Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Conformationally enforced planarization of bis[1]benzothieno[1,4]thiazines:

A rational design of redox-active fluorophores with increased radical cation stability

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1 Synthesis

1.1 General Information

1.1.1 Synthesis

All reactions were carried out in a dry and oxygen free nitrogen or argon atmosphere using standard Schlenk techniques. Furthermore, all solvents for syntheses (toluene, THF, DMF) were dried and stored under dry and oxygen free nitrogen or argon atmosphere over molecular sieve prior to use. Sodium*tert*butoxide was stored in a glove box of the manufacturer M. Braun under dry and oxygen free argon atmosphere and weight in the reaction vessel directly. Compounds, materials and solvents except the starting materials **1** and **2** and their precursors were purchased from Sigma Aldrich, BLD Pharm, Acros Organics, Alfa Aesar, Merck Millipore, Macherey-Nagel, VWR Chemicals, Carl Roth GmbH and used as received. The flash column chromatography was performed at a pressure of 2 bar under nitrogen on silica gel of size 0.040-0.060 mm. The crude products were adsorbed to Celite 535® beforehand. During recrystallization, heating was stopped after the crude product was completely dissolved. By leaving the flask in the silicone oil bath, slow cooling of the solution with the formation of high-quality crystals was ensured. The isolated products were dried for at least 12 h under a fine vacuum (10^{-2} to 10^{-3} mbar).

1.1.2 Characterization

Most of the characterization was carried out by the department CeMSA@HHU of the Heinrich-Heine university. The NMR spectra were recorded on a Bruker Avance III 300 and a Bruker Avance III 600. All ^{1}H and ^{13}C{^{1}H}, and DEPT-135 NMR spectra are referenced to the chemical shifts of residual undeuterated solvent, mostly in in THF-d_8. ^{19}F NMR spectra were referenced to standard 1,3,5-trifluorobenzene with a chemical shift of δ = –107.67 ppm in THF-d_8. The mass spectra were measured on a Finnigan MAT TSQ 7000 (EI-MS), Jeol JMS-Q1600 (EI-MS), UHR-QTOF maxis 4G (HR-ESI-MS) or MALDI-TOF Ultraflex (MALDI). EPR spectra were measured with a Miniscope MS 300 from Magnettech GmbH with *g*-factors referenced to external Mn^{2+} in ZnS (g = 2.118, 2.066, 2.027, 1.986, 1.946, 1.906). The settings were as follows: *microwave frequency* = 9.43 GHz, *center field* = 3359 G; *sweep* = 120 G; *modulation amplitude* = 2000 mG; *receiver gain* = 4; *microwave attenuation* = 0 dB; *sweep time* = 90 s. Simulations of the EPR spectrum was performed with EasySpin (v 5.2.25 for Matlab R2020). A Büchi B545 melting point analyser was used to determine the melting and decomposition points. IR spectra were recorded with a Shimadzu IR Affinity-1 spectrometer. Elemental analyses were measured on an Elementar Vario *MICRO* cube. X-ray analysis of crystals was performed using a Bruker Apex Duo CCD diffractometer with Mo-Kα radiation (λ = 0.7101 Å)

or a Rigaku XtaLAB-Synergy S diffractometer with Cu-Kα radiation (λ = 1.54184 Å). Final analysis and image plotting was performed with ORTEP,[1] Mercury[2] and Crystal explorer[3].

1.1.3 Analysis of optoelectronic properties

CVs were measured with a Potentiostat Galvanostat VersaSTAT3 from Princeton Applied Research. Measurements conditions: T = 298 K, 0.1 M [Bu_4N][PF_6], ν = 100 mV/s, Pt-working- und -counter electrode, Ag/AgCl(3 M)-reference electrode, referenced with DMFc/$DMFc^+$. Spectroelectrochemistry was recorded in a SEC cell as rhd instruments TSC 1600 closed with a Potentiostat Metrom PGSTAT204, a Hamamatsu L10290 as excitation source and TIDAS S MMS Vis/NIR as spectrometer. Measurements conditions: T = 298 K, 0.1 M [Bu_4N][PF_6], v = 100 mV/s, Pt-mesh-working- und GC-counter electrode, silver wire pseudo reference electrode. UV/vis absorption measurements were performed in a on a Perkin Elmer Spectrometer Lambda 19, whilst emission data were obtained on a FLS 1000 with a 450 W xenon gas discharge lamp for emission spectra and a pulsed diode laser EPL-450 of wavelength of 448.8 nm by Edinburgh Instruments.

1.2 Synthesis of BBTTs

1.2.1 Starting materials

The synthesis of the starting material bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane **1** and bis(2,6-dibromobenzo[*b*]thiophen-3-yl)sulfane **2** and their precursors were carried out according to literature.[4, 5]

1.2.2 General procedures

1.2.2.1 General procedure I: Buchwald-Hartwig coupling[4]

The synthesis of *anti-anti-N-ortho*-substituted-Phenyl-BBTT **3** is carried out by placing bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1.00 equivs), bis(dibenzylideneacetone)palladium, 1,1′-Bis(diphenylphosphino)ferrocene (DPPF) and sodium*tert*butoxide in a Schlenk tube. In addition, the desired *ortho*-aniline (1.00 equivs) and toluene as solvent were added. The components were allowed to react while stirring at 110 °C.

All crude products were purified by flash column chromatography and subsequent recrystallization.

1.2.2.2 General procedure II: Buchwald-Hartwig coupling

The synthesis of *anti-anti-N-ortho,ortho'*-disubstituted-Phenyl-BBTT **3** is carried out by placing bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1.00 equivs), bis(dibenzylideneacetone)palladium, 9,9-dimethyl-*9H*-xanthene-4,5-diyl)bis(diphenylphosphine (Xantphos) and sodium*tert*butoxide

in a Schlenk tube. In addition, the desired *ortho*-aniline (1.00 equivs) and toluene as solvent were added. The components were allowed to react while stirring at 110 °C.

All crude products were purified by flash column chromatography and subsequent recrystallization.

1.2.2.3 General procedure III: Buchwald-Hartwig coupling[5]

The synthesis of *anti-anti-3,9*-dibromo-*N-ortho(,ortho')*-(di)substituted-Phenyl-BBTT **4** is carried out by placing bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1.00 equivs), bis(dibenzylideneacetone)palladium, (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalin (BINAP) and sodium^{tert}butoxide in a Schlenk tube. In addition, the desired *ortho*-aniline (1.00 equivs) and toluene as solvent were added. The components were allowed to react while stirring at 110 °C.

All crude products were purified by flash column chromatography and often subsequent recrystallization or washing.

1.2.2.4 General procedure IV: Dehalogenation by transmetalation

Synthesis of *anti-anti-N-ortho(,ortho')*-(di)substituted-Phenyl-BBTT **3** was carried out in a Schlenk tube by dissolving the corresponding 3,9-dibrominated BBTT (**4**, 1.00 equivs) with TMEDA (2.40 equivs) in THF. The reaction solution was then stirred at -78°C while a solution of ^{n}butyllithium (2.40 equivs) in ^{n}hexane was added. Afterwards the reaction mixture was stirred for 2 h more, before methanol (10.0 equivs) was added and the reaction was finished by stirring at 22°C for another 30 min.

1.2.2.5 General procedure V: Kumada coupling

Anti-anti-N-ortho,ortho'-disubstituted-Phenyl-BBTT **3** were synthesized starting from their respective chlorinated BBTT **3** (1.00 eq.) by adding PEPPSI-IPr (5.00 - 15.0 mol%) to THF in a Schlenk tube. The reaction was then carried out at 65°C whilst a solution of methylmagnesium chloride (3.00 M) in THF was added gradually by a syringe pump. After complete addition, stirring was continued for 2 h to complete the reaction. The reaction was terminated by the addition of distilled water (20 mL). It was acidified with HCL solution (1 M, 1 mL), extracted with ethyl acetate (3 x 20-50 mL) and the combined organic phases were dried with anhydrous magnesium sulfate. The crude product was purified by flash column chromatography.

1.2.2.6 General procedure VI: Cyanation

The synthesis of a*nti-anti-N-ortho(,ortho')*-(di)substituted-Phenyl-BBTT **3** started from the respective chlorinated BBTT (1.00 eq.). Furthermore, PEPPSI-IPr (2.50 mol%), potassium

hexacyanoferrate(II)trihydrate (0.25-5.00 equivs) and sodium carbonate (2.50-5.00 equivs) were additionally placed with DMF in a Schlenk tube. The reaction mixture was stirred at 160°C while a solution of PEPPSI-IPr (0.1 M) in DMF was added with a drip rate of 100 µl h^{-1} using a syringe pump. After complete addition, stirring was continued for further 8 h to complete the reaction. After cooling to 22°C, the reaction solution was stirred for 0.5 h with a saturated $FeSO_4$ solution (10 mL) before the reaction mixture was filtered and the residue was washed with THF (25 mL). The filtrate was extracted with ethyl acetate (3 x 20-50 mL) and the combined organic phases were dried with magnesium sulfate (anhydrous). The crude product was purified by flash column chromatography followed by recrystallization.

1.2.3 *Anti-anti-N-ortho*-substituted-Phenyl-BBTT 3a-e

1.2.3.1 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin-6-yl)benzonitrile (3a)[4]

The product was prepared in accordance to general procedure VI.

6-(2-chlorophenyl)-6H-benzo[4,5]thieno[3,2-b]benzo[4,5]thieno[2,3-e][1,4]thiazine (3c)	**PEPPSI-IPr**	**$K_4[Fe(CN)_6] \cdot H_20$**	**Na_2CO_3**	**solvent**
1.00 mmol	2.50 mmol% + 2.50 mmol%	0.250 mmol	2.5 mmol	5.00 mL
422 mg	17.0 mg + 17.0 mg	106 mg	273 mg	DMF

The product was eluted by flash column chromatography with a gradient of ^{n}hexane/THF starting at ratio of 20:1 to 10:1 as eluent. Recrystallization was carried out in toluene (20 mL). Yield: red crystals, 211 mg, 0.511 mmol, 51%; Mp.: 236°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.16 – 7.32 (m, 2H), 7.33 – 7.44 (m, 4H), 7.60 – 7.67 (m, 2H), 7.70 – 7.79 (m, 1H), 7.88 – 8.11 (m, 3H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 101.8 ($C_{quart.}$), 115.9 ($C_{quart.}$), 116.0 ($C_{quart.}$), 120.6 (CH), 123.0 (CH), 124.6 (CH), 126.3 (CH), 131.7 (CH), 132.0 (CH), 134.6 ($C_{quart.}$), 136.1 (CH), 136.1 (CH), 137.1 ($C_{quart.}$), 140.7 ($C_{quart.}$), 145.4 ($C_{quart.}$). EI-MS (*m/z* (%)): 428 ($[C_{23}H_{12}N_2OS_3]^+$, 16), 412 ($[C_{23}H_{12}N_2S_3]^+$, 93), 380 (43), 310 ($[C_{16}H_8NS_3]^+$, 100), 278 ($[C_{16}H_8NS_2]]^+$, 28). Elemental analysis calc. for $C_{23}H_{12}N_2S_3$: C 66.96, H 2.93, N 6.79, S 23.31; found: C 66.82, H 3.11, N 6.63, S 23.24.

1.2.3.2 6-Phenyl-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3b)[4]

The product was prepared in accordance to general procedure I.

bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1)	2-chloroaniline	$Pd(dba)_2$	DPPF	sodium*tert*butoxide	solvent / reaction time
5.00 mmol	5.00 mmol	7.50 mol%	15.0 mol%	15.0 mmol	30.0 mL toluene
2.28 g	638 mg	216 mg	416 mg	1.44 g	52 h

In addition to that, saturated NaCl solution was added to the reaction mixture, followingly extraction was carried out with dichloromethane (3 x 50 mL) and the combined organic phases were dried with sodium sulfate (anhydrous). The product was eluted by flash column chromatography with a gradient of *n*hexane/triethylamine/THF starting at ratio of 100:3:0 to 100:3:3 as eluent. Recrystallization was carried out in toluene (35 mL). Yield: yellow to brownish crystals, 1.11 g, 2.64 mmol, 53%; Mp.: 180°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.14 – 7.24 (m, 2H), 7.29 – 7.41 (m, 4H), 7.51 – 7.63 (m, 4H), 7.67 – 7.74 (m, 1H), 7.74 – 7.83 (m, 1H). EI-MS (*m/z* (%)): 423 ($[C_{22}H_{12}{}^{37}ClNS_3]^+$, 37), 421 ($[C_{22}H_{12}{}^{35}ClNS_3]^+$, 93), 386 ($[C_{22}H_{12}ClNS_3]^+$, 34), 310 ($[C_{16}H_8NS_3]^+$, 100), 278 ($[C_{16}H_8NS_2]^+$, 17).

1.2.3.3 6-(2-Fluorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3c)

The product was prepared in accordance to general procedure I.

bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1)	2-fluoroaniline	$Pd(dba)_2$	DPPF	sodium*tert*butoxide	solvent / reaction time
0.500 mmol	0.500 mmol	7.50 mol%	15.0 mol%	15.0 mmol	3.00 mL toluene
228 mg	48.3 µL	21.6 mg	41.6 mg	144 mg	24 h

In addition to that, saturated NaCl solution was added to the reaction mixture, followingly extraction was carried out with dichloromethane (3 x 100 mL) and the combined organic phases were dried with magnesium sulfate (anhydrous). The product was eluted by flash column chromatography with a *n*hexane/triethylamine at ratio of 100:2 as eluent. Recrystallization was carried out in *n*hexane (60 mL). Yield: yellow needles, 135 mg, 0.33 mmol, 67%; Mp.: 182°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.17 – 7.24 (m, 2H), 7.31 – 7.47 (m, 6H), 7.57 – 7.66 (m, 2H), 7.72 – 7.79 (m, 1H). ^{13}C-{^{1}H}-NMR (151 MHz, THF-d_8) δ 100.2 (C_{quart}), 118.8 (CH, d, $^2J_{CF}$ = 19.4 Hz), 120.3 (CH), 122.9 (CH), 124.3 (CH), 126.2 (CH), 126.9 (CH, d, $^3J_{CF}$ = 4.2 Hz), 130.7 (C_{quart}, d, $^2J_{CF}$ = 12.2 Hz), 132.7 (CH), 133.3 (CH, d, $^3J_{CF}$ = 8.1 Hz), 134.4 (C_{quart}), 137.3 (C_{quart}), 141.6 (C_{quart}), 160.9 ($C_{quart,}$ d, $^1J_{CF}$ = 253.6 Hz). ^{19}F-NMR (282 MHz, THF-

d_8) δ -119.50. HR-ESI-MS calc. for $[C_{22}H_{12}FNS_3]^+$: 405.0110; found: 405.0119. IR: $\tilde{\nu}$ [cm^{-1}] = 3051 (w), 3026 (w), 1589 (w), 1568 (m), 1547 (w), 1504 (m), 1489 (m), 1456 (m), 1435 (s), 1350 (w), 1288 (m), 1275 (m), 1261 (m), 1240 (m), 1215 (w), 1204 (w), 1167 (w), 1157 (w), 1130 (w), 1105 (m), 1065 (w), 1015 (m), 953 (w), 925 (w), 865 (w), 850 (w), 826 (w), 772 (m), 758 (w), 745 (s), 719 (s), 712 (m), 687 (m). Elemental analysis calc. for $C_{22}H_{12}FNS_3$: C 65.16, H 2.98, N 3.45, S 23.72; found: C 64.88, H 3.03, N 3.50, S 23.52.

1.2.3.4 6-(*o*-Tolyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3d)

The product was prepared in accordance to general procedure IV.

3,9-dibromo-6-(*o*-tolyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4a)	**TMEDA**	**^{n}butyllithium** (1.60 M)	**methanol**	**solvent**
0.372 mmol	0.892 mmol	0.892 mmol	3.72 mmol	1.50 mL
208 mg	104 mg	558 µl	152 µl	THF

In addition to that, distilled water was added to the reaction mixture. The followingly extraction was carried out with dichloromethane (3 x 20 mL) and the combined organic phases were dried with magnesium sulfate (anhydrous). After repeated washing with ^{n}pentane (10 mL) while ultrasonification the product was isolated. Yield: orange powder, 99.2 mg, 0.247 mmol, 66 %; Mp.: 167°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 2.48 (s, 3H), 7.14 – 7.22 (m, 2H), 7.28 – 7.51 (m, 8H), 7.53 – 7.60 (m, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 17.8 (CH_3), 98.8 (C_{quart}), 120.1 (CH), 122.8 (CH), 123.9 (CH), 126.1 (CH), 129.1 (CH), 130.8 (CH), 131.4 (CH), 133.3 (CH), 134.5 (C_{quart}), 137.5 (C_{quart}), 139.4 (C_{quart}), 141.8 (C_{quart}), 142.0 (C_{quart}). EI-MS (*m/z* (%)): 401.0 ($[C_{23}H_{15}NS_3]^+$, 34), 310.0 ($[C_{16}H_8NS_3]^+$, 29), 296.0 ($[C_{16}H_8S_3]^+$, 100), 148.0 ($[C_8H_7NS]^+$, 20). IR: $\tilde{\nu}$ [cm^{-1}] = 1562 (m), 1545 (w), 1506 (s), 1452 (m), 1431 (s), 1286 (m), 1267 (m), 1244 (m), 1198 (m), 1169 (w), 1155 (w), 1113 (w), 1063 (m), 1015 (m), 955 (w), 945 (w), 857 (w), 818 (w), 745 (s), 735 (s), 728 (s), 719 (s), 689 (m), 648 (w). Elemental analysis calc. for $C_{23}H_{15}NS_3$: C 68.79, H 3.77, N 3.49, S 23.95; found: C 68.76, H 4.01, N 3.44, S 23.89.

1.2.3.5 6-(2-Methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3e)

The product was prepared in accordance to general procedure I.

bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1)	**2-Anisidine**	**$Pd(dba)_2$**	**DPPF**	**sodium^{tert}butoxide**	**solvent / reaction time**
0.500 mmol	0.500 mmol	7.50 mol%	15.0 mol%	15.0 mmol	3.00 mL toluene
228 mg	56.5 µL	21.6 mg	41.6 mg	144 mg	24 h

In addition to that, saturated NaCl solution was added to the reaction mixture, followingly extraction was carried out with dichloromethane (3 x 100 mL) and the combined organic phases were dried with magnesium sulfate (anhydrous). The product was eluted by flash column chromatography with a gradient of ^{n}hexane/dichloromethane/triethylamine starting at ratio of 100:1:2 to 100:5:2 as eluent. Recrystallization was carried out in ethanol (25 mL). Yield: yellow crystals, 45.6 mg, 0.11 mmol, 22%; Mp.: 140°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 3.82 (s, 3H), 7.09 – 7.17 (m, 3H), 7.23 – 7.28 (m, 3H), 7.32 – 7.35 (m, 2H), 7.52 – 7.57 (m, 4H). ^{13}C-{^{1}H}-NMR (151 MHz, THF-d_8) δ 56.3 (CH_3), 98.4 (C_{quart}), 114.3 (CH), 120.0 (CH), 122.2 (CH), 122.7 (CH), 123.6 (CH), 125.9 (CH), 131.1 (C_{quart}), 132.2 (CH), 132.7 (CH), 134.3 (C_{quart}), 137.6 (C_{quart}), 142.8 (C_{quart}), 158.3(C_{quart}). HR-ESI-MS calc. for $[C_{23}H_{15}NOS_3]^+$: 417.0310; found: 417.0312. IR: $\tilde{\nu}$ [cm^{-1}] = 3061 (w), 3026 (w), 2967 (w), 2938 (m), 2835 (w), 1595 (w), 1568 (w), 1555 (w), 1508 (s), 1493 (m), 1468 (w), 1456 (m), 1433 (s), 1346 (w), 1304 (w), 1297 (s), 1275 (w), 1260 (w), 1242 (m), 1182 (w), 1167 (w), 1155 (w), 1117 (w), 1063 (w), 1043 (m), 1022 (m), 993 (w), 951 (w), 904 (w), 850 (w), 836 (w), 810 (w), 754 (s), 737 (s), 722 (m), 712 (s), 691 (m), 645 (w). Elemental analysis calc. for $C_{23}H_{15}NOS_3$: C 66.16, H 3.62, N 3.35, S 23.03; found: C 65.93, H 3.47, N 3.32, S 22.93.

1.2.4 *Anti-anti-N-ortho,ortho'*-disubstituted-Phenyl-BBTT 3f-t

1.2.4.1 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine-6-yl)isophthalonitrile (3f)

The product was prepared in accordance to general procedure VI.

6-(2,6-dichlorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]-benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3g)	**PEPPSI-IPr**	**$K_4[Fe(CN)_6] \cdot H_20$**	**Na_2CO_3**	**solvent**
1.00 mmol	2.50 mmol% + 7.5 mmol%	0.500 mmol	5.00 mmol	5.00 mL
456 mg	17.0 mg + 50.9 mg	211 mg	545 mg	DMF

The product was eluted by flash column chromatography with a gradient of ^{n}hexane/THF starting at ratio of 5:1 to 5:3 as eluent. Recrystallization was carried out in toluene (20 mL). Yield: black, red and orange crystals, 201 mg, 0.458 mmol, 46%; Mp.: 302-303°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.23 – 7.36 (m, 2H), 7.37 – 7.49 (m, 4H), 7.67 (d, $^{3}J_{HH}$ = 8.05 Hz, 2H), 7.97 (t, $^{3}J_{HH}$ = 7.90 Hz, 1H), 8.36 (d, $^{3}J_{HH}$ = 7.90 Hz, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 103.3 ($C_{quart.}$), 114.6 ($C_{quart.}$), 118.3 ($C_{quart.}$), 121.1 (CH), 123.2 (CH), 125.2 (CH), 126.5 (CH), 133.0 (CH), 134.6 ($C_{quart.}$), 137.0 ($C_{quart.}$), 138.2 ($C_{quart.}$), 140.3 (CH), 170.6 ($C_{quart.}$). EI-MS (*m/z* (%)): 437 ($[C_{24}H_{11}N_3S_3]^+$, 71), 310 ($[C_{16}H_8NS_3]^+$, 100), 278 ($[C_{16}H_8NS_2]]^+$, 16). Elemental analysis calc. for $C_{24}H_{11}N_3S_3$: C 65.88, H 2.53, N 9.60, S 21.98; found: C 65.93, H 2.65, N 9.45, S 21.67.

1.2.4.2 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin-6-yl)-3-chlorobenzonitrile (3k)

The product was prepared in accordance to general procedure VI.

6-(2,6-dichlorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]-benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3g)	**PEPPSI-IPr**	**$K_4[Fe(CN)_6] \cdot H_20$**	**Na_2CO_3**	**solvent**
1.00 mmol	2.50 mmol% + 17.5 mmol%	5.00 mmol	5.00 mmol	5.00 mL
456 mg	17.0 mg + 119 mg	2.11 g	545 mg	DMF

Because general procedure VI led mostly to the formation of **3f**, the intermediate **3k** could not be isolated. Accordingly, the catalyst loading was increased as well as the reaction time after

completion of the catalyst addition reduced. Therefore, the reaction mixture was stirred for 1 h after the addition. The product was eluted by flash column chromatography with a gradient of ^{n}hexane/THF starting at ratio of 20:1 to 5:4 as eluent. Recrystallization was carried out in toluene (15 mL). Yield: dark red, 73.1 mg, 0.164 mmol, 16%; Mp.: 295-296°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.21 – 7.29 (m, 2H), 7.34 – 7.45 (m, 4H), 7.61 – 7.67 (m, 2H), 7.79 (t, $^{3}J_{HH}$ = 8.00 Hz, 1H), 7.99 – 8.09 (m, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 101.5 ($C_{quart.}$), 115.3 ($C_{quart.}$), 119.0 ($C_{quart.}$), 120.7 (CH), 123.1 (CH), 124.7 (CH), 126.4 (CH), 133.5 (CH), 134.4 (CH), 134.6 (CH), 137.2 ($C_{quart.}$), 137.4 ($C_{quart.}$), 138.2 ($C_{quart.}$), 138.8 ($C_{quart.}$), 141.6 ($C_{quart.}$). EI-MS (*m/z* (%)): 464 ([$C_{23}H_{11}{}^{37}ClN_2S_3O$]$^+$, 4), 462 ([$C_{23}H_{11}{}^{35}ClN_2S_3O$]$^+$, 9), 447 ([$C_{23}H_{11}{}^{37}ClN_2S_3$]$^+$, 20), 445 ([$C_{23}H_{11}{}^{35}ClN_2S_3$]$^+$, 7), 416 (8), 414 (20), 412 (9), 399 (12), 310 ([$C_{16}H_8NS_3$]$^+$, 100), 278 ([$C_{16}H_8NS_2$]$^+$, 22), 123 (16). IR: $\tilde{\nu}$ [cm^{-1}] = 2233 (w), 1576 (w), 1560 (w), 1522 (m), 1456 (w), 1444 (m), 1433 (m), 1279 (m), 1238 (m), 1180 (w), 1151 (w), 1057 (w), 1020 (w), 953 (w), 850 (w), 795 (m), 756 (s), 719 (s), 681 (w). Elemental analysis calc. for $C_{23}H_{11}ClN_2S_3$: C 61.80, H 2.48, N 6.27, S 21.52; found: C 62.02, H 2.74, N 6.14, S 21.46.

1.2.4.3 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine-6-yl)-3-fluorobenzonitrile (3l)

The product was prepared in accordance to general procedure VI.

6-(2-chloro-6-fluorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin (3o)	**PEPPSI-IPr**	**$K_4[Fe(CN)_6] \cdot H_20$**	**Na_2CO_3**	**solvent**
1.00 mmol	2.50 mmol% + 2.50 mmol%	0.250 mmol	2.50 mmol	5.00 mL
440 mg	17.0 mg + 17.0 mg	105.5 mg	265 mg	DMF

The product was eluted by flash column chromatography with a gradient of ^{n}hexane/THF starting at ratio of 20:1 to 5:1 as eluent. Recrystallization was carried out in toluene (10 mL). Yield: brownish crystals, 197 mg, 0.458 mmol, 46 %; Mp.: 260-264°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.21 – 7.32 (m, 2H), 7.37 – 7.46 (m, 4H), 7.63 – 7.70 (m, 2H), 7.77 – 7.92 (m, 3H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 102.0 ($C_{quart.}$), 115.0 ($C_{quart.}$, d, $^{3}J_{CF}$ = 4.3 Hz), 118.2 (CH, d, $^{4}J_{CF}$ = 1.4 Hz), 120.8 (CH), 123.1 (CH), 124.0 (CH, d, $^{2}J_{CF}$ = 20.0 Hz), 124.9 (CH), 126.4 (CH), 131.7 (CH, d, $^{3}J_{CF}$ = 3.9 Hz), 132.5 ($C_{quart.}$, d, $^{2}J_{CF}$ = 15.1 Hz), 134.4 ($C_{quart.}$), 134.5 ($C_{quart.}$), 137.1 ($C_{quart.}$), 139.5 ($C_{quart.}$), 161.7 ($C_{quart.}$, d, $^{1}J_{CF}$ = 256.6 Hz). ^{19}F-NMR (282 MHz, THF) δ -117.5. EI-MS (*m/z* (%)): 446 ([$C_{23}H_{11}FN_2S_3O$]$^+$, 5), 430 ([$C_{23}H_{11}FN_2S_3$]$^+$, 100), 398 ([$C_{22}H_{10}N_2S_3$]$^+$, 10), 310 ([$C_{16}H_8NS_3$]$^+$, 94), 278 ([$C_{16}H_8NS_2$]$^+$, 20), 215 (20). IR: $\tilde{\nu}$ [cm^{-1}] = 2237 (w), 1573 (m), 1521 (m), 1470 (m), 1456 (m), 1433 (s), 1279 (s), 1257 (m), 1238 (s), 1155 (w), 1063 (w),

1016 (w), 957 (m), 802 (s), 772 (w), 745 (s), 721 (m). Elemental analysis calc. for $C_{23}H_{11}FN_2S_3$: C 64.17, H 2.58, N 6.51, S 22.34; found: C 64.24, H 2.58, N 6.47, S 22.44.

1.2.4.4 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine-6-yl)-3-methylbenzonitrile (3m)

The product was prepared in accordance to general procedure VI.

6-(2-chloro-6-methylphenyl)-6*H*-benzo[4,5]thieno-[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin (3p)	**PEPPSI-IPr**	**$K_4[Fe(CN)_6] \cdot H_20$**	**Na_2CO_3**	**solvent**
1.38 mmol	2.50 mmol% + 2.50 mmol%	0.344 mmol + 0.344 mmol	2.50 mmol	7.00 mL
600 mg	23.4 mg + 23.4 mg	145 mg	366 mg	DMF

After the reaction was not completed by the parameters according to the method described in the general procedure VI, potassium hexacyanoferrate(II) trihydrate (145 mg, 0.344 mmol, 0.250 equivs) was added again and the reaction mixture was stirred further for 5 h at 185°C. The product was eluted by flash column chromatography with a gradient of ^{n}hexane/THF starting at ratio of 20:1 to 10:1 as eluent. Recrystallization was carried out in toluene (15 mL). Yield: yellow crystals, 112 mg, 0.262 mmol, 19% Mp.: 307°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 2.54 (s, 3H), 7.19 – 7.27 (m, 2H), 7.31 – 7.44 (m, 4H), 7.59 – 7.64 (m, 2H), 7.67 (t, $^3J_{HH}$ = 7.74 Hz, 1H), 7.76 – 7.90 (m, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 17.8 (CH_3), 100.1 ($C_{quart.}$), 116.2 ($C_{quart.}$), 117.0 ($C_{quart.}$), 120.5 (CH), 123.0 (CH), 124.5 (CH), 126.3 (CH), 132.1 (CH), 133.7 ($C_{quart.}$), 134.3 (CH), 137.4 ($C_{quart.}$), 138.0 (CH), 139.5 ($C_{quart.}$), 142.2 ($C_{quart.}$), 142.8 ($C_{quart.}$). HR-ESI-MS calc. for $[C_{24}H_{14}NS_3]^+$: 426.0319; found: 426.0316. IR: $\tilde{\nu}$ [cm^{-1}] = 2229 (w), 1570 (m), 1518 (m), 1456 (m), 1433 (s), 1377 (w), 1281 (m), 1234 (m), 1157 (w), 1060 (w), 1016 (w), 953 (w), 941 (w), 914 (w), 797 (m), 756 (s), 743 (s), 719 (s), 687 (w). Elemental analysis calc. for $C_{24}H_{14}NS_3$: C 67.58, H 3.31, N 6.57, S 22.55; found: C 67.89, H 3.36, N 6.43, S 22.29.

1.2.4.5 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin-6-yl)-3-methoxybenzonitrile (3n)

The product was prepared in accordance to general procedure VI.

6-(2-chloro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno-[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3q)	**PEPPSI-IPr**	**$K_4[Fe(CN)_6] \cdot H_20$**	**Na_2CO_3**	**solvent**
0.500 mmol	5.00 mmol% + 10.0 mmol%	0.125 mmol	2.50 mmol	3.50 mL
226 mg	16.9 mg + 33.9 mg	52.8 mg	265 mg	DMF

The product was eluted by a doubly flash column chromatography with first ^{n}hexane/THF in a ratio of 33:1 and second ^{n}hexane/dichloromethane in a ratio of 10:1 as eluent. Yield: orange powder, 21.6 mg, 0.049 mmol, 1%; Mp.: 292°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 3.88 (s, 3H), 7.21 (ddd, $^{3}J_{HH}$ = 8.3, $^{3}J_{HH}$ = 6.7, $^{4}J_{HH}$ = 1.7 Hz, 2H), 7.30 – 7.42 (m, 4H), 7.54 (dd, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.57 – 7.64 (m, 3H), 7.73 (dd, $^{3}J_{HH}$ = 8.6, $^{3}J_{HH}$ = 7.6 Hz, 1H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 57.2 (CH_3) 99.8 ($C_{quart.}$), 115.9 ($C_{quart.}$), 117.4 ($C_{quart.}$), 119.6 ($C_{quart.}$), 120.3 (CH), 122.9 (CH), 124.3 (CH), 126.1 (CH), 126.3 (CH), 132.0 (CH), 133.9 (CH), 134.1 ($C_{quart.}$), 137.3 ($C_{quart.}$), 140.7 ($C_{quart.}$), 159.3 ($C_{quart.}$). HPLC (99%) and HR-ESI-MS calc. for $[C_{24}H_{14}N_2OS_3]^+$: 442.0268; found: 442.0265. IR: $\tilde{\nu}$ [cm^{-1}] = 2955 (w), 2922 (w), 2851 (w), 1620 (w), 1602 (w), 1599 (w), 1524 (m), 1472 (m), 1456 (w), 1433 (m), 1279 (m), 1260 (m), 1238 (m), 1184 (w), 1159 (w), 1072 (m), 1016 (w), 961 (w), 955 (w), 907 (w), 797 (m), 778 (m), 746 (s), 721 (m), 694 (w), 617 (w).

1.2.4.6 6-(2,6-Chlorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3g)

The product was prepared in accordance to general procedure II.

bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1)	**2,6-dichloroaniline**	**$Pd(dba)_2$**	**Xantphos**	**sodium^{tert}butoxide**	**solvent / reaction time**
2.50 mmol	2.50 mmol	7.50 mol%	15.0 mol%	7.5 mmol	45 mL toluene
1.14 mg	405 mg	108 mg	208 mg	720 mg	46 h

In addition to that, saturated NaCl solution was added to the reaction mixture, followingly extraction was carried out with dichloromethane (3 x 75 mL) and the combined organic phases

were dried with magnesium sulfate (anhydrous). The product was eluted by flash column chromatography with a gradient of *n*hexane/toluene/THF/triethylamine starting at ratio of 100:2:0:2 to 100:2:10:2 as eluent. Recrystallization was carried out in a mixture of *n*hexane and ethanol (50 mL, ratio of 50:50). Yield: brownish crystals, 519 mg, 1.14 mmol, 46%; Mp.: 301°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.19 – 7.25 (m, 2H), 7.31 – 7.36 (m, 2H), 7.36 – 7.41 (m, 2H), 7.59 (t, $^{3}J_{HH}$ = 8.10 Hz, 1H), 7.61 (d, $^{3}J_{HH}$ = 7.98 Hz, 2H), 7.67 – 7.72 (m, 2H).^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 99.9 (C_{quart}), 120.4 (CH), 123.0 (CH), 124.3 (CH), 126.2 (CH), 131.1 (CH), 133.4 (CH), 134.2 (C_{quart}), 137.3 (C_{quart}), 137.4 (C_{quart}), 138.7 (C_{quart}), 139.3 (C_{quart}). HR-ESI-MS calc. for $[C_{22}H_{11}Cl_2NS_3]^+$: 454.9425; found: 454.9426. IR: $\tilde{\nu}$ [cm^{-1}] = 3065 (w), 2160 (w), 1576 (m), 1518 (s), 1447 (m), 1437 (s), 1344 (w), 1285 (s), 1271 (m), 1242 (s), 1192 (m), 1159 (m), 1115 (w), 1074 (m), 1061 (m), 1020 (m), 839 (m), 781 (s), 768 (m), 743 (s), 718 (s). Elemental analysis calc. for $C_{22}H_{11}Cl_2NS_3$: C 57.89, H 2.43, N 3.07, S 21.07; found: C 57.90, H 2.48, N 2.99, S 21.07.

1.2.4.7 6-(2-Chloro-6-fluorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3o)

The product was prepared in accordance to general procedure II.

bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1)	**2-chloro, 6-fluoroanilin**	**Pd(dba)$_2$**	**Xantphos**	**sodium*tert*butoxide**	**solvent / reaction time**
10.0 mmol	10.0 mmol	5.0 mol%	10.0 mol%	30.0 mmol	180 mL toluene
4.56 g	1.47 g	288 mg	576 mg	2.88 g	56 h

In addition to that, saturated NaCl solution was added to the reaction mixture, followingly extraction was carried out with ethylacetate (3 x 100 mL) and 1,2-Dichloroethane (100 mL) and the combined organic phases were dried with magnesium sulfate (anhydrous). The product was eluted by flash column chromatography with a gradient of *n*hexane/ethylacetate starting at ratio of 100:0 to 100:2 as eluent. Recrystallization was carried out in toluene (50 mL). Yield: brownish crystals, 3.43 g, 7.80 mmol, 78%; Mp.: 245°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.18 – 7.26 (m, 2H), 7.32 – 7.48 (m, 5H), 7.53 – 7.68 (m, 4H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 100.3 (C_{quart}), 117.3 (CH, d, $^{2}J_{CF}$ = 20.4 Hz), 120.5 (CH), 123.0 (CH), 124.4 (CH), 126.2 (CH), 127.9 (C_{quart}, d, $^{3}J_{CF}$ = 3.6 Hz), 128.5 (C_{quart}, d, $^{2}J_{CF}$ = 15.1 Hz), 133.7 (CH, d, $^{3}J_{CF}$ = 9.3 Hz), 134.2 (CH), 137.3 (C_{quart}), 138.1 (C_{quart}), 140.0 (C_{quart}), 162.5 (C_{quart}, d, $^{1}J_{CF}$ = 255.8 Hz). ^{19}F-NMR (282 MHz, THF) δ -116.0. EI-MS (*m/z* (%)): 441.0 ($[C_{22}H_{11}{}^{37}ClFNS_3]^+$, 27), 439.0 ($[C_{22}H_{11}{}^{35}ClFNS_3]^+$, 59), 403.9 ($[C_{22}H_{11}FNS_3]^+$, 2), 363.0 ($[C_{16}H_7{}^{37}ClFNS_3]^+$, 5), 310.0 ($[C_{18}H_8NS_3]^+$, 100), 278.0 ($[C_{16}H_8NS_2]^+$, 19), 219.5 (17). IR: $\tilde{\nu}$ [cm^{-1}] = 3076 (w), 2963 (w),

1589 (w), 1571 (w), 1518 (m), 1454 (m), 1433 (m), 1344 (w), 1269 (m), 1238 (m), 1180 (w), 1151 (w), 1109 (w), 1065 (w), 1020 (w), 951 (w), 901 (m), 839 (w), 789 (s), 743 (s), 716 (s), 683 (w). Elemental analysis calc. for $C_{22}H_{11}ClFNS_3$: C 60.06, H 2.52, N 3.18, S 21.86; found: C 60.33, H 2.64, N 3.16, S 22.82.

1.2.4.8 6-(2-chloro-6-methylphenyl)-6*H*-benzo[4,5]thieno-[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3p)

The product was prepared in accordance to general procedure V.

6-(2,6-dichlorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]-benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3g)	**PEPPSI-IPr**	**MeMgCl** (3.00 M)	**solvent**
0.500 mmol	10.0 mmol%	1.10 mmol	6.00 mL
228 mg	34.0 mg	367 µL	THF

The solution of methylmagnesium chloride in THF (3.00 M) was added at a rate of 2.00 µL min^{-1}. The product was eluted by flash column chromatography with ^{n}hexane. Recrystallization was carried out in toluene (5 mL). Yield: brownish crystals, 97.9 mg, 0.225 mmol, 45%; Mp.: 268°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 2.53 (s, 3H), 7.16 – 7.23 (m, 2H), 7.28 – 7.40 (m, 4H), 7.40 – 7.45 (m, 1H), 7.48 (t, $^{3}J_{HH}$ = 7.63 Hz, 1H), 7.51 – 7.56 (m, 1H), 7.56 – 7.63 (m, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 18.3 (CH_3), 98.6 ($C_{quart.}$), 120.2 (CH), 122.9 (CH), 124.0 (CH), 126.14 (CH), 129.9 (CH), 131.5 (CH), 132.4 (CH), 134.1 ($C_{quart.}$), 136.9 ($C_{quart.}$), 137.6 ($C_{quart.}$), 138.5 ($C_{quart.}$), 140.1 ($C_{quart.}$), 142.8 ($C_{quart.}$). HR-ESI-MS calc. for $[C_{23}H_{14}ClNS_3]^{+}$: 434.9971; found: 434.9969. IR: $\tilde{\nu}$ [cm^{-1}] = 2972 (w), 1591 (w), 1572 (m), 1514 (s), 1456 (m), 1435 (m), 1375 (w), 1348 (w), 1285 (s), 1240 (s), 1177 (w), 1155 (w), 1150 (w), 1080 (w), 1063 (m), 1018 (w), 864 (m), 839 (m), 773 (s), 743 (s), 718 (s), 681 (m). Elemental analysis calc. for $C_{22}H_{11}Cl_2NS_3$: C 63.36, H 3.24, N 3.21, S 22.06; found: C 63.16, H 3.26, N 3.19, S 21.82.

1.2.4.9 6-(2-Chloro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3q)

The product was prepared in accordance to general procedure IV.

3,9-dibromo-6-(2-chloro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4b)	**TMEDA**	***n*butyllithium**(1.60 M)	**methanol**	**solvent**
0.715 mmol	1.72 mmol	1.72 mmol	7.15 mmol	20.0 mL
436 mg	199 mg	1.11 mL	289 µl	THF

In addition to that, distilled water was added to the reaction mixture. The followingly extraction was carried out with dichloromethane (3 x 40 mL) and the combined organic phases were dried with magnesium sulfate (anhydrous). After repeated washing with *n*pentane (20 mL) while ultrasonification the product was isolated. Yield: orange powder, 313 mg, 0.692 mmol, 97 %. Mp.: 281.5°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 3.85 (s, 3H), 7.13 – 7.20 (m, 2H), 7.20 – 7.39 (m, 6H), 7.54 (t, $^{3}J_{HH}$ = 8.24 Hz, 1H), 7.54 – 7.58 (m, 2H).^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 57.0 (CH_3), 98.6 ($C_{quart.}$), 112.7 (CH), 120.1 (CH), 122.8 (CH), 123.0 (CH), 123.8 (CH), 125.9 (CH), 128.4 ($C_{quart.}$), 133.1 (CH), 134.1 ($C_{quart.}$), 137.6 ($C_{quart.}$), 137.7 ($C_{quart.}$), 141.2 ($C_{quart.}$), 160.4 ($C_{quart.}$). HR-ESI-MS calc. for $[C_{23}H_{14}ClNOS_3]^{\cdot+}$: 450.9926; found: 450.9928. IR: $\tilde{\nu}$ [cm^{-1}] = 1584 (m), 1572 (m), 1514 (s), 1454 (m), 1433 (s), 1283 (s), 1261 (m), 1242 (s), 1155 (w), 1045 (s), 943 (w), 854 (w), 785 (m), 741 (s), 718 (s). Elemental analysis calc. for $C_{23}H_{14}ClNOS_3$: C 61.12, H 3.12, N 3.10, S 21.28; found: C 61.40, H 3.31, N 3.05, S 21.16.

1.2.4.10 6-(2,6-Fluorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3h)

The product was prepared in accordance to general procedure II.

bis(2-bromobenzo[*b*]thiophen-3-yl)sulfane (1)	**2,6-difluoroanilin**	**$Pd(dba)_2$**	**Xantphos**	**sodium*tert*butoxide**	**solvent / reaction time**
0.500 mmol	0.500 mmol	7.50 mol%	15.0 mol%	15.0 mmol	9.00 mL toluene
228 mg	53.9 µL	21.6 mg	41.6 mg	144 mg	24 h

The product was eluted by flash column chromatography with *n*hexane/triethylamine in ratio of 100:2 as eluent. Recrystallization was carried out in *n*hexane (60 mL). Yield: brownish crystals,

0.14 g, 0.32 mmol, 64%; Mp.: 215-216°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 7.19 – 7.27 (m, 2H), 7.27 – 7.43 (m, 6H), 7.59 – 7.65 (m, 2H), 7.65 – 7.73 (m, 1H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 100.7 (C_{quart}), 114.2 (CH, dd, $^{2}J_{CF}$ = 20.1, $^{4}J_{CF}$ = 3.5 Hz), 119.7 (C_{quart}, t, $^{2}J_{CF}$ = 16.4 Hz), 120.5 (CH), 123.0 (CH), 124.5 (CH), 126.3 (CH), 133.62 (CH, t, $^{3}J_{CF}$ = 10.1 Hz), 134.2 (C_{quart}), 137.3 (C_{quart}), 140.6 (C_{quart}), 162.0 (C_{quart}, dd, $^{1}J_{CF}$ = 255.3, $^{3}J_{CF}$ = 3.1 Hz). ^{19}F-NMR (282 MHz, THF) δ -117.4. HR-ESI-MS calc. for $[C_{22}H_{12}FNS_3]^+$: 423.0022; found: 423.0024. IR: $\tilde{\nu}$ [cm^{-1}] = 3065 (w), 2890 (w), 2968 (w), 2901 (w), 1612 (w), 1589 (m), 1578 (m), 1555 (m), 1518 (s), 1499 (m), 1472 (s), 1456 (m), 1435 (s), 1383 (w), 1350 (w), 1304 (w), 1288 (s), 1265 (m), 1242 (s), 1158 (w), 1153 (w), 1128 (w), 1063 (m), 1023 (w), 1005 (s), 949 (m), 940 (w), 930 (w), 795 (m), 765 (w), 751 (m), 741 (s), 716 (s), 706 (m), 685 (w), 645 (w), 634 (w). Elemental analysis calc. for $C_{22}H_{11}F_2NS_3$: C 62.39, H 2.62, N 3.31, S 22.71; found: C 62.15, H 2.59, N 3.31, S 22.95.

1.2.4.11 6-(2-fluoro-6-methylphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3r)

The product was prepared in accordance to general procedure V.

6-(2-fluoro-6-methylphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]-benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3o)	**PEPPSI-IPr**	**MeMgCl** (3.00 M)	**solvent**
1.00 mmol	5.00 mmol% + 5.00 mmol%	1.20 mmol + 0.300 mmol	12.0 mL
439 mg	34.0 mg + 34.0 mg	400 µL + 100 µL	THF

The solution of methylmagnesium chloride in THF (3.00 M) was added at a rate of 4.00 µL min^{-1}. After the reaction was not complete according to the method described in the general procedure V, PEPPSI-IPr (34.0 mg, 5.00 mmol%) was added again and the reaction solution was stirred for another 0.75 h at 80°C. Further grignard reagent was then added at 8.00 µL min^{-1} and afterwards was stirred for another 0.5 h. The product was eluted by flash column chromatography with ^{n}hexane. Recrystallization was carried out in toluene (5 mL). Yield: yellow crystals, 110 mg, 0.263 mmol, 26%; Mp.: 220-221°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 2.50 (s, 3H), 7.16 – 7.23 (m, 2H), 7.23 – 7.42 (m, 6H), 7.45 – 7.55 (m, 1H), 7.55 – 7.63 (m, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 17.4 (CH_3), 99.0 (C_{quart}), 115.8 (CH, d, $^{2}J_{CF}$ = 20.0 Hz), 120.3 (CH), 122.9 (CH), 124.1 (CH), 126.2 (CH), 128.2 (CH, d, $^{4}J_{CF}$ = 3.5 Hz), 129.2 (C_{quart}, d, $^{2}J_{CF}$ = 12.7 Hz), 132.8 (CH, d, $^{3}J_{CF}$ = 8.9 Hz), 134.1 (C_{quart}), 137.6 (C_{quart}), 140.9 (C_{quart}), 142.7 (C_{quart}), 161.6 (C_{quart}, d, $^{1}J_{CF}$ = 252.4 Hz). ^{19}F-NMR (282 MHz, THF) δ -120.37. HPLC (99%) and HR-ESI-MS calc. for $[C_{23}H_{14}FNS_3]^+$: 420.0306; found: 420.0340. IR: $\tilde{\nu}$ [cm^{-1}]

= 1570 (w), 1514 (m), 1470 (w), 1514 (s), 1456 (m), 1433 (m), 1375 (w), 1279 (s), 1240 (m), 1155 (w), 1165 (w), 1016 (w), 941 (w), 783 (m), 741 (s), 716 (s).

1.2.4.12 6-(2-Fluoro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3s)

The product was prepared in accordance to general procedure IV.

3,9-dibromo-6-(2-fluoro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4c)	**TMEDA**	**^{n}butyllithium** (2.45 M)	**methanol**	**solvent**
1.34 mmol	3.22 mmol	3.22 mmol	11.3 mmol	50.0 mL
766 mg	373 mg	1.31 mL	457 µl	THF

In addition to that, distilled water was added to the reaction mixture. The followingly extraction was carried out with ethylacetate (3 x 50 mL) and the combined organic phases were dried with magnesium sulfate (anhydrous). Recrystallization was carried out in toluene (10 mL). Yield: yellow crystalls, 300 mg, 0.688 mmol, 52 %; Mp.: 196-201°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 3.85 (s, 3H), 6.93 – 7.02 (m, 1H), 7.02 – 7.10 (m, 1H), 7.12 – 7.23 (m, 2H), 7.26 – 7.41 (m, 4H), 7.49 – 7.61 (m, 3H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 57.0 (CH_3, d, $^5J_{CF}$ = 3.4 Hz, OMe), 98.9 ($C_{quart.}$), 109.6 (CH, d, $^2J_{CF}$ = 17.9 Hz), 109.7 (CH, d, $^4J_{CF}$ = 5.8 Hz), 119.1 ($C_{quart.}$, d, $^2J_{CF}$ = 14.9 Hz), 120.1 (CH), 122.8 (CH), 123.9 (CH), 126.0 (CH), 133.2 (CH, d, $^3J_{CF}$ = 10.5 Hz), 134.1 ($C_{quart.}$), 137.6 ($C_{quart.}$), 141.8 ($C_{quart.}$), 160.2 ($C_{quart.}$, d, $^3J_{CF}$ = 3.1 Hz), 162.2 ($C_{quart.}$, d, $^1J_{CF}$ = 251.8 Hz). ^{19}F-NMR (282 MHz, THF) δ -119.8. HR-ESI-MS calc. for $[C_{23}H_{14}FNOS_3]^+$: 435.0222; found: 435.0217. IR: $\tilde{\nu}$ [cm^{-1}] = 1609 (w), 1572 (m), 1514 (s), 1495 (m), 1477 (s), 1435 (s), 1302 (w), 1287 (s), 1242 (m), 1155 (w), 1083 (s), 937 (w), 791 (m), 765 (m), 739 (s), 716 (s), 637 (w). Elemental analysis calc. for $C_{23}H_{14}FNOS_3$: C 63.43, H 3.24, N 3.22, S 22.08; found: C 63.15, H 3.41, N 3.11, S 21.79.

1.2.4.13 6-(2,6-dimethylphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3i)

The product was prepared in accordance to general procedure V.

6-(2,6-dichlorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]-benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3g)	**PEPPSI-IPr**	**MeMgCl** (3.00 M)	**solvent**
1.00 mmol	10.0 mmol%	2.40 mmol	12.0 mL
456 mg	67.9 mg	800 µL	THF

The solution of methylmagnesium chloride in THF (3.00 M) was added at a rate of 4.00 µL min^{-1}. The product was eluted by flash column chromatography with a gradient of ^{n}hexane/THF in a ration from 100:0 to 100:3. Recrystallization was carried out in toluene (5 mL). Yield: orange crystals, 177 mg, 0.436 mmol, 44 %; Mp.: 226-227°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 2.46 (s, 6H), 7.13 – 7.20 (m, 2H), 7.24 – 7.30 (m, 4H), 7.32 – 7.40 (m, 3H), 7.56 (d, $^{3}J_{HH}$ = 7.94 Hz, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 18.0 (CH_3), 97.6 (C_{quart}), 120.0 (CH), 122.8 (CH), 123.8 (CH), 126.1 (CH), 130.6 (CH), 131.3 (CH), 134.0 (C_{quart}), 137.8 (C_{quart}), 139.9(C_{quart}), 140.2 (C_{quart}), 140.8 (C_{quart}). ESI-MS (*m*/*z*): 310 ([$C_{16}H_8NS_3$]$^{+}$), 415 ($C_{24}H_{17}NS_3$). IR: $\tilde{\nu}$ [cm^{-1}] = 2916 (w), 1591 (w), 1568 (m), 1510 (s), 1456 (m), 1435 (m), 1371 (m), 1348 (w), 1283 (s), 1240 (s), 1157 (m), 1130 (w), 1096 (w), 1090 (w), 1063 (m), 1018 (m), 972 (w), 951 (m), 928 (w), 766 (s), 741 (s), 718 (s), 687 (m). Elemental analysis calc. for $C_{24}H_{17}NS_3$: C 69.36, H 4.12, N 3.37, S 23.14; found: C 69.23, H 4.24, N 3.29, S 23.08.

1.2.4.14 6-(2-methoxy-6-methylphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3t)

The product was prepared in accordance to general procedure V.

6-(2-chloro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin (3q)	**PEPPSI-IPr**	**MeMgCl** (3.00 M)	**solvent**
0.609 mmol	15.0 mmol%	0.730 mmol	8.0 mL
275 mg	61.9 mg	243 µL	THF

The solution of methylmagnesium chloride in THF (3.00 M) was added at a rate of 12.0 µL min^{-1}. The product was eluted by flash column chromatography with ^{n}hexane/THF in a ratio from 100:2. After repeated washing with ^{n}pentane (25 mL) while ultrasonification the product was isolated. Yield: yellow powder, 101 mg, 0.282 mmol, 46%; Mp.: 248°C°;^{1}H NMR (300 MHz, THF-d_8) δ 2.45 (s, 3H), 3.79 (s, 3H), 6.97 – 7.08 (m, 2H), 7.10 – 7.18 (m, 2H), 7.22 – 7.28 (m, 2H), 7.29 – 7.37 (m, 2H), 7.38 – 7.46 (m, 1H), 7.51 – 7.56 (m, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 17.6 (CH_3), 56.4 (CH_3), 97.6 ($C_{quart.}$), 111.4 (CH), 119.9 (CH), 122.7 (CH), 123.5 (CH), 123.8 (CH), 125.9 (CH), 129.8 ($C_{quart.}$), 132.1 (CH), 134.1 ($C_{quart.}$), 137.8 ($C_{quart.}$), 141.4 ($C_{quart.}$), 142.1 ($C_{quart.}$), 158.8 ($C_{quart.}$). HR-ESI-MS calc. for [$C_{24}H_{17}NOS_3$]$^{+}$: 431.0472; found: 431.0471. IR: $\tilde{\nu}$ [cm^{-1}] = 1587 (w), 1570 (w), 1558 (m), 1508 (s), 1473 (m), 1456 (m), 1435 (s), 1279 (s), 1260 (m), 1240 (s), 1082 (s), 1065 (m), 1018 (w), 910 (w), 850 (w), 789 (w), 758 (m), 741 (s), 716 (s). Elemental analysis calc. for $C_{24}H_{17}NOS_3$: C 66.79, H 3.97, N 3.25, S 22.29; found: C 66.75, H 3.88, N 3.19, S 22.43.

1.2.4.15 6-(2,6-dimethoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3j)

The product was prepared in accordance to general procedure IV.

3,9-dibromo-6-(2,6-dimethoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4d)	**TMEDA**	**^{n}butyllithium** (1.60 M)	**methanol**	**solvent**
0.0758 mmol	0.182 mmol	0.182 mmol	0.758 mmol	2.50 mL
45.9 g	21.1 mg	114 µl	457 µl	THF

In addition to that, distilled water was added to the reaction mixture. The followingly extraction was carried out with dichloromethane (3 x 20 mL) and the combined organic phases were dried with magnesium sulfate (anhydrous). After repeated washing with ethylacetate (5 mL) and ^{n}pentane (20 mL) while ultrasonification the product was isolated. Yield: orange powder, 31.1 mg, 0.069 mmol, 92 %; Mp.: 267-268°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 3.82 (s, 6H), 6.79 – 6.84 (m, 2H), 7.09 – 7.16 (m, 2H), 7.19 – 7.25 (m, 2H), 7.28 – 7.35 (m, 2H), 7.43 – 7.54 (m, 3H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 56.5 (CH_3), 97.7 (C_{quart}), 105.6 (CH), 119.2 (C_{quart}), 119.8 (CH), 122.5 (CH), 123.2 (CH), 125.7 (CH), 132.5 (CH), 133.9 (C_{quart}), 137.8 (C_{quart}), 142.9 (C_{quart}), 159.6 (C_{quart}). HPLC (99%) and HR-ESI-MS calc. for $[C_{24}H_{17}NO_2S_3]^+$: 448.0455; found: 448.0499. IR: $\tilde{\nu}$ [cm^{-1}] = 2961 (w), 2837 (w), 1589 (m), 1570 (m), 1555 (w), 1512 (s), 1477 (s), 1456 (m), 1433 (s), 1346 (w), 1290 (s), 1258 (s), 1244 (m), 1175 (w), 1157 (w), 1113 (s), 1065 (w), 1034 (w), 1018 (w), 949 (w), 789 (m), 738 (s), 714 (s), 640 (w). Elemental analysis calc. for $C_{24}H_{17}NO_2S_3$: C 64.40, H 3.83, N 3.13, S 21.49; found: C 64.24, H 3.89, N 3.10, S 21.36.

1.2.5 *Anti-anti*-3,9-dibromo-*N*-*ortho(,ortho')*-(di)substituted-Phenyl-BBTT 4

1.2.5.1 3,9-Dibromo-6-(*o*-tolyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4a)

The product was prepared in accordance to general procedure III.

bis(2,6-dibromobenzo[*b*]thiophen-3-yl)sulfane (2)	**2-methylaniline**	**$Pd(dba)_2$**	**BINAP**	**sodium^{tert}butoxide**	**solvent / reaction time**
1.00 mmol	1.00 mmol	3.00 mol%	5.00 mol%	3.00 mmol	4.00 mL toluene

614 mg	107 mg	17.3 mg	31.1 mg	288 mg	24 h

The product was eluted by a doulbly flash column chromatography with first ^{n}hexane/triethylamine in a ratio of 100:1 and second ^{n}hexane as eluent. Yield: orange powder, 345 mg, 0.2617 mmol, 31%; Mp.: 167°C; ^{1}H NMR (300 MHz, THF-d_8) δ 2.46 (s, 3H), 7.20 (d, $^{3}J_{HH}$ = 8.43 Hz, 2H), 7.37 – 7.54 (m, 5H), 7.53 – 7.60 (m, 1H), 7.79 (d, $^{4}J_{HH}$ = 1.79 Hz, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 17.7 (CH_3), 98.7 (C_{quart}), 116.9 (C_{quart}), 121.4 (CH), 125.5 (CH), 129.3 (CH), 129.5 (CH), 130.6 (CH), 131.7 (CH), 133.5 (CH), 135.9 (C_{quart}), 136.2 (C_{quart}), 139.2 (C_{quart}), 141.3 (C_{quart}), 142.7 (C_{quart}). EI-MS (*m/z* (%)): 560.9 ($[C_{23}H_{13}{}^{81}Br_2NS_3]^+$, 60), 558.9 ($[C_{23}H_{13}{}^{79}Br^{81}BrNS_3]^+$, 100), 556.9 ($[C_{23}H_{13}{}^{79}Br_2NS_3]^+$, 48), 469.8 ($[C_{16}H_6{}^{81}Br_2NS_3]^+$, 39), 467.8 ($[C_{16}H_6{}^{79}Br^{81}BrNS_3]^+$, 65), 465.8 ($[C_{23}H_{13}{}^{79}Br_2NS_3]^+$, 30), 455.8 ($[C_{16}H_6{}^{81}Br_2S_3]^+$, 20), 453.8 ($[C_{16}H_6{}^{81}Br^{79}BrS_3]^+$, 32), 451.8 ($[C_{16}H_6{}^{79}Br_2S_3]^+$, 16), 388.9 ($[C_{16}H_6{}^{81}BrNS_3]^+$, 29), 386.9 ($[C_{16}H_6{}^{79}BrNS_3]^+$, 28), 308.0 ($[C_{16}H_6NS_3]^+$, 14), 293.9 ($[C_{16}H_6S_3]^+$, 15). IR: $\tilde{\nu}$ [cm^{-1}] = 1562 (w), 1544 (m), 1504 (s), 1445 (s), 1387 (w), 1285 (m), 1271 (m), 1259 (m), 1233 (m), 1132 (w), 1114 (w), 1080 (w), 1051 (w), 961 (w), 943 (w), 847 (m), 793 (s), 758 (m), 725 (m), 692 (w). Elemental analysis calc. for $C_{23}H_{13}Br_2NS_3$: C 49.39, H 2.34, N 2.50, S 17.19; found: C 49.51, H 2.54, N 2.45, S 17.38.

1.2.5.2 3,9-Dibromo-6-(2-chloro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4b)

The product was prepared in accordance to general procedure III.

bis(2,6-dibromobenzo[*b*]thiophen-3-yl)sulfane (2)	**2-chloro-6-methoxyaniline**	**Pd(dba)$_2$**	**BINAP**	**sodium^{tert}butoxide**	**solvent / reaction time**
15.0 mmol	15.0 mmol	5.00 mol%	10.00 mol%	45.0 mmol	60.0 mL toluene
9.21 g	2.36 g	216 mg	467 mg	4.32 g	42 h

In addition to that, the reaction mixture was filtrated through Celite xx, and washed with water (100 mL). Extraction of the filtrate was carried out with dichloromethane (3 x 250 mL) and the combined organic phases were dried with sodium sulfate (anhydrous). The product was eluted by a doubly flash column chromatography with first ^{n}hexane/THF in a ratio of 5:1 and second a gradient of cyclohexane/THF in a ratio of 5:1 to 5:2 as eluent. Yield: orange powder, 982 mg, 1.61 mmol, 11%; Mp.: 321-324°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 3.86 (s, 3H), 7.20 (d, $^{3}J_{HH}$ = 8.47 Hz, 2H), 7.22 – 7.29 (m, 2H), 7.50 (dd, $^{3}J_{HH}$ = 8.48, $^{4}J_{HH}$ = 1.80 Hz, 2H), 7.56 (t, $^{3}J_{HH}$ = 8.36 Hz, 1H), 7.79 (d, $^{4}J_{HH}$ = 1.77 Hz, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 57.1 (CH_3), 98.7 ($C_{quart.}$), 112.9 (CH), 116.8 ($C_{quart.}$), 121.4 (CH), 123.2 (CH), 125.5 (CH), 127.9 ($C_{quart.}$), 129.4

(CH), 133.4 (CH), 135.6 ($C_{quart.}$), 136.3 ($C_{quart.}$), 137.5 ($C_{quart.}$), 141.9 ($C_{quart.}$), 160.2 ($C_{quart.}$). ESI-MS (m/z): 606.8 ($[C_{23}H_{12}{}^{79}Br_2{}^{35}ClNOS_3]^+$), 608.8 ($[C_{23}H_{12}{}^{79}Br^{81}Br^{35}ClNOS_3]$; $[C_{23}H_{12}{}^{79}Br_2{}^{37}ClNOS_3]^+$), 610.8 ($[C_{23}H_{12}{}^{81}Br_2{}^{35}ClNOS_3]$; $[C_{23}H_{12}{}^{79}Br^{81}Br^{37}ClNOS_3]^+$), 612.8 ($[C_{23}H_{12}{}^{81}Br_2{}^{37}ClNOS_3]^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 1582 (w), 1539 (w), 1506 (m), 1445 (s), 1386 (w), 1287 (s), 1261 (m), 1237 (m), 1053 (s), 945 (w), 847 (w), 787 (s), 746 (m), 646 (w). Elemental analysis calc. for $C_{23}H_{12}Br_2ClNOS_3$: C 45.30, H 1.98, N 2.30, S 15.77; found: C 45.54, H 2.27, N 2.17, S 15.80.

1.2.5.3 3,9-Dibromo-6-(2-fluoro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4c)

The product was prepared in accordance to general procedure III.

bis(2,6-dibromobenzo[*b*]thiophen-3-yl)sulfane (2)	**2-methoxy, 6-fluoroaniline**	**$Pd(dba)_2$**	**BINAP**	**sodium*tert*butoxide**	**solvent / reaction time**
1.00 mmol	1.00 mmol	5.00 mol%	10.0 mol%	3.00 mmol	4.00 mL toluene
614 mg	141 mg	28.8 mg	62.2 mg	288 g	48 h

The product was eluted by a flash column chromatography with *n*hexane/THF in a ratio of 100:3 as eluent. Recrystallization was carried out in toluene (5 mL). Yield: orange powder, 261 mg, 0.440 mmol, 44%; Mp.: 264°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 3.87 (s, 3H), 6.95 – 7.05 (m, 1H), 7.07 – 7.14 (m, 1H), 7.16 – 7.24 (m, 2H), 7.50 (dd, $^3J_{HH}$ = 8.49, $^4J_{HH}$ = 1.82 Hz, 2H), 7.53 – 7.64 (m, 1H), 7.77 – 7.82 (m, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 57.1 (CH_3), 98.9 ($C_{quart.}$), 109.7 (CH, d, $^2J_{CF}$ = 22.7 Hz), 109.8 (CH), 116.9 ($C_{quart.}$), 118.6 ($C_{quart.}$, d, $^2J_{CF}$ = 14.8 Hz), 121.4 (CH), 125.5 (CH), 129.5 (CH), 133.6 (CH, d, $^3J_{CF}$ = 10.5 Hz), 135.6 ($C_{quart.}$), 136.3 ($C_{quart.}$), 142.5 ($C_{quart.}$), 159.9 ($C_{quart.}$, d, $^3J_{CF}$ = 2.7 Hz), 162.0 ($C_{quart.}$, d, $^1J_{CF}$ = 252.0 Hz). ^{19}F-NMR (282 MHz, THF) δ -121.67. EI-MS (*m/z* (%)): 595 ($[C_{23}H_{12}{}^{81}Br_2FNS_3]^+$, 60), 593 ($[C_{23}H_{12}{}^{79}Br^{81}BrFNS_3]^+$, 100), 591 ($[C_{23}H_{12}{}^{79}Br_2FNS_3]^+$, 56), 514 ($[C_{23}H_{12}{}^{81}BrFNS_3]^+$, 12), 512 ($[C_{23}H_{12}{}^{79}BrFNS_3]^+$, 10), 470 ($[C_{16}H_6{}^{81}Br_2NS_3]^+$, 28), 468 ($[C_{16}H_6{}^{79}Br^{81}BrNS_3]^+$, 48), 466 ($[C_{16}H_6{}^{79}Br_2NS_3]^+$, 23), 389 ($[C_{16}H_6{}^{81}BrS_3]^+$, 16), 387 ($[C_{16}H_6{}^{79}BrS_3]^+$, 14), 297 (17). Elemental analysis calc. for $C_{23}H_{12}Br_2FNOS_3$: C 46.56, H 2.04, N 2.36, S 16.21; found: C 46.87, H 2.31, N 2.30, S 16.40.

1.2.5.4 3,9-Dibrom-6-(2,6-dimethoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4d)

The product was prepared in accordance to general procedure III.

bis(2,6-dibromobenzo[*b*]thiophen-3-yl)sulfane (2)	2,6-dimethoxyaniline	$Pd(dba)_2$	BINAP	sodium*tert*butoxide	solvent / reaction time
2.00 mmol	2.00 mmol	3.00 mol%	5.00 mol%	6.00 mmol	8.00 mL toluene
1.23 g	306 mg	34.6 mg	62.2 mg	576 mg	48 h

The product was eluted by a flash column chromatography with a gradient of *n*hexane/THF in a ratio of 100:0 to 10:1 as eluent. The crude product obtained was purified by washing with *n*pentane (15 mL) while ultrasonification. A second flash column chromatographic purification was then carried out with cyclohexane/tetrahydrofuran/triethylamine in a ratio of 100:5:2. After repeated washing with *n*pentane (10 mL) while ultrasonification the product was isolated. Yield: orange powder87.7 mg, 0.145 mmol, 7%; Mp.: 252-253°C°; ^{1}H NMR (300 MHz, THF-d_8) δ 3.82 (s, 6H), 6.80 (d, $^3J_{HH}$ = 8.50 Hz, 2H), 7.12 (d, $^3J_{HH}$ = 8.44 Hz, 2H), 7.43 – 7.49 (m, 3H), 7.70 (d, $^4J_{HH}$ = 1.79 Hz, 2H). ^{13}C-{^{1}H}-NMR (75 MHz, THF-d_8) δ 56.6 (CH_3), 97.7 ($C_{quart.}$), 105.7 (CH), 116.4 ($C_{quart.}$), 118.7 ($C_{quart.}$), 121.0 (CH), 125.2 (CH), 129.1 (CH), 132.9 (CH), 135.5 ($C_{quart.}$), 136.5 ($C_{quart.}$), 143.6 ($C_{quart.}$), 159.4 ($C_{quart.}$). EI-MS (*m/z* (%)): 608.9 ($[C_{24}H_{15}{}^{81}Br_2NO_2S_3]^+$, 12), 606.9 ($[C_{24}H_{15}{}^{79}Br^{81}BrN\ O_2S_3]^+$, 25), 604.9 ($[C_{24}H_{15}{}^{79}Br_2N\ O_2S_3]^+$, 20), 455.8 ($[C_{16}H_6{}^{81}Br_2S_3]^+$, 58), 453.8 ($[C_{16}H_6{}^{79}Br^{81}BrS\ _3]^+$, 100), 451.8 ($[C_{16}H_6{}^{79}Br_2S_3]^+$, 48), 374.9 ($[C_{16}H_6{}^{81}BrS_3]^+$, 26), 372.8 ($[C_{16}H_6{}^{79}BrS_3]^+$, 24), 293.9 ($[C_{16}H_6S_3]^+$, 32), 226.9 (28), 146.9 (34). IR: $\tilde{\nu}$ [cm^{-1}] = 1587 (m), 1562 (w), 1541 (m), 1504 (m), 1481 (m), 1440 (m), 1389 (w), 1296 (m), 1261 (s), 1236 (w), 1117 (s), 1051 (w), 995 (w), 945 (m), 849 (m), 790 (s), 741 (m), 659 (w). Elemental analysis calc. for $C_{24}H_{15}Br_2NO_2S_3$: C 47.62, H 2.50, N 2.31, S 15.89; found: C 47.93, H 2.58, N 2.28, S 15.88.

1.2.6 Byproducts

1.2.6.1 Dibenzo[*d,d'*] thieno[3,2-*b'*; 4,5-*b'*]dithiophene

The product could be isolated for all syntheses according to general procedure I and II as byproduct formed by the dibrominated sulfane **1**. ^{1}H NMR (600 MHz, THF-d_8) δ 7.39 – 7.43 (m, 2H), 7.45 – 7.50 (m, 2H), 7.94 – 7.97 (m, 2H), 7.97 – 8.00 (m, 2H). ^{13}C-{^{1}H}-NMR (151 MHz, THF-d_8) δ 121.8 (CH), 125.2 (CH), 126.1 (CH), 126.3 (CH), 131.3 (C_{quat}), 134.4 (C_{quat}), 137.8 (C_{quat}), 143.2 (C_{quat}). EI-MS (*m/z* (%)): 296 ($[C_{16}H_8S_3]^+$, 100), 264 ($[C_{16}H_8S_2]^+$, 4), 149 (5), 148 ($[C_9H_8S]^+$, 20), 132 (5).

2 NMR-data

2.1 BBTTs

2.1.1 *Anti-anti-N-ortho*-substituted-Phenyl-BBTT 3a-e

2.1.1.1 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin-6-yl)benzonitrile (3a)

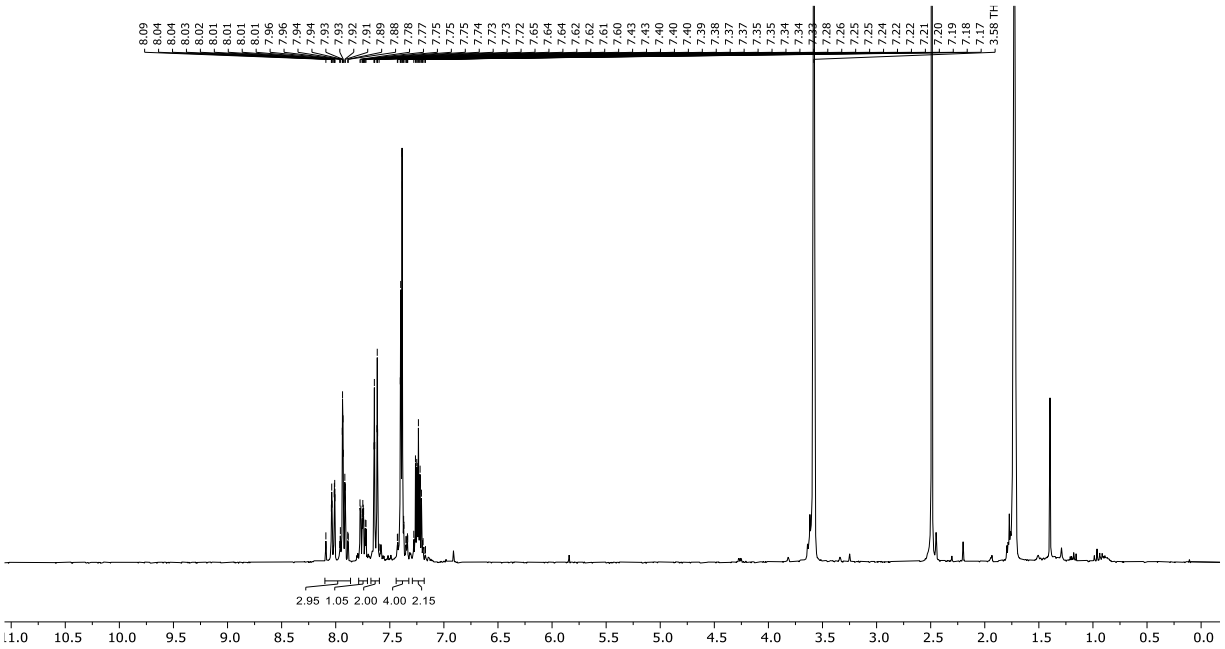


Figure 1. ^{1}H-NMR of BBTT **3a** (300 MHz, THF-d_8, 298 K).

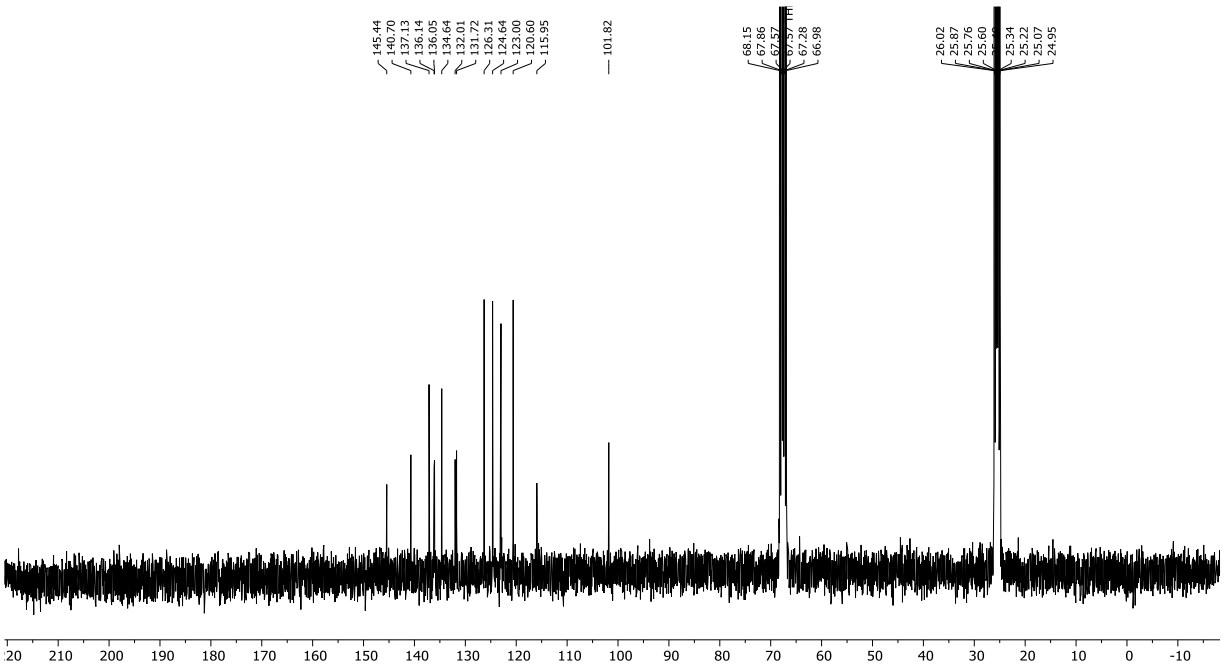


Figure 2. ^{13}C-{^{1}H}-NMR of BBTT **3a** (75 MHz, THF-d_8, 298 K).

2.1.1.2 6-Phenyl-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3b)

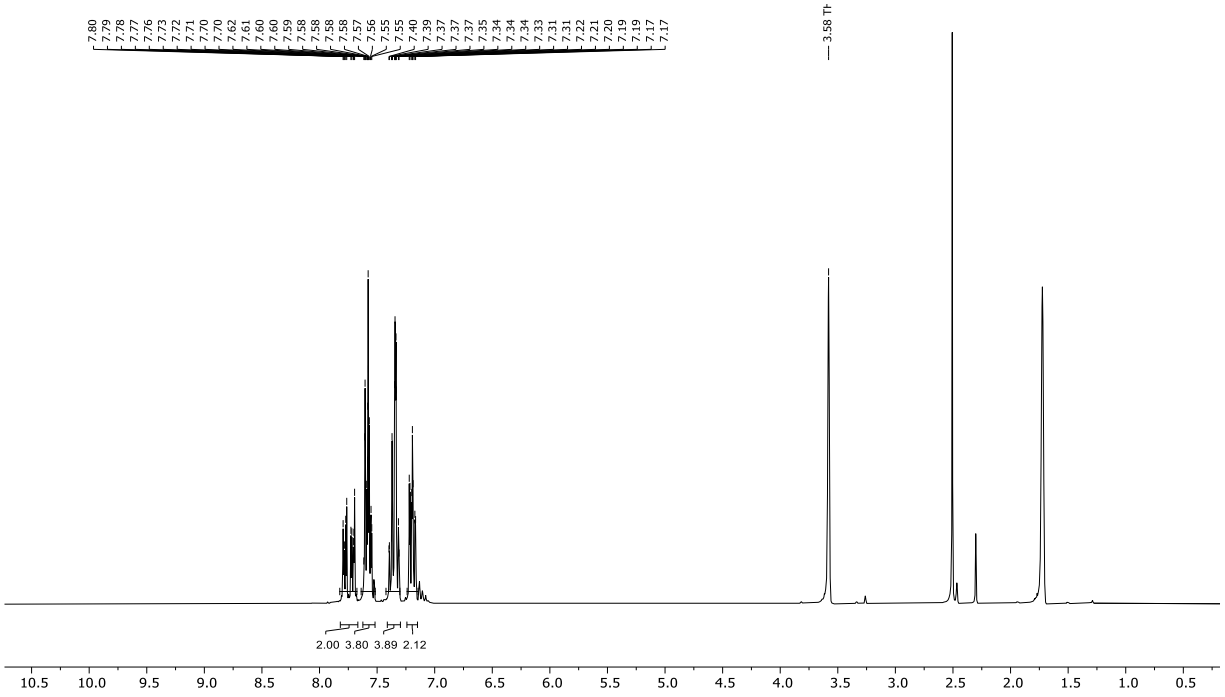


Figure 3. ^{1}H-NMR of BBTT **3b** (300 MHz, THF-d_8, 298 K).

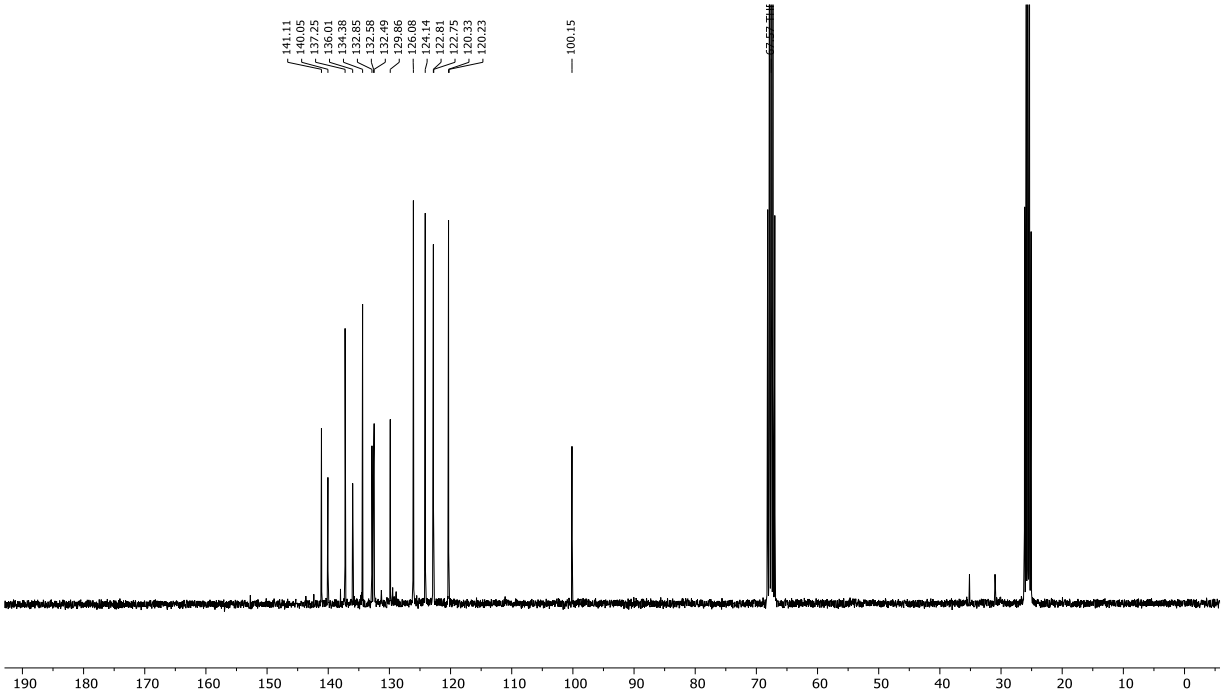


Figure 4. ^{13}C-{^{1}H}-NMR of BBTT **3b** (75 MHz, THF-d_8, 298 K).

2.1.1.3 6-(2-Fluorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5] thieno[2,3-*e*][1,4]thiazine (3c)

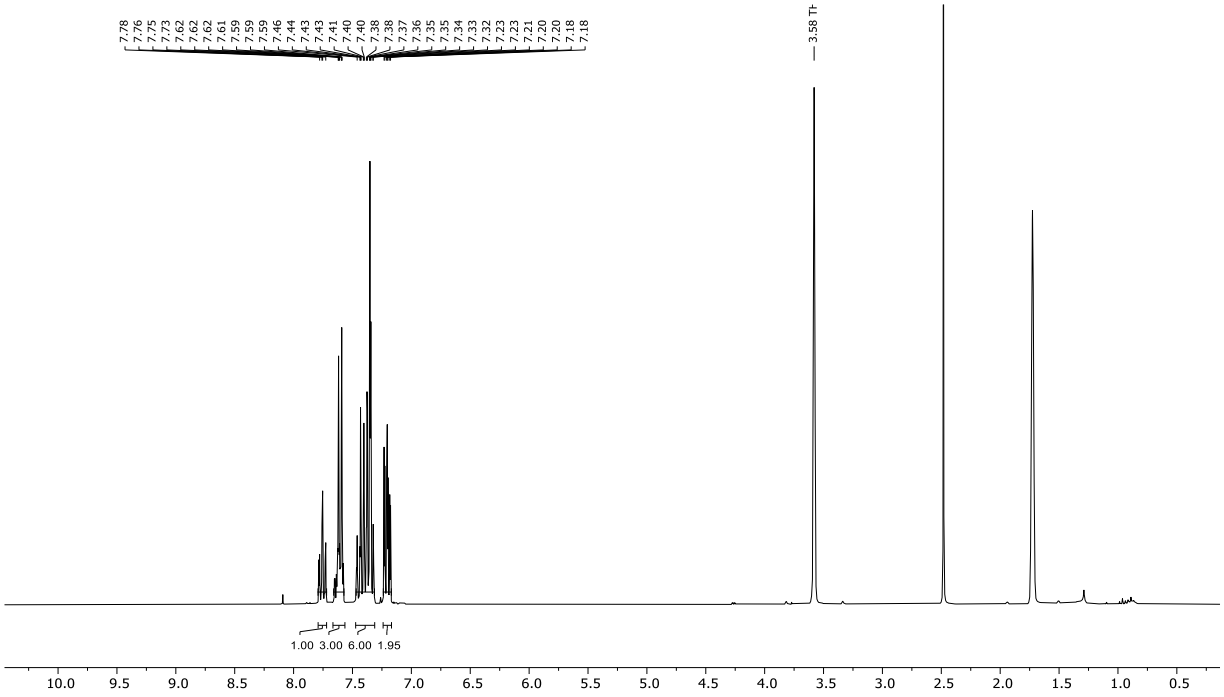


Figure 5. ^{1}H-NMR of BBTT **3c** (300 MHz, THF-d_8, 298 K).

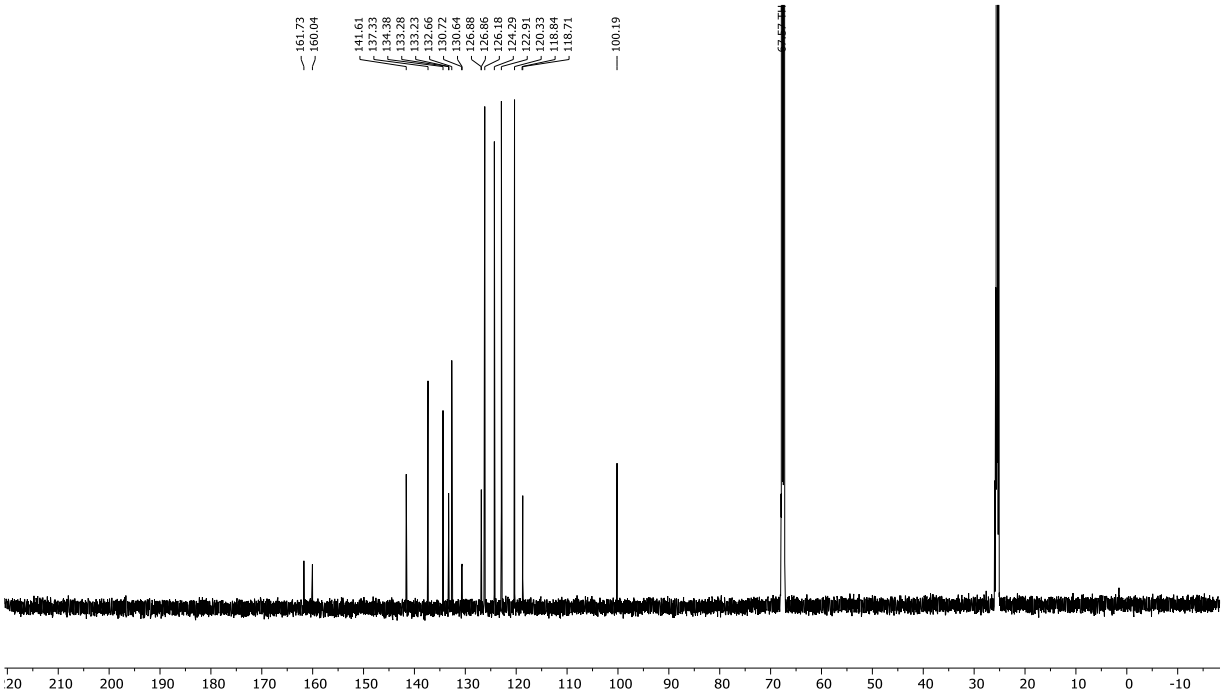


Figure 6. ^{13}C-{^{1}H}-NMR of BBTT **3c** (75 MHz, THF-d_8, 298 K).

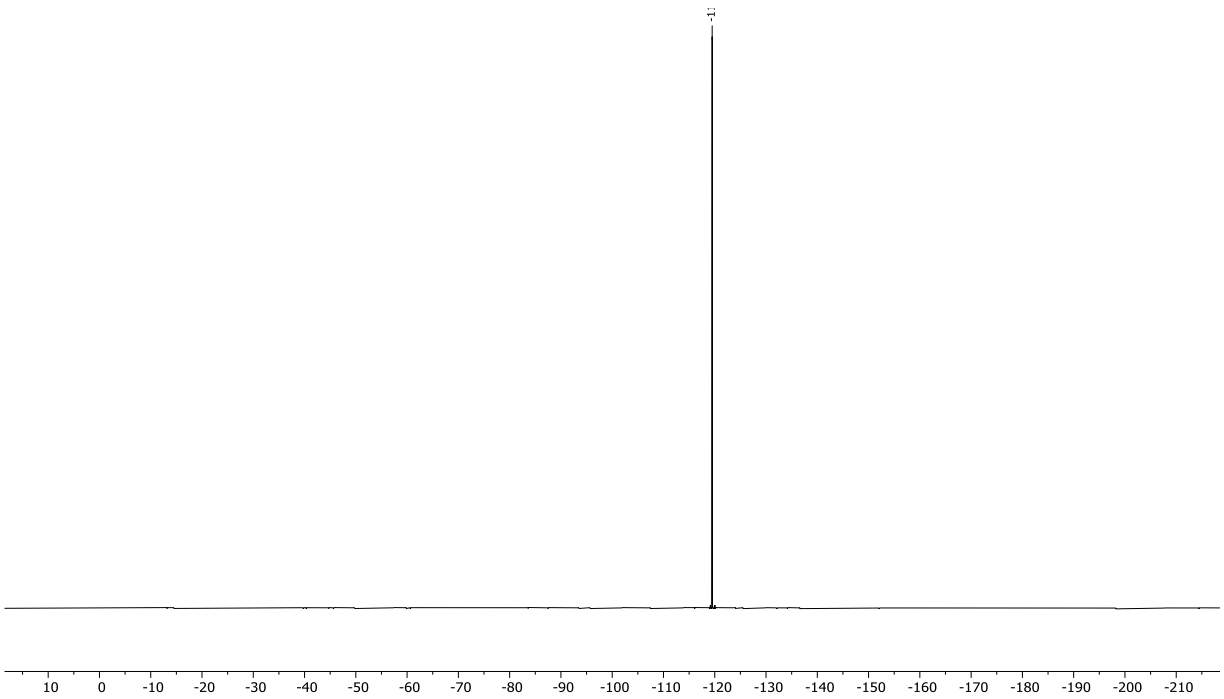


Figure 7. ^{19}F-NMR of BBTT **3c** (282 MHz, THF-d_8, 298 K).

2.1.1.4 6-(*o*-Tolyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3d)

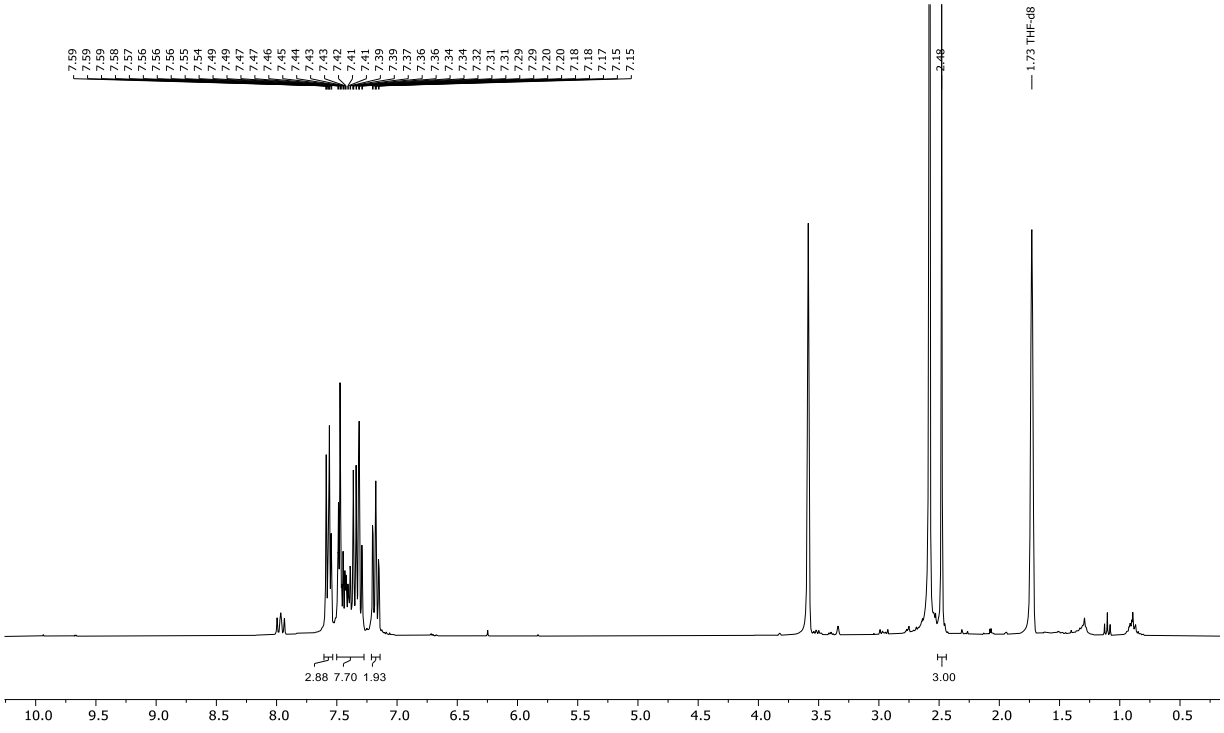


Figure 8. ^{1}H-NMR of BBTT **3d** (300 MHz, THF-d_8, 298 K).

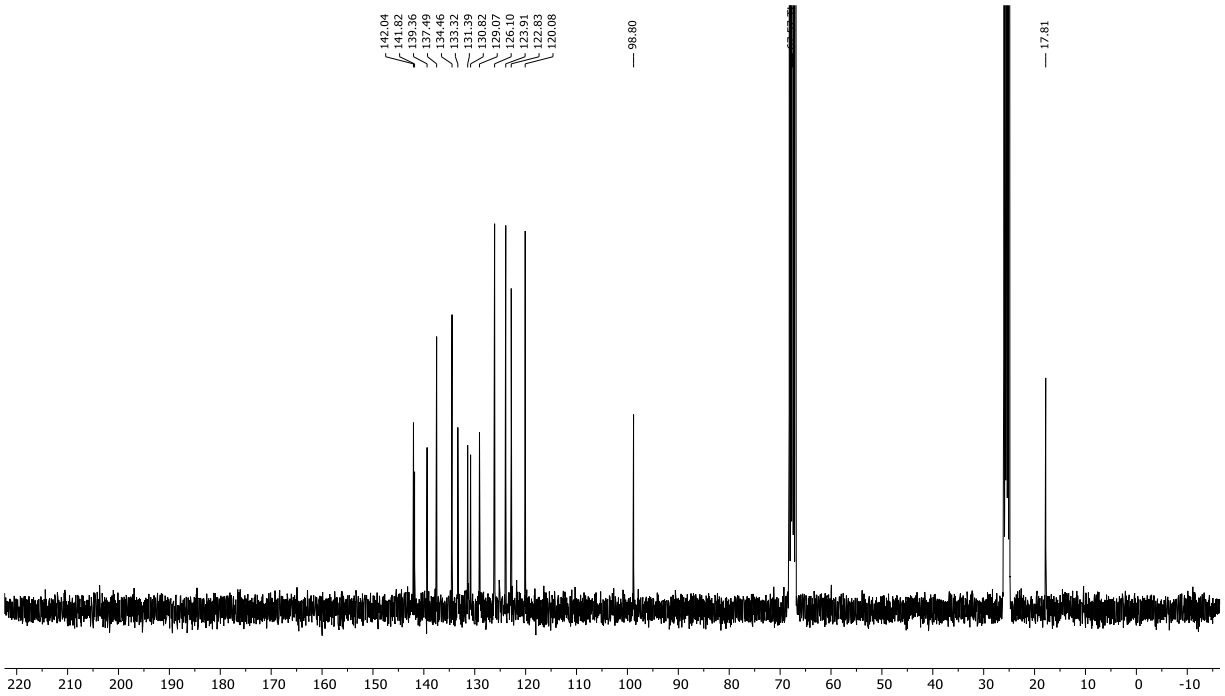


Figure 9. ^{13}C-{^{1}H}-NMR of BBTT **3d** (75 MHz, THF-d_8, 298 K).

2.1.1.5 6-(2-Methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3e)

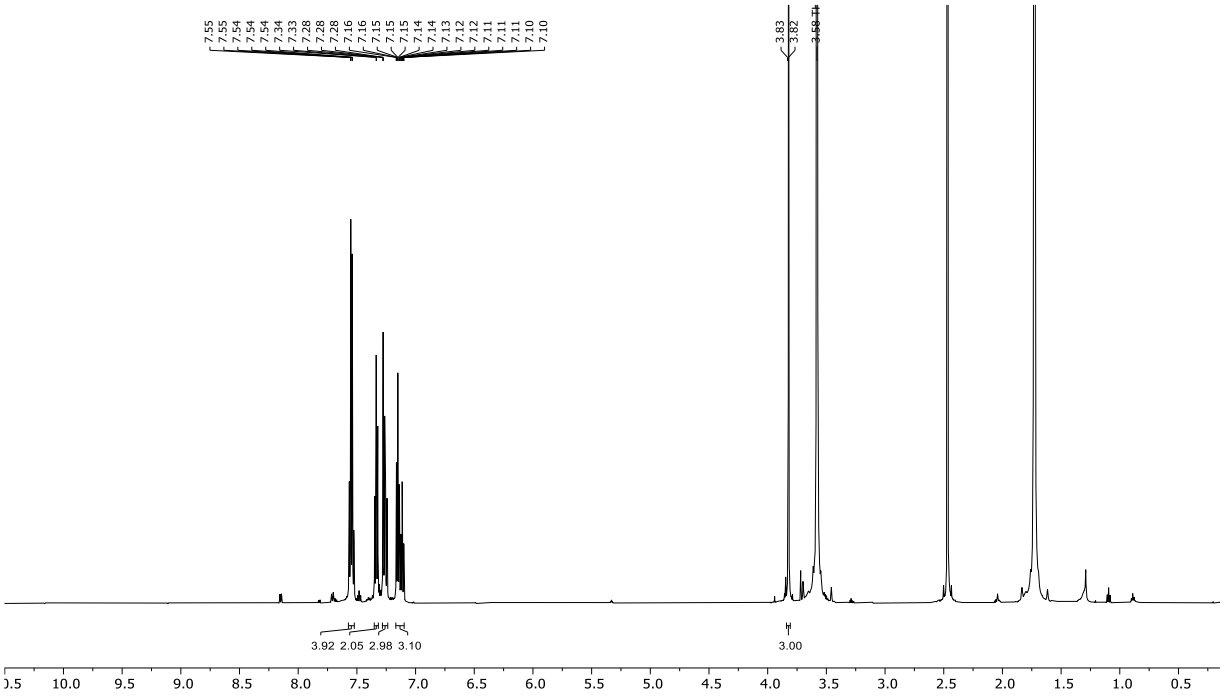


Figure 10. ^{1}H-NMR of BBTT **3e** (300 MHz, THF-d_8, 298 K).

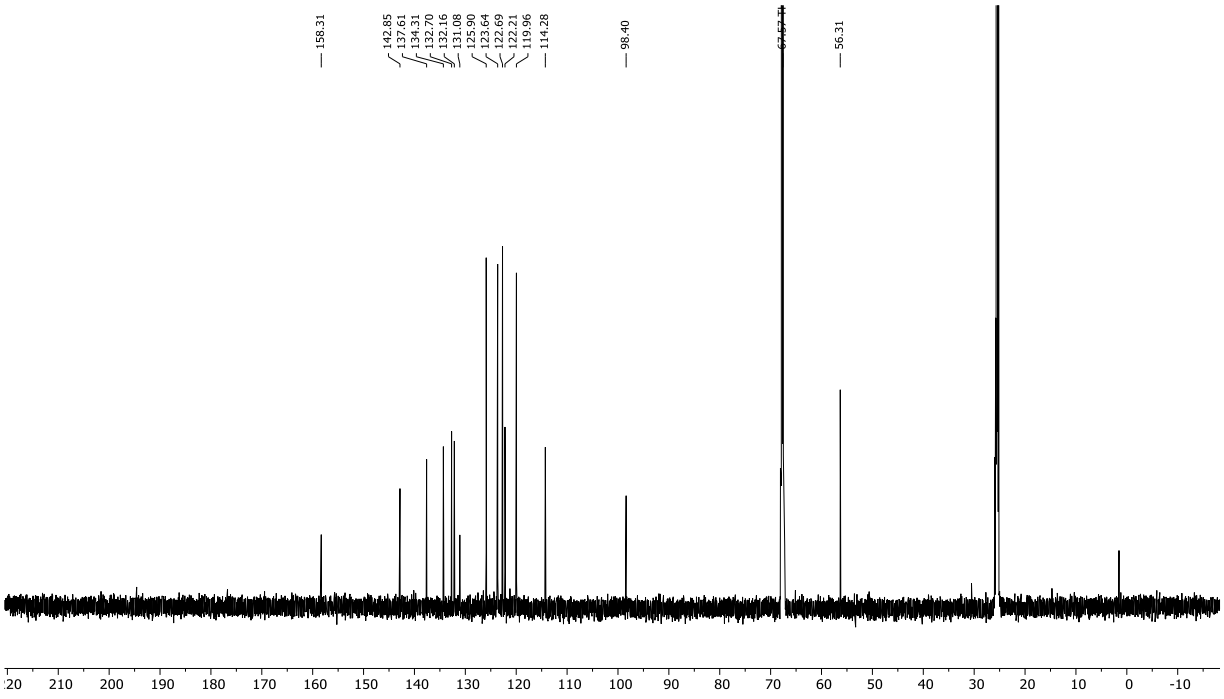


Figure 11. ^{13}C-{^{1}H}-NMR of BBTT **3e** (75 MHz, THF-d_8, 298 K).

2.1.2 *Anti-anti-N-ortho,ortho'*-disubstituted-Phenyl-BBTT

2.1.2.1 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine-6-yl)isophthalonitrile (3f)

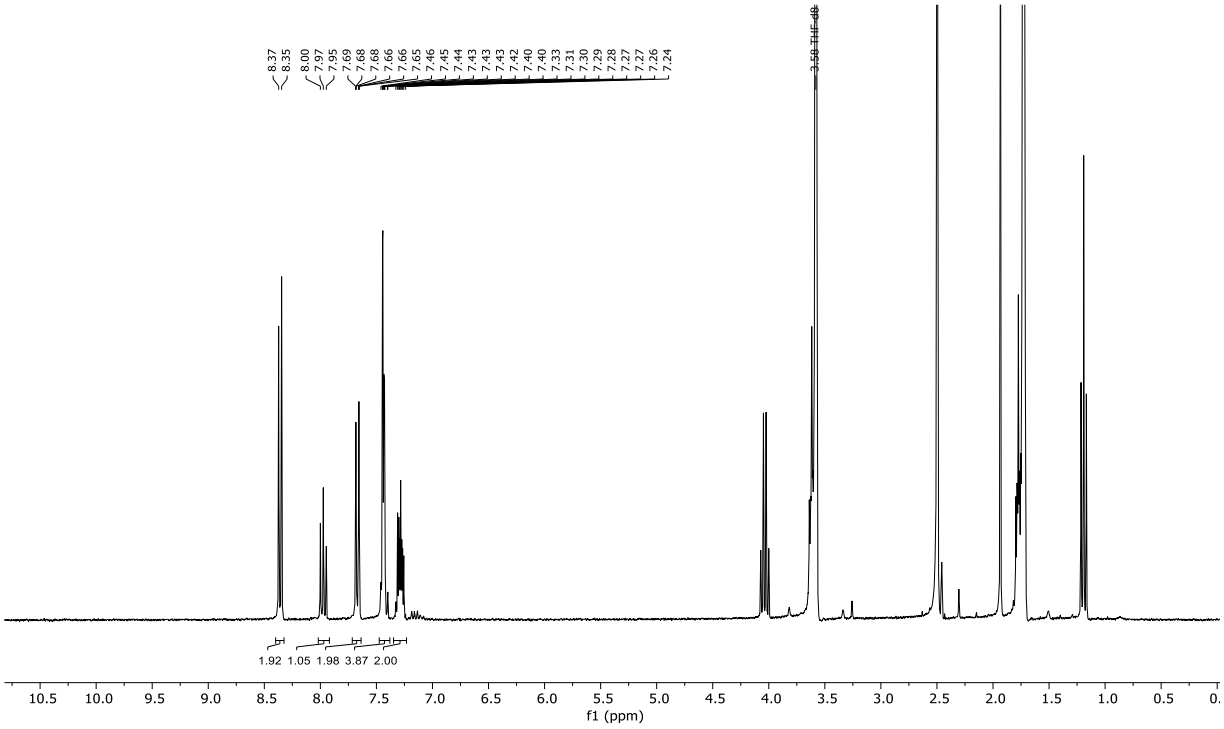


Figure 12. ^{1}H-NMR of BBTT **3f** (300 MHz, THF-d_8, 298 K).

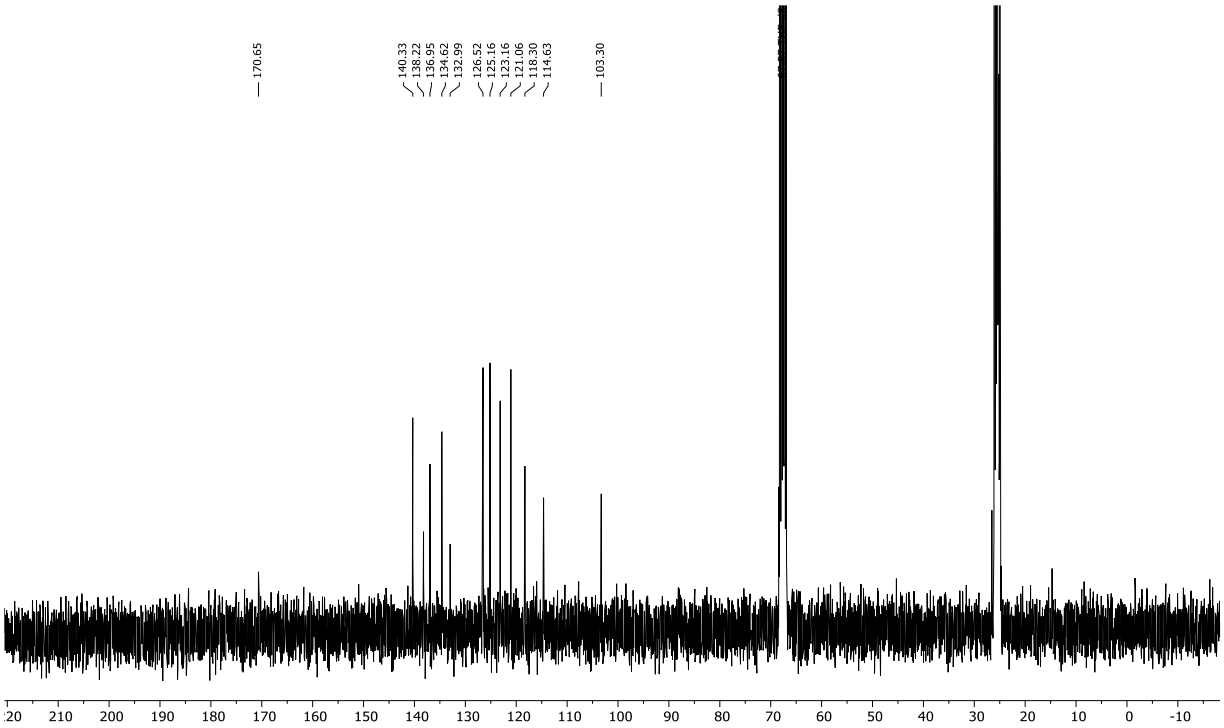


Figure 13. ^{13}C-{^{1}H}-NMR of BBTT **3f** (75 MHz, THF-d_8, 298 K).

2.1.2.2 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin-6-yl)-3-chlorobenzonitrile (3k)

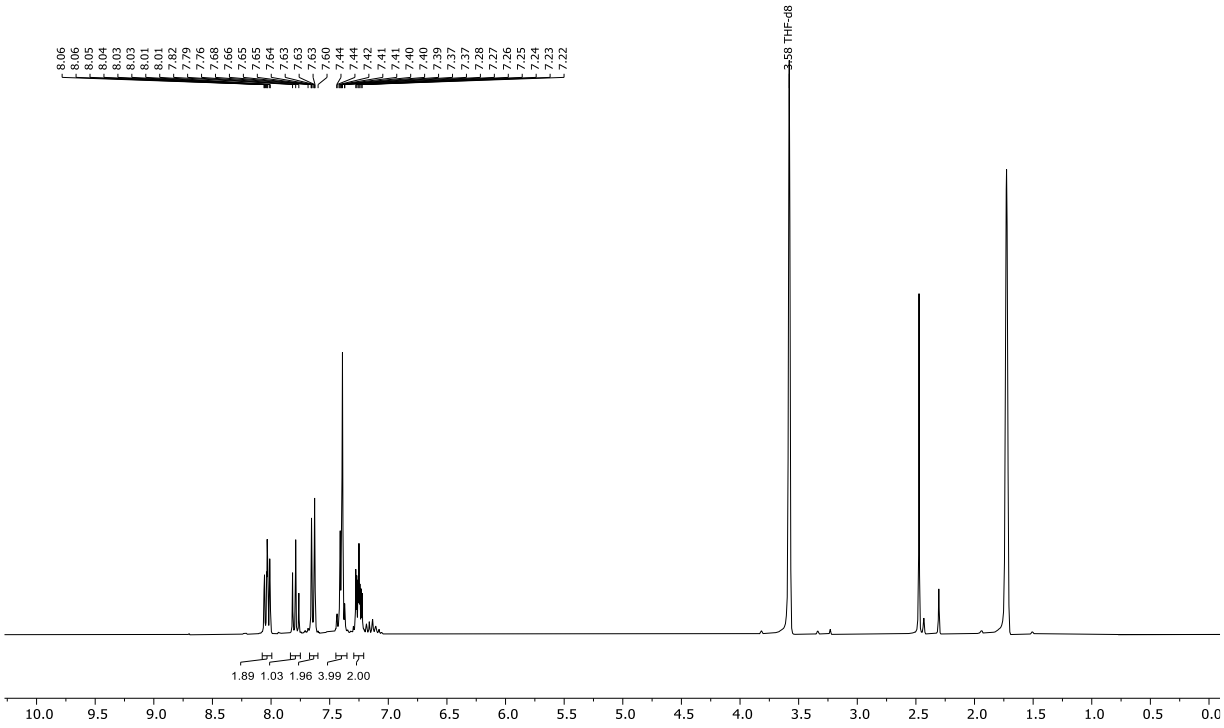


Figure 14. ^{1}H-NMR of BBTT **3k** (300 MHz, THF-d_8, 298 K).

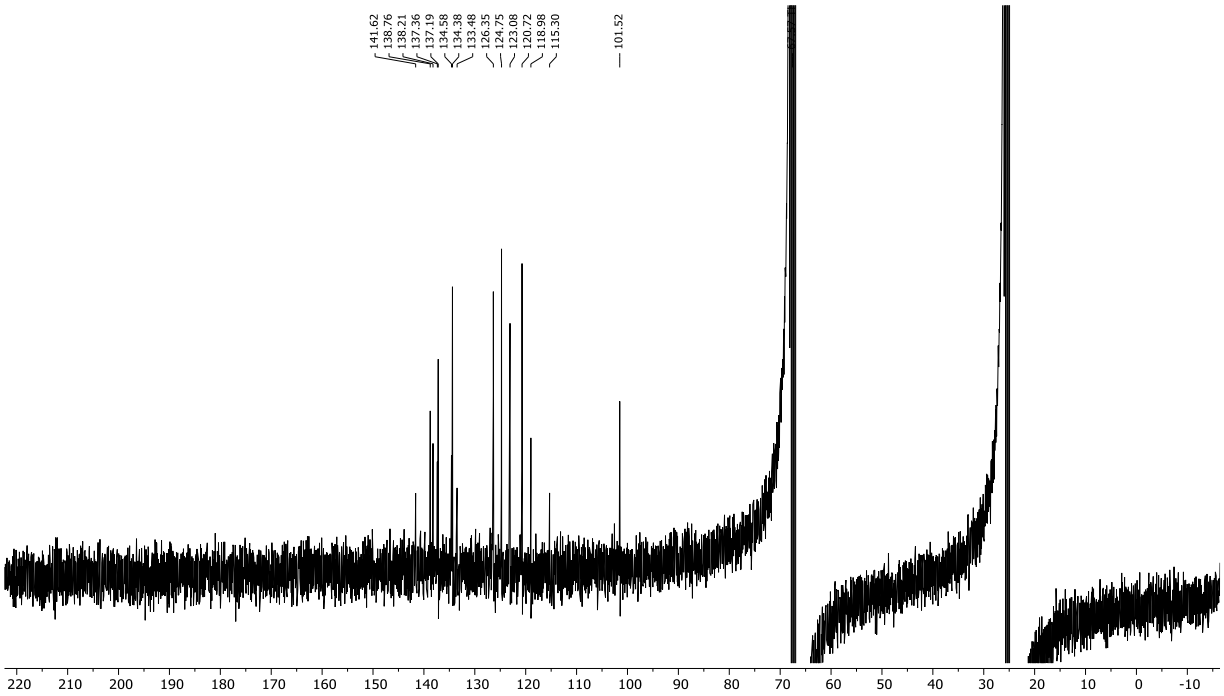


Figure 15. ^{13}C-{^{1}H}-NMR of BBTT **3k** (75 MHz, THF-d_8, 298 K).

2.1.2.3 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine-6-yl)-3-fluorobenzonitrile (3l)

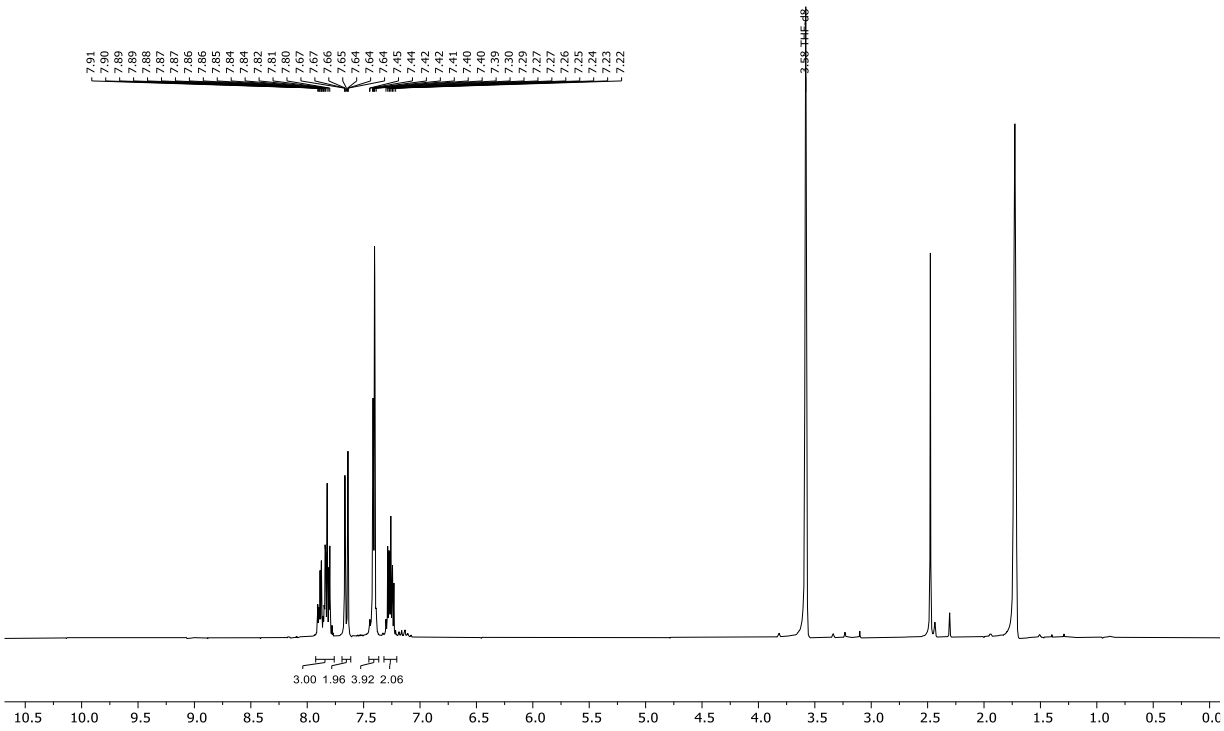


Figure 16. ^{1}H-NMR of BBTT **3l** (300 MHz, THF-d_8, 298 K).

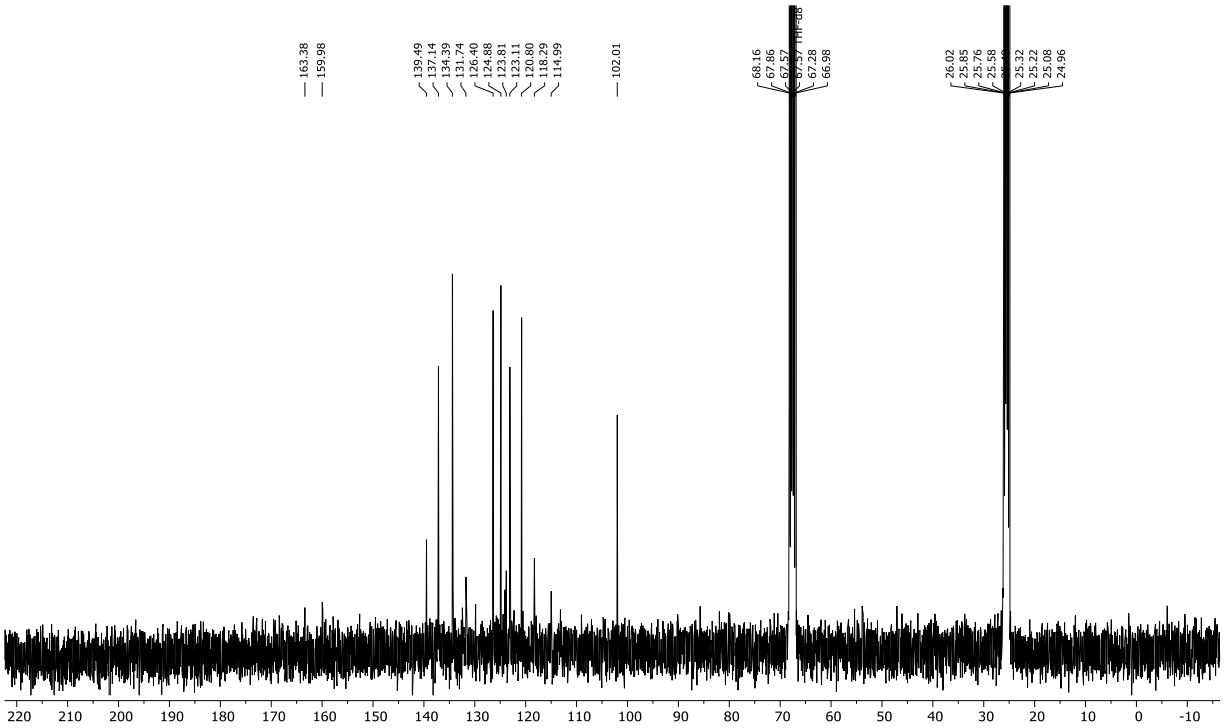


Figure 17. ^{13}C-{^{1}H}-NMR of BBTT **3l** (75 MHz, THF-d_8, 298 K).

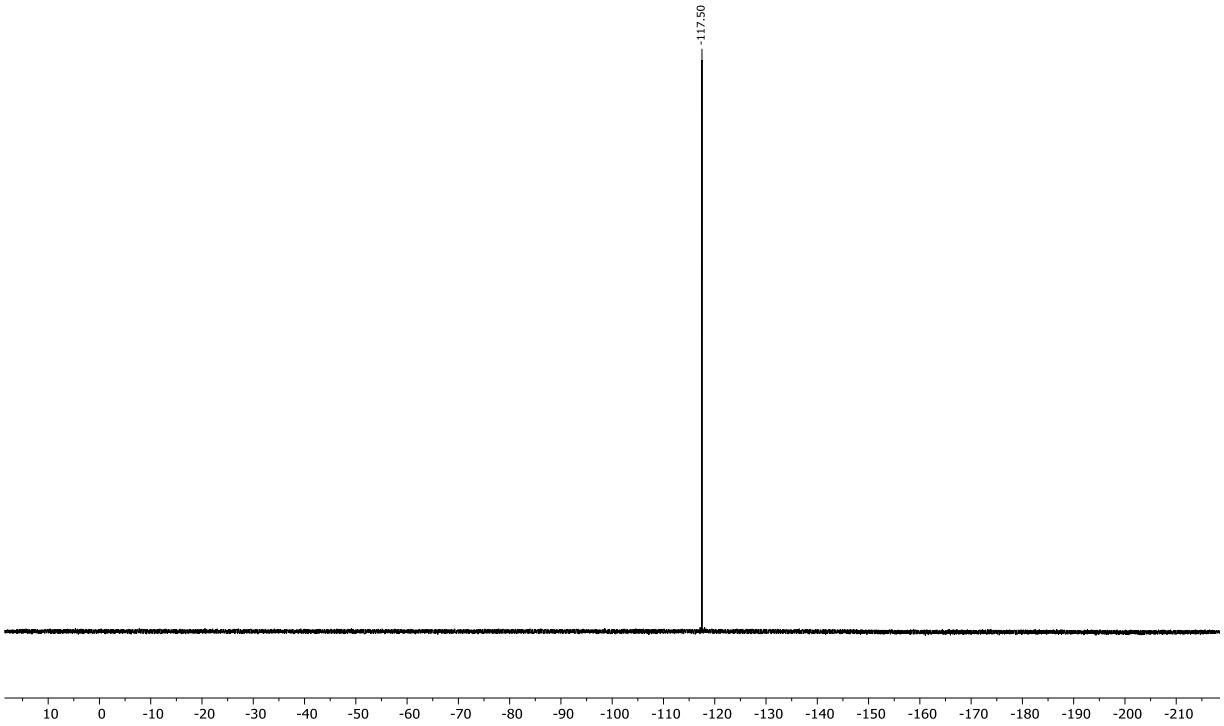


Figure 18. ^{19}F-NMR of BBTT **3l** (282 MHz, THF-d_8, 298 K).

2.1.2.4 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine-6-yl)-3-methylbenzonitrile (3m)

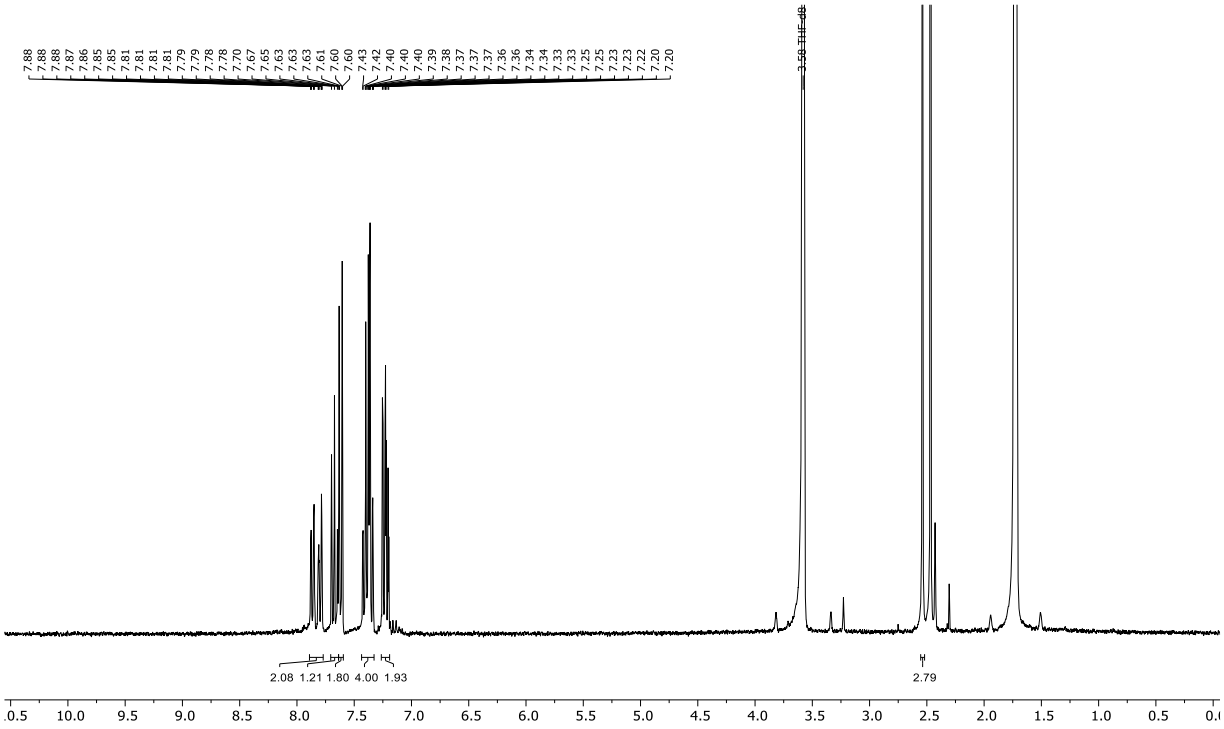


Figure 19. ^{1}H-NMR of BBTT **3m** (300 MHz, THF-d_8, 298 K).

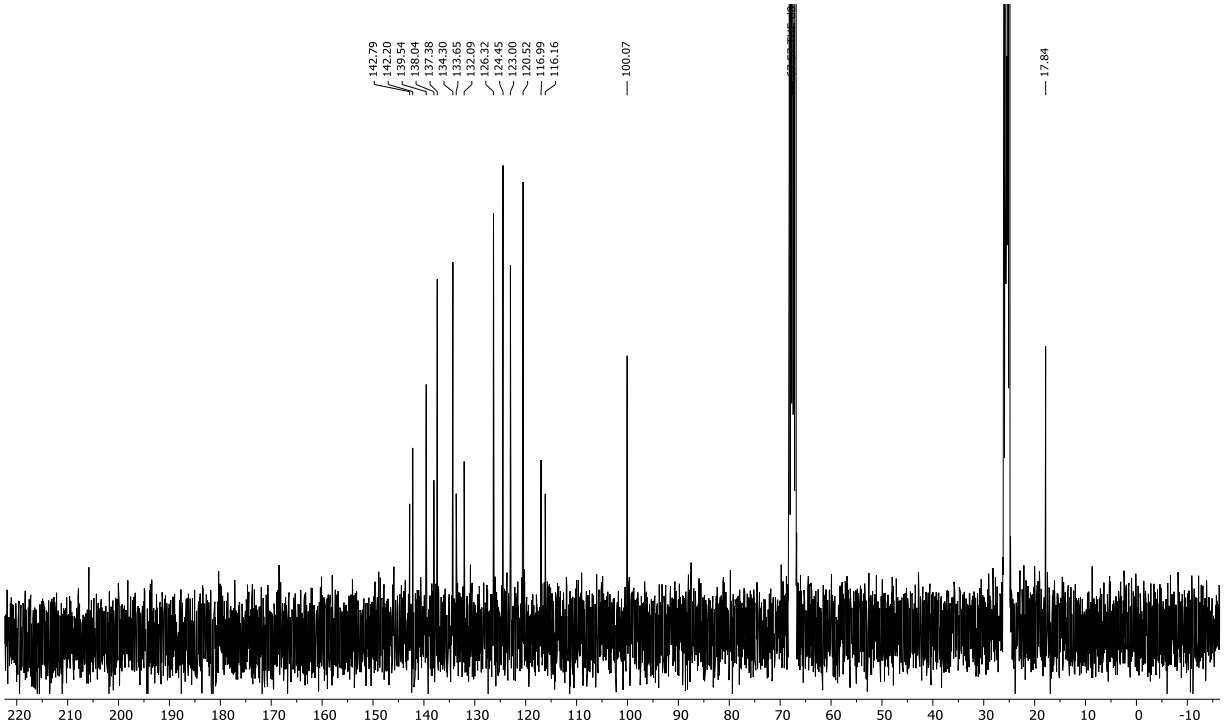


Figure 20. ^{13}C-{^{1}H}-NMR of BBTT **3m** (75 MHz, THF-d_8, 298 K).

2.1.2.5 2-(6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazin-6-yl)-3-methoxybenzonitrile (3n)

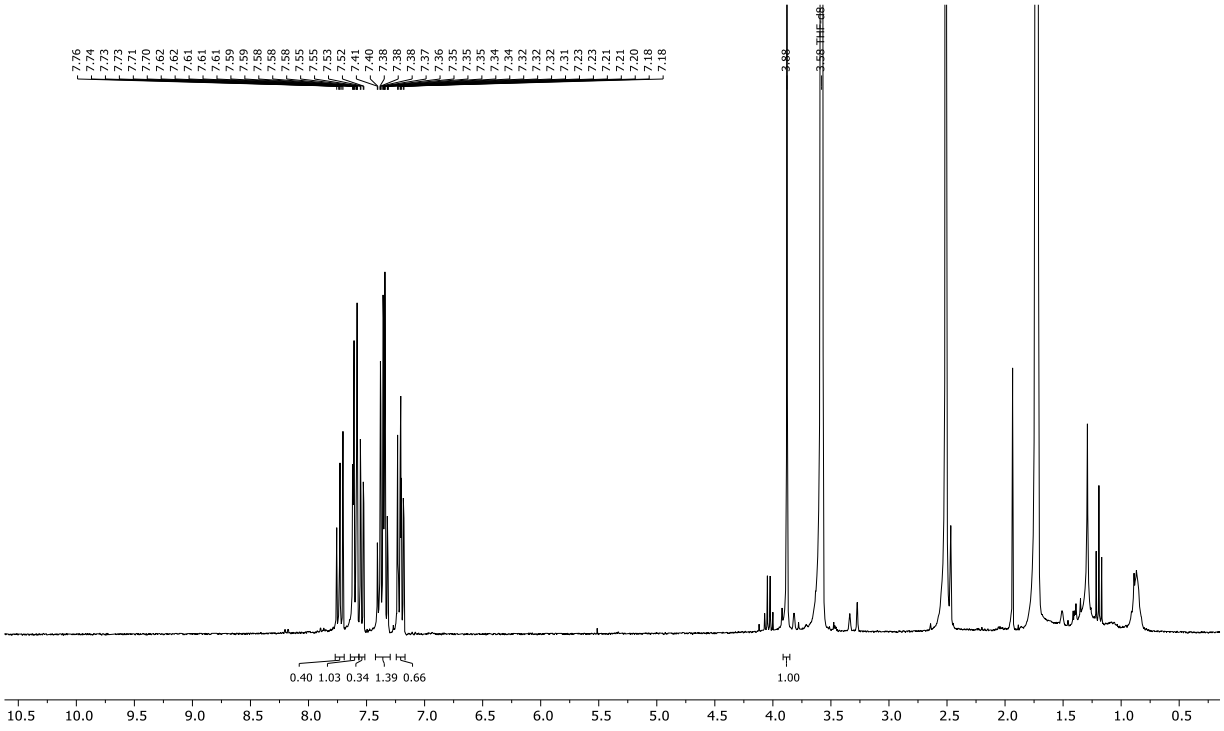


Figure 21. ^{1}H-NMR of BBTT **3n** (300 MHz, THF-d_8, 298 K).

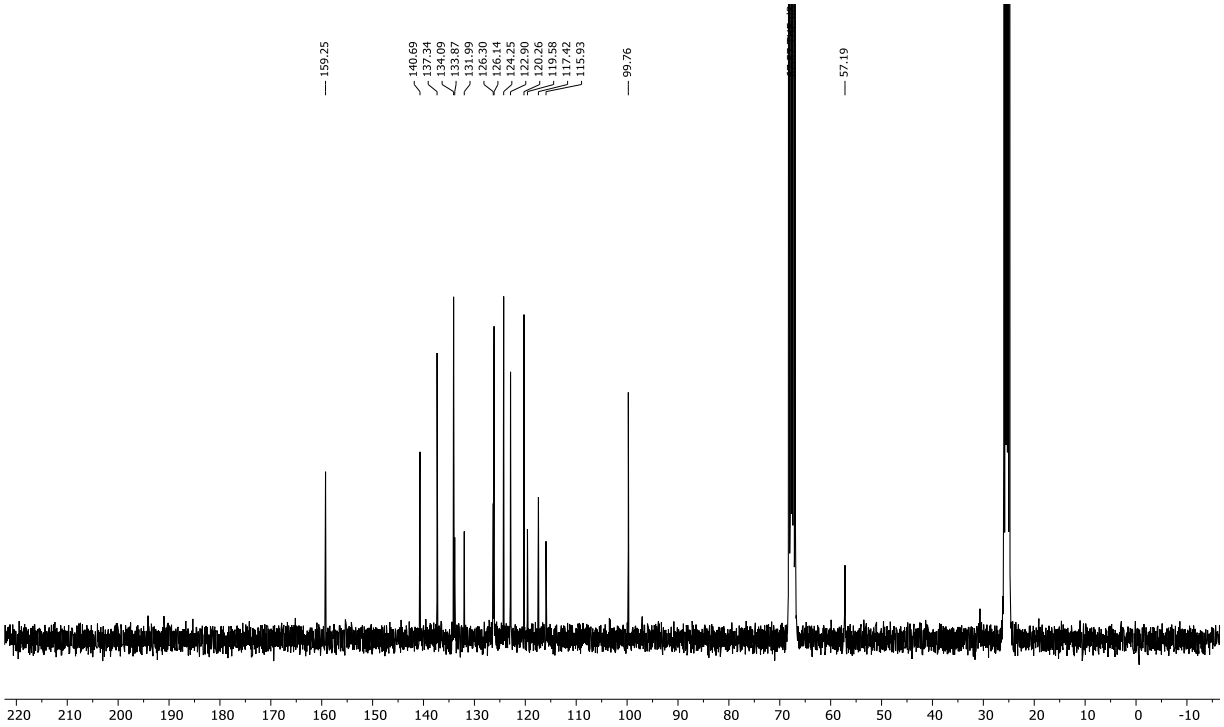


Figure 22. ^{13}C-{^{1}H}-NMR of BBTT **3n** (75 MHz, THF-d_8, 298 K).

2.1.2.6 6-(2,6-Chlorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3g)

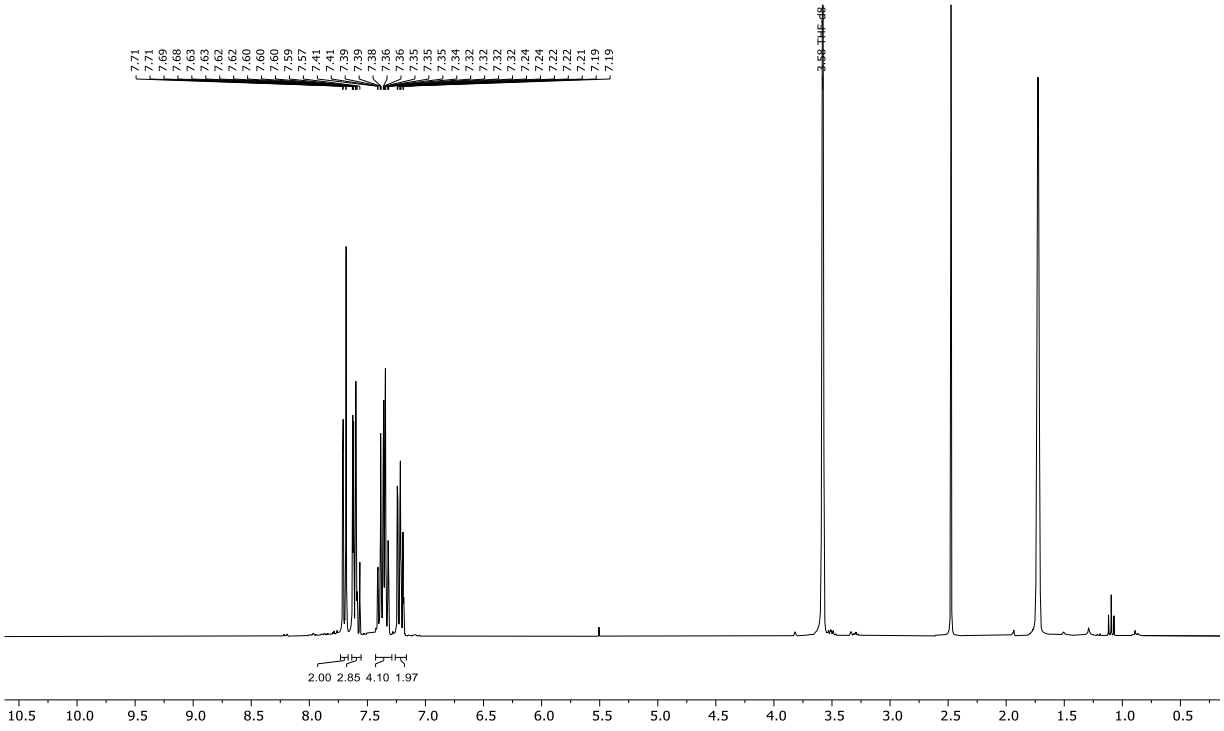


Figure 23. ^{1}H-NMR of BBTT **3g** (300 MHz, THF-d_8, 298 K).

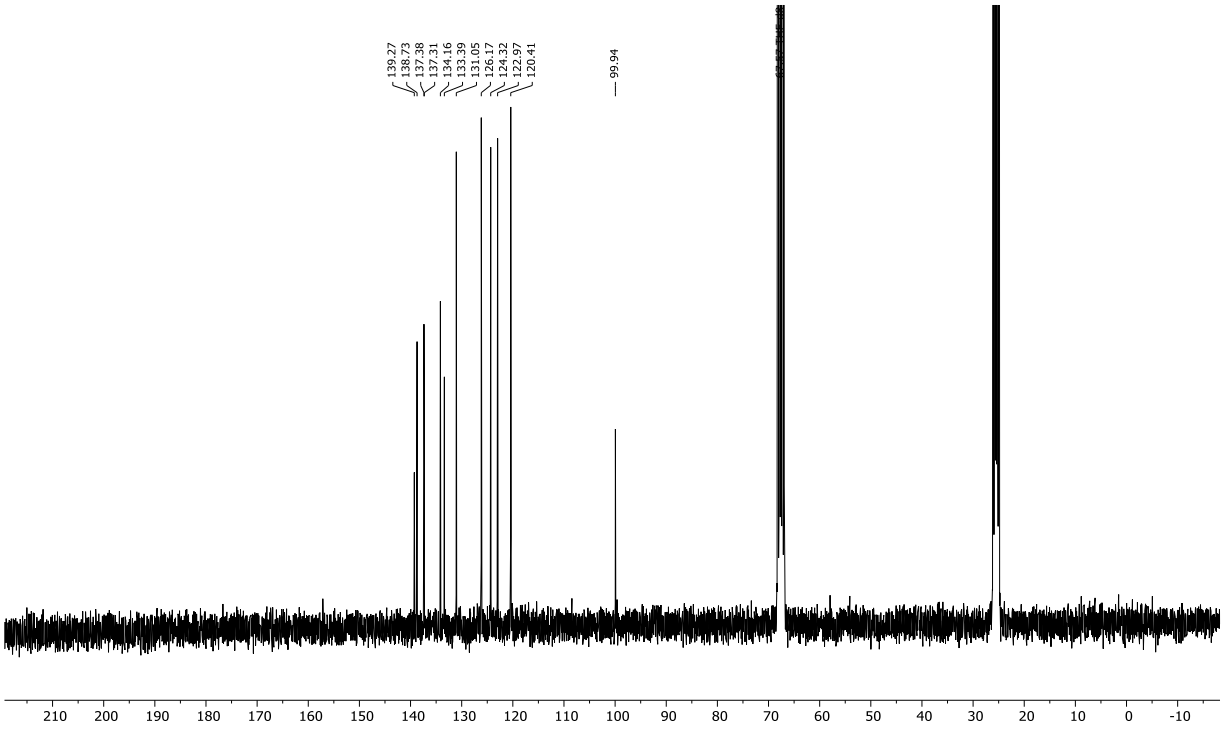


Figure 24. ^{13}C-{^{1}H}-NMR of BBTT **3g** (75 MHz, THF-d_8, 298 K).

2.1.2.7 6-(2-Chloro-6-fluorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3o)

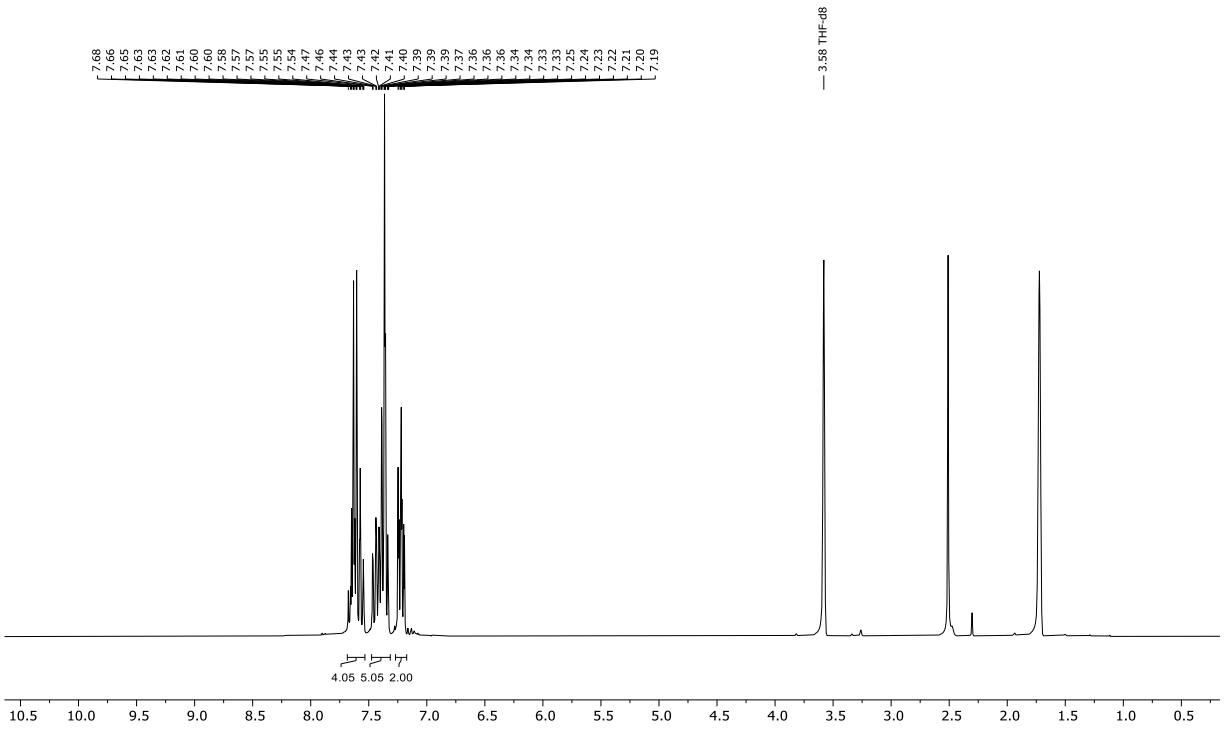


Figure 25. ^{1}H-NMR of BBTT **3o** (300 MHz, THF-d_8, 298 K).

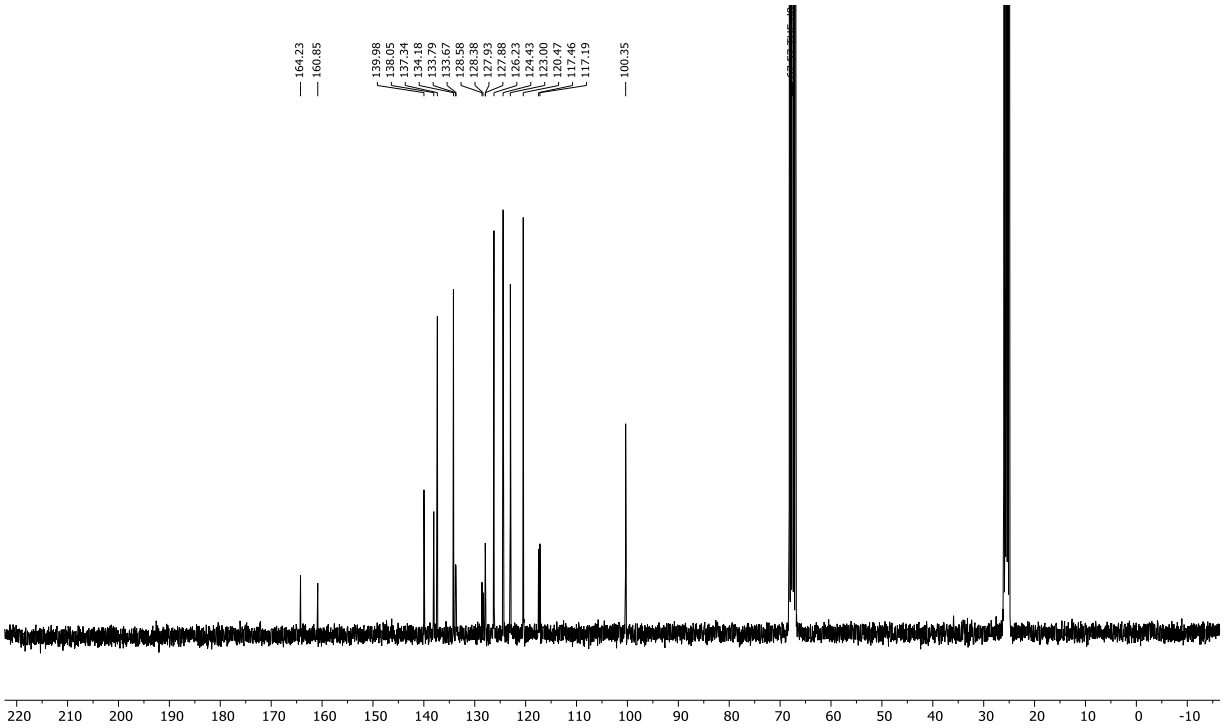


Figure 26. ^{13}C-{^{1}H}-NMR of BBTT **3o** (75 MHz, THF-d_8, 298 K).

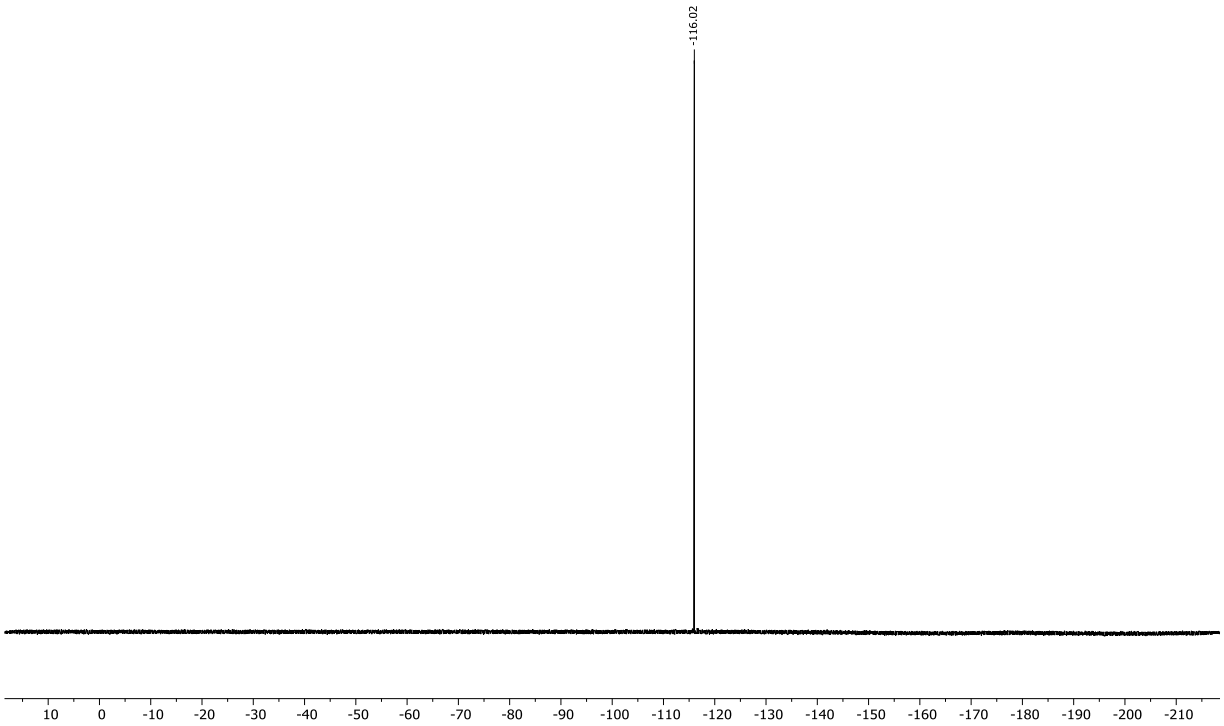


Figure 27. ^{19}F-NMR of BBTT **3o** (282 MHz, THF-d_8, 298 K).

2.1.2.8 6-(2-chloro-6-methylphenyl)-6*H*-benzo[4,5]thieno-[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3p)

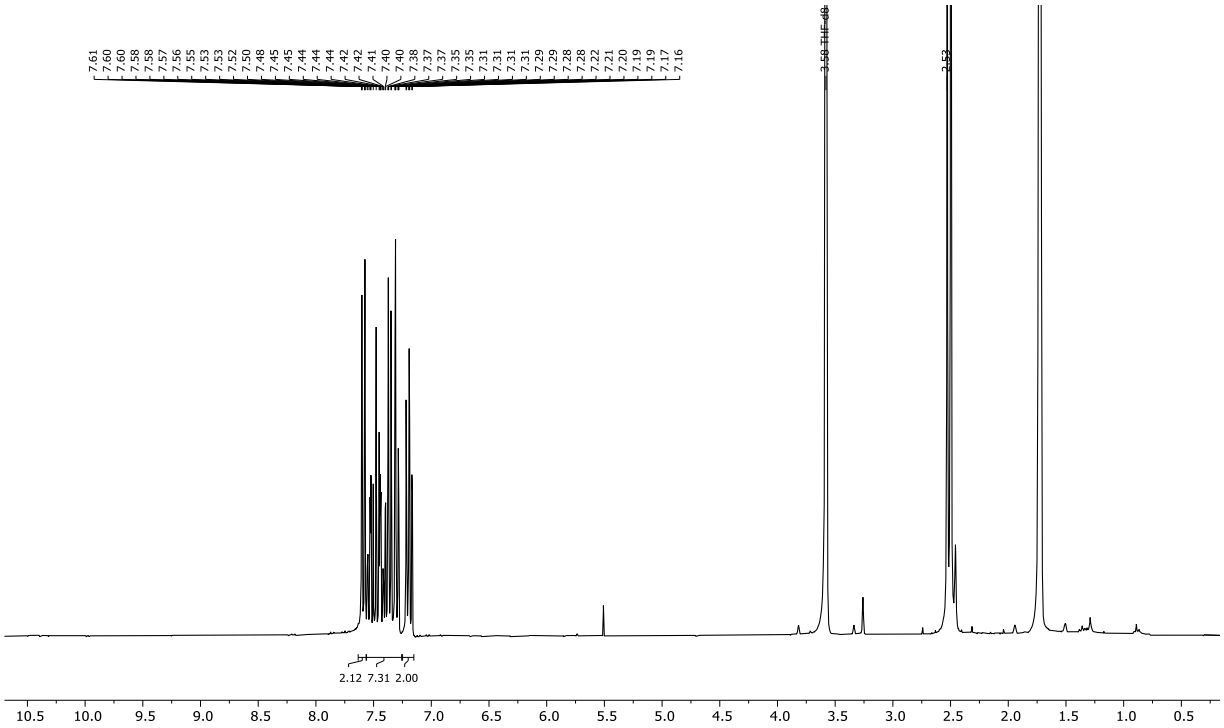


Figure 28. ^{1}H-NMR of BBTT **3p** (300 MHz, THF-d_8, 298 K).

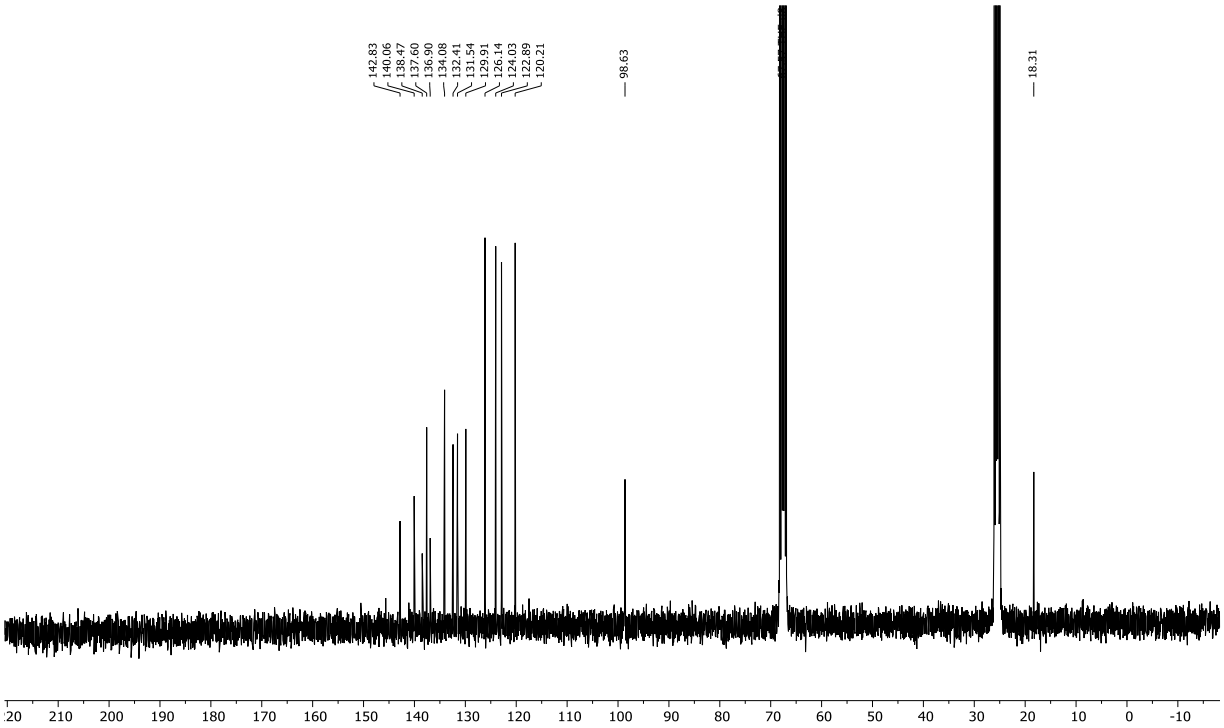


Figure 29. ^{13}C-{^{1}H}-NMR of BBTT **3p** (75 MHz, THF-d_8, 298 K).

2.1.2.9 6-(2-Chloro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3q)

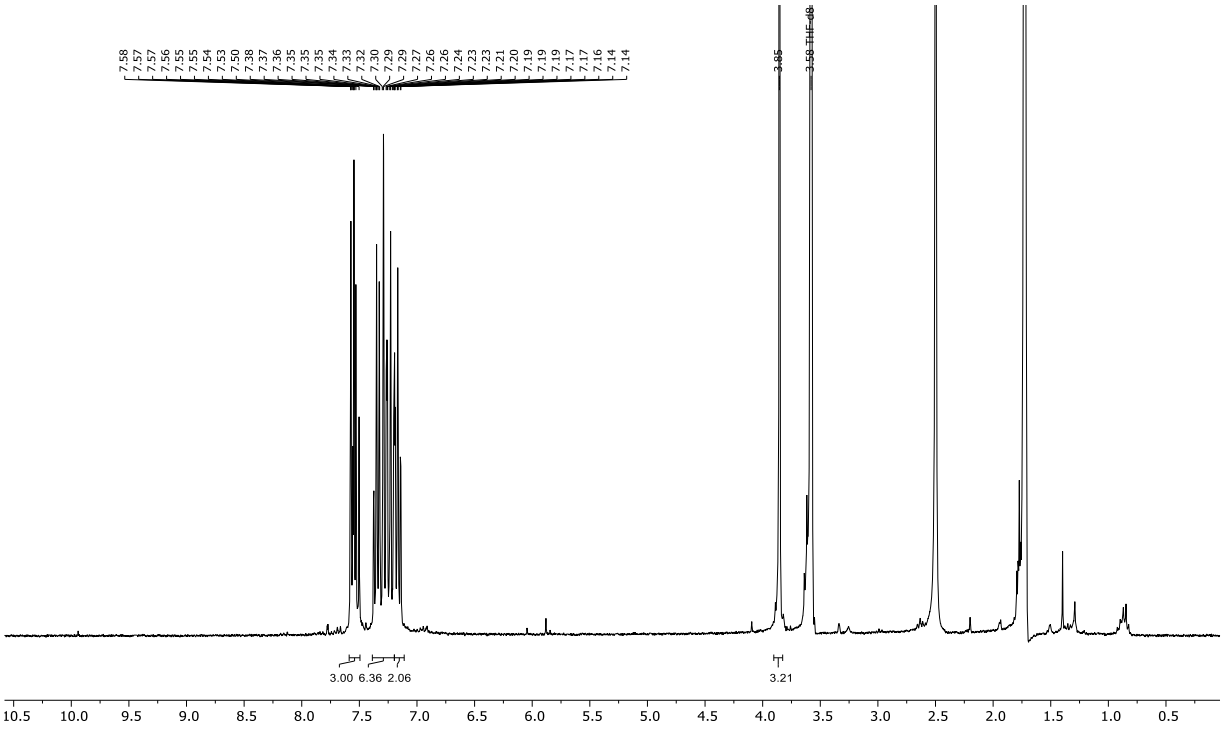


Figure 30. ^{1}H-NMR of BBTT **3q** (300 MHz, THF-d_8, 298 K).

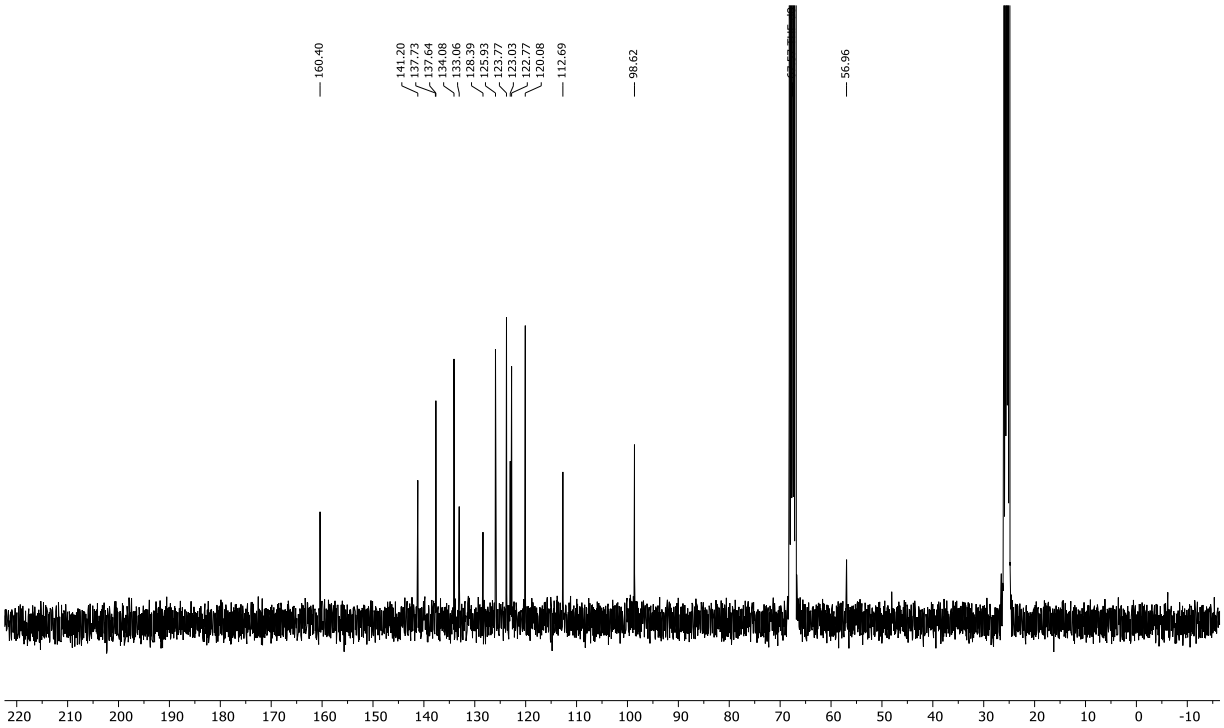


Figure 31. ^{13}C-{^{1}H}-NMR of BBTT **3q** (75 MHz, THF-d_8, 298 K).

2.1.2.10 6-(2,6-Fluorophenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5] thieno[2,3-*e*][1,4]thiazine (3h)

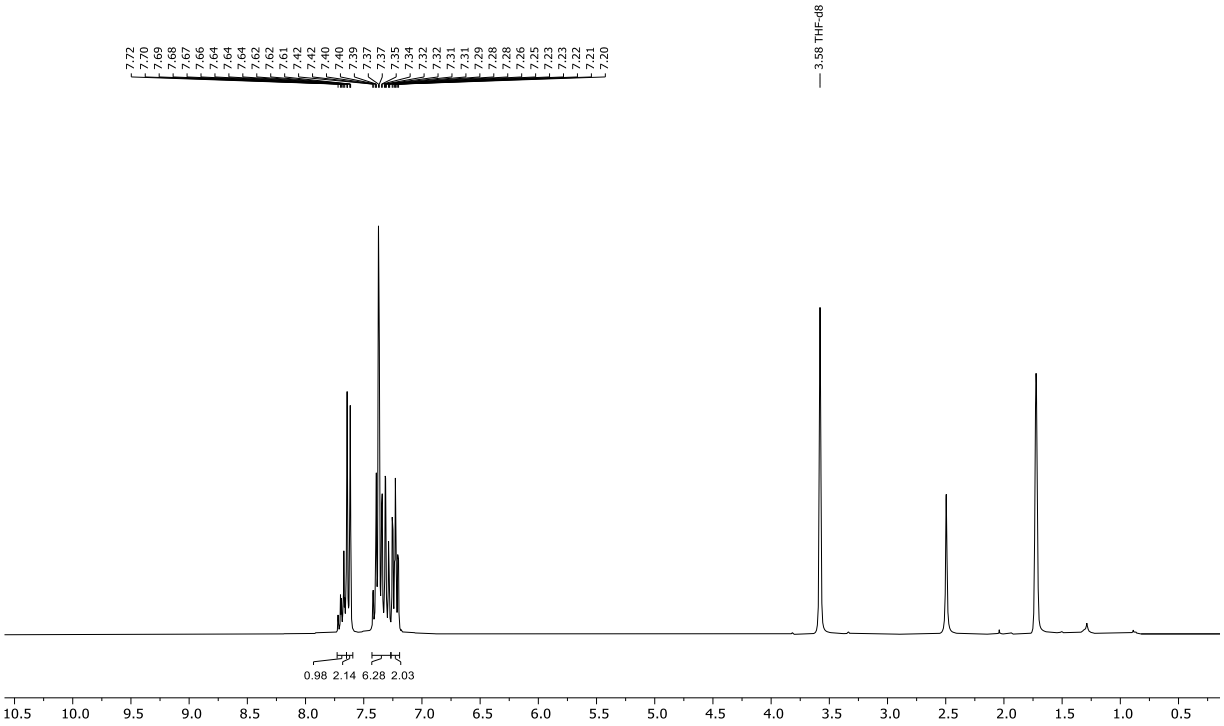


Figure 32. ^{1}H-NMR of BBTT **3h** (300 MHz, THF-d_8, 298 K).

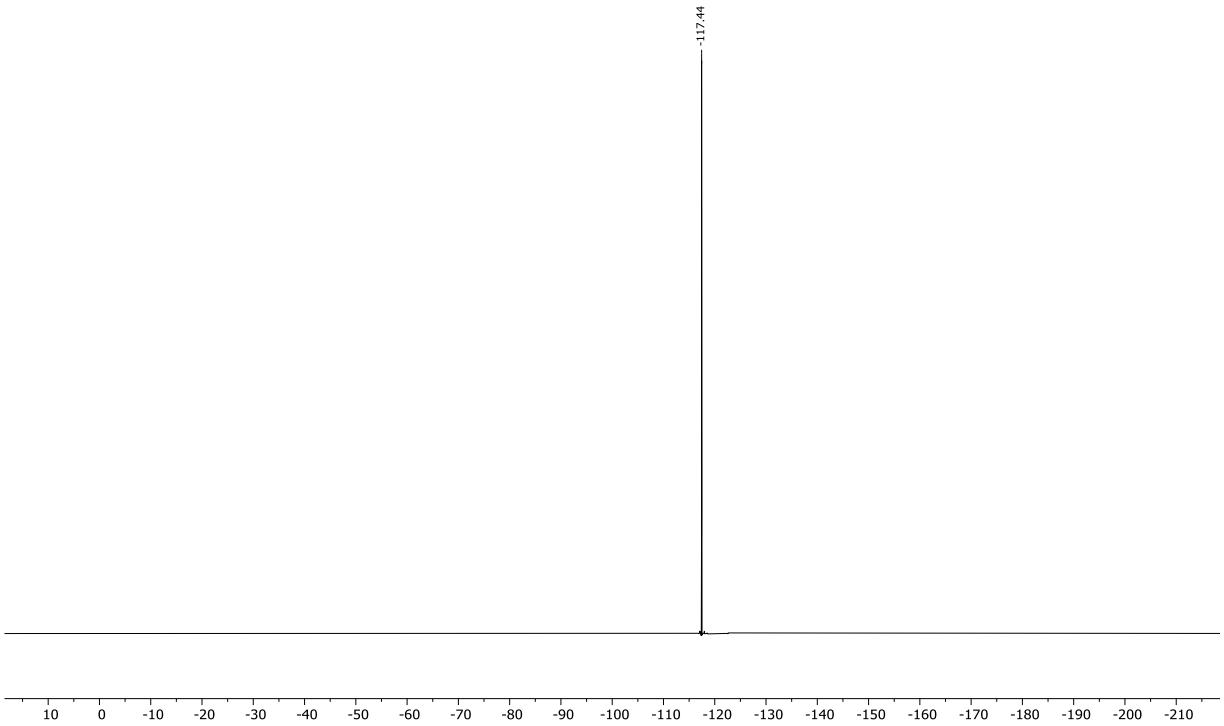


Figure 33. ^{19}F-NMR of BBTT **3h** (282 MHz, THF-d_8, 298 K).

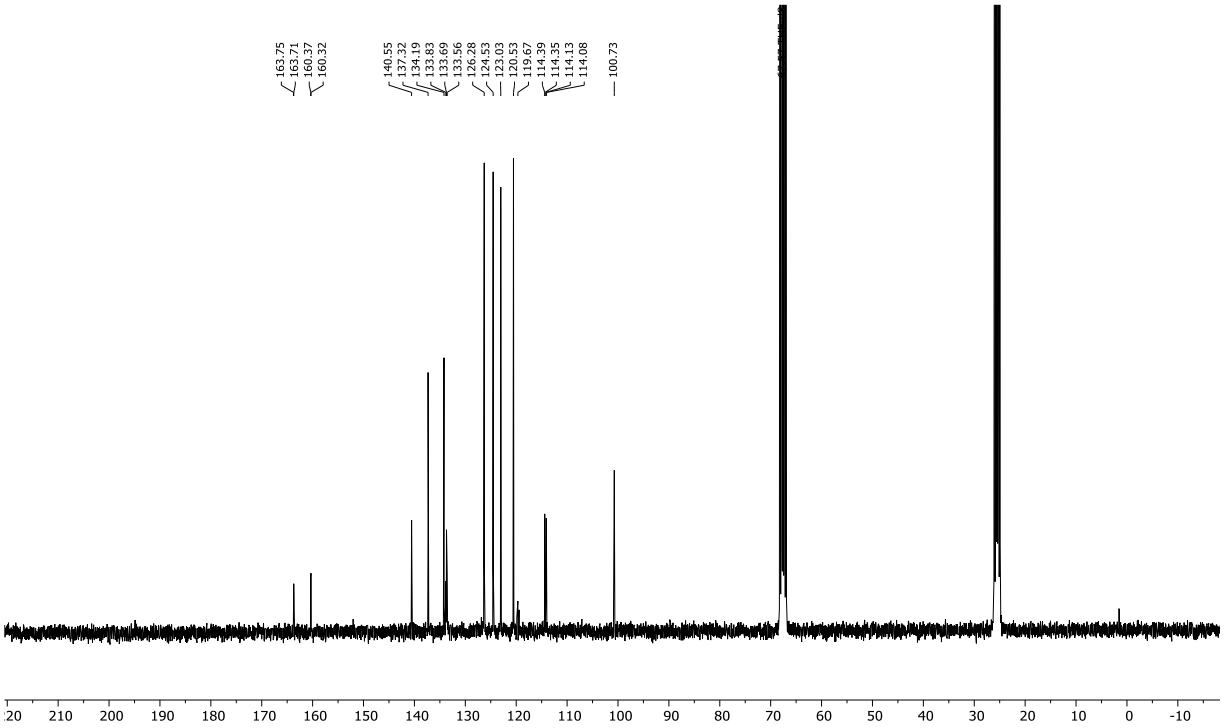


Figure 34. ^{13}C-{^{1}H}-NMR of BBTT **3h** (75 MHz, THF-d_8, 298 K).

2.1.2.11 6-(2-fluoro-6-methylphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3r)

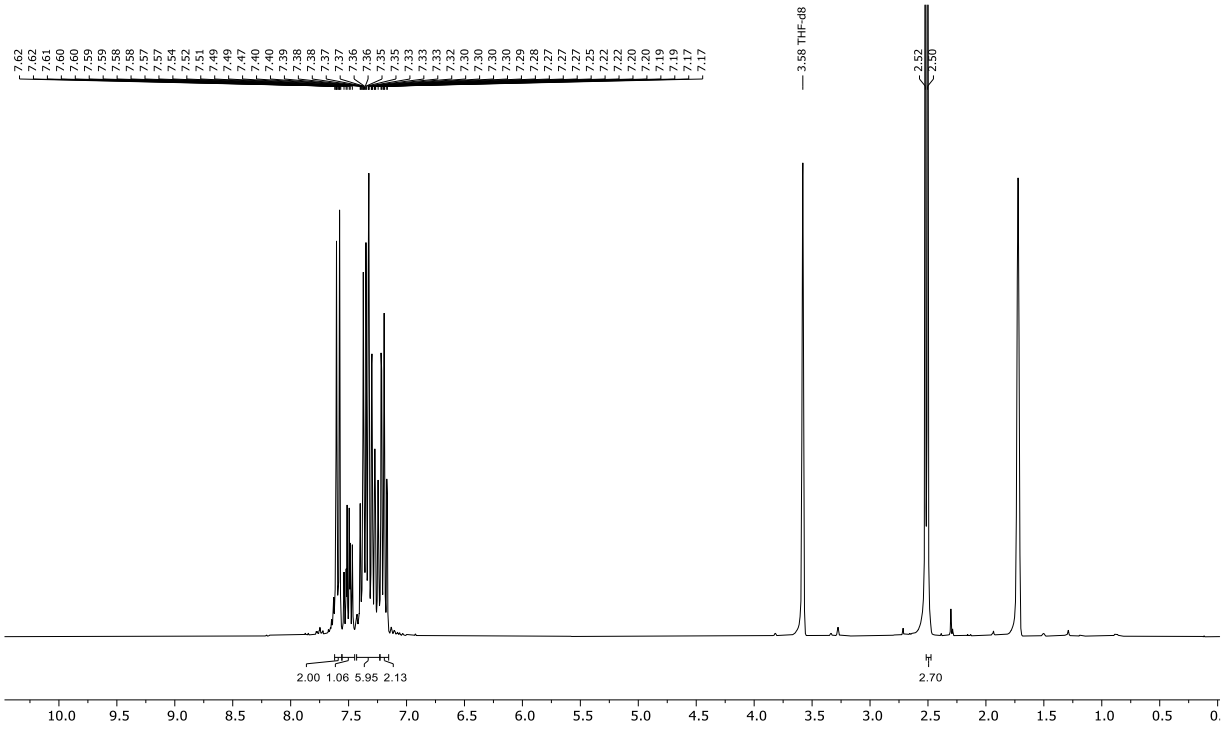


Figure 35. ^{1}H-NMR of BBTT **3r** (300 MHz, THF-d_8, 298 K).

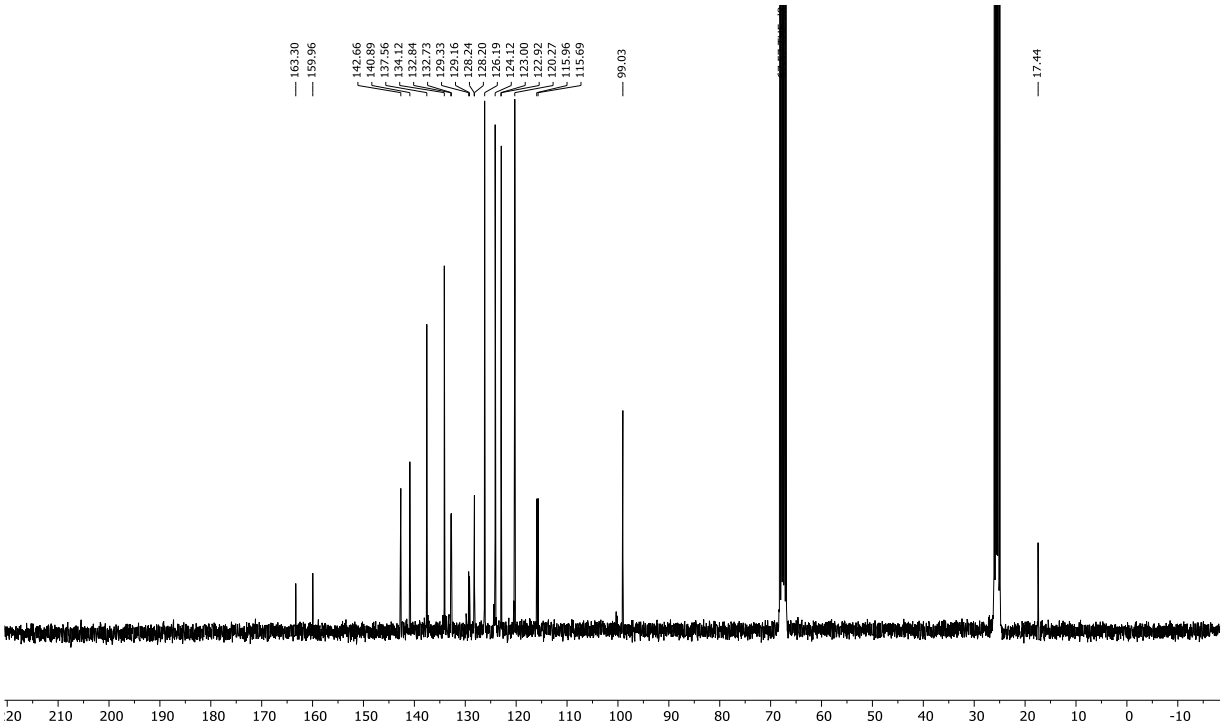


Figure 36. ^{13}C-{^{1}H}-NMR of BBTT **3r** (75 MHz, THF-d_8, 298 K).

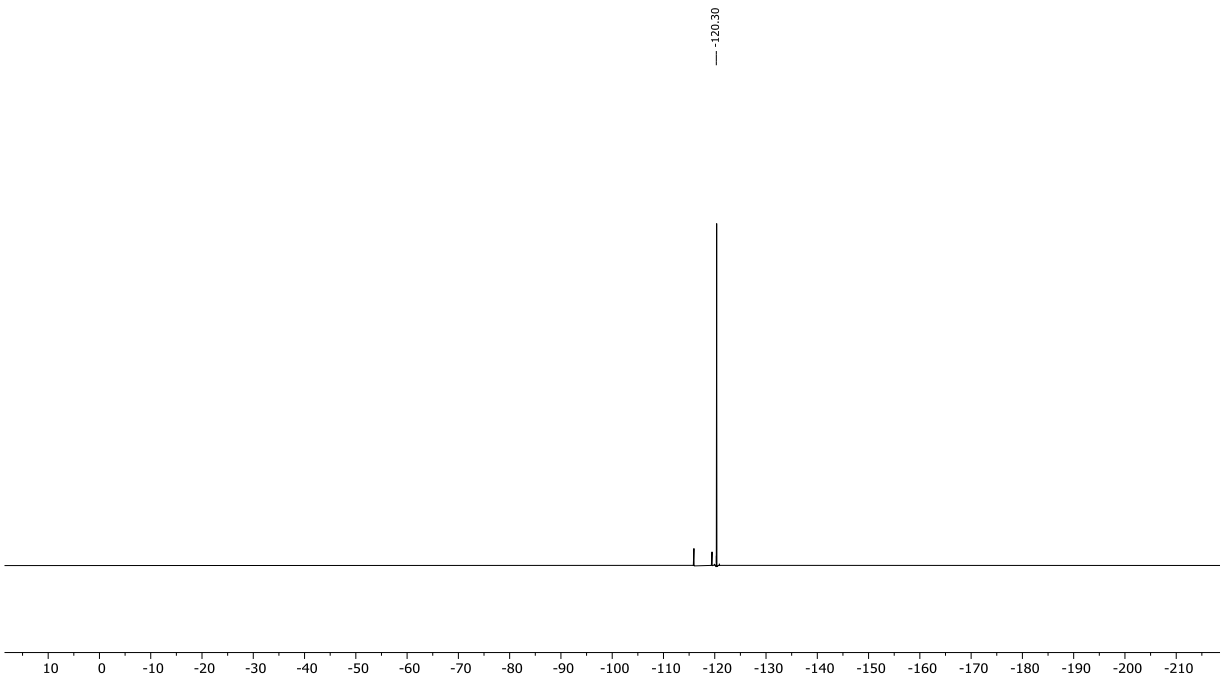


Figure 37. ^{19}F-NMR of BBTT **3r** (282 MHz, THF-d_8, 298 K).

2.1.2.12 6-(2-Fluoro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3s)

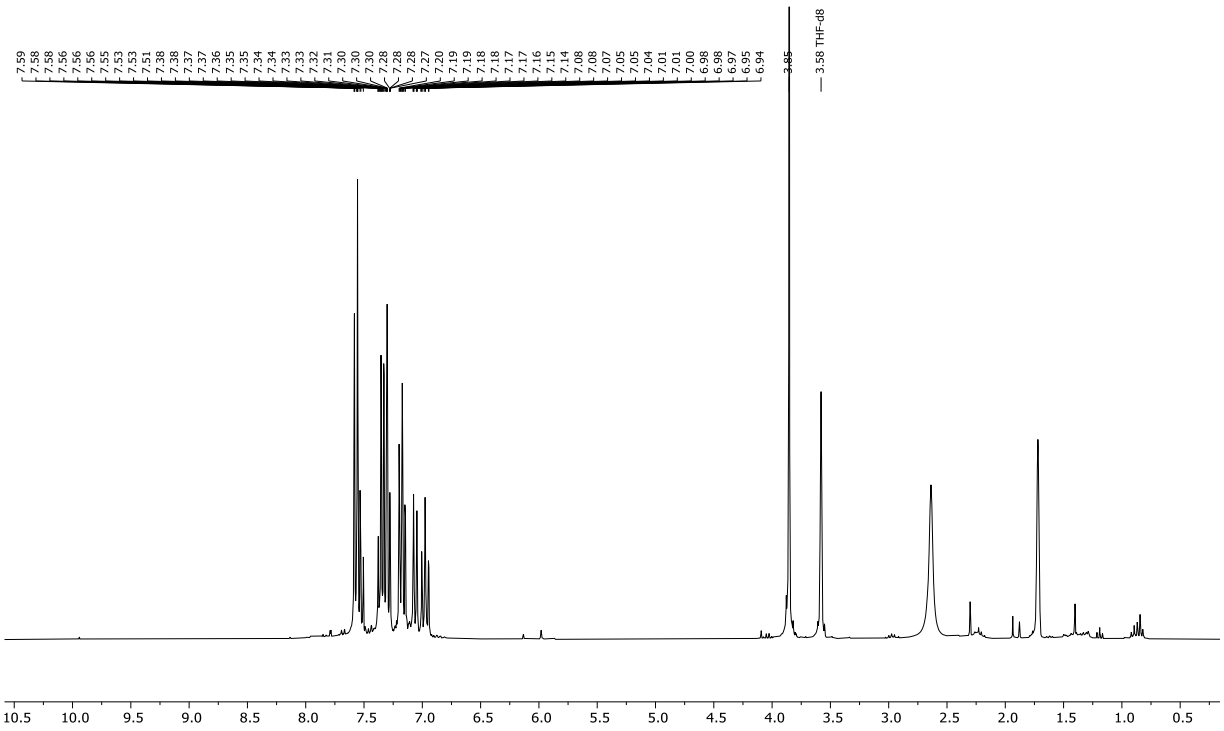


Figure 38. ^{1}H-NMR of BBTT **3s** (300 MHz, THF-d_8, 298 K).

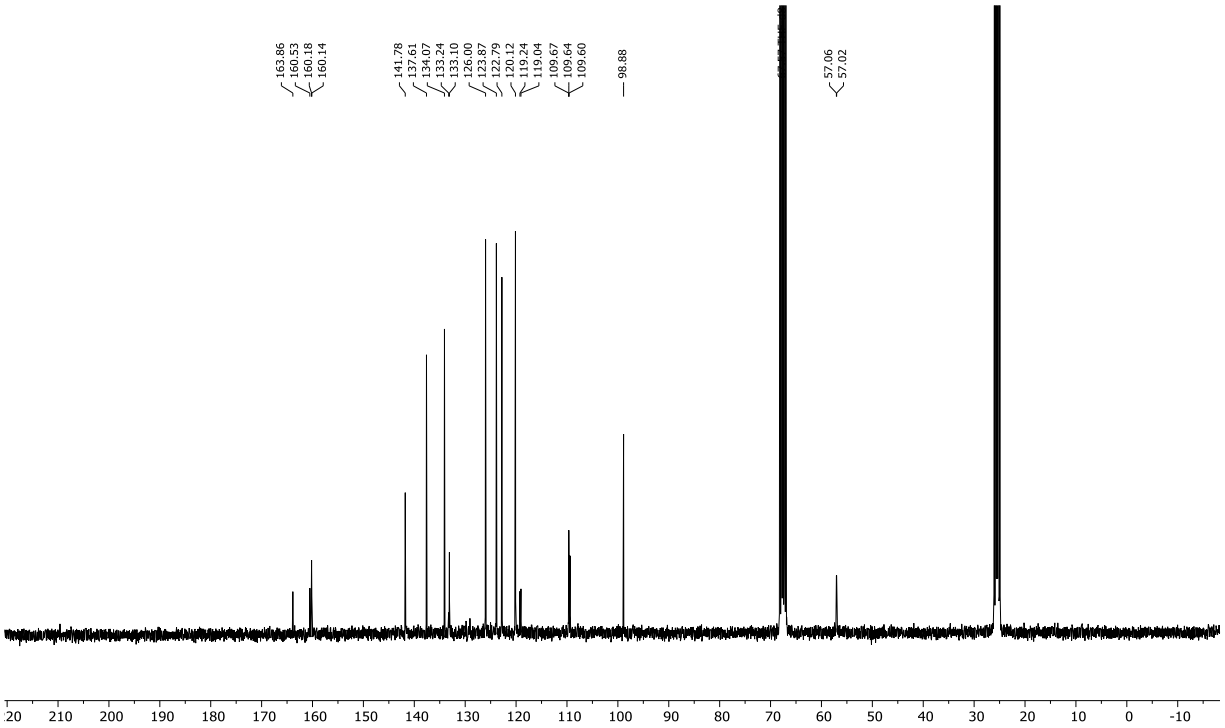


Figure 39. ^{13}C-{^{1}H}-NMR of BBTT **3s** (75 MHz, THF-d_8, 298 K).

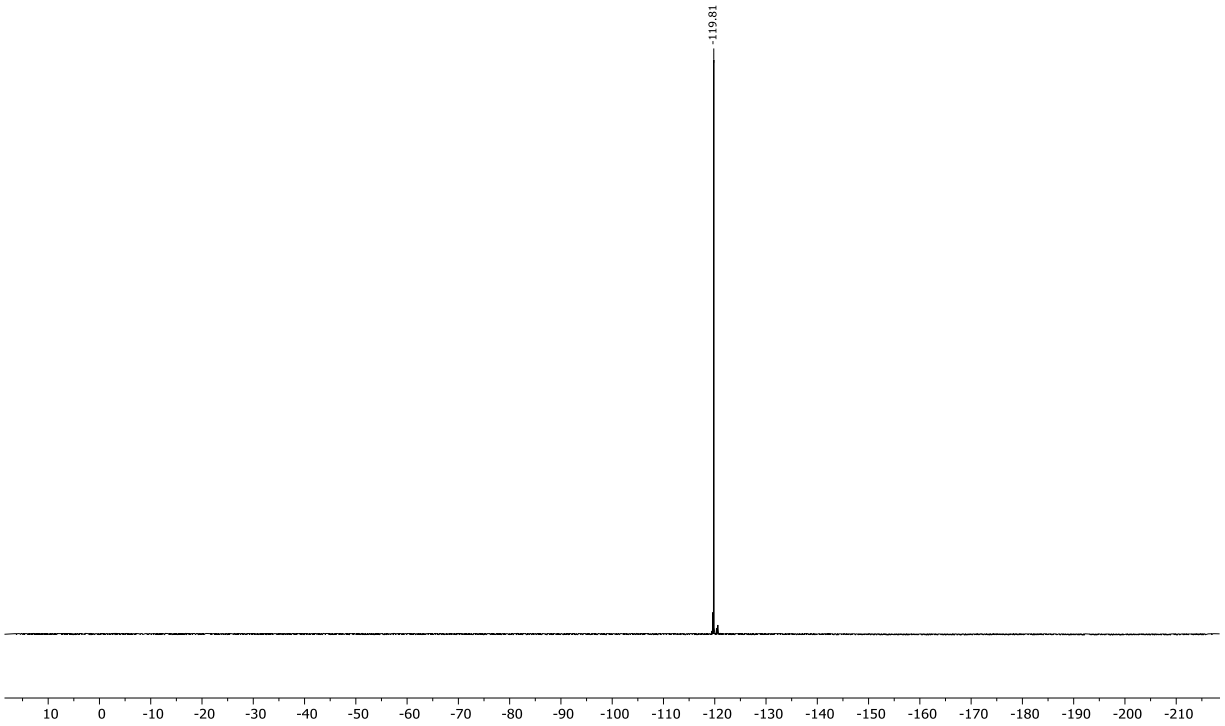


Figure 40. ^{19}F-NMR of BBTT **3s** (282 MHz, THF-d_8, 298 K).

2.1.2.13 6-(2,6-dimethylphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3i)

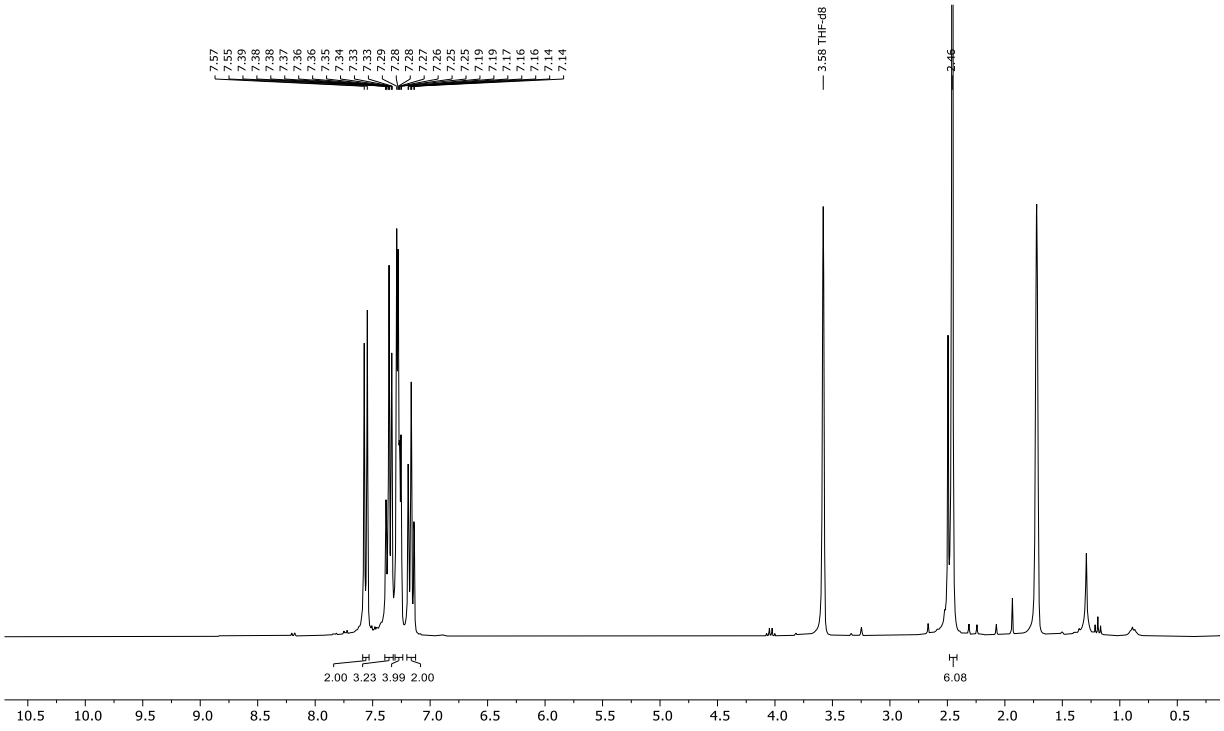


Figure 41. ^{1}H-NMR of BBTT **3i** (300 MHz, THF-d_8, 298 K).

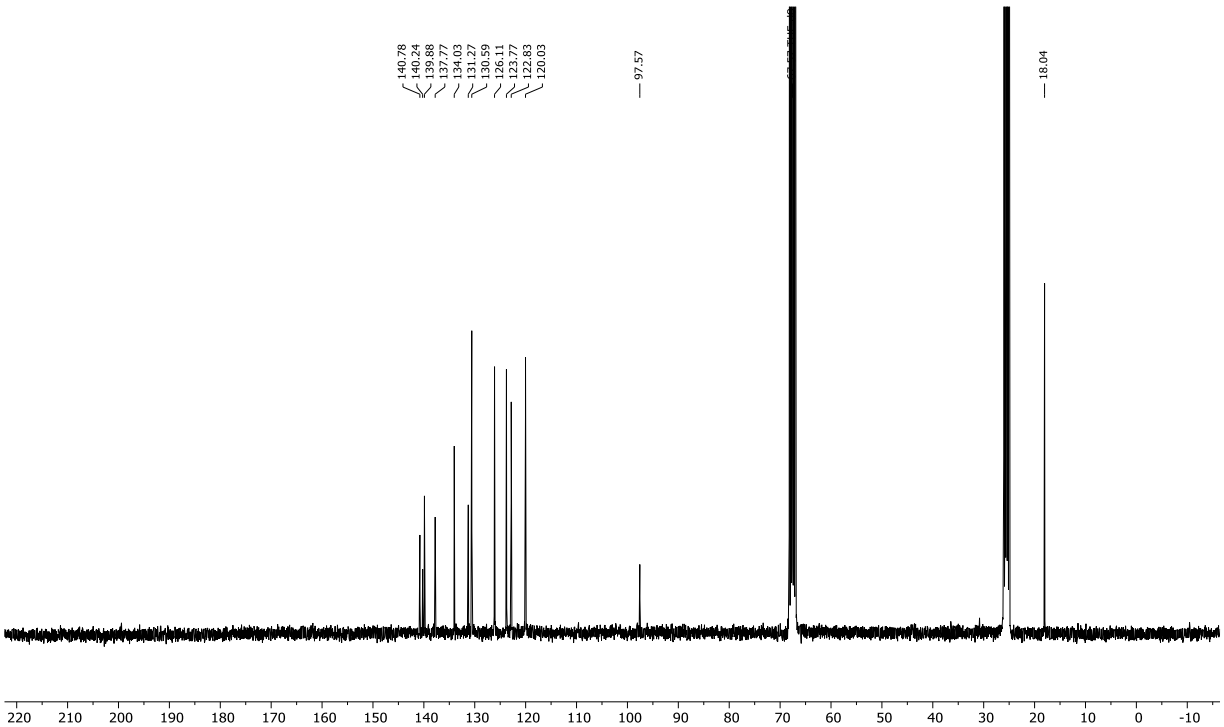


Figure 42. ^{13}C-{^{1}H}-NMR of BBTT **3i** (75 MHz, THF-d_8, 298 K).

2.1.2.14 6-(2-methoxy-6-methylphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3t)

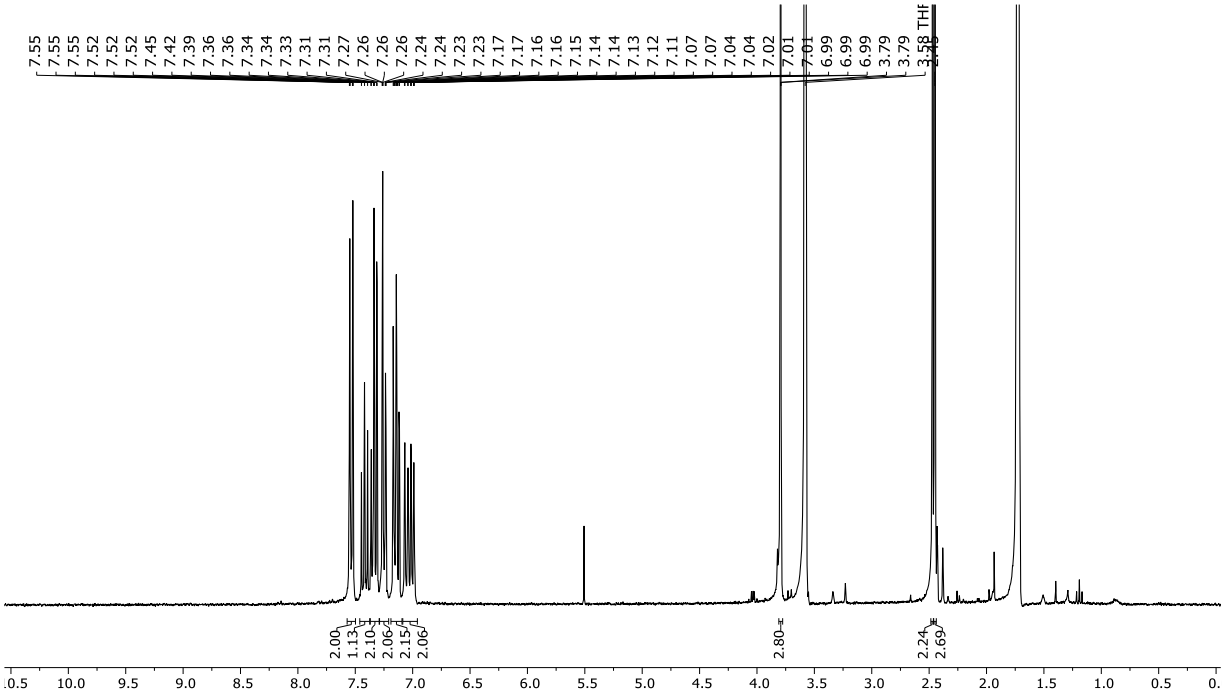


Figure 43. ^{1}H-NMR of BBTT **3t** (300 MHz, THF-d_8, 298 K).

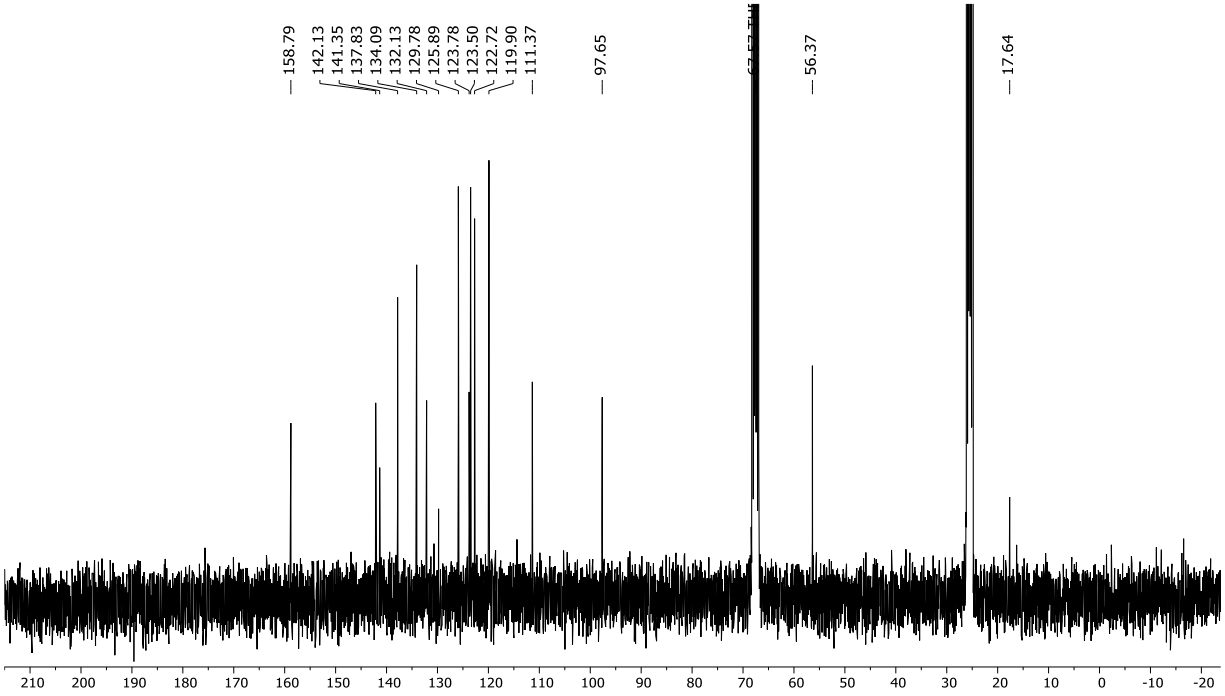


Figure 44. ^{13}C-{^{1}H}-NMR of BBTT **3t** (75 MHz, THF-d_8, 298 K).

2.1.2.15 6-(2,6-dimethoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (3j)

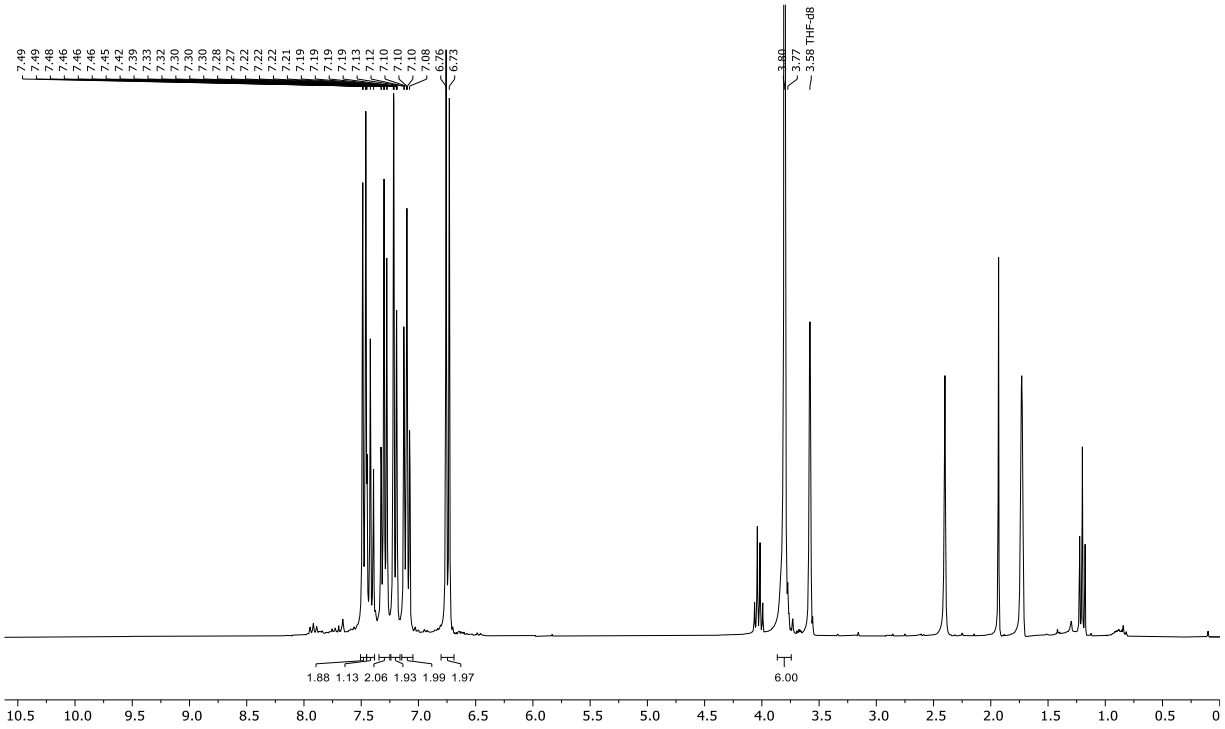


Figure 45. ^{1}H-NMR of BBTT **3j** (300 MHz, THF-d_8, 298 K).

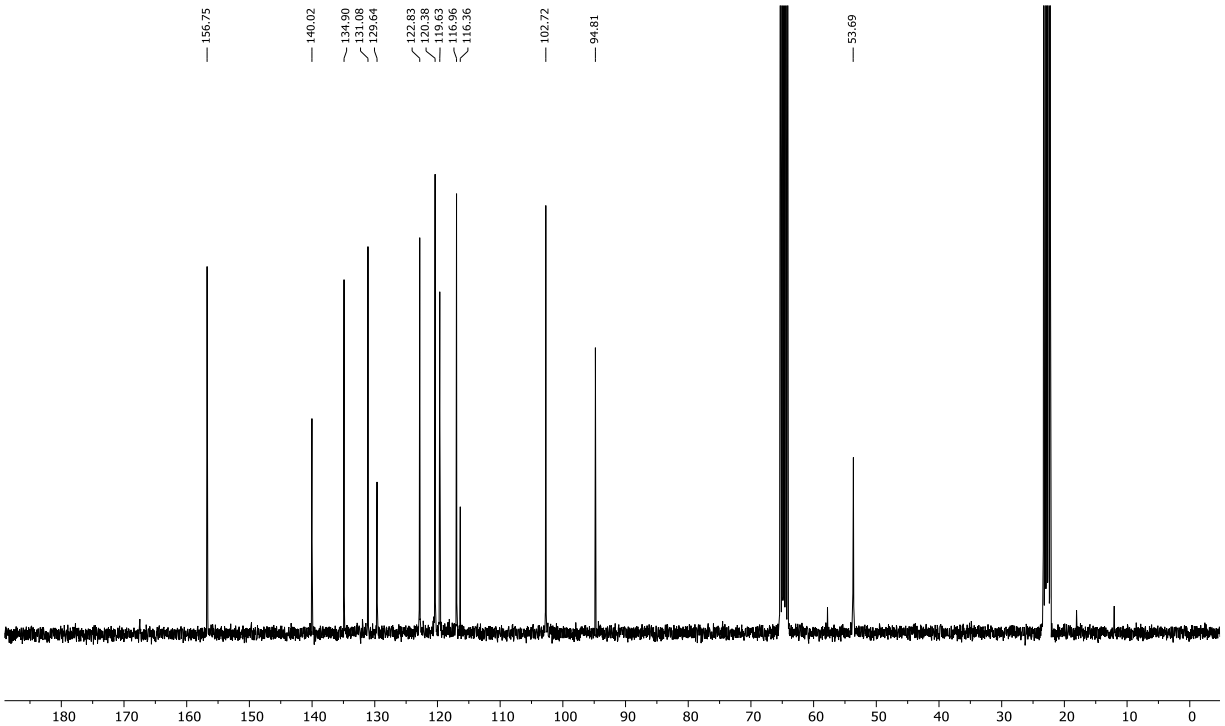


Figure 46. ^{13}C-{^{1}H}-NMR of BBTT **3j** (75 MHz, THF-d_8, 298 K).

2.1.3 *Anti-anti*-3,9-dibromo-*N-ortho(,ortho')*-(di)substituted-Phenyl-BBTT 4

2.1.3.1 3,9-Dibromo-6-(*o*-tolyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4a)

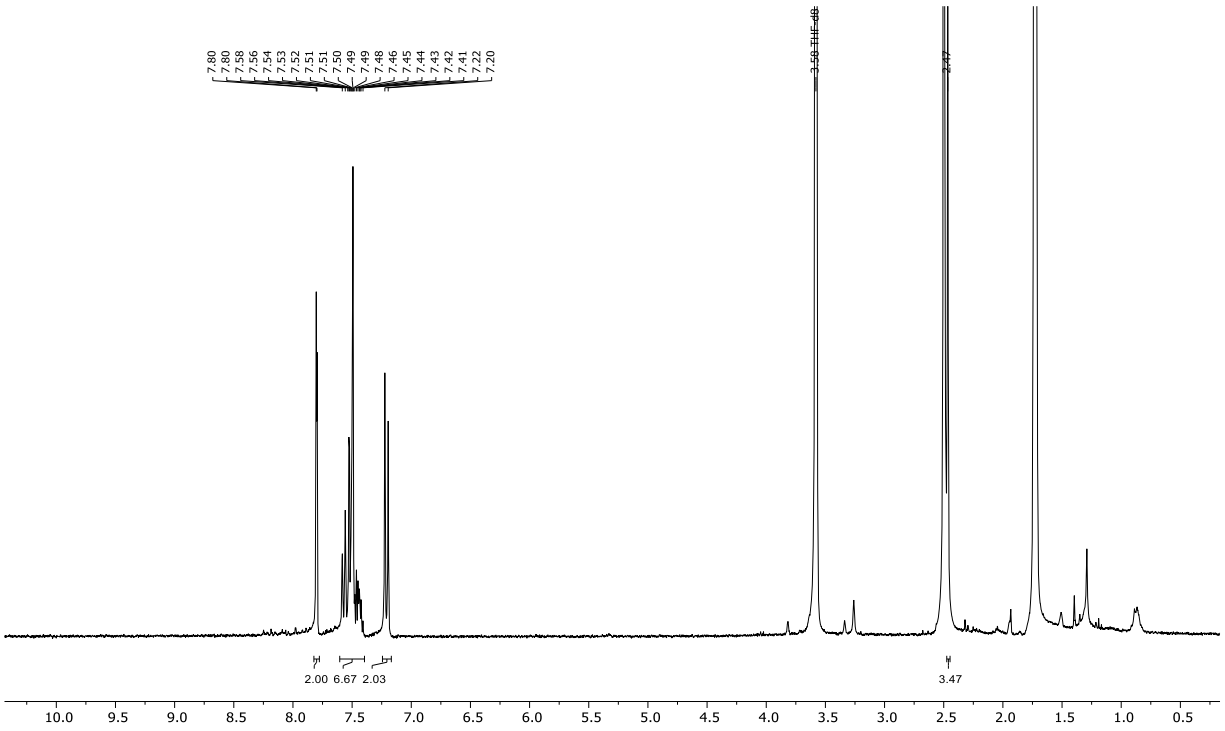


Figure 47. ^{1}H-NMR of BBTT **4a** (300 MHz, THF-d_8, 298 K).

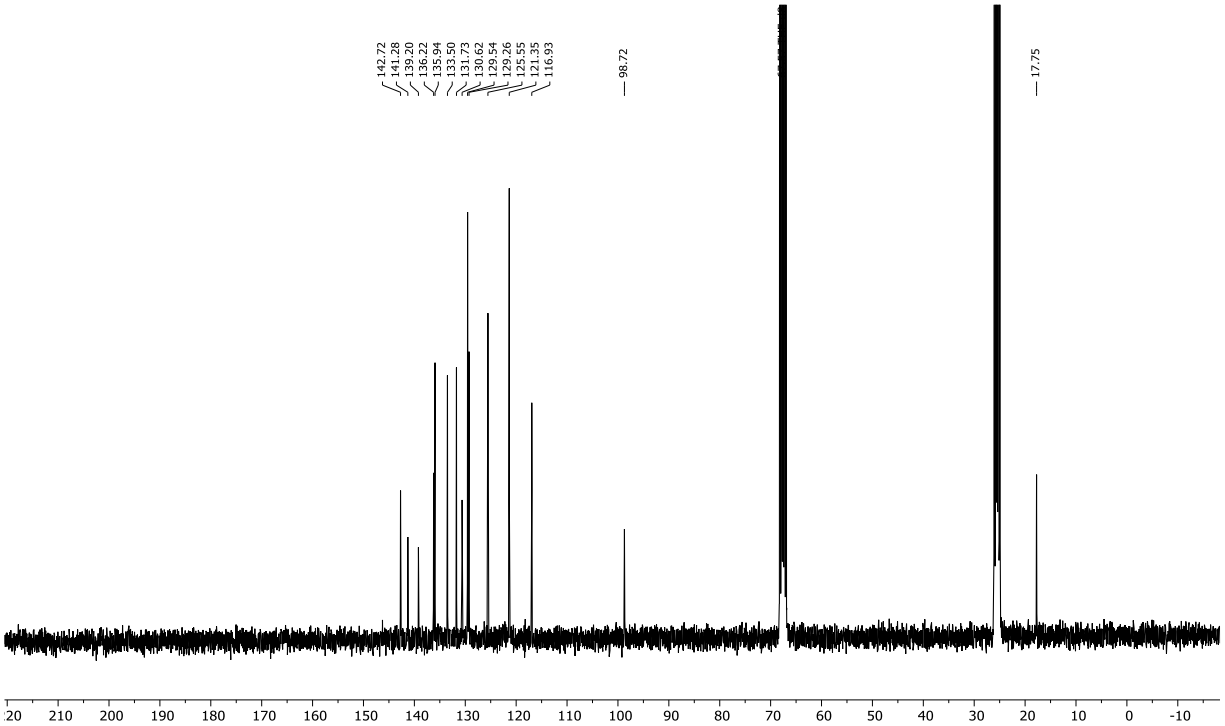


Figure 48. ^{13}C-{^{1}H}-NMR of BBTT **4a** (75 MHz, THF-d_8, 298 K).

2.1.3.2 3,9-Dibromo-6-(2-chloro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4b)

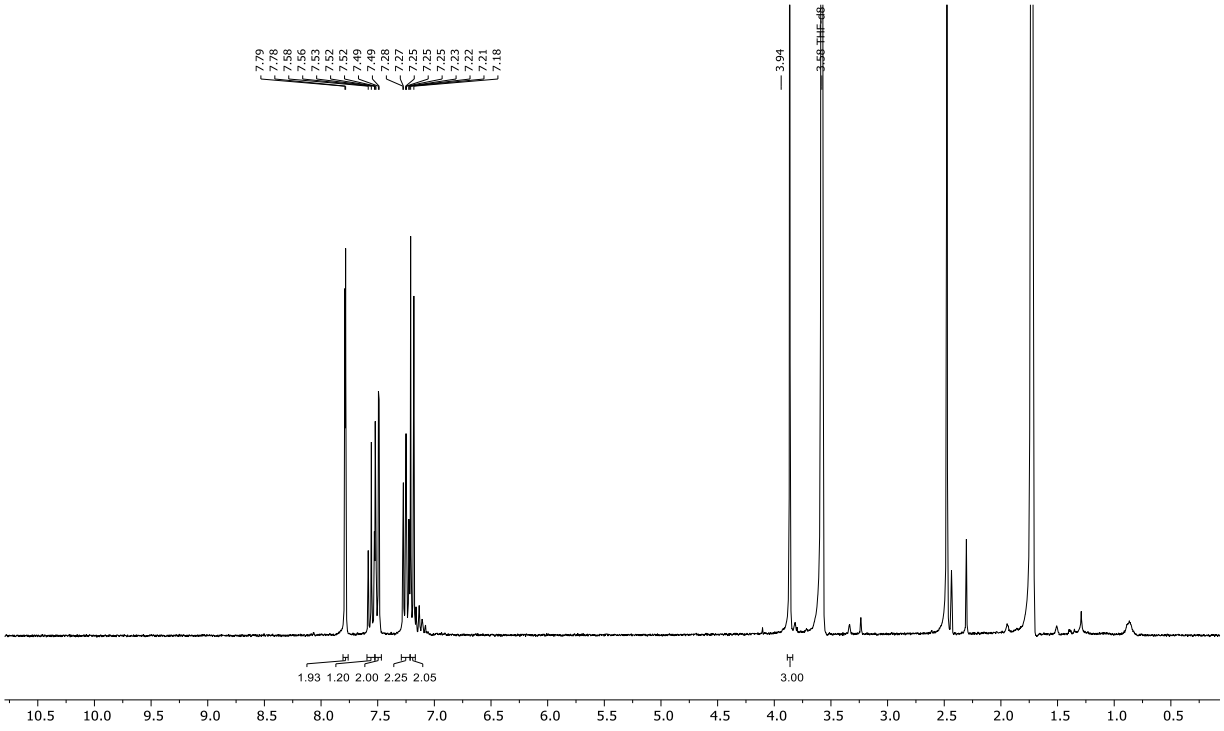


Figure 49. ^{1}H-NMR of BBTT **4b** (300 MHz, THF-d_8, 298 K).

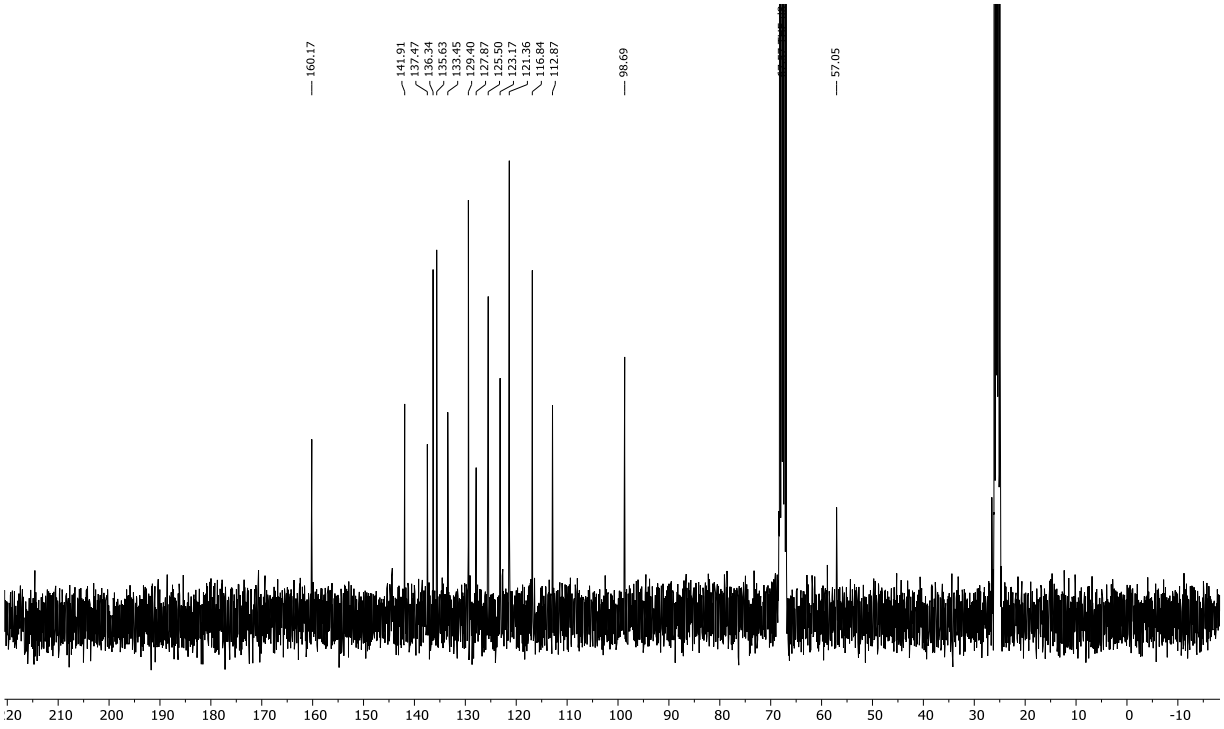


Figure 50. ^{13}C-{^{1}H}-NMR of BBTT **4b** (75 MHz, THF-d_8, 298 K).

2.1.3.3 3,9-Dibromo-6-(2-fluoro-6-methoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4c)

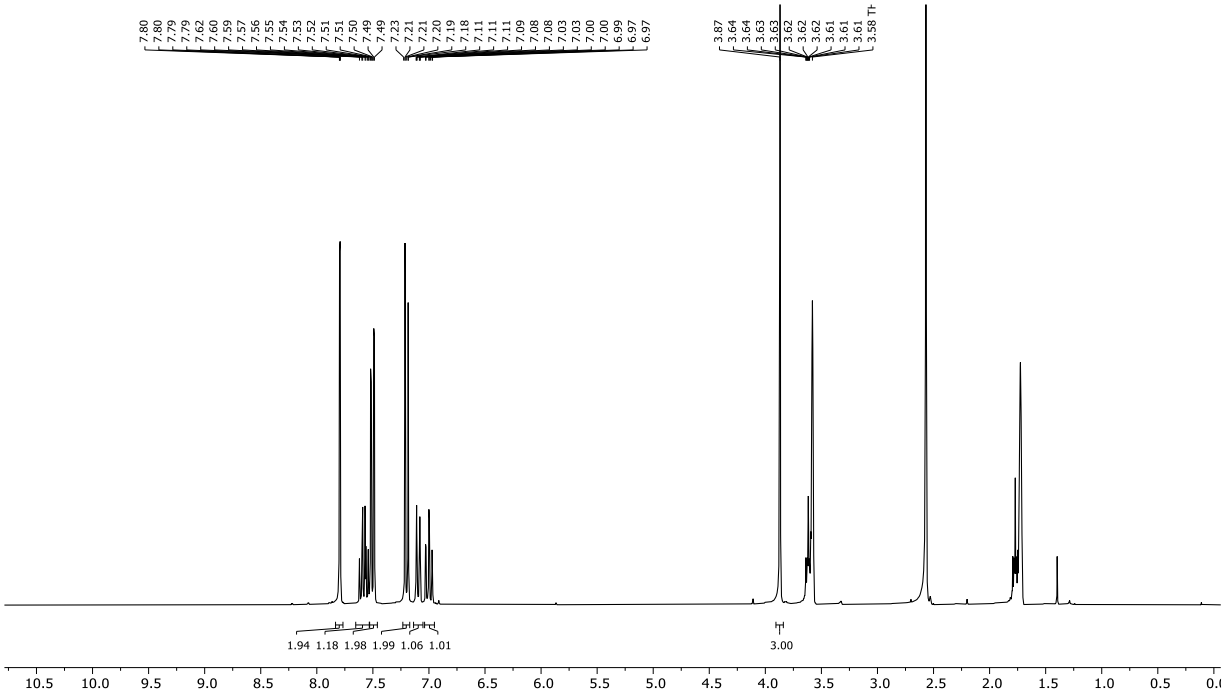


Figure 51. ^{1}H-NMR of BBTT **4c** (300 MHz, THF-d_8, 298 K).

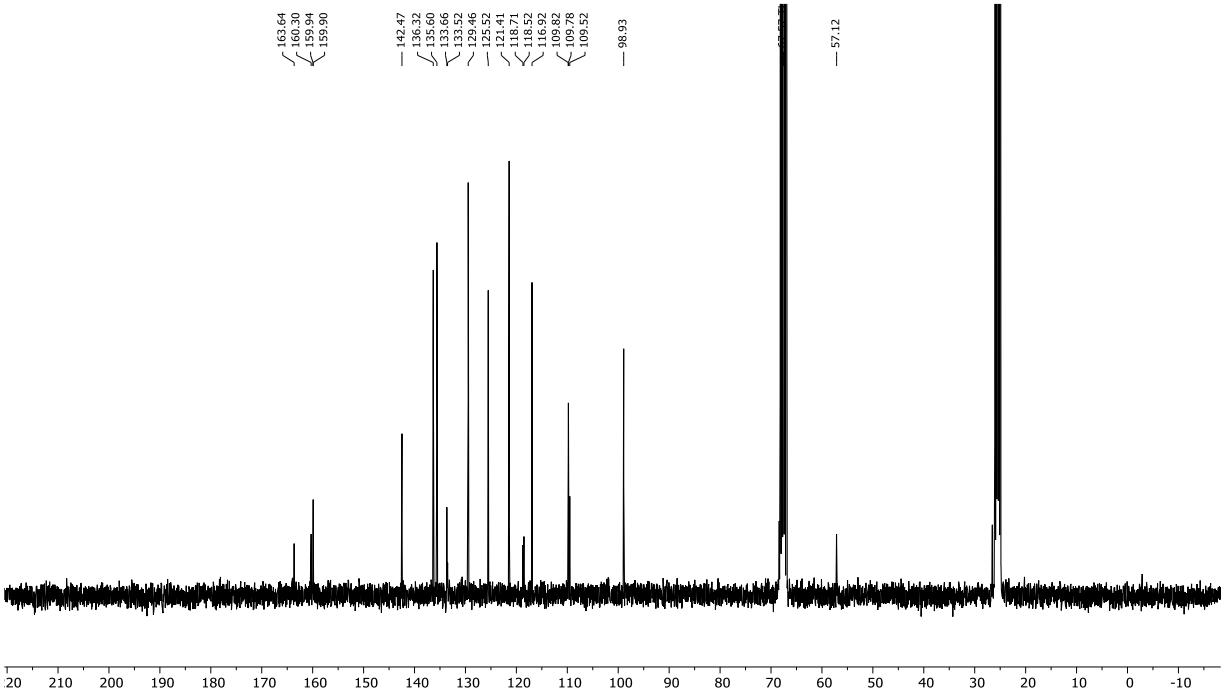


Figure 52. ^{13}C-{^{1}H}-NMR of BBTT **4c** (75 MHz, THF-d_8, 298 K).

2.1.3.4 3,9-Dibrom-6-(2,6-dimethoxyphenyl)-6*H*-benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*e*][1,4]thiazine (4d)

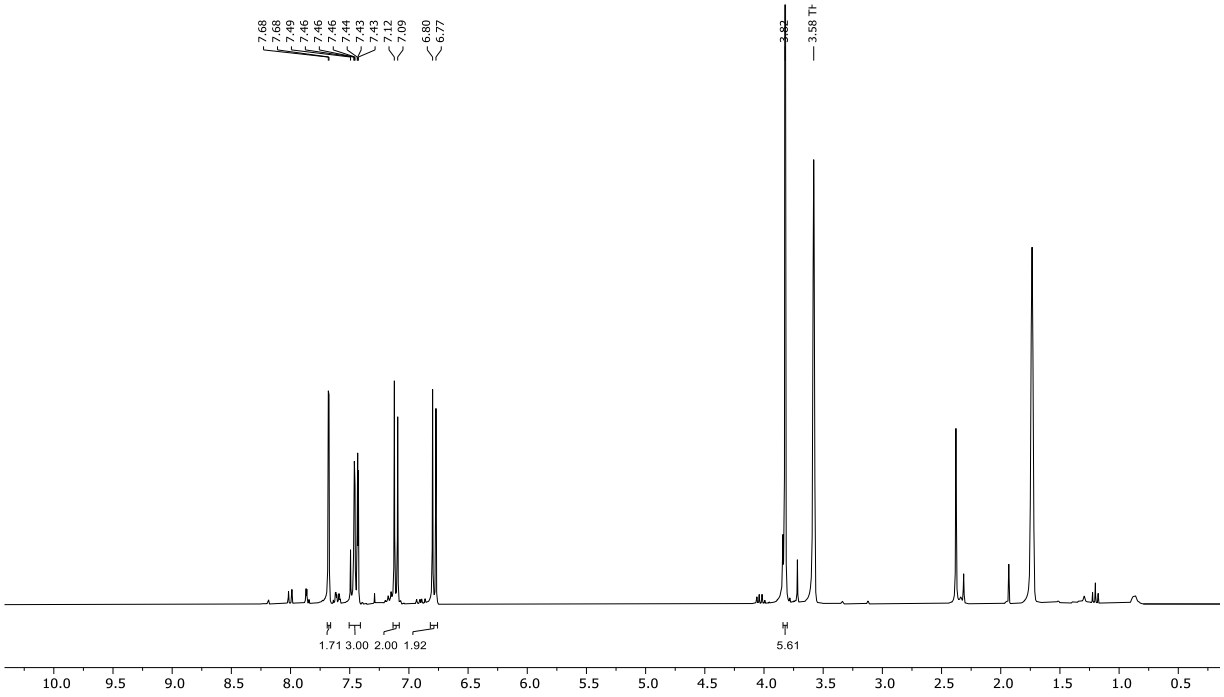


Figure 53. ^{1}H-NMR of BBTT **4d** (300 MHz, THF-d_8, 298 K).

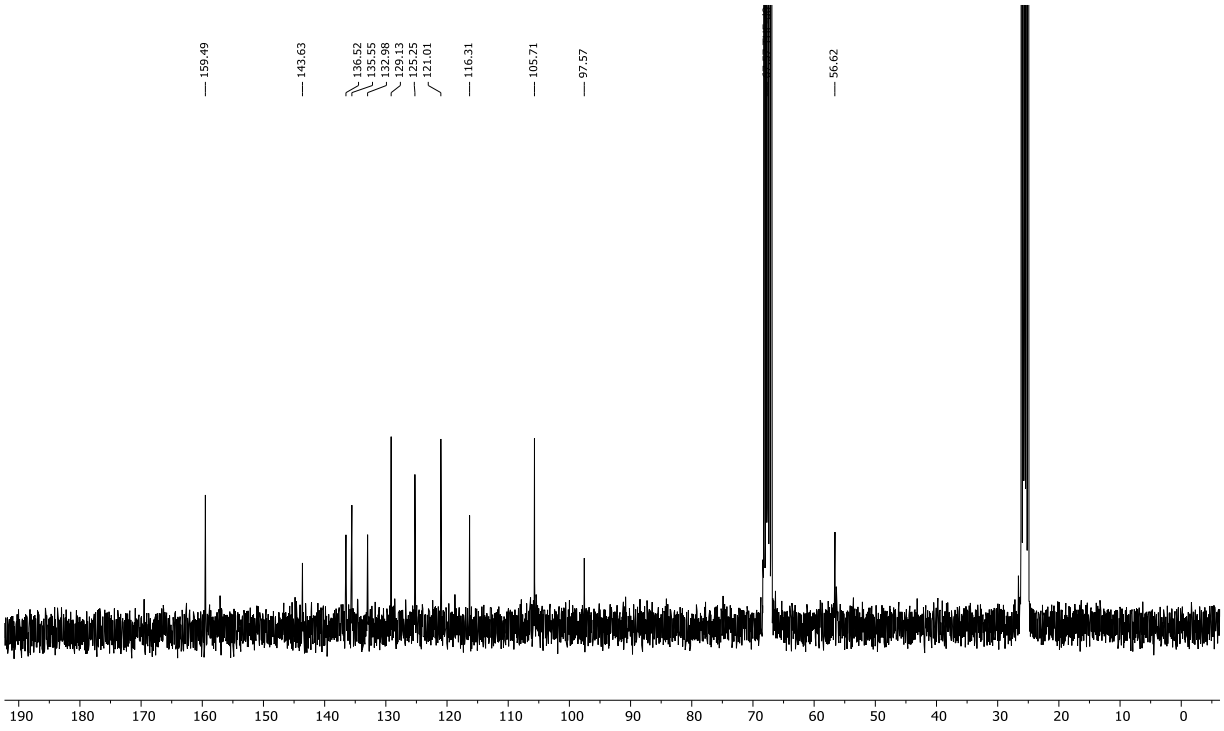
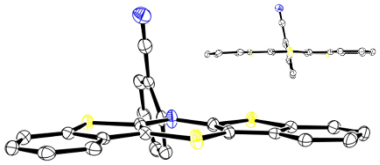


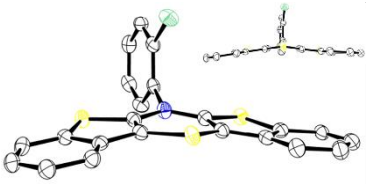
Figure 54. ^{13}C-{^{1}H}-NMR of BBTT **4d** (75 MHz, THF-d_8, 298 K).

3 Crystal structures and data

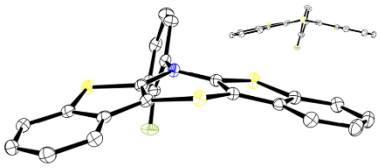
3.1 Molecular structure



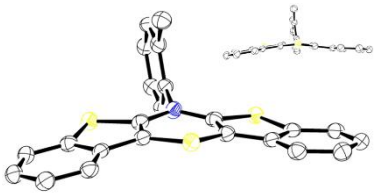
$R^1 = R^2 = H$, $R^3 = CN$ (**3a**)[b]



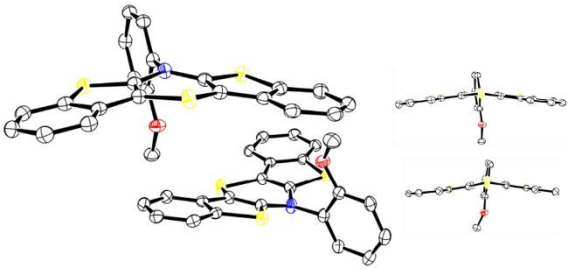
$R^1 = R^2 = H$, $R^3 = Cl$ (**3b**)[b]



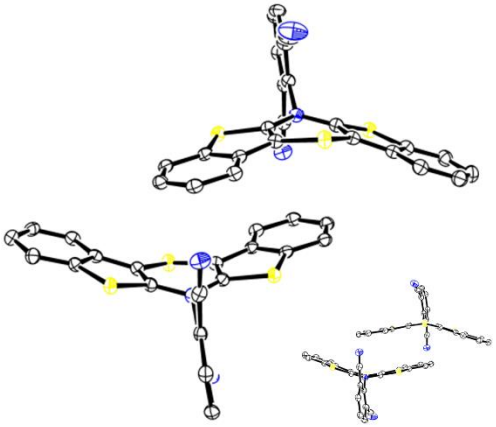
$R^1 = R^2 = H$, $R^3 = F$ (**3c**)[b]



$R^1 = R^2 = H$, $R^3 = Me$ (**3d**)[b]

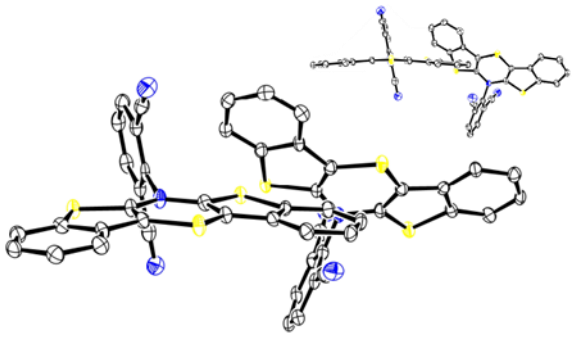


$R^1 = R^2 = H$, $R^3 = OMe$ (**3e**)[a]



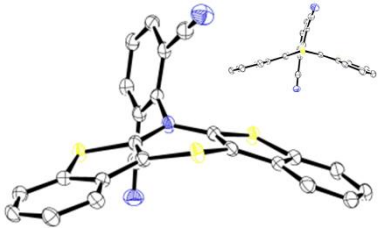
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**)[a]

(polymorph I)



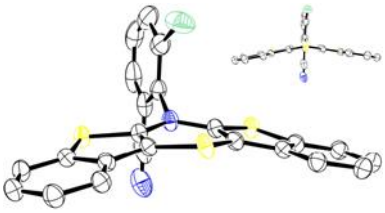
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**)[a]

(polymorph II)

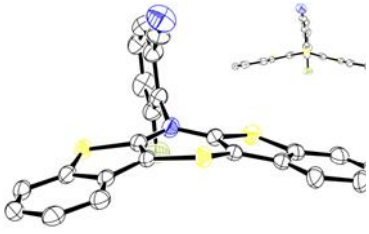


$R^1 = R^2 = H$, $R^3 = CN$ (**3f**)[b]

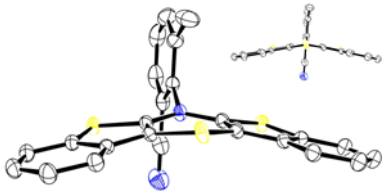
(polymorph III)



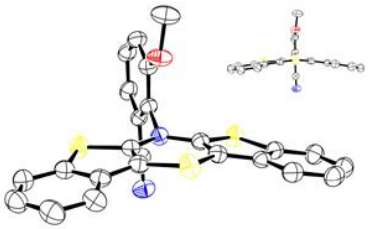
$R^1 = H$, $R^2 = CN$, $R^3 = Cl$ (**3k**)[b]



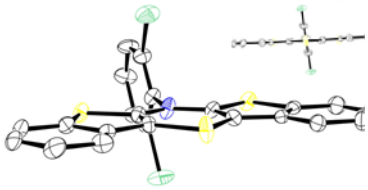
$R^1 = H$, $R^2 = CN$, $R^3 = F$ (**3l**)[b]



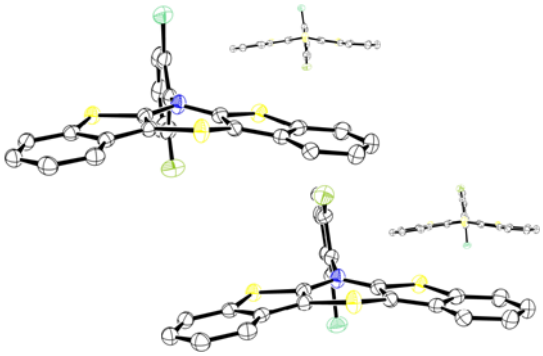
R^1 = H, R^2 = CN, R^3 = Me (**3m**)[b]



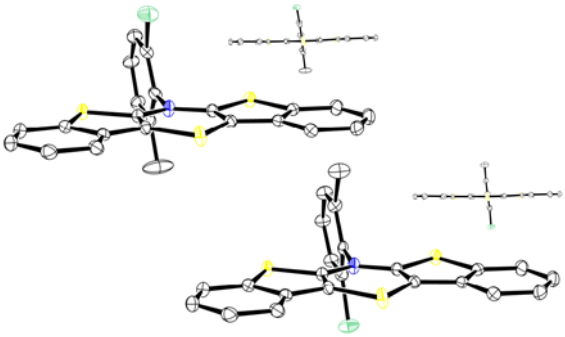
R^1 = H, R^2 = CN, R^3 = OMe (**3n**)[b]



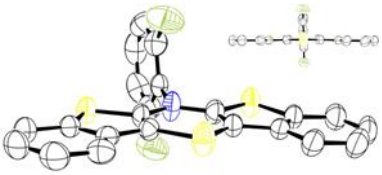
R^1 = R^2 = H, R^3 = Cl (**3g**)[b]



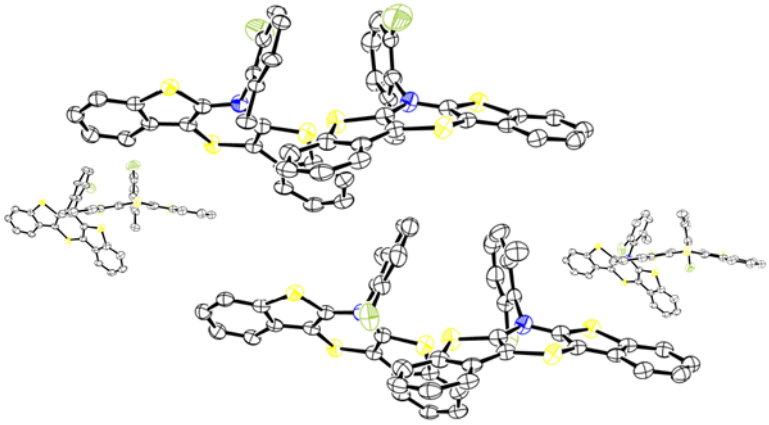
R^1 = H, R^2 = Cl, R^3 = F (**3o**)[b,c]



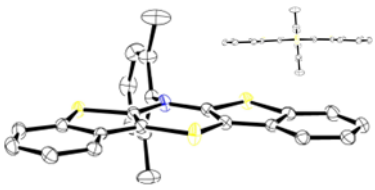
R^1 = H, R^2 = Cl, R^3 = Me (**3p**)[b,c]



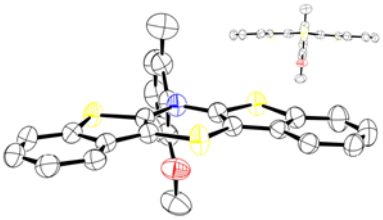
R^1 = R^2 = H, R^3 = F (**3h**)[b]



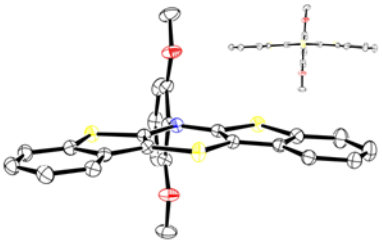
R^1 = H, R^2 = F, R^3 = Me (**3r**)[a,c]



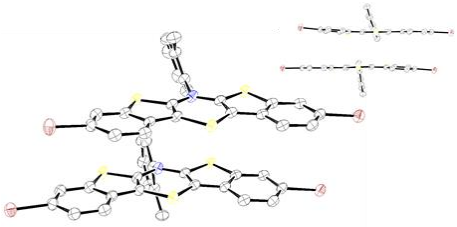
R^1 = R^2 = H, R^3 = Me (**3i**)[b]



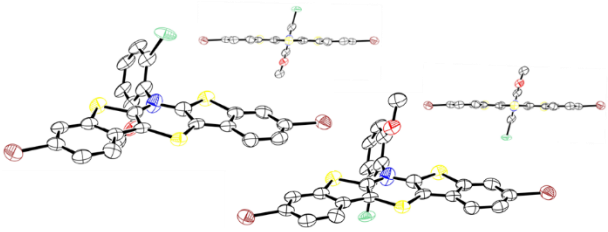
R^1 = H, R^2 = Me, R^3 = OMe (**3t**)[b]



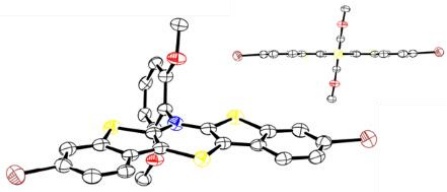
R^1 = R^2 = H, R^3 = OMe (**3j**)[b]



R^1 = Br, R^2 = H, R^3 = Me (**4a**)[a]



R^1 = Br, R^2 = Cl, R^3 = OMe (**4b**)[b,c,d]



R^1 = R^2 = Br, R^3 = OMe (**4d**)[b,d]

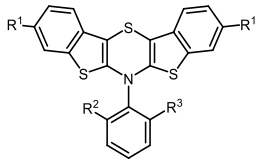
[a]The asymmetric unit consists of two BBTT molecules that differ in their arrangement of the BBTT's backbone and *N*-aryl moiety to each other. [b]The asymmetric unit consists of one BBTT molecule. [c]Each BBTT's molecule shows to conformers, that do not differ in their arrangement of the BBTT's backbone, but in the orientation of the *N*-aryl moiety. [d]The asymmetric unit consists of only half a BBTT's molecule by means of division along the *S*-*N*-axis.

Figure 55. Molecular structure of BBTTs **3** and **4**. The thermal ellipsoids are set at a 50% probability level and all hydrogen atoms are omitted for clarity.

3.1.1 Table for angles

The angles were determined analogously to the method previously defined in the literature.[6]

Table 1. Comparison of folding angles φ, torsion angles α and S–N–C_{Aryl}-angles β of of BBTTs **3** and **4** of the molecule's geometry by crystal structure analysis and DFT-calculation. (B3LYP/6-311++G**).



	folding angle / °	torsion angle / °	*S–N–C$_{aryl}$*-angle / °	density / g cm^{-3}
	φ	α	β	
R^1 = R^2 = H, R^3 = CN (**3a**) (exp.)	177.7	13.7	186.5	1.483
R^1 = R^2 = H, R^3 = CN (**3a**) (calc.)	148.4	6.8	162.1	
R^1 = R^2 = H, R^3 = Cl (**3b**) (exp.)	166.9	1.5	174.0	1.523
R^1 = R^2 = H, R^3 = Cl (**3b**) (calc.)	150.8	0.0	156.7	

$R^1 = R^2 = H$, $R^3 = F$ (**3c**) (exp.)	155.6	15.3	182.5	1.516
$R^1 = R^2 = H$, $R^3 = F$ (**3c**) (calc.)	148.6	0.0	145.1	
$R^1 = R^2 = H$, $R^3 = Me$ (**3d**) (exp.)	166.6	6.8	174.9	1.456
$R^1 = R^2 = H$, $R^3 = Me$ (**3d**) (calc.)	149.3	0.0	160.3	
$R^1 = R^2 = H$, $R^3 = OMe$ (**3e**) (exp.)	163.9 165.5	10.7 4.4	179.6 (molecule I) 175.5 (molecule II)	1.484
$R^1 = R^2 = H$, $R^3 = OMe$ (**3e**) (calc.)	155.7	0.0	175.0	
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**) (exp.) (polymorph I)	151.1 154.0	9.2 11.3	140.5 (molecule I) 142.9 (molecule II)	1.460
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**) (exp.) (polymorph II)	163.7 172.1	11.4 11.6	153.7 (molecule I) 163.4 (molecule II)	1.488
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**) (exp.) (polymorph III)	146.3	15.5	169.8	1.486
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**) (calc.)	154.5	0.04	141.5	
$R^1 = H$, $R^2 = CN$, $R^3 = Cl$ (**3k**) (exp.)	159.9	2.4	154.1	1.522
$R^1 = H$, $R^2 = CN$, $R^3 = Cl$ (**3k**) (calc.)	154.2	0.0	142.7	
$R^1 = H$, $R^2 = CN$, $R^3 = F$ (**3l**) (exp.)	157.4	6.5	156.9	1.508
$R^1 = H$, $R^2 = CN$, $R^3 = F$ (**3l**) (calc.)	149.7	0.15	156.0	
$R^1 = H$, $R^2 = CN$, $R^3 = Me$ (**3m**) (exp.)	158.9	2.93	159.9	1.440
$R^1 = H$, $R^2 = CN$, $R^3 = Me$ (**3m**) (calc.)	154.2	0.0	167.3	
$R^1 = H$, $R^2 = CN$, $R^3 = OMe$ (**3n**) (exp.)	164.9	0.5	153.7	1.446
$R^1 = H$, $R^2 = CN$, $R^3 = OMe$ (**3n**) (calc.)	155.1	0.0	140.6	

$R^1 = R^2 = H$, $R^3 = Cl$ (**3g**) (exp.)	178.9	7.0	182.6	1.580
$R^1 = R^2 = H$, $R^3 = Cl$ (**3g**) (calc.)	154.1	0.0	146.4	
$R^1 = H$, $R^2 = Cl$, $R^3 = F$ (**3o**) (exp.)	165.0 165.0	8.5 5.6	171.3 (conformer I) 186.7 (conformer II)	1.589
$R^1 = H$, $R^2 = Cl$, $R^3 = F$ (**3o**) (calc.)	151.1	0.0	139.1 (conformer I)	
$R^1 = H$, $R^2 = Cl$, $R^3 = F$ (**3o**) (calc.)	150.9	0.2	150.9 (conformer II)	
$R^1 = H$, $R^2 = Cl$, $R^3 = Me$ (**3p**) (exp.)	177.8 177.8	6.6 5.8	183.8 (conformer I) 183.8 (conformer II)	1.497
$R^1 = H$, $R^2 = Cl$, $R^3 = Me$ (**3p**) (calc.)	154.6	0.0	151.0 (conformer I)	
$R^1 = H$, $R^2 = Cl$, $R^3 = Me$ (**3p**) (calc.)	169.6	0.0	172.8 (conformer II)	
$R^1 = R^2 = H$, $R^3 = F$ (**3h**) (exp.)	178.2	1.3	170.8	1.511
$R^1 = R^2 = H$, $R^3 = F$ (**3h**) (calc.)	149.7	0.0	143.7	
$R^1 = H$, $R^2 = F$, $R^3 = Me$ (**3r**) (exp.)	161.4 161.4 161.7 161.7	8.6 0.9 6.3 0.2	153.5 (molecule I, conformer I) 162.0 (molecule I, conformer II) 157.6 (molecule II, conformer I) 160.5 (molecule II, conformer II)	1.474
$R^1 = H$, $R^2 = F$, $R^3 = Me$ (**3r**) (calc.)	150.8	0.1	159.0 (conformer I)	
$R^1 = H$, $R^2 = F$, $R^3 = Me$ (**3r**) (calc.)	169.3	0.1	168.0 (conformer II)	
$R^1 = R^2 = H$, $R^3 = Me$ (**3i**) (exp.)	176.8	2.5	185.5	1.412
$R^1 = R^2 = H$, $R^3 = Me$ (**3i**) (calc.)	166.1	0.0	171.4	
$R^1 = H$, $R^2 = Me$, $R^3 = OMe$ (**3t**) (exp.)	174.5	1.9	189.2	1.416

R^1 = H, R^2 = Me, R^3 = OMe (**3t**) (calc.)	156.2	0.0	173.0	
R^1 = R^2 = H, R^3 = OMe (**3j**) (exp.)	173.7	4.2	192.0	1.478
R^1 = R^2 = H, R^3 = OMe (**3j**) (calc.)	158.2	0.1	166.7	
R^1 = Br, R^2 = H, R^3 = Me (**4a**) (exp.)	177.3 177.3	5.5 19.5	194.2 (molecule I) 188.7 (molecule II)	1.777
R^1 = Br, R^2 = H, R^3 = Me (**4a**) (calc.)	148.4	0.1188	161.7	
R^1 = Br, R^2 = Cl, R^3 = OMe (**4b**) (exp.)	180.0 180.0	12.5 12.5	180.0 (conformer I) 180.0 (conformer II)	1.843
R^1 = Br, R^2 = Cl, R^3 = OMe (**4b**) (calc.)	158.7	0.0	172.4 (conformer I)	
R^1 = Br, R^2 = Cl, R^3 = OMe (**4b**) (calc.)	166.0	0.0	162.9 (conformer II)	
R^1 = Br, R^2 = R^3 = OMe (**4d**) (exp.)	180.0	8.3	180.0	1.790
R^1 = Br, R^2 = R^3 = OMe (**4d**) (calc.)	158.2	0.0	165.2	

3.1.2 Tables for crystallographic data

Table 2.Crystal data parameters for compounds **3a**-**d**.

	3a	**3b**	**3c**	**3d**
CCDC No.	2346002	2345988	2345990	2345982
Molecular formula	$C_{23}H_{12}N_2S_3$	$C_{22}H_{12}ClNS_3$	$C_{22}H_{12}FNS_3$	$C_{23}H_{15}NS_3$
Molecular weight [g/mol]	412.53	421.96	405.51	401.54
Crystal shape and color	block, red	block, yellow	block, yellow	block, yellow
Size [mm]	0.17 × 0.09 × 0.06	0.19 × 0.08 × 0.05	0.18 × 0.16 × 0.09	0.61 × 0.25 × 0.17
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	*Pbca*	*Pna*2_1	*C*2/*c*	*Pna*2_1

Lattice parameters [Å]	a [Å] 8.01980(10) α [°] 90	a [Å] 16.5856(2) α [°] 90	a [Å] 23.3856(4) α [°] 90	a [Å] 17.2183(2) α [°] 90
	b [Å] 13.1079(2) β [°] 90	b [Å] 17.2589(2) β [°] 90	b [Å] 7.54300(10) β [°] 106.907(2)	b [Å] 17.7363(2) β [°] 90
	c [Å] 35.1615(4) γ [°] 90	c [Å] 6.42770(10) γ [°] 90	c [Å] 21.0499(4) γ [°] 90	c [Å] 5.99740(10) γ [°] 90
Cell volume [$Å^3$]	3696.27(8)	1839.92(4)	3552.66(11)	1831.54(4)
Z	8	4	8	4
Calculated density [g/ml]	1.483	1.523	1.516	1.456
Absorption coefficient [mm^{-1}]	3.751	5.067	3.956	3.748
F (000)	1696	864	1664	832
Range Θ [°]	2.50 – 76.09	3.65 – 77.55	3.93 – 77.69	5.17 – 76.84
Array bounds	-9 ≤ h ≤ 9	-21 ≤ h ≤ 20	-26 ≤ h ≤ 29	-21 ≤ h ≤ 20
	-14 ≤ k ≤ 16	-20 ≤ k ≤ 20	-9 ≤ k ≤ 9	-21 ≤ k ≤ 22
	-40 ≤ l ≤ 42	-8 ≤ l ≤ 7	-25 ≤ l ≤ 26	-7 ≤ l ≤ 7
Measured reflections	18298	23065	20092	21850
Independent reflections	3562	3539	3624	3779
Observed reflections (I>2σ(I))	3248	3402	3332	3670
Final R-value (I>2σ(I))[a]	0.0298	0.0464	0.0287	0.0482
	0.0749	0.1226	0.0742	0.1197
R-value (whole data)[a]	0.0345	0.0481	0.0315	0.0493
	0.0772	0.1246	0.0766	0.1211
Completeness	0.999	1.000	1.000	0.999
Indep. refl/constr./parameter	3562/0/253	3539/1/244	3624/0/244	3779/1/245
Goodness-of-fit-on F^2 [b]	1.080	1.061	1.070	1.064

[a] $R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR2 = [\Sigma[w(Fo^2-Fc^2)2/\ \Sigma[(wFo^2)2]]^{1/2}$; $w = 1/[\sigma2(Fo^2)+(aP)^2+bP]$ with $P = (Fo^2+2Fc^2)/3$
[b] $GooF = S = [[\Sigma w(Fo^2-Fc^2)^2]/(m-n)]^{1/2}$. m = Number of reflexes. n = Number of parameter.

Table 3.Crystal data parameters for compounds **3e** and **3f**.

	3e	**3f (polymorph I)**	**3f (polymorph III)**	**3f (polymorph II)**
CCDC No.	2345989	2345999	2345996	2345994

Molecular formula	$C_{23}H_{15}NOS_3$	$C_{24}H_{11}N_3S_3$	$C_{24}H_{11}N_3S_3$	$C_{24}H_{11}N_3S_3$
Molecular weight [g/mol]	417.54	437.54	437.54	437.54
Crystal shape and color	block, yellow	block, yellow	block, orange	block, red
Size [mm]	0.18 × 0.13 × 0.08	0.34 × 0.27 × 0.16	0.45 × 0.28 × 0.26	0.26 × 0.17 × 0.06
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$Pna2_1$	$P\bar{1}$
Lattice parameters [Å]	a [Å] 11.52560(10) α [°] 90	a [Å] 14.60590(10) α [°] 90	a [Å] 14.60400(10) α [°] 90	a [Å] 11.7646(4) α [°] 106.573(3)
	b [Å] 26.5077(3) β [°] 107.4920(10)	b [Å] 12.08020(10) β [°] 91.3410(10)	b [Å] 15.9177(2) β [°] 90	b [Å] 14.0915(4) β [°] 105.665(3)
	c [Å] 12.8253(2) γ [°] 90	c [Å] 22.5734(2) γ [°] 90	c [Å] 8.41400(10) γ [°] 90	c [Å] 14.4094(5) γ [°] 110.564(3)
Cell volume [$Å^3$]	3737.16(8)	3981.81(6)	1955.94(4)	1952.76(12)
Z	8	8	4	4
Calculated density [g/ml]	1.484	1.460	1.486	1.488
Absorption coefficient [mm^{-1}]	3.739	3.535	3.598	3.604
F (000)	1728	1792	896	896
Range Θ [°]	3.95 – 77.39	3.57 – 77.22	2.80 – 77.06	3.41 – 77.74
Array bounds	-14 ≤ h ≤ 14	-17 ≤ h ≤ 18	-18 ≤ h ≤ 17	-14 ≤ h ≤ 12
	-33 ≤ k ≤ 29	-15 ≤ k ≤ 12	-20 ≤ k ≤ 20	-16 ≤ k ≤ 17
	-15 ≤ l ≤ 15	-28 ≤ l ≤ 28	-8 ≤ l ≤ 10	-18 ≤ l ≤ 17
Measured reflections	52097	38009	28238	36244
Independent reflections	7659	8144	3726	7871
Observed reflections (I>2σ(I))	6955	7027	3669	7093
Final R-value (I>2σ(I))[a]	0.0339	0.0484	0.0280	0.0659
	0.0846	0.1354	0.0744	0.2082
R-value (whole data)[a]	0.0375	0.0541	0.0284	0.0708
	0.0869	0.1403	0.0748	0.2105
Completeness	0.999	1.000	1.000	0.998

Indep. refl/constr./parameter	7659/0/507	8144/0/541	3726/1/271	7871/0/541
Goodness-of-fit-on F^2 [b]	1.052	1.036	1.093	1.155

[a] R1 = Σ||Fo|-|Fc||/Σ|Fo|; wR2 = [Σ[w(Fo^2-Fc^2)2/ Σ[(wFo^2)2]]$^{1/2}$; w = 1/[σ2(Fo^2)+($aP)^2$+bP] with P = (Fo^2+2Fc^2)/3
[b] GooF = S = [[Σw(Fo^2-Fc^2)^2]/(m-n)]$^{1/2}$. m = Number of reflexes. n = Number of parameter.

Table 4.Crystal data parameters for compounds **3k-n**.

	3k	**3l**	**3m**	**3n**
CCDC No.	2345983	2345987	2345959	2345998
Molecular formula	$C_{23}H_{11}ClN_2S_3$	$C_{23}H_{11}FN_2S_3$	$C_{24}H_{14}N_2S_3$	$C_{24}H_{14}N_2OS_3$
Molecular weight [g/mol]	446.97	430.52	426.55	442.55
Crystal shape and color	block, orange	block, orange	block, yellow	block, orange
Size [mm]	0.13 × 0.11 × 0.05	0.25 × 0.08 × 0.05	0.45 × 0.37 × 0.34	0.102 × 0.062 × 0.039
Temperature [K]	100(2)	100(2)	140(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*I*2/*a*	*I*2/*a*	*C*2/*c*	*I*2/*a*
Lattice parameters [Å]	a [Å] 16.3561(3) α [°] 90	a [Å] 15.1168(3) α [°] 90	a [Å] 33.709(2) α [°] 90	a [Å] 15.9604(4) α [°] 90
	b [Å] 7.66140(10) β [°] 96.415(2)	b [Å] 15.1951(3) β [°] 90.678(2)	b [Å] 7.7121(5) β [°] 112.804(3)	b [Å] 8.0872(2) β [°] 96.199(2)
	c [Å] 31.3313(6) γ [°] 90	c [Å] 16.5116(3) γ [°] 90	c [Å] 16.4250(10) γ [°] 90	c [Å] 31.6787(8) γ [°] 90
Cell volume [$Å^3$]	3901.56(12)	3792.47(13)	3936.2(4)	4065.02(18)
Z	8	8	8	8
Calculated density [g/ml]	1.522	1.508	1.440	1.446
Absorption coefficient [mm^{-1}]	4.833	3.761	0.390	3.489
F (000)	1824	1760	1760	1824
Range Θ [°]	2.82 – 77.92	3.95 – 77.49	2.49 – 36.46	5.61 – 75.80
Array bounds	-20 ≤ h ≤ 18	-18 ≤ h ≤ 18	-54 ≤ h ≤ 57	-19 ≤ h ≤ 20
	-9 ≤ k ≤ 9	-19 ≤ k ≤ 16	-12 ≤ k ≤ 12	-10 ≤ k ≤ 9
	-39 ≤ l ≤ 39	-20 ≤ l ≤ 17	-27 ≤ l ≤ 28	-39 ≤ l ≤ 39
Measured reflections	34852	13104	61119	29459

Independent reflections	4014	3606	9943	4149
Observed reflections (I>2σ(I))	3406	3178	8067	3324
Final R-value (I>2σ(I))[a]	0.0383	0.0558	0.0383	0.0539
	0.0986	0.1472	0.1027	0.1451
R-value (whole data)[a]	0.0466	0.0648	0.0504	0.0681
	0.1026	0.1526	0.1118	0.1553
Completeness	1.000	0.975	0.999	0.999
Indep. refl/constr./parameter	4014/0/262	3606/0/262	9943/0/263	4149/0/272
Goodness-of-fit-on F^2 [b]	1.062	1.066	1.026	1.050

[a] R1 = Σ||Fo|-|Fc||/Σ|Fo|; wR2 = $[\Sigma[w(Fo^2-Fc^2)2/\ \Sigma[(wFo^2)2]]^{1/2}$; w = $1/[\sigma2(Fo^2)+(aP)^2+bP]$ with P = $(Fo^2+2Fc^2)/3$
[b] GooF = S = $[[\Sigma w(Fo^2-Fc^2)^2]/(m-n)]^{1/2}$. m = Number of reflexes. n = Number of parameter.

Table 5.Crystal data parameters for compounds **3g**, **3o**, **3p** and **3h**.

	3g	**3o**	**3p**	**3h**
CCDC No.	2335542	2345948	2345958	2335553
Molecular formula	$C_{22}H_{11}Cl_2NS_3$	$C_{22}H_{11}ClFNS_3$	$C_{23}H_{14}ClNS_3$	$C_{22}H_{11}F_2NS_3$
Molecular weight [g/mol]	456.40	439.95	435.98	423.50
Crystal shape and color	block, yellow	block, orange	block, yellow	block, yellow
Size [mm]	-	0.19 × 0.13 × 0.11	0.21 × 0.15 × 0.11	0.2×0.1×0.1
Temperature [K]	273(2)	140(2)	100(2)	293(2)
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	*Pca*2_1	*P*21/*n*	*Pccn*	*P*2/*c*
Lattice parameters [Å]	a [Å] 7.8377(3) α [°] 90	a [Å] 11.1576(5) α [°] 90	a [Å] 27.1805(4) α [°] 90	a [Å] 8.1876(6) α [°] 90
	b [Å] 17.8936(4) β [°] 90	b [Å] 13.4014(5) β [°] 110.654(6)	b [Å] 17.9600(2) β [°] 90	b [Å] 8.0844(5) β [°] 90.247(4)
	c [Å] 13.6815(4) γ [°] 90	c [Å] 13.0959(8) γ [°] 90	c [Å] 7.92650(10) γ [°] 90	c [Å] 28.1173(13) γ [°] 90
Cell volume [$Å^3$]	1918.76(11)	1832.34(17)	3869.41(9)	1861.1(2)
Z	4	4	8	4
Calculated density [g/ml]	1.580	1.595	1.497	1.511

Absorption coefficient [mm^{-1}]	0.674	0.569	4.838	0.425
F (000)	928	896	1792	864
Range Θ [°]	3.0 – 30.3	1.87 – 32.12	2.94 – 76.02	3.5 – 20.5
Array bounds	-11 ≤ h ≤ 10	-16 ≤ h ≤ 13	-34 ≤ h ≤ 32	-9 ≤ h ≤ 7
	-25 ≤ k ≤ 18	-16 ≤ k ≤ 17	-22 ≤ k ≤ 16	-9 ≤ k ≤ 8
	-18 ≤ l ≤ 19	-16 ≤ l ≤ 11	-9 ≤ l ≤ 5	-33 ≤ l ≤ 35
Measured reflections	22811	25761	15834	11673
Independent reflections	5521	4666	3766	3833
Observed reflections (I>2σ(I))	4572	4019	3486	1855
Final R-value (I>2σ(I))[a]	0.0521	0.0491	0.0312	0.0592
	0.0940	0.1168	0.0782	0.0607
R-value (whole data)[a]	0.0672	0.0582	0.0335	0.1502
	0.0984	0.1225	0.0796	0.0779
Completeness	0.999	0.998	0.999	0.992
Indep. refl/constr./parameter	5521/1/254	4666/216/302	3766/92/307	3833/0/254
Goodness-of-fit-on F^2 [b]	1.146	1.062	1.033	1.024

[a] R1 = Σ||Fo|-|Fc||/Σ|Fo|; wR2 = $[\Sigma[w(Fo^2-Fc^2)2/\ \Sigma[(wFo^2)2]]^{1/2}$; w = $1/[\sigma2(Fo^2)+(aP)^2+bP]$ with P = $(Fo^2+2Fc^2)/3$
[b] GooF = S = $[[\Sigma w(Fo^2-Fc^2)^2]/(m-n)]^{1/2}$. m = Number of reflexes. n = Number of parameter.

Table 6.Crystal data parameters for compounds **3r**, **3i**, **3t** and **3j**.

	3r	**3i**	**3t**	**3j**
CCDC No.	2345985	2345957	2345992	2345956
Molecular formula	$C_{23}H_{14}FNS_3$	$C_{24}H_{17}NS_3$	$C_{24}H_{17}NOS_3$	$C_{24}H_{17}NO_2S_3$
Molecular weight [g/mol]	419.53	415.57	431.57	447.57
Crystal shape and color	block, yellow	block, yellow	block, yellow	block, orange
Size [mm]	0.16 × 0.12 × 0.07	0.28 × 0.19 × 0.07	0.23 × 0.19 × 0.14	0.36 × 0.31 × 0.25
Temperature [K]	120(2)	100(2)	200(2)	140(2)
Crystal system	triclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P\bar{1}$	*Pccn*	*Pccn*	$P2_1/c$

Lattice parameters [Å]	a [Å] 7.61560(10) α [°] 113.890(2)	a [Å] 27.1441(3) α [°] 90	a [Å] 27.9531(5) α [°] 90	a [Å] 14.2151(17) α [°] 90
	b [Å] 16.4902(3) β [°] 101.842(2)	b [Å] 17.9997(2) β [°] 90	b [Å] 18.0208(3) β [°] 90	b [Å] 18.240(2) β [°] 105.399(3)
	c [Å] 16.9288(3) γ [°] 91.0860(10)	c [Å] 8.00280(10) γ [°] 90	c [Å] 8.03800(10) γ [°] 90	c [Å] 8.0477(9) γ [°] 90
Cell volume [$Å^3$]	1890.04(6)	3910.05(8)	4049.04(11)	2011.8(4)
Z	4	8	8	4
Calculated density [g/ml]	1.474	1.412	1.416	1.478
Absorption coefficient [mm^{-1}]	3.737	3.530	3.469	0.391
F (000)	864	1728	1792	928
Range Θ [°]	2.93 – 77.57	2.92 – 75.75	2.89 – 75.85	2.68 – 37.46
Array bounds	-9 ≤ h ≤ 9	-32 ≤ h ≤ 33	-34 ≤ h ≤ 31	-22 ≤ h ≤ 22
	-20 ≤ k ≤ 19	-22 ≤ k ≤ 21	-17 ≤ k ≤ 22	-28 ≤ k ≤ 28
	-17 ≤ l ≤ 21	-9 ≤ l ≤ 9	-10 ≤ l ≤ 9	-12 ≤ l ≤ 12
Measured reflections	35586	15679	37355	123223
Independent reflections	7728	3747	4177	8050
Observed reflections (I>2σ(I))	6697	3476	3518	7090
Final R-value (I>2σ(I))[a]	0.0466	0.0322	0.0442	0.0337
	0.1281	0.0845	0.1199	0.0881
R-value (whole data)[a]	0.0523	0.0347	0.0522	0.0388
	0.1324	0.0864	0.1259	0.0918
Completeness	0.999	0.999	1.000	0.999
Indep. refl/constr./parameter	7728/150/654	3747/0/256	4177/0/264	8050/0/273
Goodness-of-fit-on F^2 [b]	1.101	1.050	1.038	1.033

[a] $R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR2 = [\Sigma[w(Fo^2-Fc^2)2/\ \Sigma[(wFo^2)2]]^{1/2}$; $w = 1/[\sigma2(Fo^2)+(aP)^2+bP]$ with $P = (Fo^2+2Fc^2)/3$
[b] $GooF = S = [[\Sigma w(Fo^2-Fc^2)^2]/(m-n)]^{1/2}$. m = Number of reflexes. n = Number of parameter.

Table 7.Crystal data parameters for compounds **4a**, **4b** and **4d**.

	4a	**4b**	**4d**
CCDC No.	2345944	2346000	2345986

Molecular formula	$C_{23}H_{13}Br_2NS_3$	$C_{23}H_{12}Br_2ClNOS_3$	$C_{24}H_{15}Br_2NO_2S_3$
Molecular weight [g/mol]	559.34	609.79	605.37
Crystal shape and color	block, yellow	block, yellow	block, yellow
Size [mm]	0.18 × 0.14 × 0.09	0.1 × 0.08 × 0.06	0.22 × 0.15 × 0.1
Temperature [K]	100(2)	100(2)	150(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	*I*2/*a*	*I*2/*a*
Lattice parameters [Å]	a [Å] 11.9165(2) α [°] 88.1270(10)	a [Å] 7.4566(2) α [°] 90	a [Å] 7.39050(10) α [°] 90
	b [Å] 13.0397(2) β [°] 89.7700(10)	b [Å] 17.8566(4) β [°] 100.776(2)	b [Å] 17.8599(3) β [°] 97.270(2)
	c [Å] 14.2173(2) γ [°] 70.184(2)	c [Å] 16.8039(4) γ [°] 90	c [Å] 17.1558(3) γ [°] 90
Cell volume [$Å^3$]	2077.21(6)	2197.98(9)	2246.25(6)
Z	4	4	4
Calculated density [g/ml]	1.789	1.843	1.790
Absorption coefficient [mm^{-1}]	7.849	8.608	7.383
F (000)	1104	1200	1200
Range Θ [°]	3.10 – 77.75	3.61 – 77.03	3.50 – 77.81
Array bounds	-14 ≤ h ≤ 15	-8 ≤ h ≤ 9	-9 ≤ h ≤ 9
	-16 ≤ k ≤ 15	-21 ≤ k ≤ 21	-22 ≤ k ≤ 16
	-18 ≤ l ≤ 17	-20 ≤ l ≤ 21	-21 ≤ l ≤ 21
Measured reflections	56317	19788	21344
Independent reflections	8243	2287	2376
Observed reflections (I>2σ(I))	7452	2177	2189
Final R-value (I>2σ(I))[a]	0.0393	0.0888	0.0369
	0.1083	0.1936	0.1018
R-value (whole data)[a]	0.0438	0.0915	0.0393
	0.1154	0.1945	0.1036
Completeness	0.998	1.000	1.000
Indep. refl/constr./parameter	8243/0/525	2287/36/157	2376/0/148
Goodness-of-fit-on F^2 [b]	1.112	1.184	1.075

[a] $R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR2 = [\Sigma[w(Fo^2-Fc^2)2/\ \Sigma[(wFo^2)2]]^{1/2}$; $w = 1/[\sigma2(Fo^2)+(aP)^2+bP]$ with $P = (Fo^2+2Fc^2)/3$
[b] $GooF = S = [[\Sigma w(Fo^2-Fc^2)^2]/(m-n)]^{1/2}$. m = Number of reflexes. n = Number of parameter.

3.2 Superimposed crystal packing patterns

The superordinate crystal packing patterns as well as Hirshfeld surface analyses are depicted for selected derivatives. More details for those and all other derivatives of **3** and **4** can be extracted from the attached cif files.

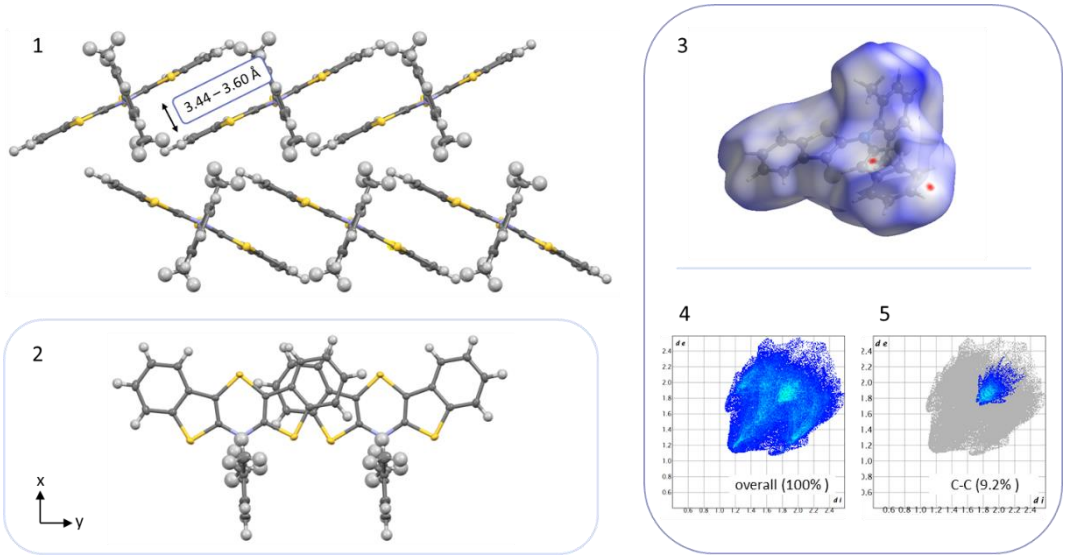


Figure 56. 1) Section of the crystal packing pattern of *anti-anti-N-ortho,ortho'*-dimethylphenyl-BBTT **3i** in the side view. 2) Section of the crystal packing pattern of *anti-anti-N-ortho,ortho'*-dimethylphenyl-BBTT **3i** in the top view. 3-5) Graphical depiction of the the Hirshfeld surface with their respective fingerprint diagrams.

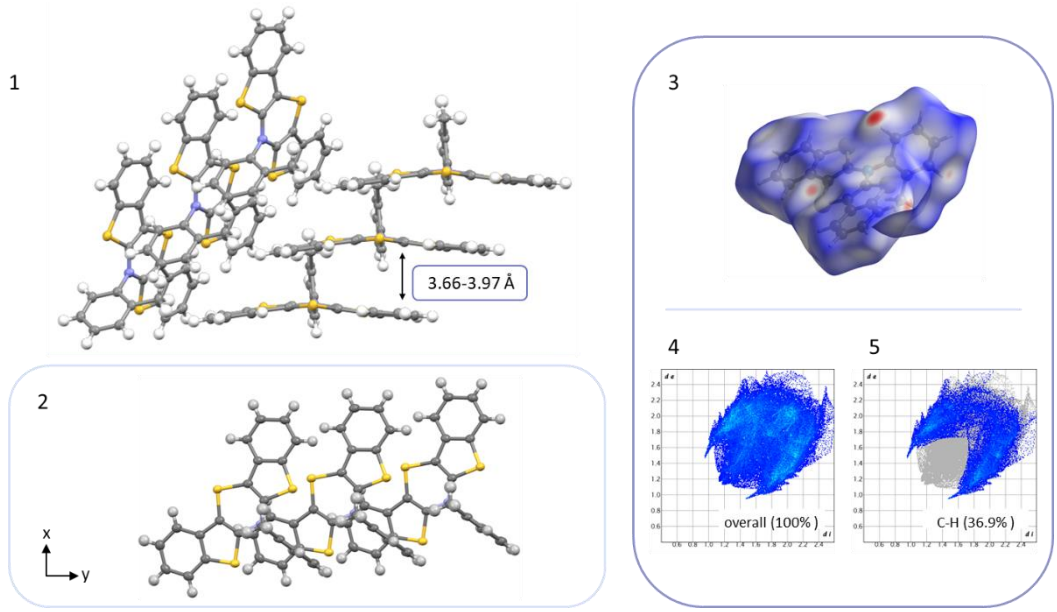


Figure 57. 1) Section of the crystal packing pattern of *anti-anti-N-ortho*-methylphenyl-BBTT **3d** in the side view. 2) Section of the crystal packing pattern of *anti-anti-N-ortho*-methylphenyl-BBTT **3d** in the top view. 3-5) Graphical depiction of the the Hirshfeld surface with their respective fingerprint diagrams.

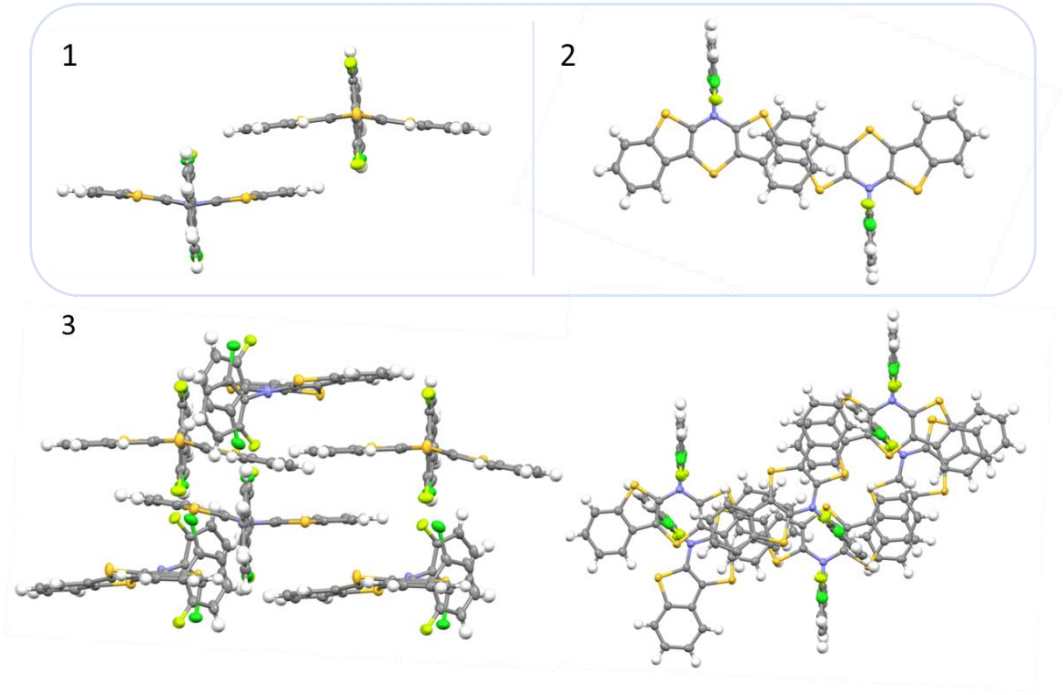


Figure 58. 1) Section of the crystal packing pattern of *anti-anti-N-ortho,ortho'*-chlorfluorphenyl-BBTT **3o** in the side view. 2) Section of the crystal packing pattern of *anti-anti-N-ortho,ortho'*-chlorfluorphenyl-BBTT **3o** in the top view. 3) Sections of the crystal packing pattern of *anti-anti-N-ortho,ortho'*-chlorfluorphenyl-BBTT **3o**.

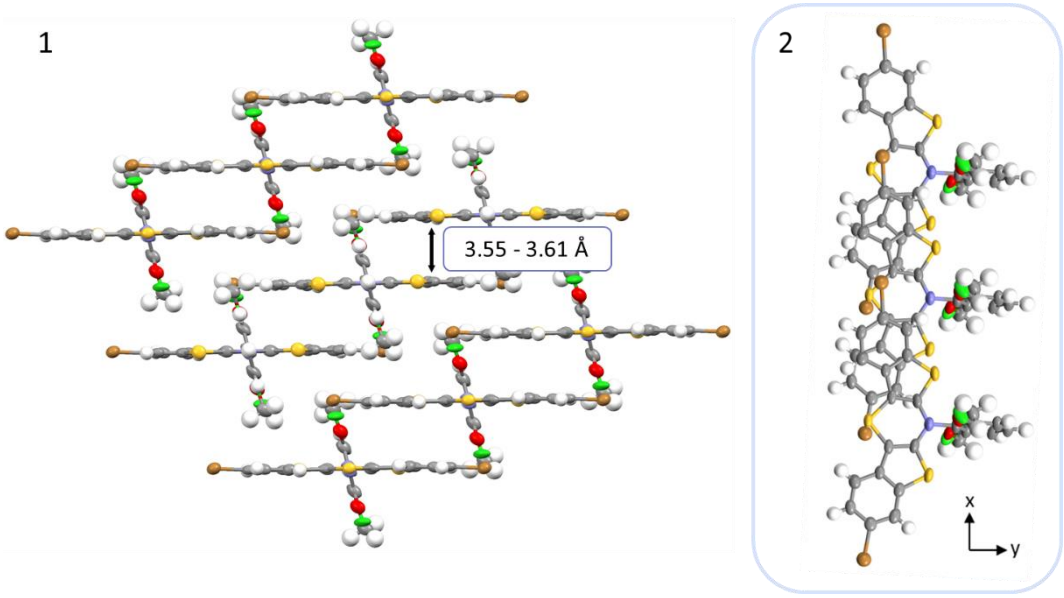
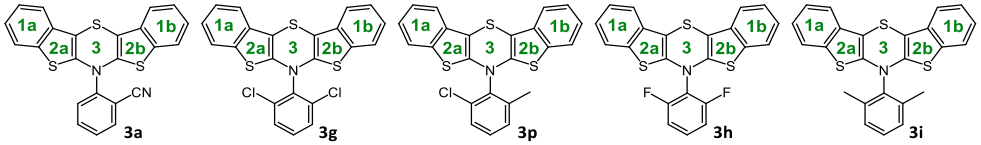


Figure 59. 1) Section of the crystal packing pattern of *anti-anti-N-ortho,ortho'*-chlormethoxyphenyl-3,9-dibromo-BBTT **4b** in the side view. 2) Section of the crystal packing pattern of *anti-anti-N-ortho,ortho'*-chlormethoxyphenyl-3,9-dibromo-BBTT **4b** in the top view.

3.3 NICS-calculations

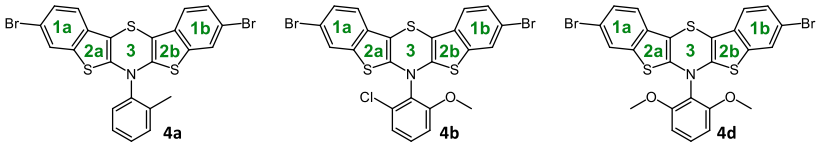
The employed DFT-calculations for producing the NICS values were used as given in the literature by the GIAO method.[7, 8]

Table 8: Quantum chemically calculated NICS-values of the roughly fully planarized BBTT **3a**, **3g**, **3p**, **3h** and **3i** (B3LYP/6-311+G**). The ghost atoms are located in the center of each of the assigned rings 1-3.



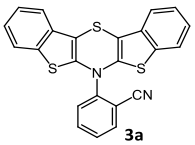
no.	$NICS_{iso}$ (0/+1/-1)						ring current (aromaticity)
	3a	**3g**	**3p**		**3h**	**3i**	
1a	–8.41/ –10.23/ –10.22	–8.37/ –10.31/ –10.25	–8.53/–10.28 /–10.27 (Conformer I)	–8.54/–10.29 /–10.34 (Conformer II)	–8.56/ –10.47/ –10.36	–8.59/ –10.29/ –10.38	diatropic (aromatic)
1b	–8.60/ –10.42/ –10.25	–8.53/ –10.43/ –10.37	–8.64/–10.43 /–10.36 (Conformer I)	–8.63/–10.41 /–10.35 (Conformer II)	–8.34/ –10.20/ –10.32	–8.39/ –10.22/ –10.17	diatropic (aromatic)
2a	–9.16/ –6.95/ –7.07	–9.74/ –7.64/ –7.63	–9.34/–7.29/ –7.17 (Conformer I)	–9.48/–7.27/ –7.25 (Conformer II)	–9.20/ –6.67/ –7.06	–8.93/ –7.12/ –7.36	diatropic (aromatic)
2b	–9.18/ –7.03/ –7.47	–9.57/ –7.56/ –7.56	–9.47/–7.62/ –7.41 (Conformer I)	–9.29/–7.53/ –7.29 (Conformer II)	–9.14/ –6.90/ –7.32	–9.20/ –7.06/ –7.02	diatropic (aromatic)
3	7.05/6.42 / 6.37	7.17/6.49 / 6.65	7.32/6.70/ 6.66 (Conformer I)	7.35/6.84/ 6.56 (Conformer II)	7.00/6.30 /6.64	7.60/6.85 /6.95	paratropic (antiaromatic)

Table 9. Quantum chemically calculated NICS-values of the roughly fully planarized BBTT **4a**, **4b** and **4d** (B3LYP/6-311+G**). The ghost atoms are located in the center of each of the assigned rings 1-3.

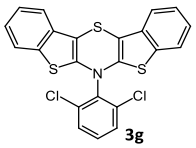


no.	$NICS_{iso}$ (0/+1/-1)					ring current (aromaticity)
	4a		4b		4d	
1a	–8.87/–9.71/ –9.78 (Conformer I)	–8.91/–10.09/ –9.88 (Conformer II)	–9.63/–7.50/ –7.54 (Conformer I)	–9.39/–7.62/ –7.48 (Conformer II)	–8.91/–9.58/ –9.68	diatropic (aromatic)
1b	–8.67/–9.39/ –9.93 (Conformer I)	–8.78/–9.83/ –9.73 (Conformer II)	–9.39/–7.48/ –7.62 (Conformer I)	–9.63/–7.53/ –7.49 (Conformer II)	–8.91/–9.68/ –9.59	diatropic (aromatic)
2a	–9.16/–6.95/ –7.13 (Conformer I)	–9.34/–7.27/ –6.76 (Conformer II)	–8.94/–9.60/ –9.76 (Conformer I)	–8.89/–9.60/ –9.74 (Conformer II)	–9.55/–7.74/ –7.73	diatropic (aromatic)
2b	–9.66/–6.97/ –7.13 (Conformer I)	–9.47/–7.27/ –6.68 (Conformer II)	–8.89/–9.73/ –9.60 (Conformer I)	–8.94/–9.76/ –9.60 (Conformer II)	–9.54/–7.72/ –7.74	diatropic (aromatic)
3	6.84/6.27/ 6.22 (Conformer I)	7.06/6.47/6.2 1 (Conformer II)	7.94/7.18/ 7.12 (Conformer I)	7.94/7.11/ 7.18 (Conformer II)	7.93/7.10/ 7.10	paratropic (antiaromatic)

Table 10: Quantum chemically calculated $NICS_{iso}$, $NICS_{in\text{-}plane}$ and $NICS_{out\text{-}of\text{-}plane}$ values of the roughly fully planarized BBTT **3a** and **3g** (B3LYP/6-311+G**). The ghost atom is located in the center of the 1,4-thiazine ring.



3a



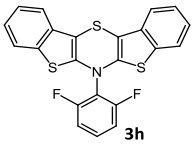
3g

Å	$NICS_{iso}$	$NICS_{in\text{-}plane}$	$NICS_{out\text{-}of\text{-}plane}$	$NICS_{iso}$	$NICS_{in\text{-}plane}$	$NICS_{out\text{-}of\text{-}plane}$
0.0	7.0473	-9.4684	16.5157	7.1675	-9.6434	16.8109
0.1	7.0507	-9.31073	16.3614	7.1838	-9.4981	16.6819
0.2	7.0986	-8.8515	15.9501	7.2486	-9.04457	16.2932
0.3	7.1726	-8.13233	15.3049	7.3381	-8.3278	15.6659
0.4	7.2445	-7.21643	14.461	7.4199	-7.4136	14.8335
0.5	7.2842	-6.178	13.4622	7.4607	-6.37787	13.8386
0.6	7.2654	-5.0915	12.3569	7.4338	-5.29563	12.7294
0.7	7.171	-4.02257	11.1936	7.3228	-4.23227	11.555
0.8	6.9945	-3.02227	10.0168	7.1232	-3.23827	10.3614

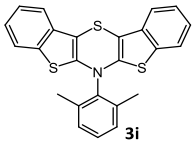
0.9	6.7394	-2.12473	8.8641	6.8408	-2.34727	9.18807
1.0	6.4164	-1.34817	7.76453	6.4888	-1.57723	8.06607
1.1	6.0408	-0.6975	6.73827	6.0842	-0.9334	7.0176
1.2	5.6294	-0.168133	5.79753	5.6449	-0.411433	6.05633
1.3	5.1984	0.250767	4.94767	5.1876	-0.0012	5.18877
1.4	4.7622	0.573333	4.18893	4.7266	0.310833	4.41577
1.5	4.3326	0.8147	3.5179	4.2733	0.5392	3.7341
1.6	3.9186	0.989733	2.9289	3.8363	0.698467	3.13787
1.7	3.5268	1.11193	2.4149	3.4219	0.802167	2.6197
1.8	3.1615	1.19307	1.96847	3.034	0.8625	2.17147
1.9	2.8251	1.243	1.5821	2.6751	0.8901	1.785
2.0	2.5184	1.26973	1.2487	2.3465	0.8941	1.4524
2.1	2.2411	1.27947	0.9616	2.0483	0.8821	1.1662
2.2	1.9918	1.27693	0.714867	1.78	0.860333	0.919667
2.3	1.7688	1.2657	0.5031	1.5404	0.8338	0.706633
2.4	1.5697	1.24827	0.321467	1.328	0.806233	0.5217
2.5	1.3923	1.22647	0.165833	1.1407	0.780567	0.360167
2.6	1.234	1.20157	0.0324333	0.9766	0.758733	0.2179
2.7	1.0927	1.17453	-0.0818667	0.8334	0.741933	0.0914667
2.8	0.9662	1.14613	-0.179933	0.709	0.730867	-0.0219
2.9	0.8528	1.11693	-0.264133	0.601	0.725533	-0.1245
3.0	0.7508	1.0874	-0.336533	0.5076	0.725667	-0.2181
3.1	0.659	1.058	-0.398967	0.4267	0.7307	-0.304
3.2	0.5762	1.0291	-0.452933	0.3567	0.739767	-0.383133
3.3	0.5013	1.00093	-0.499633	0.2959	0.752	-0.456133
3.4	0.4336	0.973833	-0.540233	0.2429	0.766333	-0.5234
3.5	0.3723	0.947867	-0.575533	0.1966	0.781767	-0.585133
3.6	0.3168	0.923133	-0.606267	0.156	0.7974	-0.641433

3.7	0.2666	0.899667	-0.633067	0.1201	0.812467	-0.6924
3.8	0.2211	0.877467	-0.656367	0.0882	0.8262	-0.738
3.9	0.1799	0.856433	-0.676533	0.0598	0.838133	-0.7783
4.0	0.1426	0.836467	-0.693833	0.0345	0.847833	-0.813367
4.1	0.1089	0.817467	-0.708533	0.0118	0.8551	-0.843333
4.2	0.0785	0.799333	-0.720833	-0.0085	0.8598	-0.868333
4.3	0.0511	0.7819	-0.7308	-0.0267	0.8619	-0.8886
4.4	0.0264	0.7651	-0.738633	-0.0429	0.861467	-0.904367
4.5	0.0043	0.748767	-0.744433	-0.0572	0.858667	-0.9159
4.6	-0.0154	0.732867	-0.748267	-0.0699	0.8536	-0.9235
4.7	-0.033	0.717267	-0.750267	-0.0809	0.846567	-0.9275
4.8	-0.0486	0.7019	-0.750533	-0.0905	0.837733	-0.928233
4.9	-0.0624	0.686767	-0.7492	-0.0987	0.8273	-0.926033
5.0	-0.0745	0.6718	-0.7463	-0.1057	0.8155	-0.9212

Table 11: Quantum chemically calculated $NICS_{iso}$, $NICS_{in\text{-}plane}$ and $NICS_{out\text{-}of\text{-}plane}$ values of the roughly fully planarized BBTT **3h** and **3i** (B3LYP/6-311+G**). The ghost atom is located in the center of the 1,4-thiazine ring.



3h



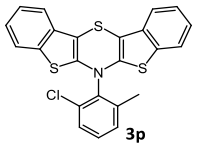
3i

Å	**$NICS_{iso}$**	**$NICS_{in\text{-}plane}$**	**$NICS_{out\text{-}of\text{-}plane}$**	**$NICS_{iso}$**	**$NICS_{in\text{-}plane}$**	**$NICS_{out\text{-}of\text{-}plane}$**
0.0	7.0043	-9.4943	16.4986	7.6017	-9.35147	16.9532
0.1	6.9836	-9.3511	16.3347	7.6379	-9.2104	16.8483
0.2	7.0139	-8.89737	15.9113	7.7116	-8.77503	16.4867
0.3	7.0758	-8.17657	15.2524	7.7983	-8.08827	15.8865
0.4	7.1401	-7.254	14.3941	7.867	-7.2116	15.0786
0.5	7.1751	-6.20593	13.3811	7.8879	-6.21547	14.1034
0.6	7.1537	-5.1085	12.2622	7.8384	-5.1693	13.0076
0.7	7.0577	-4.0285	11.0862	7.7063	-4.13393	11.8402

0.8	6.8802	-3.01763	9.89783	7.4905	-3.15717	10.6476
0.9	6.6243	-2.11043	8.73467	7.199	-2.27183	9.47087
1.0	6.3006	-1.32513	7.62577	6.8458	-1.49697	8.34273
1.1	5.9245	-0.6667	6.59123	6.4474	-0.8399	7.2873
1.2	5.5128	-0.1303	5.64307	6.0205	-0.299433	6.31993
1.3	5.0816	0.295167	4.78647	5.58	0.131633	5.4484
1.4	4.6453	0.623933	4.02143	5.1382	0.463733	4.67443
1.5	4.2157	0.871333	3.34433	4.7043	0.709133	3.9952
1.6	3.8017	1.0523	2.74937	4.2853	0.880567	3.4047
1.7	3.4098	1.1803	2.22943	3.8855	0.990467	2.89507
1.8	3.0442	1.2672	1.777	3.5078	1.05057	2.45723
1.9	2.7073	1.3227	1.3846	3.1537	1.0718	2.08187
2.0	2.4	1.3548	1.0452	2.8237	1.06403	1.75967
2.1	2.1219	1.36967	0.7523	2.5178	1.03617	1.48167
2.2	1.872	1.372	0.5	2.2356	0.995867	1.23977
2.3	1.6484	1.3653	0.283133	1.9762	0.9496	1.02663
2.4	1.449	1.35203	0.097	1.7387	0.902533	0.836133
2.5	1.2716	1.33393	-0.0623667	1.5217	0.8585	0.663233
2.6	1.1137	1.31227	-0.198567	1.3242	0.8201	0.504133
2.7	0.9732	1.2879	-0.314667	1.1449	0.788733	0.356133
2.8	0.8481	1.26143	-0.413267	0.9824	0.7648	0.217567
2.9	0.7366	1.23337	-0.496767	0.8355	0.748	0.0875333
3.0	0.6371	1.2042	-0.567067	0.7032	0.737467	-0.0342667
3.1	0.5483	1.17427	-0.626	0.5842	0.732067	-0.147833
3.2	0.469	1.1439	-0.674967	0.4777	0.730633	-0.252933
3.3	0.3982	1.11347	-0.715267	0.3826	0.732	-0.349367
3.4	0.3351	1.08313	-0.748067	0.2982	0.735167	-0.436933
3.5	0.2789	1.05317	-0.7743	0.2236	0.7392	-0.515633

3.6	0.2289	1.02367	-0.7948	0.158	0.743533	-0.585533
3.7	0.1845	0.9948	-0.8103	0.1006	0.747533	-0.6469
3.8	0.1451	0.9666	-0.821467	0.0508	0.7509	-0.7001
3.9	0.1103	0.939133	-0.8288	0.0078	0.753267	-0.7455
4.0	0.0795	0.912367	-0.832867	-0.0291	0.754533	-0.783667
4.1	0.0523	0.8863	-0.834	-0.0605	0.754533	-0.815067
4.2	0.0283	0.860967	-0.832667	-0.0871	0.7532	-0.8403
4.3	0.0071	0.836233	-0.829133	-0.1094	0.7505	-0.859867
4.4	-0.0116	0.8122	-0.823733	-0.1279	0.7464	-0.874333
4.5	-0.028	0.788767	-0.816733	-0.1432	0.741033	-0.8842
4.6	-0.0424	0.7659	-0.808333	-0.1556	0.7344	-0.889967
4.7	-0.0551	0.743667	-0.798767	-0.1655	0.7266	-0.892067
4.8	-0.0662	0.722	-0.7882	-0.1732	0.717733	-0.890967
4.9	-0.0759	0.7009	-0.776767	-0.1791	0.707933	-0.887067
5.0	-0.0843	0.680333	-0.764667	-0.1835	0.6972	-0.880733

Table 12: Quantum chemically calculated $NICS_{iso}$, $NICS_{in\text{-}plane}$ and $NICS_{out\text{-}of\text{-}plane}$ values of the roughly fully planarized BBTT **3p** (B3LYP/6-311+G**). The ghost atom is located in the center of the 1,4-thiazine ring.



3p

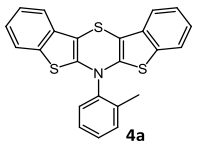
(two conformers in the asymmetric unit)

Å	**$NICS_{iso}$**	**$NICS_{in\text{-}plane}$**	**$NICS_{out\text{-}of\text{-}plane}$**	**$NICS_{iso}$**	**$NICS_{in\text{-}plane}$**	**$NICS_{out\text{-}of\text{-}plane}$**
0.0	7.3482	-9.52603	16.8743	7.3175	-9.5184	16.8359
0.1	7.3909	-9.341	16.7319	7.3305	-9.35443	16.685
0.2	7.4789	-8.85577	16.3347	7.3922	-8.88637	16.2786
0.3	7.5899	-8.11393	15.7038	7.4826	-8.1561	15.6387
0.4	7.6922	-7.1799	14.8721	7.5713	-7.2275	14.7988
0.5	7.7529	-6.12853	13.8815	7.6251	-6.17593	13.801

0.6	7.7445	-5.03417	12.7787	7.6146	-5.07757	12.6922
0.7	7.6497	-3.9617	11.6113	7.5199	-4	11.5199
0.8	7.463	-2.96107	10.4241	7.3324	-2.996	10.3284
0.9	7.1898	-2.0653	9.2551	7.0547	-2.10117	9.15587
1.0	6.8431	-1.2916	8.13467	6.6979	-1.33447	8.03233
1.1	6.4403	-0.6441	7.08443	6.2784	-0.700967	6.9794
1.2	6.0003	-0.117733	6.118	5.8153	-0.195267	6.01057
1.3	5.5406	0.298633	5.24203	5.3274	0.194733	5.13263
1.4	5.0769	0.619167	4.45777	4.8317	0.484867	4.34683
1.5	4.6216	0.859	3.76257	4.3428	0.692233	3.6506
1.6	4.1839	1.03287	3.15107	3.8722	0.833533	3.03863
1.7	3.7706	1.1541	2.6165	3.4282	0.924033	2.5042
1.8	3.3857	1.23443	2.15123	3.0168	0.977067	2.03973
1.9	3.0312	1.28363	1.74763	2.6413	1.0037	1.6376
2.0	2.7078	1.3096	1.39823	2.303	1.01277	1.2903
2.1	2.4147	1.3186	1.09607	2.0019	1.01103	0.990833
2.2	2.1503	1.31547	0.834833	1.7364	1.00357	0.732833
2.3	1.9126	1.30377	0.608867	1.5043	0.993767	0.5105
2.4	1.6992	1.28607	0.413133	1.3027	0.983933	0.318767
2.5	1.5076	1.26427	0.2433	1.1287	0.9755	0.153167
2.6	1.3353	1.23967	0.0956667	0.9789	0.969	0.00986667
2.7	1.1803	1.21327	-0.033	0.8503	0.9647	-0.114467
2.8	1.0403	1.18567	-0.145333	0.74	0.962533	-0.222567
2.9	0.9139	1.1575	-0.2436	0.6453	0.962167	-0.3168
3.0	0.7995	1.1291	-0.3296	0.564	0.963167	-0.399133
3.1	0.6959	1.10083	-0.404967	0.494	0.965133	-0.471167
3.2	0.602	1.07287	-0.470867	0.4334	0.9676	-0.5342
3.3	0.5171	1.04553	-0.528433	0.3807	0.970067	-0.589367

3.4	0.4403	1.01883	-0.578533	0.3347	0.9722	-0.6375
3.5	0.3711	0.992967	-0.6219	0.2942	0.973567	-0.6794
3.6	0.3087	0.967867	-0.659167	0.2583	0.9739	-0.715633
3.7	0.2526	0.943567	-0.6909	0.2262	0.972933	-0.746733
3.8	0.2024	0.920033	-0.7176	0.1974	0.9705	-0.773133
3.9	0.1575	0.8972	-0.7397	0.1712	0.9665	-0.795233
4.0	0.1174	0.875067	-0.757633	0.1474	0.9608	-0.813367
4.1	0.0817	0.8535	-0.771733	0.1257	0.953467	-0.827833
4.2	0.0501	0.832433	-0.7824	0.1056	0.944567	-0.8389
4.3	0.022	0.8119	-0.7899	0.0872	0.934133	-0.8469
4.4	-0.0028	0.791767	-0.794567	0.0703	0.922333	-0.852033
4.5	-0.0247	0.771967	-0.796667	0.0547	0.909267	-0.854533
4.6	-0.0439	0.752633	-0.7965	0.0404	0.895133	-0.8547
4.7	-0.0607	0.7336	-0.794267	0.0274	0.880033	-0.8527
4.8	-0.0754	0.7149	-0.790267	0.0154	0.8642	-0.848733
4.9	-0.0881	0.696533	-0.784633	0.0046	0.847667	-0.843067
5.0	-0.0991	0.6785	-0.7776	-0.0052	0.830633	-0.835833

Table 13: Quantum chemically calculated $NICS_{iso}$, $NICS_{in\text{-}plane}$ and $NICS_{out\text{-}of\text{-}plane}$ values of the roughly fully planarized BBTT **4a** (B3LYP/6-311+G**). The ghost atom is located in the center of the 1,4-thiazine ring.



4a

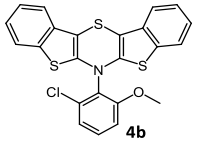
(two molecules in the asymmetric unit)

Å	**$NICS_{iso}$**	**$NICS_{in\text{-}plane}$**	**$NICS_{out\text{-}of\text{-}plane}$**	**$NICS_{iso}$**	**$NICS_{in\text{-}plane}$**	**$NICS_{out\text{-}of\text{-}plane}$**
0.0	6.8382	-9.63507	16.4733	7.0621	-9.33483	16.4608
0.1	6.848	-9.47217	16.3202	7.1398	-9.23367	16.3735
0.2	6.9	-9.0129	15.9129	7.2386	-8.78663	16.0252
0.3	6.9765	-8.29673	15.2733	7.3361	-8.0988	15.4349

0.4	7.0511	-7.38397	14.4351	7.4062	-7.2284	14.6346
0.5	7.0948	-6.34597	13.4407	7.4252	-6.24127	13.6665
0.6	7.0821	-5.25507	12.3372	7.3765	-5.2028	12.5793
0.7	6.996	-4.17597	11.1719	7.2521	-4.17067	11.4227
0.8	6.8293	-3.15973	9.98903	7.0531	-3.19083	10.2439
0.9	6.5845	-2.24167	8.8262	6.7874	-2.29617	9.0835
1.0	6.2714	-1.44153	7.71297	6.467	-1.507	7.97403
1.1	5.9043	-0.7661	6.6704	6.1058	-0.833333	6.9391
1.2	5.4994	-0.212167	5.7115	5.7167	-0.277333	5.99403
1.3	5.0726	0.229967	4.84263	5.3113	0.1642	5.1471
1.4	4.6384	0.5736	4.0648	4.8986	0.4976	4.40103
1.5	4.2087	0.8335	3.37523	4.4854	0.731067	3.75433
1.6	3.7931	1.02433	2.76877	4.0765	0.8738	3.2027
1.7	3.3983	1.1597	2.23867	3.6752	0.935467	2.73967
1.8	3.0292	1.2515	1.7777	3.2838	0.926533	2.35727
1.9	2.6885	1.3099	1.37857	2.9044	0.858167	2.04623
2.0	2.3773	1.34317	1.0341	2.5388	0.742667	1.79617
2.1	2.0956	1.3578	0.7378	2.1892	0.593567	1.5956
2.2	1.8426	1.35897	0.4836	1.8576	0.425333	1.4323
2.3	1.6164	1.35037	0.2661	1.5468	0.252933	1.2938
2.4	1.4152	1.33473	0.0805	1.259	0.0907667	1.16827
2.5	1.2366	1.31407	-0.0774333	0.9968	-0.0486333	1.04547
2.6	1.0783	1.28977	-0.211433	0.762	-0.155967	0.917933
2.7	0.9381	1.2628	-0.3247	0.5556	-0.225767	0.781367
2.8	0.8138	1.23387	-0.420067	0.3778	-0.2569	0.6347
2.9	0.7036	1.2036	-0.5	0.2276	-0.252133	0.479733
3.0	0.6058	1.17237	-0.566567	0.1032	-0.216867	0.320033

3.1	0.5189	1.14053	-0.6216	0.0019	-0.1581	0.160033
3.2	0.4418	1.10853	-0.6667	-0.0791	-0.0832667	0.00413333
3.3	0.3733	1.0765	-0.7032	-0.1428	9.66667E-4	-0.1438
3.4	0.3125	1.04477	-0.7323	-0.1919	0.0889333	-0.280833
3.5	0.2585	1.0135	-0.754933	-0.2287	0.1764	-0.405067
3.6	0.2107	0.9828	-0.772067	-0.2551	0.2604	-0.515533
3.7	0.1684	0.952833	-0.7844	-0.2729	0.339	-0.611933
3.8	0.131	0.923633	-0.7926	-0.2834	0.411167	-0.6946
3.9	0.098	0.8952	-0.797267	-0.288	0.476267	-0.7643
4.0	0.0688	0.867633	-0.798867	-0.2879	0.5341	-0.821967
4.1	0.043	0.840867	-0.797833	-0.284	0.584633	-0.868667
4.2	0.0204	0.814933	-0.794567	-0.2775	0.627933	-0.905467
4.3	0.0004	0.7898	-0.7894	-0.2691	0.664333	-0.933433
4.4	-0.0172	0.765433	-0.7826	-0.2596	0.694033	-0.9536
4.5	-0.0326	0.741833	-0.774433	-0.2494	0.717433	-0.966867
4.6	-0.0461	0.719	-0.7651	-0.2392	0.734967	-0.974167
4.7	-0.0579	0.696867	-0.754833	-0.2291	0.7471	-0.976233
4.8	-0.0683	0.6755	-0.743767	-0.2194	0.7544	-0.973833
4.9	-0.0773	0.6548	-0.732067	-0.2102	0.7574	-0.9676
5.0	-0.0851	0.644467	-0.719867	-0.2016	0.756567	-0.958167

Table 14: Quantum chemically calculated $NICS_{iso}$, $NICS_{in\text{-}plane}$ and $NICS_{out\text{-}of\text{-}plane}$ values of the roughly fully planarized BBTT **4b** (B3LYP/6-311+G**). The ghost atom is located in the center of the 1,4-thiazine ring.



4b

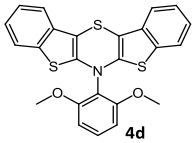
(two conformers in the asymmetric unit)

Å	**$NICS_{iso}$**	**$NICS_{in\text{-}plane}$**	**$NICS_{out\text{-}of\text{-}plane}$**	**$NICS_{iso}$**	**$NICS_{in\text{-}plane}$**	**$NICS_{out\text{-}of\text{-}plane}$**

0.0	7.9413	-9.6514	17.5927	7.9402	-9.65213	17.5923
0.1	7.9859	-9.4832	17.4691	7.9519	-9.49737	17.4493
0.2	8.0759	-9.00887	17.0848	8.0133	-9.03407	17.0474
0.3	8.1845	-8.27497	16.4595	8.1005	-8.30697	16.4075
0.4	8.2762	-7.3488	15.625	8.18	-7.38247	15.5625
0.5	8.3155	-6.30723	14.6228	8.2162	-6.3377	14.5539
0.6	8.2746	-5.22533	13.4999	8.1795	-5.2491	13.4286
0.7	8.138	-4.1674	12.3054	8.0514	-4.18327	12.2346
0.8	7.9033	-3.18207	11.0853	7.8259	-3.19117	11.0171
0.9	7.5794	-2.30057	9.87997	7.5087	-2.30633	9.81503
1.0	7.183	-1.53843	8.72147	7.1136	-1.54603	8.65963
1.1	6.7345	-0.898567	7.63307	6.6595	-0.914033	7.5735
1.2	6.2546	-0.375067	6.62963	6.1664	-0.4047	6.57113
1.3	5.762	0.0432667	5.71867	5.6537	-0.00626667	5.66
1.4	5.2721	0.3703	4.9018	5.1381	0.296067	4.84207
1.5	4.7968	0.6203	4.17647	4.6332	0.518033	4.1152
1.6	4.3442	0.806967	3.53723	4.1493	0.674833	3.4745
1.7	3.9196	0.942533	2.97703	3.6937	0.780233	2.91343
1.8	3.5257	1.0376	2.4881	3.271	0.8463	2.42467
1.9	3.1634	1.1009	2.06253	2.8838	0.883167	2.00067
2.0	2.8324	1.1397	1.69273	2.5331	0.899167	1.63393
2.1	2.5315	1.15973	1.37177	2.2185	0.901067	1.3175
2.2	2.2589	1.16563	1.09327	1.9388	0.894	1.04477
2.3	2.0126	1.16097	0.851667	1.6919	0.882067	0.8099
2.4	1.7905	1.14843	0.642033	1.4756	0.868133	0.607467
2.5	1.5903	1.13017	0.460167	1.2872	0.854467	0.4328
2.6	1.4101	1.10777	0.302333	1.1241	0.842467	0.281667

2.7	1.2479	1.08247	0.165433	0.9835	0.833067	0.150433
2.8	1.1019	1.0552	0.0467333	0.8628	0.826767	0.036
2.9	0.9706	1.02677	-0.0561333	0.7594	0.8238	-0.0644
3.0	0.8526	0.997767	-0.145133	0.671	0.824	-0.152967
3.1	0.7466	0.968667	-0.222033	0.5955	0.827133	-0.2316
3.2	0.6516	0.939933	-0.288367	0.5309	0.8327	-0.301833
3.3	0.5664	0.911833	-0.345433	0.4754	0.840267	-0.3649
3.4	0.4903	0.884633	-0.394367	0.4273	0.8491	-0.4218
3.5	0.4223	0.858533	-0.436233	0.3854	0.8587	-0.473267
3.6	0.3617	0.833567	-0.4719	0.3485	0.868367	-0.5199
3.7	0.3077	0.8099	-0.5022	0.3155	0.877567	-0.562067
3.8	0.2597	0.787467	-0.527767	0.2857	0.885867	-0.600133
3.9	0.2171	0.766367	-0.549267	0.2585	0.892867	-0.6343
4.0	0.1792	0.746433	-0.567233	0.2334	0.898167	-0.664733
4.1	0.1456	0.727667	-0.5821	0.21	0.901633	-0.6916
4.2	0.1157	0.709933	-0.594267	0.1881	0.903133	-0.715
4.3	0.0891	0.6932	-0.604067	0.1676	0.902633	-0.735067
4.4	0.0655	0.677333	-0.611833	0.1482	0.900167	-0.751933
4.5	0.0445	0.662267	-0.6178	0.1301	0.895767	-0.7657
4.6	0.0257	0.647867	-0.622133	0.1131	0.889567	-0.7765
4.7	0.009	0.634067	-0.625067	0.0972	0.881767	-0.784533
4.8	-0.0059	0.6208	-0.626667	0.0825	0.872433	-0.789933
4.9	-0.0192	0.607967	-0.627167	0.069	0.861833	-0.792867
5.0	-0.0311	0.5955	-0.626567	0.0565	0.8501	-0.793567

Table 15: Quantum chemically calculated $NICS_{iso}$, $NICS_{in\text{-}plane}$ and $NICS_{out\text{-}of\text{-}plane}$ values of the roughly fully planarized BBTT **4d** (B3LYP/6-311+G**). The ghost atom is located in the center of the 1,4-thiazine ring.

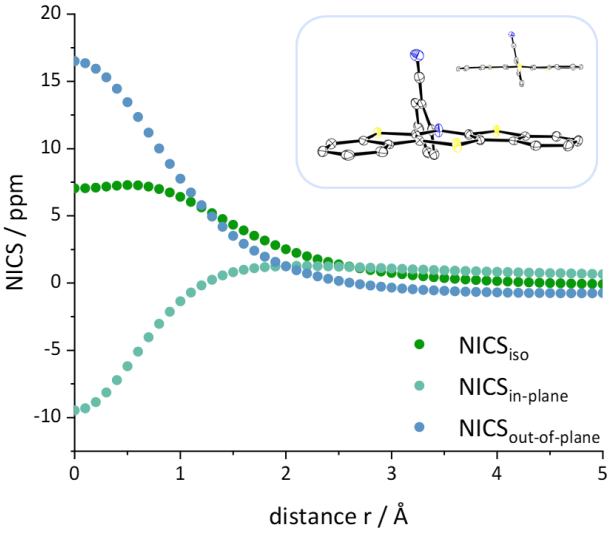


4d

Å	$NICS_{iso}$	$NICS_{in\text{-}plane}$	$NICS_{out\text{-}of\text{-}plane}$
0.0	7.9345	-9.30057	17.2351
0.1	7.9625	-9.13967	17.1022
0.2	8.0376	-8.672	16.7097
0.3	8.1345	-7.94367	16.0782
0.4	8.2184	-7.02217	15.2406
0.5	8.2536	-5.98527	14.2389
0.6	8.2112	-4.90933	13.1205
0.7	8.0737	-3.86023	11.9339
0.8	7.837	-2.88783	10.7248
0.9	7.5086	-2.02393	9.5325
1.0	7.104	-1.2841	8.38813
1.1	6.6437	-0.670567	7.3142
1.2	6.1487	-0.176167	6.32487
1.3	5.6389	0.211767	5.42713
1.4	5.1312	0.5087	4.62253
1.5	4.6389	0.7305	3.90843
1.6	4.1716	0.8921	3.27953
1.7	3.7357	1.00673	2.729
1.8	3.3348	1.08557	2.24927
1.9	2.9704	1.1377	1.8327
2.0	2.6422	1.17023	1.47193

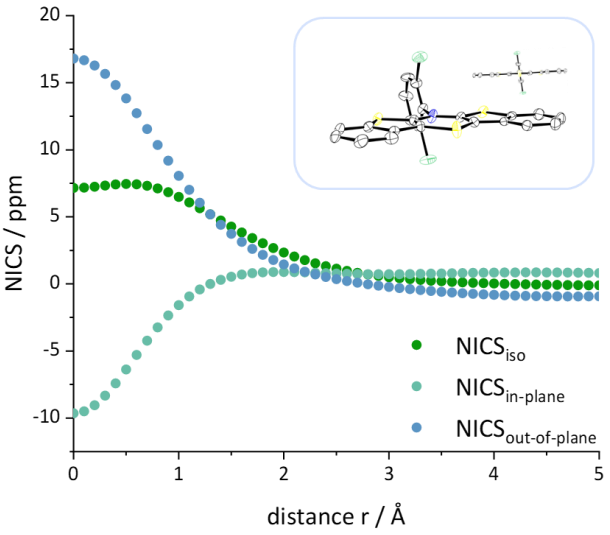
2.1	2.3487	1.18863	1.16007
2.2	2.0878	1.19687	0.8909
2.3	1.8566	1.19777	0.658833
2.4	1.6523	1.19333	0.458967
2.5	1.4718	1.1848	0.287033
2.6	1.3124	1.1731	0.139267
2.7	1.1712	1.15877	0.0124667
2.8	1.0461	1.14223	-0.0961333
2.9	0.9349	1.12383	-0.188933
3.0	0.8359	1.10387	-0.268
3.1	0.7475	1.08263	-0.335133
3.2	0.6686	1.06043	-0.391867
3.3	0.598	1.03757	-0.439533
3.4	0.5349	1.0143	-0.479367
3.5	0.4785	0.990933	-0.512433
3.6	0.428	0.967633	-0.539633
3.7	0.3828	0.944667	-0.561833
3.8	0.3424	0.9221	-0.579733
3.9	0.3062	0.900167	-0.594033
4.0	0.2737	0.878933	-0.605267
4.1	0.2445	0.858467	-0.613933
4.2	0.2183	0.8388	-0.6205
4.3	0.1946	0.819967	-0.625333
4.4	0.1733	0.801933	-0.6287
4.5	0.1539	0.784733	-0.630867
4.6	0.1362	0.768233	-0.632033
4.7	0.1201	0.752433	-0.632333

4.8	0.1054	0.7373	-0.631933
4.9	0.0919	0.722733	-0.630867
5.0	0.0794	0.708633	-0.6292



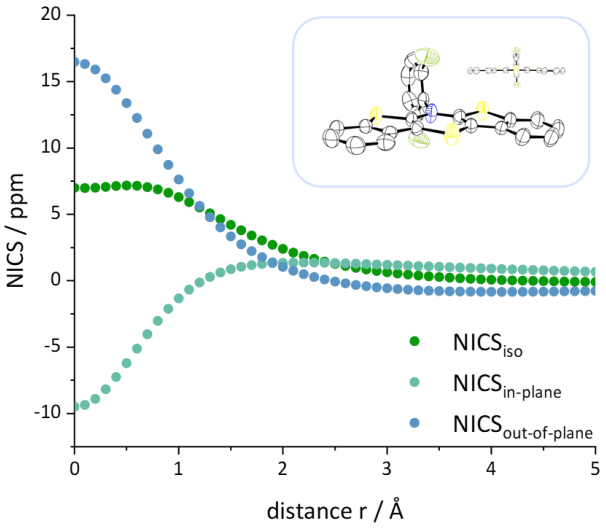
3a

Figure 60. NICS$_{iso}$, NICS$_{in-plane}$ and NICS$_{out-of-plane}$ values plotted against the distance r of the ghost atom from the center of the 1,4-thiazine as well as the underlying crystal structure geometry exemplarily for **3a** (B3LYP/6-311+G**).



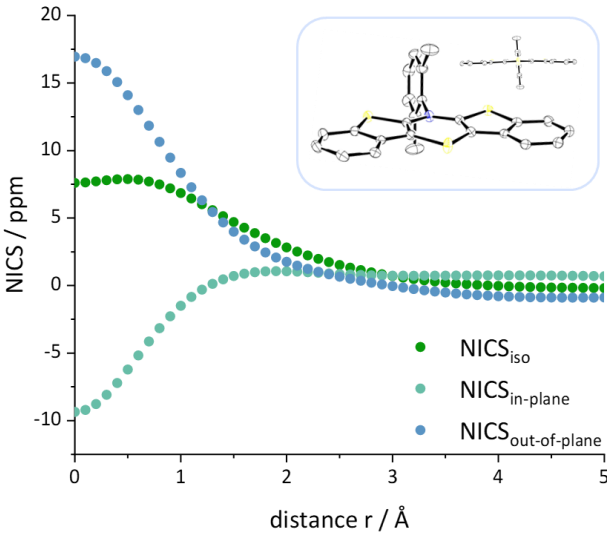
3g

Figure 61: NICS$_{iso}$, NICS$_{in-plane}$ and NICS$_{out-of-plane}$ values plotted against the distance r of the ghost atom from the center of the 1,4-thiazine as well as the underlying crystal structure geometry exemplarily for **3g** (B3LYP/6-311+G**).



3h

Figure 62. NICS$_{iso}$, NICS$_{in-plane}$ and NICS$_{out-of-plane}$ values plotted against the distance r of the ghost atom from the center of the 1,4-thiazine as well as the underlying crystal structure geometry exemplarily for **3h** (B3LYP/6-311+G**).



3i

Figure 63: NICS$_{iso}$, NICS$_{in-plane}$ and NICS$_{out-of-plane}$ values plotted against the distance r of the ghost atom from the center of the 1,4-thiazine as well as the underlying crystal structure geometry exemplarily for **3i** (B3LYP/6-311+G**).

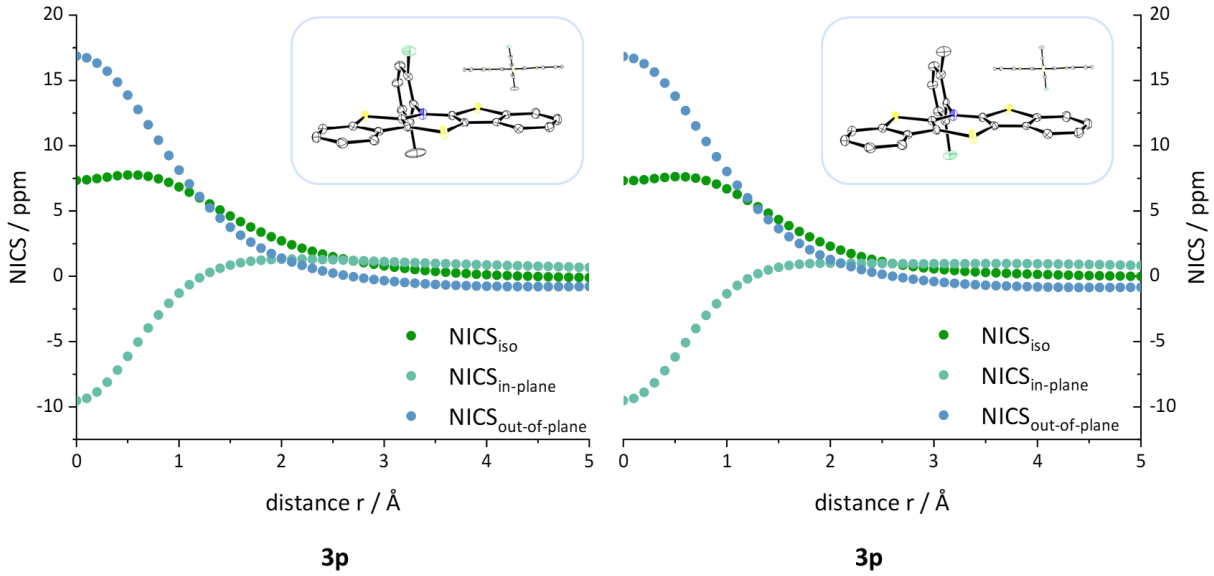


Figure 64. NICS$_{iso}$, NICS$_{in-plane}$ and NICS$_{out-of-plane}$ values plotted against the distance r of the ghost atom from the center of the 1,4-thiazine as well as the underlying crystal structure geometry exemplarily for **3p** (B3LYP/6-311+G**).

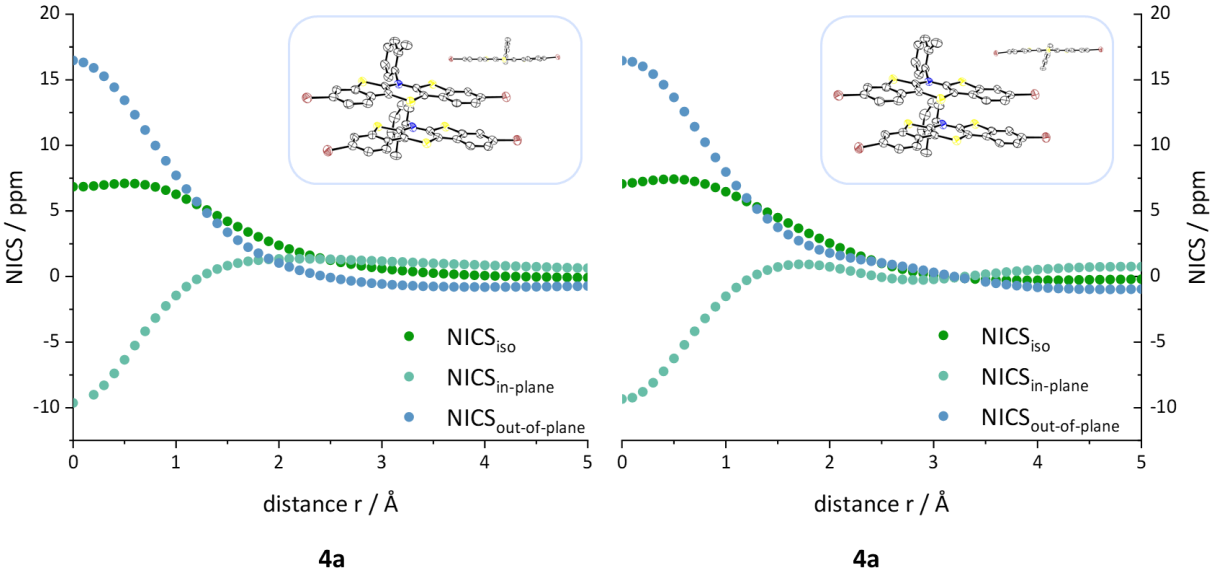


Figure 65. NICS$_{iso}$, NICS$_{in-plane}$ and NICS$_{out-of-plane}$ values plotted against the distance r of the ghost atom from the center of the 1,4-thiazine as well as the underlying crystal structure geometry exemplarily for **4a** (B3LYP/6-311+G**).

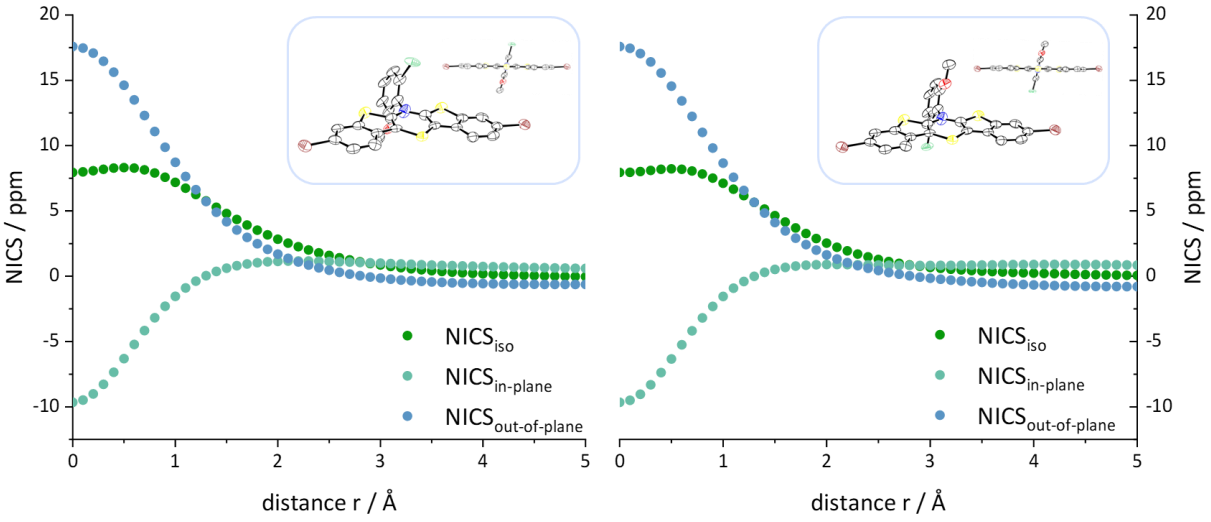


Figure 66. NICS$_{iso}$, NICS$_{in-plane}$ and NICS$_{out-of-plane}$ values plotted against the distance r of the ghost atom from the center of the 1,4-thiazine as well as the underlying crystal structure geometry exemplarily for **4b** (B3LYP/6-311+G**).

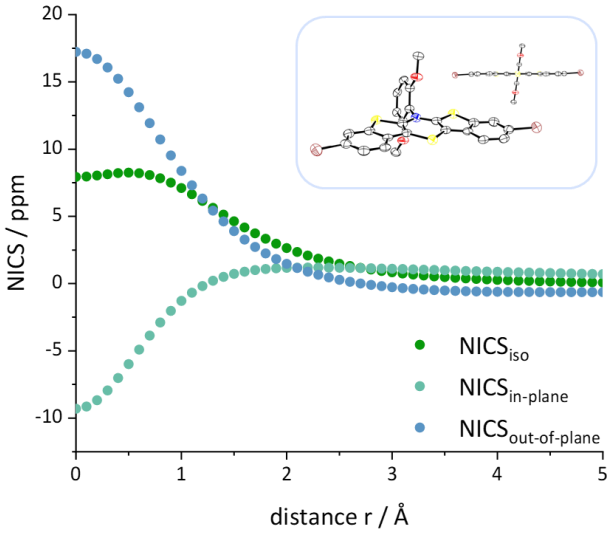


Figure 67. NICS$_{iso}$, NICS$_{in-plane}$ and NICS$_{out-of-plane}$ values plotted against the distance r of the ghost atom from the center of the 1,4-thiazine as well as the underlying crystal structure geometry exemplarily for **4d** (B3LYP/6-311+G**).

4 BBTT as a multistage redox system

4.1 Cyclic voltammetry

4.1.1 CVs

CVs were referenced with decamethylferrocene (DMFc) as internal standard since ferrocene's (Fc) redox potential signal overlaps with signals of the redox potentials of the BBTT **3**.[9-11] The difference in oxidation potentials was determinated with –546 mV for DMFc to Fc.

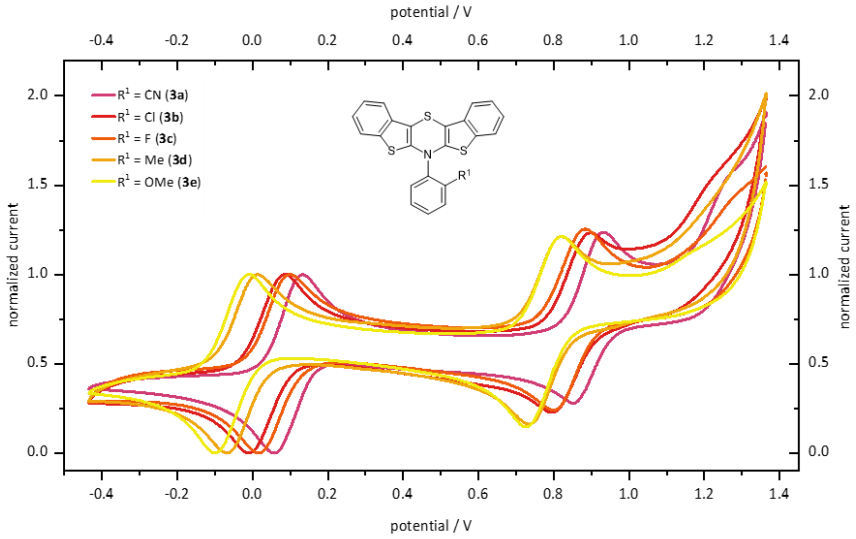


Figure 68. CVs of *anti-anti-N-ortho*-substituted-phenyl-BBTT **3a-e** (CVs recorded in CH_2Cl_2, T = 298 K, 0.1 M $[Bu_4N][PF_6]$, ν = 100 mV/s, Pt-working- und -counter electrode, Ag/AgCl(3 M)-reference electrode, referenced with $DMFc/DMFc^+$, potential vs. Fc/Fc^+ = 0.00 V).

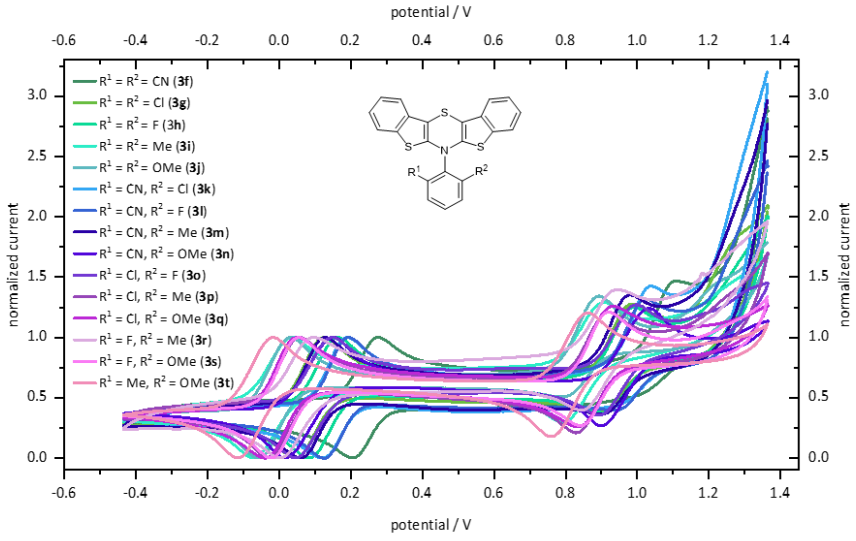


Figure 69. CVs of *anti-anti-N-ortho,ortho'*-disubstituted-phenyl-BBTT **3f-t** (CVs recorded in CH_2Cl_2, T = 298 K, 0.1 M $[Bu_4N][PF_6]$, ν = 100 mV/s, Pt-working- und -counter electrode, Ag/AgCl(3 M)-reference electrode, referenced with $DMFc/DMFc^+$, potential vs. Fc/Fc^+ = 0.00 V).

4.1.2 Nernstian reversibility

The peaks in the CVs show chemical reversibility of the native and oxidized BBTT's redox couples due to formation of signals on the forward and backwards sweep, while at the same time the signal intensity does not drop when multiple cycles are measured in a row. To account for electrochemical reversibility the peak separations of both signals on the different sweeps can be used as criterion. For one-electron processes, like for BBTTs, the difference in potentials should be 59 mV. To prove the reversibility and characterize it by means of Nernstian behavior a literature known procedure was employed, as is was before for BBTT's redox behavior.[6, 10] Therefore redox potentials were measured at different scan rates of 100, 250, 500 and 1000 mV s^{-1}, illuminating that BBTT's potentials shift upon increasing the scan rate. Also, the separation of peak potentials presents with values over 59 mV. Both of this indicates a quasi-reversible electrochemical behavior. Employing the standard redox samples ferrocene (Fc) and decamethylferrocene (DMFc) as test system, same behavior occurs, even though literature states them as fully Nernstian reversible.[9, 10] Therefore given observations seem to arise from our given setup parameters of the experiment. Literature suggests direct comparison of the values of the separation of the peak potentials of the standards Fc and DMFc with the measured samples, in this case the BBTTs, to decide on the electrochemical reversibility. To quantify this the potentials of both sweeps are plotted against the square root of the scan rate, therefore extrapolating the potentials at a scan rate of 0 mV/s by linear regression. The peak separation at 0 mV s^{-1} can be deducted by the difference in intercepts. If the peak separation of the sample, here BBTTs, falls within the range of 59 mV and the value for the known to be Nernstian reversible standards under the measuring conditions, the samples can also be treated as Nernstian and therefore electrochemically reversible. Since the test systems reveal peak separations of 93 (Fc/Fc^+) and 72 mV ($DMFc/DMFc^+$), BBTTs with values of < 95 mV fall within the same range and can therefore be indicated as Nernstian reversible.

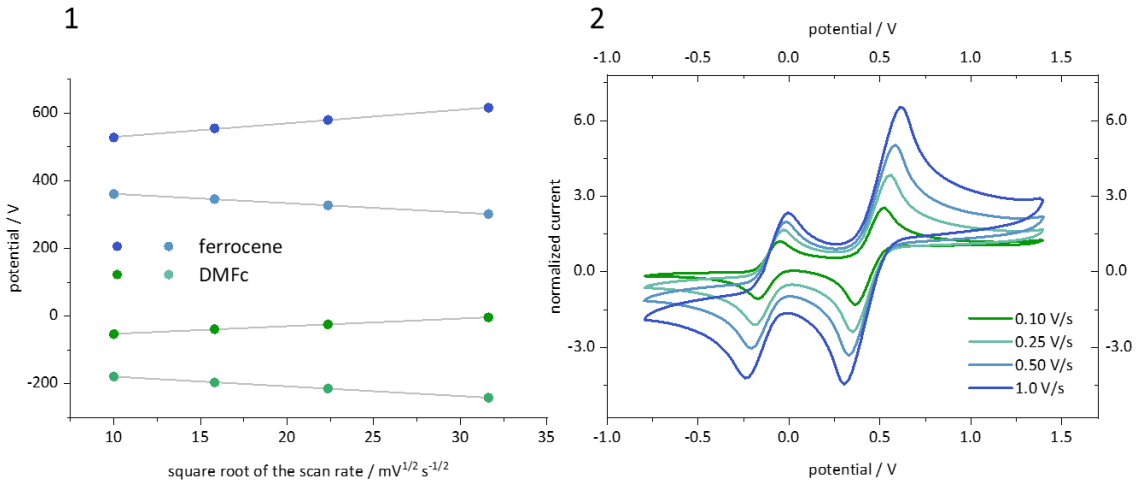


Figure 70. 1) Potentials of DMFc and Fc at v = 100, 250, 500 and 1000 mV s^{-1} plotted against the square root of that scan rate v. 2) CVs of DMFc and Fc at v = 100, 250, 500 and 1000 mV s^{-1} vs. Ag/Ag+ (3 M) = 0 mV.

4.2 DFT-examination of radical cations

CV-data reveals an increased radical cation stability due to constitutional changes from *para*- to *ortho*- to *ortho,ortho'*-substitution pattern on the *N*-aryl moiety. Because data for all BBTTs **3** and **4** reveals this, the corresponding minimum geometries of the racial cations were computed. Extraction of the Mulliken atomic spin densities and visualization of their spin density distribution overall showed a growing delocalization of the unpaired electron as discussed in the paper. Herein the comparative discussion for the data exemplarily for radical cations of *anti-anti-N-para*-methylphenyl-BBTT, *anti-anti-N-ortho*-methylphenyl-BBTT **3d**$^{\bullet+}$ and *anti-anti-N-ortho,ortho'*-methylphenyl-BBTT **3i**$^{\bullet+}$ is given.

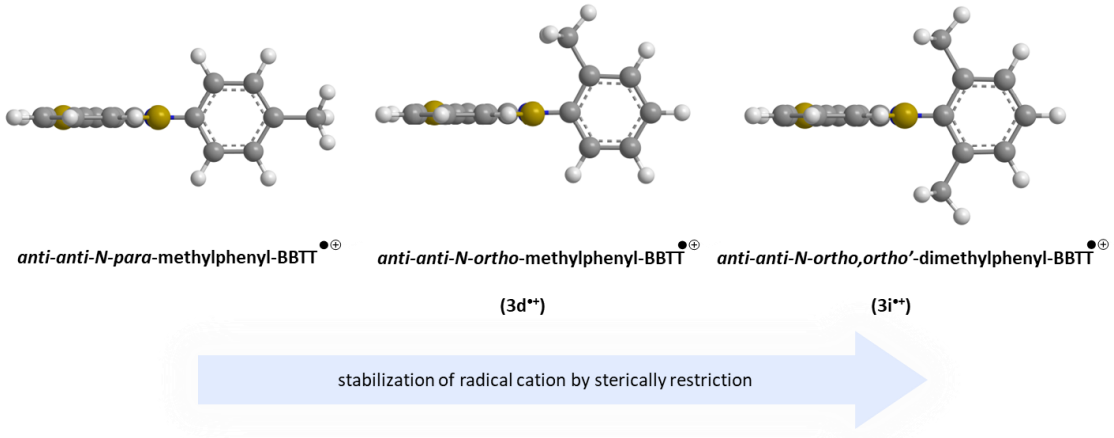


Figure 71. Radical geometries of BBTT with fully planarized BBTT's backbones exemplarily for radical cations of *anti-anti-N-para*-methylphenyl-BBTT, *anti-anti-N-ortho*-methylphenyl-BBTT **3d**$^{\bullet+}$ and *anti-anti-N-ortho,ortho'*-methylphenyl-BBTT **3i**$^{\bullet+}$ (uB3LYP/6 311++G**, IEFPCM CH_2Cl_2).

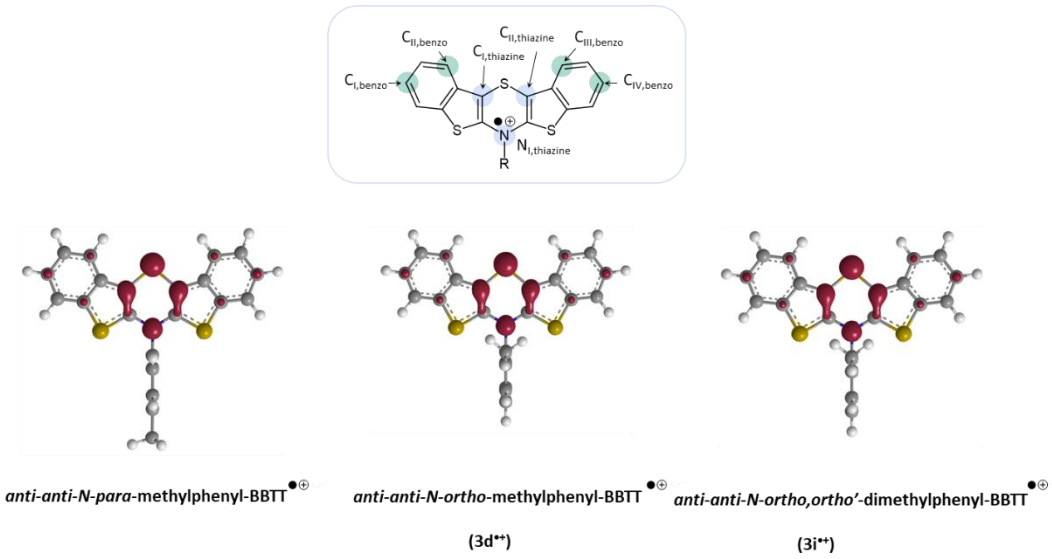
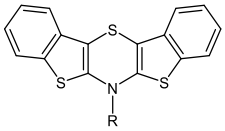


Figure 72. Quantum chemically calculated spin density distributions (uB3LYP/6 311++G**, IEFPCM CH2Cl2, isosurface value = 0.06 a.u.) (bottom) and illustration of the assignment of individual atoms for extraction of Mulliken atomic spin densities exemplarily on radical cations of *anti-anti-N-para*-methylphenyl-BBTT, *anti-anti-N-ortho*-methylphenyl-BBTT **3d**$^{\bullet+}$ and *anti-anti-N-ortho,ortho'*-methylphenyl-BBTT **3i**$^{\bullet+}$ (top).

Table 16. Mulliken atomic spin densities exemplarily for radical cations of *anti-anti-N-para*-methylphenyl-BBTT, *anti-anti-N-ortho*-methylphenyl-BBTT **3d**$^{\bullet+}$ and *anti-anti-N-ortho,ortho'*-methylphenyl-BBTT **3i**$^{\bullet+}$.



		Mulliken atomic spin density		
	$N_{I,thiazine}$	$C_{I,thiazine}$ $C_{II,thiazine}$	$C_{I,benzo}$ $C_{IV,benzo}$	$C_{II,benzo}$ $C_{III,benzo}$
radical cation$^{\bullet+}$ (R = *para*-Me-C_6H_4)	0.238	0.176 0.176	0.0716 0.0715	0.0453 0.0452
3d$^{\bullet+}$ (R = *ortho*-Me-C_6H_4)	0.232	0.171 0.171	0.0715 0.0714	0.0544 0.0547
3i$^{\bullet+}$ (R = *ortho,ortho*'-Me,Me-C_6H_3)	0.229	0.172 0.172	0.0716 0.0716	0.0555 0.0555

4.3 Computed SCF energies, Gibbs free energies and HOMO energies of *N-intra*-conformers and transition states

The Eyring equation was used to determine the rate constant k and thus the frequency of the conversion.

$$k = \frac{R\,T}{N_A\,h}\,e^{-\frac{\Delta G_A^{\neq}}{R\,T}}$$

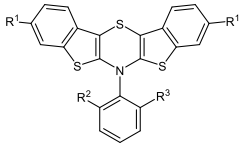
k as the rate constant with $\Delta G_A^{\neq}$ as free activation energy of both involved conformers, R as ideal gas constant, T as temperatur, N_A as Avogadro constant and h as Planck constant.

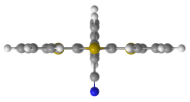
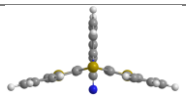
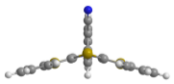
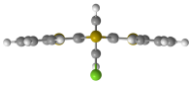
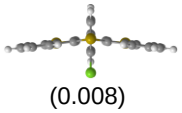
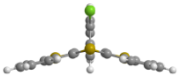
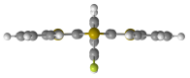
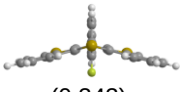
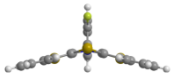
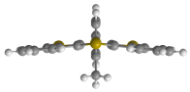
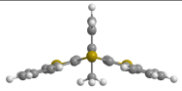
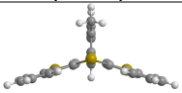
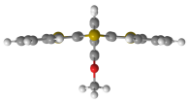
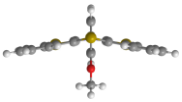
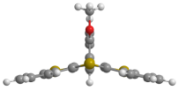
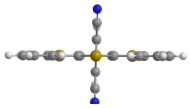
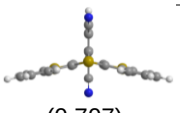
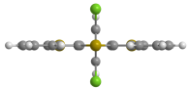
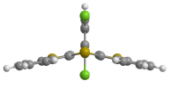
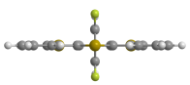
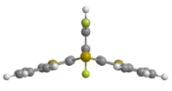
The equilibrium constant can be calculated by the connection to the Gibbs free energy.

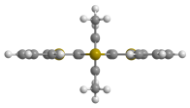
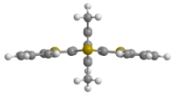
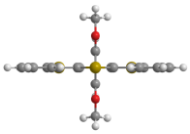
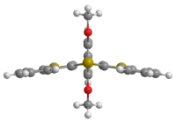
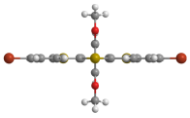
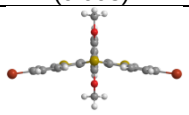
$$\Delta G = -R\,T\ln(K)$$

K as equilibrium constant with ΔG as difference of Gibbs free energies of both involved conformers, R as ideal gas constant and T as temperature.

Table 17. DFT-computational minimum structures of selected conformers of BBTT **3** and **4** by *N*-inversion and the geometry of the corresponding planar transition state as well as the SCF energy difference ΔE and free activation energy $\Delta G_A^{\neq}$ of this conversion. (B3LYP/6-311++G**, IEFPCM CH_2Cl_2).

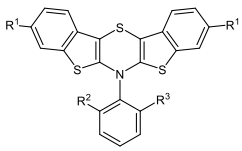
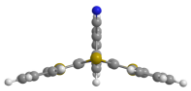
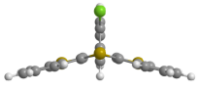
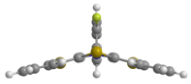
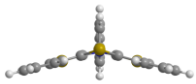
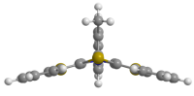
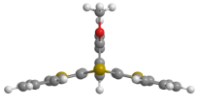
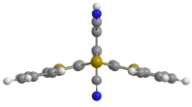


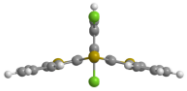
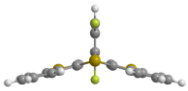
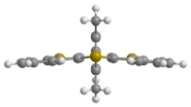
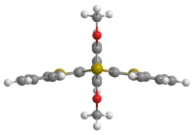
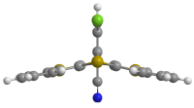
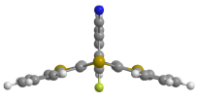
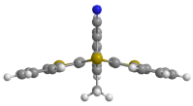
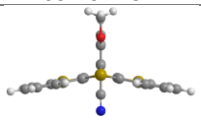
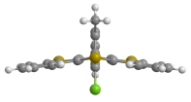
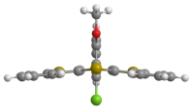
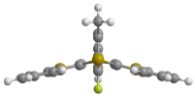
	transition state (ts)	$\Delta G_{A;\,I\text{-}II}^{\neq}$ **/ kcal mol^{-1} (k / s^{-1})**	$\Delta G_{A;\,II\text{-}I}^{\neq}$ **/ kcal mol^{-1} (k / s^{-1})**	**conformer I ($\Delta E_{I\text{-}ts}$ / kcal mol^{-1})**	**conformer II ($\Delta E_{II\text{-}ts}$ / kcal mol^{-1})**
$R^1 = R^2 = H$, $R^3 = CN$ (**3a**)		1.62 ($3.96 \cdot 10^{11}$)	1.96 ($2.27 \cdot 10^{11}$)	 (0.478)	 (0.996)
$R^1 = R^2 = H$, $R^3 = Cl$ (**3b**)		1.60 ($4.18 \cdot 10^{11}$)	2.15 ($1.64 \cdot 10^{11}$)	 (0.008)	 (0.868)
$R^1 = R^2 = H$, $R^3 = F$ (**3c**)		1.31 ($6.78 \cdot 10^{11}$)	2.21 ($1.49 \cdot 10^{11}$)	 (0.343)	 (0.785)
$R^1 = R^2 = H$, $R^3 = Me$ (**3d**)[1]		0.87 ($1.43 \cdot 10^{12}$)	1.63 ($3.97 \cdot 10^{11}$)	 (0.054)	 (1.26)
$R^1 = R^2 = H$, $R^3 =$ OMe (**3e**)		1.90 ($2.52 \cdot 10^{11}$)	2.16 ($1.61 \cdot 10^{11}$)	 (0.051)	 (0.557)
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**)		0.45 ($2.89 \cdot 10^{12}$)	-	 (0.707)	-
$R^1 = R^2 = H$, $R^3 = Cl$ (**3g**)		1.21 ($7.99 \cdot 10^{11}$)	-	 (0.174)	-
$R^1 = R^2 = H$, $R^3 = F$ (**3h**)		1.70 ($3.54 \cdot 10^{11}$)	-	 (0.590)	-

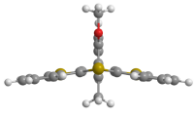
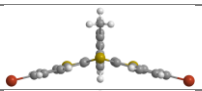
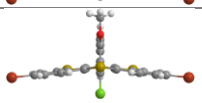
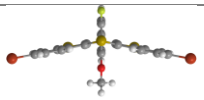
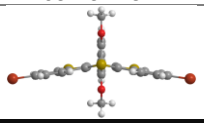
$R^1 = R^2 = H$, $R^3 = Me$ (**3i**)		1.44 ($5.46 \cdot 10^{11}$)	-	 (0.033)	-
$R^1 = R^2 = H$, $R^3 =$ OMe (**3j**)		1.62 ($4.05 \cdot 10^{11}$)	-	 (0.098)	-
$R^1 =$ Br, $R^2 = R^3 =$ OMe (**4d**)		1.86 ($2.68 \cdot 10^{11}$)	-	 (0.151)	-

[1](B3LYP/6-311G**).

Table 18. DFT-computational minimum structures of *intra*-conformers of BBTT **3** and **4** with their respective by gibbs free energy differences ΔG_{I-II} calculated percentage contributions and HOMO-Energies E_{HOMO} (B3LYP/6-311++G**, IEFPCM CH_2Cl_2).

	**thermodynamically favored minimum**	ΔG_{I-II}	K_{I-II}	**Conformer I E_{HOMO} / eV (percentage / %)**	**Conformer II E_{HOMO} / eV (percentage / %)**	E_{HOMO} / eV
$R^1 = R^2 = H$, $R^3 = CN$ (**3a**)	 conformer II	0.3307	0.5719	–5.43 (36.4)	–5.20 (63.6)	–5.28
$R^1 = R^2 = H$, $R^3 = Cl$ (**3b**)	 conformer II	0.5560	0.3908	–4.96 (28.1)	–5.12 (71.9)	–5.08
$R^1 = R^2 = H$, $R^3 = F$ (**3c**)	 conformer II	0.8986	0.2190	–5.09 (18.0)	–5.15 (82.0)	–5.14
$R^1 = R^2 = R^3 = H$ (**5**)				–5.08 (100)		–5.08
$R^1 = R^2 = H$, $R^3 = Me$ (**3d**)	 conformer II	0.0916	0.8566	–4.97 (46.1)	–5.06 (53.9)	–5.02
$R^1 = R^2 = H$, $R^3 =$ OMe (**3e**)	 conformer II	0.2667	0.6372	–4.94 (38.9)	–5.02 (61.1)	–4.98
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**)				–5.34 (100)		–5.34

$R^1 = R^2 = H$, $R^3 = Cl$ (**3g**)				–5.17 (100)		–5.17
$R^1 = R^2 = H$, $R^3 = F$ (**3h**)				–5.25 (100)		–5.25
$R^1 = R^2 = H$, $R^3 = Me$ (**3i**)				–4.88 (100)		–4.88
$R^1 = R^2 = H$, $R^3 =$ OMe (**3j**)				–4.86 (100)		–4.86
$R^1 = H$, $R^2 = CN$, $R^3 =$ Cl (**3k**)	 conformer II	0.1682	0.7526	–5.25 (42.9)	–5.30 (57.1)	–5.27
$R^1 = H$, $R^2 = CN$, $R^3 =$ F (**3l**)	 conformer I	–0.2366	1.4915	–5.24 (59.9)	–5.42 (40.1)	–5.31
$R^1 = H$, $R^2 = CN$, $R^3 =$ Me (**3m**)	 conformer I	–0.1299	1.245	–5.09 (55.5)	–5.19 (44.5)	–5.13
$R^1 = H$, $R^2 = CN$, $R^3 =$ OMe (**3n**)	 conformer II	0.1920	0.7229	–5.06 (42.0)	–5.17 (58.0)	–5.12
$R^1 = H$, $R^2 = Cl$, $R^3 =$ F (**3o**)	 conformer II	0.7913	0.2626	–5.31 (20.8)	–5.17 (79.2)	–5.20
$R^1 = H$, $R^2 = Cl$, $R^3 =$ Me (**3p**)	 conformer I	–0.2385	1.496	–4.98 (59.9)	–5.01 (40.1)	–4.99
$R^1 = H$, $R^2 = Cl$, $R^3 =$ OMe (**3q**)	 conformer II	0.1142	0.8244	–4.97 (45.2)	–4.95 (54.8)	–4.96
$R^1 = H$, $R^2 = F$, $R^3 =$ Me (**3r**)	 conformer I			–5.09 (100)	- (-)[1]	–5.09
$R^1 = H$, $R^2 = F$, $R^3 =$ OMe (**3s**)	 conformer I	–0.2416	1.504	–5.06 (60.1)	–5.02 (39.9)	–5.04

R^1 = H, R^2 = Me, R^3 = OMe (**3t**)	 conformer I	–0.5321	2.458	–4.92 (71.1)	–4.93 (28.9)	–4.92
R^1 = Br, R^2 = H, R^3 = Me (**4a**)				–5.171 (100)	-(-)[1]	
R^1 = Br, R^2 = Cl, R^3 = OMe (**4b**)	 conformer II	0.4455	0.4710	–5.10 (32.0)	–5.07 (68.0)	–5.08
R^1 = Br, R^2 = F, R^3 = OMe (**4c**)	 conformer I	–0.7298	3.432	–5.12 (77.4)	–5.16 (22.6)	–5.13
R^1 = Br, R^2 = R^3 = OMe (**4d**)				–4.99 (100)		–4.99

[1]No second *N-intra*-conformation corresponding to a minimum on the potential hypersurface was found for this derivative.

4.4 Calculation of redox potentials of 3

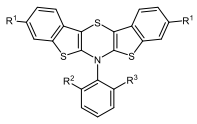
4.4.1 Computation of redox potentials of 3 by means of DFT-quantum mechanical calculation[12]

$$E_{0\,(calc.)}^{0/+1} = \mathrm{IP} + \frac{1}{\mathrm{F}}(-T\Delta S_{redox}(gas) + \Delta G_{solv}(ox) + \Delta G_{solv}(red)).$$

$E_{0\,(calc.)}^{0/+1}$ as the DFT-calculated first redox potential of respective BBTT with ionization potential (IP) as the difference of enthalpies of the radical cation and native compound in gas phase ($\Delta H_{redox}(gas)$), $\Delta S_{redox}(gas)$ as difference of entropy of the radical cation and native compound in gas phase, $\Delta G_{solv}(ox)$ as difference of SCF energy of the gas phase and under SMD variation of PCM as solvent model of the oxidized species as the radical cation and $\Delta G_{solv}(red)$ as difference of SCF energy of the gas phase and under SMD variation of PCM as solvent model of the reduced species as the native BBTT.

When there are two possible *N-intra*-conformers in solution (see Table 18), the final plotted redox potential $E_{0\,(calc.)}^{0/+1}$ is calculated from both redox potentials $E_{0\,(calc.)}^{0/+1}$ by weighing them according to the calculated percentual amount of the corresponding *N-intra*-conformers in solution.

Table 19. DFT-computed first redox potential $E_{0\,(\mathrm{calc.})}^{0/+1}$ vs. vacuum of native BBTT to the respective radical cation ((u)B3LYP/6-311++G**, (SMD CH_2Cl_2))

	ionization potential (IP) / eV	$\Delta S_{redox}(gas)$ / kcal mol^{-1}	$\Delta G_{solv}(ox)$ / kcal mol^{-1}	$\Delta G_{solv}(red)$ / kcal mol^{-1}	$E_{0\,(\mathrm{calc.})}^{0/+1}$ vs. vacuum	$E_{0\,(\mathrm{calc.})}^{0/+1}$ vs. vacuum (weighted)
$R^1 = R^2 = H$, $R^3 =$ CN (**3a**)	6.09832	–0.003424	–52.1522	–22.5457	4.8587	4.81655
	6.10833	–9.83E–4	–52.1522	–21.5148	4.79244	
$R^1 = R^2 = H$, $R^3 =$ Cl (**3b**)	6.01279	–0.001951	–49.1141	–20.211	4.78463	4.76999
	5.99059	–9.79E–4	–49.1141	–19.811	4.73252	
$R^1 = R^2 = H$, $R^3 =$ F (**3c**)	6.02569	-0.003653	-48.8098	-19.5985	4.80617	4.79798
	6.01151	-0.001998	-48.8098	-19.3672	4.76057	
$R^1 = R^2 = R^3 = H$ (**5**)	5.96678	-0.002113	-49.205	-19.5694	4.70894	4.70894
$R^1 = R^2 = H$, $R^3 =$ Me (**3d**)	5.96419	–9.25E–4	–48.9374	–19.7315	4.70963	4.67192
	5.9378	0.003146	–48.9374	–19.669	4.6279	
$R^1 = R^2 = H$, $R^3 =$ OMe (**3e**)	5.84808	–6.54E–4	–48.0724	–20.5543	4.66321	4.65541
	5.82474	–9.44E–4	–48.0724	–20.544	4.64317	
$R^1 = R^2 = H$, $R^3 =$ CN (**3f**)	6.2171	1.34E–4	–54.3789	–24.0196	4.89883	4.89883
$R^1 = R^2 = H$, $R^3 =$ Cl (**3g**)	6.02591	–4.08E–4	–48.776	–20.2586	4.79452	4.79452
$R^1 = R^2 = H$, $R^3 =$ F (**3h**)	6.0781	–9.31E–4	–48.1845	–19.1737	4.83208	4.83208
$R^1 = R^2 = H$, $R^3 =$ Me (**3i**)	5.91475	–0.001905	–48.6781	–19.6356	4.67995	4.67995
$R^1 = R^2 = H$, $R^3 =$ OMe (**3j**)	5.6951	–0.002617	–46.9857	–21.6973	4.6323	4.6323
$R^1 = H$, $R^2 =$ CN, $R^3 =$ Cl (**3k**)	6.1332	4.33E–4	–51.4918	–21.8189	4.84084	4.84334
	6.10112	–5.4E–4	–51.4918	–22.4027	4.84665	
$R^1 = H$, $R^2 =$ CN, $R^3 =$ F (**3l**)	6.16572	–1E–6	–51.3851	–21.3421	4.86291	4.89294
	6.13914	–0.003382	–51.3851	–22.104	4.91308	
$R^1 = H$, $R^2 =$ CN, $R^3 =$ Me (**3m**)	6.04878	0.001274	–51.8079	–21.8155	4.76168	4.78475
	6.00709	–0.002553	–51.8079	–22.5952	4.80329	

R^1 = H, R^2 = CN, R^3 = OMe (**3n**)	5.94677	–1.84E–4	–51.045	–22.7968	4.75416	4.75416
	5.92029	–9.3E–4	–51.045	–23.4099	4.76391	
R^1 = H, R^2 = Cl, R^3 = F (**3o**)	6.02263	–0.002186	–48.3928	–19.8285	4.8422	4.83439
	6.01776	–8E–5	–48.3928	–19.7031	4.80466	
R^1 = H, R^2 = Cl, R^3 = Me (**3p**)	5.95992	–0.003263	–48.7891	–20.231	4.76368	4.74305
	5.97712	2.5E–5	–48.7891	–20.0209	4.72926	
R^1 = H, R^2 = Cl, R^3 = OMe (**3q**)	5.86599	–0.001401	–48.1067	–21.0991	4.71292	4.71655
	5.85995	–0.001747	–48.1067	–21.3207	4.72096	
R^1 = H, R^2 = F, R^3 = Me (**3r**)	For this *N-intra*-conformer **3r** no corresponding minimum on the potential hypersurface was found.					4.78903
	6.00286	–0.002682	–48.4819	–19.6913	4.78903	
R^1 = H, R^2 = F, R^3 = OMe (**3s**)	5.87388	–0.001816	–47.6551	–20.6407	4.72588	4.72849
	5.89037	–0.001296	–47.6551	–20.5158	4.73023	
R^1 = H, R^2 = Me, R^3 = OMe (**3t**)	5.81763	–0.001058	–47.661	–20.6355	4.65935	4.66744
	5.79755	–0.003384	–47.661	–20.6676	4.67073	

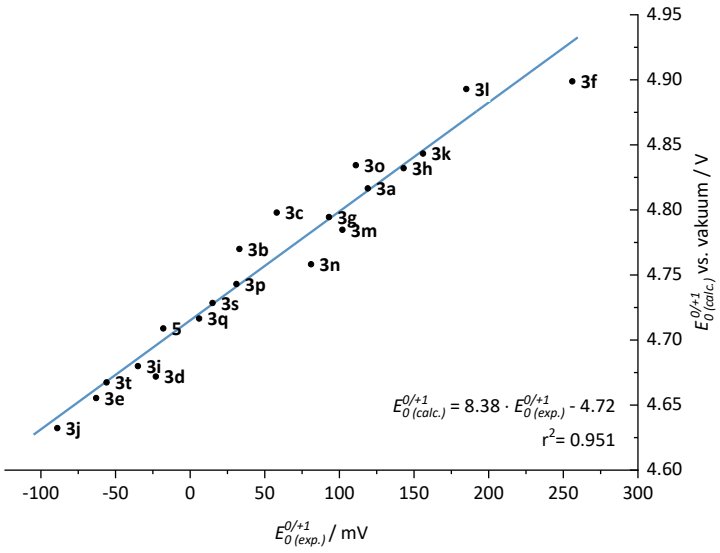


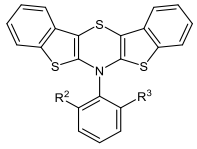
Figure 73. Linear correlation between the experimental redox potentials $E_0^{0/+1}$ and the calculated redox potentials $E_{0\,(calc.)}^{0/+1}$ of **3** ($E_{0\,(calc.)}^{0/+1} = \mathrm{IP} + \frac{1}{\mathrm{F}}(-T\Delta S_{redox}(Gas) + \Delta G_{solv}(ox) + \Delta G_{solv}(red))$).

4.4.2 Computation of redox potentials of 3f-t by means of experimental data

$$E_{0,\mathbf{3}\ (R1,R2)(calc.)} = E_{0,\mathbf{5}\ (H,H)(exp.)} + \Delta E_{0,\mathbf{3}\ (R1,H)\ (exp.)-\mathbf{5}(H,H)(exp.)} + \Delta E_{0,\mathbf{3}\ (R2,H)\ (exp.)-\mathbf{5}(H,H)(exp.)}$$

$E_{0,\mathbf{3}\ (R1,R2)(calc.)}$ as the calculated redox potential of *anti-anti-N-ortho,ortho'*-disubstituted-phenyl-BBTT **3f-t** with the two substituents R1 and R2 as the *ortho*- and *ortho'*-substituents with $E_{0,\mathbf{5}\ (H,H)(exp.)}$ as the absolute experimental redox potential of the unsubstituted *anti-anti-N*-phenyl-BBTT **5**[4, 6], $\Delta E_{0,\mathbf{3}\ (R1,H)\ (exp.)-\mathbf{5}(H,H)(exp.)}$ as the difference of the absolute experimental redox potentials of *anti-anti-N-ortho*-substituted-phenyl-BBTT **3a-e** with the *ortho*-substituent R1 and *anti-anti-N*-phenyl-BBTT **5** and $\Delta E_{0,\mathbf{3}\ (R2,H)(exp.)-\mathbf{5}(H,H)(exp.)}$ as the difference of the absolute redox potentials of *anti-anti-N-ortho*-substituted-phenyl-BBTT **3a-e** with the *ortho*-substituent R2 and *anti-anti-N*-phenyl-BBTT **5.**

Table 20. Calculated redox potential $E^{0\,/\,+1}_{0,\mathbf{3}\ (R1,R2)(calc.)}$ and $E^{+1\,/\,+2}_{0,\mathbf{3}\ (R1,R2)(calc.)}$ of BBTT **3f-t**.



	$E^{0\,/\,+1}_{0,\mathbf{3}\ (exp.)}$	$E^{+1\,/\,+2}_{0,\mathbf{3}\ (exp.)}$	$\Delta E^{0\,/\,+1}_{0,\mathbf{3}-\mathbf{5}\ (exp.)}$	$\Delta E^{+1\,/\,+2}_{0,\mathbf{3}-\mathbf{5}\ (exp.)}$	$E^{0\,/\,+1}_{0,\mathbf{3}\ (R1,R2)(calc.)}$	$E^{+1\,/\,+2}_{0,\mathbf{3}\ (R1,R2)(calc.)}$
$R^1 = R^2 = H$, $R^3 = CN$ (**3a**)	119	906	137	164	-	-
$R^1 = R^2 = H$, $R^3 = Cl$ (**3b**)	33	840	57	98	-	-
$R^1 = R^2 = H$, $R^3 = F$ (**3c**)	58	865	76	123	-	-
$R^1 = R^2 = R^3 = H$ (**5**)[4, 6]	–18	742	0	0	-	-
$R^1 = R^2 = H$, $R^3 = Me$ (**3d**)	–23	771	–5	29	-	-
$R^1 = R^2 = H$, $R^3 =$ OMe (**3e**)	–63	761	–45	19	-	-
$R^1 = R^2 = H$, $R^3 = CN$ (**3f**)	256	1073	-	-	256	1073
$R^1 = R^2 = H$, $R^3 = Cl$ (**3g**)	93	951	-	-	93	951
$R^1 = R^2 = H$, $R^3 = F$ (**3h**)	143	982	-	-	143	982
$R^1 = R^2 = H$, $R^3 = Me$ (**3i**)	–35	835	-	-	–35	835
$R^1 = R^2 = H$, $R^3 =$ OMe (**3j**)	–89	787	-	-	–89	787
$R^1 = H$, $R^2 = CN$, $R^3 =$ Cl (**3k**)	156	1019	-	-	156	1019
$R^1 = H$, $R^2 = CN$, $R^3 =$ F (**3l**)	185	1014	-	-	185	1014
$R^1 = H$, $R^2 = CN$, $R^3 =$ Me (**3m**)	102	956	-	-	102	956

R^1 = H, R^2 = CN, R^3 = OMe (**3n**)	81	948	-	-	74	925
R^1 = H, R^2 = Cl, R^3 = F (**3o**)	111	954	-	-	111	954
R^1 = H, R^2 = Cl, R^3 = Me (**3p**)	31	894	-	-	31	894
R^1 = H, R^2 = Cl, R^3 = OMe (**3q**)	6	874	-	-	6	874
R^1 = H, R^2 = F, R^3 = Me (**3r**)	56	893	-	-	56	893
R^1 = H, R^2 = F, R^3 = OMe (**3s**)	15	873	-	-	15	873
R^1 = H, R^2 = Me, R^3 = OMe (**3t**)	–56	818	-	-	–56	818

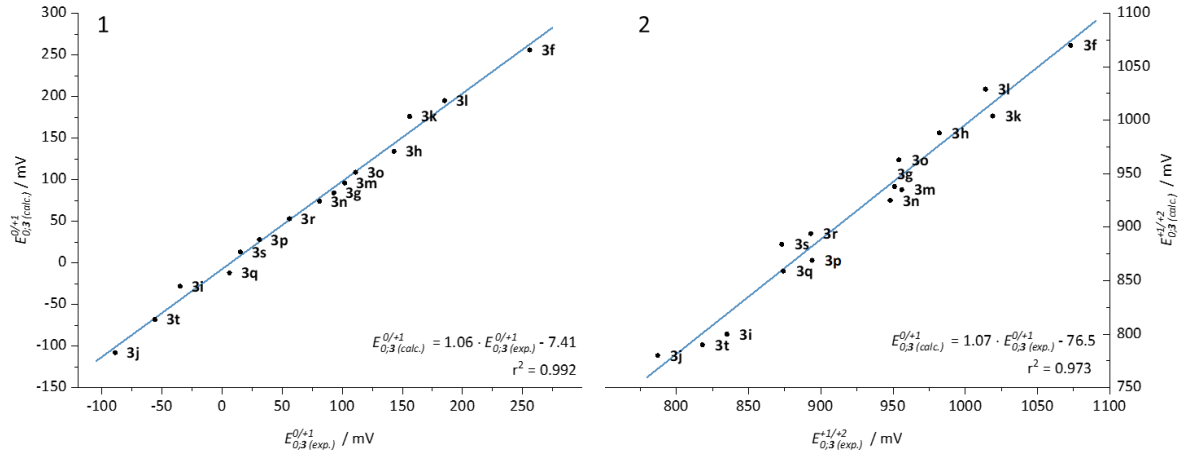


Figure 74. Linear correlation between the experimental redox potentials $E_0^{0/+1}$ (1) und $E_0^{+1/+2}$ (2) and the calculated redox potentials $E_0^{0/+1}$ und $E_0^{+1/+2}$ of **3f-t** via $E_{\mathbf{0,3}\ (R1,R2)\ (calc.)} = E_{\mathbf{0,5}\ (H,H)\ (exp.)} + \Delta E_{\mathbf{0,3}\ (R1,H)\ (exp.)-\mathbf{5}(H,H)\ (exp.)} + \Delta E_{\mathbf{0,3}\ (R2,H)\ (exp.)-\mathbf{5}(H,H)\ (exp.)}$

4.5 Spectroelectrochemistry

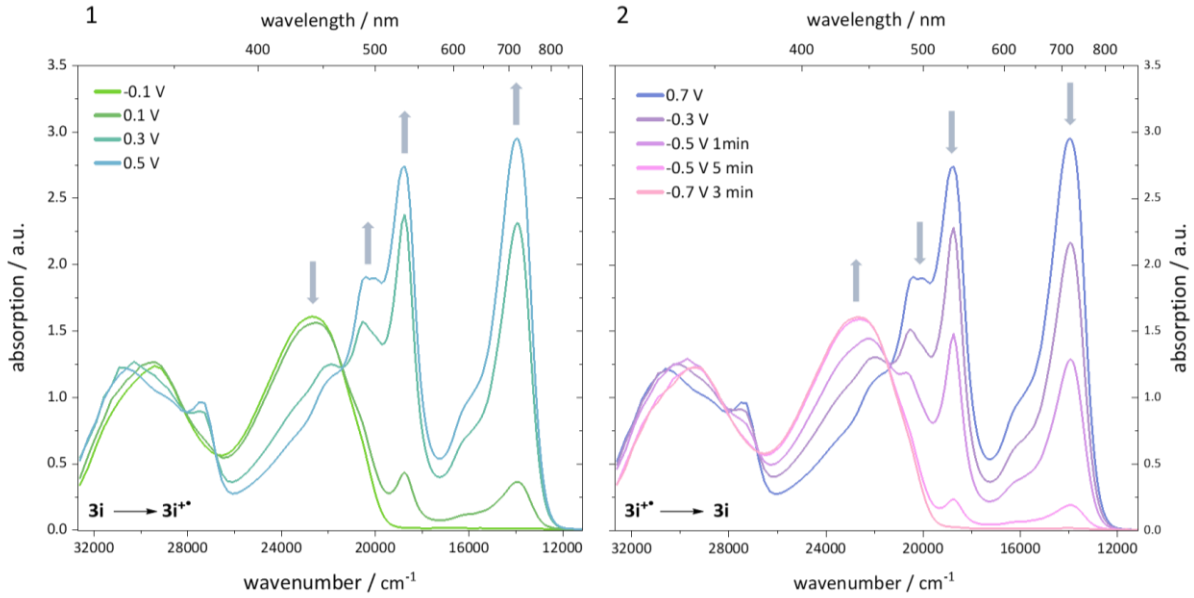


Figure 75. Spectroelectrochemical measurements of compounds **3i** forming the corresponding radical cation **3i**$^{\bullet+}$ by oxidation by increase the applied potential (1) and re-reduction by decrease of the applied potential (2) (recorded in CH_2Cl_2, $c = 5 \cdot 10^{-3}$ M, $T = 298$ K, electrolyte 0.1 M [^{n}Bu$_4$N][PF$_6$]; Pt-working electrode, GC-counter electrode and Ag/AgCl(3 M)-reference electrode).

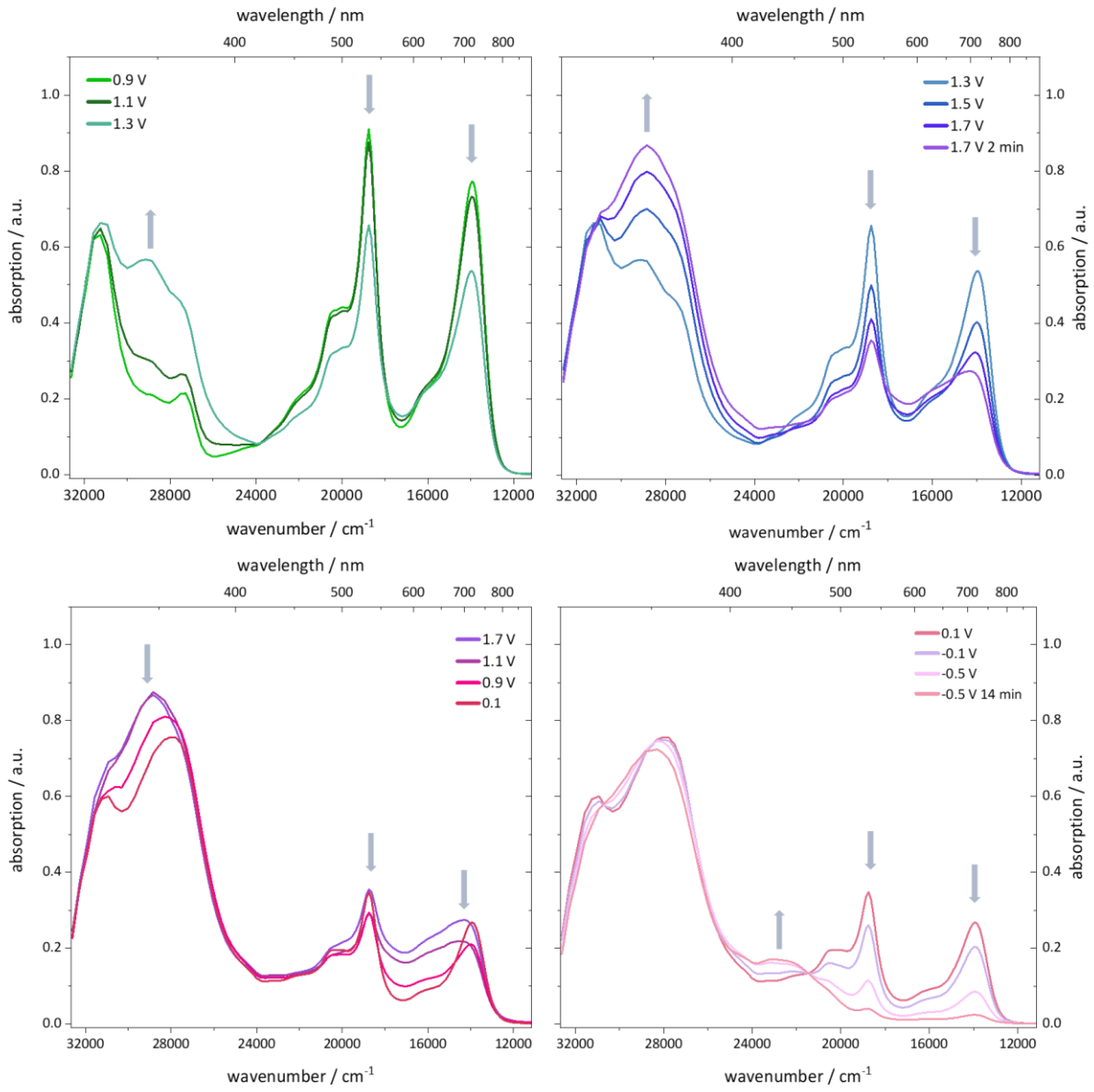


Figure 76. Spectroelectrochemical measurements of compound **3i**$^{\bullet+}$ by further oxidation by increase the applied potential and re-reduction by decrease of the applied potential. Formation of the dication **3i**$^{2+}$ cannot been seen due to presumably a fast follow-up reaction on the timescale of the experiment (recorded in CH_2Cl_2, $c = 5 \cdot 10^{-3}$ M, T = 298 K, electrolyte 0.1 M [^{n}Bu$_4$N][PF$_6$]; Pt-working electrode, GC-counter electrode and Ag/AgCl(3 M)-reference electrode).

5 Photophysics

5.1 UV/vis absorption and emission spectra

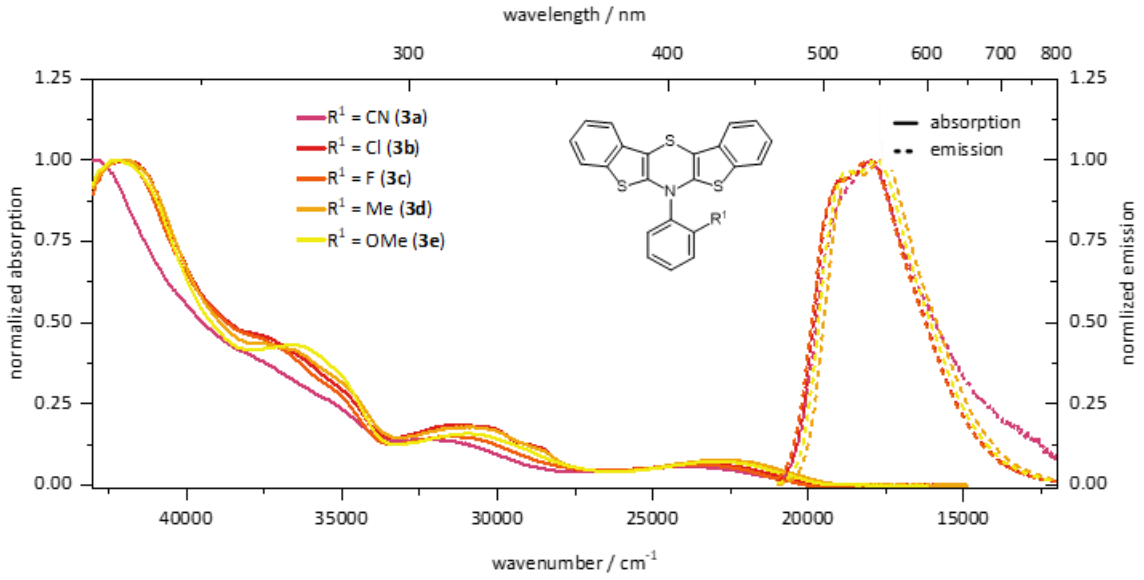


Figure 77. UV/vis-absorption and emission spectra of *anti-anti-N-ortho*-substituted-phenyl-BBTT **3a-e** in solution (recorded in CH_2Cl_2, T = 298 K, c = 10^{-5} to 10^{-7} M).

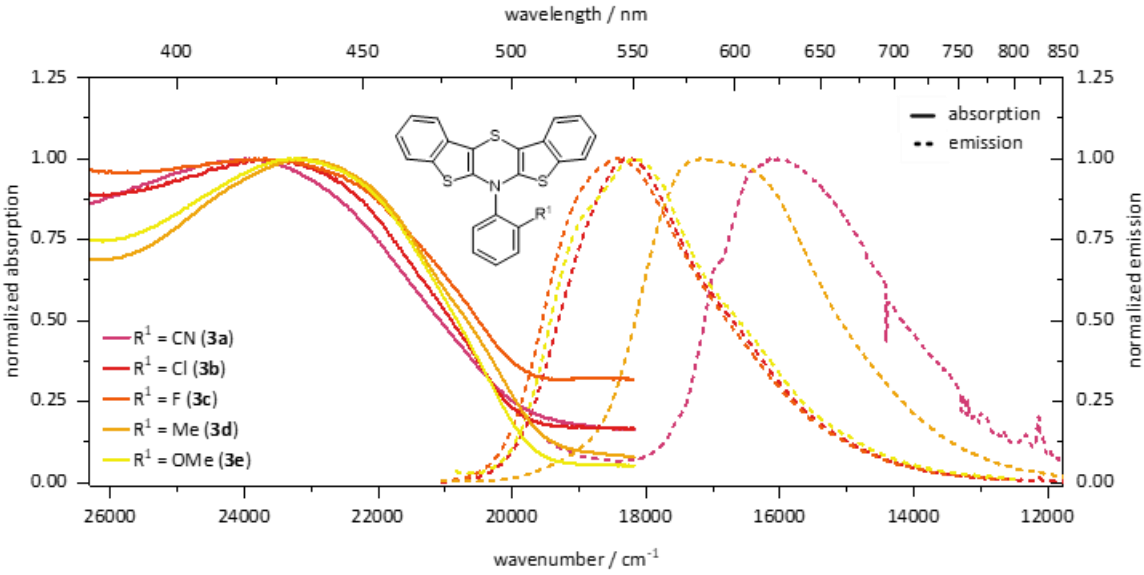


Figure 78. UV/vis-absorption and emission spectra of *anti-anti-N-ortho*-substituted-phenyl-BBTT **3a-e** in powder (T = 298 K).

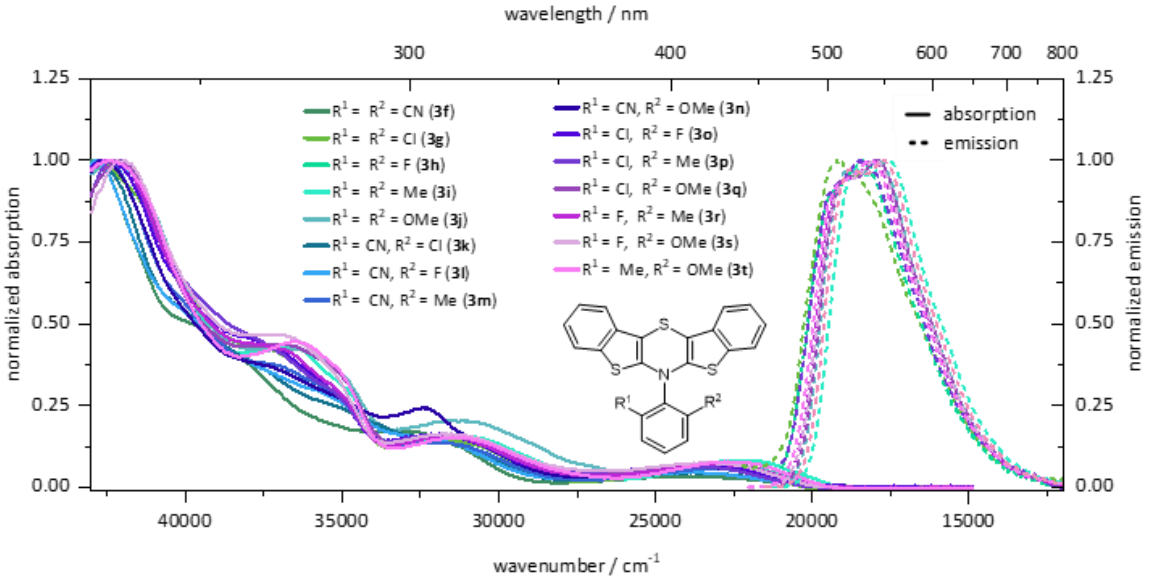


Figure 79. UV/vis-absorption and emission spectra of *anti-anti-N-ortho,ortho'*-disubstituted-phenyl-BBTT **3f-t** in solution (recorded in CH_2Cl_2, T = 298 K, c = 10^{-5} to 10^{-7} M).

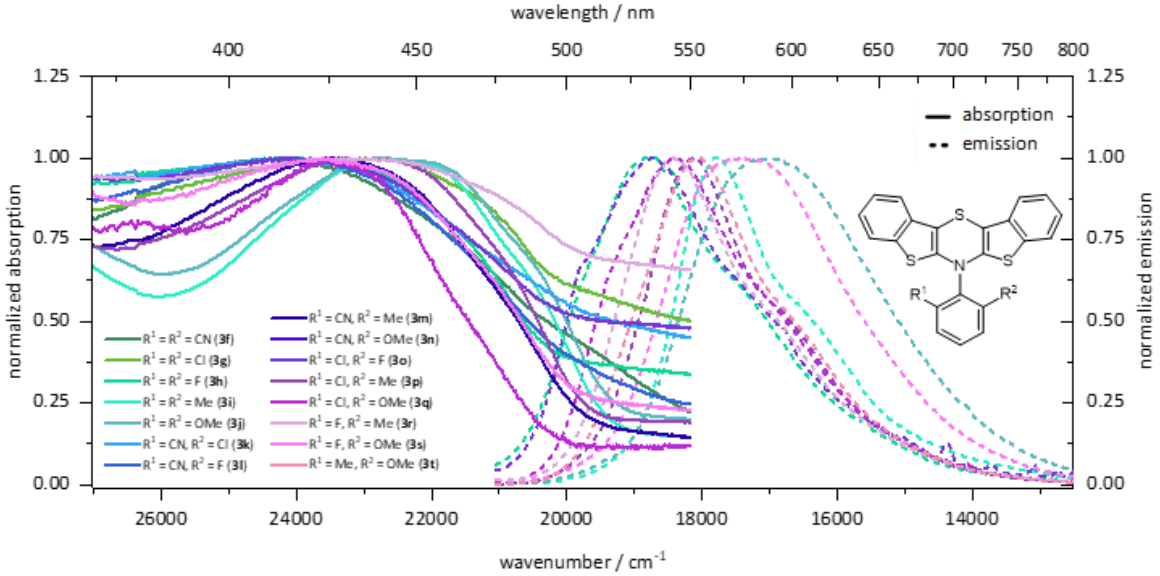
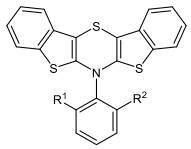


Figure 80. UV/vis-absorption and emission spectra of *anti-anti-N-ortho,ortho'*-disubstituted-phenyl-BBTT **3f-t** in powder (T = 298 K).

5.2 TD-DFT-computed and experimental UV/vis absorption and emission data

Table 21. Assignment of the experimental absorption bands to the TD-DFT simulated underlying transitions of the thermodynamically favored *N-intra*-conformer of *anti-anti-N-ortho*-substituted-phenyl-BBTT **3a-e** (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2).



	$\lambda_{exp,abs}$ / nm	$\lambda_{sim,\ abs}$ / nm	oscillator strength	most dominant contribution (%)	$\lambda_{exp,\ em}$ / nm	$\lambda_{sim,\ em}$ / nm
R^1 = H, R^2 = CN (**3a**)	233	242	0.061	HOMO−1 → LUMO+3 (55)	519, 543	494
		243	0.044	HOMO−6 → LUMO (54)		
		244	0.047	HOMO → LUMO+14 (44)		
		254	0.285	HOMO → LUMO+10 (46)		
	–	268	0.159	HOMO−2 → LUMO+1 (73)		
	309	314	0.042	HOMO−1 → LUMO (63)		
		316	0.060	HOMO → LUMO+3 (51)		
	411	403	0.115	HOMO → LUMO+1 (84)		
R^1 = H, R^2 = Cl (**3b**)	235	228	0.0653	HOMO → LUMO+17 (42)	519, 540	558
		233	0.2167	HOMO−1 → LUMO+4 (33)		
		240	0.109	HOMO−1 → LUMO+3 (51)		
	263	256	0.228	HOMO → LUMO+10 (49)		
		269	0.152	HOMO−2 → LUMO (80)		
		270	0.109	HOMO−1 → LUMO (87)		
	314	320	0.091	HOMO → LUMO+3 (73)		
	423	414	0.127	HOMO → LUMO (95)		
R^1 = H, R^2 = F (**3c**)	234	232	0.203	HOMO → LUMO+15 (36)	515 (S), 539	556
		235	0.184	HOMO−1 → LUMO+4 (41)		
	267	255	0.259	HOMO → LUMO+10 (57)		
		268	0.159	HOMO−2 → LUMO (80)		

		269	0.115	HOMO−1 → LUMO	(86)		
	282	297	0.033	HOMO → LUMO+6	(73)		
	315	318	0.097	HOMO → LUMO+3	(75)		
	418	409	0.132	HOMO → LUMO	(95)		
R^1 = H, R^2 = Me (**3d**)	234	232	0.148	HOMO → LUMO+16	(33)	525, 551	566
		234	0.342	HOMO−1 → LUMO+4	(43)		
		249	0.130	HOMO → LUMO+13	(48)		
	269	258	0.225	HOMO → LUMO+10	(64)		
		269	0.137	HOMO−2 → LUMO	(79)		
		269	0.124	HOMO−1 → LUMO	(85)		
	316	318	0.053	HOMO → LUMO+4	(71)		
		320	0.046	HOMO → LUMO+3	(72)		
	429	415	0.150	HOMO → LUMO	(96)		
R^1 = H, R^2 = OMe (**3e**)	232	232	0.475	HOMO−1 → LUMO+4	(40)	521, 547	560
	–	252	0.185	HOMO → LUMO+14	(48)		
	270	260	0.202	HOMO → LUMO+10	(64)		
		270	0.099	HOMO−1 → LUMO	(82)		
		270	0.136	HOMO−2 → LUMO	(78)		
	318	323	0.059	HOMO → LUMO+4	(66)		
		323	0.046	HOMO → LUMO+2	(66)		
	425	423	0.143	HOMO → LUMO	(96)		

The corresponding HOMOs and LUMOs referenced to their energy are depicted in the following.

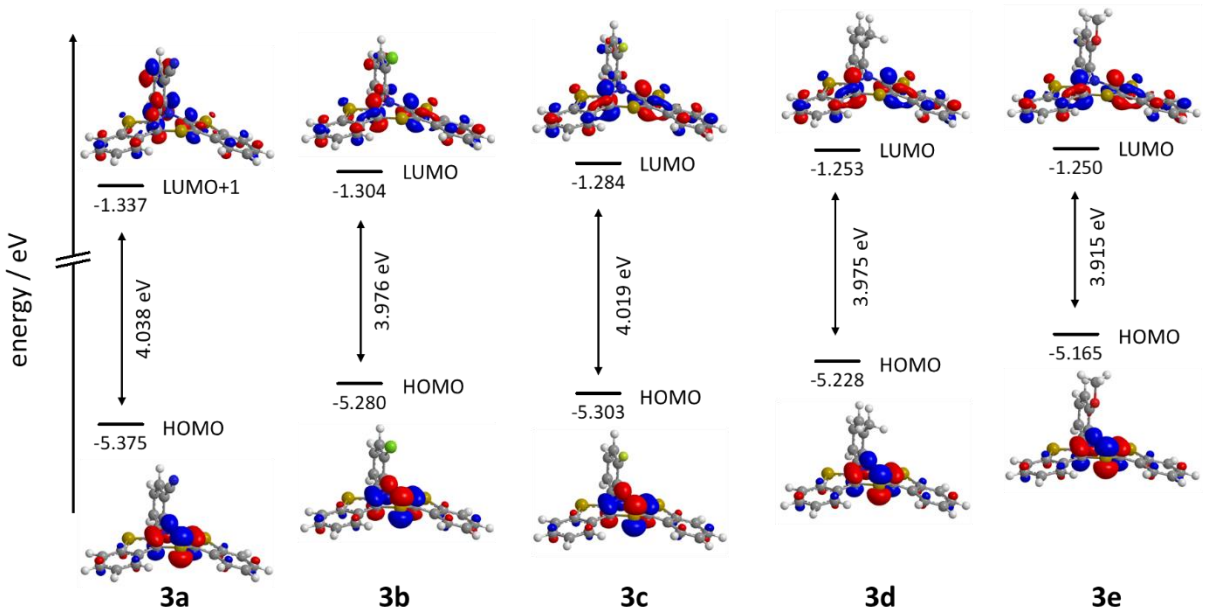
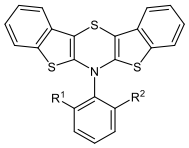


Figure 81. Selected Kohn-Sham frontier orbitals and energies using the example of **3a-e** (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2, isosurface value at 0.05 a.u.).

Table 22. Assignment of the experimental absorption bands to the TD-DFT simulated underlying transitions of *anti-anti-N-ortho,ortho'*-disubstituted-phenyl-BBTT **3f-j** with a homogenic substitution pattern (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2).



	$\lambda_{exp,abs}$ / nm	$\lambda_{sim,abs}$ / nm	oscillator strength	most dominant contribution	(%)	$\lambda_{exp,em}$ / nm	$\lambda_{sim,em}$ / nm
$R^1 = R^2 = CN$ (**3f**)	232	231	0.225	HOMO → LUMO+17	(45)	–	–
	251	248	0.354	HOMO → LUMO+13	(44)		
	260	265	0.126	HOMO–1 → LUMO+2	(74)		
	300	316	0.135	HOMO → LUMO+3	(89)		
	411	380	0.071	HOMO → LUMO+2	(96)		
$R^1 = R^2 = Cl$ (**3g**)	230	227	0.1345	HOMO → LUMO+18	(25)	509, 536 (S)	551
		232	0.2644	HOMO → LUMO+15	(30)		
	264	249	0.092	HOMO–3 → LUMO	(60)		
		255	0.270	HOMO → LUMO+11	(37)		
		276	0.155	HOMO–2 → LUMO	(89)		
	310	325	0.092	HOMO → LUMO+3	(81)		

	420	427	0.076	HOMO → LUMO	(96)		
$R^1 = R^2 = F$ (**3h**)	234	233	0.314	HOMO−1 → LUMO+4	(41)	511 (S), 525	547
		247	0.073	HOMO → LUMO+12	(45)		
	265	255	0.288	HOMO → LUMO+10	(51)		
		268	0.145	HOMO−2 → LUMO	(78)		
	279	269	0.107	HOMO−1 → LUMO	(87)		
	309	306	0.093	HOMO → LUMO+6	(45)		
	409	410	0.122	HOMO → LUMO	(93)		
$R^1 = R^2 = Me$ (**3i**)	233	231	0.1459	HOMO−1 → LUMO+6	(37)	524, 553	567
		232	0.3294	HOMO−1 → LUMO+3	(58)		
		235	0.0731	HOMO−1 → LUMO+4	(28)		
	269	259	0.433	HOMO → LUMO+13	(62)		
		266	0.105	HOMO → LUMO+10	(68)		
		269	0.132	HOMO−1 → LUMO	(88)		
		272	0.052	HOMO−2 → LUMO	(64)		
	316	315	0.109	HOMO → LUMO+4	(76)		
	434	444	0.162	HOMO → LUMO	(97)		
$R^1 = R^2 = OMe$ (**3j**)	236	233	0.375	HOMO−1 → LUMO+2	(59)	518, 544	555
	270	257	0.332	HOMO → LUMO+15	(59)		
		265	0.140	HOMO → LUMO+11	(63)		
		268	0.127	HOMO−1 → LUMO	(87)		
		271	0.057	HOMO−2 → LUMO	(63)		
	315	314	0.103	HOMO → LUMO+4	(54)		
	429	432	0.162	HOMO → LUMO	(97)		

The corresponding HOMOs and LUMOs referenced to their energy are depicted in the following.

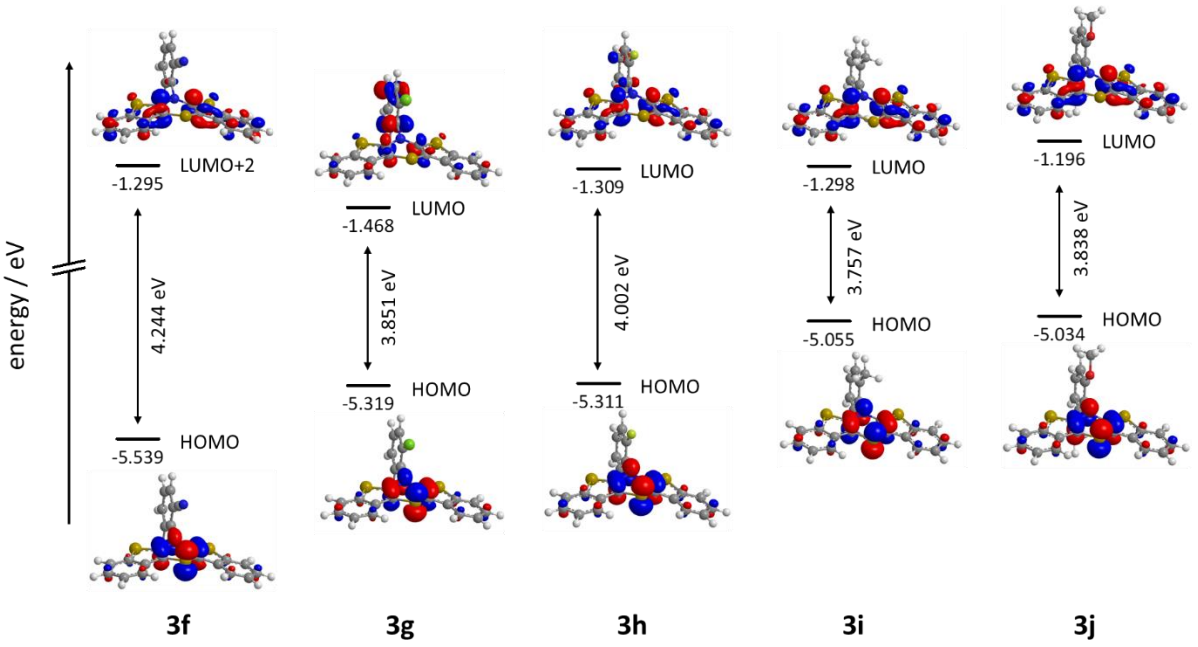


Figure 82. Selected Kohn-Sham frontier orbitals and energies using the example of **3f-j** (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2, isosurface value at 0.05 a.u.).

6 Computational details

All quantum chemical calculations were carried out with Gaussian 09.[13] The hybrid functionals (u)B3LYP and PBE1PBE were employed,[14-16] as well as the basis sets 6-311G**, 6-311+G**,and 6-311++G**.[17-20] The polarizable continuum model (PCM) with the integral equation formalism variant IEFPCM and SMD were used.[21, 22] Some calculations furthermore used time dependent methods.[23, 24]

6.1 *anti-anti-N-ortho(,ortho')*-(di)substituted-phenyl-BBTT 3

6.1.1 *anti-anti-N-ortho*-cyanophenyl-BBTT 3a

6.1.1.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt=verytight Int=UltraFine freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.334806	-0.585558	3.920145
C 0	-4.481367	-0.602447	5.033135
C 0	-3.149504	-0.230411	4.916619
C 0	-2.648521	0.162850	3.665596
C 0	-3.521715	0.163339	2.553291
C 0	-4.861286	-0.200458	2.670045
C 0	-1.330006	0.617698	3.311477
C 0	-1.204705	0.923477	1.992276
S 0	-2.695354	0.660735	1.078004
S 0	0.015189	0.817404	4.468832
C 0	1.333980	0.598066	3.284942
C 0	1.175593	0.909569	1.962696
N 0	-0.012223	1.299688	1.359960

C 0	2.652432	0.123785	3.612803
C 0	3.503215	0.111569	2.483318
S 0	2.655046	0.621295	1.024709
C 0	3.172380	-0.277000	4.853655
C 0	4.500683	-0.668650	4.943668
C 0	5.331935	-0.664176	3.813893
C 0	4.839339	-0.271956	2.573420
C 0	0.038719	2.617929	1.093853
C 0	0.036646	3.245179	-0.139577
C 0	0.036647	4.638099	-0.194617
C 0	0.036652	5.383919	0.981733
C 0	0.036655	4.742449	2.215555
C 0	0.036654	3.342649	2.279687
C 0	0.036657	2.695189	3.555713
N 0	0.036659	2.210279	4.603793
H 0	-6.372693	-0.876798	4.031492
H 0	-4.868735	-0.908058	5.998233
H 0	-2.494752	-0.245711	5.780379
H 0	-5.518810	-0.189703	1.808506
H 0	2.534812	-0.282776	5.730280
H 0	4.902645	-0.980078	5.900902
H 0	6.367429	-0.970696	3.904593
H 0	5.479656	-0.270766	1.698953
H 0	0.036643	2.655369	-1.048217
H 0	0.036645	5.137429	-1.156297
H 0	0.036653	6.466609	0.940503
H 0	0.036659	5.313339	3.135668

SCF Done: E(RB3LYP) = -2188.03798492

Sum of electronic and zero-point Energies= -2187.755678

Sum of electronic and thermal Energies= -2187.733435

Sum of electronic and thermal Enthalpies= -2187.732490

Sum of electronic and thermal Free Energies= -2187.810292

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full0 1

C 0	-5.337213	-2.292491	-0.393710
C 0	-4.503651	-3.230797	0.234307
C 0	-3.173382	-2.937271	0.495657
C 0	-2.656875	-1.685711	0.125429
C 0	-3.508464	-0.754725	-0.514800
C 0	-4.847454	-1.048298	-0.772641
C 0	-1.334889	-1.146552	0.317744
C 0	-1.189547	0.115753	-0.166447
S 0	-2.659310	0.726272	-0.934488
S 0	0.000037	-2.031507	1.100810
C 0	1.334936	-1.146518	0.317738
C 0	1.189556	0.115783	-0.166452
N 0	-0.000005	0.873288	-0.185387
C 0	2.656935	-1.685645	0.125406
C 0	3.508489	-0.754640	-0.514839
S 0	2.659291	0.726336	-0.934520
C 0	3.173480	-2.937189	0.495633
C 0	4.503753	-3.230682	0.234264
C 0	5.337280	-2.292358	-0.393770
C 0	4.847483	-1.048178	-0.772698
C 0	-0.000015	2.134637	0.521802
C 0	0.000059	2.163443	1.914935
C 0	0.000055	3.379030	2.592330
C 0	-0.000024	4.578671	1.879587
C 0	-0.000097	4.563135	0.491329
C 0	-0.000093	3.340108	-0.198717
C 0	-0.000163	3.340875	-1.630273
N 0	-0.000225	3.391341	-2.784418
H 0	-6.373813	-2.540191	-0.590420
H 0	-4.904919	-4.197061	0.517152
H 0	-2.532737	-3.667403	0.977117
H 0	-5.489946	-0.326385	-1.263031
H 0	2.532865	-3.667333	0.977114
H 0	4.905046	-4.196937	0.517102
H 0	6.373886	-2.540031	-0.590494
H 0	5.489951	-0.326250	-1.263104
H 0	0.000120	1.225658	2.457976

H 0 0.000112 3.390686 3.676088

H 0 -0.000027 5.525550 2.406183

H 0 -0.000157 5.487386 -0.072766

SCF Done: E(RB3LYP) = -2188.03837228

Sum of electronic and zero-point Energies= -2187.755888

Sum of electronic and thermal Energies= -2187.733803

Sum of electronic and thermal Enthalpies= -2187.732858

Sum of electronic and thermal Free Energies= -2187.809500

6.1.1.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt=verytight Int=UltraFine freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0 -5.343841 -2.259320 -0.526407

C 0 -4.501794 -3.253558 -0.004636

C 0 -3.168396 -2.985391 0.275569

C 0 -2.654803 -1.701764 0.026819

C 0 -3.517299 -0.715621 -0.507394

C 0 -4.858041 -0.979859 -0.780679

C 0 -1.333412 -1.183043 0.263099

C 0 -1.195077 0.122101 -0.097376

S 0 -2.677259 0.812452 -0.768232

S 0 -0.000001 -2.113905 1.004915

C 0 1.333411 -1.183044 0.263100

C 0 1.195077 0.122100 -0.097376

N 0 0.000000 0.850877 -0.053487

C 0 2.654802 -1.701765 0.026820

C 0 3.517298 -0.715623 -0.507394

S 0 2.677259 0.812450 -0.768232

C 0 3.168393 -2.985394 0.275570

C 0 4.501791 -3.253561 -0.004635

C 0 5.343839 -2.259324 -0.526407

C 0 4.858040 -0.979863 -0.780679

C 0 0.000001 2.282240 -0.134200

C 0 0.000001 2.919945 -1.370968

C 0 0.000002 4.313545 -1.440136

C 0 0.000004 5.074297 -0.273379

C 0 0.000003 4.449446 0.969678

C 0 0.000002 3.050666 1.046608

C 0 0.000001 2.410529 2.325504

N 0 -0.000001 1.918664 3.370975

H 0 -6.382312 -2.487115 -0.736034

H 0 -4.898865 -4.244196 0.184557

H 0 -2.525083 -3.758445 0.680211

H 0 -5.506319 -0.211926 -1.185960

H 0 2.525080 -3.758447 0.680212

H 0 4.898862 -4.244200 0.184557

H 0 6.382309 -2.487120 -0.736034

H 0 5.506318 -0.211931 -1.185960

H 0 0.000000 2.323433 -2.274905

H 0 0.000003 4.800968 -2.407457

H 0 0.000005 6.155917 -0.328274

H 0 0.000004 5.033907 1.880845

SCF Done: E(RB3LYP) = -2188.05063965

Sum of electronic and zero-point Energies= -2187.768205

Sum of electronic and thermal Energies= -2187.746045

Sum of electronic and thermal Enthalpies= -2187.745101

Sum of electronic and thermal Free Energies= -2187.821535

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full

scrf=(iefpcm,solvent=dichloromethane) geom=check

0 1

C 0	-5.367545	-2.260610	-0.368854
C 0	-4.523445	-3.242423	0.173698
C 0	-3.183061	-2.974306	0.415722
C 0	-2.667218	-1.704358	0.110205
C 0	-3.530551	-0.730080	-0.443639
C 0	-4.879092	-0.996022	-0.680723
C 0	-1.335638	-1.187500	0.301592
C 0	-1.192293	0.102688	-0.103063
S 0	-2.681584	0.773790	-0.781780
S 0	-0.000000	-2.139171	1.002997
C 0	1.335638	-1.187500	0.301592
C 0	1.192293	0.102688	-0.103063
N 0	0.000000	0.851682	-0.119668
C 0	2.667217	-1.704358	0.110206
C 0	3.530551	-0.730080	-0.443639
S 0	2.681584	0.773790	-0.781780
C 0	3.183061	-2.974307	0.415722
C 0	4.523445	-3.242423	0.173698
C 0	5.367545	-2.260610	-0.368854
C 0	4.879092	-0.996022	-0.680723
C 0	0.000000	2.152178	0.512335
C 0	-0.000000	2.264946	1.899842
C 0	-0.000000	3.521581	2.500492
C 0	0.000000	4.675869	1.716458
C 0	0.000000	4.577486	0.331084
C 0	0.000000	3.313280	-0.279989
C 0	0.000000	3.222886	-1.708061
N 0	0.000001	3.191162	-2.863359
H 0	-6.411319	-2.488405	-0.550608
H 0	-4.924017	-4.222126	0.406755
H 0	-2.537378	-3.737832	0.834518
H 0	-5.529949	-0.239737	-1.103110
H 0	2.537377	-3.737833	0.834518
H 0	4.924017	-4.222126	0.406755
H 0	6.411318	-2.488405	-0.550608
H 0	5.529949	-0.239737	-1.103110
H 0	-0.000000	1.365067	2.503156
H 0	-0.000000	3.599249	3.581146
H 0	0.000000	5.652539	2.184502
H 0	0.000001	5.466886	-0.285926

SCF Done: E(RB3LYP) = -2188.04981290

Sum of electronic and zero-point Energies= -2187.767427

Sum of electronic and thermal Energies= -2187.745305

Sum of electronic and thermal Enthalpies= -2187.744361

Sum of electronic and thermal Free Energies= -2187.821008

6.1.1.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	-5.321009	-2.231977	-0.540897
C 0	-4.486111	-3.239922	-0.043114
C 0	-3.155515	-2.986004	0.243719
C 0	-2.638810	-1.702366	0.025651
C 0	-3.493046	-0.701644	-0.482899
C 0	-4.831934	-0.952604	-0.764136
C 0	-1.320490	-1.196860	0.272633
C 0	-1.186588	0.114473	-0.058608
S 0	-2.653436	0.816144	-0.703921
S 0	-0.000000	-2.132693	0.993812
C 0	1.320490	-1.196860	0.272633
C 0	1.186588	0.114473	-0.058608
N 0	0.000000	0.840328	0.007812
C 0	2.638810	-1.702366	0.025651

C 0	3.493046	-0.701644	-0.482899
S 0	2.653436	0.816144	-0.703921
C 0	3.155515	-2.986004	0.243719
C 0	4.486111	-3.239922	-0.043114
C 0	5.321010	-2.231977	-0.540897
C 0	4.831934	-0.952604	-0.764136
C 0	0.000000	2.257528	-0.132201
C 0	-0.000000	2.846565	-1.389216
C 0	-0.000000	4.233376	-1.505718
C 0	-0.000000	5.032612	-0.368817
C 0	-0.000000	4.454762	0.893280
C 0	0.000000	3.064139	1.016264
C 0	0.000000	2.460504	2.309201
N 0	0.000000	1.993701	3.365089
H 0	-6.361232	-2.450531	-0.756926
H 0	-4.888738	-4.233663	0.122426
H 0	-2.513599	-3.770893	0.630980
H 0	-5.476443	-0.171218	-1.152180
H 0	2.513599	-3.770893	0.630980
H 0	4.888738	-4.233663	0.122426
H 0	6.361232	-2.450531	-0.756926
H 0	5.476443	-0.171218	-1.152180
H 0	0.000000	2.215886	-2.271564
H 0	-0.000000	4.687765	-2.490167
H 0	-0.000000	6.112632	-0.462576
H 0	-0.000000	5.070551	1.784935

SCF Done: E(RPBE1PBE) = -2186.43191596

Sum of electronic and zero-point Energies= -2186.146688

Sum of electronic and thermal Energies= -2186.124621

Sum of electronic and thermal Enthalpies= -2186.123677

Sum of electronic and thermal Free Energies= -2186.200450

6.1.1.4 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.5559 eV 485.09 nm f=0.0000

<TDDFT>HOMO -> LUMO 98.8%

<TDDFT> Excited State 2: Singlet-A 3.0788 eV 402.71 nm f=0.1146

<TDDFT>HOMO -> LUMO+1 84.2%

<TDDFT>HOMO -> LUMO+2 12.3%

<TDDFT> Excited State 3: Singlet-A 3.3421 eV 370.98 nm f=0.0143

<TDDFT>HOMO -> LUMO+1 13.2%

<TDDFT>HOMO -> LUMO+2 84.4%

<TDDFT> Excited State 4: Singlet-A 3.9209 eV 316.21 nm f=0.0181

<TDDFT>HOMO -> LUMO+5 74.3%

<TDDFT>HOMO -> LUMO+7 17.1%

<TDDFT>HOMO -> LUMO+10 2.5%

<TDDFT> Excited State 5: Singlet-A 3.9247 eV 315.91 nm f=0.0596

<TDDFT>HOMO-1 -> LUMO 34.3%

<TDDFT>HOMO -> LUMO+3 50.8%

<TDDFT>HOMO -> LUMO+4 3.8%

<TDDFT>HOMO -> LUMO+6 6.1%

<TDDFT> Excited State 6: Singlet-A 3.9459 eV 314.21 nm f=0.0417

<TDDFT>HOMO-1 -> LUMO 62.7%

<TDDFT>HOMO -> LUMO+3 34.4%

<TDDFT> Excited State 7: Singlet-A 3.9846 eV 311.16 nm f=0.0002

<TDDFT>HOMO -> LUMO+3 3.7%

<TDDFT>HOMO -> LUMO+4 91.3%

<TDDFT> Excited State 8: Singlet-A 4.0667 eV 304.88 nm f=0.0008

<TDDFT>HOMO-2 -> LUMO 96.6%

<TDDFT> Excited State 9: Singlet-A 4.1648 eV 297.69 nm f=0.0052

<TDDFT>HOMO -> LUMO+5 19.6%

<TDDFT>HOMO -> LUMO+7 69.9%

<TDDFT>HOMO -> LUMO+10 4.2%

<TDDFT> Excited State 10: Singlet-A 4.2166 eV 294.04 nm f=0.0320

<TDDFT>HOMO -> LUMO+3 6.3%

<TDDFT>HOMO -> LUMO+6 70.9%

<TDDFT>HOMO -> LUMO+8 14.0%

<TDDFT> Excited State 11: Singlet-A 4.4890 eV 276.20 nm f=0.0075

<TDDFT>HOMO -> LUMO+6 14.9%

<TDDFT>HOMO -> LUMO+8 63.8%

<TDDFT>HOMO -> LUMO+9 12.9%

<TDDFT>HOMO -> LUMO+13 4.0%

<TDDFT> Excited State 12: Singlet-A 4.5393 eV 273.13 nm f=0.0031

<TDDFT>HOMO-3 -> LUMO 98.3%

<TDDFT> Excited State 13: Singlet-A 4.5959 eV 269.77 nm f=0.0864

<TDDFT>HOMO-1 -> LUMO+1 88.9%

<TDDFT> Excited State 14: Singlet-A 4.6298 eV 267.80 nm f=0.1586

<TDDFT>HOMO-2 -> LUMO+1 73.0%

<TDDFT>HOMO-2 -> LUMO+2 8.1%

<TDDFT>HOMO-1 -> LUMO+4 2.2%

<TDDFT>HOMO -> LUMO+10 2.3%

<TDDFT>HOMO -> LUMO+14 5.4%

<TDDFT> Excited State 15: Singlet-A 4.7176 eV 262.81 nm f=0.0460

<TDDFT>HOMO-3 -> LUMO+1 2.5%

<TDDFT>HOMO-2 -> LUMO+3 2.3%

<TDDFT>HOMO-1 -> LUMO+1 3.4%

<TDDFT>HOMO-1 -> LUMO+2 85.0%

<TDDFT> Excited State 16: Singlet-A 4.8173 eV 257.37 nm f=0.0051

<TDDFT>HOMO -> LUMO+8 12.6%

<TDDFT>HOMO -> LUMO+9 77.3%

<TDDFT>HOMO -> LUMO+13 2.0%

<TDDFT>HOMO -> LUMO+15 2.4%

<TDDFT> Excited State 17: Singlet-A 4.8364 eV 256.36 nm f=0.0124

<TDDFT>HOMO-2 -> LUMO+1 16.2%

<TDDFT>HOMO-2 -> LUMO+2 75.7%

<TDDFT>HOMO -> LUMO+14 2.3%

<TDDFT> Excited State 18: Singlet-A 4.8897 eV 253.56 nm f=0.2854

<TDDFT>HOMO-2 -> LUMO+1 2.9%

<TDDFT>HOMO-2 -> LUMO+2 8.4%

<TDDFT>HOMO -> LUMO+7 2.9%

<TDDFT>HOMO -> LUMO+10 45.9%

<TDDFT>HOMO -> LUMO+14 27.0%

<TDDFT>HOMO -> LUMO+23 2.4%

<TDDFT> Excited State 19: Singlet-A 4.9813 eV 248.90 nm f=0.0078

<TDDFT>HOMO -> LUMO+11 74.5%

<TDDFT>HOMO -> LUMO+13 21.1%

<TDDFT> Excited State 20: Singlet-A 5.0271 eV 246.63 nm f=0.0084

<TDDFT>HOMO-4 -> LUMO 96.9%

<TDDFT> Excited State 21: Singlet-A 5.0679 eV 244.64 nm f=0.0362

<TDDFT>HOMO-6 -> LUMO 3.2%

<TDDFT>HOMO-4 -> LUMO+4 2.7%

<TDDFT>HOMO-3 -> LUMO+1 45.9%

<TDDFT>HOMO-3 -> LUMO+2 2.7%

<TDDFT>HOMO-2 -> LUMO+3 11.2%

<TDDFT>HOMO-2 -> LUMO+4 2.4%

<TDDFT>HOMO-1 -> LUMO+2 5.3%

<TDDFT>HOMO-1 -> LUMO+5 12.0%

<TDDFT>HOMO-1 -> LUMO+7 3.4%

<TDDFT> Excited State 22: Singlet-A 5.0917 eV 243.50 nm f=0.0474

<TDDFT>HOMO -> LUMO+7 4.6%

<TDDFT>HOMO -> LUMO+10 32.9%

<TDDFT>HOMO -> LUMO+14 44.0%

<TDDFT>HOMO -> LUMO+16 9.3%

<TDDFT> Excited State 23: Singlet-A 5.0960 eV 243.30 nm f=0.0435

<TDDFT>HOMO-6 -> LUMO 54.3%

<TDDFT>HOMO-5 -> LUMO 4.7%

<TDDFT>HOMO-5 -> LUMO+1 10.7%

<TDDFT>HOMO-5 -> LUMO+2 10.2%

<TDDFT>HOMO-3 -> LUMO+2 9.9%

<TDDFT>HOMO-2 -> LUMO+3 3.6%

<TDDFT> Excited State 24: Singlet-A 5.1183 eV 242.24 nm f=0.0609

<TDDFT>HOMO-4 -> LUMO 2.1%

<TDDFT>HOMO-2 -> LUMO+5 10.6%

<TDDFT>HOMO-2 -> LUMO+7 2.1%

<TDDFT>HOMO-1 -> LUMO+3 55.4%

<TDDFT>HOMO-1 -> LUMO+4 10.1%

<TDDFT>HOMO-1 -> LUMO+6 4.2%

6.1.1.5 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	-5.462636	-2.008844	-0.047534
C 0	-4.624264	-3.125421	0.063333
C 0	-3.249329	-2.982320	0.055018
C 0	-2.699461	-1.699541	-0.066704
C 0	-3.556455	-0.586375	-0.178305
C 0	-4.938997	-0.730340	-0.169664
C 0	-1.325081	-1.296834	-0.096574
C 0	-1.178152	0.072882	-0.227836
S 0	-2.682807	0.925131	-0.327422
S 0	0.000000	-2.402137	0.029936
C 0	1.325081	-1.296834	-0.096575
C 0	1.178152	0.072882	-0.227837
N 0	0.000000	0.756165	-0.288213
C 0	2.699461	-1.699541	-0.066705
C 0	3.556456	-0.586375	-0.178305
S 0	2.682807	0.925132	-0.327422
C 0	3.249330	-2.982320	0.055017
C 0	4.624265	-3.125420	0.063333
C 0	5.462636	-2.008843	-0.047533
C 0	4.938997	-0.730340	-0.169663
C 0	-0.000000	2.193549	-0.315732
C 0	-0.000000	2.859914	-1.530239

C 0 -0.000000 4.246760 -1.576775
C 0 -0.000000 4.967983 -0.345768
C 0 -0.000000 4.326216 0.861809
C 0 -0.000001 2.894548 0.951631
C 0 -0.000000 2.225240 2.165392
N 0 -0.000001 1.642295 3.186367
H 0 -6.538674 -2.143041 -0.037283
H 0 -5.059528 -4.113853 0.158360
H 0 -2.606299 -3.852037 0.143068
H 0 -5.590810 0.131816 -0.253706
H 0 2.606299 -3.852037 0.143067
H 0 5.059528 -4.113853 0.158360
H 0 6.538674 -2.143040 -0.037282
H 0 5.590811 0.131816 -0.253705
H 0 -0.000000 2.274636 -2.445519
H 0 -0.000000 4.765304 -2.526708
H 0 0.000000 6.053274 -0.363734
H 0 -0.000000 4.898039 1.783826

SCF Done: E(RPBE1PBE) = -2186.41903481

Sum of electronic and zero-point Energies= -2186.074867

Sum of electronic and thermal Energies= -2186.052686

Sum of electronic and thermal Enthalpies= -2186.051742

Sum of electronic and thermal Free Energies= -2186.127167

6.1.1.6 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 1.6688 eV 742.94 nm f=0.0000

<TDDFT>HOMO -> LUMO 99.4%

<TDDFT> Excited State 2: Singlet-A 2.5098 eV 494.00 nm f=0.1168

<TDDFT>HOMO -> LUMO+1 96.9%

<TDDFT> Excited State 3: Singlet-A 2.8924 eV 428.66 nm f=0.0046

<TDDFT>HOMO -> LUMO+2 97.8%

<TDDFT> Excited State 4: Singlet-A 3.5146 eV 352.77 nm f=0.0001

<TDDFT>HOMO-1 -> LUMO 83.4%

<TDDFT>HOMO -> LUMO+6 12.9%

6.1.1.7 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt=verytight Int=UltraFine freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check guess=read

0 1

C 0 -5.342755 -2.266404 -0.517250
C 0 -4.499810 -3.250807 0.021549
C 0 -3.166596 -2.976939 0.297482
C 0 -2.654063 -1.697244 0.026286
C 0 -3.517672 -0.721643 -0.525100
C 0 -4.858415 -0.990893 -0.793867
C 0 -1.334113 -1.171315 0.257053
C 0 -1.194422 0.127771 -0.124143
S 0 -2.677719 0.802899 -0.812905
S 0 0.000000 -2.087496 1.016912
C 0 1.334113 -1.171315 0.257053
C 0 1.194422 0.127771 -0.124143

N 0	-0.000000	0.856695	-0.091869
C 0	2.654063	-1.697244	0.026286
C 0	3.517672	-0.721643	-0.525100
S 0	2.677719	0.802899	-0.812905
C 0	3.166596	-2.976939	0.297482
C 0	4.499810	-3.250807	0.021549
C 0	5.342755	-2.266404	-0.517250
C 0	4.858415	-0.990893	-0.793867
C 0	-0.000000	2.291491	-0.133995
C 0	-0.000000	2.958903	-1.354833
C 0	-0.000000	4.354194	-1.390014
C 0	-0.000000	5.086470	-0.205455
C 0	-0.000000	4.432068	1.022444
C 0	-0.000000	3.031860	1.065829
C 0	-0.000000	2.364735	2.330225
N 0	-0.000000	1.853359	3.366145
H 0	-6.381300	-2.498915	-0.722999
H 0	-4.895959	-4.238620	0.228490
H 0	-2.524698	-3.743859	0.716437
H 0	-5.508687	-0.231258	-1.212462
H 0	2.524698	-3.743859	0.716437
H 0	4.895959	-4.238620	0.228490
H 0	6.381300	-2.498915	-0.722999
H 0	5.508687	-0.231258	-1.212462
H 0	-0.000000	2.385312	-2.273945
H 0	-0.000000	4.864400	-2.345976
H 0	-0.000000	6.169607	-0.233874
H 0	-0.000000	4.994151	1.947981

SCF Done: E(RB3LYP) = -2188.07391381

Sum of electronic and zero-point Energies= -2187.791589

Sum of electronic and thermal Energies= -2187.769433

Sum of electronic and thermal Enthalpies= -2187.768489

Sum of electronic and thermal Free Energies= -2187.844721

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0	-5.375026	-2.255084	-0.356883
C 0	-4.528140	-3.241161	0.173445
C 0	-3.185468	-2.976795	0.407396
C 0	-2.669915	-1.705618	0.105456
C 0	-3.536527	-0.727811	-0.436518
C 0	-4.887319	-0.989196	-0.665389
C 0	-1.336285	-1.190473	0.290640
C 0	-1.191738	0.101190	-0.108694
S 0	-2.686449	0.776781	-0.773831
S 0	-0.000000	-2.148438	0.983323
C 0	1.336285	-1.190473	0.290640
C 0	1.191738	0.101190	-0.108694
N 0	0.000000	0.850718	-0.129060
C 0	2.669915	-1.705619	0.105456
C 0	3.536526	-0.727812	-0.436518
S 0	2.686449	0.776781	-0.773831
C 0	3.185467	-2.976795	0.407397
C 0	4.528140	-3.241161	0.173445
C 0	5.375026	-2.255084	-0.356883
C 0	4.887319	-0.989197	-0.665389
C 0	0.000000	2.150739	0.507656
C 0	-0.000000	2.256196	1.895220
C 0	0.000000	3.510672	2.500873
C 0	0.000000	4.668706	1.722203
C 0	0.000000	4.577917	0.336265
C 0	0.000000	3.315844	-0.279935
C 0	0.000000	3.231547	-1.707737
N 0	0.000001	3.202796	-2.863064
H 0	-6.420691	-2.480652	-0.532330
H 0	-4.928194	-4.222016	0.404108
H 0	-2.539855	-3.745608	0.817159
H 0	-5.541230	-0.230048	-1.078941

H 0	2.539854	-3.745608	0.817160
H 0	4.928194	-4.222016	0.404108
H 0	6.420690	-2.480652	-0.532330
H 0	5.541230	-0.230048	-1.078941
H 0	-0.000000	1.352836	2.493845
H 0	-0.000000	3.583320	3.582271
H 0	0.000000	5.643555	2.194967
H 0	0.000000	5.470022	-0.277483

SCF Done: E(RB3LYP) = -2188.07265824

Sum of electronic and zero-point Energies= -2187.790377

Sum of electronic and thermal Energies= -2187.768266

Sum of electronic and thermal Enthalpies= -2187.767322

Sum of electronic and thermal Free Energies= -2187.843958

6.1.1.8 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000

0 1

C 0	5.478134	-2.051781	-0.049572
C 0	4.622860	-3.159633	0.055978
C 0	3.247462	-2.998047	0.046781
C 0	2.711250	-1.703789	-0.069560
C 0	3.589455	-0.602338	-0.174966
C 0	4.971134	-0.761556	-0.166942
C 0	1.337700	-1.283781	-0.097157
C 0	1.196746	0.090976	-0.219295
S 0	2.726226	0.932811	-0.311629
S 0	-0.000055	-2.395463	0.029973
C 0	-1.337779	-1.283745	-0.097189
C 0	-1.196788	0.091004	-0.219313
N 0	-0.000009	0.773028	-0.267109
C 0	-2.711345	-1.703712	-0.069526
C 0	-3.589519	-0.602230	-0.174850
S 0	-2.726248	0.932901	-0.311504
C 0	-3.247590	-2.997958	0.046771
C 0	-4.622993	-3.159505	0.056013
C 0	-5.478237	-2.051621	-0.049447
C 0	-4.971204	-0.761405	-0.166772
C 0	0.000008	2.223096	-0.305759
C 0	-0.000152	2.880070	-1.529187
C 0	-0.000129	4.274689	-1.554111
C 0	0.000062	4.997057	-0.362857
C 0	0.000221	4.338288	0.863401
C 0	0.000191	2.939137	0.905988
C 0	0.000319	2.238748	2.151998
N 0	0.000430	1.646690	3.143364
H 0	6.551008	-2.200733	-0.038992
H 0	5.045004	-4.152720	0.146996
H 0	2.596486	-3.860819	0.130181
H 0	5.636206	0.089473	-0.246771
H 0	-2.596636	-3.860752	0.130131
H 0	-5.045163	-4.152584	0.146984
H 0	-6.551115	-2.200542	-0.038831
H 0	-5.636252	0.089650	-0.246506
H 0	-0.000279	2.307698	-2.448979
H 0	-0.000262	4.792256	-2.505482
H 0	0.000086	6.079943	-0.386226
H 0	0.000368	4.895321	1.791708

SCF Done: E(UB3LYP) = -2187.81436354

Sum of electronic and zero-point Energies= -2187.531399

Sum of electronic and thermal Energies= -2187.509326

Sum of electronic and thermal Enthalpies= -2187.508381

Sum of electronic and thermal Free Energies= -2187.584556

6.1.1.9 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.477915	-2.059130	-0.050115
C 0	4.622635	-3.168325	0.044684
C 0	3.246404	-3.007051	0.039399
C 0	2.710180	-1.711753	-0.062554
C 0	3.587432	-0.608717	-0.157950
C 0	4.970007	-0.767838	-0.153043
C 0	1.335475	-1.293042	-0.084680
C 0	1.195667	0.082398	-0.193019
S 0	2.724070	0.926611	-0.280642
S 0	0.000001	-2.406667	0.024868
C 0	-1.335474	-1.293042	-0.084681
C 0	-1.195666	0.082397	-0.193020
N 0	0.000000	0.764907	-0.227748
C 0	-2.710178	-1.711754	-0.062555
C 0	-3.587431	-0.608719	-0.157952
S 0	-2.724069	0.926609	-0.280645
C 0	-3.246401	-3.007053	0.039397
C 0	-4.622633	-3.168327	0.044682
C 0	-5.477913	-2.059133	-0.050117
C 0	-4.970006	-0.767841	-0.153045
C 0	-0.000000	2.212535	-0.308344
C 0	0.000002	2.826447	-1.552996
C 0	0.000002	4.219426	-1.626775
C 0	-0.000000	4.984405	-0.463006
C 0	-0.000003	4.369792	0.785615
C 0	-0.000004	2.972757	0.876298
C 0	-0.000007	2.334816	2.155346
N 0	-0.000010	1.820541	3.189495
H 0	6.550918	-2.207340	-0.042999
H 0	5.044309	-4.162680	0.123918
H 0	2.595423	-3.870140	0.114279
H 0	5.633531	0.084746	-0.225305
H 0	-2.595420	-3.870141	0.114278
H 0	-5.044306	-4.162683	0.123917
H 0	-6.550916	-2.207343	-0.043001
H 0	-5.633530	0.084743	-0.225308
H 0	0.000004	2.221137	-2.450757
H 0	0.000004	4.701422	-2.596261
H 0	-0.000000	6.065434	-0.524125
H 0	-0.000005	4.960370	1.692417

SCF Done: E(UB3LYP) = -2187.87071371

Sum of electronic and zero-point Energies= -2187.587632

Sum of electronic and thermal Energies= -2187.565540

Sum of electronic and thermal Enthalpies= -2187.564596

Sum of electronic and thermal Free Energies= -2187.641331

6.1.1.10 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(SMD,solvent=dichloromethane)

0 1

C 0	5.475000	-2.072545	-0.054440
C 0	4.616788	-3.180782	0.024085
C 0	3.240914	-3.016241	0.023707
C 0	2.709332	-1.717316	-0.056426
C 0	3.589761	-0.615883	-0.138191
C 0	4.971713	-0.777600	-0.137575
C 0	1.336434	-1.294645	-0.071424
C 0	1.194718	0.081393	-0.162534
S 0	2.727363	0.923694	-0.240923
S 0	0.000237	-2.410753	0.019689
C 0	-1.336160	-1.294883	-0.071443
C 0	-1.194673	0.081190	-0.162477
N 0	-0.000045	0.764642	-0.190239
C 0	-2.708988	-1.717750	-0.056323

C 0	-3.589576	-0.616439	-0.138049
S 0	-2.727412	0.923251	-0.240900
C 0	-3.240398	-3.016745	0.023865
C 0	-4.616250	-3.181460	0.024366
C 0	-5.474618	-2.073345	-0.054175
C 0	-4.971505	-0.778337	-0.137409
C 0	-0.000239	2.210262	-0.310210
C 0	-0.000692	2.782489	-1.574918
C 0	-0.000984	4.172391	-1.692902
C 0	-0.000859	4.974430	-0.554251
C 0	-0.000435	4.401572	0.714158
C 0	-0.000137	3.007903	0.850079
C 0	0.000221	2.415561	2.150229
N 0	0.000416	1.943866	3.204321
H 0	6.547821	-2.224516	-0.050732
H 0	5.036068	-4.177690	0.086730
H 0	2.588323	-3.879889	0.084816
H 0	5.639574	0.073322	-0.197681
H 0	-2.587702	-3.880320	0.084897
H 0	-5.035389	-4.178419	0.087163
H 0	-6.547416	-2.225466	-0.050425
H 0	-5.639470	0.072491	-0.197653
H 0	-0.000833	2.146288	-2.452142
H 0	-0.001325	4.622804	-2.677906
H 0	-0.001084	6.053278	-0.650474
H 0	-0.000353	5.020169	1.602515

SCF Done: E(UB3LYP) = -2187.89747338

Sum of electronic and zero-point Energies= -2187.614475

Sum of electronic and thermal Energies= -2187.592539

Sum of electronic and thermal Enthalpies= -2187.591595

Sum of electronic and thermal Free Energies= -2187.666923

6.1.1.11 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc) freq=noraman B3LYP/6-311++g(d,p) pop=full scrf=(iefpcm,solvent=dichloromethane)

0 1

C 0	5.496972	-2.091051	-0.050899
C 0	4.630865	-3.194827	-0.060191
C 0	3.252725	-3.021924	-0.058038
C 0	2.719369	-1.721577	-0.045521
C 0	3.609563	-0.622984	-0.033623
C 0	4.992097	-0.793481	-0.038793
C 0	1.343258	-1.301165	-0.051265
C 0	1.198905	0.052326	-0.041334
S 0	2.741585	0.908847	-0.022135
S 0	0.000494	-2.480479	-0.053318
C 0	-1.342614	-1.301526	-0.051337
C 0	-1.198628	0.052022	-0.041167
N 0	-0.000116	0.778218	-0.000374
C 0	-2.718583	-1.722369	-0.045735
C 0	-3.609137	-0.624066	-0.033774
S 0	-2.741642	0.908033	-0.021978
C 0	-3.251527	-3.022884	-0.058496
C 0	-4.629615	-3.196230	-0.060799
C 0	-5.496077	-2.092738	-0.051549
C 0	-4.991614	-0.795006	-0.039154
C 0	-0.000351	2.176883	-0.329186
C 0	-0.001127	3.132567	0.704227
C 0	-0.001423	4.499499	0.390001
C 0	-0.000896	4.902376	-0.940218
C 0	-0.000073	3.953405	-1.962087
C 0	0.000190	2.593909	-1.657186
C 0	-0.001531	2.719139	2.074044
N 0	-0.001835	2.416959	3.189247
H 0	6.569379	-2.246290	-0.052050
H 0	5.043128	-4.197173	-0.069018
H 0	2.594426	-3.883354	-0.065576

H 0	5.659592	0.060050	-0.031283
H 0	-2.592955	-3.884104	-0.066119
H 0	-5.041553	-4.198709	-0.069698
H 0	-6.568435	-2.248317	-0.052976
H 0	-5.659384	0.058309	-0.031590
H 0	-0.002023	5.230056	1.188587
H 0	-0.001111	5.958814	-1.178817
H 0	0.000337	4.270518	-2.997883
H 0	0.000780	1.849750	-2.444305

SCF Done: E(RB3LYP) = -2188.04905185

Sum of electronic and zero-point Energies= -2187.766897

Sum of electronic and thermal Energies= -2187.745520

Sum of electronic and thermal Enthalpies= -2187.744576

Sum of electronic and thermal Free Energies= -2187.818411

6.1.2 *anti-anti-N-ortho*-chlorophenyl-BBTT 3b

6.1.2.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.360293	-2.298046	-0.463189
C 0	4.514236	-3.271340	0.088302
C 0	3.176251	-2.996667	0.334706
C 0	2.661589	-1.728497	0.021703
C 0	3.527877	-0.763292	-0.542653
C 0	4.873181	-1.034306	-0.781577
C 0	1.334463	-1.207588	0.215324
C 0	1.195233	0.078645	-0.205076
S 0	2.685634	0.746187	-0.883369
S 0	0.000379	-2.120580	0.975352
C 0	-1.333720	-1.208276	0.214485
C 0	-1.194932	0.078120	-0.205547
N 0	-0.000008	0.803888	-0.237016
C 0	-2.660711	-1.729478	0.021166
C 0	-3.527402	-0.764374	-0.542820
S 0	-2.685664	0.745403	-0.883510
C 0	-3.174959	-2.997774	0.334062
C 0	-4.512969	-3.272756	0.088014
C 0	-5.359435	-2.299627	-0.463172
C 0	-4.872646	-1.035785	-0.781703
C 0	-0.000352	2.234913	-0.218054
C 0	-0.000899	2.947553	0.989670
C 0	-0.001247	4.339354	0.989812
C 0	-0.001023	5.029437	-0.219834
C 0	-0.000467	4.335335	-1.427269
C 0	-0.000149	2.943451	-1.421716
Cl 0	-0.001189	2.091930	2.512775
H 0	6.402816	-2.530456	-0.646521
H 0	4.911774	-4.251175	0.326733
H 0	2.527248	-3.753814	0.759769
H 0	5.524989	-0.282145	-1.210731
H 0	-2.525704	-3.754836	0.758851
H 0	-4.910213	-4.252701	0.326495
H 0	-6.401867	-2.532369	-0.646469
H 0	-5.524624	-0.283690	-1.210757
H 0	-0.001686	4.871248	1.932566
H 0	-0.001286	6.113257	-0.213177
H 0	-0.000298	4.872113	-2.368194
H 0	0.000253	2.384368	-2.350013

SCF Done: E(RB3LYP) = -2555.39654430

Sum of electronic and zero-point Energies= -2555.122249

Sum of electronic and thermal Energies= -2555.100673

Sum of electronic and thermal Enthalpies= -2555.099729

Sum of electronic and thermal Free Energies= -2555.175399

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.342272	-2.340780	-0.417539
C 0	-4.502666	-3.319696	0.135266
C 0	-3.169743	-3.044042	0.404335
C 0	-2.655909	-1.769809	0.116653
C 0	-3.513818	-0.797789	-0.449503
C 0	-4.855186	-1.072552	-0.713138
C 0	-1.334352	-1.244028	0.340078
C 0	-1.190792	0.049320	-0.056189
S 0	-2.668338	0.711036	-0.769818
S 0	0.000380	-2.171826	1.075964
C 0	1.334969	-1.243509	0.340417
C 0	1.191040	0.049775	-0.055932
N 0	-0.000026	0.793636	-0.039306
C 0	2.656658	-1.768951	0.116847
C 0	3.514163	-0.796707	-0.449559
S 0	2.668260	0.711770	-0.769680
C 0	3.170934	-3.042984	0.404593
C 0	4.503889	-3.318219	0.135457
C 0	5.343130	-2.339079	-0.417547
C 0	4.855611	-1.071043	-0.713233
C 0	-0.000393	2.103362	0.561090
C 0	-0.000748	3.262408	-0.221896
C 0	-0.001229	4.522578	0.373662
C 0	-0.001325	4.629018	1.760555
C 0	-0.000925	3.482396	2.554094
C 0	-0.000474	2.229348	1.952692
Cl 0	-0.000462	3.150769	-1.970869
H 0	-6.380971	-2.574192	-0.620506
H 0	-4.901019	-4.303650	0.354292
H 0	-2.524496	-3.805091	0.828380
H 0	-5.502572	-0.317869	-1.144351
H 0	2.525988	-3.804200	0.828787
H 0	4.902670	-4.301986	0.354546
H 0	6.381916	-2.572181	-0.620565
H 0	5.502708	-0.316219	-1.144686
H 0	-0.001507	5.406073	-0.251658
H 0	-0.001704	5.611071	2.219055
H 0	-0.000976	3.564204	3.634480
H 0	-0.000192	1.325751	2.551445

SCF Done: E(RB3LYP) = -2555.39565431

Sum of electronic and zero-point Energies= -2555.121374

Sum of electronic and thermal Energies= -2555.099857

Sum of electronic and thermal Enthalpies= -2555.098913

Sum of electronic and thermal Free Energies= -2555.174121

6.1.2.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full

0 1

C 0	5.368391	-2.291041	-0.467288
C 0	4.522607	-3.279522	0.059079
C 0	3.181857	-3.014523	0.306162
C 0	2.664697	-1.740370	0.018613
C 0	3.531533	-0.759425	-0.518775
C 0	4.879135	-1.020687	-0.758978
C 0	1.335159	-1.227005	0.216055
C 0	1.194172	0.069297	-0.175273
S 0	2.686448	0.756701	-0.827380
S 0	-0.000016	-2.159532	0.954403
C 0	-1.335191	-1.226978	0.216086
C 0	-1.194187	0.069323	-0.175240
N 0	-0.000000	0.794289	-0.186506
C 0	-2.664731	-1.740331	0.018637

C 0	-3.531558	-0.759375	-0.518747
S 0	-2.686475	0.756767	-0.827278
C 0	-3.181896	-3.014490	0.306149
C 0	-4.522643	-3.279484	0.059038
C 0	-5.368418	-2.290992	-0.467326
C 0	-4.879155	-1.020632	-0.758980
C 0	0.000016	2.226264	-0.219666
C 0	0.000038	2.977310	0.964074
C 0	0.000056	4.367700	0.923555
C 0	0.000050	5.018514	-0.308707
C 0	0.000026	4.286314	-1.493842
C 0	0.000010	2.894774	-1.446160
Cl 0	0.000050	2.165457	2.517102
H 0	6.412359	-2.515975	-0.651308
H 0	4.922126	-4.263122	0.277755
H 0	2.535724	-3.783511	0.714182
H 0	5.530606	-0.257231	-1.167689
H 0	-2.535771	-3.783489	0.714159
H 0	-4.922165	-4.263088	0.277686
H 0	-6.412383	-2.515920	-0.651362
H 0	-5.530622	-0.257165	-1.167676
H 0	0.000075	4.931615	1.847339
H 0	0.000064	6.101688	-0.336132
H 0	0.000022	4.793178	-2.450906
H 0	-0.000007	2.309413	-2.357932

SCF Done: E(RB3LYP) = -2555.40457940

Sum of electronic and zero-point Energies= -2555.130308

Sum of electronic and thermal Energies= -2555.108750

Sum of electronic and thermal Enthalpies= -2555.107806

Sum of electronic and thermal Free Energies= -2555.183080

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0	5.466905	-2.128136	0.231661
C 0	4.605675	-3.232467	0.144104
C 0	3.236176	-3.060750	-0.012358
C 0	2.705378	-1.760866	-0.079466
C 0	3.590742	-0.661230	0.012671
C 0	4.964723	-0.830907	0.165597
C 0	1.341202	-1.339503	-0.249609
C 0	1.197459	0.015093	-0.268224
S 0	2.728894	0.871538	-0.085380
S 0	-0.000011	-2.499037	-0.487577
C 0	-1.341216	-1.339494	-0.249603
C 0	-1.197465	0.015101	-0.268220
N 0	-0.000000	0.727071	-0.380048
C 0	-2.705396	-1.760848	-0.079460
C 0	-3.590752	-0.661207	0.012675
S 0	-2.728895	0.871556	-0.085376
C 0	-3.236201	-3.060729	-0.012350
C 0	-4.605701	-3.232437	0.144114
C 0	-5.466925	-2.128100	0.231669
C 0	-4.964735	-0.830875	0.165602
C 0	0.000005	2.156357	-0.475065
C 0	0.000020	2.967508	0.669418
C 0	0.000027	4.354802	0.555084
C 0	0.000019	4.939915	-0.708614
C 0	0.000005	4.146576	-1.854960
C 0	-0.000001	2.760946	-1.734579
Cl 0	0.000033	2.244036	2.266383
H 0	6.532592	-2.282639	0.352721
H 0	5.015205	-4.234572	0.198906
H 0	2.580377	-3.921655	-0.077350
H 0	5.627493	0.023676	0.234584
H 0	-2.580408	-3.921638	-0.077340
H 0	-5.015237	-4.234540	0.198918
H 0	-6.532612	-2.282597	0.352730
H 0	-5.627499	0.023712	0.234589
H 0	0.000038	4.965872	1.448288

H 0 0.000024 6.020200 -0.792432

H 0 -0.000001 4.603244 -2.836985

H 0 -0.000012 2.125418 -2.611988

SCF Done: E(RB3LYP) = -2555.40320953

Sum of electronic and zero-point Energies= -2555.129126

Sum of electronic and thermal Energies= -2555.107500

Sum of electronic and thermal Enthalpies= -2555.106556

Sum of electronic and thermal Free Energies= -2555.182194

6.1.2.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0 5.353634 -2.258796 -0.466422

C 0 4.512997 -3.265064 0.024619

C 0 3.172437 -3.017641 0.268645

C 0 2.651502 -1.742455 0.013259

C 0 3.512245 -0.742830 -0.487230

C 0 4.860418 -0.987473 -0.725458

C 0 1.322548 -1.245062 0.213229

C 0 1.186294 0.059442 -0.145008

S 0 2.666813 0.763661 -0.756065

S 0 -0.000792 -2.190117 0.919249

C 0 -1.323465 -1.244368 0.213001

C 0 -1.186644 0.060059 -0.145128

N 0 0.000002 0.780927 -0.142332

C 0 -2.652634 -1.741216 0.013022

C 0 -3.512987 -0.741275 -0.487526

S 0 -2.666861 0.764918 -0.756340

C 0 -3.174111 -3.016047 0.268989

C 0 -4.514963 -3.262766 0.025811

C 0 -5.355286 -2.256095 -0.464872

C 0 -4.861504 -0.985111 -0.724598

C 0 0.000466 2.200951 -0.221656

C 0 0.001619 2.978862 0.940281

C 0 0.002106 4.364507 0.861251

C 0 0.001404 4.978612 -0.385676

C 0 0.000263 4.217359 -1.548531

C 0 -0.000172 2.831152 -1.463871

Cl 0 0.002358 2.207909 2.491298

H 0 6.401332 -2.472033 -0.649119

H 0 4.918544 -4.252499 0.218571

H 0 2.526334 -3.801898 0.650352

H 0 5.509576 -0.207303 -1.108237

H 0 -2.528262 -3.800536 0.650649

H 0 -4.920987 -4.249902 0.220284

H 0 -6.403262 -2.468682 -0.646746

H 0 -5.510529 -0.204741 -1.107188

H 0 0.002993 4.953414 1.770820

H 0 0.001771 6.061736 -0.442827

H 0 -0.000246 4.699404 -2.519470

H 0 -0.000942 2.218223 -2.359120

SCF Done: E(RPBE1PBE) = -2553.73298211

Sum of electronic and zero-point Energies= -2553.455862

Sum of electronic and thermal Energies= -2553.434434

Sum of electronic and thermal Enthalpies= -2553.433490

Sum of electronic and thermal Free Energies= -2553.508870

6.1.2.4 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.9958 eV 413.87 nm f=0.1274

<TDDFT>HOMO -> LUMO 94.9%

<TDDFT> Excited State 2: Singlet-A 3.3302 eV 372.31 nm f=0.0111

<TDDFT>HOMO -> LUMO+1 96.6%

<TDDFT> Excited State 3: Singlet-A 3.4939 eV 354.86 nm f=0.0009

<TDDFT>HOMO -> LUMO+2 93.2%

<TDDFT> Excited State 4: Singlet-A 3.8802 eV 319.53 nm f=0.0914

<TDDFT>HOMO -> LUMO+3 73.4%

<TDDFT>HOMO -> LUMO+4 12.0%

<TDDFT>HOMO -> LUMO+6 9.0%

<TDDFT> Excited State 5: Singlet-A 3.8941 eV 318.39 nm f=0.0203

<TDDFT>HOMO -> LUMO+2 2.9%

<TDDFT>HOMO -> LUMO+5 77.6%

<TDDFT>HOMO -> LUMO+7 13.1%

<TDDFT>HOMO -> LUMO+10 2.3%

<TDDFT> Excited State 6: Singlet-A 3.9120 eV 316.93 nm f=0.0043

<TDDFT>HOMO -> LUMO+3 13.8%

<TDDFT>HOMO -> LUMO+4 83.0%

<TDDFT> Excited State 7: Singlet-A 4.1032 eV 302.17 nm f=0.0058

<TDDFT>HOMO -> LUMO+5 17.1%

<TDDFT>HOMO -> LUMO+7 71.7%

<TDDFT>HOMO -> LUMO+10 5.9%

<TDDFT> Excited State 8: Singlet-A 4.1445 eV 299.15 nm f=0.0360

<TDDFT>HOMO -> LUMO+3 8.3%

<TDDFT>HOMO -> LUMO+4 2.1%

<TDDFT>HOMO -> LUMO+6 73.3%

<TDDFT>HOMO -> LUMO+8 11.6%

<TDDFT> Excited State 9: Singlet-A 4.4279 eV 280.01 nm f=0.0093

<TDDFT>HOMO -> LUMO+6 9.6%

<TDDFT>HOMO -> LUMO+8 73.1%

<TDDFT>HOMO -> LUMO+9 8.8%

<TDDFT>HOMO -> LUMO+14 2.5%

<TDDFT> Excited State 10: Singlet-A 4.5945 eV 269.85 nm f=0.1086

<TDDFT>HOMO-1 -> LUMO 87.2%

<TDDFT> Excited State 11: Singlet-A 4.6016 eV 269.44 nm f=0.1522

<TDDFT>HOMO-2 -> LUMO 79.7%

<TDDFT>HOMO-1 -> LUMO+4 2.1%

<TDDFT>HOMO -> LUMO+10 2.5%

<TDDFT>HOMO -> LUMO+13 5.4%

<TDDFT> Excited State 12: Singlet-A 4.6975 eV 263.94 nm f=0.0007

<TDDFT>HOMO-1 -> LUMO+1 2.7%

<TDDFT>HOMO -> LUMO+6 2.1%

<TDDFT>HOMO -> LUMO+8 6.6%

<TDDFT>HOMO -> LUMO+9 79.0%

<TDDFT>HOMO -> LUMO+12 2.7%

<TDDFT>HOMO -> LUMO+16 2.9%

<TDDFT> Excited State 13: Singlet-A 4.7900 eV 258.84 nm f=0.0148

<TDDFT>HOMO-2 -> LUMO+3 2.4%

<TDDFT>HOMO-1 -> LUMO+1 87.2%

<TDDFT>HOMO -> LUMO+9 2.9%

<TDDFT> Excited State 14: Singlet-A 4.8362 eV 256.37 nm f=0.2281

<TDDFT>HOMO-2 -> LUMO 8.7%

<TDDFT>HOMO-2 -> LUMO+1 8.1%

<TDDFT>HOMO -> LUMO+7 5.4%

<TDDFT>HOMO -> LUMO+10 49.3%

<TDDFT>HOMO -> LUMO+13 18.9%

<TDDFT> Excited State 15: Singlet-A 4.8767 eV 254.24 nm f=0.0403

<TDDFT>HOMO-2 -> LUMO+1 80.0%

<TDDFT>HOMO-1 -> LUMO+4 2.6%

<TDDFT>HOMO -> LUMO+10 7.3%

<TDDFT> Excited State 16: Singlet-A 4.8992 eV 253.07 nm f=0.0010

<TDDFT>HOMO-3 -> LUMO 6.5%

<TDDFT>HOMO-1 -> LUMO 2.1%

<TDDFT>HOMO-1 -> LUMO+1 2.1%

<TDDFT>HOMO-1 -> LUMO+2 76.4%

<TDDFT>HOMO-1 -> LUMO+5 2.0%

<TDDFT>HOMO -> LUMO+11 3.7%

<TDDFT> Excited State 17: Singlet-A 4.9168 eV 252.17 nm f=0.0060

<TDDFT>HOMO-1 -> LUMO+2 3.9%

<TDDFT>HOMO -> LUMO+11 88.7%

<TDDFT>HOMO -> LUMO+18 2.1%

<TDDFT> Excited State 18: Singlet-A 5.0061 eV 247.67 nm f=0.0284

<TDDFT>HOMO-2 -> LUMO+2 70.1%

<TDDFT>HOMO-1 -> LUMO+3 2.3%

<TDDFT>HOMO-1 -> LUMO+6 2.3%

<TDDFT>HOMO -> LUMO+10 3.0%

<TDDFT>HOMO -> LUMO+13 9.2%

<TDDFT>HOMO -> LUMO+15 2.7%

<TDDFT> Excited State 19: Singlet-A 5.0231 eV 246.83 nm f=0.0679

<TDDFT>HOMO-2 -> LUMO+2 15.4%

<TDDFT>HOMO-1 -> LUMO+3 2.9%

<TDDFT>HOMO -> LUMO+7 3.3%

<TDDFT>HOMO -> LUMO+10 19.8%

<TDDFT>HOMO -> LUMO+13 39.0%

<TDDFT>HOMO -> LUMO+15 12.1%

<TDDFT> Excited State 20: Singlet-A 5.0709 eV 244.50 nm f=0.0708

<TDDFT>HOMO-5 -> LUMO+4 2.1%

<TDDFT>HOMO-3 -> LUMO 45.2%

<TDDFT>HOMO-2 -> LUMO+3 10.2%

<TDDFT>HOMO-2 -> LUMO+4 3.2%

<TDDFT>HOMO-1 -> LUMO+1 2.9%

<TDDFT>HOMO-1 -> LUMO+2 11.4%

<TDDFT>HOMO-1 -> LUMO+5 8.8%

<TDDFT>HOMO-1 -> LUMO+7 4.0%

<TDDFT> Excited State 21: Singlet-A 5.1602 eV 240.27 nm f=0.0060

<TDDFT>HOMO -> LUMO+8 4.9%

<TDDFT>HOMO -> LUMO+12 69.1%

<TDDFT>HOMO -> LUMO+14 9.9%

<TDDFT>HOMO -> LUMO+16 5.8%

<TDDFT> Excited State 22: Singlet-A 5.1621 eV 240.18 nm f=0.1090

<TDDFT>HOMO-5 -> LUMO 2.2%

<TDDFT>HOMO-2 -> LUMO+1 3.9%

<TDDFT>HOMO-2 -> LUMO+2 7.1%

<TDDFT>HOMO-2 -> LUMO+5 9.0%

<TDDFT>HOMO-1 -> LUMO+3 51.1%

<TDDFT>HOMO-1 -> LUMO+4 10.8%

<TDDFT> Excited State 23: Singlet-A 5.2071 eV 238.10 nm f=0.0182

<TDDFT>HOMO-6 -> LUMO+1 6.0%

<TDDFT>HOMO-6 -> LUMO+2 7.4%

<TDDFT>HOMO-4 -> LUMO 14.2%

<TDDFT>HOMO-4 -> LUMO+1 9.8%

<TDDFT>HOMO-4 -> LUMO+2 6.6%

<TDDFT>HOMO-3 -> LUMO 5.7%

<TDDFT>HOMO-3 -> LUMO+1 13.6%

<TDDFT>HOMO-2 -> LUMO+3 14.5%

<TDDFT>HOMO-2 -> LUMO+4 2.5%

<TDDFT>HOMO-2 -> LUMO+6 4.6%

<TDDFT>HOMO-1 -> LUMO+7 3.7%

<TDDFT> Excited State 24: Singlet-A 5.2199 eV 237.52 nm f=0.0056

<TDDFT>HOMO -> LUMO+9 3.4%

<TDDFT>HOMO -> LUMO+12 9.2%

<TDDFT>HOMO -> LUMO+14 76.4%

6.1.2.5 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.474274	-2.111597	-0.060844
C 0	4.616530	-3.207427	0.063045
C 0	3.239803	-3.046797	0.061241
C 0	2.689026	-1.757454	-0.066771
C 0	3.577722	-0.660631	-0.192681
C 0	4.951873	-0.822876	-0.191633
C 0	1.329536	-1.342035	-0.097657
C 0	1.188155	0.057319	-0.257688
S 0	2.731693	0.881737	-0.342747
S 0	0.000624	-2.406177	0.130696
C 0	-1.328590	-1.342729	-0.099224
C 0	-1.187742	0.056528	-0.260700
N 0	0.000076	0.718591	-0.311930
C 0	-2.687927	-1.758618	-0.067544
C 0	-3.577041	-0.662281	-0.194525
S 0	-2.731607	0.880246	-0.346379
C 0	-3.238289	-3.047955	0.062402
C 0	-4.614977	-3.208922	0.065381
C 0	-5.473126	-2.113475	-0.059170
C 0	-4.951155	-0.824796	-0.192054
C 0	-0.000354	2.148359	-0.370332
C 0	-0.001244	2.901015	0.804871
C 0	-0.001725	4.287550	0.737736
C 0	-0.001383	4.913739	-0.503481
C 0	-0.000568	4.166110	-1.675513
C 0	-0.000039	2.779366	-1.609282
Cl 0	-0.001766	2.108986	2.342962
H 0	6.548859	-2.256801	-0.055866
H 0	5.033802	-4.204353	0.162396
H 0	2.589769	-3.910955	0.156922
H 0	5.611869	0.032748	-0.288147
H 0	-2.587988	-3.911813	0.158981
H 0	-5.031924	-4.205821	0.166359
H 0	-6.547663	-2.258990	-0.053128
H 0	-5.611351	0.030589	-0.289283
H 0	-0.002384	4.866599	1.653482
H 0	-0.001782	5.997280	-0.549087
H 0	-0.000297	4.659495	-2.640571
H 0	0.000654	2.171865	-2.507471

SCF Done: E(RPBE1PBE) = -2553.72087118

Sum of electronic and zero-point Energies= -2553.366158

Sum of electronic and thermal Energies= -2553.343808

Sum of electronic and thermal Enthalpies= -2553.342864

Sum of electronic and thermal Free Energies= -2553.420243

6.1.2.6 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.2222 eV 557.93 nm f=0.1140

<TDDFT>HOMO -> LUMO 98.2%

<TDDFT> Excited State 2: Singlet-A 2.7469 eV 451.36 nm f=0.0017

<TDDFT>HOMO -> LUMO+1 99.1%

<TDDFT> Excited State 3: Singlet-A 3.0225 eV 410.21 nm f=0.0022

<TDDFT>HOMO -> LUMO+2 99.2%

<TDDFT> Excited State 4: Singlet-A 3.3964 eV 365.05 nm f=0.0002

<TDDFT>HOMO -> LUMO+3 4.6%

<TDDFT>HOMO -> LUMO+5 38.2%

<TDDFT>HOMO -> LUMO+6 52.8%

<TDDFT>HOMO -> LUMO+8 2.2%

6.1.2.7 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0	5.374878	-2.285176	-0.451029
C 0	4.527187	-3.270955	0.077475
C 0	3.184391	-3.006615	0.314184
C 0	2.667042	-1.735331	0.013573
C 0	3.536131	-0.757841	-0.526324
C 0	4.885831	-1.017806	-0.756188
C 0	1.336116	-1.220536	0.201375
C 0	1.193865	0.072196	-0.200693
S 0	2.689627	0.754714	-0.853555
S 0	-0.000005	-2.147773	0.945807
C 0	-1.336129	-1.220525	0.201393
C 0	-1.193873	0.072207	-0.200675
N 0	-0.000001	0.797261	-0.219510
C 0	-2.667056	-1.735316	0.013587
C 0	-3.536141	-0.757823	-0.526311
S 0	-2.689640	0.754741	-0.853506
C 0	-3.184406	-3.006603	0.314184
C 0	-4.527199	-3.270943	0.077463
C 0	-5.374887	-2.285161	-0.451043
C 0	-4.885838	-1.017789	-0.756190
C 0	0.000005	2.231096	-0.222284
C 0	0.000019	2.956994	0.977332
C 0	0.000024	4.347433	0.968860
C 0	0.000015	5.024438	-0.249623
C 0	-0.000001	4.318296	-1.450425
C 0	-0.000006	2.925743	-1.434238
Cl 0	0.000030	2.108998	2.513986
H 0	6.420666	-2.510068	-0.626436
H 0	4.926775	-4.252377	0.307129
H 0	2.538968	-3.775104	0.724821
H 0	5.539906	-0.256989	-1.166739
H 0	-2.538984	-3.775095	0.724818
H 0	-4.926788	-4.252367	0.307106
H 0	-6.420674	-2.510052	-0.626456
H 0	-5.539911	-0.256968	-1.166736

H 0 0.000035 4.892827 1.904223

H 0 0.000019 6.108420 -0.253168

H 0 -0.000009 4.846039 -2.396601

H 0 -0.000019 2.361141 -2.359494

SCF Done: E(RB3LYP) = -2555.42875264

Sum of electronic and zero-point Energies= -2555.154571

Sum of electronic and thermal Energies= -2555.132997

Sum of electronic and thermal Enthalpies= -2555.132052

Sum of electronic and thermal Free Energies= -2555.207555

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0 5.460302 -2.165683 0.244814

C 0 4.598641 -3.261736 0.085809

C 0 3.231064 -3.079459 -0.075947

C 0 2.702380 -1.776785 -0.073938

C 0 3.588259 -0.686109 0.090817

C 0 4.960837 -0.865725 0.246999

C 0 1.341460 -1.342401 -0.242137

C 0 1.196989 0.011067 -0.187186

S 0 2.728273 0.851861 0.073235

S 0 -0.000003 -2.481904 -0.562385

C 0 -1.341464 -1.342399 -0.242132

C 0 -1.196990 0.011069 -0.187180

N 0 -0.000000 0.728034 -0.254509

C 0 -2.702384 -1.776781 -0.073933

C 0 -3.588262 -0.686103 0.090821

S 0 -2.728272 0.851864 0.073247

C 0 -3.231071 -3.079453 -0.075946

C 0 -4.598649 -3.261729 0.085807

C 0 -5.460307 -2.165674 0.244812

C 0 -4.960840 -0.865717 0.247000

C 0 0.000000 2.143467 -0.485765

C 0 0.000006 3.056297 0.578520

C 0 0.000006 4.427755 0.338226

C 0 0.000001 4.893151 -0.974083

C 0 -0.000004 3.997446 -2.042860

C 0 -0.000004 2.628916 -1.796123

Cl 0 0.000014 2.483146 2.238906

H 0 6.524710 -2.328814 0.368438

H 0 5.006444 -4.266299 0.087833

H 0 2.577459 -3.936179 -0.198178

H 0 5.624893 -0.017917 0.370967

H 0 -2.577467 -3.936175 -0.198177

H 0 -5.006454 -4.266291 0.087830

H 0 -6.524716 -2.328803 0.368435

H 0 -5.624895 -0.017907 0.370969

H 0 0.000011 5.120025 1.170848

H 0 0.000002 5.961449 -1.157326

H 0 -0.000008 4.361993 -3.063117

H 0 -0.000009 1.915578 -2.612270

SCF Done: E(RB3LYP) = -2555.42722522

Sum of electronic and zero-point Energies= -2555.153119

Sum of electronic and thermal Energies= -2555.131544

Sum of electronic and thermal Enthalpies= -2555.130600

Sum of electronic and thermal Free Energies= -2555.205987

6.1.2.8 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000

0 1

C 0 5.479722 -2.105191 -0.040648

C 0 4.626378 -3.213435 0.076765

C 0 3.250697 -3.053916 0.069085

C 0 2.712099 -1.761530 -0.057495

C 0 3.588153 -0.659118 -0.174534

C 0	4.970225	-0.817028	-0.168487
C 0	1.338127	-1.343630	-0.088594
C 0	1.195243	0.030005	-0.224928
S 0	2.722934	0.873426	-0.325489
S 0	0.000362	-2.455598	0.044800
C 0	-1.337607	-1.343885	-0.088396
C 0	-1.195016	0.029869	-0.224595
N 0	0.000026	0.710598	-0.281614
C 0	-2.711452	-1.762077	-0.057690
C 0	-3.587721	-0.659818	-0.174796
S 0	-2.722796	0.872832	-0.325405
C 0	-3.249842	-3.054602	0.068430
C 0	-4.625492	-3.214414	0.075554
C 0	-5.479031	-2.106316	-0.041775
C 0	-4.969758	-0.818004	-0.169067
C 0	-0.000041	2.156074	-0.373402
C 0	-0.001118	2.935099	0.790383
C 0	-0.001251	4.323050	0.686738
C 0	-0.000295	4.921292	-0.570771
C 0	0.000829	4.145829	-1.729380
C 0	0.000947	2.758840	-1.631419
Cl 0	-0.002058	2.179891	2.362136
H 0	6.552857	-2.252487	-0.032125
H 0	5.050242	-4.205141	0.174870
H 0	2.601126	-3.917010	0.160237
H 0	5.633720	0.034233	-0.258819
H 0	-2.600130	-3.917573	0.159734
H 0	-5.049174	-4.206251	0.173119
H 0	-6.552140	-2.253822	-0.033582
H 0	-5.633414	0.033163	-0.259112
H 0	-0.002069	4.922938	1.587605
H 0	-0.000426	6.002368	-0.641920
H 0	0.001639	4.616828	-2.704249
H 0	0.001800	2.137305	-2.519125

SCF Done: E(UB3LYP) = -2555.17610176

Sum of electronic and zero-point Energies= -2554.901124

Sum of electronic and thermal Energies= -2554.879707

Sum of electronic and thermal Enthalpies= -2554.878763

Sum of electronic and thermal Free Energies= -2554.953507

6.1.2.9 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.479089	-2.104741	-0.035606
C 0	4.625330	-3.213516	0.076884
C 0	3.248773	-3.054396	0.066480
C 0	2.710624	-1.761884	-0.058552
C 0	3.586183	-0.658884	-0.171539
C 0	4.969077	-0.816334	-0.161825
C 0	1.335419	-1.345436	-0.090425
C 0	1.193837	0.027793	-0.223657
S 0	2.720925	0.872801	-0.322436
S 0	0.000007	-2.457628	0.038293
C 0	-1.335407	-1.345441	-0.090420
C 0	-1.193829	0.027787	-0.223678
N 0	0.000003	0.708685	-0.274655
C 0	-2.710612	-1.761892	-0.058553
C 0	-3.586175	-0.658899	-0.171579
S 0	-2.720921	0.872789	-0.322507
C 0	-3.248756	-3.054401	0.066525
C 0	-4.625312	-3.213529	0.076929
C 0	-5.479075	-2.104762	-0.035609
C 0	-4.969068	-0.816357	-0.161872
C 0	-0.000001	2.153171	-0.372797
C 0	-0.000028	2.939512	0.785526

C 0	-0.000028	4.326168	0.677246
C 0	0.000003	4.917936	-0.583791
C 0	0.000031	4.136102	-1.737754
C 0	0.000029	2.749301	-1.633368
Cl 0	-0.000054	2.191181	2.365014
H 0	6.552326	-2.251123	-0.024563
H 0	5.048356	-4.205803	0.173494
H 0	2.598836	-3.917106	0.154235
H 0	5.631231	0.036046	-0.248112
H 0	-2.598814	-3.917105	0.154311
H 0	-5.048334	-4.205813	0.173582
H 0	-6.552312	-2.251149	-0.024572
H 0	-5.631226	0.036015	-0.248207
H 0	-0.000052	4.931950	1.573764
H 0	0.000005	5.998473	-0.659714
H 0	0.000057	4.601072	-2.715279
H 0	0.000043	2.122519	-2.516608

SCF Done: E(UB3LYP) = -2555.22690753

Sum of electronic and zero-point Energies= -2554.951820

Sum of electronic and thermal Energies= -2554.930417

Sum of electronic and thermal Enthalpies= -2554.929473

Sum of electronic and thermal Free Energies= -2555.004239

6.1.2.10 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(SMD,solvent=dichloromethane)

0 1

C 0	5.478027	-2.116560	-0.037422
C 0	4.622237	-3.225698	0.054023
C 0	3.245937	-3.064510	0.047720
C 0	2.711161	-1.768146	-0.051655
C 0	3.589164	-0.665460	-0.145974
C 0	4.971548	-0.824267	-0.139702
C 0	1.337419	-1.348613	-0.076554
C 0	1.193750	0.025985	-0.187661
S 0	2.723934	0.870796	-0.272684
S 0	0.001204	-2.464776	0.025665
C 0	-1.335636	-1.349437	-0.077042
C 0	-1.192787	0.025237	-0.188389
N 0	0.000249	0.707533	-0.229650
C 0	-2.709101	-1.769885	-0.052973
C 0	-3.587806	-0.667846	-0.148226
S 0	-2.723506	0.868970	-0.274958
C 0	-3.243003	-3.066581	0.046624
C 0	-4.619197	-3.228742	0.052239
C 0	-5.475706	-2.120238	-0.040071
C 0	-4.970079	-0.827622	-0.142589
C 0	-0.000083	2.148953	-0.373581
C 0	-0.003593	2.977607	0.754593
C 0	-0.003476	4.359232	0.596327
C 0	0.000090	4.903168	-0.686314
C 0	0.003417	4.079442	-1.810732
C 0	0.003333	2.697577	-1.655799
Cl 0	-0.008123	2.286493	2.363560
H 0	6.551212	-2.265828	-0.029439
H 0	5.043701	-4.220718	0.131003
H 0	2.595511	-3.929047	0.118215
H 0	5.637419	0.027416	-0.210318
H 0	-2.591969	-3.930604	0.117846
H 0	-5.040005	-4.224026	0.129388
H 0	-6.548794	-2.270244	-0.032523
H 0	-5.636527	0.023559	-0.213822
H 0	-0.006090	5.000325	1.468502
H 0	0.000182	5.980477	-0.801959
H 0	0.006093	4.508298	-2.805044
H 0	0.005807	2.035872	-2.514236

SCF Done: E(UB3LYP) = -2555.25437005

Sum of electronic and zero-point Energies= -2554.979639

Sum of electronic and thermal Energies= -2554.958156

Sum of electronic and thermal Enthalpies= -2554.957212

Sum of electronic and thermal Free Energies= -2555.032875

6.1.2.11 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc) freq=noraman B3LYP/6-311++g(d,p) pop=full scrf=(iefpcm,solvent=dichloromethane)

0 1

C 0	5.490838	-2.106465	0.111008
C 0	4.627507	-3.212328	0.128910
C 0	3.251226	-3.046800	0.038694
C 0	2.716189	-1.751379	-0.069985
C 0	3.604040	-0.650137	-0.085752
C 0	4.984253	-0.813655	0.002976
C 0	1.343508	-1.338034	-0.180375
C 0	1.197623	0.013561	-0.266373
S 0	2.735814	0.875738	-0.225550
S 0	-0.000058	-2.517728	-0.244528
C 0	-1.343567	-1.338032	-0.179449
C 0	-1.197806	0.013526	-0.266272
N 0	-0.000137	0.725834	-0.370502
C 0	-2.716278	-1.751456	-0.069593
C 0	-3.604208	-0.650290	-0.085988
S 0	-2.736078	0.875616	-0.226099
C 0	-3.251193	-3.046832	0.040194
C 0	-4.627437	-3.212383	0.130964
C 0	-5.490837	-2.106582	0.112638
C 0	-4.984360	-0.813808	0.003656
C 0	-0.000276	2.156826	-0.428891
C 0	0.001178	2.937320	0.736685
C 0	0.001258	4.326799	0.659949
C 0	-0.000721	4.945349	-0.588058
C 0	-0.002757	4.183089	-1.755036
C 0	-0.002453	2.794406	-1.671986
Cl 0	0.002223	2.168436	2.311694
H 0	6.561717	-2.256081	0.181958
H 0	5.040547	-4.210816	0.214581
H 0	2.594564	-3.909387	0.055115
H 0	5.648950	0.042109	-0.010040
H 0	-2.594458	-3.909352	0.057185
H 0	-5.040414	-4.210859	0.217060
H 0	-6.561649	-2.256180	0.184616
H 0	-5.649110	0.041910	-0.009717
H 0	0.002688	4.914005	1.569017
H 0	-0.000688	6.027488	-0.643070
H 0	-0.004541	4.665951	-2.724436
H 0	-0.003643	2.182783	-2.566207

SCF Done: E(RB3LYP) = -2555.40319694

Sum of electronic and zero-point Energies= -2555.129172

Sum of electronic and thermal Energies= -2555.108436

Sum of electronic and thermal Enthalpies= -2555.107492

Sum of electronic and thermal Free Energies= -2555.179648

6.1.3 *anti-anti-N-ortho*-fluorophenyl-BBTT 3c

6.1.3.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.361320	-2.209131	-0.426750
C 0	-4.514914	-3.190762	0.109152
C 0	-3.176358	-2.920206	0.356879
C 0	-2.661897	-1.647837	0.061565
C 0	-3.528327	-0.674015	-0.487570
C 0	-4.874379	-0.941056	-0.727440
C 0	-1.334256	-1.129962	0.262053
C 0	-1.195061	0.162418	-0.137961
S 0	-2.685759	0.839730	-0.806708
S 0	0.000139	-2.057843	1.002391
C 0	1.334469	-1.129789	0.262266
C 0	1.195186	0.162563	-0.137825
N 0	0.000016	0.889554	-0.165036
C 0	2.662156	-1.647565	0.061775
C 0	3.528509	-0.673664	-0.487355
S 0	2.685866	0.839946	-0.806536
C 0	3.176699	-2.919899	0.357112
C 0	4.515275	-3.190358	0.109435
C 0	5.361627	-2.208642	-0.426441
C 0	4.874599	-0.940620	-0.727166
C 0	-0.000090	2.314324	-0.028727
C 0	0.000494	3.146091	-1.149757
C 0	0.000433	4.531313	-1.002718
C 0	-0.000238	5.094045	0.272303
C 0	-0.000853	4.280521	1.403826
C 0	-0.000769	2.905315	1.237130
F 0	-0.001277	2.113223	2.325008
H 0	-6.404256	-2.438416	-0.611733
H 0	-4.912503	-4.173741	0.334117
H 0	-2.527062	-3.683649	0.770064
H 0	-5.526697	-0.182518	-1.144390
H 0	2.527408	-3.683392	0.770218
H 0	4.912939	-4.173317	0.334349
H 0	6.404591	-2.437835	-0.611358
H 0	5.526875	-0.182054	-1.144131
H 0	0.000985	2.690183	-2.132858
H 0	0.000898	5.167026	-1.879657
H 0	-0.000291	6.171201	0.391290
H 0	-0.001371	4.692802	2.405214

SCF Done: E(RB3LYP) = -2195.04217983

Sum of electronic and zero-point Energies= -2194.766456

Sum of electronic and thermal Energies= -2194.745222

Sum of electronic and thermal Enthalpies= -2194.744278

Sum of electronic and thermal Free Energies= -2194.819882

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.336186	-2.242141	-0.432492
C 0	-4.495316	-3.227174	0.106790
C 0	-3.164220	-2.952175	0.386297
C 0	-2.652327	-1.672190	0.121289
C 0	-3.512088	-0.694488	-0.432246
C 0	-4.851443	-0.967307	-0.704700
C 0	-1.334077	-1.146646	0.360047
C 0	-1.193568	0.153121	-0.016559
S 0	-2.670626	0.824830	-0.719811
S 0	0.000063	-2.069551	1.107142
C 0	1.334044	-1.146696	0.359909
C 0	1.193596	0.153115	-0.016652
N 0	0.000001	0.885688	0.006953
C 0	2.652335	-1.672178	0.121248
C 0	3.512127	-0.694361	-0.432080
S 0	2.670632	0.824835	-0.719686
C 0	3.164203	-2.952232	0.385983
C 0	4.495335	-3.227168	0.106587
C 0	5.336221	-2.242040	-0.432474
C 0	4.851497	-0.967168	-0.704520
C 0	-0.000038	2.274394	0.365802
C 0	-0.000043	3.263981	-0.617522

C 0	-0.000050	4.614514	-0.300127
C 0	-0.000051	4.989639	1.040131
C 0	-0.000036	4.020815	2.044104
C 0	-0.000021	2.671878	1.705239
F 0	-0.000046	2.902038	-1.916603
H 0	-6.373365	-2.475142	-0.643480
H 0	-4.891349	-4.215930	0.307811
H 0	-2.518096	-3.717932	0.800321
H 0	-5.499341	-0.207264	-1.125702
H 0	2.518032	-3.718086	0.799753
H 0	4.891359	-4.215958	0.307471
H 0	6.373445	-2.475000	-0.643433
H 0	5.499421	-0.207075	-1.125396
H 0	-0.000112	5.344924	-1.099474
H 0	-0.000012	6.041931	1.299073
H 0	-0.000056	4.315843	3.086436
H 0	0.000019	1.904729	2.470722

SCF Done: E(RB3LYP) = -2195.04162850

Sum of electronic and zero-point Energies= -2194.765903

Sum of electronic and thermal Energies= -2194.744701

Sum of electronic and thermal Enthalpies= -2194.743757

Sum of electronic and thermal Free Energies= -2194.818576

6.1.3.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	-5.365459	-2.203036	-0.444795
C 0	-4.520041	-3.200478	0.064977
C 0	-3.180083	-2.938886	0.319714
C 0	-2.663604	-1.659227	0.056967
C 0	-3.529764	-0.669138	-0.464539
C 0	-4.876847	-0.927061	-0.711735
C 0	-1.335280	-1.147792	0.268809
C 0	-1.194342	0.155682	-0.096990
S 0	-2.685356	0.853221	-0.742341
S 0	-0.000026	-2.092771	0.990581
C 0	1.335248	-1.147812	0.268820
C 0	1.194330	0.155663	-0.096980
N 0	-0.000000	0.881208	-0.096573
C 0	2.663559	-1.659274	0.056957
C 0	3.529730	-0.669203	-0.464564
S 0	2.685355	0.853181	-0.742328
C 0	3.180013	-2.938947	0.319689
C 0	4.519960	-3.200569	0.064925
C 0	5.365391	-2.203144	-0.444861
C 0	4.876802	-0.927157	-0.711789
C 0	0.000015	2.311412	-0.022993
C 0	-0.000047	3.098596	-1.176337
C 0	-0.000033	4.488576	-1.079481
C 0	0.000063	5.099131	0.173955
C 0	0.000128	4.329424	1.336756
C 0	0.000094	2.950283	1.218729
F 0	0.000178	2.193330	2.338489
H 0	-6.408815	-2.425405	-0.635314
H 0	-4.919167	-4.188291	0.264475
H 0	-2.534148	-3.714681	0.714974
H 0	-5.528193	-0.156729	-1.107529
H 0	2.534067	-3.714728	0.714957
H 0	4.919068	-4.188392	0.264412
H 0	6.408738	-2.425536	-0.635398
H 0	5.528160	-0.156838	-1.107588
H 0	-0.000106	2.609498	-2.143211
H 0	-0.000084	5.091022	-1.979317
H 0	0.000082	6.179695	0.252484
H 0	0.000202	4.781602	2.320670

SCF Done: E(RB3LYP) = -2195.05044264

Sum of electronic and zero-point Energies= -2194.774789

Sum of electronic and thermal Energies= -2194.753578

Sum of electronic and thermal Enthalpies= -2194.752634

Sum of electronic and thermal Free Energies= -2194.827334

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full

0 1

C 0	-5.381580	-2.127887	-0.464472
C 0	-4.532791	-3.200593	-0.150835
C 0	-3.188269	-2.990680	0.126856
C 0	-2.669455	-1.685353	0.086749
C 0	-3.540514	-0.618252	-0.237242
C 0	-4.891354	-0.825532	-0.508384
C 0	-1.334619	-1.221949	0.356306
C 0	-1.194668	0.125761	0.217562
S 0	-2.695346	0.928129	-0.251836
S 0	0.000003	-2.280673	0.899606
C 0	1.334623	-1.221947	0.356303
C 0	1.194668	0.125763	0.217558
N 0	0.000000	0.842327	0.347524
C 0	2.669460	-1.685347	0.086746
C 0	3.540516	-0.618245	-0.237248
S 0	2.695343	0.928133	-0.251851
C 0	3.188278	-2.990672	0.126859
C 0	4.532801	-3.200583	-0.150830
C 0	5.381587	-2.127875	-0.464470
C 0	4.891357	-0.825521	-0.508386
C 0	-0.000001	2.274092	0.380684
C 0	-0.000009	3.018814	-0.801079
C 0	-0.000012	4.404245	-0.797786
C 0	-0.000005	5.069455	0.426142
C 0	0.000003	4.351095	1.622462
C 0	0.000004	2.959730	1.597594
F 0	-0.000018	2.366246	-1.985764
H 0	-6.428167	-2.311733	-0.676867
H 0	-4.932795	-4.207664	-0.123843
H 0	-2.540385	-3.825831	0.367867
H 0	-5.544405	0.003912	-0.753131
H 0	2.540397	-3.825825	0.367872
H 0	4.932808	-4.207652	-0.123835
H 0	6.428175	-2.311718	-0.676863
H 0	5.544406	0.003924	-0.753136
H 0	-0.000019	4.939255	-1.739110
H 0	-0.000007	6.152716	0.441929
H 0	0.000007	4.872919	2.571362
H 0	0.000010	2.384659	2.515726

SCF Done: E(RB3LYP) = -2195.04973792

Sum of electronic and zero-point Energies= -2194.774113

Sum of electronic and thermal Energies= -2194.752935

Sum of electronic and thermal Enthalpies= -2194.751991

Sum of electronic and thermal Free Energies= -2194.825902

6.1.3.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	-5.338978	-2.173201	-0.489668
C 0	-4.501597	-3.198366	-0.033393
C 0	-3.165613	-2.958279	0.241106
C 0	-2.645767	-1.671187	0.052022

C 0	-3.503130	-0.652317	-0.414380
C 0	-4.846925	-0.889772	-0.682713
C 0	-1.321867	-1.178509	0.293816
C 0	-1.185834	0.141445	-0.002632
S 0	-2.660073	0.867846	-0.602716
S 0	0.000003	-2.143756	0.974491
C 0	1.321870	-1.178507	0.293814
C 0	1.185835	0.141447	-0.002633
N 0	-0.000000	0.863277	0.051588
C 0	2.645771	-1.671182	0.052022
C 0	3.503133	-0.652310	-0.414379
S 0	2.660072	0.867850	-0.602719
C 0	3.165620	-2.958273	0.241107
C 0	4.501605	-3.198357	-0.033390
C 0	5.338985	-2.173190	-0.489663
C 0	4.846929	-0.889762	-0.682709
C 0	-0.000001	2.284160	-0.002873
C 0	-0.000000	2.964185	-1.218941
C 0	-0.000002	4.353144	-1.244154
C 0	-0.000008	5.067756	-0.050818
C 0	-0.000009	4.405479	1.171654
C 0	-0.000004	3.023736	1.177639
F 0	-0.000012	2.372507	2.346485
H 0	-6.383137	-2.381055	-0.697145
H 0	-4.906051	-4.194994	0.108960
H 0	-2.522021	-3.757177	0.595707
H 0	-5.493426	-0.094781	-1.038595
H 0	2.522030	-3.757172	0.595708
H 0	4.906061	-4.194983	0.108965
H 0	6.383144	-2.381042	-0.697138
H 0	5.493428	-0.094770	-1.038591
H 0	0.000003	2.389938	-2.139543
H 0	-0.000000	4.875546	-2.193828
H 0	-0.000011	6.152173	-0.066805
H 0	-0.000014	4.942945	2.112931

SCF Done: E(RPBE1PBE) = -2193.44821361

Sum of electronic and zero-point Energies= -2193.169676

Sum of electronic and thermal Energies= -2193.148601

Sum of electronic and thermal Enthalpies= -2193.147657

Sum of electronic and thermal Free Energies= -2193.222197

6.1.3.4 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent =dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 3.0343 eV 408.61 nm f=0.1315

<TDDFT>HOMO -> LUMO 94.7%

<TDDFT> Excited State 2: Singlet-A 3.4053 eV 364.09 nm f=0.0087

<TDDFT>HOMO -> LUMO+1 97.2%

<TDDFT> Excited State 3: Singlet-A 3.6700 eV 337.84 nm f=0.0027

<TDDFT>HOMO -> LUMO+2 90.1%

<TDDFT>HOMO -> LUMO+7 4.3%

<TDDFT> Excited State 4: Singlet-A 3.8980 eV 318.07 nm f=0.0971

<TDDFT>HOMO -> LUMO+3 75.3%

<TDDFT>HOMO -> LUMO+4 10.8%

<TDDFT>HOMO -> LUMO+6 8.3%

<TDDFT> Excited State 5: Singlet-A 3.9319 eV 315.33 nm f=0.0036

<TDDFT>HOMO -> LUMO+3 12.3%

<TDDFT>HOMO -> LUMO+4 84.4%

<TDDFT> Excited State 6: Singlet-A 3.9835 eV 311.24 nm f=0.0150

<TDDFT>HOMO -> LUMO+2 4.5%

<TDDFT>HOMO -> LUMO+5 86.2%

<TDDFT>HOMO -> LUMO+7 4.8%

<TDDFT> Excited State 7: Singlet-A 4.1448 eV 299.13 nm f=0.0122

<TDDFT>HOMO -> LUMO+2 3.7%

<TDDFT>HOMO -> LUMO+5 7.9%

<TDDFT>HOMO -> LUMO+7 76.3%

<TDDFT>HOMO -> LUMO+10 7.1%

<TDDFT> Excited State 8: Singlet-A 4.1744 eV 297.01 nm f=0.0330

<TDDFT>HOMO -> LUMO+3 7.8%

<TDDFT>HOMO -> LUMO+6 73.3%

<TDDFT>HOMO -> LUMO+8 12.2%

<TDDFT> Excited State 9: Singlet-A 4.4400 eV 279.24 nm f=0.0097

<TDDFT>HOMO -> LUMO+6 11.4%

<TDDFT>HOMO -> LUMO+8 74.1%

<TDDFT>HOMO -> LUMO+9 5.1%

<TDDFT>HOMO -> LUMO+11 4.8%

<TDDFT> Excited State 10: Singlet-A 4.6091 eV 269.00 nm f=0.1151

<TDDFT>HOMO-1 -> LUMO 85.6%

<TDDFT> Excited State 11: Singlet-A 4.6211 eV 268.30 nm f=0.1588

<TDDFT>HOMO-2 -> LUMO 79.7%

<TDDFT>HOMO-1 -> LUMO+4 2.3%

<TDDFT>HOMO -> LUMO+10 2.2%

<TDDFT>HOMO -> LUMO+13 4.9%

<TDDFT> Excited State 12: Singlet-A 4.7971 eV 258.46 nm f=0.0013

<TDDFT>HOMO-1 -> LUMO 2.1%

<TDDFT>HOMO-1 -> LUMO+1 6.9%

<TDDFT>HOMO -> LUMO+8 3.5%

<TDDFT>HOMO -> LUMO+9 74.8%

<TDDFT>HOMO -> LUMO+11 6.0%

<TDDFT> Excited State 13: Singlet-A 4.8298 eV 256.71 nm f=0.0181

<TDDFT>HOMO-3 -> LUMO 3.3%

<TDDFT>HOMO-2 -> LUMO+3 2.7%

<TDDFT>HOMO-1 -> LUMO+1 80.2%

<TDDFT>HOMO -> LUMO+9 8.0%

<TDDFT> Excited State 14: Singlet-A 4.8663 eV 254.78 nm f=0.2585

<TDDFT>HOMO-2 -> LUMO 7.1%

<TDDFT>HOMO -> LUMO+7 6.0%

<TDDFT>HOMO -> LUMO+10 56.7%

<TDDFT>HOMO -> LUMO+13 19.5%

<TDDFT> Excited State 15: Singlet-A 4.9415 eV 250.90 nm f=0.0001

<TDDFT>HOMO-2 -> LUMO 2.2%

<TDDFT>HOMO-2 -> LUMO+1 89.5%

<TDDFT>HOMO-1 -> LUMO+4 2.1%

<TDDFT> Excited State 16: Singlet-A 5.0265 eV 246.66 nm f=0.0108

<TDDFT>HOMO-3 -> LUMO 20.2%

<TDDFT>HOMO-2 -> LUMO+6 4.4%

<TDDFT>HOMO-1 -> LUMO+1 2.3%

<TDDFT>HOMO-1 -> LUMO+2 58.5%

<TDDFT>HOMO-1 -> LUMO+5 4.4%

<TDDFT> Excited State 17: Singlet-A 5.0425 eV 245.88 nm f=0.0796

<TDDFT>HOMO -> LUMO+7 4.8%

<TDDFT>HOMO -> LUMO+10 20.7%

<TDDFT>HOMO -> LUMO+13 46.5%

<TDDFT>HOMO -> LUMO+15 15.7%

<TDDFT>HOMO -> LUMO+16 2.1%

<TDDFT> Excited State 18: Singlet-A 5.0717 eV 244.46 nm f=0.0198

<TDDFT>HOMO-2 -> LUMO+1 4.7%

<TDDFT>HOMO-2 -> LUMO+2 38.0%

<TDDFT>HOMO-2 -> LUMO+7 3.5%

<TDDFT>HOMO-1 -> LUMO+3 28.5%

<TDDFT>HOMO-1 -> LUMO+4 4.9%

<TDDFT>HOMO-1 -> LUMO+6 5.8%

<TDDFT> Excited State 19: Singlet-A 5.0884 eV 243.66 nm f=0.0465

<TDDFT>HOMO-3 -> LUMO 26.1%

<TDDFT>HOMO-2 -> LUMO+3 15.2%

<TDDFT>HOMO-2 -> LUMO+4 2.9%

<TDDFT>HOMO-2 -> LUMO+6 2.9%

<TDDFT>HOMO-1 -> LUMO+1 6.8%

<TDDFT>HOMO-1 -> LUMO+2 18.3%

<TDDFT>HOMO-1 -> LUMO+5 6.5%

<TDDFT>HOMO-1 -> LUMO+7 8.3%

<TDDFT>HOMO -> LUMO+12 2.0%

<TDDFT> Excited State 20: Singlet-A 5.0996 eV 243.13 nm f=0.0094

<TDDFT>HOMO -> LUMO+8 6.3%

<TDDFT>HOMO -> LUMO+9 3.2%

<TDDFT>HOMO -> LUMO+11 70.7%

<TDDFT>HOMO -> LUMO+12 8.1%

<TDDFT>HOMO -> LUMO+14 2.1%

<TDDFT>HOMO -> LUMO+20 2.8%

<TDDFT> Excited State 21: Singlet-A 5.2291 eV 237.11 nm f=0.0040

<TDDFT>HOMO -> LUMO+11 5.4%

<TDDFT>HOMO -> LUMO+12 77.1%

<TDDFT>HOMO -> LUMO+14 5.4%

<TDDFT>HOMO -> LUMO+18 3.1%

<TDDFT> Excited State 22: Singlet-A 5.2298 eV 237.07 nm f=0.0609

<TDDFT>HOMO-3 -> LUMO+4 2.4%

<TDDFT>HOMO-2 -> LUMO+2 33.4%

<TDDFT>HOMO-2 -> LUMO+5 6.9%

<TDDFT>HOMO-2 -> LUMO+7 2.9%

<TDDFT>HOMO-1 -> LUMO+3 40.0%

<TDDFT>HOMO -> LUMO+13 2.3%

<TDDFT>HOMO -> LUMO+22 2.0%

<TDDFT> Excited State 23: Singlet-A 5.2503 eV 236.14 nm f=0.0121

<TDDFT>HOMO -> LUMO+9 4.1%

<TDDFT>HOMO -> LUMO+11 3.8%

<TDDFT>HOMO -> LUMO+12 3.3%

<TDDFT>HOMO -> LUMO+14 75.9%

<TDDFT> Excited State 24: Singlet-A 5.2643 eV 235.52 nm f=0.0455

<TDDFT>HOMO-6 -> LUMO+2 3.0%

<TDDFT>HOMO-5 -> LUMO 2.9%

<TDDFT>HOMO-5 -> LUMO+1 4.1%

<TDDFT>HOMO-3 -> LUMO 22.7%

<TDDFT>HOMO-3 -> LUMO+1 10.1%

<TDDFT>HOMO-3 -> LUMO+2 2.9%

<TDDFT>HOMO-2 -> LUMO+3 23.3%

<TDDFT>HOMO-2 -> LUMO+4 2.0%

<TDDFT>HOMO-2 -> LUMO+6 6.5%

<TDDFT>HOMO-1 -> LUMO+2 7.2%

<TDDFT>HOMO -> LUMO+14 4.8%

6.1.3.5 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=3) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	-5.473782	-2.037653	-0.034511
C 0	-4.615816	-3.137563	0.043676
C 0	-3.239118	-2.977102	0.045001
C 0	-2.688401	-1.683625	-0.032593
C 0	-3.577339	-0.582615	-0.112667
C 0	-4.951496	-0.744722	-0.114744
C 0	-1.328935	-1.267445	-0.049322
C 0	-1.187853	0.137169	-0.154920
S 0	-2.731321	0.964618	-0.202716
S 0	-0.000001	-2.339870	0.136139
C 0	1.328934	-1.267446	-0.049323
C 0	1.187853	0.137169	-0.154922
N 0	0.000000	0.801322	-0.183004
C 0	2.688400	-1.683627	-0.032593
C 0	3.577338	-0.582617	-0.112667
S 0	2.731322	0.964617	-0.202717
C 0	3.239116	-2.977104	0.045001
C 0	4.615814	-3.137565	0.043677
C 0	5.473781	-2.037656	-0.034509
C 0	4.951496	-0.744725	-0.114744
C 0	0.000001	2.231384	-0.188543
C 0	0.000003	2.935629	-1.387655
C 0	0.000004	4.324078	-1.368295
C 0	0.000003	5.002120	-0.153429
C 0	0.000001	4.305522	1.050213
C 0	-0.000000	2.924454	1.017436
F 0	-0.000001	2.231820	2.160595
H 0	-6.548362	-2.182926	-0.032880
H 0	-5.032978	-4.137656	0.103982
H 0	-2.589023	-3.844442	0.104607
H 0	-5.611641	0.114058	-0.175576
H 0	2.589021	-3.844443	0.104607
H 0	5.032975	-4.137659	0.103984
H 0	6.548360	-2.182930	-0.032878
H 0	5.611641	0.114055	-0.175575
H 0	0.000003	2.383633	-2.321034
H 0	0.000005	4.875143	-2.301444
H 0	0.000004	6.086400	-0.137586
H 0	0.000001	4.814940	2.006759

SCF Done: E(RPBE1PBE) = -2193.43615101

Sum of electronic and zero-point Energies= -2193.079784

Sum of electronic and thermal Energies= -2193.057752

Sum of electronic and thermal Enthalpies= -2193.056808

Sum of electronic and thermal Free Energies= -2193.133723

6.1.3.6 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=3) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=

dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.2299 eV 556.00 nm f=0.1153

<TDDFT>HOMO -> LUMO 98.2%

<TDDFT> Excited State 2: Singlet-A 2.7993 eV 442.91 nm f=0.0025

<TDDFT>HOMO -> LUMO+1 98.8%

<TDDFT> Excited State 3: Singlet-A 3.2416 eV 382.48 nm f=0.0000

<TDDFT>HOMO -> LUMO+2 97.0%

<TDDFT> Excited State 4: Singlet-A 3.3904 eV 365.69 nm f=0.0008

<TDDFT>HOMO -> LUMO+3 4.7%

<TDDFT>HOMO -> LUMO+4 45.7%

<TDDFT>HOMO -> LUMO+6 45.8%

6.1.3.7 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0	-5.365287	-2.204002	-0.453721
C 0	-4.518797	-3.207717	0.041956
C 0	-3.178844	-2.949260	0.300444
C 0	-2.662834	-1.665861	0.054037
C 0	-3.530521	-0.670056	-0.453886
C 0	-4.877694	-0.924171	-0.704340
C 0	-1.335502	-1.154652	0.274289
C 0	-1.193766	0.153382	-0.075125
S 0	-2.686126	0.856985	-0.713547
S 0	0.000003	-2.102511	0.993443
C 0	1.335510	-1.154646	0.274300
C 0	1.193770	0.153388	-0.075114
N 0	0.000000	0.878825	-0.058612
C 0	2.662842	-1.665852	0.054045
C 0	3.530527	-0.670045	-0.453878
S 0	2.686134	0.857001	-0.713517
C 0	3.178852	-2.949253	0.300442
C 0	4.518804	-3.207710	0.041945
C 0	5.365292	-2.203992	-0.453732
C 0	4.877698	-0.924160	-0.704342
C 0	-0.000004	2.311113	-0.016917
C 0	0.000002	3.071560	-1.188419
C 0	-0.000001	4.463437	-1.121792
C 0	-0.000011	5.101937	0.117807
C 0	-0.000018	4.358921	1.298121
C 0	-0.000014	2.978133	1.209819
F 0	-0.000020	2.245144	2.348076
H 0	-6.408838	-2.424713	-0.646849
H 0	-4.917206	-4.198717	0.228365
H 0	-2.534474	-3.731738	0.685669
H 0	-5.530569	-0.149137	-1.089517
H 0	2.534483	-3.731734	0.685664
H 0	4.917213	-4.198711	0.228346
H 0	6.408841	-2.424703	-0.646865
H 0	5.530572	-0.149124	-1.089515
H 0	0.000010	2.561041	-2.144633
H 0	0.000004	5.045562	-2.035416
H 0	-0.000014	6.184403	0.172293
H 0	-0.000026	4.832939	2.272343

SCF Done: E(RB3LYP) = -2195.07337702

Sum of electronic and zero-point Energies= -2194.797809

Sum of electronic and thermal Energies= -2194.776666

Sum of electronic and thermal Enthalpies= -2194.775722

Sum of electronic and thermal Free Energies= -2194.849339

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0	-5.365882	-2.149504	-0.493038
C 0	-4.521882	-3.211774	-0.133725
C 0	-3.182922	-2.992864	0.164050
C 0	-2.664390	-1.688165	0.098019
C 0	-3.531387	-0.632563	-0.271643

C 0	-4.876911	-0.847819	-0.562271
C 0	-1.335288	-1.212476	0.378725
C 0	-1.193906	0.131057	0.205199
S 0	-2.688806	0.915351	-0.315485
S 0	-0.000000	-2.246285	0.968951
C 0	1.335288	-1.212476	0.378728
C 0	1.193906	0.131057	0.205201
N 0	-0.000000	0.849015	0.324529
C 0	2.664390	-1.688165	0.098021
C 0	3.531387	-0.632563	-0.271642
S 0	2.688808	0.915352	-0.315477
C 0	3.182921	-2.992864	0.164050
C 0	4.521881	-3.211775	-0.133727
C 0	5.365881	-2.149505	-0.493041
C 0	4.876911	-0.847820	-0.562273
C 0	-0.000000	2.280833	0.389128
C 0	0.000001	3.049793	-0.776637
C 0	0.000001	4.434438	-0.746854
C 0	-0.000001	5.074087	0.490721
C 0	-0.000002	4.331454	1.672497
C 0	-0.000002	2.940849	1.620511
F 0	0.000003	2.419620	-1.976198
H 0	-6.407992	-2.341167	-0.721504
H 0	-4.920972	-4.218797	-0.087841
H 0	-2.541343	-3.822450	0.439877
H 0	-5.525785	-0.025760	-0.842384
H 0	2.541342	-3.822451	0.439877
H 0	4.920970	-4.218798	-0.087845
H 0	6.407990	-2.341168	-0.721509
H 0	5.525784	-0.025761	-0.842385
H 0	0.000002	4.988228	-1.677745
H 0	-0.000001	6.157266	0.528531
H 0	-0.000004	4.834235	2.632130
H 0	-0.000003	2.346848	2.527071

SCF Done: E(RB3LYP) = -2195.07249215

Sum of electronic and zero-point Energies= -2194.796945

Sum of electronic and thermal Energies= -2194.775768

Sum of electronic and thermal Enthalpies= -2194.774824

Sum of electronic and thermal Free Energies= -2194.848786

6.1.3.8 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000

0 1

C 0	5.479655	-2.025051	0.000362
C 0	4.626267	-3.137542	0.064869
C 0	3.250554	-2.978504	0.051547
C 0	2.712075	-1.682322	-0.027451
C 0	3.588181	-0.575667	-0.091650
C 0	4.970254	-0.732914	-0.079025
C 0	1.337937	-1.264211	-0.052793
C 0	1.195309	0.113723	-0.134485
S 0	2.722860	0.961441	-0.186904
S 0	-0.000000	-2.381534	0.020601
C 0	-1.337937	-1.264211	-0.052792
C 0	-1.195309	0.113723	-0.134485
N 0	-0.000000	0.796131	-0.174858
C 0	-2.712075	-1.682323	-0.027451
C 0	-3.588181	-0.575668	-0.091650
S 0	-2.722860	0.961440	-0.186905
C 0	-3.250554	-2.978504	0.051547
C 0	-4.626267	-3.137542	0.064869
C 0	-5.479655	-2.025051	0.000361
C 0	-4.970253	-0.732915	-0.079026
C 0	-0.000000	2.242480	-0.197386
C 0	-0.000001	2.941745	1.010257
C 0	-0.000001	4.325843	1.036060
C 0	-0.000000	5.016867	-0.173871
C 0	0.000001	4.331856	-1.389761

C 0	0.000001	2.940924	-1.404959
F 0	-0.000002	2.244686	2.158732
H 0	6.552792	-2.172015	0.012590
H 0	5.050046	-4.132216	0.126295
H 0	2.601023	-3.844939	0.102360
H 0	5.633901	0.121601	-0.128084
H 0	-2.601023	-3.844940	0.102361
H 0	-5.050046	-4.132216	0.126295
H 0	-6.552791	-2.172015	0.012590
H 0	-5.633901	0.121601	-0.128085
H 0	-0.000002	4.838643	1.989669
H 0	-0.000000	6.100089	-0.164556
H 0	0.000002	4.879064	-2.323805
H 0	0.000002	2.392279	-2.339387

SCF Done: E(UB3LYP) = -2194.82128397

Sum of electronic and zero-point Energies= -2194.544836

Sum of electronic and thermal Energies= -2194.523782

Sum of electronic and thermal Enthalpies= -2194.522838

Sum of electronic and thermal Free Energies= -2194.596708

6.1.3.9 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.479436	-2.024740	0.007818
C 0	4.625880	-3.138209	0.057655
C 0	3.249335	-2.979734	0.040326
C 0	2.710943	-1.683117	-0.028556
C 0	3.586392	-0.575364	-0.078592
C 0	4.969269	-0.732053	-0.060996
C 0	1.335607	-1.266613	-0.054863
C 0	1.193995	0.111393	-0.122958
S 0	2.720750	0.961277	-0.164101
S 0	-0.000008	-2.385000	-0.003625
C 0	-1.335618	-1.266607	-0.054859
C 0	-1.194000	0.111399	-0.122951
N 0	-0.000001	0.793724	-0.155256
C 0	-2.710956	-1.683105	-0.028547
C 0	-3.586400	-0.575348	-0.078577
S 0	-2.720752	0.961290	-0.164084
C 0	-3.249353	-2.979720	0.040330
C 0	-4.625899	-3.138189	0.057661
C 0	-5.479450	-2.024716	0.007830
C 0	-4.969278	-0.732031	-0.060979
C 0	0.000002	2.238694	-0.194807
C 0	0.000038	2.958687	0.999808
C 0	0.000041	4.342337	1.003814
C 0	0.000009	5.013191	-0.217778
C 0	-0.000027	4.307597	-1.421604
C 0	-0.000030	2.916505	-1.413556
F 0	0.000070	2.282128	2.165356
H 0	6.552669	-2.170746	0.023334
H 0	5.049025	-4.133684	0.111157
H 0	2.599696	-3.846176	0.080532
H 0	5.631446	0.123857	-0.098543
H 0	-2.599718	-3.846165	0.080531
H 0	-5.049048	-4.133662	0.111160
H 0	-6.552684	-2.170717	0.023348
H 0	-5.631451	0.123882	-0.098521
H 0	0.000070	4.872240	1.947716
H 0	0.000011	6.096216	-0.225804
H 0	-0.000051	4.838202	-2.364957
H 0	-0.000056	2.348929	-2.336113

SCF Done: E(UB3LYP) = -2194.87264561

Sum of electronic and zero-point Energies= -2194.596343

Sum of electronic and thermal Energies= -2194.576117

Sum of electronic and thermal Free Energies= -2194.646755

Sum of electronic and thermal Enthalpies= -2194.575173

6.1.3.10 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(SMD,solvent=dichloromethane)

0 1

C 0	5.476919	-2.032998	-0.010423
C 0	4.620914	-3.144395	0.043380
C 0	3.244574	-2.982924	0.036360
C 0	2.710327	-1.684138	-0.025182
C 0	3.588495	-0.578917	-0.081301
C 0	4.970842	-0.738022	-0.074209
C 0	1.336587	-1.263985	-0.041944
C 0	1.193132	0.113197	-0.111217
S 0	2.723413	0.960463	-0.162096
S 0	-0.000001	-2.382170	0.024487
C 0	-1.336588	-1.263984	-0.041944
C 0	-1.193133	0.113198	-0.111217
N 0	-0.000000	0.796105	-0.138270
C 0	-2.710329	-1.684136	-0.025181
C 0	-3.588496	-0.578915	-0.081299
S 0	-2.723413	0.960464	-0.162094
C 0	-3.244577	-2.982922	0.036361
C 0	-4.620916	-3.144392	0.043382
C 0	-5.476921	-2.032995	-0.010420
C 0	-4.970843	-0.738019	-0.074206
C 0	0.000000	2.241770	-0.189464
C 0	0.000006	2.972486	0.998848
C 0	0.000006	4.355478	0.992474
C 0	0.000000	5.016001	-0.234842
C 0	-0.000006	4.300428	-1.432873
C 0	-0.000005	2.909393	-1.414496
F 0	0.000011	2.304921	2.172337
H 0	6.550072	-2.182500	-0.002683
H 0	5.042123	-4.141309	0.091365
H 0	2.593676	-3.849048	0.077676
H 0	5.637023	0.115396	-0.115495
H 0	-2.593679	-3.849047	0.077676
H 0	-5.042126	-4.141306	0.091367
H 0	-6.550074	-2.182496	-0.002680
H 0	-5.637024	0.115399	-0.115492
H 0	0.000011	4.892829	1.932737
H 0	0.000000	6.099473	-0.251624
H 0	-0.000010	4.823385	-2.381038
H 0	-0.000010	2.334827	-2.333220

SCF Done: E(UB3LYP) = -2194.89906730

Sum of electronic and zero-point Energies= -2194.622732

Sum of electronic and thermal Energies= -2194.601727

Sum of electronic and thermal Enthalpies= -2194.600783

Sum of electronic and thermal Free Energies= -2194.674733

6.1.3.11 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc) freq=noraman b3lyp/6-311++g(d,p) pop=full scrf=(iefpcm,solvent=dichloromethane)

0 1

C 0	5.496827	-2.018233	0.087415
C 0	4.633329	-3.122450	0.146518
C 0	3.255346	-2.956611	0.088223
C 0	2.719122	-1.662738	-0.031317

C 0	3.607119	-0.563259	-0.090464
C 0	4.988923	-0.726916	-0.031381
C 0	1.343630	-1.249081	-0.105342
C 0	1.197167	0.100408	-0.213381
S 0	2.736609	0.960794	-0.238353
S 0	-0.000119	-2.429464	-0.086743
C 0	-1.343792	-1.248959	-0.104758
C 0	-1.197278	0.100517	-0.213082
N 0	-0.000181	0.815783	-0.320946
C 0	-2.719280	-1.662608	-0.030739
C 0	-3.607288	-0.563146	-0.090028
S 0	-2.736788	0.960891	-0.238113
C 0	-3.255500	-2.956465	0.089012
C 0	-4.633485	-3.122308	0.147310
C 0	-5.496994	-2.018116	0.087964
C 0	-4.989089	-0.726806	-0.030959
C 0	-0.000147	2.245531	-0.231302
C 0	0.001320	2.881151	1.012894
C 0	0.001380	4.260075	1.134205
C 0	-0.000177	5.031855	-0.026803
C 0	-0.001752	4.424419	-1.282349
C 0	-0.001711	3.035503	-1.382585
F 0	0.002679	2.120394	2.129811
H 0	6.569010	-2.167971	0.134293
H 0	5.047491	-4.119799	0.239521
H 0	2.598870	-3.818143	0.136519
H 0	5.653984	0.127459	-0.076299
H 0	-2.599018	-3.817985	0.137445
H 0	-5.047636	-4.119641	0.240540
H 0	-6.569180	-2.167863	0.134727
H 0	-5.654154	0.127561	-0.075972
H 0	0.002559	4.709747	2.119199
H 0	-0.000161	6.112231	0.054309
H 0	-0.002962	5.029384	-2.180457
H 0	-0.002905	2.544892	-2.348472

SCF Done: E(RB3LYP) = -2195.04919169

Sum of electronic and zero-point Energies= -2194.773710

Sum of electronic and thermal Energies= -2194.753345

Sum of electronic and thermal Enthalpies= -2194.752400

Sum of electronic and thermal Free Energies= -2194.823812

6.1.4 *anti-anti-N-ortho*-methylphenyl-BBTT 3d

6.1.4.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.348030	-2.207157	-0.495302
C 0	4.503811	-3.211355	0.000902
C 0	3.169123	-2.949362	0.277371
C 0	2.655459	-1.662277	0.050942
C 0	3.519574	-0.665189	-0.459627
C 0	4.861680	-0.924387	-0.727886
C 0	1.333257	-1.150285	0.290537
C 0	1.191988	0.161078	-0.048897
S 0	2.679573	0.866106	-0.695998
S 0	0.000233	-2.093760	1.017180
C 0	-1.332950	-1.150517	0.290472
C 0	-1.191868	0.160875	-0.048904
N 0	-0.000010	0.887277	-0.016645
C 0	-2.655016	-1.662707	0.050915
C 0	-3.519345	-0.665746	-0.459558
S 0	-2.679646	0.865690	-0.695980
C 0	-3.168390	-2.949976	0.277009
C 0	-4.502967	-3.212280	0.000287
C 0	-5.347416	-2.208166	-0.495816
C 0	-4.861343	-0.925254	-0.728108
C 0	-0.000185	2.328346	-0.001567

C 0	-0.000887	3.008407	1.227943
C 0	-0.001048	4.405903	1.191615
C 0	-0.000525	5.103078	-0.015277
C 0	0.000168	4.411827	-1.223446
C 0	0.000319	3.019103	-1.213538
C 0	-0.001436	2.259641	2.535538
H 0	6.387906	-2.430217	-0.703573
H 0	4.900065	-4.205747	0.171826
H 0	2.521222	-3.730467	0.658597
H 0	5.511693	-0.148239	-1.115140
H 0	-2.520311	-3.731023	0.658054
H 0	-4.898980	-4.206804	0.170995
H 0	-6.387182	-2.431481	-0.704301
H 0	-5.511481	-0.149188	-1.115313
H 0	-0.001572	4.955148	2.127190
H 0	-0.000654	6.187314	-0.009504
H 0	0.000567	4.947880	-2.165155
H 0	0.000810	2.458486	-2.141149
H 0	-0.880028	1.614734	2.624587
H 0	0.877015	1.614648	2.625286
H 0	-0.001753	2.953851	3.377251

SCF Done: E(RB3LYP) = -2135.10606601

Sum of electronic and zero-point Energies= -2134.794731

Sum of electronic and thermal Energies= -2134.772665

Sum of electronic and thermal Enthalpies= -2134.771721

Sum of electronic and thermal Free Energies= -2134.847709

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.404768	-2.119683	0.393270
C 0	4.549892	-3.193354	0.104470
C 0	3.198375	-2.986120	-0.134653
C 0	2.677692	-1.682617	-0.080280
C 0	3.554702	-0.613943	0.219504
C 0	4.912383	-0.819353	0.451244
C 0	1.335175	-1.224733	-0.313377
C 0	1.194063	0.122899	-0.170445
S 0	2.706946	0.929693	0.256258
S 0	0.000013	-2.295536	-0.829368
C 0	-1.335154	-1.224767	-0.313318
C 0	-1.194064	0.122867	-0.170386
N 0	-0.000012	0.841975	-0.256279
C 0	-2.677660	-1.682672	-0.080201
C 0	-3.554679	-0.614014	0.219615
S 0	-2.706922	0.929619	0.256486
C 0	-3.198335	-2.986177	-0.134621
C 0	-4.549852	-3.193427	0.104483
C 0	-5.404738	-2.119771	0.393308
C 0	-4.912362	-0.819439	0.451329
C 0	-0.000054	2.280807	-0.343686
C 0	0.000105	3.072238	0.815866
C 0	0.000026	4.464189	0.643519
C 0	-0.000198	5.044474	-0.618925
C 0	-0.000361	4.240547	-1.759426
C 0	-0.000290	2.859637	-1.616759
C 0	0.000396	2.493427	2.209945
H 0	6.457574	-2.301272	0.574983
H 0	4.951034	-4.199683	0.066285
H 0	2.543817	-3.821749	-0.354884
H 0	5.570648	0.011878	0.676314
H 0	-2.543771	-3.821793	-0.354886
H 0	-4.950988	-4.199757	0.066259
H 0	-6.457544	-2.301372	0.575011
H 0	-5.570632	0.011778	0.676435
H 0	0.000134	5.098502	1.524169
H 0	-0.000257	6.124479	-0.715008
H 0	-0.000544	4.685796	-2.747349
H 0	-0.000417	2.209619	-2.483873
H 0	-0.000336	1.404907	2.208213
H 0	0.882857	2.828543	2.762270

H 0 -0.881050 2.829762 2.763136

SCF Done: E(RB3LYP) = -2135.10410238

Sum of electronic and zero-point Energies= -2134.792993

Sum of electronic and thermal Energies= -2134.771695

Sum of electronic and thermal Enthalpies= -2134.770751

Sum of electronic and thermal Free Energies= -2134.844805

6.1.4.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman b3lyp/6-311g** scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	5.348790	-2.200801	-0.506813
C 0	4.507090	-3.212437	-0.021049
C 0	3.172153	-2.956578	0.260060
C 0	2.655541	-1.667701	0.048054
C 0	3.518292	-0.662676	-0.450173
C 0	4.860763	-0.915823	-0.722890
C 0	1.333702	-1.159163	0.295483
C 0	1.190488	0.156490	-0.026533
S 0	2.675343	0.871399	-0.667210
S 0	0.000001	-2.107643	1.019166
C 0	-1.333701	-1.159164	0.295482
C 0	-1.190488	0.156490	-0.026533
N 0	-0.000000	0.881555	0.018366
C 0	-2.655540	-1.667702	0.048054
C 0	-3.518292	-0.662678	-0.450174
S 0	-2.675343	0.871398	-0.667210
C 0	-3.172152	-2.956580	0.260060
C 0	-4.507089	-3.212438	-0.021049
C 0	-5.348788	-2.200803	-0.506813
C 0	-4.860763	-0.915825	-0.722890
C 0	-0.000000	2.324101	0.002780
C 0	-0.000001	3.027421	1.219058
C 0	-0.000002	4.423918	1.154380
C 0	-0.000002	5.095953	-0.066748
C 0	-0.000000	4.380906	-1.261245
C 0	0.000000	2.988604	-1.224301
C 0	-0.000002	2.305272	2.541631
H 0	6.388870	-2.419166	-0.718229
H 0	4.905500	-4.207730	0.138535
H 0	2.528244	-3.743472	0.636014
H 0	5.508904	-0.133935	-1.100816
H 0	-2.528242	-3.743473	0.636014
H 0	-4.905498	-4.207732	0.138535
H 0	-6.388869	-2.419168	-0.718229
H 0	-5.508903	-0.133937	-1.100817
H 0	-0.000003	4.991788	2.078354
H 0	-0.000002	6.179839	-0.082809
H 0	-0.000000	4.897868	-2.213263
H 0	0.000001	2.410927	-2.141113
H 0	-0.879049	1.662915	2.643926
H 0	0.879041	1.662911	2.643925
H 0	-0.000000	3.016301	3.368492

SCF Done: E(RB3LYP) = -2135.09897123

Sum of electronic and zero-point Energies= -2134.787545

Sum of electronic and thermal Energies= -2134.765516

Sum of electronic and thermal Enthalpies= -2134.764571

Sum of electronic and thermal Free Energies= -2134.840161

Conformer II:

#p opt freq=noraman b3lyp/6-311g** scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	5.398575	-2.113352	0.419529
C 0	4.547086	-3.190562	0.132757
C 0	3.197635	-2.986875	-0.120643
C 0	2.675620	-1.682801	-0.082352
C 0	3.549943	-0.610598	0.214564
C 0	4.905873	-0.812584	0.460136
C 0	1.335657	-1.226142	-0.330499
C 0	1.192755	0.122921	-0.201930
S 0	2.701007	0.934380	0.229947
S 0	-0.000008	-2.296694	-0.853468
C 0	-1.335657	-1.226146	-0.330449
C 0	-1.192752	0.122916	-0.201880
N 0	-0.000002	0.839851	-0.297268
C 0	-2.675624	-1.682799	-0.082308
C 0	-3.549943	-0.610590	0.214599
S 0	-2.700979	0.934371	0.230095
C 0	-3.197654	-2.986865	-0.120641
C 0	-4.547115	-3.190541	0.132714
C 0	-5.398600	-2.113325	0.419475
C 0	-4.905885	-0.812563	0.460116
C 0	-0.000006	2.282262	-0.350923
C 0	0.000043	3.045518	0.827826
C 0	0.000036	4.441028	0.687197
C 0	-0.000014	5.049389	-0.562015
C 0	-0.000060	4.272255	-1.721180
C 0	-0.000058	2.888385	-1.611313
C 0	0.000085	2.436942	2.209186
H 0	6.449675	-2.292427	0.612387
H 0	4.949225	-4.196765	0.107185
H 0	2.547242	-3.825620	-0.341310
H 0	5.561352	0.020971	0.683302
H 0	-2.547266	-3.825612	-0.341314
H 0	-4.949265	-4.196739	0.107111
H 0	-6.449707	-2.292392	0.612303
H 0	-5.561359	0.020994	0.683289
H 0	0.000073	5.054505	1.581997
H 0	-0.000015	6.131061	-0.633338
H 0	-0.000102	4.740247	-2.698250
H 0	-0.000093	2.259484	-2.493562
H 0	0.000119	1.348614	2.186655
H 0	0.880845	2.763325	2.768710
H 0	-0.880684	2.763266	2.768731

SCF Done: E(RB3LYP) = -2135.09705077

Sum of electronic and zero-point Energies= -2134.785699

Sum of electronic and thermal Energies= -2134.763594

Sum of electronic and thermal Enthalpies= -2134.762649

Sum of electronic and thermal Free Energies= -2134.838949

6.1.4.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full

0 1

C 0	5.362803	-2.189689	-0.487769
C 0	4.518456	-3.207396	-0.017816
C 0	3.179184	-2.956799	0.251846
C 0	2.661364	-1.667177	0.044404
C 0	3.526817	-0.656168	-0.437578
C 0	4.872844	-0.903663	-0.699719
C 0	1.334293	-1.165200	0.279159
C 0	1.190748	0.153223	-0.034060
S 0	2.681936	0.876932	-0.649931
S 0	0.000009	-2.131176	0.976640
C 0	-1.334281	-1.165209	0.279157
C 0	-1.190744	0.153215	-0.034059
N 0	-0.000001	0.878386	0.007971
C 0	-2.661349	-1.667195	0.044400

C 0	-3.526808	-0.656190	-0.437581
S 0	-2.681937	0.876916	-0.649928
C 0	-3.179160	-2.956821	0.251835
C 0	-4.518429	-3.207427	-0.017829
C 0	-5.362783	-2.189724	-0.487781
C 0	-4.872833	-0.903694	-0.699725
C 0	-0.000007	2.321360	-0.003608
C 0	-0.000025	3.021599	1.214734
C 0	-0.000033	4.418935	1.153664
C 0	-0.000023	5.094538	-0.066176
C 0	-0.000005	4.381966	-1.262890
C 0	0.000003	2.989182	-1.228938
C 0	-0.000036	2.297758	2.536448
H 0	6.405524	-2.403868	-0.690754
H 0	4.917803	-4.202909	0.138625
H 0	2.534271	-3.748775	0.615529
H 0	5.522812	-0.117317	-1.065373
H 0	-2.534242	-3.748794	0.615517
H 0	-4.917770	-4.202943	0.138607
H 0	-6.405502	-2.403910	-0.690767
H 0	-5.522805	-0.117351	-1.065377
H 0	-0.000047	4.984706	2.079088
H 0	-0.000029	6.178589	-0.079494
H 0	0.000003	4.901132	-2.213861
H 0	0.000014	2.414258	-2.147702
H 0	-0.879246	1.655470	2.638503
H 0	0.879144	1.655431	2.638497
H 0	-0.000019	3.008262	3.363969

SCF Done: E(RB3LYP) = -2135.11318664

Sum of electronic and zero-point Energies= -2134.801951

Sum of electronic and thermal Energies= -2134.779904

Sum of electronic and thermal Enthalpies= -2134.778960

Sum of electronic and thermal Free Energies= -2134.854657

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full

0 1

C 0	5.421020	-2.099315	0.372352
C 0	4.566899	-3.182312	0.114088
C 0	3.210637	-2.985280	-0.112303
C 0	2.685053	-1.682096	-0.075715
C 0	3.562495	-0.603987	0.190662
C 0	4.924157	-0.798917	0.410775
C 0	1.337259	-1.233094	-0.296329
C 0	1.192923	0.117576	-0.179329
S 0	2.708954	0.937650	0.205909
S 0	-0.000050	-2.324784	-0.766879
C 0	-1.337324	-1.233059	-0.296310
C 0	-1.192950	0.117607	-0.179306
N 0	-0.000004	0.834812	-0.266916
C 0	-2.685126	-1.682027	-0.075670
C 0	-3.562535	-0.603897	0.190723
S 0	-2.708960	0.937720	0.205938
C 0	-3.210742	-2.985198	-0.112248
C 0	-4.567005	-3.182198	0.114172
C 0	-5.421094	-2.099179	0.372452
C 0	-4.924199	-0.798793	0.410863
C 0	0.000016	2.276872	-0.334478
C 0	0.000175	3.050870	0.837016
C 0	0.000171	4.445599	0.683670
C 0	0.000025	5.042821	-0.571547
C 0	-0.000121	4.254583	-1.724008
C 0	-0.000123	2.871233	-1.600860
C 0	0.000396	2.454203	2.223265
H 0	6.476623	-2.273062	0.544908
H 0	4.971752	-4.187544	0.089453
H 0	2.559571	-3.829177	-0.310777
H 0	5.581511	0.038953	0.611644
H 0	-2.559700	-3.829111	-0.310734
H 0	-4.971882	-4.187420	0.089545
H 0	-6.476698	-2.272901	0.545028

H 0	-5.581530	0.039093	0.611740
H 0	0.000293	5.067589	1.572749
H 0	0.000029	6.123920	-0.652780
H 0	-0.000234	4.713409	-2.705557
H 0	-0.000239	2.234708	-2.477916
H 0	0.000182	1.365556	2.209394
H 0	0.881337	2.785244	2.780089
H 0	-0.880137	2.785598	2.780520

SCF Done: E(RB3LYP) = -2135.11143582

Sum of electronic and zero-point Energies= -2134.800399

Sum of electronic and thermal Energies= -2134.778205

Sum of electronic and thermal Enthalpies= -2134.777261

Sum of electronic and thermal Free Energies= -2134.854511

6.1.4.4 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	5.344716	-2.155201	-0.497860
C 0	4.507130	-3.188708	-0.061249
C 0	3.169390	-2.955422	0.211165
C 0	2.647408	-1.666440	0.039723
C 0	3.505198	-0.638840	-0.407367
C 0	4.850483	-0.869837	-0.673238
C 0	1.321932	-1.180107	0.281832
C 0	1.182808	0.144674	0.003389
S 0	2.659908	0.882538	-0.576867
S 0	0.000000	-2.155049	0.950373
C 0	-1.321932	-1.180107	0.281831
C 0	-1.182807	0.144673	0.003389
N 0	-0.000000	0.865789	0.064431
C 0	-2.647408	-1.666441	0.039723
C 0	-3.505198	-0.638840	-0.407368
S 0	-2.659908	0.882538	-0.576868
C 0	-3.169389	-2.955423	0.211165
C 0	-4.507130	-3.188709	-0.061249
C 0	-5.344716	-2.155202	-0.497859
C 0	-4.850483	-0.869838	-0.673238
C 0	-0.000000	2.296573	-0.002816
C 0	-0.000001	3.033714	1.188273
C 0	-0.000001	4.424337	1.080966
C 0	-0.000001	5.055210	-0.158742
C 0	-0.000000	4.305111	-1.328634
C 0	0.000000	2.917877	-1.248449
C 0	-0.000001	2.348602	2.520901
H 0	6.390138	-2.357892	-0.704121
H 0	4.912723	-4.186801	0.067257
H 0	2.525815	-3.761175	0.550056
H 0	5.496821	-0.068189	-1.014349
H 0	-2.525814	-3.761175	0.550056
H 0	-4.912722	-4.186801	0.067257
H 0	-6.390137	-2.357893	-0.704121
H 0	-5.496821	-0.068190	-1.014349
H 0	-0.000002	5.021344	1.987977
H 0	-0.000001	6.139234	-0.209244
H 0	-0.000000	4.793153	-2.297062
H 0	0.000000	2.308929	-2.146816
H 0	-0.879410	1.707609	2.636627
H 0	0.879407	1.707609	2.636628
H 0	-0.000001	3.079348	3.331232

SCF Done: E(RPBE1PBE) = -2133.55187077

Sum of electronic and zero-point Energies= -2133.237778

Sum of electronic and thermal Energies= -2133.215828

Sum of electronic and thermal Enthalpies= -2133.214884

Sum of electronic and thermal Free Energies= -2133.290768

6.1.4.5 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent =dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.9850 eV 415.35 nm f=0.1496

<TDDFT>HOMO -> LUMO 96.0%

<TDDFT> Excited State 2: Singlet-A 3.5363 eV 350.60 nm f=0.0052

<TDDFT>HOMO -> LUMO+1 98.8%

<TDDFT> Excited State 3: Singlet-A 3.6699 eV 337.84 nm f=0.0034

<TDDFT>HOMO -> LUMO+2 87.4%

<TDDFT>HOMO -> LUMO+5 2.7%

<TDDFT>HOMO -> LUMO+7 5.1%

<TDDFT> Excited State 4: Singlet-A 3.8746 eV 320.00 nm f=0.0459

<TDDFT>HOMO -> LUMO+3 71.8%

<TDDFT>HOMO -> LUMO+4 22.7%

<TDDFT> Excited State 5: Singlet-A 3.8938 eV 318.42 nm f=0.0533

<TDDFT>HOMO -> LUMO+3 17.7%

<TDDFT>HOMO -> LUMO+4 70.9%

<TDDFT>HOMO -> LUMO+6 5.3%

<TDDFT>HOMO -> LUMO+8 2.4%

<TDDFT> Excited State 6: Singlet-A 3.9655 eV 312.66 nm f=0.0183

<TDDFT>HOMO -> LUMO+2 6.3%

<TDDFT>HOMO -> LUMO+5 85.3%

<TDDFT>HOMO -> LUMO+7 4.6%

<TDDFT> Excited State 7: Singlet-A 4.1012 eV 302.31 nm f=0.0112

<TDDFT>HOMO -> LUMO+2 4.2%

<TDDFT>HOMO -> LUMO+5 8.5%

<TDDFT>HOMO -> LUMO+7 74.8%

<TDDFT>HOMO -> LUMO+10 7.8%

<TDDFT> Excited State 8: Singlet-A 4.1557 eV 298.35 nm f=0.0318

<TDDFT>HOMO -> LUMO+3 6.0%

<TDDFT>HOMO -> LUMO+4 3.4%

<TDDFT>HOMO -> LUMO+6 49.8%

<TDDFT>HOMO -> LUMO+8 35.1%

<TDDFT> Excited State 9: Singlet-A 4.3336 eV 286.10 nm f=0.0097

<TDDFT>HOMO -> LUMO+6 35.4%

<TDDFT>HOMO -> LUMO+8 53.2%

<TDDFT>HOMO -> LUMO+9 3.8%

<TDDFT>HOMO -> LUMO+12 3.1%

<TDDFT> Excited State 10: Singlet-A 4.6028 eV 269.36 nm f=0.1243

<TDDFT>HOMO-2 -> LUMO+3 2.3%

<TDDFT>HOMO-1 -> LUMO 84.5%

<TDDFT> Excited State 11: Singlet-A 4.6095 eV 268.98 nm f=0.1374

<TDDFT>HOMO-3 -> LUMO+3 2.1%

<TDDFT>HOMO-2 -> LUMO 78.8%

<TDDFT>HOMO-1 -> LUMO+4 2.5%

<TDDFT>HOMO -> LUMO+10 3.4%

<TDDFT>HOMO -> LUMO+13 5.3%

<TDDFT>HOMO -> LUMO+15 2.1%

<TDDFT> Excited State 12: Singlet-A 4.7297 eV 262.14 nm f=0.0071

<TDDFT>HOMO-1 -> LUMO 2.0%

<TDDFT>HOMO -> LUMO+8 2.8%

<TDDFT>HOMO -> LUMO+9 84.6%

<TDDFT>HOMO -> LUMO+12 2.6%

<TDDFT>HOMO -> LUMO+14 3.1%

<TDDFT> Excited State 13: Singlet-A 4.8068 eV 257.94 nm f=0.2252

<TDDFT>HOMO-2 -> LUMO 7.7%

<TDDFT>HOMO -> LUMO+7 7.8%

<TDDFT>HOMO -> LUMO+10 63.7%

<TDDFT>HOMO -> LUMO+13 11.3%

<TDDFT> Excited State 14: Singlet-A 4.9620 eV 249.87 nm f=0.0007

<TDDFT>HOMO-3 -> LUMO 16.3%

<TDDFT>HOMO-2 -> LUMO+3 7.3%

<TDDFT>HOMO-2 -> LUMO+4 2.3%

<TDDFT>HOMO-1 -> LUMO+1 59.5%

<TDDFT>HOMO-1 -> LUMO+5 2.1%

<TDDFT> Excited State 15: Singlet-A 4.9835 eV 248.79 nm f=0.1302

<TDDFT>HOMO-2 -> LUMO 2.5%

<TDDFT>HOMO -> LUMO+7 3.6%

<TDDFT>HOMO -> LUMO+10 11.9%

<TDDFT>HOMO -> LUMO+13 48.3%

<TDDFT>HOMO -> LUMO+15 25.4%

<TDDFT> Excited State 16: Singlet-A 5.0129 eV 247.33 nm f=0.0041

<TDDFT>HOMO -> LUMO+11 89.3%

<TDDFT> Excited State 17: Singlet-A 5.0432 eV 245.85 nm f=0.0107

<TDDFT>HOMO-3 -> LUMO 20.8%

<TDDFT>HOMO-2 -> LUMO+6 3.7%

<TDDFT>HOMO-1 -> LUMO+1 16.6%

<TDDFT>HOMO-1 -> LUMO+2 43.8%

<TDDFT>HOMO-1 -> LUMO+5 3.4%

<TDDFT> Excited State 18: Singlet-A 5.0614 eV 244.96 nm f=0.0150

<TDDFT>HOMO-2 -> LUMO+1 43.4%

<TDDFT>HOMO-2 -> LUMO+2 17.8%

<TDDFT>HOMO-2 -> LUMO+7 3.3%

<TDDFT>HOMO-1 -> LUMO+3 8.3%

<TDDFT>HOMO-1 -> LUMO+4 10.3%

<TDDFT>HOMO-1 -> LUMO+6 4.3%

<TDDFT> Excited State 19: Singlet-A 5.0918 eV 243.50 nm f=0.0112

<TDDFT>HOMO-1 -> LUMO+1 2.1%

<TDDFT>HOMO -> LUMO+8 3.7%

<TDDFT>HOMO -> LUMO+12 81.4%

<TDDFT>HOMO -> LUMO+17 3.6%

<TDDFT> Excited State 20: Singlet-A 5.1433 eV 241.06 nm f=0.0003

<TDDFT>HOMO-5 -> LUMO 2.9%

<TDDFT>HOMO-2 -> LUMO+1 44.4%

<TDDFT>HOMO-2 -> LUMO+2 13.3%

<TDDFT>HOMO-1 -> LUMO+3 28.1%

<TDDFT>HOMO-1 -> LUMO+4 2.2%

<TDDFT> Excited State 21: Singlet-A 5.1708 eV 239.78 nm f=0.0522

<TDDFT>HOMO-4 -> LUMO+1 2.3%

<TDDFT>HOMO-3 -> LUMO 17.0%

<TDDFT>HOMO-2 -> LUMO+3 6.7%

<TDDFT>HOMO-2 -> LUMO+4 2.6%

<TDDFT>HOMO-2 -> LUMO+6 2.7%

<TDDFT>HOMO-1 -> LUMO+1 13.9%

<TDDFT>HOMO-1 -> LUMO+2 29.0%

<TDDFT>HOMO-1 -> LUMO+5 2.6%

<TDDFT>HOMO-1 -> LUMO+7 8.6%

<TDDFT>HOMO -> LUMO+12 2.5%

<TDDFT>HOMO -> LUMO+14 2.8%

<TDDFT> Excited State 22: Singlet-A 5.1956 eV 238.63 nm f=0.0149

<TDDFT>HOMO -> LUMO+9 3.9%

<TDDFT>HOMO -> LUMO+14 85.6%

<TDDFT> Excited State 23: Singlet-A 5.2389 eV 236.66 nm f=0.0002

<TDDFT>HOMO-5 -> LUMO 2.0%

<TDDFT>HOMO-2 -> LUMO+2 5.4%

<TDDFT>HOMO-1 -> LUMO+3 6.0%

<TDDFT>HOMO-1 -> LUMO+4 4.2%

<TDDFT>HOMO -> LUMO+10 3.0%

<TDDFT>HOMO -> LUMO+13 15.1%

<TDDFT>HOMO -> LUMO+15 39.9%

<TDDFT>HOMO -> LUMO+16 3.3%

<TDDFT>HOMO -> LUMO+22 5.5%

<TDDFT>HOMO -> LUMO+23 4.1%

<TDDFT> Excited State 24: Singlet-A 5.2833 eV 234.67 nm f=0.0110

<TDDFT>HOMO-6 -> LUMO+2 4.0%

<TDDFT>HOMO-4 -> LUMO 7.4%

<TDDFT>HOMO-4 -> LUMO+1 5.1%

<TDDFT>HOMO-3 -> LUMO 17.7%

<TDDFT>HOMO-3 -> LUMO+1 5.9%

<TDDFT>HOMO-2 -> LUMO+3 25.0%

<TDDFT>HOMO-2 -> LUMO+4 4.4%

<TDDFT>HOMO-2 -> LUMO+6 5.3%

<TDDFT>HOMO-1 -> LUMO+1 3.9%

<TDDFT>HOMO-1 -> LUMO+2 4.8%

<TDDFT>HOMO-1 -> LUMO+7 2.5%

6.1.4.6 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.475218	-2.026254	-0.030038
C 0	4.618362	-3.127361	0.044921
C 0	3.241415	-2.968910	0.041452
C 0	2.688683	-1.676071	-0.038313
C 0	3.576580	-0.573445	-0.114776
C 0	4.950911	-0.734082	-0.111809
C 0	1.329279	-1.261535	-0.058642
C 0	1.185279	0.143979	-0.158161
S 0	2.728861	0.972553	-0.212295
S 0	-0.000000	-2.340126	0.085118
C 0	-1.329280	-1.261535	-0.058642
C 0	-1.185279	0.143979	-0.158161
N 0	-0.000000	0.808888	-0.185228
C 0	-2.688684	-1.676071	-0.038312
C 0	-3.576580	-0.573444	-0.114776
S 0	-2.728861	0.972553	-0.212294
C 0	-3.241415	-2.968910	0.041452
C 0	-4.618363	-3.127361	0.044921
C 0	-5.475218	-2.026254	-0.030039
C 0	-4.950912	-0.734082	-0.111809
C 0	0.000000	2.248881	-0.184369
C 0	0.000001	2.923851	1.040713
C 0	0.000000	4.317915	0.988105
C 0	0.000000	4.998578	-0.224652

C 0	-0.000000	4.298739	-1.425812
C 0	-0.000000	2.910121	-1.406294
C 0	0.000001	2.182286	2.342347
H 0	6.550006	-2.170022	-0.025297
H 0	5.036680	-4.126934	0.106659
H 0	2.592566	-3.837384	0.099020
H 0	5.610004	0.125719	-0.170790
H 0	-2.592566	-3.837384	0.099020
H 0	-5.036680	-4.126934	0.106658
H 0	-6.550006	-2.170021	-0.025298
H 0	-5.610004	0.125719	-0.170790
H 0	0.000001	4.876021	1.919221
H 0	0.000000	6.083591	-0.229980
H 0	-0.000000	4.827192	-2.372562
H 0	-0.000000	2.333981	-2.325287
H 0	-0.881189	1.538815	2.429992
H 0	0.881192	1.538815	2.429991
H 0	0.000002	2.878845	3.181739

SCF Done: E(RPBE1PBE) = -2133.53993211

Sum of electronic and zero-point Energies= -2133.149497

Sum of electronic and thermal Energies= -2133.126527

Sum of electronic and thermal Enthalpies= -2133.125583

Sum of electronic and thermal Free Energies= -2133.204208

6.1.4.7 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.1923 eV 565.53 nm f=0.1246

<TDDFT>HOMO -> LUMO 98.3%

<TDDFT> Excited State 2: Singlet-A 2.9524 eV 419.94 nm f=0.0013

<TDDFT>HOMO -> LUMO+1 98.5%

<TDDFT> Excited State 3: Singlet-A 3.2658 eV 379.64 nm f=0.0000

<TDDFT>HOMO -> LUMO+2 96.7%

<TDDFT> Excited State 4: Singlet-A 3.4058 eV 364.04 nm f=0.0045

<TDDFT>HOMO -> LUMO+3 54.7%

<TDDFT>HOMO -> LUMO+5 29.0%

<TDDFT>HOMO -> LUMO+6 13.5%

6.1.4.8 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.370397	-2.186769	-0.468608
C 0	4.524156	-3.202809	0.001736
C 0	3.182319	-2.953346	0.260102
C 0	2.663564	-1.666023	0.039334
C 0	3.531566	-0.657162	-0.442638
C 0	4.880108	-0.902878	-0.693310
C 0	1.335051	-1.162670	0.265138
C 0	1.190207	0.154011	-0.055024
S 0	2.685271	0.874389	-0.669210
S 0	-0.000107	-2.125271	0.967064
C 0	-1.335121	-1.162662	0.264877
C 0	-1.190209	0.154022	-0.055246
N 0	-0.000001	0.879107	-0.020733

C 0	-2.663593	-1.666006	0.038816
C 0	-3.531501	-0.657131	-0.443298
S 0	-2.685157	0.874419	-0.669691
C 0	-3.182397	-2.953330	0.259461
C 0	-4.524185	-3.202783	0.000832
C 0	-5.370333	-2.186729	-0.469653
C 0	-4.879996	-0.902835	-0.694233
C 0	0.000004	2.323597	-0.007462
C 0	-0.000035	3.003536	1.223126
C 0	-0.000029	4.402050	1.184027
C 0	0.000010	5.097144	-0.025025
C 0	0.000048	4.404110	-1.233377
C 0	0.000046	3.010664	-1.222382
C 0	-0.000079	2.260043	2.532798
H 0	6.415219	-2.400812	-0.662367
H 0	4.924148	-4.196776	0.168092
H 0	2.538401	-3.745887	0.625153
H 0	5.532344	-0.117770	-1.058882
H 0	-2.538553	-3.745884	0.624617
H 0	-4.924213	-4.196752	0.167089
H 0	-6.415118	-2.400766	-0.663620
H 0	-5.532157	-0.117717	-1.059918
H 0	-0.000057	4.951643	2.119519
H 0	0.000012	6.181754	-0.020782
H 0	0.000080	4.938537	-2.176308
H 0	0.000079	2.451414	-2.151188
H 0	-0.879846	1.616287	2.626563
H 0	0.879669	1.616269	2.626610
H 0	-0.000095	2.959855	3.369981

SCF Done: E(RB3LYP) = -2135.13751008

Sum of electronic and zero-point Energies= -2134.826212

Sum of electronic and thermal Energies= -2134.804308

Sum of electronic and thermal Enthalpies= -2134.803364

Sum of electronic and thermal Free Energies= -2134.877863

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.440795	-2.091250	0.321353
C 0	4.584857	-3.176899	0.080820
C 0	3.222996	-2.985130	-0.115788
C 0	2.693464	-1.683481	-0.066801
C 0	3.573797	-0.603170	0.180579
C 0	4.940611	-0.792386	0.371256
C 0	1.339704	-1.237573	-0.258341
C 0	1.192727	0.112850	-0.139867
S 0	2.715604	0.936267	0.213480
S 0	0.000000	-2.340002	-0.699089
C 0	-1.339704	-1.237573	-0.258341
C 0	-1.192727	0.112850	-0.139867
N 0	-0.000000	0.830685	-0.205778
C 0	-2.693464	-1.683482	-0.066801
C 0	-3.573797	-0.603170	0.180580
S 0	-2.715604	0.936267	0.213480
C 0	-3.222996	-2.985131	-0.115788
C 0	-4.584857	-3.176900	0.080821
C 0	-5.440794	-2.091251	0.321353
C 0	-4.940611	-0.792387	0.371256
C 0	-0.000000	2.271415	-0.316019
C 0	-0.000000	3.077687	0.833807
C 0	-0.000001	4.468018	0.639872
C 0	-0.000001	5.028539	-0.632178
C 0	-0.000001	4.207546	-1.762085
C 0	-0.000001	2.828263	-1.599820
C 0	0.000001	2.520566	2.235559
H 0	6.500771	-2.261572	0.470753
H 0	4.992582	-4.180949	0.046382
H 0	2.573962	-3.833769	-0.302039
H 0	5.599734	0.047743	0.558338
H 0	-2.573961	-3.833769	-0.302039

H 0	-4.992581	-4.180950	0.046383
H 0	-6.500771	-2.261573	0.470753
H 0	-5.599734	0.047742	0.558338
H 0	-0.000000	5.115134	1.511099
H 0	-0.000001	6.107182	-0.744481
H 0	-0.000002	4.638488	-2.756560
H 0	-0.000001	2.166381	-2.458453
H 0	0.000000	1.431327	2.254578
H 0	0.880700	2.867781	2.784047
H 0	-0.880697	2.867782	2.784049

SCF Done: E(RB3LYP) = -2135.13544694

Sum of electronic and zero-point Energies= -2134.824337

Sum of electronic and thermal Energies= -2134.802312

Sum of electronic and thermal Enthalpies= -2134.801368

Sum of electronic and thermal Free Energies= -2134.877383

6.1.4.9 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p ub3lyp/6-311++g(d,p) opt=loose freq=noraman scf=maxcycle=1000 geom=check guess=read

0 1

C 0	5.479982	-2.022887	-0.041112
C 0	4.627774	-3.136056	0.027380
C 0	3.251971	-2.977261	0.033436
C 0	2.712131	-1.680626	-0.029036
C 0	3.586851	-0.572880	-0.097212
C 0	4.969078	-0.730552	-0.105141
C 0	1.337860	-1.262942	-0.035212
C 0	1.192417	0.115946	-0.106637
S 0	2.720714	0.964949	-0.176234
S 0	-0.000003	-2.381419	0.047456
C 0	-1.337864	-1.262941	-0.035215
C 0	-1.192420	0.115949	-0.106635
N 0	-0.000001	0.799830	-0.123013
C 0	-2.712135	-1.680622	-0.029034
C 0	-3.586854	-0.572874	-0.097200
S 0	-2.720715	0.964953	-0.176218
C 0	-3.251978	-2.977257	0.033431
C 0	-4.627780	-3.136050	0.027378
C 0	-5.479987	-2.022879	-0.041105
C 0	-4.969082	-0.730544	-0.105126
C 0	-0.000000	2.258115	-0.173445
C 0	0.000017	2.984387	1.026936
C 0	0.000018	4.378581	0.909841
C 0	0.000000	5.007513	-0.332755
C 0	-0.000019	4.255991	-1.506138
C 0	-0.000019	2.867820	-1.427393
C 0	0.000038	2.312169	2.376354
H 0	6.553212	-2.169632	-0.045190
H 0	5.052543	-4.131034	0.075544
H 0	2.603285	-3.844241	0.085612
H 0	5.631865	0.124345	-0.159306
H 0	-2.603293	-3.844238	0.085600
H 0	-5.052551	-4.131027	0.075536
H 0	-6.553218	-2.169621	-0.045180
H 0	-5.631868	0.124354	-0.159284
H 0	0.000032	4.977794	1.813243
H 0	0.000002	6.089883	-0.384291
H 0	-0.000033	4.742962	-2.473326
H 0	-0.000032	2.259571	-2.324451
H 0	0.882442	1.680144	2.512609
H 0	-0.000007	3.055564	3.173149
H 0	-0.882303	1.680052	2.512591

SCF Done: E(UB3LYP) = -2134.88741231

Sum of electronic and zero-point Energies= -2134.575442

Sum of electronic and thermal Energies= -2134.553485

Sum of electronic and thermal Enthalpies= -2134.552541

Sum of electronic and thermal Free Energies= -2134.628090

6.1.4.10 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt=verytight int=ultrafine freq=noraman scf=maxcycle=1000 scrf=(iefpcm,solvent=dichloromethane)

0 1

C 0	5.479780	-2.020926	-0.036582
C 0	4.627067	-3.134361	0.028375
C 0	3.250377	-2.975768	0.032876
C 0	2.710931	-1.679181	-0.028660
C 0	3.585284	-0.571063	-0.094113
C 0	4.968404	-0.728407	-0.099027
C 0	1.335519	-1.263065	-0.036033
C 0	1.191041	0.115075	-0.105256
S 0	2.718405	0.965288	-0.172613
S 0	0.000160	-2.381997	0.035828
C 0	-1.335304	-1.263204	-0.036410
C 0	-1.190995	0.114940	-0.105918
N 0	0.000011	0.798659	-0.122205
C 0	-2.710654	-1.679517	-0.029003
C 0	-3.585131	-0.571523	-0.094790
S 0	-2.718504	0.964913	-0.173545
C 0	-3.249948	-2.976144	0.033070
C 0	-4.626616	-3.134885	0.028750
C 0	-5.479466	-2.021566	-0.036547
C 0	-4.968246	-0.729025	-0.099541
C 0	-0.000204	2.255773	-0.173998
C 0	-0.002361	2.983671	1.025506
C 0	-0.002617	4.377969	0.906634
C 0	-0.000337	5.005048	-0.337433
C 0	0.001411	4.251369	-1.509797
C 0	0.001261	2.862847	-1.428830
C 0	-0.000258	2.313497	2.375290
H 0	6.553116	-2.167053	-0.038607
H 0	5.051054	-4.129812	0.075689
H 0	2.601249	-3.842046	0.083240
H 0	5.629949	0.127350	-0.149711
H 0	-2.600722	-3.842329	0.083760
H 0	-5.050494	-4.130361	0.076510
H 0	-6.552786	-2.167814	-0.038385
H 0	-5.629889	0.126645	-0.150432
H 0	-0.004888	4.978049	1.809380
H 0	-0.000680	6.087446	-0.390373
H 0	0.002504	4.735990	-2.478143
H 0	0.002148	2.251540	-2.323239
H 0	0.912570	1.731363	2.531661
H 0	-0.060655	3.058218	3.168639
H 0	-0.847180	1.631583	2.489348

SCF Done: E(UB3LYP) = -2134.93771925

Sum of electronic and zero-point Energies= -2134.625756

Sum of electronic and thermal Energies= -2134.603785

Sum of electronic and thermal Enthalpies= -2134.602841

Sum of electronic and thermal Free Energies= -2134.678469

6.1.4.11 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(SMD,solvent=dichloromethane)

0 1

C 0	5.476193	-2.031474	-0.057648
C 0	4.620559	-3.142550	0.010163
C 0	3.244378	-2.980272	0.027139

C 0	2.709610	-1.681100	-0.024307
C 0	3.587064	-0.575941	-0.095063
C 0	4.969440	-0.736379	-0.112198
C 0	1.336164	-1.260619	-0.019392
C 0	1.190257	0.117106	-0.084806
S 0	2.721531	0.963591	-0.164087
S 0	-0.000047	-2.379216	0.062979
C 0	-1.336222	-1.260583	-0.019403
C 0	-1.190278	0.117146	-0.084849
N 0	0.000000	0.801268	-0.093580
C 0	-2.709679	-1.681020	-0.024283
C 0	-3.587100	-0.575831	-0.095023
S 0	-2.721524	0.963655	-0.164073
C 0	-3.244482	-2.980179	0.027143
C 0	-4.620667	-3.142421	0.010171
C 0	-5.476269	-2.031319	-0.057618
C 0	-4.969483	-0.736238	-0.112157
C 0	0.000029	2.258386	-0.165852
C 0	0.000102	3.005675	1.022350
C 0	0.000161	4.398087	0.878847
C 0	0.000120	5.003607	-0.375881
C 0	0.000031	4.230258	-1.535796
C 0	-0.000016	2.843210	-1.432039
C 0	0.000132	2.362603	2.384355
H 0	6.549255	-2.181560	-0.068841
H 0	5.042047	-4.139752	0.049686
H 0	2.593629	-3.846013	0.078772
H 0	5.635190	0.116755	-0.165609
H 0	-2.593753	-3.845934	0.078783
H 0	-5.042186	-4.139610	0.049674
H 0	-6.549336	-2.181372	-0.068812
H 0	-5.635219	0.116909	-0.165536
H 0	0.000225	5.011739	1.772782
H 0	0.000149	6.085406	-0.447197
H 0	0.000014	4.698642	-2.512593
H 0	-0.000073	2.216071	-2.316306
H 0	0.881214	1.731551	2.534098
H 0	0.000135	3.127370	3.161787
H 0	-0.880919	1.731542	2.534155

SCF Done: E(UB3LYP) = -2134.96539898

Sum of electronic and zero-point Energies= -2134.653590

Sum of electronic and thermal Energies= -2134.631758

Sum of electronic and thermal Enthalpies= -2134.630814

Sum of electronic and thermal Free Energies= -2134.705727

6.1.4.12 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311G**, IEFPCM CH_2Cl_2)

#p opt=qst2 freq=noraman b3lyp/6-311g** scrf=(iefpcm,solvent=dichloromethane)

0 1

C 0	5.435800	-2.064830	0.346222
C 0	4.582331	-3.157697	0.134958
C 0	3.222906	-2.972582	-0.076419
C 0	2.692958	-1.670956	-0.072404
C 0	3.570220	-0.582722	0.146357
C 0	4.935199	-0.766302	0.351710
C 0	1.340523	-1.233968	-0.284326
C 0	1.192586	0.118447	-0.205330
S 0	2.710998	0.956032	0.125465
S 0	0.005927	-2.347008	-0.714605
C 0	-1.334983	-1.241331	-0.286227
C 0	-1.194324	0.112033	-0.209877
N 0	-0.002567	0.831120	-0.303024
C 0	-2.683834	-1.685543	-0.066708
C 0	-3.565735	-0.601944	0.156500
S 0	-2.715389	0.941766	0.131391
C 0	-3.206379	-2.990180	-0.066470
C 0	-4.563444	-3.182714	0.152893
C 0	-5.421844	-2.094383	0.367886

C 0	-4.928590	-0.793091	0.369367
C 0	-0.010216	2.274396	-0.326190
C 0	0.006295	3.009464	0.871709
C 0	-0.011210	4.406679	0.765245
C 0	-0.040316	5.044893	-0.470052
C 0	-0.056634	4.296453	-1.646621
C 0	-0.043079	2.909303	-1.570519
C 0	0.061507	2.357424	2.231398
H 0	6.494518	-2.229697	0.507430
H 0	4.990624	-4.161745	0.135437
H 0	2.571613	-3.823991	-0.238116
H 0	5.592078	0.079679	0.516212
H 0	-2.551125	-3.837995	-0.231011
H 0	-4.966095	-4.189032	0.156788
H 0	-6.478661	-2.265085	0.535380
H 0	-5.589294	0.049275	0.537072
H 0	-0.004743	4.998777	1.674032
H 0	-0.054200	6.127877	-0.515049
H 0	-0.082183	4.787592	-2.611910
H 0	-0.058299	2.302000	-2.467656
H 0	-0.343818	1.346004	2.223173
H 0	1.094888	2.294323	2.586197
H 0	-0.500340	2.946444	2.958566

SCF Done: E(RB3LYP) = -2135.09696437

Sum of electronic and zero-point Energies= -2134.785833

Sum of electronic and thermal Energies= -2134.764501

Sum of electronic and thermal Enthalpies= -2134.763557

Sum of electronic and thermal Free Energies= -2134.837566

6.1.5 *anti-anti-N-ortho*-methoxyphenyl-BBTT 3e

6.1.5.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.393485	-2.291213	-0.350344
C 0	4.542664	-3.254784	0.210562
C 0	3.194421	-2.988656	0.406643
C 0	2.674077	-1.739139	0.032837
C 0	3.545919	-0.783271	-0.539609
C 0	4.900747	-1.045800	-0.728084
C 0	1.335555	-1.229485	0.166831
C 0	1.192847	0.039588	-0.302719
S 0	2.696819	0.702450	-0.955470
S 0	-0.000130	-2.142400	0.924180
C 0	-1.335721	-1.229406	0.166735
C 0	-1.192880	0.039649	-0.302812
N 0	-0.000003	0.758541	-0.406478
C 0	-2.674299	-1.738924	0.032879
C 0	-3.546114	-0.783022	-0.539525
S 0	-2.696899	0.702665	-0.955562
C 0	-3.194744	-2.988344	0.406896
C 0	-4.543035	-3.254319	0.211068
C 0	-5.393834	-2.290708	-0.349827
C 0	-4.900993	-1.045401	-0.727791
C 0	0.000060	2.192687	-0.354147
C 0	0.000349	2.843818	0.897864
C 0	0.000385	4.240509	0.937547
C 0	0.000104	4.971340	-0.251445
C 0	-0.000210	4.331451	-1.485695
C 0	-0.000233	2.937122	-1.528258
O 0	0.000526	2.037073	1.984306
C 0	0.001004	2.625091	3.281478
H 0	6.443632	-2.516771	-0.494809
H 0	4.944107	-4.220575	0.495527
H 0	2.542176	-3.739152	0.838640
H 0	5.556153	-0.301095	-1.164866
H 0	-2.542482	-3.738904	0.838765

H 0	-4.944578	-4.219991	0.496228
H 0	-6.444034	-2.516161	-0.494083
H 0	-5.556365	-0.300684	-1.164564
H 0	0.000604	4.763083	1.884616
H 0	0.000130	6.054491	-0.202291
H 0	-0.000434	4.904633	-2.404488
H 0	-0.000451	2.409319	-2.474976
H 0	0.001235	1.790866	3.980028
H 0	0.896674	3.234198	3.439837
H 0	-0.894530	3.234234	3.440476

SCF Done: E(RB3LYP) = -2210.33289189

Sum of electronic and zero-point Energies= -2210.016485

Sum of electronic and thermal Energies= -2209.993563

Sum of electronic and thermal Enthalpies= -2209.992618

Sum of electronic and thermal Free Energies= -2210.070487

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.405909	-2.165118	0.446123
C 0	4.550997	-3.266490	0.293773
C 0	3.198790	-3.090734	0.033144
C 0	2.677683	-1.790753	-0.074410
C 0	3.554915	-0.692973	0.088548
C 0	4.912651	-0.867730	0.343661
C 0	1.333962	-1.365280	-0.355942
C 0	1.193140	-0.010778	-0.379489
S 0	2.705625	0.841953	-0.065652
S 0	-0.000009	-2.491818	-0.735012
C 0	-1.333828	-1.365225	-0.355831
C 0	-1.192998	-0.010711	-0.379348
N 0	0.000100	0.691504	-0.584754
C 0	-2.677649	-1.790645	-0.074707
C 0	-3.554928	-0.692870	0.087881
S 0	-2.705553	0.842044	-0.066159
C 0	-3.198829	-3.090657	0.032798
C 0	-4.550940	-3.266402	0.293275
C 0	-5.405935	-2.165034	0.445358
C 0	-4.912709	-0.867643	0.342811
C 0	0.000230	2.124884	-0.643118
C 0	-0.000487	2.882991	0.547932
C 0	-0.000298	4.279084	0.463789
C 0	0.000753	4.902608	-0.783277
C 0	0.001617	4.156321	-1.957584
C 0	0.001342	2.765489	-1.877859
O 0	-0.001201	2.179020	1.703569
C 0	-0.001794	2.882578	2.941896
H 0	6.459054	-2.322604	0.646894
H 0	4.952525	-4.269752	0.379973
H 0	2.543967	-3.947204	-0.080232
H 0	5.570726	-0.014790	0.463568
H 0	-2.543925	-3.947115	-0.080311
H 0	-4.952481	-4.269655	0.379573
H 0	-6.459234	-2.322520	0.645985
H 0	-5.570902	-0.014709	0.462452
H 0	-0.000889	4.881835	1.361822
H 0	0.000906	5.985893	-0.829252
H 0	0.002488	4.647044	-2.922950
H 0	0.001949	2.154323	-2.772738
H 0	-0.002268	2.115801	3.713823
H 0	0.893959	3.503139	3.044828
H 0	-0.897546	3.503294	3.043900

SCF Done: E(RB3LYP) = -2210.33189974

Sum of electronic and zero-point Energies= -2210.015672

Sum of electronic and thermal Energies= -2209.992704

Sum of electronic and thermal Enthalpies= -2209.991760

Sum of electronic and thermal Free Energies= -2210.069766

6.1.5.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	5.399623	-2.292874	-0.355132
C 0	4.549870	-3.271498	0.182669
C 0	3.199615	-3.013517	0.382216
C 0	2.676771	-1.756526	0.034626
C 0	3.548392	-0.785055	-0.512928
C 0	4.904693	-1.039306	-0.705582
C 0	1.336859	-1.252512	0.175975
C 0	1.191962	0.028270	-0.263683
S 0	2.696475	0.710273	-0.894185
S 0	0.000050	-2.183058	0.915004
C 0	-1.336779	-1.252574	0.175937
C 0	-1.191927	0.028214	-0.263720
N 0	0.000002	0.747151	-0.344966
C 0	-2.676672	-1.756635	0.034579
C 0	-3.548324	-0.785194	-0.512980
S 0	-2.696443	0.710138	-0.894302
C 0	-3.199479	-3.013635	0.382189
C 0	-4.549727	-3.271657	0.182655
C 0	-5.399512	-2.293064	-0.355153
C 0	-4.904620	-1.039485	-0.705618
C 0	-0.000036	2.183285	-0.354408
C 0	-0.000109	2.884107	0.870627
C 0	-0.000149	4.282134	0.850733
C 0	-0.000112	4.961534	-0.368368
C 0	-0.000039	4.270631	-1.576419
C 0	-0.000002	2.876015	-1.561128
O 0	-0.000132	2.126001	1.992113
C 0	-0.000242	2.779027	3.265944
H 0	6.450710	-2.512004	-0.501956
H 0	4.953361	-4.242016	0.447811
H 0	2.550914	-3.775608	0.799114
H 0	5.559281	-0.283269	-1.123143
H 0	-2.550754	-3.775701	0.799097
H 0	-4.953190	-4.242184	0.447812
H 0	-6.450593	-2.512227	-0.501972
H 0	-5.559230	-0.283475	-1.123194
H 0	-0.000206	4.844795	1.774271
H 0	-0.000143	6.045634	-0.364279
H 0	-0.000011	4.804946	-2.518256
H 0	0.000050	2.310546	-2.485826
H 0	-0.000259	1.979512	4.003268
H 0	0.895137	3.393649	3.391388
H 0	-0.895684	3.393580	3.391269

SCF Done: E(RB3LYP) = -2210.34223081

Sum of electronic and zero-point Energies= -2210.025957

Sum of electronic and thermal Energies= -2210.003009

Sum of electronic and thermal Enthalpies= -2210.002065

Sum of electronic and thermal Free Energies= -2210.079986

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	5.429356	-2.145858	0.401488
C 0	4.574286	-3.252925	0.289866
C 0	3.215297	-3.086142	0.055180
C 0	2.688232	-1.788844	-0.067171
C 0	3.566802	-0.685693	0.051918
C 0	4.930596	-0.850989	0.282355
C 0	1.336716	-1.371149	-0.323635
C 0	1.192233	-0.016775	-0.375071
S 0	2.710523	0.844540	-0.119776

S 0	-0.000012	-2.516268	-0.641740
C 0	-1.336726	-1.371137	-0.323624
C 0	-1.192235	-0.016764	-0.375064
N 0	0.000001	0.684931	-0.570949
C 0	-2.688247	-1.788823	-0.067172
C 0	-3.566812	-0.685666	0.051904
S 0	-2.710522	0.844560	-0.119792
C 0	-3.215321	-3.086117	0.055185
C 0	-4.574313	-3.252890	0.289861
C 0	-5.429377	-2.145818	0.401471
C 0	-4.930608	-0.850952	0.282335
C 0	0.000013	2.120888	-0.625400
C 0	0.000003	2.873065	0.569590
C 0	0.000016	4.269960	0.489071
C 0	0.000044	4.896565	-0.756576
C 0	0.000057	4.154160	-1.934937
C 0	0.000041	2.763114	-1.860287
O 0	-0.000014	2.166703	1.723887
C 0	-0.000015	2.875108	2.967818
H 0	6.487016	-2.296391	0.583183
H 0	4.980477	-4.253205	0.387516
H 0	2.563269	-3.948329	-0.027941
H 0	5.588344	0.005781	0.370769
H 0	-2.563298	-3.948309	-0.027926
H 0	-4.980511	-4.253167	0.387515
H 0	-6.487039	-2.296344	0.583160
H 0	-5.588352	0.005822	0.370739
H 0	0.000009	4.870715	1.388177
H 0	0.000055	5.979851	-0.798557
H 0	0.000079	4.648171	-2.898540
H 0	0.000049	2.156275	-2.758159
H 0	-0.000024	2.108864	3.739628
H 0	0.895424	3.494445	3.066145
H 0	-0.895446	3.494458	3.066137

SCF Done: E(RB3LYP) = -2210.34142489

Sum of electronic and zero-point Energies= -2210.025311

Sum of electronic and thermal Energies= -2210.002325

Sum of electronic and thermal Enthalpies= -2210.001381

Sum of electronic and thermal Free Energies= -2210.079561

6.1.5.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	5.387782	-2.259165	-0.343468
C 0	4.542856	-3.256753	0.157325
C 0	3.192073	-3.017033	0.348352
C 0	2.665180	-1.758626	0.028870
C 0	3.530905	-0.767318	-0.480257
C 0	4.888555	-1.004212	-0.665187
C 0	1.325034	-1.271412	0.167461
C 0	1.184577	0.018224	-0.241194
S 0	2.677659	0.718626	-0.826850
S 0	0.000001	-2.218513	0.868968
C 0	-1.325033	-1.271412	0.167461
C 0	-1.184577	0.018224	-0.241194
N 0	0.000000	0.733227	-0.314651
C 0	-2.665178	-1.758627	0.028870
C 0	-3.530904	-0.767319	-0.480257
S 0	-2.677659	0.718626	-0.826848
C 0	-3.192071	-3.017035	0.348351
C 0	-4.542854	-3.256755	0.157323
C 0	-5.387780	-2.259168	-0.343471
C 0	-4.888554	-1.004215	-0.665189
C 0	-0.000000	2.158113	-0.359052
C 0	-0.000001	2.880483	0.848419

C 0	-0.000002	4.274131	0.799298
C 0	-0.000001	4.924722	-0.431349
C 0	0.000001	4.211537	-1.622631
C 0	0.000001	2.821280	-1.578347
O 0	-0.000002	2.149315	1.976154
C 0	-0.000005	2.833651	3.219168
H 0	6.443188	-2.466011	-0.484477
H 0	4.952732	-4.231355	0.400962
H 0	2.543128	-3.795270	0.737623
H 0	5.541276	-0.230691	-1.055463
H 0	-2.543125	-3.795271	0.737622
H 0	-4.952729	-4.231358	0.400959
H 0	-6.443185	-2.466015	-0.484480
H 0	-5.541275	-0.230695	-1.055465
H 0	-0.000003	4.856776	1.712171
H 0	-0.000001	6.009755	-0.449980
H 0	0.000001	4.727248	-2.575877
H 0	0.000001	2.232836	-2.490261
H 0	-0.000007	2.058920	3.983667
H 0	0.895560	3.453153	3.328090
H 0	-0.895572	3.453152	3.328086

SCF Done: E(RPBE1PBE) = -2208.70360407

Sum of electronic and zero-point Energies= -2208.384268

Sum of electronic and thermal Energies= -2208.361433

Sum of electronic and thermal Enthalpies= -2208.360489

Sum of electronic and thermal Free Energies= -2208.438911

6.1.5.4 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.9331 eV 422.71 nm f=0.1434

<TDDFT>HOMO -> LUMO 96.3%

<TDDFT> Excited State 2: Singlet-A 3.4963 eV 354.61 nm f=0.0080

<TDDFT>HOMO -> LUMO+1 98.7%

<TDDFT> Excited State 3: Singlet-A 3.6869 eV 336.28 nm f=0.0093

<TDDFT>HOMO -> LUMO+3 84.6%

<TDDFT>HOMO -> LUMO+7 8.0%

<TDDFT>HOMO -> LUMO+10 2.7%

<TDDFT> Excited State 4: Singlet-A 3.8339 eV 323.39 nm f=0.0455

<TDDFT>HOMO -> LUMO+2 66.2%

<TDDFT>HOMO -> LUMO+4 28.4%

<TDDFT> Excited State 5: Singlet-A 3.8418 eV 322.72 nm f=0.0589

<TDDFT>HOMO -> LUMO+2 22.5%

<TDDFT>HOMO -> LUMO+4 66.2%

<TDDFT>HOMO -> LUMO+6 5.6%

<TDDFT>HOMO -> LUMO+8 2.3%

<TDDFT> Excited State 6: Singlet-A 3.9943 eV 310.40 nm f=0.0008

<TDDFT>HOMO -> LUMO+3 4.2%

<TDDFT>HOMO -> LUMO+5 80.0%

<TDDFT>HOMO -> LUMO+7 11.0%

<TDDFT> Excited State 7: Singlet-A 4.0934 eV 302.89 nm f=0.0303

<TDDFT>HOMO -> LUMO+2 7.0%

<TDDFT>HOMO -> LUMO+4 2.8%

<TDDFT>HOMO -> LUMO+6 51.3%

<TDDFT>HOMO -> LUMO+8 32.5%

<TDDFT> Excited State 8: Singlet-A 4.1260 eV 300.49 nm f=0.0183

<TDDFT>HOMO -> LUMO+3 7.8%

<TDDFT>HOMO -> LUMO+5 17.4%

<TDDFT>HOMO -> LUMO+7 64.2%

<TDDFT>HOMO -> LUMO+10 7.4%

<TDDFT> Excited State 9: Singlet-A 4.3062 eV 287.92 nm f=0.0106

<TDDFT>HOMO -> LUMO+6 33.5%

<TDDFT>HOMO -> LUMO+8 48.3%

<TDDFT>HOMO -> LUMO+9 9.8%

<TDDFT>HOMO -> LUMO+12 4.1%

<TDDFT> Excited State 10: Singlet-A 4.5863 eV 270.34 nm f=0.1363

<TDDFT>HOMO-2 -> LUMO 78.2%

<TDDFT>HOMO-1 -> LUMO+4 2.4%

<TDDFT>HOMO -> LUMO+10 2.7%

<TDDFT>HOMO -> LUMO+14 6.4%

<TDDFT>HOMO -> LUMO+15 2.4%

<TDDFT> Excited State 11: Singlet-A 4.5986 eV 269.62 nm f=0.0985

<TDDFT>HOMO-2 -> LUMO+2 2.2%

<TDDFT>HOMO-1 -> LUMO 81.9%

<TDDFT>HOMO -> LUMO+9 4.1%

<TDDFT> Excited State 12: Singlet-A 4.6609 eV 266.01 nm f=0.0112

<TDDFT>HOMO-1 -> LUMO 5.1%

<TDDFT>HOMO -> LUMO+8 8.6%

<TDDFT>HOMO -> LUMO+9 75.9%

<TDDFT>HOMO -> LUMO+12 3.2%

<TDDFT>HOMO -> LUMO+13 2.5%

<TDDFT> Excited State 13: Singlet-A 4.7770 eV 259.54 nm f=0.2015

<TDDFT>HOMO-2 -> LUMO 7.3%

<TDDFT>HOMO -> LUMO+7 10.4%

<TDDFT>HOMO -> LUMO+10 63.5%

<TDDFT>HOMO -> LUMO+14 10.7%

<TDDFT> Excited State 14: Singlet-A 4.8326 eV 256.56 nm f=0.0886

<TDDFT>HOMO-3 -> LUMO 85.4%

<TDDFT>HOMO-3 -> LUMO+1 8.0%

<TDDFT> Excited State 15: Singlet-A 4.9233 eV 251.83 nm f=0.0002

<TDDFT>HOMO-1 -> LUMO+1 2.9%

<TDDFT>HOMO -> LUMO+8 2.6%

<TDDFT>HOMO -> LUMO+11 79.0%

<TDDFT>HOMO -> LUMO+12 4.5%

<TDDFT>HOMO -> LUMO+18 4.2%

<TDDFT> Excited State 16: Singlet-A 4.9233 eV 251.83 nm f=0.1849

<TDDFT>HOMO-2 -> LUMO 4.1%

<TDDFT>HOMO -> LUMO+7 2.8%

<TDDFT>HOMO -> LUMO+10 11.6%

<TDDFT>HOMO -> LUMO+14 48.2%

<TDDFT>HOMO -> LUMO+15 26.4%

<TDDFT> Excited State 17: Singlet-A 4.9641 eV 249.76 nm f=0.0141

<TDDFT>HOMO-4 -> LUMO 12.0%

<TDDFT>HOMO-3 -> LUMO+1 3.9%

<TDDFT>HOMO-2 -> LUMO+2 6.5%

<TDDFT>HOMO-1 -> LUMO+1 57.4%

<TDDFT>HOMO -> LUMO+11 5.4%

<TDDFT> Excited State 18: Singlet-A 4.9815 eV 248.89 nm f=0.0068

<TDDFT>HOMO -> LUMO+6 2.7%

<TDDFT>HOMO -> LUMO+8 3.3%

<TDDFT>HOMO -> LUMO+11 7.0%

<TDDFT>HOMO -> LUMO+12 78.0%

<TDDFT>HOMO -> LUMO+20 4.8%

<TDDFT> Excited State 19: Singlet-A 5.0757 eV 244.27 nm f=0.0245

<TDDFT>HOMO-2 -> LUMO+1 50.3%

<TDDFT>HOMO-2 -> LUMO+3 12.8%

<TDDFT>HOMO-2 -> LUMO+7 2.0%

<TDDFT>HOMO-1 -> LUMO+2 7.5%

<TDDFT>HOMO-1 -> LUMO+4 10.8%

<TDDFT>HOMO-1 -> LUMO+6 4.2%

<TDDFT> Excited State 20: Singlet-A 5.0770 eV 244.21 nm f=0.0636

<TDDFT>HOMO-4 -> LUMO 19.8%

<TDDFT>HOMO-3 -> LUMO 8.6%

<TDDFT>HOMO-3 -> LUMO+1 39.7%

<TDDFT>HOMO-2 -> LUMO+2 4.4%

<TDDFT>HOMO-1 -> LUMO+1 4.1%

<TDDFT>HOMO-1 -> LUMO+3 8.1%

<TDDFT> Excited State 21: Singlet-A 5.1186 eV 242.22 nm f=0.0083

<TDDFT>HOMO-4 -> LUMO 9.4%

<TDDFT>HOMO-3 -> LUMO+1 21.1%

<TDDFT>HOMO-2 -> LUMO+6 5.5%

<TDDFT>HOMO-1 -> LUMO+1 12.3%

<TDDFT>HOMO-1 -> LUMO+3 34.3%

<TDDFT> Excited State 22: Singlet-A 5.1293 eV 241.72 nm f=0.0142

<TDDFT>HOMO-3 -> LUMO+1 2.4%

<TDDFT>HOMO -> LUMO+9 2.8%

<TDDFT>HOMO -> LUMO+13 86.9%

<TDDFT> Excited State 23: Singlet-A 5.1377 eV 241.32 nm f=0.0086

<TDDFT>HOMO-5 -> LUMO 2.6%

<TDDFT>HOMO-2 -> LUMO+1 38.2%

<TDDFT>HOMO-2 -> LUMO+3 12.1%

<TDDFT>HOMO-1 -> LUMO+2 30.3%

<TDDFT>HOMO-1 -> LUMO+6 2.2%

<TDDFT> Excited State 24: Singlet-A 5.1840 eV 239.17 nm f=0.0001

<TDDFT>HOMO-2 -> LUMO+3 4.0%

<TDDFT>HOMO-1 -> LUMO+4 2.5%

<TDDFT>HOMO -> LUMO+10 3.9%

<TDDFT>HOMO -> LUMO+14 17.9%

<TDDFT>HOMO -> LUMO+15 48.8%

<TDDFT>HOMO -> LUMO+16 4.4%

<TDDFT>HOMO -> LUMO+22 3.2%

<TDDFT>HOMO -> LUMO+23 4.3%

6.1.5.5 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0 5.475350 -2.140419 0.001272

C 0 4.618799 -3.232499 0.162285

C 0 3.241748 -3.075210 0.146255

C 0 2.688582 -1.792693 -0.034672

C 0 3.576158 -0.699008 -0.197399

C 0 4.950491 -0.858693 -0.181914

C 0 1.329119 -1.381085 -0.087277

C 0 1.185158 0.011081 -0.301054

S 0	2.727411	0.834784	-0.410245
S 0	-0.000001	-2.439885	0.166896
C 0	-1.329120	-1.381085	-0.087277
C 0	-1.185158	0.011081	-0.301053
N 0	0.000000	0.671632	-0.381828
C 0	-2.688583	-1.792692	-0.034673
C 0	-3.576158	-0.699006	-0.197401
S 0	-2.727410	0.834785	-0.410247
C 0	-3.241749	-3.075209	0.146255
C 0	-4.618800	-3.232497	0.162283
C 0	-5.475350	-2.140417	0.001269
C 0	-4.950491	-0.858691	-0.181917
C 0	0.000001	2.101768	-0.480249
C 0	-0.000000	2.859130	0.702530
C 0	0.000001	4.249856	0.596339
C 0	0.000005	4.851262	-0.658435
C 0	0.000006	4.093153	-1.822588
C 0	0.000004	2.706768	-1.727761
O 0	-0.000004	2.169186	1.853667
C 0	-0.000006	2.896624	3.073405
H 0	6.550201	-2.282973	0.017853
H 0	5.037433	-4.224025	0.302426
H 0	2.592968	-3.936571	0.271782
H 0	5.609330	-0.005826	-0.307458
H 0	-2.592970	-3.936569	0.271783
H 0	-5.037435	-4.224023	0.302425
H 0	-6.550202	-2.282970	0.017849
H 0	-5.609330	-0.005824	-0.307462
H 0	0.000000	4.866459	1.486344
H 0	0.000006	5.934607	-0.719026
H 0	0.000008	4.572191	-2.794574
H 0	0.000005	2.081238	-2.613956
H 0	-0.000008	2.148103	3.863378
H 0	0.895967	3.518610	3.160149
H 0	-0.895977	3.518612	3.160145

SCF Done: E(RPBE1PBE) = -2208.69188978

Sum of electronic and zero-point Energies= -2208.295261

Sum of electronic and thermal Energies= -2208.271519

Sum of electronic and thermal Enthalpies= -2208.270575

Sum of electronic and thermal Free Energies= -2208.351146

6.1.5.6 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.2143 eV 559.92 nm f=0.1259

<TDDFT>HOMO -> LUMO 98.2%

<TDDFT> Excited State 2: Singlet-A 2.9230 eV 424.17 nm f=0.0023

<TDDFT>HOMO -> LUMO+1 98.8%

<TDDFT> Excited State 3: Singlet-A 3.3553 eV 369.52 nm f=0.0042

<TDDFT>HOMO -> LUMO+2 96.0%

<TDDFT> Excited State 4: Singlet-A 3.3919 eV 365.53 nm f=0.0009

<TDDFT>HOMO -> LUMO+3 35.0%

<TDDFT>HOMO -> LUMO+4 37.8%

<TDDFT>HOMO -> LUMO+6 23.2%

6.1.5.7 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0	5.398699	-2.297641	-0.357008
C 0	4.547877	-3.276540	0.178804
C 0	3.197844	-3.017919	0.379503
C 0	2.676198	-1.759296	0.034996
C 0	3.549149	-0.788338	-0.511266
C 0	4.905370	-1.042629	-0.705079
C 0	1.337079	-1.252751	0.178728
C 0	1.191391	0.028435	-0.259787
S 0	2.697535	0.708709	-0.891663
S 0	-0.000001	-2.179517	0.923641
C 0	-1.337081	-1.252750	0.178730
C 0	-1.191392	0.028436	-0.259785
N 0	-0.000000	0.748012	-0.337134
C 0	-2.676200	-1.759294	0.034998
C 0	-3.549151	-0.788336	-0.511264
S 0	-2.697536	0.708713	-0.891659
C 0	-3.197846	-3.017917	0.379504
C 0	-4.547880	-3.276537	0.178803
C 0	-5.398701	-2.297637	-0.357009
C 0	-4.905372	-1.042626	-0.705079
C 0	0.000001	2.185337	-0.354144
C 0	0.000002	2.891024	0.868637
C 0	0.000003	4.289373	0.841512
C 0	0.000002	4.962608	-0.380945
C 0	0.000000	4.266260	-1.586363
C 0	-0.000000	2.871676	-1.565060
O 0	0.000003	2.138636	1.992281
C 0	0.000004	2.796605	3.265795
H 0	6.449802	-2.517842	-0.504513
H 0	4.950184	-4.248418	0.442086
H 0	2.550114	-3.781747	0.795285
H 0	5.561908	-0.287051	-1.121471
H 0	-2.550117	-3.781745	0.795285
H 0	-4.950187	-4.248415	0.442085
H 0	-6.449804	-2.517839	-0.504514
H 0	-5.561909	-0.287047	-1.121470
H 0	0.000005	4.856200	1.762828
H 0	0.000003	6.047226	-0.381632
H 0	-0.000000	4.796246	-2.531119
H 0	-0.000002	2.302443	-2.487870
H 0	0.000005	1.998262	4.006019
H 0	0.896272	3.410402	3.391126
H 0	-0.896263	3.410402	3.391127

SCF Done: E(RB3LYP) = -2210.36564726

Sum of electronic and zero-point Energies= -2210.049351

Sum of electronic and thermal Energies= -2210.026448

Sum of electronic and thermal Enthalpies= -2210.025503

Sum of electronic and thermal Free Energies= -2210.103255

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.420833	-2.175468	0.423278
C 0	4.566728	-3.277775	0.265535
C 0	3.210287	-3.103548	0.021358
C 0	2.683963	-1.802398	-0.062578
C 0	3.562004	-0.704724	0.103437
C 0	4.923580	-0.876956	0.342345
C 0	1.336972	-1.373584	-0.325987
C 0	1.191974	-0.018103	-0.335040
S 0	2.707790	0.832284	-0.024203
S 0	-0.000000	-2.498508	-0.711553
C 0	-1.336973	-1.373584	-0.325988
C 0	-1.191974	-0.018103	-0.335041
N 0	-0.000000	0.685245	-0.515363

C 0	-2.683963	-1.802397	-0.062578
C 0	-3.562004	-0.704724	0.103438
S 0	-2.707790	0.832284	-0.024202
C 0	-3.210287	-3.103548	0.021358
C 0	-4.566728	-3.277775	0.265536
C 0	-5.420833	-2.175467	0.423279
C 0	-4.923580	-0.876956	0.342346
C 0	-0.000000	2.117839	-0.636178
C 0	0.000001	2.923318	0.523639
C 0	0.000000	4.315490	0.377705
C 0	-0.000001	4.883461	-0.895546
C 0	-0.000001	4.087251	-2.039093
C 0	-0.000001	2.701285	-1.900472
O 0	0.000001	2.273275	1.709116
C 0	0.000003	3.040139	2.919913
H 0	6.476665	-2.332353	0.611863
H 0	4.971794	-4.281243	0.333726
H 0	2.561879	-3.964521	-0.098508
H 0	5.580769	-0.023661	0.466510
H 0	-2.561879	-3.964521	-0.098509
H 0	-4.971795	-4.281243	0.333726
H 0	-6.476665	-2.332353	0.611865
H 0	-5.580769	-0.023661	0.466512
H 0	0.000000	4.955424	1.249754
H 0	-0.000001	5.964027	-0.987590
H 0	-0.000002	4.536401	-3.024863
H 0	-0.000002	2.052735	-2.769317
H 0	0.000004	2.308545	3.726194
H 0	0.896576	3.662255	2.992289
H 0	-0.896571	3.662254	2.992292

SCF Done: E(RB3LYP) = -2210.36463875

Sum of electronic and zero-point Energies= -2210.048543

Sum of electronic and thermal Energies= -2210.025688

Sum of electronic and thermal Enthalpies= -2210.024744

Sum of electronic and thermal Free Energies= -2210.101649

6.1.5.8 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000

0 1

C 0	-5.480398	-2.130108	0.008265
C 0	-4.628536	-3.233740	0.170959
C 0	-3.252534	-3.076413	0.155629
C 0	-2.712182	-1.791307	-0.025026
C 0	-3.586313	-0.692920	-0.186768
C 0	-4.968757	-0.849263	-0.172909
C 0	-1.337522	-1.377024	-0.074631
C 0	-1.192209	-0.010472	-0.267993
S 0	-2.718839	0.830766	-0.402168
S 0	-0.000080	-2.484201	0.098978
C 0	1.337411	-1.377082	-0.074613
C 0	1.192154	-0.010519	-0.267990
N 0	-0.000008	0.666689	-0.361390
C 0	2.712049	-1.791431	-0.025074
C 0	3.586226	-0.693094	-0.186917
S 0	2.718818	0.830621	-0.402346
C 0	3.252349	-3.076552	0.155638
C 0	4.628344	-3.233942	0.170919
C 0	5.480252	-2.130363	0.008104
C 0	4.968663	-0.849506	-0.173133
C 0	0.000025	2.111448	-0.483558
C 0	0.000182	2.881593	0.695874
C 0	0.000200	4.274168	0.572490
C 0	0.000034	4.861757	-0.691341
C 0	-0.000147	4.089341	-1.850870
C 0	-0.000152	2.702349	-1.743222
O 0	0.000280	2.193801	1.857352
C 0	0.000578	2.919690	3.095002
H 0	-6.553753	-2.275492	0.022741
H 0	-5.053685	-4.220070	0.309674
H 0	-2.603841	-3.935831	0.281340

H 0	-5.631121	-0.001604	-0.299017
H 0	2.603621	-3.935936	0.281402
H 0	5.053452	-4.220279	0.309711
H 0	6.553600	-2.275799	0.022532
H 0	5.631061	-0.001895	-0.299381
H 0	0.000345	4.900798	1.453675
H 0	0.000042	5.942909	-0.765452
H 0	-0.000283	4.558431	-2.826159
H 0	-0.000261	2.073958	-2.626337
H 0	0.000774	2.162417	3.875181
H 0	0.897223	3.538277	3.183066
H 0	-0.896035	3.538261	3.183497

SCF Done: E(UB3LYP) = -2210.11857907

Sum of electronic and zero-point Energies= -2209.801469

Sum of electronic and thermal Energies= -2209.778650

Sum of electronic and thermal Enthalpies= -2209.777705

Sum of electronic and thermal Free Energies= -2209.855263

6.1.5.9 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	-5.479832	-2.126569	0.027051
C 0	-4.627409	-3.231790	0.178529
C 0	-3.250567	-3.076068	0.151901
C 0	-2.710880	-1.790936	-0.029449
C 0	-3.584822	-0.691056	-0.181067
C 0	-4.967929	-0.845581	-0.154948
C 0	-1.335210	-1.378819	-0.086163
C 0	-1.191073	-0.012350	-0.275549
S 0	-2.717492	0.831606	-0.398676
S 0	-0.000033	-2.487384	0.076727
C 0	1.335163	-1.378845	-0.086172
C 0	1.191052	-0.012374	-0.275562
N 0	-0.000004	0.665057	-0.366712
C 0	2.710826	-1.790989	-0.029474
C 0	3.584788	-0.691128	-0.181109
S 0	2.717486	0.831551	-0.398715
C 0	3.250488	-3.076131	0.151880
C 0	4.627327	-3.231882	0.178491
C 0	5.479771	-2.126679	0.026995
C 0	4.967893	-0.845682	-0.155006
C 0	0.000008	2.109504	-0.487011
C 0	0.000054	2.878310	0.693420
C 0	0.000060	4.271327	0.572491
C 0	0.000023	4.859918	-0.691021
C 0	-0.000020	4.088423	-1.851649
C 0	-0.000029	2.700819	-1.746046
O 0	0.000083	2.191372	1.854959
C 0	0.000231	2.920495	3.092422
H 0	-6.553281	-2.270074	0.051361
H 0	-5.051748	-4.218419	0.318255
H 0	-2.601123	-3.935741	0.269439
H 0	-5.628993	0.004169	-0.271329
H 0	2.601028	-3.935790	0.269434
H 0	5.051648	-4.218518	0.318219
H 0	6.553217	-2.270207	0.051293
H 0	5.628973	0.004054	-0.271400
H 0	0.000089	4.896534	1.454483
H 0	0.000028	5.941232	-0.763221
H 0	-0.000047	4.557887	-2.826790
H 0	-0.000062	2.072232	-2.628478
H 0	0.000285	2.164155	3.873339
H 0	0.896471	3.539095	3.177713
H 0	-0.895953	3.539151	3.177898

SCF Done: E(UB3LYP) = -2210.16814005

Sum of electronic and zero-point Energies= -2209.851063

Sum of electronic and thermal Enthalpies= -2209.827304

Sum of electronic and thermal Energies= -2209.828249

Sum of electronic and thermal Free Energies= -2209.905057

6.1.5.10 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(SMD,solvent=dichloromethane)

0 1

C 0	-5.478606	-2.131457	0.022270
C 0	-4.624218	-3.234338	0.179662
C 0	-3.247593	-3.076643	0.156133
C 0	-2.710699	-1.790549	-0.028842
C 0	-3.587000	-0.693504	-0.186771
C 0	-4.969759	-0.849438	-0.163389
C 0	-1.336300	-1.375794	-0.082897
C 0	-1.190164	-0.010399	-0.275048
S 0	-2.719318	0.830822	-0.408370
S 0	-0.000098	-2.484037	0.088643
C 0	1.336171	-1.375868	-0.082863
C 0	1.190131	-0.010453	-0.274945
N 0	-0.000003	0.667827	-0.360901
C 0	2.710553	-1.790726	-0.028920
C 0	3.586928	-0.693730	-0.186712
S 0	2.719292	0.830729	-0.408091
C 0	3.247368	-3.076887	0.155799
C 0	4.623988	-3.234675	0.179255
C 0	5.478443	-2.131818	0.022096
C 0	4.969672	-0.849729	-0.163310
C 0	0.000030	2.112500	-0.483469
C 0	0.000184	2.880823	0.697786
C 0	0.000314	4.273887	0.575793
C 0	0.000253	4.860772	-0.688512
C 0	0.000061	4.088782	-1.849518
C 0	-0.000048	2.701017	-1.744292
O 0	0.000142	2.194394	1.858480
C 0	0.000306	2.923475	3.098243
H 0	-6.552042	-2.277712	0.044378
H 0	-5.047225	-4.221679	0.321241
H 0	-2.598110	-3.936058	0.279334
H 0	-5.634176	-0.002302	-0.284347
H 0	2.597850	-3.936296	0.278846
H 0	5.046929	-4.222085	0.320544
H 0	6.551870	-2.278139	0.044201
H 0	5.634137	-0.002594	-0.284018
H 0	0.000387	4.898041	1.459086
H 0	0.000345	5.942476	-0.761384
H 0	0.000021	4.558524	-2.825027
H 0	-0.000199	2.069716	-2.625690
H 0	0.000168	2.164376	3.878278
H 0	0.897636	3.540883	3.186392
H 0	-0.896800	3.541193	3.186429

SCF Done: E(UB3LYP) = -2210.19518736

Sum of electronic and zero-point Energies= -2209.878225

Sum of electronic and thermal Energies= -2209.855540

Sum of electronic and thermal Enthalpies= -2209.854596

Sum of electronic and thermal Free Energies= -2209.931331

6.1.5.11 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc) freq=noraman b3lyp/6-311++g(d,p) pop=full scrf=(iefpcm,solvent=dichloromethane)

0 1

C 0	5.487268	-2.100700	0.188841
C 0	4.626017	-3.205536	0.266916
C 0	3.250460	-3.049984	0.148706
C 0	2.713939	-1.765808	-0.049423
C 0	3.599684	-0.664917	-0.124675
C 0	4.978837	-0.818858	-0.007901
C 0	1.342032	-1.363256	-0.200494
C 0	1.193364	-0.020028	-0.374397
S 0	2.729534	0.846622	-0.371223
S 0	-0.000069	-2.546033	-0.217944
C 0	-1.342047	-1.363104	-0.201051
C 0	-1.193204	-0.019883	-0.374968
N 0	0.000077	0.683189	-0.555688
C 0	-2.714012	-1.765493	-0.050095
C 0	-3.599621	-0.664492	-0.125317
S 0	-2.729257	0.846965	-0.371606
C 0	-3.250722	-3.049642	0.147716
C 0	-4.626317	-3.205055	0.265676
C 0	-5.487441	-2.100134	0.187433
C 0	-4.978828	-0.818320	-0.009031
C 0	0.000211	2.120375	-0.544874
C 0	-0.000826	2.814224	0.685077
C 0	-0.000192	4.212729	0.672727
C 0	0.001700	4.898577	-0.541895
C 0	0.002984	4.214298	-1.754576
C 0	0.002264	2.820713	-1.747483
O 0	-0.002140	2.050578	1.801901
C 0	-0.003056	2.694947	3.080442
H 0	6.557571	-2.242440	0.281835
H 0	5.040019	-4.195361	0.421484
H 0	2.595227	-3.911495	0.212194
H 0	5.641778	0.036349	-0.067961
H 0	-2.595604	-3.911247	0.211129
H 0	-5.040453	-4.194847	0.420097
H 0	-6.557785	-2.241778	0.280110
H 0	-5.641672	0.036951	-0.069250
H 0	-0.000865	4.769563	1.599727
H 0	0.002198	5.982628	-0.531658
H 0	0.004529	4.754347	-2.693120
H 0	0.003222	2.258205	-2.673768
H 0	-0.003981	1.890416	3.812237
H 0	0.892490	3.308178	3.210692
H 0	-0.898402	3.308803	3.209113

SCF Done: E(RB3LYP) = -2210.34134395

Sum of electronic and zero-point Energies= -2210.025191

Sum of electronic and thermal Energies= -2210.003135

Sum of electronic and thermal Enthalpies= -2210.002191

Sum of electronic and thermal Free Energies= -2210.076538

6.1.6 *anti-anti-N-ortho,ortho'*-dicyanophenyl-BBTT 3f

6.1.6.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.383806	-2.296311	-0.453858
C 0	-4.532991	-3.295903	0.041568
C 0	-3.188029	-3.039616	0.264827
C 0	-2.673174	-1.763391	-0.011624
C 0	-3.543478	-0.771583	-0.518851
C 0	-4.896630	-1.025401	-0.737093
C 0	-1.335434	-1.260250	0.170567
C 0	-1.199392	0.040566	-0.198434
S 0	-2.695962	0.737716	-0.830981
S 0	-0.000351	-2.245192	0.817482
C 0	1.335156	-1.260528	0.170919

C 0	1.199550	0.040291	-0.198263
N 0	0.000145	0.780881	-0.220364
C 0	2.672847	-1.763979	-0.010774
C 0	3.543517	-0.772362	-0.517735
S 0	2.696403	0.737023	-0.830237
C 0	3.187340	-3.040304	0.265891
C 0	4.532296	-3.296903	0.042989
C 0	5.383466	-2.297525	-0.452249
C 0	4.896674	-1.026515	-0.735641
C 0	0.000233	2.130729	0.259668
C 0	0.001480	3.191762	-0.660348
C 0	0.001628	4.521765	-0.212413
C 0	0.000419	4.798454	1.147845
C 0	-0.000937	3.758969	2.071078
C 0	-0.001013	2.426990	1.635482
C 0	-0.002253	1.382734	2.613937
N 0	-0.003232	0.579917	3.443634
C 0	0.002413	2.934138	-2.069582
N 0	0.003084	2.790442	-3.215230
H 0	-6.431784	-2.515509	-0.621770
H 0	-4.932506	-4.280995	0.252751
H 0	-2.535669	-3.816829	0.646148
H 0	-5.552337	-0.254534	-1.124644
H 0	2.534701	-3.817341	0.647088
H 0	4.931556	-4.282052	0.254384
H 0	6.431444	-2.516952	-0.619801
H 0	5.552670	-0.255804	-1.122998
H 0	0.002623	5.323067	-0.940434
H 0	0.000501	5.825591	1.491163
H 0	-0.001899	3.964951	3.134160

SCF Done: E(RB3LYP) = -2280.29487954

Sum of electronic and zero-point Energies= -2280.014224

Sum of electronic and thermal Energies= -2279.990194

Sum of electronic and thermal Enthalpies= -2279.989250

Sum of electronic and thermal Free Energies= -2280.069687

6.1.6.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full

0 1

C 0	-5.396114	-2.289005	-0.435626
C 0	-4.541892	-3.308829	0.012121
C 0	-3.192796	-3.064439	0.229975
C 0	-2.677640	-1.779246	-0.005666
C 0	-3.552185	-0.767181	-0.464395
C 0	-4.908990	-1.008111	-0.676036
C 0	-1.337049	-1.285106	0.179141
C 0	-1.200966	0.028386	-0.143717
S 0	-2.705519	0.755023	-0.720962
S 0	0.000071	-2.293563	0.793159
C 0	1.337112	-1.285043	0.179077
C 0	1.200941	0.028442	-0.143773
N 0	-0.000028	0.762235	-0.154465
C 0	2.677713	-1.779114	-0.005829
C 0	3.552171	-0.767007	-0.464636
S 0	2.705406	0.755149	-0.721155
C 0	3.192956	-3.064278	0.229788
C 0	4.542048	-3.308598	0.011839
C 0	5.396183	-2.288733	-0.435983
C 0	4.908973	-1.007869	-0.676373
C 0	-0.000049	2.141000	0.232803
C 0	-0.000320	3.142784	-0.750495
C 0	-0.000390	4.498524	-0.386691
C 0	-0.000166	4.857301	0.954410
C 0	0.000142	3.877651	1.941201
C 0	0.000199	2.521891	1.586229
C 0	0.000521	1.530029	2.617473

N 0	0.000799	0.756104	3.474425
C 0	-0.000484	2.790873	-2.138803
N 0	-0.000598	2.552053	-3.268607
H 0	-6.446563	-2.498994	-0.599114
H 0	-4.941508	-4.300216	0.191066
H 0	-2.540361	-3.857753	0.576582
H 0	-5.567353	-0.221466	-1.024841
H 0	2.540589	-3.857621	0.576455
H 0	4.941730	-4.299961	0.190768
H 0	6.446631	-2.498669	-0.599545
H 0	5.567269	-0.221192	-1.025234
H 0	-0.000605	5.255741	-1.159879
H 0	-0.000218	5.903116	1.233304
H 0	0.000335	4.152602	2.988088

SCF Done: E(RB3LYP) = -2280.31091202

Sum of electronic and zero-point Energies= -2280.030173

Sum of electronic and thermal Energies= -2280.006142

Sum of electronic and thermal Enthalpies= -2280.005197

Sum of electronic and thermal Free Energies= -2280.085865

6.1.6.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	-5.380649	-2.251413	-0.424930
C 0	-4.532409	-3.274217	0.017249
C 0	-3.183971	-3.040015	0.224635
C 0	-2.665176	-1.761672	-0.016420
C 0	-3.532429	-0.746201	-0.468523
C 0	-4.889656	-0.977585	-0.670237
C 0	-1.325178	-1.277458	0.156450
C 0	-1.192519	0.032736	-0.172269
S 0	-2.684552	0.756723	-0.732211
S 0	-0.000000	-2.283710	0.753830
C 0	1.325177	-1.277458	0.156449
C 0	1.192518	0.032736	-0.172269
N 0	0.000000	0.765031	-0.197987
C 0	2.665176	-1.761672	-0.016420
C 0	3.532428	-0.746202	-0.468522
S 0	2.684552	0.756722	-0.732211
C 0	3.183971	-3.040015	0.224635
C 0	4.532409	-3.274217	0.017250
C 0	5.380649	-2.251413	-0.424929
C 0	4.889655	-0.977586	-0.670237
C 0	-0.000000	2.120307	0.236935
C 0	0.000001	3.151419	-0.707523
C 0	0.000000	4.489804	-0.299536
C 0	-0.000001	4.799755	1.050732
C 0	-0.000002	3.788637	2.001243
C 0	-0.000001	2.451298	1.598315
C 0	-0.000001	1.416766	2.581610
N 0	0.000002	0.598049	3.394688
C 0	0.000002	2.836583	-2.101055
N 0	0.000003	2.621806	-3.234831
H 0	-6.434517	-2.455192	-0.580949
H 0	-4.938317	-4.263386	0.200334
H 0	-2.532046	-3.837051	0.567859
H 0	-5.545396	-0.186042	-1.016094
H 0	2.532046	-3.837052	0.567858
H 0	4.938317	-4.263386	0.200334
H 0	6.434517	-2.455192	-0.580948
H 0	5.545396	-0.186042	-1.016093
H 0	0.000001	5.274006	-1.047129
H 0	-0.000001	5.836040	1.366838
H 0	-0.000002	4.025840	3.058567

SCF Done: E(RPBE1PBE) = -2278.58657624

Sum of electronic and zero-point Energies= -2278.302931

Sum of electronic and thermal Enthalpies= -2278.278061

Sum of electronic and thermal Energies= -2278.279006

Sum of electronic and thermal Free Energies= -2278.358758

6.1.6.4 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.3337 eV 531.27 nm f=0.0006

<TDDFT>HOMO -> LUMO 95.4%

<TDDFT>HOMO -> LUMO+1 4.2%

<TDDFT> Excited State 2: Singlet-A 2.4176 eV 512.83 nm f=0.0058

<TDDFT>HOMO -> LUMO 4.1%

<TDDFT>HOMO -> LUMO+1 94.9%

<TDDFT> Excited State 3: Singlet-A 3.2645 eV 379.80 nm f=0.0709

<TDDFT>HOMO -> LUMO+2 96.3%

<TDDFT> Excited State 4: Singlet-A 3.6364 eV 340.95 nm f=0.0010

<TDDFT>HOMO-1 -> LUMO 98.6%

<TDDFT> Excited State 5: Singlet-A 3.7271 eV 332.66 nm f=0.0125

<TDDFT>HOMO-2 -> LUMO 98.8%

<TDDFT> Excited State 6: Singlet-A 3.7895 eV 327.18 nm f=0.0001

<TDDFT>HOMO-1 -> LUMO+1 93.8%

<TDDFT>HOMO -> LUMO+3 4.3%

<TDDFT> Excited State 7: Singlet-A 3.8683 eV 320.51 nm f=0.0421

<TDDFT>HOMO-2 -> LUMO+1 97.1%

<TDDFT> Excited State 8: Singlet-A 3.9209 eV 316.21 nm f=0.1350

<TDDFT>HOMO-1 -> LUMO+1 4.4%

<TDDFT>HOMO -> LUMO+3 88.8%

<TDDFT> Excited State 9: Singlet-A 4.0064 eV 309.47 nm f=0.0019

<TDDFT>HOMO -> LUMO+5 61.6%

<TDDFT>HOMO -> LUMO+7 29.4%

<TDDFT>HOMO -> LUMO+11 2.7%

<TDDFT> Excited State 10: Singlet-A 4.0998 eV 302.41 nm f=0.0015

<TDDFT>HOMO-3 -> LUMO 4.4%

<TDDFT>HOMO -> LUMO+4 89.4%

<TDDFT> Excited State 11: Singlet-A 4.1635 eV 297.79 nm f=0.0100

<TDDFT>HOMO-3 -> LUMO 85.8%

<TDDFT>HOMO -> LUMO+4 4.8%

<TDDFT>HOMO -> LUMO+6 6.7%

<TDDFT> Excited State 12: Singlet-A 4.2192 eV 293.86 nm f=0.0000

<TDDFT>HOMO -> LUMO+5 32.6%

<TDDFT>HOMO -> LUMO+7 60.0%

<TDDFT>HOMO -> LUMO+11 2.4%

<TDDFT> Excited State 13: Singlet-A 4.2266 eV 293.35 nm f=0.0114

<TDDFT>HOMO-3 -> LUMO 6.6%

<TDDFT>HOMO -> LUMO+6 83.0%

<TDDFT> Excited State 14: Singlet-A 4.3364 eV 285.91 nm f=0.0488

<TDDFT>HOMO-3 -> LUMO+1
95.0%

<TDDFT> Excited State 15: Singlet-A
4.6595 eV 266.09 nm f=0.0634

<TDDFT>HOMO-4 -> LUMO
73.4%

<TDDFT>HOMO-2 -> LUMO+2
20.9%

<TDDFT> Excited State 16: Singlet-A
4.6704 eV 265.47 nm f=0.0063

<TDDFT>HOMO-1 -> LUMO+2 2.3%

<TDDFT>HOMO -> LUMO+6 2.8%

<TDDFT>HOMO -> LUMO+8
52.6%

<TDDFT>HOMO -> LUMO+9
35.9%

<TDDFT> Excited State 17: Singlet-A
4.6742 eV 265.25 nm f=0.0636

<TDDFT>HOMO-4 -> LUMO
25.6%

<TDDFT>HOMO-2 -> LUMO+2
55.9%

<TDDFT>HOMO-1 -> LUMO+3 3.2%

<TDDFT>HOMO -> LUMO+13 4.0%

<TDDFT> Excited State 18: Singlet-A
4.6799 eV 264.93 nm f=0.1262

<TDDFT>HOMO-2 -> LUMO+3 3.7%

<TDDFT>HOMO-2 -> LUMO+4 2.6%

<TDDFT>HOMO-1 -> LUMO+2
73.8%

<TDDFT>HOMO -> LUMO+8 6.2%

<TDDFT> Excited State 19: Singlet-A
4.7610 eV 260.42 nm f=0.0100

<TDDFT>HOMO-1 -> LUMO+2 5.5%

<TDDFT>HOMO -> LUMO+8
17.3%

<TDDFT>HOMO -> LUMO+9
49.6%

<TDDFT>HOMO -> LUMO+10
19.6%

<TDDFT>HOMO -> LUMO+14 4.9%

<TDDFT> Excited State 20: Singlet-A
4.8418 eV 256.07 nm f=0.0265

<TDDFT>HOMO-4 -> LUMO+1
96.2%

<TDDFT> Excited State 21: Singlet-A
4.8939 eV 253.34 nm f=0.0063

<TDDFT>HOMO-7 -> LUMO
18.7%

<TDDFT>HOMO-6 -> LUMO
31.2%

<TDDFT>HOMO-5 -> LUMO+1
46.4%

<TDDFT> Excited State 22: Singlet-A
4.9579 eV 250.08 nm f=0.0079

<TDDFT>HOMO -> LUMO+8
13.5%

<TDDFT>HOMO -> LUMO+9 6.5%

<TDDFT>HOMO -> LUMO+10
68.1%

<TDDFT> Excited State 23: Singlet-A
4.9924 eV 248.35 nm f=0.3543

<TDDFT>HOMO-2 -> LUMO+2 9.5%

<TDDFT>HOMO-1 -> LUMO+3 9.3%

<TDDFT>HOMO -> LUMO+11
23.2%

<TDDFT>HOMO -> LUMO+13
44.0%

<TDDFT>HOMO -> LUMO+24 2.4%

<TDDFT> Excited State 24: Singlet-A
5.0486 eV 245.58 nm f=0.0189

<TDDFT>HOMO-4 -> LUMO+4 3.1%

<TDDFT>HOMO-3 -> LUMO+2
25.5%

<TDDFT>HOMO-2 -> LUMO+3
39.5%

<TDDFT>HOMO-1 -> LUMO+2 5.8%

<TDDFT>HOMO-1 -> LUMO+5 9.9%

<TDDFT>HOMO-1 -> LUMO+7 3.0%

6.1.6.5 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	-5.461873	-2.113406	-0.003807
C 0	-4.621798	-3.233908	0.014872
C 0	-3.247105	-3.089000	0.008921
C 0	-2.699441	-1.799942	-0.016385
C 0	-3.558561	-0.683494	-0.035309
C 0	-4.940719	-0.828310	-0.029054
C 0	-1.325311	-1.394046	-0.024343
C 0	-1.181563	-0.018621	-0.049650
S 0	-2.686974	0.835758	-0.067197
S 0	-0.000002	-2.504334	0.001315
C 0	1.325308	-1.394048	-0.024351
C 0	1.181561	-0.018623	-0.049658
N 0	-0.000000	0.667626	-0.067643
C 0	2.699437	-1.799946	-0.016400
C 0	3.558559	-0.683499	-0.035328
S 0	2.686973	0.835754	-0.067212
C 0	3.247100	-3.089005	0.008904
C 0	4.621793	-3.233915	0.014849
C 0	5.461870	-2.113414	-0.003833
C 0	4.940717	-0.828317	-0.029078
C 0	0.000002	2.097524	0.008941
C 0	-0.000015	2.868466	-1.158332
C 0	-0.000011	4.257968	-1.107868
C 0	0.000011	4.885156	0.173044
C 0	0.000027	4.152671	1.325298
C 0	0.000022	2.719015	1.312933
C 0	0.000038	1.968095	2.479921
N 0	0.000052	1.318677	3.456868
C 0	-0.000038	2.210531	-2.426277
N 0	-0.000056	1.677238	-3.450965
H 0	-6.537656	-2.249616	0.001889
H 0	-5.055535	-4.227302	0.035062
H 0	-2.603105	-3.962203	0.024552
H 0	-5.593739	0.036798	-0.042565
H 0	2.603099	-3.962207	0.024538
H 0	5.055528	-4.227309	0.035038
H 0	6.537652	-2.249625	0.001857
H 0	5.593738	0.036790	-0.042592
H 0	-0.000023	4.835330	-2.021762
H 0	0.000015	5.967688	0.230692
H 0	0.000043	4.654413	2.286913

SCF Done: E(RPBE1PBE) = -2278.57401012

Sum of electronic and zero-point Energies= -2278.241201

Sum of electronic and thermal Energies= -2278.217051

Sum of electronic and thermal Enthalpies= -2278.216107

Sum of electronic and thermal Free Energies= -2278.295980

6.1.6.6 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 1.4155 eV 875.93 nm f=0.0000

<TDDFT>HOMO -> LUMO 96.8%

<TDDFT>HOMO -> LUMO+1 2.9%

<TDDFT> Excited State 2: Singlet-A 1.8838 eV 658.17 nm f=0.0004

<TDDFT>HOMO -> LUMO 3.0%

<TDDFT>HOMO -> LUMO+1 96.7%

<TDDFT> Excited State 3: Singlet-A 2.5654 eV 483.30 nm f=0.1037

<TDDFT>HOMO -> LUMO+2 98.1%

<TDDFT> Excited State 4: Singlet-A 3.2204 eV 385.00 nm f=0.0010

<TDDFT>HOMO-1 -> LUMO 97.8%

6.1.6.7 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromethane) pop=full geom=checkpoint guess=read

0 1

C 0	-5.385315	-2.330671	-0.385385
C 0	-4.518521	-3.341680	0.058219
C 0	-3.169167	-3.086154	0.262264
C 0	-2.666426	-1.797799	0.016299
C 0	-3.554214	-0.795318	-0.437479
C 0	-4.911194	-1.046656	-0.635567
C 0	-1.328006	-1.290713	0.186055
C 0	-1.203126	0.022150	-0.143748
S 0	-2.721333	0.732881	-0.709124
S 0	0.021957	-2.285568	0.795892
C 0	1.347250	-1.272570	0.163395
C 0	1.196590	0.037747	-0.165557
N 0	-0.007674	0.765557	-0.163776
C 0	2.689096	-1.760096	-0.033434
C 0	3.551746	-0.745939	-0.509735
S 0	2.689676	0.767890	-0.771988
C 0	3.217332	-3.038700	0.210487
C 0	4.566702	-3.273224	-0.016835
C 0	5.408546	-2.250770	-0.481877
C 0	4.908796	-0.976355	-0.731200
C 0	-0.011900	2.142198	0.237739
C 0	-0.090104	3.153622	-0.732912
C 0	-0.104522	4.505714	-0.355038
C 0	-0.036667	4.851641	0.987460
C 0	0.048543	3.863631	1.961930
C 0	0.059082	2.511794	1.592738
C 0	0.142279	1.512329	2.612184
N 0	0.207402	0.725290	3.454341
C 0	-0.147160	2.817296	-2.123608
N 0	-0.190111	2.589229	-3.254751
H 0	-6.435765	-2.550143	-0.538288
H 0	-4.908200	-4.335970	0.244828
H 0	-2.509156	-3.874887	0.605763
H 0	-5.579962	-0.266933	-0.981514
H 0	2.577278	-3.835916	0.571850
H 0	4.976455	-4.259504	0.169133
H 0	6.459633	-2.453849	-0.651980
H 0	5.558261	-0.187521	-1.092961
H 0	-0.165644	5.269659	-1.119958
H 0	-0.047141	5.894946	1.276963
H 0	0.104280	4.127483	3.010628

SCF Done: E(RB3LYP) = -2280.33315718

Sum of electronic and zero-point Energies= -2280.052415

Sum of electronic and thermal Energies= -2280.028444

Sum of electronic and thermal Enthalpies= -2280.027499

Sum of electronic and thermal Free Energies= -2280.107597

6.1.6.8 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.477515	-2.155261	-0.000277
C 0	-4.620636	-3.266698	-0.000266
C 0	-3.245450	-3.103052	-0.000035
C 0	-2.711115	-1.802883	0.000061
C 0	-3.591493	-0.698416	-0.000094
C 0	-4.972673	-0.858684	-0.000168
C 0	-1.337946	-1.380427	0.000211
C 0	-1.199661	-0.000722	0.000124

S 0	-2.729439	0.843647	-0.000354
S 0	0.000089	-2.497645	0.000379
C 0	1.338068	-1.380355	-0.000127
C 0	1.199683	-0.000669	-0.000341
N 0	-0.000009	0.682973	-0.000136
C 0	2.711273	-1.802715	-0.000113
C 0	3.591572	-0.698187	-0.000371
S 0	2.729401	0.843819	-0.000373
C 0	3.245699	-3.102846	0.000178
C 0	4.620897	-3.266394	0.000203
C 0	5.477699	-2.154897	-0.000188
C 0	4.972764	-0.858356	-0.000504
C 0	-0.000046	2.127249	0.000132
C 0	-0.000052	2.822094	1.218909
C 0	-0.000178	4.223872	1.209109
C 0	-0.000328	4.912463	0.000655
C 0	-0.000329	4.224328	-1.208055
C 0	-0.000201	2.822548	-1.218381
C 0	-0.000035	2.098883	-2.451673
N 0	-0.000069	1.498144	-3.437296
C 0	-0.000073	2.097948	2.451923
N 0	0.000054	1.496800	3.437297
H 0	-6.550163	-2.306064	-0.000324
H 0	-5.041200	-4.264579	-0.000427
H 0	-2.593385	-3.969021	0.000117
H 0	-5.639020	-0.004975	-0.000059
H 0	2.593695	-3.968859	0.000334
H 0	5.041534	-4.264245	0.000509
H 0	6.550357	-2.305627	-0.000300
H 0	5.639048	-0.004598	-0.000928
H 0	-0.000182	4.758120	2.150708
H 0	-0.000448	5.995408	0.000857
H 0	-0.000418	4.758929	-2.149453

SCF Done: E(UB3LYP) = -2280.06686189

Sum of electronic and zero-point Energies= -2279.785726

Sum of electronic and thermal Energies= -2279.761720

Sum of electronic and thermal Enthalpies= -2279.760776

Sum of electronic and thermal Free Energies= -2279.841276

6.1.6.9 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	-5.477329	-2.157206	-0.000241
C 0	-4.620582	-3.269143	-0.000155
C 0	-3.244550	-3.106446	-0.000086
C 0	-2.710251	-1.806471	-0.000095
C 0	-3.589460	-0.701258	-0.000182
C 0	-4.971636	-0.860837	-0.000259
C 0	-1.335741	-1.385598	-0.000021
C 0	-1.199224	-0.006197	-0.000054
S 0	-2.727313	0.839754	-0.000185
S 0	0.000000	-2.502779	0.000124
C 0	1.335742	-1.385598	0.000084
C 0	1.199225	-0.006197	0.000054
N 0	0.000000	0.677896	0.000005
C 0	2.710251	-1.806471	0.000101
C 0	3.589460	-0.701258	0.000093
S 0	2.727315	0.839754	0.000060
C 0	3.244550	-3.106446	0.000113
C 0	4.620582	-3.269144	0.000117
C 0	5.477329	-2.157208	0.000112
C 0	4.971637	-0.860838	0.000100
C 0	-0.000001	2.121950	0.000025
C 0	-0.000279	2.820309	1.216167
C 0	-0.000285	4.222012	1.207397
C 0	0.000004	4.910536	0.000061

C 0	0.000290	4.222045	-1.207293
C 0	0.000279	2.820341	-1.216098
C 0	0.000543	2.108973	-2.457116
N 0	0.000726	1.537959	-3.460172
C 0	-0.000547	2.108905	2.457163
N 0	-0.000739	1.537864	3.460203
H 0	-6.550095	-2.306978	-0.000297
H 0	-5.040849	-4.267181	-0.000141
H 0	-2.592692	-3.971986	-0.000023
H 0	-5.636341	-0.006242	-0.000332
H 0	2.592692	-3.971986	0.000110
H 0	5.040848	-4.267182	0.000120
H 0	6.550095	-2.306980	0.000118
H 0	5.636342	-0.006244	0.000096
H 0	-0.000510	4.757888	2.147270
H 0	0.000006	5.992725	0.000076
H 0	0.000517	4.757945	-2.147152

SCF Done: E(UB3LYP) = -2280.12738416

Sum of electronic and zero-point Energies= -2279.846196

Sum of electronic and thermal Energies= -2279.822138

Sum of electronic and thermal Enthalpies= -2279.821194

Sum of electronic and thermal Free Energies= -2279.903899

6.1.6.10 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane)

0 1

C 0	-5.472392	-2.170805	0.000193
C 0	-4.610919	-3.279155	0.000472
C 0	-3.235539	-3.111012	0.000316
C 0	-2.708406	-1.807983	-0.000130
C 0	-3.592409	-0.707002	-0.000424
C 0	-4.973724	-0.871307	-0.000257
C 0	-1.336534	-1.381359	-0.000244
C 0	-1.199045	-0.002447	-0.000559
S 0	-2.734118	0.837875	-0.000899
S 0	-0.000057	-2.498720	0.000082
C 0	1.336464	-1.381408	-0.000304
C 0	1.199034	-0.002499	-0.000603
N 0	-0.000002	0.682687	-0.000556
C 0	2.708322	-1.808094	-0.000347
C 0	3.592371	-0.707153	-0.000721
S 0	2.734149	0.837763	-0.001047
C 0	3.235399	-3.111145	-0.000021
C 0	4.610770	-3.279348	-0.000048
C 0	5.472293	-2.171034	-0.000424
C 0	4.973680	-0.871516	-0.000780
C 0	0.000038	2.128012	0.000332
C 0	0.000530	2.827268	1.216935
C 0	0.000691	4.229107	1.209318
C 0	0.000265	4.918253	0.002319
C 0	-0.000288	4.230811	-1.205635
C 0	-0.000371	2.828958	-1.215278
C 0	-0.000759	2.120182	-2.457112
N 0	-0.001070	1.548795	-3.459777
C 0	0.000772	2.116660	2.457706
N 0	0.000871	1.543661	3.459450
H 0	-6.544729	-2.326038	0.000354
H 0	-5.027333	-4.279155	0.000830
H 0	-2.580257	-3.974804	0.000575
H 0	-5.644162	-0.020315	-0.000413
H 0	2.580076	-3.974907	0.000238
H 0	5.027141	-4.279366	0.000230
H 0	6.544623	-2.326315	-0.000439
H 0	5.644153	-0.020551	-0.001099
H 0	0.001090	4.762379	2.151311
H 0	0.000374	6.001047	0.003071

H 0 -0.000620 4.765440 -2.146863

SCF Done: E(UB3LYP) = -2280.15352013

Sum of electronic and zero-point Energies= -2279.872126

Sum of electronic and thermal Energies= -2279.848207

Sum of electronic and thermal Enthalpies= -2279.847263

Sum of electronic and thermal Free Energies= -2279.927836

6.1.6.11 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc,tight) freq=noraman B3LYP/6-311++g(d,p) pop=full scrf=(iefpcm,solvent=dichloromethane)

0 1

C 0	5.497340	-2.171269	-0.027755
C 0	4.630071	-3.274119	-0.022169
C 0	3.252264	-3.100093	-0.013928
C 0	2.720406	-1.799244	-0.011291
C 0	3.612014	-0.702203	-0.017409
C 0	4.994294	-0.873104	-0.025258
C 0	1.344289	-1.378008	-0.002769
C 0	1.204654	-0.025224	-0.002240
S 0	2.745908	0.831237	-0.013600
S 0	0.000001	-2.555600	-0.000005
C 0	-1.344288	-1.378009	0.002757
C 0	-1.204653	-0.025224	0.002223
N 0	-0.000000	0.695715	-0.000013
C 0	-2.720405	-1.799245	0.011284
C 0	-3.612013	-0.702206	0.017400
S 0	-2.745908	0.831235	0.013582
C 0	-3.252262	-3.100095	0.013928
C 0	-4.630068	-3.274121	0.022174
C 0	-5.497339	-2.171273	0.027758
C 0	-4.994293	-0.873107	0.025254
C 0	-0.000001	2.121534	0.000002
C 0	0.039721	2.835335	1.209606
C 0	0.041058	4.237281	1.205278
C 0	-0.000001	4.928065	0.000031
C 0	-0.041060	4.237305	-1.205229
C 0	-0.039724	2.835359	-1.209586
C 0	0.074533	2.129766	2.454436
N 0	0.101105	1.584844	3.471968
C 0	-0.074537	2.129816	-2.454431
N 0	-0.101110	1.584916	-3.471975
H 0	6.569519	-2.327706	-0.034119
H 0	5.041338	-4.276859	-0.024214
H 0	2.593082	-3.960784	-0.009457
H 0	5.662556	-0.020254	-0.029669
H 0	-2.593079	-3.960786	0.009459
H 0	-5.041335	-4.276862	0.024224
H 0	-6.569517	-2.327709	0.034126
H 0	-5.662556	-0.020258	0.029664
H 0	0.072548	4.772479	2.145341
H 0	-0.000000	6.010441	0.000042
H 0	-0.072550	4.772523	-2.145282

SCF Done: E(RB3LYP) = -2280.30978569

Sum of electronic and zero-point Energies= -2280.029525

Sum of electronic and thermal Energies= -2280.006119

Sum of electronic and thermal Enthalpies= -2280.005175

Sum of electronic and thermal Free Energies= -2280.085148

6.1.7 *anti-anti-N-ortho,ortho'*-cyanochlorophenyl-BBTT 3k

6.1.7.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.383940	-2.340188	-0.439336
C 0	-4.532735	-3.334424	0.066041
C 0	-3.187391	-3.075830	0.285446
C 0	-2.672227	-1.802822	-0.005594
C 0	-3.543213	-0.816029	-0.522298
C 0	-4.896413	-1.072424	-0.736624
C 0	-1.335590	-1.296527	0.169225
C 0	-1.197894	-0.000645	-0.217123
S 0	-2.696224	0.690006	-0.850565
S 0	-0.000179	-2.262696	0.847492
C 0	1.335403	-1.296644	0.169324
C 0	1.197791	-0.000784	-0.217085
N 0	0.000007	0.736707	-0.249420
C 0	2.671973	-1.803094	-0.005597
C 0	3.542999	-0.816418	-0.522458
S 0	2.696206	0.689652	-0.850753
C 0	3.187050	-3.076107	0.285594
C 0	4.532371	-3.334823	0.066205
C 0	5.383628	-2.340713	-0.439303
C 0	4.896188	-1.072952	-0.736750
C 0	0.000116	2.104534	0.174078
C 0	0.000170	3.131113	-0.790664
C 0	0.000269	4.477369	-0.402848
C 0	0.000374	4.804158	0.946756
C 0	0.000372	3.803576	1.913902
C 0	0.000244	2.465484	1.527543
Cl 0	0.000146	1.230642	2.757927
C 0	0.000180	2.810646	-2.186914
N 0	0.000342	2.611207	-3.324425
H 0	-6.432012	-2.561056	-0.604348
H 0	-4.932015	-4.317439	0.287396
H 0	-2.534178	-3.849584	0.672539
H 0	-5.552248	-0.305730	-1.132247
H 0	2.533815	-3.849734	0.672882
H 0	4.931552	-4.317871	0.287592
H 0	6.431691	-2.561671	-0.604316
H 0	5.552079	-0.306349	-1.132454
H 0	0.000287	5.248416	-1.162278
H 0	0.000455	5.843628	1.251767
H 0	0.000454	4.050964	2.967737

SCF Done: E(RB3LYP) = -2647.65520226

Sum of electronic and zero-point Energies= -2647.382496

Sum of electronic and thermal Energies= -2647.359135

Sum of electronic and thermal Enthalpies= -2647.358191

Sum of electronic and thermal Free Energies= -2647.437016

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.381321	-2.347575	-0.477209
C 0	-4.529147	-3.364442	-0.021064
C 0	-3.184410	-3.115326	0.212522
C 0	-2.670436	-1.828802	-0.014190
C 0	-3.542276	-0.819262	-0.482614
C 0	-4.894903	-1.065939	-0.710608
C 0	-1.334964	-1.330775	0.190416
C 0	-1.198520	-0.016409	-0.129094
S 0	-2.696176	0.702507	-0.735669
S 0	-0.000036	-2.327450	0.824150
C 0	1.334941	-1.330776	0.190674
C 0	1.198663	-0.016378	-0.128776
N 0	0.000059	0.718520	-0.112255
C 0	2.670463	-1.828844	-0.013588
C 0	3.542454	-0.819271	-0.481740
S 0	2.696526	0.702489	-0.734793
C 0	3.184305	-3.115437	0.212973
C 0	4.529091	-3.364583	-0.020352
C 0	5.381403	-2.347712	-0.476132

C 0	4.895109	-1.066016	-0.709494
C 0	-0.000087	2.086135	0.303015
C 0	0.000521	3.126138	-0.633648
C 0	0.000282	4.460874	-0.229737
C 0	-0.000556	4.774203	1.124246
C 0	-0.001151	3.763975	2.078920
C 0	-0.000927	2.425045	1.673012
C 0	-0.001517	1.400345	2.672240
Cl 0	0.001667	2.768504	-2.343415
N 0	-0.002019	0.609914	3.514008
H 0	-6.429291	-2.560873	-0.652631
H 0	-4.927452	-4.357471	0.152130
H 0	-2.531076	-3.905669	0.564037
H 0	-5.551780	-0.280771	-1.066400
H 0	2.530822	-3.905834	0.564128
H 0	4.927271	-4.357690	0.152688
H 0	6.429421	-2.561008	-0.651284
H 0	5.552110	-0.280859	-1.065086
H 0	0.000744	5.240897	-0.979931
H 0	-0.000740	5.812023	1.434726
H 0	-0.001777	3.997902	3.135783

SCF Done: E(RB3LYP) = -2647.65395838

Sum of electronic and zero-point Energies= -2647.381391

Sum of electronic and thermal Energies= -2647.357956

Sum of electronic and thermal Enthalpies= -2647.357012

Sum of electronic and thermal Free Energies= -2647.436300

6.1.7.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0	-5.401969	-2.324281	-0.411167
C 0	-4.547193	-3.337893	0.049218
C 0	-3.196101	-3.092651	0.254479
C 0	-2.679362	-1.813049	-0.007044
C 0	-3.554835	-0.806880	-0.477433
C 0	-4.913218	-1.048808	-0.676843
C 0	-1.336939	-1.318493	0.159788
C 0	-1.198606	-0.011536	-0.187937
S 0	-2.706596	0.709104	-0.763725
S 0	-0.000005	-2.315358	0.794528
C 0	1.336929	-1.318502	0.159781
C 0	1.198614	-0.011542	-0.187941
N 0	0.000004	0.721836	-0.221289
C 0	2.679352	-1.813063	-0.007032
C 0	3.554841	-0.806898	-0.477400
S 0	2.706609	0.709095	-0.763695
C 0	3.196081	-3.092671	0.254485
C 0	4.547175	-3.337917	0.049241
C 0	5.401965	-2.324308	-0.411124
C 0	4.913224	-1.048829	-0.676796
C 0	0.000006	2.104557	0.151059
C 0	0.000041	3.096789	-0.849927
C 0	0.000050	4.456097	-0.512765
C 0	0.000017	4.829657	0.825283
C 0	-0.000022	3.864534	1.828029
C 0	-0.000025	2.513772	1.488696
Cl 0	-0.000063	1.318361	2.762135
C 0	0.000060	2.718823	-2.231162
N 0	0.000057	2.458769	-3.356689
H 0	-6.453838	-2.534731	-0.564736
H 0	-4.947707	-4.325236	0.247706
H 0	-2.543109	-3.881627	0.609954
H 0	-5.572032	-0.266880	-1.035370
H 0	2.543082	-3.881648	0.609944
H 0	4.947681	-4.325266	0.247724

H 0	6.453834	-2.534763	-0.564680
H 0	5.572045	-0.266901	-1.035307
H 0	0.000080	5.202087	-1.296357
H 0	0.000022	5.878829	1.092860
H 0	-0.000047	4.152884	2.871157

SCF Done: E(RB3LYP) = -2647.66710246

Sum of electronic and zero-point Energies= -2647.394359

Sum of electronic and thermal Energies= -2647.370997

Sum of electronic and thermal Enthalpies= -2647.370053

Sum of electronic and thermal Free Energies= -2647.448900

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0	-5.392216	-2.336390	-0.465898
C 0	-4.538263	-3.370364	-0.051377
C 0	-3.189963	-3.132600	0.179337
C 0	-2.674588	-1.839577	-0.009762
C 0	-3.549234	-0.812657	-0.435063
C 0	-4.904876	-1.047427	-0.659744
C 0	-1.336439	-1.350220	0.197375
C 0	-1.199364	-0.025755	-0.080733
S 0	-2.703017	0.718222	-0.637654
S 0	0.000265	-2.365913	0.804133
C 0	1.336744	-1.350000	0.197244
C 0	1.199419	-0.025559	-0.080868
N 0	-0.000033	0.703614	-0.049815
C 0	2.674962	-1.839131	-0.009985
C 0	3.549407	-0.812065	-0.435343
S 0	2.702905	0.718655	-0.637936
C 0	3.190571	-3.132061	0.179107
C 0	4.538900	-3.369596	-0.051680
C 0	5.392652	-2.335480	-0.466257
C 0	4.905080	-1.046602	-0.660086
C 0	-0.000144	2.093356	0.283722
C 0	-0.000509	3.082102	-0.704818
C 0	-0.000667	4.436096	-0.369401
C 0	-0.000439	4.818006	0.966914
C 0	-0.000081	3.859032	1.974165
C 0	0.000047	2.502570	1.634515
C 0	0.000390	1.520247	2.674891
Cl 0	-0.000935	2.633089	-2.395059
N 0	0.000674	0.749707	3.535386
H 0	-6.442114	-2.541107	-0.639399
H 0	-4.937421	-4.367789	0.091798
H 0	-2.537777	-3.936863	0.500377
H 0	-5.562917	-0.249299	-0.982376
H 0	2.538541	-3.936430	0.500198
H 0	4.938238	-4.366951	0.091485
H 0	6.442575	-2.540019	-0.639815
H 0	5.562964	-0.248365	-0.982768
H 0	-0.000988	5.179404	-1.155785
H 0	-0.000569	5.870038	1.222855
H 0	0.000082	4.150648	3.016211

SCF Done: E(RB3LYP) = -2647.66626235

Sum of electronic and zero-point Energies= -2647.393697

Sum of electronic and thermal Energies= -2647.370249

Sum of electronic and thermal Enthalpies= -2647.369305

Sum of electronic and thermal Free Energies= -2647.448632

6.1.7.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=check guess=read

0 1

C 0	-5.407696	-2.322294	-0.400874
C 0	-4.551574	-3.341154	0.045305
C 0	-3.198895	-3.100215	0.246080
C 0	-2.681598	-1.818664	-0.006162
C 0	-3.559144	-0.807928	-0.462373
C 0	-4.919005	-1.044758	-0.657255
C 0	-1.337965	-1.325755	0.159565
C 0	-1.198757	-0.015524	-0.175690
S 0	-2.710020	0.710666	-0.738444
S 0	0.000001	-2.329568	0.783091
C 0	1.337966	-1.325755	0.159564
C 0	1.198757	-0.015524	-0.175691
N 0	-0.000000	0.717239	-0.203997
C 0	2.681599	-1.818663	-0.006164
C 0	3.559144	-0.807926	-0.462375
S 0	2.710019	0.710667	-0.738446
C 0	3.198896	-3.100214	0.246078
C 0	4.551576	-3.341152	0.045302
C 0	5.407697	-2.322292	-0.400878
C 0	4.919005	-1.044756	-0.657258
C 0	-0.000000	2.106744	0.144215
C 0	-0.000004	3.082640	-0.873443
C 0	-0.000004	4.447633	-0.559713
C 0	-0.000001	4.842983	0.771751
C 0	0.000002	3.895707	1.791497
C 0	0.000002	2.539855	1.474327
Cl 0	0.000006	1.363493	2.769450
C 0	-0.000005	2.682265	-2.247851
N 0	-0.000006	2.401082	-3.368151
H 0	-6.460866	-2.530344	-0.550923
H 0	-4.952236	-4.330199	0.236583
H 0	-2.547334	-3.895325	0.591195
H 0	-5.579383	-0.258658	-1.005014
H 0	2.547335	-3.895324	0.591193
H 0	4.952238	-4.330197	0.236580
H 0	6.460866	-2.530342	-0.550928
H 0	5.579382	-0.258656	-1.005018
H 0	-0.000007	5.179494	-1.357286
H 0	-0.000002	5.896837	1.022004
H 0	0.000004	4.205325	2.829038

SCF Done: E(RB3LYP) = -2647.68997296

Sum of electronic and zero-point Energies= -2647.417330

Sum of electronic and thermal Energies= -2647.393968

Sum of electronic and thermal Enthalpies= -2647.393024

Sum of electronic and thermal Free Energies= -2647.471813

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=check guess=read

0 1

C 0	-5.383840	-2.349999	-0.479969
C 0	-4.531858	-3.379838	-0.051097
C 0	-3.186249	-3.138718	0.192368
C 0	-2.671254	-1.845593	0.000871
C 0	-3.544636	-0.823405	-0.438132
C 0	-4.897606	-1.060773	-0.675646
C 0	-1.336932	-1.350095	0.220701
C 0	-1.198797	-0.026261	-0.060415
S 0	-2.699631	0.709701	-0.638980
S 0	0.000167	-2.355784	0.845724
C 0	1.337122	-1.349953	0.220622
C 0	1.198825	-0.026136	-0.060495
N 0	-0.000023	0.702899	-0.016183
C 0	2.671486	-1.845306	0.000716
C 0	3.544732	-0.823026	-0.438342
S 0	2.699542	0.709986	-0.639159
C 0	3.186636	-3.138371	0.192204
C 0	4.532260	-3.379343	-0.051326
C 0	5.384105	-2.349414	-0.480253

C 0	4.897717	-1.060244	-0.675919
C 0	-0.000096	2.100873	0.284868
C 0	-0.000360	3.065987	-0.727111
C 0	-0.000489	4.428162	-0.428767
C 0	-0.000334	4.843730	0.897297
C 0	-0.000053	3.911323	1.928889
C 0	0.000054	2.546148	1.624964
C 0	0.000340	1.598006	2.696172
Cl 0	-0.000588	2.574428	-2.408702
N 0	0.000576	0.857958	3.582747
H 0	-6.431646	-2.558327	-0.663510
H 0	-4.930450	-4.377654	0.093195
H 0	-2.538099	-3.941889	0.525100
H 0	-5.554481	-0.265405	-1.008871
H 0	2.538592	-3.941610	0.524978
H 0	4.930971	-4.377113	0.092958
H 0	6.431926	-2.557626	-0.663841
H 0	5.554487	-0.264806	-1.009183
H 0	-0.000716	5.152712	-1.233424
H 0	-0.000438	5.902365	1.126444
H 0	0.000073	4.229115	2.963575

SCF Done: E(RB3LYP) = -2647.68965927

Sum of electronic and zero-point Energies= -2647.417100

Sum of electronic and thermal Energies= -2647.393703

Sum of electronic and thermal Enthalpies= -2647.392759

Sum of electronic and thermal Free Energies= -2647.471464

6.1.7.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.478359	-2.197680	-0.018237
C 0	-4.622993	-3.310025	-0.045915
C 0	-3.247573	-3.148021	-0.048577
C 0	-2.711397	-1.848802	-0.023477
C 0	-3.589956	-0.742969	0.003982
C 0	-4.971509	-0.902229	0.007238
C 0	-1.337853	-1.427739	-0.018326
C 0	-1.197941	-0.048183	0.012036
S 0	-2.726436	0.797569	0.035267
S 0	0.000132	-2.545446	-0.041520
C 0	1.338014	-1.427628	-0.018338
C 0	1.198001	-0.048044	0.011786
N 0	0.000009	0.635006	0.026834
C 0	2.711572	-1.848581	-0.023968
C 0	3.590063	-0.742661	0.002528
S 0	2.726459	0.797777	0.033838
C 0	3.247842	-3.147773	-0.048493
C 0	4.623274	-3.309672	-0.046317
C 0	5.478567	-2.197245	-0.019783
C 0	4.971627	-0.901817	0.005171
C 0	-0.000096	2.076700	0.084495
C 0	-0.001297	2.838001	-1.086347
C 0	-0.001409	4.230798	-1.009201
C 0	-0.000016	4.855941	0.233130
C 0	0.001350	4.110140	1.408598
C 0	0.001248	2.714334	1.341424
C 0	0.002057	1.922753	2.532250
Cl 0	-0.002425	2.058791	-2.641212
N 0	0.002650	1.263739	3.480206
H 0	-6.551211	-2.347091	-0.015575
H 0	-5.044902	-4.307188	-0.064475
H 0	-2.596591	-4.014603	-0.068582
H 0	-5.636613	-0.047808	0.030044
H 0	2.596918	-4.014418	-0.067696
H 0	5.045248	-4.306818	-0.064342
H 0	6.551433	-2.346565	-0.017650
H 0	5.636683	-0.047332	0.026991
H 0	-0.002525	4.811390	-1.922654
H 0	-0.000020	5.937849	0.284320

H 0 0.002426 4.595943 2.375628

SCF Done: E(UB3LYP) = -2647.43029471

Sum of electronic and zero-point Energies= -2647.157079

Sum of electronic and thermal Energies= -2647.133744

Sum of electronic and thermal Enthalpies= -2647.132800

Sum of electronic and thermal Free Energies= -2647.211832

6.1.7.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane)

0 1

C 0	-5.474922	-2.206053	-0.038144
C 0	-4.616499	-3.316777	-0.043036
C 0	-3.240648	-3.152437	-0.029492
C 0	-2.709784	-1.851049	-0.010786
C 0	-3.590726	-0.747160	-0.005243
C 0	-4.972442	-0.908158	-0.019045
C 0	-1.336928	-1.427807	0.005986
C 0	-1.197311	-0.049234	0.027025
S 0	-2.728624	0.795689	0.021489
S 0	0.000045	-2.545663	0.001734
C 0	1.336981	-1.427760	0.006023
C 0	1.197312	-0.049198	0.027084
N 0	-0.000008	0.634445	0.046890
C 0	2.709852	-1.850967	-0.010691
C 0	3.590772	-0.747065	-0.005077
S 0	2.728630	0.795795	0.021654
C 0	3.240740	-3.152344	-0.029428
C 0	4.616595	-3.316660	-0.042934
C 0	5.474996	-2.205920	-0.037983
C 0	4.972490	-0.908034	-0.018855
C 0	-0.000036	2.076642	0.085827
C 0	0.000082	2.820391	-1.095280
C 0	0.000021	4.213395	-1.046733
C 0	-0.000176	4.860919	0.183502
C 0	-0.000294	4.137279	1.372285
C 0	-0.000209	2.740717	1.329923
C 0	-0.000286	1.986105	2.544506
Cl 0	0.000260	2.010879	-2.641193
N 0	-0.000346	1.379526	3.526690
H 0	-6.547661	-2.358183	-0.048731
H 0	-5.035591	-4.315585	-0.057051
H 0	-2.587703	-4.018006	-0.032169
H 0	-5.640489	-0.055268	-0.014768
H 0	2.587812	-4.017926	-0.032163
H 0	5.035706	-4.315460	-0.056968
H 0	6.547738	-2.358027	-0.048551
H 0	5.640523	-0.055134	-0.014544
H 0	0.000109	4.780041	-1.969091
H 0	-0.000233	5.943514	0.214837
H 0	-0.000438	4.641223	2.329785

SCF Done: E(UB3LYP) = -2647.51235209

Sum of electronic and zero-point Energies= -2647.238999

Sum of electronic and thermal Energies= -2647.215738

Sum of electronic and thermal Enthalpies= -2647.214794

Sum of electronic and thermal Free Energies= -2647.293751

6.1.8 *anti-anti-N-ortho,ortho'*-cyanofluorophenyl-BBTT 3l

6.1.8.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.356981	-2.326538	-0.419512
C 0	-4.514798	-3.290112	0.156053
C 0	-3.178064	-3.011382	0.400761
C 0	-2.663153	-1.749417	0.065692
C 0	-3.524061	-0.793477	-0.521919
C 0	-4.869309	-1.070772	-0.762244
C 0	-1.334613	-1.224624	0.253513
C 0	-1.194882	0.053578	-0.186227
S 0	-2.676791	0.699908	-0.900965
S 0	-0.000027	-2.150230	0.984930
C 0	1.334620	-1.224570	0.253683
C 0	1.194958	0.053675	-0.186040
N 0	0.000017	0.801744	-0.213401
C 0	2.663185	-1.749367	0.066035
C 0	3.524199	-0.793469	-0.521426
S 0	2.676937	0.700001	-0.900615
C 0	3.178068	-3.011469	0.401089
C 0	4.514781	-3.290200	0.156386
C 0	5.357037	-2.326604	-0.419105
C 0	4.869447	-1.070807	-0.761757
C 0	-0.000094	2.119083	0.351834
C 0	0.000315	3.261576	-0.469152
C 0	0.000227	4.545107	0.095658
C 0	-0.000294	4.694088	1.477134
C 0	-0.000725	3.576113	2.307743
C 0	-0.000612	2.314804	1.733505
F 0	-0.000995	1.237455	2.534528
C 0	0.000767	3.124186	-1.894616
N 0	0.001097	3.067496	-3.048120
H 0	-6.398561	-2.562735	-0.603629
H 0	-4.914445	-4.264529	0.411939
H 0	-2.531388	-3.760899	0.842669
H 0	-5.518373	-0.328588	-1.212042
H 0	2.531320	-3.760950	0.842898
H 0	4.914412	-4.264649	0.412179
H 0	6.398594	-2.562882	-0.603225
H 0	5.518551	-0.328600	-1.211457
H 0	0.000539	5.409702	-0.555080
H 0	-0.000366	5.685860	1.912457
H 0	-0.001126	3.665219	3.387040

SCF Done: E(RB3LYP) = -2287.30139835

Sum of electronic and zero-point Energies= -2287.027198

Sum of electronic and thermal Energies= -2287.004215

Sum of electronic and thermal Enthalpies= -2287.003271

Sum of electronic and thermal Free Energies= -2287.081508

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.346475	-2.329077	-0.506265
C 0	4.500825	-3.324606	0.005271
C 0	3.166734	-3.056530	0.276649
C 0	2.655961	-1.772225	0.031015
C 0	3.521382	-0.784841	-0.494088
C 0	4.863397	-1.049569	-0.759008
C 0	1.333106	-1.255308	0.264384
C 0	1.198524	0.050044	-0.090763
S 0	2.681339	0.740346	-0.758858
S 0	-0.000785	-2.198130	0.983715
C 0	-1.334271	-1.254564	0.264570
C 0	-1.199114	0.050766	-0.090516
N 0	-0.000077	0.779664	-0.054028
C 0	-2.657664	-1.770554	0.032499
C 0	-3.522916	-0.782494	-0.491766
S 0	-2.682154	0.742083	-0.757102
C 0	-3.169132	-3.054485	0.278614
C 0	-4.503647	-3.321607	0.008542
C 0	-5.349048	-2.325491	-0.502306
C 0	-4.865226	-1.046294	-0.755523

C 0	0.000608	2.197781	0.065864
C 0	0.004274	2.833020	1.324917
C 0	0.005302	4.229619	1.417419
C 0	0.002461	5.001416	0.259779
C 0	-0.001199	4.395899	-0.992214
C 0	-0.001973	3.010119	-1.068024
F 0	-0.005159	2.430816	-2.279902
C 0	0.006959	2.049383	2.522404
N 0	0.009164	1.453954	3.511649
H 0	6.386146	-2.556983	-0.710179
H 0	4.895938	-4.316420	0.192335
H 0	2.517858	-3.830245	0.670791
H 0	5.514784	-0.280718	-1.157937
H 0	-2.520338	-3.828694	0.671925
H 0	-4.899354	-4.313065	0.196232
H 0	-6.389145	-2.552618	-0.705293
H 0	-5.516456	-0.277092	-1.154056
H 0	0.008209	4.696125	2.393915
H 0	0.003184	6.082047	0.333130
H 0	-0.003306	4.973792	-1.907888

SCF Done: E(RB3LYP) = -2287.30039449

Sum of electronic and zero-point Energies= -2287.026384

Sum of electronic and thermal Energies= -2287.003239

Sum of electronic and thermal Enthalpies= -2287.002294

Sum of electronic and thermal Free Energies= -2287.082139

6.1.8.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full Guess=Read geom=chec

k

SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	-5.371749	-2.313664	-0.406180
C 0	-4.525063	-3.297426	0.128693
C 0	-3.183437	-3.030580	0.365022
C 0	-2.668625	-1.759909	0.060713
C 0	-3.534798	-0.784050	-0.485318
C 0	-4.884645	-1.048070	-0.716164
C 0	-1.335774	-1.244644	0.247446
C 0	-1.196134	0.046182	-0.154406
S 0	-2.687826	0.721694	-0.821455
S 0	0.000006	-2.198215	0.944699
C 0	1.335782	-1.244639	0.247444
C 0	1.196136	0.046186	-0.154408
N 0	-0.000001	0.789877	-0.180604
C 0	2.668634	-1.759898	0.060710
C 0	3.534803	-0.784037	-0.485320
S 0	2.687825	0.721705	-0.821456
C 0	3.183452	-3.030568	0.365019
C 0	4.525078	-3.297408	0.128689
C 0	5.371761	-2.313641	-0.406184
C 0	4.884652	-1.048050	-0.716167
C 0	-0.000004	2.125932	0.339641
C 0	-0.000011	3.242238	-0.517868
C 0	-0.000015	4.543418	0.003223
C 0	-0.000012	4.735345	1.380193
C 0	-0.000006	3.644971	2.246697
C 0	-0.000002	2.366648	1.712368
F 0	0.000004	1.309415	2.546458
C 0	-0.000017	3.052873	-1.936745
N 0	-0.000022	2.940972	-3.086551
H 0	-6.416508	-2.540555	-0.583257
H 0	-4.924743	-4.277755	0.360608
H 0	-2.536036	-3.795522	0.778459
H 0	-5.537420	-0.290012	-1.132312
H 0	2.536053	-3.795512	0.778455

H 0	4.924763	-4.277734	0.360604
H 0	6.416521	-2.540530	-0.583260
H 0	5.537423	-0.289989	-1.132315
H 0	-0.000022	5.388705	-0.671854
H 0	-0.000016	5.739901	1.783675
H 0	-0.000004	3.772114	3.321966

SCF Done: E(RB3LYP) = -2287.31347154

Sum of electronic and zero-point Energies= -2287.039285

Sum of electronic and thermal Energies= -2287.016303

Sum of electronic and thermal Enthalpies= -2287.015358

Sum of electronic and thermal Free Energies= -2287.093533

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full Guess=Read geom=chec

k SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	5.358207	-2.309016	-0.510374
C 0	4.512129	-3.329704	-0.049581
C 0	3.174563	-3.078467	0.225711
C 0	2.661036	-1.785051	0.034247
C 0	3.528025	-0.771885	-0.437932
C 0	4.872928	-1.019464	-0.706971
C 0	1.334281	-1.282489	0.276829
C 0	1.198347	0.037912	-0.021208
S 0	2.687131	0.764853	-0.631583
S 0	-0.000029	-2.258467	0.954546
C 0	-1.334294	-1.282467	0.276798
C 0	-1.198359	0.037935	-0.021228
N 0	-0.000002	0.764933	0.047181
C 0	-2.661074	-1.784994	0.034292
C 0	-3.528065	-0.771835	-0.437885
S 0	-2.687154	0.764900	-0.631552
C 0	-3.174586	-3.078412	0.225789
C 0	-4.512157	-3.329654	-0.049480
C 0	-5.358240	-2.308973	-0.510281
C 0	-4.872970	-1.019421	-0.706905
C 0	0.000016	2.189390	0.053750
C 0	0.000096	2.914362	1.263315
C 0	0.000121	4.313105	1.257385
C 0	0.000046	4.997939	0.045221
C 0	-0.000043	4.303813	-1.159871
C 0	-0.000049	2.916519	-1.134917
F 0	-0.000144	2.244726	-2.302047
C 0	0.000156	2.209308	2.508190
N 0	0.000209	1.664703	3.526698
H 0	6.399750	-2.524215	-0.718062
H 0	4.909131	-4.327841	0.094859
H 0	2.528160	-3.872331	0.582253
H 0	5.524338	-0.231208	-1.065423
H 0	-2.528173	-3.872265	0.582336
H 0	-4.909160	-4.327788	0.094981
H 0	-6.399785	-2.524178	-0.717954
H 0	-5.524387	-0.231177	-1.065370
H 0	0.000187	4.852330	2.195271
H 0	0.000055	6.080480	0.039594
H 0	-0.000103	4.816933	-2.113132

SCF Done: E(RB3LYP) = -2287.31318713

Sum of electronic and zero-point Energies= -2287.039163

Sum of electronic and thermal Energies= -2287.016065

Sum of electronic and thermal Enthalpies= -2287.015120

Sum of electronic and thermal Free Energies= -2287.093910

6.1.8.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=checkpoint guess=read

0 1

C 0	-5.362817	-2.327466	-0.420203
C 0	-4.517553	-3.303811	0.130362
C 0	-3.178955	-3.030774	0.376927
C 0	-2.665551	-1.760762	0.066734
C 0	-3.530495	-0.793235	-0.495648
C 0	-4.877544	-1.062647	-0.736535
C 0	-1.336220	-1.237877	0.261011
C 0	-1.195278	0.049482	-0.151241
S 0	-2.684104	0.712194	-0.840312
S 0	-0.000001	-2.178395	0.976712
C 0	1.336220	-1.237878	0.261011
C 0	1.195277	0.049481	-0.151241
N 0	0.000000	0.794190	-0.173738
C 0	2.665550	-1.760762	0.066735
C 0	3.530494	-0.793236	-0.495648
S 0	2.684104	0.712193	-0.840312
C 0	3.178954	-3.030775	0.376928
C 0	4.517552	-3.303812	0.130363
C 0	5.362816	-2.327467	-0.420203
C 0	4.877544	-1.062648	-0.736535
C 0	0.000000	2.132500	0.343522
C 0	0.000001	3.249116	-0.514603
C 0	0.000001	4.550848	0.004752
C 0	0.000001	4.743522	1.381690
C 0	0.000000	3.653916	2.249100
C 0	0.000000	2.375961	1.715139
F 0	-0.000000	1.317598	2.551326
C 0	0.000001	3.060098	-1.932845
N 0	0.000002	2.946146	-3.082364
H 0	-6.405384	-2.559725	-0.605110
H 0	-4.915811	-4.283939	0.367131
H 0	-2.534643	-3.791723	0.802951
H 0	-5.530153	-0.310915	-1.165356
H 0	2.534642	-3.791724	0.802951
H 0	4.915810	-4.283941	0.367131
H 0	6.405383	-2.559727	-0.605109
H 0	5.530152	-0.310917	-1.165356
H 0	0.000002	5.394752	-0.672740
H 0	0.000001	5.748671	1.784636
H 0	0.000000	3.781951	3.324798

SCF Done: E(RB3LYP) = -2287.33540914

Sum of electronic and zero-point Energies= -2287.061403

Sum of electronic and thermal Energies= -2287.038409

Sum of electronic and thermal Enthalpies= -2287.037465

Sum of electronic and thermal Free Energies= -2287.115586

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=checkpoint guess=read

0 1

C 0	5.355821	-2.319377	-0.505151
C 0	4.509479	-3.328183	-0.019188
C 0	3.172413	-3.069784	0.252364
C 0	2.659512	-1.780939	0.029942
C 0	3.526989	-0.780442	-0.467731
C 0	4.871631	-1.034365	-0.732500
C 0	1.335052	-1.268887	0.267961
C 0	1.197727	0.044613	-0.057978
S 0	2.685791	0.752483	-0.697628
S 0	-0.000159	-2.225439	0.972355
C 0	-1.335092	-1.268872	0.267488
C 0	-1.197723	0.044693	-0.058211
N 0	0.000017	0.772407	-0.004038
C 0	-2.659568	-1.780843	0.029405
C 0	-3.527099	-0.780190	-0.467864
S 0	-2.685835	0.752754	-0.697563

C 0	-3.172501	-3.069711	0.251632
C 0	-4.509661	-3.327964	-0.019598
C 0	-5.356069	-2.318982	-0.505073
C 0	-4.871827	-1.033970	-0.732326
C 0	0.000097	2.196874	0.061812
C 0	0.000040	2.878382	1.297724
C 0	0.000059	4.276217	1.342175
C 0	0.000295	5.004398	0.155149
C 0	0.000435	4.354766	-1.074320
C 0	0.000311	2.967841	-1.097880
F 0	0.000617	2.336847	-2.290644
C 0	-0.000242	2.130800	2.516891
N 0	-0.000445	1.549911	3.514984
H 0	6.397170	-2.540653	-0.709084
H 0	4.905981	-4.323166	0.148747
H 0	2.528049	-3.856075	0.629623
H 0	5.524129	-0.255582	-1.110464
H 0	-2.528030	-3.856164	0.628371
H 0	-4.906171	-4.322969	0.148199
H 0	-6.397504	-2.540120	-0.708715
H 0	-5.524374	-0.255078	-1.109977
H 0	-0.000070	4.780307	2.299881
H 0	0.000363	6.086917	0.188897
H 0	0.000668	4.901526	-2.009252

SCF Done: E(RB3LYP) = -2287.33561944

Sum of electronic and zero-point Energies= -2287.061635

Sum of electronic and thermal Energies= -2287.038590

Sum of electronic and thermal Enthalpies= -2287.037646

Sum of electronic and thermal Free Energies= -2287.115768

6.1.8.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.478474	-2.136432	-0.043690
C 0	4.623187	-3.248538	-0.006932
C 0	3.247757	-3.086664	-0.005528
C 0	2.711500	-1.787745	-0.041577
C 0	3.590125	-0.682234	-0.078712
C 0	4.971601	-0.841199	-0.080149
C 0	1.337885	-1.366769	-0.045975
C 0	1.198220	0.012563	-0.084130
S 0	2.726016	0.858506	-0.118740
S 0	-0.000194	-2.483640	0.000553
C 0	-1.338163	-1.366673	-0.046606
C 0	-1.198394	0.012663	-0.085032
N 0	-0.000064	0.696178	-0.092812
C 0	-2.711807	-1.787527	-0.041435
C 0	-3.590360	-0.681945	-0.078219
S 0	-2.726130	0.858732	-0.118261
C 0	-3.248166	-3.086381	-0.004558
C 0	-4.623614	-3.248120	-0.004790
C 0	-5.478819	-2.135954	-0.041537
C 0	-4.971847	-0.840782	-0.078928
C 0	0.000021	2.136576	-0.112109
C 0	0.001507	2.874052	1.088366
C 0	0.001536	4.270960	1.037271
C 0	0.000052	4.920576	-0.195753
C 0	-0.001456	4.199579	-1.385875
C 0	-0.001478	2.813434	-1.328167
F 0	-0.002733	2.097169	-2.459506
C 0	0.002942	2.180277	2.338253
N 0	0.003869	1.598015	3.335157
H 0	6.551338	-2.285746	-0.043076
H 0	5.045188	-4.245424	0.021568
H 0	2.596886	-3.953047	0.024176
H 0	5.636695	0.013090	-0.107328
H 0	-2.597360	-3.952828	0.024737
H 0	-5.045687	-4.244950	0.024595
H 0	-6.551696	-2.285170	-0.040318
H 0	-5.636877	0.013547	-0.106432

H 0 0.002737 4.835434 1.960430

H 0 0.000062 6.003029 -0.229035

H 0 -0.002607 4.688333 -2.352122

SCF Done: E(UB3LYP) = -2287.07531311

Sum of electronic and zero-point Energies= -2286.800607

Sum of electronic and thermal Energies= -2286.777629

Sum of electronic and thermal Enthalpies= -2286.776685

Sum of electronic and thermal Free Energies= -2286.854922

6.1.8.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0 5.474365 -2.150874 -0.042786

C 0 4.615428 -3.260876 -0.015406

C 0 3.239648 -3.095565 -0.006784

C 0 2.709426 -1.793942 -0.026125

C 0 3.590784 -0.690850 -0.055343

C 0 4.972471 -0.852769 -0.063312

C 0 1.336633 -1.369968 -0.023597

C 0 1.197147 0.008514 -0.048727

S 0 2.729005 0.852336 -0.079106

S 0 -0.000042 -2.487629 0.001148

C 0 -1.336681 -1.369930 -0.023720

C 0 -1.197145 0.008546 -0.048844

N 0 0.000006 0.693189 -0.051523

C 0 -2.709493 -1.793865 -0.026261

C 0 -3.590822 -0.690757 -0.055495

S 0 -2.728963 0.852438 -0.079207

C 0 -3.239768 -3.095466 -0.006919

C 0 -4.615558 -3.260721 -0.015567

C 0 -5.474458 -2.150693 -0.042969

C 0 -4.972511 -0.852605 -0.063483

C 0 0.000034 2.132690 -0.120906

C 0 -0.000107 2.925851 1.044528

C 0 -0.000036 4.319054 0.931718

C 0 0.000208 4.913235 -0.328543

C 0 0.000356 4.140287 -1.484518

C 0 0.000253 2.759712 -1.362820

F 0 0.000426 1.991462 -2.465975

C 0 -0.000334 2.310853 2.334739

N 0 -0.000452 1.822390 3.380703

H 0 6.547037 -2.303745 -0.048108

H 0 5.034076 -4.259856 -0.000355

H 0 2.586278 -3.960554 0.014666

H 0 5.640938 -0.000456 -0.084260

H 0 -2.586443 -3.960487 0.014596

H 0 -5.034240 -4.259687 -0.000525

H 0 -6.547135 -2.303528 -0.048320

H 0 -5.640934 -0.000259 -0.084409

H 0 -0.000187 4.923949 1.828804

H 0 0.000306 5.992988 -0.409441

H 0 0.000560 4.585950 -2.471641

SCF Done: E(UB3LYP) = -2287.15720050

Sum of electronic and zero-point Energies= -2286.882213

Sum of electronic and thermal Energies= -2286.859411

Sum of electronic and thermal Enthalpies= -2286.858466

Sum of electronic and thermal Free Energies= -2286.935886

6.1.9 *anti-anti-N-ortho,ortho'*-cyanomethylphenyl-BBTT 3m

6.1.9.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.387582	-2.278712	-0.404730
C 0	-4.535088	-3.301275	0.037713
C 0	-3.188431	-3.057135	0.266351
C 0	-2.672782	-1.769678	0.047602
C 0	-3.545252	-0.753769	-0.407177
C 0	-4.899574	-0.995971	-0.629475
C 0	-1.336283	-1.274638	0.247261
C 0	-1.196520	0.042163	-0.066056
S 0	-2.699297	0.770123	-0.646814
S 0	0.000006	-2.271942	0.884312
C 0	1.336290	-1.274618	0.247301
C 0	1.196514	0.042170	-0.066006
N 0	-0.000015	0.774594	-0.062005
C 0	2.672831	-1.769638	0.047649
C 0	3.545270	-0.753717	-0.407121
S 0	2.699314	0.770189	-0.646713
C 0	3.188453	-3.057107	0.266284
C 0	4.535117	-3.301263	0.037542
C 0	5.387575	-2.278690	-0.404922
C 0	4.899566	-0.995934	-0.629560
C 0	-0.000010	2.157884	0.334918
C 0	-0.000101	3.154205	-0.658572
C 0	-0.000124	4.508813	-0.297583
C 0	-0.000028	4.854809	1.046030
C 0	0.000092	3.864135	2.025305
C 0	0.000092	2.505386	1.694659
C 0	0.000158	1.446890	2.766516
C 0	-0.000129	2.805310	-2.047836
N 0	-0.000144	2.576541	-3.180098
H 0	-6.436483	-2.488733	-0.578342
H 0	-4.934112	-4.295550	0.202080
H 0	-2.534278	-3.852930	0.604083
H 0	-5.556148	-0.206899	-0.977042
H 0	2.534306	-3.852922	0.603981
H 0	4.934126	-4.295556	0.201824
H 0	6.436447	-2.488727	-0.578693
H 0	5.556117	-0.206864	-0.977174
H 0	-0.000202	5.266179	-1.070936
H 0	-0.000044	5.899678	1.333363
H 0	0.000190	4.147721	3.072211
H 0	0.000273	1.903305	3.757112
H 0	-0.878148	0.800911	2.686642
H 0	0.878370	0.800809	2.686476

SCF Done: E(RB3LYP) = -2227.36672020

Sum of electronic and zero-point Energies= -2227.056797

Sum of electronic and thermal Energies= -2227.032994

Sum of electronic and thermal Enthalpies= -2227.032050

Sum of electronic and thermal Free Energies= -2227.111329

Conformer II:

#p opt=verytight freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.426812	-2.214850	-0.390754
C 0	4.571304	-3.279676	-0.072825
C 0	3.214965	-3.069381	0.133263
C 0	2.690531	-1.771743	0.016532
C 0	3.568568	-0.713050	-0.310925
C 0	4.930804	-0.920452	-0.511523
C 0	1.340545	-1.312741	0.205680
C 0	1.199193	0.026134	0.007283
S 0	2.714536	0.823388	-0.424207
S 0	0.007573	-2.378401	0.732505
C 0	-1.330444	-1.320172	0.203980
C 0	-1.196085	0.019488	0.006196
N 0	-0.000405	0.747635	0.063695
C 0	-2.676503	-1.787269	0.007161
C 0	-3.558707	-0.733984	-0.326619
S 0	-2.713086	0.807273	-0.437587

C 0	-3.193746	-3.087978	0.121631
C 0	-4.547501	-3.306547	-0.092424
C 0	-5.407471	-2.246985	-0.416018
C 0	-4.918559	-0.949749	-0.534857
C 0	-0.005977	2.179684	0.005504
C 0	-0.030119	2.902571	1.217304
C 0	-0.039071	4.299767	1.205446
C 0	-0.024412	4.970149	-0.013193
C 0	-0.002099	4.255314	-1.203694
C 0	0.008349	2.852637	-1.224303
C 0	0.041515	2.129370	-2.547922
C 0	-0.045165	2.211824	2.471027
N 0	-0.057493	1.693722	3.503183
H 0	6.483602	-2.398664	-0.544759
H 0	4.975954	-4.281368	0.015375
H 0	2.560706	-3.898296	0.378012
H 0	5.589824	-0.095977	-0.757840
H 0	-2.535926	-3.912731	0.370857
H 0	-4.946707	-4.310568	-0.005909
H 0	-6.462201	-2.437256	-0.576193
H 0	-5.581026	-0.129446	-0.785791
H 0	-0.057784	4.842089	2.142112
H 0	-0.032426	6.053617	-0.031658
H 0	0.006293	4.789511	-2.147970
H 0	-0.748191	2.503780	-3.204124
H 0	0.998283	2.300538	-3.049843
H 0	-0.089839	1.054952	-2.437494

SCF Done: E(RB3LYP) = -2227.36511570

Sum of electronic and zero-point Energies= -2227.055538

Sum of electronic and thermal Energies= -2227.031463

Sum of electronic and thermal Enthalpies= -2227.030518

Sum of electronic and thermal Free Energies= -2227.111616

6.1.9.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full Guess=Read geom=chec k SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	-5.413109	-2.249616	-0.364148
C 0	-4.557103	-3.293165	0.020494
C 0	-3.202611	-3.066159	0.225718
C 0	-2.682982	-1.774150	0.040378
C 0	-3.560299	-0.737205	-0.354641
C 0	-4.921589	-0.961256	-0.553158
C 0	-1.337755	-1.295600	0.223318
C 0	-1.196821	0.031596	-0.042454
S 0	-2.710066	0.792530	-0.549228
S 0	0.000001	-2.332322	0.794514
C 0	1.337755	-1.295599	0.223316
C 0	1.196821	0.031596	-0.042455
N 0	-0.000000	0.761162	-0.040340
C 0	2.682983	-1.774149	0.040377
C 0	3.560299	-0.737204	-0.354641
S 0	2.710067	0.792532	-0.549228
C 0	3.202612	-3.066158	0.225715
C 0	4.557104	-3.293164	0.020489
C 0	5.413109	-2.249614	-0.364152
C 0	4.921590	-0.961254	-0.553159
C 0	0.000000	2.156648	0.313308
C 0	-0.000002	3.121009	-0.712740
C 0	-0.000002	4.487157	-0.399597
C 0	0.000000	4.875390	0.933258
C 0	0.000003	3.917325	1.944421
C 0	0.000002	2.546841	1.659904
C 0	0.000004	1.524712	2.766183
C 0	-0.000005	2.720146	-2.087037

N 0	-0.000009	2.437855	-3.207708
H 0	-6.467444	-2.446226	-0.519032
H 0	-4.959113	-4.290030	0.159756
H 0	-2.549064	-3.878666	0.522500
H 0	-5.581060	-0.155581	-0.853351
H 0	2.549065	-3.878666	0.522497
H 0	4.959114	-4.290030	0.159751
H 0	6.467444	-2.446224	-0.519037
H 0	5.581061	-0.155579	-0.853352
H 0	-0.000004	5.220860	-1.195045
H 0	0.000000	5.928699	1.186109
H 0	0.000005	4.235967	2.980755
H 0	0.000004	2.014198	3.740154
H 0	-0.879439	0.877768	2.707767
H 0	0.879450	0.877771	2.707766

SCF Done: E(RB3LYP) = -2227.37832470

Sum of electronic and zero-point Energies= -2227.068536

Sum of electronic and thermal Energies= -2227.044651

Sum of electronic and thermal Enthalpies= -2227.043707

Sum of electronic and thermal Free Energies= -2227.123464

Conformer II:

#p opt=verytight freq=noraman rb3lyp/6-311++g(d,p) pop=full Guess=Read

geom=check SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	5.412828	-2.237153	-0.421627
C 0	4.557838	-3.294799	-0.075579
C 0	3.203895	-3.076884	0.143709
C 0	2.682277	-1.778761	0.011094
C 0	3.559840	-0.727368	-0.343652
C 0	4.919777	-0.942273	-0.557278
C 0	1.336671	-1.310069	0.208726
C 0	1.196970	0.026900	-0.008620
S 0	2.709616	0.810665	-0.473034
S 0	0.000000	-2.360078	0.762177
C 0	-1.336670	-1.310069	0.208726
C 0	-1.196970	0.026900	-0.008620
N 0	0.000000	0.750824	0.044636
C 0	-2.682277	-1.778761	0.011094
C 0	-3.559839	-0.727368	-0.343652
S 0	-2.709616	0.810665	-0.473034
C 0	-3.203894	-3.076884	0.143709
C 0	-4.557837	-3.294799	-0.075579
C 0	-5.412828	-2.237153	-0.421627
C 0	-4.919777	-0.942273	-0.557278
C 0	-0.000000	2.186214	0.014888
C 0	-0.000000	2.882038	1.244221
C 0	-0.000000	4.278416	1.269509
C 0	-0.000000	4.976757	0.065406
C 0	-0.000000	4.289971	-1.141125
C 0	-0.000000	2.886463	-1.197561
C 0	-0.000000	2.200646	-2.540835
C 0	-0.000000	2.156549	2.477305
N 0	-0.000000	1.597730	3.488785
H 0	6.466898	-2.426844	-0.586470
H 0	4.960495	-4.296208	0.023901
H 0	2.552000	-3.900622	0.411640
H 0	5.578117	-0.124527	-0.825921
H 0	-2.551999	-3.900622	0.411640
H 0	-4.960495	-4.296208	0.023901
H 0	-6.466898	-2.426844	-0.586470
H 0	-5.578117	-0.124527	-0.825921
H 0	-0.000000	4.800887	2.217279
H 0	-0.000000	6.059918	0.072547
H 0	-0.000000	4.846628	-2.071855
H 0	-0.880997	2.497889	-3.115808
H 0	0.880998	2.497888	-3.115807
H 0	-0.000001	1.115844	-2.456477

SCF Done: E(RB3LYP) = -2227.37757700

Sum of electronic and zero-point Energies= -2227.067987

Sum of electronic and thermal Enthalpies= -2227.043029

Sum of electronic and thermal Energies= -2227.043973

Sum of electronic and thermal Free Energies= -2227.123671

6.1.9.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full

0 1

C 0	-5.392903	-2.290064	-0.366956
C 0	-4.531643	-3.325027	0.029220
C 0	-3.180055	-3.087506	0.242857
C 0	-2.668584	-1.792368	0.054366
C 0	-3.552011	-0.764713	-0.350620
C 0	-4.910360	-0.998504	-0.557889
C 0	-1.328210	-1.301069	0.243833
C 0	-1.194267	0.026489	-0.024471
S 0	-2.712574	0.772266	-0.543141
S 0	0.016850	-2.322832	0.827035
C 0	1.348029	-1.286257	0.238464
C 0	1.197714	0.039478	-0.029678
N 0	-0.001866	0.762942	-0.016881
C 0	2.692325	-1.762811	0.040109
C 0	3.561478	-0.725774	-0.372071
S 0	2.703235	0.801476	-0.561671
C 0	3.219421	-3.051945	0.226967
C 0	4.572147	-3.274630	0.004862
C 0	5.419188	-2.230552	-0.397963
C 0	4.920948	-0.944735	-0.587683
C 0	-0.009877	2.164300	0.318245
C 0	-0.047703	3.114850	-0.721498
C 0	-0.065146	4.485507	-0.429398
C 0	-0.043557	4.892712	0.897634
C 0	-0.002287	3.950100	1.922029
C 0	0.015310	2.574605	1.658918
C 0	0.069535	1.574520	2.782309
C 0	-0.063098	2.696148	-2.089709
N 0	-0.074161	2.397767	-3.206084
H 0	-6.444716	-2.495920	-0.529092
H 0	-4.927082	-4.324620	0.170025
H 0	-2.524817	-3.895665	0.548636
H 0	-5.574240	-0.198887	-0.866102
H 0	2.575331	-3.866956	0.538315
H 0	4.979727	-4.269494	0.144498
H 0	6.472168	-2.424848	-0.566566
H 0	5.573882	-0.138246	-0.901293
H 0	-0.094334	5.206201	-1.236821
H 0	-0.057552	5.949862	1.135608
H 0	0.015093	4.283288	2.953846
H 0	0.000544	2.079964	3.746297
H 0	-0.746508	0.850217	2.715456
H 0	1.006164	1.009056	2.761111

SCF Done: E(RB3LYP) = -2227.40148536

Sum of electronic and zero-point Energies= -2227.091632

Sum of electronic and thermal Energies= -2227.067897

Sum of electronic and thermal Enthalpies= -2227.066953

Sum of electronic and thermal Free Energies= -2227.145923

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=checkpoint guess=read

0 1

C 0	5.381957	-2.278798	-0.475190
C 0	4.530683	-3.312061	-0.053711

C 0	3.185853	-3.073064	0.197647
C 0	2.669465	-1.778092	0.020083
C 0	3.543038	-0.752364	-0.411291
C 0	4.894696	-0.987245	-0.655757
C 0	1.335565	-1.285797	0.242810
C 0	1.195727	0.040914	-0.030098
S 0	2.699535	0.785836	-0.587674
S 0	0.000017	-2.286071	0.884581
C 0	-1.335560	-1.285802	0.242865
C 0	-1.195739	0.040910	-0.030041
N 0	-0.000007	0.767036	0.019978
C 0	-2.669463	-1.778107	0.020170
C 0	-3.543053	-0.752383	-0.411181
S 0	-2.699566	0.785823	-0.587579
C 0	-3.185836	-3.073084	0.197738
C 0	-4.530669	-3.312090	-0.053592
C 0	-5.381961	-2.278832	-0.475048
C 0	-4.894715	-0.987274	-0.655620
C 0	-0.000013	2.204452	0.041151
C 0	0.000100	2.860921	1.293777
C 0	0.000091	4.255557	1.365538
C 0	-0.000035	4.993395	0.184854
C 0	-0.000149	4.347058	-1.043425
C 0	-0.000140	2.945419	-1.146824
C 0	-0.000292	2.309667	-2.513693
C 0	0.000248	2.099838	2.504545
N 0	0.000368	1.510949	3.498692
H 0	6.429077	-2.485448	-0.664379
H 0	4.929234	-4.311530	0.079273
H 0	2.538695	-3.879329	0.524804
H 0	5.550570	-0.188263	-0.982492
H 0	-2.538664	-3.879346	0.524875
H 0	-4.929210	-4.311563	0.079395
H 0	-6.429083	-2.485490	-0.664216
H 0	-5.550601	-0.188297	-0.982339
H 0	0.000184	4.745261	2.331057
H 0	-0.000045	6.076192	0.228266
H 0	-0.000253	4.933231	-1.956270
H 0	-0.880873	2.629344	-3.078434
H 0	0.880154	2.629353	-3.078637
H 0	-0.000284	1.221765	-2.475084

SCF Done: E(RB3LYP) = -2227.40112348

Sum of electronic and zero-point Energies= -2227.091307

Sum of electronic and thermal Energies= -2227.067556

Sum of electronic and thermal Enthalpies= -2227.066612

Sum of electronic and thermal Free Energies= -2227.145356

6.1.9.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.478592	-2.121164	-0.011983
C 0	4.623983	-3.234283	0.009372
C 0	3.248503	-3.073704	-0.008608
C 0	2.711492	-1.775177	-0.049301
C 0	3.589049	-0.668352	-0.070766
C 0	4.970741	-0.826517	-0.052133
C 0	1.337660	-1.355625	-0.070682
C 0	1.195370	0.023994	-0.106210
S 0	2.724632	0.871852	-0.114048
S 0	-0.000004	-2.474662	-0.042094
C 0	-1.337665	-1.355622	-0.070680
C 0	-1.195371	0.023997	-0.106204
N 0	0.000000	0.708037	-0.131479
C 0	-2.711499	-1.775167	-0.049312
C 0	-3.589047	-0.668334	-0.070785
S 0	-2.724630	0.871852	-0.114062
C 0	-3.248518	-3.073691	-0.008622
C 0	-4.623999	-3.234261	0.009348
C 0	-5.478601	-2.121136	-0.012013

C 0	-4.970741	-0.826493	-0.052160
C 0	0.000004	2.160898	-0.119424
C 0	-0.000018	2.811446	1.130121
C 0	-0.000007	4.208293	1.173474
C 0	0.000027	4.925598	-0.018230
C 0	0.000048	4.265247	-1.242860
C 0	0.000036	2.866186	-1.327069
C 0	0.000051	2.165771	-2.662033
C 0	-0.000044	2.040233	2.334223
N 0	-0.000064	1.393141	3.290712
H 0	6.551492	-2.269414	0.004394
H 0	5.046576	-4.230805	0.042112
H 0	2.598033	-3.940691	0.010668
H 0	5.635260	0.028604	-0.065767
H 0	-2.598054	-3.940681	0.010659
H 0	-5.046599	-4.230781	0.042086
H 0	-6.551502	-2.269379	0.004358
H 0	-5.635255	0.028632	-0.065798
H 0	-0.000024	4.712789	2.131006
H 0	0.000038	6.008525	0.009124
H 0	0.000072	4.841728	-2.160703
H 0	0.000051	2.892750	-3.473690
H 0	0.882538	1.531506	-2.782282
H 0	-0.882423	1.531491	-2.782295

SCF Done: E(UB3LYP) = -2227.14376359

Sum of electronic and zero-point Energies= -2226.833475

Sum of electronic and thermal Energies= -2226.809603

Sum of electronic and thermal Enthalpies= -2226.808659

Sum of electronic and thermal Free Energies= -2226.888544

6.1.9.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0	5.478915	-2.129079	-0.006667
C 0	4.622473	-3.241354	0.009613
C 0	3.246270	-3.079520	-0.000595
C 0	2.712650	-1.779251	-0.027834
C 0	3.591363	-0.673475	-0.045445
C 0	4.973608	-0.832540	-0.034547
C 0	1.339110	-1.358617	-0.041352
C 0	1.195198	0.020061	-0.068593
S 0	2.726706	0.867447	-0.081350
S 0	0.003534	-2.479145	-0.028433
C 0	-1.334070	-1.361143	-0.046656
C 0	-1.193190	0.017818	-0.073906
N 0	0.000568	0.703131	-0.085942
C 0	-2.706587	-1.785075	-0.043097
C 0	-3.587861	-0.681532	-0.069272
S 0	-2.726779	0.861527	-0.101665
C 0	-3.236930	-3.086703	-0.018041
C 0	-4.612724	-3.252140	-0.018355
C 0	-5.471846	-2.142071	-0.042817
C 0	-4.969759	-0.844241	-0.068760
C 0	-0.001016	2.155182	-0.126011
C 0	-0.032936	2.853652	1.101965
C 0	-0.039298	4.248980	1.101503
C 0	-0.013201	4.926971	-0.115064
C 0	0.019183	4.226348	-1.312467
C 0	0.027416	2.821516	-1.352966
C 0	0.079979	2.113259	-2.680647
C 0	-0.056383	2.140442	2.340093
N 0	-0.075250	1.564126	3.340959
H 0	6.551970	-2.279127	0.003073
H 0	5.043413	-4.239282	0.031271
H 0	2.595013	-3.946271	0.013066

H 0	5.640008	0.021634	-0.045925
H 0	-2.583411	-3.951635	0.002118
H 0	-5.031270	-4.251109	0.001587
H 0	-6.544556	-2.294903	-0.041192
H 0	-5.638364	0.008094	-0.086695
H 0	-0.064120	4.785244	2.041319
H 0	-0.019160	6.010383	-0.123025
H 0	0.038306	4.768283	-2.251511
H 0	-0.679715	2.520341	-3.352052
H 0	1.053354	2.277501	-3.153438
H 0	-0.076273	1.037837	-2.601026

SCF Done: E(UB3LYP) = -2227.22632477

Sum of electronic and zero-point Energies= -2226.915769

Sum of electronic and thermal Energies= -2226.892133

Sum of electronic and thermal Enthalpies= -2226.891189

Sum of electronic and thermal Free Energies= -2226.970144

6.1.10 *anti-anti-N-ortho,ortho'*-cyanomethoxyphenyl-BBTT 3n

6.1.10.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman b3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.392328	-2.353832	-0.400550
C 0	4.540756	-3.334960	0.129139
C 0	3.192747	-3.074447	0.330615
C 0	2.674869	-1.813004	-0.003513
C 0	3.546502	-0.839164	-0.544186
C 0	4.902069	-1.097619	-0.740324
C 0	1.335251	-1.306533	0.144602
C 0	1.194609	-0.023983	-0.283166
S 0	2.696732	0.652645	-0.923873
S 0	0.000053	-2.256691	0.845933
C 0	-1.335209	-1.306608	0.144620
C 0	-1.194721	-0.024030	-0.283175
N 0	-0.000036	0.713801	-0.352533
C 0	-2.674803	-1.813123	-0.003312
C 0	-3.546549	-0.839312	-0.543824
S 0	-2.696809	0.652573	-0.923519
C 0	-3.192581	-3.074642	0.330708
C 0	-4.540595	-3.335202	0.129304
C 0	-5.392268	-2.354074	-0.400223
C 0	-4.902107	-1.097797	-0.739911
C 0	-0.000065	2.082763	0.075967
C 0	-0.000330	3.122629	-0.863272
C 0	-0.000389	4.463205	-0.446399
C 0	-0.000169	4.748988	0.910228
C 0	0.000118	3.728634	1.860647
C 0	0.000180	2.391765	1.452214
O 0	0.000437	1.330678	2.285399
C 0	-0.000482	2.830429	-2.266015
N 0	-0.000571	2.651958	-3.407105
C 0	0.000673	1.551064	3.694348
H 0	6.442223	-2.576031	-0.551944
H 0	4.941473	-4.309624	0.382801
H 0	2.539117	-3.838795	0.735445
H 0	5.557920	-0.341195	-1.155398
H 0	-2.538879	-3.839000	0.735400
H 0	-4.941227	-4.309924	0.382862
H 0	-6.442163	-2.576317	-0.551539
H 0	-5.558016	-0.341385	-1.154911
H 0	-0.000586	5.252992	-1.185625
H 0	-0.000216	5.780780	1.241450
H 0	0.000271	3.979776	2.912585
H 0	0.000881	0.560038	4.142632
H 0	0.896970	2.094941	4.008206
H 0	-0.895646	2.094714	4.008541

SCF Done: E(RB3LYP) = -2302.59336040

Sum of electronic and zero-point Energies= -2302.278647

Sum of electronic and thermal Energies= -2302.253850

Sum of electronic and thermal Enthalpies= -2302.252906

Sum of electronic and thermal Free Energies= -2302.334885

Conformer II:

#p opt=verytight freq=noraman b3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.423481	-2.273458	-0.423585
C 0	4.565601	-3.366499	-0.233289
C 0	3.208734	-3.179221	-0.008619
C 0	2.686056	-1.875979	0.023850
C 0	3.566635	-0.787907	-0.175618
C 0	4.929056	-0.973017	-0.395541
C 0	1.334884	-1.439605	0.253432
C 0	1.196538	-0.087056	0.208138
S 0	2.714023	0.751551	-0.113987
S 0	-0.000000	-2.558828	0.644254
C 0	-1.334885	-1.439605	0.253432
C 0	-1.196538	-0.087056	0.208138
N 0	-0.000000	0.629524	0.368168
C 0	-2.686056	-1.875979	0.023850
C 0	-3.566635	-0.787906	-0.175618
S 0	-2.714023	0.751551	-0.113987
C 0	-3.208734	-3.179221	-0.008619
C 0	-4.565601	-3.366498	-0.233289
C 0	-5.423481	-2.273457	-0.423584
C 0	-4.929056	-0.973016	-0.395540
C 0	0.000000	2.053726	0.275396
C 0	0.000000	2.835130	1.440488
C 0	0.000001	4.234446	1.362692
C 0	0.000000	4.841082	0.114370
C 0	-0.000000	4.083698	-1.054603
C 0	-0.000000	2.686010	-0.986223
O 0	-0.000001	1.863715	-2.054634
C 0	0.000001	2.203029	2.725676
N 0	0.000001	1.740408	3.783671
C 0	-0.000000	2.423968	-3.366583
H 0	6.480661	-2.439915	-0.594036
H 0	4.968845	-4.372336	-0.259634
H 0	2.552624	-4.029884	0.136271
H 0	5.589793	-0.126531	-0.542928
H 0	-2.552624	-4.029884	0.136271
H 0	-4.968846	-4.372336	-0.259634
H 0	-6.480661	-2.439915	-0.594035
H 0	-5.589794	-0.126531	-0.542927
H 0	0.000001	4.821519	2.271305
H 0	0.000000	5.922457	0.043803
H 0	-0.000000	4.583495	-2.013561
H 0	-0.000000	1.573646	-4.044827
H 0	-0.896606	3.027463	-3.537433
H 0	0.896606	3.027463	-3.537432

SCF Done: E(RB3LYP) = -2302.59242715

Sum of electronic and zero-point Energies= -2302.277734

Sum of electronic and thermal Energies= -2302.252877

Sum of electronic and thermal Enthalpies= -2302.251933

Sum of electronic and thermal Free Energies= -2302.334266

6.1.10.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman b3lyp/6-311++g(d,p) pop=full scrf=(iefpcm,solvent=

dichloromethane)

0 1

C 0	5.424220	-2.327969	-0.331797
C 0	4.566846	-3.344537	0.116676
C 0	3.209001	-3.108855	0.287573

C 0	2.687587	-1.835877	0.002796
C 0	3.566424	-0.826349	-0.454784
C 0	4.930848	-1.058719	-0.619678
C 0	1.337584	-1.351852	0.132257
C 0	1.196050	-0.048614	-0.229319
S 0	2.712937	0.681135	-0.768674
S 0	0.000053	-2.358676	0.751907
C 0	-1.337536	-1.351891	0.132300
C 0	-1.196070	-0.048646	-0.229309
N 0	-0.000007	0.681547	-0.301834
C 0	-2.687508	-1.835970	0.002877
C 0	-3.566399	-0.826497	-0.454707
S 0	-2.712941	0.681028	-0.768628
C 0	-3.208872	-3.108965	0.287689
C 0	-4.566712	-3.344691	0.116845
C 0	-5.424138	-2.328159	-0.331616
C 0	-4.930813	-1.058898	-0.619545
C 0	-0.000026	2.076696	0.029116
C 0	-0.000212	3.046334	-0.985547
C 0	-0.000282	4.413338	-0.672386
C 0	-0.000131	4.795781	0.661997
C 0	0.000085	3.848831	1.683979
C 0	0.000126	2.482890	1.378577
O 0	0.000362	1.489796	2.289948
C 0	-0.000298	2.643686	-2.359898
N 0	-0.000346	2.362198	-3.480561
C 0	0.000037	1.824646	3.684581
H 0	6.481117	-2.530850	-0.458805
H 0	4.970346	-4.326984	0.332934
H 0	2.554460	-3.900806	0.633591
H 0	5.591561	-0.274157	-0.969046
H 0	-2.554292	-3.900890	0.633693
H 0	-4.970171	-4.327150	0.333123
H 0	-6.481034	-2.531075	-0.458570
H 0	-5.591562	-0.274366	-0.968913
H 0	-0.000425	5.148924	-1.465226
H 0	-0.000171	5.848511	0.917196
H 0	0.000225	4.179202	2.713526
H 0	-0.000199	0.872860	4.209910
H 0	0.896378	2.390962	3.949232
H 0	-0.896320	2.391147	3.948771

SCF Done: E(RB3LYP) = -2302.60722690

Sum of electronic and zero-point Energies= -2302.292446

Sum of electronic and thermal Energies= -2302.267651

Sum of electronic and thermal Enthalpies= -2302.266707

Sum of electronic and thermal Free Energies= -2302.348644

Conformer II:

#p opt freq=noraman b3lyp/6-311++g(d,p) pop=full scrf=(iefpcm,solvent=

dichloromethane)

0 1

C 0	5.417792	-2.281024	-0.455161
C 0	4.563089	-3.373261	-0.240939
C 0	3.207737	-3.184648	-0.003268
C 0	2.684364	-1.880594	0.017826
C 0	3.562098	-0.793613	-0.204222
C 0	4.922892	-0.979787	-0.437598
C 0	1.335762	-1.439935	0.256332
C 0	1.195774	-0.087064	0.195734
S 0	2.709611	0.747304	-0.153848
S 0	-0.000132	-2.550346	0.676303
C 0	-1.335901	-1.439825	0.256196
C 0	-1.195784	-0.086967	0.195614
N 0	-0.000012	0.628532	0.353856
C 0	-2.684566	-1.880364	0.017777
C 0	-3.562220	-0.793291	-0.204189
S 0	-2.709637	0.747533	-0.153796
C 0	-3.208053	-3.184374	-0.003287
C 0	-4.563432	-3.372875	-0.240892
C 0	-5.418046	-2.280563	-0.455078
C 0	-4.923031	-0.979367	-0.437526

C 0	0.000082	2.056685	0.290344
C 0	0.000226	2.810758	1.475323
C 0	0.000328	4.210081	1.436486
C 0	0.000325	4.846508	0.200995
C 0	0.000202	4.118586	-0.985113
C 0	0.000070	2.717696	-0.954927
O 0	0.000006	1.925969	-2.044810
C 0	0.000211	2.139329	2.739652
N 0	0.000202	1.629776	3.776521
C 0	0.000178	2.528912	-3.346510
H 0	6.472852	-2.448581	-0.636895
H 0	4.967028	-4.378940	-0.259492
H 0	2.556049	-4.035326	0.160928
H 0	5.580552	-0.134860	-0.604683
H 0	-2.556424	-4.035107	0.160863
H 0	-4.967462	-4.378526	-0.259421
H 0	-6.473129	-2.448021	-0.636755
H 0	-5.580632	-0.134390	-0.604587
H 0	0.000418	4.777196	2.357459
H 0	0.000419	5.928811	0.156580
H 0	0.000228	4.643104	-1.930466
H 0	0.000130	1.698815	-4.048523
H 0	-0.896107	3.136132	-3.494628
H 0	0.896630	3.135922	-3.494483

SCF Done: E(RB3LYP) = -2302.60706417

Sum of electronic and zero-point Energies= -2302.292304

Sum of electronic and thermal Energies= -2302.267496

Sum of electronic and thermal Enthalpies= -2302.266551

Sum of electronic and thermal Free Energies= -2302.348338

6.1.10.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt freq=noraman b3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dic

hloromethane)

0 1

C 0	5.428944	-2.324899	-0.321801
C 0	4.570019	-3.343959	0.118079
C 0	3.210791	-3.110878	0.282610
C 0	2.689569	-1.836965	0.000334
C 0	3.570472	-0.825715	-0.448977
C 0	4.936209	-1.054820	-0.607646
C 0	1.338305	-1.353756	0.124396
C 0	1.195696	-0.049414	-0.232839
S 0	2.716152	0.682526	-0.762487
S 0	-0.000081	-2.366776	0.733135
C 0	-1.338245	-1.353730	0.123950
C 0	-1.195486	-0.049395	-0.233243
N 0	0.000119	0.681604	-0.307070
C 0	-2.689484	-1.836893	-0.000514
C 0	-3.570219	-0.825617	-0.450097
S 0	-2.715735	0.682588	-0.763410
C 0	-3.210830	-3.110780	0.281653
C 0	-4.570023	-3.343810	0.116760
C 0	-5.428785	-2.324728	-0.323380
C 0	-4.935920	-1.054677	-0.609137
C 0	0.000090	2.077600	0.027144
C 0	0.000962	3.051156	-0.984825
C 0	0.001095	4.417019	-0.667155
C 0	0.000338	4.794293	0.669186
C 0	-0.000599	3.844612	1.688412
C 0	-0.000724	2.479528	1.377741
O 0	-0.001549	1.484669	2.285122
C 0	0.001632	2.653661	-2.360041
N 0	0.002186	2.375166	-3.481360
C 0	-0.003539	1.817378	3.681625
H 0	6.487024	-2.526525	-0.443586
H 0	4.973286	-4.327120	0.333111

H 0	2.557280	-3.906737	0.622520
H 0	5.598940	-0.268601	-0.950835
H 0	-2.557446	-3.906656	0.621764
H 0	-4.973385	-4.326949	0.331713
H 0	-6.486842	-2.526313	-0.445436
H 0	-5.598528	-0.268442	-0.952526
H 0	0.001763	5.154798	-1.458717
H 0	0.000449	5.846778	0.927400
H 0	-0.001167	4.168283	2.720723
H 0	-0.004564	0.863538	4.205608
H 0	0.893198	2.382012	3.949859
H 0	-0.900739	2.382528	3.947209

SCF Done: E(RB3LYP) = -2302.62968937

Sum of electronic and zero-point Energies= -2302.314978

Sum of electronic and thermal Energies= -2302.290175

Sum of electronic and thermal Enthalpies= -2302.289231

Sum of electronic and thermal Free Energies= -2302.371287

Conformer II:

#p opt freq=noraman b3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dic

hloromethane)

0 1

C 0	5.401510	-2.307632	-0.507160
C 0	4.551124	-3.390414	-0.234629
C 0	3.200983	-3.192590	0.025015
C 0	2.677983	-1.887939	0.009468
C 0	3.552019	-0.811276	-0.271023
C 0	4.907827	-1.006025	-0.526015
C 0	1.336326	-1.433603	0.265040
C 0	1.195213	-0.083237	0.160527
S 0	2.702689	0.732551	-0.261641
S 0	0.000052	-2.514726	0.757248
C 0	-1.336220	-1.433667	0.264953
C 0	-1.195234	-0.083285	0.160564
N 0	0.000015	0.632393	0.313677
C 0	-2.677847	-1.888072	0.009386
C 0	-3.551980	-0.811470	-0.270948
S 0	-2.702706	0.732465	-0.261494
C 0	-3.200740	-3.192764	0.024784
C 0	-4.550875	-3.390657	-0.234822
C 0	-5.401370	-2.307911	-0.507159
C 0	-4.907784	-1.006263	-0.525894
C 0	-0.000042	2.062732	0.321725
C 0	-0.000136	2.760714	1.542319
C 0	-0.000191	4.159925	1.570859
C 0	-0.000124	4.854358	0.366531
C 0	-0.000028	4.184235	-0.852692
C 0	-0.000017	2.782707	-0.890431
O 0	-0.000020	2.045554	-2.017412
C 0	-0.000114	2.032366	2.773997
N 0	-0.000065	1.473835	3.785163
C 0	-0.000217	2.710918	-3.290397
H 0	6.452515	-2.483049	-0.705979
H 0	4.954331	-4.396800	-0.225056
H 0	2.555601	-4.038319	0.235262
H 0	5.561935	-0.167976	-0.738365
H 0	-2.555274	-4.038463	0.234893
H 0	-4.954006	-4.397068	-0.225346
H 0	-6.452371	-2.483390	-0.705931
H 0	-5.561965	-0.168235	-0.738088
H 0	-0.000286	4.681343	2.518938
H 0	-0.000134	5.938070	0.373729
H 0	0.000014	4.753168	-1.772425
H 0	-0.000282	1.914129	-4.031724
H 0	-0.897375	3.323483	-3.411007
H 0	0.896865	3.323542	-3.411263

SCF Done: E(RB3LYP) = -2302.62973321

Sum of electronic and zero-point Energies= -2302.315040

Sum of electronic and thermal Energies= -2302.290233

Sum of electronic and thermal Enthalpies= -2302.289289

Sum of electronic and thermal Free Energies= -2302.371597

6.1.10.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.479527	-2.222029	0.078782
C 0	-4.625776	-3.333537	0.151997
C 0	-3.250021	-3.173621	0.143235
C 0	-2.711937	-1.877710	0.060369
C 0	-3.588405	-0.772233	-0.011880
C 0	-4.970358	-0.929981	-0.004100
C 0	-1.337562	-1.459378	0.033967
C 0	-1.195097	-0.082600	-0.055969
S 0	-2.722312	0.764154	-0.112071
S 0	-0.000078	-2.576426	0.099412
C 0	1.337487	-1.459452	0.033947
C 0	1.195095	-0.082686	-0.056094
N 0	-0.000033	0.598875	-0.109321
C 0	2.711816	-1.877864	0.060148
C 0	3.588348	-0.772446	-0.012355
S 0	2.722270	0.763981	-0.112590
C 0	3.249862	-3.173797	0.143065
C 0	4.625605	-3.333767	0.151749
C 0	5.479408	-2.222300	0.078423
C 0	4.970292	-0.930240	-0.004568
C 0	0.000004	2.040561	-0.191346
C 0	-0.000277	2.670583	-1.447158
C 0	-0.000244	4.066303	-1.520902
C 0	0.000104	4.805812	-0.342213
C 0	0.000383	4.187883	0.904579
C 0	0.000315	2.789780	0.998033
O 0	0.000610	2.082486	2.142219
C 0	-0.000565	1.872511	-2.634215
N 0	-0.000760	1.209182	-3.579264
C 0	0.000982	2.780043	3.398759
H 0	-6.552630	-2.369695	0.085006
H 0	-5.049108	-4.328353	0.214389
H 0	-2.600073	-4.039486	0.198170
H 0	-5.634192	-0.076217	-0.062892
H 0	2.599877	-4.039626	0.198146
H 0	5.048902	-4.328603	0.214074
H 0	6.552504	-2.370009	0.084772
H 0	5.634155	-0.076511	-0.063523
H 0	-0.000466	4.552374	-2.487169
H 0	0.000147	5.887933	-0.393327
H 0	0.000658	4.793153	1.800547
H 0	0.001222	2.002964	4.158800
H 0	0.898482	3.394738	3.500647
H 0	-0.896484	3.394705	3.501171

SCF Done: E(UB3LYP) = -2302.37433191

Sum of electronic and zero-point Energies= -2302.058966

Sum of electronic and thermal Energies= -2302.034209

Sum of electronic and thermal Enthalpies= -2302.033264

Sum of electronic and thermal Free Energies= -2302.115156

6.1.10.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane)

0 1

C 0	5.477279	-2.227100	-0.102631
C 0	4.621632	-3.339284	-0.142064
C 0	3.245364	-3.179128	-0.115112
C 0	2.710690	-1.880851	-0.047202
C 0	3.588713	-0.775132	-0.005626

C 0	4.970839	-0.932522	-0.033940
C 0	1.336732	-1.461586	-0.008596
C 0	1.193865	-0.085008	0.066769
S 0	2.723432	0.763720	0.083773
S 0	0.000064	-2.580122	-0.047643
C 0	-1.336647	-1.461654	-0.008449
C 0	-1.193837	-0.085014	0.066872
N 0	-0.000043	0.596842	0.127914
C 0	-2.710549	-1.881001	-0.046725
C 0	-3.588656	-0.775350	-0.004864
S 0	-2.723432	0.763545	0.084470
C 0	-3.245143	-3.179321	-0.114605
C 0	-4.621399	-3.339580	-0.141336
C 0	-5.477119	-2.227458	-0.101718
C 0	-4.970767	-0.932840	-0.033056
C 0	-0.000016	2.039371	0.197200
C 0	0.000630	2.690957	1.444118
C 0	0.000698	4.086915	1.498351
C 0	0.000032	4.808393	0.307410
C 0	-0.000663	4.172583	-0.928421
C 0	-0.000658	2.772103	-1.002235
O 0	-0.001203	2.051402	-2.135196
C 0	0.001143	1.927928	2.653640
N 0	0.001600	1.317353	3.633778
C 0	-0.001744	2.735436	-3.404489
H 0	6.550380	-2.375643	-0.124352
H 0	5.042992	-4.335983	-0.193143
H 0	2.595045	-4.046154	-0.143962
H 0	5.636577	-0.078336	-0.002631
H 0	-2.594745	-4.046280	-0.143729
H 0	-5.042702	-4.336308	-0.192318
H 0	-6.550211	-2.376068	-0.123398
H 0	-5.636574	-0.078714	-0.001613
H 0	0.001224	4.587874	2.456954
H 0	0.000045	5.891297	0.342466
H 0	-0.001181	4.762937	-1.834485
H 0	-0.001720	1.946252	-4.153379
H 0	-0.900012	3.347274	-3.512754
H 0	0.896050	3.347857	-3.513282

SCF Done: E(UB3LYP) = -2302.45567727

Sum of electronic and zero-point Energies= -2302.140141

Sum of electronic and thermal Energies= -2302.115521

Sum of electronic and thermal Enthalpies= -2302.114577

Sum of electronic and thermal Free Energies= -2302.196022

6.1.11 *anti-anti-N-ortho,ortho'*-dichlorophenyl-BBTT 3g

6.1.11.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.385613	-2.383293	-0.456983
C 0	-4.532741	-3.396180	0.006519
C 0	-3.186385	-3.146385	0.230924
C 0	-2.671271	-1.863379	-0.013285
C 0	-3.544058	-0.857418	-0.488651
C 0	-4.897984	-1.105123	-0.707329
C 0	-1.335069	-1.364097	0.178108
C 0	-1.196641	-0.054059	-0.159527
S 0	-2.697581	0.660457	-0.761106
S 0	0.000020	-2.348095	0.834012
C 0	1.335113	-1.364059	0.178096
C 0	1.196665	-0.054022	-0.159541
N 0	0.000001	0.679596	-0.159585
C 0	2.671330	-1.863313	-0.013263
C 0	3.544105	-0.857340	-0.488627
S 0	2.697585	0.660492	-0.761181
C 0	3.186469	-3.146302	0.230986
C 0	4.532838	-3.396067	0.006622
C 0	5.385697	-2.383168	-0.456873
C 0	4.898043	-1.105015	-0.707261

C 0	-0.000026	2.056792	0.221613
C 0	-0.000011	3.075182	-0.744427
C 0	-0.000041	4.419433	-0.383823
C 0	-0.000099	4.763482	0.963180
C 0	-0.000125	3.780491	1.947722
C 0	-0.000088	2.441625	1.572900
Cl 0	-0.000089	1.216495	2.816796
Cl 0	0.000026	2.662505	-2.444671
H 0	-6.434694	-2.596923	-0.625288
H 0	-4.931481	-4.386870	0.192013
H 0	-2.532066	-3.934293	0.586339
H 0	-5.555318	-0.323084	-1.069237
H 0	2.532159	-3.934219	0.586398
H 0	4.931596	-4.386744	0.192145
H 0	6.434788	-2.596774	-0.625147
H 0	5.555365	-0.322970	-1.069175
H 0	-0.000021	5.178897	-1.154197
H 0	-0.000125	5.808613	1.249410
H 0	-0.000175	4.041824	2.997665

SCF Done: E(RB3LYP) = -3015.01346748

Sum of electronic and zero-point Energies= -3014.748899

Sum of electronic and thermal Energies= -3014.726115

Sum of electronic and thermal Enthalpies= -3014.725171

Sum of electronic and thermal Free Energies= -3014.803008

6.1.11.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full geom=check guess=read

0 1

C 0	-5.410093	-2.358021	-0.418128
C 0	-4.553774	-3.396366	-0.020067
C 0	-3.200064	-3.165489	0.185853
C 0	-2.681286	-1.875054	-0.012674
C 0	-3.558914	-0.843352	-0.420470
C 0	-4.919410	-1.071351	-0.620354
C 0	-1.337114	-1.393073	0.167816
C 0	-1.197626	-0.069104	-0.113225
S 0	-2.709116	0.683959	-0.633840
S 0	0.000019	-2.418107	0.760057
C 0	1.337136	-1.393057	0.167807
C 0	1.197631	-0.069089	-0.113234
N 0	-0.000002	0.659034	-0.107468
C 0	2.681312	-1.875023	-0.012690
C 0	3.558927	-0.843311	-0.420490
S 0	2.709111	0.683990	-0.633855
C 0	3.200106	-3.165452	0.185835
C 0	4.553818	-3.396313	-0.020092
C 0	5.410123	-2.357958	-0.418157
C 0	4.919425	-1.071295	-0.620380
C 0	-0.000011	2.055471	0.191672
C 0	-0.000037	3.018825	-0.829271
C 0	-0.000048	4.380564	-0.543991
C 0	-0.000033	4.797649	0.782781
C 0	-0.000008	3.870863	1.821392
C 0	0.000001	2.514689	1.519132
Cl 0	0.000032	1.353542	2.828495
Cl 0	-0.000068	2.508624	-2.505766
H 0	-6.464037	-2.557277	-0.572421
H 0	-4.955146	-4.391957	0.129858
H 0	-2.546270	-3.973737	0.493527
H 0	-5.579260	-0.269627	-0.930236
H 0	2.546323	-3.973708	0.493511
H 0	4.955202	-4.391899	0.129830
H 0	6.464069	-2.557202	-0.572455
H 0	5.579265	-0.269562	-0.930265
H 0	-0.000070	5.099290	-1.352413

H 0 -0.000042 5.856586 1.010648

H 0 0.000003 4.193043 2.854136

SCF Done: E(RB3LYP) = -3015.02144862

Sum of electronic and zero-point Energies= -3014.756988

Sum of electronic and thermal Energies= -3014.734149

Sum of electronic and thermal Enthalpies= -3014.733205

Sum of electronic and thermal Free Energies= -3014.811524

6.1.11.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0 -5.407457 -2.307030 -0.378342

C 0 -4.556495 -3.361448 -0.025085

C 0 -3.199926 -3.151466 0.156542

C 0 -2.674194 -1.865092 -0.022035

C 0 -3.545748 -0.816623 -0.383008

C 0 -4.909790 -1.024347 -0.559232

C 0 -1.326478 -1.403301 0.138973

C 0 -1.190028 -0.075293 -0.113692

S 0 -2.692059 0.694802 -0.571859

S 0 -0.000201 -2.447598 0.674362

C 0 1.326217 -1.403500 0.138961

C 0 1.189929 -0.075480 -0.113695

N 0 0.000017 0.647680 -0.117659

C 0 2.673877 -1.865455 -0.022074

C 0 3.545549 -0.817083 -0.383056

S 0 2.692036 0.694453 -0.571865

C 0 3.199469 -3.151890 0.156481

C 0 4.556013 -3.362023 -0.025174

C 0 5.407088 -2.307701 -0.378440

C 0 4.909563 -1.024960 -0.559312

C 0 0.000176 2.034991 0.175501

C 0 0.000233 2.988982 -0.848468

C 0 0.000420 4.348433 -0.566351

C 0 0.000527 4.766038 0.756810

C 0 0.000456 3.845586 1.796700

C 0 0.000283 2.491444 1.499282

Cl 0 0.000198 1.335186 2.785953

Cl 0 0.000115 2.466094 -2.499403

H 0 -6.467522 -2.491918 -0.514691

H 0 -4.966556 -4.356798 0.109508

H 0 -2.546485 -3.973848 0.430490

H 0 -5.567258 -0.206956 -0.835086

H 0 2.545941 -3.974201 0.430435

H 0 4.965963 -4.357419 0.109404

H 0 6.467130 -2.492710 -0.514810

H 0 5.567120 -0.207641 -0.835171

H 0 0.000483 5.065592 -1.377838

H 0 0.000672 5.826677 0.982205

H 0 0.000538 4.170507 2.829893

SCF Done: E(RPBE1PBE) = -3013.19146340

Sum of electronic and zero-point Energies= -3012.924096

Sum of electronic and thermal Energies= -3012.901395

Sum of electronic and thermal Enthalpies= -3012.900451

Sum of electronic and thermal Free Energies= -3012.979222

6.1.11.4 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent =dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.9032 eV 427.06 nm f=0.0764

<TDDFT>HOMO -> LUMO 96.0%

<TDDFT> Excited State 2: Singlet-A 3.2100 eV 386.25 nm f=0.0235

<TDDFT>HOMO -> LUMO+1 91.2%

<TDDFT>HOMO -> LUMO+2 6.6%

<TDDFT> Excited State 3: Singlet-A 3.4495 eV 359.42 nm f=0.0178

<TDDFT>HOMO -> LUMO+1 7.4%

<TDDFT>HOMO -> LUMO+2 89.0%

<TDDFT> Excited State 4: Singlet-A 3.8197 eV 324.59 nm f=0.0918

<TDDFT>HOMO -> LUMO+3 80.7%

<TDDFT>HOMO -> LUMO+4 5.1%

<TDDFT>HOMO -> LUMO+6 9.1%

<TDDFT> Excited State 5: Singlet-A 3.8681 eV 320.53 nm f=0.0108

<TDDFT>HOMO -> LUMO+5 70.7%

<TDDFT>HOMO -> LUMO+7 20.4%

<TDDFT>HOMO -> LUMO+11 2.9%

<TDDFT> Excited State 6: Singlet-A 3.9392 eV 314.75 nm f=0.0054

<TDDFT>HOMO -> LUMO+3 6.0%

<TDDFT>HOMO -> LUMO+4 90.6%

<TDDFT> Excited State 7: Singlet-A 4.0837 eV 303.61 nm f=0.0008

<TDDFT>HOMO -> LUMO+5 24.4%

<TDDFT>HOMO -> LUMO+7 66.5%

<TDDFT>HOMO -> LUMO+11 4.6%

<TDDFT> Excited State 8: Singlet-A 4.1079 eV 301.82 nm f=0.0431

<TDDFT>HOMO -> LUMO+3 9.2%

<TDDFT>HOMO -> LUMO+6 79.9%

<TDDFT>HOMO -> LUMO+9 2.8%

<TDDFT> Excited State 9: Singlet-A 4.3954 eV 282.08 nm f=0.0093

<TDDFT>HOMO-1 -> LUMO 5.3%

<TDDFT>HOMO -> LUMO+6 3.8%

<TDDFT>HOMO -> LUMO+8 84.4%

<TDDFT>HOMO -> LUMO+13 2.4%

<TDDFT> Excited State 10: Singlet-A 4.4845 eV 276.47 nm f=0.0674

<TDDFT>HOMO-1 -> LUMO 87.8%

<TDDFT>HOMO -> LUMO+8 6.4%

<TDDFT> Excited State 11: Singlet-A 4.4979 eV 275.65 nm f=0.1554

<TDDFT>HOMO-2 -> LUMO 88.6%

<TDDFT>HOMO -> LUMO+12 3.2%

<TDDFT> Excited State 12: Singlet-A 4.6066 eV 269.15 nm f=0.0027

<TDDFT>HOMO -> LUMO+6 3.9%

<TDDFT>HOMO -> LUMO+9 68.6%

<TDDFT>HOMO -> LUMO+10 17.3%

<TDDFT>HOMO -> LUMO+16 5.1%

<TDDFT> Excited State 13: Singlet-A 4.6861 eV 264.58 nm f=0.0278

<TDDFT>HOMO-1 -> LUMO+1 88.2%

<TDDFT>HOMO-1 -> LUMO+2 2.1%

<TDDFT> Excited State 14: Singlet-A 4.7250 eV 262.40 nm f=0.0038

<TDDFT>HOMO-2 -> LUMO 2.5%

<TDDFT>HOMO-2 -> LUMO+1 76.8%

<TDDFT>HOMO-2 -> LUMO+2 4.2%

<TDDFT>HOMO-1 -> LUMO+3 2.1%

<TDDFT>HOMO -> LUMO+12 4.9%

<TDDFT> Excited State 15: Singlet-A 4.8254 eV 256.94 nm f=0.0033

<TDDFT>HOMO-1 -> LUMO+1 2.2%

<TDDFT>HOMO-1 -> LUMO+2 4.4%

<TDDFT>HOMO -> LUMO+9 16.2%

<TDDFT>HOMO -> LUMO+10 68.1%

<TDDFT>HOMO -> LUMO+19 2.0%

<TDDFT> Excited State 16: Singlet-A 4.8536 eV 255.45 nm f=0.2702

<TDDFT>HOMO-2 -> LUMO 2.9%

<TDDFT>HOMO-2 -> LUMO+1 10.6%

<TDDFT>HOMO -> LUMO+7 2.8%

<TDDFT>HOMO -> LUMO+11 37.2%

<TDDFT>HOMO -> LUMO+12 35.5%

<TDDFT>HOMO -> LUMO+22 2.1%

<TDDFT> Excited State 17: Singlet-A 4.8740 eV 254.38 nm f=0.0006

<TDDFT>HOMO-3 -> LUMO 17.8%

<TDDFT>HOMO-2 -> LUMO+3 3.8%

<TDDFT>HOMO-1 -> LUMO+1 3.3%

<TDDFT>HOMO-1 -> LUMO+2 56.1%

<TDDFT>HOMO-1 -> LUMO+5 2.6%

<TDDFT>HOMO -> LUMO+9 2.6%

<TDDFT>HOMO -> LUMO+10 6.2%

<TDDFT> Excited State 18: Singlet-A 4.9659 eV 249.67 nm f=0.0095

<TDDFT>HOMO-2 -> LUMO+1 4.8%

<TDDFT>HOMO-2 -> LUMO+2 72.0%

<TDDFT>HOMO -> LUMO+11 11.8%

<TDDFT> Excited State 19: Singlet-A 4.9787 eV 249.03 nm f=0.0923

<TDDFT>HOMO-3 -> LUMO 60.4%

<TDDFT>HOMO-1 -> LUMO+2 28.5%

<TDDFT>HOMO-1 -> LUMO+5 3.6%

<TDDFT> Excited State 20: Singlet-A 5.0001 eV 247.96 nm f=0.0176

<TDDFT>HOMO-6 -> LUMO+1 9.8%

<TDDFT>HOMO-6 -> LUMO+2 6.9%

<TDDFT>HOMO-4 -> LUMO 46.6%

<TDDFT>HOMO-4 -> LUMO+1 10.4%

<TDDFT>HOMO-4 -> LUMO+2 4.9%

<TDDFT>HOMO-3 -> LUMO+1 15.9%

<TDDFT> Excited State 21: Singlet-A 5.0238 eV 246.80 nm f=0.0860

<TDDFT>HOMO-2 -> LUMO+2 10.2%

<TDDFT>HOMO -> LUMO+7 4.7%

<TDDFT>HOMO -> LUMO+11 28.9%

<TDDFT>HOMO -> LUMO+12 42.4%

<TDDFT>HOMO -> LUMO+15 6.0%

<TDDFT> Excited State 22: Singlet-A 5.1110 eV 242.58 nm f=0.0961

<TDDFT>HOMO-2 -> LUMO+1 3.5%

<TDDFT>HOMO-2 -> LUMO+2 2.7%

<TDDFT>HOMO-2 -> LUMO+5 8.6%

<TDDFT>HOMO-1 -> LUMO+3 63.1%

<TDDFT>HOMO-1 -> LUMO+4 2.4%

<TDDFT>HOMO-1 -> LUMO+6 3.4%

<TDDFT> Excited State 23: Singlet-A 5.1304 eV 241.67 nm f=0.0015

<TDDFT>HOMO-4 -> LUMO 4.1%

<TDDFT>HOMO-3 -> LUMO 6.2%

<TDDFT>HOMO-3 -> LUMO+1 14.9%

<TDDFT>HOMO-3 -> LUMO+2 3.3%

<TDDFT>HOMO-2 -> LUMO+3 35.6%

<TDDFT>HOMO-2 -> LUMO+4 2.4%

<TDDFT>HOMO-2 -> LUMO+6 4.8%

<TDDFT>HOMO-2 -> LUMO+8 2.7%

<TDDFT>HOMO-1 -> LUMO+2 2.6%

<TDDFT>HOMO-1 -> LUMO+5 2.4%

<TDDFT>HOMO-1 -> LUMO+7 7.0%

<TDDFT> Excited State 24: Singlet-A 5.1975 eV 238.55 nm f=0.0120

<TDDFT>HOMO -> LUMO+8 2.6%

<TDDFT>HOMO -> LUMO+13 74.9%

<TDDFT>HOMO -> LUMO+17 14.2%

6.1.11.5 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=

dichloromethane) geom=check guess=read

0 1

C 0	-5.472940	-2.243579	-0.070314
C 0	-4.615598	-3.346018	-0.028540
C 0	-3.239186	-3.185651	-0.005803
C 0	-2.688793	-1.890301	-0.023806
C 0	-3.576940	-0.787093	-0.067830
C 0	-4.950989	-0.948582	-0.091704
C 0	-1.328933	-1.473624	-0.010219
C 0	-1.189350	-0.066846	-0.057900
S 0	-2.730662	0.762437	-0.077420
S 0	0.000001	-2.550720	0.146869
C 0	1.328937	-1.473624	-0.010195
C 0	1.189354	-0.066845	-0.057879
N 0	0.000002	0.596624	-0.059882
C 0	2.688797	-1.890300	-0.023762
C 0	3.576945	-0.787092	-0.067776
S 0	2.730666	0.762438	-0.077383
C 0	3.239191	-3.185650	-0.005750
C 0	4.615603	-3.346017	-0.028466
C 0	5.472945	-2.243577	-0.070229
C 0	4.950993	-0.948580	-0.091631
C 0	0.000001	2.018490	0.026597
C 0	0.000043	2.799300	-1.133243
C 0	0.000048	4.184549	-1.050159
C 0	-0.000003	4.790757	0.198166
C 0	-0.000052	4.033895	1.364082
C 0	-0.000041	2.650578	1.273240
Cl 0	-0.000137	1.691880	2.710424
Cl 0	0.000119	2.030117	-2.680944
H 0	-6.547403	-2.388833	-0.085992
H 0	-5.033031	-4.347660	-0.014389
H 0	-2.589047	-4.054475	0.023932
H 0	-5.610820	-0.088107	-0.124707
H 0	2.589051	-4.054474	0.023977
H 0	5.033037	-4.347658	-0.014307
H 0	6.547408	-2.388830	-0.085892
H 0	5.610824	-0.088105	-0.124627
H 0	0.000089	4.775841	-1.957481
H 0	-0.000006	5.872854	0.265209
H 0	-0.000099	4.507516	2.337949

SCF Done: E(RPBE1PBE) = -3013.18026874

Sum of electronic and zero-point Energies= -3012.834168

Sum of electronic and thermal Energies= -3012.810614

Sum of electronic and thermal Enthalpies= -3012.809670

Sum of electronic and thermal Free Energies= -3012.890008

6.1.11.6 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent= dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.2495 eV 551.17 nm f=0.1036

<TDDFT>HOMO -> LUMO 97.8%

<TDDFT> Excited State 2: Singlet-A 2.5796 eV 480.63 nm f=0.0029

<TDDFT>HOMO -> LUMO+1 98.9%

<TDDFT> Excited State 3: Singlet-A 2.8933 eV 428.52 nm f=0.0032

<TDDFT>HOMO -> LUMO+2 99.4%

<TDDFT> Excited State 4: Singlet-A 3.3194 eV 373.51 nm f=0.0023

<TDDFT>HOMO -> LUMO+3 37.6%

<TDDFT>HOMO -> LUMO+4 48.3%

<TDDFT>HOMO -> LUMO+6 10.0%

6.1.11.7 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet hane) pop=full geom=check guess=read

0 1

C 0	-5.406668	-2.365021	-0.428385
C 0	-4.551997	-3.400192	-0.018453
C 0	-3.199697	-3.167600	0.195507
C 0	-2.680590	-1.877643	-0.007092
C 0	-3.557303	-0.849704	-0.425791
C 0	-4.916412	-1.078677	-0.633944
C 0	-1.338041	-1.391684	0.179913
C 0	-1.197466	-0.068644	-0.104884
S 0	-2.707845	0.678767	-0.640389
S 0	-0.000086	-2.411952	0.780432
C 0	1.337952	-1.391747	0.179995
C 0	1.197457	-0.068699	-0.104800
N 0	0.000013	0.659902	-0.093558
C 0	2.680483	-1.877775	-0.006966
C 0	3.557261	-0.849878	-0.425634
S 0	2.707894	0.678644	-0.640233
C 0	3.199515	-3.167761	0.195634
C 0	4.551809	-3.400422	-0.018289
C 0	5.406545	-2.365293	-0.428190
C 0	4.916363	-1.078923	-0.633755
C 0	0.000043	2.059350	0.194016
C 0	0.000195	3.015123	-0.834408
C 0	0.000230	4.379098	-0.562365
C 0	0.000102	4.807069	0.760891
C 0	-0.000044	3.889947	1.808077
C 0	-0.000066	2.531748	1.517028
Cl 0	-0.000271	1.380937	2.839193
Cl 0	0.000432	2.490079	-2.508757
H 0	-6.459488	-2.566681	-0.589287
H 0	-4.953474	-4.395677	0.133905
H 0	-2.549667	-3.975544	0.512750
H 0	-5.575409	-0.279022	-0.952411
H 0	2.549434	-3.975675	0.512851
H 0	4.953229	-4.395929	0.134072
H 0	6.459359	-2.567007	-0.589064
H 0	5.575411	-0.279299	-0.952197
H 0	0.000366	5.092622	-1.376224
H 0	0.000129	5.868233	0.980079
H 0	-0.000140	4.223997	2.837437

SCF Done: E(RB3LYP) = -3015.04575158

Sum of electronic and zero-point Energies= -3014.781320

Sum of electronic and thermal Enthalpies= -3014.757564

Sum of electronic and thermal Energies= -3014.758508

Sum of electronic and thermal Free Energies= -3014.835518

6.1.11.8 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.479411	-2.236685	0.000272
C 0	4.625606	-3.350674	-0.000179
C 0	3.249923	-3.190588	-0.000240
C 0	2.711849	-1.891854	0.000156
C 0	3.588496	-0.783959	0.000547
C 0	4.970468	-0.941902	0.000643
C 0	1.337857	-1.472161	-0.000044
C 0	1.196359	-0.092049	0.000148
S 0	2.723415	0.755687	0.000747
S 0	-0.000084	-2.590944	-0.000037
C 0	-1.337963	-1.472090	-0.000007
C 0	-1.196390	-0.091987	-0.000193
N 0	0.000003	0.590714	-0.000042
C 0	-2.711980	-1.891710	-0.000182
C 0	-3.588566	-0.783768	-0.000553
S 0	-2.723403	0.755833	-0.000765
C 0	-3.250127	-3.190414	0.000223
C 0	-4.625819	-3.350423	0.000195
C 0	-5.479563	-2.236387	-0.000233
C 0	-4.970547	-0.941633	-0.000612
C 0	0.000037	2.032264	0.000001
C 0	-0.000497	2.738817	1.212000
C 0	-0.000379	4.129011	1.212690
C 0	0.000253	4.812466	0.000070
C 0	0.000779	4.129072	-1.212584
C 0	0.000702	2.738877	-1.211962
Cl 0	0.001315	1.873387	-2.723991
Cl 0	-0.001223	1.873251	2.723986
H 0	6.552506	-2.384472	0.000322
H 0	5.048952	-4.347426	-0.000529
H 0	2.600065	-4.058282	-0.000551
H 0	5.634304	-0.086139	0.001025
H 0	-2.600319	-4.058146	0.000521
H 0	-5.049221	-4.347151	0.000551
H 0	-6.552666	-2.384114	-0.000256
H 0	-5.634335	-0.085832	-0.000974
H 0	-0.000679	4.662629	2.153799
H 0	0.000328	5.895811	0.000098
H 0	0.001167	4.662737	-2.153666

SCF Done: E(UB3LYP) = -3014.79258736

Sum of electronic and zero-point Energies= -3014.527355

Sum of electronic and thermal Energies= -3014.504667

Sum of electronic and thermal Enthalpies= -3014.503723

Sum of electronic and thermal Free Energies= -3014.581366

6.1.11.9 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpc

m,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.479362	-2.234833	0.000172
C 0	4.625356	-3.349163	-0.000067
C 0	3.248858	-3.189811	-0.000137
C 0	2.710718	-1.891304	0.000038
C 0	3.587008	-0.783010	0.000254

C 0	4.969725	-0.940057	0.000334
C 0	1.335990	-1.473142	-0.000065
C 0	1.195483	-0.093653	0.000049
S 0	2.721517	0.755876	0.000277
S 0	-0.000008	-2.592238	-0.000018
C 0	-1.336000	-1.473135	0.000037
C 0	-1.195484	-0.093648	-0.000076
N 0	0.000001	0.589219	-0.000022
C 0	-2.710733	-1.891288	-0.000052
C 0	-3.587013	-0.782987	-0.000265
S 0	-2.721511	0.755893	-0.000302
C 0	-3.248885	-3.189790	0.000136
C 0	-4.625385	-3.349129	0.000081
C 0	-5.479380	-2.234791	-0.000154
C 0	-4.969731	-0.940020	-0.000327
C 0	0.000004	2.030591	0.000003
C 0	-0.000254	2.738482	1.210869
C 0	-0.000236	4.128290	1.212216
C 0	0.000048	4.811704	0.000045
C 0	0.000305	4.128327	-1.212147
C 0	0.000279	2.738519	-1.210842
Cl 0	0.000573	1.873046	-2.724862
Cl 0	-0.000587	1.872964	2.724864
H 0	6.552571	-2.381805	0.000222
H 0	5.048405	-4.346077	-0.000213
H 0	2.599036	-4.057003	-0.000306
H 0	5.632404	-0.083757	0.000512
H 0	-2.599073	-4.056990	0.000303
H 0	-5.048443	-4.346039	0.000236
H 0	-6.552591	-2.381753	-0.000191
H 0	-5.632401	-0.083712	-0.000501
H 0	-0.000423	4.663174	2.152221
H 0	0.000065	5.894615	0.000061
H 0	0.000507	4.663239	-2.152136

SCF Done: E(UB3LYP) = -3014.84268293

Sum of electronic and zero-point Energies= -3014.577593

Sum of electronic and thermal Energies= -3014.554812

Sum of electronic and thermal Enthalpies= -3014.553868

Sum of electronic and thermal Free Energies= -3014.632235

6.1.11.10 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane)

0 1

C 0	-5.476966	-2.240673	-0.000472
C 0	-4.620818	-3.353208	0.000404
C 0	-3.244514	-3.191513	0.000584
C 0	-2.710753	-1.891156	-0.000153
C 0	-3.589366	-0.784908	-0.001034
C 0	-4.971526	-0.943773	-0.001171
C 0	-1.337162	-1.470288	0.000294
C 0	-1.195487	-0.091577	-0.000139
S 0	-2.724307	0.756217	-0.001362
S 0	-0.000259	-2.589007	0.000331
C 0	1.336814	-1.470499	0.000067
C 0	1.195397	-0.091764	0.000337
N 0	0.000007	0.591868	0.000143
C 0	2.710318	-1.891630	0.000314
C 0	3.589150	-0.785555	0.000977
S 0	2.724384	0.755737	0.001297
C 0	3.243797	-3.192100	-0.000420
C 0	4.620066	-3.354095	-0.000458
C 0	5.476438	-2.241735	0.000194
C 0	4.971280	-0.944725	0.000890
C 0	0.000159	2.032887	0.000009
C 0	0.001340	2.742846	-1.209700

C 0	0.001742	4.131695	-1.213504
C 0	0.000954	4.814634	-0.000397
C 0	-0.000240	4.132065	1.212914
C 0	-0.000653	2.743202	1.209530
Cl 0	-0.001852	1.873587	2.725902
Cl 0	0.001999	1.872725	-2.725764
H 0	-6.550070	-2.390618	-0.000633
H 0	-5.041990	-4.351263	0.000981
H 0	-2.593271	-4.058390	0.001269
H 0	-5.637771	-0.089426	-0.001794
H 0	2.592351	-4.058825	-0.000953
H 0	5.041032	-4.352237	-0.001045
H 0	6.549513	-2.391902	0.000182
H 0	5.637729	-0.090537	0.001334
H 0	0.002729	4.669050	-2.152728
H 0	0.001260	5.898086	-0.000566
H 0	-0.000964	4.669723	2.151963

SCF Done: E(UB3LYP) = -3014.87031681

Sum of electronic and zero-point Energies= -3014.604809

Sum of electronic and thermal Energies= -3014.582254

Sum of electronic and thermal Enthalpies= -3014.581309

Sum of electronic and thermal Free Energies= -3014.658359

6.1.11.11 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc) freq=noraman B3LYP/6-311++g(d,p) scrf=(iefp

cm,solvent=dichloromethane)

0 1

C 0	5.499630	-2.248803	0.000172
C 0	4.635201	-3.353885	0.000231
C 0	3.256688	-3.183349	0.000213
C 0	2.720778	-1.883832	0.000125
C 0	3.609731	-0.783716	0.000055
C 0	4.992320	-0.951937	0.000083
C 0	1.344638	-1.465492	0.000159
C 0	1.200104	-0.111926	0.000119
S 0	2.739472	0.747181	-0.000024
S 0	-0.000000	-2.644960	0.000612
C 0	-1.344639	-1.465492	0.000114
C 0	-1.200105	-0.111927	0.000042
N 0	-0.000001	0.606985	0.000101
C 0	-2.720780	-1.883830	-0.000111
C 0	-3.609729	-0.783710	-0.000303
S 0	-2.739477	0.747176	-0.000226
C 0	-3.256691	-3.183347	-0.000225
C 0	-4.635203	-3.353881	-0.000505
C 0	-5.499630	-2.248797	-0.000688
C 0	-4.992319	-0.951932	-0.000595
C 0	-0.000001	2.030146	0.000052
C 0	0.000522	2.756270	-1.202773
C 0	0.000562	4.146320	-1.210736
C 0	0.000003	4.832480	-0.000046
C 0	-0.000555	4.146406	1.210693
C 0	-0.000518	2.756355	1.202825
Cl 0	0.001042	1.896215	-2.725967
Cl 0	-0.001039	1.896401	2.726075
H 0	6.572307	-2.402210	0.000195
H 0	5.049039	-4.355659	0.000295
H 0	2.599813	-4.045915	0.000255
H 0	5.658316	-0.097165	0.000041
H 0	-2.599816	-4.045914	-0.000101
H 0	-5.049043	-4.355654	-0.000594
H 0	-6.572307	-2.402202	-0.000909
H 0	-5.658314	-0.097159	-0.000756
H 0	0.000995	4.679798	-2.151701
H 0	0.000003	5.915657	-0.000085
H 0	-0.000984	4.679950	2.151621

SCF Done: E(RB3LYP) = -3015.02117147

Sum of electronic and zero-point Energies= -3014.756927

Sum of electronic and thermal Energies= -3014.734866

Sum of electronic and thermal Enthalpies= -3014.733922

Sum of electronic and thermal Free Energies= -3014.809589

6.1.12 *anti-anti-N-ortho,ortho'*-chlorofluorophenyl-BBTT 3o

6.1.12.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.358071	-2.365358	-0.465305
C 0	-4.511371	-3.344087	0.076033
C 0	-3.173627	-3.071063	0.324222
C 0	-2.660393	-1.799252	0.024388
C 0	-3.526969	-0.828404	-0.529775
C 0	-4.872436	-1.098455	-0.771375
C 0	-1.333728	-1.278545	0.224228
C 0	-1.196224	0.011761	-0.182212
S 0	-2.684067	0.681145	-0.861062
S 0	0.000963	-2.201629	0.967776
C 0	1.335396	-1.277419	0.225040
C 0	1.197142	0.012806	-0.181503
N 0	0.000157	0.742027	-0.195528
C 0	2.662623	-1.797055	0.026161
C 0	3.528786	-0.825620	-0.527434
S 0	2.684975	0.683237	-0.859458
C 0	3.176737	-3.068419	0.326706
C 0	4.514906	-3.340314	0.079696
C 0	5.361188	-2.360944	-0.461199
C 0	4.874696	-1.094538	-0.767912
C 0	-0.000690	2.154206	-0.009770
C 0	0.001966	3.012640	-1.113635
C 0	0.001008	4.392642	-0.991031
C 0	-0.002890	4.944297	0.286098
C 0	-0.005612	4.130464	1.416159
C 0	-0.004393	2.747850	1.263238
Cl 0	-0.007786	1.730043	2.679565
F 0	0.005448	2.471602	-2.345735
H 0	-6.400387	-2.596848	-0.651022
H 0	-4.908281	-4.326564	0.304228
H 0	-2.523713	-3.832362	0.740547
H 0	-5.524683	-0.342929	-1.193695
H 0	2.527110	-3.830246	0.742390
H 0	4.912450	-4.322439	0.308330
H 0	6.403885	-2.591488	-0.645962
H 0	5.526642	-0.338505	-1.189852
H 0	0.003144	5.005755	-1.882915
H 0	-0.003688	6.021221	0.404630
H 0	-0.008421	4.557864	2.410000

SCF Done: E(RB3LYP) = -2654.65983256

Sum of electronic and zero-point Energies= -2654.393786

Sum of electronic and thermal Energies= -2654.371319

Sum of electronic and thermal Enthalpies= -2654.370375

Sum of electronic and thermal Free Energies= -2654.448176

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.357181	-2.376887	-0.441087
C 0	4.512776	-3.362955	0.091165
C 0	3.175343	-3.093810	0.343761
C 0	2.661368	-1.818785	0.059829
C 0	3.524616	-0.839977	-0.485159

C 0	4.870333	-1.107479	-0.732363
C 0	1.334220	-1.300789	0.269454
C 0	1.194245	-0.005012	-0.117000
S 0	2.678836	0.669439	-0.802374
S 0	0.000081	-2.245771	0.979834
C 0	-1.334255	-1.300804	0.269528
C 0	-1.194325	-0.004990	-0.116891
N 0	-0.000053	0.736518	-0.112824
C 0	-2.661417	-1.818784	0.060056
C 0	-3.524728	-0.839827	-0.484606
S 0	-2.679039	0.669442	-0.801891
C 0	-3.175318	-3.093899	0.343737
C 0	-4.512737	-3.363041	0.091212
C 0	-5.357248	-2.376868	-0.440726
C 0	-4.870487	-1.107384	-0.731748
C 0	0.000077	2.073889	0.393812
C 0	0.000541	2.310648	1.772844
C 0	0.000671	3.582681	2.318157
C 0	0.000361	4.673300	1.452674
C 0	-0.000009	4.488724	0.073519
C 0	-0.000187	3.196424	-0.445650
Cl 0	-0.000717	2.978500	-2.180993
F 0	0.000814	1.248831	2.597341
H 0	6.399470	-2.605294	-0.631022
H 0	4.911203	-4.347423	0.307708
H 0	2.526966	-3.860374	0.752694
H 0	5.521356	-0.346885	-1.147439
H 0	-2.526829	-3.860514	0.752410
H 0	-4.911110	-4.347576	0.307508
H 0	-6.399542	-2.605274	-0.630629
H 0	-5.521643	-0.346675	-1.146407
H 0	0.000970	3.701351	3.394091
H 0	0.000413	5.678673	1.856386
H 0	-0.000210	5.334385	-0.600939

SCF Done: E(RB3LYP) = -2654.65963517

Sum of electronic and zero-point Energies= -2654.393519

Sum of electronic and thermal Energies= -2654.371140

Sum of electronic and thermal Enthalpies= -2654.370196

Sum of electronic and thermal Free Energies= -2654.446997

6.1.12.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full geom=check guess=read

0 1

C 0	-5.380917	-2.340403	-0.453521
C 0	-4.531390	-3.356585	0.010612
C 0	-3.186917	-3.107794	0.253381
C 0	-2.669930	-1.821651	0.024966
C 0	-3.540763	-0.812698	-0.449770
C 0	-4.892129	-1.057977	-0.686134
C 0	-1.335736	-1.322832	0.230056
C 0	-1.197121	-0.009257	-0.097184
S 0	-2.695066	0.714544	-0.689736
S 0	0.000101	-2.300468	0.904024
C 0	1.335852	-1.322760	0.229978
C 0	1.197161	-0.009193	-0.097264
N 0	0.000002	0.716607	-0.080124
C 0	2.670105	-1.821469	0.025003
C 0	3.540891	-0.812441	-0.449663
S 0	2.695059	0.714693	-0.689819
C 0	3.187200	-3.107550	0.253523
C 0	4.531728	-3.356212	0.010920
C 0	5.381199	-2.339960	-0.453157
C 0	4.892307	-1.057593	-0.685874

C 0	-0.000065	2.139544	-0.029788
C 0	0.000086	2.893179	-1.207744
C 0	0.000010	4.277482	-1.213955
C 0	-0.000245	4.943086	0.008162
C 0	-0.000410	4.236878	1.209462
C 0	-0.000310	2.847111	1.183023
Cl 0	-0.000481	1.957958	2.687847
F 0	0.000289	2.234203	-2.385487
H 0	-6.427689	-2.553435	-0.635657
H 0	-4.930879	-4.349273	0.183251
H 0	-2.537971	-3.898608	0.612237
H 0	-5.546335	-0.273215	-1.047213
H 0	2.538298	-3.898417	0.612342
H 0	4.931298	-4.348852	0.183642
H 0	6.428005	-2.552887	-0.635222
H 0	5.546481	-0.272771	-1.046883
H 0	0.000137	4.809126	-2.156521
H 0	-0.000313	6.025907	0.027530
H 0	-0.000612	4.757334	2.157666

SCF Done: E(RB3LYP) = -2654.66820606

Sum of electronic and zero-point Energies= -2654.402297

Sum of electronic and thermal Energies= -2654.379806

Sum of electronic and thermal Enthalpies= -2654.378862

Sum of electronic and thermal Free Energies= -2654.456479

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full geom=check guess=read

0 1

C 0	5.369559	-2.364231	-0.432724
C 0	4.522577	-3.365997	0.066833
C 0	3.181134	-3.107038	0.313783
C 0	2.666244	-1.826096	0.055597
C 0	3.532914	-0.831566	-0.455377
C 0	4.882276	-1.087906	-0.696377
C 0	1.335456	-1.316313	0.264396
C 0	1.194951	-0.011147	-0.090535
S 0	2.686376	0.686189	-0.736982
S 0	-0.000196	-2.282788	0.947806
C 0	-1.335700	-1.316141	0.264346
C 0	-1.195014	-0.010994	-0.090588
N 0	0.000018	0.726725	-0.082435
C 0	-2.666551	-1.825749	0.055515
C 0	-3.533078	-0.831108	-0.455481
S 0	-2.686329	0.686529	-0.737087
C 0	-3.181615	-3.106622	0.313695
C 0	-4.523086	-3.365407	0.066711
C 0	-5.369926	-2.363532	-0.432866
C 0	-4.882469	-1.087270	-0.696510
C 0	0.000100	2.078182	0.386181
C 0	0.000034	2.350454	1.758018
C 0	0.000126	3.633841	2.272965
C 0	0.000325	4.702110	1.379123
C 0	0.000455	4.483710	0.004145
C 0	0.000290	3.179185	-0.481306
Cl 0	0.000608	2.914827	-2.213497
F 0	-0.000150	1.302620	2.608351
H 0	6.414244	-2.584802	-0.618141
H 0	4.921768	-4.354331	0.263153
H 0	2.533463	-3.885864	0.700128
H 0	5.535292	-0.315325	-1.084749
H 0	-2.534055	-3.885531	0.700059
H 0	-4.922409	-4.353688	0.263025
H 0	-6.414635	-2.583966	-0.618308
H 0	-5.535376	-0.314605	-1.084896
H 0	0.000041	3.782897	3.344980
H 0	0.000379	5.716897	1.757405
H 0	0.000571	5.314509	-0.688359

SCF Done: E(RB3LYP) = -2654.66778754

Sum of electronic and zero-point Energies= -2654.401762

Sum of electronic and thermal Energies= -2654.379369

Sum of electronic and thermal Free Energies= -2654.455218

Sum of electronic and thermal Enthalpies= -2654.378425

6.1.12.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane) geom=check guess=read

0 1

C 0	-5.385264	-2.338269	-0.445622
C 0	-4.535130	-3.353988	0.018597
C 0	-3.189326	-3.106719	0.255984
C 0	-2.671403	-1.821921	0.020929
C 0	-3.543431	-0.814020	-0.453747
C 0	-4.896127	-1.057076	-0.684706
C 0	-1.336667	-1.321796	0.223048
C 0	-1.196853	-0.009176	-0.106877
S 0	-2.696254	0.712541	-0.701272
S 0	0.000009	-2.296501	0.900841
C 0	1.336693	-1.321773	0.223097
C 0	1.196868	-0.009156	-0.106831
N 0	0.000001	0.717241	-0.088015
C 0	2.671427	-1.821895	0.020967
C 0	3.543450	-0.813990	-0.453710
S 0	2.696287	0.712593	-0.701141
C 0	3.189346	-3.106703	0.255984
C 0	4.535142	-3.353978	0.018559
C 0	5.385266	-2.338249	-0.445658
C 0	4.896140	-1.057050	-0.684709
C 0	-0.000012	2.140726	-0.027663
C 0	0.000006	2.901601	-1.200815
C 0	-0.000003	4.285294	-1.200869
C 0	-0.000032	4.943871	0.024945
C 0	-0.000051	4.231855	1.223279
C 0	-0.000041	2.842749	1.188798
Cl 0	-0.000059	1.943296	2.690817
F 0	0.000043	2.246763	-2.383254
H 0	-6.433200	-2.550968	-0.623254
H 0	-4.935289	-4.345856	0.196197
H 0	-2.542369	-3.899023	0.615974
H 0	-5.551544	-0.272610	-1.045564
H 0	2.542389	-3.899011	0.615966
H 0	4.935302	-4.345850	0.196132
H 0	6.433204	-2.550936	-0.623295
H 0	5.551552	-0.272584	-1.045573
H 0	0.000014	4.821770	-2.141261
H 0	-0.000039	6.027027	0.050307
H 0	-0.000072	4.750296	2.173128

SCF Done: E(RB3LYP) = -2654.69143133

Sum of electronic and zero-point Energies= -2654.425610

Sum of electronic and thermal Energies= -2654.403134

Sum of electronic and thermal Enthalpies= -2654.402189

Sum of electronic and thermal Free Energies= -2654.479682

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane) geom=check guess=read

0 1

C 0	5.377062	-2.358166	-0.422667
C 0	4.528090	-3.365905	0.061375
C 0	3.184371	-3.112041	0.301856
C 0	2.668791	-1.829540	0.051408
C 0	3.538060	-0.829593	-0.444268
C 0	4.889658	-1.080106	-0.678455

C 0	1.336548	-1.321892	0.258656
C 0	1.195067	-0.013685	-0.084686
S 0	2.690068	0.690100	-0.718210
S 0	0.000054	-2.294820	0.933184
C 0	-1.336480	-1.321942	0.258665
C 0	-1.195049	-0.013729	-0.084676
N 0	-0.000005	0.723274	-0.071917
C 0	-2.668706	-1.829636	0.051426
C 0	-3.538013	-0.829720	-0.444243
S 0	-2.690076	0.690002	-0.718197
C 0	-3.184240	-3.112155	0.301879
C 0	-4.527953	-3.366065	0.061410
C 0	-5.376964	-2.358354	-0.422626
C 0	-4.889605	-1.080279	-0.678420
C 0	-0.000032	2.079462	0.384401
C 0	-0.000015	2.364879	1.753395
C 0	-0.000043	3.651818	2.257867
C 0	-0.000093	4.712321	1.355040
C 0	-0.000125	4.482542	-0.018304
C 0	-0.000086	3.174082	-0.491604
Cl 0	-0.000156	2.895450	-2.224500
F 0	0.000037	1.323374	2.614197
H 0	6.423653	-2.575583	-0.602769
H 0	4.927575	-4.355662	0.251565
H 0	2.537727	-3.897418	0.677267
H 0	5.544945	-0.302977	-1.054978
H 0	-2.537568	-3.897509	0.677287
H 0	-4.927404	-4.355834	0.251605
H 0	-6.423549	-2.575807	-0.602718
H 0	-5.544921	-0.303172	-1.054939
H 0	-0.000022	3.810161	3.329122
H 0	-0.000111	5.730687	1.724507
H 0	-0.000163	5.308908	-0.716776

SCF Done: E(RB3LYP) = -2654.69103402

Sum of electronic and zero-point Energies= -2654.425119

Sum of electronic and thermal Energies= -2654.402731

Sum of electronic and thermal Enthalpies= -2654.401787

Sum of electronic and thermal Free Energies= -2654.478458

6.1.12.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.479716	-2.182790	-0.029126
C 0	-4.626229	-3.295622	0.025596
C 0	-3.250514	-3.135664	0.028493
C 0	-2.712191	-1.838154	-0.023858
C 0	-3.588605	-0.731373	-0.078526
C 0	-4.970527	-0.889144	-0.082186
C 0	-1.337995	-1.418822	-0.033024
C 0	-1.196551	-0.040079	-0.091796
S 0	-2.722911	0.807138	-0.139383
S 0	0.000003	-2.536222	0.024111
C 0	1.337998	-1.418820	-0.033024
C 0	1.196552	-0.040077	-0.091796
N 0	-0.000000	0.642874	-0.111316
C 0	2.712195	-1.838150	-0.023858
C 0	3.588607	-0.731367	-0.078526
S 0	2.722909	0.807142	-0.139384
C 0	3.250521	-3.135659	0.028493
C 0	4.626236	-3.295614	0.025595
C 0	5.479721	-2.182781	-0.029126
C 0	4.970529	-0.889136	-0.082186
C 0	-0.000003	2.080405	-0.185824
C 0	-0.000005	2.699816	-1.438817
C 0	-0.000006	4.076247	-1.571794
C 0	-0.000006	4.851034	-0.414272
C 0	-0.000005	4.266123	0.850636
C 0	-0.000004	2.880358	0.966054
Cl 0	-0.000002	2.132171	2.537330

F 0 -0.000004 1.917055 -2.528111
H 0 -6.552803 -2.330568 -0.030532
H 0 -5.049843 -4.291433 0.065971
H 0 -2.600966 -4.002545 0.070598
H 0 -5.634191 -0.034325 -0.124693
H 0 2.600975 -4.002541 0.070598
H 0 5.049852 -4.291424 0.065970
H 0 6.552808 -2.330557 -0.030533
H 0 5.634192 -0.034315 -0.124694
H 0 -0.000007 4.517277 -2.560138
H 0 -0.000007 5.931001 -0.497561
H 0 -0.000005 4.875613 1.744342

SCF Done: E(UB3LYP) = -2654.43796099

Sum of electronic and zero-point Energies= -2654.171205

Sum of electronic and thermal Energies= -2654.148890

Sum of electronic and thermal Enthalpies= -2654.147945

Sum of electronic and thermal Free Energies= -2654.224708

6.1.12.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0 -5.476768 -2.190700 -0.025577
C 0 -4.620374 -3.302384 0.011999
C 0 -3.244140 -3.140110 0.016641
C 0 -2.710742 -1.840083 -0.017045
C 0 -3.589531 -0.734806 -0.057012
C 0 -4.971625 -0.894180 -0.061042
C 0 -1.337076 -1.418972 -0.022734
C 0 -1.195661 -0.041072 -0.067139
S 0 -2.724620 0.806300 -0.102017
S 0 0.000002 -2.536949 0.013646
C 0 1.337079 -1.418970 -0.022733
C 0 1.195663 -0.041070 -0.067138
N 0 0.000000 0.642576 -0.082130
C 0 2.710746 -1.840080 -0.017042
C 0 3.589533 -0.734802 -0.057008
S 0 2.724619 0.806303 -0.102013
C 0 3.244145 -3.140107 0.016643
C 0 4.620379 -3.302378 0.012001
C 0 5.476772 -2.190693 -0.025573
C 0 4.971627 -0.894174 -0.061037
C 0 -0.000001 2.077673 -0.191207
C 0 0.000003 2.665870 -1.458949
C 0 0.000003 4.036135 -1.632353
C 0 -0.000002 4.842229 -0.496965
C 0 -0.000007 4.293038 0.784161
C 0 -0.000006 2.912013 0.935593
Cl 0 -0.000012 2.205815 2.533838
F 0 0.000007 1.850376 -2.530715
H 0 -6.549816 -2.341038 -0.027897
H 0 -5.041242 -4.300234 0.037553
H 0 -2.592746 -4.006396 0.044902
H 0 -5.638116 -0.040548 -0.090579
H 0 2.592752 -4.006393 0.044903
H 0 5.041248 -4.300228 0.037555
H 0 6.549820 -2.341029 -0.027892
H 0 5.638117 -0.040541 -0.090572
H 0 0.000006 4.450611 -2.632375
H 0 -0.000002 5.919382 -0.609894
H 0 -0.000010 4.931413 1.657653

SCF Done: E(UB3LYP) = -2654.51507983

Sum of electronic and zero-point Energies= -2654.248364

Sum of electronic and thermal Energies= -2654.226112

Sum of electronic and thermal Enthalpies= -2654.225168

Sum of electronic and thermal Free Energies= -2654.301914

6.1.13 *anti-anti-N-ortho,ortho'*-chloromethylphenyl-BBTT 3p

6.1.13.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.480703	-2.207508	-0.187459
C 0	-4.616748	-3.296233	-0.001734
C 0	-3.243616	-3.112108	0.086073
C 0	-2.711111	-1.816050	-0.015966
C 0	-3.599033	-0.732374	-0.207019
C 0	-4.976576	-0.914334	-0.291377
C 0	-1.341469	-1.385345	0.057739
C 0	-1.197570	-0.039057	-0.084988
S 0	-2.734478	0.797666	-0.313593
S 0	0.000087	-2.525813	0.365466
C 0	1.341571	-1.385274	0.057713
C 0	1.197615	-0.038986	-0.084991
N 0	0.000003	0.681820	-0.103695
C 0	2.711238	-1.815908	-0.015951
C 0	3.599118	-0.732187	-0.206944
S 0	2.734483	0.797819	-0.313484
C 0	3.243812	-3.111943	0.086058
C 0	4.616956	-3.295992	-0.001722
C 0	5.480862	-2.207220	-0.187391
C 0	4.976671	-0.914068	-0.291283
C 0	-0.000059	2.113219	-0.131737
C 0	-0.000014	2.791126	-1.366124
C 0	-0.000096	4.188419	-1.353988
C 0	-0.000211	4.899483	-0.157610
C 0	-0.000251	4.231746	1.062156
C 0	-0.000173	2.841245	1.067311
Cl 0	-0.000203	1.998767	2.599942
C 0	0.000067	2.031119	-2.668994
H 0	-6.550006	-2.371194	-0.251671
H 0	-5.027423	-4.296393	0.075890
H 0	-2.584585	-3.960970	0.228679
H 0	-5.641991	-0.070969	-0.435405
H 0	2.584823	-3.960845	0.228616
H 0	5.027679	-4.296134	0.075882
H 0	6.550175	-2.370852	-0.251580
H 0	5.642042	-0.070662	-0.435270
H 0	-0.000074	4.723004	-2.297106
H 0	-0.000273	5.983412	-0.172038
H 0	-0.000338	4.772758	1.999228
H 0	0.880407	1.389434	-2.755436
H 0	-0.880186	1.389320	-2.755438
H 0	0.000028	2.722966	-3.512344

SCF Done: E(RB3LYP) = -2594.72350812

Sum of electronic and zero-point Energies= -2594.421972

Sum of electronic and thermal Energies= -2594.398546

Sum of electronic and thermal Enthalpies= -2594.397602

Sum of electronic and thermal Free Energies= -2594.477517

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.392761	-2.315222	-0.415507
C 0	4.538403	-3.356604	-0.023663
C 0	3.189816	-3.123874	0.206552
C 0	2.673319	-1.828723	0.039900
C 0	3.548033	-0.793295	-0.364246
C 0	4.903913	-1.024353	-0.587583
C 0	1.335827	-1.344127	0.252278
C 0	1.195321	-0.014754	-0.006358
S 0	2.701780	0.739129	-0.542928

S 0	-0.000021	-2.363032	0.857839
C 0	-1.335731	-1.344176	0.252242
C 0	-1.195293	-0.014789	-0.006346
N 0	0.000007	0.713150	0.030917
C 0	-2.673228	-1.828800	0.039854
C 0	-3.547990	-0.793416	-0.364268
S 0	-2.701758	0.739113	-0.542895
C 0	-3.189673	-3.123970	0.206496
C 0	-4.538262	-3.356748	-0.023705
C 0	-5.392658	-2.315400	-0.415539
C 0	-4.903851	-1.024509	-0.587620
C 0	-0.000028	2.106626	0.378462
C 0	-0.000079	2.485735	1.734428
C 0	-0.000110	3.846692	2.045716
C 0	-0.000097	4.814391	1.044489
C 0	-0.000066	4.443389	-0.294655
C 0	-0.000039	3.089871	-0.619764
Cl 0	-0.000047	2.633062	-2.312254
C 0	-0.000125	1.441785	2.821463
H 0	6.443342	-2.516123	-0.589879
H 0	4.937546	-4.356664	0.100862
H 0	2.534556	-3.934035	0.505867
H 0	5.562079	-0.219793	-0.894553
H 0	-2.534379	-3.934117	0.505777
H 0	-4.937367	-4.356821	0.100840
H 0	-6.443225	-2.516336	-0.589915
H 0	-5.562035	-0.219984	-0.894641
H 0	-0.000137	4.149449	3.086831
H 0	-0.000113	5.866156	1.306911
H 0	-0.000068	5.184392	-1.083126
H 0	-0.878533	0.794463	2.751941
H 0	0.878169	0.794319	2.751911
H 0	-0.000079	1.913266	3.805050

SCF Done: E(RB3LYP) = -2594.72415714

Sum of electronic and zero-point Energies= -2594.422418

Sum of electronic and thermal Energies= -2594.399179

Sum of electronic and thermal Enthalpies= -2594.398234

Sum of electronic and thermal Free Energies= -2594.476587

6.1.13.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt=verytight int=ultrafine freq=noraman rb3lyp/6-311++g(d,p) scrf=

(pcm,solvent=dichloromethane) pop=full geom=checkpoint guess=read

0 1

C 0	-5.435186	-2.263710	-0.354080
C 0	-4.577908	-3.320028	-0.009981
C 0	-3.217268	-3.106634	0.169807
C 0	-2.691536	-1.814539	-0.001125
C 0	-3.571724	-0.764145	-0.353214
C 0	-4.937797	-0.974714	-0.527372
C 0	-1.338649	-1.351402	0.152543
C 0	-1.195571	-0.019315	-0.092923
S 0	-2.715551	0.765464	-0.531126
S 0	-0.000000	-2.410361	0.686090
C 0	1.338649	-1.351402	0.152543
C 0	1.195571	-0.019315	-0.092924
N 0	-0.000000	0.702467	-0.096964
C 0	2.691536	-1.814540	-0.001125
C 0	3.571724	-0.764146	-0.353214
S 0	2.715551	0.765464	-0.531127
C 0	3.217268	-3.106634	0.169806
C 0	4.577908	-3.320028	-0.009981
C 0	5.435185	-2.263710	-0.354080
C 0	4.937797	-0.974714	-0.527373
C 0	0.000000	2.136117	-0.069084
C 0	-0.000000	2.875517	-1.264932

C 0	-0.000000	4.274133	-1.177682
C 0	0.000000	4.922436	0.050159
C 0	0.000001	4.191508	1.237444
C 0	0.000000	2.806621	1.166753
Cl 0	0.000001	1.880481	2.657490
C 0	-0.000001	2.216855	-2.622975
H 0	-6.494266	-2.449677	-0.488272
H 0	-4.983838	-4.316772	0.118983
H 0	-2.563555	-3.929646	0.435718
H 0	-5.598105	-0.158111	-0.794752
H 0	2.563555	-3.929646	0.435717
H 0	4.983838	-4.316772	0.118983
H 0	6.494266	-2.449677	-0.488273
H 0	5.598104	-0.158111	-0.794752
H 0	-0.000001	4.855921	-2.092641
H 0	0.000000	6.005330	0.092151
H 0	0.000001	4.686468	2.199600
H 0	-0.000001	1.130444	-2.559642
H 0	-0.880894	2.525235	-3.192375
H 0	0.880891	2.525235	-3.192376

SCF Done: E(RB3LYP) = -2594.73117397

Sum of electronic and zero-point Energies= -2594.429700

Sum of electronic and thermal Energies= -2594.406290

Sum of electronic and thermal Enthalpies= -2594.405346

Sum of electronic and thermal Free Energies= -2594.484798

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0	5.459462	-2.218838	-0.274909
C 0	4.599363	-3.312802	-0.094578
C 0	3.231851	-3.128526	0.064659
C 0	2.701856	-1.826858	0.040047
C 0	3.585760	-0.737858	-0.146042
C 0	4.958092	-0.919952	-0.300828
C 0	1.340711	-1.391852	0.200436
C 0	1.196459	-0.039561	0.118523
S 0	2.724746	0.798576	-0.157731
S 0	0.000032	-2.523731	0.548698
C 0	-1.340675	-1.391878	0.200457
C 0	-1.196443	-0.039585	0.118547
N 0	0.000001	0.678548	0.185298
C 0	-2.701817	-1.826901	0.040087
C 0	-3.585738	-0.737913	-0.145995
S 0	-2.724741	0.798533	-0.157713
C 0	-3.231795	-3.128575	0.064712
C 0	-4.599307	-3.312869	-0.094503
C 0	-5.459423	-2.218917	-0.274825
C 0	-4.958069	-0.920025	-0.300760
C 0	-0.000014	2.107632	0.299848
C 0	0.000032	2.701352	1.576263
C 0	0.000023	4.095851	1.659109
C 0	-0.000029	4.885725	0.512223
C 0	-0.000079	4.301669	-0.750394
C 0	-0.000073	2.914567	-0.847433
Cl 0	-0.000167	2.179503	-2.442044
C 0	0.000130	1.849043	2.819134
H 0	6.523657	-2.382911	-0.396518
H 0	5.008214	-4.316543	-0.078507
H 0	2.576852	-3.981442	0.202381
H 0	5.620086	-0.073583	-0.441550
H 0	-2.576783	-3.981482	0.202428
H 0	-5.008144	-4.316616	-0.078420
H 0	-6.523618	-2.383004	-0.396419
H 0	-5.620075	-0.073665	-0.441479
H 0	0.000058	4.566003	2.635710
H 0	-0.000032	5.966010	0.598462
H 0	-0.000126	4.906759	-1.647288
H 0	-0.879344	1.200593	2.856451
H 0	0.879895	1.200990	2.856563

H 0 -0.000062 2.475873 3.711119

SCF Done: E(RB3LYP) = -2594.73163155

Sum of electronic and zero-point Energies= -2594.430253

Sum of electronic and thermal Energies= -2594.406833

Sum of electronic and thermal Enthalpies= -2594.405889

Sum of electronic and thermal Free Energies= -2594.485178

6.1.13.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt=verytight int=ultrafine freq=noraman rb3lyp/6-311++g(d,p) scrf=

(smd,solvent=dichloromethane) pop=full geom=checkpoint guess=read

0 1

C 0	-5.432025	-2.269958	-0.366546
C 0	-4.576444	-3.321439	-0.003590
C 0	-3.216927	-3.105649	0.182968
C 0	-2.690842	-1.814950	0.000443
C 0	-3.570078	-0.769894	-0.368904
C 0	-4.934971	-0.982317	-0.550619
C 0	-1.339324	-1.347082	0.158396
C 0	-1.195032	-0.017080	-0.097547
S 0	-2.714634	0.760204	-0.554522
S 0	-0.000000	-2.397562	0.708440
C 0	1.339323	-1.347082	0.158396
C 0	1.195032	-0.017080	-0.097547
N 0	-0.000000	0.705568	-0.098010
C 0	2.690842	-1.814950	0.000443
C 0	3.570078	-0.769895	-0.368904
S 0	2.714634	0.760204	-0.554522
C 0	3.216926	-3.105649	0.182968
C 0	4.576443	-3.321440	-0.003590
C 0	5.432025	-2.269959	-0.366546
C 0	4.934971	-0.982318	-0.550619
C 0	0.000000	2.140207	-0.062678
C 0	0.000000	2.886802	-1.254631
C 0	0.000000	4.285254	-1.158633
C 0	0.000001	4.925954	0.072989
C 0	0.000001	4.188573	1.256859
C 0	0.000000	2.804567	1.176981
Cl 0	0.000000	1.867578	2.664432
C 0	-0.000000	2.238121	-2.616287
H 0	-6.490224	-2.458708	-0.506254
H 0	-4.982713	-4.317178	0.134033
H 0	-2.566903	-3.927019	0.463674
H 0	-5.594521	-0.169080	-0.831438
H 0	2.566903	-3.927020	0.463674
H 0	4.982712	-4.317178	0.134033
H 0	6.490224	-2.458709	-0.506255
H 0	5.594521	-0.169080	-0.831438
H 0	0.000000	4.871675	-2.071004
H 0	0.000001	6.008978	0.121837
H 0	0.000001	4.680696	2.220943
H 0	0.000000	1.150574	-2.565295
H 0	-0.880859	2.551151	-3.184474
H 0	0.880857	2.551152	-3.184474

SCF Done: E(RB3LYP) = -2594.75574819

Sum of electronic and zero-point Energies= -2594.454185

Sum of electronic and thermal Energies= -2594.430925

Sum of electronic and thermal Enthalpies= -2594.429981

Sum of electronic and thermal Free Energies= -2594.508852

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane) geom=check guess=read

0 1

C 0	5.443368	-2.243845	-0.326998
C 0	4.584703	-3.328115	-0.089367
C 0	3.221953	-3.134181	0.097668
C 0	2.694995	-1.831952	0.042520
C 0	3.577653	-0.753424	-0.201880
C 0	4.945646	-0.944591	-0.383572
C 0	1.340187	-1.383995	0.225523
C 0	1.195884	-0.034811	0.101686
S 0	2.720719	0.785539	-0.248236
S 0	0.000007	-2.488643	0.654345
C 0	-1.340177	-1.384004	0.225513
C 0	-1.195881	-0.034819	0.101673
N 0	-0.000001	0.684784	0.165127
C 0	-2.694983	-1.831968	0.042513
C 0	-3.577646	-0.753445	-0.201891
S 0	-2.720720	0.785521	-0.248256
C 0	-3.221935	-3.134200	0.097670
C 0	-4.584685	-3.328139	-0.089361
C 0	-5.443355	-2.243875	-0.326996
C 0	-4.945639	-0.944619	-0.383575
C 0	-0.000008	2.111264	0.323938
C 0	-0.000019	2.667656	1.617918
C 0	-0.000038	4.059605	1.740867
C 0	-0.000038	4.883045	0.617996
C 0	-0.000023	4.336749	-0.661506
C 0	-0.000008	2.953087	-0.798440
Cl 0	0.000013	2.267799	-2.418840
C 0	0.000000	1.784642	2.837765
H 0	6.503992	-2.415981	-0.469599
H 0	4.991003	-4.332546	-0.050472
H 0	2.570479	-3.981601	0.280906
H 0	5.606945	-0.105966	-0.569482
H 0	-2.570457	-3.981616	0.280912
H 0	-4.990980	-4.332572	-0.050460
H 0	-6.503979	-2.416016	-0.469592
H 0	-5.606942	-0.105997	-0.569486
H 0	-0.000056	4.499420	2.731720
H 0	-0.000054	5.960638	0.735855
H 0	-0.000022	4.970052	-1.539162
H 0	-0.879686	1.134956	2.862366
H 0	0.879908	1.135258	2.862535
H 0	-0.000184	2.390813	3.744724

SCF Done: E(RB3LYP) = -2594.75606243

Sum of electronic and zero-point Energies= -2594.454897

Sum of electronic and thermal Energies= -2594.431428

Sum of electronic and thermal Enthalpies= -2594.430484

Sum of electronic and thermal Free Energies= -2594.510818

6.1.13.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.479831	-2.166510	0.001871
C 0	4.626978	-3.280489	0.043922
C 0	3.251184	-3.122115	0.027514
C 0	2.712004	-1.825147	-0.032192
C 0	3.587517	-0.716948	-0.074219
C 0	4.969666	-0.873603	-0.057691
C 0	1.337743	-1.407535	-0.058372
C 0	1.193777	-0.028482	-0.117666
S 0	2.721388	0.821131	-0.142252
S 0	0.000041	-2.526954	-0.013682
C 0	-1.337694	-1.407573	-0.058422
C 0	-1.193764	-0.028516	-0.117647
N 0	-0.000003	0.654360	-0.154685
C 0	-2.711942	-1.825230	-0.032188
C 0	-3.587497	-0.717061	-0.074061
S 0	-2.721403	0.821072	-0.142045
C 0	-3.251078	-3.122225	0.027345

C 0	-4.626867	-3.280648	0.043760
C 0	-5.479760	-2.166693	0.001887
C 0	-4.969638	-0.873761	-0.057516
C 0	-0.000035	2.104480	-0.197035
C 0	-0.000164	2.757396	-1.441429
C 0	-0.000286	4.154367	-1.430597
C 0	-0.000216	4.868883	-0.235768
C 0	-0.000055	4.210557	0.989970
C 0	0.000008	2.821161	1.007611
Cl 0	0.000104	1.977618	2.536601
C 0	-0.000028	1.988665	-2.738940
H 0	6.553025	-2.312919	0.016372
H 0	5.051200	-4.275793	0.090561
H 0	2.601995	-3.989654	0.061425
H 0	5.632801	-0.017809	-0.088655
H 0	-2.601859	-3.989747	0.061133
H 0	-5.051053	-4.275975	0.090259
H 0	-6.552948	-2.313141	0.016404
H 0	-5.632801	-0.017983	-0.088335
H 0	-0.000442	4.686210	-2.374584
H 0	-0.000293	5.952230	-0.256096
H 0	-0.000002	4.759252	1.922482
H 0	0.883251	1.350382	-2.829528
H 0	-0.881833	1.348230	-2.828595
H 0	-0.001305	2.674847	-3.585414

SCF Done: E(UB3LYP) = -2594.50503760

Sum of electronic and zero-point Energies= -2594.202726

Sum of electronic and thermal Energies= -2594.179523

Sum of electronic and thermal Enthalpies= -2594.178579

Sum of electronic and thermal Free Energies= -2594.256943

6.1.13.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0	5.469872	-2.188390	-0.023449
C 0	4.611504	-3.298347	0.023517
C 0	3.235547	-3.133915	0.016612
C 0	2.704091	-1.833616	-0.038154
C 0	3.584548	-0.729832	-0.087530
C 0	4.966594	-0.892018	-0.080153
C 0	1.331374	-1.410436	-0.053152
C 0	1.190796	-0.032382	-0.113014
S 0	2.722762	0.811928	-0.156579
S 0	-0.007947	-2.526216	-0.000579
C 0	-1.342139	-1.403994	-0.046652
C 0	-1.194401	-0.026515	-0.104339
N 0	-0.000481	0.653476	-0.138592
C 0	-2.717137	-1.819656	-0.022966
C 0	-3.591693	-0.710713	-0.060755
S 0	-2.721802	0.826353	-0.127480
C 0	-3.255971	-3.117085	0.028617
C 0	-4.632835	-3.273512	0.042930
C 0	-5.485094	-2.158476	0.006709
C 0	-4.974547	-0.864781	-0.045946
C 0	0.003796	2.102196	-0.196480
C 0	-0.020256	2.751990	-1.440543
C 0	-0.006266	4.152548	-1.430993
C 0	0.024790	4.869542	-0.241968
C 0	0.044904	4.214253	0.988809
C 0	0.034472	2.828850	1.005387
Cl 0	0.058363	1.985736	2.543208
C 0	-0.079388	2.010543	-2.751388
H 0	6.542712	-2.340210	-0.015717
H 0	5.030644	-4.296375	0.066372
H 0	2.582610	-3.998743	0.053109

H 0	5.634620	-0.039757	-0.115669
H 0	-2.608190	-3.986078	0.056334
H 0	-5.057453	-4.269350	0.082676
H 0	-6.558728	-2.304149	0.019505
H 0	-5.637592	-0.008338	-0.073270
H 0	-0.021209	4.679189	-2.378488
H 0	0.034553	5.953143	-0.264451
H 0	0.068734	4.768804	1.917858
H 0	0.102121	0.940653	-2.651670
H 0	-1.064089	2.140906	-3.211449
H 0	0.658883	2.417887	-3.445928

SCF Done: E(UB3LYP) = -2594.58278791

Sum of electronic and zero-point Energies= -2594.280473

Sum of electronic and thermal Energies= -2594.257395

Sum of electronic and thermal Enthalpies= -2594.256451

Sum of electronic and thermal Free Energies= -2594.334399

6.1.14 *anti-anti-N-ortho,ortho'*-chloromethoxyphenyl-BBTT 3q

6.1.14.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt=verytight freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.400954	-2.391736	-0.403824
C 0	-4.546656	-3.399097	0.068786
C 0	-3.195532	-3.152131	0.267728
C 0	-2.676690	-1.877576	-0.011441
C 0	-3.551433	-0.876829	-0.495290
C 0	-4.909601	-1.121896	-0.688518
C 0	-1.335252	-1.382203	0.148708
C 0	-1.193795	-0.080439	-0.219023
S 0	-2.700907	0.630346	-0.809884
S 0	0.000000	-2.361608	0.812117
C 0	1.335252	-1.382203	0.148708
C 0	1.193795	-0.080439	-0.219023
N 0	-0.000000	0.653333	-0.258221
C 0	2.676690	-1.877576	-0.011442
C 0	3.551433	-0.876829	-0.495290
S 0	2.700907	0.630346	-0.809885
C 0	3.195532	-3.152130	0.267729
C 0	4.546656	-3.399096	0.068786
C 0	5.400954	-2.391735	-0.403823
C 0	4.909600	-1.121896	-0.688518
C 0	-0.000000	2.033698	0.120419
C 0	-0.000000	3.058511	-0.827625
C 0	-0.000001	4.400392	-0.449639
C 0	-0.000001	4.713373	0.902932
C 0	-0.000001	3.717834	1.878486
C 0	0.000000	2.376139	1.492523
O 0	0.000001	1.328352	2.345417
C 0	0.000001	1.577156	3.748876
Cl 0	0.000000	2.664733	-2.534104
H 0	-6.453429	-2.603099	-0.552925
H 0	-4.947628	-4.383684	0.280535
H 0	-2.540114	-3.936511	0.629052
H 0	-5.567776	-0.344095	-1.058155
H 0	2.540114	-3.936511	0.629052
H 0	4.947628	-4.383684	0.280536
H 0	6.453429	-2.603098	-0.552925
H 0	5.567776	-0.344095	-1.058155
H 0	-0.000001	5.173091	-1.206093
H 0	-0.000001	5.753597	1.207762
H 0	-0.000001	3.991468	2.924367
H 0	0.000002	0.595600	4.217929
H 0	0.896028	2.127662	4.052041
H 0	-0.896026	2.127660	4.052042

SCF Done: E(RB3LYP) = -2669.95097796

Sum of electronic and zero-point Energies= -2669.644375

Sum of electronic and thermal Energies= -2669.620166

Sum of electronic and thermal Enthalpies= -2669.619222

Sum of electronic and thermal Free Energies= -2669.700168

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.419824	-2.337282	0.426392
C 0	-4.563264	-3.421495	0.186115
C 0	-3.207492	-3.224970	-0.037944
C 0	-2.684205	-1.921539	-0.018554
C 0	-3.563344	-0.842155	0.231734
C 0	-4.924725	-1.036852	0.449992
C 0	-1.335553	-1.475207	-0.239561
C 0	-1.195315	-0.125078	-0.136170
S 0	-2.710637	0.698310	0.233666
S 0	0.000087	-2.572467	-0.690954
C 0	1.335639	-1.475139	-0.239551
C 0	1.195334	-0.125015	-0.136132
N 0	-0.000007	0.593374	-0.252448
C 0	2.684324	-1.921393	-0.018557
C 0	3.563409	-0.841959	0.231678
S 0	2.710639	0.698440	0.233629
C 0	3.207725	-3.224788	-0.038068
C 0	4.563522	-3.421205	0.185833
C 0	5.420039	-2.336944	0.426038
C 0	4.924850	-1.036569	0.449759
C 0	-0.000061	2.017669	-0.214049
C 0	-0.000261	2.776073	-1.388702
C 0	-0.000332	4.168351	-1.354808
C 0	-0.000193	4.806007	-0.120514
C 0	-0.000010	4.084287	1.070843
C 0	0.000029	2.687630	1.032178
O 0	0.000129	1.887769	2.120613
C 0	0.000257	2.480361	3.417060
Cl 0	-0.000401	1.964262	-2.935218
H 0	-6.476018	-2.510563	0.596344
H 0	-4.966430	-4.427687	0.173584
H 0	-2.552137	-4.068942	-0.220803
H 0	-5.584227	-0.197222	0.637216
H 0	2.552426	-4.068826	-0.220838
H 0	4.966736	-4.427378	0.173212
H 0	6.476240	-2.510160	0.595866
H 0	5.584299	-0.196903	0.636982
H 0	-0.000479	4.730380	-2.278642
H 0	-0.000228	5.889321	-0.082562
H 0	0.000068	4.609087	2.015889
H 0	0.000380	1.647776	4.117255
H 0	0.896375	3.088856	3.572863
H 0	-0.895883	3.088773	3.573067

SCF Done: E(RB3LYP) = -2669.95084561

Sum of electronic and zero-point Energies= -2669.644182

Sum of electronic and thermal Energies= -2669.619944

Sum of electronic and thermal Enthalpies= -2669.619000

Sum of electronic and thermal Free Energies= -2669.700111

6.1.14.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt=verytight freq=noraman rb3lyp/6-311++g(d,p) pop=full Guess=Read geom=check SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	-5.476092	-2.309523	-0.185310

C 0	-4.614558	-3.390031	0.057497
C 0	-3.242114	-3.201009	0.159208
C 0	-2.709009	-1.908692	0.013130
C 0	-3.594340	-0.833495	-0.235812
C 0	-4.971363	-1.020068	-0.333054
C 0	-1.341922	-1.470141	0.099533
C 0	-1.196236	-0.129918	-0.092718
S 0	-2.728406	0.691899	-0.393963
S 0	-0.000000	-2.588671	0.482336
C 0	1.341922	-1.470141	0.099533
C 0	1.196236	-0.129918	-0.092718
N 0	0.000000	0.590443	-0.130446
C 0	2.709009	-1.908692	0.013130
C 0	3.594340	-0.833495	-0.235812
S 0	2.728406	0.691899	-0.393963
C 0	3.242114	-3.201009	0.159208
C 0	4.614558	-3.390031	0.057497
C 0	5.476092	-2.309523	-0.185310
C 0	4.971363	-1.020068	-0.333054
C 0	0.000000	2.011739	0.000705
C 0	0.000000	2.851182	-1.117954
C 0	0.000000	4.236790	-0.988575
C 0	0.000000	4.784743	0.289625
C 0	0.000000	3.981357	1.427521
C 0	0.000000	2.590751	1.291284
O 0	0.000000	1.716172	2.319328
C 0	0.000000	2.223148	3.660348
Cl 0	0.000000	2.148595	-2.725264
H 0	-6.544104	-2.476713	-0.260620
H 0	-5.025914	-4.386802	0.167832
H 0	-2.586446	-4.043912	0.346580
H 0	-5.634941	-0.184463	-0.522417
H 0	2.586446	-4.043912	0.346580
H 0	5.025914	-4.386802	0.167832
H 0	6.544104	-2.476714	-0.260620
H 0	5.634941	-0.184463	-0.522417
H 0	0.000000	4.865192	-1.868557
H 0	0.000000	5.862377	0.403776
H 0	0.000000	4.439041	2.406517
H 0	0.000000	1.345001	4.301610
H 0	0.895942	2.818900	3.851970
H 0	-0.895942	2.818900	3.851970

SCF Done: E(RB3LYP) = -2669.96079300

Sum of electronic and zero-point Energies= -2669.654211

Sum of electronic and thermal Energies= -2669.629967

Sum of electronic and thermal Enthalpies= -2669.629023

Sum of electronic and thermal Free Energies= -2669.710431

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full Guess=Read geom=chec

k
SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	-5.437192	-2.320099	0.396839
C 0	-4.581328	-3.411718	0.184730
C 0	-3.220457	-3.223987	-0.021150
C 0	-2.692492	-1.921382	-0.011667
C 0	-3.571937	-0.834644	0.207159
C 0	-4.937760	-1.020228	0.408611
C 0	-1.338113	-1.482213	-0.213950
C 0	-1.194792	-0.130062	-0.131036
S 0	-2.713909	0.703908	0.195885
S 0	-0.000075	-2.597896	-0.618018
C 0	1.338020	-1.482271	-0.213982
C 0	1.194762	-0.130114	-0.131072
N 0	-0.000000	0.587261	-0.241380
C 0	2.692386	-1.921499	-0.011727
C 0	3.571883	-0.834795	0.207066
S 0	2.713914	0.703791	0.195845
C 0	3.220287	-3.224129	-0.021219
C 0	4.581162	-3.411919	0.184605

C 0	5.437074	-2.320332	0.396682
C 0	4.937701	-1.020437	0.408472
C 0	0.000038	2.013671	-0.203227
C 0	0.000003	2.769828	-1.379822
C 0	0.000041	4.160344	-1.353148
C 0	0.000126	4.800731	-0.118059
C 0	0.000176	4.082929	1.074873
C 0	0.000131	2.685281	1.042305
O 0	0.000211	1.890823	2.133590
C 0	0.000337	2.495992	3.432764
Cl 0	-0.000110	1.947356	-2.927427
H 0	-6.496361	-2.486736	0.553894
H 0	-4.988391	-4.416335	0.179992
H 0	-2.568383	-4.074752	-0.183733
H 0	-5.596389	-0.175650	0.573923
H 0	2.568147	-4.074840	-0.183805
H 0	4.988193	-4.416548	0.179871
H 0	6.496243	-2.487011	0.553700
H 0	5.596374	-0.175889	0.573764
H 0	0.000006	4.722818	-2.276667
H 0	0.000163	5.883815	-0.082917
H 0	0.000259	4.611301	2.017629
H 0	0.000384	1.668105	4.137714
H 0	0.896221	3.104357	3.580004
H 0	-0.895498	3.104390	3.580164

SCF Done: E(RB3LYP) = -2669.96099766

Sum of electronic and zero-point Energies= -2669.654418

Sum of electronic and thermal Energies= -2669.630170

Sum of electronic and thermal Enthalpies= -2669.629226

Sum of electronic and thermal Free Energies= -2669.710249

6.1.14.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt=verytight int=ultrafine freq=noraman rb3lyp/6-311++g(d,p) scrf=

(smd,solvent=dichloromethane) pop=full geom=check guess=read

0 1

C 0	-5.453510	-2.339873	-0.279257
C 0	-4.593843	-3.398386	0.052120
C 0	-3.227647	-3.191728	0.195971
C 0	-2.699516	-1.903492	0.002703
C 0	-3.582824	-0.851119	-0.334526
C 0	-4.954244	-1.054669	-0.473810
C 0	-1.340492	-1.444794	0.122001
C 0	-1.195212	-0.115255	-0.132171
S 0	-2.722959	0.672799	-0.540659
S 0	-0.000000	-2.517608	0.620704
C 0	1.340491	-1.444794	0.122001
C 0	1.195211	-0.115255	-0.132171
N 0	-0.000000	0.608840	-0.171409
C 0	2.699516	-1.903492	0.002703
C 0	3.582824	-0.851120	-0.334526
S 0	2.722959	0.672798	-0.540659
C 0	3.227646	-3.191729	0.195971
C 0	4.593842	-3.398387	0.052120
C 0	5.453509	-2.339875	-0.279258
C 0	4.954243	-1.054670	-0.473811
C 0	0.000000	2.022402	0.045761
C 0	0.000000	2.931740	-1.016566
C 0	0.000001	4.306408	-0.799981
C 0	0.000001	4.771590	0.510946
C 0	0.000001	3.897748	1.595488
C 0	0.000000	2.518632	1.370638
O 0	0.000000	1.580538	2.339415
C 0	0.000001	2.000897	3.711921
Cl 0	0.000000	2.336124	-2.670113
H 0	-6.516720	-2.521451	-0.386913

H 0	-5.001806	-4.392295	0.197729
H 0	-2.574650	-4.019177	0.450809
H 0	-5.617243	-0.236609	-0.731562
H 0	2.574648	-4.019178	0.450809
H 0	5.001805	-4.392296	0.197728
H 0	6.516719	-2.521453	-0.386913
H 0	5.617243	-0.236611	-0.731563
H 0	0.000001	4.991143	-1.637552
H 0	0.000001	5.840146	0.693434
H 0	0.000001	4.290246	2.602707
H 0	0.000001	1.081782	4.294994
H 0	0.896867	2.581481	3.943484
H 0	-0.896864	2.581482	3.943485

SCF Done: E(RB3LYP) = -2669.98460158

Sum of electronic and zero-point Energies= -2669.678382

Sum of electronic and thermal Energies= -2669.653980

Sum of electronic and thermal Enthalpies= -2669.653036

Sum of electronic and thermal Free Energies= -2669.736608

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=check guess=read

0 1

C 0	-5.456138	-2.308068	0.351270
C 0	-4.598138	-3.403989	0.172811
C 0	-3.231954	-3.222699	-0.002181
C 0	-2.700492	-1.921110	0.005463
C 0	-3.583011	-0.830328	0.188994
C 0	-4.953800	-1.009121	0.360049
C 0	-1.340447	-1.486924	-0.169542
C 0	-1.195057	-0.134183	-0.102878
S 0	-2.720308	0.706812	0.177474
S 0	0.000031	-2.617017	-0.525448
C 0	1.340490	-1.486894	-0.169570
C 0	1.195072	-0.134157	-0.102904
N 0	-0.000002	0.582519	-0.204812
C 0	2.700544	-1.921057	0.005455
C 0	3.583042	-0.830255	0.188970
S 0	2.720319	0.706873	0.177376
C 0	3.232005	-3.222642	-0.002156
C 0	4.598192	-3.403938	0.172837
C 0	5.456163	-2.307990	0.351290
C 0	4.953825	-1.009041	0.360051
C 0	-0.000022	2.009749	-0.195537
C 0	-0.000047	2.742637	-1.387468
C 0	-0.000070	4.132641	-1.390842
C 0	-0.000071	4.797267	-0.167892
C 0	-0.000051	4.104727	1.039583
C 0	-0.000024	2.705980	1.037031
O 0	-0.000012	1.934375	2.142880
C 0	0.000007	2.565265	3.432185
Cl 0	-0.000041	1.886469	-2.919760
H 0	-6.519600	-2.470355	0.483955
H 0	-5.007811	-4.407828	0.169078
H 0	-2.581500	-4.079397	-0.140372
H 0	-5.614800	-0.161131	0.498602
H 0	2.581514	-4.079310	-0.140349
H 0	5.007941	-4.407745	0.169149
H 0	6.519627	-2.470259	0.483994
H 0	5.614832	-0.161056	0.498594
H 0	-0.000086	4.678055	-2.325099
H 0	-0.000092	5.881343	-0.154935
H 0	-0.000058	4.653270	1.971119
H 0	0.000017	1.750057	4.153396
H 0	0.896829	3.174912	3.569426
H 0	-0.896809	3.174912	3.569455

SCF Done: E(RB3LYP) = -2669.98482238

Sum of electronic and zero-point Energies= -2669.678426

Sum of electronic and thermal Energies= -2669.654130

Sum of electronic and thermal Enthalpies= -2669.653186

Sum of electronic and thermal Free Energies= -2669.734831

6.1.14.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.480406	-2.259977	0.057158
C 0	4.628222	-3.374338	0.100225
C 0	3.252232	-3.216344	0.088953
C 0	2.712122	-1.919691	0.033888
C 0	3.586830	-0.810856	-0.008470
C 0	4.969130	-0.967317	0.002456
C 0	1.337492	-1.502485	0.013512
C 0	1.193450	-0.123711	-0.042986
S 0	2.719256	0.726231	-0.073641
S 0	-0.000060	-2.621449	0.052882
C 0	-1.337573	-1.502424	0.013672
C 0	-1.193453	-0.123674	-0.042962
N 0	0.000003	0.558447	-0.080373
C 0	-2.712227	-1.919585	0.033811
C 0	-3.586901	-0.810751	-0.009142
S 0	-2.719262	0.726337	-0.074626
C 0	-3.252373	-3.216205	0.089253
C 0	-4.628371	-3.374168	0.100249
C 0	-5.480520	-2.259810	0.056500
C 0	-4.969204	-0.967178	0.001449
C 0	0.000012	2.000501	-0.104178
C 0	0.000551	2.700876	-1.314569
C 0	0.000678	4.090903	-1.321225
C 0	0.000242	4.766322	-0.104487
C 0	-0.000281	4.089193	1.112469
C 0	-0.000362	2.692417	1.125956
O 0	-0.000613	1.918042	2.228841
C 0	-0.001156	2.544721	3.520766
Cl 0	0.000934	1.824298	-2.822044
H 0	6.553736	-2.405940	0.065789
H 0	5.052939	-4.369670	0.141974
H 0	2.603448	-4.084243	0.121889
H 0	5.631703	-0.111181	-0.031703
H 0	-2.603613	-4.084101	0.122719
H 0	-5.053116	-4.369471	0.142380
H 0	-6.553855	-2.405750	0.064874
H 0	-5.631751	-0.111046	-0.033300
H 0	0.001120	4.625898	-2.260946
H 0	0.000327	5.849880	-0.103529
H 0	-0.000659	4.647346	2.038012
H 0	-0.001626	1.727736	4.237966
H 0	0.895845	3.153683	3.656881
H 0	-0.898124	3.153925	3.655993

SCF Done: E(UB3LYP) = -2669.73616547

Sum of electronic and zero-point Energies= -2669.428658

Sum of electronic and thermal Energies= -2669.404595

Sum of electronic and thermal Enthalpies= -2669.403651

Sum of electronic and thermal Free Energies= -2669.483931

6.1.14.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0	5.478855	-2.263178	0.071311
C 0	4.624928	-3.377095	0.098723
C 0	3.248252	-3.218392	0.082432
C 0	2.711443	-1.920000	0.037735

C 0	3.587622	-0.812026	0.008562
C 0	4.970169	-0.968412	0.026047
C 0	1.336903	-1.501991	0.014560
C 0	1.192334	-0.124249	-0.034523
S 0	2.719666	0.726837	-0.049661
S 0	0.000076	-2.621446	0.038992
C 0	-1.336799	-1.502055	0.014511
C 0	-1.192300	-0.124303	-0.034579
N 0	0.000002	0.558377	-0.074692
C 0	-2.711316	-1.920133	0.037609
C 0	-3.587553	-0.812208	0.008361
S 0	-2.719666	0.726701	-0.049829
C 0	-3.248053	-3.218555	0.082306
C 0	-4.624721	-3.377336	0.098524
C 0	-5.478708	-2.263466	0.071045
C 0	-4.970093	-0.968671	0.025783
C 0	-0.000033	2.000188	-0.112452
C 0	0.000081	2.690103	-1.329264
C 0	0.000042	4.077773	-1.356205
C 0	-0.000125	4.766241	-0.144878
C 0	-0.000251	4.104007	1.078779
C 0	-0.000199	2.706226	1.110182
O 0	-0.000284	1.947423	2.220860
C 0	-0.000676	2.593345	3.508485
Cl 0	0.000249	1.791395	-2.832340
H 0	6.552268	-2.410508	0.084754
H 0	5.047938	-4.373851	0.132457
H 0	2.599040	-4.086528	0.102879
H 0	5.634584	-0.112846	0.004593
H 0	-2.598789	-4.086651	0.102816
H 0	-5.047680	-4.374114	0.132256
H 0	-6.552113	-2.410855	0.084433
H 0	-5.634558	-0.113145	0.004284
H 0	0.000138	4.605825	-2.300204
H 0	-0.000160	5.850074	-0.156285
H 0	-0.000373	4.672964	1.997893
H 0	-0.000703	1.784032	4.235627
H 0	0.896802	3.202902	3.635143
H 0	-0.898414	3.202609	3.634730

SCF Done: E(UB3LYP) = -2669.81282837

Sum of electronic and zero-point Energies= -2669.505319

Sum of electronic and thermal Energies= -2669.481304

Sum of electronic and thermal Enthalpies= -2669.480360

Sum of electronic and thermal Free Energies= -2669.560759

6.1.15 *anti-anti-N-ortho,ortho'*-difluorophenyl-BBTT 3h

6.1.15.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

#

p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.346438	-2.312898	-0.427911
C 0	-4.504607	-3.275908	0.148406
C 0	-3.170727	-2.993242	0.405726
C 0	-2.657295	-1.727812	0.081107
C 0	-3.518214	-0.772819	-0.508497
C 0	-4.860291	-1.052932	-0.759542
C 0	-1.334356	-1.197683	0.285844
C 0	-1.195215	0.083277	-0.147127
S 0	-2.674259	0.728932	-0.869170
S 0	-0.000017	-2.102305	1.050267
C 0	1.334323	-1.197714	0.285805
C 0	1.195199	0.083249	-0.147163
N 0	0.000001	0.818837	-0.164591
C 0	2.657258	-1.727856	0.081075
C 0	3.518188	-0.772871	-0.508525
S 0	2.674231	0.728861	-0.869271
C 0	3.170683	-2.993282	0.405720

C 0	4.504567	-3.275953	0.148427
C 0	5.346409	-2.312951	-0.427887
C 0	4.860271	-1.052988	-0.759538
C 0	0.000023	2.204253	0.173021
C 0	0.000011	3.199493	-0.807990
C 0	0.000035	4.551562	-0.500862
C 0	0.000072	4.930953	0.838526
C 0	0.000084	3.977024	1.854170
C 0	0.000061	2.637423	1.503547
F 0	0.000069	1.706011	2.471352
F 0	-0.000025	2.824816	-2.100220
H 0	-6.385857	-2.551659	-0.620694
H 0	-4.902226	-4.253328	0.396146
H 0	-2.524286	-3.741946	0.849291
H 0	-5.509109	-0.310071	-1.208765
H 0	2.524235	-3.741977	0.849289
H 0	4.902180	-4.253371	0.396186
H 0	6.385830	-2.551718	-0.620655
H 0	5.509095	-0.310137	-1.208770
H 0	0.000025	5.278118	-1.302833
H 0	0.000090	5.983385	1.094991
H 0	0.000111	4.253636	2.900523

SCF Done: E(RB3LYP) = -2294.30564770

Sum of electronic and zero-point Energies= -2294.038015

Sum of electronic and thermal Energies= -2294.015982

Sum of electronic and thermal Enthalpies= -2294.015037

Sum of electronic and thermal Free Energies= -2294.091373

6.1.15.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full SCRF=(IEFPCM,Solvent =Dichloromethane)

0 1

C 0	-5.363964	-2.290747	-0.434849
C 0	-4.518252	-3.289670	0.071999
C 0	-3.178774	-3.028003	0.327746
C 0	-2.663752	-1.746958	0.069930
C 0	-3.529756	-0.755585	-0.448798
C 0	-4.876851	-1.013785	-0.697604
C 0	-1.335587	-1.234787	0.285575
C 0	-1.196433	0.069642	-0.073783
S 0	-2.685373	0.766226	-0.723163
S 0	-0.000010	-2.186587	0.994338
C 0	1.335564	-1.234810	0.285535
C 0	1.196426	0.069621	-0.073822
N 0	0.000002	0.799059	-0.065272
C 0	2.663735	-1.746982	0.069933
C 0	3.529756	-0.755608	-0.448763
S 0	2.685357	0.766170	-0.723258
C 0	3.178758	-3.028017	0.327798
C 0	4.518250	-3.289675	0.072122
C 0	5.363979	-2.290751	-0.434697
C 0	4.876868	-1.013796	-0.697492
C 0	0.000010	2.204574	0.169051
C 0	0.000105	3.129031	-0.879030
C 0	0.000114	4.498128	-0.668330
C 0	0.000013	4.968979	0.642503
C 0	-0.000089	4.088678	1.723589
C 0	-0.000082	2.729543	1.465523
F 0	-0.000182	1.860657	2.495968
F 0	0.000194	2.658344	-2.143673
H 0	-6.406995	-2.513431	-0.626782
H 0	-4.916860	-4.278390	0.267703
H 0	-2.532244	-3.804710	0.720182
H 0	-5.528543	-0.242903	-1.091555
H 0	2.532218	-3.804722	0.720223
H 0	4.916859	-4.278388	0.267861
H 0	6.407019	-2.513431	-0.626586

H 0 5.528568 -0.242918 -1.091438

H 0 0.000191 5.170064 -1.516524

H 0 0.000014 6.036336 0.824864

H 0 -0.000167 4.441003 2.746782

SCF Done: E(RB3LYP) = -2294.31412733

Sum of electronic and zero-point Energies= -2294.046735

Sum of electronic and thermal Energies= -2294.024627

Sum of electronic and thermal Enthalpies= -2294.023682

Sum of electronic and thermal Free Energies= -2294.100790

6.1.15.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichlor

omethane) pop=full geom=check guess=read

0 1

C 0 -5.369631 -2.193768 -0.454060

C 0 -4.527133 -3.263278 -0.127468

C 0 -3.182497 -3.058257 0.132596

C 0 -2.658994 -1.760560 0.061020

C 0 -3.522584 -0.696801 -0.274213

C 0 -4.874443 -0.899394 -0.529180

C 0 -1.323053 -1.302165 0.305627

C 0 -1.188554 0.039739 0.136786

S 0 -2.675252 0.830805 -0.327290

S 0 -0.000003 -2.348979 0.848255

C 0 1.323043 -1.302173 0.305601

C 0 1.188548 0.039732 0.136761

N 0 0.000001 0.758300 0.242041

C 0 2.658986 -1.760569 0.061004

C 0 3.522579 -0.696810 -0.274220

S 0 2.675237 0.830788 -0.327363

C 0 3.182490 -3.058264 0.132602

C 0 4.527132 -3.263284 -0.127436

C 0 5.369634 -2.193774 -0.454020

C 0 4.874444 -0.899401 -0.529156

C 0 0.000005 2.170141 0.165396

C 0 0.000004 2.841626 -1.058819

C 0 0.000009 4.219964 -1.147324

C 0 0.000013 4.958111 0.030024

C 0 0.000013 4.335793 1.272925

C 0 0.000010 2.955477 1.318468

F 0 0.000010 2.334837 2.499242

F 0 0.000003 2.108486 -2.175380

H 0 -6.420312 -2.375439 -0.652808

H 0 -4.934370 -4.267555 -0.076174

H 0 -2.535542 -3.892464 0.385027

H 0 -5.524492 -0.069544 -0.784698

H 0 2.535533 -3.892470 0.385031

H 0 4.934371 -4.267559 -0.076126

H 0 6.420318 -2.375444 -0.652753

H 0 5.524494 -0.069553 -0.784678

H 0 0.000010 4.694320 -2.121067

H 0 0.000016 6.040904 -0.021942

H 0 0.000016 4.902457 2.196047

SCF Done: E(RPBE1PBE) = -2292.62289617

Sum of electronic and zero-point Energies= -2292.352556

Sum of electronic and thermal Energies= -2292.330616

Sum of electronic and thermal Enthalpies= -2292.329671

Sum of electronic and thermal Free Energies= -2292.405735

6.1.15.4 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent =dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 3.0205 eV 410.48 nm f=0.1223

<TDDFT>HOMO -> LUMO 93.3%

<TDDFT>HOMO -> LUMO+1 2.9%

<TDDFT> Excited State 2: Singlet-A 3.2617 eV 380.12 nm f=0.0087

<TDDFT>HOMO -> LUMO 3.1%

<TDDFT>HOMO -> LUMO+1 96.0%

<TDDFT> Excited State 3: Singlet-A 3.7254 eV 332.81 nm f=0.0014

<TDDFT>HOMO -> LUMO+2 85.1%

<TDDFT>HOMO -> LUMO+5 5.6%

<TDDFT>HOMO -> LUMO+7 5.6%

<TDDFT> Excited State 4: Singlet-A 3.8627 eV 320.98 nm f=0.0301

<TDDFT>HOMO -> LUMO+3 34.8%

<TDDFT>HOMO -> LUMO+4 11.3%

<TDDFT>HOMO -> LUMO+6 50.0%

<TDDFT> Excited State 5: Singlet-A 3.9339 eV 315.17 nm f=0.0094

<TDDFT>HOMO -> LUMO+3 31.5%

<TDDFT>HOMO -> LUMO+4 64.3%

<TDDFT> Excited State 6: Singlet-A 3.9491 eV 313.95 nm f=0.0184

<TDDFT>HOMO -> LUMO+2 11.5%

<TDDFT>HOMO -> LUMO+5 73.9%

<TDDFT>HOMO -> LUMO+7 10.2%

<TDDFT> Excited State 7: Singlet-A 4.0515 eV 306.02 nm f=0.0927

<TDDFT>HOMO -> LUMO+3 29.3%

<TDDFT>HOMO -> LUMO+4 21.2%

<TDDFT>HOMO -> LUMO+6 45.1%

<TDDFT> Excited State 8: Singlet-A 4.1055 eV 301.99 nm f=0.0077

<TDDFT>HOMO -> LUMO+2 2.1%

<TDDFT>HOMO -> LUMO+5 16.7%

<TDDFT>HOMO -> LUMO+7 71.2%

<TDDFT>HOMO -> LUMO+10 5.0%

<TDDFT> Excited State 9: Singlet-A 4.4532 eV 278.42 nm f=0.0087

<TDDFT>HOMO -> LUMO+8 86.0%

<TDDFT>HOMO -> LUMO+9 2.9%

<TDDFT>HOMO -> LUMO+13 5.0%

<TDDFT> Excited State 10: Singlet-A 4.6090 eV 269.00 nm f=0.1067

<TDDFT>HOMO-1 -> LUMO 87.1%

<TDDFT> Excited State 11: Singlet-A 4.6231 eV 268.19 nm f=0.1454

<TDDFT>HOMO-2 -> LUMO 77.9%

<TDDFT>HOMO-2 -> LUMO+1 2.3%

<TDDFT>HOMO-1 -> LUMO+4 2.2%

<TDDFT>HOMO -> LUMO+10 2.4%

<TDDFT>HOMO -> LUMO+12 6.2%

<TDDFT> Excited State 12: Singlet-A 4.7135 eV 263.04 nm f=0.0242

<TDDFT>HOMO-1 -> LUMO+1 92.8%

<TDDFT> Excited State 13: Singlet-A 4.7985 eV 258.38 nm f=0.0001

<TDDFT>HOMO-2 -> LUMO 5.8%

<TDDFT>HOMO-2 -> LUMO+1 83.8%

<TDDFT> Excited State 14: Singlet-A 4.8092 eV 257.81 nm f=0.0062

<TDDFT>HOMO -> LUMO+9 72.4%

<TDDFT>HOMO -> LUMO+11 20.0%

<TDDFT> Excited State 15: Singlet-A 4.8656 eV 254.82 nm f=0.2878

<TDDFT>HOMO-2 -> LUMO 5.4%

<TDDFT>HOMO-2 -> LUMO+1 4.6%

<TDDFT>HOMO-1 -> LUMO+6 2.8%

<TDDFT>HOMO -> LUMO+7 3.3%

<TDDFT>HOMO -> LUMO+10 51.3%

<TDDFT>HOMO -> LUMO+12 23.0%

<TDDFT>HOMO -> LUMO+21 2.3%

<TDDFT> Excited State 16: Singlet-A 5.0285 eV 246.56 nm f=0.0725

<TDDFT>HOMO-1 -> LUMO+6 3.7%

<TDDFT>HOMO -> LUMO+7 5.2%

<TDDFT>HOMO -> LUMO+10 27.5%

<TDDFT>HOMO -> LUMO+12 44.5%

<TDDFT>HOMO -> LUMO+15 10.7%

<TDDFT> Excited State 17: Singlet-A 5.0432 eV 245.85 nm f=0.0136

<TDDFT>HOMO-4 -> LUMO+4 2.3%

<TDDFT>HOMO-3 -> LUMO 39.7%

<TDDFT>HOMO-2 -> LUMO+3 5.1%

<TDDFT>HOMO-2 -> LUMO+4 2.1%

<TDDFT>HOMO-2 -> LUMO+6 2.9%

<TDDFT>HOMO-1 -> LUMO 2.4%

<TDDFT>HOMO-1 -> LUMO+2 24.5%

<TDDFT>HOMO-1 -> LUMO+5 10.3%

<TDDFT> Excited State 18: Singlet-A 5.0825 eV 243.94 nm f=0.0018

<TDDFT>HOMO -> LUMO+8 5.8%

<TDDFT>HOMO -> LUMO+9 16.7%

<TDDFT>HOMO -> LUMO+11 67.6%

<TDDFT>HOMO -> LUMO+13 3.4%

<TDDFT>HOMO -> LUMO+18 2.1%

<TDDFT> Excited State 19: Singlet-A 5.1297 eV 241.70 nm f=0.0473

<TDDFT>HOMO-2 -> LUMO+1 4.8%

<TDDFT>HOMO-2 -> LUMO+2 14.6%

<TDDFT>HOMO-2 -> LUMO+5 3.7%

<TDDFT>HOMO-2 -> LUMO+7 3.0%

<TDDFT>HOMO-1 -> LUMO+3 31.6%

<TDDFT>HOMO-1 -> LUMO+4 8.5%

<TDDFT>HOMO-1 -> LUMO+6 18.5%

<TDDFT>HOMO -> LUMO+15 2.2%

<TDDFT>HOMO -> LUMO+21 2.8%

<TDDFT> Excited State 20: Singlet-A 5.1509 eV 240.70 nm f=0.0081

<TDDFT>HOMO-3 -> LUMO+1 11.1%

<TDDFT>HOMO-2 -> LUMO+3 14.4%

<TDDFT>HOMO-2 -> LUMO+4 6.2%

<TDDFT>HOMO-2 -> LUMO+6 22.6%

<TDDFT>HOMO-1 -> LUMO+1 2.5%

<TDDFT>HOMO-1 -> LUMO+2 19.0%

<TDDFT>HOMO-1 -> LUMO+7 12.9%

<TDDFT> Excited State 21: Singlet-A 5.2202 eV 237.51 nm f=0.0131

<TDDFT>HOMO -> LUMO+8 2.7%

<TDDFT>HOMO -> LUMO+9 3.1%

<TDDFT>HOMO -> LUMO+11 3.5%

<TDDFT>HOMO -> LUMO+13 81.8%

<TDDFT> Excited State 22: Singlet-A 5.2266 eV 237.22 nm f=0.0301

<TDDFT>HOMO-3 -> LUMO 28.5%

<TDDFT>HOMO-3 -> LUMO+1 15.1%

<TDDFT>HOMO-2 -> LUMO+3 2.1%

<TDDFT>HOMO-2 -> LUMO+6 5.2%

<TDDFT>HOMO-1 -> LUMO+2 40.7%

<TDDFT> Excited State 23: Singlet-A 5.2520 eV 236.07 nm f=0.0080

<TDDFT>HOMO-4 -> LUMO 10.5%

<TDDFT>HOMO-3 -> LUMO+3 3.2%

<TDDFT>HOMO-2 -> LUMO+2 7.9%

<TDDFT>HOMO-2 -> LUMO+5 3.7%

<TDDFT>HOMO-1 -> LUMO+4 8.7%

<TDDFT>HOMO-1 -> LUMO+6 18.6%

<TDDFT>HOMO -> LUMO+10 2.3%

<TDDFT>HOMO -> LUMO+15 15.5%

<TDDFT>HOMO -> LUMO+16 8.2%

<TDDFT>HOMO -> LUMO+21 11.4%

<TDDFT> Excited State 24: Singlet-A 5.2921 eV 234.28 nm f=0.0332

<TDDFT>HOMO-4 -> LUMO 2.8%

<TDDFT>HOMO-3 -> LUMO+4 2.8%

<TDDFT>HOMO-2 -> LUMO+2 25.7%

<TDDFT>HOMO-2 -> LUMO+5 7.1%

<TDDFT>HOMO-2 -> LUMO+7 6.4%

<TDDFT>HOMO-1 -> LUMO+3 20.9%

<TDDFT>HOMO-1 -> LUMO+6 13.1%

<TDDFT>HOMO -> LUMO+12 5.4%

<TDDFT>HOMO -> LUMO+15 4.6%

<TDDFT>HOMO -> LUMO+21 2.1%

6.1.15.5 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent= dichloromethane) geom=check guess=read

0 1

C 0	-5.474510	-2.122242	-0.034205
C 0	-4.616949	-3.225140	-0.016108
C 0	-3.240325	-3.065793	-0.002008
C 0	-2.688967	-1.770201	-0.004805
C 0	-3.577794	-0.666334	-0.024141
C 0	-4.951837	-0.826985	-0.038943
C 0	-1.329438	-1.354286	0.005784
C 0	-1.189601	0.053997	-0.012000
S 0	-2.730810	0.883628	-0.021946
S 0	-0.000001	-2.437135	0.098464
C 0	1.329437	-1.354287	0.005784
C 0	1.189601	0.053997	-0.012000
N 0	0.000000	0.718305	-0.012083
C 0	2.688965	-1.770202	-0.004806
C 0	3.577793	-0.666337	-0.024140
S 0	2.730810	0.883626	-0.021943
C 0	3.240323	-3.065795	-0.002009
C 0	4.616947	-3.225142	-0.016110
C 0	5.474508	-2.122245	-0.034204
C 0	4.951836	-0.826988	-0.038942
C 0	0.000001	2.140975	0.004271
C 0	0.000003	2.872363	-1.181157

C 0 0.000003 4.253204 -1.183927
C 0 0.000003 4.918740 0.036183
C 0 0.000001 4.225224 1.240968
C 0 -0.000001 2.845024 1.206125
F 0 -0.000001 2.147611 2.342059
F 0 0.000002 2.202002 -2.333405
H 0 -6.549091 -2.266960 -0.044479
H 0 -5.034541 -4.226846 -0.013736
H 0 -2.590771 -3.935472 0.010400
H 0 -5.611540 0.034119 -0.053114
H 0 2.590768 -3.935474 0.010397
H 0 5.034538 -4.226849 -0.013738
H 0 6.549089 -2.266964 -0.044478
H 0 5.611539 0.034116 -0.053111
H 0 0.000004 4.785919 -2.126899
H 0 0.000004 6.002591 0.048593
H 0 0.000001 4.735982 2.195998

SCF Done: E(RPBE1PBE) = -2292.61099711

Sum of electronic and zero-point Energies= -2292.261424

Sum of electronic and thermal Energies= -2292.238472

Sum of electronic and thermal Enthalpies= -2292.237528

Sum of electronic and thermal Free Energies= -2292.317031

6.1.15.6 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=

dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.2662 eV 547.11 nm f=0.1098

<TDDFT>HOMO -> LUMO 98.3%

<TDDFT> Excited State 2: Singlet-A 2.7426 eV 452.07 nm f=0.0003

<TDDFT>HOMO -> LUMO+1 99.2%

<TDDFT> Excited State 3: Singlet-A 3.3047 eV 375.17 nm f=0.0004

<TDDFT>HOMO -> LUMO+2 98.5%

<TDDFT> Excited State 4: Singlet-A 3.3244 eV 372.95 nm f=0.0002

<TDDFT>HOMO -> LUMO+4 83.3%

<TDDFT>HOMO -> LUMO+6 14.6%

6.1.15.7 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt=verytight Int=UltraFine freq=noraman rb3lyp/6-311++g(d,p) pop=f

ull scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0 -5.351978 -2.308494 -0.443640
C 0 -4.508631 -3.291148 0.098012
C 0 -3.172906 -3.018659 0.362039
C 0 -2.659267 -1.742686 0.076985
C 0 -3.522783 -0.768737 -0.477697
C 0 -4.866509 -1.036975 -0.734450
C 0 -1.335966 -1.217711 0.296244
C 0 -1.195329 0.077000 -0.095245
S 0 -2.678922 0.747893 -0.786772
S 0 0.000000 -2.141475 1.041406
C 0 1.335966 -1.217711 0.296244
C 0 1.195329 0.077000 -0.095245
N 0 0.000000 0.808828 -0.090617
C 0 2.659267 -1.742686 0.076985

C 0	3.522783	-0.768737	-0.477696
S 0	2.678923	0.747893	-0.786772
C 0	3.172906	-3.018659	0.362039
C 0	4.508632	-3.291148	0.098013
C 0	5.351978	-2.308494	-0.443639
C 0	4.866509	-1.036975	-0.734449
C 0	-0.000000	2.210366	0.175900
C 0	0.000001	3.156401	-0.852074
C 0	0.000001	4.520654	-0.615685
C 0	-0.000000	4.964247	0.704697
C 0	-0.000001	4.062566	1.768376
C 0	-0.000001	2.709706	1.482470
F 0	-0.000002	1.818555	2.496642
F 0	0.000002	2.708330	-2.127664
H 0	-6.392366	-2.540003	-0.641150
H 0	-4.906183	-4.276129	0.315296
H 0	-2.530161	-3.784197	0.782251
H 0	-5.517411	-0.279463	-1.155764
H 0	2.530161	-3.784197	0.782251
H 0	4.906183	-4.276129	0.315296
H 0	6.392367	-2.540003	-0.641149
H 0	5.517412	-0.279463	-1.155762
H 0	0.000001	5.209912	-1.450698
H 0	-0.000001	6.028024	0.909146
H 0	-0.000002	4.394214	2.798911

SCF Done: E(RB3LYP) = -2294.33620295

Sum of electronic and zero-point Energies= -2294.068893

Sum of electronic and thermal Energies= -2294.046831

Sum of electronic and thermal Enthalpies= -2294.045887

Sum of electronic and thermal Free Energies= -2294.122185

6.1.15.8 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.479883	-2.112524	-0.000308
C 0	-4.626261	-3.226602	-0.000040
C 0	-3.250561	-3.066800	0.000035
C 0	-2.712375	-1.768148	-0.000131
C 0	-3.588987	-0.660252	-0.000364
C 0	-4.970882	-0.817693	-0.000479
C 0	-1.338089	-1.348906	-0.000012
C 0	-1.196950	0.031088	-0.000105
S 0	-2.723083	0.879880	-0.000419
S 0	-0.000034	-2.467566	0.000067
C 0	1.338044	-1.348934	0.000040
C 0	1.196938	0.031064	0.000092
N 0	0.000000	0.714544	-0.000005
C 0	2.712319	-1.768210	0.000139
C 0	3.588958	-0.660335	0.000320
S 0	2.723090	0.879818	0.000344
C 0	3.250472	-3.066874	-0.000012
C 0	4.626169	-3.226711	0.000029
C 0	5.479819	-2.112654	0.000248
C 0	4.970850	-0.817810	0.000402
C 0	0.000014	2.151989	0.000009
C 0	0.000980	2.869716	-1.199595
C 0	0.001058	4.252877	-1.216770
C 0	0.000112	4.933533	0.000039
C 0	-0.000881	4.252850	1.216833
C 0	-0.000894	2.869691	1.199630
F 0	-0.001741	2.176522	2.346747
F 0	0.001804	2.176573	-2.346728
H 0	-6.552988	-2.260186	-0.000395
H 0	-5.049802	-4.223258	0.000119
H 0	-2.600897	-3.934627	0.000205
H 0	-5.634699	0.038066	-0.000729
H 0	2.600787	-3.934685	-0.000146
H 0	5.049686	-4.223377	-0.000120
H 0	6.552920	-2.260341	0.000310

H 0 5.634688 0.037932 0.000612

H 0 0.001807 4.774045 -2.165167

H 0 0.000147 6.016529 0.000051

H 0 -0.001596 4.773999 2.165242

SCF Done: E(UB3LYP) = -2294.08281247

Sum of electronic and zero-point Energies= -2293.814566

Sum of electronic and thermal Energies= -2293.792615

Sum of electronic and thermal Enthalpies= -2293.791671

Sum of electronic and thermal Free Energies= -2293.867565

6.1.15.9 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpc

m,solvent=dichloromethane) geom=check guess=read

0 1

C 0 5.479887 -2.110878 0.008690

C 0 4.626221 -3.225247 0.006279

C 0 3.249629 -3.066074 0.004075

C 0 2.711460 -1.767647 0.004230

C 0 3.587316 -0.659230 0.006673

C 0 4.970078 -0.816119 0.008941

C 0 1.335817 -1.350102 0.001660

C 0 1.195934 0.029242 0.002064

S 0 2.721087 0.879796 0.006222

S 0 0.000007 -2.468503 0.000017

C 0 -1.335808 -1.350108 -0.001644

C 0 -1.195932 0.029236 -0.002053

N 0 -0.000000 0.712870 0.000006

C 0 -2.711449 -1.767659 -0.004225

C 0 -3.587311 -0.659247 -0.006683

S 0 -2.721089 0.879783 -0.006234

C 0 -3.249612 -3.066089 -0.004070

C 0 -4.626203 -3.225269 -0.006287

C 0 -5.479874 -2.110905 -0.008712

C 0 -4.970071 -0.816143 -0.008965

C 0 -0.000003 2.149491 0.000004

C 0 -0.024874 2.869172 1.197627

C 0 -0.025343 4.251560 1.216008

C 0 -0.000027 4.932608 -0.000001

C 0 0.025305 4.251556 -1.216008

C 0 0.024862 2.869169 -1.197622

F 0 0.048381 2.177103 -2.349063

F 0 -0.048389 2.177110 2.349070

H 0 6.553107 -2.257612 0.010322

H 0 5.049222 -4.222187 0.006087

H 0 2.600094 -3.933429 0.002176

H 0 5.632379 0.040435 0.010816

H 0 -2.600072 -3.933441 -0.002161

H 0 -5.049199 -4.222211 -0.006094

H 0 -6.553093 -2.257644 -0.010354

H 0 -5.632377 0.040408 -0.010852

H 0 -0.044997 4.773681 2.163307

H 0 -0.000039 6.015185 -0.000002

H 0 0.044948 4.773675 -2.163309

SCF Done: E(UB3LYP) = -2294.13424385

Sum of electronic and zero-point Energies= -2293.866144

Sum of electronic and thermal Energies= -2293.844145

Sum of electronic and thermal Enthalpies= -2293.843201

Sum of electronic and thermal Free Energies= -2293.919413

6.1.15.10 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0	-5.475893	-2.120693	-0.008737
C 0	-4.618683	-3.232345	-0.005569
C 0	-3.242519	-3.069283	-0.003150
C 0	-2.710091	-1.768401	-0.003912
C 0	-3.589726	-0.663154	-0.007463
C 0	-4.971740	-0.823263	-0.009807
C 0	-1.336784	-1.346515	-0.001427
C 0	-1.195512	0.032192	-0.002224
S 0	-2.725713	0.879071	-0.008876
S 0	-0.000033	-2.465199	-0.000012
C 0	1.336719	-1.346554	0.001368
C 0	1.195451	0.032161	0.002120
N 0	-0.000037	0.716557	-0.000006
C 0	2.710012	-1.768494	0.003872
C 0	3.589706	-0.663298	0.007414
S 0	2.725714	0.878922	0.008751
C 0	3.242348	-3.069411	0.003178
C 0	4.618498	-3.232583	0.005670
C 0	5.475781	-2.120984	0.008840
C 0	4.971717	-0.823520	0.009824
C 0	-0.000032	2.153836	0.000016
C 0	0.026737	2.875569	-1.197012
C 0	0.028034	4.257186	-1.215952
C 0	0.000415	4.938273	0.000069
C 0	-0.027478	4.257155	1.216058
C 0	-0.026731	2.875530	1.197061
F 0	-0.051814	2.183099	2.351082
F 0	0.051667	2.183175	-2.351055
H 0	-6.548852	-2.271667	-0.010238
H 0	-5.038844	-4.230826	-0.004826
H 0	-2.590550	-3.935613	-0.000359
H 0	-5.638920	0.030346	-0.012134
H 0	2.590274	-3.935660	0.000358
H 0	5.038599	-4.231089	0.004975
H 0	6.548735	-2.272021	0.010407
H 0	5.638984	0.030023	0.012146
H 0	0.049248	4.778829	-2.164184
H 0	0.000612	6.021414	0.000086
H 0	-0.048556	4.778759	2.164315

SCF Done: E(UB3LYP) = -2294.15959933

Sum of electronic and zero-point Energies= -2293.891335

Sum of electronic and thermal Energies= -2293.869500

Sum of electronic and thermal Enthalpies= -2293.868556

Sum of electronic and thermal Free Energies= -2293.943977

6.1.15.11 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc) freq=noraman b3lyp/6-311++g(d,p) pop=full s

crf=(iefpcm,solvent=dichloromethane)

0 1

C 0	5.500256	-2.122927	0.003442
C 0	4.636243	-3.228260	0.003539
C 0	3.257645	-3.058208	0.001999
C 0	2.721341	-1.758937	0.000362
C 0	3.609917	-0.658506	0.000229
C 0	4.992528	-0.826182	0.001745
C 0	1.344786	-1.341175	-0.001441
C 0	1.200291	0.012148	-0.002731

S 0	2.738698	0.872611	-0.002151
S 0	0.000043	-2.520646	0.000781
C 0	-1.344713	-1.341178	-0.001498
C 0	-1.200240	0.012159	-0.003175
N 0	-0.000079	0.731627	-0.004887
C 0	-2.721252	-1.758986	-0.001469
C 0	-3.609873	-0.658592	-0.003212
S 0	-2.738709	0.872554	-0.005313
C 0	-3.257512	-3.058277	0.000193
C 0	-4.636105	-3.228382	0.000367
C 0	-5.500160	-2.123085	-0.001105
C 0	-4.992478	-0.826321	-0.002871
C 0	-0.000121	2.152739	-0.000407
C 0	-0.006312	2.883435	1.192825
C 0	-0.006532	4.267114	1.220197
C 0	-0.000029	4.954973	0.008169
C 0	0.006431	4.274529	-1.208006
C 0	0.006126	2.890661	-1.189139
F 0	-0.012175	2.198871	2.352742
F 0	0.011977	2.213396	-2.353315
H 0	6.572975	-2.275967	0.004648
H 0	5.050437	-4.229874	0.004829
H 0	2.601087	-3.921007	0.002048
H 0	5.658290	0.028761	0.001685
H 0	-2.600922	-3.921051	0.001444
H 0	-5.050262	-4.230013	0.001405
H 0	-6.572875	-2.276166	-0.000571
H 0	-5.658270	0.028597	-0.004116
H 0	-0.011525	4.784574	2.170501
H 0	0.000005	6.037808	0.011468
H 0	0.011466	4.797791	-2.155127

SCF Done: E(RB3LYP) = -2294.31318747

Sum of electronic and zero-point Energies= -2294.046035

Sum of electronic and thermal Energies= -2294.024700

Sum of electronic and thermal Enthalpies= -2294.023755

Sum of electronic and thermal Free Energies= -2294.098086

6.1.16 *anti-anti-N-ortho,ortho'*-fluoromethylphenyl-BBTT 3r

6.1.16.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.479940	-2.139262	-0.166662
C 0	4.616034	-3.230217	0.005400
C 0	3.243101	-3.046846	0.098031
C 0	2.710887	-1.749478	0.014373
C 0	3.598629	-0.663538	-0.163891
C 0	4.976079	-0.844625	-0.251929
C 0	1.341518	-1.319154	0.099860
C 0	1.197479	0.028660	-0.023559
S 0	2.733974	0.868013	-0.248108
S 0	0.000249	-2.463201	0.393780
C 0	-1.341191	-1.319430	0.099774
C 0	-1.197390	0.028419	-0.023647
N 0	-0.000021	0.750577	-0.041621
C 0	-2.710444	-1.749994	0.013934
C 0	-3.598301	-0.664216	-0.164780
S 0	-2.733973	0.867454	-0.248948
C 0	-3.242462	-3.047459	0.097591
C 0	-4.615334	-3.231068	0.004630
C 0	-5.479372	-2.140273	-0.167761
C 0	-4.975711	-0.845570	-0.253093
C 0	-0.000281	2.178037	0.063724
C 0	-0.001749	2.772293	1.327927
C 0	-0.002188	4.145404	1.502069
C 0	-0.001195	4.948029	0.365112
C 0	0.000156	4.379416	-0.906500
C 0	0.000674	2.992295	-1.083648

C 0	0.003003	2.384396	-2.463588
F 0	-0.002785	1.975268	2.413348
H 0	6.549076	-2.302356	-0.235075
H 0	5.026523	-4.231459	0.068574
H 0	2.584043	-3.897367	0.230267
H 0	5.641574	0.000421	-0.385310
H 0	-2.583287	-3.897844	0.230122
H 0	-5.025677	-4.232363	0.067834
H 0	-6.548472	-2.303555	-0.236460
H 0	-5.641322	-0.000657	-0.386740
H 0	-0.003329	4.558539	2.502668
H 0	-0.001606	6.026498	0.473212
H 0	0.000717	5.020983	-1.780176
H 0	-0.007673	3.165816	-3.224513
H 0	0.889552	1.765194	-2.622929
H 0	-0.870190	1.745527	-2.618052

SCF Done: E(RB3LYP) = -2234.36949655

Sum of electronic and zero-point Energies= -2234.066518

Sum of electronic and thermal Energies= -2234.043420

Sum of electronic and thermal Enthalpies= -2234.042476

Sum of electronic and thermal Free Energies= -2234.122518

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.361857	-2.268215	-0.472700
C 0	-4.514114	-3.293915	-0.028888
C 0	-3.175370	-3.046452	0.240475
C 0	-2.661263	-1.752226	0.060358
C 0	-3.529265	-0.733117	-0.397043
C 0	-4.875437	-0.978195	-0.658951
C 0	-1.334208	-1.253717	0.302372
C 0	-1.194738	0.069532	0.013857
S 0	-2.687224	0.802387	-0.583876
S 0	-0.000294	-2.234082	0.974869
C 0	1.333751	-1.254081	0.302117
C 0	1.194551	0.069199	0.013665
N 0	0.000020	0.794921	0.070118
C 0	2.660587	-1.752961	0.059603
C 0	3.528689	-0.734100	-0.398144
S 0	2.686998	0.801643	-0.584672
C 0	3.174415	-3.047326	0.239609
C 0	4.513006	-3.295130	-0.030222
C 0	5.360859	-2.269663	-0.474363
C 0	4.874713	-0.979527	-0.660498
C 0	0.000364	2.222560	0.180454
C 0	-0.001211	3.010480	-0.971992
C 0	-0.000887	4.395139	-0.923704
C 0	0.001141	5.006954	0.325238
C 0	0.002783	4.242174	1.490425
C 0	0.002433	2.846065	1.441499
C 0	0.004497	2.017669	2.699736
F 0	-0.003044	2.402356	-2.175943
H 0	-6.404780	-2.480453	-0.676972
H 0	-4.910734	-4.293688	0.105763
H 0	-2.524788	-3.844360	0.580062
H 0	-5.528005	-0.185675	-1.006571
H 0	2.523716	-3.845048	0.579427
H 0	4.909445	-4.294996	0.104284
H 0	6.403649	-2.482201	-0.679000
H 0	5.527375	-0.187189	-1.008361
H 0	-0.002175	4.961759	-1.846057
H 0	0.001410	6.088865	0.389938
H 0	0.004309	4.735580	2.455663
H 0	0.001578	2.658832	3.582079
H 0	-0.871525	1.365098	2.746296
H 0	0.885461	1.371781	2.747548

SCF Done: E(RB3LYP) = -2234.37059664

Sum of electronic and zero-point Energies= -2234.067657

Sum of electronic and thermal Energies= -2234.044580

Sum of electronic and thermal Free Energies= -2234.122561

Sum of electronic and thermal Enthalpies= -2234.043636

6.1.16.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

No minimum found on the potential hyper surface.

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=di

chloromethane) pop=full geom=check guess=read

0 1

C 0	-5.384126	-2.232951	-0.460468
C 0	-4.535016	-3.284493	-0.082547
C 0	-3.189647	-3.058282	0.177648
C 0	-2.670413	-1.758402	0.054020
C 0	-3.541404	-0.713030	-0.334820
C 0	-4.893267	-0.936349	-0.588058
C 0	-1.335210	-1.279814	0.293016
C 0	-1.194025	0.056624	0.070721
S 0	-2.694538	0.828293	-0.450342
S 0	0.000003	-2.305789	0.894877
C 0	1.335214	-1.279810	0.293020
C 0	1.194027	0.056627	0.070720
N 0	-0.000000	0.779567	0.149081
C 0	2.670417	-1.758396	0.054017
C 0	3.541404	-0.713024	-0.334831
S 0	2.694535	0.828296	-0.450355
C 0	3.189652	-3.058276	0.177648
C 0	4.535021	-3.284488	-0.082544
C 0	5.384129	-2.232944	-0.460471
C 0	4.893268	-0.936343	-0.588068
C 0	-0.000001	2.212414	0.170536
C 0	-0.000010	2.926446	-1.029408
C 0	-0.000013	4.309864	-1.072349
C 0	-0.000005	4.999154	0.136887
C 0	0.000005	4.309983	1.348706
C 0	0.000006	2.912940	1.390344
C 0	0.000016	2.168531	2.699951
F 0	-0.000019	2.236199	-2.194381
H 0	-6.431432	-2.429016	-0.657921
H 0	-4.935415	-4.287612	0.008866
H 0	-2.541511	-3.877020	0.469129
H 0	-5.546731	-0.123650	-0.882825
H 0	2.541514	-3.877008	0.469139
H 0	4.935428	-4.287603	0.008870
H 0	6.431434	-2.429008	-0.657924
H 0	5.546730	-0.123646	-0.882839
H 0	-0.000021	4.819146	-2.027494
H 0	-0.000007	6.082698	0.132447
H 0	0.000011	4.864448	2.279879
H 0	0.000029	2.866812	3.537285
H 0	-0.879347	1.525009	2.790191
H 0	0.879371	1.524996	2.790172

SCF Done: E(RB3LYP) = -2234.37848338

Sum of electronic and zero-point Energies= -2234.075669

Sum of electronic and thermal Energies= -2234.052632

Sum of electronic and thermal Enthalpies= -2234.051688

Sum of electronic and thermal Free Energies= -2234.129989

6.1.16.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

No minimum found on the potential hyper surface.

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=checkpoint guess=read

0 1

C 0	-5.368870	-2.256462	-0.481718
C 0	-4.522480	-3.293618	-0.060098
C 0	-3.181719	-3.056125	0.214127
C 0	-2.664228	-1.758673	0.059824
C 0	-3.532853	-0.728492	-0.372553
C 0	-4.880365	-0.962243	-0.639550
C 0	-1.335199	-1.266211	0.308329
C 0	-1.193181	0.063852	0.051393
S 0	-2.688782	0.812851	-0.519952
S 0	0.000160	-2.263682	0.957334
C 0	1.335451	-1.265968	0.308532
C 0	1.193241	0.064062	0.051568
N 0	-0.000025	0.788098	0.121474
C 0	2.664560	-1.758250	0.060104
C 0	3.533020	-0.728025	-0.372463
S 0	2.688817	0.813213	-0.519775
C 0	3.182096	-3.055723	0.214190
C 0	4.522807	-3.293329	-0.060135
C 0	5.369097	-2.256008	-0.481630
C 0	4.880538	-0.961814	-0.639439
C 0	-0.000162	2.221109	0.180822
C 0	-0.000076	2.965218	-1.000449
C 0	-0.000198	4.348809	-1.011683
C 0	-0.000434	5.008384	0.214214
C 0	-0.000536	4.290043	1.409099
C 0	-0.000399	2.892025	1.418067
C 0	-0.000528	2.119080	2.709966
F 0	0.000180	2.302099	-2.184245
H 0	-6.412466	-2.462271	-0.690239
H 0	-4.921250	-4.295361	0.053877
H 0	-2.538052	-3.865783	0.539829
H 0	-5.531777	-0.160371	-0.968123
H 0	2.538088	-3.865251	0.539557
H 0	4.921708	-4.295013	0.053807
H 0	6.412753	-2.461648	-0.690030
H 0	5.531995	-0.159926	-0.967894
H 0	-0.000110	4.880738	-1.954895
H 0	-0.000540	6.092177	0.235939
H 0	-0.000728	4.820733	2.354396
H 0	-0.000714	2.800940	3.561339
H 0	-0.880360	1.473669	2.787624
H 0	0.879391	1.473821	2.787886

SCF Done: E(RB3LYP) = -2234.40197679

Sum of electronic and zero-point Energies= -2234.099202

Sum of electronic and thermal Energies= -2234.076235

Sum of electronic and thermal Enthalpies= -2234.075291

Sum of electronic and thermal Free Energies= -2234.152726

6.1.16.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

SCF Done: E(UB3LYP) = -2234.15059498

0 1

C 0	-5.479812	-2.102346	-0.037268
C 0	-4.627224	-3.217245	-0.027835
C 0	-3.251508	-3.058628	-0.008101

C 0	-2.712141	-1.760425	0.003087
C 0	-3.587468	-0.651305	-0.006429
C 0	-4.969476	-0.808136	-0.026926
C 0	-1.337794	-1.342501	0.021604
C 0	-1.193852	0.037722	0.026023
S 0	-2.720852	0.888428	0.005108
S 0	-0.000030	-2.462693	0.033537
C 0	1.337761	-1.342534	0.021503
C 0	1.193885	0.037696	0.026015
N 0	0.000002	0.721884	0.046298
C 0	2.712097	-1.760473	0.002990
C 0	3.587410	-0.651333	-0.006456
S 0	2.720837	0.888314	0.005088
C 0	3.251472	-3.058676	-0.008216
C 0	4.627186	-3.217280	-0.027834
C 0	5.479769	-2.102368	-0.037153
C 0	4.969432	-0.808169	-0.026828
C 0	0.000011	2.170216	0.016814
C 0	0.000065	2.801874	-1.228344
C 0	0.000102	4.179447	-1.341293
C 0	0.000015	4.928951	-0.167799
C 0	-0.000039	4.309628	1.080987
C 0	0.000009	2.917869	1.206084
C 0	0.000054	2.248845	2.556710
F 0	0.000086	2.034077	-2.333035
H 0	-6.552940	-2.249018	-0.053541
H 0	-5.051567	-4.213538	-0.037007
H 0	-2.602564	-3.926995	-0.002375
H 0	-5.632439	0.048301	-0.035934
H 0	2.602530	-3.927045	-0.002602
H 0	5.051543	-4.213567	-0.037002
H 0	6.552899	-2.249036	-0.053321
H 0	5.632387	0.048275	-0.035787
H 0	0.000149	4.637492	-2.321964
H 0	0.000009	6.010595	-0.229224
H 0	-0.000171	4.916015	1.978729
H 0	-0.000208	2.994854	3.350846
H 0	-0.882087	1.616681	2.692361
H 0	0.882684	1.617353	2.692327

Sum of electronic and zero-point Energies= -2233.846844

Sum of electronic and thermal Energies= -2233.823979

Sum of electronic and thermal Enthalpies= -2233.823035

Sum of electronic and thermal Free Energies= -2233.900686

6.1.16.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0	-5.487296	-2.086628	-0.062336
C 0	-4.636571	-3.203147	-0.037782
C 0	-3.259747	-3.047907	-0.010229
C 0	-2.719421	-1.750111	-0.007089
C 0	-3.592379	-0.639688	-0.032825
C 0	-4.975182	-0.792439	-0.060489
C 0	-1.344034	-1.335628	0.018079
C 0	-1.194083	0.042854	0.015574
S 0	-2.720179	0.897487	-0.026116
S 0	-0.012178	-2.461069	0.040585
C 0	1.328927	-1.346705	0.026188
C 0	1.190802	0.032848	0.025816
N 0	0.000825	0.722415	0.035882
C 0	2.700762	-1.772985	0.015551
C 0	3.583563	-0.670130	0.004939
S 0	2.724793	0.874805	0.011152
C 0	3.229131	-3.075641	0.011810
C 0	4.604663	-3.243324	-0.002183
C 0	5.465461	-2.134312	-0.012643

C 0	4.965202	-0.835516	-0.009325
C 0	0.010052	2.170785	0.019738
C 0	0.076713	2.811600	-1.220819
C 0	0.099822	4.186111	-1.332504
C 0	0.057357	4.932541	-0.155252
C 0	-0.007788	4.309466	1.087366
C 0	-0.036674	2.915068	1.209570
C 0	-0.145642	2.267013	2.564115
F 0	0.121828	2.044173	-2.333508
H 0	-6.560902	-2.231499	-0.083578
H 0	-5.062418	-4.199254	-0.040397
H 0	-2.613189	-3.918088	0.008409
H 0	-5.636864	0.065265	-0.080375
H 0	2.574127	-3.939681	0.019067
H 0	5.021654	-4.243159	-0.005601
H 0	6.537897	-2.288773	-0.023871
H 0	5.635122	0.015980	-0.018096
H 0	0.152071	4.648214	-2.310302
H 0	0.078077	6.014476	-0.213170
H 0	-0.035829	4.910109	1.989114
H 0	0.359576	2.877468	3.314137
H 0	-1.196397	2.185403	2.862340
H 0	0.284057	1.264770	2.591181

SCF Done: E(UB3LYP) = -2234.22785580

Sum of electronic and zero-point Energies= -2233.924175

Sum of electronic and thermal Energies= -2233.901396

Sum of electronic and thermal Enthalpies= -2233.900452

Sum of electronic and thermal Free Energies= -2233.977881

6.1.17 *anti-anti-N-ortho,ortho'*-fluoromethoxyphenyl-BBTT 3s

6.1.17.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.402466	-2.289231	0.460766
C 0	4.547784	-3.374818	0.219380
C 0	3.197045	-3.178236	-0.032289
C 0	2.676777	-1.873581	-0.039605
C 0	3.553405	-0.792672	0.213197
C 0	4.910410	-0.987597	0.458104
C 0	1.334510	-1.426421	-0.296153
C 0	1.195179	-0.074887	-0.214068
S 0	2.704416	0.749739	0.181859
S 0	-0.000171	-2.518596	-0.762110
C 0	-1.334675	-1.426229	-0.295972
C 0	-1.195133	-0.074677	-0.213768
N 0	-0.000160	0.638926	-0.354368
C 0	-2.676978	-1.873308	-0.039533
C 0	-3.553575	-0.792296	0.213104
S 0	-2.704359	0.750004	0.181855
C 0	-3.197337	-3.177881	-0.032177
C 0	-4.548257	-3.374315	0.219320
C 0	-5.402811	-2.288670	0.460501
C 0	-4.910558	-0.987015	0.457832
C 0	0.000049	2.060118	-0.442519
C 0	0.000134	2.866376	0.718731
C 0	0.000370	4.259308	0.594520
C 0	0.000568	4.841467	-0.671996
C 0	0.000509	4.069191	-1.827798
C 0	0.000202	2.689928	-1.685496
F 0	0.000254	1.921854	-2.788651
O 0	0.000036	2.196088	1.891063
C 0	-0.000066	2.933958	3.110758
H 0	6.454837	-2.462685	0.652951
H 0	4.948801	-4.381913	0.227501
H 0	2.542556	-4.022703	-0.215961
H 0	5.568453	-0.147084	0.646482
H 0	-2.542935	-4.022467	-0.215590

H 0 -4.949245 -4.381414 0.227885

H 0 -6.455286 -2.461914 0.652217

H 0 -5.568564 -0.146451 0.646103

H 0 0.000461 4.889634 1.472504

H 0 0.000798 5.922071 -0.754851

H 0 0.000682 4.507209 -2.817049

H 0 -0.000317 2.187640 3.902281

H 0 0.896043 3.556263 3.195540

H 0 -0.896012 3.556539 3.195219

SCF Done: E(RB3LYP) = -2309.59667376

Sum of electronic and zero-point Energies= -2309.288652

Sum of electronic and thermal Energies= -2309.264737

Sum of electronic and thermal Enthalpies= -2309.263793

Sum of electronic and thermal Free Energies= -2309.344320

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0 -5.386928 -2.368038 -0.374584

C 0 -4.536273 -3.347341 0.159226

C 0 -3.189927 -3.084236 0.370110

C 0 -2.671510 -1.821816 0.039687

C 0 -3.542832 -0.849987 -0.505865

C 0 -4.896203 -1.110186 -0.710104

C 0 -1.335306 -1.312595 0.197914

C 0 -1.194528 -0.028979 -0.229696

S 0 -2.694400 0.647618 -0.874223

S 0 -0.000015 -2.243221 0.932065

C 0 1.335286 -1.312597 0.197931

C 0 1.194521 -0.028971 -0.229669

N 0 0.000008 0.697157 -0.289999

C 0 2.671453 -1.821865 0.039618

C 0 3.542788 -0.850054 -0.506002

S 0 2.694349 0.647580 -0.874285

C 0 3.189871 -3.084262 0.370077

C 0 4.536223 -3.347413 0.159101

C 0 5.386855 -2.368150 -0.374782

C 0 4.896116 -1.110282 -0.710290

C 0 0.000013 2.115477 -0.136158

C 0 0.000182 2.700551 1.150549

C 0 0.000188 4.091754 1.281705

C 0 0.000051 4.893568 0.140393

C 0 -0.000102 4.342092 -1.134734

C 0 -0.000128 2.958545 -1.243851

F 0 -0.000253 2.405361 -2.472199

O 0 0.000266 1.826266 2.179152

C 0 0.000265 2.326821 3.513923

H 0 -6.435672 -2.591723 -0.531711

H 0 -4.936459 -4.322991 0.410245

H 0 -2.537291 -3.846812 0.779800

H 0 -5.551279 -0.354001 -1.127087

H 0 2.537270 -3.846799 0.779895

H 0 4.936407 -4.323033 0.410237

H 0 6.435559 -2.591867 -0.532069

H 0 5.551204 -0.354104 -1.127272

H 0 0.000293 4.553096 2.259216

H 0 0.000060 5.971408 0.253468

H 0 -0.000205 4.950761 -2.029113

H 0 0.000240 1.447017 4.153829

H 0 0.896209 2.923346 3.711623

H 0 -0.895652 2.923390 3.711610

SCF Done: E(RB3LYP) = -2309.59730724

Sum of electronic and zero-point Energies= -2309.289199

Sum of electronic and thermal Energies= -2309.265343

Sum of electronic and thermal Enthalpies= -2309.264399

Sum of electronic and thermal Free Energies= -2309.344678

6.1.17.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt=verytight Int=UltraFine freq=noraman rb3lyp/6-311++g(d,p) pop=f

ull scrf=(iefpcm,solvent=dichloromethane) Geom=check guess=read

0 1

C 0	5.410825	-2.288299	0.452327
C 0	4.557538	-3.375516	0.208950
C 0	3.203878	-3.181172	-0.034092
C 0	2.680827	-1.876863	-0.030649
C 0	3.556786	-0.794465	0.221835
C 0	4.916084	-0.986736	0.459407
C 0	1.336298	-1.429925	-0.277736
C 0	1.194642	-0.077927	-0.192204
S 0	2.704668	0.747576	0.198249
S 0	0.000001	-2.524778	-0.739101
C 0	-1.336297	-1.429926	-0.277736
C 0	-1.194641	-0.077927	-0.192204
N 0	-0.000000	0.635795	-0.323947
C 0	-2.680826	-1.876864	-0.030649
C 0	-3.556786	-0.794466	0.221835
S 0	-2.704668	0.747575	0.198249
C 0	-3.203877	-3.181173	-0.034092
C 0	-4.557537	-3.375518	0.208949
C 0	-5.410824	-2.288301	0.452327
C 0	-4.916083	-0.986738	0.459407
C 0	-0.000000	2.057139	-0.440804
C 0	-0.000001	2.888957	0.702454
C 0	-0.000001	4.279003	0.542073
C 0	-0.000001	4.830122	-0.737647
C 0	-0.000001	4.030743	-1.877302
C 0	-0.000000	2.658020	-1.698200
F 0	0.000000	1.854704	-2.784236
O 0	-0.000001	2.249440	1.891223
C 0	-0.000001	3.025034	3.096514
H 0	6.464545	-2.459939	0.638082
H 0	4.961108	-4.381542	0.209273
H 0	2.552788	-4.027654	-0.220987
H 0	5.572961	-0.145994	0.649335
H 0	-2.552787	-4.027655	-0.220987
H 0	-4.961107	-4.381543	0.209273
H 0	-6.464544	-2.459942	0.638082
H 0	-5.572961	-0.145996	0.649334
H 0	-0.000002	4.931010	1.403697
H 0	-0.000001	5.908145	-0.846023
H 0	-0.000001	4.447806	-2.875546
H 0	-0.000001	2.300260	3.907136
H 0	0.895880	3.647729	3.160191
H 0	-0.895883	3.647729	3.160190

SCF Done: E(RB3LYP) = -2309.60707001

Sum of electronic and zero-point Energies= -2309.299163

Sum of electronic and thermal Energies= -2309.275262

Sum of electronic and thermal Enthalpies= -2309.274318

Sum of electronic and thermal Free Energies= -2309.354407

Conformer II:

#p opt=verytight Int=UltraFine freq=noraman rb3lyp/6-311++g(d,p) pop=f

ull scrf=(iefpcm,solvent=dichloromethane) Geom=check guess=read

0 1

C 0	-5.405615	-2.353616	-0.353258
C 0	-4.553049	-3.362986	0.119636
C 0	-3.200955	-3.118670	0.322800
C 0	-2.679231	-1.843999	0.044922
C 0	-3.553708	-0.841654	-0.437945
C 0	-4.912008	-1.082424	-0.634368
C 0	-1.336898	-1.351112	0.203525

C 0	-1.194673	-0.048098	-0.164131
S 0	-2.702100	0.671407	-0.738662
S 0	0.000000	-2.326443	0.879961
C 0	1.336898	-1.351112	0.203525
C 0	1.194672	-0.048098	-0.164131
N 0	0.000000	0.675220	-0.205700
C 0	2.679231	-1.843999	0.044922
C 0	3.553708	-0.841654	-0.437945
S 0	2.702100	0.671407	-0.738662
C 0	3.200955	-3.118670	0.322800
C 0	4.553049	-3.362986	0.119636
C 0	5.405615	-2.353616	-0.353258
C 0	4.912008	-1.082424	-0.634368
C 0	0.000000	2.101082	-0.154721
C 0	0.000000	2.777607	1.086592
C 0	0.000000	4.175613	1.110920
C 0	0.000000	4.889469	-0.086798
C 0	-0.000000	4.245875	-1.320172
C 0	-0.000000	2.860303	-1.322630
F 0	-0.000000	2.208559	-2.507987
O 0	0.000000	1.985194	2.178758
C 0	0.000000	2.594953	3.475935
H 0	-6.458072	-2.562899	-0.504408
H 0	-4.955889	-4.346947	0.330503
H 0	-2.549943	-3.904728	0.688439
H 0	-5.568638	-0.302823	-1.002271
H 0	2.549943	-3.904728	0.688439
H 0	4.955889	-4.346947	0.330502
H 0	6.458072	-2.562899	-0.504408
H 0	5.568638	-0.302823	-1.002271
H 0	0.000000	4.709770	2.050332
H 0	0.000000	5.972430	-0.053833
H 0	-0.000000	4.789169	-2.255661
H 0	-0.000000	1.769635	4.183913
H 0	0.895821	3.204012	3.620679
H 0	-0.895820	3.204013	3.620679

SCF Done: E(RB3LYP) = -2309.60741440

Sum of electronic and zero-point Energies= -2309.299410

Sum of electronic and thermal Energies= -2309.275542

Sum of electronic and thermal Enthalpies= -2309.274598

Sum of electronic and thermal Free Energies= -2309.354792

6.1.17.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt=verytight Int=UltraFine freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0	5.421862	-2.278689	0.434753
C 0	4.568329	-3.369387	0.208136
C 0	3.211835	-3.180565	-0.024201
C 0	2.685614	-1.877054	-0.026619
C 0	3.562995	-0.791630	0.207646
C 0	4.924727	-0.977930	0.435310
C 0	1.337957	-1.432734	-0.264423
C 0	1.194549	-0.080212	-0.189535
S 0	2.708325	0.749690	0.178938
S 0	-0.000001	-2.533904	-0.708413
C 0	-1.337958	-1.432734	-0.264422
C 0	-1.194550	-0.080211	-0.189535
N 0	0.000000	0.632919	-0.321041
C 0	-2.685615	-1.877053	-0.026618
C 0	-3.562996	-0.791629	0.207647
S 0	-2.708325	0.749691	0.178938
C 0	-3.211836	-3.180564	-0.024200
C 0	-4.568330	-3.369386	0.208137
C 0	-5.421863	-2.278687	0.434754

C 0	-4.924727	-0.977929	0.435310
C 0	0.000000	2.055225	-0.435467
C 0	0.000001	2.883981	0.710510
C 0	0.000001	4.274735	0.552485
C 0	0.000001	4.827876	-0.726341
C 0	0.000000	4.031241	-1.868829
C 0	0.000000	2.659192	-1.691302
F 0	-0.000000	1.855002	-2.779771
O 0	0.000001	2.242148	1.896033
C 0	0.000002	3.015266	3.104962
H 0	6.477747	-2.446877	0.612869
H 0	4.973936	-4.374869	0.213018
H 0	2.563991	-4.032539	-0.198785
H 0	5.581672	-0.134038	0.612830
H 0	-2.563992	-4.032539	-0.198784
H 0	-4.973937	-4.374868	0.213019
H 0	-6.477747	-2.446875	0.612869
H 0	-5.581672	-0.134036	0.612830
H 0	0.000001	4.923449	1.417316
H 0	0.000001	5.906420	-0.832965
H 0	-0.000000	4.450578	-2.866685
H 0	0.000002	2.286023	3.913082
H 0	0.897033	3.636592	3.172988
H 0	-0.897029	3.636593	3.172989

SCF Done: E(RB3LYP) = -2309.62956682

Sum of electronic and zero-point Energies= -2309.321684

Sum of electronic and thermal Energies= -2309.297892

Sum of electronic and thermal Enthalpies= -2309.296948

Sum of electronic and thermal Free Energies= -2309.376181

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full

0 1

C 0	-5.426889	-2.323454	-0.327277
C 0	-4.577012	-3.338567	0.138311
C 0	-3.222006	-3.103203	0.333132
C 0	-2.694288	-1.831027	0.053870
C 0	-3.566593	-0.823603	-0.422296
C 0	-4.927808	-1.054778	-0.610432
C 0	-1.348357	-1.344519	0.206031
C 0	-1.199566	-0.042013	-0.160915
S 0	-2.707248	0.685300	-0.727842
S 0	-0.013257	-2.325380	0.880010
C 0	1.326914	-1.358592	0.195777
C 0	1.188999	-0.054628	-0.169970
N 0	-0.001506	0.675315	-0.204182
C 0	2.666240	-1.859302	0.032291
C 0	3.545252	-0.861197	-0.451200
S 0	2.699180	0.656844	-0.750153
C 0	3.182428	-3.137005	0.307563
C 0	4.533117	-3.387134	0.101586
C 0	5.389957	-2.381227	-0.371123
C 0	4.902297	-1.107205	-0.650371
C 0	0.006521	2.102028	-0.153696
C 0	0.035415	2.779094	1.087610
C 0	0.038819	4.177570	1.109115
C 0	0.016474	4.889396	-0.089636
C 0	-0.008964	4.245048	-1.322933
C 0	-0.013116	2.860362	-1.322029
F 0	-0.036315	2.204424	-2.507579
O 0	0.058490	1.987312	2.178317
C 0	0.130676	2.596027	3.476237
H 0	-6.481879	-2.526486	-0.471404
H 0	-4.984279	-4.320718	0.350706
H 0	-2.575526	-3.895615	0.693780
H 0	-5.583038	-0.270952	-0.973196
H 0	2.530298	-3.922201	0.673770
H 0	4.931366	-4.373687	0.310724
H 0	6.441474	-2.595625	-0.523960
H 0	5.563096	-0.330647	-1.018564

H 0 0.057520 4.713721 2.047692
H 0 0.019281 5.972880 -0.058013
H 0 -0.025176 4.787196 -2.259516
H 0 0.147152 1.769007 4.183642
H 0 1.045162 3.185931 3.579997
H 0 -0.745856 3.221021 3.665176

SCF Done: E(RB3LYP) = -2309.63000118

Sum of electronic and zero-point Energies= -2309.322050

Sum of electronic and thermal Energies= -2309.298246

Sum of electronic and thermal Enthalpies= -2309.297302

Sum of electronic and thermal Free Energies= -2309.376708

6.1.17.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0 5.479918 -2.210594 0.023704
C 0 4.627610 -3.321004 0.125558
C 0 3.251661 -3.162378 0.120589
C 0 2.711763 -1.869032 0.012210
C 0 3.586734 -0.764154 -0.089141
C 0 4.968915 -0.921197 -0.084917
C 0 1.337189 -1.452074 -0.014905
C 0 1.193561 -0.077178 -0.132879
S 0 2.719032 0.769540 -0.217058
S 0 -0.000647 -2.566728 0.087656
C 0 -1.338046 -1.451583 -0.015178
C 0 -1.193867 -0.076773 -0.133341
N 0 -0.000042 0.604195 -0.189922
C 0 -2.712788 -1.867966 0.012674
C 0 -3.587357 -0.762753 -0.088421
S 0 -2.719095 0.770645 -0.216575
C 0 -3.253160 -3.161043 0.121894
C 0 -4.629173 -3.319076 0.127959
C 0 -5.481076 -2.208358 0.026083
C 0 -4.969598 -0.919229 -0.083474
C 0 0.000190 2.040551 -0.291847
C 0 0.001860 2.831883 0.876135
C 0 0.002028 4.222970 0.740971
C 0 0.000673 4.796911 -0.529386
C 0 -0.000893 4.025472 -1.688763
C 0 -0.001114 2.650057 -1.545633
F 0 -0.002555 1.857091 -2.629773
O 0 0.003157 2.152374 2.038387
C 0 0.004582 2.884907 3.273682
H 0 6.553197 -2.357087 0.028514
H 0 5.052204 -4.313829 0.208174
H 0 2.602782 -4.027281 0.198855
H 0 5.631625 -0.068215 -0.164596
H 0 -2.604593 -4.026209 0.199850
H 0 -5.054135 -4.311672 0.211441
H 0 -6.554413 -2.354407 0.031495
H 0 -5.631994 -0.066034 -0.163476
H 0 0.003242 4.858591 1.614920
H 0 0.000820 5.876861 -0.615474
H 0 -0.001950 4.464917 -2.677199
H 0 0.005766 2.130483 4.056398
H 0 0.901573 3.503282 3.356649
H 0 -0.892394 3.502971 3.358939

SCF Done: E(UB3LYP) = -2309.38149613

Sum of electronic and zero-point Energies= -2309.072621

Sum of electronic and thermal Energies= -2309.048876

Sum of electronic and thermal Enthalpies= -2309.047932

Sum of electronic and thermal Free Energies= -2309.127595

6.1.17.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0	5.478748	-2.211451	0.059480
C 0	4.624682	-3.323317	0.130228
C 0	3.248093	-3.165443	0.105066
C 0	2.711169	-1.869932	0.007233
C 0	3.587591	-0.764134	-0.065666
C 0	4.970073	-0.919711	-0.039494
C 0	1.336611	-1.453029	-0.033060
C 0	1.192405	-0.078147	-0.135157
S 0	2.720027	0.771655	-0.185275
S 0	-0.000213	-2.570744	0.036228
C 0	-1.336894	-1.452863	-0.033363
C 0	-1.192471	-0.078025	-0.135562
N 0	0.000008	0.603408	-0.195944
C 0	-2.711515	-1.869559	0.007298
C 0	-3.587810	-0.763677	-0.065661
S 0	-2.720020	0.772057	-0.185666
C 0	-3.248601	-3.164963	0.105682
C 0	-4.625206	-3.322630	0.131327
C 0	-5.479140	-2.210680	0.060350
C 0	-4.970303	-0.919047	-0.039244
C 0	0.000101	2.039578	-0.303471
C 0	0.000615	2.836035	0.861530
C 0	0.000756	4.227326	0.719526
C 0	0.000419	4.794867	-0.552655
C 0	-0.000100	4.018496	-1.710533
C 0	-0.000256	2.646074	-1.558511
F 0	-0.000730	1.844752	-2.645341
O 0	0.000744	2.164855	2.025999
C 0	0.001158	2.908812	3.259247
H 0	6.552130	-2.358001	0.081237
H 0	5.047514	-4.317910	0.205397
H 0	2.599055	-4.032183	0.159598
H 0	5.634573	-0.065710	-0.093824
H 0	-2.599681	-4.031788	0.160269
H 0	-5.048152	-4.317132	0.207087
H 0	-6.552537	-2.357081	0.082362
H 0	-5.634693	-0.064984	-0.093900
H 0	0.001049	4.864839	1.592510
H 0	0.000515	5.874574	-0.643751
H 0	-0.000379	4.454873	-2.700822
H 0	0.001293	2.157414	4.046324
H 0	0.898914	3.526278	3.338345
H 0	-0.896499	3.526353	3.338724

SCF Done: E(UB3LYP) = -2309.45743929

Sum of electronic and zero-point Energies= -2309.148706

Sum of electronic and thermal Energies= -2309.125065

Sum of electronic and thermal Enthalpies= -2309.124121

Sum of electronic and thermal Free Energies= -2309.203167

6.1.18 *anti-anti-N-ortho,ortho'*-dimethylphenyl-BBTT 3i

6.1.18.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311G**) + energies of *N*-inversion relaxed geometry PES scan

#p opt freq=noraman rb3lyp/6-311g** scrf=(iefpcm,solvent=dichlorometha

ne) pop=full guess=read geom=check

0 1

C 0	-5.480265	-2.121848	-0.198220
C 0	-4.619792	-3.220001	-0.054706
C 0	-3.246983	-3.043337	0.051912
C 0	-2.711305	-1.744419	0.011789
C 0	-3.596428	-0.650696	-0.135512
C 0	-4.973740	-0.826027	-0.238756
C 0	-1.343238	-1.318241	0.115653
C 0	-1.193973	0.033732	0.034444
S 0	-2.728191	0.882653	-0.168638
S 0	-0.000002	-2.469155	0.397646
C 0	1.343238	-1.318240	0.115678
C 0	1.193974	0.033733	0.034469
N 0	0.000000	0.752568	0.062260
C 0	2.711303	-1.744421	0.011804
C 0	3.596428	-0.650699	-0.135502
S 0	2.728198	0.882655	-0.168558
C 0	3.246977	-3.043342	0.051901
C 0	4.619783	-3.220010	-0.054744
C 0	5.480257	-2.121858	-0.198263
C 0	4.973737	-0.826036	-0.238778
C 0	0.000000	2.196733	0.070082
C 0	0.000005	2.886935	-1.155302
C 0	0.000005	4.284202	-1.113441
C 0	0.000003	4.962437	0.101172
C 0	-0.000001	4.257451	1.301015
C 0	-0.000003	2.860587	1.309238
C 0	0.000000	2.092330	2.606762
C 0	0.000005	2.157192	-2.476136
H 0	-6.549146	-2.280114	-0.278663
H 0	-5.032776	-4.221701	-0.025826
H 0	-2.591684	-3.899967	0.161892
H 0	-5.636366	0.024117	-0.350316
H 0	2.591676	-3.899971	0.161879
H 0	5.032764	-4.221712	-0.025883
H 0	6.549136	-2.280127	-0.278722
H 0	5.636364	0.024108	-0.350331
H 0	0.000008	4.840315	-2.044161
H 0	0.000004	6.046564	0.112911
H 0	-0.000001	4.792481	2.244019
H 0	0.879161	1.447438	2.689450
H 0	0.000001	2.776003	3.456331
H 0	-0.879159	1.447437	2.689452
H 0	0.000008	2.867896	-3.303233
H 0	0.879602	1.516917	-2.580594
H 0	-0.879595	1.516923	-2.580596

SCF Done: E(RB3LYP) = -2174.42480481

Sum of electronic and zero-point Energies= -2174.086279

Sum of electronic and thermal Energies= -2174.062331

Sum of electronic and thermal Enthalpies= -2174.061387

Sum of electronic and thermal Free Energies= -2174.141631

Relaxed PES Scan via:

#p rb3lyp/6-311G** opt=ModRedundant nosymm scrf=(iefpcm,solvent=dichloromethane)

with D 8 13 21 22 S 180 1.0

HF=-2174.4248039,-2174.4248014,-2174.4247

937,-2174.4247806,-2174.424762,-2174.4247323,-2174.4247079,-2174.42466

65,-2174.4246301,-2174.4245761,-2174.4245266,-2174.4244643,-2174.42438

89,-2174.4243177,-2174.4242265,-2174.4241396,-2174.4240312,-2174.42392

7,-2174.4238067,-2174.4236765,-2174.4235361,-2174.423385,-2174.4232229

,-2174.4230497,-2174.4228652,-2174.4226692,-2174.4224613,-2174.4222411

,-2174.4220082,-2174.4217619,-2174.4215018,-2174.4212274,-2174.4209383

,-2174.420634,-2174.4203143,-2174.419979,-2174.4196277,-2174.4192605,-

2174.418877,-2174.4184772,-2174.41867,-2174.4182828,-2174.4178942,-217

4.4174852,-2174.4170618,-2174.4166241,-2174.4161722,-2174.4157061,-217

4.4152261,-2174.4147323,-2174.4142249,-2174.4137042,-2174.4131702,-217

4.4126229,-2174.4120621,-2174.4114879,-2174.4109001,-2174.4102989,-217

4.4096847,-2174.4090582,-2174.40842,-2174.4077711,-2174.4071122,-2174.

4064443,-2174.4057685,-2174.405086,-2174.4043976,-2174.4037045,-2174.4

030081,-2174.4023097,-2174.4016117,-2174.4009158,-2174.4002229,-2174.3

995355,-2174.3988556,-2174.3981853,-2174.3975247,-2174.3968731,-2174.3

962332,-2174.3956109,-2174.395016,-2174.3944564,-2174.3939272,-2174.39

34219,-2174.392938,-2174.392477,-2174.3920403,-2174.3916264,-2174.3912

311,-2174.3908507,-2174.390486,-2174.3901402,-2174.3898146,-2174.38950

83,-2174.3892194,-2174.3889466,-2174.3886892,-2174.3884457,-2174.38821

49,-2174.3879977,-2174.3877962,-2174.3876104,-2174.3874405,-2174.38728

55,-2174.387148,-2174.3870351,-2174.386945,-2174.3868764,-2174.3868225

,-2174.3867781,-2174.3867416,-2174.3867138,-2174.3866934,-2174.3866783

,-2174.3866674,-2174.3866608,-2174.3866591,-2174.3866632,-2174.3866722

,-2174.3866863,-2174.3867097,-2174.3867476,-2174.4093738,-2174.4100428

,-2174.4106946,-2174.4113291,-2174.4119465,-2174.4125469,-2174.4131302

,-2174.4136967,-2174.4142465,-2174.4147796,-2174.4152963,-2174.4157966

,-2174.4162805,-2174.4167484,-2174.4172001,-2174.4176359,-2174.4180559

,-2174.4184603,-2174.4188493,-2174.4192232,-2174.4195822,-2174.4199266

,-2174.4202565,-2174.4205722,-2174.4208739,-2174.4211618,-2174.4214362

,-2174.4216974,-2174.4219456,-2174.4221811,-2174.4224041,-2174.4226149

,-2174.4228136,-2174.4230007,-2174.4231762,-2174.4233405,-2174.4234939

,-2174.4236368,-2174.4237693,-2174.4238919,-2174.4240048,-2174.4241084

,-2174.4242032,-2174.4242896,-2174.4243681,-2174.4244421,-2174.4245075

,-2174.4245653,-2174.4246159,-2174.4246598,-2174.4246974,-2174.4247296

,-2174.4247567,-2174.4247784,-2174.4247944,-2174.4248044,-2174.4248087

,-2174.4248072,-2174.4248001

6.1.18.2 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0 -5.468830 -2.138534 -0.235249

C 0 -4.606617 -3.229494 -0.054426

C 0	-3.236673	-3.044461	0.073060
C 0	-2.705299	-1.745032	0.015842
C 0	-3.591275	-0.658644	-0.171376
C 0	-4.965746	-0.841984	-0.294426
C 0	-1.340418	-1.312058	0.138353
C 0	-1.194374	0.038393	0.029078
S 0	-2.728794	0.876136	-0.222887
S 0	0.000081	-2.446547	0.476664
C 0	1.340468	-1.312011	0.138087
C 0	1.194409	0.038448	0.028896
N 0	-0.000012	0.759822	0.055554
C 0	2.705383	-1.744931	0.015757
C 0	3.591347	-0.658493	-0.171222
S 0	2.728806	0.876251	-0.222794
C 0	3.236803	-3.044347	0.072905
C 0	4.606768	-3.229311	-0.054422
C 0	5.468966	-2.138301	-0.235035
C 0	4.965841	-0.841768	-0.294150
C 0	-0.000047	2.202564	0.084829
C 0	0.000082	2.912516	-1.128943
C 0	0.000082	4.309115	-1.065670
C 0	-0.000168	4.969173	0.158703
C 0	-0.000385	4.245293	1.347147
C 0	-0.000287	2.848590	1.333208
C 0	-0.000295	2.059539	2.618002
C 0	0.000097	2.203651	-2.461215
H 0	-6.535610	-2.303089	-0.331379
H 0	-5.016113	-4.232303	-0.012679
H 0	-2.578456	-3.894883	0.210139
H 0	-5.629658	0.003082	-0.435768
H 0	2.578601	-3.894809	0.209813
H 0	5.016300	-4.232108	-0.012720
H 0	6.535762	-2.302814	-0.331054
H 0	5.629730	0.003339	-0.435360
H 0	0.000280	4.879607	-1.987969
H 0	-0.000201	6.053242	0.187088
H 0	-0.000636	4.765770	2.298622
H 0	0.879065	1.413514	2.689733
H 0	-0.000451	2.729278	3.479282
H 0	-0.879422	1.413197	2.689634
H 0	-0.000029	2.927697	-3.277355
H 0	0.880348	1.565960	-2.575574
H 0	-0.879913	1.565647	-2.575432

SCF Done: E(RB3LYP) = -2174.43238922

Sum of electronic and zero-point Energies= -2174.093791

Sum of electronic and thermal Energies= -2174.069890

Sum of electronic and thermal Enthalpies= -2174.068946

Sum of electronic and thermal Free Energies= -2174.148934

6.1.18.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0	-5.485325	-2.119440	-0.177291
C 0	-4.623886	-3.219344	-0.048430
C 0	-3.249093	-3.043957	0.047436
C 0	-2.713036	-1.744642	0.011436
C 0	-3.599056	-0.649256	-0.120886
C 0	-4.977709	-0.822777	-0.213935
C 0	-1.343025	-1.320302	0.104023
C 0	-1.193510	0.032973	0.031380
S 0	-2.730049	0.883043	-0.149602
S 0	-0.000015	-2.477875	0.351536
C 0	1.343012	-1.320308	0.104109
C 0	1.193511	0.032969	0.031471
N 0	0.000001	0.752624	0.056698
C 0	2.713019	-1.744661	0.011522

C 0	3.599050	-0.649282	-0.120800
S 0	2.730070	0.883037	-0.149333
C 0	3.249059	-3.043984	0.047455
C 0	4.623845	-3.219387	-0.048464
C 0	5.485296	-2.119491	-0.177324
C 0	4.977695	-0.822820	-0.213919
C 0	0.000004	2.197287	0.062660
C 0	0.000115	2.885312	-1.164026
C 0	0.000123	4.283159	-1.124987
C 0	0.000021	4.964018	0.088911
C 0	-0.000085	4.260668	1.290431
C 0	-0.000093	2.863198	1.300960
C 0	-0.000199	2.098857	2.600858
C 0	0.000238	2.153659	-2.483677
H 0	-6.555051	-2.276503	-0.249674
H 0	-5.037152	-4.221099	-0.022302
H 0	-2.594131	-3.902329	0.146294
H 0	-5.640924	0.028455	-0.314189
H 0	2.594087	-3.902352	0.146293
H 0	5.037099	-4.221148	-0.022383
H 0	6.555017	-2.276566	-0.249735
H 0	5.640921	0.028407	-0.314145
H 0	0.000211	4.837863	-2.056691
H 0	0.000030	6.048301	0.098758
H 0	-0.000161	4.797597	2.232499
H 0	0.879263	1.454553	2.685911
H 0	-0.000261	2.785623	3.448137
H 0	-0.879678	1.454561	2.685776
H 0	0.000299	2.863509	-3.311715
H 0	0.880136	1.513403	-2.587335
H 0	-0.879627	1.513382	-2.587482

SCF Done: E(RB3LYP) = -2174.43933315

Sum of electronic and zero-point Energies= -2174.101021

Sum of electronic and thermal Energies= -2174.077064

Sum of electronic and thermal Enthalpies= -2174.076119

Sum of electronic and thermal Free Energies= -2174.156320

6.1.18.4 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichlor

omethane) pop=full geom=check guess=read

0 1

C 0	-5.459858	-2.088146	-0.201472
C 0	-4.607809	-3.193149	-0.090490
C 0	-3.236870	-3.029148	0.022096
C 0	-2.696530	-1.735489	0.020764
C 0	-3.571835	-0.634676	-0.092767
C 0	-4.947670	-0.797339	-0.203297
C 0	-1.330327	-1.321464	0.131244
C 0	-1.184809	0.031379	0.089214
S 0	-2.702491	0.881152	-0.080842
S 0	-0.000029	-2.472907	0.364537
C 0	1.330292	-1.321484	0.131271
C 0	1.184795	0.031360	0.089240
N 0	-0.000002	0.747202	0.144755
C 0	2.696492	-1.735528	0.020825
C 0	3.571813	-0.634726	-0.092702
S 0	2.702484	0.881111	-0.080852
C 0	3.236816	-3.029193	0.022191
C 0	4.607756	-3.193211	-0.090354
C 0	5.459822	-2.088220	-0.201330
C 0	4.947648	-0.797407	-0.203192
C 0	0.000017	2.178624	0.063355
C 0	0.000155	2.788538	-1.199276
C 0	0.000171	4.182204	-1.243596
C 0	0.000056	4.930845	-0.073696
C 0	-0.000072	4.302539	1.165213

C 0	-0.000089	2.911676	1.257397
C 0	-0.000241	2.217923	2.586616
C 0	0.000326	1.973894	-2.458726
H 0	-6.530624	-2.238016	-0.287661
H 0	-5.027667	-4.193598	-0.091701
H 0	-2.584798	-3.892913	0.106911
H 0	-5.605171	0.061085	-0.290144
H 0	2.584732	-3.892949	0.107004
H 0	5.027603	-4.193665	-0.091537
H 0	6.530588	-2.238104	-0.287489
H 0	5.605160	0.061008	-0.290043
H 0	0.000285	4.680768	-2.207931
H 0	0.000072	6.014878	-0.128086
H 0	-0.000162	4.894421	2.075197
H 0	0.879563	1.577201	2.700466
H 0	-0.000322	2.945163	3.400085
H 0	-0.880082	1.577218	2.700273
H 0	0.000438	2.624720	-3.334416
H 0	0.881055	1.326938	-2.515321
H 0	-0.880377	1.326925	-2.515553

SCF Done: E(RPBE1PBE) = -2172.83021417

Sum of electronic and zero-point Energies= -2172.488935

Sum of electronic and thermal Energies= -2172.465097

Sum of electronic and thermal Enthalpies= -2172.464153

Sum of electronic and thermal Free Energies= -2172.544270

6.1.18.5 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent =dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.7935 eV 443.83 nm f=0.1620

<TDDFT>HOMO -> LUMO 97.3%

<TDDFT> Excited State 2: Singlet-A 3.2920 eV 376.62 nm f=0.0013

<TDDFT>HOMO -> LUMO+1 96.8%

<TDDFT> Excited State 3: Singlet-A 3.6630 eV 338.48 nm f=0.0055

<TDDFT>HOMO -> LUMO+2 83.0%

<TDDFT>HOMO -> LUMO+5 3.6%

<TDDFT>HOMO -> LUMO+7 8.2%

<TDDFT> Excited State 4: Singlet-A 3.7222 eV 333.10 nm f=0.0120

<TDDFT>HOMO -> LUMO+3 83.4%

<TDDFT>HOMO -> LUMO+4 14.2%

<TDDFT> Excited State 5: Singlet-A 3.7841 eV 327.64 nm f=0.0049

<TDDFT>HOMO -> LUMO+4 6.5%

<TDDFT>HOMO -> LUMO+6 81.9%

<TDDFT>HOMO -> LUMO+8 6.6%

<TDDFT> Excited State 6: Singlet-A 3.8470 eV 322.29 nm f=0.0092

<TDDFT>HOMO -> LUMO+2 14.8%

<TDDFT>HOMO -> LUMO+5 14.1%

<TDDFT>HOMO -> LUMO+7 59.1%

<TDDFT>HOMO -> LUMO+10 7.5%

<TDDFT> Excited State 7: Singlet-A 3.8704 eV 320.34 nm f=0.0018

<TDDFT>HOMO -> LUMO+5 80.9%

<TDDFT>HOMO -> LUMO+7 15.3%

<TDDFT> Excited State 8: Singlet-A 3.9299 eV 315.49 nm f=0.1094

<TDDFT>HOMO -> LUMO+3
12.1%

<TDDFT>HOMO -> LUMO+4
76.0%

<TDDFT>HOMO -> LUMO+6 7.7%

<TDDFT> Excited State 9: Singlet-A
4.1535 eV 298.51 nm f=0.0041

<TDDFT>HOMO -> LUMO+6 6.3%

<TDDFT>HOMO -> LUMO+8
82.8%

<TDDFT>HOMO -> LUMO+9 4.0%

<TDDFT>HOMO -> LUMO+12 2.5%

<TDDFT> Excited State 10: Singlet-A
4.5528 eV 272.32 nm f=0.0523

<TDDFT>HOMO-2 -> LUMO
64.1%

<TDDFT>HOMO-1 -> LUMO+4 2.2%

<TDDFT>HOMO -> LUMO+10 6.8%

<TDDFT>HOMO -> LUMO+13
19.1%

<TDDFT>HOMO -> LUMO+15 2.0%

<TDDFT> Excited State 11: Singlet-A
4.5578 eV 272.03 nm f=0.0022

<TDDFT>HOMO -> LUMO+8 3.3%

<TDDFT>HOMO -> LUMO+9
83.4%

<TDDFT>HOMO -> LUMO+12 6.1%

<TDDFT>HOMO -> LUMO+14 2.9%

<TDDFT> Excited State 12: Singlet-A
4.6161 eV 268.59 nm f=0.1323

<TDDFT>HOMO-2 -> LUMO+3 3.7%

<TDDFT>HOMO-1 -> LUMO
87.7%

<TDDFT> Excited State 13: Singlet-A
4.6640 eV 265.83 nm f=0.1047

<TDDFT>HOMO-2 -> LUMO 9.9%

<TDDFT>HOMO -> LUMO+7
11.2%

<TDDFT>HOMO -> LUMO+10
68.1%

<TDDFT>HOMO -> LUMO+15 2.2%

<TDDFT>HOMO -> LUMO+21 2.4%

<TDDFT> Excited State 14: Singlet-A
4.7828 eV 259.23 nm f=0.4325

<TDDFT>HOMO-2 -> LUMO
16.7%

<TDDFT>HOMO -> LUMO+13
61.6%

<TDDFT>HOMO -> LUMO+15
12.3%

<TDDFT> Excited State 15: Singlet-A
4.8541 eV 255.42 nm f=0.0011

<TDDFT>HOMO -> LUMO+11
89.2%

<TDDFT>HOMO -> LUMO+17 3.2%

<TDDFT> Excited State 16: Singlet-A
4.8773 eV 254.21 nm f=0.0017

<TDDFT>HOMO -> LUMO+8 4.0%

<TDDFT>HOMO -> LUMO+9 3.6%

<TDDFT>HOMO -> LUMO+11 2.5%

<TDDFT>HOMO -> LUMO+12
81.5%

<TDDFT>HOMO -> LUMO+20 2.4%

<TDDFT> Excited State 17: Singlet-A
4.9647 eV 249.73 nm f=0.0008

<TDDFT>HOMO-2 -> LUMO+6 5.7%

<TDDFT>HOMO-1 -> LUMO+1
86.5%

<TDDFT>HOMO-1 -> LUMO+7 2.6%

<TDDFT> Excited State 18: Singlet-A
4.9972 eV 248.11 nm f=0.0008

<TDDFT>HOMO-2 -> LUMO+1
64.6%

<TDDFT>HOMO-1 -> LUMO+6
10.5%

<TDDFT>HOMO -> LUMO+15 7.7%

<TDDFT>HOMO -> LUMO+16 3.5%

<TDDFT>HOMO -> LUMO+21 4.3%

<TDDFT> Excited State 19: Singlet-A
5.0129 eV 247.33 nm f=0.0073

<TDDFT>HOMO -> LUMO+9 4.8%

<TDDFT>HOMO -> LUMO+14
89.2%

<TDDFT> Excited State 20: Singlet-A 5.0156 eV 247.20 nm f=0.0045

<TDDFT>HOMO-2 -> LUMO+1 18.2%

<TDDFT>HOMO -> LUMO+10 5.1%

<TDDFT>HOMO -> LUMO+13 6.2%

<TDDFT>HOMO -> LUMO+15 37.7%

<TDDFT>HOMO -> LUMO+16 11.2%

<TDDFT>HOMO -> LUMO+21 13.7%

<TDDFT>HOMO -> LUMO+26 2.1%

<TDDFT> Excited State 21: Singlet-A 5.0566 eV 245.19 nm f=0.0146

<TDDFT>HOMO-5 -> LUMO+3 2.2%

<TDDFT>HOMO-3 -> LUMO 56.4%

<TDDFT>HOMO-2 -> LUMO+4 8.1%

<TDDFT>HOMO-1 -> LUMO 2.4%

<TDDFT>HOMO-1 -> LUMO+2 17.5%

<TDDFT>HOMO-1 -> LUMO+5 3.7%

<TDDFT> Excited State 22: Singlet-A 5.1267 eV 241.84 nm f=0.0005

<TDDFT>HOMO-1 -> LUMO+6 2.7%

<TDDFT>HOMO -> LUMO+13 7.2%

<TDDFT>HOMO -> LUMO+15 29.9%

<TDDFT>HOMO -> LUMO+16 41.1%

<TDDFT>HOMO -> LUMO+21 13.4%

<TDDFT> Excited State 23: Singlet-A 5.2188 eV 237.57 nm f=0.0291

<TDDFT>HOMO-6 -> LUMO+2 11.6%

<TDDFT>HOMO-6 -> LUMO+5 13.8%

<TDDFT>HOMO-4 -> LUMO 3.4%

<TDDFT>HOMO-4 -> LUMO+1 66.6%

<TDDFT> Excited State 24: Singlet-A 5.2681 eV 235.35 nm f=0.0008

<TDDFT>HOMO-4 -> LUMO 95.0%

<TDDFT>HOMO-4 -> LUMO+1 2.3%

6.1.18.6 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	-5.476665	-2.098178	-0.000140
C 0	-4.621098	-3.202985	-0.000139
C 0	-3.244019	-3.046609	-0.000066
C 0	-2.689279	-1.751974	0.000005
C 0	-3.576059	-0.645545	0.000013
C 0	-4.950515	-0.804164	-0.000058
C 0	-1.329607	-1.338613	0.000080
C 0	-1.184450	0.070427	0.000172
S 0	-2.726248	0.902950	0.000106
S 0	0.000000	-2.426154	-0.000032
C 0	1.329607	-1.338612	0.000118
C 0	1.184450	0.070427	0.000205
N 0	-0.000000	0.736423	0.000141
C 0	2.689279	-1.751973	0.000076
C 0	3.576059	-0.645545	0.000091
S 0	2.726248	0.902950	0.000144
C 0	3.244019	-3.046609	0.000022
C 0	4.621098	-3.202984	-0.000017
C 0	5.476665	-2.098177	-0.000009
C 0	4.950515	-0.804163	0.000050
C 0	-0.000000	2.178008	-0.000006
C 0	0.000125	2.838218	-1.233075
C 0	0.000132	4.231986	-1.206722
C 0	-0.000001	4.920468	-0.000309

C 0	-0.000134	4.232239	1.206252
C 0	-0.000126	2.838478	1.232919
C 0	-0.000310	2.077812	2.524785
C 0	0.000312	2.077263	-2.524769
H 0	-6.551647	-2.240539	-0.000199
H 0	-5.040733	-4.203920	-0.000193
H 0	-2.596431	-3.917940	-0.000050
H 0	-5.608472	0.058551	-0.000060
H 0	2.596432	-3.917939	0.000029
H 0	5.040734	-4.203919	-0.000056
H 0	6.551648	-2.240538	-0.000046
H 0	5.608472	0.058552	0.000050
H 0	0.000248	4.777429	-2.144997
H 0	-0.000002	6.005685	-0.000418
H 0	-0.000250	4.777892	2.144405
H 0	0.880886	1.433687	2.605383
H 0	-0.000424	2.763872	3.372838
H 0	-0.881536	1.433694	2.605141
H 0	0.000425	2.763122	-3.372984
H 0	0.881536	1.433123	-2.604969
H 0	-0.880880	1.433111	-2.605213

SCF Done: E(RPBE1PBE) = -2172.81924299

Sum of electronic and zero-point Energies= -2172.401627

Sum of electronic and thermal Energies= -2172.376829

Sum of electronic and thermal Enthalpies= -2172.375885

Sum of electronic and thermal Free Energies= -2172.458635

6.1.18.7 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent= dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.1874 eV 566.82 nm f=0.1257

<TDDFT>HOMO -> LUMO 98.4%

<TDDFT> Excited State 2: Singlet-A 2.9780 eV 416.33 nm f=0.0000

<TDDFT>HOMO -> LUMO+1 98.4%

<TDDFT> Excited State 3: Singlet-A 3.3739 eV 367.48 nm f=0.0023

<TDDFT>HOMO -> LUMO+2 91.6%

<TDDFT>HOMO -> LUMO+4 7.2%

<TDDFT> Excited State 4: Singlet-A 3.4051 eV 364.11 nm f=0.0106

<TDDFT>HOMO -> LUMO+3 80.4%

<TDDFT>HOMO -> LUMO+5 17.8%

6.1.18.8 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di chloromethane)

0 1

C 0	-5.409622	-2.205625	-0.412917
C 0	-4.558129	-3.266314	-0.067440
C 0	-3.205260	-3.051747	0.164238
C 0	-2.680610	-1.752776	0.045150
C 0	-3.555628	-0.698261	-0.309077
C 0	-4.914152	-0.909778	-0.534109
C 0	-1.337388	-1.283887	0.256996
C 0	-1.191139	0.056061	0.050881
S 0	-2.703958	0.841374	-0.419373
S 0	0.000226	-2.333021	0.816517
C 0	1.337710	-1.283643	0.257089

C 0	1.191287	0.056302	0.051009
N 0	-0.000011	0.778559	0.102326
C 0	2.680993	-1.752337	0.045219
C 0	3.555862	-0.697683	-0.308929
S 0	2.703938	0.841889	-0.418984
C 0	3.205847	-3.051252	0.164128
C 0	4.558733	-3.265590	-0.067654
C 0	5.410062	-2.204743	-0.413062
C 0	4.914400	-0.908952	-0.534073
C 0	-0.000203	2.224083	0.150108
C 0	-0.000350	2.960705	-1.046337
C 0	-0.000665	4.359507	-0.949541
C 0	-0.000811	4.991137	0.286924
C 0	-0.000648	4.238933	1.461747
C 0	-0.000345	2.844699	1.416508
C 0	-0.000067	2.317696	-2.412024
C 0	-0.000232	2.032455	2.685938
H 0	-6.462550	-2.393489	-0.588954
H 0	-4.962134	-4.268633	0.020369
H 0	-2.558619	-3.880506	0.430938
H 0	-5.569760	-0.088993	-0.802228
H 0	2.559345	-3.880142	0.430759
H 0	4.962891	-4.267860	0.020013
H 0	6.463002	-2.392446	-0.589196
H 0	5.569863	-0.088037	-0.802148
H 0	-0.000792	4.949038	-1.860535
H 0	-0.001049	6.074617	0.340253
H 0	-0.000780	4.737354	2.425029
H 0	0.000027	1.229549	-2.369033
H 0	-0.880279	2.631637	-2.981159
H 0	0.880356	2.631784	-2.980765
H 0	-0.000559	2.689200	3.557481
H 0	-0.879514	1.384306	2.748711
H 0	0.879469	1.384897	2.748980

SCF Done: E(RB3LYP) = -2174.46368061

Sum of electronic and zero-point Energies= -2174.125247

Sum of electronic and thermal Energies= -2174.101523

Sum of electronic and thermal Enthalpies= -2174.100579

Sum of electronic and thermal Free Energies= -2174.179559

6.1.18.9 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.480451	-2.093707	-0.000063
C 0	-4.628519	-3.209253	0.000047
C 0	-3.252565	-3.051505	0.000076
C 0	-2.712147	-1.753549	0.000017
C 0	-3.586564	-0.643425	-0.000100
C 0	-4.968972	-0.799974	-0.000152
C 0	-1.337607	-1.336581	0.000015
C 0	-1.191139	0.044020	-0.000110
S 0	-2.719491	0.896156	-0.000160
S 0	0.000004	-2.458456	0.000132
C 0	1.337614	-1.336578	0.000006
C 0	1.191141	0.044023	-0.000113
N 0	0.000000	0.728911	-0.000159
C 0	2.712154	-1.753542	0.000011
C 0	3.586569	-0.643416	-0.000085
S 0	2.719491	0.896163	-0.000117
C 0	3.252576	-3.051497	0.000054
C 0	4.628530	-3.209240	0.000028
C 0	5.480460	-2.093692	-0.000062
C 0	4.968977	-0.799961	-0.000133
C 0	-0.000001	2.190238	0.000009
C 0	0.000001	2.851729	-1.239039
C 0	-0.000007	4.248235	-1.208301
C 0	-0.000009	4.937605	0.000324
C 0	-0.000008	4.247960	1.208787

C 0	-0.000008	2.851445	1.239214
C 0	0.000018	2.104513	-2.549598
C 0	-0.000040	2.103960	2.549614
H 0	-6.553806	-2.239682	-0.000080
H 0	-5.053626	-4.205283	0.000107
H 0	-2.604086	-3.920256	0.000123
H 0	-5.631416	0.056971	-0.000249
H 0	2.604100	-3.920250	0.000084
H 0	5.053640	-4.205270	0.000074
H 0	6.553815	-2.239664	-0.000076
H 0	5.631419	0.056986	-0.000212
H 0	-0.000012	4.795647	-2.143671
H 0	-0.000012	6.021368	0.000443
H 0	-0.000004	4.795155	2.144285
H 0	0.882536	1.466725	-2.653075
H 0	-0.882246	1.466349	-2.652906
H 0	-0.000208	2.804479	-3.384875
H 0	0.000316	2.803759	3.385033
H 0	-0.882636	1.466265	2.653010
H 0	0.882152	1.465669	2.652750

SCF Done: E(UB3LYP) = -2174.21558438

Sum of electronic and zero-point Energies= -2173.876243

Sum of electronic and thermal Energies= -2173.852528

Sum of electronic and thermal Enthalpies= -2173.851583

Sum of electronic and thermal Free Energies= -2173.930666

6.1.18.10 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpc

m,solvent=dichloromethane) geom=check guess=read

0 1

C 0	-5.480626	-2.091982	-0.000054
C 0	-4.628212	-3.207649	-0.000009
C 0	-3.251432	-3.050218	0.000005
C 0	-2.711047	-1.752420	-0.000025
C 0	-3.585473	-0.642243	-0.000072
C 0	-4.968584	-0.798173	-0.000087
C 0	-1.335834	-1.336766	-0.000009
C 0	-1.190371	0.043033	-0.000034
S 0	-2.718021	0.896082	-0.000135
S 0	0.000006	-2.458482	0.000058
C 0	1.335842	-1.336761	0.000004
C 0	1.190374	0.043038	-0.000019
N 0	-0.000000	0.727646	-0.000027
C 0	2.711056	-1.752410	0.000017
C 0	3.585478	-0.642230	-0.000011
S 0	2.718020	0.896092	-0.000103
C 0	3.251446	-3.050206	0.000059
C 0	4.628227	-3.207631	0.000079
C 0	5.480636	-2.091961	0.000055
C 0	4.968590	-0.798155	0.000008
C 0	-0.000003	2.188227	0.000031
C 0	0.000094	2.849785	-1.238724
C 0	0.000086	4.246620	-1.208735
C 0	-0.000018	4.936342	0.000113
C 0	-0.000113	4.246545	1.208917
C 0	-0.000106	2.849706	1.238830
C 0	0.000233	2.102731	-2.548282
C 0	-0.000247	2.102592	2.548352
H 0	-6.554082	-2.237371	-0.000069
H 0	-5.052792	-4.203961	0.000014
H 0	-2.602819	-3.918375	0.000034
H 0	-5.630010	0.059204	-0.000136
H 0	2.602836	-3.918366	0.000074
H 0	5.052811	-4.203942	0.000114
H 0	6.554093	-2.237346	0.000066

H 0	5.630013	0.059226	-0.000028
H 0	0.000161	4.792927	-2.144658
H 0	-0.000023	6.020182	0.000145
H 0	-0.000192	4.792793	2.144874
H 0	0.881973	1.464108	-2.649325
H 0	-0.881240	1.463745	-2.649325
H 0	0.000091	2.804144	-3.382584
H 0	0.000016	2.803969	3.382684
H 0	-0.882053	1.464063	2.649421
H 0	0.881161	1.463505	2.649326

SCF Done: E(UB3LYP) = -2174.26511508

Sum of electronic and zero-point Energies= -2173.926087

Sum of electronic and thermal Energies= -2173.902264

Sum of electronic and thermal Enthalpies= -2173.901320

Sum of electronic and thermal Free Energies= -2173.980917

6.1.18.11 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0	5.476923	-2.101999	-0.000330
C 0	4.621028	-3.214911	-0.000005
C 0	3.244612	-3.053404	0.000183
C 0	2.710044	-1.753139	0.000027
C 0	3.587825	-0.646033	-0.000310
C 0	4.970382	-0.805657	-0.000487
C 0	1.336447	-1.332956	0.000195
C 0	1.190186	0.046404	-0.000036
S 0	2.722662	0.894943	-0.000335
S 0	0.000047	-2.454189	0.000619
C 0	-1.336387	-1.332998	0.000196
C 0	-1.190169	0.046365	-0.000022
N 0	-0.000002	0.731554	-0.000029
C 0	-2.709972	-1.753222	0.000016
C 0	-3.587785	-0.646142	-0.000307
S 0	-2.722668	0.894860	-0.000292
C 0	-3.244501	-3.053504	0.000138
C 0	-4.620911	-3.215052	-0.000075
C 0	-5.476839	-2.102165	-0.000389
C 0	-4.970338	-0.805808	-0.000508
C 0	-0.000041	2.192642	0.000102
C 0	-0.000081	2.854006	1.240268
C 0	-0.000129	4.251311	1.209471
C 0	-0.000145	4.940900	0.000402
C 0	-0.000114	4.251607	-1.208799
C 0	-0.000057	2.854279	-1.239897
C 0	-0.000114	2.110178	2.551716
C 0	0.000055	2.110777	-2.551538
H 0	6.550118	-2.251555	-0.000452
H 0	5.042508	-4.212898	0.000106
H 0	2.593661	-3.920559	0.000435
H 0	5.636336	0.049039	-0.000686
H 0	-2.593522	-3.920638	0.000377
H 0	-5.042362	-4.213052	0.000006
H 0	-6.550030	-2.251753	-0.000533
H 0	-5.636319	0.048867	-0.000699
H 0	-0.000161	4.795665	2.147048
H 0	-0.000191	6.025324	0.000550
H 0	-0.000134	4.796142	-2.146270
H 0	-0.881114	1.470421	2.656638
H 0	0.880635	1.470058	2.656508
H 0	0.000088	2.816394	3.382326
H 0	-0.000579	2.817217	-3.381956
H 0	0.881328	1.471448	-2.656767
H 0	-0.880420	1.470294	-2.656365

SCF Done: E(UB3LYP) = -2174.29315793

Sum of electronic and zero-point Energies= -2173.954038

Sum of electronic and thermal Enthalpies= -2173.929323

Sum of electronic and thermal Energies= -2173.930267

Sum of electronic and thermal Free Energies= -2174.009286

6.1.18.12 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2) + energies of ringinversion relaxed geometry PES scan

#p opt=(ts,noeigen,calcfc) freq=noraman B3LYP/6-311++g(d,p) pop=full s crf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	5.501229	-2.102511	-0.000013
C 0	4.638761	-3.208983	0.000011
C 0	3.259664	-3.041111	0.000017
C 0	2.720601	-1.742443	-0.000002
C 0	3.607957	-0.640230	-0.000027
C 0	4.990530	-0.806436	-0.000032
C 0	1.344950	-1.326764	0.000006
C 0	1.193733	0.028179	-0.000016
S 0	2.734263	0.889609	-0.000045
S 0	0.000003	-2.508812	0.000064
C 0	-1.344945	-1.326767	0.000005
C 0	-1.193731	0.028176	-0.000018
N 0	0.000000	0.747498	-0.000020
C 0	-2.720596	-1.742449	-0.000008
C 0	-3.607955	-0.640238	-0.000040
S 0	-2.734263	0.889603	-0.000060
C 0	-3.259656	-3.041118	0.000012
C 0	-4.638752	-3.208993	0.000000
C 0	-5.501223	-2.102523	-0.000030
C 0	-4.990527	-0.806447	-0.000051
C 0	-0.000002	2.191964	0.000012
C 0	-0.000022	2.868739	1.232548
C 0	-0.000027	4.266420	1.207948
C 0	-0.000011	4.958463	0.000078
C 0	0.000009	4.266477	-1.207824
C 0	0.000014	2.868797	-1.232492
C 0	-0.000047	2.119213	2.541331
C 0	0.000043	2.119337	-2.541315
H 0	6.574236	-2.253724	-0.000017
H 0	5.054409	-4.210087	0.000026
H 0	2.604527	-3.905066	0.000037
H 0	5.654900	0.049748	-0.000050
H 0	-2.604517	-3.905071	0.000036
H 0	-5.054398	-4.210098	0.000016
H 0	-6.574229	-2.253739	-0.000038
H 0	-5.654900	0.049735	-0.000074
H 0	-0.000042	4.812278	2.144862
H 0	-0.000015	6.042796	0.000103
H 0	0.000021	4.812379	-2.144713
H 0	0.879628	1.476574	2.634385
H 0	0.000044	2.816196	3.380218
H 0	-0.879842	1.476743	2.634441
H 0	-0.000025	2.816365	-3.380164
H 0	0.879827	1.476857	-2.634447
H 0	-0.879643	1.476720	-2.634414

SCF Done: E(RB3LYP) = -2174.43927996

Sum of electronic and zero-point Energies= -2174.101140

Sum of electronic and thermal Energies= -2174.078039

Sum of electronic and thermal Enthalpies= -2174.077095

Sum of electronic and thermal Free Energies= -2174.154025

Relaxed PES scan via:

#p b3lyp/6-311G** opt=ModRedundant nosymm scrf=(iefpcm,solvent=dichloromethane)
With D 7 8 13 21 S 60 1.0

HF=-2174.4247453,-2174.4247788,-2174.4247869,-2174.4247926,-

2174.4247961,-2174.4247974,-2174.4247965,-2174.4247934,-2174.4247882,-

2174.4247809,-2174.4247717,-2174.4247608,-2174.4247486,-2174.4247358,-

2174.4247228,-2174.4247089,-2174.4246934,-2174.424672,-2174.4246566,-2

174.4246352,-2174.4246118,-2174.4245862,-2174.4245582,-2174.4245275,-2

174.4244939,-2174.4244572,-2174.4244175,-2174.4243747,-2174.4243287,-2

174.4242794,-2174.4242264,-2174.4241695,-2174.4241088,-2174.4240441,-2

174.4239758,-2174.4239043,-2174.4238299,-2174.4238914,-2174.4238079,-2

174.4237192,-2174.4236249,-2174.4235245,-2174.4234176,-2174.4233036,-2

174.4231822,-2174.4230529,-2174.4229155,-2174.4227697,-2174.4226153,-2

174.4224655,-2174.4222993,-2174.4221241,-2174.4219416,-2174.4217498,-2

174.421548,-2174.4213361,-2174.4211136,-2174.4208805,-2174.4206364,-21

74.4203813,-2174.4201204

Relaxed PES scan via:

#p b3lyp/6-311G** opt=ModRedundant nosymm scrf=(iefpcm,solvent=dichloromethane)

With D 7 8 13 21 S 60 -1.0

HF=-2174.4247453,-2174.4247779,-2174.4247861,-2174.4247921,-2174.

4247958,-2174.4247972,-2174.4247966,-2174.4247937,-2174.4247887,-2174.

4247816,-2174.4247725,-2174.4247617,-2174.4247496,-2174.4247369,-2174.

424724,-2174.4247102,-2174.4246948,-2174.4246776,-2174.4246584,-2174.4

246372,-2174.424614,-2174.4245886,-2174.4245608,-2174.4245302,-2174.42

44968,-2174.4244604,-2174.4244209,-2174.4243784,-2174.4243326,-2174.42

42836,-2174.4242309,-2174.4241744,-2174.424114,-2174.4240498,-2174.424

1213,-2174.424051,-2174.4239766,-2174.423898,-2174.4238148,-2174.42372

66,-2174.4236328,-2174.423533,-2174.4234266,-2174.4233132,-2174.423192

4,-2174.4230637,-2174.4229271,-2174.422782,-2174.4226283,-2174.4224787

,-2174.4223133,-2174.4221389,-2174.4219568,-2174.4217659,-2174.421565,

-2174.4213539,-2174.4211324,-2174.4209001,-2174.420657,-2174.4204029,-

2174.4201426

6.1.19 *anti-anti-N-ortho,ortho'*-methylmethoxyphenyl-BBTT 3t

6.1.19.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.463748	-2.249210	-0.243391
C 0	-4.607222	-3.293897	0.132738
C 0	-3.241228	-3.084737	0.265735
C 0	-2.708286	-1.809499	0.015053
C 0	-3.587564	-0.770820	-0.370560

C 0	-4.958766	-0.977193	-0.497030
C 0	-1.348294	-1.353516	0.114236
C 0	-1.198062	-0.038202	-0.203207
S 0	-2.722568	0.737930	-0.645051
S 0	-0.014407	-2.401195	0.675941
C 0	1.327474	-1.367171	0.108745
C 0	1.188603	-0.050327	-0.207276
N 0	-0.001284	0.676432	-0.284050
C 0	2.681319	-1.837854	-0.003814
C 0	3.567596	-0.808862	-0.399573
S 0	2.716549	0.708686	-0.668170
C 0	3.202837	-3.118812	0.241824
C 0	4.564900	-3.342952	0.094436
C 0	5.428799	-2.307723	-0.291187
C 0	4.935175	-1.030428	-0.540173
C 0	0.009098	2.109125	-0.176513
C 0	-0.010511	2.915798	-1.320079
C 0	0.007613	4.307917	-1.149953
C 0	0.040794	4.867612	0.118741
C 0	0.059869	4.065976	1.260328
C 0	0.045105	2.679320	1.116656
O 0	0.062165	1.796768	2.144086
C 0	0.100114	2.293172	3.478293
C 0	-0.069412	2.329605	-2.709515
H 0	-6.527624	-2.431432	-0.340722
H 0	-5.018001	-4.278911	0.322897
H 0	-2.586198	-3.898912	0.554410
H 0	-5.618505	-0.168603	-0.790238
H 0	2.541928	-3.925651	0.537685
H 0	4.966920	-4.332328	0.280638
H 0	6.489497	-2.501678	-0.399803
H 0	5.600500	-0.229335	-0.841095
H 0	-0.002092	4.948077	-2.024846
H 0	0.055415	5.946062	0.231383
H 0	0.087257	4.522660	2.240021
H 0	0.107465	1.412619	4.117550
H 0	1.005988	2.881351	3.656440
H 0	-0.784456	2.898510	3.700769
H 0	0.280855	1.298659	-2.735556
H 0	-1.097028	2.338949	-3.086846
H 0	0.539348	2.920126	-3.397645

SCF Done: E(RB3LYP) = -2249.65972404

Sum of electronic and zero-point Energies= -2249.316191

Sum of electronic and thermal Energies= -2249.291350

Sum of electronic and thermal Enthalpies= -2249.290406

Sum of electronic and thermal Free Energies= -2249.373190

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.413121	-2.248199	0.436610
C 0	-4.558017	-3.342503	0.240683
C 0	-3.203969	-3.156702	-0.002452
C 0	-2.680971	-1.853702	-0.047645
C 0	-3.558504	-0.763261	0.158298
C 0	-4.918035	-0.948049	0.395873
C 0	-1.334964	-1.417256	-0.299108
C 0	-1.192441	-0.063053	-0.258113
S 0	-2.706693	0.776075	0.082469
S 0	0.000146	-2.527994	-0.720774
C 0	1.334870	-1.417264	-0.298628
C 0	1.192448	-0.063054	-0.257972
N 0	0.000008	0.648348	-0.422298
C 0	2.680876	-1.853700	-0.047073
C 0	3.558440	-0.763285	0.158820
S 0	2.706632	0.776137	0.082676
C 0	3.203811	-3.156700	-0.001799
C 0	4.557859	-3.342558	0.241230
C 0	5.413029	-2.248278	0.437011
C 0	4.918027	-0.948103	0.396235
C 0	-0.000031	2.083828	-0.430272

C 0	0.000299	2.788009	-1.639808
C 0	0.000231	4.189220	-1.593665
C 0	-0.000007	4.858955	-0.379087
C 0	-0.000296	4.161168	0.828615
C 0	-0.000341	2.766830	0.809300
O 0	-0.000618	1.981206	1.913031
C 0	-0.000788	2.595756	3.197194
C 0	0.001578	2.082353	-2.972848
H 0	-6.467859	-2.413345	0.623003
H 0	-4.960896	-4.348209	0.278725
H 0	-2.549160	-4.008092	-0.149524
H 0	-5.576236	-0.100629	0.549892
H 0	2.548917	-4.008042	-0.148711
H 0	4.960695	-4.348264	0.279354
H 0	6.467870	-2.413497	0.623327
H 0	5.576282	-0.100732	0.550198
H 0	0.000339	4.749501	-2.521994
H 0	-0.000067	5.943228	-0.361439
H 0	-0.000508	4.702579	1.764529
H 0	-0.000939	1.776744	3.913621
H 0	0.894784	3.208018	3.343340
H 0	-0.896354	3.208091	3.343075
H 0	-0.009179	0.999413	-2.864590
H 0	-0.873298	2.376016	-3.560053
H 0	0.889255	2.358932	-3.549226

SCF Done: E(RB3LYP) = -2249.65966831

Sum of electronic and zero-point Energies= -2249.316146

Sum of electronic and thermal Energies= -2249.292189

Sum of electronic and thermal Enthalpies= -2249.291245

Sum of electronic and thermal Free Energies= -2249.370978

6.1.19.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt=verytight freq=noraman rb3lyp/6-311++g(d,p) pop=full Int=UltraF ine SCRF=(IEFPCM,Solvent=Dichloromethane) geom=check

0 1

C 0	-5.453615	-2.274559	-0.257261
C 0	-4.595228	-3.323993	0.104157
C 0	-3.229026	-3.114262	0.243251
C 0	-2.698700	-1.833065	0.013237
C 0	-3.580351	-0.789296	-0.355878
C 0	-4.951447	-0.996272	-0.488976
C 0	-1.339833	-1.375073	0.118723
C 0	-1.192506	-0.052974	-0.175840
S 0	-2.718029	0.726966	-0.605090
S 0	-0.000001	-2.431974	0.655260
C 0	1.339831	-1.375075	0.118722
C 0	1.192505	-0.052975	-0.175841
N 0	-0.000000	0.665907	-0.241803
C 0	2.698698	-1.833068	0.013236
C 0	3.580349	-0.789299	-0.355879
S 0	2.718029	0.726963	-0.605091
C 0	3.229023	-3.114265	0.243249
C 0	4.595225	-3.323997	0.104154
C 0	5.453612	-2.274564	-0.257265
C 0	4.951446	-0.996277	-0.488979
C 0	0.000001	2.102639	-0.186907
C 0	-0.000000	2.867222	-1.359766
C 0	0.000001	4.265167	-1.238151
C 0	0.000003	4.868494	0.011188
C 0	0.000004	4.107894	1.181812
C 0	0.000003	2.716969	1.087912
O 0	0.000004	1.873030	2.148137
C 0	0.000007	2.426623	3.467647
C 0	-0.000004	2.239072	-2.732119
H 0	-6.516844	-2.457273	-0.359578

H 0	-5.004326	-4.312511	0.278780
H 0	-2.574872	-3.932438	0.522841
H 0	-5.612740	-0.184915	-0.769863
H 0	2.574868	-3.932440	0.522840
H 0	5.004322	-4.312515	0.278777
H 0	6.516841	-2.457279	-0.359582
H 0	5.612739	-0.184920	-0.769867
H 0	0.000000	4.874109	-2.135113
H 0	0.000004	5.950147	0.086810
H 0	0.000006	4.599976	2.144393
H 0	0.000008	1.573318	4.142178
H 0	0.895236	3.030245	3.639765
H 0	-0.895219	3.030246	3.639769
H 0	0.000010	1.151181	-2.690285
H 0	-0.880578	2.558878	-3.296073
H 0	0.880551	2.558900	-3.296088

SCF Done: E(RB3LYP) = -2249.66884333

Sum of electronic and zero-point Energies= -2249.325447

Sum of electronic and thermal Energies= -2249.300581

Sum of electronic and thermal Enthalpies= -2249.299637

Sum of electronic and thermal Free Energies= -2249.382814

Conformer II:

#p opt=verytight freq=noraman rb3lyp/6-311++g(d,p) pop=full Guess=Read

geom=check SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	-5.429411	-2.234677	0.415166
C 0	-4.575230	-3.334402	0.241524
C 0	-3.216354	-3.155786	0.014912
C 0	-2.688327	-1.854034	-0.035983
C 0	-3.566057	-0.758513	0.145069
C 0	-4.929771	-0.935526	0.367065
C 0	-1.337113	-1.423480	-0.271424
C 0	-1.191364	-0.068278	-0.246838
S 0	-2.708339	0.778359	0.061754
S 0	0.000001	-2.549416	-0.652281
C 0	1.337114	-1.423479	-0.271424
C 0	1.191364	-0.068278	-0.246838
N 0	-0.000000	0.642795	-0.400558
C 0	2.688327	-1.854033	-0.035983
C 0	3.566058	-0.758512	0.145069
S 0	2.708339	0.778360	0.061754
C 0	3.216355	-3.155785	0.014912
C 0	4.575231	-3.334400	0.241524
C 0	5.429412	-2.234676	0.415166
C 0	4.929771	-0.935525	0.367065
C 0	-0.000000	2.080230	-0.420533
C 0	-0.000000	2.757281	-1.647696
C 0	-0.000001	4.156176	-1.632984
C 0	-0.000001	4.850887	-0.427503
C 0	-0.000001	4.179783	0.793085
C 0	-0.000001	2.782071	0.804673
O 0	-0.000001	2.022182	1.926285
C 0	-0.000002	2.672685	3.200753
C 0	0.000000	1.994285	-2.947983
H 0	-6.486976	-2.394306	0.589496
H 0	-4.982007	-4.338311	0.283807
H 0	-2.565176	-4.012566	-0.116891
H 0	-5.586828	-0.084505	0.503400
H 0	2.565177	-4.012565	-0.116890
H 0	4.982009	-4.338310	0.283808
H 0	6.486977	-2.394304	0.589496
H 0	5.586828	-0.084503	0.503400
H 0	-0.000001	4.698219	-2.571401
H 0	-0.000001	5.935134	-0.431816
H 0	-0.000001	4.741025	1.717066
H 0	-0.000002	1.872047	3.936987
H 0	0.895258	3.287199	3.327865
H 0	-0.895262	3.287199	3.327864
H 0	-0.879080	1.349390	-3.031200

H 0 -0.000000 2.681797 -3.794565

H 0 0.879081 1.349391 -3.031200

SCF Done: E(RB3LYP) = -2249.66960096

Sum of electronic and zero-point Energies= -2249.326122

Sum of electronic and thermal Energies= -2249.301356

Sum of electronic and thermal Enthalpies= -2249.300412

Sum of electronic and thermal Free Energies= -2249.381966

6.1.19.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

Conformer I:

#p opt=verytight int=ultrafine freq=noraman rb3lyp/6-311++g(d,p) scrf=

(smd,solvent=dichloromethane) pop=full geom=checkpoint guess=read

0 1

C 0 -5.455228 -2.269845 -0.271118

C 0 -4.599441 -3.311671 0.117759

C 0 -3.234253 -3.099179 0.263985

C 0 -2.702375 -1.822102 0.013928

C 0 -3.581903 -0.786618 -0.382213

C 0 -4.952133 -0.995739 -0.522733

C 0 -1.344534 -1.359542 0.122325

C 0 -1.193907 -0.043032 -0.194631

S 0 -2.718238 0.725920 -0.652993

S 0 -0.006084 -2.403780 0.687200

C 0 1.335353 -1.365189 0.119101

C 0 1.189466 -0.048172 -0.197862

N 0 -0.000765 0.674574 -0.266326

C 0 2.690945 -1.833486 0.007500

C 0 3.573823 -0.801984 -0.391553

S 0 2.715777 0.714014 -0.661109

C 0 3.218019 -3.112575 0.257338

C 0 4.581969 -3.330893 0.108221

C 0 5.441191 -2.292962 -0.283486

C 0 4.942843 -1.016964 -0.535024

C 0 0.002711 2.111368 -0.175427

C 0 -0.000645 2.906725 -1.328060

C 0 0.003647 4.301344 -1.167548

C 0 0.011484 4.870234 0.098169

C 0 0.015569 4.078690 1.248459

C 0 0.011021 2.690535 1.116435

O 0 0.014413 1.817069 2.150651

C 0 0.042611 2.329383 3.488167

C 0 -0.007815 2.317143 -2.716726

H 0 -6.517768 -2.455376 -0.378730

H 0 -5.009670 -4.297158 0.307909

H 0 -2.584257 -3.913580 0.564538

H 0 -5.612180 -0.190396 -0.824673

H 0 2.565254 -3.923914 0.560176

H 0 4.988491 -4.317925 0.298345

H 0 6.502715 -2.482995 -0.393276

H 0 5.605589 -0.214633 -0.839063

H 0 0.001103 4.934449 -2.047963

H 0 0.014764 5.949798 0.202978

H 0 0.021837 4.544071 2.224654

H 0 0.050048 1.453851 4.135295

H 0 0.945607 2.920624 3.663916

H 0 -0.846268 2.930613 3.698818

H 0 -0.006809 1.227837 -2.708130

H 0 -0.891762 2.651668 -3.267922

H 0 0.869568 2.653201 -3.277397

SCF Done: E(RB3LYP) = -2249.69265995

Sum of electronic and zero-point Energies= -2249.349367

Sum of electronic and thermal Energies= -2249.324643

Sum of electronic and thermal Enthalpies= -2249.323699

Sum of electronic and thermal Free Energies= -2249.405477

Conformer II:

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=checkpoint guess=read

0 1

C 0	-5.416757	-2.254979	0.451575
C 0	-4.564791	-3.349047	0.235489
C 0	-3.209766	-3.164224	-0.009196
C 0	-2.682601	-1.860976	-0.034728
C 0	-3.558732	-0.771832	0.188709
C 0	-4.918767	-0.954487	0.428611
C 0	-1.336933	-1.420195	-0.285785
C 0	-1.190806	-0.065649	-0.230418
S 0	-2.704187	0.768758	0.132335
S 0	0.000059	-2.524696	-0.727196
C 0	1.337003	-1.420152	-0.285744
C 0	1.190830	-0.065610	-0.230375
N 0	0.000003	0.645750	-0.383221
C 0	2.682681	-1.860889	-0.034664
C 0	3.558773	-0.771716	0.188786
S 0	2.704177	0.768845	0.132410
C 0	3.209890	-3.164119	-0.009130
C 0	4.564918	-3.348898	0.235569
C 0	5.416845	-2.254802	0.451666
C 0	4.918812	-0.954326	0.428702
C 0	-0.000022	2.083473	-0.439188
C 0	0.000038	2.731900	-1.682748
C 0	0.000012	4.131192	-1.699482
C 0	-0.000076	4.853650	-0.510041
C 0	-0.000140	4.211242	0.725747
C 0	-0.000113	2.813665	0.770125
O 0	-0.000182	2.081789	1.908753
C 0	-0.000285	2.761647	3.169773
C 0	0.000140	1.944105	-2.967403
H 0	-6.471364	-2.420089	0.639945
H 0	-4.970354	-4.354359	0.258415
H 0	-2.563239	-4.019038	-0.174783
H 0	-5.573960	-0.107503	0.598231
H 0	2.563394	-4.018954	-0.174730
H 0	4.970515	-4.354196	0.258495
H 0	6.471456	-2.419877	0.640047
H 0	5.573975	-0.107321	0.598330
H 0	0.000061	4.650433	-2.651034
H 0	-0.000097	5.938017	-0.539365
H 0	-0.000212	4.792766	1.637459
H 0	-0.000332	1.976323	3.923961
H 0	0.895807	3.377776	3.285304
H 0	-0.896408	3.377755	3.285169
H 0	-0.879338	1.297710	-3.041655
H 0	0.000182	2.617896	-3.825613
H 0	0.879657	1.297749	-3.041536

SCF Done: E(RB3LYP) = -2249.69336649

Sum of electronic and zero-point Energies= -2249.350011

Sum of electronic and thermal Energies= -2249.325295

Sum of electronic and thermal Enthalpies= -2249.324351

Sum of electronic and thermal Free Energies= -2249.405527

6.1.19.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.480855	-2.187722	0.053486
C 0	-4.629712	-3.300426	0.139604
C 0	-3.253601	-3.144971	0.113538
C 0	-2.712372	-1.852637	-0.000846
C 0	-3.585824	-0.745092	-0.086026
C 0	-4.968290	-0.899438	-0.060231
C 0	-1.337393	-1.438709	-0.046399

C 0	-1.190819	-0.063544	-0.162297
S 0	-2.717069	0.787619	-0.218660
S 0	-0.000071	-2.556782	0.037448
C 0	1.337296	-1.438755	-0.046361
C 0	1.190779	-0.063589	-0.162288
N 0	-0.000008	0.616867	-0.236835
C 0	2.712258	-1.852739	-0.000781
C 0	3.585759	-0.745233	-0.085921
S 0	2.717068	0.787515	-0.218562
C 0	3.253427	-3.145098	0.113618
C 0	4.629529	-3.300614	0.139720
C 0	5.480724	-2.187945	0.053659
C 0	4.968218	-0.899636	-0.060049
C 0	0.000015	2.067249	-0.304117
C 0	0.000194	2.713362	-1.547236
C 0	0.000237	4.110828	-1.540523
C 0	0.000116	4.817038	-0.341600
C 0	-0.000077	4.163761	0.888149
C 0	-0.000106	2.768214	0.918874
O 0	-0.000254	2.007329	2.035935
C 0	0.000026	2.654706	3.315685
C 0	0.000630	1.938827	-2.841070
H 0	-6.554284	-2.331648	0.075279
H 0	-5.055378	-4.292354	0.227587
H 0	-2.605512	-4.011388	0.181022
H 0	-5.630124	-0.044547	-0.126250
H 0	2.605296	-4.011484	0.181090
H 0	5.055149	-4.292563	0.227695
H 0	6.554146	-2.331917	0.075515
H 0	5.630092	-0.044769	-0.125976
H 0	0.000352	4.644566	-2.483017
H 0	0.000105	5.900669	-0.360252
H 0	-0.000254	4.736303	1.805086
H 0	0.000295	1.850801	4.047862
H 0	0.896430	3.267036	3.442055
H 0	-0.896435	3.266861	3.442500
H 0	-0.881124	1.297595	-2.927868
H 0	0.000118	2.620543	-3.691170
H 0	0.883394	1.298946	-2.927937

SCF Done: E(UB3LYP) = -2249.44738377

Sum of electronic and zero-point Energies= -2249.102905

Sum of electronic and thermal Energies= -2249.078295

Sum of electronic and thermal Enthalpies= -2249.077350

Sum of electronic and thermal Free Energies= -2249.158527

6.1.19.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane)

0 1

C 0	-5.465202	-2.219626	0.042758
C 0	-4.606707	-3.327812	0.119597
C 0	-3.230778	-3.164626	0.091096
C 0	-2.698880	-1.867671	-0.016473
C 0	-3.579328	-0.765269	-0.095119
C 0	-4.961361	-0.926835	-0.065691
C 0	-1.326151	-1.445702	-0.059064
C 0	-1.185673	-0.070391	-0.167892
S 0	-2.718111	0.773000	-0.225140
S 0	0.015390	-2.558489	0.017294
C 0	1.346933	-1.433058	-0.049851
C 0	1.193199	-0.058995	-0.157594
N 0	0.001072	0.615982	-0.232553
C 0	2.723703	-1.840697	0.005474
C 0	3.593072	-0.728684	-0.060535
S 0	2.716974	0.800665	-0.194324
C 0	3.268938	-3.132039	0.114257
C 0	4.646265	-3.280104	0.156312

C 0	5.493383	-2.162421	0.091995
C 0	4.976381	-0.874908	-0.017415
C 0	-0.006609	2.065734	-0.307814
C 0	0.021388	2.712515	-1.548897
C 0	0.003353	4.113160	-1.539310
C 0	-0.034039	4.816555	-0.341757
C 0	-0.057390	4.161767	0.889616
C 0	-0.044433	2.767896	0.918107
O 0	-0.064167	2.006249	2.033261
C 0	-0.113679	2.655151	3.314958
C 0	0.091340	1.966532	-2.856575
H 0	-6.538007	-2.370090	0.067537
H 0	-5.025620	-4.323478	0.202653
H 0	-2.578023	-4.028235	0.151378
H 0	-5.629279	-0.075698	-0.123961
H 0	2.625565	-4.003270	0.164444
H 0	5.075130	-4.271459	0.240208
H 0	6.567457	-2.301221	0.127241
H 0	5.635115	-0.016056	-0.066221
H 0	0.020799	4.645681	-2.483273
H 0	-0.046425	5.900792	-0.358156
H 0	-0.086050	4.733028	1.807093
H 0	-0.117644	1.850172	4.047403
H 0	0.766277	3.284840	3.466737
H 0	-1.026152	3.248169	3.415261
H 0	-0.104601	0.898923	-2.754651
H 0	-0.631228	2.378634	-3.564798
H 0	1.084122	2.081762	-3.303495

SCF Done: E(UB3LYP) = -2249.52333632

Sum of electronic and zero-point Energies= -2249.178861

Sum of electronic and thermal Energies= -2249.154436

Sum of electronic and thermal Enthalpies= -2249.153492

Sum of electronic and thermal Free Energies= -2249.234029

6.1.20 *anti-anti-N-ortho,ortho'*-dimethoxyphenyl-BBTT 3j

6.1.20.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.425501	-2.388192	-0.375860
C 0	4.568988	-3.457963	-0.077975
C 0	3.211246	-3.250993	0.124834
C 0	2.685551	-1.952098	0.024615
C 0	3.564610	-0.887168	-0.284200
C 0	4.927796	-1.092425	-0.480175
C 0	1.336307	-1.495612	0.215058
C 0	1.192919	-0.153357	0.033525
S 0	2.709090	0.648760	-0.382072
S 0	-0.000195	-2.565805	0.727782
C 0	-1.336615	-1.495343	0.215256
C 0	-1.193060	-0.153098	0.033718
N 0	-0.000007	0.567841	0.084441
C 0	-2.686041	-1.951548	0.025469
C 0	-3.565034	-0.886415	-0.282841
S 0	-2.709234	0.649309	-0.381159
C 0	-3.211953	-3.250349	0.125847
C 0	-4.569821	-3.457024	-0.076333
C 0	-5.426284	-2.387045	-0.373627
C 0	-4.928370	-1.091375	-0.478126
C 0	0.000285	1.993921	0.125594
C 0	0.001470	2.654561	1.368304
C 0	0.001848	4.052913	1.414532
C 0	0.000912	4.768573	0.221330
C 0	-0.000361	4.137326	-1.018022
C 0	-0.000679	2.738337	-1.068805
O 0	-0.001873	2.012063	-2.210864
C 0	-0.002556	2.692688	-3.461874
O 0	0.002203	1.849792	2.455050
C 0	0.003384	2.440201	3.751531
H 0	6.483038	-2.569079	-0.529037

H 0	4.973404	-4.461075	-0.003920
H 0	2.555849	-4.084136	0.352174
H 0	5.587129	-0.264097	-0.713235
H 0	-2.556584	-4.083625	0.352777
H 0	-4.974397	-4.460058	-0.002069
H 0	-6.483972	-2.567663	-0.526086
H 0	-5.587669	-0.262883	-0.710693
H 0	0.002785	4.578484	2.358769
H 0	0.001196	5.852218	0.258807
H 0	-0.001024	4.726339	-1.924007
H 0	-0.003431	1.911207	-4.219049
H 0	-0.898030	3.311584	-3.575759
H 0	0.893238	3.310875	-3.577090
H 0	0.003671	1.606646	4.451001
H 0	0.899318	3.048836	3.908992
H 0	-0.891941	3.049376	3.910365

SCF Done: E(RB3LYP) = -2324.88713770

Sum of electronic and zero-point Energies= -2324.538575

Sum of electronic and thermal Energies= -2324.512873

Sum of electronic and thermal Enthalpies= -2324.511929

Sum of electronic and thermal Free Energies= -2324.596228

6.1.20.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0	5.454372	-2.354575	-0.304136
C 0	4.597785	-3.440707	-0.068999
C 0	3.231765	-3.250991	0.099021
C 0	2.698992	-1.952066	0.026888
C 0	3.579526	-0.870487	-0.215066
C 0	4.950010	-1.058251	-0.377802
C 0	1.339818	-1.511658	0.184497
C 0	1.192311	-0.163366	0.048858
S 0	2.715496	0.663804	-0.279300
S 0	0.000008	-2.621947	0.602438
C 0	-1.339807	-1.511664	0.184499
C 0	-1.192308	-0.163370	0.048863
N 0	0.000000	0.556263	0.096736
C 0	-2.698981	-1.952077	0.026897
C 0	-3.579521	-0.870503	-0.215051
S 0	-2.715498	0.663793	-0.279284
C 0	-3.231747	-3.251006	0.099027
C 0	-4.597767	-3.440728	-0.068989
C 0	-5.454360	-2.354599	-0.304122
C 0	-4.950004	-1.058273	-0.377785
C 0	-0.000003	1.985385	0.096334
C 0	0.000001	2.680285	1.321236
C 0	-0.000000	4.079205	1.325591
C 0	-0.000010	4.758434	0.110438
C 0	-0.000018	4.092002	-1.111277
C 0	-0.000011	2.692570	-1.121984
O 0	-0.000028	1.933300	-2.242582
C 0	-0.000040	2.584167	-3.517557
O 0	0.000010	1.908395	2.432631
C 0	0.000016	2.545661	3.714712
H 0	6.517424	-2.522358	-0.431043
H 0	5.008025	-4.442708	-0.016130
H 0	2.579653	-4.098055	0.280145
H 0	5.609329	-0.217726	-0.560736
H 0	-2.579631	-4.098068	0.280147
H 0	-5.008001	-4.442730	-0.016121
H 0	-6.517411	-2.522387	-0.431027
H 0	-5.609327	-0.217750	-0.560716
H 0	0.000006	4.633097	2.253317
H 0	-0.000014	5.842528	0.115979
H 0	-0.000030	4.655175	-2.033376

H 0	-0.000043	1.783019	-4.253187
H 0	-0.895392	3.198262	-3.644517
H 0	0.895305	3.198269	-3.644532
H 0	0.000018	1.736515	4.441561
H 0	0.895363	3.158385	3.848219
H 0	-0.895330	3.158386	3.848227

SCF Done: E(RB3LYP) = -2324.89871922

Sum of electronic and zero-point Energies= -2324.550188

Sum of electronic and thermal Energies= -2324.524511

Sum of electronic and thermal Enthalpies= -2324.523567

Sum of electronic and thermal Free Energies= -2324.607431

6.1.20.3 Minimum geometry of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent=dichlor

omethane) pop=full geom=check guess=read

0 1

C 0	5.434692	-2.317919	-0.274279
C 0	4.586986	-3.411864	-0.064083
C 0	3.223238	-3.235998	0.104928
C 0	2.685098	-1.942411	0.058772
C 0	3.555534	-0.852595	-0.157288
C 0	4.924652	-1.027139	-0.321907
C 0	1.327681	-1.515034	0.218321
C 0	1.183841	-0.166054	0.109265
S 0	2.689741	0.665150	-0.191282
S 0	-0.000001	-2.626829	0.604650
C 0	-1.327682	-1.515034	0.218320
C 0	-1.183842	-0.166054	0.109264
N 0	-0.000000	0.550593	0.175616
C 0	-2.685099	-1.942410	0.058771
C 0	-3.555534	-0.852594	-0.157289
S 0	-2.689741	0.665151	-0.191283
C 0	-3.223240	-3.235996	0.104928
C 0	-4.586988	-3.411862	-0.064084
C 0	-5.434693	-2.317917	-0.274280
C 0	-4.924653	-1.027137	-0.321908
C 0	0.000000	1.966181	0.072489
C 0	0.000000	2.745010	1.240359
C 0	0.000001	4.137016	1.140254
C 0	0.000001	4.720859	-0.119725
C 0	0.000001	3.968919	-1.286990
C 0	0.000001	2.576747	-1.192819
O 0	0.000001	1.738114	-2.242629
C 0	0.000004	2.295387	-3.547901
O 0	-0.000000	2.062099	2.397230
C 0	-0.000001	2.799029	3.610197
H 0	6.500002	-2.476580	-0.402617
H 0	5.004593	-4.412770	-0.031337
H 0	2.573915	-4.090679	0.267338
H 0	5.578725	-0.177380	-0.486218
H 0	-2.573917	-4.090678	0.267338
H 0	-5.004595	-4.412768	-0.031338
H 0	-6.500004	-2.476577	-0.402618
H 0	-5.578725	-0.177378	-0.486219
H 0	0.000000	4.759635	2.025108
H 0	0.000002	5.803497	-0.194758
H 0	0.000002	4.462423	-2.249791
H 0	0.000004	1.447980	-4.231037
H 0	-0.895584	2.900688	-3.718004
H 0	0.895592	2.900688	-3.718001
H 0	-0.000002	2.056972	4.406550
H 0	0.895530	3.422373	3.693123
H 0	-0.895532	3.422374	3.693122

SCF Done: E(RPBE1PBE) = -2323.13491391

Sum of electronic and zero-point Energies= -2322.782952

Sum of electronic and thermal Energies= -2322.757451

Sum of electronic and thermal Free Energies= -2322.840394

Sum of electronic and thermal Enthalpies= -2322.756507

6.1.20.4 TD-DFT calculation of ground state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p td=(singlets,nstates=24) PBE1PBE/6-311++g(d,p) scrf=(iefpcm,solvent =dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.8697 eV 432.04 nm f=0.1620

<TDDFT>HOMO -> LUMO 96.7%

<TDDFT> Excited State 2: Singlet-A 3.3854 eV 366.23 nm f=0.0032

<TDDFT>HOMO -> LUMO+1 96.2%

<TDDFT> Excited State 3: Singlet-A 3.6890 eV 336.09 nm f=0.0108

<TDDFT>HOMO -> LUMO+3 83.8%

<TDDFT>HOMO -> LUMO+6 7.1%

<TDDFT>HOMO -> LUMO+11 2.3%

<TDDFT> Excited State 4: Singlet-A 3.7460 eV 330.98 nm f=0.0130

<TDDFT>HOMO -> LUMO+2 79.2%

<TDDFT>HOMO -> LUMO+4 18.3%

<TDDFT> Excited State 5: Singlet-A 3.7886 eV 327.26 nm f=0.0174

<TDDFT>HOMO -> LUMO+2 5.3%

<TDDFT>HOMO -> LUMO+4 24.2%

<TDDFT>HOMO -> LUMO+5 58.7%

<TDDFT>HOMO -> LUMO+7 8.4%

<TDDFT> Excited State 6: Singlet-A 3.9244 eV 315.93 nm f=0.0060

<TDDFT>HOMO -> LUMO+3 12.3%

<TDDFT>HOMO -> LUMO+6 65.5%

<TDDFT>HOMO -> LUMO+8 7.1%

<TDDFT>HOMO -> LUMO+11 9.7%

<TDDFT> Excited State 7: Singlet-A 3.9506 eV 313.83 nm f=0.1026

<TDDFT>HOMO -> LUMO+2 12.6%

<TDDFT>HOMO -> LUMO+4 54.3%

<TDDFT>HOMO -> LUMO+5 26.6%

<TDDFT>HOMO -> LUMO+7 2.9%

<TDDFT> Excited State 8: Singlet-A 4.1924 eV 295.73 nm f=0.0055

<TDDFT>HOMO -> LUMO+5 8.9%

<TDDFT>HOMO -> LUMO+7 65.2%

<TDDFT>HOMO -> LUMO+9 18.8%

<TDDFT>HOMO -> LUMO+13 2.4%

<TDDFT> Excited State 9: Singlet-A 4.2614 eV 290.95 nm f=0.0099

<TDDFT>HOMO -> LUMO+6 12.9%

<TDDFT>HOMO -> LUMO+8 85.1%

<TDDFT> Excited State 10: Singlet-A 4.5115 eV 274.82 nm f=0.0013

<TDDFT>HOMO -> LUMO+7 17.2%

<TDDFT>HOMO -> LUMO+9 71.1%

<TDDFT>HOMO -> LUMO+12 5.9%

<TDDFT>HOMO -> LUMO+13 2.2%

<TDDFT> Excited State 11: Singlet-A 4.5822 eV 270.58 nm f=0.0565

<TDDFT>HOMO-2 -> LUMO 62.8%

<TDDFT>HOMO-1 -> LUMO+4 2.2%

<TDDFT>HOMO -> LUMO+11 10.0%

<TDDFT>HOMO -> LUMO+14 5.1%

<TDDFT>HOMO -> LUMO+15 11.7%

<TDDFT> Excited State 12: Singlet-A 4.6262 eV 268.01 nm f=0.1265

<TDDFT>HOMO-2 -> LUMO+2 3.9%

<TDDFT>HOMO-1 -> LUMO 86.5%

<TDDFT> Excited State 13: Singlet-A 4.6803 eV 264.90 nm f=0.1403

<TDDFT>HOMO-2 -> LUMO 14.9%

<TDDFT>HOMO -> LUMO+6 8.2%

<TDDFT>HOMO -> LUMO+8 3.7%

<TDDFT>HOMO -> LUMO+11 63.4%

<TDDFT>HOMO -> LUMO+14 2.2%

<TDDFT> Excited State 14: Singlet-A 4.7548 eV 260.76 nm f=0.0005

<TDDFT>HOMO -> LUMO+10 93.0%

<TDDFT>HOMO -> LUMO+17 3.1%

<TDDFT> Excited State 15: Singlet-A 4.8100 eV 257.77 nm f=0.0035

<TDDFT>HOMO -> LUMO+7 4.9%

<TDDFT>HOMO -> LUMO+9 2.3%

<TDDFT>HOMO -> LUMO+12 82.4%

<TDDFT>HOMO -> LUMO+20 3.4%

<TDDFT> Excited State 16: Singlet-A 4.8325 eV 256.56 nm f=0.3322

<TDDFT>HOMO-2 -> LUMO 11.6%

<TDDFT>HOMO -> LUMO+6 2.1%

<TDDFT>HOMO -> LUMO+11 2.9%

<TDDFT>HOMO -> LUMO+14 17.0%

<TDDFT>HOMO -> LUMO+15 59.4%

<TDDFT> Excited State 17: Singlet-A 4.8533 eV 255.47 nm f=0.0116

<TDDFT>HOMO-3 -> LUMO 88.3%

<TDDFT>HOMO-3 -> LUMO+1 8.5%

<TDDFT> Excited State 18: Singlet-A 4.9144 eV 252.29 nm f=0.0765

<TDDFT>HOMO-5 -> LUMO+8 7.7%

<TDDFT>HOMO-3 -> LUMO 10.3%

<TDDFT>HOMO-3 -> LUMO+1 70.5%

<TDDFT>HOMO-1 -> LUMO+1 5.3%

<TDDFT> Excited State 19: Singlet-A 4.9833 eV 248.80 nm f=0.0003

<TDDFT>HOMO-3 -> LUMO+1 3.9%

<TDDFT>HOMO-2 -> LUMO+5 4.2%

<TDDFT>HOMO-1 -> LUMO+1 50.9%

<TDDFT>HOMO-1 -> LUMO+6 2.7%

<TDDFT>HOMO -> LUMO+13 30.8%

<TDDFT> Excited State 20: Singlet-A 4.9853 eV 248.70 nm f=0.0123

<TDDFT>HOMO-1 -> LUMO+1 27.2%

<TDDFT>HOMO -> LUMO+9 3.6%

<TDDFT>HOMO -> LUMO+13 58.8%

<TDDFT> Excited State 21: Singlet-A 5.0190 eV 247.03 nm f=0.0090

<TDDFT>HOMO-2 -> LUMO+1 44.4%

<TDDFT>HOMO-1 -> LUMO+4 2.6%

<TDDFT>HOMO-1 -> LUMO+5 9.9%

<TDDFT>HOMO -> LUMO+14 16.4%

<TDDFT>HOMO -> LUMO+15 7.6%

<TDDFT>HOMO -> LUMO+18 4.1%

<TDDFT>HOMO -> LUMO+24 4.4%

<TDDFT> Excited State 22: Singlet-A 5.0337 eV 246.31 nm f=0.0039

<TDDFT>HOMO-2 -> LUMO+1 30.5%

<TDDFT>HOMO -> LUMO+11 3.6%

<TDDFT>HOMO -> LUMO+14 37.7%

<TDDFT>HOMO -> LUMO+15 11.4%

<TDDFT>HOMO -> LUMO+18 3.6%

<TDDFT>HOMO -> LUMO+24 3.8%

<TDDFT> Excited State 23: Singlet-A 5.0534 eV 245.35 nm f=0.0183

<TDDFT>HOMO-4 -> LUMO 54.6%

<TDDFT>HOMO-2 -> LUMO+4 7.2%

<TDDFT>HOMO-1 -> LUMO 2.5%

<TDDFT>HOMO-1 -> LUMO+3 21.9%

<TDDFT> Excited State 24: Singlet-A 5.1296 eV 241.70 nm f=0.0052

<TDDFT>HOMO-2 -> LUMO+1 3.1%

<TDDFT>HOMO-1 -> LUMO+5 5.1%

<TDDFT>HOMO -> LUMO+14 17.3%

<TDDFT>HOMO -> LUMO+15 3.4%

<TDDFT>HOMO -> LUMO+18 40.3%

<TDDFT>HOMO -> LUMO+22 2.5%

<TDDFT>HOMO -> LUMO+24 19.3%

6.1.20.5 Minimum geometry of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent= dichloromethane) geom=check guess=read

0 1

C 0	5.477400	-2.300541	-0.000058
C 0	4.622415	-3.405740	-0.000066
C 0	3.245091	-3.250297	-0.000055
C 0	2.689234	-1.955741	-0.000024
C 0	3.575513	-0.848294	-0.000022
C 0	4.949939	-1.006439	-0.000038
C 0	1.329685	-1.542730	-0.000010
C 0	1.184074	-0.134608	-0.000012
S 0	2.723185	0.698864	0.000017
S 0	-0.000001	-2.630791	0.000196
C 0	-1.329686	-1.542729	-0.000008
C 0	-1.184075	-0.134607	-0.000010
N 0	0.000000	0.531523	-0.000020
C 0	-2.689235	-1.955739	-0.000022
C 0	-3.575514	-0.848292	-0.000018
S 0	-2.723185	0.698866	0.000021
C 0	-3.245093	-3.250295	-0.000053
C 0	-4.622417	-3.405737	-0.000064
C 0	-5.477402	-2.300537	-0.000055
C 0	-4.949940	-1.006436	-0.000035
C 0	0.000001	1.960525	-0.000004
C 0	0.000003	2.646181	1.222347
C 0	0.000004	4.041303	1.217058
C 0	0.000003	4.709919	0.000013
C 0	-0.000000	4.041316	-1.217037
C 0	-0.000001	2.646192	-1.222349
O 0	-0.000004	1.878724	-2.323219
C 0	-0.000006	2.521445	-3.589787
O 0	0.000005	1.878695	2.323213
C 0	0.000008	2.521394	3.589789
H 0	6.552510	-2.442206	-0.000067
H 0	5.042665	-4.406489	-0.000087
H 0	2.598148	-4.122143	-0.000070
H 0	5.607364	-0.143256	-0.000035
H 0	-2.598151	-4.122141	-0.000068

H 0 -5.042668 -4.406485 -0.000084
H 0 -6.552512 -2.442202 -0.000063
H 0 -5.607365 -0.143252 -0.000031
H 0 0.000007 4.600132 2.143344
H 0 0.000004 5.794975 0.000018
H 0 -0.000001 4.600157 -2.143317
H 0 -0.000008 1.720466 -4.326570
H 0 -0.895909 3.136003 -3.718585
H 0 0.895896 3.136003 -3.718589
H 0 0.000009 1.720409 4.326566
H 0 0.895910 3.135951 3.718600
H 0 -0.895892 3.135953 3.718604

SCF Done: E(RPBE1PBE) = -2323.12400312

Sum of electronic and zero-point Energies= -2322.693963

Sum of electronic and thermal Energies= -2322.667564

Sum of electronic and thermal Enthalpies= -2322.666620

Sum of electronic and thermal Free Energies= -2322.752904

6.1.20.6 TD-DFT calculation of excited state of native BBTT under IEFPCM variation of PCM (PBE1PBE/6-311++G**, IEFPCM CH_2Cl_2)

#p opt td=(nstates=4) PBE1PBE/6-311++g(d,p) freq scrf=(iefpcm,solvent=

dichloromethane) geom=check guess=read

<TDDFT> Excited State 1: Singlet-A 2.2344 eV 554.89 nm f=0.1315

<TDDFT>HOMO -> LUMO 98.3%

<TDDFT> Excited State 2: Singlet-A 3.0161 eV 411.07 nm f=0.0000

<TDDFT>HOMO -> LUMO+1 98.2%

<TDDFT> Excited State 3: Singlet-A 3.3784 eV 366.99 nm f=0.0001

<TDDFT>HOMO -> LUMO+5 93.9%

<TDDFT>HOMO -> LUMO+6 3.6%

<TDDFT> Excited State 4: Singlet-A 3.3981 eV 364.86 nm f=0.0114

<TDDFT>HOMO -> LUMO+2 79.0%

<TDDFT>HOMO -> LUMO+4 19.2%

6.1.20.7 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(smd,solvent=dichloromet

hane) pop=full geom=checkpoint guess=read

0 1

C 0 5.470625 -2.338195 -0.253408
C 0 4.612325 -3.431495 -0.061881
C 0 3.241975 -3.250055 0.079267
C 0 2.706454 -1.950999 0.023763
C 0 3.589552 -0.862340 -0.173248
C 0 4.963976 -1.041657 -0.309710
C 0 1.342063 -1.517871 0.156363
C 0 1.192195 -0.167378 0.047032
S 0 2.720960 0.671197 -0.222805
S 0 0.000007 -2.649310 0.508343
C 0 -1.342060 -1.517870 0.156413
C 0 -1.192195 -0.167377 0.047082
N 0 0.000001 0.551613 0.088666
C 0 -2.706452 -1.951000 0.023833
C 0 -3.589555 -0.862342 -0.173166
S 0 -2.720970 0.671199 -0.222704
C 0 -3.241968 -3.250058 0.079330
C 0 -4.612320 -3.431501 -0.061810
C 0 -5.470623 -2.338203 -0.253325
C 0 -4.963979 -1.041663 -0.309624

C 0	0.000001	1.981398	0.078388
C 0	0.000054	2.685097	1.299105
C 0	0.000059	4.084414	1.291593
C 0	0.000001	4.753289	0.070513
C 0	-0.000057	4.077948	-1.146598
C 0	-0.000053	2.678198	-1.146934
O 0	-0.000113	1.910178	-2.259597
C 0	-0.000175	2.549351	-3.542602
O 0	0.000112	1.922414	2.415187
C 0	0.000168	2.568958	3.694812
H 0	6.537111	-2.500289	-0.359582
H 0	5.024622	-4.433507	-0.021685
H 0	2.591558	-4.105115	0.227942
H 0	5.625337	-0.195698	-0.459282
H 0	-2.591548	-4.105117	0.227991
H 0	-5.024613	-4.433515	-0.021619
H 0	-6.537110	-2.500299	-0.359492
H 0	-5.625344	-0.195705	-0.459183
H 0	0.000106	4.645972	2.215067
H 0	0.000002	5.837948	0.067486
H 0	-0.000104	4.634194	-2.073257
H 0	-0.000228	1.740096	-4.270928
H 0	-0.896441	3.160836	-3.677478
H 0	0.896093	3.160810	-3.677580
H 0	0.000220	1.763633	4.427488
H 0	0.896424	3.181245	3.826081
H 0	-0.896093	3.181218	3.826176

SCF Done: E(RB3LYP) = -2324.92171459

Sum of electronic and zero-point Energies= -2324.573159

Sum of electronic and thermal Energies= -2324.547525

Sum of electronic and thermal Enthalpies= -2324.546581

Sum of electronic and thermal Free Energies= -2324.630484

6.1.20.8 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.481580	-2.287456	-0.000097
C 0	-4.631043	-3.403868	-0.000103
C 0	-3.254728	-3.247333	-0.000085
C 0	-2.712579	-1.950412	-0.000070
C 0	-3.585279	-0.839035	-0.000076
C 0	-4.967946	-0.994604	-0.000084
C 0	-1.337260	-1.534839	-0.000011
C 0	-1.190617	-0.155075	-0.000008
S 0	-2.715179	0.698388	-0.000054
S 0	0.000023	-2.655522	0.000001
C 0	1.337291	-1.534821	0.000009
C 0	1.190626	-0.155059	0.000011
N 0	0.000000	0.528243	0.000001
C 0	2.712617	-1.950371	0.000068
C 0	3.585299	-0.838980	0.000078
S 0	2.715174	0.698430	0.000059
C 0	3.254788	-3.247284	0.000078
C 0	4.631105	-3.403796	0.000094
C 0	5.481624	-2.287370	0.000092
C 0	4.967969	-0.994526	0.000085
C 0	-0.000008	1.971196	0.000000
C 0	0.000075	2.656028	-1.228768
C 0	0.000049	4.053298	-1.220613
C 0	-0.000066	4.722851	-0.000002
C 0	-0.000156	4.053299	1.220611
C 0	-0.000134	2.656028	1.228769
O 0	-0.000206	1.876881	2.330368
C 0	-0.000359	2.501011	3.622137
O 0	0.000170	1.876884	-2.330368
C 0	0.000327	2.501027	-3.622130
H 0	-6.555160	-2.432024	-0.000097
H 0	-5.057123	-4.399523	-0.000119
H 0	-2.607066	-4.116728	-0.000109

H 0	-5.629282	-0.136745	-0.000082
H 0	2.607140	-4.116690	0.000099
H 0	5.057202	-4.399444	0.000106
H 0	6.555206	-2.431920	0.000091
H 0	5.629290	-0.136656	0.000087
H 0	0.000097	4.613181	-2.144614
H 0	-0.000083	5.806614	-0.000002
H 0	-0.000227	4.613184	2.144610
H 0	-0.000480	1.683348	4.338838
H 0	0.896203	3.110472	3.759544
H 0	-0.896928	3.110514	3.759324
H 0	0.000494	1.683370	-4.338837
H 0	-0.896255	3.110456	-3.759547
H 0	0.896876	3.110565	-3.759296

SCF Done: E(UB3LYP) = -2324.67872265

Sum of electronic and zero-point Energies= -2324.329056

Sum of electronic and thermal Energies= -2324.303582

Sum of electronic and thermal Enthalpies= -2324.302638

Sum of electronic and thermal Free Energies= -2324.385693

6.1.20.9 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpcm,solvent=dichloromethane) geom=check guess=read

0 1

C 0	-5.482498	-2.284887	-0.000021
C 0	-4.632167	-3.402009	-0.000012
C 0	-3.254876	-3.246749	-0.000006
C 0	-2.712125	-1.950110	-0.000009
C 0	-3.584235	-0.837961	-0.000017
C 0	-4.967724	-0.992056	-0.000024
C 0	-1.335563	-1.536653	-0.000004
C 0	-1.189859	-0.157417	-0.000005
S 0	-2.713291	0.698456	-0.000014
S 0	-0.000008	-2.657461	0.000000
C 0	1.335554	-1.536659	0.000003
C 0	1.189856	-0.157423	0.000005
N 0	-0.000000	0.526013	0.000000
C 0	2.712114	-1.950122	0.000008
C 0	3.584229	-0.837977	0.000017
S 0	2.713291	0.698443	0.000015
C 0	3.254859	-3.246764	0.000004
C 0	4.632150	-3.402030	0.000011
C 0	5.482485	-2.284911	0.000021
C 0	4.967717	-0.992078	0.000024
C 0	0.000004	1.968759	0.000000
C 0	0.000020	2.653566	-1.228707
C 0	0.000027	4.051097	-1.221118
C 0	0.000015	4.720396	0.000000
C 0	-0.000003	4.051097	1.221118
C 0	-0.000008	2.653566	1.228707
O 0	-0.000022	1.876108	2.331531
C 0	-0.000063	2.505004	3.622528
O 0	0.000027	1.876109	-2.331531
C 0	0.000091	2.505006	-3.622527
H 0	-6.556265	-2.428167	-0.000027
H 0	-5.058187	-4.397764	-0.000010
H 0	-2.607781	-4.116030	0.000001
H 0	-5.627356	-0.133273	-0.000031
H 0	2.607760	-4.116042	-0.000003
H 0	5.058164	-4.397786	0.000008
H 0	6.556252	-2.428196	0.000027
H 0	5.627352	-0.133298	0.000033
H 0	0.000041	4.610228	-2.145377
H 0	0.000020	5.804111	0.000000
H 0	-0.000012	4.610229	2.145377
H 0	-0.000088	1.689368	4.341379

H 0	0.895996	3.115073	3.756591
H 0	-0.896128	3.115076	3.756533
H 0	0.000116	1.689372	-4.341379
H 0	-0.895959	3.115086	-3.756600
H 0	0.896165	3.115069	-3.756519

SCF Done: E(UB3LYP) = -2324.72683778

Sum of electronic and zero-point Energies= -2324.377352

Sum of electronic and thermal Energies= -2324.351815

Sum of electronic and thermal Enthalpies= -2324.350871

Sum of electronic and thermal Free Energies= -2324.434437

6.1.20.10 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt freq=noraman ub3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=di

chloromethane)

0 1

C 0	5.480242	-2.290084	0.028172
C 0	4.628056	-3.405708	0.021093
C 0	3.250991	-3.248555	0.013921
C 0	2.711928	-1.950342	0.013755
C 0	3.586038	-0.839968	0.020987
C 0	4.969020	-0.995489	0.028247
C 0	1.336719	-1.534235	0.006437
C 0	1.189313	-0.155660	0.007109
S 0	2.715100	0.698616	0.018796
S 0	0.000010	-2.655189	-0.000002
C 0	-1.336704	-1.534241	-0.006446
C 0	-1.189307	-0.155666	-0.007120
N 0	0.000001	0.528223	-0.000006
C 0	-2.711909	-1.950360	-0.013759
C 0	-3.586028	-0.839993	-0.020991
S 0	-2.715102	0.698600	-0.018806
C 0	-3.250958	-3.248577	-0.013921
C 0	-4.628022	-3.405745	-0.021089
C 0	-5.480218	-2.290129	-0.028169
C 0	-4.969009	-0.995528	-0.028248
C 0	-0.000001	1.971655	0.000001
C 0	-0.025208	2.655668	1.229841
C 0	-0.024143	4.053402	1.221518
C 0	-0.000018	4.721879	0.000016
C 0	0.024113	4.053415	-1.221492
C 0	0.025191	2.655680	-1.229833
O 0	0.047352	1.877742	-2.331161
C 0	0.098936	2.506338	-3.623804
O 0	-0.047364	1.877719	2.331162
C 0	-0.099000	2.506311	3.623803
H 0	6.553947	-2.436027	0.033545
H 0	5.052701	-4.402389	0.021091
H 0	2.602887	-4.117828	0.008208
H 0	5.632057	-0.138508	0.033617
H 0	-2.602845	-4.117844	-0.008206
H 0	-5.052658	-4.402429	-0.021084
H 0	-6.553922	-2.436082	-0.033540
H 0	-5.632056	-0.138554	-0.033619
H 0	-0.041325	4.613397	2.145583
H 0	-0.000022	5.806232	0.000022
H 0	0.041285	4.613422	-2.145549
H 0	0.109764	1.689233	-4.342498
H 0	-0.783652	3.128460	-3.789088
H 0	1.009074	3.101614	-3.729347
H 0	-0.109826	1.689205	4.342496
H 0	0.783566	3.128456	3.789115
H 0	-1.009157	3.101565	3.729319

SCF Done: E(UB3LYP) = -2324.75359912

Sum of electronic and zero-point Energies= -2324.403886

Sum of electronic and thermal Energies= -2324.378512

Sum of electronic and thermal Enthalpies= -2324.377568

Sum of electronic and thermal Free Energies= -2324.460623

6.1.20.11 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc,tight) freq=noraman b3lyp/6-311++g(d,p) scrf =(iefpcm,solvent=dichloromethane)

0 1

C 0	-5.502930	-2.301182	-0.000000
C 0	-4.642180	-3.408926	-0.000001
C 0	-3.262686	-3.242968	-0.000004
C 0	-2.721339	-1.945292	-0.000006
C 0	-3.607081	-0.841346	-0.000006
C 0	-4.989802	-1.005864	-0.000002
C 0	-1.345080	-1.531559	-0.000009
C 0	-1.193235	-0.177113	-0.000010
S 0	-2.730139	0.686919	-0.000009
S 0	-0.000003	-2.713450	-0.000016
C 0	1.345076	-1.531562	-0.000011
C 0	1.193233	-0.177115	-0.000010
N 0	0.000000	0.540883	-0.000016
C 0	2.721335	-1.945297	-0.000005
C 0	3.607079	-0.841352	0.000000
S 0	2.730140	0.686914	-0.000002
C 0	3.262680	-3.242973	-0.000005
C 0	4.642173	-3.408934	0.000000
C 0	5.502925	-2.301191	0.000006
C 0	4.989800	-1.005872	0.000006
C 0	0.000001	1.969115	0.000001
C 0	0.000004	2.669721	-1.221981
C 0	0.000006	4.068840	-1.218746
C 0	0.000006	4.741300	0.000033
C 0	0.000003	4.068813	1.218796
C 0	0.000000	2.669694	1.221999
O 0	-0.000003	1.903212	2.337031
O 0	0.000003	1.903265	-2.337031
C 0	0.000017	2.546349	-3.616303
C 0	-0.000007	2.546266	3.616319
H 0	-6.576227	-2.450641	0.000002
H 0	-5.059287	-4.409472	0.000001
H 0	-2.608833	-4.107945	-0.000004
H 0	-5.652914	-0.148625	-0.000002
H 0	2.608825	-4.107949	-0.000010
H 0	5.059278	-4.409481	0.000000
H 0	6.576222	-2.450652	0.000010
H 0	5.652913	-0.148634	0.000010
H 0	0.000008	4.627692	-2.143498
H 0	0.000009	5.825415	0.000045
H 0	0.000004	4.627644	2.143561
H 0	0.895410	3.159586	-3.746843
H 0	0.000018	1.740564	-4.346846
H 0	-0.895369	3.159594	-3.746858
H 0	-0.000022	1.740463	4.346843
H 0	0.895388	3.159493	3.746888
H 0	-0.895390	3.159513	3.746873

SCF Done: E(RB3LYP) = -2324.89856337

Sum of electronic and zero-point Energies= -2324.550109

Sum of electronic and thermal Energies= -2324.525312

Sum of electronic and thermal Enthalpies= -2324.524368

Sum of electronic and thermal Free Energies= -2324.604854

6.2 *anti-anti-N-para*-substituted-phenyl-BBTT

6.2.1 *anti-anti-N-para*-cyanophenyl-BBTT

6.2.1.1 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=verytight int=ultrafine freq=noraman rb3lyp/6-311++g(d,p) scrf=

(iefpcm,solvent=dichloromethane) pop=full

0 1

C 0	-2.919510	-5.038823	0.278623
C 0	-3.447568	-4.287939	-0.784635
C 0	-2.909430	-3.054007	-1.119249
C 0	-1.822281	-2.554672	-0.384527
C 0	-1.310756	-3.317621	0.691731
C 0	-1.848387	-4.562250	1.025055
C 0	-1.088663	-1.324728	-0.549610
C 0	-0.065875	-1.175282	0.334382
S 0	0.016875	-2.499272	1.508499
S 0	-1.519013	0.000000	-1.662601
C 0	-1.088662	1.324729	-0.549610
C 0	-0.065875	1.175282	0.334382
N 0	0.716266	-0.000000	0.422742
C 0	-1.822280	2.554673	-0.384527
C 0	-1.310755	3.317621	0.691731
S 0	0.016876	2.499271	1.508499
C 0	-2.909428	3.054009	-1.119249
C 0	-3.447566	4.287941	-0.784635
C 0	-2.919507	5.038825	0.278624
C 0	-1.848384	4.562251	1.025056
C 0	2.097389	-0.000001	0.127089
C 0	2.800013	1.209451	-0.022010
C 0	4.158867	1.208279	-0.289125
C 0	4.859644	-0.000001	-0.420478
C 0	4.158867	-1.208281	-0.289123
C 0	2.800013	-1.209452	-0.022009
C 0	6.259369	-0.000001	-0.691210
N 0	7.395910	-0.000002	-0.910833
H 0	-3.353251	-6.001051	0.524271
H 0	-4.285588	-4.678448	-1.349896
H 0	-3.320759	-2.478014	-1.940199
H 0	-1.446142	-5.140245	1.848446
H 0	-3.320758	2.478016	-1.940199
H 0	-4.285585	4.678451	-1.349895
H 0	-3.353248	6.001053	0.524272
H 0	-1.446139	5.140245	1.848446
H 0	2.287091	2.156122	0.062247
H 0	4.680420	2.150578	-0.401765
H 0	4.680419	-2.150580	-0.401763
H 0	2.287090	-2.156123	0.062249

SCF Done: E(RB3LYP) = -2188.05490327

Sum of electronic and zero-point Energies= -2187.772054

Sum of electronic and thermal Energies= -2187.750159

Sum of electronic and thermal Enthalpies= -2187.749215

Sum of electronic and thermal Free Energies= -2187.824810

6.2.1.2 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpc

m,solvent=dichloromethane)

0 1

C 0	-5.482014	-2.339393	0.000068
C 0	-4.628687	-3.454185	0.000386
C 0	-3.252113	-3.295502	0.000374

C 0	-2.713317	-1.997142	0.000028
C 0	-3.588637	-0.888219	-0.000253
C 0	-4.971653	-1.044976	-0.000255
C 0	-1.337857	-1.580686	0.000058
C 0	-1.194682	-0.200892	-0.000196
S 0	-2.722446	0.650259	-0.000518
S 0	-0.003791	-2.702482	0.000176
C 0	1.333435	-1.584432	0.000041
C 0	1.194011	-0.204240	-0.000029
N 0	0.000626	0.479610	-0.000119
C 0	2.707779	-2.004601	0.000053
C 0	3.586031	-0.897986	-0.000053
S 0	2.724017	0.642746	-0.000132
C 0	3.243225	-3.304366	0.000074
C 0	4.619388	-3.466599	0.000010
C 0	5.475630	-2.354036	-0.000080
C 0	4.968625	-1.058303	-0.000113
C 0	0.002719	1.933043	-0.000012
C 0	0.003626	2.607882	1.218732
C 0	0.005558	3.997003	1.218579
C 0	0.006542	4.690506	0.000168
C 0	0.005612	3.997164	-1.218328
C 0	0.003690	2.608038	-1.218657
C 0	0.008512	6.122885	0.000250
N 0	0.010100	7.277816	0.000323
H 0	-6.555293	-2.485735	0.000089
H 0	-5.052100	-4.450959	0.000666
H 0	-2.602884	-4.163124	0.000621
H 0	-5.633761	-0.188222	-0.000478
H 0	2.591805	-4.170349	0.000153
H 0	5.040205	-4.464472	0.000014
H 0	6.548522	-2.503183	-0.000129
H 0	5.632887	-0.203221	-0.000182
H 0	0.002844	2.055943	2.149998
H 0	0.006296	4.540355	2.154235
H 0	0.006385	4.540634	-2.153916
H 0	0.002992	2.056213	-2.149990

SCF Done: E(UB3LYP) = -2187.87382936

Sum of electronic and zero-point Energies= -2187.590657

Sum of electronic and thermal Energies= -2187.568582

Sum of electronic and thermal Enthalpies= -2187.567638

Sum of electronic and thermal Free Energies= -2187.644848

6.2.2 *anti-anti-N-para*-chlorophenyl-BBTT

6.2.2.1 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0	2.626949	-5.348614	-0.464710
C 0	3.648931	-4.504258	-0.004134
C 0	3.397377	-3.168641	0.281894
C 0	2.102406	-2.654690	0.100776
C 0	1.087150	-3.520127	-0.371747
C 0	1.335478	-4.862679	-0.650334
C 0	1.598559	-1.331823	0.356365
C 0	0.274707	-1.192301	0.067334
S 0	-0.453177	-2.680538	-0.549874
S 0	2.567328	0.003151	1.047861
C 0	1.595115	1.335654	0.356471
C 0	0.271681	1.192604	0.067298
N 0	-0.450749	-0.000833	0.133785
C 0	2.095427	2.659858	0.100755
C 0	1.077856	3.522411	-0.372053
S 0	-0.460095	2.678723	-0.550208
C 0	3.388976	3.177401	0.281899
C 0	3.636882	4.513636	-0.004325

C 0	2.612647	5.355122	-0.465193
C 0	1.322567	4.865632	-0.650923
C 0	-1.889684	-0.002507	0.144365
C 0	-2.568488	-0.001983	1.363545
C 0	-3.959728	-0.003437	1.386957
C 0	-4.654656	-0.005422	0.180159
C 0	-3.992867	-0.005989	-1.043294
C 0	-2.599692	-0.004488	-1.056980
Cl 0	-6.414129	-0.007228	0.203926
H 0	2.842018	-6.388483	-0.680763
H 0	4.648562	-4.900743	0.131842
H 0	4.192486	-2.523586	0.638319
H 0	0.545811	-5.512779	-1.008418
H 0	4.185853	2.534611	0.638473
H 0	4.635395	4.912876	0.131736
H 0	2.824906	6.395574	-0.681316
H 0	0.531156	5.513454	-1.009277
H 0	-2.007360	-0.000437	2.290054
H 0	-4.494161	-0.003046	2.327966
H 0	-4.551357	-0.007521	-1.970120
H 0	-2.068312	-0.004763	-2.000944

SCF Done: E(RB3LYP) = -2555.40668359

Sum of electronic and zero-point Energies= -2555.132567

Sum of electronic and thermal Energies= -2555.110958

Sum of electronic and thermal Enthalpies= -2555.110014

Sum of electronic and thermal Free Energies= -2555.186001

6.2.2.2 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpc

m,solvent=dichloromethane)

0 1

C 0	2.395252	5.500970	0.000289
C 0	3.517655	4.657592	0.000024
C 0	3.371285	3.279592	-0.000147
C 0	2.077784	2.729060	-0.000008
C 0	0.960865	3.594368	0.000160
C 0	1.105599	4.978762	0.000326
C 0	1.672992	1.350063	-0.000152
C 0	0.294312	1.194986	-0.000162
S 0	-0.570028	2.715093	0.000051
S 0	2.805130	0.024396	0.000243
C 0	1.696523	-1.320906	0.000112
C 0	0.315332	-1.190739	-0.000026
N 0	-0.378153	-0.003901	-0.000045
C 0	2.126148	-2.692263	0.000025
C 0	1.025405	-3.577988	-0.000198
S 0	-0.521579	-2.726405	-0.000324
C 0	3.429664	-3.218364	0.000139
C 0	3.601929	-4.593340	-0.000002
C 0	2.495424	-5.457428	-0.000274
C 0	1.196186	-4.959490	-0.000380
C 0	-1.831532	-0.016409	-0.000017
C 0	-2.510435	-0.023694	1.216351
C 0	-3.901420	-0.035480	1.216686
C 0	-4.579815	-0.039673	0.000064
C 0	-3.901504	-0.032572	-1.216588
C 0	-2.510511	-0.020753	-1.216337
Cl 0	-6.332623	-0.053969	0.000088
H 0	2.531997	6.575536	0.000471
H 0	4.510642	5.089882	-0.000080
H 0	4.244839	2.638296	-0.000409
H 0	0.242727	5.632899	0.000529
H 0	4.290743	-2.560452	0.000344
H 0	4.602804	-5.007024	0.000105
H 0	2.652127	-6.529268	-0.000422
H 0	0.345981	-5.630058	-0.000629

H 0 -1.961934 -0.019994 2.150016

H 0 -4.447595 -0.041164 2.150452

H 0 -4.447755 -0.036113 -2.150322

H 0 -1.962114 -0.014864 -2.150047

SCF Done: E(UB3LYP) = -2555.22987215

Sum of electronic and zero-point Energies= -2554.954937

Sum of electronic and thermal Energies= -2554.933470

Sum of electronic and thermal Enthalpies= -2554.932526

Sum of electronic and thermal Free Energies= -2555.008364

6.2.3 *anti-anti-N-para*-fluorophenyl-BBTT

6.2.3.1 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0 -5.352724 -2.348514 -0.479077

C 0 -4.509104 -3.378662 -0.035664

C 0 -3.172727 -3.133453 0.252360

C 0 -2.657123 -1.836508 0.090703

C 0 -3.521933 -0.812813 -0.364527

C 0 -4.865205 -1.054964 -0.645177

C 0 -1.333030 -1.338611 0.351401

C 0 -1.191974 -0.010647 0.082238

S 0 -2.680511 0.728932 -0.519955

S 0 0.001090 -2.319837 1.026887

C 0 1.334362 -1.337414 0.351423

C 0 1.192126 -0.009576 0.082208

N 0 -0.000211 0.713279 0.158064

C 0 2.658909 -1.834156 0.090863

C 0 3.522872 -0.809724 -0.364298

S 0 2.680111 0.731307 -0.519821

C 0 3.175663 -3.130636 0.252629

C 0 4.512285 -3.374665 -0.035266

C 0 5.355029 -2.343797 -0.478660

C 0 4.866371 -1.050682 -0.644837

C 0 -0.000974 2.152367 0.173744

C 0 -0.002627 2.825686 1.396973

C 0 -0.003465 4.216832 1.426644

C 0 -0.002599 4.900382 0.219782

C 0 -0.000979 4.259347 -1.008521

C 0 -0.000176 2.866254 -1.026411

F 0 -0.003410 6.257419 0.243764

H 0 -6.393215 -2.558787 -0.696951

H 0 -4.906763 -4.379750 0.085315

H 0 -2.528343 -3.935006 0.595328

H 0 -5.514671 -0.258888 -0.989999

H 0 2.531982 -3.932756 0.595591

H 0 4.910812 -4.375400 0.085786

H 0 6.395726 -2.553152 -0.696426

H 0 5.515157 -0.254039 -0.989628

H 0 -0.003234 2.259087 2.319981

H 0 -0.004747 4.763226 2.361089

H 0 -0.000400 4.836499 -1.924229

H 0 0.000963 2.336535 -1.971145

SCF Done: E(RB3LYP) = -2195.05316484

Sum of electronic and zero-point Energies= -2194.777701

Sum of electronic and thermal Energies= -2194.756498

Sum of electronic and thermal Enthalpies= -2194.755554

Sum of electronic and thermal Free Energies= -2194.830132

6.2.3.2 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpc

m,solvent=dichloromethane)

0 1

C 0	-5.479636	-2.182689	-0.000039
C 0	-4.626130	-3.297375	0.000206
C 0	-3.249531	-3.138368	0.000239
C 0	-2.710824	-1.839951	0.000022
C 0	-3.586136	-0.730775	-0.000207
C 0	-4.969182	-0.888313	-0.000253
C 0	-1.335540	-1.422983	0.000100
C 0	-1.192566	-0.042991	-0.000080
S 0	-2.720399	0.807930	-0.000381
S 0	-0.000000	-2.543437	0.000279
C 0	1.335540	-1.422985	0.000071
C 0	1.192566	-0.042990	0.000073
N 0	0.000001	0.640470	0.000030
C 0	2.710821	-1.839952	0.000035
C 0	3.586134	-0.730774	0.000013
S 0	2.720400	0.807919	0.000070
C 0	3.249530	-3.138369	-0.000092
C 0	4.626129	-3.297377	-0.000208
C 0	5.479635	-2.182690	-0.000216
C 0	4.969180	-0.888315	-0.000110
C 0	-0.000003	2.093744	0.000043
C 0	-0.000030	2.772107	1.217930
C 0	-0.000025	4.162872	1.219588
C 0	0.000006	4.824466	0.000086
C 0	0.000027	4.162910	-1.219436
C 0	0.000024	2.772144	-1.217823
F 0	0.000008	6.175378	0.000106
H 0	-6.552920	-2.329161	-0.000057
H 0	-5.049361	-4.294256	0.000383
H 0	-2.600142	-4.005910	0.000415
H 0	-5.631374	-0.031567	-0.000439
H 0	2.600140	-4.005909	-0.000091
H 0	5.049361	-4.294256	-0.000311
H 0	6.552919	-2.329162	-0.000318
H 0	5.631374	-0.031569	-0.000134
H 0	-0.000054	2.221675	2.150333
H 0	-0.000035	4.724980	2.144187
H 0	0.000039	4.725045	-2.144019
H 0	0.000038	2.221748	-2.150248

SCF Done: E(UB3LYP) = -2194.87671878

Sum of electronic and zero-point Energies= -2194.600413

Sum of electronic and thermal Energies= -2194.579337

Sum of electronic and thermal Enthalpies= -2194.578393

Sum of electronic and thermal Free Energies= -2194.652961

6.2.4 *anti-anti-N*-phenyl-BBTT 5

6.2.4.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.331272	-2.115762	-0.512030
C 0	4.489261	-3.136094	-0.045875
C 0	3.159576	-2.880389	0.258930
C 0	2.648540	-1.583251	0.092008
C 0	3.510341	-0.569579	-0.388817
C 0	4.847689	-0.822647	-0.685225
C 0	1.331876	-1.076050	0.369852
C 0	1.192453	0.248428	0.086137
S 0	2.674226	0.973250	-0.552038

S 0	0.000108	-2.037529	1.074051
C 0	-1.331896	-1.076066	0.369640
C 0	-1.192466	0.248410	0.085905
N 0	-0.000015	0.972312	0.163993
C 0	-2.648501	-1.583309	0.091858
C 0	-3.510313	-0.569644	-0.388966
S 0	-2.674147	0.973181	-0.552158
C 0	-3.159651	-2.880433	0.258928
C 0	-4.489381	-3.136033	-0.045695
C 0	-5.331387	-2.115685	-0.511821
C 0	-4.847681	-0.822625	-0.685274
C 0	-0.000027	2.410646	0.217664
C 0	-0.000073	3.052383	1.456844
C 0	-0.000065	4.443502	1.512604
C 0	-0.000037	5.190791	0.334732
C 0	0.000007	4.547045	-0.900928
C 0	0.000041	3.154338	-0.963200
H 0	6.367357	-2.334072	-0.742982
H 0	4.883319	-4.138176	0.079013
H 0	2.513211	-3.673650	0.616922
H 0	5.496062	-0.033732	-1.048687
H 0	-2.513288	-3.673675	0.616888
H 0	-4.883498	-4.138080	0.079300
H 0	-6.367533	-2.333902	-0.742557
H 0	-5.495991	-0.033749	-1.048931
H 0	-0.000101	2.456767	2.362071
H 0	-0.000086	4.943525	2.474297
H 0	-0.000050	6.273861	0.380859
H 0	0.000044	5.126031	-1.817166
H 0	0.000195	2.642390	-1.918278

SCF Done: E(RB3LYP) = -2095.77731924

Sum of electronic and zero-point Energies= -2095.493485

Sum of electronic and thermal Energies= -2095.473094

Sum of electronic and thermal Enthalpies= -2095.472150

Sum of electronic and thermal Free Energies= -2095.545164

6.2.4.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloro

methane) pop=full

0 1

C 0	5.353537	-2.087300	-0.499120
C 0	4.510433	-3.125595	-0.074111
C 0	3.174027	-2.886196	0.218843
C 0	2.657584	-1.586756	0.080703
C 0	3.521974	-0.554610	-0.356206
C 0	4.865202	-0.791152	-0.641589
C 0	1.333468	-1.094164	0.349960
C 0	1.191240	0.238527	0.103829
S 0	2.679732	0.989133	-0.484731
S 0	0.000003	-2.086210	1.011118
C 0	-1.333464	-1.094168	0.349957
C 0	-1.191239	0.238523	0.103827
N 0	-0.000001	0.960175	0.192939
C 0	-2.657578	-1.586763	0.080700
C 0	-3.521970	-0.554619	-0.356208
S 0	-2.679731	0.989124	-0.484741
C 0	-3.174019	-2.886204	0.218842
C 0	-4.510424	-3.125606	-0.074111
C 0	-5.353531	-2.087312	-0.499120
C 0	-4.865198	-0.791164	-0.641589
C 0	-0.000004	2.401847	0.214559
C 0	-0.000018	3.067872	1.440963
C 0	-0.000023	4.460589	1.466656
C 0	-0.000012	5.182476	0.272312
C 0	0.000002	4.512520	-0.950235
C 0	0.000005	3.118338	-0.983472
H 0	6.394049	-2.293144	-0.721121

H 0	4.908517	-4.128574	0.028629
H 0	2.530163	-3.694163	0.547478
H 0	5.514161	0.011368	-0.972212
H 0	-2.530153	-3.694170	0.547477
H 0	-4.908506	-4.128585	0.028629
H 0	-6.394043	-2.293159	-0.721121
H 0	-5.514159	0.011355	-0.972213
H 0	-0.000026	2.493629	2.359810
H 0	-0.000034	4.980693	2.417411
H 0	-0.000016	6.266134	0.295244
H 0	0.000009	5.071590	-1.878531
H 0	0.000015	2.588557	-1.928717

SCF Done: E(RB3LYP) = -2095.78481036

Sum of electronic and zero-point Energies= -2095.501019

Sum of electronic and thermal Energies= -2095.480659

Sum of electronic and thermal Enthalpies= -2095.479714

Sum of electronic and thermal Free Energies= -2095.552165

6.2.4.3 Minimum geometry of native BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full scrf=(SMD,solvent=dichloromethane) geom=check

0 1

C 0	5.350531	-2.095585	-0.499558
C 0	4.508311	-3.127876	-0.058189
C 0	3.172885	-2.884673	0.236752
C 0	2.656193	-1.586791	0.083040
C 0	3.520373	-0.561328	-0.369846
C 0	4.862657	-0.800902	-0.657104
C 0	1.333942	-1.088087	0.352652
C 0	1.190456	0.241675	0.091792
S 0	2.678513	0.982441	-0.514148
S 0	0.000001	-2.067814	1.032672
C 0	-1.333942	-1.088087	0.352656
C 0	-1.190456	0.241675	0.091796
N 0	-0.000000	0.963788	0.175459
C 0	-2.656192	-1.586792	0.083042
C 0	-3.520373	-0.561330	-0.369843
S 0	-2.678515	0.982441	-0.514138
C 0	-3.172883	-2.884675	0.236751
C 0	-4.508307	-3.127880	-0.058193
C 0	-5.350528	-2.095590	-0.499562
C 0	-4.862656	-0.800906	-0.657105
C 0	-0.000000	2.406577	0.214441
C 0	0.000003	3.056963	1.449556
C 0	0.000003	4.449361	1.491105
C 0	-0.000002	5.185184	0.304915
C 0	-0.000006	4.529859	-0.925657
C 0	-0.000005	3.135881	-0.975895
H 0	6.390279	-2.305201	-0.723138
H 0	4.906352	-4.129944	0.055829
H 0	2.532118	-3.690007	0.578510
H 0	5.511117	-0.002776	-1.000533
H 0	-2.532115	-3.690009	0.578509
H 0	-4.906347	-4.129949	0.055823
H 0	-6.390276	-2.305207	-0.723144
H 0	-5.511117	-0.002780	-1.000533
H 0	0.000007	2.471391	2.361728
H 0	0.000006	4.958452	2.448258
H 0	-0.000002	6.268965	0.340652
H 0	-0.000010	5.099854	-1.847752
H 0	-0.000009	2.617582	-1.927899

SCF Done: E(RB3LYP) = -2095.80850503

Sum of electronic and zero-point Energies= -2095.524556

Sum of electronic and thermal Energies= -2095.504320

Sum of electronic and thermal Enthalpies= -2095.503376

Sum of electronic and thermal Free Energies= -2095.574657

6.2.4.4 Minimum geometry of radical cation of BBTT in gas phase (B3LYP/6-311++G**)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000

0 1

C 0	5.479297	-1.937864	-0.000175
C 0	4.625872	-3.052354	-0.000147
C 0	3.250235	-2.892802	-0.000041
C 0	2.711637	-1.594062	0.000048
C 0	3.587481	-0.485231	-0.000015
C 0	4.969757	-0.643467	-0.000116
C 0	1.337780	-1.175369	0.000031
C 0	1.193803	0.205589	-0.000073
S 0	2.722967	1.055011	-0.000106
S 0	-0.000004	-2.296303	0.000484
C 0	-1.337786	-1.175370	0.000168
C 0	-1.193806	0.205598	-0.000054
N 0	-0.000006	0.888908	-0.000050
C 0	-2.711637	-1.594058	0.000021
C 0	-3.587480	-0.485221	-0.000315
S 0	-2.722961	1.055002	-0.000495
C 0	-3.250245	-2.892795	0.000268
C 0	-4.625882	-3.052340	0.000173
C 0	-5.479303	-1.937847	-0.000175
C 0	-4.969756	-0.643452	-0.000429
C 0	0.000002	2.345893	0.000070
C 0	-0.000362	3.022605	1.218250
C 0	-0.000358	4.415301	1.210310
C 0	0.000009	5.108300	0.000306
C 0	0.000373	4.415514	-1.209814
C 0	0.000370	3.022814	-1.217992
H 0	6.552447	-2.085298	-0.000255
H 0	5.049698	-4.048918	-0.000232
H 0	2.600664	-3.760725	0.000012
H 0	5.633407	0.212500	-0.000120
H 0	-2.600679	-3.760721	0.000481
H 0	-5.049713	-4.048902	0.000380
H 0	-6.552454	-2.085274	-0.000249
H 0	-5.633403	0.212517	-0.000734
H 0	-0.000622	2.471157	2.151028
H 0	-0.000646	4.955993	2.148864
H 0	0.000011	6.191765	0.000402
H 0	0.000664	4.956363	-2.148277
H 0	0.000632	2.471526	-2.150864

SCF Done: E(UB3LYP) = -2095.55859696

Sum of electronic and zero-point Energies= -2095.274032

Sum of electronic and thermal Energies= -2095.253820

Sum of electronic and thermal Enthalpies= -2095.252875

Sum of electronic and thermal Free Energies= -2095.324885

6.2.4.5 Minimum geometry of radical cation of BBTT under SMD variation of PCM (B3LYP/6-311++G**, SMD CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(SMD,s

olvent=dichloromethane)

0 1

C 0	5.477113	-1.940378	0.000033
C 0	4.621543	-3.053578	-0.000015
C 0	3.245131	-2.892494	-0.000015
C 0	2.710198	-1.592390	0.000020
C 0	3.587624	-0.484951	0.000072
C 0	4.970272	-0.644205	0.000082
C 0	1.336501	-1.172741	-0.000009
C 0	1.190898	0.206560	-0.000008

S 0	2.722157	1.055794	0.000092
S 0	-0.000015	-2.293900	0.000009
C 0	-1.336518	-1.172731	0.000043
C 0	-1.190896	0.206574	0.000038
N 0	0.000000	0.889533	0.000044
C 0	-2.710216	-1.592365	-0.000034
C 0	-3.587635	-0.484920	-0.000122
S 0	-2.722153	1.055812	-0.000113
C 0	-3.245163	-2.892464	0.000043
C 0	-4.621577	-3.053536	0.000031
C 0	-5.477139	-1.940330	-0.000065
C 0	-4.970283	-0.644161	-0.000143
C 0	0.000016	2.346591	0.000021
C 0	-0.000493	3.020617	1.219690
C 0	-0.000480	4.413623	1.210735
C 0	0.000039	5.106458	-0.000009
C 0	0.000546	4.413596	-1.210738
C 0	0.000538	3.020590	-1.219665
H 0	6.550347	-2.089638	0.000036
H 0	5.043343	-4.051427	-0.000059
H 0	2.594449	-3.759842	-0.000024
H 0	5.636029	0.210625	0.000148
H 0	-2.594489	-3.759818	0.000088
H 0	-5.043384	-4.051382	0.000111
H 0	-6.550374	-2.089581	-0.000082
H 0	-5.636033	0.210675	-0.000242
H 0	-0.000850	2.465737	2.150480
H 0	-0.000858	4.954140	2.149780
H 0	0.000050	6.190508	-0.000022
H 0	0.000933	4.954093	-2.149794
H 0	0.000884	2.465693	-2.150445

SCF Done: E(UB3LYP) = -2095.63701017

Sum of electronic and zero-point Energies= -2095.352156

Sum of electronic and thermal Energies= -2095.332113

Sum of electronic and thermal Enthalpies= -2095.331169

Sum of electronic and thermal Free Energies= -2095.402396

6.2.5 *anti-anti-N-para*-methylphenyl-BBTT

6.2.5.1 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=di

chloromethane) pop=full

0 1

C 0	-5.369779	-2.326538	-0.483112
C 0	-4.531567	-3.368851	-0.058331
C 0	-3.192747	-3.136885	0.229763
C 0	-2.668752	-1.840916	0.086842
C 0	-3.528474	-0.804509	-0.349448
C 0	-4.873912	-1.033694	-0.630139
C 0	-1.340662	-1.355932	0.349575
C 0	-1.191178	-0.024516	0.099796
S 0	-2.677380	0.733940	-0.483836
S 0	-0.012155	-2.354645	1.010919
C 0	1.326126	-1.369310	0.349210
C 0	1.190024	-0.036463	0.099474
N 0	0.003083	0.692224	0.184573
C 0	2.649218	-1.867617	0.086333
C 0	3.519296	-0.839976	-0.350171
S 0	2.683578	0.706915	-0.484760
C 0	3.160049	-3.168758	0.229581
C 0	4.496507	-3.414281	-0.058226
C 0	5.345231	-2.380523	-0.483059
C 0	4.862441	-1.082776	-0.630505
C 0	0.010586	2.133779	0.179965
C 0	0.013224	2.827462	1.391015
C 0	0.017795	4.218205	1.389610
C 0	0.021180	4.941967	0.188983

C 0	0.015290	4.228401	-1.013917
C 0	0.011033	2.834356	-1.025644
C 0	0.050771	6.450208	0.199812
H 0	-6.412243	-2.526575	-0.701251
H 0	-4.935333	-4.369186	0.048089
H 0	-2.552838	-3.948087	0.558188
H 0	-5.519061	-0.227984	-0.960515
H 0	2.511830	-3.973306	0.558077
H 0	4.890196	-4.418591	0.048500
H 0	6.385691	-2.591065	-0.700892
H 0	5.515761	-0.283685	-0.960915
H 0	0.008926	2.274811	2.323230
H 0	0.016688	4.750020	2.335236
H 0	0.011818	4.766141	-1.955850
H 0	0.005288	2.293993	-1.965073
H 0	-0.613583	6.854209	0.967473
H 0	1.059553	6.816275	0.417878
H 0	-0.249166	6.861095	-0.765779

SCF Done: E(RB3LYP) = -2135.11307644

Sum of electronic and zero-point Energies= -2134.802203

Sum of electronic and thermal Energies= -2134.779957

Sum of electronic and thermal Enthalpies= -2134.779013

Sum of electronic and thermal Free Energies= -2134.856097

6.2.5.2 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpc

m,solvent=dichloromethane)

0 1

C 0	5.483631	-2.189461	-0.000493
C 0	4.632599	-3.306094	-0.000501
C 0	3.255624	-3.150080	-0.000276
C 0	2.713878	-1.852880	-0.000027
C 0	3.586595	-0.741500	-0.000031
C 0	4.970065	-0.896347	-0.000266
C 0	1.337764	-1.438915	0.000192
C 0	1.191437	-0.059107	0.000313
S 0	2.717715	0.795328	0.000210
S 0	0.004040	-2.562047	0.000371
C 0	-1.333204	-1.443132	0.000199
C 0	-1.191348	-0.062873	0.000314
N 0	-0.001057	0.622400	0.000437
C 0	-2.707963	-1.861517	0.000046
C 0	-3.584322	-0.753012	0.000098
S 0	-2.720361	0.786677	0.000308
C 0	-3.245324	-3.160518	-0.000195
C 0	-4.621758	-3.321179	-0.000363
C 0	-5.476493	-2.207389	-0.000304
C 0	-4.967274	-0.912551	-0.000082
C 0	-0.003401	2.077662	0.000259
C 0	-0.002226	2.759033	-1.214508
C 0	0.000151	4.150106	-1.203810
C 0	-0.000462	4.866949	-0.000165
C 0	0.001457	4.150519	1.203636
C 0	-0.000924	2.759374	1.214752
C 0	-0.027134	6.373826	-0.000650
H 0	6.557262	-2.333521	-0.000677
H 0	5.058043	-4.302059	-0.000697
H 0	2.608145	-4.019082	-0.000308
H 0	5.630269	-0.038028	-0.000284
H 0	-2.594848	-4.027271	-0.000268
H 0	-5.043873	-4.318559	-0.000554
H 0	-6.549639	-2.355025	-0.000445
H 0	-5.630452	-0.056522	-0.000057
H 0	0.000128	2.210112	-2.148430
H 0	0.004975	4.684821	-2.146849
H 0	0.007330	4.685491	2.146516

H 0 0.002395 2.210748 2.148845

H 0 -1.060042 6.737505 -0.008299

H 0 0.457272 6.780148 0.889052

H 0 0.469919 6.779635 -0.883648

SCF Done: E(UB3LYP) = -2134.93852249

Sum of electronic and zero-point Energies= -2134.626868

Sum of electronic and thermal Energies= -2134.604712

Sum of electronic and thermal Enthalpies= -2134.603767

Sum of electronic and thermal Free Energies= -2134.681372

6.2.6 *anti-anti-N-para*-methoxyphenyl-BBTT

6.2.6.1 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) scrf=(iefpcm,solvent=dichloromethane) pop=full

0 1

C 0 2.579773 -5.363757 -0.531287

C 0 3.639817 -4.519091 -0.167710

C 0 3.418161 -3.179599 0.125660

C 0 2.114182 -2.661324 0.049884

C 0 1.059570 -3.527656 -0.325580

C 0 1.278801 -4.873638 -0.611138

C 0 1.638681 -1.333032 0.328636

C 0 0.295392 -1.190328 0.147578

S 0 -0.487326 -2.683122 -0.382571

S 0 2.667042 0.000859 0.931333

C 0 1.637740 1.334083 0.328781

C 0 0.294567 1.190352 0.147712

N 0 -0.424289 -0.000196 0.264166

C 0 2.112317 2.662643 0.049726

C 0 1.057159 3.528130 -0.326114

S 0 -0.489137 2.682611 -0.383103

C 0 3.415871 3.181933 0.125957

C 0 3.636604 4.521551 -0.167424

C 0 2.576025 5.365386 -0.531424

C 0 1.275466 4.874259 -0.611672

C 0 -1.864260 -0.000617 0.290932

C 0 -2.535519 0.000054 1.518565

C 0 -3.920172 -0.000250 1.553668

C 0 -4.656289 -0.001257 0.358673

C 0 -3.988176 -0.001956 -0.870207

C 0 -2.593366 -0.001602 -0.895609

O 0 -6.007975 -0.001520 0.496977

C 0 -6.820256 -0.002373 -0.680535

H 0 2.772168 -6.406653 -0.754154

H 0 4.646094 -4.918393 -0.112941

H 0 4.243338 -2.534874 0.406405

H 0 0.459087 -5.523683 -0.894102

H 0 4.241429 2.537904 0.407182

H 0 4.642573 4.921610 -0.112505

H 0 2.767718 6.408393 -0.754378

H 0 0.455361 5.523642 -0.895026

H 0 -1.965033 0.000826 2.439768

H 0 -4.453315 0.000272 2.496611

H 0 -4.532932 -0.002739 -1.803960

H 0 -2.075263 -0.002052 -1.847379

H 0 -7.849467 -0.002341 -0.328282

H 0 -6.640002 0.892185 -1.283136

H 0 -6.639695 -0.897590 -1.282067

SCF Done: E(RB3LYP) = -2210.34389757

Sum of electronic and zero-point Energies= -2210.027841

Sum of electronic and thermal Energies= -2210.004878

Sum of electronic and thermal Enthalpies= -2210.003934

Sum of electronic and thermal Free Energies= -2210.082049

6.2.6.2 Minimum geometry of radical cation of BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p ub3lyp/6-311++g(d,p) opt freq=noraman scf=maxcycle=1000 scrf=(iefpc

m,solvent=dichloromethane)

0 1

C 0	-2.450535	-5.480023	-0.055899
C 0	-3.565914	-4.627670	-0.078570
C 0	-3.408446	-3.250907	-0.065554
C 0	-2.111136	-2.710757	-0.028590
C 0	-1.000893	-3.584752	-0.005888
C 0	-1.157297	-4.967973	-0.019711
C 0	-1.695868	-1.335149	-0.009502
C 0	-0.316321	-1.190806	0.025699
S 0	0.536636	-2.717509	0.038122
S 0	-2.816751	0.000435	-0.023118
C 0	-1.695454	1.335675	-0.009406
C 0	-0.315955	1.190846	0.025530
N 0	0.367759	-0.000082	0.048723
C 0	-2.110257	2.711447	-0.028495
C 0	-0.999667	3.585018	-0.006012
S 0	0.537521	2.717306	0.037740
C 0	-3.407379	3.252092	-0.065172
C 0	-3.564317	4.628918	-0.078138
C 0	-2.448599	5.480839	-0.055722
C 0	-1.155558	4.968298	-0.019792
C 0	1.819947	-0.000288	0.109453
C 0	2.453315	-0.000565	1.355567
C 0	3.835756	-0.000796	1.412082
C 0	4.593479	-0.000748	0.229098
C 0	3.948266	-0.000414	-1.014632
C 0	2.557096	-0.000189	-1.069736
O 0	5.935382	-0.001025	0.391904
C 0	6.777004	-0.001063	-0.768366
H 0	-2.595669	-6.553458	-0.066797
H 0	-4.562011	-5.051884	-0.106843
H 0	-4.276359	-2.602212	-0.084173
H 0	-0.299947	-5.629245	-0.002744
H 0	-4.275560	2.603740	-0.083646
H 0	-4.560253	5.053522	-0.106177
H 0	-2.593302	6.554334	-0.066608
H 0	-0.297943	5.629223	-0.002984
H 0	1.866813	-0.000602	2.266332
H 0	4.351274	-0.001031	2.364183
H 0	4.510590	-0.000353	-1.937527
H 0	2.053399	0.000074	-2.028725
H 0	7.796279	-0.001425	-0.389682
H 0	6.609353	-0.896460	-1.372293
H 0	6.609857	0.894635	-1.371983

SCF Done: E(UB3LYP) = -2210.16956529

Sum of electronic and zero-point Energies= -2209.852604

Sum of electronic and thermal Energies= -2209.829798

Sum of electronic and thermal Enthalpies= -2209.828854

Sum of electronic and thermal Free Energies= -2209.906713

6.3 *anti-anti-N-ortho(,ortho')*-(di)substituted-phenyl-3,9-dibromo-BBTT 4a-d

6.3.1 *anti-anti-N-ortho*-methylphenyl-3,9-dibromo-BBTT 4a

6.3.1.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.336002	-1.575240	-0.148774
C 0	-4.508706	-2.551979	0.418526
C 0	-3.174113	-2.266883	0.670031
C 0	-2.654702	-1.003055	0.349755
C 0	-3.517994	-0.044743	-0.230835
C 0	-4.861860	-0.312785	-0.480451
C 0	-1.331845	-0.478208	0.547487
C 0	-1.190768	0.804770	0.111803
S 0	-2.678990	1.463309	-0.581587
S 0	0.000248	-1.364917	1.343560
C 0	1.332270	-0.477993	0.547572
C 0	1.191051	0.804955	0.111829
N 0	0.000079	1.531752	0.090939
C 0	2.655190	-1.002705	0.349967
C 0	3.518411	-0.044327	-0.230607
S 0	2.679328	1.463603	-0.581460
C 0	3.174736	-2.266411	0.670472
C 0	4.509381	-2.551388	0.419092
C 0	5.336576	-1.574607	-0.148249
C 0	4.862335	-0.312233	-0.480070
C 0	-0.000158	2.967747	-0.038361
C 0	0.002076	3.533484	-1.313614
C 0	0.001940	4.918195	-1.461758
C 0	-0.000544	5.725696	-0.327887
C 0	-0.002841	5.152369	0.942555
C 0	-0.002663	3.765449	1.118045
C 0	-0.005108	3.149587	2.493298
Br 0	-7.178030	-1.992209	-0.484100
Br 0	7.178702	-1.991429	-0.483520
H 0	-4.913011	-3.526212	0.659878
H 0	-2.533087	-3.023657	1.107284
H 0	-5.514548	0.428930	-0.921926
H 0	2.533767	-3.023210	1.107771
H 0	4.913799	-3.525525	0.660634
H 0	5.515003	0.429541	-0.921457
H 0	0.003797	2.883387	-2.180941
H 0	0.003687	5.358024	-2.451968
H 0	-0.000694	6.805070	-0.429932
H 0	-0.004726	5.792205	1.818559
H 0	0.872175	2.515178	2.647330
H 0	-0.884735	2.517914	2.645385
H 0	-0.004825	3.923350	3.262325

SCF Done: E(RB3LYP) = -7282.18968236

Sum of electronic and zero-point Energies= -7281.898930

Sum of electronic and thermal Energies= -7281.873677

Sum of electronic and thermal Enthalpies= -7281.872733

Sum of electronic and thermal Free Energies= -7281.958391

Conformer II:

No minimum on the potential hyper surface could be found.

6.3.1.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full SCRF=(IEFPCM,Solvent =Dichloromethane)

0 1

C 0	-5.346701	-1.563757	-0.149222
C 0	-4.521469	-2.559374	0.387328
C 0	-3.182583	-2.286358	0.633026
C 0	-2.660106	-1.017154	0.336893
C 0	-3.524511	-0.039941	-0.211473
C 0	-4.872291	-0.294850	-0.455677
C 0	-1.332607	-0.504358	0.532212
C 0	-1.189596	0.789332	0.127142
S 0	-2.681063	1.472313	-0.532402
S 0	0.000092	-1.419564	1.296631
C 0	1.332775	-0.504211	0.532323

C 0	1.189643	0.789471	0.127276
N 0	0.000004	1.515938	0.119299
C 0	2.660294	-1.016941	0.337051
C 0	3.524699	-0.039706	-0.211286
S 0	2.681252	1.472526	-0.532323
C 0	3.182836	-2.286071	0.633391
C 0	4.521739	-2.559070	0.387765
C 0	5.346917	-1.563474	-0.148900
C 0	4.872492	-0.294601	-0.455445
C 0	-0.000090	2.951405	-0.035445
C 0	0.000875	3.493574	-1.321376
C 0	0.000859	4.875945	-1.493154
C 0	-0.000160	5.703064	-0.372523
C 0	-0.001138	5.151899	0.908352
C 0	-0.001103	3.767520	1.108264
C 0	-0.002060	3.177718	2.495011
Br 0	-7.198029	-1.965132	-0.477939
Br 0	7.198264	-1.964906	-0.477794
H 0	-4.926146	-3.537669	0.610992
H 0	-2.544235	-3.057060	1.049112
H 0	-5.523601	0.462087	-0.872305
H 0	2.544509	-3.056750	1.049555
H 0	4.926493	-3.537276	0.611672
H 0	5.523810	0.462335	-0.872048
H 0	0.001582	2.830257	-2.178440
H 0	0.001610	5.298297	-2.490810
H 0	-0.000191	6.780447	-0.492982
H 0	-0.001901	5.806952	1.772772
H 0	0.876624	2.548029	2.660488
H 0	-0.881508	2.548868	2.659657
H 0	-0.002068	3.966459	3.248230

SCF Done: E(RB3LYP) = -7282.19719407

Sum of electronic and zero-point Energies= -7281.906635

Sum of electronic and thermal Energies= -7281.881362

Sum of electronic and thermal Enthalpies= -7281.880418

Sum of electronic and thermal Free Energies= -7281.965859

Conformer II:

No minimum on the potential hyper surface could be found.

6.3.2 *anti-anti-N-ortho,ortho'*-chloromethoxyphenyl-3,9-dibromo-BBTT 4b

6.3.2.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.395148	-1.758360	0.135742
C 0	4.557017	-2.821039	-0.221794
C 0	3.204715	-2.593872	-0.435479
C 0	2.678310	-1.300939	-0.287812
C 0	3.554831	-0.254198	0.081128
C 0	4.915152	-0.464573	0.292318
C 0	1.333989	-0.832241	-0.478819
C 0	1.194098	0.500913	-0.239644
S 0	2.705522	1.278762	0.234535
S 0	0.000003	-1.868447	-1.059483
C 0	-1.333989	-0.832236	-0.478840
C 0	-1.194092	0.500917	-0.239669
N 0	0.000001	1.226026	-0.289164
C 0	-2.678307	-1.300938	-0.287827
C 0	-3.554832	-0.254200	0.081125
S 0	-2.705528	1.278768	0.234538
C 0	-3.204712	-2.593869	-0.435497
C 0	-4.557015	-2.821041	-0.221800
C 0	-5.395145	-1.758370	0.135749

C 0	-4.915147	-0.464579	0.292325
C 0	-0.000001	2.648268	-0.192104
C 0	-0.000036	3.453442	-1.335617
C 0	-0.000044	4.842758	-1.244939
C 0	-0.000013	5.429236	0.014742
C 0	0.000021	4.659757	1.175646
C 0	0.000024	3.265659	1.080601
O 0	0.000043	2.422121	2.135947
Br 0	7.262146	-2.096841	0.421177
Br 0	-7.262135	-2.096853	0.421211
Cl 0	-0.000071	2.703956	-2.913018
C 0	0.000075	2.962584	3.456072
H 0	4.966195	-3.816716	-0.331218
H 0	2.556502	-3.418040	-0.710050
H 0	5.576895	0.344890	0.571353
H 0	-2.556500	-3.418036	-0.710076
H 0	-4.966189	-3.816719	-0.331235
H 0	-5.576891	0.344880	0.571367
H 0	-0.000072	5.442285	-2.144898
H 0	-0.000017	6.510043	0.096919
H 0	0.000040	5.145688	2.141135
H 0	0.000093	2.102504	4.122100
H 0	0.896210	3.564150	3.635899
H 0	-0.896053	3.564147	3.635943

SCF Done: E(RB3LYP) = -7817.03483333

Sum of electronic and zero-point Energies= -7816.748867

Sum of electronic and thermal Energies= -7816.721398

Sum of electronic and thermal Enthalpies= -7816.720454

Sum of electronic and thermal Free Energies= -7816.811375

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.393841	-1.767531	-0.113313
C 0	-4.555517	-2.761769	0.405608
C 0	-3.203013	-2.503831	0.577852
C 0	-2.678069	-1.250090	0.228420
C 0	-3.553279	-0.273463	-0.300847
C 0	-4.914710	-0.515015	-0.472827
C 0	-1.334642	-0.753012	0.351002
C 0	-1.193360	0.526933	-0.087920
S 0	-2.703538	1.211966	-0.701107
S 0	0.000001	-1.698359	1.063695
C 0	1.334643	-0.753012	0.351003
C 0	1.193359	0.526932	-0.087921
N 0	-0.000002	1.253716	-0.176759
C 0	2.678073	-1.250088	0.228421
C 0	3.553281	-0.273463	-0.300847
S 0	2.703542	1.211967	-0.701111
C 0	3.203013	-2.503830	0.577854
C 0	4.555519	-2.761769	0.405610
C 0	5.393844	-1.767530	-0.113310
C 0	4.914712	-0.515015	-0.472827
C 0	-0.000000	2.665041	0.060480
C 0	0.000009	3.589271	-0.986501
C 0	0.000010	4.961931	-0.743734
C 0	0.000001	5.407917	0.571204
C 0	-0.000009	4.515207	1.641511
C 0	-0.000009	3.141600	1.391752
O 0	-0.000019	2.183846	2.344382
Br 0	-7.261031	-2.146464	-0.338853
Br 0	7.261035	-2.146462	-0.338842
Cl 0	0.000015	3.025185	-2.643957
C 0	-0.000038	2.570623	3.717061
H 0	-4.964882	-3.727849	0.669966
H 0	-2.553675	-3.275054	0.976002
H 0	-5.576634	0.239943	-0.876358
H 0	2.553675	-3.275051	0.976005
H 0	4.964884	-3.727849	0.669967
H 0	5.576636	0.239942	-0.876360
H 0	0.000017	5.655703	-1.573259

H 0	0.000001	6.473354	0.770439
H 0	-0.000017	4.892236	2.654715
H 0	-0.000050	1.640122	4.280569
H 0	0.896043	3.148294	3.963591
H 0	-0.896123	3.148300	3.963565

SCF Done: E(RB3LYP) = -7817.03485758

Sum of electronic and zero-point Energies= -7816.748887

Sum of electronic and thermal Energies= -7816.721452

Sum of electronic and thermal Enthalpies= -7816.720508

Sum of electronic and thermal Free Energies= -7816.811263

6.3.2.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	5.412075	-1.740045	0.127091
C 0	4.576558	-2.819582	-0.182995
C 0	3.218511	-2.606830	-0.378303
C 0	2.687270	-1.312119	-0.259229
C 0	3.564160	-0.248573	0.060161
C 0	4.929757	-0.443654	0.253612
C 0	1.336232	-0.857185	-0.435369
C 0	1.193643	0.483260	-0.236224
S 0	2.709348	1.284720	0.178534
S 0	-0.000001	-1.926142	-0.953084
C 0	-1.336232	-0.857184	-0.435361
C 0	-1.193637	0.483262	-0.236223
N 0	0.000001	1.206238	-0.289643
C 0	-2.687268	-1.312117	-0.259230
C 0	-3.564164	-0.248571	0.060151
S 0	-2.709357	1.284728	0.178523
C 0	-3.218508	-2.606828	-0.378300
C 0	-4.576559	-2.819581	-0.182996
C 0	-5.412077	-1.740046	0.127082
C 0	-4.929760	-0.443652	0.253599
C 0	0.000002	2.629702	-0.181839
C 0	0.000016	3.441464	-1.321059
C 0	0.000018	4.828628	-1.226494
C 0	0.000004	5.407821	0.038710
C 0	-0.000010	4.633176	1.195356
C 0	-0.000010	3.238600	1.095190
O 0	-0.000018	2.391594	2.146128
Br 0	7.289962	-2.060248	0.387824
Br 0	-7.289964	-2.060247	0.387816
Cl 0	0.000031	2.693882	-2.905722
C 0	-0.000033	2.933089	3.473774
H 0	4.987733	-3.816512	-0.271184
H 0	2.573809	-3.444396	-0.618112
H 0	5.589226	0.379219	0.495902
H 0	-2.573805	-3.444396	-0.618100
H 0	-4.987731	-3.816513	-0.271187
H 0	-5.589232	0.379221	0.495879
H 0	0.000029	5.435573	-2.121401
H 0	0.000005	6.487890	0.126523
H 0	-0.000019	5.114982	2.162677
H 0	-0.000041	2.071768	4.137379
H 0	0.895900	3.533476	3.649917
H 0	-0.895970	3.533476	3.649897

SCF Done: E(RB3LYP) = -7817.04500995

Sum of electronic and zero-point Energies= -7816.759173

Sum of electronic and thermal Energies= -7816.731694

Sum of electronic and thermal Enthalpies= -7816.730750

Sum of electronic and thermal Free Energies= -7816.821860

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	-5.451141	-1.719702	-0.061372
C 0	-4.610052	-2.796970	0.240901
C 0	-3.240510	-2.594151	0.346132
C 0	-2.704152	-1.311670	0.145345
C 0	-3.587105	-0.250365	-0.163595
C 0	-4.963745	-0.435403	-0.267612
C 0	-1.339969	-0.868384	0.226787
C 0	-1.195051	0.461862	-0.027753
S 0	-2.724591	1.266279	-0.386004
S 0	-0.000001	-1.959291	0.685392
C 0	1.339969	-0.868385	0.226779
C 0	1.195047	0.461861	-0.027756
N 0	-0.000001	1.180580	-0.088739
C 0	2.704151	-1.311670	0.145339
C 0	3.587104	-0.250363	-0.163595
S 0	2.724593	1.266281	-0.386001
C 0	3.240507	-2.594153	0.346117
C 0	4.610050	-2.796973	0.240887
C 0	5.451138	-1.719702	-0.061374
C 0	4.963745	-0.435401	-0.267609
C 0	-0.000001	2.606639	-0.008286
C 0	0.000002	3.406616	-1.155611
C 0	0.000001	4.795637	-1.072958
C 0	-0.000002	5.386592	0.186004
C 0	-0.000004	4.622779	1.350755
C 0	-0.000004	3.228404	1.262220
O 0	-0.000002	2.388636	2.318469
Br 0	-7.344201	-2.025940	-0.199562
Br 0	7.344204	-2.025940	-0.199556
Cl 0	0.000006	2.649813	-2.737945
C 0	-0.000008	2.939761	3.642347
H 0	-5.025582	-3.784449	0.392280
H 0	-2.592199	-3.430763	0.579456
H 0	-5.628022	0.385682	-0.502773
H 0	2.592195	-3.430766	0.579435
H 0	5.025579	-3.784453	0.392255
H 0	5.628024	0.385685	-0.502761
H 0	0.000003	5.394078	-1.973517
H 0	-0.000002	6.467481	0.263306
H 0	-0.000004	5.114030	2.313415
H 0	-0.000012	2.083210	4.312110
H 0	0.896026	3.541335	3.813844
H 0	-0.896042	3.541336	3.813835

SCF Done: E(RB3LYP) = -7817.04479756

Sum of electronic and zero-point Energies= -7816.758876

Sum of electronic and thermal Energies= -7816.731429

Sum of electronic and thermal Enthalpies= -7816.730485

Sum of electronic and thermal Free Energies= -7816.821150

6.3.3 *anti-anti-N-ortho,ortho'*-fluoromethoxyphenyl-3,9-dibromo-BBTT 4c

6.3.3.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

Conformer I:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.387631	-1.692191	0.137525
C 0	4.550234	-2.767485	-0.181994
C 0	3.200229	-2.547197	-0.416312
C 0	2.675204	-1.248433	-0.326890
C 0	3.550707	-0.188700	0.005546
C 0	4.908997	-0.392179	0.235797
C 0	1.333389	-0.785569	-0.548348

C 0	1.194092	0.556371	-0.365003
S 0	2.702924	1.350699	0.090332
S 0	0.000004	-1.839196	-1.097982
C 0	-1.333385	-0.785569	-0.548358
C 0	-1.194086	0.556370	-0.365015
N 0	0.000001	1.278907	-0.450020
C 0	-2.675201	-1.248434	-0.326896
C 0	-3.550704	-0.188702	0.005543
S 0	-2.702928	1.350701	0.090326
C 0	-3.200224	-2.547197	-0.416328
C 0	-4.550229	-2.767488	-0.182005
C 0	-5.387624	-1.692198	0.137524
C 0	-4.908993	-0.392185	0.235799
C 0	-0.000004	2.703235	-0.415930
C 0	-0.000031	3.437362	-1.600359
C 0	-0.000043	4.823563	-1.622207
C 0	-0.000027	5.492556	-0.403504
C 0	-0.000000	4.803362	0.808102
C 0	0.000009	3.405040	0.811421
O 0	0.000032	2.634212	1.920071
Br 0	7.251425	-2.021838	0.452299
Br 0	-7.251417	-2.021850	0.452319
F 0	-0.000046	2.766592	-2.764991
C 0	0.000032	3.261806	3.201072
H 0	4.958242	-3.767562	-0.246177
H 0	2.552499	-3.380953	-0.661506
H 0	5.570066	0.427144	0.486157
H 0	-2.552495	-3.380950	-0.661530
H 0	-4.958236	-3.767565	-0.246199
H 0	-5.570063	0.427135	0.486163
H 0	-0.000064	5.346084	-2.569522
H 0	-0.000034	6.576218	-0.392605
H 0	0.000012	5.355405	1.737326
H 0	0.000041	2.448482	3.923437
H 0	0.896108	3.874102	3.339709
H 0	-0.896051	3.874088	3.339715

SCF Done: E(RB3LYP) = -7456.68066093

Sum of electronic and zero-point Energies= -7456.393170

Sum of electronic and thermal Energies= -7456.366084

Sum of electronic and thermal Enthalpies= -7456.365140

Sum of electronic and thermal Free Energies= -7456.454905

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	-5.376912	-1.725399	-0.100345
C 0	-4.543146	-2.684619	0.486992
C 0	-3.196221	-2.407830	0.673859
C 0	-2.671678	-1.170563	0.269517
C 0	-3.542374	-0.229979	-0.328580
C 0	-4.898235	-0.489744	-0.515110
C 0	-1.334408	-0.657562	0.392456
C 0	-1.193602	0.598701	-0.110819
S 0	-2.694751	1.240992	-0.787221
S 0	-0.000002	-1.545615	1.178769
C 0	1.334409	-0.657565	0.392460
C 0	1.193608	0.598699	-0.110814
N 0	-0.000003	1.318522	-0.218776
C 0	2.671682	-1.170563	0.269529
C 0	3.542377	-0.229975	-0.328565
S 0	2.694752	1.240997	-0.787199
C 0	3.196228	-2.407823	0.673882
C 0	4.543155	-2.684609	0.487020
C 0	5.376916	-1.725391	-0.100327
C 0	4.898238	-0.489739	-0.515097
C 0	0.000000	2.745016	-0.178425
C 0	0.000021	3.497102	-1.350065
C 0	0.000026	4.884665	-1.350342
C 0	0.000008	5.534557	-0.122266
C 0	-0.000016	4.825708	1.079001
C 0	-0.000021	3.428563	1.058599
O 0	-0.000043	2.637034	2.151975

Br 0	-7.236350	-2.129707	-0.345067
Br 0	7.236356	-2.129704	-0.345065
F 0	0.000036	2.846936	-2.529804
C 0	-0.000061	3.240928	3.444274
H 0	-4.951704	-3.638592	0.793316
H 0	-2.550406	-3.151727	1.125998
H 0	-5.556369	0.238074	-0.971281
H 0	2.550417	-3.151718	1.126030
H 0	4.951718	-3.638575	0.793358
H 0	5.556371	0.238079	-0.971270
H 0	0.000043	5.421086	-2.289798
H 0	0.000012	6.617901	-0.094578
H 0	-0.000029	5.363294	2.016786
H 0	-0.000083	2.414101	4.151173
H 0	0.895937	3.850823	3.594099
H 0	-0.896051	3.850842	3.594067

SCF Done: E(RB3LYP) = -7456.68115992

Sum of electronic and zero-point Energies= -7456.393592

Sum of electronic and thermal Energies= -7456.366552

Sum of electronic and thermal Enthalpies= -7456.365607

Sum of electronic and thermal Free Energies= -7456.455156

6.3.3.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

Conformer I:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full SCRF=(IEFPCM,Solvent=Dichloromethane)

0 1

C 0	5.401686	-1.675556	0.130685
C 0	4.567372	-2.764491	-0.148355
C 0	3.212520	-2.556626	-0.369300
C 0	2.683032	-1.257313	-0.306635
C 0	3.558481	-0.184089	-0.017036
C 0	4.921126	-0.374273	0.200850
C 0	1.335373	-0.806232	-0.516719
C 0	1.193609	0.540851	-0.368917
S 0	2.706077	1.354456	0.033927
S 0	0.000003	-1.886136	-1.013236
C 0	-1.335367	-0.806233	-0.516718
C 0	-1.193602	0.540849	-0.368920
N 0	0.000002	1.261515	-0.458874
C 0	-2.683027	-1.257315	-0.306631
C 0	-3.558477	-0.184092	-0.017032
S 0	-2.706079	1.354457	0.033928
C 0	-3.212513	-2.556627	-0.369307
C 0	-4.567366	-2.764496	-0.148363
C 0	-5.401678	-1.675562	0.130683
C 0	-4.921121	-0.374278	0.200852
C 0	-0.000002	2.687566	-0.406398
C 0	-0.000019	3.434420	-1.583025
C 0	-0.000027	4.818638	-1.594056
C 0	-0.000018	5.474533	-0.366118
C 0	-0.000002	4.773790	0.838248
C 0	0.000005	3.374891	0.829612
O 0	0.000021	2.594765	1.930379
Br 0	7.275073	-1.989713	0.428270
Br 0	-7.275068	-1.989723	0.428277
F 0	-0.000025	2.768236	-2.757557
C 0	-0.000002	3.217014	3.222059
H 0	4.977051	-3.764932	-0.192741
H 0	2.568637	-3.401358	-0.584899
H 0	5.579362	0.456055	0.419885
H 0	-2.568629	-3.401358	-0.584910
H 0	-4.977045	-3.764936	-0.192760
H 0	-5.579360	0.456047	0.419889
H 0	-0.000039	5.353537	-2.534405
H 0	-0.000023	6.557745	-0.344107

H 0 0.000005 5.317257 1.772251

H 0 -0.000013 2.398443 3.937740

H 0 0.895901 3.827139 3.360674

H 0 -0.895913 3.827135 3.360644

SCF Done: E(RB3LYP) = -7456.69106787

Sum of electronic and zero-point Energies= -7456.403814

Sum of electronic and thermal Energies= -7456.376699

Sum of electronic and thermal Enthalpies= -7456.375755

Sum of electronic and thermal Free Energies= -7456.465503

Conformer II:

#p opt=tight freq=noraman rb3lyp/6-311++g(d,p) pop=full SCRF=(IEFPCM,S

olvent=Dichloromethane)

0 1

C 0 -5.391383 -1.717536 -0.094934

C 0 -4.558375 -2.713601 0.428416

C 0 -3.206256 -2.455949 0.609793

C 0 -2.678922 -1.201693 0.262904

C 0 -3.552080 -0.223886 -0.269568

C 0 -4.912563 -0.463251 -0.450532

C 0 -1.335710 -0.706548 0.389153

C 0 -1.193679 0.575143 -0.048634

S 0 -2.701556 1.267975 -0.653688

S 0 0.000001 -1.646982 1.114902

C 0 1.335711 -0.706548 0.389152

C 0 1.193680 0.575143 -0.048633

N 0 -0.000002 1.294011 -0.132242

C 0 2.678922 -1.201694 0.262901

C 0 3.552080 -0.223887 -0.269572

S 0 2.701558 1.267975 -0.653693

C 0 3.206255 -2.455952 0.609786

C 0 4.558373 -2.713604 0.428410

C 0 5.391384 -1.717537 -0.094936

C 0 4.912563 -0.463252 -0.450533

C 0 -0.000001 2.720100 -0.187925

C 0 0.000008 3.389867 -1.409572

C 0 0.000010 4.771488 -1.509077

C 0 0.000003 5.503977 -0.326095

C 0 -0.000007 4.881108 0.921377

C 0 -0.000009 3.485112 1.000604

O 0 -0.000018 2.774093 2.147023

Br 0 -7.260982 -2.097058 -0.333530

Br 0 7.260983 -2.097057 -0.333522

F 0 0.000015 2.650705 -2.542101

C 0 -0.000010 3.476806 3.396746

H 0 -4.967136 -3.680277 0.691577

H 0 -2.562470 -3.227925 1.014947

H 0 -5.570244 0.294071 -0.856164

H 0 2.562468 -3.227928 1.014936

H 0 4.967133 -3.680281 0.691565

H 0 5.570245 0.294070 -0.856163

H 0 0.000018 5.244470 -2.481992

H 0 0.000005 6.586399 -0.373238

H 0 -0.000013 5.483847 1.818418

H 0 -0.000005 2.705117 4.162754

H 0 0.895903 4.094474 3.496431

H 0 -0.895922 4.094474 3.496442

SCF Done: E(RB3LYP) = -7456.69127954

Sum of electronic and zero-point Energies= -7456.404121

Sum of electronic and thermal Energies= -7456.376954

Sum of electronic and thermal Enthalpies= -7456.376009

Sum of electronic and thermal Free Energies= -7456.466666

6.3.4 *anti-anti-N-ortho,ortho'*-dimethoxyphenyl-3,9-dibromo-BBTT 4d

6.3.4.1 Minimum geometry of native BBTT in gas phase (B3LYP/6-311++G**)

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full

0 1

C 0	5.410298	-1.779330	-0.108516
C 0	4.571794	-2.835041	0.267318
C 0	3.214539	-2.608704	0.449968
C 0	2.683877	-1.323994	0.252546
C 0	3.561476	-0.284090	-0.134748
C 0	4.926209	-0.493844	-0.314933
C 0	1.335259	-0.856661	0.408988
C 0	1.191701	0.468753	0.128813
S 0	2.707179	1.238992	-0.347882
S 0	-0.000043	-1.884754	1.003269
C 0	-1.335333	-0.856635	0.409002
C 0	-1.191770	0.468792	0.128828
N 0	-0.000054	1.191436	0.125288
C 0	-2.683968	-1.323950	0.252657
C 0	-3.561581	-0.284025	-0.134557
S 0	-2.707243	1.239037	-0.347715
C 0	-3.214639	-2.608657	0.450004
C 0	-4.571923	-2.834973	0.267431
C 0	-5.410432	-1.779266	-0.108360
C 0	-4.926299	-0.493760	-0.314711
C 0	0.000009	2.618827	0.097568
C 0	0.000204	3.336943	1.308004
C 0	0.000291	4.735745	1.287711
C 0	0.000167	5.393240	0.061390
C 0	-0.000022	4.703932	-1.146740
C 0	-0.000090	3.304293	-1.131583
O 0	-0.000237	2.523568	-2.237141
Br 0	7.284860	-2.115268	-0.349453
Br 0	-7.284830	-2.115199	-0.349394
O 0	0.000295	2.583238	2.430518
C 0	-0.000357	3.142922	-3.520705
C 0	0.000534	3.233599	3.698928
H 0	4.984025	-3.824543	0.414954
H 0	2.565796	-3.427775	0.738371
H 0	5.588593	0.310012	-0.608458
H 0	-2.565894	-3.427767	0.738291
H 0	-4.984081	-3.824515	0.415010
H 0	-5.588705	0.310107	-0.608165
H 0	0.000442	5.305760	2.205821
H 0	0.000228	6.477372	0.046971
H 0	-0.000104	5.249490	-2.079467
H 0	-0.000478	2.325425	-4.238726
H 0	-0.896016	3.754979	-3.664690
H 0	0.895325	3.754895	-3.664897
H 0	0.000593	2.433486	4.436284
H 0	0.896276	3.848871	3.827734
H 0	-0.895088	3.848989	3.828007

SCF Done: E(RB3LYP) = -7471.97169389

Sum of electronic and zero-point Energies= -7471.643681

Sum of electronic and thermal Energies= -7471.614789

Sum of electronic and thermal Enthalpies= -7471.613844

Sum of electronic and thermal Free Energies= -7471.707456

6.3.4.2 Minimum geometry of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt freq=noraman rb3lyp/6-311++g(d,p) pop=full SCRF=(IEFPCM,Solvent =Dichloromethane)

0 1

C 0	5.430596	-1.758355	-0.093544
C 0	4.594459	-2.835909	0.220621
C 0	3.230620	-2.627384	0.378348
C 0	2.694419	-1.339065	0.217162
C 0	3.572717	-0.277028	-0.105546
C 0	4.943498	-0.468105	-0.261250
C 0	1.337886	-0.889092	0.353517

C 0	1.191128	0.447050	0.125100
S 0	2.711572	1.248367	-0.273993
S 0	0.000040	-1.960897	0.864483
C 0	-1.337858	-0.889121	0.353572
C 0	-1.191113	0.446988	0.125123
N 0	0.000065	1.167975	0.128175
C 0	-2.694370	-1.339114	0.217151
C 0	-3.572658	-0.277076	-0.105593
S 0	-2.711556	1.248321	-0.274043
C 0	-3.230532	-2.627446	0.378354
C 0	-4.594366	-2.835960	0.220559
C 0	-5.430507	-1.758420	-0.093652
C 0	-4.943438	-0.468168	-0.261421
C 0	-0.000017	2.597247	0.082873
C 0	-0.000170	3.328300	1.286632
C 0	-0.000233	4.726527	1.248495
C 0	-0.000141	5.368016	0.012880
C 0	-0.000013	4.664916	-1.188070
C 0	0.000038	3.265891	-1.156849
O 0	0.000134	2.472654	-2.253383
Br 0	7.316739	-2.071773	-0.301979
Br 0	-7.316733	-2.071830	-0.302041
O 0	-0.000207	2.589153	2.419715
C 0	0.000280	3.084168	-3.548241
C 0	-0.000330	3.263735	3.683020
H 0	5.009227	-3.827964	0.341362
H 0	2.585536	-3.463740	0.621570
H 0	5.604025	0.353317	-0.505908
H 0	-2.585461	-3.463781	0.621662
H 0	-5.009203	-3.827983	0.341360
H 0	-5.603899	0.353217	-0.506295
H 0	-0.000329	5.308640	2.158799
H 0	-0.000184	6.451749	-0.014720
H 0	0.000036	5.199743	-2.126813
H 0	0.000400	2.260613	-4.258646
H 0	-0.895119	3.693942	-3.693811
H 0	0.895675	3.694003	-3.693582
H 0	-0.000343	2.476089	4.433041
H 0	0.895053	3.879940	3.798164
H 0	-0.895790	3.879850	3.798041

SCF Done: E(RB3LYP) = -7471.98306877

Sum of electronic and zero-point Energies= -7471.655254

Sum of electronic and thermal Energies= -7471.626343

Sum of electronic and thermal Enthalpies= -7471.625399

Sum of electronic and thermal Free Energies= -7471.718893

6.3.4.3 Transition state of native BBTT under IEFPCM variation of PCM (B3LYP/6-311++G**, IEFPCM CH_2Cl_2)

#p opt=(ts,noeigen,calcfc) freq=noraman B3LYP/6-311++g(d,p) pop=full s crf=(iefpcm,solvent=dichloromethane)

0 1

Br 0	-7.388575	-1.975426	-0.000002
S 0	-0.000001	-2.136498	0.000026
S 0	-2.727542	1.267390	-0.000007
O 0	0.000003	2.479551	2.336634
N 0	-0.000000	1.118174	0.000003
C 0	0.000021	4.645791	1.219033
C 0	-2.719378	-1.364638	0.000002
C 0	0.000017	3.246836	1.222635
C 0	0.000001	2.547185	0.000003
C 0	-1.192171	0.400700	-0.000013
C 0	-1.343929	-0.954157	-0.000006
C 0	-3.265564	-2.659240	0.000012
C 0	0.000005	5.317891	0.000003
C 0	-3.602998	-0.259106	-0.000000

C 0	-4.986730	-0.413490	0.000006
C 0	-4.643765	-2.830579	0.000016
C 0	-5.483635	-1.711322	0.000014
C 0	0.000092	3.121559	3.616984
Br 0	7.388573	-1.975429	-0.000017
S 0	2.727541	1.267388	-0.000010
O 0	0.000001	2.479551	-2.336628
C 0	-0.000013	4.645791	-1.219026
C 0	2.719376	-1.364640	0.000010
C 0	-0.000012	3.246836	-1.222629
C 0	1.192169	0.400699	0.000020
C 0	1.343927	-0.954158	0.000026
C 0	3.265561	-2.659242	0.000010
C 0	3.602996	-0.259108	-0.000007
C 0	4.986728	-0.413492	-0.000023
C 0	4.643762	-2.830581	-0.000004
C 0	5.483633	-1.711324	-0.000021
C 0	-0.000084	3.121560	-3.616978
H 0	0.000030	5.204780	2.143666
H 0	-2.619592	-3.529605	0.000017
H 0	0.000006	6.401957	0.000003
H 0	-5.650656	0.440917	0.000011
H 0	-5.066323	-3.826625	0.000021
H 0	0.000131	2.314914	4.346543
H 0	-0.895389	3.734535	3.747779
H 0	0.895571	3.734511	3.747661
H 0	-0.000020	5.204780	-2.143660
H 0	2.619589	-3.529606	0.000019
H 0	5.650654	0.440914	-0.000042
H 0	5.066320	-3.826627	-0.000001
H 0	-0.000124	2.314915	-4.346537
H 0	0.895399	3.734532	-3.747772
H 0	-0.895561	3.734513	-3.747656

SCF Done: E(RB3LYP) = -7471.98282800

Sum of electronic and zero-point Energies= -7471.655106

Sum of electronic and thermal Energies= -7471.627066

Sum of electronic and thermal Enthalpies= -7471.626122

Sum of electronic and thermal Free Energies= -7471.715927

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