Supporting Information

for RSC Advances

Photophysical behaviour of BODIPY-phenylacetylene macrocyclic dyads for light-harvesting applications

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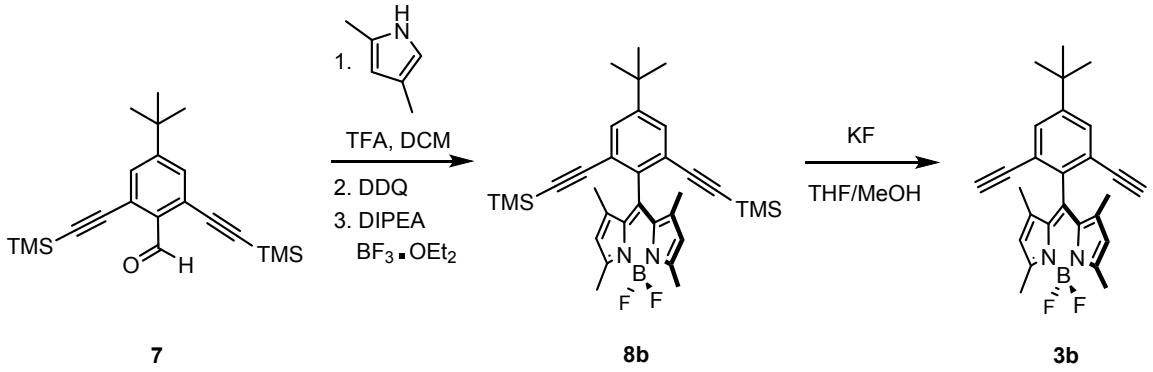
General Considerations

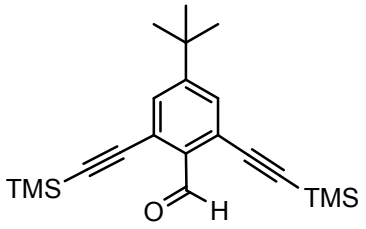
All reagents were purchased from Aldrich except $PdCl_2$ (Pressure Chemical Co., Pittsburg, PA). $PdCl_2$ was reacted with PPh_3 to make catalyst $PdCl_2(PPh_3)_2$. Purification by column chromatography was carried out using silica (Silicycle: ultrapure flash silica). Analytical thin-layer chromatography was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. Routine ^{1}H, $^{13}C\{1H\}$, $^{11}B\{1H\}$ and ^{19}F NMR spectra were recorded at 400, 100, 128 and 376 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to a residual nondeuterated solvent ($CHCl_3$) for ^{1}H and ^{13}C nuclei and BF_3•OEt_2 (^{11}B nucleus; δ = 0 ppm) C_6F_6 (^{19}F nucleus; δ = 0 ppm). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; t = triplet; q = quartet and br = broad. High resolution mass spectroscopy (HRMS) results were obtained from Queen's University, Kingston, Ontario. Electron impact (EI) mass spectrometry and Electrospray ionization (ESI) techniques were used for the ionization; time of flight (TOF) was used for analysis. UV-Vis data was taken using Cary Series UV-Vis-NIR Spectrophotometer from Agilent Technologies and dichloromethane (having the onset peak at 230 nm) was used as a solvent.

The GAUSSIAN 09 computational package[1] was used to perform ground-state geometry optimization calculations employing Becke's[2] three-parameter hybrid exchange functional and the Lee–Yang-Parr[3] non-local correlation functional B3LYP.[4] The 6-31G(d) basis set was used for all the atoms. Time-dependent density functional theory calculations were performed using the long-range corrected version of the Becke-3-parameter-Lee-Yang-Parr, the CAM-B3LYP hybrid functional[5] and the first 40 singlet excited states were calculated. The Grimme's dispersion corrections (DFT-D3) were included in all calculations.[6] Compounds 1, 2a, 3a, 4a, 9a, 10a, 11a, 12a, 13a, 14a, 15a and 16a have been previously synthesized and reported.[7]

Synthesis

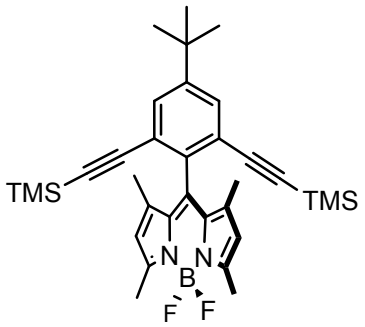


Scheme 1. Synthesis of BODIPY terminal alkyne **3b**.



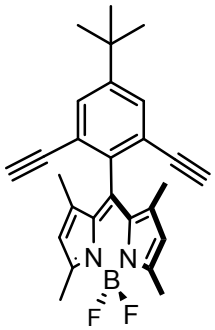
7

Synthesis of 7. 4-(*tert*-butyl)-2,6-diiodobenzaldehyde[1] (1.0 g, 2.42 mmol) was dissolved in THF:NEt_3 (18 mL, 2:1) in a 250 mL flask followed by the addition of $PdCl_2(PPh_3)_2$ (0.168 g, 0.24 mmol), CuI (0.09 g, 0.48 mmol) and TMS-acetylene (0.52 g, 5.31 mmol). The mixture was stirred overnight at RT. The solution was filtered and volatiles from the filtrate were removed *in vacuo*. The residue was redissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:EtOAc (19:1, R_f = 0.70) as the eluent to yield an orange-yellow crystalline solid (0.78 g, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.59 (s, 1H), 7.52 (s, 2H), 1.32 (s, 9H), 0.29 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 190.24, 156.00, 134.74, 131.64, 124.78, 101.92, 101.29, 35.05, 30.76, -0.21. HRMS (EI-TOF): *m*/*z* 354.1831 ($[MH]^+$), calcd for $C_{21}H_{30}OSi_2$: *m*/*z* 354.1835.



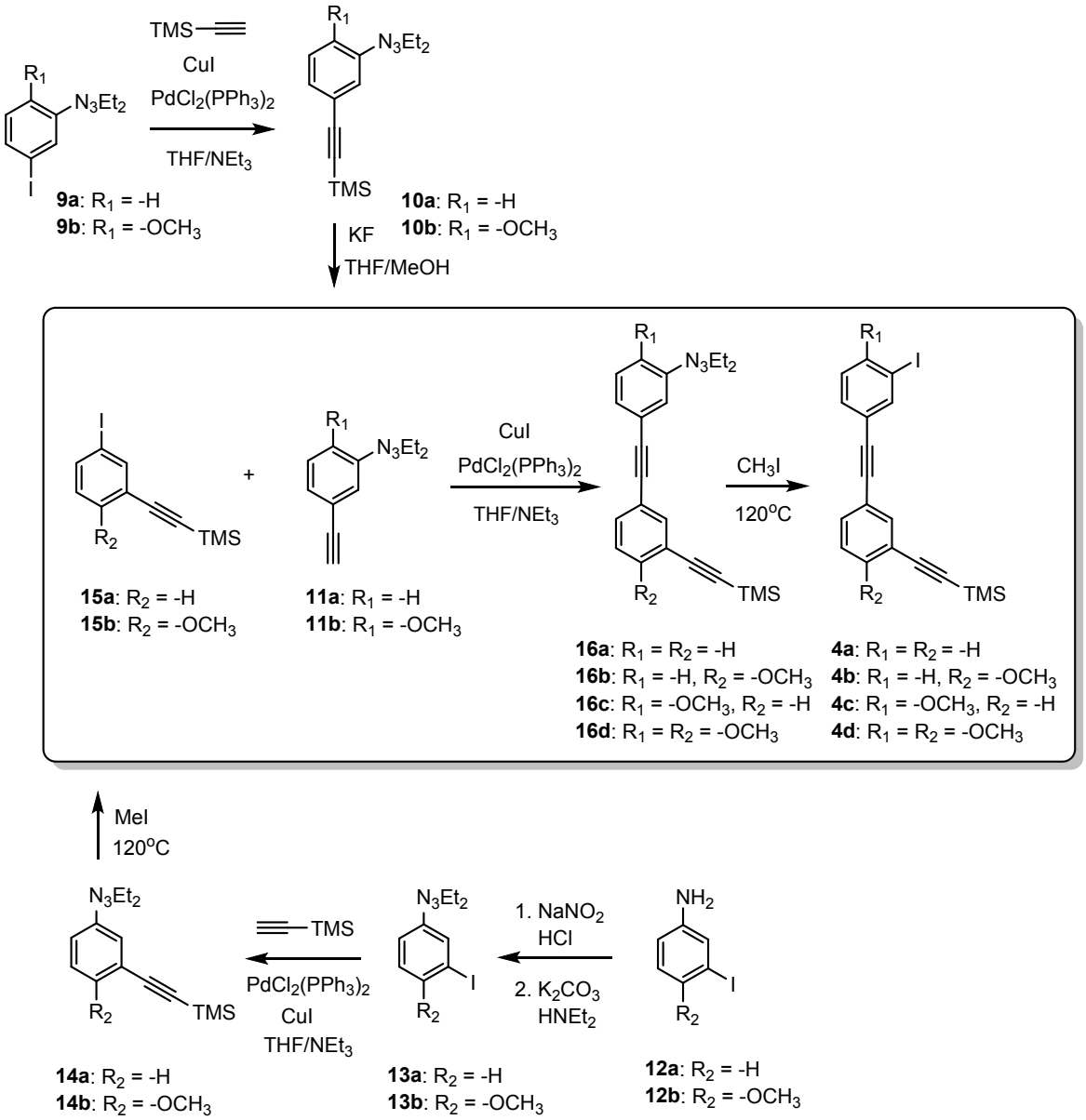
8b

Synthesis of 8b. To a solution of pyrrole **2.6** (0.82 g, 8.59 mmol, 2.5 eq) in dry DCM (120 mL), benzaldehyde derivative **7** (1.22 g, 3.44 mmol, 1 eq) was added followed by a catalytic amount of trifluoroacetic acid (TFA). After overnight stirring, DDQ (1.17 g, 1.5 eq) was added and the reddish mixture was stirred for ~3 hours. After the TLC analysis revealed the completion of oxidation, DIPEA (3.6 mL) and $BF_3{\cdot}OEt_2$ (4.2 mL) were added. After stirring for 6 hours, the mixture was concentrated in *vacuo*, redissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by column chromatography using toluene (R_f = 0.69) as the eluent to yield an orange powder (0.91 g, 42 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52 (s, 2H), 5.94 (s, 2H), 2.54 (s, 6H), 1.45 (s, 6H), 1.33 (s, 9H), 0.02 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 156.64, 156.17, 143.91, 141.52, 139.67, 137.11, 130.37, 121.34, 96.67, 89.71, 85.33, 34.67, 31.45, 14.76, 13.59, -0.01. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.76 (t, J_{FB} = 32 Hz). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = -146.36 (q). HRMS (DART-TOF): calcd for $C_{33}H_{43}BF_2N_2Si_2$, 572.3026; found 572.3029.

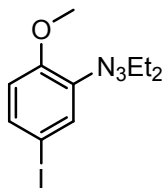


3b

Synthesis of 3b. BODIPY derivative **8b** (0.275 g, 0.48 mmol) was dissolved in MeOH:THF (10 mL, 1:1) and stirred with excess KF (0.14 g, 5 eq) overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The residue was chromatographed using toluene (R_f = 0.49) as the eluent to give a reddish solid (0.134 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64 (s, 2H), 5.98 (d, *J*=4.0 Hz, 2H), 3.01 (s, 2H), 2.57 (s, 6H), 1.44 (s, 6H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 158.14, 157.13, 142.27, 140.21, 138.99, 138.44, 130.71, 122.84, 96.06, 88.56, 86.66, 34.23, 31.37, 14.36, 13.38. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -146.55 (q). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.82 (t, J_{FB} = 83 Hz). HRMS (EI-TOF): *m*/*z* 428.2241 ($[MH]^+$), calcd for $C_{27}H_{27}BF_2N_2$: *m*/*z* 428.2235.

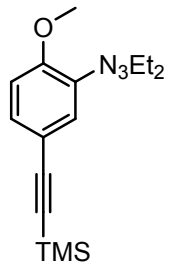


Scheme 2. Synthesis of macrocycle arms **4b, 4c and 4d.** Synthesis of 4a, 9a, 10a, 12a, 13a, 14a, 15a and 16a have already been reported.[6]



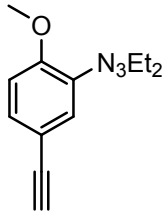
9b

Synthesis of 9b. To a solution of 5-iodo-2-methoxyaniline (1.0 g, 4.570 mmol) in concentrated HCl (35%, 6 mL) was added a solution of $NaNO_2$ (0.35 g, 5.02 mmol) in water (1.0 mL) at 0 °C. After stirring at 0 °C for 30 min, the resulting mixture was added dropwise to a suspension of K_2CO_3 (5.09 g, 36.84 mmol), diethylamine (0.5 g, 6.80 mmol), and water (18 mL) kept at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1.5 hours. After extraction with EtOAc, volatiles were removed *in vacuo*, affording a brown viscous liquid (1.31 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 2.4, 8.8, 1H), 6.67 (d, *J* = 8.8, 1H), 3.86 (s, 3H), 3.78 (q, *J* = 7.12, 4H), 1.28 (t, *J* = 7.12, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 153.06, 142.41, 134.20, 127.18, 114.52, 83.84, 56.44, 14.11, 12.20. HRMS (EI-TOF): *m*/*z* 333.0332, calcd for $C_6H_3I_2NO_2$: *m*/*z* 333.0338.



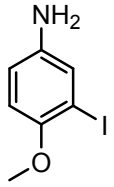
10b

Synthesis of 10b. Triazine **9b** (1.31 g, 3.932 mmol) was dissolved in THF:NEt_3 (12 mL, 2:1) in a 100 mL flask and sparged with N_2 for 15 minutes prior to the addition of $PdCl_2(PPh_3)_2$ (0.138 g, 0.197 mmol), CuI (0.075 mg, 0.393 mmol) and TMS-acetylene (0.463 g, 4.718 mmol). The mixture was stirred overnight at RT. The solution was filtered and the solvent was removed from the filtrate *in vacuo*. The residue was re-dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:EtOAc (15:1, R_f = 0.25) as the eluent to yield a light brown viscous liquid (1.10 g, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39 (d, *J* = 2.0 Hz, 1H), 7.22 (dd, *J* = 2.0, 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.78 (q, *J* = 7.12, 7.12, 4H), 1.27 (t, *J* = 7.12, 6H), 0.23 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 153.52, 144.46, 140.64, 129.80, 122.21, 115.40, 111.79, 105.64, 91.95, 56.22, 30.90, 0.10. HRMS (EI-TOF): *m*/*z* 303.1762, calcd for $C_{16}H_{25}N_3OSi$: *m*/*z* 303.1767.



11b

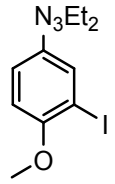
Synthesis of 11b. The TMS-protected alkyne **10b** (1.10 g, 3.625 mmol) was dissolved in 14 mL of MeOH:THF (1:1) and stirred with excess KF (0.63 g, 10.874 mmol) overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was chromatographed using Hex:EtOAc (9:1, R_f = 0.41) as the eluent to give **11b** (0.641 g, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.44 (d, *J* = 2.0 Hz, 1H), 7.25 (dd, *J* = 1.6, 8.2 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 3.76 (q, *J* = 7.2 Hz, 4H), 2.98 (s, 1H), 1.27 (t, *J* = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 153.69, 140.78, 129.85, 122.33, 114.32, 111.98, 84.07, 75.38, 56.25, 12.86. HRMS (EI-TOF): *m*/*z* 231.1380, calcd for $C_{13}H_{17}N_3O$: *m*/*z* 231.1372.



12b

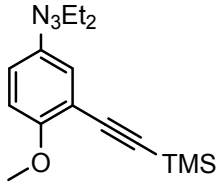
Synthesis of 12b. 2-iodo-1-methoxy-4-nitrobenzene (4 g, 14.34 mmol) was dissolved in methanol (50 mL) in a 500 mL flask prior to the addition of a solution of NH_4Cl (3.83 g, 71.7 mmol) in water (40 mL) and powdered Fe (2.36 g, 42.2 mmol). The mixture was refluxed for 3.5 h. The precipitate was filtered and the filtrate was evaporated until MeOH was removed. The mixture was diluted with water, alkalinized with Na_2CO_3 and extracted with EtOAc. The organic layer was washed with brine and water, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:EtOAc (2:1, *Rf* = 0.40) as the eluent to yield a brown viscous liquid (3.68 g, 50%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.15 (d, *J* = 1.92 Hz, 1H), 6.68-6.62 (m, 2H), 3.79 (s, 3H), 3.42 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 151.59, 141.45, 126.18,

116.16, 112.46, 86.73, 57.10. HRMS (EI-TOF): *m*/*z* 374.8246, calcd for $C_6H_3I_2NO_2$: *m*/*z* 374.8253.



13b

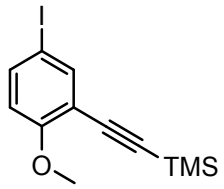
Synthesis of 13b. To a solution of **12b** (3.0 g, 13.7 mmol) in concentrated HCl (35%, 17.7 mL) was added a solution of $NaNO_2$ (1.04 g, 15.07 mmol) in water (3.0 mL) at 0 °C. After stirring at 0°C for 30 min, the resulting mixture was added dropwise to a suspension of K_2CO_3 (15.27 g, 110.51 mmol), diethylamine (1.49 g, 20.4 mmol), and water (55.5 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1.5 hours. After extraction with EtOAc, volatiles were removed in *vacuo* and the residue was chromatographed using Hex:EtOAc (15:1, R_f = 0.42) as the eluent to yield an orange liquid (4.78 g, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89 (d, *J* = 2.36 Hz, 1H), 7.35 (dd, *J* = 2.36, 8.72 Hz, 1H), 6.78 (d, *J* = 2.36, 8.72 Hz, 1H), 3.86 (s, 3H), 3.73 (q, *J* = 7.12 Hz, 4H), 1.25 (t, *J* = 7.12 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 155.72, 146.24, 130.59, 121.90, 110.80, 86.22, 56.65, 12.90. HRMS (EI-TOF): *m*/*z* 333.0331, calcd for $C_{11}H_{16}IN_3O$: *m*/*z* 333.0338.



14b

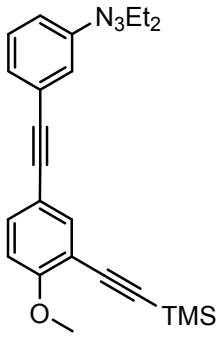
Synthesis of 14b. Triazine **13b** (2.75 g, 8.25 mmol) was dissolved in THF:NEt_3 (138 mL, 2:1) in a 500 mL flask followed by the addition of $PdCl_2(PPh_3)_2$ (290 mg, 0.41 mmol), CuI (157 mg, 0.82 mmol), and TMS-acetylene (0.97 g, 9.90 mmol). The mixture was stirred overnight at RT. The mixture was filtered and the solvent removed from the filtrate. The residue was re-dissolved in EtOAc, washed with H_4Cl (sat) and brine, dried

over $MgSO_4$, and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:EtOAc (15:1, R_f = 0.40) as the eluent to yield an orange viscous liquid (1.55 g, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (d, *J* = 2.40 Hz, 1H), 7.34 (dd, *J* = 2.40, 8.84 Hz, 1H), 6.81 (d, *J* = 8.84 Hz, 1H), 3.87 (s, 3H), 3.72 (q, *J* = 7.2 Hz, 4H), 1.24 (t, *J* = 7.2 Hz, 6H), 0.26 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 158.09, 144.62, 125.60, 122.30, 112.36, 110.99, 101.59, 97.96, 56.16, 12.87, 0.12. HRMS (EI-TOF): *m*/*z* 303.1762, calcd for $C_{16}H_{25}N_3OSi$: *m*/*z* 303.1767.



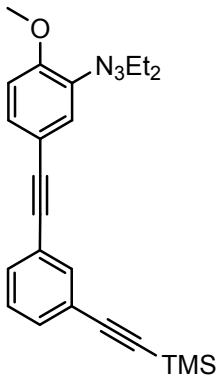
15b

Synthesis of 15b. Compound **14b** (1.0 g, 3.30 mmol) and methyl iodide (5 mL) were sealed in a heavy walled flask (*i.e.*, microwave tube) and heated to 120 ^{o}C for 12 hours. The reaction mixture was quenched with water, extracted with DCM, dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed using hexane as the eluent (R_f = 0.65) to yield a yellow viscous liquid (0.97 g, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71 (d, *J* = 2.20 Hz, 1H), 7.53 (dd, *J* = 2.20, 8.76 Hz, 1H), 6.61 (d, *J* = 8.76 Hz, 1H), 3.83 (s, 3H), 0.26 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 160.21, 142.14, 138.56, 114.92, 112.85, 100.15, 99.44, 81.68, 55.97, -0.02. HRMS (EI-TOF): *m*/*z* 329.9932, calcd for $C_{12}H_{15}IOSi$: *m*/*z* 329.9937.



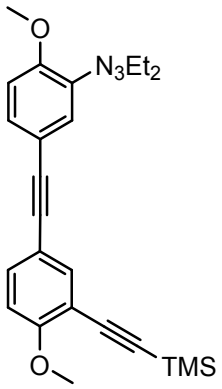
16b

Synthesis of 16b. To a mixture of **15b** (1.00 g, 3.028 mmol), $Pd(PPh_3)_4$ (0.106 g, 0.151 mmol) and CuI (0.058 mg, 0.303 mmol) in THF:NEt_3 (15 mL, 2:1) was added **11a** (0.735 g, 3.634 mmol). The mixture was stirred at RT for 3 hrs, filtered and the solvent was removed from the filtrate. The residue was dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed using Hex:EtOAc (9:1, R_f = 0.5) as the eluent to give a yellow viscous liquid (1.232 g, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.63 (d, *J* = 2.0 Hz, 1H), 7.56 (s, 1H), 7.45 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.77 (q, *J* = 7.0 Hz, 4H), 1.27 (t, *J* = 7.0 Hz, 6H), 0.27 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 160.06, 151.20, 137.40, 133.28, 128.75, 128.01, 123.64, 123.23, 120.79, 115.66, 112.69, 110.71, 100.29, 99.12, 88.89, 87.88, 55.99, 0.03. HRMS (EI-TOF): *m*/*z* 403.2069 ([MH]$^+$), calcd for $C_{24}H_{29}N_3OSi$: *m*/*z* 403.2080.



16c

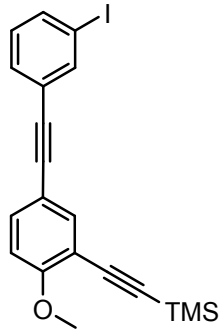
Synthesis of 16c. To a mixture of **15a** (1.00 g, 3.331 mmol), $PdCl_2(PPh_3)_2$ (0.117 g, 0.167 mmol) and CuI (0.063 g, 0.333 mmol) in THF:NEt_3 (15 mL, 2:1)was added **11b** (0.925 g, 3.997 mmol). The mixture was stirred at RT for 10 hrs, filtered and the solvent from the filtrate was removed *in vacuo*. The residue was dissolved in EtOAc and washed with an NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:EtOAc (9:1, R_f = 0.31) as the eluent to give a light yellow viscous liquid (1.236 g, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.63 (s, 1H), 7.45 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.27 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 3.81 (q, *J* = 7.0 Hz, 4H), 1.29 (t, *J* = 7.0 Hz, 6H), 0.25 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 153.51, 140.84, 134.89, 131.36, 131.13, 129.39, 128.25, 124.01, 123.36, 121.87, 115.26, 112.05, 104.32, 94.73, 90.47, 86.87, 56.28, -0.07. HRMS (EI-TOF): *m/z* 403.2088 ([MH]$^+$), calcd for $C_{24}H_{29}N_3OSi$: m/z 403.2080.



16d

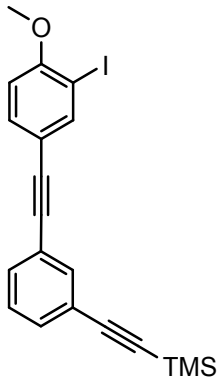
Synthesis of 16d. A mixture **15b** (0.85 g, 2.574 mmol) and **11b** (0.655 g, 2.831 mmol) in THF:NEt_3 (12 mL, 2:1) was sparged with N_2 for 20 minutes. $PdCl_2(PPh_3)_2$ (0.090 g, 0.129 mmol) and CuI (0.049 g, 0.257 mmol) were added and the mixture was stirred at RT for 11 hrs. The solution was filtered and the solvent removed from the filtrate. The residue was re-dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:AcOEt (9:1, R_f = 0.29) as the eluent to give an off-white solid (0.74 g, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.61 (s, 1H), 7.44 (s, 1H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.79 (q, *J* = 7.0 Hz, 4H), 1.28 (t, *J* = 7.0 Hz, 6H), 0.27 (s,

9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 159.87, 153.30, 140.82, 137.22, 133.12, 129.21, 121.72, 115.96, 115.62, 112.63, 112.09, 110.72, 100.39, 99.00, 88.86, 86.69, 56.29, 55.96, 12.88, 0.04. HRMS (EI-TOF): *m*/*z* 433.2190, calcd for $C_{25}H_{31}N_3O_2Si$: *m*/*z* 433.2186.



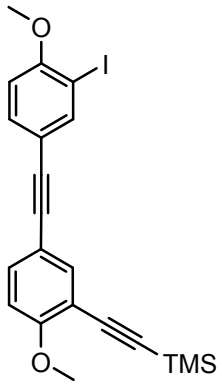
4b

Synthesis of 4b. Compound **16b** (1.469 g, 3.641 mmol) and MeI (5.0 mL) were sealed in a heavy walled microwave vial and heated to 120 °C for 8 hrs. The reaction mixture was cooled to RT, quenched with water and extracted with DCM. The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by column chromatography using Hex:EtOAc (9:1, R_f = 0.30) as the eluent to yield a light yellow liquid (1.285 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (s, 1H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.44 (t, *J* = 7.0 Hz, 2H), 7.06 (t, *J* = 7.0 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H), 0.28 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 160.40, 140.03, 137.44, 137.06. 133.33, 130.54, 129.85, 125.48, 114.91, 112.87, 110.78, 100.11, 99.38, 93.72, 89.87, 86.81, 56.01, 0.05. HRMS (EI-TOF): *m*/*z* 430.0240 ($[MH]^+$), calcd for $C_{20}H_{19}OISi$: *m*/*z* 430.0250.



4c

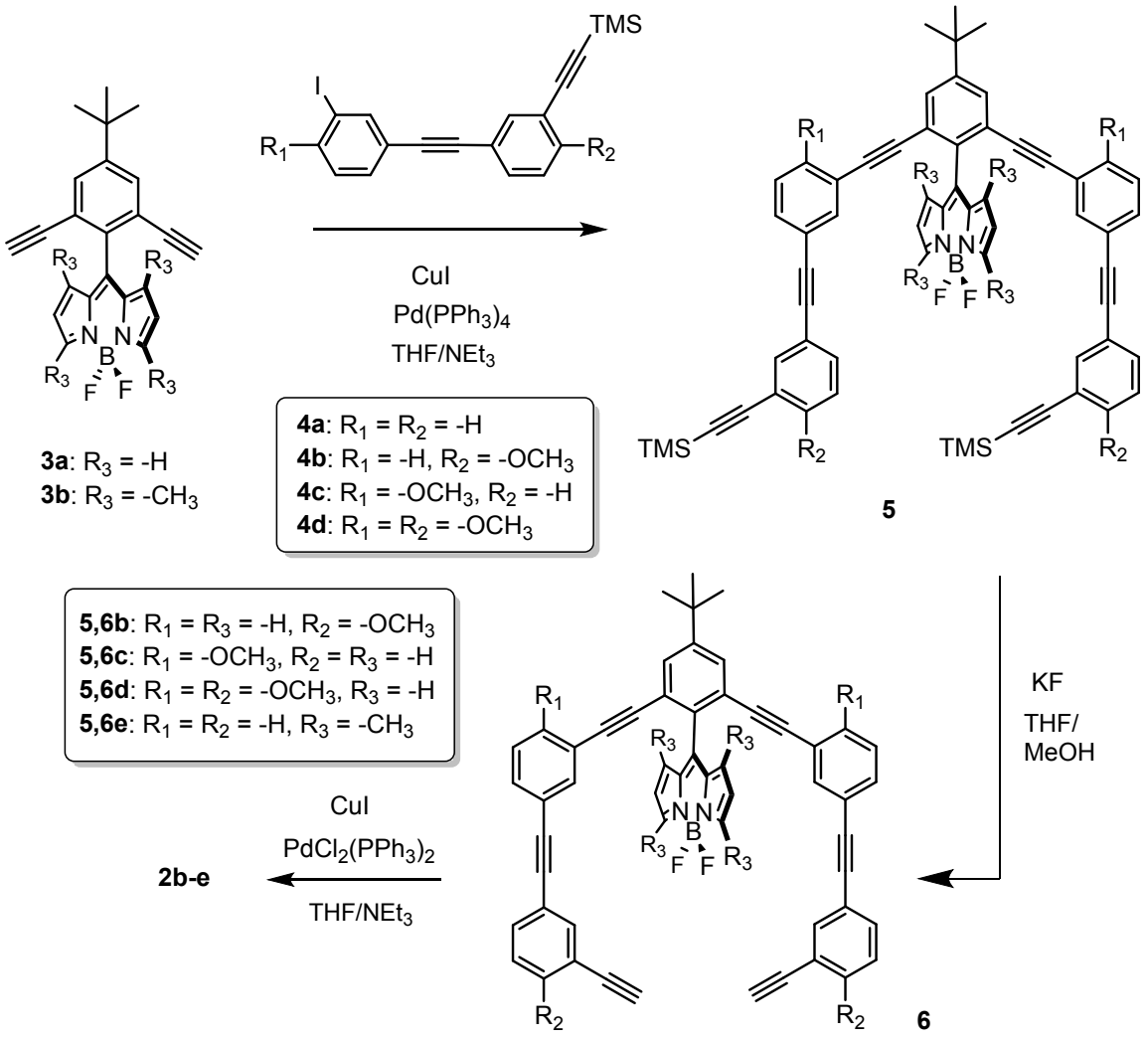
Synthesis of 4c. Compound **16c** (1.163 g, 2.883 mmol) and MeI (5.0 mL) were sealed in a heavy walled microwave vial under N_2 and heated to 120 ^oC for 12 h. The reaction mixture was cooled to RT and quenched with water and extracted with DCM. The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by column chromatography using Hex:EtOAc (9:1, R_f = 0.63) as the eluent to yield a yellowish liquid (1.154 g, 93%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 1H), 7.62 (s, 1H), 7.48-7.40 (m, 3H), 7.29-7.25 (m, 1H), 6.78 (d, J = 8.5 Hz, 1H), 3.91 (s, 3H), 0.25 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 158.36, 142.40, 134.93, 133.00, 131.51, 131.33, 128.34, 123.50, 123.42, 117.20, 104.12, 94.98, 88.22, 85.52, 56.45, -0.09. HRMS (EI-TOF): *m*/*z* 430.0248 ($[MH]^+$), calcd for $C_{20}H_{19}OISi$: *m*/*z* 430.0250.



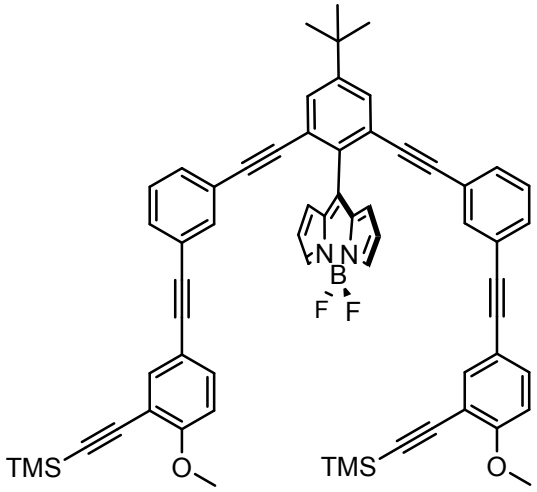
4d

Synthesis of 4d. Compound **16d** (0.74 g, 1.707 mmol) and MeI (3.5 mL) were sealed in a heavy walled microwave vial and heated to 120 ^oC for 8 h. The reaction mixture was cooled to RT, quenched with water and extracted with DCM. The organic phase was

dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by column chromatography using Hex:EtOAc (9:1, R_f = 0.38) as the eluent to yield a white fluffy solid (0.676 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.41 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 6H), 0.27 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 160.13, 158.11, 142.24, 137.28, 133.12, 132.79, 117.58, 115.33, 112.78, 110.75, 110.44, 100.19, 99.23, 88.12, 86.69, 85.49, 56.43, 55.99, 0.02. HRMS (EI-TOF): *m*/*z* 460.0361, calcd for $C_{21}H_{21}O_2ISi$: *m*/*z* 460.0356.

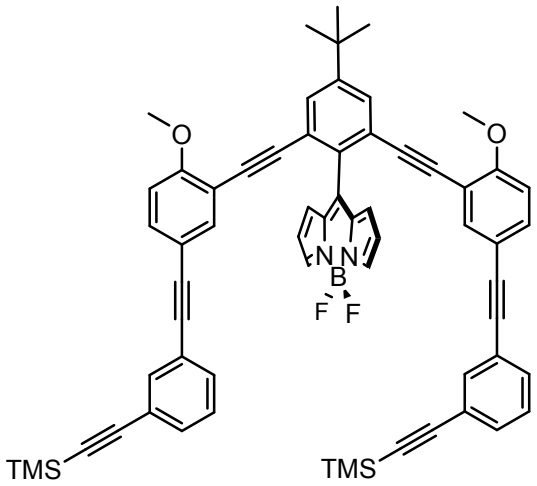


Scheme 3. Synthesis of BODIPY-Macrocycles **2b-e.**



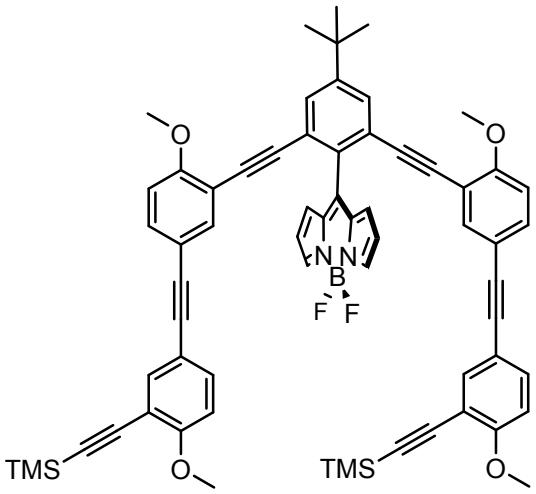
5b

Synthesis of 5b. To a mixture of **3a** (300 mg, 0.806 mmol), $Pd(PPh_3)_4$ (93 mg, 0.081 mmol) and CuI (31 mg, 0.161 mmol) in 15 mL of THF:NEt_3 (2:1) was added **4b** (763 mg, 1.773 mmol). The mixture was stirred at RT for 6 hrs, filtered and the solvent was removed from the filtrate *in vacuo*. The residue was dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:DCM (1:1, R_f = 0.44) as the eluent to give a red solid (394 mg, 50%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 2H), 7.67 (s, 2H), 7.61 (s, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.37 (m, 4H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.92 (d, 4.0 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 4.0 Hz, 2H), 3.91 (s, 6H), 1.44 (s, 9H), 0.27 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 160.27, 152.96, 144.48, 137.39, 134.29, 133.42, 131.45, 131.24, 129.23, 128.46, 123.63, 122.76, 112.76, 110.79, 100.18, 99.26, 93.99, 89.10, 87.73, 87.54, 77.22, 56.01, 34.94, 31.07, 0.02. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.44 (q). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.47 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m/z* 977.39260 ($[M+H]^+$), calcd for $C_{63}H_{56}BF_2N_2O_2$: *m/z* 977.39360.



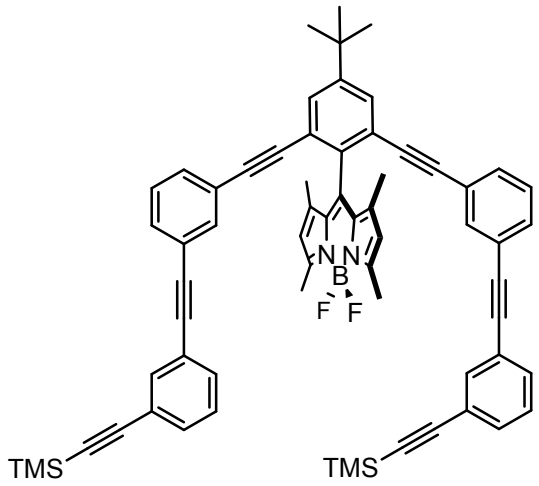
5c

Synthesis of 5c. To a mixture of **3a** (300 mg, 0.806 mmol), $PdCl_2(PPh_3)_2$ (57 mg, 0.081 mmol) and CuI (31 mg, 0.161 mmol) in 12 mL of THF:NEt_3 (2:1) was added **4c** (763 mg, 1.773 mmol). The mixture was stirred at RT for 12 hrs, filtered and the solvent from the filtrate removed *in vacuo*. The residue was dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:DCM (1:1, R_f = 0.52) as the eluent to give a red solid (200 mg, 25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.94 (s, 2H), 7.68 (s, 2H), 7.47 (d, J = 7.0 Hz, 2H), 7.41-7.35 (m, 4H), 7.29-7.26 (m, 4H), 6.91 (d, J = 4.0 Hz, 2H), 6.74 (d, J = 9.0 Hz, 2H), 6.48 (d, J = 4.0 Hz, 2H), 3.73 (s, 6H), 1.44 (s, 9H), 0.26 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 160.00, 144.07, 136.90, 134.88, 133.38, 131.45, 131.34, 131.16, 129.41, 128.34, 123.70, 123.41, 115.13, 112.15, 110.69, 94.83, 91.61, 90.03, 89.01, 87.60, 77.21, 55.90, 34.92, 31.08, -0.08. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -144.75 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.45 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): m/z 977.39111 ([M+H]$^+$), calcd for $C_{63}H_{56}BF_2N_2O_2$: m/z 977.39360.



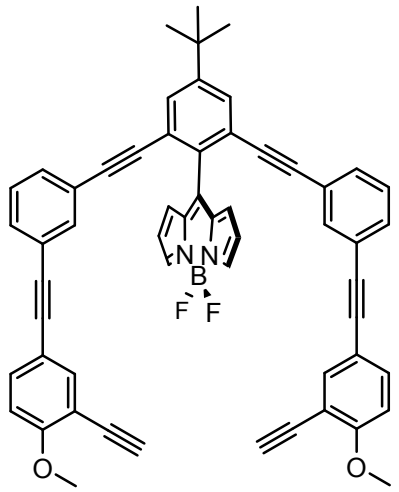
5d

Synthesis of 5d. Compound **3a** (220 mg, 0.591 mmol) was dissolved in 9 mL of THF:NEt_3 (2:1) and sparged with N_2 for 20 minutes prior to the addition of $Pd(PPh_3)_4$ (68 mg, 0.059 mmol), CuI (23 mg, 0.118 mmol) and **4d** (680 mg, 1.478 mmol). The mixture was stirred at RT for 6 hrs, filtered and the solvent from the filtrate removed *in vacuo*. The residue was dissolved in EtOAc and washed with NH_4Cl (sat). The extract was then washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:DCM (1:3, R_f = 0.40) as the eluent to give a red solid (360 mg, 59%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.94 (s, 2H), 7.68 (s, 2H), 7.61 (d, *J* = 2.5 Hz, 2H), 7.46 (dd, *J* = 2.5, 8.5 Hz, 2H), 7.34 (dd, *J* = 2.5, 8.5 Hz, 2H), 7.28-7.24 (m, 2H), 6.91 (d, *J* = 4.0 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 4.0 Hz, 2H), 3.89 (s, 6H), 3.72 (s, 6H), 1.44 (s, 9H), 0.28 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 160.02, 159.76, 152.69, 144.97, 144.09, 137.20, 136.75, 133.28, 133.18, 129.38, 124.05, 115.64, 115.51, 112.67, 112.08, 110.82, 110.69, 100.36, 99.09, 91.56, 90.16, 87.49, 77.25, 55.99, 55.88, 31.09. 0.05. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.23 (q). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.65 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m*/*z* 1036.40987 ($[M–F]^-$), calcd for $C_{65}H_{59}BF_2N_2O_4Si_2$: *m*/*z* 1036.40690.



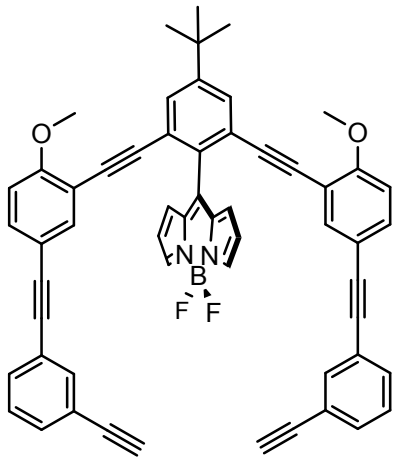
5e

Synthesis of 5e. To a mixture of **3b** (409 g, 0.955 mmol), $PdCl_2(PPh_3)_2$ (67 mg, 0.096 mmol) and CuI (36 mg, 0.191 mmol) in 11 mL of THF:NEt_3 (2:1) was added **4a** (803 mg, 2.006 mmol). The mixture was stirred at RT overnight, filtered and the solvent from the filtrate was removed *in vacuo*. The residue was dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:DCM (1:1, R_f = 0.70) as the eluent to give a red solid (725 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.68 (s, 4H), 7.51-7.42 (m, 8H), 7.33-7.20 (m, 6H), 6.00 (s, 2H), 2.62 (s, 6H), 1.57 (s, 6H), 1.44 (s, 9H), 0.28 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 155.43, 152.97, 142.24, 140.19, 139.19, 137.43, 137.29, 135.10, 134.70, 131.90, 131.77, 131.69, 131.55, 130.72, 129.89, 129.13, 128.51, 128.39, 125.1, 123.51, 123.30, 123.19, 123.03, 122.98, 121.01, 104.15, 95.01, 93.05, 89.08, 89.02, 87.49, 34.90, 31.19, 22.68, 14.74 14.15, 13.68, -0.06. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -146.24 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 1.00 (t, J_{FB} = 30 Hz). HRMS (ESI-TOF): *m*/*z* 972.4284 ([M–F]$^-$), calcd for $C_{65}H_{59}BFN_2Si_2$: *m*/*z* 972.4278.



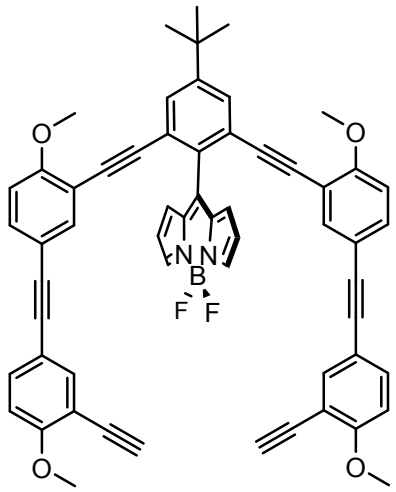
6b

Synthesis of 6b. Compound **5b** (390 mg, 0.399 mmol) was dissolved in MeOH:THF (1:1, 8.0 mL) with KF (116 mg, 1.998 mmol). The mixture was stirred for 2.5 hrs at RT, quenched with water and extracted with DCM. The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was chromatographed using Hex:DCM (1:2, R_f = 0.43) as the eluent to give a red viscous liquid (82 mg, 25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 2H), 7.67 (s, 2H), 7.63 (d, *J* = 2.0 Hz, 2H), 7.51 (dd, *J* = 2.0, 9.0 Hz, 2H) 7.37 (d, *J* = 9.0 Hz, 2H), 7.34 (s, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 4.0 Hz, 2H), 6.89 (d, *J* = 8.0, 2H), 6.50 (d, *J* = 4.0 Hz, 2H), 3.93 (s, 6H), 3.32 (s, 2H), 1.44 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 160.55, 152.98, 144.49, 137.30, 134.37, 133.79, 131.46, 131.26, 131.13, 129.21, 128.47, 123.74, 123.55, 122.65, 115.36, 111.67, 110.81, 93.98, 88.90, 87.76, 81.66, 79.11, 77.21, 56.05, 34.95, 31.07. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.43 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.48 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m*/*z* 833.31819 ($[M+H]^+$), calcd for $C_{57}H_{40}BF_2N_2O_2$: *m*/*z* 833.31454.



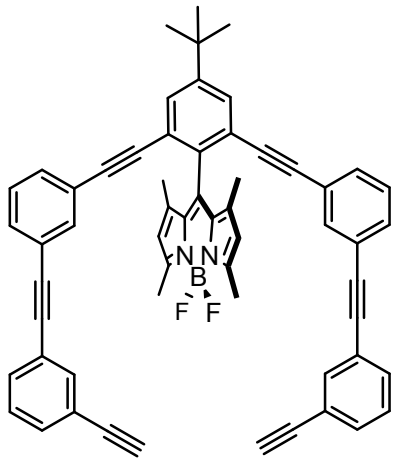
6c

Synthesis of 6c. Compound **5c** (200 mg, 0.205 mmol) was dissolved in MeOH:THF (1:1, 6.0mL) with KF (59 mg, 1.023 mmol). The mixture was stirred for 2 hrs at RT, quenched with water and extracted with DCM. The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was chromatographed using Hex:DCM (1:2, R_f = 0.57) as the eluent to give a red sticky solid (103 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.95 (s, 2H), 7.69 (s, 2H), 7.64 (s, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.37 (dd, *J* = 2.5, 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 2.5 Hz, 2H), 6.91 (d, *J* = 4.0 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.49 (d, *J* = 4.0 Hz, 2H), 3.74 (s, 6H), 3.09 (s, 2H), 1.44 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 160.01, 152.72, 144.11, 136.97, 134.94, 133.40, 131.82, 131.57, 131.16, 129.38, 128.46, 123.99, 123.85, 122.41, 115.06, 112.16, 110.69, 91.64, 90.05, 89.17, 87.45, 82.89, 77.67, 77.21, 55.91, 34.93, 31.08. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -144.77 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.46 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m*/*z* 813.30798 ([M–F]$^-$), calcd for $C_{57}H_{39}BFN_2O_2$: *m*/*z* 813.30831.



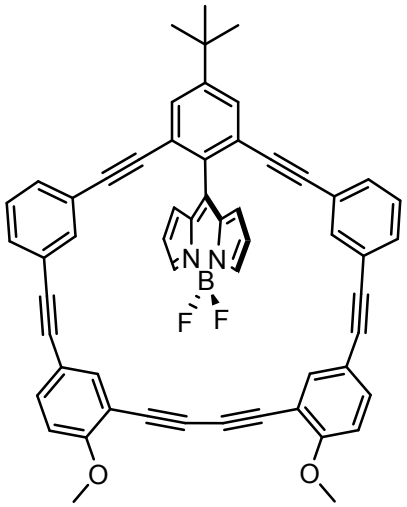
6d

Synthesis of 6d. Compound **5d** (353 mg, 0.341 mmol) was dissolved in MeOH:THF (1:1, 7 mL) with KF (99 mg, 1.704 mmol). The mixture was stirred for 2 hrs, quenched with water and extracted with DCM. The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was chromatographed using Hex:DCM (1:3, R_f = 0.30) as the eluent to give a red viscous liquid (100 mg, 28%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.94 (s, 2H), 7.68 (s, 2H), 7.62 (d, *J* = 2.0 Hz, 2H), 7.51 (dd, *J* = 2.0, 8.5 Hz, 2H), 7.35 (dd, *J* = 2.0, 8.5 Hz, 2H), 7.26 (s, 2H), 6.91-6.87 (m, 4H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 2.0 Hz, 2H), 3.93 (s, 6H), 3.73 (s, 6H), 3.31 (s, 2H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 160.29, 159.77, 152.69, 144.09, 137.10, 136.82, 135.95, 133.63, 133.19, 131.16, 129.36, 124.02, 118.34, 115.83, 115.42, 112.10, 111.57, 110.81, 110.67, 91.58, 90.14, 87.63, 87.29, 81.53, 79.24, 56.03, 55.89, 34.92, 31.08. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -144.76 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.63 (t, J_{FB} = 30 Hz). HRMS (ESI-TOF): *m*/*z* 893.33438 ([M+H]$^+$), calcd for $C_{59}H_{44}BF_2N_2O_4$: *m*/*z* 893.33567.



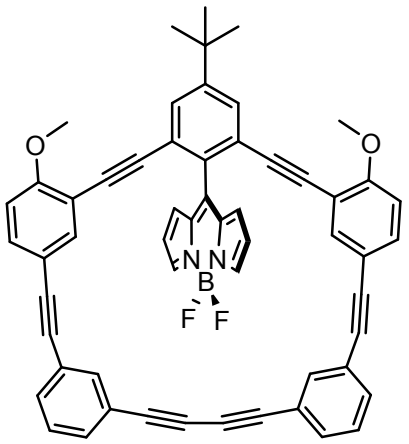
6e

Synthesis of 6e. Compound **5e** (958 mg, 0.984 mmol) was dissolved in MeOH:THF (1:1, 20 mL) with KF (286 mg, 4.921 mmol). The mixture was stirred overnight at RT, quenched with water and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was chromatographed using Hex:EtOAc (9:1, R_f = 0.23) as the eluent to give a reddish viscous liquid (555 mg, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (s, 4H), 7.75-7.72 (m, 4H), 7.50-7.46 (m, 6H), 7.38-7.28 (m, 4H), 6.03 (s, 2H), 3.15 (s, 2H), 2.66 (s, 6H), 1.61 (s, 6H), 1.46 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 155.38, 152.95, 152.93, 142.20, 139.15, 137.33, 135.36, 135.12, 134.70, 131.91, 131.88, 131.75, 131.52, 129.08, 128.47, 128.46, 123.44, 123.17, 122.96, 122.95, 122.45, 121.02, 92.99, 89.18, 88.81, 87.47, 82.74, 77.79, 34.88, 31.16, 14.73, 13.66. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -146.30 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.46 (t, J_{FB} = 30 Hz). HRMS (EI-TOF): *m*/*z* 828.3490 ([MH]$^+$), calcd for $C_{59}H_{43}BF_2N_2$: *m*/*z* 828.3487.



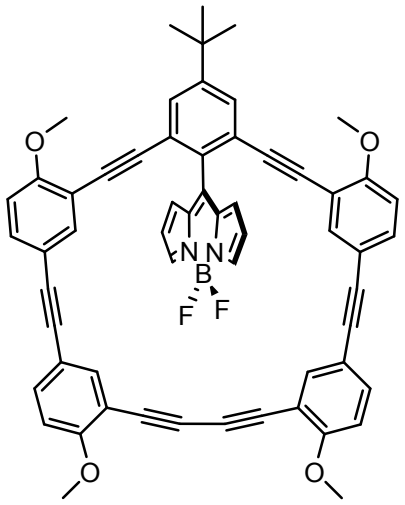
2b

Synthesis of 2b. Compound **6b** (82 mg, 0.098 mmol) was dissolved in THF:NEt_3 (2:1, 98 mL) and sparged with N_2 for 30 minutes prior to the addition of $PdCl_2(PPh_3)_2$ (34 mg, 0.049 mmol) and CuI (19 mg, 0.098 mmol). The mixture was stirred at RT for 34 hrs, filtered and the solvent from the filtrate was removed *in vacuo*. The residue was dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:DCM (1:1, R_f = 0.29) as the eluent to give a dark red solid (19 mg, 23%). ^{1}H NMR $CDCl_3$, 400 MHz): δ = 8.12 (s, 2H), 8.10 (s, 2H), 7.68 (s, 2H), 7.38 (dd, *J* = 4 Hz, 8Hz, 2H), 7.33 (s, 2H), 7.31 (s, 2H), 7.23 (t, *J* = 8 Hz, 2H), 7.10 (s, 2H), 6.94 (d, *J* = 4.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.49 (s, 2H), 3.93 (s, 6H), 1.45 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 159.91, 152.89, 144.76, 141.90, 137.05, 135.61, 131.94, 131.02, 129.87, 129.57, 129.09, 128.19, 123.96, 123.82, 122.71, 118.57, 112.48, 110.73, 94.04, 89.80, 88.37, 88.07, 79.60, 78.93, 77.22, 56.03, 34.94, 31.08. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.86 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.71 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m*/*z* 811.29202 ([M–F]), calcd for $C_{57}H_{37}BFN_2O_2$: *m*/*z* 811.29266.



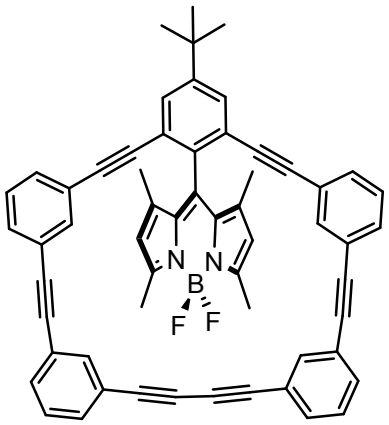
2c

Synthesis of 2c. Compound **6c** (103 mg, 0.124 mmol) was dissolved in THF:NEt_3 (2:1, 124 mL) and sparged with N_2 for 30 minutes prior to the addition of $PdCl_2(PPh_3)_2$ (44 mg, 0.062 mmol) and CuI (24 mg, 0.124 mmol). The mixture was stirred at RT for 32 hrs, filtered and the solvent from the filtrated was removed *in vacuo*. The residue was dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:DCM (1:1, R_f = 0.35) as the eluent to give a red solid (25 mg, 24%). ^{1}H NMR $CDCl_3$, h400 MHz): δ = 8.11 (m, 4H), 7.71 (s, 2H), 7.40- 7.33 (m, 6H), 7.30 (t, *J* = 4.0 Hz, 2H), 7.06 (d, *J* = 2.0 Hz, 2H), 6.94 (d, *J* = 4.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 4.0 Hz, 2H), 3.92 (s, 6H), 1.44 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 159.17, 144.58, 139.81, 139.13, 129.96, 129.19, 128.31, 124.08, 123.87, 122.59, 115.58, 112.18, 110.35, 92.01, 90.32, 89.75, 88.23, 82.56, 75.13, 55.95, 34.97, 31.08. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.90 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.70 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m*/*z* 811.29349 ([M–F]$^-$), calcd for $C_{57}H_{37}BFN_2O_2$: *m*/*z* 811.29266.



2d

Synthesis of 2d. Compound **6d** (93 mg, 0.104 mmol) was dissolved in THF:NEt_3 (2:1, 105 mL) and sparged with N_2 for 45 minutes prior to the addition of $PdCl_2(PPh_3)_2$ (8.3 mg, 0.012 mmol) and CuI (4.5 mg, 0.024 mmol). The mixture was stirred at RT for 21 hrs, filtered and the solvent from the filtrate was removed *in vacuo*. The residue was dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:DCM (1:2, R_f = 0.26) as the eluent to give a dark red solid (21 mg, 23%). ^{1}H NMR $CDCl_3$, 400 MHz): δ = 8.10 (s, 2H), 8.05 (d, *J* = 2.0 Hz, 2H), 7.70 (s, 2H), 7.36 (dd, *J* = 2.0, 8.5 Hz, 2H), 7.31 (dd, *J* = 2.0, 8.5 Hz, 2H), 7.03 (d, *J* = 2.0 Hz, 2H), 6.93 (d, *J* = 4.0 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 4.0 Hz, 2H), 3.92 (s, 6H), 3.91 (s, 6H), 1.44 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 159.51, 158.84, 152.66, 144.62, 141.53, 138.79, 135.20, 131.55, 131.09, 129.21, 128.95, 128.92, 128.91, 123.89, 118.50, 116.16, 116.00, 112.36, 112.10, 110.67, 110.31, 91.94, 90.40, 88.16, 88.13, 79.74, 78.86, 56.00, 55.92, 34.96, 31.06. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.84 (q). ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ = 0.87 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m*/*z* 890.31413 ([M+H]$^+$), calcd for $C_{59}H_{41}BF_2N_2O_4$: *m*/*z* 890.31220.



2e

Synthesis of 2e. Compound **6e** (199 mg, 0.240 mmol) was dissolved in THF:NEt_3 (2:1, 120 mL) and sparged with N_2 for 15 minutes prior to the addition of $PdCl_2(PPh_3)_2$ (25 mg, 0.036 mmol) and CuI (46 mg, 0.240 mmol). The mixture was stirred overnight at RT, filtered and the solvent from the filtrate was removed *in vacuo*. The residue was re-dissolved in EtOAc, washed with NH_4Cl (sat) and brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was chromatographed using Hex:DCM (2:1, R_f = 0.35) as the eluent to give a dark red solid (32 mg, 16%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.72 (s, 2H), 7.68 (s, 2H), 7.57-7.49 (m, 6H), 7.43- 7.35 (m, 6H), 7.28-7.24 (m, 2H), 6.01 (s, Hz, 2H), 2.63 (s, 6H), 1.57 (s, 6H), 1.43 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 155.39, 152.92, 142.18, 139.13, 135.35, 134.65, 132.25, 131.46, 129.02, 128.60, 128.44, 123.64, 122.95, 122.05, 121.03, 93.01, 89.44, 88.68, 87.50, 80.89, 74.39, 34.88, 31.15, 14.75, 13.66. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -146.9 (q). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128 MHz): δ = 0.99 (t, J_{FB} = 31 Hz).

DFT Calculations and FMOs

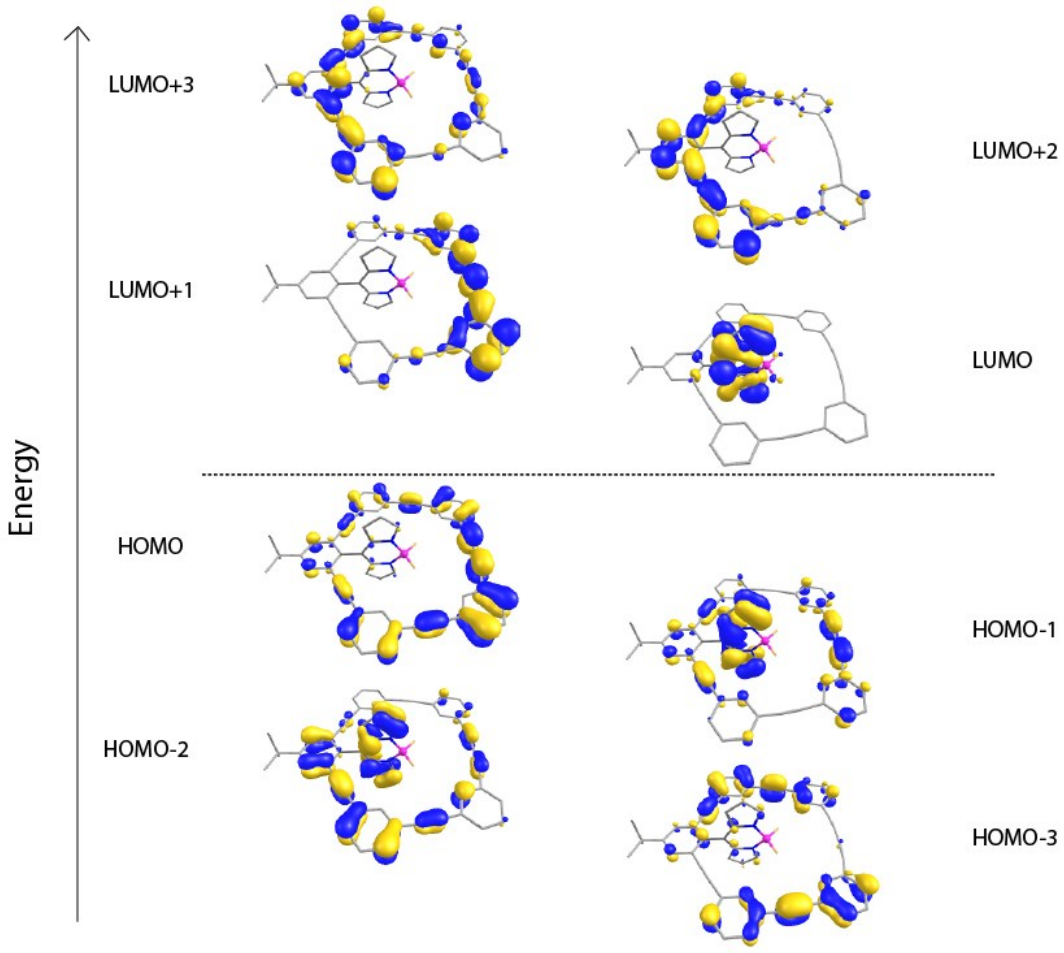


Table S1. Selected TD–DFT optical transitions[a] for **2a**. The most relevant FMOs of **2a** are shown above.

λ (nm) (exp.)	λ (nm) (calc.)	Oscillator Strength *(f)*	Active MOs (Transitions)	Molecular Contributions (%)
512	421	0.435	HOMO-2 → LUMO	36.0
			HOMO-1 → LUMO	45.0
489	358	0.678	HOMO-1 → LUMO+1	14.0
			HOMO → LUMO+1	52.0
338	332	0.407	HOMO-2 → LUMO+1	25.0
			HOMO-1 → LUMO+3	35.0
			HOMO → LUMO+3	15.0
305	297	1.553	HOMO-3 → LUMO+1	29.0
292	285	2.055	HOMO → LUMO+2	50.7
			HOMO-3 → LUMO+2	24.0

[a] TD-DFT (6-31G*/CAM-B3LYP) level of theory on geometry optimized structure.

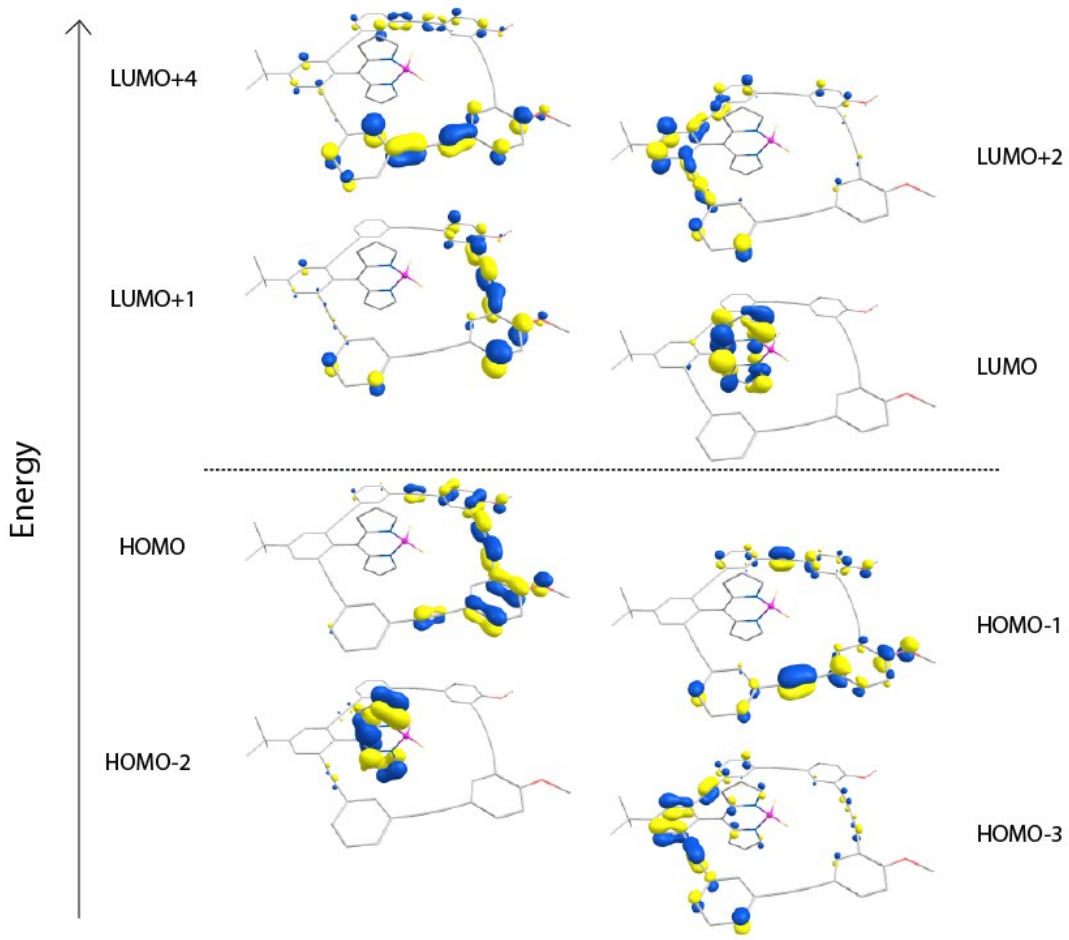


Table S2. Selected TD–DFT optical transitions[a] for **2b**. The most relevant FMOs of **2b** are shown above.

λ (nm) (exp.)	λ (nm) (calc.)	Oscillator Strength *(f)*	Active MOs (Transitions)	Molecular Contributions (%)
511	414	0.468	HOMO-2 → LUMO	88.8
			HOMO-3 → LUMO	7.5
486	363	0.014	HOMO-3 → LUMO	67.9
			HOMO → LUMO	11.6
364	329	0.811	HOMO → LUMO+1	48.8
			HOMO → LUMO+2	10.6
313	293	0.257	HOMO-1 → LUMO+4	23.7
			HOMO → LUMO+5	12.7
291	288	1.971	HOMO-1 → LUMO+1	34.8
			HOMO → LUMO+4	13.1
283	282	0.979	HOMO-1 → LUMO+2	12.6
			HOMO-3 → LUMO+2	10.4

[a] TD-DFT (6-31G*/CAM-B3LYP) level of theory on geometry optimized structure.

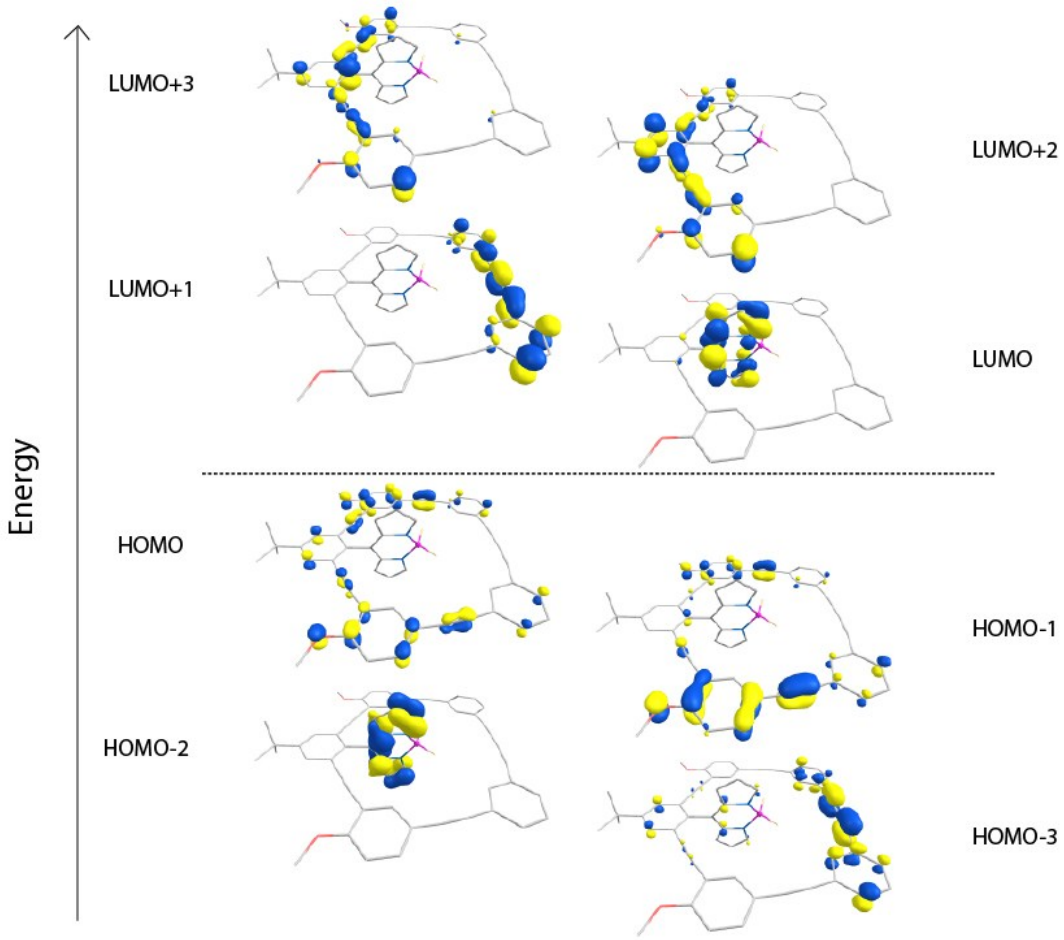


Table S3. Selected TD–DFT optical transitions[a] for **2c**. The most relevant FMOs of **2c** are shown above.

λ (nm) (exp.)	λ (nm) (calc.)	Oscillator Strength *(f)*	Active MOs (Transitions)	Molecular Contributions (%)
511	415	0.448	HOMO-2 → LUMO	82.1
			HOMO → LUMO	8.7
486	380	0.032	HOMO → LUMO	57.1
			HOMO-3 → LUMO	20.7
337	315	0.393	HOMO-3 → LUMO+1	36.3
			HOMO-4 → LUMO+1	8.5
313	301	1.646	HOMO-1 → LUMO+2	28.0
			HOMO → LUMO+3	31.1
295	286	2.290	HOMO-1 → LUMO+1	27.9
			HOMO → LUMO+4	27.0

[a] TD-DFT (6-31G*/CAM-B3LYP) level of theory on geometry optimized structure.

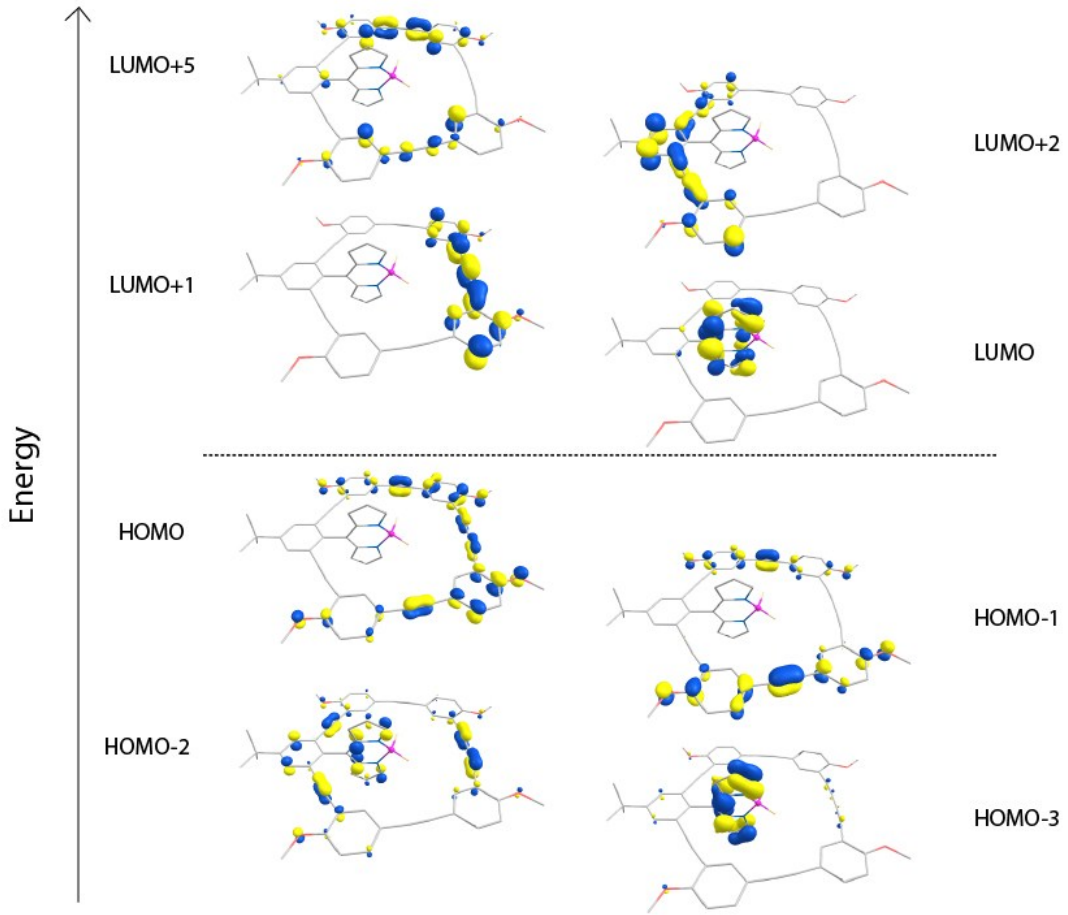


Table S4. Selected TD–DFT optical transitions[a] for **2d** and the FMOs are shown above.

λ (nm) (exp.)	λ (nm) (calc.)	Oscillator Strength *(f)*	Active MOs (Transitions)			Molecular Contributions (%)
511	415	0.446	HOMO-3	→	LUMO	56.0
			HOMO-2	→	LUMO	37.8
487	383	0.032	HOMO	→	LUMO	44.8
			HOMO-3	→	LUMO	23.5
376	330	0.774	HOMO-2	→	LUMO+1	18.6
			HOMO	→	LUMO+1	48.6
348	303	1.277	HOMO-1	→	LUMO+2	25.3
			HOMO	→	LUMO+3	18.9
317	292	1.018	HOMO-1	→	LUMO+1	29.3
			HOMO	→	LUMO+4	12.1
			HOMO11	→	LUMO	16.7
300	283	1.269	HOMO-1	→	LUMO+5	24.0
			HOMO	→	LUMO+4	24.5

[a] TD-DFT (6-31G*/CAM-B3LYP) level of theory on geometry optimized structure.

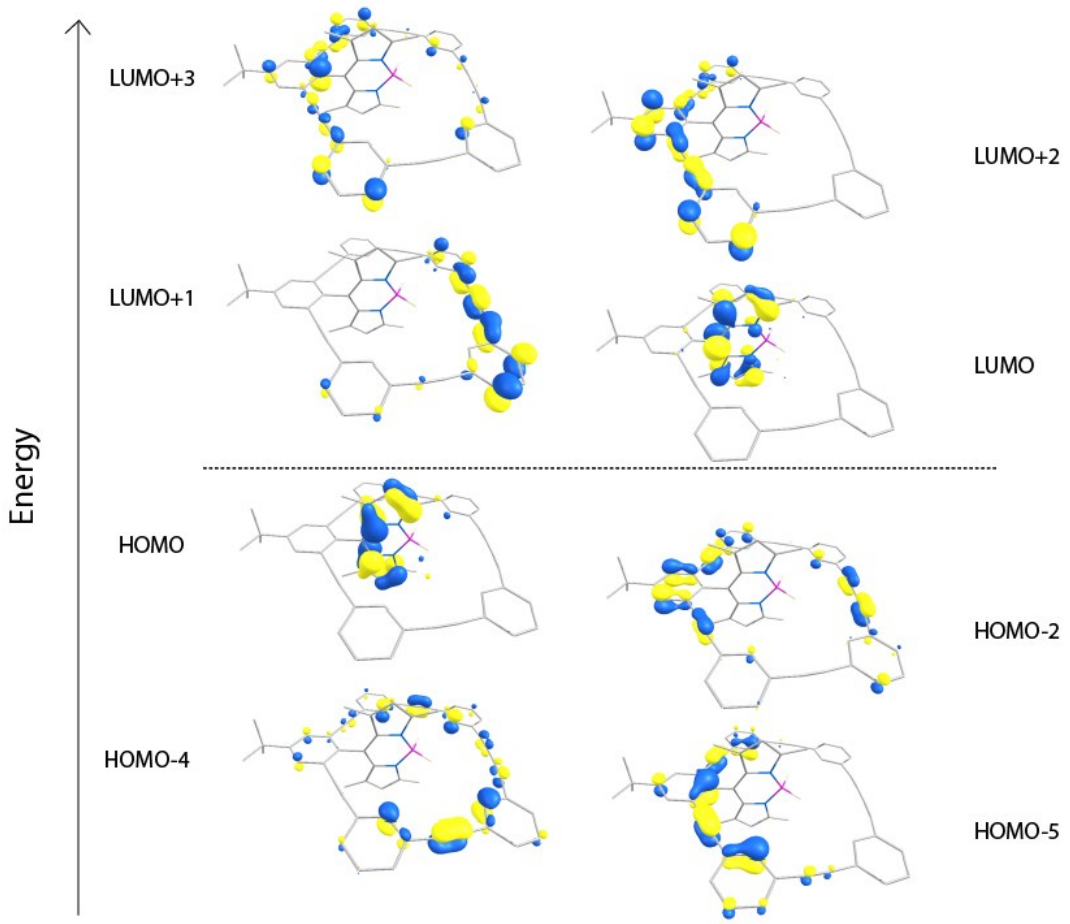


Table S5. Selected TD–DFT optical transitions[a] for **2e** and the FMOs are shown above.

λ (nm) (exp.)	λ (nm) (calc.)	Oscillator Strength *(f)*	Active MOs (Transitions)			Molecular Contributions (%)
510	430	0.552	HOMO	→	LUMO	98.0
335	315	0.647	HOMO-5	→	LUMO	79.0
			HOMO-2	→	LUMO	11.0
306	294	0.211	HOMO	→	LUMO+2	60.0
290	280	1.691	HOMO-5	→	LUMO+3	08.0
			HOMO-4	→	LUMO+2	13.0
			HOMO-3	→	LUMO+1	07.0
			HOMO-3	→	LUMO+2	06.0
			HOMO-3	→	LUMO+5	07.0
			HOMO-2	→	LUMO+2	13.0
			HOMO-2	→	LUMO+4	05.0
			HOMO-1	→	LUMO+4	10.0
			HOMO	→	LUMO+2	07.9

[a] TD-DFT (6-31G*/CAM-B3LYP) level of theory on geometry optimized structure.

Table S6. Molar extinction coefficients (ε) of **2b**, **2c**, **2d** and **2e** along with their corresponding wavelengths.

2b		**2c**		**2d**		**2e**	
λ_{abs} *(nm)*	ε *($LM^{-1}cm^{-1}$)*	λ_{abs} *(nm)*	ε *($LM^{-1}cm^{-1}$)*	λ_{abs} *(nm)*	ε *($LM^{-1}cm^{-1}$)*	λ_{abs} *(nm)*	ε *($LM^{-1}cm^{-1}$)*
294	96990	295	102845	300	109400	290	120000
312	75375	314	67222	318	72350	306	103550
364	26470	337	46960	376	26350	335	31220

X-Rays Crystallography

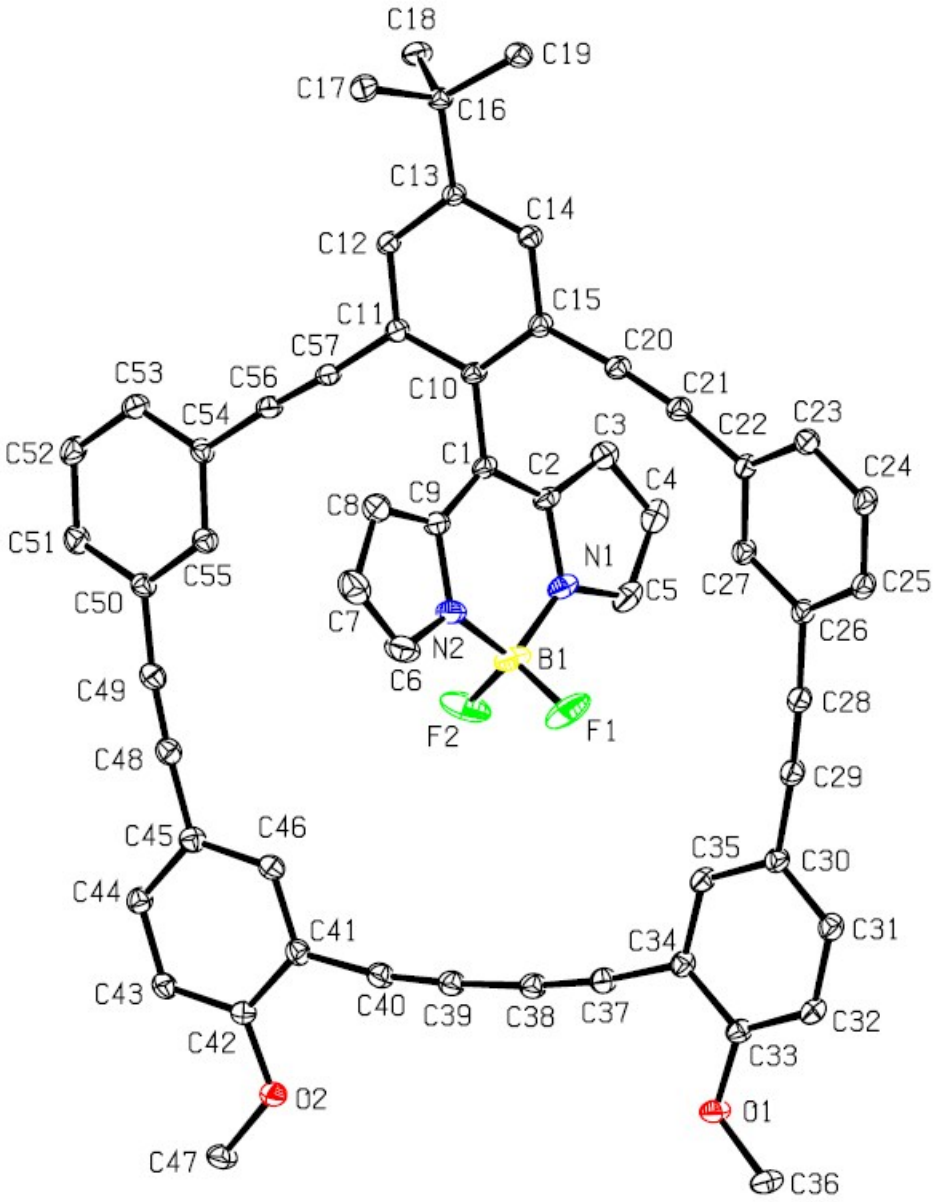


Figure 1. Crystal structure of BODIPY-macrocycle **2b**

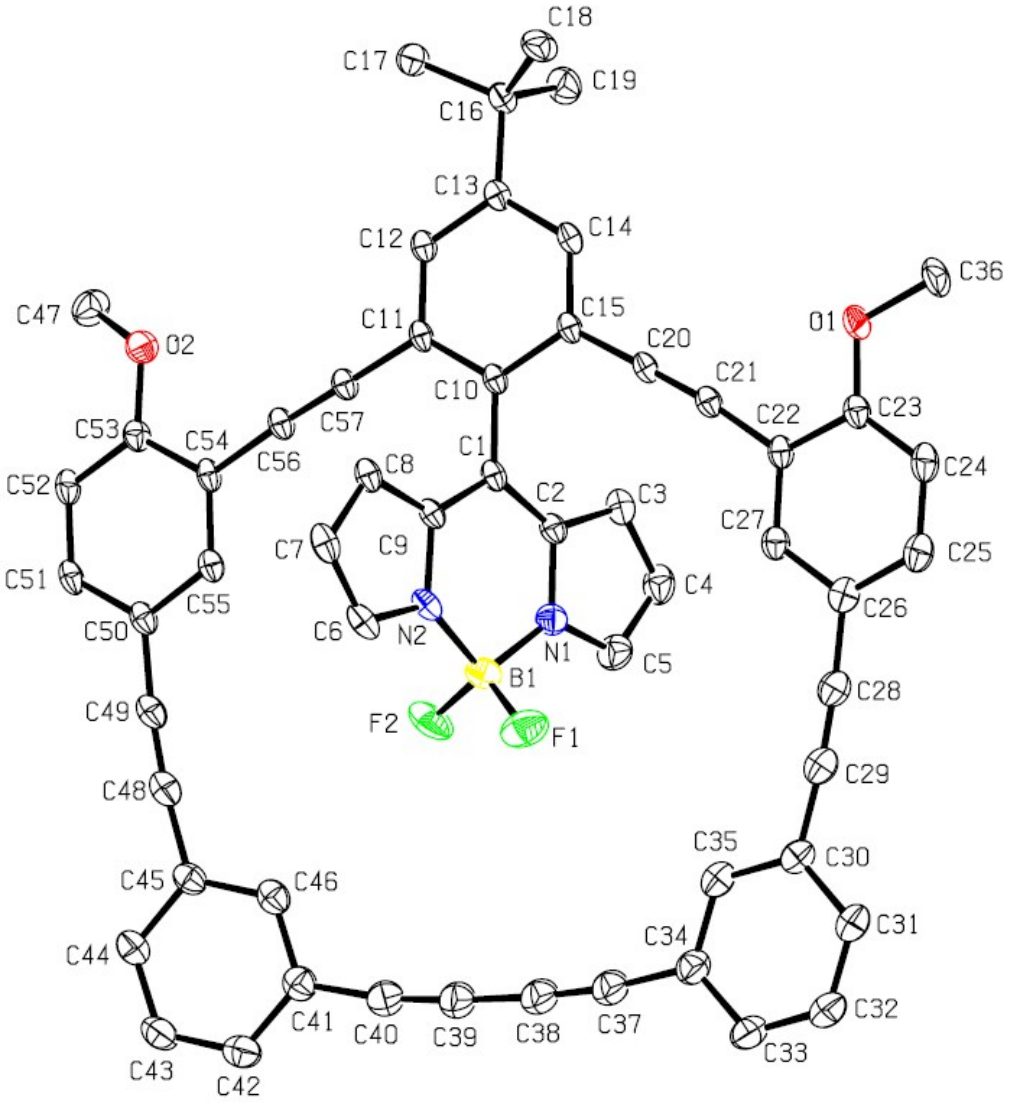


Figure 2. Crystal structure of BODIPY-macrocycle **2c**

NMR Spect

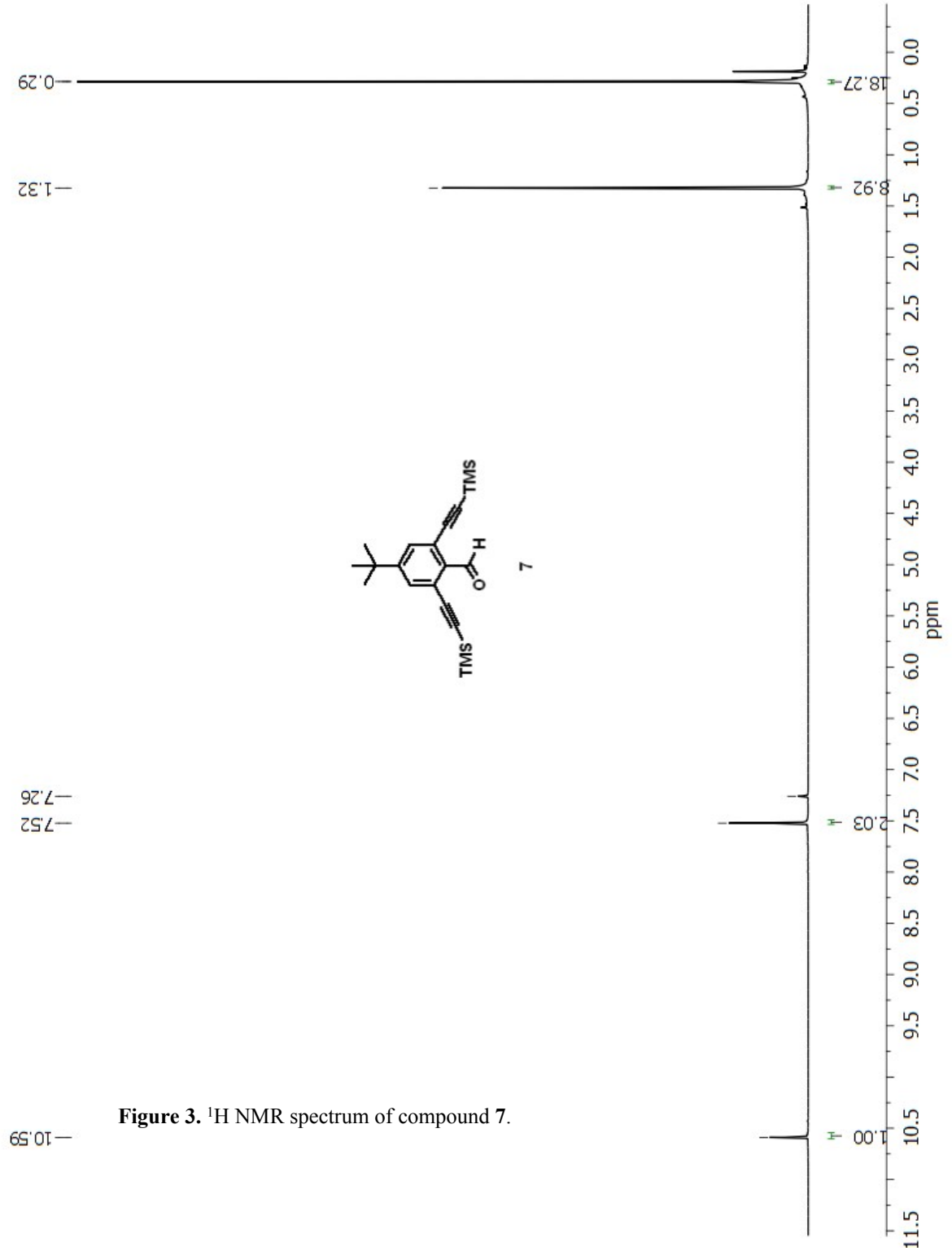


Figure 3. ^{1}H NMR spectrum of compound **7**.

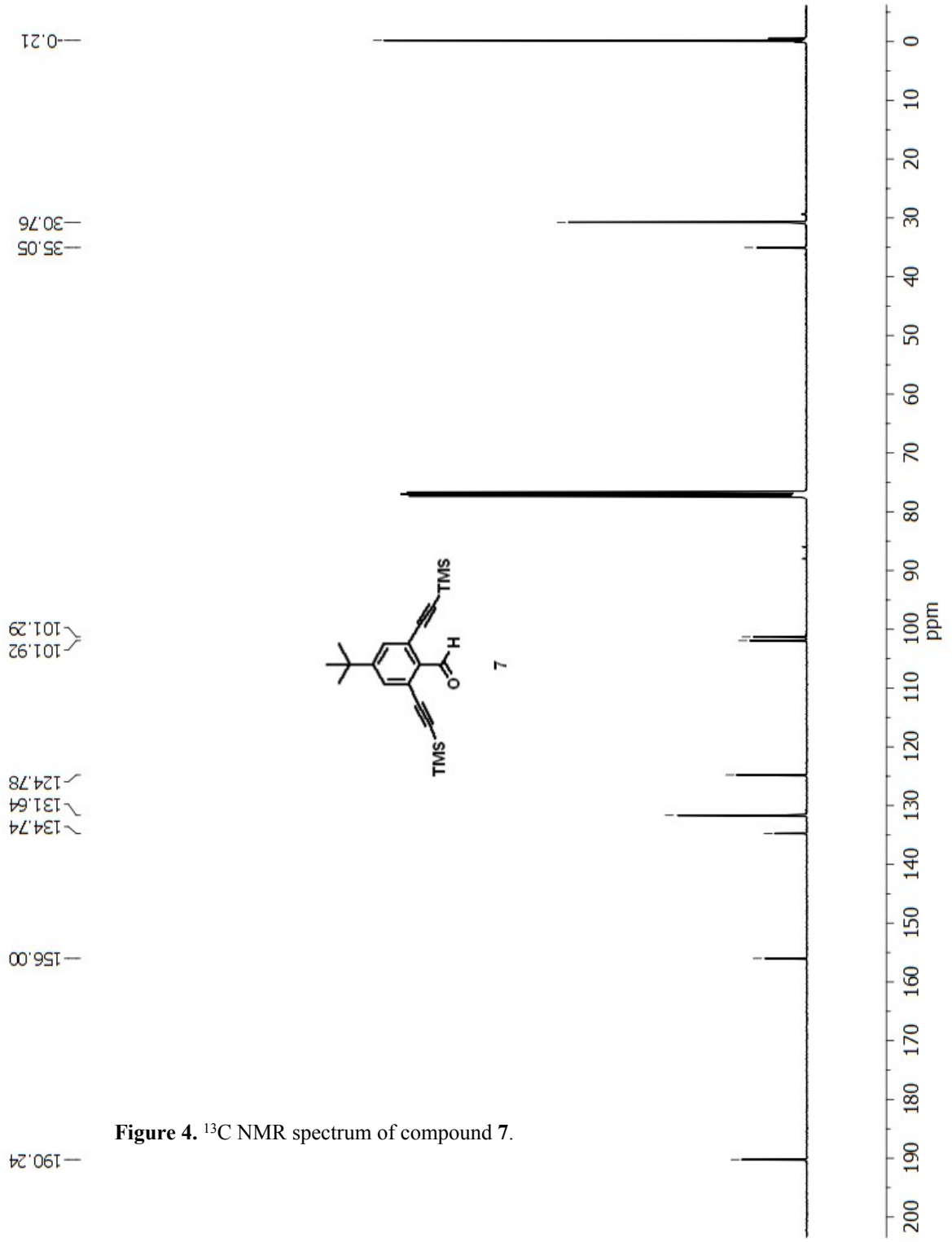


Figure 4. ^{13}C NMR spectrum of compound **7**.

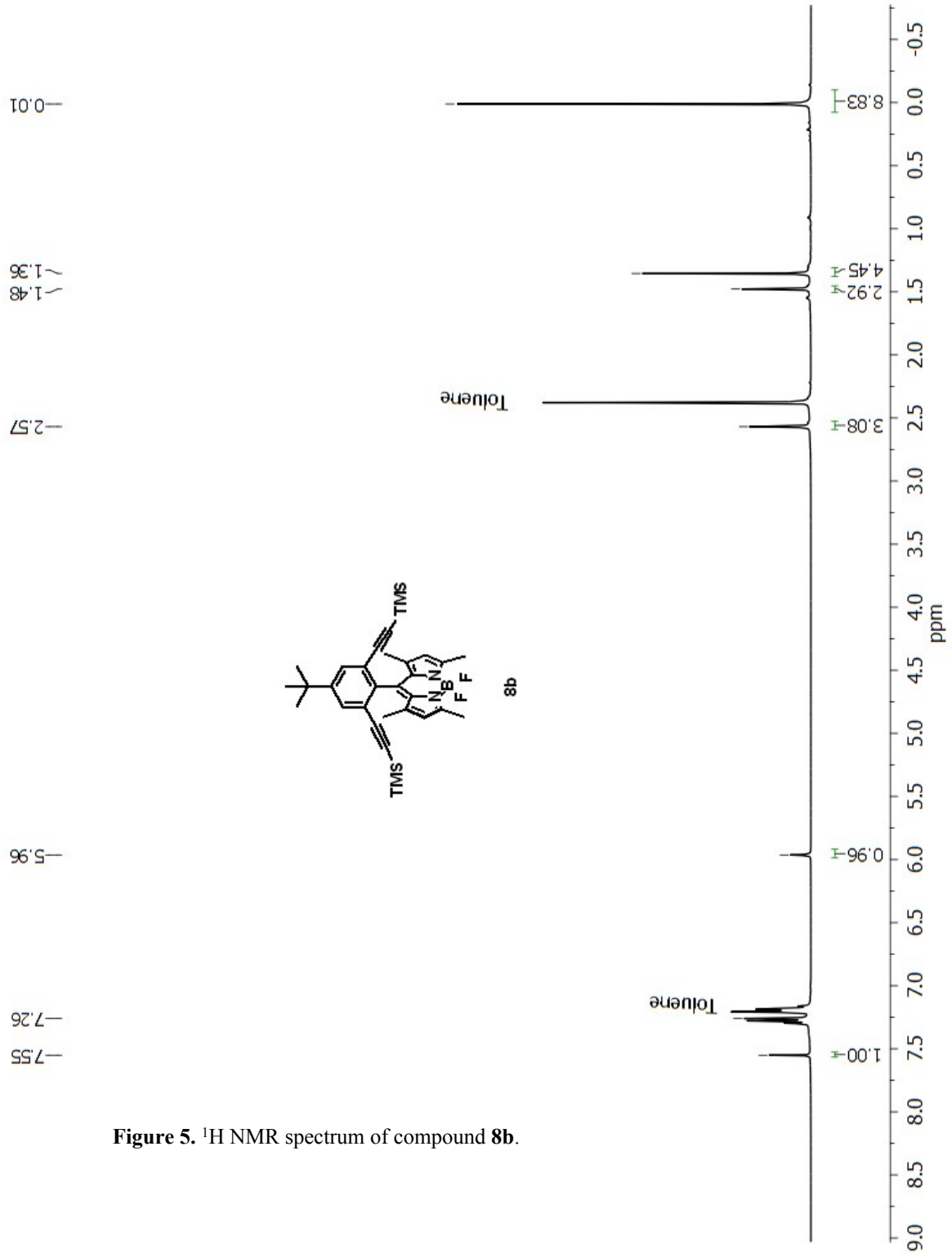


Figure 5. [1]H NMR spectrum of compound **8b**.

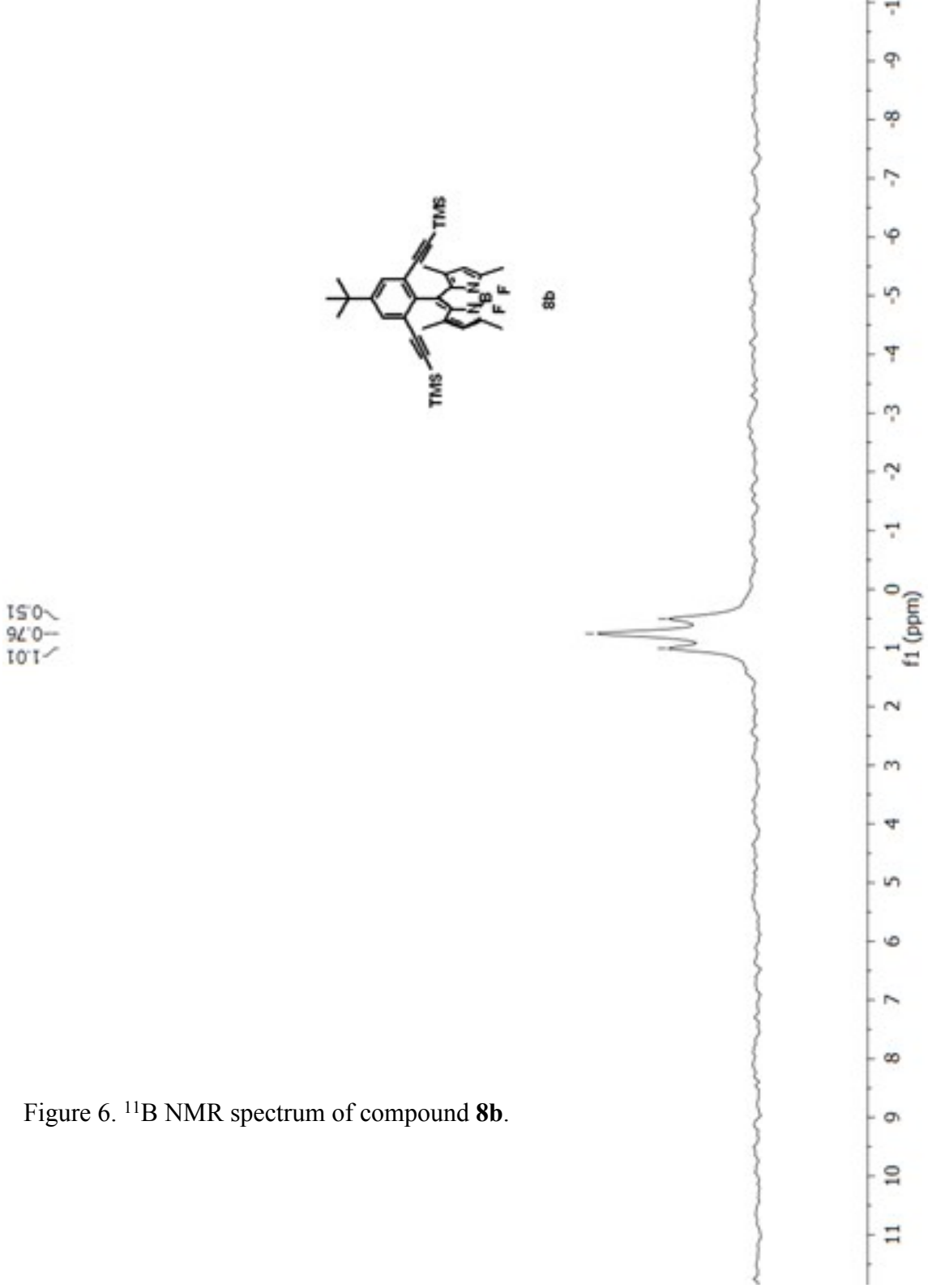


Figure 6. ^{11}B NMR spectrum of compound **8b**.

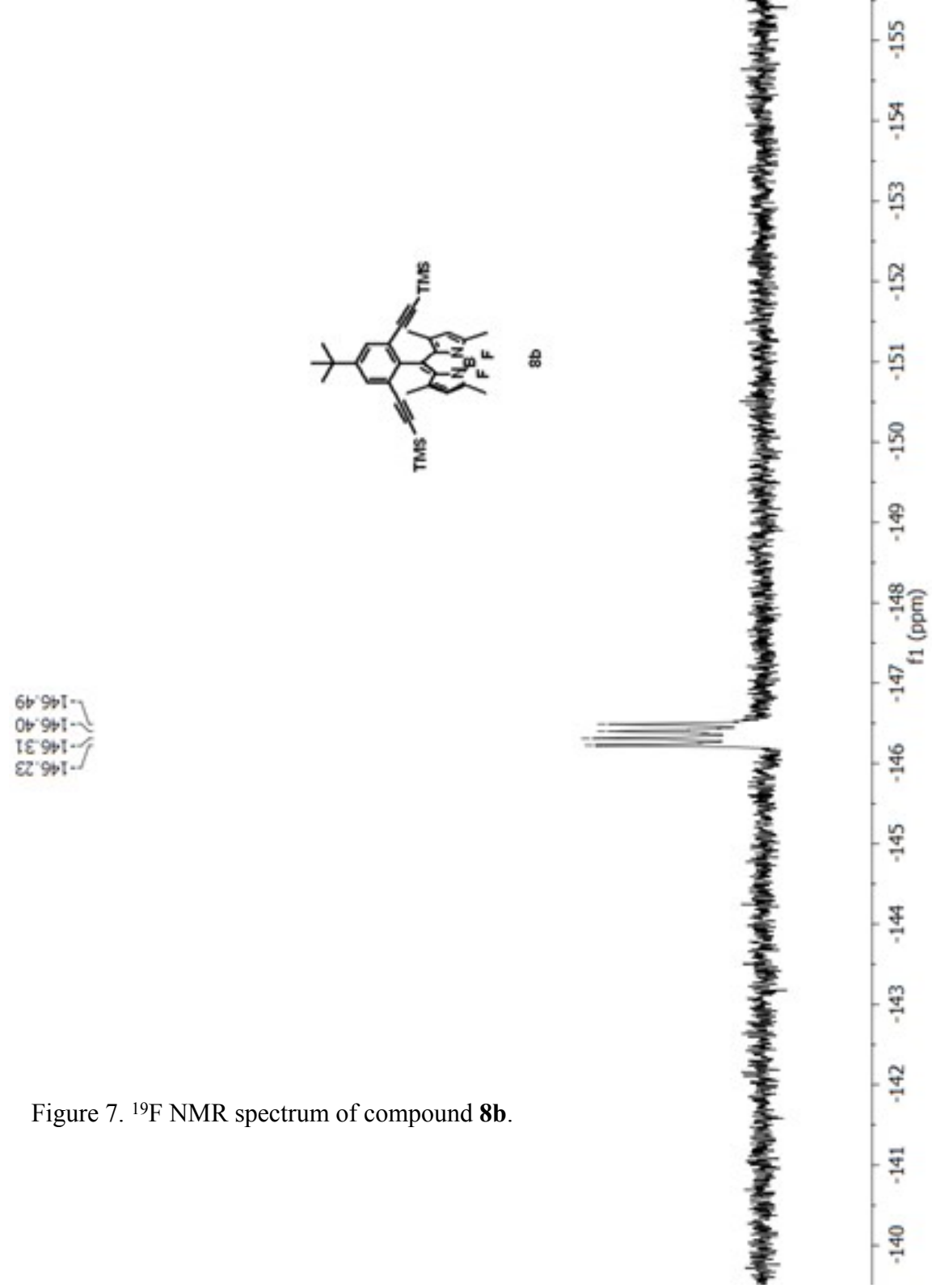


Figure 7. ^{19}F NMR spectrum of compound **8b**.

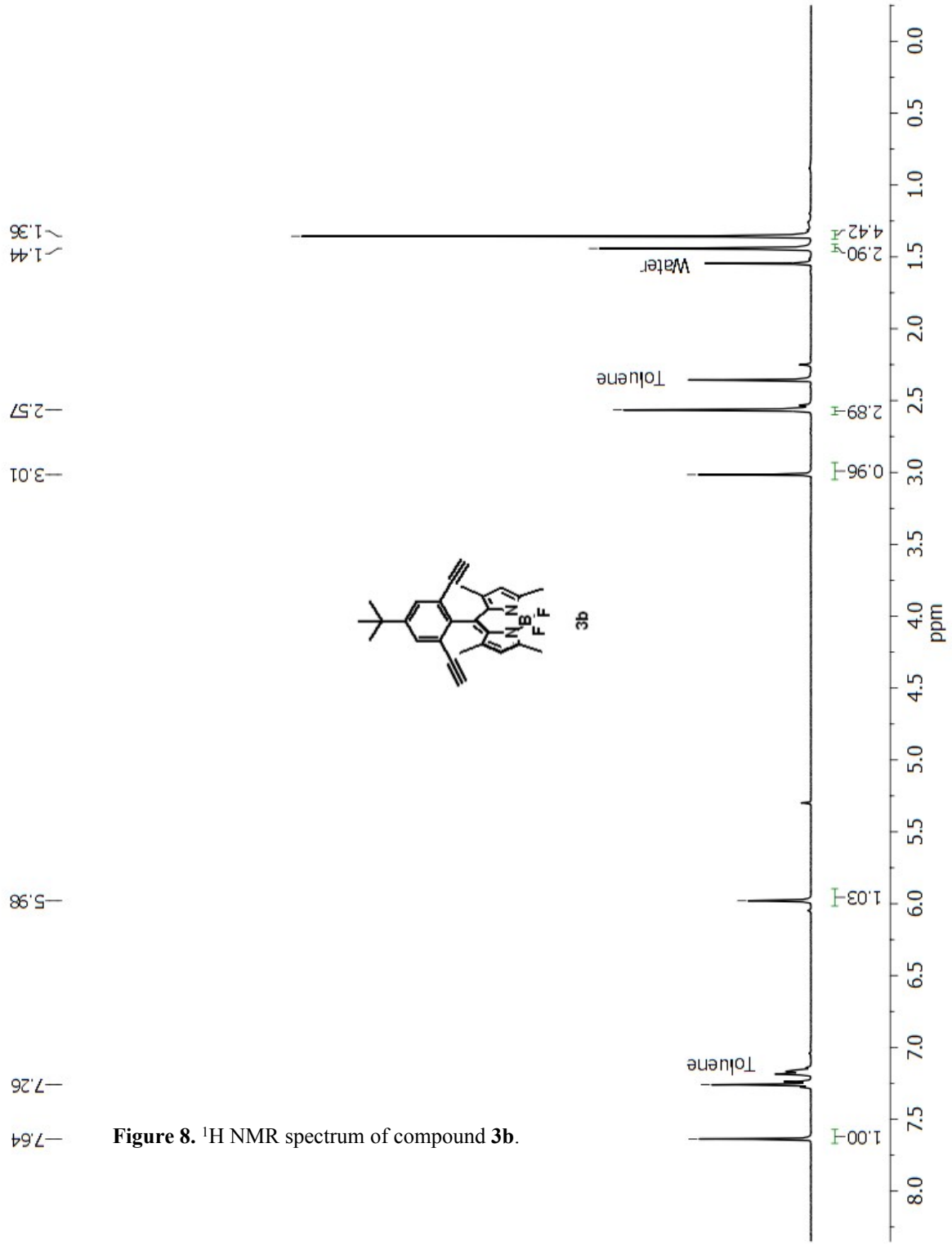


Figure 8. ^{1}H NMR spectrum of compound **3b**.

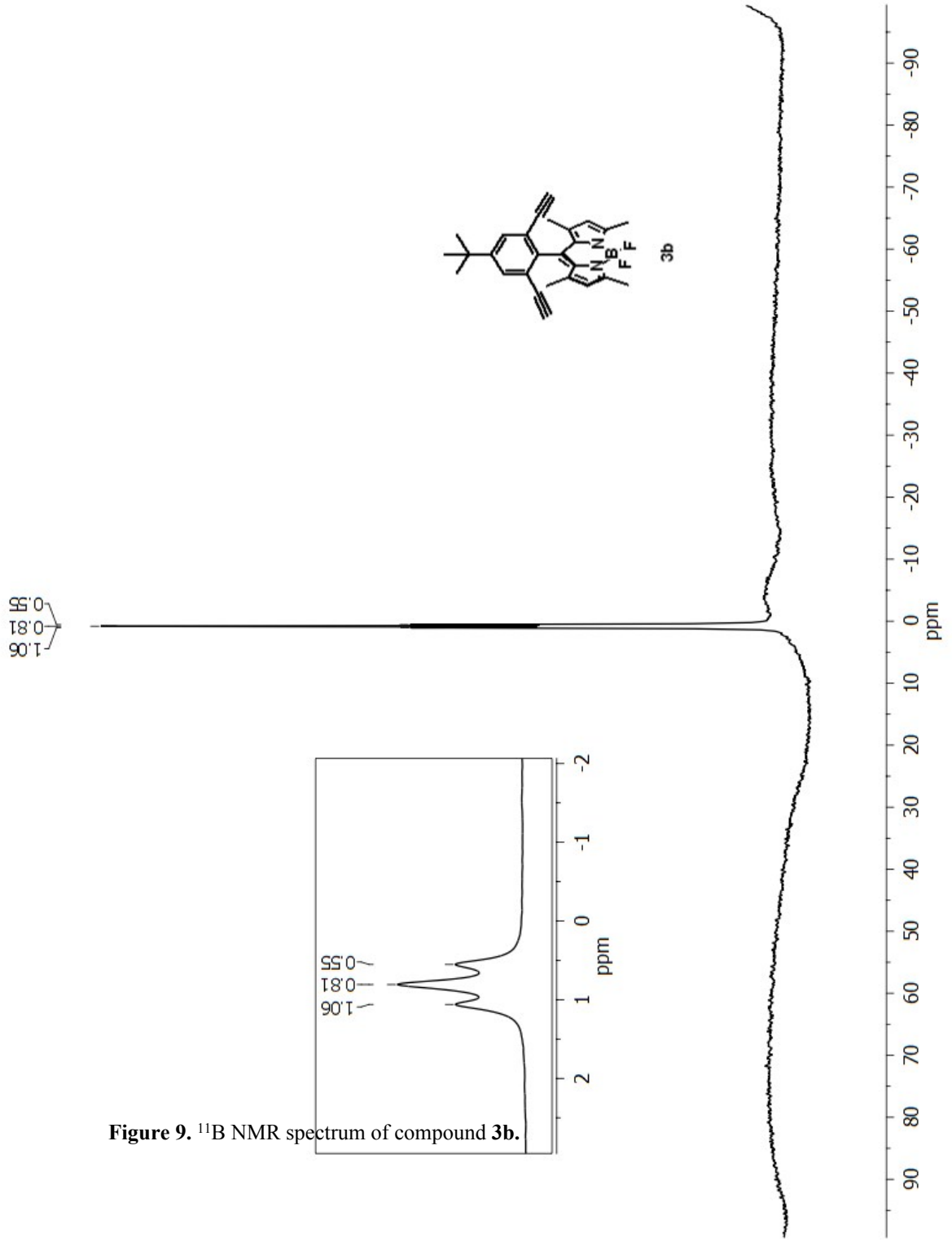


Figure 9. ^{11}B NMR spectrum of compound **3b.**

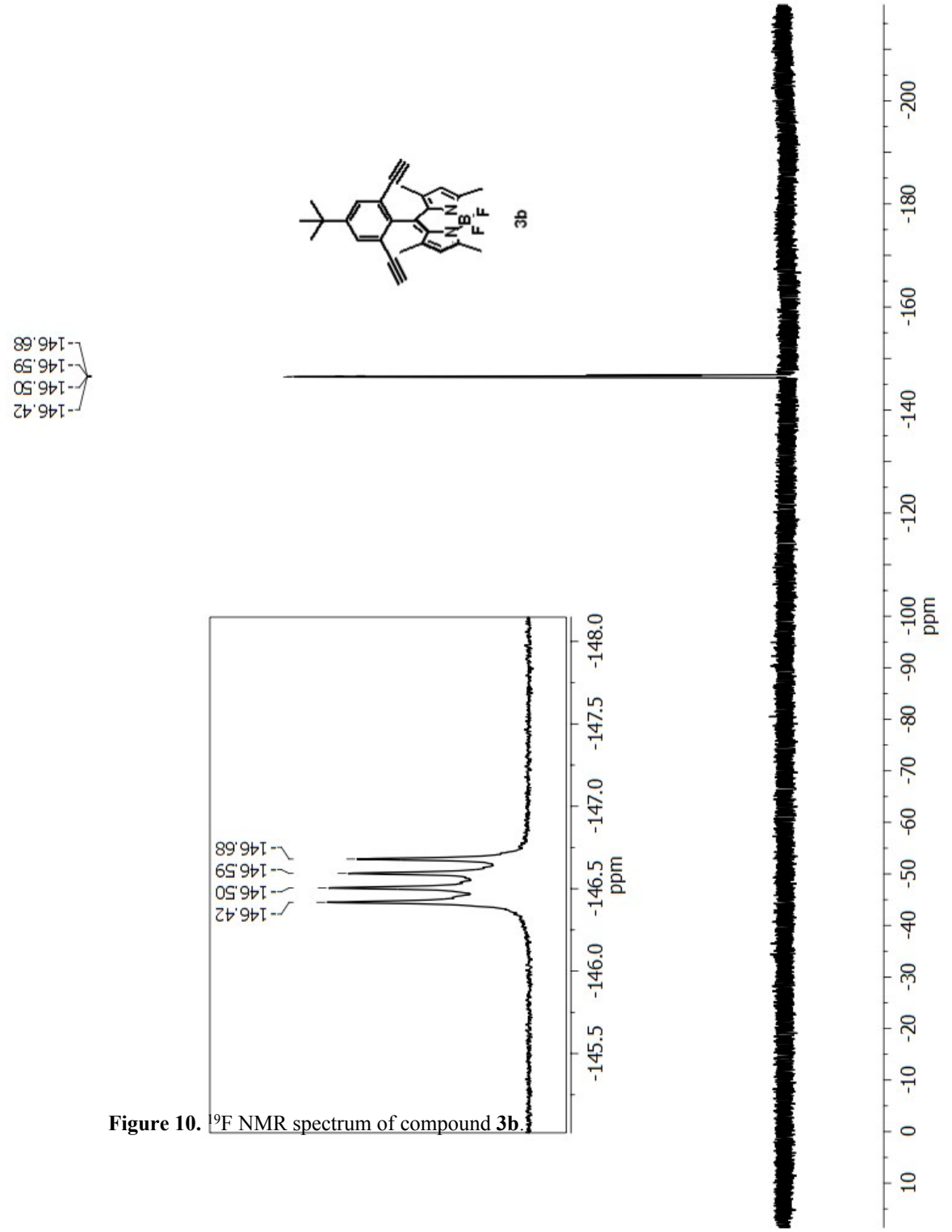


Figure 10. ^{19}F NMR spectrum of compound **3b**.

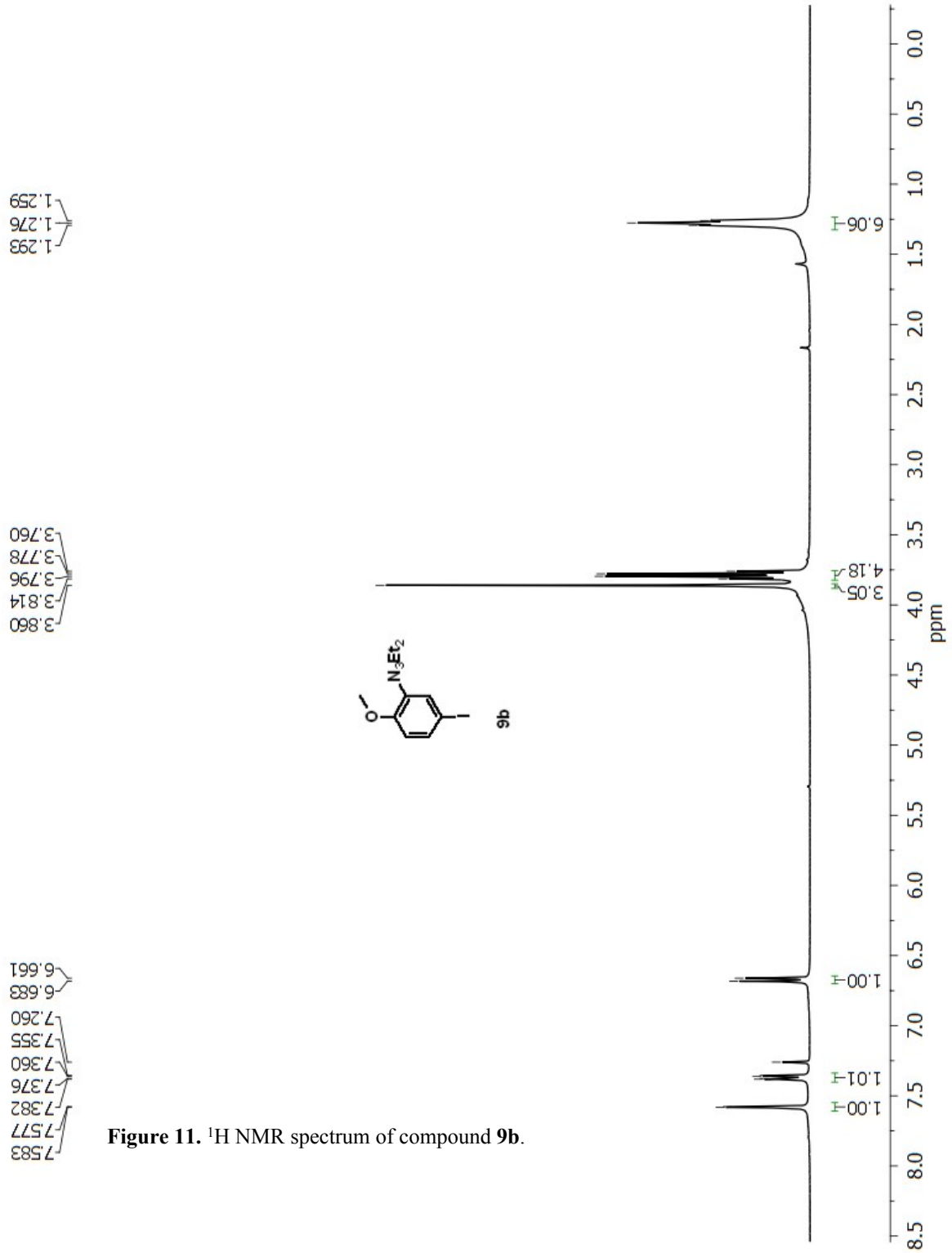


Figure 11. [1]H NMR spectrum of compound **9b**.

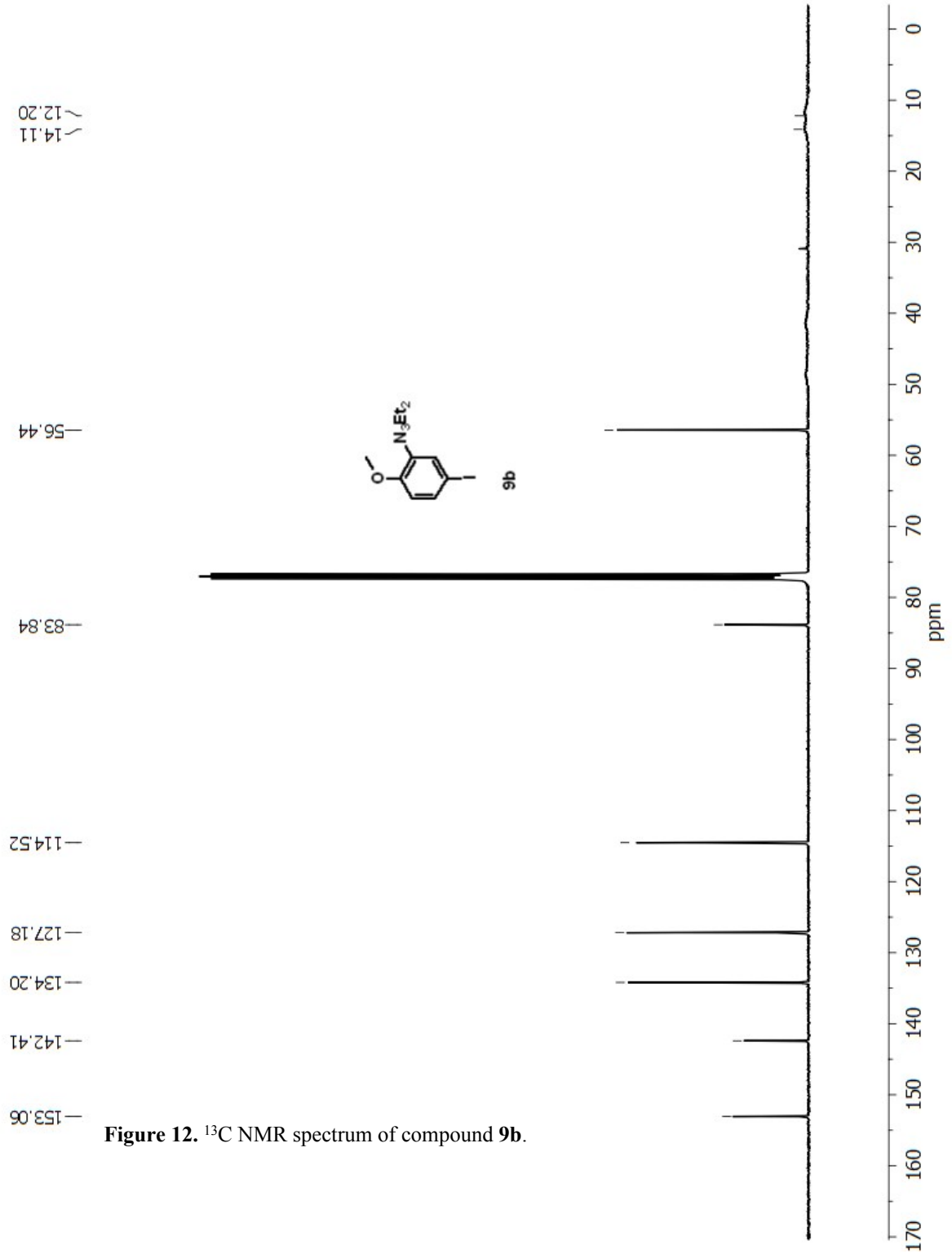


Figure 12. ^{13}C NMR spectrum of compound **9b**.

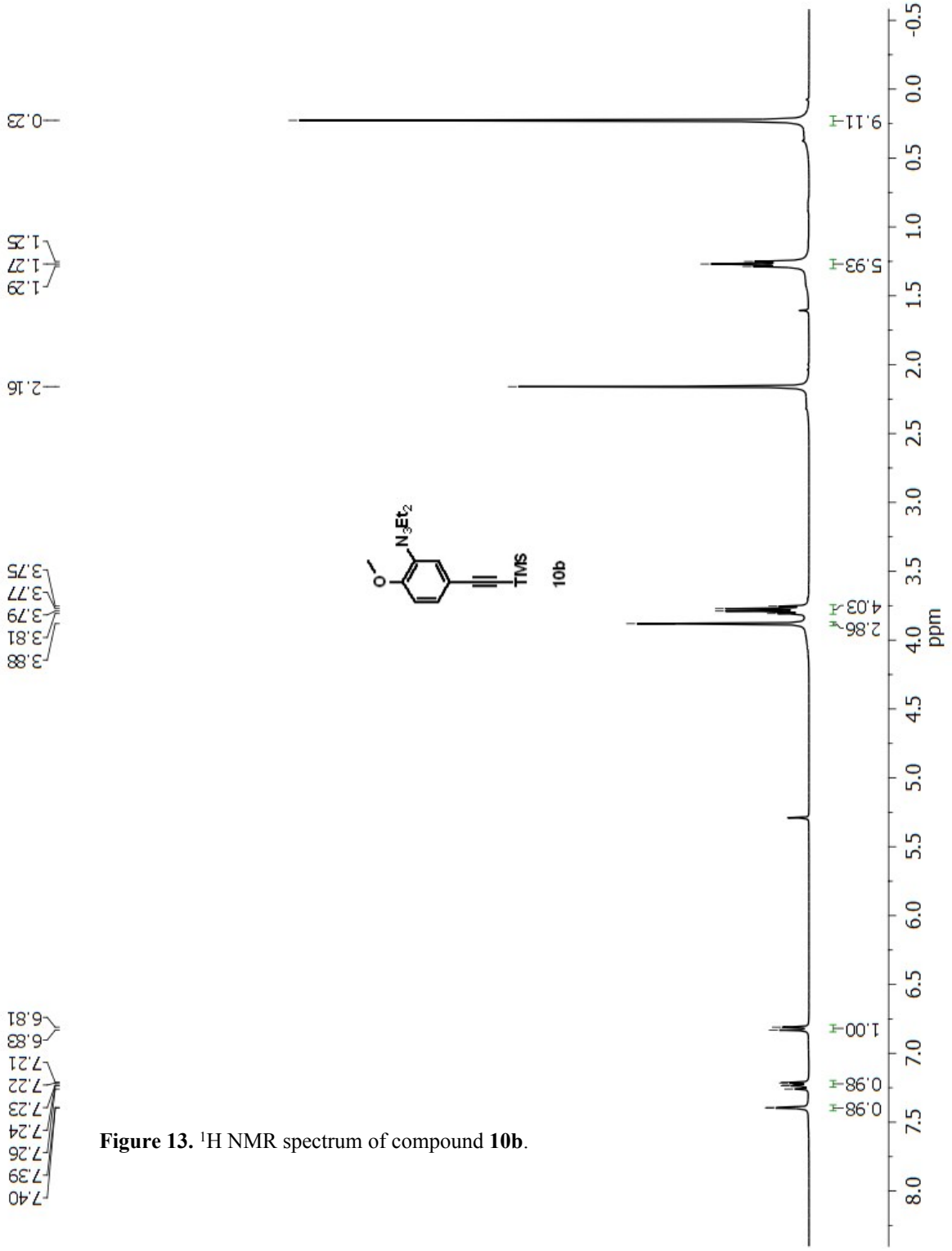


Figure 13. [1]H NMR spectrum of compound **10b**.

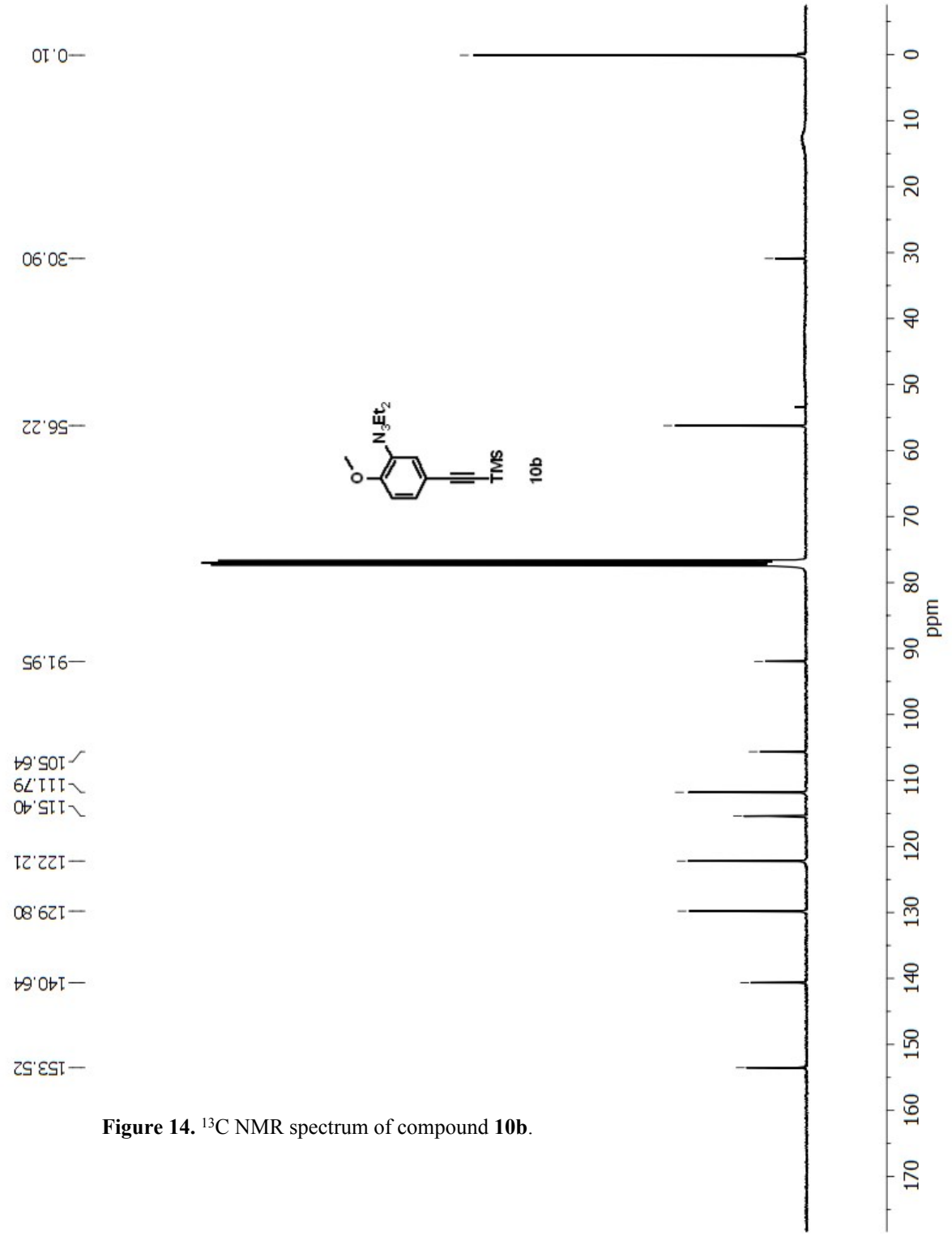


Figure 14. ^{13}C NMR spectrum of compound **10b**.

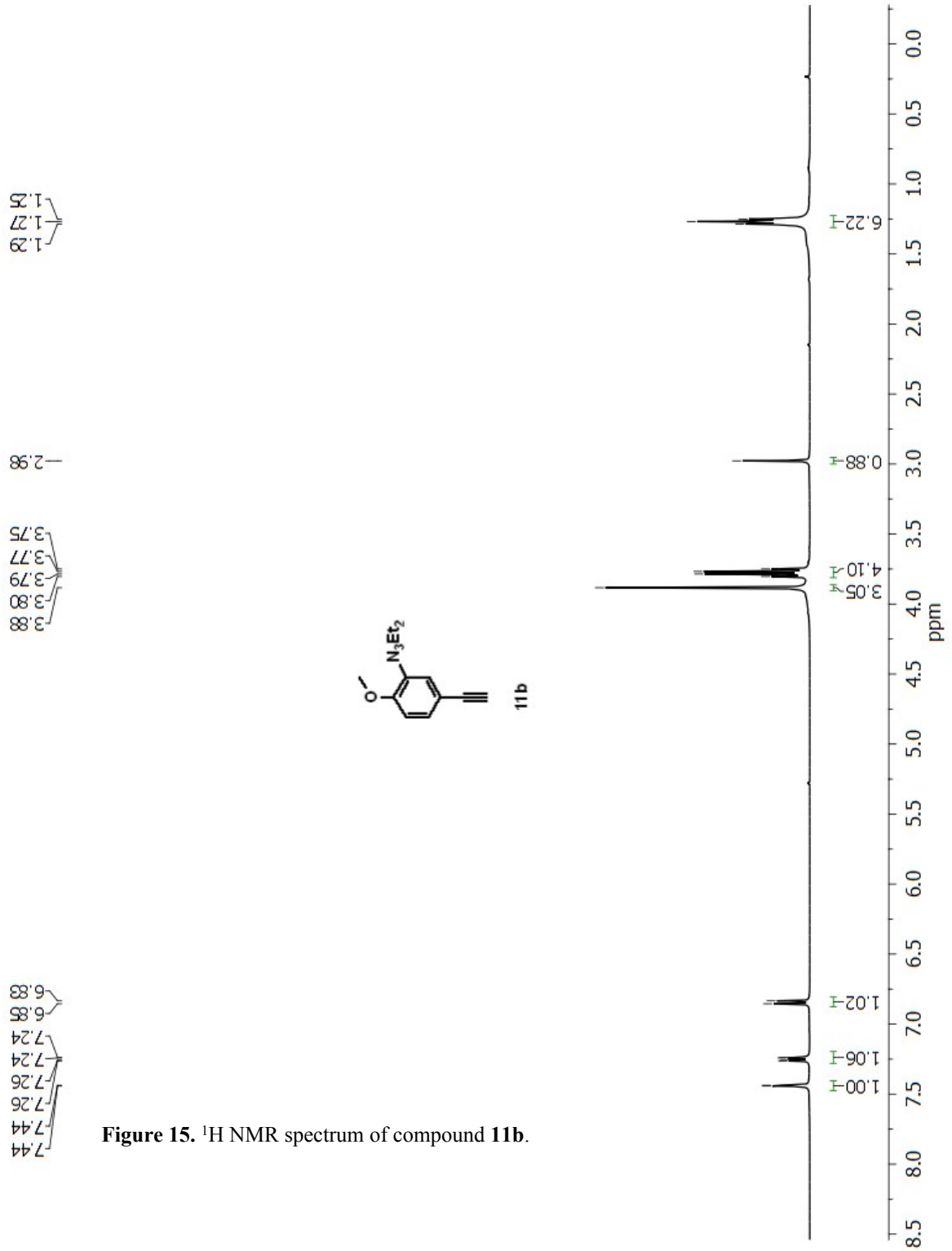


Figure 15. [1]H NMR spectrum of compound **11b**.

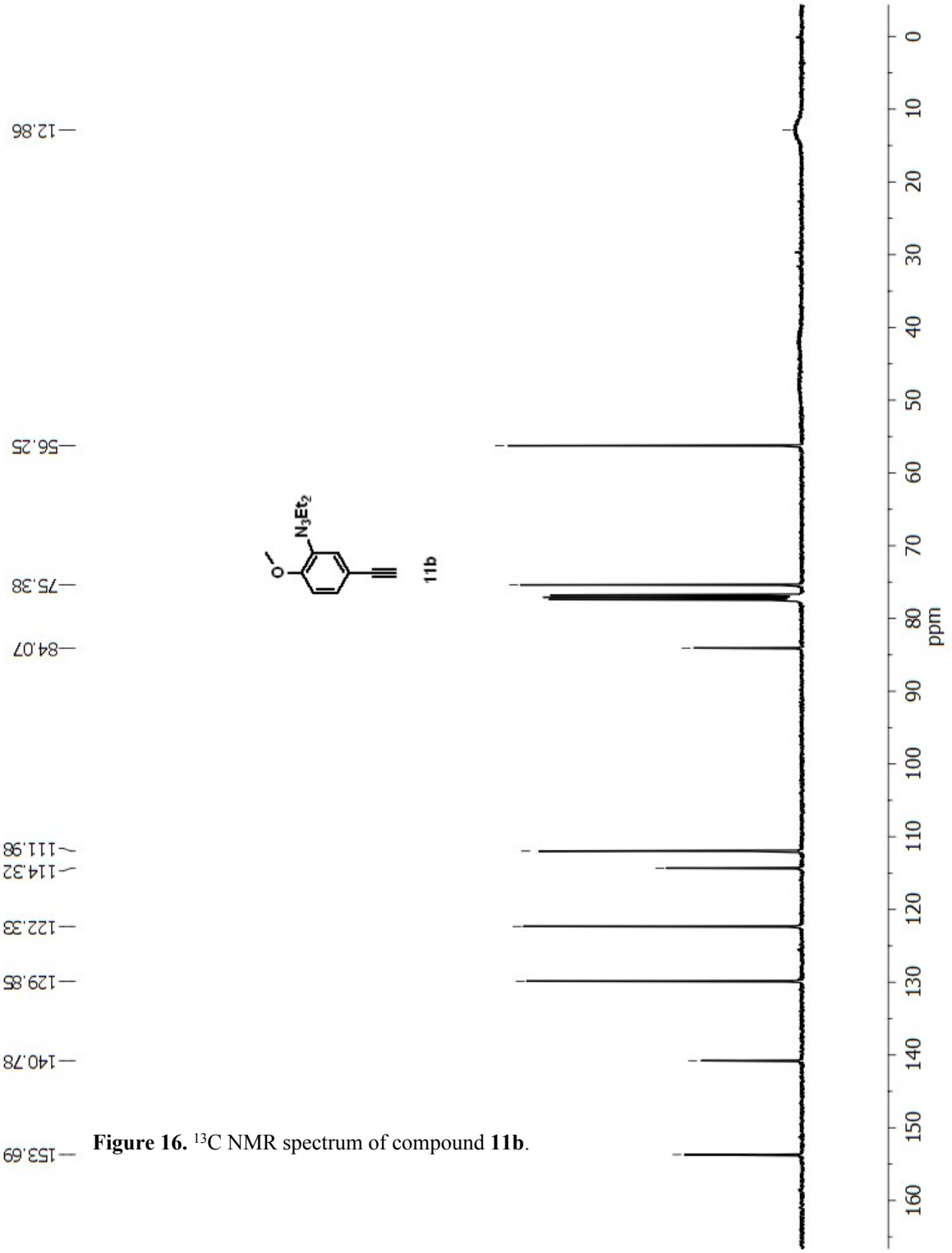


Figure 16. ^{13}C NMR spectrum of compound **11b**.

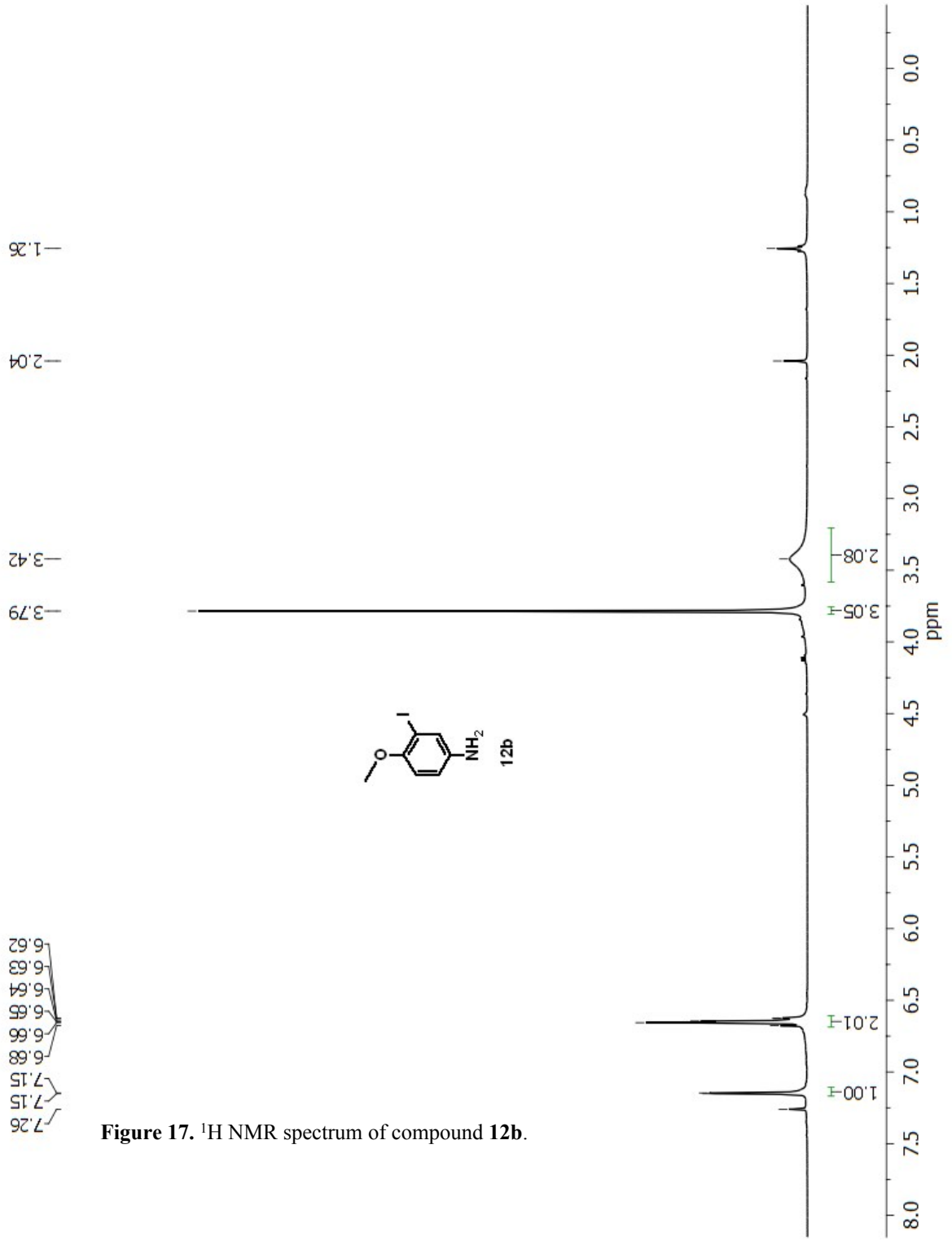


Figure 17. ^{1}H NMR spectrum of compound **12b**.

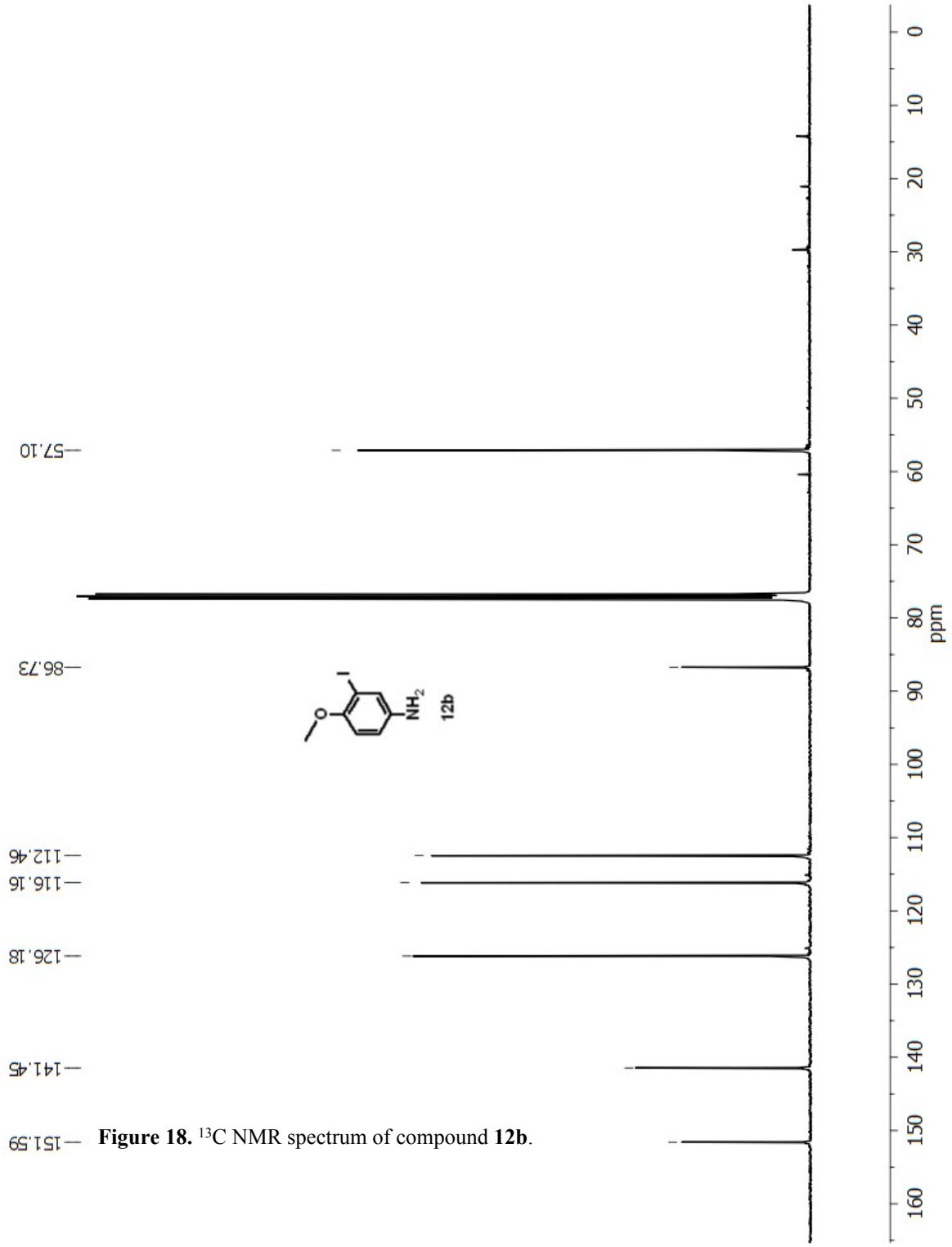


Figure 18. ^{13}C NMR spectrum of compound **12b**.

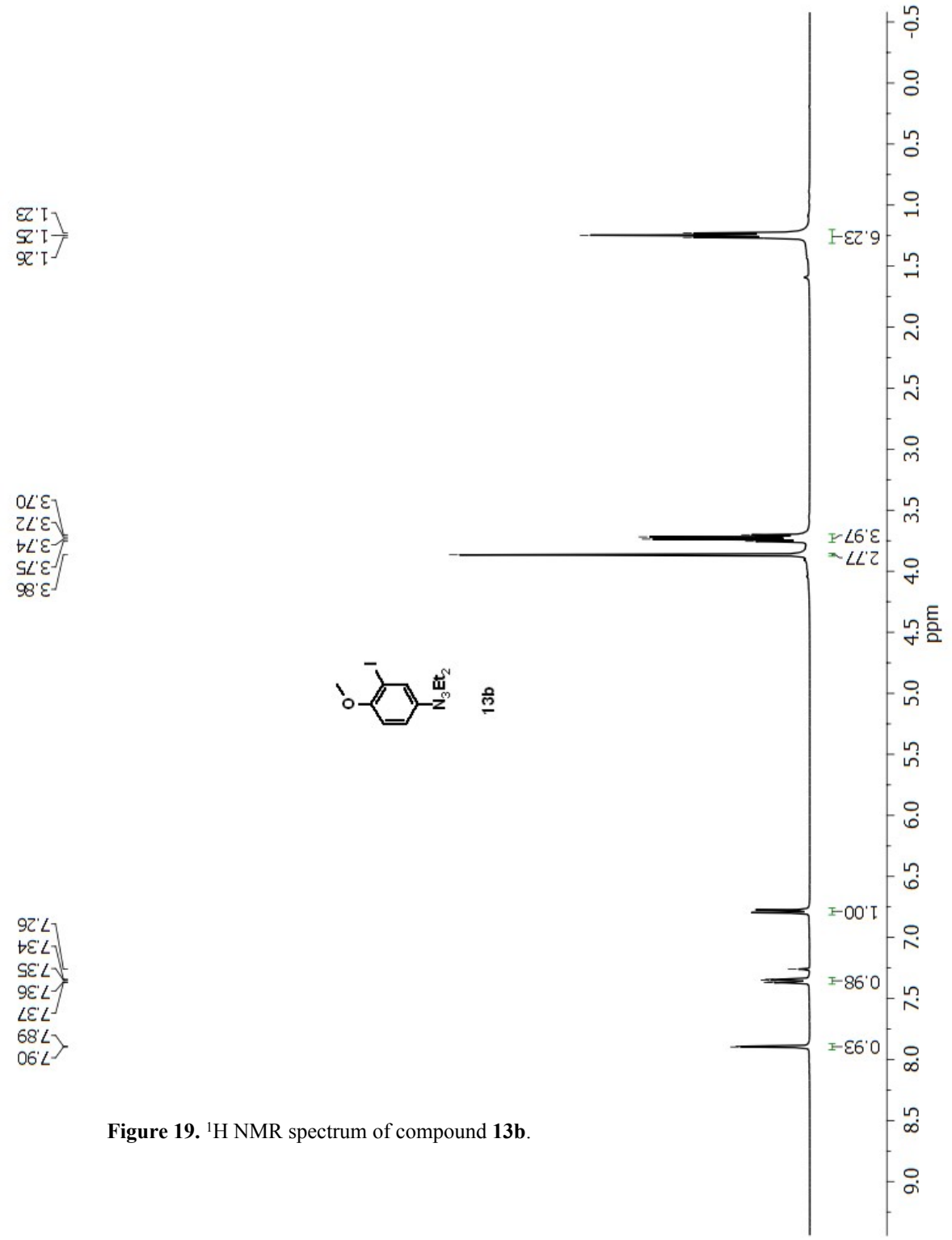


Figure 19. [1]H NMR spectrum of compound **13b**.

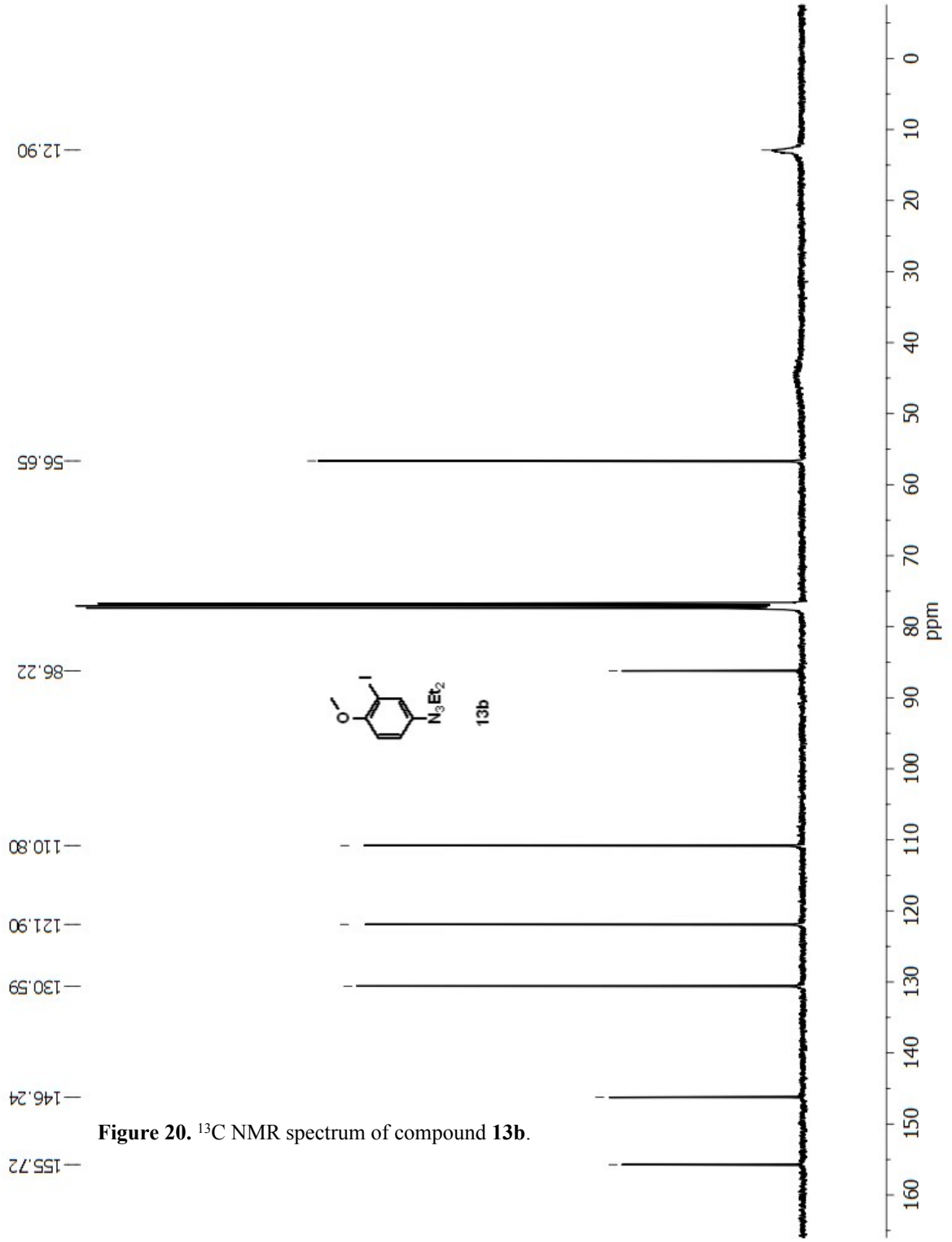


Figure 20. ^{13}C NMR spectrum of compound **13b**.

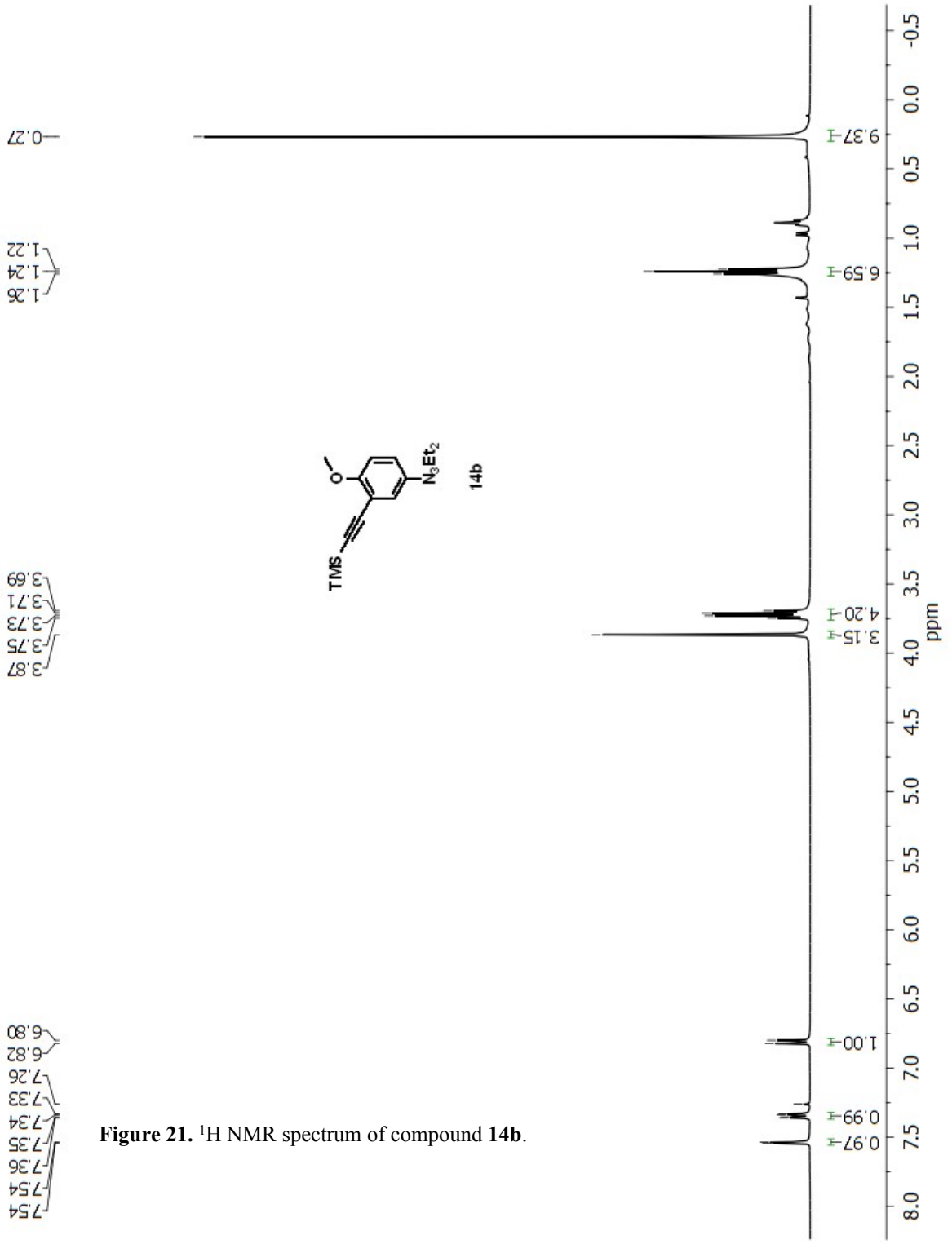


Figure 21. ^{1}H NMR spectrum of compound **14b**.

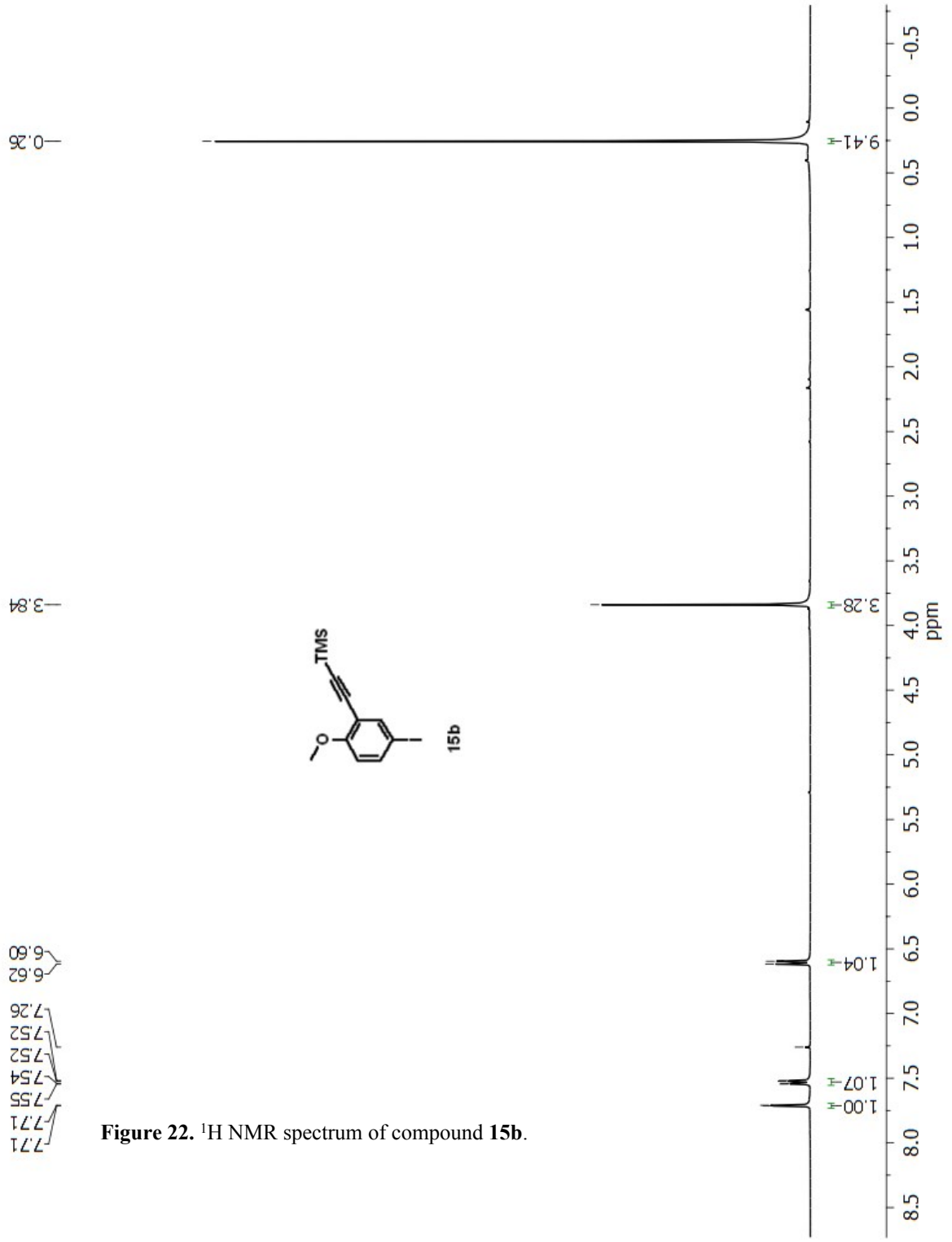


Figure 22. [1]H NMR spectrum of compound **15b**.

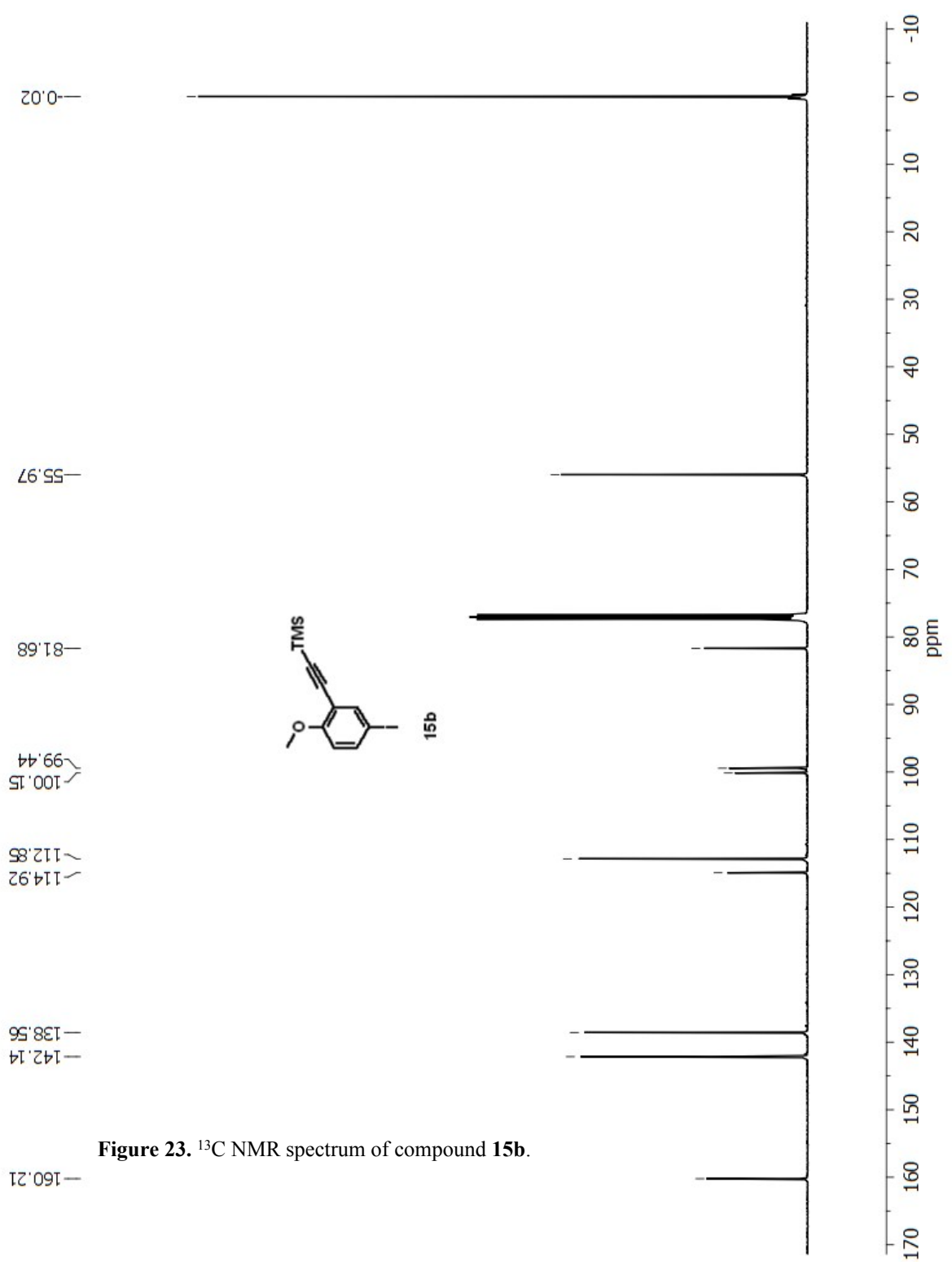


Figure 23. ^{13}C NMR spectrum of compound **15b**.

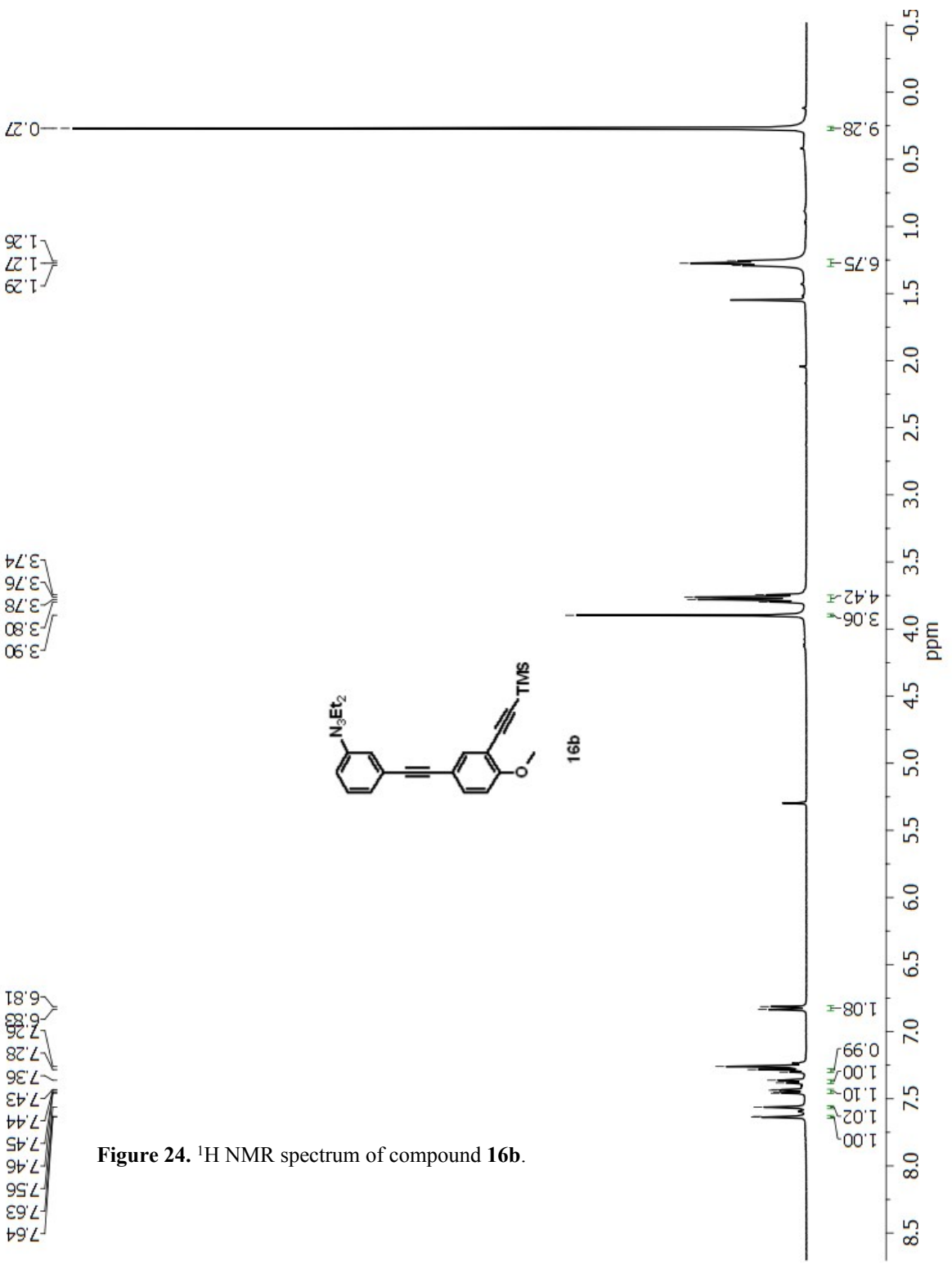


Figure 24. ^{1}H NMR spectrum of compound **16b**.

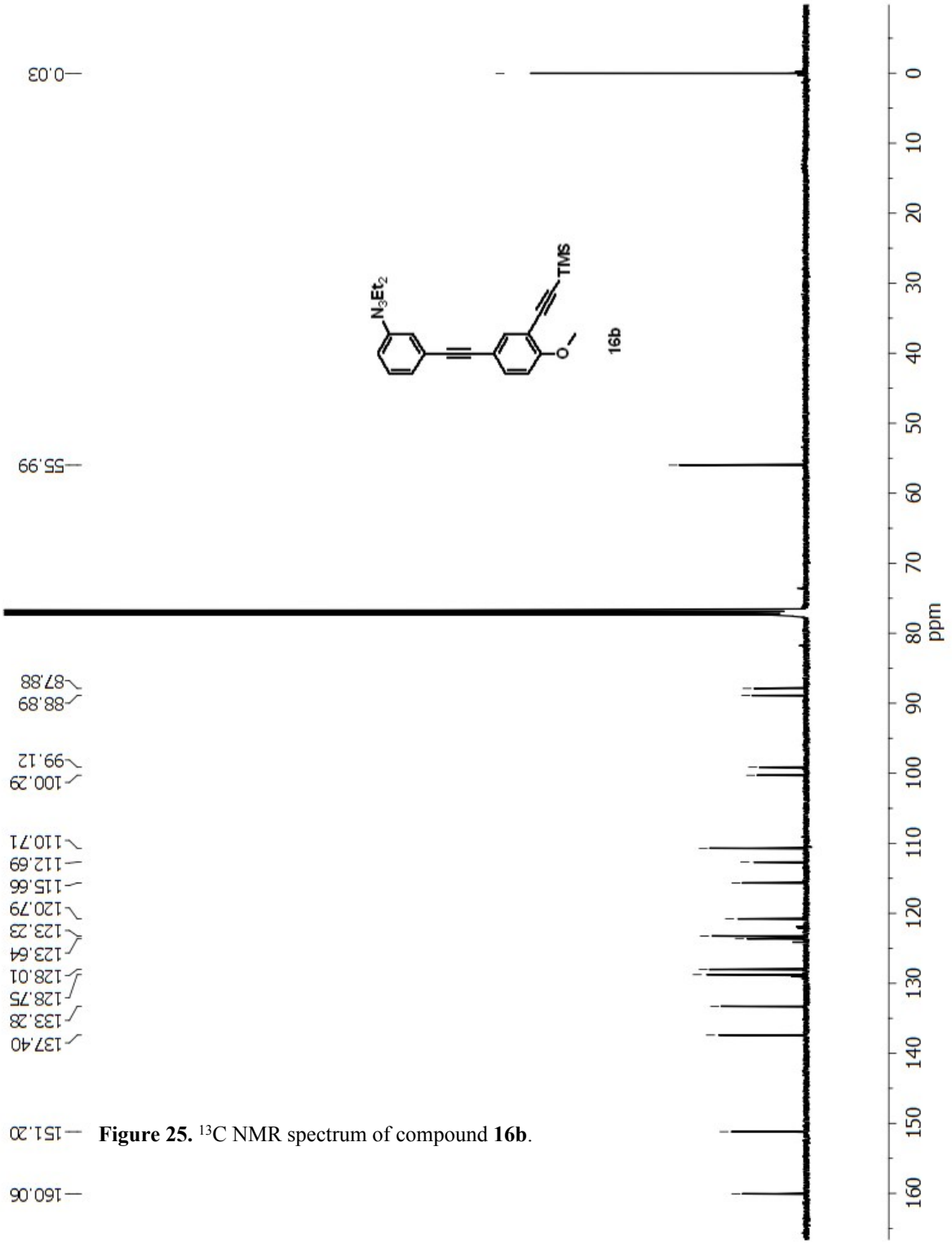


Figure 25. ^{13}C NMR spectrum of compound **16b**.

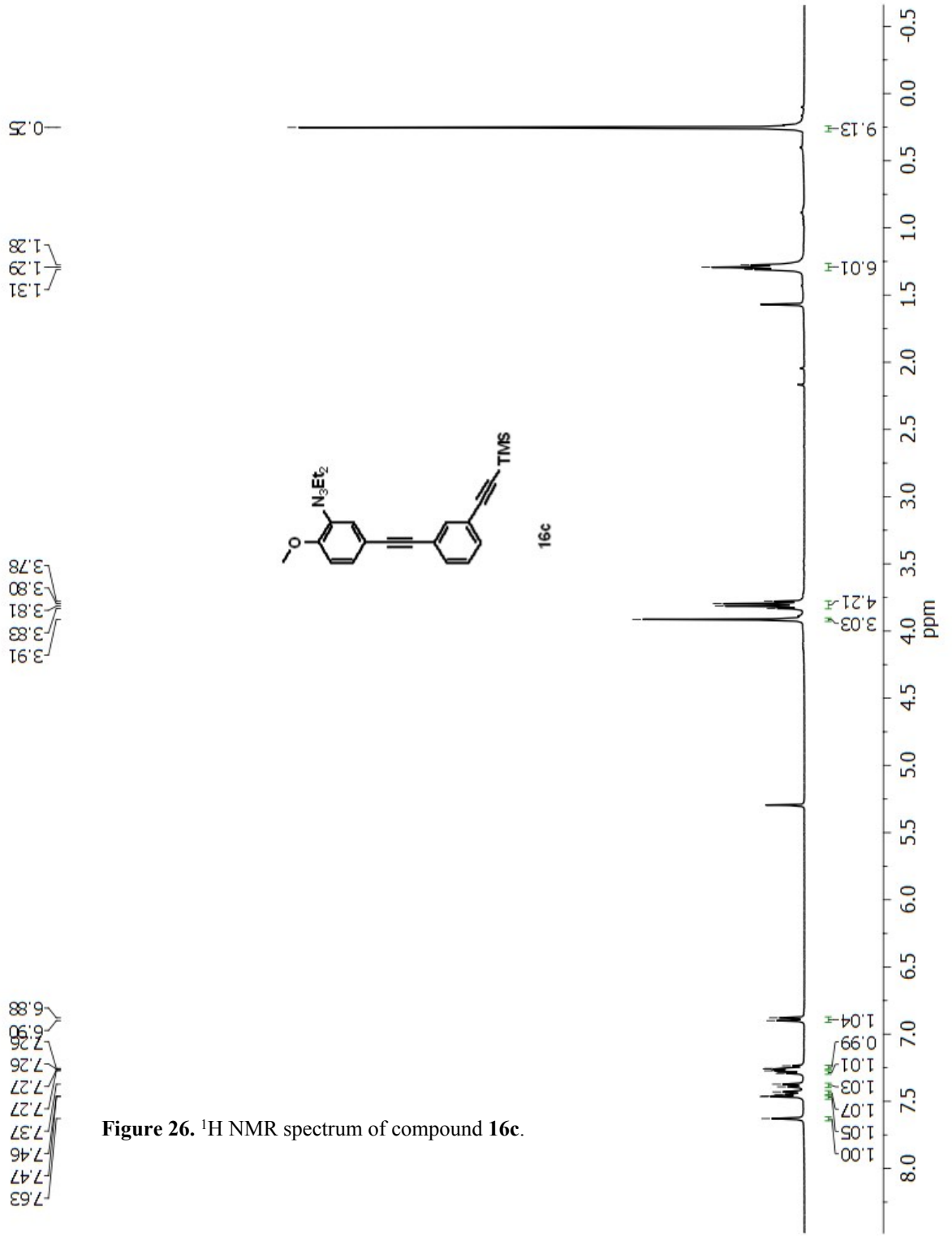


Figure 26. [1]H NMR spectrum of compound **16c**.

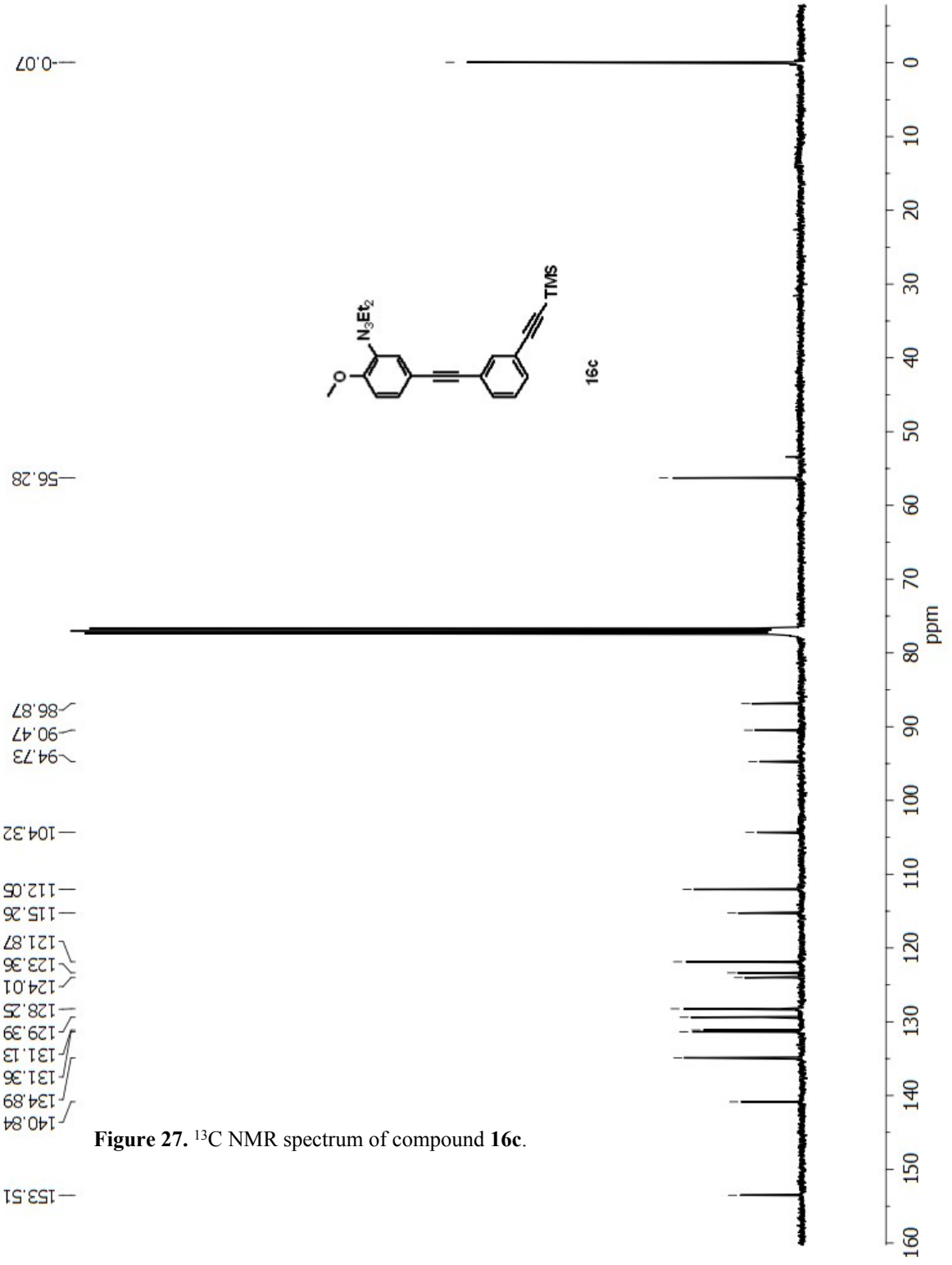


Figure 27. ^{13}C NMR spectrum of compound **16c**.

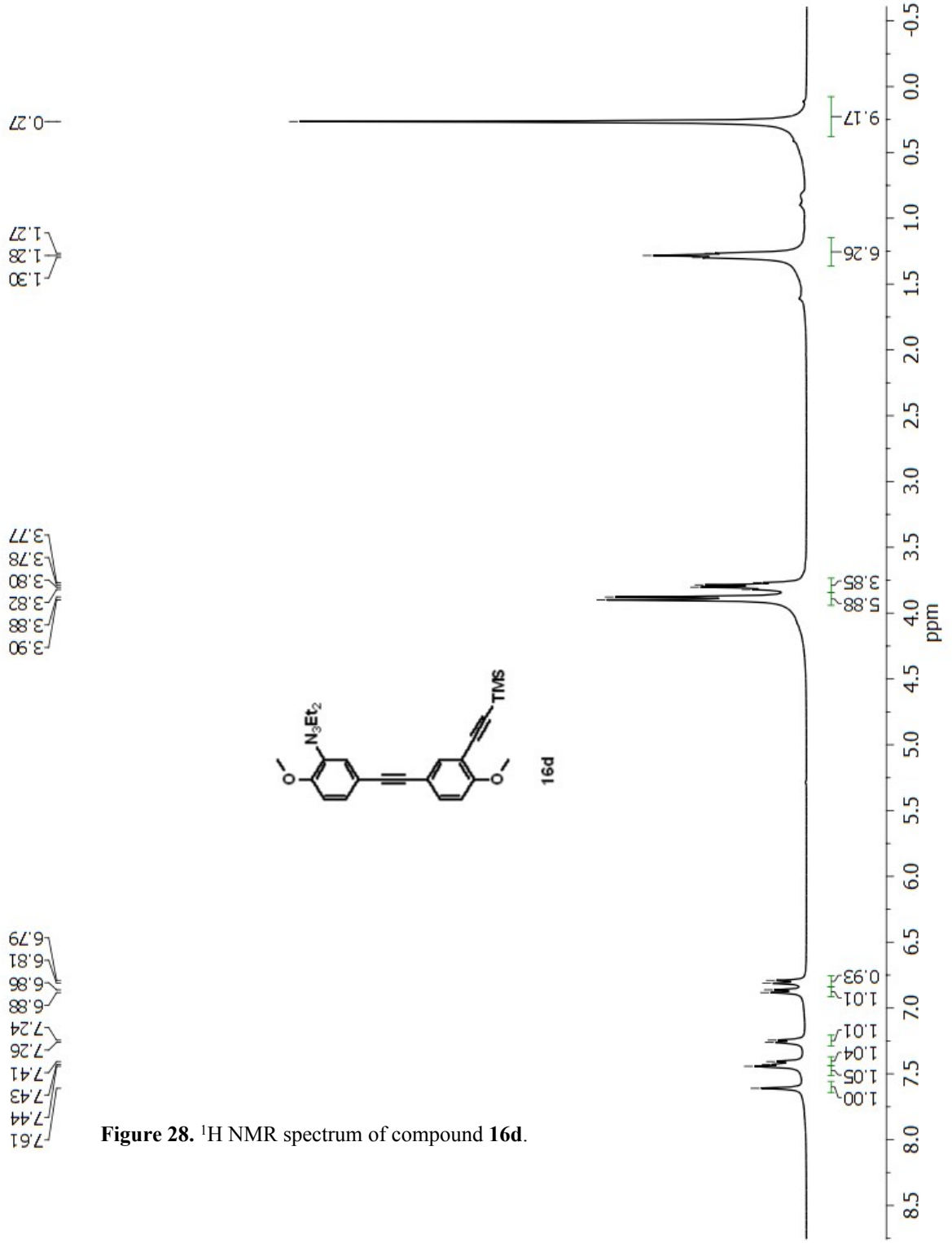


Figure 28. [1]H NMR spectrum of compound **16d**.

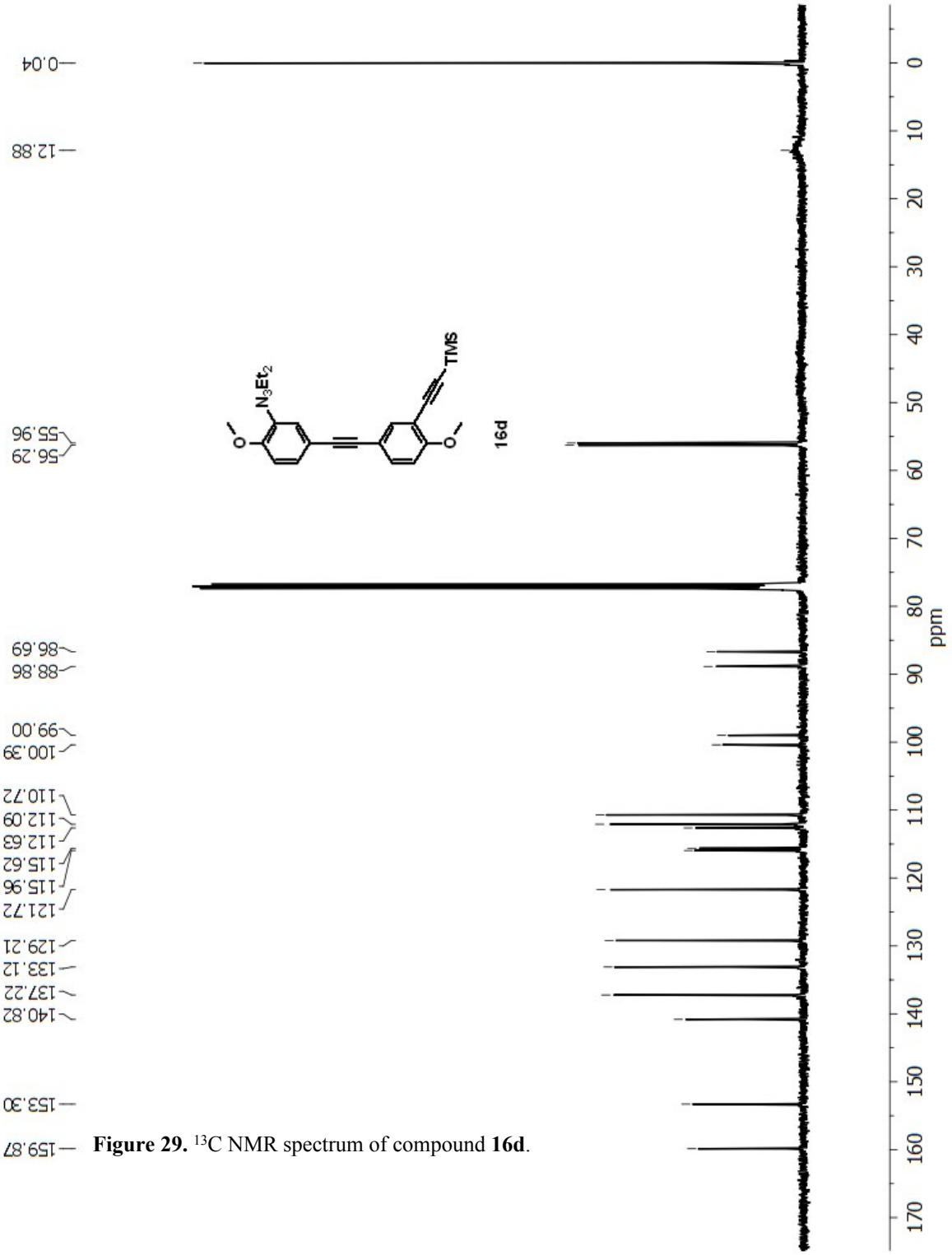


Figure 29. ^{13}C NMR spectrum of compound **16d**.

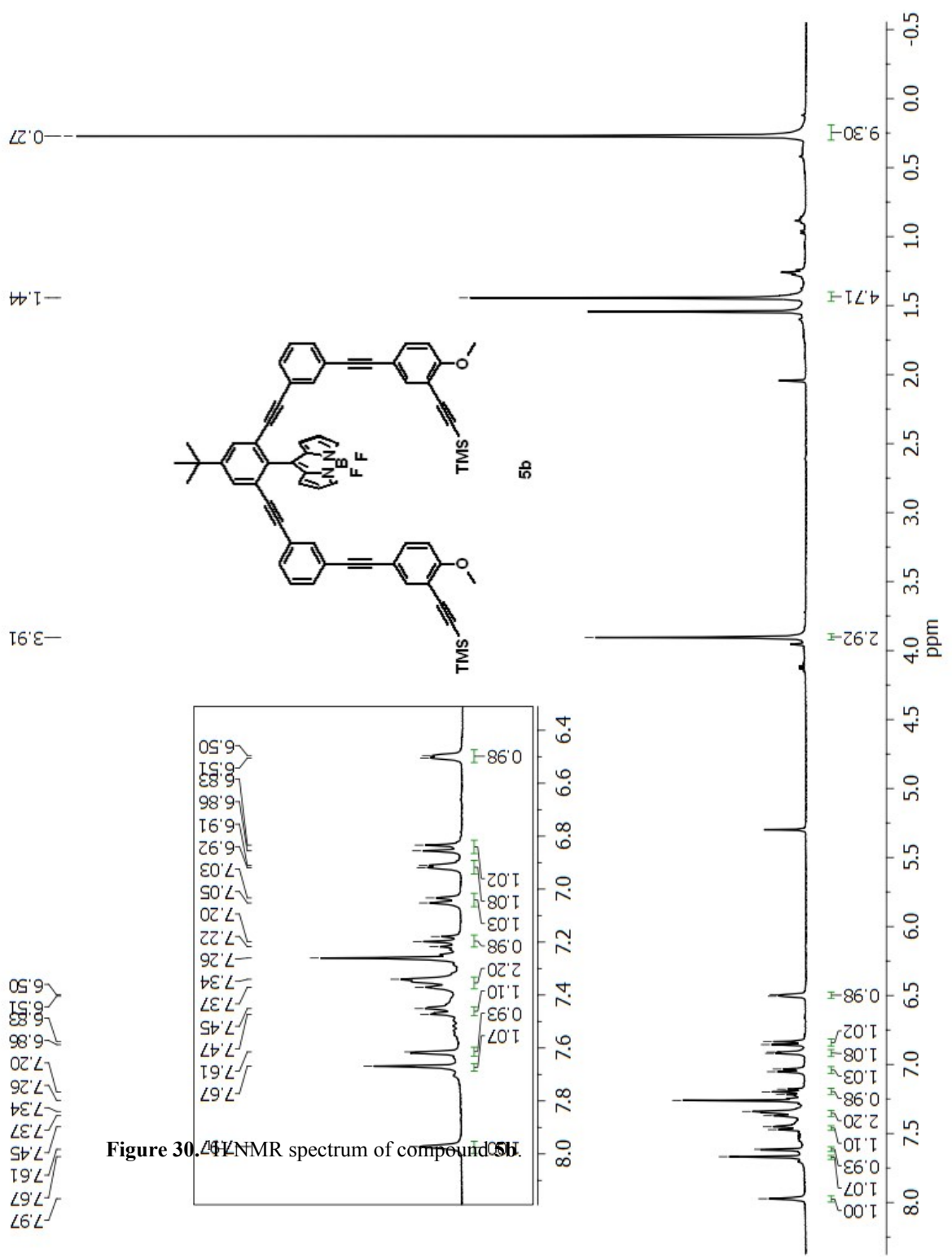


Figure 30. ^{1}H NMR spectrum of compound **5b**.

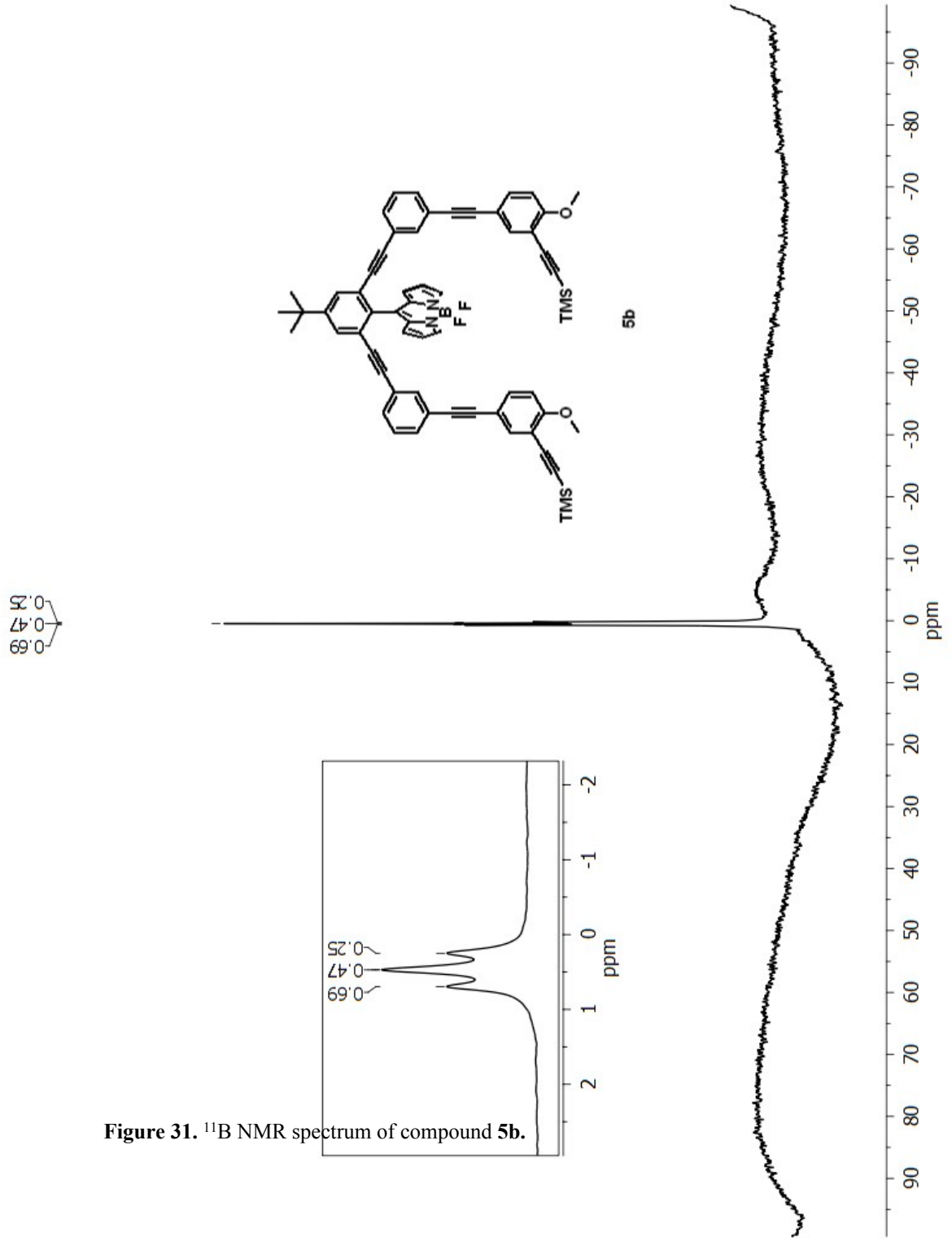


Figure 31. ^{11}B NMR spectrum of compound **5b.**

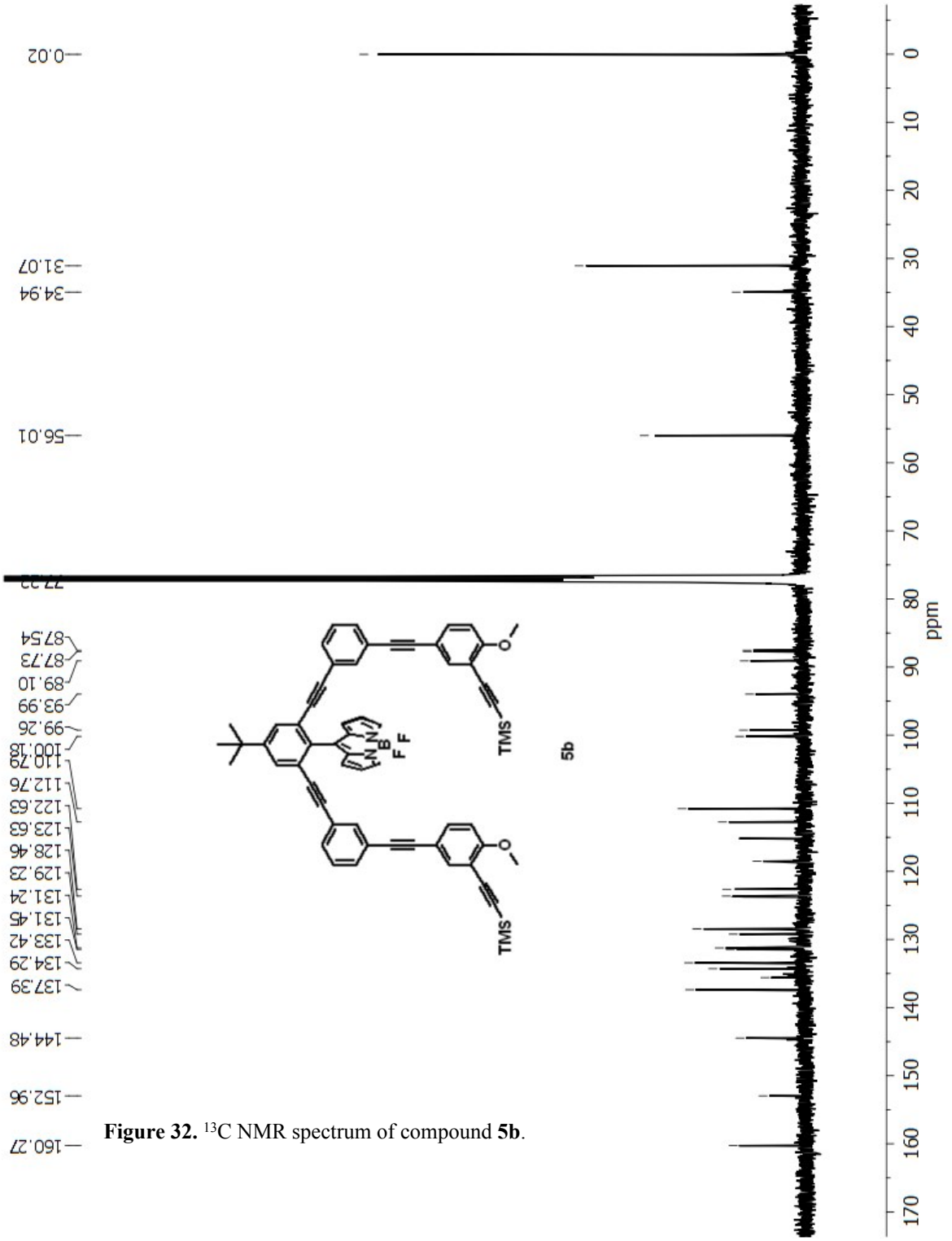


Figure 32. ^{13}C NMR spectrum of compound **5b**.

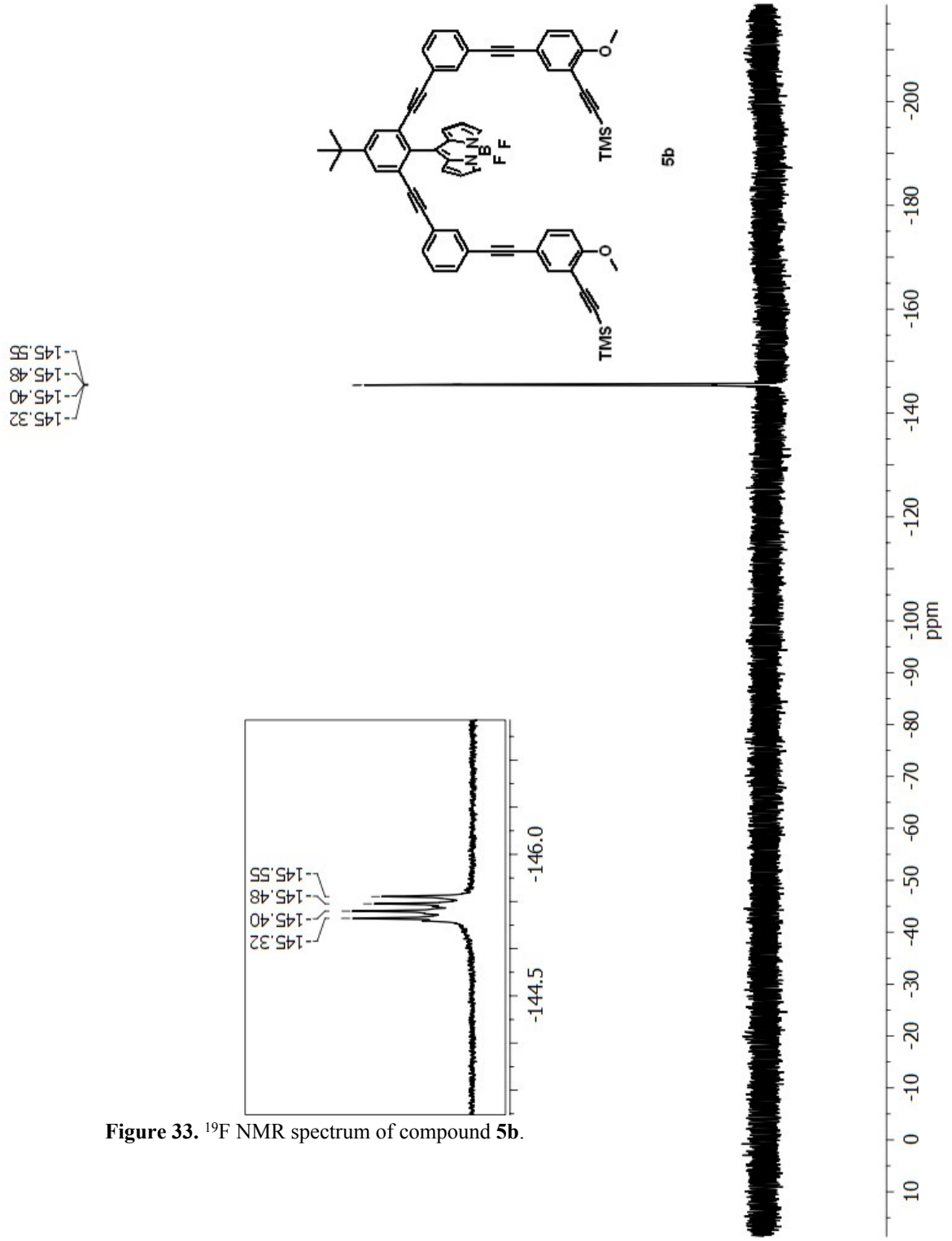


Figure 33. ^{19}F NMR spectrum of compound **5b**.

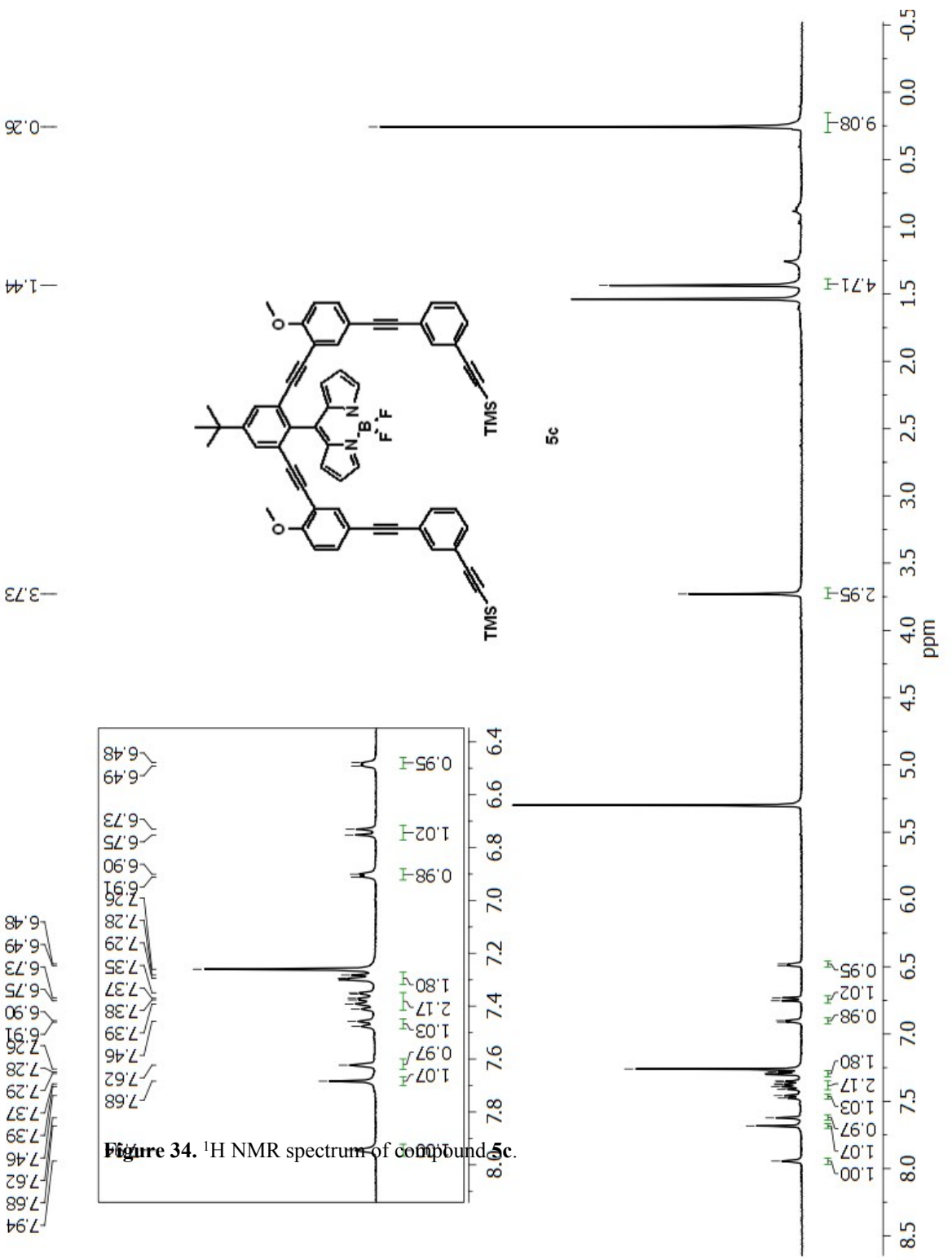


Figure 34. [1]H NMR spectrum of compound **5c**.

Figure 35. ^{11}B NMR spectrum of compound **5c**.

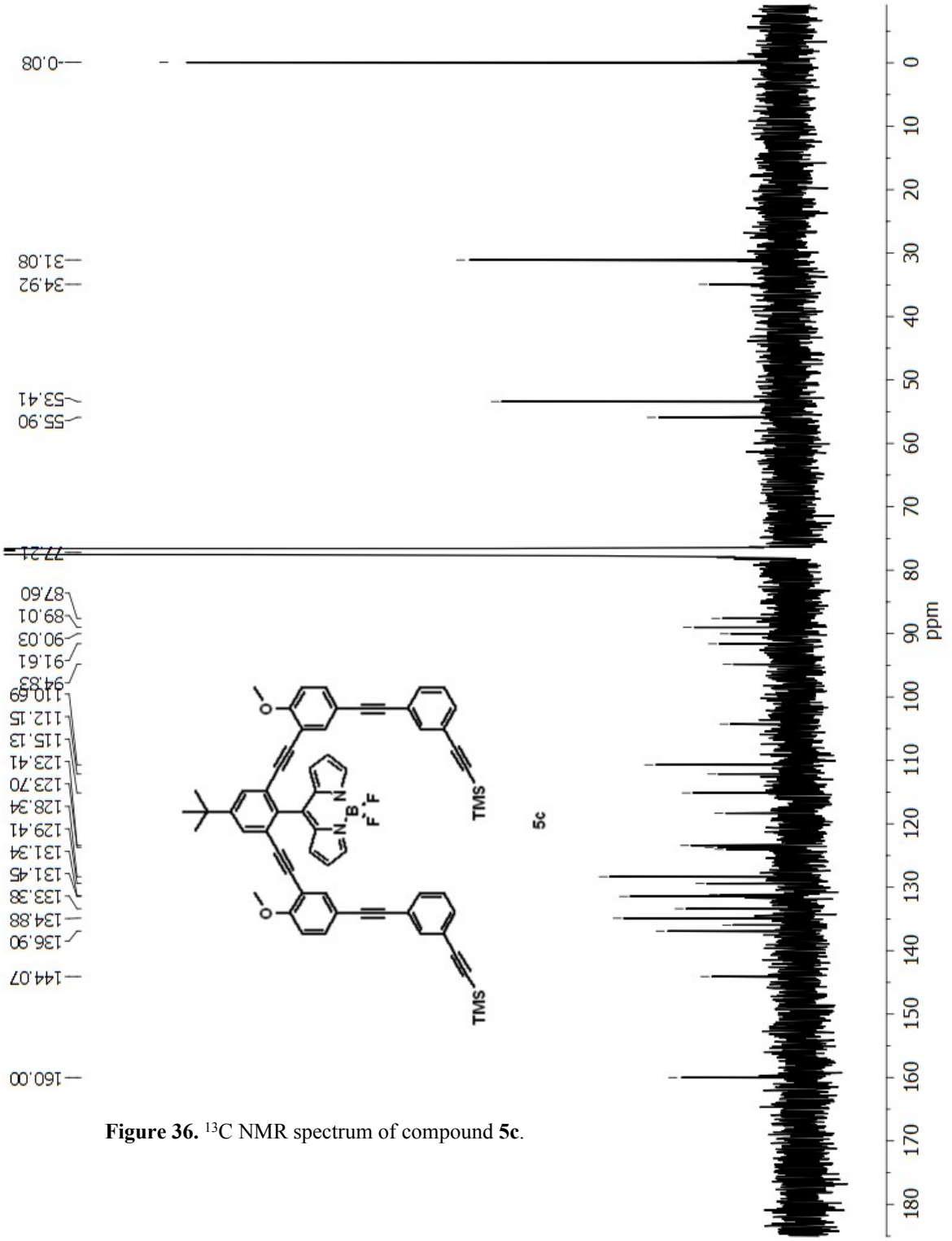


Figure 36. ^{13}C NMR spectrum of compound **5c**.

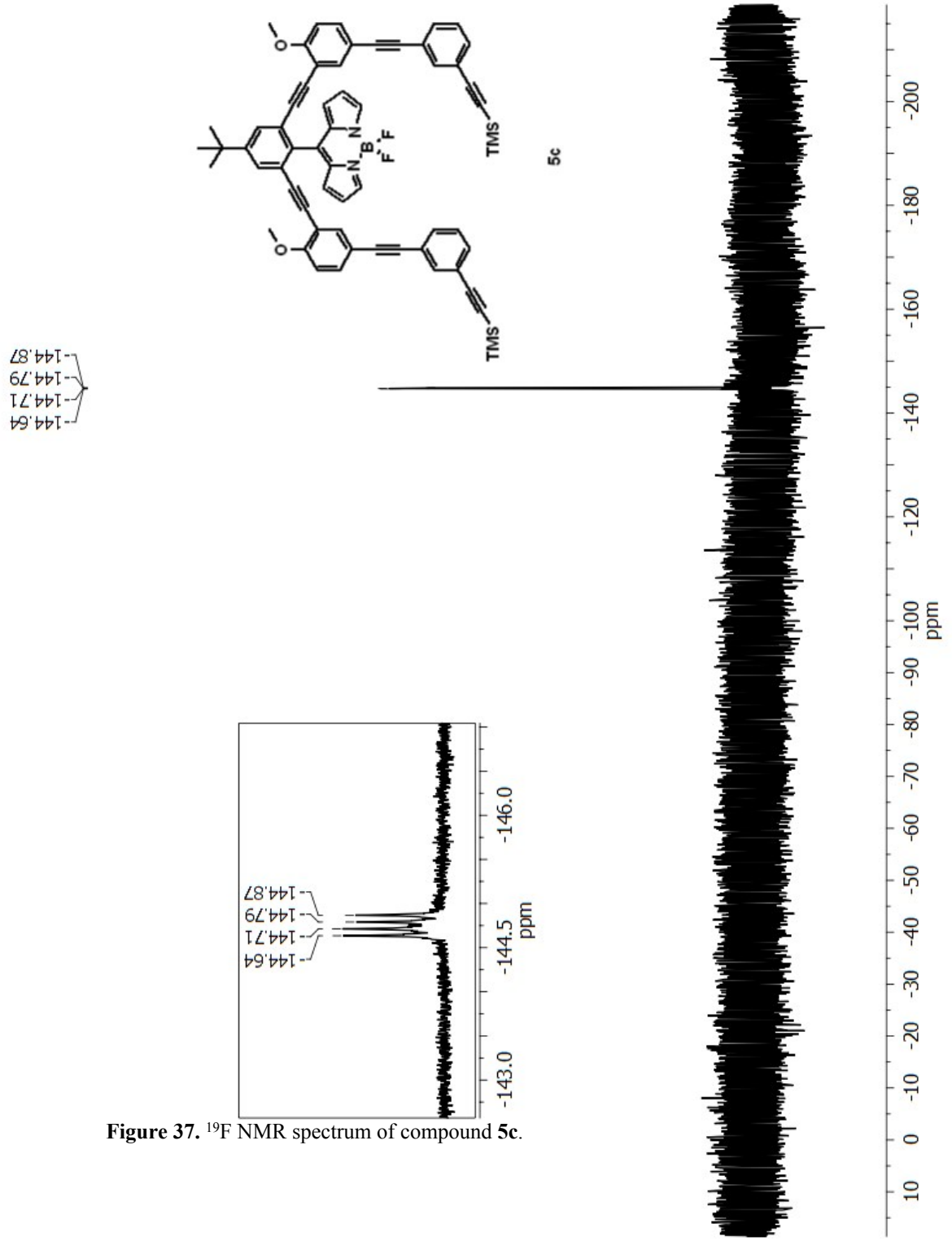


Figure 37. ^{19}F NMR spectrum of compound **5c**.

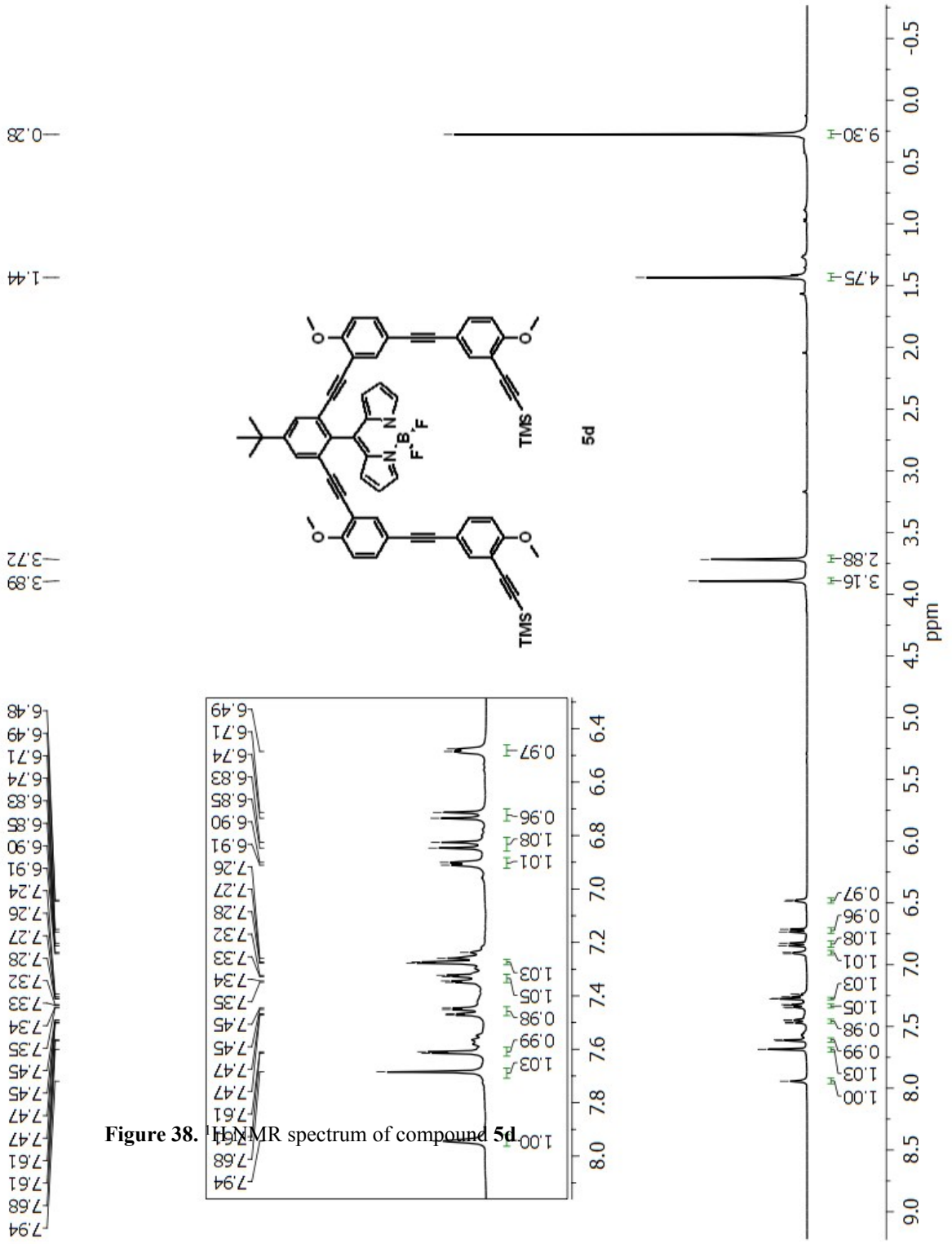


Figure 38. ^{1}H NMR spectrum of compound **5d**

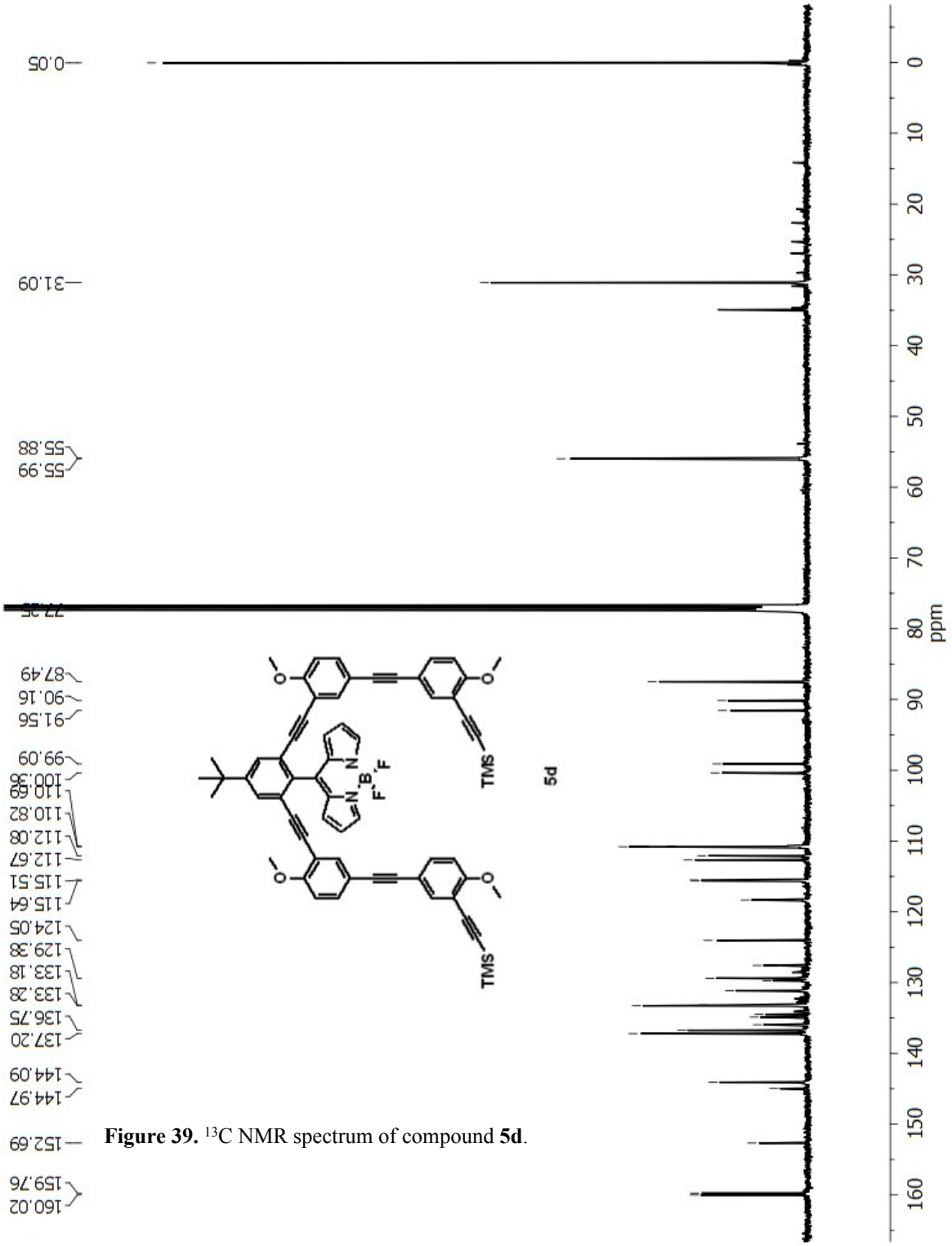


Figure 39. ^{13}C NMR spectrum of compound **5d**.

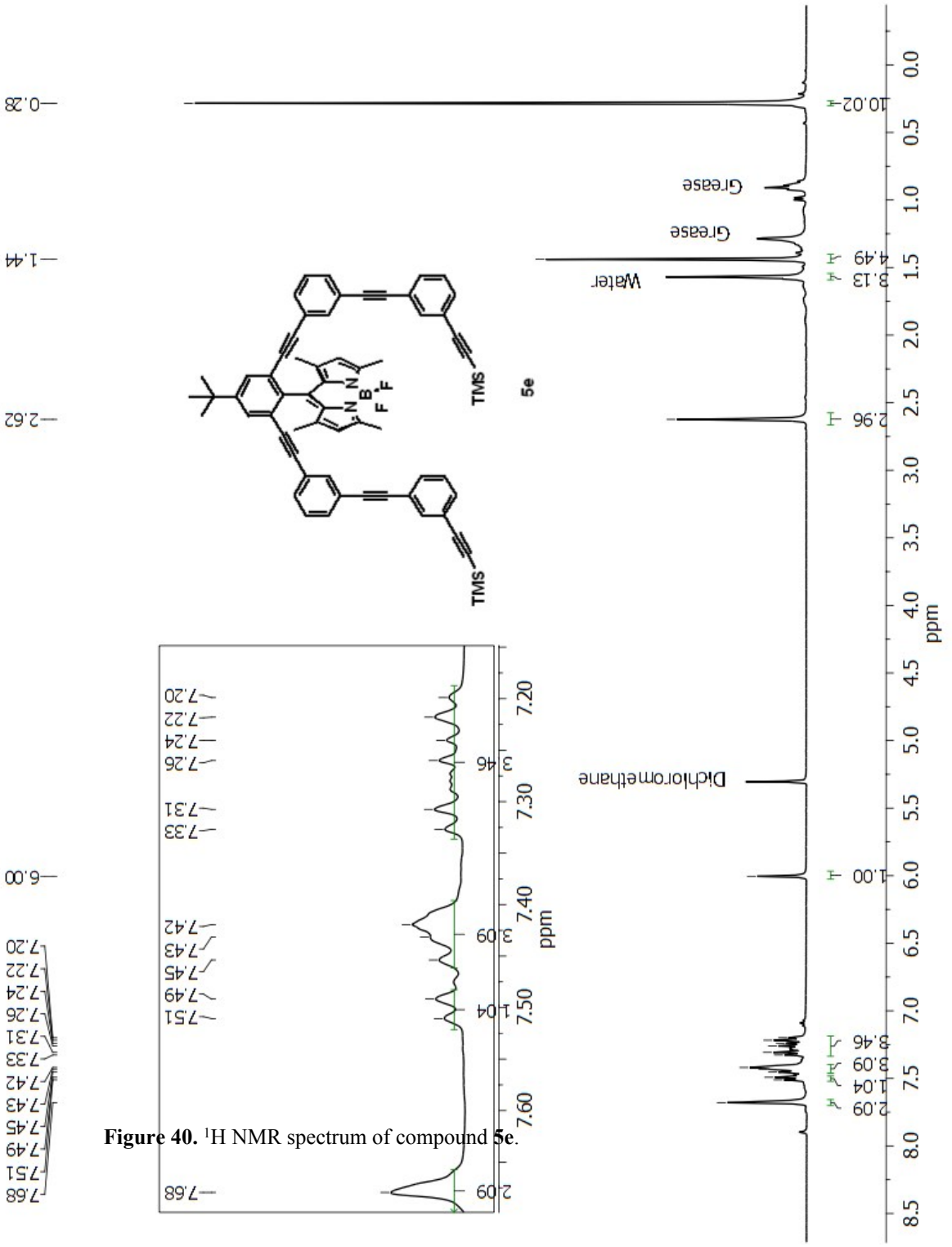


Figure 40. ^{1}H NMR spectrum of compound **5e**.

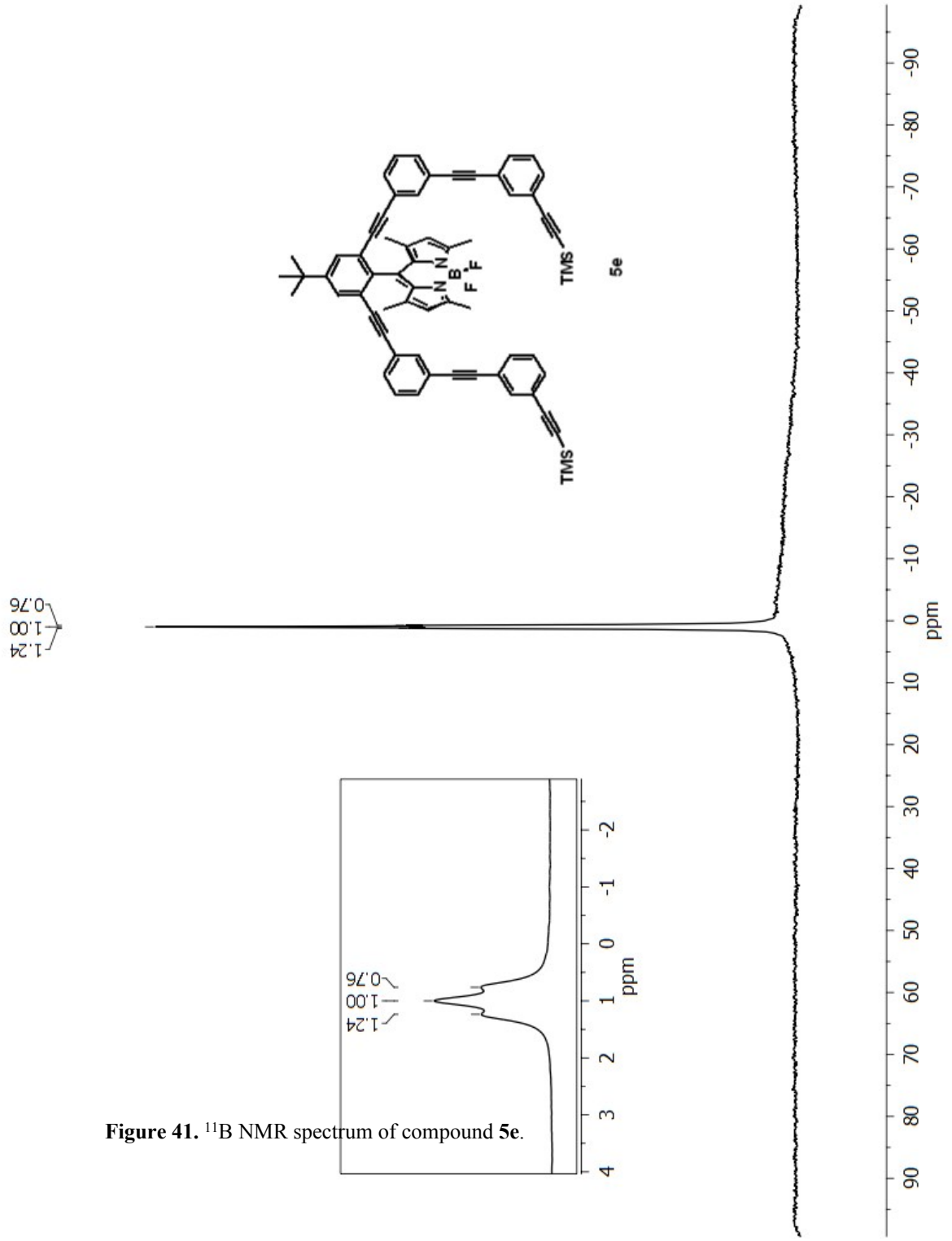


Figure 41. ^{11}B NMR spectrum of compound **5e**.

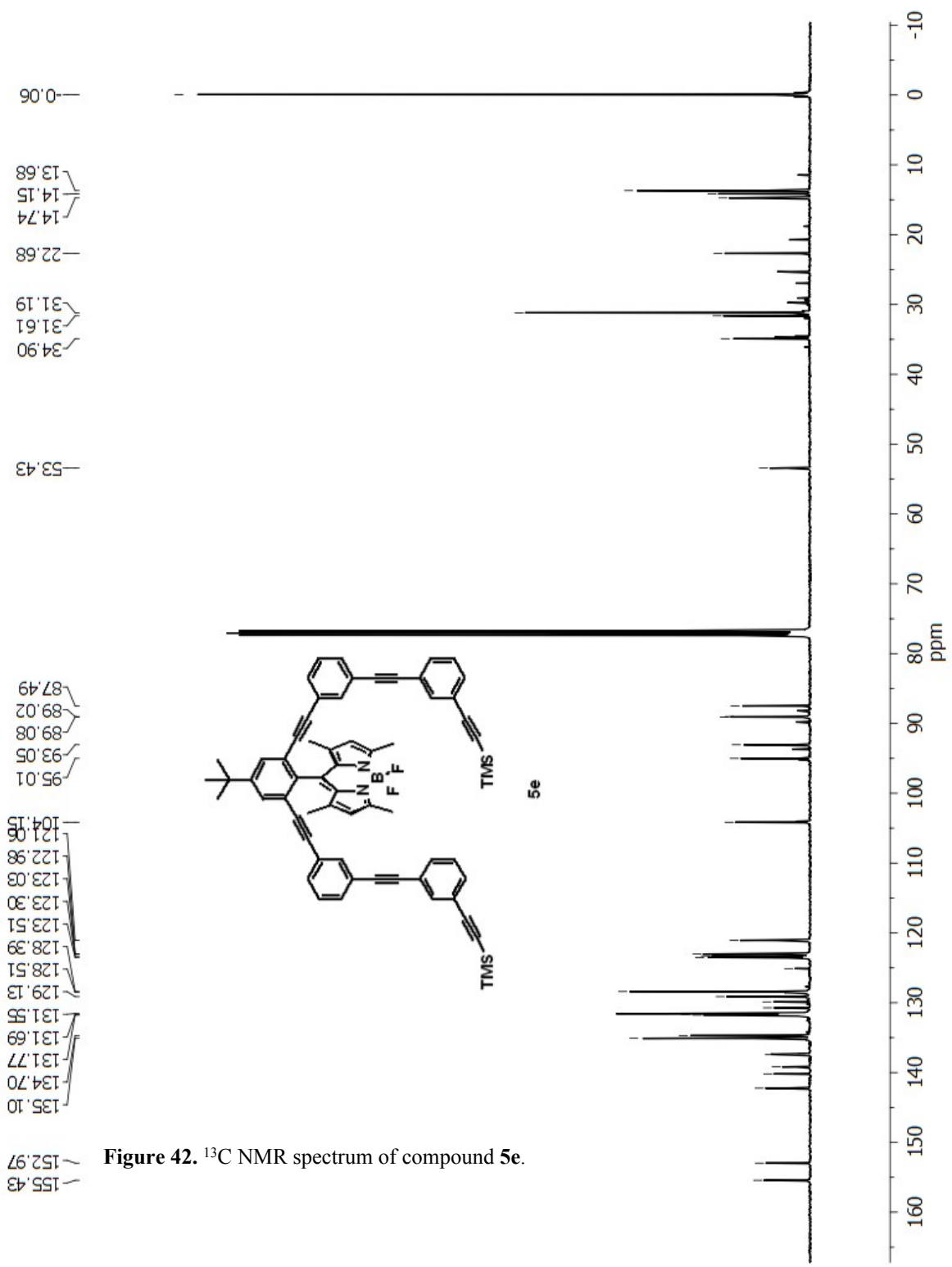


Figure 42. ^{13}C NMR spectrum of compound **5e**.

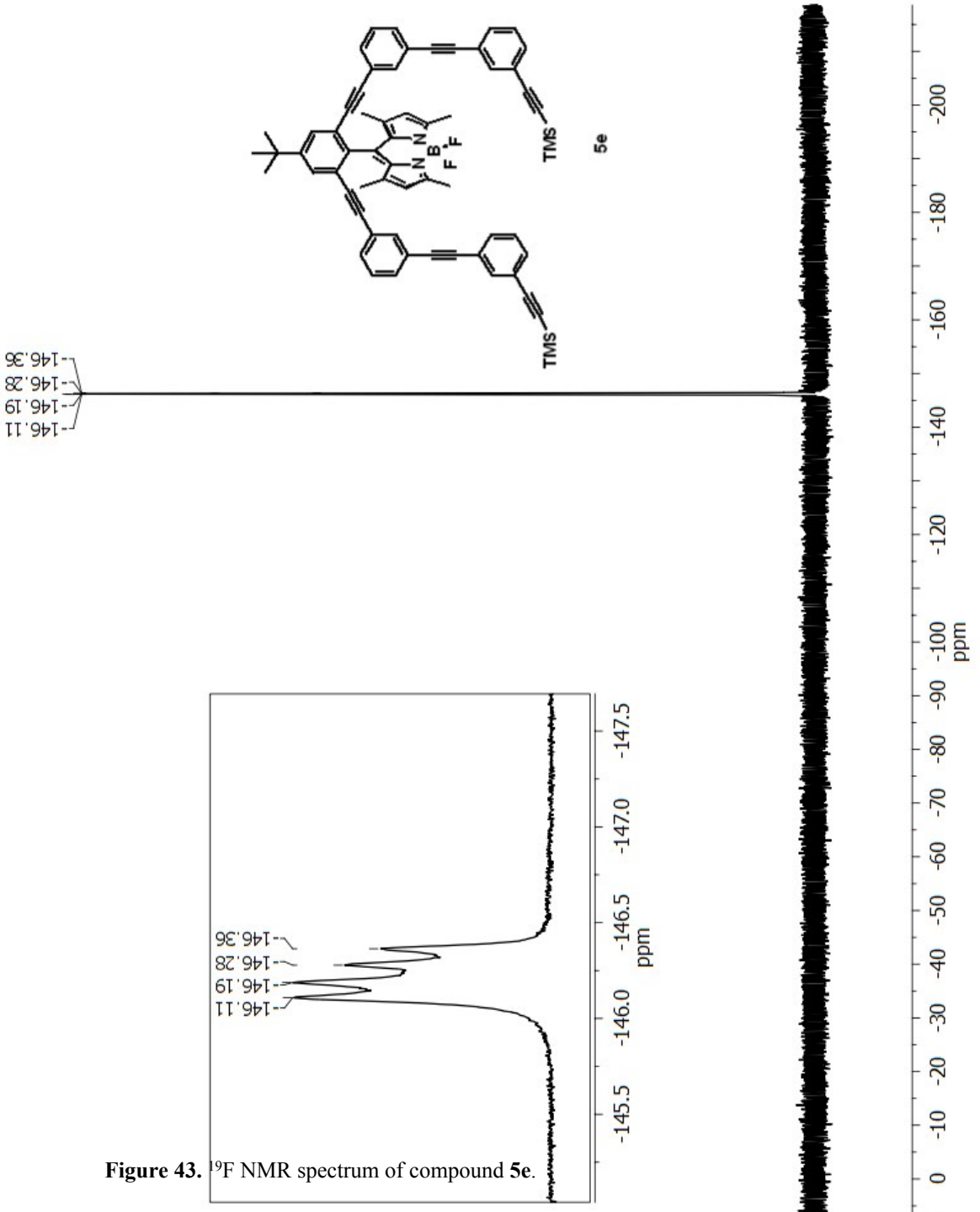


Figure 43. ^{19}F NMR spectrum of compound **5e**.

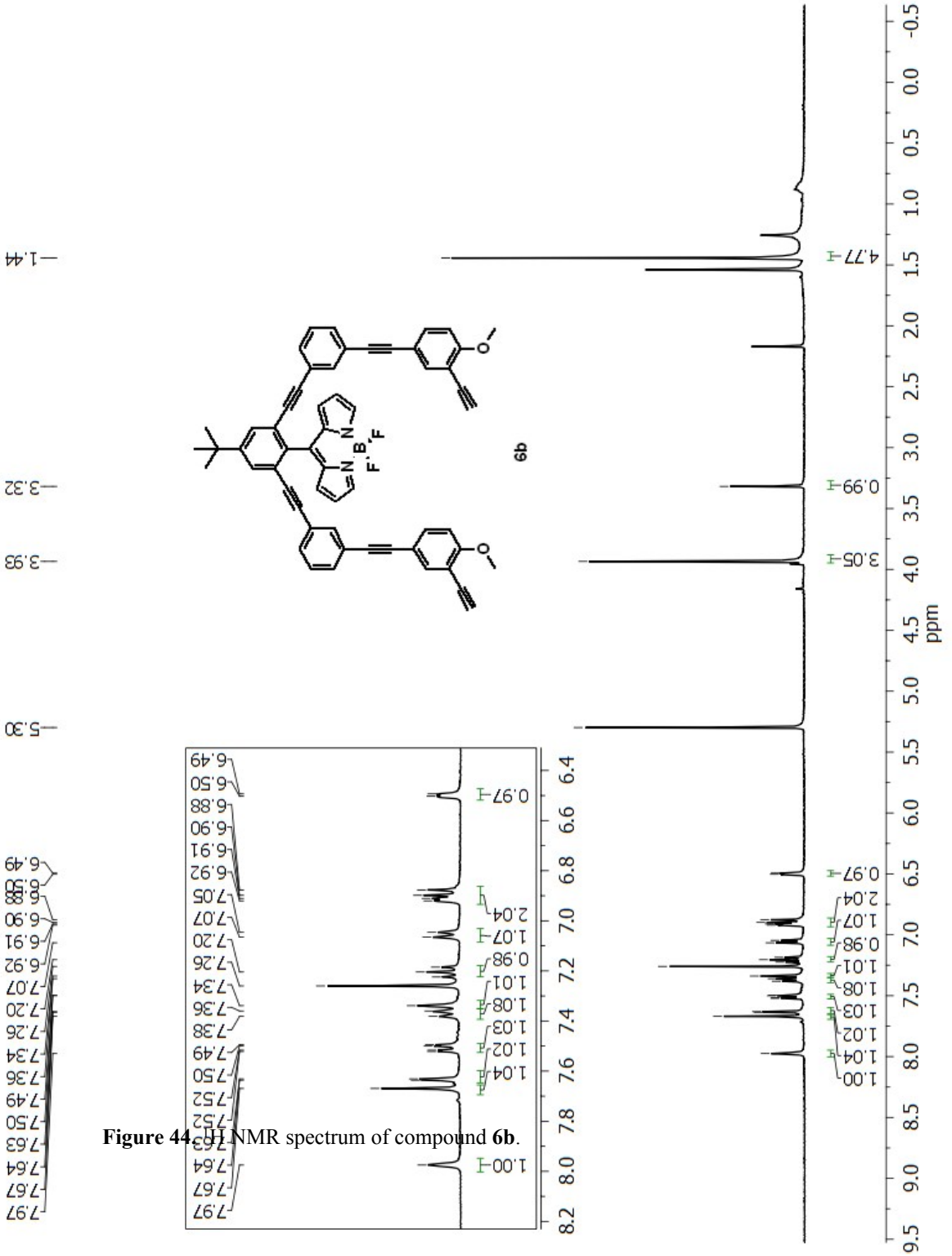


Figure 44. ^{1}H NMR spectrum of compound **6b**.

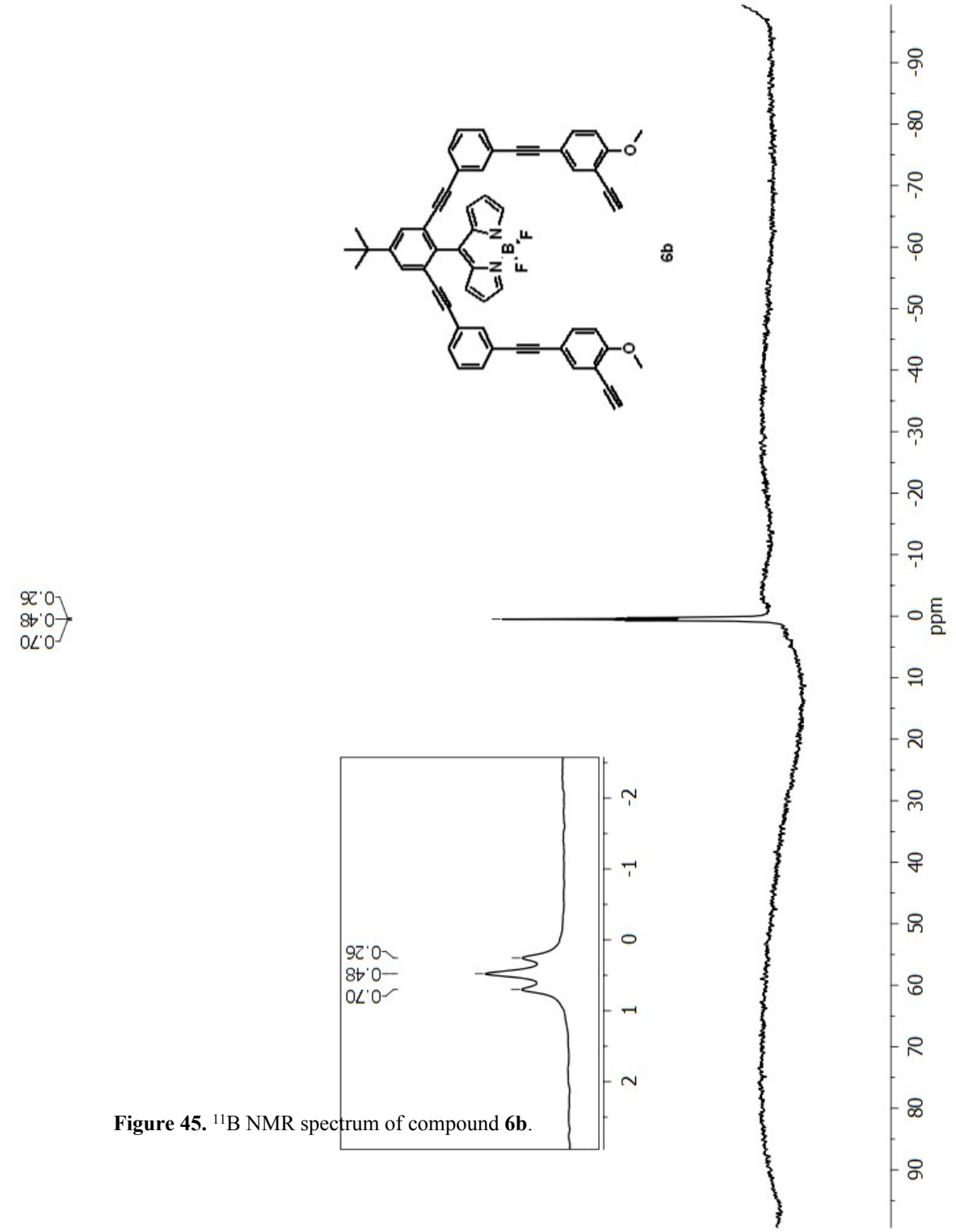


Figure 45. ^{11}B NMR spectrum of compound **6b**.

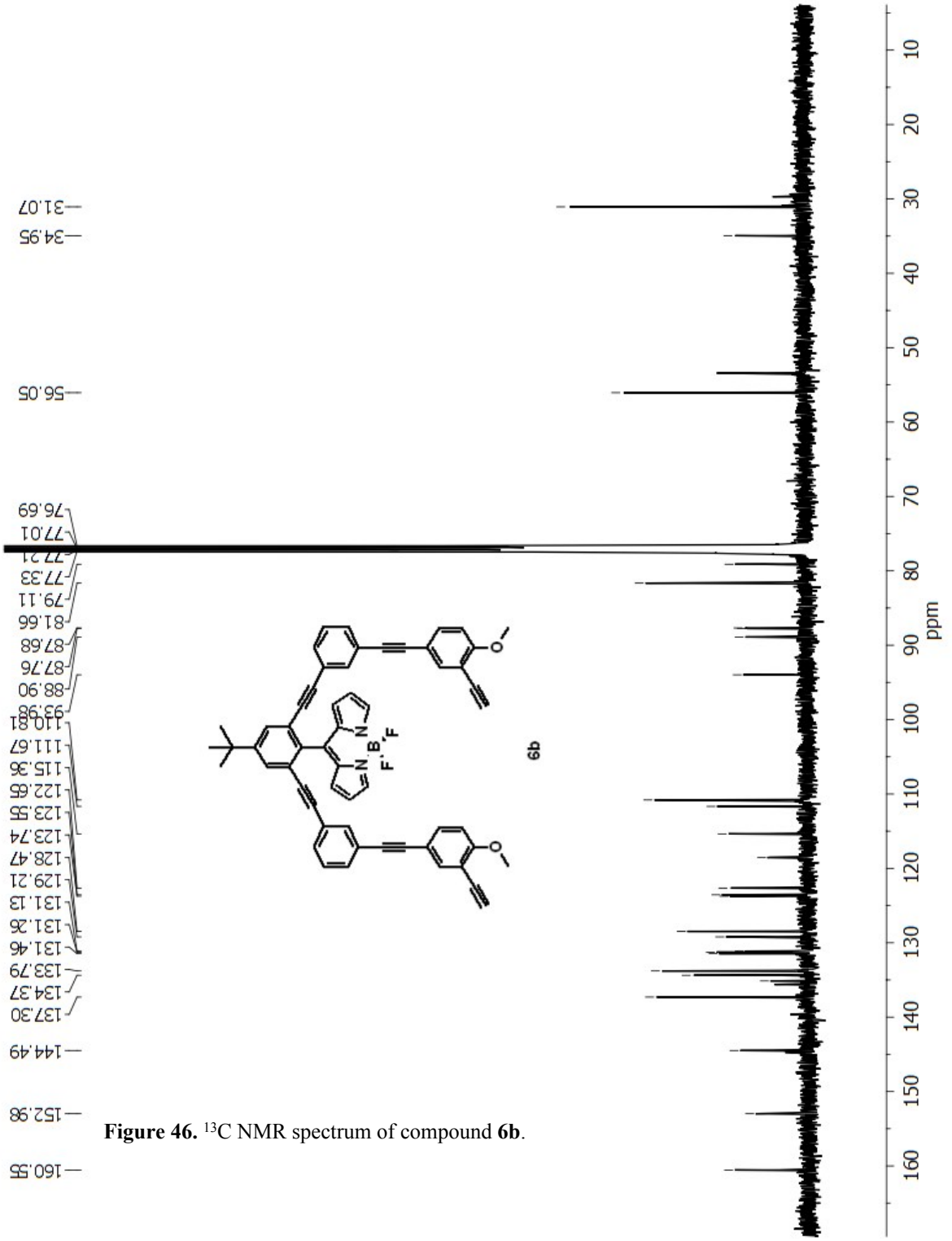


Figure 46. ^{13}C NMR spectrum of compound **6b**.

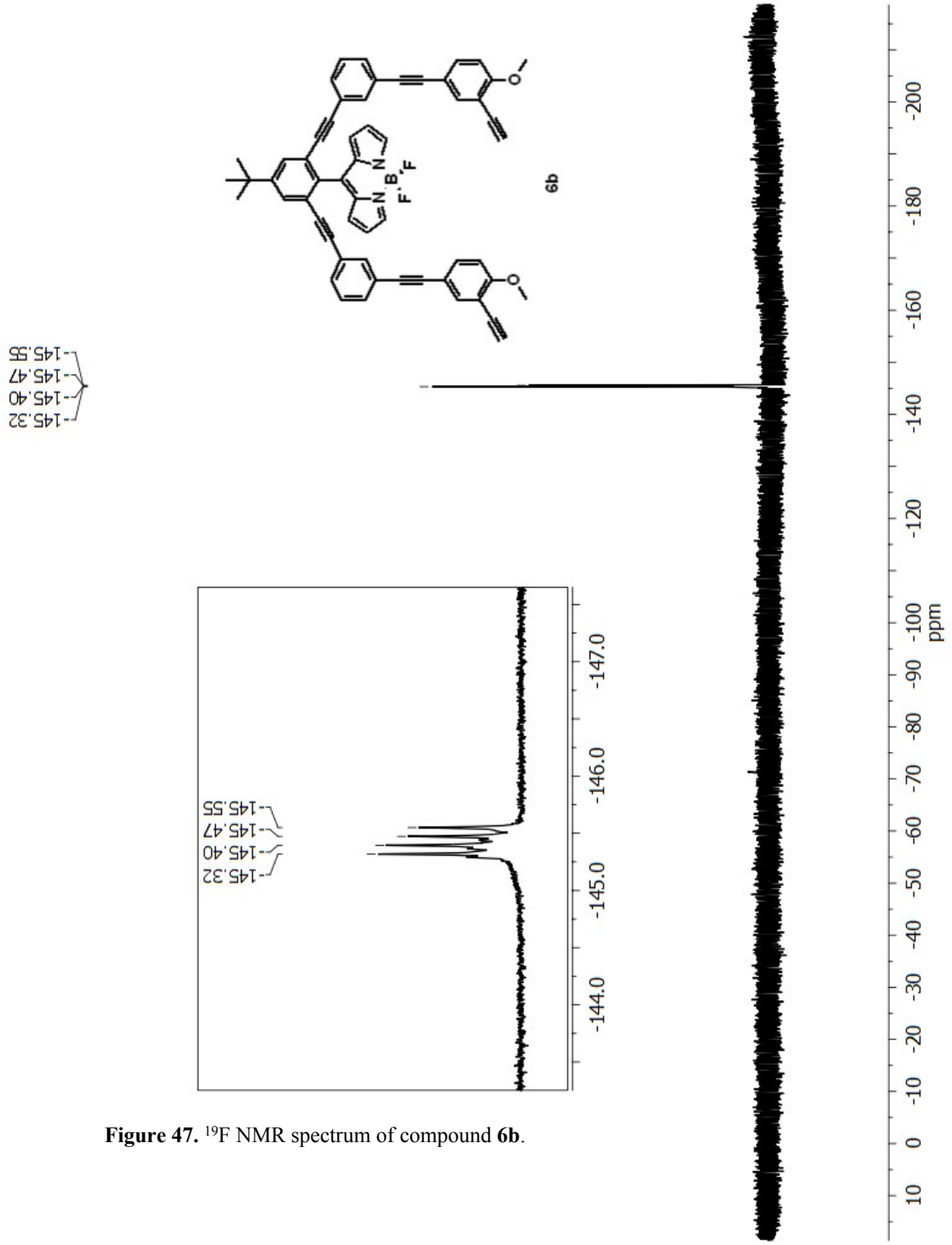


Figure 47. ^{19}F NMR spectrum of compound **6b**.

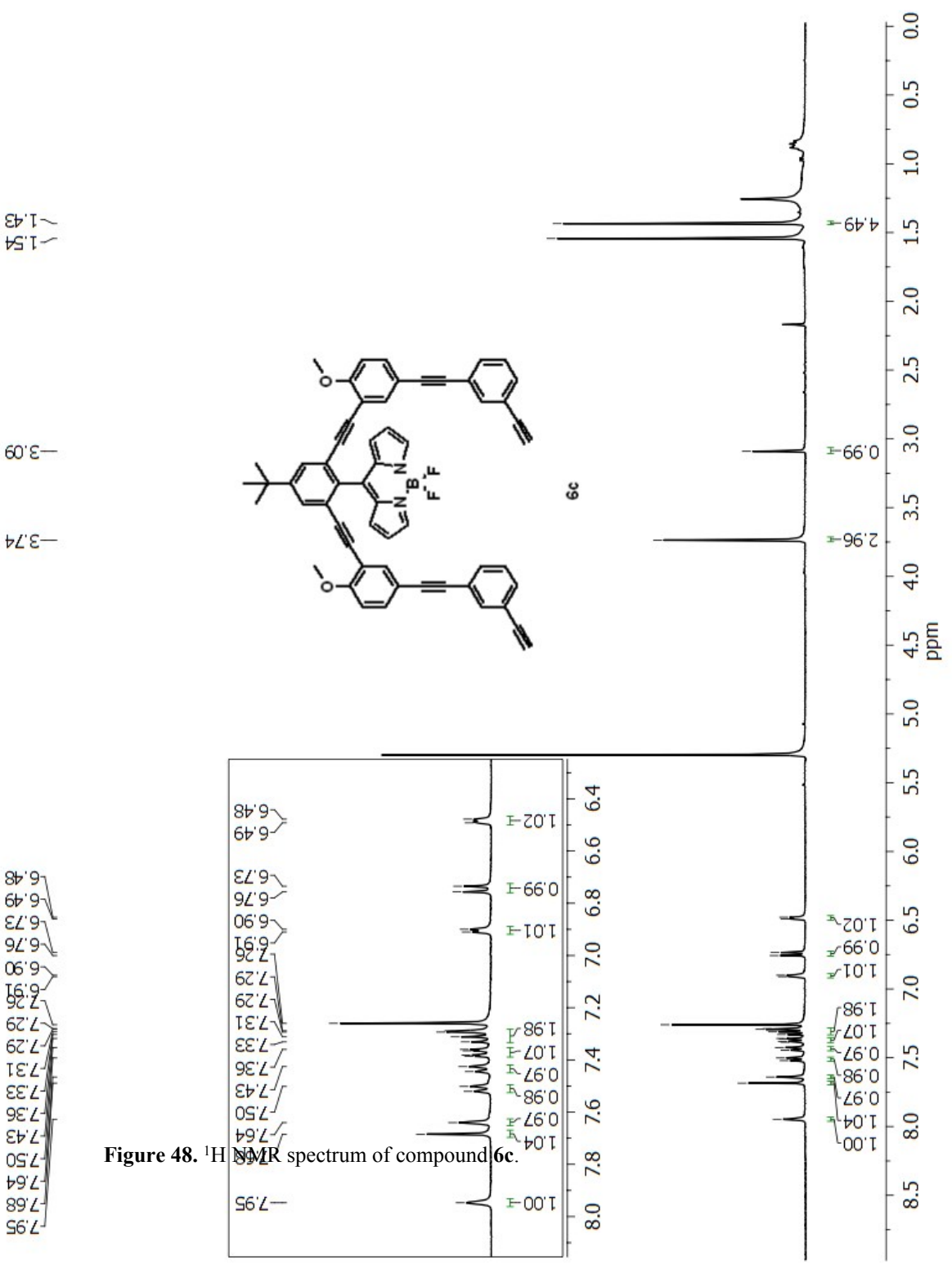


Figure 48. ^{1}H NMR spectrum of compound **6c**.

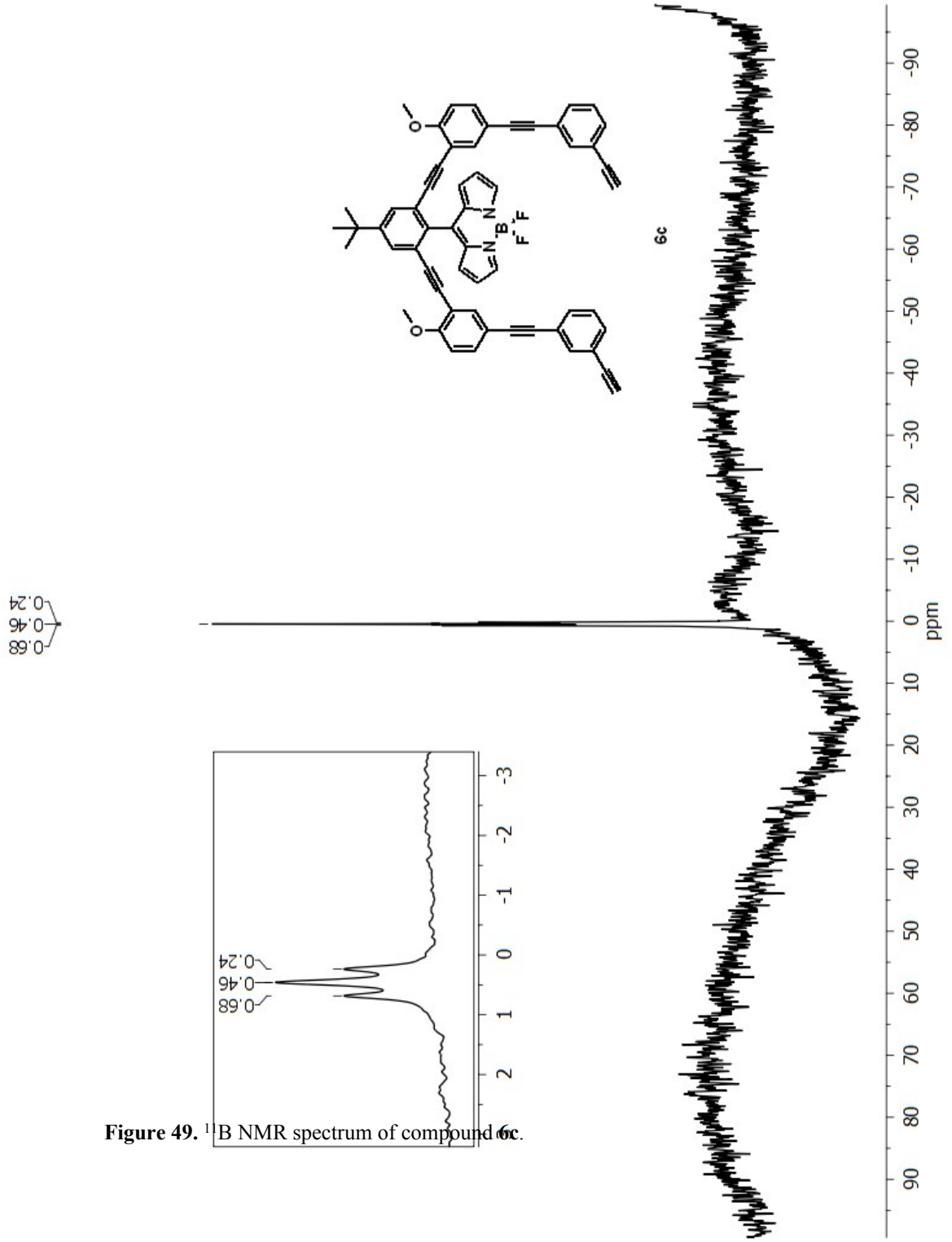


Figure 49. ^{11}B NMR spectrum of compound **6c**.

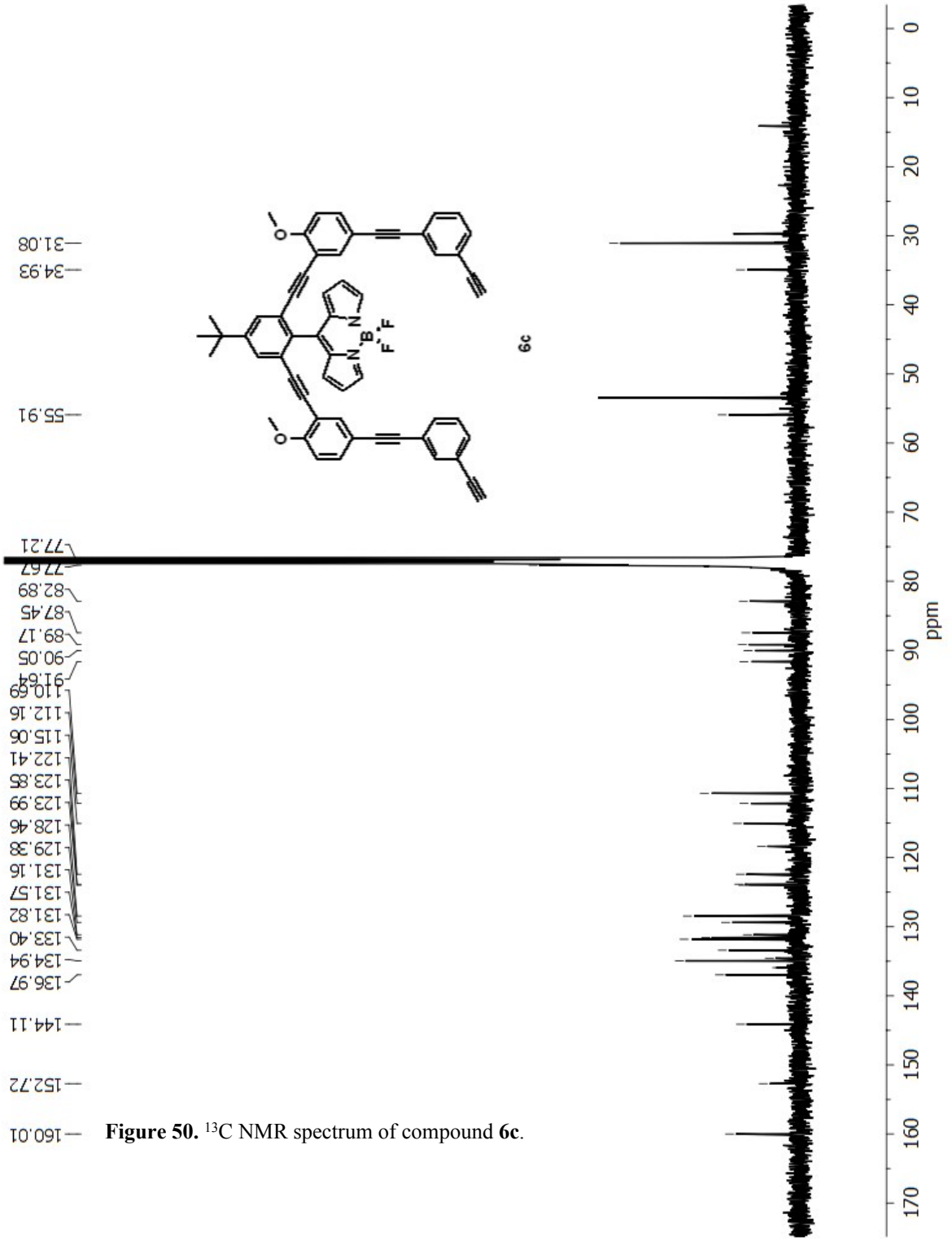


Figure 50. ^{13}C NMR spectrum of compound **6c**.

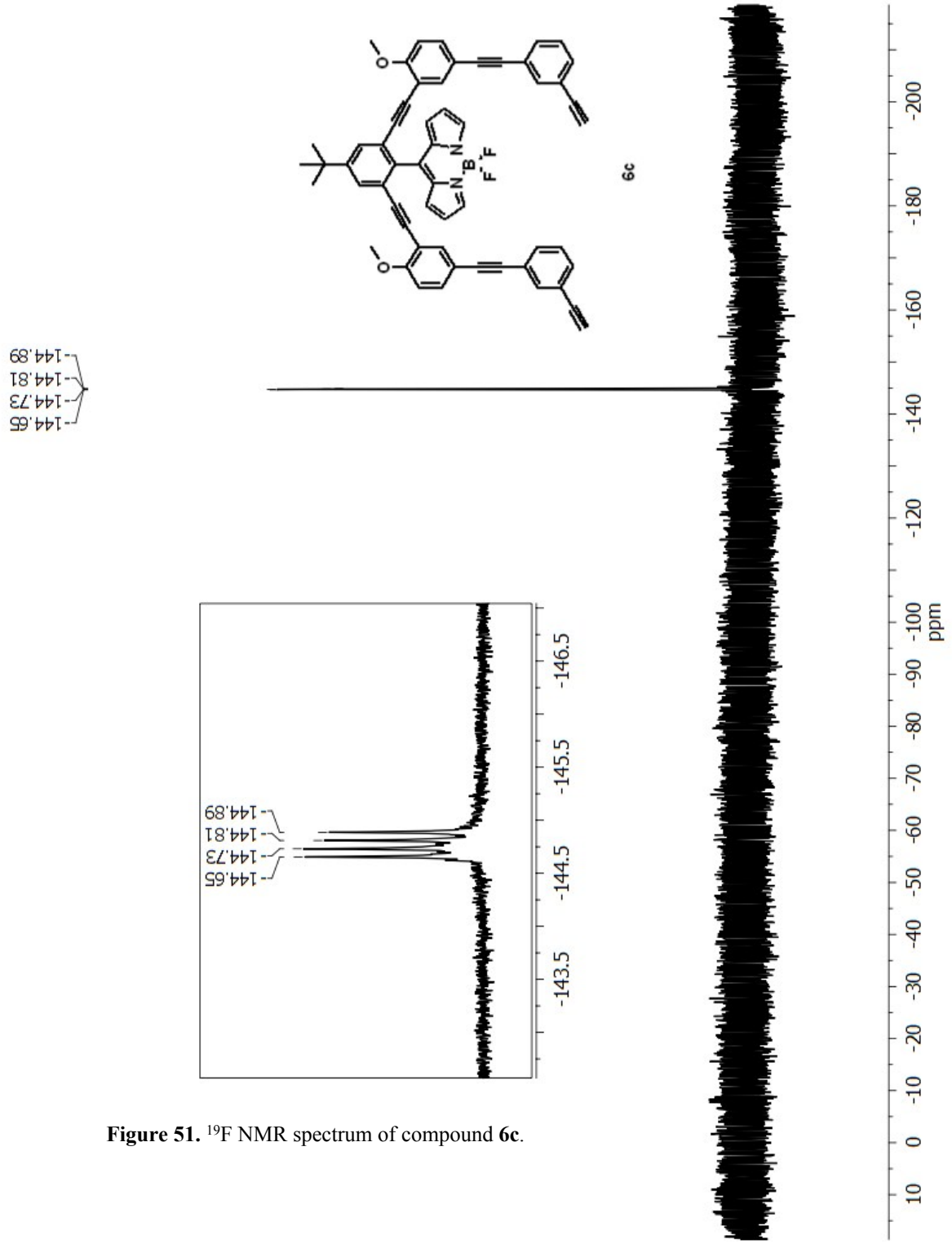


Figure 51. ^{19}F NMR spectrum of compound **6c**.

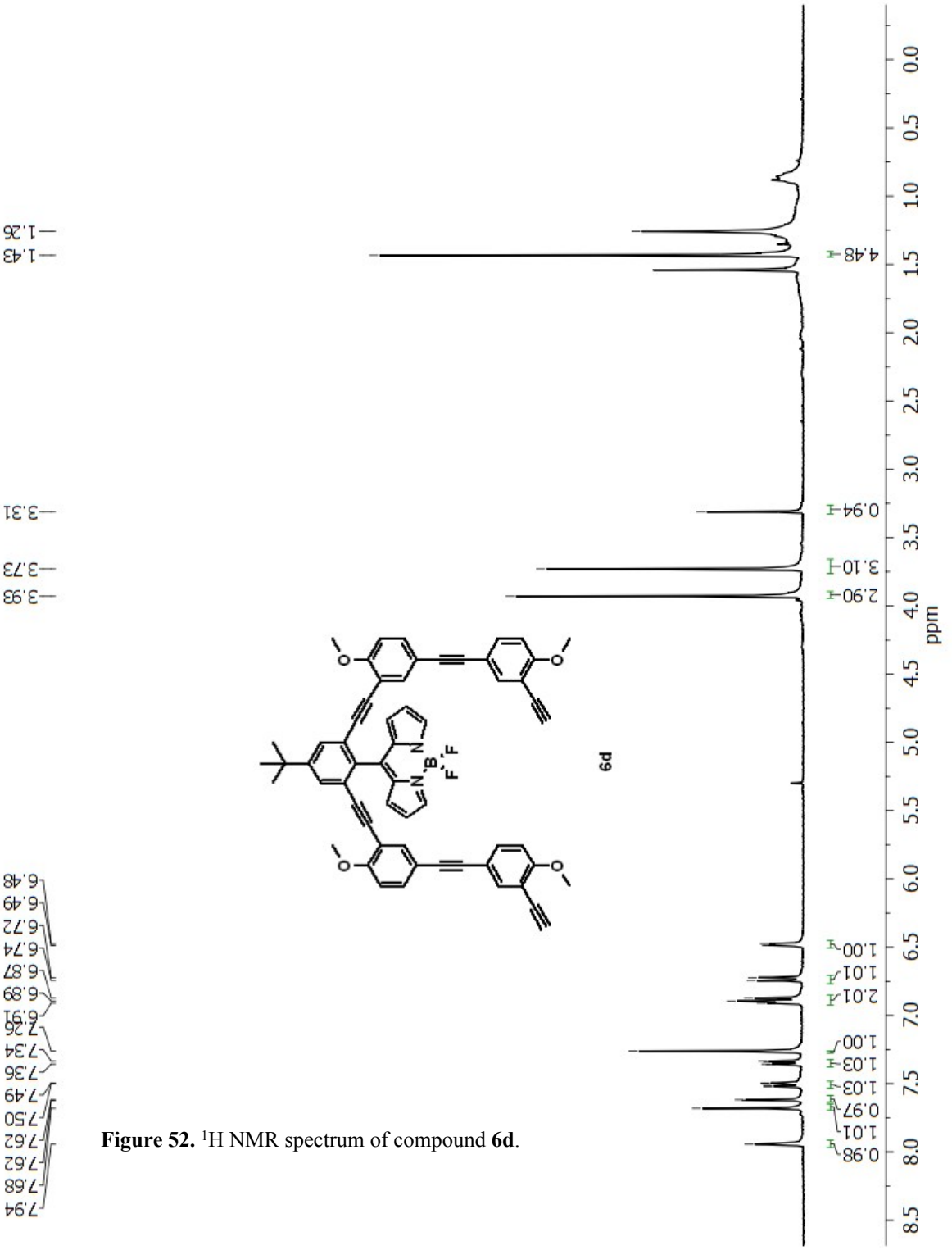


Figure 52. ^{1}H NMR spectrum of compound **6d**.

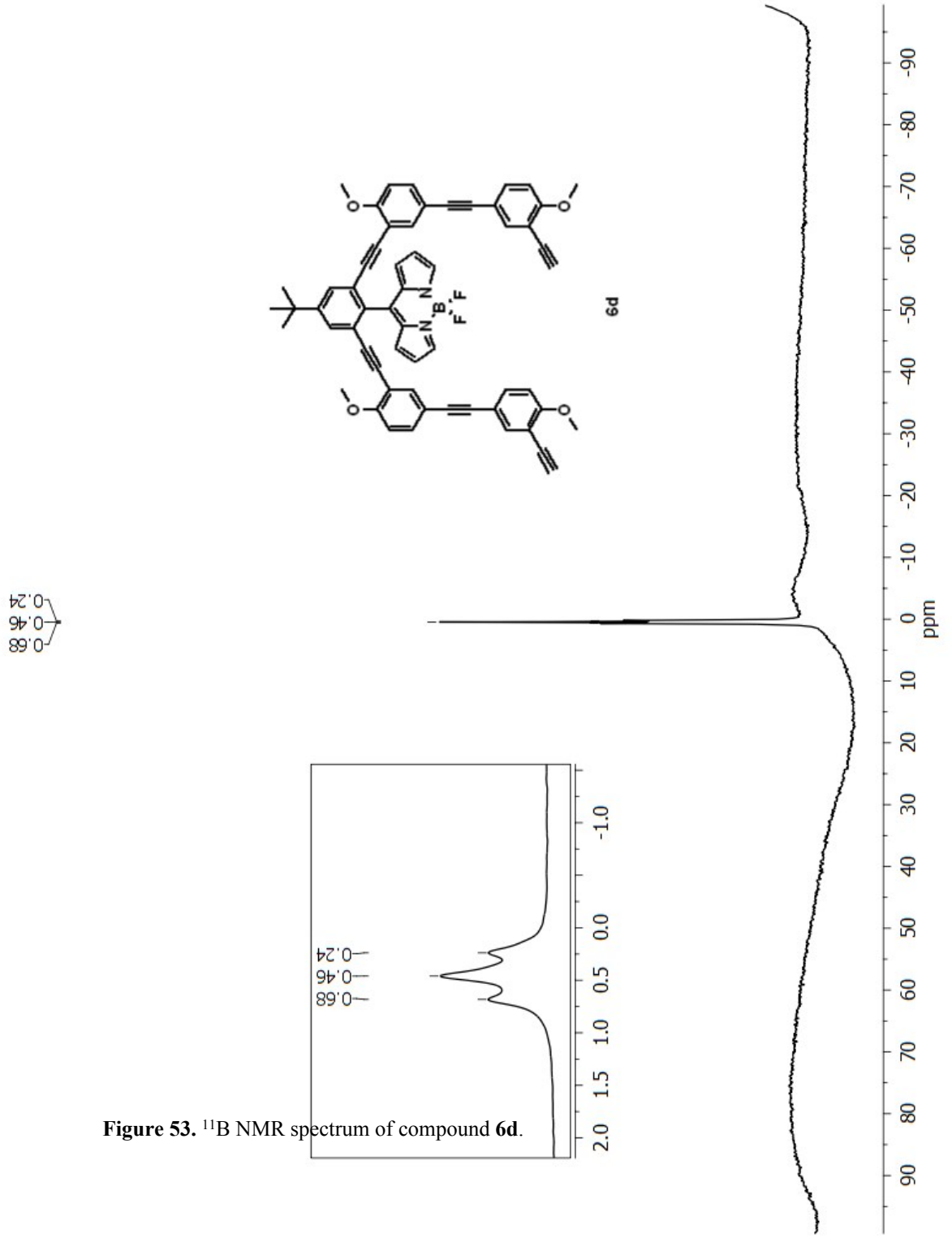


Figure 53. ^{11}B NMR spectrum of compound **6d**.

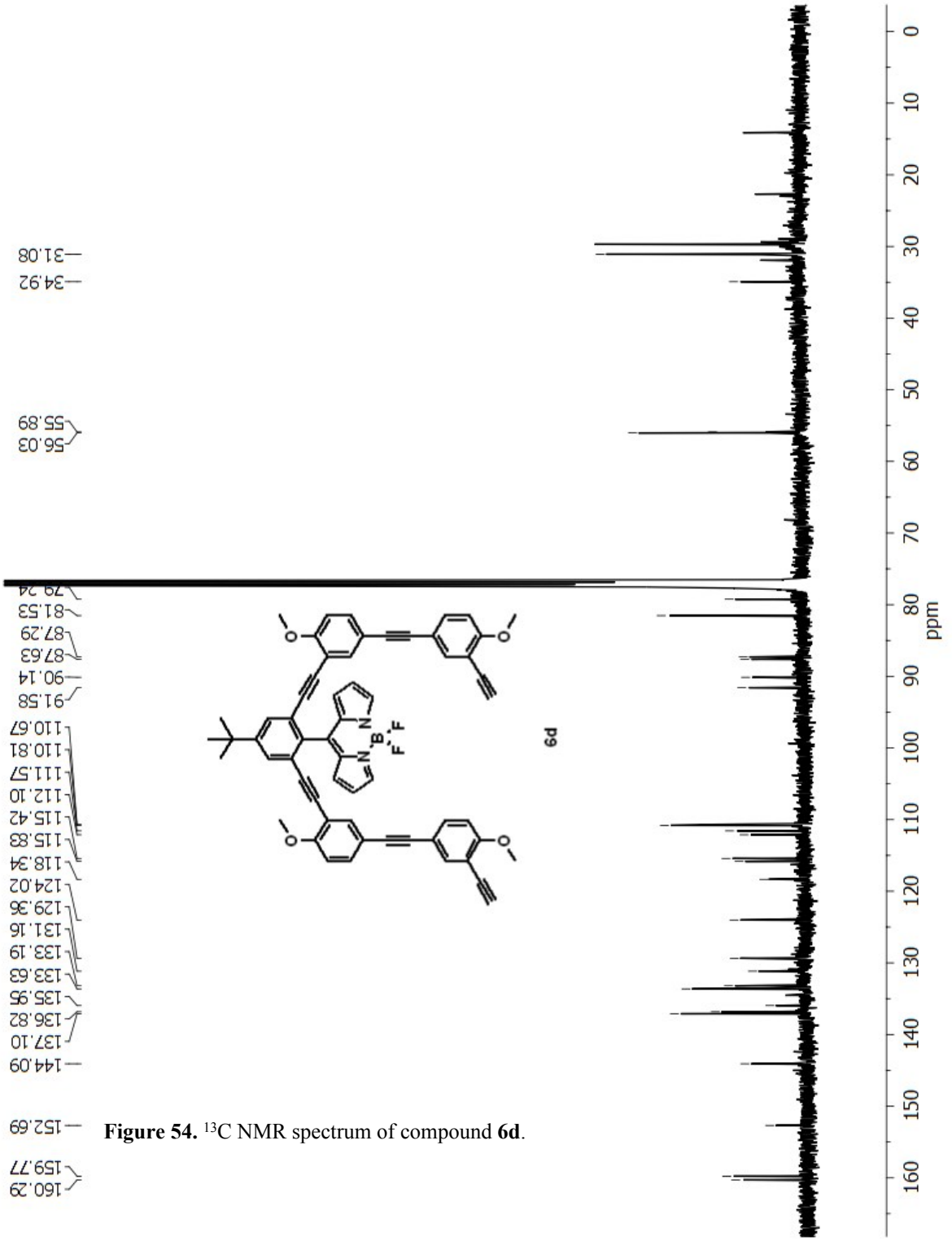


Figure 54. ^{13}C NMR spectrum of compound **6d**.

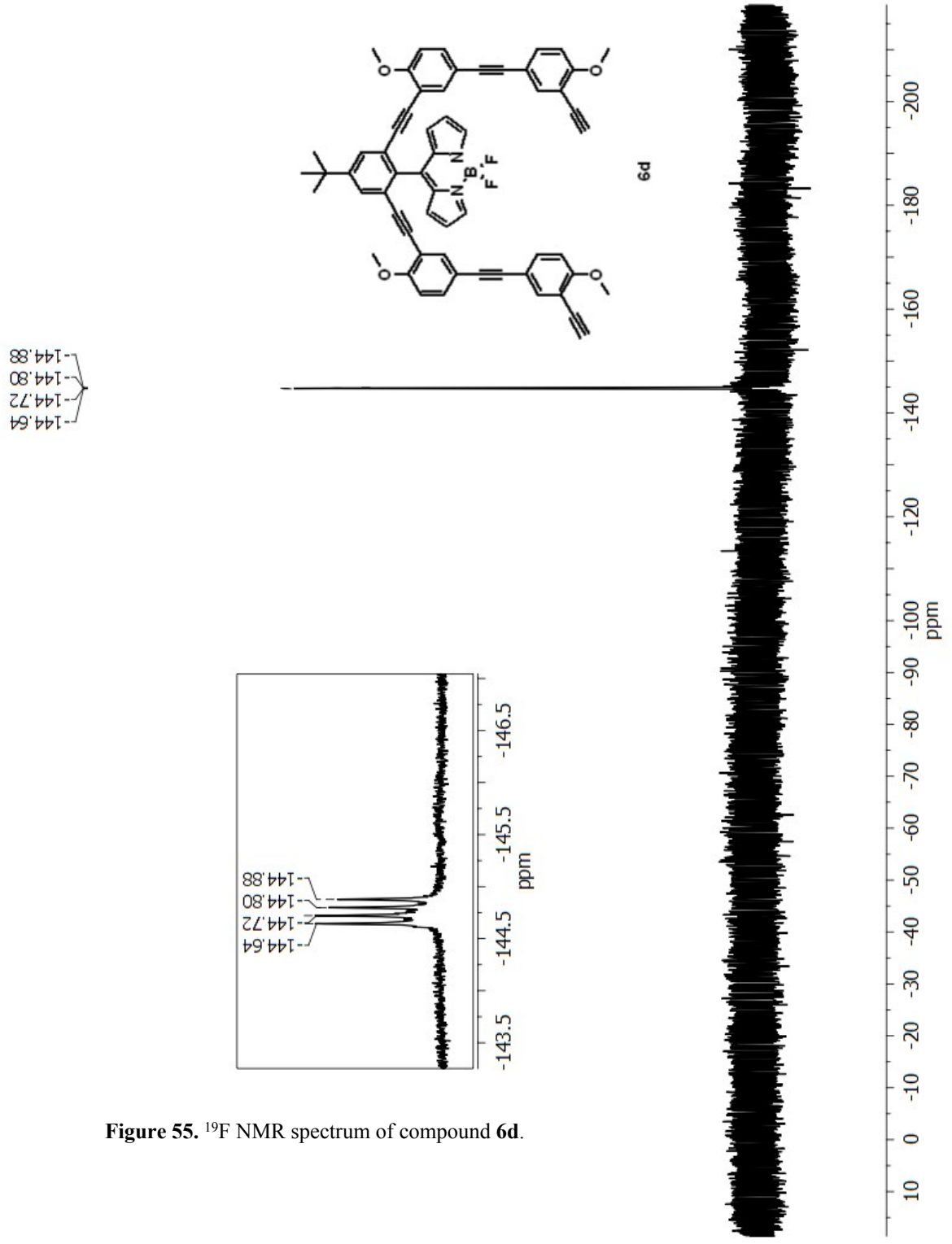


Figure 55. ^{19}F NMR spectrum of compound **6d**.

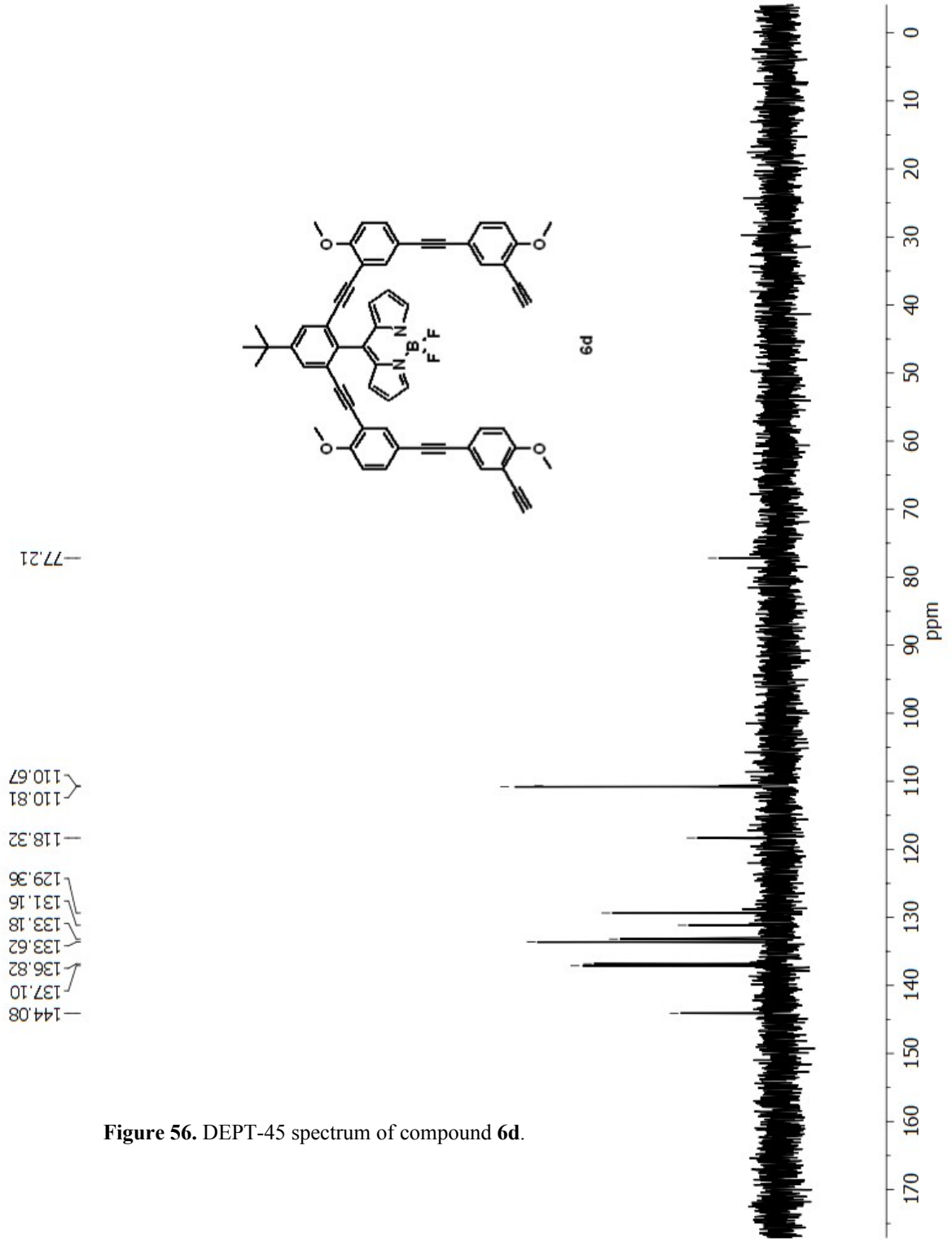


Figure 56. DEPT-45 spectrum of compound **6d**.

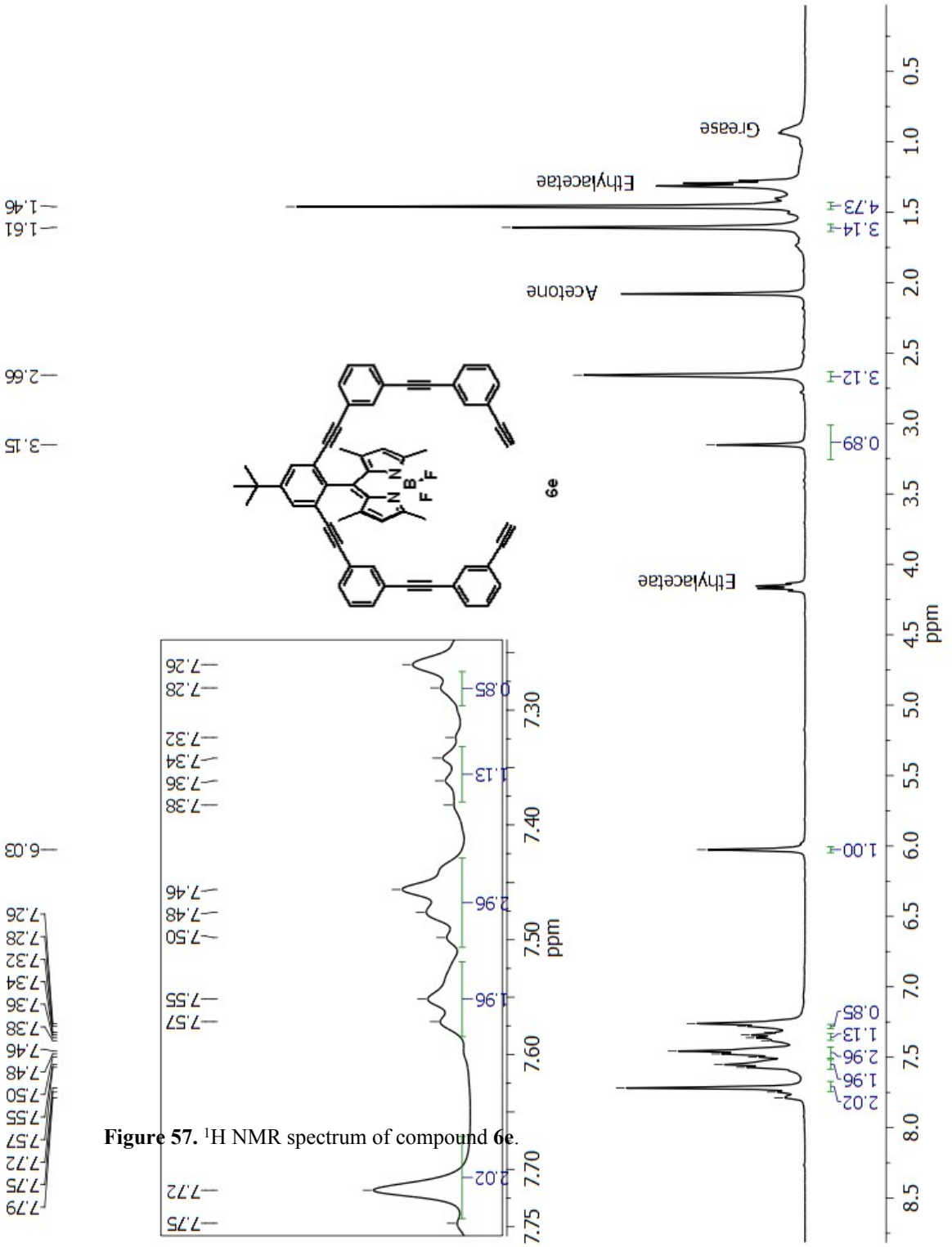


Figure 57. ^{1}H NMR spectrum of compound **6e**.

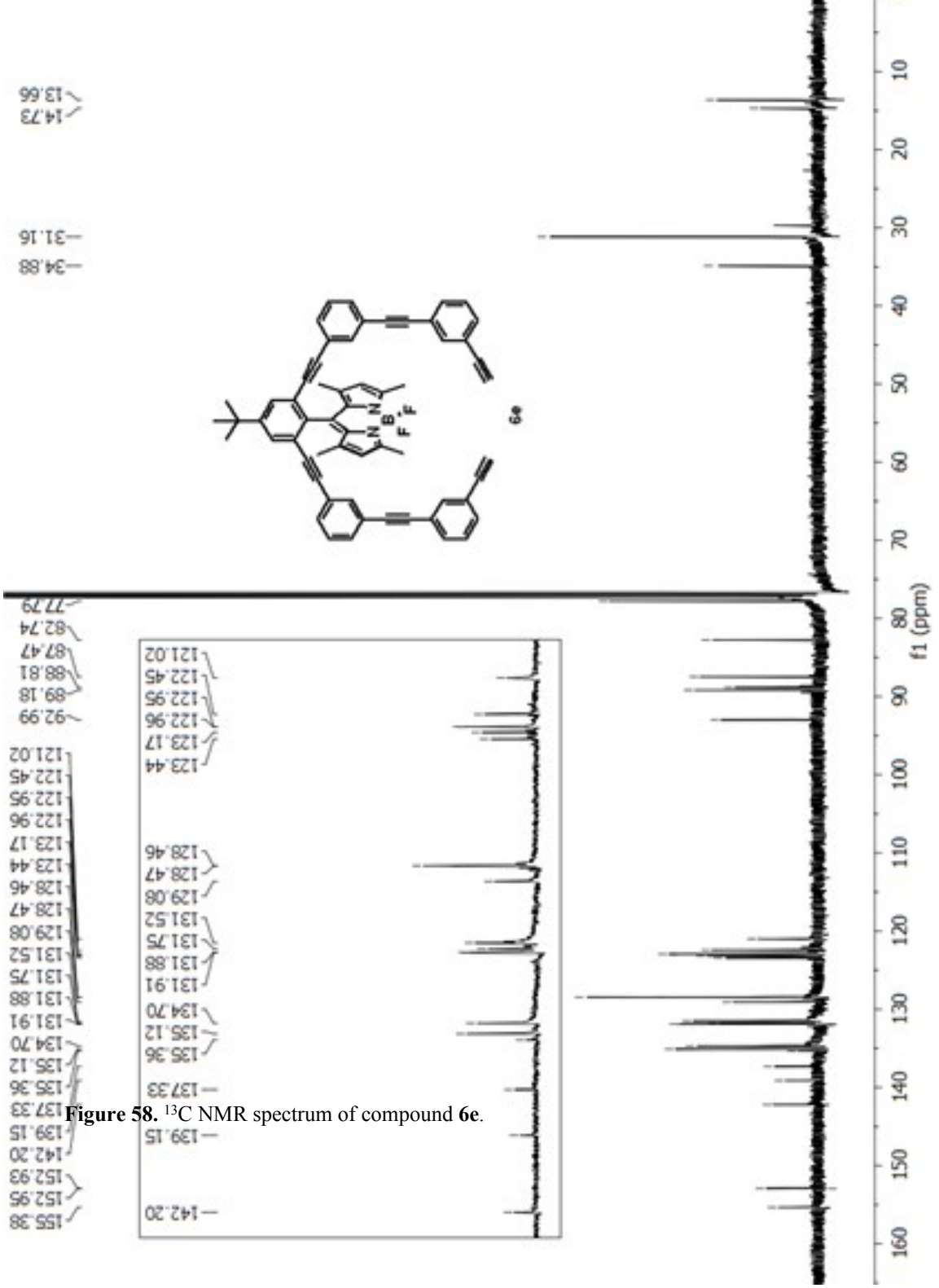


Figure 58. ^{13}C NMR spectrum of compound **6e**.

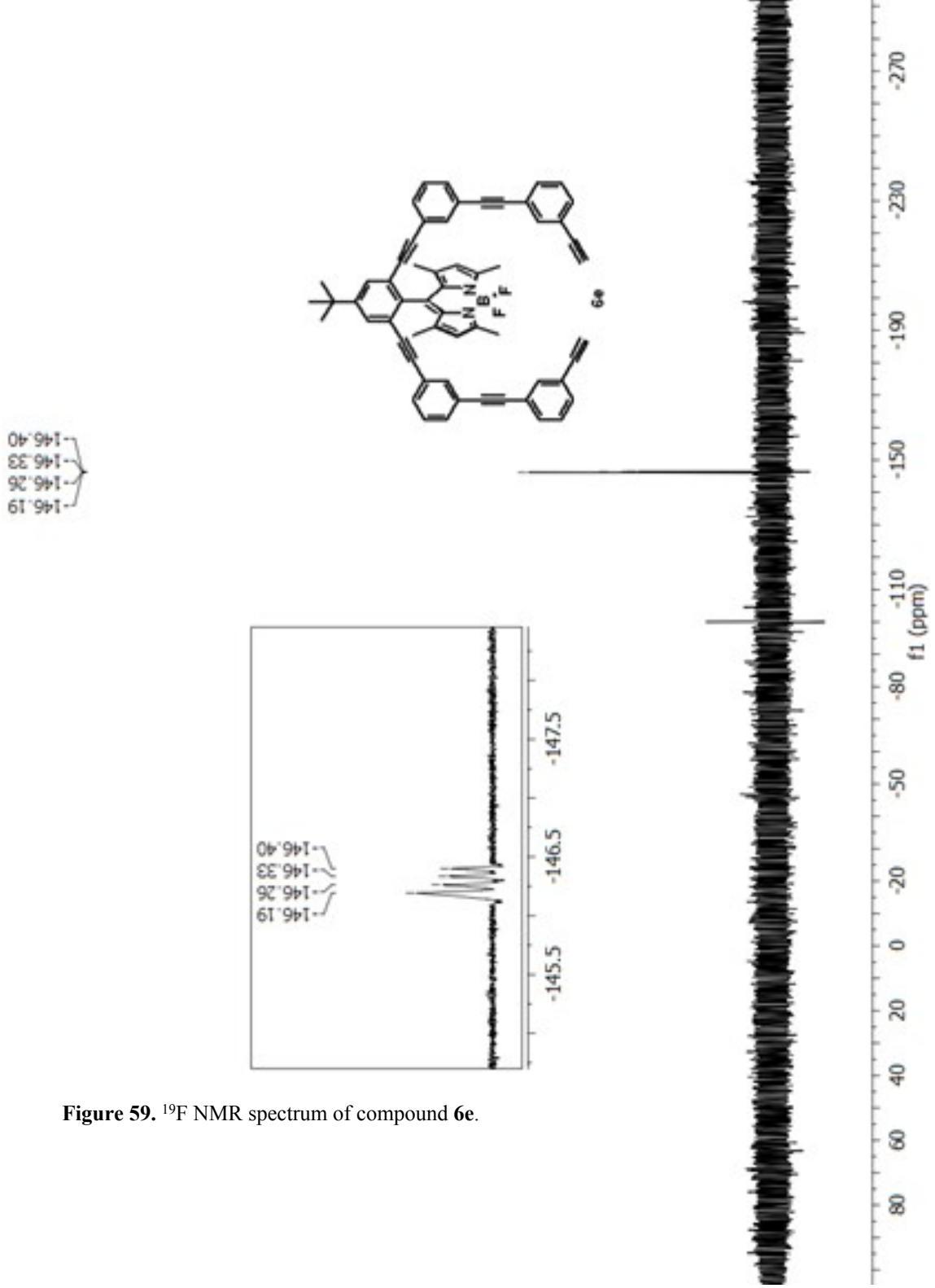


Figure 59. ^{19}F NMR spectrum of compound **6e**.

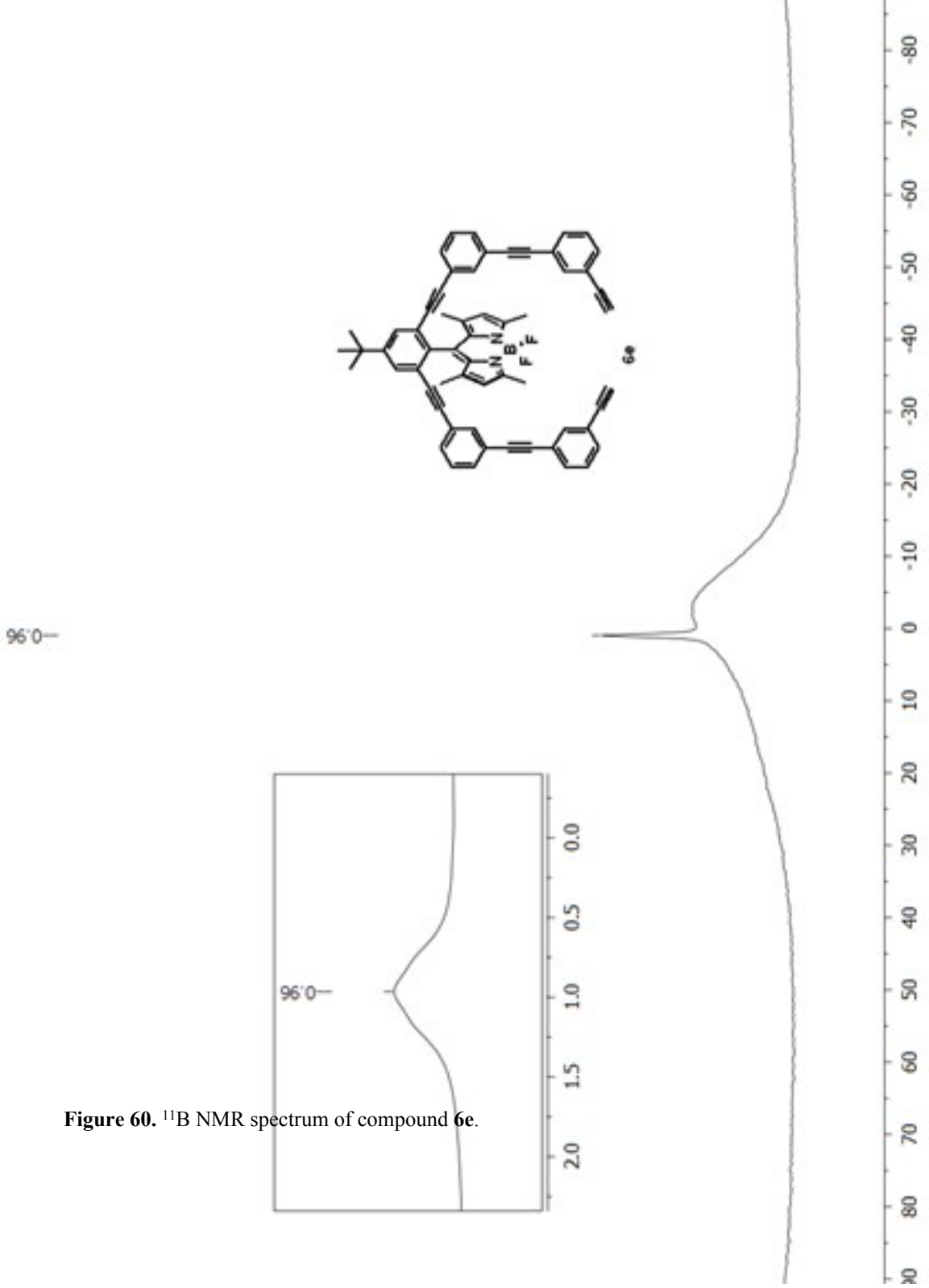


Figure 60. ^{11}B NMR spectrum of compound **6e**.

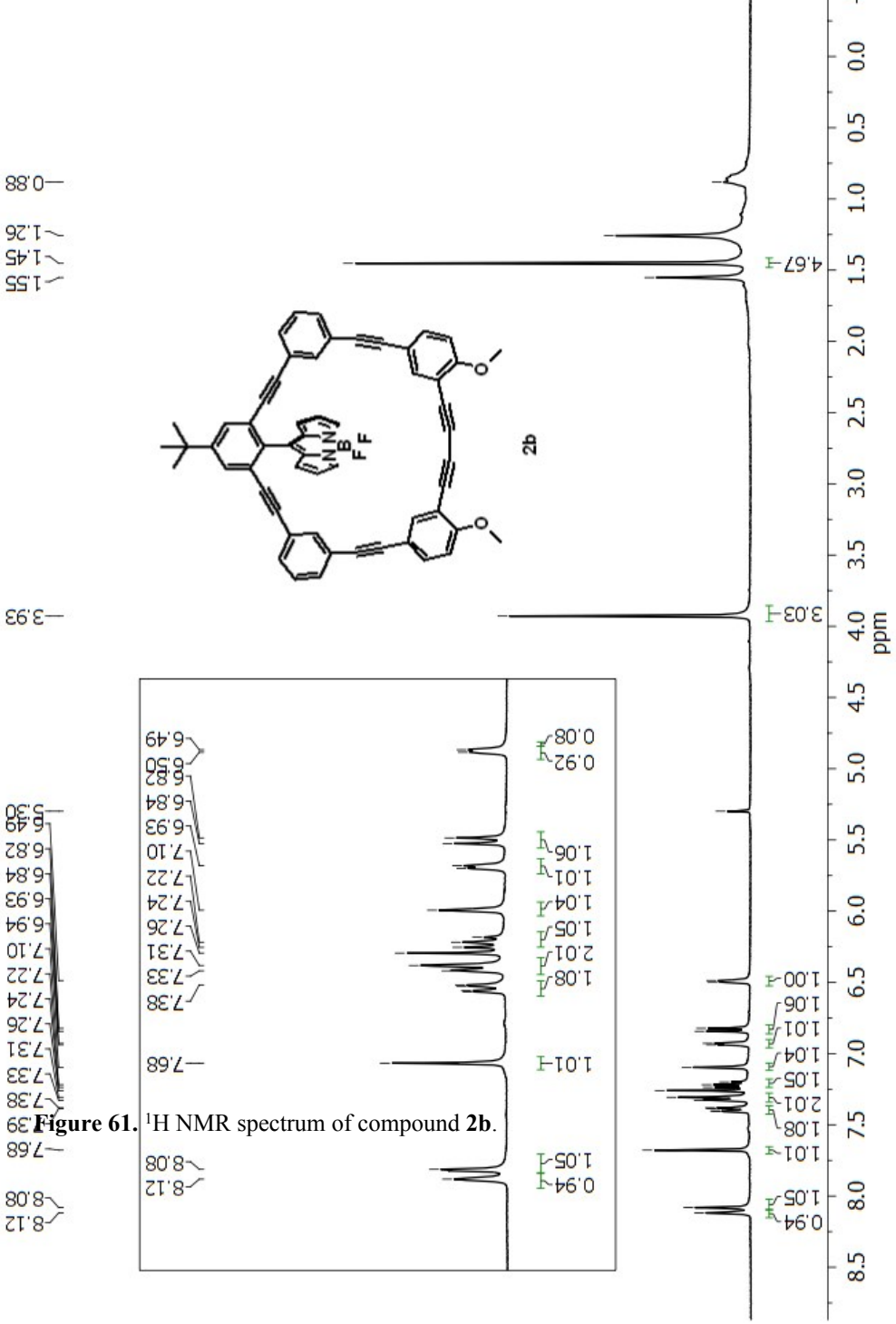


Figure 61. ^{1}H NMR spectrum of compound **2b**.

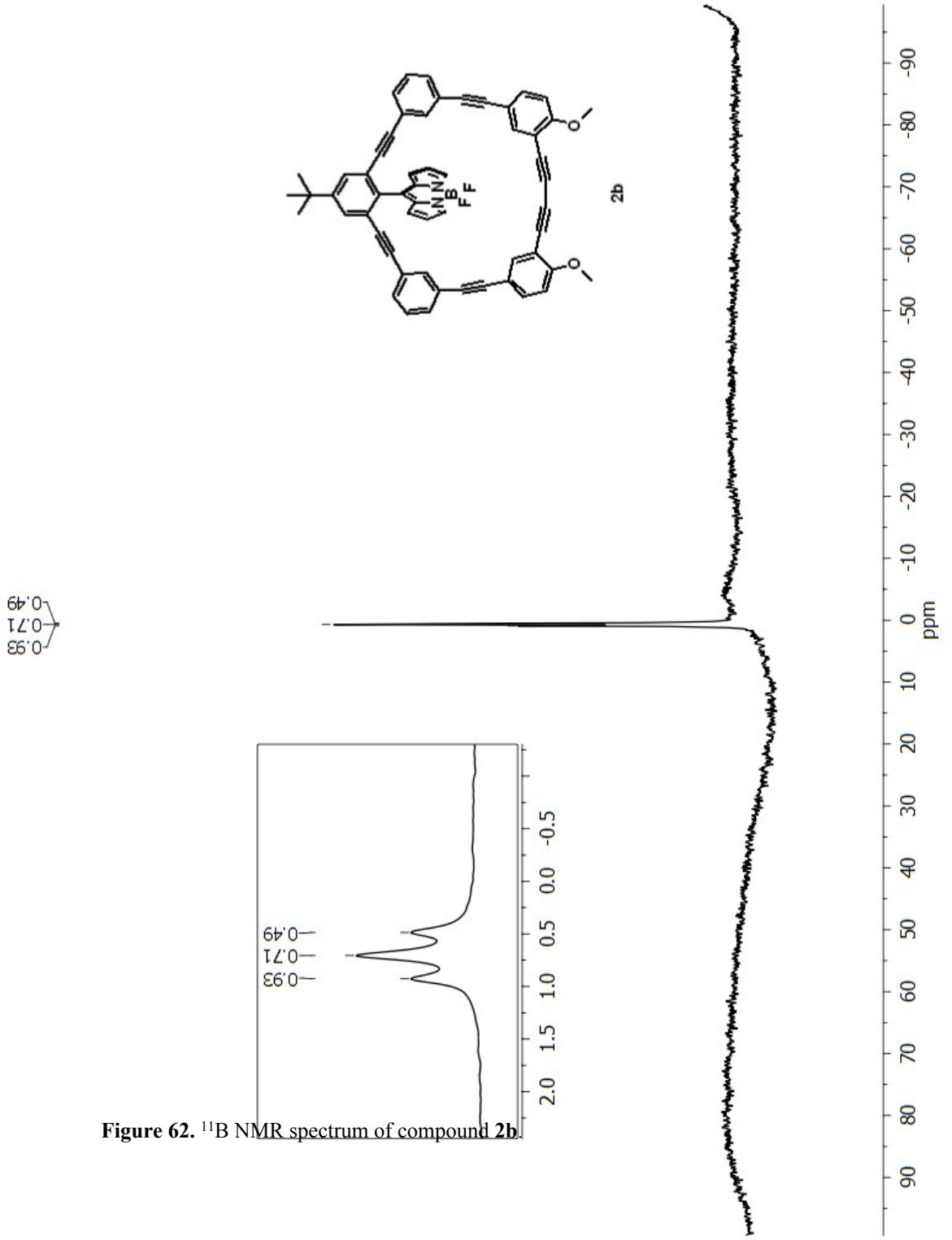


Figure 62. ^{11}B NMR spectrum of compound **2b**.

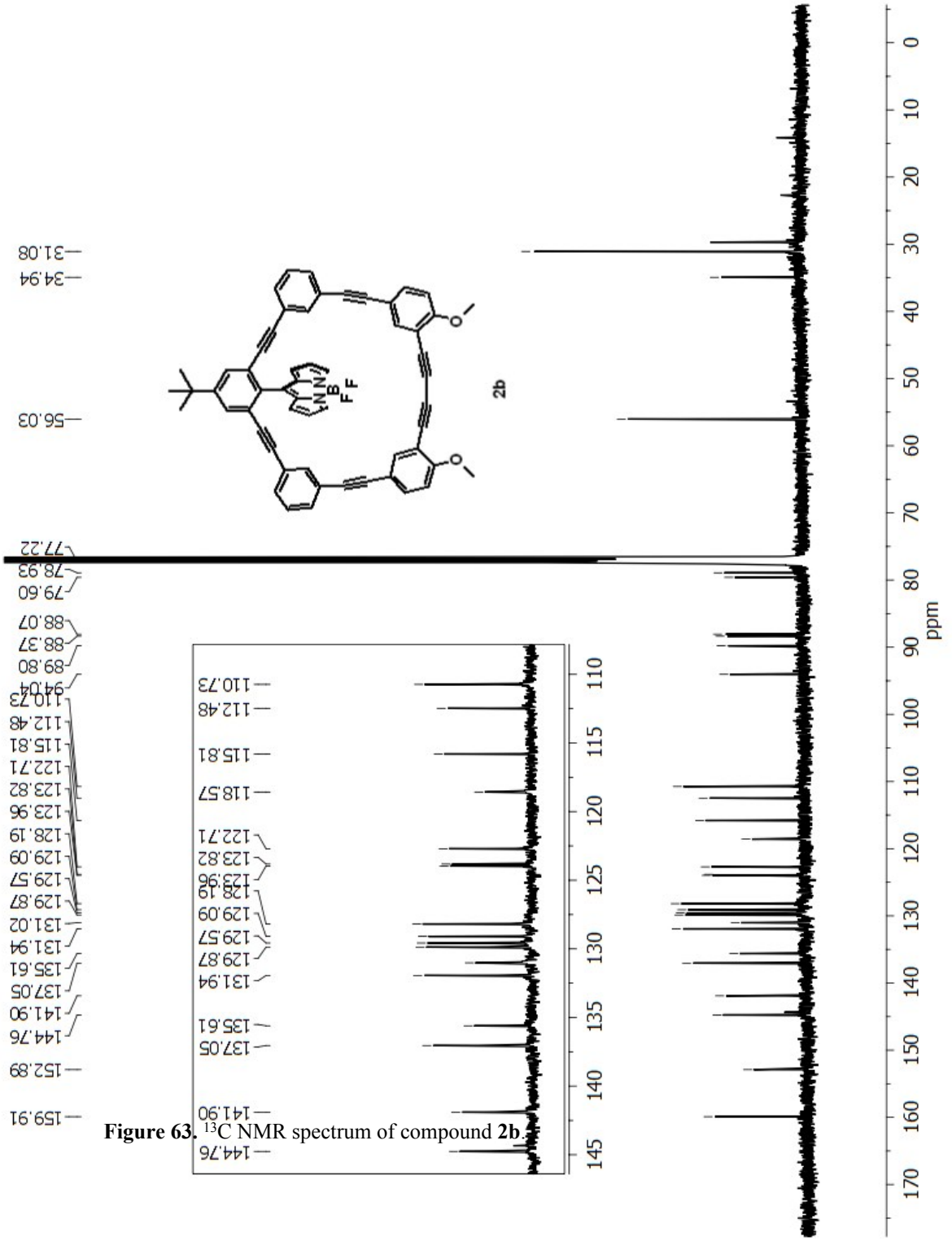


Figure 63. ^{13}C NMR spectrum of compound **2b**.

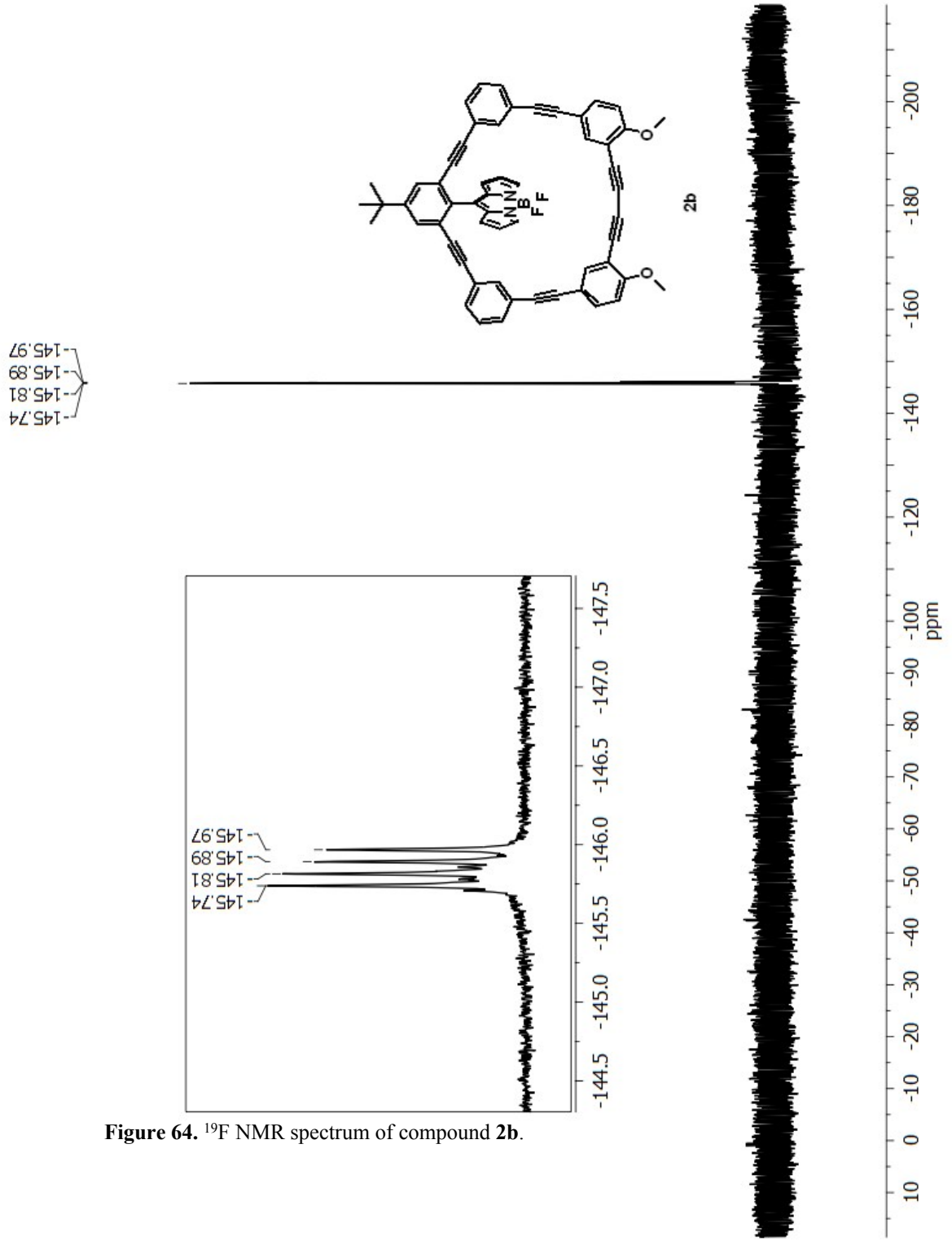


Figure 64. ^{19}F NMR spectrum of compound **2b**.

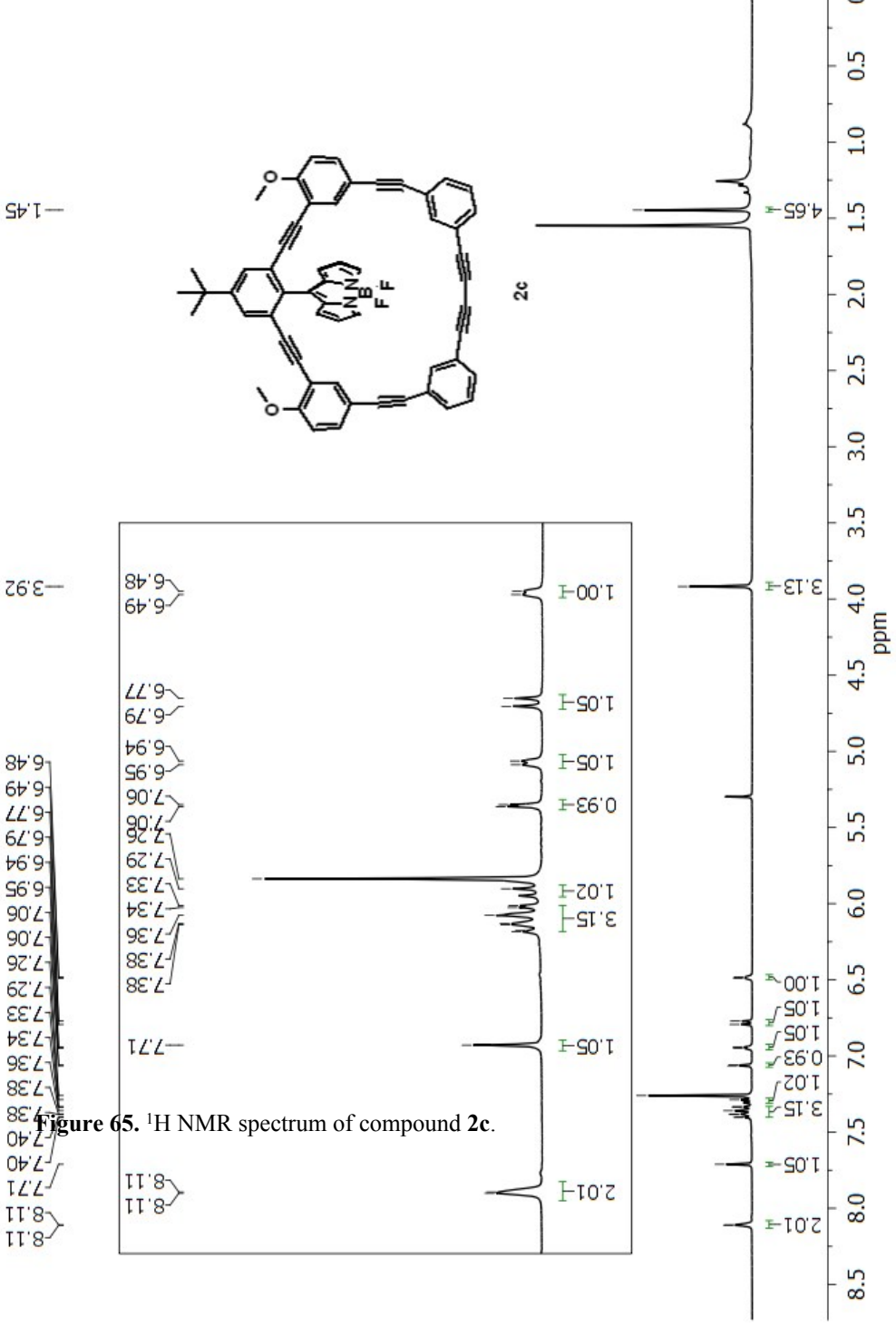


Figure 65. [1]H NMR spectrum of compound **2c**.

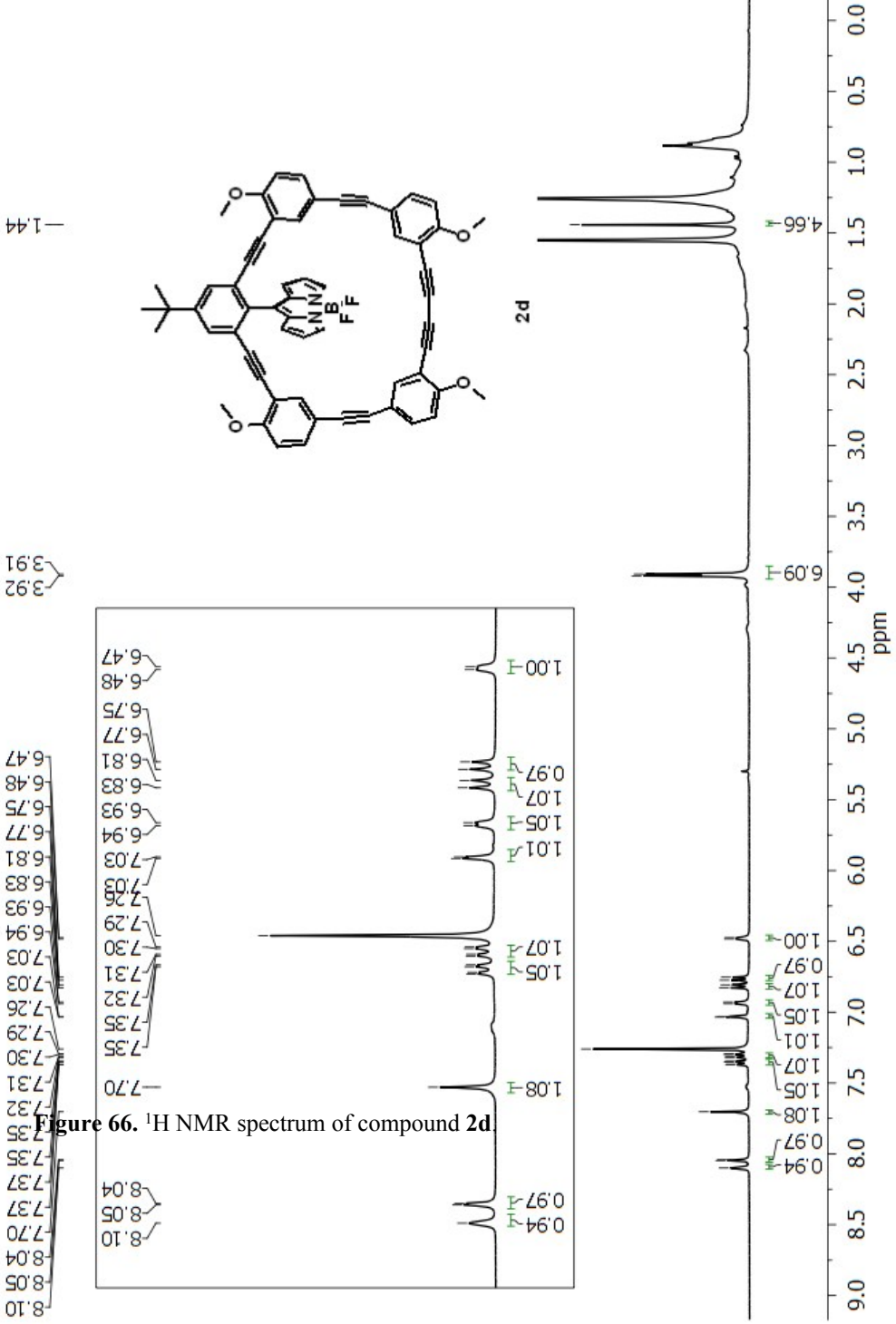


Figure 66. [1]H NMR spectrum of compound **2d**.

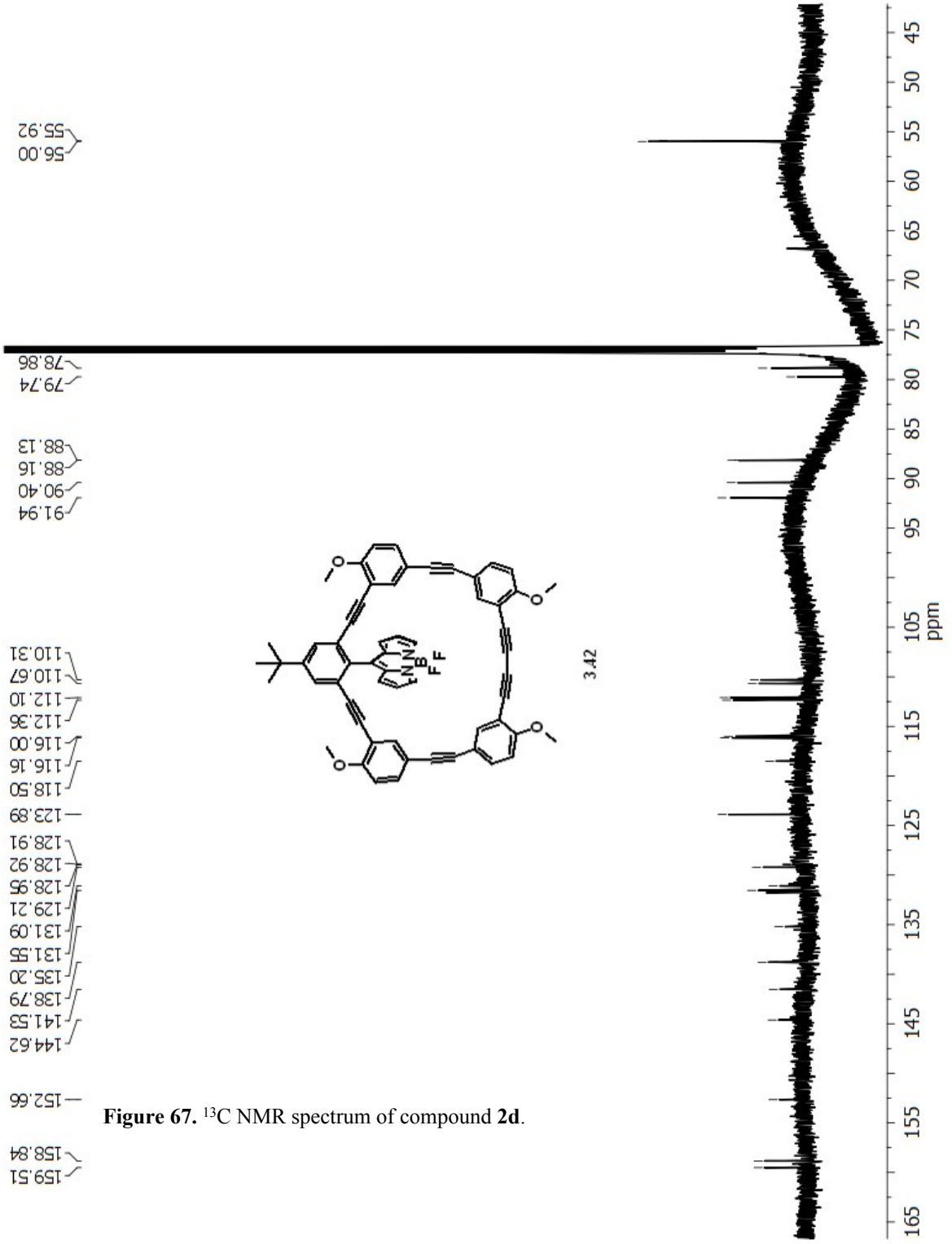


Figure 67. ^{13}C NMR spectrum of compound **2d**.

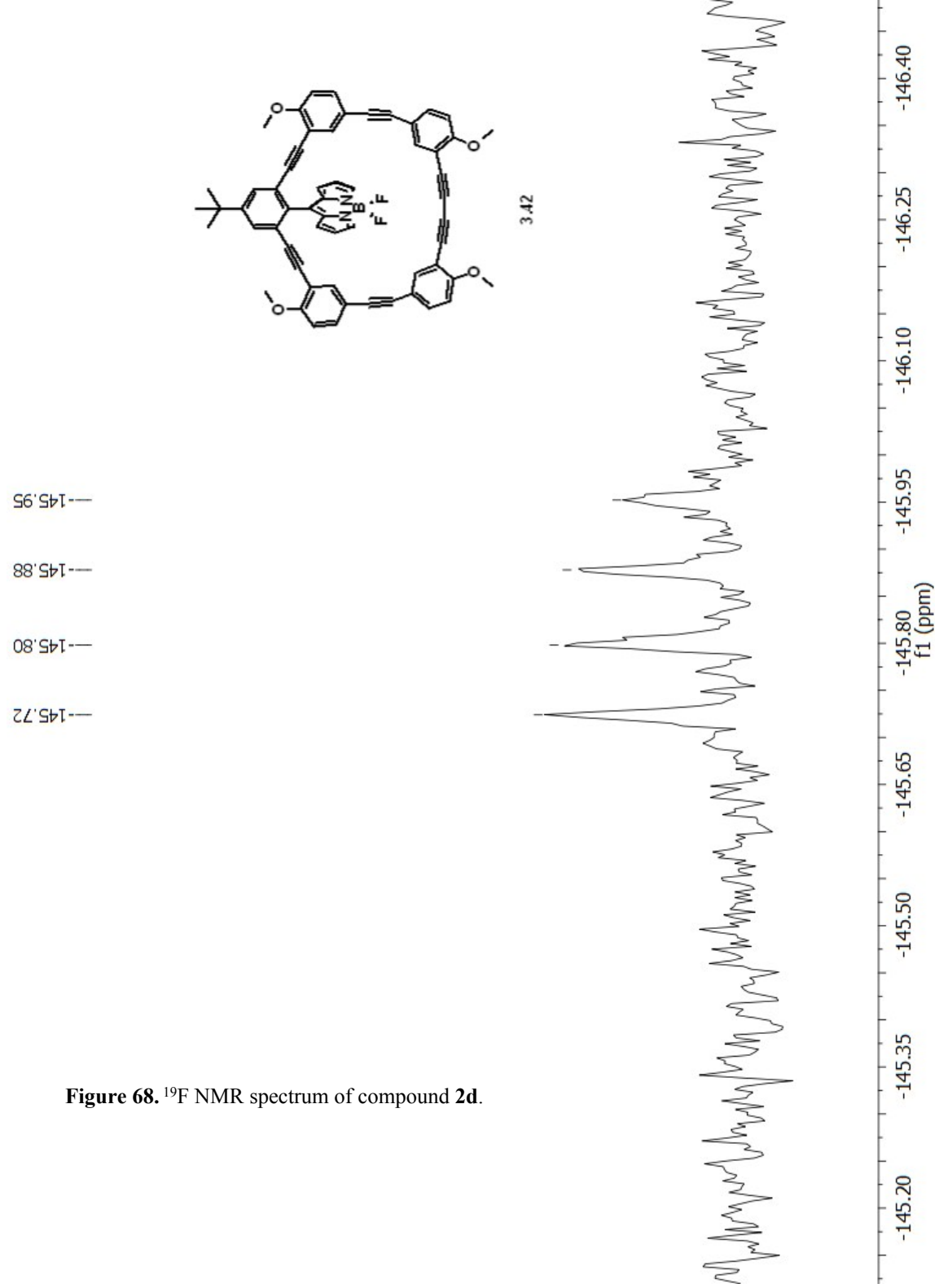


Figure 68. ^{19}F NMR spectrum of compound **2d**.

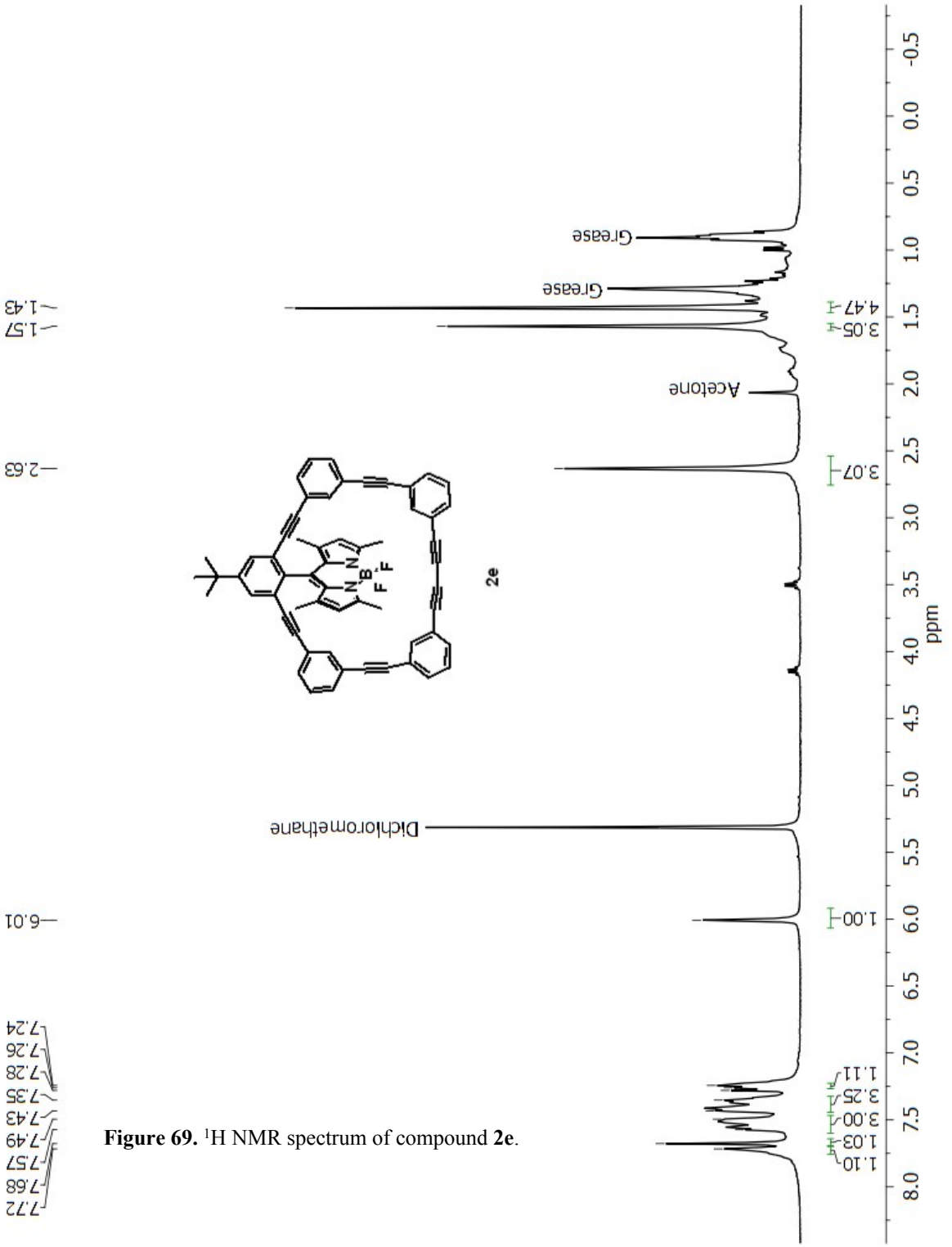


Figure 69. [1]H NMR spectrum of compound **2e**.

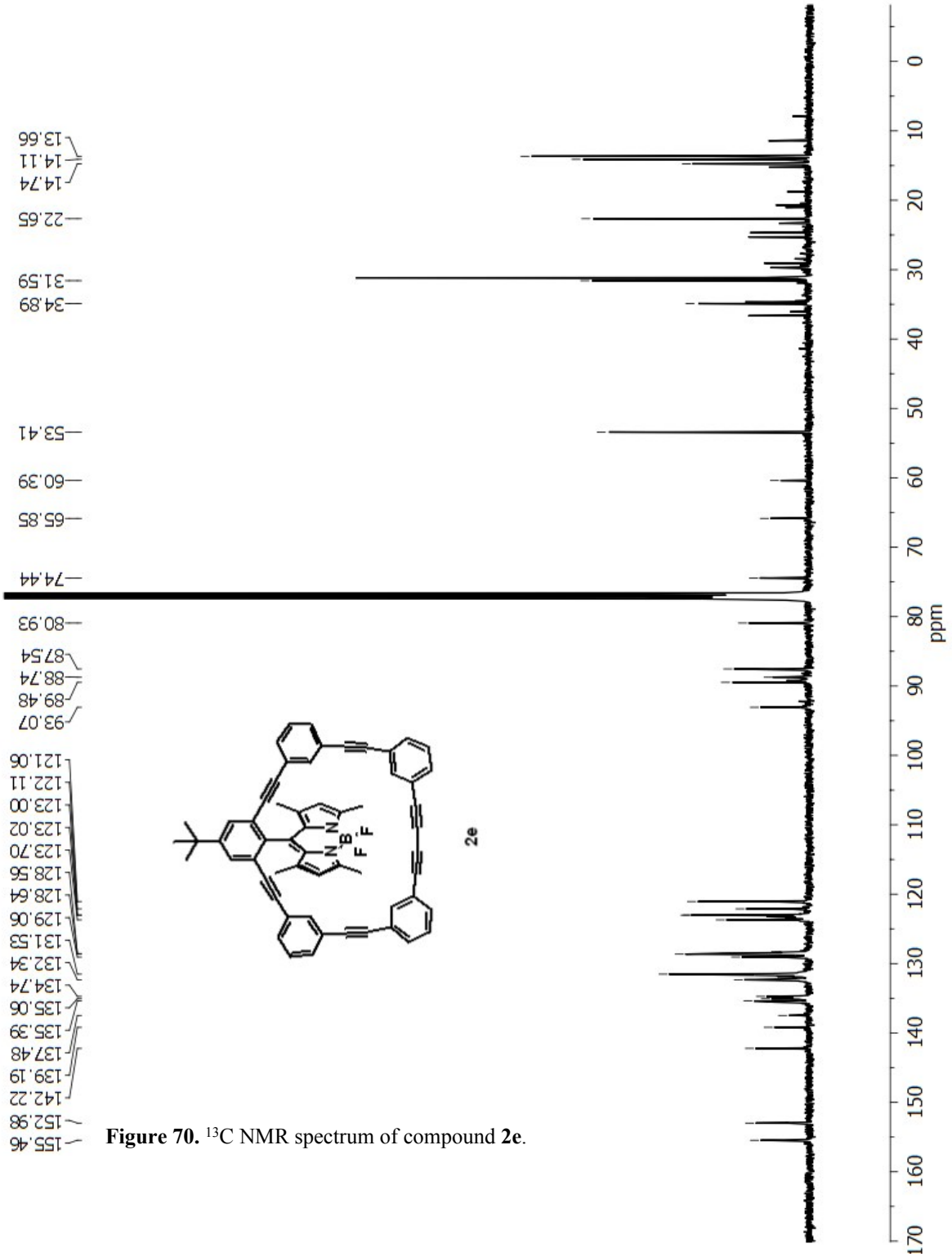


Figure 70. ^{13}C NMR spectrum of compound **2e**.

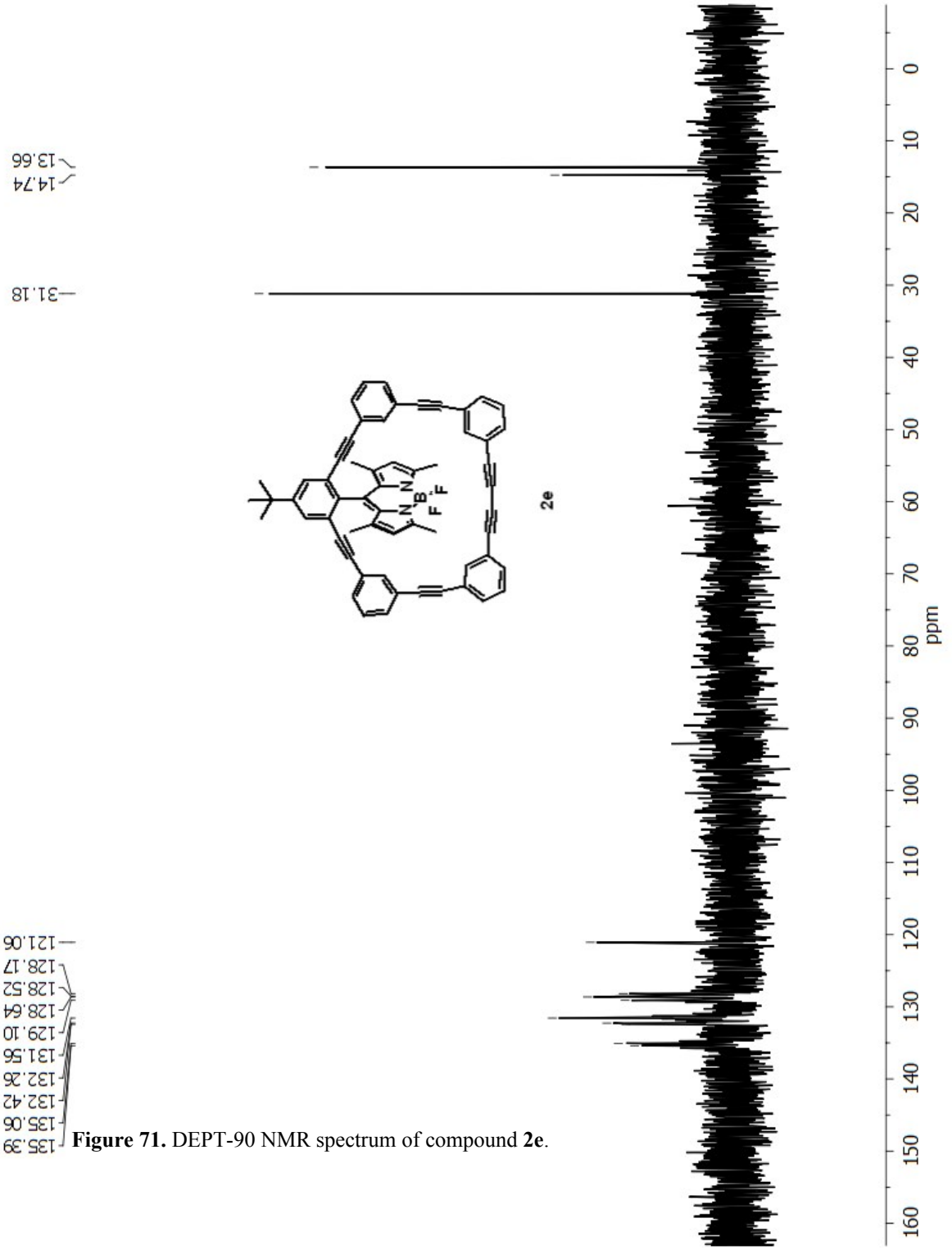


Figure 71. DEPT-90 NMR spectrum of compound **2e**.

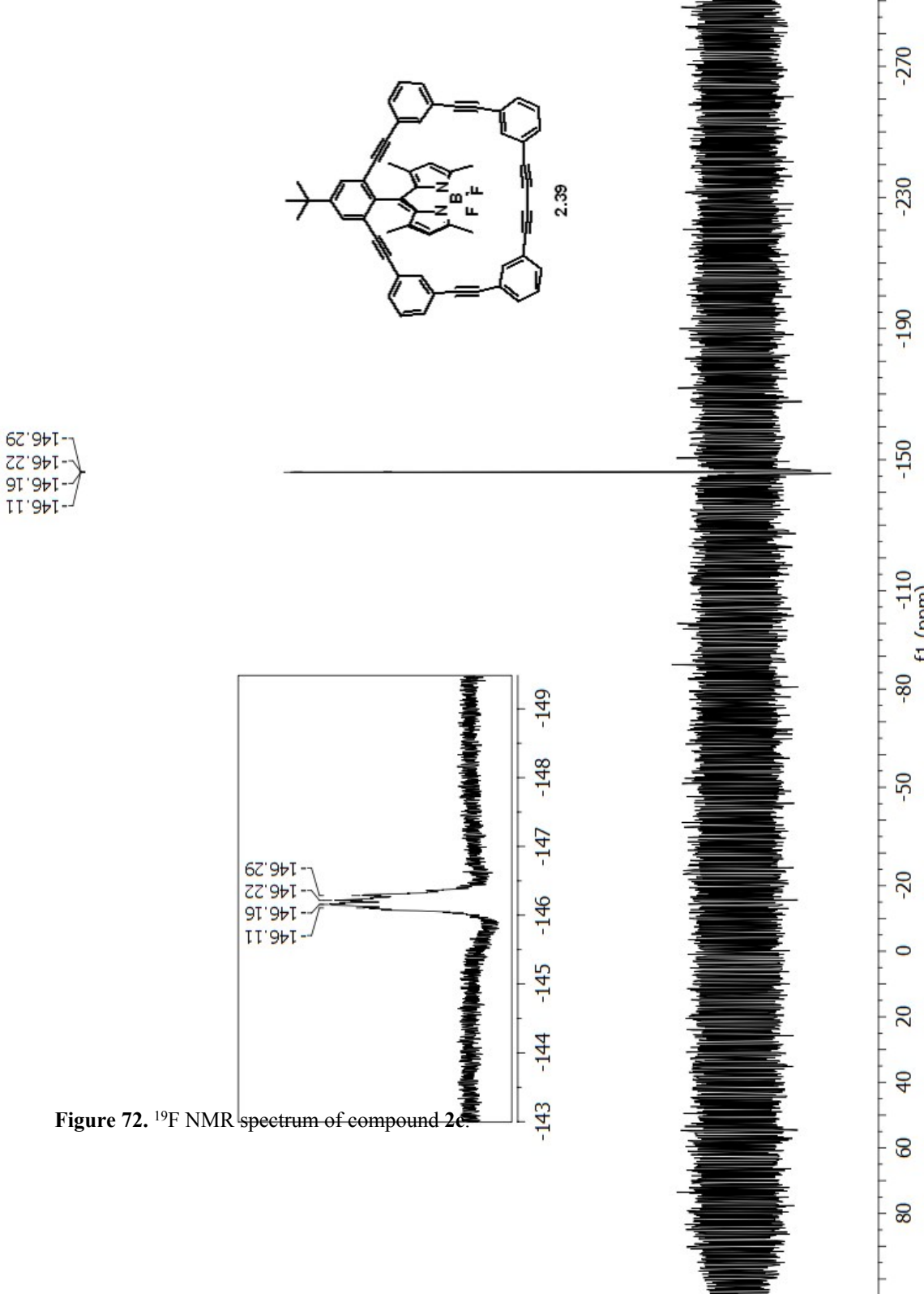


Figure 72. ^{19}F NMR spectrum of compound **2c**.

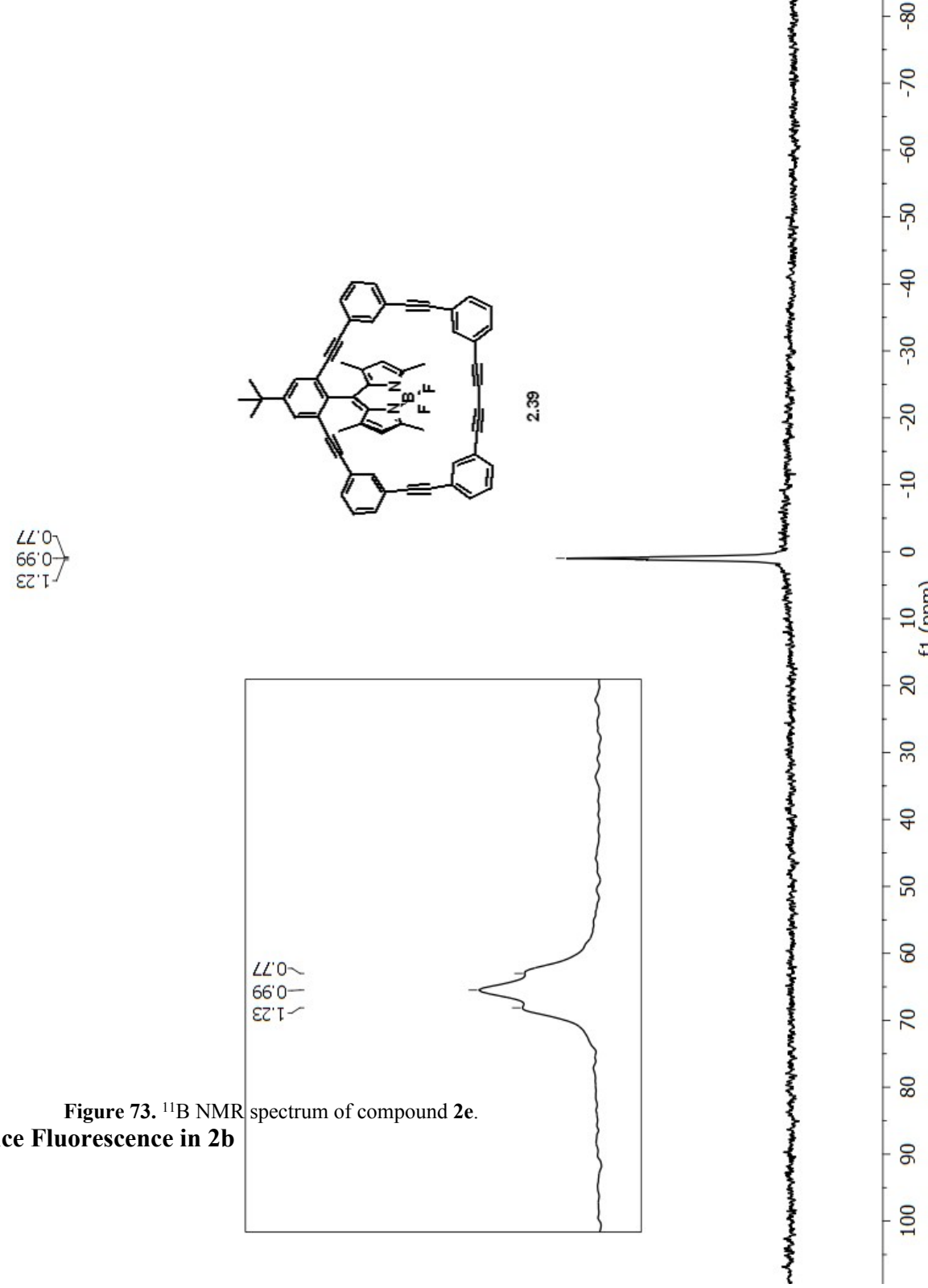


Figure 73. ^{11}B NMR spectrum of compound **2e**.

Solvent dependence Fluorescence in 2b

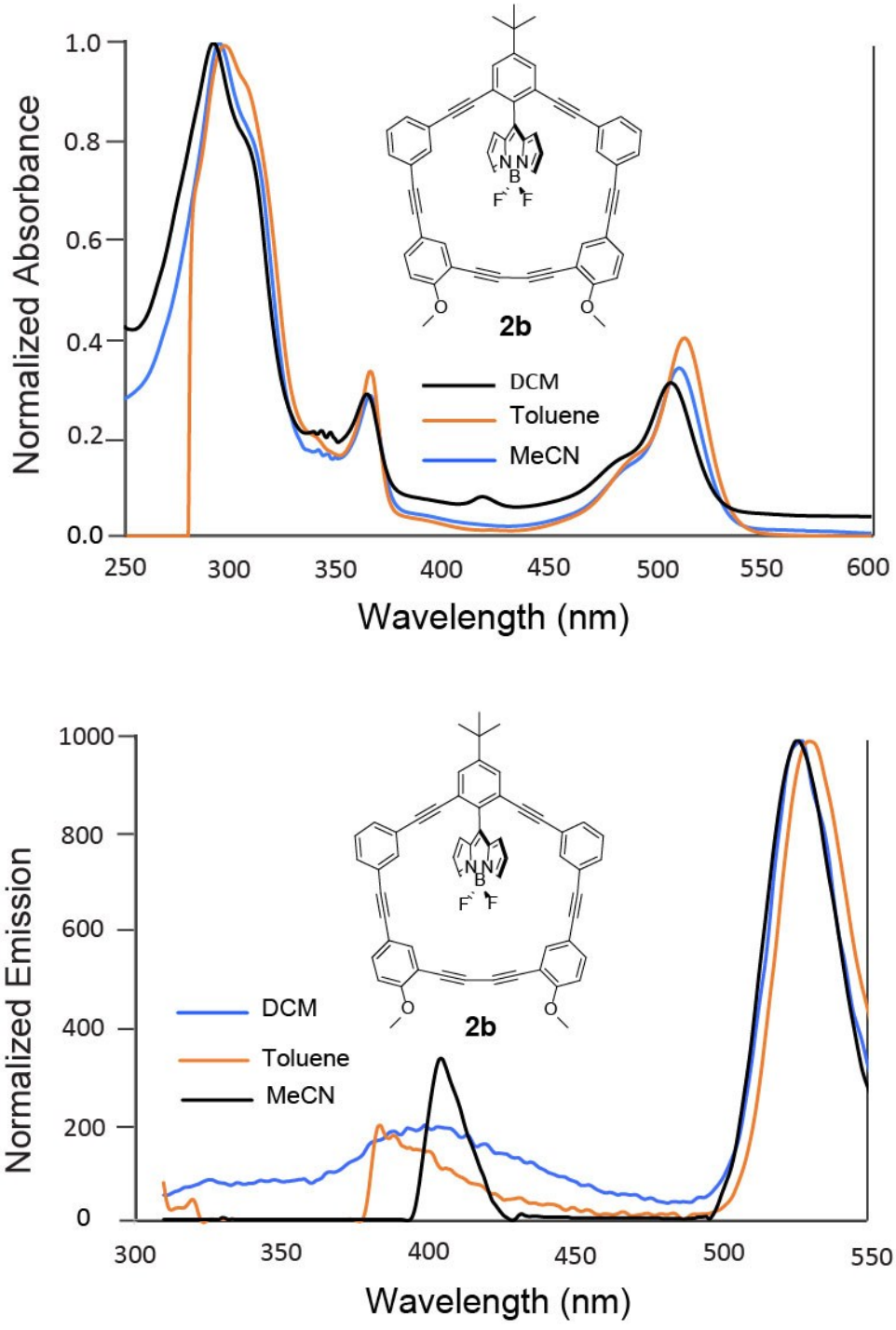


Figure 74. Absorption and normalized (BODIPY) emission (excitation at 295 nm) profiles for **2b**, showing the sensitivity of the ~400 nm emission as a function of solvent polarity. Similar behaviour is seen for **2d**.

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Theoretical rationale and calculations supporting enery transfer in 2d & 2e

In order to rationalize how the energy transfer phenomenon from the phenylacetylene macrocycle (Donor (D)) to the BODIPY (Acceptor (A)) occurs in the studied systems, we chose compounds **2d** and **2e**, which were studied by means of excited state calculations. The Fermi golden rule stablishes an expression to measure the energy transfer rate [Fermi, E. Nuclear Physics: A Course Given by Enrico Fermi at the University of Chicago; University of Chicago Press: Chicago, 1950]. It is known that this rate is related to the transition probability, which increases when the coupling between the initial and final states is stronger, as shown by the spectral overlap integral (*J*), which is calculated as:

$$J = \int g_D(E) g_A(E) dE$$

In this expression $g_D(E)$ and $g_A(E)$ are functions that describe the emission and absorption spectra of D and A, respectively. In our systems, the coupling between both states would be located in a common area defined by the overlap between the absorption of the BODIPY dye and the emission of the phenylacetylene macrocycle. In this sense, this overlap generates a density of states, which is directly proportional to the amount of energy transfer. Furthermore, this calculated value can be related with the experimental quantum yields. Hence, a greater overlap is related to a greater energy transfer [J Spiegel, M Kleinschmidt, A Larbig, J Tatchen, C Marian. J Chem Theory Comput., 2015, 11, 4316−4327].

Regarding the obtained results, the absorption of the free BODIPY fragment, which appears around 500 nm, is in good agreement with the reported experimental data for this compound. In addition, this absorption is in good agreement to the experimental emission wavelength of the phenylacetylene macrocycle and an overlap between the UV-Vis absorption spectrum of the Acceptor fragment (BODIPY) and the emission spectrum of the Donor fragment (the macrocyclic ring) is observed (see Figure 75). This supports the fact that energy charge transfer can occur followed by the emission of the BODIPY motif in the whole compound.

The theoretical spectral overlap integrals were calculated for **2d** and **2e**, and a value of $5.3*10^9$ and $3.1*10^{10}$ were obtained respectively (in $nm^4M^{-1}cm^{-1}$). The observed overlap integral data correlate with the measured quantum yields, which strongly agrees that **2e** has a greater value than **2d**.

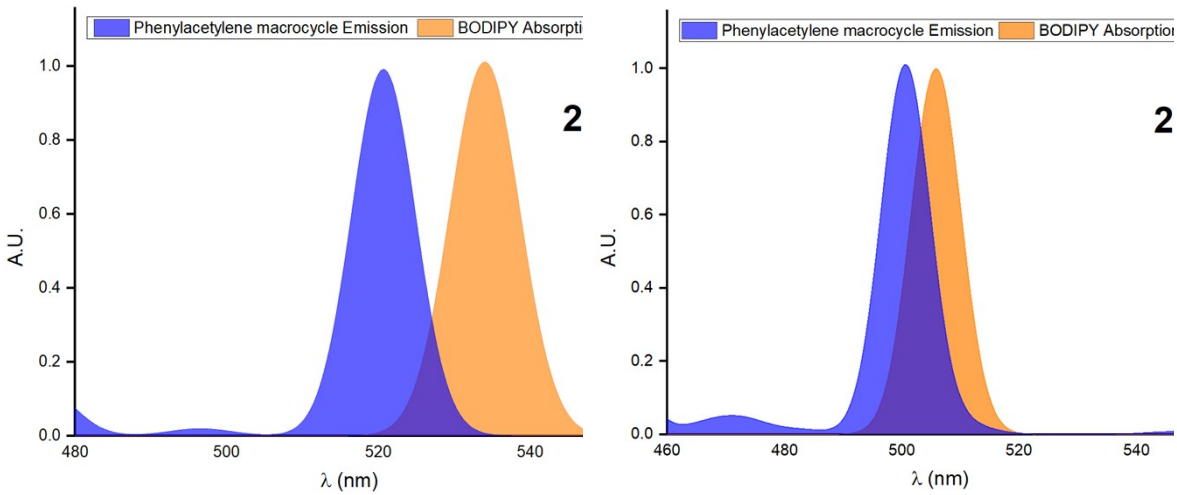
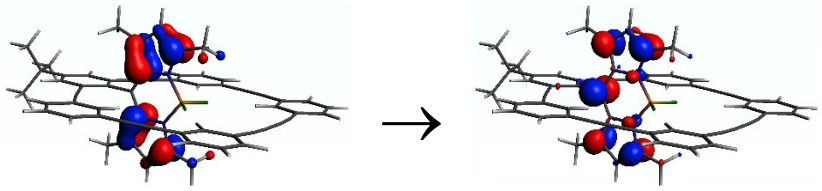


Figure 75. Overlap for the emission of the phenylacetylene macrocycle relative to the absorption of the BODIPY dye for **2d** and **2e**.

Finally, for compound **2e**, the UV-Vis absorption and emission spectra which can be seen in Figure 75. In case of the band at 357 nm, which displays the highest oscillator strength and agrees with the experimental spectrum (see Figure 6), the transition is composed by $\pi \rightarrow \pi^*$ orbitals (decomposed in transitions between the HOMO-3→LUMO+5(32%), HOMO-4→LUMO+4(30%) and HOMO-5→LUMO+3(25%)), all of them located on the phenylacetylene macrocycle. This band is relevant, since corresponds to the chosen excitation wavelength for the emission experiments. On the other hand, the emissive state is composed by the transition between orbitals located both in the BODIPY fragment of the dye as shown in the supplementary information, see Figure 76. This fact supports that the BODIPY is the emitting fragment in the system.

Computational details: The ground and singlet excited states (for systems **2d** and **2e**) were optimized using the Amsterdam Density Functional (ADF) 2017 package.[Baerends, E. J.; Ziegler, T.; Autschbach, J.; Bashford, D.; Berces, A.; Bickelhaupt, F. M.; Bo, C.; Boerrigter, P. M.; Cavallo, L.; Chong, D. P.; et al. Amsterdam Density Functional; SCM, Theoretical Chemistry, Vrije University: Amsterdam, Netherlands, 2012. http// www.scm.com.] The scalar relativistic effects were incorporated including in all the calculations the two-component Hamiltonian with the zeroth-order regular approximation (ZORA).[van Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic Regular Two-component Hamiltonians. J. Chem. Phys. 1993, 99, 4597−4610. (63) Wang, F.; Hong, G.; Li, L. A Simplified Scheme for Relativistic Density Functional Computation in the Zeroth-Order Regular Approximation. Chem. Phys. Lett. 2000, 316, 318−323.] The exchange and correlation functional, rPBE,[Hammer, B.; Hansen, L. B.; Nørskov, J. K. Phys. Rev. B 1999, 59, 7413−7421] was employed in combination with standard Slater-type orbital (STO) basis set and the triple-ξ quality plus one polarization function for all of the atoms (TZP).[Perdew, J. P.; Yue, W. Accurate and Simple Density Functional for the Electronic Exchange Energy: Generalized Gradient Approximation. Phys. Rev. B: Condens. Matter Mater. Phys. 1986, 33, 8800; Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865.; Van Lenthe, E.; Baerends, E. J.

Optimized Slater-Type Basis Sets for the Elements 1−118. J. Comput. Chem. 2003, 24, 1142−1156.] In all obtained minima, the eigenvalues of the hessian matrix were calculated, obtaining only positive values, this procedure was performed in order to verify the quality of the minimum found. Once the optimization process has been performed, the fragmentation scheme proposed by Caprasecca et al. and Marian et al.[S Caprasecca, B Mennucci. J Phys Chem A., 2014, 118, 6484−6491 AND J Spiegel, M Kleinschmidt, A Larbig, J Tatchen, C Marian. J Chem Theory Comput., 2015, 11, 4316−4327] was applied on the structures in order to treat the Phenylacetylene macrocycle and BODIPY fragment separately as energy donor (D) and energy acceptor (A) respectively. The methodology to obtain the herein reported results was: First, all the fragments were defined. Thus, for both studied systems the fragments used were the Phenylacetylene macrocycle and the BODIPY fragments, respectively, and the valence vacancies of the monomers were saturated with hydrogens. Then, the probability of energy transfer was estimated calculating the spectral overlap integral between the UV-Vis absorption spectrum of A and the emission spectrum of D. The spectra were computed using relativistic time-dependent density functional theory (SR-TDDFT) with the model LB94 proposed by van Leeuwen and Baerends, which incorporates corrected asymptotic behavior of V_{XC}, this model is thought to improve the calculations of properties dependent on the outer reaches of V_{XC}.[R. van Leeuwen and E. J. Baerends, "Exchange-correlation potential with correct asymptotic behavior", Phys. Rev. A 49, 2421 (1994).] This functional has proven to be successfully applied in BODIPY compounds to determine this kind of transitions improving, in this way, the limitations of the TDDFT.[Thomas S. Teets, James B. Updegraff III, Arthur J. Esswein, and Thomas G. Gray, Three-Coordinate, Phosphine-Ligated Azadipyrromethene Complexes of Univalent Group 11 Metals Inorg. Chem. 2009, 48, 8134–8144]. To obtain the spectral overlap integral (*J*) both, absorption and emission spectra, were normalized and numerical integration was performed employing the trapezoid rule. All of these spectra were built using a Lorentzian line shape.



HOMO LUMO

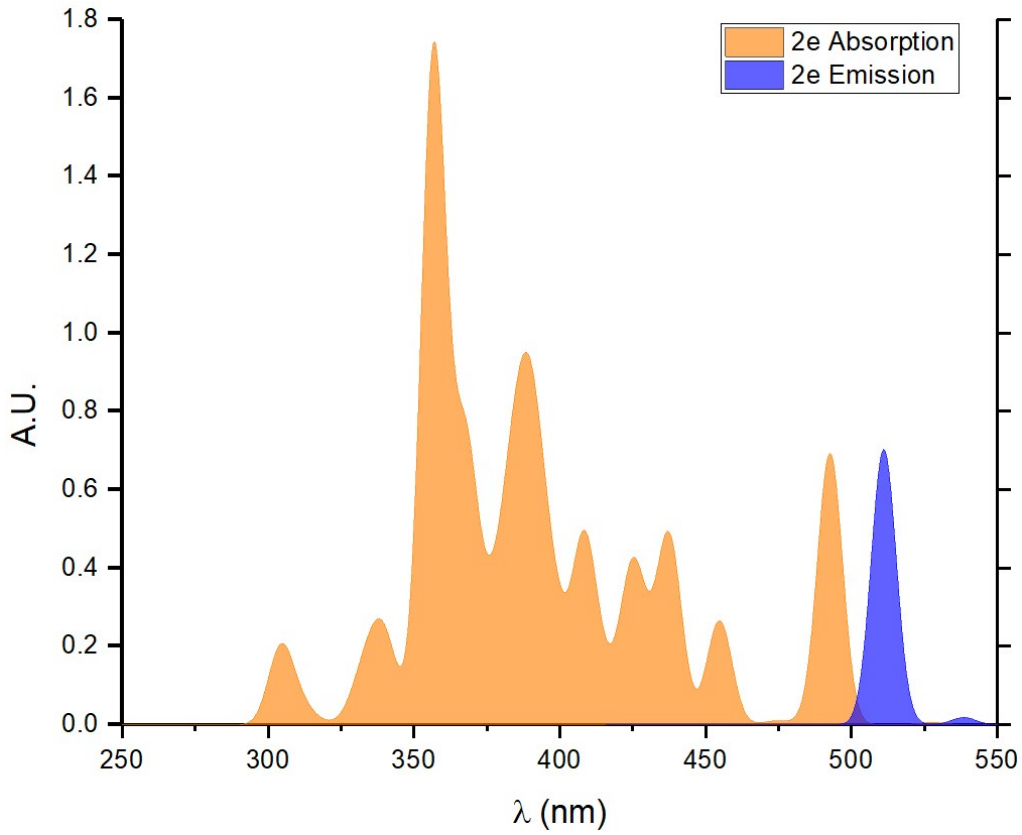


Figure 76. *Top*. Involved MOs in the emission process. *Bottom*. Calculated absorption and emission profile for **2e**.