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Supporting Information for the

Dalton Transactions

Manuscript entitled

Molecular Lemmings: Strategies to avoid when designing BODIPY ferrocene dyads for dye-sensitized solar cell applications

By

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Experimental

General Considerations

All reagents were purchased from Aldrich except $Pd(PPh_3)_4$ (Pressure Chemical Co., Pittsburg, PA). 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 F_{254} adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. Routine ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$ 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 $BF_3{\cdot}OEt_2$ (^{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; m = multiplet; br = broad. High resolution mass spectroscopy (HRMS) results were obtained from Queen 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. Cyclic voltammetry data was collected using a MetrOhm μ-Autolab Type III potentiostat/galvanostat and 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

Ethynyl ferrocene was prepared using a procedure from literature[1]

The synthesis and characterization of compounds **4a**[2], **4c**[2], **4d**[3], **5a**[4], **5c**[4], **6a**[5] and **12**[6] were reported elsewhere.

Theoretical Calculations

All DFT and TD-DFT calculation was done use Gaussian 09M version C software. All structures were optimized at ground state default spin using the B3LYP exchange correlation function. These calculations were done in the gas phase in the absence of solvent. For TD-DFT calculations were done at TD-SCF using the B3LYP exchange correlation function. All calculations were optimized using 3.21 G basis set (6.31 G basis set when mentioned).

References

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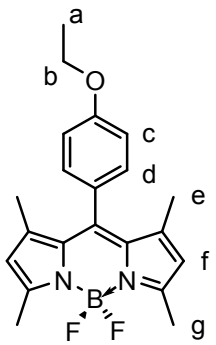
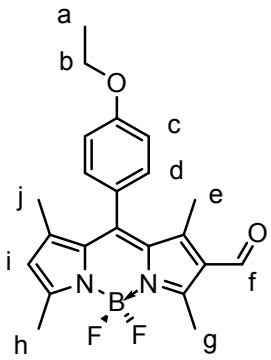
Synthetic details

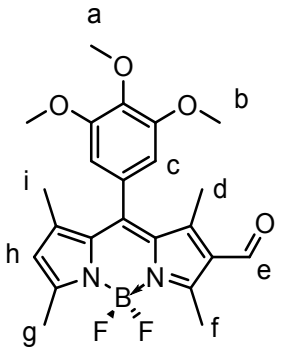


4c: To a solution of 2, 4-dimethyl-1H-pyrrole (0.790 g, 8.32 mmol) in dry DCM (120 mL), 4-ethoxybenzaldehyde (0.500 g, 3.33 mmol,) was added followed by a catalytic amount of TFA. After stirring for 12 h, DDQ (1.13 g, 1.5 eq) was added to the red mixture and stirred at RT until TLC analysis revealed the completion of the reaction (3 h). DIPEA (4.0 mL) and $BF_3{\cdot}OEt_2$ (4.7 mL) were added to the mixture and stirred for 6 h before being concentrated *in vacuo*, dissolved 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 (toluene) yielded a red powder (367 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, ^3J = 8.6 Hz, 2H, H_c), 7.00 (d, ^3J = 8.6 Hz, 2H, H_d), 5.97 (s, 2H, H_f), 4.09 (q, ^3J = 7.0 Hz, 2H, H_b), 2.55 (s, 6H, H_g), 1.47 (t, ^3J = 7.0 Hz, 3H, H_a), 1.43 (s, 6H, H_e). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.52, 155.23, 143.18, 141.96, 131.87, 129.11, 128.23 , 126.90, 121.07, 115.04, 63.56, 14.78, 14.56. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 0.79 (t, ^1J = 33 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.3 (q). HRMS: m/z 368.1875 [M^+], calculated for $C_{21}H_{23}BF_2N_2O_2$: m/z 368.1872

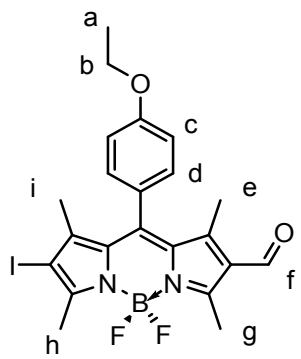


5c: A solution of 10 mL of dry DMF in 30 mL of dry DCM was cooled in an ice bath and 12 mL of $POCl_3$ was added dropwise. The mixture was warmed to room temperature and stirred 30 min. **4b** (0.200 mg, 0.543 mmol) was added in one portion and the mixture was stirred for 3 h before the addition of 30 mL of $NaHCO_3$ (sat) and cooled to 0°C. The mixture was stirred 30 min at room temperature and the organic layer was separated. The aqueous layer was extracted with DCM (3 ×

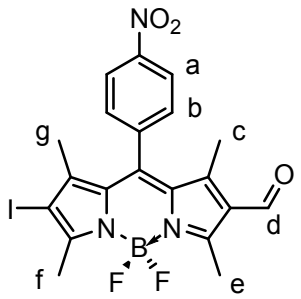
25 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and volatiles were removed *in vacuo*. The residue was purified by column chromatography using DCM as the eluent to afford an orange powder (0.153 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H, H_f), 7.13 (d, ^3J = 8.6 Hz, 2H, H_c), 7.01 (d, ^3J = 8.6 Hz, 2H, H_d), 6.13 (s, 1H, H_i), 4.16 – 3.99 (q, ^3J = 6.9 Hz, 3H, H_b), 2.79 (s, 3H, H_g), 2.58 (s, 3H, H_e), 1.70 (s, 3H, H_h), 1.47 (s, 3H, H_j), 1.44 (t, ^3J = 7.0 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 185.88, 161.35, 159.97, 156.27, 147.35, 143.88, 142.86, 134.51, 130.21, 128.99, 126.27, 125.91, 123.88, 115.38, 63.66, 15.04, 14.71, 12.97, 11.73. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.70 (t, ^1J = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.7 (q). HRMS: m/z 396.1821 [M^+], calculated for $C_{22}H_{23}BF_2N_2O_2$: m/z 396.1821.



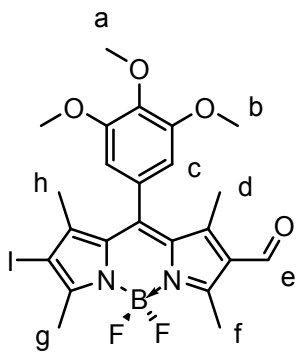
5d: A solution of 10 mL of dry DMF in 30 mL of dry DCM was cooled in an ice bath and 12 mL of $POCl_3$ was added dropwise. The mixture was warmed to room temperature and stirred for 30 min. **4d** (0.300 mg, 0.724 mmol) was added in one portion and the mixture was stirred for 3 h before the addition of 30 mL of $NaHCO_3$ (sat) and then cooled to 0 ˚C. The mixture was stirred for 30 min at room temperature and the organic layer was separated. The aqueous layer was extracted with DCM (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and volatiles were removed *in vacuo*. The residue was purified by column chromatography using DCM as the eluent to afford an orange powder (0.258 g, 81%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H, H_e), 6.54 (s, 2H, H_c), 6.19 (s, 1H, H_h), 3.94 (s, 3H, H_a), 3.86 (s, 6H, H_b), 2.83 (s, 3H, H_f), 2.63 (s, 3H, H_d), 1.83 (s, 3H, H_g), 1.61 (s, 3H, H_i). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 185.85, 161.76, 156.59, 154.51, 147.18, 143.21, 142.78, 139.19, 134.03, 129.72, 129.13, 126.35, 123.99, 104.99, 61.38, 56.46, 53.41, 15.07, 14.71, 12.97, 11.54. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.68 (t, ^1J = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.8 (q). HRMS: m/z 442.1902 [(M^+], calculated for $C_{23}H_{25}BF_2N_2O_4$: m/z 442.1875.



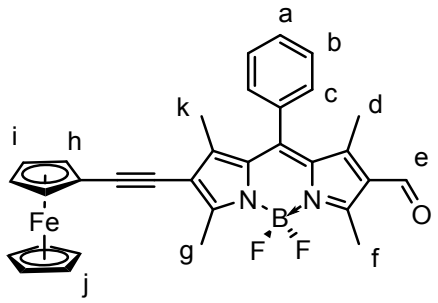
6c: BODIPY **5c** (0.104 g, 0.262 mmol) was dissolved in a minimum amount of DCM and NIS (0.071 g, 0.317 mmol) was added in one portion. The mixture was stirred 12 h in the absence of light. Volatiles were removed *in vacuo* and the residue was purified via column chromatography using DCM as the eluent, affording an orange solid (0.086 g, 63%).^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H, H_f), 7.14 (d, ^{3}J = 8.0 Hz, 2H, H_c), 7.05 (d, ^{3}J = 8.0 Hz, 2H, H_d), 4.12 (q, ^{3}J = 8.0 Hz, 2H, H_a), 2.82 (s, 3H, H_g), 2.69 (s, 3H, H_e), 1.72 (s, 3H, H_h), 1.50 (s, 3H, H_i), 1.48 (t, ^{3}J = 8.0 Hz, 3H, H_a). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.93, 160.57, 160.34, 157.95, 148.00, 145.44, 144.26, 134.06, 130.54, 129.09, 127.11, 126.03, 115.70, 88.25, 63.89, 17.71, 16.50, 15.22, 14.87, 13.41, 12.18. ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = -144.42 (q, *J* = 34 Hz). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ = 0.63 (t, *J*= 32 Hz). HRMS: m/z 522.0799 [M^+], calculated for $C_{22}H_{22}BF_2IN_2O_2$: m/z 522.0787



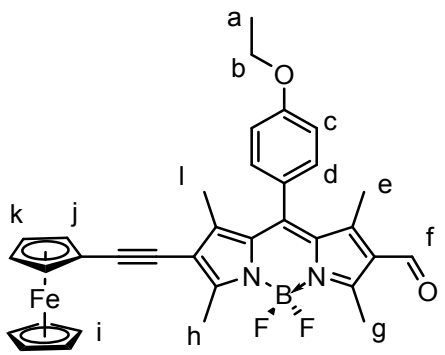
6a: BODIPY **5a** (0.200 g, 0.503 mmol) was dissolved in a minimum amount of DCM and NIS (0.136 g, 0.604 mmol) was added in one portion. The mixture was stirred 12 h in the absence of light. Volatiles were removed *in vacuo* and the residue was purified via column chromatography using DCM as the eluent, affording an orange solid (0.171 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H, H_d), 8.47 (d, ^{3}J = 8.2 Hz, 2H, H_a), 7.58 (d, ^{3}J = 8.3 Hz, 2H, H_b), 2.85 (s, 3H, H_e), 2.74 (s, 3H, H_c), 1.67 (s, 3H, H_f), 1.45 (s, 3H, H_g). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 185.47 (s), 162.12 (s), 158.81 (s), 148.80 (s), 147.10 (s), 144.52 (s), 140.87 (s), 140.21, 132.80, 129.56, 129.29, 127.26, 124.81, 77.33, 77.01, 76.70, 17.71, 16.55, 13.29, 12.20. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.58 (t, *J* = 31 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.3 (q). HRMS: m/z 523.0386 [M^+], calculated for $C_{20}H_{17}BF_2IN_3O_3$: m/z 523.0376.



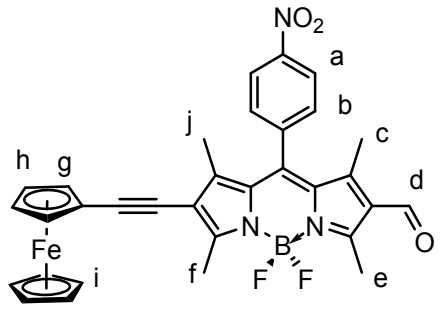
6d: BODIPY **5d** (0.200 g, 0.452 mmol) was dissolved in a minimum amount of DCM and NIS (0.122 g, 0.543 mmol) was added in one portion. The mixture was stirred 12 h in the absence of light. Volatiles were removed *in vacuo* and the residue was purified via column chromatography using DCM:hexanes (4:1) as the eluent, affording an orange solid (0.203 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H, H_e), 6.51 (s, 2H, H_c), 3.93 (s, 3H, H_a), 3.84 (s, 6H, H_b), 2.82 (s, 3H, H_f), 2.61 (s, 3H, H_d), 1.81 (s, 3H, H_g), 1.59 (s, 3H, H_h). ^{13}C{^{1}H} NMR (101 MHz): δ 185, 171.1, 160.8, 158.0, 154.7, 147.8, 145.1, 143.4, 139.4, 133.4, 129.9, 129.0, 127.0, 104.8, 61.4 60.4, 56.5, 21.0, 17.3, 16.38, 14.2 13.3, 11.8. ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ 0.60 (t, ^{1}J = 32 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ -144.5 (q). HRMS: m/z 568.0832 [(M^+], calculated for $C_{23}H_{24}BF_2IN_2O_4$: m/z 568.0842.



7b: In a 100 mL Schlenk flask under a nitrogen atmosphere, BODIPY **6b** (0.100 g, 0.209 mmol) and ethynyl ferrocene (0.066 g, 0.314 mmol) were solubilized in 25 mL of THF:DIPEA (3:2). The solution was degassed for 30 min prior to the addition of $Pd(PPh_3)_2Cl_2$ (0.022 g, 0.031 mmol) and CuI (0.005 g, 0.021 mmol). The mixture was stirred at 35 °C for 12h. Solvents were then removed *in vacuo* and the residue was purified via column chromatography using hexanes:EtOAc (4:1) as the eluent, affording the desired product as dark purple solid (0.044 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H, H_e), 7.60 – 7.51 (m, 3H, H_a, H_b), 7.34 – 7.28 (m, 2H, H_c), 4.45 (s, 2H, H_h), 4.25 (s, 2H, H_i), 4.19 (m, 5H, H_j), 2.84 (s, 3H, H_f), 2.74 (s, 3H, H_d), 1.68 (s, 3H, H_g), 1.52 (m, 3H, H_k). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 185.78, 162.43, 157.41, 146.11, 143.88, 134.12 , 129.62, 127.72, 97.00, 77.33, 77.02, 76.70, 71.52, 70.05, 69.09, 64.69, 13.83, 11.70.^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.66 (t, ^{1}J = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.9 (q). HRMS: m/z 560.1545 [M^+], calculated for $C_{32}H_{27}BF_2FeN_2O$: m/z 560.1534.

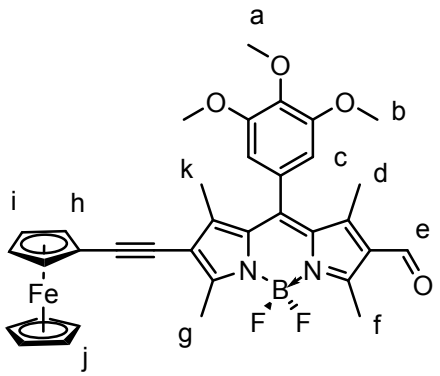


7c: In a 100 mL Schlenk flask under a nitrogen atmosphere, BODIPY **6c** (0.108 g, 0.206 mmol) and ethynyl ferrocene (0.048 g, 0.227 mmol) were solubilized in 25 mL of THF:DIPEA (3:2). The solution was degassed for 30 min prior to the addition of $Pd(PPh_3)_2Cl_2$ (0.022 g, 0.032 mmol) and CuI(0.004 g, 0.023 mmol). The mixture was stirred at 35 ˚C for 12h. The solvents were removed *in vacuo* and the residue was purified via column chromatography using hexanes:EtOAc (4:1) as the eluent, affording the desired product as dark purple solid (0.054 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H, H_f), 7.17 (d, ^3J = 8.7 Hz, 2H, H_c), 7.05 (d, ^3J = 8.7 Hz, 2H, H_d), 4.47 – 4.43 (m, 2H, H_k), 4.26 – 4.23 (m, 2H, H_j), 4.20 (s, 5H, H_i), 4.12 (q, ^3J = 7.0 Hz, 2H, H_a), 2.83 (s, 3H, H_g), 2.73 (s, 3H, H_e), 1.74 (s, 3H, H_h), 1.59 (s, 3H, H_l), 1.48 (t, ^3J = 7.0 Hz, 3H, H_b). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 185.98, 162.30, 160.24, 157.41, 146.35, 144.34, 144.09, 133.62, 130.98, 129.16, 126.75 , 126.00, 115.59, 96.99, 71.67, 70.19, 69.22, 64.89, 63.85, 14.88, 14.21, 13.29, 12.08. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 0.66 (t, ^1J = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.9 (q). HRMS: m/z 604.1802 [M^+], calculated for $C_{34}H_{31}BF_2FeN_2O_2$: m/z 604.1803.

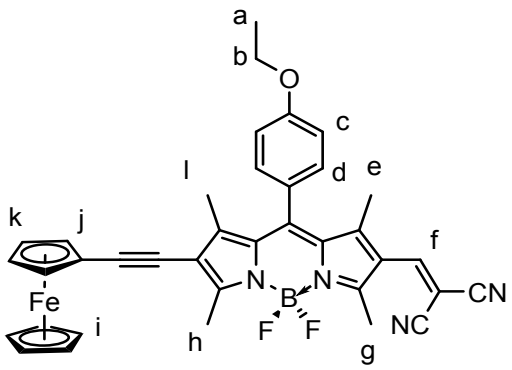


7a: In a 100 mL Schlenk flask under a nitrogen atmosphere, BODIPY **6a** (0.100 g, 0.191 mmol) and ethynyl ferrocene (0.048 g, 0.229 mmol) were solubilized in 25 mL of THF:DIPEA 3:2. The solution was degassed for 30 min prior to the addition of $Pd(PPh_3)_2Cl_2$ (0.020 g, 0.029 mmol) and CuI(0.004 g, 0.019 mmol). The mixture was stirred at 35 ˚C for 12h. The solvents were removed *in vacuo* and the residue was purified via column chromatography using hexanes:EtOAc (4:1) as the eluent, affording the desired product as dark purple solid. (0.072 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H, H_d), 8.48 (d, ^3J = 8.5 Hz, 2H, H_a), 7.59 (d, ^3J = 8.3 Hz, 2H, H_b), 4.49 (d, ^3J = 1.7 Hz, 2H, H_g), 4.29 (d, ^3J = 1.7 Hz, 2H, H_h), 4.22 (s, 5H, H_i), 2.87 (s, 3H, H_e), 2.78 (s, 3H, H_c), 1.70 (s, 3H, H_f), 1.53 (s, 3H, H_j). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 185.57, 163.83, 158.20, 148.76, 144.97, 143.09, 140.89,

140.26, 129.47, 126.85, 124.72, 98.09, 71.58, 70.09, 69.26, 29.69, 14.17, 12.13.^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.60 (t, ^{1}J = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.8 (q). HRMS: m/z 605.1378 [M$^+$], calculated for $C_{32}H_{26}BF_2FeN_3O_3$: m/z 605.1385.

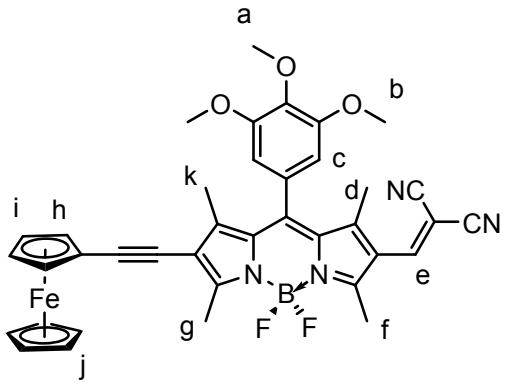


7d: In a 100 mL Schlenk flask under a nitrogen atmosphere, BODIPY **6d** (0.100 g, 0.191 mmol) and ethynyl ferrocene (0.048 g, 0.229 mmol) were solubilized in 25 mL of THF:DIPEA (3:2). The solution was degassed for 30 min prior to the addition of $Pd(PPh_3)_2Cl_2$ (0.020 g, 0.029 mmol) and CuI (0.004 g, 0.019 mmol). The mixture was stirred at 35 ˚C for 12h. The solvents were removed *in vacuo* and the residue was purified via column chromatography using hexanes:EtOAc (9:1) as the eluent, affording the desired product as dark purple solid (0.105 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H, H_e), 6.55 (s, 2H, H_c), 4.48 (s, 2H, H_h), 4.28 (s, 2H, H_i), 4.23 (s, 5H, H_j), 3.97 (s, 3H, H_a), 3.88 (s, 6H, H_b), 2.86 (s, 3H, H_f), 2.76 (s, 3H, H_d), 1.86 (s, 3H, H_g), 1.72 (s, 3H, H_k). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 185.80, 162.57, 157.46, 154.56, 145.94, 143.75, 143.43, 139.26, 133.02, 130.31, 129.04, 126.61, 104.90, 97.20, 71.53, 70.07, 69.14, 64.61, 61.43, 56.47, 14.09, 13.81, 13.16, 11.72.^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.64 (t, ^{1}J = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.9 (q). HRMS: m/z 650.1852 [M$^+$], calculated for $C_{35}H_{33}BF_2FeN_2O_4$: m/z 650.1851.

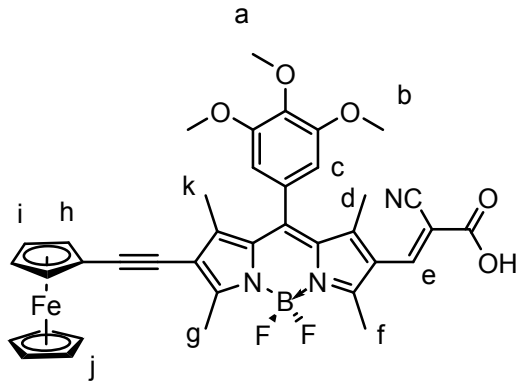


8c: 7c (0.048 g, 0.077 mmol) was dissolved in a minimum amount of $CHCl_3$ and malononitrile (0.015 g, 0.173 mmol) was added, followed by NEt_3 (2 drops). The mixture was refluxed for 12 h and after being cooled to room temperature, the organic layer was washed with HCl 1N (3 × 25 mL), dried over $MgSO_4$, filtered, and volatiles were removed *in vacuo*. The residue was purified via column chromatography using DCM as the eluent affording a dark purple solid (0.015 g, 28%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H, H_f), 7.17 (d, ^{3}J = 8.4 Hz, 2H, H_c), 7.06 (d, ^{3}J = 8.4 Hz, 2H, H_d),

4.46 (s, 2H, H_k), 4.26 (s, 2H, H_j), 4.20 (s, 5H, H_i), 4.12 (q, ^3J = 6.8 Hz, 2H, H_a), 2.74 (s, 3H, H_g), 2.65 (s, 3H, H_e), 1.60 (s, 3H, H_h), 1.53 (s, 3H, H_l), 1.48 (t, ^3J = 6.9 Hz, 3H, H_b). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 207.04, 163.73 , 160.43, 153.43, 147.09, 143.66, 140.16, 129.19, 125.62, 115.77, 114.50, 113.30, 97.71, 82.59, 71.70, 70.22, 69.32, 63.89, 31.04, 29.84, 14.89, 14.37.$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 0.59 (t, ^1J = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.6 (q). HRMS: m/z 652.1919 [M^+], calculated for $C_{37}H_{31}BF_2FeN_4O$: m/z 652.1908.

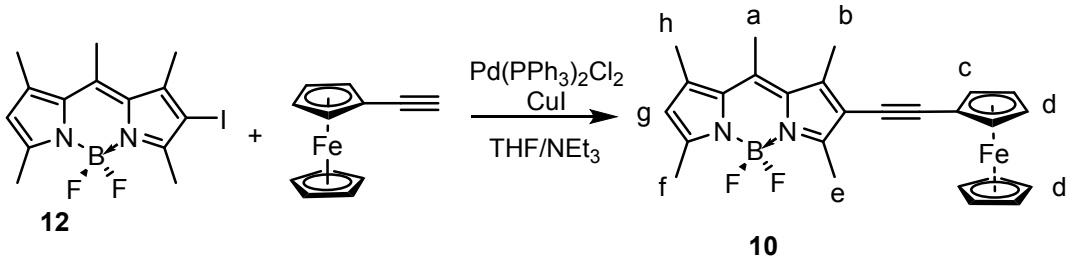


8d: 7d (0.050 g, 0.077 mmol) was dissolved in a minimum amount of $CHCl_3$ and malononitrile (0.011 mg, 0.173 mmol) was added, followed by NEt_3 (2 drops). The mixture was refluxed for 12 h and after being cooled to room temperature, the organic layer was washed with HCl 1N (3 × 25 mL), dried over $MgSO_4$, filtered, and volatiles were removed *in vacuo*. The residue was purified via column chromatography using DCM as the eluent affording a dark purple solid (0.018 g, 33%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H, H_e), 6.55 (s, 2H, H_c), 4.49 (s, 2H, H_h), 4.29 (s, 2H, H_h), 4.23 (s, 5H, H_j), 3.97 (s, 3H, H_a), 3.88 (s, 6H, H_b), 2.77 (s, 3H, H_f), 2.68 (s, 3H, H_d), 1.73 (s, 3H, H_g), 1.65 (s, 3H, H_k). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.97, 154.66, 153.19, 142.73, 139.89, 139.37, 128.67, 114.22, 113.14, 104.81, 97.91, 82.91, 71.58, 70.10, 69.25, 61.47 , 56.50, 14.23 , 13.99. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 0.55 (t, ^1J = 32 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.6 (q). HRMS: m/z 698.1979 [M^+], calculated for $C_{38}H_{33}BF_2FeN_4O_3$: m/z 698.1963.

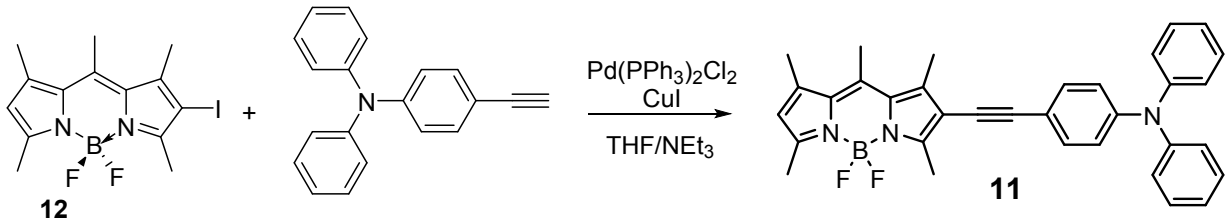


3d: 7d (0.060 g, 0.092 mmol) was dissolved in a minimum amount of $CHCl_3$ and cyanoacetic acid (0.016 mg, 0.185 mmol) was added, followed by piperidine (2 µL, 0.02 mmol). The mixture was refluxed for 12 h and after being cooled to room temperature, organic layer was washed with HCl

1N (3 × 25 mL), dried over $MgSO_4$, filtered, and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:EtOAc (10:1), affording a dark purple solid (0.037 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H, H_e), 6.56 (s, 2H, H_c), 4.62 (m, 2H, H_h), 4.48 (s, 2H, H_i), 4.28 (s, 5H, H_j), 3.97 (s, 3H, H_a), 3.88 (s, 6H, H_b), 2.75 (s, 3H, H_f), 2.69 (s, 3H, H_d), 1.72 (s, 3H, H_g), 1.67 (s, 3H, H_k). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.63 (t, ^1J = 30 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.7 (q). HRMS: m/z 717.1896 [M$^+$], calculated for $C_{38}H_{34}BF_2FeN_3O_5$: m/z 717.1904.



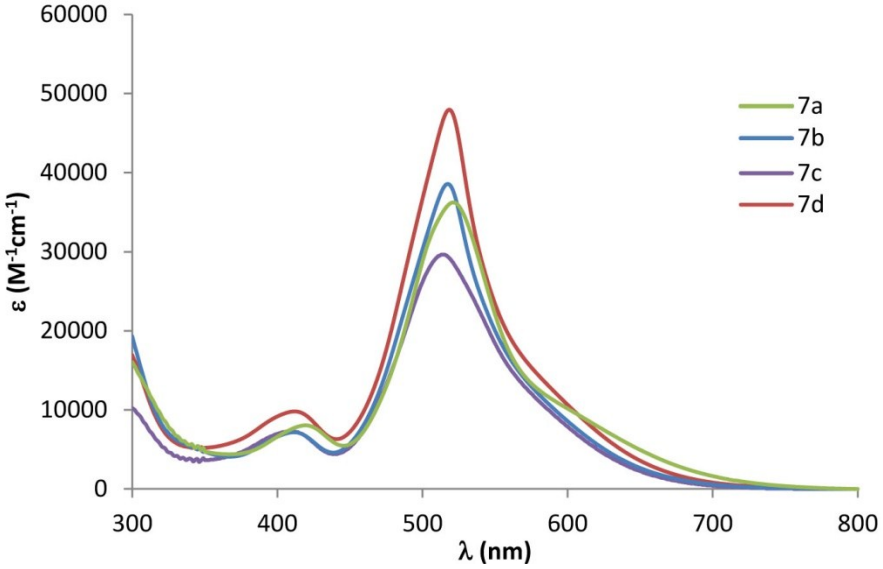
10: In a flame dried 200 mL Schlenk flask under nitrogen, **12** (0.388 g, 1.030 mmol) was dissolved in 7 mL dry THF and dry NEt_3 (3.6 mL). The mixture was degassed for 10 minutes under nitrogen. The oil bath was set to 40°C and $Pd(PPh_3)_2Cl_2$ (0.070 g, 0.100 mmol), and CuI (0.038 g, 0.200 mmol) were added. To the mixture was then added ethynyl ferrocene(0.236 g, 1.125 mmol). The reaction was stirred at 60°C. After 26 h, the reaction was cooled to room temperature. Solvents were removed under high vacuum and the crude product was dissolved in EtOAc and washed with sat. ammonium chloride. The combined organic layers were dried over $MgSO_4$, filtered, and solvent was removed *in vacuo*. The crude was purified by column chromatography using hexanes:DCM (3:1) to (1:1) as the eluent to afford a dark red-brown solid (0.173 g, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (s, 1H,H_g), 4.50 (t, 2H, ^3J = 4.0 Hz, H_c), 4.24 (s, 7H, H_d), 2.65 (s, 3H, H_h), 2.62 (s, 3H, H_f), 2.53 (s, 6H, H_e), 2.43 (s, 3H, H_b). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.42, 155.06, 142.36, 141.76, 140.37, 133.10, 131.17, 122.10, 115.97, 94.44, 78.08, 71.59, 70.15, 68.94, 65.77, 17.60, 16.78, 16.09, 14.69, 13.63. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 0.52 (t, ^1J = 30.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.60 (q) HRMS m/z 470.1438 (M$^+$) calculated for $C_{26}H_{25}BF_2FeN_2$: m/z 470.1428.



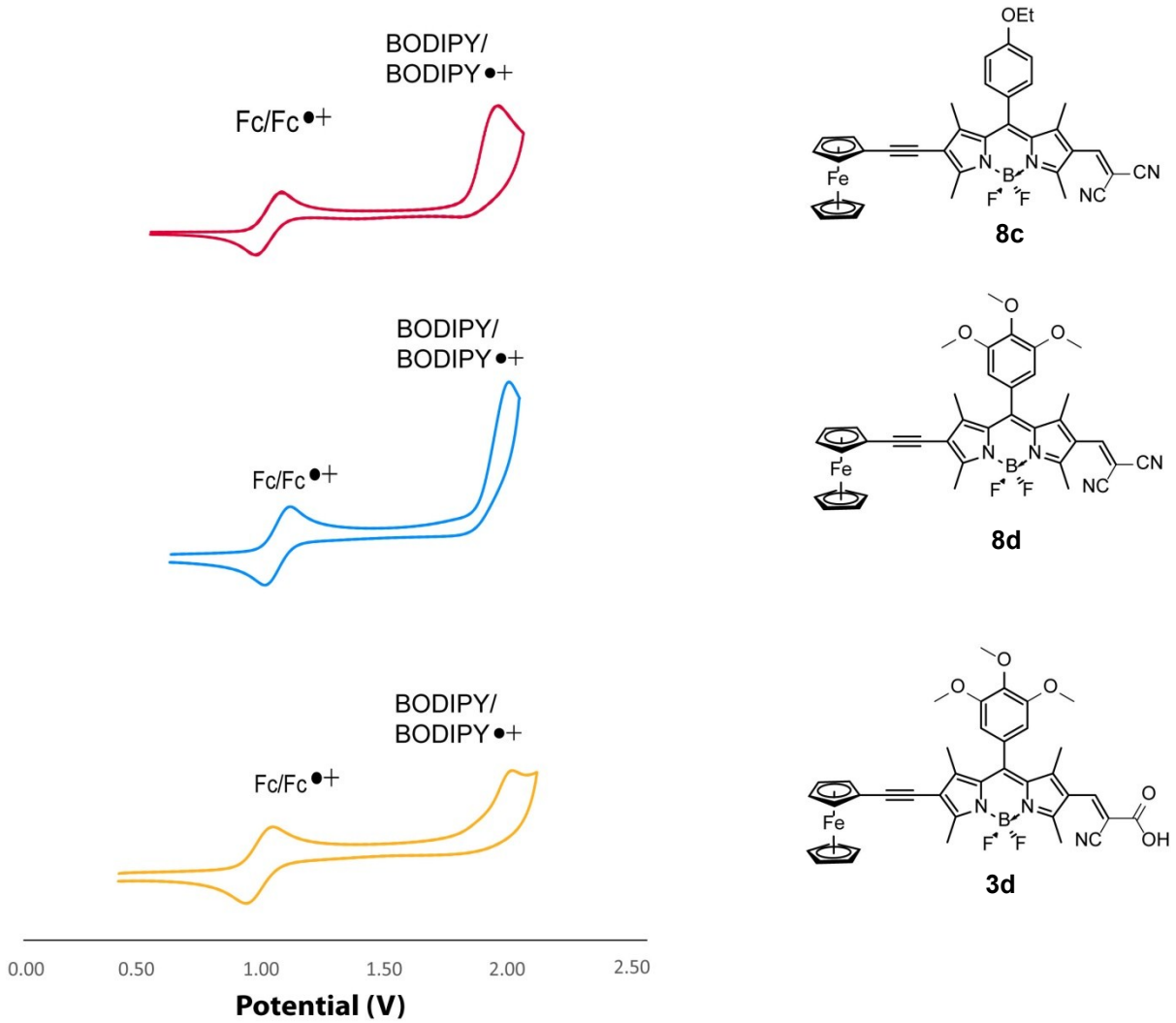
11: A 200 mL flame dried Schlenk flask was charged with a stir bar, **12** (0.203 g, 0.522 mmol), dry THF (6.6 mL), and dry NEt_3 (2.8 mL). The solution was degassed with nitrogen for 5 min. The mixture was then heated to 68°C and $Pd(PPh_3)_2Cl_2$ (0.018 g, 0.026 mmol) and CuI (0.010 g, 0.052 mmol) were added together in one portion, followed by ethynyl TPA (0.155 g, 0.575 mmol). The reaction was monitored by TLC and allowed to cool to room temperature after 6 h. The solvent was removed under high vacuum, the crude material was dissolved in EtOAc and washed with sat.

$NH_4Cl$and then with brine. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated to give a crude red oil. The crude material was purified by column chromatography using hexanes:DCM (6:2) as the eluent to afford the red solid powder product (0.062 g, 23%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, 2H, *J* = 8.4 Hz), 7.28 (t, 4H, *J* = 8.0 Hz), 7.11 (d, 4H, *J* = 8.0 Hz), 7.06 (t, 2H, J = 7.2 Hz), 7.01 (d, 2H, *J* = 8.8 Hz), 2.65 (s, 3H), 2.62 (s, 3H), 2.54 (s, 6H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.62, 147.87, 147.71, 142.46, 141.80, 140.35, 133.19, 132.43, 129.53, 125.01, 123.61, 122.20, 116.78, 96.11, 81.39, 29.85, 22.84, 17.63, 16.81, 16.07, 14.71, 13.61. ^{19}F NMR ($CDCl_3$, 376.5 MHz) δ -146.83 (q, J_{BF} = 30.0 Hz). ^{11}B NMR ($CDCl_3$, 128 MHz) δ 0.52 (t, J_{FB} = 30.7 Hz).

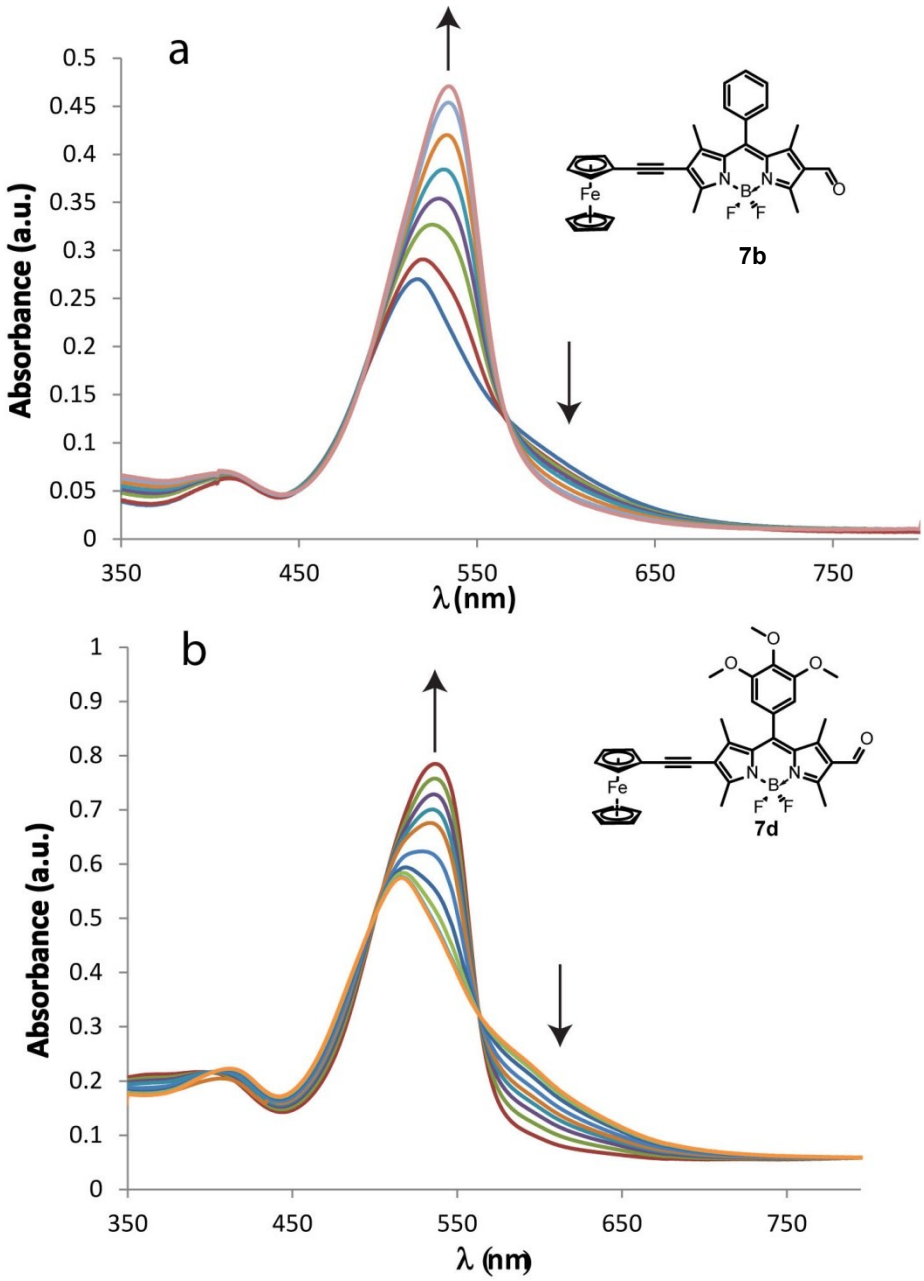
Appendices



Supplementary Figure 1: UV-Vis spectra (in DCM) for **7a-d**



Supplementary Figure 2: Cyclic voltammograms of ferrocenyl-BODIPY dyes **3d, 8c,** and **8d**. Data collected in DCM using 0.1 M [nBu_4N][PF_6] at 100 mV/s and reference to a [Fc/Fc^+] internal standard (+0.765 V vs. NHE in DCM)



Supplementary Figure 3:. UV-Vis changes over time at a constant potential of 1.0V; Data collected using an OTTLE cell in DCM using 0.1 M [nBu_4N][PF_6]. A) molecule **7b**, B) molecule **7d**

NMR Spectra fo

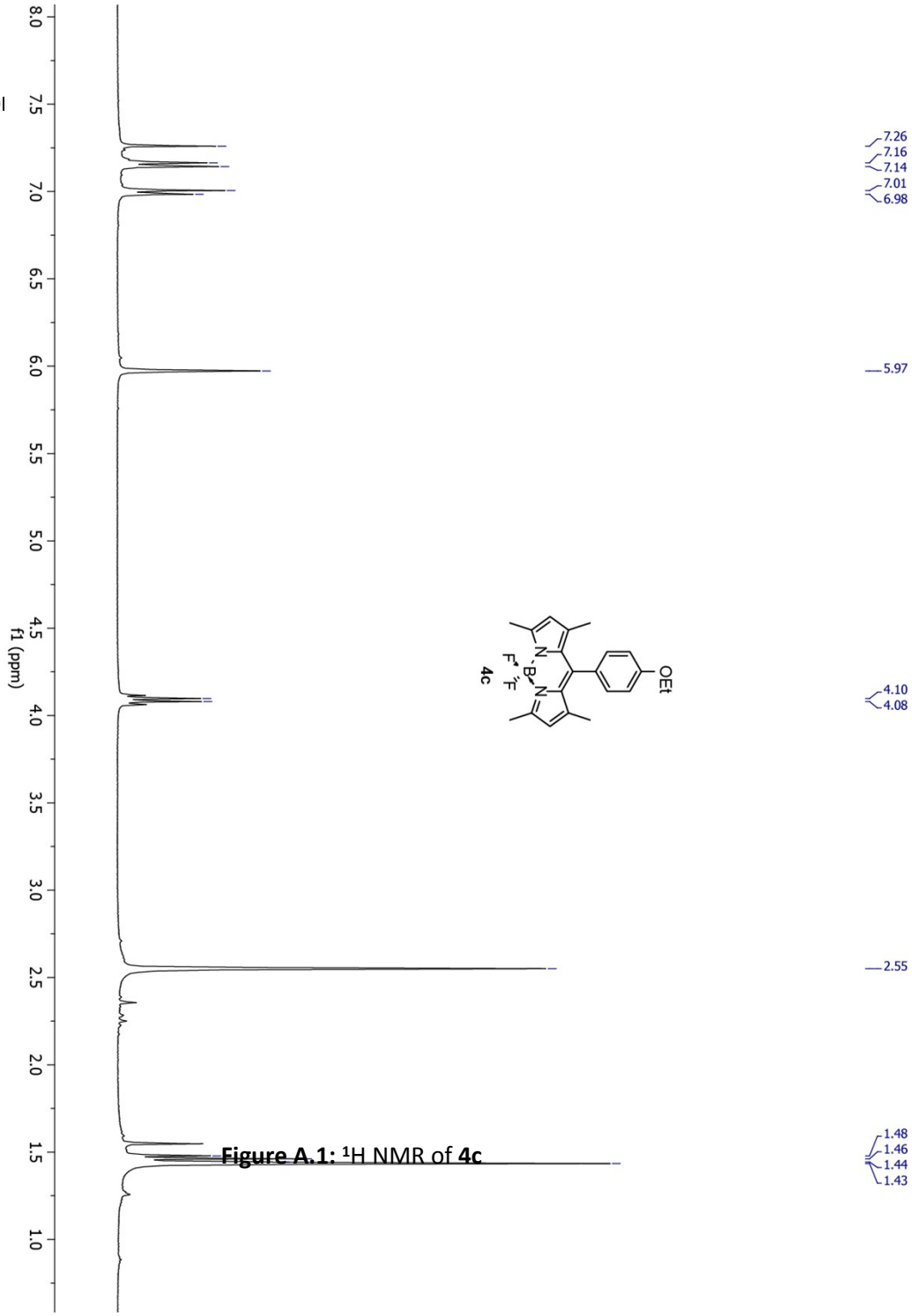


Figure A.1: ^{1}H NMR of **4c**

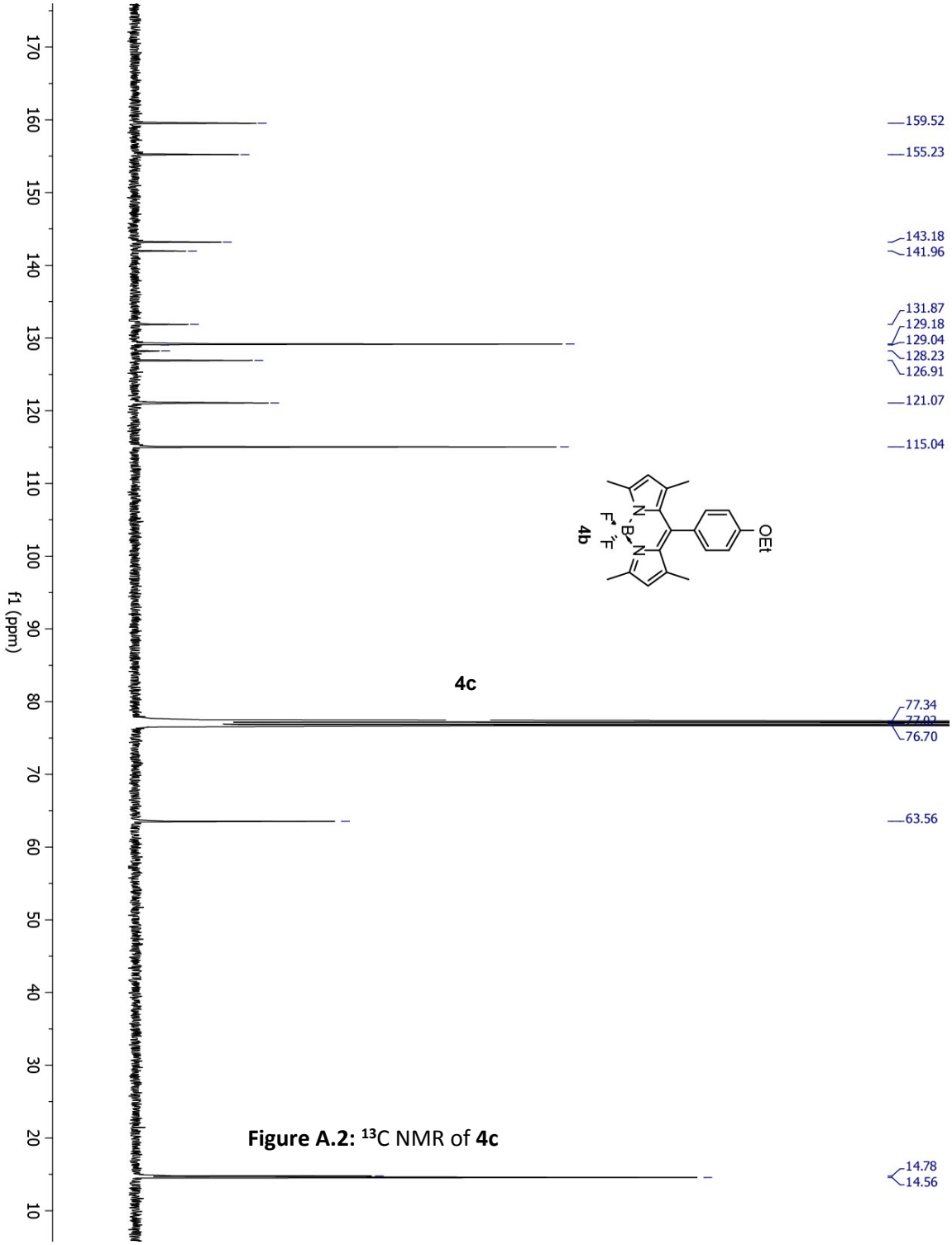


Figure A.2: ^{13}C NMR of **4c**

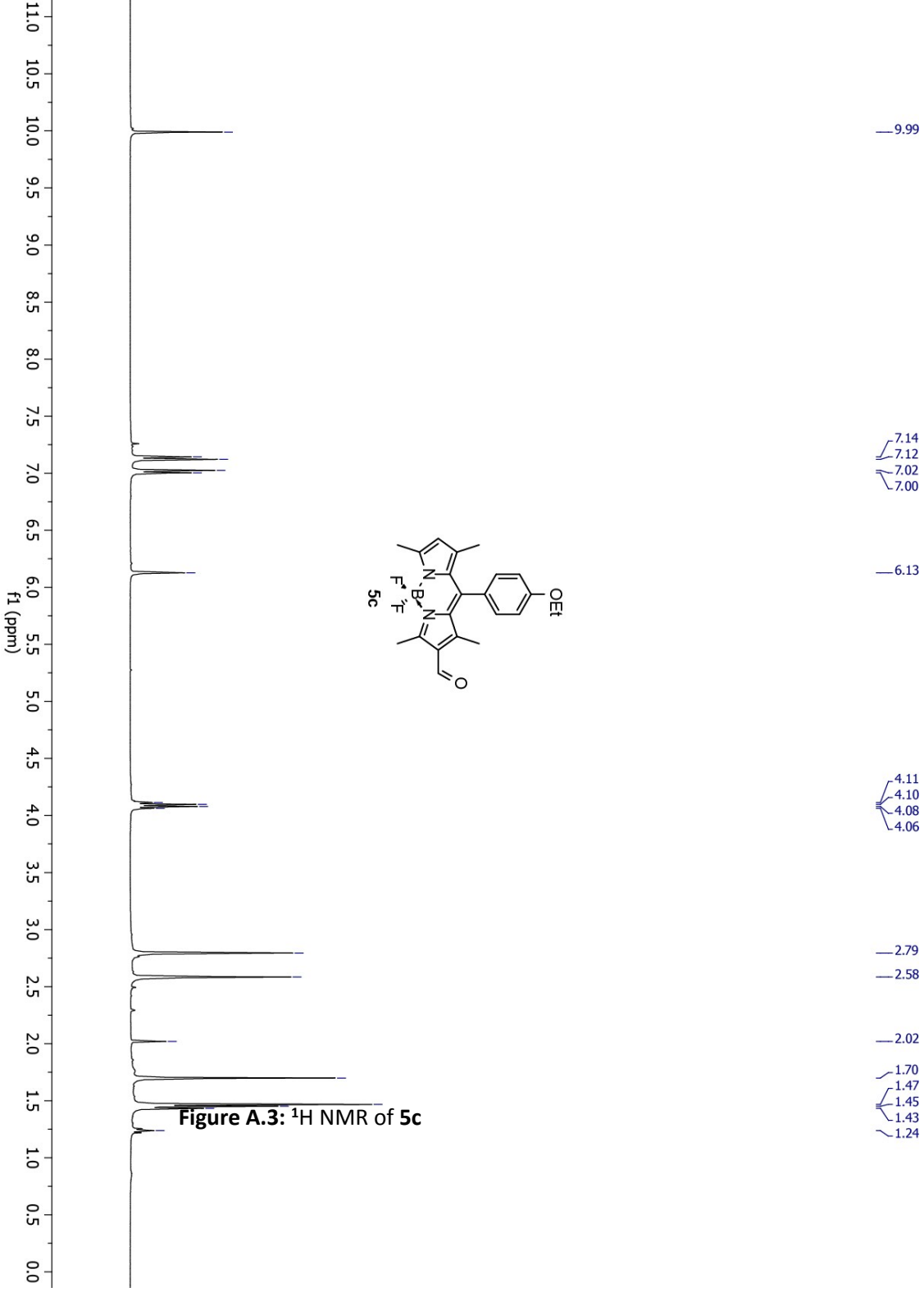


Figure A.3: ^{1}H NMR of **5c**

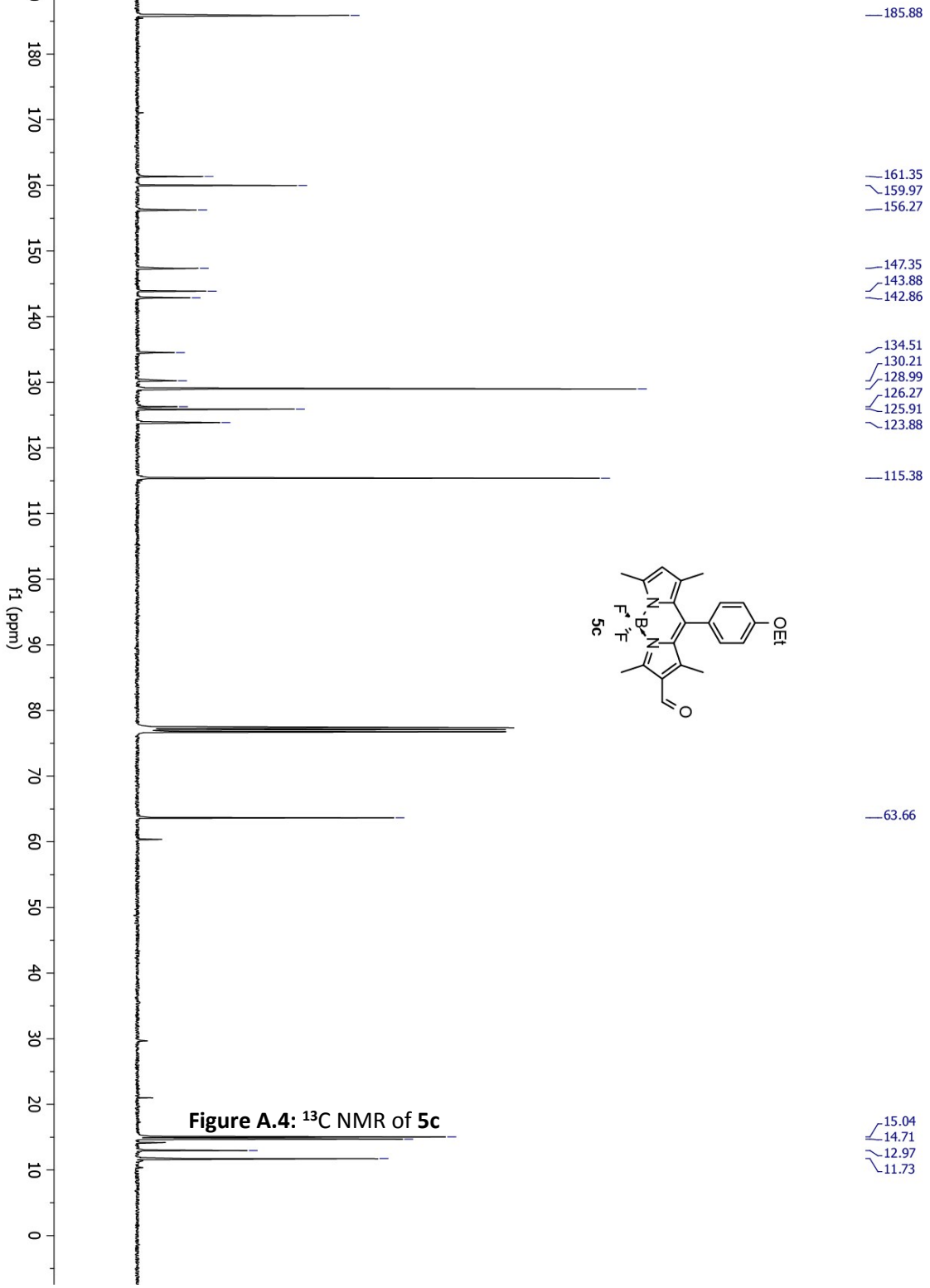


Figure A.4: ^{13}C NMR of **5c**

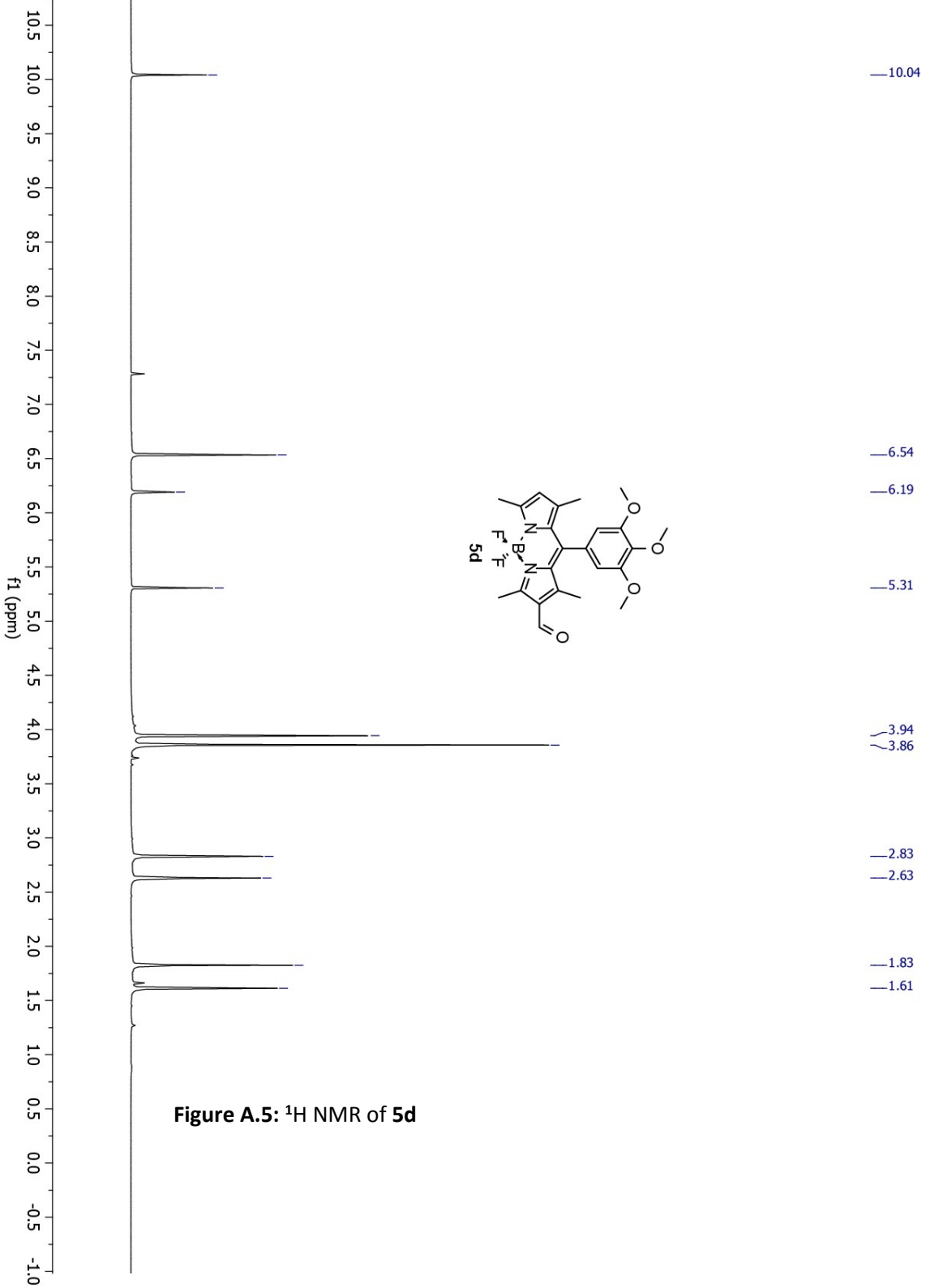


Figure A.5: ^{1}H NMR of **5d**

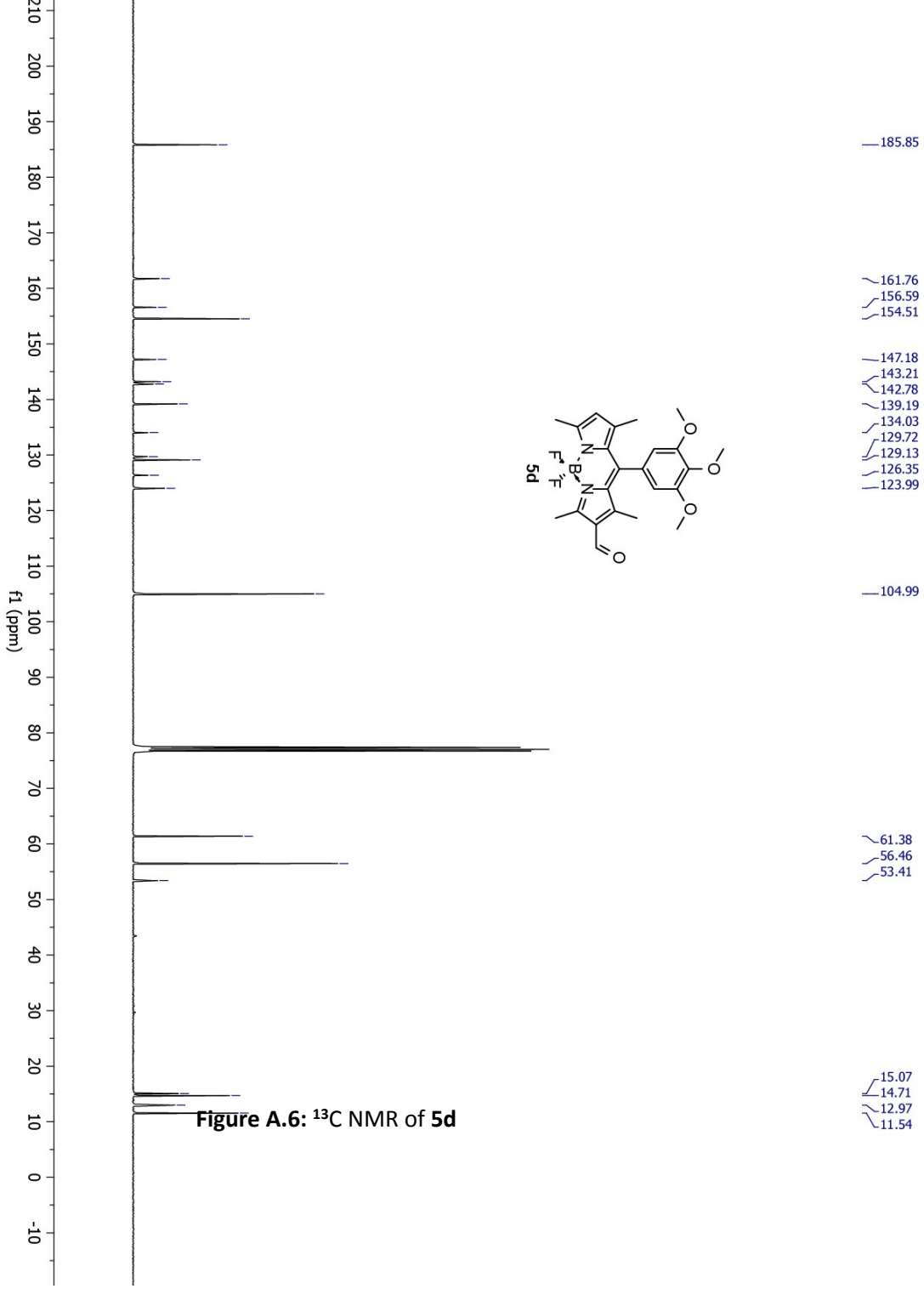


Figure A.6: ^{13}C NMR of **5d**

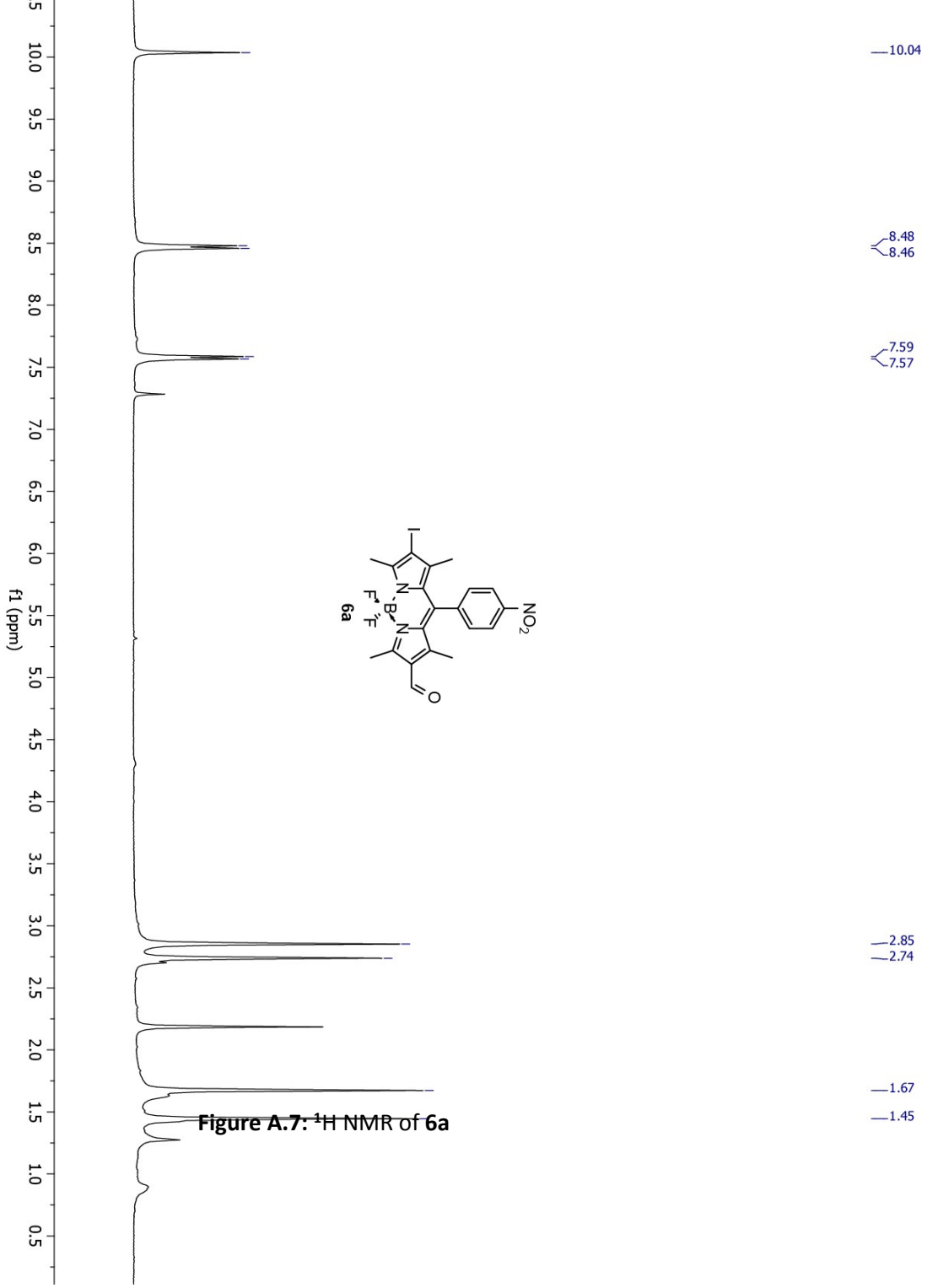


Figure A.7: ^{1}H NMR of **6a**

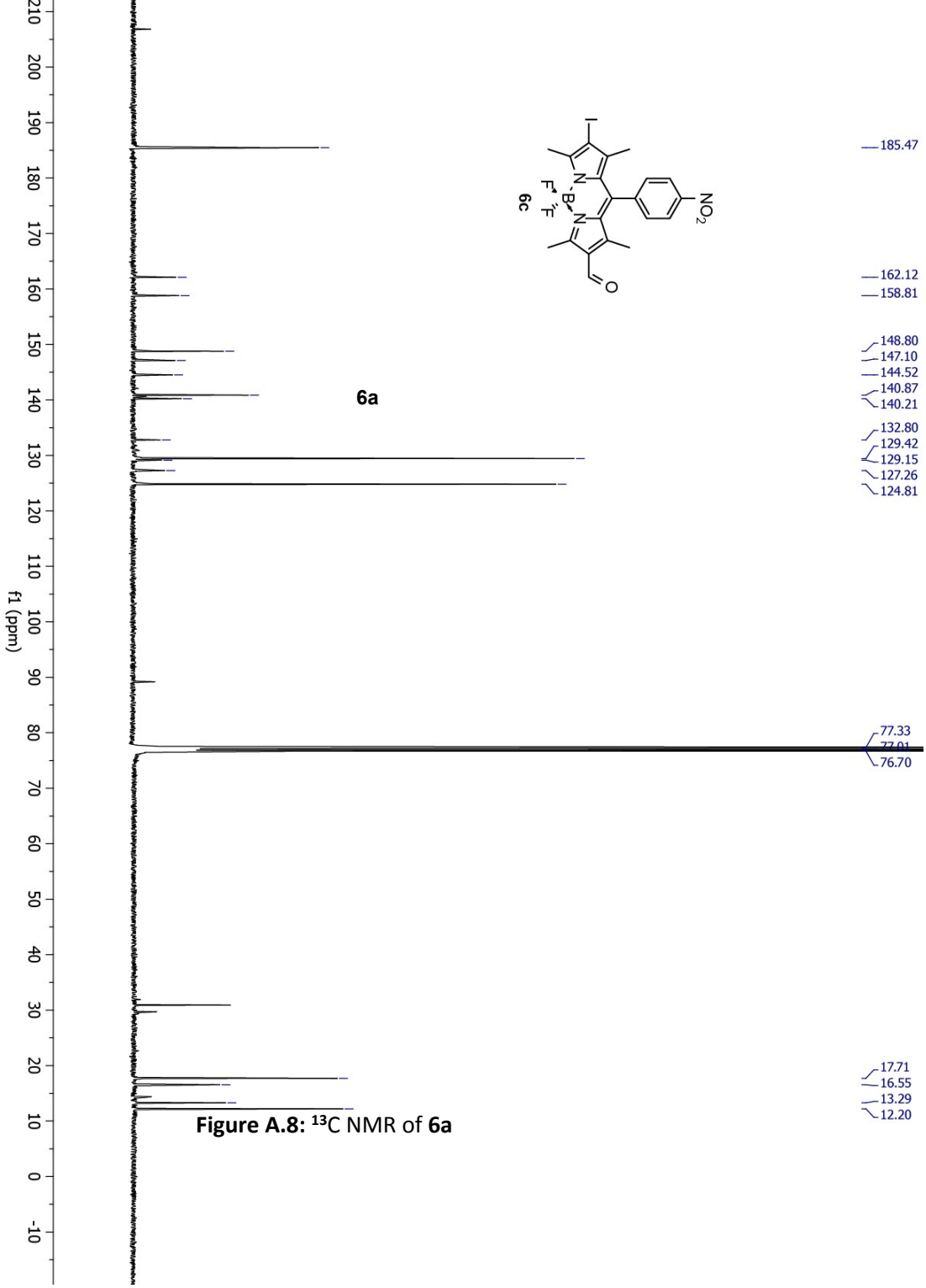


Figure A.8: ^{13}C NMR of **6a**

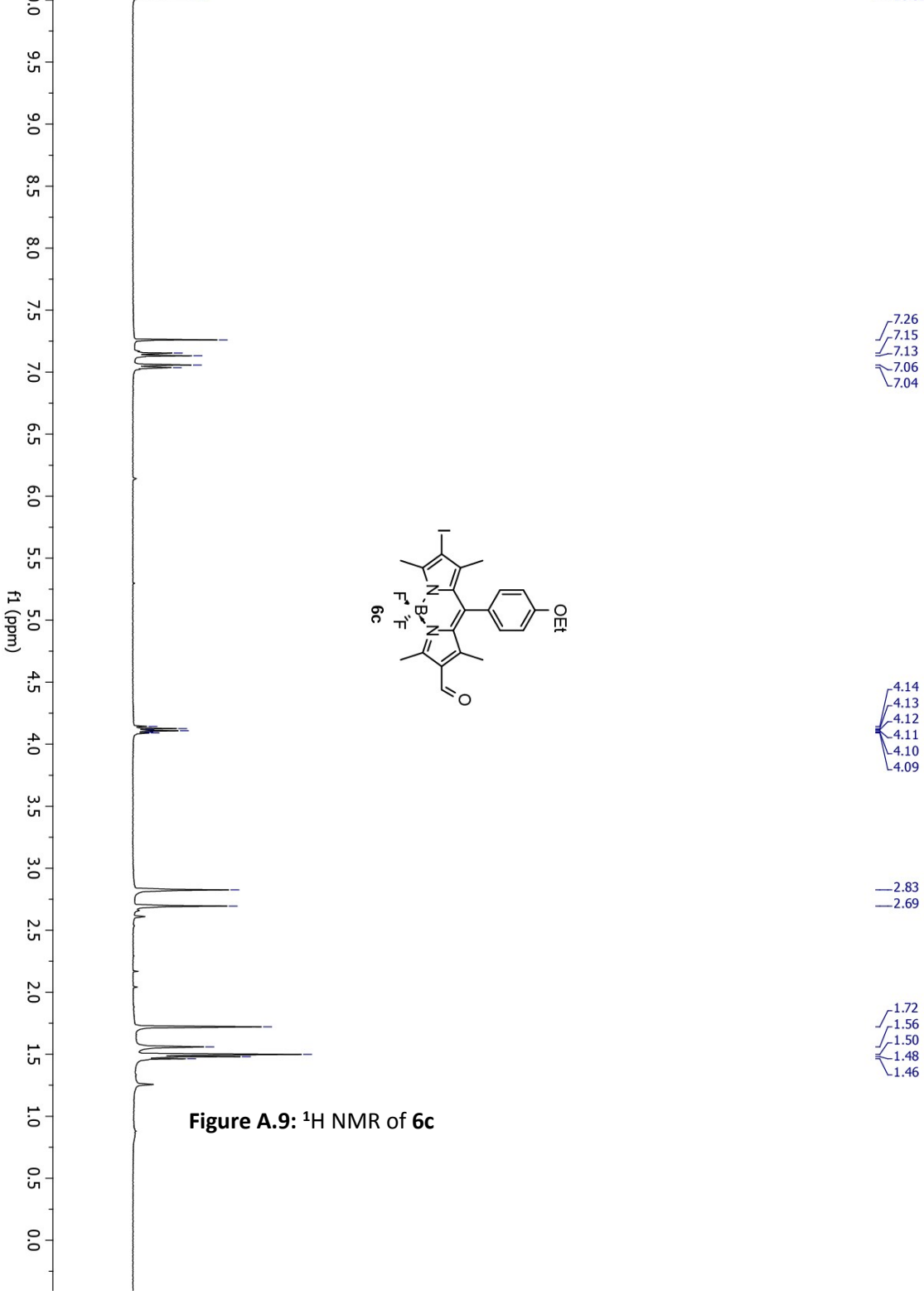


Figure A.9: ^{1}H NMR of **6c**

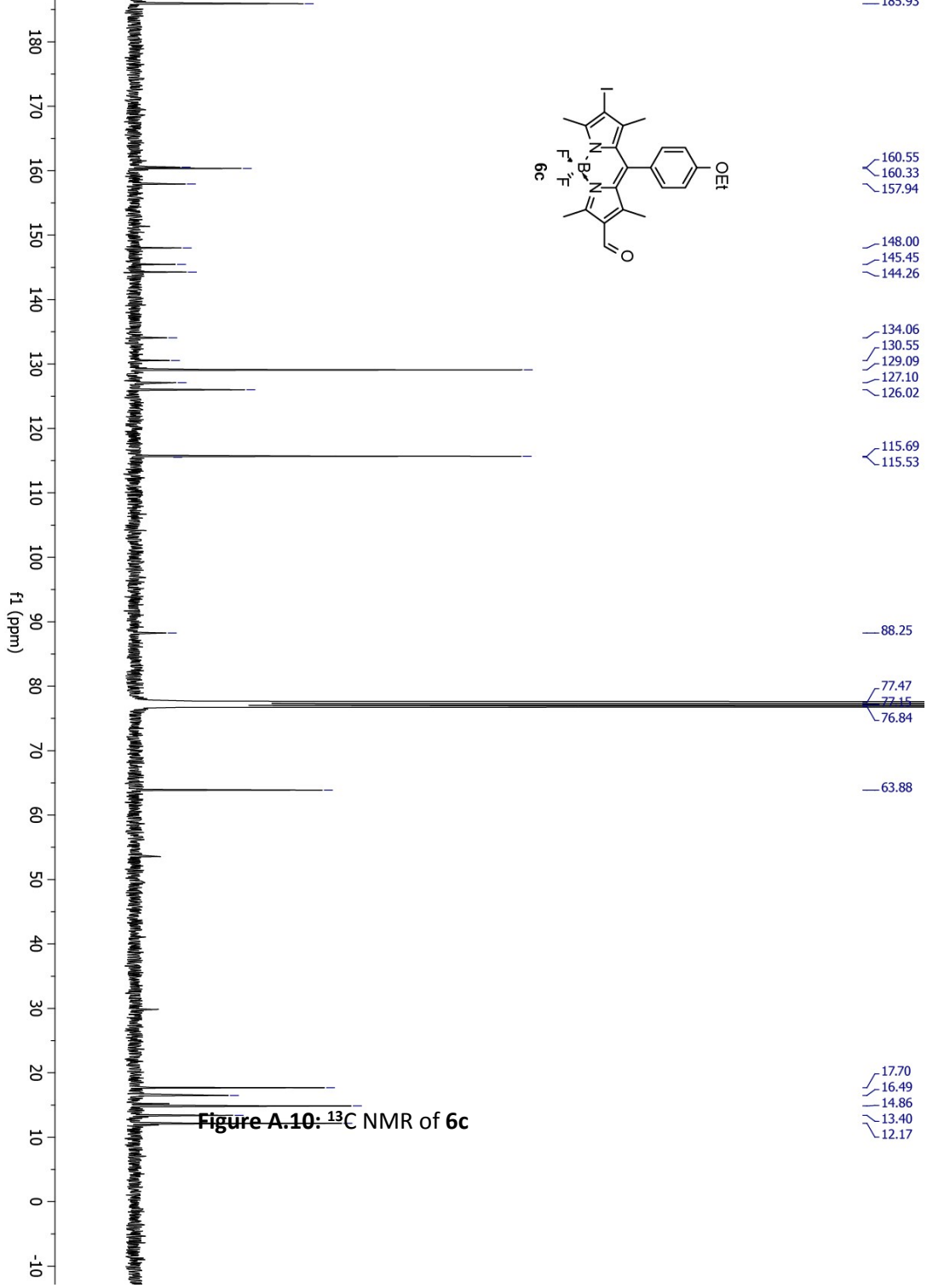


Figure A.10: ^{13}C NMR of **6c**

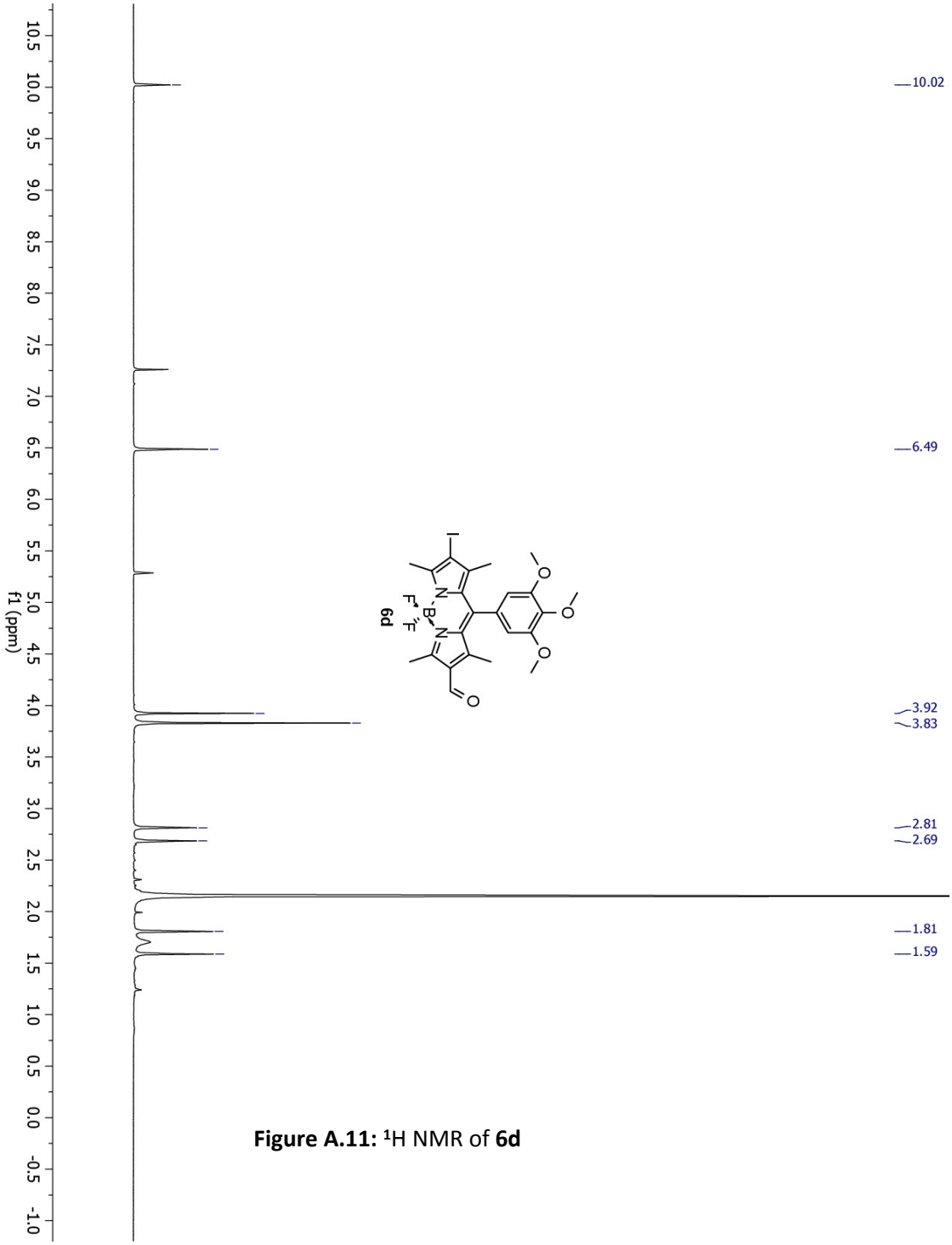


Figure A.11: ^{1}H NMR of **6d**

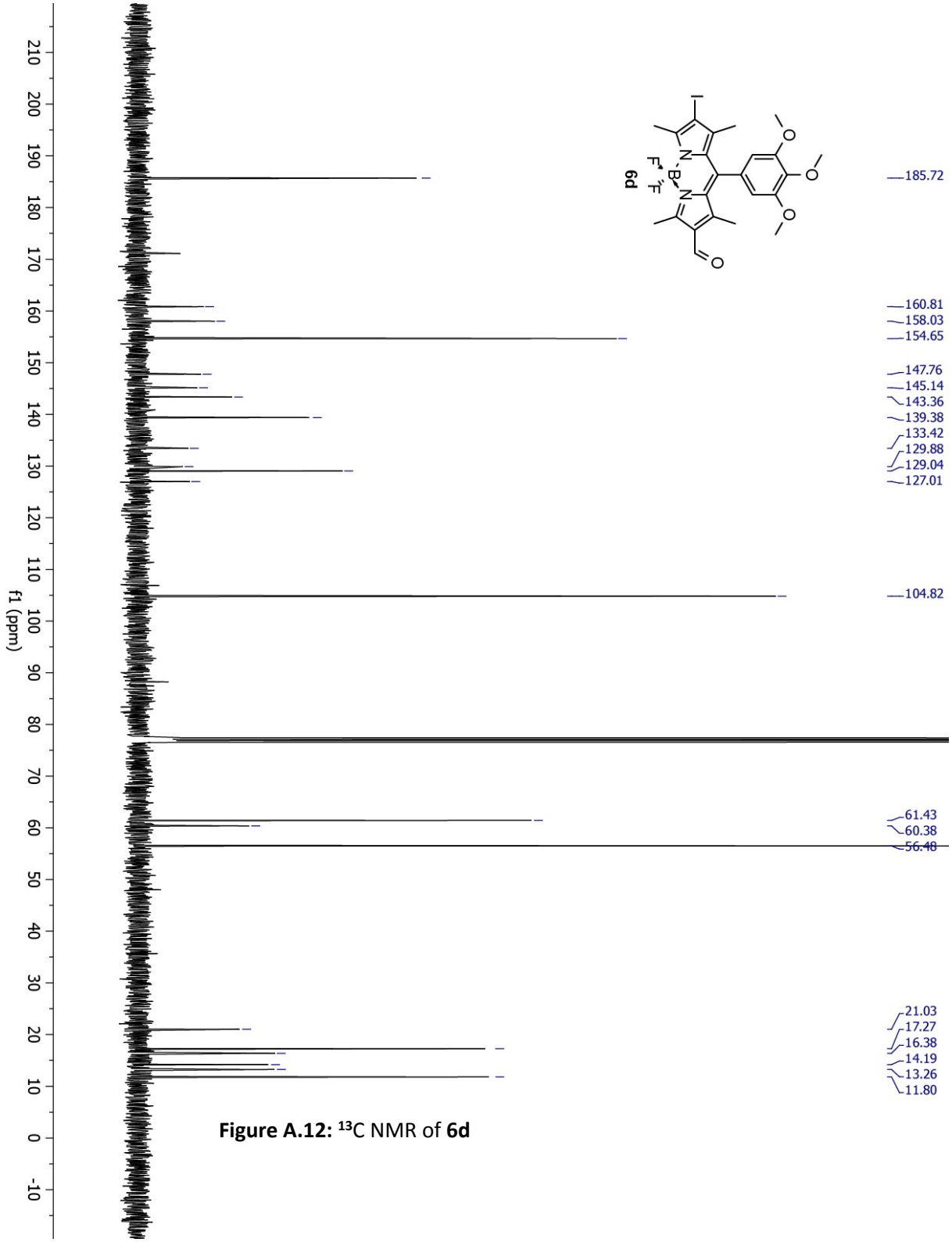


Figure A.12: ^{13}C NMR of **6d**

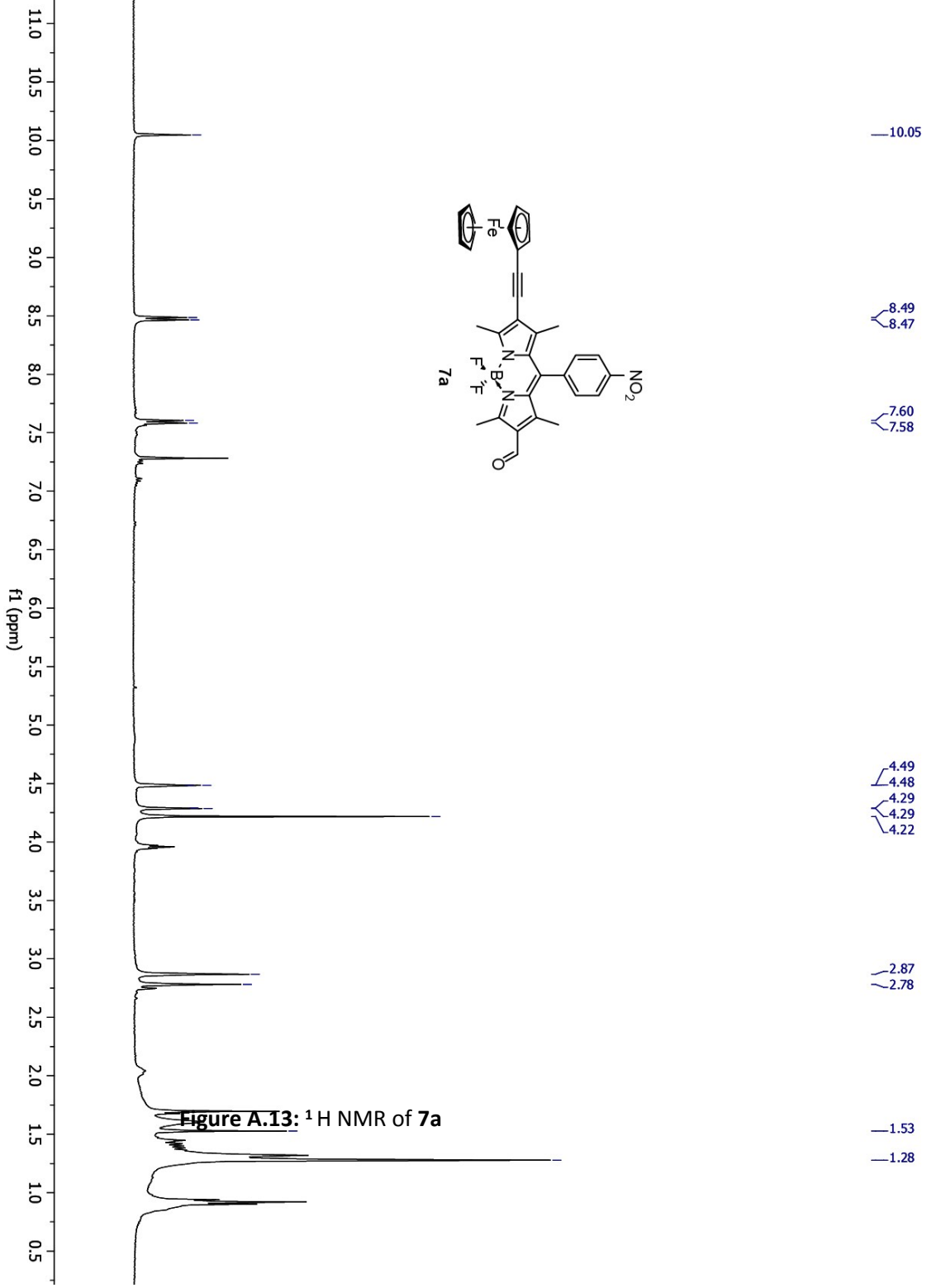


Figure A.13: ^{1}H NMR of **7a**

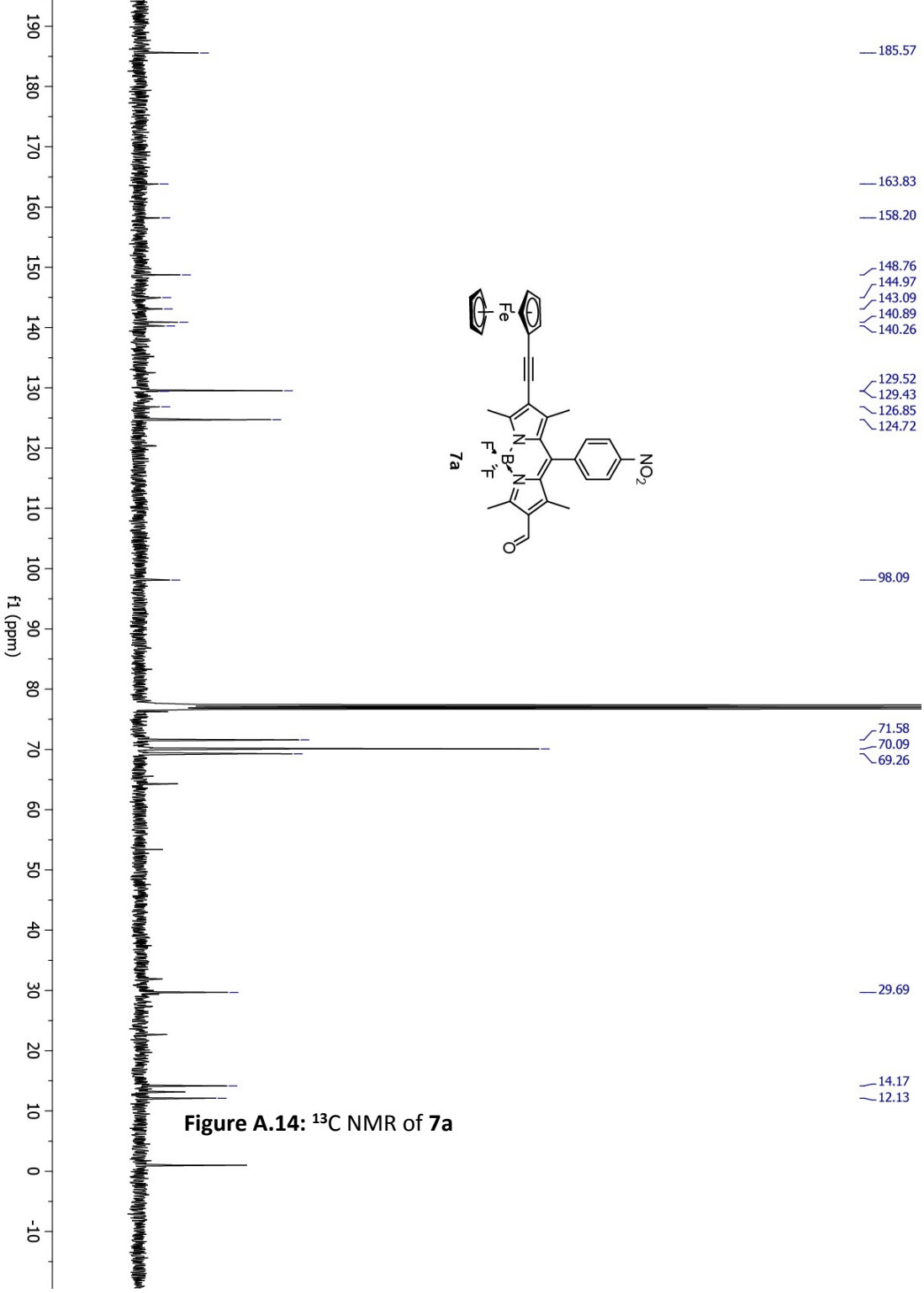


Figure A.14: ^{13}C NMR of **7a**

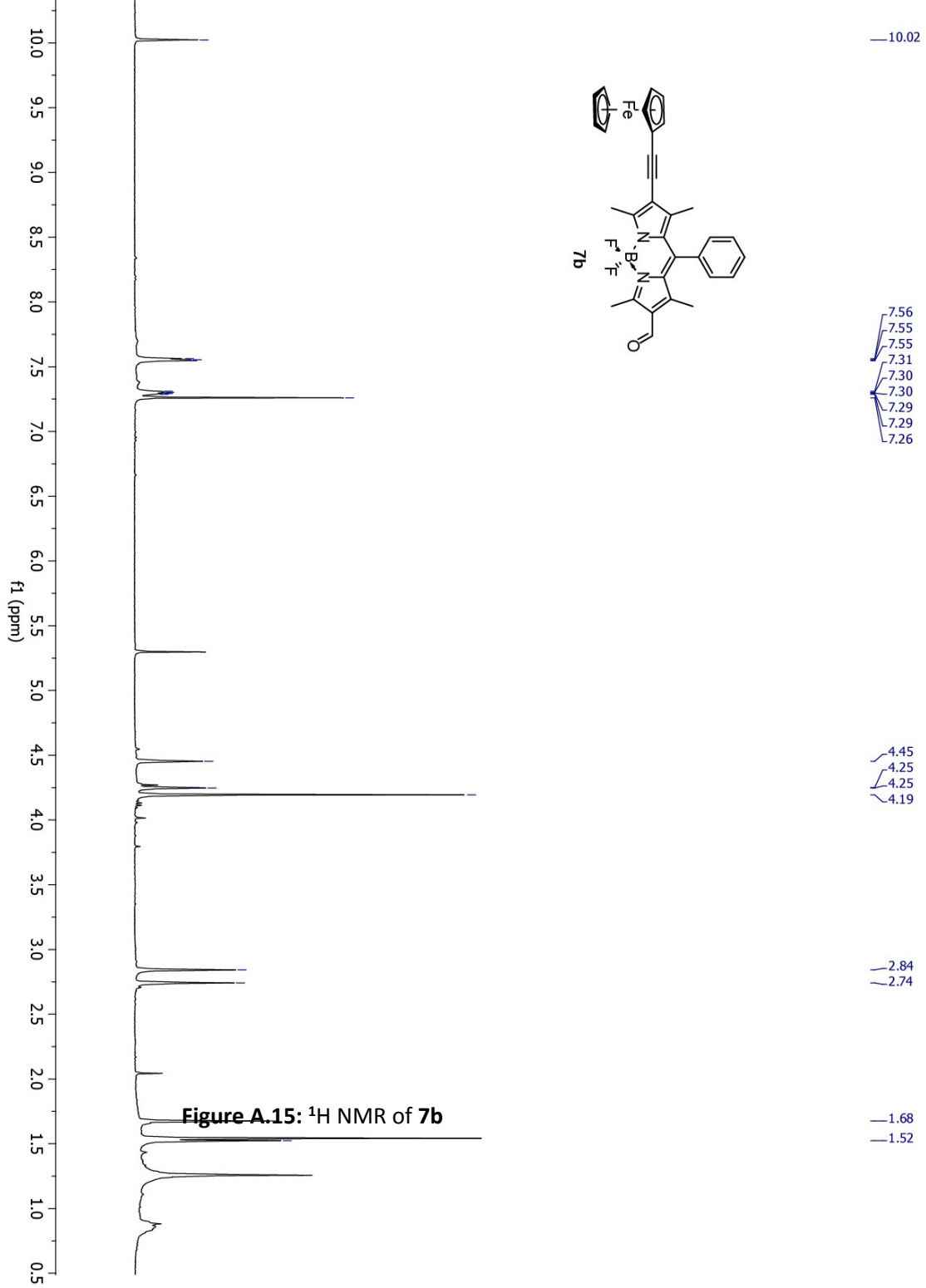


Figure A.15: ^{1}H NMR of **7b**

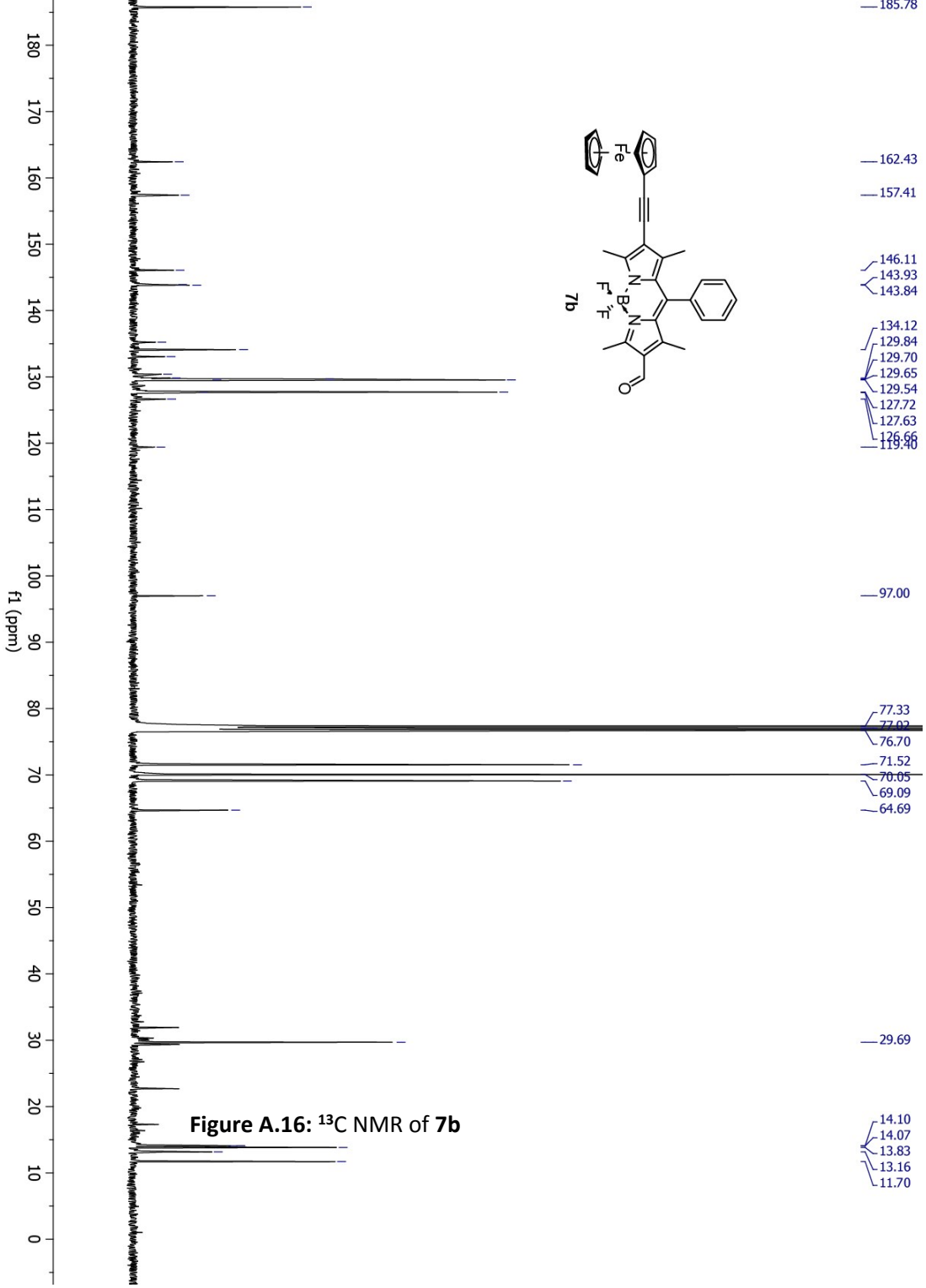


Figure A.16: ^{13}C NMR of **7b**

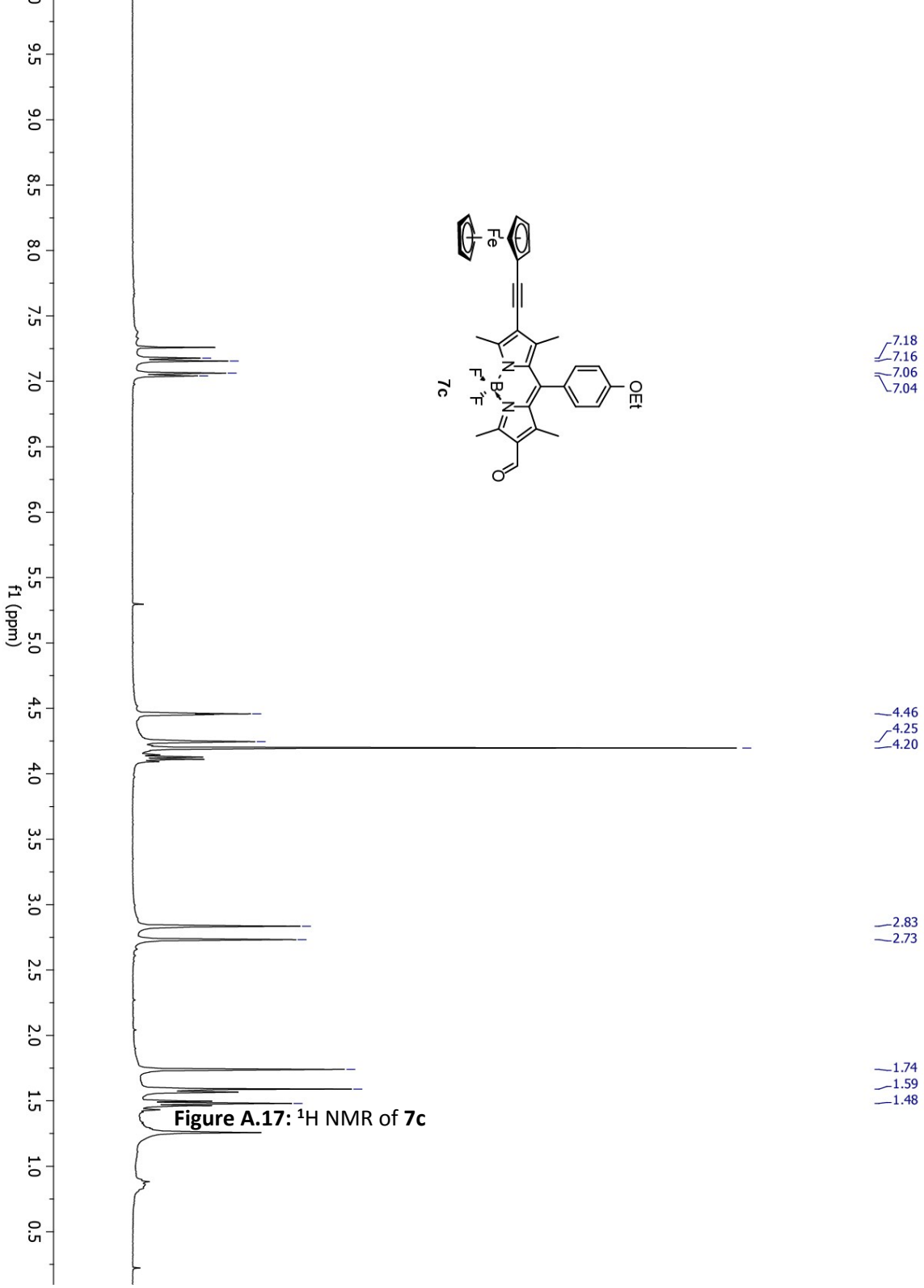


Figure A.17: ^{1}H NMR of **7c**

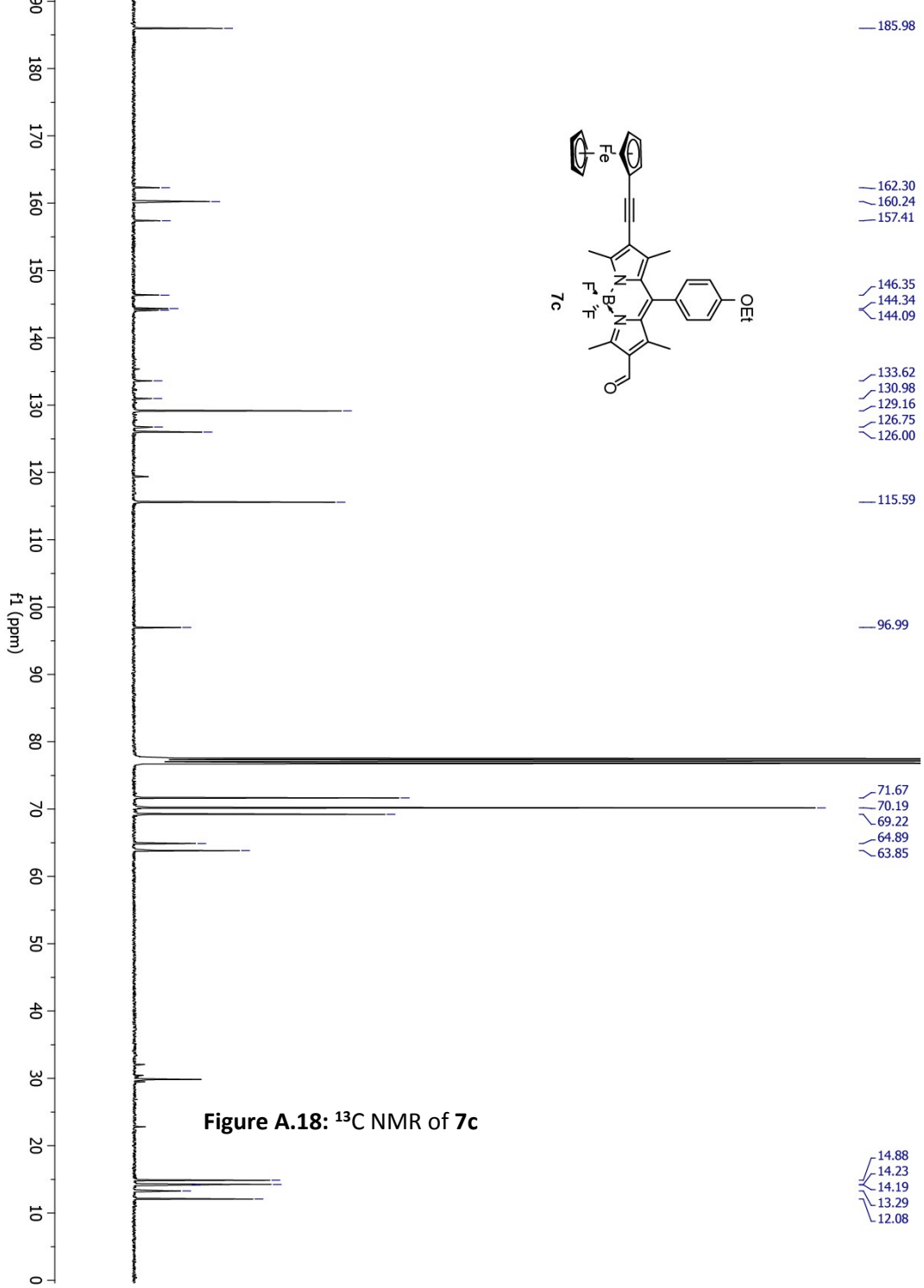


Figure A.18: ^{13}C NMR of **7c**

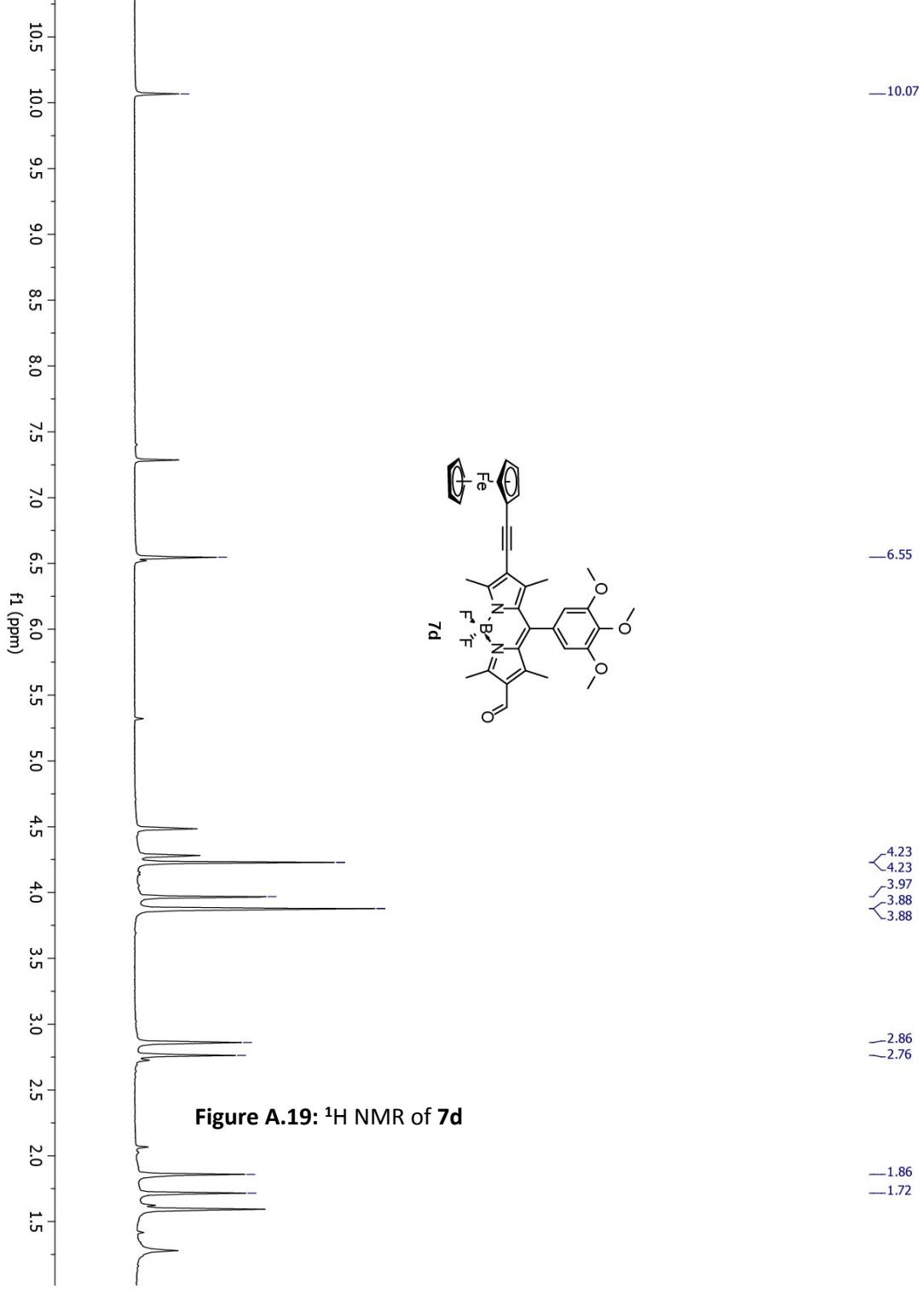


Figure A.19: ^{1}H NMR of **7d**

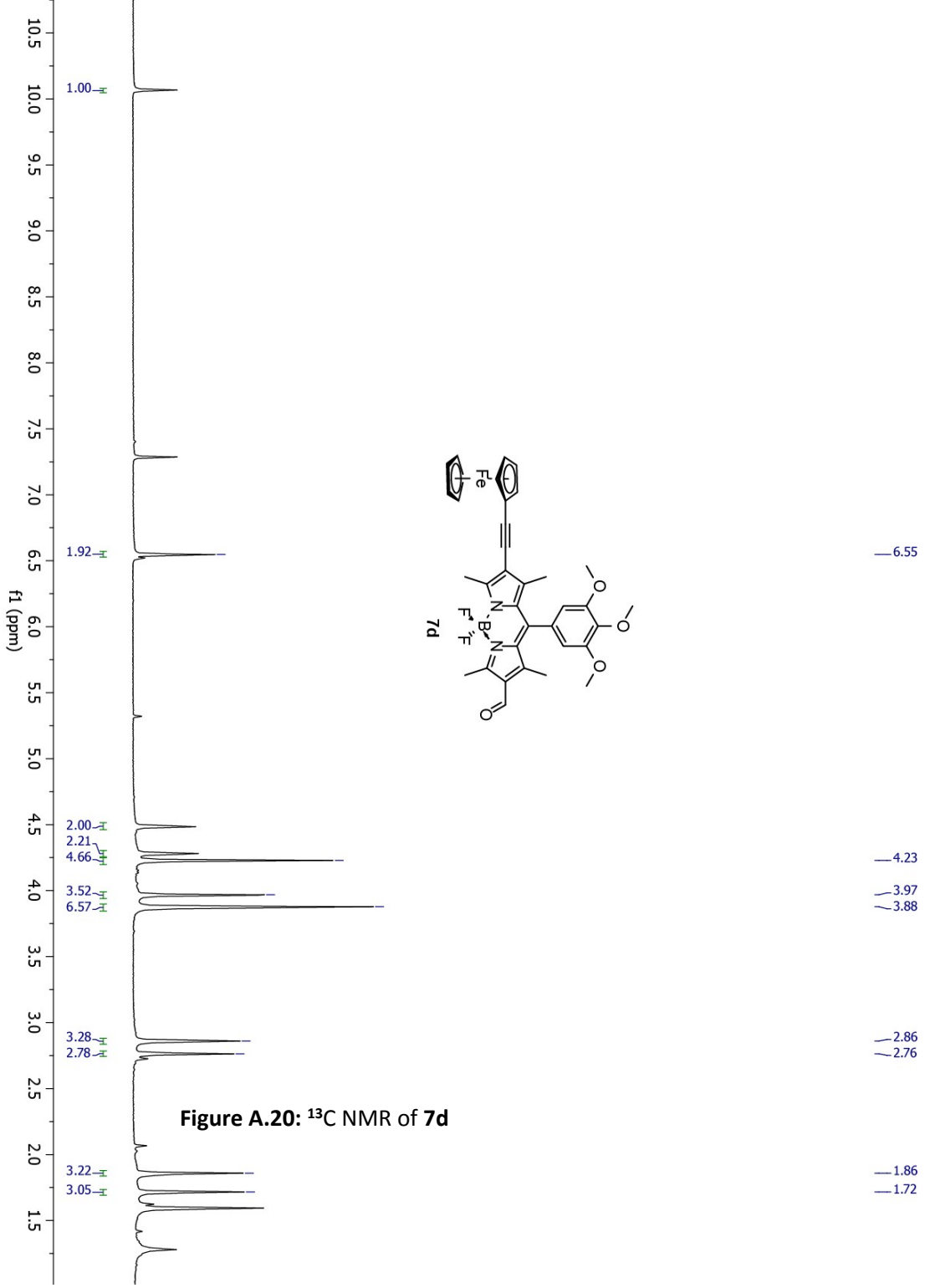


Figure A.20: ^{13}C NMR of **7d**

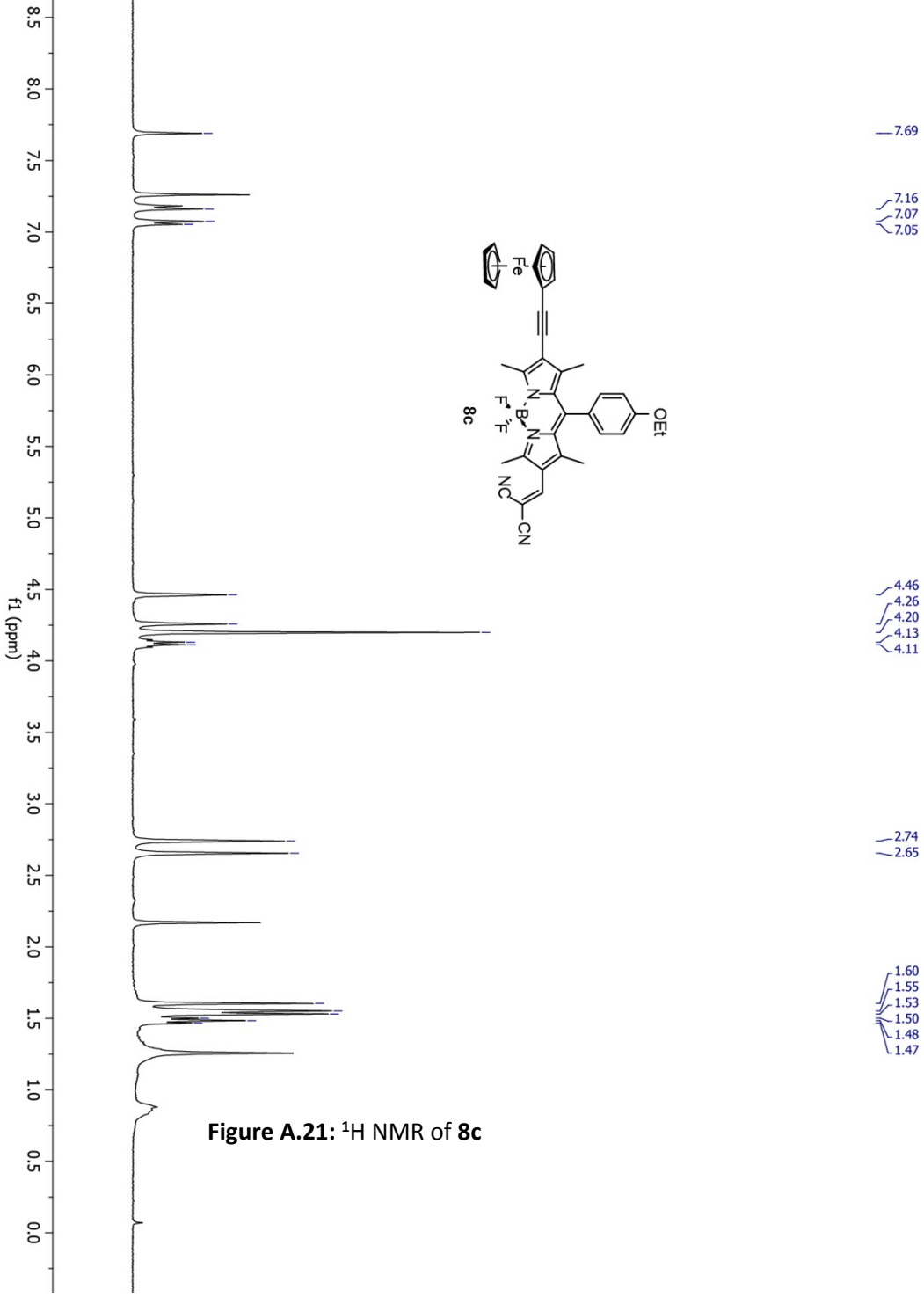


Figure A.21: ^{1}H NMR of **8c**

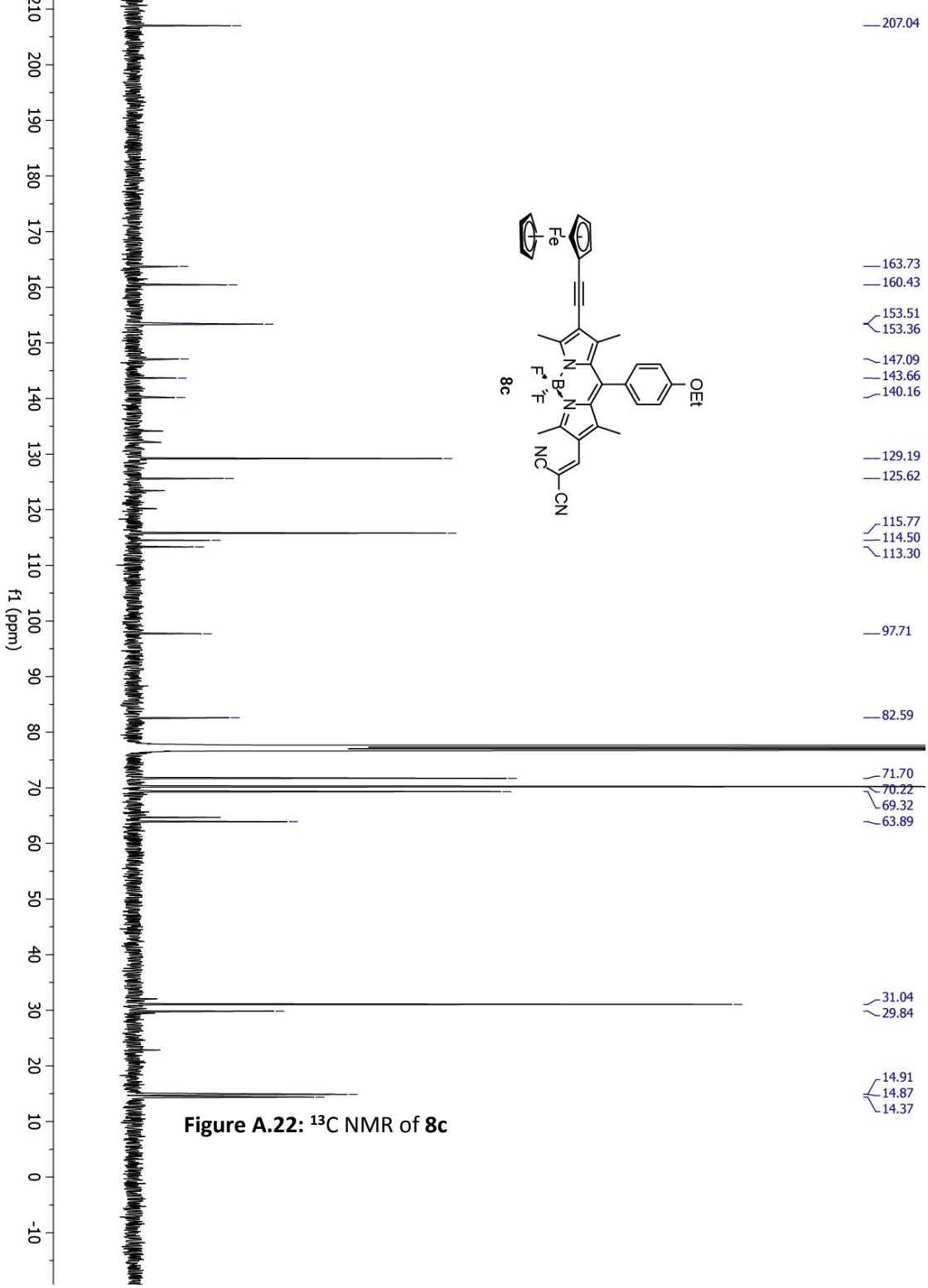


Figure A.22: ^{13}C NMR of **8c**

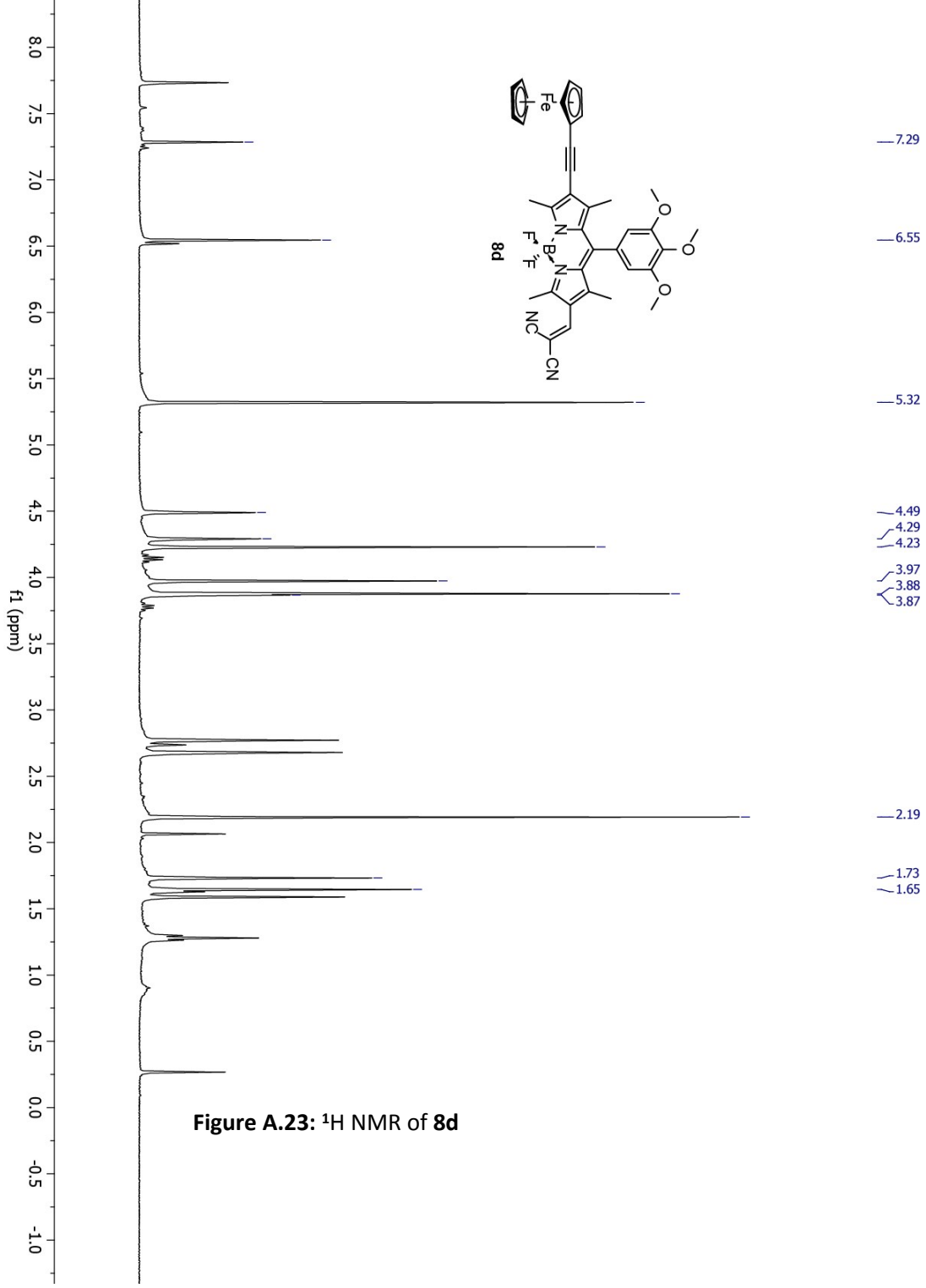


Figure A.23: ^{1}H NMR of **8d**

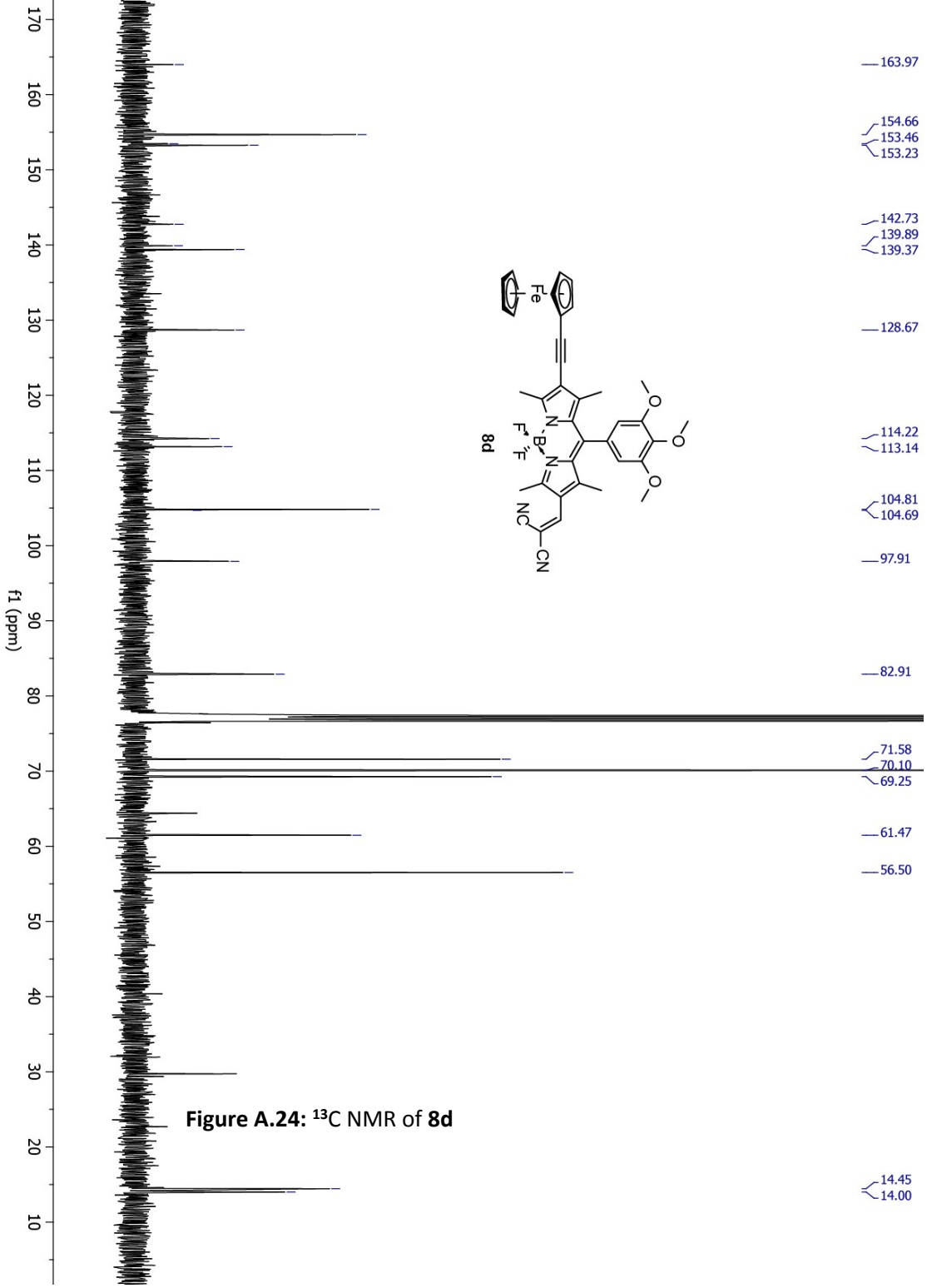


Figure A.24: ^{13}C NMR of **8d**

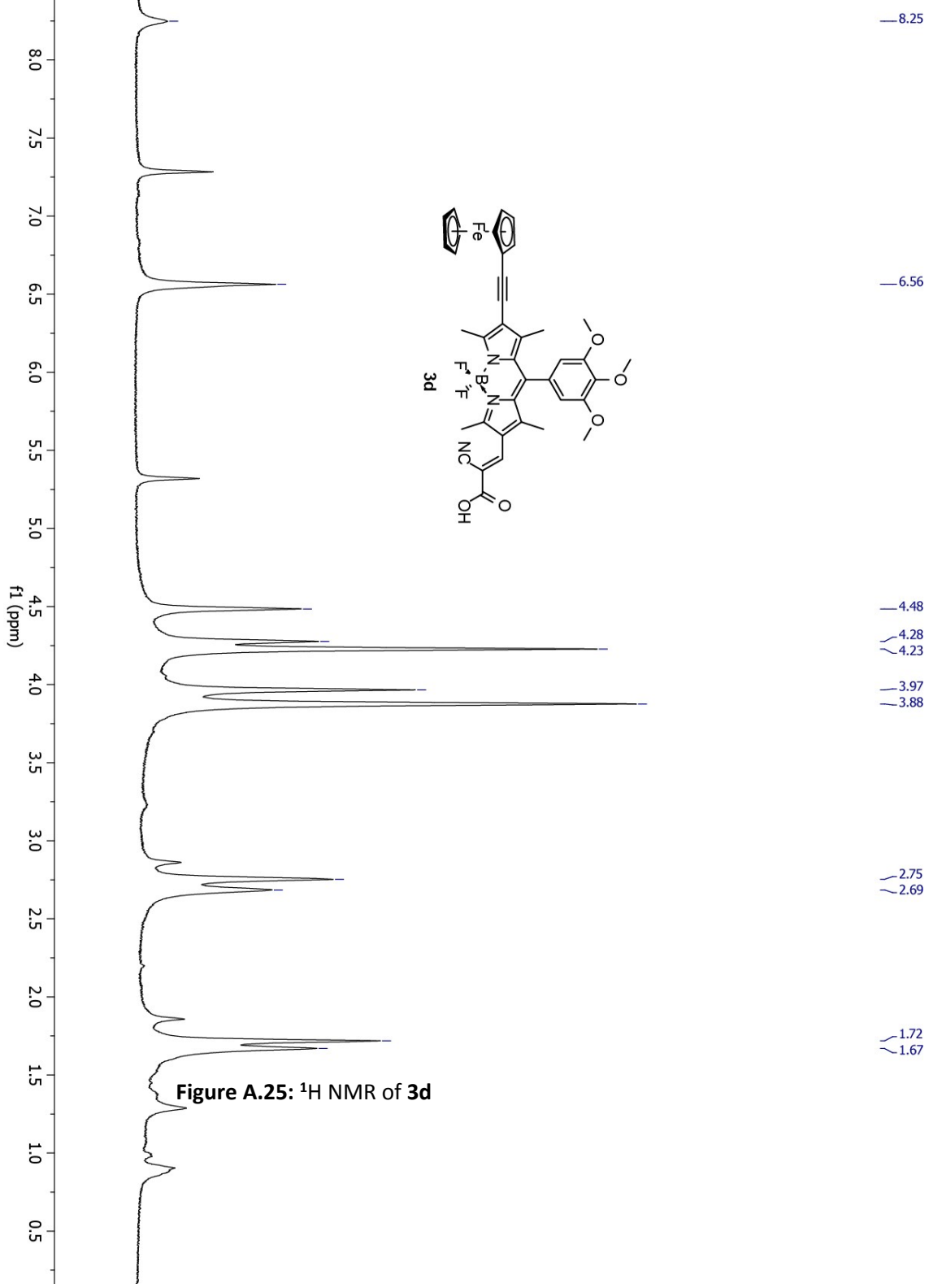


Figure A.25: ^{1}H NMR of **3d**

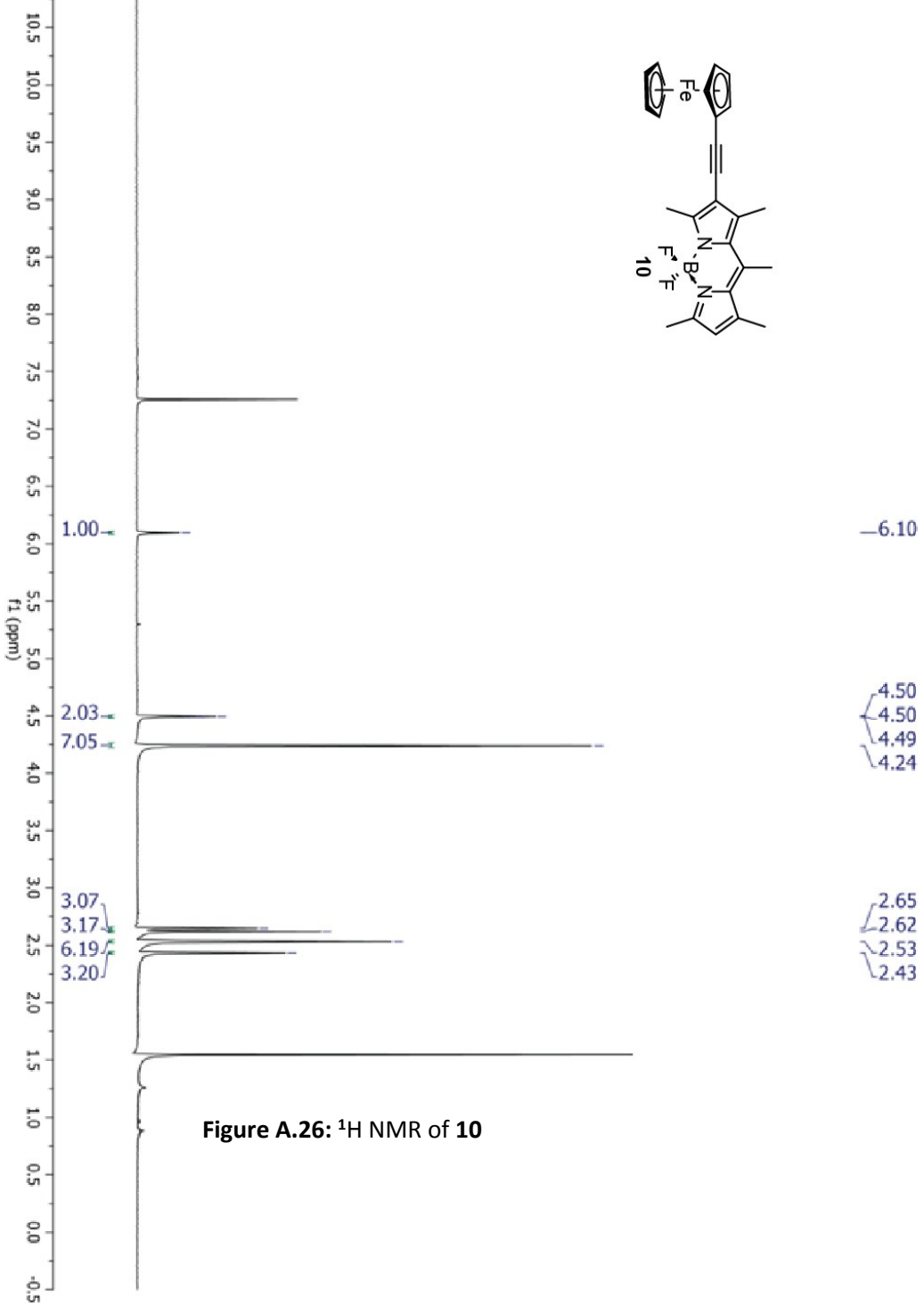


Figure A.26: ^{1}H NMR of **10**

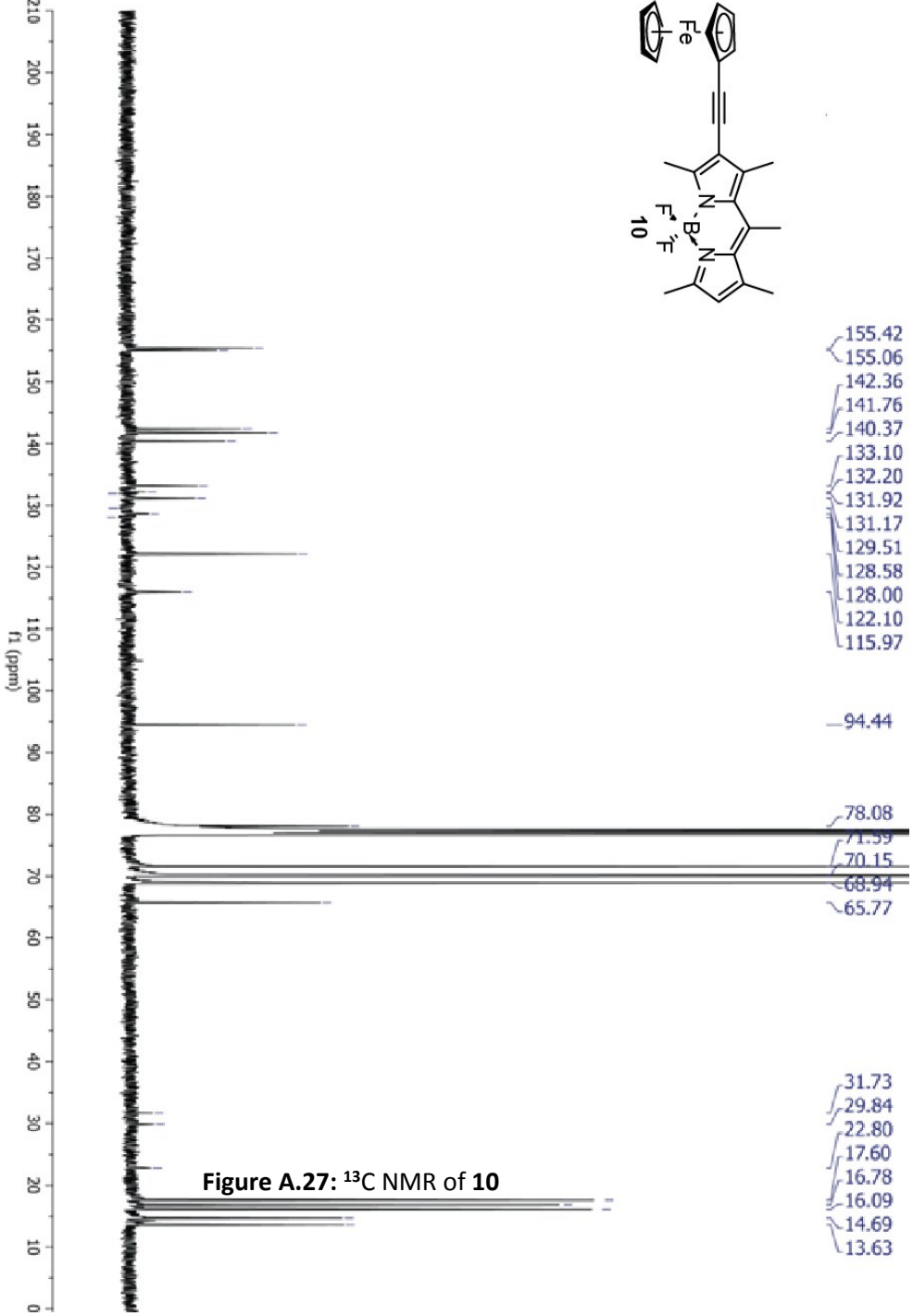


Figure A.27: ^{13}C NMR of **10**