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Supporting Information

Ruthenium Half-Sandwich Complexes as Protein Kinase Inhibitors: Derivatization of the Pyridocarbazole Pharmacophore Ligand

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A) Synthesis of Ruthenium Pyridocarbazoles

All reactions were carried out using oven-dried glassware and conducted under a positive pressure of argon unless otherwise specified. NMR spectra were recorded on a DMX-360 (360 MHz) or Bruker AM-500 (500 MHz) spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. Low-resolution mass spectra were obtained on an LC platform from Micromass using ESI technique. ES-TOF spectra were measured by Waters Micromass MS Technologies. High-resolution mass spectra were obtained with a Micromass AutoSpec instrument using either CI or ES ionization. Commerical pyridines **9a**, **9b** and **9d** were purchased and used as supplied from Aldrich. Pyridines **9c**[1,2], **9e**[3,4], **9f**[5], **9g**[6], **9h**[7] and **9i**[8] were individually prepared according to literature protocols. Reagents and solvents were used as received from standard suppliers. Chromatographic separations were performed using Silia-P Flash silica gel from Silicycle Inc.

Compound 6b. A biphasic suspension of **8a** (157 mg, 0.604 mmol), **9b** (100 mg, 0.549 mmol), bis(triphenylphosphine)palladium(II) chloride (38.5 mg, 0.055 mmol) and 2 M Na_2CO_3 (3.1 mL) in 1,2-dimethoxyethane (5.5 mL) and water (0.6 mL) was purged with argon and refluxed overnight. The reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (15:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6b**. The resulting white-yellow solid (116 mg) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (1.16 g) using rotary evaporation. The white powder was heated to 80 ^oC overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (15:1). The combined product eluents were dried *in vacuo* to provide **6b** (82 mg, 57% over two steps) as a white solid. ^1H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.51 (s, 1H), 8.82 (m, 1H), 7.89 (m, 2H), 7.68 (dd, J = 8.0, 0.9 Hz, 1H) 7.45 (dd, J = 8.2, 0.9 Hz, 1H), 7.28 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.15 (m, 2H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 153.5, 146.0 (q_{C-F}, J = 4.1 Hz), 137.2, 135.4, 133.9 (q_{C-F}, J = 3.4 Hz), 129.1, 124.6 (q_{C-F}, J = 33.2 Hz), 124.4, 123.9 (q_{C-F}, J = 271.7 Hz), 121.8, 120.8, 119.4, 111.8, 103.0. IR (film): ν (cm^{-1}) 3419, 1605, 1563, 1425, 1335, 1225, 1165, 1126, 1084, 1010, 937, 847, 804, 770, 750, 701. HRMS calcd for $C_{14}H_{10}F_3N_2$ $(M+H)^+$ 263.0796, found $(M+H)^+$ 263.0802.

Compound 6c. A biphasic suspension of **8a** (166 mg, 0.636 mmol), **9c** (128 mg, 0.424 mmol), tetrakis(triphenylphosphine)palladium(0) (49 mg, 0.042 mmol) and Na_2CO_3 (124 mg, 1.17 mmol) in 1,2-dimethoxyethane (1.25 mL) and water (0.35 mL) was purged with argon and refluxed overnight. The resulting brown solution was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using $MgSO_4$, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and chromatographed using hexanes:EtOAc (15:1). The combined product eluents were dried *in vacuo* to provide the Boc-protected pyridoindole (164 mg, 88%) as a pale orange oil. ^1H NMR (360 MHz, $CDCl_3$) δ (ppm) = 8.62 (dd, J = 2.2, 0.6 Hz, 1H), 8.19 (dd, J = 8.4, 0.8 Hz, 1H), 7.73 (dd, J = 8.0, 2.2 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.49 (dd, J = 8.0, 0.5 Hz, 1H), 7.36 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.26 (m, 1H), 6.77 (d, J = 0.5 Hz, 1H), 4.82 (s, 2H), 1.36 (s, 9H), 0.97 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 152.2, 150.2, 147.3, 139.5, 137.9, 135.5, 134.2, 129.1, 125.0, 123.02, 123.00, 121.1, 115.2, 111.0, 83.5, 62.8, 27.8, 26.0, 18.5, -5.1. IR (film) ν (cm^{-1}) = 2954, 2928, 2857, 1736, 1600, 1451, 1368, 1328, 1254, 1228, 1162, 1136, 1096, 842, 776, 745. HRMS calcd for $C_{25}H_{34}N_2O_3NaSi$ $(M+Na)^+$ 461.2236, found $(M+Na)^+$ 461.2253. The Boc-protected

pyridoindole (150 mg) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (1.50 g) using rotary evaporation. The powder was heated to 80 °C overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate dried *in vacuo* to provide **6c** (109 mg, 95%) as a yellow-brown viscous oil. Trace impurity was removed by adsorption of the material onto silica gel and purification by silica gel chromatography with hexanes:EtOAc (10:1) as the eluting solvent. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) = 10.19 (s, 1H), 8.58 (dd, *J* = 2.2, 0.7 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.74 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.24 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.16 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 7.06 (dd, *J* = 1.9, 0.6 Hz, 1H), 4.80 (s, 2H), 1.01 (s, 9H), 0.18 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) = 149.6, 147.3, 137.0, 136.9, 135.3, 135.1, 129.3, 123.2, 121.3, 120.2, 119.8, 111.6, 100.6, 62.9, 26.1, 18.6, -5.1. IR (film) ν (cm^{-1}) = 3420, 2950, 2924, 2854, 1600, 1469, 1426, 1256, 1099, 1021, 908, 838. HRMS calcd for $C_{20}H_{26}N_2OSi$ $(M)^+$ 338.1814, found $(M)^+$ 338.1803.

Compound 6d. A biphasic suspension of **8c** (2.06 g, 6.39 mmol), **9d** (1.00 g, 5.81 mmol), tetrakis(triphenylphosphine)palladium(0) (672 mg, 0.58 mmol) and Na_2CO_3 (1.70 g, 16.0 mmol) in 1,2-dimethoxyethane (25 mL) and water (7.5 mL) was purged with argon and refluxed overnight. The resulting yellow reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1 to 8:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6d**. The resulting white solid (1.48 g) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (14.8 g) using rotary evaporation. The white powder was heated to 80 ^{o}C overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate dried *in vacuo* to provide **6d** (1.10 g, 91% over two steps) as a white-yellow solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.49 (s, 1H), 8.41 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.53 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.20 (ddd, *J* = 8.0, 7.2, 0.9 Hz, 1H), 7.10 (ddd, *J* = 7.8, 7.2, 0.6 Hz, 1H), 6.96 (d, *J* = 1.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 149.6, 148.1, 137.4, 137.2, 136.7, 131.8, 129.5, 123.1, 121.2, 120.3, 119.6, 111.5, 100.1, 18.5. IR (film): ν (cm^{-1}) 3422, 3047, 2914, 2856, 1645, 1598, 1554, 1467, 1450, 1417, 1338, 1301, 1230, 1182, 1134, 1111, 1052, 1024, 930, 836, 798, 742. HRMS calcd for $C_{14}H_{12}N_2$ $(M)^+$ 208.1000, found $(M)^+$ 208.0997.

Compound 6e. A biphasic suspension of **8c** (1.57 g, 4.87 mmol), **9e** (900 mg, 4.43 mmol), tetrakis(triphenylphosphine)palladium(0) (512 mg, 0.44 mmol) and Na_2CO_3 (1.29 g, 12.2 mmol) in 1,2-dimethoxyethane (19.3 mL) and water (5.9 mL) was purged with argon and refluxed overnight. The resulting orange reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (3:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6e**. The resulting yellow solid (1.24 g) was dissolved into EtOAc and adsorbed onto silica gel (12.4 g) using rotary evaporation. The dark yellow powder was heated to 80 °C overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate dried *in vacuo* to provide **6e** (900 mg, 86% over two steps) as a yellow solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.52 (s, 1H), 8.11 (d, *J* = 2.7 Hz, 1H), 7.66 (dd, *J* = 8.8, 0.6 Hz, 1H), 7.61 (m, 1H), 7.37 (m, 1H), 7.16 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.07 (m, 2H), 6.81 (dd, *J* = 2.1, 0.9 Hz, 1H), 3.02 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 145.4, 139.3, 137.9, 136.5, 133.9, 129.8, 122.2, 120.7, 120.4, 120.0, 119.7, 111.2,

97.8, 40.3. IR (film): ν (cm^{-1}) 3133, 3064, 2888, 1593, 1557, 1492, 1444, 1423, 1364, 1301, 1219, 1061, 1007, 944, 905, 827, 788, 740. HRMS calcd for $C_{15}H_{16}N_3$ $(M+H)^+$ 238.1344, found $(M+H)^+$ 238.1334.

Compound 6f. A biphasic suspension of **8c** (1.89 g, 5.85 mmol), **9f** (1.00 g, 5.32 mmol), tetrakis(triphenylphosphine)palladium(0) (615 mg, 0.53 mmol) and Na_2CO_3 (1.55 g, 14.6 mmol) in 1,2-dimethoxyethane (23 mL) and water (7 mL) was purged with argon and refluxed overnight. The resulting orange reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (4:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6f**. The resulting white-yellow solid (1.62 g) was dissolved into EtOAc and adsorbed onto silica gel (16.2 g) using rotary evaporation. The white powder was heated to 80 ^oC overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate dried *in vacuo* to provide **6f** (1.12 g, 85% over two steps) as a yellow solid. ^1H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.62 (s, 1H), 8.29 (d, J = 2.9 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.25 (dd, J = 8.7, 2.9 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.89 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 155.1, 143.7, 137.1, 136.7, 136.5, 130.0, 122.8, 122.0, 121.1, 120.6, 120.2, 111.4, 99.2, 56.0. IR (film): ν (cm^{-1}) 3421, 3041, 2968, 2830, 1564, 1471, 1425, 1382, 1356, 1270, 1235, 1181, 1141, 1059, 1022, 933, 911, 834, 797, 743, 662. HRMS calcd for $C_{14}H_{13}N_2O$ $(M+H)^+$ 225.1028, found $(M+H)^+$ 225.1030.

Compound 6g. A biphasic suspension of **8a** (1.55 g, 5.96 mmol), **9g** (1.20 g, 5.00 mmol), bis(triphenylphosphine)palladium(II) chloride (351 mg, 0.500 mmol) and 2 M Na_2CO_3 (30 mL) in 1,2-dimethoxyethane (54 mL) and water (6 mL) was purged with argon and refluxed overnight. The resulting orange reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6g**. The resulting white solid (1.06 mg) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (10.6 g) using rotary evaporation. The white powder was heated to 80 ^oC overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate dried *in vacuo* to provide **6g** (750 mg, 66% over two steps) as a yellow solid. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.43 (s, 1H), 7.66 (m, 3H), 7.42 (dd, J = 8.2, 0.7 Hz, 1H), 7.25 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 7.18 (d, J = 7.5, 1.0 Hz, 1 H), 7.13 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 151.2, 139.3, 136.9, 135.8, 129.1, 124.0, 122.3, 121.6, 120.6, 118.2, 111.7, 101.9. IR (film): ν (cm^{-1}) 3403, 3060, 1787, 1580, 1545, 1435, 1418, 1382, 1360, 1334, 1303, 1228, 1158, 1132, 1066, 982, 938. HRMS calcd for $C_{13}H_9ClN_2$ $(M)^+$ 228.0454, found $(M)^+$ 228.0444.

Compound 6h. A biphasic suspension of **8a** (442 mg, 1.70 mmol), **9h** (440 mg, 1.55 mmol), tetrakis(triphenylphosphine)palladium(0) (179 mg, 0.155 mmol) and Na_2CO_3 (452 mg, 4.26 mmol) in 1,2-dimethoxyethane (6.6 mL) and water (1.9 mL) was purged with argon and refluxed overnight. The resulting light yellow reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1). The combined product eluents were isolated as a mixture of Boc-

protected pyridoindole and **6h**. The resulting white solid (311 mg) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (3.11 g) using rotary evaporation. The white powder was heated to 80 ^oC overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (15:1 to 10:1). The combined product eluents were dried *in vacuo* to provide **6h** (220 mg, 52% over two steps) as a white solid. ^1H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.43 (s, 1H), 7.67 (m, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.41 (dd, J = 8.2, 0.9 Hz, 1H), 7.32 (dd, J = 7.8, 0.8 Hz, 1 H), 7.26 (ddd, J = 8.2, 5.9, 1.1 Hz, 1H), 7.15 (ddd, J = 8.0, 6.0, 1.0 Hz, 1H), 7.01 (dd, J = 2.1, 0.9 Hz, 1 H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 151.6, 141.9, 139.0, 136.8, 135.2, 129.1, 126.0, 124.0, 121.5, 120.6, 118.5, 111.7, 101.9. IR (film): ν (cm^{-1}) 3417, 1582, 1543, 1434, 1413, 1360, 1337, 1306, 1229, 1158, 1126, 1067, 982, 938, 786, 751, 730. HRMS calcd for $C_{13}H_8BrN_2$ $(M-H)^-$ 270.9871, found $(M-H)^-$ 270.9881.

Compound 6i. A biphasic suspension of **8a** (302 mg, 1.16 mmol), **9i** (316 mg, 1.05 mmol), tetrakis(triphenylphosphine)palladium(0) (121 mg, 0.105 mmol) and Na_2CO_3 (306 mg, 2.89 mmol) in 1,2-dimethoxyethane (4.5 mL) and water (1.3 mL) was purged with argon and refluxed overnight. The resulting light orange reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (15:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6i**. The resulting white solid (300 mg) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (3.00 g) using rotary evaporation. The white powder was heated to 80 ^oC overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (20:1 to 15:1). The combined product eluents were dried *in vacuo* to provide **6i** (237 mg, 67% over two steps) as a white solid. ^1H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.64 (s, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.69 (m, 2H), 7.43 (m, 2H) 7.26 (ddd, J = 8.2, 5.8, 1.2 Hz, 1H), 7.16 (ddd, J = 8.0, 6.0, 1.0 Hz, 1 H), 7.04 (dd, J = 2.1, 0.9 Hz, 1H), 4.94 (s, 2H), 1.05 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 161.1, 149.3, 137.4, 137.0, 136.6, 129.4, 123.3, 121.3, 120.3, 118.5, 118.1, 111.5, 100.6, 66.4, 26.2, 18.7, -5.1. IR (film): ν (cm^{-1}) 3421, 3049, 2931, 2895, 2857, 1594, 1572, 1461, 1399, 1348, 1308, 1253, 1152, 1116, 1075, 1005, 962, 935, 836, 788, 740. HRMS calcd for $C_{20}H_{26}N_2OSi$ $(M)^+$ 338.1814, found $(M)^+$ 338.1801.

Compound 6k (from **8b**). A biphasic suspension of **8b** (5.54 g, 15.1 mmol), **9b** (2.50 g, 13.7 mmol), tetrakis(triphenylphosphine)palladium(0) (1.58 g, 1.37 mmol) and Na_2CO_3 (4.00 g, 37.7 mmol) in 1,2-dimethoxyethane (59 mL) and water (17 mL) was purged with argon and refluxed overnight. The orange reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (15:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6k**. The resulting white-yellow solid (3.04 g) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (30.4 g) using rotary evaporation. The white powder was heated to 80 ^oC overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and dried *in vacuo* to provide **6k** (2.60 g, 52% over two steps) as a yellow solid. Crystallization in EtOAc yields **6k** as white crystals. ^1H NMR (360 MHz, DMSO-d_6): δ (ppm) 11.72 (s, 1H), 8.93 (s, 1H), 8.20 (dd, J = 8.9, 2.3 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H) 7.40

(m, 6H), 7.22 (d, J = 1.6 Hz, 1H), 7.16 (d, J = 2.4 Hz, 1H), 6.91 (dd, J = 8.8, 2.4 Hz, 1H), 5.10 (s, 2H). ^{13}C NMR (90 MHz, DMSO-d_6): δ (ppm) 153.9, 152.8, 146.0 (q_{C-F}, J = 3.8 Hz), 137.6, 135.9, 134.2, 133.1, 128.4, 128.3, 127.6, 127.5, 123.9 (q_{C-F}, J = 271.8 Hz), 122.6 (q_{C-F}, J = 32.4 Hz), 119.5, 114.8, 113.1, 103.4, 102.9, 69.6. IR (film): ν (cm^{-1}) 3420, 2884, 1607, 1462, 1444, 1426, 1343, 1327, 1299, 1207, 1154, 1127, 1101, 1083, 1035, 1013, 938, 842, 811. HRMS calcd for $C_{21}H_{15}F_3N_2O$ $(M)^+$ 368.1136, found $(M)^+$ 368.1125.

Compound 6k (using **8d**). A biphasic suspension of **8d** (259 mg, 0.604 mmol), **9b** (100 mg, 0.549 mmol), tetrakis(triphenylphosphine)palladium(0) (64 mg, 0.055 mmol) and Na_2CO_3 (160 mg, 1.51 mmol) in 1,2-dimethoxyethane (2.4 mL) and water (0.70 mL) was purged with argon and refluxed overnight. The resulting yellow reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (8:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6k**. The resulting white-yellow solid (163 mg) was dissolved into EtOAc and adsorbed onto silica gel (1.63 g) using rotary evaporation. The white powder was heated to 80 °C overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with 20:1 CH_2Cl_2:MeOH and dried *in vacuo* to provide **6k** (147 mg, 73% over two steps) as a yellow solid.

Compound 6l. A biphasic suspension of **8b** (5.56 g, 15.2 mmol), **9c** (3.05 g, 10.1 mmol), tetrakis(triphenylphosphine)palladium(0) (1.17 g, 1.01 mmol) and Na_2CO_3 (2.94 g, 27.8 mmol) in 1,2-dimethoxyethane (44.4 mL) and water (12.6 mL) was purged with argon and refluxed overnight. The resulting brown solution was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using $MgSO_4$, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and chromatographed using hexanes:EtOAc (8:1). The combined product eluents were dried *in vacuo* to provide the Boc-protected pyridoindole (3.74 g, 68%) as a light orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.61 (s, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.47 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 6.8 Hz, 1H), 7.12 (d, J = 2.5 Hz, 1H), 7.07 (dd, J = 9.0, 2.5 Hz, 1H), 6.69 (s, 1H), 5.14 (s, 2H), 4.82 (s, 2H), 1.35 (s, 9H), 0.96 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) = 155.4, 152.2, 150.2, 147.3, 140.1, 137.5, 135.5, 134.2, 132.9, 129.8, 128.7, 128.0, 127.7, 123.2, 116.1, 114.8, 111.1, 105.0, 83.5, 70.8, 62.9, 27.8, 26.1, 18.5, -5.1. IR (film) ν (cm^{-1}) = 2958, 2920, 2883, 2855, 1731, 1599, 1454, 1369, 1327, 1256, 1219, 1162, 1124, 1096, 1026, 838, 809, 781, 743, 696. HRMS calcd for $C_{32}H_{41}N_2O_4Si$ $(M+H)^+$ 545.2836, found $(M+H)^+$ 545.2844. The Boc-protected pyridoindole (3.20 g) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (32.0 g) using rotary evaporation. The powder was heated to 80 °C overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc and the filtrate dried *in vacuo* to provide **6l** (2.61 g, 100%) as a yellow-brown viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.83 (s, 1H), 8.53 (d, J = 1.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.70 (dd, J = 8.2, 2.1 Hz, 1H), 7.51 (m, 2H), 7.42 (m, 2H), 7.34 (m, 2H), 7.29 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 2.3 Hz, 1H), 6.98 (dd, J = 8.8, 2.4 Hz, 1H), 6.94 (d, J = 1.4 Hz, 1H), 5.14 (s, 2H), 4.79 (s, 2H), 0.98 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) = 153.8, 149.5, 147.4, 137.9, 137.6, 135.2, 135.1, 132.3, 129.7, 128.7, 127.9, 127.7, 119.6, 114.6, 112.3, 104.2, 100.4, 71.0, 62.9, 26.1, 18.6, -5.0. IR (film) ν (cm^{-1}) = 3429, 3201, 3060, 3034, 2955, 2929, 2885, 2859, 1622, 1600, 1548, 1464, 1455, 1429, 1385, 1298, 1254, 1205, 1153, 1096, 1026, 837, 780, 736. HRMS calcd for $C_{27}H_{33}N_2O_2Si$ $(M+H)^+$ 445.2311, found $(M+H)^+$ 445.2332.

Compound 9j. A solution of 6-bromonicotinic acid (30 mg, 0.149 mmol), pyridine (24.1 µl, 0.30 mmol), and 2-trimethylsilyl ethanol (21.3 µl, 0.149 mmol) in CH_3CN (300 µl) was cooled to 0 °C and *N,N'*-dicyclohexylcarbodiimide (32.6 mg, 0.158 mmol) was added. The reaction was allowed to warm naturally to room temperature and stir for a total of 6 hours yielding a white suspension. The suspension was filtered through celite using acetonitile and the filtrate was concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (15:1 to 8:1). The combined product eluents were dried *in vacuo* to provide **9j** (27 mg, 60%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.91 (d, *J* = 2.1 Hz, 1H), 8.10 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 4.42 (t, *J* = 8.4 Hz, 2H), 1.11 (t, *J* = 8.4 Hz, 2H), 0.06 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 164.8, 151.6, 146.8, 139.3, 128.2, 126.1, 64.3, 17.7, -1.2. IR (film) *ν* (cm^{-1}) = 2951, 1714, 1580, 1446, 1277, 1251, 1117, 1013, 844, 766. HRMS calcd for $C_{11}H_{17}BrNO_2Si$ $(M+H)^+$ 302.0212, found $(M+H)^+$ 302.0226.

Compound 6m. A biphasic suspension of **8b** (627 mg, 1.71 mmol), **9j** (430 mg, 1.42 mmol), tetrakis(triphenylphosphine)palladium(0) (164 mg, 0.142 mmol) and Na_2CO_3 (414 mg, 3.91 mmol) in 1,2-dimethoxyethane (6.1 mL) and water (1.7 mL) was purged with argon and refluxed overnight. The resulting solution was cooled to room temperature, diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried using $MgSO_4$, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and chromatographed with hexanes:EtOAc (10:1 to 8:1). The combined product eluents were isolated as a mixture of Boc-protected pyridoindole and **6m**. The mixture (400 mg) was dissolved into CH_2Cl_2 and adsorbed onto silica gel (4.00 g) using rotary evaporation. The powder was heated to 80 °C overnight under high vacuum. The silica gel was cooled to room temperature, filtered through celite with EtOAc in addition to CH_2Cl_2:MeOH (2:1) and the filtrate concentrated to dryness *in vacuo* to provide **6m** (300 mg, 47% over two steps) as an off-white solid. ^{1}H NMR (360 MHz, DMSO-d_6) δ (ppm) = 11.71 (s, 1H), 9.07 (d, *J* = 2.1 Hz, 1H), 8.27 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.47 (m, 2H), 7.39 (m, 3H), 7.31 (m, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.1 (s, 2H), 4.42 (t, *J* = 8.2 Hz, 2H), 1.12 (t, *J* = 8.2 Hz, 2H), 0.07 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C) δ (ppm) = 164.2, 153.5, 152.7, 149.5, 137.4, 136.8, 136.2, 133.1, 128.3, 127.8, 127.1, 127.0, 123.2, 118.8, 114.4, 112.5, 103.8, 102.4, 69.9, 62.6, 16.6, -1.9. IR (KBr) *ν* (cm^{-1}) = 3376, 2955, 2888, 1694, 1594, 1546, 1450, 1421, 1383, 1278, 1226, 1211, 1135, 1116, 1039, 1025, 843, 805, 776, 729. HRMS calcd for $C_{26}H_{29}N_2O_3Si$ $(M+H)^+$ 445.1947, found $(M+H)^+$ 445.1926.

Compound 12k. A suspension of **6k** (2.34 g, 6.36 mmol) in ethanol (140 mL) was purged with argon for 15 minutes. Following thorough argon purge, palladium (10 wt% on activated carbon, wet, Degussa type E101 NE/W) (2.34 g) was added and the reaction mixture was carefully purged with hydrogen gas and stirred at 40 °C under an atmosphere of hydrogen overnight. The resulting dark blue reaction mixture was cooled, filtered through celite with EtOAc and the filtrate concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (3:1 to 1:1). The combined product eluents were dried *in vacuo* to provide **12k** (1.21 g, 68%) as a tan solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 11.54 (s, 1H), 8.91 (s, 1H), 8.80 (s, 1H), 8.18 (dd, *J* = 8.5, 1.8 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H) 7.29 (d, *J* = 8.7 Hz, 1H), 7.13 (d, *J* = 1.3 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.3 Hz, 1H). ^{13}C NMR (90 MHz, DMSO-d_6): δ (ppm) 154.0, 151.2, 145.9 (q_{C-F}, *J* = 4.0 Hz), 135.7, 134.2 (q_{C-F}, *J* = 3.2 Hz), 132.5, 128.9, 123.9 (q_{C-F}, *J* = 271.7 Hz), 122.4 (q_{C-F}, *J* = 32.4 Hz), 119.4, 114.4, 112.7, 104.1, 102.3. IR (film): ν (cm^{-1}) 3448, 3418, 3189, 1700, 1605, 1565, 1546, 1441, 1421, 1332, 1207, 1173, 1128, 1083, 1000, 949, 844, 800, 765, 735, 700. HRMS calcd for $C_{14}H_9F_3N_2O$ $(M)^+$ 278.0667, found $(M)^+$ 278.0662.

Compound 12l. A solution of **6l** (1.14 g, 2.58 mmol) in ethanol (55 mL) was purged with argon for 15 minutes. Following thorough argon purge, palladium (10 wt% on activated carbon, wet, Degussa type E101 NE/W) (555 mg) was added and the heterogeneous mixture was carefully purged with hydrogen gas and stirred at room temperature under an atmosphere of hydrogen for 2 hours. The crude material was filtered through celite with EtOAc and the filtrate concentrated to dryness *in vacuo* to provide **12l** (0.82 g, 90%) as an off-white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.57 (s, 1H), 8.52 (d, *J* = 1.1 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 1.5 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.78 (s, 2H), 0.97 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 150.0, 149.4, 147.5, 137.9, 135.3, 132.2, 130.1, 119.7, 113.4, 112.2, 105.4, 99.9, 63.0, 26.1, 18.6, -5.0. IR (film) ν (cm^{-1}) = 2953, 2930, 2861, 1603, 1547, 1448, 1253, 1201, 1101, 837, 781, 673, 616, 573. HRMS calcd for $C_{20}H_{27}N_2O_2Si$ $(M+H)^+$ 355.1841, found $(M+H)^+$ 355.1842.

Compound 12m. A suspension of **6m** (250 mg, 0.560 mmol) in glacial acetic acid (11 mL) was purged with argon for 15 minutes. Following thorough argon purge, palladium (10 wt.% on activated carbon, wet, Degussa type E101 NE/W) (125 mg) was added and the reaction mixture was carefully purged with hydrogen gas and stirred at 50 °C under an atmosphere of hydrogen for 6 hours. The reaction mixture was cooled, filtered through celite with MeOH and the filtrate concentrated to dryness *in vacuo* to provide **12m** (185 mg, 93%) as a light brown solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) = 9.05 (s, 1H), 8.81 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 1H), 7.11 (s, 1H), 6.87 (s, 1H), 6.70 (d, *J* = 8.7 Hz, 1H), 4.40 (t, *J* = 8.8 Hz, 2H), 1.12 (t, *J* = 9.0 Hz, 2H), 0.07 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6,) δ (ppm) = 164.7, 154.0, 151.2, 149.9, 137.3, 136.1, 132.6, 129.0, 123.2, 119.3, 114.4, 112.7, 104.0, 102.3, 63.1, 16.8, -1.4. IR (film) ν (cm^{-1}) = 3266, 2957, 2527, 1698, 1595, 1544, 1450, 1417, 1384, 1291, 1277, 1254, 1216, 1118, 1020, 842, 777, 664. HRMS calcd for $C_{19}H_{22}N_2O_3Si$ $(M)^+$ 354.1400, found $(M)^+$ 354.1407.

Compound 13k. A solution of **12k** (1.02 g, 3.67 mmol) in DMF (13.6 mL) was cooled to 0 °C and *N*,*N*-diisopropylethylamine (3.20 mL, 18.4 mmol) was added dropwise. After stirring for 10 minutes at 0 °C, *tert*-butyldimethylsilyl trifluoromethanesulfonate (924 µL, 4.04 mmol) was added dropwise over 15 minutes and the reaction mixture was stirred at room temperature for an additional hour. The resulting yellow solution was cooled to 0 °C and 1 M NH_4OAc (20 mL) was carefully added. The mixture was then diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (15:1). The combined product eluents were dried *in vacuo* to provide **13k** (1.17 g, 81%) as a white solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.64 (s, 1H), 8.82 (s, 1H), 7.88 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H) 7.13 (d, *J* = 2.3 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.3 Hz, 1H), 1.07 (s, 9H), 0.27 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 153.6, 150.1, 146.4 (q_{C-F}, *J* = 4.1 Hz), 136.0, 133.8 (q_{C-F}, *J* = 3.3 Hz), 133.0, 129.8, 124.4 (q_{C-F}, *J* = 33.1 Hz), 123.9 (q_{C-F}, *J* = 271.9 Hz), 119.2, 119.2, 112.2, 110.6, 102.5, 26.0, 18.5, -4.2. IR (film): ν (cm^{-1}) 3449, 3429, 2928, 2888, 2856, 1606, 1551, 1468, 1448, 1426, 1330, 1286, 1239, 1166, 1133, 1084, 1011, 969, 945, 891, 860, 839, 778, 763. HRMS calcd for $C_{20}H_{23}F_3N_2OSi$ $(M)^+$ 392.1532, found $(M)^+$ 392.1523.

Compound 13l. A solution of **12l** (1.60 mg, 4.53 mmol) in DMF (16 mL) was cooled to 0 °C and *N*,*N*-diisopropylethylamine (3.84 mL, 22.7 mmol) was added dropwise. After stirring for 10 minutes at 0 °C, *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.15 mL, 4.98 mmol) was added dropwise over 15 minutes and the reaction mixture was stirred at room temperature for an additional 45 minutes. The solution was cooled to 0 °C and 1 M NH_4OAc (25 mL) was

carefully added. The mixture was then diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried using $MgSO_4$, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1). The combined product eluents were dried *in vacuo* to provide **13l** (1.62 g, 77%) as an off-white solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) = 9.52 (s, 1H), 8.51 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.70 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 6.91 (d, *J* = 1.6 Hz, 1H), 6.80 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.78 (s, 2H), 1.02 (s, 9H), 0.96 (s, 9H), 0.22 (s, 6H), 0.14 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 149.8, 149.5, 147.3, 137.5, 135.2, 135.1, 132.6, 129.9, 119.7, 117.9, 111.9, 110.4, 100.2, 62.9, 26.1, 26.0, 18.6, 18.5, -4.2, -5.0. IR (film) *v* (cm^{-1}) = 3202, 2959, 2931, 2884, 2856, 1624, 1600, 1549, 1469, 1427, 1287, 1254, 1217, 1151, 1095, 964, 890, 838, 782, 670. HRMS calcd for $C_{26}H_{41}N_2O_2Si_2$ $(M+H)^+$ 469.2707, found $(M+H)^+$ 469.2701.

Compound 13m. A solution of **12m** (173 mg, 0.490 mmol) in DMF (1.73 mL) was cooled to 0 °C and *N*,*N*-diisopropylethylamine (436 µL, 2.44 mmol) was added dropwise. After stirring for 10 minutes at 0 °C, *tert*-butyldimethylsilyl trifluoromethanesulfonate (169 µL, 0.74 mmol) was added dropwise over 15 minutes and the reaction mixture was stirred at room temperature for an additional 2 hours. The resulting yellow suspension was cooled to 0 °C and 1 M NH_4OAc (5 mL) was carefully added. The mixture was then diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried using $MgSO_4$, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1). The combined product eluents were dried *in vacuo* to provide **13m** (140 mg, 61%) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 9.48 (s, 1H), 9.16 (d, *J* = 2.0 Hz, 1H), 8.28 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 7.02 (d, *J* = 1.5 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.47 (m, 2H), 1.17 (m, 2H), 1.02 (s, 9H), 0.22 (s, 6H), 0.11 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 165.7, 153.6, 150.9, 150.0, 137.7, 136.5, 132.9, 129.8, 124.3, 119.08, 119.06, 112.1, 110.6, 102.4, 63.9, 26.0, 18.5, 17.7, -1.2, -4.2. IR (film) *v* (cm^{-1}) = 3397, 2956, 2929, 2857, 1696, 1593, 1543, 1454, 1283, 1229, 1139, 1117, 892, 838, 780. HRMS calcd for $C_{25}H_{37}N_2O_3Si_2$ $(M+H)^+$ 469.2343, found $(M+H)^+$ 469.2344.

Compound 14b. A solution of **6b** (675 mg, 2.58 mmol) in THF (8.5 mL) was prepared after drying **6b** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (7.74 mL, 7.74 mmol) was added dropwise over 15 minutes and the resulting yellow suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (1.00 g, 2.71 mmol) in THF (8.5 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 20 minutes and room temperature overnight. The resulting dark purple reaction mixture was carefully poured into stirring ice cold 10% HCl (60 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (6:1). The combined product eluents were dried *in vacuo* to provide **6b** (653 mg, 46%) as an orange solid. The unstable material was immediately subjected to photocyclization step.

Compound 14c. A solution of **6c** (90 mg, 0.268 mmol) in THF (720 µL) was prepared after drying **6c** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (670 µL, 0.670 mmol) was added dropwise over 15 minutes and the resulting orange suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (99 mg, 0.268 mmol) in THF (2.5 µL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 30 minutes and room temperature for 1.5 hours. The resulting dark purple reaction mixture was carefully poured into stirring ice cold 10%

HCl (10 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using $MgSO_4$, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (6:1). The combined product eluents were dried *in vacuo* to provide **14c** (90 mg, 78% based on recovered **6c**) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 10.38 (s, 1H), 8.54 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.26 (m, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 4.75 (s, 2H), 1.03 (s, 9H), 0.97 (s, 9H), 0.51 (s, 6H), 0.14 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 173.5, 171.1, 148.3, 147.4, 141.8, 136.7, 136.3, 136.1, 134.7, 127.3, 126.1, 124.1, 122.3, 121.3, 121.2, 112.2, 101.9, 62.6, 26.5, 26.1, 19.1, 18.5, -4.2, -5.1. IR (film) ν (cm^{-1}) = 3325, 2952, 2932, 2856, 1700, 1312, 1254, 1092, 1063, 843, 742. HRMS calcd for $C_{30}H_{41}BrN_3O_3Si_2$ $(M+H)^+$ 626.1870, found $(M+H)^+$ 626.1862.

Compound 14d. A solution of **6d** (200 mg, 0.962 mmol) in THF (2.5 mL) was prepared after drying **6d** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (2.9 mL, 2.89 mmol) was added dropwise over 15 minutes and the resulting light yellow suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (372 mg, 1.01 mmol) in THF (2.5 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 20 minutes and room temperature overnight. The resulting dark purple reaction mixture was carefully poured into stirring ice cold 10% HCl (50 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (5:1 to 2:1). The combined product eluents were dried *in vacuo* to provide **14d** (320 mg, 67%) as a bright orange solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.87 (s, 1H), 8.46 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.44 (m, 2H), 7.24 (m, 3H), 2.37 (s, 3H), 1.01 (s, 9H), 0.50 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 173.4, 171.0, 150.2, 147.1, 141.8, 137.1, 137.0, 135.9, 132.9, 127.5, 126.5, 124.1, 122.2, 121.3, 121.3, 112.0, 101.4, 26.6, 19.1, 18.6, -4.2. IR (film): ν (cm^{-1}) 3326, 3048, 2934, 2850, 1757, 1701, 1642, 1525, 1448, 1364, 1312, 1255, 1208, 1064, 976, 911, 824, 740. HRMS calcd for $C_{24}H_{27}BrN_3O_2Si$ $(M+H)^+$ 496.1056, found $(M+H)^+$ 496.1065.

Compound 14e. A solution of **6e** (200 mg, 0.844 mmol) in THF (2.5 mL) was prepared after drying **6e** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (2.5 mL, 2.53 mmol) was added dropwise over 15 minutes and the resulting yellow-brown suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (326 mg, 0.886 mmol) in THF (2.5 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 20 minutes and room temperature overnight. The resulting dark purple reaction mixture was carefully poured into stirring ice cold water and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (3:1 to 1:1). The combined product eluents were dried *in vacuo* to provide **14e** (300 mg, 68%) as a brick red solid. ^{1}H NMR (360 MHz, $CDCl_3$:CD_3OD 3:1): δ (ppm) 7.91 (d, *J* = 2.9 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.05 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 6.97 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 2.86 (s, 6H), 0.81 (s, 9H), 0.28 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD 3:1): δ (ppm) 173.5, 171.5, 145.2, 142.6, 138.5, 137.9, 136.3, 133.9, 126.9, 123.5, 122.9, 122.7, 120.6, 120.4, 118.6, 111.6, 99.8, 39.6, 26.1, 18.8, -4.7. IR (film): ν (cm^{-1}) 3342, 2930, 2855, 1760, 1701, 1633, 1589, 1498, 1443, 1396, 1361, 1310, 1255, 1207, 1137,

1084, 1063, 1005, 975, 939, 910, 847, 823, 738. HRMS calcd for $C_{25}H_{28}BrN_4O_2Si$ $(M-H)^-$ 523.1165, found $(M-H)^-$ 523.1185.

Compound 14f. A solution of **6f** (200 mg, 0.893 mmol) in THF (2.5 mL) was prepared after drying **6f** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (2.7 mL, 2.68 mmol) was added dropwise over 15 minutes and the resulting bright yellow suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (345 mg, 0.938 mmol) in THF (2.5 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 20 minutes and room temperature overnight. The resulting dark purple reaction mixture was carefully poured into stirring ice cold water and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (3:1 to 100% EtOAc). The combined product eluents were dried *in vacuo* to provide **14f** (355 mg, 78%) as a bright orange solid. ^{1}H NMR (360 MHz, $CDCl_3$:CD_3OD 3:1): δ (ppm) 8.10 (d, J = 3.0 Hz, 1H), 7.33 (m, 3H), 7.08 (m, 2H), 6.99 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H), 3.72 (s, 3H), 0.80 (s, 9H), 0.28 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$:CD_3OD 3:1): δ (ppm) 173.5, 171.4, 155.0, 143.0, 142.4, 137.4, 137.2, 136.4, 126.8, 124.0, 123.2, 122.8, 120.9, 120.8, 120.6, 111.8, 100.9, 55.5, 26.1, 18.8, -4.7. IR (film): ν (cm^{-1}) 3335, 2935, 2850, 1756, 1699, 1650, 1578, 1482, 1455, 1395, 1313, 1257, 1231, 1087, 1064, 1029, 846, 822, 793, 740. HRMS calcd for $C_{24}H_{27}BrN_3O_3Si$ $(M+H)^+$ 512.1005, found $(M+H)^+$ 512.1027.

Compound 14g. A solution of **6g** (745 mg, 3.27 mmol) in THF (8.5 mL) was prepared after drying **6g** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (9.81 mL, 9.81 mmol) was added dropwise over 15 minutes and the resulting yellow-orange suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (1.27 g, 3.43 mmol) in THF (8.5 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 20 minutes and room temperature overnight. The resulting dark purple reaction mixture was carefully poured into stirring ice cold 10% HCl (100 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (6:1 to 1:1). The combined product eluents were dried *in vacuo* to provide **14g** (668 mg, 40%) as a yellow-orange solid. The unstable material was immediately subjected to photocyclization step.

Compound 14h. A solution of **6h** (170 mg, 0.441 mmol) in THF (1.2 mL) was prepared after drying **6h** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (926 µL, 0.926 mmol) was added dropwise over 15 minutes and the resulting orange suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (171 mg, 0.463 mmol) in THF (1.2 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 20 minutes and room temperature overnight. The resulting dark purple reaction mixture was carefully poured into stirring ice cold 10% HCl (20 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (6:1 to 1:1). The combined product eluents were dried to provide **14h** (83 mg, 34%) as a yellow-orange solid. The unstable material was immediately subjected to photocyclization step.

Compound 14i. A solution of **6i** (775 mg, 2.29 mmol) in THF (6.0 mL) was prepared after drying **6i** under high vacuum. After cooling the solution to -15 °C, lithium

bis(trimethylsilyl)amide (1 M solution in hexanes) (4.81 mL, 4.81 mmol) was added dropwise over 15 minutes and the resulting suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (886 mg, 2.40 mmol) in THF (6.0 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 20 minutes and room temperature overnight. The resulting dark purple reaction mixture was carefully poured into stirring ice cold 10% HCl (50 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (5:1). The combined product eluents were dried to provide **14i** (983 mg, 69%) as an orange solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.94 (s, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.45 (m, 2H), 7.28 (ddd, J = 8.1, 6.0, 1.1 Hz, 1H), 7.20 (m, 2H), 4.89 (s, 2H), 1.00 (s, 9H), 0.99 (s, 9H), 0.49 (s, 6H), 0.16 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 173.3, 171.0, 161.5, 148.3, 141.6, 137.3, 136.7, 135.8, 130.4, 127.5, 126.7, 124.3, 121.4, 121.3, 121.0, 119.5, 112.0, 101.8, 66.2, 26.5, 26.2, 19.1, 18.6, -4.2, -5.1. IR (film): ν (cm^{-1}) 3342, 3061, 2954, 2930, 2885, 2858, 1764, 1741, 1700, 1640, 1593, 1575, 1531, 1493, 1467, 1442, 1412, 1362, 1312, 1257, 1212, 1117, 1089, 1065, 1009, 982, 910, 843, 792, 779, 742, 680. HRMS calcd for $C_{30}H_{39}BrN_3O_3Si_2$ $(M-H)^-$ 624.1713, found $(M-H)^-$ 624.1718.

Compound 14k. A solution of **13k** (800 mg, 2.04 mmol) in THF (5.3 mL) was prepared after drying **13k** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (6.12 mL, 6.12 mmol) was added dropwise over 15 minutes and the resulting yellow suspension was stirred at -15 °C for an additional 45 minutes. A solution of **7** (598 mg, 1.62 mmol) in THF (5.3 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 20 minutes and room temperature overnight. The resulting dark purple reaction mixture was carefully poured into stirring ice cold 10% HCl (50 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using Na_2SO_4, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (8:1). The combined product eluents were dried *in vacuo* to provide **14k** (940 mg, 68%) as a yellow-orange solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.88 (s, 1H), 7.68 (dd, J = 8.3, 1.9 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 8.7 Hz, 1H) 6.93 (d, J = 2.2 Hz, 1H), 6.83 (dd, J = 8.7, 2.3 Hz, 1H), 1.02 (s, 9H), 1.01 (s, 9H), 0.51 (s, 6H), 0.27 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 173.8, 170.9, 152.6, 150.9, 146.4 (q_{C-F}, J = 3.4 Hz), 141.6, 135.3, 133.7 (q_{C-F}, J = 3.3 Hz), 132.0, 128.0, 126.3, 125.0 (q_{C-F}, J = 33.4 Hz), 123.5 (q_{C-F}, J = 272.2 Hz), 121.2, 120.0, 112.7, 110.6, 103.3. IR (film): ν (cm^{-1}) 3333, 2956, 2931, 2886, 2859, 1765, 1743, 1698, 1642, 1604, 1575, 1525, 1471, 1461, 1391, 1364, 1327, 1268, 1218, 1180, 1133, 1077, 1057, 1014, 972, 939, 897, 842, 828, 803, 780, 734. HRMS calcd for $C_{30}H_{36}BrF_3N_3O_3Si_2$ $(M-H)^-$ 678.1431, found $(M-H)^-$ 678.1425.

Compound 14l. A solution of **13l** (1.60 g, 3.43 mmol) in THF (9.0 mL) was prepared after drying **13l** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (6.85 mL, 6.85 mmol) was added dropwise over 15 minutes and the resulting orange suspension was stirred at -15 °C for an additional 30 minutes. A solution of **7** (1.33 mg, 3.60 mmol) in THF (9.0 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 10 minutes and room temperature for 1.5 hours. The resulting dark purple reaction mixture was carefully poured into stirring ice cold 10% HCl (125 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using $MgSO_4$, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (8:1). The combined product eluents were dried *in*

vacuo to provide **14l** (2.34 g, 90%) as an orange solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) = 10.05 (s, 1H), 8.52 (d, *J* = 1.4 Hz, 1H), 7.55 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.24 (m, 2H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.80 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.73 (s, 2H), 0.989 (s, 9H), 0.986 (s, 9H), 0.93, (s, 9H), 0.46 (s, 6H), 0.20 (s, 6H), 0.10 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) = 173.4, 171.1, 150.5, 148.5, 147.5, 141.8, 137.5, 136.2, 134.6, 131.6, 128.2, 125.6, 122.3, 118.8, 112.5, 110.8, 101.4, 62.7, 26.6, 26.1, 26.0, 19.1, 18.6, 18.5, -4.2 (2C), -5.1. IR (film) *v* (cm^{-1}) = 3298, 2950, 2932, 2854, 1700, 1635, 1461, 1313, 1256, 1182, 1086, 1060, 973, 895, 838. HRMS calcd for $C_{36}H_{55}BrN_3O_4Si_3$ $(M+H)^+$ 756.2684, found $(M+H)^+$ 756.2648.

Compound 14m. A solution of **13m** (60 mg, 0.139 mmol) in THF (0.4 mL) was prepared after drying **13m** under high vacuum. After cooling the solution to -15 °C, lithium bis(trimethylsilyl)amide (1 M solution in hexanes) (417 µL, 0.417 mmol) was added dropwise over 15 minutes and the resulting orange suspension was stirred at -15 °C for an additional 15 minutes. A solution of **7** (54 mg, 0.146 mmol) in THF (0.4 mL) cooled to 0 °C was added and the reaction mixture was stirred at -15 °C for 10 minutes and room temperature for 3 hours. The resulting purple-brown reaction mixture was carefully poured into stirring ice cold 10% HCl (5 mL) and extracted with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine, dried using $MgSO_4$, filtered and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1 to 6:1). The combined product eluents were dried *in vacuo* to provide **14m** (65 mg, 77% based on recovered **13m**) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 10.00 (s, 1H), 9.16 (s, 1H), 8.15 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.2 Hz, 1H), 4.47 (m, 2H), 1.16 (m, 2H), 1.03 (s, 9H), 1.02 (s, 9H), 0.52 (s, 6H), 0.14 (s, 6H), 0.11 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 173.5, 170.9, 165.2, 152.6, 150.8, 150.7, 141.5, 137.5, 135.9, 132.0, 128.2, 126.4, 125.0, 121.5, 119.9, 112.7, 110.8, 103.1, 64.1, 26.6, 26.0, 19.1, 18.5, 17.7, -1.2, -4.12, -4.15. IR (film) *v* (cm^{-1}) = 3305, 3238, 2952, 2923, 2856, 1727, 1698, 1593, 1469, 1317, 1264, 1183, 1116, 1083, 1059, 1031, 973, 897, 840, 782. HRMS calcd for $C_{35}H_{51}BrN_3O_5Si_3$ $(M+H)^+$ 756.2320, found $(M+H)^+$ 756.2328.

Compound 4b. An orange solution of **14b** (40 mg, 0.073 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 1 hour with constant argon flow through the solution. The resulting orange solution was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (8:1). The combined product eluents were dried *in vacuo* to provide **4b** (21 mg, 62%) as a yellow solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 10.12 (s, 1H), 9.73 (d, *J* = 1.2 Hz, 1H), 9.20 (d, *J* = 2.1 Hz, 1H), 9.10 (d, *J* = 8.0 Hz, 1H) 7.69 (d, *J* = 8.1 Hz, 1H), 7.64 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 1.08 (s, 9H), 0.65 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 175.1, 174.0, 153.5, 146.5, 139.9, 139.4, 139.1, 132.6 (q_{C-F}, *J* = 3.3 Hz), 131.9, 128.5, 126.1, 125.5 (q_{C-F}, *J* = 33.0 Hz), 123.7, (q_{C-F}, *J* = 272.7 Hz), 122.5, 122.3, 121.2, 120.1, 116.9, 111.9, 26.7, 19.4, -3.8. IR (film): ν (cm^{-1}) 2929, 2862, 1690, 1656, 1610, 1564, 1543, 1522, 1493, 1460, 1443, 1393, 1309, 1254, 1185, 1116, 1089, 989, 918, 843, 826, 745. HRMS calcd for $C_{24}H_{21}F_3N_3O_2Si$ $(M-H)^-$ 468.1355, found $(M-H)^-$ 468.1334.

Compound 4c. An orange solution of **14c** (95 mg, 0.152 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 3 hours with constant argon flow through the solution. The resulting orange solution was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (8:1 to 3:1). The combined product eluents were rechromatographed using CH_2Cl_2:MeOH (100% CH_2Cl_2 to 100:1) providing **4c** (20 mg, 24%) as an orange solid containing inseparable impurities. The impure material was used in the

subsequent step. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 10.26 (s, 1H), 9.30 (m, 1H), 9.10 (m, 2H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.57 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.1, 6.6, 1.5 Hz, 1H), 5.03 (s, 2H), 1.09 (s, 9H), 0.99 (s, 9H), 0.65 (s, 6H), 0.18 (s, 6H).

Compound 4d. An orange suspension of **14d** (300 mg, 0.606 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 3 hours with constant argon flow through the solution. The resulting yellow suspension was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (5:1 to 2:1). The combined product eluents were dried *in vacuo* to provide **4d** (176 mg, 70%) as a yellow solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 10.12 (s, 1H), 9.20 (dd, *J* = 2.1, 1.0 Hz, 1H), 9.07 (d, *J* = 7.9 Hz, 1H), 8.44 (d, *J* = 2.1 Hz, 1H), 7.57 (m, 2H), 7.43 (ddd, *J* = 8.1, 6.7, 1.4 Hz, 1H), 2.61 (s, 3H), 1.08 (s, 9H), 0.65 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 175.9, 174.6, 152.6, 140.5, 139.6, 136.8, 133.3, 133.1, 130.8, 127.4, 125.7, 122.7, 122.0, 121.9, 120.5, 114.8, 111.5, 26.7, 19.4, 19.3, -3.7. IR (film): ν (cm^{-1}) 3286, 2931, 2852, 1750, 1690, 1603, 1563, 1513, 1464, 1396, 1340, 1309, 1250, 1064, 1013, 826, 744. HRMS calcd for $C_{24}H_{26}N_3O_2Si$ $(M+H)^+$ 416.1794, found $(M+H)^+$ 416.1791.

Compound 4e. A red-orange suspension of **14e** (200 mg, 0.382 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 2 hours with constant argon flow through the solution. The resulting bright orange suspension was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (3:1 to 1:1). The combined product eluents were dried *in vacuo* to provide **4e** (116 mg, 69%) as a bright orange solid. ^{1}H NMR (360 MHz, $CDCl_3$:CD_3OD 3:1): δ (ppm) 8.81 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 3.0 Hz, 1H), 8.23 (d, *J* = 3.0 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.33 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.19 (ddd, *J* = 8.1, 7.1, 0.9 Hz, 1H), 3.04 (s, 6H), 0.88 (s, 9H), 0.44 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD 3:1): δ (ppm) 176.0, 174.7, 145.2, 140.8, 139.8, 139.8, 130.9, 130.1, 126.3, 124.6, 123.7, 122.2, 121.0, 118.2, 112.8, 111.3, 110.3, 40.0, 26.3, 18.9, -4.2. IR (film): ν (cm^{-1}) 3457, 2929, 2850, 1740, 1683, 1592, 1563, 1458, 1409, 1376, 1313, 1275, 1246, 1178, 1116, 1063, 1044, 1005, 914, 843, 745, 722. HRMS calcd for $C_{25}H_{29}N_4O_2Si$ $(M+H)^+$ 445.2060, found $(M+H)^+$ 445.2075.

Compound 4f. An orange suspension of **14f** (252 mg, 0.493 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 2.5 hours with constant argon flow through the solution. The resulting yellow-orange suspension was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (5:1 to 1:1). The combined product eluents were dried *in vacuo* to provide **4f** (153 mg, 73%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.73 (s, 1H), 9.06 (d, *J* = 8.0 Hz, 1H), 8.75 (d, *J* = 3.0 Hz, 1H), 8.71 (d, *J* = 3.0, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.43 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 4.07 (s, 3H), 1.08 (s, 9H), 0.64 (s, 6H). IR (film): ν (cm^{-1}) 3447, 2927, 2853, 1743, 1686, 1611, 1567, 1520, 1450, 1409, 1372, 1347, 1305, 1244, 1219, 1046, 873, 848, 827. HRMS calcd for $C_{24}H_{26}N_3O_3Si$ $(M+H)^+$ 432.1743, found $(M+H)^+$ 432.1745.

Compound 4g. An orange suspension of **14g** (300 mg, 0.583 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 3 hours with constant argon flow through the solution. The resulting orange suspension was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes: EtOAc (10:1 to 8:1). The combined product eluents were dried *in vacuo* to provide **4g** (220 mg, 87%) as a yellow solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 13.17 (s, 1H), 9.27 (d, *J* = 8.8 Hz, 1H), 8.88 (d, *J* = 8.1 Hz, 1H), 7.87 (d,

J = 8.8 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 0.99 (s, 9H), 0.56 (s, 6H). IR (film): ν (cm^{-1}) 2924, 2855, 1754, 1690, 1592, 1518, 1469, 1454, 1405, 1336, 1302, 1272, 1253, 1209, 1120, 1100, 1066, 1042, 1007, 973, 938, 845, 825, 776, 742. HRMS calcd for $C_{23}H_{22}ClN_3O_2Si$ $(M)^+$ 435.1170, found $(M)^+$ 435.1181.

Compound 4h. A yellow solution of **14h** (92 mg, 0.165 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 1.5 hours with constant argon flow through the solution. The resulting orange solution was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1 to 8:1). The combined product eluents were dried *in vacuo* to provide **4h** (76 mg, 96%) as a yellow solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 13.20 (s, 1H), 9.18 (d, *J* = 8.7 Hz, 1H), 8.91 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1 H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.1 Hz, 1H), 1.00 (s, 9H), 0.56 (s, 6H). IR (film): ν (cm^{-1}) 2923, 2854, 1686, 1585, 1510, 1464, 1447, 1402, 1334, 1302, 1247, 1206, 1097, 1066, 1014, 844, 741. HRMS calcd for $C_{23}H_{21}BrN_3O_2Si$ $(M-H)^-$ 478.0586, found $(M-H)^-$ 478.0570.

Compound 4i. An orange solution of **14i** (325 mg, 0.520 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 3 hours with constant argon flow through the solution. The resulting orange solution was concentrated to dryness *in vacuo* and the crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1 to 8:1). The combined product eluents were dried *in vacuo* to provide **4i** (243 mg, 86%) as a yellow solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.93 (s, 1H), 9.40 (d, *J* = 8.3 Hz, 1H), 9.06 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.7, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56 (m, 1H), 7.43 (ddd, *J* = 8.0, 5.9, 1.1 Hz, 1H), 5.08 (s, 2H), 1.08 (s, 9H), 1.00 (s, 9H), 0.64 (s, 6H), 0.18 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 175.7, 174.6, 162.9, 140.0, 139.6, 137.7, 134.8, 130.2, 127.5, 125.7, 122.6, 121.9, 121.2, 121.0, 120.6, 115.4, 111.6. IR (film): ν (cm^{-1}) 3454, 2954, 2888, 2856, 1749, 1693, 1600, 1527, 1462, 1400, 1339, 1301, 1259, 1214, 1112, 1005, 844, 777, 742. HRMS calcd for $C_{30}H_{40}N_3O_3Si_2$ $(M+H)^+$ 546.2608, found $(M+H)^+$ 546.2608.

Compound 4k. A yellow solution of **14k** (300 mg, 0.442 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 3 hours with constant argon flow through the solution. The resulting red solution was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1). The combined product eluents were dried *in vacuo* to provide **4k** (206 mg, 78%) as a yellow-orange solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 10.19 (s, 1H), 9.69 (s, 1H), 9.14 (d, *J* = 2.1 Hz, 1H), 8.59 (d, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H) 7.17 (dd, *J* = 8.7, 2.4 Hz, 1H), 1.08 (s, 9H), 1.07 (s, 9H), 0.66 (s, 6H), 0.34 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 175.2, 173.7, 151.4, 146.4 (q_{C-F}, *J* = 3.2 Hz), 139.9, 139.4, 135.1, 132.4 (q_{C-F}, *J* = 3.9 Hz), 131.9, 125.3 (q_{C-F}, *J* = 33.2 Hz), 123.8 (q_{C-F}, *J* = 272.9 Hz), 123.0, 122.4, 120.6, 120.0, 116.6, 114.9, 112.2, 26.7, 26.1, 19.3, 18.6, -3.8, -4.1. IR (film): ν (cm^{-1}) 3453, 3237, 3079, 2953, 2891, 2860, 1752, 1696, 1622, 1573, 1520, 1471, 1401, 1311, 1264, 1217, 1178, 1138, 1087, 1047, 1002, 961, 926, 883, 831, 779, 736, 700. HRMS calcd for $C_{30}H_{35}F_3N_3O_3Si_2$ $(M-H)^-$ 598.2169, found $(M-H)^-$ 598.2172.

Compound 4l. A suspension of **14l** (290 mg, 0.390 mmol) in hexanes (225 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 3 hours with constant argon flow through the solution. The resulting orange suspension was concentrated to dryness *in vacuo* and subjected to silica gel chromatography with hexanes:EtOAc (5:1 to 3:1) using CH_2Cl_2 as the loading solvent. The combined product eluents were dried *in vacuo* to provide **4l** (124 mg, 47%) as an orange solid. ^{1}H NMR (360

MHz, $CDCl_3$) δ (ppm) = 10.27 (s, 1H), 9.28 (m, 1H), 9.09 (d, *J* = 2.1 Hz, 1H), 8.62 (d, *J* = 2.4 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.13 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.02 (s, 2H), 1.08 (s, 9H), 1.07 (s, 9H), 0.99 (s, 9H), 0.64 (s, 6H), 0.34 (s, 6H), 0.18 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) = 175.8, 174.2, 151.0, 150.3, 140.9, 137.8, 136.2, 134.9, 131.3, 131.1, 123.3, 121.6, 121.4, 120.3, 115.1, 114.8, 112.0, 63.6, 26.7, 26.1 (2C), 19.3, 18.6, -3.8, -4.1, -5.0. IR (film) *v* (cm^{-1}) = 2950, 2933, 2856, 1694, 1472, 1310, 1285, 1255, 1216, 1161, 1097, 965, 896, 837, 777. HRMS calcd for $C_{36}H_{54}N_3O_4Si_3$ $(M+H)^+$ 676.3422, found $(M+H)^+$ 676.3425.

Compound 4m. A yellow solution of **14m** (50 mg, 0.066 mmol) in toluene (250 mL) was irradiated with a medium pressure Hg lamp using a uranium filter (50% transmission at 350 nm) for 1 hour with constant argon flow through the solution. The resulting red-orange solution was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (6:1). The combined product eluents were dried *in vacuo* to provide **4m** (22 mg, 49%) as an orange solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) = 10.03 (s, 1H), 9.99 (d, *J* = 2.1 Hz, 1H), 9.55 (d, *J* = 2.1 Hz, 1H), 8.64 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.56 (m, 2H), 1.26 (m, 2H), 1.08 (s, 9H), 1.07 (s, 9H), 0.65 (s, 6H), 0.34 (s, 6H), 0.14 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 175.2, 173.9, 165.5, 151.3, 150.9, 140.2, 139.9, 136.3, 135.2, 131.6, 125.2, 123.2, 122.3, 121.3, 120.5, 116.5, 114.9, 112.2, 64.4, 26.7, 26.1, 19.3, 18.6, 17.9, -1.2, -3.8, -4.1. IR (film) *v* (cm^{-1}) = 3380, 2949, 2858, 1691, 1466, 1398, 1255, 1164, 1104, 962, 884, 838, 774. HRMS calcd for $C_{35}H_{48}N_3O_5Si_3$ $(M-H)^-$ 674.2902, found $(M-H)^-$ 674.2870.

Compound 4n. To a solution of **1** (43.0 mg, 0.107 mmol) in $CHCl_3$:MeOH (1:1) (4 mL) was added *N*-chlorosuccinimide (15.8 mg, 0.118 mmol) and the yellow solution was refluxed for 1 hour. The reaction mixture was concentrated to dryness *in vacuo*, adsorbed onto silica gel and purified via silica gel chromatography with hexanes:EtOAc (6:1 to 4:1). The combined product eluents were dried *in vacuo* to provide **4n** (20 mg, 43%, 92% based on recovered **1**) as a yellow solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) = 10.48 (s, 1H), 9.41 (dd, *J* = 8.5, 1.6 Hz, 1H), 9.03 (m, 1H), 9.00 (dd, *J* = 4.3, 1.7 Hz, 1H), 7.66 (dd, *J* = 8.5, 4.3 Hz, 1H), 7.48 (m, 2H), 1.09 (s, 9H), 0.66 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) = 175.4, 174.1, 150.8, 140.7, 138.5, 137.9, 134.6, 130.7, 127.8, 127.4, 125.0, 123.5, 123.4, 122.2, 121.4, 114.5, 112.6, 26.7, 19.3, -3.8. IR (film) *v* (cm^{-1}) = 3149, 3079, 2956, 2929, 2859, 1752, 1695, 1597, 1558, 1527, 1457, 1409, 1338, 1307, 1281, 1083, 1061, 1043, 977, 938, 907, 845, 828, 735, 696, 678, 647. HRMS calcd for $C_{23}H_{21}ClN_3O_2Si$ $(M-H)^-$ 434.1092, found $(M-H)^-$ 434.1108.

Compound 4o. To a solution of **1** (35.0 mg, 0.087 mmol) was stirred in $CHCl_3$:MeOH (1:1) was added *N*-bromosuccinimide (15.5 mg, 0.087 mmol) and the solution was stirred at room temperature for 30 minutes. The reaction mixture was concentrated to dryness *in vacuo*, adsorbed onto silica gel and purified via silica gel chromatography with hexanes:EtOAc (5:1 to 3:1). The combined product eluents were dried *in vacuo* to provide **4o** (29 mg, 71%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 10.56 (s, 1H), 9.40 (dd, *J* = 8.5, 1.6 Hz, 1H), 9.16 (d, *J* = 1.9 Hz, 1H), 9.00 (dd, *J* = 4.3, 1.7 Hz, 1H), 7.65 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.62 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 1H), 1.09 (s, 9H), 0.66 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 175.4, 174.0, 150.8, 140.4, 138.5, 138.3, 134.7, 130.7, 130.4, 128.0, 124.0, 123.4, 122.2, 121.4, 114.9, 114.3, 113.1, 26.7, 19.3, -3.8. IR (film) *v* (cm^{-1}) = 2925, 2852, 1749, 1694, 1594, 1526, 1453, 1403, 1335, 1308, 1281, 1071, 1049, 826, 799. HRMS calcd for $C_{23}H_{22}BrNaN_3O_2Si$ $(M+Na)^+$ 502.0562, found $(M+Na)^+$ 502.0570.

Compound 15c. A suspension of ligand **4c** (20 mg, 0.037 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (20 mg, 0.048 mmol) and K_2CO_3 (5.6 mg, 0.041 mmol) in CH_3CN:CH_2Cl_2:MeOH (2:1:1) (1.6 mL) was stirred at room temperature overnight. The resulting purple reaction mixture was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (8:1). The combined

product eluents were dried *in vacuo* to provide **15c** (14 mg, 52%) as a purple film containing inseparable impurities. The impure material was used in the subsequent step. ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) = 9.06 (m, 1H), 9.03 (d, *J* = 1.6 Hz, 1H), 8.90 (ddd, *J* = 7.9, 1.2, 0.7 Hz, 1H), 7.58 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.48 (ddd, *J* = 8.2, 1.0, 0.7 Hz, 1H), 7.39 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 5.22 (s, 5H), 5.00 (d, *J* = 3.5 Hz, 2H), 1.06 (s, 9H), 1.01 (s, 9H), 0.64 (s, 6H), 0.20 (d, *J* = 4.5 Hz, 6H).

Compound 15d. A suspension of ligand **4d** (20 mg, 0.048 mmol), $[RuCp(CO)(CH_3CN)_2]^+$ PF_6^- (30 mg, 0.072 mmol) and K_2CO_3 (7.3 mg, 0.053 mmol) in CH_3CN:CH_3OH (3:1) (2 mL) was stirred at room temperature overnight. The resulting purple reaction mixture was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (4:1 to 3:1). The combined product eluents were dried *in vacuo* to provide **15d** (28 mg, 91%) as a dark red film. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.08 (dd, *J* = 1.6, 0.9 Hz, 1H), 8.88 (d, *J* = 7.9 Hz, 1H), 8.77 (d, *J* = 1.6 Hz, 1H), 7.55 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.45 (dt, *J* = 8.1, 0.9, 0.9 Hz, 1H), 7.37 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 5.21 (s, 5H), 2.61 (s, 3H), 1.06 (s, 9H), 0.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 200.0, 176.0, 175.2, 155.7, 153.4, 143.6, 134.1, 133.3, 132.5, 126.6, 125.3, 124.5, 121.9, 119.9, 115.3, 115.2, 113.8, 80.8, 26.7, 19.4, 19.4, -3.7, (*one hidden carbon*). IR (film): ν (cm^{-1}) 2928, 2856, 1955, 1742, 1685, 1580, 1563, 1496, 1469, 1416, 1383, 1339, 1293, 1263, 1233, 1169, 1049, 1006, 910, 828, 746.

Compound 15e. A suspension of ligand **4e** (20 mg, 0.045 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (29 mg, 0.068 mmol) and K_2CO_3 (7.0 mg, 0.050 mmol) in CH_3CN:CH_3OH (3:1) (2 mL) was stirred at room temperature overnight. The resulting light purple reaction mixture was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (3:1 to 1:1). The combined product eluents were dried *in vacuo* to provide **15e** (23 mg, 79%) as a purple film. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 8.82 (d, *J* = 7.8 Hz, 1H), 8.55 (d, *J* = 2.5 Hz, 1H), 8.36 (d, *J* = 2.5 Hz, 1H), 7.49 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.32 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 1H), 5.19 (s, 5H), 3.18 (s, 6H), 1.06 (s, 9H), 0.62 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 200.4, 176.0, 175.4, 156.7, 153.4, 146.2, 143.4, 138.1, 133.6, 125.5, 125.0, 124.8, 123.2, 119.6, 114.7, 113.6, 112.9, 80.7, 41.1, 26.8, 19.4, -3.5, (*one hidden carbon*). IR (film): ν (cm^{-1}) 2931, 2857, 1953, 1738, 1681, 1631, 1570, 1496, 1470, 1425, 1366, 1310, 1272, 1241, 1170, 1109, 1046, 1007, 909, 829, 736, 692, 656.

Compound 15f. A suspension of ligand **4f** (15 mg, 0.035 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (22 mg, 0.053 mmol) and K_2CO_3 (5.4 mg, 0.039 mmol) in CH_3CN:CH_3OH (3:1) (1.5 mL) was stirred at room temperature overnight. The resulting dark red reaction mixture was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (3:1). The combined product eluents were dried *in vacuo* to provide **15f** (15 mg, 68%) as a red film. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 8.86 (d, *J* = 7.8 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.65 (d, *J* = 2.4 Hz, 1H), 7.54 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.36 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.21 (s, 5H), 4.07 (s, 3H), 1.06 (s, 9H), 0.63 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 199.9, 176.0, 175.1, 156.1, 155.0, 153.5, 147.9, 140.1, 133.2, 126.0, 125.3, 124.5, 122.4, 119.9, 115.0, 114.8, 113.4, 112.9, 80.7, 56.6, 26.8, 19.4, -3.6. IR (film): ν (cm^{-1}) 2929, 2856, 1957, 1741, 1684, 1631, 1565, 1515, 1497, 1469, 1418, 1349, 1308, 1262, 1220, 1110, 1046, 910, 878, 828, 746, 690.

Compound 15k. A suspension of ligand **4k** (25 mg, 0.042 mmol), $[RuCp(CO)(CH_3CN)_2]^+$ PF_6^- (27 mg, 0.063 mmol) and K_2CO_3 (6.3 mg, 0.046 mmol) in CH_3CN:CH_3OH (3:1) (2.5 mL) was stirred at room temperature overnight. The resulting dark purple reaction mixture

was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1). The combined product eluents were dried *in vacuo* to provide **15k** (22 mg, 67%) as a purple film. ^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 9.50 (s, 1H), 9.07 (s, 1H), 8.41 (d, J = 2.2 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H) 7.20 (dd, J = 8.8, 2.4 Hz, 1H), 5.25 (s, 5H), 1.08 (s, 9H), 1.06 (s, 9H), 0.63 (s, 6H), 0.33 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ (ppm) 199.0, 175.4, 174.4, 154.4, 150.6, 149.7 (q_{C-F}, J = 3.6 Hz), 149.2, 146.3, 134.3, 132.1 (q_{C-F}, J = 3.6 Hz), 124.7, 124.7 (q_{C-F}, J = 33.5 Hz), 123.4 (q_{C-F}, J = 272.4 Hz), 121.4, 120.2, 116.9, 115.9, 114.7, 113.8, 80.7, 26.7, 26.2, 19.4, 18.7, -3.7, -4.0. IR (film): ν (cm^{-1}) 3070, 2956, 2930, 2886, 2858, 1965, 1744, 1691, 1608, 1568, 1550, 1503, 1462, 1419, 1392, 1347, 1314, 1299, 1253, 1209, 1198, 1172, 1138, 1085, 1048, 1006, 973, 931, 904, 828, 814, 779, 734, 701.

Compound 15l. A suspension of ligand **4l** (23 mg, 0.034 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (16 mg, 0.038 mmol) and K_2CO_3 (5.1 mg, 0.037 mmol) in CH_3CN:CH_2Cl_2:MeOH (2:1:1) (2.0 mL) was stirred at room temperature overnight. The resulting purple reaction mixture was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (10:1). The combined product eluents were dried *in vacuo* to provide **15l** (20 mg, 68%) as a purple film. ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) = 9.04 (s, 1H), 8.98 (s, 1H), 8.38 (d, J = 2.5 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 7.14 (dd, J = 8.7, 2.5 Hz, 1H), 5.21 (s, 5H), 4.99 (d, J = 3.3 Hz, 2H), 1.08 (s, 9H), 1.06 (s, 9H), 1.01 (s, 9H), 0.63 (s, 6H), 0.33 (d, J = 0.8 Hz, 6H), 0.19 (d, J = 4.5 Hz, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) = 199.9, 175.9, 174.8, 155.6, 153.6, 149.9, 148.8, 144.8, 135.6, 133.6, 131.4, 124.8, 121.5, 120.3, 115.4, 114.6, 113.4, 80.7, 63.4, 26.8, 26.23, 26.15, 19.4, 18.65, 18.63, -3.7, -4.0, -4.9. IR (film) ν (cm^{-1}) = 2950, 2926, 2855, 1961, 1744, 1689, 1601, 1562, 1499, 1459, 1420, 1325, 1305, 1293, 1257, 1210, 1147, 1100, 1048, 1005, 973, 942, 906, 835, 780.

Compound 15m. A suspension of ligand **4m** (20 mg, 0.030 mmol), $[RuCp(CO)(CH_3CN)_2]^+$ PF_6^- (16 mg, 0.038 mmol) and K_2CO_3 (4.6 mg, 0.033 mmol) in CH_3CN:2-trimethylsilylethanol:CH_2Cl_2 (8:2:1) (1.2 mL) was stirred at room temperature overnight. An additional equivalent of $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ and K_2CO_3 were added and the reaction was warmed to 45 °C for 3 hours. The resulting purple reaction mixture was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (8:1) using CH_2Cl_2 to assist in loading the column. The combined product eluents were dried *in vacuo* to provide **15m** (20 mg, 78%) as a purple film. ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) = 9.80 (dd, J = 1.6, 0.3 Hz, 1H), 9.47 (dd, J = 1.6, 0.3 Hz, 1H), 8.41 (d, J = 2.5 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.19 (dd, J = 8.7, 2.5 Hz, 1H), 4.55 (m, 2H), 1.27 (m, 2H), 1.08 (s, 9H), 1.07 (s, 9H), 0.64 (s, 6H), 0.33 (d, J = 1.0 Hz, 6H), 0.15 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 199.4, 175.4, 174.5, 165.0, 154.9, 154.5, 150.3, 149.4, 146.5, 136.0, 134.0, 124.8, 124.6, 121.3, 120.4, 116.8, 115.8, 114.6, 114.5, 80.8, 64.6, 26.8, 26.2, 19.4, 18.7, 18.0, -1.2, -3.7, -4.0. IR (film) ν (cm^{-1}) = 2956, 2929, 2856, 1961, 1715, 1688, 1602, 1461, 1312, 1271, 1234, 1153, 835.

Compound 15n. A suspension of ligand **4n** (14 mg, 0.032 mmol), $[RuCp(CO)(CH_3CN)_2]^+$ PF_6^- (18 mg, 0.042 mmol) and K_2CO_3 (4.9 mg, 0.035 mmol) in CH_3CN:CH_2Cl_2:MeOH (3:2:1) (1.2 mL) was stirred at room temperature overnight. The resulting red suspension was concentrated to dryness *in vacuo*, adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (3:1). The combined product eluents were dried *in vacuo* to provide **15n** (18.5 mg, 92%) as a red solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) = 9.27 (dd, J = 8.3, 1.0 Hz, 1H), 8.92 (dd, J = 5.1, 1.1 Hz, 1H), 8.87 (d, J = 2.1 Hz, 1H), 7.50 (m, 2H), 7.38 (d, J = 8.7 Hz, 1H), 5.22 (s, 5H), 1.06 (s, 9H), 0.64 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) = 175.6, 174.8, 155.7, 154.8, 151.7, 145.5, 134.7, 133.4, 126.5, 125.4, 125.1,

124.5, 122.33, 122.29, 116.2, 115.1, 115.0, 80.8, 26.7, 19.4, -3.7. IR (film) ν (cm^{-1}) = 2929, 2855, 1959, 1741, 1688, 1519, 1495, 1445, 1417, 1334, 1293, 1269, 1224, 1088, 1043, 825.

Compound 3b. A suspension of ligand **4b** (30 mg, 0.064 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (41 mg, 0.096 mmol) and K_2CO_3 (9.7 mg, 0.070 mmol) in CH_3CN:CH_3OH (3:1) (3 mL) was stirred at room temperature overnight. The resulting dark purple reaction mixture was concentrated to dryness *in vacuo* and dissolved in CH_2Cl_2 (4 mL), purging with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (96 µL, 0.096 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The resulting dark purple reaction mixture was cooled to 0 °C and glacial acetic acid (5.5 µL, 0.096 mmol) was added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with hexanes:EtOAc (6:1 to 4:1). The combined product eluents were dried *in vacuo* to provide **3b** (20 mg, 57% over two steps) as a purple solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 11.21 (s, 1H), 9.65 (d, J = 1.1 Hz, 1H), 9.27 (s, 1H), 8.66 (d, J = 7.8 Hz, 1H) 7.67 (d, J = 8.2 Hz, 1H), 7.59 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.39 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 5.58 (s, 5H). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 200.3, 170.4, 170.1, 153.2, 153.1, 151.3, 144.8, 131.6, 130.2, 126.7, 124.2, 123.6 (q_{C-F}, J = 33.1 Hz), 123.2, 123.1 (q_{C-F}, J = 271.9 Hz), 120.0, 119.0, 116.2, 115.9, 112.6, 81.7. IR (film): ν (cm^{-1}) 3230, 1954, 1748, 1709, 1613, 1575, 1497, 1469, 1420, 1388, 1328, 1296, 1254, 1229, 1171, 1131, 1085, 1051, 1027, 988, 974, 811, 744, 710.

Compound 3c. A solution of **15c** (14.2 mg, 0.019 mmol) in CH_2Cl_2 (1 mL) was purged with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (60 µL, 0.060 mmol) and the reaction mixture was stirred at room temperature for 1.5 hours and 40 °C for an additional 2 hours. The reaction was again cooled to 0 °C, quenched with the careful addition of saturated NH_4Cl and extracted with EtOAc. The organic layer was washed with 1 M HCl followed by brine, dried over Na_2SO_4 and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (1:1 to 100% EtOAc). The combined product eluents were dried *in vacuo* to provide **3c** (4 mg, 41%) as a dark purple film. ^{1}H NMR (500 MHz, acetone-d_6) δ (ppm) = 9.75 (s, 1H), 9.29 (d, J = 1.4 Hz, 1H), 9.17 (s, 1H), 8.79 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.53 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.33 (ddd, J = 7.9, 6.9, 1.0 Hz, 1H), 5.49 (s, 5H), 4.99 (d, J = 5.7 Hz, 2H), 4.75 (t, J = 5.7 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm) = 201.1, 170.8, 170.5, 155.5, 154.4, 152.8, 142.8, 138.0, 130.9, 130.4, 125.9, 123.8, 123.4, 120.8, 119.3, 115.7, 114.3, 112.2, 81.6, 60.6. IR (film) ν (cm^{-1}) = 3196, 2920, 1946, 1746, 1702, 1582, 1564, 1493, 1422, 1342, 1231, 1023, 992, 743.

Compound 3d. A solution of **15d** (28 mg, 0.040 mmol) in CH_2Cl_2 (2.5 mL) was purged with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (60 µL, 0.060 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The reaction was again cooled to 0 °C, quenched with the careful addition of saturated NH_4Cl and extracted with EtOAc. The organic layer was washed with 1 M HCl followed by brine, dried over Na_2SO_4 and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (2:1 to 1:1). The combined product eluents were dried *in vacuo* to provide **3d** (21 mg, 91%) as a purple solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 11.00 (s, 1H), 9.21 (d, J = 1.3 Hz, 1H), 8.88 (s, 1H), 8.63 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.51 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.31 (ddd, J = 7.9, 6.9, 1.0 Hz, 1H), 5.51 (s, 5H), 2.61 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 201.2, 170.8, 170.6, 157.3, 154.5, 152.7, 142.0, 133.3, 132.1, 130.8, 125.8, 123.7, 123.4, 120.9, 119.2, 115.6, 114.0, 111.8, 81.6, 18.6. IR (film): ν

(cm^{-1}) 2923, 1952, 1747, 1701, 1652, 1566, 1520, 1491, 1462, 1421, 1346, 1261, 1222, 1108, 1071, 1017.

Compound 3e. A solution of **15e** (22 mg, 0.035 mmol) in CH_2Cl_2 (2.5 mL) was purged with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (53 µL, 0.053 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The reaction was again cooled to 0 °C, quenched with the careful addition of saturated NH_4Cl and extracted with EtOAc. The organic layer was washed with 1 M HCl followed by brine, dried over Na_2SO_4 and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (1:1). The combined product eluents were dried *in vacuo* to provide **3e** (18 mg, 100%) as a purple solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 10.84 (s, 1H), 8.87 (d, J = 2.4 Hz, 1H), 8.55 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 2.4 Hz, 1H), 7.45 (m, 2H), 7.24 (ddd, J = 7.9, 6.3, 1.5 Hz, 1H), 5.51 (s, 5H), 3.16 (s, 6H). ^{13}C NMR (90 MHz, DMSO-d_6): δ (ppm) 201.5, 171.0, 170.6, 155.6, 152.7, 146.0, 144.9, 136.0, 131.0, 125.2, 123.7, 123.3, 122.4, 118.8, 115.1, 112.2, 110.3, 109.4, 81.6, 40.1. IR (film): ν (cm^{-1}) 3158, 3034, 2914, 1939, 1679, 1567, 1483, 1426, 1325, 1234, 1173, 1108, 1063, 1005, 935, 852.

Compound 3f. A solution of **15f** (15 mg, 0.024 mmol) in CH_2Cl_2 (2 mL) was purged with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (36 µL, 0.036 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The reaction was again cooled to 0 °C, quenched with the careful addition of saturated NH_4Cl and extracted with EtOAc. The organic layer was washed with 1 M HCl followed by brine, dried over Na_2SO_4 and concentrated to dryness *in vacuo*. The crude material was adsorbed onto silica gel and subjected to silica gel chromatography with hexanes:EtOAc (2:1 to 1:1). The combined product eluents were dried *in vacuo* to provide **3f** (10 mg, 83%) as a purple solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 11.00 (s, 1H), 9.14 (d, J = 2.4 Hz, 1H), 8.61 (d, J = 7.6 Hz, 1H), 8.47 (d, J = 2.4 Hz, 1H), 7.51 (m, 2H), 7.30 (ddd, J = 8.0, 6.6, 1.5 Hz, 1H), 5.52 (s, 5H), 4.06 (s, 3H). ^{13}C NMR (90 MHz, DMSO-d_6): δ (ppm) 201.1, 170.8, 170.4, 154.8, 154.8, 152.8, 148.7, 138.6, 130.9, 125.7, 123.7, 123.4, 121.5, 119.1, 115.4, 113.5, 111.8, 111.2, 81.6, 55.2. IR (film): ν (cm^{-1}) 1954, 1740, 1676, 1578, 1560, 1514, 1491, 1467, 1411, 1337, 1290, 1266, 1228, 1162, 1109, 1065, 1026, 1002, 901.

Compound 3g. A suspension of ligand **4g** (50 mg, 0.115 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (53 mg, 0.126 mmol) and K_2CO_3 (17 mg, 0.126 mmol) in CH_3CN:CH_3OH (3:1) (5 mL) was stirred at room temperature for 48 hours. The resulting purple reaction mixture was concentrated to dryness *in vacuo* and dissolved in CH_2Cl_2 (4 mL), purging with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (173 µL, 0.173 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The resulting purple reaction mixture was cooled to 0 °C and glacial acetic acid (9.9 µL, 0.173 mmol) was added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with toluene:acetone (20:1). The combined product eluents were dried to provide **3g** (18 mg, 31% over two steps) as a purple solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 11.13 (s, 1H), 9.08 (d, J = 8.7 Hz, 1H), 8.68 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1 H), 7.65 (d, J = 8.2 Hz, 1H), 7.56 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.36 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H), 5.55 (s, 5H). ^{13}C NMR (90 MHz, DMSO-d_6): δ (ppm) 200.4, 170.6, 170.4, 155.3, 154.1, 152.9, 144.6, 135.7, 130.3, 126.4, 124.0, 123.7, 123.2, 119.6, 119.1, 115.8, 112.5, 82.6. IR (film): ν (cm^{-1}) 2923, 1952, 1753, 1697, 1644, 1579, 1492, 1419, 1340, 1292, 1244, 1201, 1127, 1053, 1009, 896, 870, 836, 796.

Compound 3h. A suspension of **4h** (35 mg, 0.073 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (46 mg, 0.110 mmol) and K_2CO_3 (11 mg, 0.080 mmol) in CH_3CN:CH_3OH (3:1) (3 mL) was stirred at room temperature for 48 hours. The resulting purple reaction mixure was concentrated to dryness *in vacuo* and dissolved in CH_2Cl_2 (3 mL), purging with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (110 µL, 0.110 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The resulting purple reaction mixture was cooled to 0 °C and glacial acetic acid (6.3 µL, 0.173 mmol) was added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with toluene:acetone (20:1). The combined product eluents were dried to provide **3h** (14 mg, 34% over two steps) as a purple solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 11.11 (s, 1H), 8.97 (d, J = 8.7 Hz, 1H), 8.69 (d, J = 7.9 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1 H), 7.63 (d, J = 8.2 Hz, 1H), 7.56 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.36 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 5.53 (s, 5H). ^{13}C NMR (90 MHz, DMSO-d_6): δ (ppm) 200.6, 170.5, 170.3, 154.4, 152.8, 148.6, 144.6, 135.0, 130.3, 127.5, 126.4, 124.0, 123.1, 119.6, 119.4, 115.9, 115.9, 112.5, 82.3. IR (film): ν (cm^{-1}) 3387, 1950, 1749, 1695, 1645, 1631, 1576, 1494, 1466, 1418, 1340, 1287, 1243, 1200, 1109, 1003, 806.

Compound 3i. A suspension of **4i** (50 mg, 0.092 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (58 mg, 0.138 mmol) and K_2CO_3 (14 mg, 0.101 mmol) in CH_3CN:CH_3OH (3:1) (5 mL) was stirred at room temperature for 48 hours. The resulting purple reaction mixure was concentrated to dryness *in vacuo* and dissolved in CH_2Cl_2 (5 mL), purging with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (230 µL, 0.230 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The resulting purple reaction mixture was cooled to 0 °C and glacial acetic acid (13.1 µL, 0.230 mmol) was added, allowed to warm to room temperature, concentrated to dryness *in vacuo*, and redissolved in EtOAc. The purple solution was washed with 1 M HCl followed by brine, dried using Na_2SO_4, filtered and evaporated. The crude material was subjected to silica gel chromatography with toluene:acetone (5:1). The combined product eluents were dried to provide **3i** (10 mg, 18% over two steps) as a purple solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 11.01 (s, 1H), 9.15 (d, J = 8.6 Hz, 1H), 8.67 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1 H), 7.63 (d, J = 8.3 Hz, 1H), 7.53 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 6.02 (t, J = 7.4 Hz, 1H) 5.52 (s, 5H) 4.88 (m, 2H). ^{13}C NMR (90 MHz, DMSO-d_6): δ (ppm) 200.5, 170.8, 170.6, 166.8, 154.1, 152.7, 143.8, 133.5, 130.1, 125.9, 123.9, 123.5, 120.8, 120.0, 119.2, 115.7, 114.8, 112.7, 82.0, 67.4. IR (film): ν (cm^{-1}) 3410, 1946, 1746, 1695, 1644, 1536, 1498, 1471, 1419, 1344, 1292, 1231, 1190, 1136, 1023, 993, 746.

Compound 3k. A solution of **15k** (21 mg, 0.027 mmol) in CH_2Cl_2 (2 mL) was purged with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (68 µL, 0.068 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The resulting dark blue reaction mixture was cooled to 0 °C and glacial acetic acid (3.9 µL, 0.068 mmol) was added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with CH_2Cl_2:CH_3OH (50:1). The combined product eluents were dried *in vacuo* to provide **3k** (13 mg, 87%) as a blue-green solid. ^{1}H NMR (360 MHz, DMSO-d_6): δ (ppm) 11.16 (s, 1H) 9.58 (s, 1H), 9.32 (s, 1H), 9.22 (s, 1H) 8.11 (d, J = 2.1 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H) 7.13 (dd, J = 8.8, 2.5 Hz, 1H), 5.56 (s, 5H). ^{13}C NMR (90 MHz, DMSO-d_6): δ (ppm) 200.2, 170.5, 170.2, 152.9, 152.1, 150.8, 147.4, 145.2, 132.0, 129.7 (q_{C-F}, J = 4.4 Hz), 123.8, 123.2 (q_{C-F}, J = 272.7 Hz), 123.2 (q_{C-F}, J = 33.1 Hz), 119.1, 117.3, 116.7, 115.6, 111.1, 108.1, 81.7. IR (film): ν (cm^{-1}) 3449, 3291, 2918, 2851, 1962, 1751, 1710, 1608, 1500, 1474, 1425, 1388, 1336, 1301, 1255, 1217, 1168, 1118, 1085, 905, 809, 702.

Compound 3l. A solution of **15l** (15 mg, 0.017 mmol) in CH_2Cl_2 (1 mL) was purged with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (69 µL, 0.069 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The resulting turbid purple solution was cooled to 0 °C and glacial acetic acid (3.4 µL, 0.069 mmol) was added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with CH_2Cl_2:MeOH (50:1 to 20:1). The combined product eluents were dried *in vacuo* to provide **3l** (6.8 mg, 75%) as a dark purple solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) = 9.16 (s, 1H), 9.02 (s, 1H), 8.08 (d, J = 2.4 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 7.05 (dd, J = 8.7, 2.5 Hz, 1H), 5.48 (s, 5H), 4.80 (d, J = 2.1 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm) = 201.1, 171.0, 170.8, 154.9, 154.2, 151.5, 147.0, 143.2, 137.5, 131.3, 130.2, 123.9, 120.8, 116.1, 116.0, 114.1, 110.8, 108.2, 81.6, 60.7. IR (film) v (cm^{-1}) = 3354, 3283, 3248, 3213, 3160, 2922, 2869, 1946, 1743, 1699, 1563, 1470, 1338, 1210, 1153, 1021.

Compound 3m. A solution of **15m** (14 mg, 0.016 mmol) in THF (400 µL) was purged with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (80 µL, 0.080 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The reaction mixture was cooled to 0 °C and a few drops of glacial acetic acid were added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with EtOAc:MeOH (2:1) and rechromatographed with CH_2Cl_2:MeOH (2:1) to obtain an analytically pure material. The combined product eluents were dried *in vacuo* to provide **3m** (3.1 mg, 36%) as a green film. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) = 10.90 (s, 1H), 9.52 (s, 1H), 9.46 (s, 1H), 9.12 (s, 1H), 8.08 (d, J = 2.2 Hz, 1H), 7.41 (d, J = 8.7 Hz, 1H), 7.05 (dd, J = 8.8, 2.3 Hz, 1H), 5.47 (s, 5H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm) = 201.2, 170.74, 170.72, 166.0, 157.4, 154.0, 151.4, 147.1, 144.0, 133.2, 131.1, 123.9, 120.4, 116.3, 116.1, 114.3, 111.7, 108.1, 81.6 (*one carbon hidden*). IR (film) v (cm^{-1}) = 3619, 3592, 3187, 1950, 1702, 1562, 1423, 1378, 1342. HRMS calcd for $C_{24}H_{12}N_3O_6Ru$ (M-H)$^-$ 539.9770, found (M-H)$^-$ 539.9783.

Compound 3n. A solution of **15n** (14 mg, 0.022 mmol) in CH_2Cl_2 (1.1 mL) was purged with argon while cooling to 0 °C. To the solution was added tetrabutylammonium fluoride (1 M solution in THF) (33 µL, 0.033 mmol) and the reaction mixture was allowed to slowly warm to room temperature. The reaction mixture was cooled to 0 °C and glacial acetic acid (1.9 µL, 0.033 mmol) was added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with hexanes:EtOAc (3:1 to 1:1), then finally hexanes:EtOAc:CH_2Cl_2 (1:1:1) due to solubility issues. The combined product eluents were dried *in vacuo* to provide **3n** (10 mg, 87%) as a pink film. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) = 11.13 (s, 1H), 9.31 (d, J = 4.6 Hz, 1H), 9.08 (d, J = 8.1 Hz, 1H), 8.60 (d, J = 2.1 Hz, 1H), 7.76 (dd, J = 8.4, 5.1 Hz, 1H), 7.62 (d, J = 8.7 Hz, 1H), 7.51 (dd, J = 8.7, 2.2 Hz, 1H), 5.51 (s, 5H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm) = 200.9, 170.6, 170.4, 156.5, 154.7, 151.1, 144.0, 133.3, 131.0, 125.6, 124.1, 123.45, 123.35, 122.6, 121.4, 117.2, 113.5, 113.4, 81.7. IR (film) v (cm^{-1}) = 3349, 2923, 2853, 1948, 1701, 1653, 1557, 1540, 1522, 1509, 1457, 1418, 1340, 1270, 1222, 1022, 796.

Compound 3o. A yellow suspension of **4o** (18.5 mg, 0.039 mmol), $[RuCp(CO)(CH_3CN)_2]^+$ PF_6^- (16.2 mg, 0.039 mmol) and K_2CO_3 (5.3 mg, 0.039 mmol) in CH_3CN:MeOH (2:1) (2.4 mL) was stirred at room temperature overnight. To the resulting red solution was added tetrabutylammonium fluoride (1 M solution in THF) (193 µl, 0.193 mmol) and the solution stirred for 10 minutes at room temperature. The reaction mixture was cooled to 0°C and glacial acetic acid (3.3 µL, 0.058 mmol) was added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with hexanes:EtOAc (1:2). The combined product eluents were dried *in*

vacuo to provide **3o** (13 mg, 50%) as a red film. ^{1}H NMR (360 MHz, DMSO-d_6) δ (ppm) = 11.18 (s, 1H), 9.33 (dd, J = 5.1, 1.1 Hz, 1H), 9.09 (dd, J = 8.4, 1.1 Hz, 1H), 8.75 (dd, J = 1.9, 0.5 Hz, 1H), 7.77 (dd, J = 8.4, 5.1 Hz, 1H), 7.63 (dd, J = 8.7, 2.0 Hz, 1H), 7.58 (dd, J = 8.7, 0.5 Hz, 1H), 5.52 (s, 5H). ^{13}C NMR (90 MHz, DMSO-d_6) δ (ppm) = 200.9, 170.7, 170.5, 156.7, 154.6, 151.3, 144.0, 133.3, 131.0, 128.2, 125.7, 124.8, 123.6, 121.4, 117.8, 113.5, 113.4, 111.2, 81.7. IR (film) v (cm^{-1}) = 3346, 3248, 1944, 1693, 1664, 1643, 1334, 1087, 840.

Compound 3p. A suspension of **4p** (25 mg, 0.041 mmol), $[RuCp(CO)(CH_3CN)_2]^+PF_6^-$ (17 mg, 0.041 mmol) and K_2CO_3 (6.0 mg, 0.041 mmol) in CH_3CN:MeOH (3:1) (3 mL) was stirred at room temperature overnight. To the resulting red-purple reaction mixture was added tetrabutylammonium fluoride (1 M solution in THF) (193 µl, 0.193 mmol) and the solution stirred for 30 minutes at room temperature. The reaction mixture was cooled to 0 °C and a few drops of glacial acetic acid were added, allowed to warm to room temperature and concentrated to dryness *in vacuo*. The crude material was subjected to silica gel chromatography with CH_2Cl_2:MeOH (100:1). The combined product eluents were dried *in vacuo* to provide **3p** (16 mg, 70%) as a purple solid. ^{1}H NMR (360 MHz, DMSO-d_6) δ (ppm) = 11.18 (s, 1H), 9.33 (dd, J = 5.1, 1.1 Hz, 1H), 9.09 (dd, J = 8.4, 1.1 Hz, 1H), 8.75 (dd, J = 1.9, 0.5 Hz, 1H), 7.77 (dd, J = 8.4, 5.1 Hz, 1H), 7.63 (dd, J = 8.7, 2.0 Hz, 1H), 7.58 (dd, J = 8.7, 0.5 Hz, 1H), 5.52 (s, 5H). ^{13}C NMR (90 MHz, DMSO-d_6) δ (ppm) = 200.9, 170.7, 170.5, 156.7, 154.6, 151.3, 144.0, 133.3, 131.0, 128.2, 125.7, 124.8, 123.6, 121.4, 117.8, 113.5, 113.4, 111.2, 81.7. IR (film) v (cm^{-1}) = 3346, 3248, 1944, 1693, 1664, 1643, 1334, 1087, 840.

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B) NMR Spectra

Compound **11b**
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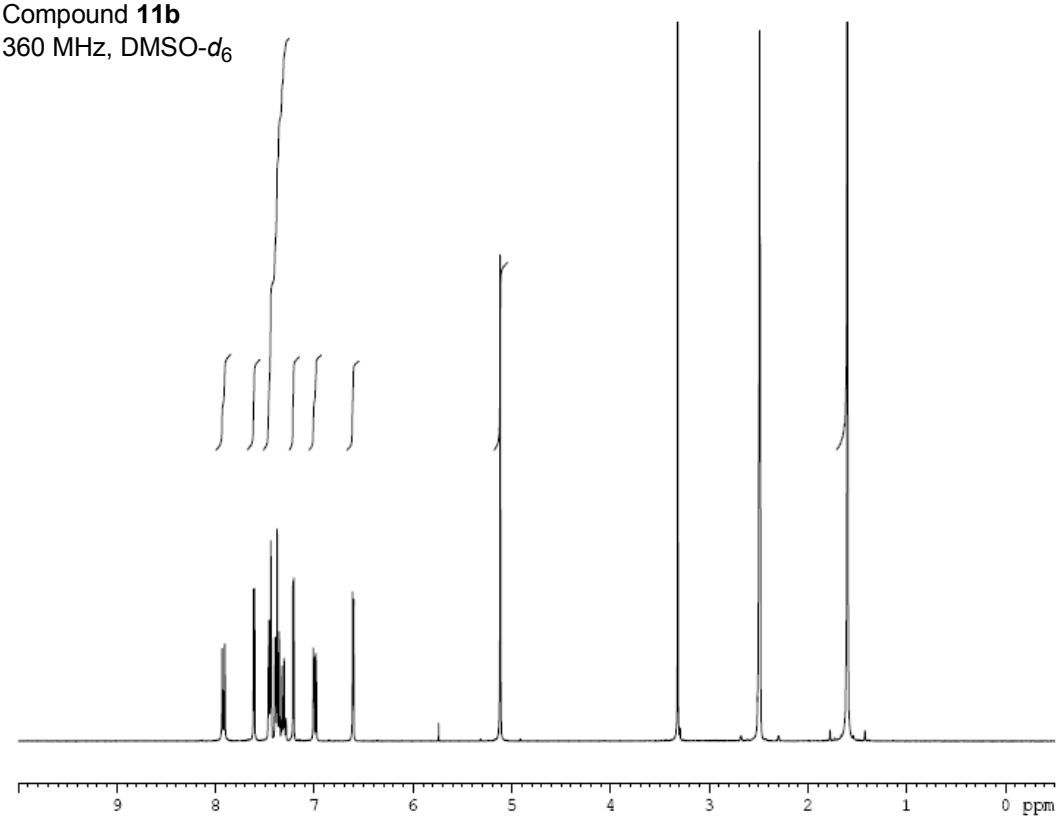

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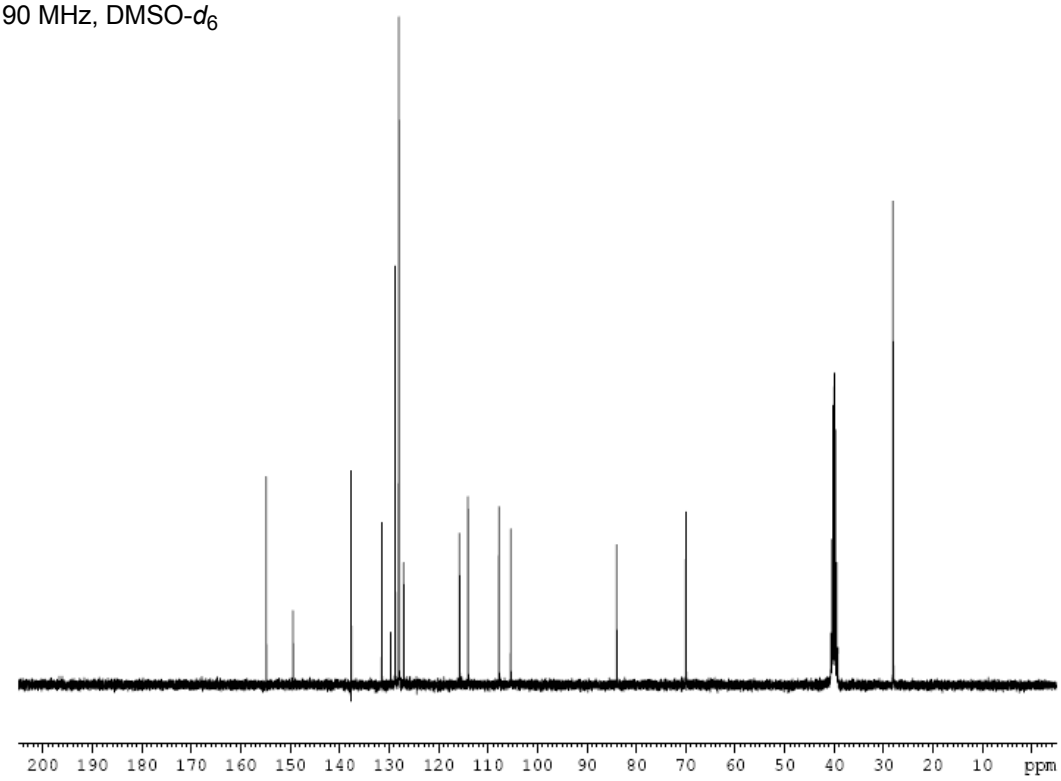
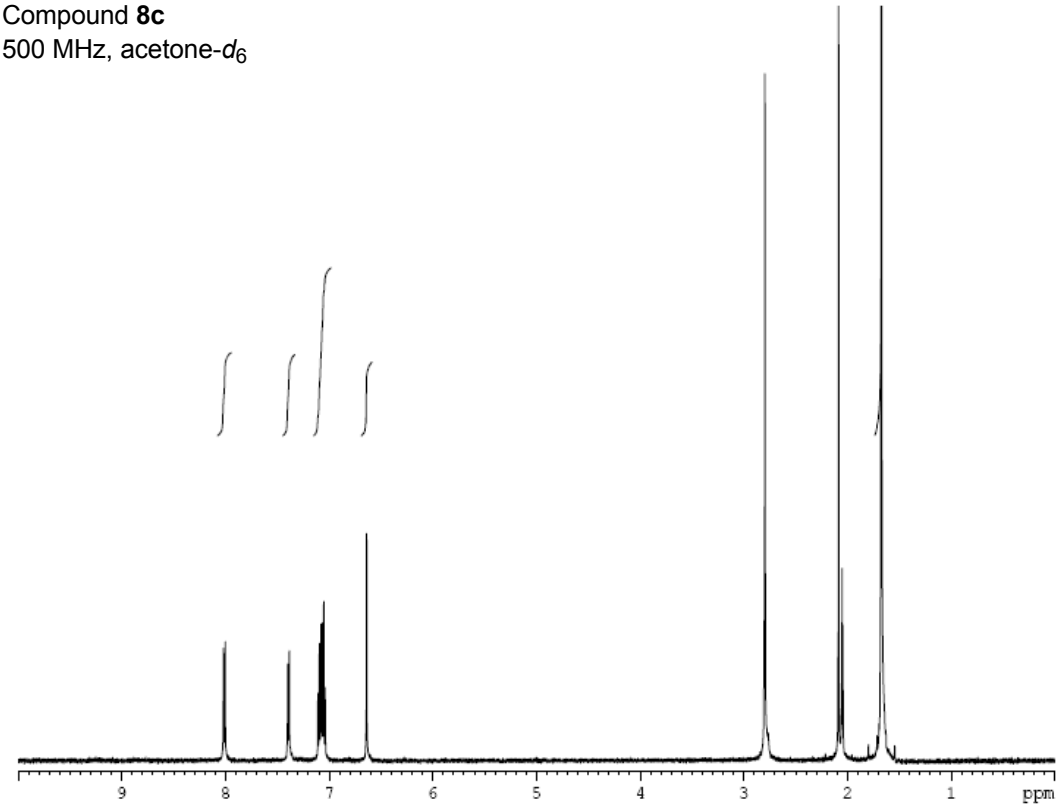
90 MHz, DMSO-d_6



Compound **8c**
500 MHz, acetone-d_6



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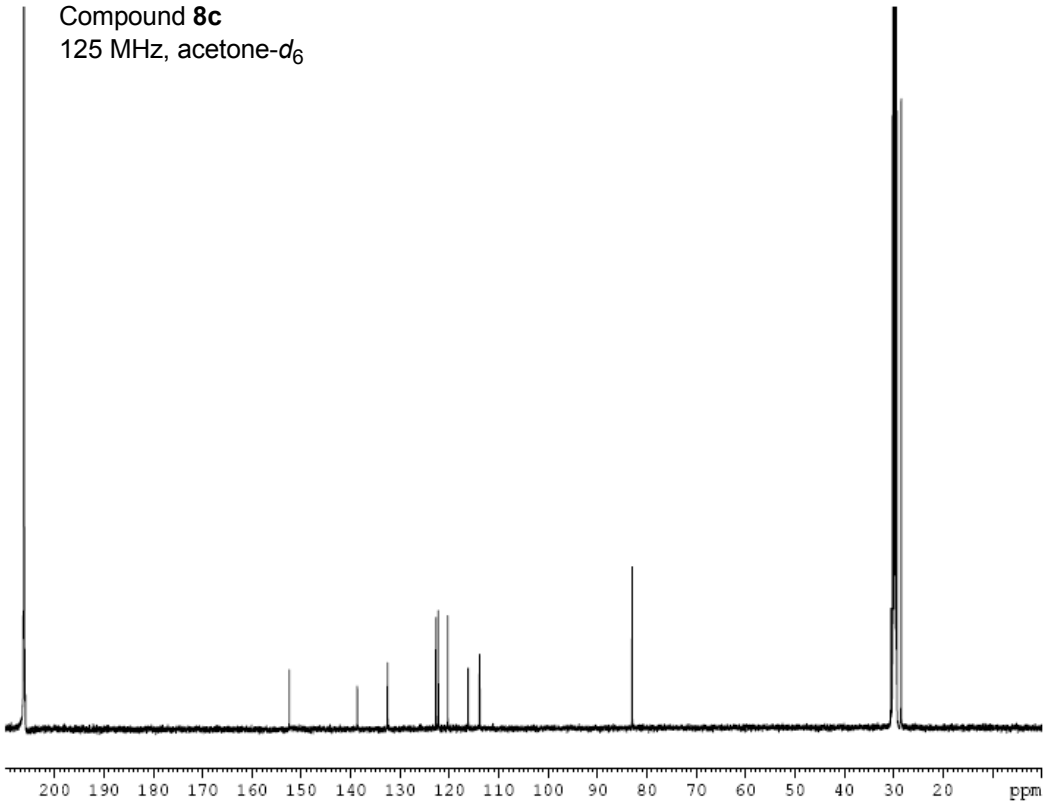

Compound **8d**
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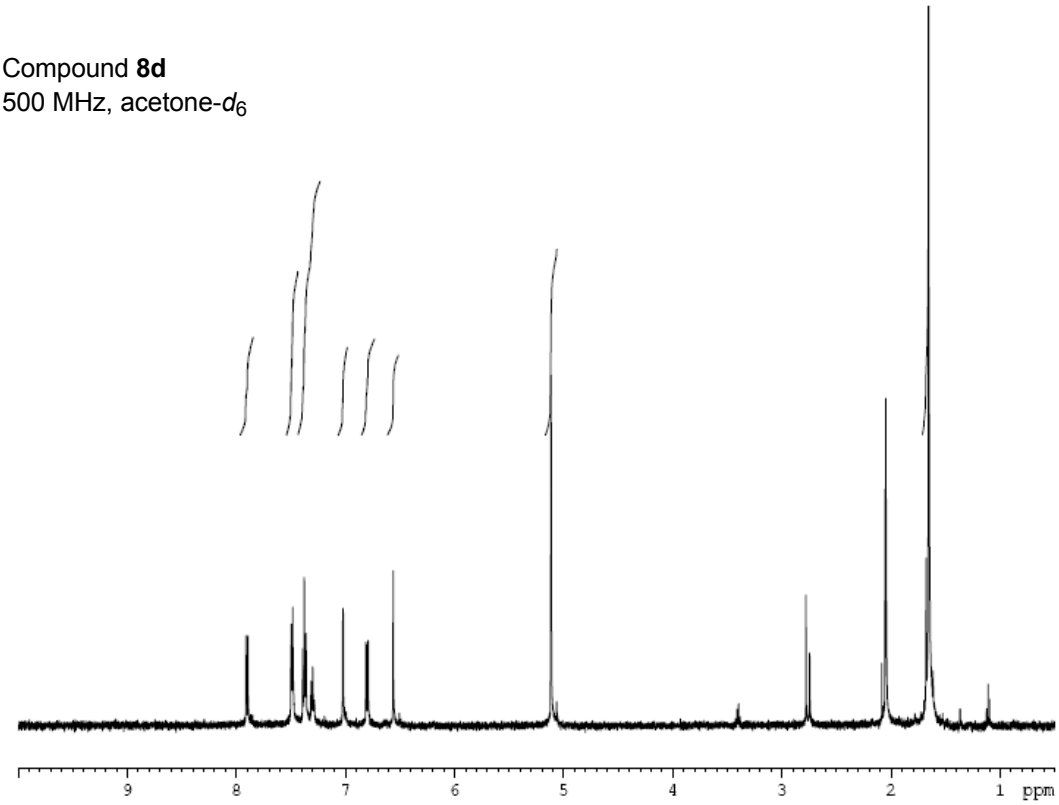

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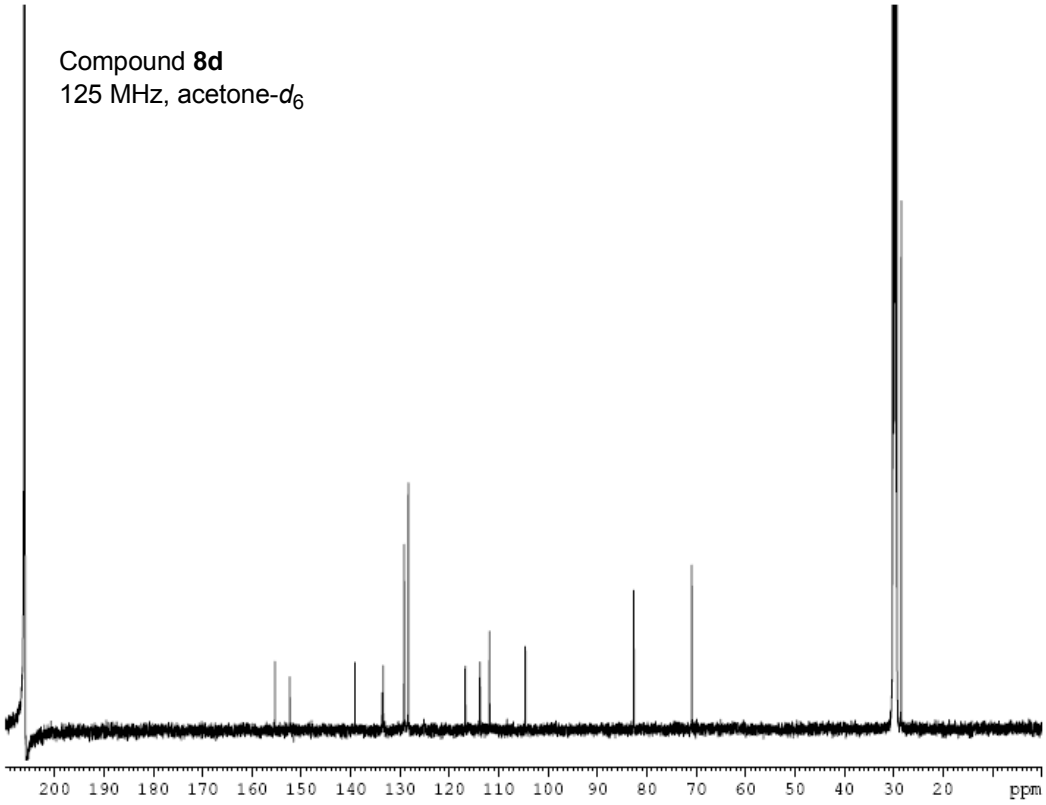
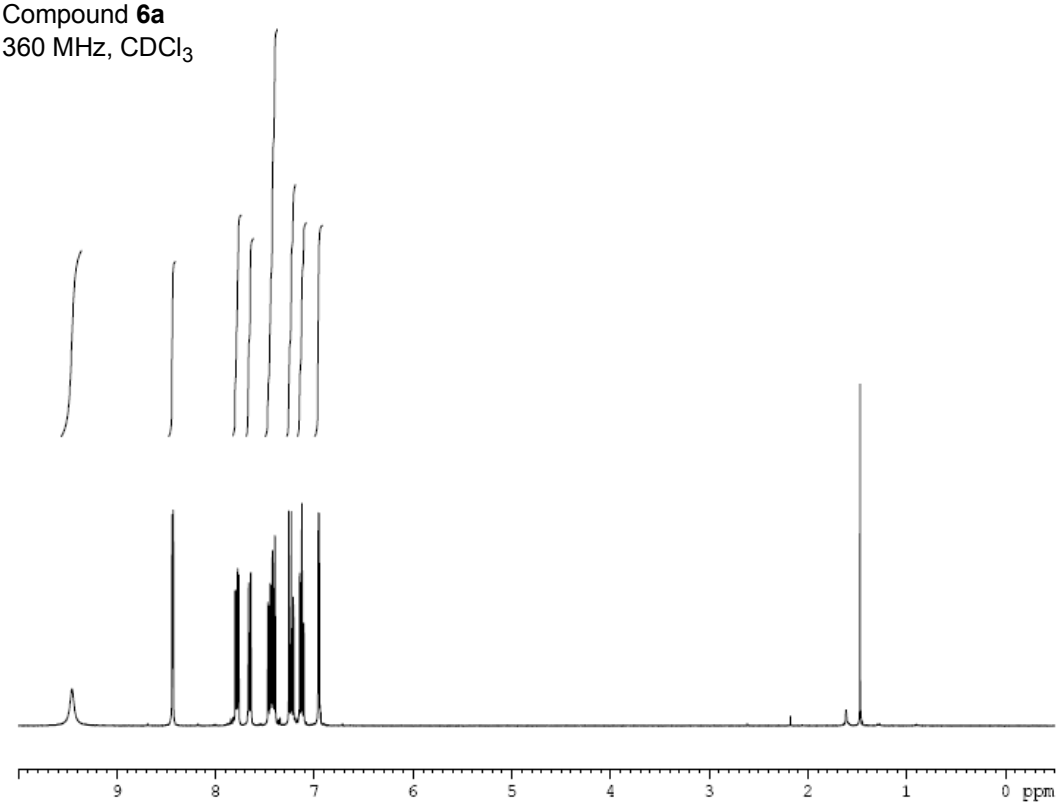


Compound **6a**
360 MHz, $CDCl_3$



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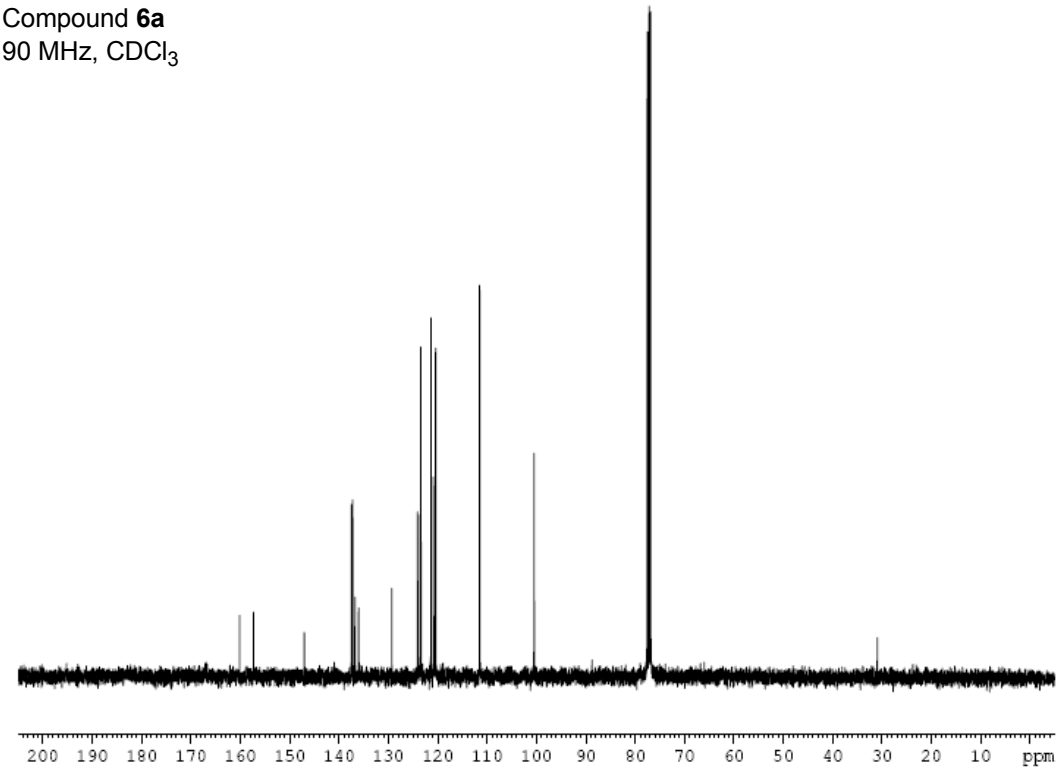

Compound **6b**
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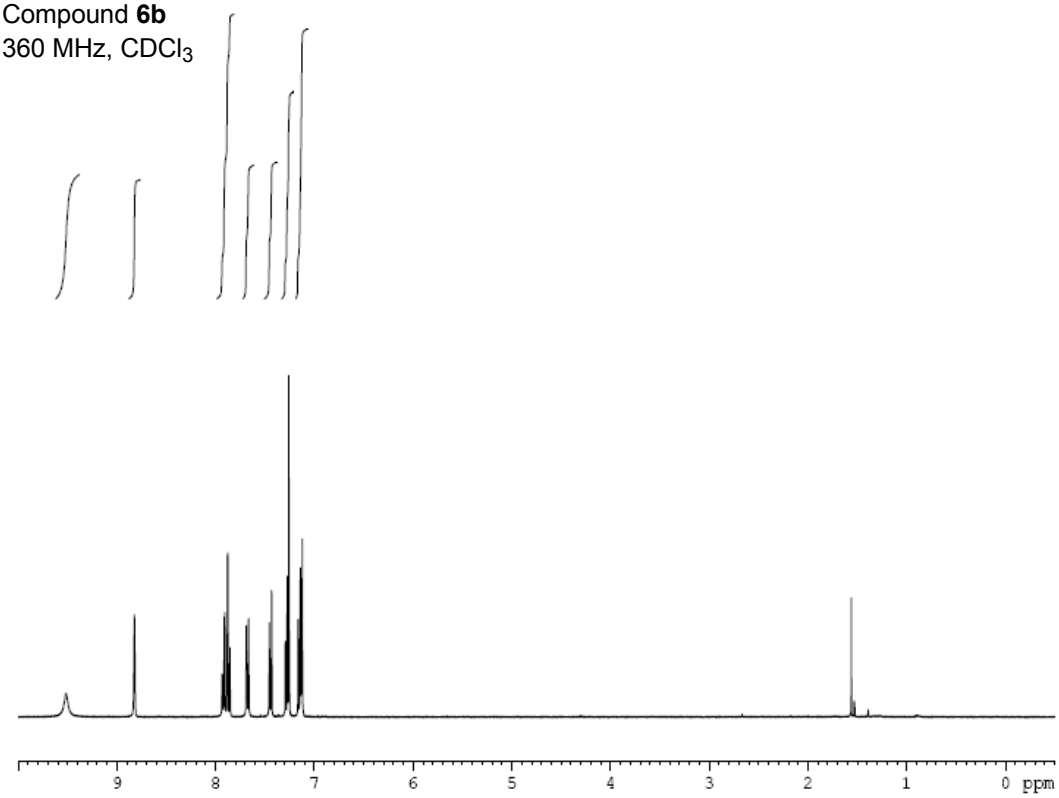

Compound **6b**
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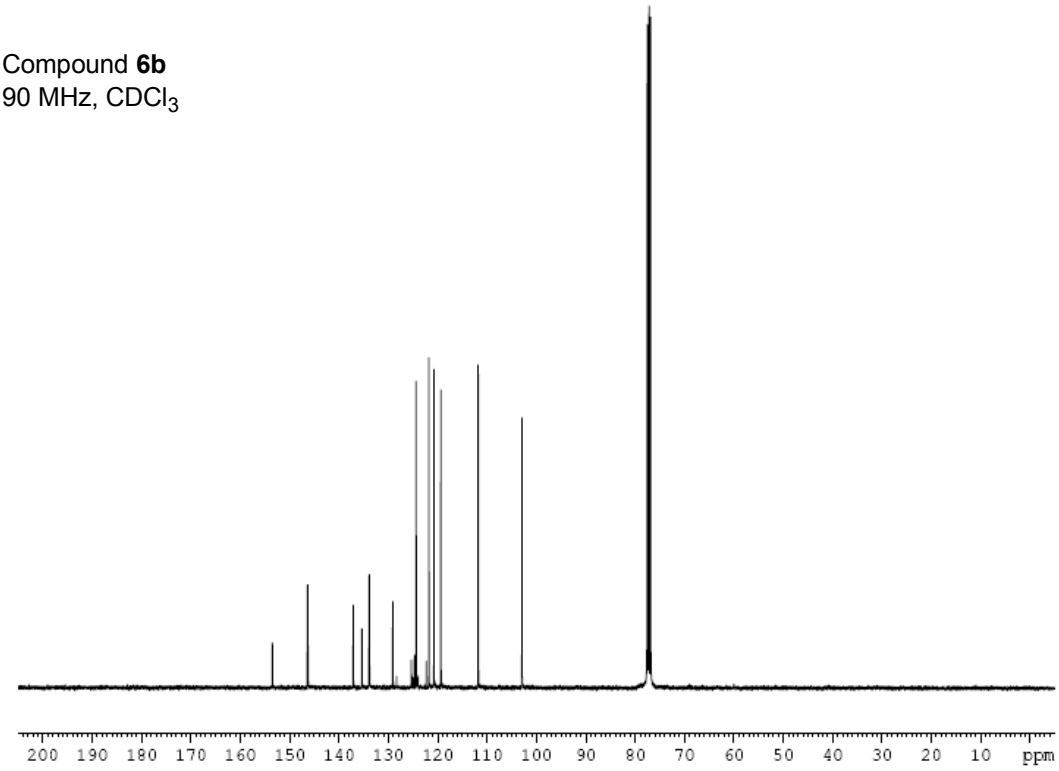
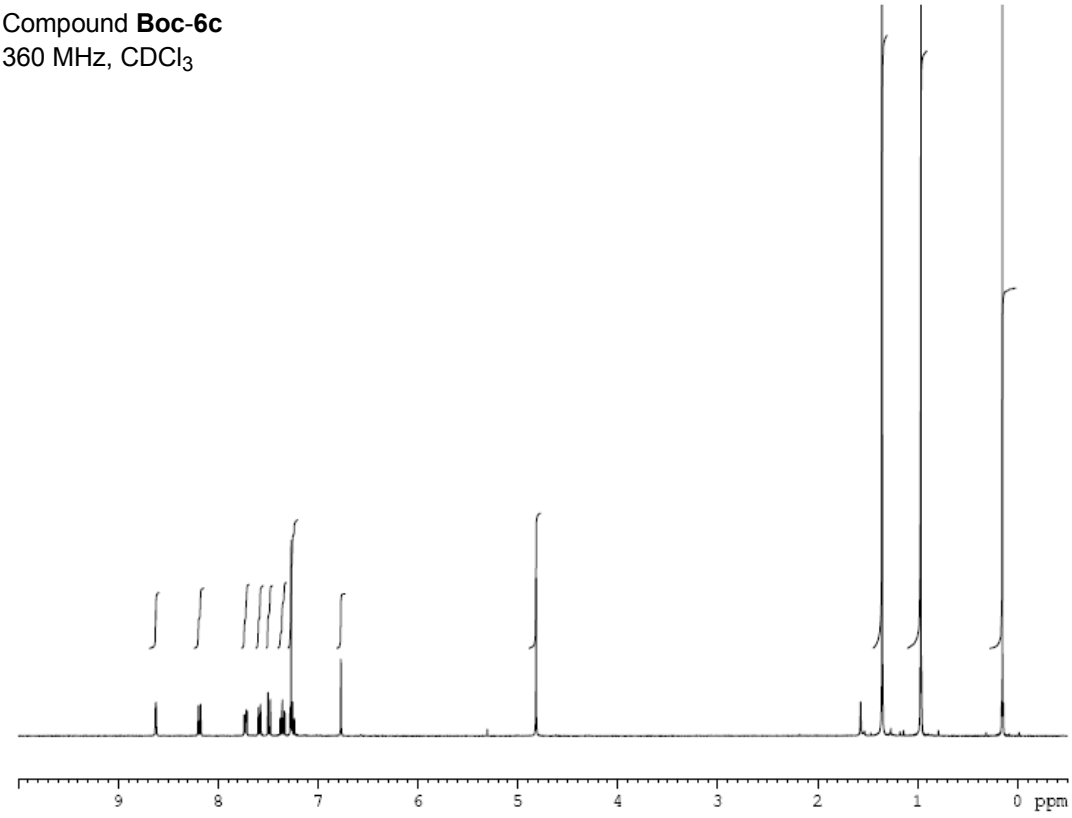


Compound **Boc-6c**
360 MHz, $CDCl_3$



Compound **Boc-6c**
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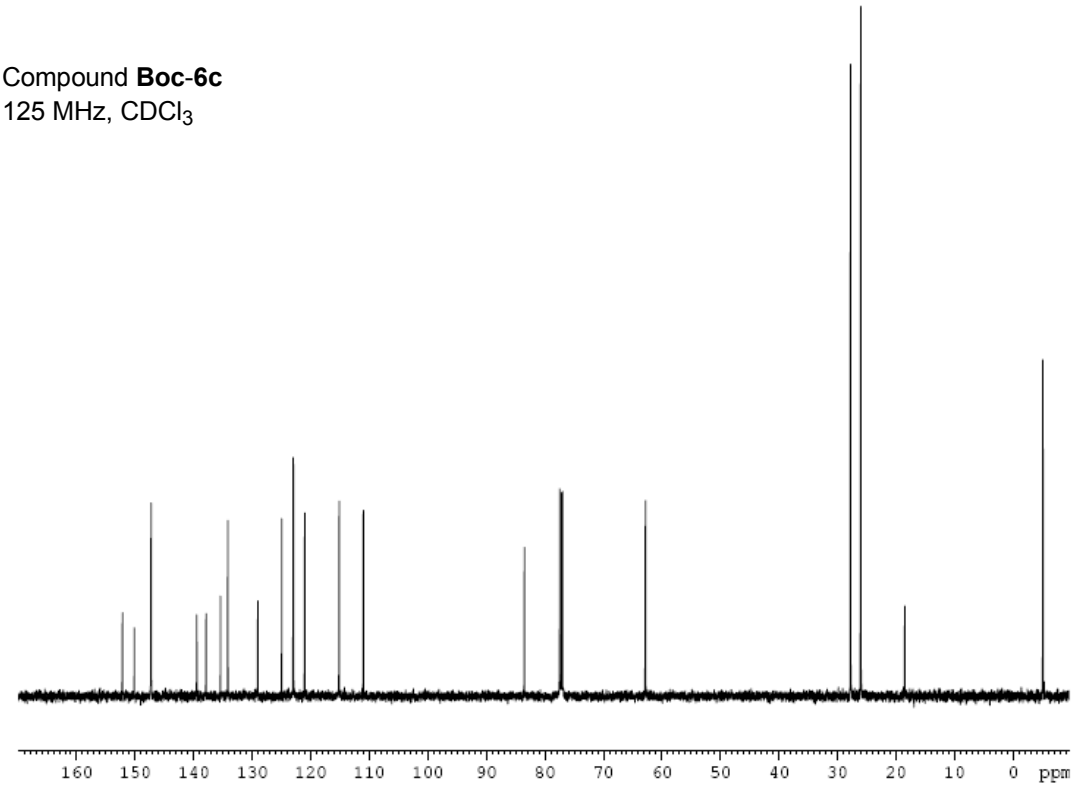

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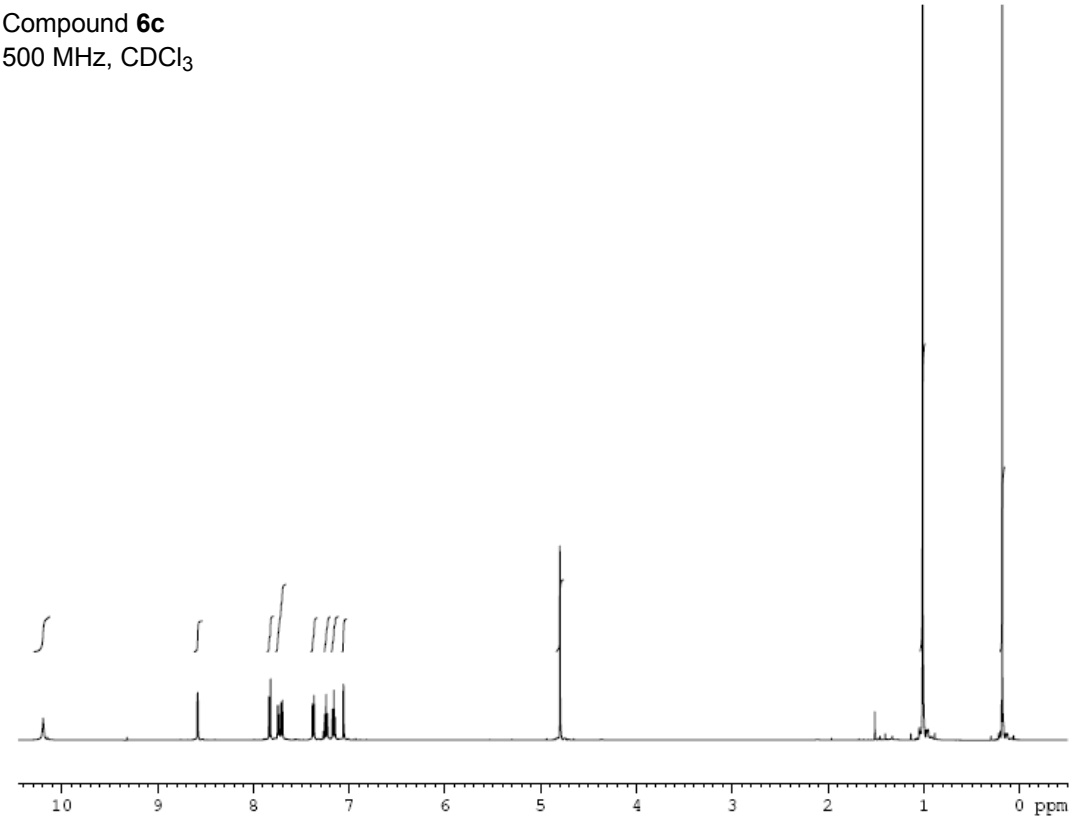

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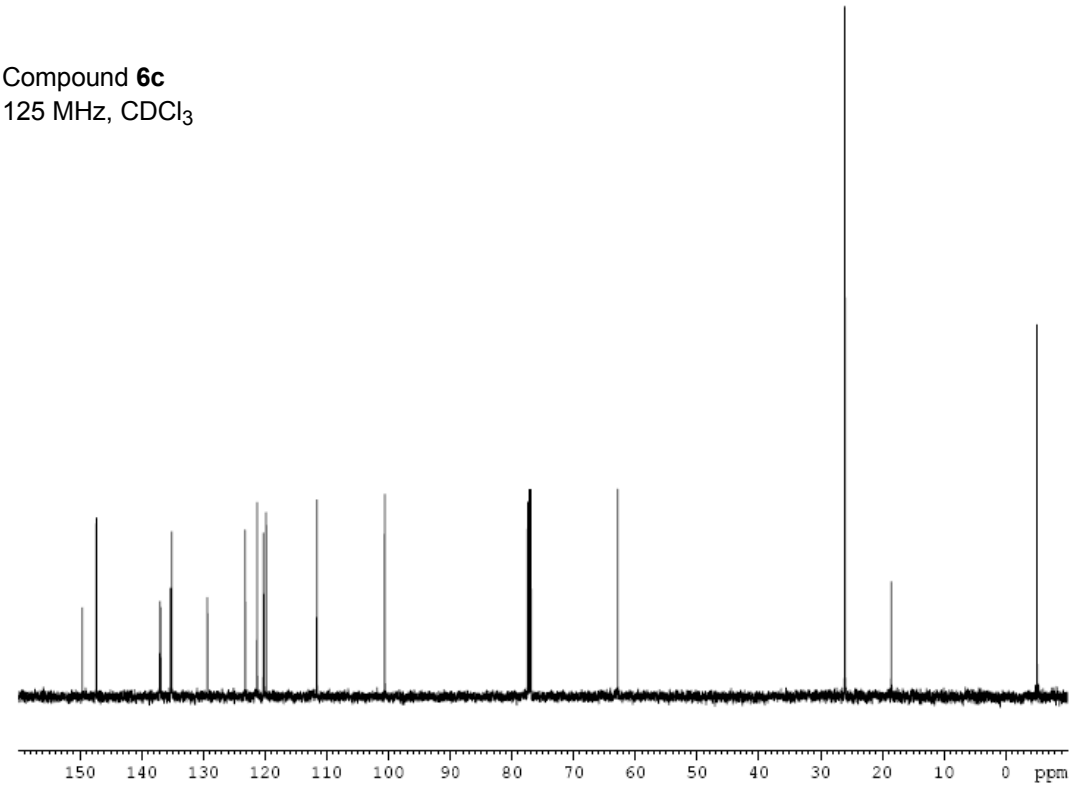
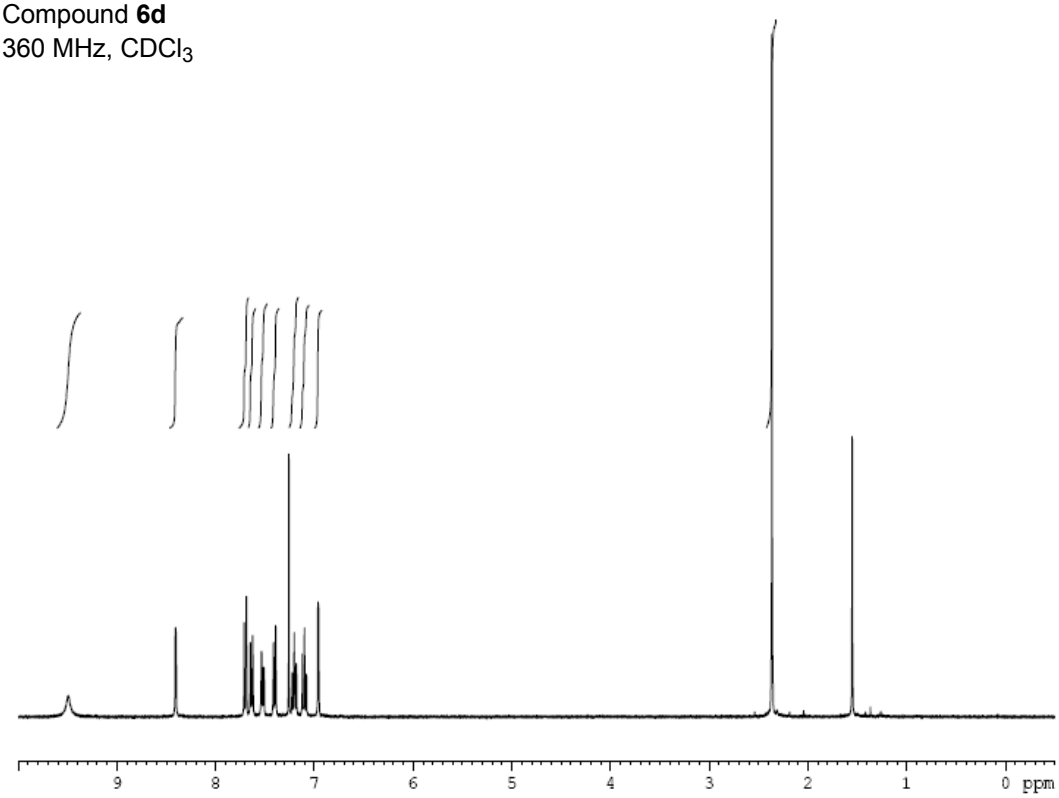


Compound **6d**
360 MHz, $CDCl_3$



Compound **6d**
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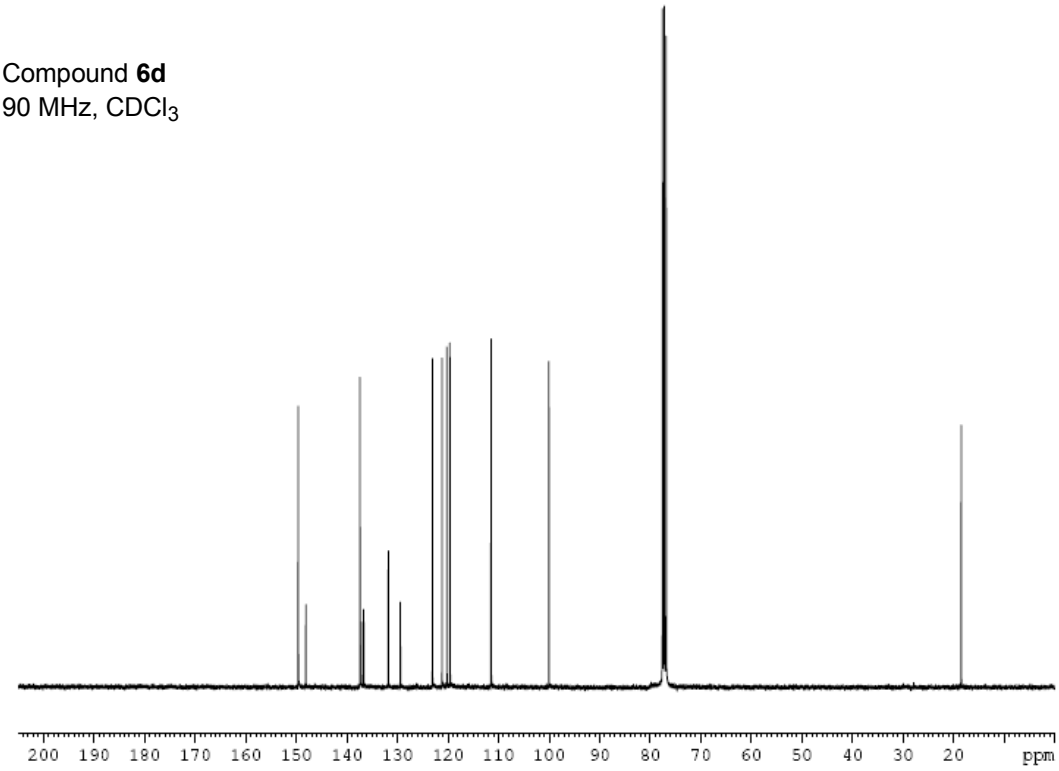

Compound **6e**
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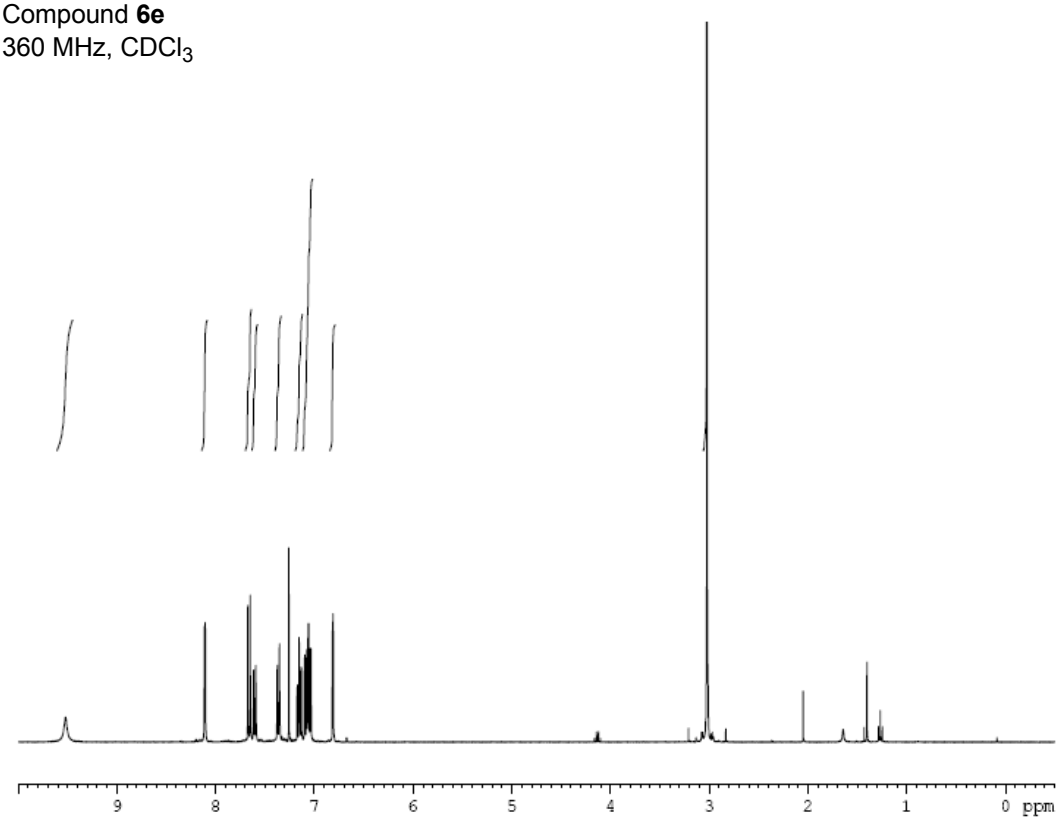

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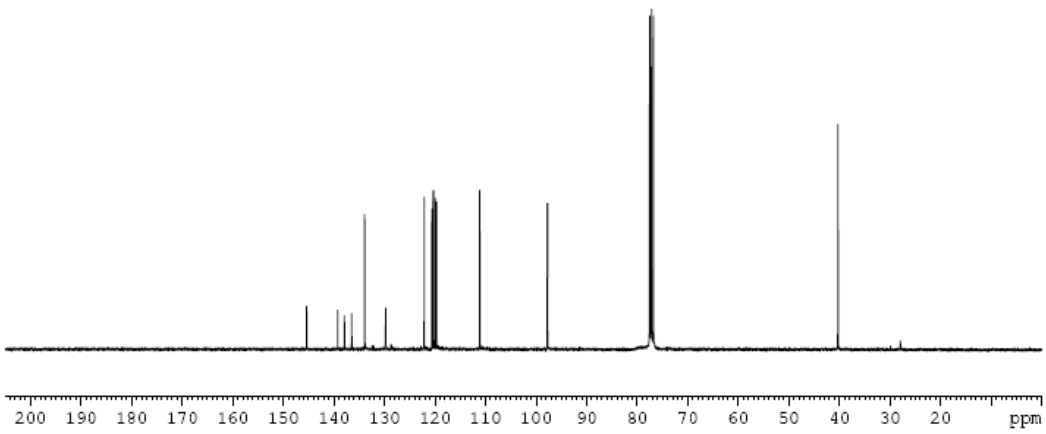

Compound **6f**
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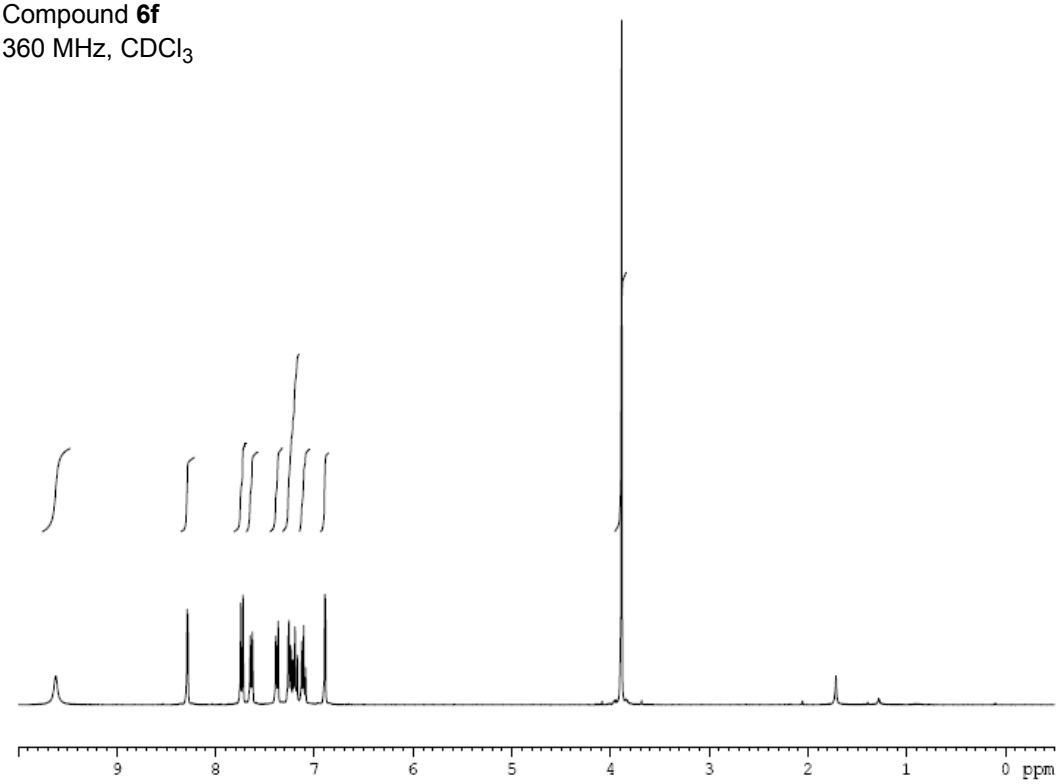

Compound **6f**
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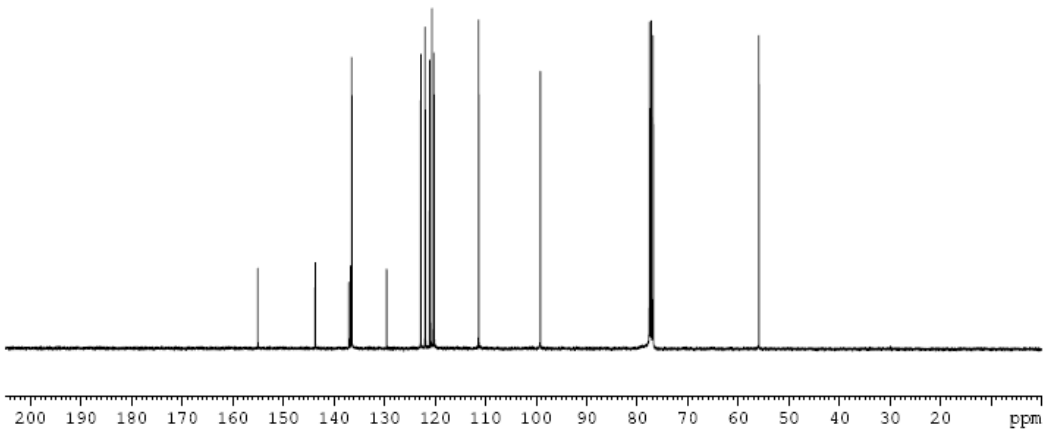
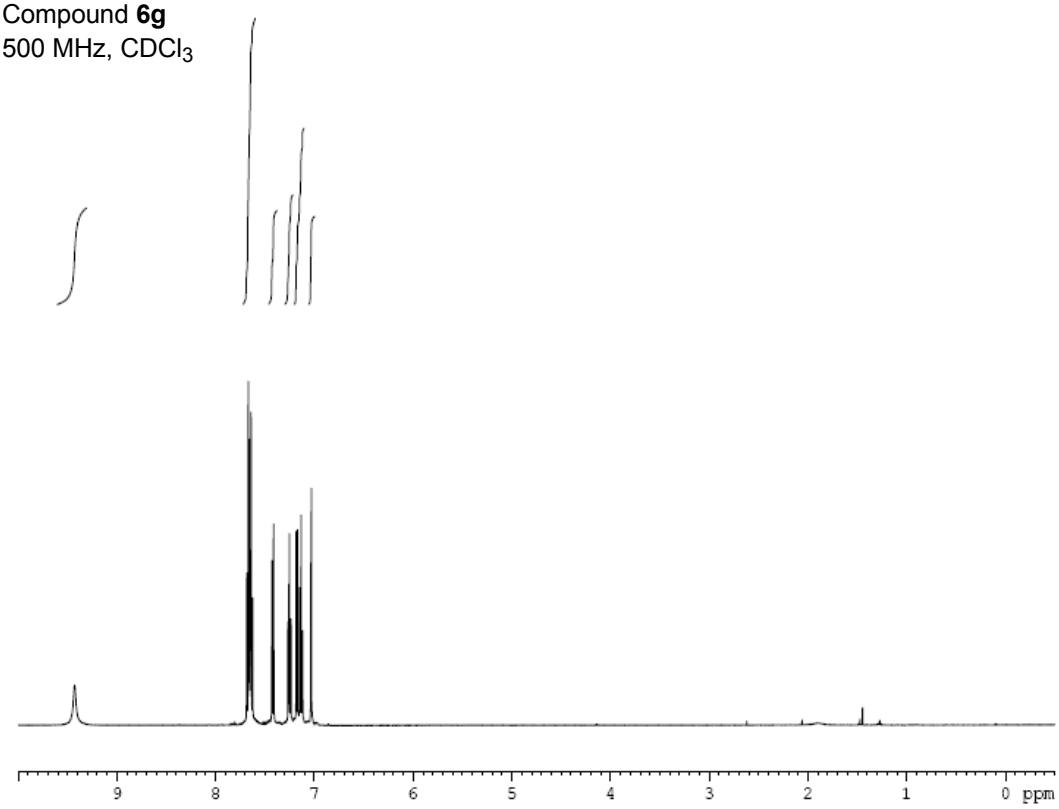


Compound **6g**
500 MHz, $CDCl_3$



Compound **6g**
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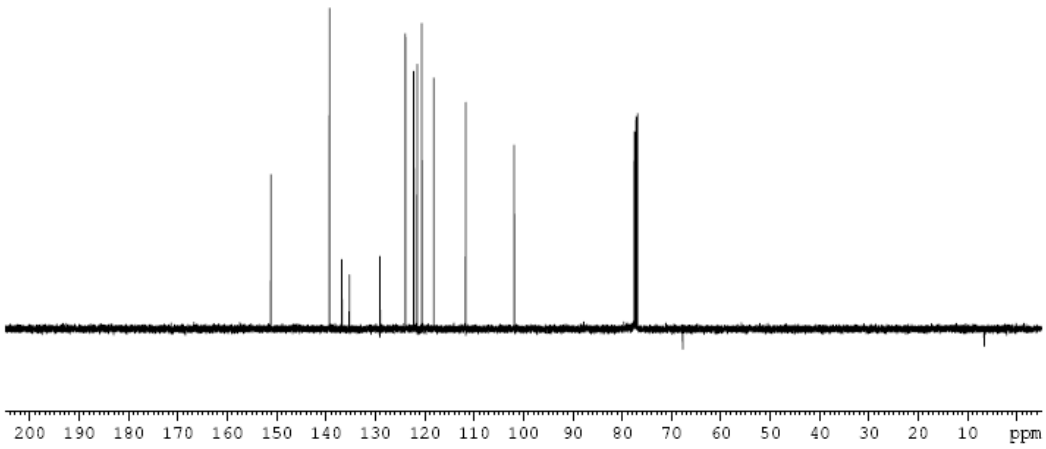

Compound **6h**
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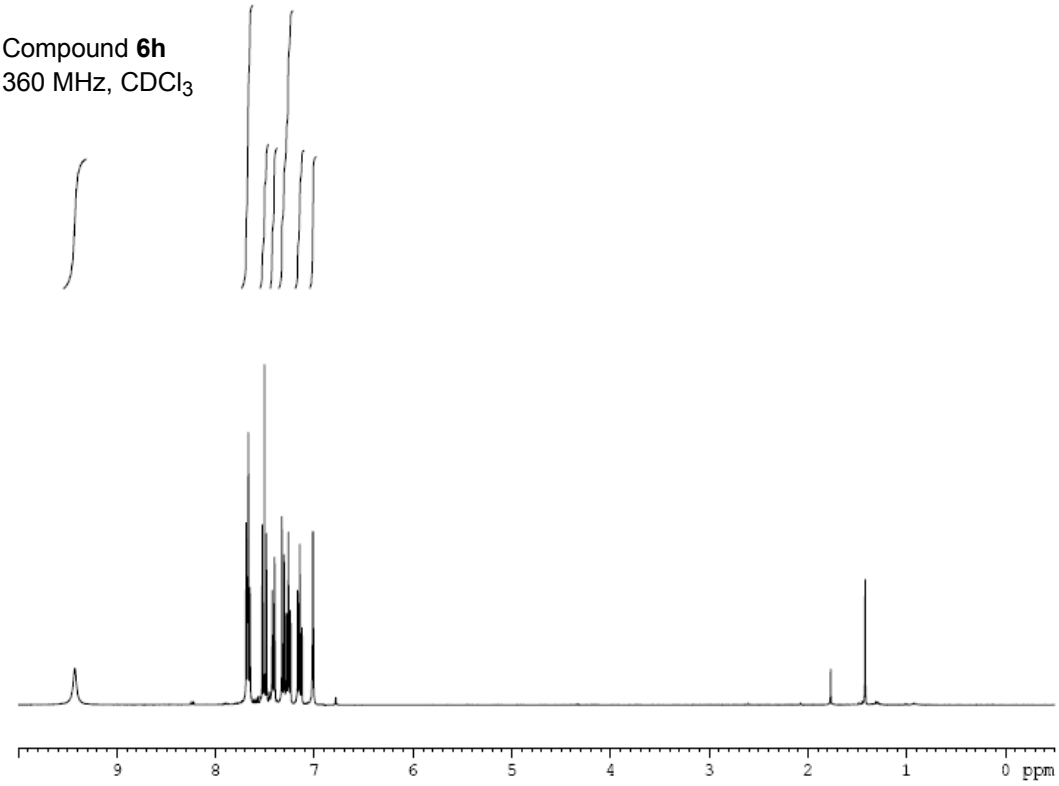

Compound **6h**
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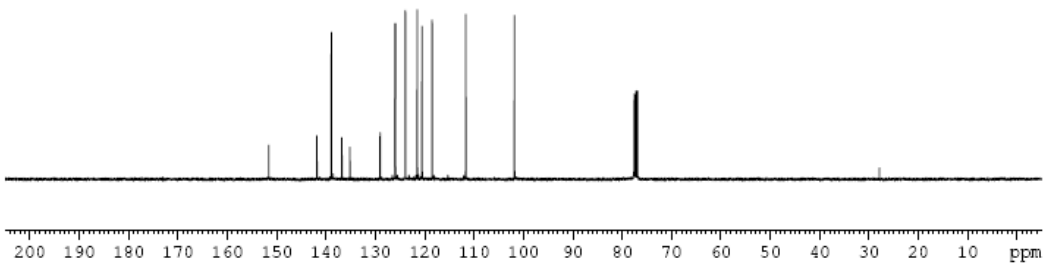

Compound **6i**
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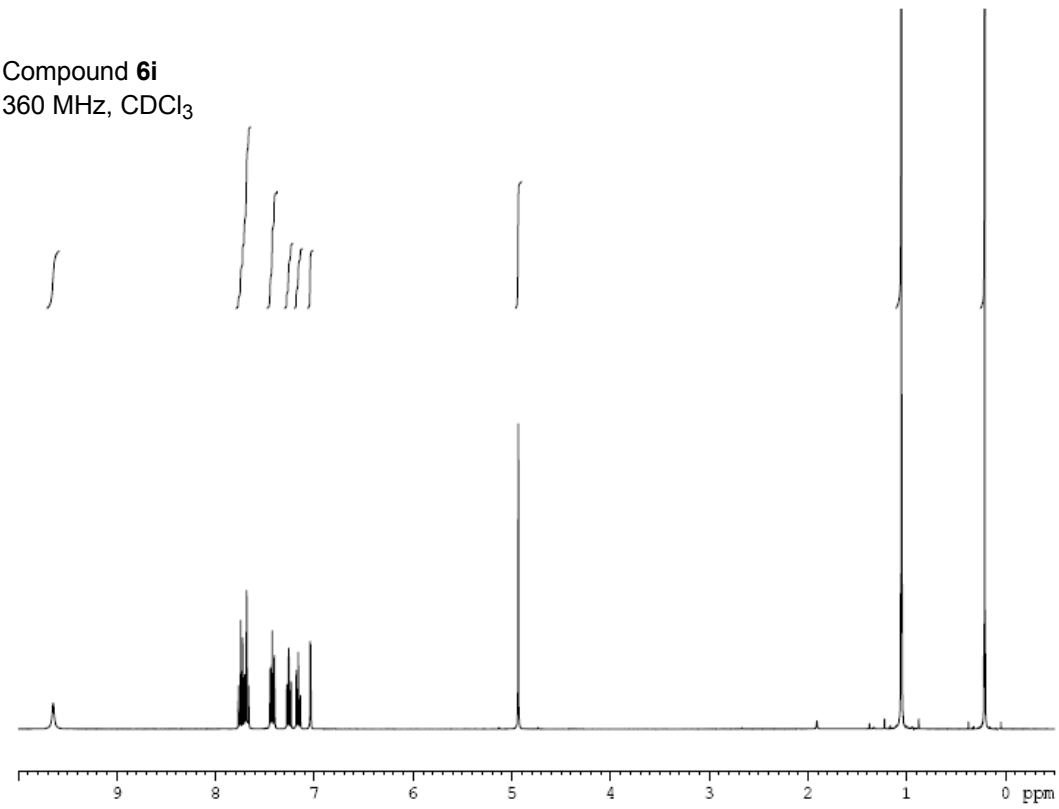

Compound **6i**
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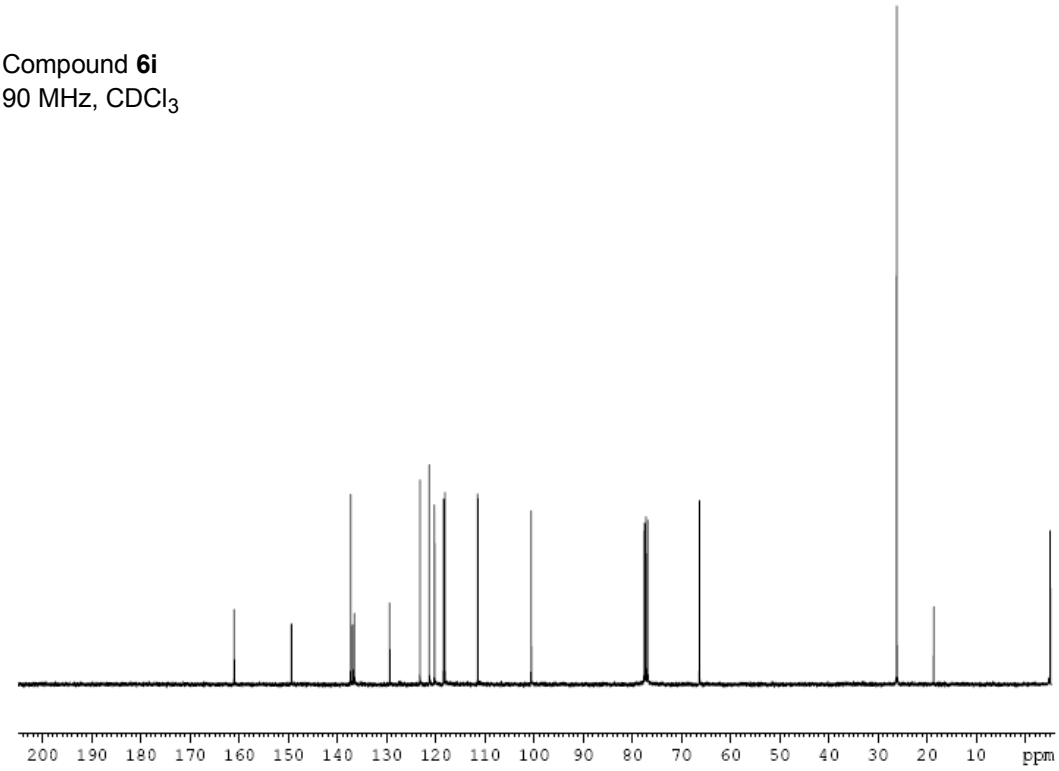

Compound **6j**
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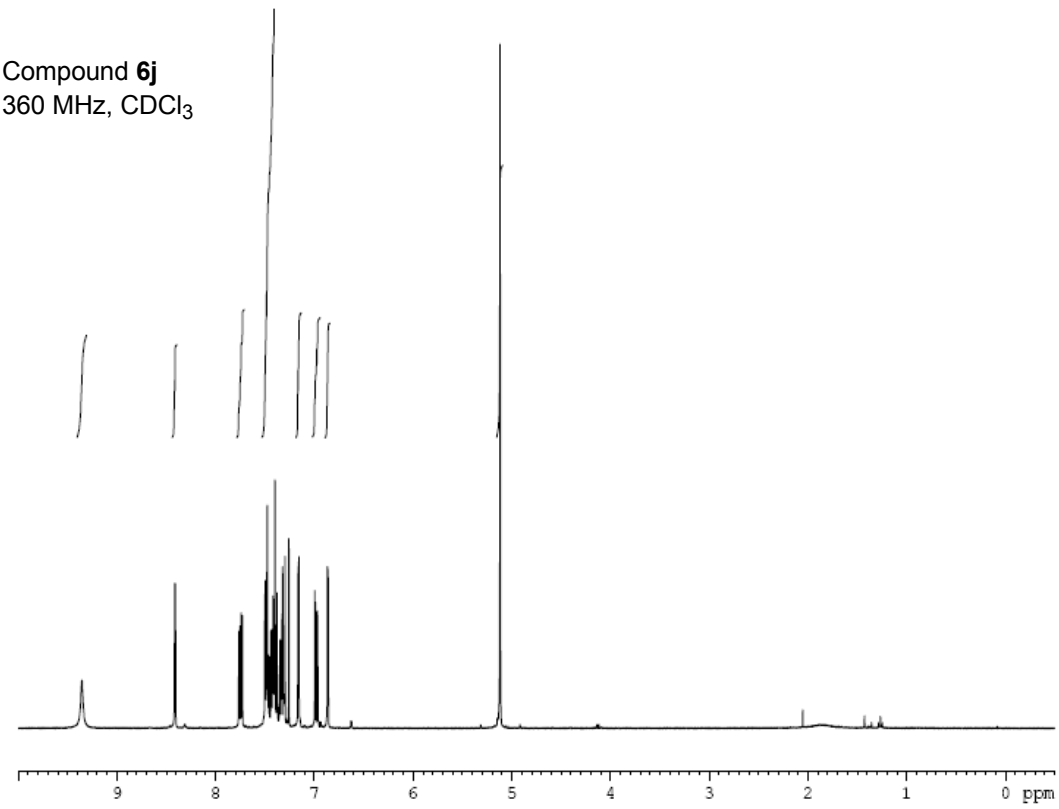
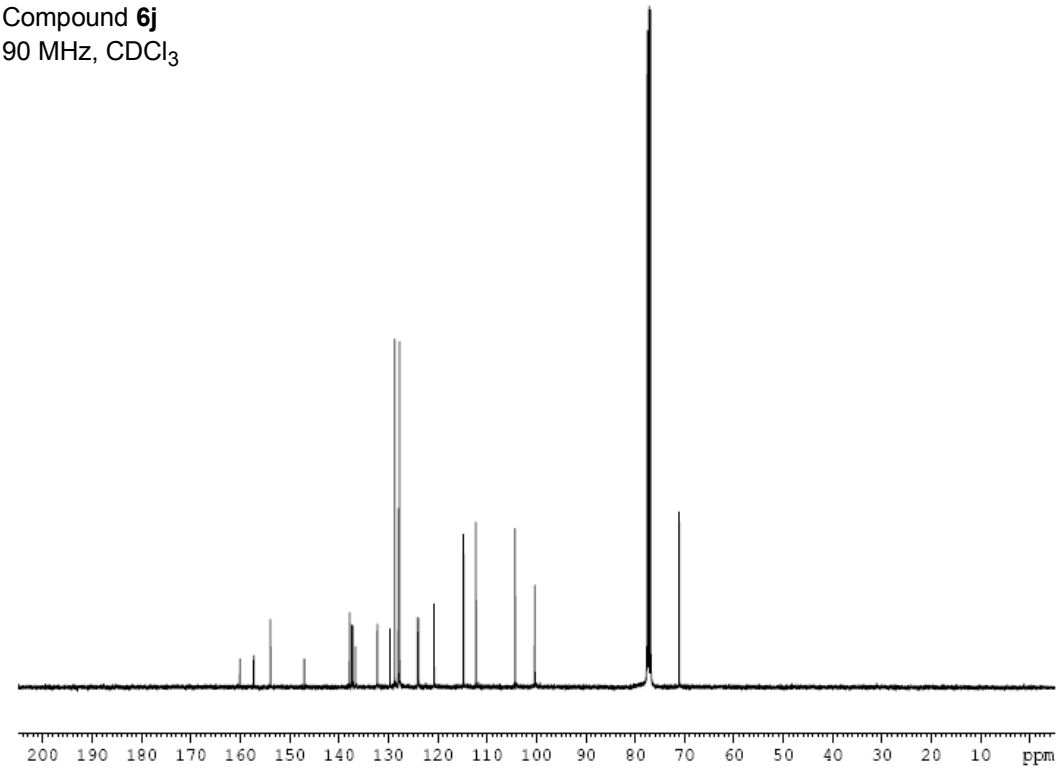


Compound **6j**
90 MHz, $CDCl_3$



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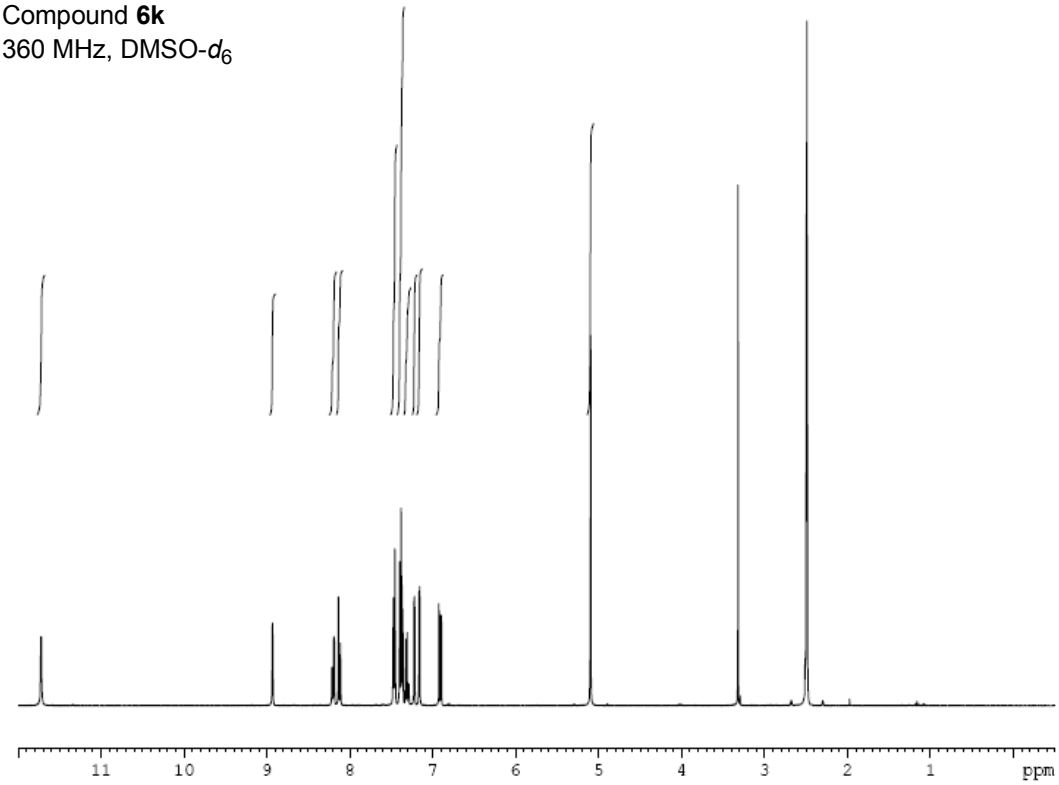
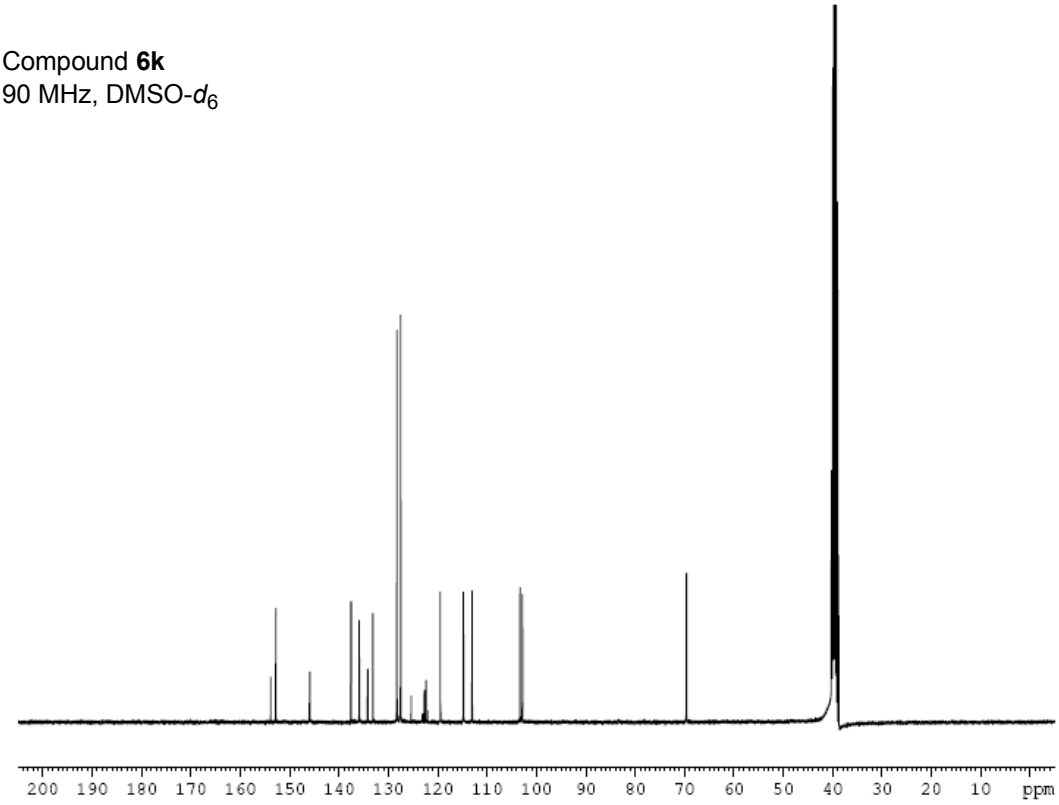
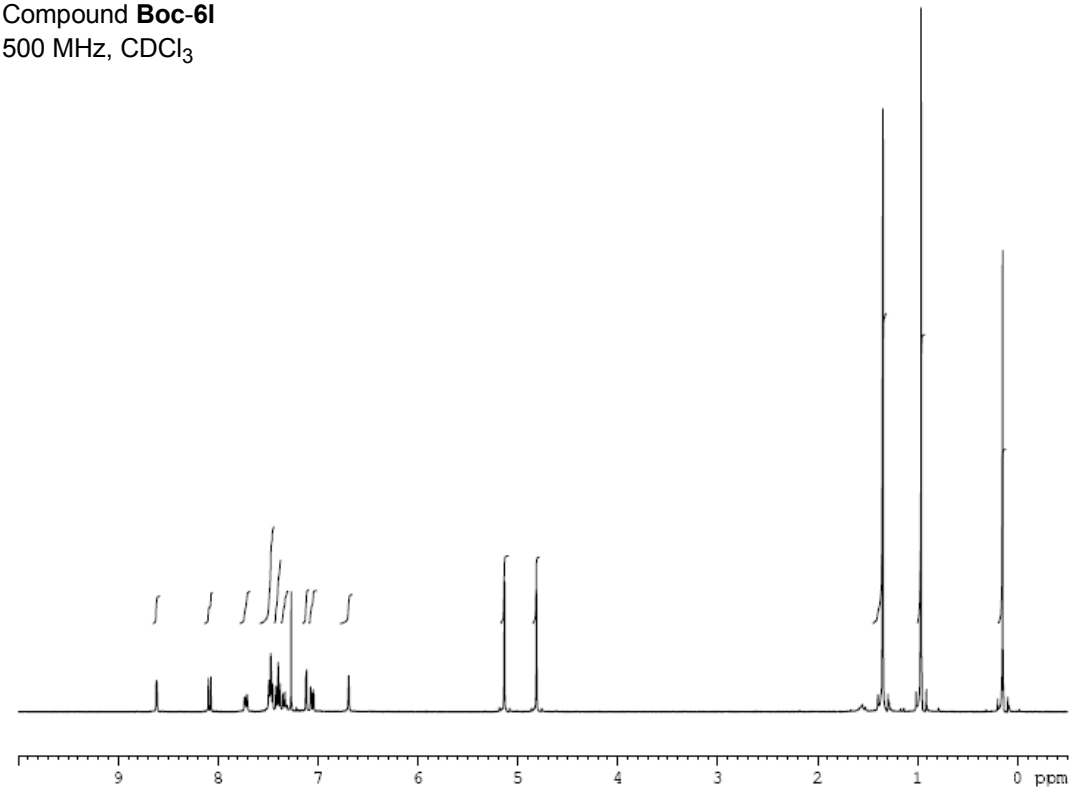
Compound **6k**
360 MHz, DMSO-d_6



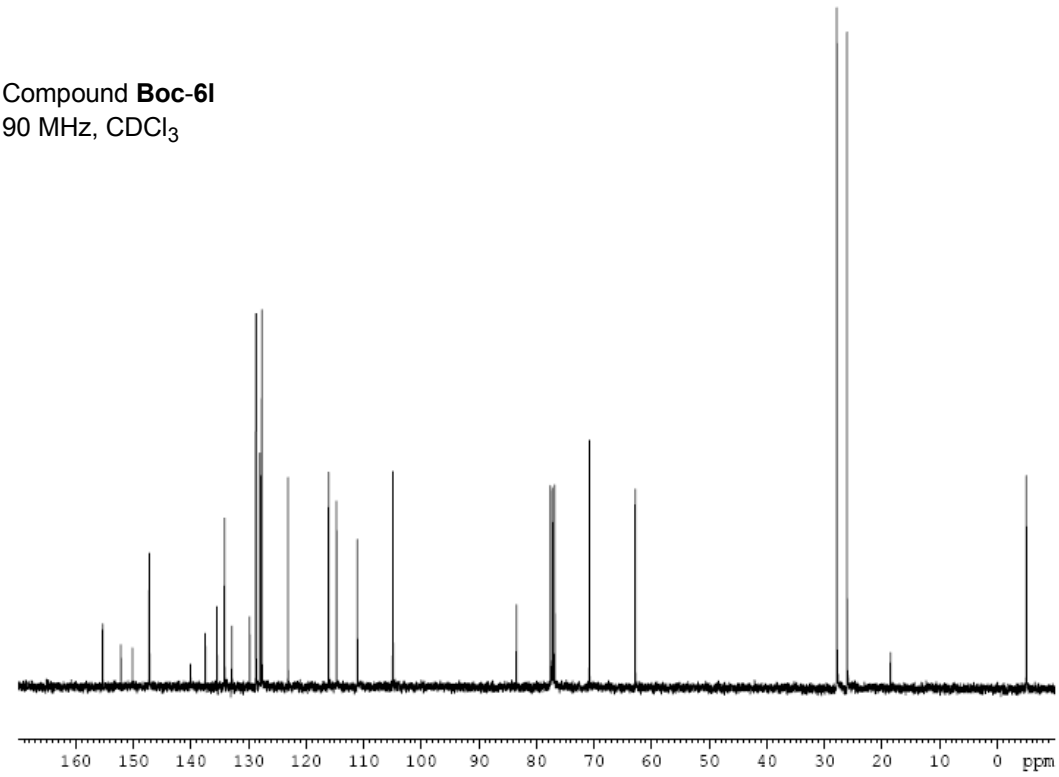
Compound **6k**
90 MHz, DMSO-d_6



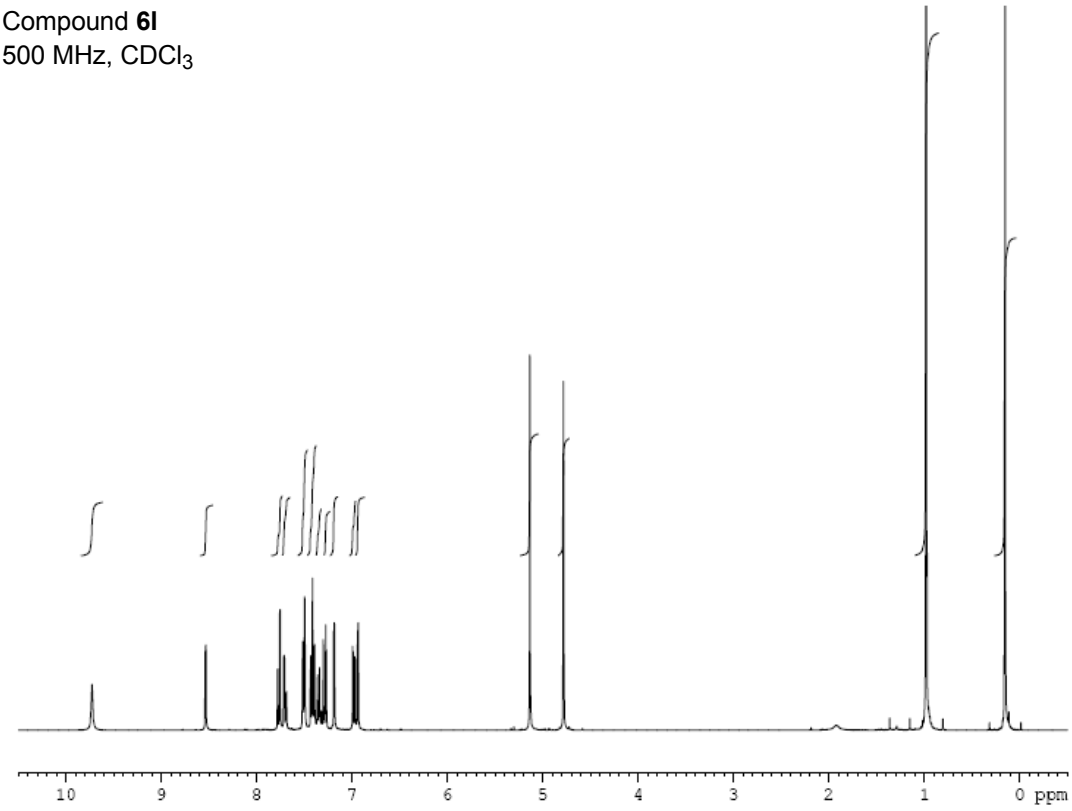
Compound **Boc-6l**
500 MHz, $CDCl_3$



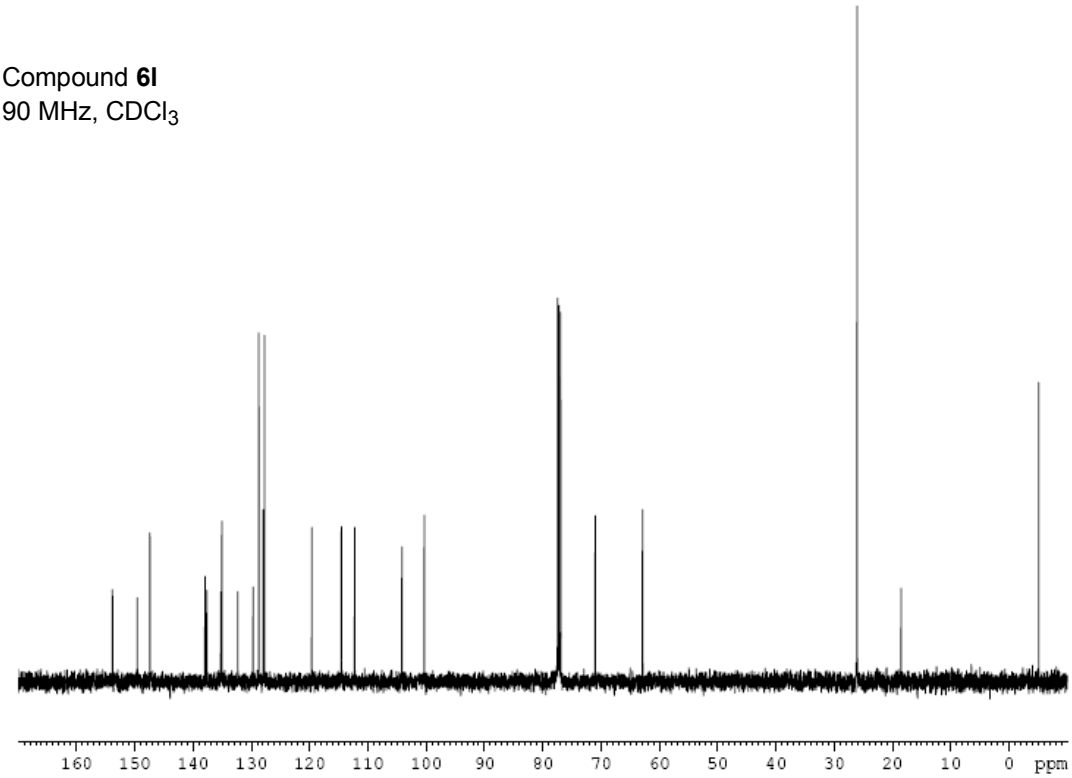
Compound **Boc-6l**
90 MHz, $CDCl_3$



Compound **6l**
500 MHz, $CDCl_3$



Compound **6l**
90 MHz, $CDCl_3$



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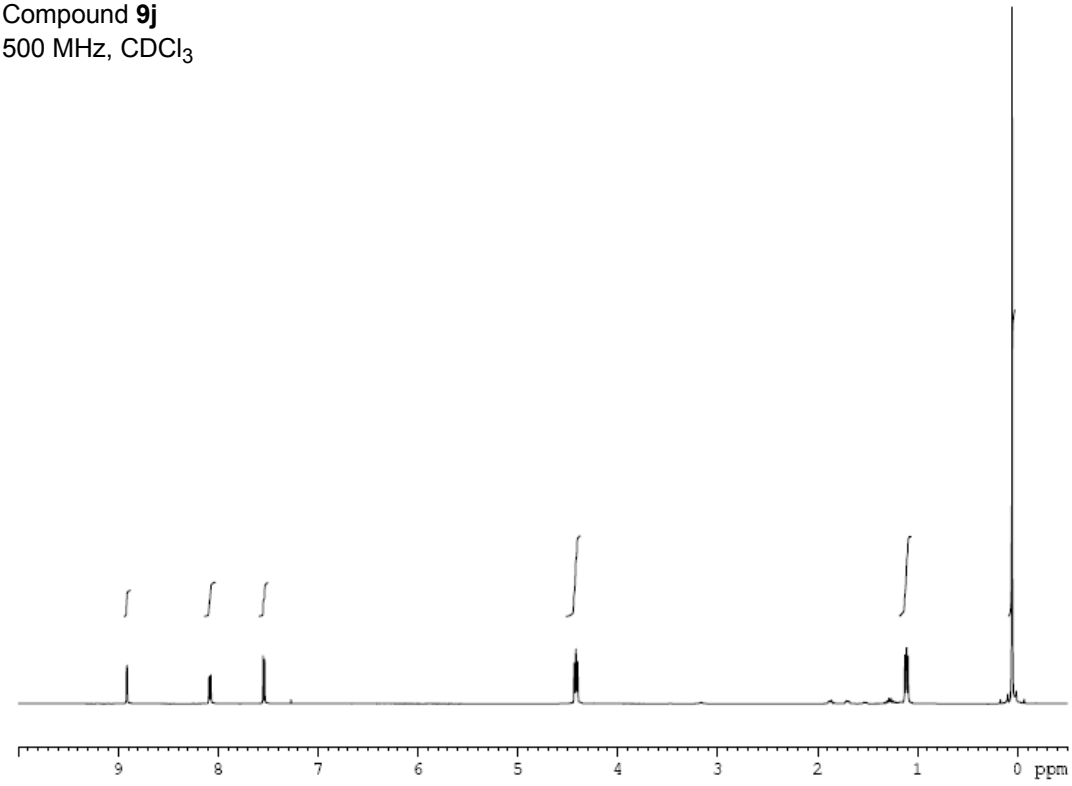
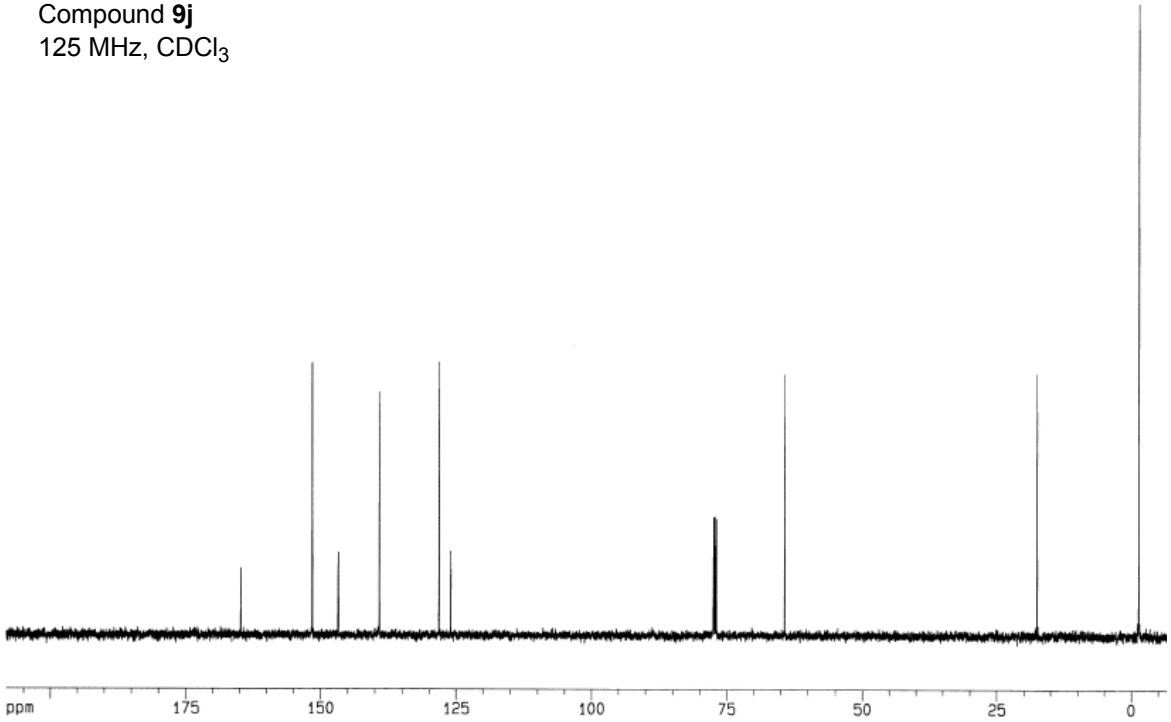
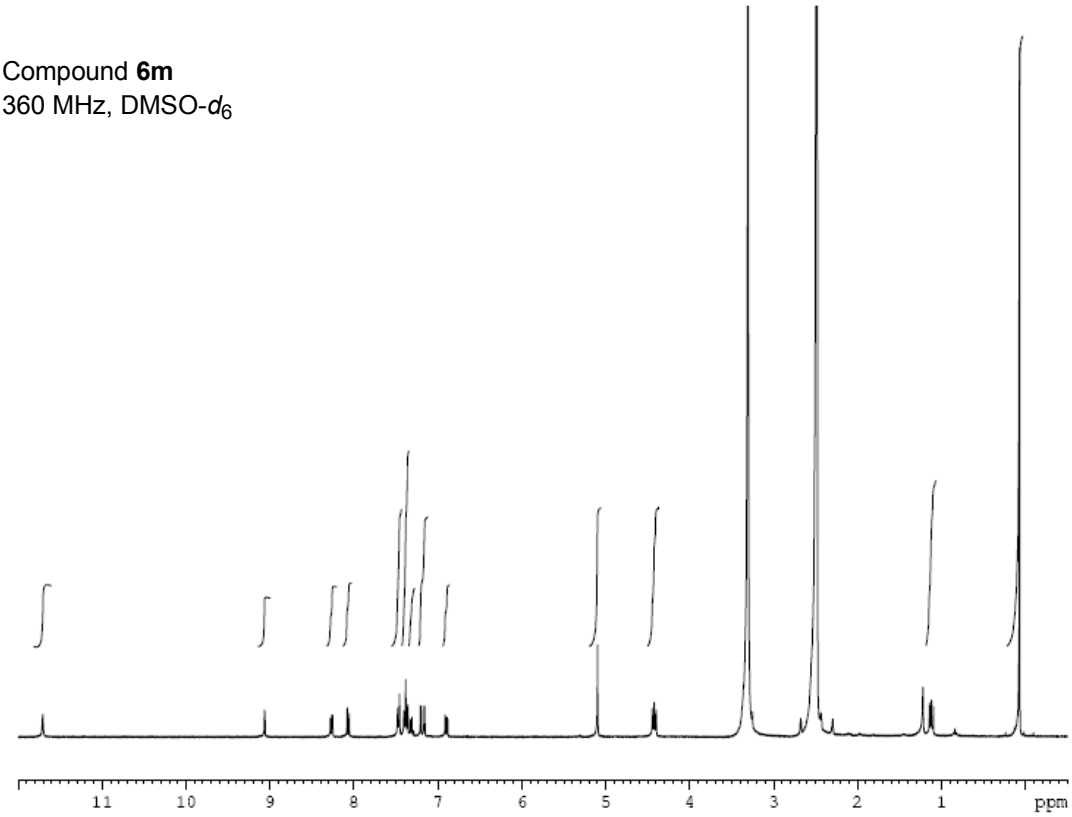
Compound **9j**
500 MHz, $CDCl_3$



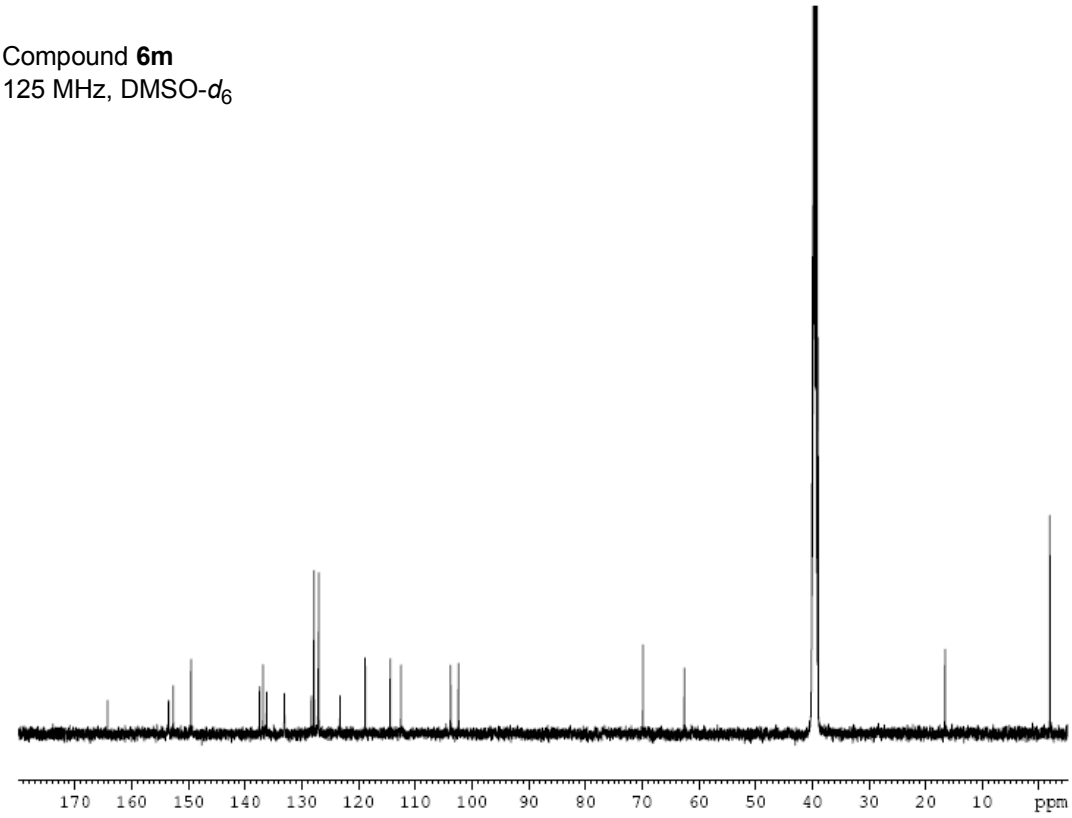
Compound **9j**
125 MHz, $CDCl_3$



Compound **6m**
360 MHz, DMSO-d_6



Compound **6m**
125 MHz, DMSO-d_6



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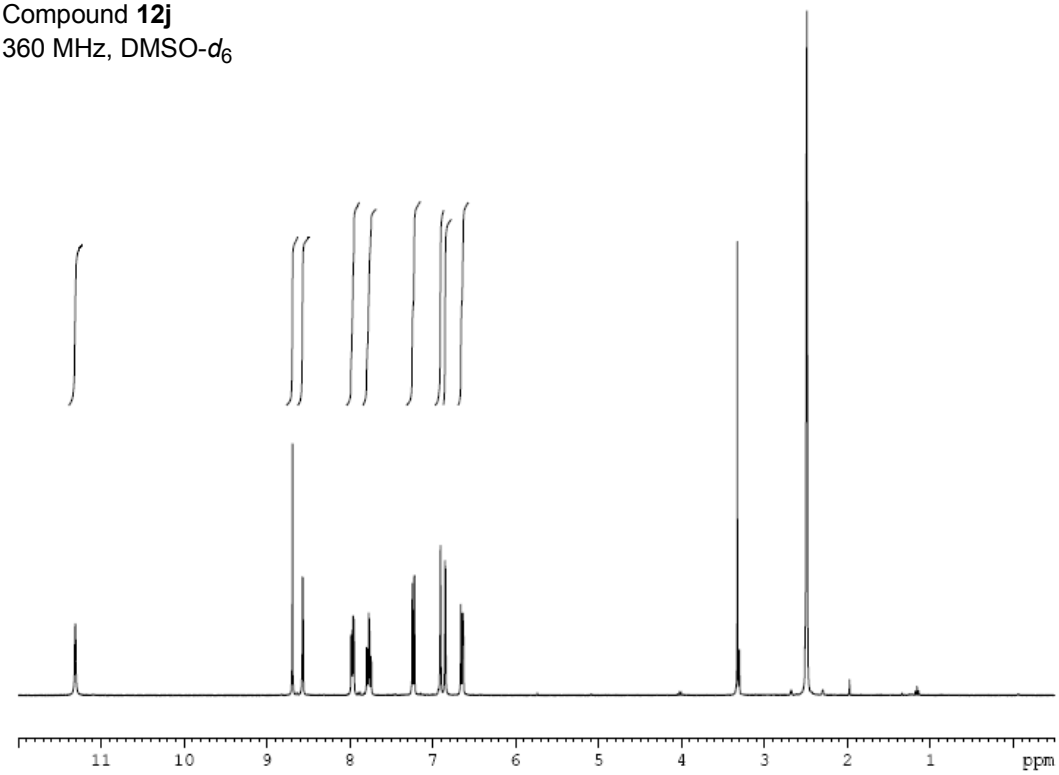
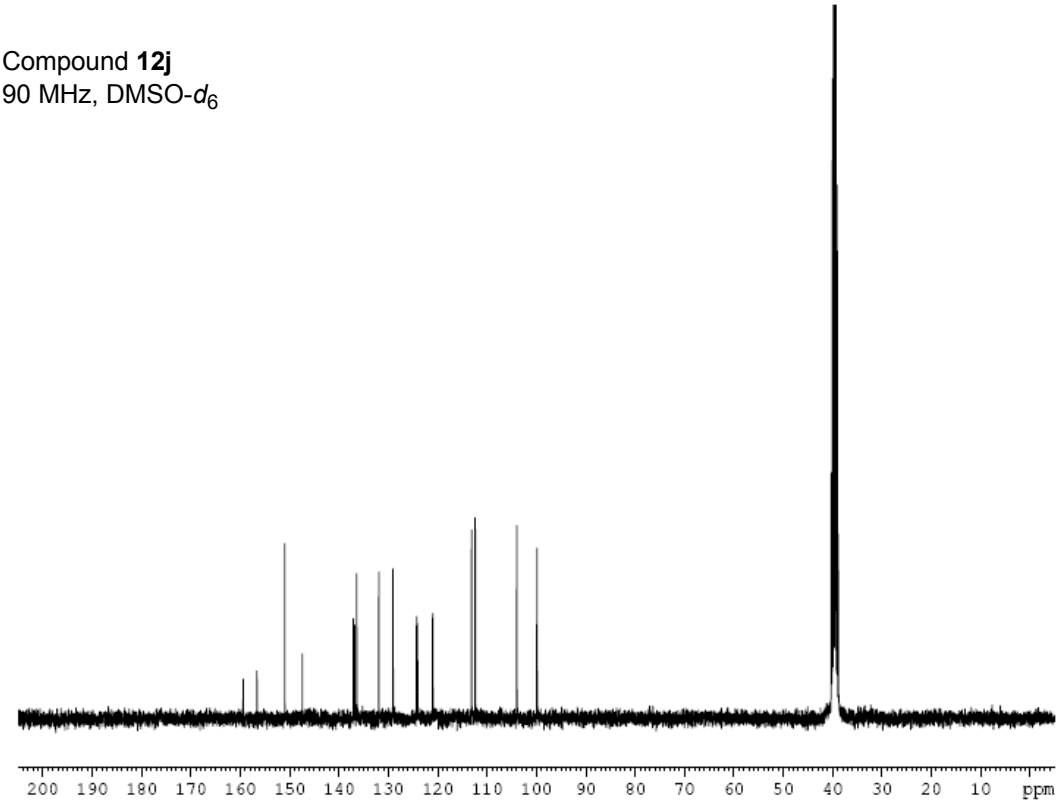
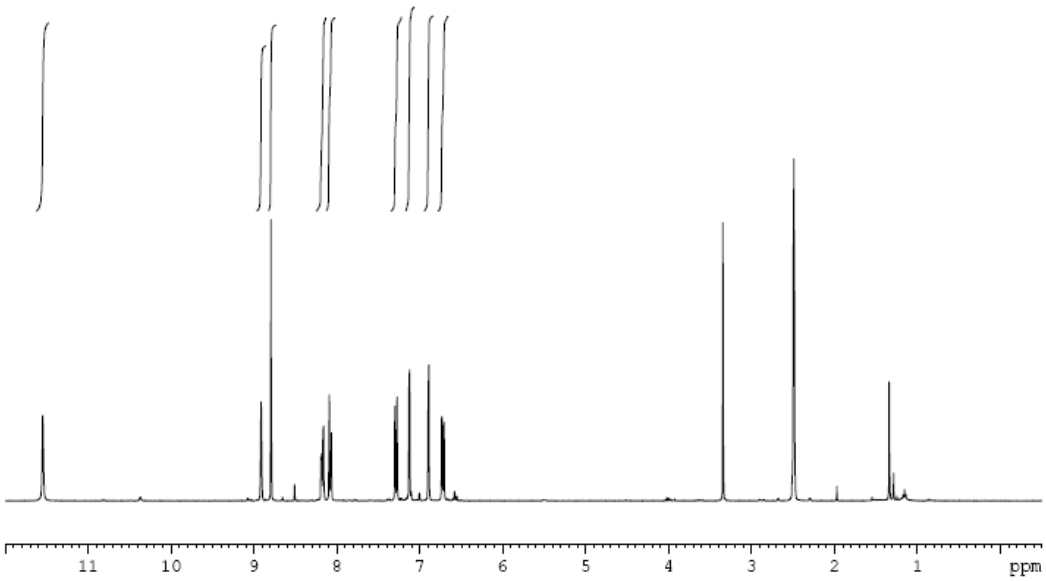
Compound **12j**
360 MHz, DMSO-d_6



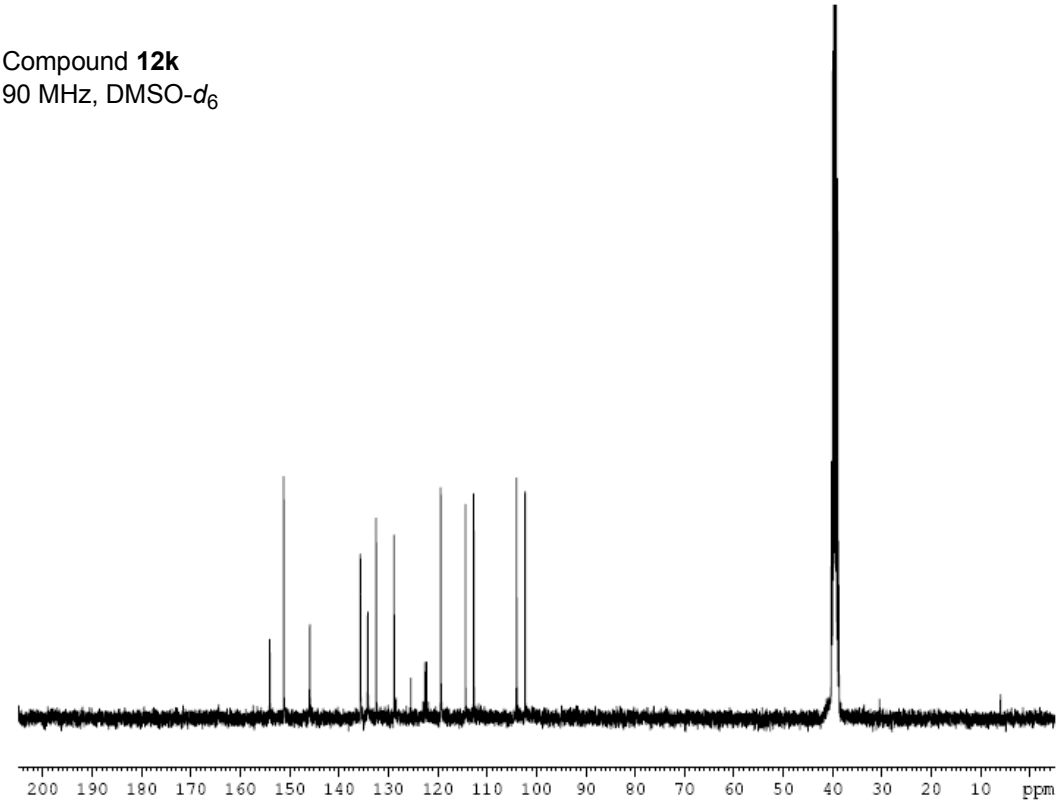
Compound **12j**
90 MHz, DMSO-d_6



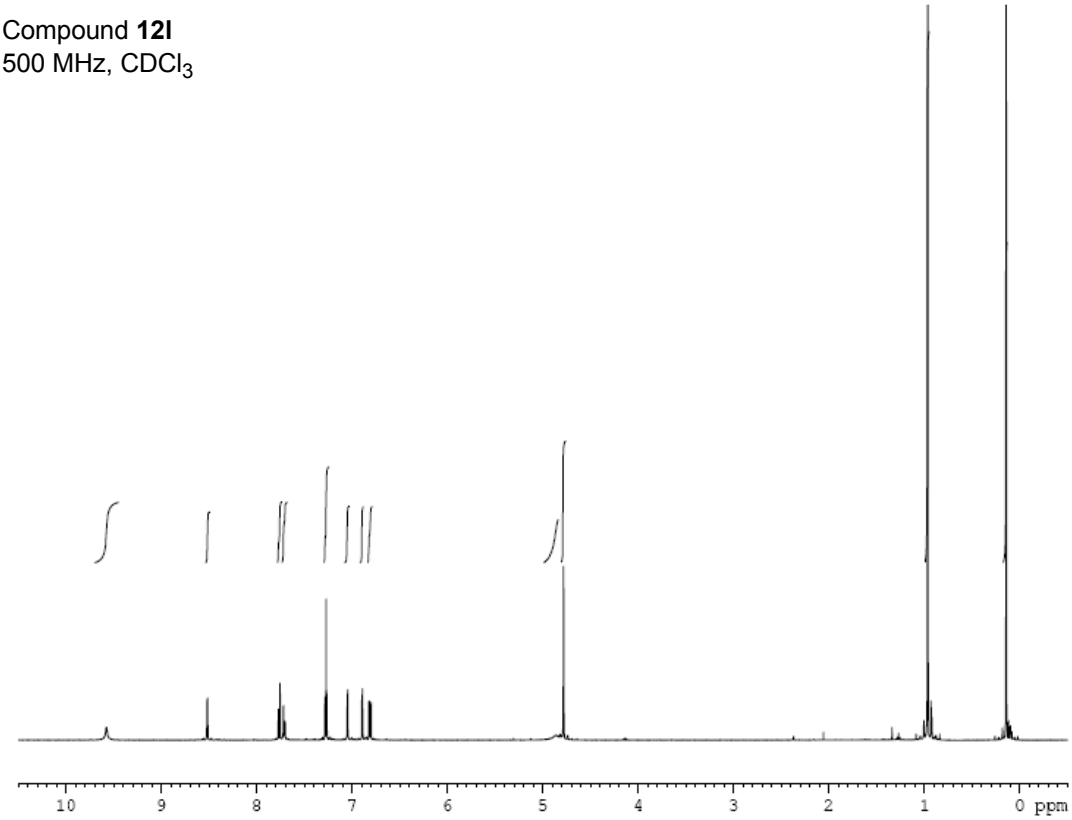
Compound **12k**
360 MHz, DMSO-d_6



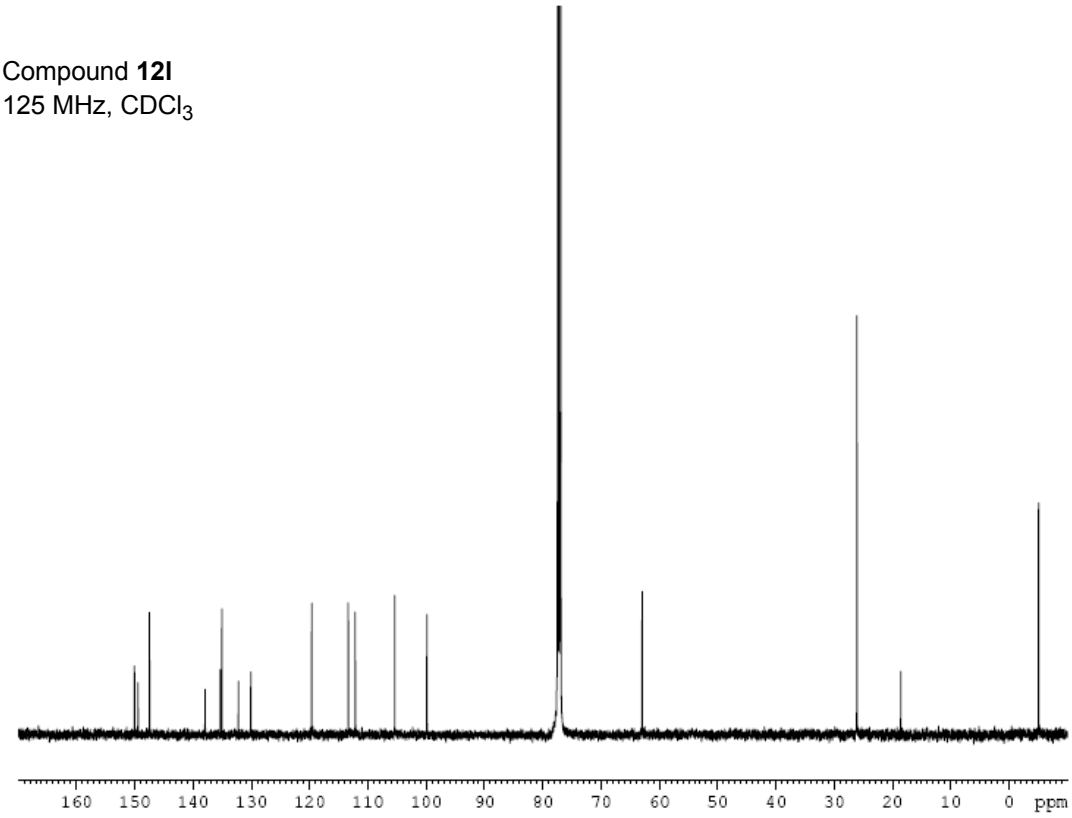
Compound **12k**
90 MHz, DMSO-d_6



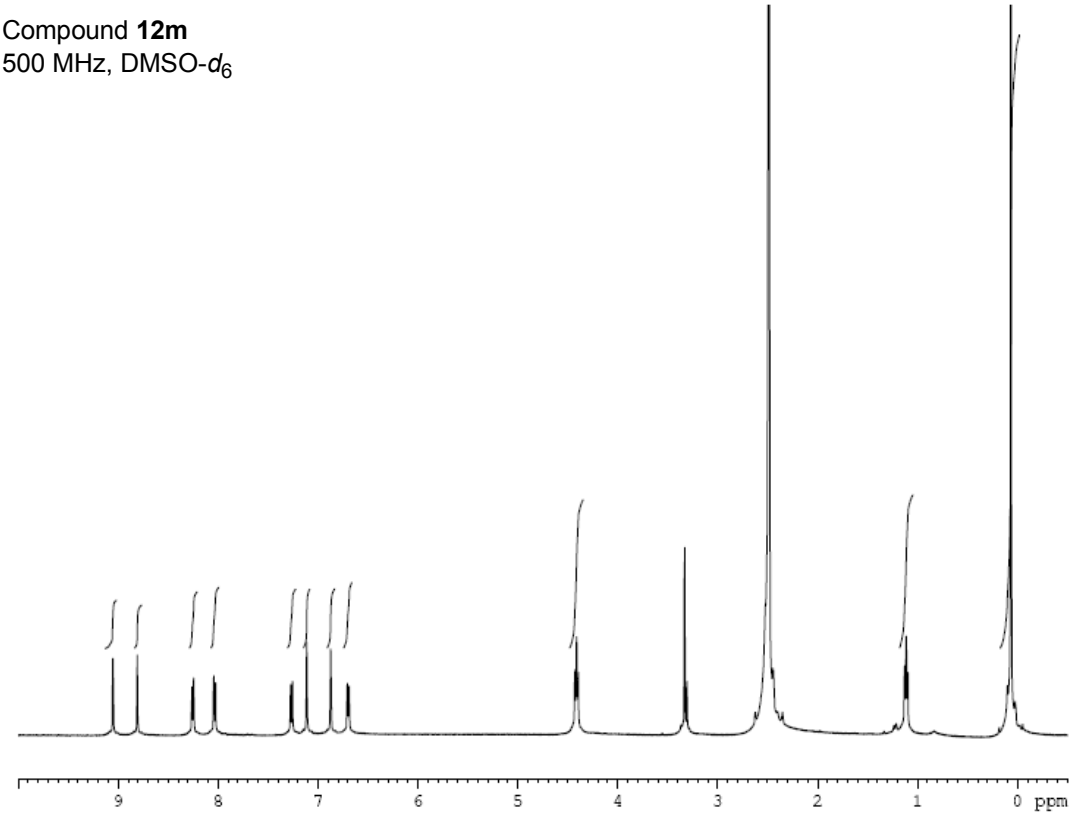
Compound **12l**
500 MHz, $CDCl_3$



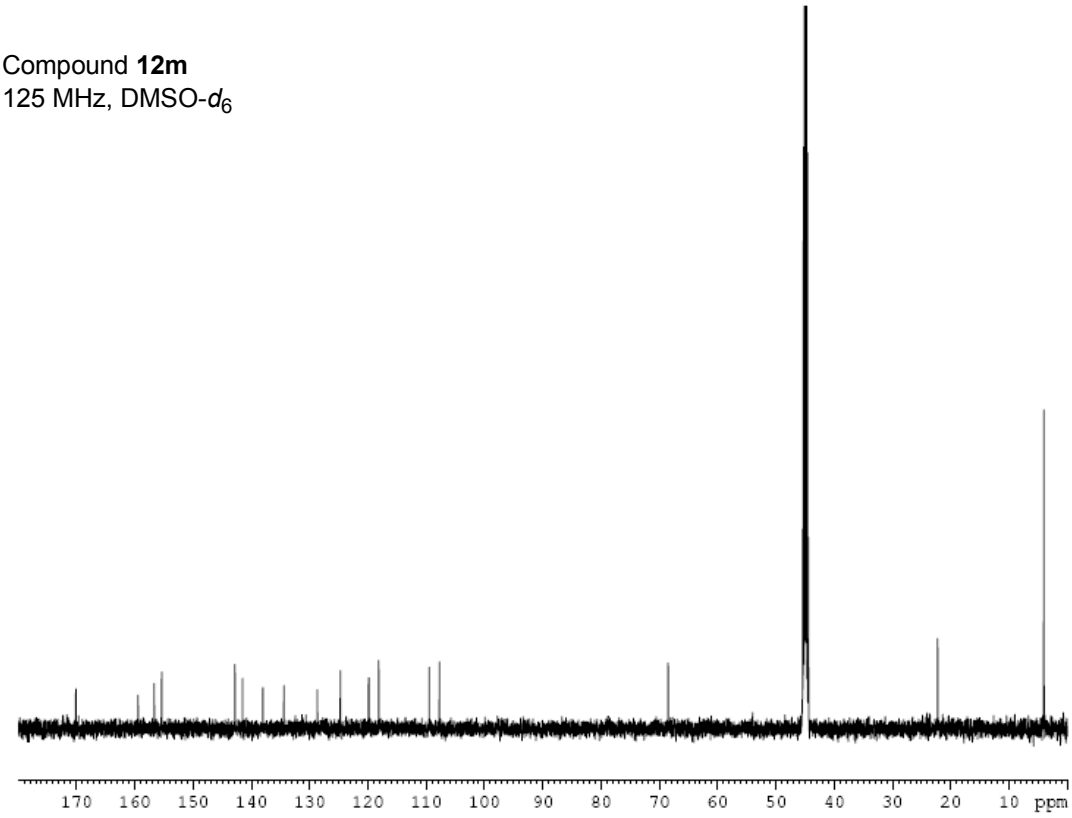
Compound **12l**
125 MHz, $CDCl_3$



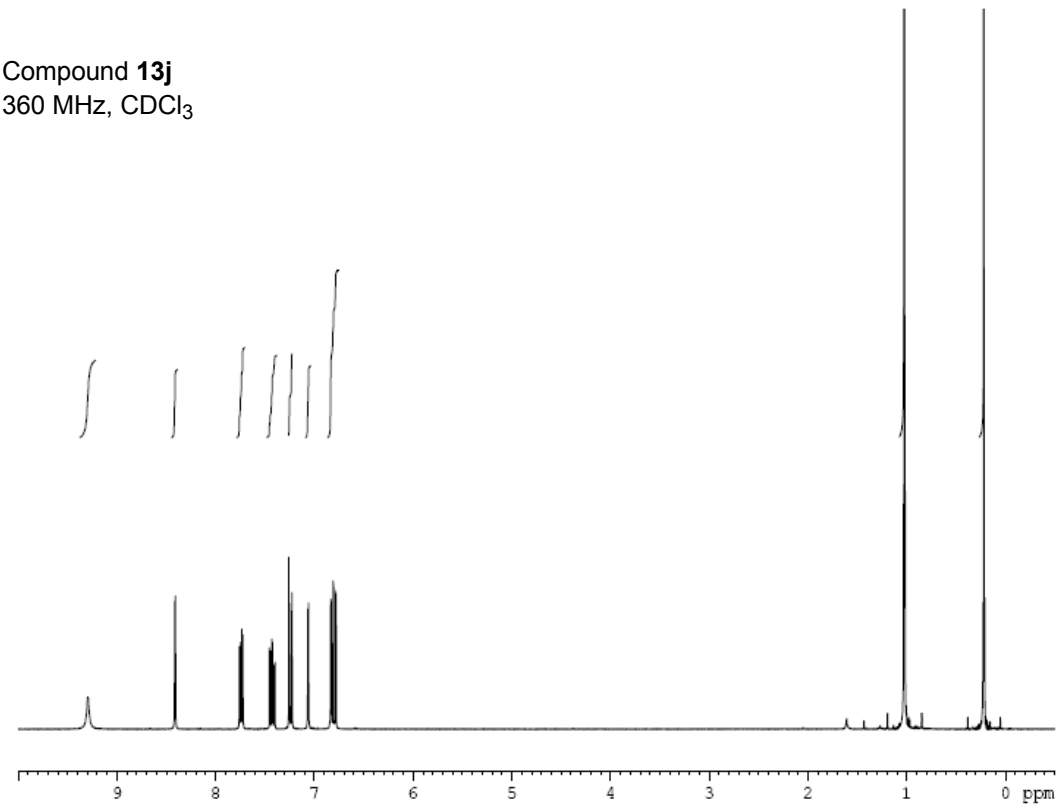
Compound **12m**
500 MHz, DMSO-d_6



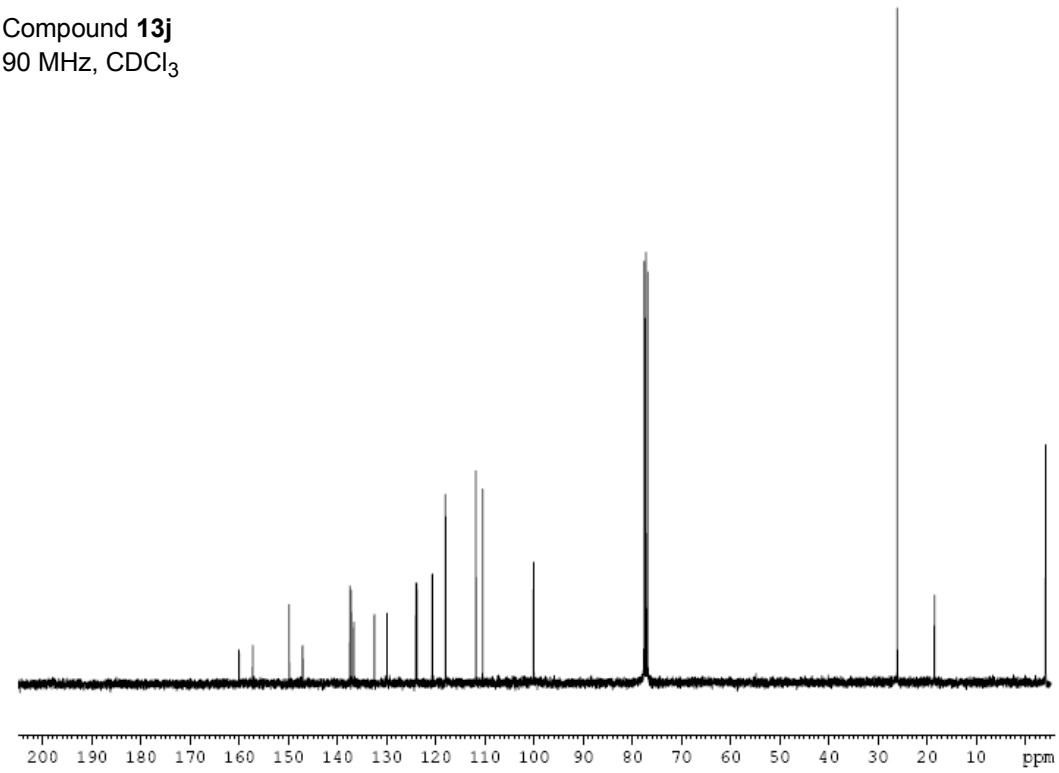
Compound **12m**
125 MHz, DMSO-d_6



Compound **13j**
360 MHz, $CDCl_3$



Compound **13j**
90 MHz, $CDCl_3$



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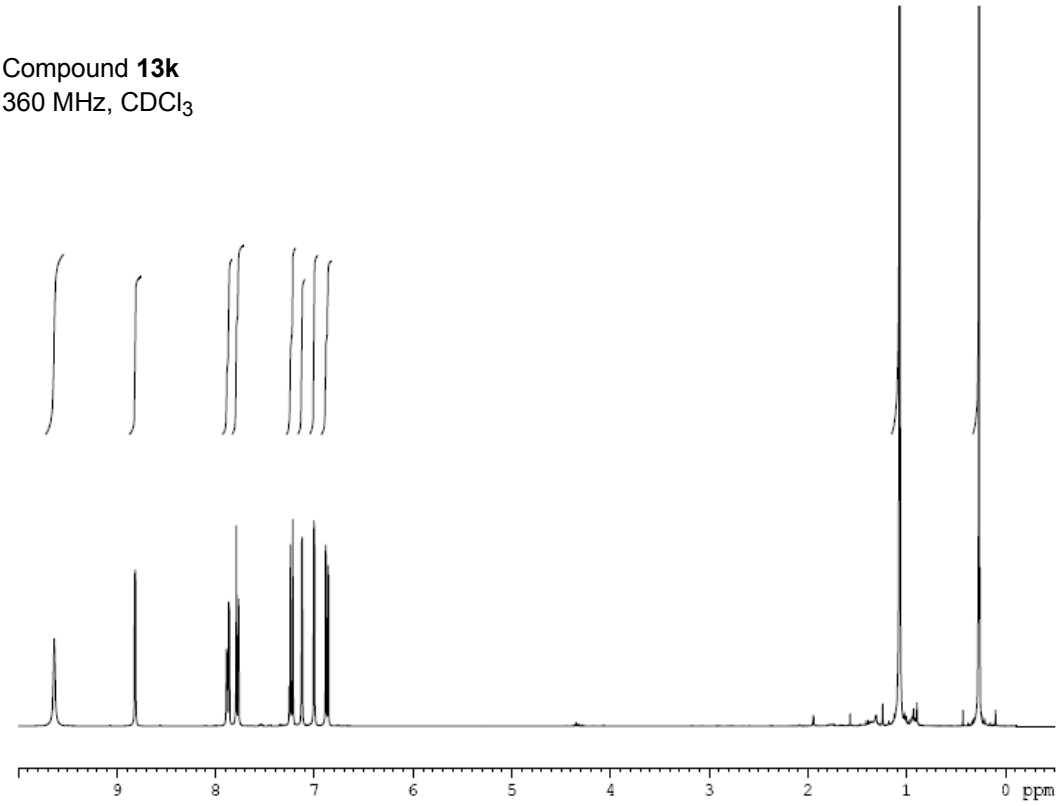
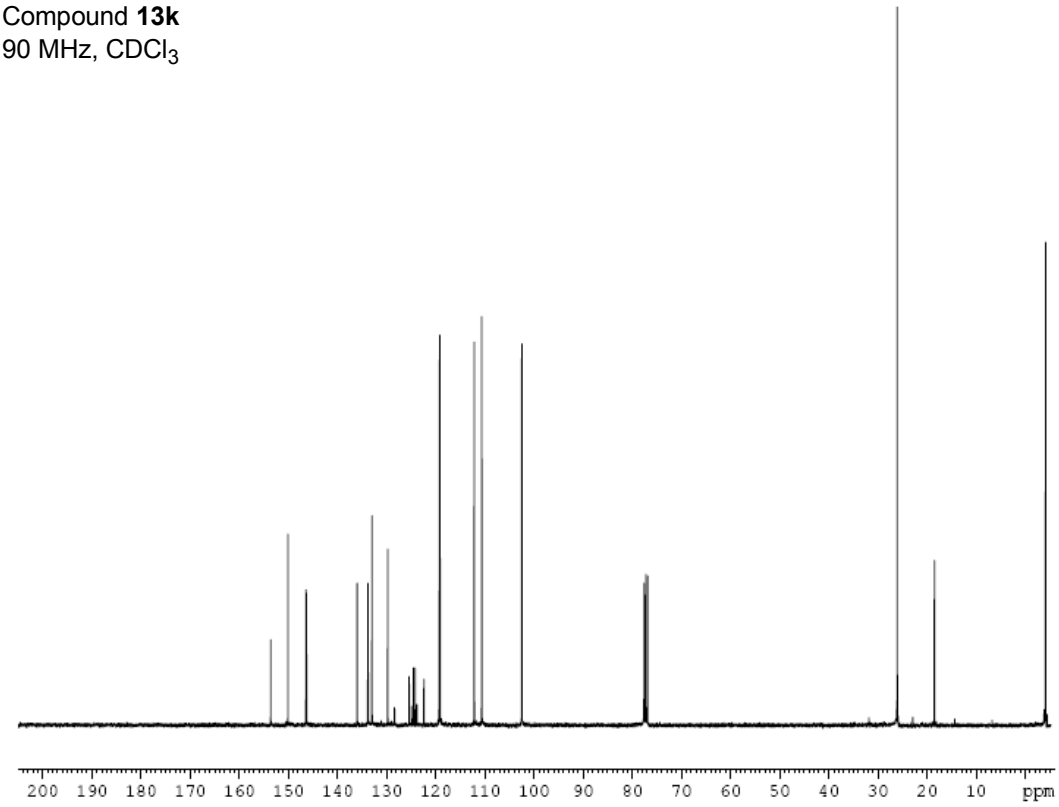
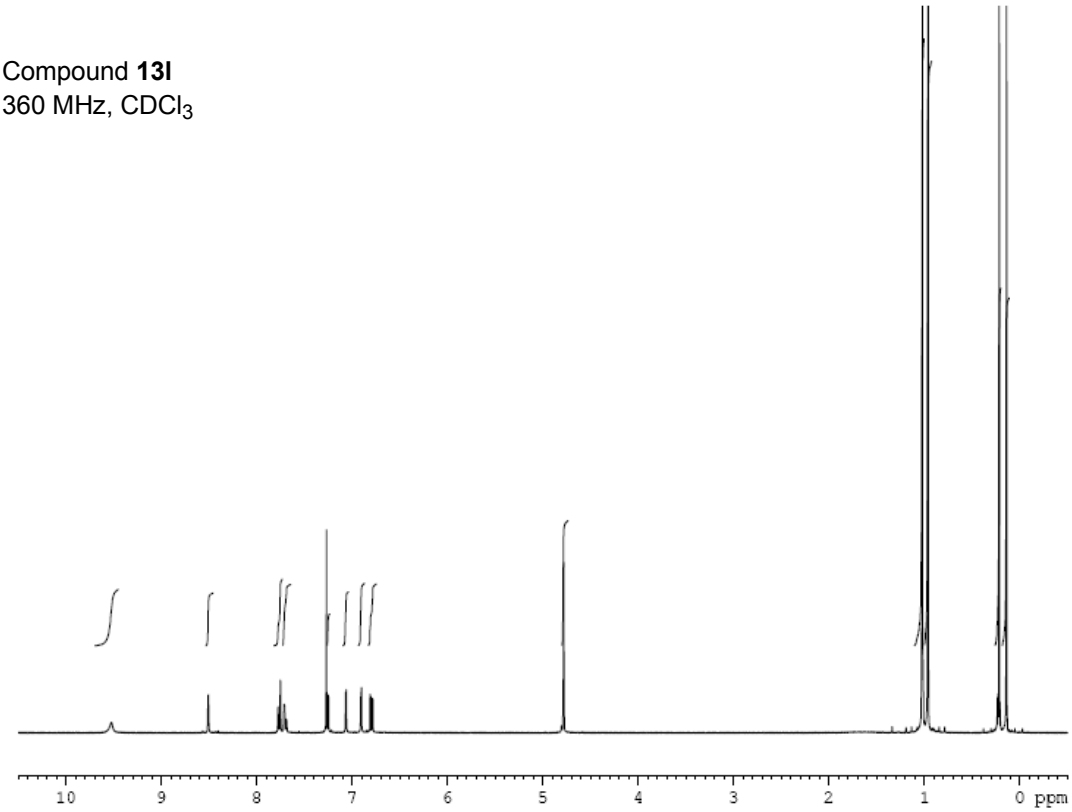
Compound **13k**
360 MHz, $CDCl_3$



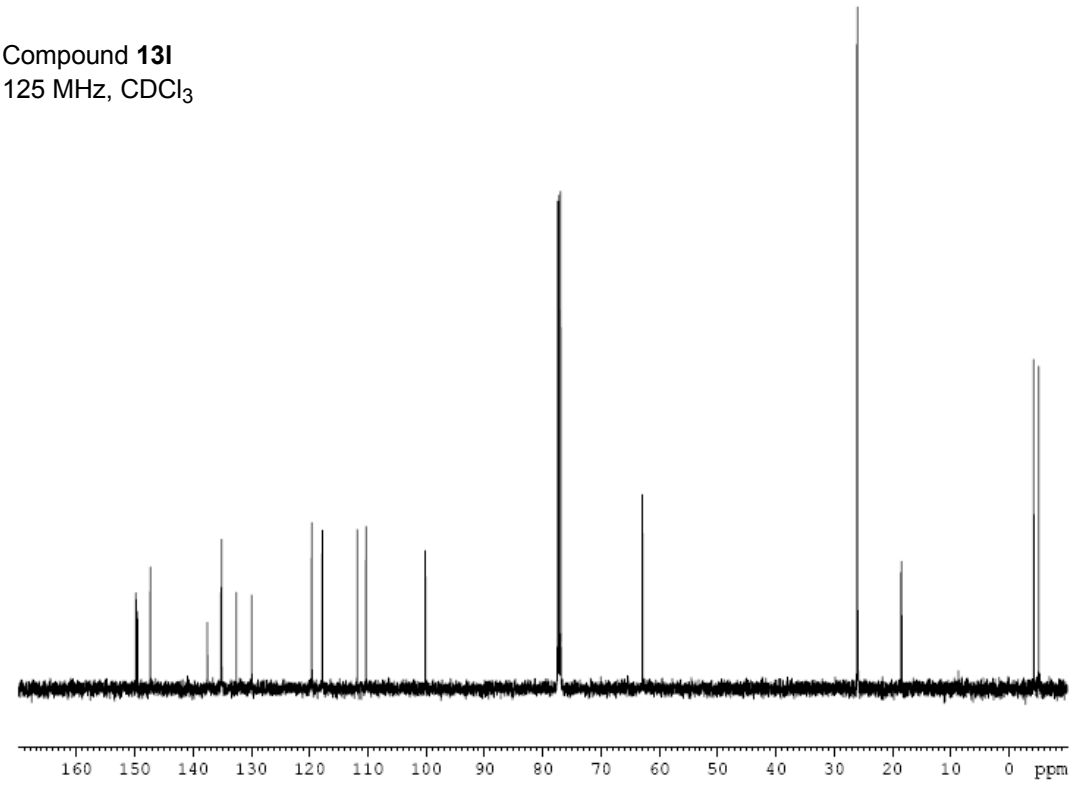
Compound **13k**
90 MHz, $CDCl_3$



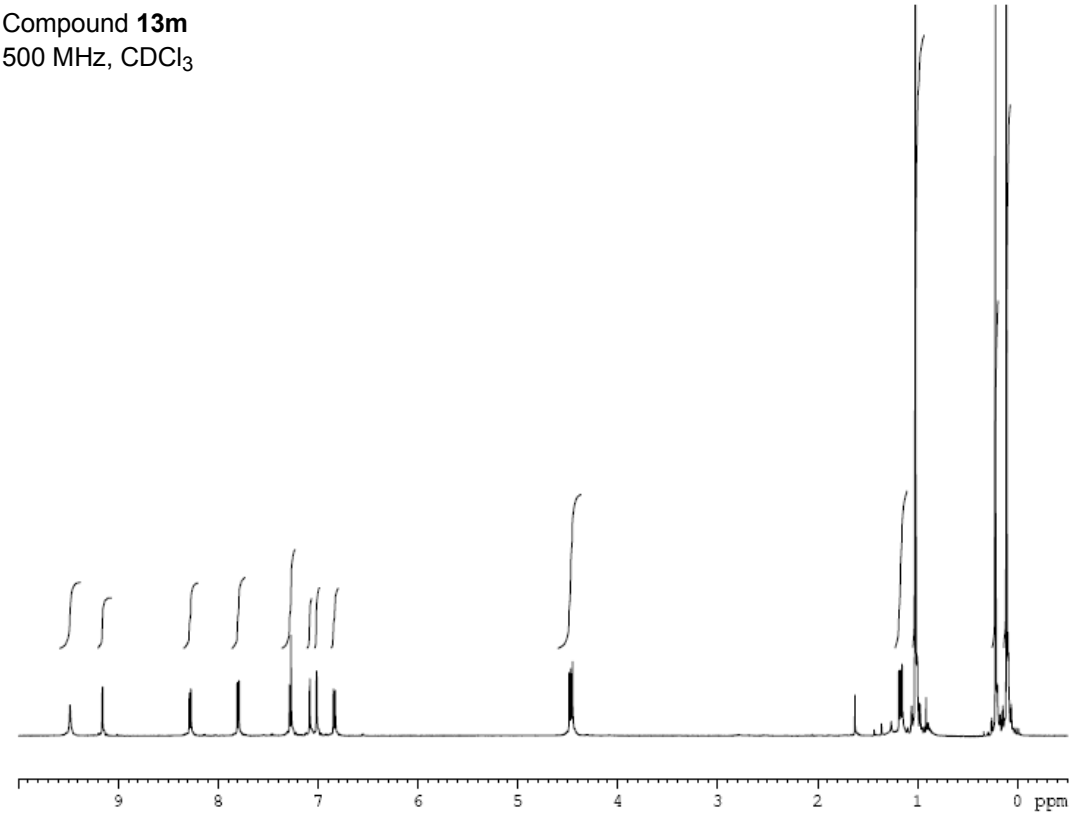
Compound **13l**
360 MHz, $CDCl_3$



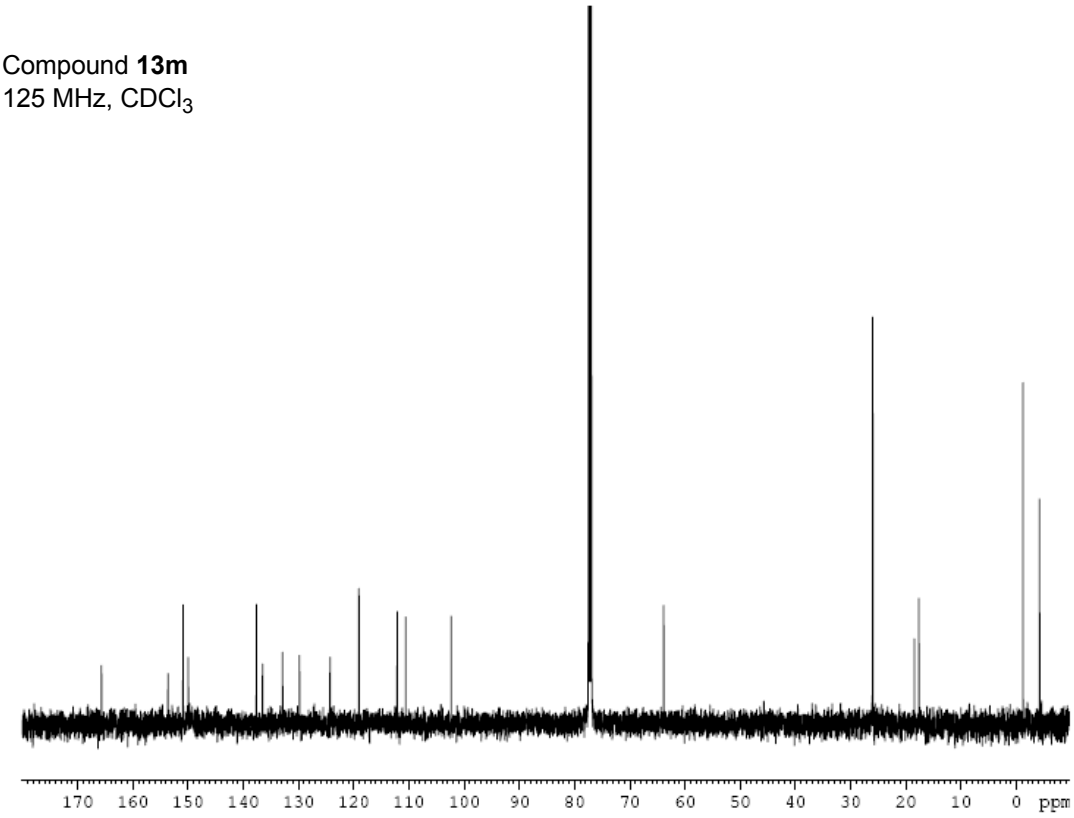
Compound **13l**
125 MHz, $CDCl_3$



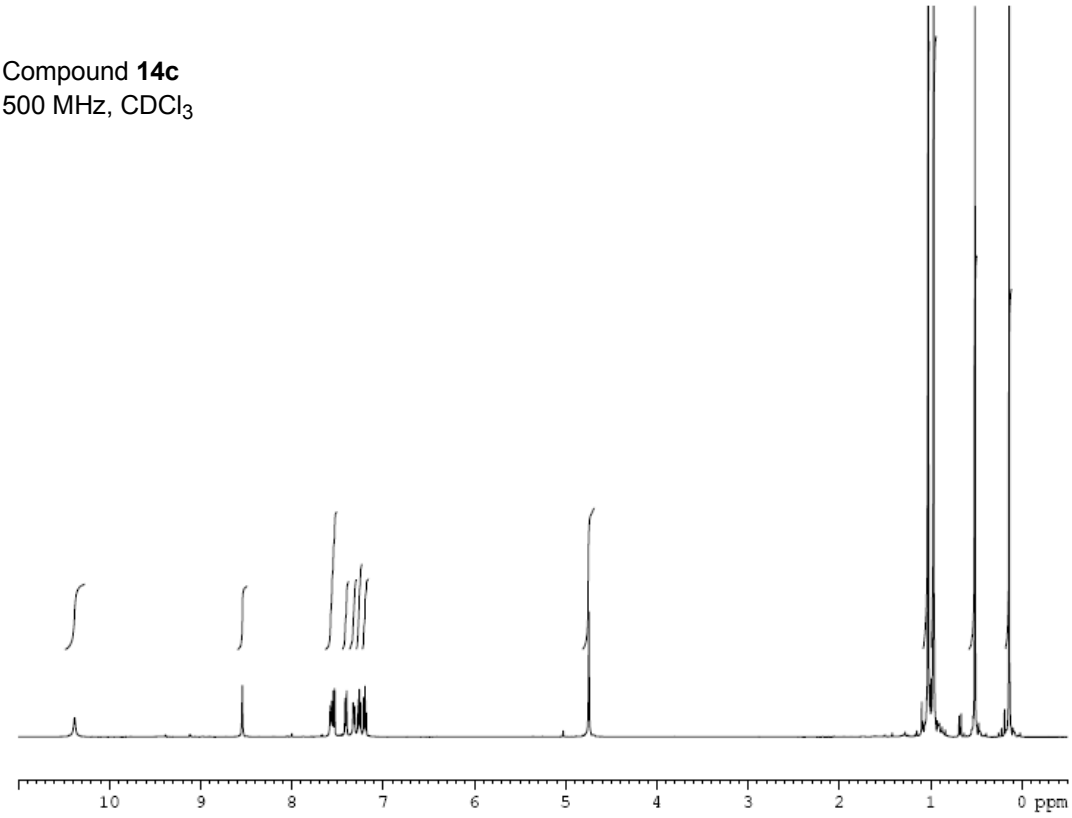
Compound **13m**
500 MHz, $CDCl_3$



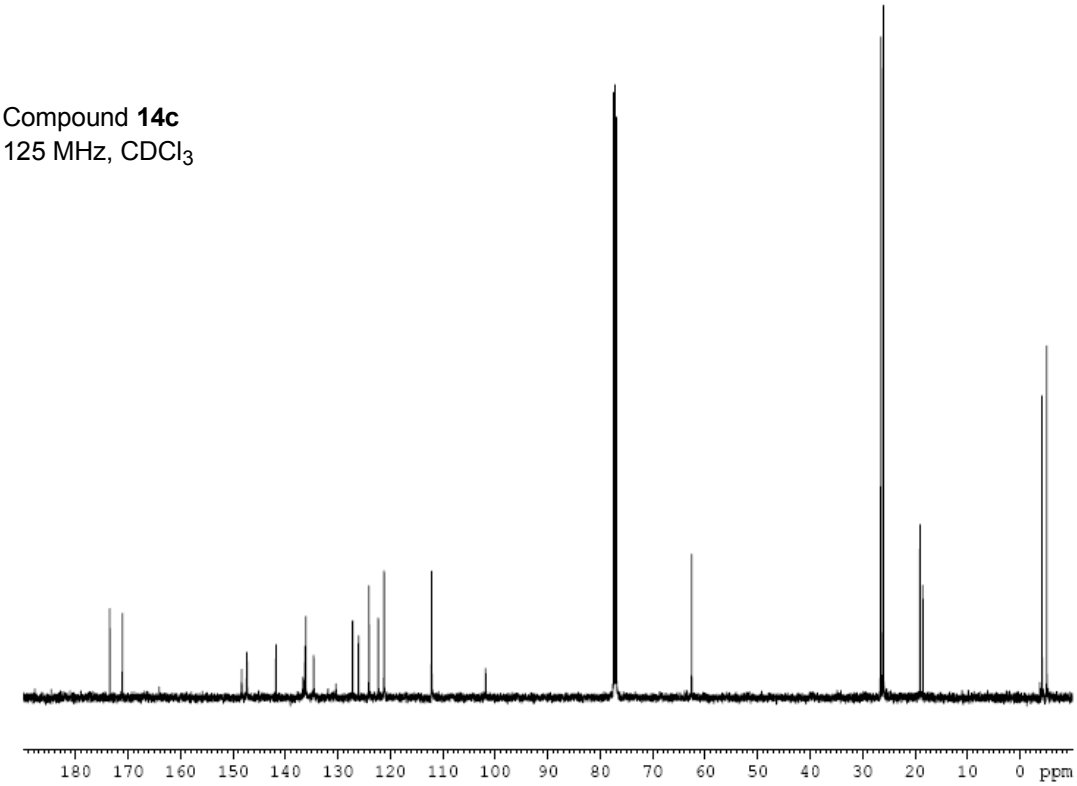
Compound **13m**
125 MHz, $CDCl_3$



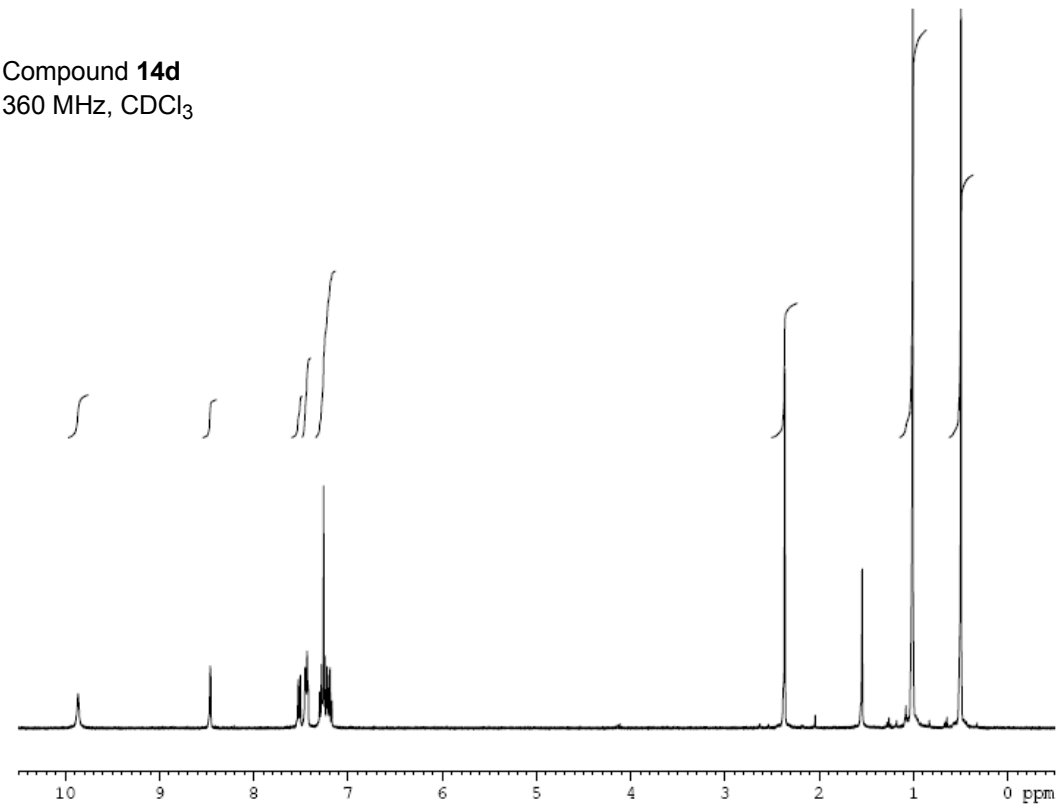
Compound **14c**
500 MHz, $CDCl_3$



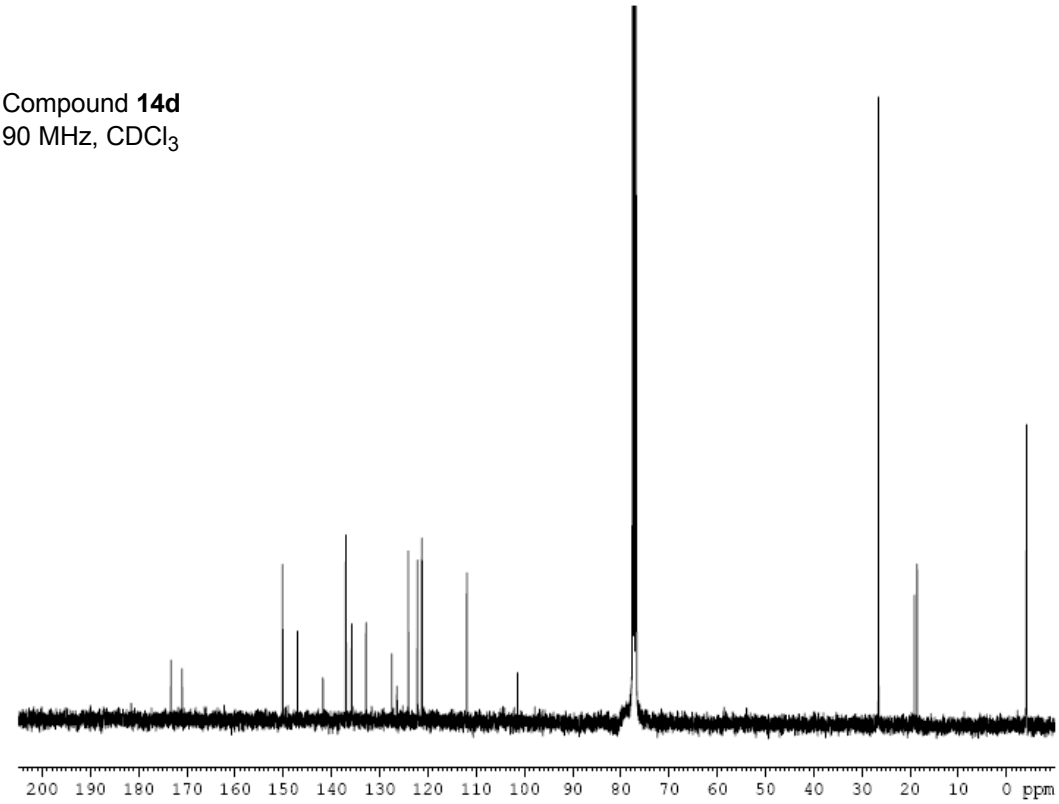
Compound **14c**
125 MHz, $CDCl_3$



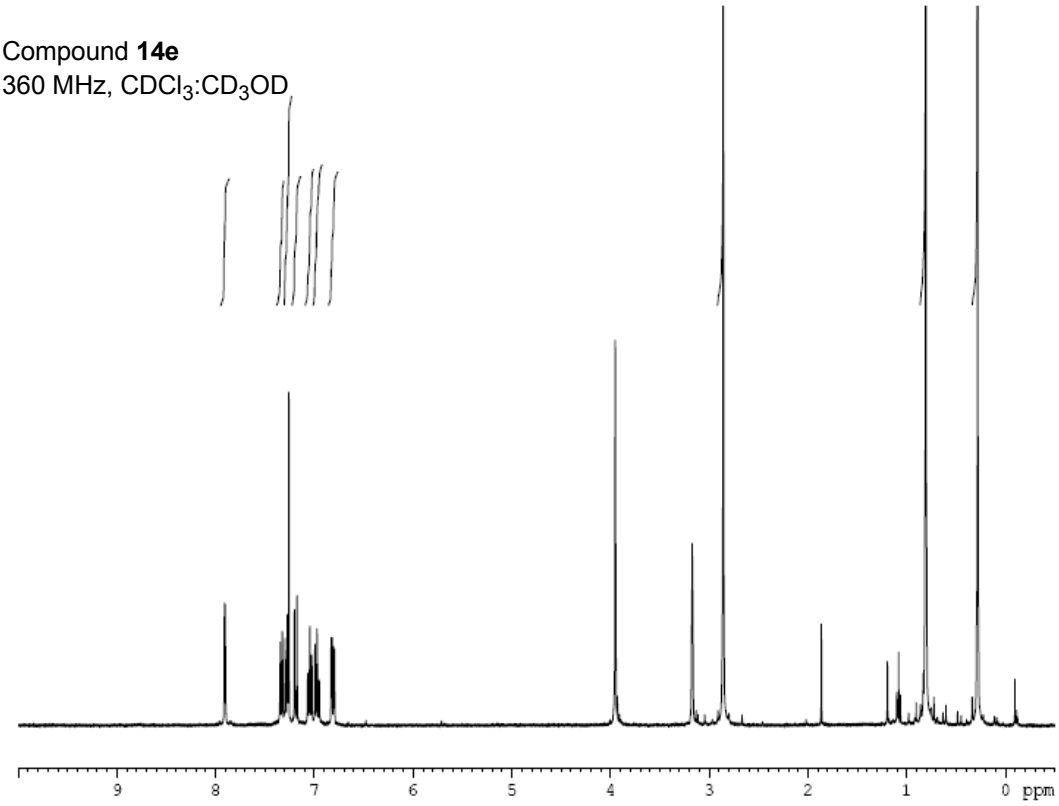
Compound **14d**
360 MHz, $CDCl_3$



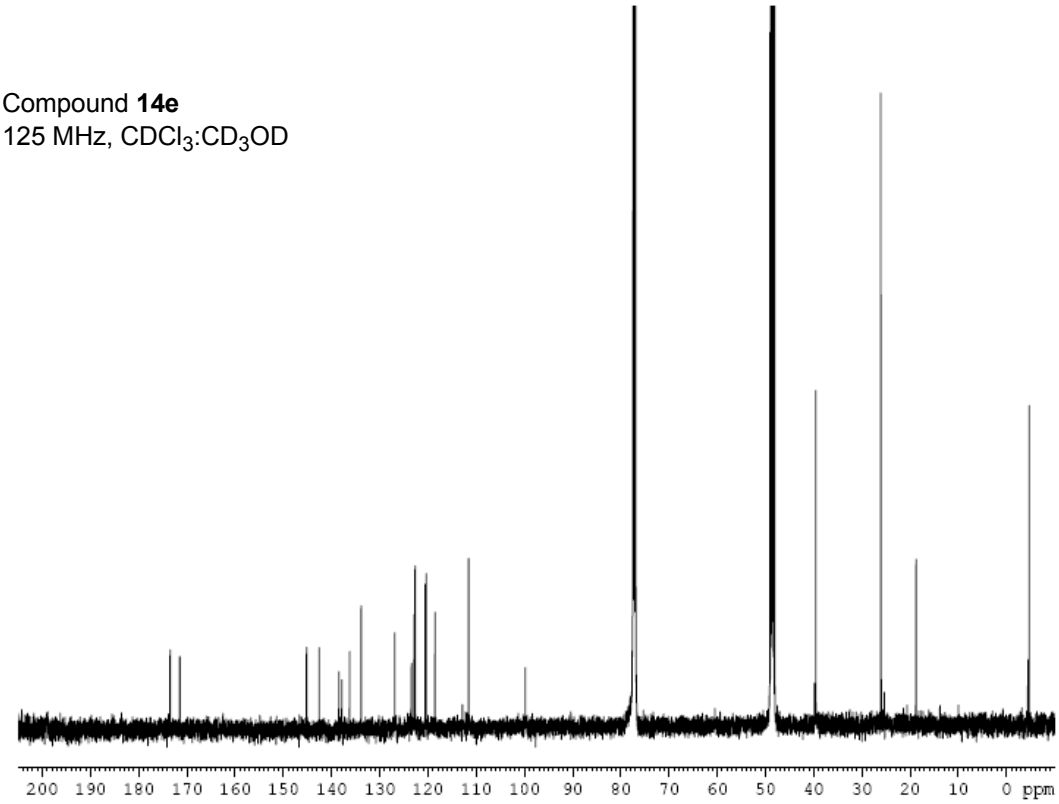
Compound **14d**
90 MHz, $CDCl_3$



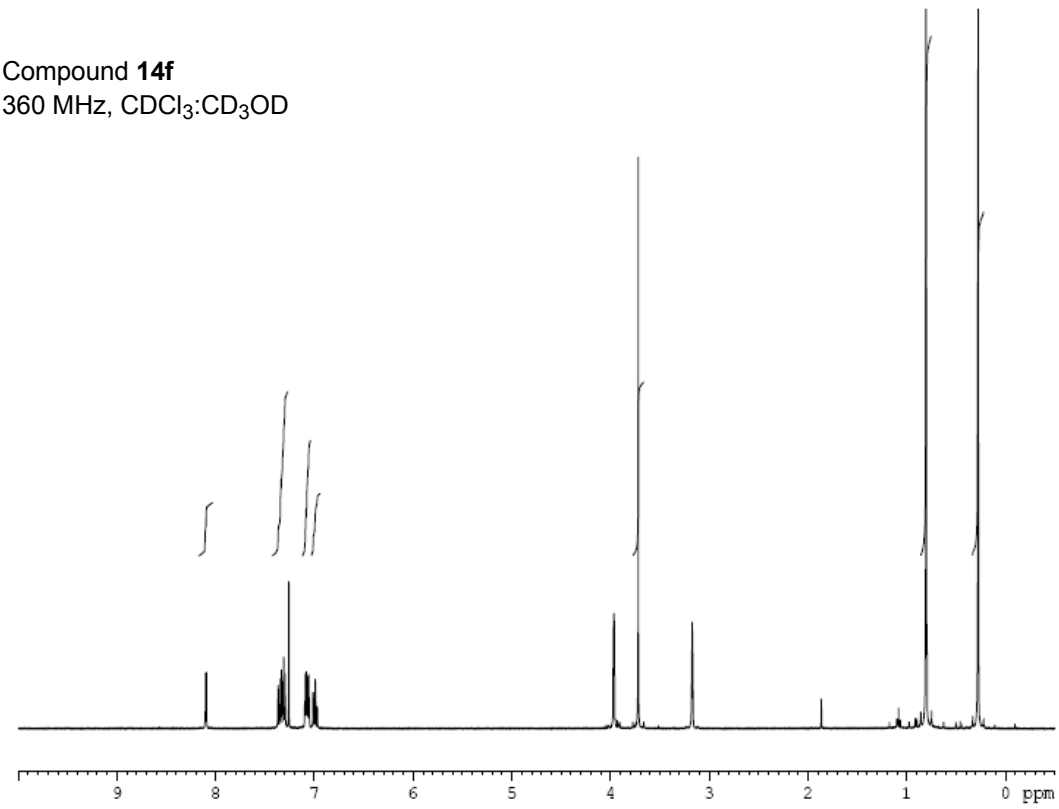
Compound **14e**
360 MHz, $CDCl_3$:CD_3OD



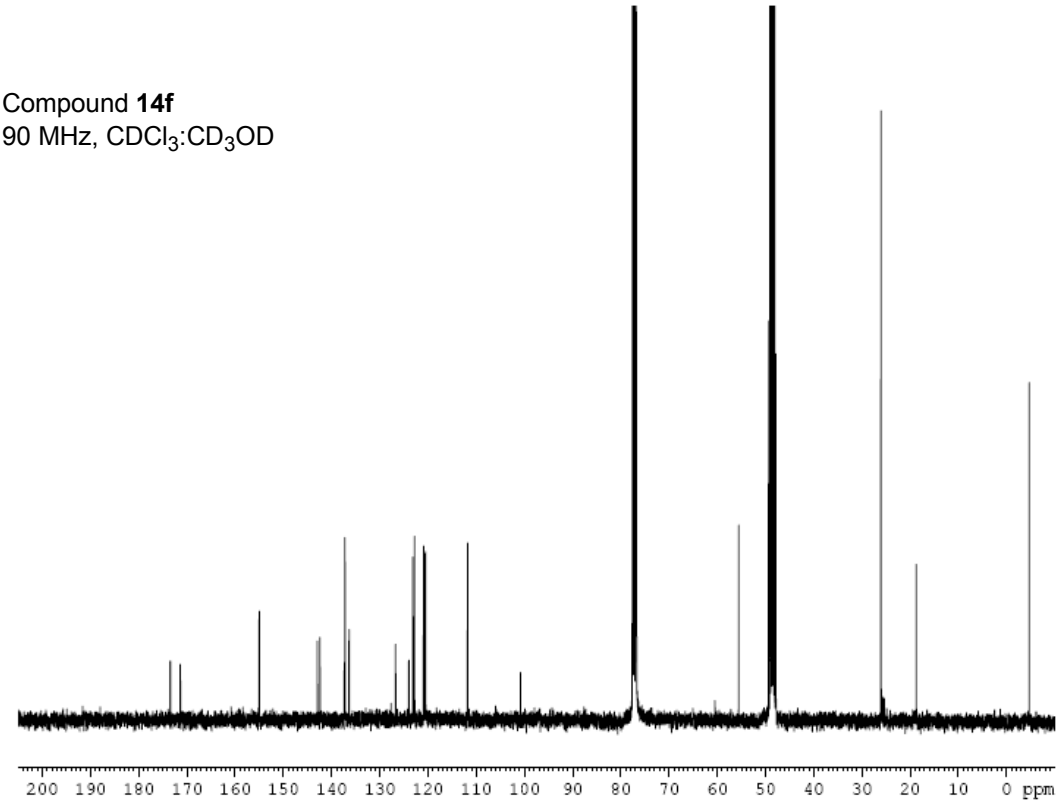
Compound **14e**
125 MHz, $CDCl_3$:CD_3OD



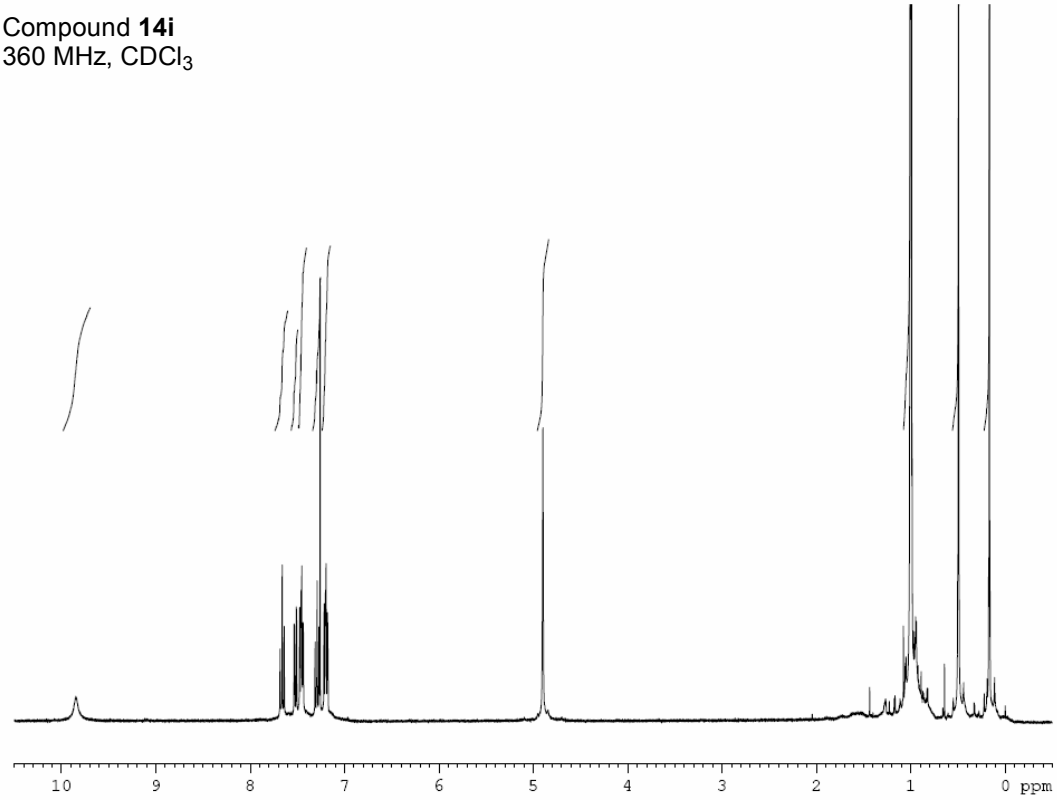
Compound **14f**
360 MHz, $CDCl_3$:CD_3OD



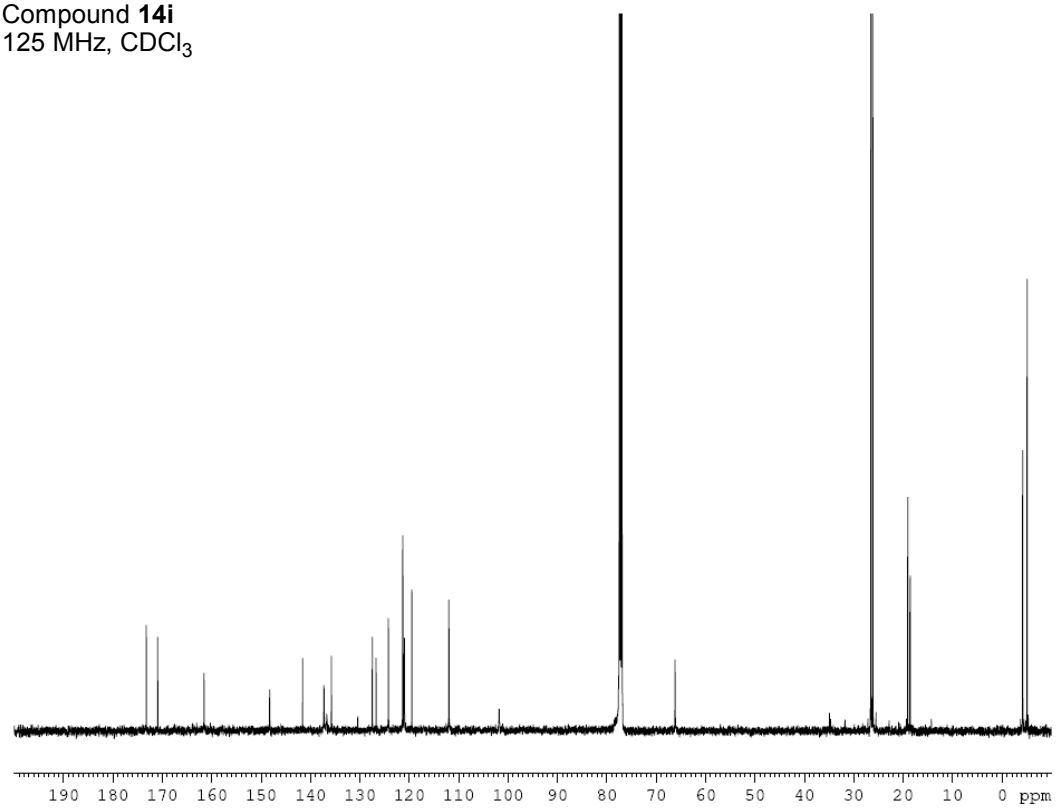
Compound **14f**
90 MHz, $CDCl_3$:CD_3OD



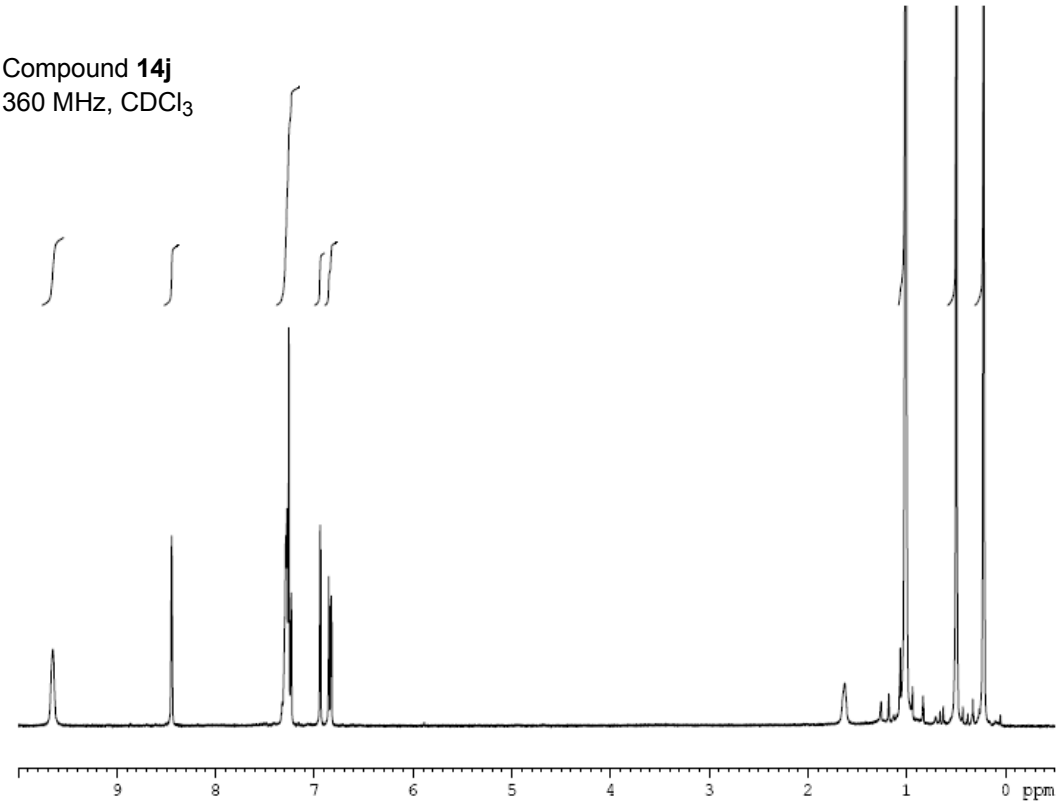
Compound **14i**
360 MHz, $CDCl_3$



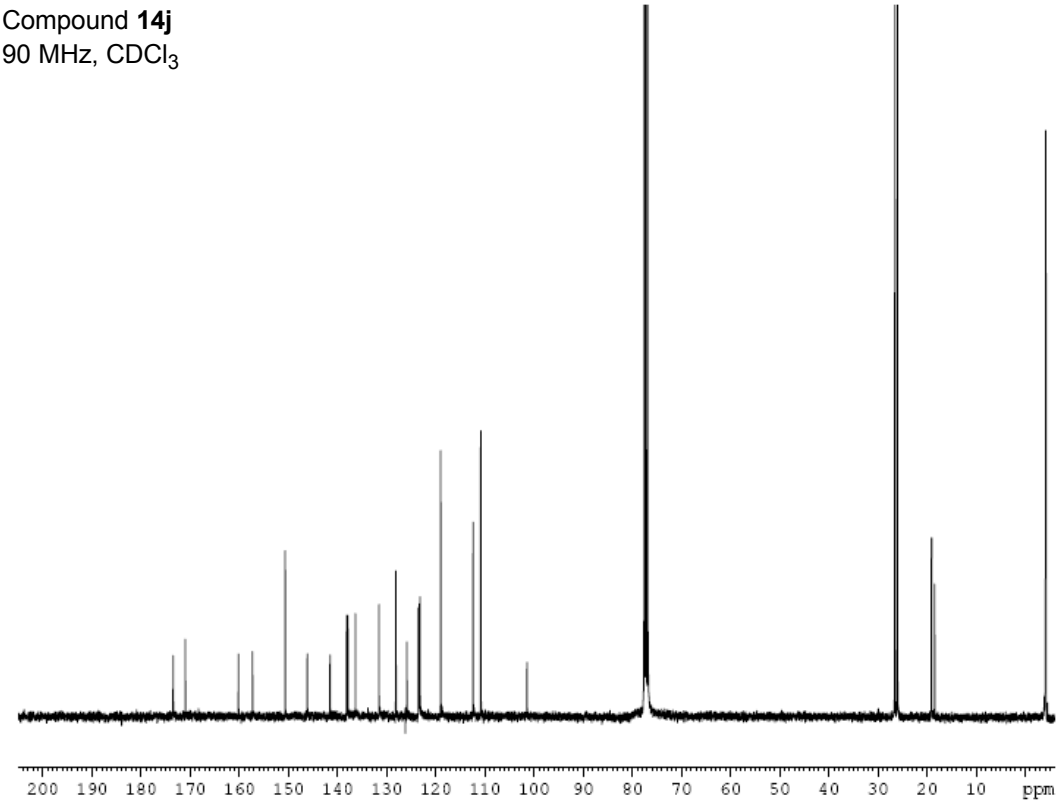
Compound **14i**
125 MHz, $CDCl_3$



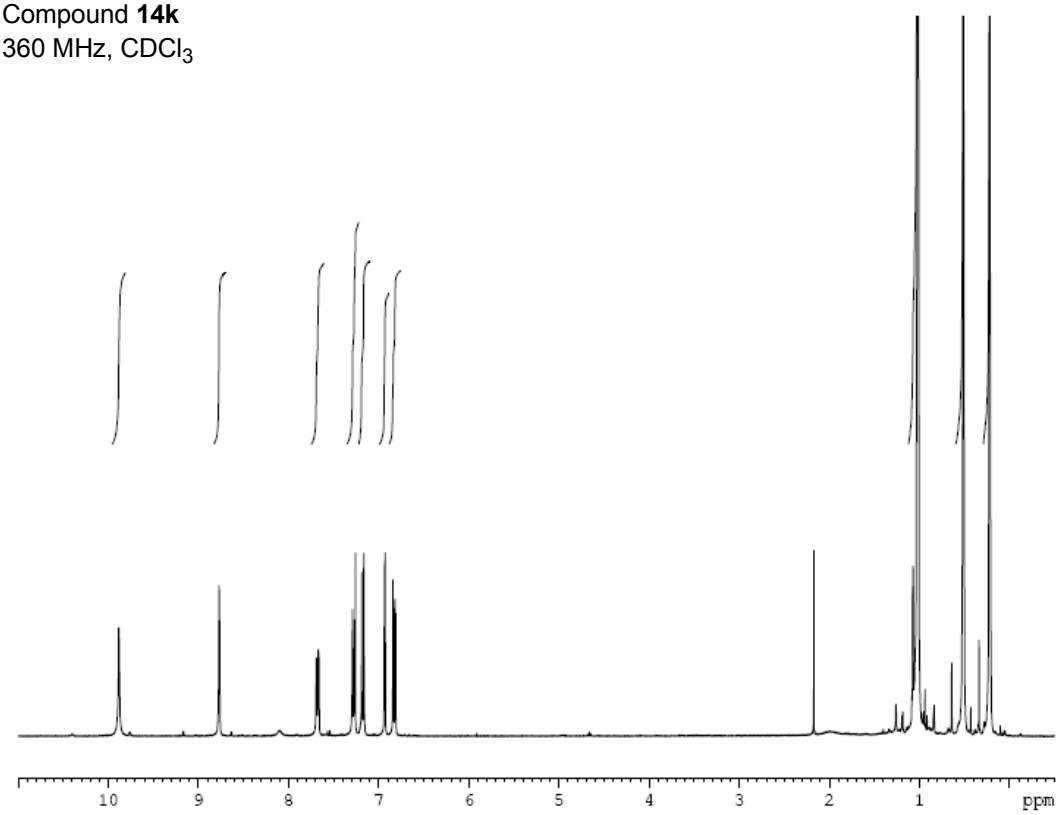
Compound **14j**
360 MHz, $CDCl_3$



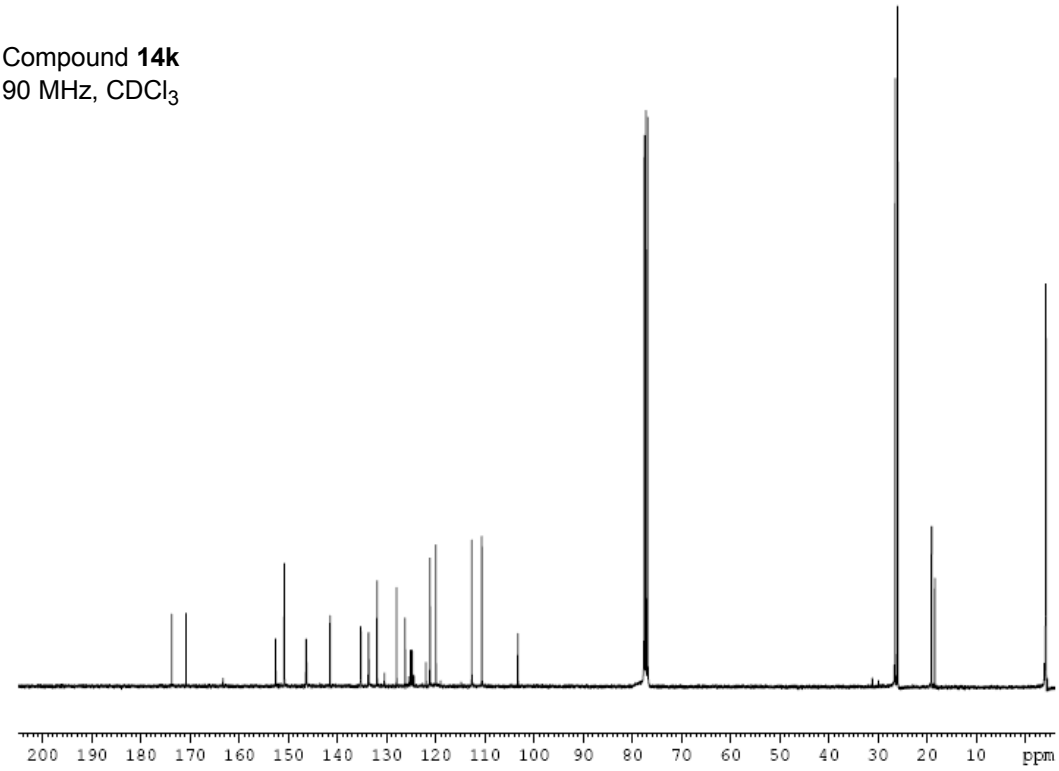
Compound **14j**
90 MHz, $CDCl_3$



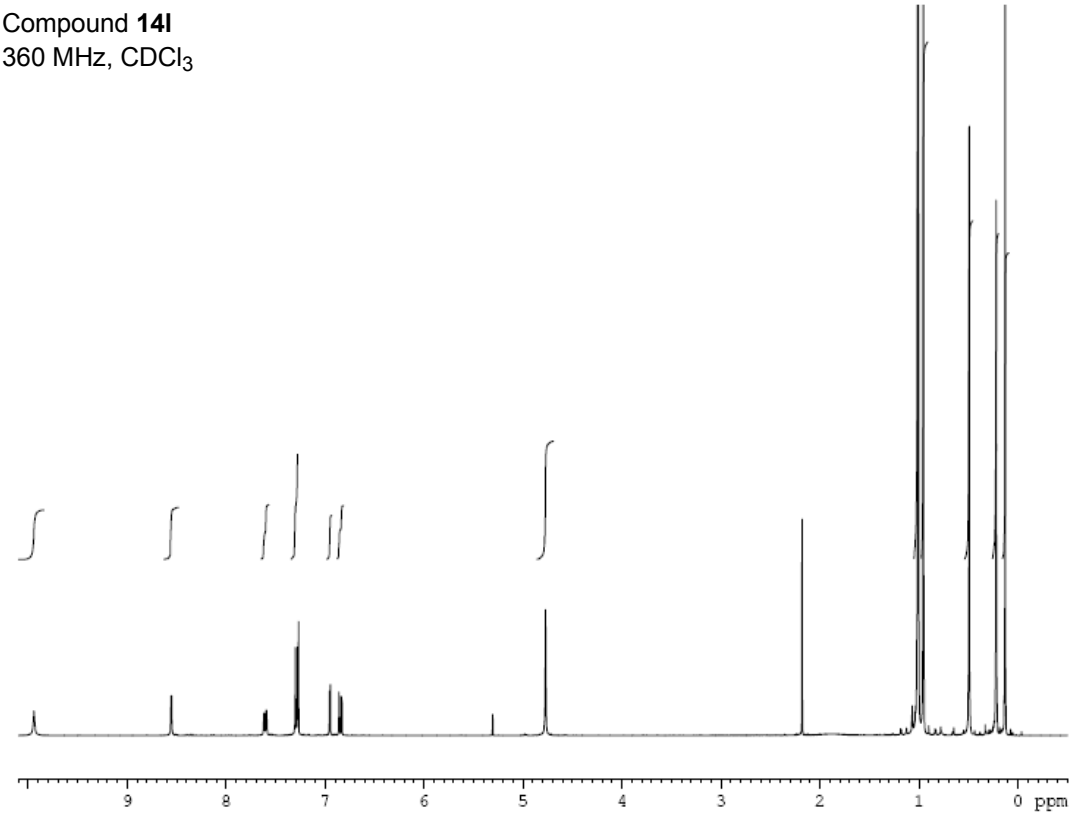
Compound **14k**
360 MHz, $CDCl_3$



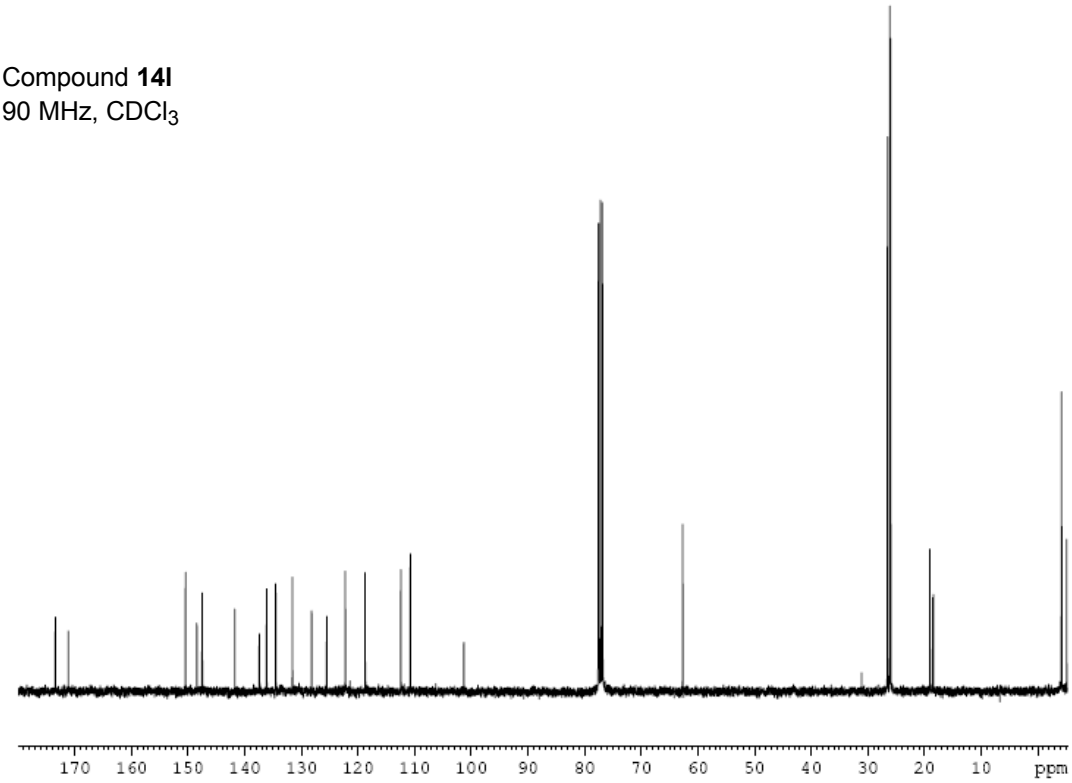
Compound **14k**
90 MHz, $CDCl_3$



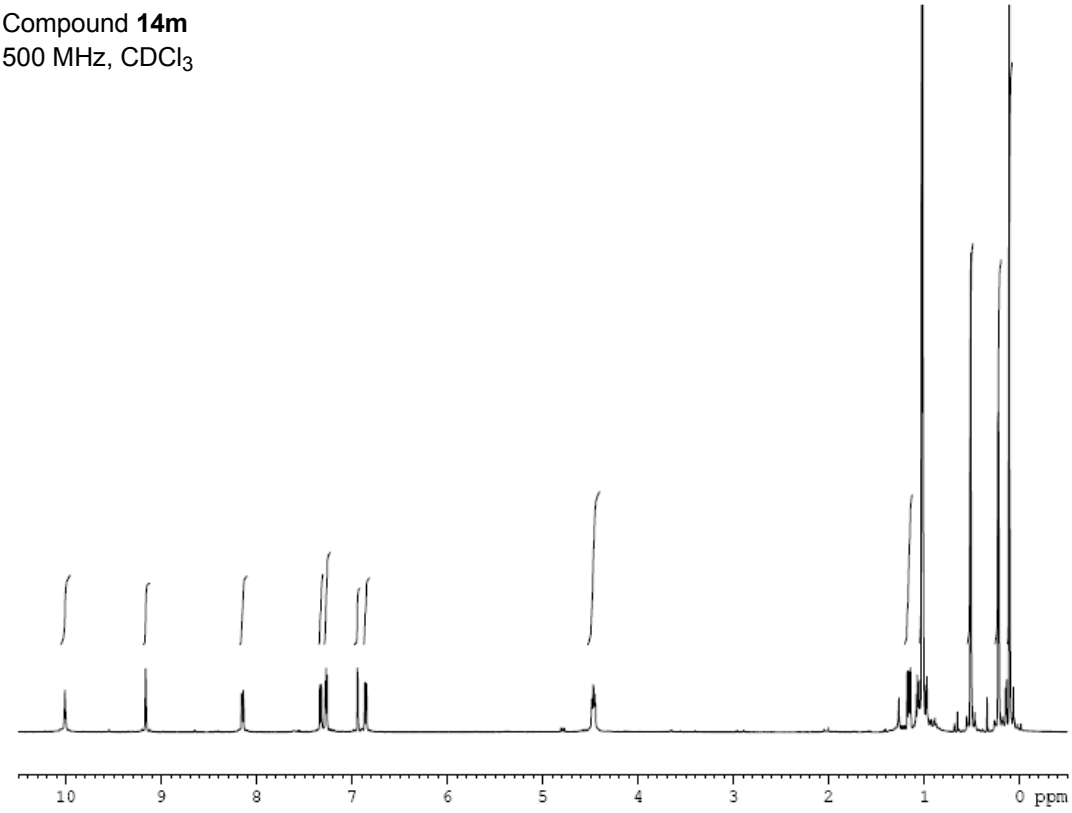
Compound **14l**
360 MHz, $CDCl_3$



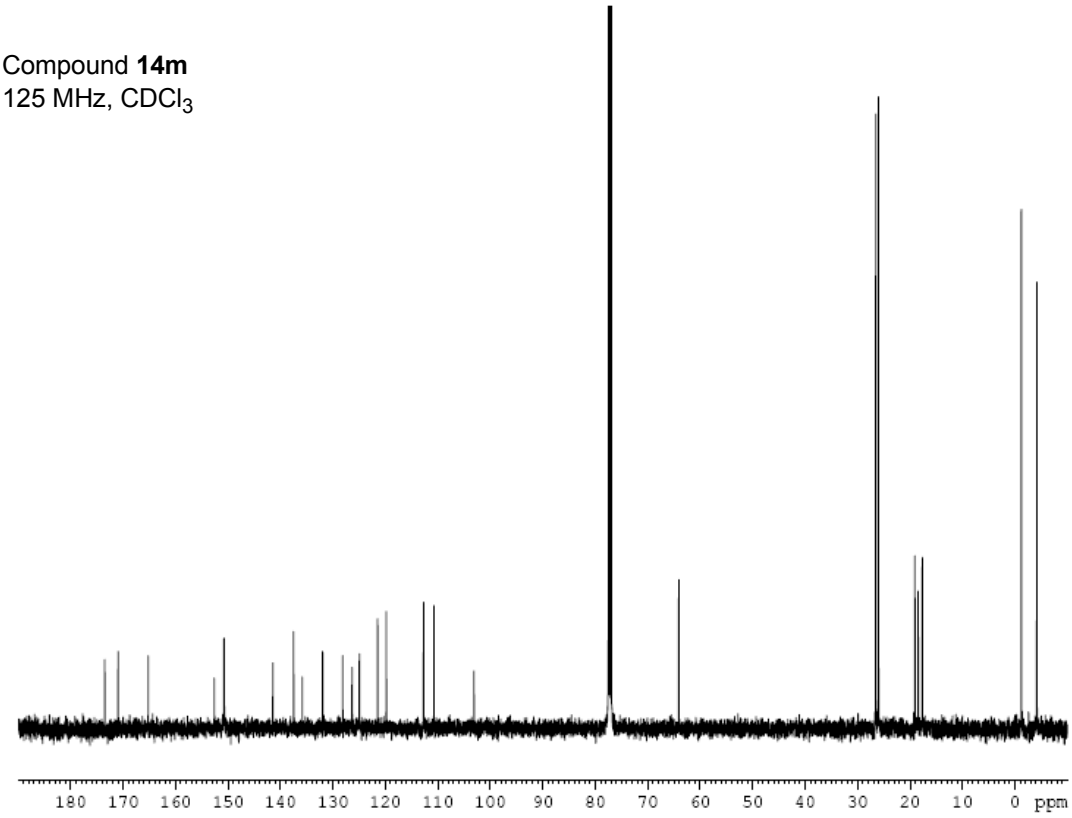
Compound **14l**
90 MHz, $CDCl_3$



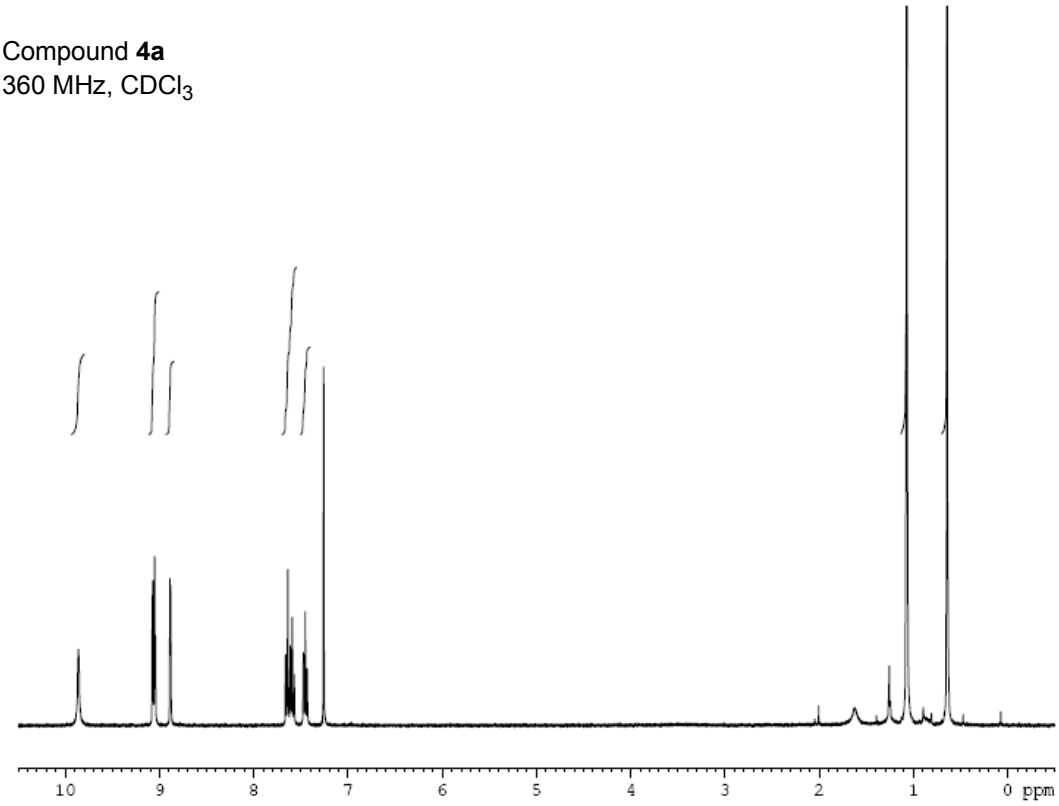
Compound **14m**
500 MHz, $CDCl_3$



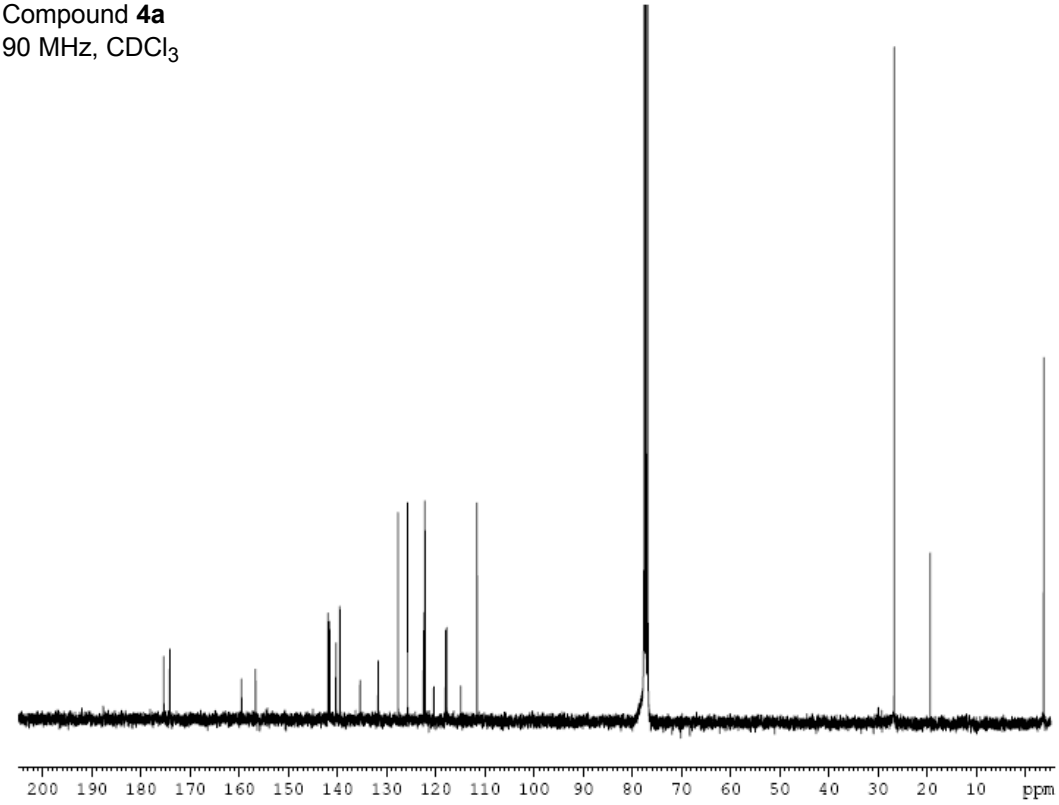
Compound **14m**
125 MHz, $CDCl_3$



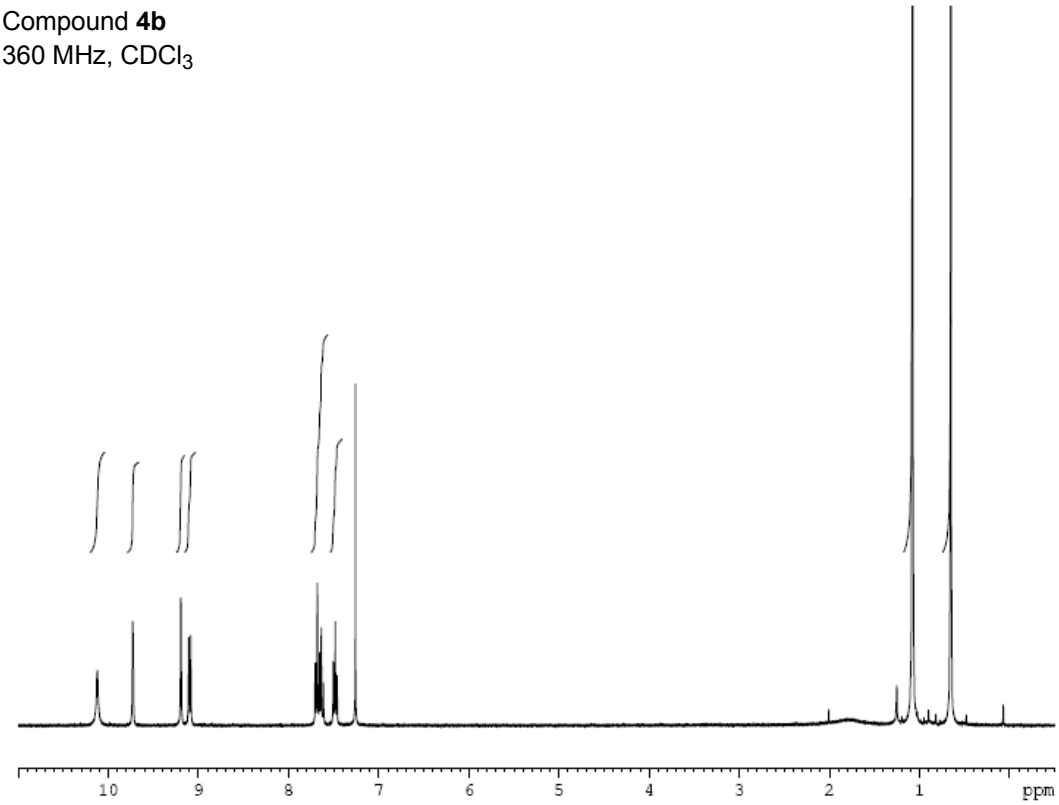
Compound **4a**
360 MHz, $CDCl_3$



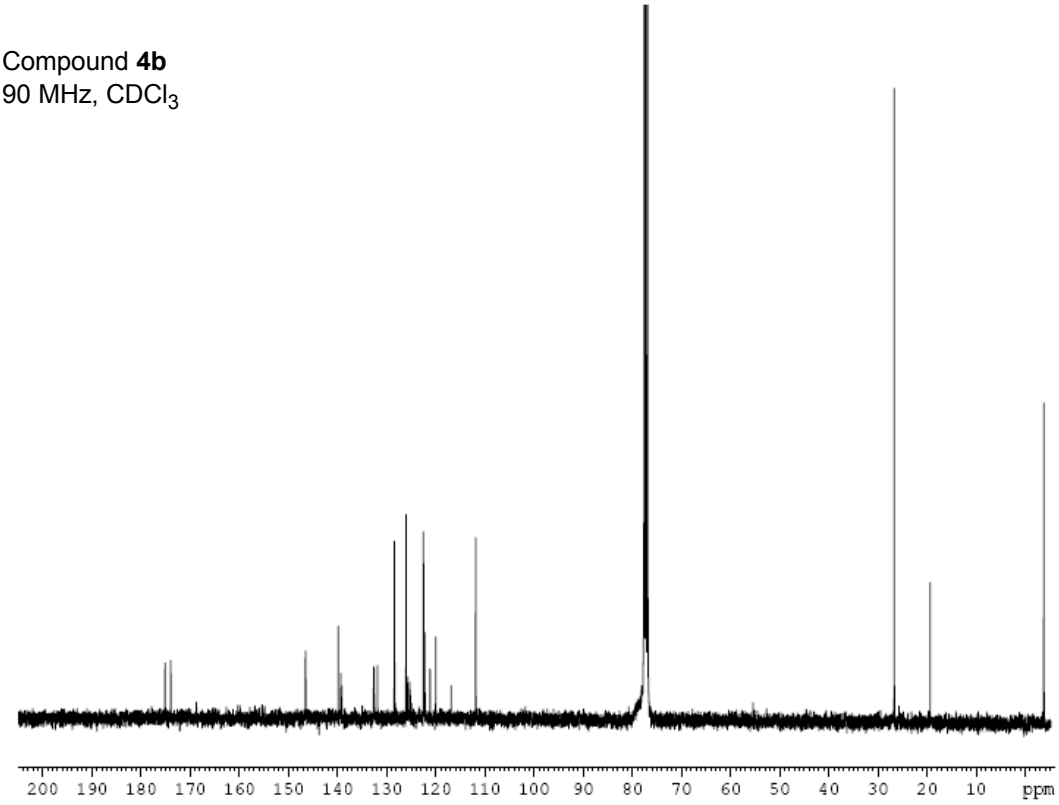
Compound **4a**
90 MHz, $CDCl_3$



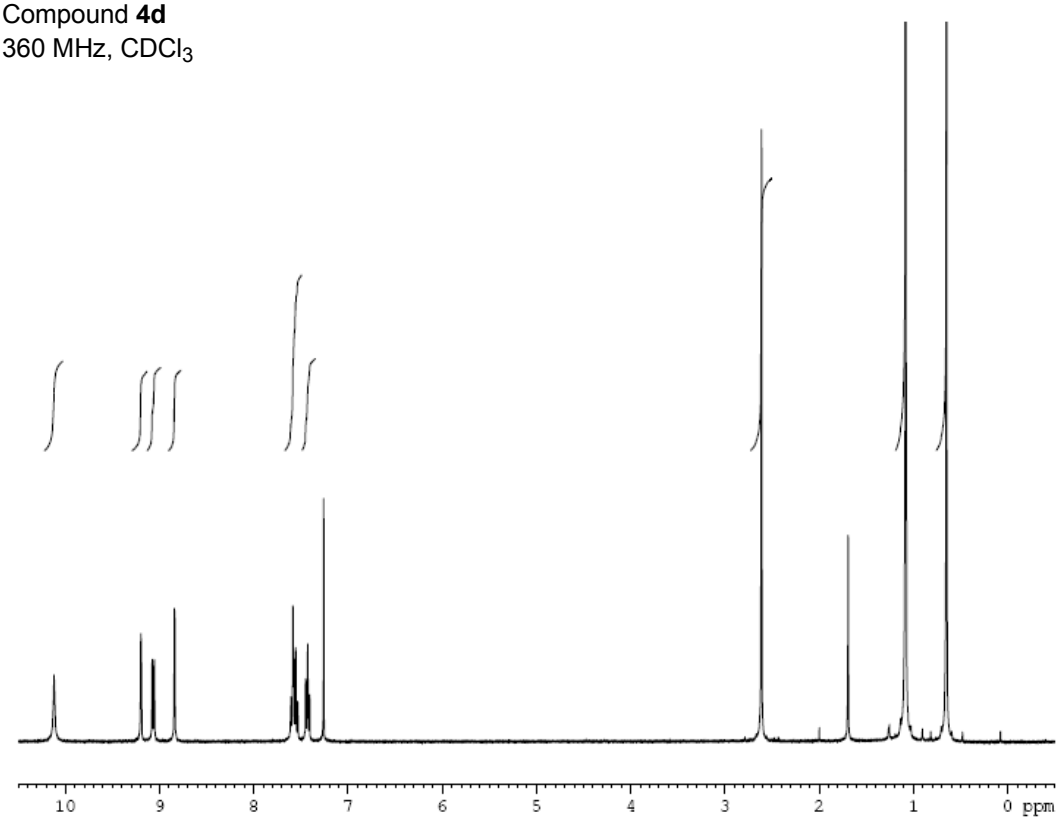
Compound **4b**
360 MHz, $CDCl_3$



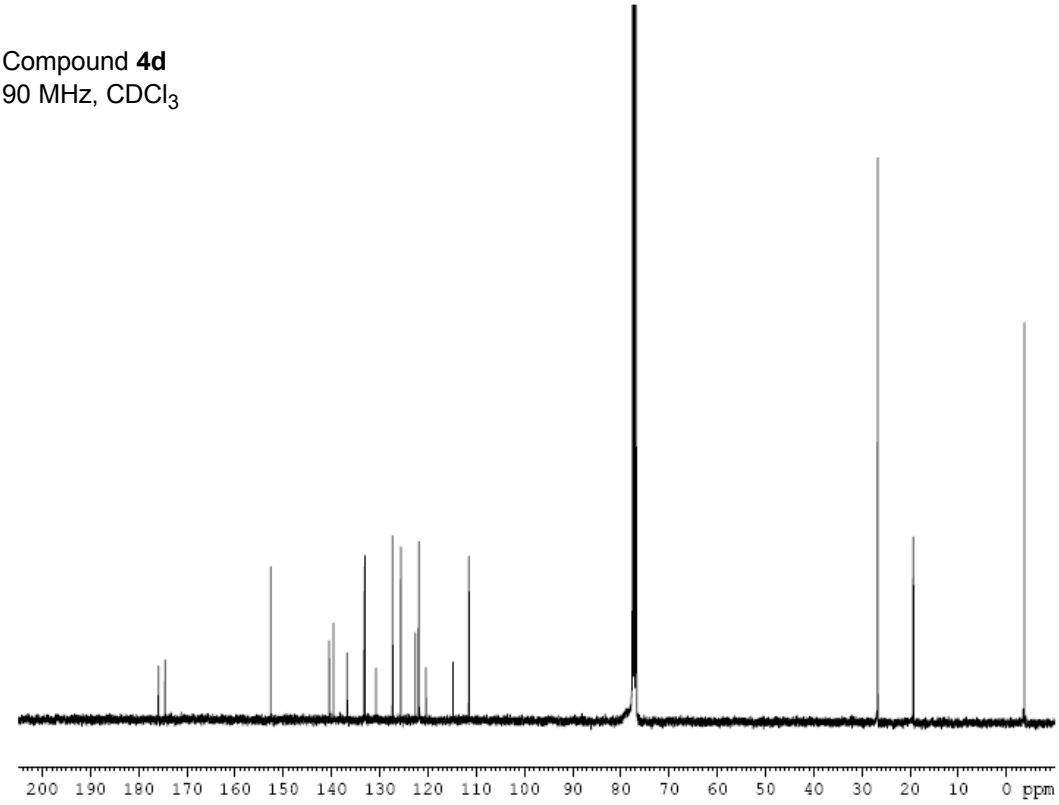
Compound **4b**
90 MHz, $CDCl_3$



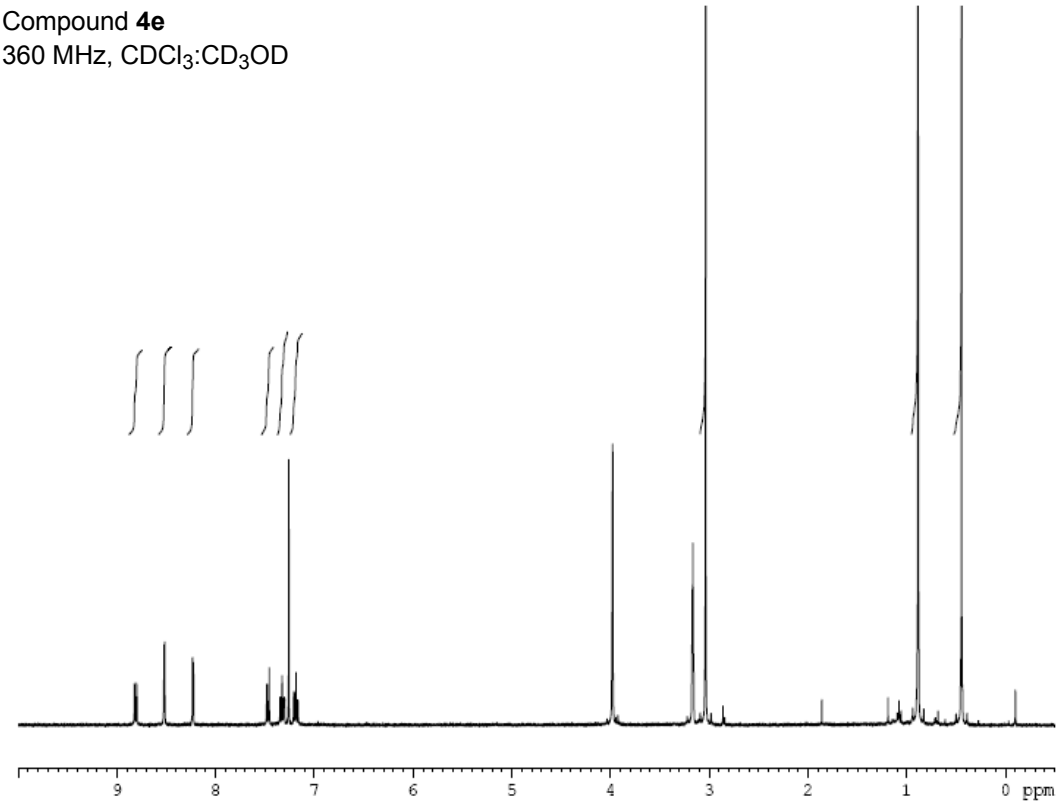
Compound **4d**
360 MHz, $CDCl_3$



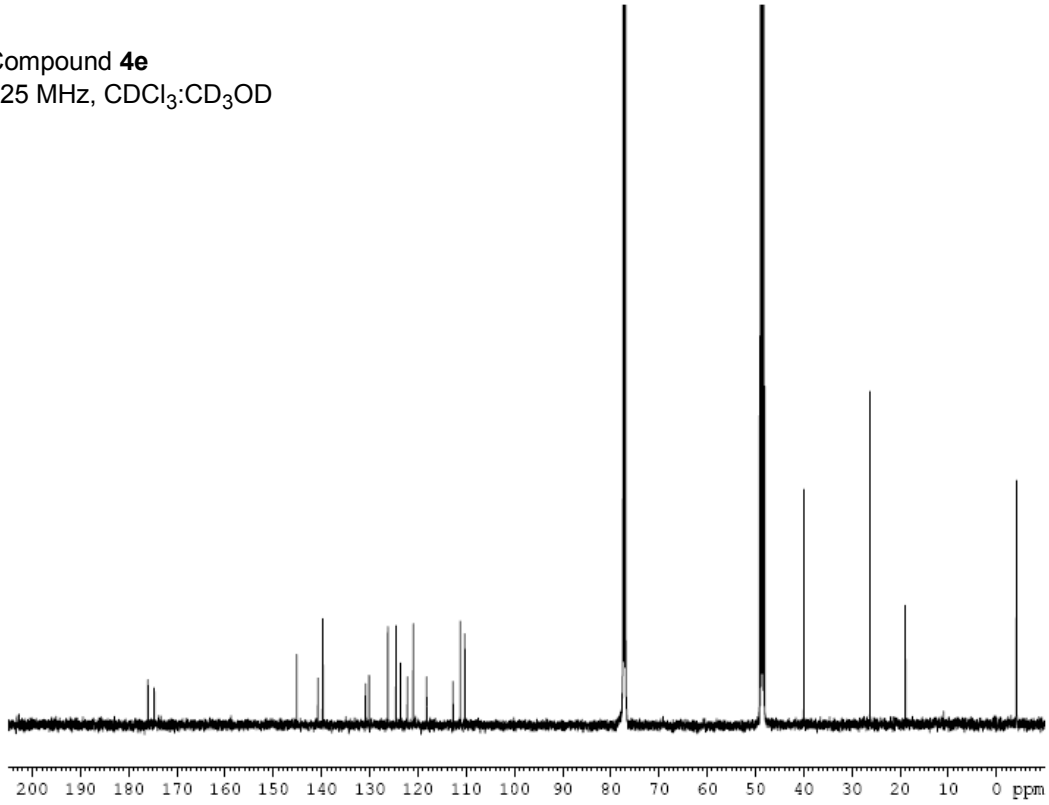
Compound **4d**
90 MHz, $CDCl_3$



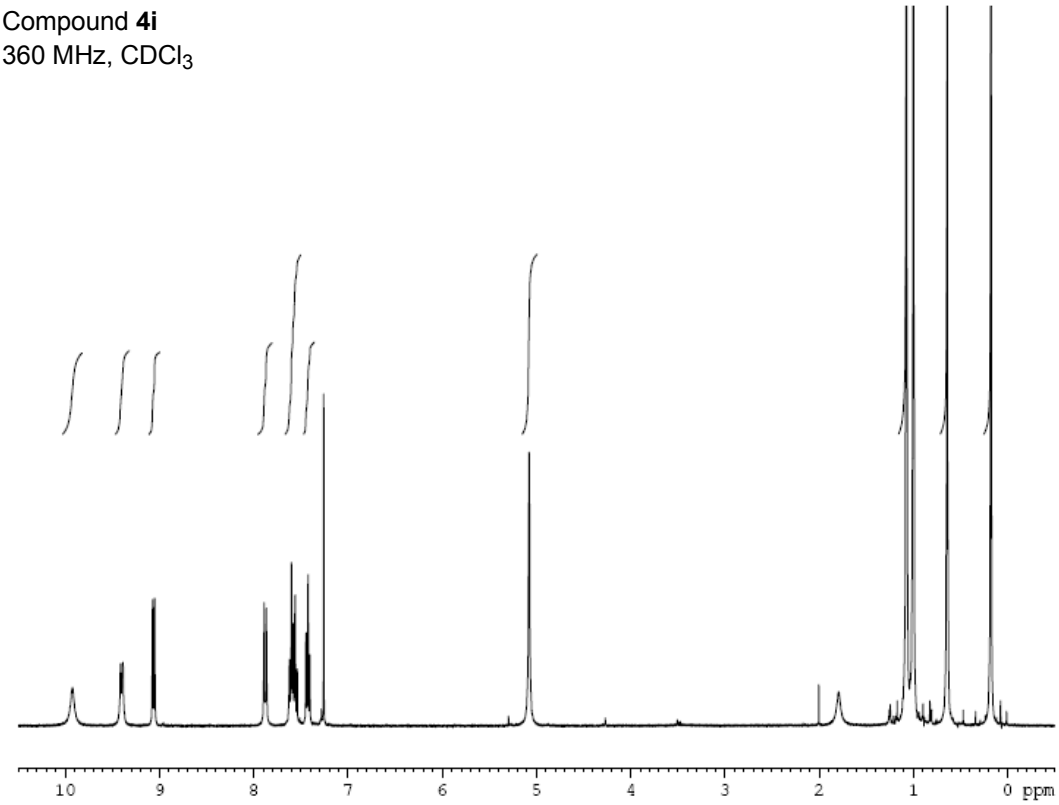
Compound **4e**
360 MHz, $CDCl_3$:CD_3OD



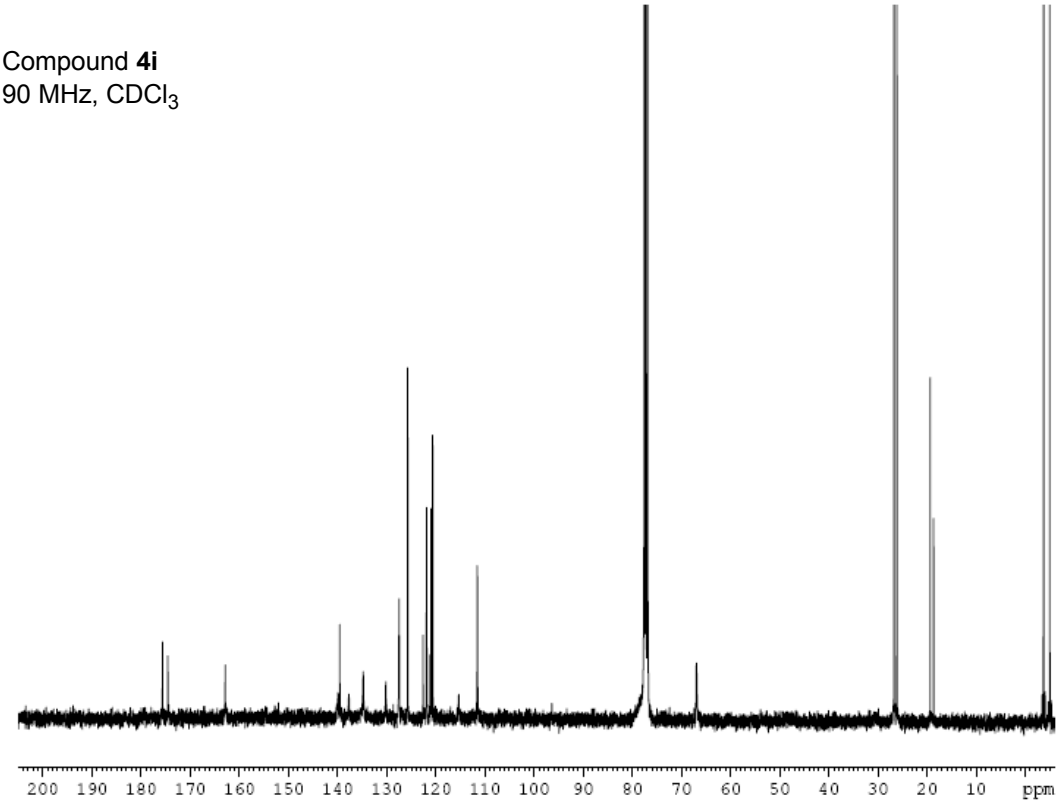
Compound **4e**
125 MHz, $CDCl_3$:CD_3OD



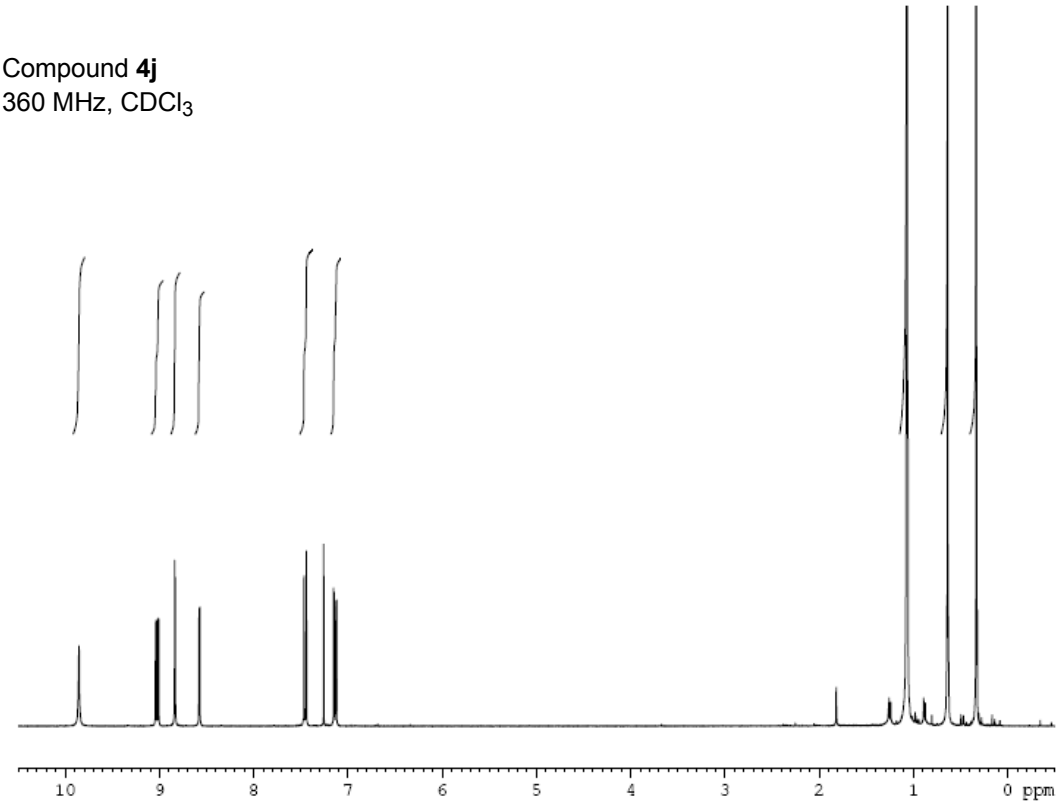
Compound **4i**
360 MHz, $CDCl_3$



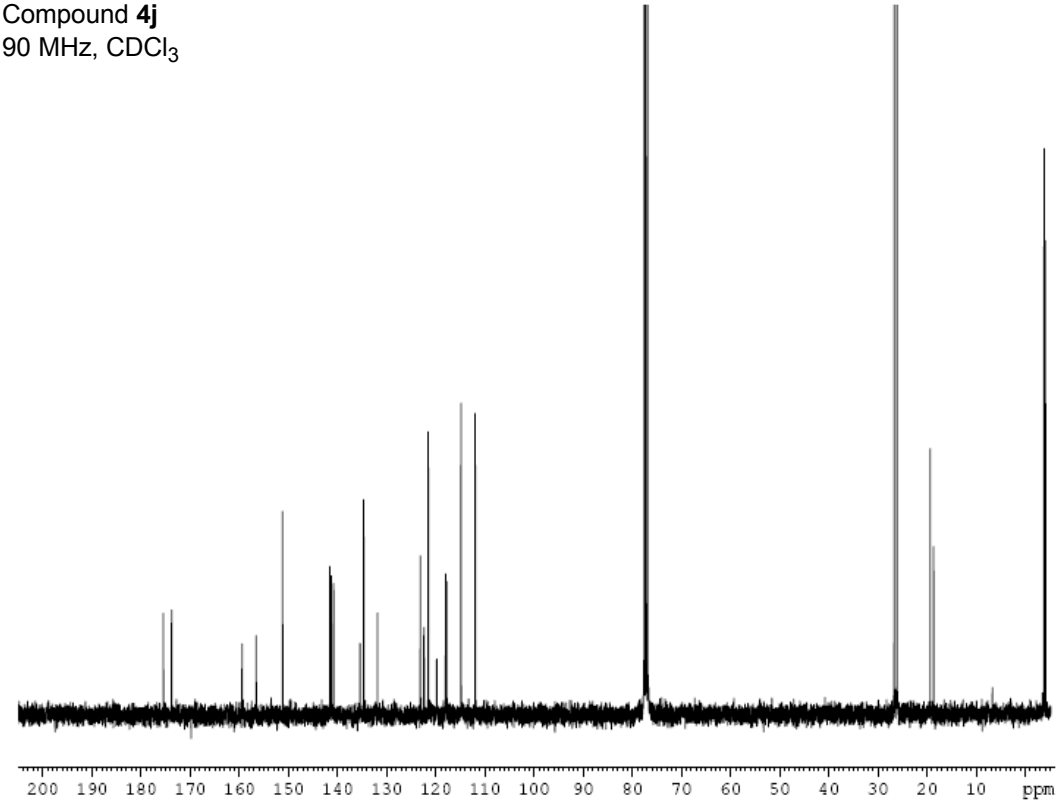
Compound **4i**
90 MHz, $CDCl_3$



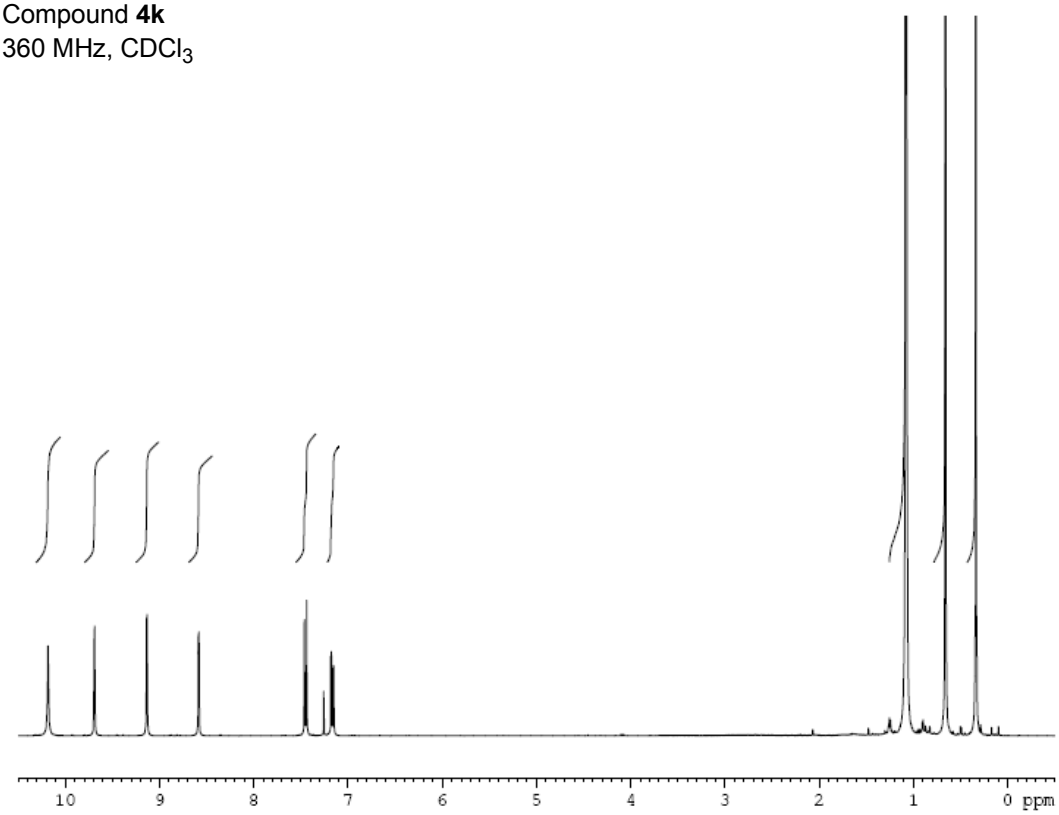
Compound **4j**
360 MHz, $CDCl_3$



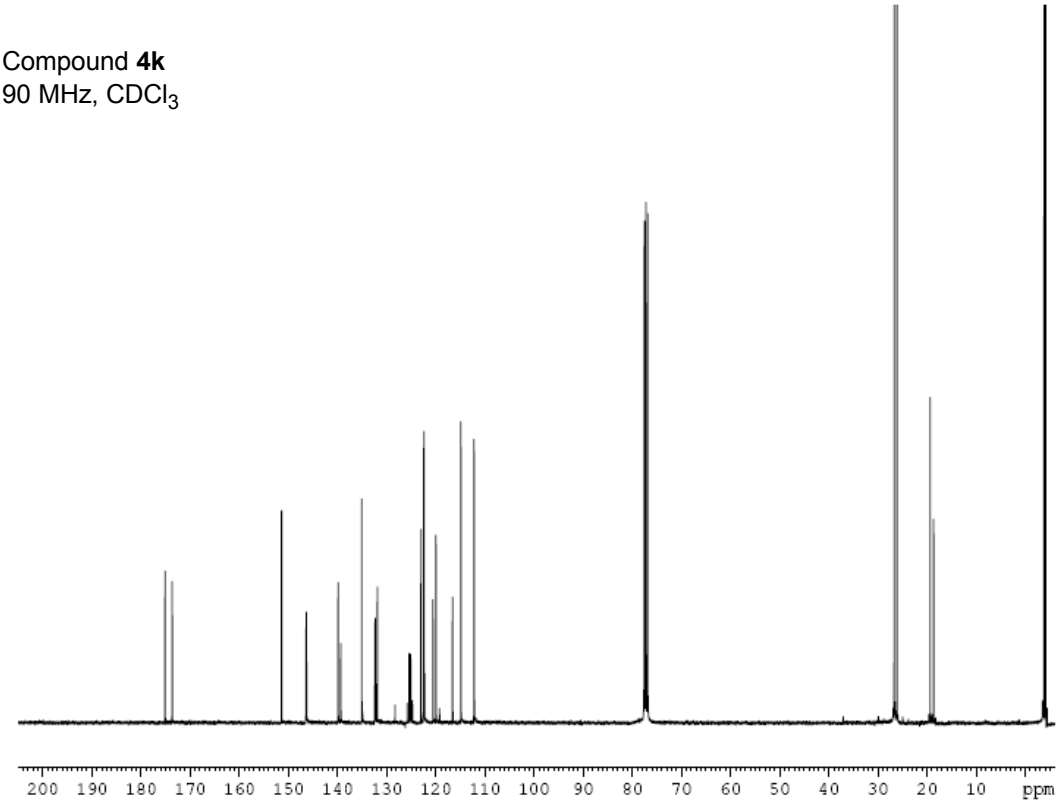
Compound **4j**
90 MHz, $CDCl_3$



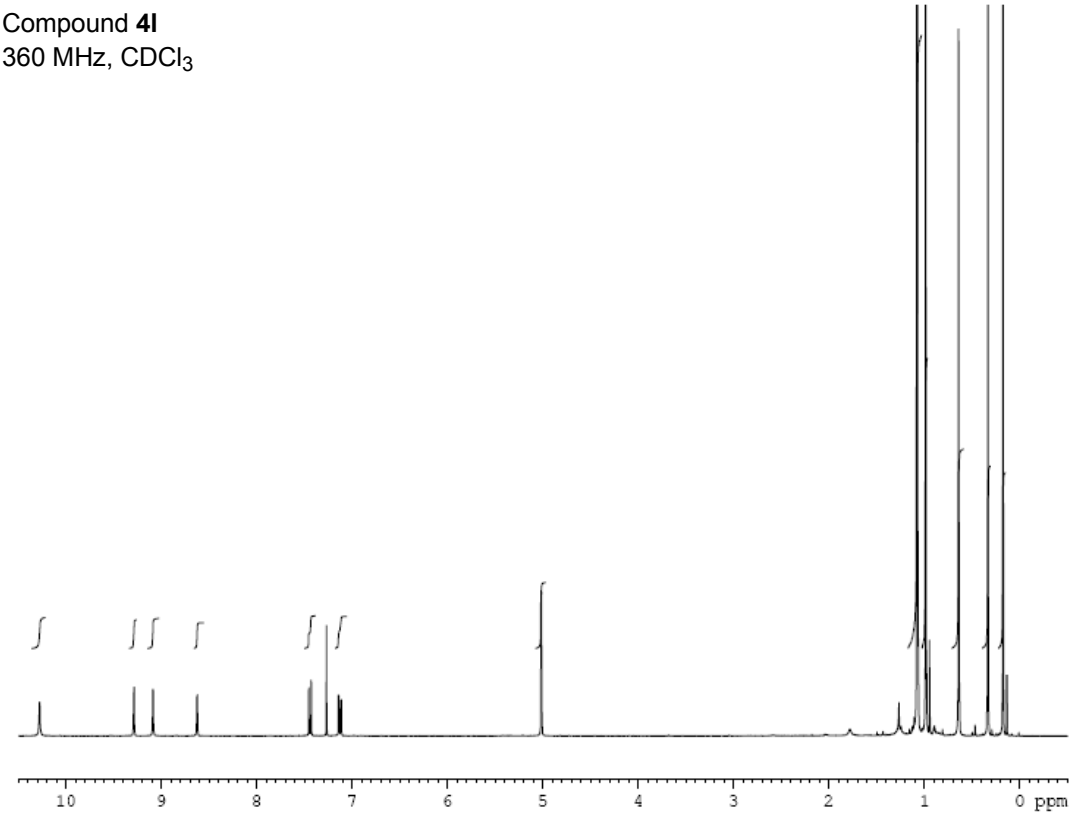
Compound **4k**
360 MHz, $CDCl_3$



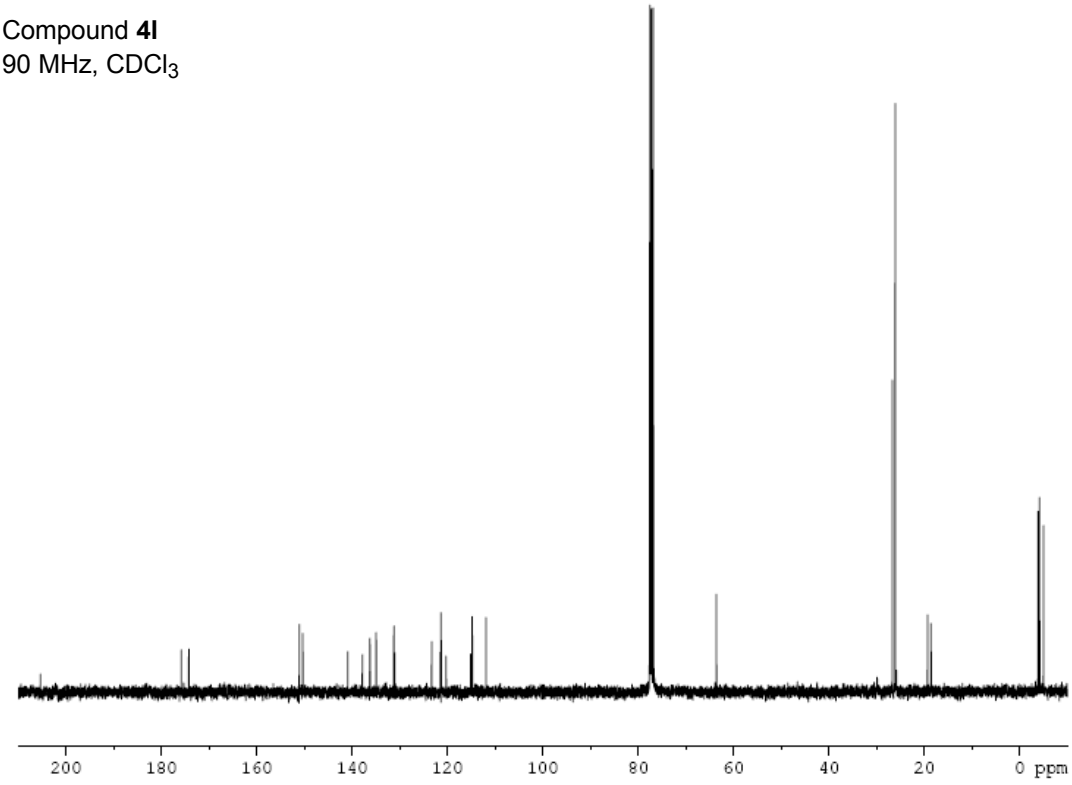
Compound **4k**
90 MHz, $CDCl_3$



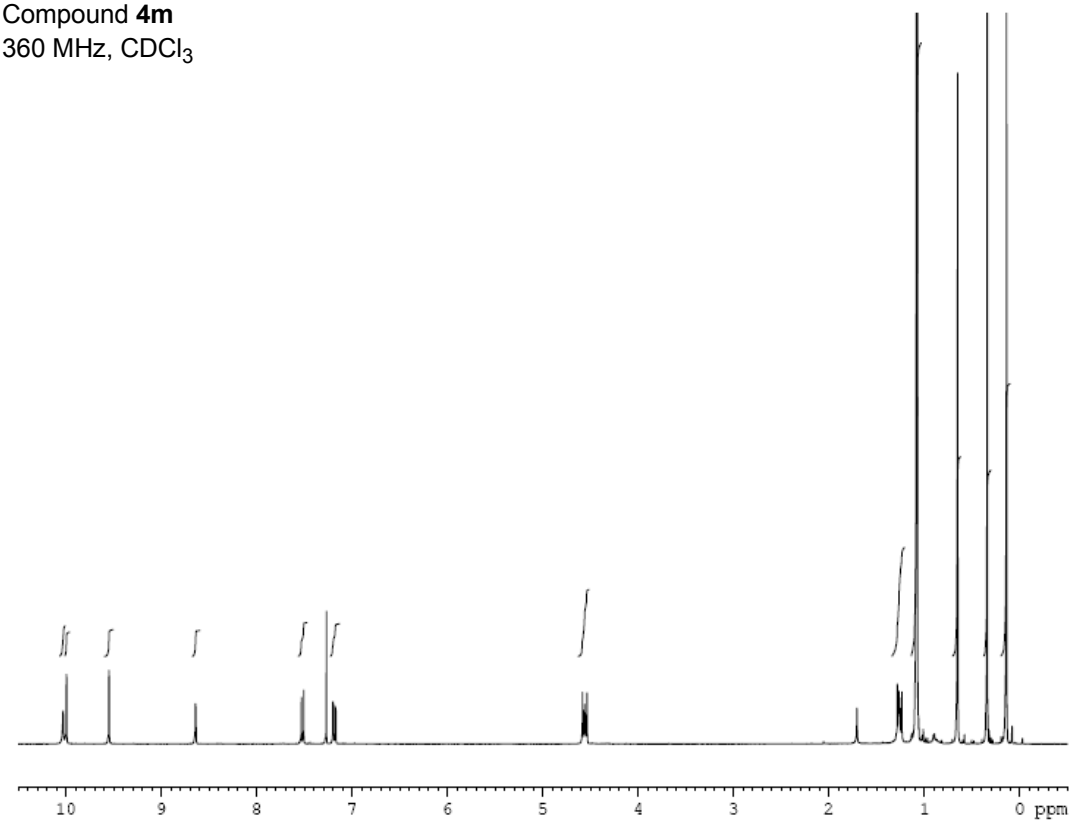
Compound **4l**
360 MHz, $CDCl_3$



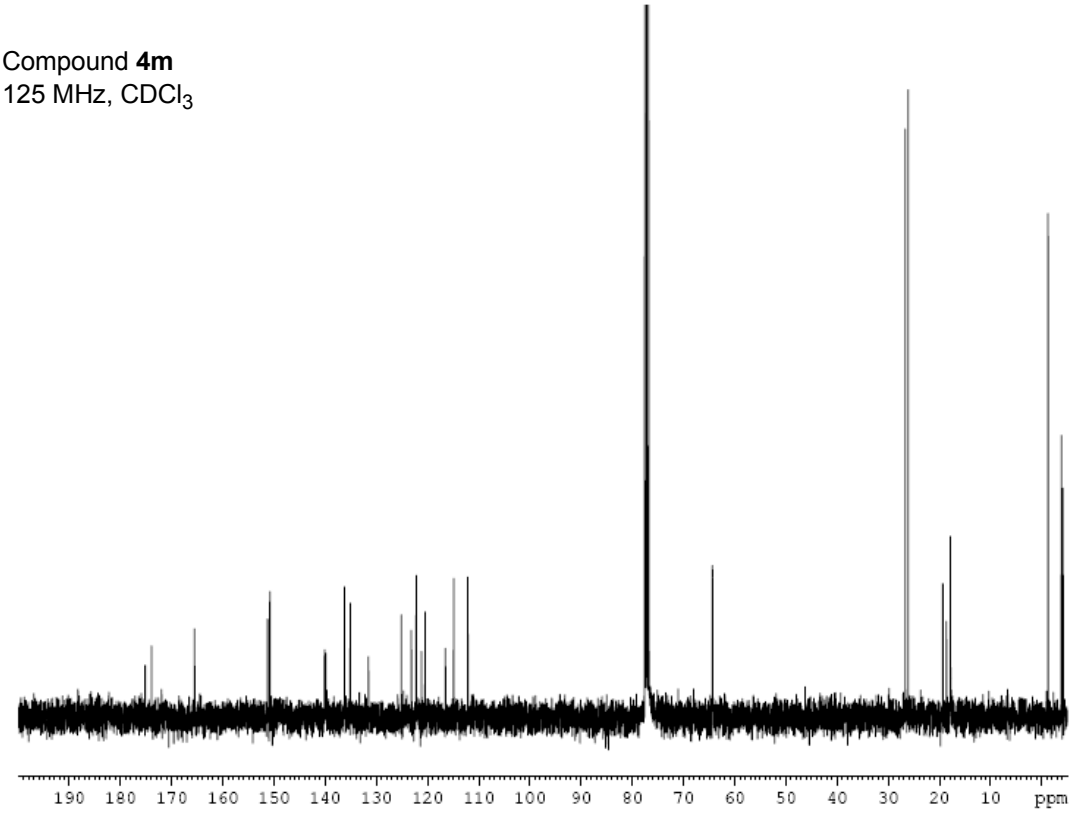
Compound **4l**
90 MHz, $CDCl_3$



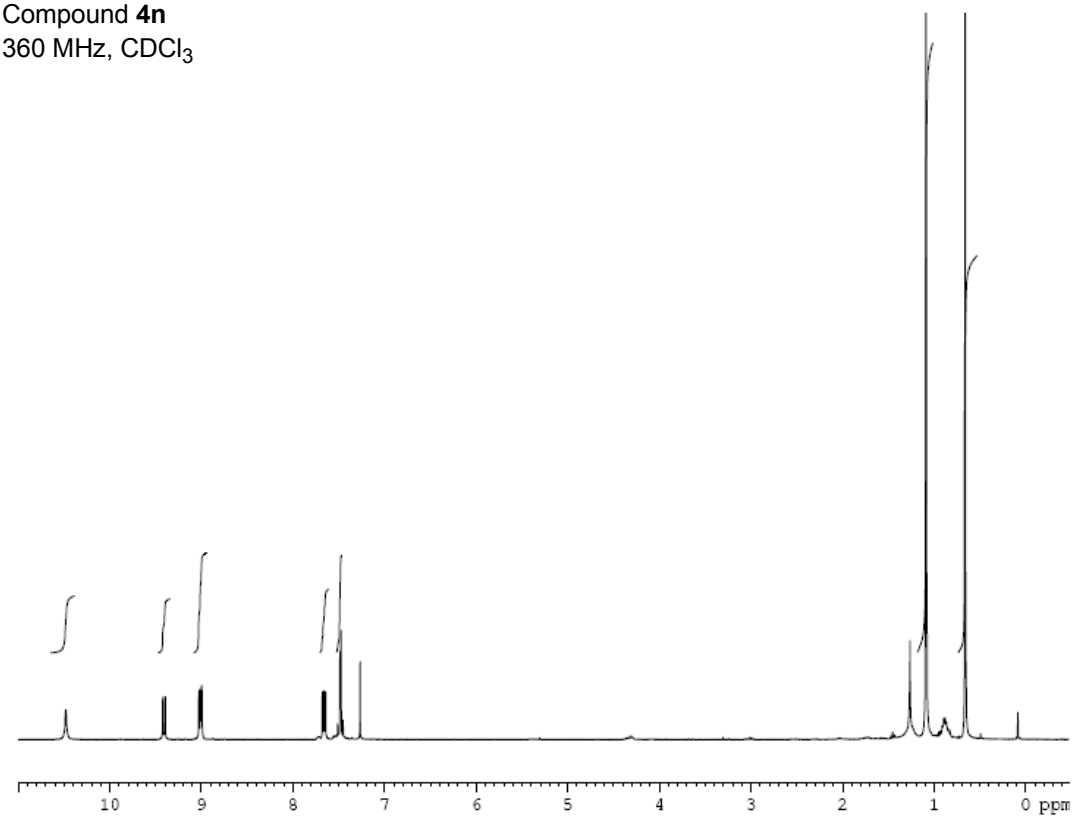
Compound **4m**
360 MHz, $CDCl_3$



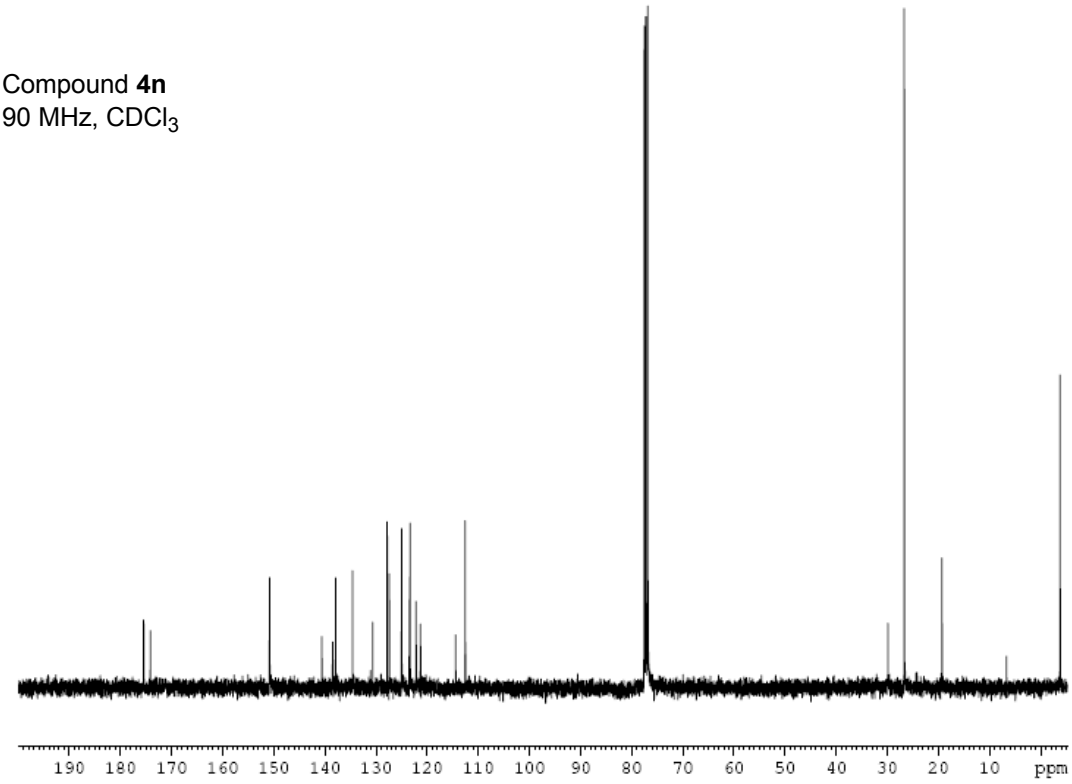
Compound **4m**
125 MHz, $CDCl_3$



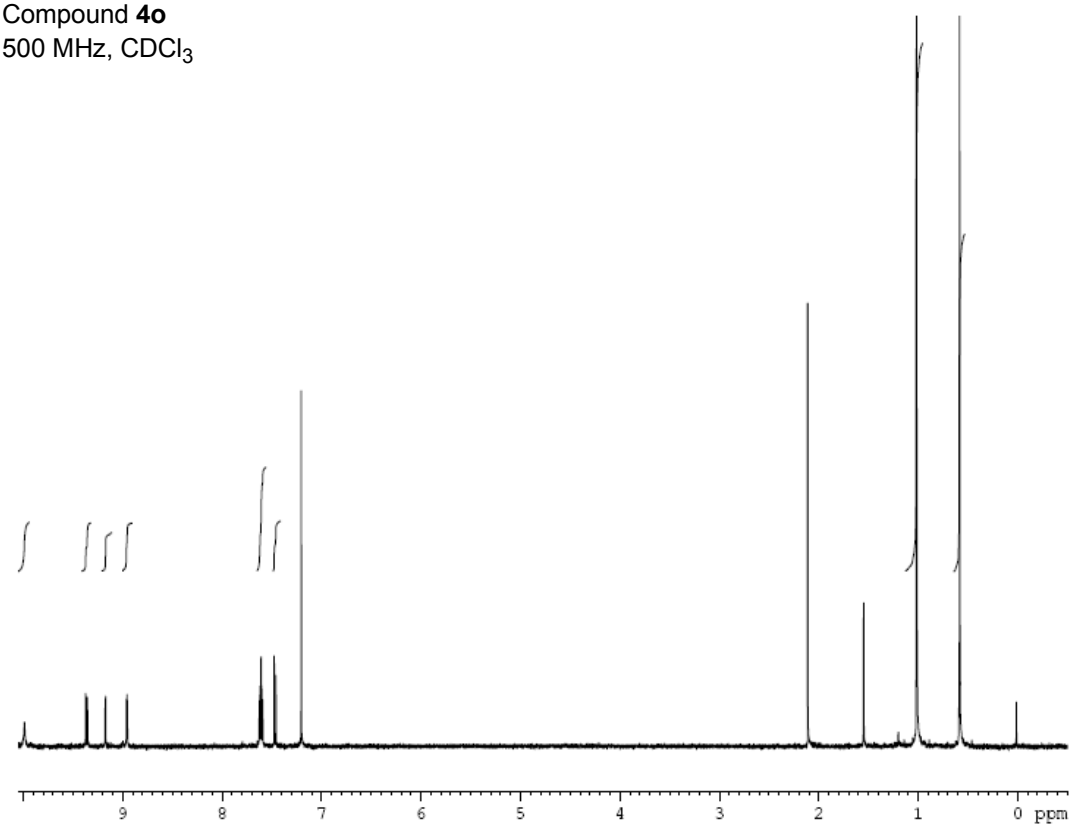
Compound **4n**
360 MHz, $CDCl_3$



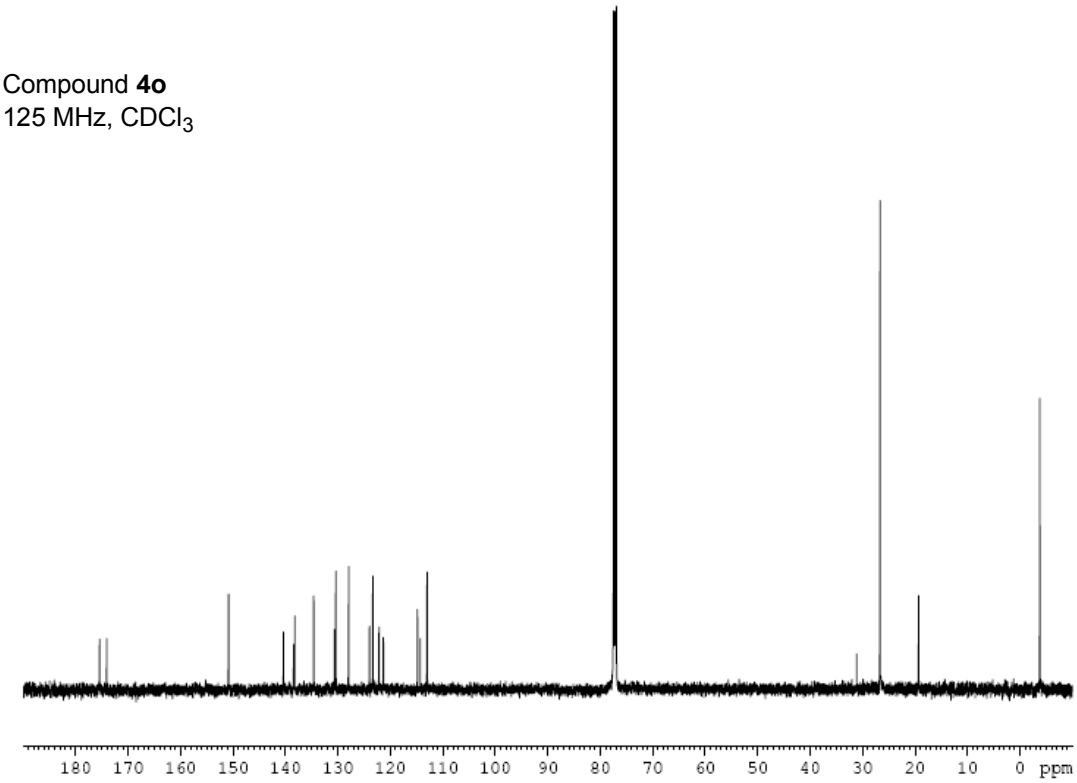
Compound **4n**
90 MHz, $CDCl_3$



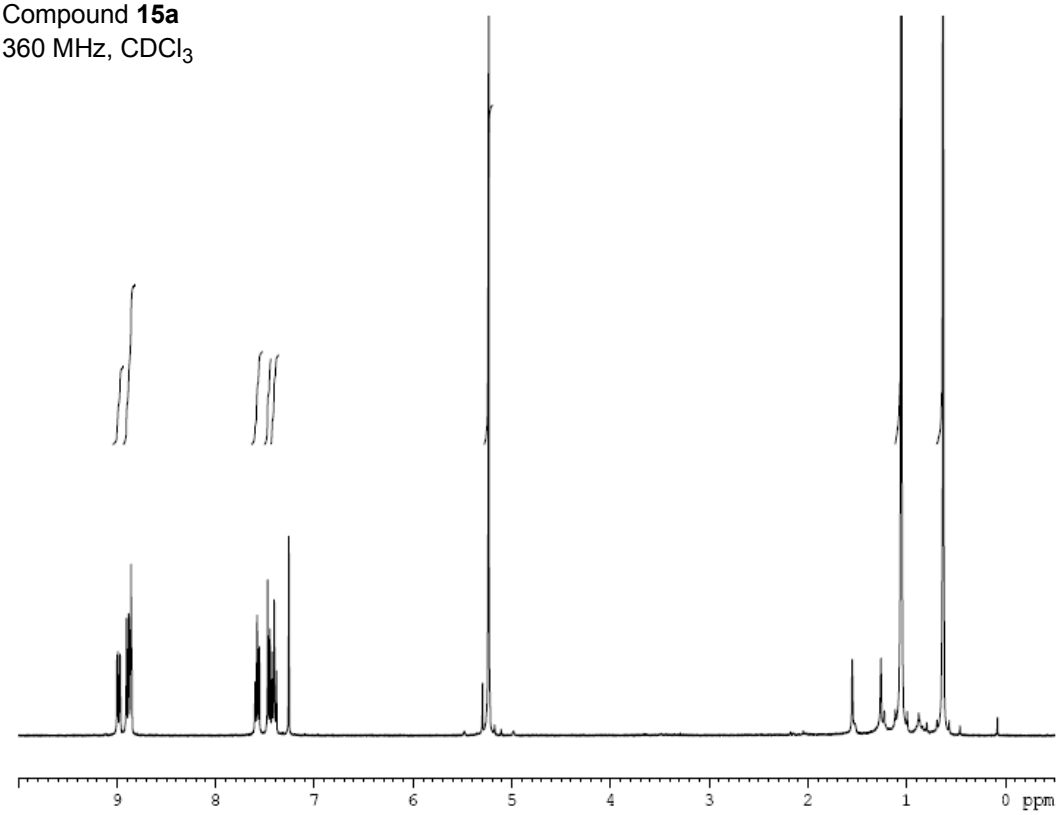
Compound **4o**
500 MHz, $CDCl_3$



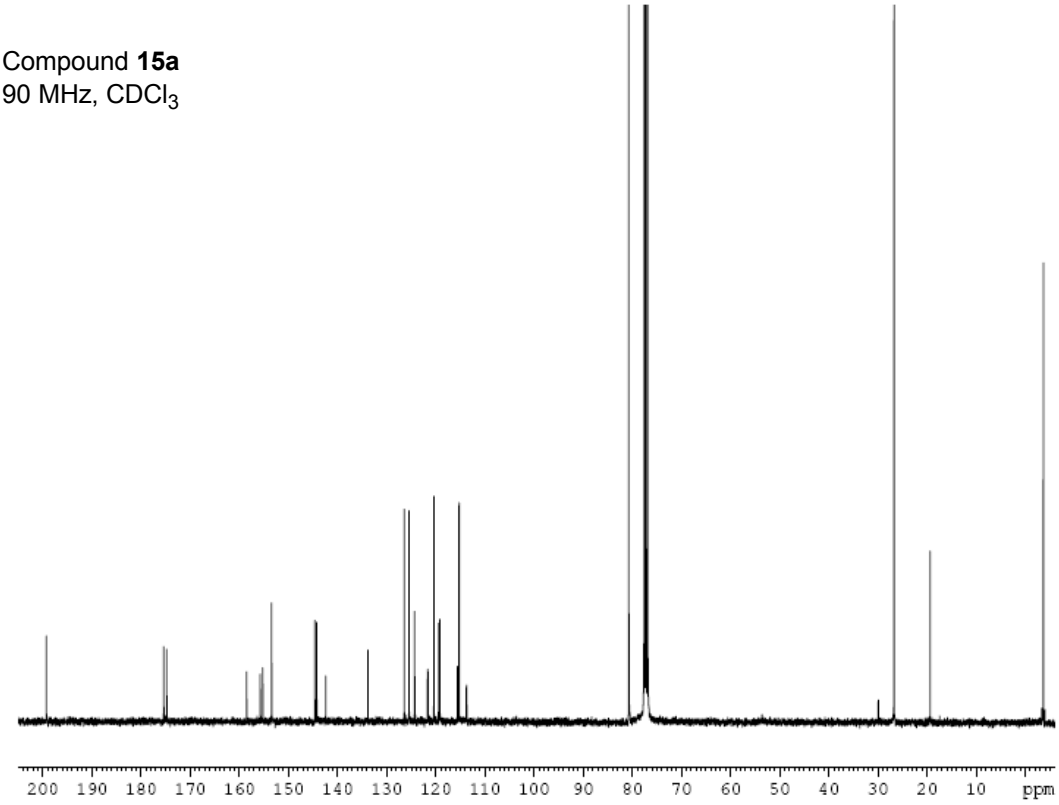
Compound **4o**
125 MHz, $CDCl_3$



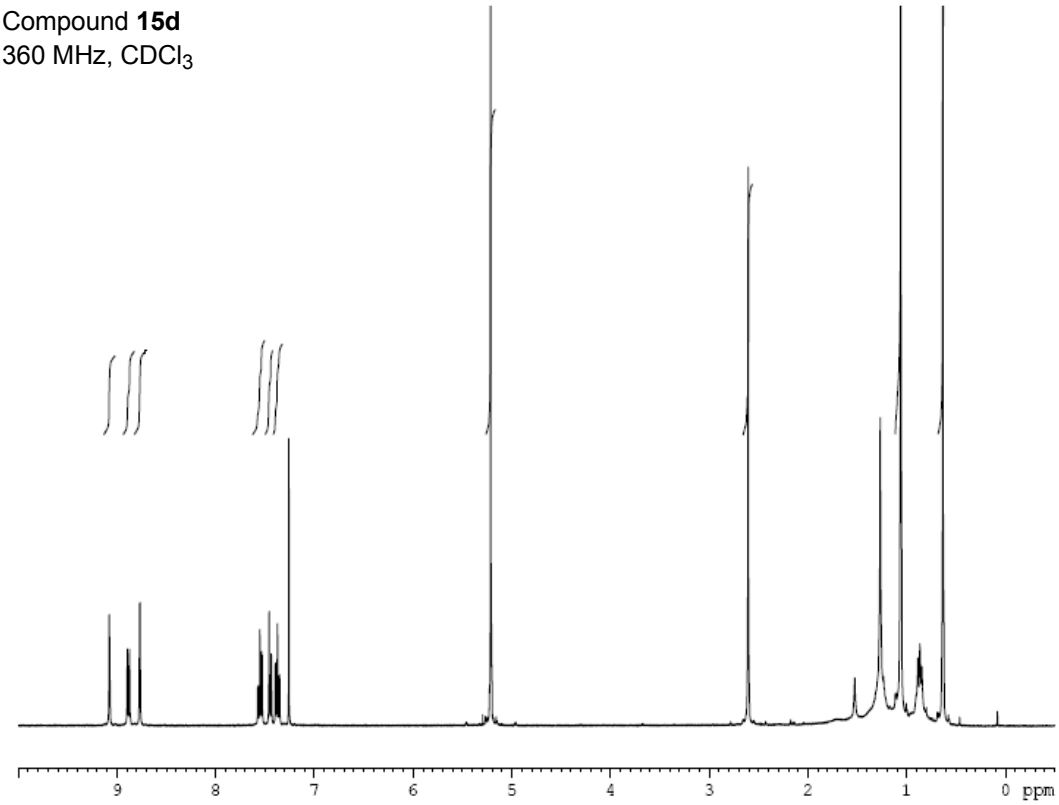
Compound **15a**
360 MHz, $CDCl_3$



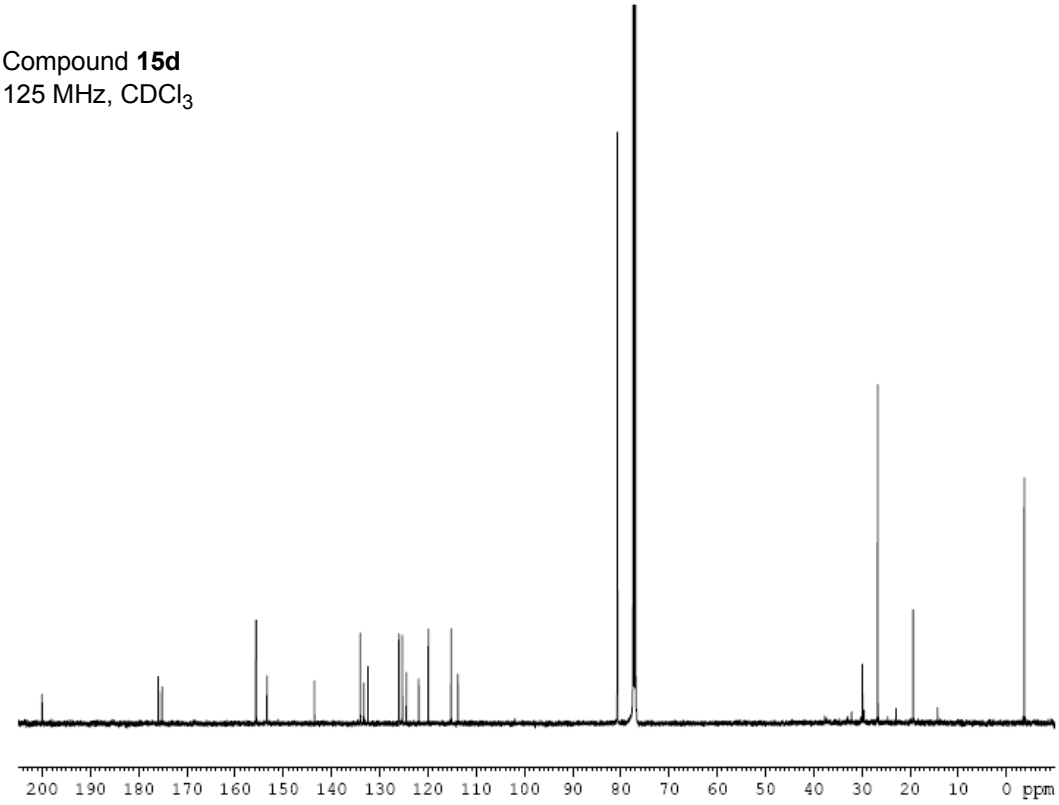
Compound **15a**
90 MHz, $CDCl_3$



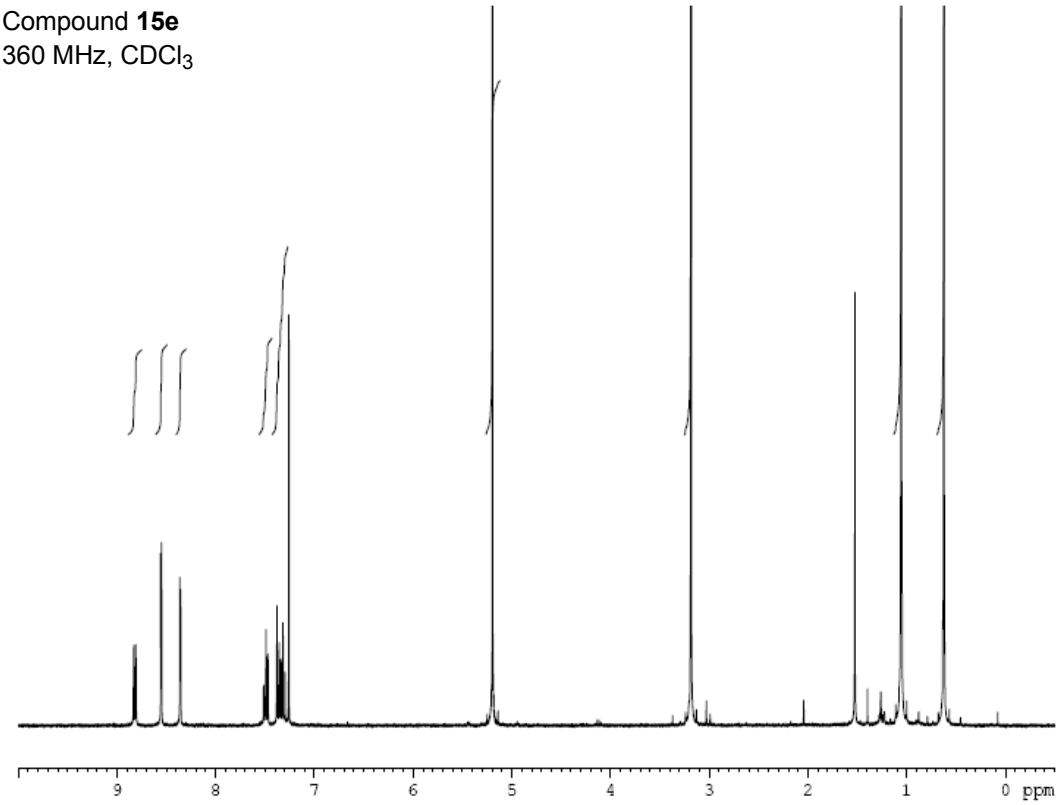
Compound **15d**
360 MHz, $CDCl_3$



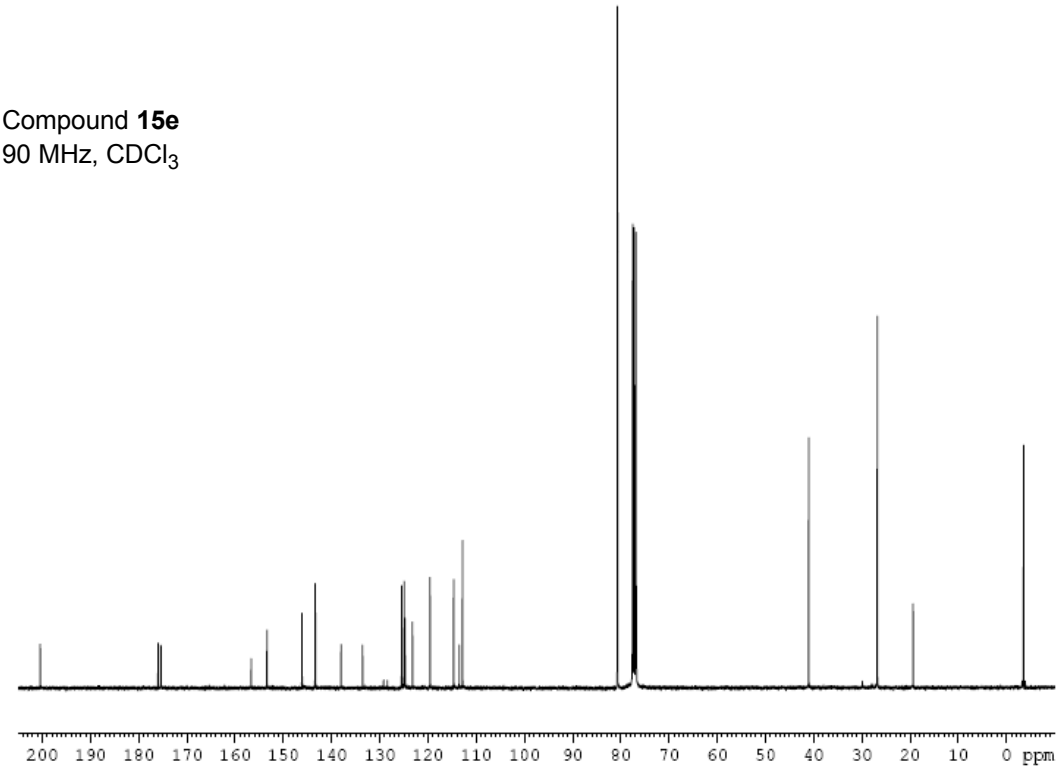
Compound **15d**
125 MHz, $CDCl_3$



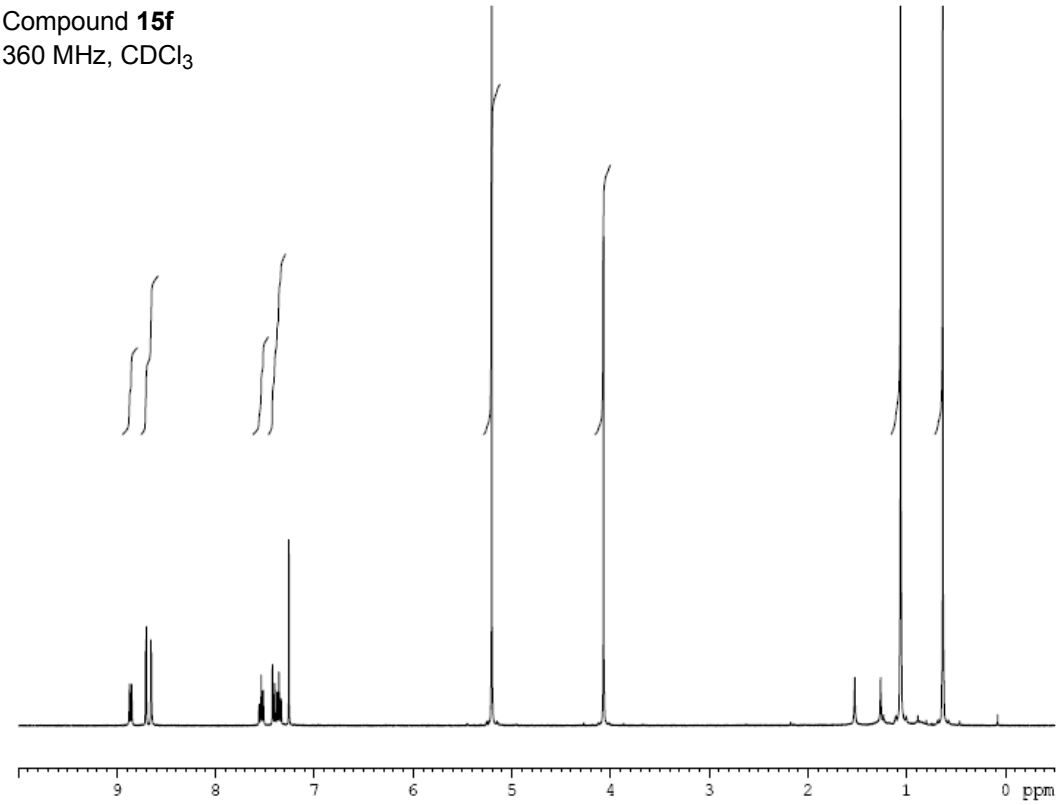
Compound **15e**
360 MHz, $CDCl_3$



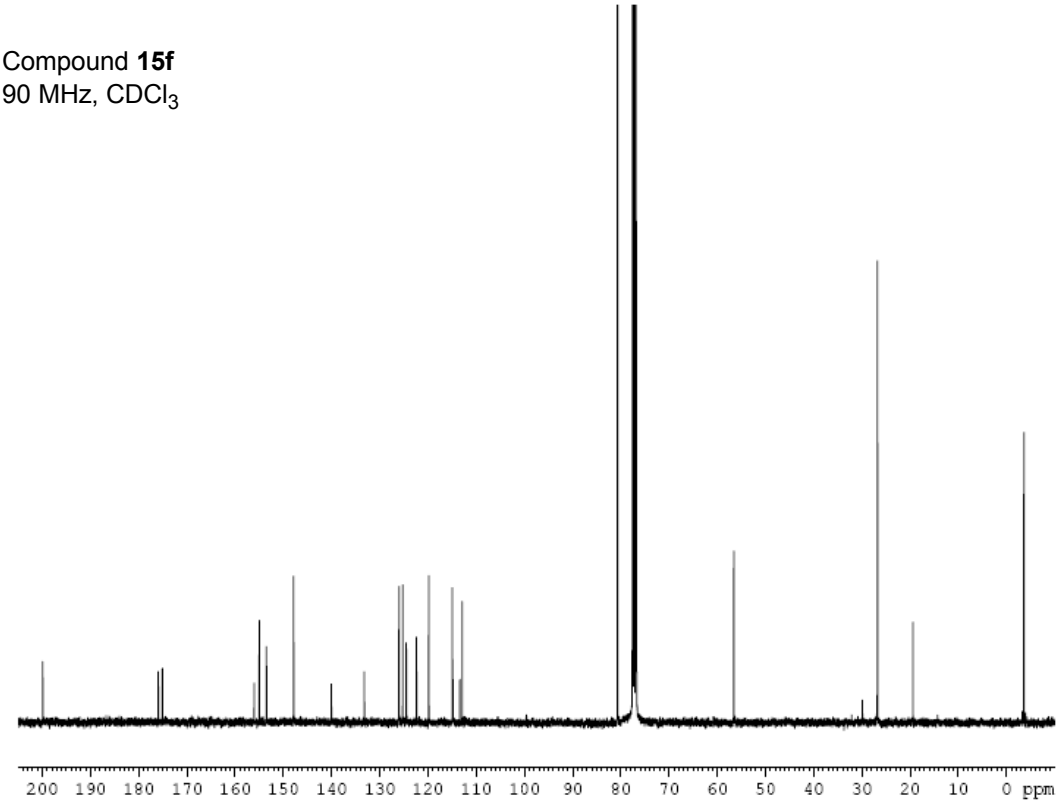
Compound **15e**
90 MHz, $CDCl_3$



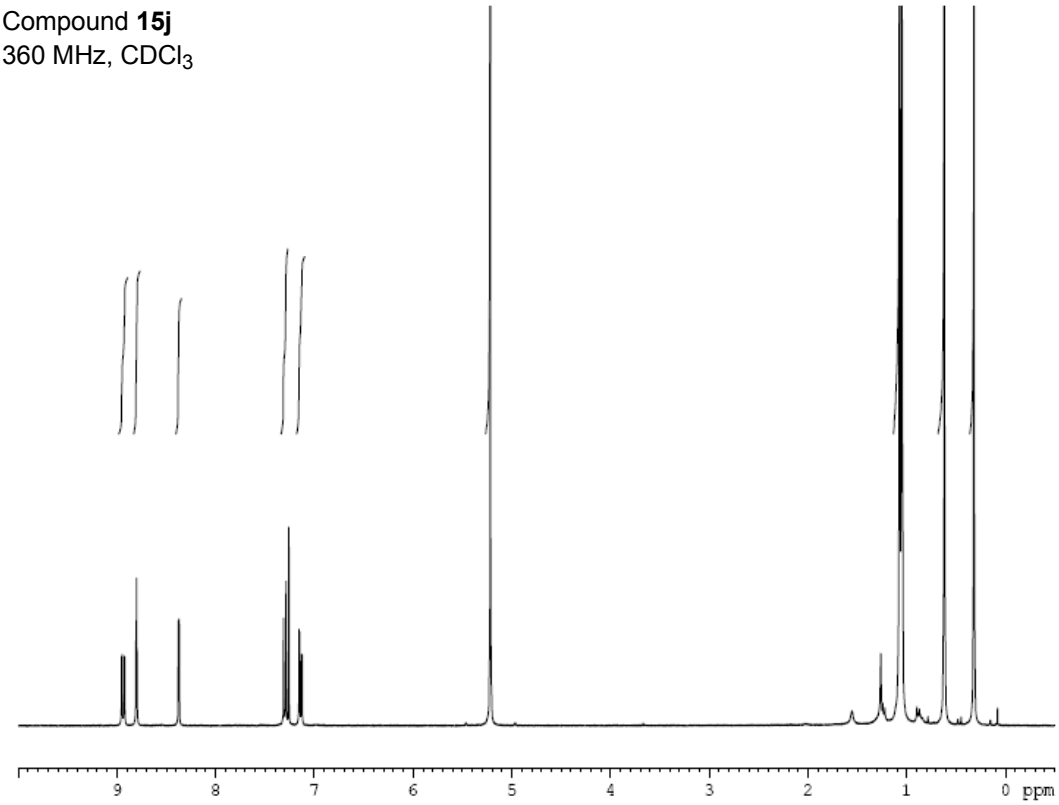
Compound **15f**
360 MHz, $CDCl_3$



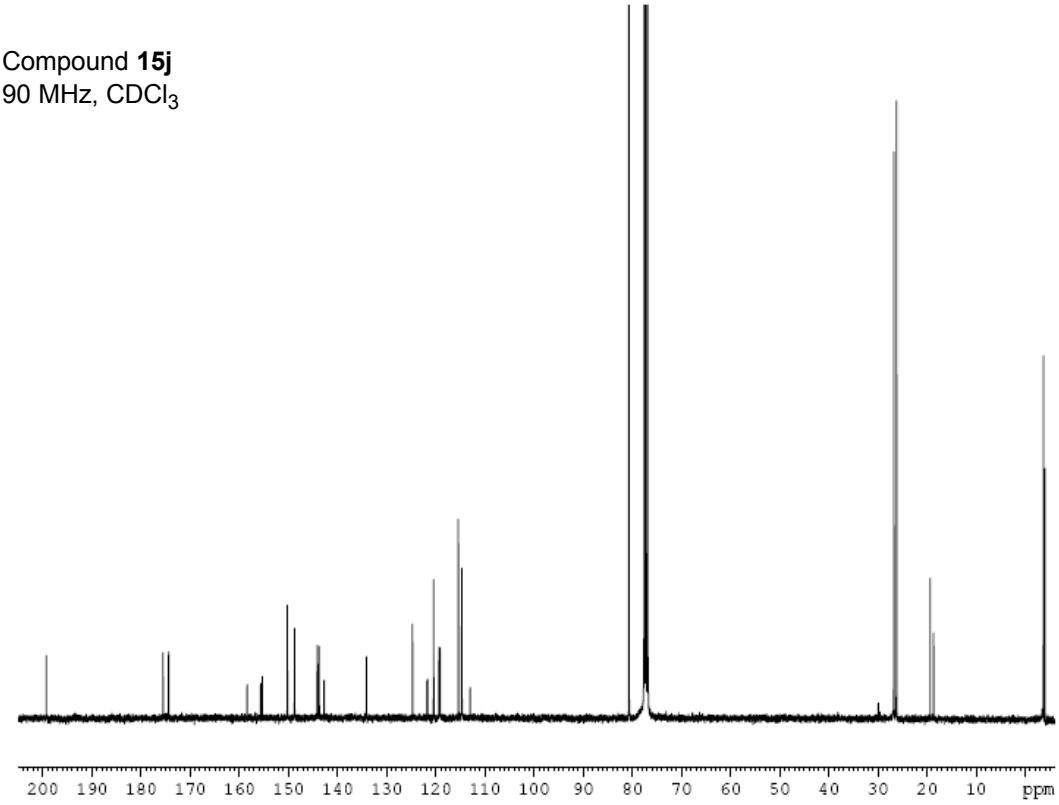
Compound **15f**
90 MHz, $CDCl_3$



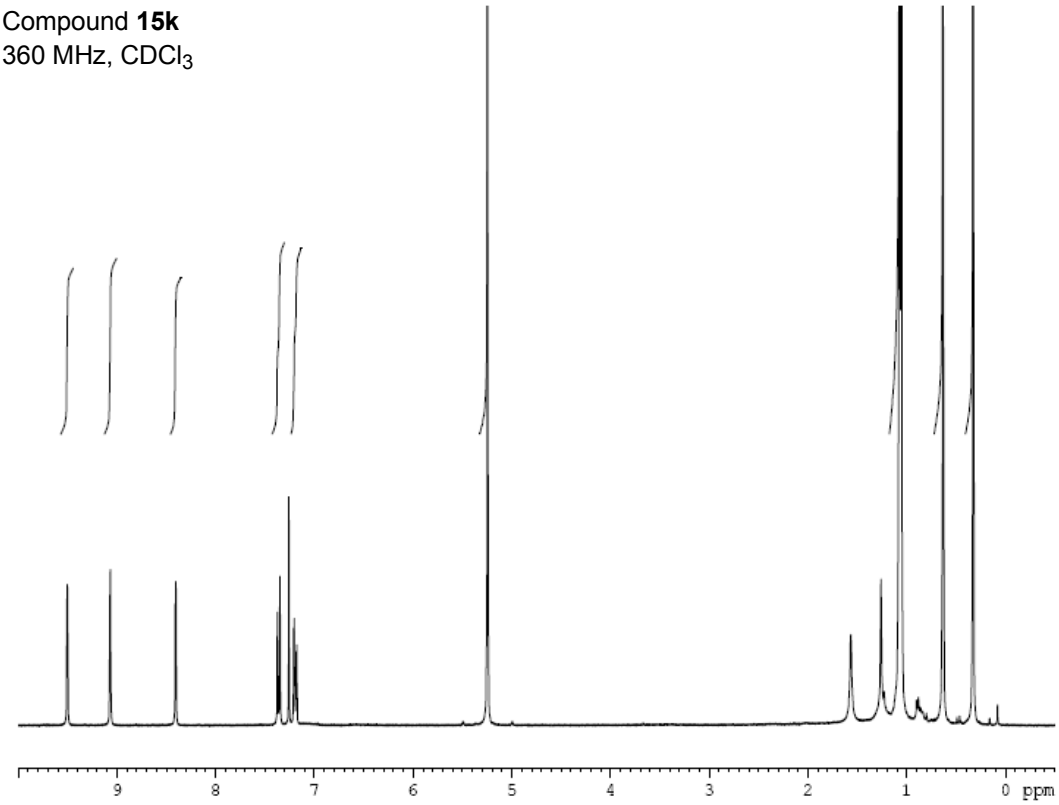
Compound **15j**
360 MHz, $CDCl_3$



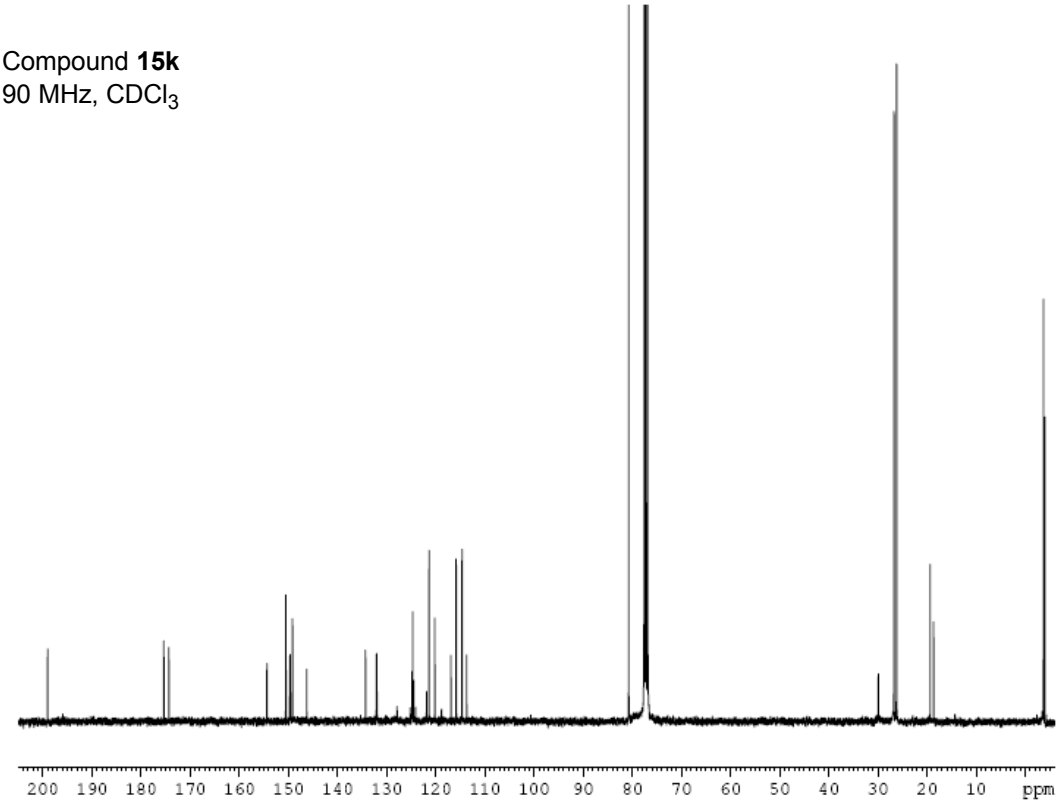
Compound **15j**
90 MHz, $CDCl_3$



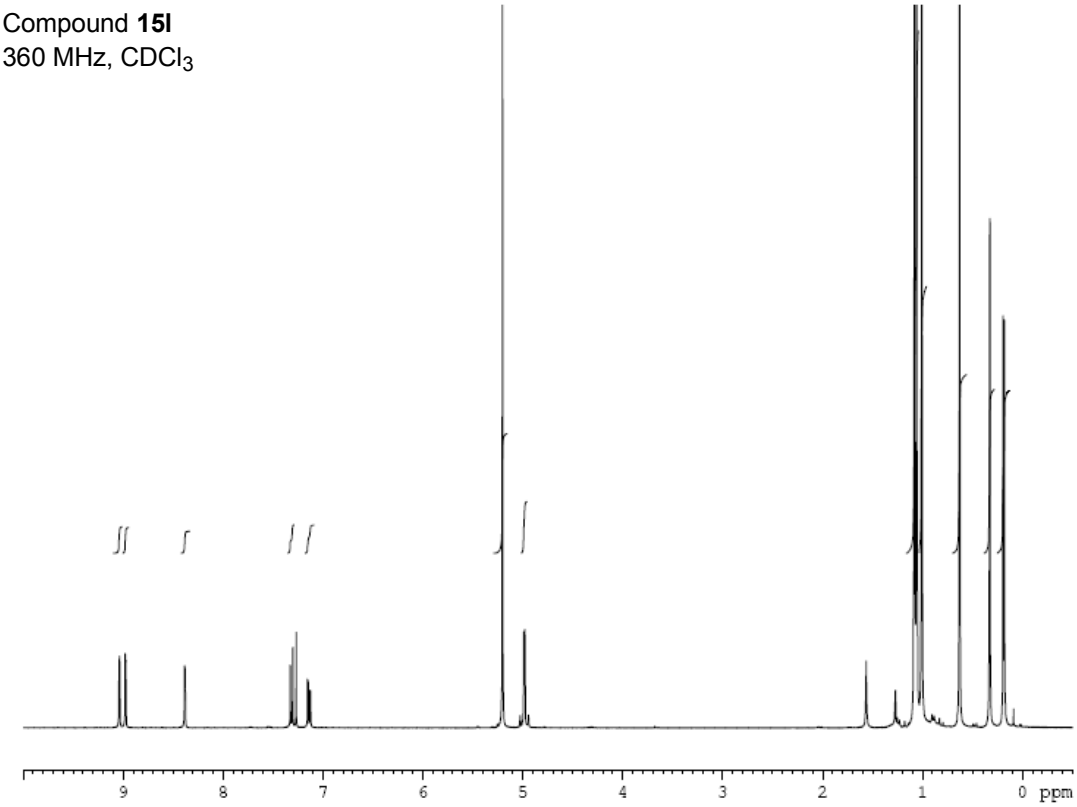
Compound **15k**
360 MHz, $CDCl_3$



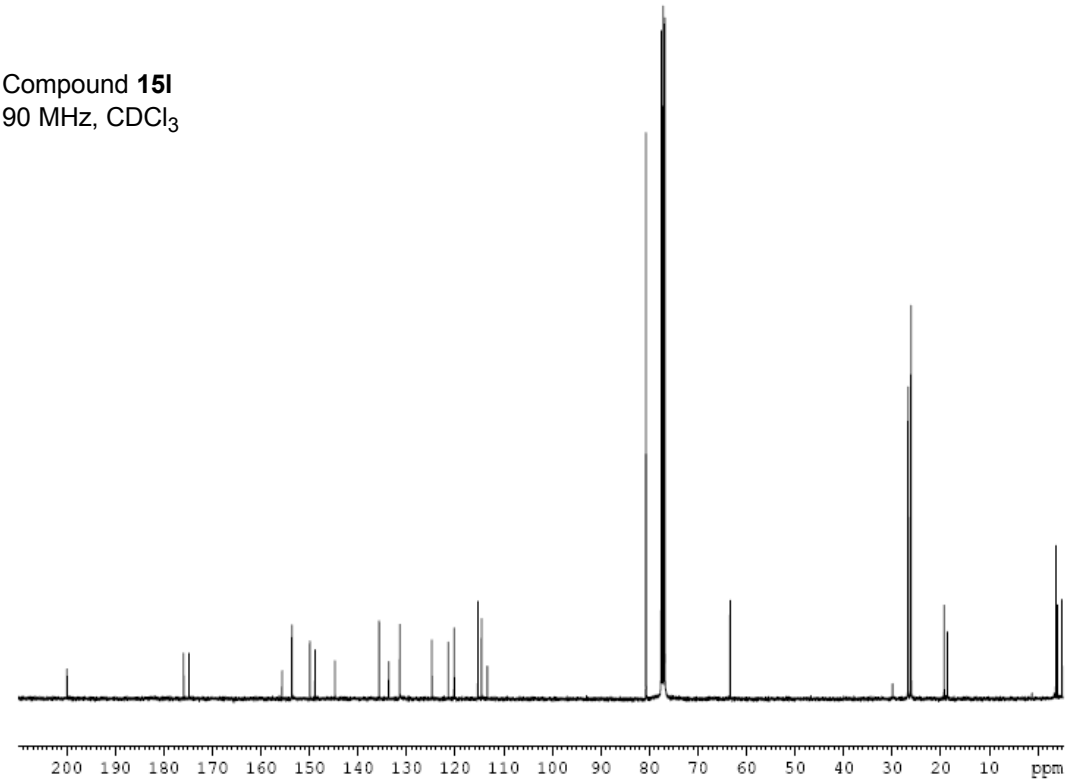
Compound **15k**
90 MHz, $CDCl_3$



Compound **15l**
360 MHz, $CDCl_3$



Compound **15l**
90 MHz, $CDCl_3$



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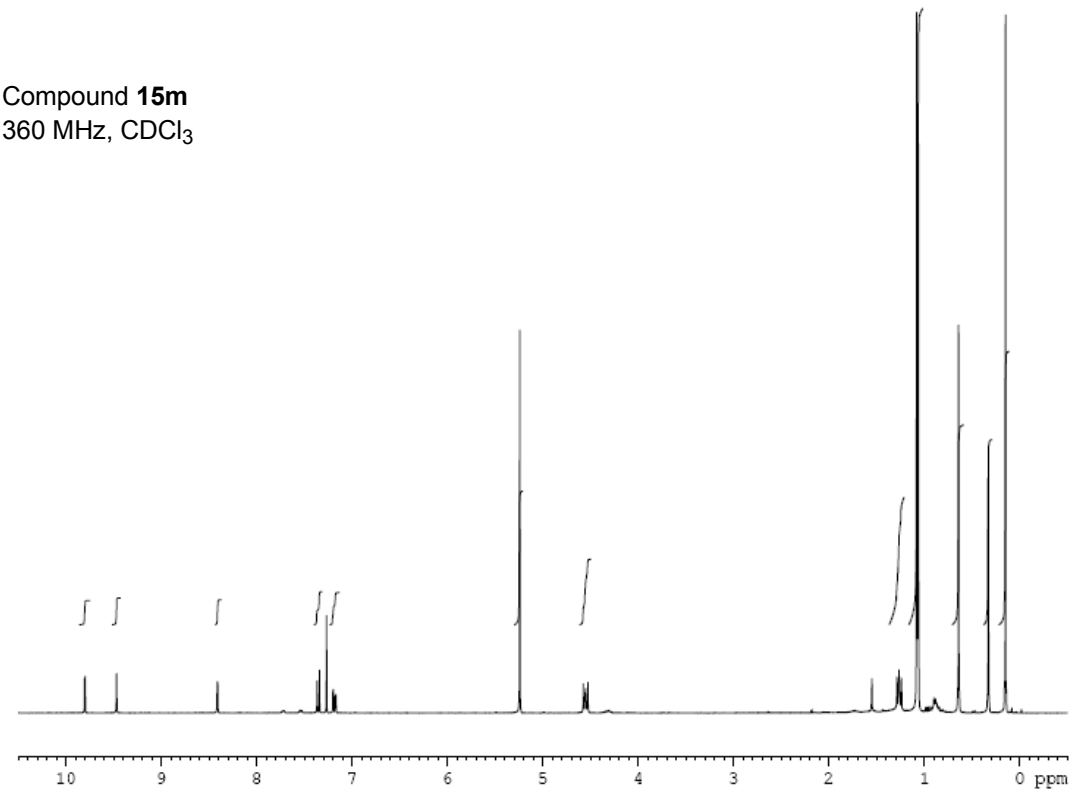
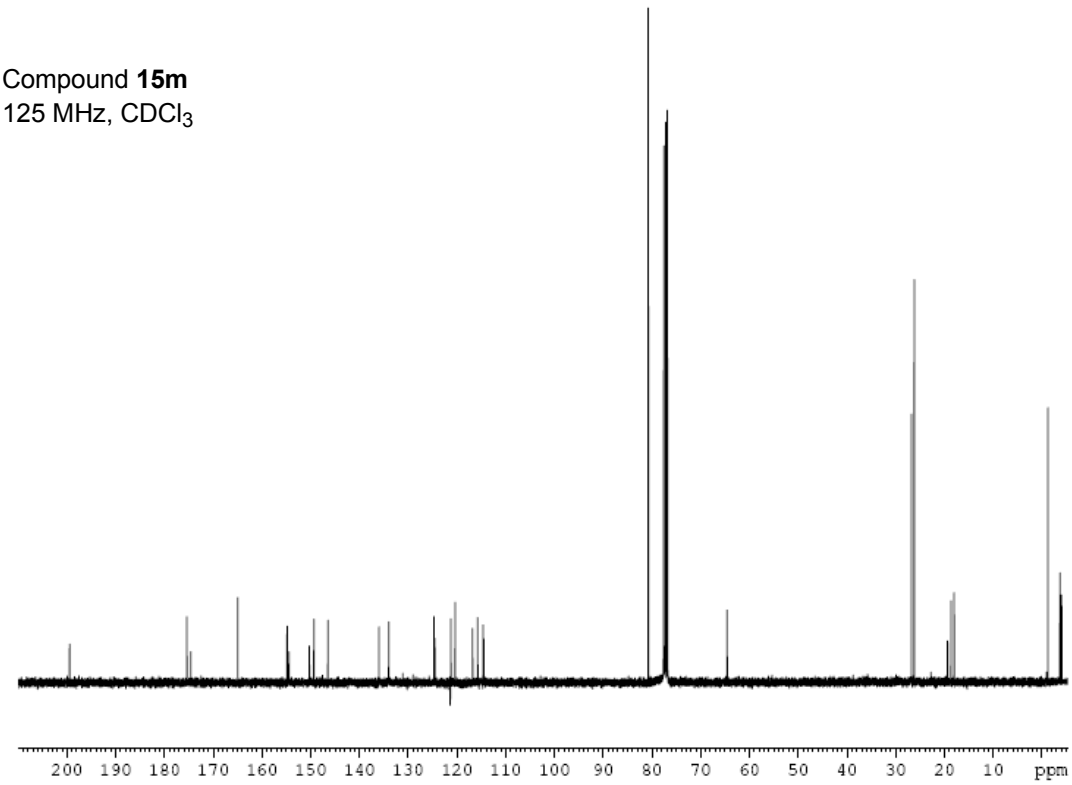
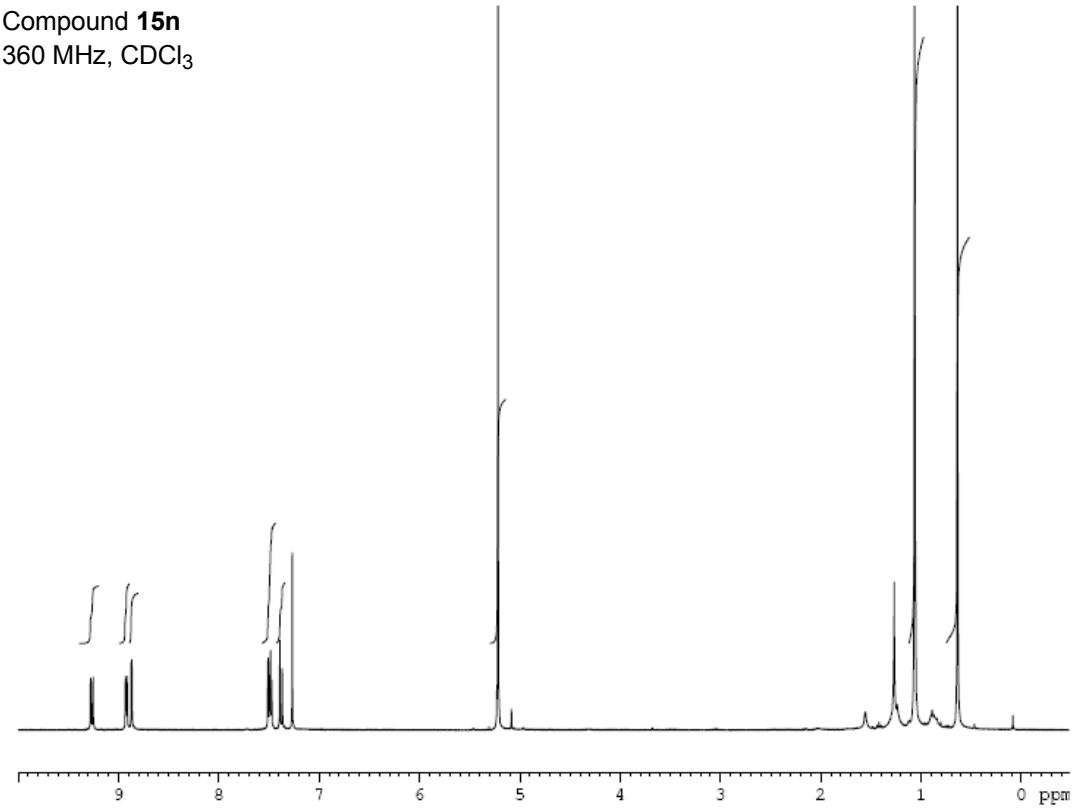
Compound **15m**
360 MHz, $CDCl_3$



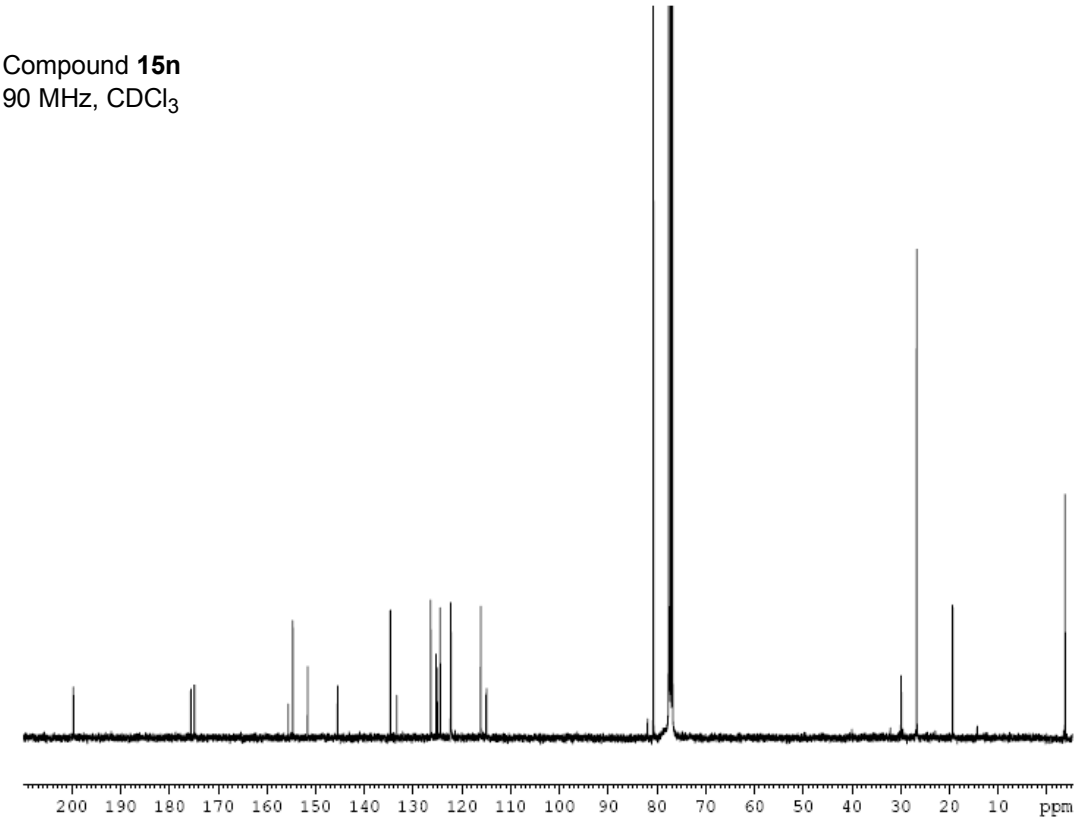
Compound **15m**
125 MHz, $CDCl_3$



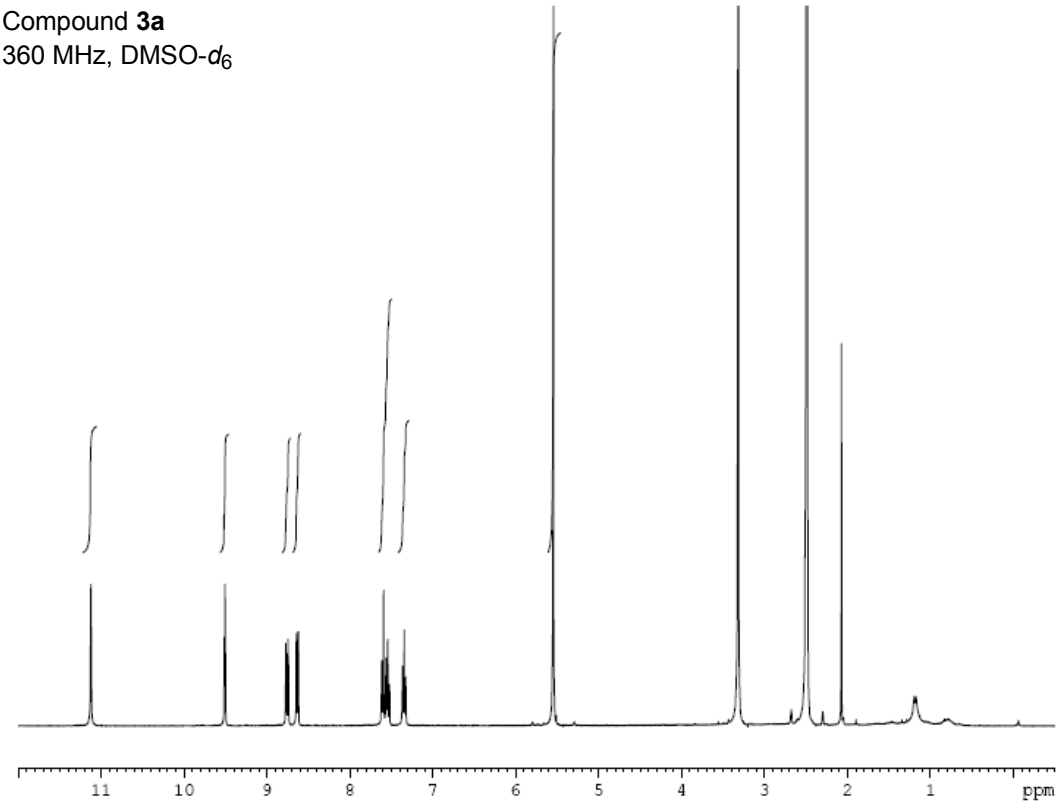
Compound **15n**
360 MHz, $CDCl_3$



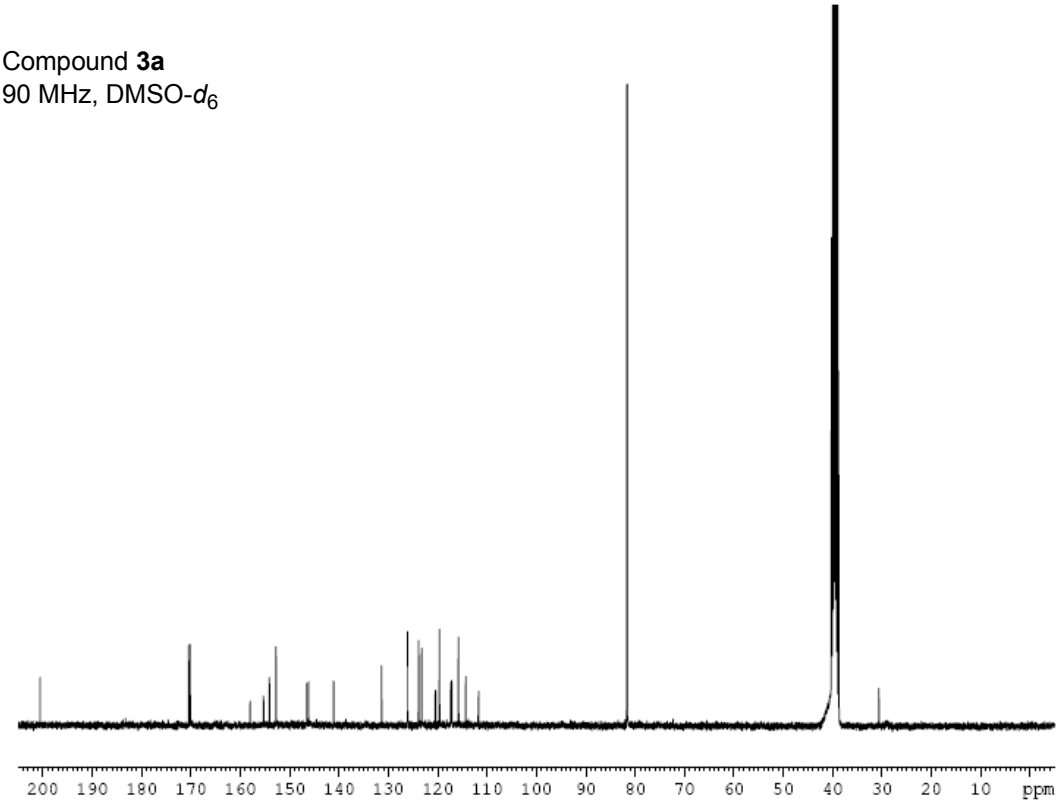
Compound **15n**
90 MHz, $CDCl_3$



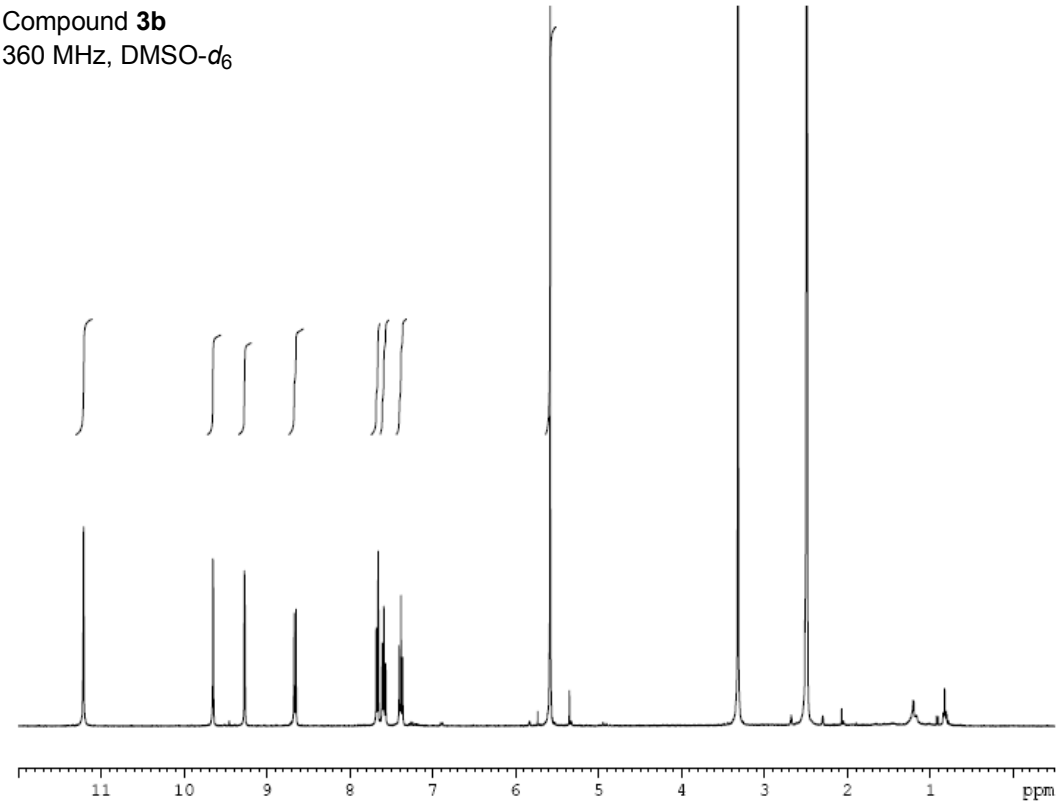
Compound **3a**
360 MHz, DMSO-d_6



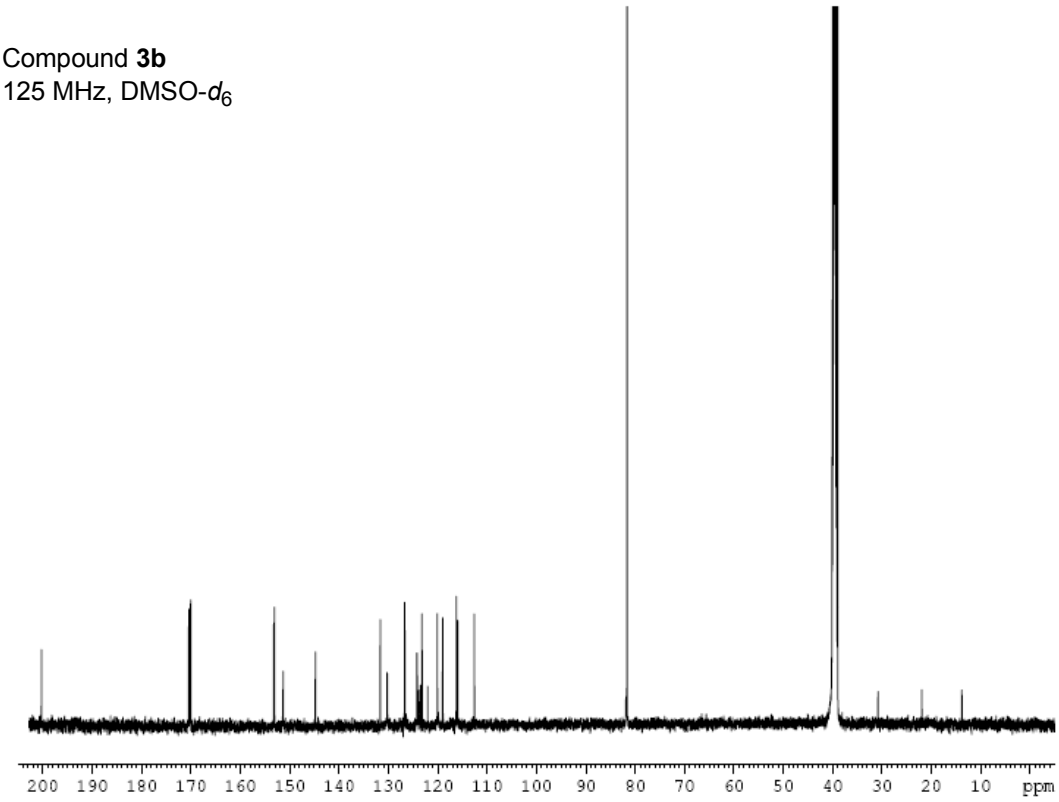
Compound **3a**
90 MHz, DMSO-d_6



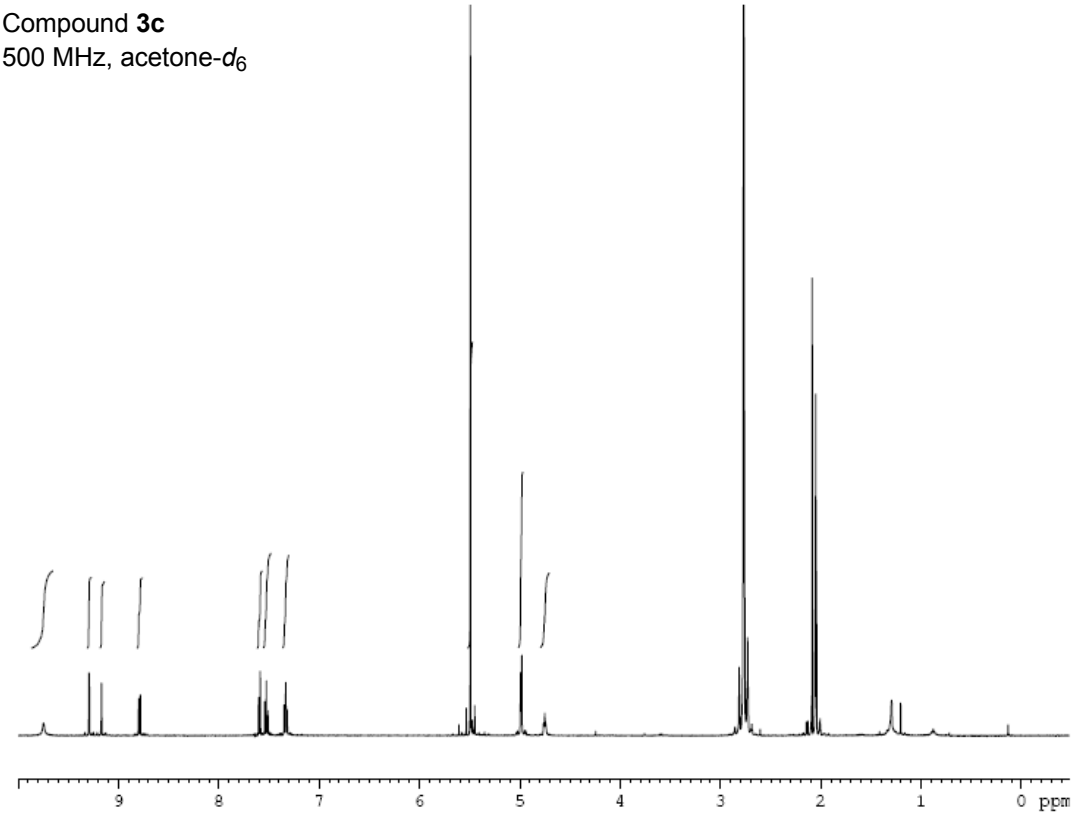
Compound **3b**
360 MHz, DMSO-d_6



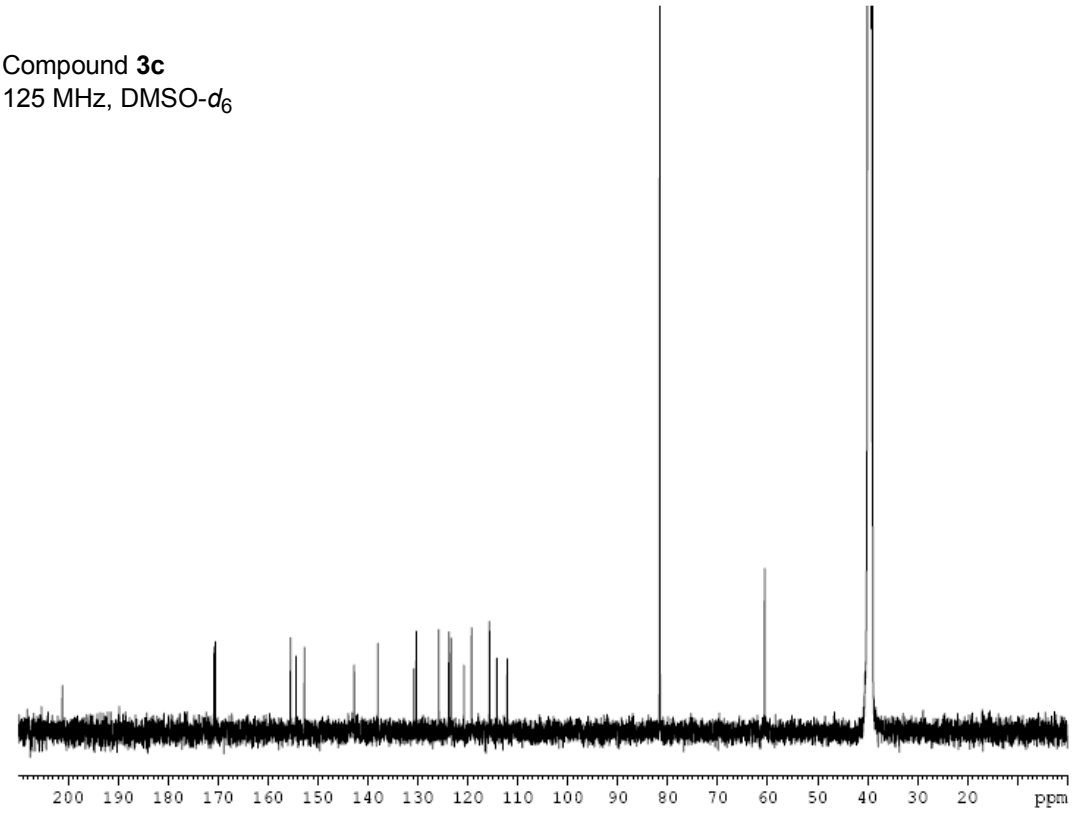
Compound **3b**
125 MHz, DMSO-d_6



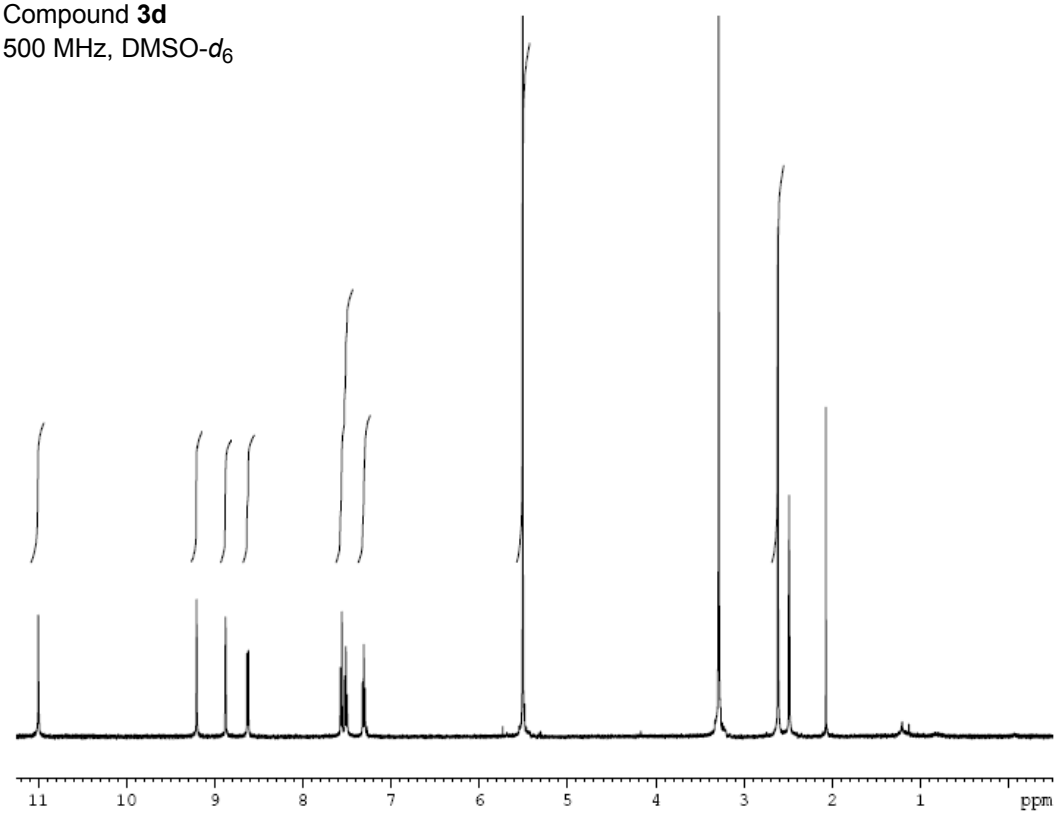
Compound **3c**
500 MHz, acetone-d_6



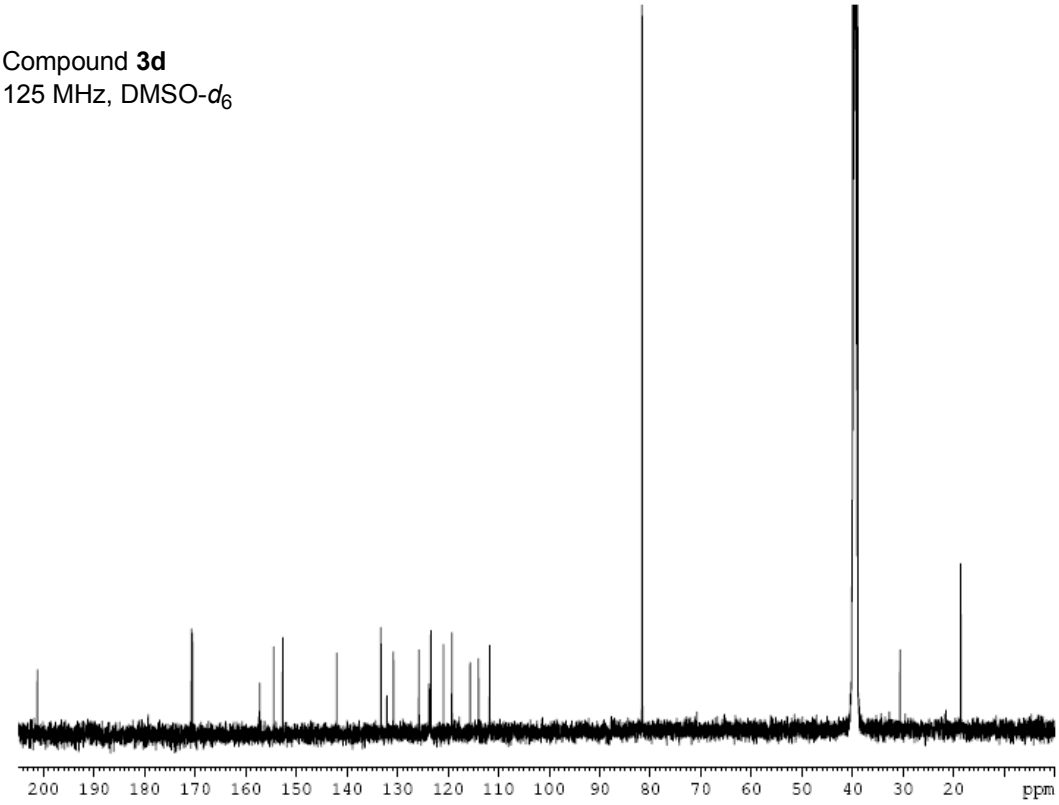
Compound **3c**
125 MHz, DMSO-d_6



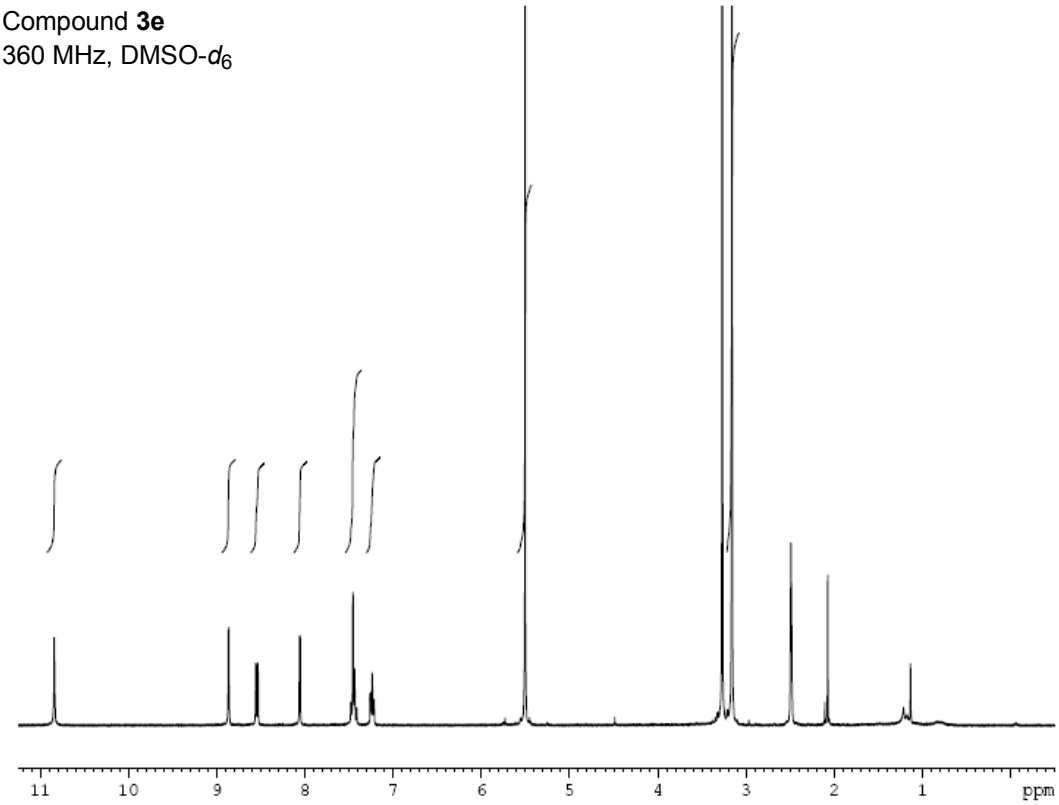
Compound **3d**
500 MHz, DMSO-d_6



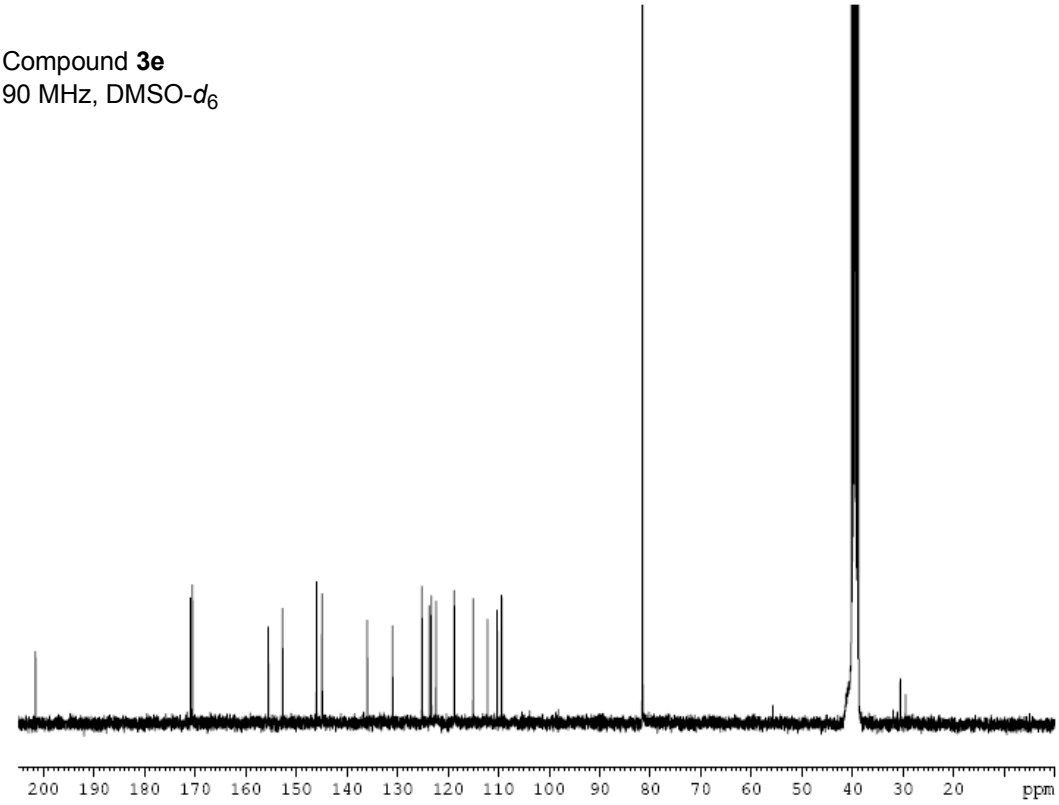
Compound **3d**
125 MHz, DMSO-d_6



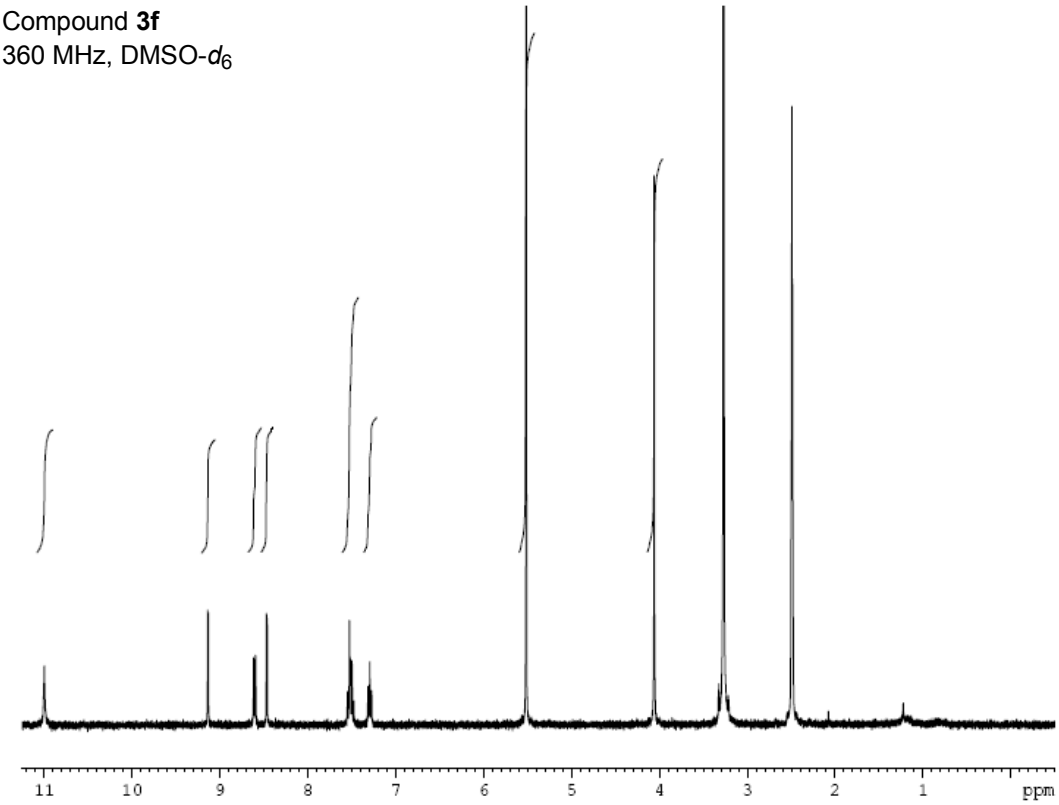
Compound **3e**
360 MHz, DMSO-d_6



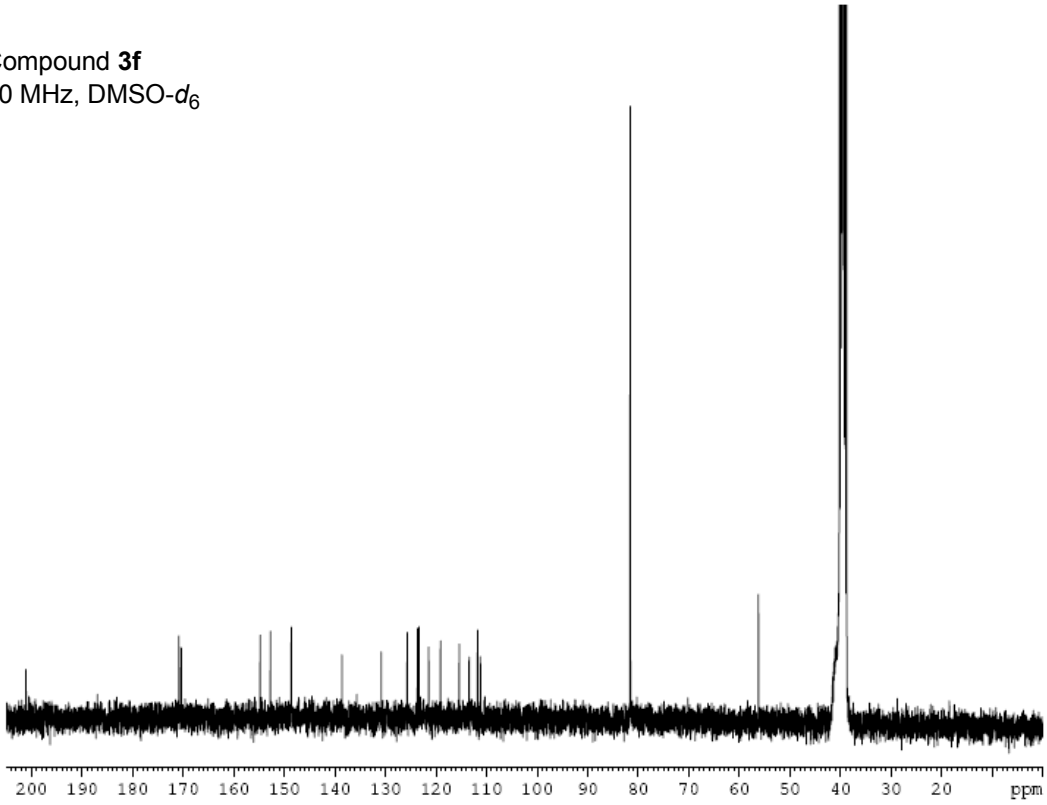
Compound **3e**
90 MHz, DMSO-d_6



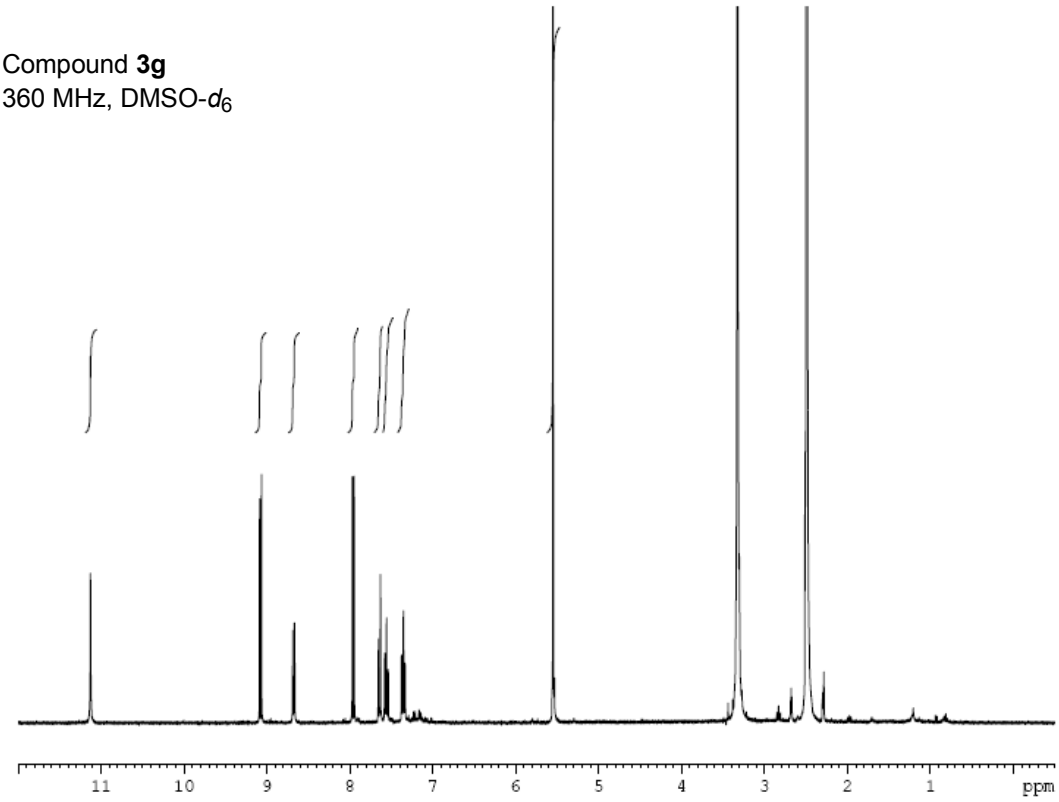
Compound **3f**
360 MHz, DMSO-d_6



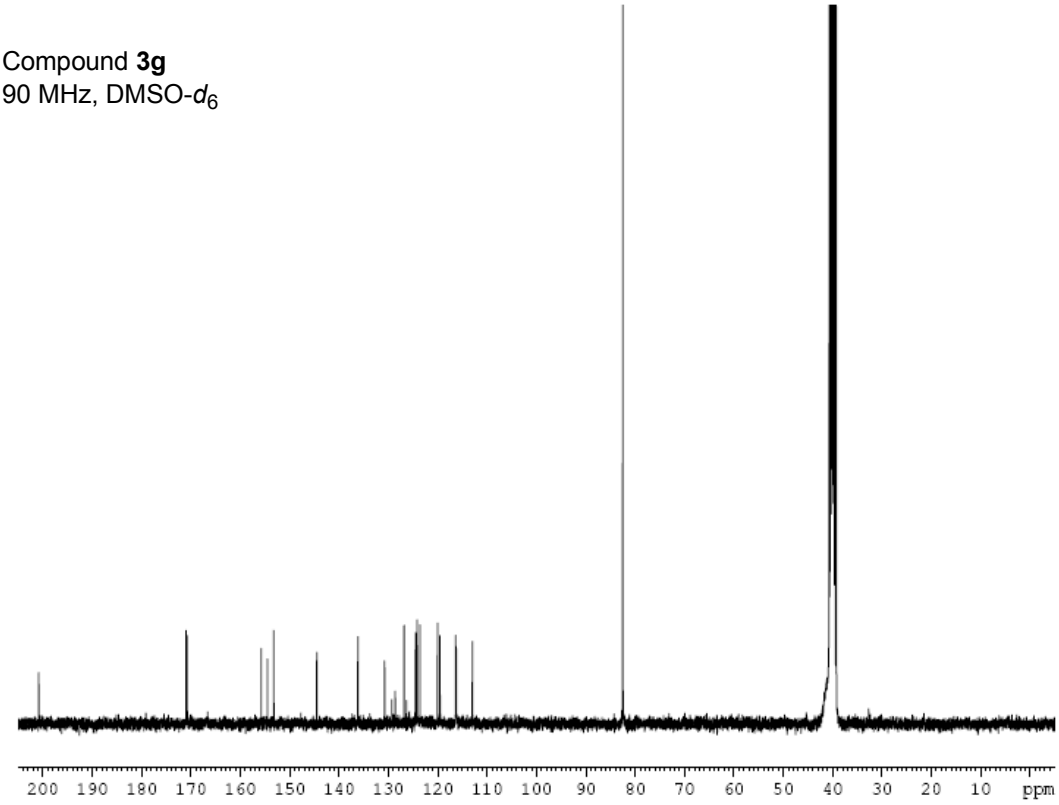
Compound **3f**
90 MHz, DMSO-d_6



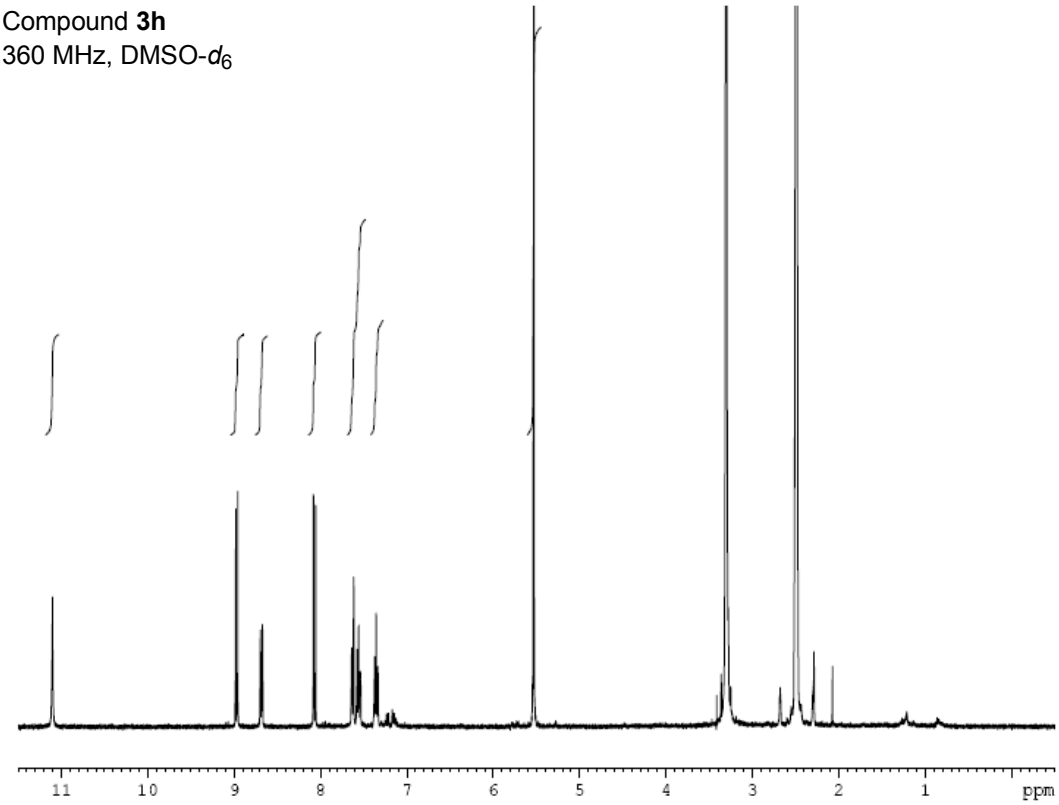
Compound **3g**
360 MHz, DMSO-d_6



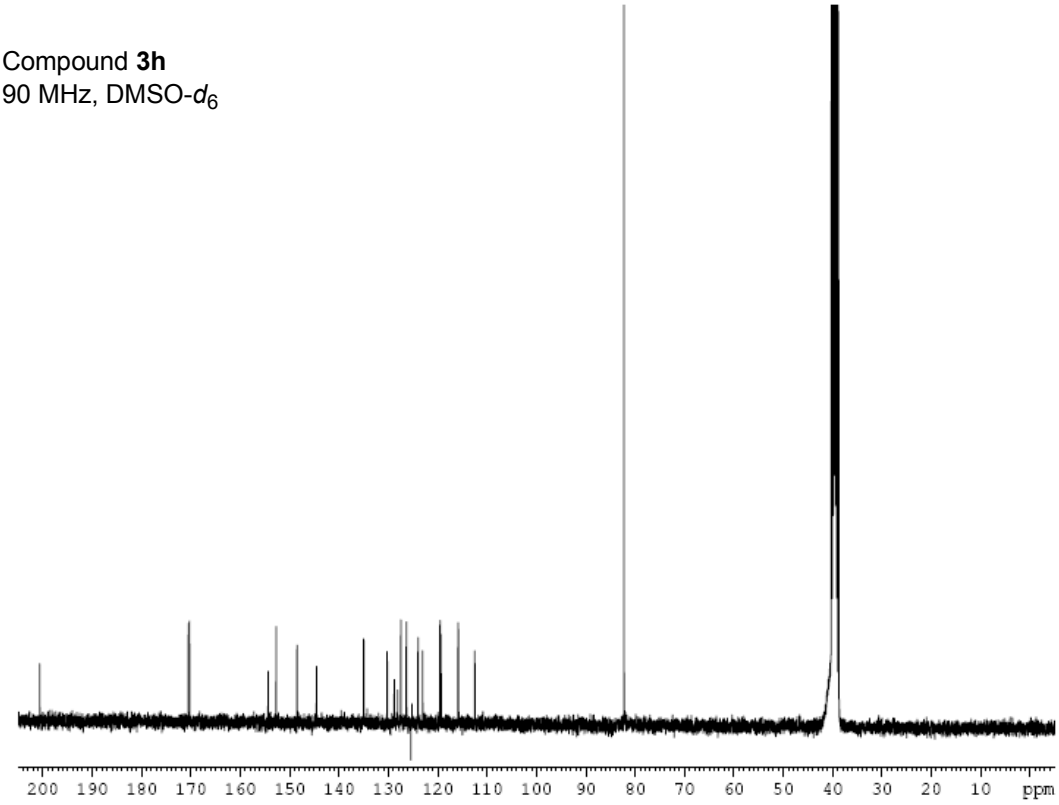
Compound **3g**
90 MHz, DMSO-d_6



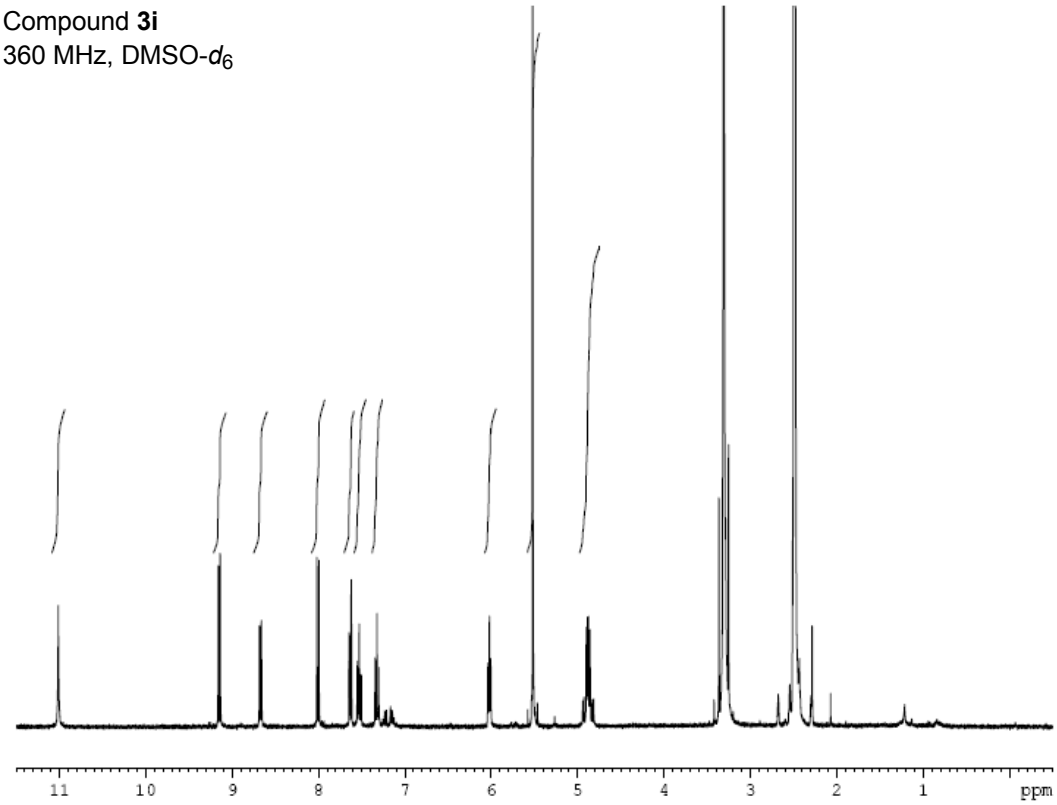
Compound **3h**
360 MHz, DMSO-d_6



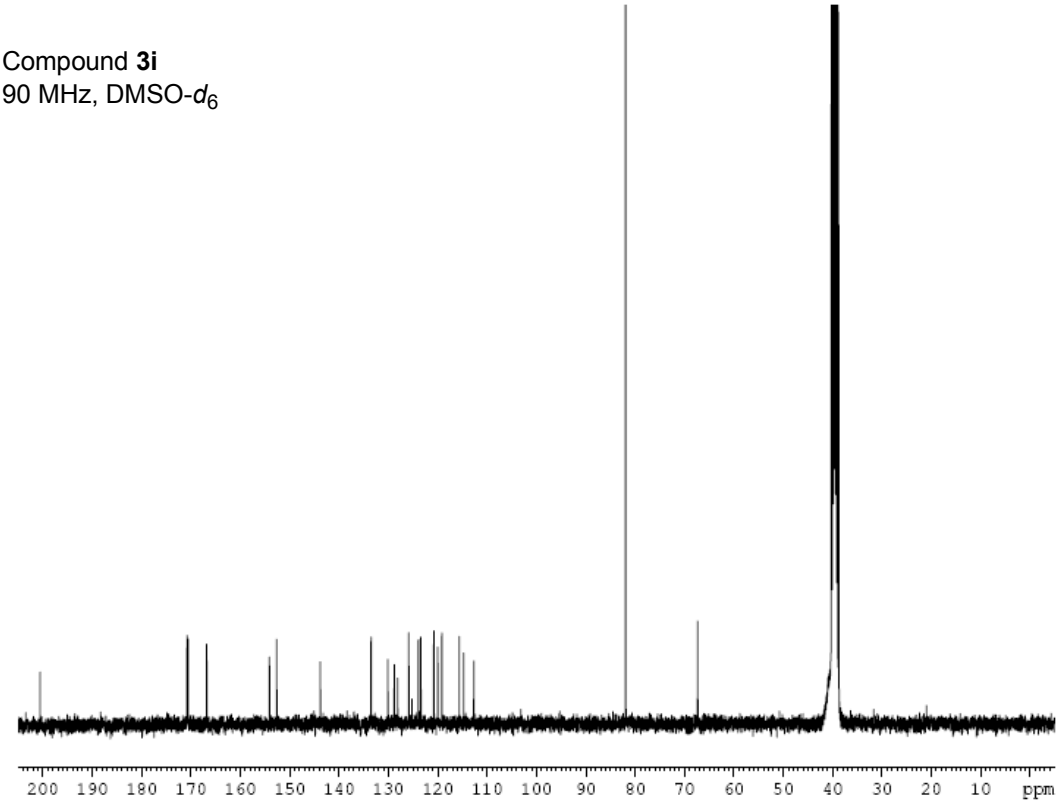
Compound **3h**
90 MHz, DMSO-d_6



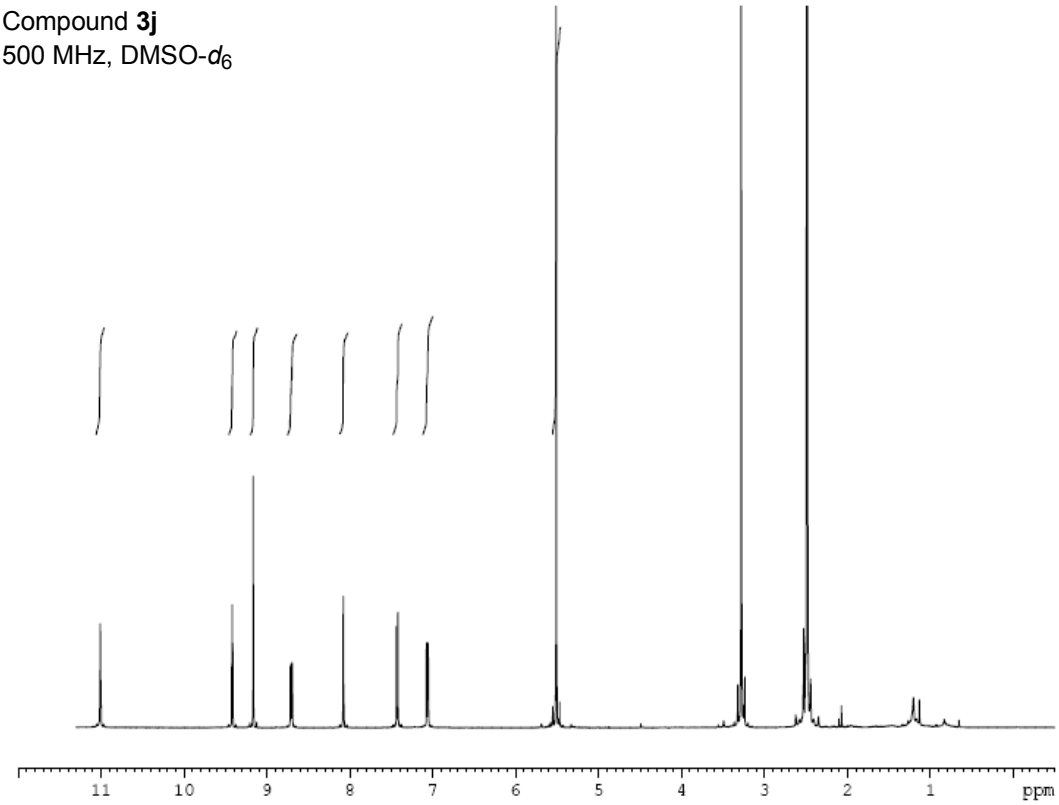
Compound **3i**
360 MHz, DMSO-d_6



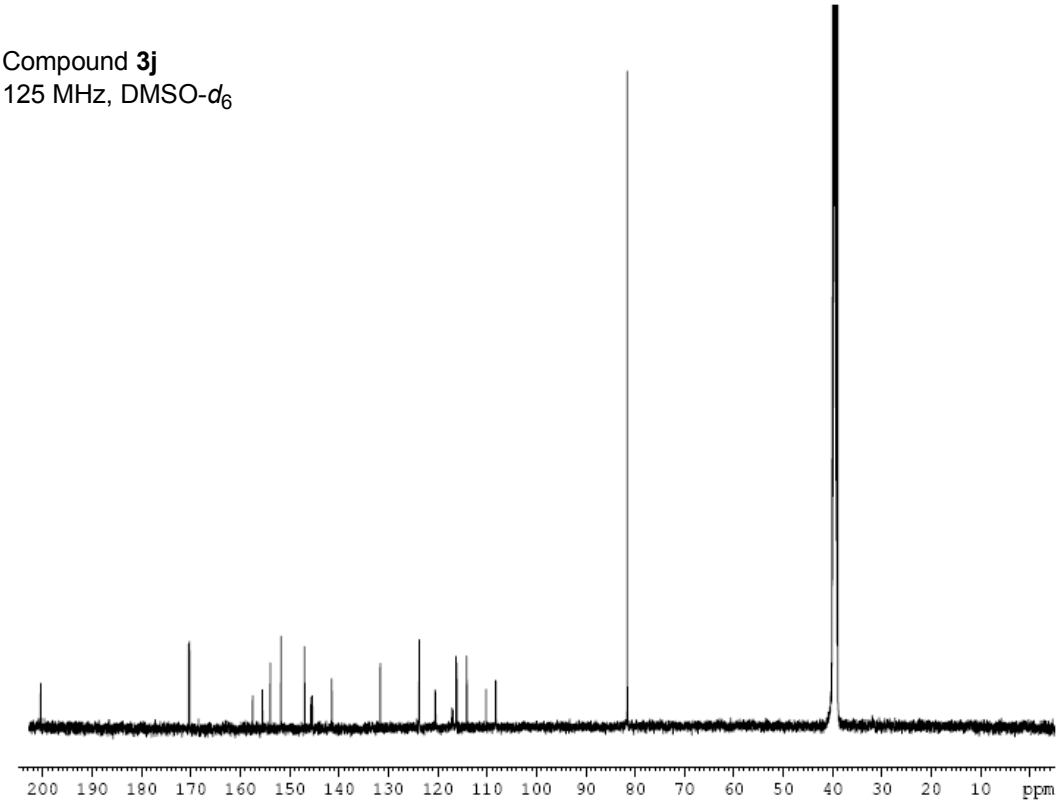
Compound **3i**
90 MHz, DMSO-d_6



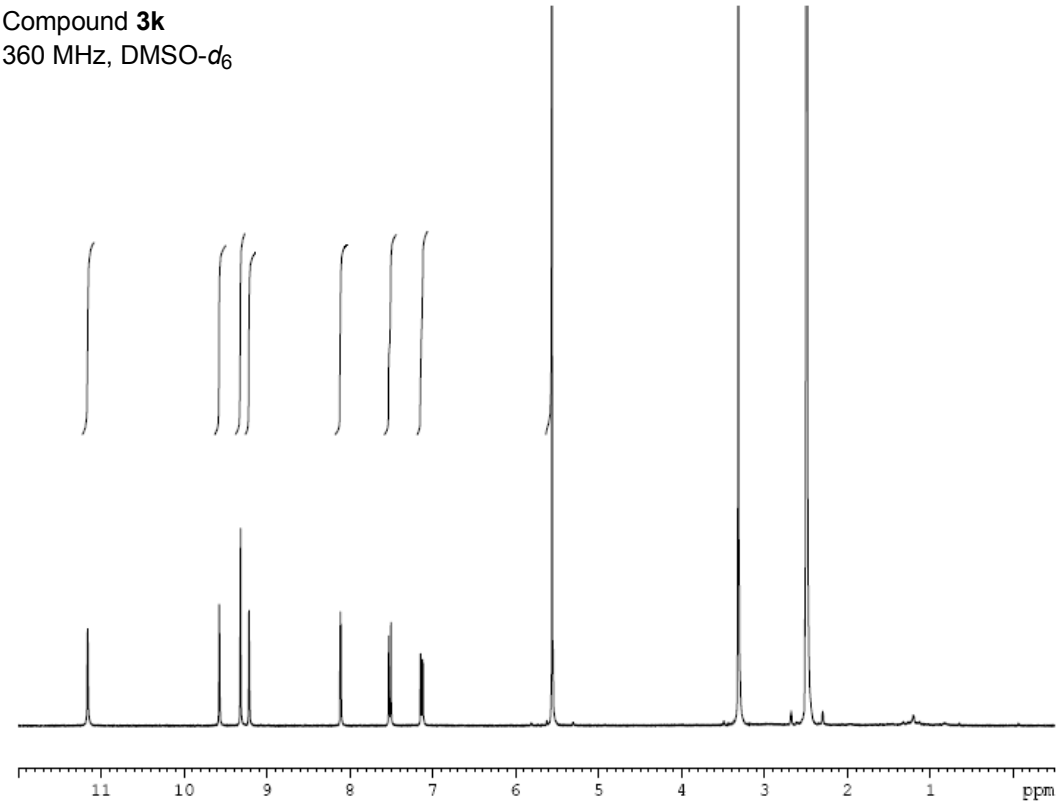
Compound **3j**
500 MHz, DMSO-d_6



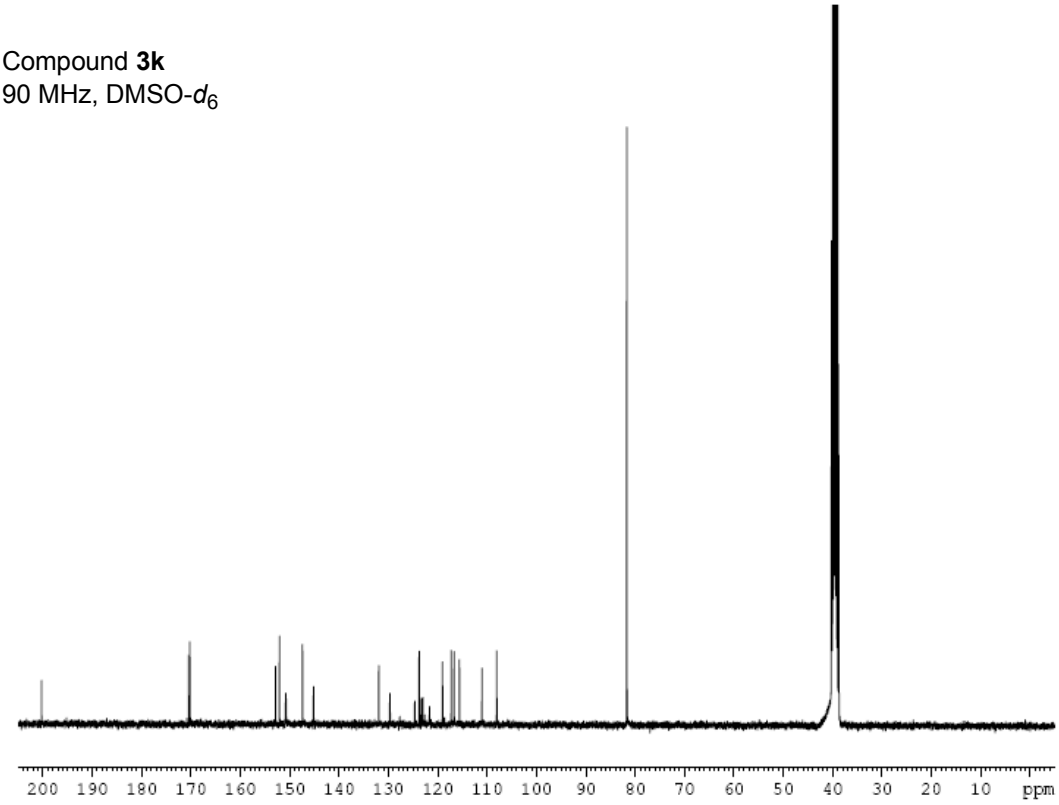
Compound **3j**
125 MHz, DMSO-d_6



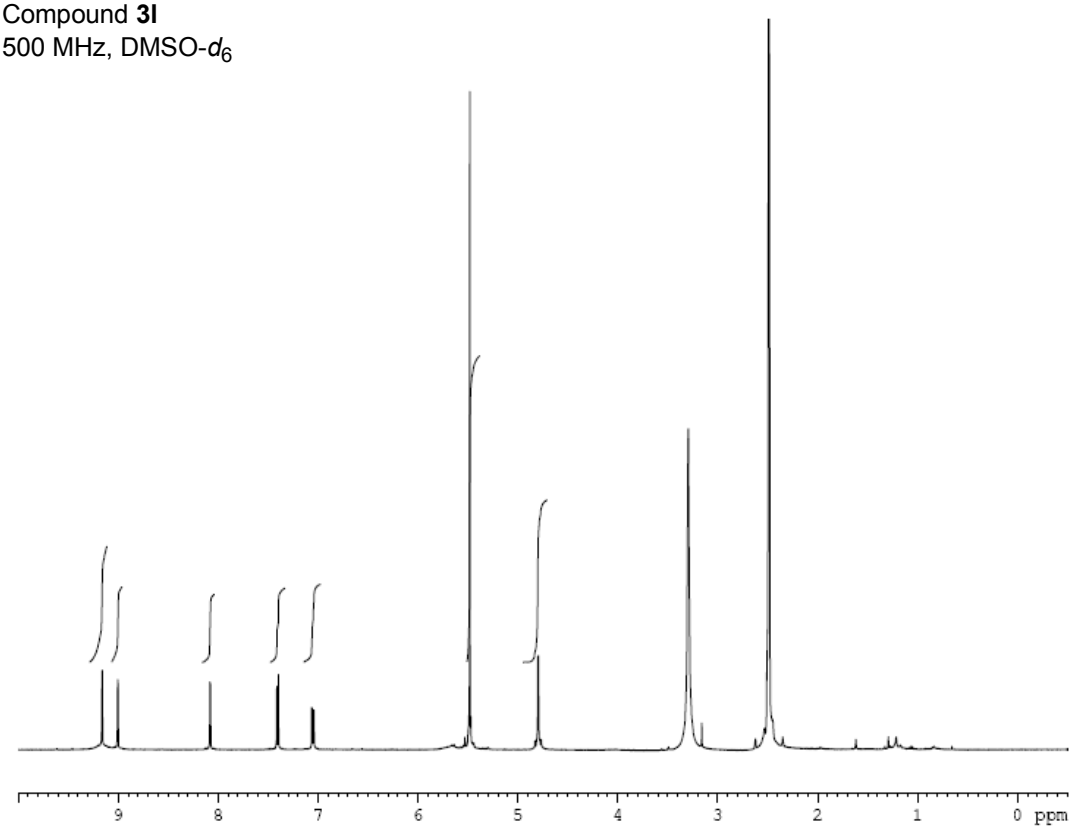
Compound **3k**
360 MHz, DMSO-d_6



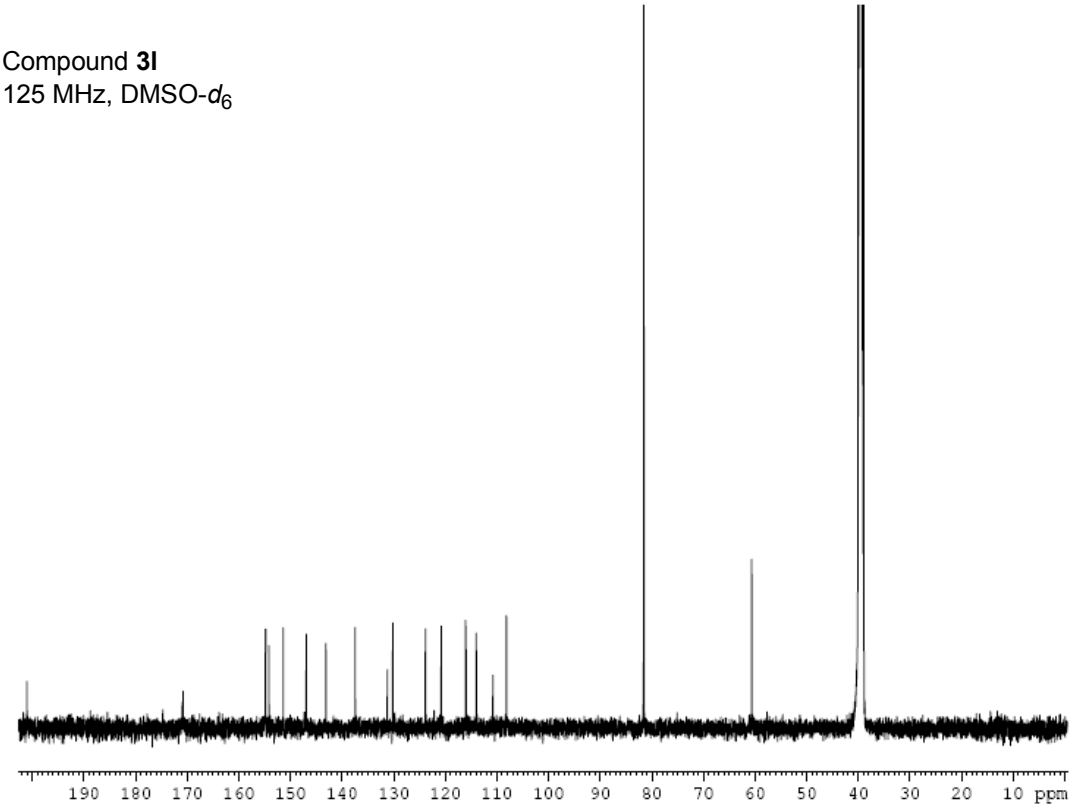
Compound **3k**
90 MHz, DMSO-d_6



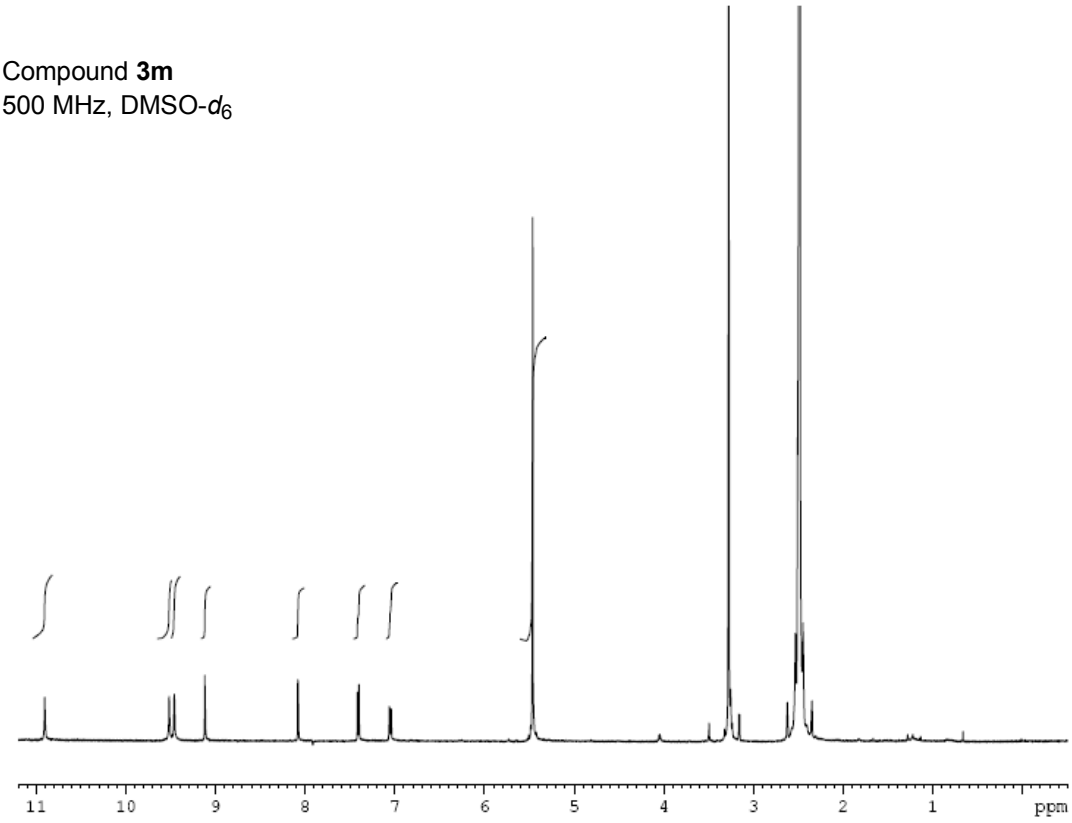
Compound **3l**
500 MHz, DMSO-d_6



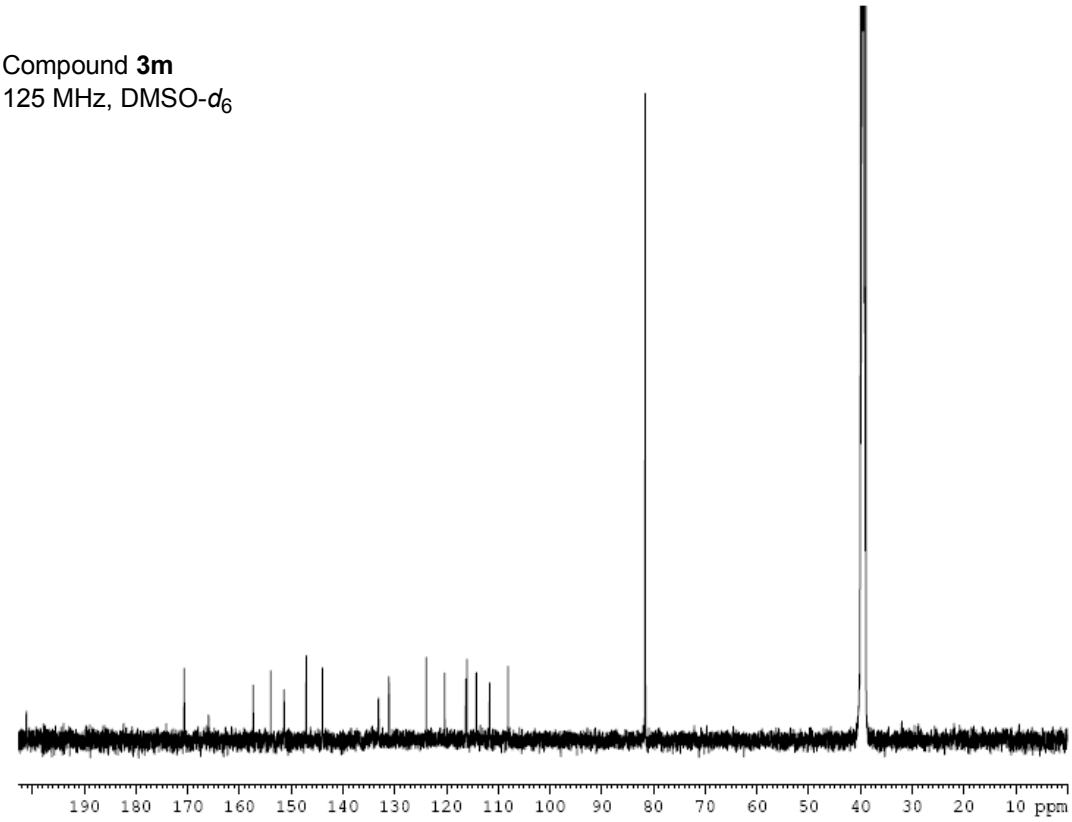
Compound **3l**
125 MHz, DMSO-d_6



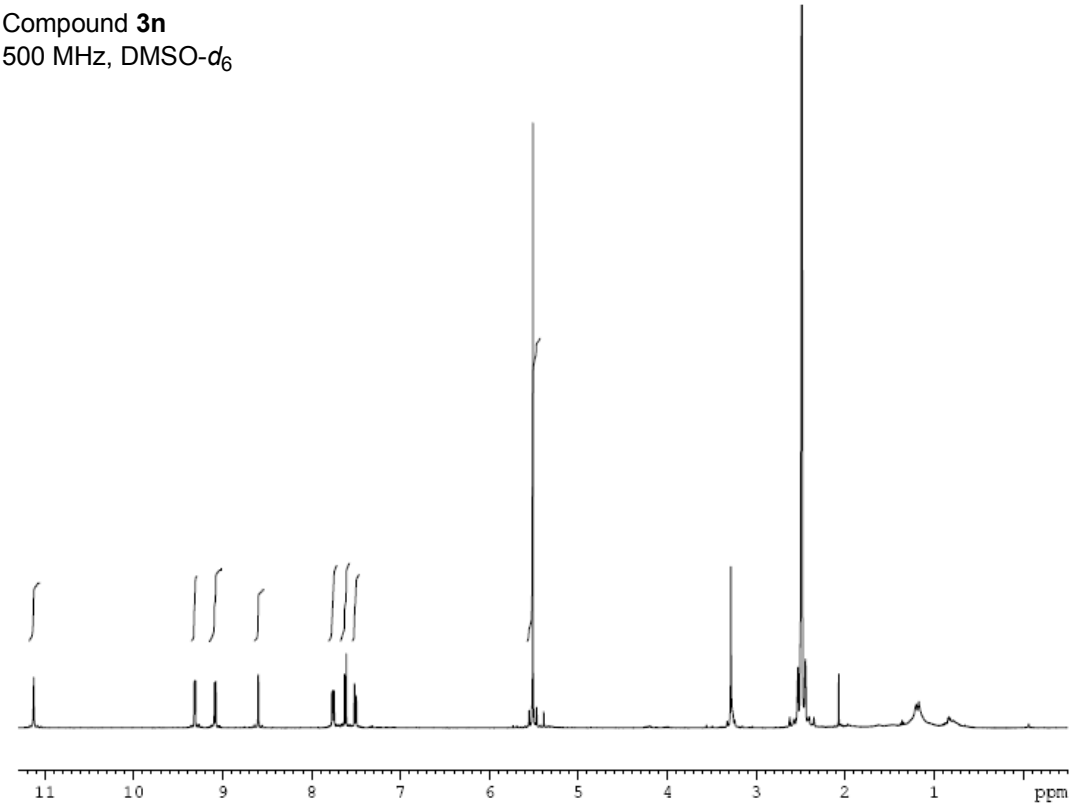
Compound **3m**
500 MHz, DMSO-d_6



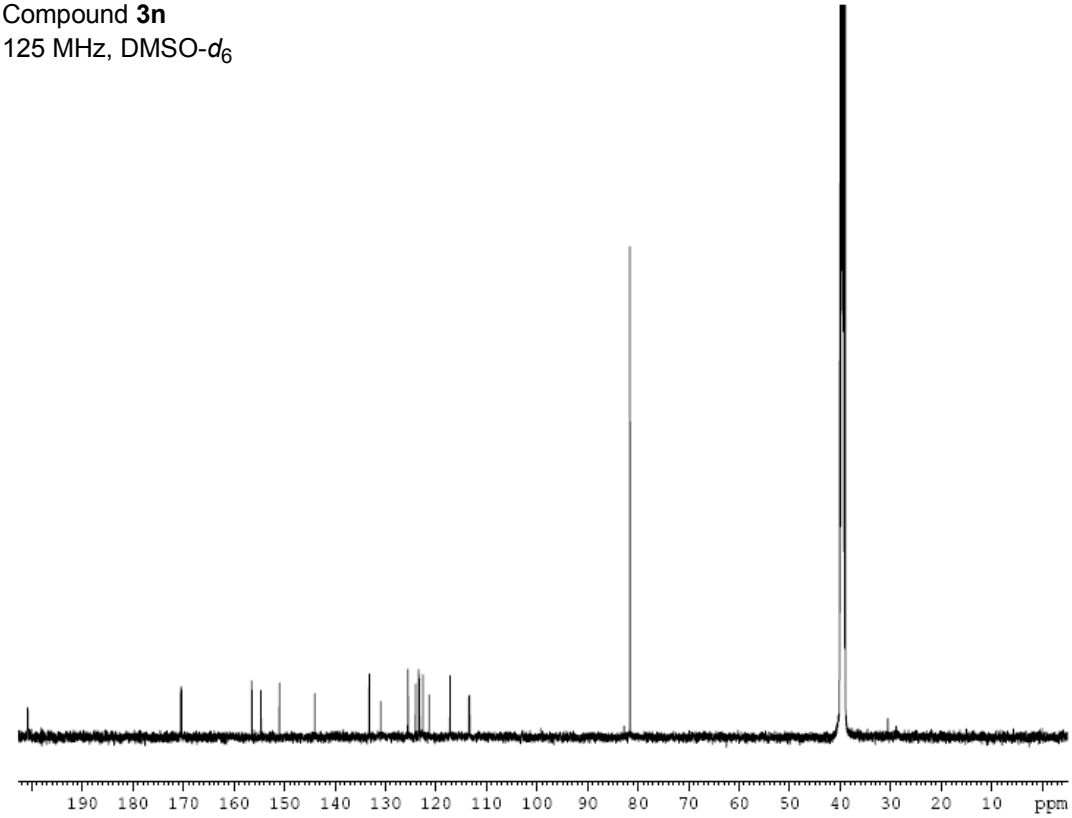
Compound **3m**
125 MHz, DMSO-d_6



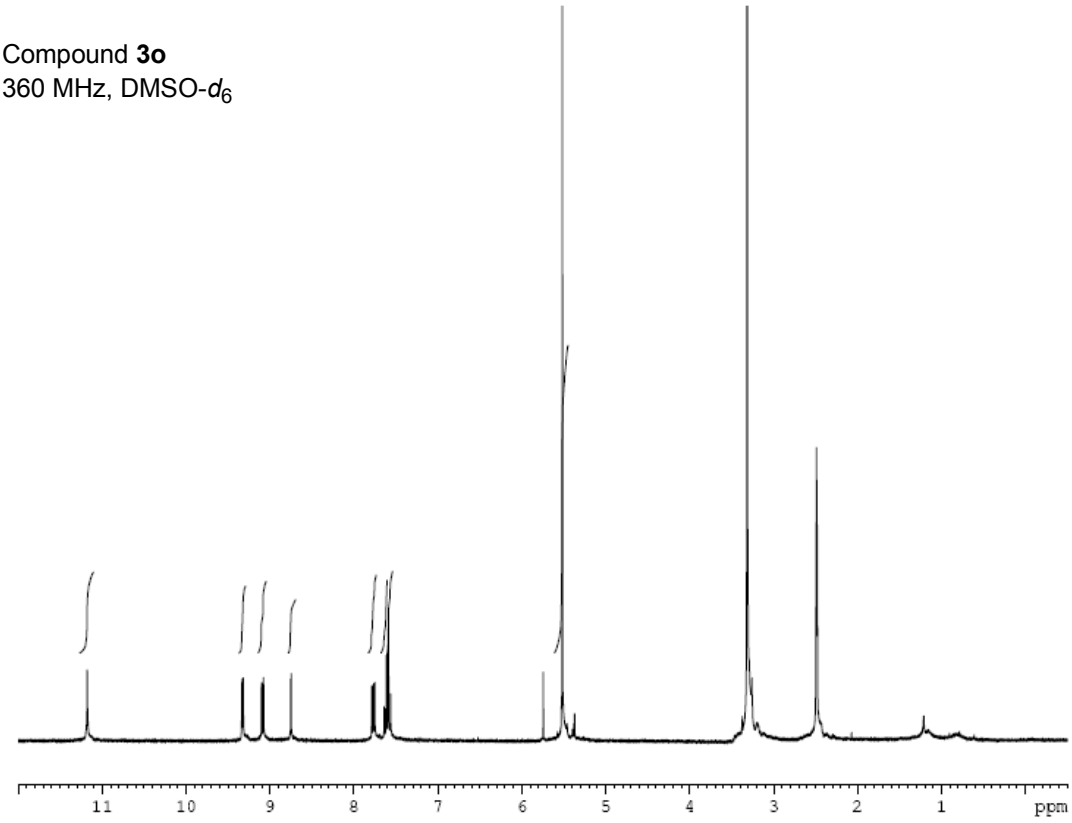
Compound **3n**
500 MHz, DMSO-d_6



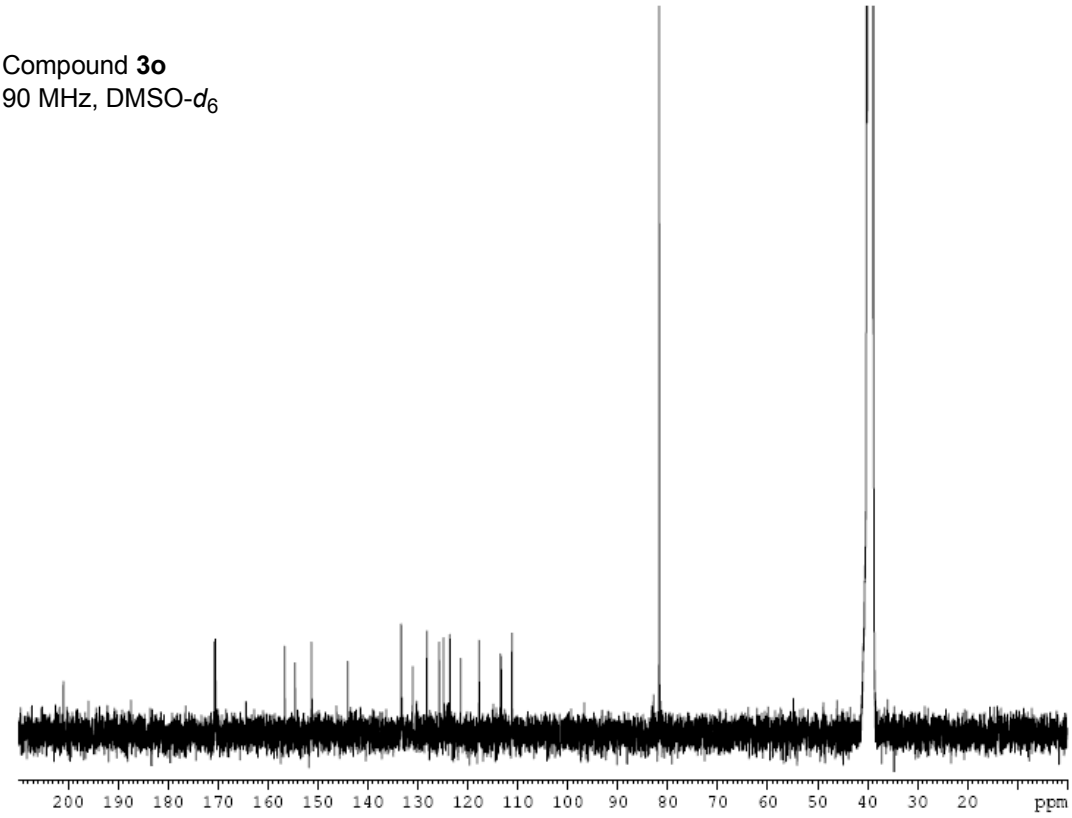
Compound **3n**
125 MHz, DMSO-d_6



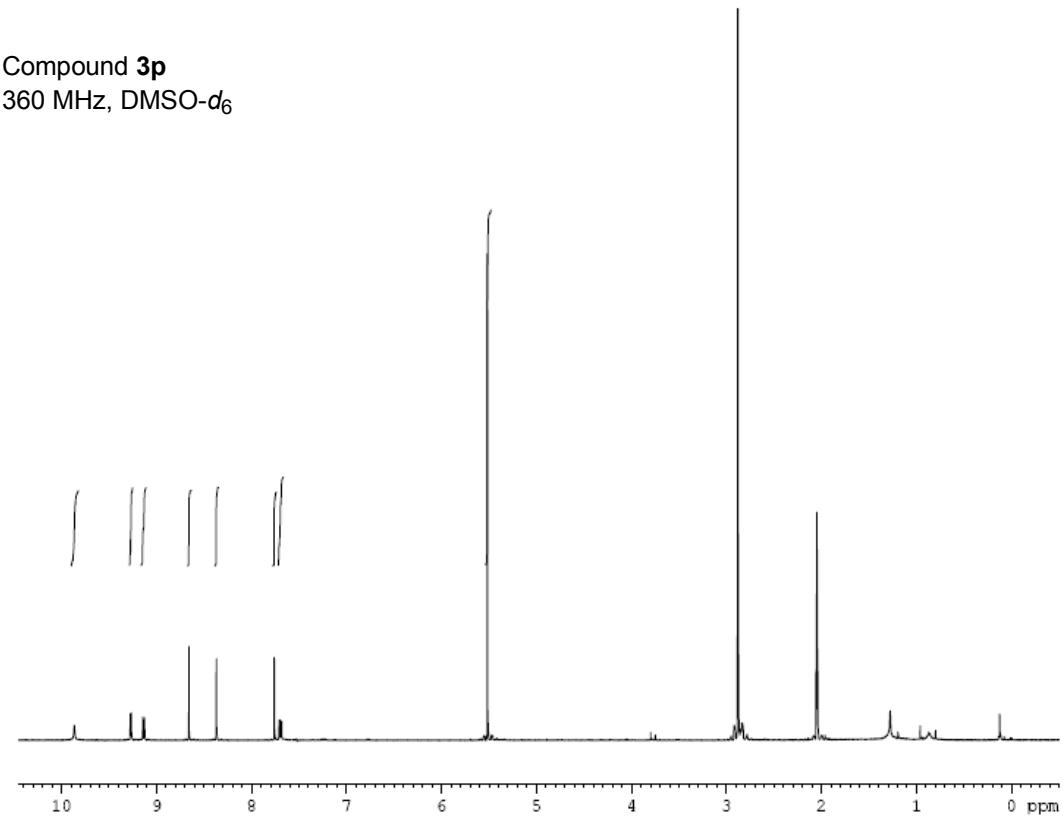
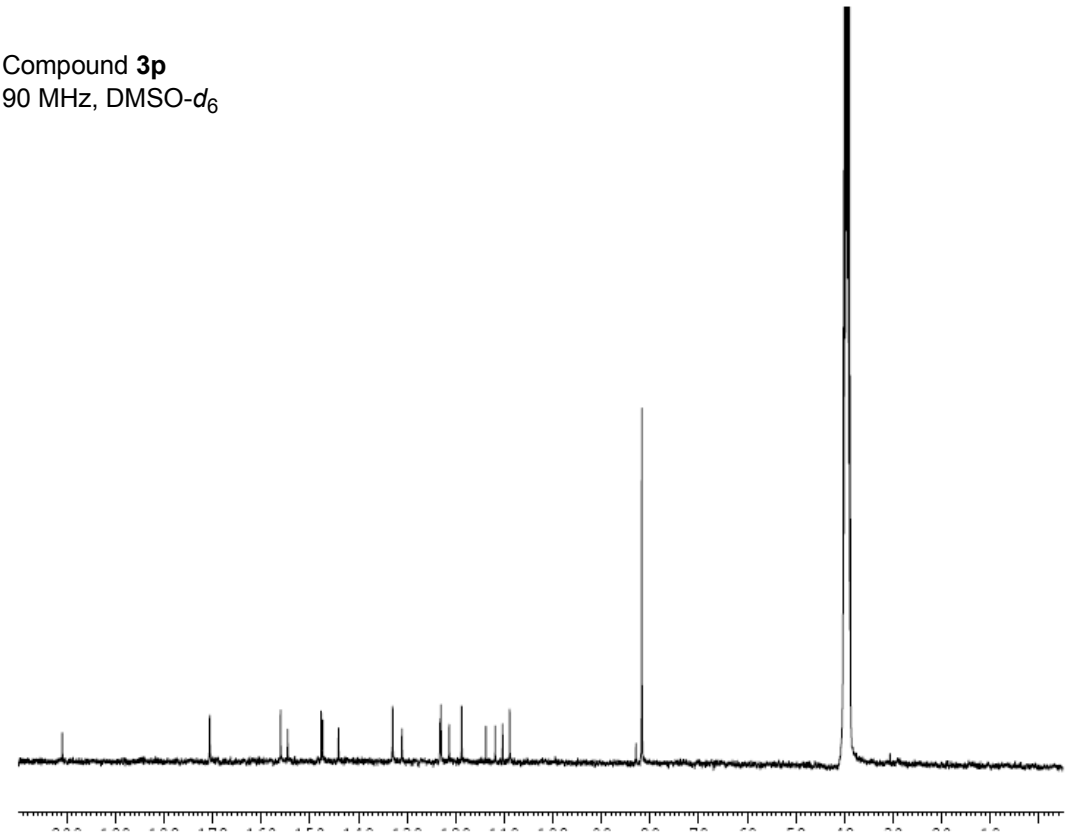
Compound **3o**
360 MHz, DMSO-d_6



Compound **3o**
90 MHz, DMSO-d_6



Compound **3p**
360 MHz, DMSO-d_6



Compound **3p**
90 MHz, DMSO-d_6