Supporting Information

Thiophene-based twisted bistricyclic aromatic ene with tricoordinate boron: a new n-type semiconductor

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Experimental

General

All reactions were carried out under dry argon. For the reaction solvents, toluene, diethyl ether, dichloromethane, dioxane, and DMSO were purchased from Kanto Chemical Co., Ltd. and were distilled from calcium hydride and stored over activated molecular sieves under argon until use. All other chemicals were purchased from Wako Pure Chemical Industries, Ltd. and TCI Co., Ltd. Starting material bis(2-bromothiophen-3-yl)methane was prepared according to literature.[S1] Room-temperature NMR spectra were recorded on Varian System 500 and 400MR spectrometers, whereas VT-NMR experiments were performed on a JEOL JNM-ECA500 spectrometer. Abbreviations Th and ^{F}Mes used for the following NMR assignments stand for fused thiophene ring and 1,3,5-tris(trifluoromethyl)phenyl group, respectively. High-resolution mass spectra were obtained on a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer at N-BARD, Hiroshima University. ESR spectra of **dDTCB** solutions in benzene (1.0 mmol/L) and pyridine (2.0 mmol/L) were recorded on a JEOL JES-RE1X spectrometer (X-band) in the dark at room temperature with a Mn^{2+}/MgO standard sample to calibrate the magnetic fields. DSC analysis was carried out under gentle nitrogen flow at a heating rate of 10 ºC/min using the SII DSC6200 analyzer. The measurements of single-crystal X-ray diffraction, VT-NMR, and HR-MS were made at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University.

XRD measurements

Single crystal X-ray diffraction data was collected at 123 K on a Bruker AXS SMART APEX II ULTRA diffractometer at Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University, using MoKα radiation monochromated with a multilayered confocal mirror. The structure was solved by Intrinsic Phasing on the SHELXT-2014/4 program and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were included but not refined (SHELXL-2014/6). All other calculations were performed using the APEXII crystallographic software package of Bruker AXS. Graphical crystal structures were generated using Mercury 3.10.3 (Cambridge Crystallographic Data Centre). Powder XRD patterns were obtained on a Rigaku Ultima IV multipurpose

X-ray diffraction system.

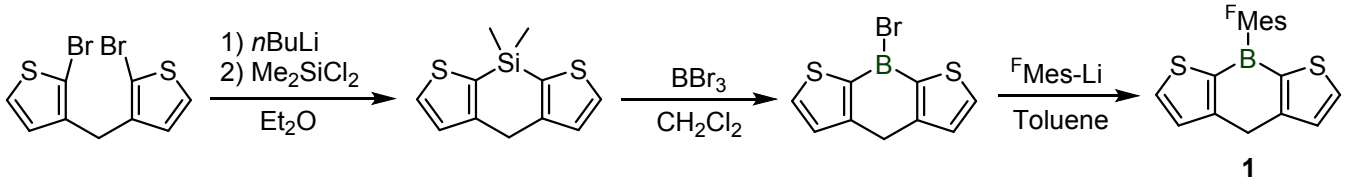
Photophysical measurements

Room-temperature UV–vis absorption spectra were measured with a HITACHI U-2910 spectrophotometer, whereas VT-absorption spectra were acquired with a Shimadzu UV-3600 plus spectrometer. The concentration of the samples was 10 μmol/L. In the titration experiments, aliquots of a tetrabutylammonium cyanide (TBACN) solution in toluene (5 μL, 3.0 mmol/L, 0.5 equivalents) were added to a solution of **dDTCB** in toluene (10 μmol/L, 3.0 mL) every 5 minutes. Cyclic voltammetry measurements were performed with an AMETEK VersaSTAT 4 potentiostat/galvanostat in a 1.0 mM solution in dichloromethane containing 0.1 M nBu_4NPF_6 at a 100 mV s^{-1} scan rate using a three-electrode system which was composed of a Pt plate as the counter electrode, a Pt wire as the working electrode, and an Ag wire as the pseudo-reference electrode. The potentials were corrected using ferrocene as the internal standard.

DFT calculations

All geometrical optimizations and TD-DFT calculations were performed on a Gaussian 16 program at the B3LYP/6-311+G(d,p) level of theory.[S2] No imaginary frequencies were found for all the ground state optimized structures, whereas only one imaginary frequency was observed for the TS geometry. The intrinsic reaction coordinate (IRC) calculation was performed on the TS structure at the same level to confirm that the transition state connects the twisted and folded conformers. The ground state geometries of the twisted and folded conformers of **dDTCB** were optimized with C_2 symmetry. NMR chemical shifts were calculated using GIAO method at the B3LYP/6-311+G(2d,p) level.

Synthesis



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Synthesis of 8,8-dimethyl-4,8-dihydrosilino[2,3-*b*:6,5-*b*']dithiophene

To a solution of bis(2-bromothiophen-3-yl)methane (8.74 g, 25.8 mmol) in 50 mL of diethyl ether was slowly added 18.9 mL (52.9 mmol) of 2.8 mol/L *n*BuLi in hexane at –78 °C for 20 min, and the mixture was stirred for 30 min at the temperature. Dimethyldichlorosilane (3.28 mL, 27.1 mmol) was then added slowly to the mixture at –78 °C. The mixture was warmed to room temperature and then stirred overnight. The resulting mixture was hydrolyzed with water, and the organic layer was washed twice with water and then once with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The crude product was purified by silica gel chromatography using a 10:1 mixture of hexane/dichloromethane as the eluent to give 3.97 g (16.8 mmol, 65% yield) of the title compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 4.6 Hz, 2H, Th), 7.13 (d, J = 4.6 Hz, 2H, Th), 4.26 (s, 2H, CH_2), 0.50 (s, 6H, $SiMe_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 130.7, 129.0, 128.4, 32.0, 1.2. HRMS (APCI, positive) Calcd for $C_{11}H_{12}S_2Si$: M^+: 236.01442, Found 236.01416. m.p. 61.5-63.5°C.

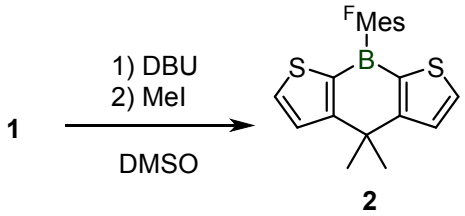
Synthesis of 8-bromo-4,8-dihydroborinino[2,3-*b*:6,5-*b*']dithiophene.

To a solution of 8,8-dimethyl-4,8-dihydrosilino[2,3-*b*:6,5-*b*']dithiophene (3.09 g, 13.1 mmol) in 15 mL of dichloromethane was slowly added 14.5 mL (14.5 mmol) of 1.0 mol/L BBr_3 in dichloromethane at –78 °C for 5 min. The mixture was gradually warmed to room temperature and stirred overnight. All volatiles were removed in vacuum to give the product quantitively as a brown solid. The product was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J = 4.7 Hz, 2H, Th), 7.36 (d, J = 4.7 Hz, 2H, Th), 4.24 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.2, 136.7, 128.8, 32.8. One signal for B−C was not detected, probably due to its low intensity as a result of quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 45.9.

Synthesis of 1.

To a solution of 1,3,5-tris(trifluoromethyl)benzene (4.63 g, 16.4 mmol) in 50 mL of ether were slowly added 10.6 mL (16.4 mmol) of 1.55 mol/L *n*BuLi in hexane at –78 °C for 5 min. The mixture was stirred for 3 hours at room temperature, then the solvent was removed in vacuum to give the lithium salt. The solid was redissolved in 20 mL of toluene at 0 ℃, then cooled to –78 °C. A solution of 8-bromo-4,8-

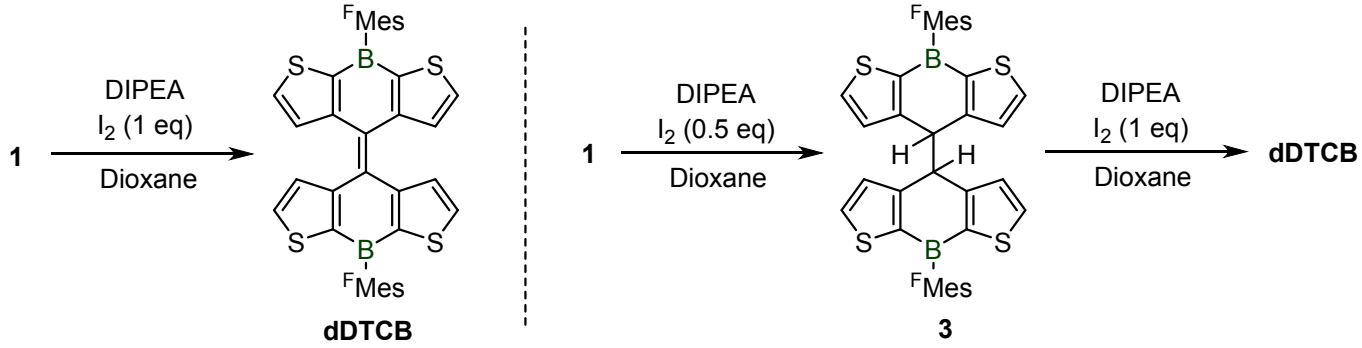
dihydroborinino[2,3-*b*:6,5-*b*']dithiophene (13.1 mmol) in 20 mL of toluene was slowly added to the above solution, then the mixture was stirred overnight at room temperature. The resulting mixture was hydrolyzed with saturated NH_4Cl aqueous solution, and the organic layer was washed twice with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The crude product was purified by silica gel chromatography using a 10:1 mixture of hexanes/dichloromethane as the eluent to give 3.82 g (8.11 mmol, 49% yield) of the title compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (s, 2H, ^{F}Mes), 7.88 (d, J = 4.7 Hz, 2H, Th), 7.36 (d, J = 4.7 Hz, 2H, Th), 4.42 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.1, 143.1 (br, B−C), 137.8 (br, B−C), 136.4, 134.6 (q, $J_{C\text{-}F}$ = 32 Hz, *o*-$\underline{C}CF_3$), 131.7 (q, $J_{C\text{-}F}$ = 34 Hz, *p*-$\underline{C}CF_3$), 128.3, 126.0 (m), 123.4 (q, $J_{C\text{-}F}$ = 275 Hz, *o*-CF_3), 122.9 (q, $J_{C\text{-}F}$ = 273 Hz, *p*-CF_3), 32.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 47.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −57.6, −63.1. HRMS (APCI, positive) Calcd for $C_{18}H_8BF_9S_2$: M^+: 470.00146, Found 470.00052. m.p. 131.9-134.3°C.



Synthesis of 2.

To a solution of **1** (78.1 mg, 0.166 mmol) in 4 mL of DMSO were added 74.5 μL (0.498 mmol) of DBU at room temperature and stirred for 30 min. Then methyl iodide (52 μL, 0.835 mmol) was added to the mixture and the mixture was stirred for additional 2 hours. The resulting mixture was hydrolyzed with water and extracted with hexane. The organic layer was washed three times with water and then once with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The crude product was purified by silica gel chromatography using hexanes as the eluent to give 66.3 mg (0.133 mmol, 80% yield) of **2** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (s, 2H, ^{F}Mes), 7.87 (d, J = 4.8 Hz, 2H, Th), 7.45 (d, J = 4.8 Hz, 2H, Th), 1.68 (s, 6H, CH_3). ^{13}C NMR (100 MHz, cdcl$_3$) δ = 164.8, 143.1 (br, B−C), 136.8, 135.9 (br, B−C), 134.7 (q, $J_{C\text{-}F}$ = 32 Hz, *o*-$\underline{C}CF_3$), 131.7 (q, $J_{C\text{-}F}$ = 34 Hz, *p*-$\underline{C}CF_3$), 127.0, 126.0 (m), 123.5 (q, $J_{C\text{-}F}$ = 275 Hz, *o*-CF_3), 122.9 (q, $J_{C\text{-}F}$ = 273 Hz, *p*-CF_3), 42.3, 31.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ: 47.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −57.6, −63.1. HRMS (APCI, positive) Calcd for $C_{20}H_{12}BF_9S_2$: M^+: 498.03280, Found

498.03259. m.p. 130.8-133.6°C.



Synthesis of dDTCB.

To a solution of **1** (105 mg, 0.224 mmol) and I_2 (58.0 mg, 0.229 mmol) in 5 mL of dioxane was added 190 μL (1.12 mmol) of DIPEA at room temperature and the mixture was stirred overnight. The resulting mixture was hydrolyzed with water and extracted with dichloromethane. The organic layer was washed once with saturated sodium thiosulfate aqueous solution, twice with water, then once with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The crude product was purified by silica gel chromatography using hexanes as the eluent to give 99.7 mg (0.106 mmol, 95 % yield) of **dDTCB** as a black powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (s, 4H, ^{F}Mes), 7.74 (d, J = 5.0 Hz, 4H, Th), 7.54 (d, J = 5.0 Hz, 4H, Th). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.9 (Th), 143.3 (br, B−C_{Th}), 142.3 (br, B−C_{FMes}), 138.6 (C=C), 135.0 (q, $J_{C\text{-}F}$ = 32 Hz, *o*-$\underline{C}CF_3$), 133.7 (Th), 133.2 (Th), 131.9 (q, $J_{C\text{-}F}$ = 35 Hz, *p*-$\underline{C}CF_3$), 126.1 (m, ^{F}Mes), 123.5 (q, $J_{C\text{-}F}$ = 276 Hz, *o*-CF_3), 122.9 (q, $J_{C\text{-}F}$ = 273 Hz, *p*-CF_3). ^{11}B NMR (160 MHz, $CDCl_3$) δ: 45.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ: −57.4, −63.0. HRMS (APCI, positive) Calcd for $C_{36}H_{12}B_2F_{18}S_4$: M^+: 935.97260, Found 935.97412. s.p. 336°C (DSC).

Synthesis of 3.

Compound **3** was prepared from 48.1 mg (0.102 mmol) of **1**, 13.1 mg (51.6 μmol) of I_2, and 87 μL (0.512 mmol) of DIPEA in 3 mL of dioxane in a manner similar to that above. The product was obtained as a white solid (34.1 mg, 36.3 μmol, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.18 (s, 2H, ^{F}Mes), 8.16 (s, 2H, ^{F}Mes), 7.79 (d, J = 4.8, 4H, Th), 6.98 (br s, 4H, Th), 5.42 (s, 2H, CH). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.6, 142.7 (br, B−C), 138.9 (br, B−C), 137.0, 134.6 (m, *o*-$\underline{C}CF_3$), 131.7 (q, $J_{C\text{-}F}$ = 34 Hz, *p*-$\underline{C}CF_3$), 127.7,

126.0 (m), 125.7 (m), 123.6 (m, *o*-CF_3), 122.8 (q, $J_{C\text{-}F}$ = 273 Hz, *p*-CF_3), 49.2. ^{11}B NMR (160 MHz, $CDCl_3$) δ: 48.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ: −57.3, −57.4, −63.1. HRMS (ESI, positive) Calcd for $C_{36}H_{14}B_2F_{18}S_4$: $[M+Na]^+$: 960.97816, Found 960.97882.

Synthesis of dDTCB from 3.

Compound **dDTCB** was prepared from 50.7 mg (54.0 μmol) of **3**, 15.0 mg (59.1 μmol) of I_2, and 46 μL (0.270 mmol) of DIPEA in 5 mL of dioxane in a manner similar to that above. The product was obtained as a black powder (44.9 mg, 48.0 μmol, 89 % yield).

Fabrication of OFETs

Fig. S20 shows the schematic illustration of top-gate/bottom-contact **dDTCB** OFET, along with the chemical structures of the organic materials used in the OFETs. The glass substrates were sequentially washed with acetone and isopropyl alcohol (IPA) in ultrasonic baths, followed by exposure to UV/O_3. An insulating polymer of poly (4-vinylphenol) (PVP, Sigma-Aldrich) mixed with a cross-linking agent of poly (melamine-co-formaldehyde) (PMF, Sigma-Aldrich) in a weight ratio of 2:1 was dissolved in propylene glycol monomethyl ether acetate. The PVP:PMF solution was deposited onto the glass substrates by spin coating in ambient air, and the PVP:PMF thin films were cured at 200 °C under vacuum for 1 h to form cross-linked PVP thin films. After the fabrication of 30-nm-thick Au source-drain electrodes with 2-nm-thick Cr adhesion layers on the substrates by vacuum evaporation using a shadow mask, a thin layer of poly(ethyleneimine) (PEI), an electron-injection layer, was spun onto the surface of the substrate with source and drain Au electrodes from 0.1-wt% ethanol solution at 2000 rpm for 30 s. The substrate was then annealed in ambient atmosphere for 10 min at 150 °C. The channel length (L) and width (W) were 100 μm and 1.5 mm, respectively.

0.5 wt% **dDTCB** toluene solution was spin-coated on the substrates at 500 rpm for 5 s and then at 1000 rpm for 60 s in N_2 atmosphere. After drying **dDTCB** thin films at room temperature for 1 h and then at 100℃ for 10 min, an amorphous fluoropolymer solution, CYTOP™ (CTL-809 M, AGC), diluted at 6 wt% using a dilution solvent (CT-SOLV180, AGC) was spin-coated on the **dDTCB** thin films at 500 rpm for 10 s and then at 4000 rpm for 60 s, and was dried overnight in N_2 atmosphere to form a gate insulator with thickness of

~300 nm. Finally, 40-nm-thick Al gate electrodes were fabricated on the CYTOP layers by shadow-mask evaporation. The organic films, except for the cross-linked PVP films, were prepared in glove boxes filled with N_2.

Of key importance in the fabrication of n-channel OFETs is the coating of a thin polyethyleneimine (PEI) layer of approximately 1 nm thickness on source and drain electrodes in OFETs with the top-gate configuration.[S3] The PEI layer reduces the electron injection barrier from Au source electrode to **dDTCB** because of the formation of dipole moment.[S4]

Electrical characterization of OFETs

The electrical characteristics of the **dDTCB** OFET were measured using Keithley 6430 and 2400 source meters in an N_2-filled glove box at room temperature. The field-effect mobility, μ_{FE}, and the threshold voltage, V_{th}, were determined by the following standard FET equation using the transfer characteristics measured in the saturation regime:

$$I_D = \frac{\mu_{FE} C_i W}{2L}(V_G - V_{th})^2 \quad (1)$$

where I_D is the drain current, C_i is the capacitance per unit area for the gate insulator, and V_G is the gate voltage.

References

[S1] J. C. Bijleveld, M. Shahid, J. Gilot, M. M. Wienk, R. A. J. Janssen, *Adv. Funct. Mater.* **2009**, *19*, 3262–3270.

[S2] *Gaussian 16,* Revision A.03; Gaussian, Inc.: Wallingford, CT, 2016, https://gaussian.com/gaussian16/

[S3] K. Takagi, T. Nagase, T. Kobayashi, H. Naito, *Organic Electronics* **2016**, *32*, 65-69.

[S4] M. Takada, T. Nagase, T. Kobayashi, H. Naito, *Organic Electronics* **2017**, *50*, 290-295.

Supporting Figures and Tables

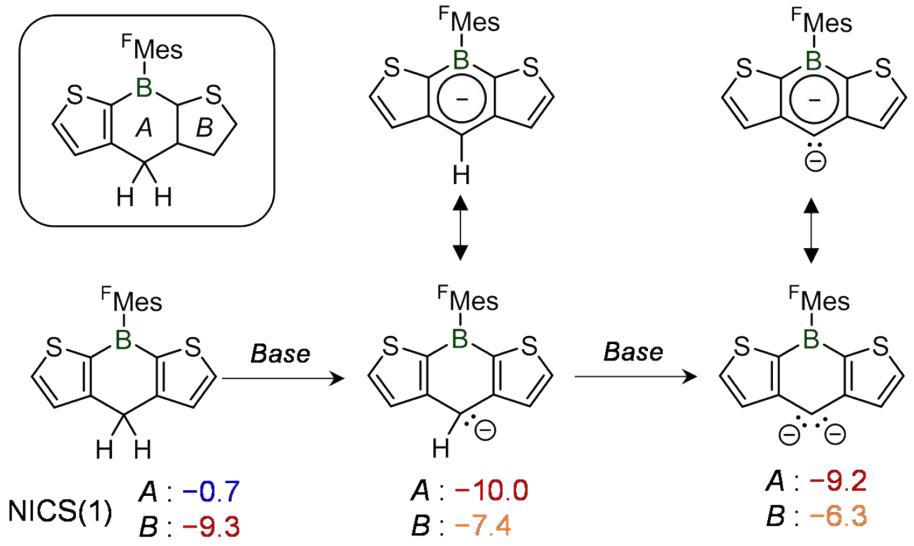


Figure S1. NICS(1) values of thiophene-annulated dihydroborinines calculated at the B3LYP/6-311+G(2d,p) level.

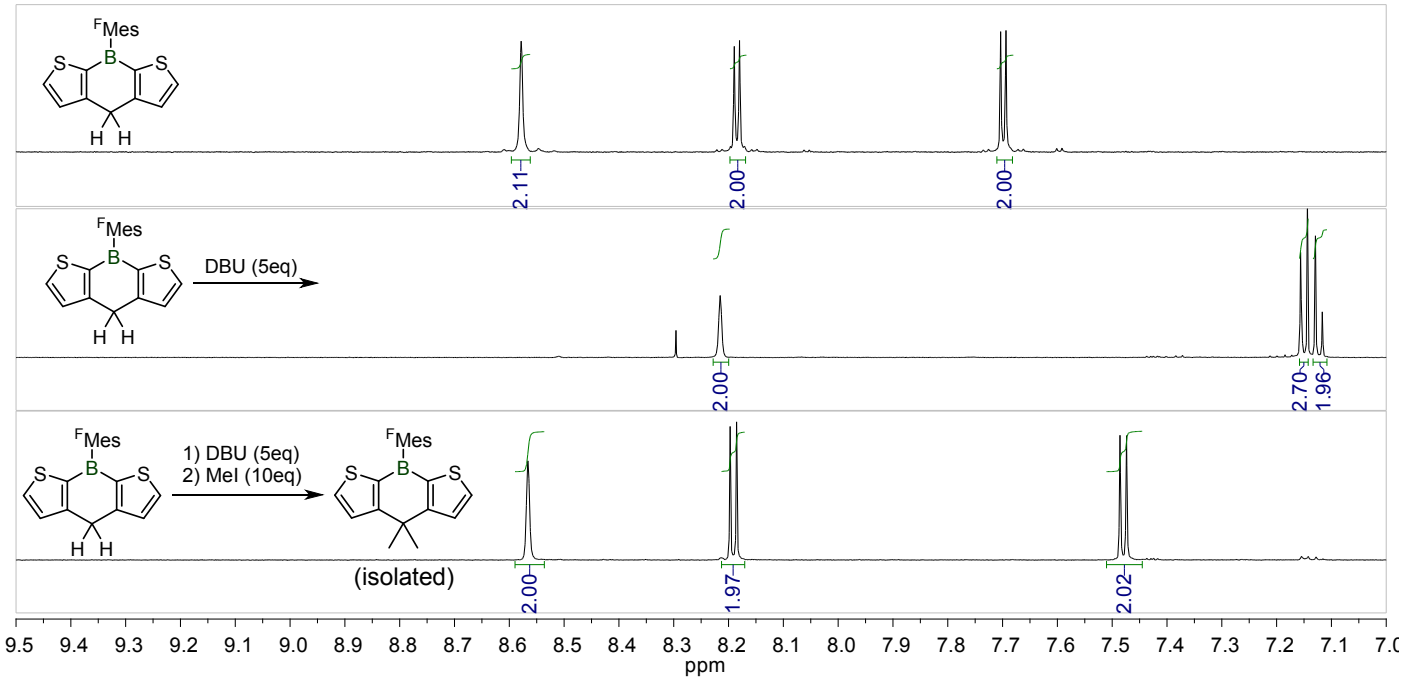


Figure S2. Partial ^{1}H NMR spectra of **1** in the presence and absence of DBU, and methylated product **2** in DMSO-d_6.

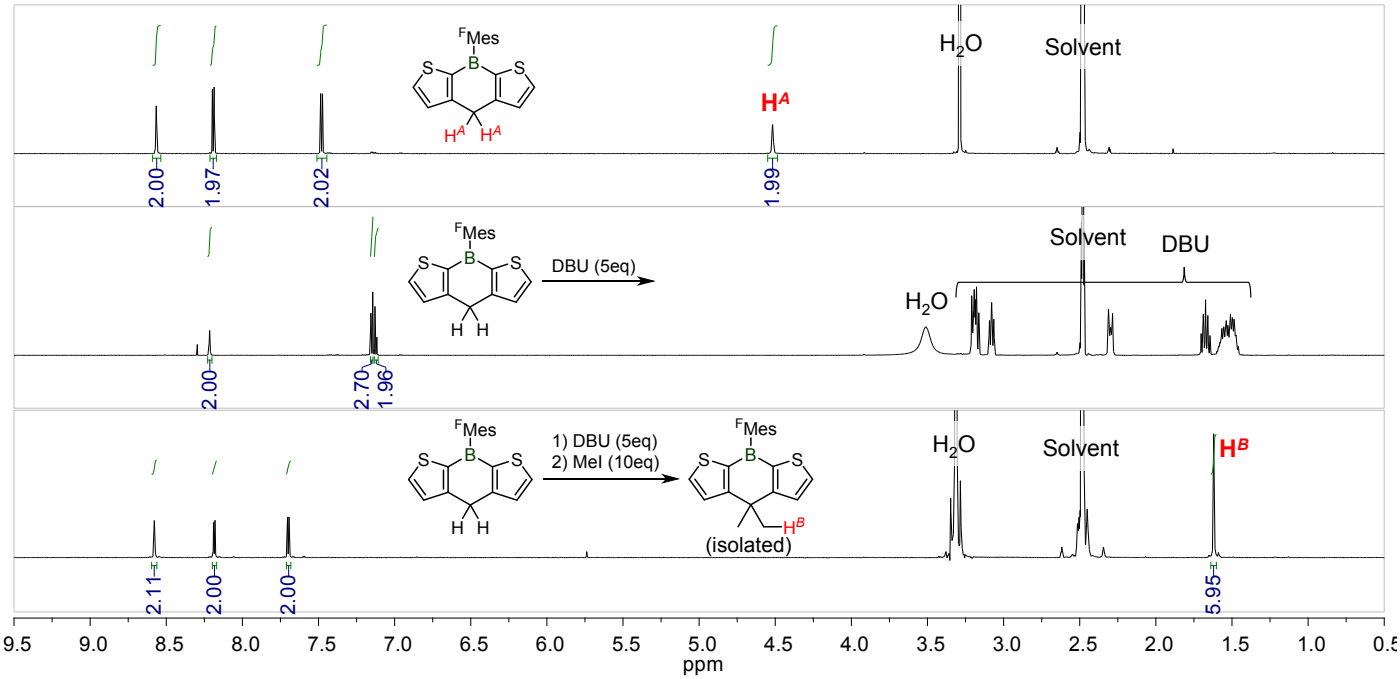


Figure S3. Full ^{1}H NMR spectra of **1** in the presence and absence of DBU, and methylated product **2** in DMSO-d_6.

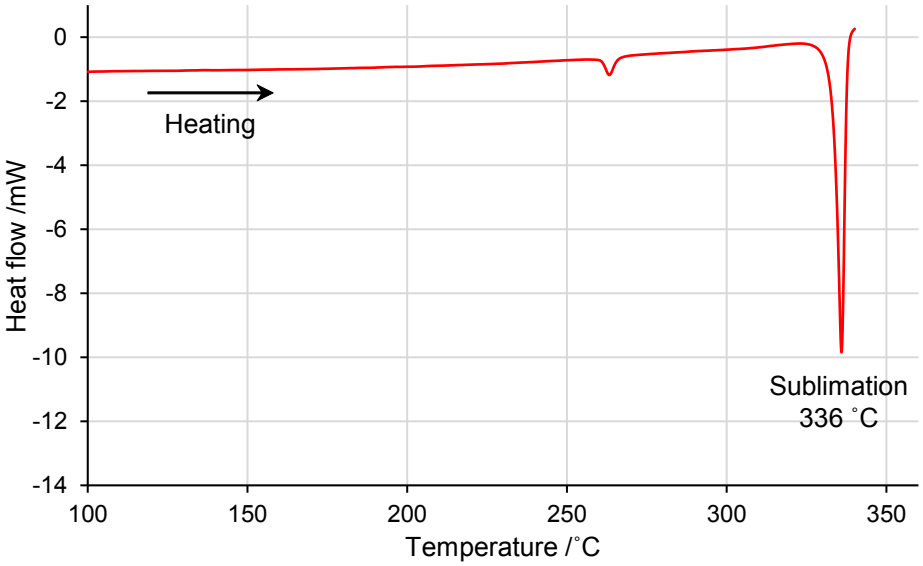


Figure S4. DSC curve of **dDTCB** at a heating rate of 10 ℃ min^{-1}.

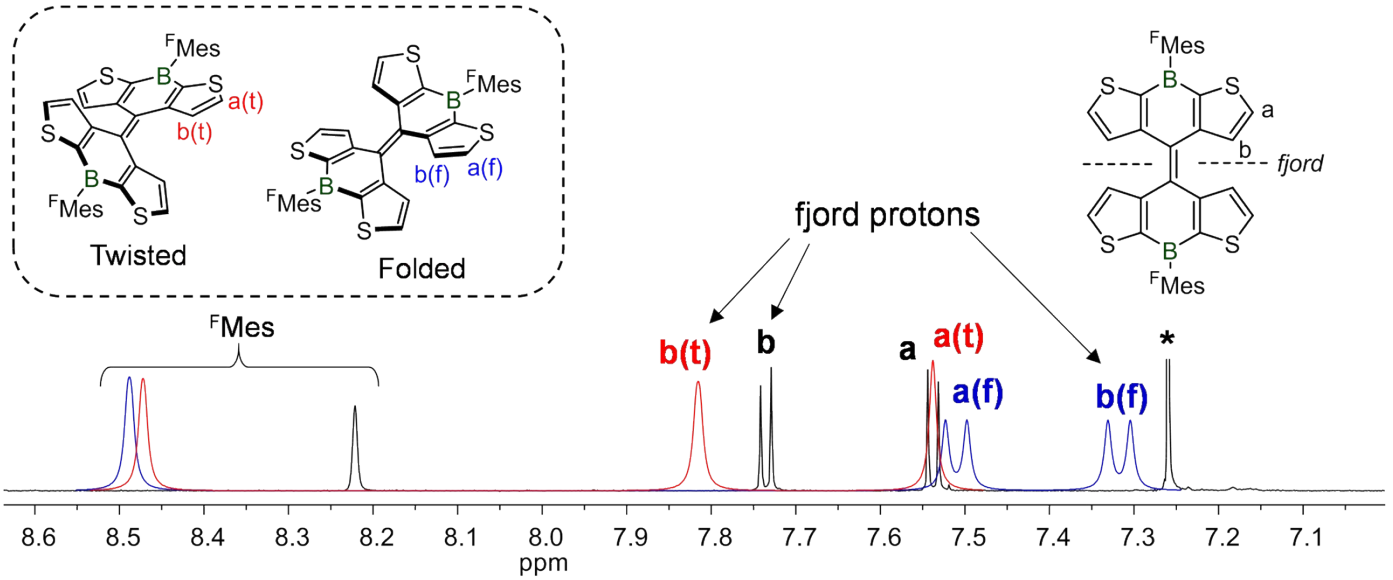


Figure S5. Experimental ^{1}H NMR spectrum of **dDTCB** in $CDCl_3$ at room temperature (black) and GIAO-DFT-calculated ^{1}H NMR spectra of twisted (red) and folded (blue) conformers of **dDTCB** at the B3LYP/6-311+G(2d,p) level.

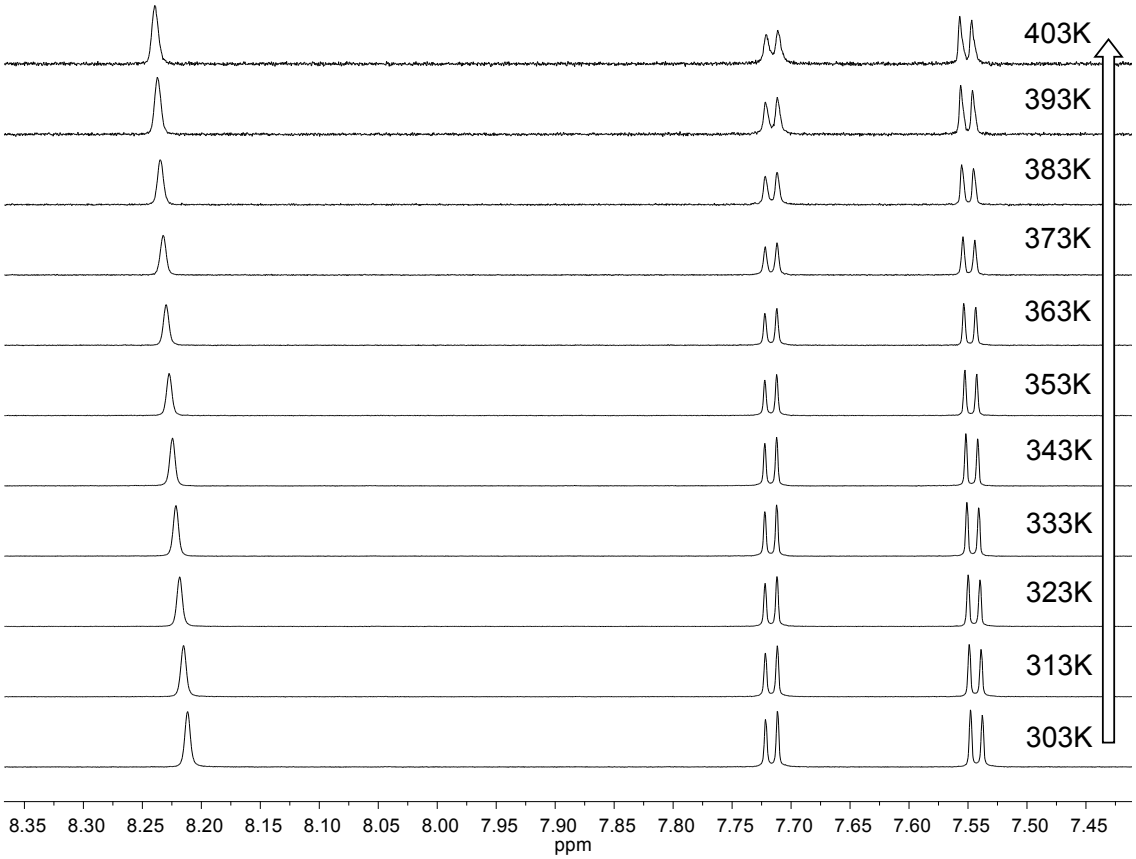


Figure S6. Variable temperature ^{1}H NMR spectra of **dDTCB** in $C_2D_2Cl_4$.

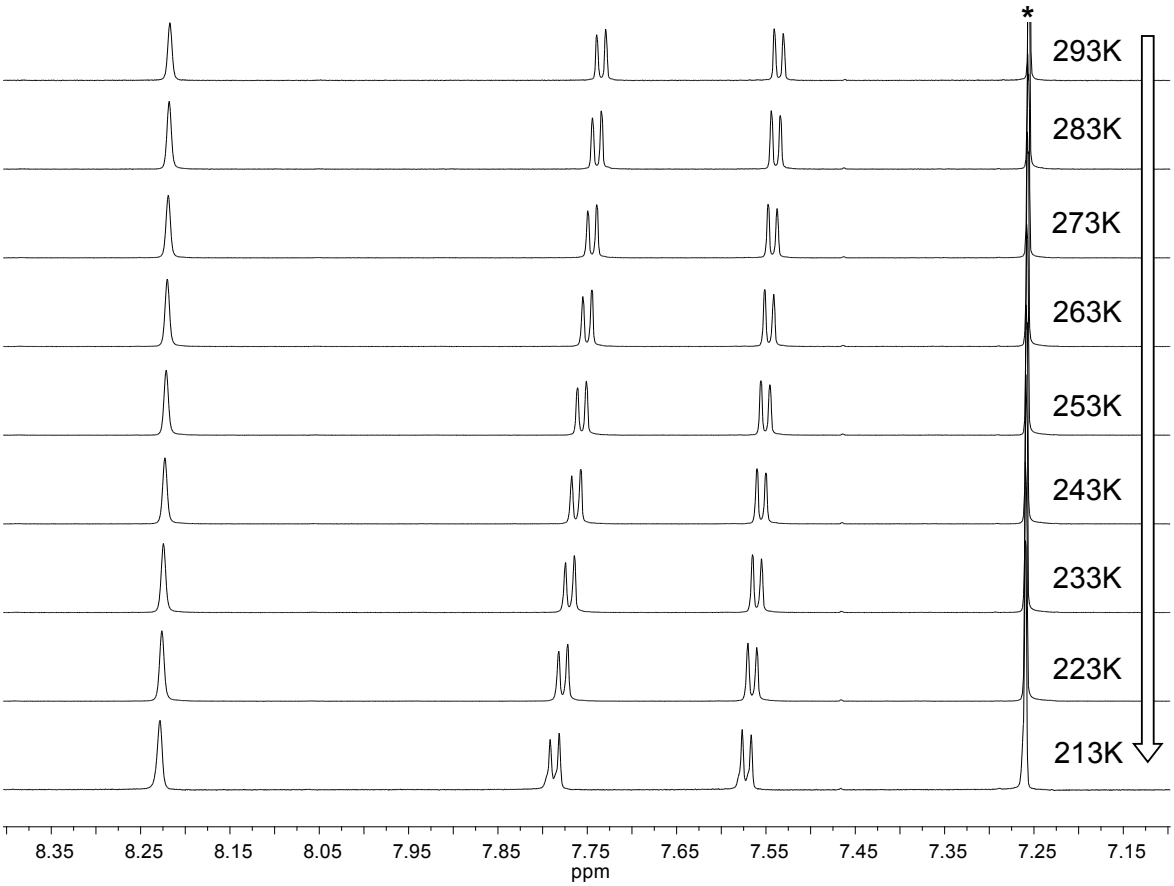


Figure S7. Variable temperature ^{1}H NMR spectra of **dDTCB** in $CDCl_3$.

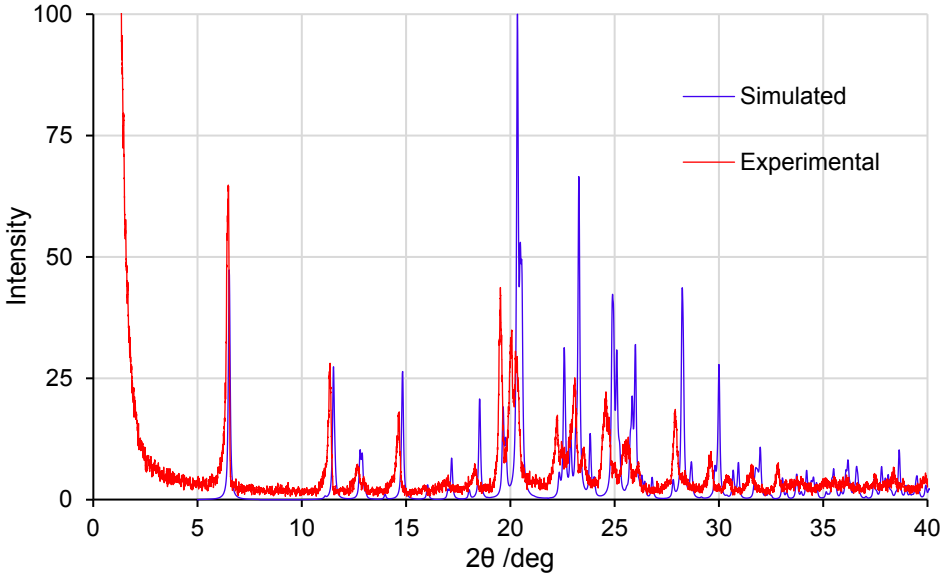


Figure S8. XRD patterns of a powder sample recorded at room temperature and simulated patterns from the single crystal XRD measured at 77K for **dDTCB**.

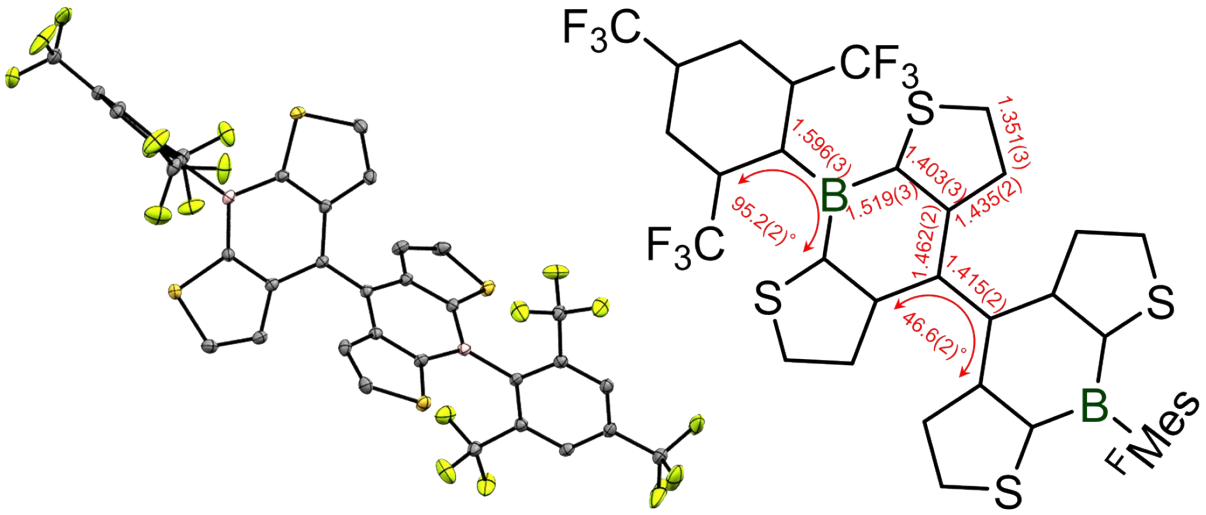


Figure S9. Crystal structure of **dDTCB** obtained at 123 K. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

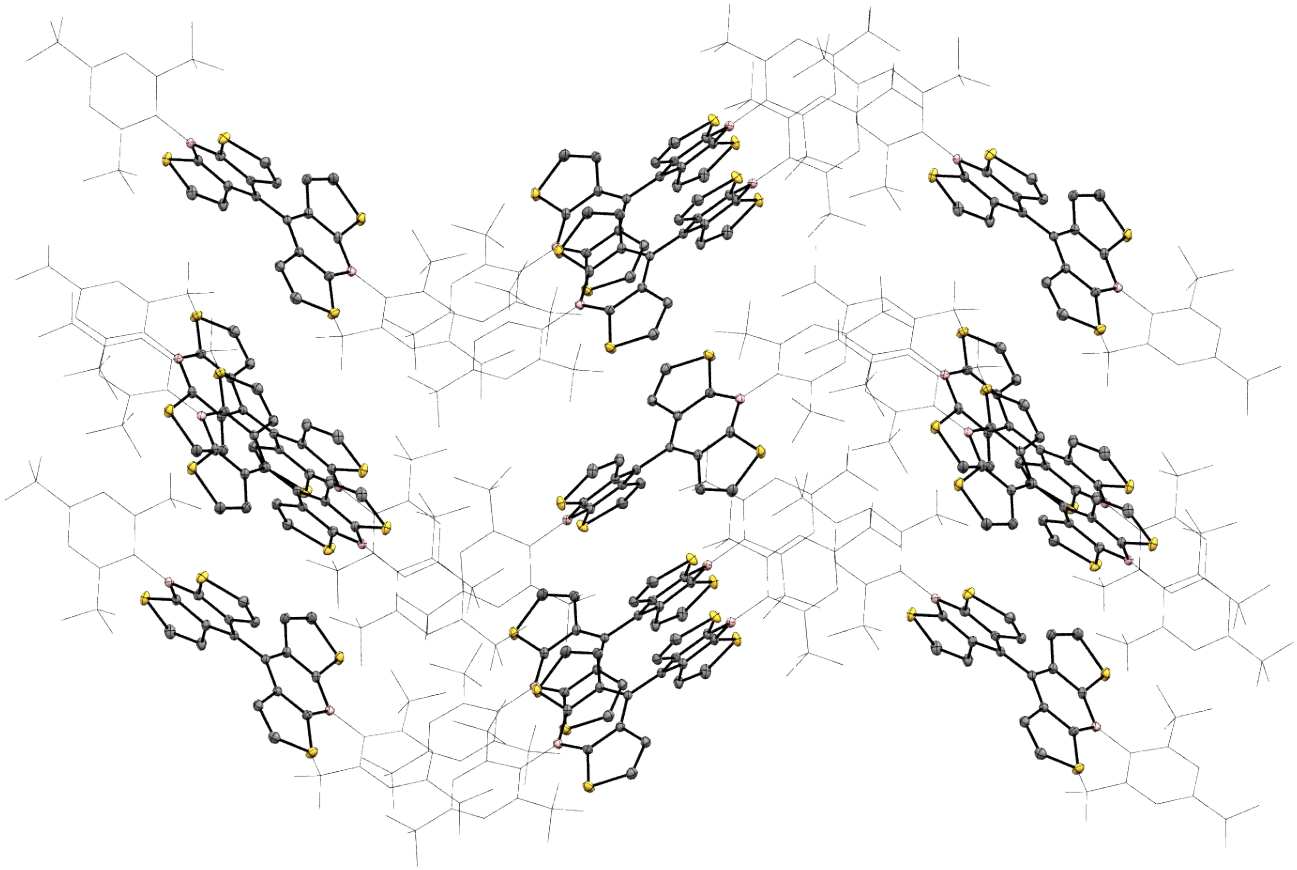


Figure S10. Crystal packing structure of **dDTCB** obtained at 123 K. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity. ^{F}Mes groups are shown in wireframe style.

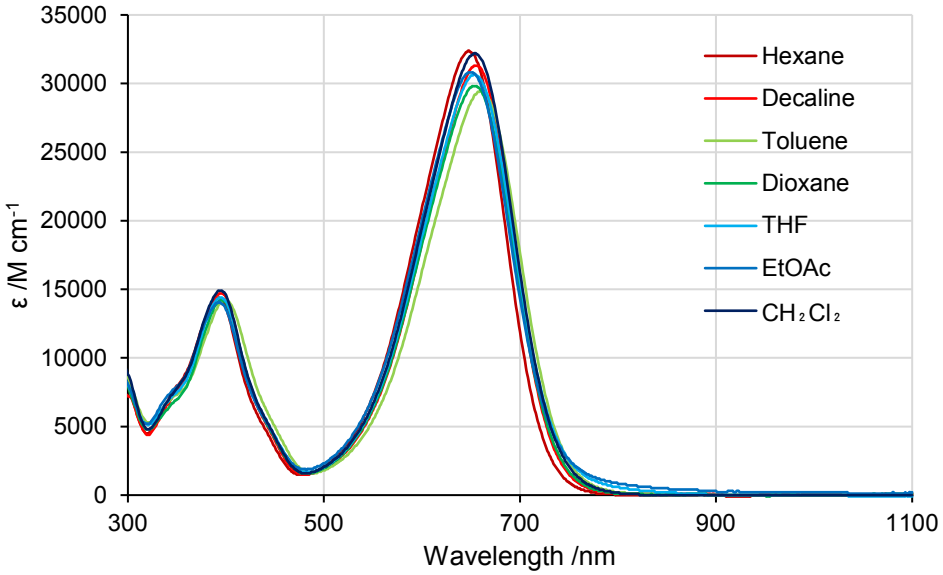


Figure S11. Absorption spectra of **dDTCB** in relatively non-polar solvents at room temperature.

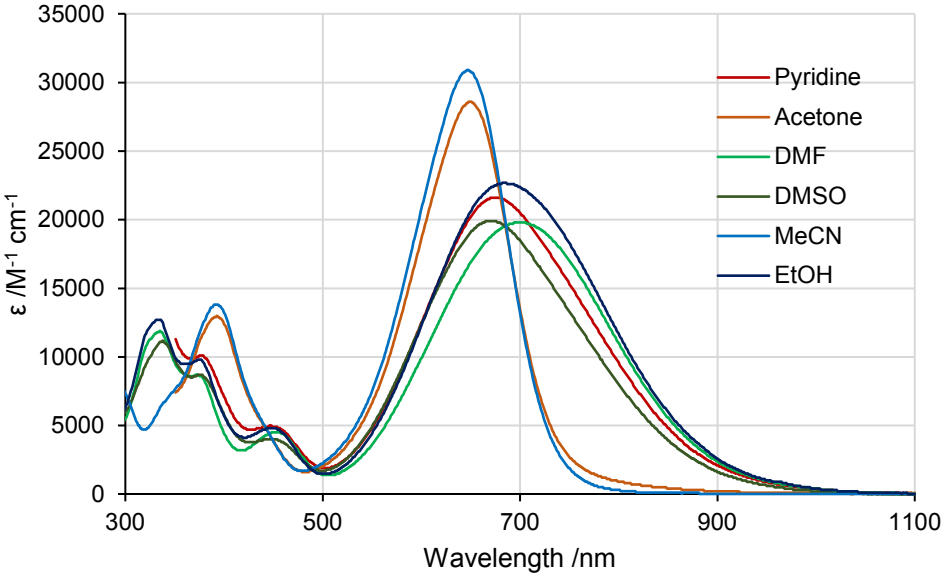


Figure S12. Absorption spectra of **dDTCB** in highly polar solvents at room temperature.

Table S1. Absorption maxima and coefficient of **dDTCB** in various solvents.

Solvent	λ_{max} /nm	ε /10^4 M^{-1} cm^{-1}
Hexane	648	3.2
Decaline	657	3.1
Toluene	661	3.0
Dioxane	656	3.0
THF	654	3.1
EtOAc	652	3.1
Pyridine	681	2.2
DCM	655	3.2
Acetone	651	2.9
DMF	706	2.0
DMSO	676	2.0
ACN	648	3.1
EtOH	686	2.3

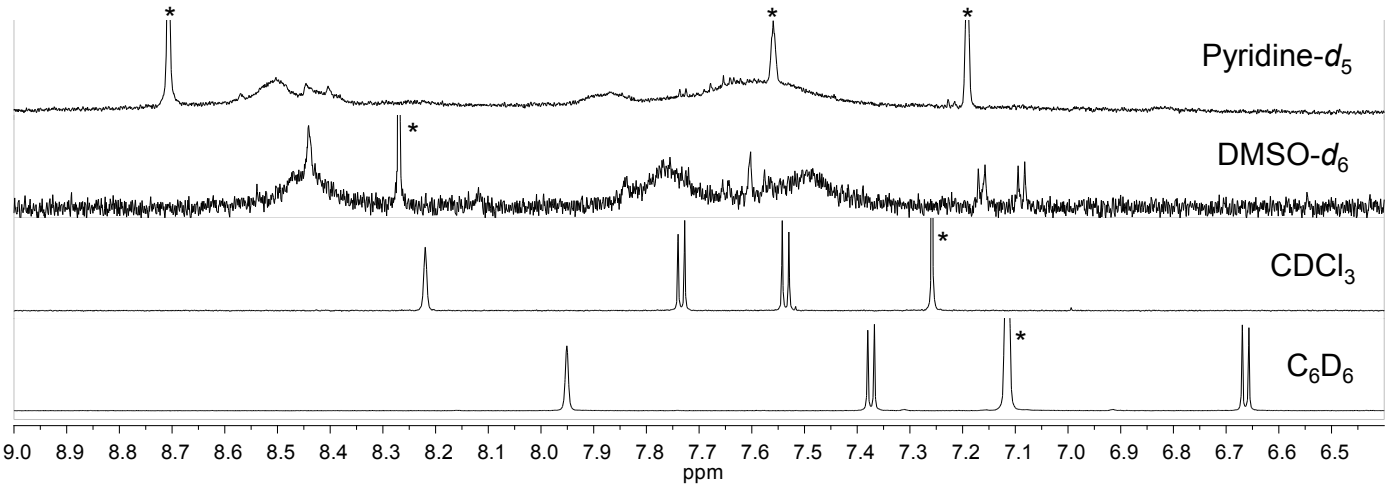


Figure S13. ^{1}H NMR spectra of **dDTCB** in various *d*-solvents at room temperature. The solvent peaks are denoted by asterisk.

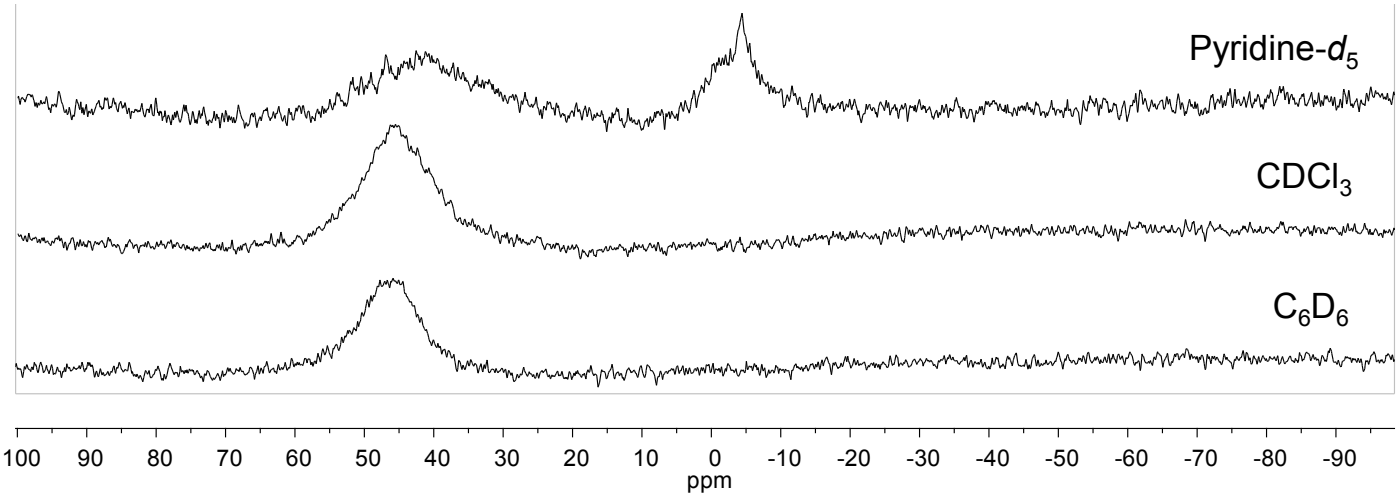


Figure S14. ^{11}B NMR spectra of **dDTCB** in various *d*-solvents at room temperature.

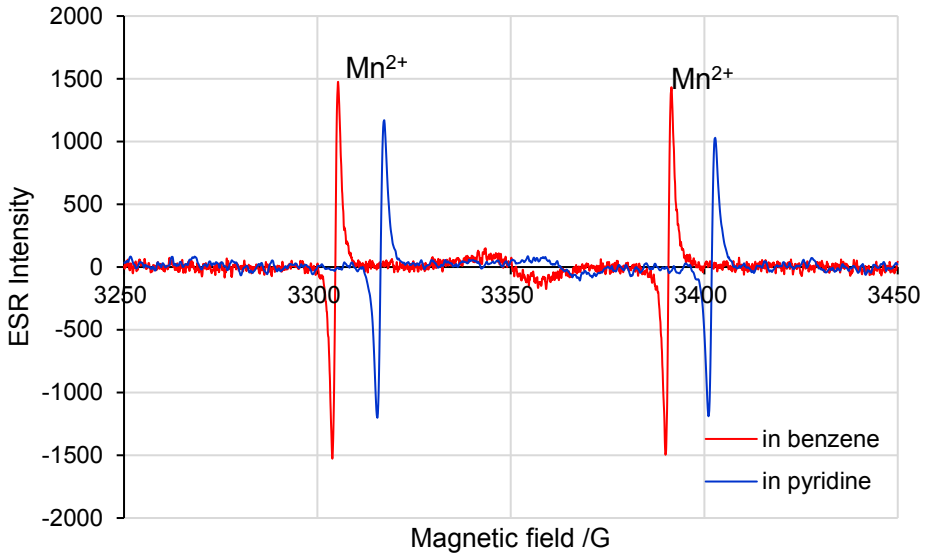


Figure S15. ESR spectra of **dDTCB** in benzene and in pyridine at room temperature. The sharp signals correspond to Mn^{2+} reference.

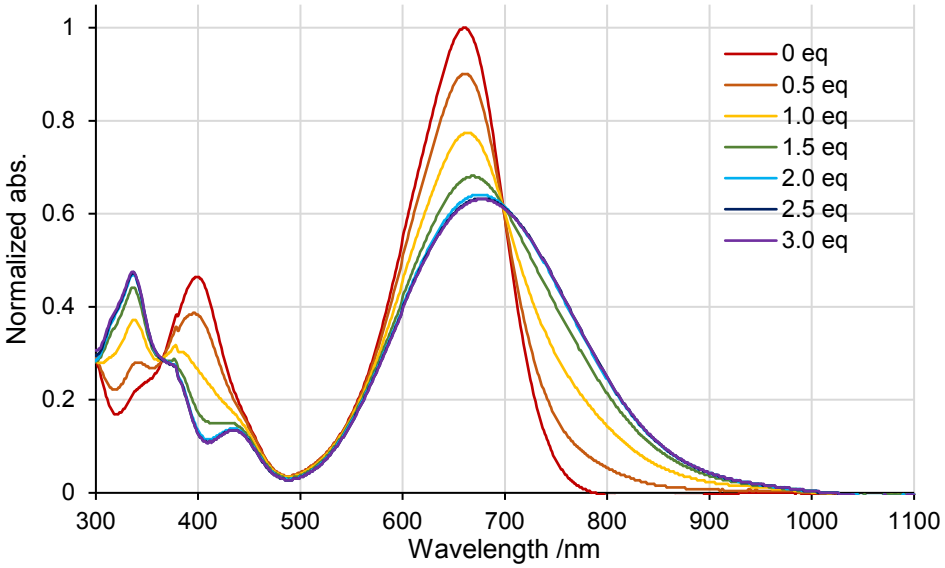


Figure S16. Absorption spectra for titrations of **dDTCB** with TBACN in toluene.

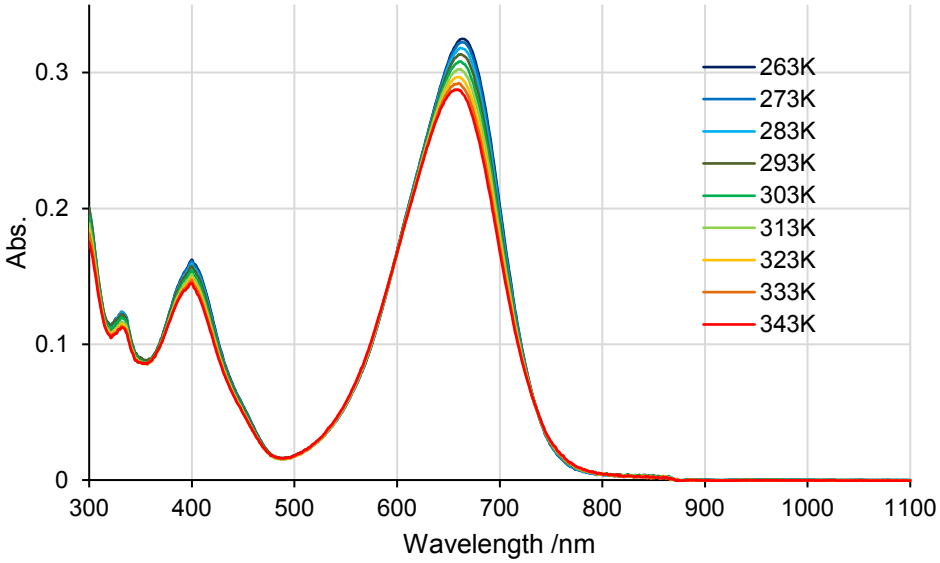


Figure S17. Absorption spectra of **dDTCB** in toluene at variable temperatures.

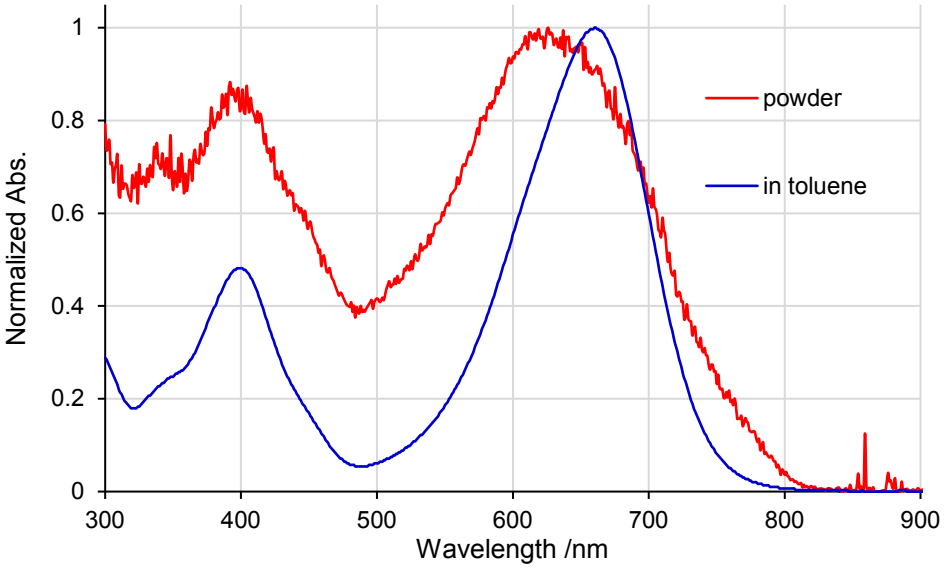


Figure S18. Normalized absorption spectra of **dDTCB** in toluene and as solids.

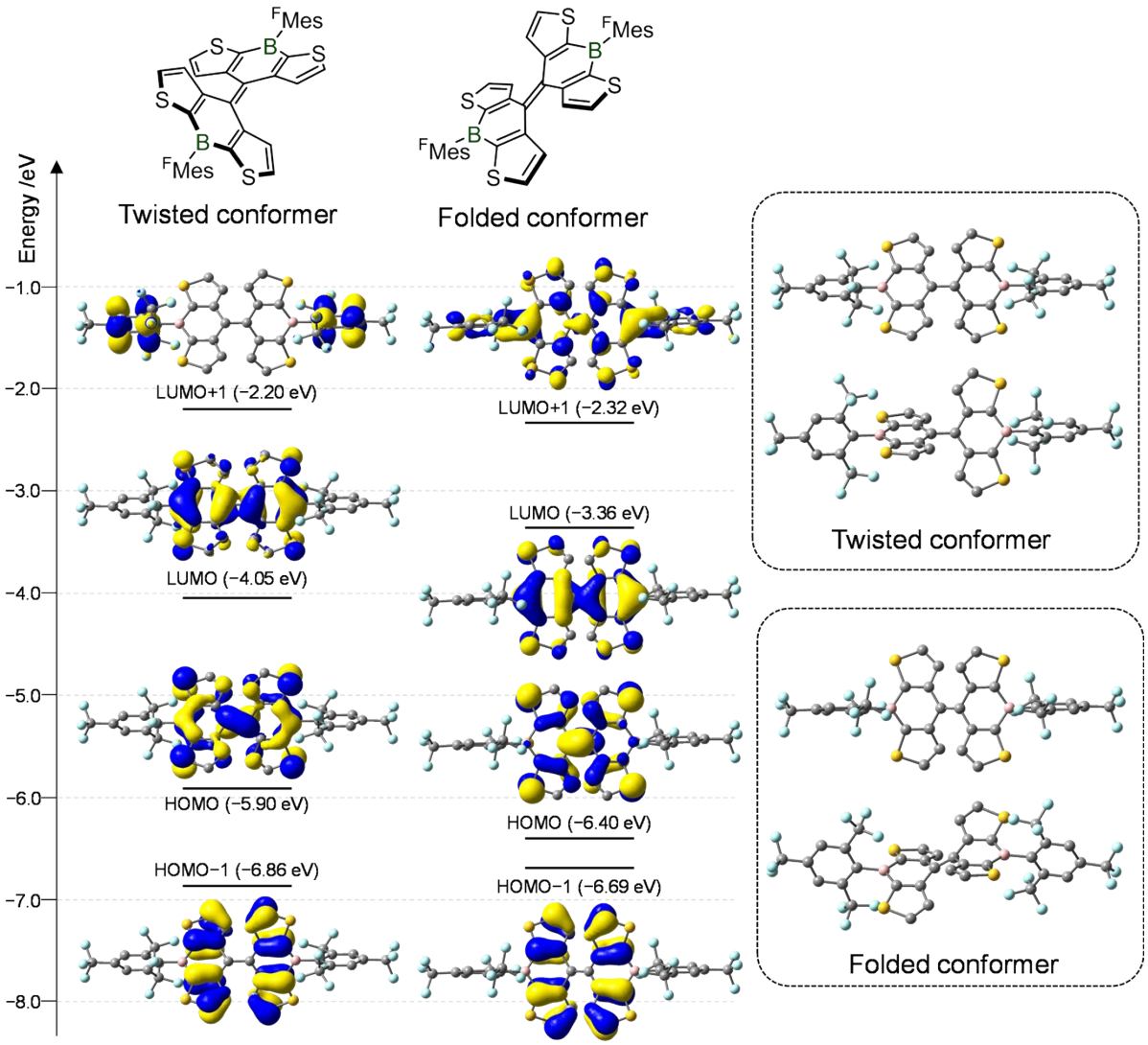


Figure S19. DFT-calculated Kohn–Sham orbitals of the two conformers of **dDTCB** at the B3LYP/6-311+G(d,p) level (isovalue = 0.03). Hydrogen atoms are omitted for clarity.

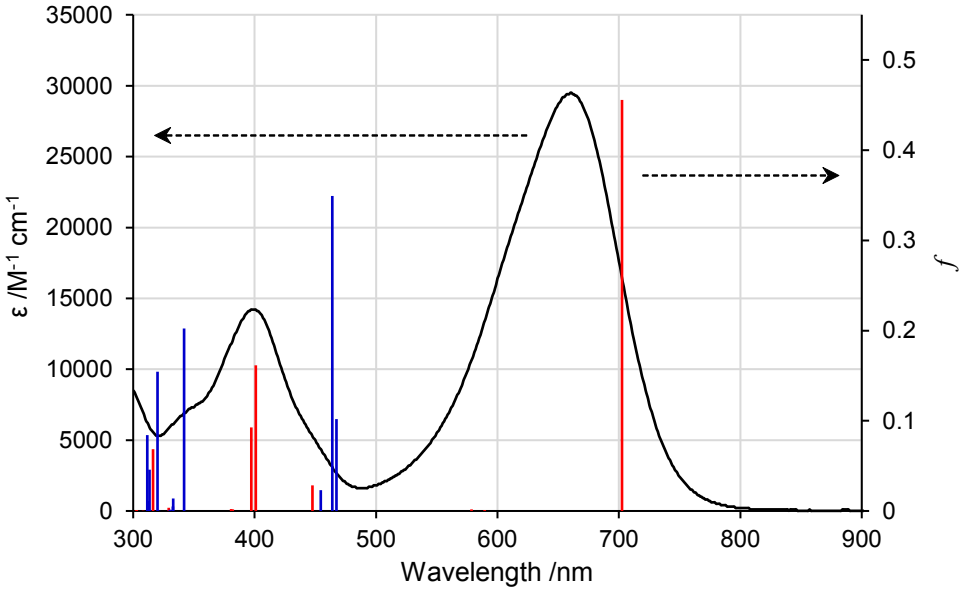


Figure S20. Experimental absorption spectrum in toluene (black line) and calculated TD-DFT results of twisted (red) and folded (blue) conformers at the B3LYP/6-311+G(d,p) level for **dDTCB**.

Table S2. TD-DFT data for the twisted conformer of **dDTCB**.

Excited state	Composition [a]	CI	Excitation energy /eV	Wavelength /nm	f [b]
S0→S1	H→L	0.717	1.77	702	0.46
	H→L	-0.156			
S0→S5	H-4→L	0.696	3.09	401	0.16
S0→S6	H-5→L	0.696	3.12	397	0.09

[a] H and L denote HOMO and LUMO, respectively. [b] Oscillator strength.

Table S3. TD-DFT data for the folded conformer of **dDTCB**.

Excited state	Composition [a]	CI	Excitation energy /eV	Wavelength /nm	f [b]
S0→S1	H-1→L	0.606	2.65	467	0.10
	H→L	-0.349			
S0→S2	H-1→L	0.348	2.67	464	0.35
	H→L	0.608			
S0→S6	H-4→L	0.692	3.63	342	0.20
S0→S13	H-5→L	0.291	3.87	320	0.15
	H-2→L+2	-0.144			
	H-2→L+4	0.214			
	H-1→L+1	0.553			
	H-1→L+5	0.154			
S0→S18	H-5→L	-0.134	3.98	312	0.08
	H-2→L+4	0.396			
	H-1→L+1	-0.176			
	H-1→L+3	0.174			
	H-1→L+5	0.499			

[a] H and L denote HOMO and LUMO, respectively. [b] Oscillator strength.

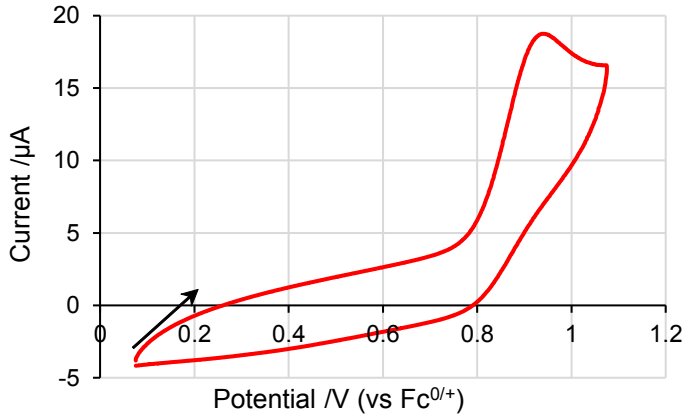


Figure S21. Anodic cyclic voltammetry data of **dDTCB** in dichloromethane containing 0.1 M Bu_4NPF_6 at the scan rate of 100 mV s^{-1}.

Table S4. Optical/electrochemical properties of **dDTCB** in solution.

λ_{max} [a]/nm	E_{red}^1 [b]/V	E_{red}^2 [b]/V	E_{ox} [c]/V	LUMO [d]/eV	HOMO [e]/eV	E_g(CV) [f]/eV	E_g(Opt) [g]/eV
661	−0.81	−1.17	0.79	−3.99	−5.59	1.60	1.88

[a] Absorption maxima in toluene; [b] $E_{red} = 0.5\ (E_{pc} + E_{pa})$ vs Fc/Fc^+; [c] Onset potential vs Fc/Fc^+; [d] Determined as $-(4.8 - E_{red}^1)$; [e] Determined as $-(4.8 + E_{ox})$; [f] $E_g(CV) = E_{ox} - E_{red}^1$; [g] Obtained from the absorption onset in toluene.

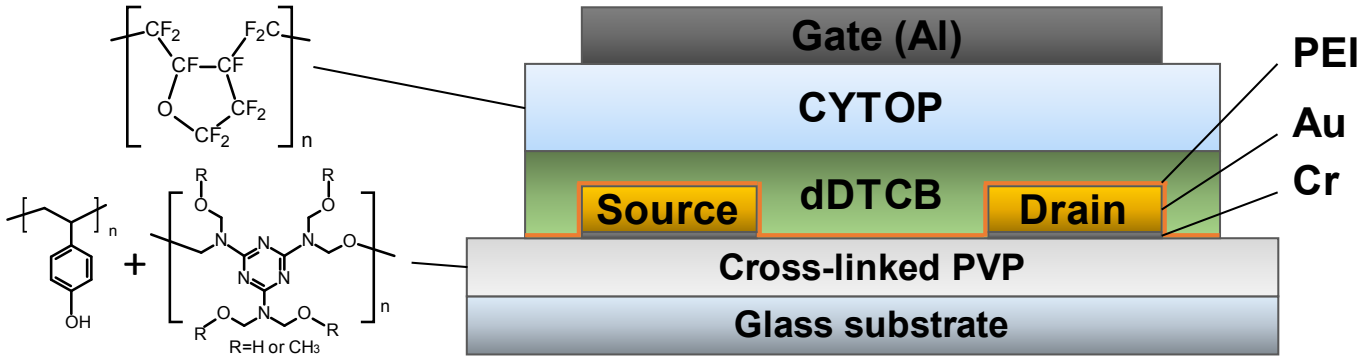


Figure S22. Schematic illustration of a top-gate/bottom-contact **dDTCB** OFET, along with the chemical structures of the organic materials.

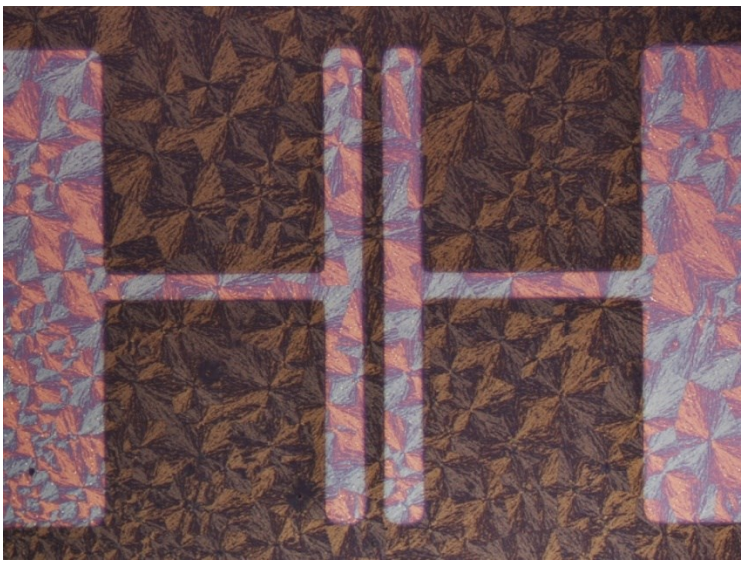


Figure S23. Polarized light microscopy image of **dDTCB** thin film coated on glass substrate with source and drain electrodes after annealing at 100 ℃ for 10 min.

NMR and MS spectra

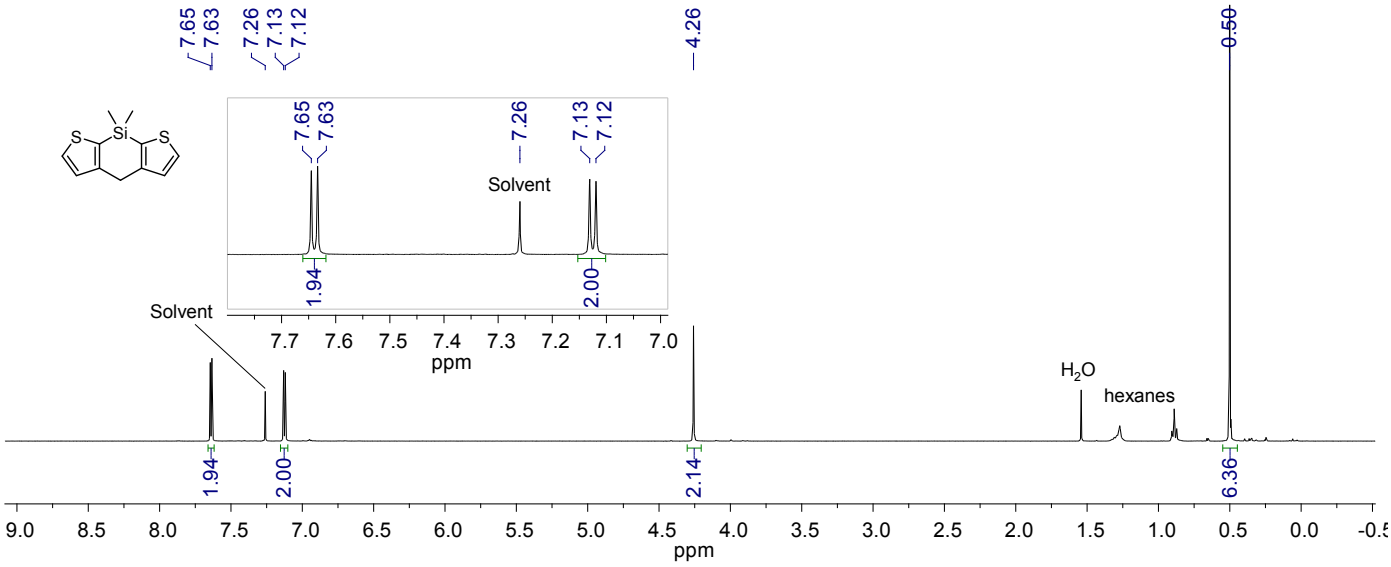


Figure S24. ^{1}H NMR spectrum of 8,8-dimethyl-4,8-dihydrosilino[2,3-*b*:6,5-*b*']dithiophene in $CDCl_3$ at room temperature (400 MHz).

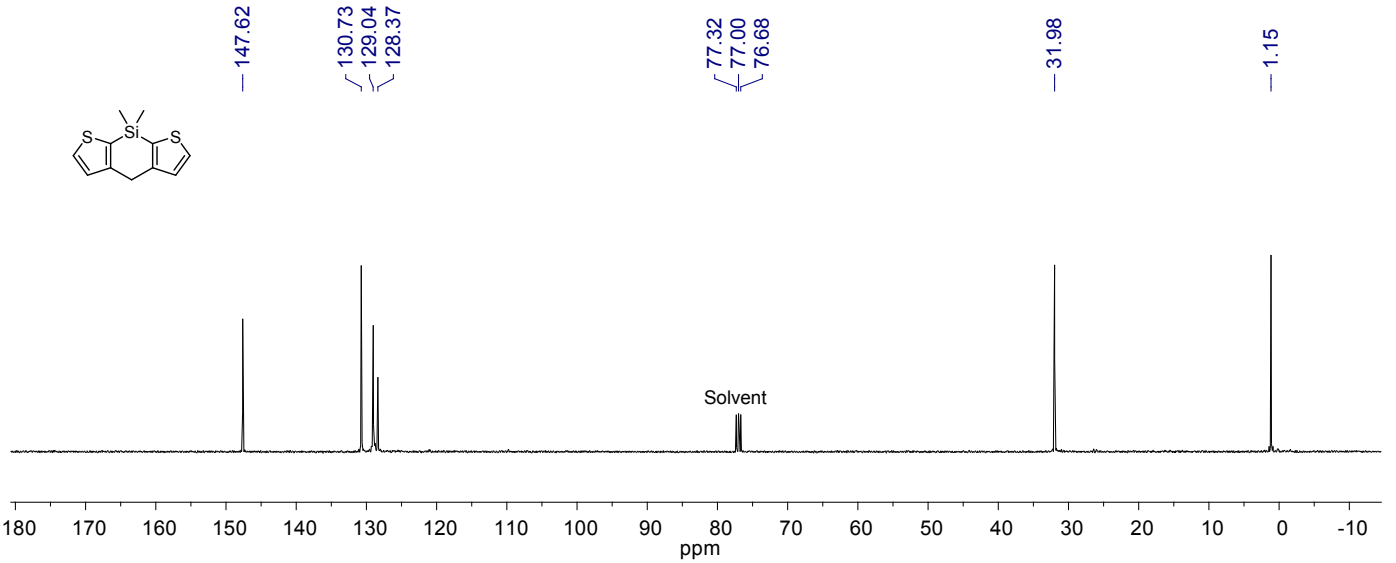


Figure S25. ^{13}C NMR spectrum of 8,8-dimethyl-4,8-dihydrosilino[2,3-*b*:6,5-*b*']dithiophene in $CDCl_3$ at room temperature (100 MHz).

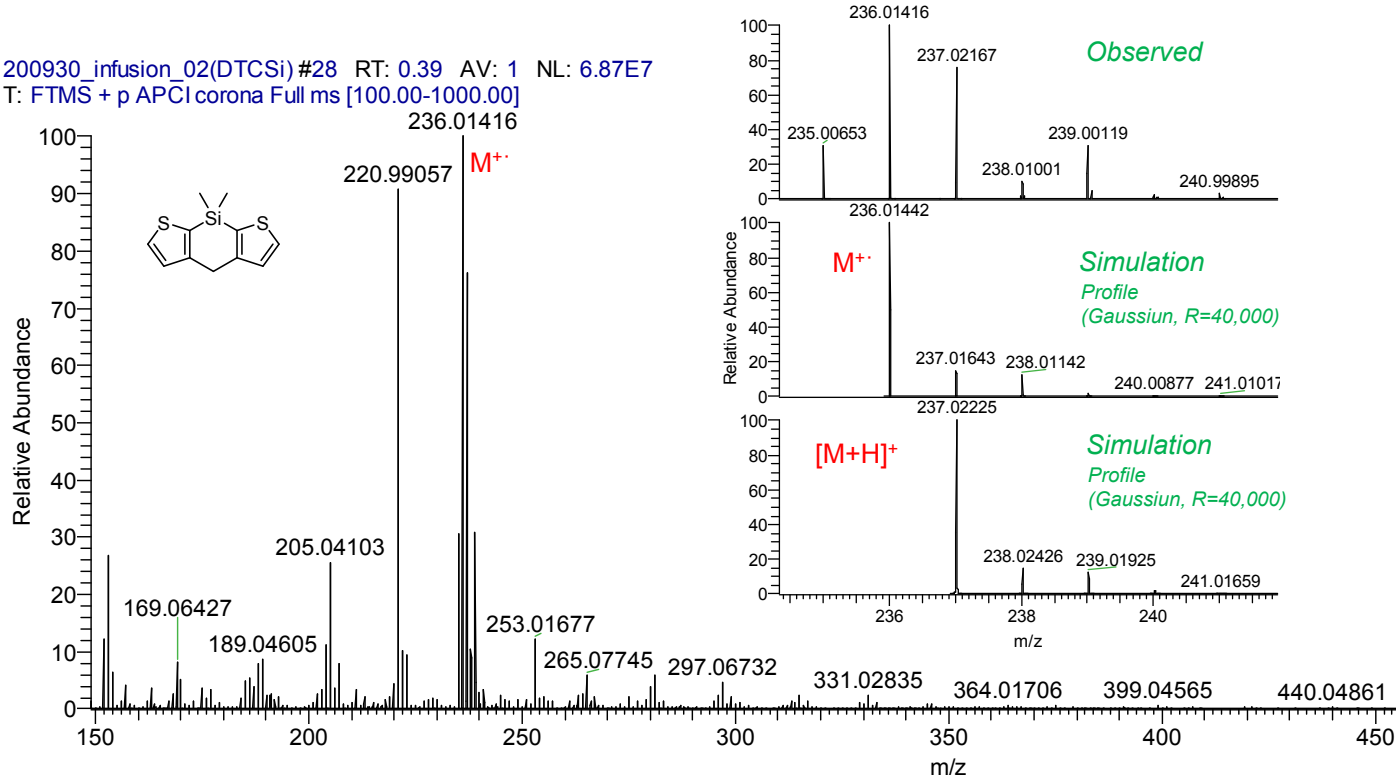


Figure S26. APCI mass spectrum of 8,8-dimethyl-4,8-dihydrosilino[2,3-*b*:6,5-*b*']dithiophene (positive mode).

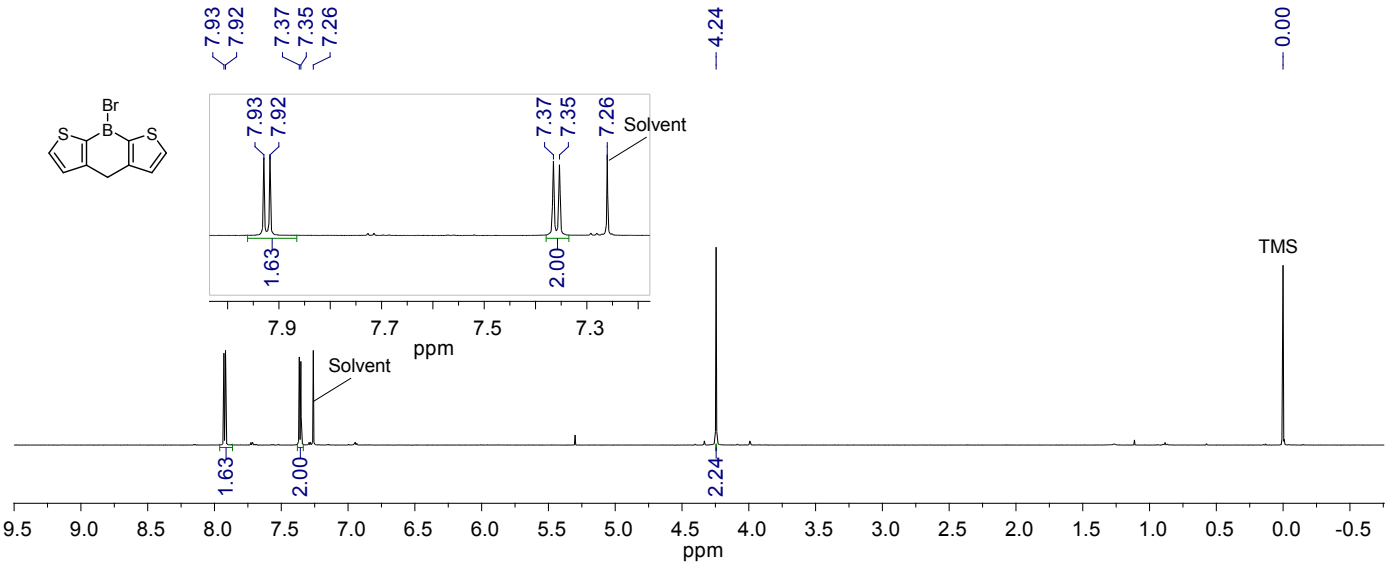


Figure S27. ^{1}H NMR spectrum of 8-bromo-4,8-dihydroborinino[2,3-*b*:6,5-*b*']dithiophene in $CDCl_3$ at room temperature (400 MHz).

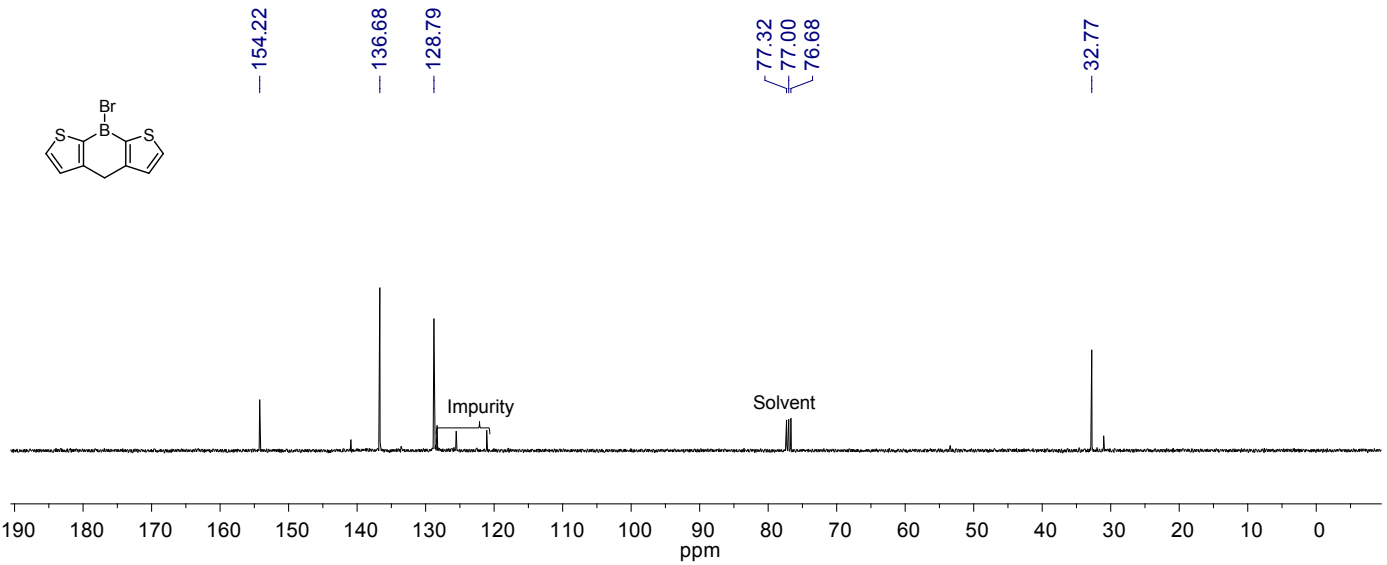


Figure S28. ^{13}C NMR spectrum of 8,8-dimethyl-4,8-dihydrosilino[2,3-*b*:6,5-*b*']dithiophene in $CDCl_3$ at room temperature (100 MHz).

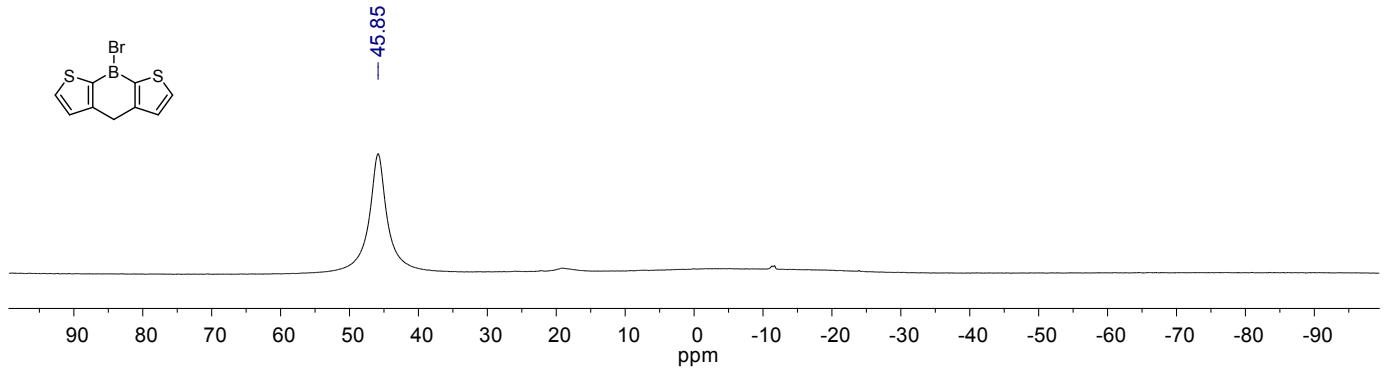


Figure S29. ^{11}B NMR spectrum of 8,8-dimethyl-4,8-dihydrosilino[2,3-*b*:6,5-*b*']dithiophene in $CDCl_3$ at room temperature (128 MHz).

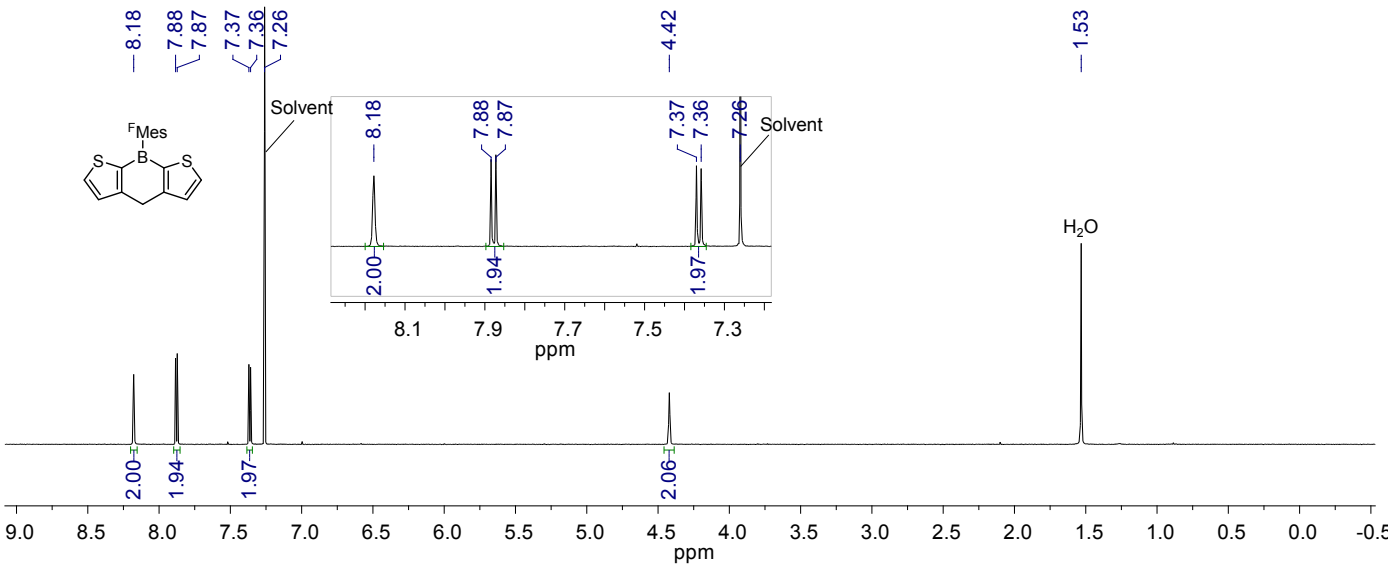


Figure S30. ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature (400 MHz).

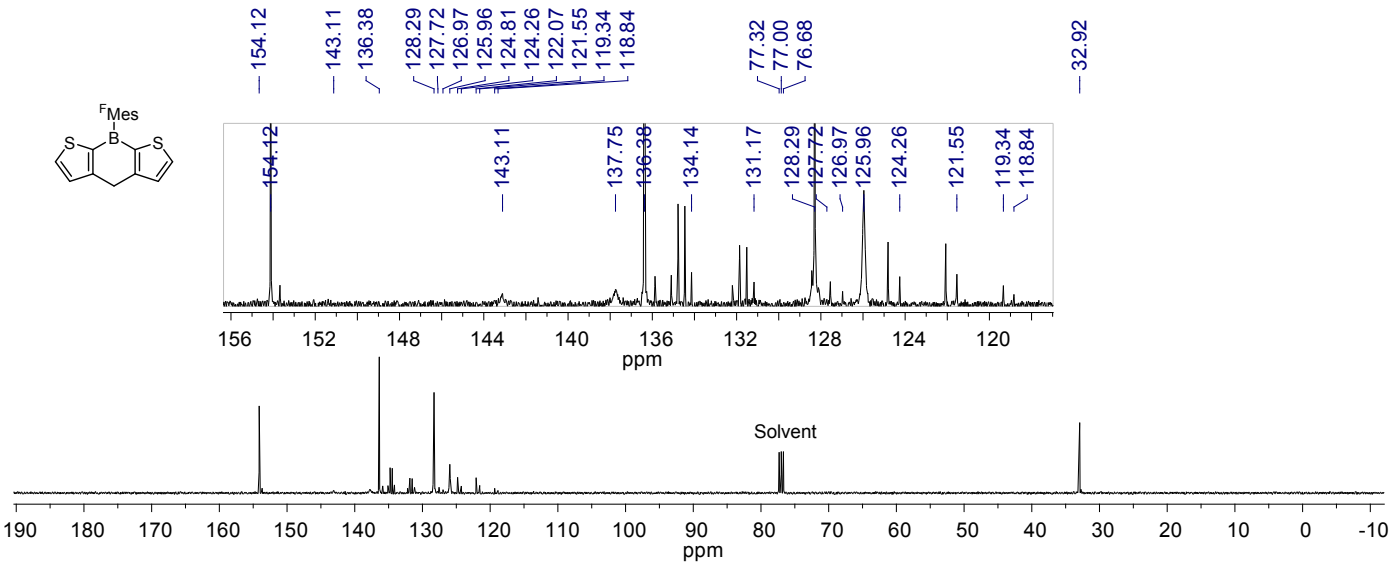


Figure S31. ^{13}C NMR spectrum of **1** in $CDCl_3$ at room temperature (100 MHz).

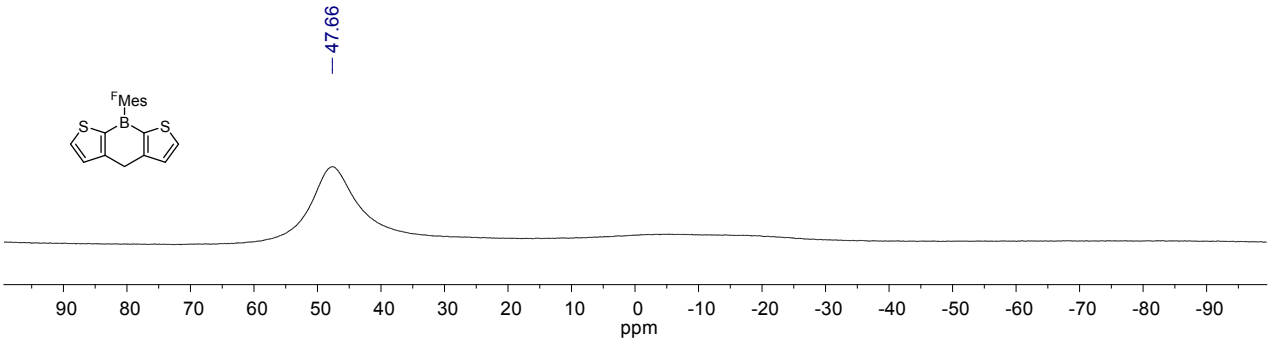


Figure S32. ^{11}B NMR spectrum of **1** in $CDCl_3$ at room temperature (128 MHz).

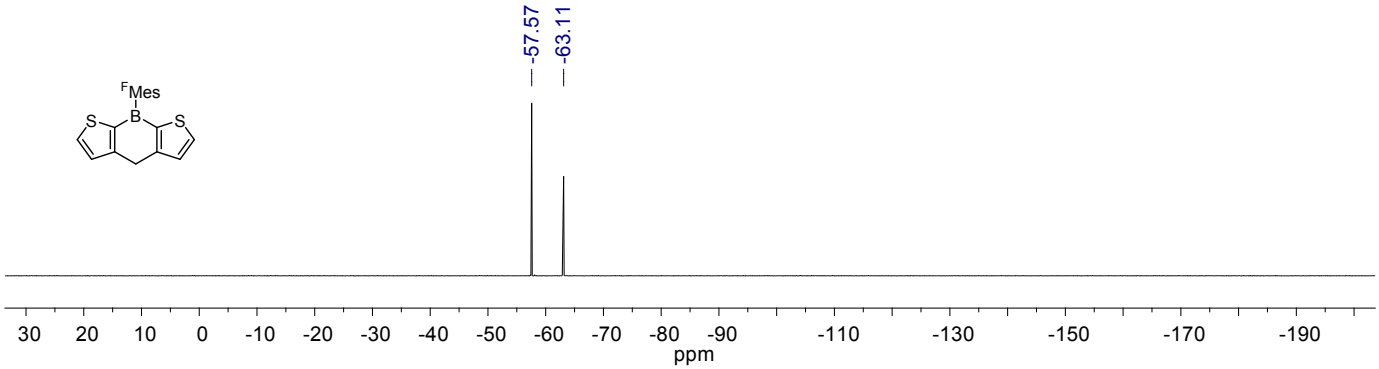


Figure S33. ^{19}F NMR spectrum of **1** in $CDCl_3$ at room temperature (376 MHz).

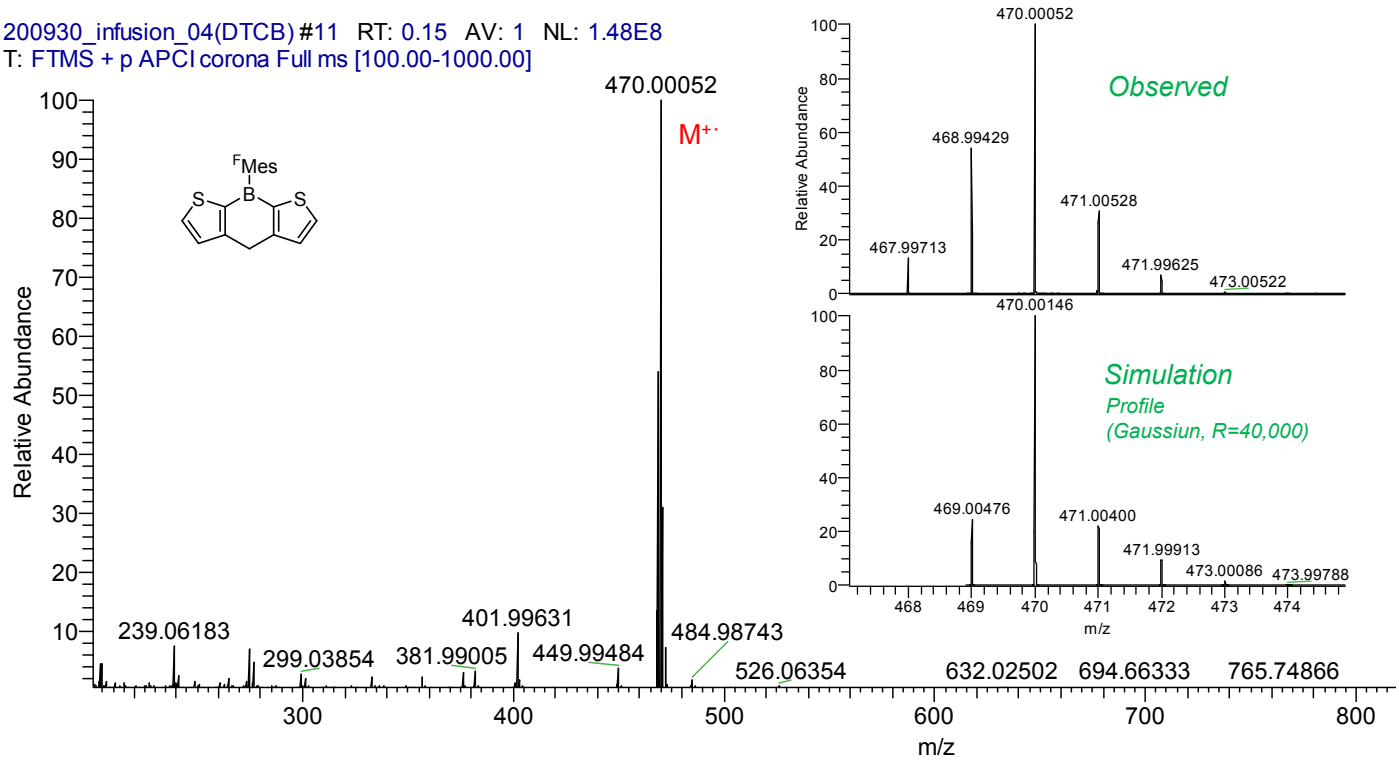


Figure S34. APCI mass spectrum of **1** (positive mode).

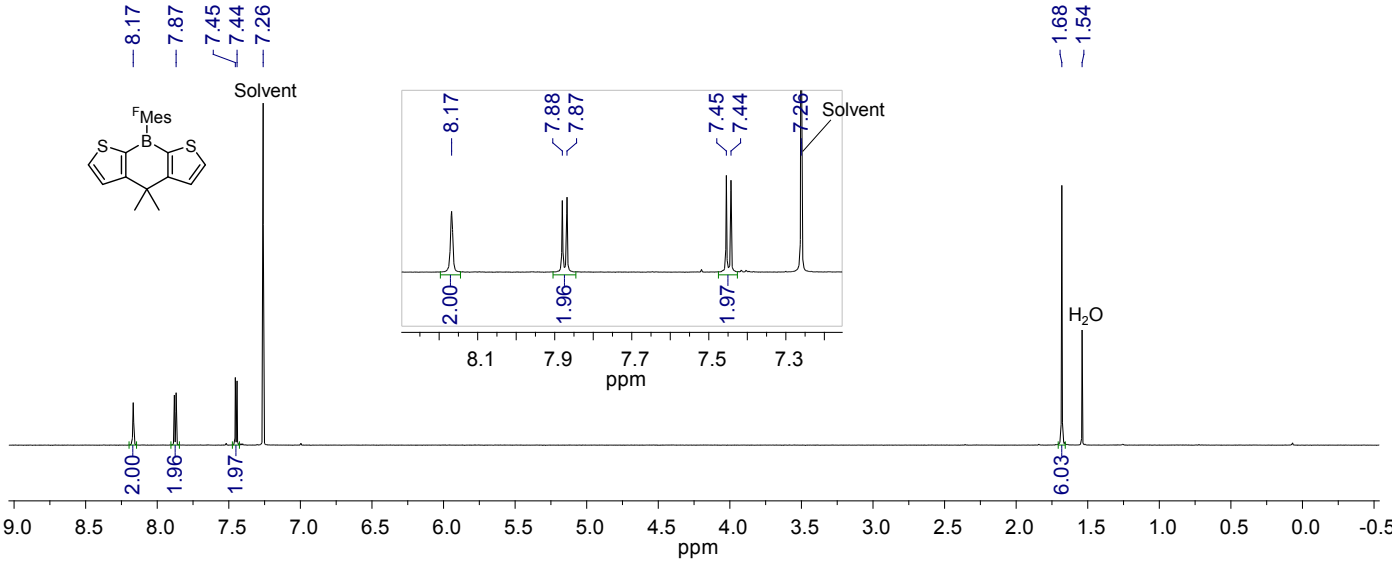


Figure S35. ^{1}H NMR spectrum of **2** in $CDCl_3$ at room temperature (400 MHz).

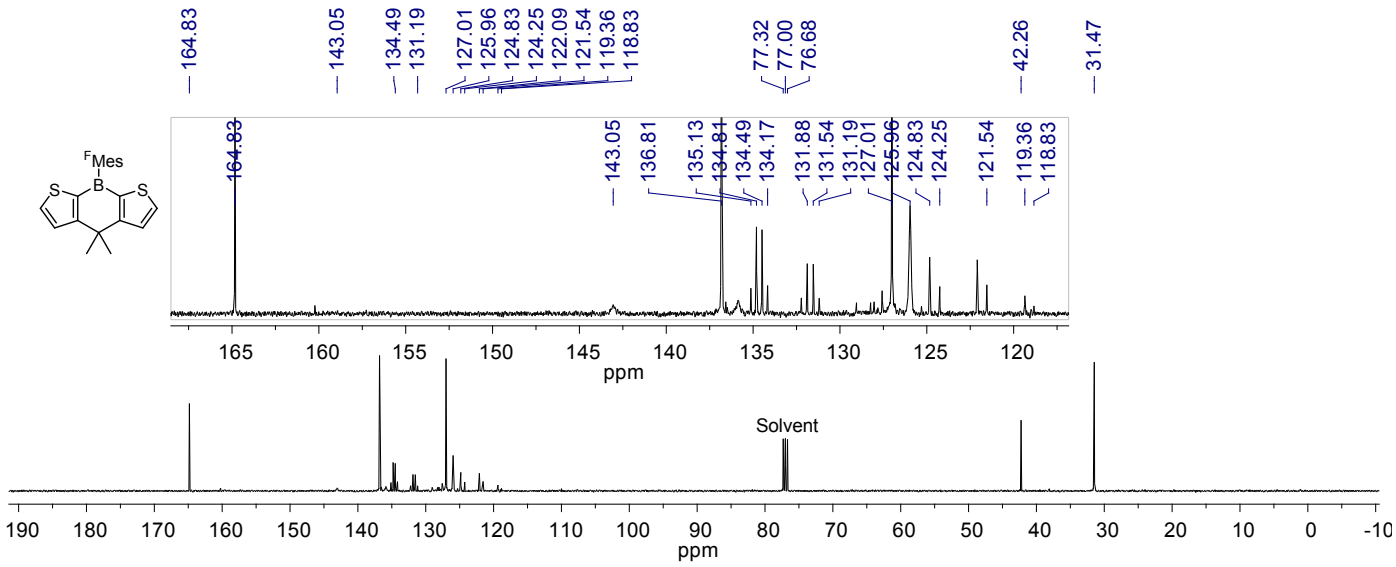


Figure S36. ^{13}C NMR spectrum of **2** in $CDCl_3$ at room temperature (100 MHz).

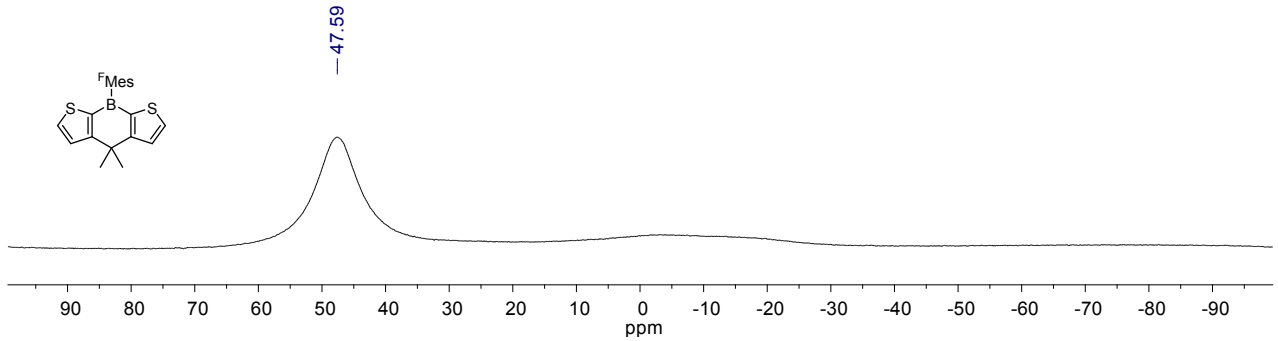


Figure S37. ^{11}B NMR spectrum of **2** in $CDCl_3$ at room temperature (128 MHz).

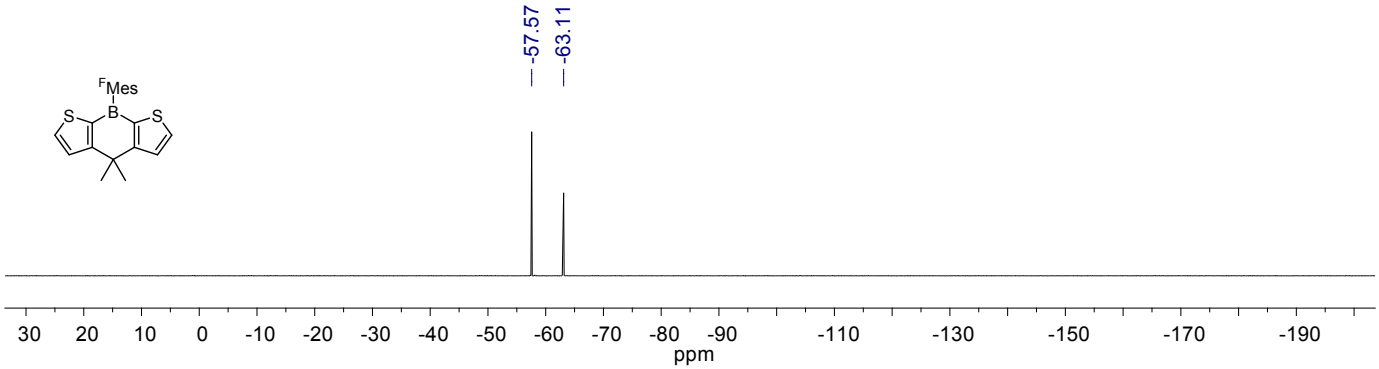


Figure S38. ^{19}F NMR spectrum of **2** in $CDCl_3$ at room temperature (376 MHz).

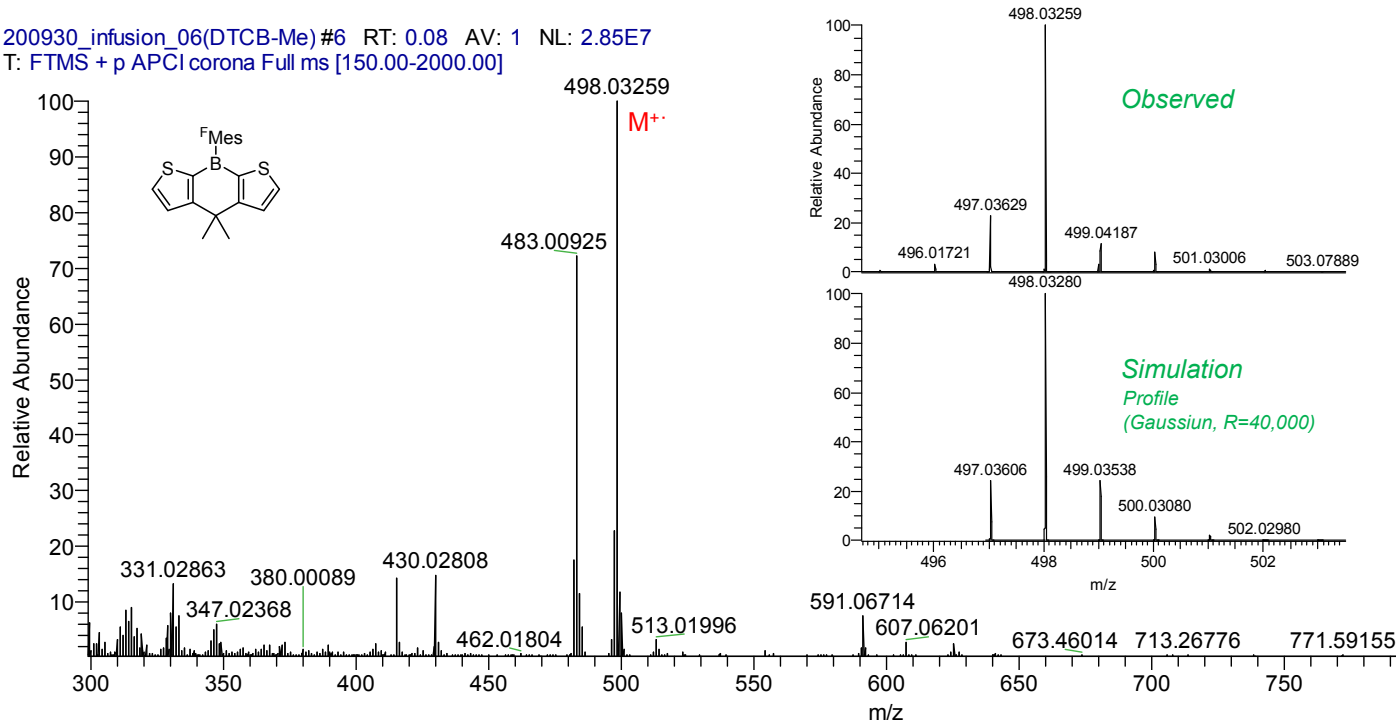


Figure S39. APCI mass spectrum of **2** (positive mode).

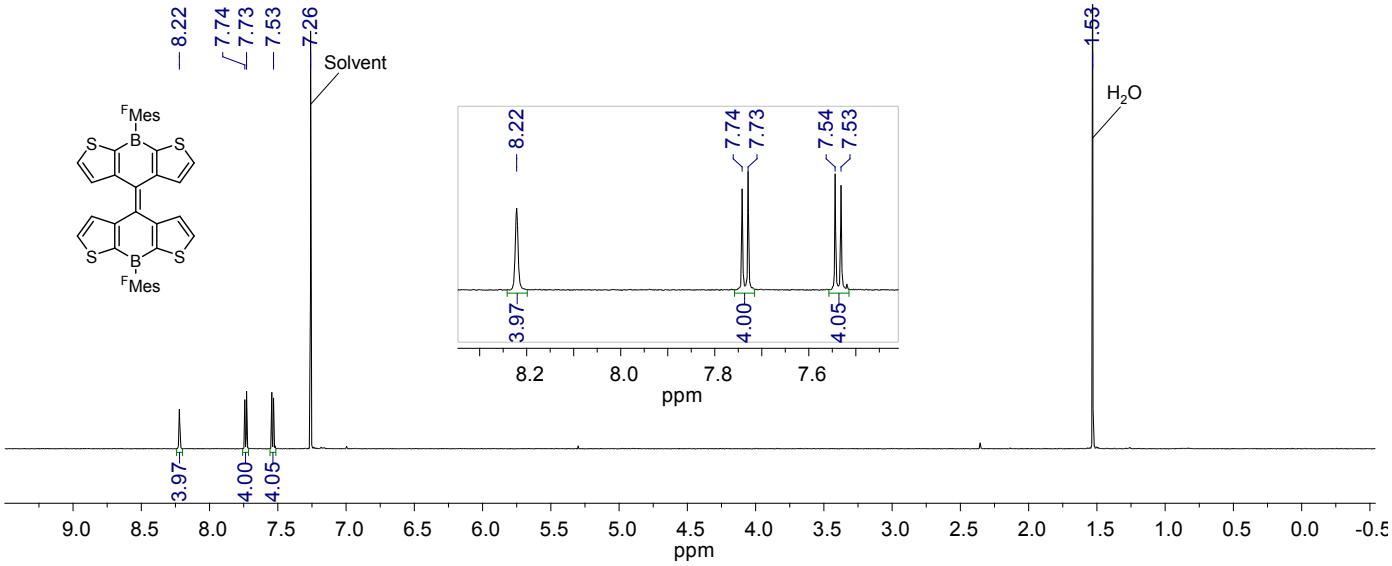


Figure S40. ^{1}H NMR spectrum of **dDTCB** in $CDCl_3$ at room temperature (400 MHz).

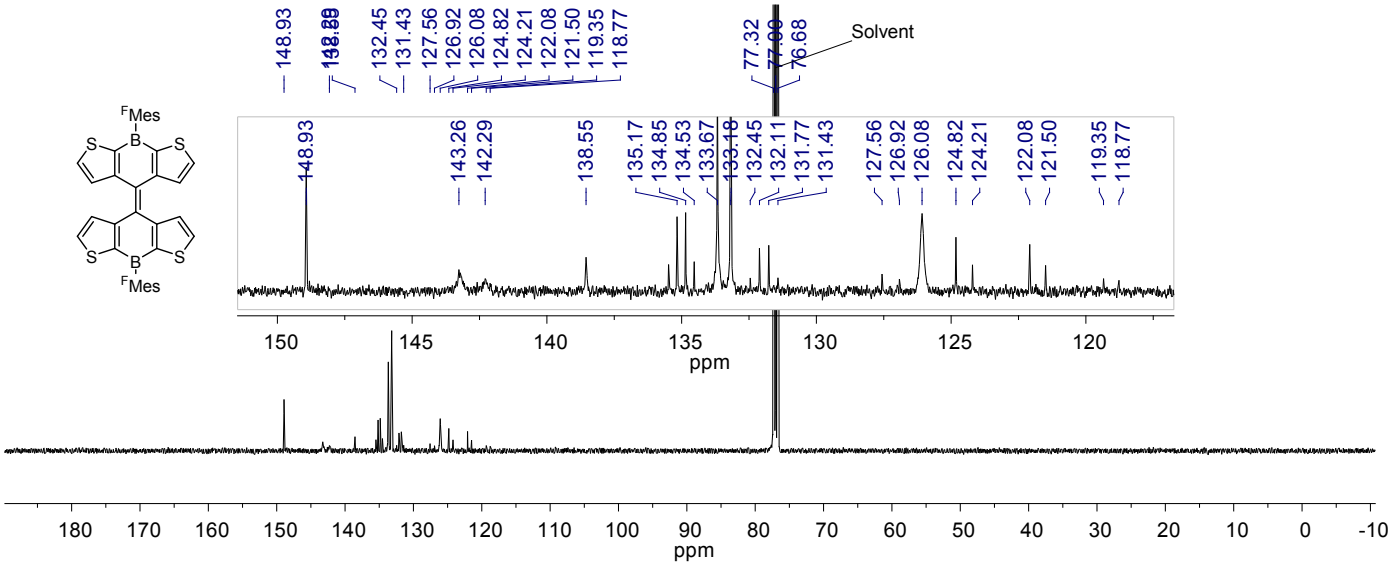


Figure S41. ^{13}C NMR spectrum of **dDTCB** in $CDCl_3$ at room temperature (100 MHz).

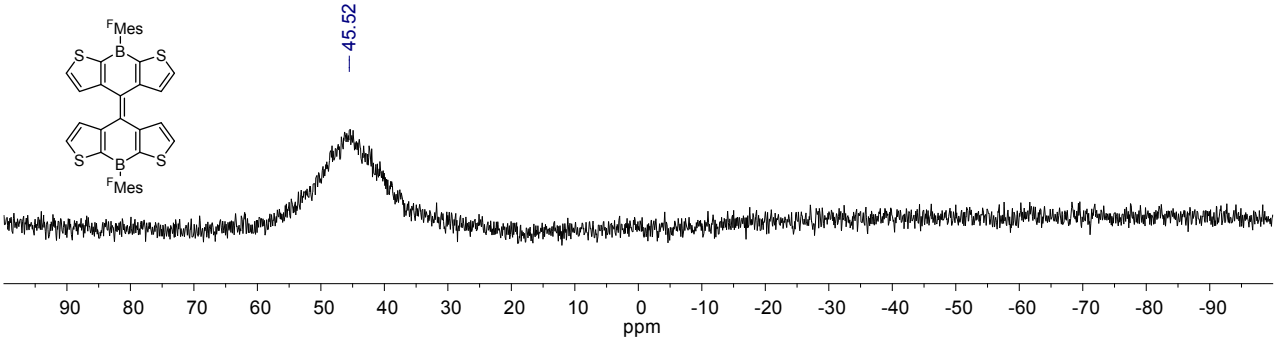


Figure S42. ^{11}B NMR spectrum of **dDTCB** in $CDCl_3$ at room temperature (160 MHz).

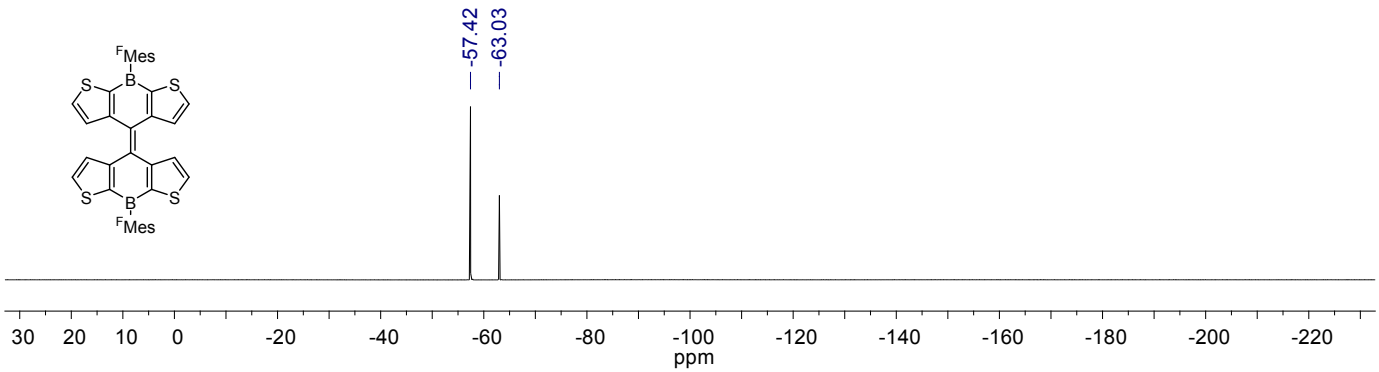


Figure S43. ^{19}F NMR spectrum of **dDTCB** in $CDCl_3$ at room temperature (470 MHz).

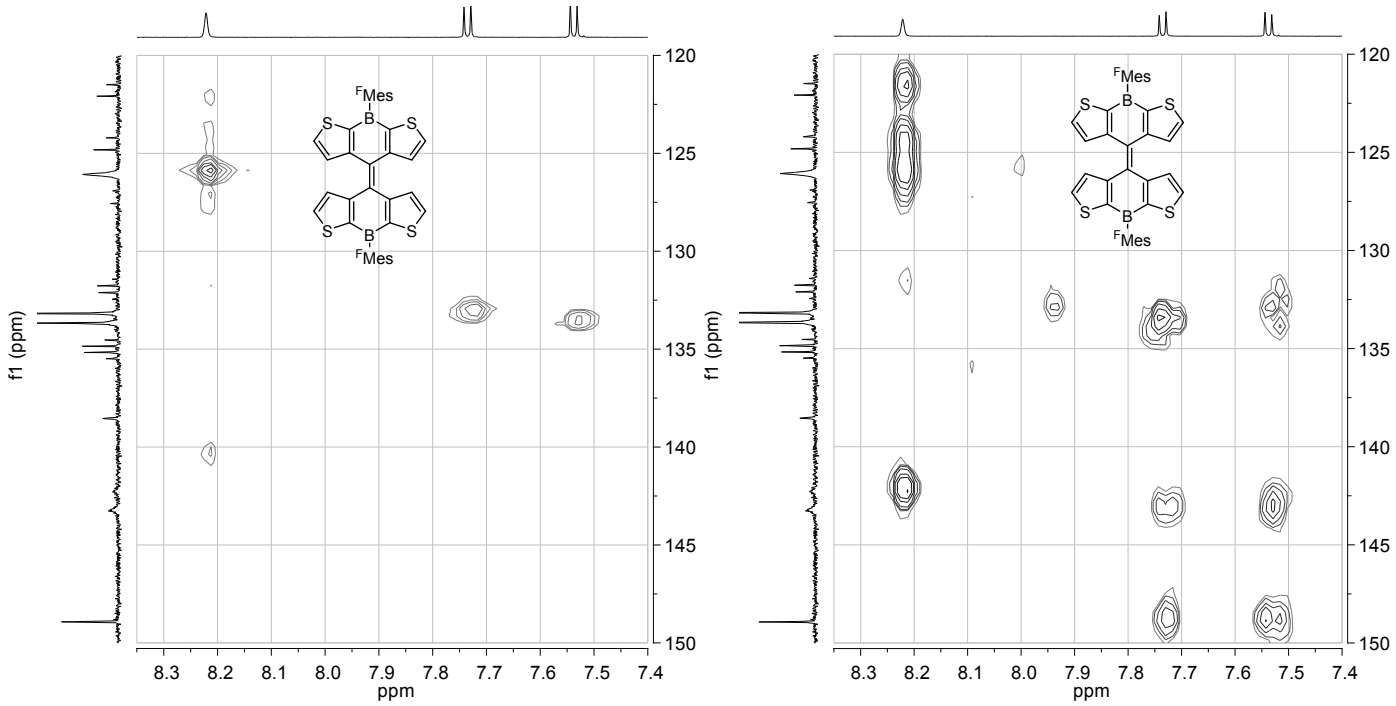


Figure S44. HMQC (left) and HMBC (right) NMR spectra of **dDTCB** in $CDCl_3$ at room temperature.

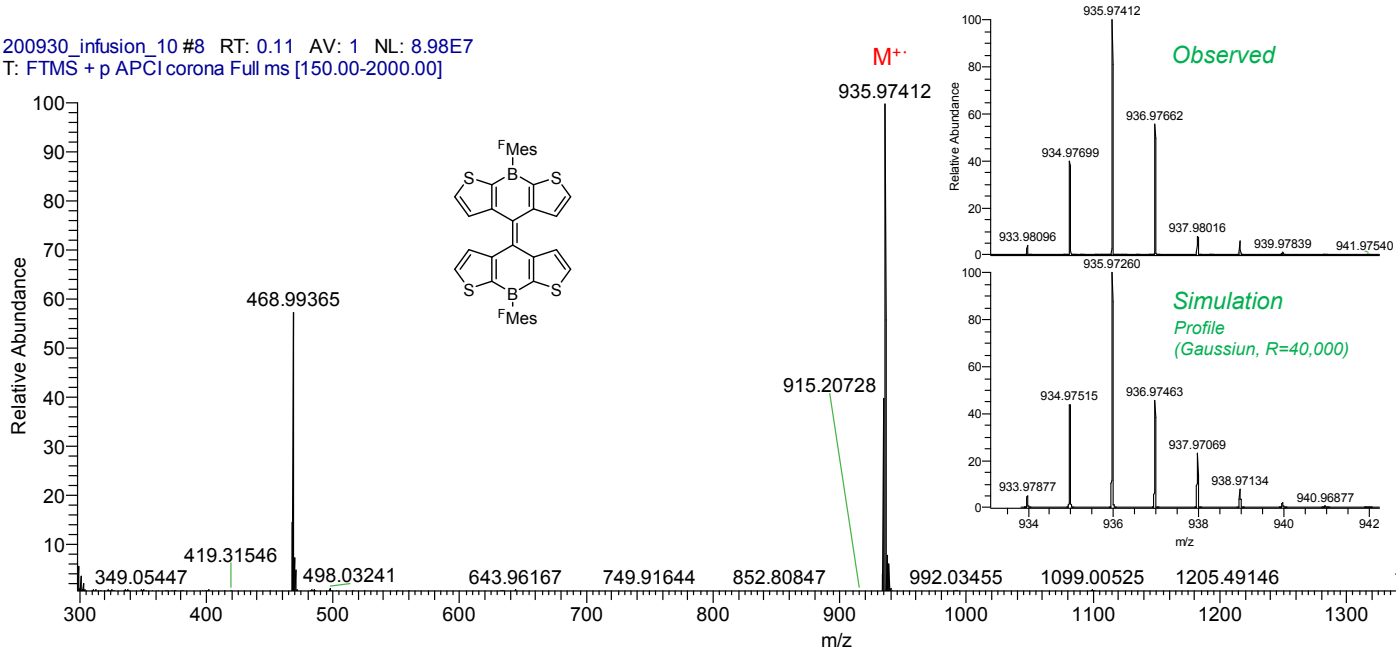


Figure S45. APCI mass spectrum of **dDTCB** (positive mode).

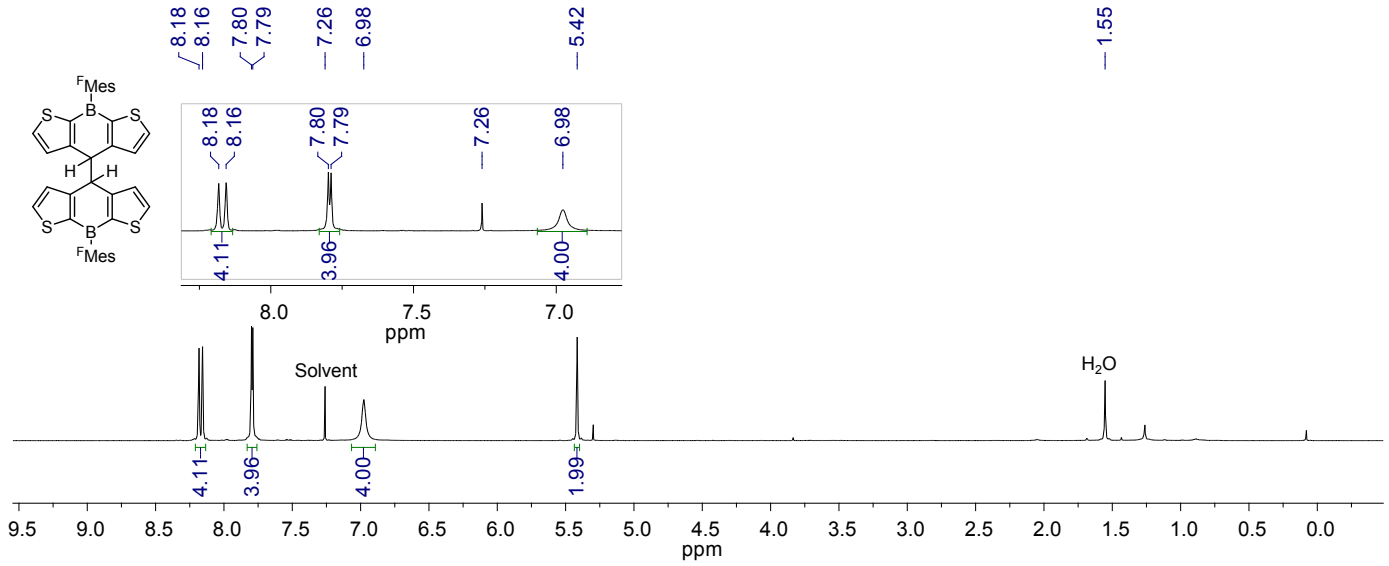


Figure S46. ^{1}H NMR spectrum of **3** in $CDCl_3$ at room temperature (500 MHz).

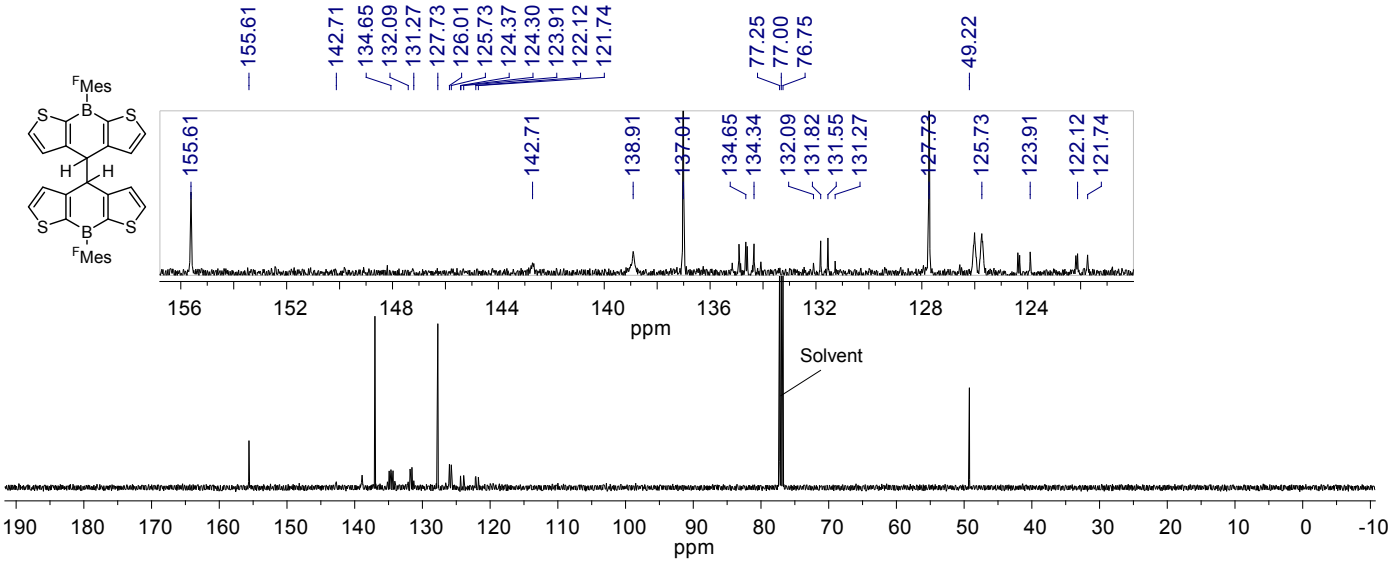


Figure S47. ^{13}C NMR spectrum of **3** in $CDCl_3$ at room temperature (125 MHz).

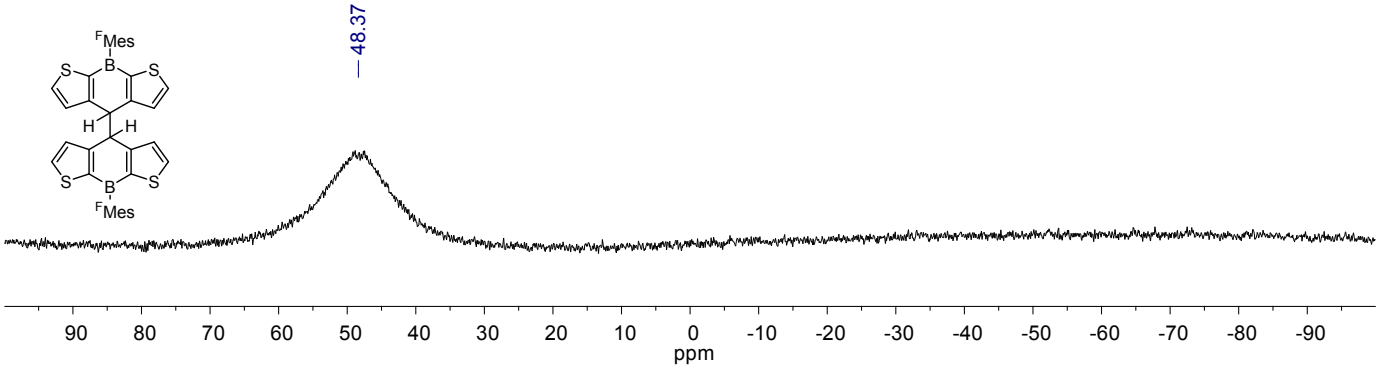


Figure S48. ^{11}B NMR spectrum of **3** in $CDCl_3$ at room temperature (160 MHz).

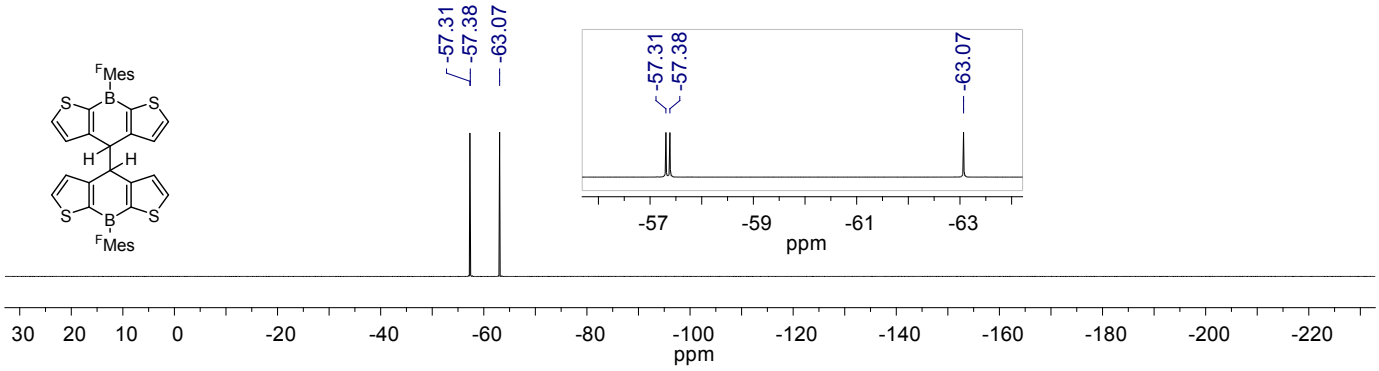


Figure S49. ^{19}F NMR spectrum of **3** in $CDCl_3$ at room temperature (470 MHz).

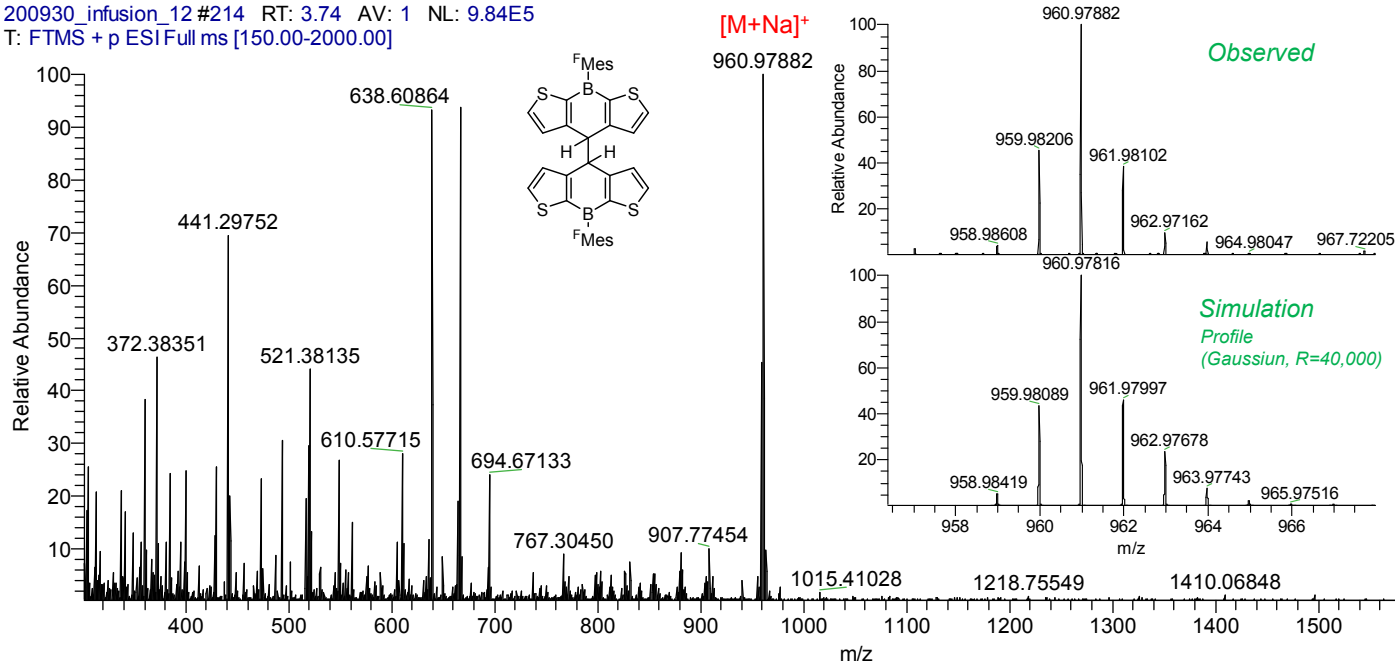


Figure S50. ESI mass spectrum of **3** (positive mode).

Cartesian Coordinates for Optimized Structures

Table S5. Coordinates for optimized structure of the twisted conformer of **dDTCB** in the ground state (S_0).
Total Energy: −4819.78083319 Hartree
opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.129691	1.466768	-0.520626
2	6	0	1.135815	2.869498	-0.530504
3	6	0	-0.002550	0.708502	0.002170
4	6	0	-1.140356	1.458591	0.524788
5	6	0	-1.156077	2.861313	0.535870
6	6	0	-2.248787	0.906554	1.253360
7	6	0	-3.096348	1.854896	1.740182
8	16	0	-2.559058	3.456610	1.372113
9	5	0	-0.012906	3.715553	0.003268
10	16	0	2.533321	3.475248	-1.368334
11	6	0	3.081146	1.877536	-1.738505
12	6	0	2.240985	0.922952	-1.251054
13	6	0	2.248787	-0.906554	1.253360
14	6	0	3.096348	-1.854896	1.740182
15	16	0	2.559058	-3.456610	1.372113
16	5	0	0.012906	-3.715553	0.003268
17	16	0	-2.533321	-3.475248	-1.368334
18	6	0	-3.081146	-1.877536	-1.738505
19	6	0	-2.240985	-0.922952	-1.251054
20	6	0	-1.135815	-2.869498	-0.530504
21	6	0	-1.129691	-1.466768	-0.520626
22	6	0	0.002550	-0.708502	0.002170
23	6	0	1.156077	-2.861313	0.535870
24	6	0	1.140356	-1.458591	0.524788
25	6	0	-0.017178	5.312310	0.003848
26	6	0	0.406187	6.065064	1.120388
27	6	0	0.404179	7.458936	1.125130
28	6	0	-0.027025	8.157203	0.005600
29	6	0	-0.451593	7.457306	-1.115312
30	6	0	-0.445795	6.063403	-1.111581
31	6	0	-0.882655	5.411873	-2.407593
32	9	0	0.112114	5.429349	-3.327401
33	9	0	-1.929560	6.065377	-2.961587
34	9	0	-1.257052	4.126336	-2.258033
35	6	0	0.840595	5.413640	2.417294
36	9	0	-0.162680	5.409784	3.327869
37	9	0	1.871954	6.080047	2.984909
38	9	0	1.236751	4.135026	2.263623
39	6	0	0.017178	9.663452	-0.012968
40	9	0	-0.153409	10.188565	1.218463
41	9	0	-0.935992	10.185817	-0.812767
42	9	0	1.207975	10.118811	-0.472378
43	6	0	0.017178	-5.312310	0.003848
44	6	0	-0.406187	-6.065064	1.120388
45	6	0	-0.404179	-7.458936	1.125130
46	6	0	0.027025	-8.157203	0.005600
47	6	0	0.451593	-7.457306	-1.115312
48	6	0	0.445795	-6.063403	-1.111581

49	6	0	0.882655	-5.411873	-2.407593
50	9	0	1.929560	-6.065377	-2.961587
51	9	0	1.257052	-4.126336	-2.258033
52	9	0	-0.112114	-5.429349	-3.327401
53	6	0	-0.840595	-5.413640	2.417294
54	9	0	-1.871954	-6.080047	2.984909
55	9	0	-1.236751	-4.135026	2.263623
56	9	0	0.162680	-5.409784	3.327869
57	6	0	-0.017178	-9.663452	-0.012968
58	9	0	0.153409	-10.188565	1.218463
59	9	0	0.935992	-10.185817	-0.812767
60	9	0	-1.207975	-10.118811	-0.472378
61	1	0	-2.402348	-0.149402	1.418995
62	1	0	-3.999727	1.702001	2.311343
63	1	0	3.984682	1.731379	-2.311179
64	1	0	2.401604	-0.131814	-1.417649
65	1	0	2.402348	0.149402	1.418995
66	1	0	3.999727	-1.702001	2.311343
67	1	0	-3.984682	-1.731379	-2.311179
68	1	0	-2.401604	0.131814	-1.417649
69	1	0	0.735732	7.996055	2.004152
70	1	0	-0.797409	7.993146	-1.989662
71	1	0	-0.735732	-7.996055	2.004152
72	1	0	0.797409	-7.993146	-1.989662

Table S6. Coordinates for optimized structure of the folded conformer of **dDTCB** in the ground state (S_0).

Total Energy: −4819.76998237 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.678144	1.351491	1.260986
2	6	0	-0.555769	2.740955	1.287847
3	6	0	-0.326941	0.605332	0.025134
4	6	0	-0.667294	1.349064	-1.215152
5	6	0	-0.526291	2.736589	-1.244219
6	6	0	-1.201822	0.827880	-2.429418
7	6	0	-1.418633	1.796302	-3.371572
8	16	0	-0.972586	3.362796	-2.807901
9	5	0	-0.340250	3.575942	0.021716
10	16	0	-0.989454	3.361223	2.856540
11	6	0	-1.417349	1.790127	3.424155
12	6	0	-1.199655	0.825258	2.479691
13	6	0	1.199655	-0.825258	2.479691
14	6	0	1.417349	-1.790127	3.424155
15	16	0	0.989454	-3.361223	2.856540
16	5	0	0.340250	-3.575942	0.021716
17	16	0	0.972586	-3.362796	-2.807901
18	6	0	1.418633	-1.796302	-3.371572
19	6	0	1.201822	-0.827880	-2.429418
20	6	0	0.526291	-2.736589	-1.244219
21	6	0	0.667294	-1.349064	-1.215152
22	6	0	0.326941	-0.605332	0.025134
23	6	0	0.555769	-2.740955	1.287847
24	6	0	0.678144	-1.351491	1.260986
25	6	0	-0.069324	5.147853	0.005910
26	6	0	-1.084469	6.117268	0.107318

27	6	0	-0.810985	7.487027	0.105837
28	6	0	0.495535	7.934399	-0.003935
29	6	0	1.529303	7.010989	-0.122848
30	6	0	1.247514	5.649309	-0.120967
31	6	0	2.420526	4.716317	-0.336838
32	9	0	2.273277	3.538432	0.307850
33	9	0	3.582063	5.255602	0.090824
34	9	0	2.587127	4.425832	-1.649677
35	6	0	-2.551471	5.763385	0.236397
36	9	0	-3.301812	6.471465	-0.640578
37	9	0	-3.023777	6.060199	1.470921
38	9	0	-2.809406	4.461889	0.014493
39	6	0	0.810985	9.407150	0.046361
40	9	0	-0.252169	10.166005	-0.288233
41	9	0	1.820953	9.732082	-0.789609
42	9	0	1.194567	9.789292	1.288430
43	6	0	0.069324	-5.147853	0.005910
44	6	0	-1.247514	-5.649309	-0.120967
45	6	0	-1.529303	-7.010989	-0.122848
46	6	0	-0.495535	-7.934399	-0.003935
47	6	0	0.810985	-7.487027	0.105837
48	6	0	1.084469	-6.117268	0.107318
49	6	0	2.551471	-5.763385	0.236397
50	9	0	3.023777	-6.060199	1.470921
51	9	0	2.809406	-4.461889	0.014493
52	9	0	3.301812	-6.471465	-0.640578
53	6	0	-2.420526	-4.716317	-0.336838
54	9	0	-3.582063	-5.255602	0.090824
55	9	0	-2.587127	-4.425832	-1.649677
56	9	0	-2.273277	-3.538432	0.307850
57	6	0	-0.810985	-9.407150	0.046361
58	9	0	-1.194567	-9.789292	1.288430
59	9	0	0.252169	-10.166005	-0.288233
60	9	0	-1.820953	-9.732082	-0.789609
61	1	0	-1.442295	-0.212036	-2.592308
62	1	0	-1.829761	1.671340	-4.362140
63	1	0	-1.820544	1.662215	4.417540
64	1	0	-1.429222	-0.216906	2.643417
65	1	0	1.429222	0.216906	2.643417
66	1	0	1.820544	-1.662215	4.417540
67	1	0	1.829761	-1.671340	-4.362140
68	1	0	1.442295	0.212036	-2.592308
69	1	0	-1.622814	8.198970	0.180349
70	1	0	2.551710	7.350843	-0.221581
71	1	0	-2.551710	-7.350843	-0.221581
72	1	0	1.622814	-8.198970	0.180349

Table S7. Coordinates for optimized structure of **dDTCB** in the triplet state (T_1).

Total Energy: −4819.77377296 Hartree

opt ub3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.678144	1.351491	1.260986
2	6	0	-0.555769	2.740955	1.287847
3	6	0	-0.326941	0.605332	0.025134
4	6	0	-0.667294	1.349064	-1.215152

5	6	0	-0.526291	2.736589	-1.244219
6	6	0	-1.201822	0.827880	-2.429418
7	6	0	-1.418633	1.796302	-3.371572
8	16	0	-0.972586	3.362796	-2.807901
9	5	0	-0.340250	3.575942	0.021716
10	16	0	-0.989454	3.361223	2.856540
11	6	0	-1.417349	1.790127	3.424155
12	6	0	-1.199655	0.825258	2.479691
13	6	0	1.199655	-0.825258	2.479691
14	6	0	1.417349	-1.790127	3.424155
15	16	0	0.989454	-3.361223	2.856540
16	5	0	0.340250	-3.575942	0.021716
17	16	0	0.972586	-3.362796	-2.807901
18	6	0	1.418633	-1.796302	-3.371572
19	6	0	1.201822	-0.827880	-2.429418
20	6	0	0.526291	-2.736589	-1.244219
21	6	0	0.667294	-1.349064	-1.215152
22	6	0	0.326941	-0.605332	0.025134
23	6	0	0.555769	-2.740955	1.287847
24	6	0	0.678144	-1.351491	1.260986
25	6	0	-0.069324	5.147853	0.005910
26	6	0	-1.084469	6.117268	0.107318
27	6	0	-0.810985	7.487027	0.105837
28	6	0	0.495535	7.934399	-0.003935
29	6	0	1.529303	7.010989	-0.122848
30	6	0	1.247514	5.649309	-0.120967
31	6	0	2.420526	4.716317	-0.336838
32	9	0	2.273277	3.538432	0.307850
33	9	0	3.582063	5.255602	0.090824
34	9	0	2.587127	4.425832	-1.649677
35	6	0	-2.551471	5.763385	0.236397
36	9	0	-3.301812	6.471465	-0.640578
37	9	0	-3.023777	6.060199	1.470921
38	9	0	-2.809406	4.461889	0.014493
39	6	0	0.810985	9.407150	0.046361
40	9	0	-0.252169	10.166005	-0.288233
41	9	0	1.820953	9.732082	-0.789609
42	9	0	1.194567	9.789292	1.288430
43	6	0	0.069324	-5.147853	0.005910
44	6	0	-1.247514	-5.649309	-0.120967
45	6	0	-1.529303	-7.010989	-0.122848
46	6	0	-0.495535	-7.934399	-0.003935
47	6	0	0.810985	-7.487027	0.105837
48	6	0	1.084469	-6.117268	0.107318
49	6	0	2.551471	-5.763385	0.236397
50	9	0	3.023777	-6.060199	1.470921
51	9	0	2.809406	-4.461889	0.014493
52	9	0	3.301812	-6.471465	-0.640578
53	6	0	-2.420526	-4.716317	-0.336838
54	9	0	-3.582063	-5.255602	0.090824
55	9	0	-2.587127	-4.425832	-1.649677
56	9	0	-2.273277	-3.538432	0.307850
57	6	0	-0.810985	-9.407150	0.046361
58	9	0	-1.194567	-9.789292	1.288430
59	9	0	0.252169	-10.166005	-0.288233
60	9	0	-1.820953	-9.732082	-0.789609
61	1	0	-1.442295	-0.212036	-2.592308
62	1	0	-1.829761	1.671340	-4.362140
63	1	0	-1.820544	1.662215	4.417540
64	1	0	-1.429222	-0.216906	2.643417
65	1	0	1.429222	0.216906	2.643417

66	1	0	1.820544	-1.662215	4.417540
67	1	0	1.829761	-1.671340	-4.362140
68	1	0	1.442295	0.212036	-2.592308
69	1	0	-1.622814	8.198970	0.180349
70	1	0	2.551710	7.350843	-0.221581
71	1	0	-2.551710	-7.350843	-0.221581
72	1	0	1.622814	-8.198970	0.180349

Table S8. Coordinates for optimized structure of **dDTCB** in the transition state (TS).

Total Energy: −4819.75453097 Hartree

opt=(readfc,ts) b3lyp/6-311+g(d,p) scf=(vshift=700,maxcycle=100) geom=allcheck guess=read

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.725342	2.186102	0.145389
2	6	0	-3.064988	1.758012	0.033233
3	6	0	-0.666856	1.148362	0.239631
4	6	0	-1.137646	-0.146422	0.795334
5	6	0	-2.465487	-0.568117	0.760846
6	6	0	-0.306657	-1.049894	1.533598
7	6	0	-0.984310	-2.137809	2.002881
8	16	0	-2.653511	-2.098385	1.566402
9	5	0	-3.572306	0.338239	0.262922
10	16	0	-4.133788	3.085032	-0.302546
11	6	0	-2.848899	4.217762	-0.220749
12	6	0	-1.648829	3.608907	0.013376
13	6	0	1.632980	3.617541	0.008633
14	6	0	2.829565	4.232121	0.245528
15	16	0	4.120978	3.106409	0.321087
16	5	0	3.574789	0.358902	-0.256812
17	16	0	2.669039	-2.077544	-1.569390
18	6	0	0.999991	-2.124477	-2.005599
19	6	0	0.316401	-1.042172	-1.531931
20	6	0	2.472712	-0.551517	-0.757786
21	6	0	1.142529	-0.137041	-0.790271
22	6	0	0.664835	1.152868	-0.229222
23	6	0	3.059807	1.774923	-0.021176
24	6	0	1.717650	2.195905	-0.130628
25	6	0	-5.087400	-0.120234	0.061464
26	6	0	-6.088027	0.069312	1.033879
27	6	0	-7.409100	-0.336169	0.834443
28	6	0	-7.774289	-0.953183	-0.351502
29	6	0	-6.815677	-1.171881	-1.335060
30	6	0	-5.501536	-0.765477	-1.127180
31	6	0	-4.509427	-1.111550	-2.217870
32	9	0	-3.528326	-0.190914	-2.344425
33	9	0	-5.102517	-1.219615	-3.425828
34	9	0	-3.900530	-2.298646	-1.977704
35	6	0	-5.819909	0.750395	2.360215
36	9	0	-6.418958	0.090694	3.378979
37	9	0	-6.315386	2.011669	2.376649
38	9	0	-4.511278	0.835076	2.661188
39	6	0	-9.207159	-1.347310	-0.601563
40	9	0	-9.891446	-1.527801	0.546319
41	9	0	-9.296013	-2.492625	-1.311720
42	9	0	-9.865812	-0.397445	-1.308880
43	6	0	5.091940	-0.093963	-0.057964

44	6	0	5.509056	-0.742401	1.128287
45	6	0	6.824897	-1.142812	1.334423
46	6	0	7.783407	-0.912804	0.352781
47	6	0	7.415108	-0.294888	-0.831235
48	6	0	6.091862	0.105875	-1.028622
49	6	0	5.821066	0.797118	-2.349099
50	9	0	6.300829	2.064513	-2.351367
51	9	0	4.512545	0.868409	-2.654299
52	9	0	6.431957	0.154979	-3.372098
53	6	0	4.519307	-1.094038	2.219436
54	9	0	5.114346	-1.204289	3.426180
55	9	0	3.913504	-2.282074	1.976122
56	9	0	3.535653	-0.176738	2.350293
57	6	0	9.197659	-1.385872	0.569906
58	9	0	9.612450	-1.155189	1.834904
59	9	0	10.070496	-0.779473	-0.259454
60	9	0	9.312215	-2.719525	0.359941
61	1	0	0.743069	-0.886978	1.728471
62	1	0	-0.594379	-2.953467	2.593047
63	1	0	-3.035455	5.275999	-0.324636
64	1	0	-0.771603	4.202446	0.160283
65	1	0	0.752229	4.206645	-0.134905
66	1	0	3.010057	5.290878	0.354691
67	1	0	0.614438	-2.939949	-2.598893
68	1	0	-0.734249	-0.884333	-1.725990
69	1	0	-8.145182	-0.177681	1.611777
70	1	0	-7.090061	-1.661847	-2.259688
71	1	0	7.103689	-1.625130	2.261941
72	1	0	8.152571	-0.120549	-1.603665

Table S9. Coordinates for optimized structure of the folded conformer of **m1** in the ground state (S_0).

Total Energy: −2362.34629980 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.232525	-2.454547	0.869543
2	6	0	2.265763	-3.339412	0.828696
3	16	0	3.630064	-2.697110	-0.036416
4	16	0	3.630279	2.697064	-0.036018
5	6	0	2.266089	3.339291	0.829321
6	6	0	1.232774	2.454508	0.870030
7	6	0	2.790745	1.207954	-0.332000
8	6	0	1.515814	1.223259	0.185761
9	6	0	0.676994	0.000080	0.089815
10	6	0	2.790658	-1.207882	-0.332172
11	6	0	1.515727	-1.223164	0.185585
12	6	0	-1.515727	-1.223164	-0.185586
13	6	0	-2.790658	-1.207882	0.332172
14	6	0	-0.676994	0.000080	-0.089815
15	6	0	-1.515814	1.223259	-0.185761
16	6	0	-2.790745	1.207954	0.332000
17	6	0	-1.232775	2.454508	-0.870030
18	6	0	-2.266090	3.339291	-0.829322
19	16	0	-3.630279	2.697065	0.036018
20	16	0	-3.630064	-2.697110	0.036416
21	6	0	-2.265763	-3.339412	-0.828696

22	6	0	-1.232525	-2.454547	-0.869544
23	6	0	3.413670	0.000059	-0.978061
24	6	0	-3.413670	0.000059	0.978061
25	1	0	0.304239	-2.659445	1.381785
26	1	0	2.319742	-4.326942	1.260231
27	1	0	2.320186	4.326713	1.261088
28	1	0	0.304551	2.659368	1.382395
29	1	0	-0.304551	2.659368	-1.382397
30	1	0	-2.320187	4.326713	-1.261089
31	1	0	-2.319742	-4.326942	-1.260231
32	1	0	-0.304239	-2.659444	-1.381786
33	1	0	4.499094	0.000010	-0.850108
34	1	0	3.227904	0.000145	-2.061597
35	1	0	-3.227904	0.000145	2.061597
36	1	0	-4.499094	0.000010	0.850108

Table S10. Coordinates for optimized structure of the twisted conformer of **m1** in the ground state (S_0).

Total Energy: −2362.34205647 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.988351	-2.310239	1.158493
2	6	0	-1.963018	-3.131358	1.621841
3	16	0	-3.549781	-2.514351	1.266141
4	16	0	-3.549628	2.514451	-1.266214
5	6	0	-1.962825	3.131558	-1.621558
6	6	0	-0.988209	2.310389	-1.158191
7	6	0	-2.872246	1.125485	-0.469816
8	6	0	-1.490243	1.149732	-0.458205
9	6	0	-0.698328	-0.000013	0.000008
10	6	0	-2.872309	-1.125481	0.469654
11	6	0	-1.490306	-1.149706	0.458244
12	6	0	1.490272	-1.149763	-0.458214
13	6	0	2.872275	-1.125487	-0.469797
14	6	0	0.698328	-0.000041	0.000014
15	6	0	1.490277	1.149675	0.458235
16	6	0	2.872279	1.125480	0.469672
17	6	0	0.988279	2.310221	1.158430
18	6	0	1.962919	3.131370	1.621784
19	16	0	3.549704	2.514370	1.266163
20	16	0	3.549705	-2.514432	-1.266191
21	6	0	1.962924	-3.131547	-1.621615
22	6	0	0.988280	-2.310407	-1.158254
23	6	0	-3.740297	-0.000045	-0.000246
24	6	0	3.740297	0.000064	-0.000221
25	1	0	0.060733	-2.507740	1.317698
26	1	0	-1.855086	-4.059096	2.162344
27	1	0	-1.854830	4.059394	-2.161881
28	1	0	0.060892	2.507955	-1.317192
29	1	0	-0.060813	2.507712	1.317588
30	1	0	1.854956	4.059123	2.162255
31	1	0	1.854960	-4.059368	-2.161970
32	1	0	-0.060811	-2.507984	-1.317301
33	1	0	-4.404401	-0.328218	-0.812306
34	1	0	-4.404756	0.328059	0.811549
35	1	0	4.404386	0.328256	-0.812287

36	1	0	4.404771	-0.328020	0.811569

Table S11. Coordinates for optimized structure of the folded conformer of **m2** in the ground state (S_0).

Total Energy: −2334.65758091 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.270857	0.723860	2.455512
2	6	0	-1.591542	1.671769	3.390169
3	16	0	-1.307963	3.272011	2.814022
4	16	0	-1.307943	3.272004	-2.814025
5	6	0	-1.591508	1.671760	-3.390173
6	6	0	-1.270830	0.723854	-2.455511
7	6	0	-0.786473	2.684866	-1.259409
8	6	0	-0.786473	1.288746	-1.239474
9	6	0	-0.375861	0.576347	0.000005
10	6	0	-0.786482	2.684869	1.259412
11	6	0	-0.786482	1.288748	1.239480
12	6	0	0.786482	-1.288748	1.239480
13	6	0	0.786482	-2.684869	1.259412
14	6	0	0.375861	-0.576347	0.000005
15	6	0	0.786473	-1.288746	-1.239474
16	6	0	0.786473	-2.684866	-1.259409
17	6	0	1.270830	-0.723854	-2.455511
18	6	0	1.591508	-1.671760	-3.390173
19	16	0	1.307943	-3.272004	-2.814025
20	16	0	1.307963	-3.272011	2.814022
21	6	0	1.591542	-1.671769	3.390169
22	6	0	1.270857	-0.723860	2.455512
23	1	0	-1.403713	-0.334047	2.626069
24	1	0	-1.995618	1.509522	4.378308
25	1	0	-1.995572	1.509510	-4.378317
26	1	0	-1.403677	-0.334054	-2.626068
27	1	0	1.403677	0.334054	-2.626068
28	1	0	1.995572	-1.509510	-4.378317
29	1	0	1.995618	-1.509522	4.378308
30	1	0	1.403713	0.334047	2.626069
31	5	0	0.671015	-3.542290	0.000001
32	1	0	0.651530	-4.731325	-0.000000
33	5	0	-0.671015	3.542290	0.000001
34	1	0	-0.651530	4.731325	-0.000000

Table S12. Coordinates for optimized structure of the twisted conformer of **m2** in the ground state (S_0).

Total Energy: −2334.66912825 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.922156	2.249738	1.248676
2	6	0	1.879318	3.090063	1.734044
3	16	0	3.475693	2.543289	1.354435
4	16	0	3.475717	-2.543272	-1.354536

5	6	0	1.879348	-3.090052	-1.734158
6	6	0	0.922178	-2.249752	-1.248764
7	6	0	2.867820	-1.147981	-0.515169
8	6	0	1.464055	-1.140055	-0.514870
9	6	0	0.707958	-0.000028	-0.000003
10	6	0	2.867810	1.147964	0.515116
11	6	0	1.464046	1.140019	0.514825
12	6	0	-1.464043	1.140024	-0.514823
13	6	0	-2.867807	1.147974	-0.515111
14	6	0	-0.707958	-0.000026	0.000006
15	6	0	-1.464059	-1.140051	0.514872
16	6	0	-2.867823	-1.147971	0.515174
17	6	0	-0.922185	-2.249749	1.248767
18	6	0	-1.879358	-3.090045	1.734164
19	16	0	-3.475725	-2.543268	1.354526
20	16	0	-3.475685	2.543293	-1.354444
21	6	0	-1.879307	3.090071	-1.734038
22	6	0	-0.922149	2.249741	-1.248673
23	1	0	-0.132132	2.409990	1.419289
24	1	0	1.732017	3.992769	2.307951
25	1	0	1.732056	-3.992740	-2.308096
26	1	0	-0.132108	-2.410009	-1.419386
27	1	0	0.132100	-2.410008	1.419391
28	1	0	-1.732069	-3.992731	2.308105
29	1	0	-1.732003	3.992779	-2.307942
30	1	0	0.132140	2.409991	-1.419283
31	5	0	-3.722133	0.000005	0.000025
32	1	0	-4.911623	0.000016	0.000029
33	5	0	3.722133	-0.000011	-0.000013
34	1	0	4.911622	0.000000	-0.000026

Table S13. Coordinates for optimized structure of the folded conformer of **m3** in the ground state (S_0).

Total Energy: −1079.29893998 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.036756	3.412317	-1.143015
2	6	0	-3.230278	3.435386	-0.422251
3	6	0	-3.578648	2.344731	0.371787
4	6	0	-2.736225	1.237057	0.464381
5	6	0	-1.509801	1.230350	-0.225280
6	6	0	-1.184542	2.316666	-1.046341
7	6	0	-2.736233	-1.237046	0.464379
8	6	0	-1.509810	-1.230350	-0.225284
9	6	0	-0.671207	-0.000003	-0.108406
10	6	0	-3.578668	-2.344712	0.371778
11	6	0	-3.230312	-3.435365	-0.422267
12	6	0	-2.036790	-3.412303	-1.143035
13	6	0	-1.184565	-2.316663	-1.046354
14	6	0	0.671187	-0.000004	0.108405
15	6	0	1.509794	1.230342	0.225274
16	6	0	2.736207	1.237039	-0.464411
17	6	0	2.736204	-1.237055	-0.464407
18	6	0	1.509792	-1.230352	0.225280
19	6	0	1.184570	2.316647	1.046361
20	6	0	2.036814	3.412275	1.143049

21	6	0	3.230327	3.435331	0.422271
22	6	0	3.578659	2.344687	-0.371800
23	6	0	3.578654	-2.344704	-0.371791
24	6	0	3.230322	-3.435343	0.422288
25	6	0	2.036812	-3.412279	1.143070
26	6	0	1.184570	-2.316650	1.046377
27	1	0	-1.772040	4.244573	-1.785467
28	1	0	-3.896058	4.288057	-0.495118
29	1	0	-4.520595	2.345975	0.911158
30	1	0	-0.262131	2.301862	-1.613166
31	1	0	-4.520613	-2.345949	0.911152
32	1	0	-3.896102	-4.288027	-0.495140
33	1	0	-1.772085	-4.244558	-1.785493
34	1	0	-0.262155	-2.301865	-1.613180
35	1	0	0.262167	2.301855	1.613198
36	1	0	1.772127	4.244524	1.785523
37	1	0	3.896132	4.287981	0.495153
38	1	0	4.520597	2.345923	-0.911187
39	1	0	4.520591	-2.345945	-0.911181
40	1	0	3.896125	-4.287994	0.495173
41	1	0	1.772125	-4.244522	1.785551
42	1	0	0.262169	-2.301851	1.613218
43	6	0	3.104625	-0.000010	-1.254494
44	1	0	4.168101	-0.000011	-1.502494
45	1	0	2.557247	-0.000010	-2.208459
46	6	0	-3.104701	0.000003	1.254432
47	1	0	-2.557410	0.000006	2.208448
48	1	0	-4.168199	0.000007	1.502340

Table S14. Coordinates for optimized structure of the twisted conformer of **m3** in the ground state (S_0).

Total Energy: −1079.26857756 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.522318	-3.180282	1.907769
2	6	0	-2.918786	-3.217937	1.828915
3	6	0	-3.578726	-2.184637	1.183279
4	6	0	-2.881203	-1.136055	0.569855
5	6	0	-1.469544	-1.127394	0.569902
6	6	0	-0.823178	-2.148882	1.310869
7	6	0	-2.880218	1.137700	-0.571745
8	6	0	-1.468531	1.129372	-0.569279
9	6	0	-0.707544	0.000594	0.000244
10	6	0	-3.576906	2.187238	-1.184508
11	6	0	-2.916117	3.221741	-1.827315
12	6	0	-1.519518	3.184391	-1.903976
13	6	0	-0.821175	2.152175	-1.307562
14	6	0	0.707544	-0.000325	0.000137
15	6	0	1.468219	-1.129238	-0.569535
16	6	0	2.879895	-1.138075	-0.571910
17	6	0	2.881527	1.135680	0.569690
18	6	0	1.469856	1.127531	0.569642
19	6	0	0.820513	-2.151634	-1.308071
20	6	0	1.518520	-3.183896	-1.904801
21	6	0	2.915112	-3.221667	-1.828237
22	6	0	3.576244	-2.187595	-1.185085

23	6	0	3.579388	2.184278	1.182709
24	6	0	2.919790	3.218011	1.827994
25	6	0	1.523314	3.180783	1.906935
26	6	0	0.823839	2.149431	1.310349
27	1	0	-0.984680	-3.945952	2.455752
28	1	0	-3.477807	-4.021050	2.295354
29	1	0	-4.664478	-2.170643	1.159982
30	1	0	0.251409	-2.119852	1.421294
31	1	0	-4.662693	2.172966	-1.163071
32	1	0	-3.474506	4.025579	-2.293261
33	1	0	-0.981086	3.951050	-2.449795
34	1	0	0.253592	2.123669	-1.416225
35	1	0	-0.254249	-2.122734	-1.416703
36	1	0	0.979839	-3.950232	-2.450828
37	1	0	3.473241	-4.025503	-2.294498
38	1	0	4.662035	-2.173692	-1.163633
39	1	0	4.665136	2.169910	1.159430
40	1	0	3.479070	4.021124	2.294123
41	1	0	0.985924	3.946780	2.454704
42	1	0	-0.250753	2.120800	1.420799
43	6	0	-3.682436	0.000006	-0.003197
44	1	0	-4.349127	-0.380382	-0.789204
45	1	0	-4.354541	0.379034	0.778780
46	6	0	3.682439	-0.001106	-0.002407
47	1	0	4.353103	-0.380772	0.780520
48	1	0	4.350575	0.378647	-0.787469

Table S15. Coordinates for optimized structure of the folded conformer of **m4** in the ground state (S_0).

Total Energy: −1051.56368575 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.474728	1.893604	1.107823
2	6	0	-3.575138	3.063987	0.355084
3	6	0	-2.492571	3.468373	-0.420001
4	6	0	-1.303608	2.719281	-0.462737
5	6	0	-1.248338	1.487318	0.241764
6	6	0	-2.327173	1.105202	1.043892
7	6	0	1.303562	2.719210	-0.462864
8	6	0	1.248294	1.487250	0.241642
9	6	0	-0.000047	0.671366	0.127350
10	6	0	2.492579	3.468223	-0.420262
11	6	0	3.575220	3.063746	0.354674
12	6	0	3.474840	1.893342	1.107383
13	6	0	2.327222	1.105020	1.043588
14	6	0	-0.000053	-0.671366	-0.127350
15	6	0	-1.248350	-1.487308	-0.241765
16	6	0	-1.303630	-2.719270	0.462737
17	6	0	1.303540	-2.719220	0.462864
18	6	0	1.248281	-1.487260	-0.241642
19	6	0	-2.327182	-1.105183	-1.043893
20	6	0	-3.474744	-1.893576	-1.107823
21	6	0	-3.575163	-3.063957	-0.355084
22	6	0	-2.492599	-3.468353	0.420001
23	6	0	2.492551	-3.468243	0.420262
24	6	0	3.575195	-3.063776	-0.354673

25	6	0	3.474825	-1.893371	-1.107383
26	6	0	2.327213	-1.105039	-1.043588
27	1	0	-4.295079	1.588956	1.748672
28	1	0	-4.478104	3.662914	0.394695
29	1	0	-2.545842	4.397029	-0.979186
30	1	0	-2.273305	0.195257	1.628110
31	1	0	2.545844	4.396881	-0.979444
32	1	0	4.478234	3.662610	0.394175
33	1	0	4.295263	1.588613	1.748101
34	1	0	2.273379	0.195048	1.627768
35	1	0	-2.273307	-0.195238	-1.628110
36	1	0	-4.295092	-1.588920	-1.748672
37	1	0	-4.478134	-3.662877	-0.394695
38	1	0	-2.545878	-4.397008	0.979187
39	1	0	2.545808	-4.396902	0.979444
40	1	0	4.478204	-3.662646	-0.394175
41	1	0	4.295250	-1.588648	-1.748101
42	1	0	2.273377	-0.195066	-1.627768
43	5	0	-0.000062	-3.305114	1.044689
44	1	0	-0.000079	-4.261344	1.759868
45	5	0	-0.000035	3.305114	-1.044690
46	1	0	-0.000044	4.261344	-1.759868

Table S16. Coordinates for optimized structure of the twisted conformer of **m4** in the ground state (S_0).

Total Energy: −1051.56368575 Hartree

opt b3lyp/6-311+g(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.443593	-3.122036	2.007493
2	6	0	-2.837277	-3.218714	1.916458
3	6	0	-3.532500	-2.234738	1.229521
4	6	0	-2.873817	-1.172517	0.580366
5	6	0	-1.447703	-1.120221	0.607294
6	6	0	-0.766921	-2.083849	1.389751
7	6	0	-2.873786	1.172499	-0.580451
8	6	0	-1.447671	1.120192	-0.607322
9	6	0	-0.714386	-0.000023	-0.000013
10	6	0	-3.532433	2.234738	-1.229613
11	6	0	-2.837172	3.218725	-1.916497
12	6	0	-1.443484	3.122043	-2.007469
13	6	0	-0.766846	2.083837	-1.389720
14	6	0	0.714386	-0.000020	0.000011
15	6	0	1.447708	-1.120215	-0.607295
16	6	0	2.873823	-1.172505	-0.580365
17	6	0	2.873780	1.172512	0.580451
18	6	0	1.447666	1.120198	0.607321
19	6	0	0.766931	-2.083847	-1.389752
20	6	0	1.443609	-3.122031	-2.007493
21	6	0	2.837293	-3.218702	-1.916456
22	6	0	3.532511	-2.234724	-1.229519
23	6	0	3.532422	2.234753	1.229615
24	6	0	2.837156	3.218736	1.916499
25	6	0	1.443469	3.122048	2.007468
26	6	0	0.766836	2.083840	1.389718
27	1	0	-0.885380	-3.852223	2.583321
28	1	0	-3.363704	-4.029273	2.407745

29	1	0	-4.616902	-2.260627	1.200804
30	1	0	0.304076	-2.012727	1.521581
31	1	0	-4.616836	2.260634	-1.200942
32	1	0	-3.363572	4.029299	-2.407789
33	1	0	-0.885241	3.852242	-2.583252
34	1	0	0.304157	2.012712	-1.521499
35	1	0	-0.304065	-2.012729	-1.521584
36	1	0	0.885400	-3.852221	-2.583322
37	1	0	3.363724	-4.029259	-2.407743
38	1	0	4.616914	-2.260607	-1.200801
39	1	0	4.616825	2.260654	1.200945
40	1	0	3.363551	4.029312	2.407791
41	1	0	0.885221	3.852244	2.583252
42	1	0	-0.304167	2.012710	1.521496
43	5	0	-3.667524	-0.000011	-0.000069
44	1	0	-4.862541	-0.000005	-0.000089
45	5	0	3.667524	0.000005	0.000070
46	1	0	4.862541	0.000016	0.000092
