Supporting Information

The role of steric hindrance in intramolecular oxidative aromatic coupling of pyrrolo[3,2-*b*]pyrroles

Maciej Krzeszewski,[a] Paweł Świder,[a] Łukasz Dobrzycki,[b] Michał Cyrański,[b*] Witold Danikiewicz,[a*] and Daniel T. Gryko[a*]

[a] *Institute of Organic Chemistry PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland*
E-mail: dtgryko@icho.edu.pl

[b] *The Czochralski Laboratory of Advanced Crystal Engineering, Faculty of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02089 Warsaw, Poland*

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1. General remarks.

All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. DMF was dried over magnesium sulfate, then distilled and stored under argon. Transformations with moisture and oxygen sensitive compounds were performed under a stream of argon. The reaction progress was monitored by means of thin layer chromatography (TLC), which was performed on aluminium foil plates, covered with Silica gel 60 F_{254} (Merck) or Aluminium oxide 60 F_{254} (neutral, Merck). Products purification was done by means of column chromatography with Kieselgel 60 (Merck) or Aluminium oxide (Fluka). Occasionally, dry column vacuum chromatography (DCVC**)** for purification of products obtained was performed using Silica gel Type D 5F. The identity and purity of prepared compounds were proved by ^{1}H NMR and ^{13}C NMR spectrometry as well as by MS-spectrometry (*via* EI-MS or ESI-MS). NMR spectra were measured on Bruker AM 500 MHz, Bruker AM 600 MHz, Varian 600 MHz, Varian 400 MHz or Varian 200 MHz instruments with TMS as internal standard. All chemical shifts are given in ppm. All melting points for crystalline products were measured with automated melting point apparatus EZ-MELT and were given without correction. The absorbance and fluorescence spectra were measured in dichloromethane on Perkin – Elmer Lambda 25 UV/VIS and Hitachi F-7000 respectively.

Linear optical measurements

Steady-state fluorescence measurements were performed with dilute solutions (10^{-6}M, optical density<0.1) contained in standard 1 cm quartz cuvettes at room temperature. Compounds were dissolved in dichloromethane unless otherwise noted. Emission spectra were obtained, for each compound, under excitation at λ=310 nm. Fluorescence quantum yields were measured by using quinine hemisulfate monohydrate in 0.5M sulfuric acid as a standard. For spiro derivatives emission spectra were obtained, under excitation at λ=500 nm. Fluorescence quantum yields were measured by Rhodamine 6g in ethanol as a standard.

2. Experimental section

Compounds **4a** and **5a** were synthesized according to procedures published in [1]

General procedures for the synthesis of aldehydes (1b-f)

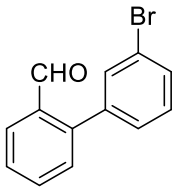
METHOD A SUZUKI-MIYAURA COUPLING

Synthesis of **1b, 1c and 1f**. 1-bromo-3-iodobenzene/ 3-methoxybromobenzene/ 3,5-dimethoxybromobenzene (20 mmol), 2-formylphenylboronic acid (24 mmol), K_2CO_3 (40 mmol), PPh_3 (20% mol), $Pd(OAc)_2$ (10% mol) were placed in a 100 mL Schlenk flask, which was flushed with argon prior to use. Then 50 mL of 1:1 v/v mixture of toluene and water was added, and the resulting mixture was stirred at 80 °C for 16 h. After cooling two layers were separated, water layer was extracted with ethyl acetate (3× 20 mL). Organic layers were combined and dried, solvent was evaporated and crude products were purified by means of flash column chromatography.
In case of **1e** different ratio of substrates was applied. Synthesis of **1e**. 1,3,5-tribromobenzene (50 mmol), 2-formylphenylboronic acid (20 mmol), K_2CO_3 (40 mmol), PPh_3 (20% mol), $Pd(OAc)_2$ (10% mol).

METHOD B SUZUKI-MIYAURA COUPLING

Synthesis of **1d**. 2-bromobenzaldehyde (20 mmol), 3,5-dimethylphenylboronic acid (24 mmol), K_2CO_3 (40 mmol), PPh_3 (20% mol), $Pd(OAc)_2$ (10% mol) were placed in a 100 mL Schlenk flask, which was flushed with argon prior to use. Then 50 mL of 1:1 v/v mixture of toluene and water was added, and the resulting mixture was stirred at 80 °C for 16 h. After cooling two layers were separated, water layer was extracted with ethyl acetate (3× 20 mL). Organic layers were combined and dried, solvent was evaporated and crude products were purified by means of flash column chromatography.

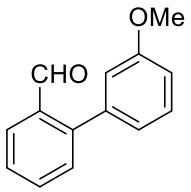
1b



Beige solid. Yield 3.12 g (60%). R_f= 0.52 (SiO_2, DCM/hexanes, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.03 (dt, *J* 7.8, 1.1 Hz, 1H), 7.64 (dd, *J* 7.5, 1.4 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.53 (t, *J* 7.6 Hz, 1H), 7.41 (dd, *J* 7.7, 0.7 Hz, 1H), 7.34 (t, *J* 7.7 Hz, 1H), 7.32 – 7.28 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 144.2, 139.9, 133.7, 132.7, 131.2, 130.6, 129.8, 128.8, 128.3, 127.9, 122.6. HRMS (EI) calcd for $C_{13}H_9OBr$: 259.9837 [M^+], found: 259.9842.

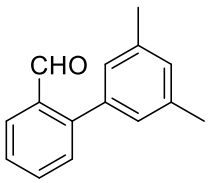
[1] Krzeszewski, M.; Gryko, D. T. *J. Org. Chem.* **2015**, *80*, 2893−2899.

1c



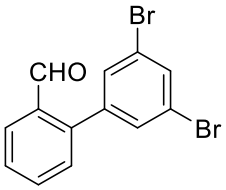
Colorless oil. Yield 5.56 g (88%). R_f= 0.46 (SiO_2, DCM/hexanes, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.02 (dd, *J* 7.8, 0.5 Hz, 1H), 7.63 (td, *J* 7.5, 0.8 Hz, 1H), 7.49 (t, *J* 7.6 Hz, 1H), 7.45 (dd, *J* 7.6, 0.4 Hz, 1H), 7.37 (t, *J* 7.9 Hz, 1H), 6.98 (dd, *J* 8.2, 2.2 Hz, 1H), 6.95 (d, *J* 7.5 Hz, 1H), 6.93 – 6.91 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 159.5, 145.8, 139.2, 133.8, 133.5, 130.6, 129.4, 127.8, 127.4, 122.7, 115.7, 113.6, 55.3. HRMS (EI) calcd for $C_{14}H_{12}O$: 212.0837 [M^+], found: 212.0841.

1d



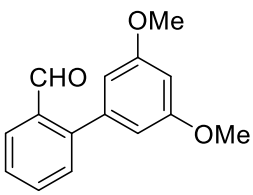
White solid. Yield 4.12 g (98%). R_f= 0.42 (SiO_2, DCM/hexanes, 1:2). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 9.99 (s, 1H), 8.01 (d, *J* 7.8 Hz, 1H), 7.60 (dd, *J* 7.5, 1.2 Hz, 1H), 7.47 (t, *J* 7.6 Hz, 1H), 7.43 (d, *J* 7.7 Hz, 1H), 7.07 (s, 1H), 6.99 (s, 2H), 2.38 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 192.7, 146.3, 138.0, 137.7, 133.8, 133.4, 130.7, 129.7, 128.0, 127.5, 127.4, 21.27. HRMS (EI) calcd for $C_{15}H_{14}O$: 210.1045 [M^+], found: 210.1043.

1e



Beige solid. Yield 4.39 g (65%). R_f= 0.48 (SiO_2, DCM/hexanes, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.03 (dd, *J* 7.8, 0.8 Hz, 1H), 7.76 (t, *J* 1.7 Hz, 1H), 7.66 (td, *J* 7.6, 1.4 Hz, 1H), 7.55 (t, *J* 7.6 Hz, 1H), 7.48 (d, *J* 1.7 Hz, 2H), 7.38 (dd, *J* 7.7, 0.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 191.1, 142.5, 141.4, 133.8, 133.7, 133.6, 131.6, 130.6, 128.8, 128.3, 123.0. HRMS (EI) calcd for $C_{13}H_8Br_2O$: 337.8942 [M^+], found: 337.8952.

1f

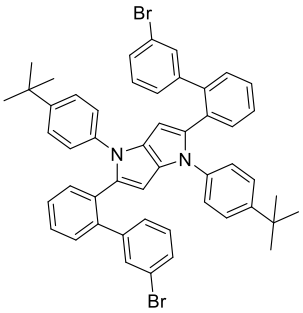


White solid. Yield 5.24 g (83%). R_f= 0.38 (SiO_2, DCM/hexanes, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.01 (dd, *J* 7.8, 0.9 Hz, 1H), 7.62 (td, *J* 7.6, 1.4 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.45 (dd, *J* 7.6, 0.6 Hz, 1H), 6.54 (t, *J* 2.2 Hz, 1H), 6.51 (d, *J* 2.2 Hz, 2H), 3.82 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 160.7, 145.9, 139.8, 133.8, 133.4, 130.4, 127.9, 127.3, 108.5, 100.1, 55.5. HRMS (EI) calcd for $C_{15}H_{14}O_3$: 242.0943 [M^+], found: 242.0940.

General procedure for the synthesis of tetraarylpyrrolopyrroles (4b-e)

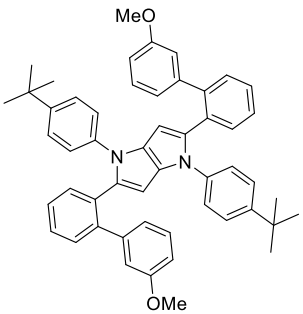
In a 25 mL round-bottom flask equipped with a reflux condenser and magnetic stir bar, 6 mL glacial acetic acid was placed followed by the addition of arylamine (8 mmol), aldehyde (8 mmol) and TsOH (0.8 mmol). The mixture was stirred at 90 °C for 30 min. After that time butane-2,3-dione (4 mmol) was slowly added via syringe and the resulting mixture was stirred at 90 °C for 3 h. The reaction mixture was then cooled to room temperature. The precipitate of the obtained dye was then filtered off and washed with cooled glacial acetic acid. Recrystallization from AcOEt and drying under vacuum afforded pure product.

4b



Off-white solid. Yield 1.42 g (43%). R_f= 0.40 (SiO_2, DCM/hexanes, 1:4). mp 296-298 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* 7.5, 1.1 Hz, 2H), 7.39 (td, *J* 7.5, 1.4 Hz, 2H), 7.35 (td, *J* 7.5, 1.4 Hz, 2H), 7.23 (dd, *J* 8.0, 0.9 Hz, 2H), 7.15 (dd, *J* 7.5, 1.1 Hz, 2H), 7.05 (d, *J* 8.6 Hz, 4H), 6.91 (t, *J* 7.9 Hz, 2H), 6.69 (t, *J* 1.6 Hz, 2H), 6.61 (d, *J* 7.8 Hz, 2H), 6.51 (d, *J* 8.6 Hz, 4H), 6.26 (s, 2H), 1.31 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 143.4, 139.3, 136.4, 133.9, 132.6, 131.09, 131.02, 129.9, 129.7, 128.93, 128.89, 127.9, 127.8, 127.1, 125.3, 122.4, 121.6, 95.7, 34.3, 31.4. HRMS (ESI- TOF) calcd for $C_{50}H_{44}N_2Br_2$: 830.1871 [M^+], found: 830.1852.

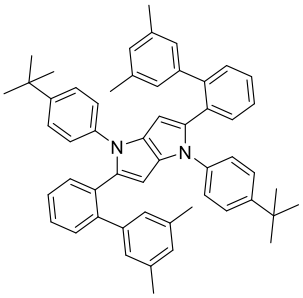
4c



Off-white solid. Yield 1.00 g (34%). R_f= 0.44 (SiO_2, DCM/hexanes, 1:2). mp 249-251 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.58 (dd, *J* 7.5, 1.0 Hz, 2H), 7.24 (dd, *J* 7.5, 1.1 Hz, 2H), 7.20 – 7.17 (m, 2H), 7.15 – 7.10 (m, 2H), 6.92-6.88 (m, 6H), 6.74 (d, *J* 8.5 Hz, 4H), 6.71 – 6.65 (m, 2H), 6.51 – 6.46 (m, 4H), 6.31 (s, 2H), 3.34 (s, 6H), 1.20 (s, 18H). ^{13}C NMR (125 MHz, C_6D_6) δ 159.9, 147.0, 143.2,

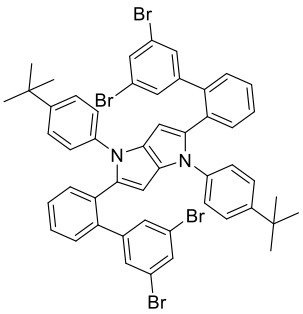
141.3, 137.5, 134.9, 133.2, 131.6, 130.45, 130.39, 128.7, 128.3, 128.1, 127.9, 127.6, 125.4, 123.1, 121.4, 114.4, 112.3, 96.3, 54.7, 34.2, 31.4. HRMS (ESI- TOF) calcd for $C_{52}H_{50}N_2O_2$: 734.3872 [M^+], found: 734.3878.

4d



Pale yellow solid. Yield 1.17 g (40%). R_f= 0.40 (SiO_2, DCM/hexanes, 1:4). mp 254-255 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.36 – 7.27 (m, 4H), 7.20 – 7.14 (m, 2H), 7.02 (d, *J* 8.6 Hz, 4H), 6.74 (s, 2H), 6.53 (d, *J* 8.6 Hz, 4H), 6.28 (s, 4H), 6.20 (s, 2H), 2.10 (s, 12H), 1.29 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 141.2, 141.0, 137.0, 136.6, 134.6, 132.6, 131.1, 130.16, 130.06, 127.6, 127.3, 127.0, 126.3, 124.9, 122.7, 95.6, 34.3, 31.5, 21.5. HRMS (ESI- TOF) calcd for $C_{54}H_{54}N_2$: 730.4287 [M^+], found: 730.4291.

4e

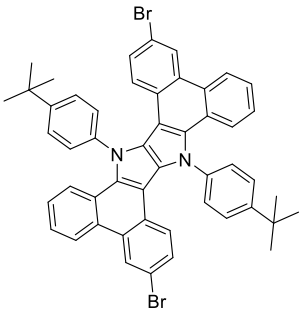


Pale yellow solid. Yield 1.54 g (39%). R_f= 0.70 (SiO_2, DCM/hexanes, 1:2). mp 288-290 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* 7.5 Hz, 2H), 7.44 - 7.38 (m, 4H), 7.34 (td, *J* 7.6, 1.1 Hz, 2H), 7.11 (d, *J* 8.4 Hz, 6H), 6.70 (d, *J* 1.6 Hz, 4H), 6.59 (d, *J* 8.6 Hz, 4H), 6.29 (s, 2H), 1.33 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 144.8, 137.8, 136.6, 133.8, 132.5, 131.6, 131.3, 130.5, 130.08, 129.95, 128.4, 127.7, 125.5, 122.6, 121.9, 96.2, 34.4, 31.4. HRMS (ESI- TOF) calcd for $C_{50}H_{43}Br_4N_2$: 987.0160 [M+H^+], found: 987.0149.

General procedure for the synthesis of π-expanded PPs (5b-c) and spiro compounds (6d-e)

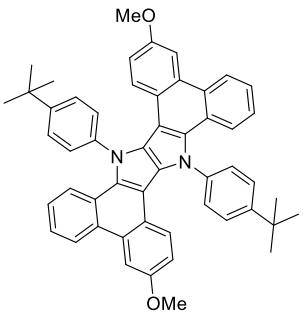
To a flushed with argon prior to use 50 mL round-bottom flask equipped with magnetic stir bar and septum, 12 mL of dry methylene chloride and 1 mmol of adequate TAPP (**4b-e**) were placed. To suspended substrate, 20 mmol of iron(III) chloride dissolved in 12 mL of dry nitromethane were added via syringe. Reaction was conducted at room temperature for 30 min. Then 20 mL of water was added, and resulting mixture was stirred for another 15 min. Two layers were separated, water layer was extracted with methylene chloride (3 × 10 mL). Organic layers were combined and dried, solvent was evaporated and crude product was purified by means of flash column chromatography.

5b



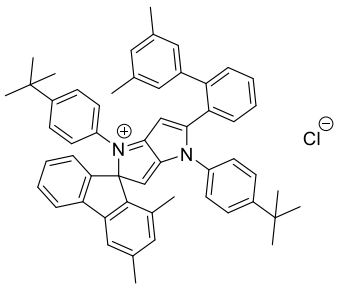
Yellow solid. Yield 413 mg (50%). R_f= 0.45 (SiO_2, DCM/hexanes, 1:2). mp >400 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* 1.0 Hz, 2H), 8.60 (d, *J* 8.2 Hz, 2H), 7.77 (d, *J* 8.4 Hz, 4H), 7.73 (d, *J* 8.4 Hz, 4H), 7.52 – 7.40 (m, 4H), 7.23 (d, *J* 7.6 Hz, 2H), 7.01 (dd, *J* 8.9, 1.7 Hz, 2H), 6.57 (d, *J* 8.8 Hz, 2H), 1.60 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 151.6, 140.6, 130.5, 128.7, 128.0, 127.2, 126.5, 125.8, 124.5, 123.8, 122.8, 122.0, 120.9, 117.3, 99.7, 35.3, 31.7. (EI) calcd for $C_{50}H_{40}N_2Br_2$: 826.1558 [M^+], found: 826.1531.

5c



Pale yellow solid. Yield 511 mg (70%). R_f= 0.40 (SiO_2, DCM/hexanes, 1:2). Mp 396-397 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 8.65 (d, *J* 7.9 Hz, 2H), 8.16 (s, 2H), 7.96 (d, *J* 8.2 Hz, 2H), 7.58 (d, *J* 8.2 Hz, 4H), 7.33 (d, *J* 8.4 Hz, 4H), 7.27 (t, *J* 7.0 Hz, 2H), 7.15 (t, *J* 7.0 Hz, 2H) 6.99 (s, 4H), 3.54 (s, 6H), 1.31 (s, 18H). HRMS (ESI- TOF) calcd for $C_{52}H_{46}N_2O_2$: 730.3559 [M^+], found: 730.3552. ^{13}C NMR was not recorded due to very poor solubility of the compound.

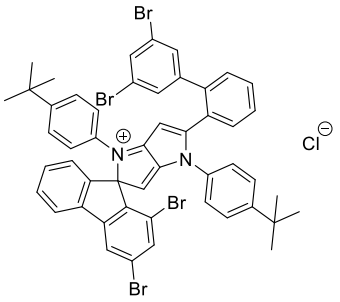
6d



Red solid. Yield 688 mg (90%). R_f= 0.30 (SiO_2, DCM/methanol, 9:1). mp 145 °C (decomp.). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.07 (s, 1H), 7.80 (d, *J* 7.5 Hz, 1H), 7.70 (s, 2H), 7.54 – 7.50 (m, 2H), 7.34 (d, *J* 6.4 Hz, 2H), 7.31 (d, *J* 6.4 Hz, 2H), 7.21 – 7.10 (m, 3H), 6.99 (d, *J* 6.5 Hz, 4H), 6.72 (s, 1H), 6.67 (s, 1H), 6.46 (s, 2H), 6.42 (d, *J* 7.1 Hz, 2H), 2.44 (s, 3H), 2.23 (s, 6H), 2.07 (d, *J* 5.8 Hz, 3H), 1.26 (s, 9H), 1.22 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 164.5, 152.36, 152.31, 143.6, 142.97, 142.90, 142.7, 142.3, 136.0, 134.33, 134.21, 133.6, 132.5, 131.9, 131.59, 131.56, 131.2, 130.0, 129.4, 128.7, 128.5, 128.2, 127.49, 127.42, 127.1, 126.7, 126.4, 123.9, 123.5, 122.3, 122.0,

120.8, 120.6, 97.2, 93.9, 35.00, 34.97, 31.3, 31.1, 21.64, 21.55, 17.6. HRMS (ESI- TOF) calcd for $C_{54}H_{53}N_2$: 729.4209 [M^+], found: 729.4218.

6e



Red solid. Yield 918 mg (90%). R_f= 0.30 (SiO_2, DCM/methanol, 9:1). mp 160 °C (decomp.). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.32 (d, *J* 7.6 Hz, 1H), 7.93 (d, *J* 1.5 Hz, 1H), 7.78 (d, *J* 7.8 Hz, 2H), 7.73 (t, *J* 7.3 Hz, 2H), 7.69 – 7.63 (m, 2H), 7.56 (t, *J* 7.5 Hz, 1H), 7.47 (t, *J* 7.6 Hz, 1H), 7.32 (d, *J* 8.7 Hz, 2H), 7.29 (d, *J* 7.6 Hz, 1H), 7.23 (d, *J* 8.6 Hz, 2H), 7.06 (d, *J* 8.7 Hz, 2H), 6.92 (s, 2H), 6.72 (s, 1H), 6.67 (s, 1H), 6.54 (d, *J* 8.5 Hz, 2H), 1.30 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 178.4, 152.7, 146.7, 143.2, 140.4, 138.4, 135.4, 133.81, 133.71, 132.95, 132.0, 131.2, 130.8, 130.3, 130.1, 129.3, 127.6, 127.3, 127.1, 126.9, 124.3, 124.1, 123.3, 122.7, 122.0, 97.6, 93.7, 35.1, 31.29, 31.13. HRMS (ESI- TOF) calcd for $C_{50}H_{41}Br_4N_2$: 985.0003 [M^+], found: 984.9980.

3. X-ray crystallography

Experimental

The X-ray measurement of **6e** was performed at 100(2) K on a Bruker D8 Venture Photon100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ=1.54178 Å). A total of 4810 frames were collected with Bruker APEX2 program **[2]**. The frames were integrated with the Bruker SAINT software package **[3]** using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 33604 reflections to a maximum θ angle of 65.30° (0.85 Å resolution), of which 7712 were independent (average redundancy 4.357, completeness = 99.5%, R_{int} = 6.86%, R_{sig} = 5.03%) and 5942 (77.05%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.9254(12) Å, b = 13.4449(14) Å, c = 15.8457(17) Å, α = 95.900(4)°, β = 100.524(4)°, γ = 95.947(4)°, V = 2258.4(4) Å^3, are based upon the refinement of the XYZ-centroids of 9926 reflections above 20 $\sigma(I)$ with 5.717° < 2θ < 130.3°. Data were corrected for absorption effects using the multi-scan method (SADABS) **[4]**. The ratio of minimum to maximum apparent transmission was 0.782. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3230 and 0.7670.

The structure was solved and refined using SHELXTL Software Package **[5]** using the space group P-1, with Z=1 for the formula unit, $C_{104}H_{92}Br_8Cl_2N_4O$. The final anisotropic full-matrix least-squares refinement on F^2 with 656 variables converged at $R1$ = 5.38%, for the observed data and $wR2$ = 14.69% for all data. The goodness-of-fit was 1.045. The largest peak in the final difference electron density synthesis was 1.214 e$^-$/Å^3 and the largest hole was -0.476 e$^-$/Å^3 with an RMS deviation of 0.100 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.562 g/cm^3 and F(000), 1066 e$^-$.

The investigated crystal was quite small and weakly diffracting thus it was not possible to collect reflections above 2θ=130.3°.

The structure contains disordered Et_2O molecule located at the centre of symmetry. Moreover, in the organic cation di-bromo substituted fluorene moiety is disordered over two sites with refined occupancy ratio yielding 0.968(2):0.032(2). Such a minimal degree of disorder was only possible to detect due to the presence of Br substituents. In addition one of the t-butyl group in the cation is disordered as well. There are two alternative positions of this group with refined occupancy ration equal to 0.726(16):0.274(16). To preserve reasonable shape of disordered moieties number of geometry restraints were used.

Most of non-hydrogen atoms were refined anisotropically. The isotropic approach was applied for atoms of low-occupancy disordered fluorene fragment in the organic cation. All hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of

the hydrogen atoms were not refined and were set to be equal to either 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. The atomic scattering factors were taken from the International Tables **[6]**.

References

[2] APEX2,. Bruker AXS Inc., Madison, Wisconsin, USA, **2013**.

[3] SAINT,. Bruker AXS Inc., Madison, Wisconsin, USA, **2013**.

[4] SADABS,. Bruker AXS Inc., Madison, Wisconsin, USA, **2012**.

[5] G. M. Sheldrick, *Acta Crystallogr*. **1990**, A46, 467-473; Sheldrick, G. M. *Acta Cryst*., **2008**, A64, 112–122.

[6] *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer: Dordrecht, **1992**, Vol.C.

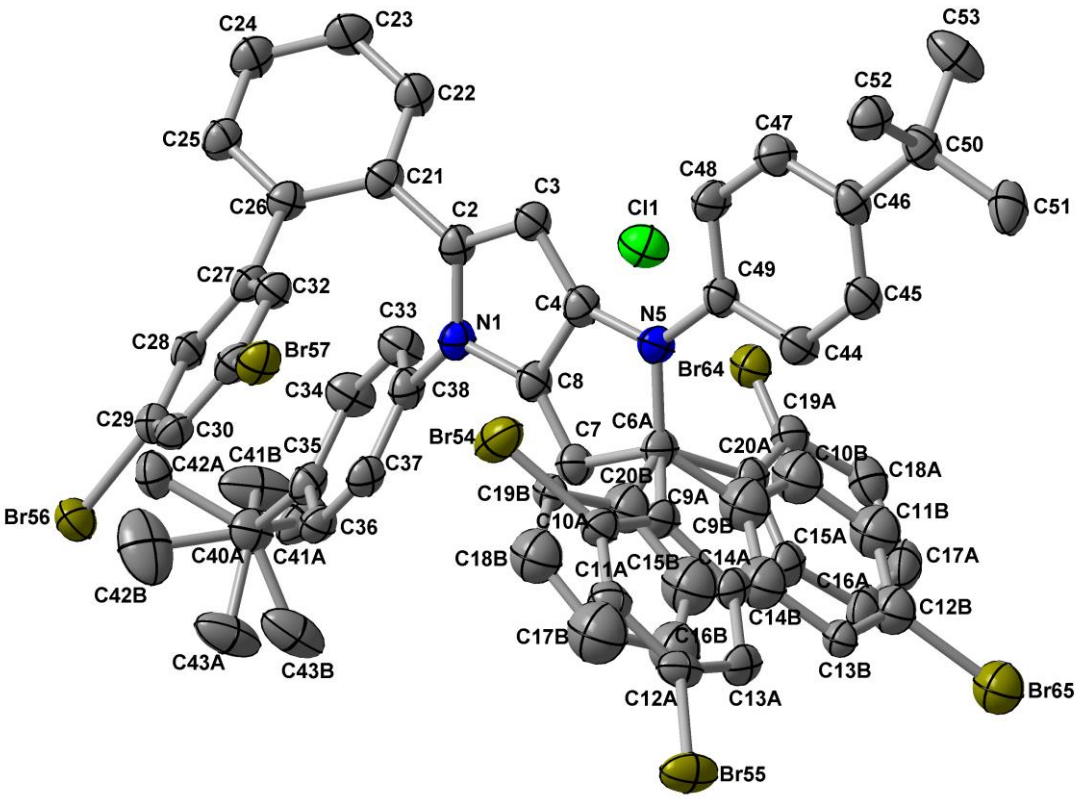


Figure S1. Atom numbering and thermal ellipsoid plot drawn at the 33% probability level. H atoms and disordered Et_2O molecule omitted for clarity.

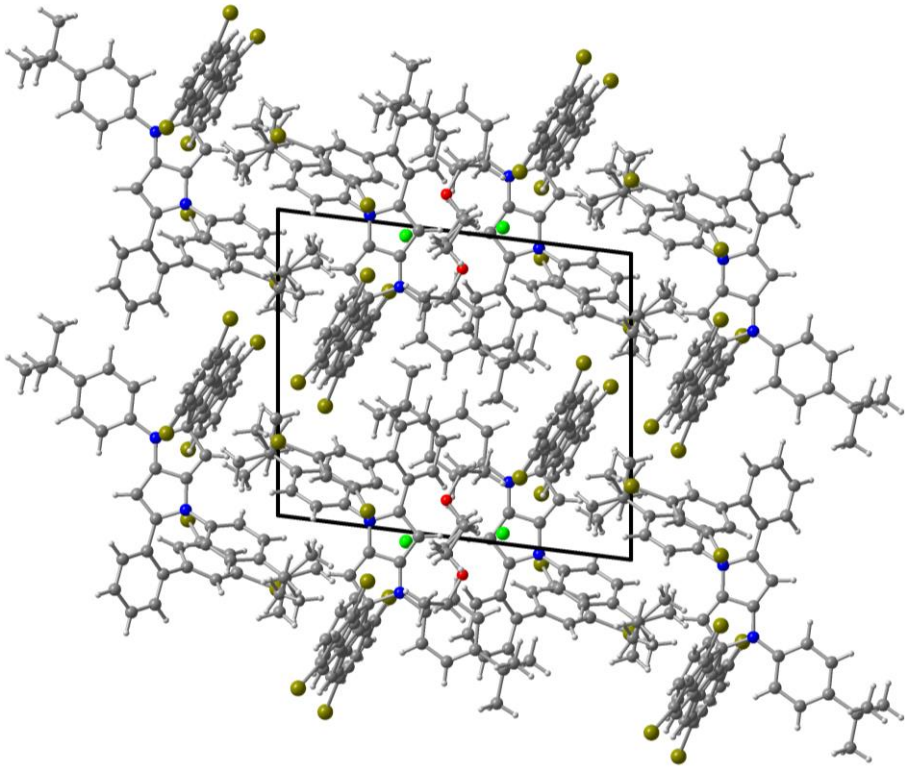
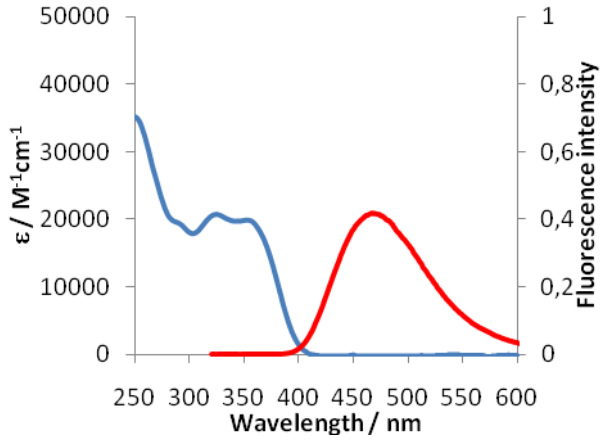


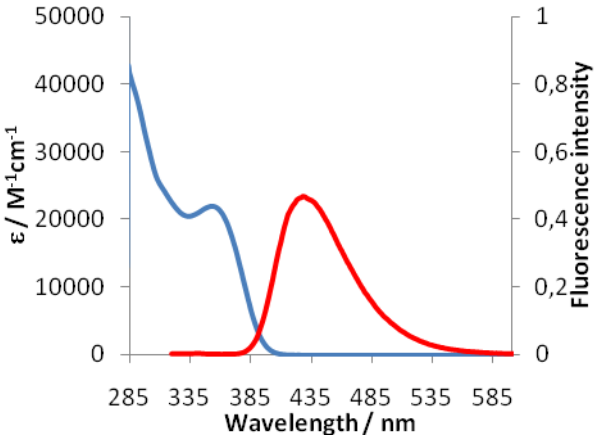
Figure S2. Packing diagram of **6e**, view along [100] direction.

4. Normalized absorption and emission spectra for synthesized compounds.

4b



4c (in toluene)



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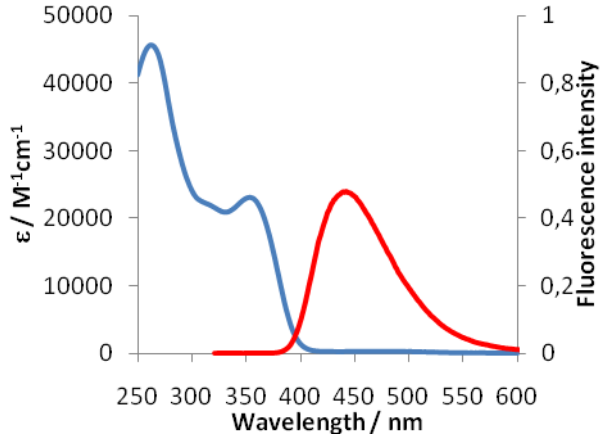
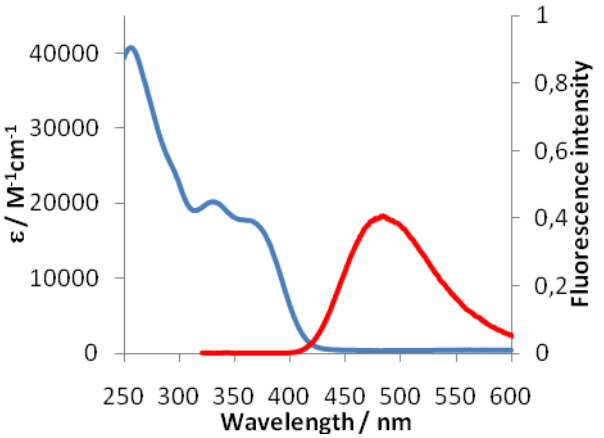
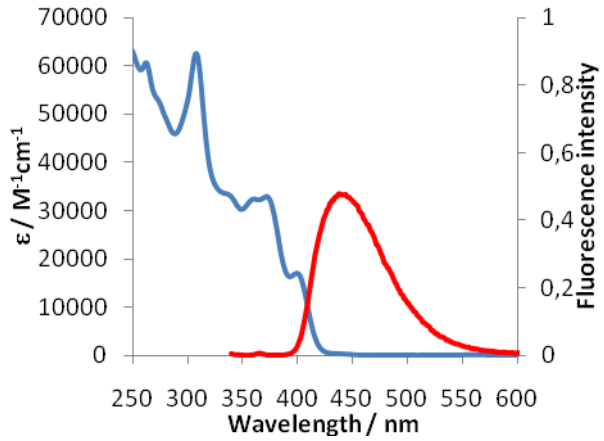


4e



5b



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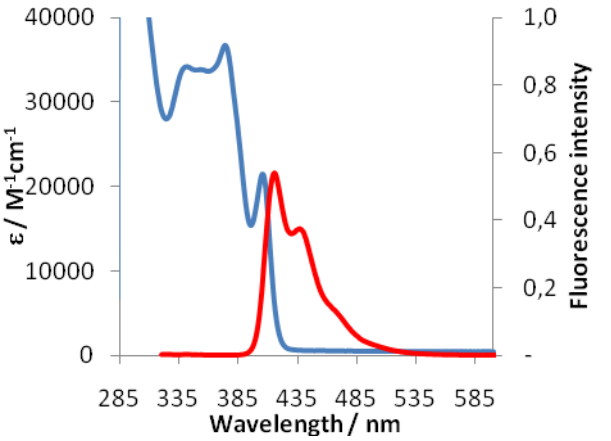
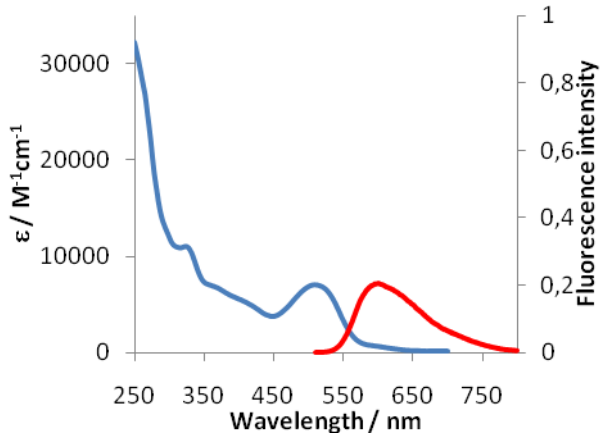


6d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20000
10000
0
ε / M-1cm-1
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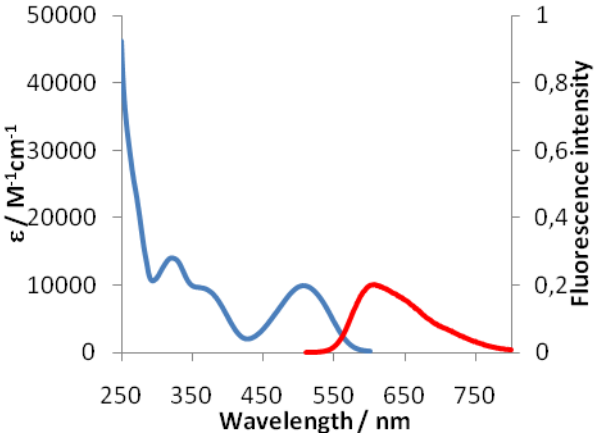
0,6
0,4
0,2
0
Fluorescence intensity
250 350 450 550 650 750
Wavelength / nm

6e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20000
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ε / M-1cm-1
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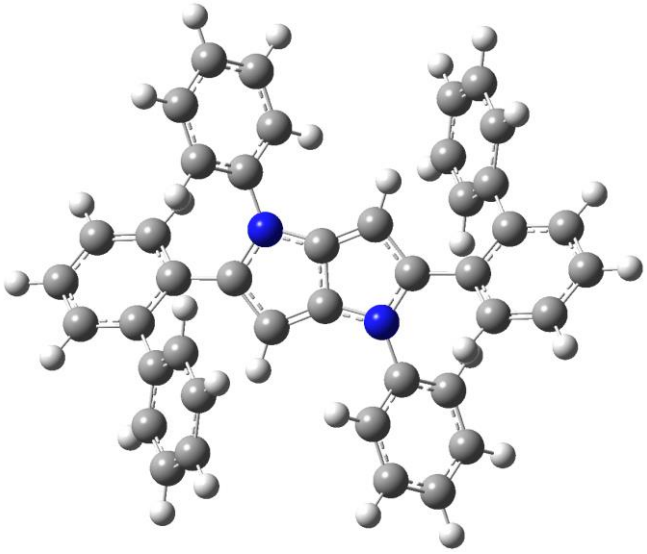
0,8
0,6
0,4
0,2
0
Fluorescence intensity
250 350 450 550 650 750
Wavelength / nm

5. Cartesians coordinates of calculated structures

Cartesian coordinates of molecules without bromine atoms in structures:

Substrate (compound 7a):
conformer 1 (16 %)



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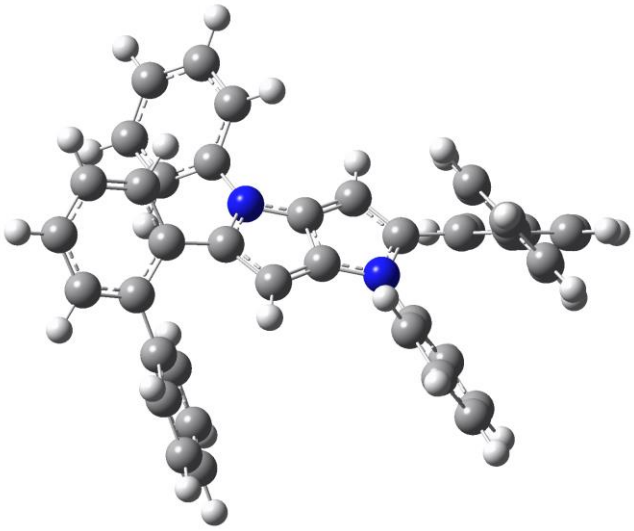
conformer 2 (19 %)



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H	6.67109100	2.61783700	-2.13868100
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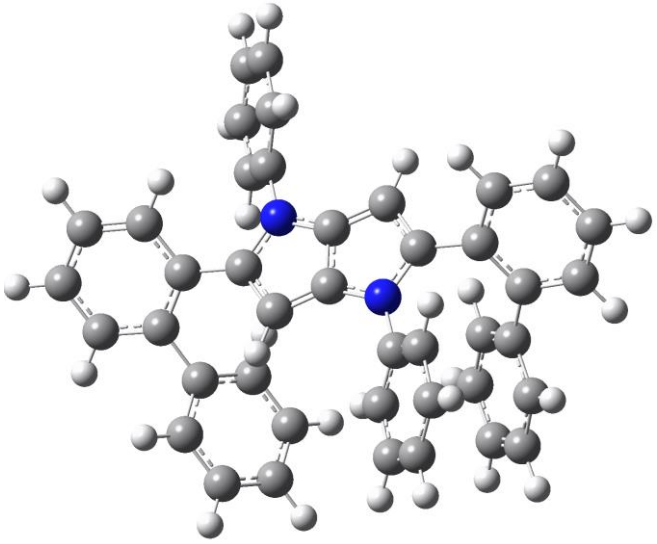

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H	1.10020900	-1.62085800	-1.31893700
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C	-3.36366100	3.29774900	-0.87489100
C	-4.06842400	1.34817200	0.40962400
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H	-2.57996200	3.83429600	-1.39561800
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C	-5.65703600	3.08376900	-0.20205100
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C	2.67638000	3.71687600	-0.24691500
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C	3.44970500	4.73847800	0.29581200
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C	4.33543400	3.20561500	1.93555300
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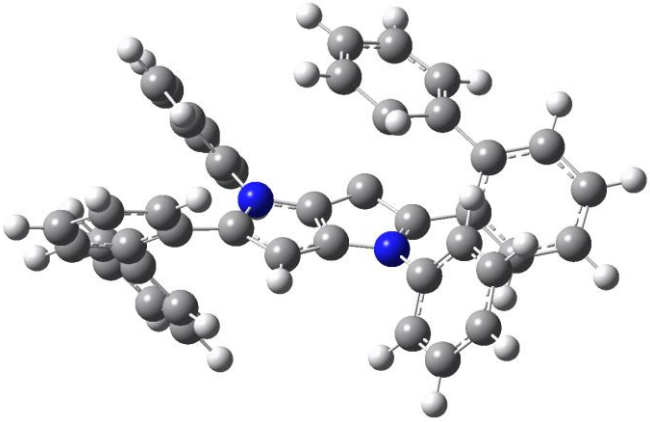
C	2.28014800	-2.23824900	1.38215400
C	1.80719600	-4.69701100	0.16760100
H	3.30993200	-4.10855800	-1.25438200
C	1.33157900	-3.10406800	1.91389300
H	2.47744600	-1.28805200	1.86499200
C	1.08710400	-4.33225500	1.30232500
H	0.35022900	-5.00785800	1.71725500
C	-3.78804400	0.10015100	1.16113400
C	-4.64573800	-0.99696200	1.03632800
C	-2.69355800	0.01380700	2.02799400
C	-4.40722700	-2.16240000	1.75489900
H	-5.48161800	-0.94310100	0.34965600
C	-2.45593800	-1.15336800	2.74569800
H	-2.04690200	0.87326700	2.16305400
C	-3.31060200	-2.24461000	2.60905800
H	-3.13080600	-3.14958600	3.17525600
H	1.62744000	-5.65333900	-0.30599300
H	0.79085900	-2.82677600	2.80984900
H	-1.61786000	-1.20140900	3.42980900
H	-5.07448300	-3.00741700	1.64406300

Transition state (TS-6 (7a)):

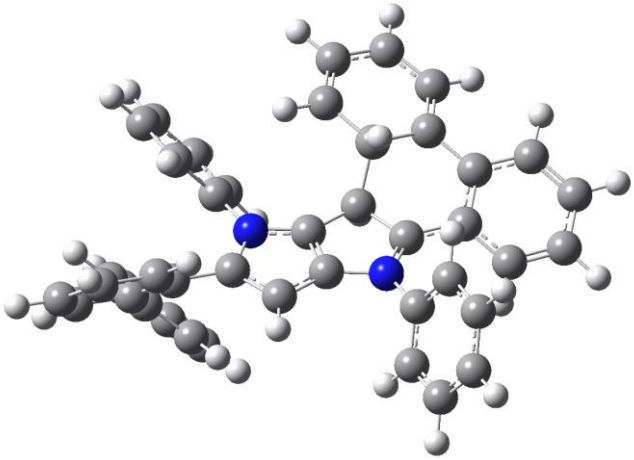


Zero-point correction=0.608054 (Hartree/Particle)
Thermal correction to Energy=0.640488
Thermal correction to Enthalpy=0.641432
Thermal correction to Gibbs Free Energy=0.542658
SCF Done:E(UM052X) = -1727.65182050

C	2.36208500	-0.03990900	0.46751500
C	1.20264600	-0.92919400	0.29224000
C	0.11476200	-0.00033800	0.05728100
C	0.61493200	1.27898900	-0.01249100
C	-1.54357900	1.36796800	-0.51590100
C	-0.41501700	2.16720200	-0.38097400
H	1.10243700	-1.79289300	0.93694900
H	-0.39118900	3.23771500	-0.49648300
C	3.72685100	-0.53489600	0.60396500
C	4.71681900	0.15707100	1.30714400
C	4.01748100	-1.78182200	-0.00312900
C	5.99866500	-0.36837100	1.39838300
H	4.47698200	1.09179600	1.79604000
C	5.31758200	-2.28010300	0.08654200
C	6.29905700	-1.58033000	0.77941000
H	6.76090700	0.16590300	1.94898100
H	5.56304900	-3.21077200	-0.40823800
H	7.30229300	-1.98150700	0.83618100
C	-2.90519800	1.81824200	-0.86346800
C	-3.04263000	2.60552800	-2.01145600
C	-4.04043900	1.49969400	-0.09267800
C	-4.28793100	3.06808800	-2.41715900
H	-2.15958800	2.83277400	-2.59622100
C	-5.28596600	1.96265500	-0.52613900
C	-5.41566600	2.73618300	-1.67347300
H	-4.37618500	3.67448500	-3.30894600
H	-6.15880700	1.73641400	0.07328700
H	-6.39270800	3.08862300	-1.97707300
N	-1.20966500	0.04155100	-0.26549800
N	1.99963600	1.22370600	0.22528100
C	-2.03499200	-1.11513600	-0.38480200
C	-2.80590300	-1.30559300	-1.52856600

C	-2.00991100	-2.06062600	0.63513700
C	-3.56359600	-2.46633700	-1.64383600
H	-2.81083300	-0.55475600	-2.30819900
C	-2.75909700	-3.22365700	0.50098100
H	-1.44845700	-1.85955600	1.53856100
C	-3.53595200	-3.42834000	-0.63624500
H	-4.17003400	-2.62145300	-2.52663400
H	-2.75273100	-3.95786400	1.29594000
H	-4.12570200	-4.33041100	-0.73404500
C	2.84670500	2.37270400	0.06531800
C	3.83710900	2.37185900	-0.91085200
C	2.61406700	3.47947600	0.87383800
C	4.62557900	3.50612600	-1.06339800
H	3.98418700	1.50077100	-1.53631100
C	3.40769300	4.60993600	0.70672800
H	1.83102300	3.44777000	1.62123200
C	4.41270100	4.62178900	-0.25649200
H	5.40025300	3.52087300	-1.81837800
H	3.24050200	5.47783900	1.33042400
H	5.02748700	5.50303000	-0.38289400
C	-3.96882800	0.71037500	1.16427200
C	-3.03349300	1.01090900	2.15980100
C	-4.86941200	-0.33803700	1.37587600
C	-2.99662500	0.27188500	3.33747800
H	-2.34944900	1.83864200	2.01679500
C	-4.83121100	-1.07711200	2.55288900
H	-5.58189400	-0.58923200	0.59952900
C	-3.89337900	-0.77570300	3.53623100
H	-3.86819300	-1.34519600	4.45656000
C	2.93612500	-2.52995600	-0.66472400
C	2.81629900	-3.89805500	-0.53917800
C	1.82743800	-1.76072100	-1.23948500
C	1.68687700	-4.57682100	-1.02255100
H	3.58937100	-4.45406300	-0.02399000
C	0.72730900	-2.51064200	-1.81409300
H	2.10859300	-0.87473400	-1.80744600
C	0.64929800	-3.87067000	-1.65968500
H	-0.20392500	-4.40665000	-2.05434700
H	-0.04829900	-1.96746400	-2.33607900
H	1.61743400	-5.64885800	-0.90399300
H	-2.28031200	0.52553800	4.10899400
H	-5.53154500	-1.88942500	2.69979900

Product (6-membered ring, compound 8a):
conformer 1 (97.8 %)

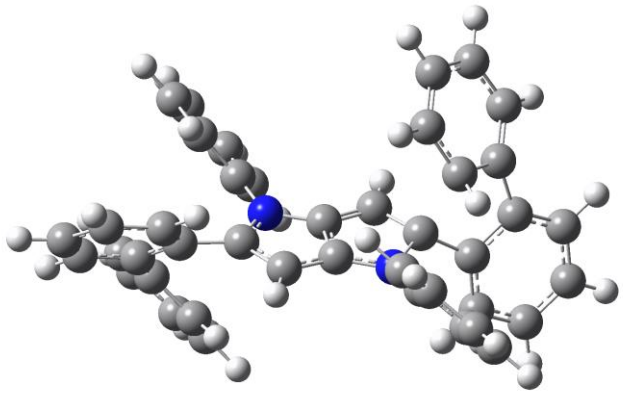


Zero-point correction=0.608887 (Hartree/Particle)
Thermal correction to Energy=0.641734
Thermal correction to Enthalpy=0.642678
Thermal correction to Gibbs Free Energy=0.541918
SCF Done:E(UM052X) = -1727.66033623

C	2.42054800	0.03904000	0.25563300
C	1.26923600	-0.93750800	0.09192900
C	0.14124500	0.00481800	-0.16288500
C	0.60018600	1.29233900	-0.14647200
C	-1.57473400	1.37648500	-0.53865200
C	-0.45854400	2.18703800	-0.39471600
H	1.15223000	-1.52069900	1.01133200
H	-0.45548800	3.26324100	-0.43515700
C	3.76278000	-0.43973500	0.45781700
C	4.76834200	0.34991400	1.04821600
C	4.01805000	-1.79555800	0.09869000
C	6.02333000	-0.17653500	1.27312900
H	4.54753900	1.36113300	1.35862100
C	5.31927400	-2.28497700	0.31510200
C	6.29752300	-1.49580100	0.88960600
H	6.78897900	0.42718800	1.74027100
H	5.57127000	-3.28766400	0.00138600
H	7.28843100	-1.90393300	1.04009600
C	-2.95649900	1.81814200	-0.81600500
C	-3.14902800	2.63948700	-1.93157300
C	-4.05512100	1.46698600	-0.00788700
C	-4.41371800	3.10538200	-2.26841000
H	-2.29338200	2.89262300	-2.54561500
C	-5.32131800	1.93396600	-0.37183200
C	-5.50563800	2.74251300	-1.48705700
H	-4.54451700	3.73913800	-3.13562600
H	-6.16575000	1.68259400	0.25749300
H	-6.49704500	3.09768100	-1.73605800
N	-1.19874500	0.04256600	-0.39970700
N	1.99697800	1.27882600	0.09058100

C	-2.03938700	-1.10729500	-0.50021500
C	-2.85315200	-1.27679400	-1.61628000
C	-1.98569700	-2.06225600	0.50911200
C	-3.62578000	-2.42955900	-1.71516900
H	-2.87704200	-0.51842200	-2.38791500
C	-2.75025900	-3.21671700	0.39148800
H	-1.38498100	-1.87902100	1.39061500
C	-3.57005600	-3.40154600	-0.71850200
H	-4.26462000	-2.57106600	-2.57701000
H	-2.71928500	-3.96041700	1.17684500
H	-4.16994900	-4.29808000	-0.80478800
C	2.77597900	2.48501900	0.00116100
C	3.69848300	2.62491800	-1.02975000
C	2.53931800	3.49611800	0.92441000
C	4.42015000	3.80925200	-1.11895900
H	3.84586300	1.82208900	-1.74050700
C	3.26878800	4.67684500	0.82103500
H	1.80605500	3.35449600	1.70834300
C	4.20746100	4.83124000	-0.19555200
H	5.14278800	3.93626300	-1.91369900
H	3.10157400	5.47297200	1.53383800
H	4.77082000	5.75155000	-0.27247400
C	-3.92562400	0.63853800	1.21902900
C	-2.95591200	0.91749000	2.18773600
C	-4.80903900	-0.42393100	1.43211400
C	-2.86879700	0.14333800	3.34004600
H	-2.28596500	1.75652300	2.04507400
C	-4.72051000	-1.19802600	2.58352600
H	-5.54746000	-0.65838500	0.67486100
C	-3.74900500	-0.91789900	3.54020100
H	-3.68495500	-1.51455000	4.44130300
C	2.97443000	-2.61726300	-0.49317600
C	3.04105800	-3.99913900	-0.52551900
C	1.74961400	-1.90837000	-1.03026100
C	2.00468900	-4.78025100	-1.03780000
H	3.89963600	-4.50268600	-0.10231900
C	0.66819000	-2.82276200	-1.51697900
H	2.05087100	-1.26283800	-1.87326900
C	0.81686900	-4.16706100	-1.53197400
H	0.02027000	-4.78883100	-1.91924300
H	-0.23100200	-2.36308900	-1.90424900
H	2.09607700	-5.85643000	-1.03850400
H	-2.12686100	0.38059300	4.09251200
H	-5.40808400	-2.02102000	2.73158600

Transition state (TS-5 (7a)):

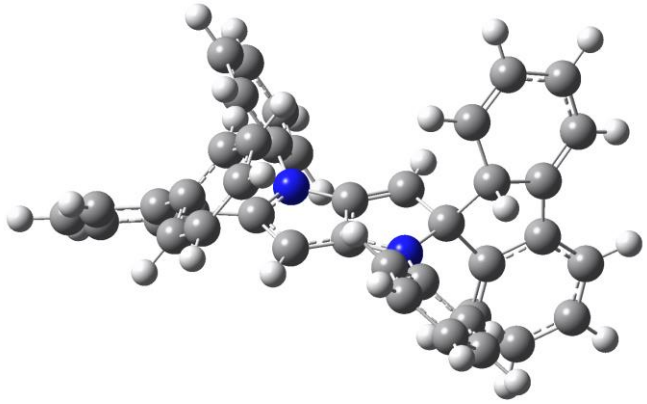


Zero-point correction=0.606598 (Hartree/Particle)
Thermal correction to Energy=0.639310
Thermal correction to Enthalpy=0.640254
Thermal correction to Gibbs Free Energy=0.540042
SCF Done:E(UM052X) = -1727.64595018

C	-2.24446200	-0.32162000	-0.12841400
C	-1.01756600	-1.07457000	0.16094300
C	0.00788100	-0.18384700	0.13976400
C	-0.49517500	1.11013700	-0.20004800
C	1.69667900	1.26028600	0.16825600
C	0.56363300	2.01985400	-0.15983700
H	-1.01597900	-2.13051500	0.38277500
H	0.57453000	3.07069900	-0.39432100
C	-3.30066900	-1.01703500	-0.94822700
C	-3.33031700	-1.10858500	-2.33449200
C	-4.21973900	-1.72690500	-0.15989400
C	-4.31279300	-1.89550500	-2.93060100
H	-2.59809900	-0.58449800	-2.93725400
C	-5.18772900	-2.52919900	-0.76096700
C	-5.23328400	-2.59791500	-2.14882400
H	-4.35561100	-1.97395200	-4.00895000
H	-5.90572000	-3.06899800	-0.15696500
H	-5.99024900	-3.20300300	-2.63007800
C	3.05700200	1.79848900	0.31396000
C	3.19872700	2.92916400	1.12780600
C	4.18402500	1.23461100	-0.31609300
C	4.44820600	3.48774700	1.35680400
H	2.32073800	3.34588000	1.60549600
C	5.43188200	1.81192500	-0.06842400
C	5.56978500	2.91895500	0.76065800
H	4.54516300	4.35506200	1.99603000
H	6.29961900	1.39998700	-0.56756300
H	6.54991200	3.34665800	0.92647200
N	1.36545500	-0.06058500	0.36854300
N	-1.82348600	1.02111600	-0.44724900
C	2.19489700	-1.13219800	0.81561300
C	3.01811300	-0.96548900	1.92513200

C	2.13406300	-2.34463700	0.13582300
C	3.80745100	-2.03104100	2.34330100
H	3.04039500	-0.01839500	2.44763200
C	2.91279300	-3.40824500	0.57675600
H	1.52100100	-2.43302900	-0.75214000
C	3.75335900	-3.25216500	1.67526100
H	4.45517800	-1.90966100	3.20158300
H	2.87685000	-4.35148500	0.04785000
H	4.36474000	-4.07934600	2.01108600
C	-2.69345200	2.15301300	-0.51160200
C	-2.47870300	3.21048800	0.37497500
C	-3.74706900	2.19554700	-1.42225200
C	-3.31417200	4.32004100	0.33717000
H	-1.66771300	3.15653200	1.09052000
C	-4.58713500	3.30494400	-1.43809500
H	-3.90404900	1.38196800	-2.11415200
C	-4.37189100	4.36821700	-0.56704600
H	-3.14487700	5.14017800	1.02221700
H	-5.40515100	3.34006900	-2.14518200
H	-5.02480400	5.23039000	-0.59180000
C	4.09442500	0.09018600	-1.25690200
C	3.14486200	0.07048700	-2.28322100
C	4.99441000	-0.97361400	-1.14210900
C	3.09181300	-0.99914700	-3.17066300
H	2.46710400	0.90791100	-2.40213200
C	4.94083400	-2.04137200	-2.03019800
H	5.71451700	-0.97486900	-0.33291700
C	3.98811200	-2.05807400	-3.04520300
H	3.95077900	-2.88585000	-3.74176100
C	-3.92104700	-1.51845100	1.25576300
C	-3.92096400	-2.45945200	2.26249000
C	-3.24782400	-0.23604300	1.42659300
C	-3.25668900	-2.18431000	3.46532800
H	-4.37826900	-3.42775500	2.10195900
C	-2.57946200	0.00631100	2.68357300
H	-3.81566400	0.61861200	1.04997100
C	-2.57594500	-0.96221000	3.65536100
H	-2.08128700	-0.77710800	4.59982000
H	5.63903800	-2.86197500	-1.92618100
H	2.36468500	-0.99646600	-3.97294500
H	-2.12480800	0.97277500	2.86080300
H	-3.24693900	-2.92616200	4.25178200

Product (5-membered ring, compound 9a):
conformer 1 (36.8 %)

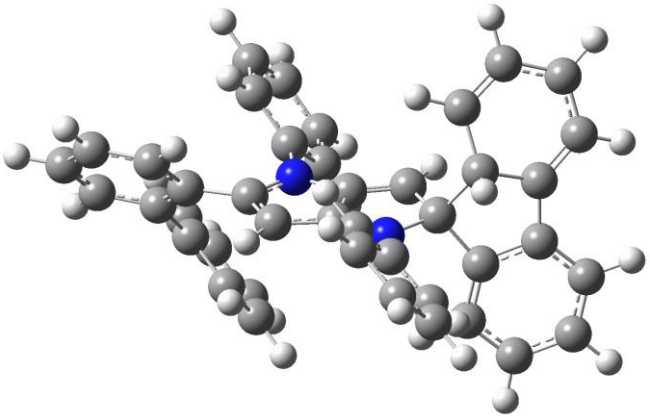


Zero-point correction=0.607524 (Hartree/Particle)
Thermal correction to Energy=0.640733
Thermal correction to Enthalpy=0.641677
Thermal correction to Gibbs Free Energy=0.538516
SCF Done:E(UM052X) = -1727.65375513

C	-2.24574200	-0.24232700	-0.08991100
C	-1.30515000	-1.40973000	0.10324400
C	-0.07125500	-0.99665700	-0.21596100
C	-0.10188000	0.40291200	-0.58024500
C	2.00135500	-0.31844800	-0.65231700
C	1.19892700	0.81268600	-0.85781500
H	-1.65733600	-2.37914600	0.42282700
H	1.56072400	1.77856800	-1.16226600
C	-3.35336700	-0.63996800	-1.06313100
C	-3.27995500	-0.76596600	-2.44081000
C	-4.50287600	-1.00162600	-0.34291700
C	-4.40353000	-1.23865300	-3.11741900
H	-2.37954900	-0.49198800	-2.97863600
C	-5.61719000	-1.49174700	-1.02831900
C	-5.55643500	-1.59975900	-2.41280700
H	-4.38327700	-1.33059700	-4.19520000
H	-6.51774700	-1.76502000	-0.49364300
H	-6.41769900	-1.96526500	-2.95663200
C	3.45206000	-0.39089900	-0.85737000
C	3.97883600	-1.47247700	-1.57640400
C	4.29396200	0.65791200	-0.43453900
C	5.32766900	-1.51507900	-1.89340100
H	3.32037900	-2.26390300	-1.91009700
C	5.64918300	0.59195300	-0.76372200
C	6.16361700	-0.47805100	-1.48629300
H	5.72300800	-2.34790500	-2.45902400
H	6.30411000	1.38424700	-0.42410500
H	7.21861400	-0.50590700	-1.72574500
N	1.25204600	-1.41275700	-0.28284900
N	-1.35388300	0.85647700	-0.52803500
C	1.69243700	-2.70555900	0.14316500
C	2.65714300	-2.82692400	1.13886700

C	1.10852200	-3.82773200	-0.43737800
C	3.05043900	-4.09661100	1.54512400
H	3.09507100	-1.94208700	1.58174500
C	1.49727300	-5.09325700	-0.00910000
H	0.37115100	-3.70675900	-1.22151600
C	2.47005800	-5.22833700	0.97706000
H	3.80402200	-4.20083100	2.31423800
H	1.04756100	-5.97046100	-0.45460900
H	2.77595200	-6.21329600	1.30327300
C	-1.71669300	2.23329100	-0.59851100
C	-0.88117100	3.17477800	0.00478600
C	-2.88473500	2.62594400	-1.25045600
C	-1.20882800	4.52279400	-0.07049100
H	0.00587200	2.85626900	0.53942700
C	-3.20842300	3.97790200	-1.29972800
H	-3.52153100	1.88992300	-1.72093100
C	-2.37233100	4.92736200	-0.71933500
H	-0.55853900	5.25348800	0.39241900
H	-4.11382000	4.28781500	-1.80431000
H	-2.62829400	5.97728100	-0.76961600
C	3.79912900	1.81033100	0.36454400
C	3.11380200	1.61407300	1.56763400
C	4.01985100	3.11430900	-0.08659400
C	2.64183800	2.69965500	2.29602400
H	2.96243100	0.60679800	1.93893300
C	3.54020700	4.20170100	0.63854000
H	4.54971900	3.27245300	-1.01830000
C	2.84768800	3.99693300	1.82843600
H	2.48510700	4.84283500	2.39838300
C	-4.26410800	-0.79431600	1.07489100
C	-4.87430700	-1.33172500	2.17817600
C	-3.05273300	0.09435600	1.20158800
C	-4.28694800	-1.17469200	3.44560100
H	-5.76908100	-1.93279100	2.06946700
C	-2.36285100	-0.00020500	2.52191100
H	-3.38499800	1.13665000	1.04494900
C	-3.00716200	-0.55789200	3.57971600
H	-2.53660300	-0.55329900	4.55480600
H	3.71159300	5.20667800	0.27526200
H	2.12774100	2.53645800	3.23473000
H	-1.39234800	0.46745700	2.63785000
H	-4.76735500	-1.59522400	4.31650600

conformer 2 (58.4 %)



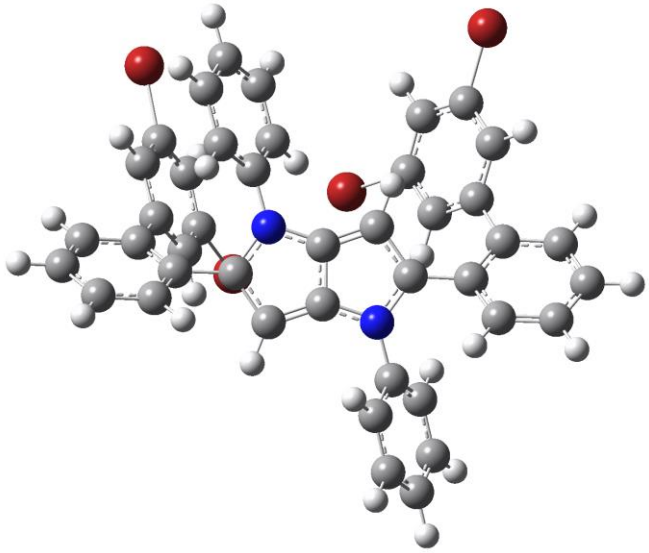
Zero-point correction=0.607367 (Hartree/Particle)
Thermal correction to Energy=0.640386
Thermal correction to Enthalpy=0.641330
Thermal correction to Gibbs Free Energy=0.539903
SCF Done:E(UM052X) = -1727.65557752

C	-2.28236000	-0.27517800	0.11756800
C	-1.01274900	-0.98555400	0.52088000
C	0.00317800	-0.12467900	0.36964100
C	-0.50266900	1.15883200	-0.06916200
C	1.70762200	1.28459300	0.18674900
C	0.57532800	2.03957900	-0.16352300
H	-1.01130400	-2.01762300	0.83845100
H	0.59686300	3.06413600	-0.49276600
C	-2.98321800	-1.07186200	-0.98064400
C	-2.63833600	-1.17629200	-2.31864700
C	-4.01445900	-1.83995300	-0.41767000
C	-3.37351600	-2.04759600	-3.12105000
H	-1.82821400	-0.58693100	-2.73308400
C	-4.73322900	-2.72449700	-1.22586500
C	-4.40800000	-2.81364900	-2.57410400
H	-3.14060000	-2.13566300	-4.17384900
H	-5.54000800	-3.31663300	-0.81340700
H	-4.96647700	-3.48469600	-3.21355000
C	3.07553900	1.81795000	0.24615400
C	3.24309400	3.01295000	0.95760500
C	4.18210400	1.18584800	-0.35476500
C	4.50417900	3.56800200	1.12024900
H	2.37939500	3.48168000	1.41240100
C	5.44096900	1.76490500	-0.17836300
C	5.60695700	2.93386600	0.55527800
H	4.62468300	4.48388200	1.68282100
H	6.29395100	1.30184500	-0.65762200
H	6.59532900	3.35949800	0.66898800
N	1.37722300	-0.00400700	0.51806500
N	-1.82039300	1.08502500	-0.24840200
C	2.21116000	-1.04448600	1.03219900
C	3.06068100	-0.79427400	2.10520200

C	2.12334000	-2.30657700	0.45399500
C	3.85124800	-1.83009400	2.59061400
H	3.10099500	0.19171800	2.54893100
C	2.90469300	-3.33797200	0.96203600
H	1.48579300	-2.46327100	-0.40684400
C	3.77193200	-3.10047400	2.02466400
H	4.51851300	-1.64621600	3.42223700
H	2.84799900	-4.32106800	0.51381200
H	4.38365600	-3.90363100	2.41369500
C	-2.67724600	2.20150100	-0.48173000
C	-2.45209400	3.37701100	0.23466500
C	-3.72330200	2.11150900	-1.39848900
C	-3.27021400	4.47857600	0.01452400
H	-1.65538800	3.41765300	0.96718600
C	-4.54410600	3.21690300	-1.59644000
H	-3.88590800	1.19846100	-1.95323200
C	-4.31800900	4.40007000	-0.89883600
H	-3.09775200	5.39189100	0.56822000
H	-5.35748400	3.15265700	-2.30683100
H	-4.95833700	5.25635300	-1.06332500
C	4.05506900	-0.02682800	-1.19925500
C	3.08352600	-0.10584500	-2.20193400
C	4.93659200	-1.09674400	-1.01807300
C	2.98690200	-1.24176500	-2.99838600
H	2.42487300	0.73696400	-2.37802400
C	4.83833700	-2.23126600	-1.81460500
H	5.67566500	-1.04876200	-0.22764000
C	3.86219400	-2.30783500	-2.80449300
H	3.79138600	-3.18855200	-3.42985100
C	-4.10752300	-1.55071400	1.00275300
C	-4.64143200	-2.27602300	2.03578300
C	-3.35614900	-0.26745500	1.24979800
C	-4.37153200	-1.90146700	3.36340200
H	-5.21326400	-3.17379200	1.83456900
C	-2.90685500	-0.08615400	2.66151700
H	-4.02499600	0.56853600	0.97561800
C	-3.45806900	-0.84250700	3.64603600
H	-3.18934100	-0.65426000	4.67779000
H	5.52071700	-3.05690700	-1.65909500
H	2.24378400	-1.28668900	-3.78452400
H	-2.21570100	0.71606600	2.89094800
H	-4.79410300	-2.46988200	4.17866400

Cartesian coordinates of molecules with bromine atoms in structures:

Substrate (compound 7e):
conformer 1 (98.9 %)

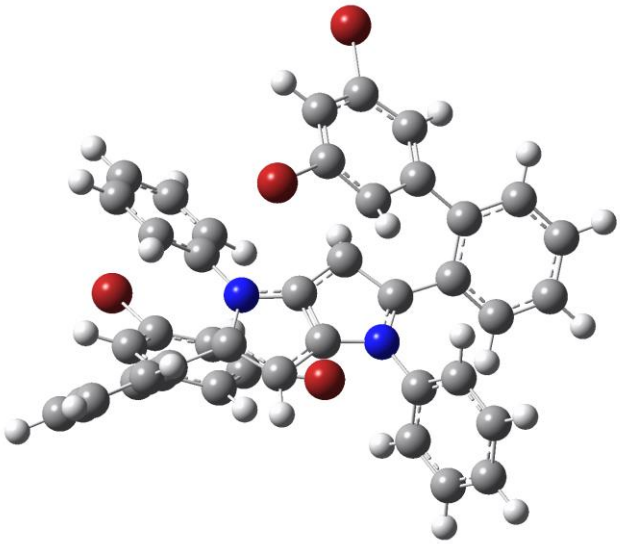


Zero-point correction=0.567662 (Hartree/Particle)
Thermal correction to Energy=0.606899
Thermal correction to Enthalpy=0.607843
Thermal correction to Gibbs Free Energy=0.490280
SCF Done:E(UM052X) = -12012.0561899

C	0.96826700	-2.65560500	-1.19043700
C	-0.16094900	-3.38729700	-0.72097300
C	-1.20699900	-2.48901000	-0.73160200
C	-0.73765200	-1.23965200	-1.21885900
C	-2.91841300	-1.06269100	-0.77537500
C	-1.78355300	-0.35291100	-1.28089900
H	-0.13341400	-4.41663500	-0.40394900
H	-1.79846200	0.65921800	-1.64671500
C	2.30313400	-3.21857300	-1.42038800
C	2.35886300	-4.39387400	-2.18211500
C	3.49362300	-2.62591100	-0.95684800
C	3.57965000	-4.95542100	-2.52951400
H	1.43647000	-4.83995700	-2.53283700
C	4.71052400	-3.20007700	-1.32498900
C	4.75895000	-4.34723100	-2.10991000
H	3.60927000	-5.85538800	-3.12874700
H	5.62630300	-2.75683000	-0.95470000
H	5.71634800	-4.77615100	-2.37473700
C	-4.28940900	-0.57272800	-0.66925100
C	-5.34795100	-1.43901700	-0.99219500
C	-4.57237700	0.77227400	-0.33147600
C	-6.65889000	-0.99164300	-0.98617300
H	-5.13368100	-2.45802900	-1.28331000
C	-5.90036900	1.19929100	-0.32832700
C	-6.93702100	0.33075700	-0.64858600

H	-7.45922900	-1.66921500	-1.25059300
H	-6.11646900	2.22211500	-0.04695200
H	-7.95904500	0.68553400	-0.63329500
N	-2.55203100	-2.35332300	-0.45066500
N	0.60902800	-1.36563400	-1.48791600
C	-3.30527100	-3.35665800	0.24162100
C	-3.39617900	-4.62502400	-0.32255600
C	-3.89283000	-3.06438000	1.46826000
C	-4.09223000	-5.61943600	0.35795100
H	-2.93923300	-4.82074800	-1.28494000
C	-4.59921800	-4.06151400	2.13054200
H	-3.79773500	-2.07300900	1.89237700
C	-4.69660200	-5.33740500	1.57964600
H	-4.16908000	-6.60925500	-0.07181000
H	-5.06358700	-3.84437000	3.08308300
H	-5.24194700	-6.11103800	2.10346600
C	1.41564200	-0.28441200	-1.96625100
C	2.17505900	-0.42977800	-3.12098600
C	1.40023900	0.90588800	-1.24370700
C	2.95582600	0.64146900	-3.54563900
H	2.15646100	-1.36090000	-3.67217000
C	2.17139300	1.97229400	-1.68974300
H	0.83885400	0.97519000	-0.31964500
C	2.95542600	1.83869500	-2.83335400
H	3.55656000	0.54223100	-4.44016800
H	2.18761800	2.89459100	-1.12383700
H	3.56912100	2.66553200	-3.16543400
C	-3.50796500	1.74983300	0.00918300
C	-3.46471200	2.97205500	-0.66620500
C	-2.52029700	1.44493100	0.94886100
C	-2.42410500	3.85834500	-0.41374000
H	-4.21294200	3.21681100	-1.40812000
C	-1.47832600	2.33706900	1.15232800
H	-2.54461800	0.51456100	1.50040000
C	-1.40898000	3.55325600	0.48503500
H	-0.59176500	4.23918200	0.65568700
C	3.50157300	-1.46720900	-0.02940000
C	4.28388000	-0.34814500	-0.31923800
C	2.77468400	-1.51928600	1.16271000
C	4.29475000	0.71941800	0.56626100
H	4.83559900	-0.28842400	-1.24726600
C	2.85006600	-0.45237200	2.04762400
H	2.19809600	-2.39706000	1.42256400
C	3.58989500	0.68853000	1.76334100
H	3.62612200	1.51793700	2.45481700
Br	-0.07460600	1.82116300	2.30869500
Br	-2.35704200	5.49148300	-1.35343400
Br	1.95828900	-0.57445500	3.71029900
Br	5.27217300	2.26911600	0.11327200

Transition state (TS-6 (7e)):

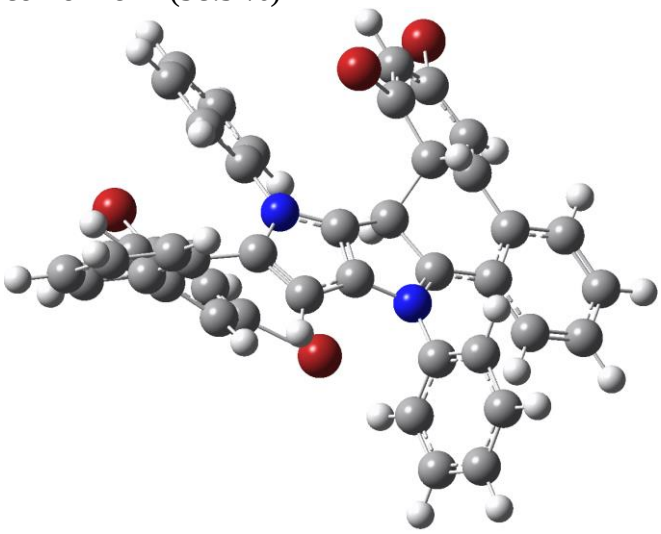


Zero-point correction=0.567861 (Hartree/Particle)
Thermal correction to Energy=0.606198
Thermal correction to Enthalpy=0.607142
Thermal correction to Gibbs Free Energy=0.491920
SCF Done:E(UM052X) = -12012.0134278

C	2.21594000	-1.16627500	-0.32806500
C	1.34999400	-0.00747200	-0.04999700
C	0.25010900	-0.59344400	0.68313700
C	0.53479200	-1.91589800	0.94485400
C	-1.46124200	-1.47154600	1.79320800
C	-0.51695100	-2.48704500	1.68460700
H	1.20571200	0.73145400	-0.82632900
H	-0.65723800	-3.50620000	2.00379100
C	3.52163600	-1.04576400	-0.96756100
C	4.08983800	-2.06480700	-1.73663800
C	4.20220900	0.18687500	-0.80526500
C	5.33202800	-1.87648100	-2.32947400
H	3.55177900	-2.99004400	-1.89030300
C	5.45483600	0.34701900	-1.39507600
C	6.01635600	-0.67672300	-2.15073900
H	5.76463400	-2.66544400	-2.92945500
H	5.99962300	1.26956200	-1.24131600
H	6.99067100	-0.53751700	-2.59995600
C	-2.88004600	-1.63610700	2.18386300
C	-3.19413000	-1.98051700	3.49790600
C	-3.91026500	-1.50710200	1.22583100
C	-4.51649800	-2.17426800	3.88389800
H	-2.39201900	-2.08094600	4.21879900
C	-5.23153400	-1.69062700	1.63408000
C	-5.53604300	-2.02113900	2.95077100
H	-4.74748400	-2.43863800	4.90734900
H	-6.02425500	-1.60454200	0.90112000
H	-6.56739400	-2.16999000	3.24212500

N	-0.97535200	-0.31073500	1.20644200
N	1.74830500	-2.23567500	0.31905300
C	-1.65115100	0.93655000	1.06990600
C	-2.34601900	1.47825400	2.14675500
C	-1.60834900	1.58771800	-0.15954600
C	-3.02716700	2.67778700	1.97337500
H	-2.35013800	0.96625600	3.09947800
C	-2.28579800	2.79152700	-0.31950400
H	-1.10766800	1.11920800	-0.99685400
C	-3.00061500	3.33413400	0.74463600
H	-3.57598900	3.10262200	2.80343200
H	-2.28481700	3.28284300	-1.28356000
H	-3.53734600	4.26482700	0.61716800
C	2.31219300	-3.55798300	0.35325400
C	3.44644500	-3.81450900	1.11149600
C	1.66893000	-4.54780600	-0.38255600
C	3.95821000	-5.10817900	1.12168600
H	3.91545400	-3.01858400	1.67551200
C	2.19047000	-5.83707800	-0.35937400
H	0.79953800	-4.29104900	-0.97673400
C	3.33213100	-6.11439600	0.38978500
H	4.84235100	-5.32981900	1.70403200
H	1.70865400	-6.62071200	-0.92856400
H	3.73463400	-7.11848000	0.40400600
C	-3.60376500	-1.16565500	-0.18940900
C	-2.52792000	-1.77844600	-0.83844400
C	-4.31119800	-0.16048400	-0.85215400
C	-2.11346500	-1.30895600	-2.07029100
H	-1.97949800	-2.57406600	-0.35984100
C	-3.91006000	0.23425500	-2.12291500
H	-5.12377800	0.35745100	-0.36080000
C	-2.79769400	-0.31262500	-2.75313100
H	-2.46613900	0.04811100	-3.71588900
C	3.55283500	1.27023200	-0.04874100
C	3.61427100	2.58253600	-0.45534800
C	2.61571000	0.87636600	1.00426700
C	2.85282700	3.56508500	0.19975100
H	4.22080900	2.86735400	-1.30432200
C	1.97239100	1.95412400	1.72108900
H	2.91983700	0.05040300	1.64341900
C	2.03603100	3.25630500	1.29795400
H	1.50423100	4.03739600	1.82261400
Br	-4.81588700	1.65843400	-2.97052100
Br	-0.45992600	-1.96057800	-2.75164400
Br	1.01371200	1.49047300	3.26382500
Br	2.93934500	5.33535100	-0.40219300

Product (6-membered ring, compound 8e):
conformer 1 (98.9 %)

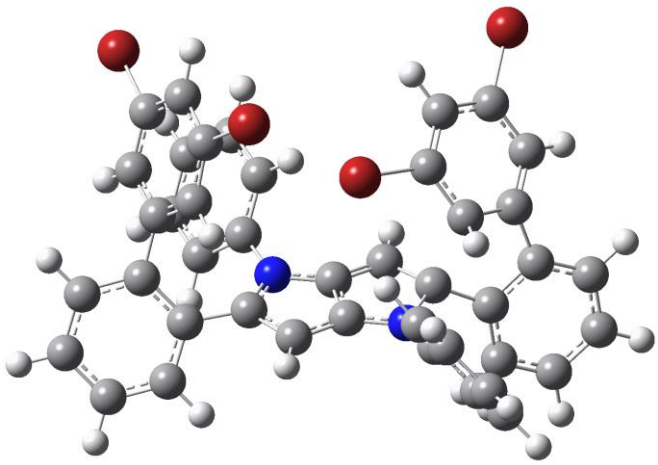


Zero-point correction=0.568151 (Hartree/Particle)
Thermal correction to Energy=0.606966
Thermal correction to Enthalpy=0.607910
Thermal correction to Gibbs Free Energy=0.490690
SCF Done:E(UM052X) = -12012.0229071

C	2.50941900	-0.95874100	0.12516700
C	1.40050800	0.03755900	0.44455600
C	0.34733200	-0.86915400	0.99642600
C	0.79938500	-2.16035300	0.94699900
C	-1.35405100	-2.25050400	1.41094800
C	-0.24282400	-3.05891000	1.23880000
H	1.08307900	0.45450000	-0.51946200
H	-0.24348200	-4.13604400	1.22867000
C	3.79003700	-0.50878200	-0.37160100
C	4.75124500	-1.36240000	-0.94820000
C	4.03103700	0.89412600	-0.32260200
C	5.92365900	-0.84572000	-1.46649600
H	4.57085700	-2.42326100	-1.01809700
C	5.23587600	1.38359900	-0.84394400
C	6.16660400	0.52964600	-1.41018200
H	6.65065900	-1.50952300	-1.91366100
H	5.45419500	2.43996800	-0.76702400
H	7.09265300	0.93092400	-1.80033700
C	-2.76292900	-2.70419600	1.43300800
C	-3.22435900	-3.48071400	2.49510300
C	-3.62121300	-2.41542100	0.35017700
C	-4.53242600	-3.95456700	2.51102900
H	-2.55216200	-3.69760600	3.31626600
C	-4.93418900	-2.88435500	0.38967000
C	-5.38972600	-3.64810000	1.45984800
H	-4.87934500	-4.55449400	3.34188600
H	-5.59304800	-2.67274500	-0.44359800
H	-6.40874200	-4.01179900	1.46458000

N	-0.98625700	-0.91244700	1.27669000
N	2.11261700	-2.17813200	0.42988200
C	-1.86977100	0.20599300	1.35723000
C	-2.85042600	0.24712400	2.34371000
C	-1.72673100	1.24825600	0.44784500
C	-3.70612100	1.34080700	2.40057100
H	-2.93272800	-0.55817900	3.06051000
C	-2.58059100	2.34322500	0.51950400
H	-0.98810500	1.18769800	-0.33942900
C	-3.57315700	2.39005400	1.49360900
H	-4.47102300	1.37786400	3.16498900
H	-2.48598200	3.14258900	-0.20392800
H	-4.24257600	3.23844800	1.54505200
C	2.79296400	-3.42945500	0.21325300
C	3.67075900	-3.91442900	1.17272000
C	2.50161000	-4.12243100	-0.95668600
C	4.30069300	-5.13221700	0.93301000
H	3.85967900	-3.34881700	2.07574300
C	3.13966600	-5.33785900	-1.18002300
H	1.80886200	-3.69568300	-1.67233400
C	4.03790900	-5.83786800	-0.23898000
H	4.99380800	-5.52889100	1.66248700
H	2.93509500	-5.89143500	-2.08645700
H	4.53185300	-6.78347300	-0.41822200
C	-3.14999400	-1.60561500	-0.80545700
C	-1.90211600	-1.86095600	-1.38279900
C	-3.90010200	-0.52023900	-1.26080000
C	-1.39563800	-0.98445700	-2.32385600
H	-1.31131100	-2.70485400	-1.06180900
C	-3.37903300	0.30814900	-2.24732700
H	-4.84946200	-0.27796800	-0.80250100
C	-2.11501700	0.10794700	-2.79005000
H	-1.70567500	0.78877900	-3.52216600
C	3.05287000	1.79298300	0.27638900
C	2.89800800	3.09476600	-0.13789500
C	2.09346000	1.17053500	1.26444700
C	1.90292500	3.91290400	0.41165400
H	3.51940700	3.49726800	-0.92625300
C	1.17252700	2.17342400	1.88384600
H	2.64770400	0.67970000	2.07480900
C	1.06673800	3.45544200	1.46399000
H	0.38163100	4.13926700	1.94561600
Br	-4.35888700	1.83673900	-2.76564700
Br	0.40489600	-1.23882100	-2.90124600
Br	0.24013700	1.59758100	3.40770300
Br	1.68530400	5.65642300	-0.22969500

Transition state (TS-5 (7e)):

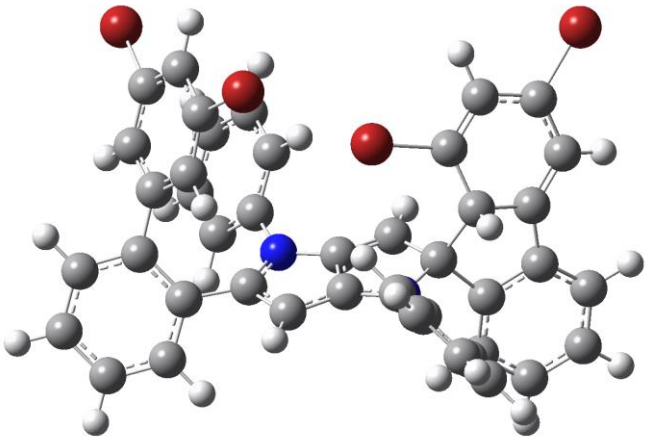


Zero-point correction=0.566268 (Hartree/Particle)
Thermal correction to Energy=0.604791
Thermal correction to Enthalpy=0.605735
Thermal correction to Gibbs Free Energy=0.490912
SCF Done:E(UM052X) = -12012.0153804

C	2.77804200	-0.90559900	-0.86549500
C	1.61856700	-0.45344900	-1.63804500
C	0.57070600	-1.22718800	-1.25146400
C	1.02971600	-2.24158700	-0.35593600
C	-1.15221700	-2.51086000	-0.68799800
C	-0.05239300	-3.05076800	-0.00726400
H	1.64693600	0.38866400	-2.31233100
H	-0.08514400	-3.90983700	0.64107100
C	4.16379800	-0.89738400	-1.44700300
C	4.65945500	-1.87072900	-2.30848400
C	4.92879900	0.23537300	-1.13743600
C	5.94182900	-1.72030100	-2.82736600
H	4.05035100	-2.72535000	-2.57796400
C	6.21027800	0.38767000	-1.66588700
C	6.71394900	-0.60229800	-2.49980100
H	6.34051400	-2.46959300	-3.49829700
H	6.80719500	1.25526000	-1.41546000
H	7.71159800	-0.50388300	-2.90654800
C	-2.49604600	-3.11353200	-0.76607200
C	-2.55684300	-4.42622000	-1.24783700
C	-3.68150300	-2.43042800	-0.44647000
C	-3.78098300	-5.04998400	-1.45285700
H	-1.63559800	-4.94046600	-1.49101900
C	-4.90307300	-3.06776400	-0.66918000
C	-4.95766600	-4.36211900	-1.17465400
H	-3.81414000	-6.06186700	-1.83372900
H	-5.81586400	-2.54682500	-0.40870300
H	-5.91695700	-4.83697800	-1.33274100
N	-0.78645500	-1.40405100	-1.42376700
N	2.35539200	-2.07986600	-0.15158300
C	-1.61208300	-0.48479000	-2.14252600

C	-1.58208300	0.85039000	-1.74551100
C	-2.41099400	-0.91567500	-3.19450500
C	-2.37108000	1.77360600	-2.42002400
H	-0.98843800	1.12864400	-0.88231000
C	-3.21057800	0.01690300	-3.85048900
H	-2.40901900	-1.95776000	-3.48683700
C	-3.19108100	1.35547400	-3.46643300
H	-2.37746000	2.80908000	-2.10641200
H	-3.84291300	-0.30348600	-4.66796000
H	-3.81937200	2.07328000	-3.97694800
C	3.07716400	-2.71774000	0.91009900
C	4.25305000	-3.42151800	0.66101900
C	2.55972000	-2.62445600	2.20390900
C	4.91685000	-4.02843100	1.72200200
H	4.63697900	-3.50453800	-0.34428300
C	3.22673200	-3.24596500	3.25351100
H	1.66307500	-2.04427100	2.37943800
C	4.40586100	-3.94610300	3.01419700
H	5.82978400	-4.57727300	1.53338500
H	2.82825000	-3.17461900	4.25674500
H	4.92534700	-4.42680500	3.83248500
C	-3.68018600	-1.08549900	0.18194500
C	-2.99439800	-0.87344900	1.38020300
C	-4.42090700	-0.04975700	-0.38887200
C	-3.07734300	0.36877800	1.99401300
H	-2.45000500	-1.67879400	1.85522200
C	-4.43456000	1.19340500	0.22574600
H	-4.94064300	-0.19896100	-1.32540800
C	-3.77577600	1.42672700	1.42680400
H	-3.81861800	2.39184900	1.91025600
C	4.14429700	1.18171100	-0.35099800
C	4.14193100	2.54916100	-0.51948700
C	3.09707400	0.49438900	0.39131400
C	3.08615300	3.29916300	0.00657800
H	4.90734300	3.03621500	-1.10877700
C	2.00429200	1.32612800	0.83004500
H	3.43882700	-0.23876600	1.12446800
C	1.99354500	2.68293500	0.64570900
H	1.16906500	3.28244900	1.00518000
Br	-5.34830600	2.61662400	-0.61520800
Br	-2.25512500	0.60966000	3.68112900
Br	0.52997100	0.50851600	1.67405400
Br	3.07049500	5.15699200	-0.21851900

Product (5-membered ring, compound 9e):
conformer 1 (97.1 %)

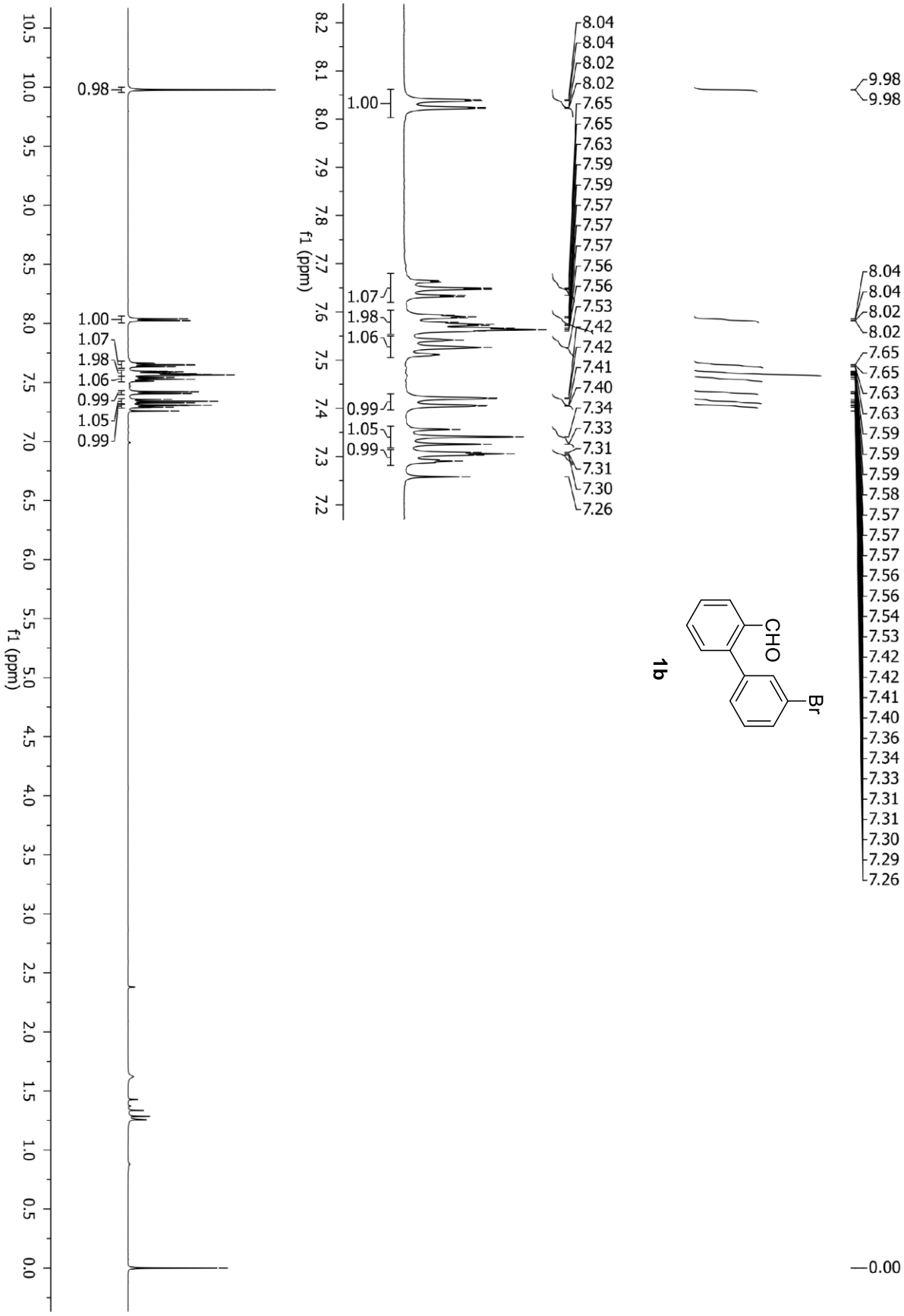


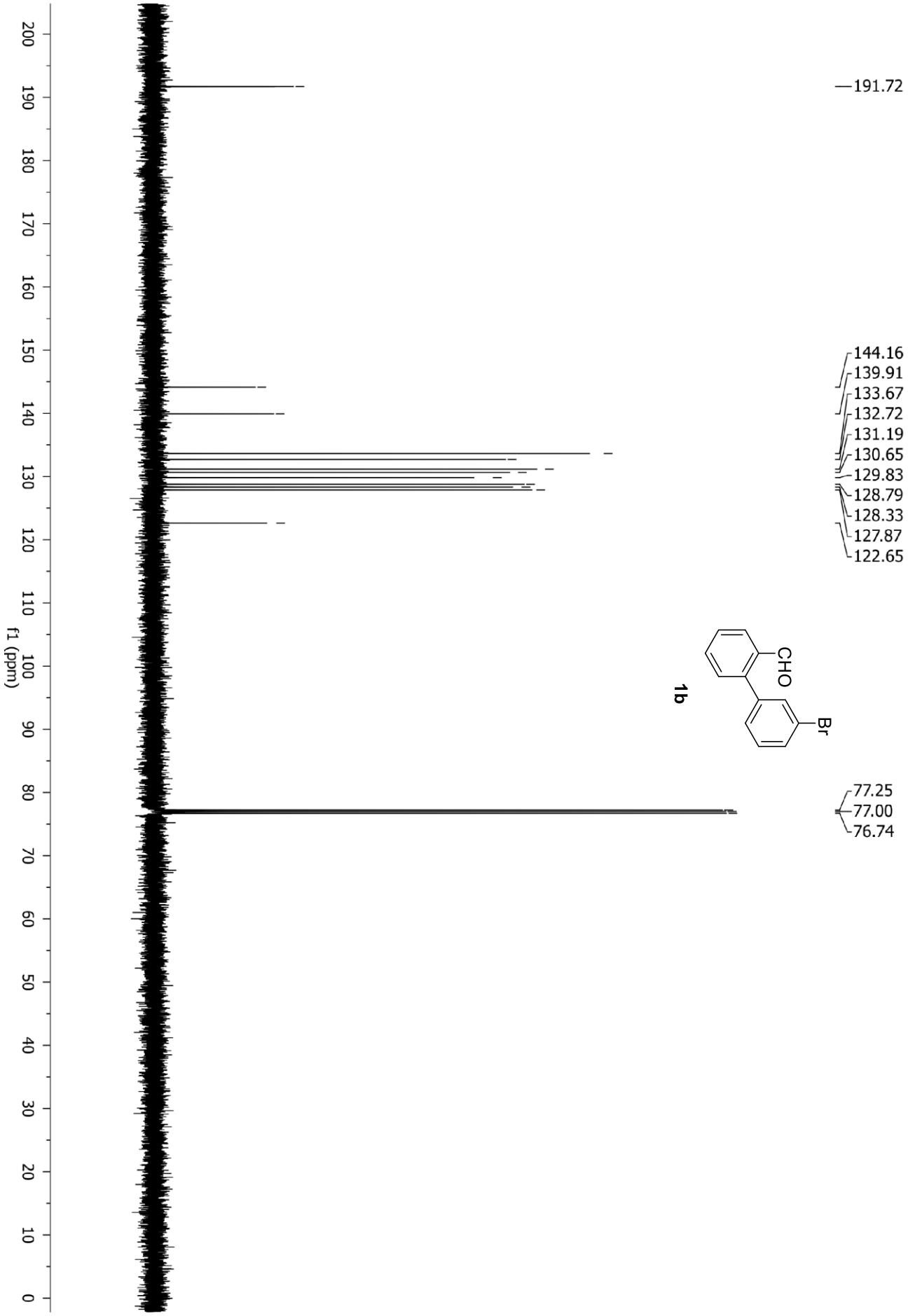
Zero-point correction=0.567226 (Hartree/Particle)
Thermal correction to Energy=0.605923
Thermal correction to Enthalpy=0.606867
Thermal correction to Gibbs Free Energy=0.491892
SCF Done:E(UM052X) = -12012.0294531

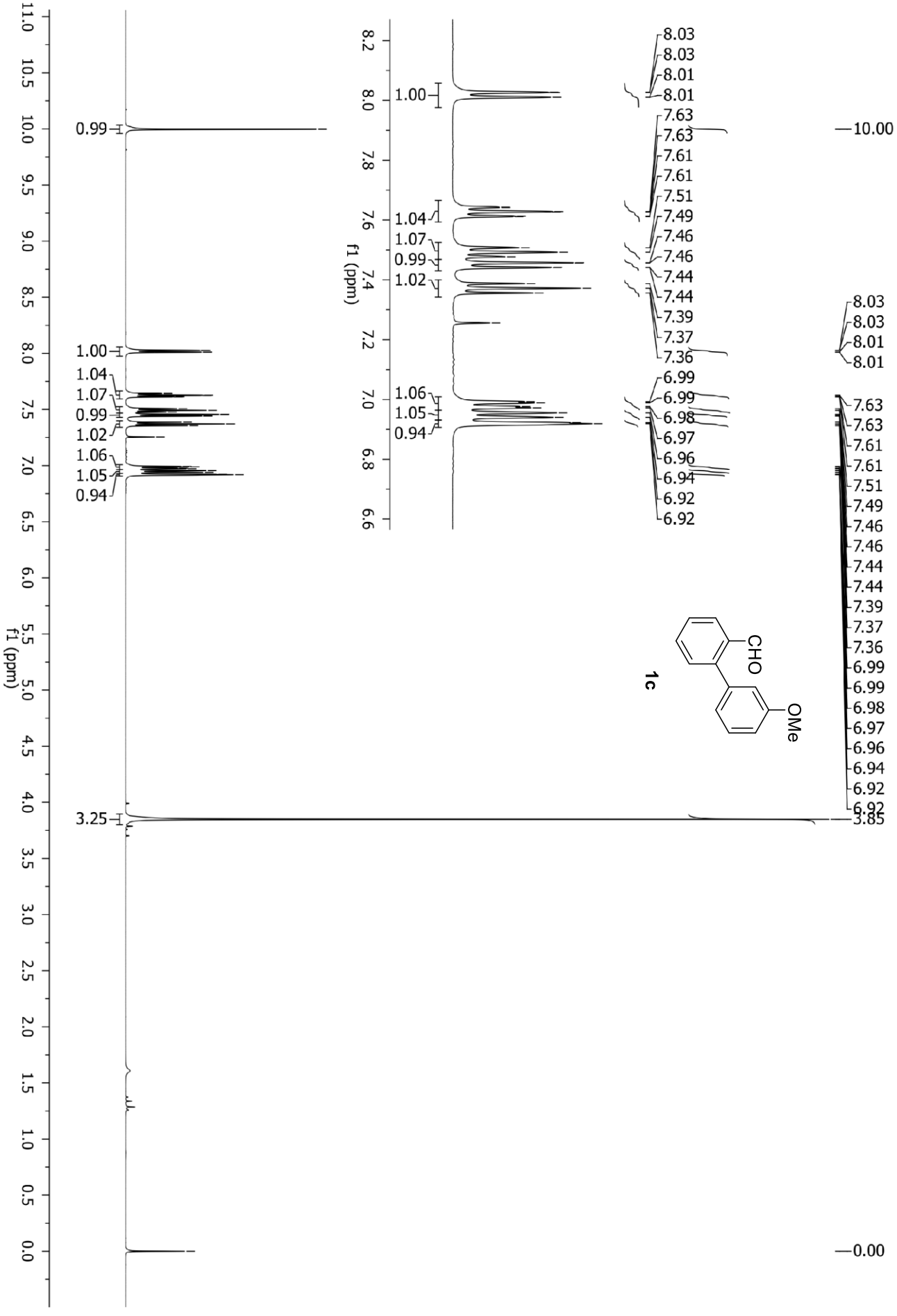
C	2.52648800	-1.06767400	-0.66631400
C	1.32310100	-0.61336800	-1.45812000
C	0.26358500	-1.29664600	-1.00734900
C	0.67315800	-2.22047000	0.02780200
C	-1.51449300	-2.42962700	-0.32025400
C	-0.45090400	-2.94059400	0.43765900
H	1.38924900	0.13861100	-2.23053900
H	-0.53681400	-3.70806800	1.18763000
C	3.62726400	-1.58910400	-1.58563100
C	3.63598700	-2.77088900	-2.31017000
C	4.65156100	-0.64206000	-1.70707600
C	4.72000000	-3.01957800	-3.14910200
H	2.82681000	-3.48643500	-2.21926300
C	5.72896800	-0.89089200	-2.56147000
C	5.75476900	-2.08522200	-3.26982100
H	4.76136200	-3.94023200	-3.71558700
H	6.53483400	-0.17495600	-2.65856400
H	6.58798400	-2.29771100	-3.92656600
C	-2.89251500	-2.95257900	-0.30167200
C	-3.03856300	-4.31586100	-0.58160400
C	-4.02558000	-2.15489300	-0.06555100
C	-4.30248500	-4.88444100	-0.67294100
H	-2.15566700	-4.91737700	-0.75859600
C	-5.28664200	-2.74298500	-0.16642900
C	-5.42845200	-4.09151000	-0.47574600
H	-4.40559900	-5.93688100	-0.90004600
H	-6.16097600	-2.13703600	0.03550400
H	-6.41742400	-4.52531600	-0.54255800
N	-1.10145000	-1.44361200	-1.18275000
N	1.97565500	-2.09398700	0.25082200

C	-1.88023500	-0.54797800	-1.98198800
C	-1.73810200	0.81621800	-1.73454200
C	-2.73914100	-1.03012300	-2.96161400
C	-2.48356200	1.71607000	-2.48555500
H	-1.08706300	1.14674200	-0.93256800
C	-3.49250100	-0.11657800	-3.69415900
H	-2.81892500	-2.09436100	-3.14097900
C	-3.36705700	1.25021000	-3.45757800
H	-2.40166400	2.77707600	-2.29028300
H	-4.17117100	-0.47489400	-4.45687500
H	-3.96100900	1.95365200	-4.02576700
C	2.66993300	-2.64387000	1.37298600
C	3.83050000	-3.39328400	1.19565700
C	2.15596100	-2.39415600	2.64562600
C	4.47649200	-3.90463000	2.31664500
H	4.21307900	-3.58190600	0.20250400
C	2.80492400	-2.92361300	3.75485600
H	1.28398800	-1.76147600	2.75327000
C	3.96424200	-3.67725400	3.59126400
H	5.37771800	-4.48975300	2.19067200
H	2.41292300	-2.73416500	4.74523400
H	4.47101800	-4.08298400	4.45668200
C	-3.91556100	-0.73661200	0.35343500
C	-3.09393400	-0.38989600	1.42852800
C	-4.66216200	0.24600900	-0.29968100
C	-3.03314800	0.93611100	1.83249900
H	-2.54423100	-1.14631200	1.97270000
C	-4.54329900	1.56657400	0.10676300
H	-5.28429300	-0.00752500	-1.14699300
C	-3.73653500	1.93719100	1.17623100
H	-3.66854000	2.96761700	1.49360800
C	4.33412800	0.51447100	-0.89026400
C	4.78490100	1.80172400	-0.98346600
C	3.24421200	0.10634400	0.07673300
C	4.11411200	2.81193600	-0.27509900
H	5.59589100	2.06649900	-1.64904900
C	2.44537600	1.27881000	0.54006500
H	3.71736300	-0.36673700	0.95480600
C	2.90678500	2.54827800	0.43009100
H	2.35859200	3.37254900	0.86564200
Br	-5.46621600	2.91090100	-0.84342700
Br	-1.99431500	1.38390200	3.34728500
Br	0.83771400	0.95280700	1.48602500
Br	4.73406500	4.57591100	-0.36366600

6. ^{1}H and ^{13}C NMR spectra of synthesized compounds.




191.72
144.16
139.91
133.67
132.72
131.19
130.65
129.83
128.79
128.33
127.87
122.65
CHO
Br
1b
77.25
77.00
76.74
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


f1 (ppm)
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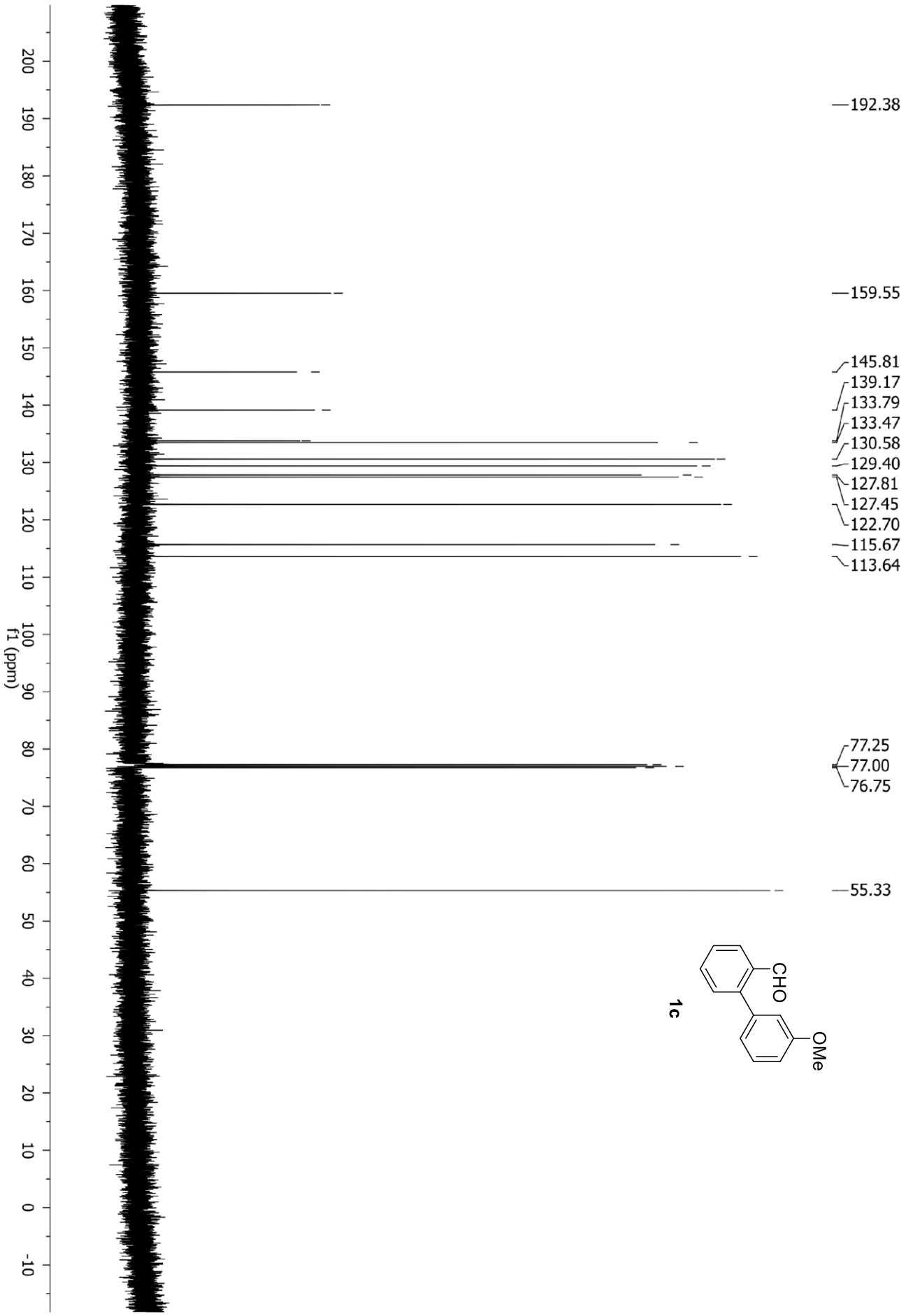
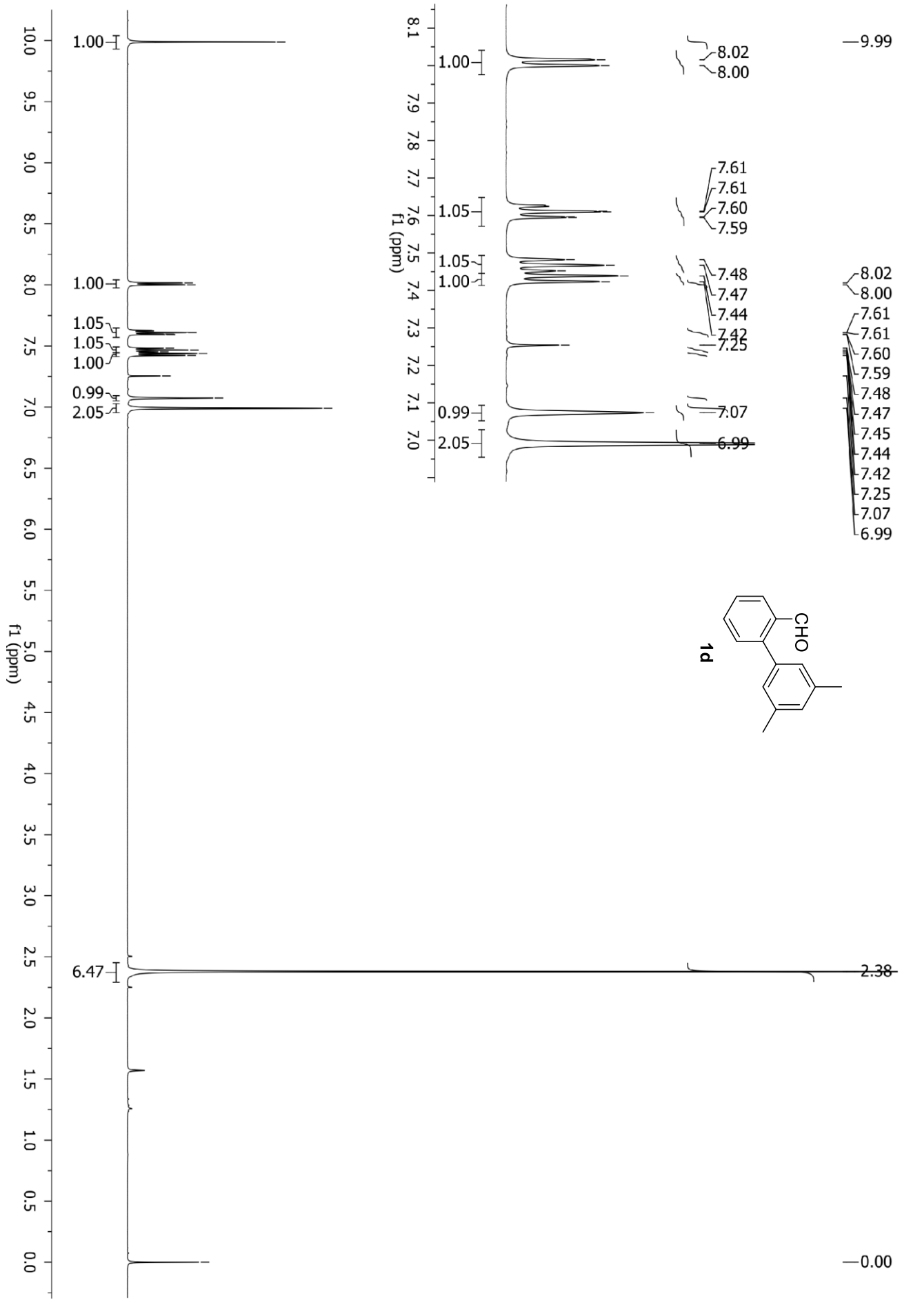
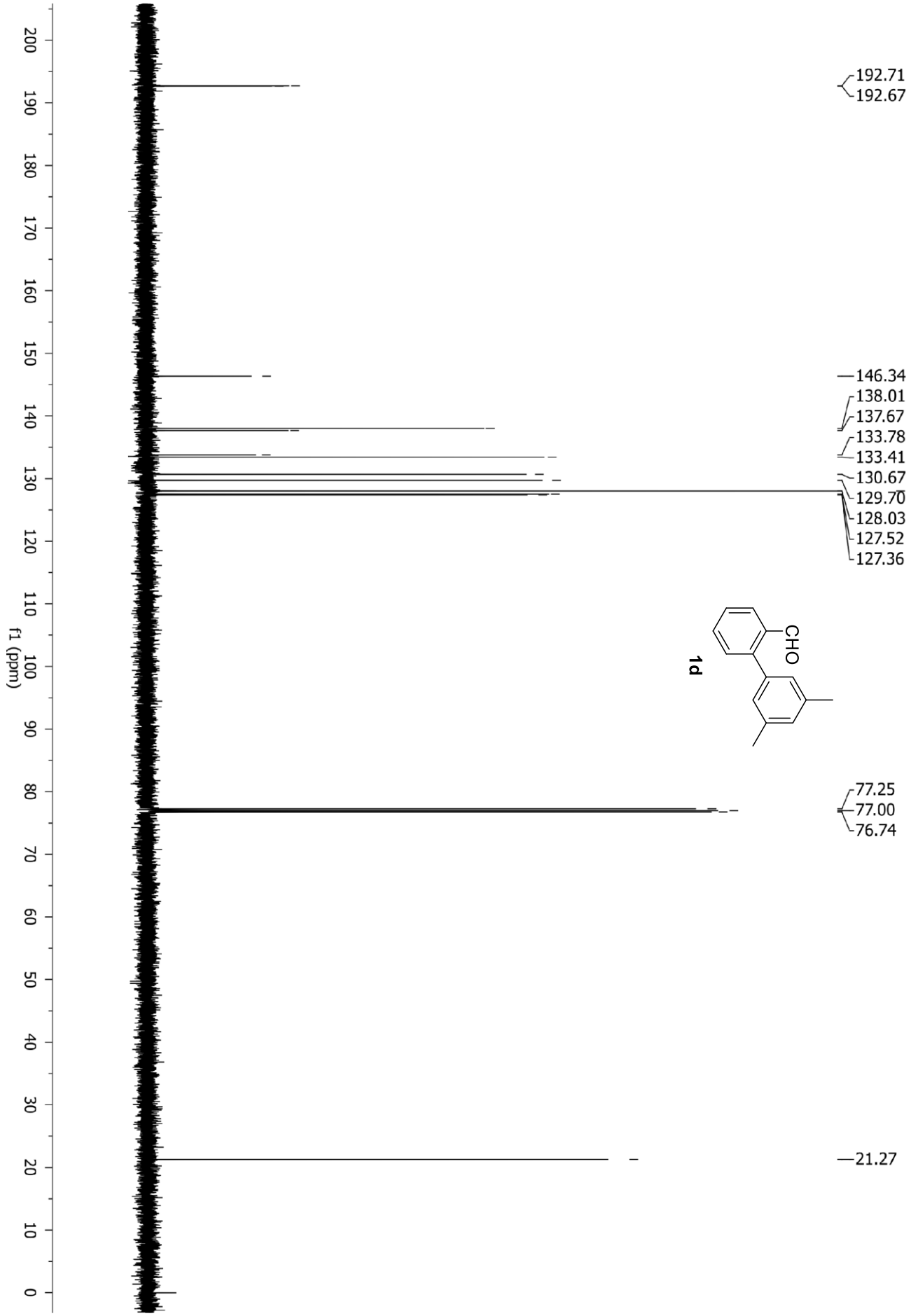
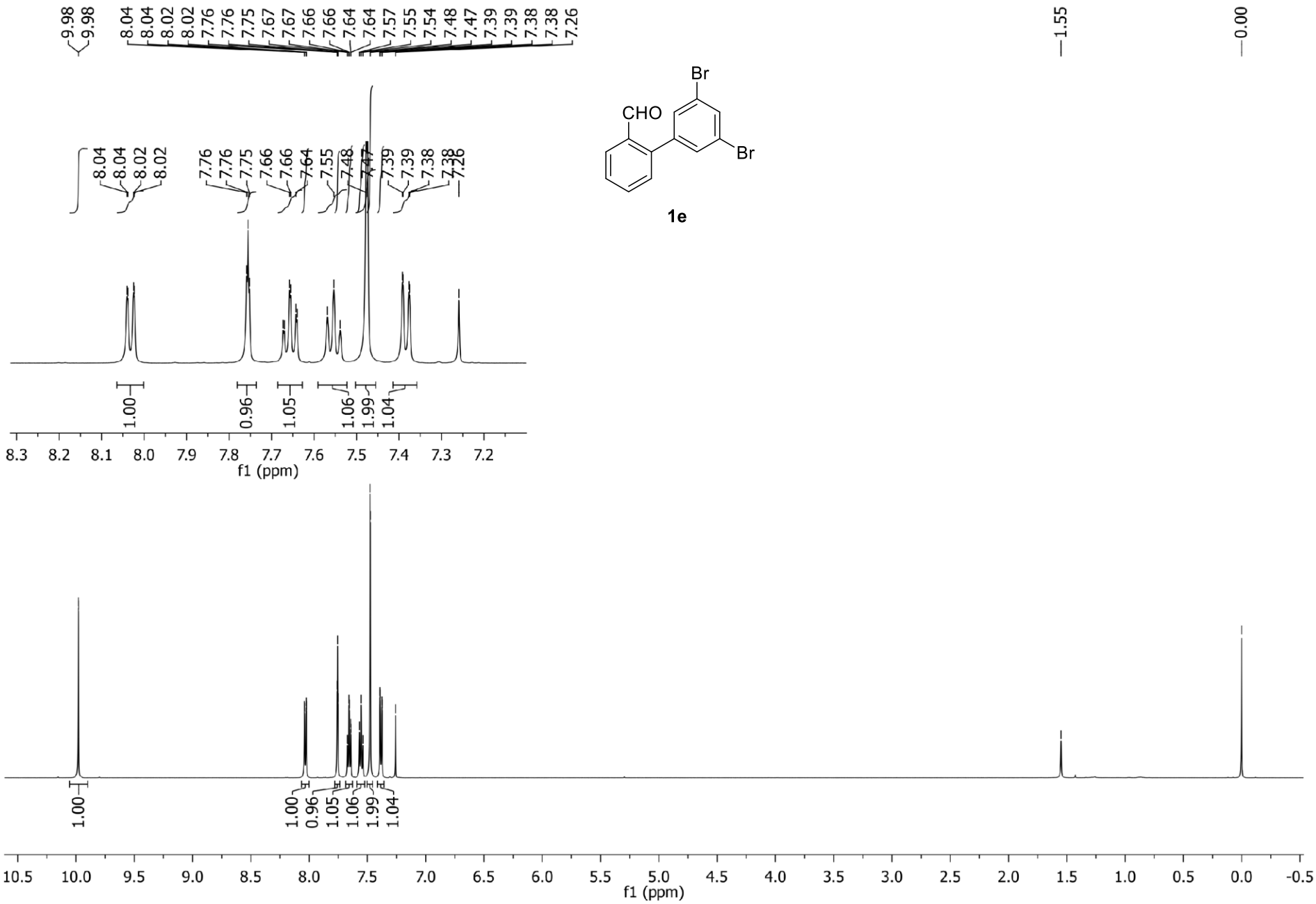
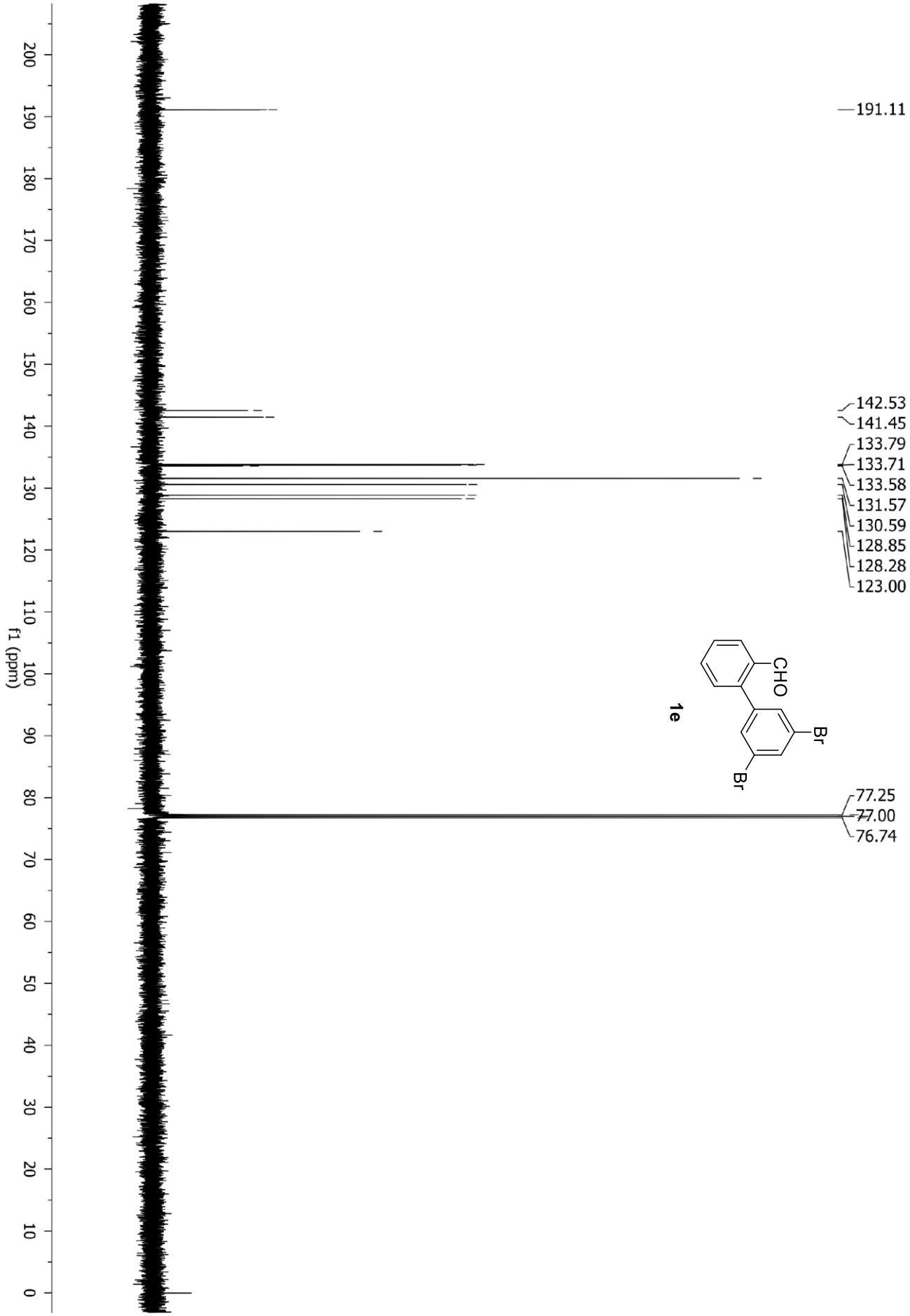
1.00
1.04
1.07
0.99
1.02
1.06
1.05
0.94
3.25
1.00
1.04
1.07
0.99
1.02
1.06
1.05
0.94
8.03
8.03
8.01
8.01
7.63
7.63
7.61
7.61
7.51
7.49
7.46
7.46
7.44
7.44
7.39
7.37
7.36
6.99
6.99
6.98
6.97
6.96
6.94
6.92
6.92
10.00
8.03
8.03
8.01
8.01
7.63
7.63
7.61
7.61
7.51
7.49
7.46
7.46
7.44
7.44
7.39
7.37
7.36
6.99
6.99
6.98
6.97
6.96
6.94
6.92
6.92
3.85
0.00
CHO
OMe
1c

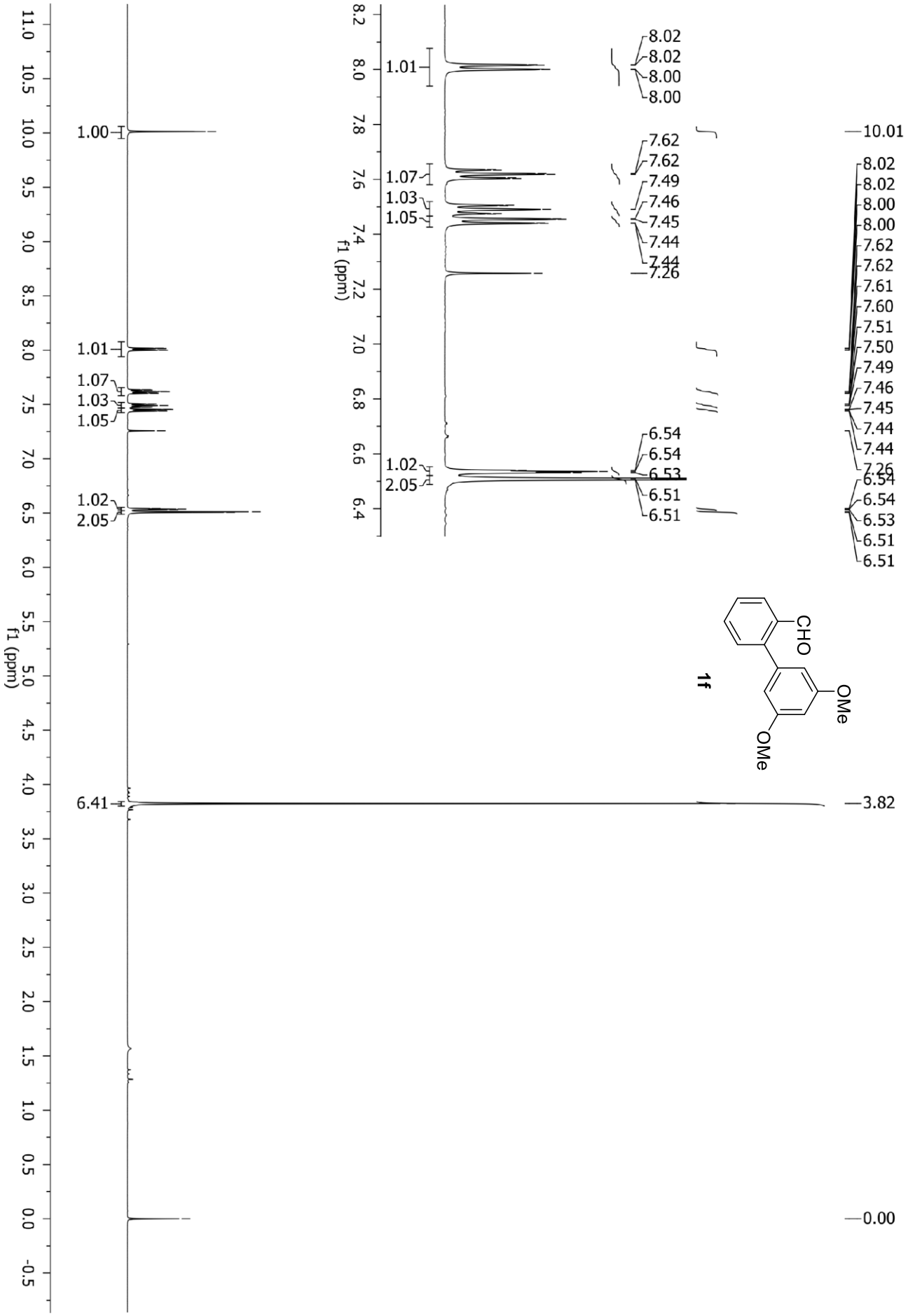

192.38
159.55
145.81
139.17
133.79
133.47
130.58
129.40
127.81
127.45
122.70
115.67
113.64
77.25
77.00
76.75
55.33
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
CHO
OMe
1c

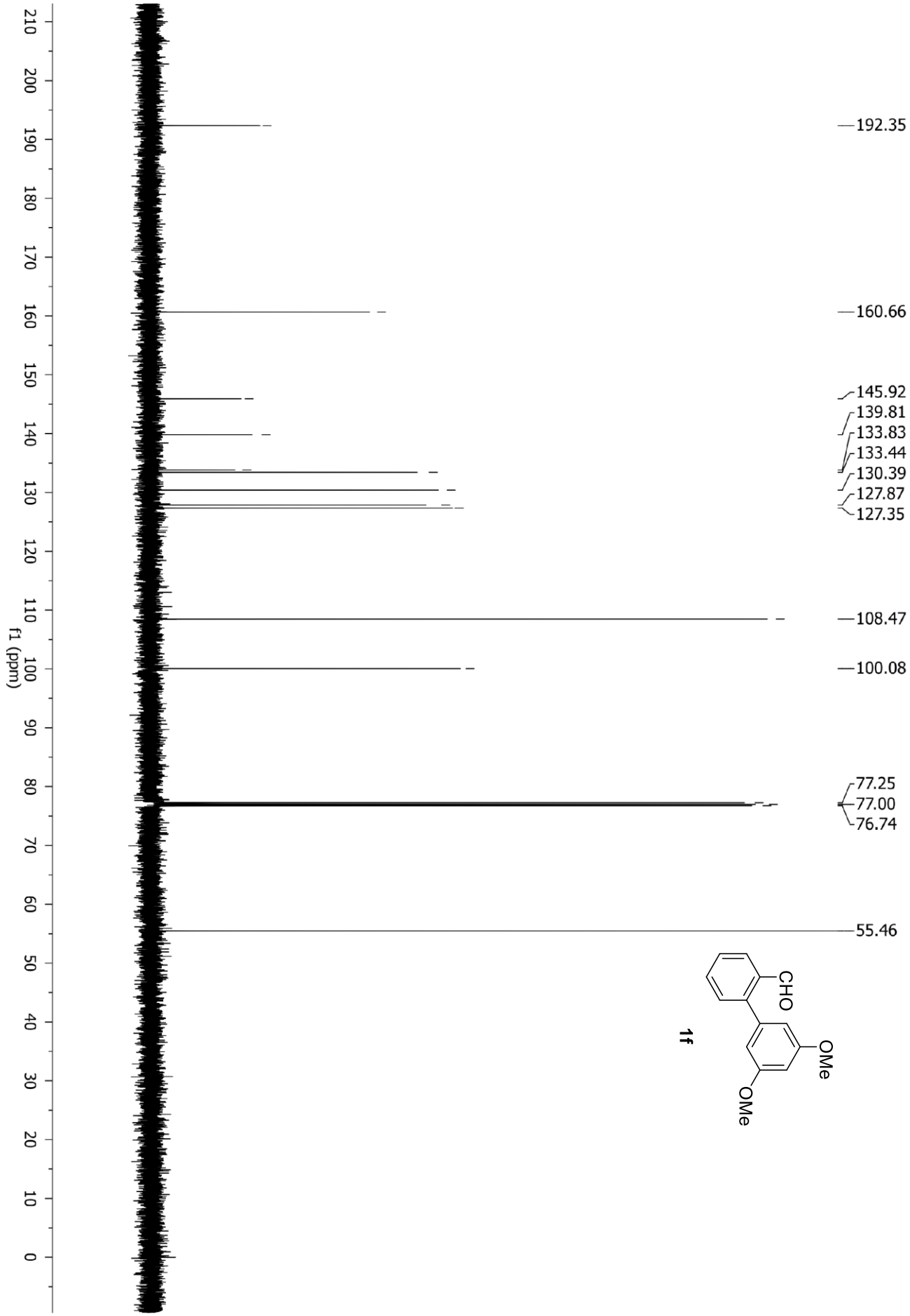

9.99
8.02
8.00
7.61
7.61
7.60
7.59
7.48
7.47
7.44
7.42
7.25
7.07
6.99
2.38
0.00
1.00
1.00
1.05
1.05
1.00
0.99
2.05
6.47
f1 (ppm)
CHO
1d

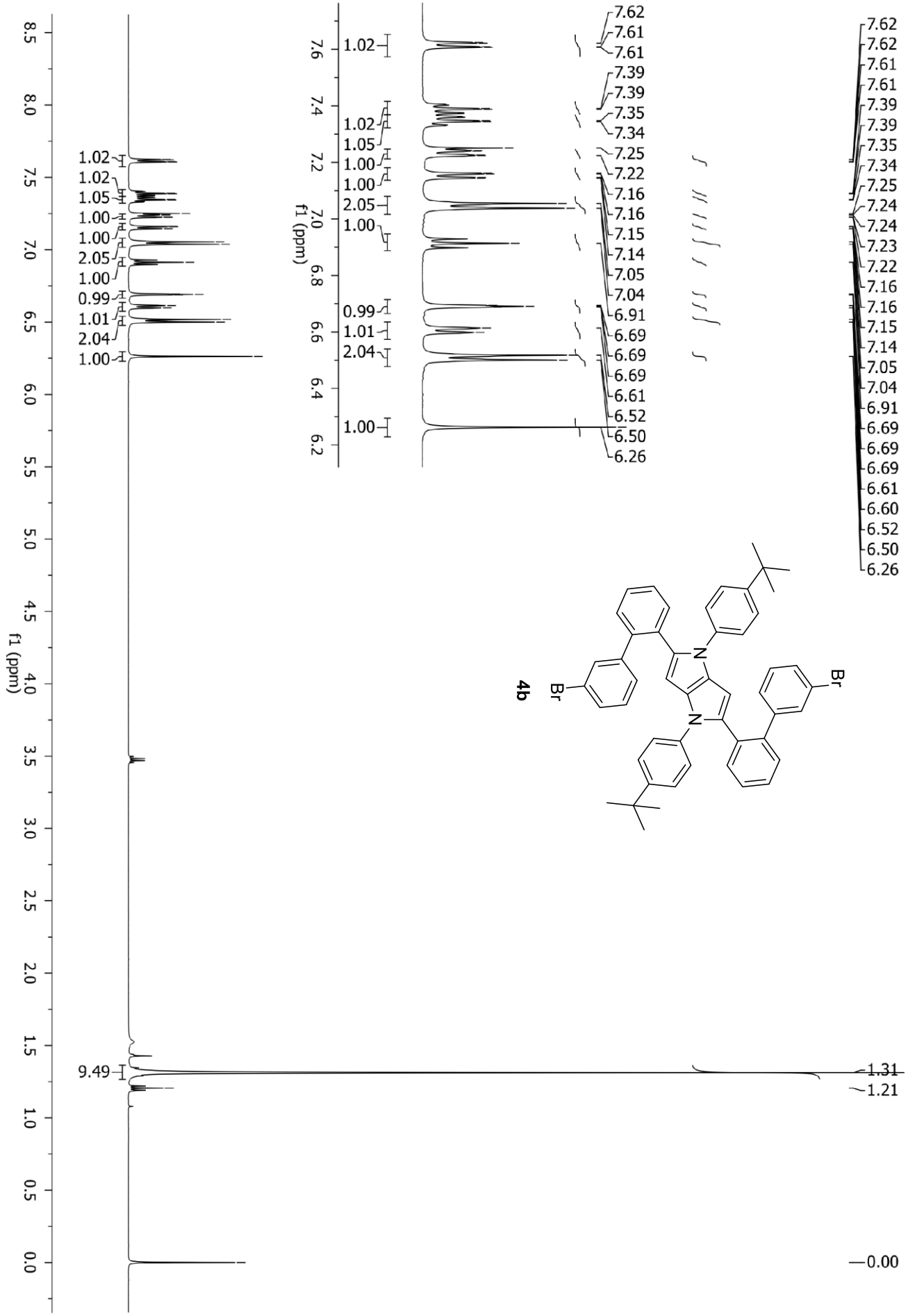

192.71
192.67
146.34
138.01
137.67
133.78
133.41
130.67
129.70
128.03
127.52
127.36
CHO
1d
77.25
77.00
76.74
21.27
f1 (ppm)


9.98
8.04
8.02
7.76
7.75
7.67
7.66
7.64
7.57
7.55
7.54
7.48
7.47
7.39
7.38
7.26
1.55
0.00
Br
CHO
Br
1e
1.00
0.96
1.05
1.06
1.99
1.04
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


191.11
142.53
141.45
133.79
133.71
133.58
131.57
130.59
128.85
128.28
123.00
77.25
77.00
76.74
CHO
Br
Br
1e
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


f1 (ppm)
1.00
1.01
1.07
1.03
1.05
1.02
2.05
6.41
1.01
1.07
1.03
1.05
1.02
2.05
8.02
8.02
8.00
8.00
7.62
7.62
7.49
7.46
7.45
7.44
7.44
7.26
6.54
6.54
6.53
6.51
6.51
10.01
8.02
8.02
8.00
8.00
7.62
7.62
7.61
7.60
7.51
7.50
7.49
7.46
7.45
7.44
7.44
7.26
6.54
6.54
6.53
6.51
6.51
3.82
0.00
CHO
OMe
OMe
1f


192.35
160.66
145.92
139.81
133.83
133.44
130.39
127.87
127.35
108.47
100.08
77.25
77.00
76.74
55.46
f1 (ppm)
CHO
OMe
OMe
1f


f1 (ppm)
1.02
1.02
1.05
1.00
1.00
2.05
1.00
0.99
1.01
2.04
1.00
9.49
1.31
1.21
0.00
7.62
7.61
7.61
7.39
7.39
7.35
7.34
7.25
7.22
7.16
7.16
7.15
7.14
7.05
7.04
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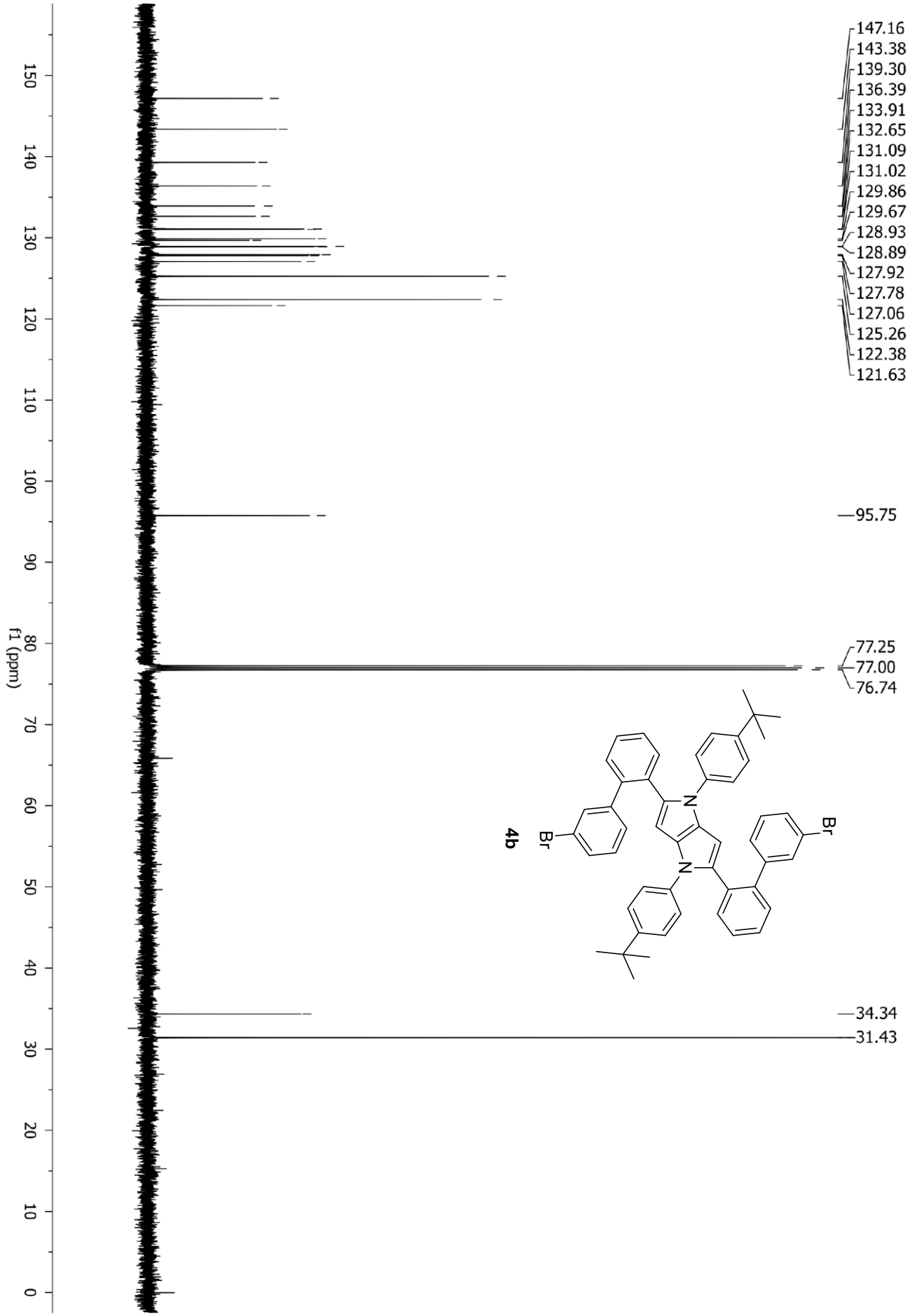
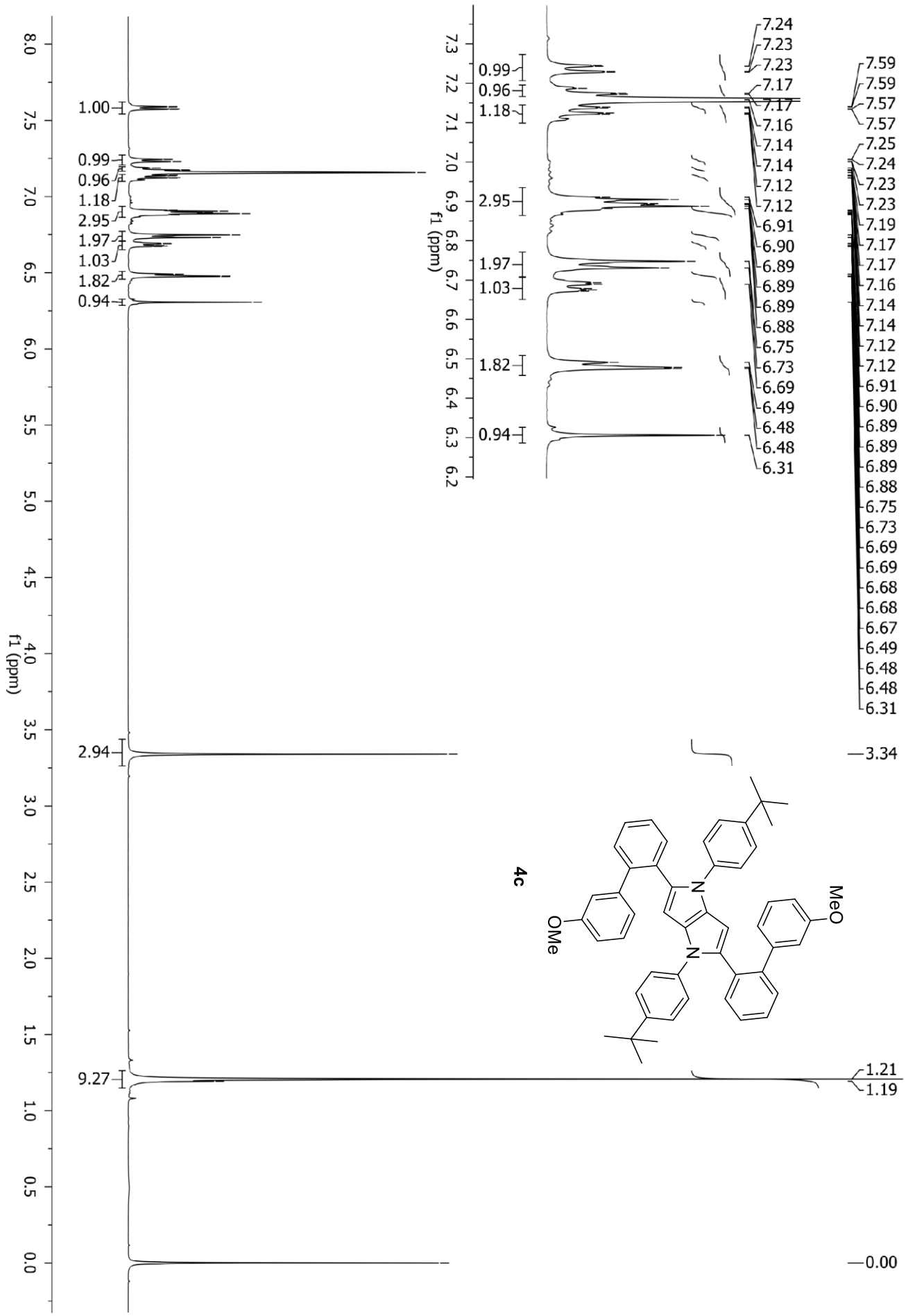
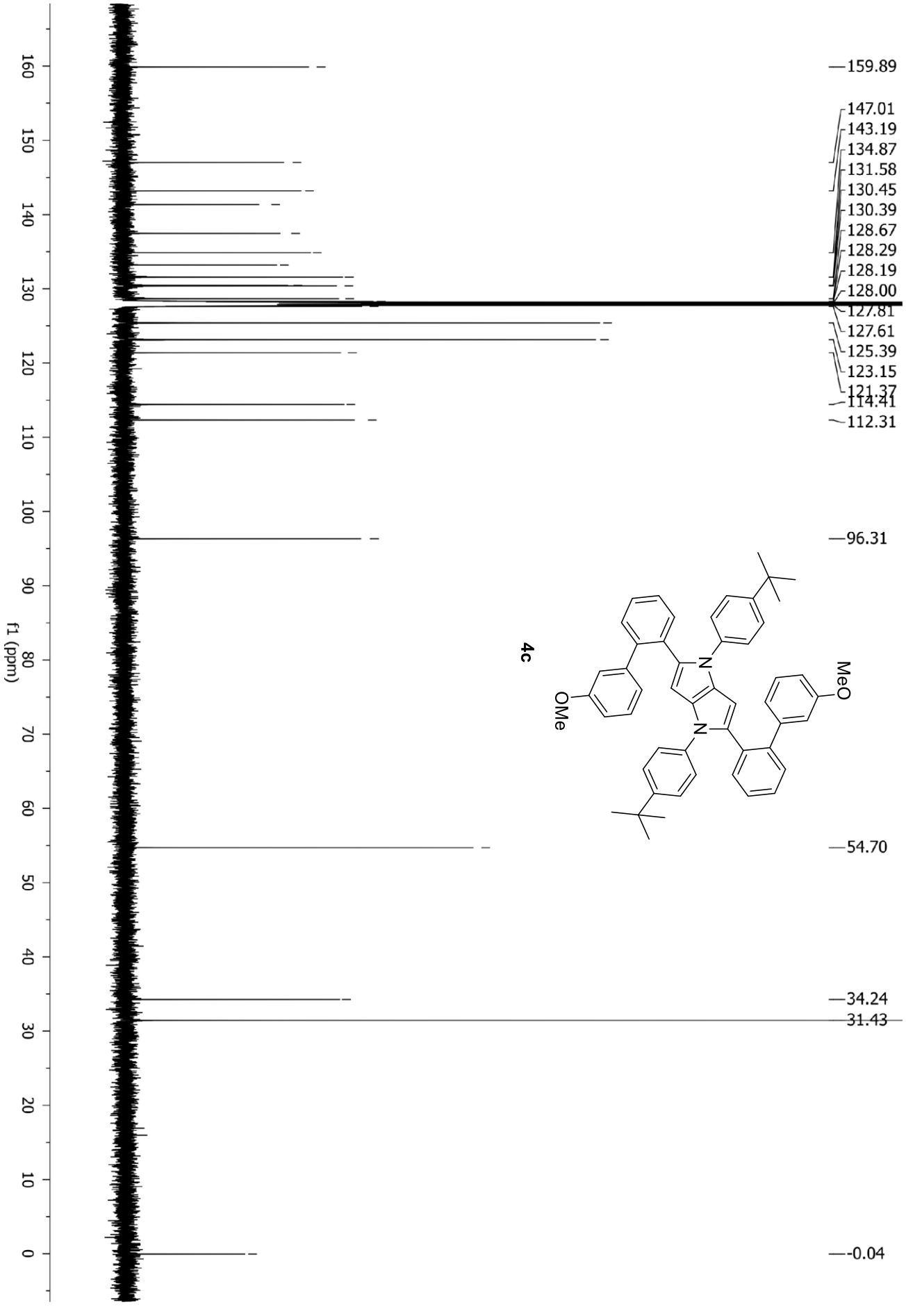
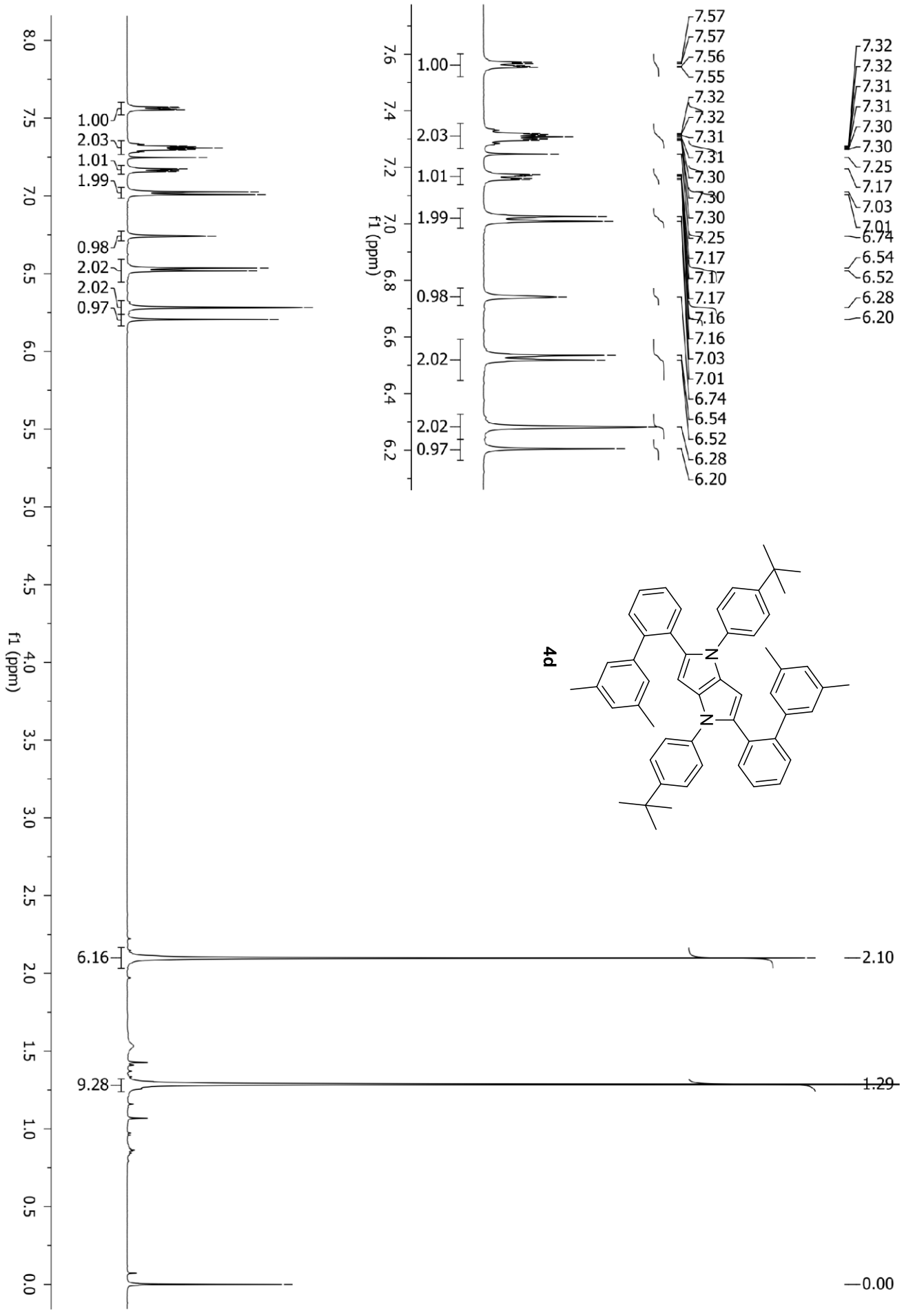
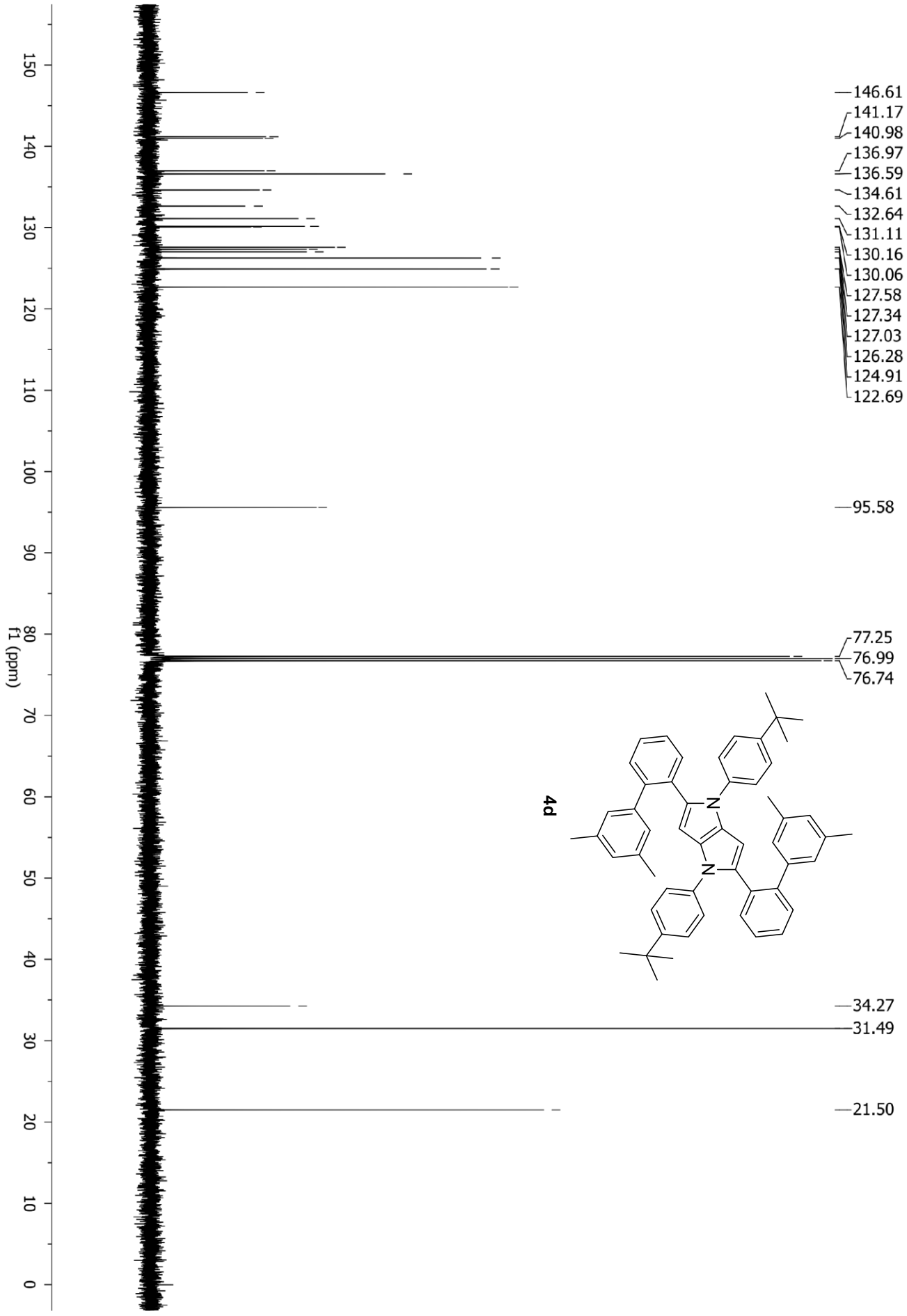
6.69
6.69
6.61
6.52
6.50
6.26
Br
Br
N
N
4b

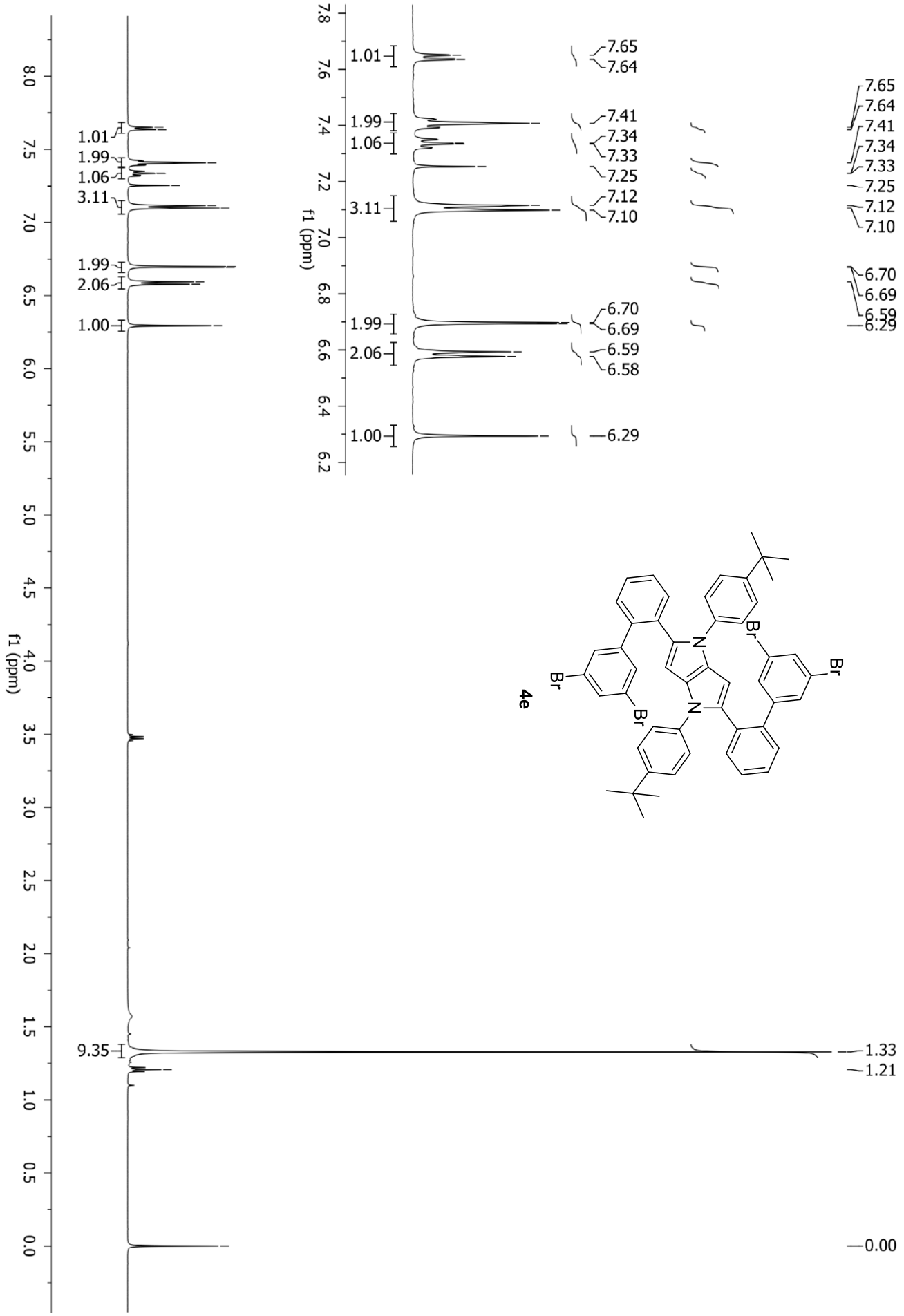

147.16
143.38
139.30
136.39
133.91
132.65
131.09
131.02
129.86
129.67
128.93
128.89
127.92
127.78
127.06
125.26
122.38
121.63
95.75
77.25
77.00
76.74
34.34
31.43
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Br
Br
N
N
4b

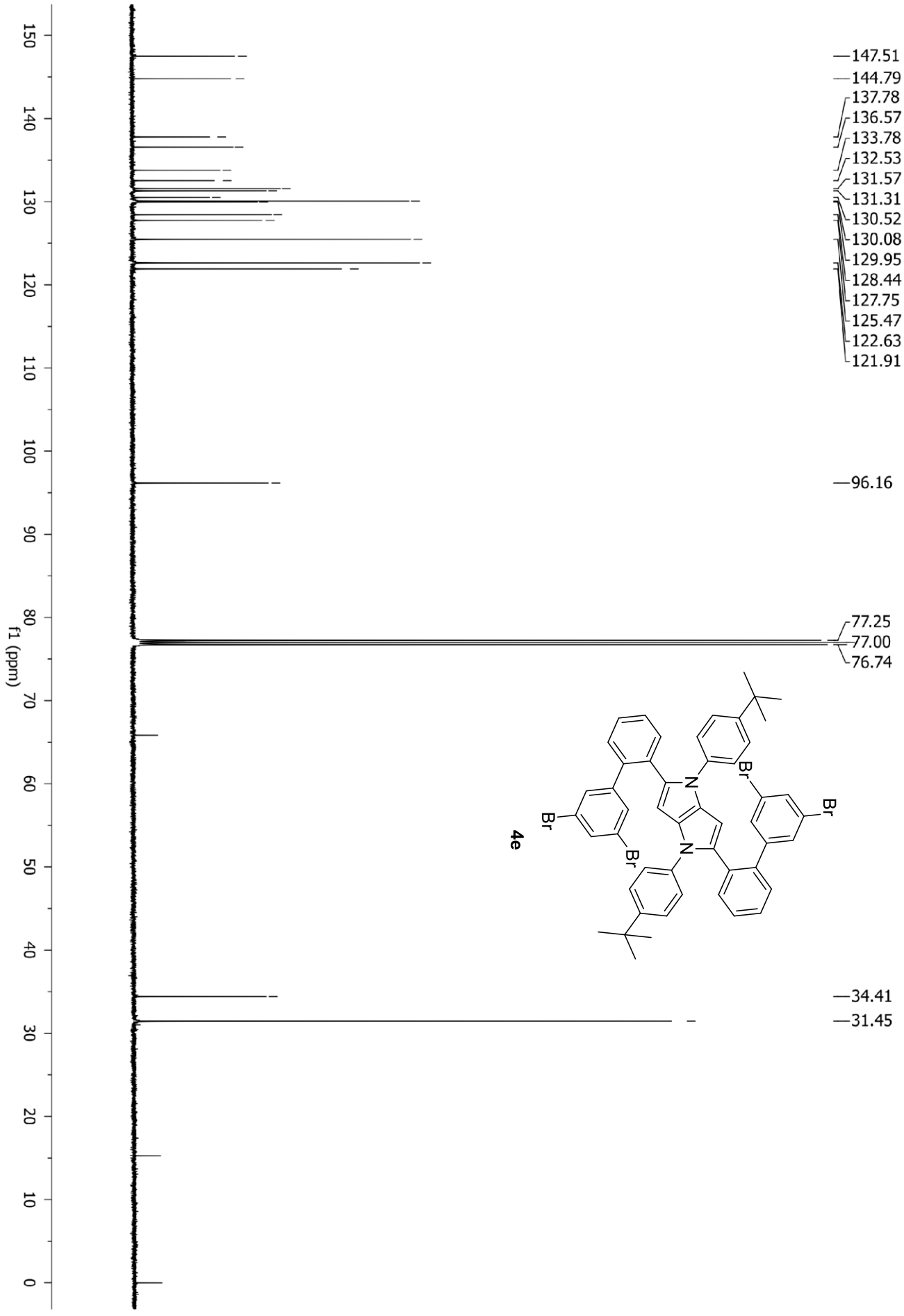

f1 (ppm)
1.00
0.99
0.96
1.18
2.95
1.97
1.03
1.82
0.94
2.94
9.27
7.24
7.23
7.23
7.17
7.17
7.16
7.14
7.14
7.12
7.12
6.91
6.90
6.89
6.89
6.89
6.88
6.75
6.73
6.69
6.49
6.48
6.48
6.31
7.59
7.59
7.57
7.57
7.25
7.24
7.23
7.23
7.19
7.17
7.17
7.16
7.14
7.14
7.12
7.12
6.91
6.90
6.89
6.89
6.89
6.88
6.75
6.73
6.69
6.69
6.68
6.68
6.67
6.49
6.48
6.48
6.31
3.34
1.21
1.19
0.00
4c
OMe
MeO
N
N

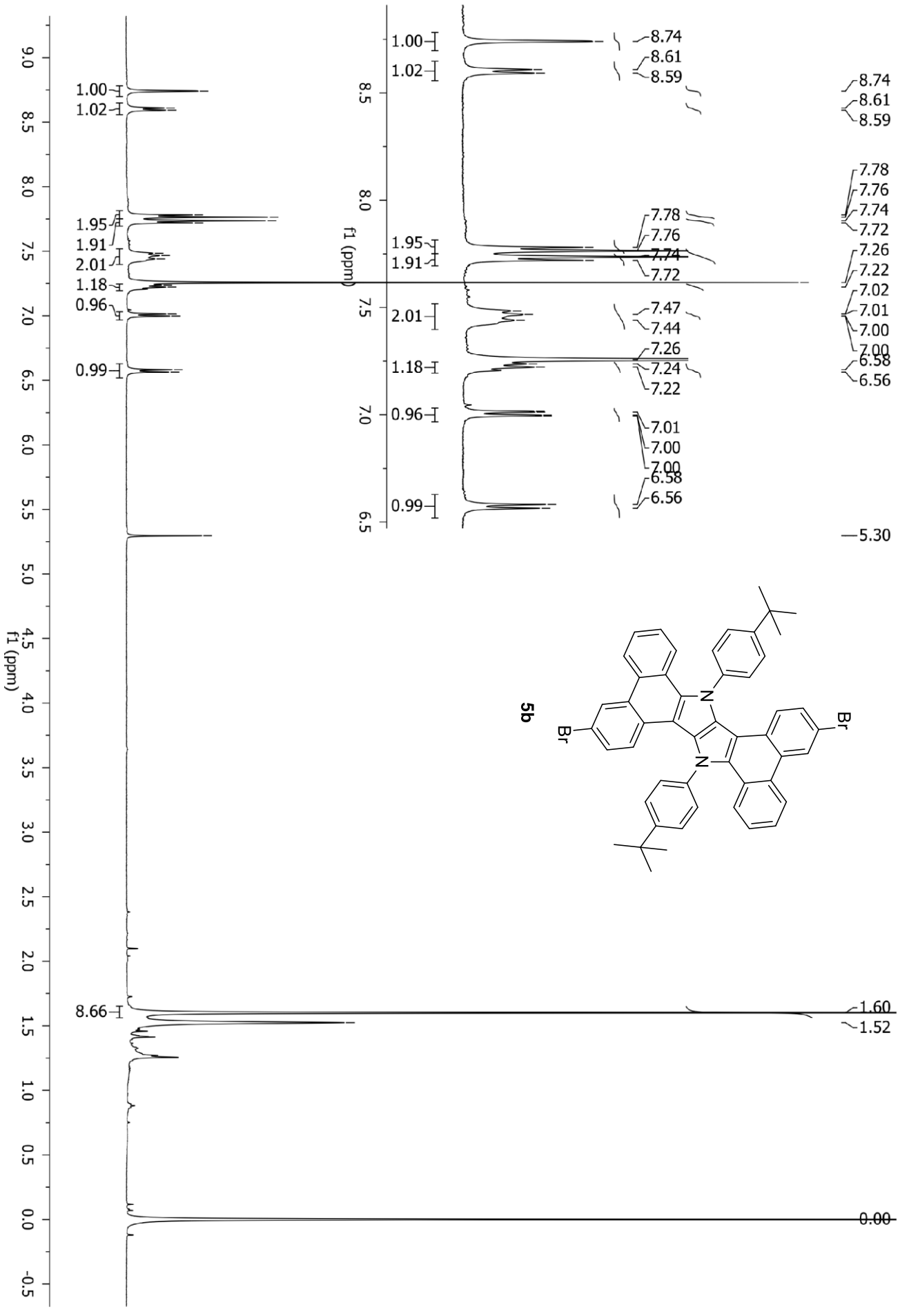

159.89
147.01
143.19
134.87
131.58
130.45
130.39
128.67
128.29
128.19
128.00
127.81
127.61
125.39
123.15
121.37
114.41
112.31
96.31
54.70
34.24
31.43
-0.04
f1 (ppm)
4c
OMe
MeO
N
N

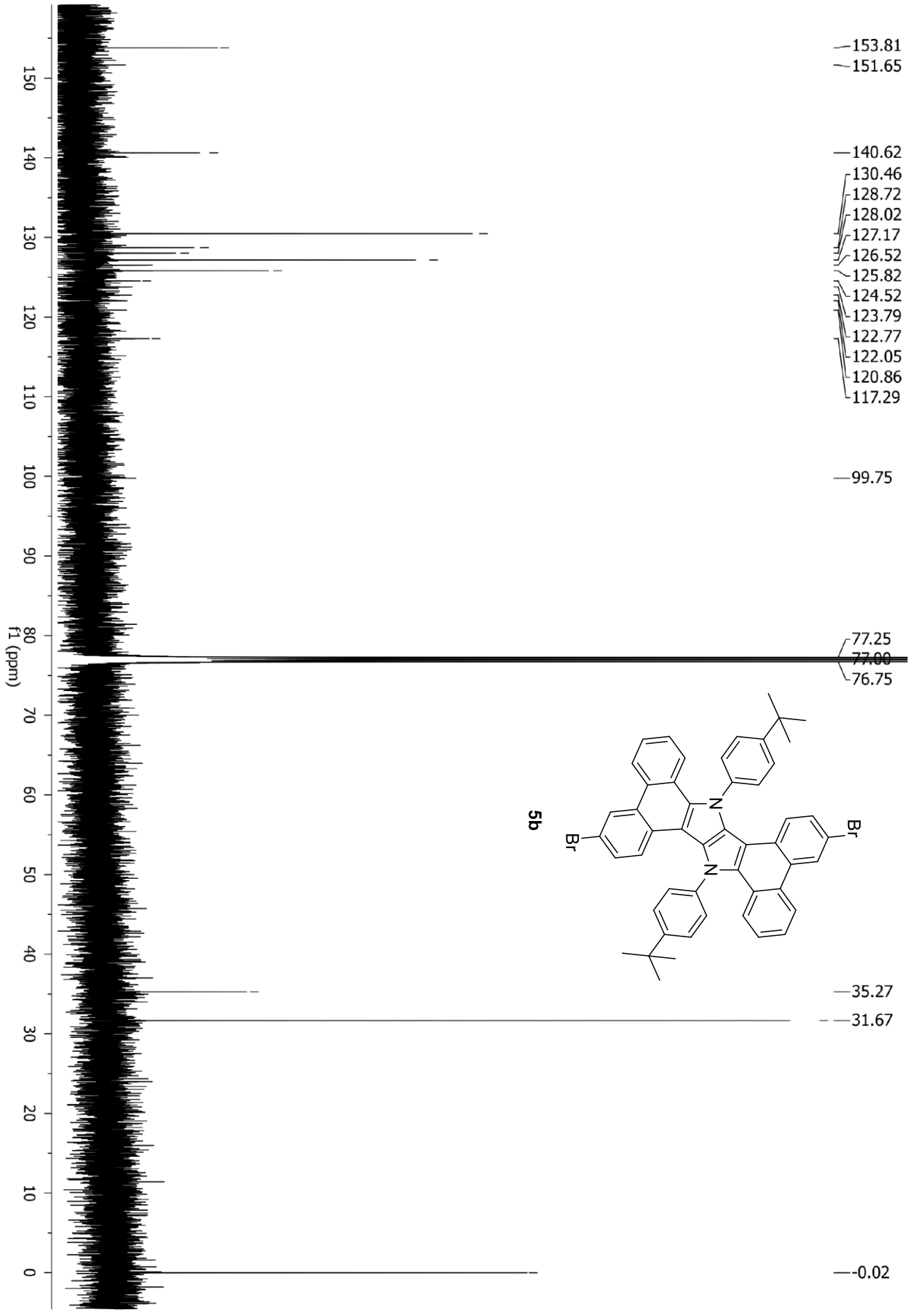

f1 (ppm)
1.00
2.03
1.01
1.99
0.98
2.02
2.02
0.97
6.16
9.28
2.10
1.29
0.00
7.57
7.56
7.55
7.32
7.31
7.30
7.25
7.17
7.03
7.01
6.74
6.54
6.52
6.28
6.20
4d

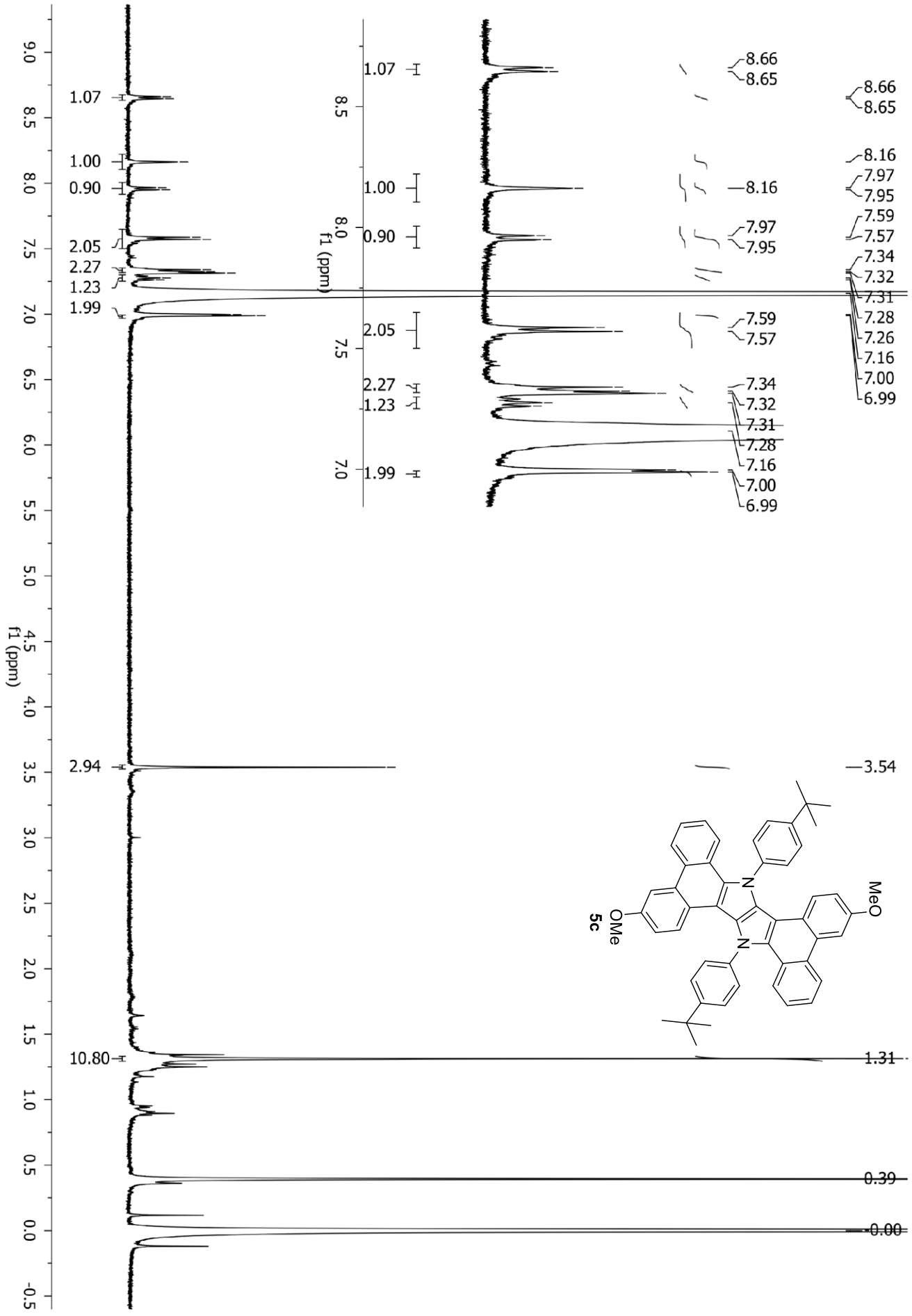

146.61
141.17
140.98
136.97
136.59
134.61
132.64
131.11
130.16
130.06
127.58
127.34
127.03
126.28
124.91
122.69
95.58
77.25
76.99
76.74
34.27
31.49
21.50
f1 (ppm)
4d

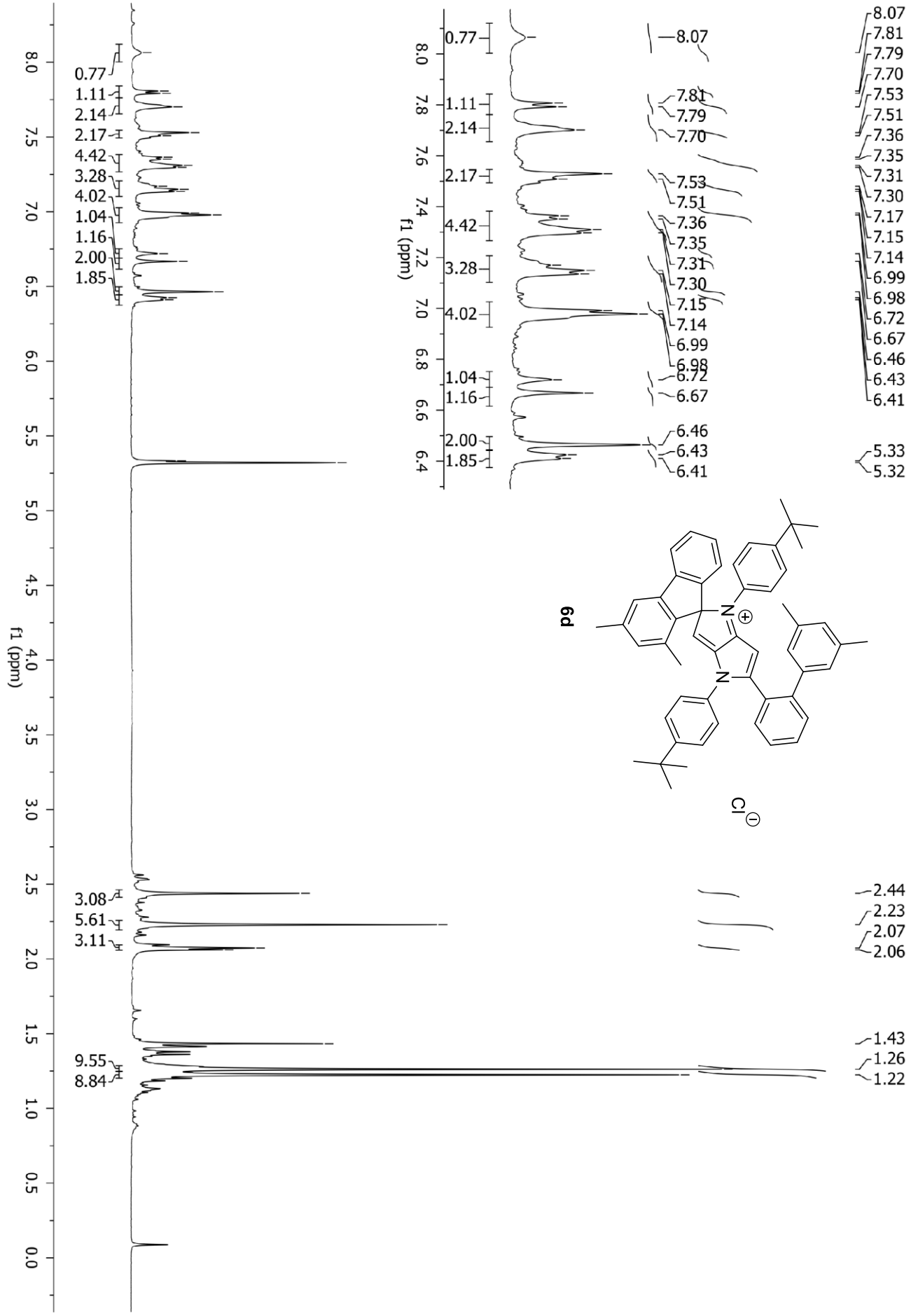

1.01
1.99
1.06
3.11
1.99
2.06
1.00
9.35
f1 (ppm)
7.65
7.64
7.41
7.34
7.33
7.25
7.12
7.10
6.70
6.69
6.59
6.58
6.29
1.33
1.21
0.00
4e
Br
N

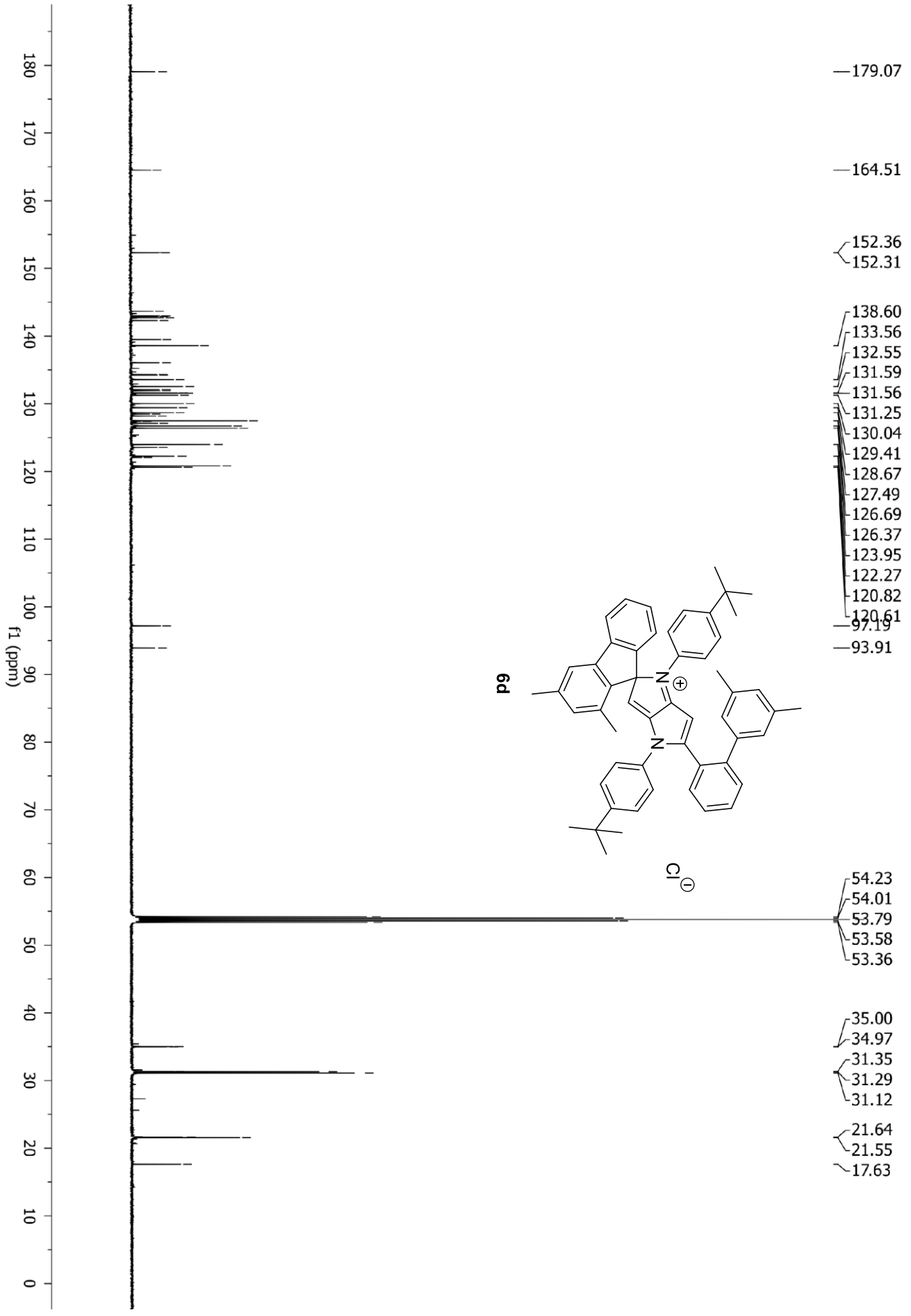

147.51
144.79
137.78
136.57
133.78
132.53
131.57
131.31
130.52
130.08
129.95
128.44
127.75
125.47
122.63
121.91
96.16
77.25
77.00
76.74
34.41
31.45
f1 (ppm)
4e

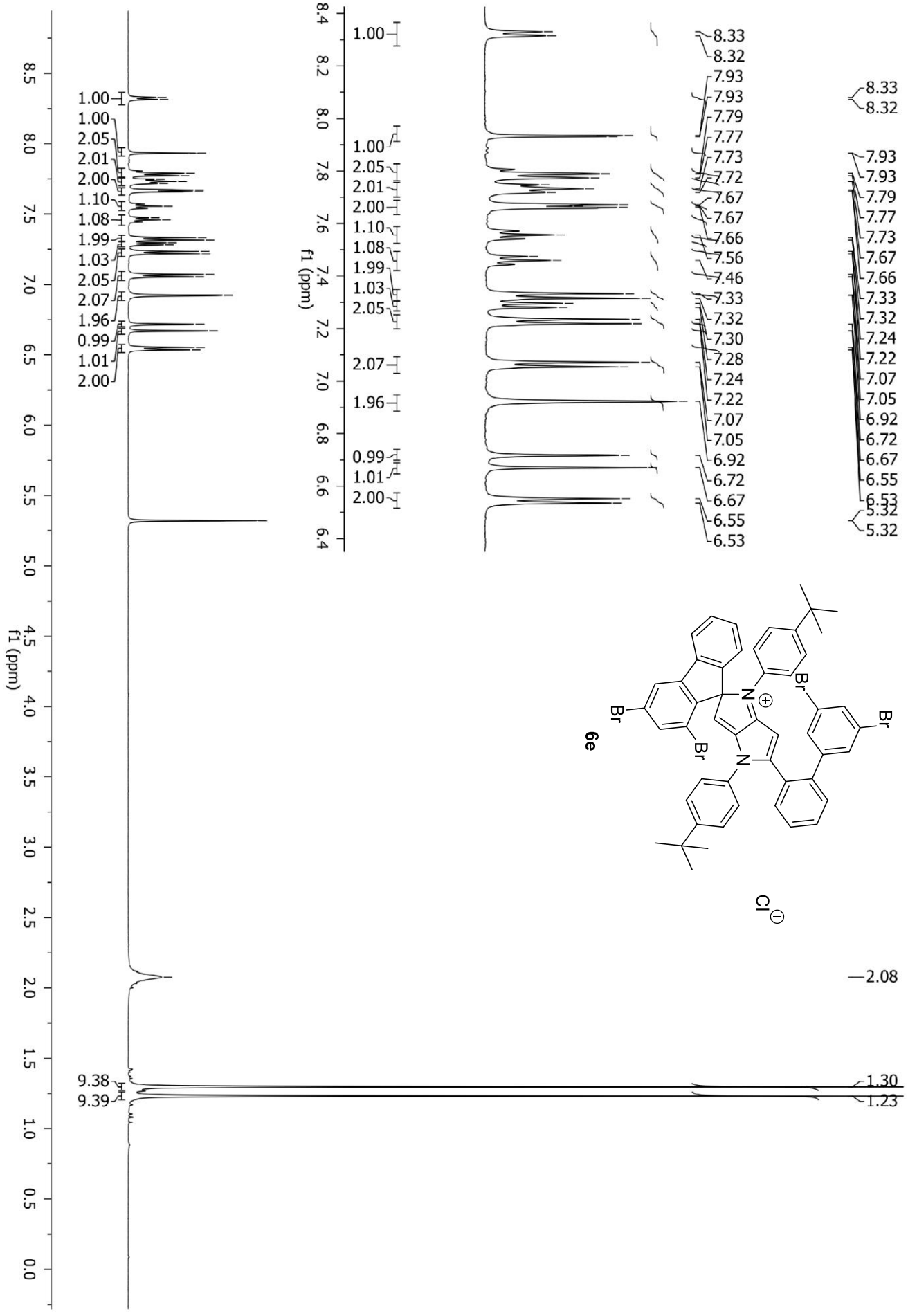

f1 (ppm)
1.00
1.02
1.95
1.91
2.01
1.18
0.96
0.99
8.66
8.74
8.61
8.59
7.78
7.76
7.74
7.72
7.47
7.44
7.26
7.24
7.22
7.01
7.00
7.00
6.58
6.56
5.30
1.60
1.52
0.00
5b
Br
Br
N
N

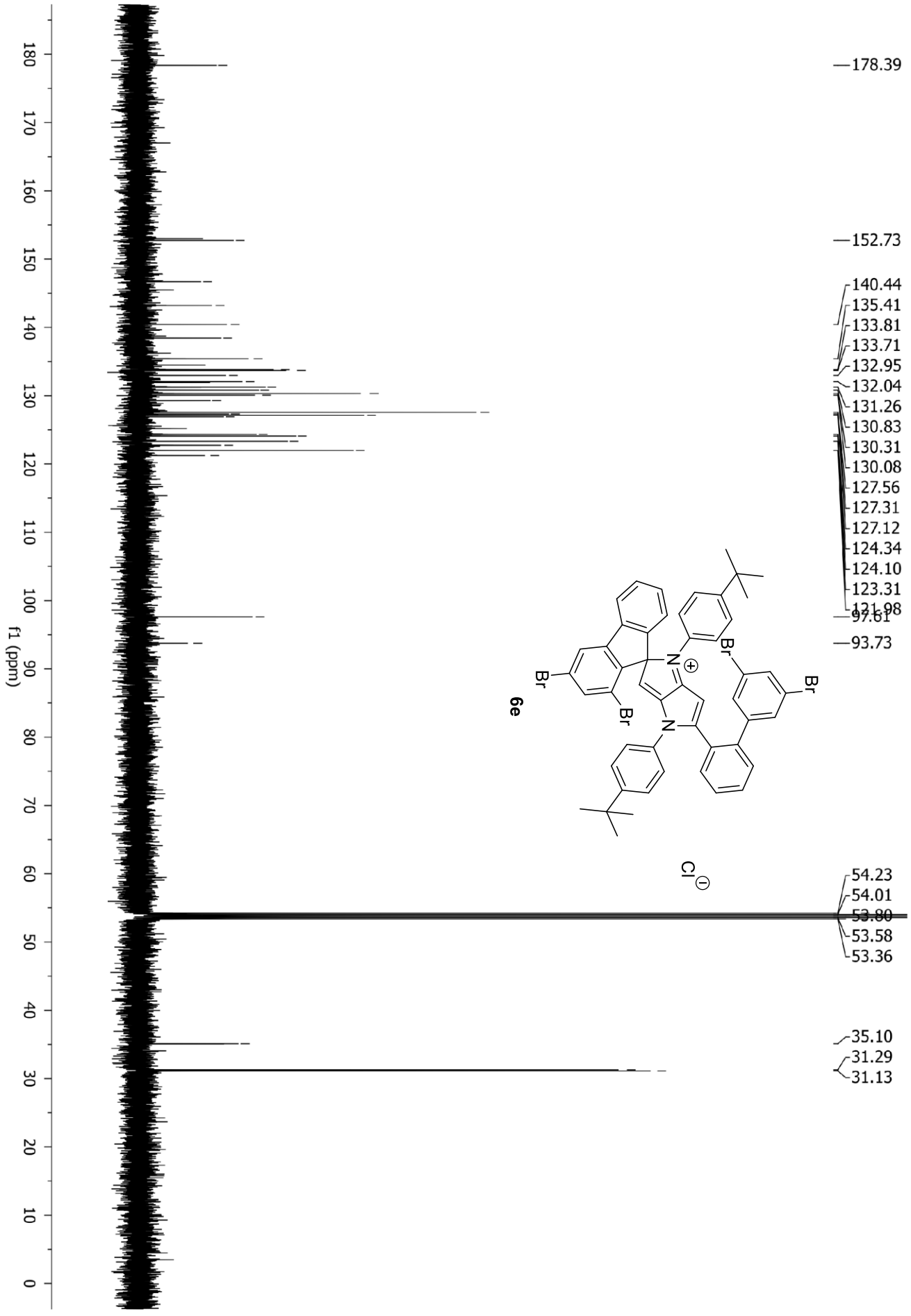

153.81
151.65
140.62
130.46
128.72
128.02
127.17
126.52
125.82
124.52
123.79
122.77
122.05
120.86
117.29
99.75
77.25
77.00
76.75
35.27
31.67
-0.02
f1 (ppm)
5b
Br
Br
N
N


f1 (ppm)
1.07
1.00
0.90
2.05
2.27
1.23
1.99
2.94
10.80
8.66
8.65
8.16
7.97
7.95
7.59
7.57
7.34
7.32
7.31
7.28
7.16
7.00
6.99
3.54
1.31
0.39
0.00
MeO
OMe
5c


8.07
7.81
7.79
7.70
7.53
7.51
7.36
7.35
7.31
7.30
7.17
7.15
7.14
6.99
6.98
6.72
6.67
6.46
6.43
6.41
5.33
5.32
2.44
2.23
2.07
2.06
1.43
1.26
1.22
0.77
1.11
2.14
2.17
4.42
3.28
4.02
1.04
1.16
2.00
1.85
3.08
5.61
3.11
9.55
8.84
f1 (ppm)
6d
Cl


179.07
164.51
152.36
152.31
138.60
133.56
132.55
131.59
131.56
131.25
130.04
129.41
128.67
127.49
126.69
126.37
123.95
122.27
120.82
120.61
97.19
93.91
54.23
54.01
53.79
53.58
53.36
35.00
34.97
31.35
31.29
31.12
21.64
21.55
17.63
f1 (ppm)
6d


f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1.00 1.00 2.05 2.01 2.00 1.10 1.08 1.99 1.03 2.05 2.07 1.96 0.99 1.01 2.00
9.38 9.39
2.08
1.30 1.23
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
8.33 8.32 7.93 7.93 7.79 7.77 7.73 7.72 7.67 7.67 7.66 7.56 7.46 7.33 7.32 7.30 7.28 7.24 7.22 7.07 7.05 6.92 6.72 6.67 6.55 6.53
5.32 5.32
Br Br Br Br
N N
Cl
6e


178.39
152.73
140.44
135.41
133.81
133.71
132.95
132.04
131.26
130.83
130.31
130.08
127.56
127.31
127.12
124.34
124.10
123.31
121.98
97.61
93.73
54.23
54.01
53.80
53.58
53.36
35.10
31.29
31.13
f1 (ppm)
6e
Cl⊖