SUPPORTING INFORMATION

A Route to Annulated Indoles *via* a Palladium-Catalyzed Sequential Alkylation/Direct Arylation Reaction

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General. The following includes general experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for new compounds. Melting points were recorded using a Fisher-Johns melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained using either Varian Gemini 300 MHz or Varian Unity 400 MHz spectrometers. ^{1}H spectra were referenced to tetramethylsilane (TMS, 0 ppm) and ^{13}C spectra were referenced to solvent carbons (77.23 ppm for $CDCl_3$). No special notation is used for equivalent carbons. IR spectra were obtained using a Nicolet DX FT IR spectrometer as thin films on NaCl plates. High-resolution mass spectra were obtained using a VG 70-250S (double focusing) mass spectrometer at 70 eV unless otherwise noted.

Dichloromethane and acetonitrile were distilled under nitrogen from CaH_2 immediately prior to use. Dimethyl sulfoxide (DMSO) was stored under 4 Å molecular sieves. Anhydrous *N,N*-dimethylformamide (Sigma-Aldrich) was used as received. Neutral silica (Silicycle, Quebec, Canada) for flash chromatography was used as received. All reagents, metal catalysts and ligands were purchased from Sigma-Aldrich or Strem-Chemical Company and used as received unless otherwise noted. Reactions were performed under an atmosphere of nitrogen. The cyclization reactions were carried out in an oil bath using Biotage Microwave Vials (2-5 mL).

Synthesis of Bromoalkyl Indoles

General Procedure for the Alkylation of Indoles

Method A:

To a solution of indole (20 mmol, 1 equiv) and 3-bromo-1-(*tert*-butyldimethyl)silyloxypropane (22 mmol, 1.1 equiv) in DMF (50 mL) was added in one portion potassium hydroxide (flakes crushed into a powder, 22 mmol, 1.1 equiv). The reaction was stirred at rt for 1.5 h and then quenched with water (50 mL). The aqueous layer was washed with ether (3×) and the combined organic extracts were dried with anhydrous $MgSO_4$ and filtered. Removal of the solvent gave a crude product that was purified by flash chromatography.

Method B:

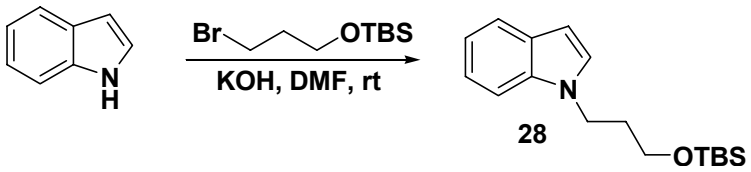
To a solution of indole (13.2 mmol, 1 equiv) in DMSO (25 mL) was added in one portion potassium hydroxide (flakes crushed into a powder, 14.5 mmol, 1.1 equiv). The reaction was submitted to an ultrasonic bath for 10 min. Then 3-bromo-1-(*tert*-butyldimethyl)silyloxypropane (14.5 mmol, 1.1 equiv) in DMSO (25 mL) was added *via* cannula. The reaction was stirred at rt for 1 h and then quenched with water (50 mL). The aqueous layer was washed with ether (3×) and the combined organic extracts were dried with anhydrous $MgSO_4$ and filtered. Removal of the solvent gave a crude product that was purified by flash chromatography.

Method C:

To a solution of indole (20 mmol, 1 equiv) and 2-bromo-1-(*tert*-butyldimethyl)silyloxyethane (22 mmol, 1.1 equiv) in DMF (50 mL) was added in one portion cesium carbonate (22 mmol, 1.1 equiv). The mixture was heated at 75 °C and stirred for 4 days. The reaction was cooled to rt and then quenched with water (50 mL). The aqueous layer was washed with ether (3×) and the combined organic extracts were dried with anhydrous $MgSO_4$ and filtered. Removal of the

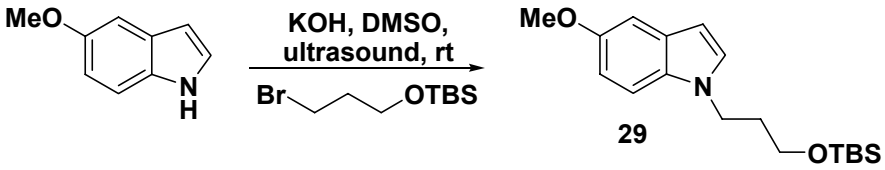
solvent gave a crude product that was purified by flash chromatography.

1-(3-{[*tert*-Butyl(dimethyl)silyl]oxy}propyl)-1*H*-indole (28).



Following Method A of the general procedure for the alkylation using indole, **28** was isolated as a colourless oil (5.4 g, 99%) by flash chromatography using 5% EtOAc/hexanes as eluant. R_f = 0.74 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3055, 2992, 1463, 1253, 1101 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, 1H, *J* = 8.2, 0.9 Hz), 7.37 (dd, 1H, *J* = 8.2, 0.9 Hz), 7.19 (td, 1H, *J* = 8.2, 0.9 Hz), 7.10 (d, 1H, *J* = 3.1 Hz), 7.08 (td, 1H, *J* = 8.2, 0.9 Hz), 6.48 (dd, 1H, *J* = 3.1, 0.9 Hz), 4.25 (t, 2H, *J* = 5.9 Hz), 3.56 (t, 2H, *J* = 5.9 Hz), 2.00 (quint, 2H, *J* = 5.9 Hz), 0.93 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 128.5, 128.1, 121.2, 120.8, 119.1, 109.4, 100.8, 59.5, 42.7, 32.9, 25.9, 18.2, -5.4; HRMS calcd for $C_{17}H_{27}NOSi$ $[M]^+$ 289.1861, found 289.1864.

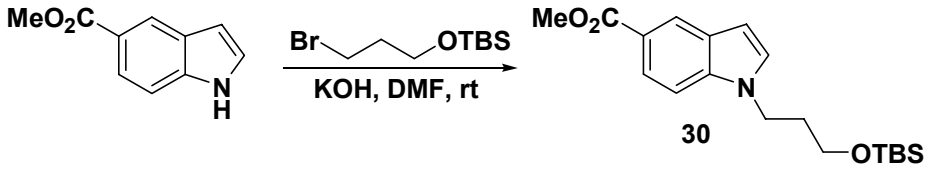
1-(3-{[*tert*-Butyl(dimethyl)silyl]oxy}propyl)-5-methoxy-1*H*-indole (29).



Following Method B of the general procedure for the alkylation using 5-methoxyindole, **29** was isolated as a colourless oil (4.23 g, 96%) by flash chromatography using 5% EtOAc/hexanes as eluant. R_f = 0.65 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3099, 2952, 1488, 1239, 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 1H), 7.08 (m, 2H), 6.85 (dd, 1H, *J* = 9.0, 2.4 Hz), 6.39 (d, 1H, *J* = 3.1 Hz), 4.21 (t, 2H, *J* = 5.8 Hz), 3.84 (s, 3H), 3.55 (t, 2H, *J* = 5.8 Hz), 1.98 (quint, 2H, *J* = 5.8 Hz), 0.93 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 131.2,

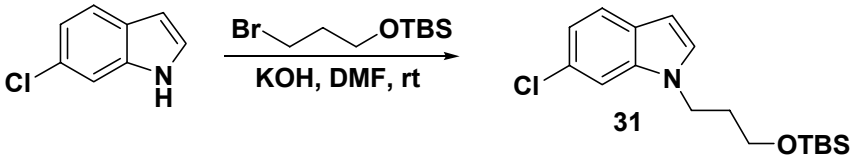
128.7, 128.6, 111.6, 110.1, 102.3, 100.3, 59.4, 55.8, 42.7, 33.0, 25.9, 18.2, -5.4; HRMS calcd for $C_{18}H_{29}NO_2Si$ $[M]^+$ 319.1967, found 319.1962.

Methyl 1-(3-{[*tert*-butyl(dimethyl)silyl]oxy}propyl)-1*H*-indole-5-carboxylate (30).



Following Method A of the general procedure for the alkylation using methyl indole-5-carboxylate (12 mmol scale), **30** was isolated as a colourless oil (4.11 g, 99%) by flash chromatography using 5% EtOAc/hexanes as eluant. R_f = 0.58 on silica gel (5% EtOAc/hexanes). IR (neat) ν = 2951, 1713, 1259, 1087 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.89 (d, 1H, *J* = 8.5 Hz), 7.37 (d, 1H, *J* = 8.5 Hz), 7.16 (d, 1H, *J* = 3.1 Hz), 6.58 (d, 1H, *J* = 3.1 Hz), 4.27 (t, 2H, *J* = 5.9 Hz), 3.92 (s, 3H), 3.55 (t, 2H, *J* = 5.9Hz), 2.00 (quint, 2H, *J* = 5.9Hz), 0.93 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 138.5, 129.4, 128.0, 123.9, 122.7, 121.2, 109.0, 102.6, 59.2, 51.7, 42.8, 32.9, 25.8, 18.2, -5.4; HRMS calcd for $C_{19}H_{29}NO_3Si$ $[M]^+$ 347.1916, found 347.1923.

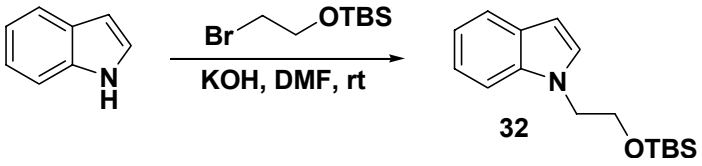
1-(3-{[*tert*-Butyl(dimethyl)silyl]oxy}propyl)-6-chloro-1*H*-indole (31).



Following Method A of the general procedure for the alkylation using methyl indole-5-carboxylate (12 mmol scale), **31** was isolated as a yellow oil (3.61 g, 93%) by flash chromatography using 5% EtOAc/hexanes as eluant. R_f = 0.91 on silica gel (20% EtOAc/hexanes). IR (neat) ν = 2953, 1463, 1256, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50

(d, 1H, *J* = 8.3 Hz), 7,37 (s, 1H), 7.08 (d, 1H, *J* = 3.1 Hz), 7.04 (d, 1H, *J* = 8.3 Hz), 6.45 (d, 1H, *J* = 3.1 Hz), 4.21 (t, 2H, *J* = 5.9 Hz), 3.54 (t, 2H, *J* = 5.9 Hz), 1.97 (quint, 2H, *J* = 5.9 Hz), 0.93 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 128.7, 127.3, 127.0, 121.6, 119.8, 109.5, 101.1, 59.2, 42.6, 32.9, 25.9, 18.2, -5.4; HRMS calcd for $C_{17}H_{26}NO_2SiCl$ $[M]^+$ 323.1472, found 323.1475.

1-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)-1*H*-indole (32).

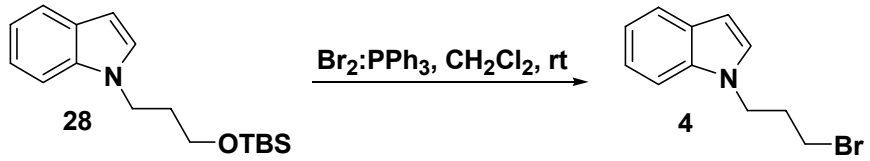


Following Method C of the general procedure for the alkylation using indole, **32** was isolated as a colourless oil (3.90 g, 71%) by flash chromatography using 5% ether/hexanes as eluant. R_f = 0.52 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3056, 2929, 1463, 1316, 1114 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, 1H, *J* = 6.9 Hz), 7.34 (d, 1H, *J* = 6.9 Hz), 7.19 (t, 1H, *J* = 6.9 Hz), 7.14 (d, 1H, *J* = 3.3 Hz), 7.08 (t, 1H, *J* = 6.9 Hz), 6.48 (d, 1H, *J* = 3.3Hz), 4.23 (t, 2H, *J* = 6.0 Hz), 3.91 (t, 2H, *J* = 6.0 Hz), 0.83 (s, 9H), -0.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 128.8, 128.7, 121.5, 121.1, 119.4, 109.5, 101.2, 62.5, 48.9, 26.0, 18.4, -5.5; HRMS calcd for $C_{16}H_{25}NOSi$ $[M]^+$ 275.1705, found 275.1702.

General Procedure for Bromination

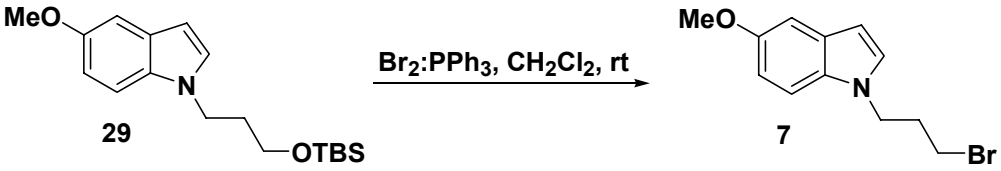
To a suspension of dibromophosphorane (22 mmol, 1.1 equiv) in CH_2Cl_2 (70 mL) was added a solution of alkylated indole (20 mmol, 1 equiv) in CH_2Cl_2 (35 mL). The reaction was stirred for 5 min and then quenched with water (25 mL). The organic layer was washed with water (2×) and then dried with anhydrous $MgSO_4$ and filtered. Removal of the solvent gave a crude product that was purified by flash chromatography.

1-(3-Bromopropyl)-1*H*-indole (4).



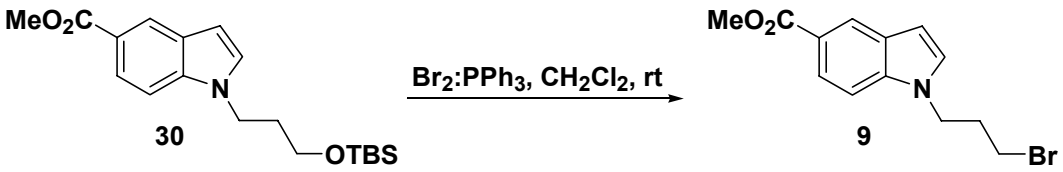
Following the general procedure for bromination using **28**, **4** was isolated as a colourless oil (4.56 g, 96%) by flash chromatography using 10% EtOAc/hexanes as eluant. R_f = 0.58 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3053, 2938, 1463, 1315, 1228 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 77.63 (dd, 1H, *J* = 7.0, 0.8 Hz), 7.37 (dd, 1H, *J* = 7.0, 0.8 Hz), 7.21 (td, 1H, *J* = 7.0, 0.8 Hz), 7.14 (d, 1H, *J* = 3.1 Hz), 7.11 (td, 1H, *J* = 7.0, 0.8 Hz), 6.50 (dd, 1H, *J* = 3.1, 0.8 Hz), 4.33 (t, 2H, *J* = 6.3 Hz), 3.30 (t, 2H, *J* = 6.3 Hz), 2.35 (quint, 2H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 128.6, 127.9, 121.6, 121.0, 119.4, 109.2, 101.5, 43.9, 32.6, 30.4; HRMS calcd for $C_{11}H_{12}NBr$ $[M]^+$ 237.0153, found 237.0155.

1-(3-Bromopropyl)-5-methoxy-1*H*-indole (7).



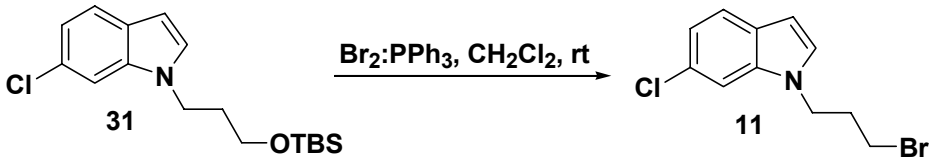
Following the general procedure for bromination using **29** (12 mmol scale), **7** was isolated as a colourless oil (2.82 g, 87%) by flash chromatography using 10% EtOAc/hexanes as eluant. R_f = 0.56 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3098, 2944, 1485, 1237, 1150, 1030 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, 1H, *J* = 8.8 Hz), 7.12 (d, 1H, *J* = 3.1 Hz), 7.09 (d, 1H, *J* = 3.1 Hz), 6.88 (dd, 1H, *J* = 8.8, 3.1 Hz), 6.42 (d, 1H, *J* = 3.1 Hz), 4.30 (t, 2H, *J* = 6.2 Hz), 3.85 (s, 3H), 3.29 (t, 2H, *J* = 6.2 Hz), 2.33 (quint, 2H, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 131.0, 128.9, 128.5, 111.9, 109.9, 102.5, 100.9, 55.7, 44.0, 32.6, 30.5; HRMS calcd for $C_{12}H_{14}NOBr$ $[M]^+$ 267.0258, found 267.0267.

Methyl 1-(3-bromopropyl)-1*H*-indole-5-carboxylate (9).



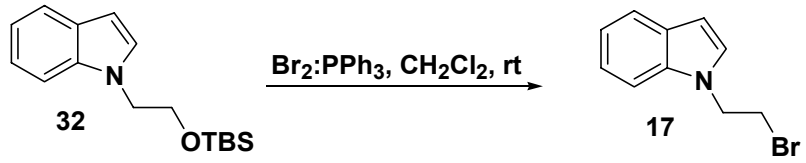
Following the general procedure for bromination using **30** (7.2 mmol scale), **9** was isolated as a colourless oil (1.95 g, 92%) by flash chromatography using 10% EtOAc/hexanes as eluant. R_f = 0.27 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3101, 2948, 1700, 1449, 1360, 1311, 1255, 1195, 1096 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, 1H, *J* = 1.4 Hz), 7.92 (dd, 1H, *J* = 8.8, 1.4 Hz), 7.38 (d, 1H, *J* = 8.8 Hz), 7.20 (d, 1H, *J* = 3.1 Hz), 6.60 (d, 1H, *J* = 3.1 Hz), 4.36 (t, 2H, *J* = 8.1 Hz), 3.93 (s, 3H), 3.29 (t, 2H, *J* = 8.1 Hz), 2.36 (quint, 2H, *J* = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 138.2, 129.2, 128.0, 123.9, 122.9, 121.5, 108.8, 103.1, 51.7, 44.0, 32.5, 30.0; HRMS calcd for $C_{13}H_{14}NO_2Br$ $[M]^+$ 295.0207, found 295.0207.

1-(3-Bromopropyl)-6-chloro-1*H*-indole (11).



Following the general procedure for bromination using **31** (10.7 mmol scale), **11** was isolated as a colourless oil (2.61 g, 90%) by flash chromatography using 10% EtOAc/hexanes as eluant. R_f = 0.62 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3100, 2948, 1463, 1319, 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 1H, *J* = 8.6 Hz), 7,35 (d, 1H, *J* = 2 Hz), 7.13 (d, 1H, *J* = 3.1 Hz), 7.07 (d, 1H, *J* = 8.6, 2 Hz), 6.47 (d, 1H, *J* = 3.1 Hz), 4.29 (t, 2H, *J* = 6.1 Hz), 3.29 (t, 2H, *J* = 6.1 Hz), 2.33 (quint, 2H, *J* = 6.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 128.7, 127.6, 127.1, 121.8, 120.2, 109.2, 101.7, 44.0, 32.4, 30.2; HRMS calcd for $C_{11}H_{11}NClBr$ $[M]^+$ 270.9763, found 270.9760.

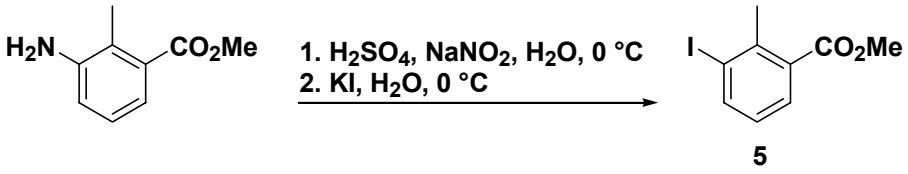
1-(2-Bromoethyl)-1*H*-indole (17).



Following the general procedure for bromination using **32** (8.0 mmol scale), **17** was isolated as a colourless oil (1.73 g, 97%) by flash chromatography using 10% EtOAc/hexanes as eluant. R_f = 0.75 on silica gel (20% EtOAc/hexanes). IR (neat) ν = 3053, 2960, 1514, 1463, 1314, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, 1H, *J* = 7.8 Hz), 7.34 (m, 1H), 7.23 (m, 1H), 7.13 (m, 2H), 6.53 (d, 1H, *J* = 3.1 Hz), 4.53 (t, 2H, *J* = 7.0 Hz), 3.64 (t, 2H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 128.7, 121.8, 121.2, 119.7, 108.8, 101.9, 47.8, 29.7; HRMS calcd for $C_{10}H_{10}NBr$ $[M]^+$ 222.9996, found 223.0003.

Synthesis of Aryl Iodides

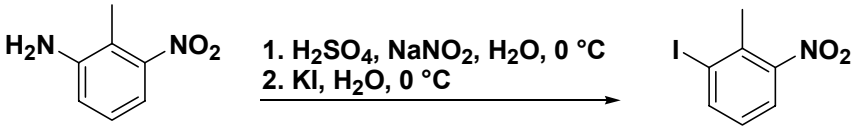
Methyl 3-iodo-2-methylbenzoate (5).



To a solution of methyl-3-amino-2-methylbenzoate (5 mL, 34.7 mmol, 1 equiv) in water (35 mL) was added a solution of H_2SO_4 (7 mL) in water (35 mL). The mixture was cooled to 0 °C, then a solution of sodium nitrite (2.51 g, 36.4 mmol, 1.05 mmol) in water (35 mL) was added dropwise. The mixture was stirred for 1 h, then a solution of potassium iodide (8.64 g, 52.0 mmol, 1.5 equiv) in water (35mL) was added dropwise. The reaction was stirred for 1 h and then extracted with CH_2Cl_2 (3×). The combined organic extracts were washed with saturated aqueous $Na_2S_2O_3$, dried with anhydrous $MgSO_4$, filtred and concentated. The crude mixture was purified by flash chromatography using 10% EtOAc/hexanes as eluant to yield **5** (9.00 g, 94%) as a colourless

solid, mp = 23-25 °C. R_f = 0.75 (20% EtOAc/hexanes). IR (neat) ν = 3060, 2948, 1727, 1431, 1281, 1252, 1090, 1001 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 1H, *J* = 7.7 Hz), 7.73 (d, 1H, *J* = 7.7 Hz), 6.92 (t, 1H, *J* = 7.7 Hz), 3.90 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 142.4, 141.3, 131.6, 129.8, 126.9, 104.0, 52.2, 26.4; HRMS calcd for $C_9H_9O_2I$ $[M]^+$ 275.9647, found 275.9649.

2-Methyl-3-nitro-iodobenzene (13).



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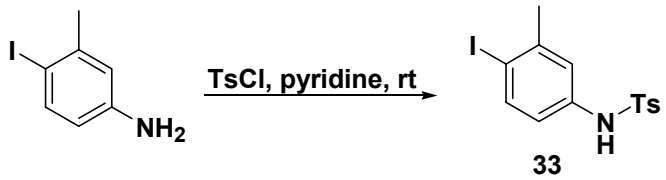
To a solution of 2-methyl-3-nitroaniline (3.00 g, 19.7 mmol, 1 equiv) in water (20 mL) was added a solution of H_2SO_4 (4 mL) in water (20 mL). The mixture was cooled to 0 °C, then a solution of sodium nitrite (1.43 g, 20.72 mmol, 1.05 mmol) in water (20 mL) was added dropwise. The mixture was stirred for 1 h, then a solution of potassium iodide (4.91 g, 29.6 mmol, 1.5 equiv) in water (20 mL) was added dropwise. The reaction was stirred for 1 h and then extracted with CH_2Cl_2 (3×). The combined organic extracts were washed with saturated aqueous $Na_2S_2O_3$, dried with anhydrous $MgSO_4$, filtred and concentated. The crude mixture was purified by flash chromatography using 10% EtOAc/hexanes as eluant to yield **13** (3.73 g, 72%) as a yellow solid, mp = 35-37 °C. R_f = 0.78 (20% EtOAc/hexanes). IR (neat) ν = 3080, 2863, 1518, 1443, 1360 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, 1H, *J* = 7.9, 1.0 Hz), 7.72 (dd, 1H, *J* = 7.9, 1.0 Hz), 7.03 (t, 1H, *J* = 7.9 Hz), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 143.0, 134.9, 127.9, 123.8, 103.5, 24.9; HRMS calcd for $C_7H_6NO_2I$ $[M]^+$ 262.9443, found 262.9444.

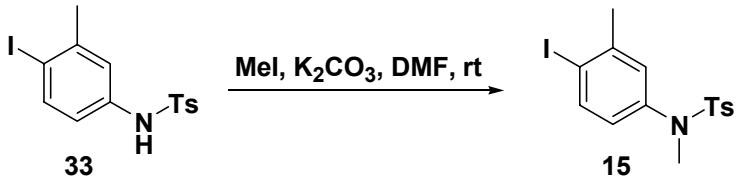
***N N*-(4-Iodo-3-methylphenyl)-4-methylbenzenesulfonamide (33).**



33

To a solution of 3-methyl-4-iodoaniline[1] (2.33 g, 10.0 mmol, 1 equiv) in pyridine (20 mL) was added in one portion *p*-toluenesulfonyl chloride (2.00 g, 10.5 mmol, 1.05 equiv). The reaction was stirred at rt for 1.5 h then quenched with water (20 mL). The solution was extracted with CH_2Cl_2 (3×) and the combined organic extracts were washed with a 10% aqueous $CuSO_4$ (2×), dried with anhydrous $MgSO_4$, filtered and concentrated. The crude mixture was purified by flash chromatography using 25% EtOAc/hexanes as eluant to yield **33** (2.89 g, 75%) as a white solid, mp = 167-170 °C. R_f = 0.39 (30% EtOAc/hexanes). IR (neat) ν = 3250, 1636, 1159 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, 2H, *J* = 7.9 Hz), 7.60 (d, 1H, *J* = 8.2 Hz), 7.24 (d, 2H, *J* = 7.9 Hz), 6.99 (s, 1H, NH), 6.97 (d, 1H, *J* = 2.6 Hz), 6,63 (dd, 1H, *J* = 8.2, 2.6 Hz), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.8, 139.7, 136.9, 135.9, 130.0, 127.4, 122.5, 120.2, 96.2, 28.3, 21.8; HRMS calcd for $C_{14}H_{14}NO_2IS$ $[M]^+$ 386.9790, found 386.9796.

***N*-(4-Iodo-3-methylphenyl)-*N*,4-dimethylbenzenesulfonamide (15).**

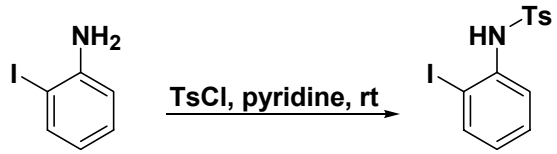


33 15

To a solution of **33** (1.00 g, 2.58 mmol, 1 equiv) in DMF (10 mL) was added K_2CO_3 (1.07 g, 7.75 mmol, 3 equiv) and iodomethane (320 μL, 5.17 mmol, 2 equiv). The reaction was stirred at rt for 1 h then quenched with water (10 mL). The aqueous layer was extracted with ether (3×) and the combined organic extracts were dried with anhydrous $MgSO_4$, filtered and concentrated.. The crude mixture was purified by flash chromatography using 10% EtOAc/hexanes as eluant to yield

15 (1.00 g, 97%) as a white solid, mp = 97-98 °C. R_f = 0.74 (30% EtOAc/hexanes). IR (neat) ν = 3062, 2975, 1470, 1349, 1168, 1015, 814 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 1H, *J* = 8.3 Hz), 7.44 (d, 2H, *J* = 8.3 Hz), 7.25 (d, 2H, *J* = 8.3 Hz), 7.06 (d, 1H, *J* = 2.7 Hz), 6.55 (dd, 1H, *J* = 8.3, 2.7 Hz), 3.11 (s, 3H), 2.43 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.1, 141.7, 139.0, 133.2, 129.3, 128.1, 127.7, 124.9, 99.1, 37.8, 28.8, 21.5; HRMS calcd for $C_{15}H_{16}NO_2IS$ $[M]^+$ 400.9946, found 400.9939.

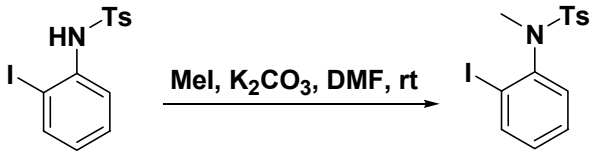
***N*-(2-Iodophenyl)-4-methylbenzenesulfonamide (34).**



34

To a solution of 3-methyl-4-iodoaniline (1.00 g, 4.57 mmol, 1 equiv) in pyridine (10 mL) was added in one portion *p*-toluenesulfonyl chloride (914 mg, 4.79 mmol, 1.05 equiv). The reaction was stirred at rt for 1.5 h then quenched with water (10 mL). The solution was extracted with CH_2Cl_2 (3×) and the combined organic extracts were washed with a 10% aqueous $CuSO_4$ (2×), dried with anhydrous $MgSO_4$, filtered and concentrated. The crude mixture was purified by flash chromatography using 25% EtOAc/hexanes as eluant to yield **34** (1.62 g, 95%) as a white solid. Spectral data match the previously reported data.[2]

***N*-(2-Iodophenyl)-*N*,4-dimethylbenzenesulfonamide (21).**

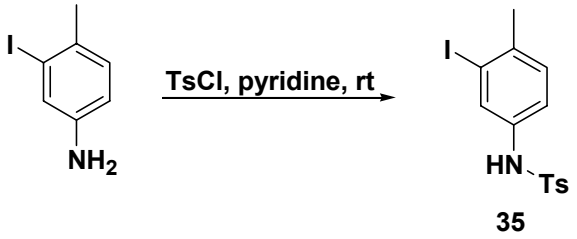


34 **21**

To a solution of **34** (400 mg, 1.07 mmol, 1 equiv) in DMF (5 mL) was added K_2CO_3 (444 mg, 3.21 mmol, 3 equiv) and iodomethane (133 μL, 2.14 mmol, 2 equiv). The reaction was stirred at

rt for 1 h then quenched with water (5 mL). The aqueous layer was extracted with ether (3×) and the combined organic extracts were dried with anhydrous $MgSO_4$, filtered and concentrated. The crude mixture was purified by flash chromatography using 10% EtOAc/hexanes as eluant to yield **21** (406 g, 98%) as a white solid, mp = 105-106 °C. R_f = 0.67 (25% EtOAc/hexanes). IR (neat) ν = 3052, 2965, 2870, 1580, 1432, 1318, 1162 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 1H), 7.69 (m, 2H), 7.30 (m, 3H), 6.97 (m, 2H), 3.12/3.13 (two s, 3H, rotamers), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 143.7, 140.2, 135.5, 129.8, 129.9, 129.0, 128.6, 128.1, 101.8, 36.7, 21.5; HRMS calcd for $C_{14}H_{14}INO_2S$ $[M]^+$ 386.9790, found 386.9787.

***N*-(3-Iodo-4-methylphenyl)-4-methylbenzenesulfonamide (35).**

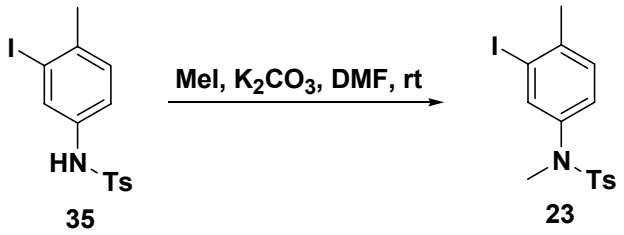


35

To a solution of 4-methyl-3-iodoaniline (2.50 g, 10.7 mmol, 1 equiv) in pyridine (20 mL) was added in one portion *p*-toluenesulfonyl chloride (2.14 g, 11.3 mmol, 1.1 equiv). The reaction was stirred at rt for 1.5 h then quenched with water (20 mL). The solution was extracted with CH_2Cl_2 (3×) and the combined organic extracts were washed with a 10% aqueous $CuSO_4$ (2×), dried with anhydrous $MgSO_4$, filtered and concentated. The crude mixture was purified by flash chromatography using 10% EtOAc/hexanes as eluant to yield **35** (4.10 g, 99%) as a white solid, mp = 1211-124 °C. R_f = 0.49 (20% EtOAc/hexanes). IR (neat) ν = 3249, 1595, 1483, 1318, 1156 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 2H, *J* = 6.3 Hz), 7.47 (d, 1H, *J* = 2.4 Hz), 7.25 (d, 2H, *J* = 6.3 Hz), 7.08 (d, 1H, *J* = 8.3 Hz), 6.99 (dd, 1H, *J* = 8.3, 2.4 Hz), 6.49 (s, NH), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 138.4, 135.6, 134.9, 131.5, 129.76,

129.72, 127.2,121.3, 100.6, 27.2, 21.5; HRMS calcd for $C_{14}H_{14}NO_2IS$ $[M]^+$ 386.9790, found 386.9790.

***N*-(3-Iodo-4-methylphenyl)-*N*,4-dimethylbenzenesulfonamide (23).**



To a solution of **35** (1.50 g, 3.88 mmol, 1 equiv) in DMF (15mL) was added K_2CO_3 (1.60 g, 11.6 mmol, 3 equiv) and iodomethane (485 μL, 7.76 mmol, 2 equiv). The reaction was stirred at rt for 1 h then quenched with water (15 mL). The aqueous layer was extracted with ether (3×) and the combined organic extracts were dried with anhydrous $MgSO_4$, filtered and concentrated. The crude mixture was purified by flash chromatography using 10% EtOAc/hexanes as eluant to yield **23** (1.55 g, 99%) as a white solid, mp = 71-73 °C. R_f = 0.65 (20% EtOAc/hexanes). IR (neat) ν = 3050, 2983, 1641, 1484, 1384, 1171 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 3H), 7.27 (d, 2H, *J*= 7.2Hz), 7.16 (d, 1H, *J*= 6.2Hz), 7.03 (dd, 1H, *J*= 6.2-2.2Hz), 3.10 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.0, 139.6, 136.2, 132.5, 129.0, 127.3, 125.6, 99.7, 37.6, 27.1, 21.1; HRMS calcd for $C_{15}H_{16}NO_2IS$ $[M]^+$ 400.9946, found 400.9950.

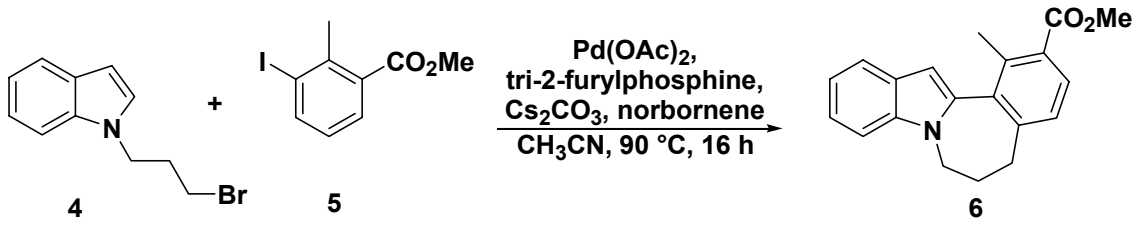
Cyclization Reactions

General Procedure for the Cyclization Reaction

A vial equipped with a stir bar was charged with Cs_2CO_3 (0.400 mmol, 2 equiv), $Pd(OAc)_2$ (0.020 mmol, 10 mol%), tri-2-furylphosphine (0.044 mmol, 22 mol%), and norbornene (0.400 mmol, 2 equiv). A solution of bromoindole (0.400 mmol, 2 equiv) and aryl iodide (0.200 mmol, 1 equiv) in CH_3CN (2 mL) was added. The vial was capped and purged with nitrogen. The

resulting mixture was heated in an oil bath at 90 °C for 16 h, cooled and then filtered through a short plug of silica. Removal of the solvent gave a crude product that was purified by flash chromatography.

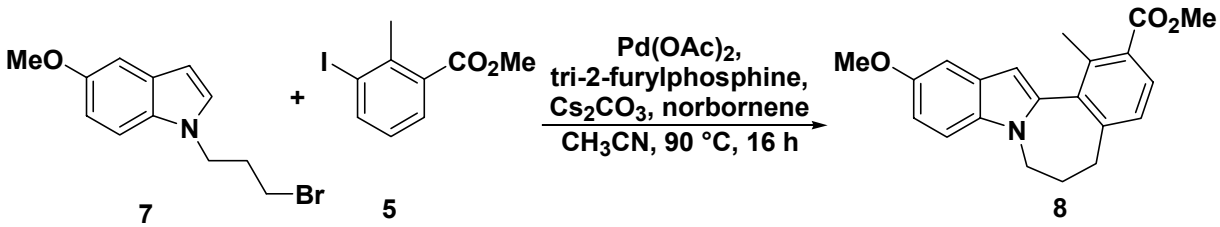
Methyl 1-methyl-5,6-dihydroindolo[2,1-*a*]isoquinoline-2-carboxylate (6).



4 5 6

Following the general procedure for the cyclization reaction using **4** and **5**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **6** (48.8 mg, 80%) as a thick colourless oil. R_f = 0.68 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3052, 2947, 1719, 1458, 1270, 1203, 1076 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 1H, *J*= 7.2Hz), 7.68 (d, 1H, *J*= 7.2Hz), 7.36 (d, 1H, *J*= 8.0Hz), 7.22 (t, 1H, *J*= 8.0Hz), 7.15 (d, 1H, *J*= 8.0Hz), 7.12 (t, 1H, *J*= 8.0Hz), 6.55 (s, 1H), 4.37 (dd, 1H, *J*= 14.8-6.4Hz), 3.91 (s, 3H), 3.75 (td, 1H, *J*= 12.4-6.0Hz), 2.69 (s, 3H), 2.60 (m, 1H), 2.35 (m, 2H), 2.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 143.4, 138.0, 137.2, 135.4, 134.0, 130.5, 130.2, 127.9, 126.5, 121.6, 120.9, 119.6, 108.8, 103.4, 52.3, 40.2, 31.8, 30.6, 19.3; HRMS calcd for $C_{13}H_{14}NO_2Br$ $[M]^+$ 305.1415, found 305.1416.

Methyl 10-methoxy-1-methyl-5,6-dihydroindolo[2,1-*a*]isoquinoline-2-carboxylate (8).

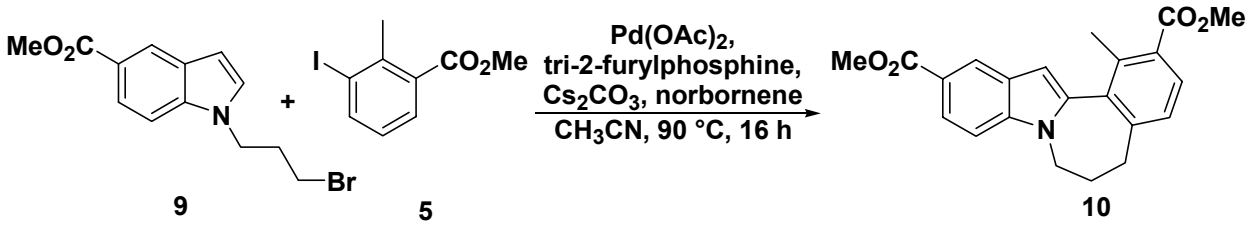


7 5 8

Following the general procedure for the cyclization reaction using **7** and **5**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **8** (54.7 mg, 83%) as a white

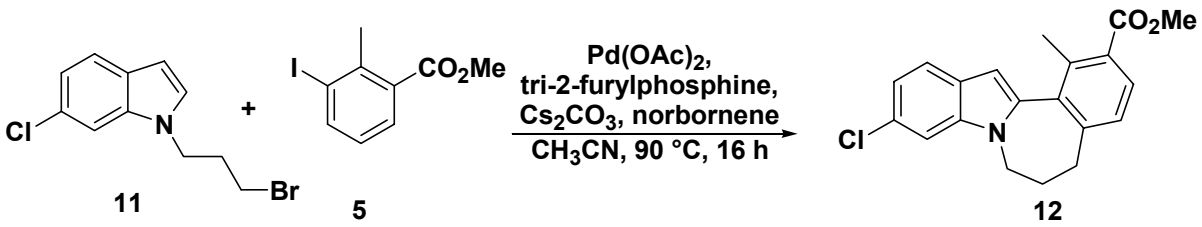
solid, mp = 129-133 °C. R_f = 0.23 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 2947, 1718, 1486, 1448, 1270, 1236, 1219 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 1H, *J* = 8.0 Hz), 7.24 (d, 1H, *J* = 8.0 Hz), 7.15 (d, 1H, *J* = 8.8 Hz), 7.14 (s, 1H), 6.90 (dd, 1H, *J* = 8.8, 2.4 Hz), 6.48 (s, 1H), 4.31 (dd, 1H, *J* = 14.8, 4.8 Hz), 3.92 (s, 3H), 3.87 (s, 3H), 3.85 (m, 1H), 3.74 (td, 1H, *J* = 14.8, 8.4 Hz), 2.68 (s, 3H), 2.63 (dd, 1H, *J* = 12.0, 6.8 Hz), 2.34 (m, 2H), 2.00 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 154.2, 143.3, 137.9, 137.7, 134.1, 130.8, 130.5, 130.1, 128.1, 126.4, 112.2, 109.5, 102.9, 102.3, 56.1, 52.2, 40.3, 31.8, 30.7, 19.2; HRMS calcd for $C_{21}H_{21}NO_3$ $[M]^+$ 335.1521, found 335.1526.

Dimethyl 1-methyl-5,6-dihydroindolo[2,1-*a*]isoquinoline-2,10-dicarboxylate (10).



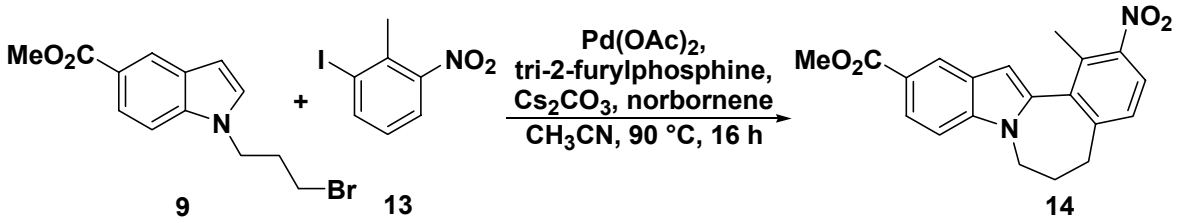
Following the general procedure for the cyclization reaction using **9** and **5**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **10** (52.9 mg, 79%) as a white solid, mp = 202-203 °C. R_f = 0.58 on silica gel (30% EtOAc/hexanes). IR (neat) ν = 2948, 1711, 1610, 1451, 1433, 1307, 1255, 1202, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, 1H, *J* = 1.8 Hz), 7.94 (dd, 1H, *J* = 9.0, 1.8 Hz), 7.81 (d, 1H, *J* = 7.8 Hz), 7.37 (d, 1H, *J* = 9.0 Hz), 7.18 (d, 1H, *J* = 7.8 Hz), 6.65 (s, 1H), 4.41 (dd, 1H, *J* = 14.4, 6.6 Hz), 3.94 (s, 3H), 3.93 (s, 3H), 3.76 (m, 1H), 2.68 (s, 3H), 2.67 (m, 1H), 2.35 (m, 2H), 2.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.1, 142.9, 138.5, 137.8, 137.6, 133.1, 130.4, 130.3, 127.1, 126.3, 123.7, 122.8, 121.4, 108.2, 104.6, 52.0, 51.8, 40.3, 31.4, 30.0, 18.9; HRMS calcd for $C_{22}H_{21}NO_4$ $[M]^+$ 363.1470, found 363.1458.

Methyl 9-chloro-1-methyl-5,6-dihydroindolo[2,1-*a*]isoquinoline-2-carboxylate (12).



Following the general procedure for the cyclization reaction using **11** and **5**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **12** (37.4 mg, 54%) as a pale yellow oil. R_f = 0.30 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 2947, 1719, 1608, 1463, 1266, 1058 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, 1H, *J* = 7.8 Hz), 7.56 (d, 1H, *J* = 7.8 Hz), 7.34 (s, 1H), 7.16 (d, 1H, *J* = 7.8 Hz), 7.08 (dd, 1H, *J* = 7.8, 1.8 Hz), 6.52 (s, 1H), 4.28 (dd, 1H, *J* = 14.7, 6.3 Hz), 3.92 (s, 3H), 3.73 (m, 1H), 2.67 (s, 3H), 2.63 (m, 1H), 2.32 (m, 2H), 2.02 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 143.2, 138.1, 138.0, 135.8, 133.5, 130.6, 130.4, 127.7, 126.5, 126.4, 121.7, 120.3, 108.9, 103.5, 52.2, 40.4, 31.7, 30.3, 19.1; HRMS calcd for $C_{20}H_{18}NO_2Cl$ $[M]^+$ 339.1026, found 339.1025.

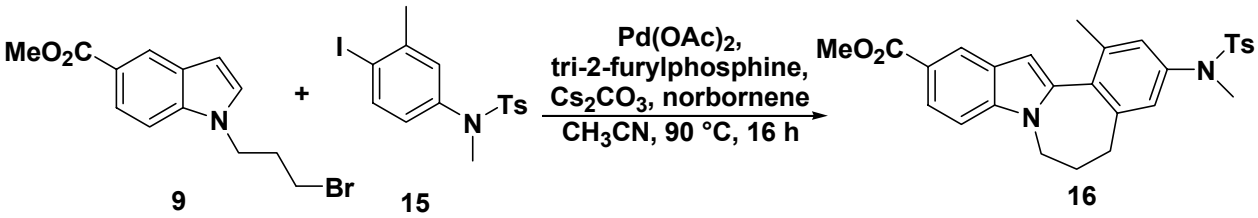
Methyl 1-methyl-2-nitro-5,6-dihydroindolo[2,1-*a*]isoquinoline-10-carboxylate (14).



Following the general procedure for the cyclization reaction using **9** and **13**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **14** (60.2 mg, 86%) as a yellow solid, mp = 175-177 °C. R_f = 0.50 on silica gel (30% EtOAc/hexanes). IR (neat) ν = 2949, 1709, 1519, 1350, 1307, 1253, 1159, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.97 (d, 1H, *J* = 8.7 Hz), 7.81 (d, 1H, *J* = 8.1 Hz), 7.38 (d, 1H, *J* = 8.7 Hz), 7.27 (d, 1H, *J* = 8.1 Hz),

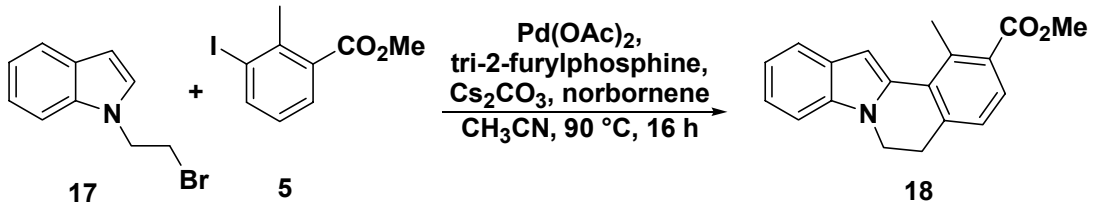
6.69 (s, 1H), 4.45 (dd, 1H, J = 14.7, 6.3 Hz), 3.95 (s, 3H), 3.77 (m, 1H), 2.74 (dd, 1H, J = 12.6, 6.0 Hz), 2.62 (s, 3H), 2.39 (m, 2H), 2.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 150.4, 144.1, 137.7, 137.0, 134.2, 131.2, 127.1, 126.9, 124.1, 124.0, 123.4, 121.8, 108.4, 105.2, 51.8, 40.3, 31.4, 29.9, 17.6; HRMS calcd for $C_{20}H_{18}N_2O_4$ $[M]^+$ 350.1266, found 350.1274.

Methyl 1-methyl-3-{methyl[(4-methylphenyl)sulfonyl]amino}-5,6-dihydroindolo[2,1-*a*]isoquinoline-10-carboxylate (16).



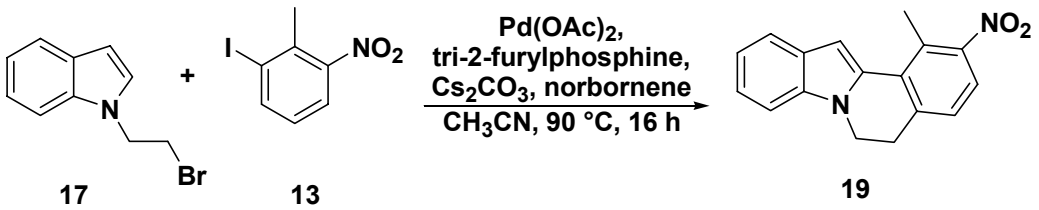
Following the general procedure for the cyclization reaction using **9** and **15**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **16** (83.9 mg, 85%) as a colourless oil. R_f = 0.29 on silica gel (30% EtOAc/hexanes). IR (neat) ν = 2949, 1708, 1610, 1468, 1351, 1307, 1252, 1164, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, 1H, J = 1.5 Hz), 7.93 (dd, 1H, J = 8.7, 1.5 Hz), 7.52 (d, 2H, J = 8.4 Hz), 7.36 (d, 1H, J = 8.7 Hz), 7.29 (d, 2H, J = 8.4 Hz), 6.96 (d, 1H, J = 2.1 Hz), 6.91 (d, 1H, J = 2.1 Hz), 6.64 (s, 1H), 4.38 (br, 1H), 3.94 (s, 3H), 3.38 (br, 1H), 3.18 (s, 3H), 2.44 (s, 3H), 2.43 (br, 3H), 2.42 (s, 3H), 2.03 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 143.7, 141.3, 139.7, 138.7, 137.9, 137.6, 133.7, 130.5, 129.4, 128.0, 127.2, 126.8, 124.9, 123.7, 122.9, 121.4, 108.2, 104.0, 51.9, 40.5, 38.1, 31.2, 30.3, 21.6, 21.3; HRMS calcd for $C_{28}H_{28}N_2O_4S$ $[M]^+$ 488.1769, found 488.1771.

Methyl 1-methyl-5,6-dihydroindolo[2,1-a]isoquinoline-2-carboxylate (18).



Following the general procedure for the cyclization reaction using **17** and **5**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **18** (46.0 mg, 79%) as a white solid, mp = 112-114 °C. R_f = 0.35 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 2948, 1719, 1431, 1316, 1265, 1210, 1075 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, 1H, *J* = 7.9 Hz), 7.63 (d, 1H, *J* = 7.9 Hz), 7.35 (d, 1H, *J* = 8.1 Hz), 7.25 (dt, 1H, *J* = 8.1, 1.1 Hz), 7.18 (d, 1H, *J* = 8.1 Hz), 7.11 (dt, 1H, *J* = 8.1, 1.1 Hz), 6.93 (s, 1H), 4.25 (t, 2H, *J* = 6.2 Hz), 3.93 (s, 3H), 3.12 (t, 2H, *J* = 6.2 Hz), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 137.9, 136.0, 135.3, 133.1, 131.7, 130.1, 128.2, 128.0, 125.6, 122.2, 120.9, 119.7, 108.7, 103.5, 52.1, 39.5, 31.2, 19.6; HRMS calcd for $C_{19}H_{17}NO_2$ $[M]^+$ 291.1259, found 291.1266.

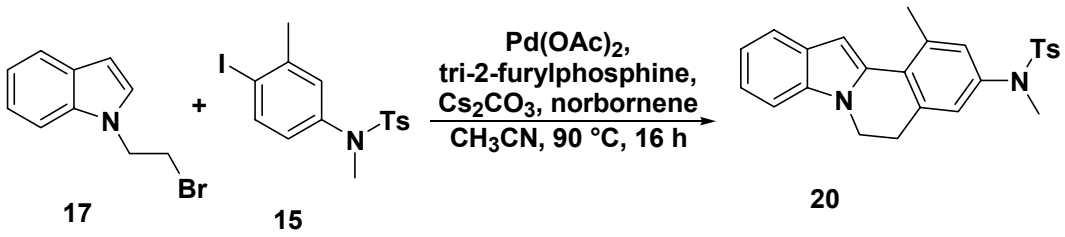
1-Methyl-2-nitro-5,6-dihydroindolo[2,1-a]isoquinoline (19).



Following the general procedure for the cyclization reaction using **17** and **13**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **19** (48.9 mg, 88%) as a white solid, mp = 113-115 °C. R_f = 0.28 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3054, 2925, 2876, 1519, 1350 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 1H, *J*= 7.9Hz), 7.62 (d, 1H, *J*= 7.9Hz), 7.37 (m, 1H), 7.28 (m, 2H), 7.14 (t, 1H, *J*= 6.8Hz), 6.96 (s, 1H), 4.28 (t, 2H, *J*= 6.1Hz), 3.17 (t, 2H, *J*= 6.1Hz), 2.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 138.6, 135.4, 131.9,

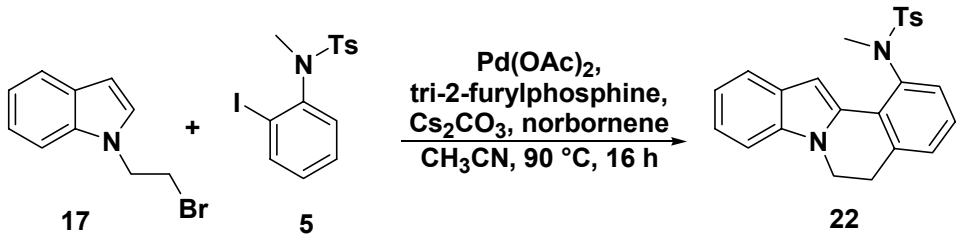
131.0, 129.0, 127.7, 126.4, 122.8, 121.9, 121.2, 120.0, 108.9, 104.1, 39.2, 31.0, 18.0; HRMS calcd for $C_{17}H_{14}N_2O_2$ $[M]^+$ 278.1055, found 278.1050.

N,4-Dimethyl-N-(1-methyl-5,6-dihydroindolo[2,1-a]isoquinolin-3-yl)benzenesulfonamide (20).



Following the general procedure for the cyclization reaction using **17** and **15**, and purification by flash chromatography using 20% EtOAc/hexanes as eluant resulted **20** (77.4 mg, 93%) as a colourless oil. R_f = 0.13 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3053, 2953, 1597, 1470, 1347, 1166, 1088 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, 1H, *J* = 7.9 Hz), 7.50 (d, 2H, *J* = 8.1 Hz), 7.34 (d, 1H, *J* = 7.9 Hz), 7.25 (m, 3H), 7.11 (t, 1H, *J* = 7.9 Hz), 6.99 (d, 1H, *J* = 2.0 Hz), 6.87 (s, 1H), 6.85 (d, 1H, *J* = 2.0 Hz), 4.22 (t, 2H, *J* = 6.4 Hz), 3.17 (s, 3H), 3.09 (t, 2H, *J* = 6.4 Hz), 2.58 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 139.6, 135.9, 135.4, 134.6, 133.6, 133.4, 129.3, 128.1, 127.9, 127.4, 127.2, 124.4, 122.1, 120.8, 119.6, 108.7, 102.2, 39.7, 37.9, 30.6, 22.9, 21.5; HRMS calcd for $C_{25}H_{24}N_2O_2S$ $[M]^+$ 416.1558, found 416.1562.

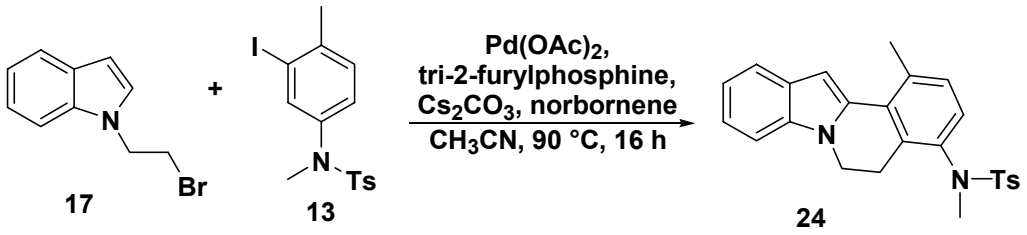
N-5,6-Dihydroindolo[2,1-a]isoquinolin-1-yl-N,4-dimethylbenzenesulfonamide (22).



Following the general procedure for the cyclization reaction using **17** and **5**, and purification by flash chromatography using 20% EtOAc/hexanes as eluant resulted **22** (61.1 mg, 76%) as a white

solid, mp = 193-199 °C. R_f = 0.29 on silica gel (20% EtOAc/hexanes). IR (neat) ν = 3053, 2931, 1478, 1345, 1154 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 3H), 7.43 (s, 1H), 7.25 (m, 5H), 7.10 (td, 1H, *J*= 7.9-1.0Hz), 7.08 (t, 1H, *J*= 8.8Hz), 6.78 (dd, 1H, *J*= 7.9-1.0Hz), 4.23 (m, 2H), 3.23 (s, 3H), 3.18 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 138.0, 135.8, 135.6 , 135.1, 130.9, 129.3, 128.9, 128.6, 128.2, 127.0, 126.0, 122.1, 121.4, 119.6, 108.6, 102.9, 39.6, 38.3, 30.1, 21.5; HRMS calcd for $C_{24}H_{22}N_2O_2S$ $[M]^+$ 402.1402, found 402.1401.

N,4-Dimethyl-N-(1-methyl-5,6-dihydroindolo[2,1-a]isoquinolin-4-yl)benzenesulfonamide (24).



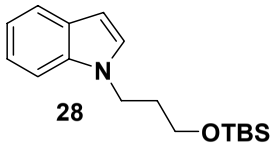
Following the general procedure for the cyclization reaction using **17** and **13**, and purification by flash chromatography using 10% EtOAc/hexanes as eluant resulted **24** (31.6 mg, 38%) as a thick white oil. R_f = 0.30 on silica gel (10% EtOAc/hexanes). IR (neat) ν = 3053, 2924, 1741, 1487, 1463, 1346, 1232, 1154 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, 1H, *J*= 7.8Hz), 7.60 (d, 2H, *J*= 8.4Hz), 7.38 (d, 1H, *J*= 8.1Hz), 7.32 (d, 2H, *J*= 8.4Hz), 7.26 (t, 1H, *J*= 7.8Hz), 7.12 (t, 1H, *J*= 7.8Hz), 7.05 (d, 1H, *J*= 8.1Hz), 6.90 (s, 1H), 6.45 (d, 1H, *J*= 8.1Hz), 4.27 (m, 1H), 4.14 (m, 1H), 3.44 (m, 1H), 3.27 (m, 1H), 3.17 (s, 3H), 2.66 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.5, 135.5, 135.4, 134.4, 133.6, 130.3, 1130.1, 129.6, 128.2, 128.1, 124.7, 122.2, 120.9, 119.7, 109.0, 102.6, 39.6, 39.2, 26.1, 23.1, 21.7; HRMS calcd for $C_{25}H_{24}N_2O_2S$ $[M]^+$ 416.1558, found 416.1557.

References

1. Kajigaeshi, S.; Kakinami, T.; Yamasaki, H. ; Fujisaki, S.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600-602.

2. Zenner, J. M.; Larock, R. C. *J. Org. Chem.* **1999**, *64*, 7312-7322.

1H NMR (400 MHz, CDCl3)



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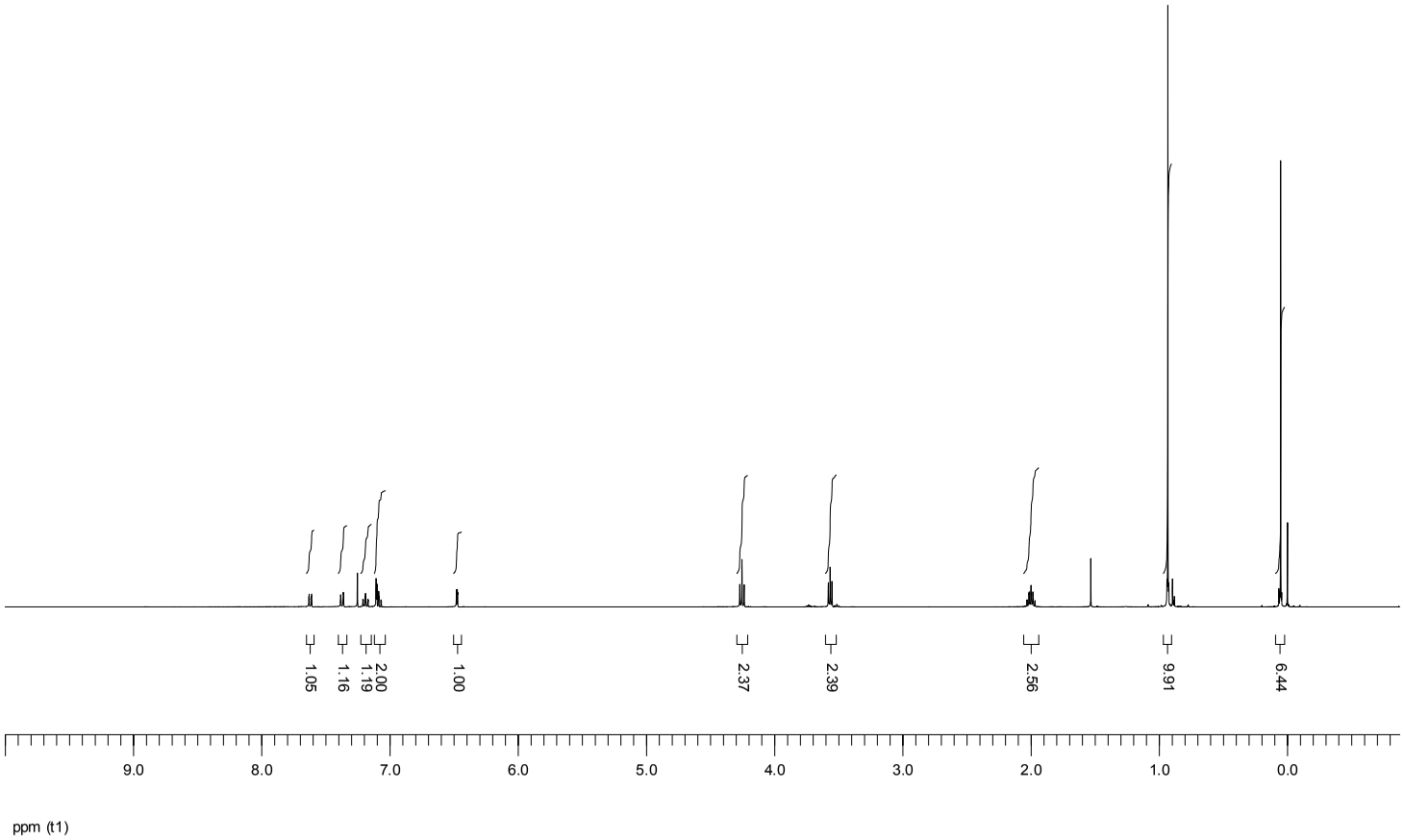
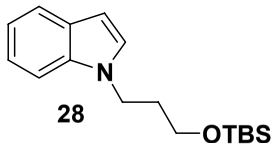


13C NMR (100 MHz, CDCl3)



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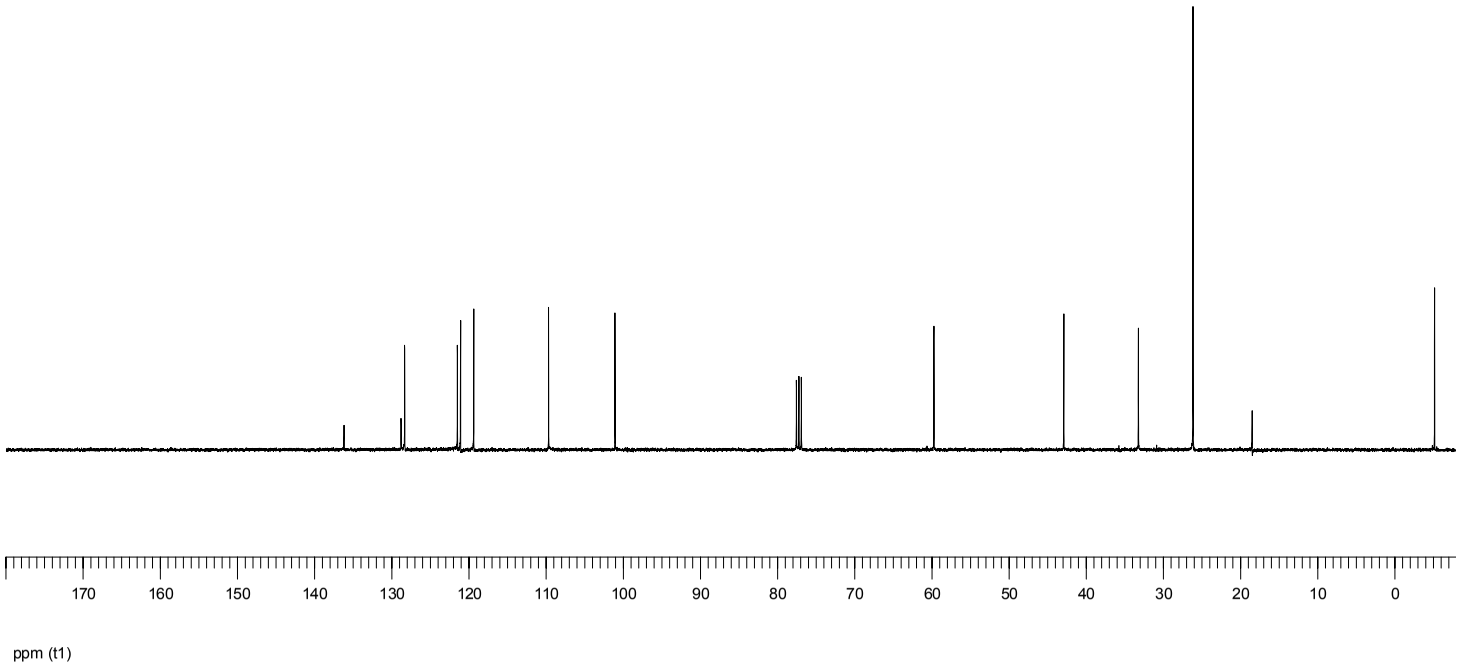
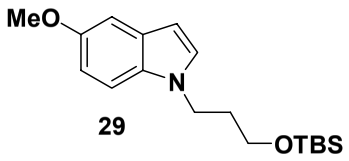


1H NMR (400 MHz, CDCl3)



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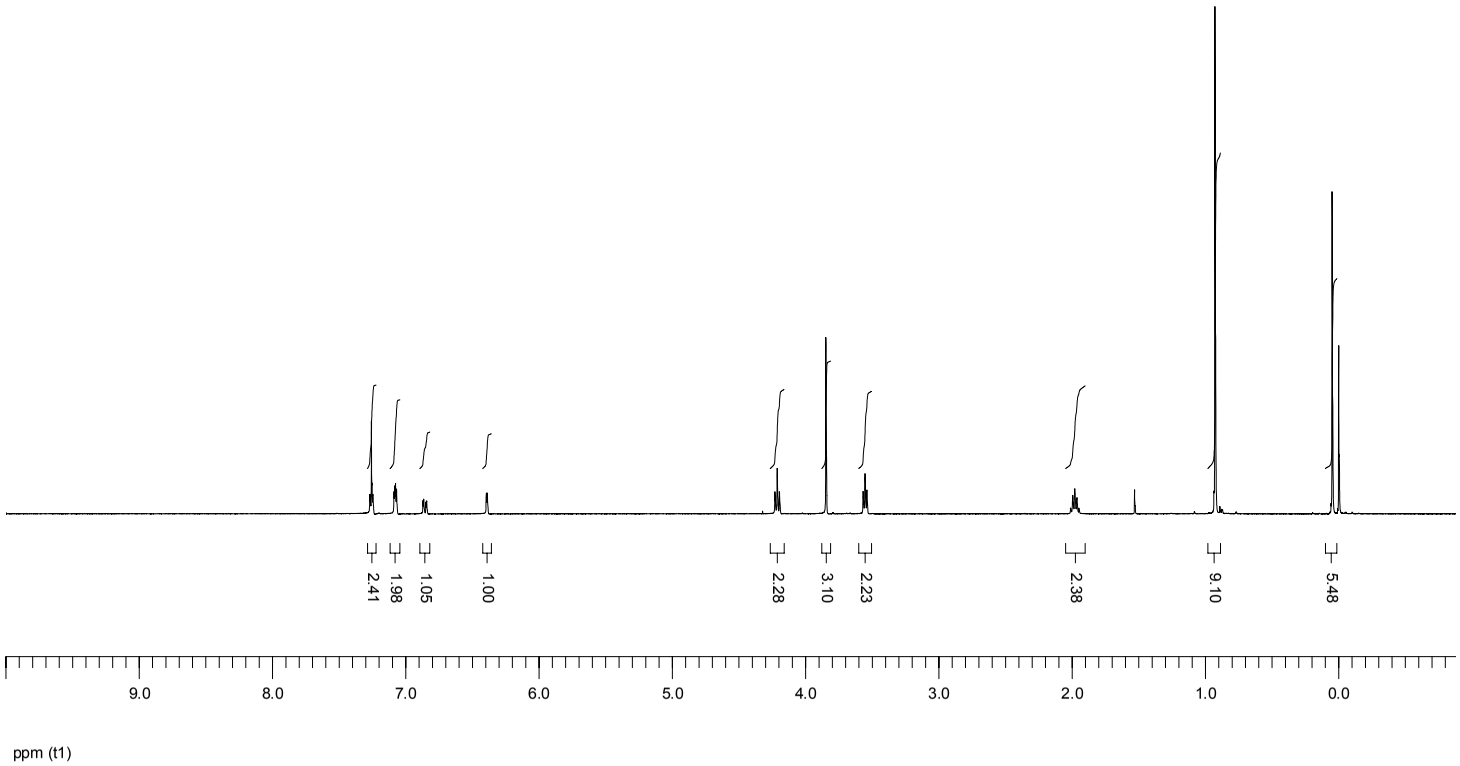
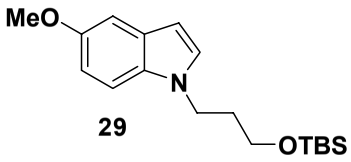


13C NMR (100 MHz, CDCl3)



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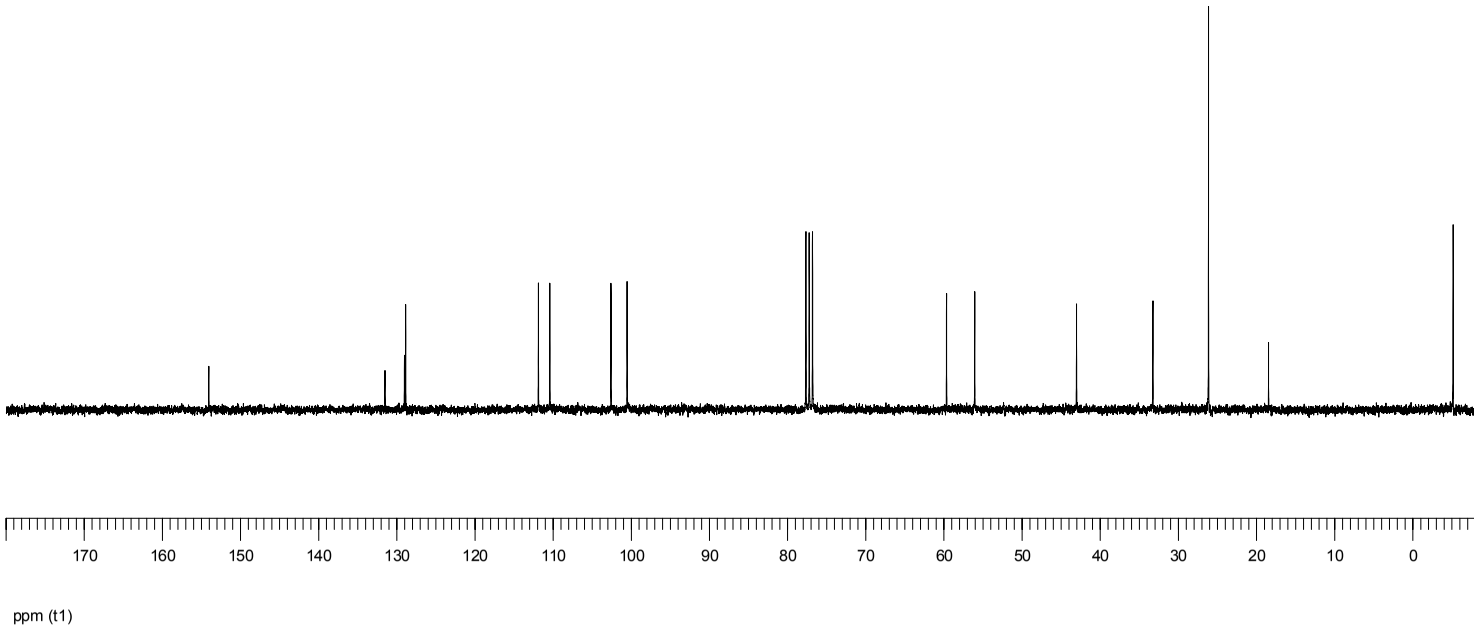
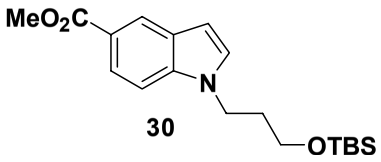


1H NMR (400 MHz, CDCl3)



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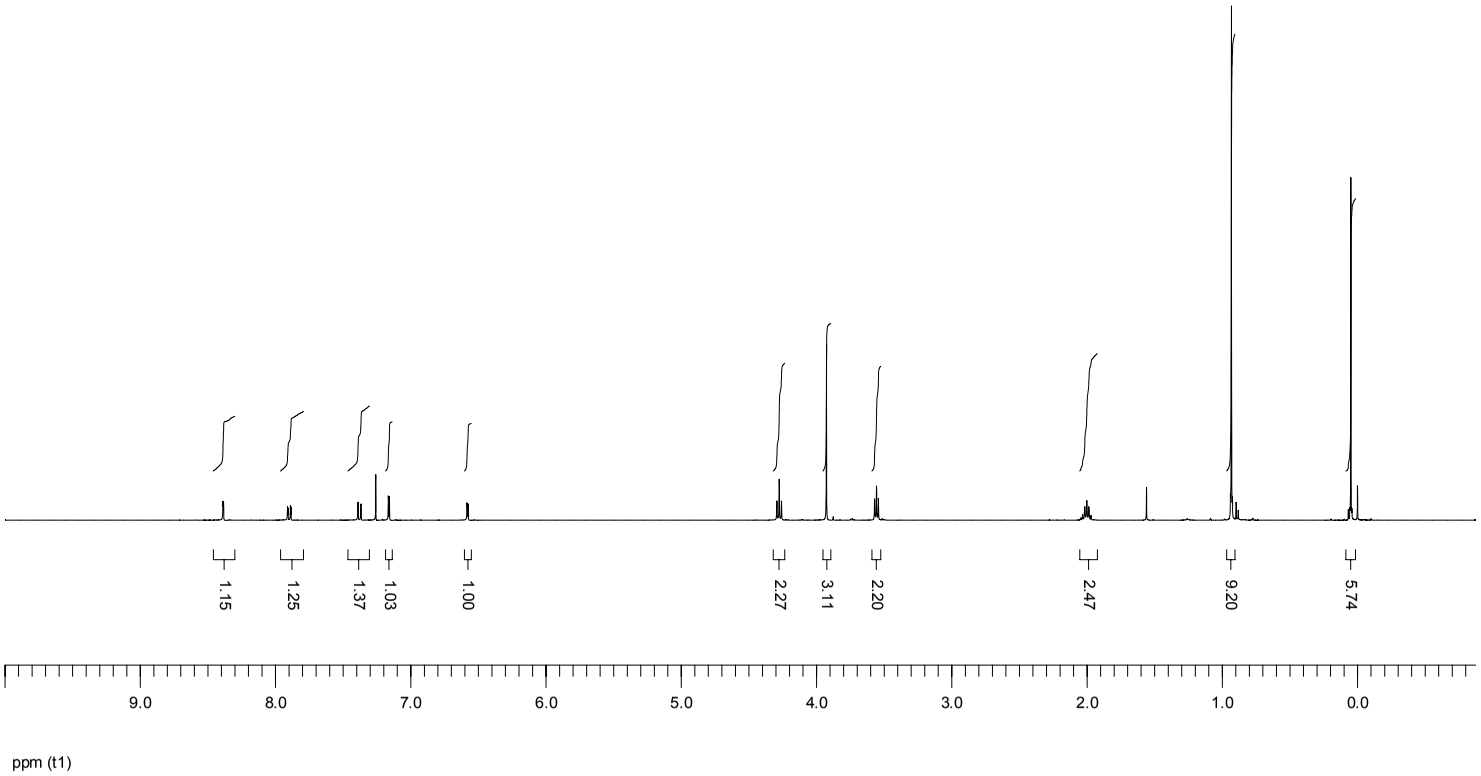
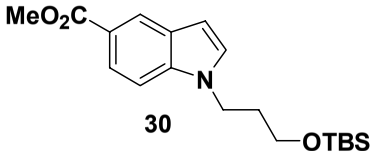


13C NMR (100 MHz, CDCl3)



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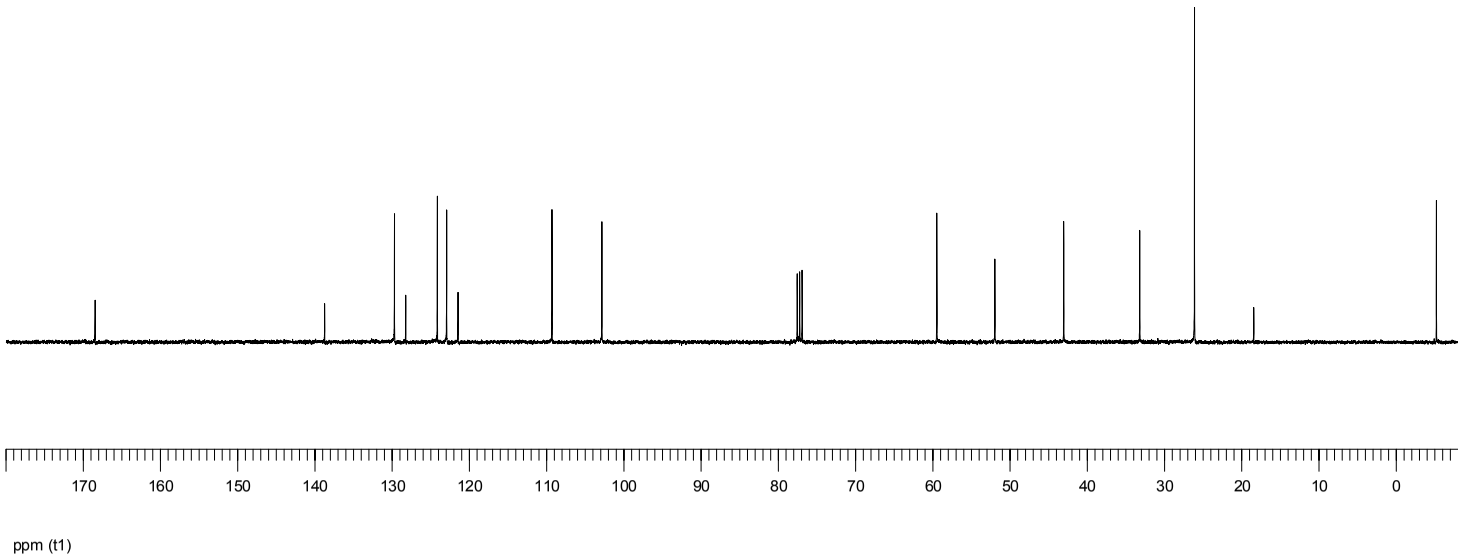
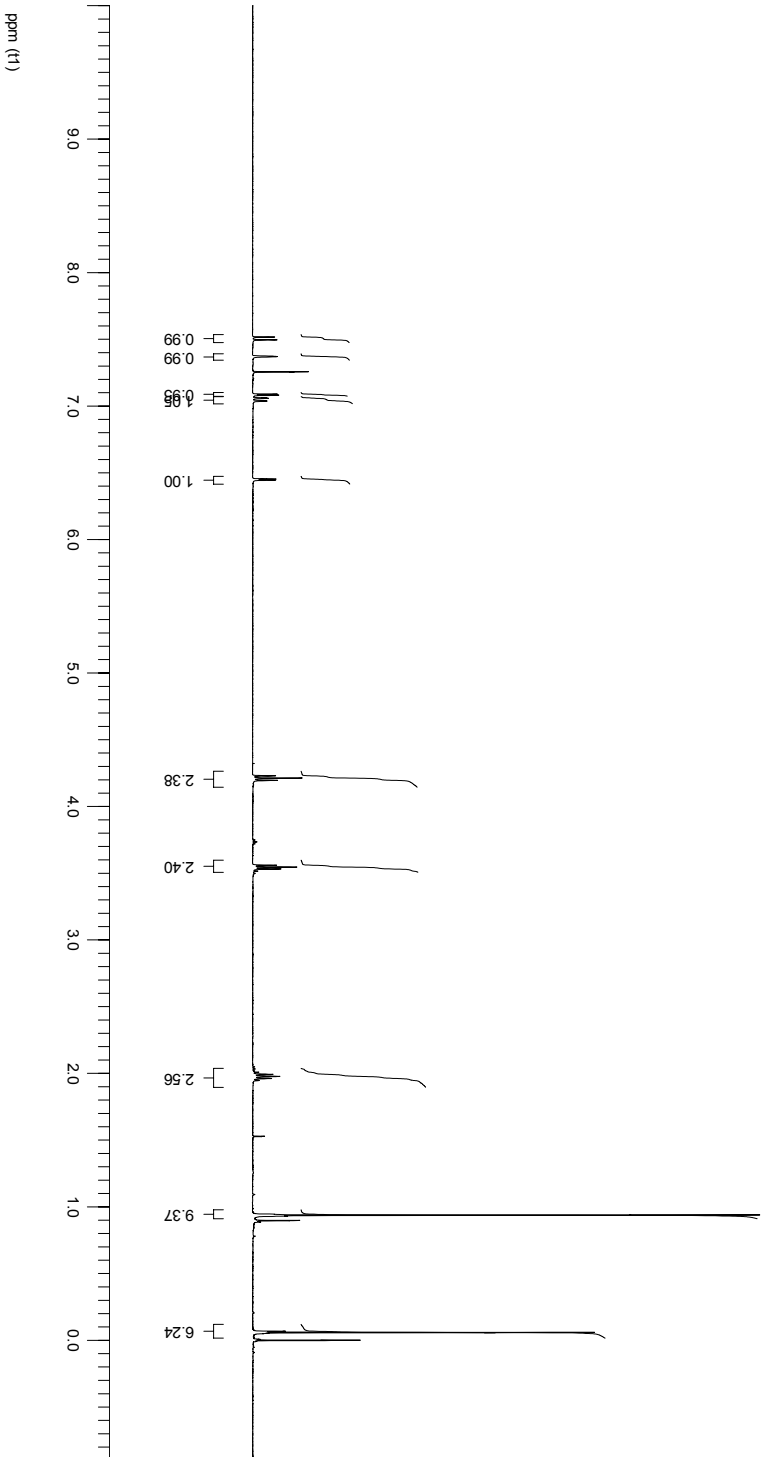
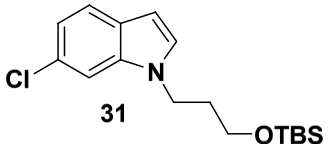



1H NMR (400 MHz, CDCl3)
Cl
N
OTBS
31
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.99
0.99
1.06
0.98
1.00
2.38
2.40
2.56
9.37
6.24

13C NMR (100 MHz, CDCl3)



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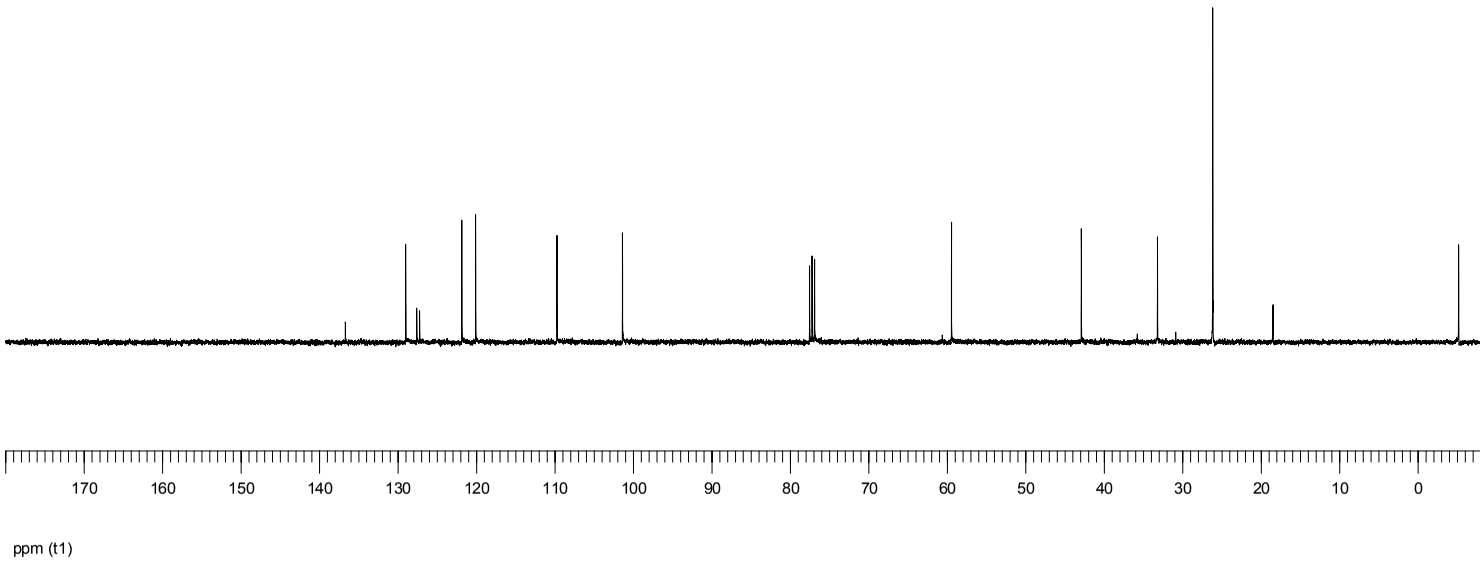

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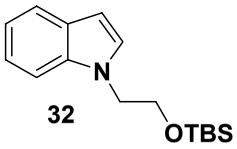

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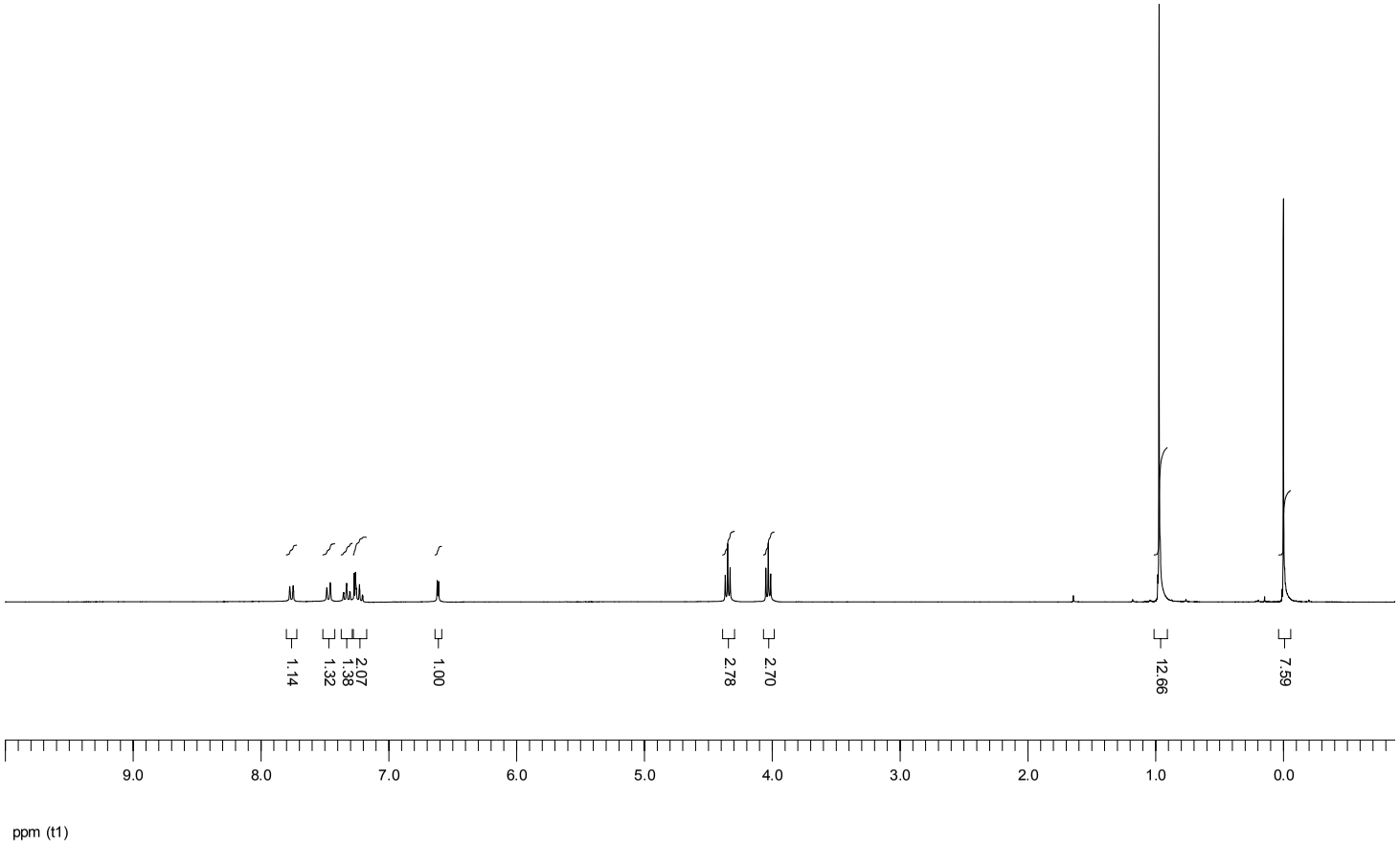
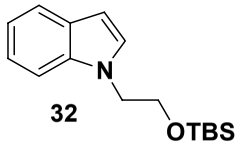


13C NMR (100 MHz, CDCl3)



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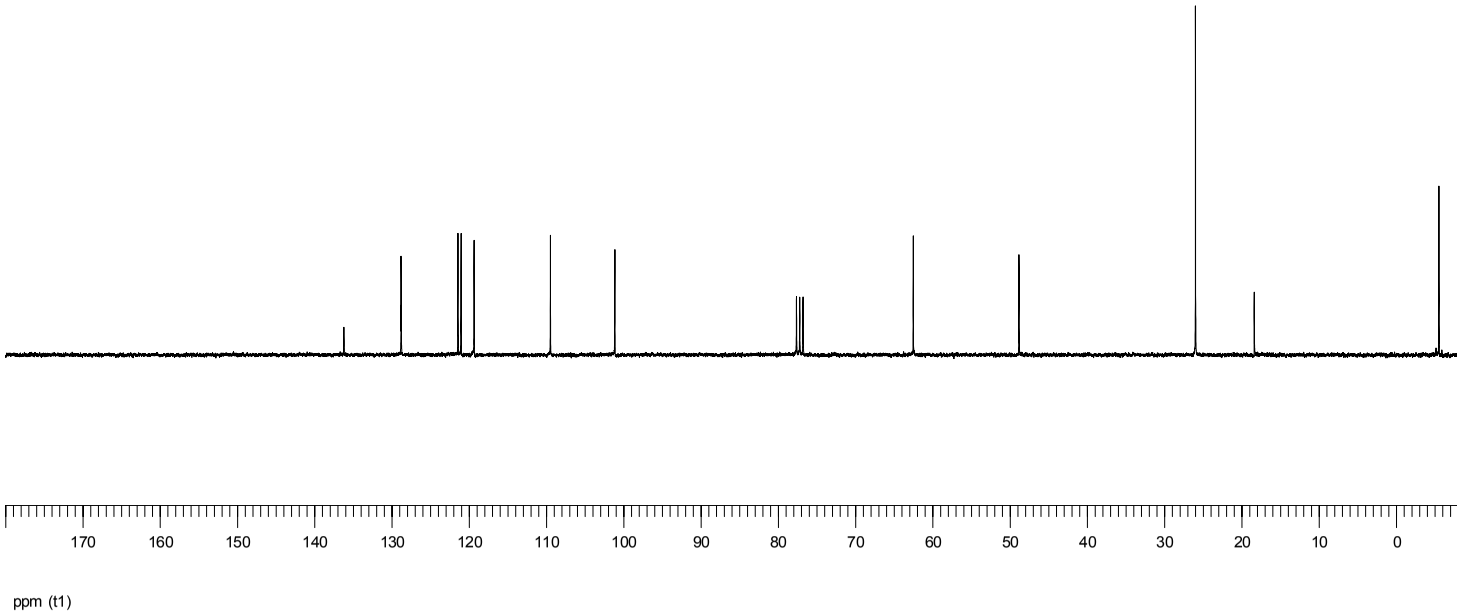
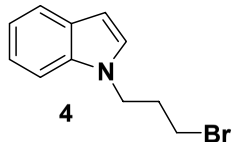


1H NMR (400 MHz, CDCl3)



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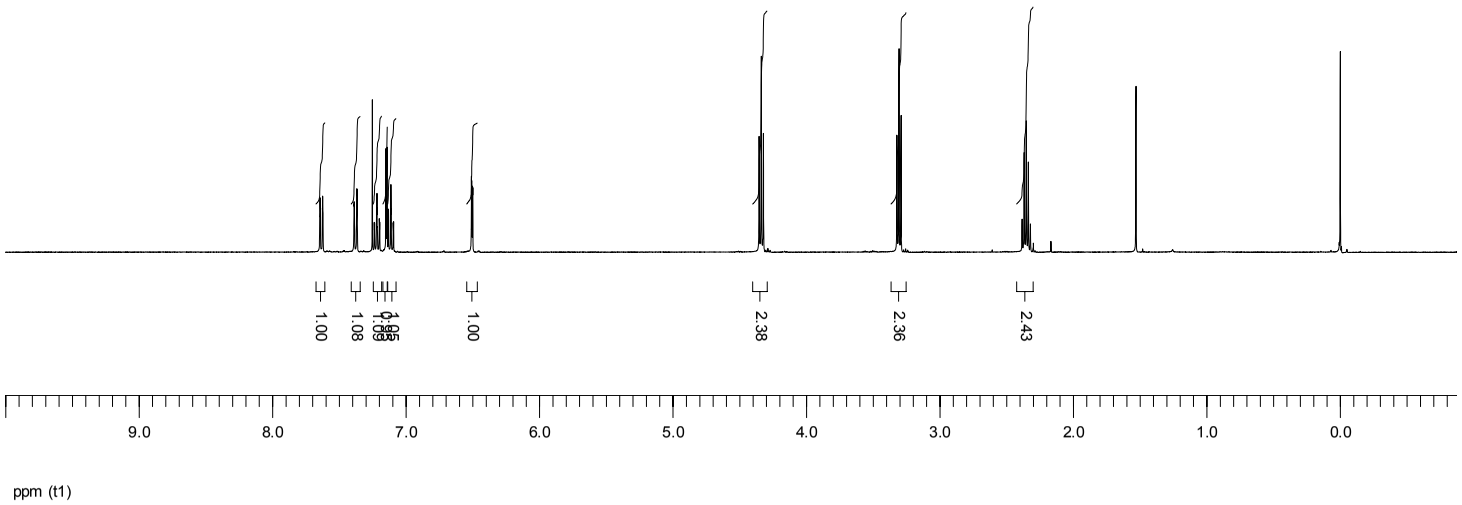
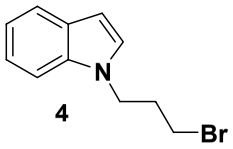


13C NMR (100 MHz, CDCl3)



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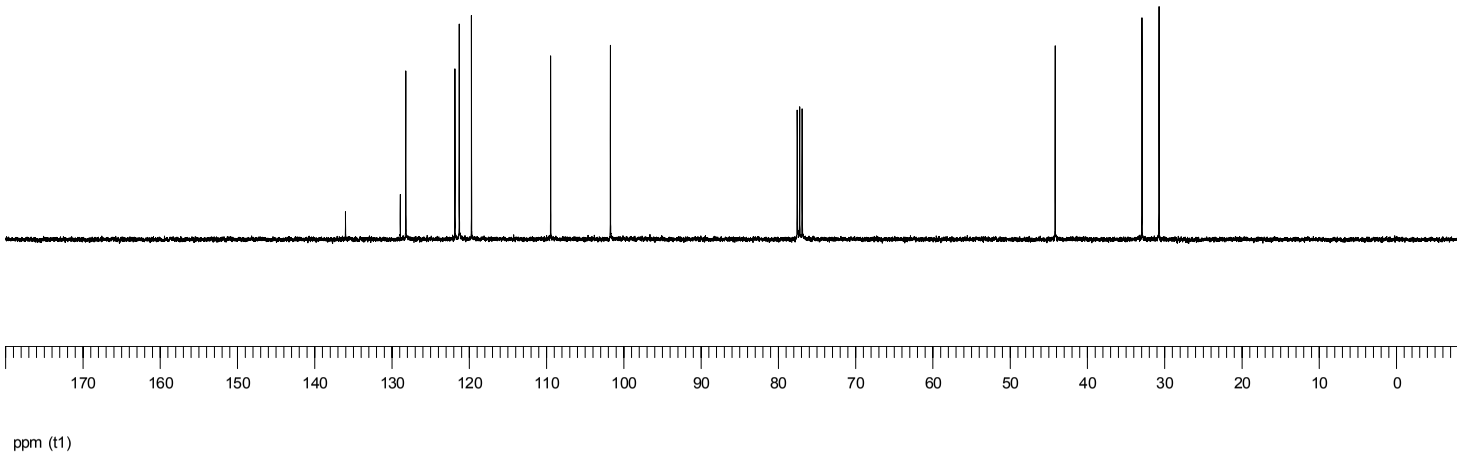
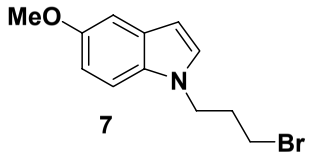


1H NMR (400 MHz, CDCl3)



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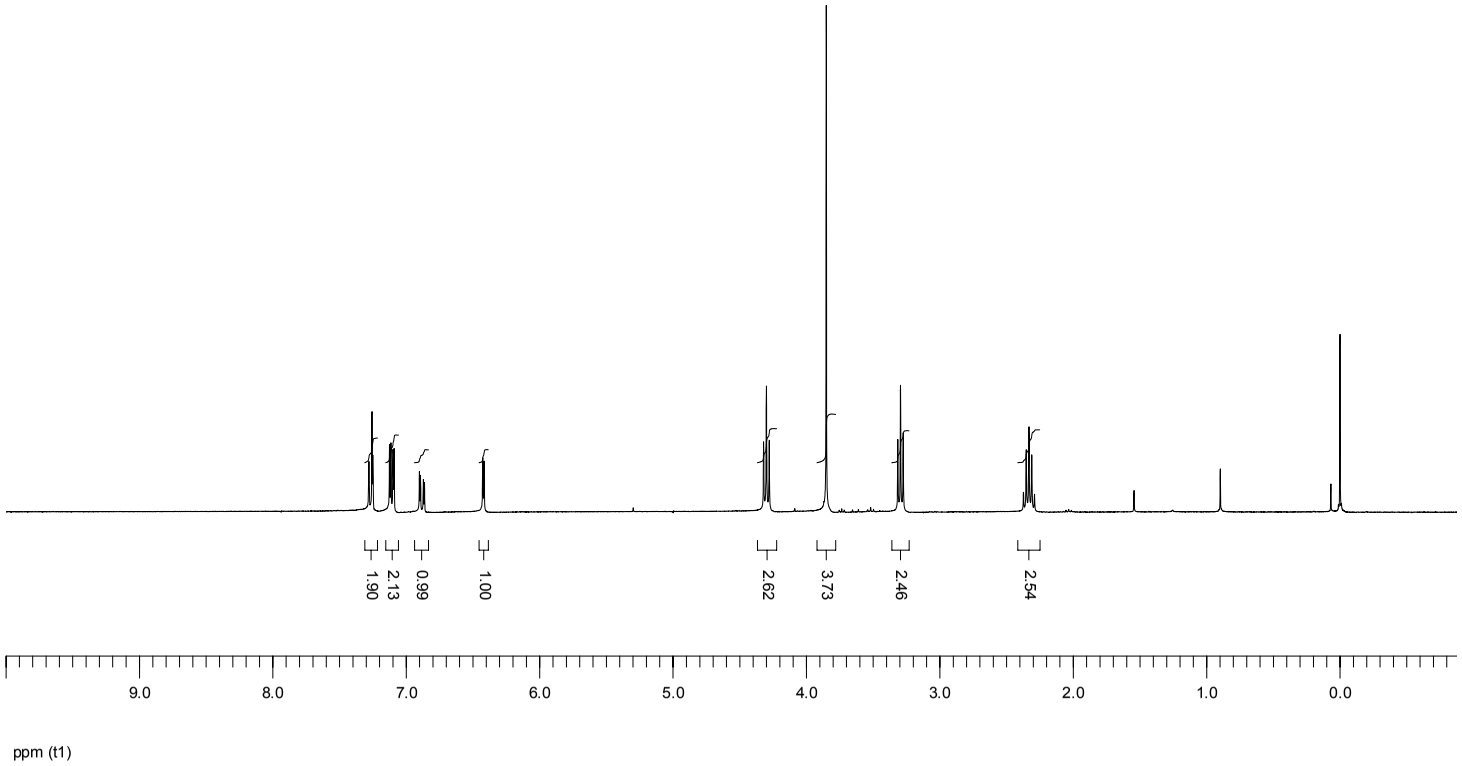
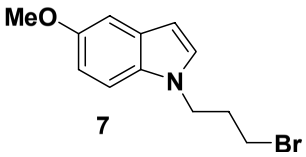


13C NMR (100 MHz, CDCl3)



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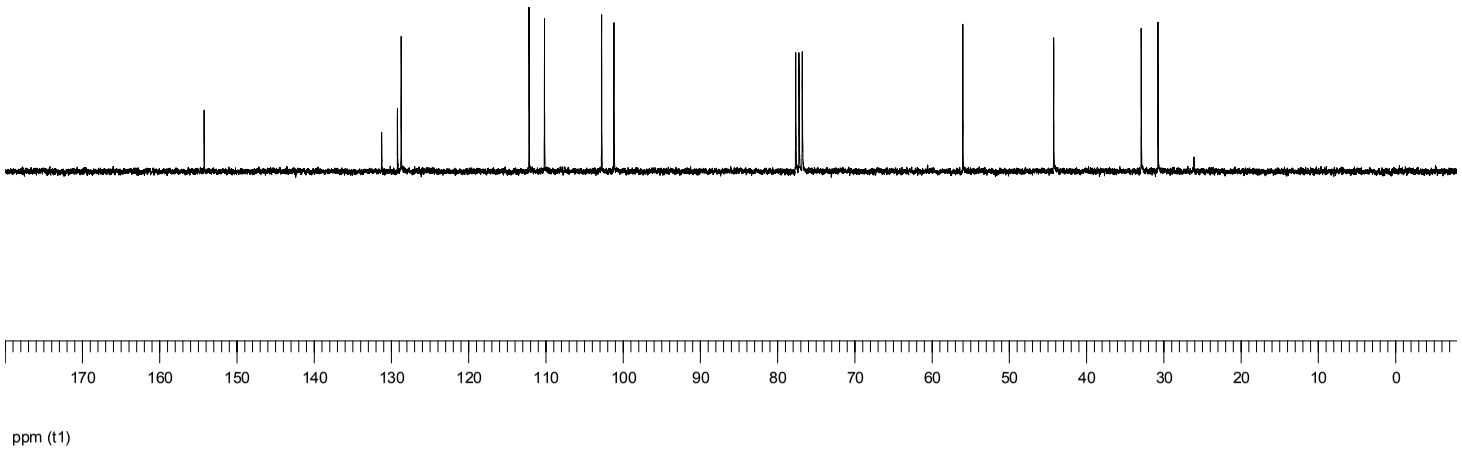
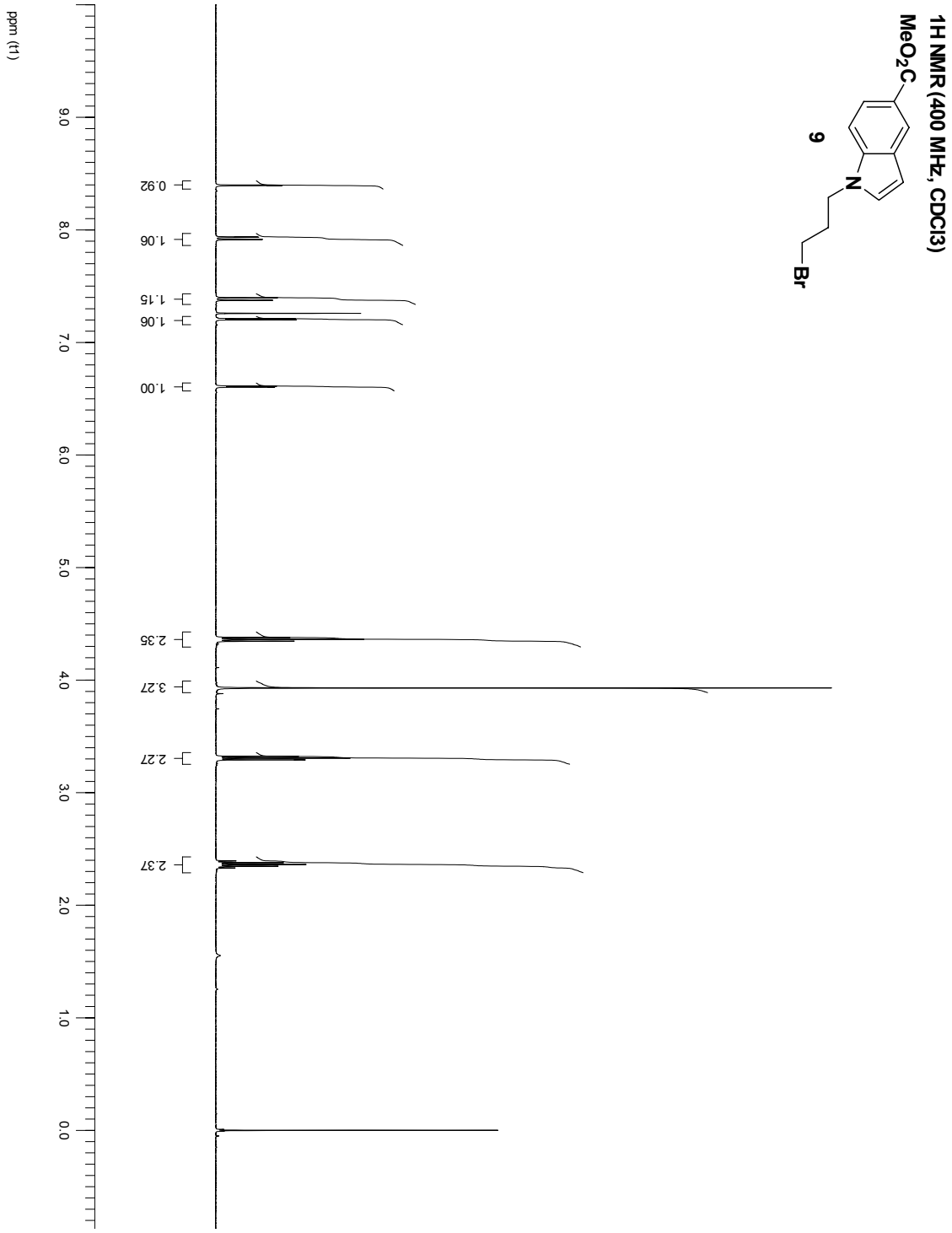
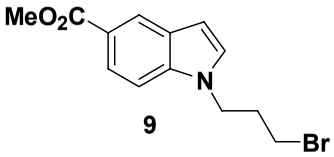



1H NMR (400 MHz, CDCl3)
MeO2C
9
N
Br
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.92
1.06
1.15
1.06
1.00
2.35
3.27
2.27
2.37

13C NMR (100 MHz, CDCl3)



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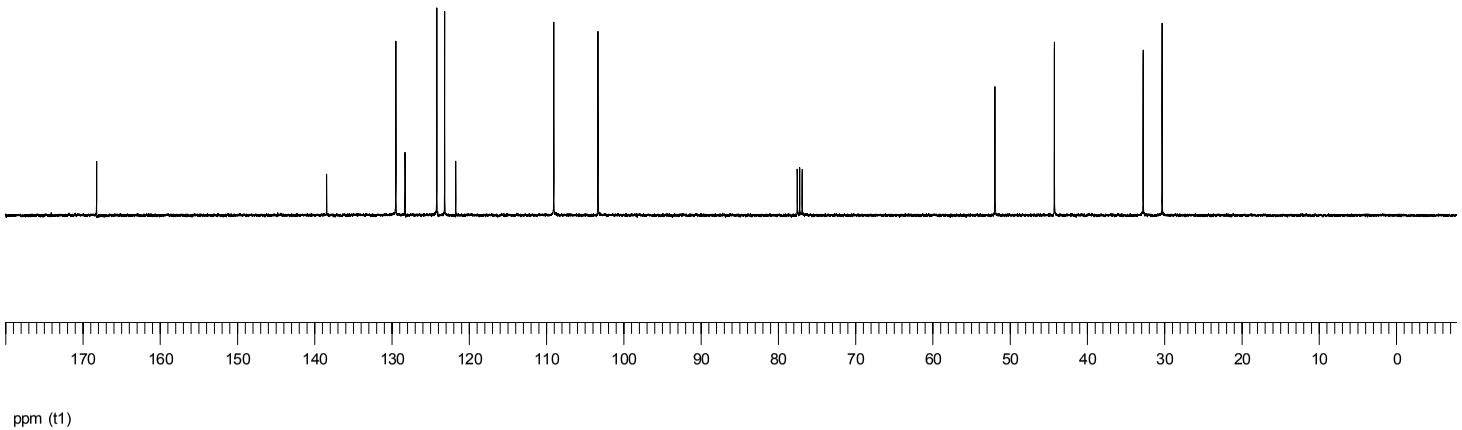
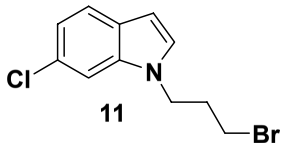


1H NMR (400 MHz, CDCl3)



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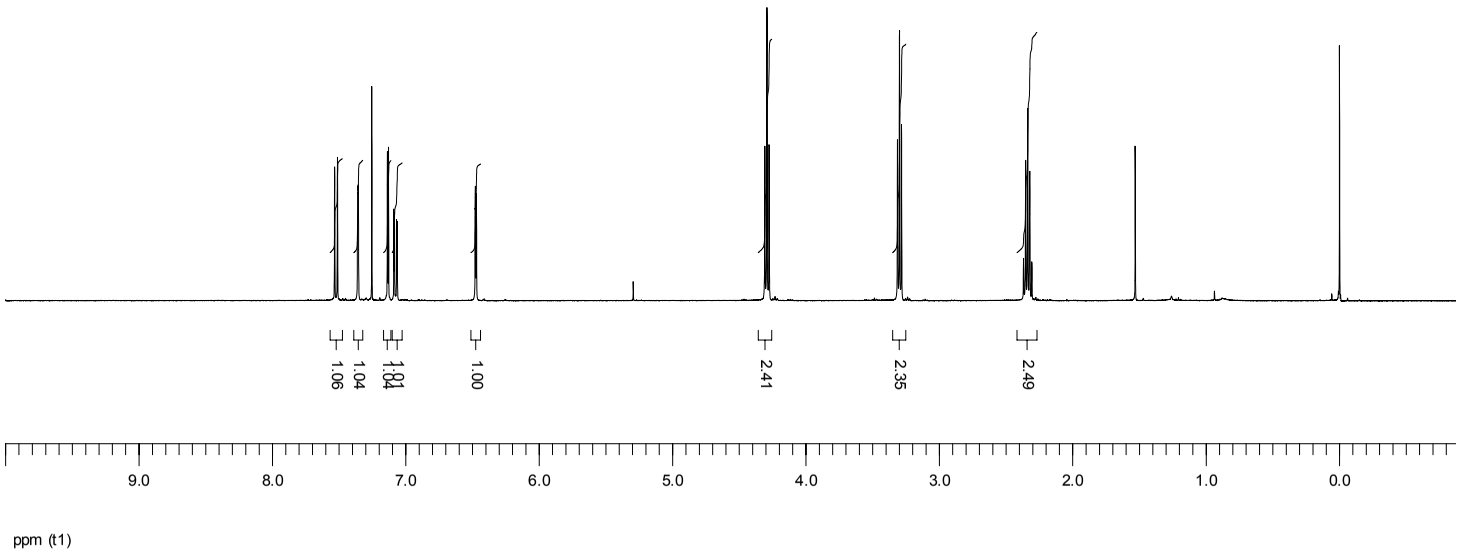
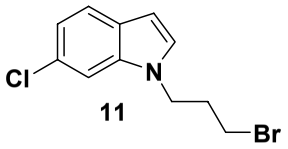


13C NMR (100 MHz, CDCl3)



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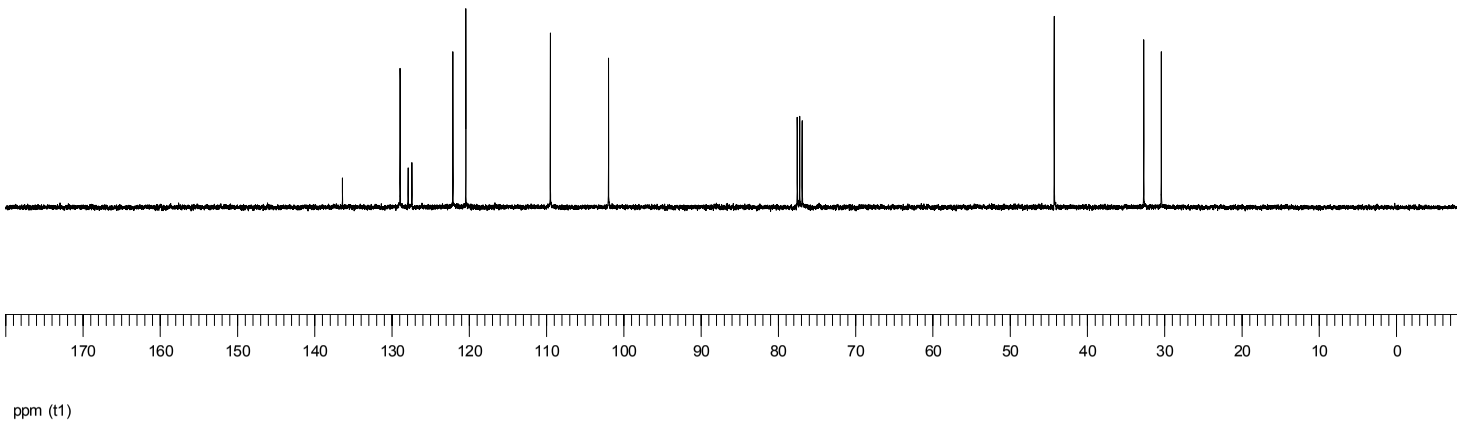
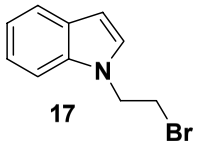


1H NMR (400 MHz, CDCl3)



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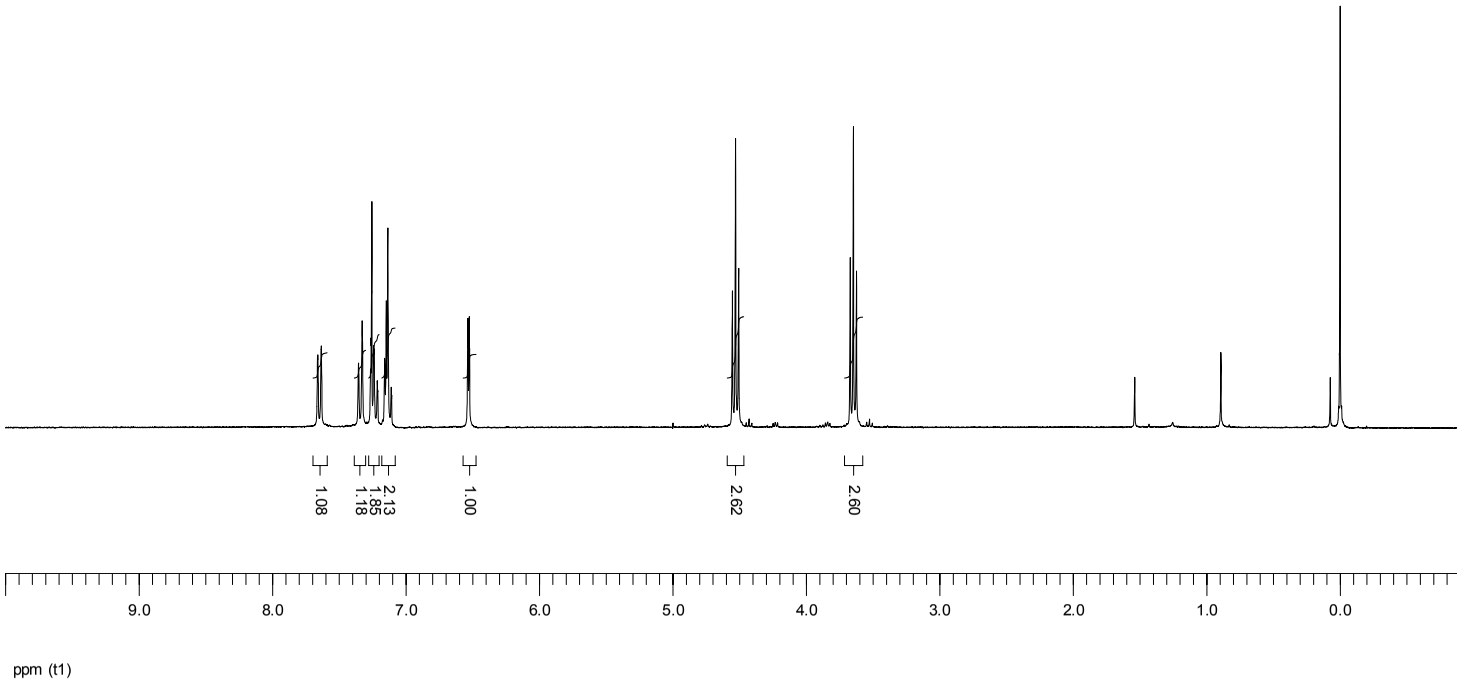
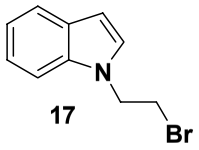


13C NMR (100 MHz, CDCl3)



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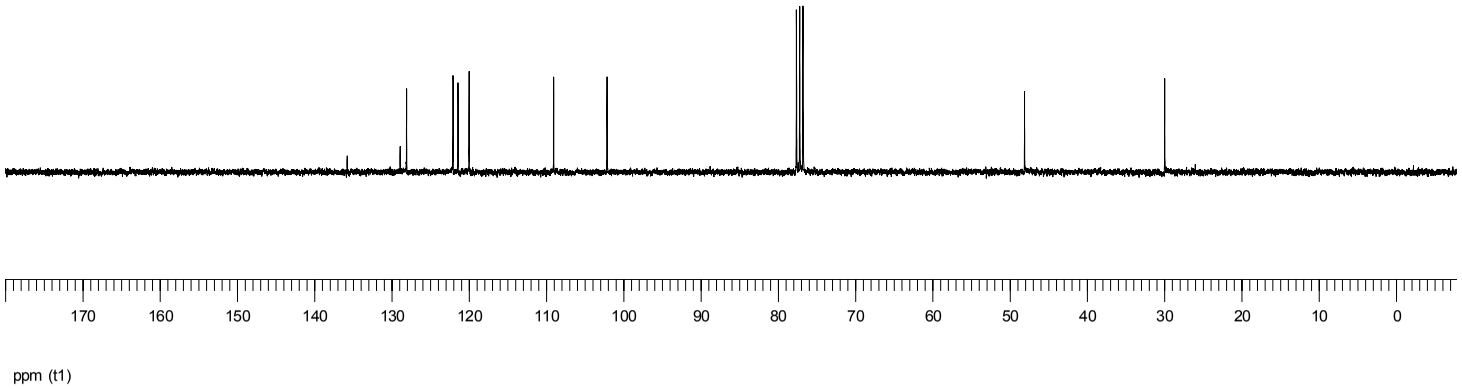
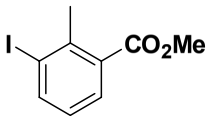


1H NMR (400 MHz, CDCl3)



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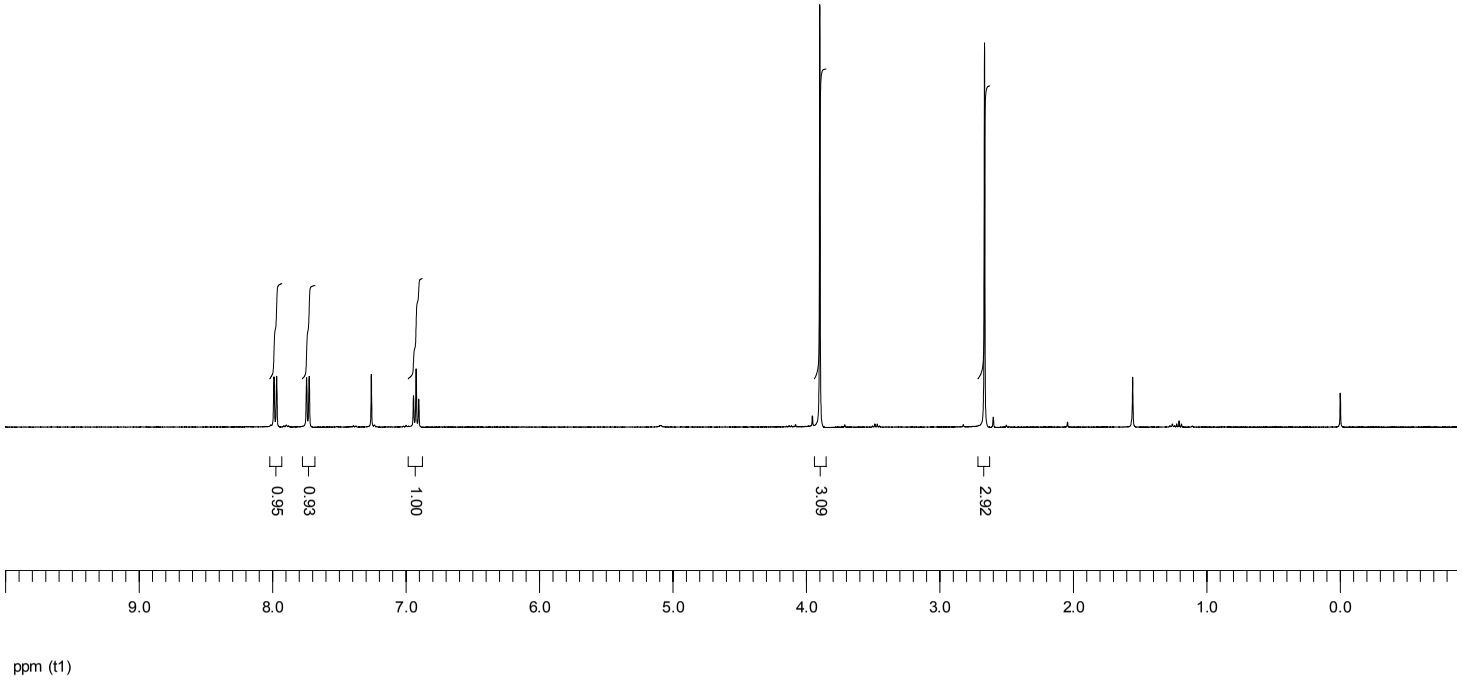
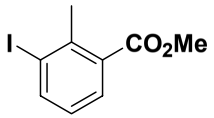


13C NMR (100 MHz, CDCl3)



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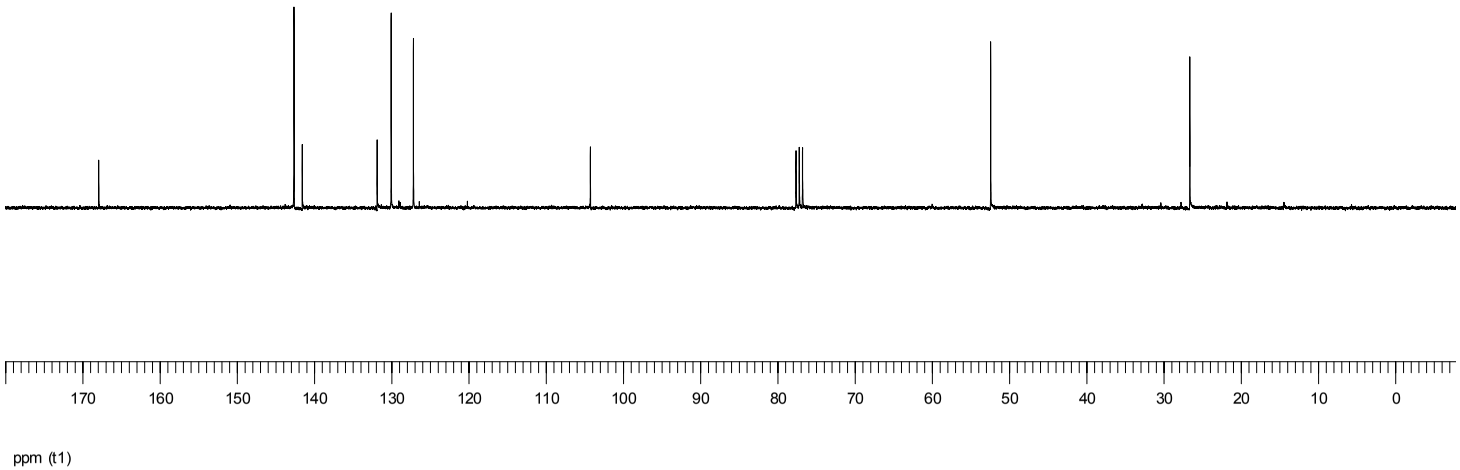
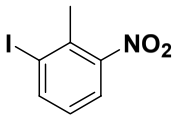


1H NMR (400 MHz, CDCl3)



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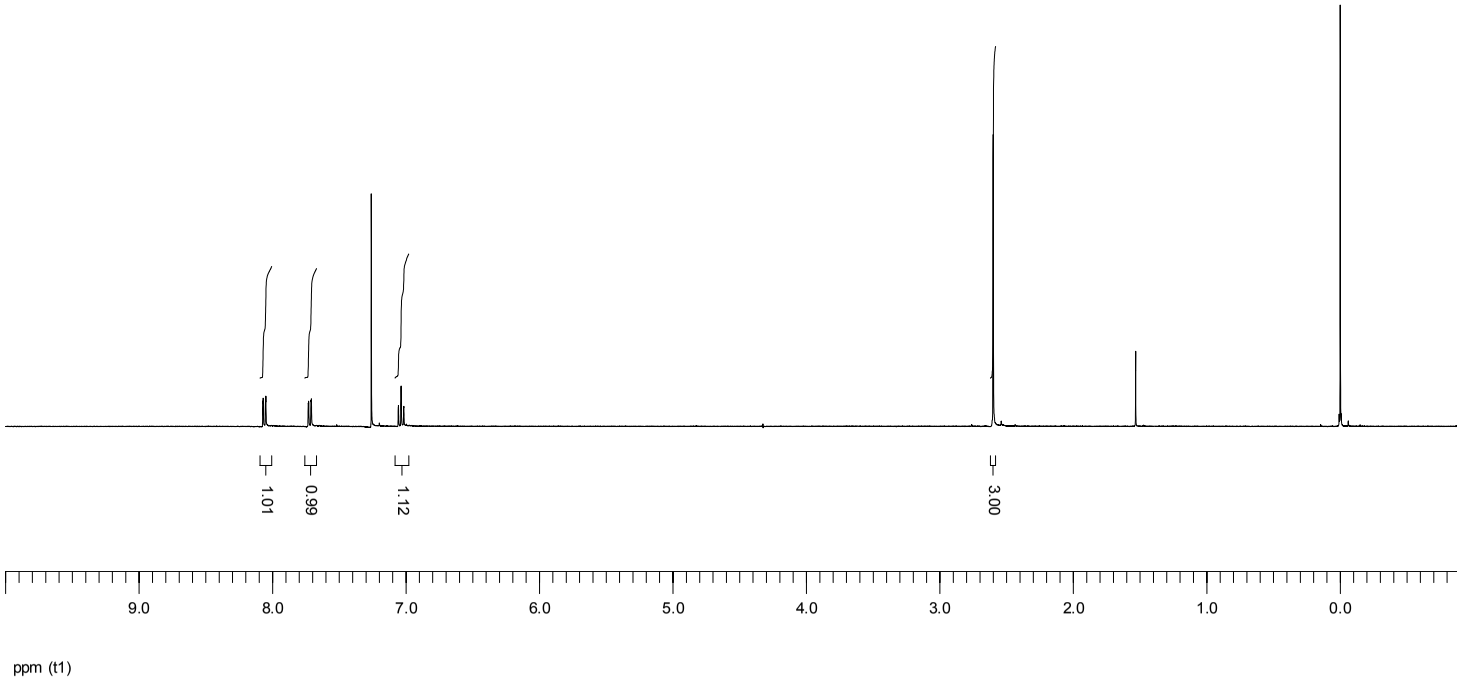

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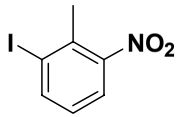

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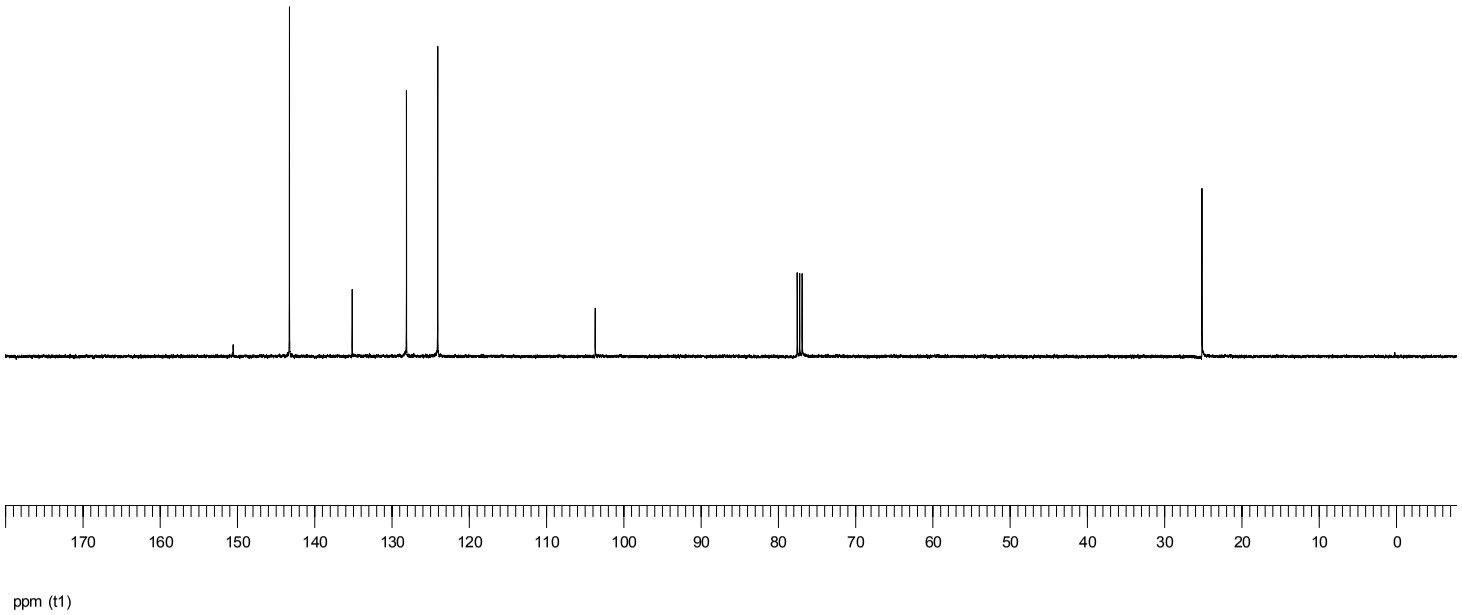

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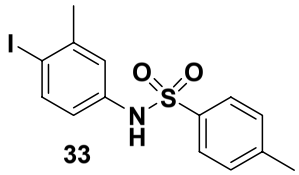

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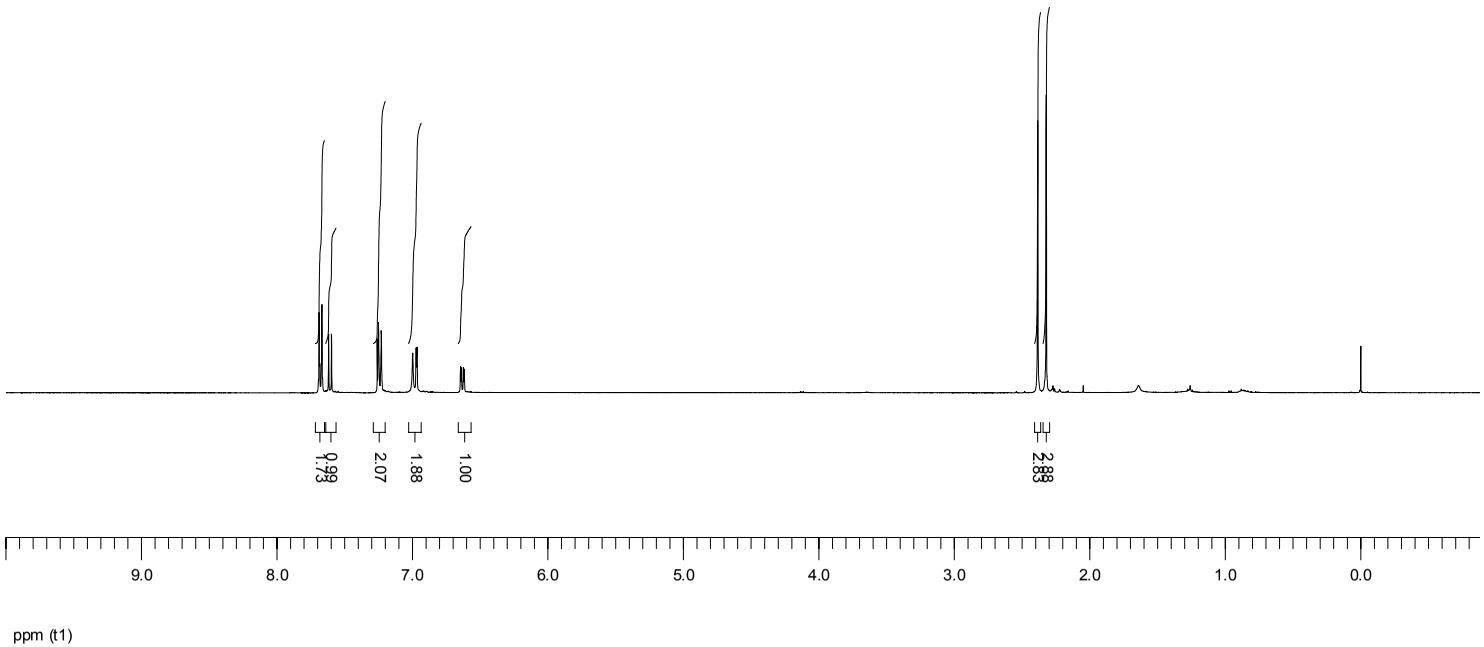

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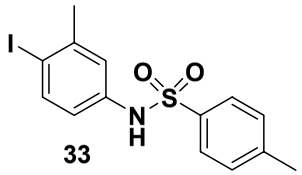

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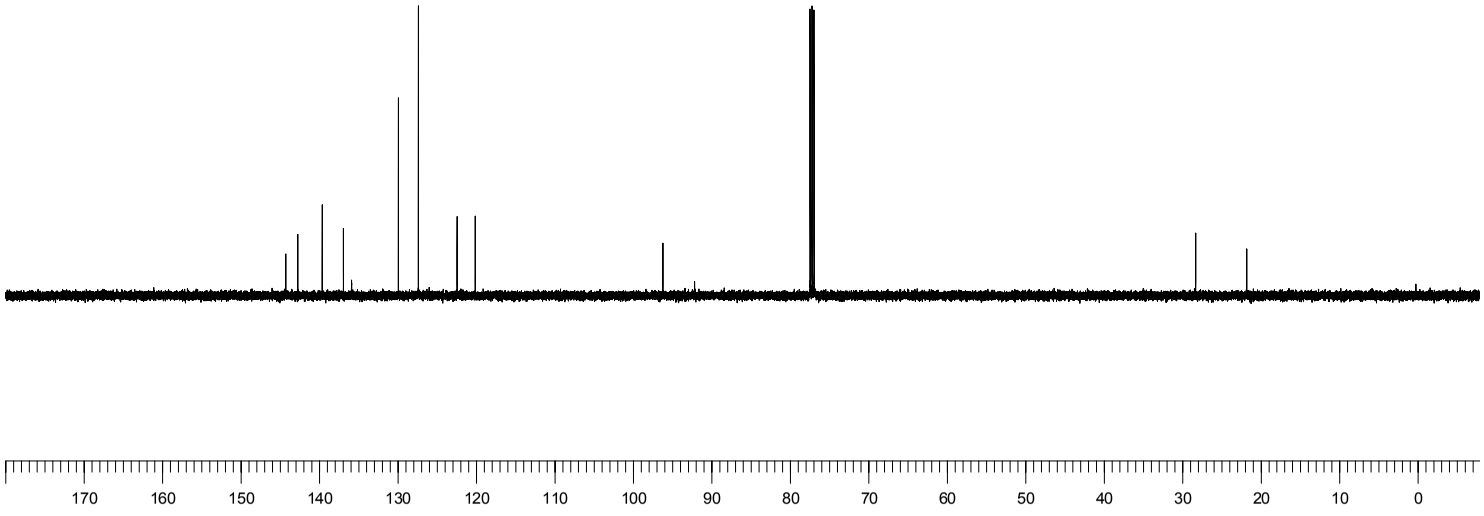

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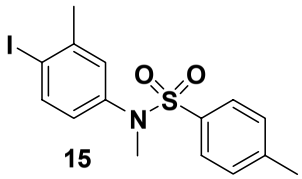

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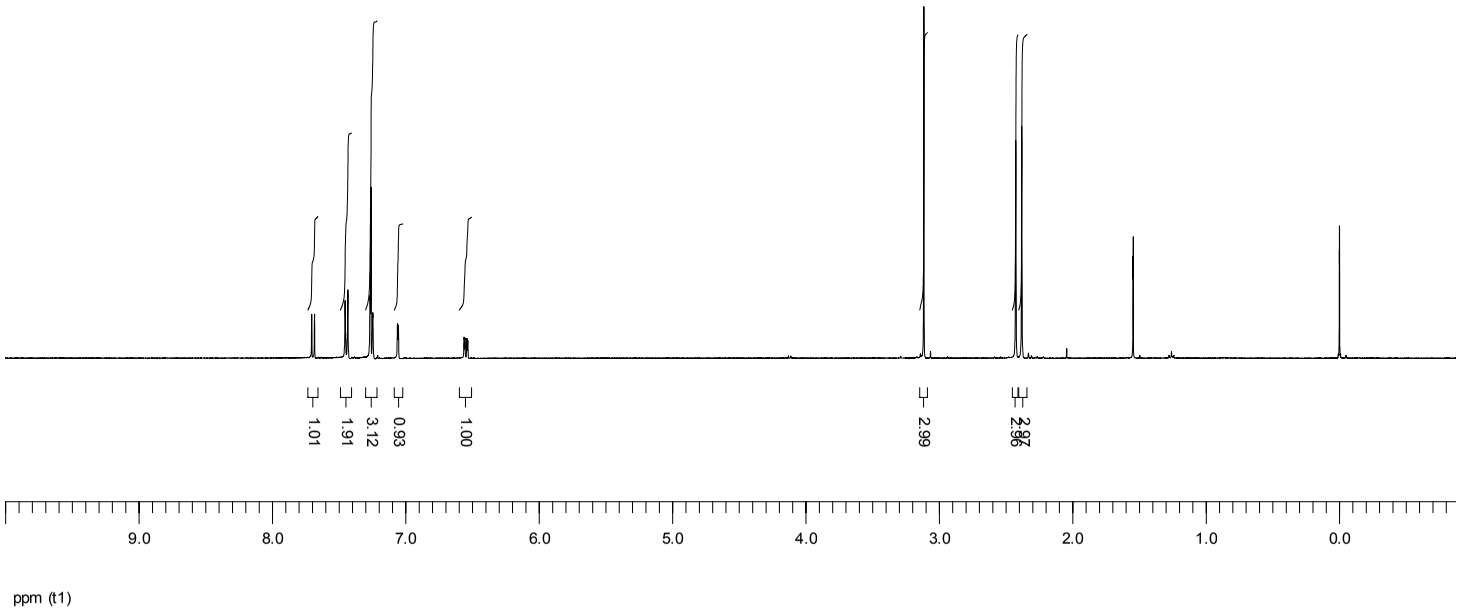

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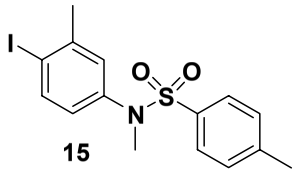

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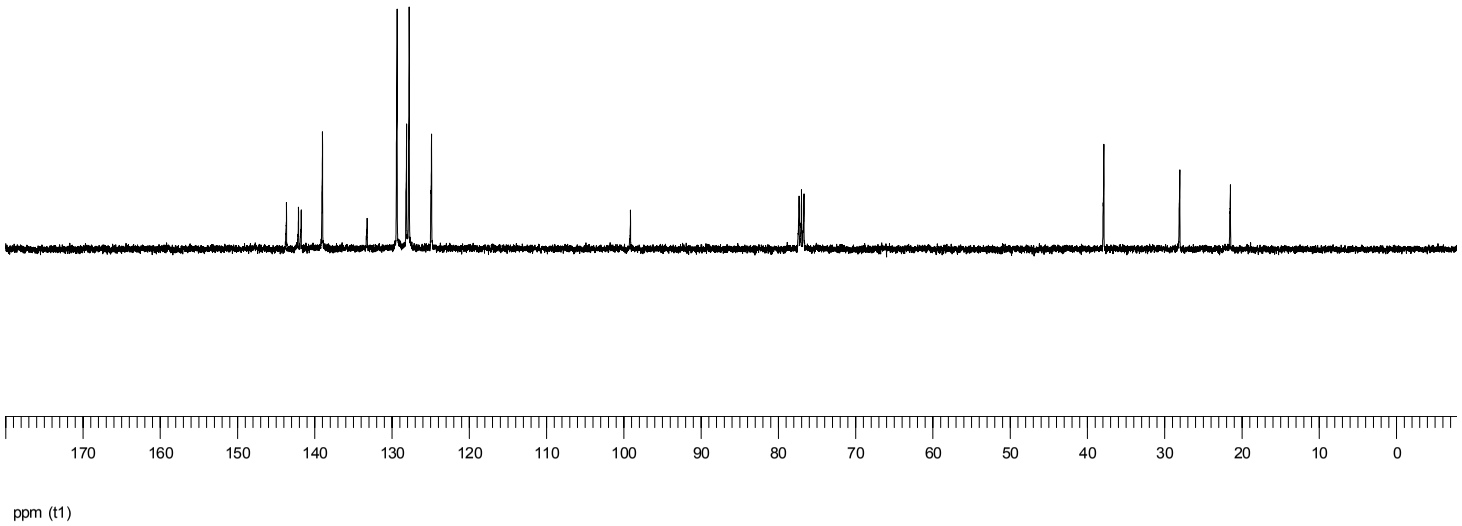

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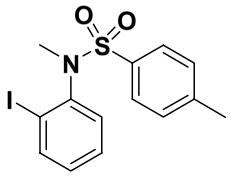

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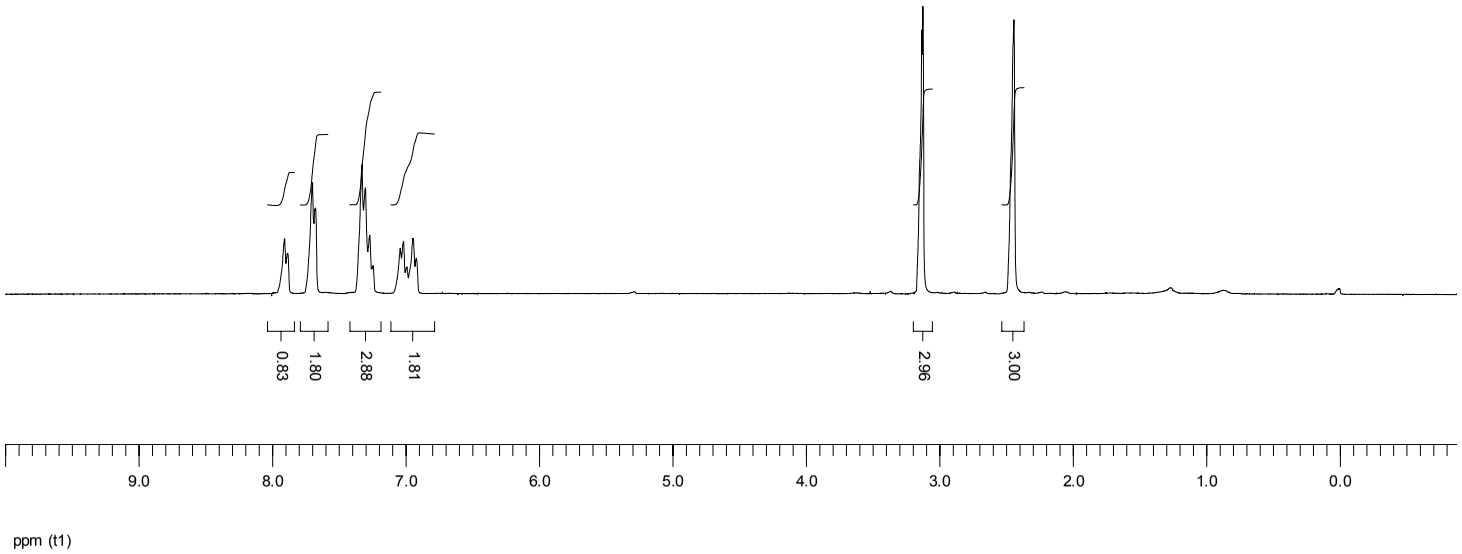
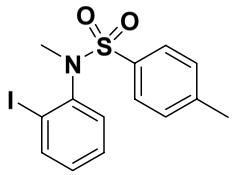


13C NMR (100 MHz, CDCl3)



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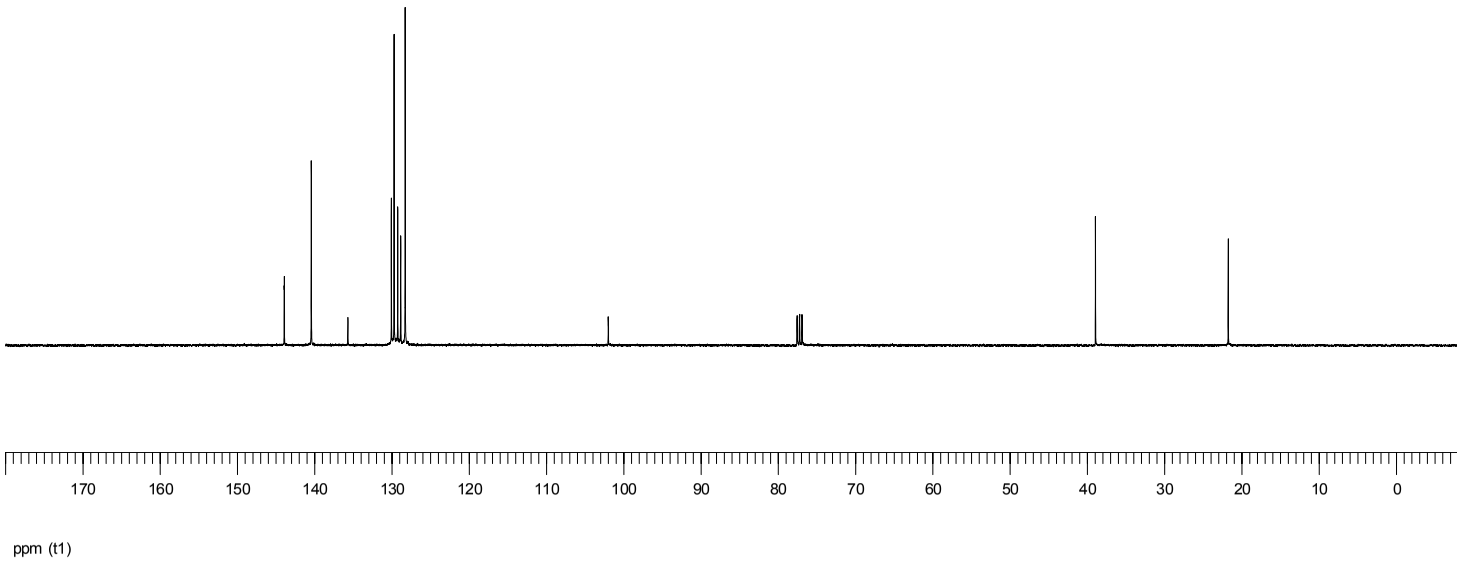

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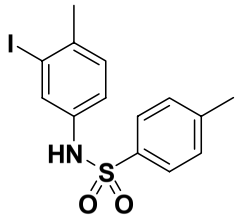

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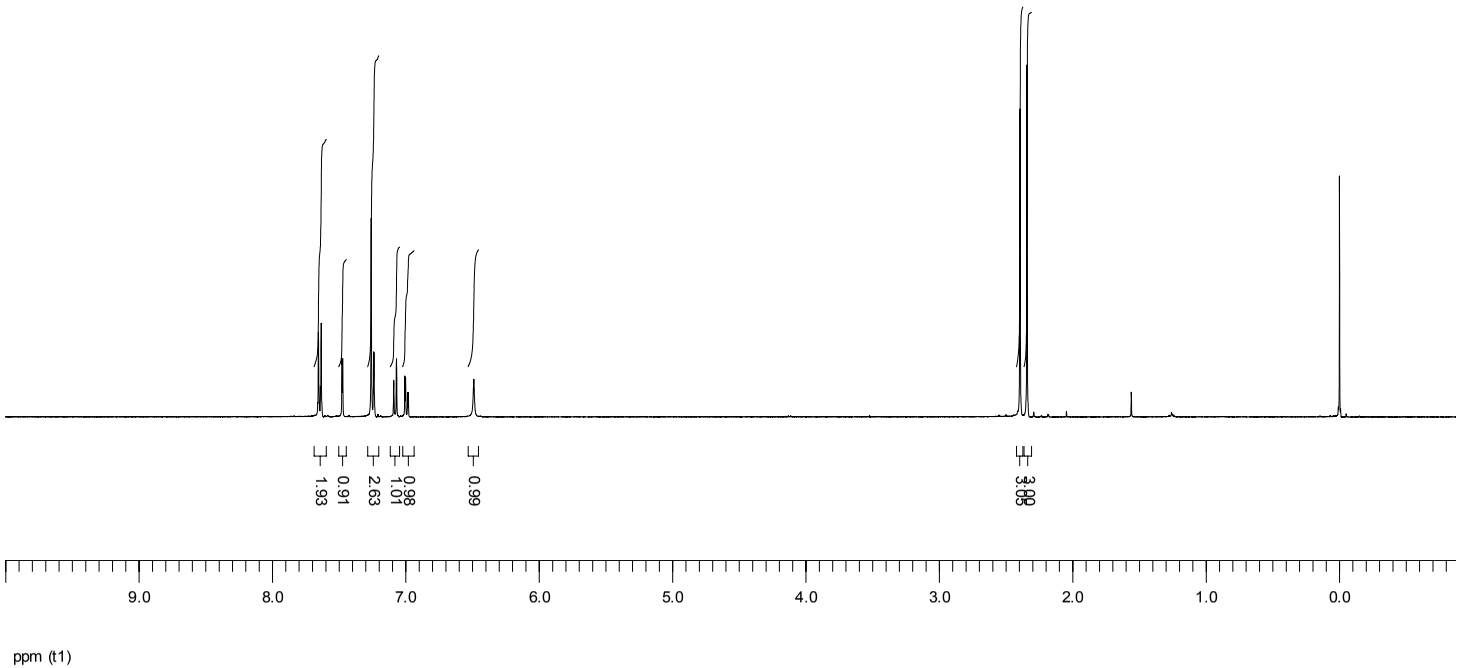

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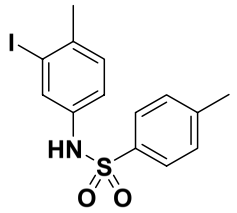

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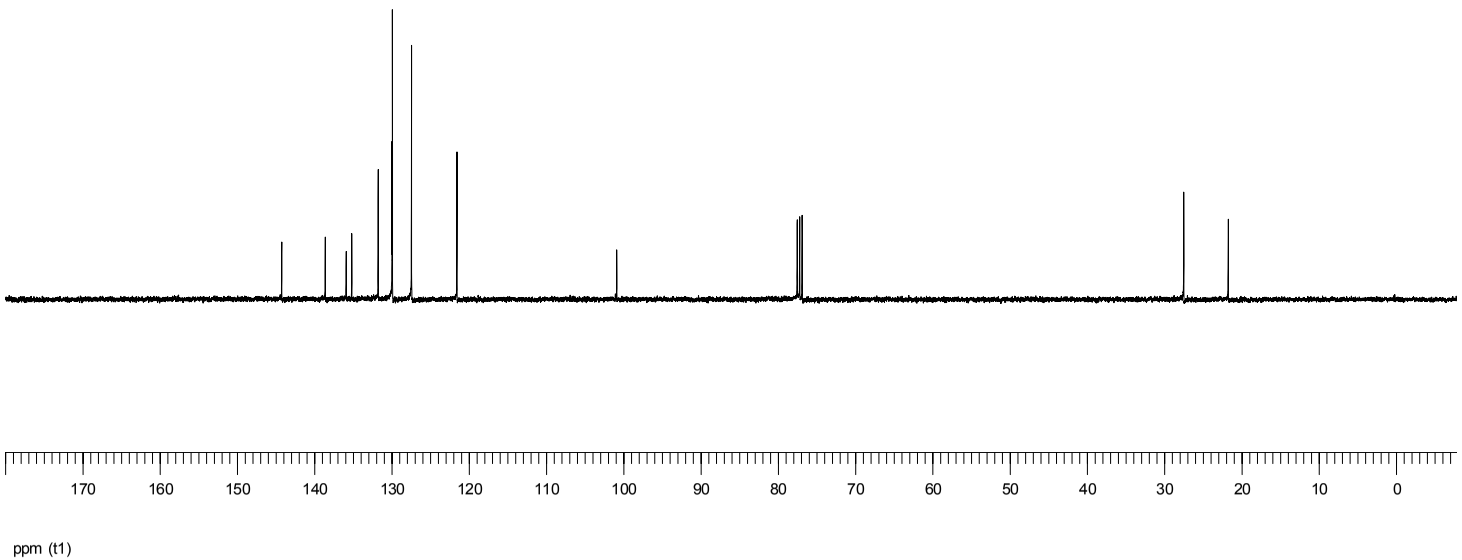

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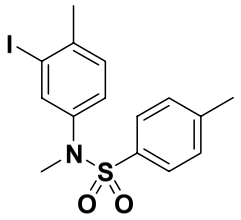

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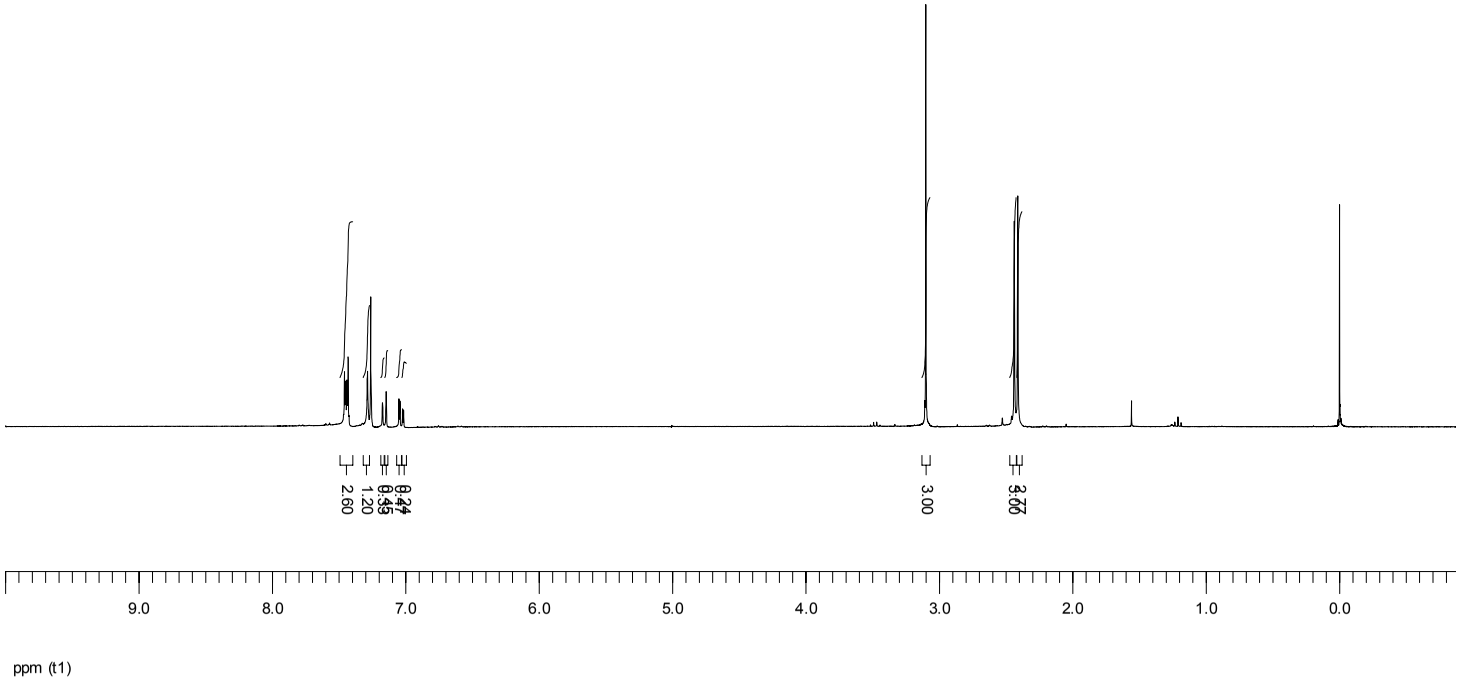

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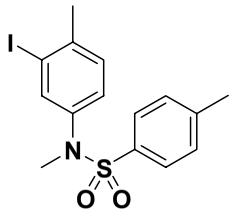

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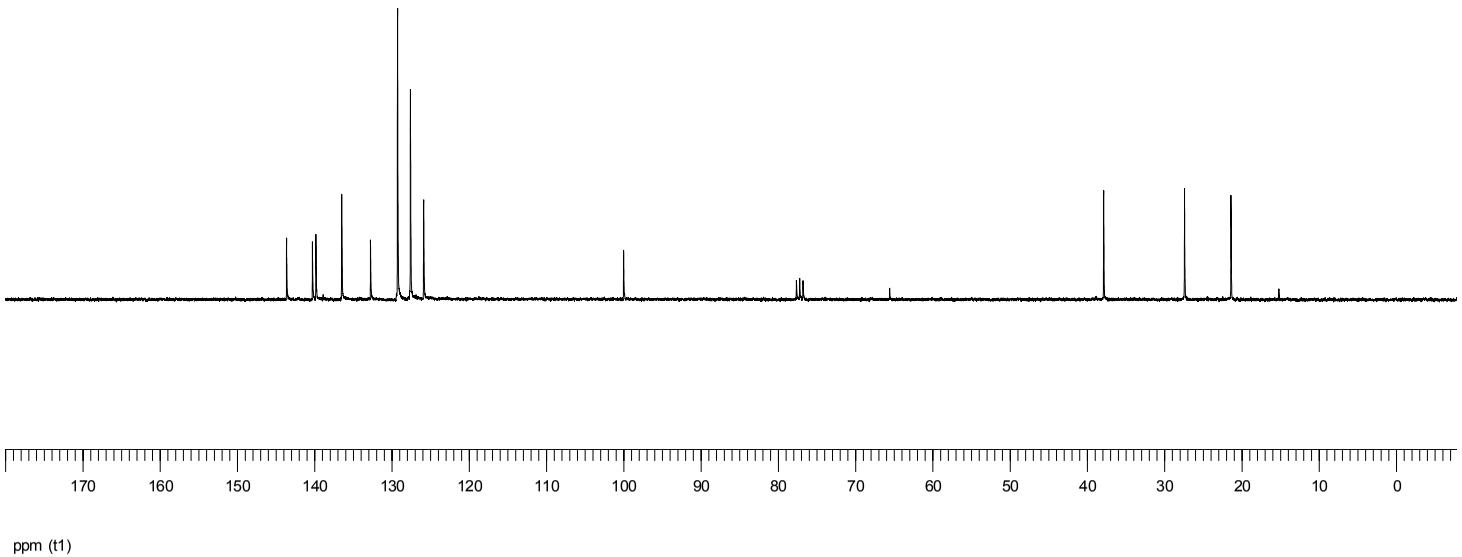

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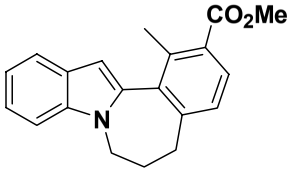

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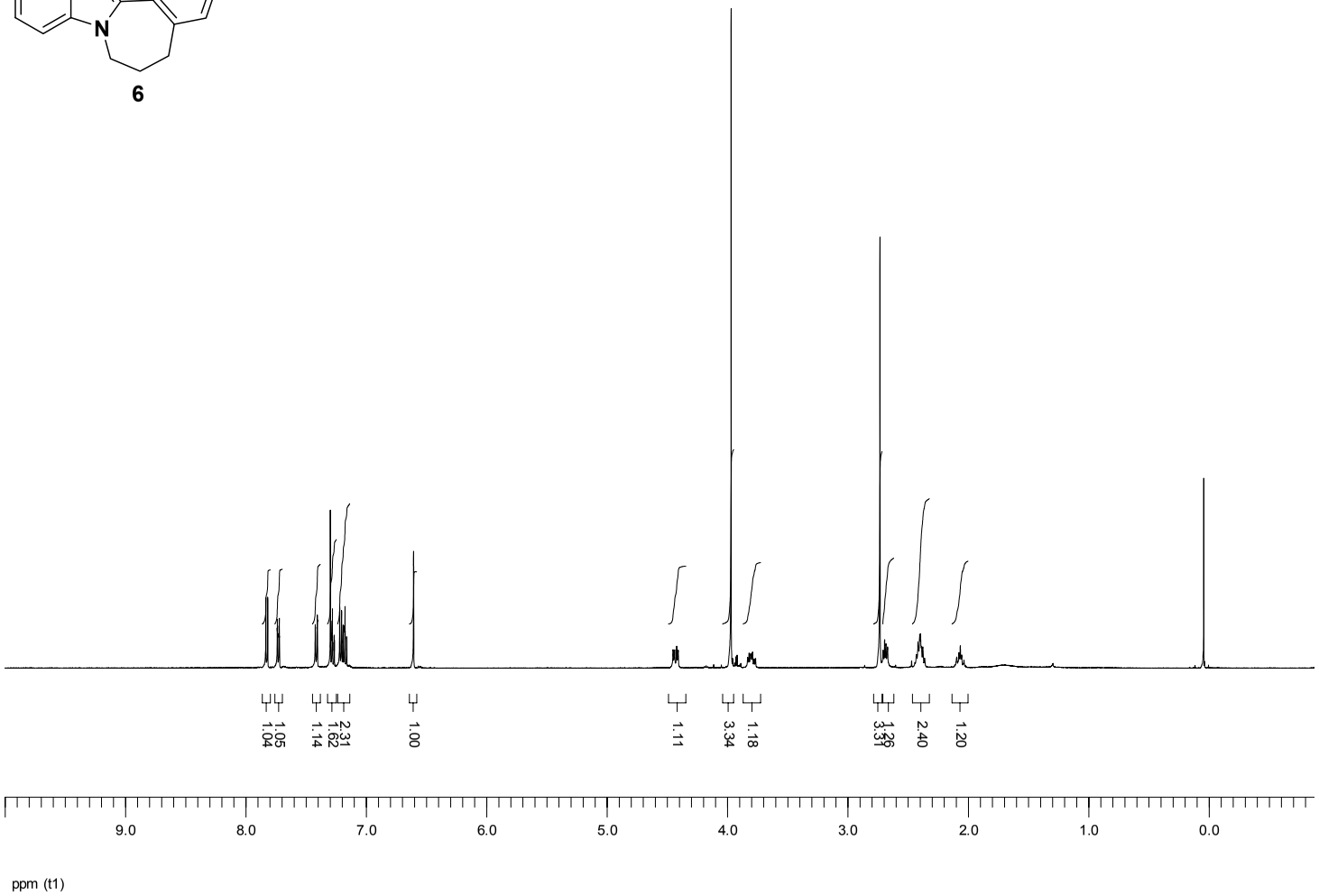

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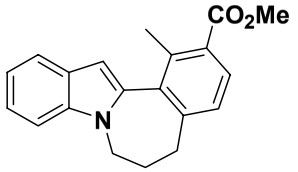

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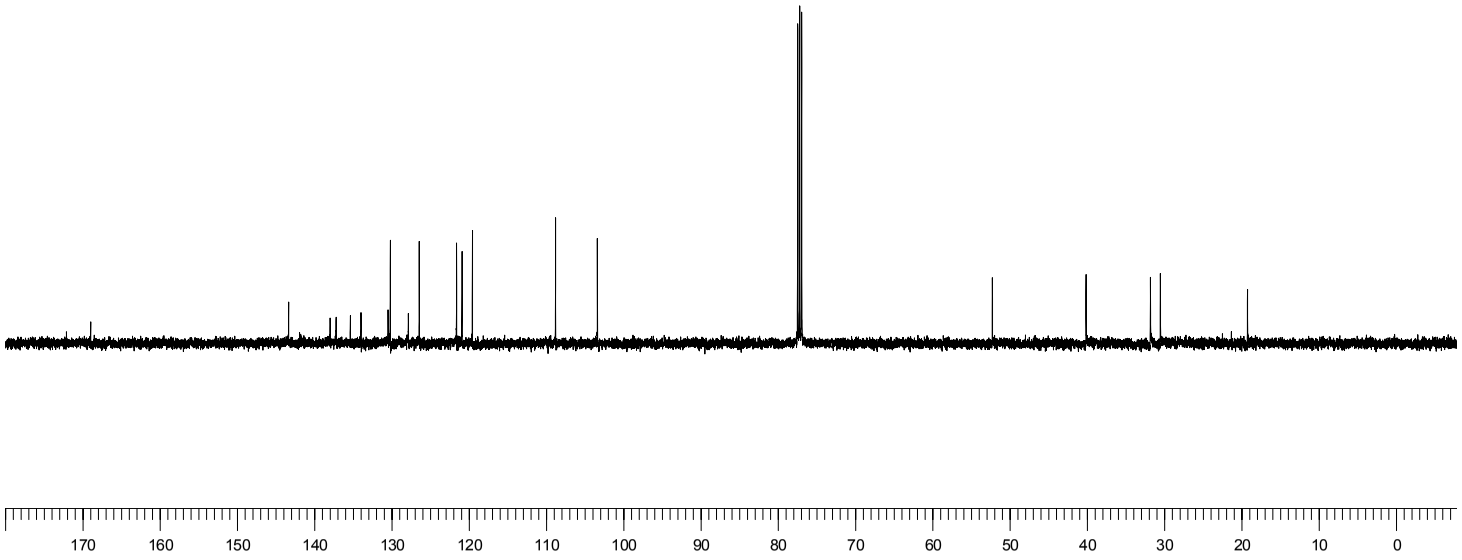

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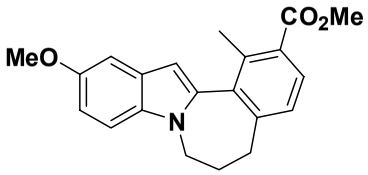

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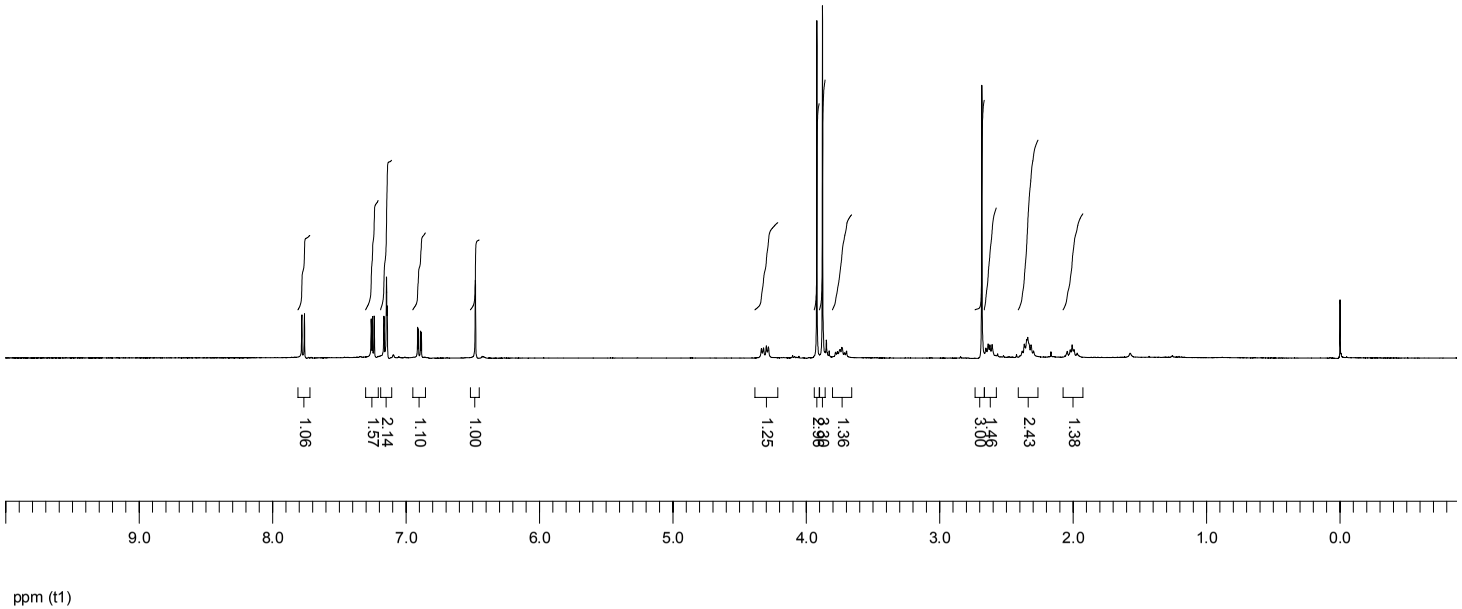
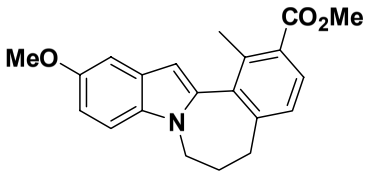


13C NMR (100 MHz, CDCl3)



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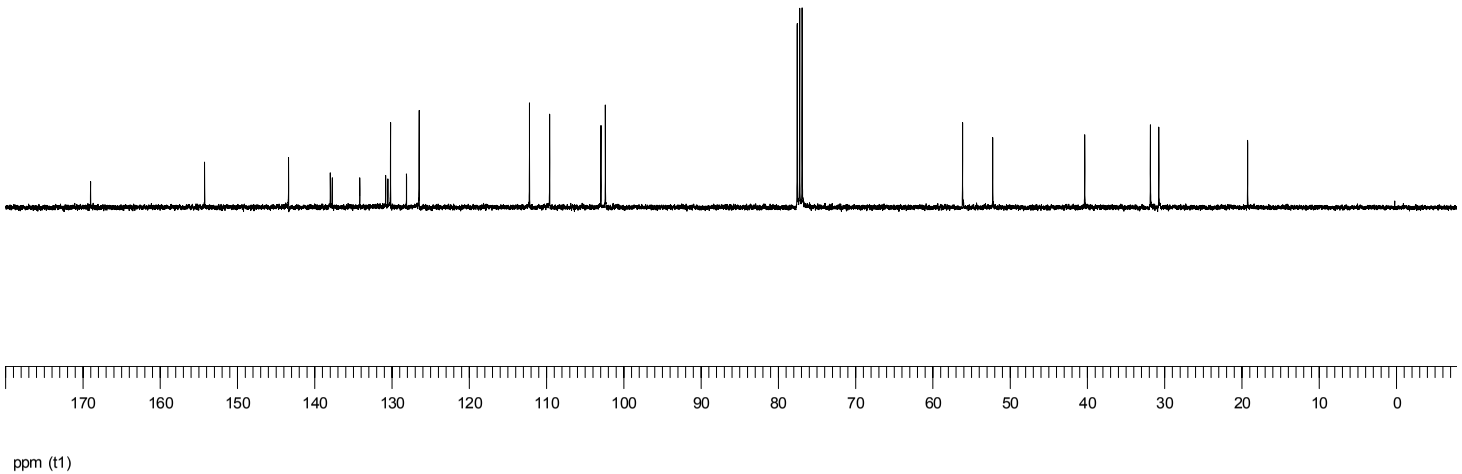

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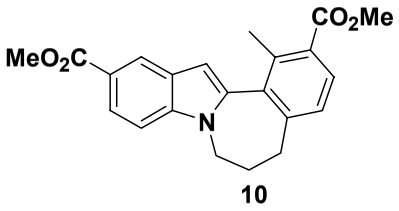

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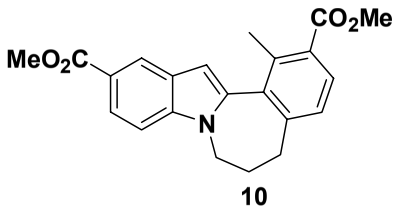
13C NMR (100 MHz, CDCl3)



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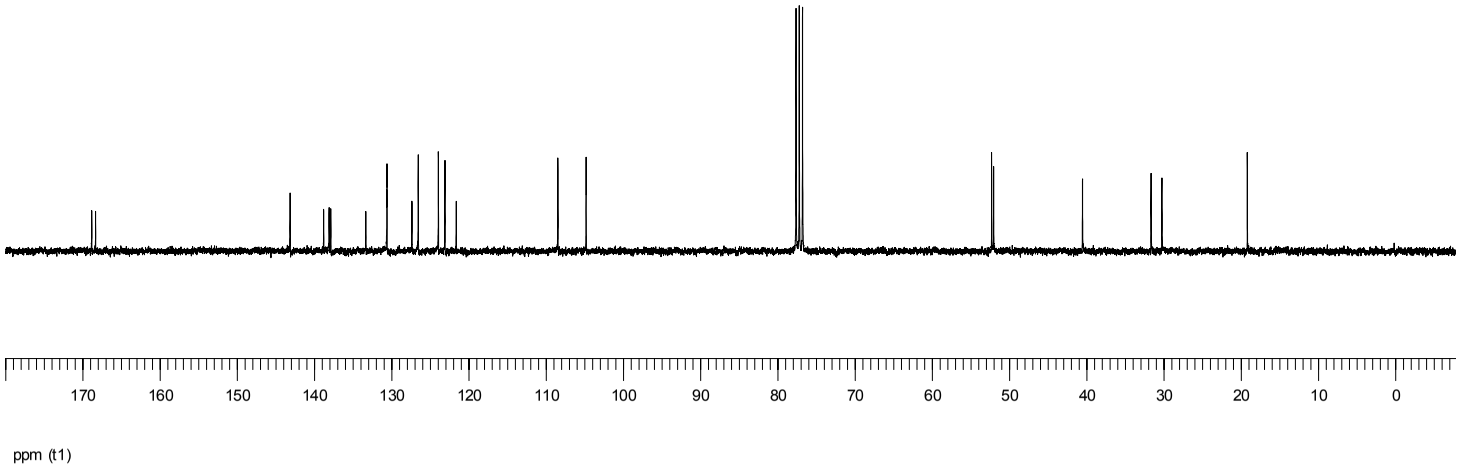

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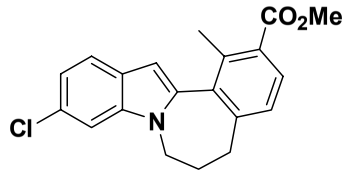

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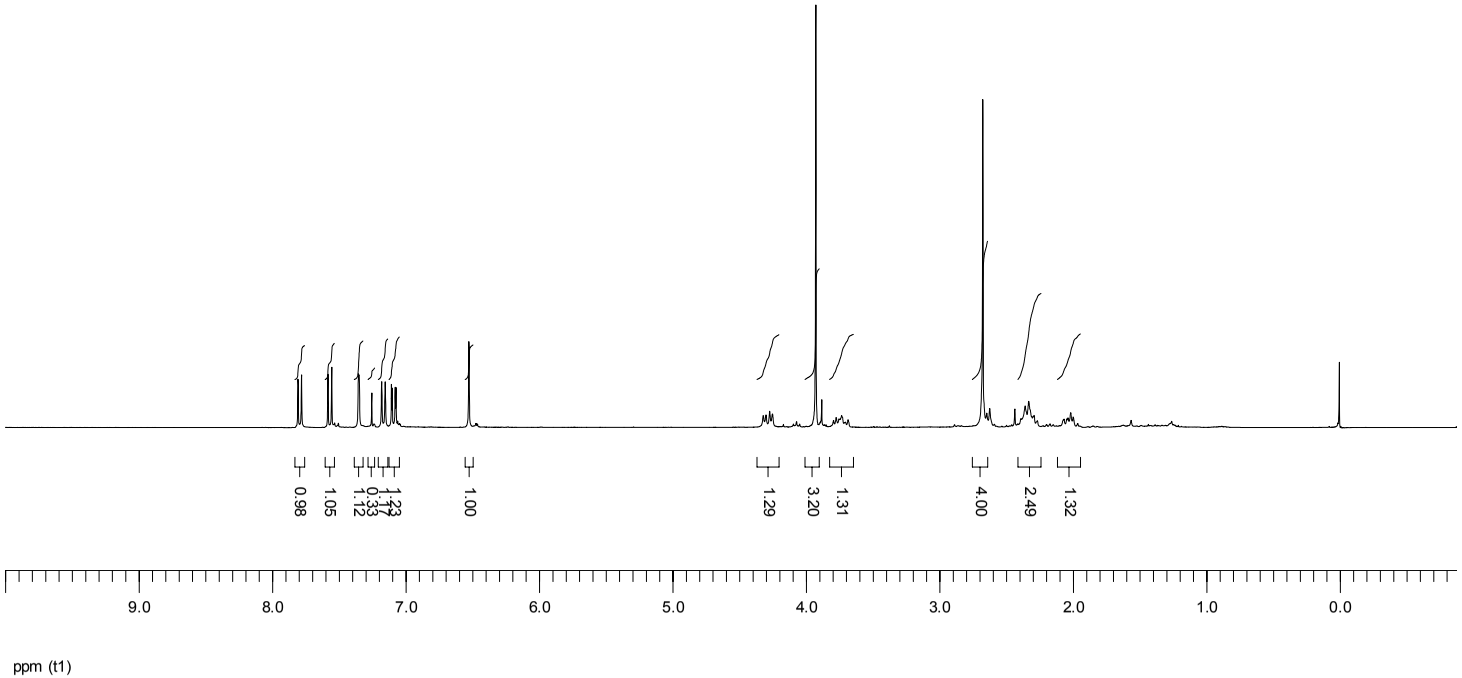
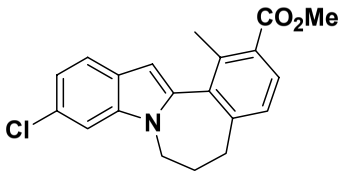


13C NMR (75 MHz, CDCl3)



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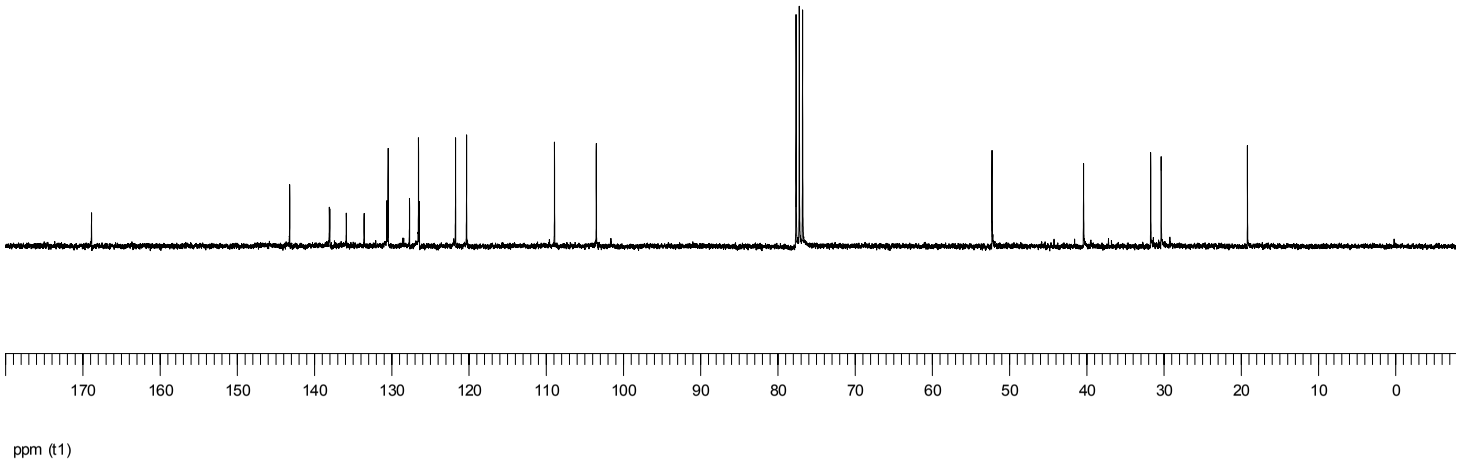
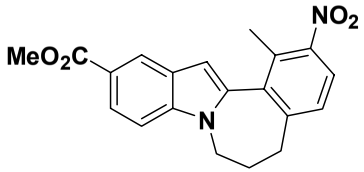


1H NMR (400 MHz, CDCl3)



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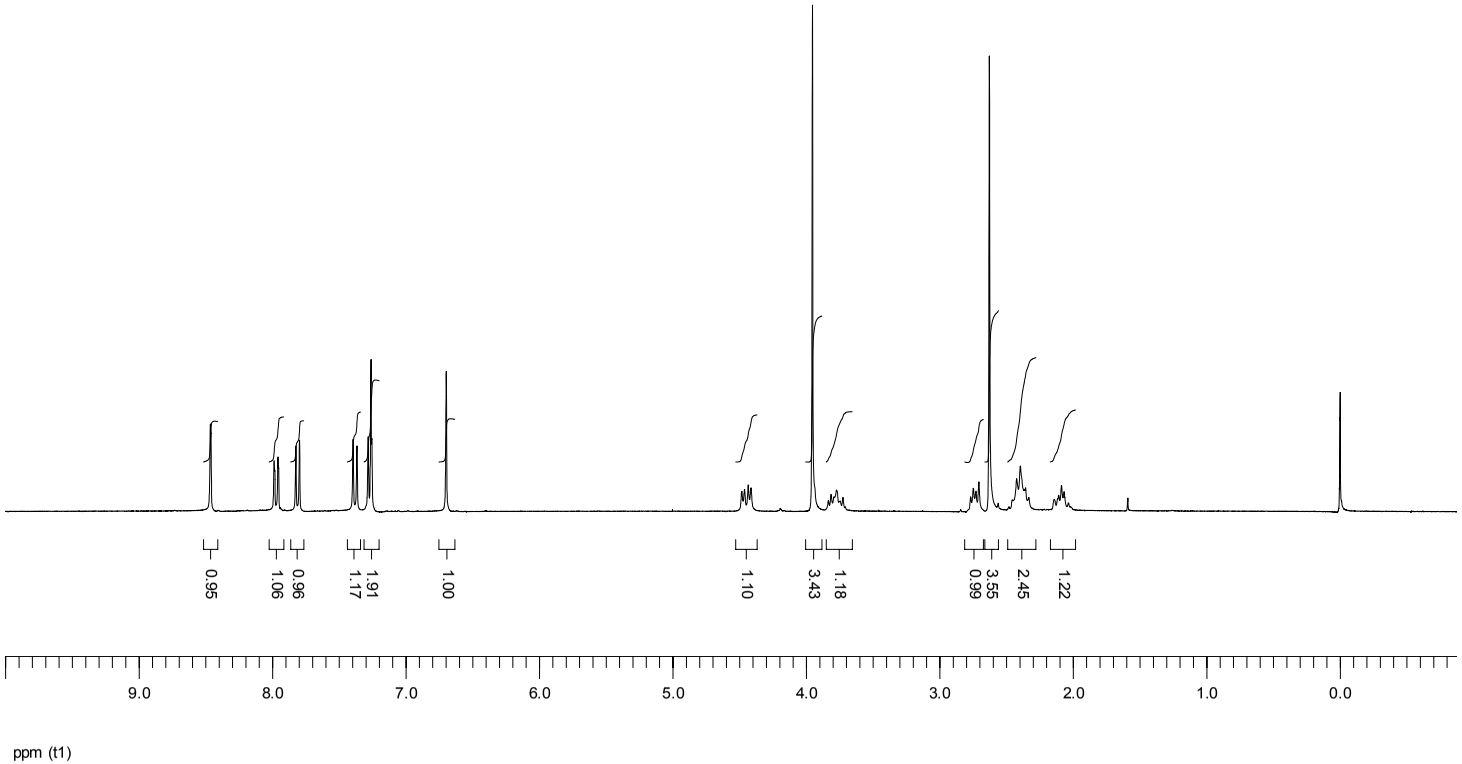
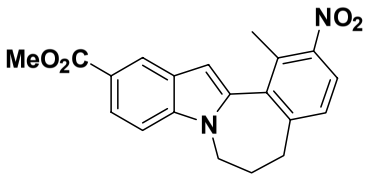


13C NMR (100 MHz, CDCl3)



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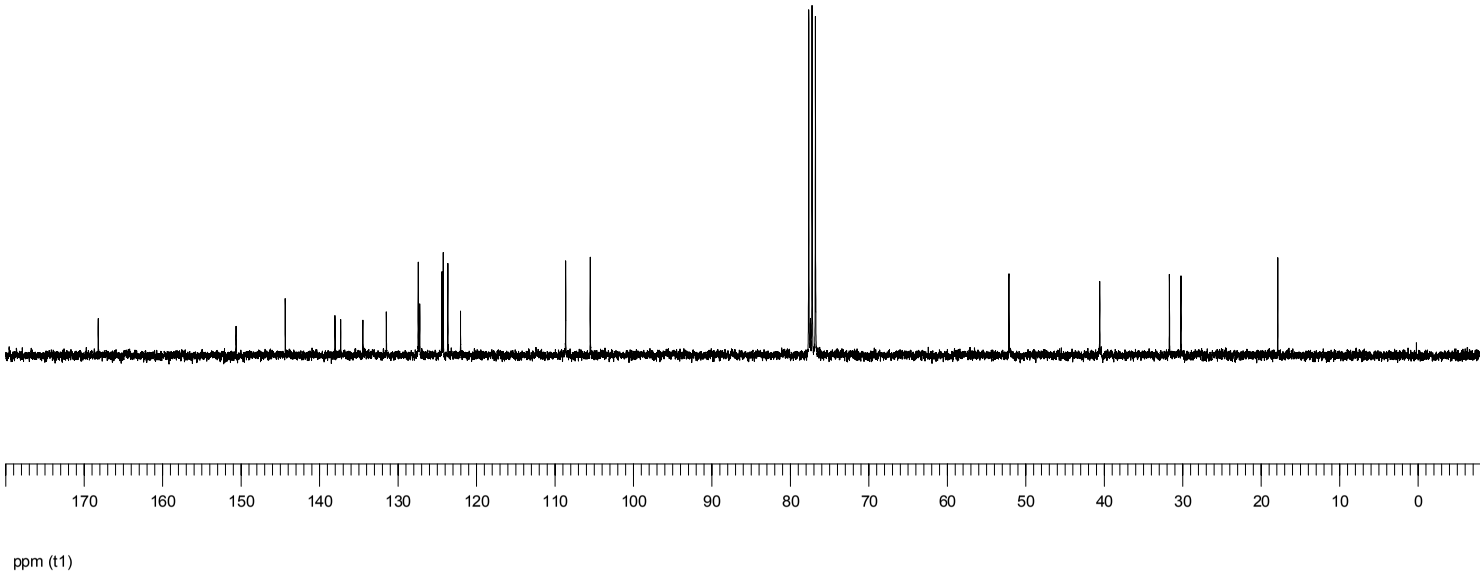
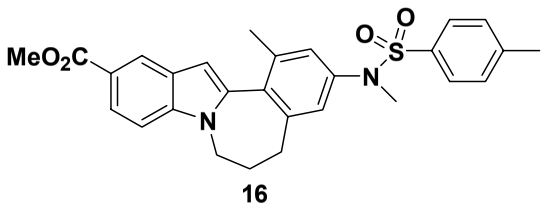


1H NMR (400 MHz, CDCl3)



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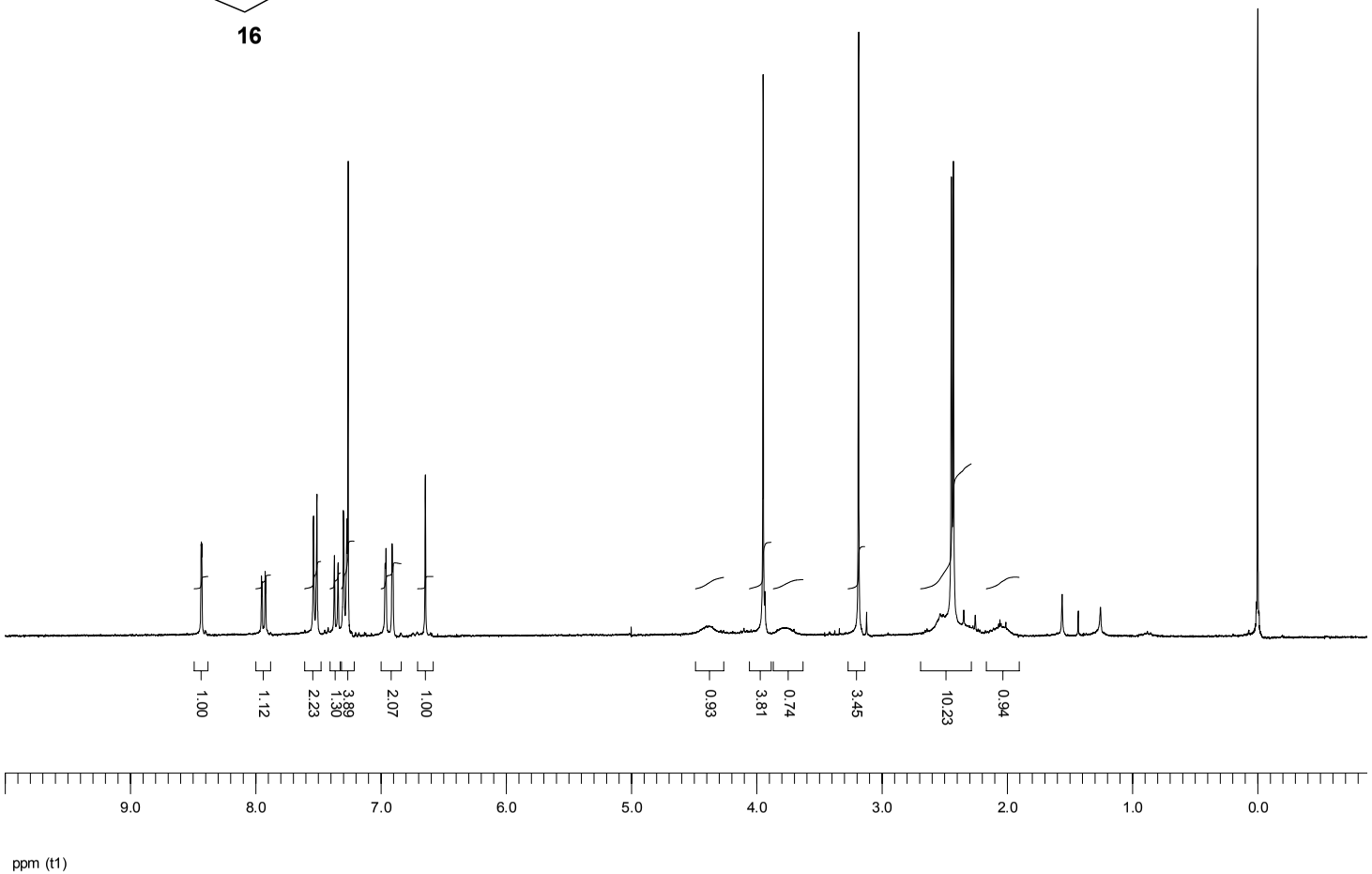
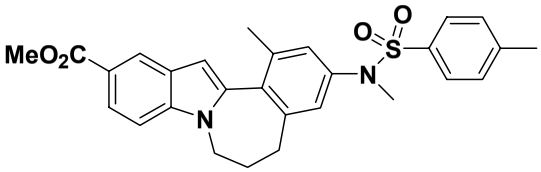


13C NMR (100 MHz, CDCl3)



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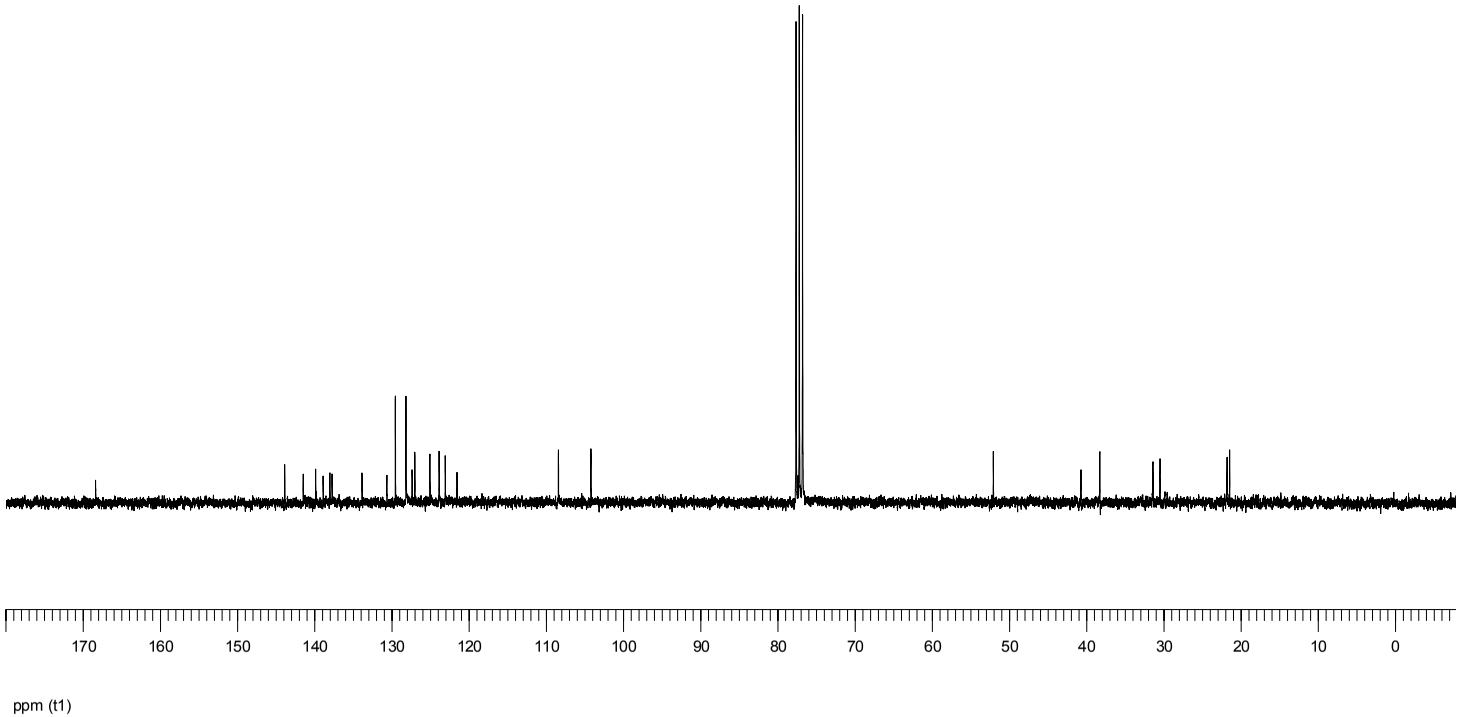
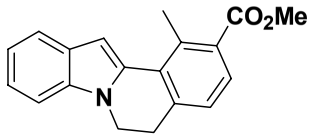


1H NMR (400 MHz, CDCl3)



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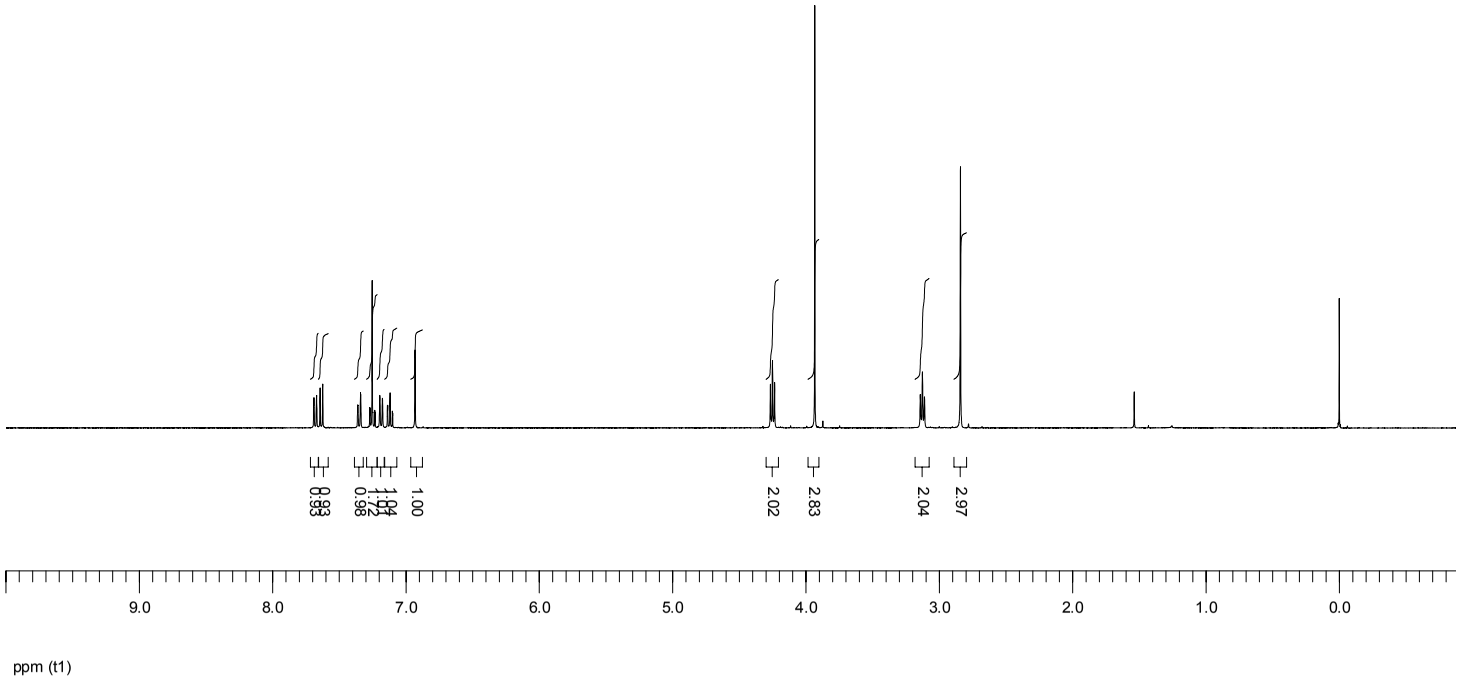
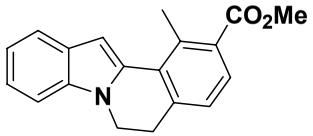


13C NMR (100 MHz, CDCl3)



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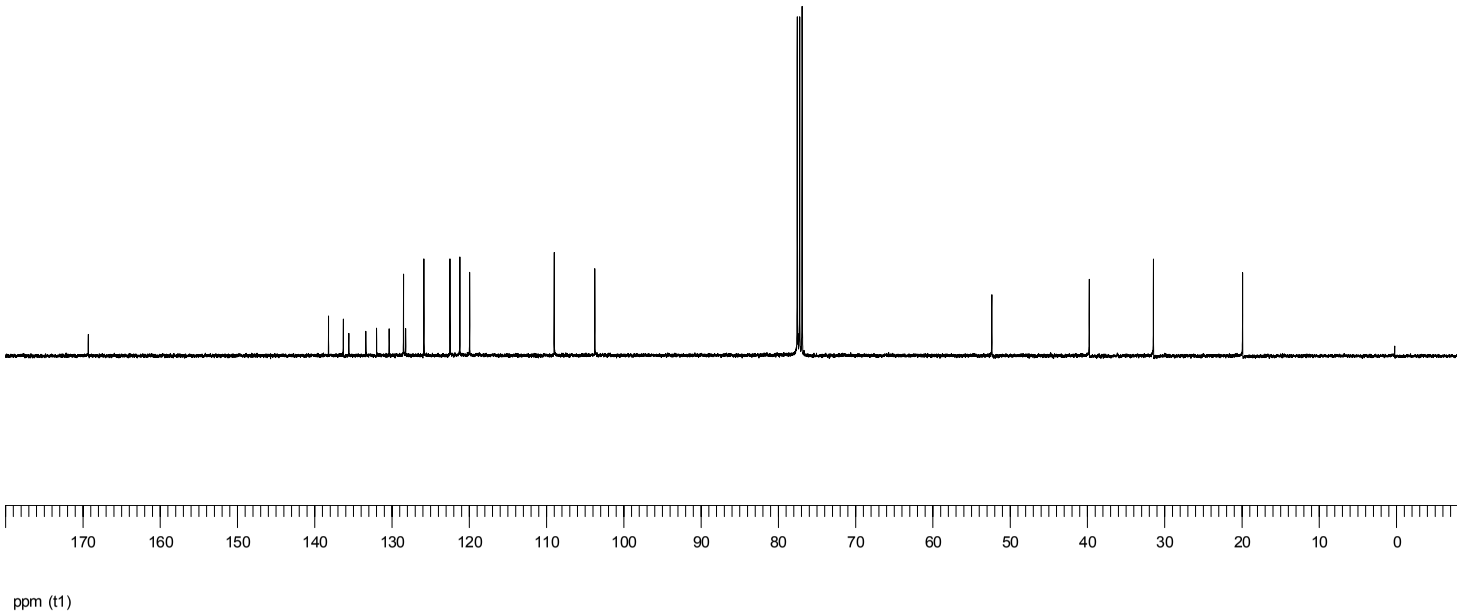

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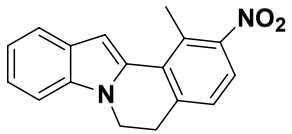

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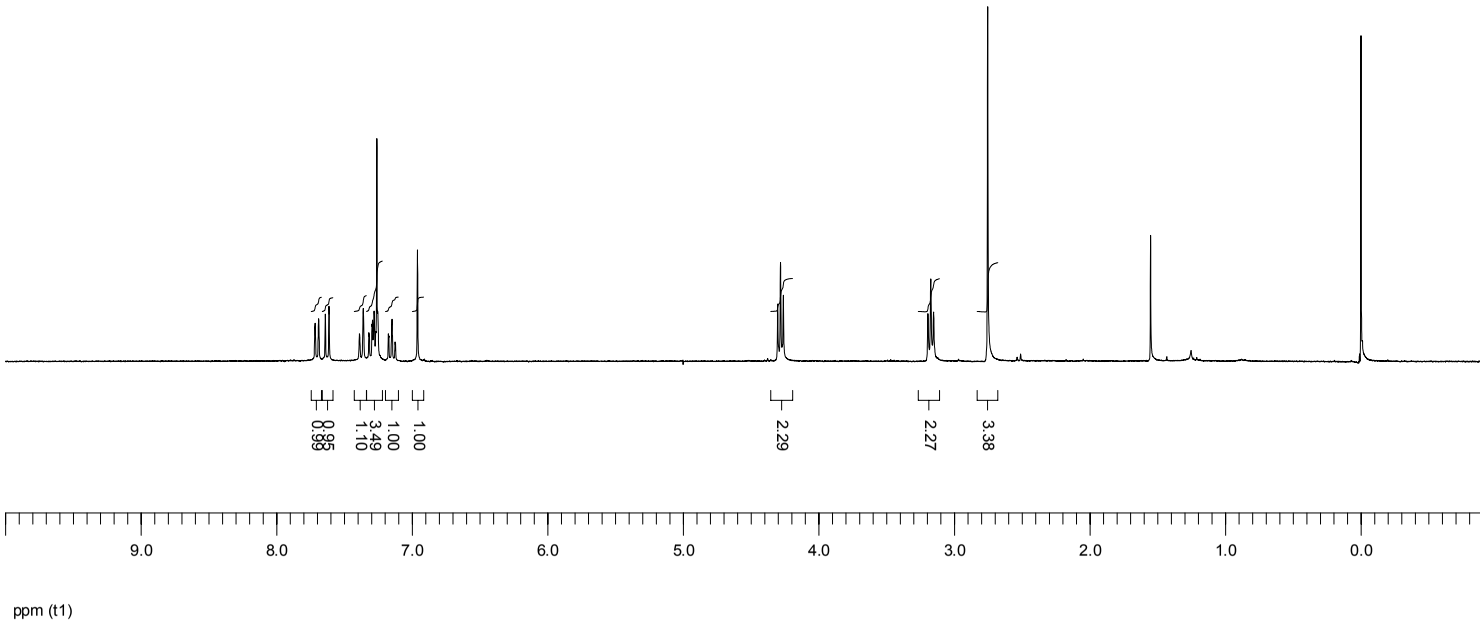

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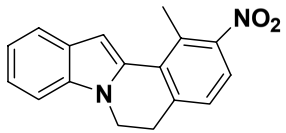

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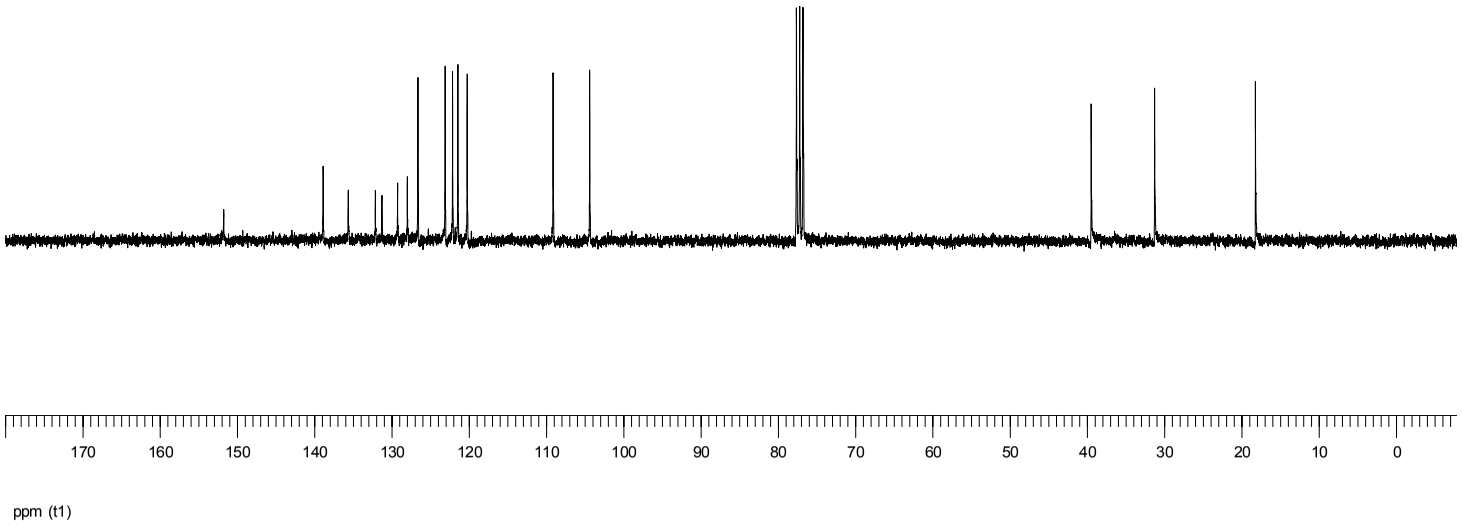
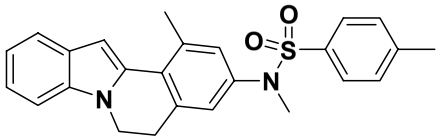


1H NMR (400 MHz, CDCl3)



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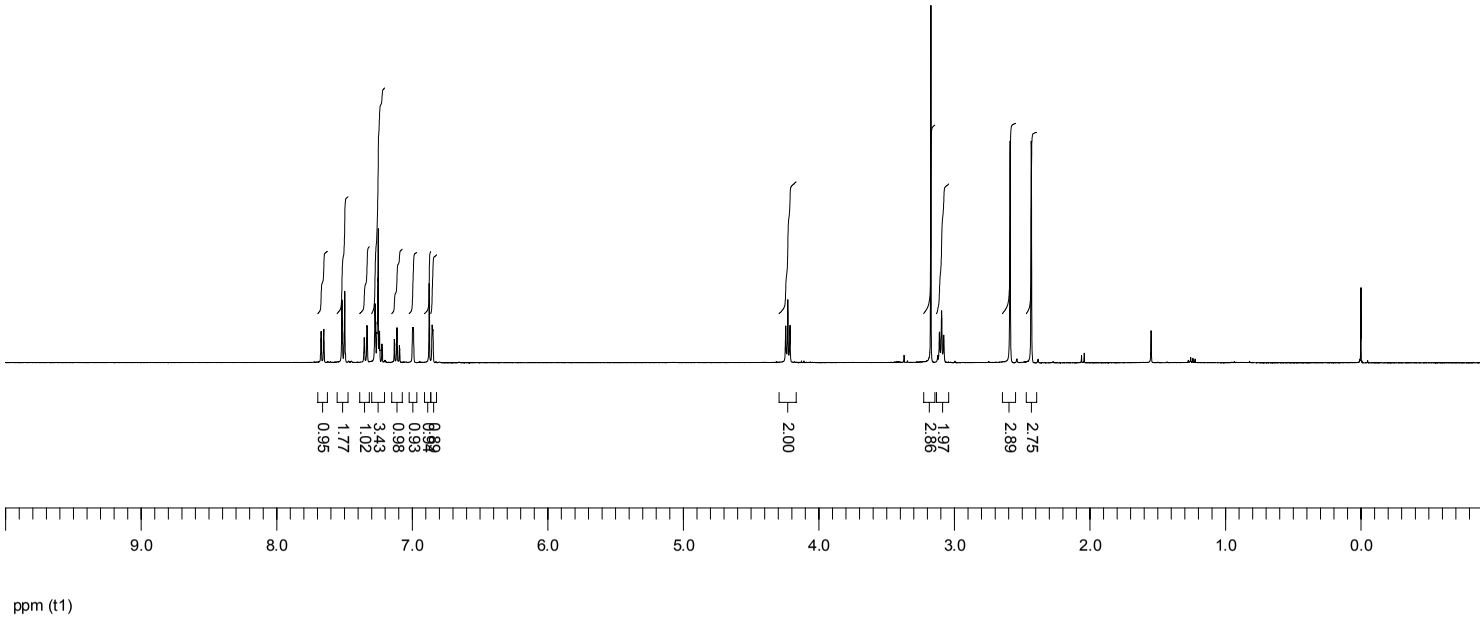
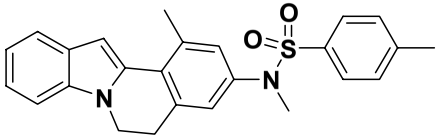


13C NMR (75 MHz, CDCl3)



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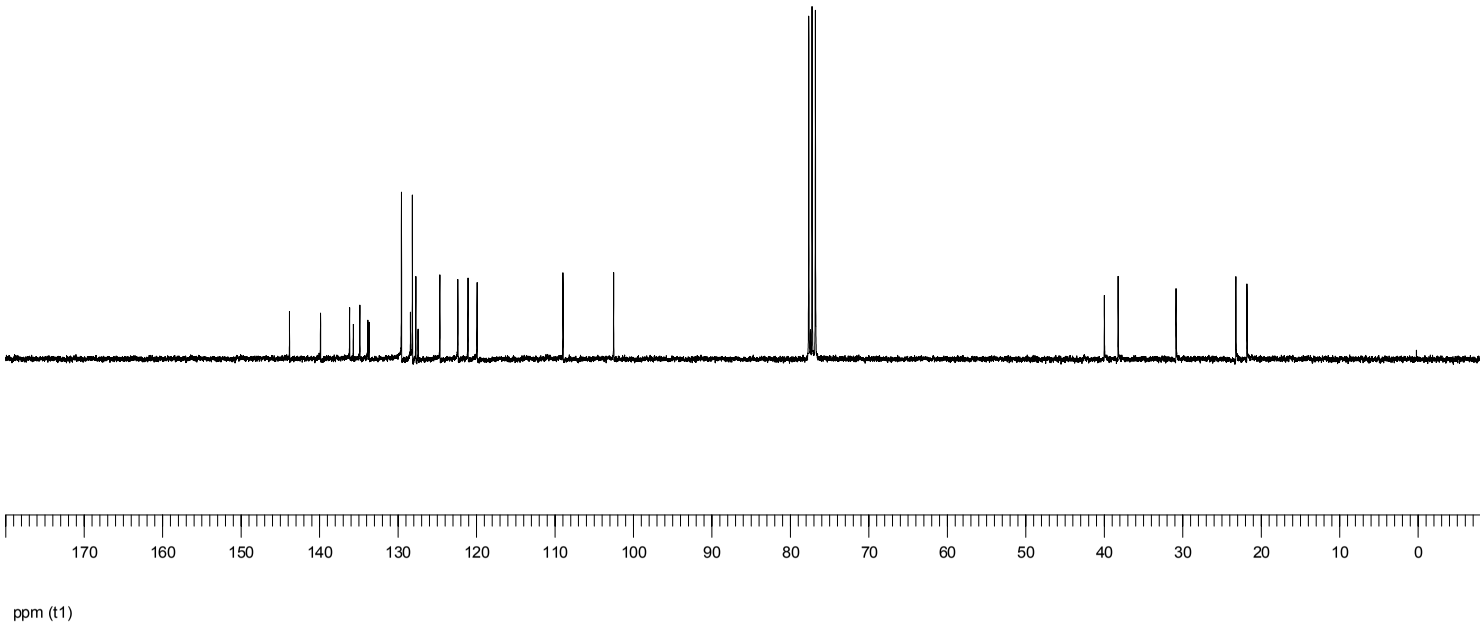
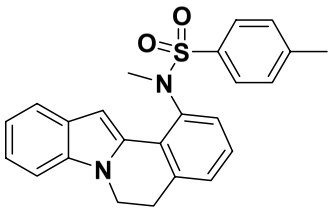


1H NMR (400 MHz, CDCl3)



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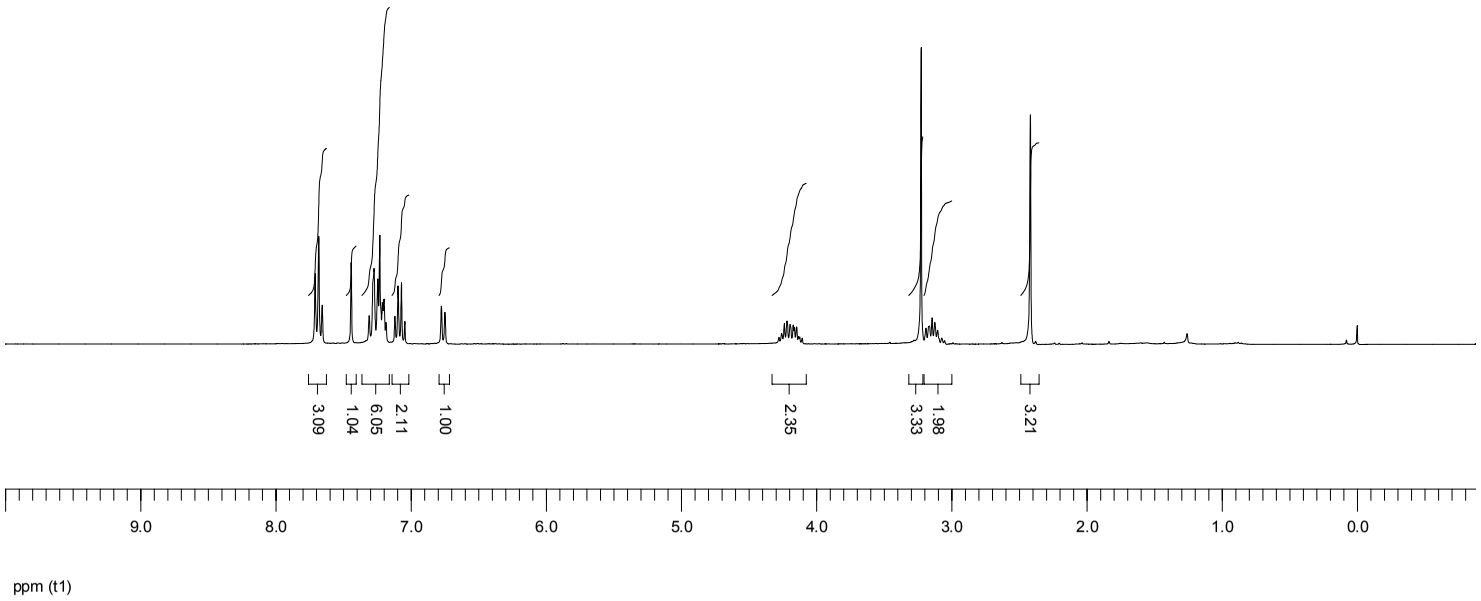
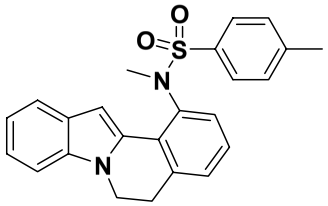
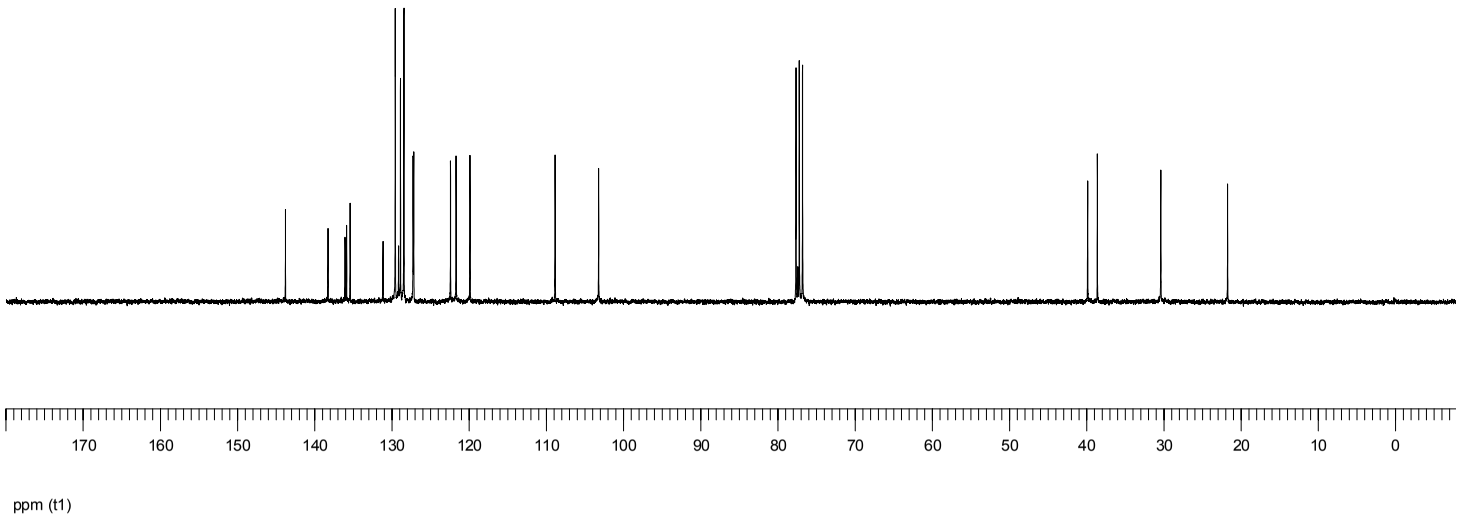


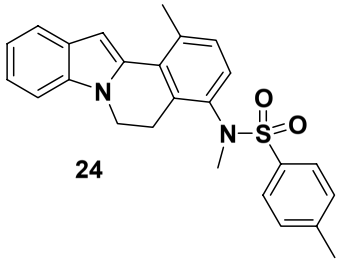
13C NMR (100 MHz, CDCl3)



22



1H NMR (400 MHz, CDCl3)



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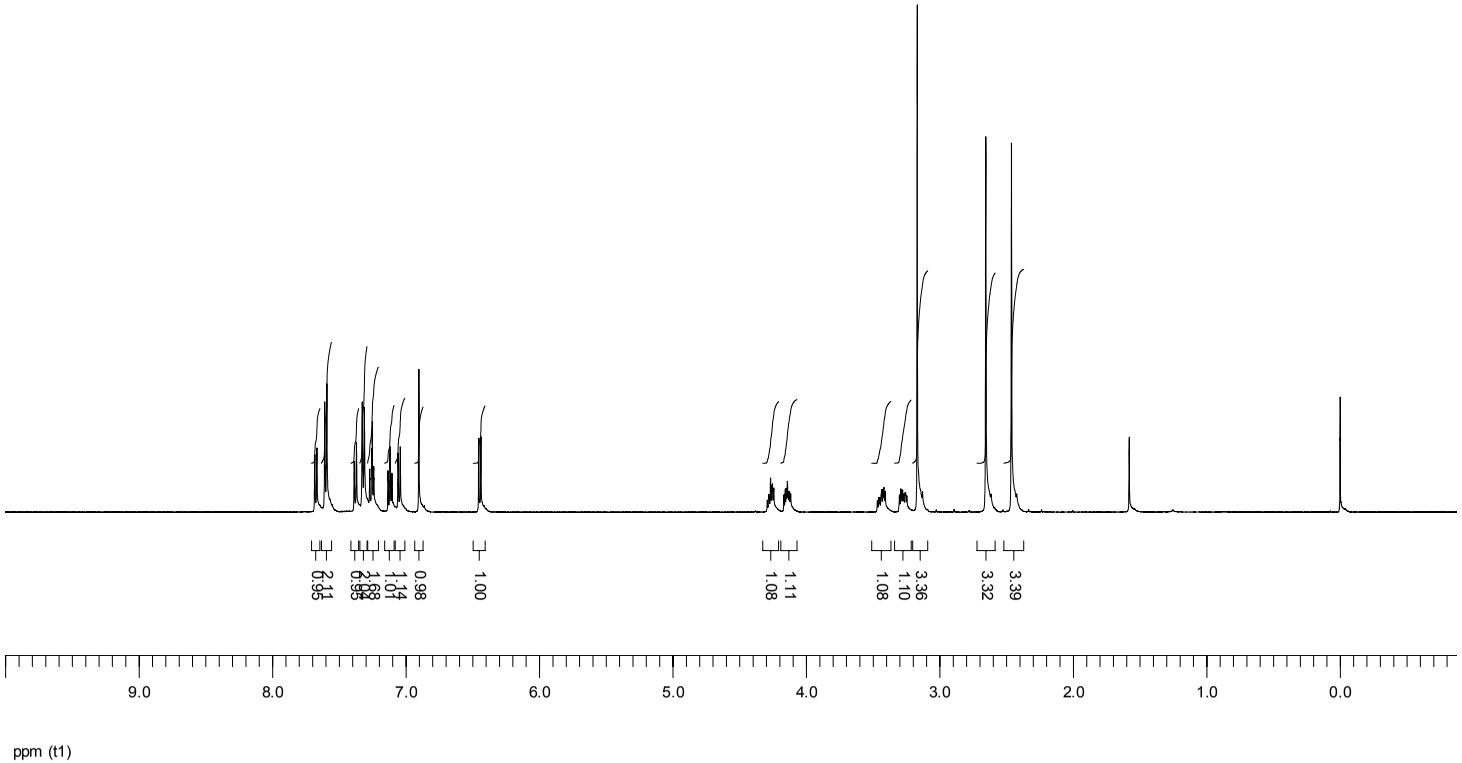
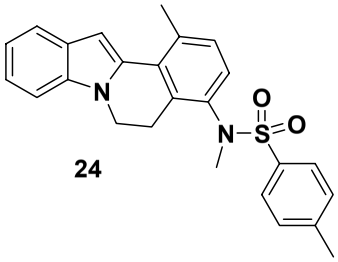


13C NMR (100 MHz, CDCl3)



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