Synthesis and Optoelectronic Properties of 2,6-Bis(2-anilinoethynyl)pyridine Scaffolds

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Supporting Information

Table of Contents

General Methods. Compounds **6-9** were prepared according to the previously published literature reports.[1-5] ^{1}H and ^{13}C NMR spectra were obtained on a Varian 300 MHz spectrometer (^{1}H 299.95 Hz, ^{13}C 75.43 Hz), Inova 500 MHz spectrometer (^{1}H 500.10 MHz, ^{13}C 125.75 MHz) or Varian 600 MHz spectrometer. Chemical shifts (δ) are expressed in ppm from solvent signal using non-deuterated solvent present in the bulk deuterated solvent (DMSO-d6: ^{1}H 2.5 ppm, ^{13}C 39.52 ppm). Unless otherwise specified, solvents were obtained from distillation using published literature procedures directly before use. Mass spectra were acquired Waters LCT Premier ESI-MS in positive mode in MeCN solvent. UV-Vis spectra were acquired with a Hewlett-Packard 8453 UV-Visible spectrophotometer equipped with a 250 nm cutoff filter. Fluorescence data was acquired with a Horiba Jobin-Yvon FluoroMax-4 fluorescence spectrophotometer equipped with an integrating sphere. Absolute photoluminescence quantum yields were taken in triplicate in O_2- containing (no inert gas purging) MeCN.

General TMS Deprotection Procedure A. To a solution of 4-substituted-2-(trimethylsilylethynyl)aniline (**6-9**, 1 equiv) in 2:1 MeOH/Et_2O (0.1 M) was added K_2CO_3 (5 equiv) at room temperature. After stirring for 30 min, the reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the desilylated product which was used without further purification.

General Cross Coupling Procedure B. To an Ar degassed solution of 2,6-dibromopyridine (1 equiv) in 1:1 THF/DIPA (0.05 M) were added CuI (0.2 equiv) and $Pd(PPh_3)_4$ (0.1 equiv) at room temperature. The solution was degassed with Ar for an additional 30 min and then heated to 50 °C. To this solution a second degassed solution of 2-ethynyl-4-substituted aniline (2.2 equiv) in THF (20 mL) was cannula transferred. After stirring for 16 h, the reaction mixture was cooled, diluted with CH_2Cl_2, and filtered through a 4 cm pad of silica. The filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography over silica gel to give the desired dianiline product.

General Urea Formation Procedure C. To a stirred solution of 2,6-bis(2-anilinoethynyl)pyridine (**6-9**, 1 equiv) in dry toluene (0.01 M) was added the appropriate phenylisocyanate reagent (3-10 equiv). The reaction was stirred at rt-80 °C for 3 h- 2 d. The resulting suspension was diluted in hexanes and the solid precipitate was collected via vacuum filtration. The solid was redissolved in a minimal amount of 10:1 acetone/TFA and hexanes was added until the solution became cloudy. The resulting suspension was cooled and the precipitate was collected via vacuum filtration affording the desired product.

***t*-Butyl dianiline 6:** Aniline **10**[1,2] (3.88 g, 15.8 mmol) was deprotected according to general procedure A and reacted with 2,6-dibromopyridine (1.62 g, 6.85 mmol), CuI (150 mg, 0.78 mmol), and $Pd(PPh_3)_4$ (250 mg, 0.22 mmol) using general procedure B. The crude product was then dissolved in EtOAc and triturated with hexanes until cloudy. The resulting suspension was cooled in an ice bath for 1 h and the product was filtered and dried to give **6** (2.19 g, 76%) as a yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.39 (m, 4H), 7.21 (dd, *J* = 8.5, 1.8 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 4.31 (s, 4H), 1.28 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.43, 144.10, 140.88, 136.51, 129.47, 128.21, 125.89, 114.54, 106.15, 93.37, 87.61, 34.07, 31.51. UV-vis

(MeCN) λ_{max} 360 nm (17225 $cm^{-1}M^{-1}$). HRMS (EI+) calcd for $C_{29}H_{31}N_3^{\bullet+}$ [$M^{\bullet+}$] 421.2513, found 421.2511.

Ester dianiline 7[3]**:** Benzoate **11** (2.13 g, 11.3 mmol) was deprotected according to general procedure A and reacted with 2,6-dibromopyridine (1.21 g, 5.13 mmol), CuI (150 mg, 0.79 mmol), and $Pd(PPh_3)_4$ (250 mg, 0.22 mmol) using general procedure B. The crude product was then dissolved in EtOAc and triturated with hexanes until cloudy. The resulting suspension was cooled in an ice bath for 1 h and the product was filtered and dried to give **7** (1.50 g, 64%) as a yellow solid: ^1H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.9 Hz, 2H), 7.85 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 4.85 (s, 4H), 4.33 (q, *J* = 7.1 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.09, 152.20, 143.77, 136.77, 135.19, 132.45, 126.36, 119.95, 113.60, 105.66, 93.93, 85.90, 60.71, 14.56. UV-vis (MeCN) λ_{max} 354 nm (23149 $cm^{-1}M^{-1}$). HRMS (EI+) calcd for $C_{27}H_{24}N_3O_4^+$ [MH^+] 454.1761, found 454.1745.

Trifluoromethyl dianiline 8: Aniline **12**[4] (0.631 g, 3.41 mmol) was deprotected according to general procedure A and reacted with 2,6-dibromopyridine (0.337 g, 1.55 mmol), CuI (59 mg, 0.31 mmol), and $Pd(PPh_3)_4$ (179 mg, 0.16 mmol) using general procedure B. The crude product was then dissolved in EtOAc and triturated with hexanes until cloudy. The resulting suspension was cooled in an ice bath for 1 h and the product was filtered and dried to give **8** (0.48 g, 70%) as an off-white solid: ^1H NMR (600 MHz, $CDCl_3$) δ 7.72 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (dd, *J* = 8.5, 1.8 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.78 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.14, 143.59, 136.87, 130.28 (q, *J* = 3.9 Hz), 127.66 (q, *J* = 3.6 Hz), 126.48, 124.38 (d, J = 270.7 Hz), 119.93 (q, J = 33.2 Hz), 114.08, 105.90, 94.29, 85.47. UV-vis (MeCN) λ_{max} 351 nm (23078 $cm^{-1}M^{-1}$). HRMS (EI+) calcd for $C_{23}H_{13}F_6N_3^{\bullet+}$ [$M^{\bullet+}$] 445.1008, found 445.1014.

Methoxy dianiline 9: Aniline **13**[5] (1.46 g, 9.91 mmol) was deprotected according to general procedure A and reacted with 2,6-dibromopyridine (1.118 g, 4.72 mmol), CuI (150 mg, 0.79 mmol), and $Pd(PPh_3)_4$ (250 mg, 0.22 mmol) using general procedure B. The crude product was then dissolved in EtOAc and triturated with hexanes until cloudy. The resulting suspension was cooled in an ice bath for 1 h and the product was filtered and dried to give **9** (1.50 g, 86%) as a light brown solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 2.9 Hz, 2H), 6.81 (dd, J = 8.8, 2.9 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 4.15 (s, 4H), 3.75 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.90, 143.93, 143.13, 136.59, 126.10, 118.88, 116.27, 116.08, 107.08, 93.66, 87.02, 55.97. UV-vis (MeCN) λ_{max} 373 nm (17226 $cm^{-1}M^{-1}$). HRMS (EI+) calcd for $C_{23}H_{19}N_3O_2^{\bullet+}$ [$M^{\bullet+}$] 369.1472, found 369.1477.

Bis-urea 2a: Dianiline **6** (100 mg, 0.238 mmol) and 4-methoxyphenyl isocyanate (88.6 mg, 0.594 mmol) were reacted at 80 °C for 16 h using general procedure C to afford the desired product **2a** (160 mg, 93%) as an yellow solid^{1}H NMR (600 MHz, DMSO-d6) δ 9.27 (s, 2H), 8.22 (s, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.99 (t, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 2.3 Hz, 2H), 7.47 (dd, J = 8.8, 2.3 Hz, 2H), 7.37 (d, J = 9.0 Hz, 4H), 6.87 (d, J = 9.0 Hz, 4H), 3.71 (s, 6H), 1.29 (s, 18H). ^{13}C NMR (151 MHz, DMSO-d6) δ 154.61, 152.36, 144.51, 142.82, 138.46, 137.41, 132.42, 129.02, 127.59, 127.25, 120.16, 119.88, 114.04, 109.99, 93.46, 85.87, 55.14, 33.95, 30.97. UV-vis (MeCN) λ_{max} 336 nm (22541 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{45}H_{46}N_5O_4^+$ [MH^+] 720.3544, found 720.3550.

Bis-urea 2b: Dianiline **6** (100 mg, 0.238 mmol) and 4-nitrophenyl isocyanate (97.5 mg, 0.594 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (166 mg, 93%). ^{1}H NMR (600 MHz, DMSO-d6) δ 10.12 (s, 2H), 8.53 (s, 2H), 8.19 (d, *J* = 9.2 Hz, 4H), 8.02 – 7.96 (m, 3H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 9.2 Hz, 4H), 7.57 (d, *J* = 2.3 Hz, 2H), 7.51 (dd, *J* = 8.8, 2.3 Hz, 2H), 1.30 (s, 18H). ^{13}C NMR (151 MHz, DMSO-d6) δ 151.78, 146.08, 145.58, 142.75, 141.16, 137.49, 129.20, 127.68, 127.38, 125.15, 120.52, 117.56, 111.02, 93.55, 85.67, 34.04, 30.93. UV-vis (MeCN) λ_{max} 337 nm (37271 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{43}H_{40}N_7O_6^+$ [MH^+] 750.3035, found 750.2986.

Bis-urea 2c: Dianiline **6** (800 mg, 1.9 mmol) and phenyl isocyanate (679 mg, 5.7 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (1.15 g, 92%). ^{1}H NMR (600 MHz, DMSO-d6) δ 9.44 (s, 2H), 8.32 (s, 2H), 8.05 – 7.95 (m, 3H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 2.3 Hz, 2H), 7.51 – 7.43 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 4H), 6.99 (t, *J* = 7.6 Hz, 2H), 1.30 (s, 18H). ^{13}C NMR (151 MHz, DMSO-d6) δ 152.22, 144.77, 142.82, 139.46, 138.24, 137.45, 129.07, 128.84, 127.61, 127.30, 122.05, 120.11, 118.29, 110.26, 93.46, 85.85, 33.98, 30.96. UV-vis (MeCN) λ_{max} 334 nm (15310 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{43}H_{42}N_5O_2^+$ [MH^+] 660.3333, found 660.3325.

Bis-urea 2d: Dianiline **6** (75.3 mg, 0.169 mmol) and pentafluorophenyl isocyanate (66 µL, 0.507 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (115 mg, 81%). ^{1}H

NMR (600 MHz, DMSO-d6) δ 9.34 (s, 2H), 8.64 (s, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 1.8 Hz, 2H), 7.49 (dd, *J* = 8.7, 11.8 Hz, 2H), 1.29 (s, 18H). ^{13}C NMR (151 MHz, dmso) δ 151.67, 145.48, 142.78, 143.64 – 141.64 (m), 139.36 – 137.49 (m), 137.67, 137.45, 138.20 – 136.16 (m), 129.17, 127.72, 127.33, 120.07, 113.84 – 113.42 (m), 110.77, 93.52, 85.59, 34.02, 30.92. UV-vis (MeCN) λ_{max} 333 nm (14836 cm^{-1}M^{-1}). HRMS (TOF MS ES+) calcd for $C_{43}H_{32}F_{10}N_5O_2^+$ [MH$^+$] 840.2391, found 840.2435.

Bis-urea 3a: Dianiline **7** (43.3 mg, 0.095 mmol) and 4-methoxyphenyl isocyanate (120 µL, 0.96 mmol) were reacted at 80 °C for 16 h using general procedure C to afford the desired product **3a** (47.5 mg, 57%) as an orange solid. ^{1}H NMR (600 MHz, DMSO-d6) δ 9.56 (s, 2H), 8.57 (s, 2H), 8.36 (d, *J* = 8.9 Hz, 2H), 8.12 (d, *J* = 1.9 Hz, 2H), 8.05 (t, *J* = 7.8 Hz, 1H), 7.98 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 4H), 6.89 (d, *J* = 8.9 Hz, 4H), 4.31 (q, *J* = 7.1 Hz, 4H), 3.72 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 164.58, 154.96, 151.80, 144.88, 142.49, 137.60, 133.93, 131.84, 131.24, 127.90, 123.00, 120.50, 118.61, 114.10, 109.54, 94.51, 84.02, 60.71, 55.15, 14.16. UV-vis (MeCN) λ_{max} 335 nm (13710 cm^{-1}M^{-1}). HRMS (TOF MS ES+) calcd for $C_{43}H_{38}N_5O_8^+$ [MH$^+$] 752.2715, found 752.2681.

Bis-urea 3b: Dianiline **7** (89 mg, 0.196 mmol) and 4-nitrophenyl isocyanate (193 mg, 1.18 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (46.5 mg, 30%). ^{1}H NMR (300 MHz, DMSO-d6) δ 10.37 (s, 2H), 8.84 (s, 2H), 8.34 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 9.1 Hz, 4H), 8.14 (d, *J* = 1.9 Hz, 2H), 8.11 – 7.97 (m, 3H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 9.1 Hz, 4H), 4.32 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d6) δ 164.98, 151.88, 146.05, 144.46, 142.91, 141.97, 138.14, 134.44, 131.77, 128.52, 125.64, 124.37, 119.70, 118.36, 110.90, 95.18, 84.36, 61.32, 14.63. UV-vis (MeCN) λ_{max} 337 nm (53369 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{41}H_{32}N_7O_{10}^+$ [MH^+] 782.2205, found 782.2221.

Bis-urea 3c: Dianiline **7** (44.4 mg, 0.0979 mmol) and phenyl isocyanate (110 µL, 0.979 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (20.7 mg, 26%). ^{1}H NMR (500 MHz, DMSO-d6) δ 9.74 (s, 2H), 8.67 (s, 2H), 8.36 (d, *J* = 8.9 Hz, 2H), 8.13 (d, *J* = 1.9 Hz, 2H), 8.05 (t, *J* = 7.8 Hz, 1H), 7.99 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 4H), 7.31 (t, *J* = 7.7 Hz, 4H), 7.03 (t, *J* = 7.7 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d6) δ 164.57, 151.70, 144.69, 142.49, 138.95, 137.63, 133.96, 131.25, 128.91, 127.96, 123.22, 122.56, 118.83, 118.60, 109.79, 94.54, 84.02, 60.75, 14.16. UV-vis (MeCN) λ_{max} 340 nm (10677 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{41}H_{34}N_5O_6^+$ [MH^+] 692.2504, found 692.2505.

Bis-urea 3d: Dianiline **7** (31.6 mg, 0.0697 mmol) and pentafluorophenyl isocyanate (50 µL, 0.42 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (52 mg, 76%). ^{1}H NMR (600 MHz, DMSO-d6) δ 10.05 (s, 2H), 9.18 (s, 2H), 8.29 (d, *J* = 8.9 Hz, 2H), 8.14 (d, *J* = 1.9 Hz, 2H), 8.08 – 8.01 (m, 3H), 7.99 (dd, *J* = 8.9, 1.9 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 164.50, 151.50, 144.09, 142.41, 137.45, 133.97, 131.27, 128.03, 123.86, 119.00, 110.37, 94.71, 83.78, 60.81, 14.11. UV-vis (MeCN) λ_{max} 323 nm (11895 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{41}H_{24}F_{10}N_5O_6^+$ [MH^+] 872.1561, found 872.1612.

Bis-urea 4a: Dianiline **8** (29.6 mg, 0.067 mmol) and 4-methoxyphenyl isocyanate (90 µL, 0.67 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (9 mg, 16%). ^{1}H NMR (600 MHz, DMSO-d6) δ 9.54 (s, 2H), 8.58 (s, 2H), 8.42 (d, *J* = 8.9 Hz, 2H), 8.06 (t, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 1.5 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.77 (dd, *J* = 8.9, 1.5 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 4H), 6.89 (d, *J* = 9.0 Hz, 4H), 3.72 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 154.97, 151.89, 144.23, 142.39, 137.66, 131.82, 129.77, 128.09, 127.13, 124.77, 122.97, 122.14 (q, *J* = 32.4 Hz), 120.51, 119.35, 114.11, 110.06, 94.91, 83.64, 55.16. UV-vis (MeCN) λ_{max} 332 nm (16404 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{39}H_{28}F_6N_5O_4^+$ [MH^+] 744.2040, found 744.2059.

Bis-urea 4b: Dianiline **8** (102 mg, 0.023 mmol) and 4-nitrophenyl isocyanate (188 mg, 1.14 mmol) were reacted at 70 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (59.3 mg, 34%). ^{1}H NMR (600 MHz, DMSO-d6) δ 10.35 (s, 2H), 8.87 (s, 2H), 8.39 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 9.3 Hz, 4H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.99 (s, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 9.3 Hz, 4H). ^{13}C NMR (151 MHz, DMSO-d6) δ 151.48, 145.52, 143.36, 142.33, 141.54, 137.72, 129.89 (t, *J* = 6.1 Hz), 128.21, 127.24 (t, *J* = 6.6 Hz), 125.15, 124.05 (t, *J* = 407.7 Hz), 123.09 (q, *J* = 32.7 Hz), 120.03, 117.92, 111.04, 95.07, 83.50. UV-vis (MeCN) λ_{max} 330 nm (9749 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{37}H_{22}F_6N_7O_6^+$ [MH^+] 774.1530, found 774.1553.

Bis-urea 4c: Dianiline **8** (22.7 mg, 0.051 mmol) and phenyl isocyanate (60 μL, 0.51 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (14.9 mg, 37%). ^{1}H NMR (300 MHz, DMSO-d6) δ 9.71 (s, 2H), 8.68 (s, 2H), 8.41 (d, *J* = 8.8 Hz, 2H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.94 (m, 4H), 7.79 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 4H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.03 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d6) δ 152.24, 144.51, 142.85, 139.39, 138.12, 130.28 (q, *J* = 3.8 Hz), 129.36, 128.59, 127.61 (q, *J* = 3.2 Hz), 124.30 (q, *J* = 271.1 Hz), 123.01, 122.82 (q, *J* = 32.6 Hz), 120.04, 119.05, 110.78, 95.39, 84.09. UV-vis (MeCN) λ_{max} 329 nm (11661 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{37}H_{24}F_6N_5O_2^+$ [MH^+] 684.1829, found 684.1850.

Bis-urea 4d: Dianiline **8** (24.5 mg, 0.055 mmol) and pentafluorophenyl isocyanate (72 μL, 0.55 mmol) were reacted at 80 °C for 16 h using general procedure C. Purification using general procedure C afforded the desired product (40.3 mg, 75%). ^{1}H NMR (600 MHz, DMSO-d6) δ 9.65 (s, 2H), 9.00 (s, 2H), 8.35 (d, *J* = 8.9 Hz, 2H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 1.6 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.80 (dd, *J* = 8.9, 1.6 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d6) δ 151.41, 143.42, 143.65 – 141.64 (m), 142.34, 139.82 – 137.37 (m), 137.69, 137.23 (dt, *J* = 32.1, 19.1 Hz), 129.97 – 129.74 (m, *J* = 3.8 Hz), 128.14, 127.45 – 127.21 (m, *J* = 3.5 Hz), 123.74 (q, *J* = 271.2 Hz), 123.08 (q, *J* = 33.6 Hz), 119.61, 113.12 (t, *J* = 13.8 Hz), 110.85, 95.05, 83.40. UV-vis (MeCN) λ_{max} 331 nm (9291 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{37}H_{14}F_{16}N_5O_2^+$ [MH^+] 864.0887, found 864.0952.

Bis-urea 5a: Dianiline **9** (116 mg, 0.314 mmol) and 4-methoxyphenyl isocyanate (121 μL, 0.94 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (133 g, 64%). ^{1}H NMR (300 MHz, DMSO-d6) δ 9.17 (s, 2H), 8.15 (s, 2H), 8.04 – 7.95 (m, 1H), 7.92 (d, *J* = 9.1 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 4H), 7.13 (d, *J* = 3.0 Hz, 2H), 7.04 (dd, *J* = 9.1, 3.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 4H), 3.77 (s, 6H), 3.71 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 154.55, 154.18, 152.62, 142.70, 137.48, 134.32, 132.55, 127.42, 122.40, 120.14, 117.18, 116.19, 114.03, 112.03, 93.47, 85.47, 55.46, 55.14. UV-vis (MeCN) λ_{max} 342 nm (10529 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{39}H_{34}N_5O_6^+$ [MH^+] 668.2504, found 668.2509.

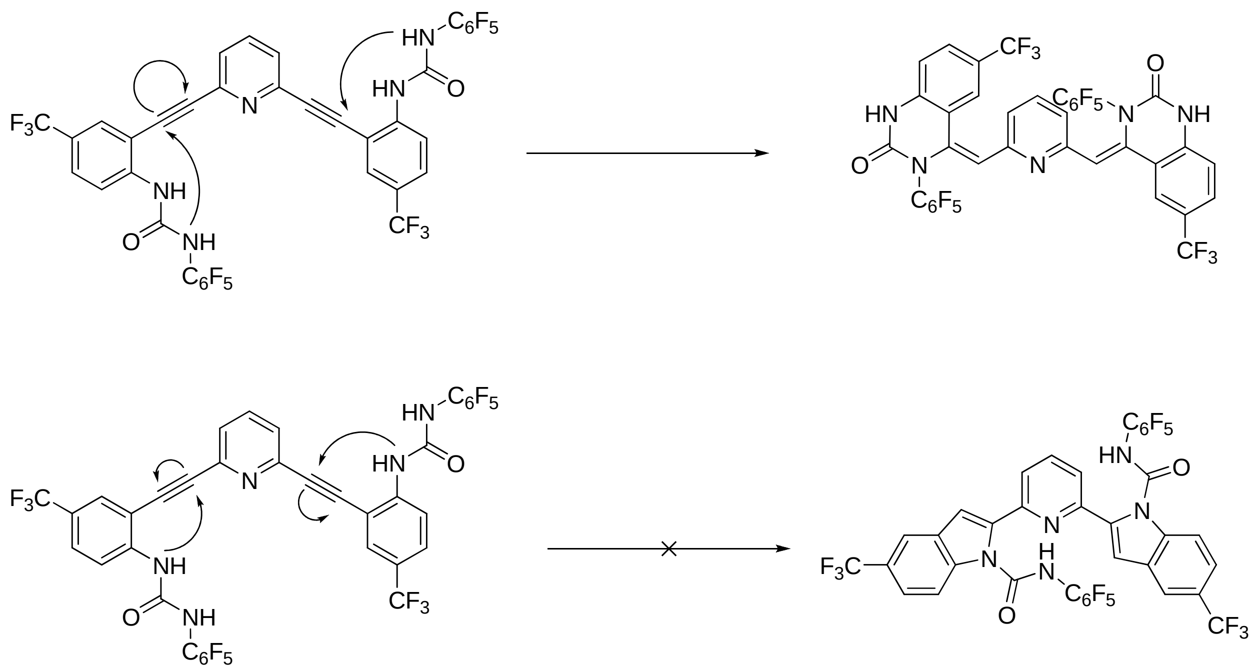
Bis-urea 5b: Dianiline **9** (214 mg, 0.58 mmol) and 4-nitrophenyl isocyanate (285 mg, 1.74 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (0.346 g, 86%). ^{1}H NMR (300 MHz, DMSO-d6) δ 10.02 (s, 2H), 8.49 (s, 2H), 8.19 (d, *J* = 9.3 Hz, 4H), 7.99 (t, *J* = 7.8 Hz 1H), 7.88 (d, *J* = 9.1 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 9.3 Hz, 4H), 7.16 (d, *J* = 3.0 Hz, 2H), 7.08 (dd, *J* = 9.1, 3.0 Hz, 2H), 3.79 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 154.95, 152.03, 146.23, 142.63, 141.08, 137.58, 133.20, 127.51, 125.16, 123.21, 117.51, 117.11, 116.47, 113.33, 93.49, 85.32, 55.52. UV-vis (MeCN) λ_{max} 341 nm (29956 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{37}H_{28}N_7O_8^+$ [MH^+] 698.1994, found 698.2028.

Bis-urea 5c: Dianiline **9** (36.3 mg, 0.098 mmol) and phenyl isocyanate (110 µL, 0.983 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (44.1 mg, 62%). ^{1}H NMR (600 MHz, DMSO-d6) δ 9.30 (s, 2H), 8.24 (s, 2H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 9.1 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 4H), 7.28 (t, *J* = 7.5 Hz, 4H), 7.14 (d, *J* =

3.0 Hz, 2H), 7.05 (dd, *J* = 9.1, 3.0 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 2H), 3.78 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 154.36, 152.46, 142.70, 139.58, 137.50, 134.06, 128.81, 127.45, 122.65, 121.93, 118.25, 117.17, 116.24, 112.34, 93.45, 85.45, 55.47. UV-vis (MeCN) λ_{max} 339 nm (7270 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{37}H_{30}N_5O_4^+$ [MH^+] 608.2292, found 608.2294.

Bis-urea 5d: Dianiline **9** (37 mg, 0.100 mmol) and pentafluorophenyl isocyanate (40 µL, 0.300 mmol) were reacted at rt for 16 h using general procedure C. Purification using general procedure C afforded the desired product (55.7 mg, 71%). ^{1}H NMR (600 MHz, DMSO-d6) δ 9.17 (s, 2H), 8.56 (s, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 2.6 Hz, 2H), 7.05 (dd, *J* = 9.1, 2.6 Hz, 2H), 3.78 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 155.30, 152.36, 144.32–141.92 (m), 143.12, 139.90–137.47 (m), 137.95, 138.72–136.48 (m), 133.88, 127.90, 123.19, 117.57, 116.88, 114.25 (t, *J* = 15.8 Hz), 113.53, 93.93, 85.67, 55.94. UV-vis (MeCN) λ_{max} 342 nm (7945 $cm^{-1}M^{-1}$). HRMS (TOF MS ES+) calcd for $C_{37}H_{20}F_{10}N_5O_4^+$ [MH^+] 788.1350, found 788.1398

Discussion of 2-quinazolinone side-product:



SCHEME S1. Observed 6-*exo*-dig cyclization pathway (top); typical but unobserved 5-*endo*-dig cyclization pathway (bottom).

While attempting to synthesize **4d** a small amount of an unexpected 2-quinazolinone was isolated and its crystal structure was solved. To our knowledge this is the first reported example of a 2-quinazolinone resulting from a 6-*exo*-dig cyclization pathway with an internal alkyne (Scheme S1) as typically a 5-*endo*-dig cyclization occurs. Additionally, the x-ray crystal structure shows that one of the resulting alkenes is in the *E* conformation, which the other is in a *Z* conformation, resulting in an unusual twisted structure (Figure S1). CCDC-844849 contains the supplementary crystallographic data for this molecule, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

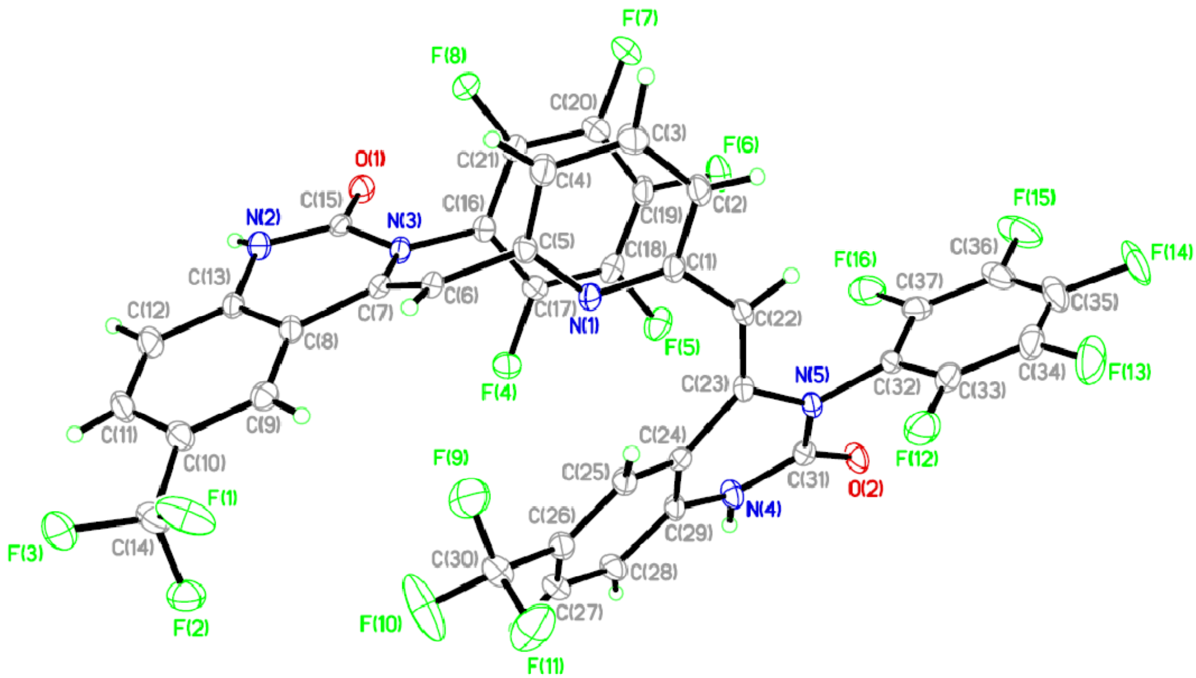
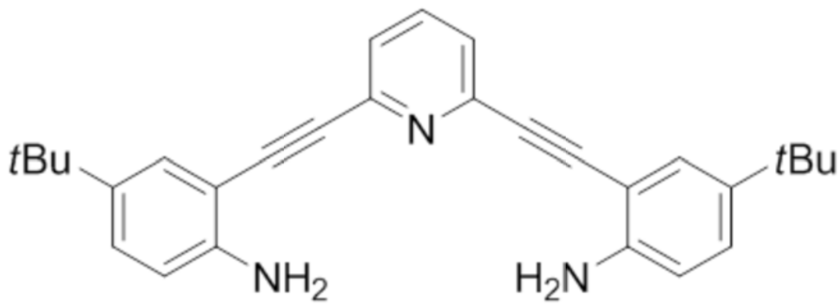


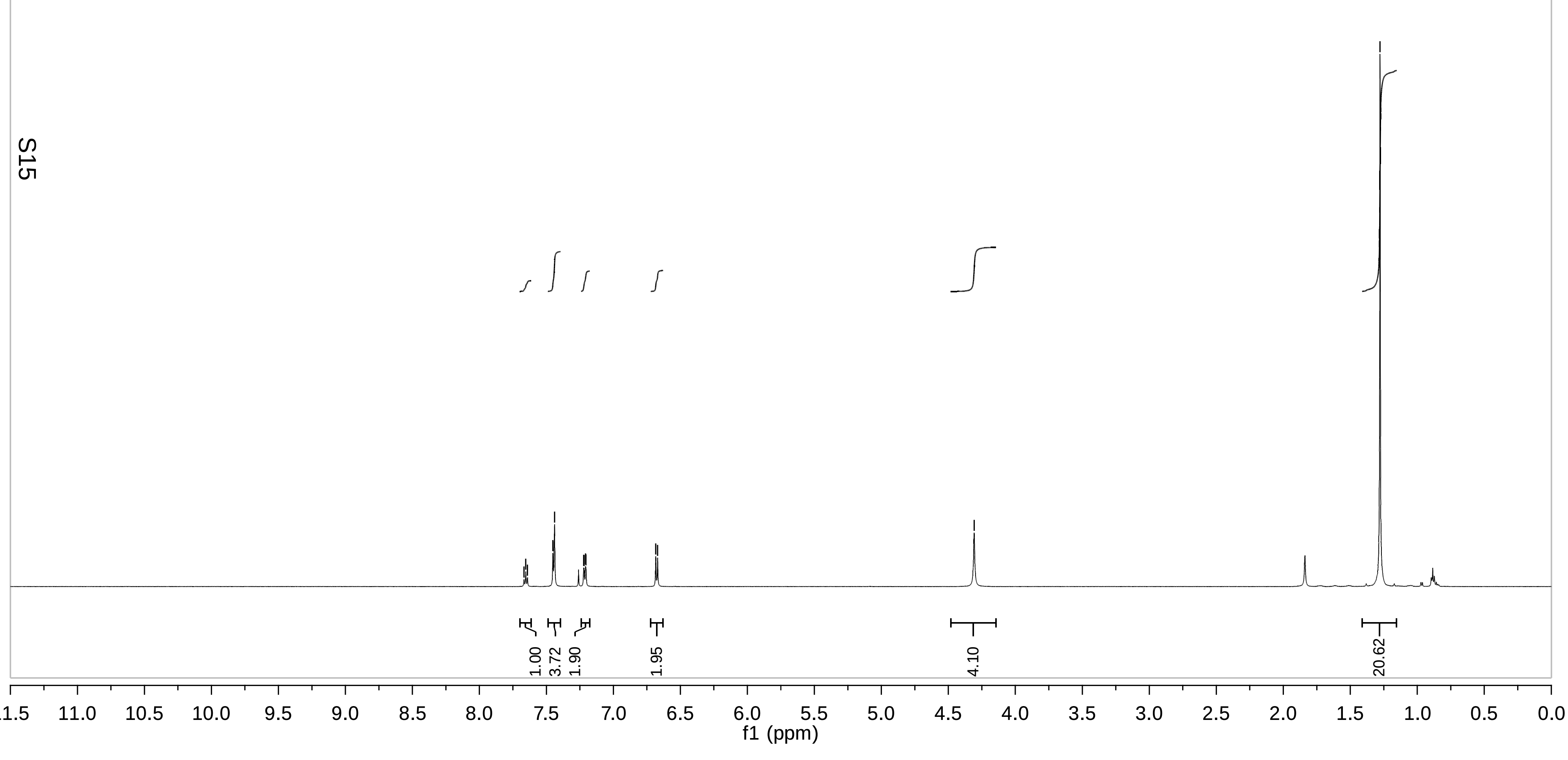
FIGURE S1. 2-Quinazolinone side product formed while attempting to synthesize **4d**.

1. C. N. Carroll, B. A. Coombs, S. P. McClintock, C. A. Johnson II, O. B. Berryman, D. W. Johnson, and M. M. Haley, *Chem. Commun.*, 2011, **47**, 5539.
2. C. N. Carroll, O. B. Berryman, C. A. Johnson II, L. N. Zakharov, M. M. Haley, and D. W. Johnson, *Chem. Commun.*, 2009, **18**, 2520.
3. A. Isobe, J. Takagi, T. Katagiri, and K. Uneyama, *Org. Lett.*, 2008, **10**, 2657.
4. Y. Ohta, H. Chiba, S. Oishi, N. Fujii, and H. Ohno, *J. Org. Chem.*, 2009, **74**, 7052.
5. D. B. Kimball, T. J. R. Weakley, and M. M. Haley, *J. Org. Chem.*, 2002, **67**, 6395.

Compound 6

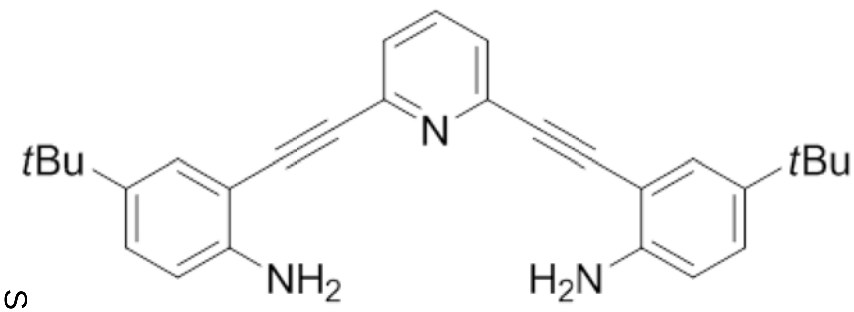
[1]H NMR (600 MHz, $CDCl_3$) δ 7.65 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.39 (m, 4H), 7.21 (dd, *J* = 8.5, 1.8 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 4.31 (s, 4H), 1.28 (s, 18H).

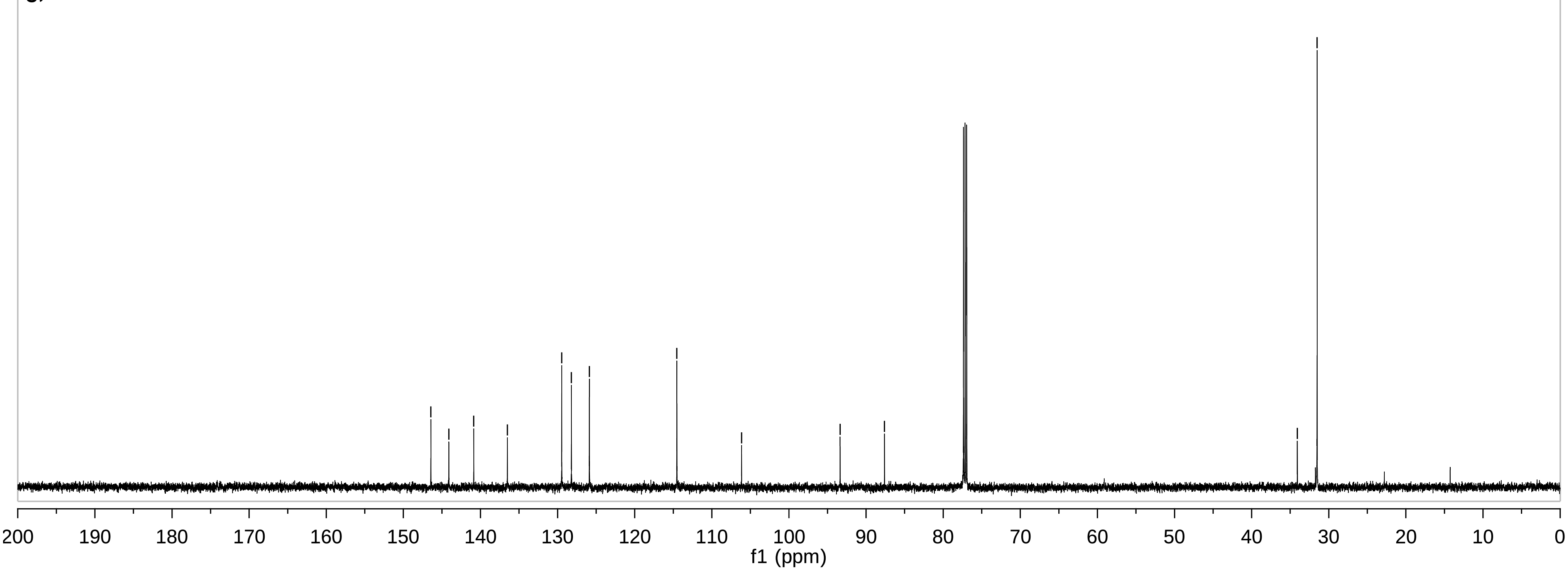




Compound 6

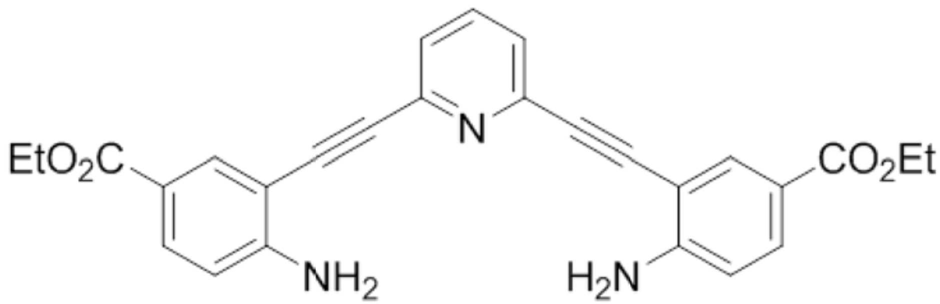
^{13}C NMR (151 MHz, $CDCl_3$) δ 146.43, 144.10, 140.88, 136.51, 129.47, 128.21, 125.89, 114.54, 106.15, 93.37, 87.61, 34.07, 31.51.

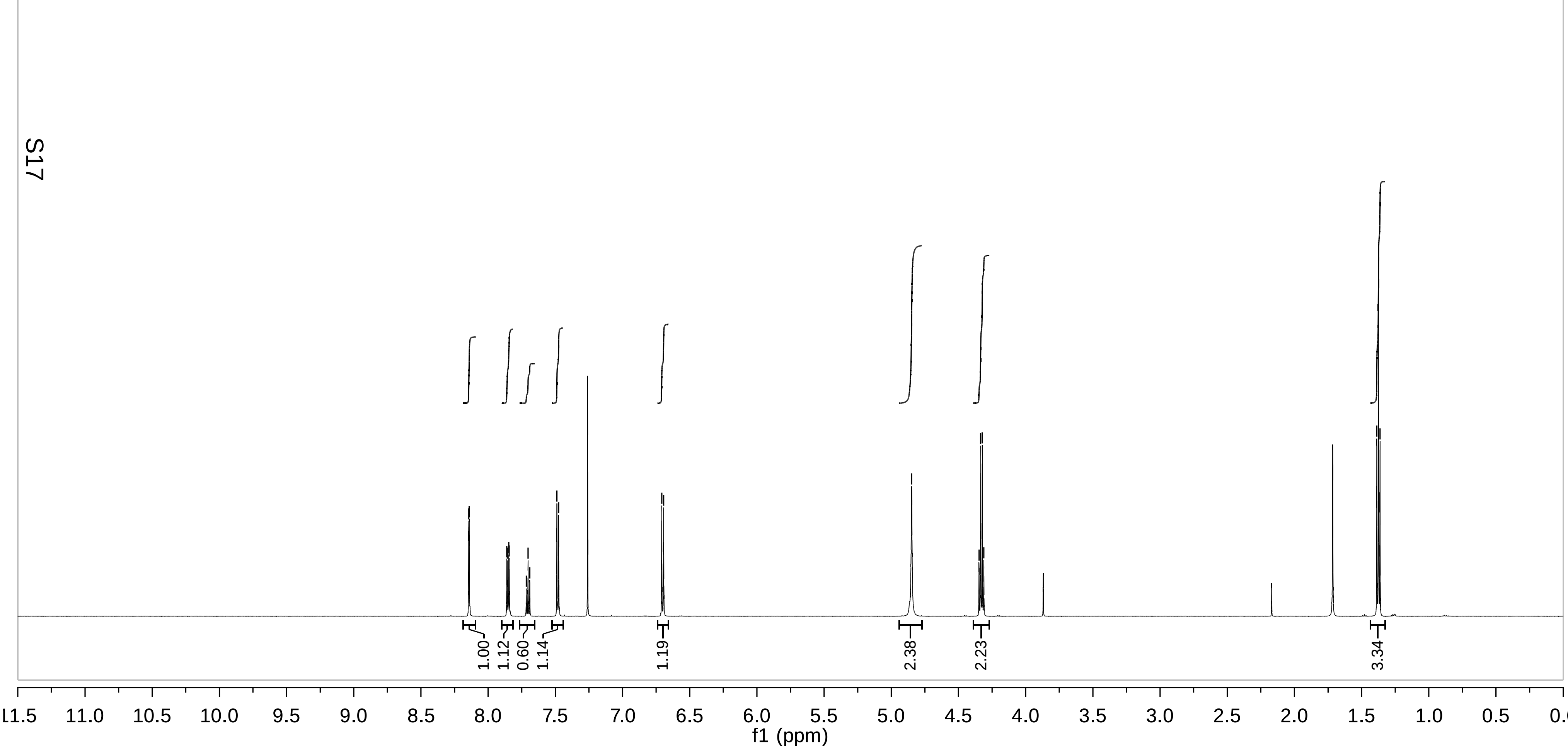




Compound 7

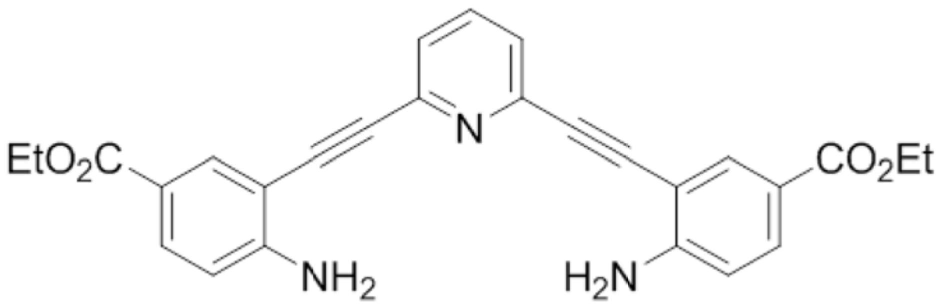
[1]H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.9 Hz, 2H), 7.85 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 6.70 (d, *J* = 8.6 Hz, 2H), 4.85 (s, 4H), 4.33 (q, *J* = 7.1 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 6H).

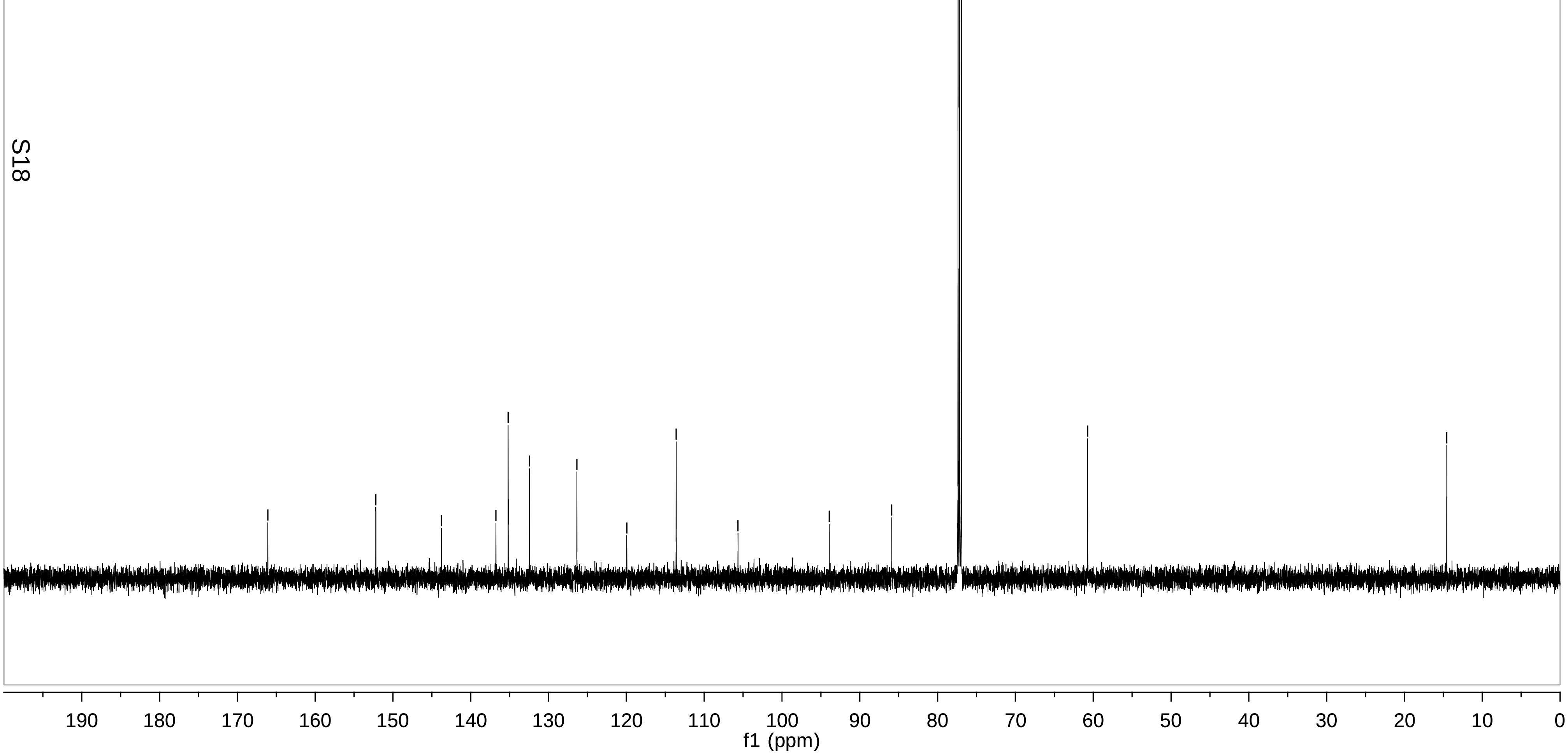




Compound 7

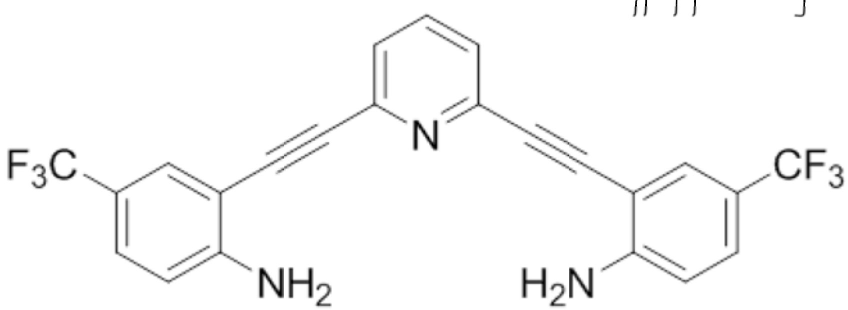
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.09, 152.20, 143.77, 136.77, 135.19, 132.45, 126.36, 119.95, 113.60, 105.66, 93.93, 85.90, 60.71, 14.56.

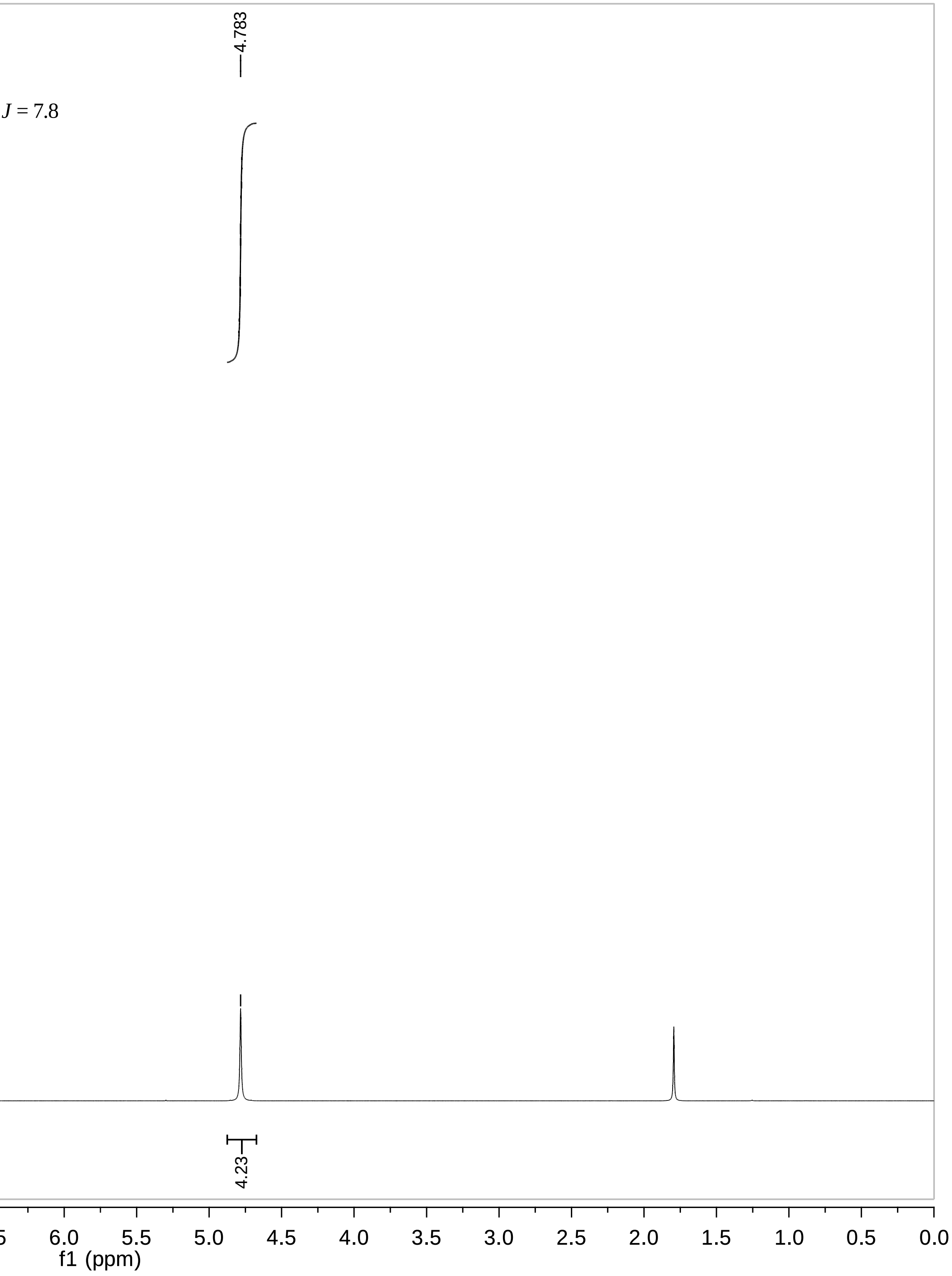




Compound 8

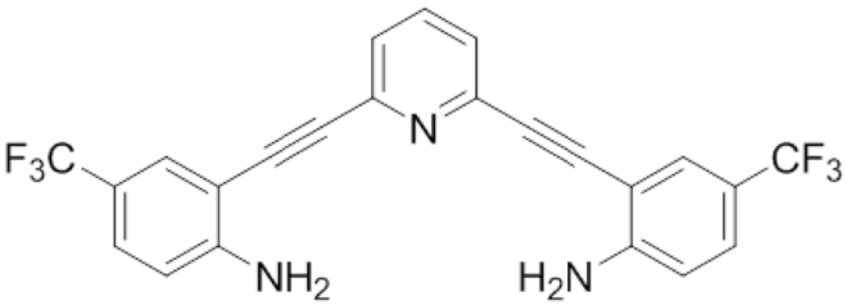
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (dd, *J* = 8.6, 1.8 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 4.78 (s, 4H).

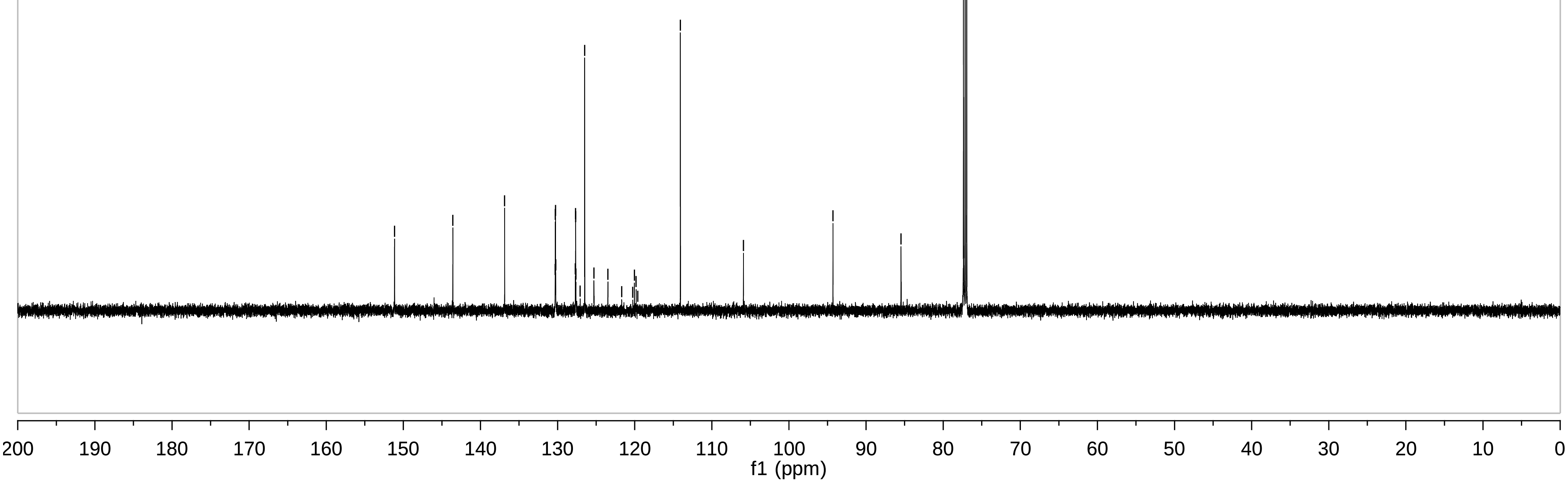




Compound 8

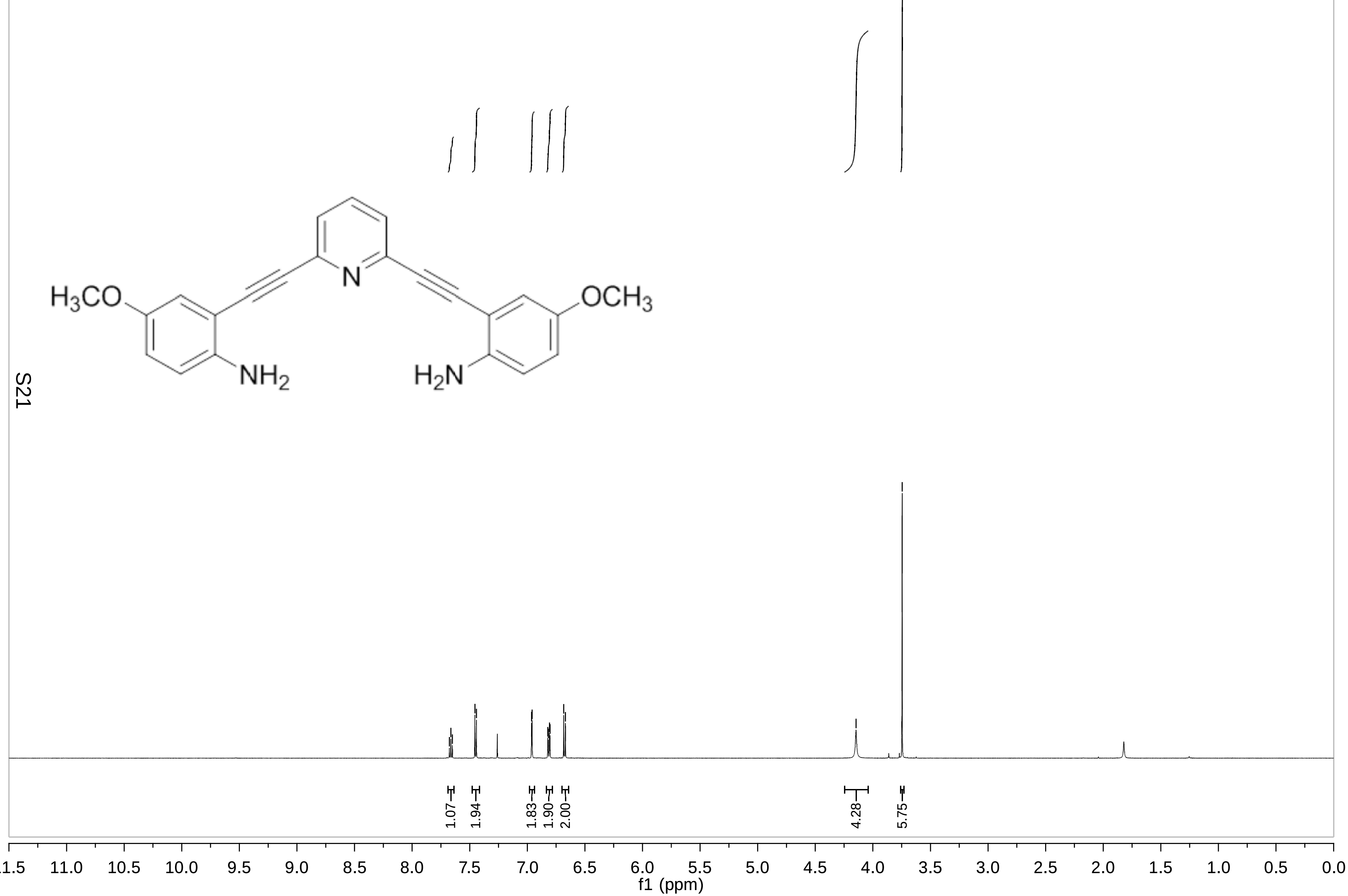
^{13}C NMR (151 MHz, CDCl$_3$) δ 151.14, 143.59, 136.87, 130.28 (q, *J* = 3.9 Hz), 127.66 (q, *J* = 3.6 Hz), 126.48, 124.38 (q, *J* = 270.8 Hz), 119.93 (q, *J* = 33.2 Hz), 114.08, 105.90, 94.29, 85.47.





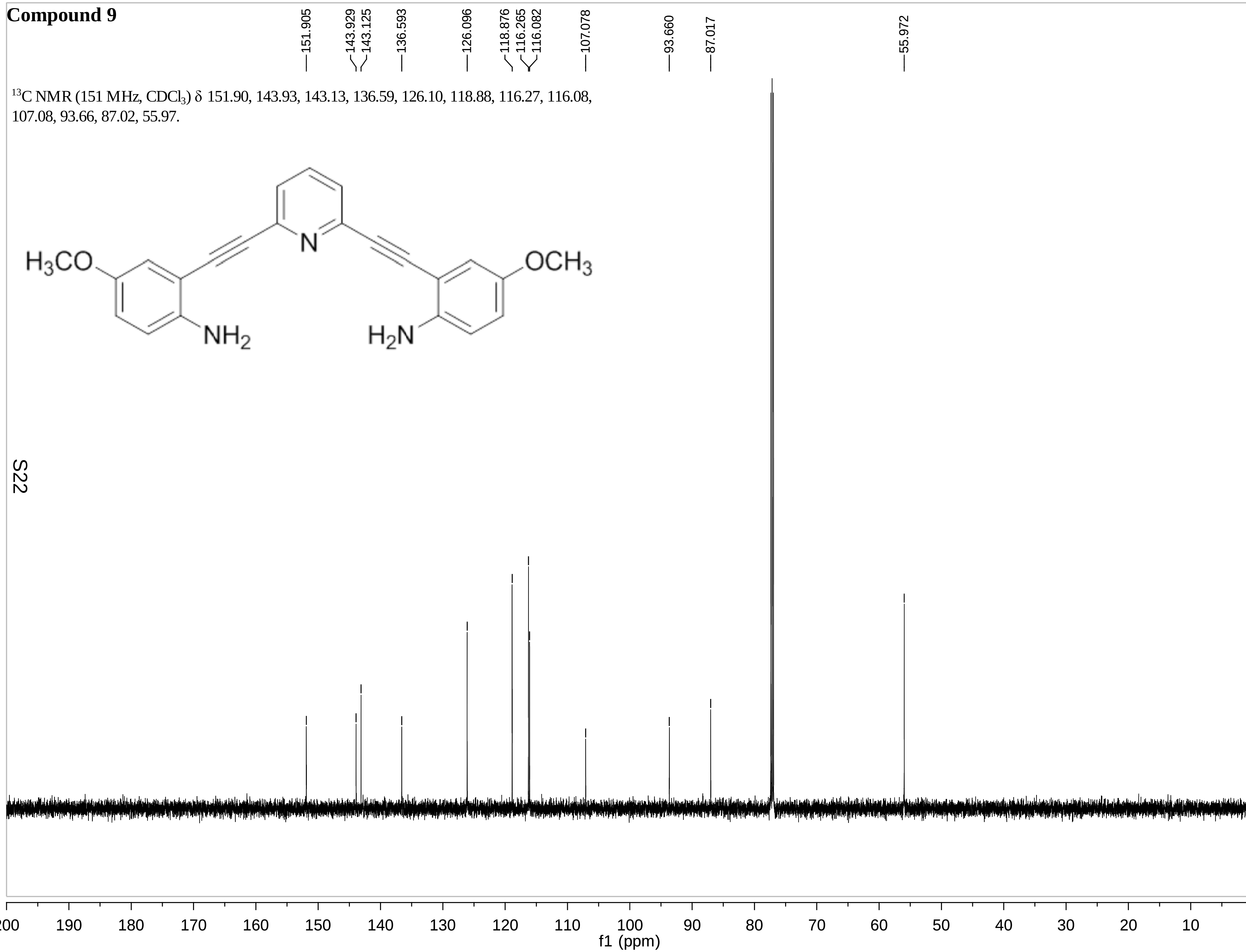
Compound 9

[1]H NMR (600 MHz, $CDCl_3$) δ 7.66 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 2.9 Hz, 2H), 6.81 (dd, J = 8.8, 2.9 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 4.15 (s, 4H), 3.75 (s, 6H).



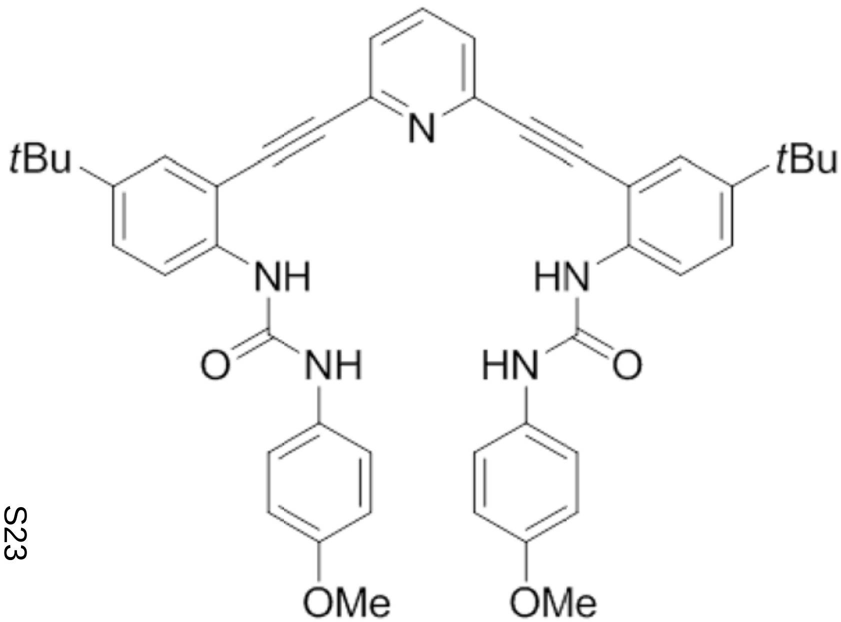
Compound 9

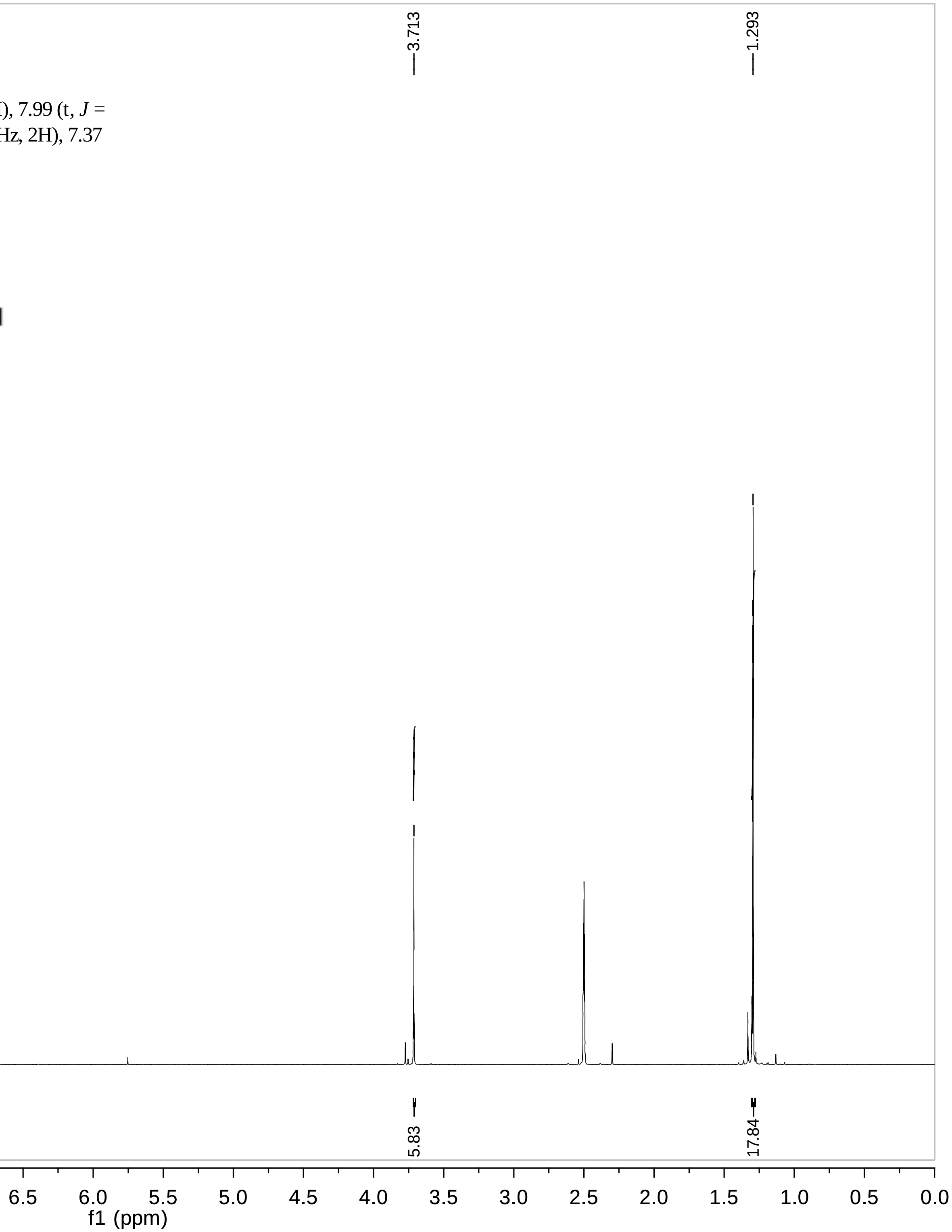
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.90, 143.93, 143.13, 136.59, 126.10, 118.88, 116.27, 116.08, 107.08, 93.66, 87.02, 55.97.



Compound 2a

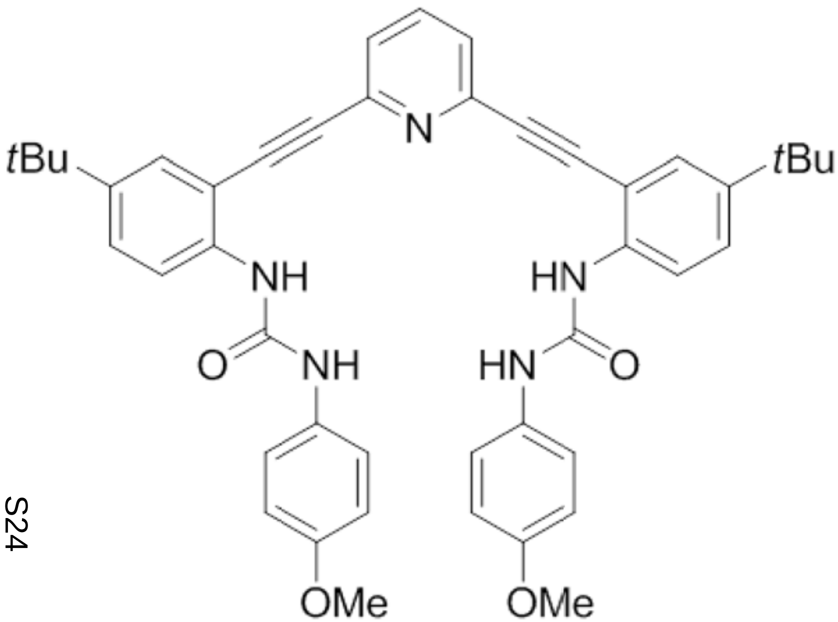
[1]H NMR (600 MHz, DMSO-d6) δ 9.27 (s, 2H), 8.22 (s, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.99 (t, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 2.3 Hz, 2H), 7.47 (dd, J = 8.8, 2.3 Hz, 2H), 7.37 (d, J = 9.0 Hz, 4H), 6.87 (d, J = 9.0 Hz, 4H), 3.71 (s, 6H), 1.29 (s, 18H).

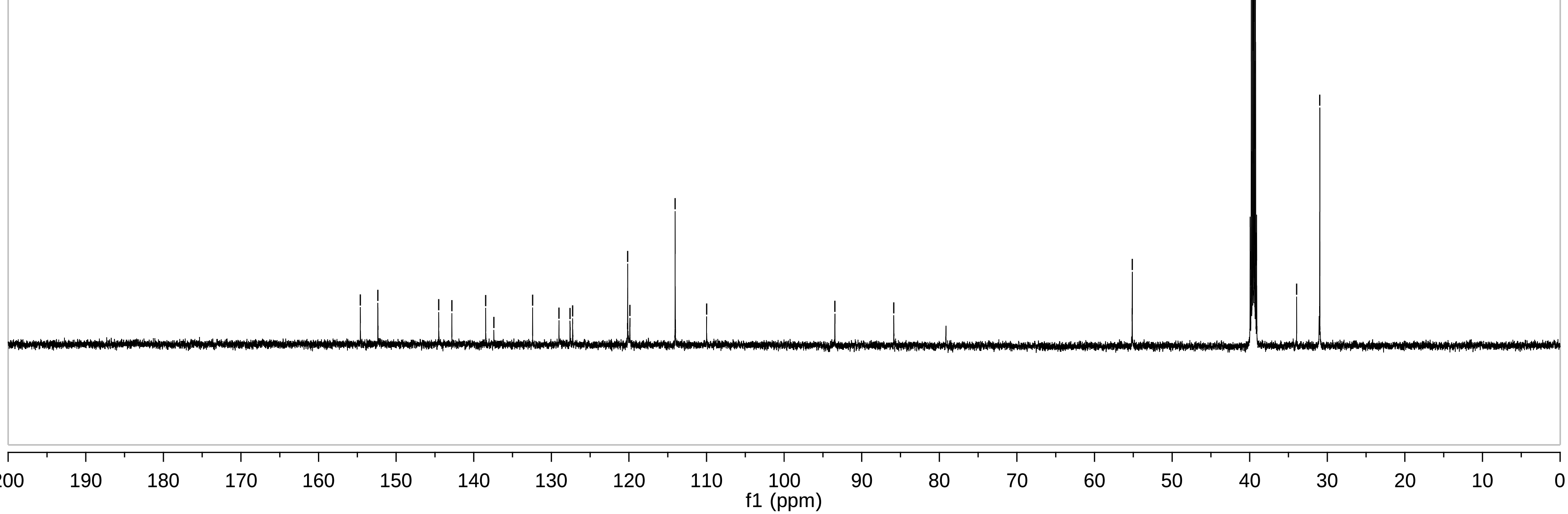




Compound 2a

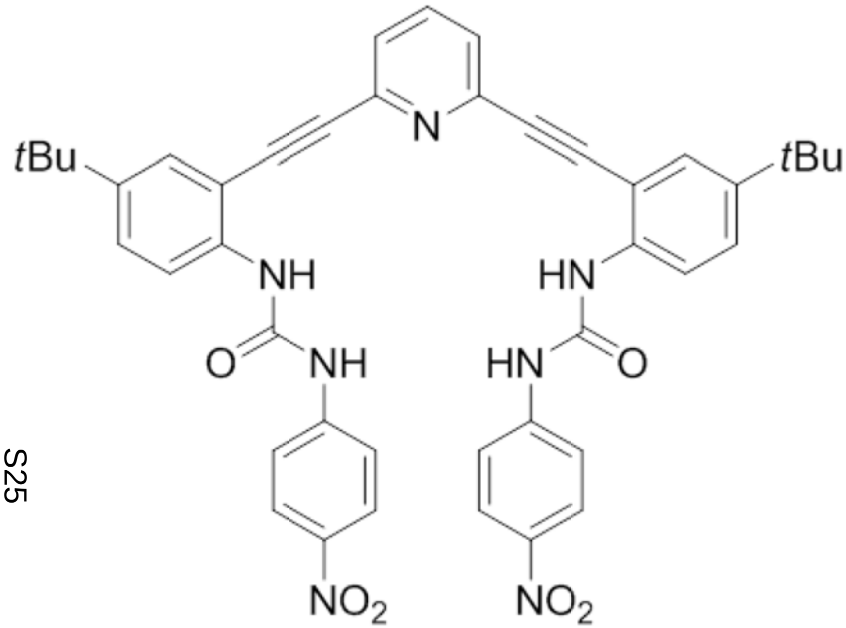
^{13}C NMR (151 MHz, DMSO-d6) δ 154.61, 152.36, 144.51, 142.82, 138.46, 137.41, 132.42, 129.02, 127.59, 127.25, 120.16, 119.88, 114.04, 109.99, 93.46, 85.87, 55.14, 33.95, 30.97.

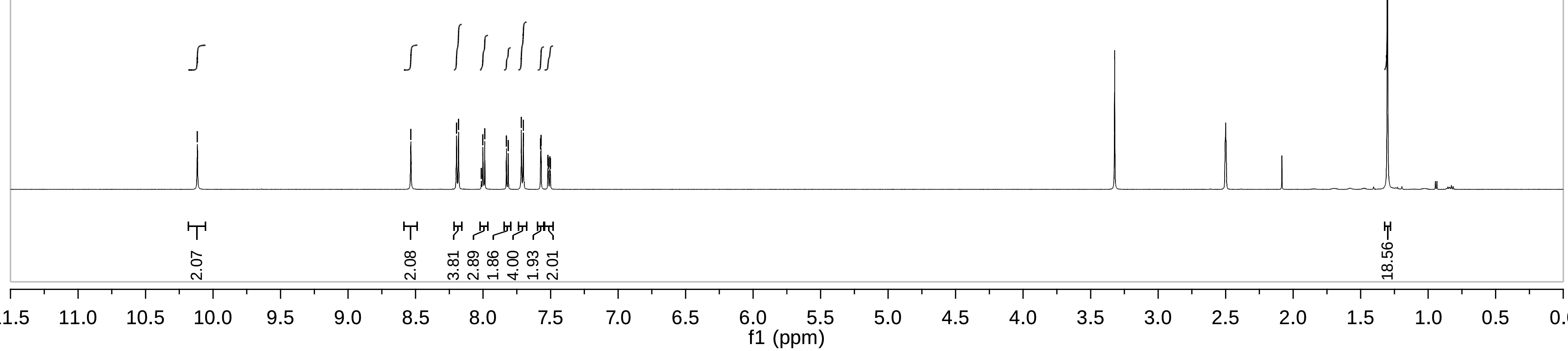




Compound 2b

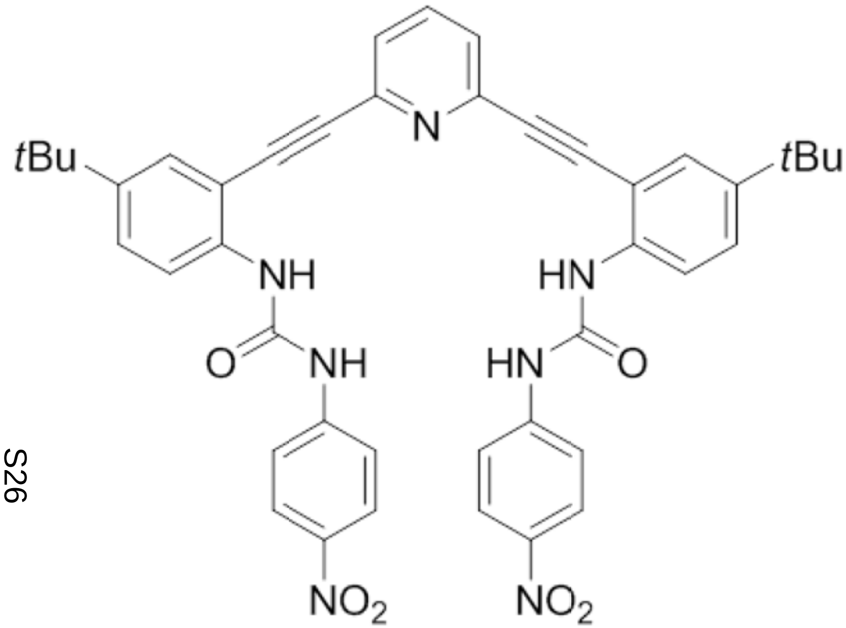
[1]H NMR (600 MHz, DMSO-d6) δ 10.12 (s, 2H), 8.53 (s, 2H), 8.19 (d, *J* = 9.2 Hz, 4H), 8.02 – 7.96 (m, 3H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 9.2 Hz, 4H), 7.57 (d, *J* = 2.3 Hz, 2H), 7.51 (dd, *J* = 8.8, 2.3 Hz, 2H), 1.30 (s, 18H).

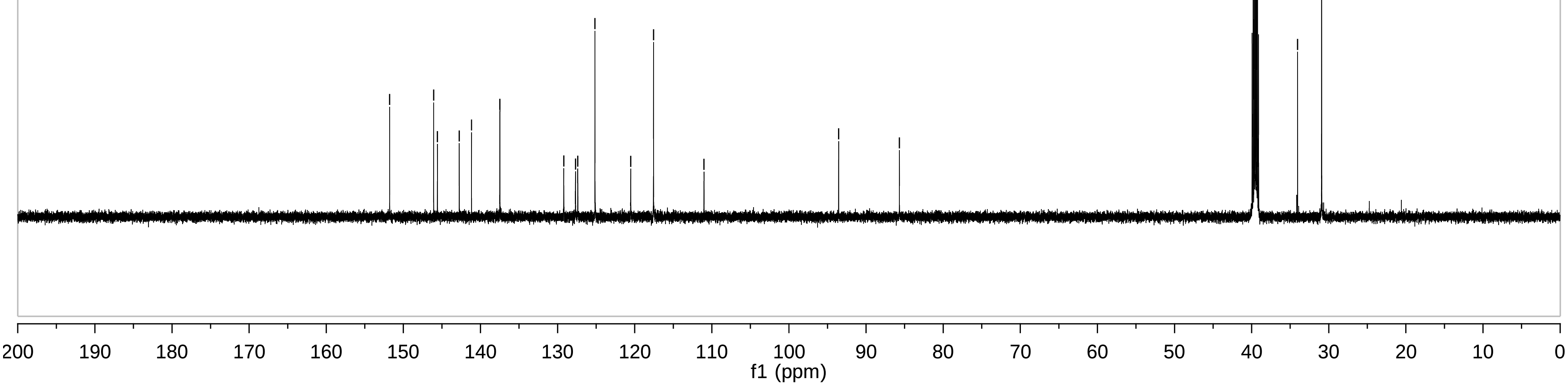




Compound 2b

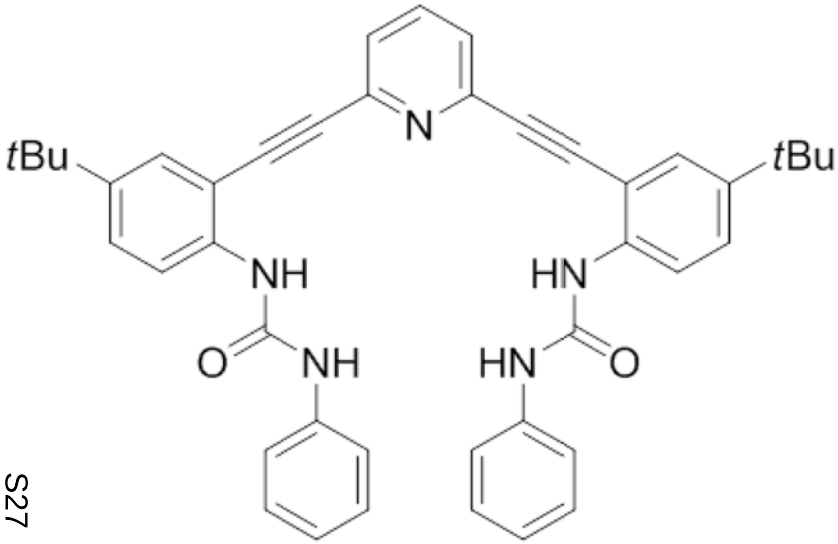
^{13}C NMR (151 MHz, DMSO-d6) δ 151.78, 146.08, 145.58, 142.75, 141.16, 137.49, 129.20, 127.68, 127.38, 125.15, 120.52, 117.56, 111.02, 93.55, 85.67, 34.04, 30.93.

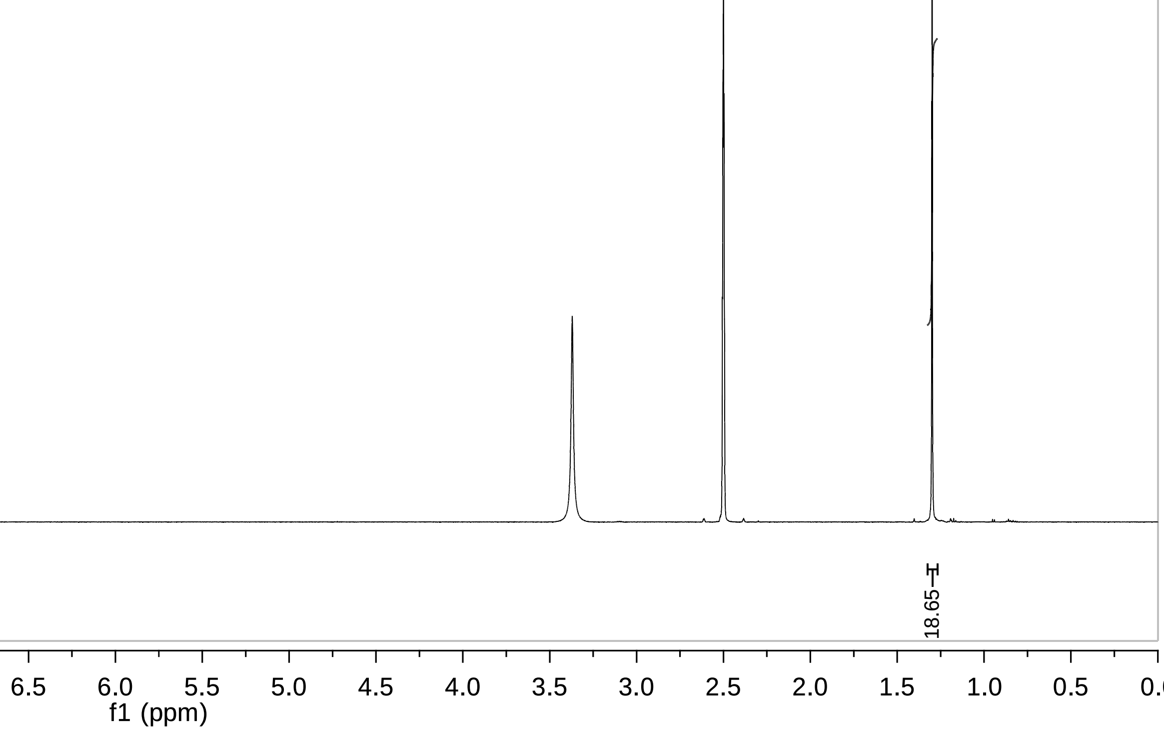




Compound 2c

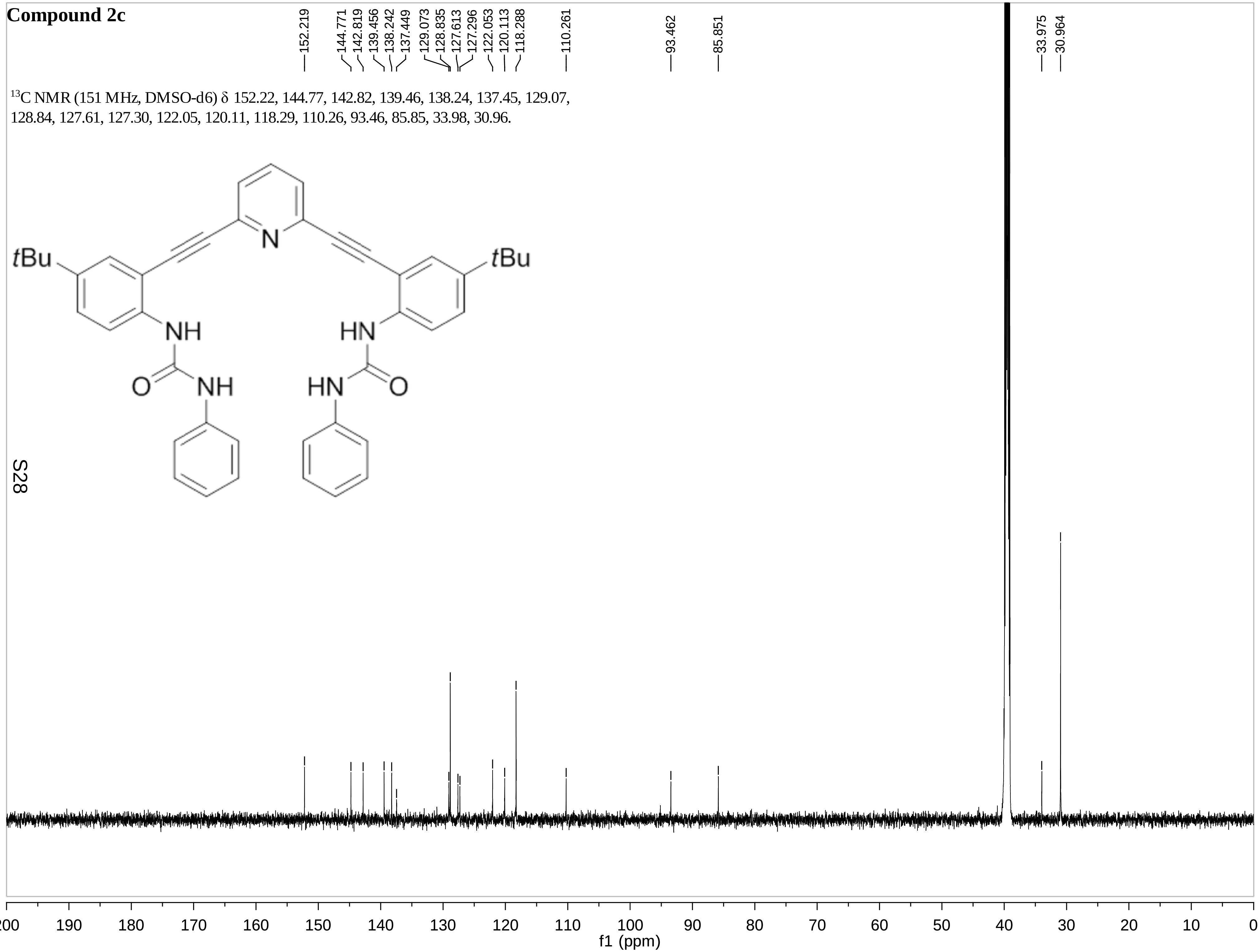
[1]H NMR (600 MHz, DMSO-d6) δ 9.44 (s, 2H), 8.32 (s, 2H), 8.05 – 7.95 (m, 3H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 2.3 Hz, 2H), 7.51 – 7.43 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 4H), 6.99 (t, *J* = 7.6 Hz, 2H), 1.30 (s, 18H).





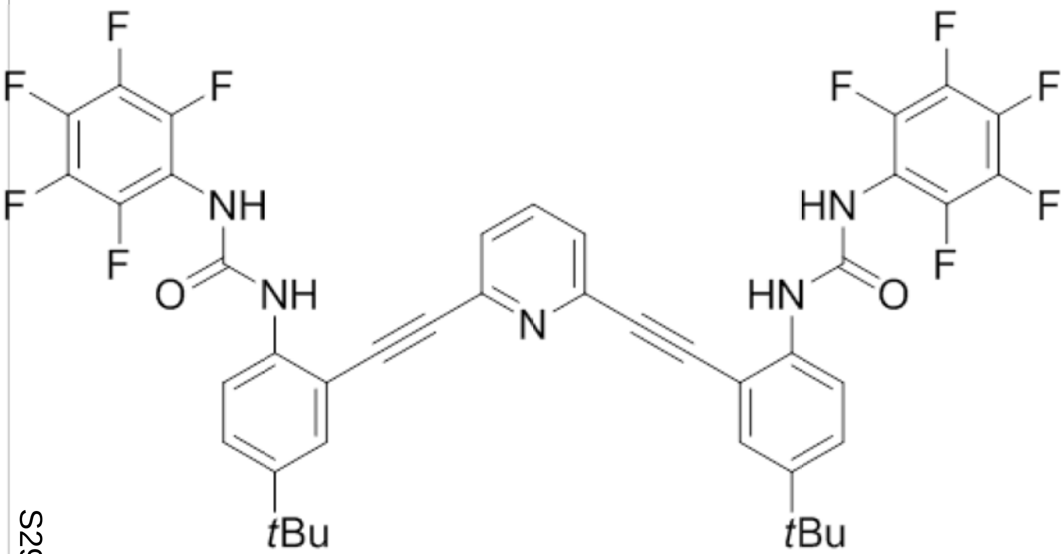
Compound 2c

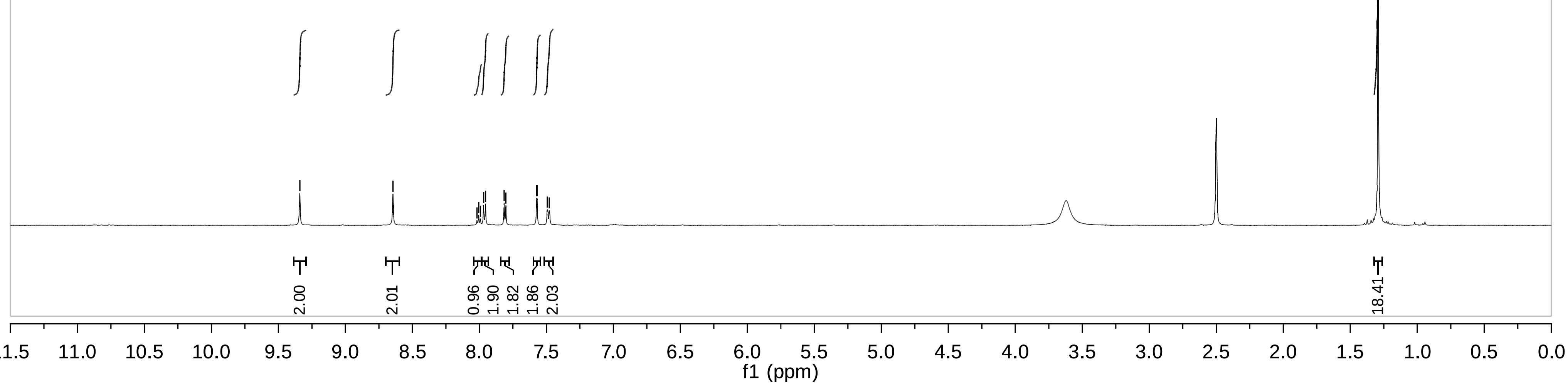
^{13}C NMR (151 MHz, DMSO-d6) δ 152.22, 144.77, 142.82, 139.46, 138.24, 137.45, 129.07, 128.84, 127.61, 127.30, 122.05, 120.11, 118.29, 110.26, 93.46, 85.85, 33.98, 30.96.



Compound 2d

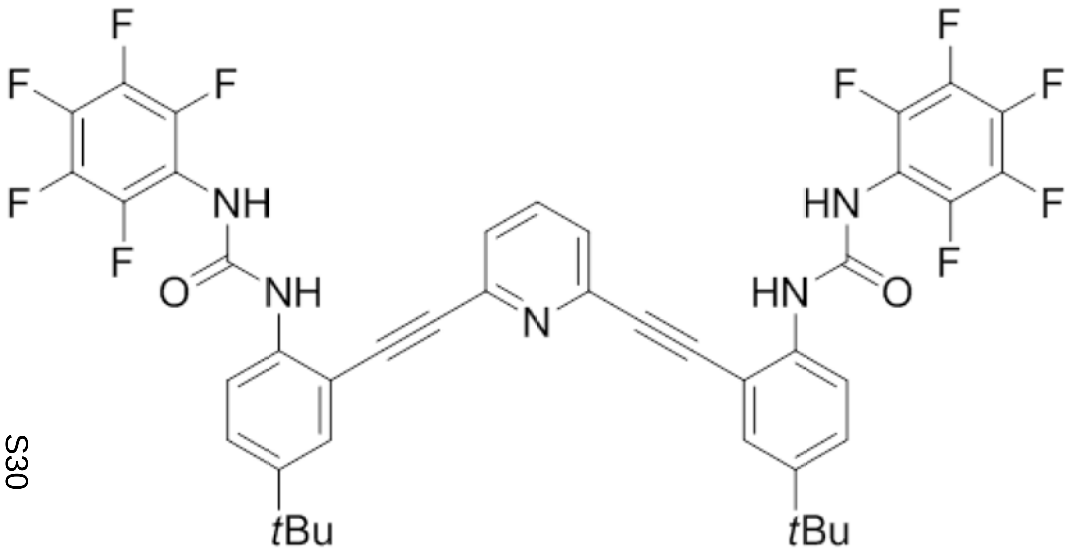
[1]H NMR (600 MHz, DMSO-d6) δ 9.34 (s, 2H), 8.64 (s, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 1.8 Hz, 2H), 7.49 (dd, *J* = 8.7, 11.8 Hz, 2H), 1.29 (s, 18H).

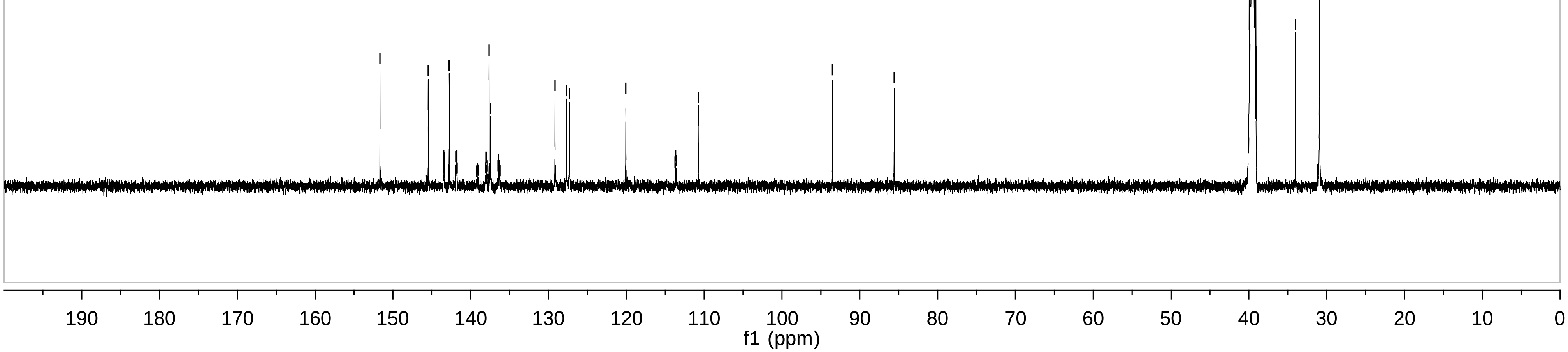




Compound 2d

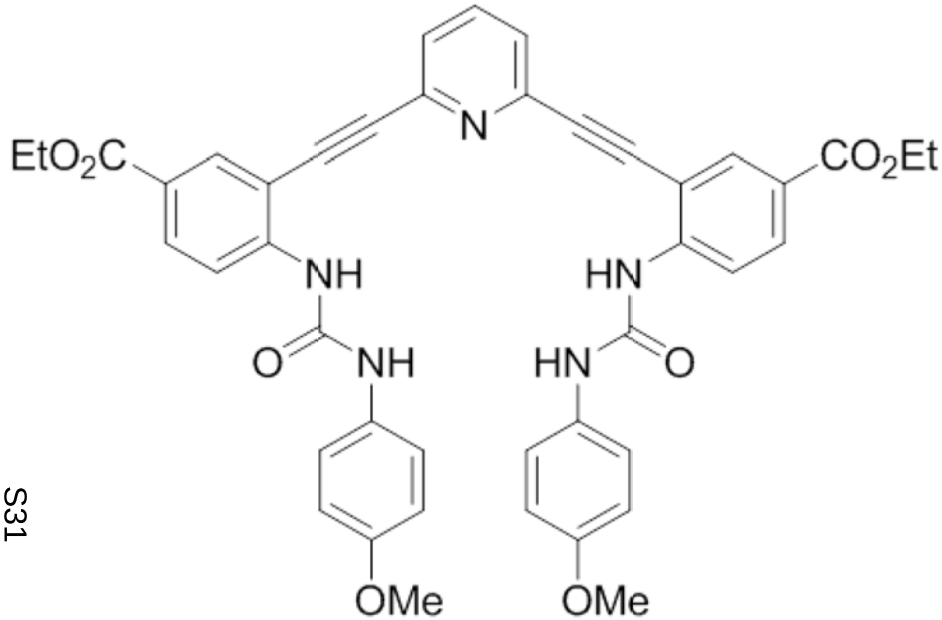
^{13}C NMR (151 MHz, DMSO-d6) δ 151.67, 145.48, 142.78, 143.64 – 141.64 (m), 139.36 – 137.49 (m), 137.67, 137.45, 138.20 – 136.16 (m), 129.17, 127.72, 127.33, 120.07, 113.84 – 113.42 (m), 110.77, 93.52, 85.59, 34.02, 30.92.

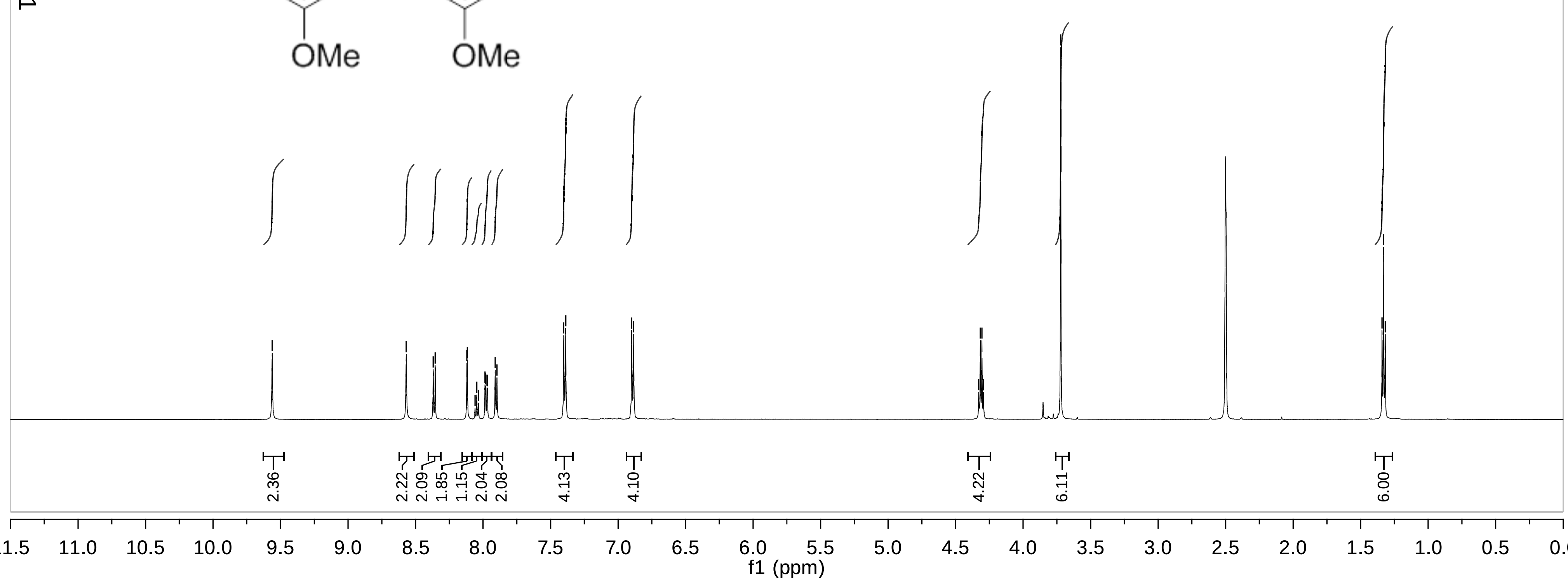




Compound 3a

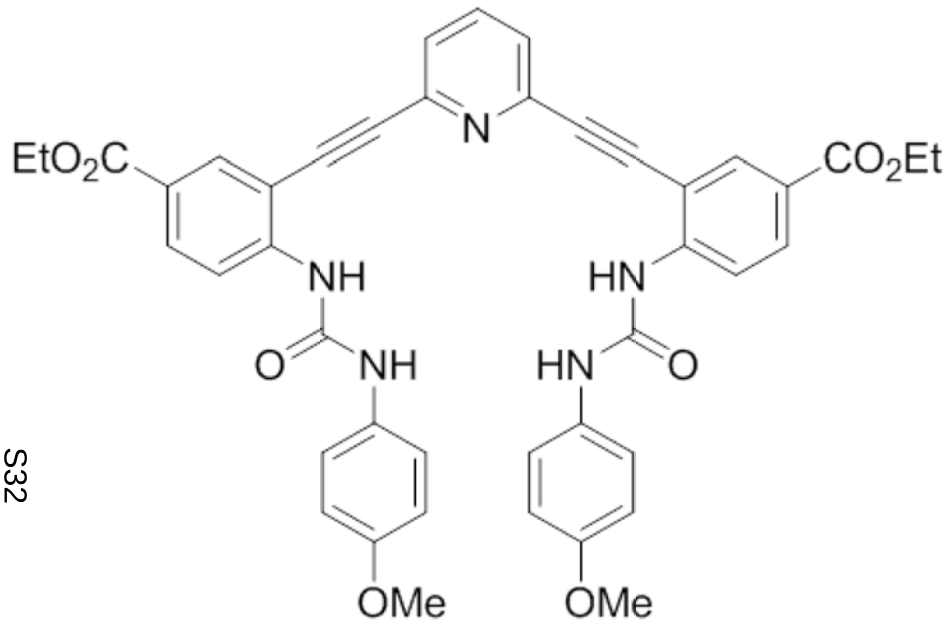
[1]H NMR (600 MHz, DMSO-d6) δ 9.56 (s, 2H), 8.57 (s, 2H), 8.36 (d, *J* = 8.9 Hz, 2H), 8.12 (d, *J* = 1.9 Hz, 2H), 8.05 (t, *J* = 7.8 Hz, 1H), 7.98 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 4H), 6.89 (d, *J* = 8.9 Hz, 4H), 4.31 (q, *J* = 7.1 Hz, 4H), 3.72 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 6H).

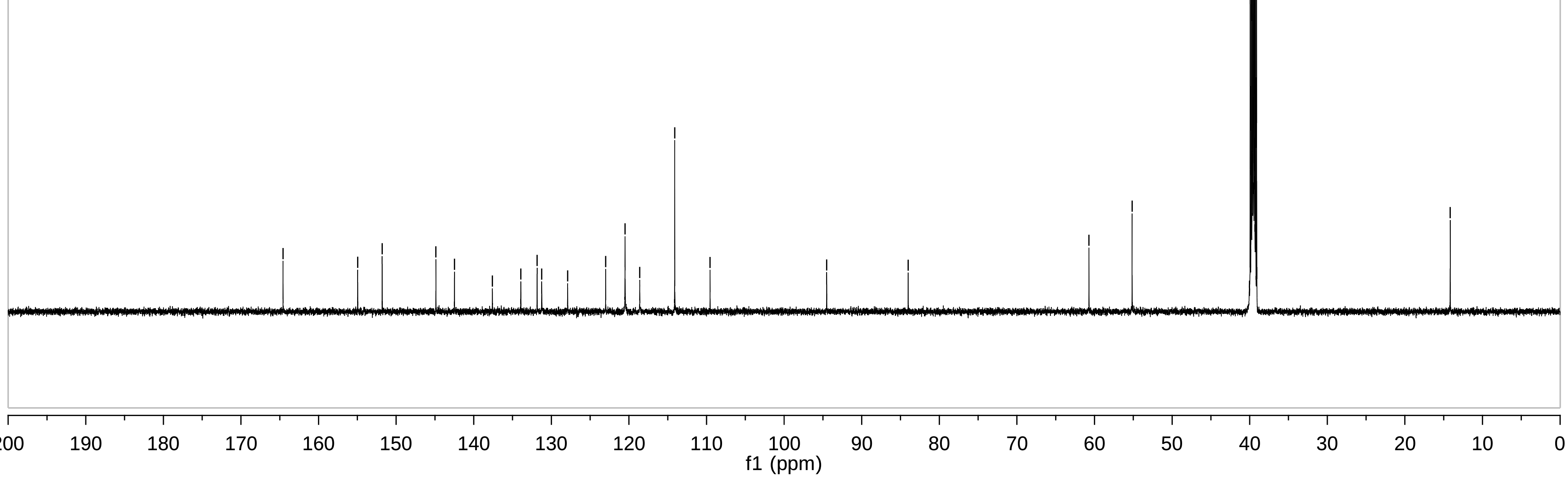




Compound 3a

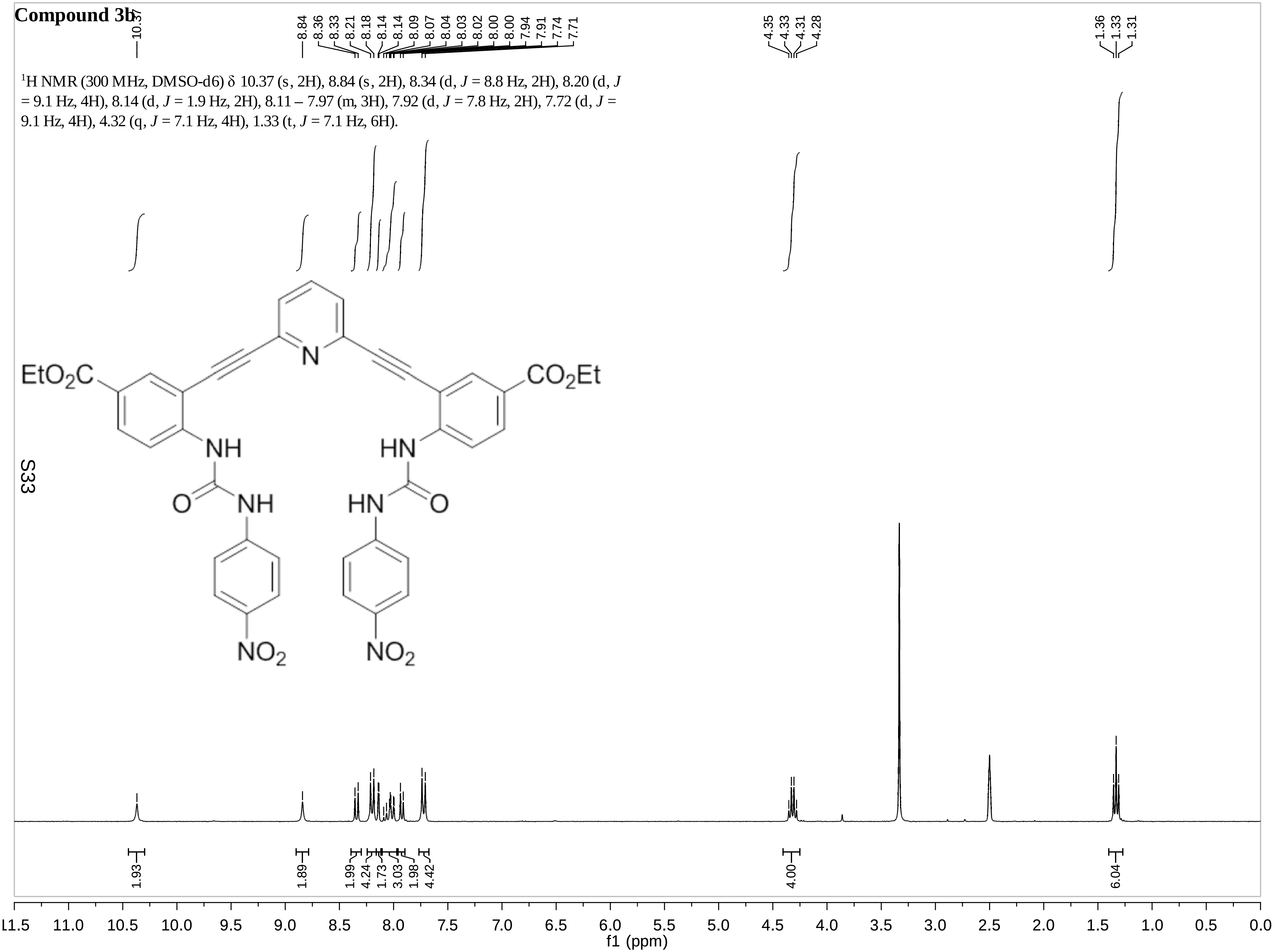
^{13}C NMR (151 MHz, DMSO-d6) δ 164.58, 154.96, 151.80, 144.88, 142.49, 137.60, 133.93, 131.84, 131.24, 127.90, 123.00, 120.50, 118.61, 114.10, 109.54, 94.51, 84.02, 60.71, 55.15, 14.16.





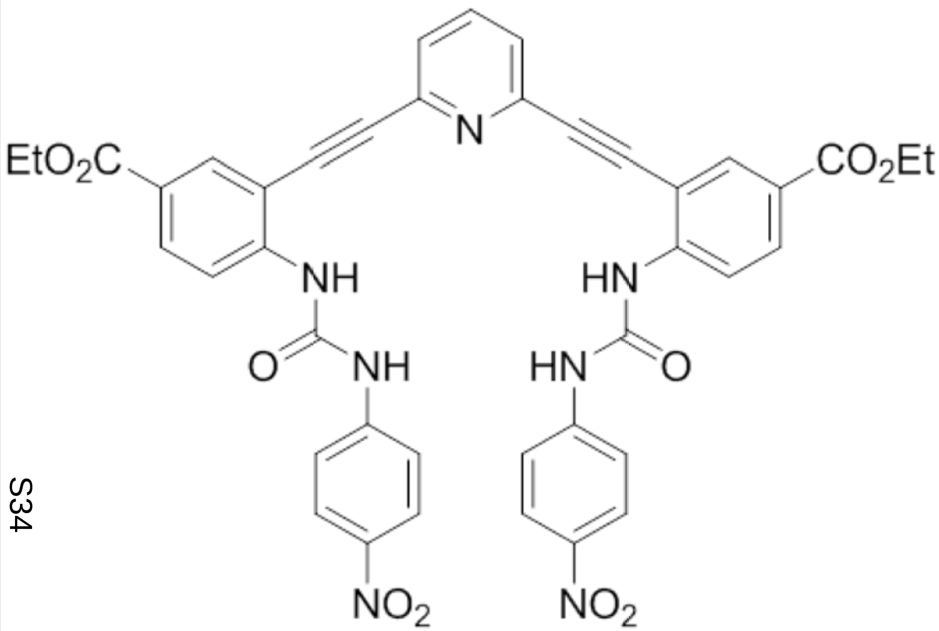
Compound 3b

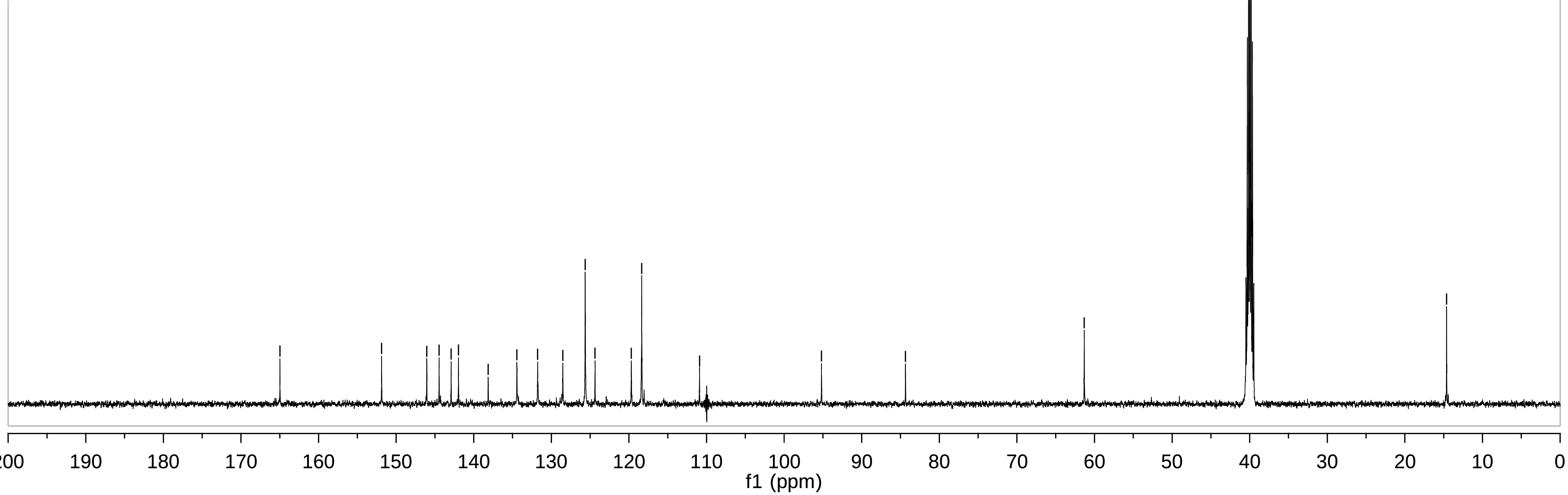
[1]H NMR (300 MHz, DMSO-d6) δ 10.37 (s, 2H), 8.84 (s, 2H), 8.34 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 9.1 Hz, 4H), 8.14 (d, *J* = 1.9 Hz, 2H), 8.11 – 7.97 (m, 3H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 9.1 Hz, 4H), 4.32 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 6H).



Compound 3b

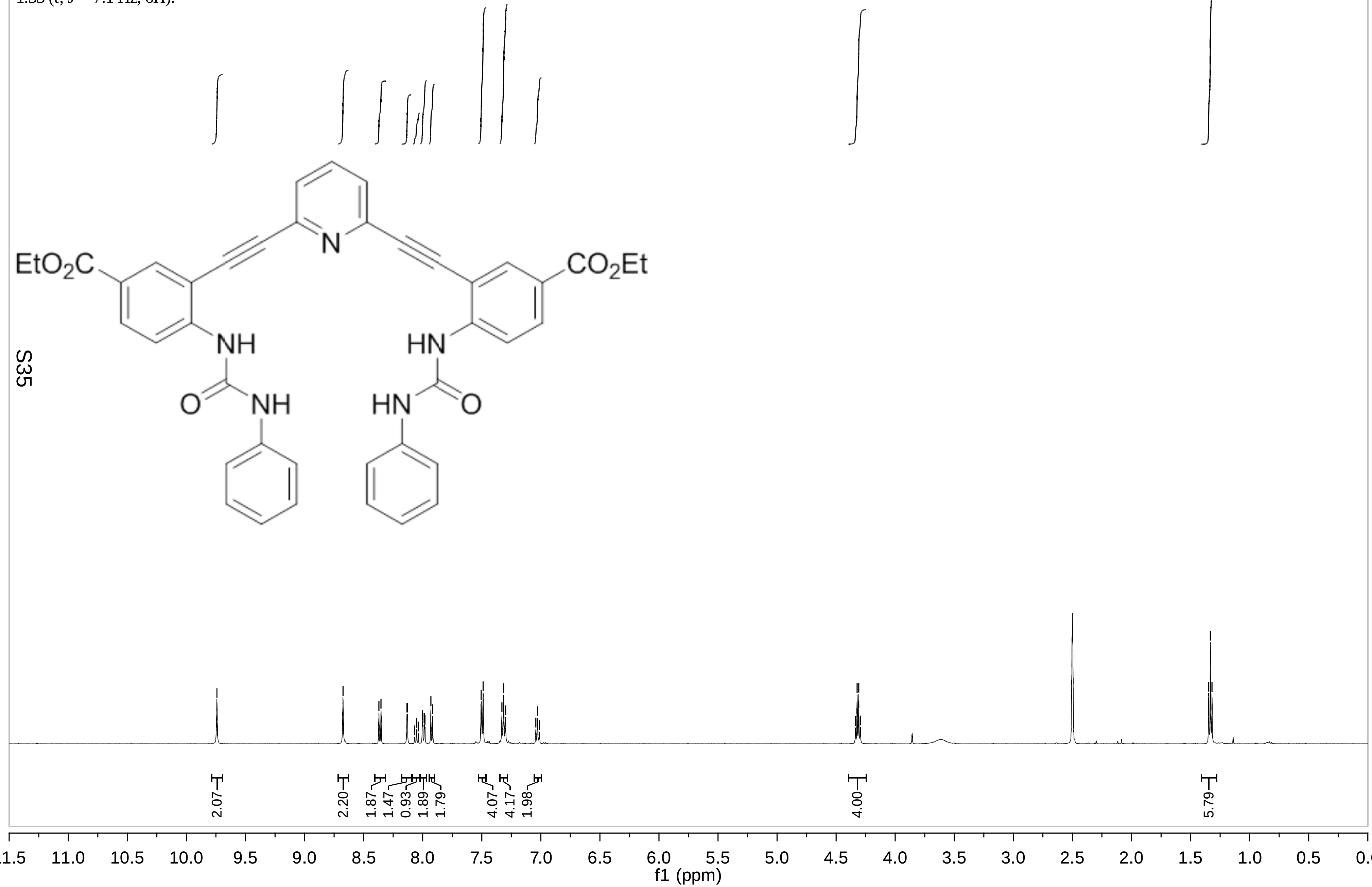
^{13}C NMR (126 MHz, DMSO-d6) δ 164.98, 151.88, 146.05, 144.46, 142.91, 141.97, 138.14, 134.44, 131.77, 128.52, 125.64, 124.37, 119.70, 118.36, 110.90, 95.18, 84.36, 61.32, 14.63.





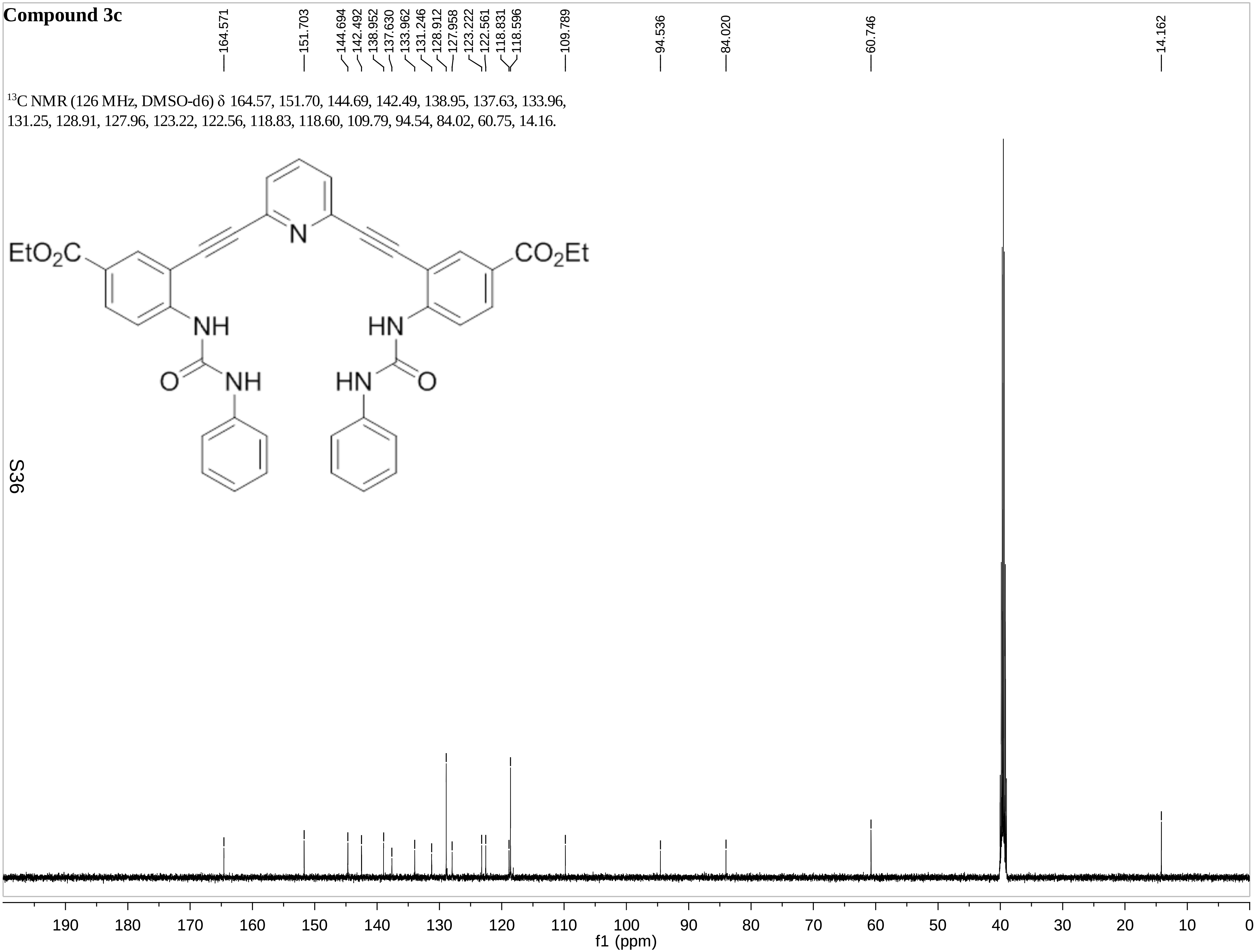
Compound 3c

[1]H NMR (500 MHz, DMSO-d6) δ 9.74 (s, 2H), 8.67 (s, 2H), 8.36 (d, *J* = 8.9 Hz, 2H), 8.13 (d, *J* = 1.9 Hz, 2H), 8.05 (t, *J* = 7.8 Hz, 1H), 7.99 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 4H), 7.31 (t, *J* = 7.7 Hz, 4H), 7.03 (t, *J* = 7.7 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 6H).



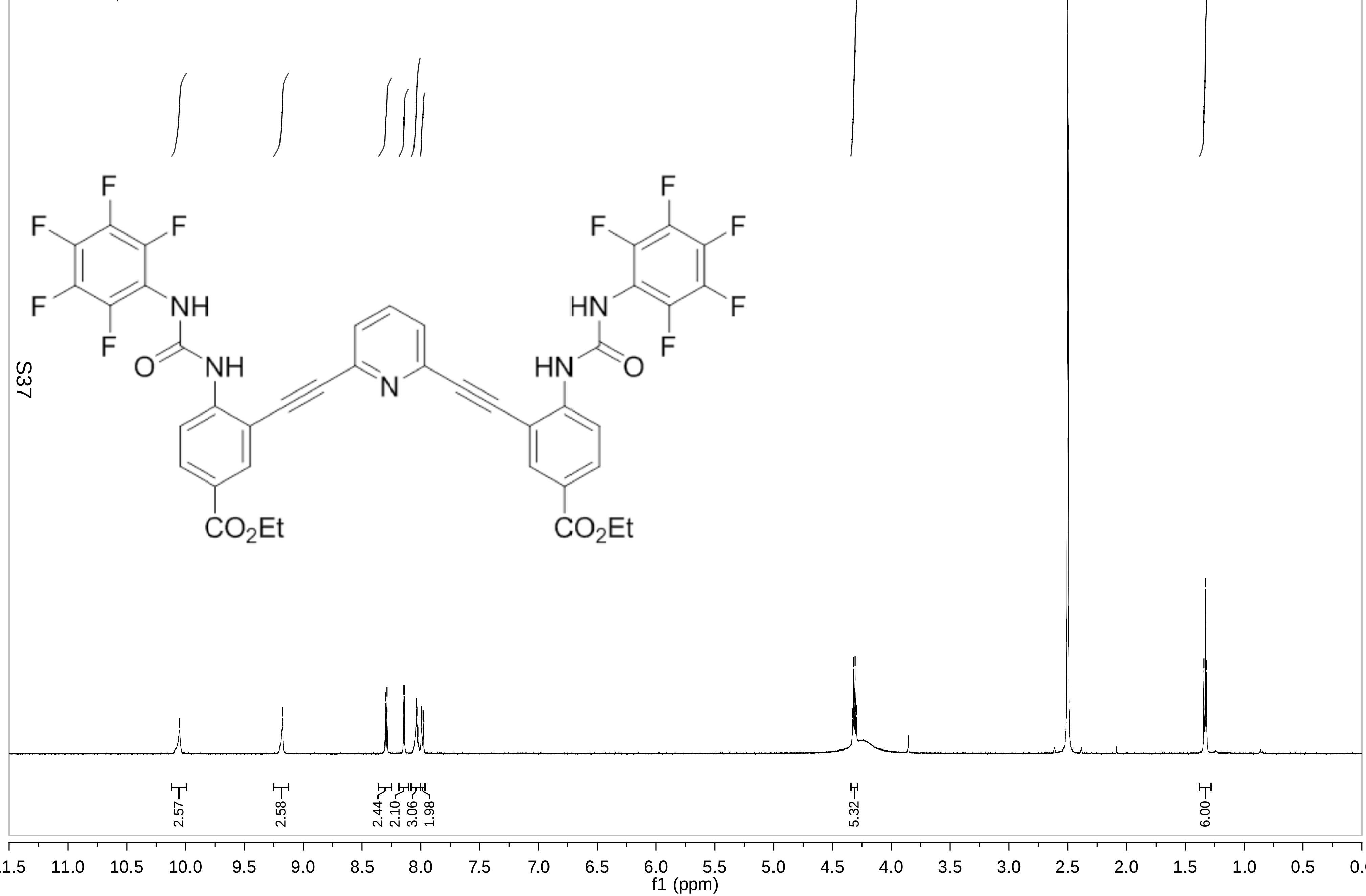
Compound 3c

^{13}C NMR (126 MHz, DMSO-d6) δ 164.57, 151.70, 144.69, 142.49, 138.95, 137.63, 133.96, 131.25, 128.91, 127.96, 123.22, 122.56, 118.83, 118.60, 109.79, 94.54, 84.02, 60.75, 14.16.



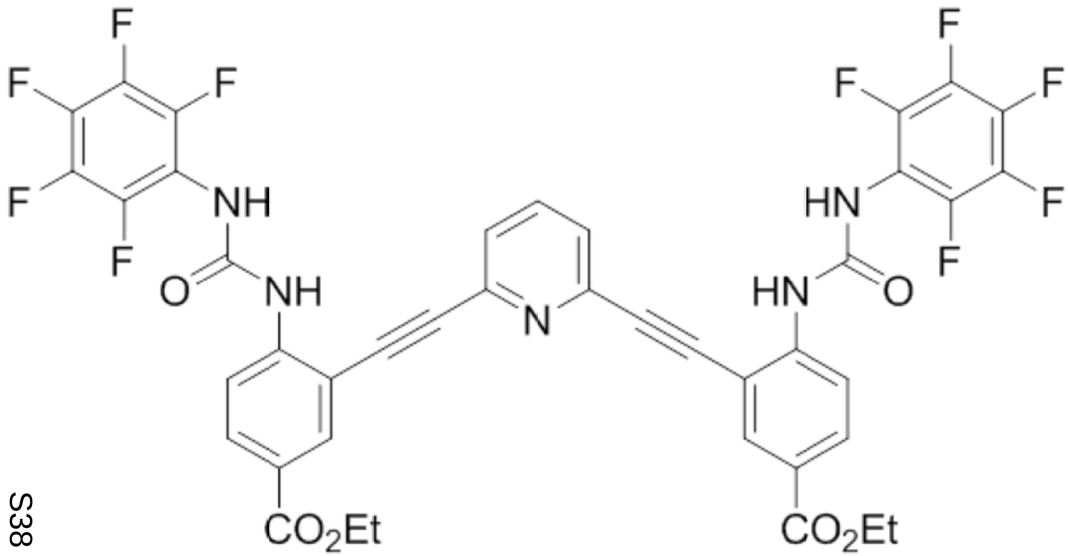
Compound 3d

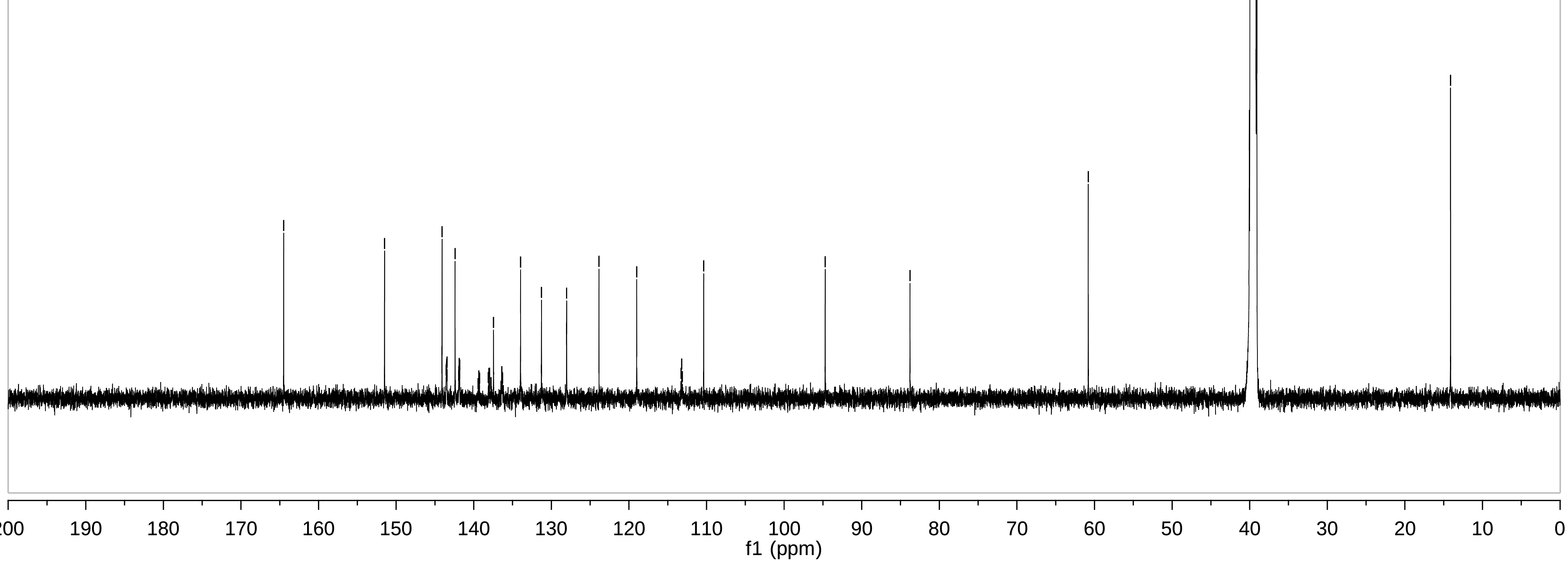
[1]H NMR (600 MHz, DMSO-d6) δ 10.05 (s, 2H), 9.18 (s, 2H), 8.29 (d, *J* = 8.9 Hz, 2H), 8.14 (d, *J* = 1.9 Hz, 2H), 8.08 – 8.01 (m, 3H), 7.99 (dd, *J* = 8.9, 1.9 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 4H), 1.33 (t, *J* = 7.1 Hz, 6H).



Compound 3d

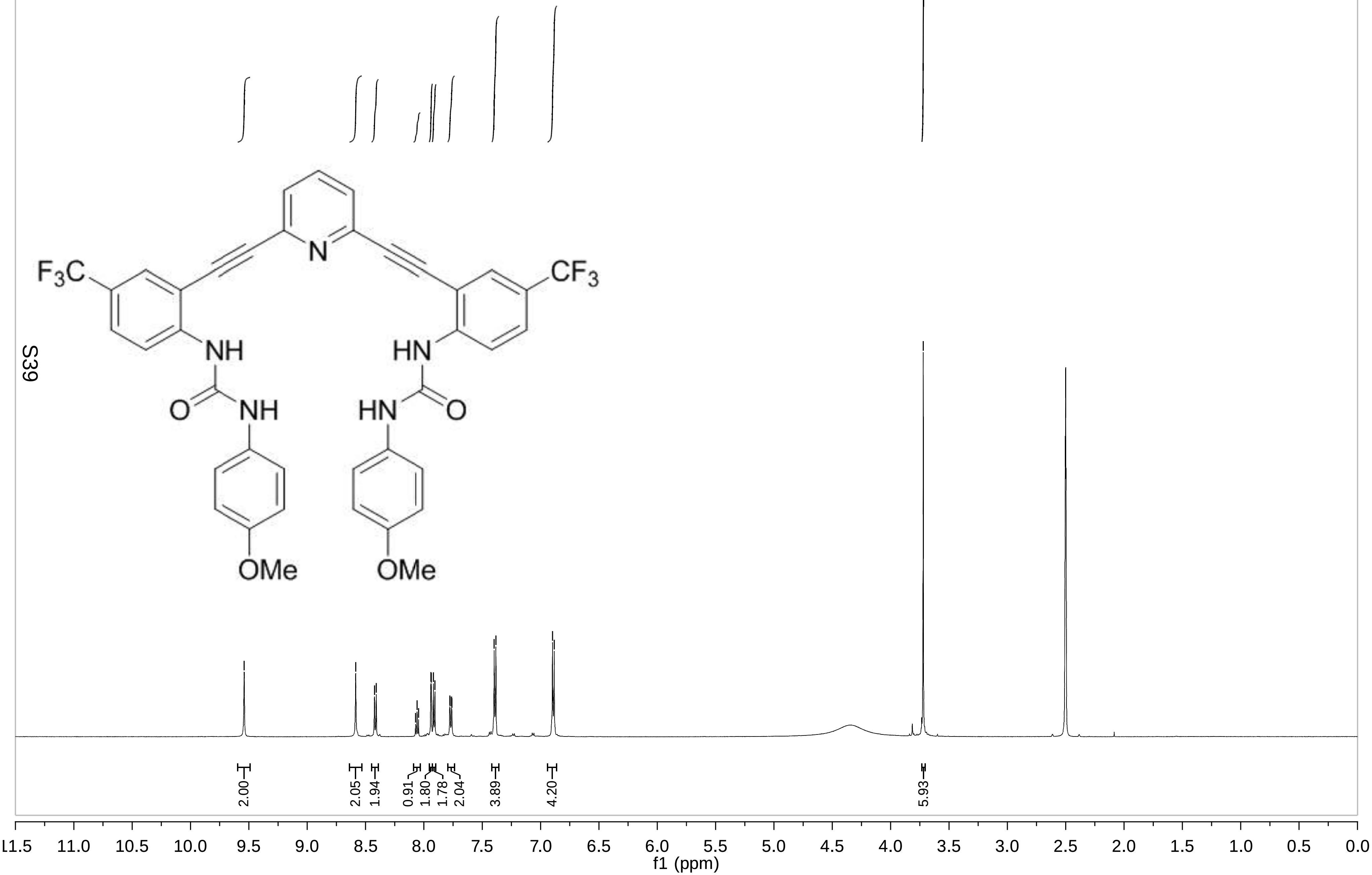
^{13}C NMR (151 MHz, DMSO-d6) δ 164.50 (s), 151.50 (s), 144.09 (s), 143.79 – 141.44 (m), 142.41 (s), 139.62 – 137.53 (m), 137.45 (s), 138.38 – 135.82 (m), 133.97 (s), 131.27 (s), 128.03 (s), 123.86 (s), 119.00 (s), 113.20 (t, J = 12.6 Hz), 110.37 (s), 94.71 (s), 83.78, 60.81, 14.11.





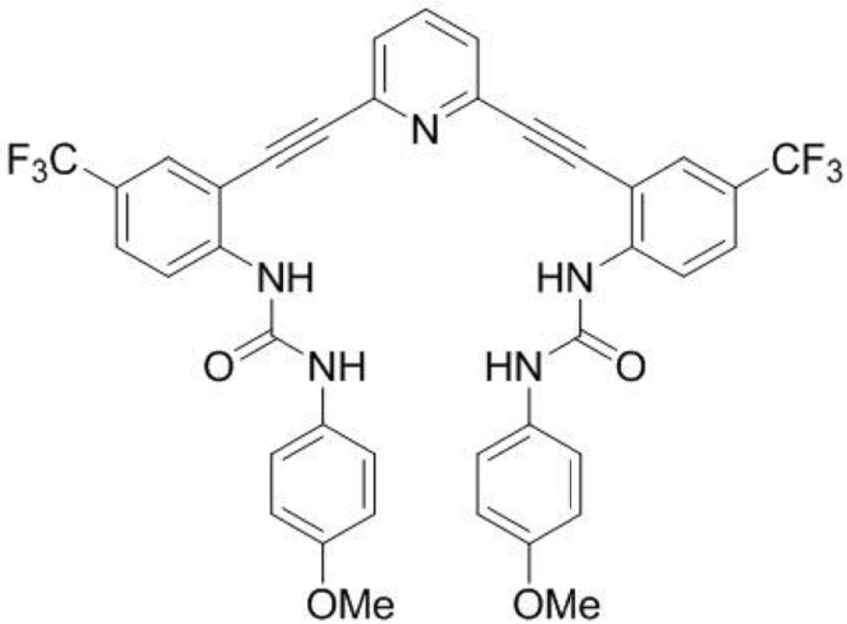
Compound 4a

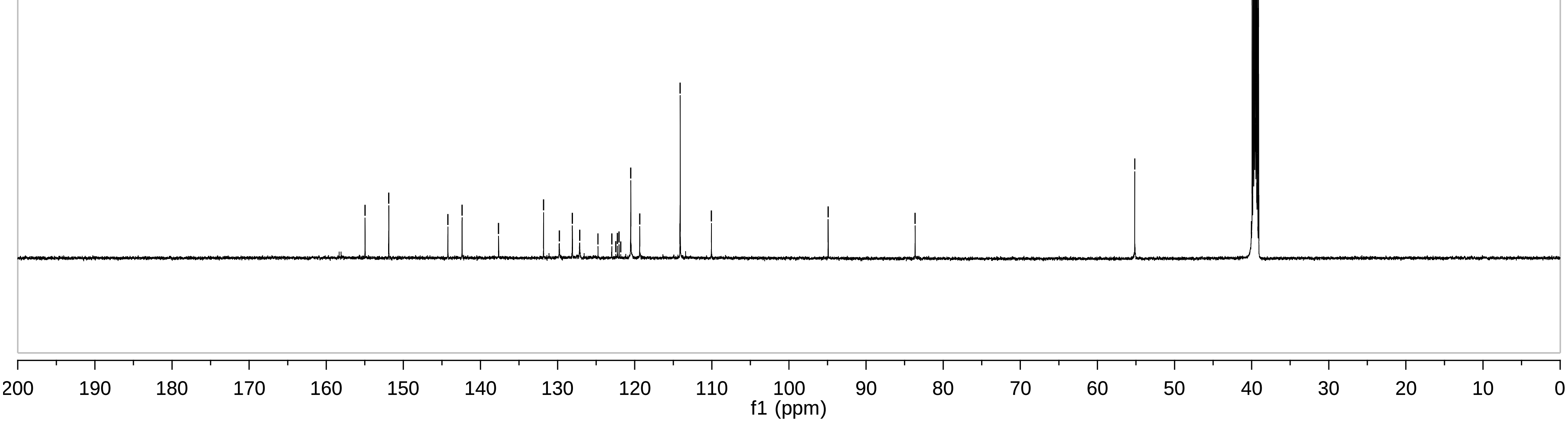
[1]H NMR (600 MHz, DMSO-d6) δ 9.54 (s, 2H), 8.58 (s, 2H), 8.42 (d, *J* = 8.9 Hz, 2H), 8.06 (t, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 1.5 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.77 (dd, *J* = 8.9, 1.5 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 4H), 6.89 (d, *J* = 9.0 Hz, 4H), 3.72 (s, 6H).



Compound 4a

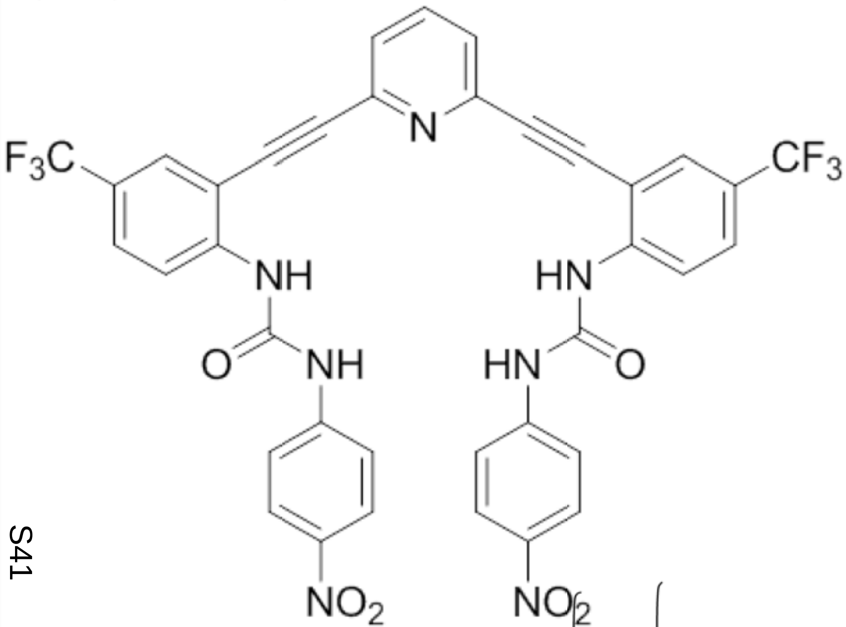
^{13}C NMR (151 MHz, DMSO-d6) δ 154.97, 151.89, 144.23, 142.39, 137.66, 131.82, 129.77, 128.09, 127.13, 124.77, 122.97, 122.14 (q, *J* = 32.4 Hz), 120.51, 119.35, 114.11, 110.06, 94.91, 83.64, 55.16.

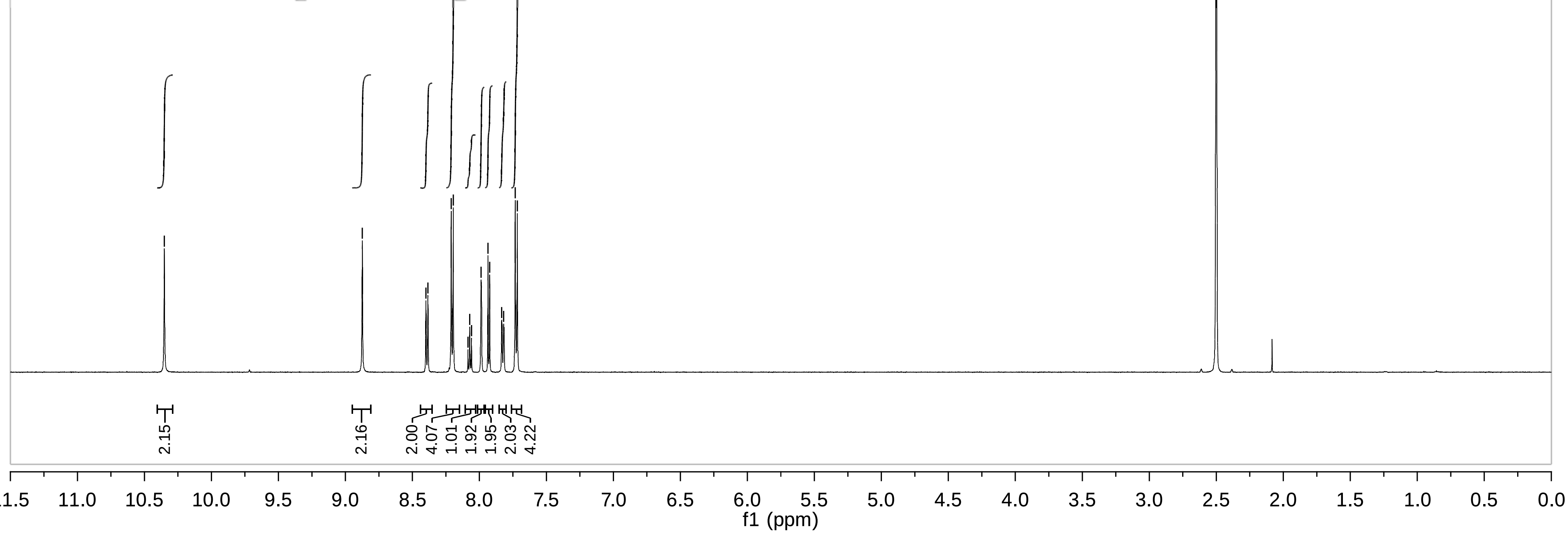




Compound 4b

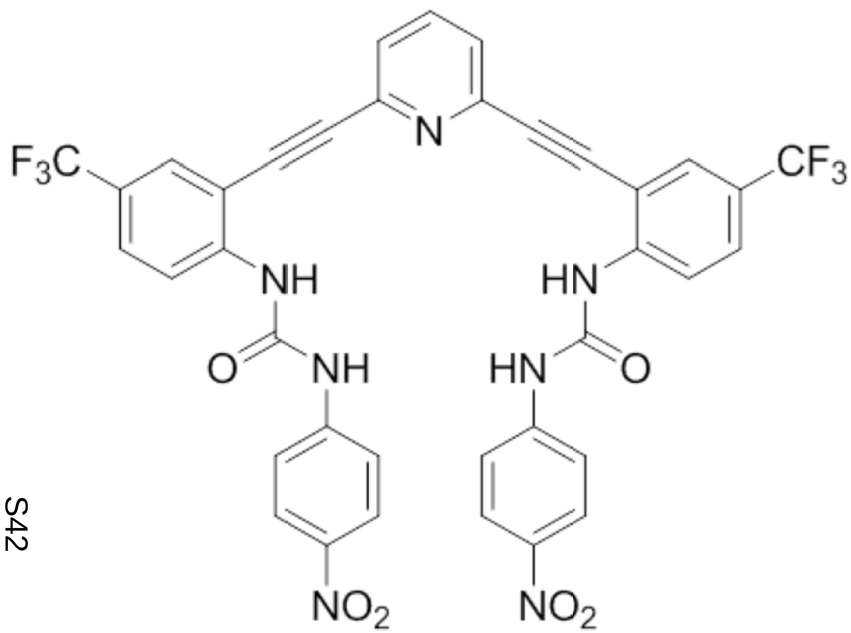
[1]H NMR (600 MHz, DMSO-d6) δ 10.35 (s, 2H), 8.87 (s, 2H), 8.39 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 9.3 Hz, 4H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.99 (s, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 9.3 Hz, 4H).

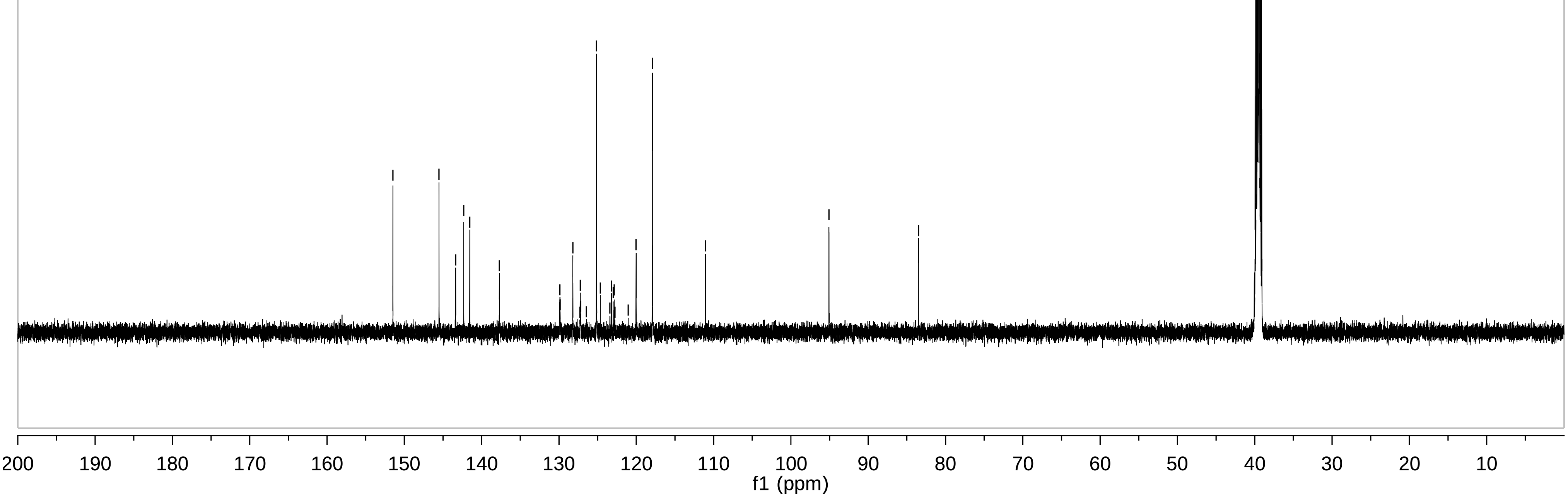




Compound 4b

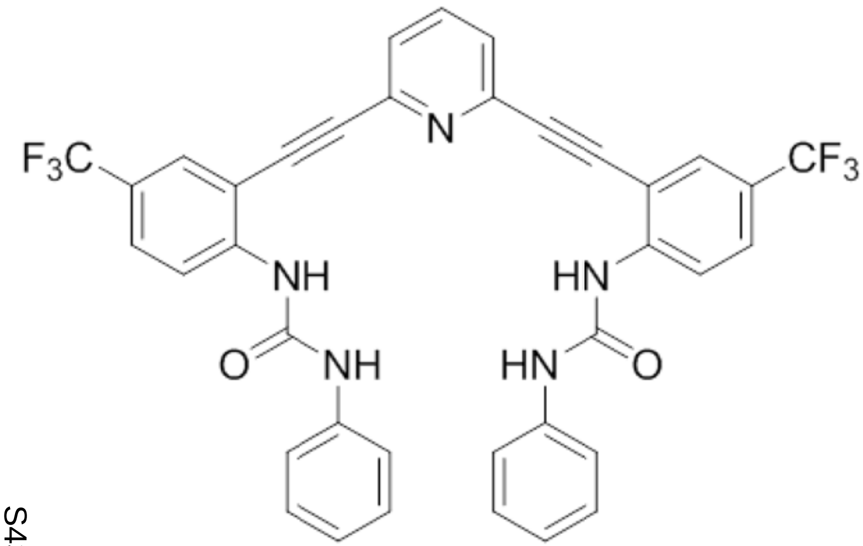
^{13}C NMR (151 MHz, DMSO-d6) δ 151.48, 145.52, 143.36, 142.33, 141.54, 137.72, 129.89 (t, *J* = 6.1 Hz), 128.21, 127.24 (t, *J* = 6.6 Hz), 125.15, 124.05 (t, *J* = 407.7 Hz), 123.09 (q, *J* = 32.7 Hz), 120.03, 117.92, 111.04, 95.07, 83.50.

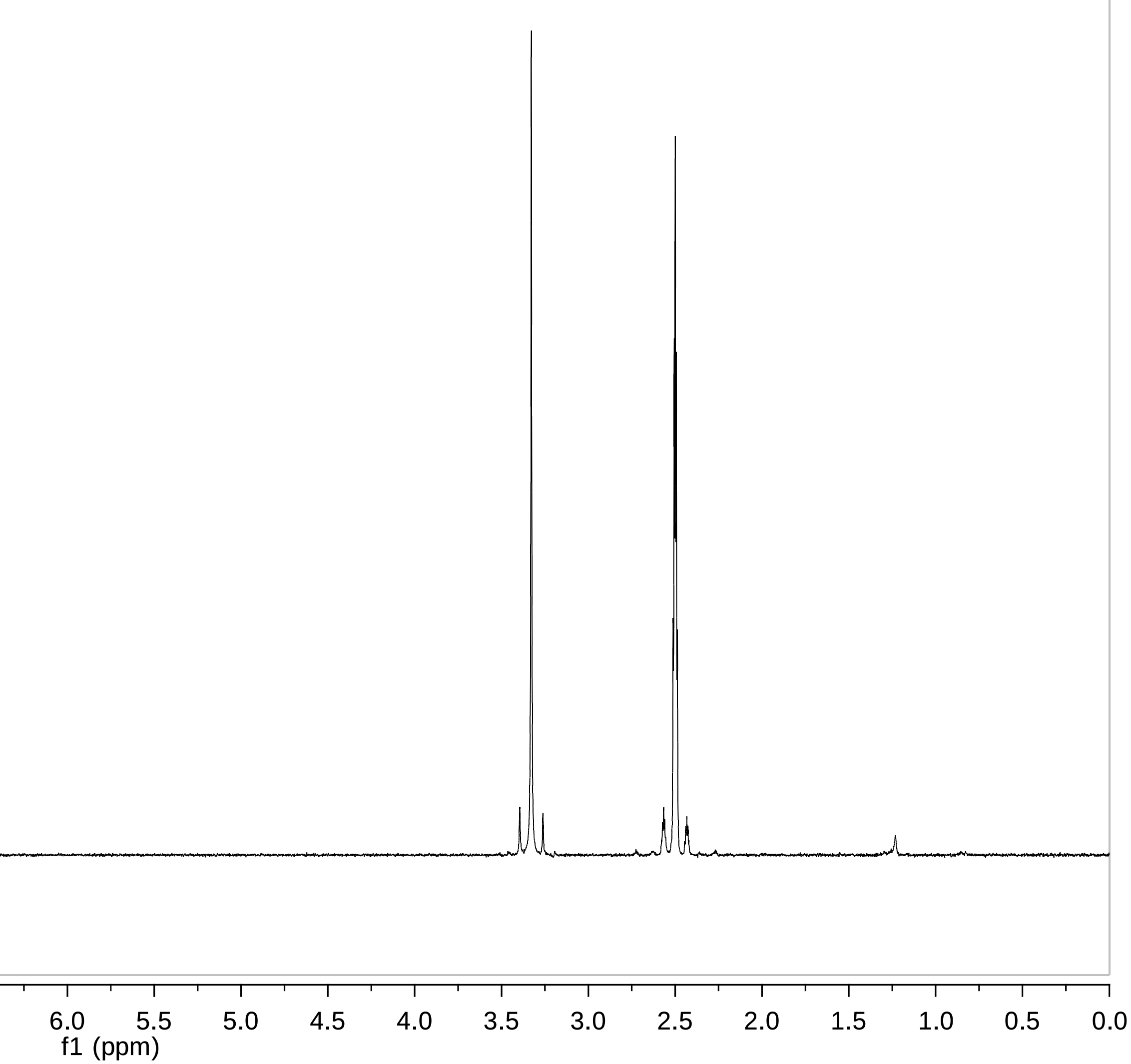




Compound 4c

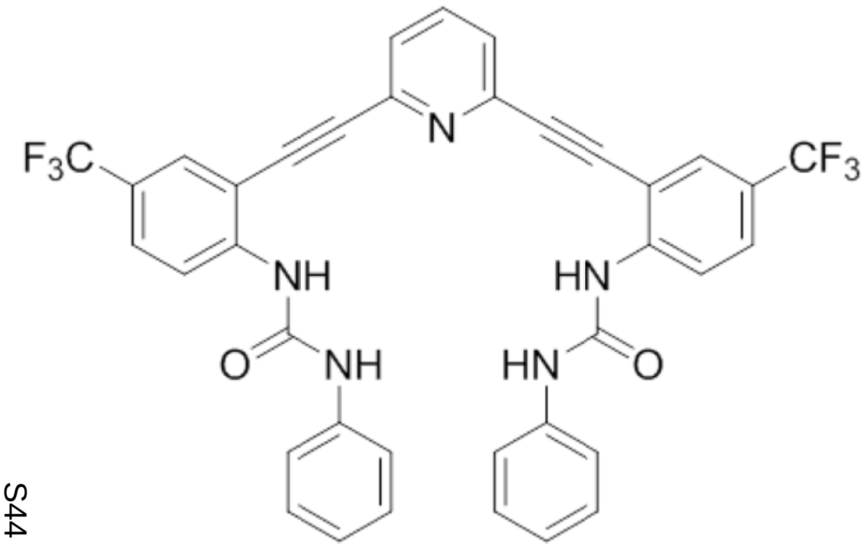
[1]H NMR (300 MHz, DMSO-d6) δ 9.71 (s, 2H), 8.68 (s, 2H), 8.41 (d, *J* = 8.8 Hz, 2H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.94 (m, 4H), 7.79 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 4H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.03 (t, *J* = 7.5 Hz, 2H).

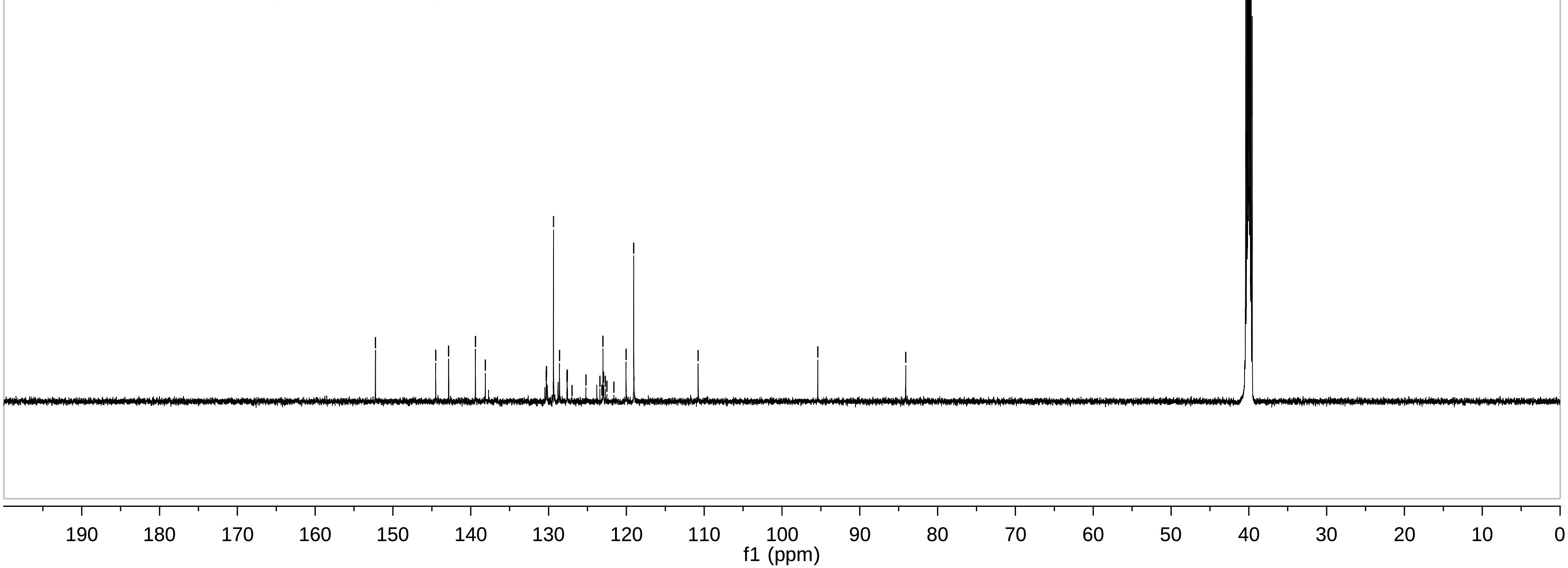




Compound 4c

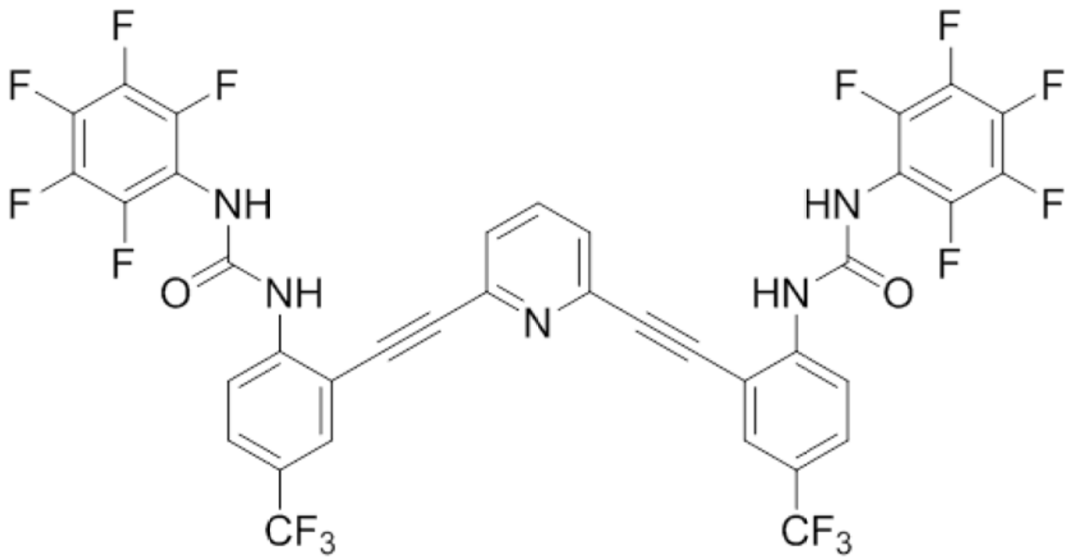
^{13}C NMR (151 MHz, DMSO-d6) δ 152.24, 144.51, 142.85, 139.39, 138.12, 130.28 (q, J = 3.8 Hz), 129.36, 128.59, 127.61 (q, J = 3.2 Hz), 124.30 (q, J = 271.1 Hz), 123.01, 122.82 (q, J = 32.6 Hz), 120.04, 119.05, 110.78, 95.39, 84.09.

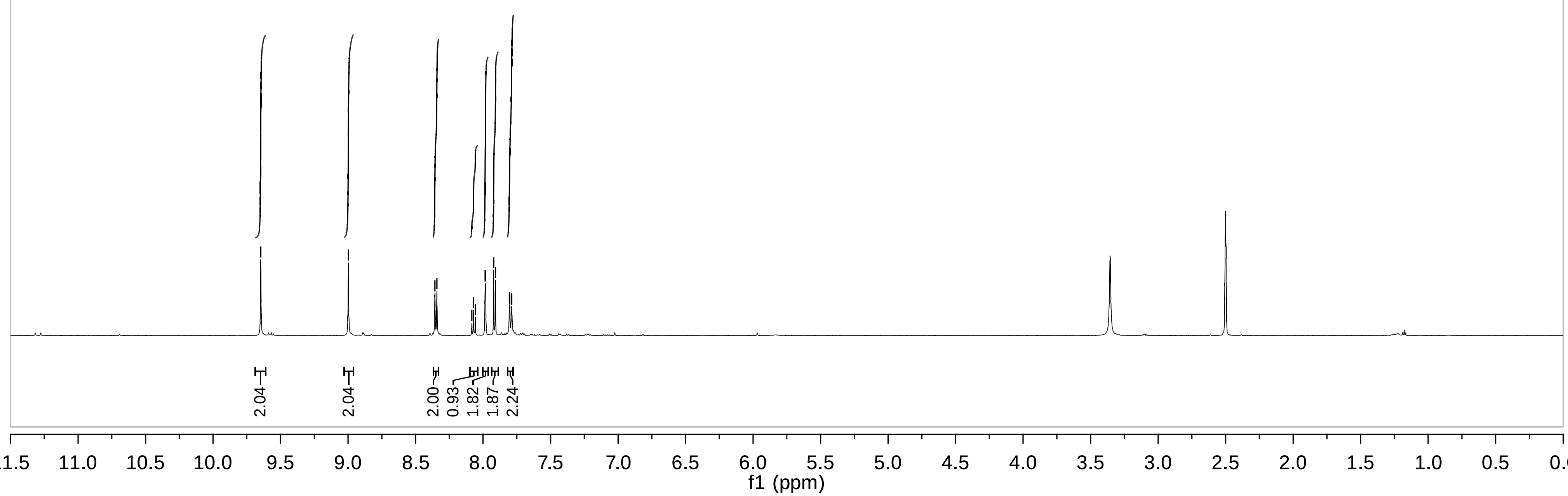




Compound 4d

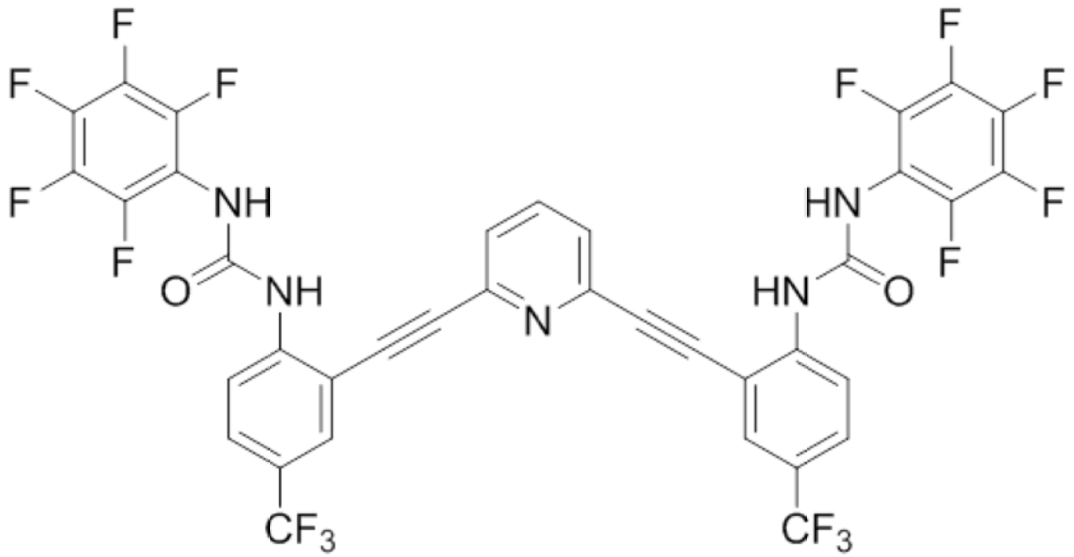
[1]H NMR (600 MHz, DMSO-d6) δ 9.65 (s, 2H), 9.00 (s, 2H), 8.35 (d, *J* = 8.9 Hz, 2H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 1.6 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.80 (dd, *J* = 8.9, 1.6 Hz, 2H).

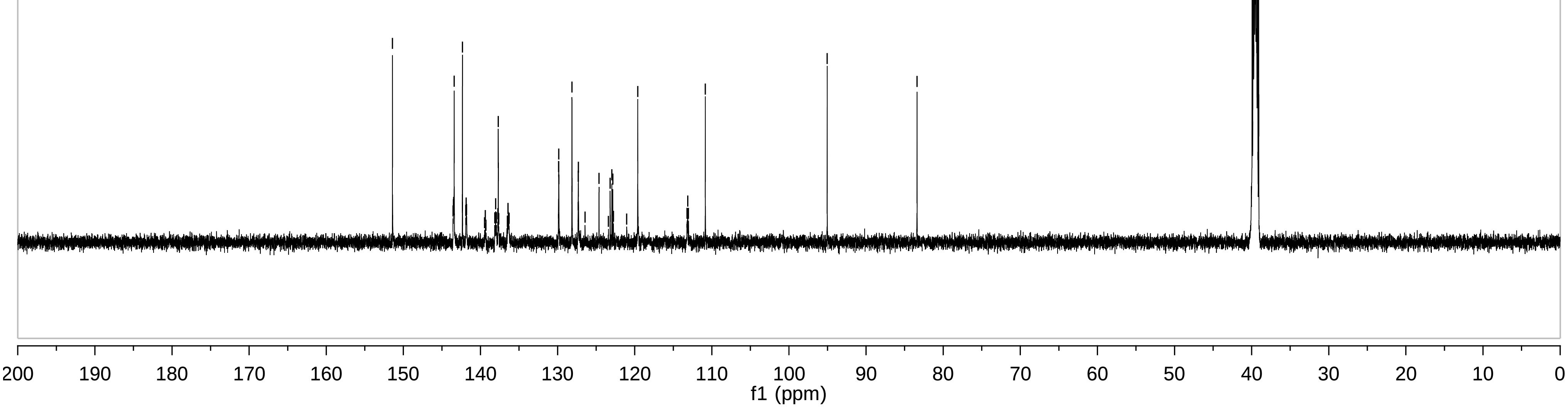




Compound 4d

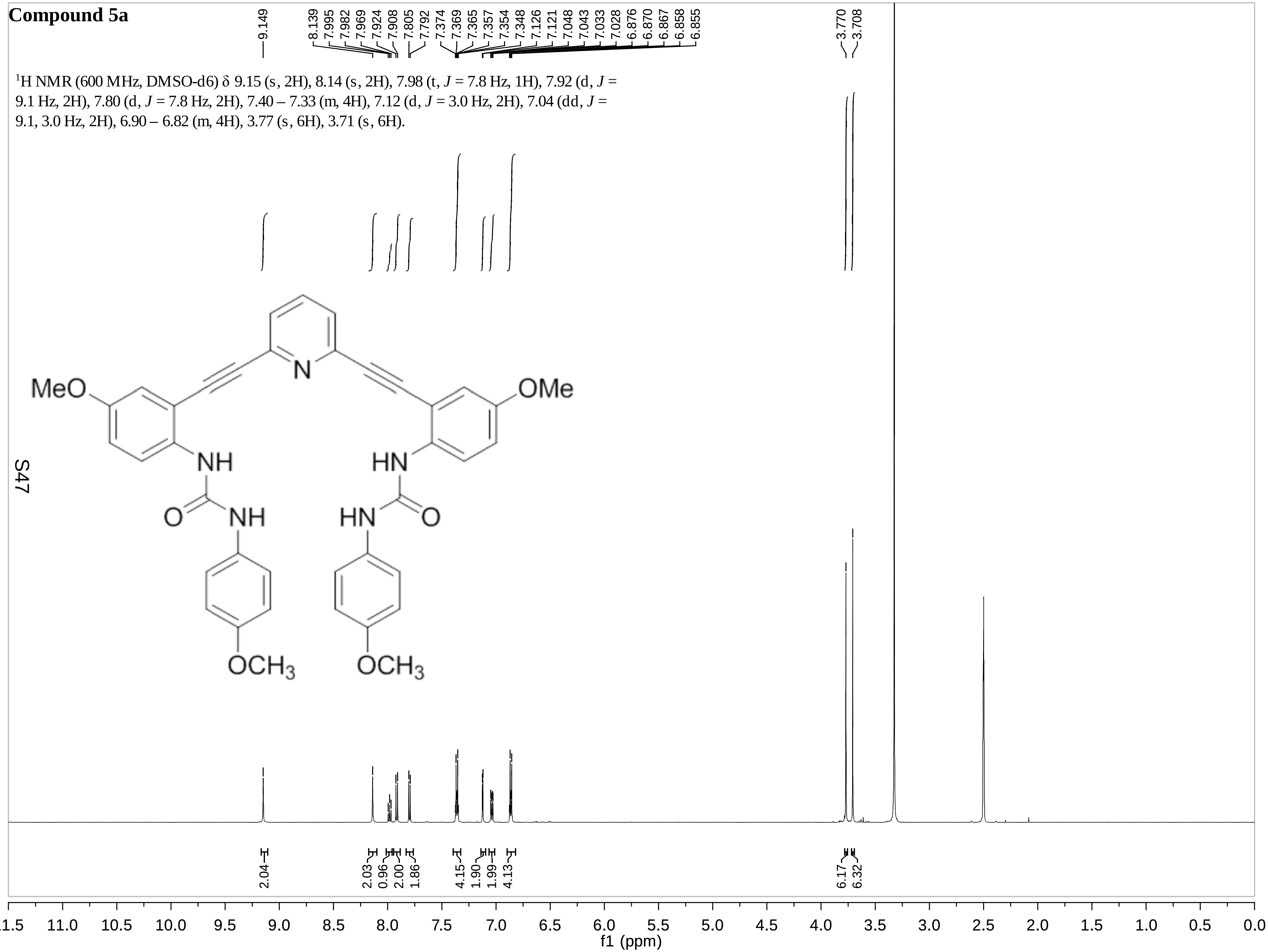
^{13}C NMR (151 MHz, DMSO-d6) δ 151.41, 143.42, 143.65 – 141.64 (m), 142.34, 139.82 – 137.37 (m), 137.69, 137.23 (dt, *J* = 32.1, 19.1 Hz), 129.97 – 129.74 (m, *J* = 3.8 Hz), 128.14, 127.45 – 127.21 (m, *J* = 3.5 Hz), 123.74 (q, *J* = 271.2 Hz), 123.08 (q, *J* = 33.6 Hz), 119.61, 113.12 (t, *J* = 13.8 Hz), 110.85, 95.05, 83.40.





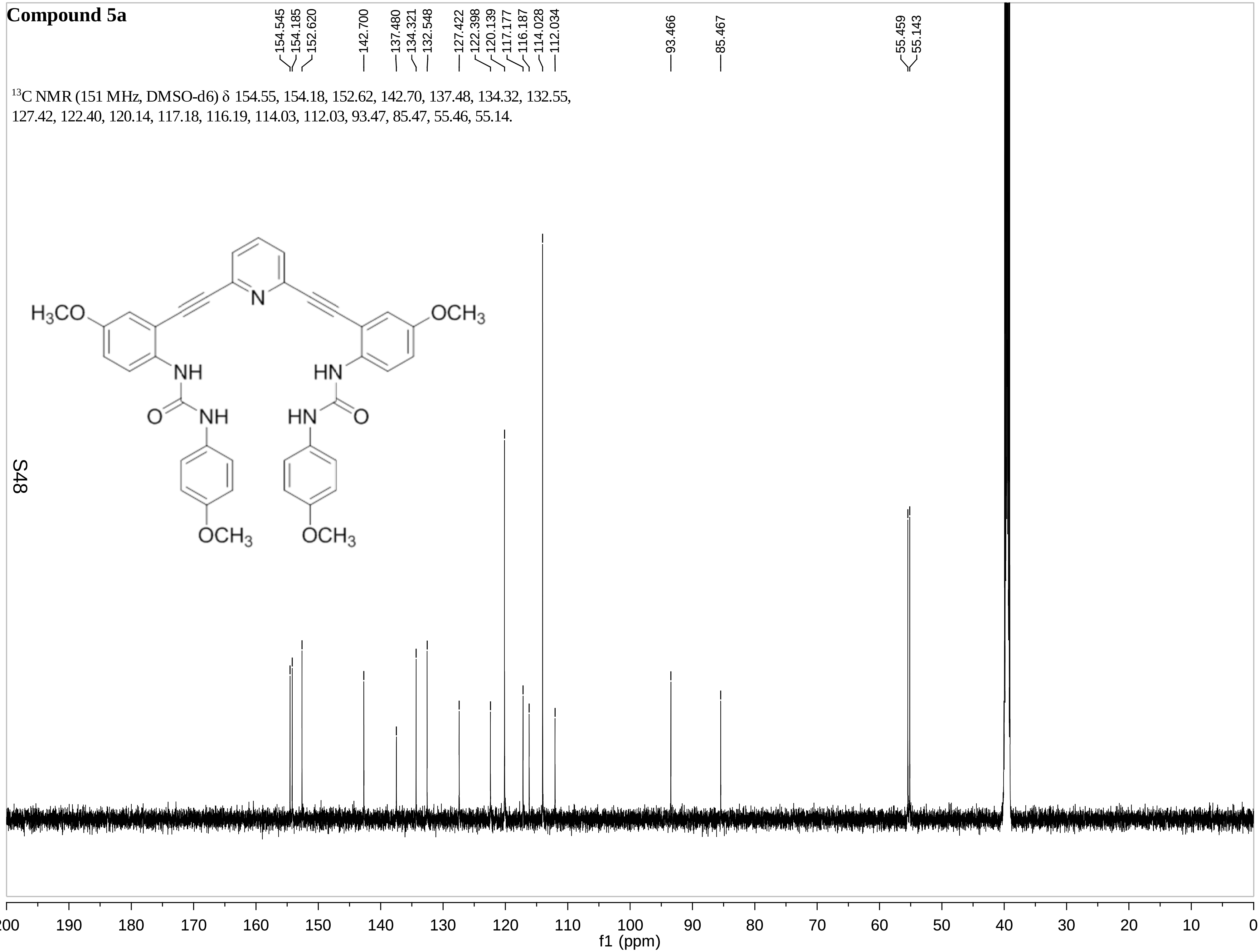
Compound 5a

[1]H NMR (600 MHz, DMSO-d6) δ 9.15 (s, 2H), 8.14 (s, 2H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 9.1 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.12 (d, *J* = 3.0 Hz, 2H), 7.04 (dd, *J* = 9.1, 3.0 Hz, 2H), 6.90 – 6.82 (m, 4H), 3.77 (s, 6H), 3.71 (s, 6H).



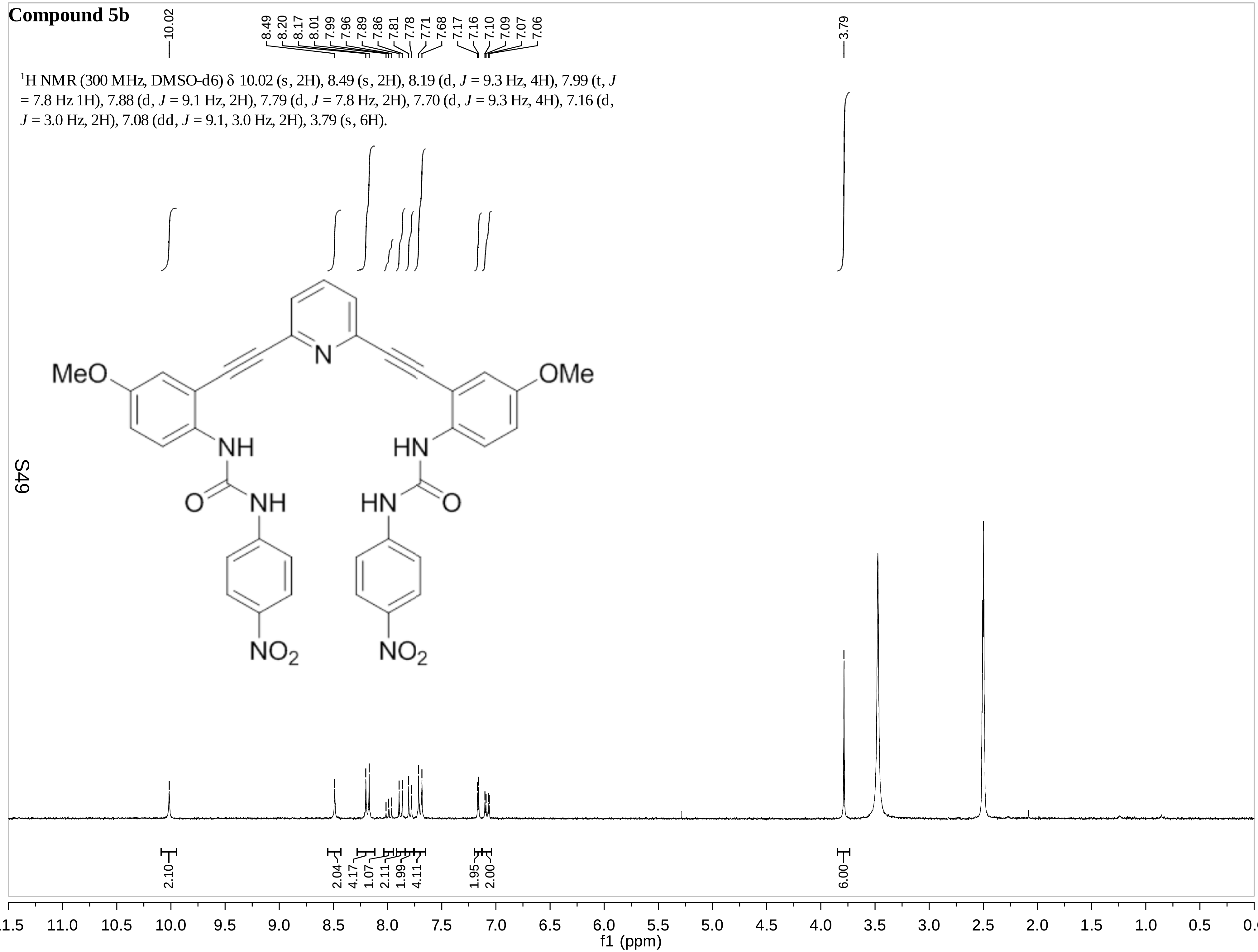
Compound 5a

^{13}C NMR (151 MHz, DMSO-d6) δ 154.55, 154.18, 152.62, 142.70, 137.48, 134.32, 132.55, 127.42, 122.40, 120.14, 117.18, 116.19, 114.03, 112.03, 93.47, 85.47, 55.46, 55.14.



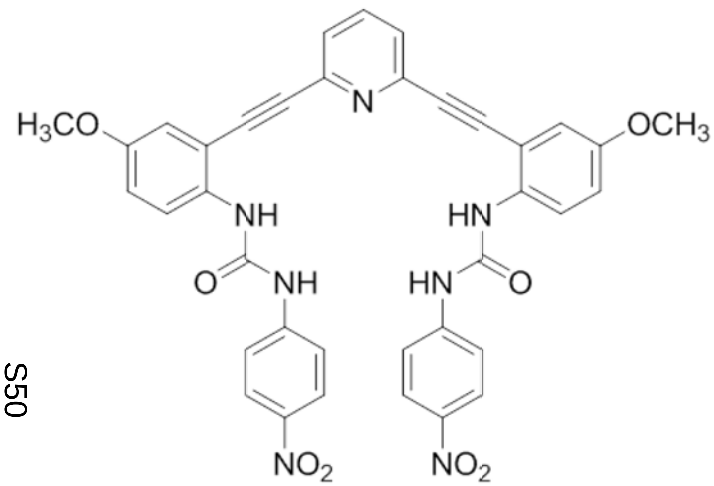
Compound 5b

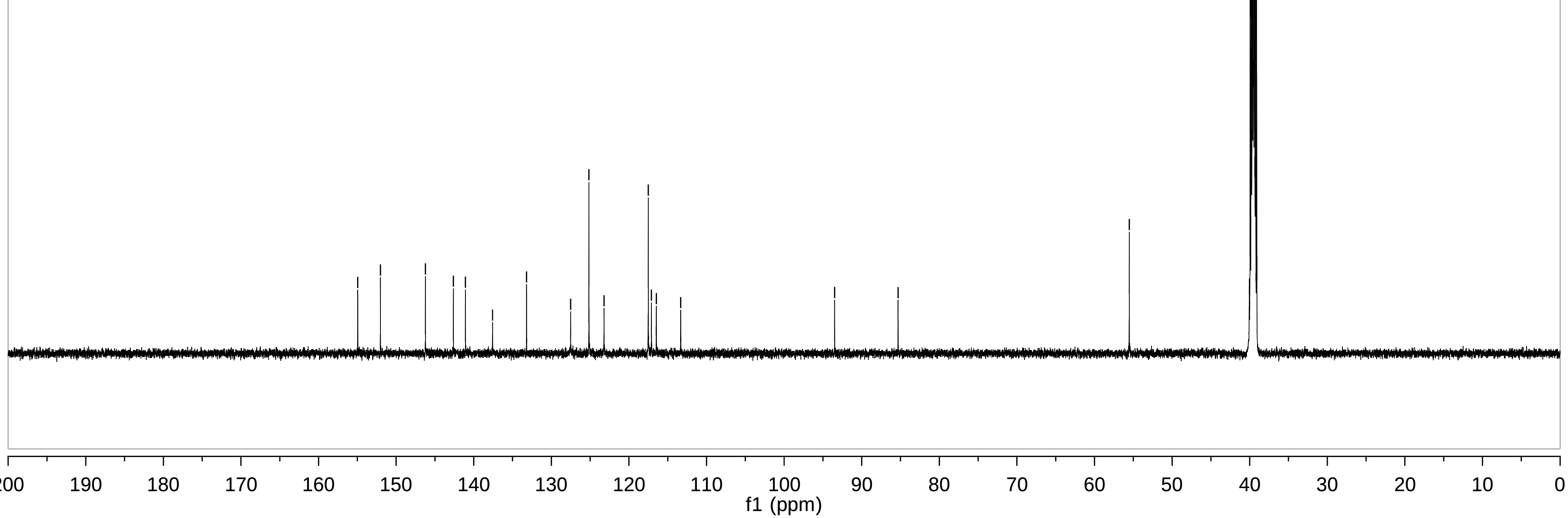
^{1}H NMR (300 MHz, DMSO-d6) δ 10.02 (s, 2H), 8.49 (s, 2H), 8.19 (d, *J* = 9.3 Hz, 4H), 7.99 (t, *J* = 7.8 Hz 1H), 7.88 (d, *J* = 9.1 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 9.3 Hz, 4H), 7.16 (d, *J* = 3.0 Hz, 2H), 7.08 (dd, *J* = 9.1, 3.0 Hz, 2H), 3.79 (s, 6H).



Compound 5b

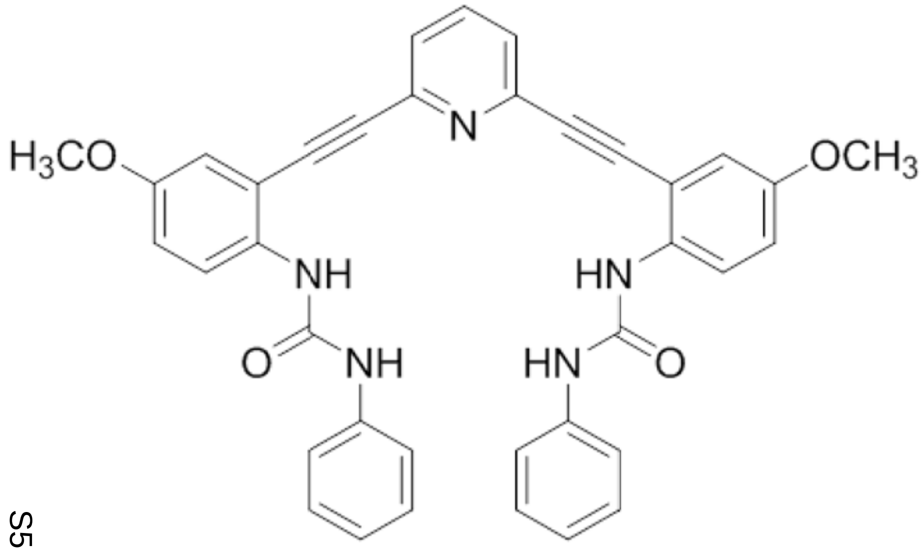
^{13}C NMR (151 MHz, DMSO-d6) δ 154.95, 152.03, 146.23, 142.63, 141.08, 137.58, 133.20, 127.51, 125.16, 123.21, 117.51, 117.11, 116.47, 113.33, 93.49, 85.32, 55.52.

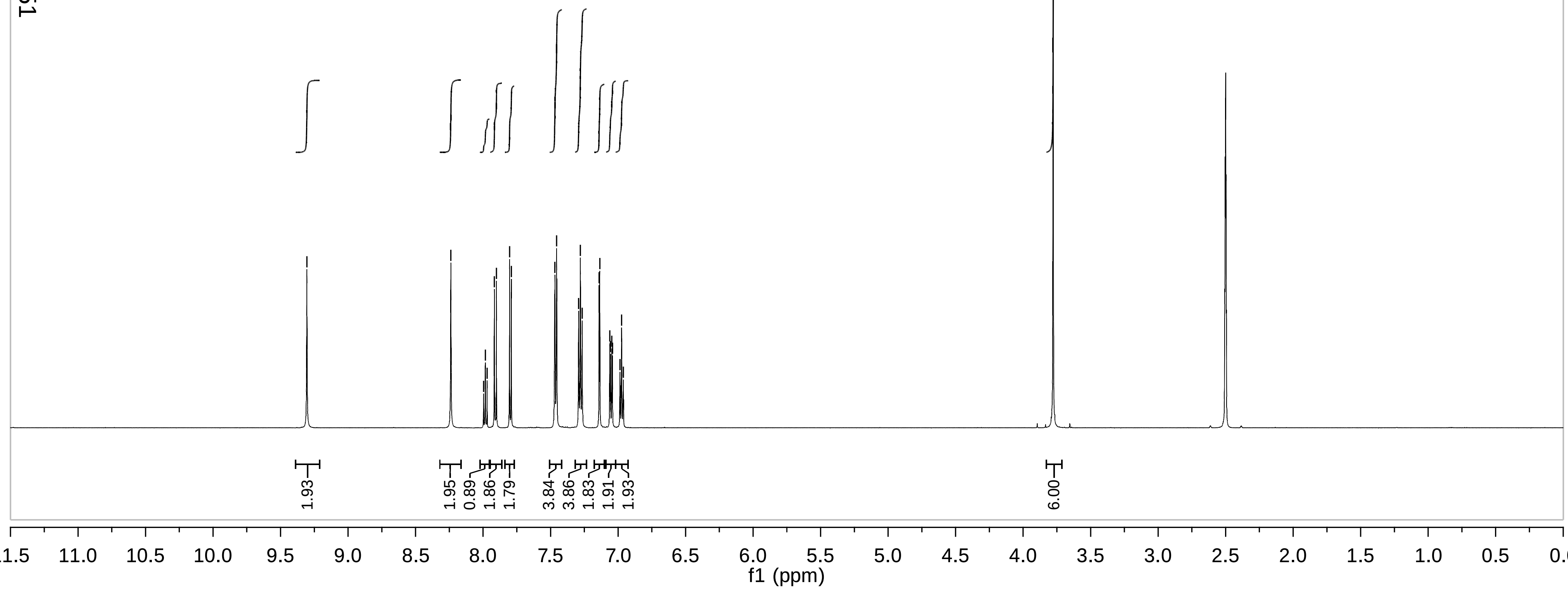




Compound 5c

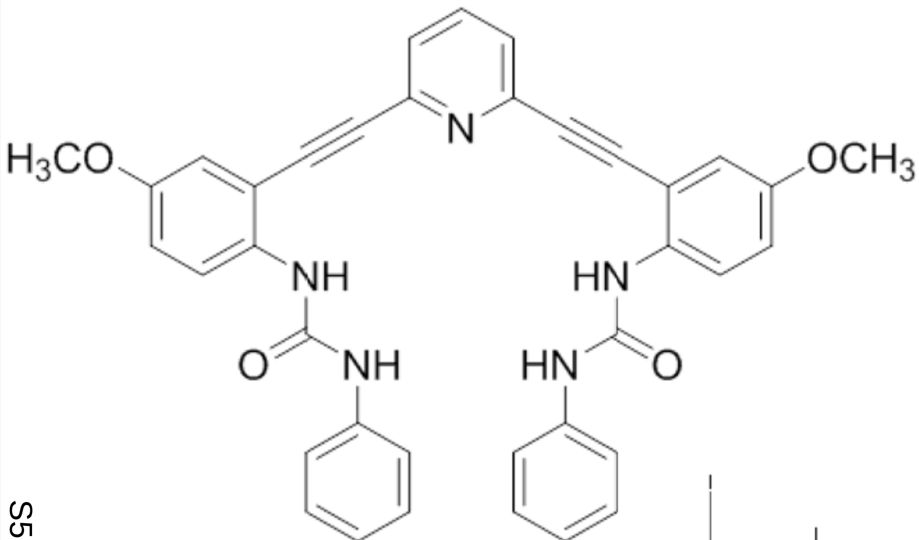
[1]H NMR (600 MHz, DMSO-d6) δ 9.30 (s, 2H), 8.24 (s, 2H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 9.1 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 4H), 7.28 (t, *J* = 7.5 Hz, 4H), 7.14 (d, *J* = 3.0 Hz, 2H), 7.05 (dd, *J* = 9.1, 3.0 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 2H), 3.78 (s, 6H).

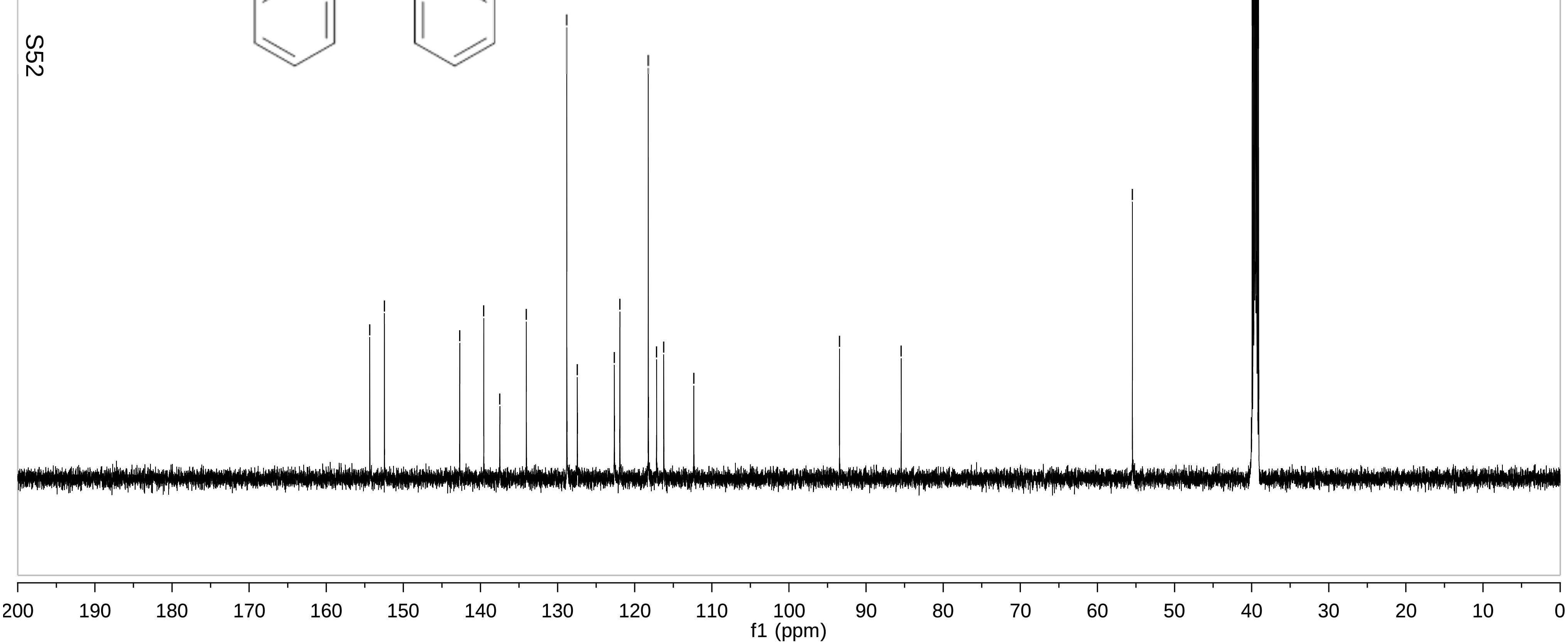




Compound 5c

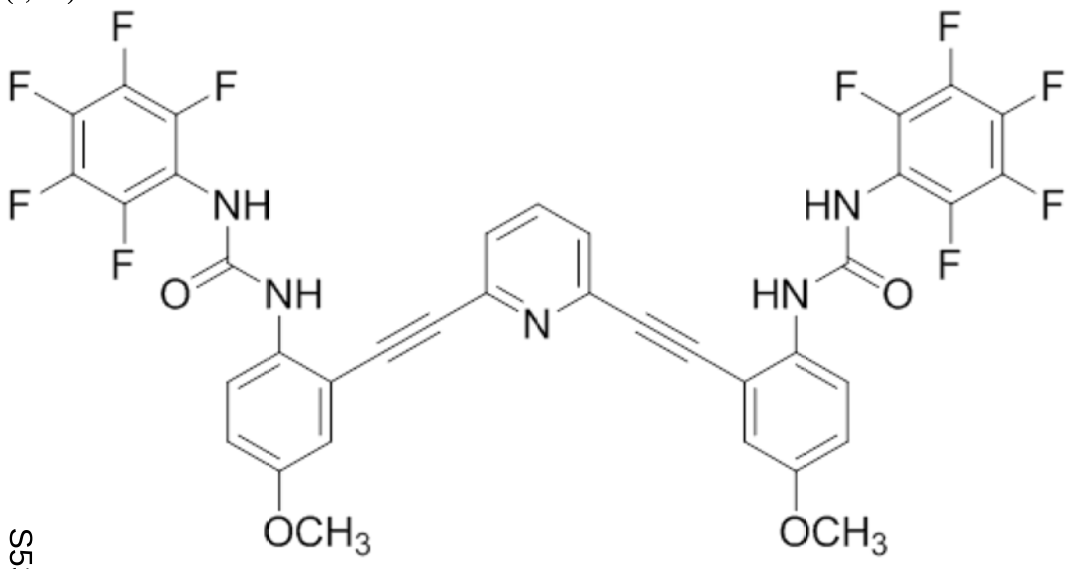
^{13}C NMR (151 MHz, DMSO-d6) δ 154.36, 152.46, 142.70, 139.58, 137.50, 134.06, 128.81, 127.45, 122.65, 121.93, 118.25, 117.17, 116.24, 112.34, 93.45, 85.45, 55.47.

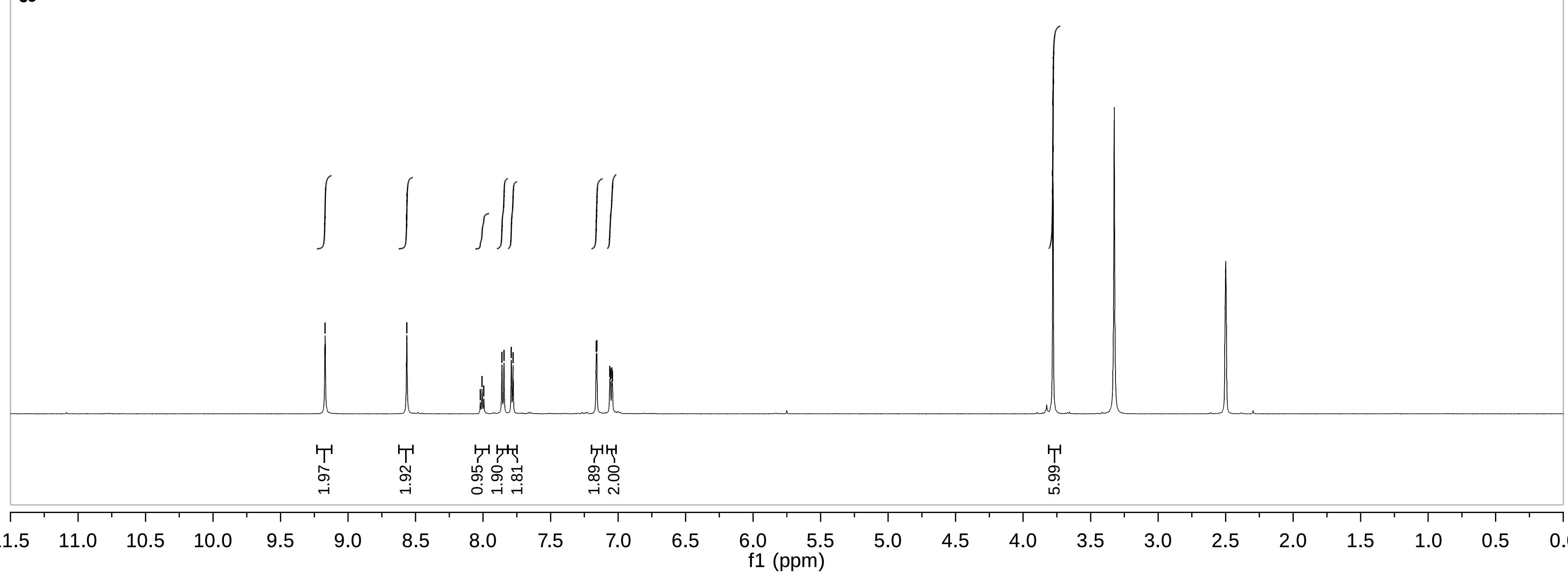




Compound 5d

[1]H NMR (600 MHz, DMSO-d6) δ 9.17 (s, 2H), 8.56 (s, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 2.6 Hz, 2H), 7.05 (dd, *J* = 9.1, 2.6 Hz, 2H), 3.78 (s, 6H).





Compound 5d

^{13}C NMR (151 MHz, DMSO-d6) δ 155.30, 152.36, 144.32 – 141.92 (m), 143.12, 139.90 – 137.47 (m), 137.95, 138.72 – 136.48 (m), 133.88, 127.90, 123.19, 117.57, 116.88, 114.25 (t, J = 15.8 Hz), 113.53, 93.93, 85.67, 55.94.