Supporting Information

Two-Component Approach Toward Fully-Substituted N-Fused Pyrrole Ring

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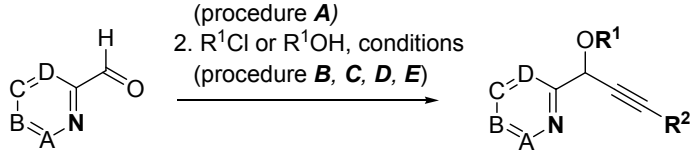
Content

General Information

NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz) and Bruker Avance DRX-400 (400 MHz). HRMS analysis was performed on Micromass 70 VSE high resolution mass spectrometer[1]. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). IR spectra were recorded on a JASCO FTIR-4100 spectrometer and are reported in frequency of absorption (cm^{-1}). Melting points were determined using Thomas Hoover capillary melting point apparatus and are uncorrected.

Column chromatography was carried out employing Silicycle Silica-P Flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Anhydrous solvents were purchased from Aldrich and stored over calcium hydride. Iodo- and bromoarenes were commercially available and purchased from Aldrich, Strem Chemicals Inc. or Acros Organics. All manipulations with air sensitive materials were conducted under argon atmosphere using a combination of glovebox and standard Schlenk techniques.

Preparation of starting materials



1, R^1 = Piv
3, R^1 = Ac
5, R^1 = Ph
7, R^1 = TBS

R^1 = Piv (procedure ***B***)
Ac (procedure ***C***)
Ph (procedure ***D***)
TBS (procedure ***E***)
R^2 = *n*-Bu, *n*-Hex, *n*- Oct,
t-Bu, CH_2CH_2Ph,
Ph, *p*-Tol, *c*-Hexenyl
Heterocycles are: pyridine, quinoline, and isoquinoline

A. To a stirring solution of the terminal alkyne (3.6 mmol, 1.2 equiv) in THF (1.0 M) was added ethylmagnesium bromide (3.3 mmol, 3.0 M in THF, 1.1 equiv) at room temperature. The resulting solution was stirred for 30 min. This solution was then added slowly by syringe to a solution of heteroarylcarboxaldehyde (3.0 mmol, 1.0 equiv) in THF (0.5 M) at 0°C and stirred for 1 h. The reaction mixture was quenched at 0°C by addition of saturated aqueous ammonium chloride (30 mL) and extracted three times with ethyl acetate (20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporation to yield the propargylic alcohol, which was used directly without further purification.

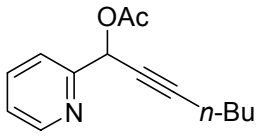
[1] The 70-VSE mass spectrometer was purchased in part with a grant from the Division of Research Resources, National Institutes of Health (RR 04648).

B. To a solution of the crude propargylic alcohol in dichloromethane (0.2 M) at room temperature were added triethylamine (3.0 equiv) and dimethylaminopyridine (10 mol%), and pivaloyl chloride (1.25 equiv) and the reaction mixture was stirred for 3 h. The solution was then washed with saturated aqueous ammonium chloride and brine, then dried over Na_2SO_4 and concentrated by rotary evaporation. The crude products were purified by flash chromatography (8:1 hexanes/EtOAc) to yield the desired propargylic pivalates.

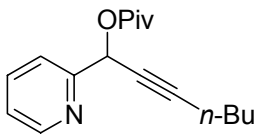
C. Acylation of propargyl alcohols was done using standard AcCl/NEt_3/DMAP protocol. In a typical procedure, to a stirred solution of propargyl alcohol (1.00 equiv.) in DCM successively were added DMAP (0.10 equiv.) and triethylamine (1.5 equiv.). The solution was cooled down to 0°C and AcCl (1.2 equiv.) was added dropwise. The reaction was allowed to warm up to room temperature and stirred until completion as monitored by TLC and/or GC-MS. The solvent was removed under reduced pressure and the residue was purified on silica gel column using (4:1 hexanes/EtOAc) mixture as eluent.

D. To a solution of the crude propargylic alcohol in THF (0.25 M) at room temperature were added phenol (1.0 equiv.), triphenylphosphine (1.3 equiv.). The solution was cooled down to 0°C and DIAD (1.3 equiv.) was added dropwise and the reaction mixture was stirred for 3 h at 0°C, the was allowed to warm up to room temperature and stirred until completion as monitored by GC/MS. The solution was then washed with saturated aqueous ammonium chloride and brine, then dried over Na_2SO_4 and concentrated. The crude products were purified by flash chromatography (10:1 hexanes/EtOAc) to yield the desired propargylic ethers.

E. *t*-Butyldimetylsilyl (TBS) protection of propargyl alcohols was done *via* typical procedure: a solution of alcohol (1.00 equiv.) in small amount of DCM was added to a stirred solution of TBSCl (1.05 equiv.) and imidazole (1.10 equiv.) in THF. The mixture was stirred at room temperature for 4 hours. The solvent was removed under reduced pressure and the residue was purified on silica gel column using 10:1 hexanes/EtOAc mixture as eluent.

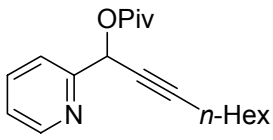


1a: Yellowish oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.58 (ddd, *J*=4.86, 1.74, 0.92 Hz, 1 H), 7.70 (td, *J*=7.70, 1.83 Hz, 1 H), 7.53 (dt, *J*=7.75, 0.89 Hz, 1 H), 7.22 (ddd, *J*=7.57, 4.81, 1.19 Hz, 1 H), 6.44 (t, *J*=2.11 Hz, 1 H), 2.23 (td, *J*=7.15, 2.20 Hz, 2 H), 2.11 (s, 3 H), 1.43 - 1.53 (m, 2 H), 1.30 - 1.42 (m, 2 H), 0.86 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 169.6, 156.4, 149.5, 136.9, 123.3, 121.6, 88.8, 75.8, 67.0, 30.3, 21.8, 21.0, 18.5, 13.5; IR (neat) υ_{max} 2969.84, 2933.20, 1740.44, 1590.02, 1217.83, 758.85 cm^{-1}.

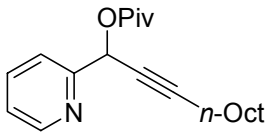


1b: Yellowish oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.59 (ddd, *J*=4.77, 1.65, 0.92 Hz, 1 H), 7.70 (td, *J*=7.70, 1.83 Hz, 1 H), 7.50 - 7.53 (m, 1 H), 7.22 (ddd, *J*=7.52, 4.77, 1.10 Hz, 1 H),

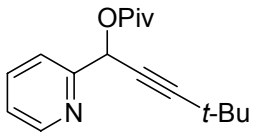
6.45 (t, *J*=2.11 Hz, 1 H), 2.20 - 2.28 (m, 2 H), 1.44 - 1.55 (m, 2 H), 1.32 - 1.42 (m, 2 H), 1.23 (s, 9 H), 0.87 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.9, 157.0, 149.4, 136.8, 123.1, 121.1, 88.3, 76.2, 66.9, 38.7, 30.4, 27.0, 21.8, 18.5, 13.5; IR (neat) υ_{max} 2969.84, 2957.30, 2935.13, 1737.55, 1435.74, 1365.35, 1132.97, 747.28 cm^{-1}.



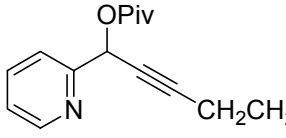
1c: Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.58 (ddd, *J*=4.81, 1.70, 0.83 Hz, 1 H), 7.70 (td, *J*=7.70, 1.83 Hz, 1 H), 7.49 - 7.52 (m, 1 H), 7.22 (ddd, *J*=7.57, 4.81, 1.01 Hz, 1 H), 6.45 (t, *J*=2.11 Hz, 1 H), 2.22 (td, *J*=7.15, 2.20 Hz, 2 H), 1.44 - 1.53 (m, 2 H), 1.30 - 1.38 (m, 2 H), 1.21 - 1.29 (m, 13 H), 0.85 (t, *J*=7.05 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.9, 157.0, 149.4, 136.8, 123.1, 121.1, 88.3, 76.2, 66.9, 38.7, 31.2, 28.4, 28.3, 27.0, 22.5, 18.8, 14.0; IR (neat) υ_{max} 2957.30, 2931.27, 2858.95, 1735.62, 1590.02, 1132.97, 747.28 cm^{-1}.



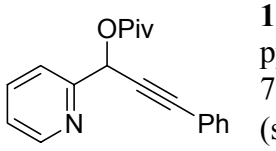
1d: Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.59 (ddd, *J*=4.81, 1.79, 0.92 Hz, 1 H), 7.70 (td, *J*=7.70, 1.83 Hz, 1 H), 7.49 - 7.53 (m, 1 H), 7.22 (ddd, *J*=7.52, 4.77, 1.10 Hz, 1 H), 6.45 (t, *J*=2.02 Hz, 1 H), 2.23 (td, *J*=7.11, 2.11 Hz, 2 H), 1.45 - 1.54 (m, 2 H), 1.20 - 1.37 (m, 19 H), 0.86 (t, *J*=7.00 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.9, 157.0, 149.4, 136.8, 123.1, 121.1, 88.3, 76.2, 66.9, 38.7, 31.8, 29.1, 29.0, 28.7, 28.3, 27.0, 22.6, 18.9, 14.1; IR (neat) υ_{max} 2956.34, 2926.45, 285.06, 1736.58, 1590.02, 1272.79, 1133.94, 747.28 cm^{-1}.



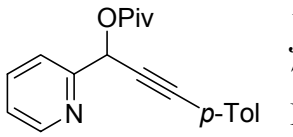
1e: Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.56 (ddd, *J*=4.81, 1.70, 0.83 Hz, 1 H), 7.69 (td, *J*=7.70, 1.83 Hz, 1 H), 7.52 - 7.55 (m, 1 H), 7.21 (ddd, *J*=7.52, 4.77, 1.10 Hz, 1 H), 6.45 (br. s., 1 H), 1.20 (s, 9 H), 1.19 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.8, 157.0, 149.3, 136.8, 123.0, 121.2, 96.2, 74.7, 66.8, 38.6, 30.6, 27.4, 26.9; IR (neat) υ_{max} 2965.98, 1737.55, 1590.02, 1221.68, 1138.76, 747.28 cm^{-1}.



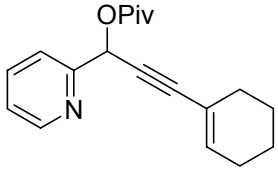
1f: Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.59 - 8.61 (m, 1 H), 7.69 (td, *J*=7.70, 1.83 Hz, 1 H), 7.41 - 7.46 (m, 1 H), 7.14 - 7.28 (m, 6 H), 6.46 (t, *J*=1.93 Hz, 1 H), 2.83 (t, *J*=7.52 Hz, 2 H), 2.51 - 2.57 (m, 2 H), 1.24 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.8, 156.8, 149.3, 140.4, 136.8, 128.4, 128.2, 126.2, 123.1, 121.1, 87.3, 66.7, 38.7, 34.6, 27.0, 21.0; IR (neat) υ_{max} 2971.28, 1731.58, 1589.2, 1273.18, 747.09 cm^{-1}.



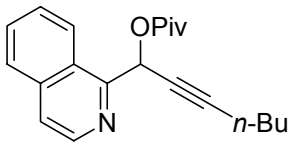
1g: Bright yellow solid; **mp** 57-58^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.63 (ddd, *J*=4.81, 1.70, 0.83 Hz, 1 H), 7.73 - 7.77 (m, 1 H), 7.58 - 7.63 (m, 1 H), 7.45 - 7.48 (m, 2 H), 7.23 - 7.33 (m, 4 H), 6.72 (s, 1 H), 1.27 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.9, 156.5, 149.5, 137.0, 131.9, 128.7, 128.2, 123.3, 122.2, 121.3, 87.0, 85.1, 67.0, 38.8, 27.0; IR (neat) υ_{max} 2973.52, 1722.71, 1475.47, 1270.48, 1029.80, 748.24 cm^{-1}.



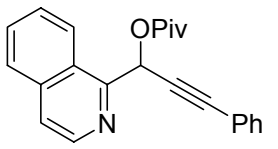
1h: Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.62 (ddd, *J*=4.77, 1.65, 0.92 Hz, 1 H), 7.73 (td, *J*=7.70, 1.83 Hz, 1 H), 7.58 - 7.62 (m, 1 H), 7.32 - 7.36 (m, 2 H), 7.25 (ddd, *J*=7.52, 4.77, 1.10 Hz, 1 H), 7.07 - 7.12 (m, 2 H), 6.71 (s, 1 H), 2.32 (s, 3 H), 1.26 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.8, 156.6, 149.4, 138.8, 136.9, 131.8, 128.9, 123.2, 121.2, 119.0, 87.1, 84.4, 67.0, 38.8, 27.0, 21.4.



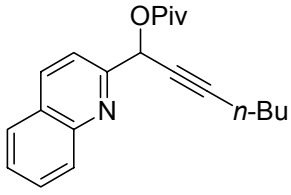
1i: Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.58 (ddd, *J*=4.81, 1.70, 0.83 Hz, 1 H), 7.70 (td, *J*=7.70, 1.65 Hz, 1 H), 7.51 - 7.55 (m, 1 H), 7.22 (ddd, *J*=7.52, 4.77, 1.10 Hz, 1 H), 6.58 (br. s., 1 H), 6.12 - 6.17 (m, 1 H), 2.02 - 2.13 (m, 4 H), 1.49 - 1.63 (m, 4 H), 1.22 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.9, 156.8, 149.4, 136.9, 136.3, 123.1, 121.2, 119.8, 88.9, 82.3, 67.0, 38.7, 28.8, 27.0, 25.6, 22.1, 21.3; IR (neat) υ_{max} 2930.31, 1734.66, 1589.06, 1132.97, 747.28 cm^{-1}.



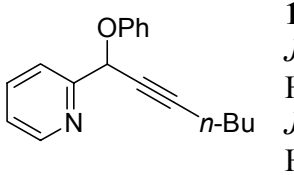
1j: Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.45 - 8.54 (m, 2 H), 7.81 - 7.87 (m, 1 H), 7.66 - 7.71 (m, 1 H), 7.59 - 7.65 (m, 2 H), 7.00 (t, *J*=2.11 Hz, 1 H), 2.18 - 2.24 (m, 2 H), 1.41 - 1.49 (m, 2 H), 1.29 - 1.38 (m, 2 H), 1.19 (s, 9 H), 0.83 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.9, 155.6, 141.6, 137.0, 130.0, 127.3, 127.1, 125.7, 121.6, 89.9, 76.1, 67.3, 38.8, 30.3, 27.0, 21.8, 18.6, 13.5; IR (neat) υ_{max} 2968.70, 2932.63, 1736.20, 1365.36, 1216.67, 826.73 cm^{-1}.



1k: Bright brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.59 - 8.63 (m, 1 H), 8.53 (d, *J*=5.69 Hz, 1 H), 7.87 (d, *J*=7.52 Hz, 1 H), 7.65 - 7.74 (m, 3 H), 7.39 - 7.44 (m, 2 H), 7.23 - 7.31 (m, 4 H), 1.24 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.8, 155.1, 141.6, 137.0, 131.9, 130.1, 128.7, 128.1, 127.4, 127.3, 125.8, 125.5, 122.1, 121.8, 88.4, 85.0, 67.4, 38.9, 27.0; IR (neat) υ_{max} 2972.73, 1733.69, 1272.79, 1130.08, 753.07 cm^{-1}.

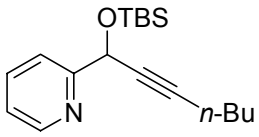


1l: Brownish oil; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 8.26 (d, *J*=8.33 Hz, 1 H), 7.68 - 7.82 (m, 2 H), 7.36 - 7.49 (m, 2 H), 7.18 - 7.30 (m, 2 H), 2.02 - 2.07 (m, 2 H), 1.26 - 1.36 (m, 13 H), 0.75 - 0.80 (m, 3 H); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 176.8, 158.0, 148.5, 137.4, 130.5, 130.1, 128.0, 127.2, 119.4, 89.2, 77.9, 68.5, 39.3, 31.0, 27.6, 22.4, 19.1, 14.0.



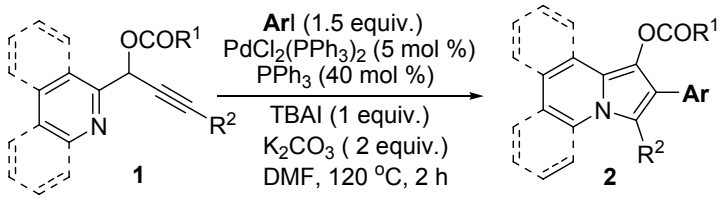
1m: Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.61 (ddd, *J*=4.86, 1.74, 0.92 Hz, 1 H), 7.69 - 7.78 (m, 2 H), 7.23 - 7.31 (m, 3 H), 7.06 - 7.10 (m, 2 H), 6.97 (tt, *J*=7.34, 1.01 Hz, 1 H), 5.95 (t, *J*=2.02 Hz, 1 H), 2.23 (td, *J*=7.15, 2.02 Hz, 2 H), 1.43 - 1.51 (m, 2 H), 1.30 - 1.38 (m, 2 H), 0.85 (t, *J*=7.24 Hz, 3 H); ^{13}C NMR (126

MHz, $CDCl_3$) δ ppm 158.0, 157.2, 149.1, 137.1, 129.2, 123.2, 121.5, 121.3, 116.1, 89.6, 76.9, 71.6, 30.3, 21.8, 18.6, 13.5; IR (neat) υ_{max} 2957.30, 2931.27, 1737.55, 1587.13, 1219.76, 748.25 cm^{-1}.

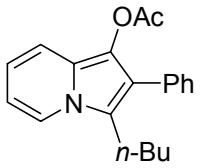


1n: Yellowish oil; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.52 (ddd, *J*=4.77, 1.65, 0.92 Hz, 1 H), 7.70 (td, *J*=7.70, 1.83 Hz, 1 H), 7.59 - 7.63 (m, 1 H), 7.17 (ddd, *J*=7.43, 4.86, 1.10 Hz, 1 H), 5.53 (t, *J*=2.02 Hz, 1 H), 2.17 - 2.23 (m, 2 H), 1.42 - 1.51 (m, 2 H), 1.32 - 1.42 (m, 2 H), 0.93 (s, 9 H), 0.87 (t, *J*=7.34 Hz, 3 H), 0.18 (s, 3 H), 0.14 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.4, 148.6, 136.9, 122.4, 119.8, 86.3, 80.4, 66.6 , 30.5, 25.8, 21.9, 18.6, 13.5, -4.6, -5.0; IR (neat) υ_{max} 2956.34, 2929.34, 2857.02, 1470.46, 1250.61, 1063.55, 748.25 cm^{-1}.

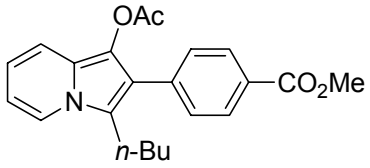
Arylation/Cyclization Cascade Reactions of Propargylic Pivalates and Acetates (1)



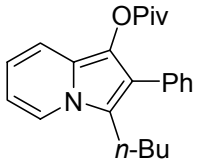
General Procedure: In a dry and argon flushed Wheaton 3mL V-vial, equipped with a magnetic stirring bar and a screw cap, propargylic ester **1** (0.5 mmol, 1 equiv.), TBAI (185 mg, 0.5 mmol, 1 equiv.), K_2CO_3 (138 mg, 1.0 mmol, 2 equiv.) PPh_3 (52 mg, 0.2 mmol, 40 mol%), $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol, 5 mol %) **Ar**I (only added at this point if solid) were added in a glovebox under inert atmosphere. Subsequently, anhydrous DMF (1.5 mL, 0.33 M), and **Ar**I (0.75 mmol, 1.5 equiv.) were added and the reaction mixture was stirred at 120 °C until GC/MS analysis showed full conversion of the propargylic ester **1** (1-6 hours). The reaction mixture was cooled to room temperature followed by addition of water (15 mL) and extracted three times with ethyl acetate (15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporation to give the crude material, which was purified by column chromatography on silica gel to afford desired indolizine product **2**.



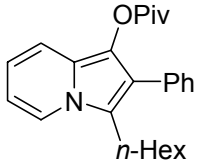
2a: Yellow solid, 72 % yield; **mp** 73-74°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.71 - 7.75 (m, 1 H), 7.40 - 7.49 (m, 4 H), 7.33 - 7.37 (m, 1 H), 7.21 (dt, *J*=8.99, 1.10 Hz, 1 H), 6.64 (ddd, *J*=8.99, 6.42, 0.73 Hz, 1 H), 6.51 (dd, *J*=13.66, 1.19 Hz, 1 H), 2.88 - 2.97 (m, 2 H), 2.25 (s, 3 H), 1.60 - 1.71 (m, 2 H), 1.29 - 1.43 (m, 2 H), 0.91 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 170.0, 133.3, 129.7, 128.3, 126.6, 123.6, 121.7, 121.4, 119.7, 119.3, 115.9, 115.6, 110.3, 29.8, 23.9, 22.5, 20.5, 13.6; IR (neat) υ_{max} 2956.34, 2928.38, 2864.74, 1760.69, 1364.39, 1202.40, 728.96 cm^{-1}; HRMS (EI+) calculated for $C_{20}H_{21}NO_2$ (M^+): 307.15723, Found: 307.15693.



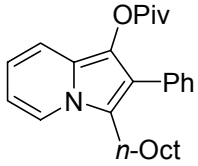
2b: Grey solid, 76 % yield; **mp** 106-107°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.07 - 8.12 (m, 2 H), 7.69 - 7.73 (m, 1 H), 7.42 - 7.49 (m, 2 H), 7.18 (dt, *J*=9.12, 1.03 Hz, 1 H), 6.61 - 6.67 (m, 1 H), 6.48 - 6.54 (m, 1 H), 3.94 (s, 3 H), 2.85 - 2.95 (m, 2 H), 2.23 (s, 3 H), 1.56 - 1.68 (m, 2 H), 1.25 - 1.41 (m, 2 H), 0.87 (t, *J*=7.43 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 169.8, 167.1, 138.5, 129.6, 129.5, 128.3, 123.5, 122.1, 121.4, 119.5, 118.8, 116.1, 116.0, 110.7, 52.0, 29.8, 23.9, 22.5, 20.5, 13.6; IR (neat) υ_{max} 2963.09, 2934.27, 2858.95, 1718.26, 1606.41, 1271.82, 1197.58, 724.14 cm^{-1}; HRMS (EI+) calculated for $C_{22}H_{23}O_4N$ (M^+): 365.16271, Found: 365.16087.



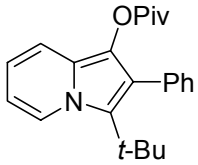
2c: Grey solid, 94 % yield; **mp** 91-92°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.72 (d, *J*=7.15 Hz, 1 H), 7.38 - 7.45 (m, 4 H), 7.29 - 7.35 (m, 1 H), 7.14 (dt, *J*=8.99, 1.10 Hz, 1 H), 6.62 (ddd, *J*=8.99, 6.42, 0.73 Hz, 1 H), 6.49 (td, *J*=6.79, 1.28 Hz, 1 H), 2.88 - 2.96 (m, 2 H), 1.59 - 1.71 (m, 2 H), 1.31 - 1.42 (m, 2 H), 1.30 (s, 9 H), 0.90 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 133.3, 129.9, 128.1, 126.6, 123.7, 121.7, 121.3, 119.9, 119.1, 115.9, 115.3, 110.2, 38.9, 29.8, 27.2, 23.9, 22.5, 13.7; IR (neat) υ_{max} 2960.20, 2927.41, 2869.56, 1743.33, 1365.35, 1113.69, 727.03 cm^{-1}; HRMS (EI+) calculated for $C_{23}H_{27}O_2N$ (M^+): 349.20418, Found: 349.20536.



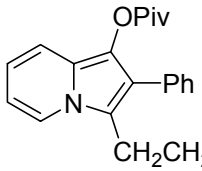
2d: Yellow oil, 77 % yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.71 - 7.74 (m, 1 H), 7.40 - 7.46 (m, 4 H), 7.31 - 7.36 (m, 1 H), 7.16 (dt, *J*=9.03, 1.17 Hz, 1 H), 6.63 (ddd, *J*=8.99, 6.42, 0.92 Hz, 1 H), 6.50 (ddd, *J*=7.29, 6.28, 1.28 Hz, 1 H), 2.88 - 2.97 (m, 2 H), 1.62 - 1.72 (m, 2 H), 1.23 - 1.42 (m, 15 H), 0.89 (t, *J*=7.01 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 133.3, 129.9, 128.1, 126.6, 123.7, 121.6, 121.3, 119.9, 119.2, 115.9, 115.3, 110.2, 38.9, 31.4, 29.1, 27.6, 27.2, 24.1, 22.5, 14.0; IR (neat) υ_{max} 2956.34, 2927.41, 2855.10, 1749.12, 1363.43, 1113.69, 728.00 cm^{-1}; HRMS (EI+) calculated for $C_{25}H_{31}O_2N$ (M^+): 377.23548, Found: 377.23451.



2e: Yellow oil, 94 % yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.68 - 7.73 (m, 1 H), 7.36 - 7.44 (m, 4 H), 7.29 - 7.34 (m, 1 H), 7.11 - 7.14 (m, 1 H), 6.61 (ddd, *J*=8.99, 6.42, 0.73 Hz, 1 H), 6.48 (td, *J*=6.79, 1.28 Hz, 1 H), 2.87 - 2.93 (m, 2 H), 1.59 - 1.70 (m, 2 H), 1.18 - 1.38 (m, 19 H), 0.89 (t, *J*=7.06 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 133.3, 129.9, 128.1, 126.6, 123.8, 123.7, 121.7, 121.4, 119.9, 119.2, 115.9, 115.3, 110.2, 39.0, 31.8, 29.4, 29.2, 27.7,27.3, 24.1, 22.6, 14.1; IR (neat) υ_{max} 2954.41, 2924.52, 2853.17, 1749.12, 1363.43 1112.73, 727.03 cm^{-1}; HRMS (EI+) calculated for $C_{27}H_{35}O_2N$ (M^+): 405.26678, Found: 405.26604.

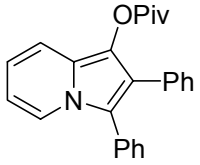


2f: Yellow oil, 50 % yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.08 - 8.13 (m, 1 H), 7.25 - 7.33 (m, 5 H), 7.12 (dt, *J*=8.99, 1.28 Hz, 1 H), 6.61 (ddd, *J*=8.94, 6.37, 0.83 Hz, 1 H), 6.46 (ddd, *J*=7.61, 6.33, 1.47 Hz, 1 H), 1.37 (s, 9 H), 1.05 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.3, 135.8, 131.2, 127.0, 126.7, 125.6, 125.3, 124.6, 122.1, 120.4, 115.9, 115.0, 109.5, 109.5, 38.8, 33.8, 30.0, 26.9; IR (neat) υ_{max} 2962.13, 1749.12, 1478.17, 1342.21, 1117.55, 741.50 cm^{-1}; HRMS (EI+) calculated for $C_{23}H_{27}O_2N$ (M^+): 349.20418, Found: 349.20602.

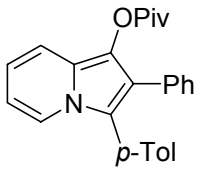


2g: Yellowish solid, 94 % yield; **mp** 121-122°C ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.72 (d, *J*=7.15 Hz, 1 H), 7.36 - 7.43 (m, 2 H), 7.25 - 7.35 (m, 5 H), 7.19 - 7.24 (m, 1 H), 7.10 - 7.18 (m, 3 H), 6.64 (dd, *J*=8.53, 6.51 Hz, 1 H), 6.48 - 6.53 (m, 1 H), 3.19 - 3.26 (m, 2 H), 2.92 - 2.99 (m, 2 H), 1.30 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.3, 140.9, 133.0, 129.8, 128.5, 128.3, 128.1, 126.7, 126.2, 123.9, 121.9, 121.2, 120.4, 117.9, 116.0, 115.6, 110.4, 39.0, 34.1, 27.2, 26.4; IR (neat)

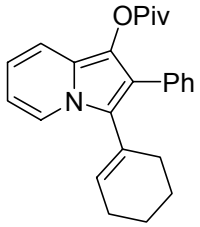
υ_{max} 2968.87, 2958.48, 2929.30, 2358.52, 1744.30, 1602.56, 1363.43, 1113.69, 728.00 cm^{-1}; HRMS (EI+) calculated for $C_{27}H_{27}O_2N$ (M^+): 397.20418, Found: 397.20262.



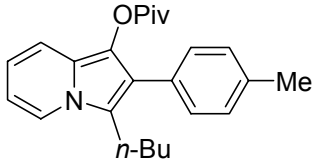
2h: White solid, 69 % yield; **mp** 182-183°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.96 - 7.99 (m, 1 H), 7.30 - 7.41 (m, 5 H), 7.16 - 7.24 (m, 5 H), 7.14 (dt, *J*=9.12, 1.03 Hz, 1 H), 6.66 (ddd, *J*=8.99, 6.42, 0.92 Hz, 1 H), 6.40 (ddd, *J*=7.29, 6.28, 1.28 Hz, 1 H), 1.33 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 132.7, 130.9, 130.7, 130.1, 128.9, 127.9, 127.6, 126.5, 124.7, 122.8,121.7, 120.3, 119.4, 117.0, 115.9, 110.7, 39.1, 27.3; IR (neat) υ_{max} 2972.73, 2956.34, 2855.10, 1743.33, 1396.21, 1124.31, 737.64 cm^{-1}; HRMS (EI+) calculated for $C_{25}H_{23}O_2N$ (M^+): 369.17288, Found: 369.17176.



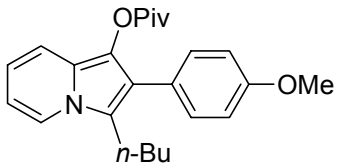
2i: White solid, 68 % yield; **mp** 127-128°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.95 - 7.98 (m, 1 H), 7.17 - 7.28 (m, 9 H), 7.15 (dt, *J*=8.99, 1.06 Hz, 1 H), 6.66 (ddd, *J*=8.99, 6.43, 0.80 Hz, 1 H), 6.37 - 6.43 (m, 1 H), 2.39 (s, 3 H), 1.35 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.2, 137.4, 132.7, 130.5, 130.0, 129.6, 127.9, 127.7, 126.4, 124.5, 122.6, 121.7, 120.0, 119.4, 116.8, 115.8, 110.6, 39.0, 27.3, 21.3; IR (neat) υ_{max} 2977.57, 1750.86, 1353.79, 1246.00, 1112.73 cm^{-1}; HRMS (EI+) calculated for $C_{26}H_{25}O_2N$ (M^+): 383.18853, Found: 383.18966.



2j: Grey solid, 96 % yield; **mp** 146-147°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.90 - 7.95 (m, 1 H), 7.44 - 7.49 (m, 2 H), 7.32 - 7.38 (m, 2 H), 7.23 - 7.28 (m, 1 H), 7.07 (dt, *J*=9.03, 1.17 Hz, 1 H), 6.56 - 6.61 (m, 1 H), 6.37 - 6.44 (m, 1 H), 6.00 - 6.09 (m, 1 H), 2.21 - 2.29 (m, 2 H), 2.00 - 2.07 (m, 2 H), 1.61 - 1.76 (m, 4 H), 1.33 (s, 9 H)^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.1, 133.4, 132.6, 129.2, 128.8, 127.9, 126.4, 124.0, 122.3, 121.9, 121.4, 118.5, 116.0, 115.8, 110.1, 39.0, 28.7, 27.3, 25.8, 23.0, 22.0; IR (neat) υ_{max} 2921.83, 2436.54, 1750.28, 1110.80, 728.57 cm^{-1}; HRMS (EI+) calculated for $C_{25}H_{27}O_2N$ (M^+): 373.20418, Found: 373.20281.

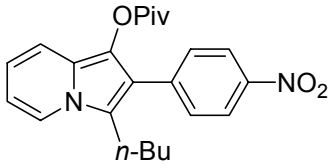


2k: Yellowish solid, 87 % yield; **mp** 91-92°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.69 - 7.72 (m, 1 H), 7.27 - 7.31 (m, 2 H), 7.21 - 7.24 (m, 2 H), 7.12 (dt, *J*=8.99, 1.10 Hz, 1 H), 6.60 (ddd, *J*=8.99, 6.42, 0.73 Hz, 1 H), 6.48 (td, *J*=6.79, 1.28 Hz, 1 H), 2.87 - 2.94 (m, 2 H), 2.40 (s, 3 H), 1.59 - 1.68 (m, 2 H), 1.32 - 1.41 (m, 2 H), 1.31 (s, 9 H), 0.91 (t, *J*=7.43 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 136.1, 130.2, 129.7, 128.8, 123.7, 121.6, 121.3, 119.8, 119.1, 115.8, 115.2, 110.1, 39.0, 29.9, 27.3, 24.0, 22.6, 21.2, 13.7; IR (neat) υ_{max} 2964.05, 2928.38, 1743.33, 1363.43, 1119.48, 725.10 cm^{-1}; HRMS (EI+) calculated for $C_{24}H_{29}O_2N$ (M^+): 363.21983, Found: 363.22028.

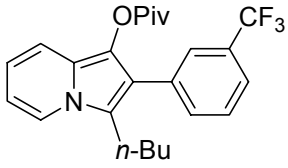


2l: Grey solid, 53 % yield; **mp** 106-107°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.68 - 7.72 (m, 1 H), 7.28 - 7.33 (m, 2 H), 7.11 (dt, *J*=8.99, 1.19 Hz, 1 H), 6.93 - 6.99 (m, 2 H), 6.60 (ddd, *J*=8.99, 6.42, 0.92 Hz, 1 H), 6.47 (td, *J*=6.79, 1.28 Hz,

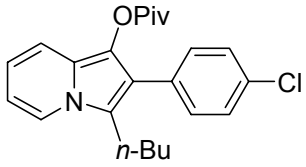
1 H), 3.85 (s, 3 H), 2.86 - 2.93 (m, 2 H), 1.58 - 1.68 (m, 2 H), 1.31 - 1.40 (m, 2 H), 1.30 (s, 9 H), 0.90 (t, *J*=7.43 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.3, 158.4, 130.9, 125.6, 123.8, 121.6, 121.3, 119.6, 119.1, 115.8, 115.2, 113.6, 110.0, 55.2, 39.0, 29.9, 27.3, 23.9, 22.6, 13.7; IR (neat) υ_{max} 2960.20, 2934.16, 2874.38, 1744.30, 1113.69, 735.71 cm^{-1}; HRMS (EI+) calculated for $C_{24}H_{29}O_3N$ (M^+): 379.21475, Found: 379.21380.



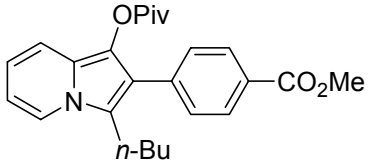
2m: Orange solid, 70 % yield; **mp** 119-120°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.26 - 8.31 (m, 2 H), 7.72 (d, *J*=7.15 Hz, 1 H), 7.52 - 7.58 (m, 2 H), 7.10 - 7.16 (m, 1 H), 6.61 - 6.70 (m, 1 H), 6.49 - 6.57 (m, 1 H), 2.86 - 2.95 (m, 2 H), 1.57 - 1.68 (m, 2 H), 1.28 - 1.40 (m, 11 H), 0.89 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.1, 146.4, 140.8, 130.3, 123.5, 122.1, 121.4, 119.5, 117.8, 116.2, 116.1, 111.0, 39.0, 29.8, 27.2, 23.9, 22.5, 13.6; IR (neat) υ_{max} 2956.34, 2928.38, 2868.59, 1746.23, 1597.73, 1344.14, 1104.05, 729.93 cm^{-1}; HRMS (EI+) calculated for $C_{23}H_{26}O_4N_2$ (M^+): 394.18926, Found: 394.18835.



2n: Yellowish oil, 90 % yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.70 - 7.75 (m, 2 H), 7.58 - 7.62 (m, 2 H), 7.52 - 7.57 (m, 1 H), 7.13 - 7.17 (m, 1 H), 6.64 (ddd, *J*=8.99, 6.42, 0.73 Hz, 1 H), 6.49 - 6.54 (m, 1 H), 2.87 - 2.95 (m, 2 H), 1.61 - 1.71 (m, 2 H), 1.33 - 1.41 (m, 2 H), 1.31 (s, 9 H), 0.91 (t, *J*=7.43 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 134.3, 133.0, 130.6 (q, *J*=32.5 Hz), 28.6, 126.5, 125.3, 123.6, 123.3 (d, *J*=3.7 Hz), 123.1, 121.9, 121.4, 119.3, 118.4, 116.0, 115.8, 110.6, 39.0, 29.8, 27.1, 23.8, 22.5, 13.6; IR (neat) υ_{max} 2966.95, 2929.34, 1745.26, 1320.04, 1107.90, 728.00 cm^{-1}; HRMS (EI+) calculated for $C_{24}H_{26}O_2NF_3$ (M^+): 417.19156, Found: 417.19250.

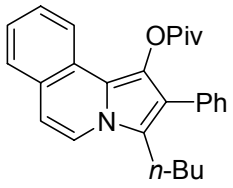


2o: Grey solid, 93 % yield; **mp** 96-97°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.72 (d, *J*=7.15 Hz, 1 H), 7.39 - 7.44 (m, 2 H), 7.32 - 7.37 (m, 2 H), 7.15 (d, *J*=8.99 Hz, 1 H), 6.63 (dd, *J*=8.99, 6.42 Hz, 1 H), 6.47 - 6.52 (m, 1 H), 2.85 - 2.92 (m, 2 H), 1.58 - 1.67 (m, 2 H), 1.29 - 1.40 (m, 11 H), 0.91 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 132.6, 131.9, 131.1, 128.3, 123.6, 121.7, 121.3, 119.1, 118.7, 115.9, 115.5, 110.4, 38.9, 29.8, 27.2, 23.8, 22.5, 13.6; IR (neat) υ_{max} 2956.34, 2931.27, 2868.59, 1745.26, 1364.39, 1089.58, 729.93 cm^{-1}; HRMS (EI+) calculated for $C_{23}H_{26}O_2NCl$ (M^+): 383.16520, Found: 383.16605.

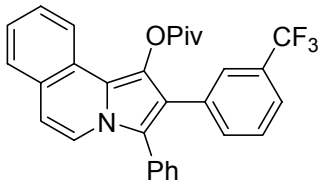


2p: Grey solid, 88 % yield; **mp** 101-102°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.06 - 8.12 (m, 2 H), 7.71 (d, *J*=7.15 Hz, 1 H), 7.44 - 7.48 (m, 2 H), 7.09 - 7.14 (m, 1 H), 6.62 (dd, *J*=8.80, 6.60 Hz, 1 H), 6.50 (t, *J*=6.79 Hz, 1 H), 3.94 (s, 3 H), 2.85 - 2.94 (m, 2 H), 1.56 - 1.67 (m, 2 H), 1.29 - 1.37 (m, 2 H), 1.28 (s, 9 H), 0.88 (t, *J*=7.34 Hz, 3 H); ^{13}C

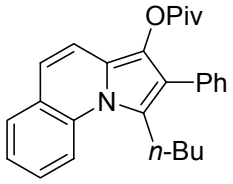
NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 167.1, 138.5, 129.7, 129.5, 128.2, 123.6, 121.9, 121.4, 119.4, 118.9, 116.1, 115.7, 110.6, 52.0, 39.0, 29.8, 27.3, 23.9, 22.5, 13.7; IR (neat) υ_{max} 2960.40, 1725.02, 1610.08, 1275.68, 1110.04, 728.96 cm^{-1}; HRMS (EI+) calculated for $C_{25}H_{29}O_4N$ (M^+): 407.20966, Found: 407.21039.



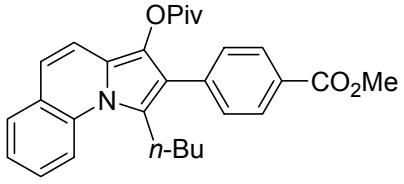
2q: Yellow oil, 71 % yield; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.03 - 8.07 (m, 1 H), 7.63 (d, *J*=7.52 Hz, 1 H), 7.52 - 7.56 (m, 1 H), 7.39 - 7.46 (m, 5 H), 7.30 - 7.37 (m, 2 H), 6.71 (d, *J*=7.52 Hz, 1 H), 2.86 - 2.93 (m, 2 H), 1.59 - 1.69 (m, 2 H), 1.30 - 1.39 (m, 11 H), 0.89 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.7, 133.2, 130.2, 128.4, 128.1, 127.1, 126.7, 126.6, 126.6, 125.8, 125.0, 121.9, 121.7, 121.1, 119.5, 117.2, 110.5, 39.0, 30.9, 27.3, 23.7, 22.4, 13.7; IR (neat) υ_{max} 2950.55, 2368.16, 1741.41, 1363.43, 1102.12, 702.93 cm^{-1}; HRMS (EI+) calculated for $C_{27}H_{29}O_2N$ (M^+): 399.21983, Found: 399.21894.



2r: White solid, 74 % yield; **mp** 207-208°C; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.06 - 8.11 (m, 1 H), 7.75 (d, *J*=7.52 Hz, 1 H), 7.58 - 7.61 (m, 1 H), 7.52 - 7.56 (m, 1 H), 7.29 - 7.49 (m, 10 H), 6.66 (d, *J*=7.34 Hz, 1 H), 1.35 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 176.8, 133.7, 133.5, 131.0, 130.0, 29.0, 128.7, 128.5, 128.3, 127.4, 127.4, 126.8, 126.7, 125.8, 125.5, 123.3, 123.2, 123.1, 122.5, 122.2, 121.5, 118.6, 111.4, 39.1, 27.3; IR (neat) υ_{max} 2969.95, 1749.51, 1460.63, 1326.60, 1128.93 cm^{-1}; HRMS (EI+) calculated for $C_{30}H_{24}O_2NF_3$ (M^+): 487.17591, Found: 487.17714.



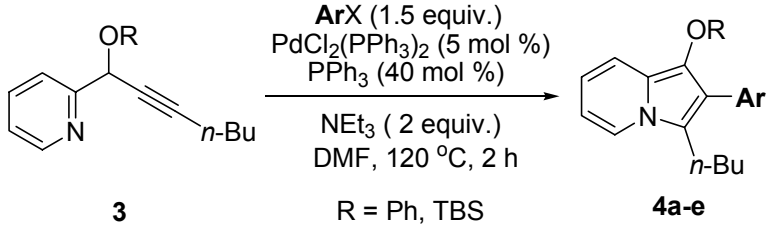
2s: Yellow oil, 78 % yield; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.16 (d, *J*=8.62 Hz, 1 H), 7.61 (dd, *J*=7.79, 1.56 Hz, 1 H), 7.46 (ddd, *J*=8.62, 7.15, 1.65 Hz, 1 H), 7.39 - 7.44 (m, 2 H), 7.28 - 7.38 (m, 4 H), 7.04 (d, *J*=9.17 Hz, 1 H), 6.91 (d, *J*=9.17 Hz, 1 H), 3.20 - 3.27 (m, 2 H), 1.69 - 1.78 (m, 2 H), 1.29 - 1.39 (m, 2 H), 1.24 (s, 9 H), 0.86 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.2, 135.1, 133.3, 130.5, 128.7, 128.0, 127.3, 127.1, 126.8, 125.9, 125.8, 123.2, 121.5, 121.4, 118.1, 116.5, 115.3, 39.0, 31.2, 27.7, 27.2, 22.2, 13.7; IR (neat) υ_{max} 2952.50, 2951.34, 1753.18, 1362.27, 1111.09, 779.49 cm^{-1}; HRMS (EI+) calculated for $C_{27}H_{29}NO_2$ (M^+): 399.21983, Found: 399.21831.



2t: Yellow oil, 88 % yield; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.14 (d, *J*=8.62 Hz, 1 H), 8.10 - 8.13 (m, 2 H), 7.61 (dd, *J*=7.89, 1.47 Hz, 1 H), 7.44 - 7.49 (m, 3 H), 7.29 - 7.33 (m, 1 H), 7.04 (d, *J*=9.35 Hz, 1 H), 6.92 (d, *J*=9.35 Hz, 1 H), 3.95 (s, 3 H), 3.19 - 3.27 (m, 2 H), 1.69 - 1.78 (m, 2 H), 1.28 - 1.36 (m, 2 H), 1.26 (s, 9 H), 0.85 (t, *J*=7.43 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 177.0, 167.1, 138.4, 134.9, 130.4, 129.4, 128.8, 128.4, 127.2, 126.9, 125.8, 125.8, 123.4, 121.6, 120.5, 118.5, 116.5, 115.2, 52.0, 39.0, 31.0, 27.6, 27.2, 22.1, 13.6. IR (neat) υ_{max} 2967.92, 2958.09, 2917.21,

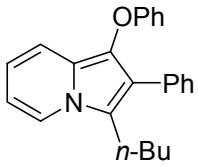
1725.98, 1272.98, 1119.48 cm^{-1}; HRMS (EI+) calculated for $C_{29}H_{31}NO_4$ (M^+): 457.22531, Found: 457.22625

Arylation/Cyclization Cascade Reactions of Propargylic Ethers (3)

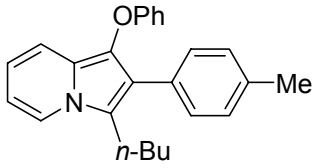


3 **4a-e**

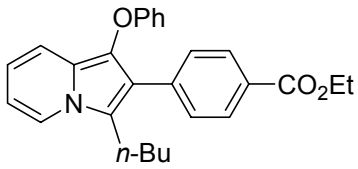
General Procedure: In a dry and argon flushed Wheaton 3mL V-vial, equipped with a magnetic stirring bar and a screw cap, propargylic ether **3** (0.5 mmol, 1 equiv.), PPh_3 (52 mg, 0.2 mmol, 40 mol%), $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol, 5 mol %) **Ar**X (only added at this point if solid) were added in a glovebox under inert atmosphere. Subsequently, anhydrous DMF (1.5 mL, 0.33 M), NEt_3 (101 mg, 139 µL, 1.0 mmol, 2 equiv.), and **Ar**X (0.75 mmol, 1.5 equiv.) were added and the reaction mixture was stirred at 120 °C until GC/MS analysis showed full conversion of the propargylic ether **1** (2 hours). The reaction mixture was cooled to room temperature followed by addition of water (15 mL) and extracted three times with ethyl acetate (15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporation to give the crude material, which was purified by column chromatography on silica gel to afford desired indolizine product **4**.



4a: Bright yellow solid, 78 % yield (when, **Ar**X = PhBr); 83 % yield (when, **Ar**X = PhI); **mp** 116-117°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.77 (d, *J*=6.97 Hz, 1 H), 7.42 - 7.47 (m, 2 H), 7.34 - 7.40 (m, 2 H), 7.15 - 7.30 (m, 4 H), 6.92 - 6.96 (m, 3 H), 6.49 - 6.57 (m, 2 H), 2.96 - 3.02 (m, 2 H), 1.67 - 1.76 (m, 2 H), 1.37 - 1.47 (m, 2 H), 0.95 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.0, 133.4, 129.7, 129.2, 128.2, 126.4, 121.8, 121.3, 121.2, 120.1, 119.1, 116.5, 115.3, 114.7, 110.3, 29.9, 24.0, 22.6, 13.7; IR (neat) υ_{max} 2951.50, 2925.11, 1589.25, 1488.01, 1206.45 cm^{-1}; HRMS (EI+) calculated for $C_{24}H_{23}ON$ (M^+): 341.17797, Found: 341.17734.

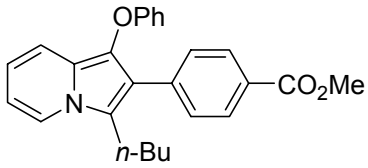


4b: Yellow oil, 81 % yield (when, **Ar**X = *p*-TolBr); 76 % yield (when, **Ar**X = *p*-TolI); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.74 - 7.78 (m, 1 H), 7.30 - 7.35 (m, 2 H), 7.14 - 7.24 (m, 5 H), 6.90 - 6.97 (m, 3 H), 6.47 - 6.56 (m, 2 H), 2.94 - 3.01 (m, 2 H), 2.36 (s, 3 H), 1.66 - 1.75 (m, 2 H), 1.37 - 1.47 (m, 2 H), 0.95 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.0, 136.0, 130.4, 129.6, 129.2, 128.9, 127.9, 121.8, 121.2, 121.2, 120.1, 119.0, 116.5, 115.3, 114.6, 110.1, 29.9, 24.1, 22.6, 21.2, 13.8; IR (neat) υ_{max} 2953.46, 2915.47, 2869.19, 1587.52, 1363.24, 1205.49, 817.86 cm^{-1}; HRMS (EI+) calculated for $C_{25}H_{25}ON$ (M^+): 355.19362, Found: 355.19464.

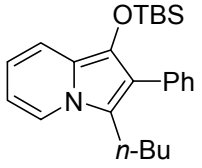


4c: Bright yellow solid, 89 % yield (when, **Ar**X = *p*-CO_2Et-C_6H_4Br); **mp** 131-132°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.02 - 8.07 (m, 2 H), 7.76 (d, *J*=6.97 Hz, 1 H), 7.50 -

7.55 (m, 2 H), 7.16 - 7.23 (m, 3 H), 6.88 - 6.95 (m, 3 H), 6.48 - 6.58 (m, 2 H), 4.38 (q, *J*=7.15 Hz, 2 H), 2.94 - 3.01 (m, 2 H), 1.65 - 1.77 (m, 2 H), 1.34 - 1.46 (m, 5 H), 0.94 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.0, 159.7, 138.4, 129.5, 129.2, 127.9, 127.8, 122.1, 121.4, 121.3, 119.3, 118.9, 116.6, 115.1, 110.6, 51.9, 29.8, 24.0, 22.5, 13.7; IR (neat) υ_{max} 2938.52, 2921.45, 2858.00, 1706.89, 1361.69, 1176.75, 775.05 cm^{-1}; HRMS (EI+) calculated for $C_{27}H_{27}O_3N$ (M^+): 413.19910, Found: 413.19813.

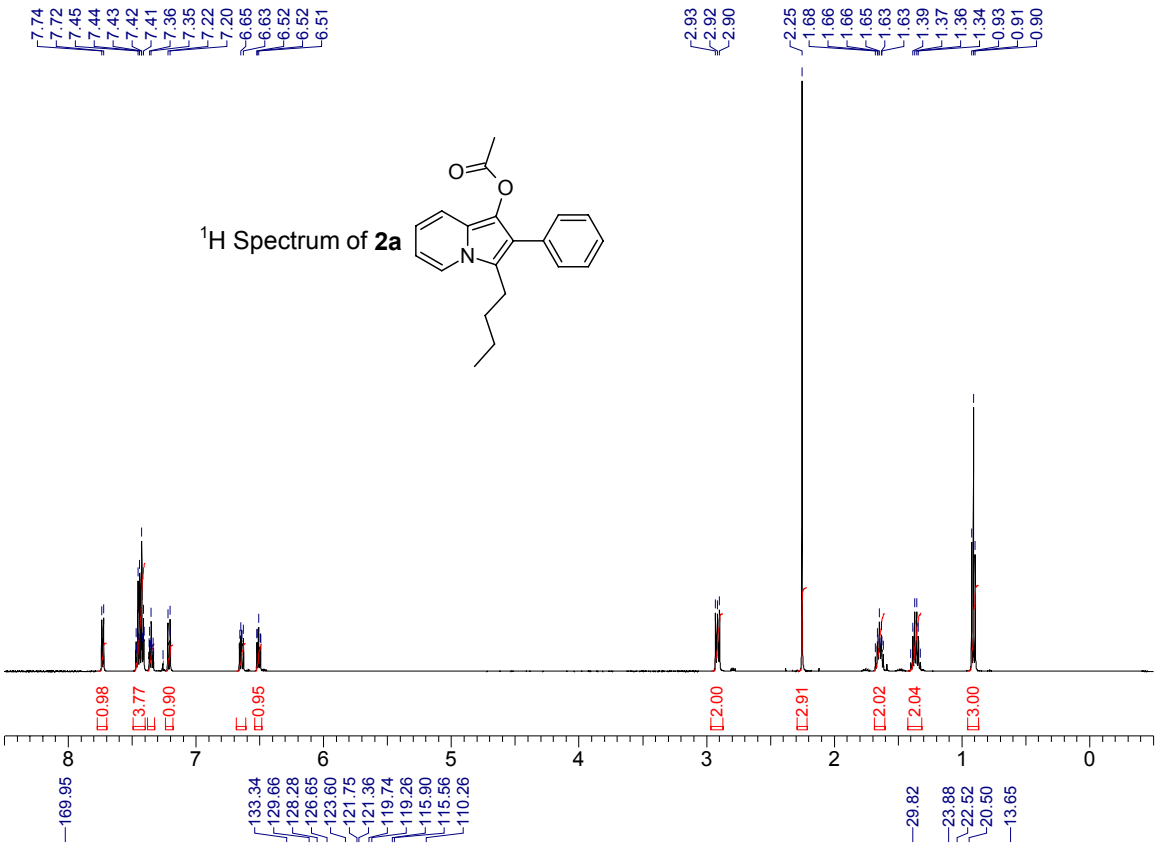


4d: Bright yellow solid, 94 % yield (when, **Ar**X = *p*-CO_2Me-C_6H_4I); **mp** 113-114°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.01 - 8.07 (m, 2 H), 7.76 (d, *J*=6.97 Hz, 1 H), 7.50 - 7.56 (m, 2 H), 7.16 - 7.23 (m, 3 H), 6.87 - 6.97 (m, 3 H), 6.49 - 6.59 (m, 2 H), 3.91 (s, 3 H), 2.94 - 3.02 (m, 2 H), 1.64 - 1.76 (m, 2 H), 1.34 - 1.45 (m, 2 H), 0.94 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.0, 159.7, 138.4, 129.5, 129.2, 127.9, 127.8, 122.1, 121.4, 121.3, 119.3, 118.9, 116.6, 115.1, 110.6, 51.9, 29.8, 24.0, 22.5, 13.7; IR (neat) υ_{max} 2925.50, 1714.03 1606.80, 1258.33, 1109.06, 751.52 cm^{-1}; HRMS (EI+) calculated for $C_{26}H_{25}O_3N$ (M^+): 399.18345, Found: 399.18250.

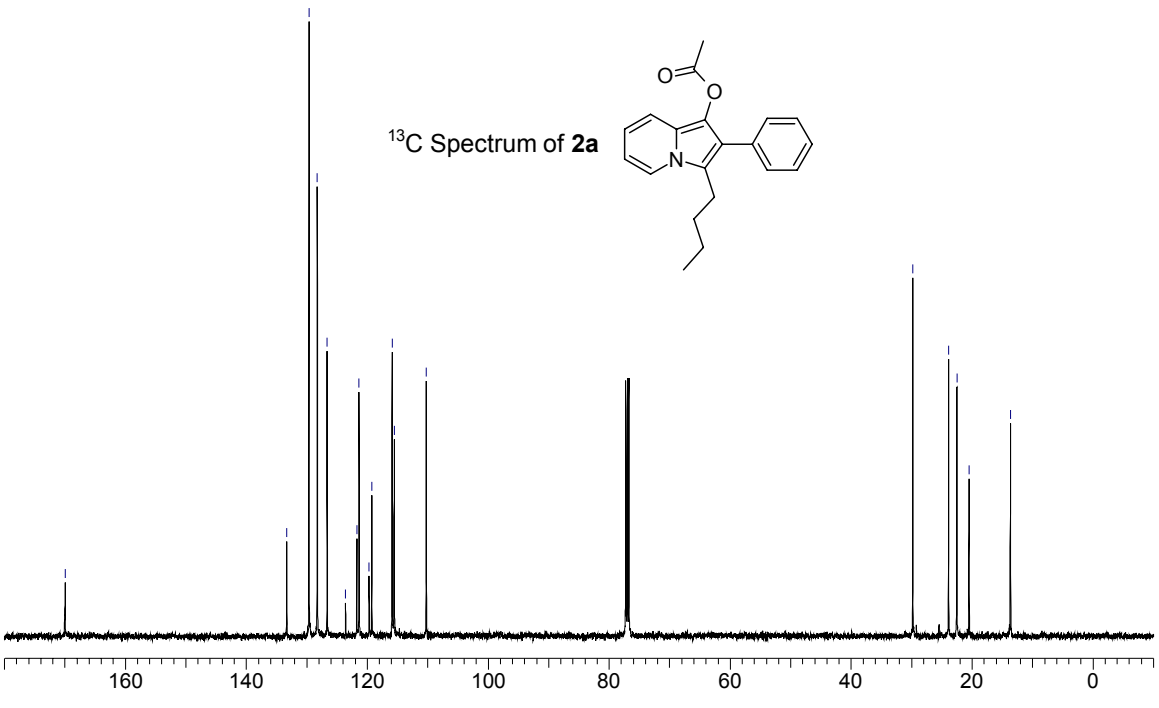


4e[a]: Yellow oil, 73 % yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.58 - 7.62 (m, 1 H), 7.37 - 7.46 (m, 4 H), 7.25 - 7.31 (m, 2 H), 6.42 (ddd, *J*=8.94, 6.28, 0.92 Hz, 1 H), 6.36 (ddd, *J*=7.29, 6.19, 1.38 Hz, 1 H), 2.83 - 2.92 (m, 2 H), 1.52 - 1.63 (m, 2 H), 1.24 - 1.36 (m, 2 H), 0.92 (s, 9 H), 0.86 (t, *J*=7.34 Hz, 3 H), -0.24 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 134.7, 130.6, 129.2, 128.0, 126.1, 120.8, 120.5, 119.0, 118.1, 117.0, 112.5, 109.6, 29.8, 25.8, 24.0, 22.5, 18.1, 13.7, -4.8; IR (neat) υ_{max} 2956.34, 2928.38, 2852.20, 1717.30, 1552.42, 1250.61, 728.96 cm^{-1}; HRMS (EI+) calculated for $C_{24}H_{33}ONSi$ (M^+): 379.23315, Found: 379.23239.

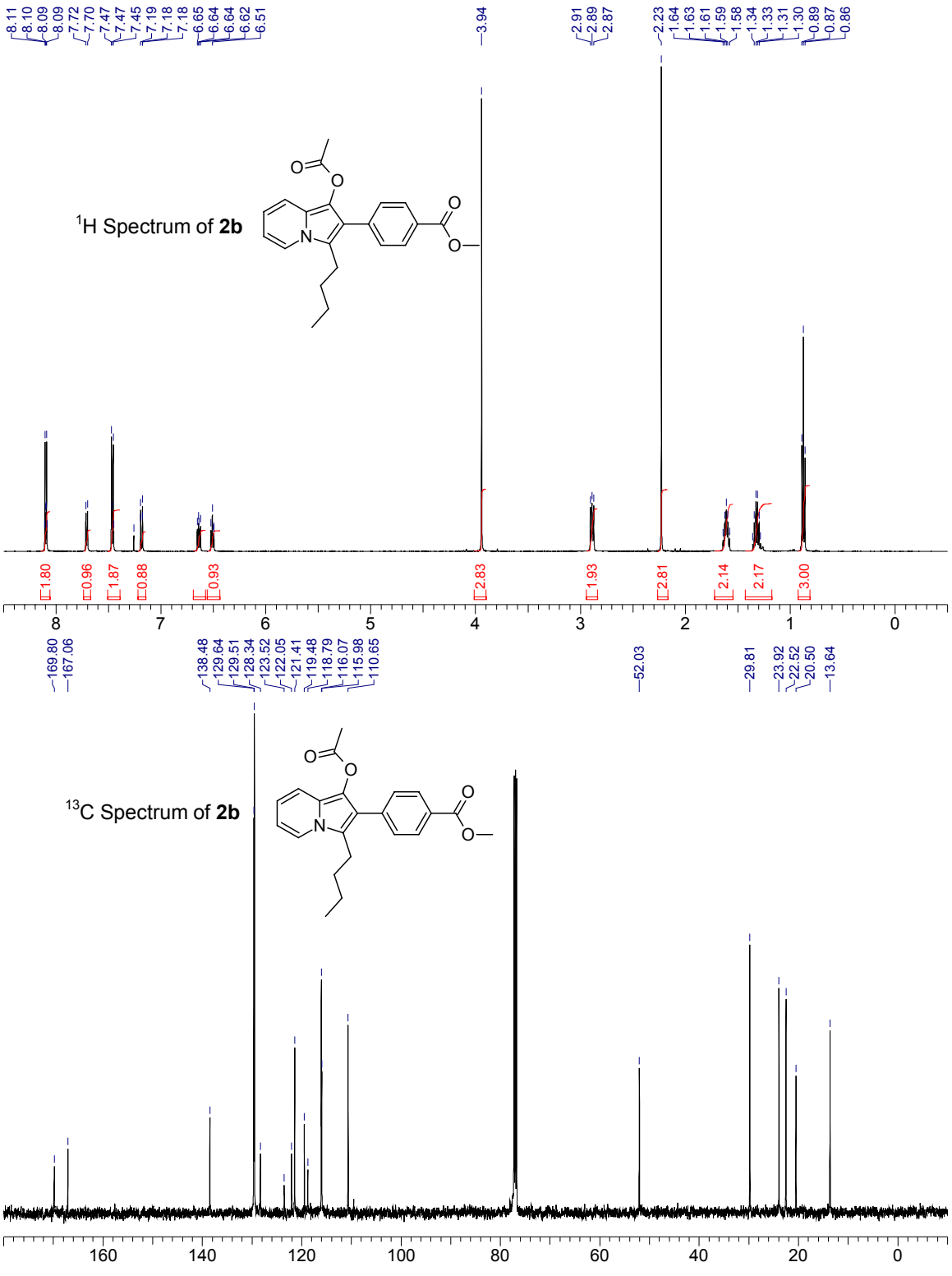
[a] Reaction was performed under conditons reported on page S7

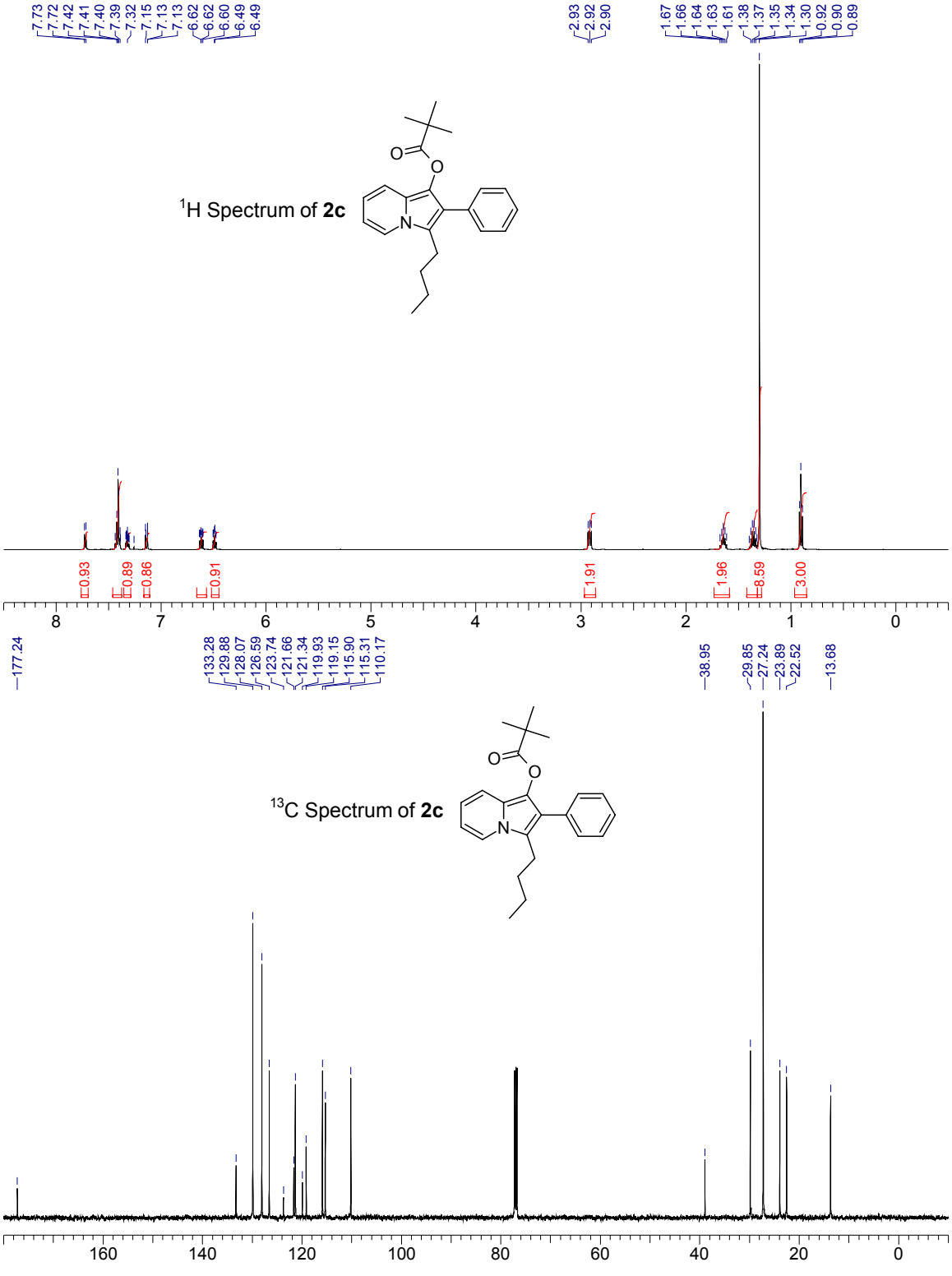


^{1}H Spectrum of **2a**



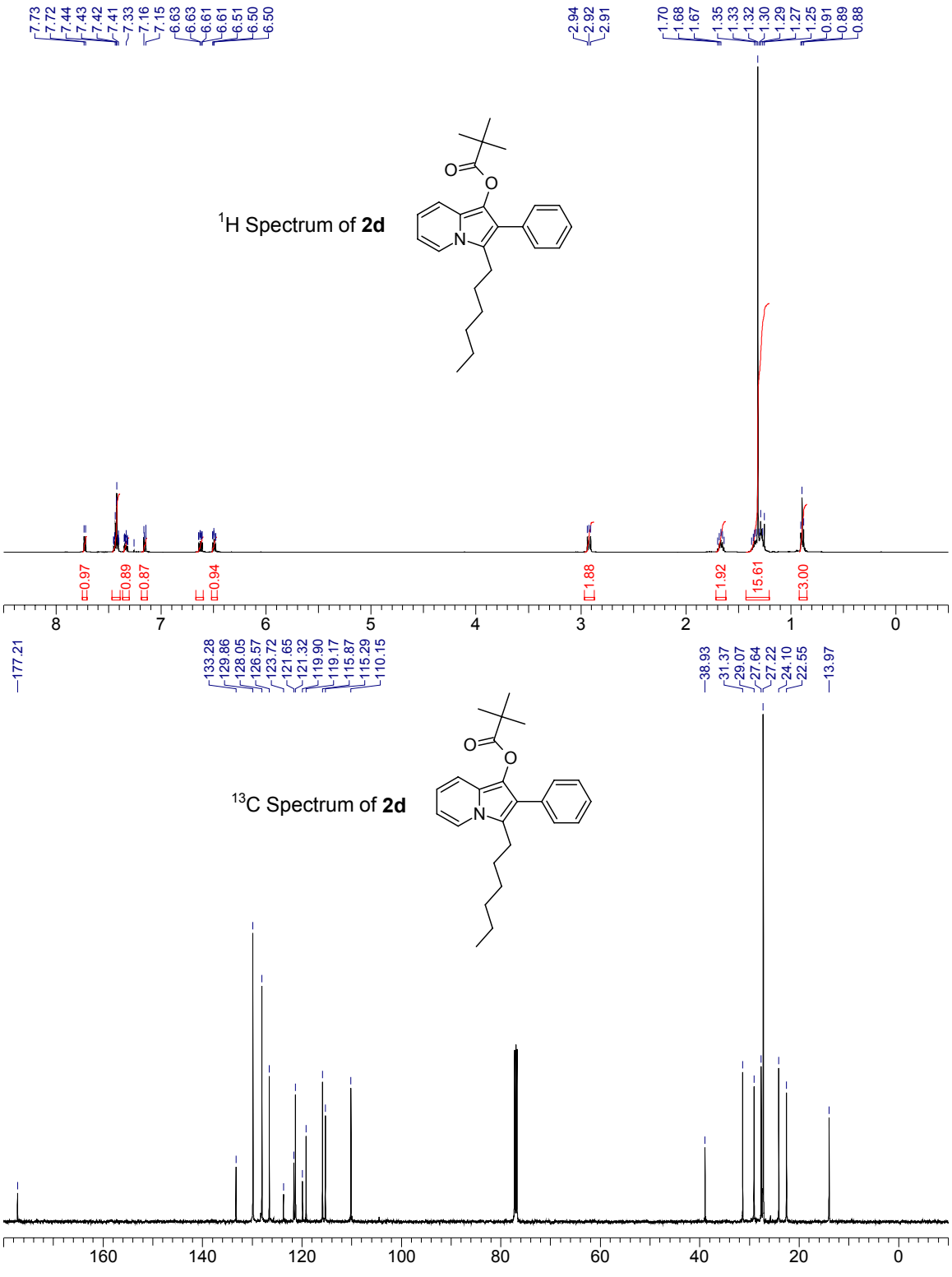
^{13}C Spectrum of **2a**

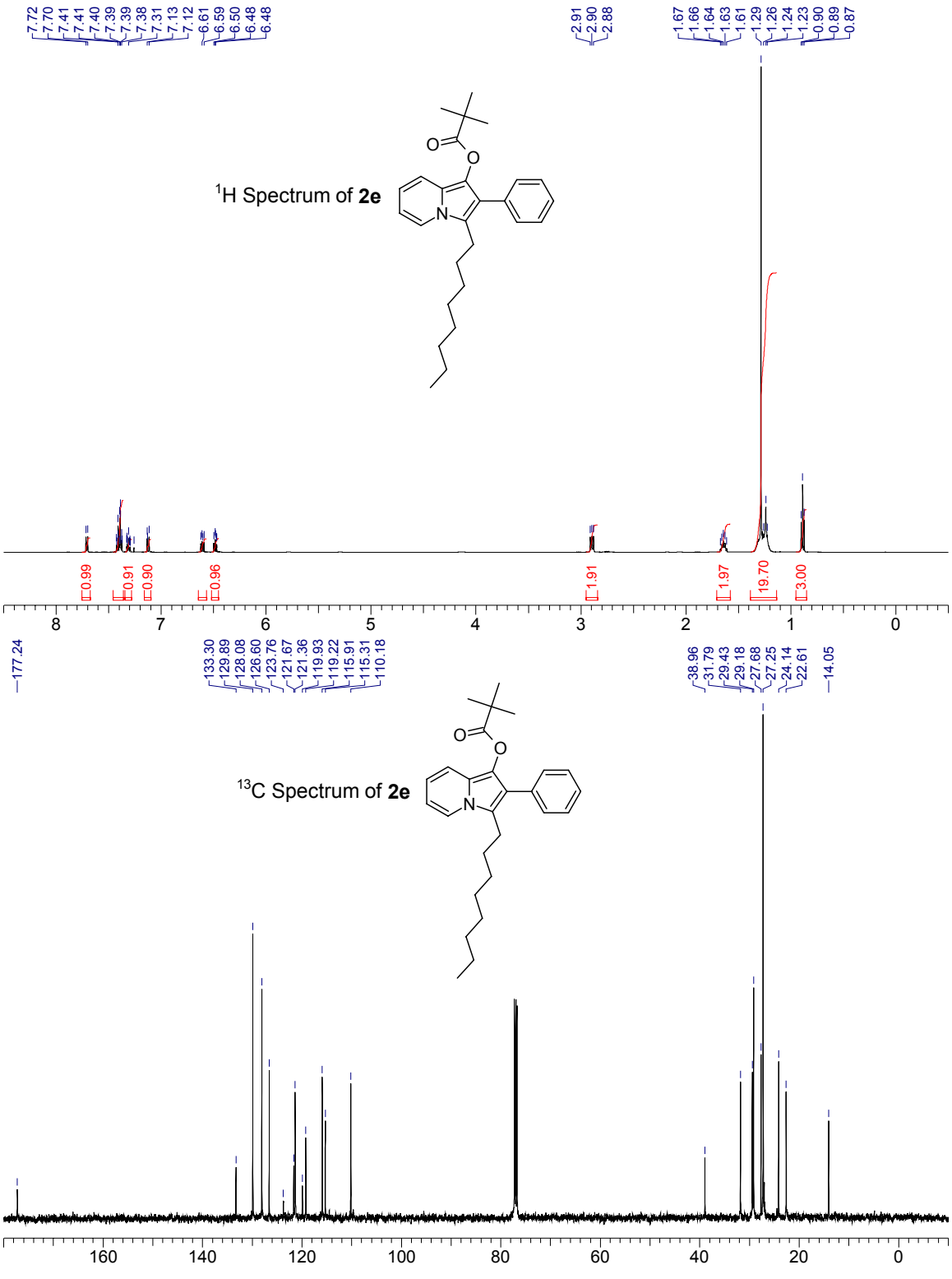

8.11
8.10
8.09
8.09
7.72
7.70
7.47
7.47
7.45
7.19
7.18
7.18
6.65
6.64
6.64
6.62
6.51
3.94
2.91
2.89
2.87
2.23
1.64
1.63
1.61
1.59
1.58
1.34
1.33
1.31
1.30
0.89
0.87
0.86
1H Spectrum of 2b
1.80
0.96
1.87
0.88
0.93
2.83
1.93
2.81
2.14
2.17
3.00
8
7
6
5
4
3
2
1
0
169.80
167.06
138.48
129.64
129.51
128.34
123.52
122.05
121.41
119.48
118.79
116.07
115.98
110.65
52.03
29.81
23.92
22.52
20.50
13.64
13C Spectrum of 2b
160
140
120
100
80
60
40
20
0



^{1}H Spectrum of **2c**

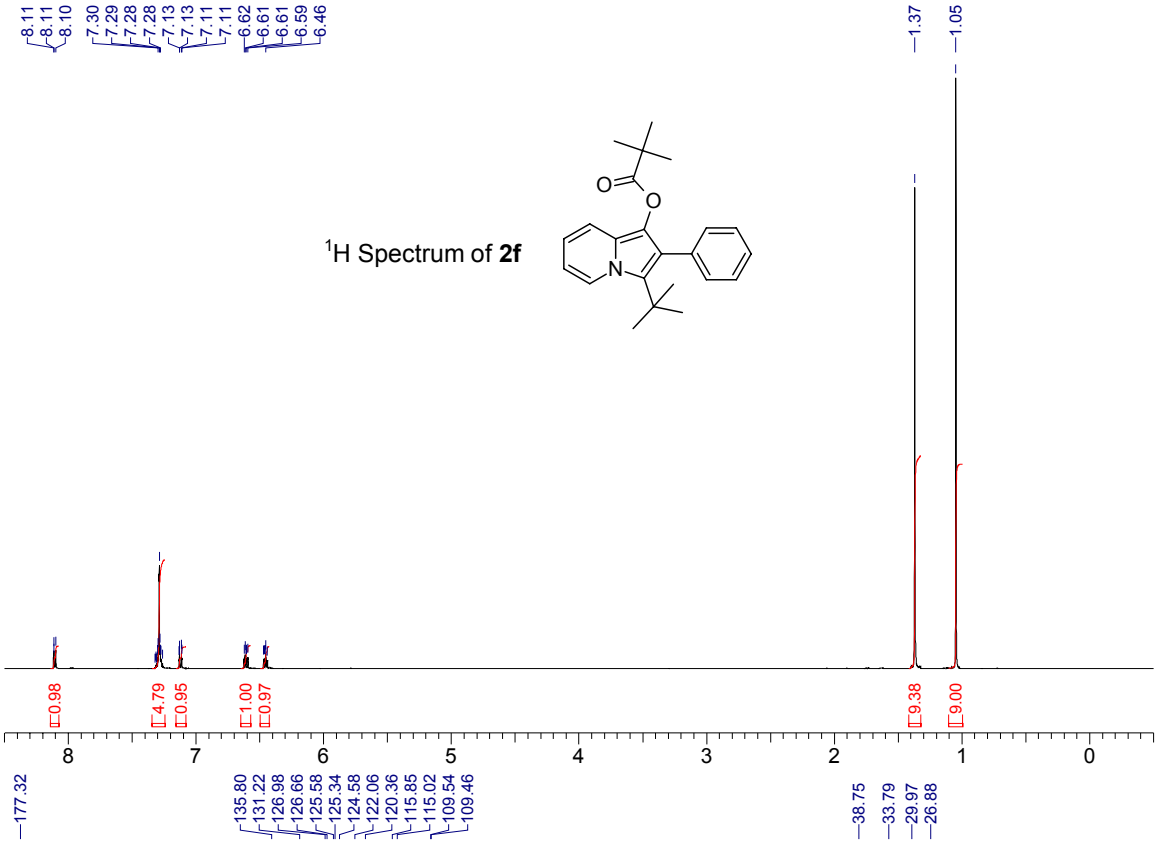
^{13}C Spectrum of **2c**


7.73
7.72
7.44
7.43
7.42
7.41
7.33
7.16
7.15
6.63
6.63
6.61
6.61
6.51
6.50
6.50
2.94
2.92
2.91
1.70
1.68
1.67
1.35
1.33
1.32
1.30
1.29
1.27
1.25
0.91
0.89
0.88
O
O
N
1H Spectrum of 2d
0.97
0.89
0.87
0.94
1.88
1.92
15.61
3.00
8
7
6
5
4
3
2
1
0
177.21
133.28
129.86
128.05
126.57
123.72
121.65
121.32
119.90
119.17
115.87
115.29
110.15
38.93
31.37
29.07
27.64
27.22
24.10
22.55
13.97
O
O
N
13C Spectrum of 2d
160
140
120
100
80
60
40
20
0

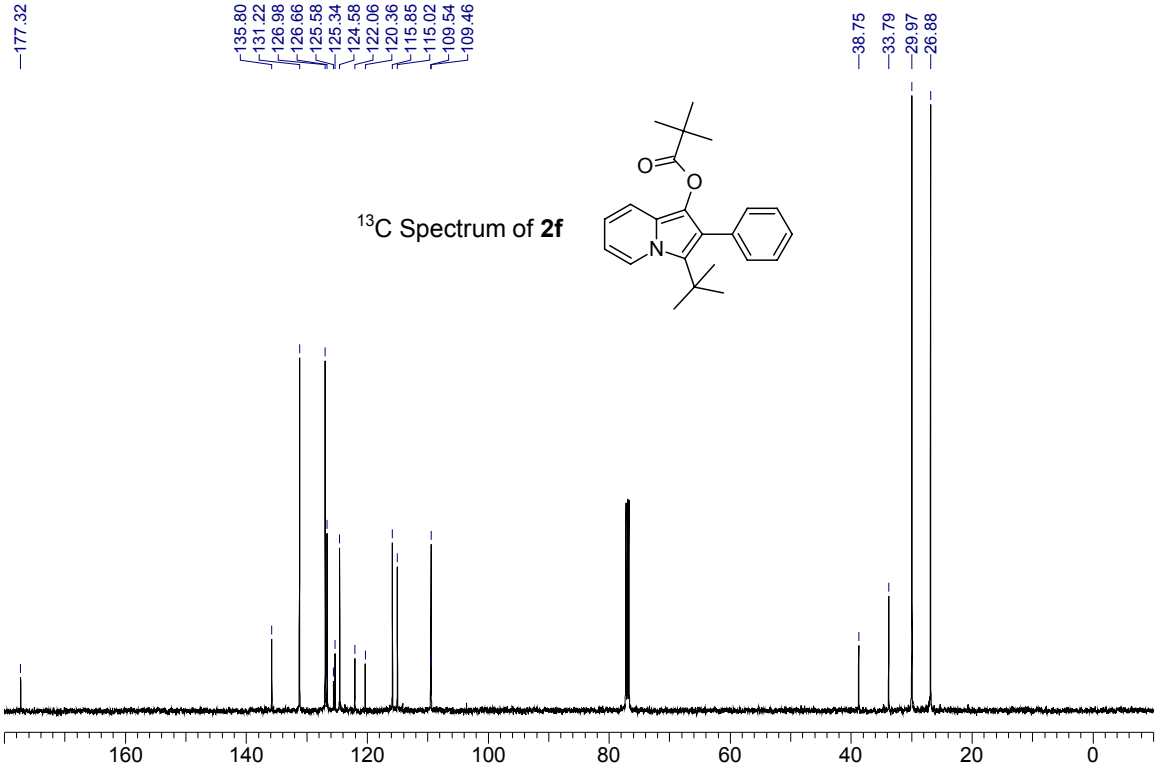


^{1}H Spectrum of **2e**

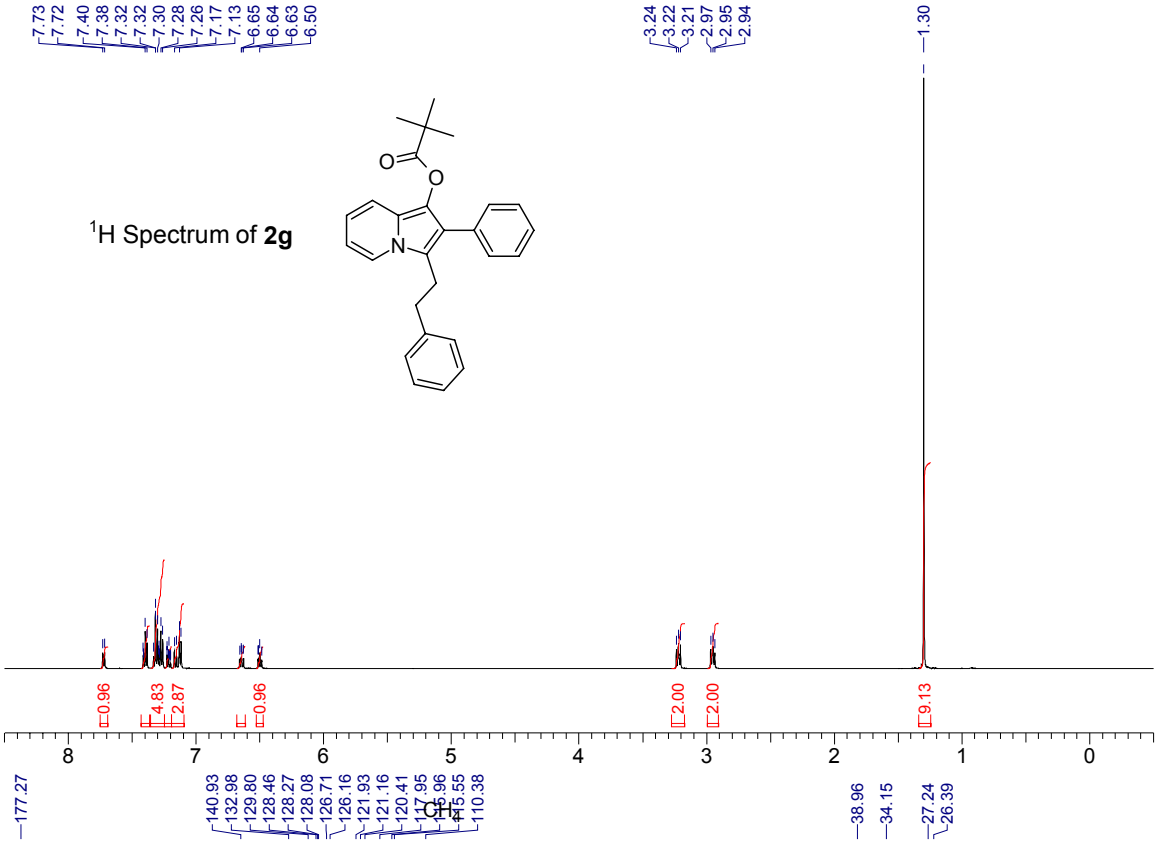
^{13}C Spectrum of **2e**



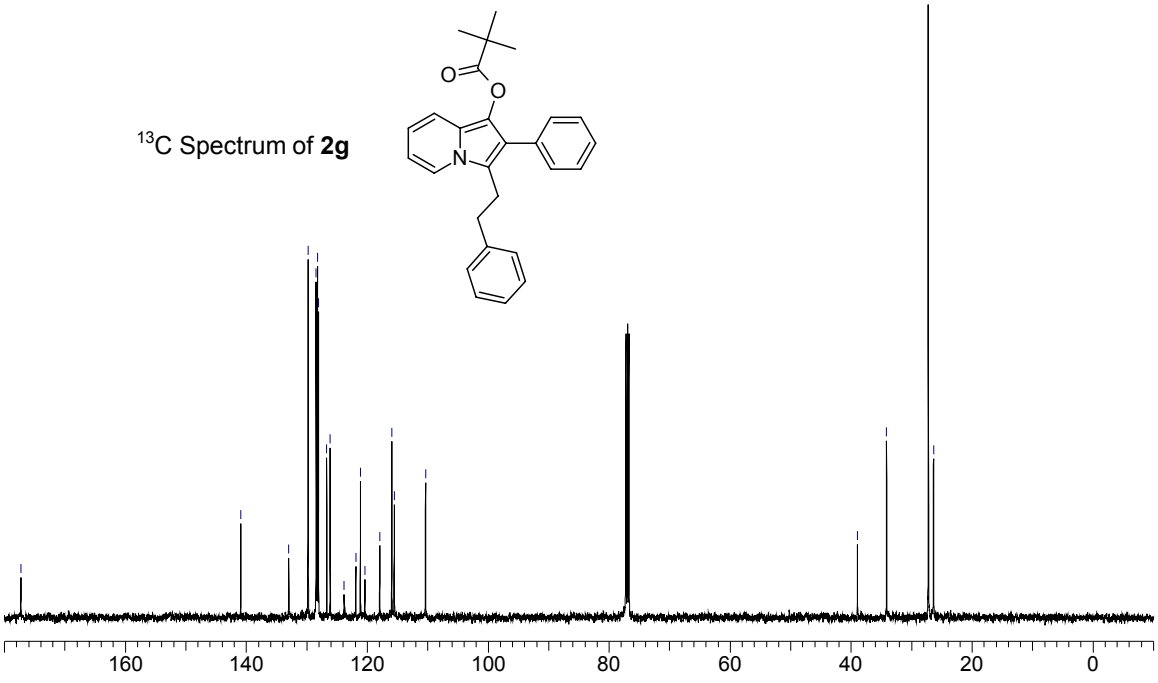
^{1}H Spectrum of **2f**



^{13}C Spectrum of **2f**

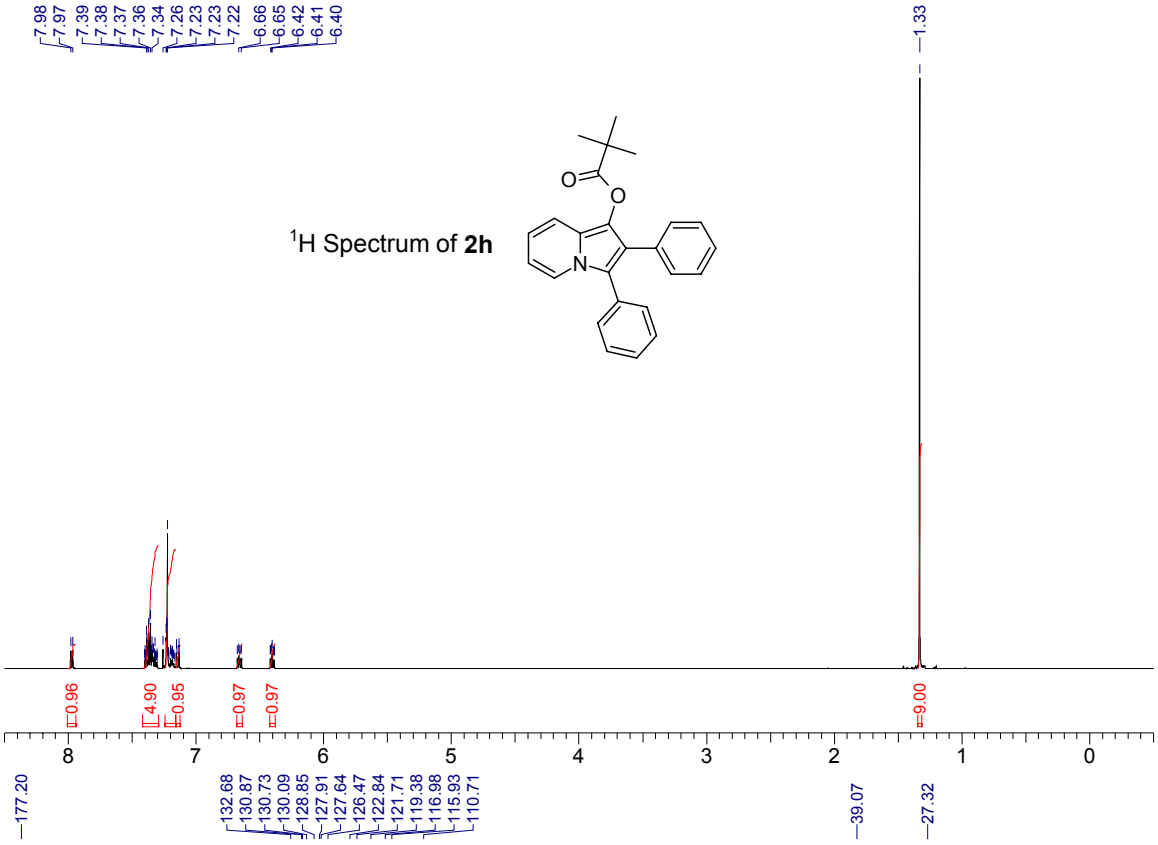


^{1}H Spectrum of **2g**

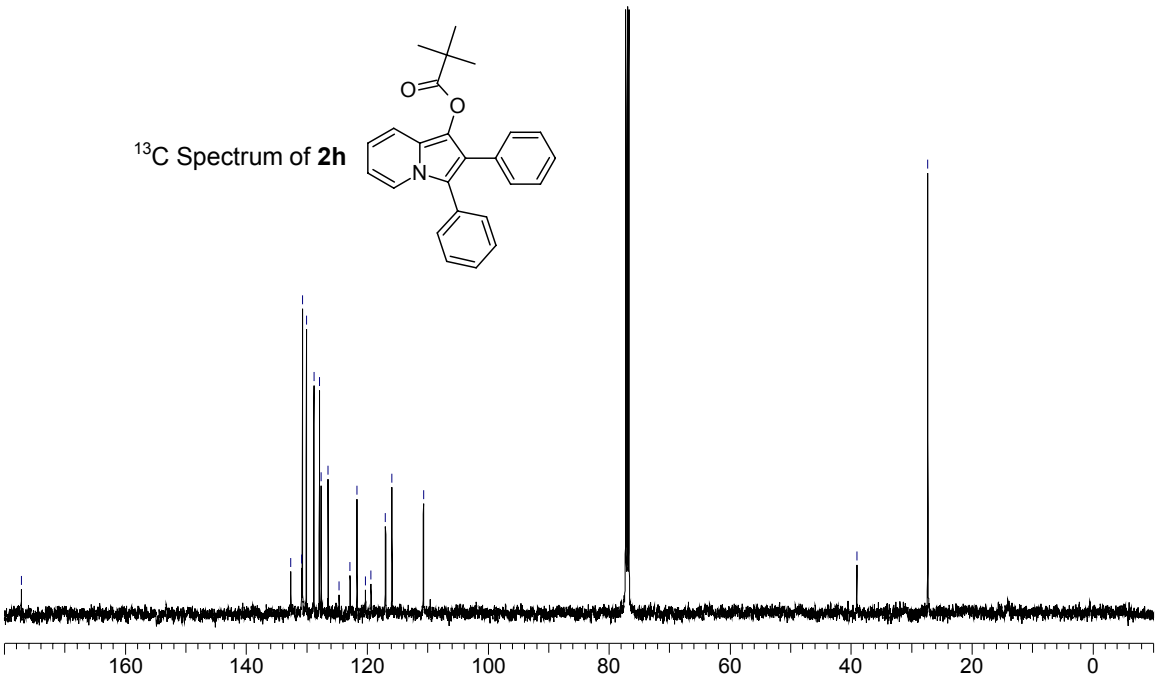


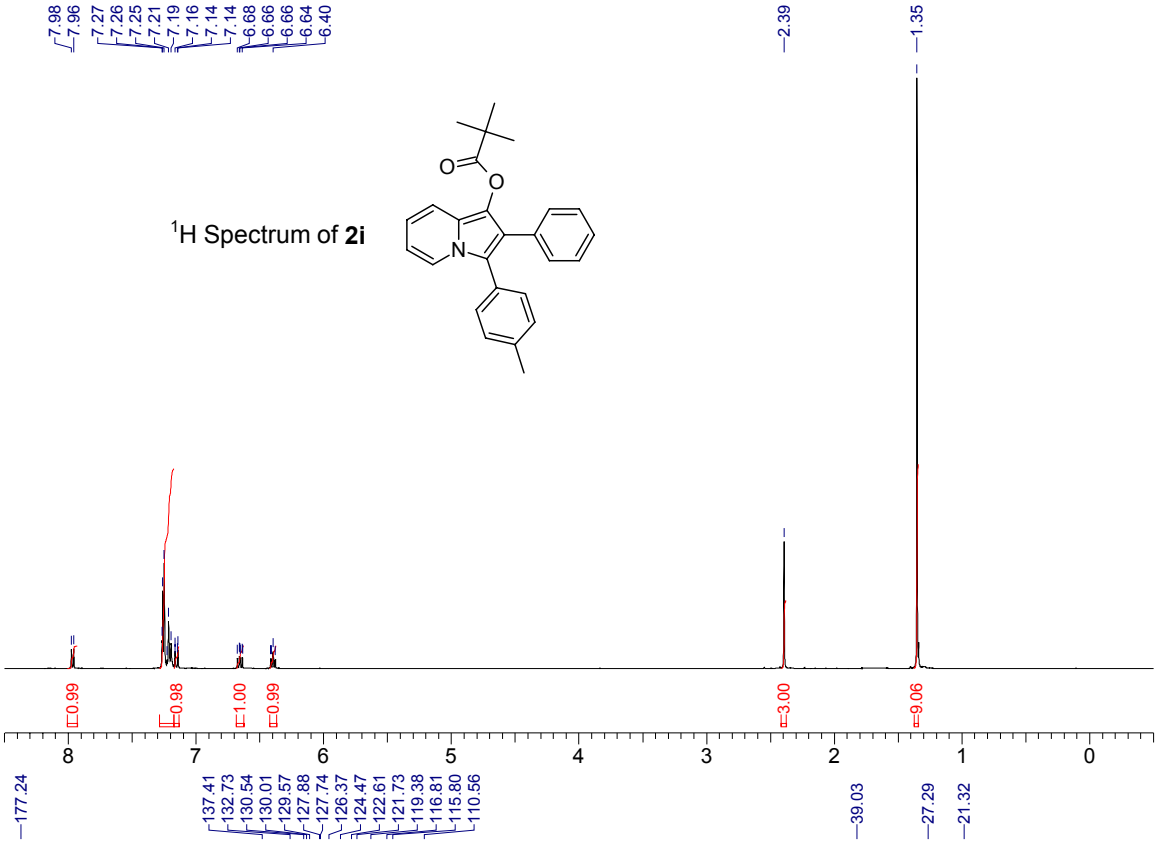
^{13}C Spectrum of **2g**

^{1}H Spectrum of **2h**

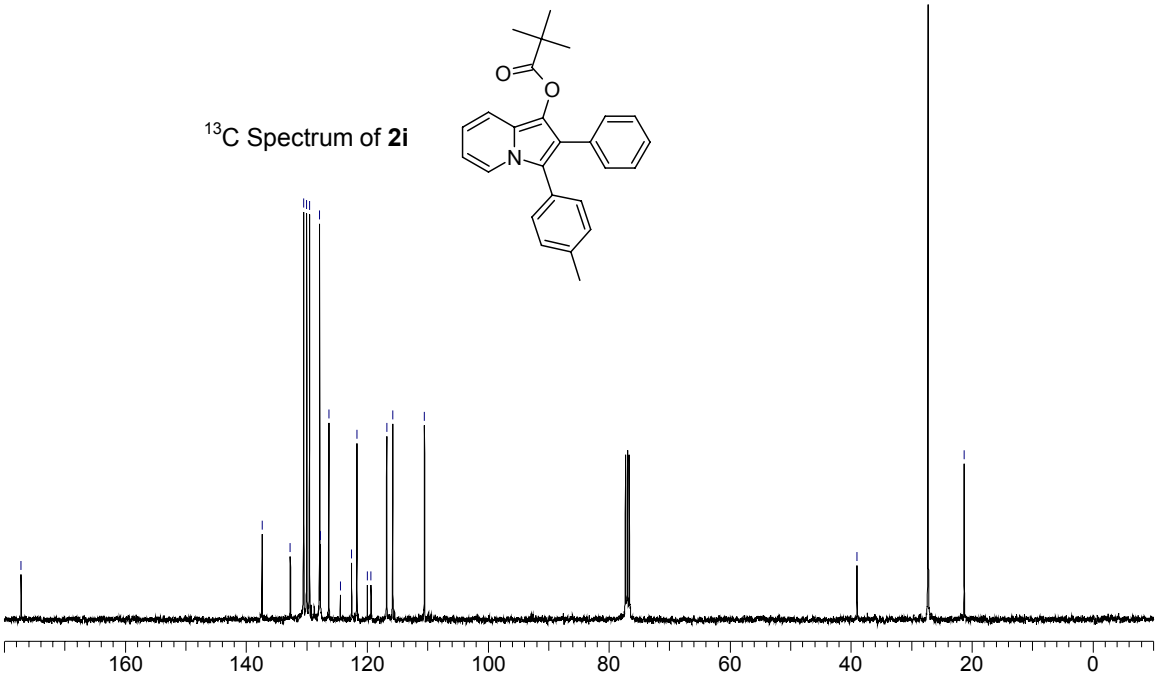


^{13}C Spectrum of **2h**



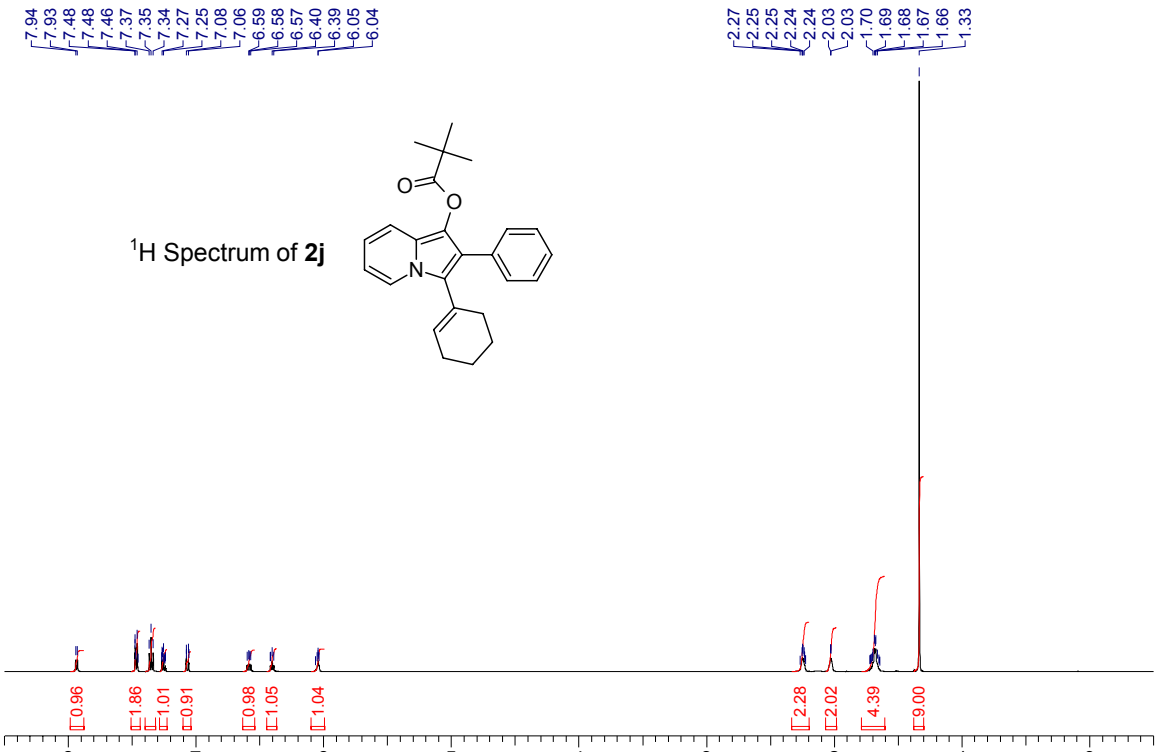


^{1}H Spectrum of **2i**

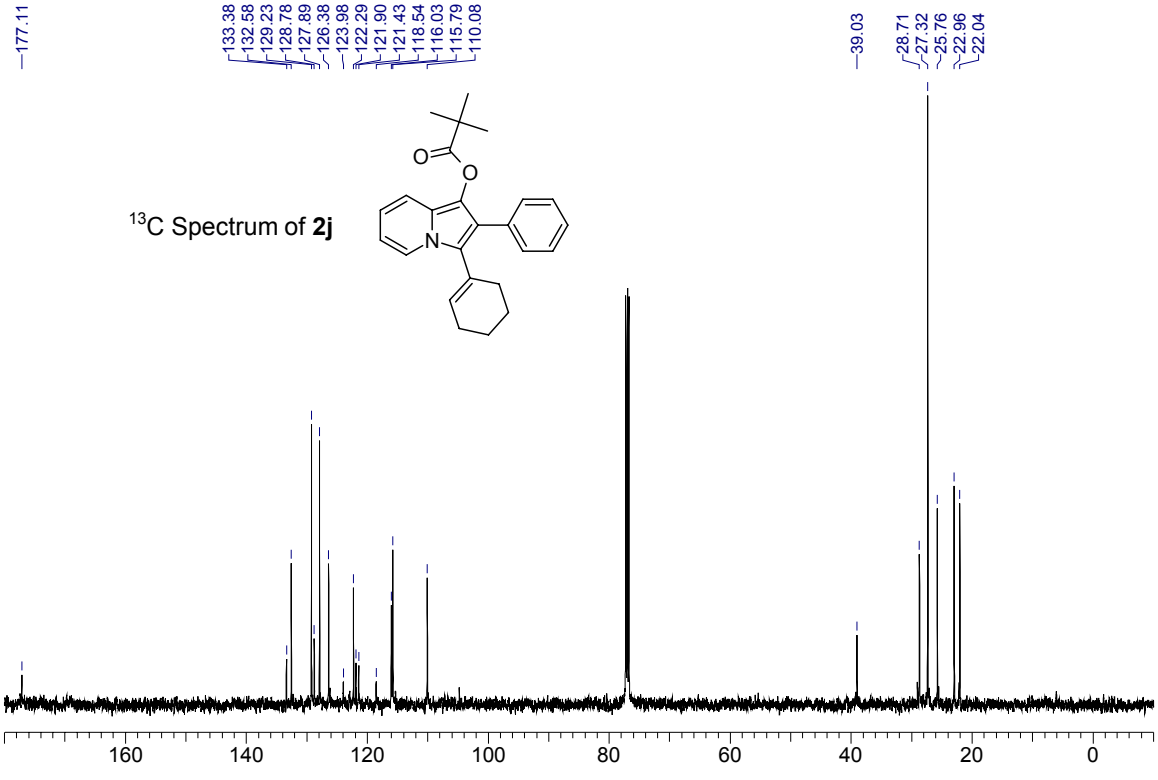


^{13}C Spectrum of **2i**

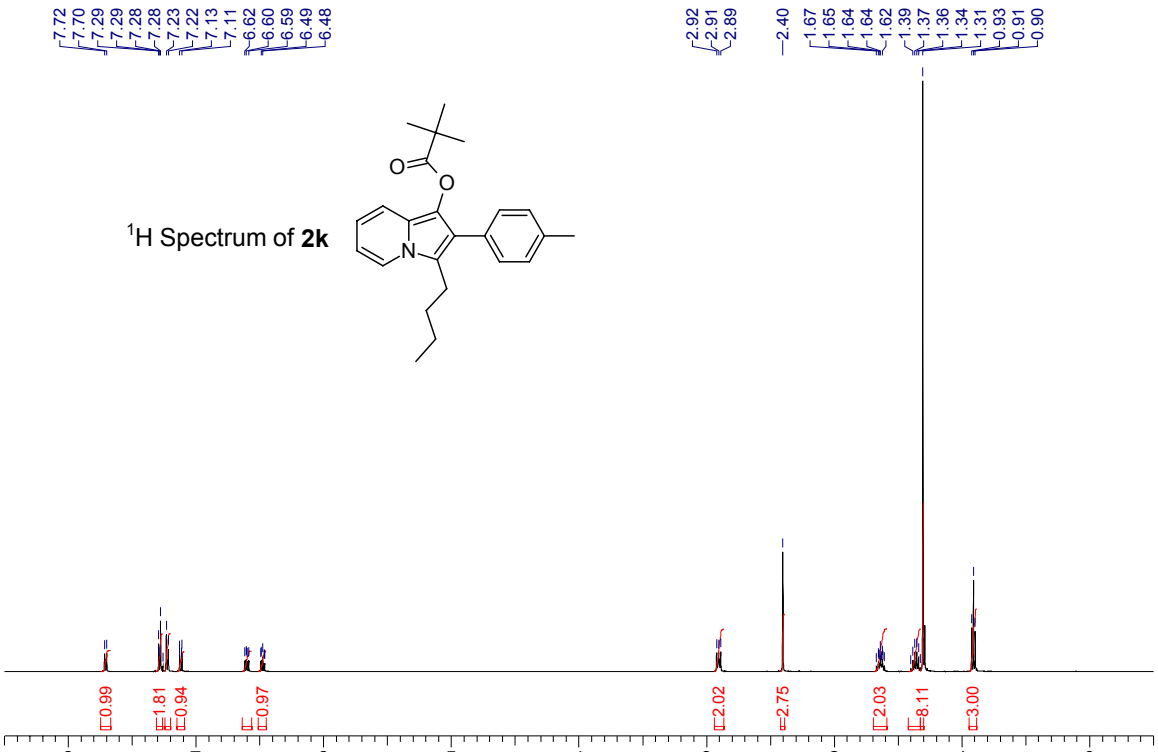
^{1}H Spectrum of **2j**



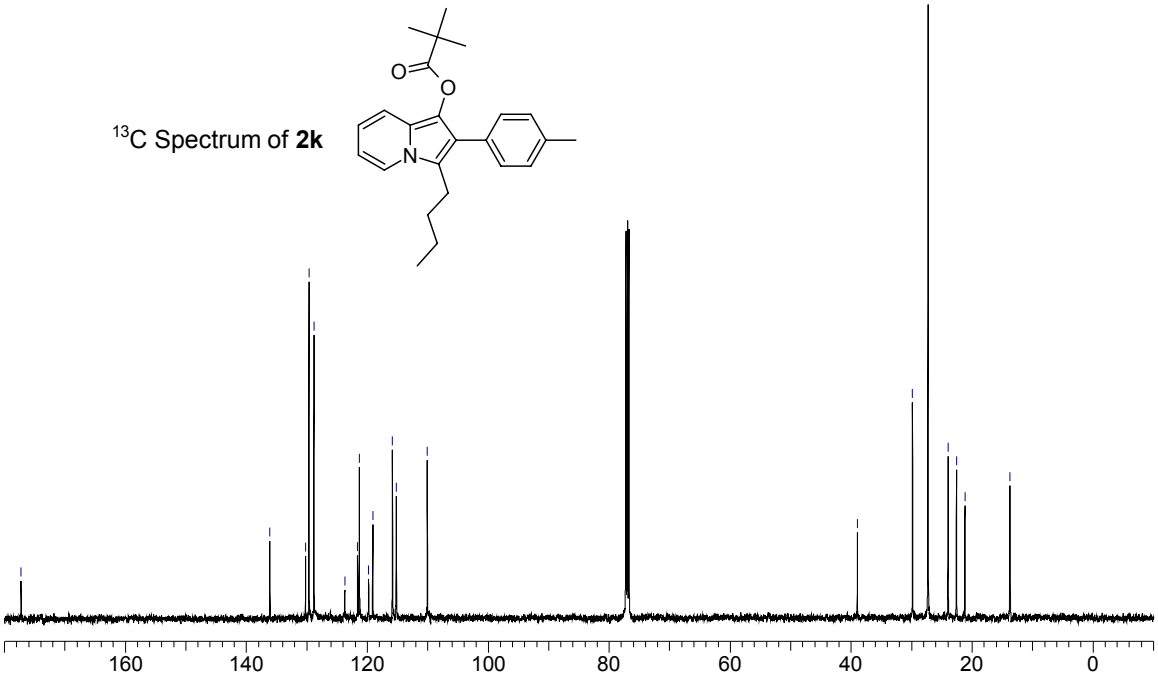
^{13}C Spectrum of **2j**



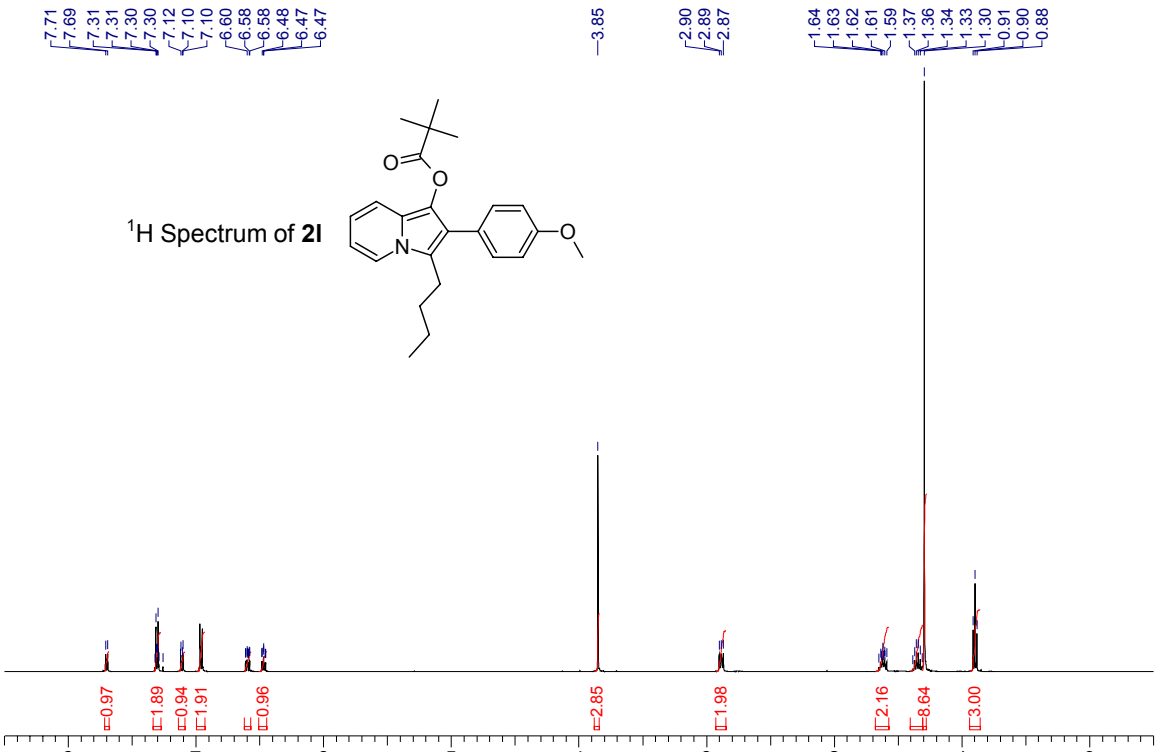
^{1}H Spectrum of **2k**



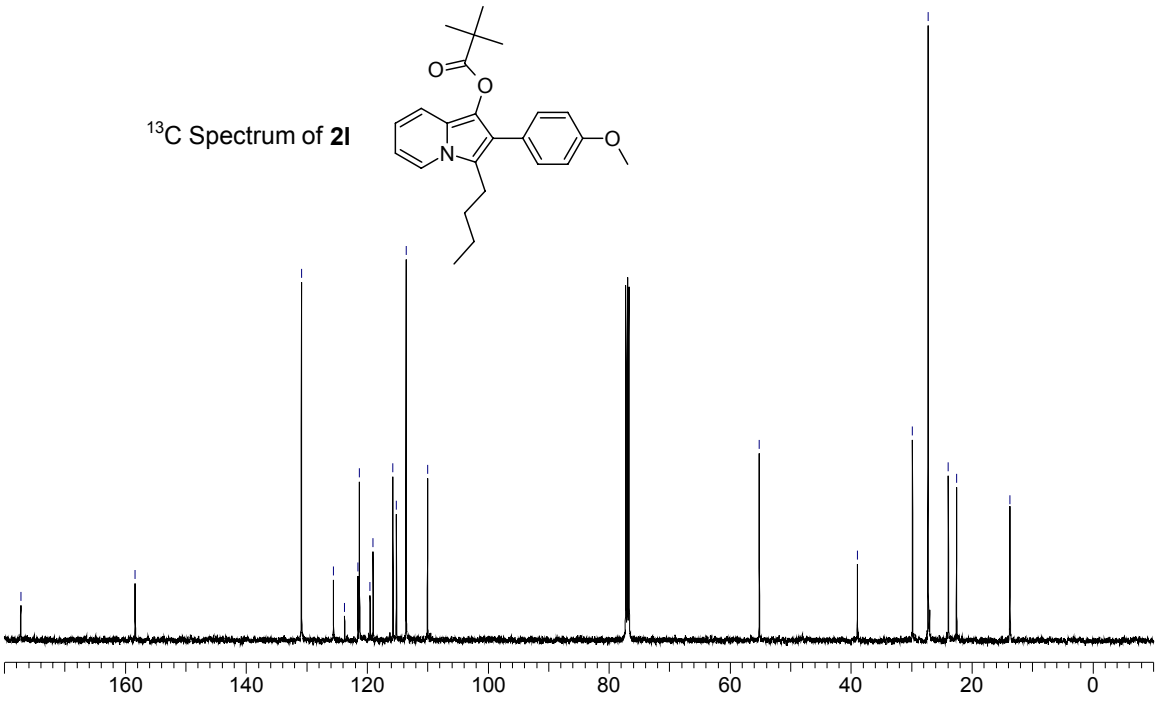
^{13}C Spectrum of **2k**



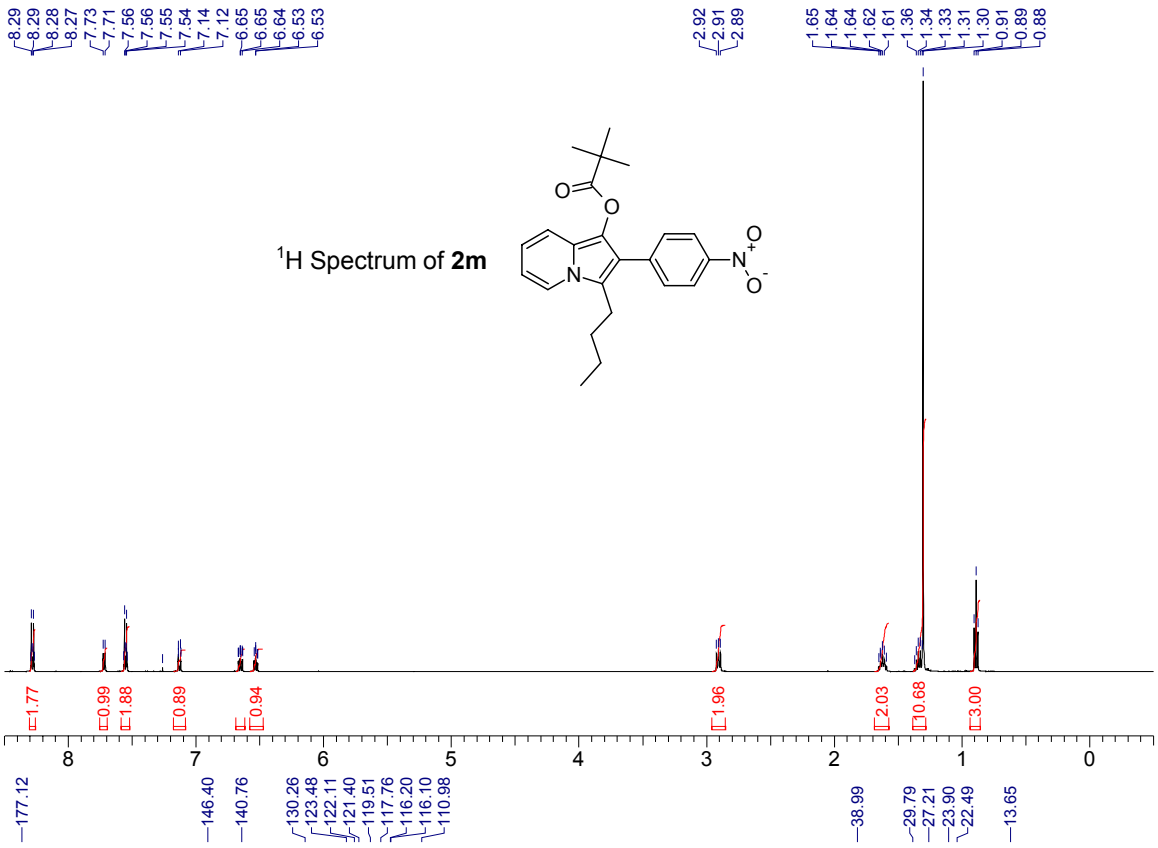
^{1}H Spectrum of **2l**



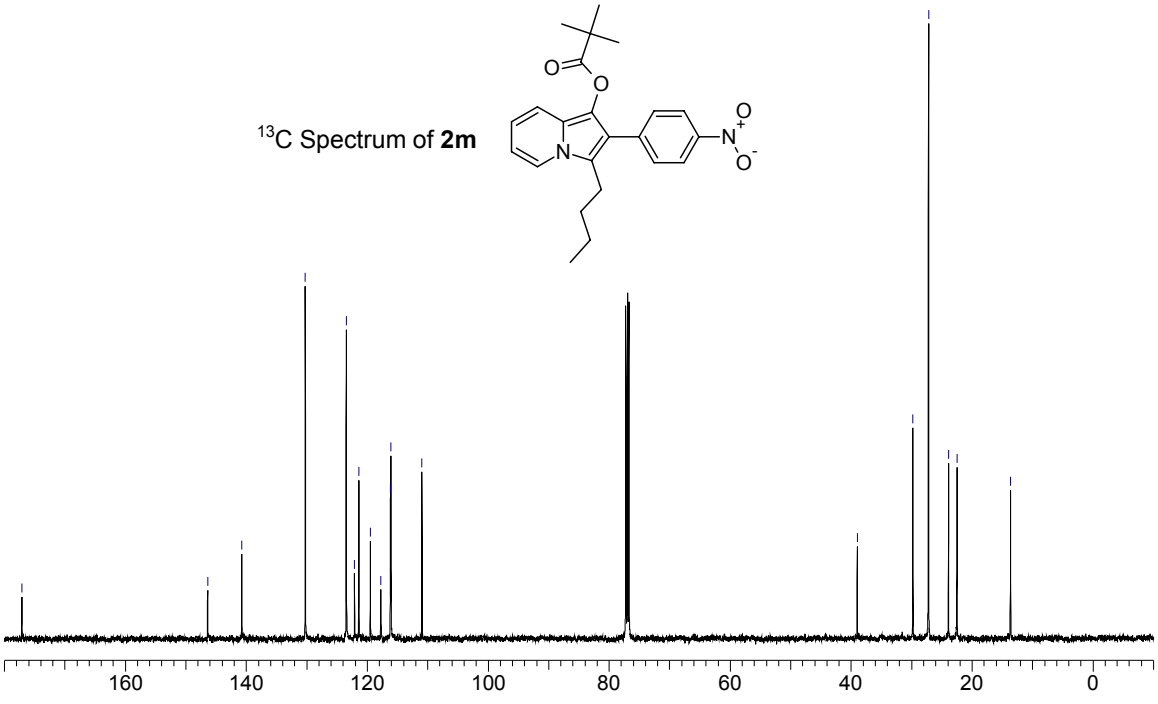
^{13}C Spectrum of **2l**



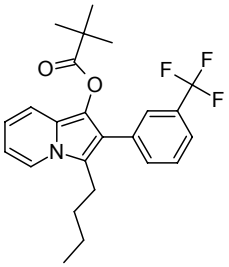
^{1}H Spectrum of **2m**



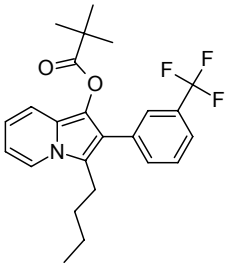
^{13}C Spectrum of **2m**

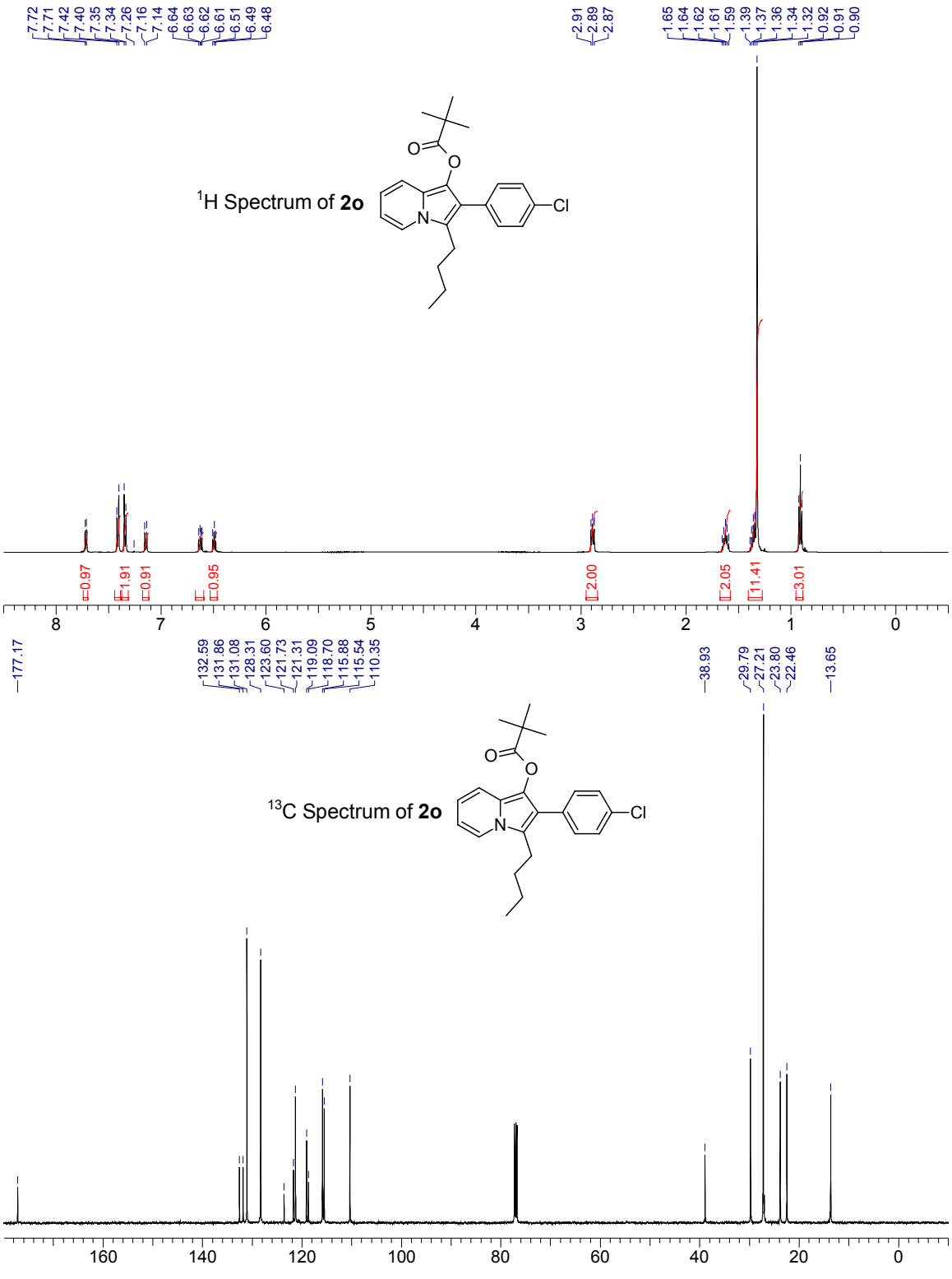


^{1}H Spectrum of **2n**

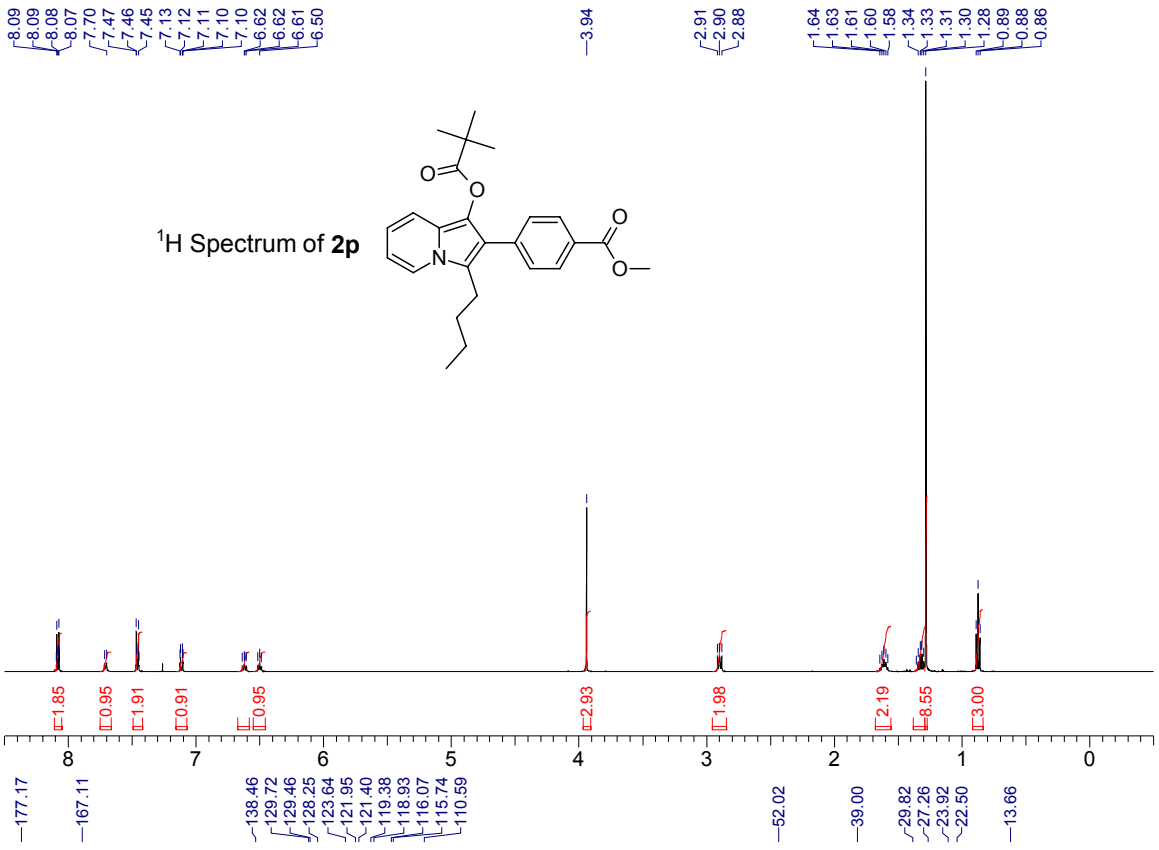


^{13}C Spectrum of **2n**

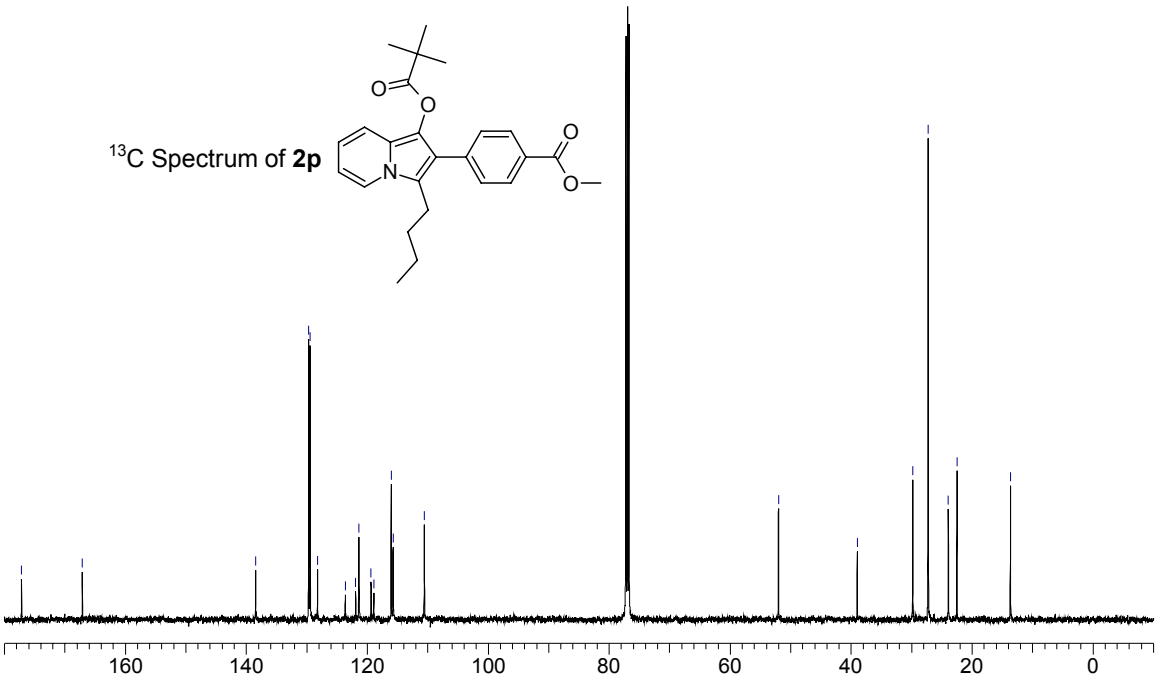


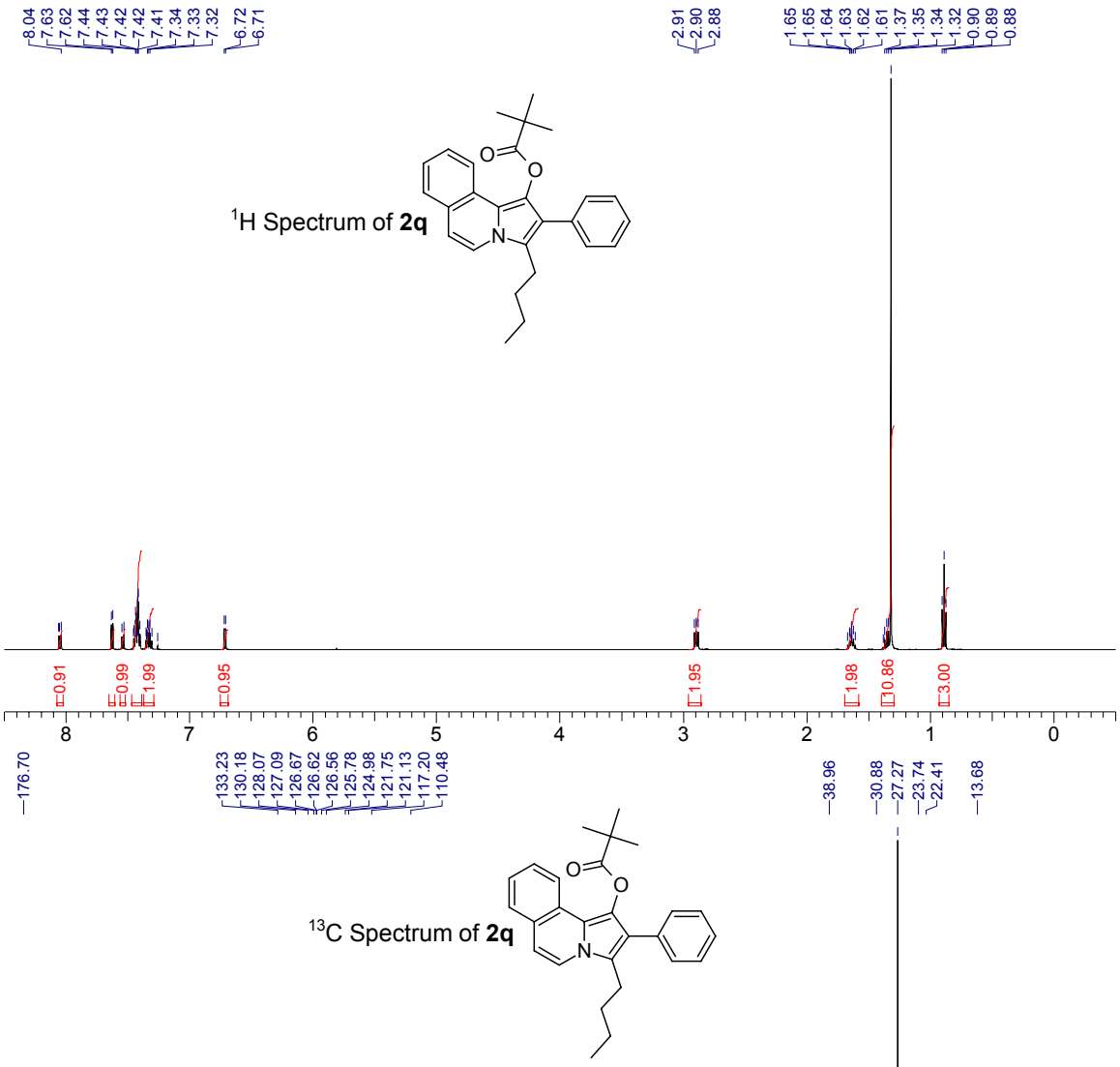

7.72
7.71
7.42
7.40
7.35
7.34
7.26
7.16
7.14
6.64
6.63
6.62
6.61
6.51
6.49
6.48
2.91
2.89
2.87
1.65
1.64
1.62
1.61
1.59
1.39
1.37
1.36
1.34
1.32
0.92
0.91
0.90
1H Spectrum of 2o
O
O
N
Cl
0.97
1.91
0.91
0.95
2.00
2.05
11.41
3.01
8
7
6
5
4
3
2
1
0
177.17
132.59
131.86
131.08
128.31
123.60
121.73
121.31
119.09
118.70
115.88
115.54
110.35
38.93
29.79
27.21
23.80
22.46
13.65
13C Spectrum of 2o
O
O
N
Cl
160
140
120
100
80
60
40
20
0

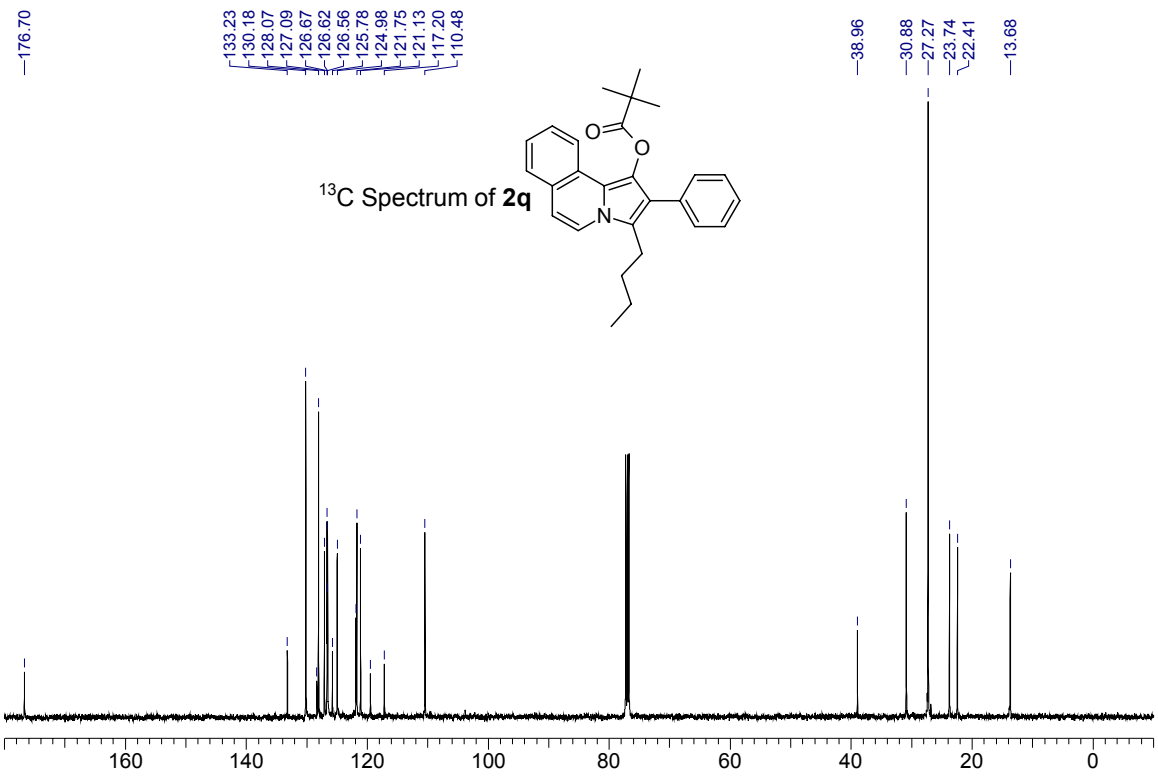
^{1}H Spectrum of **2p**

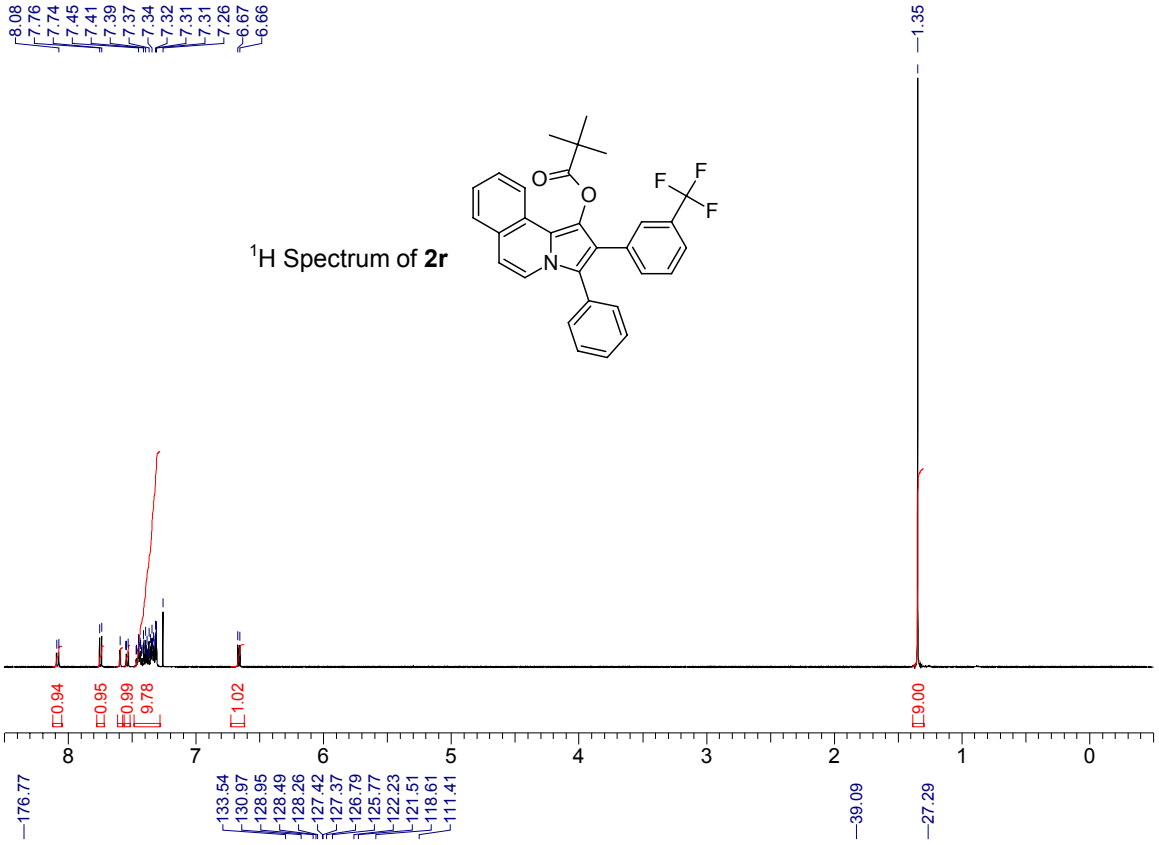


^{13}C Spectrum of **2p**

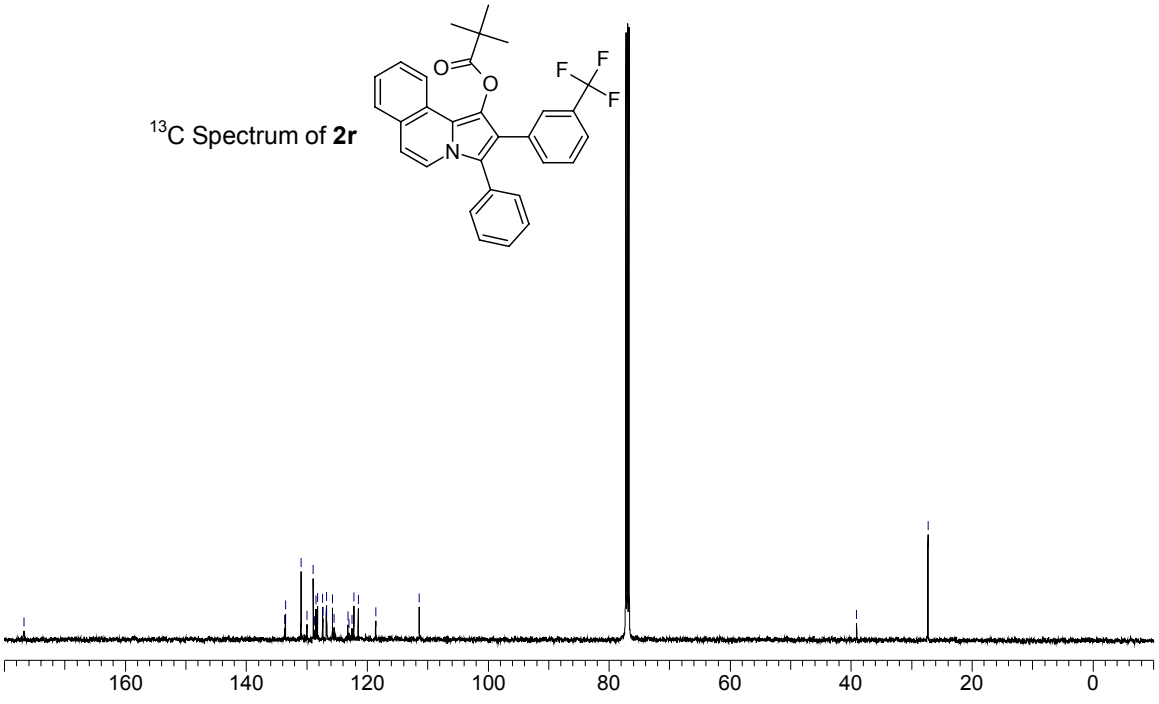



8.04
7.63
7.62
7.44
7.43
7.42
7.42
7.41
7.34
7.33
7.32
6.72
6.71
2.91
2.90
2.88
1.65
1.65
1.64
1.63
1.62
1.61
1.37
1.35
1.34
1.32
0.90
0.89
0.88
O
O
N
1H Spectrum of 2q
0.91
0.99
1.99
0.95
1.95
1.98
10.86
3.00
8
7
6
5
4
3
2
1
0

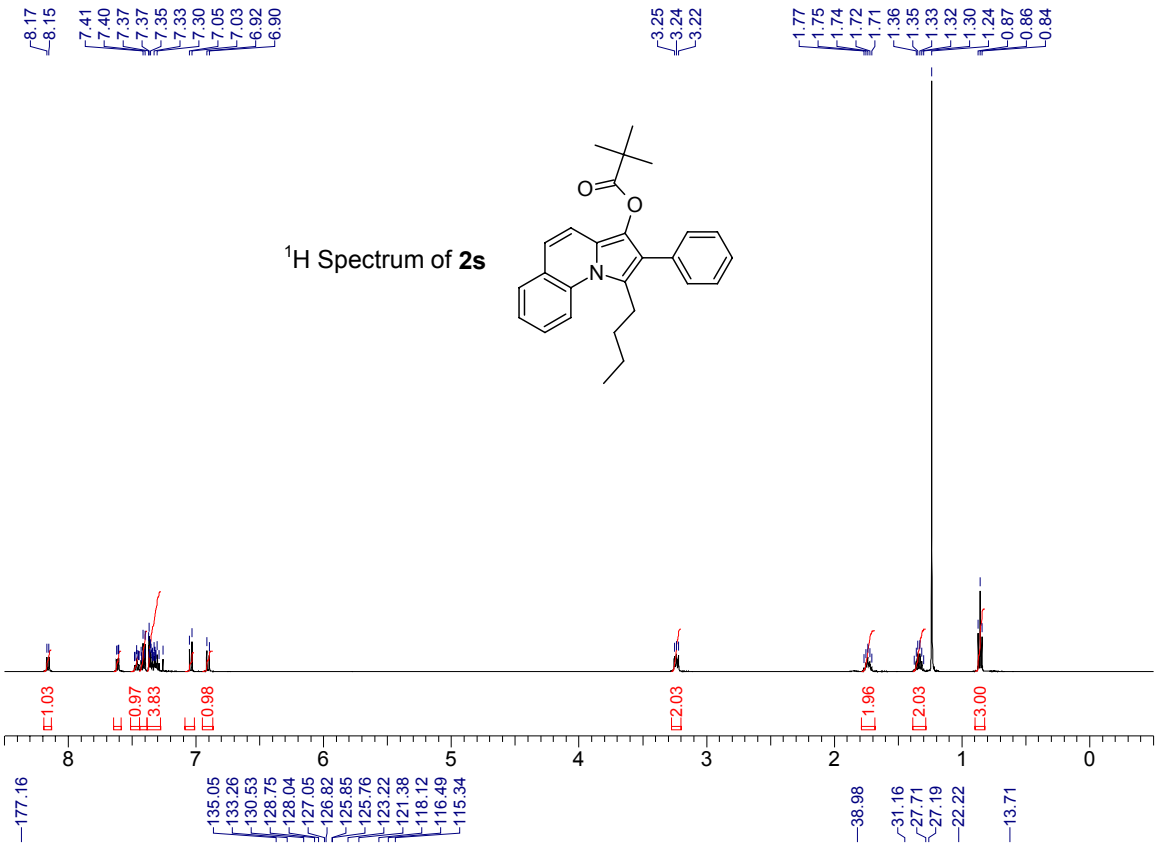

176.70
133.23
130.18
128.07
127.09
126.67
126.62
126.56
125.78
124.98
121.75
121.13
117.20
110.48
38.96
30.88
27.27
23.74
22.41
13.68
O
O
N
13C Spectrum of 2q
160
140
120
100
80
60
40
20
0

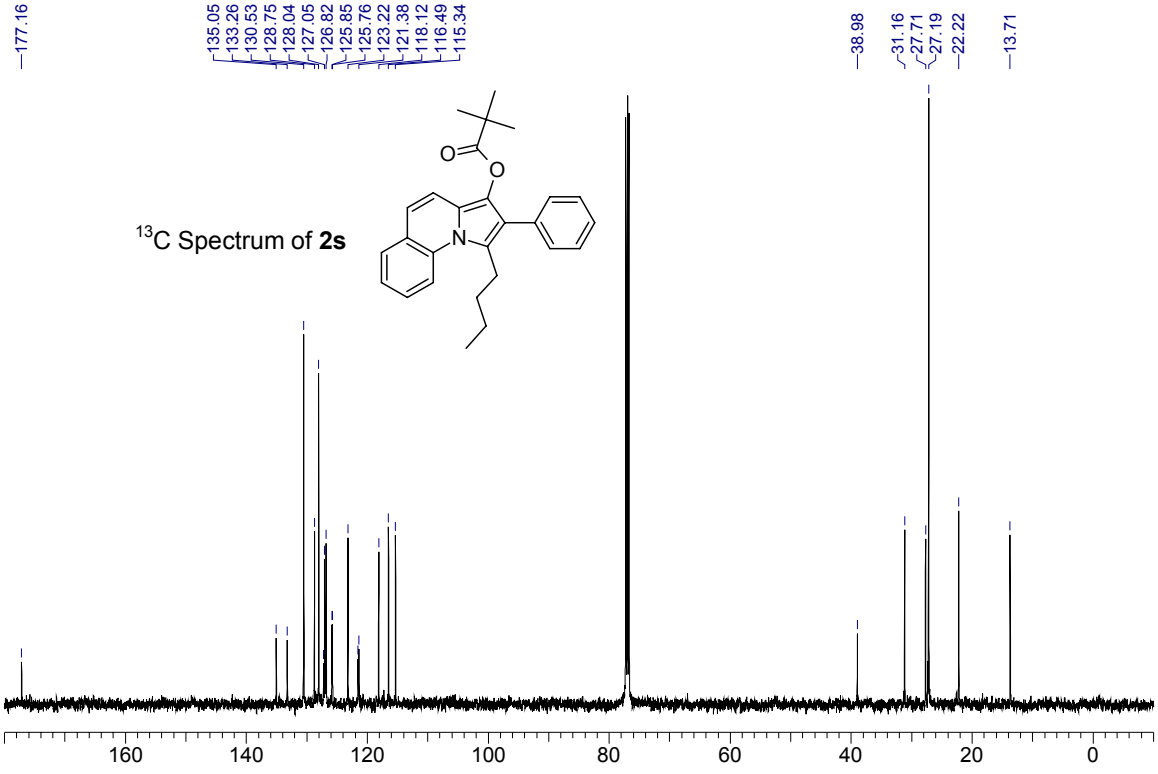


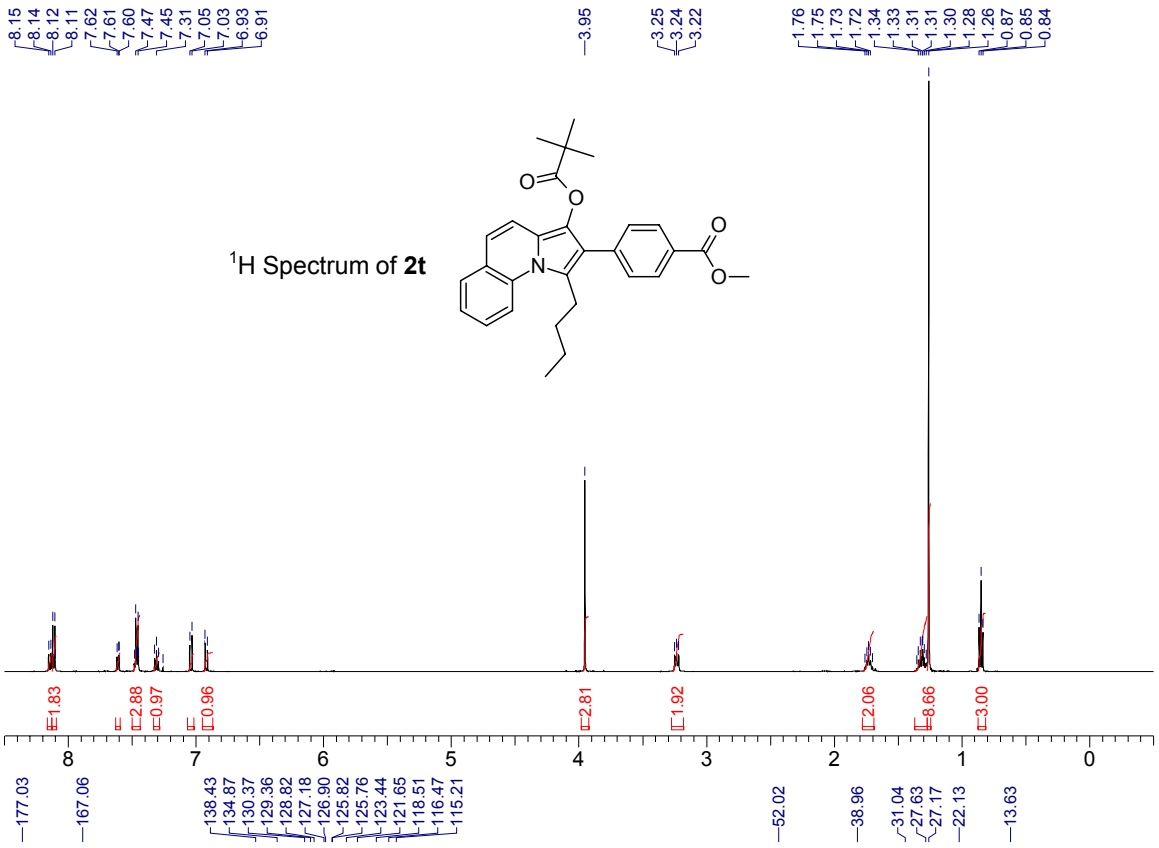
^{1}H Spectrum of **2r**

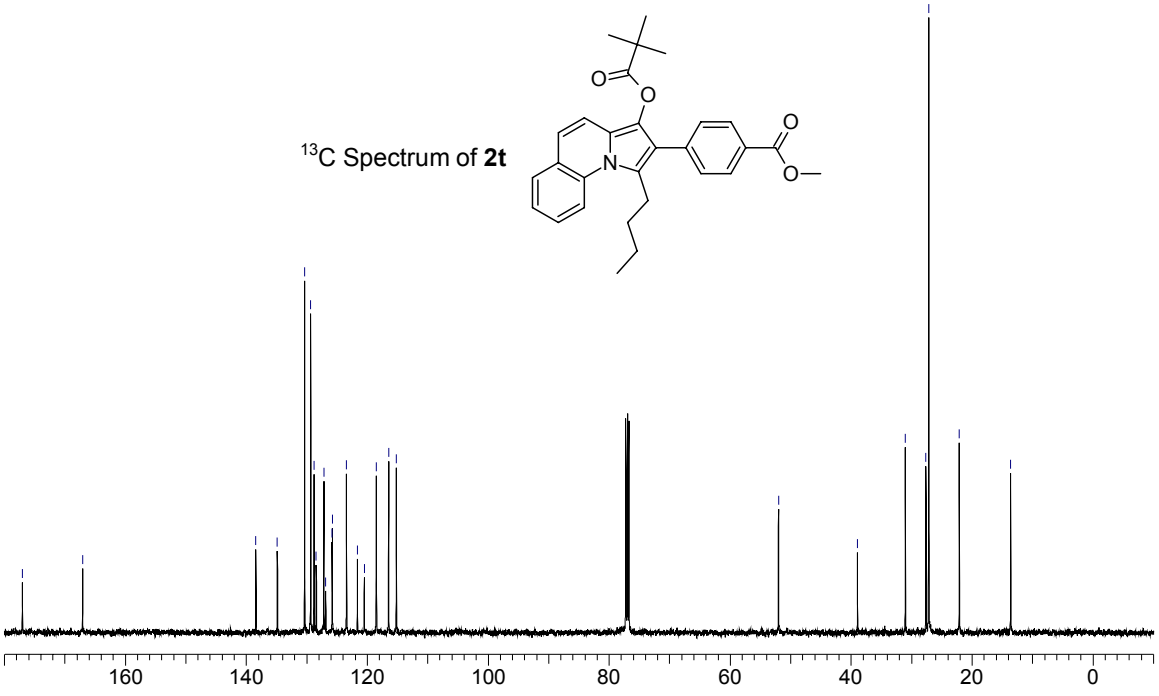


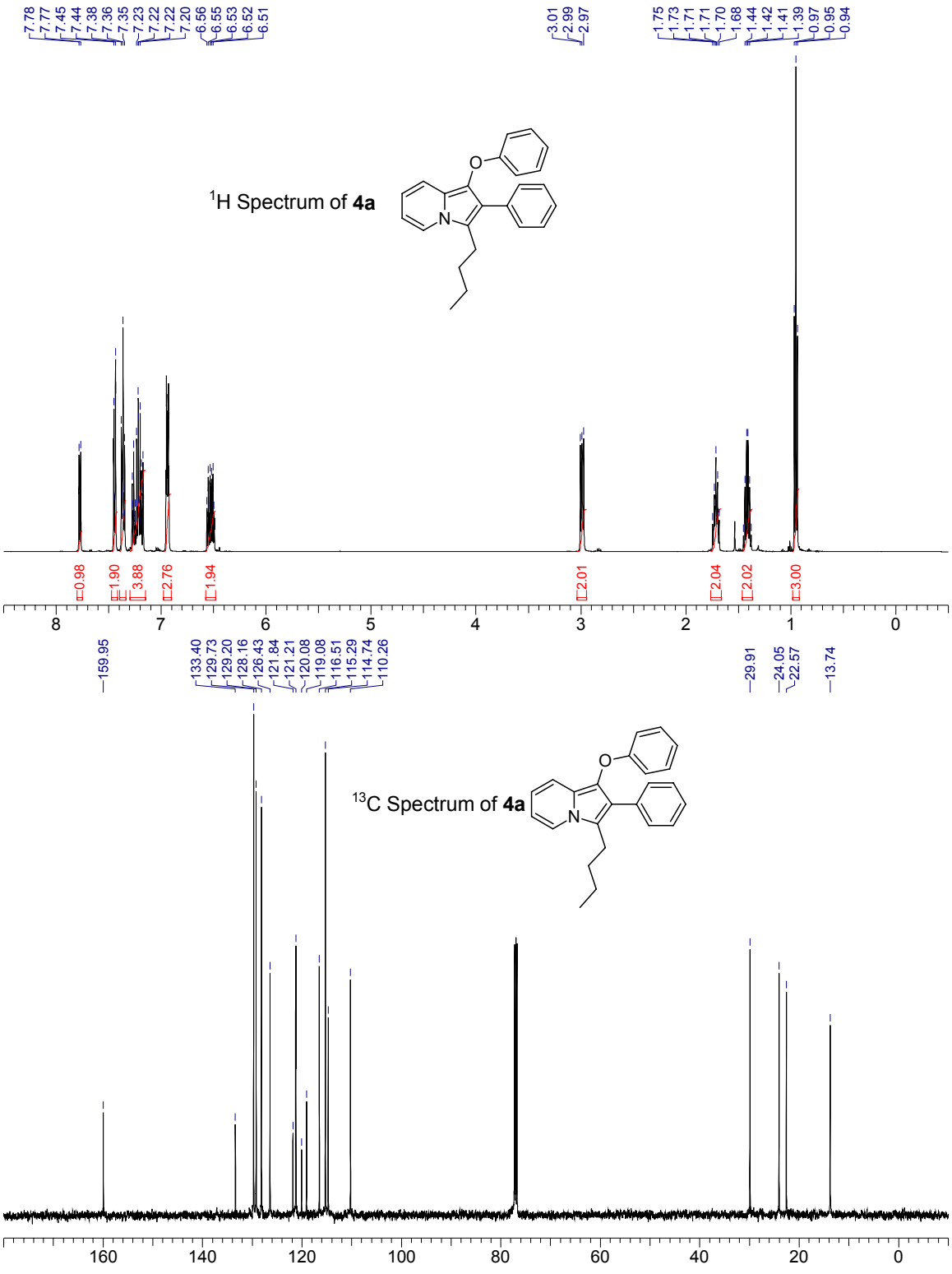
^{13}C Spectrum of **2r**


8.17
8.15
7.41
7.40
7.37
7.37
7.35
7.33
7.30
7.05
7.03
6.92
6.90
3.25
3.24
3.22
1.77
1.75
1.74
1.72
1.71
1.36
1.35
1.33
1.32
1.30
1.24
0.87
0.86
0.84
1H Spectrum of 2s
O
O
N
1.03
0.97
3.83
0.98
2.03
1.96
2.03
3.00
8
7
6
5
4
3
2
1
0


177.16
135.05
133.26
130.53
128.75
128.04
127.05
126.82
125.85
125.76
123.22
121.38
118.12
116.49
115.34
38.98
31.16
27.71
27.19
22.22
13.71
13C Spectrum of 2s
O
O
N
160
140
120
100
80
60
40
20
0

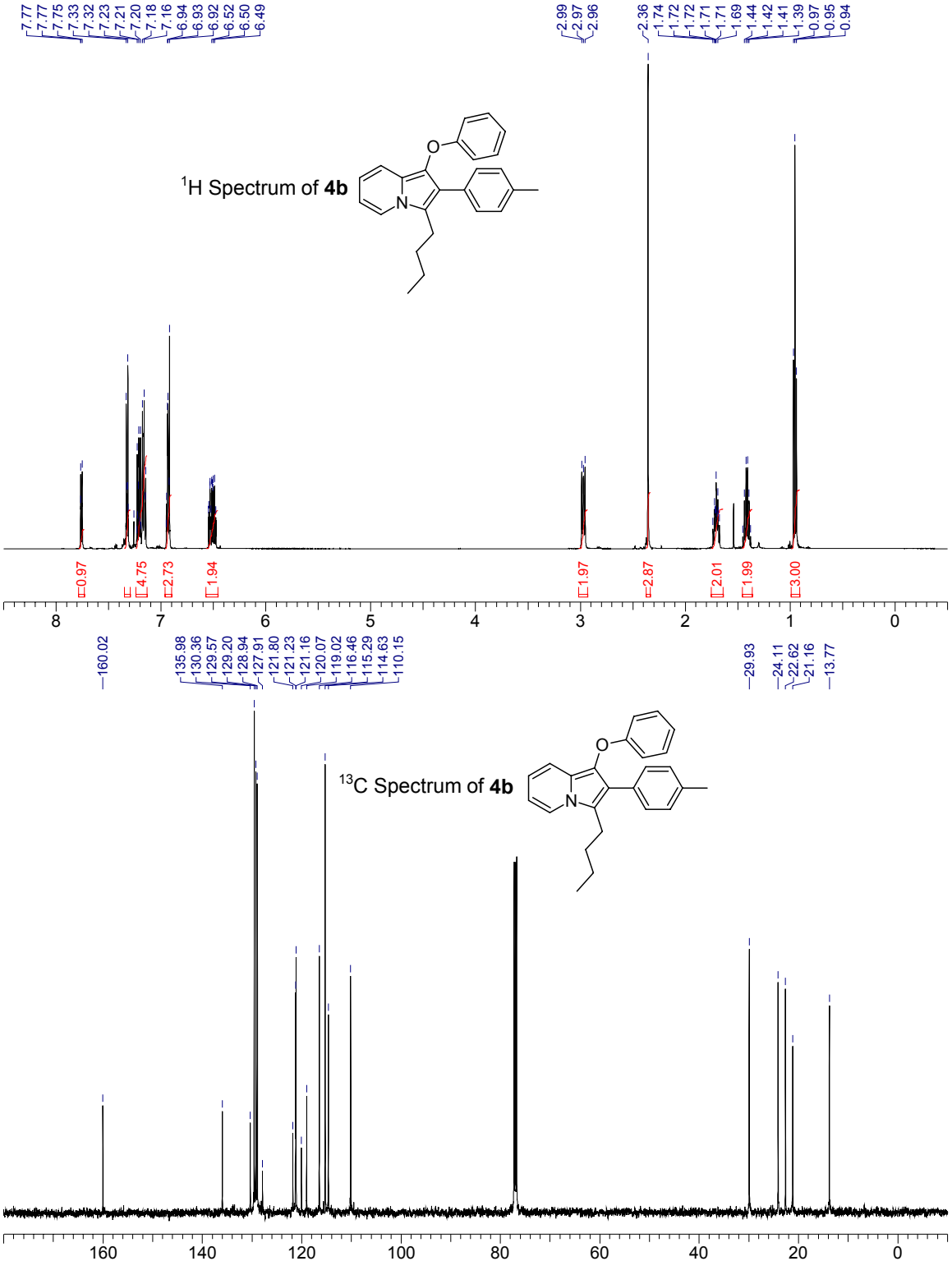

8.15
8.14
8.12
8.11
7.62
7.61
7.60
7.47
7.45
7.31
7.05
7.03
6.93
6.91
3.95
3.25
3.24
3.22
1.76
1.75
1.73
1.72
1.34
1.33
1.31
1.31
1.30
1.28
1.26
0.87
0.85
0.84
1H Spectrum of 2t
1.83
2.88
0.97
0.96
2.81
1.92
2.06
8.66
3.00
8
7
6
5
4
3
2
1
0

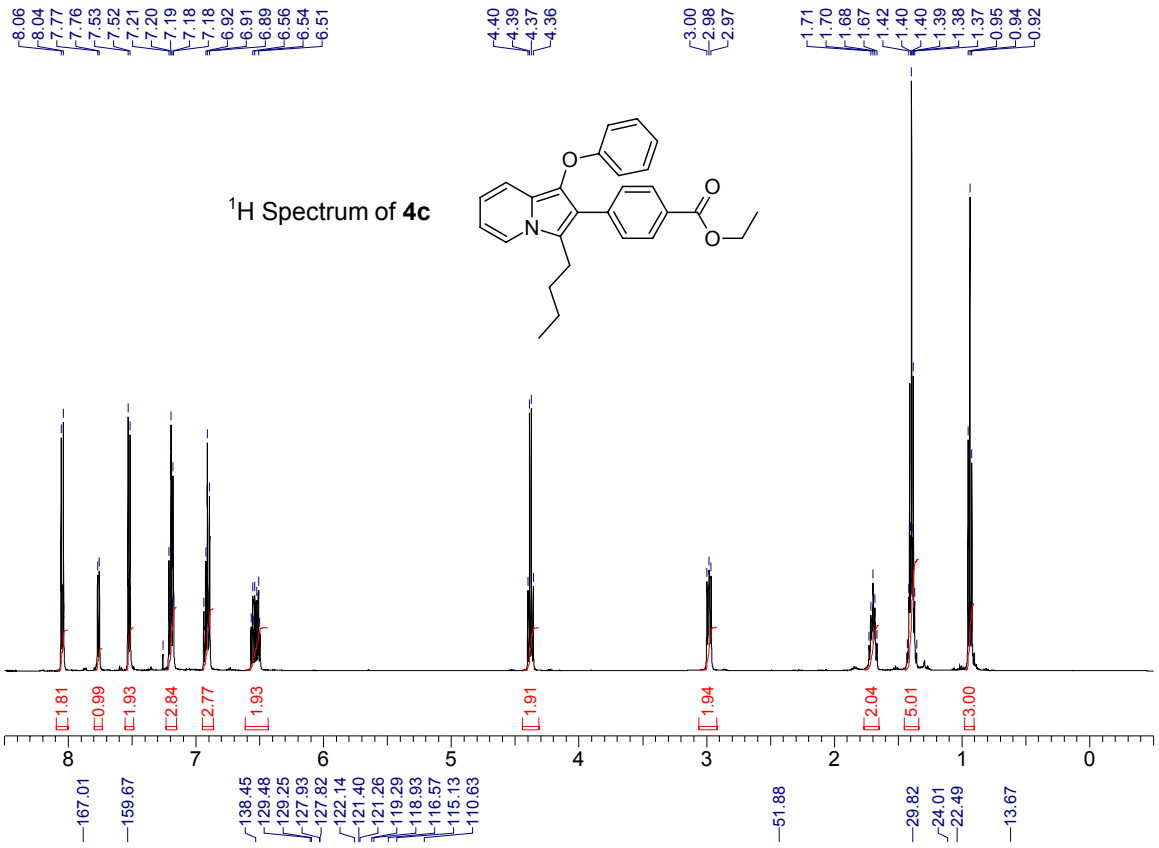

177.03
167.06
138.43
134.87
130.37
129.36
128.82
127.18
126.90
125.82
125.76
123.44
121.65
118.51
116.47
115.21
52.02
38.96
31.04
27.63
27.17
22.13
13.63
13C Spectrum of 2t
160
140
120
100
80
60
40
20
0

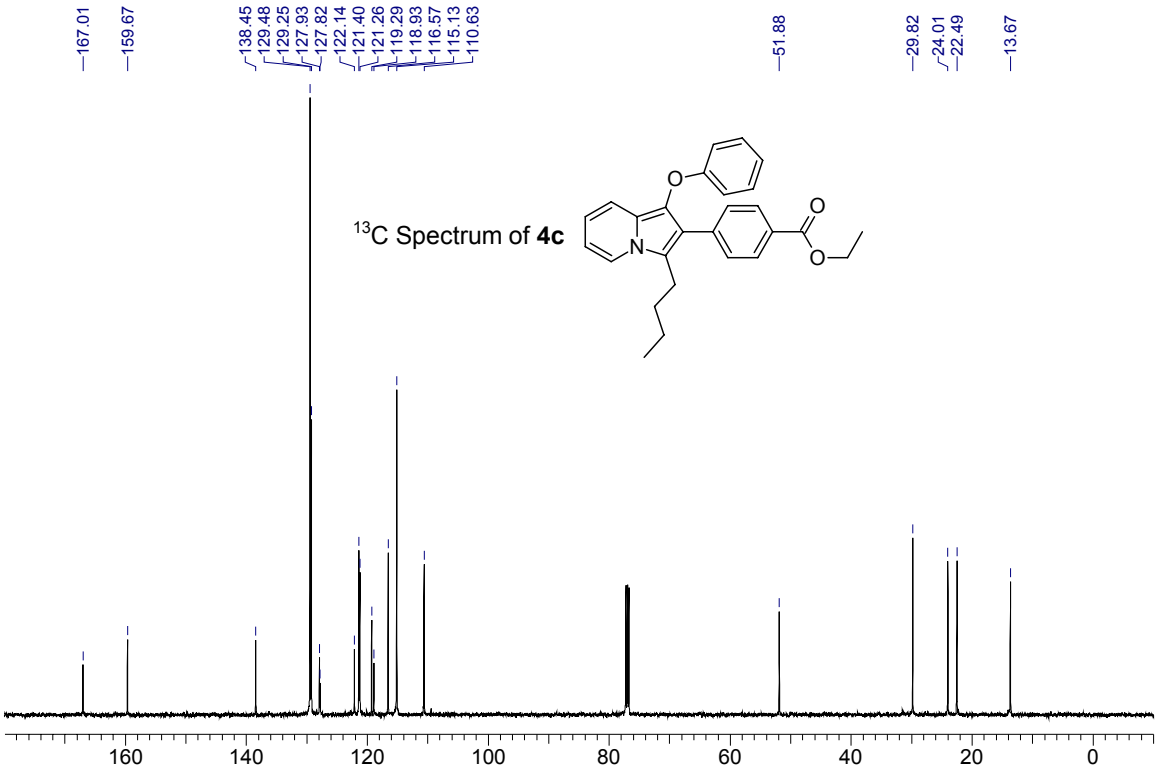


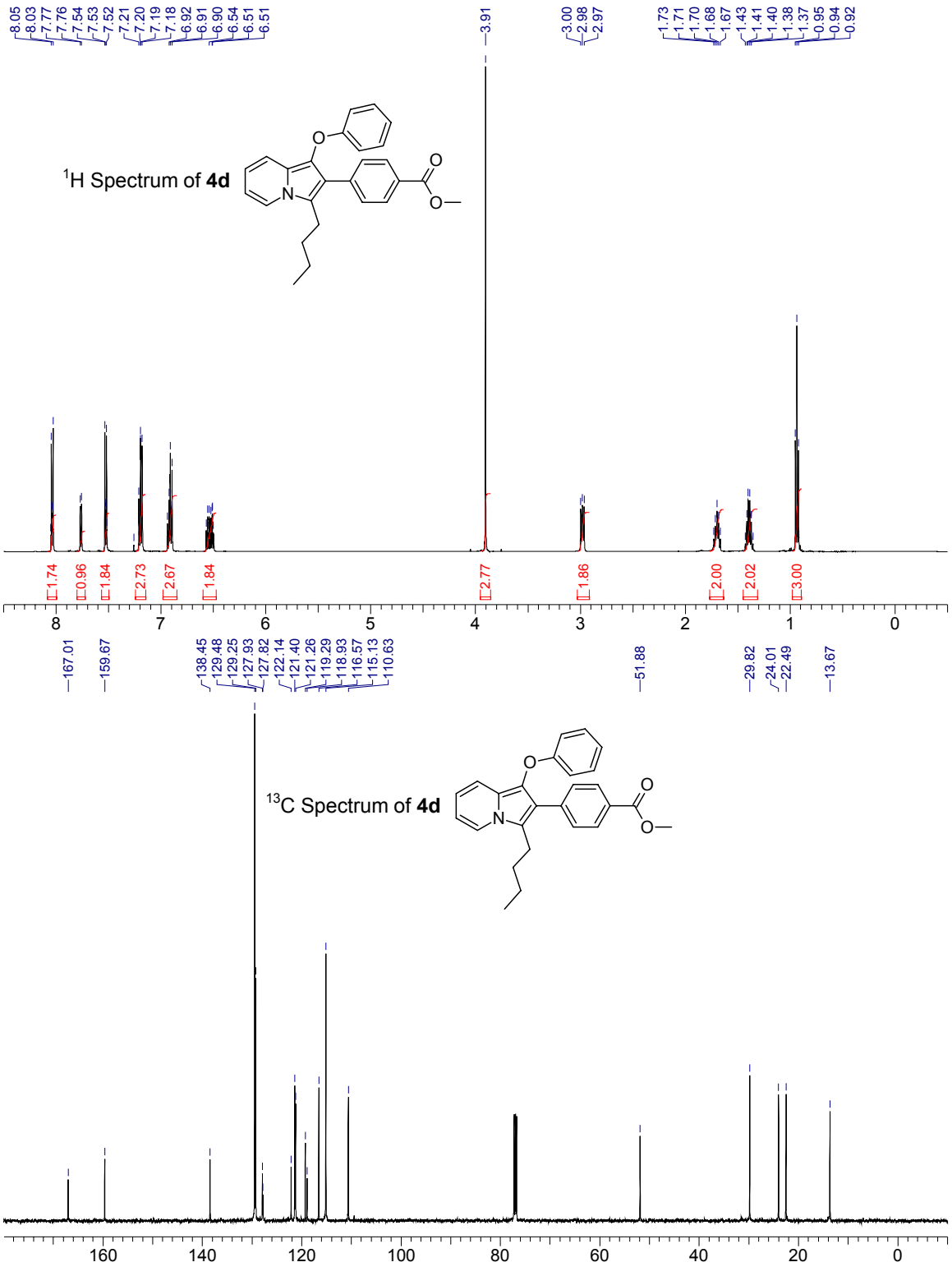
^{1}H Spectrum of **4a**

^{13}C Spectrum of **4a**

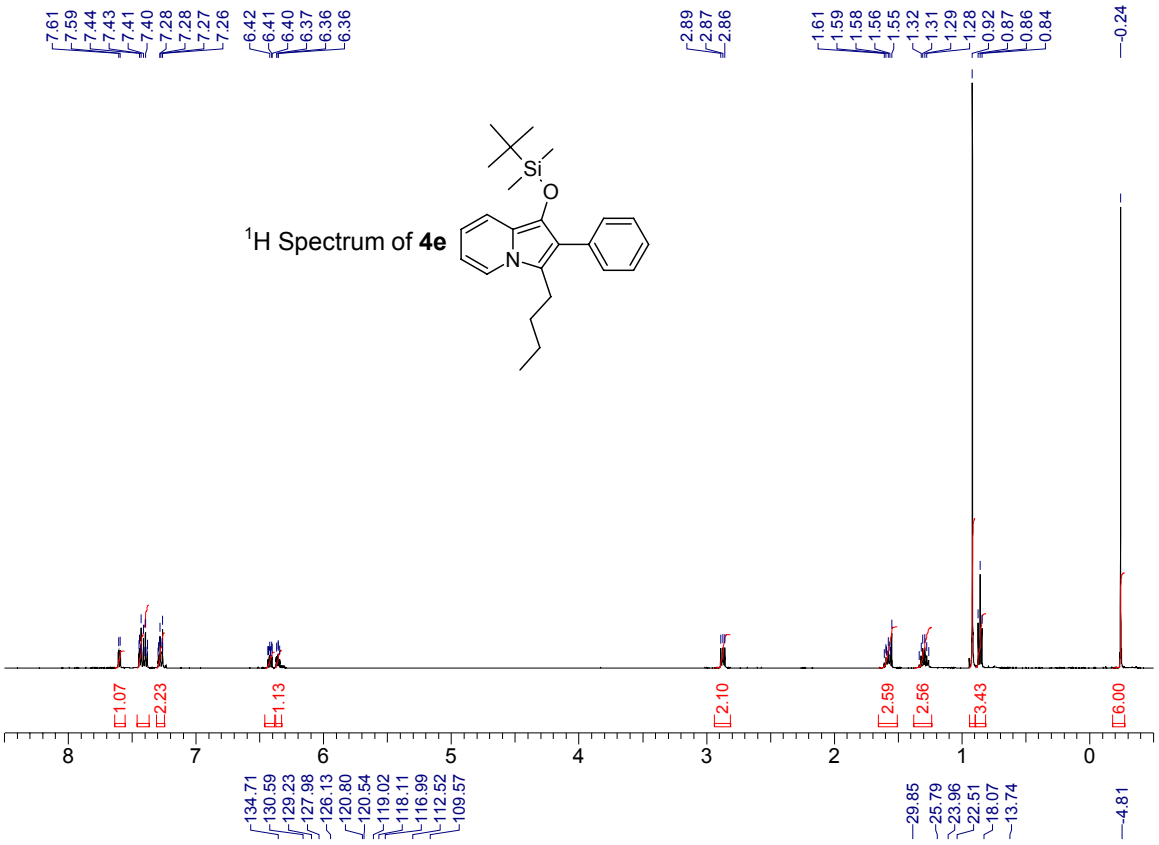

7.77
7.77
7.75
7.75
7.33
7.32
7.23
7.21
7.20
7.18
7.16
6.94
6.93
6.92
6.52
6.50
6.49
2.99
2.97
2.96
2.36
1.74
1.72
1.72
1.71
1.71
1.69
1.44
1.42
1.41
1.39
0.97
0.95
0.94
¹H Spectrum of 4b
O
N
0.97
4.75
2.73
1.94
1.97
2.87
2.01
1.99
3.00
8
7
6
5
4
3
2
1
0
160.02
135.98
130.36
129.57
129.20
128.94
127.91
121.80
121.23
121.16
120.07
119.02
116.46
115.29
114.63
110.15
29.93
24.11
22.62
21.16
13.77
¹³C Spectrum of 4b
O
N
160
140
120
100
80
60
40
20
0


8.06
8.04
7.77
7.76
7.53
7.52
7.21
7.20
7.19
7.18
7.18
6.92
6.91
6.89
6.56
6.54
6.51
4.40
4.39
4.37
4.36
3.00
2.98
2.97
1.71
1.70
1.68
1.67
1.42
1.40
1.40
1.39
1.38
1.37
0.95
0.94
0.92
1H Spectrum of 4c
O
O
O
N
1.81
0.99
1.93
2.84
2.77
1.93
1.91
1.94
2.04
5.01
3.00
8
7
6
5
4
3
2
1
0


167.01
159.67
138.45
129.48
129.25
127.93
127.82
122.14
121.40
121.26
119.29
118.93
116.57
115.13
110.63
51.88
29.82
24.01
22.49
13.67
13C Spectrum of 4c
O
O
O
N
160
140
120
100
80
60
40
20
0


8.05
8.03
7.77
7.76
7.54
7.53
7.52
7.21
7.20
7.19
7.18
6.92
6.91
6.90
6.54
6.51
6.51
3.91
3.00
2.98
2.97
1.73
1.71
1.70
1.68
1.67
1.43
1.41
1.40
1.38
1.37
0.95
0.94
0.92
1H Spectrum of 4d
O
O
O
N
1.74
0.96
1.84
2.73
2.67
1.84
2.77
1.86
2.00
2.02
3.00
8
7
6
5
4
3
2
1
0
167.01
159.67
138.45
129.48
129.25
127.93
127.82
122.14
121.40
121.26
119.29
118.93
116.57
115.13
110.63
51.88
29.82
24.01
22.49
13.67
13C Spectrum of 4d
O
O
O
N
160
140
120
100
80
60
40
20
0

^{1}H Spectrum of **4e**



^{13}C Spectrum of **4e**