

Supporting Information

Synthesis of Carbazoles by Copper-Catalyzed Intramolecular C–H/N–H Coupling

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Instrumentation and Chemicals

¹H, ¹³C, and ¹⁹F NMR spectra were recorded at 400 MHz, 100 MHz, and 376 MHz, respectively, for DMSO-*d*₆ solutions. HRMS data were obtained by EI or APCI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakosil C-200, Wako Pure Chemical Co.) was used for column chromatography. Microwave irradiation was conducted with Initiator⁺ (Biotage).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous Cu(OAc)₂ and MnO₂ were purchased from Wako Pure Chemical Co. The starting 2-aminobiphenyls **1** were prepared through the Suzuki-Miyaura coupling of 2-bromoanilines with arylboronic acids¹ followed by the condensation with picolinoyl chloride. All reactions were carried out under atmospheric conditions without any special cautions unless otherwise noted.

¹ a) Youn, S. W.; Bihn, J. H. *Tetrahedron Lett.* **2009**, *50*, 4598. (b) Suzuki, C.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2013**, *15*, 3990.

Experimental Procedures

Preparation of the Starting Materials 1

Synthesis of **1r** is representative. Thiophen-2-ylboronic acid (1.2 g, 9.0 mmol), PdCl₂(PPh₃)₂ (420 mg, 0.60 mmol), and potassium carbonate (830 mg, 6.0 mmol) were placed in a 100 mL two-necked reaction flask equipped with a reflux condenser, and the flask was flushed with nitrogen. *N,N*-Dimethylformamide (DMF, 30 mL), water (6 mL), and 2-bromoaniline (1.0 g, 6.0 mmol) were added, and the resulting solution was stirred at 80 °C for 24 h. After cooling, the reaction mixture was diluted with ethyl acetate and aqueous saturated NaHCO₃, and filtered off through a short pad of Celite. The filtrate was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (5:1, v/v) gave 2-(thiophen-2-yl)aniline (860 mg, 4.9 mmol) in 82% yield.

Pyridine-2-carbonyl chloride hydrochloride (960 mg, 5.4 mmol) and *N,N*-dimethyl-4-aminopyridine (180 mg, 1.5 mmol) were placed in a 50 mL two-necked reaction flask, and the flask was flushed with nitrogen. Dichloromethane (12 mL), triethylamine (1.1 g, 11 mmol), and 2-(thiophen-2-yl)aniline (860 mg, 4.9 mmol) obtained above were added, and the mixture was stirred at room temperature for 24 h. The resulting mixture was then quenched with water. The mixture was extracted with dichloromethane, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (3:1, v/v) gave *N*-{2-(thiophen-2-yl)phenyl}picolinamide (**1r**, 1.3 g, 4.5 mmol) in 92% yield.

Cu-Catalyzed Intramolecular C-H/N-H Coupling of 2-Aminobiphenyls 1

Synthesis of **2a**: Cu(OAc)₂ (14 mg, 0.075 mmol), *N*-{(1,1'-biphenyl)-2-yl}picolinamide (**1a**, 69 mg, 0.25 mmol), acetic acid (15 mg, 0.25 mmol), manganese dioxide (43 mg, 0.50 mmol), and *N,N*-dimethylformamide (DMF, 1.5 mL) were placed in a 2 mL microwave vessel. The vessel was sealed with a cap and the mixture was irradiated under microwave reactor conditions at 200 °C for 1 h. The resulting mixture was then quenched with water and ethylenediamine (ca. 1 mL). The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (5:1, v/v) gave 9*H*- carbazole (**2a**, 40 mg, 0.24 mmol) in 96% yield.

Synthesis of **2f**: Cu(OAc)₂ (91 mg, 0.50 mmol), *N*-{4'-(dimethylamino)-(1,1'-biphenyl)-2-yl}picolinamide (**1f**, 79 mg, 0.25 mmol), acetic acid (15 mg,

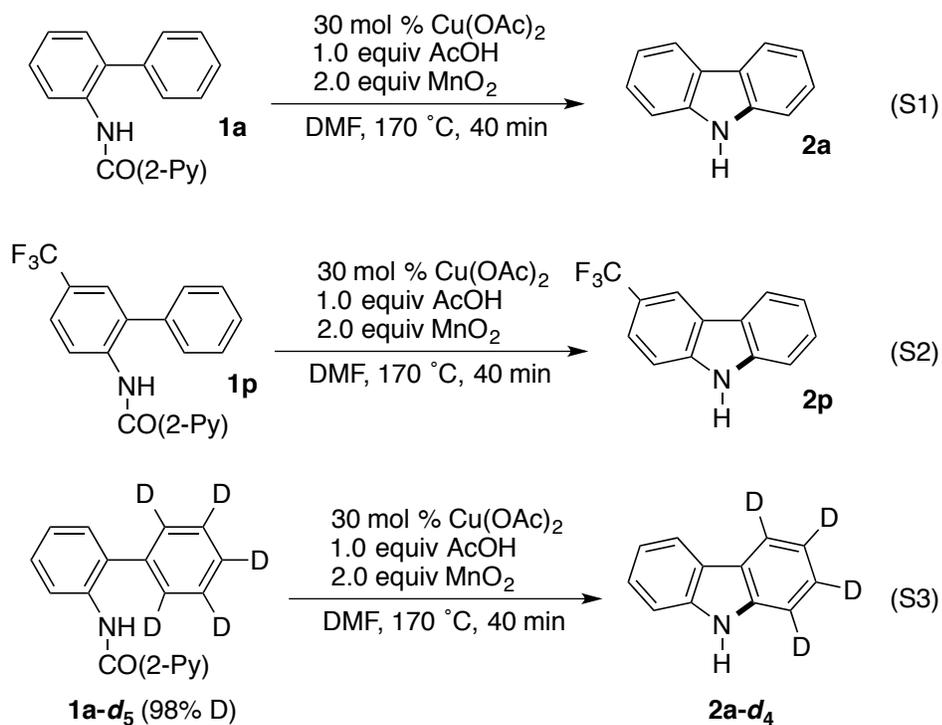
0.25 mmol), and *N,N*-dimethylformamide (DMF, 1.5 mL) were placed in a 2 mL microwave vessel. The vessel was sealed with a cap, and the mixture was irradiated under microwave reactor conditions at 200 °C for 1 h. The resulting mixture was then quenched with water. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate. The dried solution was concentrated in vacuo. To the residue, ethanol (10 mL) and 6 M NaOH aq. (3 mL) were added, and the resulting solution was stirred at room temperature for additional 4 h. The resulting mixture was neutralized with 1 M HCl aq. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (3:1, v/v) gave *N,N*-dimethyl-9*H*-carbazol-2-amine (**2f**, 43 mg, 0.21 mmol) in 82% yield.

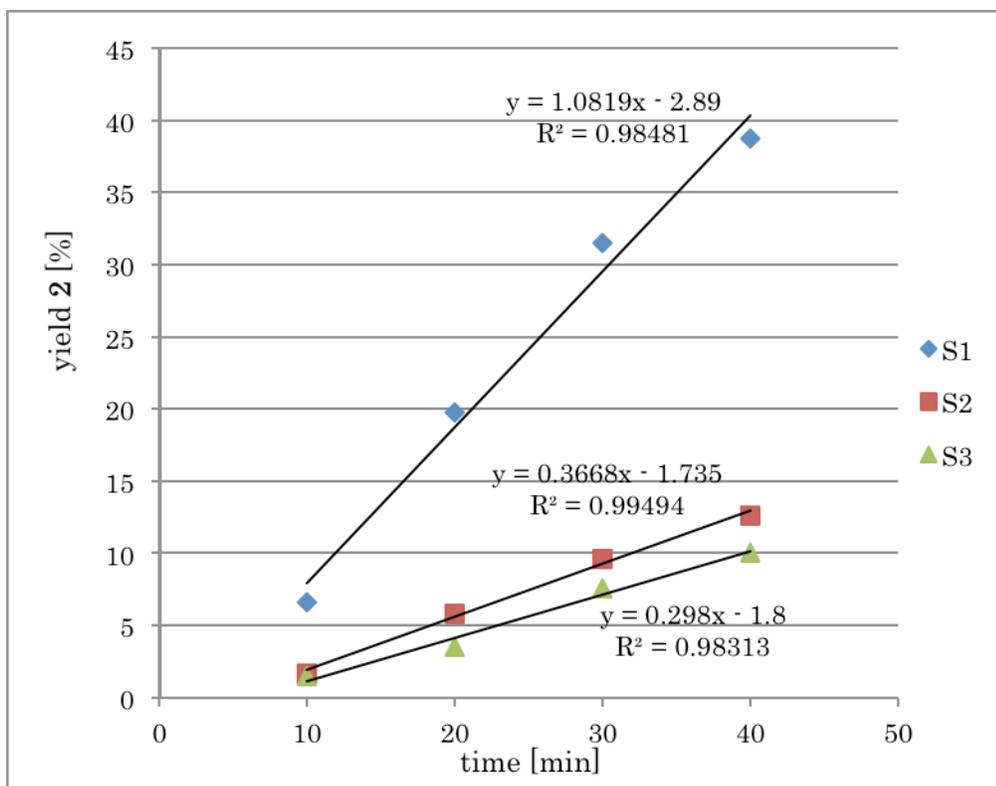
Synthesis of **2v**: Cu(OAc)₂ (27 mg, 0.15 mmol), *N,N'*-{(2,2'-bithiophene)-5,5'-diylbis(4-chloro-2,1-phenylene)}dipicolinamide (**1v**, 160 mg, 0.25 mmol), acetic acid (30 mg, 0.50 mmol), manganese dioxide (87 mg, 1.0 mmol), and *N,N*-dimethylformamide (DMF, 1.5 mL) were placed in a 2 mL microwave vessel. The vessel was sealed with a cap and the mixture was irradiated under microwave reactor conditions at 200 °C for 1 h. The resulting mixture was diluted with hot ethyl acetate and filtered off through a short pad of Celite. To the filtrate, water and ethylenediamine (ca. 1 mL) were added, and the mixture was extracted with ethyl acetate before the combined organic layer was dried over sodium sulfate. The dried solution was concentrated in vacuo. The residual solid was collected and washed with hexane to provide 7,7'-dichloro-4*H*,4'*H*-2,2'-bithieno[3,2-*b*]indole (**2v**, 78 mg, 0.19 mmol) in 75% yield.

Kinetic Studies

All kinetic experiments were carried out under the conventional heating conditions with an oil-bath, because under microwave-assisted conditions the reaction proceeded in the course of preheating time up to 200 °C, and the conversion at an early stage was difficult to be monitored.

The initial reaction rates of **1a**, **1p**, and **1a-d₅** were obtained by plotting the products yields along the reaction time (eqs S1–S3).



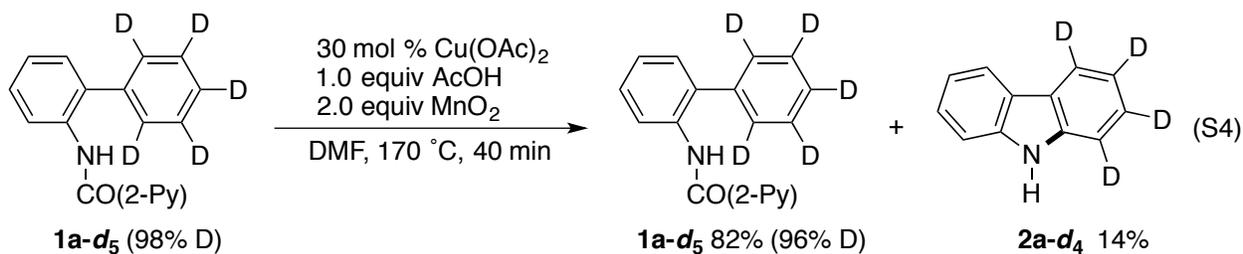


According to the above data, the ratios of initial rate constants were calculated as follows.

$$k_{\text{H}}/k_{\text{CF}_3} = 1.0819/0.3668 = 2.9 \quad (\text{eq S1 vs eq S2})$$

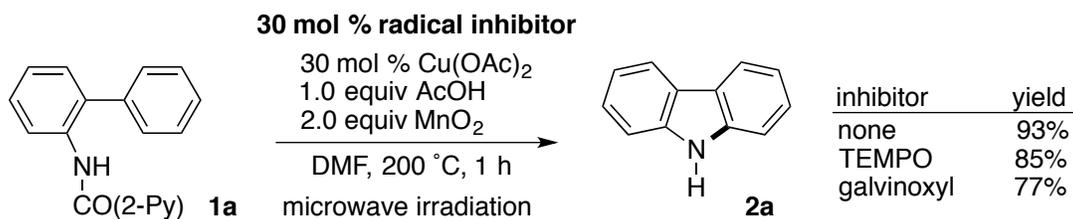
$$k_{\text{H}}/k_{\text{D}} = 1.0819/0.298 = 3.6 \quad (\text{eq S1 vs eq S3})$$

Additionally, we confirmed that at the early stage (40 min) of the reaction with **1a-d₅** negligible H/D exchange occurred eq (S4). Thus, the C–H cleavage appeared to be irreversible.



Control Experiments in the Presence of Radical Inhibitors

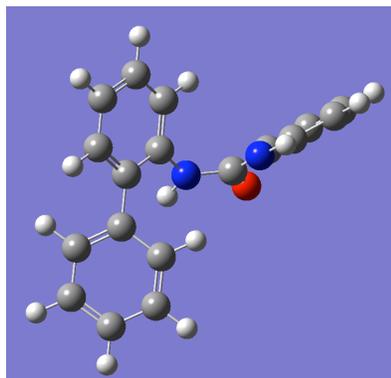
The control experiments in the presence of radical inhibitors, TEMPO and galvinoxyl, were carried out (Scheme S1). We observed only minor effects on the reaction efficiency.



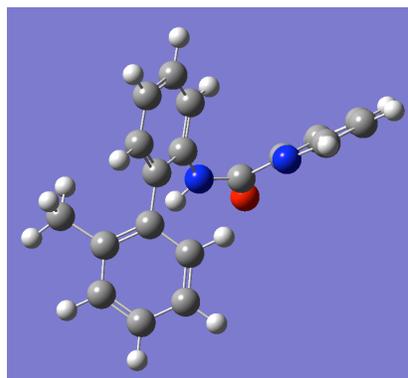
Scheme S1. Control experiments in the presence of radical inhibitors.

DFT Calculation about Stable Conformations of **1a** and **1k**

The most stable conformations of **1a** and **1k** were calculated by DFT at the RB3LYP/6-31G(d) level of theory. We observed the relatively large dihedral angle of two phenyl rings in **1k** that bears the Me group at the 2' position (Figure. S1).



1a: dihedral angle = 57.7915°



1k: dihedral angle = 61.2636°

Figure S1. The most stable conformations of **1a** (left) and **1k** (right) calculated by DFT at the RB3LYP/6-31G(d) level of theory.

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Characterization Data for Products

^1H , ^{13}C , and ^{19}F NMR spectra for all compounds are attached in the last part.

9H-Carbazole (2a) white solid; m.p. 243.0-244.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.15 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 2H), 7.38 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 2H), 7.48 (td, $J = 0.8, 8.0$ Hz, 2H), 8.10 (td, $J = 0.8, 8.0$ Hz, 2H), 11.22 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 110.87, 118.41, 120.08, 122.33, 125.43, 139.66; HRMS (EI) m/z (M^+) calcd for $\text{C}_{12}\text{H}_9\text{N}$: 167.0735, found: 167.0733.

2-Methyl-9H-carbazole (2b) white solid; m.p. 244.0-246.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 2.47 (s, 3H), 6.97 (dd, $J = 0.8, 8.0$ Hz, 1H), 7.11 (ddd, 0.8, 7.2, 8.0 Hz, 1H), 7.26 (d, $J = 0.8$ Hz, 1H), 7.33 (ddd, $J = 1.2, 7.2, 8.0$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 11.10 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 21.68, 110.76, 110.86, 118.32, 119.75, 119.82, 119.99, 120.13, 122.46, 124.91, 134.94, 139.67, 140.16; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_{11}\text{N}$: 181.0891, found: 181.0891.

2-Methoxy-9H-carbazole (2c) white solid; m.p. 237.0-238.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 3.84 (s, 3H) 6.77 (dd, $J = 2.4, 8.0$ Hz, 1H), 6.96 (d, $J = 2.4$ Hz, 1H), 7.10 (t, $J = 8.0$ Hz, 1H), 7.28 (dt, $J = 1.2, 8.0$ Hz, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 11.08 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 55.22, 94.42, 107.64, 110.56, 116.15, 118.49, 119.19, 120.84, 122.63, 124.06, 139.69, 141.06, 158.46; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_{11}\text{NO}$: 197.0841, found: 197.0839.

2-(Trifluoromethyl)-9H-carbazole (2d) white solid; m.p. 206.0-208.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.24 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.47 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.50 (dd, $J = 0.8, 8.4$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 0.8$ Hz, 1H), 8.23 (d, $J = 8.0$ Hz, 1H), 8.34 (d, $J = 8.4$ Hz, 1H), 11.62 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 107.95 (q, $J = 3.7$ Hz), 111.50, 114.75 (q, $J = 3.7$), 119.30, 121.00, 121.03, 125.08 (q, $J = 271.9$ Hz), 125.31, 125.60 (q, $J = 31.2$ Hz), 127.02, 129.14, 138.75, 140.81; ^{19}F NMR (376 MHz, DMSO- d_6) δ -59.24; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_8\text{F}_3\text{N}$: 235.0609, found: 235.0608.

2-Chloro-9H-carbazole (2e) white solid; m.p. 235.5-237.5 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.17 (dd, $J = 2.0, 8.4$ Hz, 1H), 7.18 (ddd, $J = 1.2, 7.2, 8.4$ Hz, 1H), 7.41 (ddd, $J = 1.2, 7.2, 8.4$ Hz, 1H), 7.51

(d, $J = 8.4$ Hz, 1H), 7.52 (d, $J = 2.0$ Hz, 1H), 8.12 (d, $J = 8.4$, 2H), 11.39 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 110.55, 111.17, 118.63, 119.04, 120.28, 121.28, 121.51, 121.76, 125.92, 129.83, 140.05, 140.26; HRMS (EI) m/z (M^+) calcd for $\text{C}_{12}\text{H}_8\text{ClN}$: 201.0345, found: 201.0344.

***N,N*-Dimethyl-9*H*-carbazol-2-amine (2f)** cream-colored solid; m.p. 224.5-226.5 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 2.97 (s, 6H), 6.67 (s, 1H), 6.68 (dd, $J = 2.4, 9.2$ Hz, 1H), 7.04 (ddd, $J = 0.8, 7.2, 7.6$ Hz, 1H), 7.20 (ddd, $J = 0.8, 7.2$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 9.2$ Hz, 1H), 7.88 (d, $J = 7.6$ Hz, 1H), 10.82 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 40.76, 93.30, 106.42, 110.13, 113.29, 118.18, 118.54, 120.50, 123.18, 123.22, 139.47, 141.81, 149.81; HRMS (EI) m/z (M^+) calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2$: 210.1157, found: 210.1153.

(9*H*-Carbazol-2-yl)(phenyl)methanone (2g) yellow solid; m.p. 165.0-166.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.23 (t, $J = 7.2$ Hz, 1H), 7.48 (ddd, $J = 1.2, 7.2, 8.4$ Hz, 1H), 7.56-7.61 (m, 4H), 7.69 (dt, $J = 0.8, 7.2$ Hz, 1H), 7.78-7.80 (m, 2H), 7.89 (s, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 8.28 (d, $J = 8.4$ Hz, 1H), 11.55 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 111.42, 113.33, 119.21, 120.08, 120.17, 121.16, 121.60, 125.93, 127.10, 128.44, 129.54, 132.17, 133.80, 138.11, 138.86, 141.20, 196.08; HRMS (EI) m/z (M^+) calcd for $\text{C}_{19}\text{H}_{13}\text{NO}$: 271.0997, found: 271.0999.

Methyl 9*H*-carbazole-2-carboxylate (2h) white solid; m.p. 186.0-188.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 3.90 (s, 3H), 7.21 (ddd, $J = 1.2, 6.8, 8.0$ Hz, 1H), 7.47 (ddd, $J = 1.2, 6.8, 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.78 (dd, $J = 1.2, 8.0$ Hz, 1H), 8.12 (d, $J = 1.2$ Hz, 1H), 8.21 (d, $J = 8.0$ Hz, 1H), 8.23 (d, $J = 8.0$ Hz, 1H), 11.56 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 52.05, 111.41, 112.31, 119.14, 119.21, 120.15, 121.10, 121.57, 126.17, 126.27, 127.05, 139.01, 141.06, 166.91; HRMS (EI) m/z (M^+) calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_2$: 225.0790, found: 225.0789.

9*H*-Carbazole-2-carbonitrile (2i) white solid; m.p. 135.0-137.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.24 (t, $J = 8.0$ Hz, 1H), 7.50 (t, $J = 8.0$ Hz, 1H), 7.53 (d, 8.0 Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.98 (s, 1H), 8.24 (d, $J = 8.0$ Hz, 1H), 8.32 (dd, $J = 2.4, 8.0$ Hz, 1H), 11.74 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 106.79, 111.60, 115.22, 119.51, 120.14, 121.30 (2C), 121.34, 121.52, 125.94, 127.56, 138.54, 141.00; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_8\text{N}_2$: 192.0687, found: 192.0689.

2-Phenyl-9*H*-carbazole (2j) white solid; m.p. 285.0-287.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.17

(t, $J = 7.2$ Hz, 1H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.45-7.52 (m, 4H), 7.72 (s, 1H), 7.75 (d, $J = 7.2$ Hz, 2H), 8.13 (d, $J = 8.0$ Hz, 1H), 8.18 (d, $J = 8.0$ Hz, 1H), 11.32 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 108.85, 110.97, 117.81, 118.67, 120.23, 120.58, 121.80, 122.15, 125.60, 126.98, 127.04, 128.91, 137.82, 140.26, 140.35, 141.20; HRMS (EI) m/z (M^+) calcd for $\text{C}_{18}\text{H}_{13}\text{N}$: 243.1048, found: 243.1047.

4-Methyl-9H-carbazole (2k) light yellow solid; m.p. 126.0-128.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 2.80 (s, 3H), 6.94 (td, $J = 0.8, 7.6$ Hz, 1H), 7.17 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.38 (ddd, $J = 1.2, 7.2, 8.4$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 11.28 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 20.48, 108.53, 110.69, 118.50, 119.89, 120.84, 122.09, 122.87, 124.87, 125.31, 132.34, 139.67, 139.71; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_{11}\text{N}$: 181.0891, found: 181.0893.

3-Methyl-9H-carbazole (2l, 2o) white solid; m.p. 206.0-207.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 2.46 (s, 3H), 7.11 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.20 (dd, $J = 0.8, 8.0$ Hz, 1H), 7.34 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.89 (s, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 11.09 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 21.11, 110.62, 110.84, 118.22, 119.90, 120.02, 122.20, 122.52, 125.28, 126.81, 127.06, 137.94, 139.96; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_{11}\text{N}$: 181.0891, found: 181.0891.

3-(Trifluoromethyl)-9H-carbazole (2m, 2p) white solid; m.p. 163.5.0-164.5 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.24 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.47 (ddd, $J = 1.2, 7.2, 8.4$ Hz, 1H), 7.56 (td, $J = 0.8, 8.0$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.69 (dd, $J = 1.2, 8.4$ Hz, 1H), 8.29 (td, $J = 1.2, 8.4$ Hz, 1H), 8.57 (t, $J = 1.2$ Hz, 1H), 11.72 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 111.39, 111.41, 117.89 (q, $J = 3.9$ Hz), 119.09 (q, $J = 31.1$ Hz), 119.41, 120.84, 121.97 (q, $J = 3.9$ Hz), 121.98, 122.09, 125.53 (q, $J = 269.5$ Hz), 126.60, 140.37, 141.41; ^{19}F NMR (376 MHz, DMSO- d_6) δ -58.12; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_8\text{F}_3\text{N}$: 235.0609, found: 235.0607.

5H-Benzo[b]carbazole (2n) light brown solid; m.p. 309.5-311.5 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.16-7.23 (m, 1H), 7.36 (ddd, $J = 1.2, 6.8, 8.0$ Hz, 1H), 7.43-7.50 (m, 3H), 7.85 (s, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 8.05 (dd, $J = 0.4, 8.0$ Hz, 1H), 8.25 (d, $J = 8.0$ Hz, 1H), 8.68 (s, 1H), 11.20 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 105.06, 110.53, 118.26, 118.54, 121.02, 122.12, 122.28, 124.75, 125.10,

126.89, 127.27, 127.45, 128.25, 132.21, 139.61, 142.43; HRMS (EI) m/z (M^+) calcd for $C_{16}H_{11}N$: 217.0891, found: 217.0892.

3-Chloro-9H-carbazole (2q) white solid; m.p. 198.0-199.0 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.17 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.38 (dd, $J = 2.0, 8.4$ Hz, 1H), 7.41 (ddd, $J = 0.4, 7.2, 7.6$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.50 (d, $J = 7.6$ Hz, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 8.22 (d, $J = 2.0$ Hz, 1H), 11.42 (s, 1H); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 112.20, 112.37, 118.85, 119.76, 120.68, 121.55, 122.80, 123.72, 125.25, 126.30, 138.10, 140.29; HRMS (EI) m/z (M^+) calcd for $C_{12}H_8ClN$: 201.0345, found: 201.0346.

4H-Thieno[3,2-b]indole (2r) white solid; m.p. 175.5-177.5 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.08 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.20 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.20 (d, $J = 5.2$ Hz, 1H), 7.48 (td, $J = 0.8, 8.0$ Hz, 1H), 7.57 (d, $J = 5.2$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 11.39 (s, 1H); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 112.20, 112.29, 115.62, 118.25, 118.76, 121.20, 122.19, 127.42, 141.20, 143.80; HRMS (EI) m/z (M^+) calcd for $C_{10}H_7NS$: 173.0299, found: 173.0298.

10H-Benzo[4,5]thieno[3,2-b]indole (2s) white solid; m.p. 254.0-256.0 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.15 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.28 (ddd, $J = 1.2, 7.2, 8.0$ Hz, 1H), 7.39 (ddd, $J = 1.2, 7.2, 8.0$ Hz, 1H), 7.49 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 12.13 (s, 1H); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 112.62, 113.82, 118.83, 119.38, 120.16, 121.51, 122.85, 124.31, 124.44, 124.55, 126.66, 137.49, 140.58, 141.96; HRMS (EI) m/z (M^+) calcd for $C_{14}H_9NS$: 223.0456, found: 223.0455.

10H-Benzofuro[3,2-b]indole (2t) white solid; m.p. 196.5-197.5 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.15 (ddd, $J = 0.8, 7.2, 8.0$ Hz, 1H), 7.24 (ddd, $J = 1.2, 7.2, 8.4$ Hz, 1H), 7.35-7.38 (m, 2H), 7.56 (td, $J = 0.8, 8.0$ Hz, 1H), 7.70-7.72 (m, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.78-7.81 (m, 1H), 11.51 (s, 1H); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 112.60, 112.76, 113.06, 116.36, 118.32, 118.53, 119.48, 122.36, 122.92, 123.95, 125.30, 139.30, 142.03, 158.57; HRMS (EI) m/z (M^+) calcd for $C_{14}H_9NO$: 207.0684, found: 207.0685.

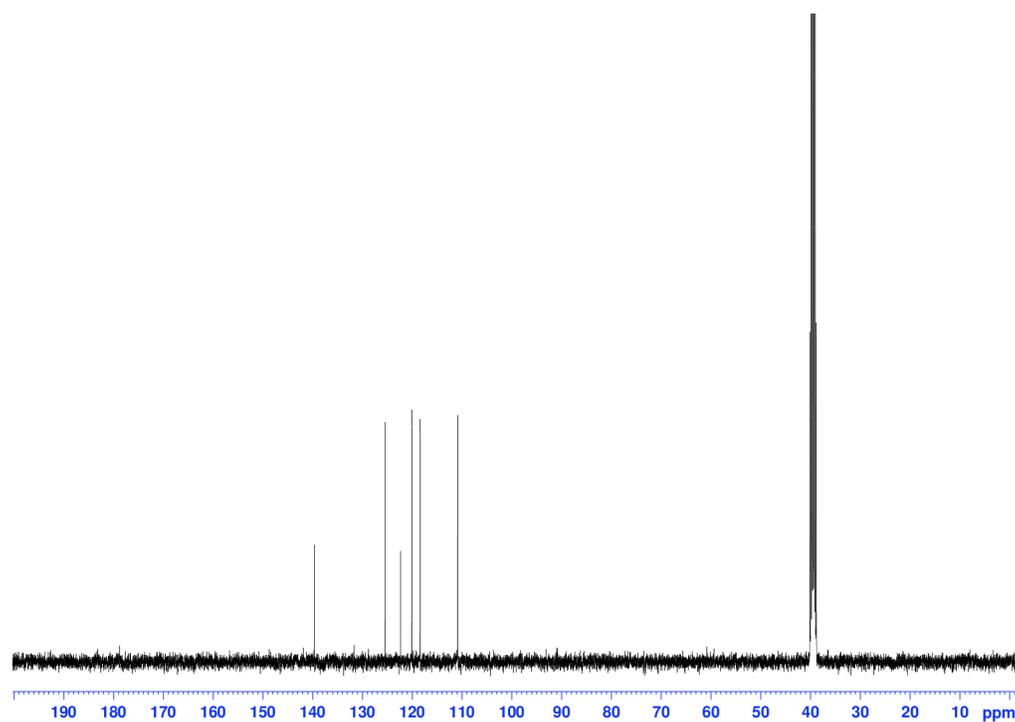
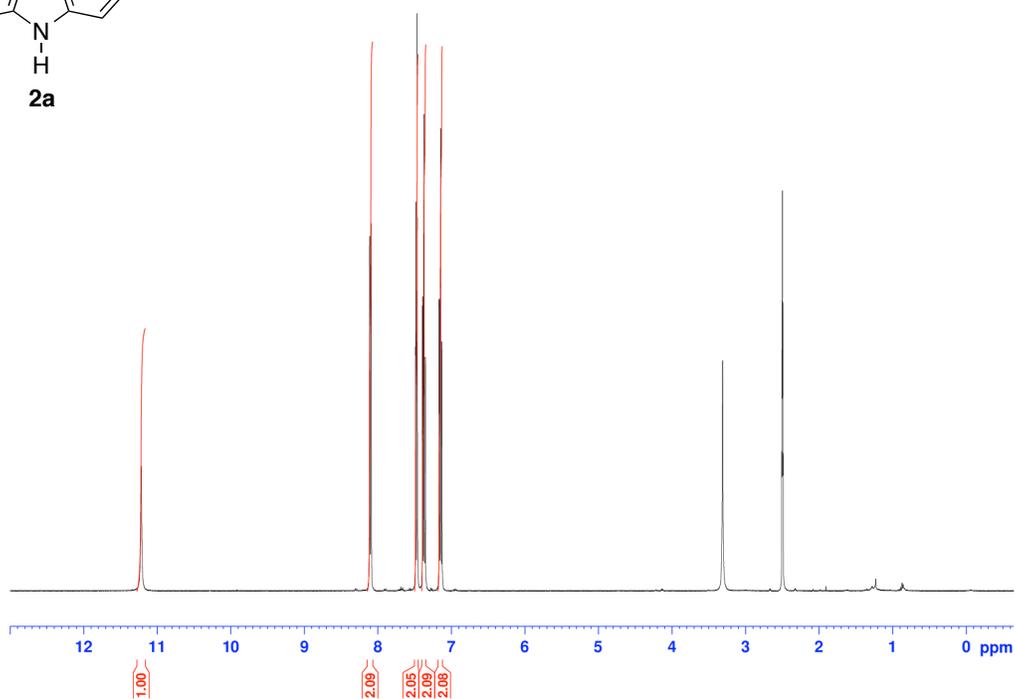
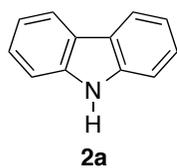
3-Methyl-3,10-dihydropyrrolo[3,2-a]carbazole (2u) light green solid; m.p. 215.5-217.5 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 3.87 (s, 3H), 6.74 (dd, $J = 0.8, 3.2$ Hz, 1H), 7.12 (ddd, $J = 0.8, 7.2, 8.0$ Hz,

1H), 7.24 (dd, $J = 0.8, 8.0$ Hz, 1H), 7.26 (ddd, $J = 1.2, 7.2, 8.0$ Hz, 1H), 7.31 (d, $J = 3.2$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 11.52 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 33.01, 97.95, 102.48, 110.68, 113.33, 113.56, 113.92, 118.36, 118.80, 122.90, 123.95, 127.48, 133.23, 135.54, 138.38; HRMS (EI) m/z (M^+) calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2$: 220.1000, found: 220.1002.

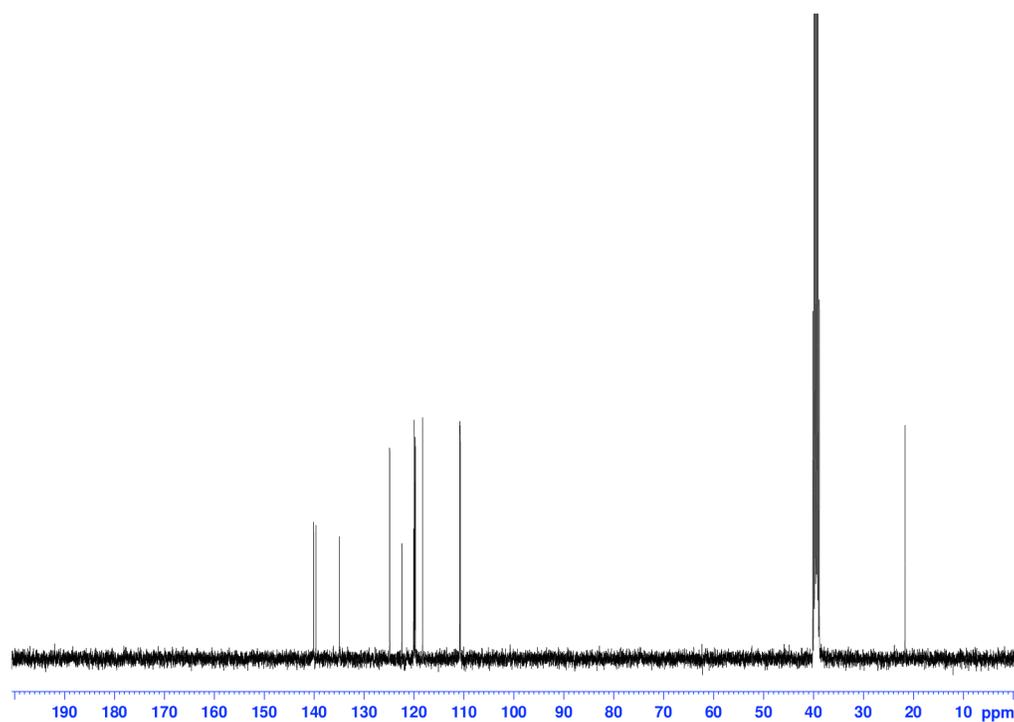
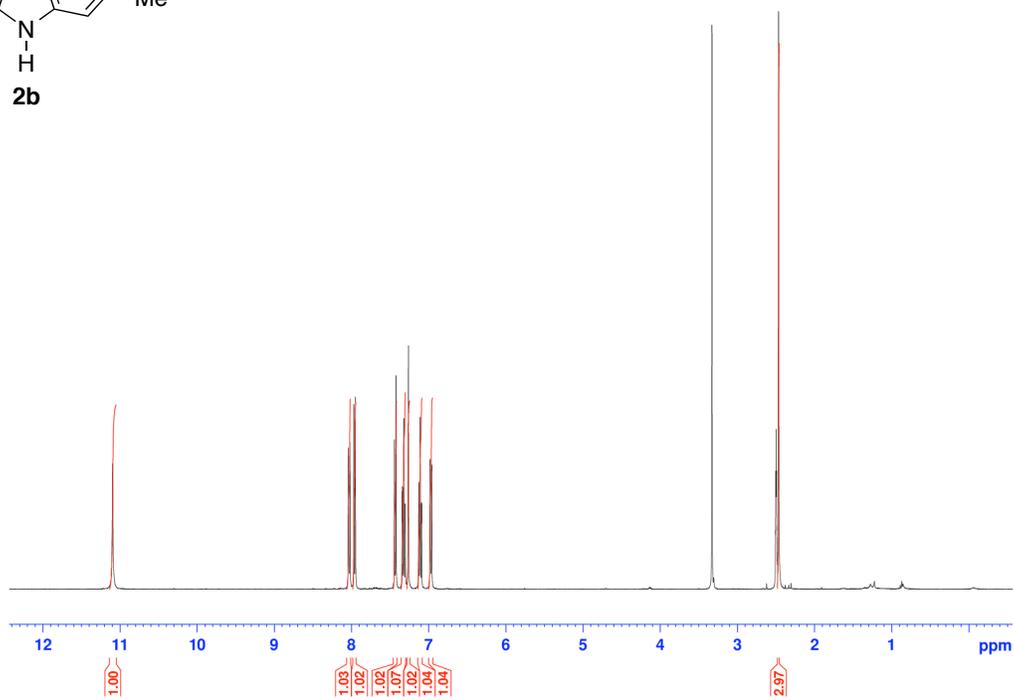
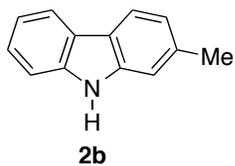
1-Methyl-1,9-dihydropyrrolo[2,3-*b*]carbazole (2u') white solid; m.p. 249.0-251.0 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 3.81 (s, 3H), 6.50 (dd, $J = 0.8, 3.2$ Hz, 1H), 7.08 (ddd, $J = 1.2, 6.8, 8.0$ Hz, 1H), 7.27-7.31 (m, 3H), 7.39 (d, $J = 8.0$ Hz, 1H), 8.07 (d, $J = 7.6$ Hz, 1H), 8.22, (s, 1H), 10.85 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 32.67, 89.29, 100.08, 110.00, 110.63, 117.68, 118.27, 119.39, 123.08, 123.12, 124.46, 128.87, 136.95, 137.80, 140.67; HRMS (EI) m/z (M^+) calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2$: 220.1000, found: 220.0998.

7,7'-Dichloro-4*H*,4'*H*-2,2'-bithieno[3,2-*b*]indole (2v) ocher solid; m.p. >300 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 7.21 (dd, $J = 2.0, 8.8$ Hz, 2H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.55 (s, 2H), 7.86 (d, $J = 2.0$ Hz, 2H), 11.68 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 108.70, 113.66, 113.89, 117.75, 122.14, 122.39, 123.61, 139.53, 139.72, 144.74; HRMS (APCI) m/z ($[\text{M}+\text{H}]^+$) calcd for $\text{C}_{20}\text{H}_{11}\text{Cl}_2\text{N}_2\text{S}_2$: 412.9735, found: 412.9745.

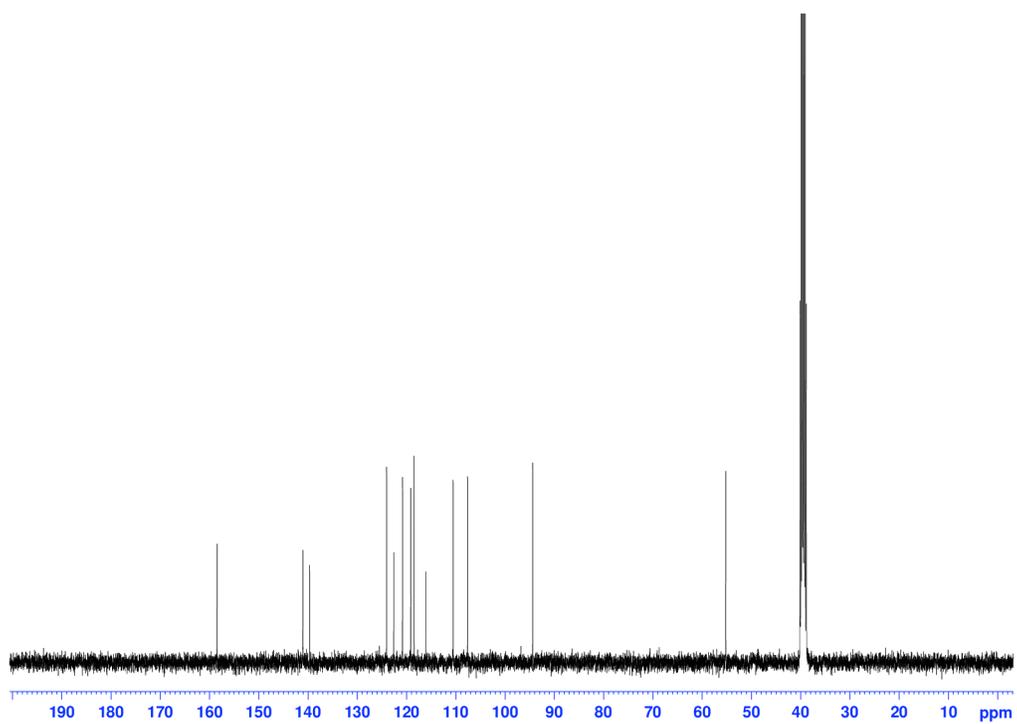
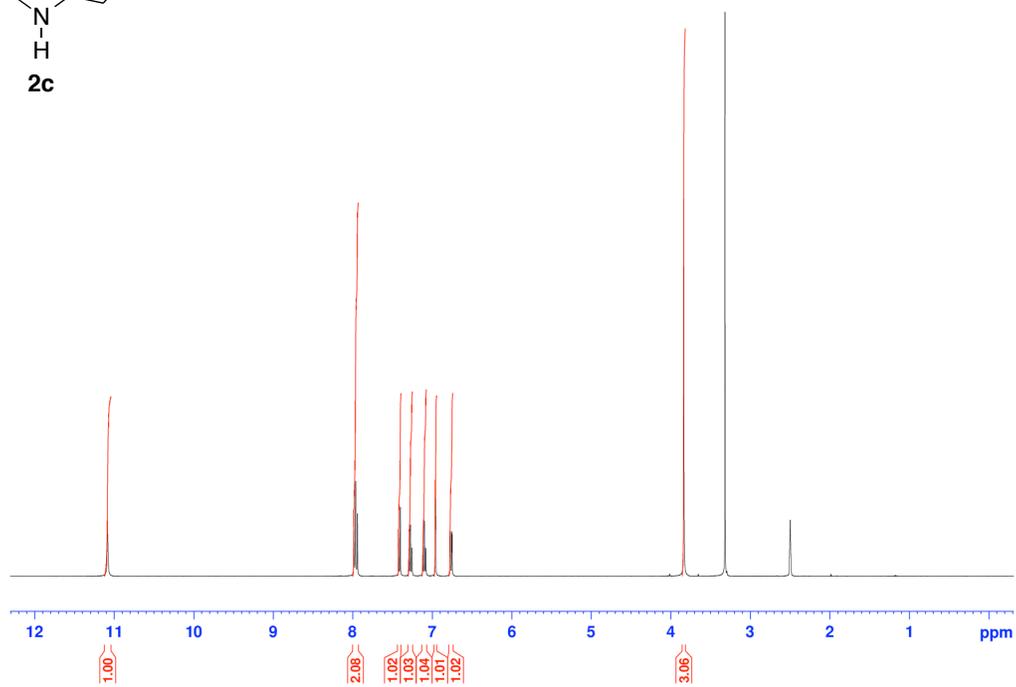
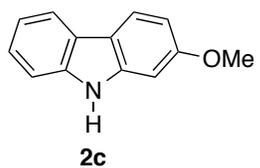
[¹H and ¹³C NMR Spectra of **2a**]



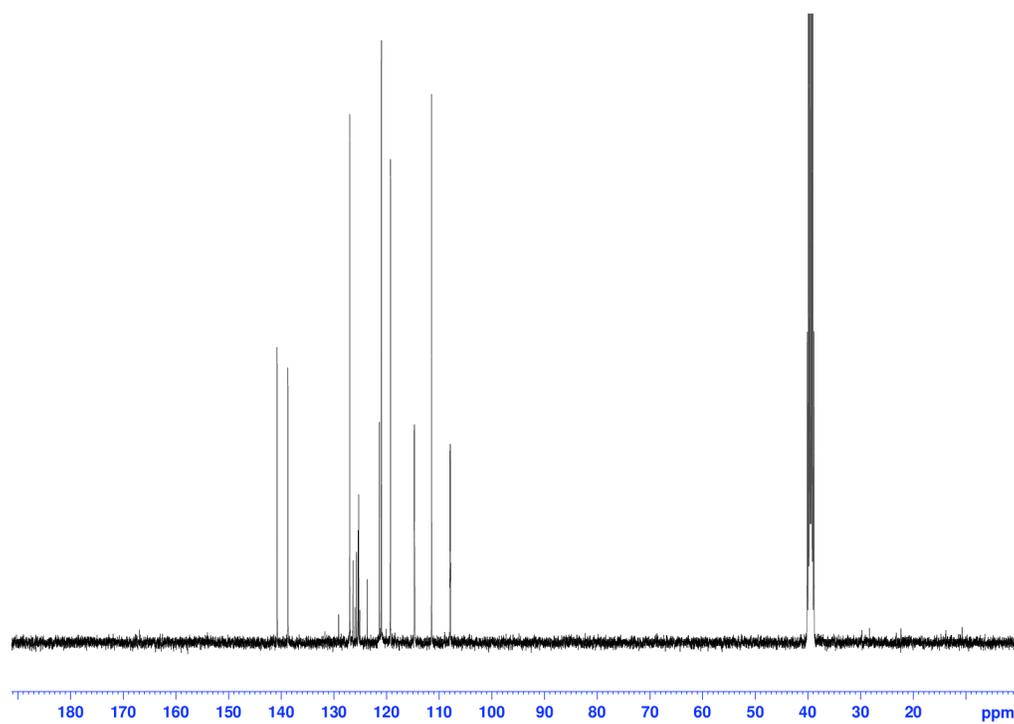
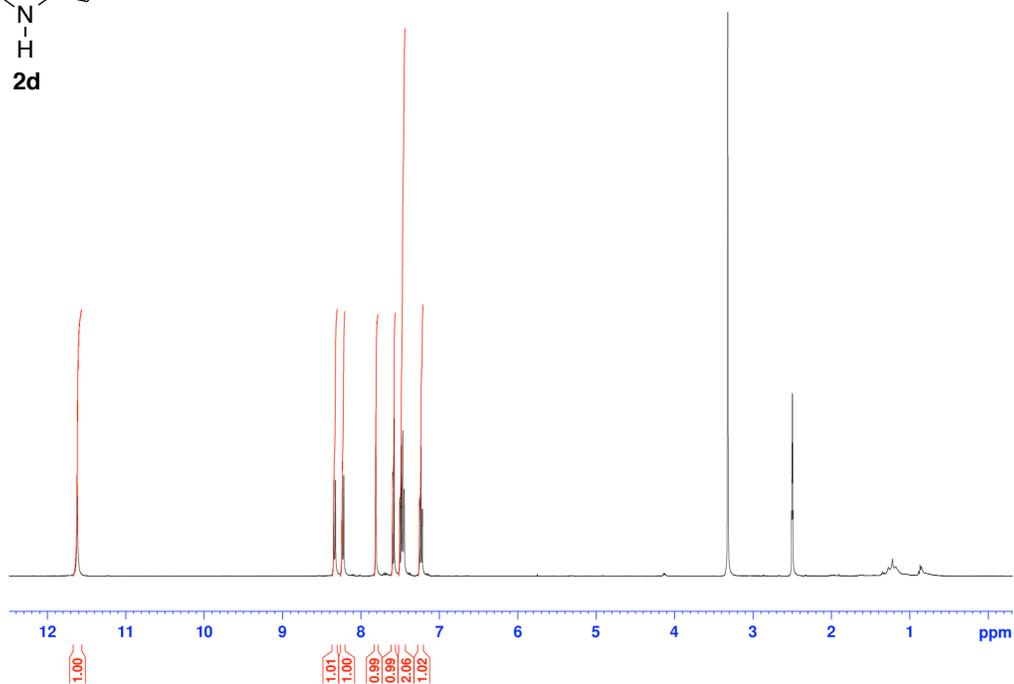
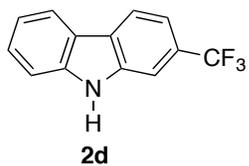
[¹H and ¹³C NMR Spectra of **2b**]

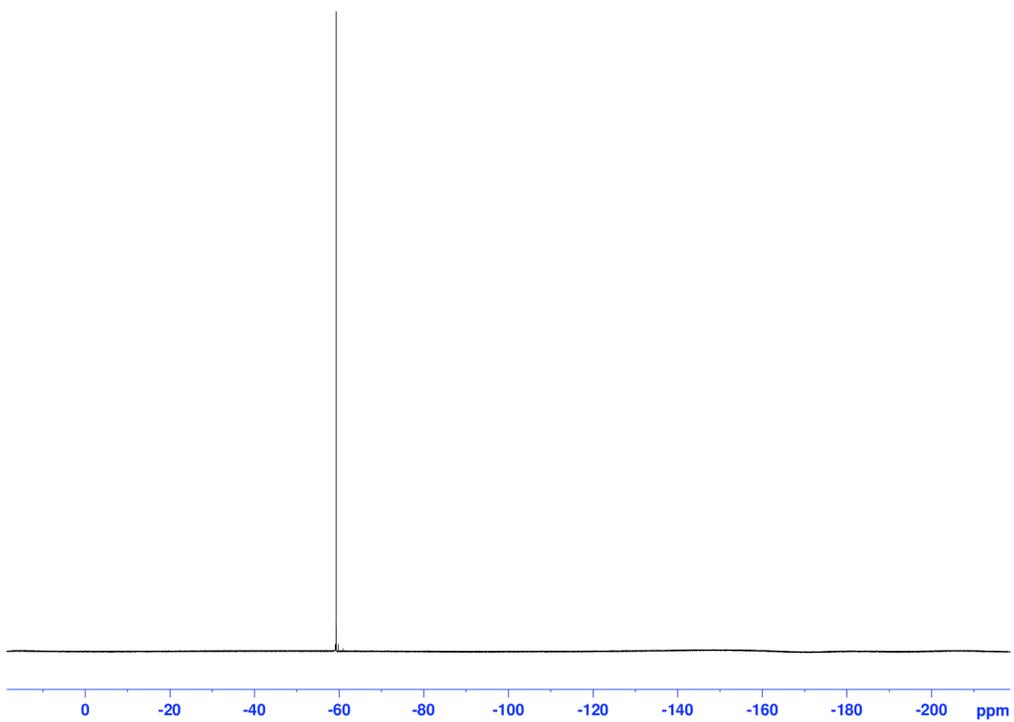


[¹H and ¹³C NMR Spectra of **2c**]

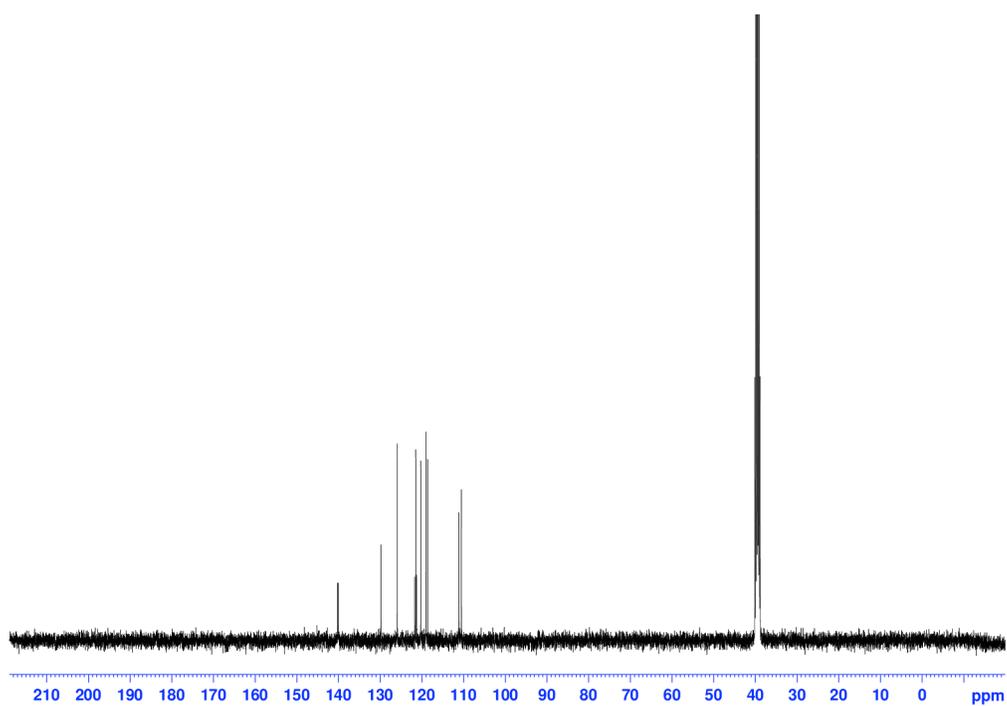
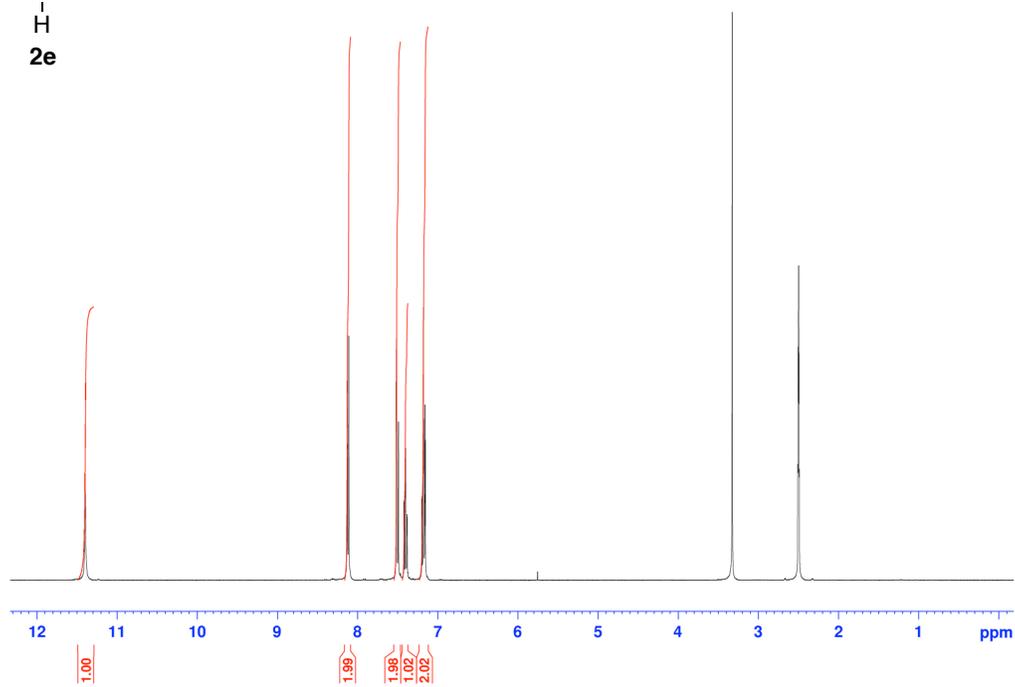
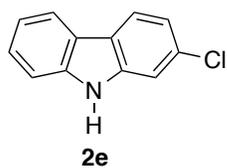


[^1H , ^{13}C , and ^{19}F NMR Spectra of **2d**]

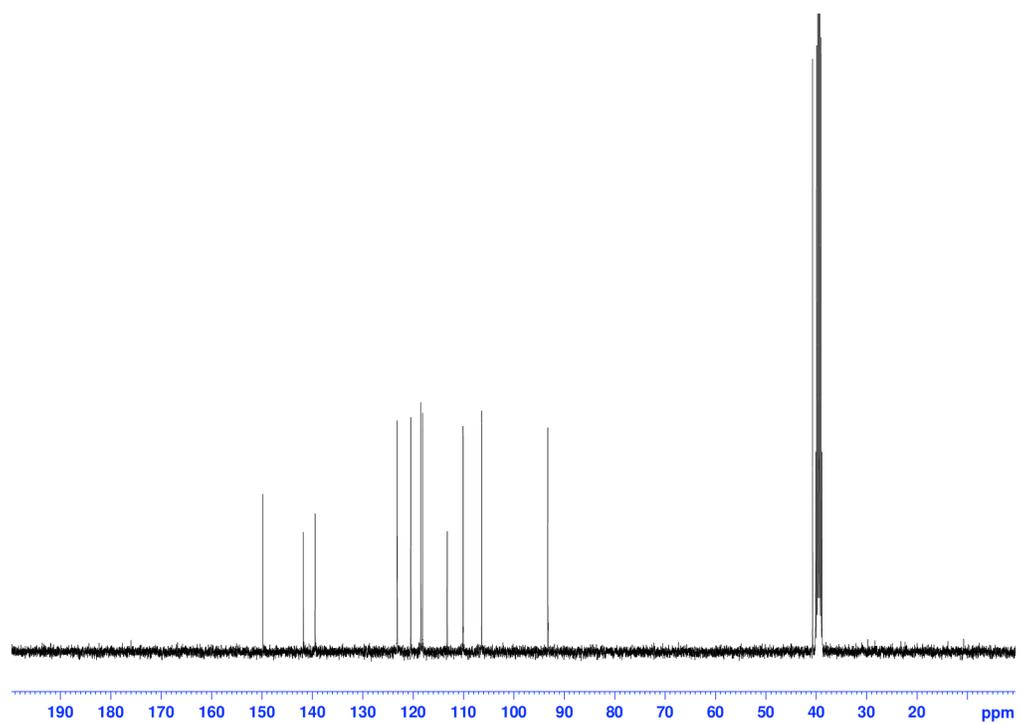
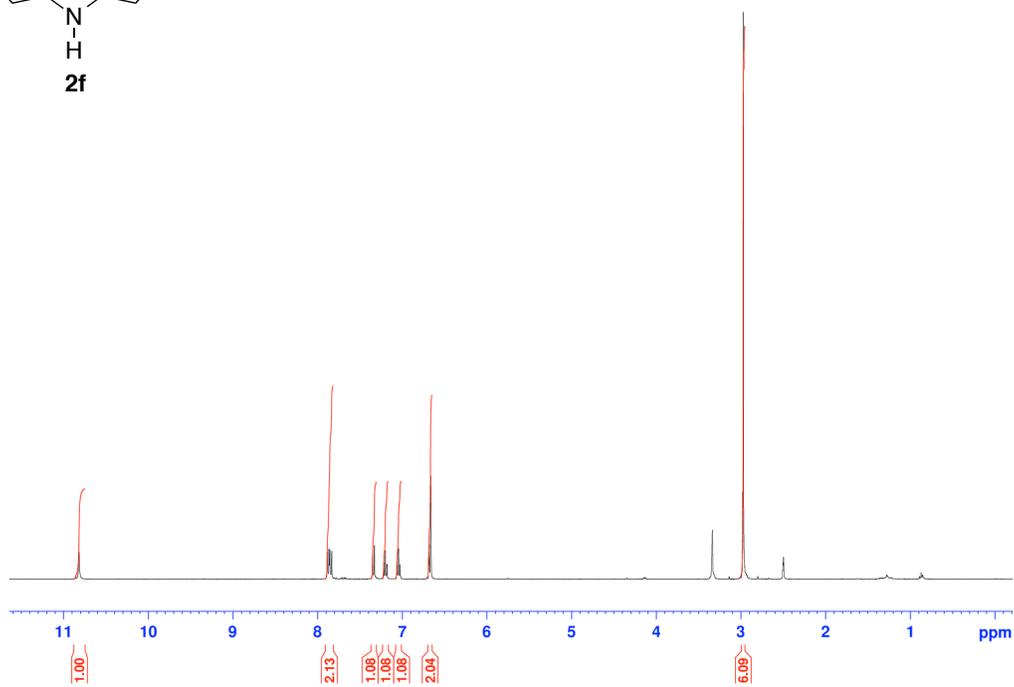
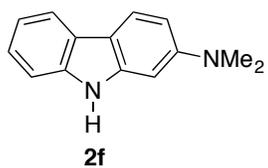




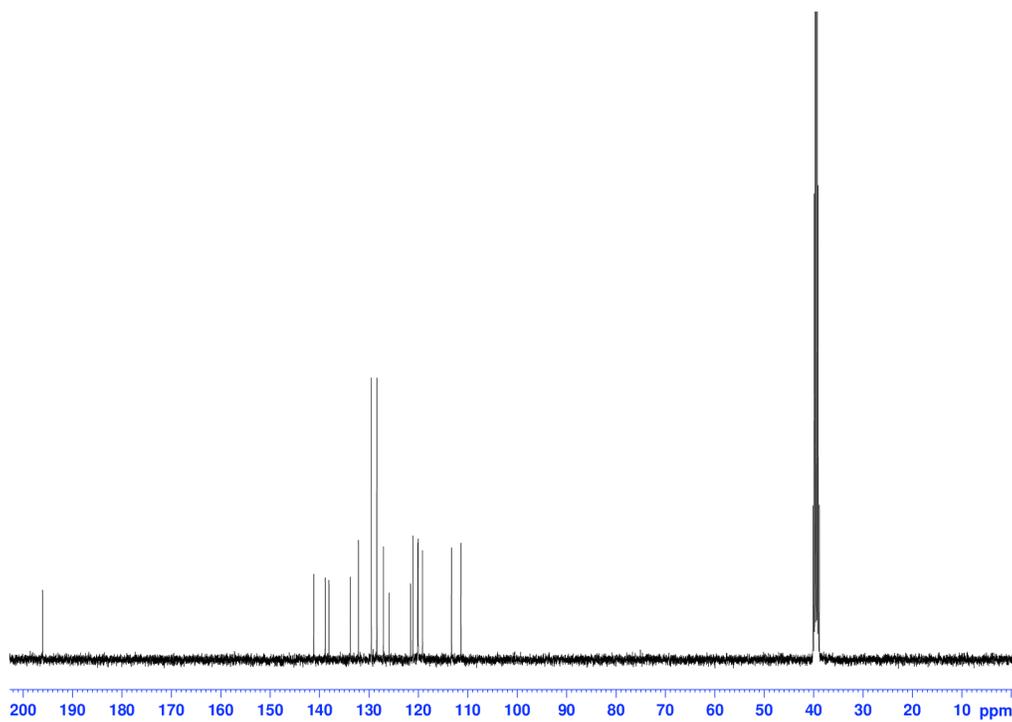
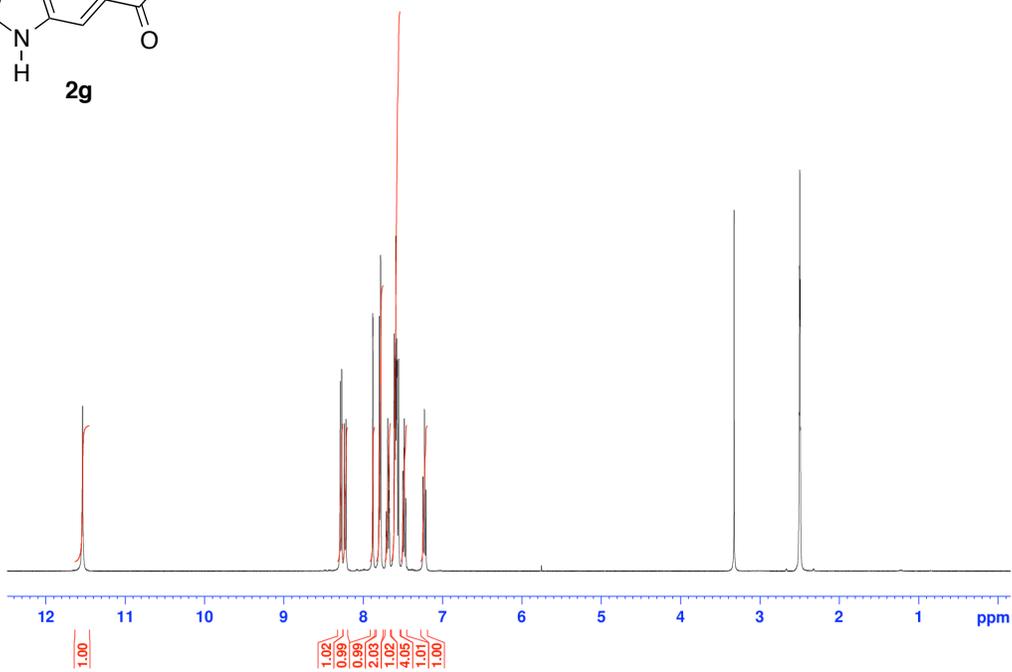
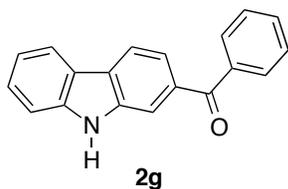
[¹H and ¹³C NMR Spectra of **2e**]



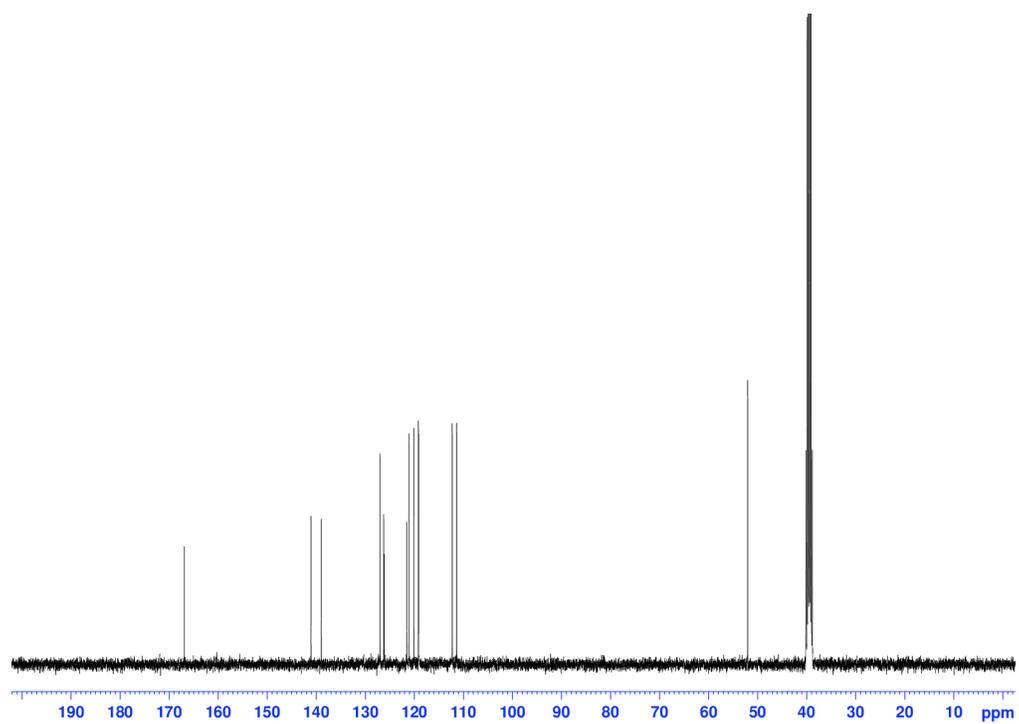
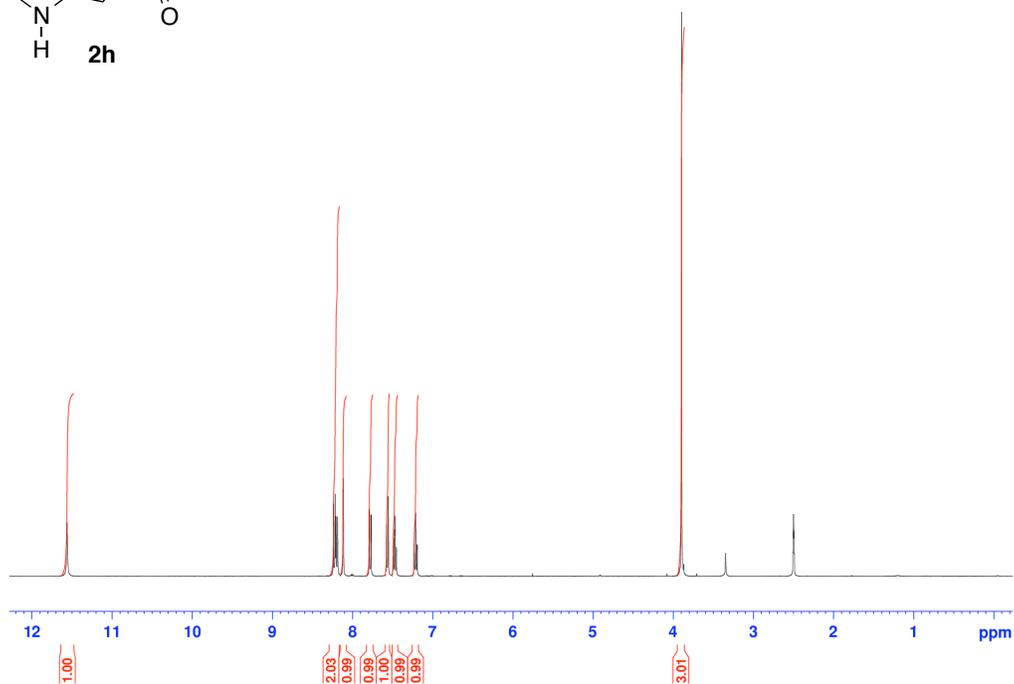
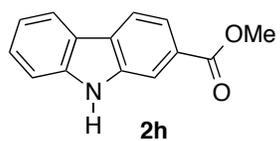
[¹H and ¹³C NMR Spectra of **2f**]



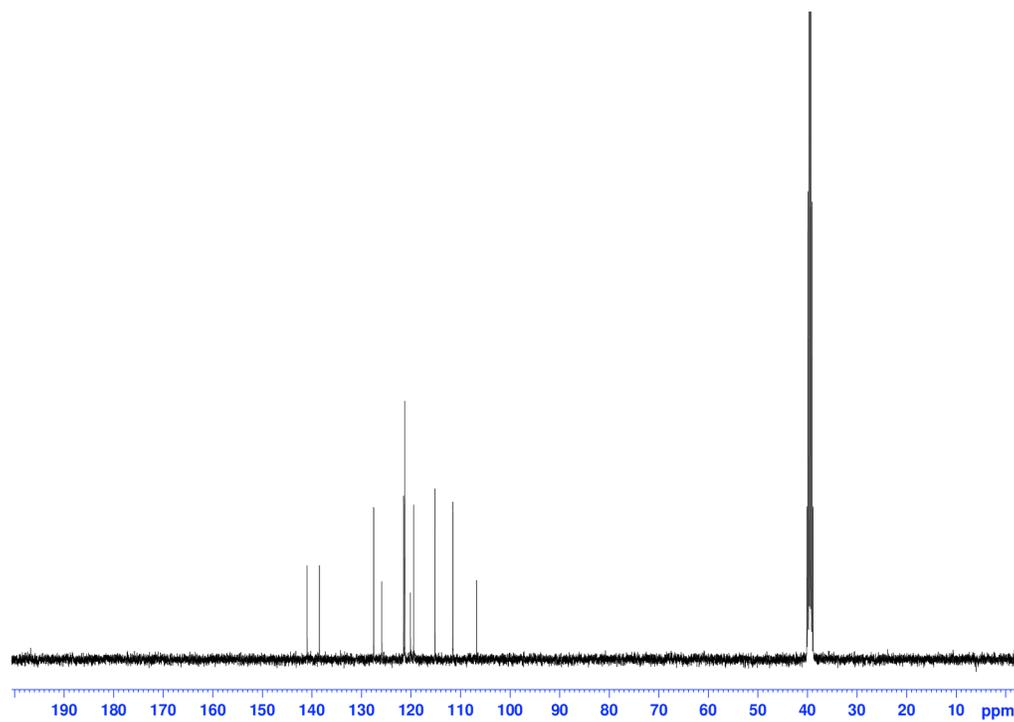
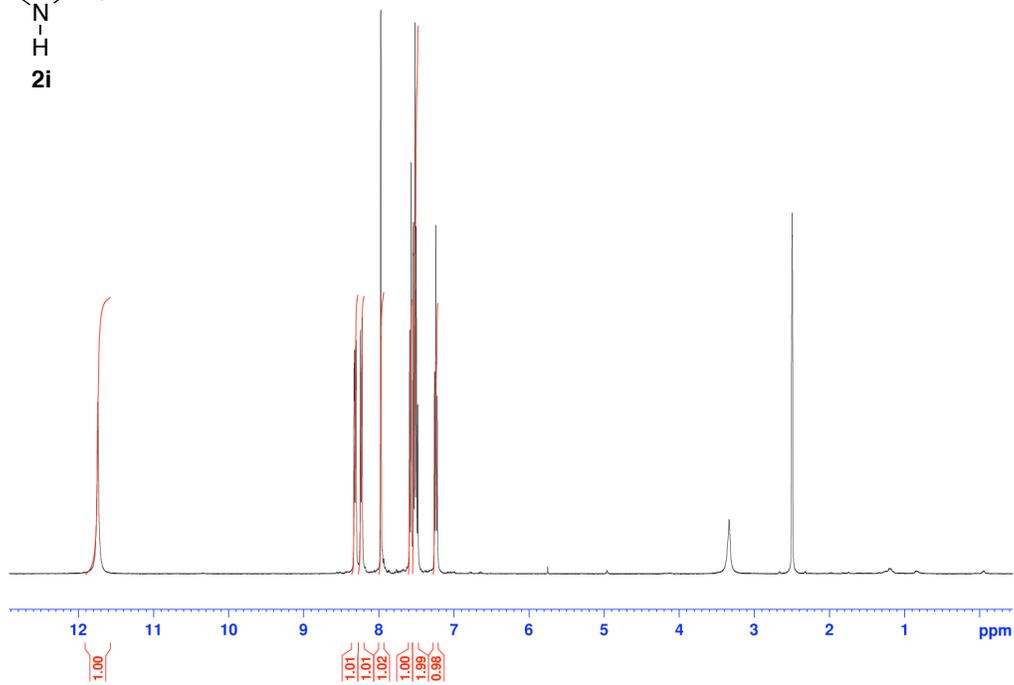
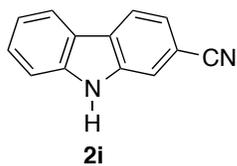
[¹H and ¹³C NMR Spectra of **2g**]



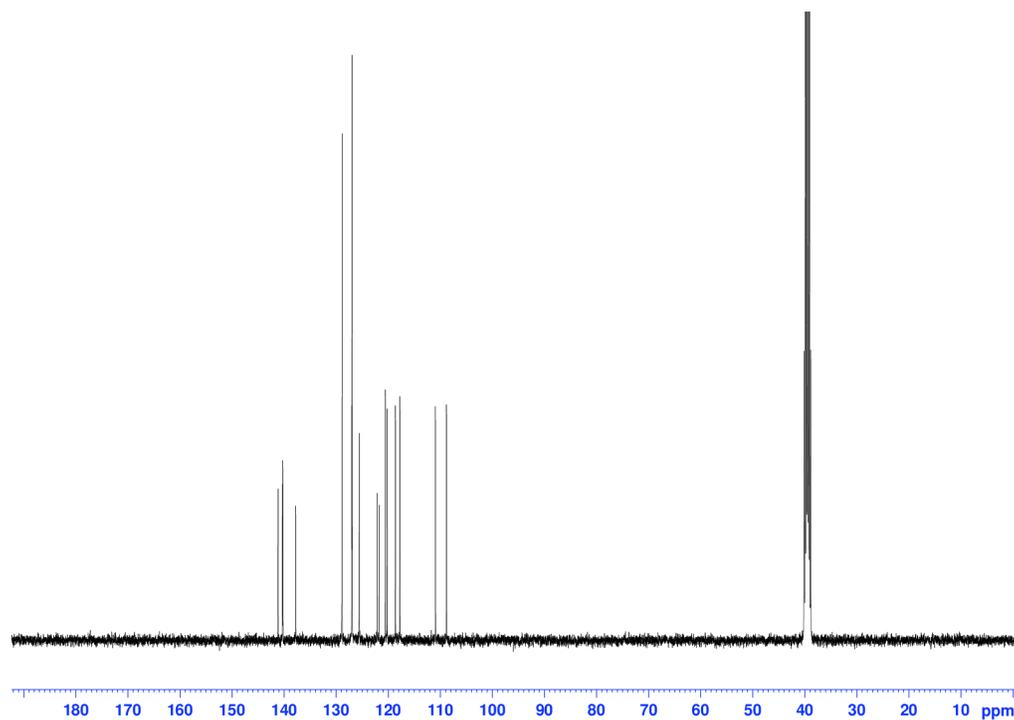
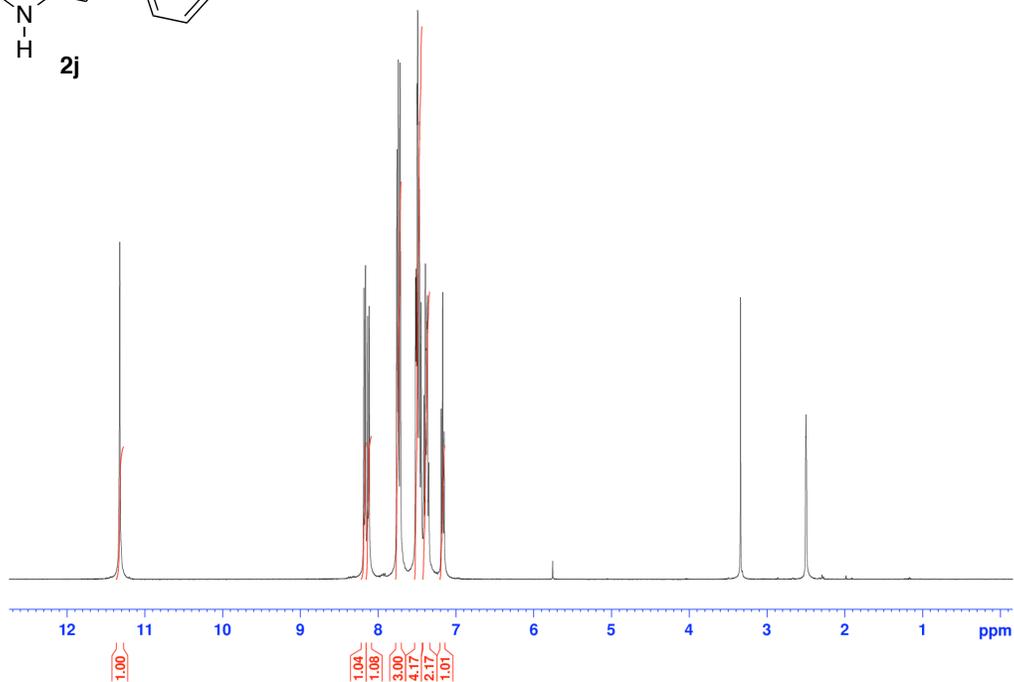
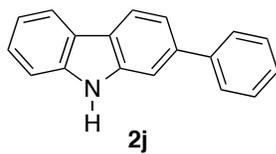
[¹H and ¹³C NMR Spectra of **2h**]



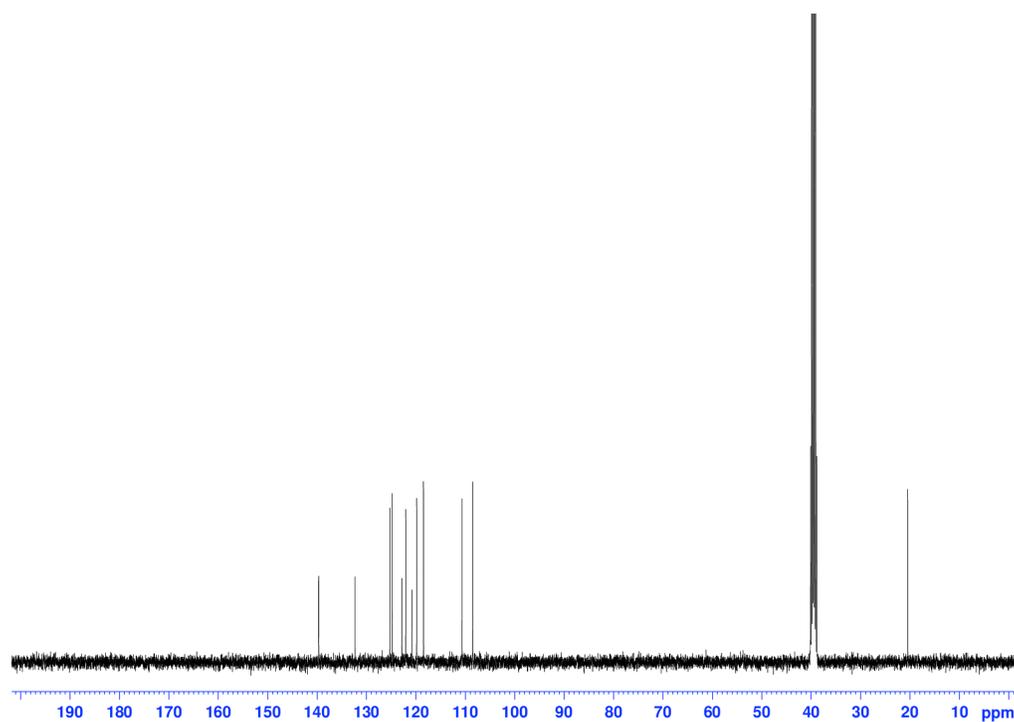
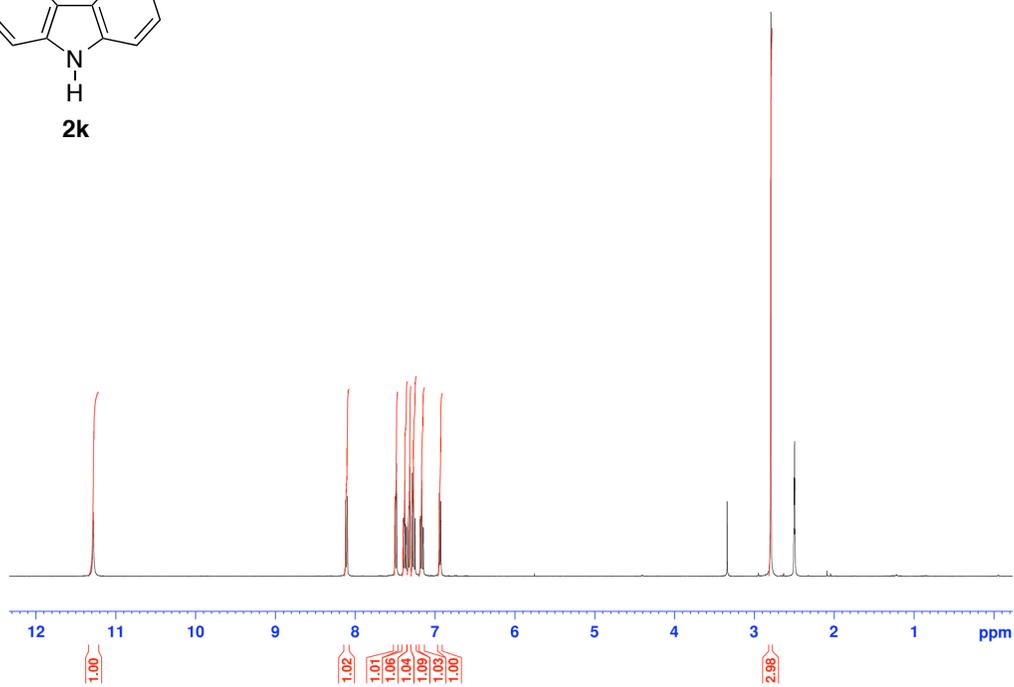
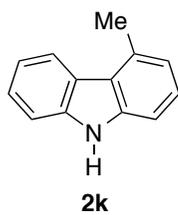
[¹H and ¹³C NMR Spectra of **2i**]



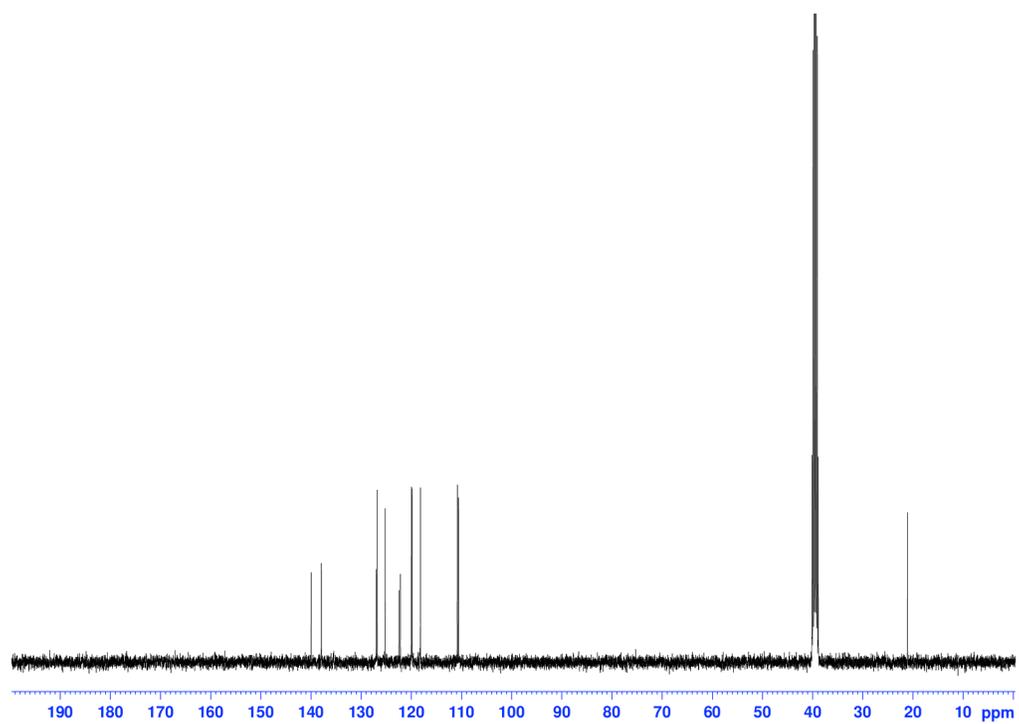
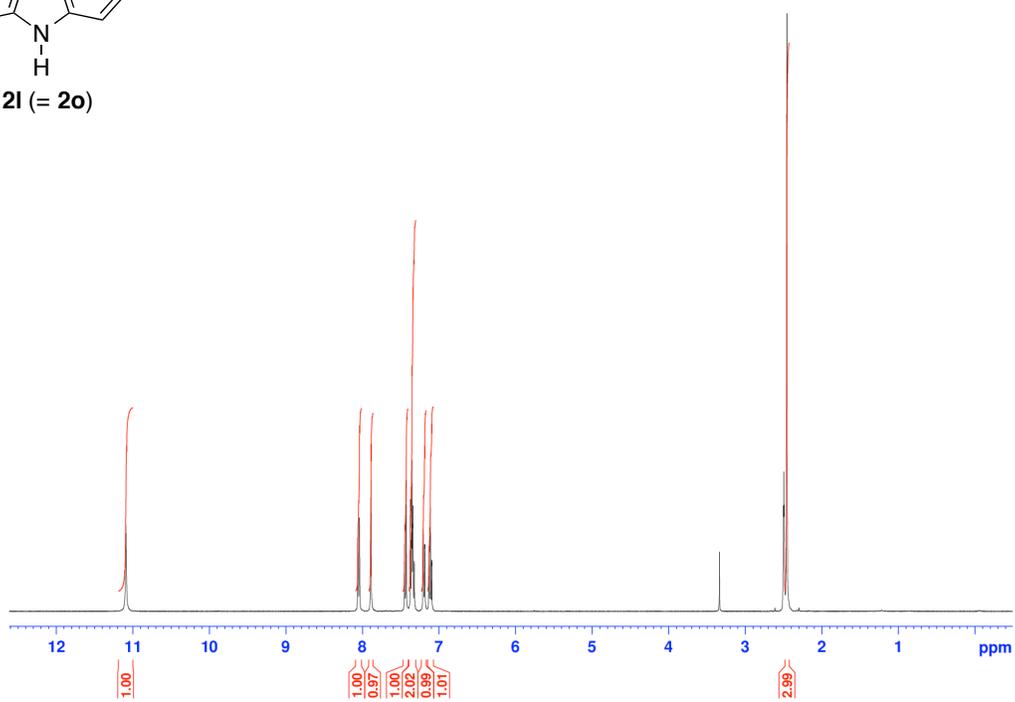
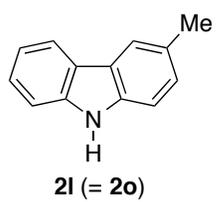
[¹H and ¹³C NMR Spectra of **2j**]



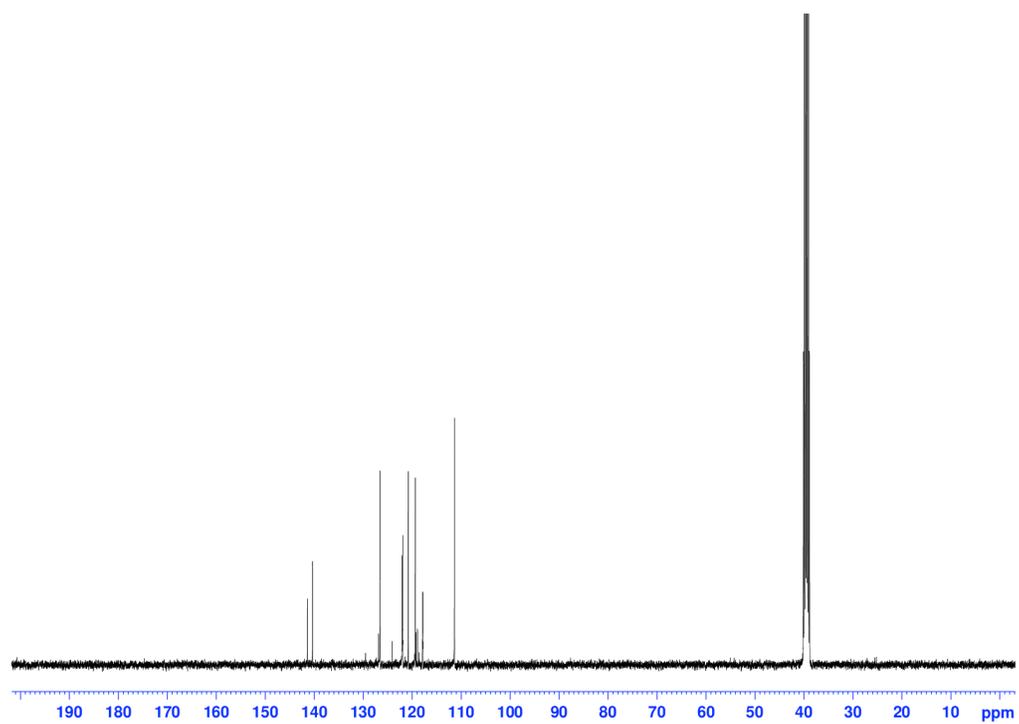
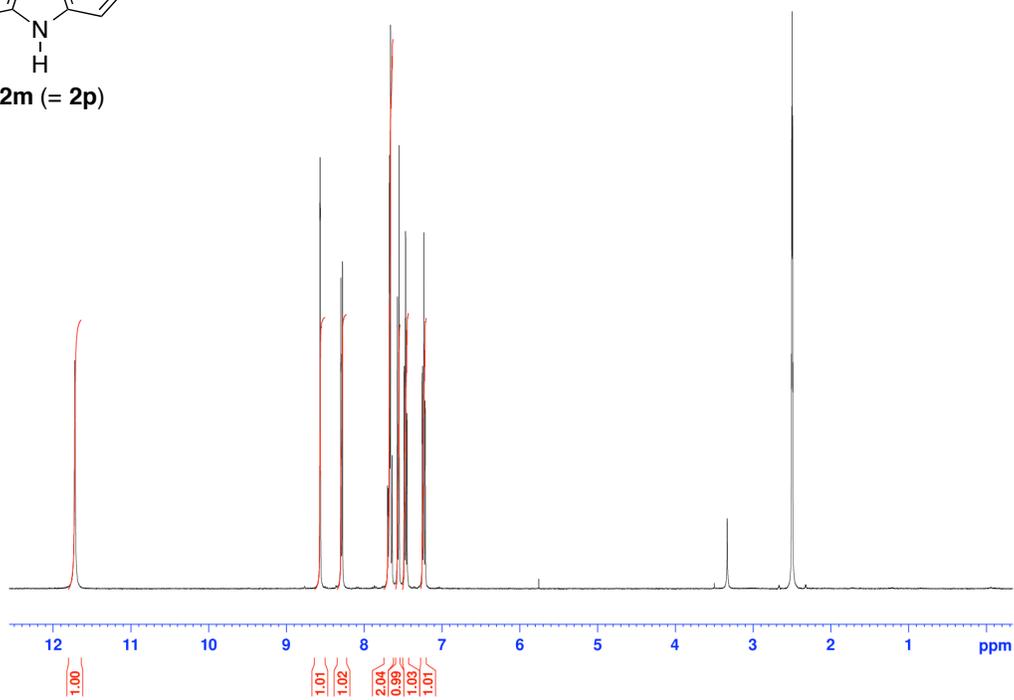
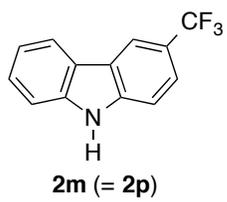
[¹H and ¹³C NMR Spectra of **2k**]

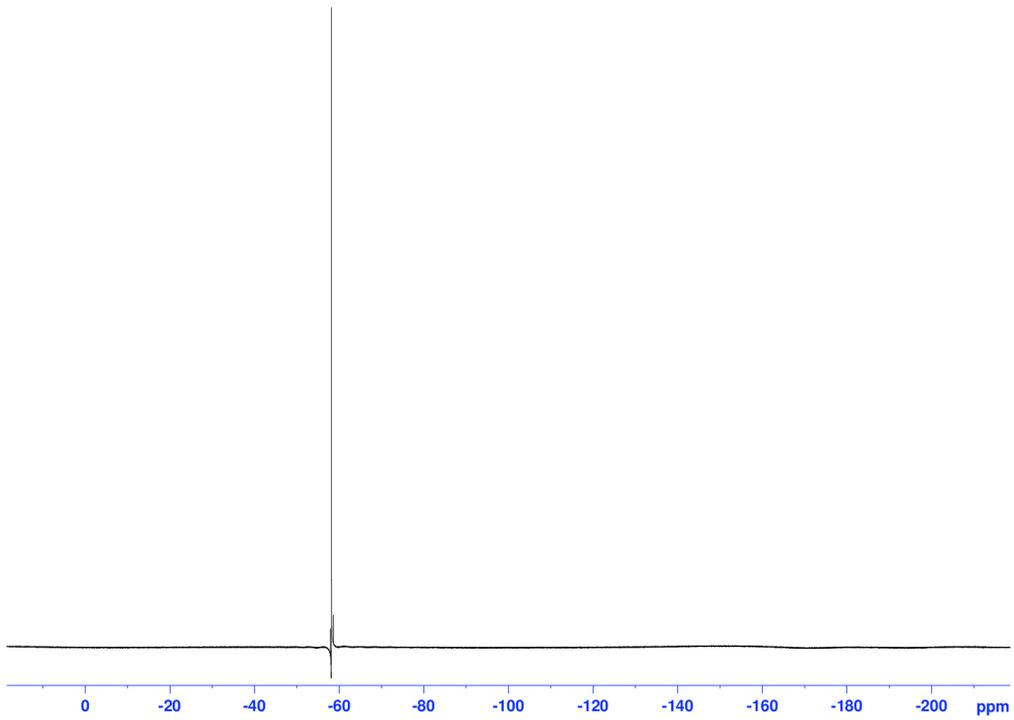


[¹H and ¹³C NMR Spectra of **2l** (**2o**)]

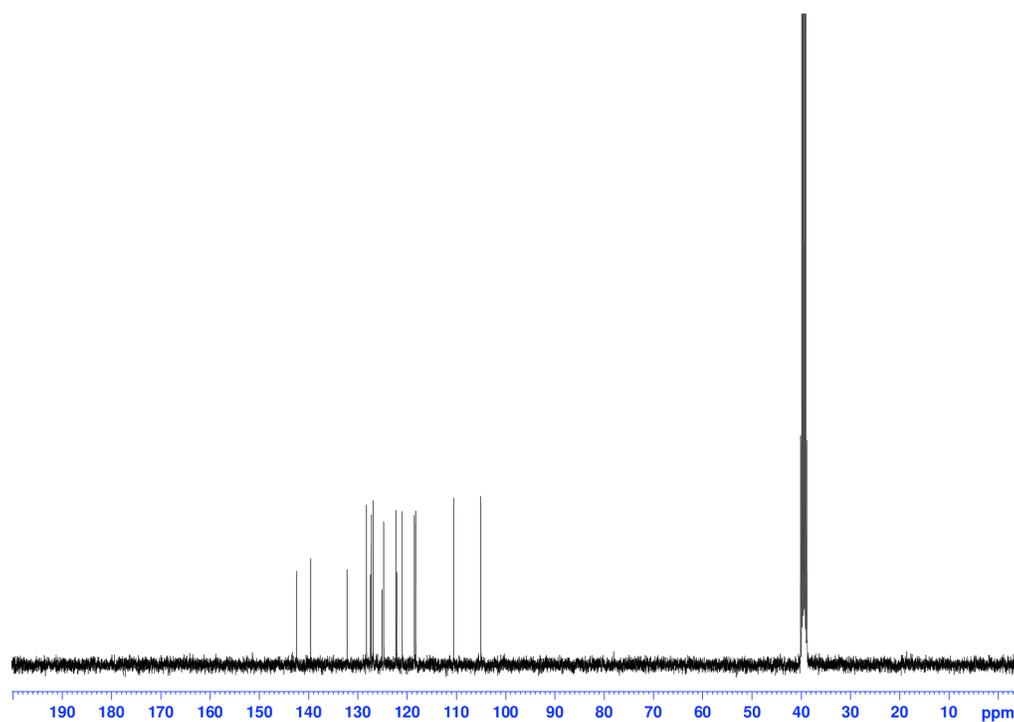
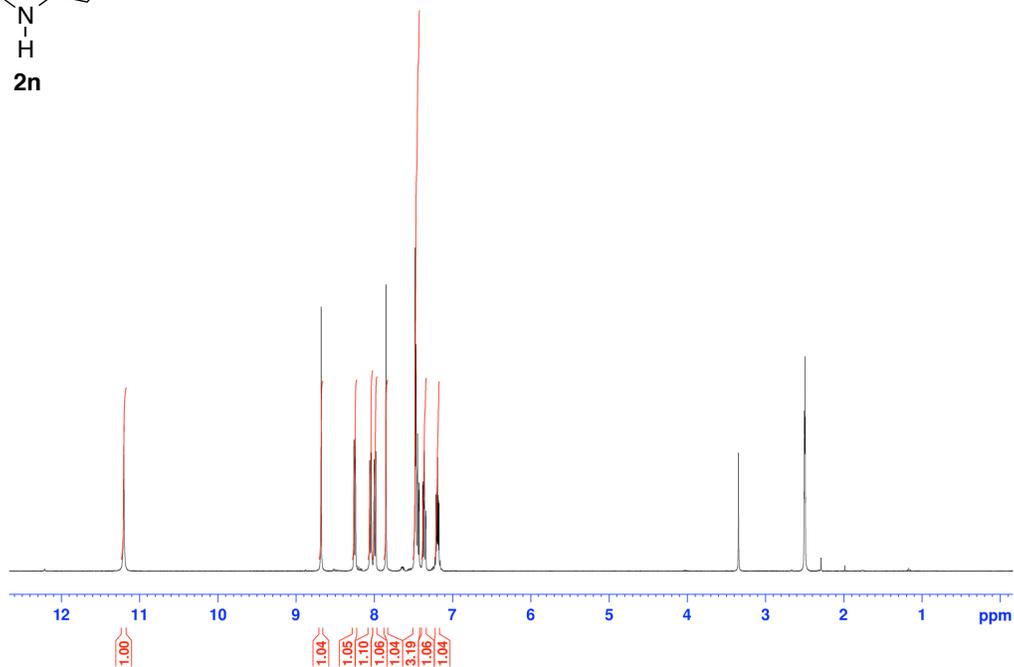
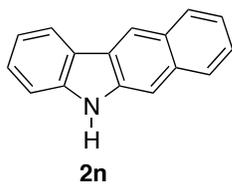


[^1H , ^{13}C , and ^{19}F NMR Spectra of **2m** (**2p**)]

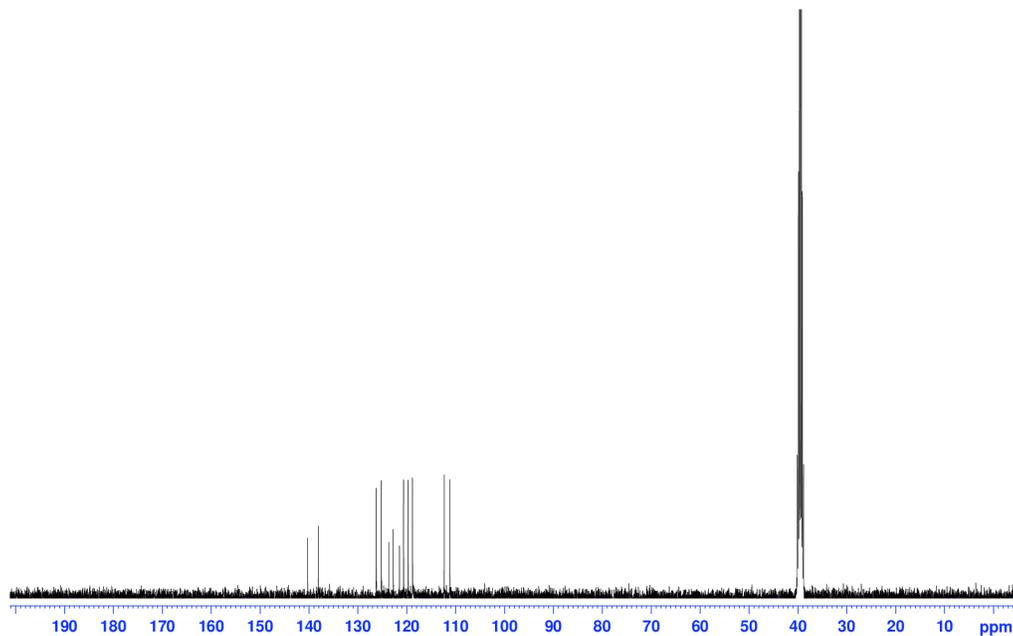
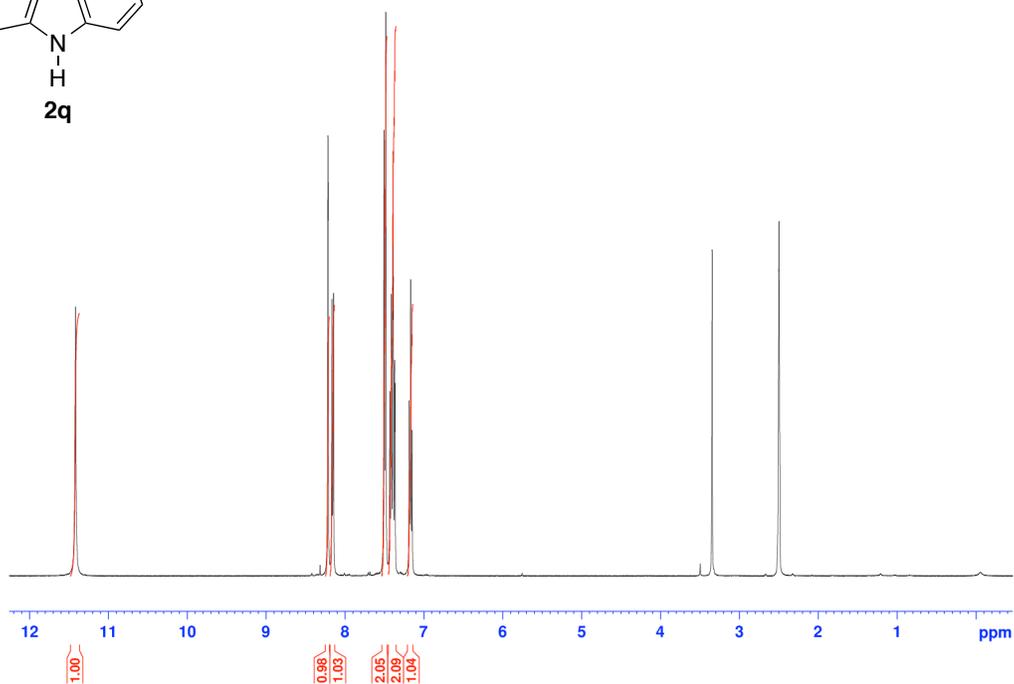
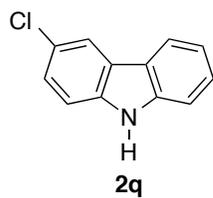




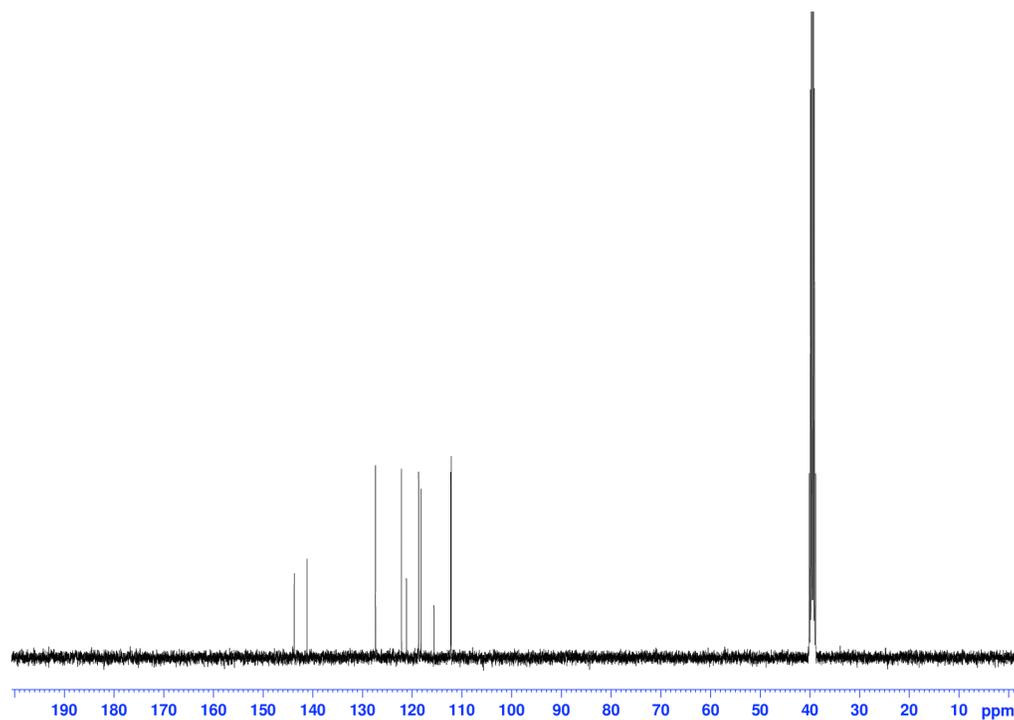
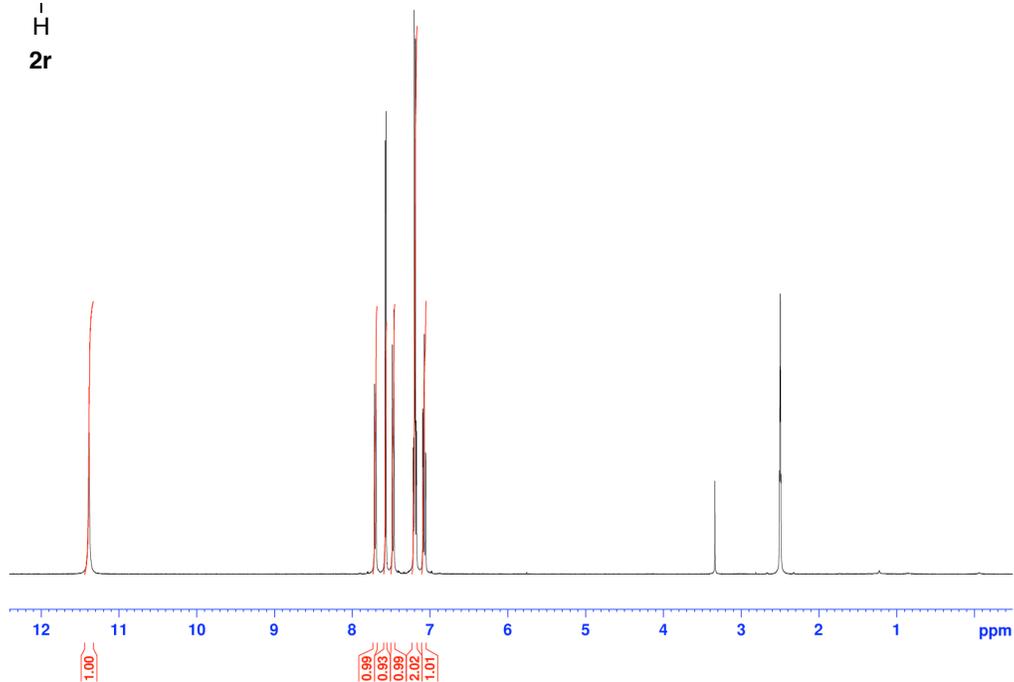
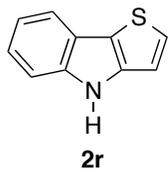
[¹H and ¹³C NMR Spectra of **2n**]



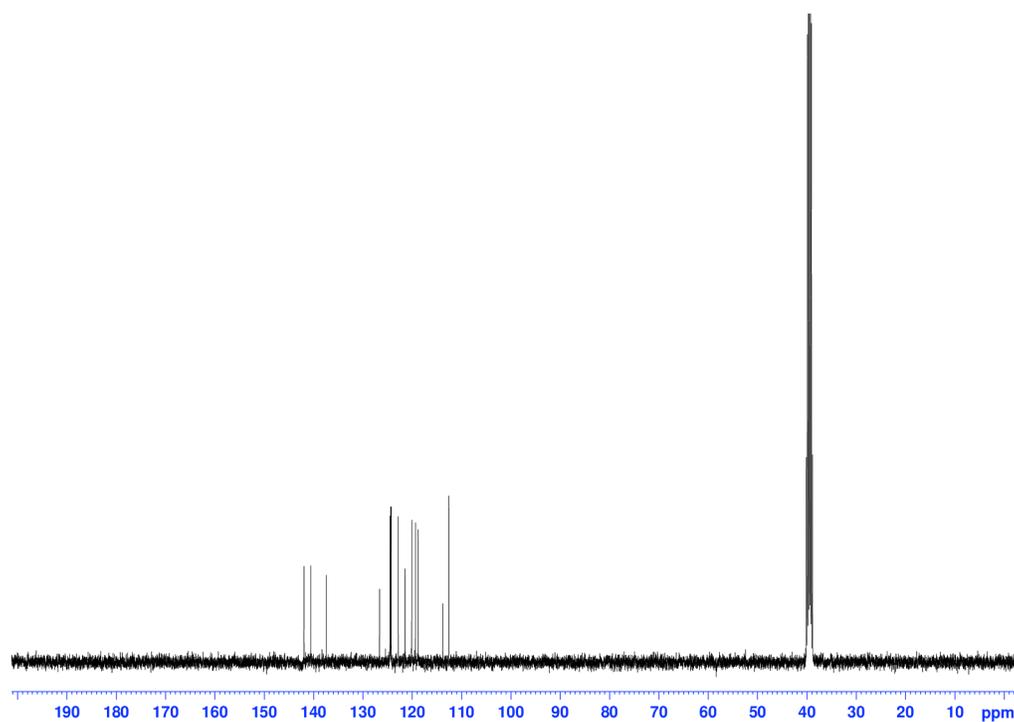
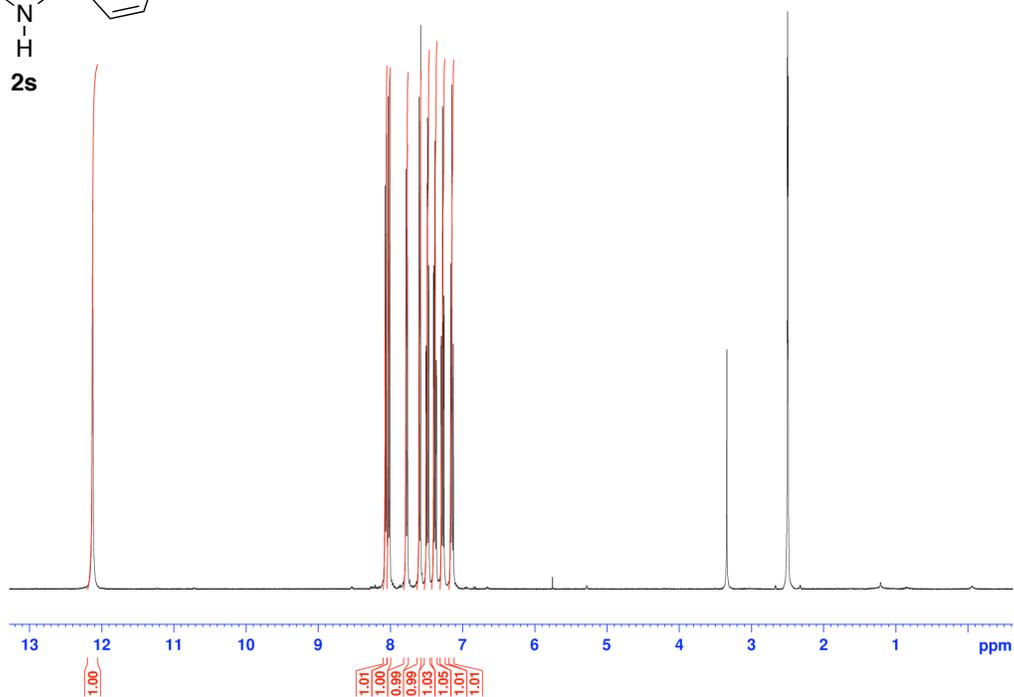
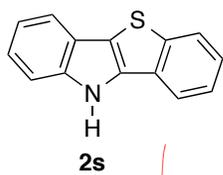
[¹H and ¹³C NMR Spectra of **2q**]



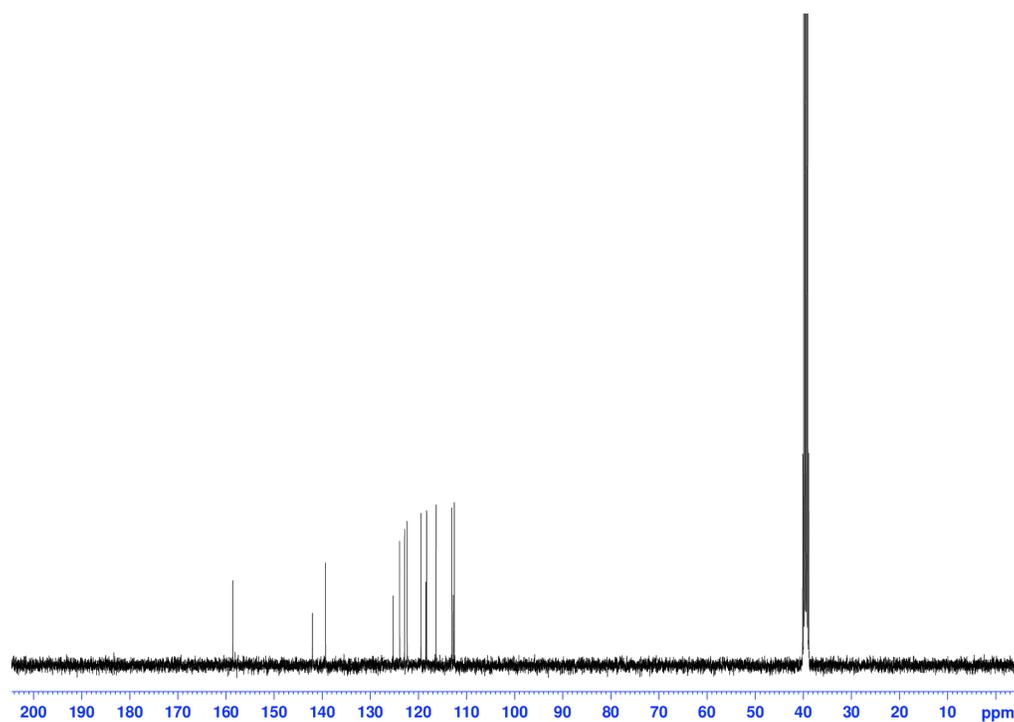
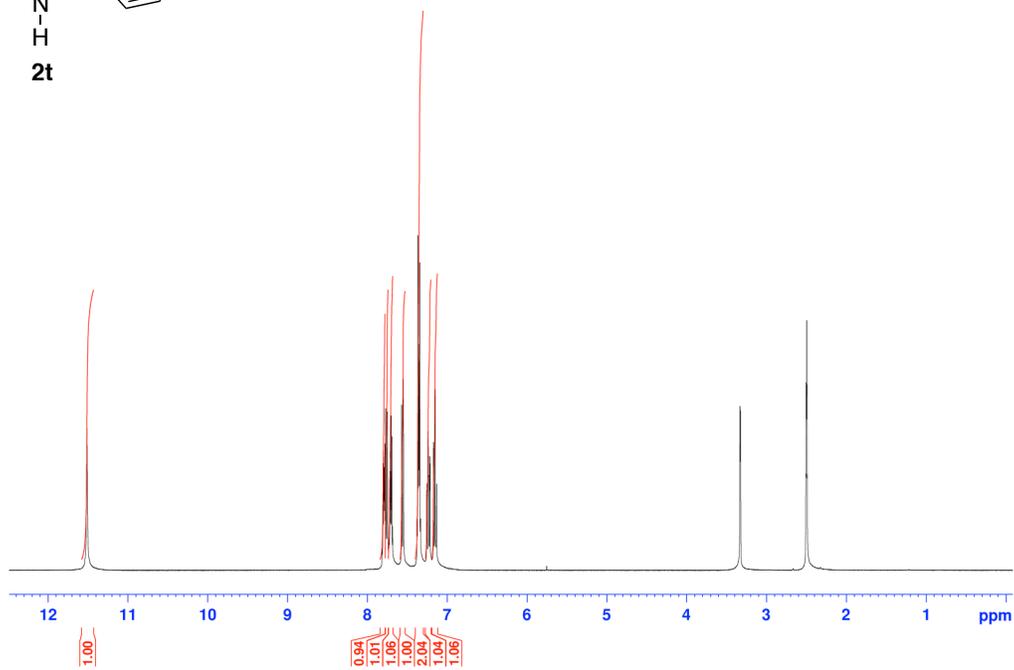
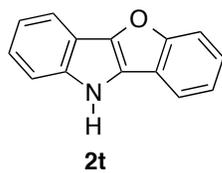
[¹H and ¹³C NMR Spectra of **2r**]



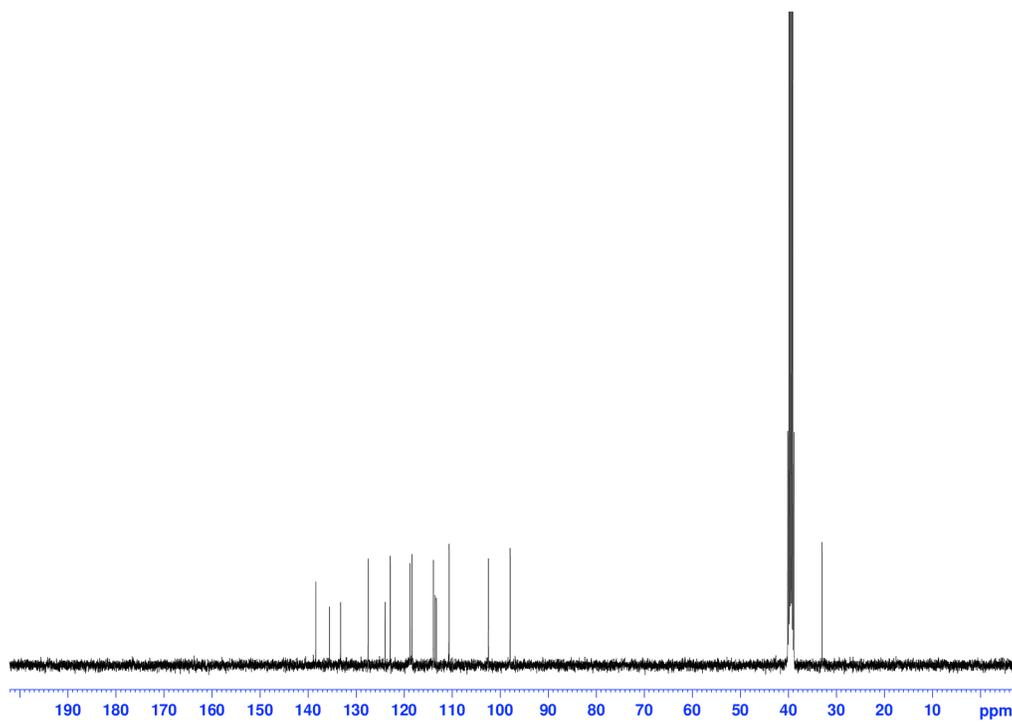
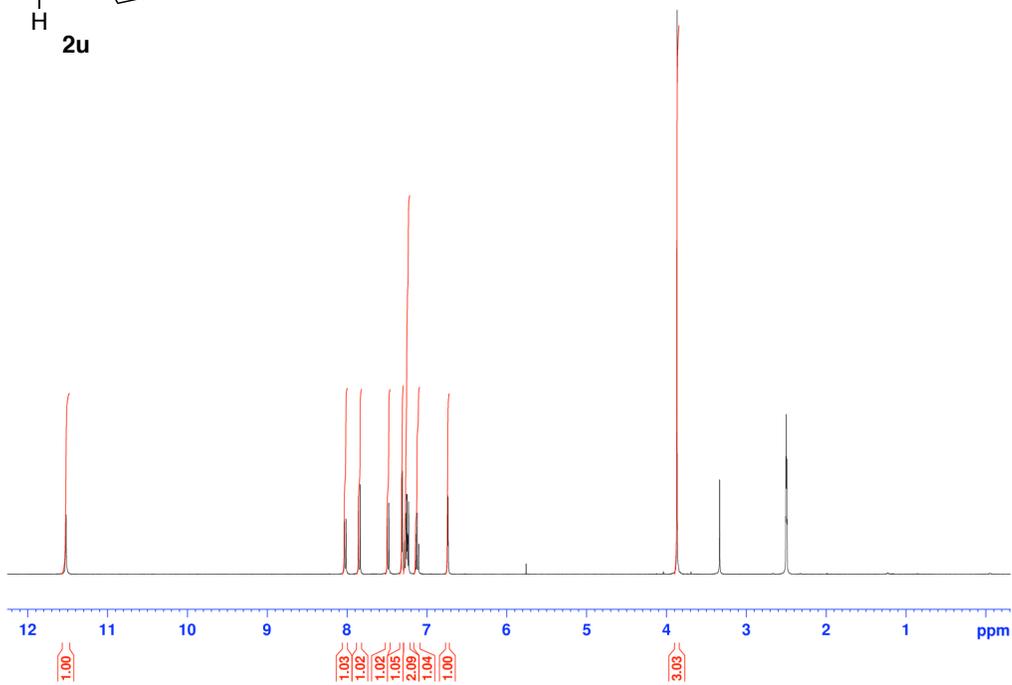
[¹H and ¹³C NMR Spectra of 2s]



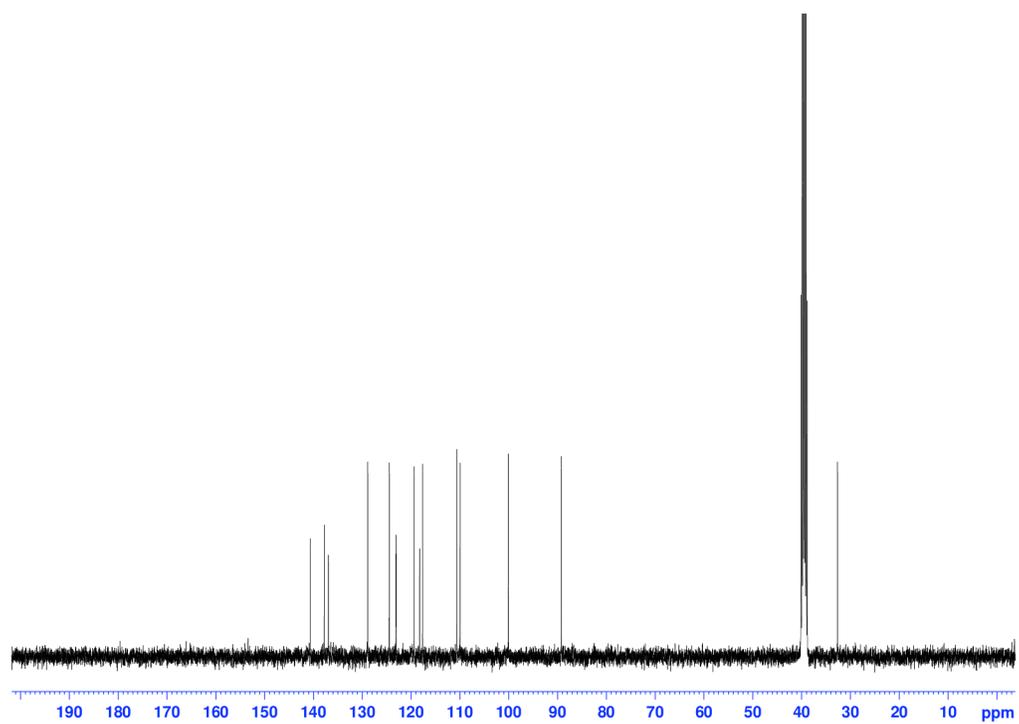
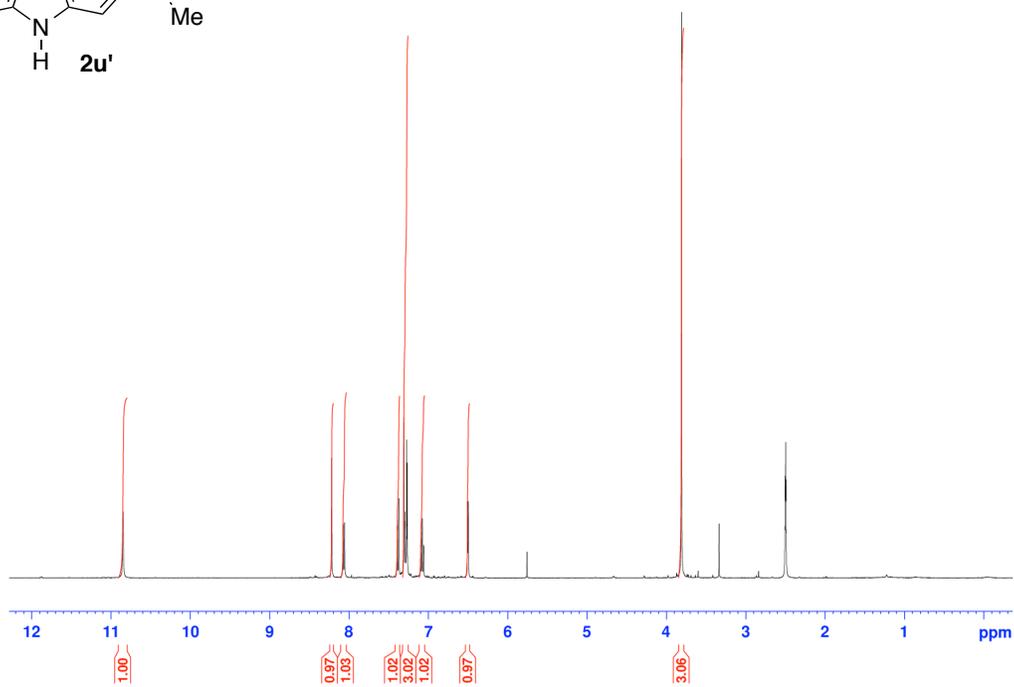
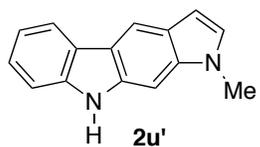
[^1H and ^{13}C NMR Spectra of **2t**]



[¹H and ¹³C NMR Spectra of **2u**]



[¹H and ¹³C NMR Spectra of **2u'**]



[¹H and ¹³C NMR Spectra of **2v**]

