Supporting Information

Regiodivergent metal-catalyzed rearrangement of 3-imino cyclopropenes into N-fused heterocycles

Stepan Chuprakov and Vladimir Gevorgyan*

Department of Chemistry, University of Illinois at Chicago,
845 West Taylor Street, Chicago, Illinois 60607-7061

Content

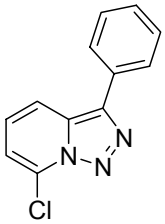
General Information

NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz) or DPX-400 instruments. (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. 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). HPLC analysis was performed using Gilson 321 pump interfaced with Gilson Holochrome variable band UV-detector tuned for 254 nm. Chiralcel OD-H column (250 x 4.6 mm) was used for chiral HPLC analysis. Column chromatography was carried out employing Silicycle Silia-P Flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Melting points were determined using Thomas Hoover capillary melting points apparatus and are uncorrected. Anhydrous solvents were purchased from Aldrich and stored over calcium hydride. Alkynes and metal catalysts were commercially available and purchased from Aldrich, Strem Chemicals Inc. or Acros Organics, or synthesized via known literature procedures.

Starting materials

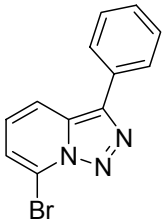
Preparation of triazoles **1d** and **1e** was previously described,[1] while compounds **1a-c** were prepared via analogous methods for the first time.

7-Chloro-3-phenyl[1,2,3]triazolo[1,5-a]pyridine (**1a**)



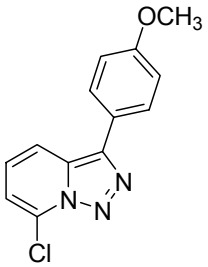
1a: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.89 - 8.02 (m, 3 H), 7.46 - 7.57 (m, 2 H), 7.38 - 7.45 (m, 1 H), 7.28 (dd, *J*=8.89, 7.06 Hz, 1 H), 7.10 (dd, *J*=7.06, 1.01 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 139.54, 132.13, 131.02, 129.08 (+), 128.27 (+), 127.77, 126.92 (+), 126.02 (+), 116.78 (+), 115.26 (+); FT-IR (KBr): 3396, 3078, 1622, 1512 cm^{-1}; mp 128°C (hexane-dichloromethane); Found: C 63.00, H 3.64; Calcd for $C_{12}H_8ClN_3$ C 62.76, H 3.51.

7-Bromo-3-phenyl[1,2,3]triazolo[1,5-a]pyridine (**1b**)



1b: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.01 (dd, *J*=8.71, 1.01 Hz, 1 H), 7.92 - 7.97 (m, 2 H), 7.49 - 7.56 (m, 2 H), 7.38 - 7.46 (m, 1 H), 7.26 - 7.30 (m, 1 H), 7.21 (dd, *J*=8.80, 6.97 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 139.69, 132.00, 131.15, 129.08 (+), 128.25 (+), 126.94 (+), 126.12 (+), 119.48 (+), 117.35 (+), 115.64; FT-IR (KBr): 3079, 1618, 1509, 1418, 1217 cm^{-1}; mp 125-126°C (hexane-dichloromethane); HR EI MS *m/z* 272.9909, Calcd for $C_{12}H_8BrN_3$ 272.99016.

7-Chloro-3-(4-methoxyphenyl)[1,2,3]triazolo[1,5-a]pyridine (**1c**)

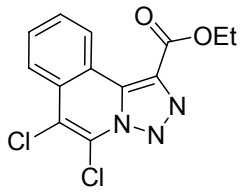


1c: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.96 (dd, *J*=8.99, 0.92 Hz, 1 H), 7.87 - 7.93 (m, 2 H), 7.29 (dd, *J*=8.80, 1.83 Hz, 1 H), 7.12 (dd, *J*=7.15, 0.92 Hz, 1 H), 7.06 - 7.11 (m, 2 H), 3.91 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.71, 139.54, 131.73, 128.23 (+), 127.62, 125.53 (+), 123.57, 116.82 (+), 115.16 (+), 114.53 (+), 55.40 (+); mp 151°C (hexane-dichloromethane); FT-IR (KBr): 3085, 1616, 1517, 1542, 1462, 1246 cm^{-1}; HR EI MS *m/z* 259.0510, Calcd for $C_{13}H_{10}ClN_3O$ 259.05124.

[1] Chuprakov, S.; Hwang. F. W.; Gevorgyan, V. *Angew. Chem. Int. Ed*. **2007**, *46*, 4757.

Oxazolyl diazocompound was prepared as previously described[2] and its analytical data corresponded to the literature. Triazoloisoquinoline **1f** was prepared from ethyl (3,4-dichloroisoquinolin-1-yl)acetate[3] via diazotransfer reaction with *p*-ABSA.[2]

Ethyl 5,6-dichloro[1,2,3]triazolo[5,1-a]isoquinoline-1-carboxylate **(1f)**



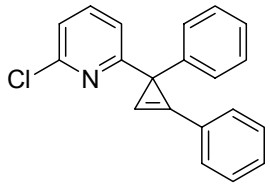
1f: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.77 (d, *J*=7.89 Hz, 1 H), 8.21 (d, *J*=8.07 Hz, 1 H), 7.64 - 7.96 (m, 2 H), 4.60 (q, *J*=7.15 Hz, 2 H), 1.54 (t, *J*=7.06 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.8, 133.7, 133.5, 131.5 (+), 129.9 (+), 129.2, 128.3 (+), 124.7 (+), 123.7, 122.9, 120.7, 62.1 (-), 14.4 (+); HR EI MS *m/z* 309.0069, Calcd for $C_{13}H_9Cl_2N_3O_2$ 309.0072.

Rh_2(*S*-DOSP)$_4$-Catalyzed Cyclopropenation of N-fused 1,2,3-Triazoles

Note: Due to relative instability of cyclopropenes prepared during these studies, all these compounds were purified via short-path flash chromatography. Generally, this allowed for purities of ~95% as judged by NMR integration, except for the compound ***3m*** *(~88% purity). The obtained cyclopropenes were used for further transformations without any additional purification.*

Typical Preparative Procedure. To an oven dried 5 ml Wheaton vial were added 7-chloro-3-phenyl[1,2,3]triazolo[1,5-*a*]pyridine (0.230 g, 1.0 mmol) and Rh_2(*S*-DOSP)$_4$ (4.6 mg, 0.0025 mmol) under N_2 atmosphere. 2ml of dry toluene and phenylacetylene (0.306 g, 3.0 mmol) were added to the same vial and reaction mixture was stirred at room temperature for 6h until judged complete by TLC analysis. The reaction mixture was filtered through short Silica path (dichloromethane – eluent), all solvents were removed in vacuo, and the residue was purified via flash SiO_2 chromatography (1:20 EtOAc/Hexanes) to afford 0.245 g (0.81 mmol, 81%) of 2-chloro-6-(1,2-diphenylcycloprop-2-en-1-yl) pyridine **3a** as yellow oil.

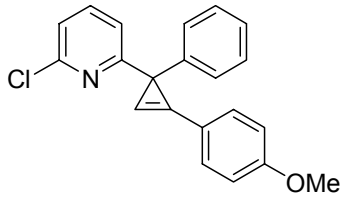
2-Chloro-6-(1,2-diphenylcycloprop-2-en-1-yl)pyridine **(3a)**



3a: (81%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.63 - 7.70 (m, 2 H), 7.52 (s, 1 H), 7.34 - 7.45 (m, 3 H), 7.17 - 7.33 (m, 6 H), 7.13 (dd, *J*=7.79, 0.83 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 165.91, 150.76, 144.50, 138.50 (+), 129.77 (+, 2C), 129.53 (+), 128.78 (+), 128.22 (+), 128.12 (+), 126.68, 126.14 (+), 121.64 (+), 121.35 (+), 120.21, 104.83, 104.80 (+), 36.84; HR EI MS *m/z* 303.0800, Calcd for $C_{20}H_{14}ClN$ 303.0815.

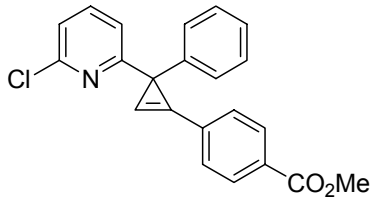
[2] Davies, H. M. L.; Townsend, R. J. *J. Org. Chem.* **2001**, *66*, 6595.
[3] Kemetani, T.; Kigasawa, K.; Hiiragi, M. *Chem. Pharm. Bull.* **1967**, *15*, 704.

2-Chloro-6-[2-(4-methoxyphenyl)-1-phenylcycloprop-2-en-1-yl]pyridine **(3b)**



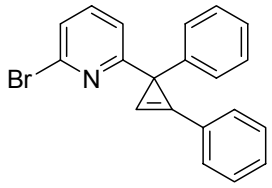
3b: (79%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.57 - 7.65 (m, 2 H), 7.51 (t, *J*=7.70 Hz, 1 H), 7.35 (s, 1 H), 7.15 - 7.32 (m, 6 H), 7.12 (dd, *J*=7.79, 0.83 Hz, 1 H), 6.89 - 6.98 (m, 2 H), 3.82 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.19, 160.63, 150.69, 144.75, 138.48 (+), 131.37 (+), 128.15 (+), 128.07 (+), 125.99 (+), 121.54 (+), 121.24 (+), 119.62, 119.20, 114.32 (+), 101.94 (+), 101.91, 55.38 (+), 36.57; HR EI MS *m/z* 333.0921, Calcd for $C_{16}H_{12}ClNO_2$ 333.09204.

Methyl 4-[3-(6-chloropyridin-2-yl)-3-phenylcycloprop-1-en-1-yl]benzoate **(3c)**



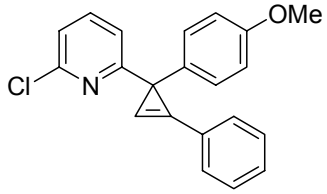
3c: (65%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.98 - 8.15 (m, 2 H), 7.69 - 7.78 (m, 2 H), 7.67 (s, 1 H), 7.53 (t, *J*=7.70 Hz, 1 H), 7.18 - 7.35 (m, 6 H), 7.14 (dd, *J*=7.70, 0.55 Hz, 1 H), 3.92 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.52, 165.39, 150.87, 143.96, 138.60 (+), 131.02, 130.67, 130.00 (+), 129.57 (+), 128.36 (+), 128.09 (+), 126.41 (+), 121.67 (+), 121.56 (+), 119.89, 107.91 (+), 52.29 (+), 37.19; HR EI MS *m/z* 361.0875, Calcd for $C_{22}H_{16}ClNO_2$ 361.08696.

2-Bromo-6-(1,2-diphenylcycloprop-2-en-1-yl)pyridine **(3d)**



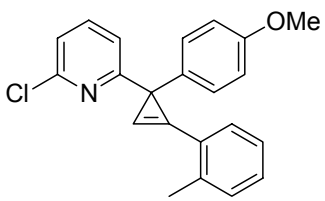
3d: (88%); 8% ee (1% *i*-PrOH in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.63 - 7.69 (m, 3 H), 7.51 (s, 1 H), 7.34 - 7.46 (m, 4 H), 7.24 - 7.32 (m, 4 H), 7.17 - 7.23 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.43, 144.46, 138.23 (+), 129.75 (+), 129.53 (+), 128.78 (+, 2C), 128.20 (+, 2C), 128.09 (+, 2C), 126.67, 126.12 (+), 125.18 (+), 122.00 (+), 120.17, 104.84 (+), 36.84; HR EI MS *m/z* 347.0317, Calcd for $C_{20}H_{14}BrN$ 347.0310.

2-Chloro-6-[1-(4-methoxyphenyl)-2-phenylcycloprop-2-en-1-yl]pyridine **(3e)**



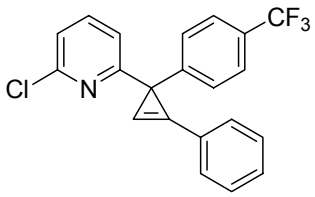
3e: (67%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.60 - 7.74 (m, 2 H), 7.51 (s, 1 H), 7.31 - 7.46 (m, 3 H), 7.19 - 7.27 (m, 3 H), 7.12 (dd, *J*=7.79, 0.64 Hz, 1 H), 6.73 - 6.92 (m, 2 H), 3.79 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.23, 157.96, 150.64, 138.40, 136.59, 129.65 (+, 2C), 129.40 (+), 129.15 (+, 2C), 128.71 (+, 2C), 126.73, 121.46 (+), 121.15 (+), 120.50, 113.61 (+), 105.06, 105.03 (+), 55.22 (+), 36.16; HR EI MS *m/z* 333.0929, Calcd for $C_{21}H_{16}ClNO$ 333.09204.

2-Chloro-6-[1-(4-methoxyphenyl)-2-(2-methylphenyl)cycloprop-2-en-1-yl]pyridine **(3f)**



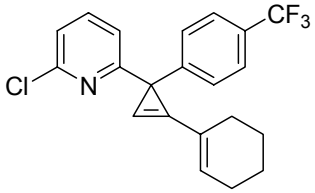
3f: (45%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.45 - 7.62 (m, 3 H), 7.16 - 7.33 (m, 6 H), 7.12 (dd, *J*=7.70, 0.73 Hz, 1 H), 6.78 - 6.90 (m, 2 H), 3.78 (s, 3 H), 2.53 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.36, 157.97, 150.64, 140.23, 138.49 (+), 136.81, 130.31 (+), 130.21 (+), 129.45 (+), 129.20 (+, 2C), 126.00 (+), 125.43, 121.54 (+), 121.21 (+), 119.44, 113.64 (+), 107.50 (+), 55.29 (+), 34.95, 20.28 (+); HR EI MS *m/z* 299.0705, Calcd for $C_{17}H_{14}ClNO_2$ 299.0713.

2-Chloro-6-{2-phenyl-1-[4-(trifluoromethyl)phenyl]cycloprop-2-en-1-yl}pyridine **(3g)**



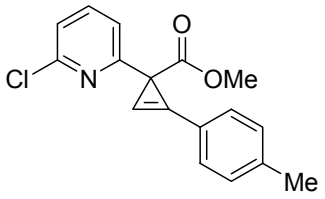
3g: (68%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.62 - 7.73 (m, 2 H), 7.47 - 7.61 (m, 4 H), 7.34 - 7.47 (m, 5 H), 7.22 (dd, *J*=7.61, 0.64 Hz, 1 H), 7.17 (dd, *J*=7.79, 0.64 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.89, 150.83, 148.66, 138.86 (+), 129.98 (+), 129.84 (+), 128.97 (+), 128.34 (+), 128.06, 125.10 (+, q, J_{FC} = 2.77 Hz), 124.38 (q, J_{FC} = 271.88 Hz), 121.78 (+), 121.24 (+), 119.93, 104.01 (+), 36.49; HR EI MS *m/z* 371.0686, Calcd for $C_{21}H_{13}ClF_3N$ 371.06886.

2-Chloro-6-{2-cyclohex-1-en-1-yl-1-[4-(trifluoromethyl)phenyl]cycloprop-2-en-1-yl}pyridine **(3h)**



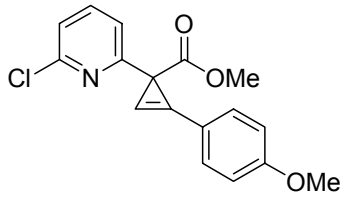
3h: (93%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.44 - 7.61 (m, 3 H), 7.33 (d, *J*=8.07 Hz, 2 H), 7.03 - 7.21 (m, 3 H), 6.16 - 6.36 (m, 1 H), 2.25 (br.m, 4 H), 1.48 - 1.88 (br.m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 165.32, 150.59, 149.05, 138.64 (+), 135.52 (+), 128.28 (+), 124.91 (+, q, J_{FC} = 2.77 Hz), 124.67, 124.42 (q, J_{FC} = 271.88 Hz), 121.42 (+), 121.16 (+), 101.99 (+), 36.30, 26.86 (-), 25.71 (-), 22.24 (-), 21.76 (-); HR EI MS *m/z* 375.1001, Calcd for $C_{21}H_{17}ClF_3N$ 375.10016.

Methyl 1-(6-chloropyridin-2-yl)-2-(4-methylphenyl)cycloprop-2-ene-1-carboxylate **(3i)**



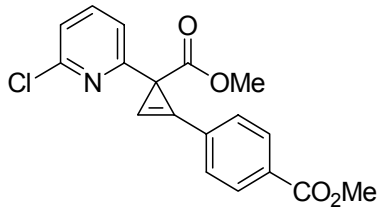
3i: (93%); 86% ee (3% *i*-PrOH in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.49 - 7.61 (m, 3 H), 7.46 (dd, *J*=7.70, 0.73 Hz, 1 H), 7.21 - 7.26 (m, 2 H), 7.15 (dd, *J*=7.79, 0.83 Hz, 1 H), 7.13 (s, 1 H), 3.71 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 174.06, 160.89, 150.50, 140.62, 138.59 (+), 130.08 (+), 129.61 (+), 122.09 (+), 121.86 (+), 115.38, 97.03 (+), 52.27 (+), 35.14, 21.62 (+); HR EI MS *m/z* 299.070661, Calcd for $C_{17}H_{14}ClNO_2$ 299.0713.

Methyl 1-(6-chloropyridin-2-yl)-2-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (**3j**)



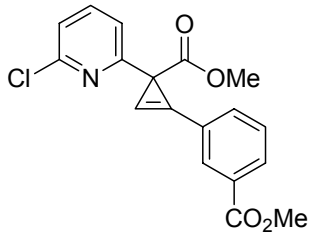
3j: (67%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.51 - 7.64 (m, 3 H), 7.44 (dd, *J*=7.70, 0.73 Hz, 1 H), 7.15 (dd, *J*=7.79, 0.83 Hz, 1 H), 7.04 (s, 1 H), 6.87 - 6.99 (m, 2 H), 3.83 (s, 3 H), 3.71 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 174.16, 161.12, 161.04, 150.48, 138.59 (+), 131.78 (+), 122.07 (+), 121.75 (+), 117.45, 115.07, 114.40 (+), 95.46 (+), 55.41 (+), 52.26 (+), 35.16; HR EI MS *m/z* 315.0670, Calcd for $C_{17}H_{14}ClNO_3$ 315.0662.

Methyl 4-[3-(6-chloropyridin-2-yl)-3-(methoxycarbonyl)cycloprop-1-en-1-yl]benzoate (**3k**)



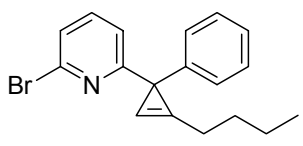
3k: (72%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.06 - 8.11 (m, 2 H); 7.68 - 7.74 (m, 2 H); 7.59 (t, *J*=7.70 Hz, 1 H); 7.49 (dd, *J*=7.52, 0.54 Hz, 1 H); 7.34 (s, 1 H); 7.17 (dd, *J*=7.89, 0.55 Hz, 1 H); 3.93 (s, 3 H); 3.72 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.53, 166.36, 160.16, 150.63 , 138.73 (+) 131.29 , 130.00 (+) 129.17 , 122.38 (+) 121.92 (+) 114.96 , 109.59 , 101.23 (+) 101.20 , 52.43 (+), 52.37 (+), 35.48; HR EI MS *m/z* 343.0600, Calcd for $C_{18}H_{14}ClNO_4$ 343.0611.

Methyl 3-[3-(6-chloropyridin-2-yl)-3-(methoxycarbonyl)cycloprop-1-en-1-yl]benzoate (**3l**)



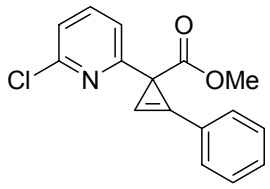
3l: (87%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.29 (t, *J*=1.56 Hz, 1 H), 8.04 - 8.09 (m, 1 H), 7.83 (dt, *J*=7.66, 1.40 Hz, 1 H), 7.59 (t, *J*=7.79 Hz, 1 H), 7.51 (t, *J*=8.07 Hz, 1 H), 7.28 (s, 1 H), 7.17 (dd, *J*=7.89, 0.73 Hz, 1 H), 3.93 (s, 1 H), 3.72 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.67, 166.29, 160.28, 150.60, 138.73 (+), 134.23 (+), 131.06 (+), 130.95, 130.00 (+), 129.03 (+), 125.52, 122.34 (+), 121.96 (+), 114.87, 99.76, 99.73 (+), 52.40 (+), 35.49; HR EI MS *m/z* 343.0613; Calcd for $C_{18}H_{14}ClNO_4$ 343.0611.

2-Bromo-6-(2-butyl-1-phenylcycloprop-2-en-1-yl)pyridine (**3m**)



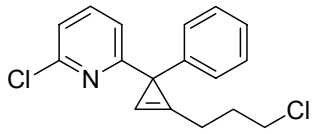
3m: (69%) ^{1}H NMR (500 MHz, CDCl3) δ ppm 7.36 (t, *J*=7.70 Hz, 1 H), 7.27 - 7.33 (m, 2 H), 7.16 - 7.27 (m, 4 H), 7.09 (dd, *J*=7.61, 0.83 Hz, 1 H), 6.91 (t, *J*=1.38 Hz, 1 H), 2.65 (td, *J*=7.34, 1.28 Hz, 2 H), 1.55 - 1.65 (m, 2 H), 1.29 - 1.42 (m, 2 H), 0.88 (t, *J*=7.43 Hz, 3 H); ^{13}C NMR (126 MHz, CDCl3) δ ppm 167.96, 145.31, 141.51, 137.95 (+), 128.20 (+), 125.87 (+), 124.51 (+), 123.50, 121.82 (+), 101.16 (+), 36.07, 29.22 (-), 24.48 (-), 22.35 (-), 13.79 (+); HR EI MS *m/z* 327.0631, Calcd for $C_{18}H_{18}BrN$ 327.0631.

Methyl 1-(6-chloropyridin-2-yl)-2-phenylcycloprop-2-ene-1-carboxylate[1] (**3n**)



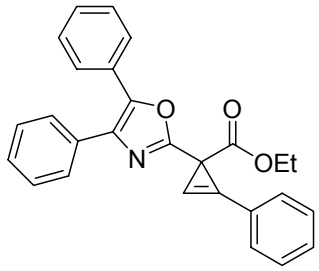
3n: (86%); 84% ee (3% *i*-PrOH in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J*=7.75, 1.61 Hz, 2 H), 7.57 (t, *J*=7.75 Hz, 1 H), 7.48 (dd, *J*=7.75, 0.73 Hz, 1 H), 7.36 - 7.46 (m, 3 H), 7.20 (s, 1 H), 7.15 (dd, *J*=7.75, 0.73 Hz, 1 H), 3.71 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.94, 160.69, 150.54, 138.63 (+), 130.19 (+), 130.11 (+), 128.86 (+), 124.95, 122.18 (+), 121.91 (+), 115.54, 98.25 (+,) 52.32 (+), 35.28; HR EI MS *m/z* 285.0547, Calcd for $C_{16}H_{12}ClNO_2$ 285.0557.

2-Chloro-6-[2-(3-chloropropyl)-1-phenylcycloprop-2-en-1-yl]pyridine (**3o**)



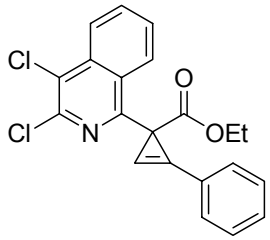
3o: (68%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.46 (t, *J*=7.79 Hz, 1 H), 7.28 - 7.34 (m, 2 H), 7.18 - 7.25 (m, 3 H), 7.09 (dd, *J*=7.79, 0.64 Hz, 1 H), 7.05 (dd, *J*=7.70, 0.55 Hz, 1 H), 6.99 (t, *J*=1.28 Hz, 1 H), 3.52 - 3.64 (m, 2 H), 2.76 - 2.93 (m, 2 H), 2.04 - 2.16 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.00, 150.70, 144.81, 138.31 (+), 128.37 (+), 128.20 (+), 126.14 (+), 122.23, 121.53 (+), 120.87 (+), 102.36 (+), 44.26 (-), 36.16, 30.08 (-), 22.20 (-); HR EI MS *m/z* 303.05815, Calcd for $C_{17}H_{15}Cl_2N$ 303.0582.

Ethyl 2-phenyl-1-(4,5-diphenyl-1,3-oxazol-2-yl)cycloprop-2-ene-1-carboxylate (**3p**)



3p: (64%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.70 - 7.85 (m, 2 H), 7.61 - 7.69 (m, 2 H), 7.55 - 7.61 (m, 2 H), 7.40 - 7.54 (m, 3 H), 7.27 - 7.41 (m, 6 H), 7.20 (s, 1 H), 4.16 - 4.36 (m, 2 H), 1.27 (t, *J*=7.06 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.89, 162.00, 145.38, 135.34, 132.53, 130.56 (+), 130.45 (+), 129.12, 128.92, (+), 128.60 (+), 128.47 (+), 128.39 (+), 128.11 (+), 128.00 (+), 126.56 (+), 124.30, 114.32, 96.58 (+), 61.59 (-), 27.90, 14.32 (+);

Ethyl 1-(3,4-dichloroisoquinolin-1-yl)-2-phenylcycloprop-2-ene-1-carboxylate (**3r**)

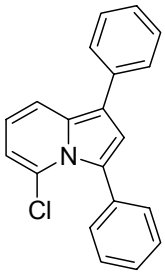


3r: (64%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.31 (dt, *J*=8.34, 0.96 Hz, 1 H), 8.24 (dt, *J*=8.57, 0.85 Hz, 1 H), 7.86 - 7.91 (m, 2 H), 7.81 (ddd, *J*=8.44, 7.06, 1.19 Hz, 1 H), 7.69 (ddd, *J*=8.34, 7.06, 1.10 Hz, 1 H), 7.39 - 7.49 (m, 3 H), 7.34 (s, 1 H), 4.09 - 4.21 (m, 2 H), 1.09 (t, *J*=7.06 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.99, 159.25, 142.68, 135.90, 131.53 (+), 130.51 (+), 130.18 (+), 128.65 (+), 127.69 (+), 127.31, 126.52 (+), 125.42, 124.89, 124.53 (+), 116.99, 99.62 (+), 61.38 (-) 35.01, 14.19 (+); HR EI MS *m/z* 383.0481, Calcd for $C_{21}H_{15}Cl_2NO_2$ 383.04798.

$Rh(PPh_3)_3Cl$-Catalyzed Rearrangement of Cyclopropenes

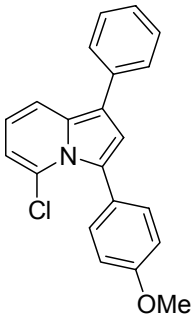
Typical Preparative Procedure. To an oven dried 3 ml Wheaton vial were added 2-chloro-6-(1,2-diphenylcycloprop-2-en-1-yl)pyridine **3a** (0.152 g, 0.5 mmol) and Wilkinson's catalyst (9.2 mg, 0.01 mmol) under N_2 atmosphere. 1 ml of dry dimethylformamide was then added, and reaction mixture was stirred 24h until judged complete by TLC analysis. The reaction mixture was quenched with 50 ml of saturated NH_4Cl solution and thoroughly extracted with hexanes. The organic phase was washed with brine, and dried over $MgSO_4$. After removal of solvents in vacuo, the residue was purified via flash Silica chromatography (1% triethylamine in hexanes) to afford 0.129 g (0.425 mmol, 85%) of 5-chloro-1,3-diphenylindolizine **2a** as yellow oil.

5-Chloro-1,3-diphenylindolizine **(2a)**



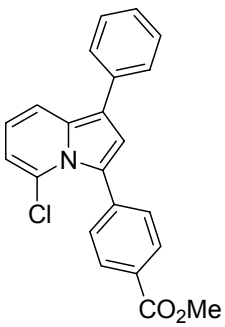
2a: (85%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.77 (dd, *J*=8.89, 1.19 Hz, 1 H), 7.56 - 7.70 (m, 2 H), 7.43 - 7.51 (m, 4 H), 7.37 - 7.42 (m, 3 H), 7.28 - 7.33 (m, 1 H), 7.00 (s, 1 H), 6.71 (dd, *J*=8.99, 6.97 Hz, 1 H), 6.62 (dd, *J*=6.79, 1.10 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 135.71, 134.45, 132.68, 130.90 (+), 128.83 (+), 128.09 (+), 127.51, 127.43 (+), 126.91 (+), 126.56, 125.99 (+), 117.82 (+), 117.53 (+), 117.06 (+), 116.28, 113.15 (+); HR EI MS *m/z* 303.0814, Calcd for $C_{20}H_{14}ClN$ 303.08148.

5-Chloro-3-(4-methoxyphenyl)-1-phenylindolizine **(2b)**



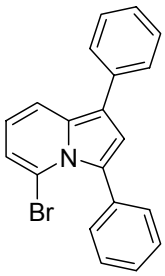
2b: (91%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.75 (dd, *J*=8.89, 1.19 Hz, 1 H), 7.54 - 7.66 (m, 2 H), 7.33 - 7.52 (m, 4 H), 7.27 - 7.33 (m, 1 H), 6.87 - 7.01 (m, 3 H), 6.67 (dd, *J*=8.99, 6.79 Hz, 1 H), 6.59 (dd, *J*=6.88, 1.19 Hz, 1 H), 3.89 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.20, 135.78, 132.42, 132.20 (+), 128.80 (+), 128.06 (+), 127.29, 126.86, 126.56, 125.91 (+), 117.55 (+), 117.30 (+), 117.01 (+), 116.00, 113.03 (+), 112.33 (+), 55.32 (+); mp 139°C; HR EI MS *m/z* 333.0932, Calcd for $C_{21}H_{16}ClNO$ 333.09204.

Methyl 4-(5-chloro-1-phenylindolizin-3-yl)benzoate **(2c)**



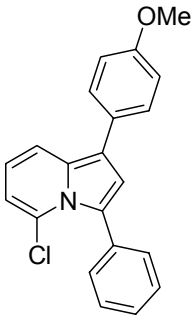
2c: (79%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.07 (s, 2 H), 7.77 (dd, *J*=8.99, 1.10 Hz, 1 H), 7.41 - 7.64 (m, 6 H), 7.31 (s, 1 H), 7.03 (s, 1 H), 6.75 (dd, *J*=8.80, 6.97 Hz, 1 H), 6.67 (dd, *J*=6.97, 0.92 Hz, 1 H), 3.96 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.04, 138.86, 135.38, 133.45, 130.31 (+), 128.87 (+), 128.66, 128.20 (+), 128.09 (+), 126.49, 126.31, 126.20 (+), 118.46 (+), 118.17 (+), 117.15 (+), 116.95, 113.58 (+), 52.18 (+); mp 121-122°C; HR EI MS *m/z* 361.0872, Calcd for $C_{22}H_{16}ClNO_2$ 361.08696.

5-Bromo-1,3-diphenylindolizine **(2d)**



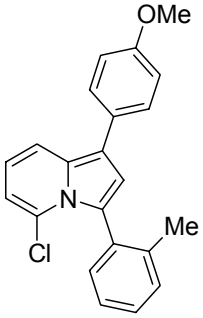
2d: (87%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.81 (dd, *J*=8.99, 1.10 Hz, 1 H), 7.54 - 7.70 (m, 2 H), 7.34 - 7.55 (m, 7 H), 7.27 - 7.36 (m, 1 H), 7.00 (s, 1 H), 6.83 (dd, *J*=6.97, 1.10 Hz, 1 H), 6.61 (dd, *J*=8.89, 6.88 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 135.70, 134.17, 132.75, 131.27 (+), 128.83 (+), 128.56, 128.12 (+), 127.64 (+), 126.94 (+), 126.00 (+), 118.23 (+), 117.85 (+), 117.67 (+), 116.13, 113.59; HR EI MS *m/z* 347.0321, Calcd for $C_{20}H_{14}BrN$ 347.03096.

5-Chloro-1-(4-methoxyphenyl)-3-phenylindolizine **(2e)**



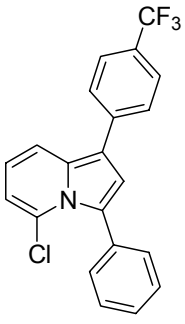
2e: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.70 (dd, *J*=8.99, 1.10 Hz, 1 H), 7.50 - 7.58 (m, 2 H), 7.45 - 7.50 (m, 2 H), 7.39 (s, 3 H), 6.98 - 7.07 (m, 2 H), 6.94 (s, 1 H), 6.67 (dd, *J*=8.90, 6.88 Hz, 1 H), 6.59 (dd, *J*=6.97, 1.10 Hz, 1 H), 3.87 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.11, 134.50, 132.43, 130.87 (+), 129.17 (+), 128.23, 127.36 (+), 127.26, 126.88 (+), 126.41, 117.68 (+), 117.07 (+), 116.05, 114.31 (+), 112.99 (+), 55.38 (+); HR EI MS *m/z* 333.0931, Calcd for $C_{21}H_{16}ClNO$ 333.09204.

5-Chloro-1-(4-methoxyphenyl)-3-(2-methylphenyl)indolizine **(2f)**



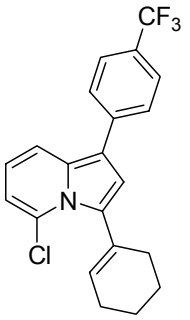
2f: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.69 (dd, *J*=8.99, 1.10 Hz, 1 H), 7.49 - 7.58 (m, 2 H), 7.39 (dd, *J*=7.43, 1.19 Hz, 1 H), 7.29 - 7.36 (m, 1 H), 7.18 - 7.25 (m, 2 H), 6.96 - 7.06 (m, 2 H), 6.85 (s, 1 H), 6.64 (dd, *J*=8.99, 6.97 Hz, 1 H), 6.54 (dd, *J*=6.88, 1.19 Hz, 1 H), 3.87 (s, 3 H), 2.09 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.05, 139.56, 134.68, 131.87, 131.53 (+), 129.09 (+), 128.78 (+), 128.39, 128.28 (+), 126.38, 126.20, 124.53 (+), 117.12 (+), 116.87 (+), 116.70 (+), 115.62, 114.34 (+), 112.51 (+), 55.39 (+), 20.42 (+);

5-Chloro-3-phenyl-1-[4-(trifluoromethyl)phenyl]indolizine **(2g)**



2g: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.76 (dd, *J*=8.99, 1.10 Hz, 1 H), 7.71 (s, 4 H), 7.44 - 7.52 (m, 2 H), 7.37 - 7.45 (m, 3 H), 7.01 (s, 1 H), 6.77 (dd, *J*=8.99, 6.97 Hz, 1 H), 6.66 (dd, *J*=6.97, 1.10 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 139.42, 134.14, 133.01, 130.92 (+), 128.07, 127.89 (+), 127.67 (+), 127.00 (+), 126.95, 125.76 (+, q, J_{FC} = 2.77 Hz), 124.48 (q, J_{FC} = 271.88 Hz), 118.56 (+), 117.75 (+), 116.61 (+), 114.68, 113.51 (+); HR EI MS *m/z* 371.0684, Calcd for $C_{21}H_{13}ClF_3N$ 371.06886.

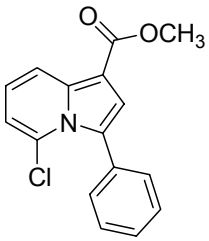
***5-Chloro-3-cyclohex-1-en-1-yl-1-[4-(trifluoromethyl)phenyl]indolizine* (2h)**



2h: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.66 (s, 4 H), 7.64 (dd, *J*=8.89, 1.19 Hz, 1 H), 6.79 (s, 1 H), 6.67 (dd, *J*=8.99, 6.97 Hz, 1 H), 6.60 (dd, *J*=6.90, 1.17 Hz, 1 H), 5.84 - 5.90 (m, 1 H), 2.04 - 2.84 (m, 4 H), 1.53 - 2.01 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 139.65, 132.32, 131.73, 130.79, 130.33 (+), 127.68 (+), 126.81, 125.65 (+, q, J_{FC} = 2.78 Hz), 124.32 (q, J_{FC} = 271.88 Hz), 118.08 (+), 116.45 (+), 115.54 (+), 113.92, 112.88 (+), 32.71 (-), 25.71 (-), 22.62 (-), 21.87 (-); HR EI MS *m/z* 375.1001, Calcd for $C_{21}H_{17}ClF_3N$ 375.10016.

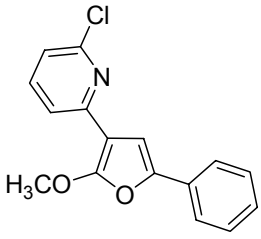
$Rh(PPh_3)_3Cl$-Catalyzed rearrangement of cyclopropene 3n. To an oven dried 3 ml Wheaton vial were added methyl 1-(6-chloropyridin-2-yl)-2-phenylcycloprop-2-ene-1-carboxylate **3n** (0.285 g, 1.0 mmol) and Wilkinson's catalyst (18.4 mg, 0.02 mmol) under N_2 atmosphere. Dry dimethylformamide (2 ml) was then added, and reaction the mixture was stirred for 24h until judged complete by TLC analysis. The reaction mixture was quenched with 100 mL of saturated NH_4Cl solution and thoroughly extracted with diethyl ether. The organic phase was washed with brine, and dried over $MgSO_4$. After removal of solvents in vacuo, the residue was purified via flash Silica chromatography (2:1 hexanes/benzene) to afford 0.038 g (0.133 mmol, 13%) of methyl 5-chloro-3-phenylindolizine-1-carboxylate **5**[1] and 0.184 g (0.646 mmol, 65%) of 2-chloro-6-(2-methoxy-5-phenyl-3-furyl)pyridine **6**.

***Methyl 5-chloro-3-phenylindolizine-1-carboxylate* (5)**



5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J*=8.92, 1.32 Hz, 1 H), 7.29 - 7.43 (m, 5 H), 7.20 (s, 1 H), 6.98 (dd, *J*=9.06, 7.02 Hz, 1 H), 6.74 (dd, *J*=7.16, 1.32 Hz, 1 H), 3.88 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.93, 138.77, 133.62, 131.01 (+, 2C), 128.09, 127.96 (+), 127.66, 127.04 (+, 2C), 121.99 (+), 119.51 (+), 118.52 (+), 114.75 (+), 104.60, 51.11 (+); mp 110°C (dichloromethane-hexane); HR EI MS *m/z* 285.0556 Calcd for $C_{16}H_{12}ClNO_2$ 285.05566.

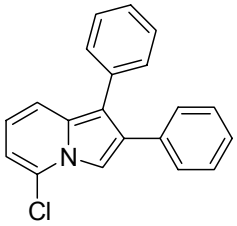
***2-Chloro-6-(2-methoxy-5-phenyl-3-furyl)pyridine* (6)**



6: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.54 - 7.70 (m, 4 H), 7.37 – 7.39 (m, 2 H), 7.27 (s, 1 H), 7.22 – 7.24 (m, 1 H), 7.07 (d, *J*=7.52 Hz, 1 H), 4.21 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 157.5, 152.4, 150.8, 144.1, 138.7 (+), 130.3, 128.7 (+), 126.8 (+), 122.7 (+), 120.1 (+), 118.8 (+), 106.0 (+), 100.7, 58.1 (+); mp 99-100°C; LR EI MS *m/z* 284.90 (M+).

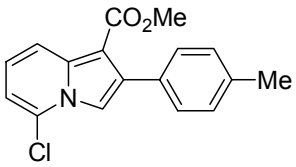
CuI-Catalyzed Rearrangement of Cyclopropenes

Typical experimental procedure. To an oven dried 3 ml Wheaton vial were added 2-chloro-6-(1,2-diphenylcycloprop-2-en-1-yl)pyridine **3a** (0.152 g, 0.5 mmol) and CuI (4.8 mg, 0.025 mmol) under N_2 atmosphere. 1 ml of dry dimethylformamide was then added, and reaction mixture was stirred 10h, when judged complete by TLC analysis, quenched with 50 ml of saturated NH_4Cl solution and thoroughly extracted with hexanes. The organic phase was washed with brine, and dried over $MgSO_4$. After removal of solvents in vacuo, the residue was purified via flash Silica chromatography (1% triethylamine in hexanes) to afford 0.112 g (0.375 mmol, 75%) of 5-chloro-1,2-diphenylindolizine **4a** as yellow oil.



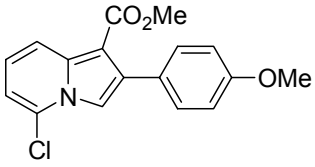
4a: (75%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.73 (s, 1 H), 7.48 (dd, *J*=7.70, 2.20 Hz, 1 H), 7.20 - 7.41 (m, 10 H), 6.63 - 6.76 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 134.80, 132.83, 130.32 (+), 129.20 (+), 128.84, 128.44 (+), 128.34 (+), 126.65 (+), 126.13 (+), 125.50, 117.87 (+), 116.41 (+), 114.59, 110.58 (+), 110.11 (+); HR EI MS *m/z* 303.0799 Calcd for $C_{20}H_{14}ClN$ 303.0815.

Methyl 5-chloro-2-(4-methylphenyl)indolizine-1-carboxylate (**4b**)



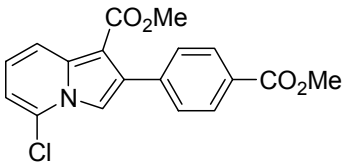
4b: (83%) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.24 (d, *J*=9.06 Hz, 1 H), 7.55 (s, 1 H), 7.44 (m, 2 H), 7.24 (m, 2 H), 7.04 (dd, *J*=9.06, 7.16 Hz, 1 H), 6.86 (dd, *J*=7.16, 1.02 Hz, 1 H), 3.80 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 165.2, 138.2, 137.1, 133.1, 131.5, 129.7 (+), 128.5 (+), 126.3 (+), 122.3 (+), 118.6 (+), 112.3 (+), 112.2 (+), 103.3, 50.8 (+), 21.3 (+); mp 101-102°C (hexane); HR EI MS *m/z* 299.0714, Calcd for $C_{17}H_{14}O_2NCl$ 299.0713.

Methyl 5-chloro-2-(4-methoxyphenyl)indolizine-1-carboxylate (**4c**)



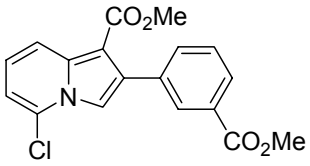
4c: (95%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.23 (d, *J*=9.17 Hz, 1 H) 7.53 (s, 1 H) 7.44 - 7.51 (m, 2 H) 7.04 (dd, *J*=8.99, 7.15 Hz, 1 H) 6.92 - 7.00 (m, 2 H) 6.86 (dd, *J*=7.24, 1.01 Hz, 1 H) 3.87 (s, 3 H) 3.81 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 165.21, 159.09, 138.19, 132.85, 131.00 (+), 126.79, 126.30, 122.34 (+), 118.54 (+), 113.26 (+), 112.30 (+), 112.12 (+), 103.18, 55.31 (+), 50.81 (+); HR EI MS *m/z* 315.0649 Calcd for $C_{17}H_{14}ClNO_3$ 315.0662; mp 94-95°C (dichloromethane-hexane).

Methyl 5-chloro-2-[4-(methoxycarbonyl)phenyl]indolizine-1-carboxylate (**4d**)



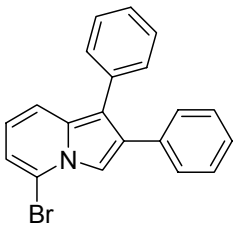
4d: (73%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.27 (d, *J*=8.99 Hz, 1 H), 8.06 - 8.13 (m, 2 H), 7.57 - 7.64 (m, 3 H), 7.09 (dd, *J*=9.08, 7.24 Hz, 1 H), 6.91 (dd, *J*=7.15, 0.92 Hz, 1 H), 3.95 (s, 3 H), 3.78 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.12, 164.92, 139.48, 138.36, 131.90, 129.90 (+), 129.01 (+), 128.95, 126.48, 122.83 (+), 118.67 (+), 112.65 (+), 112.45 (+), 103.31, 52.14 (+) 50.86 (+); mp 136-137°C (dichloromethane-hexane).

Methyl 5-chloro-2-[3-(methoxycarbonyl)phenyl]indolizine-1-carboxylate (**4e**)



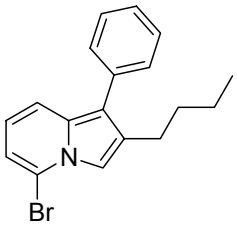
4e: (81%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.14 - 8.35 (m, 2 H), 8.05 (dd, *J*=7.89, 1.10 Hz, 1 H), 7.75 (dd, *J*=7.70, 1.10 Hz, 1 H), 7.60 (s, 1 H), 7.49 (t, *J*=7.79 Hz, 1 H), 7.08 (dd, *J*=8.99, 7.34 Hz, 1 H), 6.90 (dd, *J*=7.15, 0.73 Hz, 1 H), 3.94 (s, 3 H), 3.78 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.13, 164.95, 138.26, 134.91, 134.61 (+), 131.96, 130.88 (+), 129.75, 129.00, 128.56 (+), 127.72 (+), 126.48, 122.72 (+), 118.66 (+), 112.57 (+), 112.44 (+), 52.15 (+), 50.82 (+); HR EI MS *m/z* 345.0591 Calcd for $C_{18}H_{14}ClNO_4$ 345.0582; mp 111-112°C (dichloromethane-hexane).

5-Bromo-1,2-diphenylindolizine (**4f**)



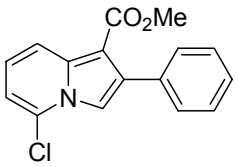
4f: (78%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.78 (s, 1 H), 7.53 (d, *J*=8.99 Hz, 1 H), 7.20 - 7.43 (m, 10 H), 6.85 (dd, *J*=6.97, 0.92 Hz, 1 H), 6.61 (dd, *J*=8.99, 6.97 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 134.87, 134.77, 132.79, 130.33 (+), 129.21 (+), 128.64, 128.45 (+), 128.34 (+), 126.65 (+), 126.14 (+), 125.55, 117.96 (+), 116.98 (+), 114.97, 114.79 (+) 114.39, 112.43 (+), 112.41; HR EI MS *m/z* 347.0297, Calcd for $C_{20}H_{14}BrN$ 347.0310.

5-Bromo-2-butyl-1-phenylindolizine (**4g**)



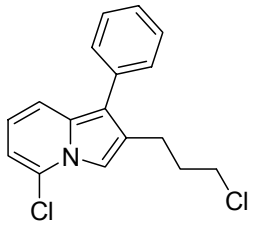
4g: (71%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.51 (s, 1 H), 7.39 - 7.49 (m, 5 H), 7.28 - 7.37 (m, 1 H), 6.77 (dd, *J*=6.88, 0.83 Hz, 1 H), 6.54 (dd, *J*=8.90, 6.88 Hz, 1 H), 2.77 (s, 2 H), 1.58 - 1.69 (m, 2 H), 1.32 - 1.44 (m, 2 H), 0.90 (t, *J*=7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 135.45, 132.06, 129.81, 129.00 (+), 128.48 (+), 126.02 (+), 117.19 (+), 116.30 (+), 115.87, 114.17, 114.06 (+), 111.95 (+), 32.92 (-), 25.63 (-), 22.73 (-), 13.98 (+); HR EI MS *m/z* 327.0619 Calcd for $C_{18}H_{18}BrN$ 327.0623.

Methyl 5-chloro-2-phenylindolizine-1-carboxylate (**4h**)



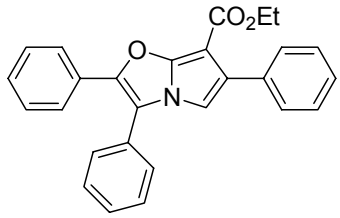
4h: (67%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.26 (dd, *J*=9.17, 0.37 Hz, 1 H), 7.57 (s, 1 H), 7.51 - 7.56 (m, 2 H), 7.33 - 7.46 (m, 3 H), 7.05 (dd, *J*=8.44, 1.28 Hz, 1 H), 6.88 (dd, *J*=7.24, 0.83 Hz, 1 H), 3.79 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 165.14, 138.21, 134.55, 133.08, 129.89 (+), 127.74 (+), 127.39 (+), 126.39, 122.46 (+), 118.62 (+), 112.39 (+), 103.31, 50.80 (+); HR EI MS *m/z* 285.0555, Calcd for $C_{16}H_{12}O_2NCl$ 285.0557.

5-Chloro-2-(3-chloropropyl)-1-phenylindolizine (**4i**)



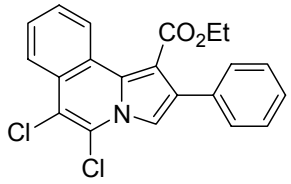
4i: (73%) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 - 7.55 (m, 7 H), 6.58 - 6.69 (m, 2 H), 3.52 (t, *J*=6.43 Hz, 2 H), 2.96 (s, 2 H), 1.98 - 2.13 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 135.01, 132.28, 129.73 (+) 128.63 (+) 126.90, 126.26 (+), 125.27, 117.43 (+), 115.87, 115.79 (+), 109.95 (+), 109.79 (+), 44.61 (-), 33.22 (-), 23.15 (-).

Ethyl 2,3,6-triphenylpyrrolo[2,1-b][1,3]oxazole-7-carboxylate (**4j**)

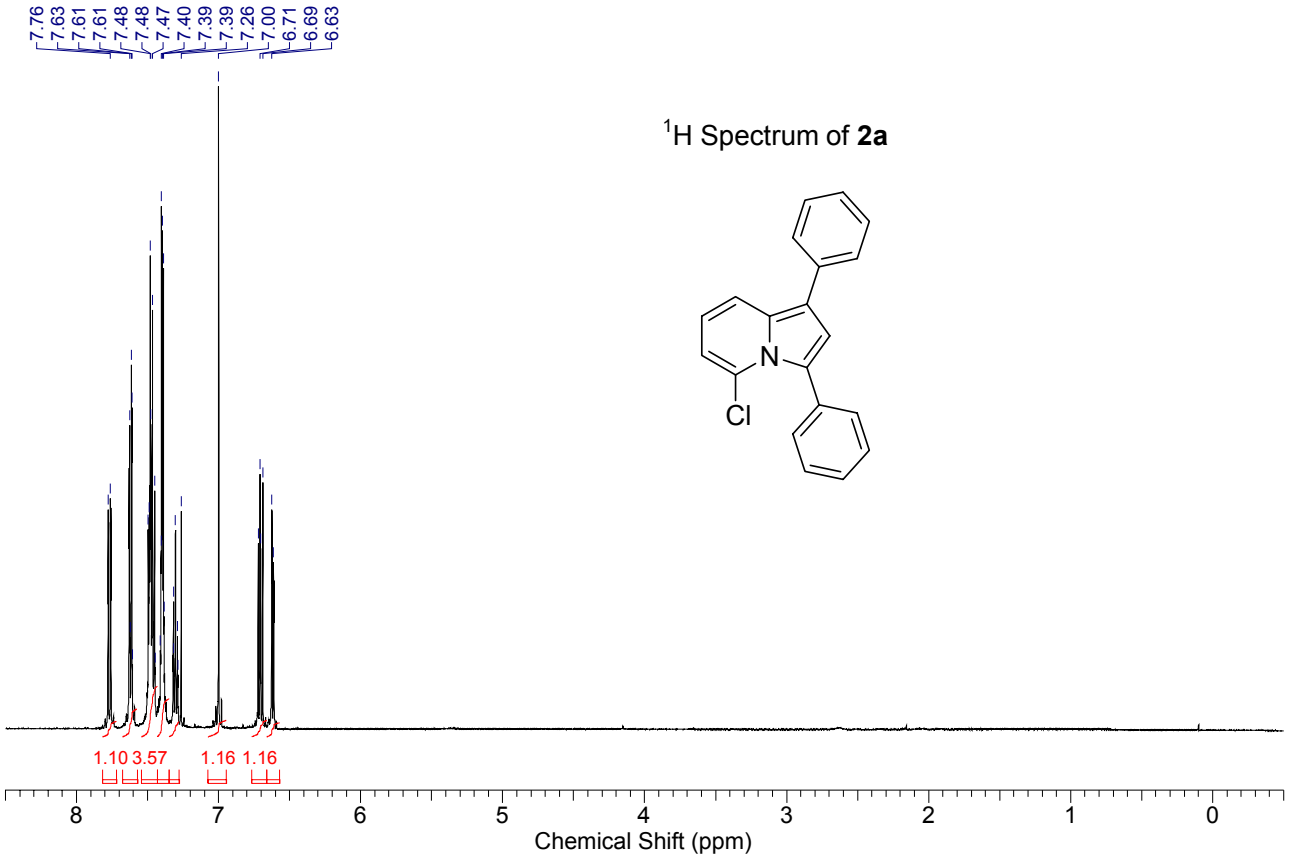


4j: (71%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.59 - 7.69 (m, 4 H), 7.48 - 7.59 (m, 5 H), 7.32 - 7.43 (m, 5 H), 7.27 - 7.33 (m, 1 H), 6.65 (s, 1 H), 4.33 (q, *J*=7.15 Hz, 2 H), 1.35 (t, *J*=7.15 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.31, 150.00, 145.27, 134.84, 130.84, 129.98 (+), 129.57 (+), 129.48 (+), 128.96 (+), 128.73 (+), 128.05, 127.70 (+), 126.95 (+), 126.59, 125.95 (+), 119.72, 101.72 (+), 59.45 (-), 14.55 (+); mp 129-130°C (dichloromethane-hexane); HR EI MS *m/z* 407.1523, Calcd for $C_{27}H_{21}O_3N$ 407.1521.

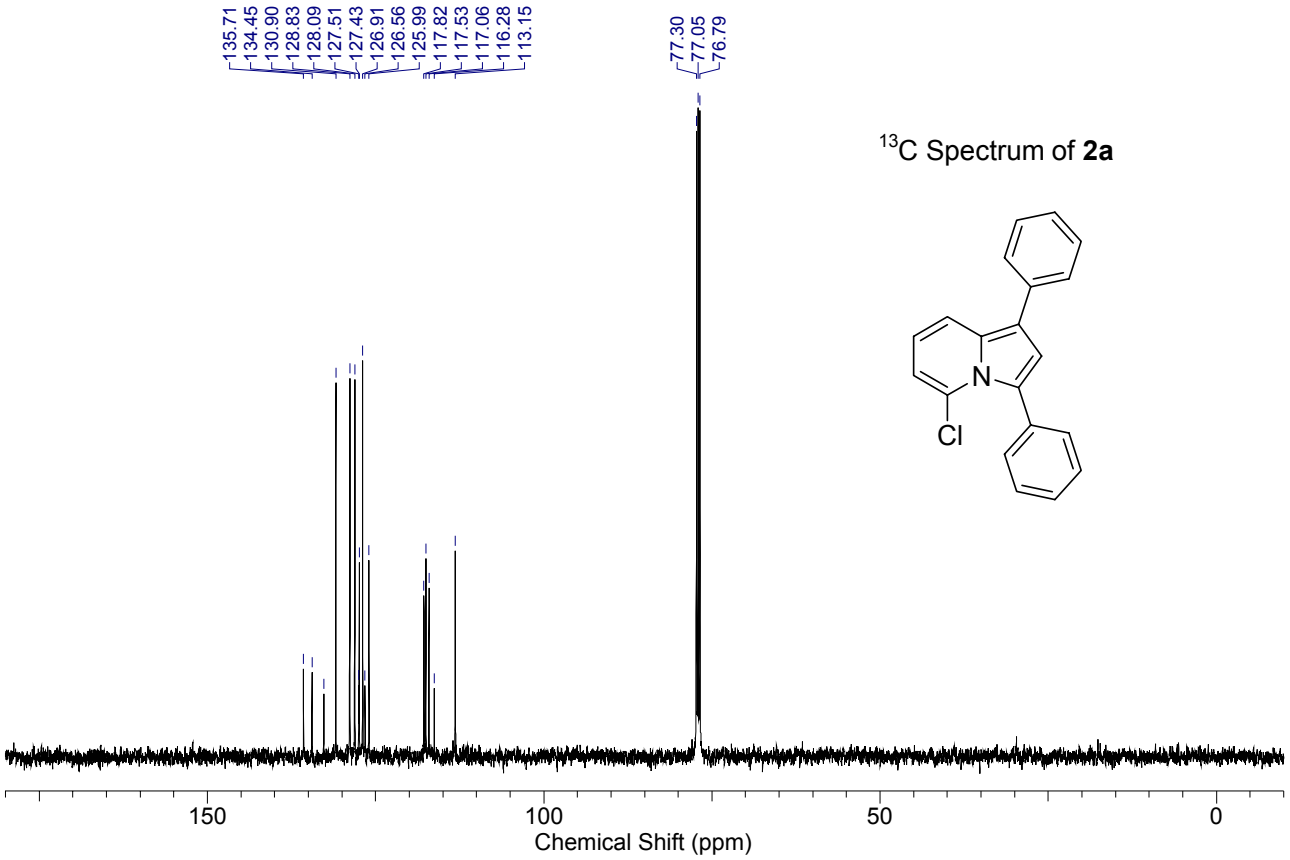
Ethyl 5,6-dichloro-2-phenylpyrrolo[2,1-a]isoquinoline-1-carboxylate (**4k**)



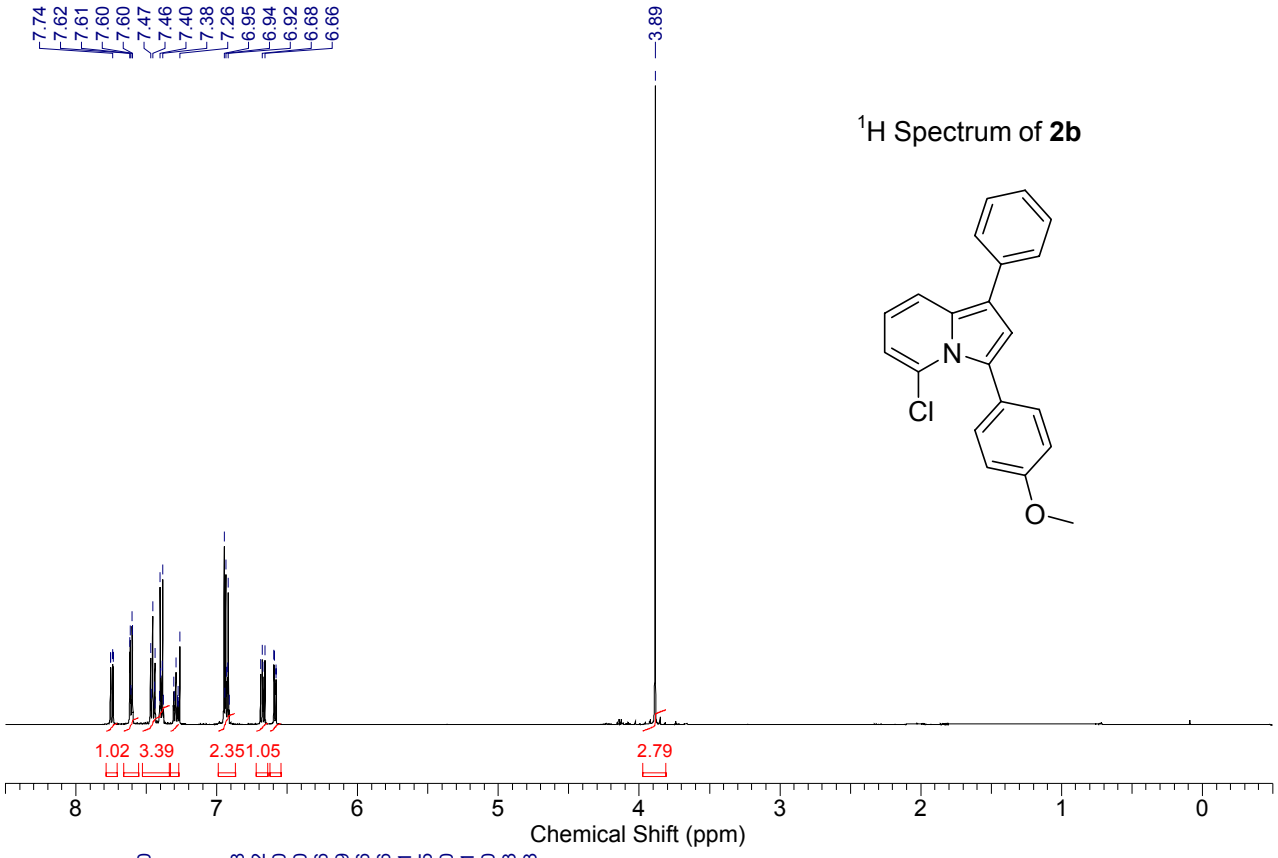
4k: (88%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 (d, *J*=8.44 Hz, 1 H), 8.08 (d, *J*=7.52 Hz, 1 H), 7.70 (s, 1 H), 7.52 - 7.66 (m, 2 H), 7.31 - 7.53 (m, 5 H), 4.27 (q, *J*=7.09 Hz, 2 H), 1.08 (t, *J*=7.15 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.17, 134.61, 130.03, 129.64, 128.87 (+), 128.55 (+), 128.18 (+), 127.77 (+), 127.20 (+), 126.31, 124.58 (+),124.54 (+), 123.92, 123.64, 117.58, 113.70 (+), 110.49, 61.09 (-), 13.70 (+); mp 105°C (hexanes); HR EI MS *m/z* 383.0478, Calcd for $C_{21}H_{15}Cl_2NO_2$ 383.0480.



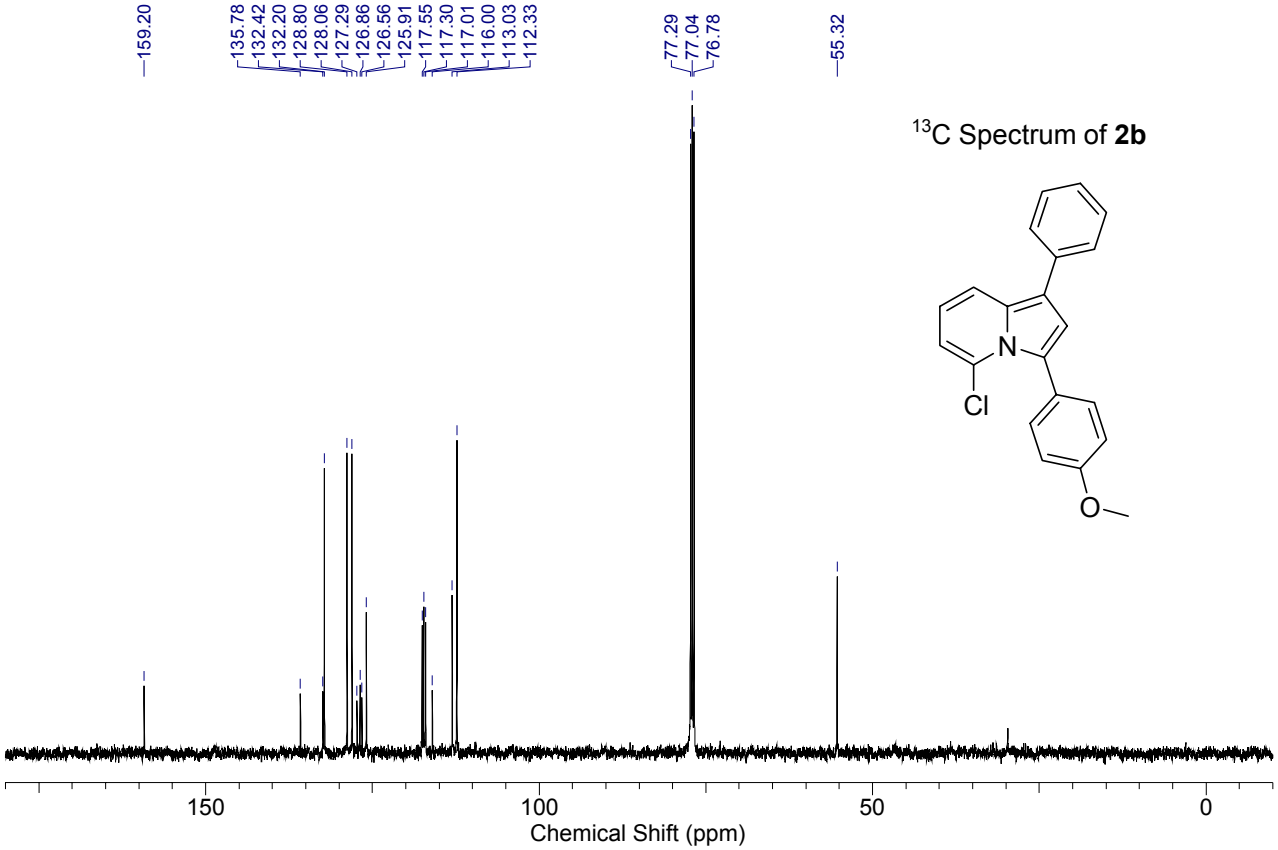
^{1}H Spectrum of **2a**



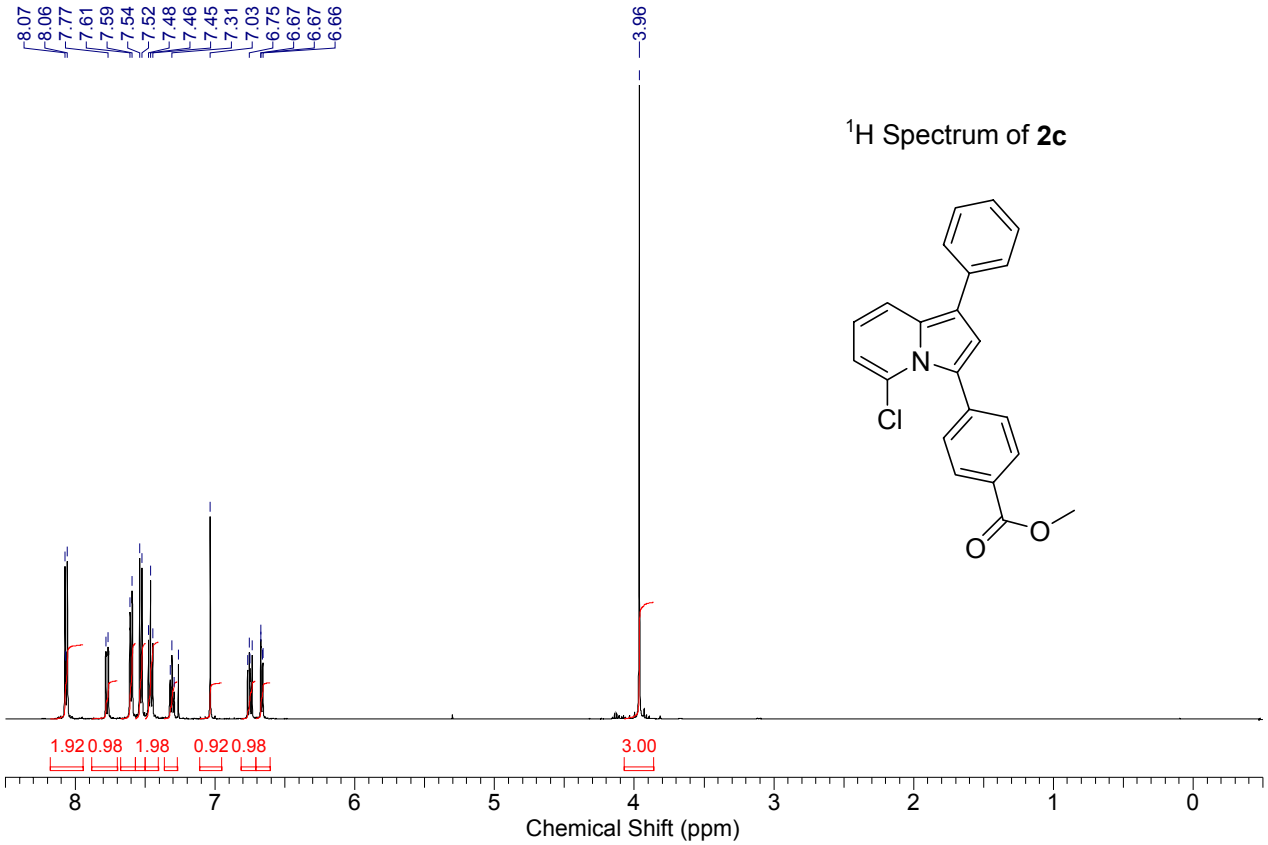
^{13}C Spectrum of **2a**



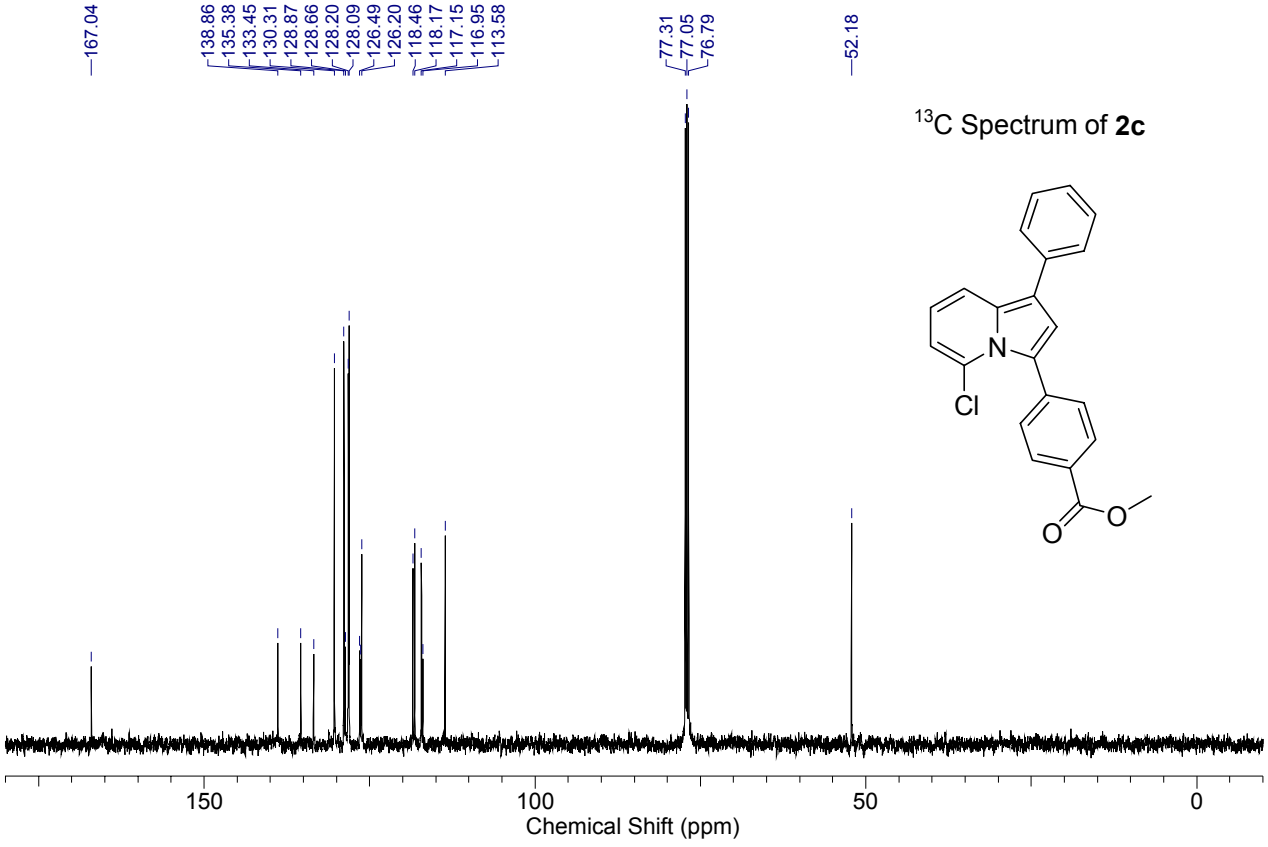
^{1}H Spectrum of **2b**



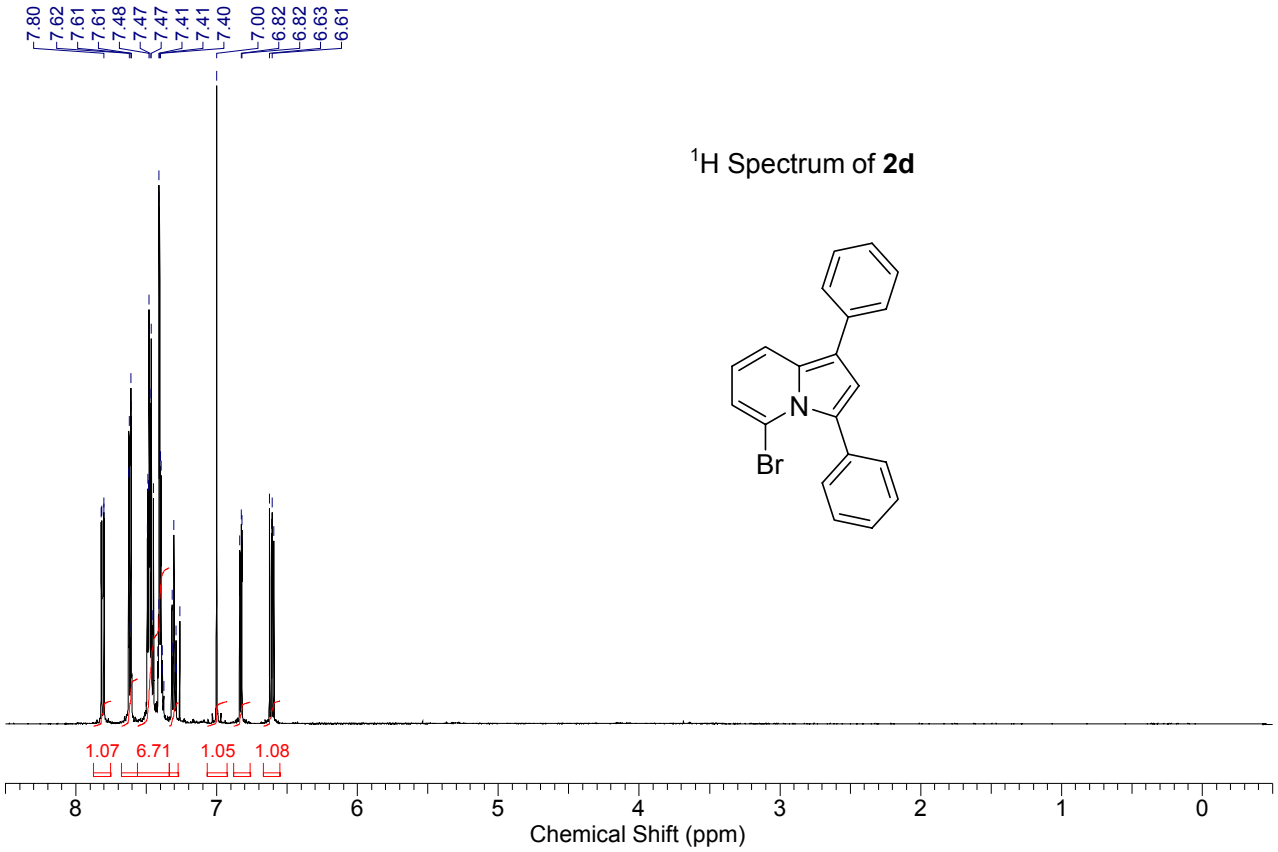
^{13}C Spectrum of **2b**



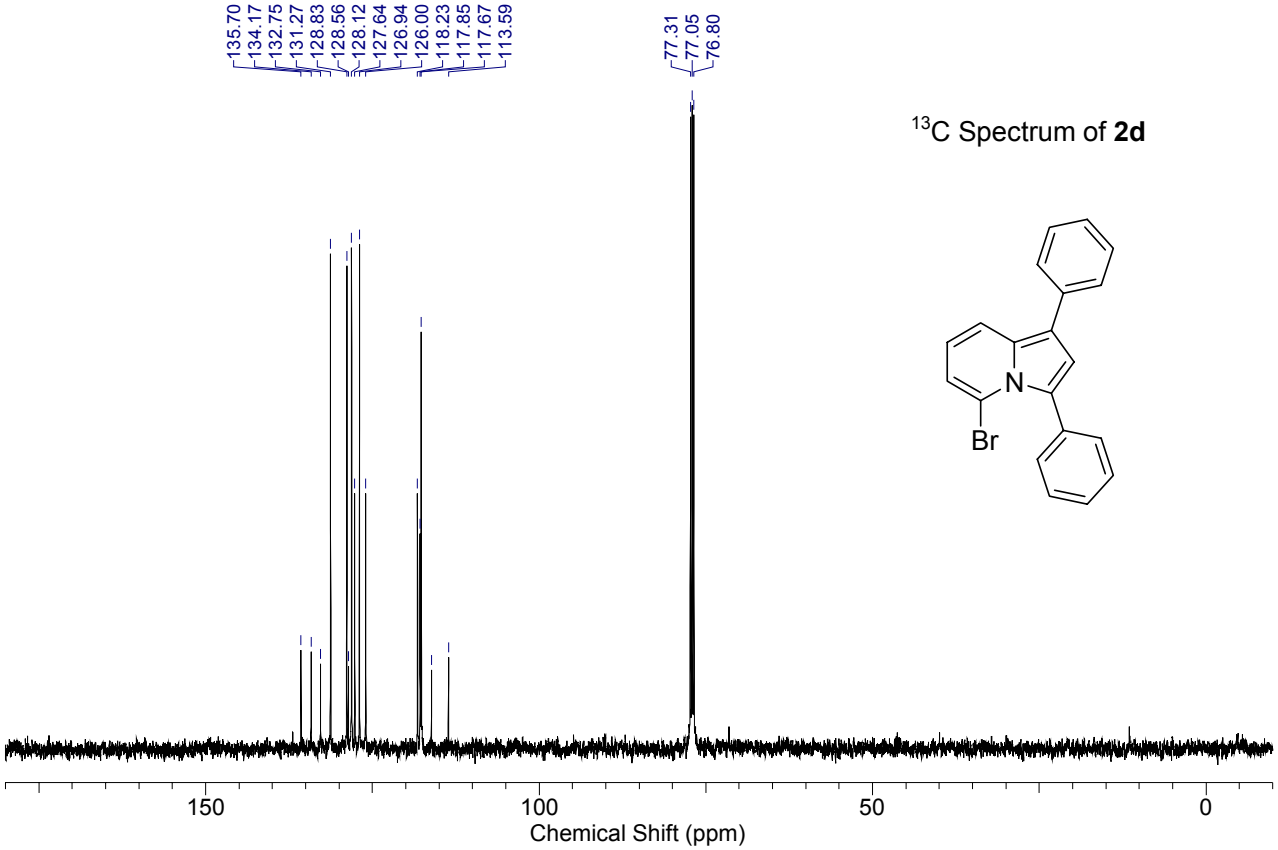
^{1}H Spectrum of **2c**



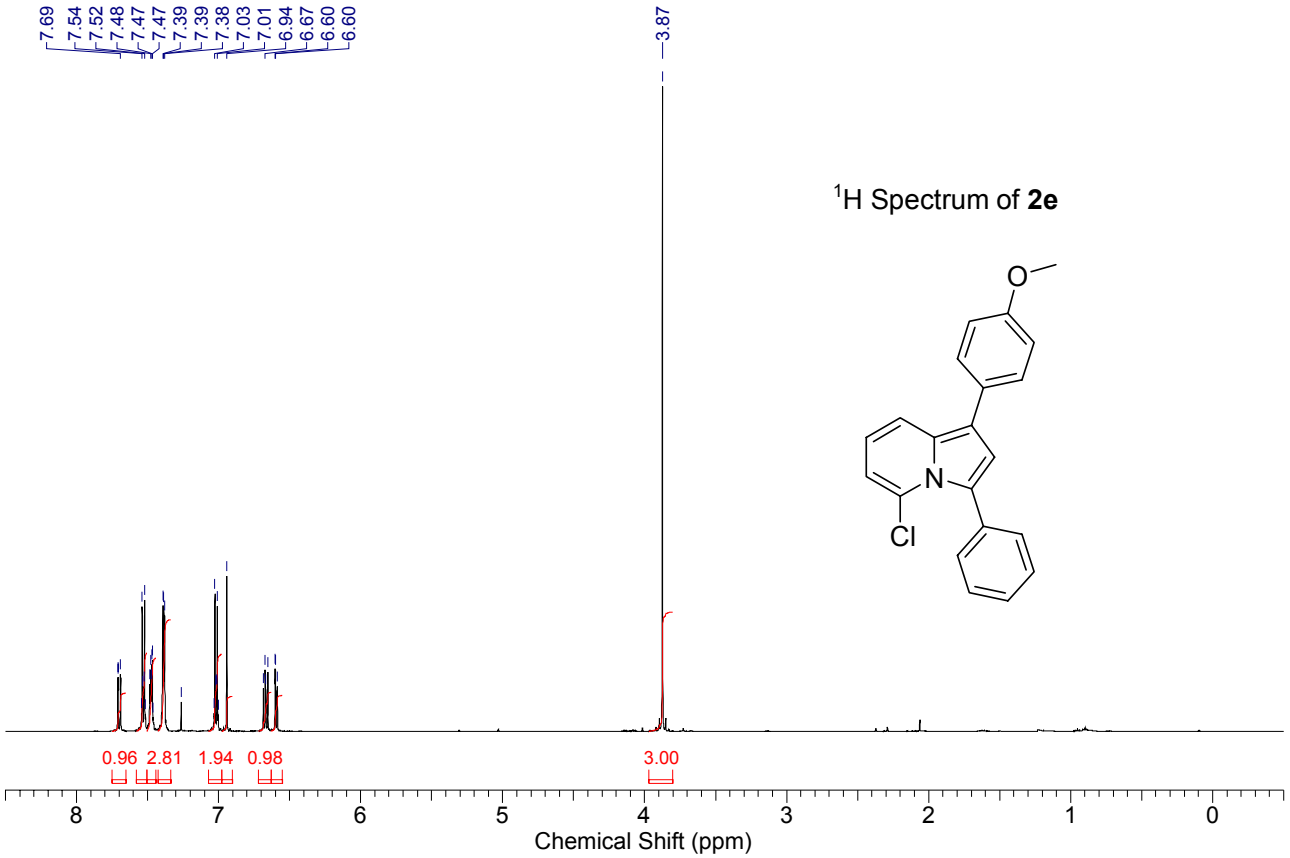
^{13}C Spectrum of **2c**



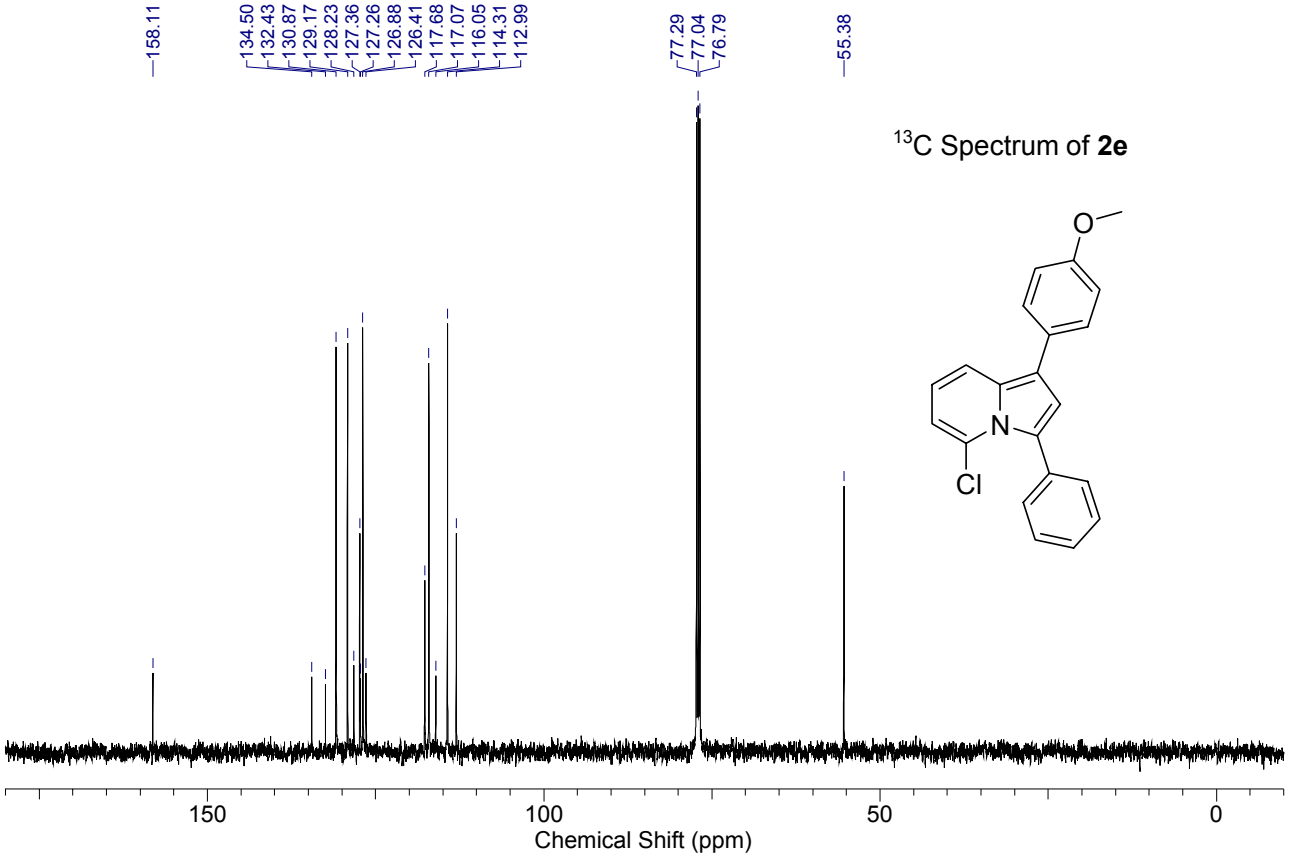
^{1}H Spectrum of **2d**



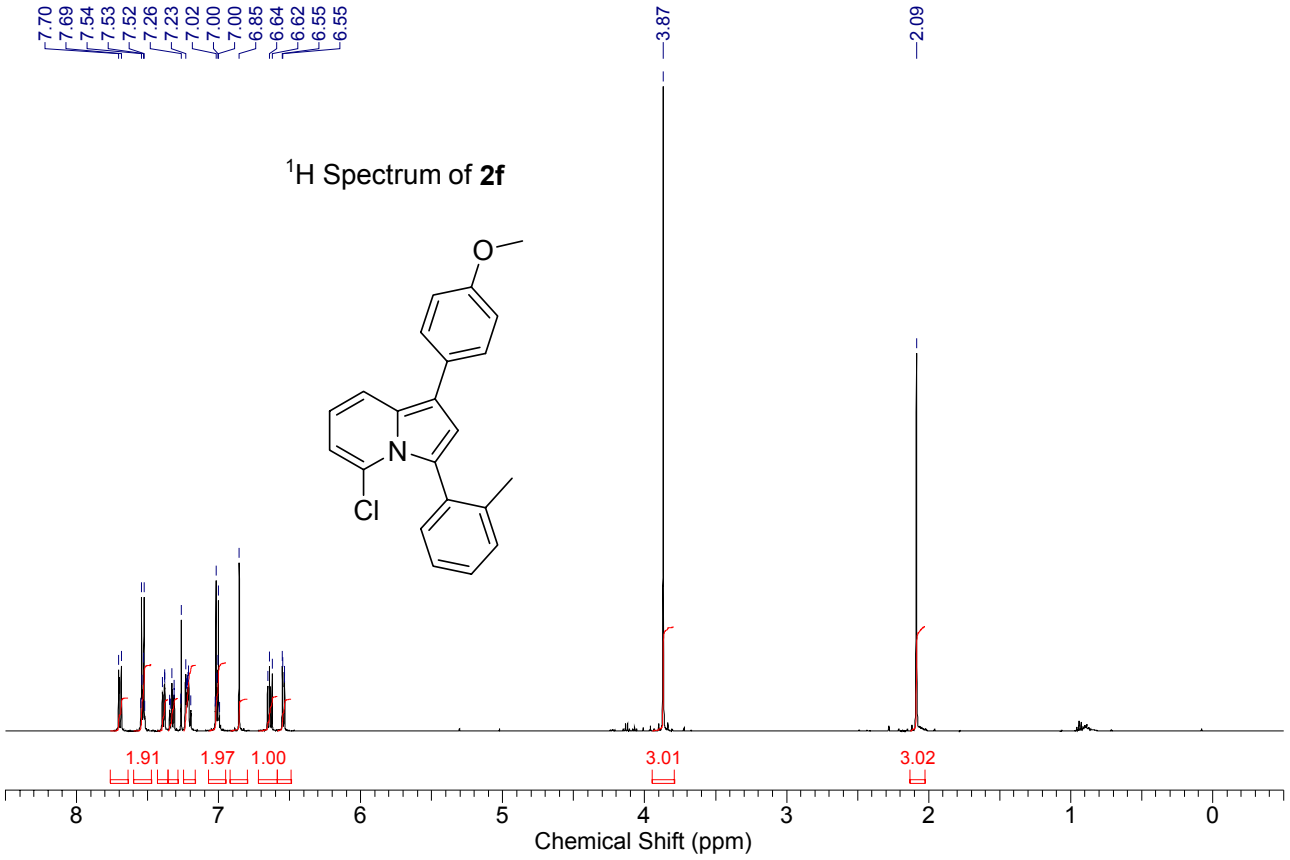
^{13}C Spectrum of **2d**

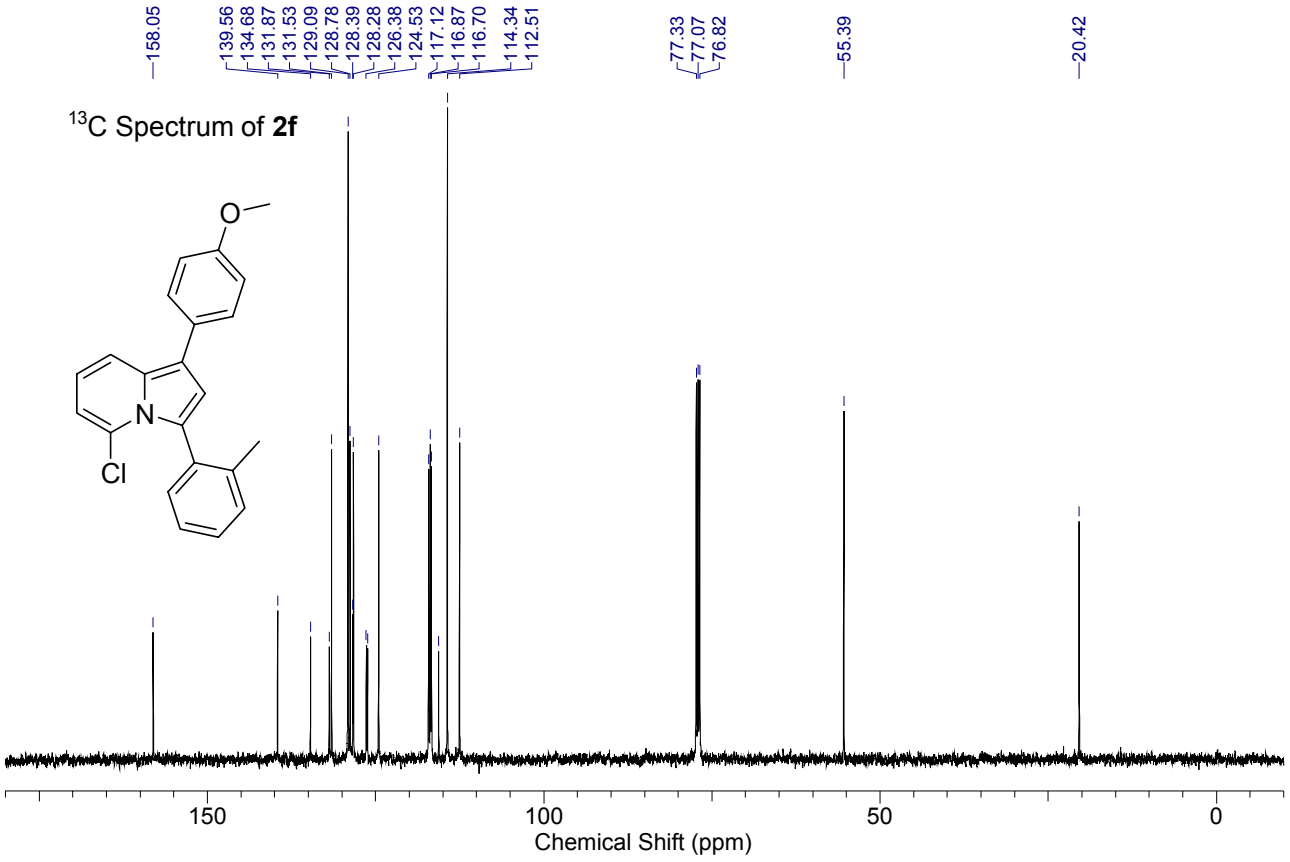


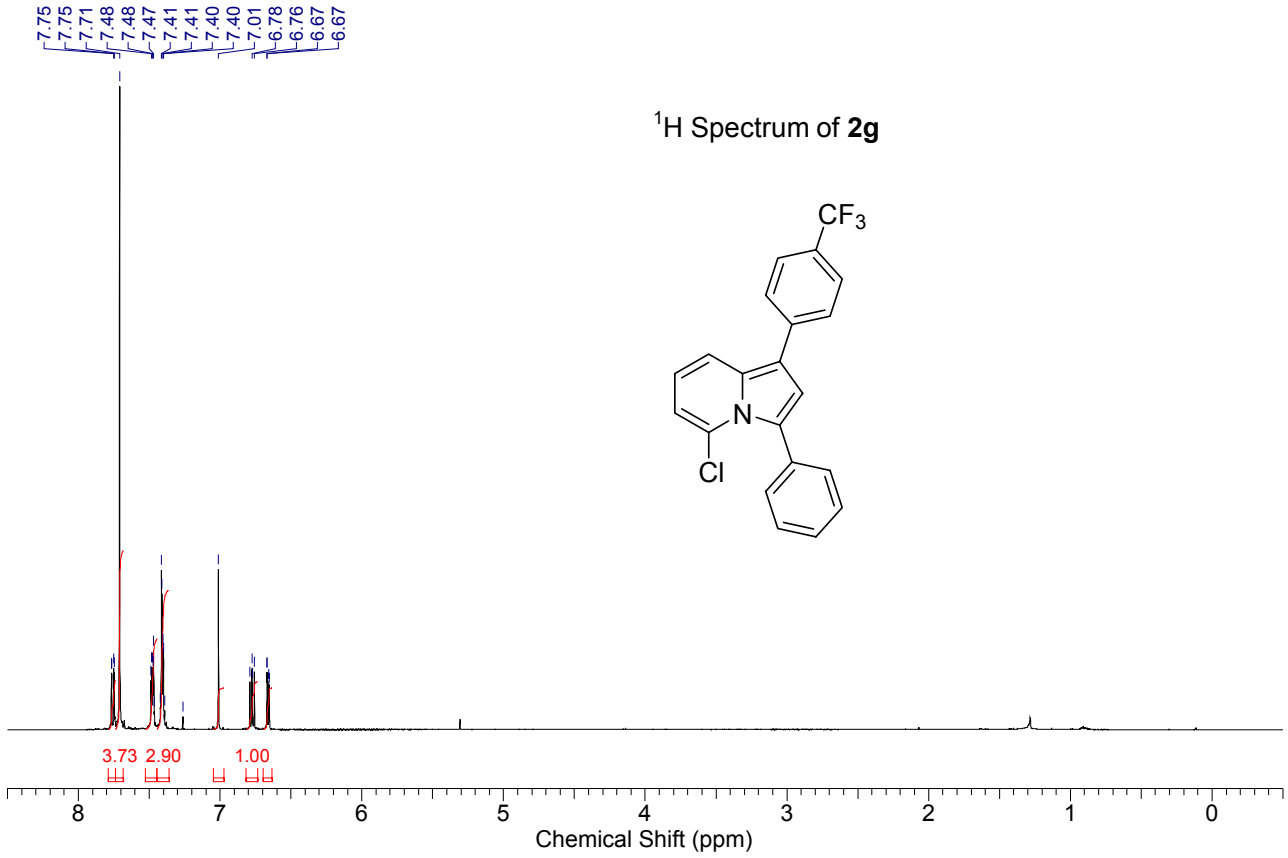
^{1}H Spectrum of **2e**



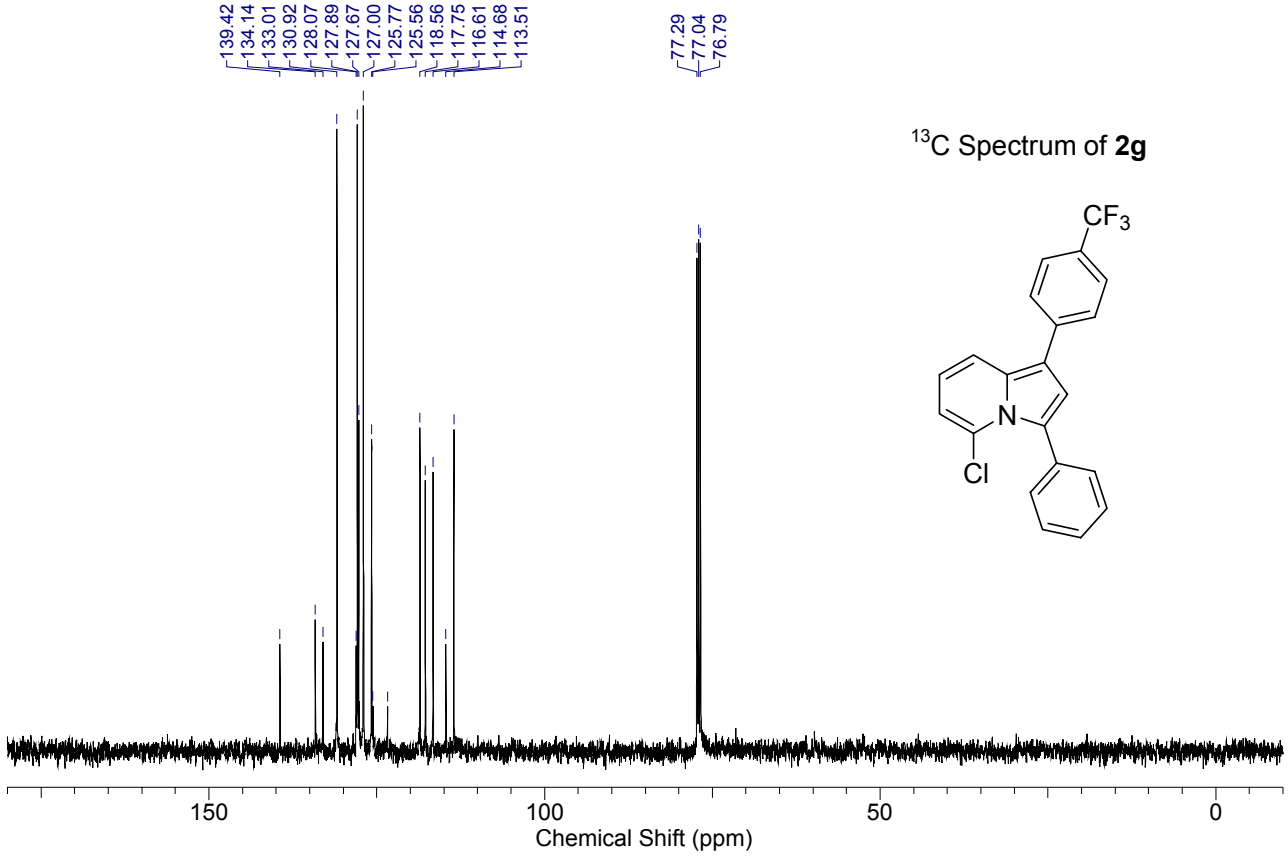
^{13}C Spectrum of **2e**


7.70
7.69
7.54
7.53
7.52
7.26
7.23
7.02
7.00
7.00
6.85
6.64
6.62
6.55
6.55
3.87
2.09
1H Spectrum of 2f
O
N
Cl
1.91
1.97
1.00
3.01
3.02
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

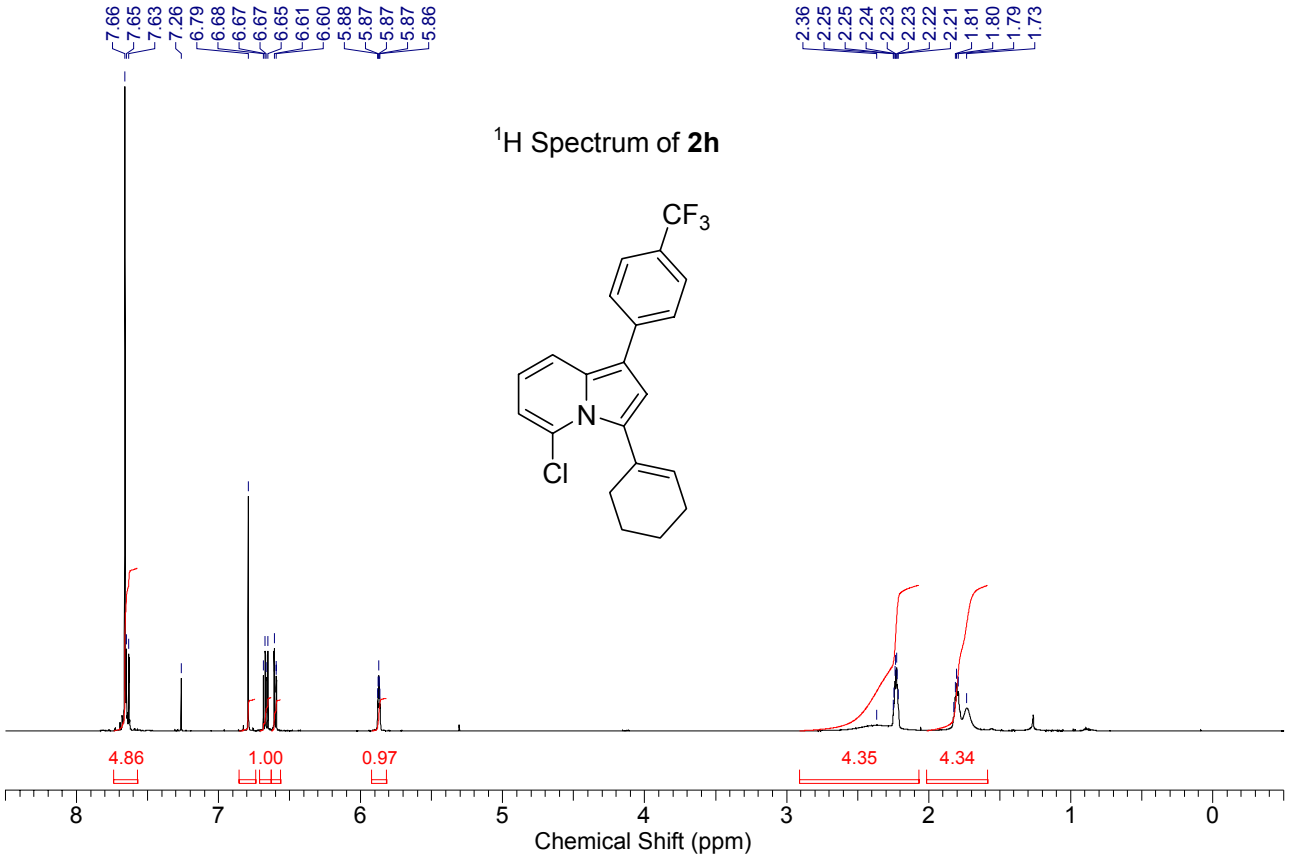

158.05
139.56
134.68
131.87
131.53
129.09
128.78
128.39
128.28
126.38
124.53
117.12
116.87
116.70
114.34
112.51
77.33
77.07
76.82
55.39
20.42
13C Spectrum of 2f
O
N
Cl
150
100
50
0
Chemical Shift (ppm)



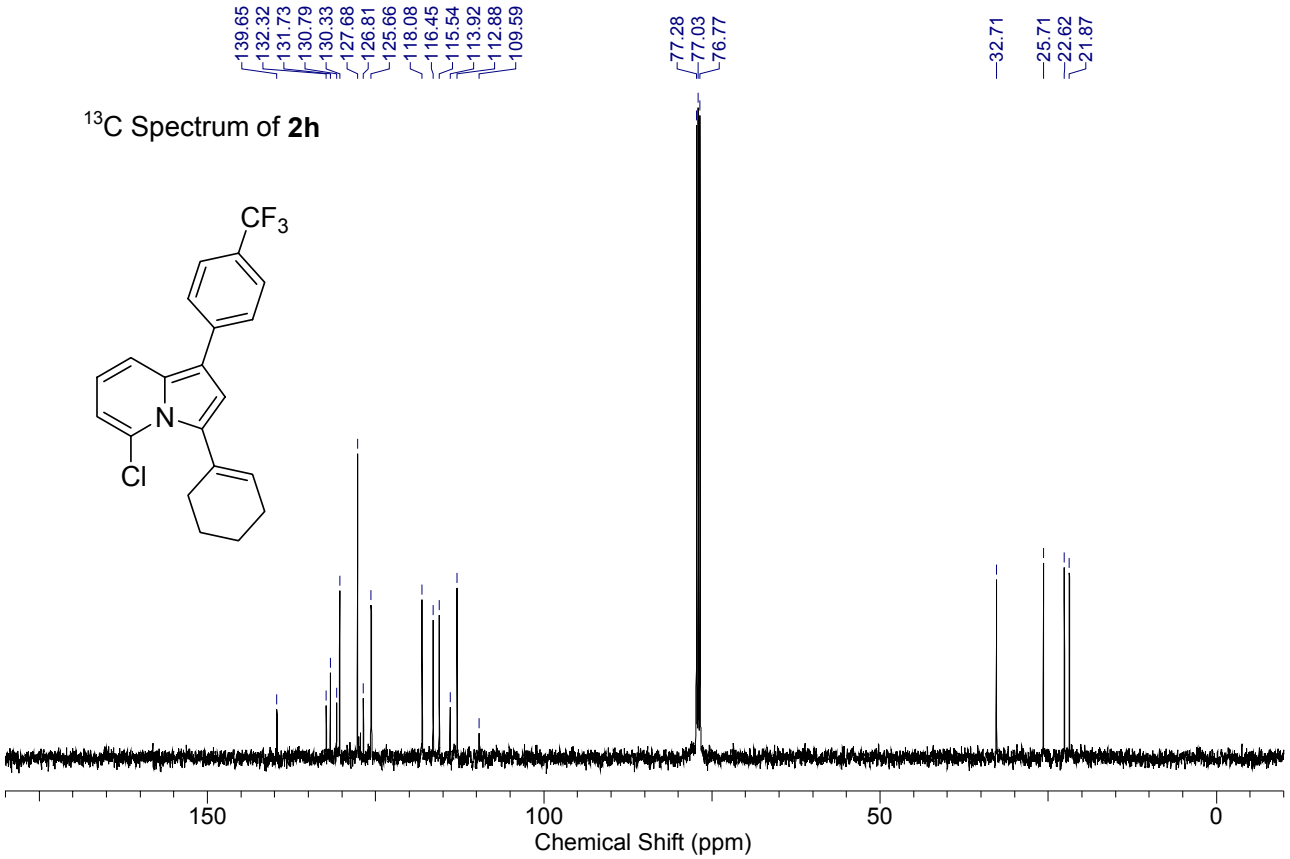
^{1}H Spectrum of **2g**



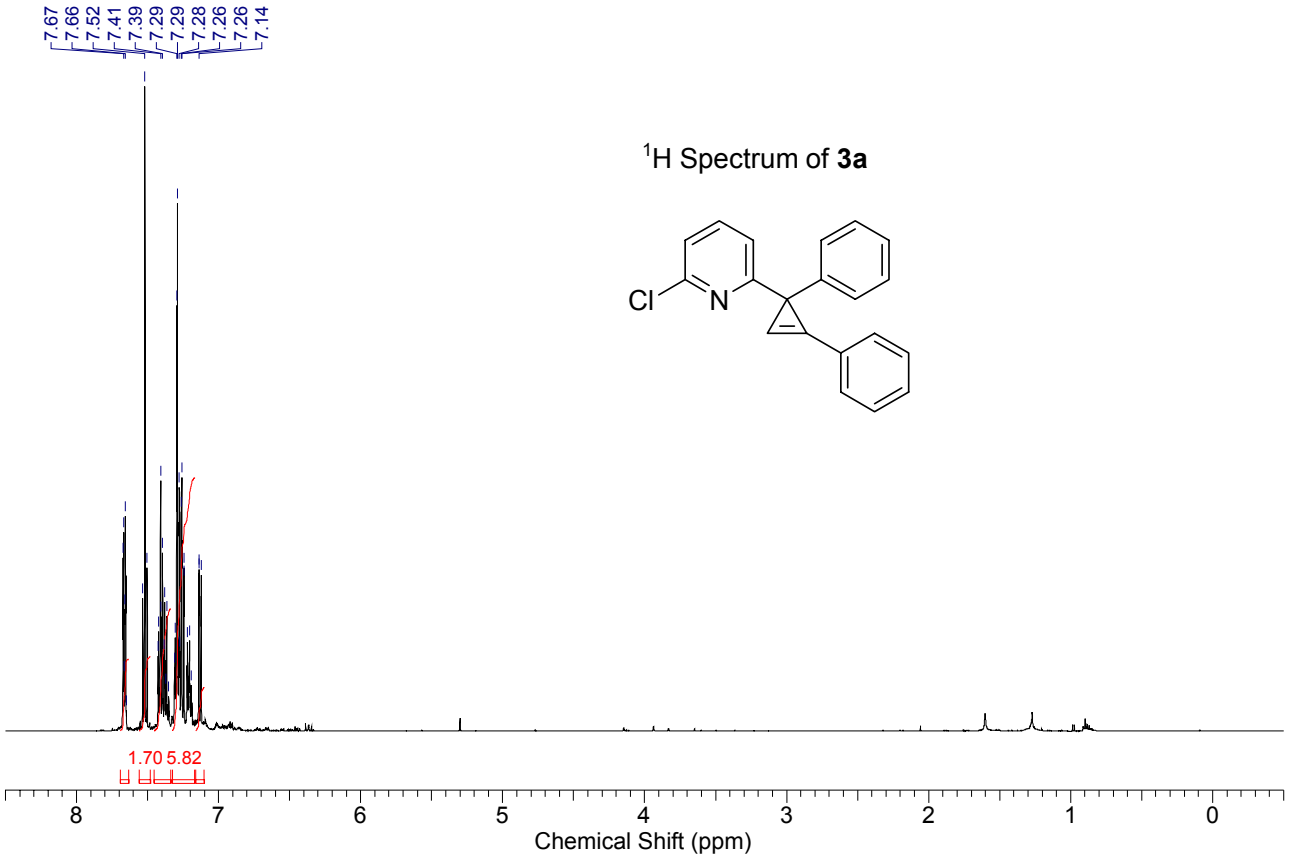
^{13}C Spectrum of **2g**



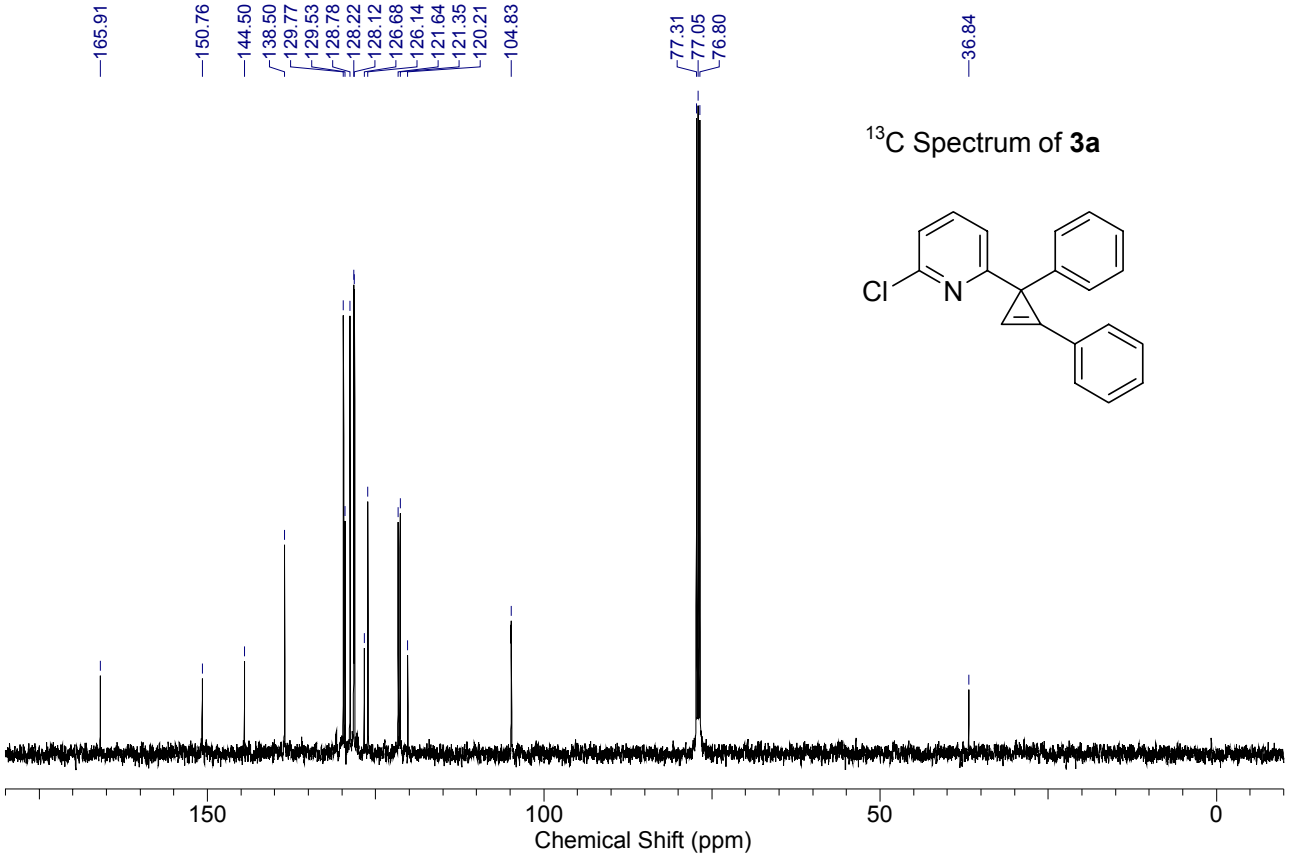
^{1}H Spectrum of **2h**



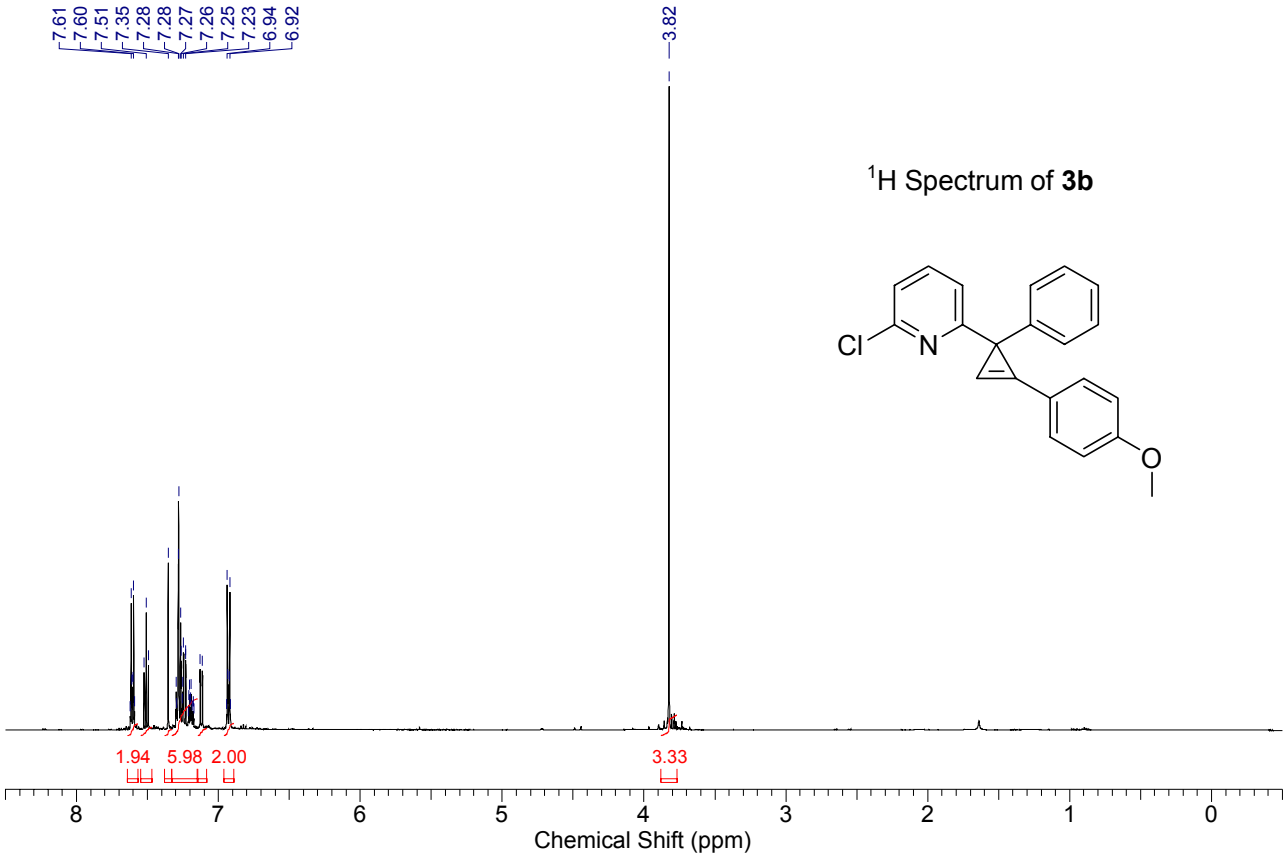
^{13}C Spectrum of **2h**



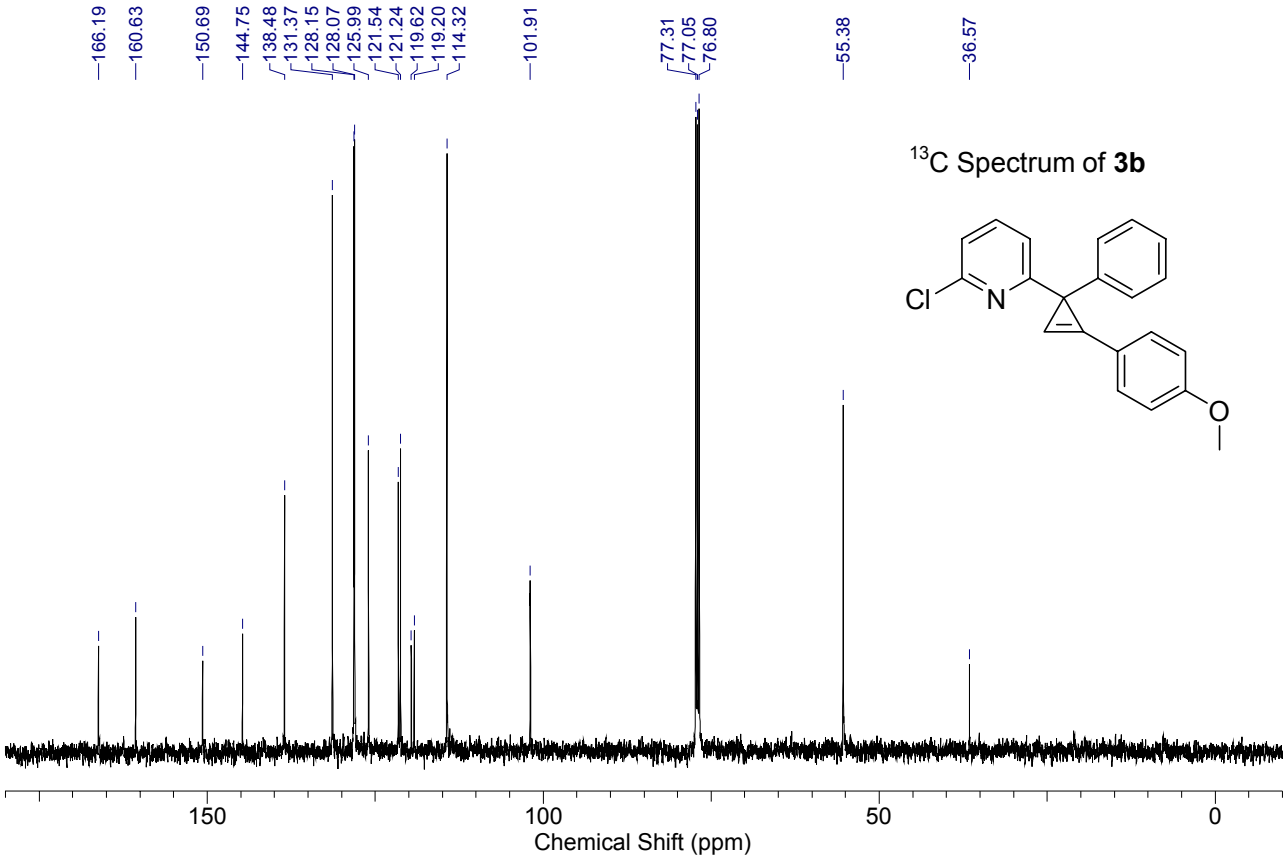
^{1}H Spectrum of **3a**



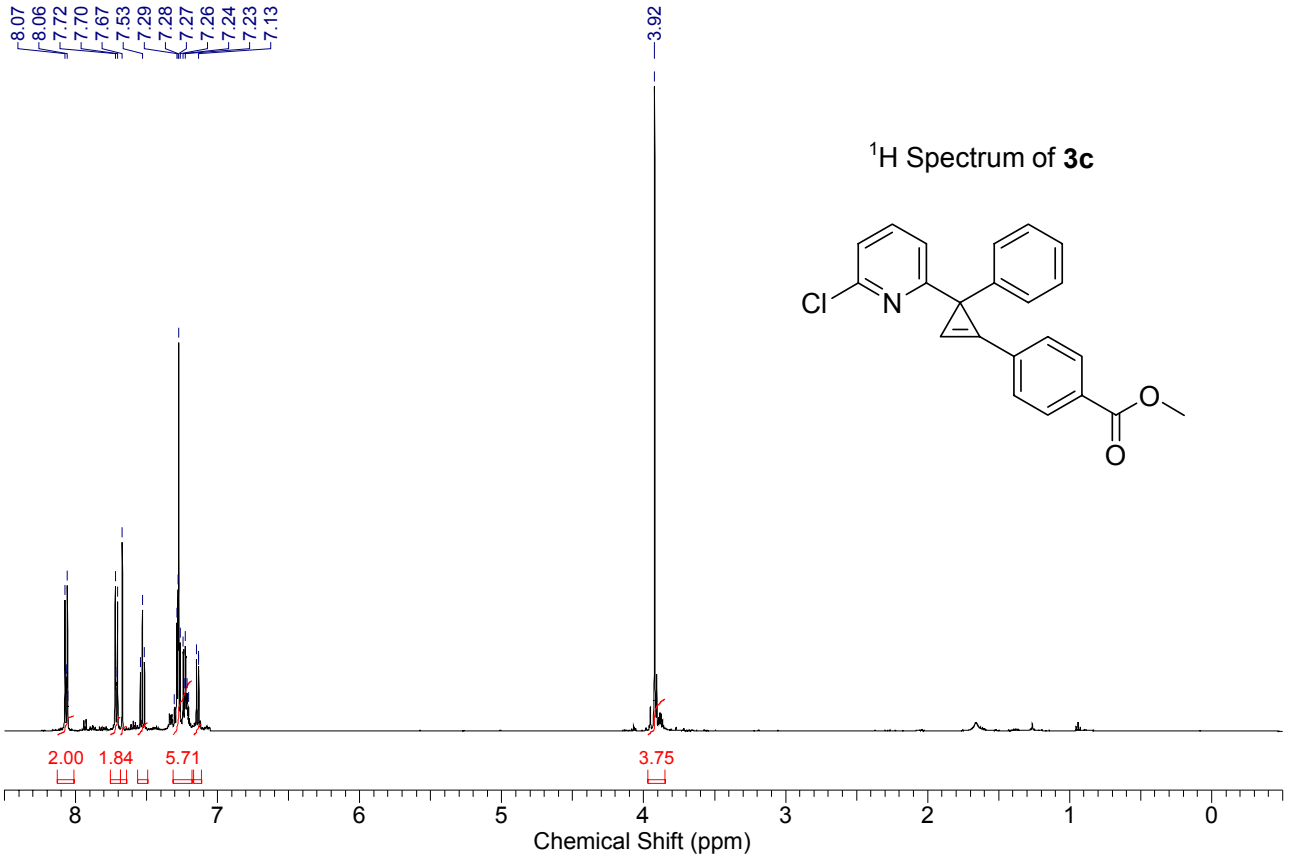
^{13}C Spectrum of **3a**



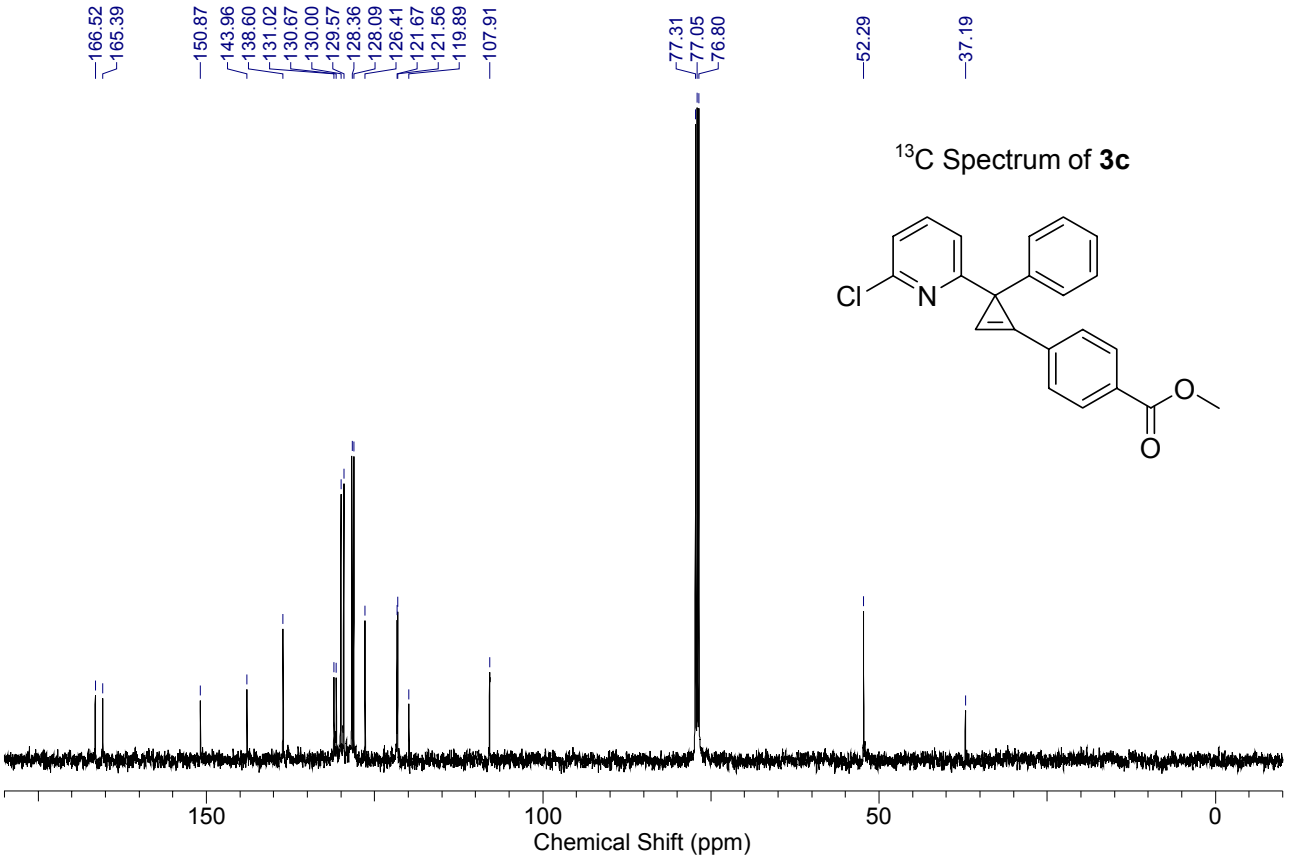
^{1}H Spectrum of **3b**



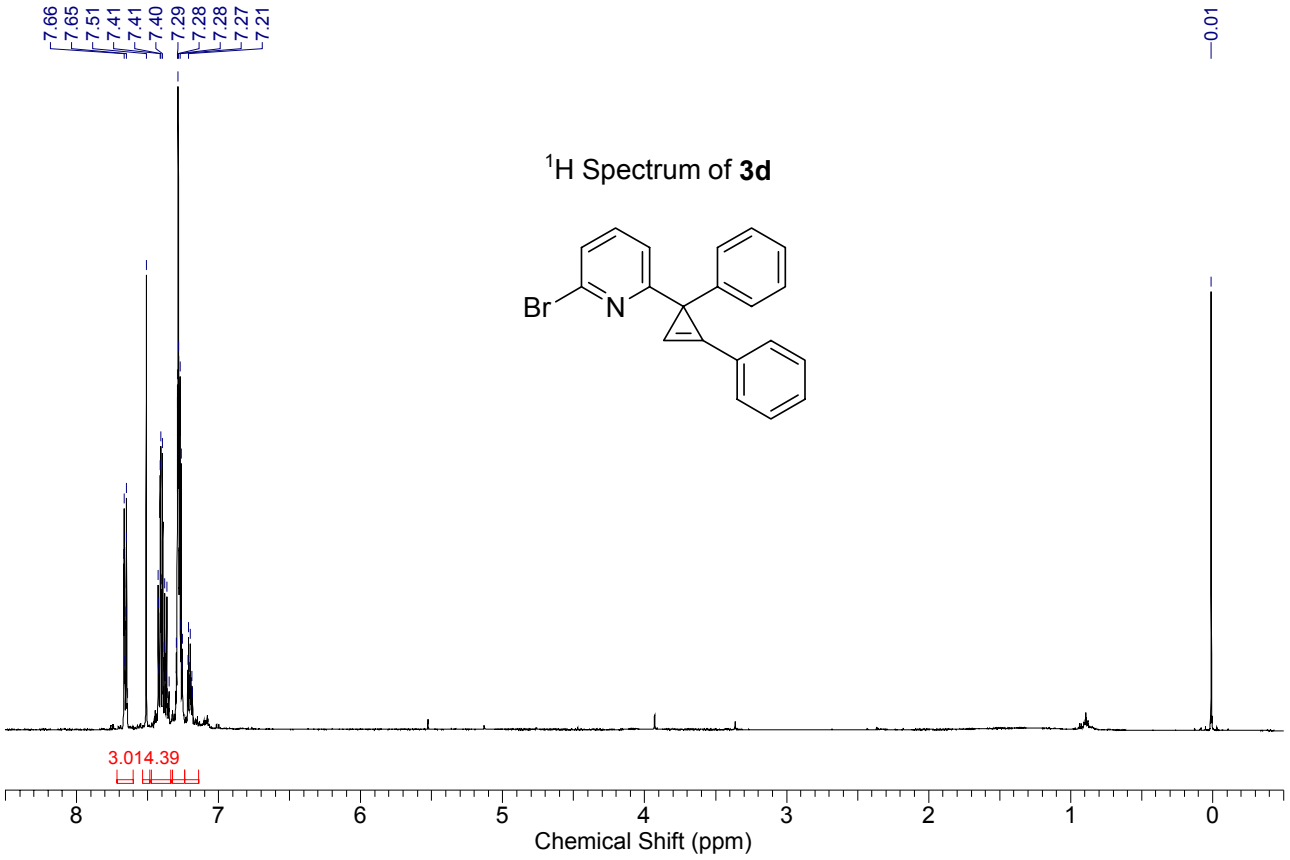
^{13}C Spectrum of **3b**



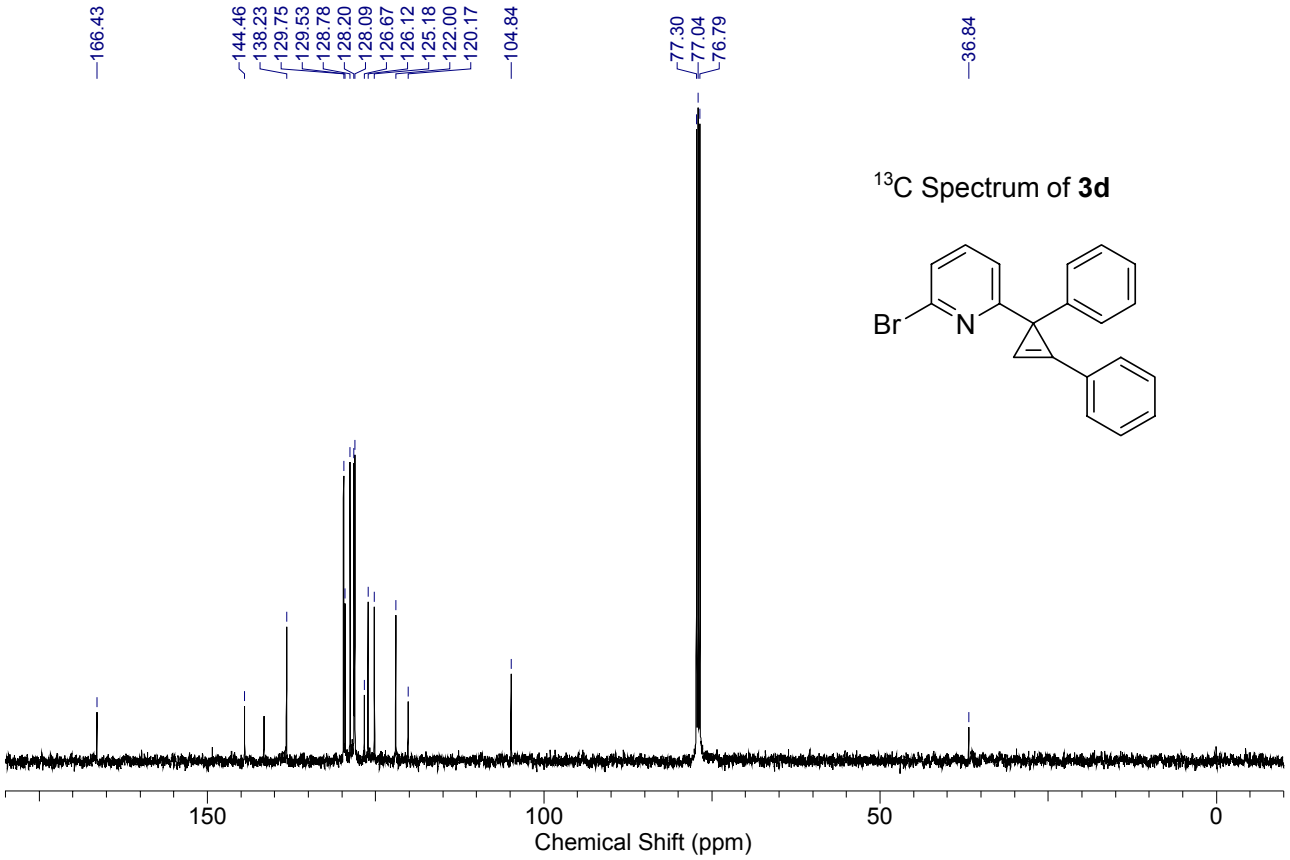
^{1}H Spectrum of **3c**



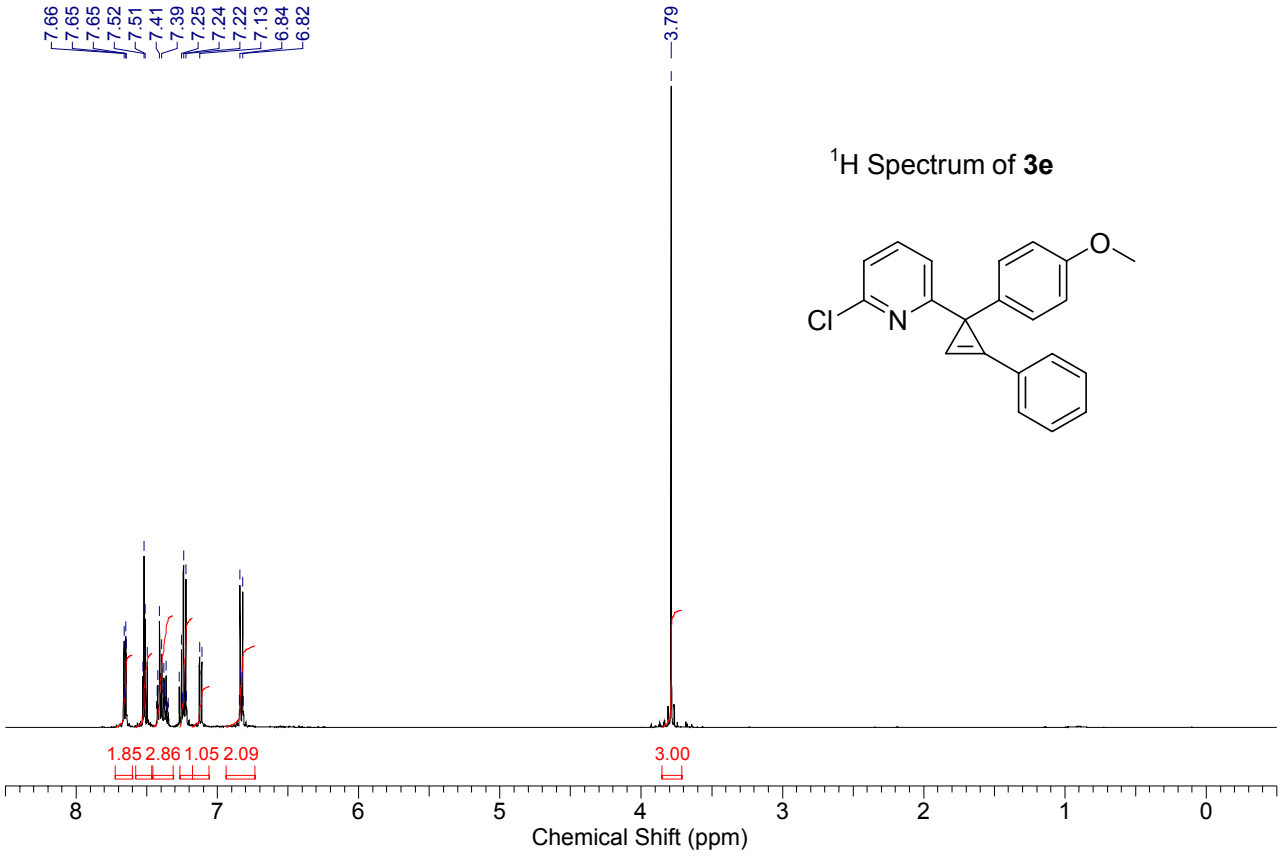
^{13}C Spectrum of **3c**



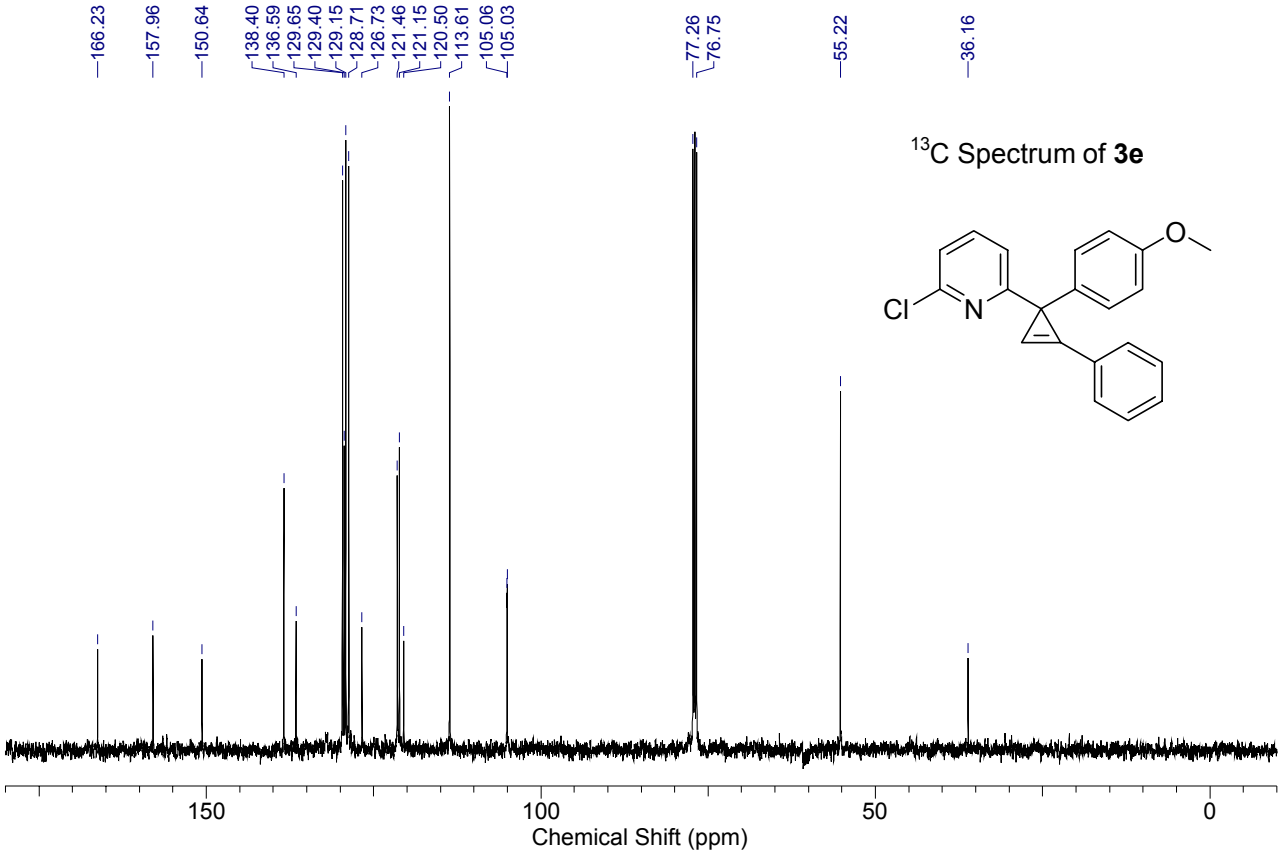
^{1}H Spectrum of **3d**



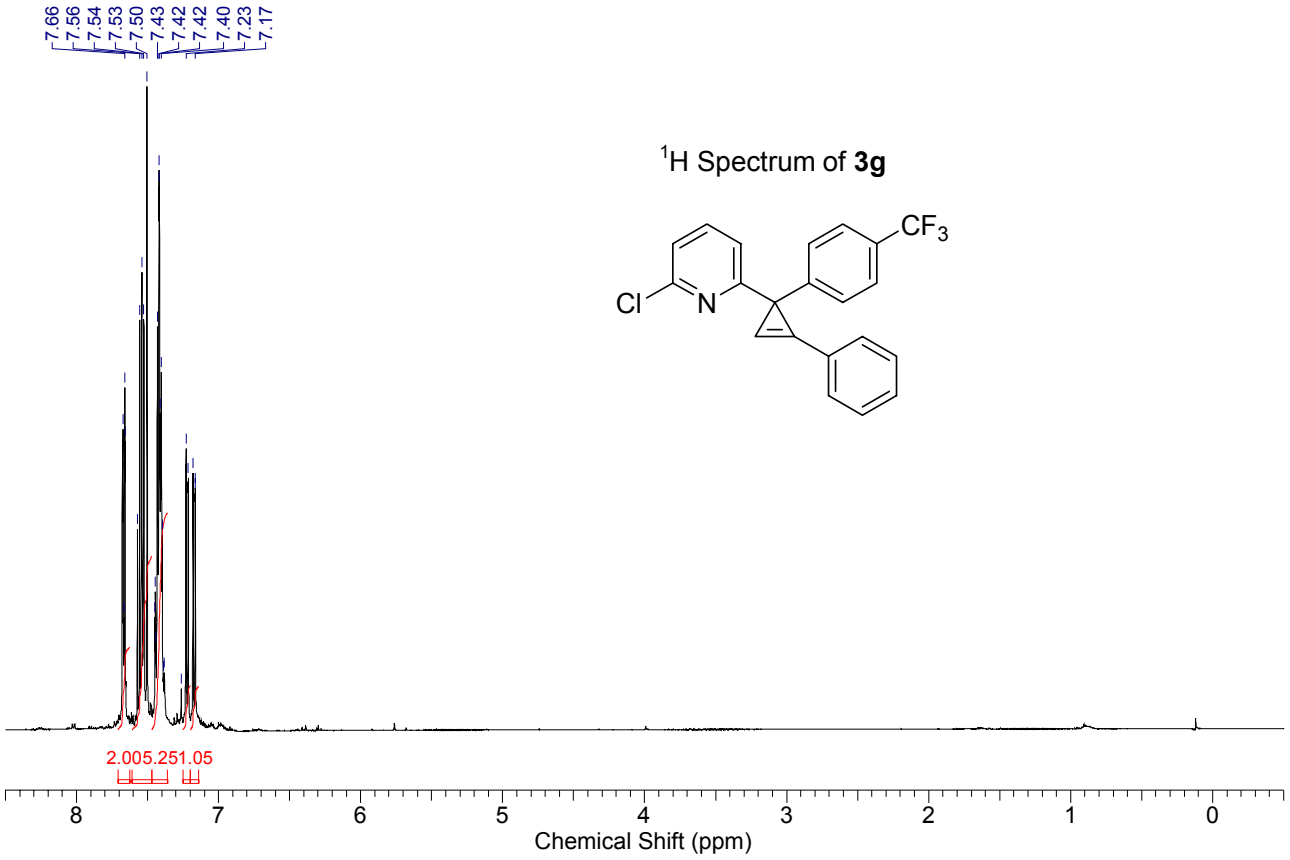
^{13}C Spectrum of **3d**



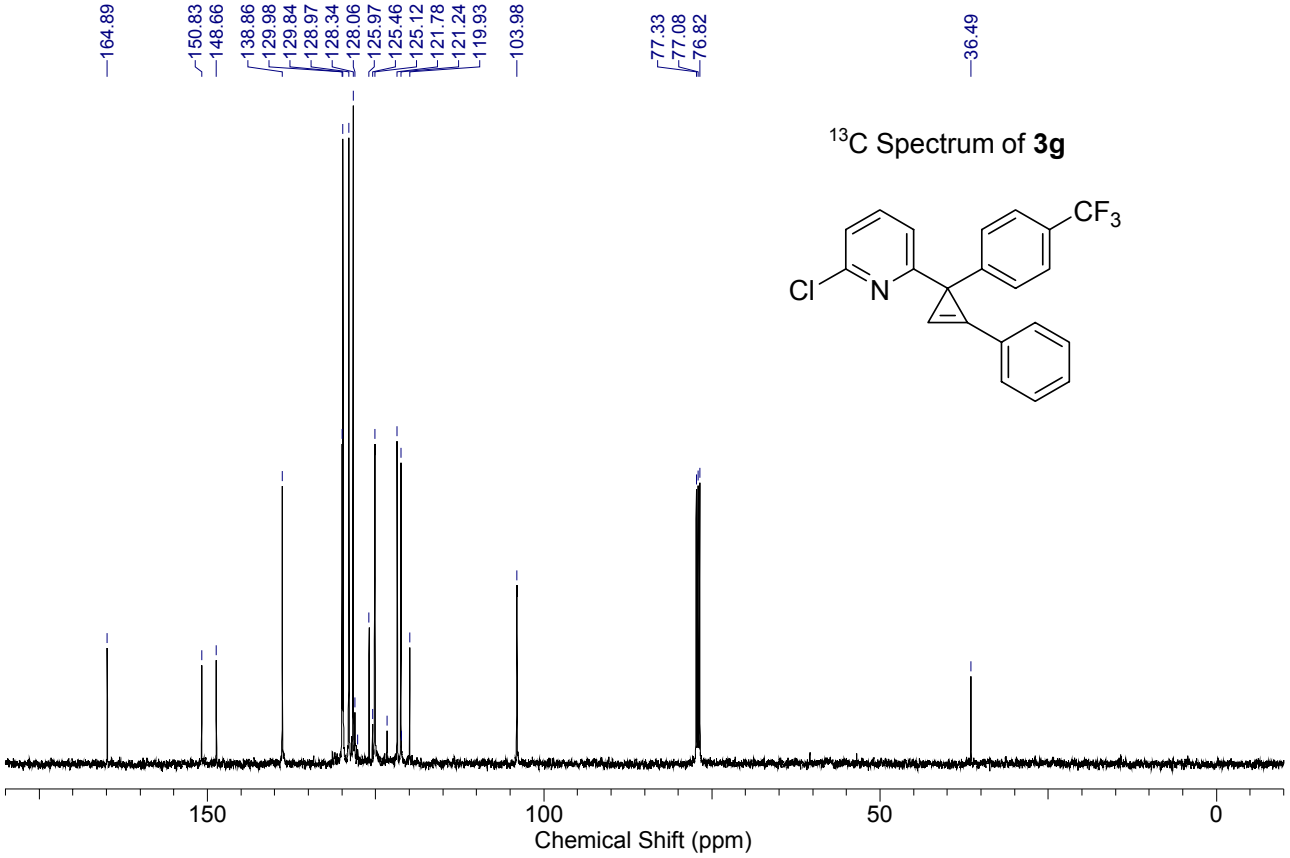
^{1}H Spectrum of **3e**



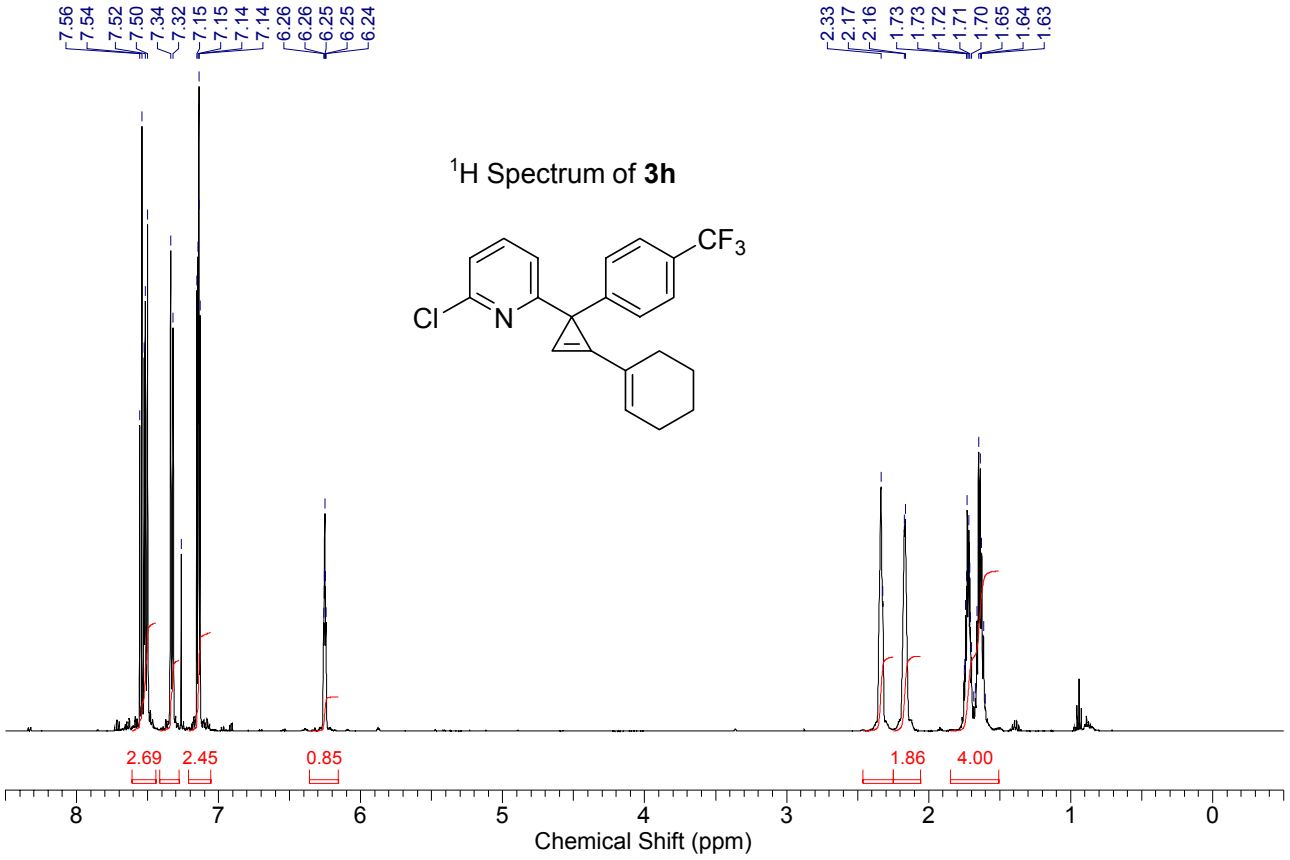
^{13}C Spectrum of **3e**



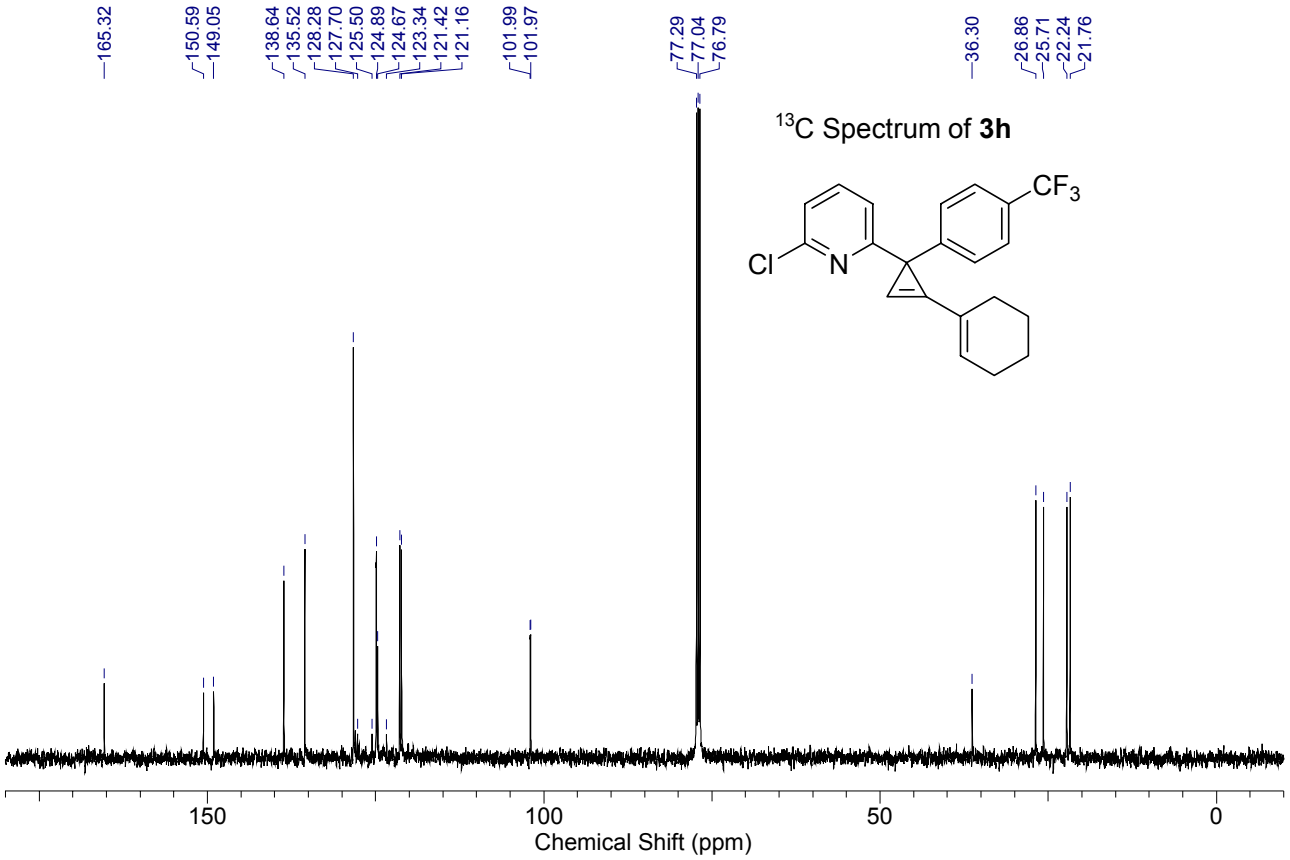
^{1}H Spectrum of **3g**



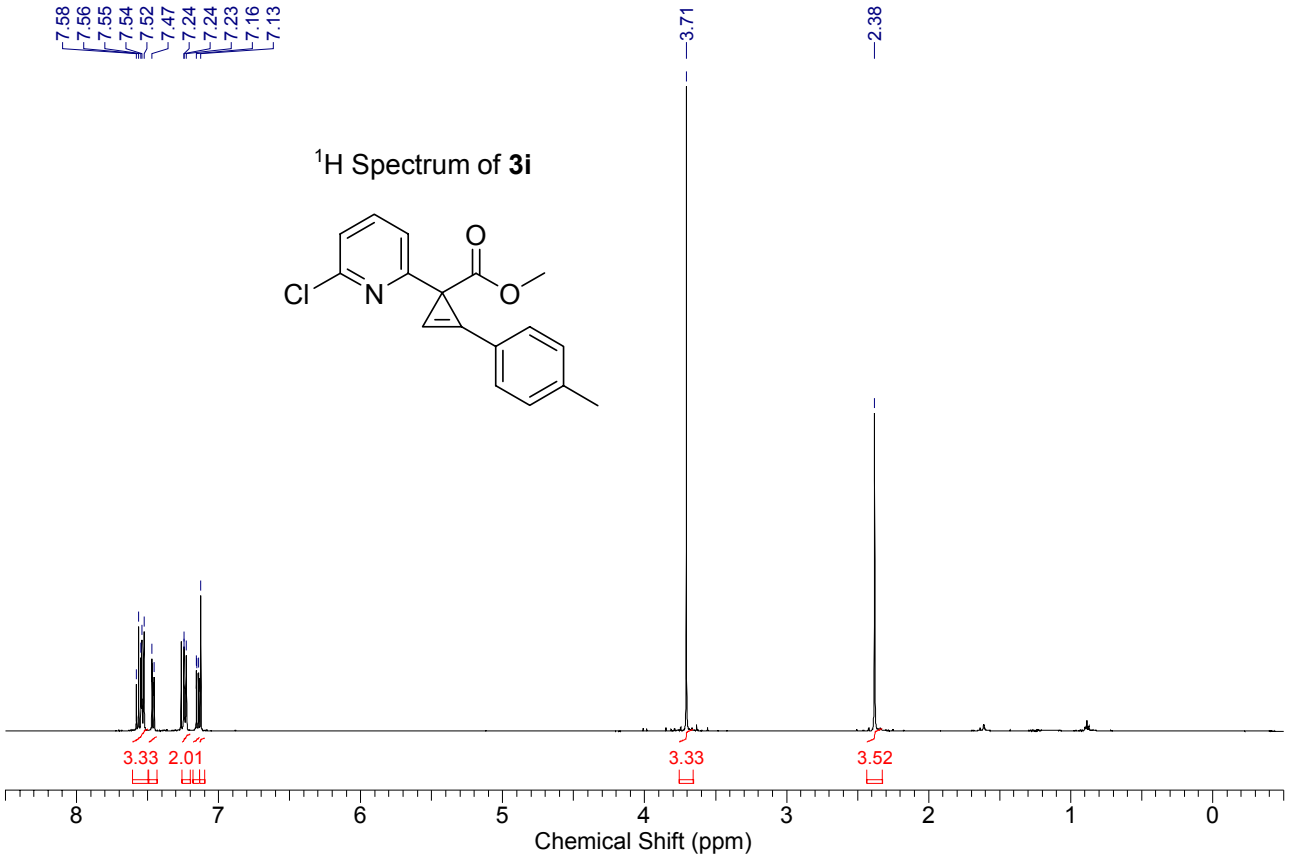
^{13}C Spectrum of **3g**



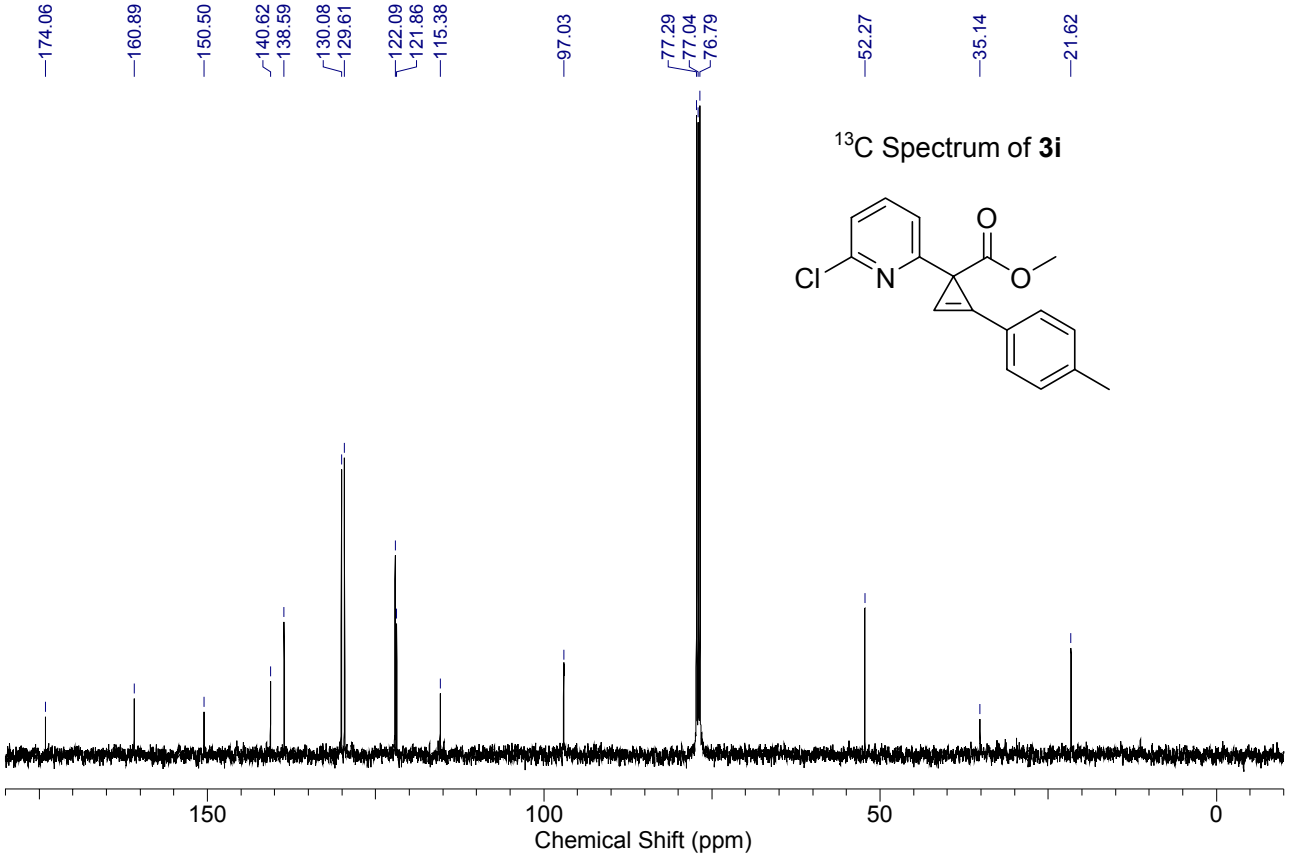
^{1}H Spectrum of **3h**



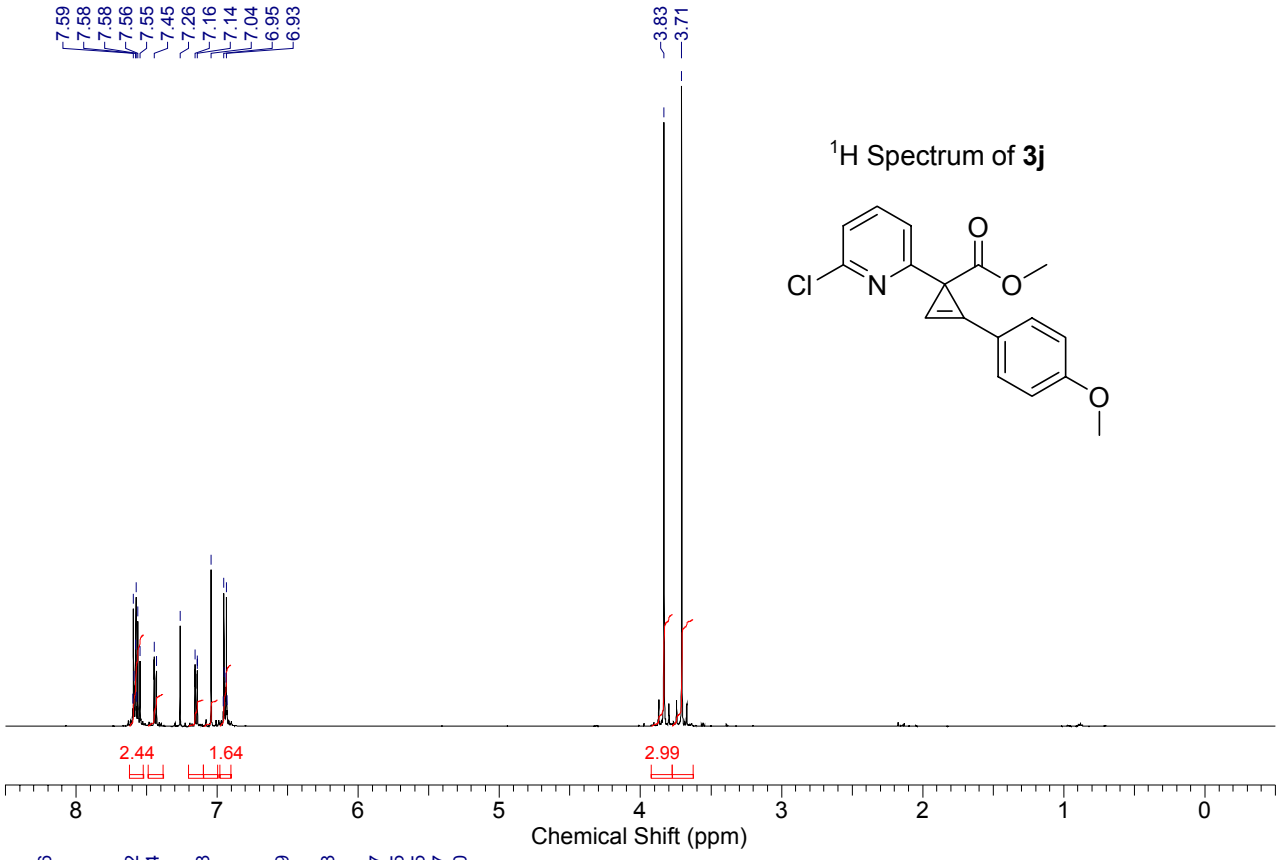
^{13}C Spectrum of **3h**



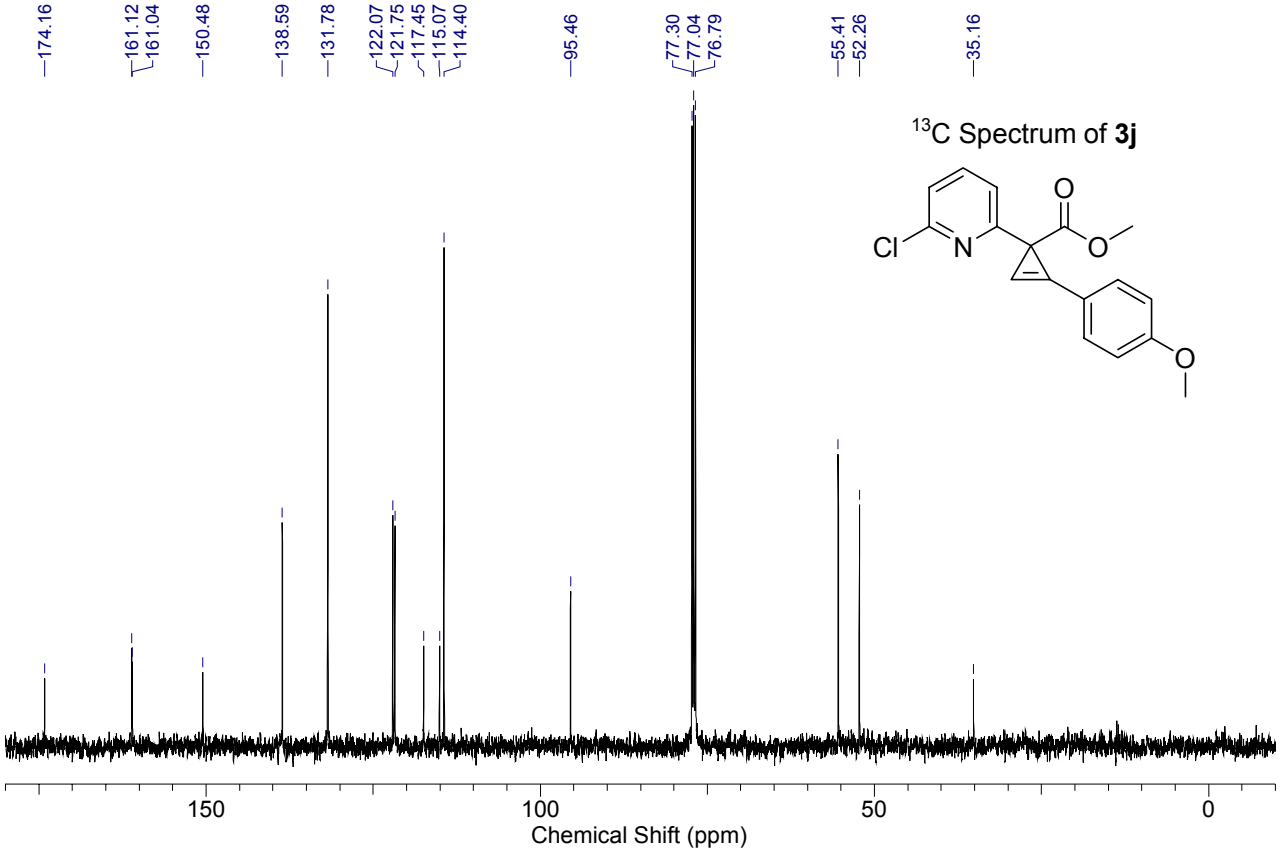
^{1}H Spectrum of **3i**



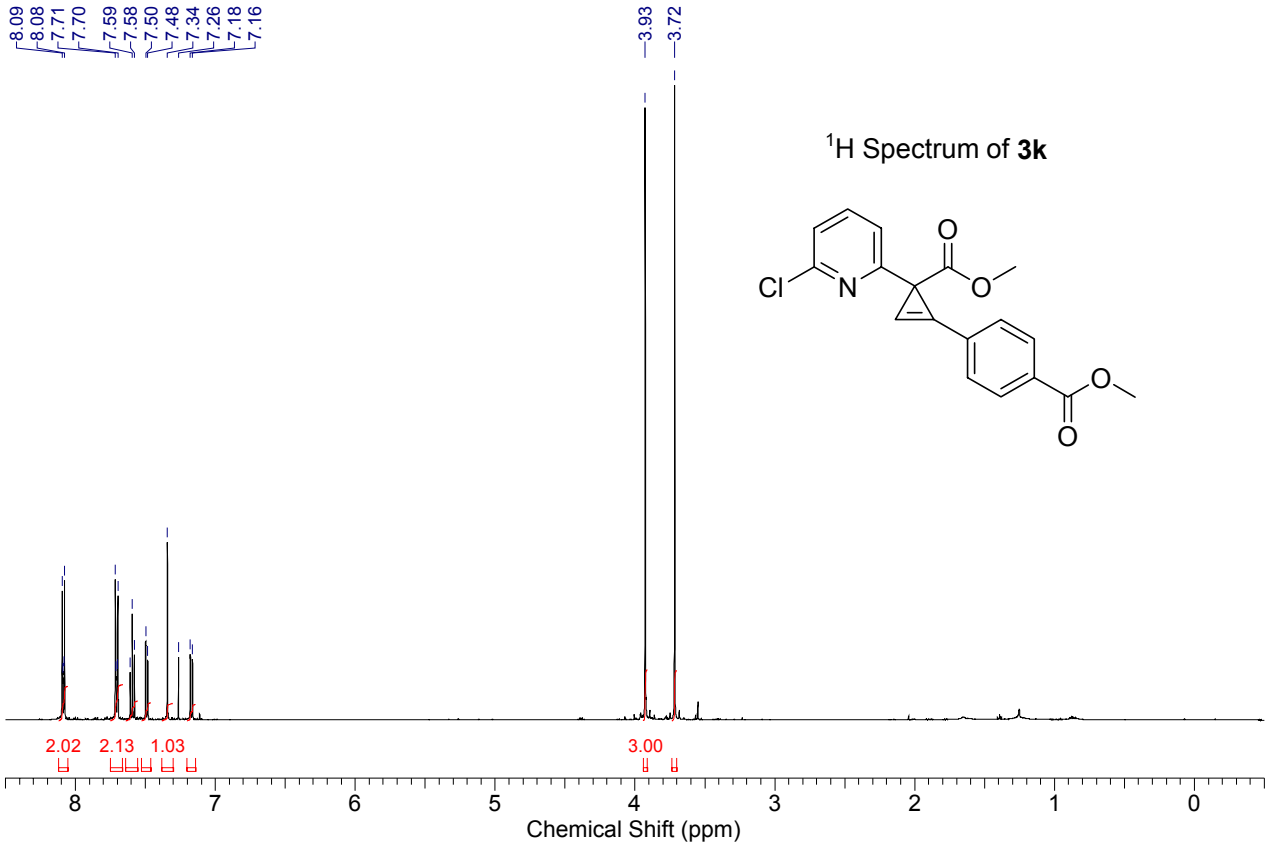
^{13}C Spectrum of **3i**



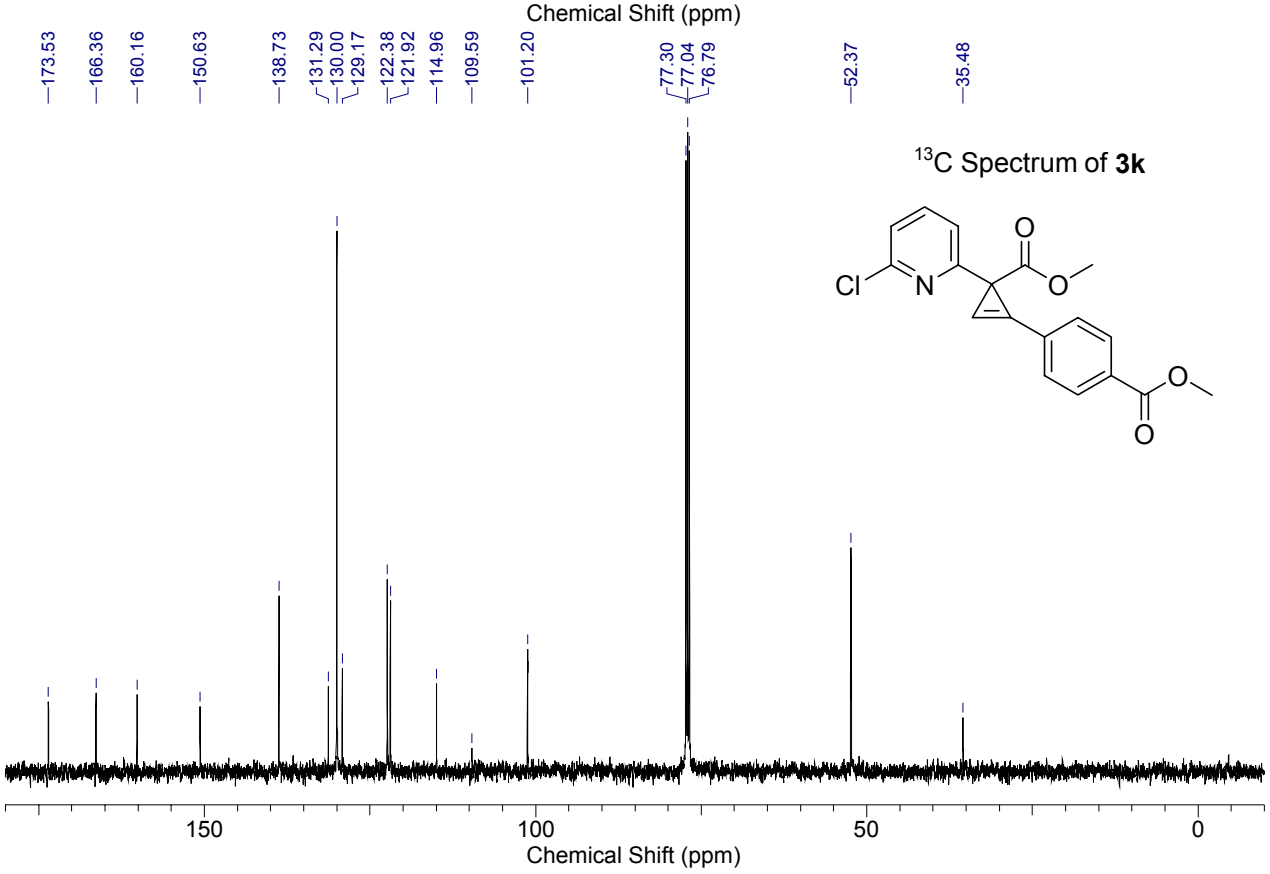
^{1}H Spectrum of **3j**



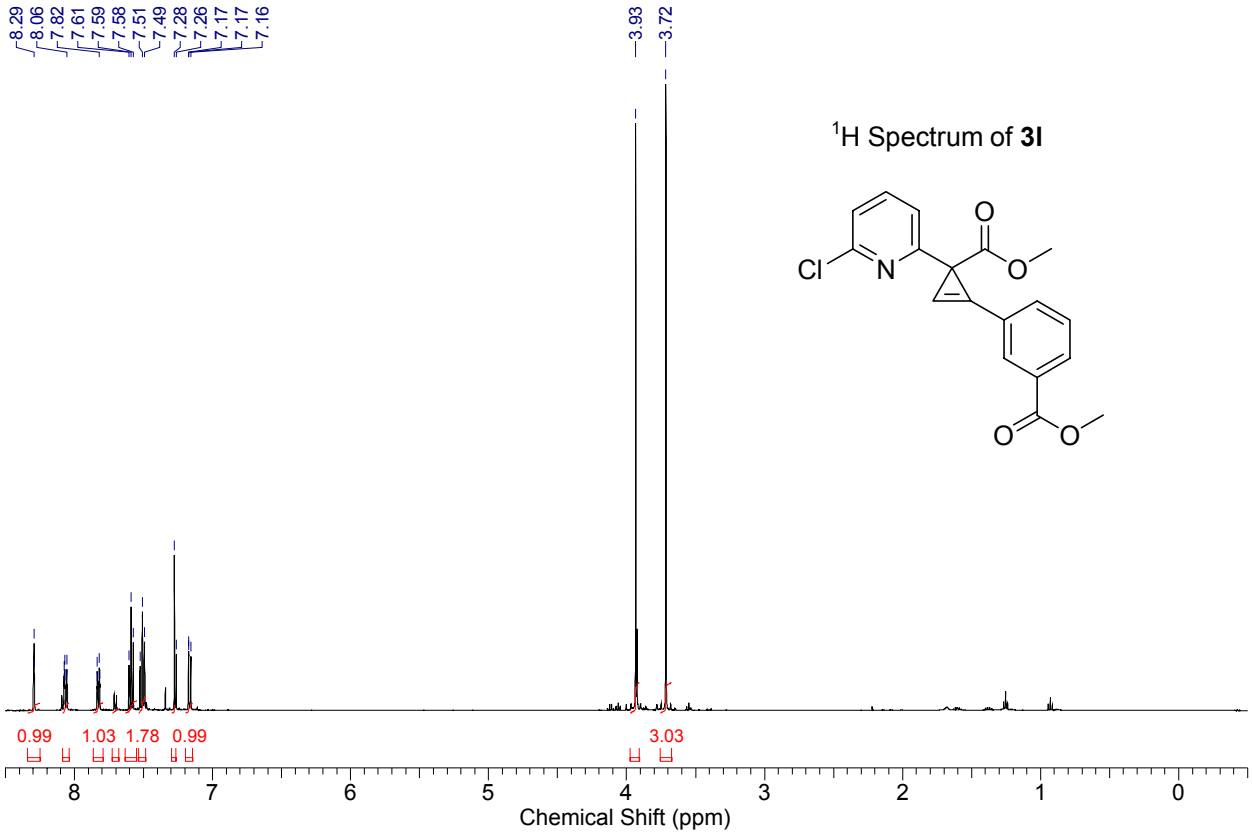
^{13}C Spectrum of **3j**



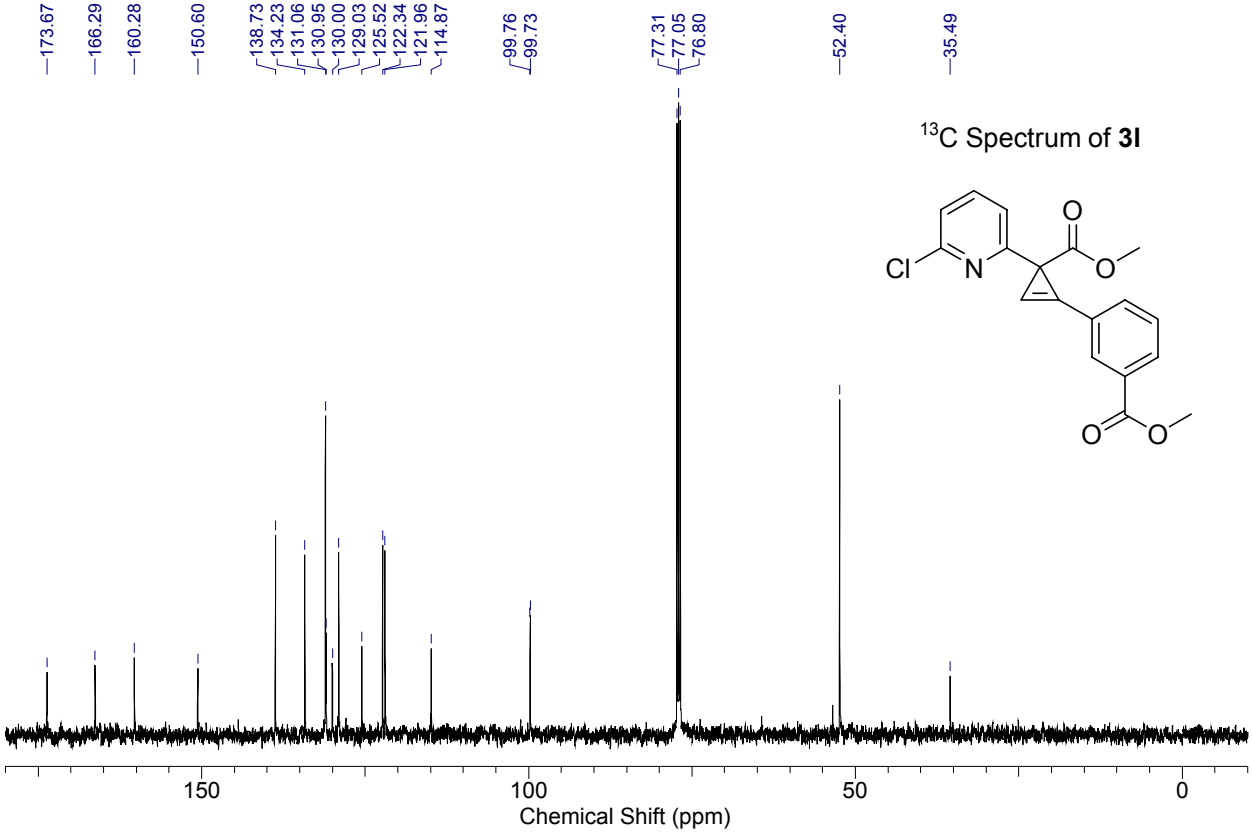
^{1}H Spectrum of **3k**



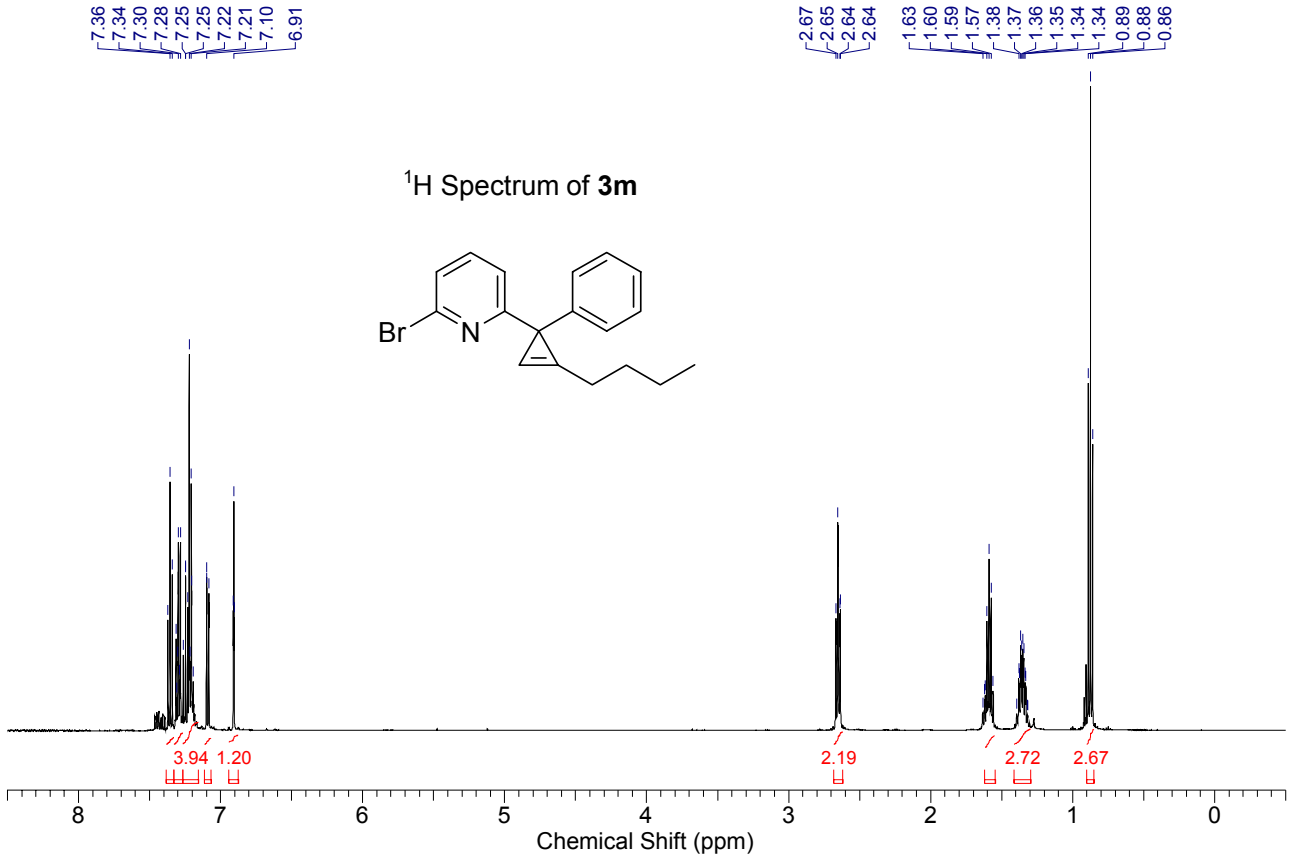
^{13}C Spectrum of **3k**



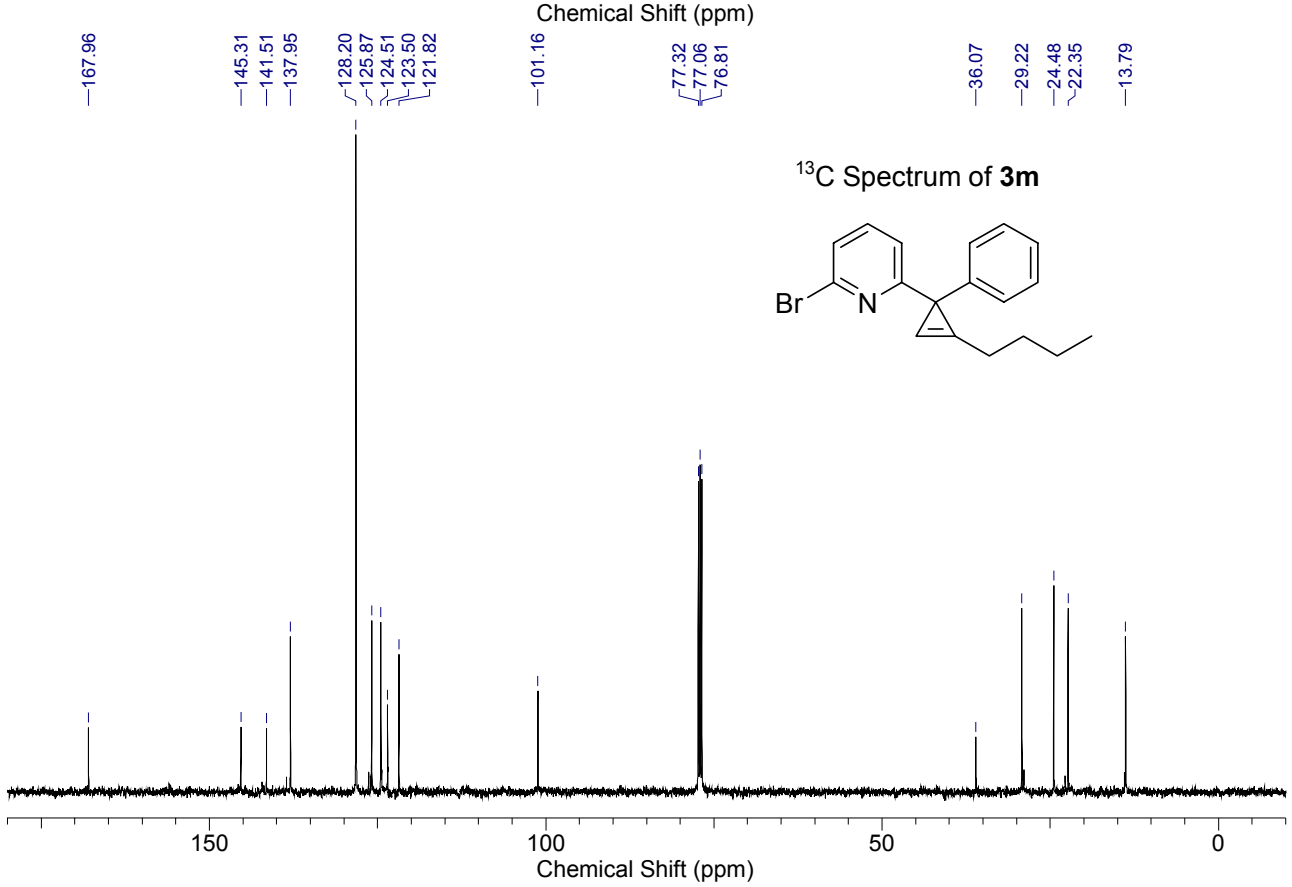
^{1}H Spectrum of **3l**



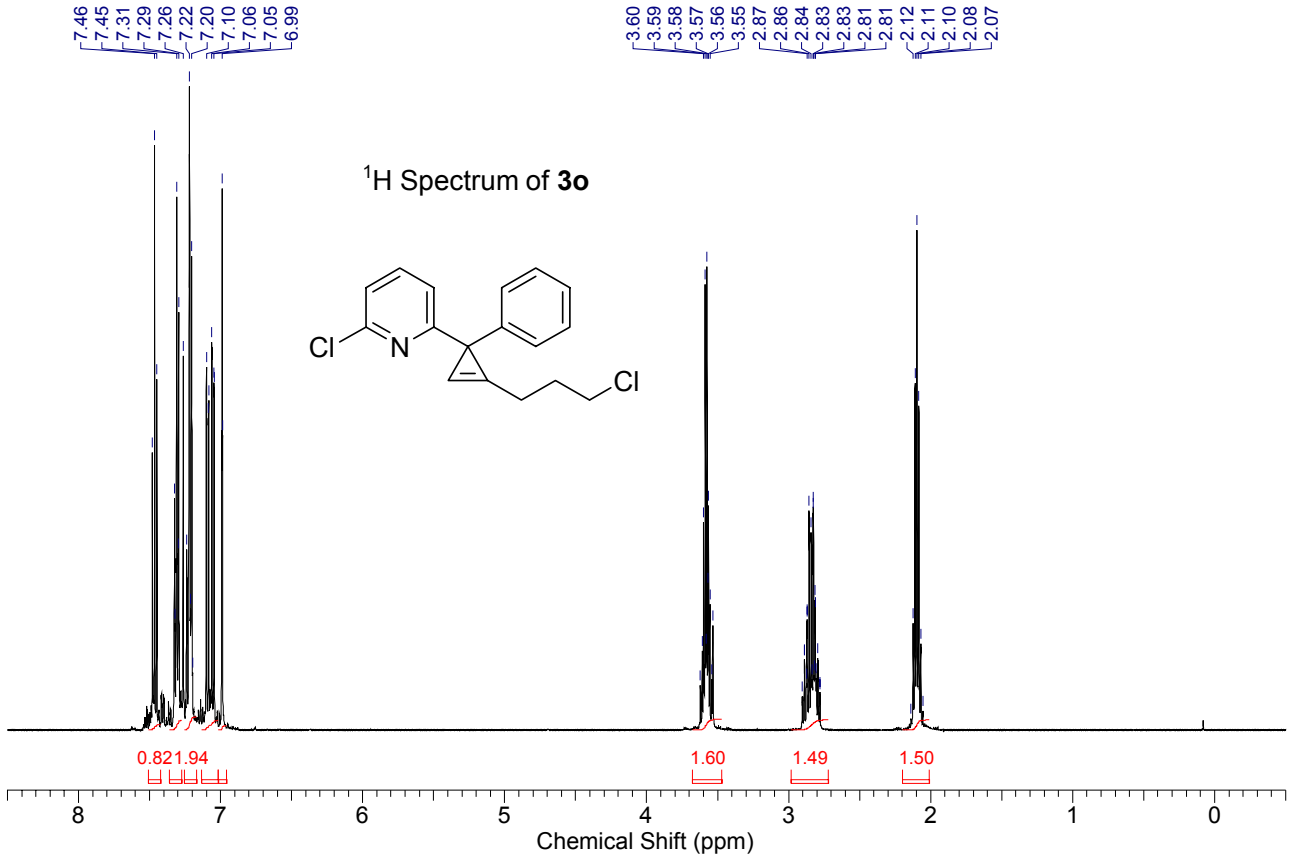
^{13}C Spectrum of **3l**



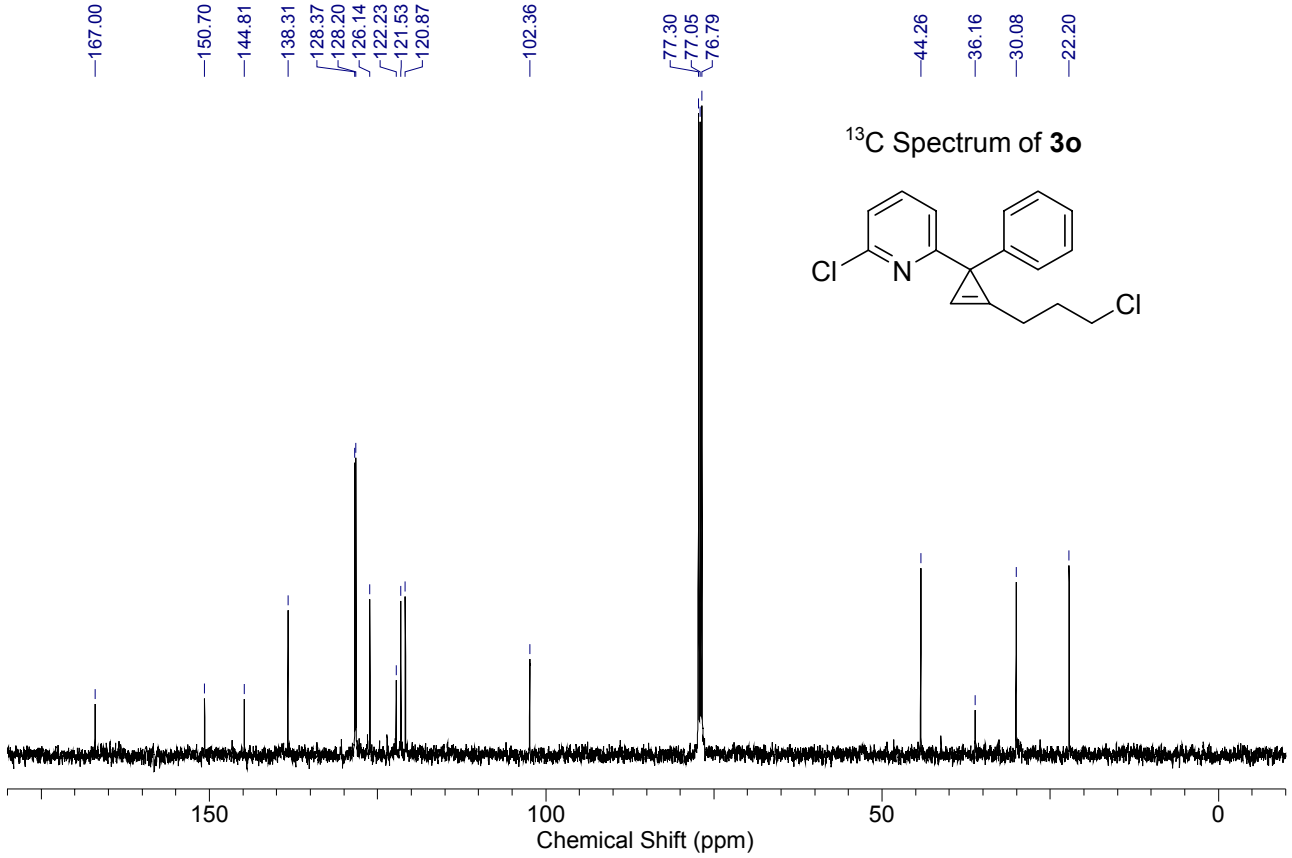
^{1}H Spectrum of **3m**



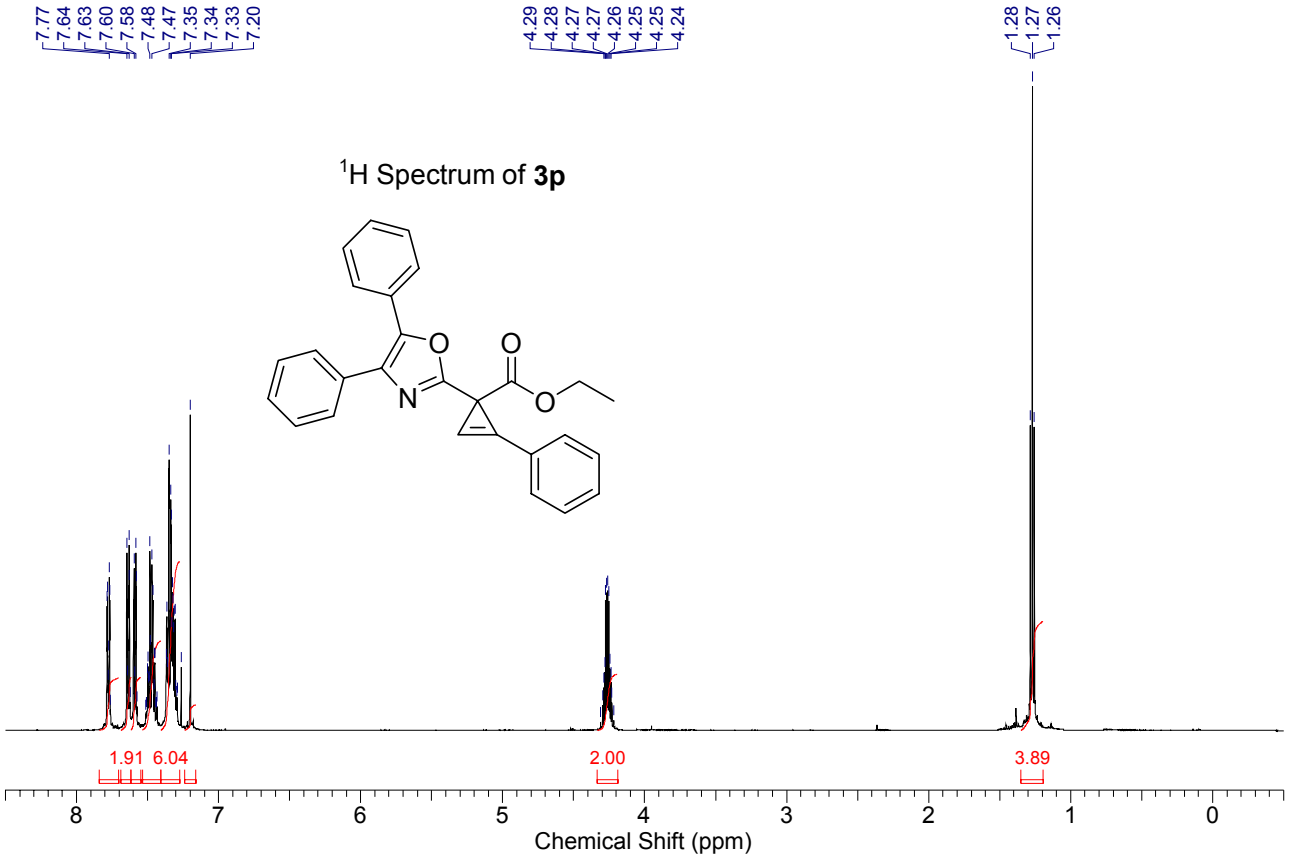
^{13}C Spectrum of **3m**

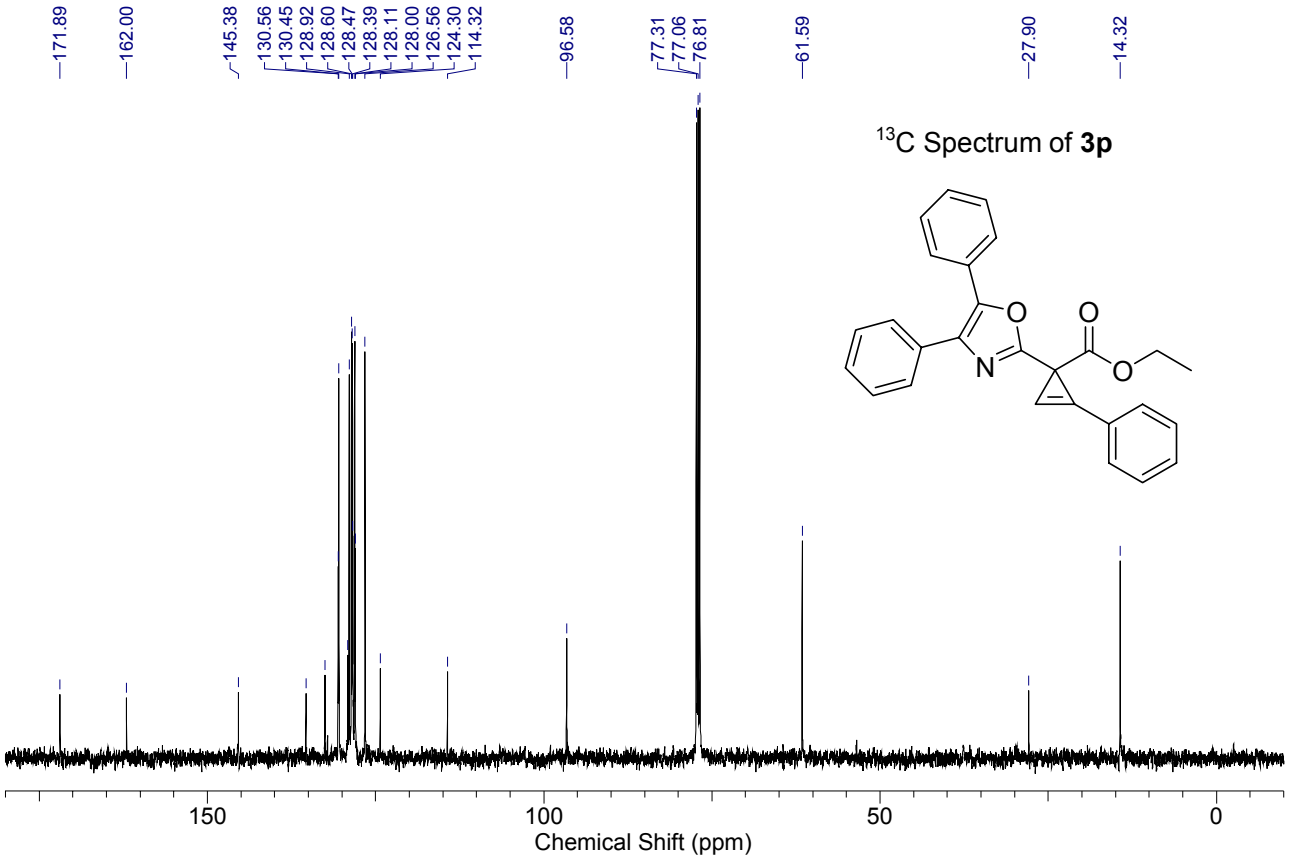


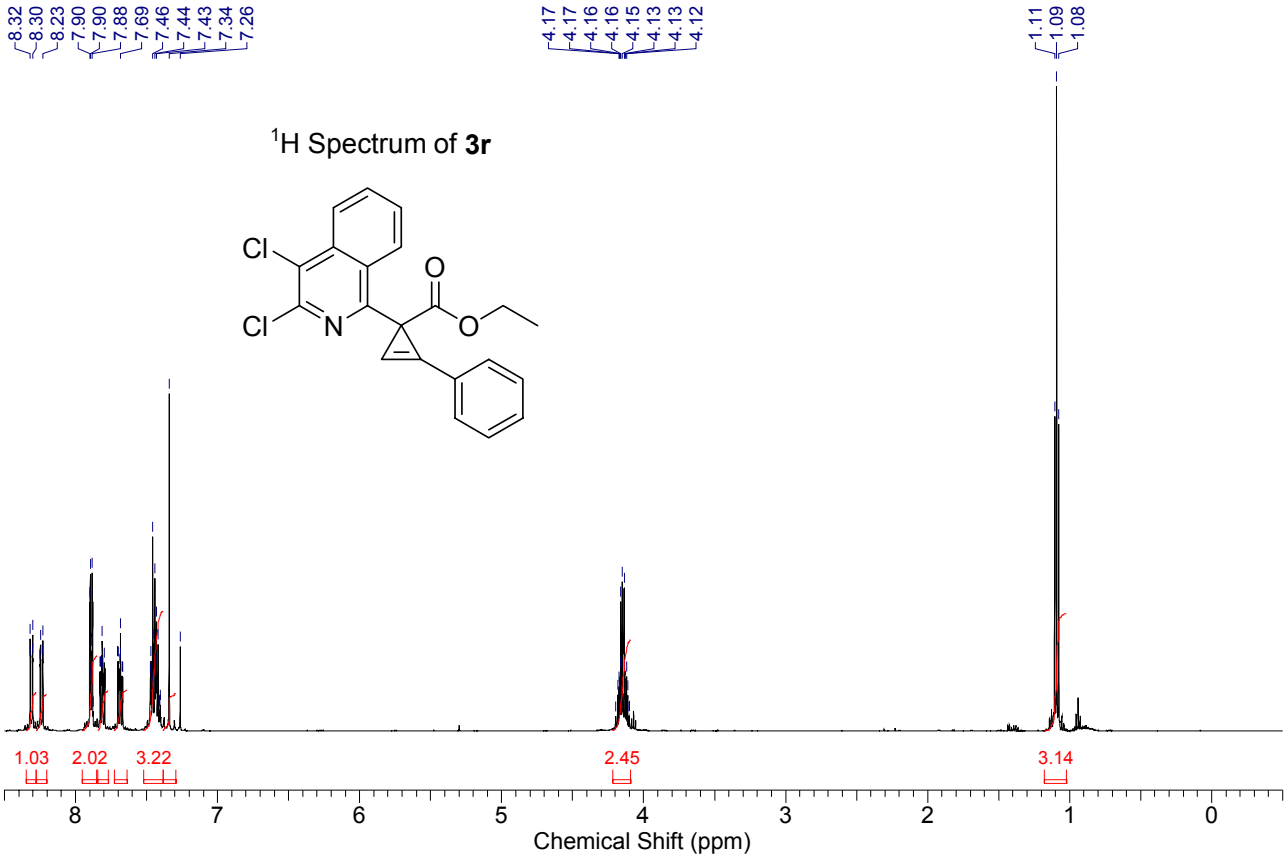
^{1}H Spectrum of **3o**

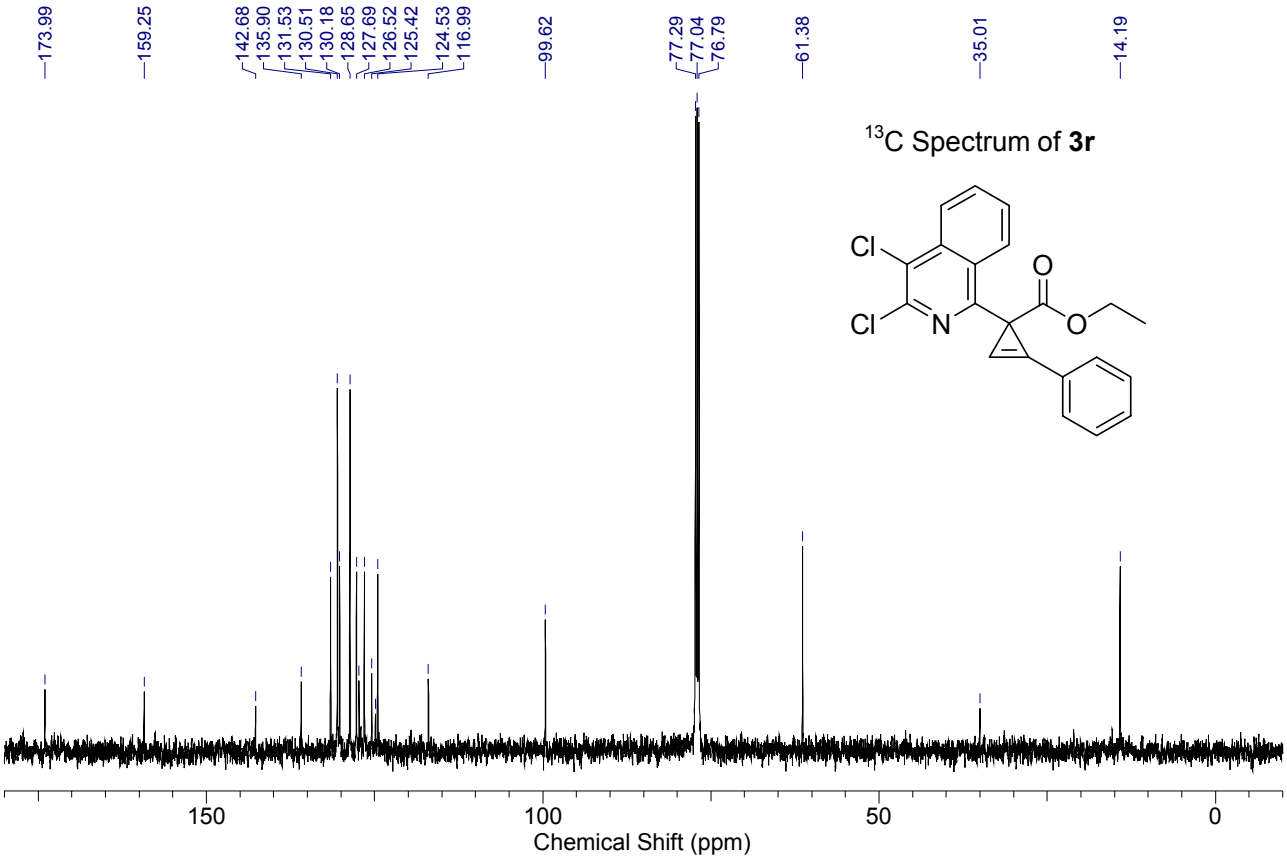


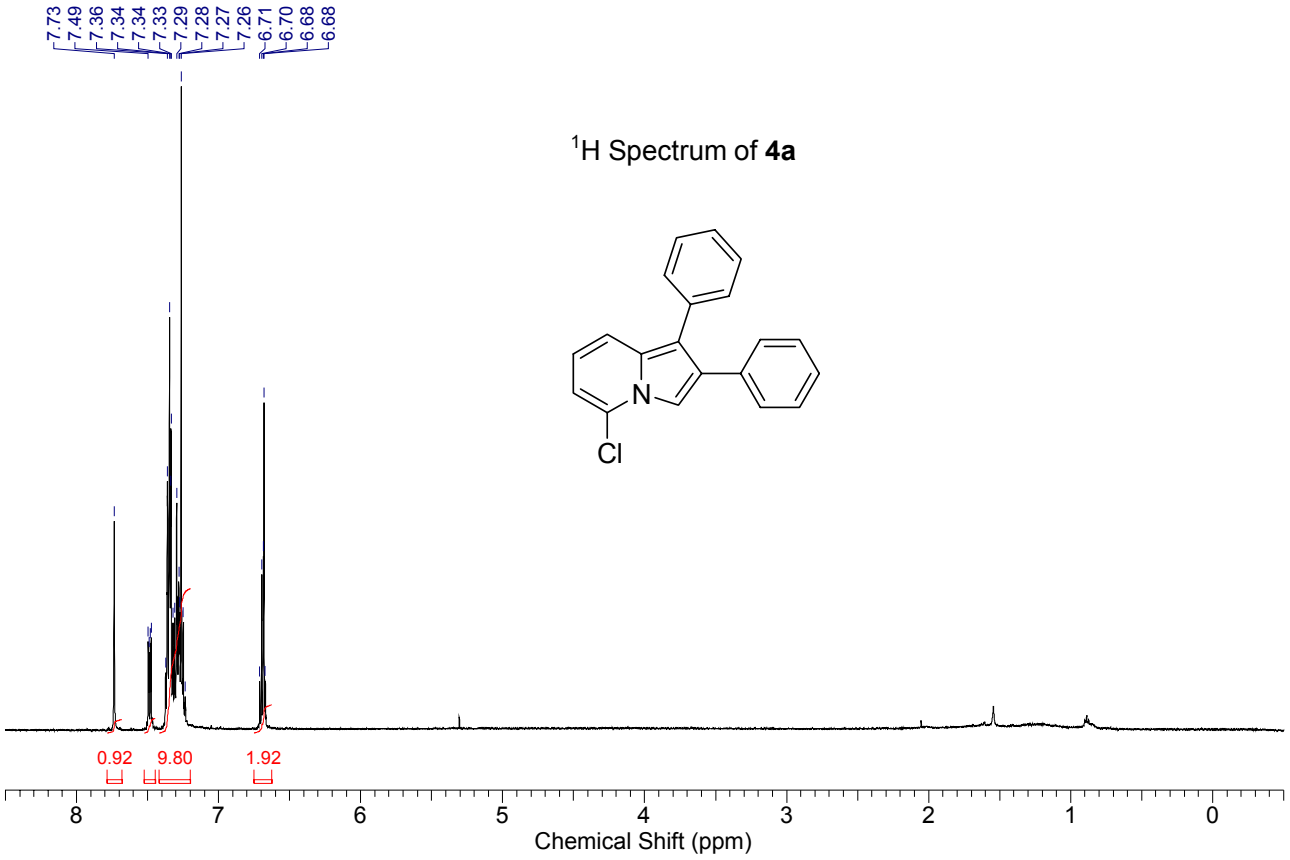
^{13}C Spectrum of **3o**


7.77
7.64
7.63
7.60
7.58
7.48
7.47
7.35
7.34
7.33
7.20
4.29
4.28
4.27
4.27
4.26
4.25
4.25
4.24
1.28
1.27
1.26
1H Spectrum of 3p
O
O
N
O
1.91
6.04
2.00
3.89
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

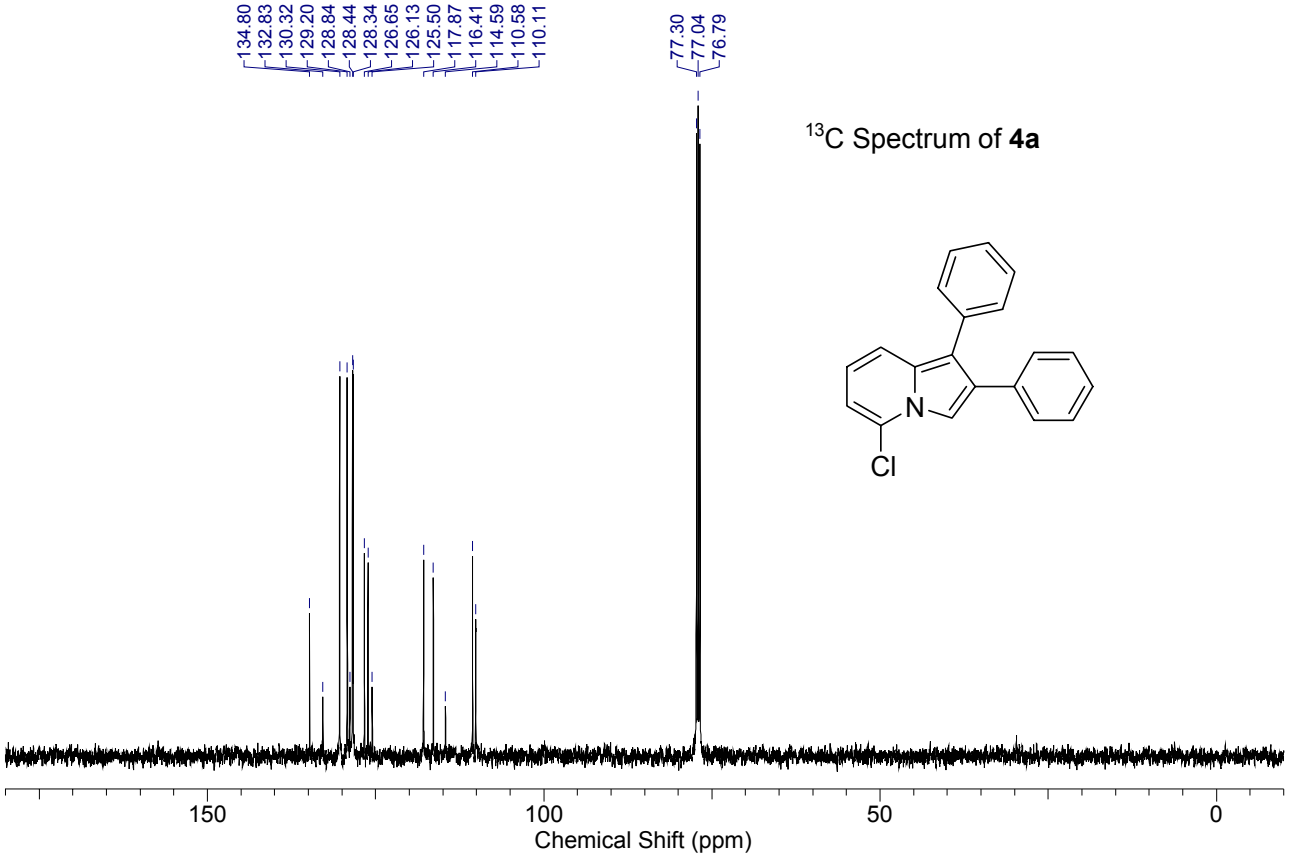

171.89
162.00
145.38
130.56
130.45
128.92
128.60
128.47
128.39
128.11
128.00
126.56
124.30
114.32
96.58
77.31
77.06
76.81
61.59
27.90
14.32
13C Spectrum of 3p
O
O
N
O
150
100
50
0
Chemical Shift (ppm)


8.32
8.30
8.23
7.90
7.90
7.88
7.69
7.46
7.44
7.43
7.34
7.26
4.17
4.17
4.16
4.16
4.15
4.13
4.13
4.12
1.11
1.09
1.08
1H Spectrum of 3r
Cl
Cl
N
O
O
1.03
2.02
3.22
2.45
3.14
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

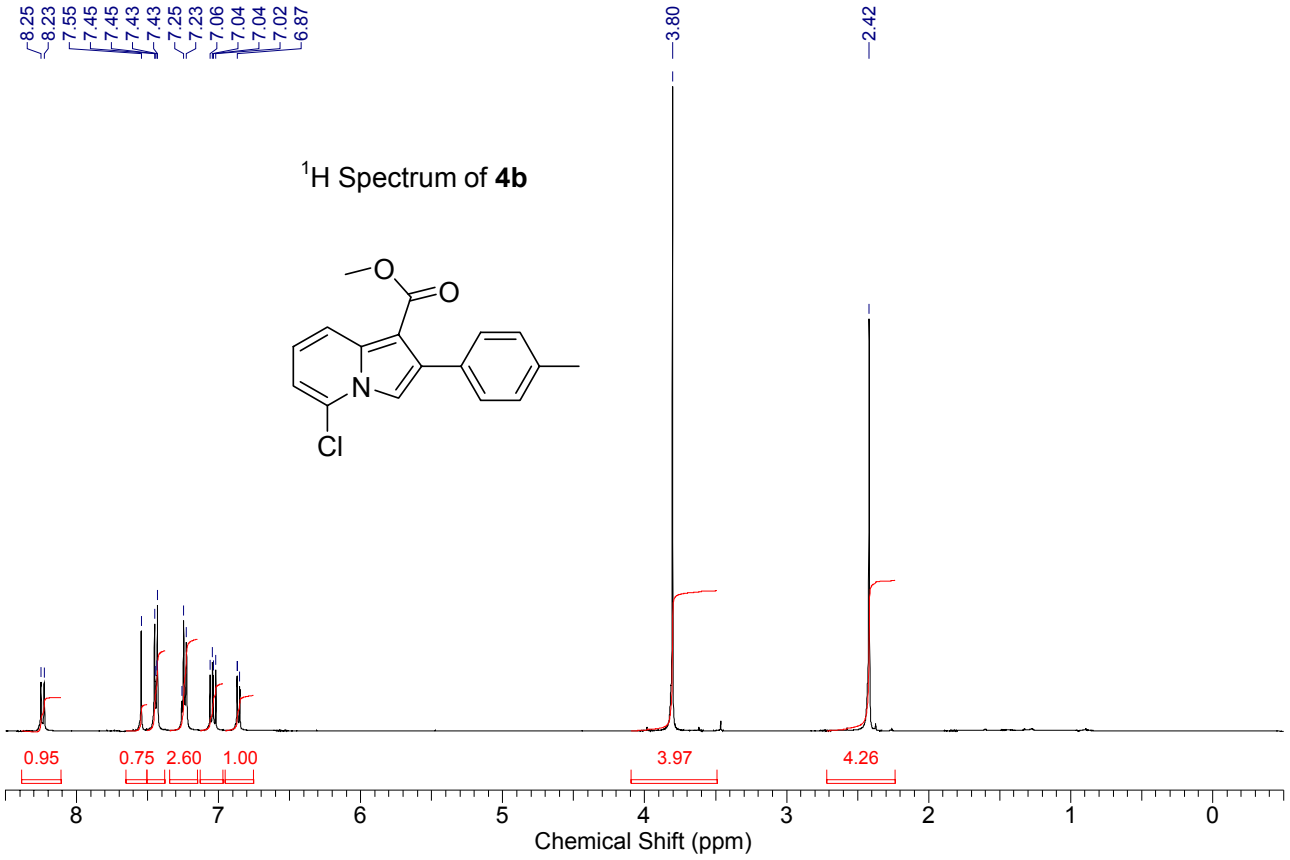

173.99
159.25
142.68
135.90
131.53
130.51
130.18
128.65
127.69
126.52
125.42
124.53
116.99
99.62
77.29
77.04
76.79
61.38
35.01
14.19
13C Spectrum of 3r
Cl
Cl
N
O
O
150
100
50
0
Chemical Shift (ppm)



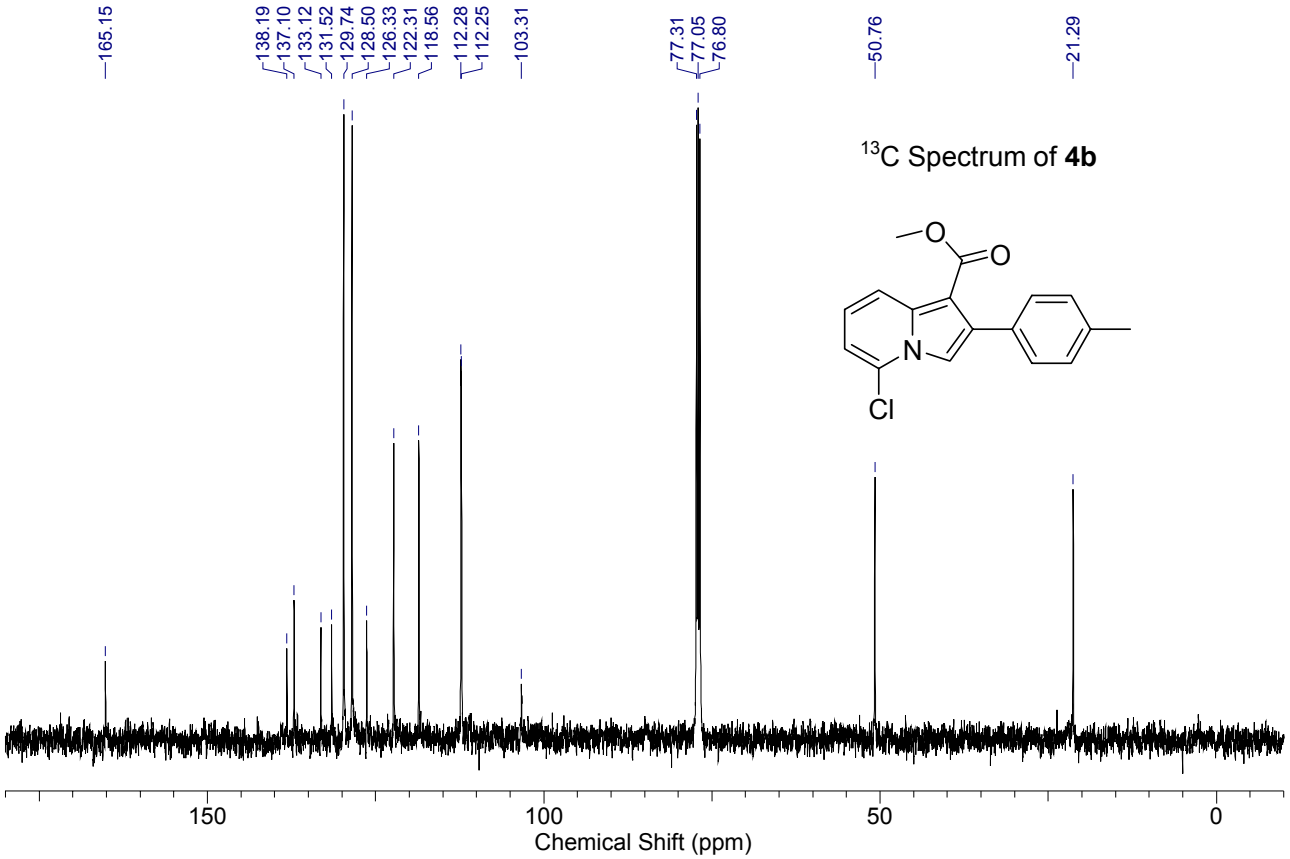
^{1}H Spectrum of **4a**



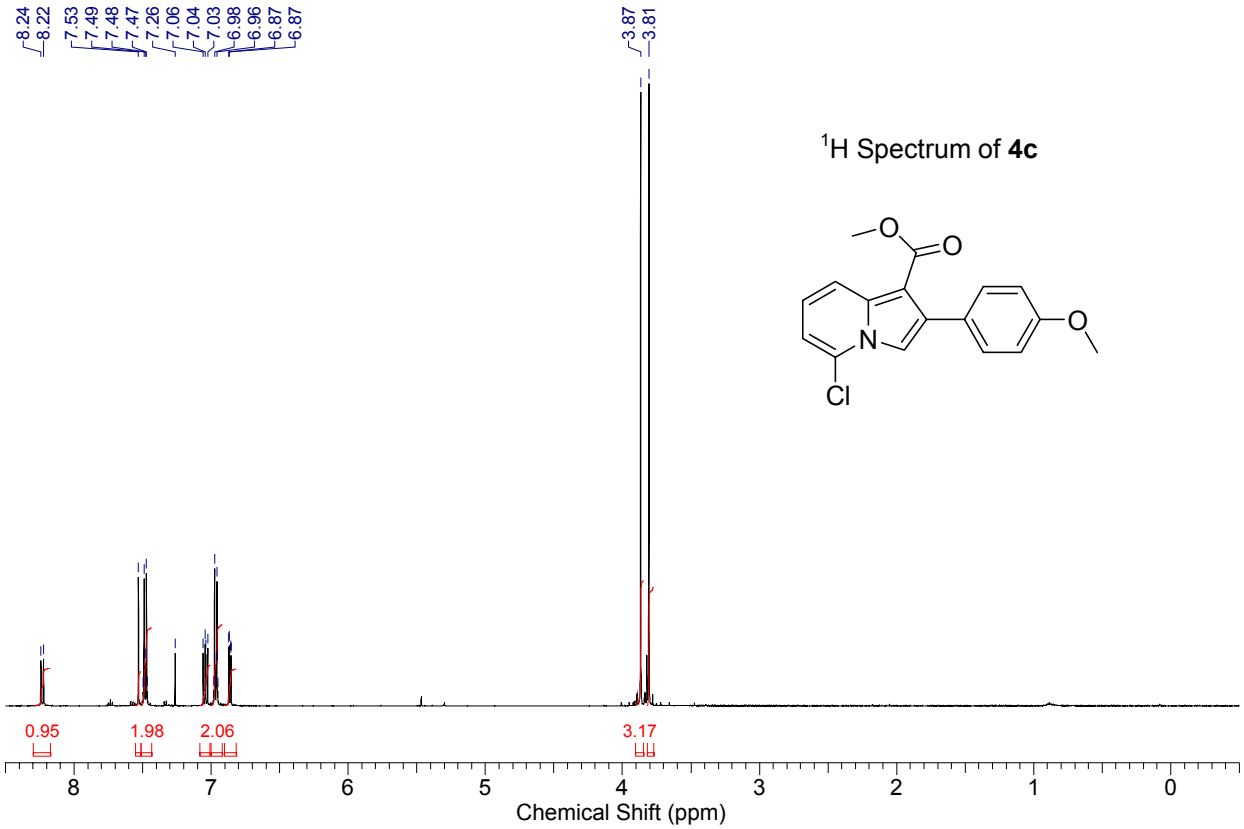
^{13}C Spectrum of **4a**



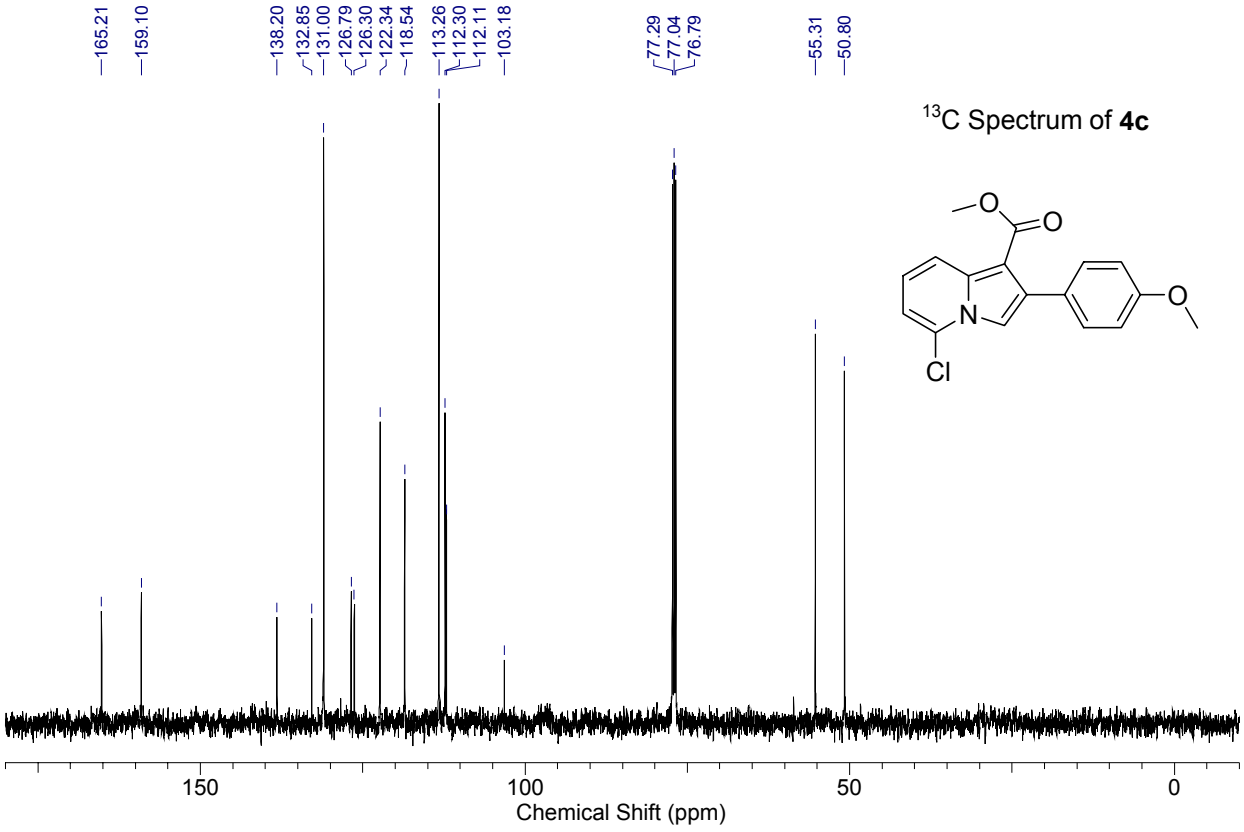
^{1}H Spectrum of **4b**



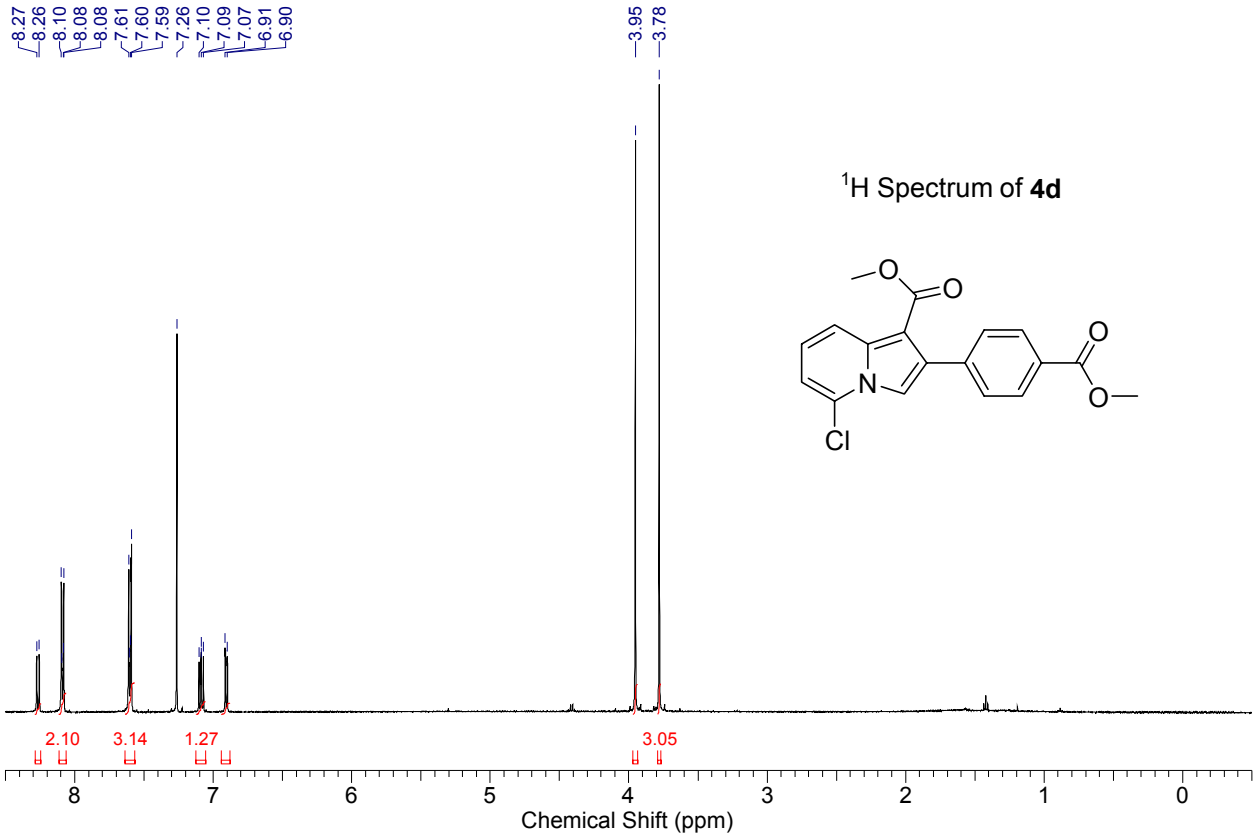
^{13}C Spectrum of **4b**



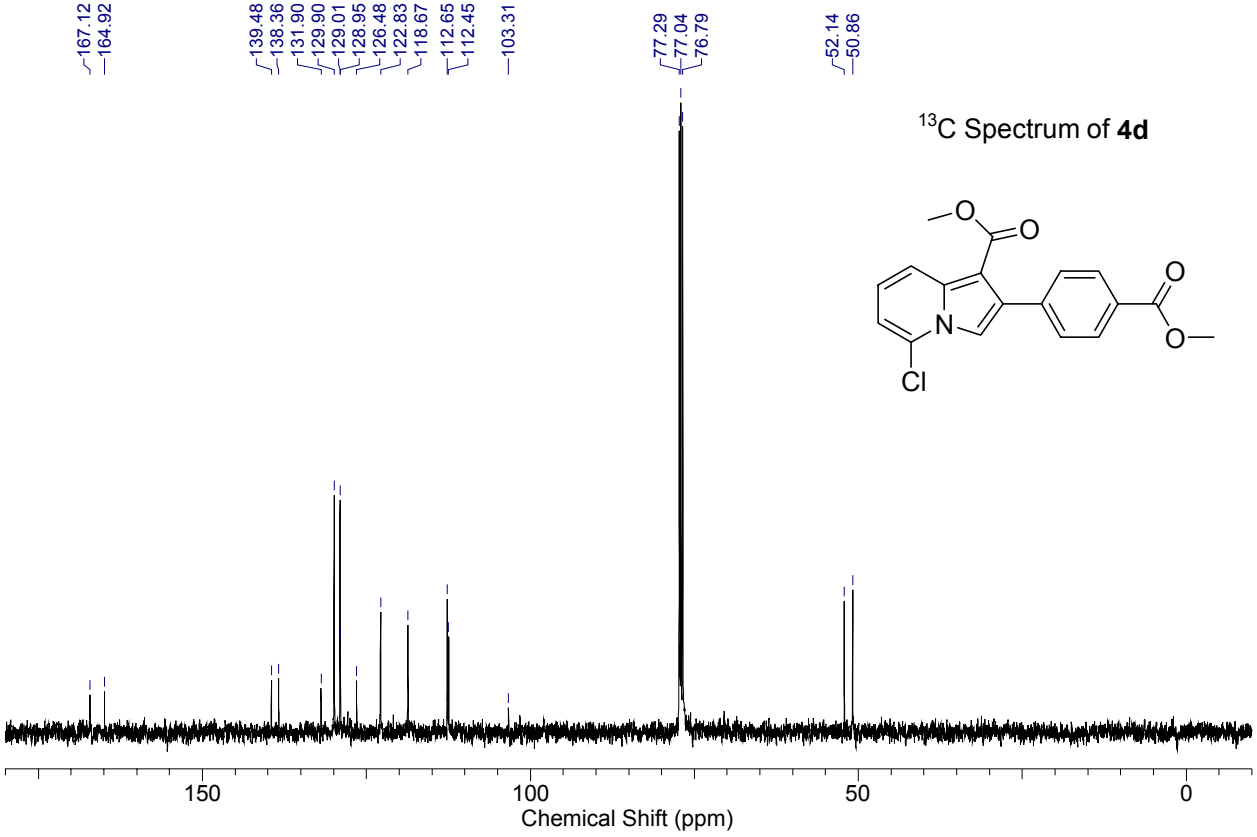
^{1}H Spectrum of **4c**



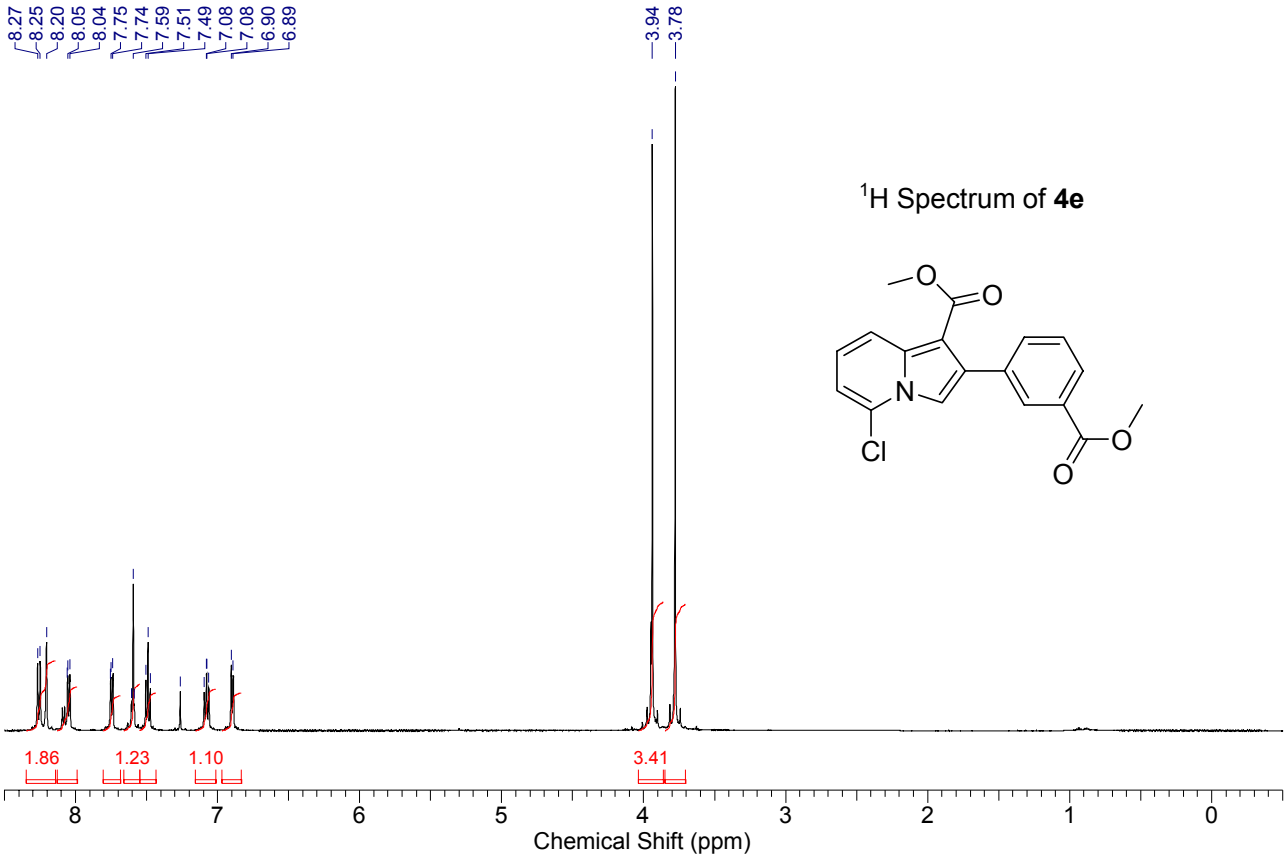
^{13}C Spectrum of **4c**



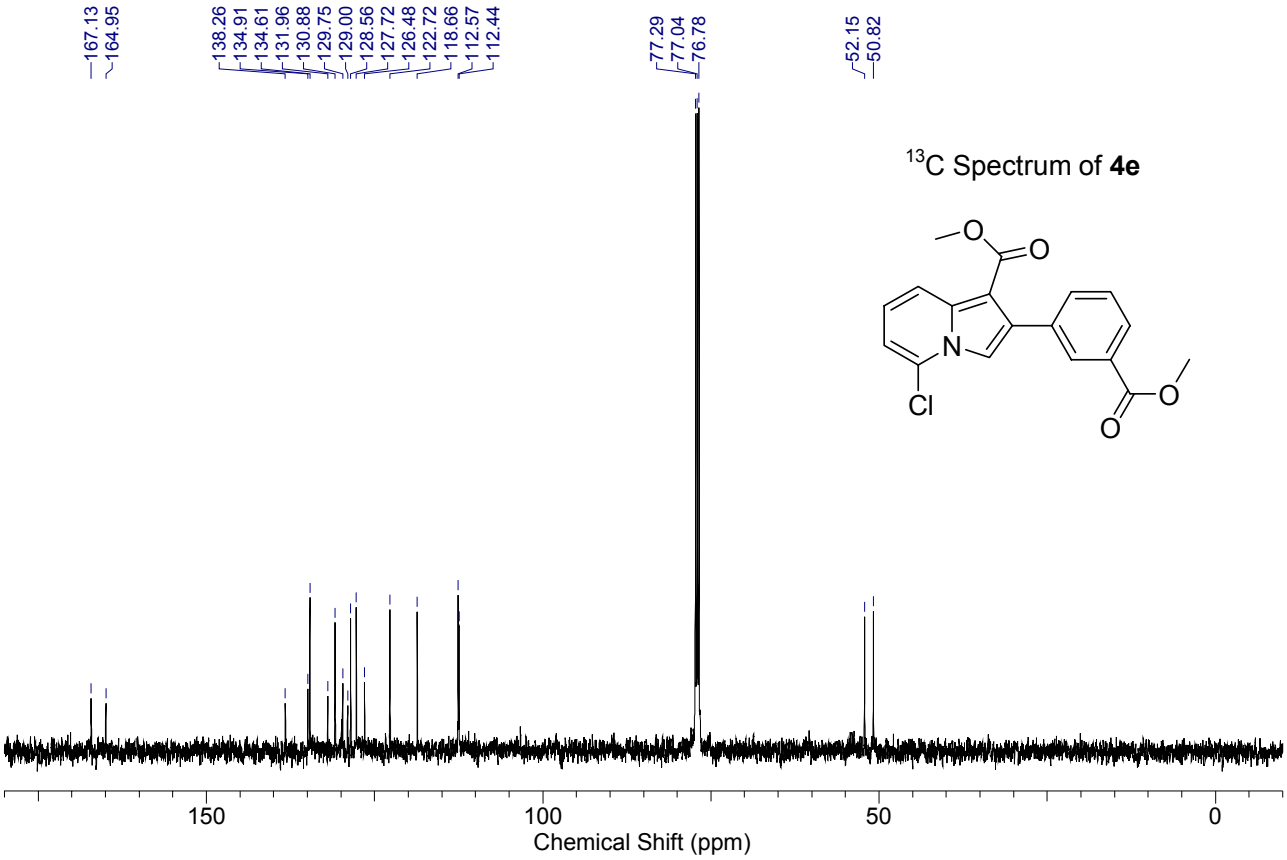
^{1}H Spectrum of **4d**



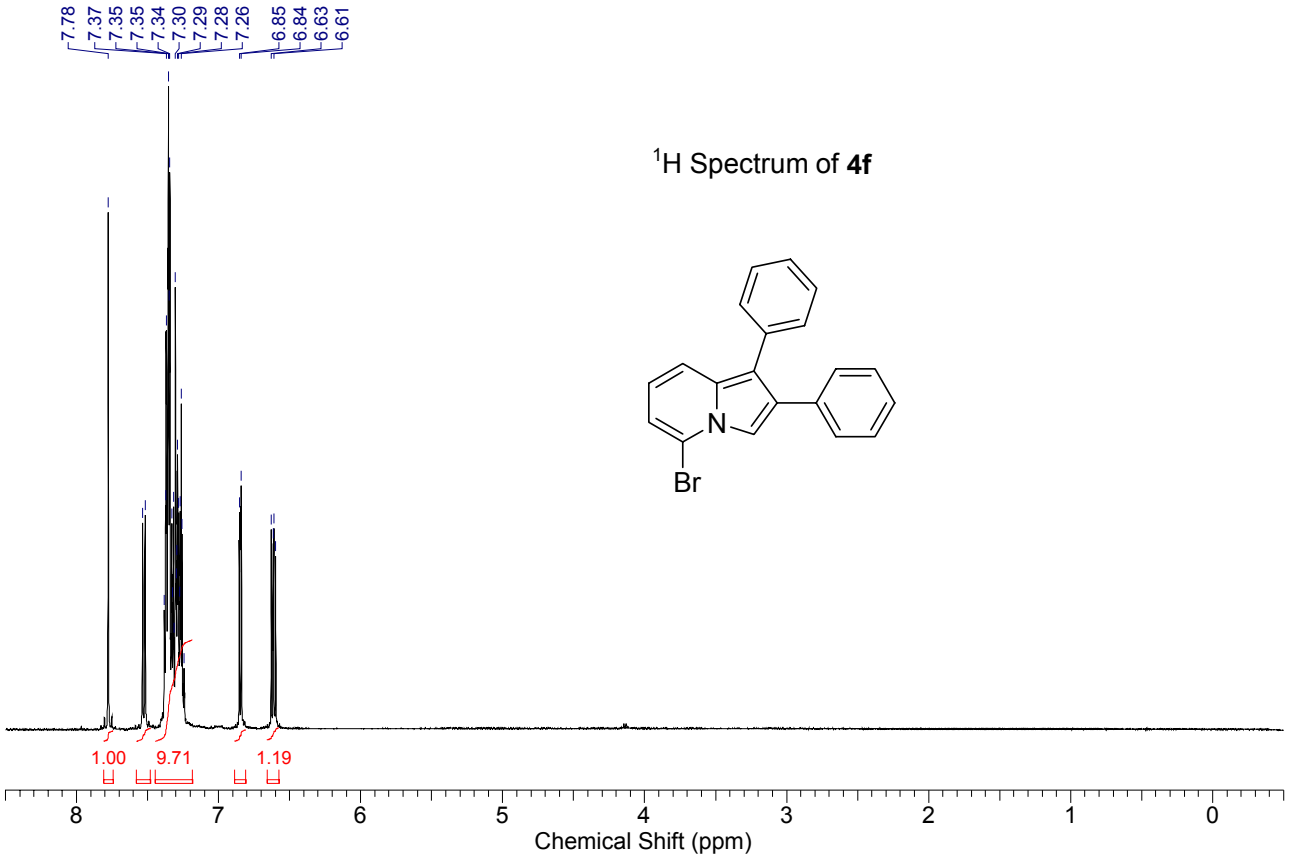
^{13}C Spectrum of **4d**



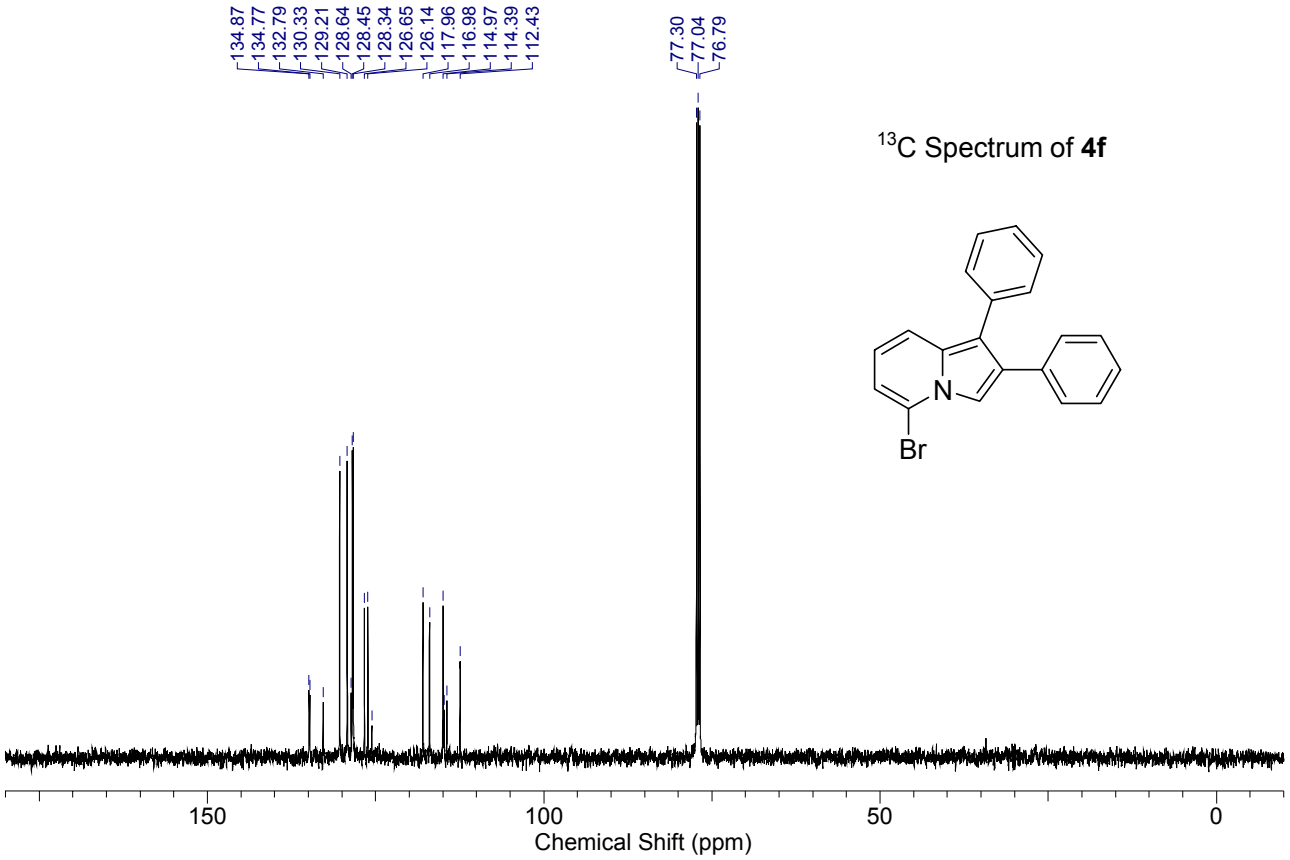
^{1}H Spectrum of **4e**



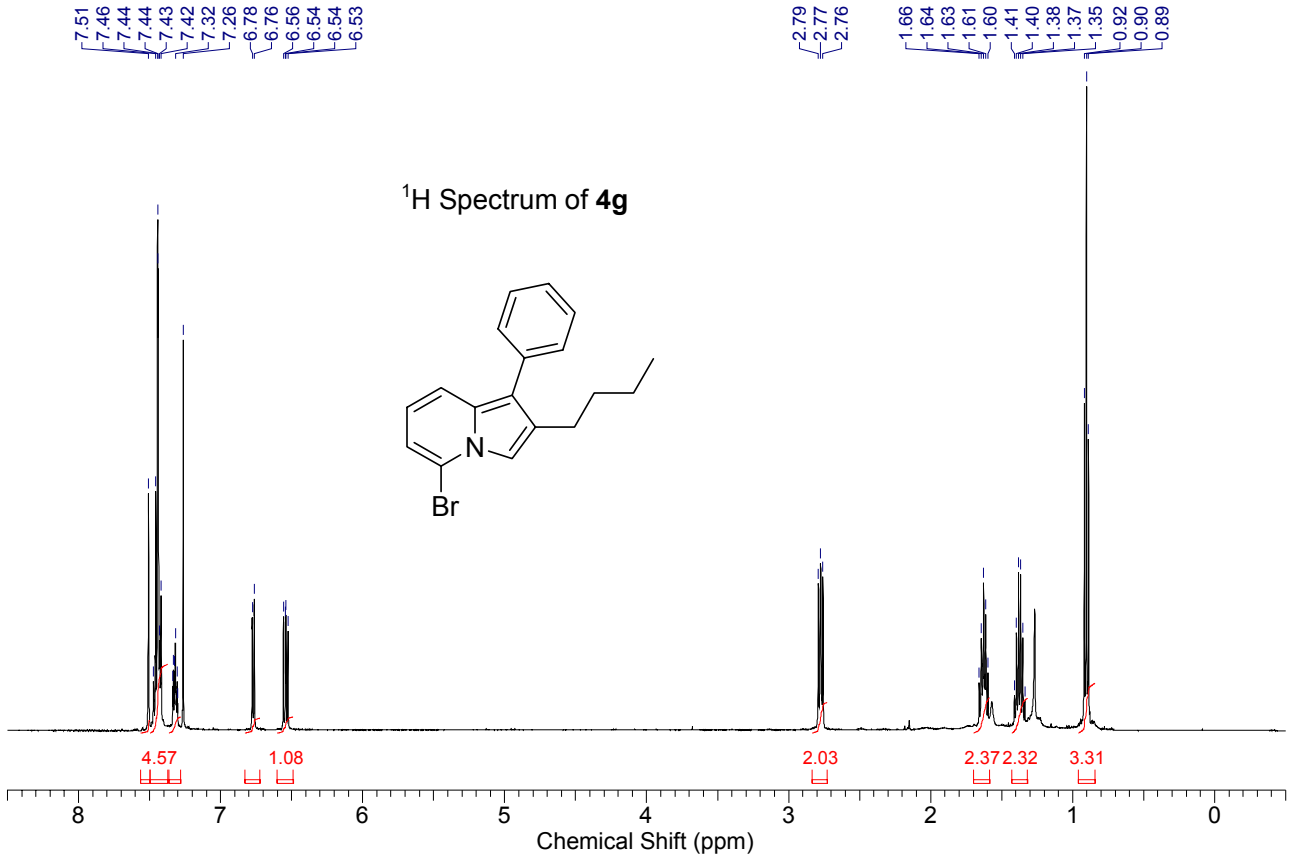
^{13}C Spectrum of **4e**



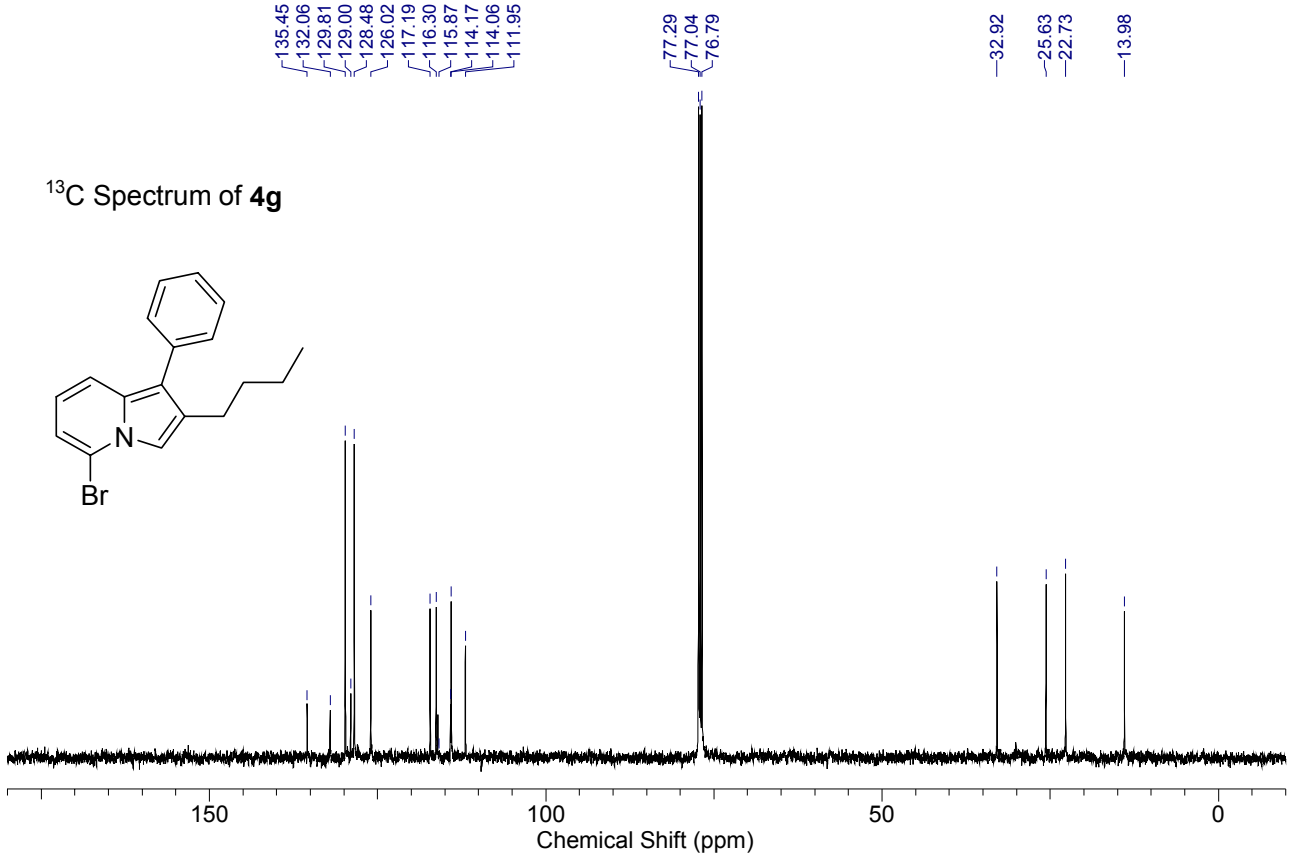
^{1}H Spectrum of **4f**



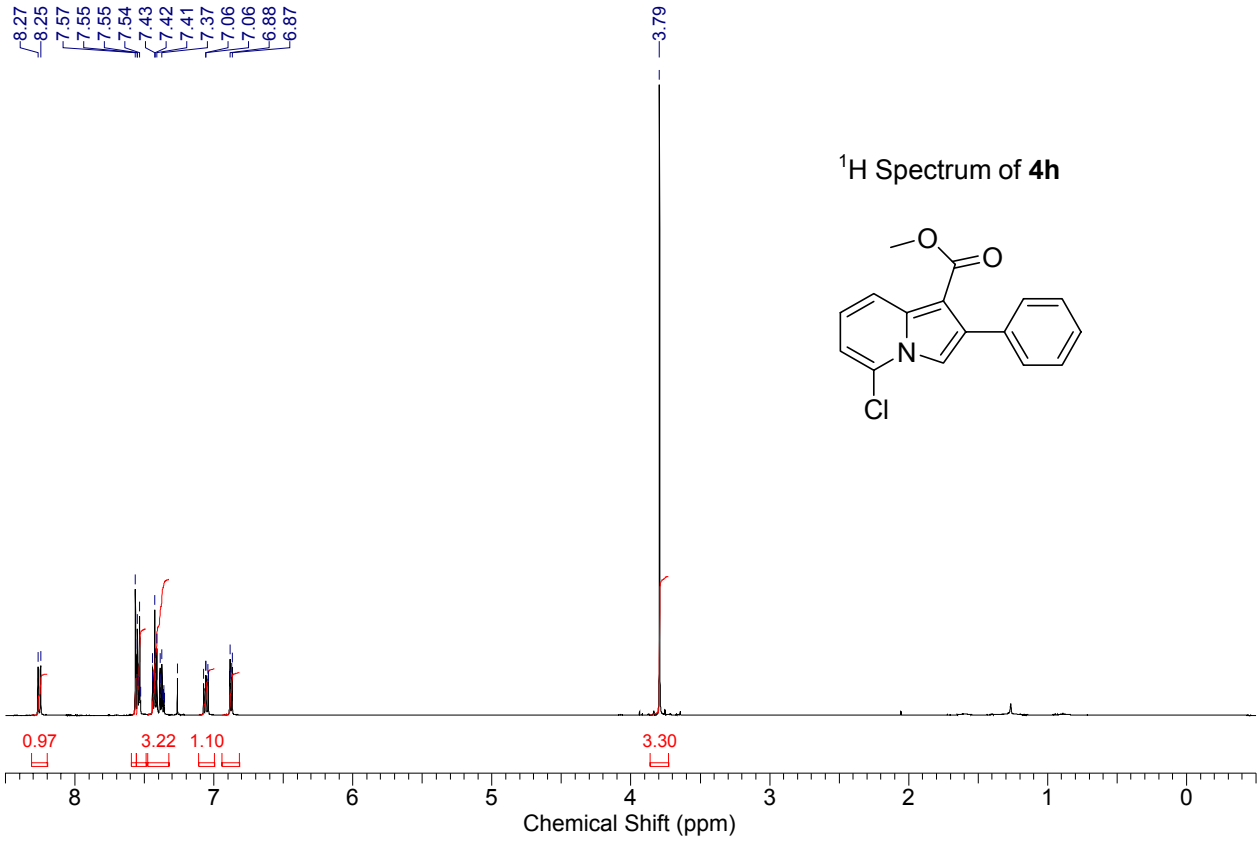
^{13}C Spectrum of **4f**



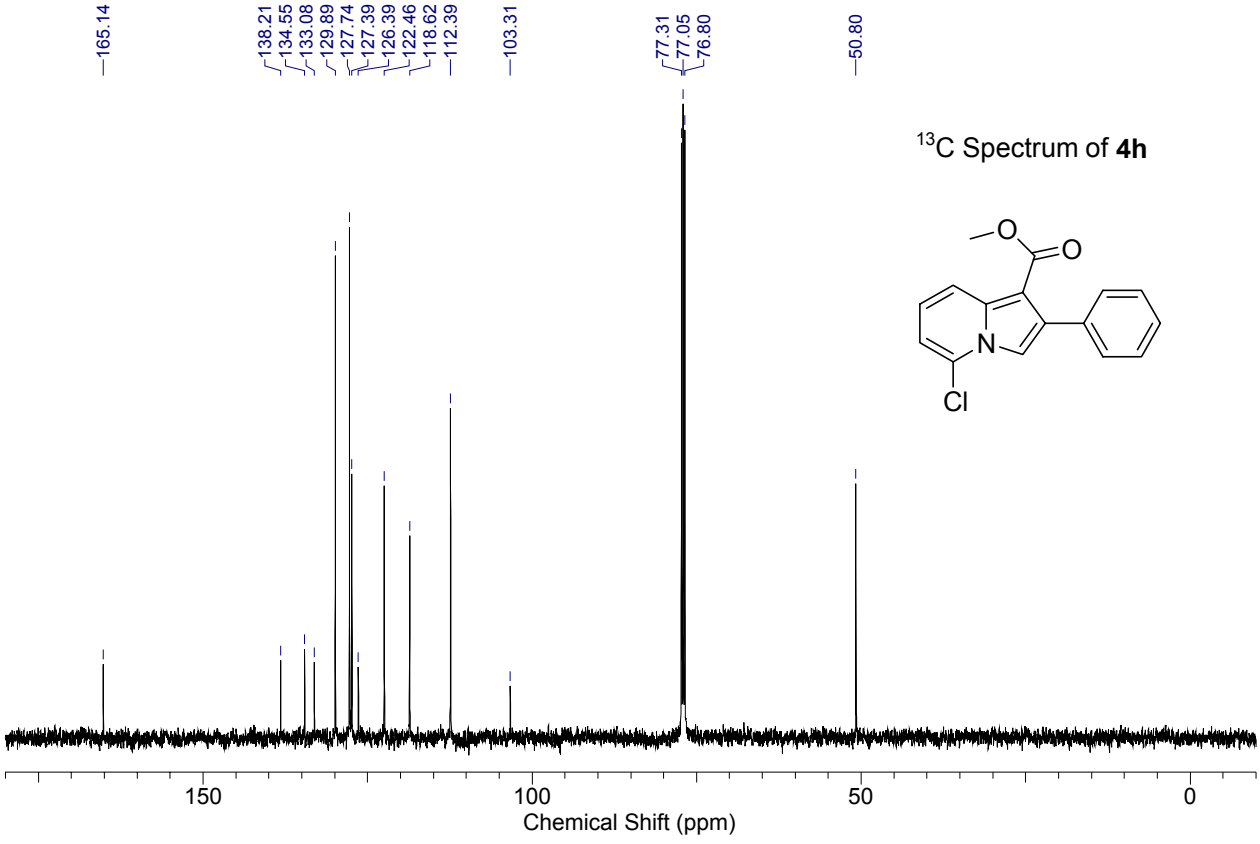
^{1}H Spectrum of **4g**



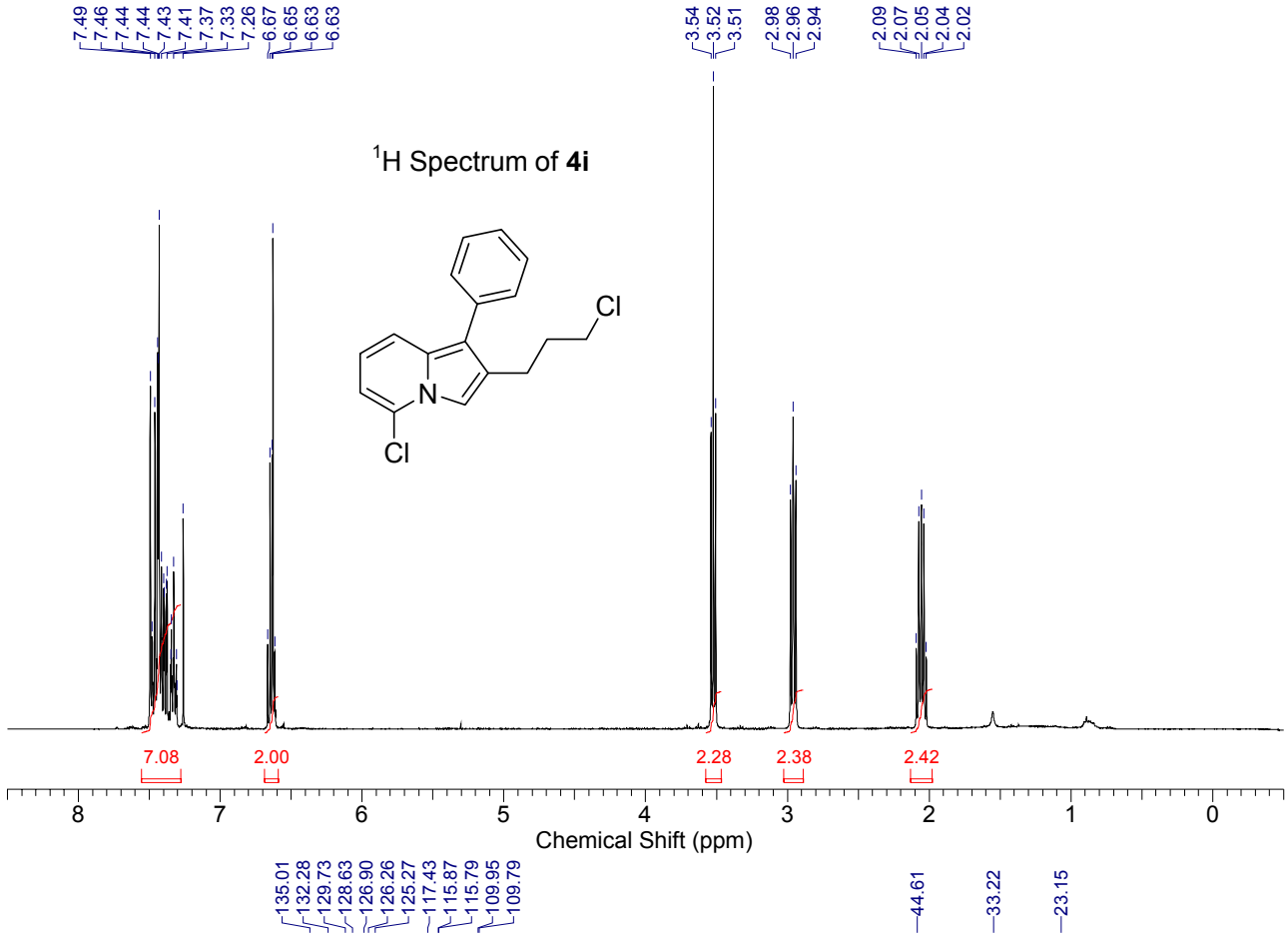
^{13}C Spectrum of **4g**

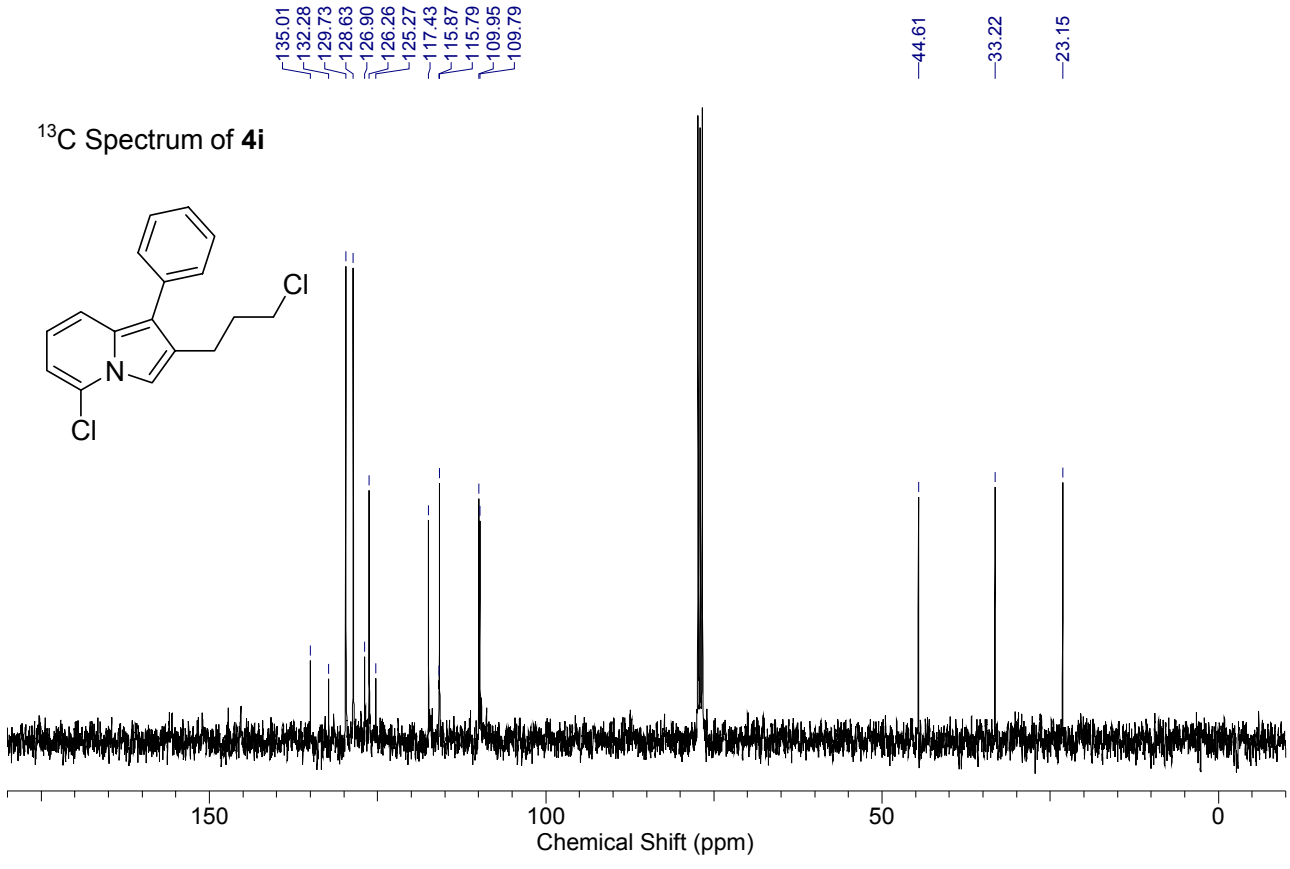


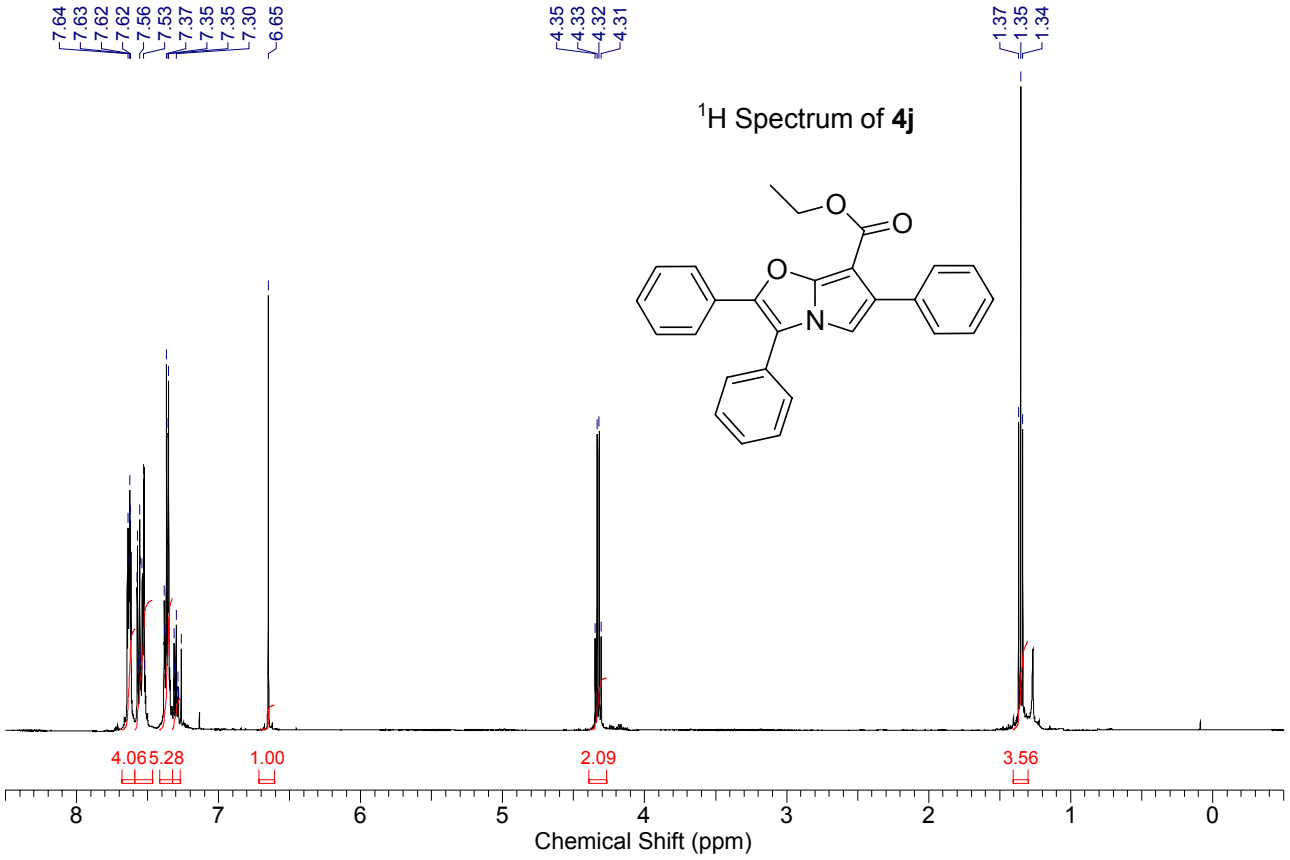
^{1}H Spectrum of **4h**



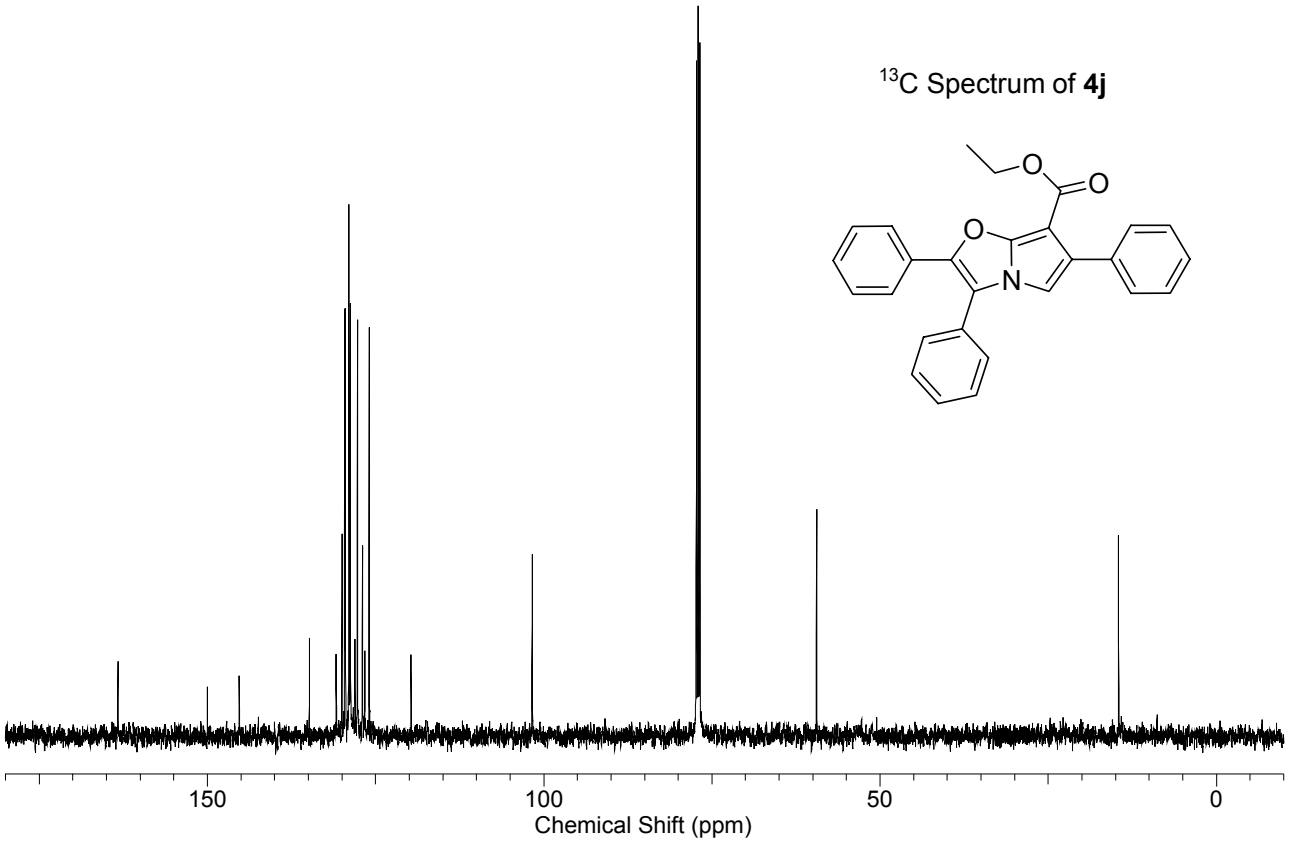
^{13}C Spectrum of **4h**


7.49
7.46
7.44
7.44
7.43
7.41
7.37
7.33
7.26
6.67
6.65
6.63
6.63
3.54
3.52
3.51
2.98
2.96
2.94
2.09
2.07
2.05
2.04
2.02
1H Spectrum of 4i
Cl
N
Cl
7.08
2.00
2.28
2.38
2.42
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

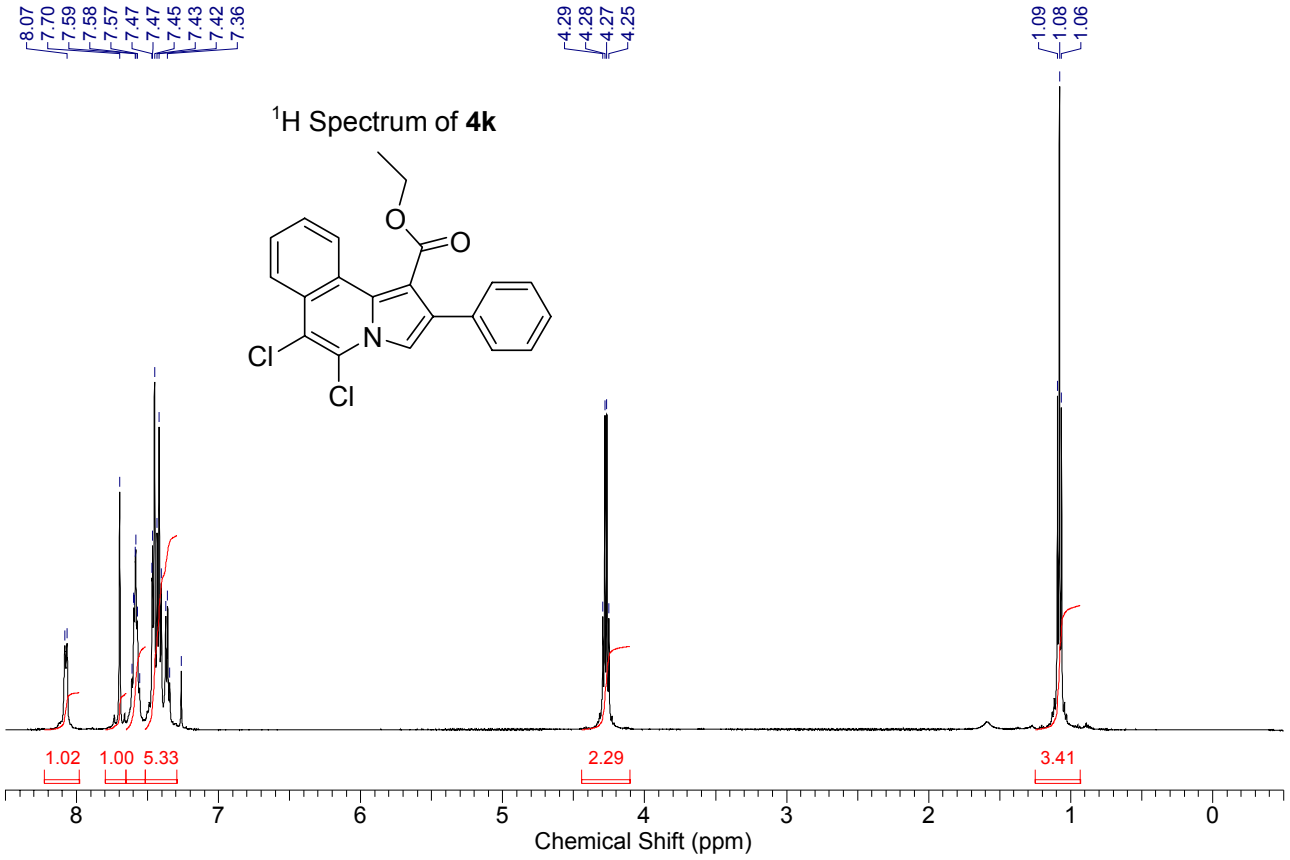

135.01
132.28
129.73
128.63
126.90
126.26
125.27
117.43
115.87
115.79
109.95
109.79
44.61
33.22
23.15
13C Spectrum of 4i
Cl
N
Cl
150
100
50
0
Chemical Shift (ppm)

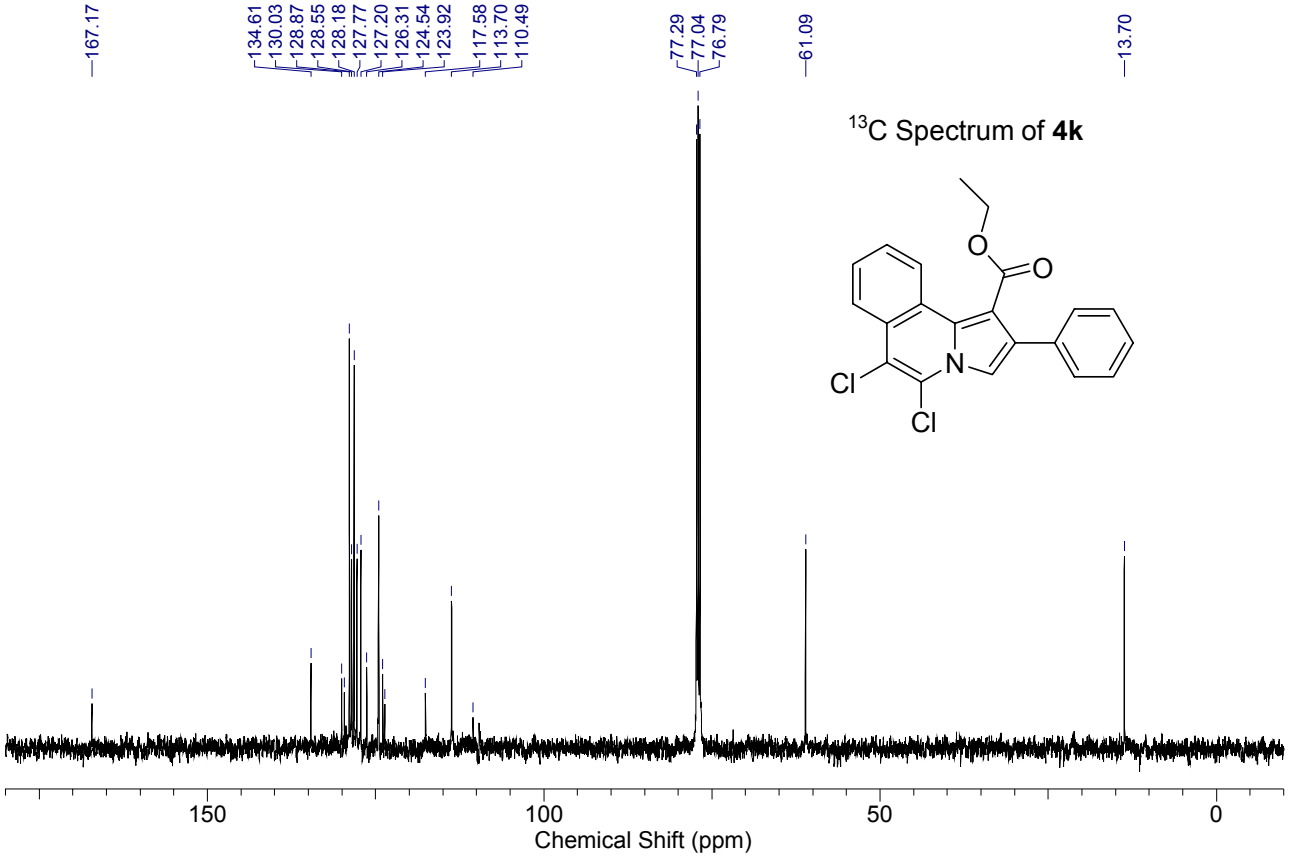


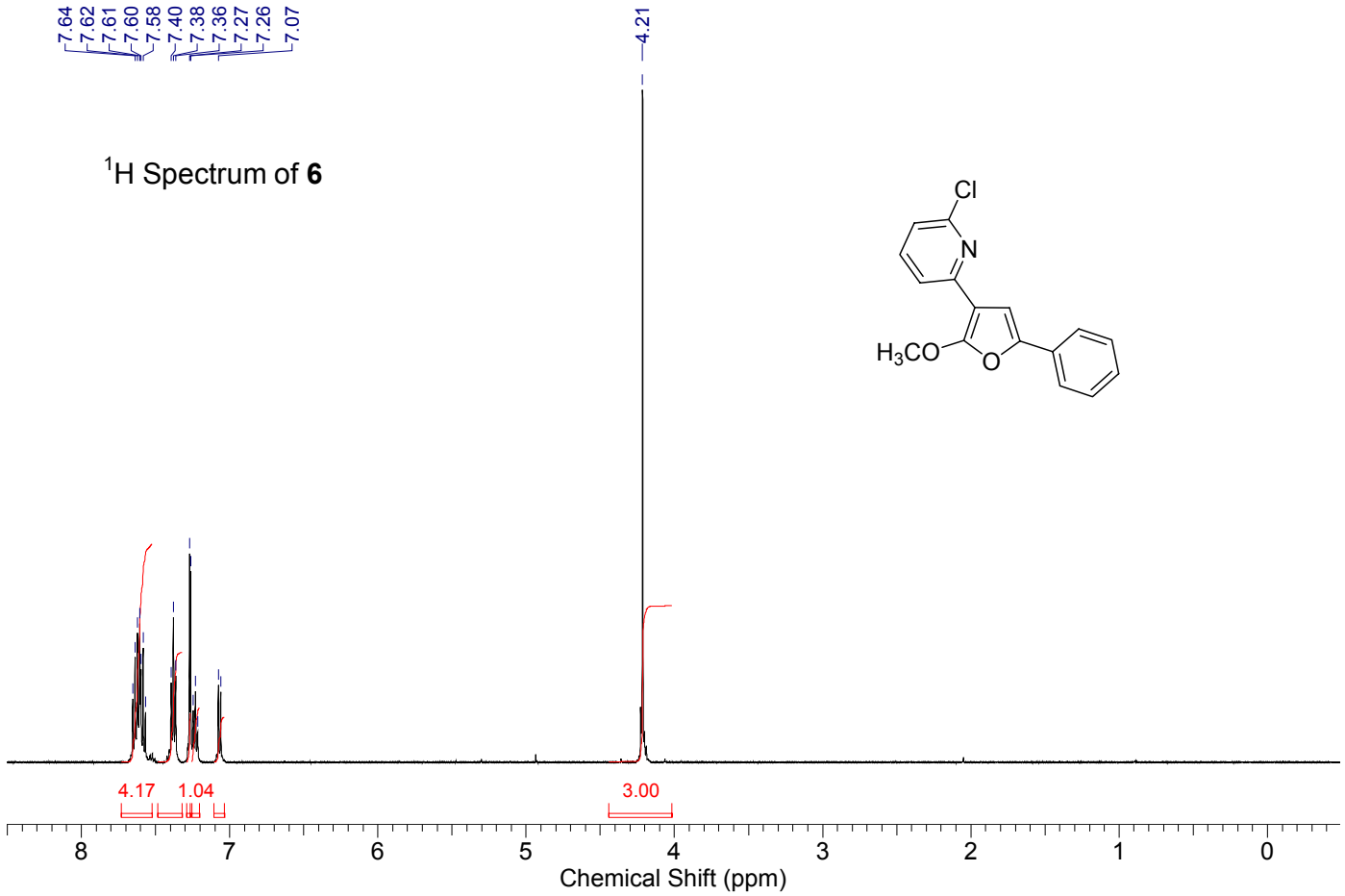
^{1}H Spectrum of **4j**



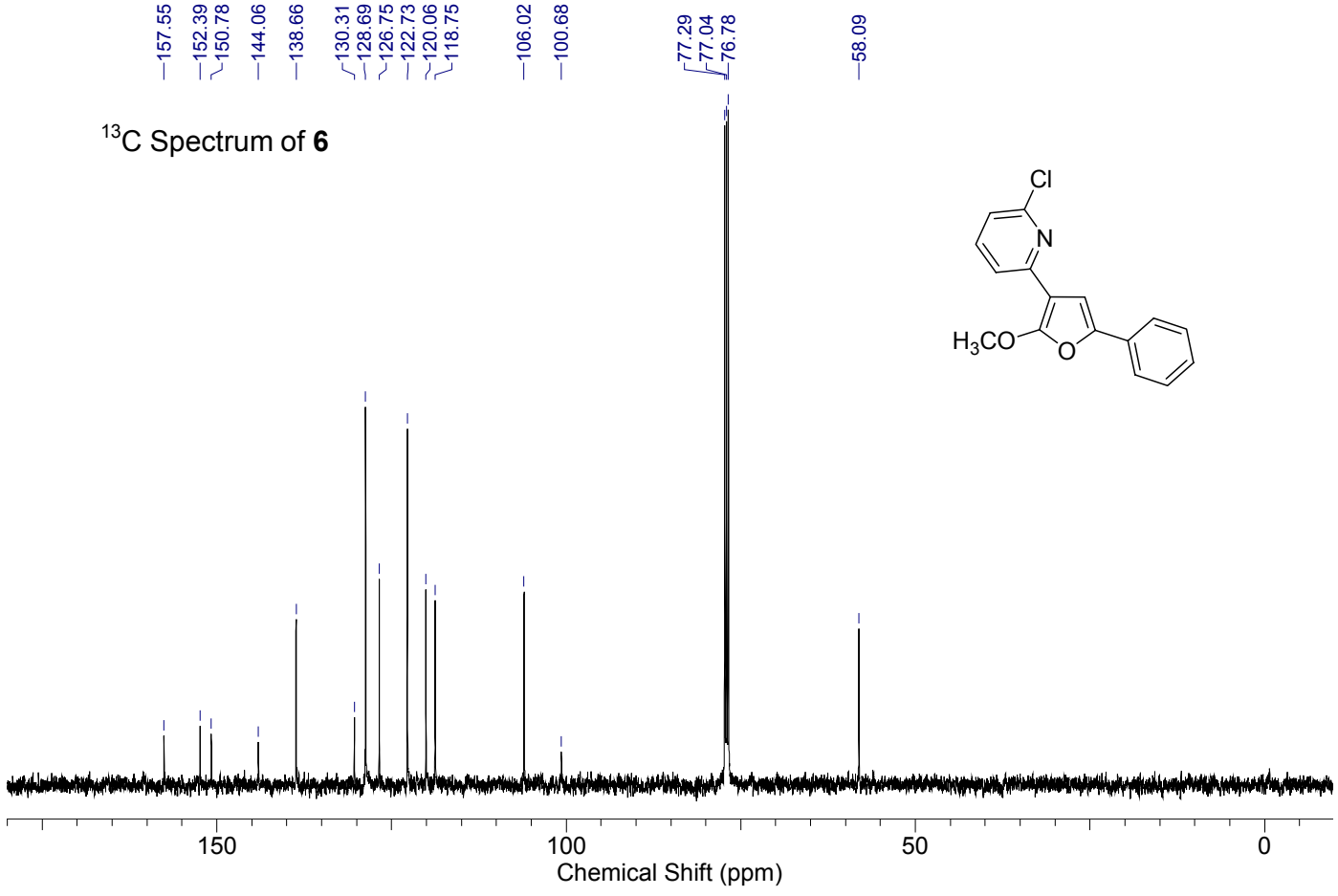
^{13}C Spectrum of **4j**


8.07
7.70
7.59
7.58
7.57
7.47
7.47
7.45
7.43
7.42
7.36
4.29
4.28
4.27
4.25
1.09
1.08
1.06
^{1}H Spectrum of **4k**
O
O
N
Cl
Cl
1.02
1.00
5.33
2.29
3.41
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


167.17
134.61
130.03
128.87
128.55
128.18
127.77
127.20
126.31
124.54
123.92
117.58
113.70
110.49
77.29
77.04
76.79
61.09
13.70
^{13}C Spectrum of **4k**
O
O
N
Cl
Cl
150
100
50
0
Chemical Shift (ppm)



^{1}H Spectrum of **6**



^{13}C Spectrum of **6**