Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cu-Catalyzed Transannulation Reaction of Pyridotriazoles – General Access to Fused Polycyclic Indolizines

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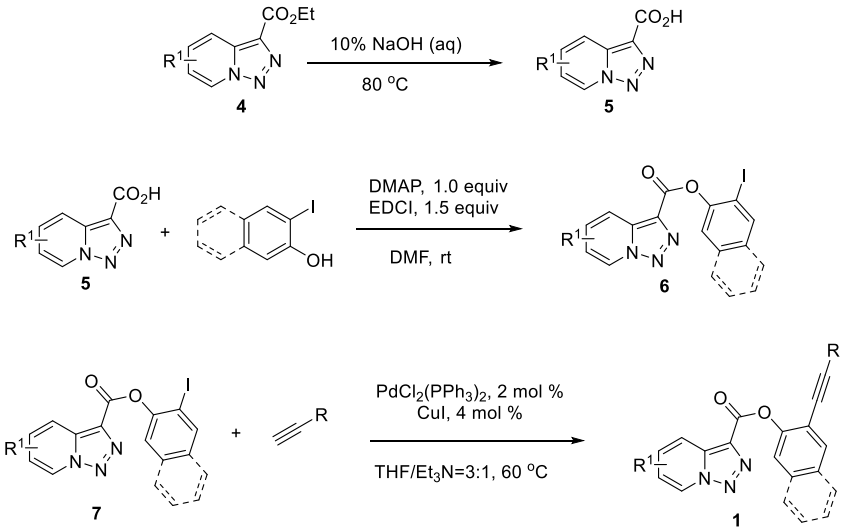
General Information

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). NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument (Overlapping signals in ^{13}C spectrum exist in some compounds due to highly aromatic structure). LRMS and HRMS analyses were performed on Micromass 70 VSE mass spectrometer. 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. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques unless otherwise noted. Anhydrous DCM, toluene, ethyl ether and THF (BHT-free) was purchased from Aldrich, degassed with argon, and dried by passage through activated alumina on an Innovative Technology PureSolv system. Other dry solvent were prepared using CaH_2. All commercially available compounds were purchased from Acros Organics, Strem Chemicals, Aldrich, Gelest Inc., Alfa Aesar, Oakwood Products, Inc., Ark Pharm, Inc., AK Scientific Inc., Matrix Scientific, or Chem-Impex International and used without further purification.

Part I. Preparation of Pyridoriazoles

General Procedure A – synthesis of ester/amide tethered pyridotriazoles



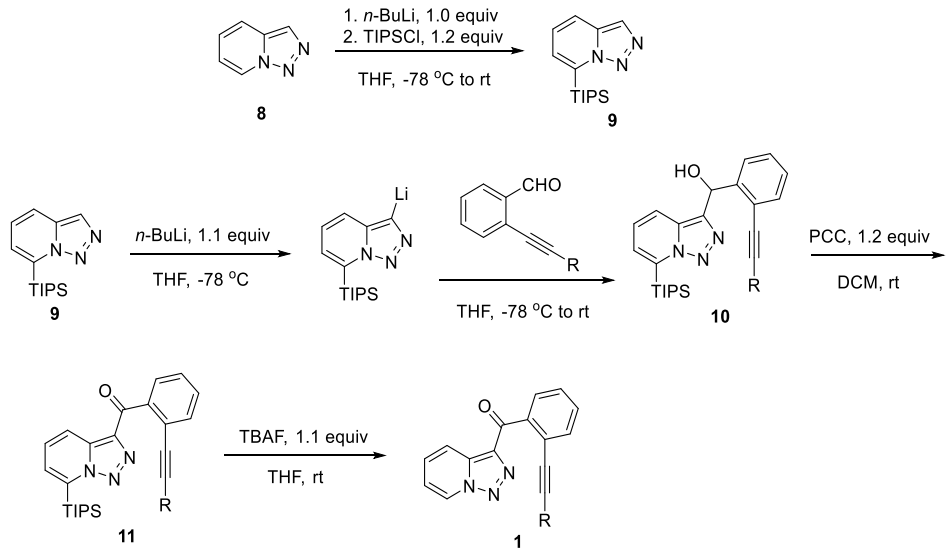
Pyridotriazole **4** was known and prepared according to literature report[1].

Carboxylic acid **5** was prepared via hydrolysis of ester **4** under basic conditions. A suspension of pyridotriazole **4** (20 mmol) in 10% NaOH aqueous solution (20 mL) was heated at 80 °C until a clear solution is formed (about 1 h). Then, the reaction mixture was allowed to cool down to room temperature, and 2 M HCl was added to pH=2. White precipitate (carboxylic acid **5**) formed during acidification and was collected by filtration. It can be used directly in the next step without purification.

To a stirred suspension of compound **5** (10 mmol, 1.0 equiv), 2-iodophenol (12 mmol, 1.2 equiv), and 4-(dimethylamino)pyridine (DMAP, 10 mmol, 1.0 equiv) in DMF was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 15 mmol, 1.5 equiv). The mixture was stirred at room temperature for 2 h (until a clear solution is formed). Then water was added. The mixture was extracted with ethyl acetate twice, and the combined organic layers were washed with 1 M HCl, water, saturated aqueous Na_2CO_3, brine, and dried over anhydrous Na_2SO_4. Evaporation of solvent afforded yellow solid, which can be used directly in the next step without purification.

Alkynyl pyridotriazole **1** was prepared from compound **7** and terminal alkyne via Sonogashira cross-coupling reaction. A round-bottom flask equipped with a stirring bar was charged with $PdCl_2(PPh_3)_2$ (2 mol %), CuI (4 mol %), compound **7** (0.5 mmol, 1.0 equiv), terminal alkyne (0.75 mmol, 1.5 equiv), and solvent (THF/Et_3N=3:1) under N_2 atmosphere. The reaction mixture was stirred at 60 °C. Upon completion (about 4 h), the reaction mixture was cooled to room temperature, filtered through a short path of silica gel, concentrated under reduced pressure, and the crude product was purified by column chromatography to afford the corresponding alkynyl pyridotriazole substrate.

General Procedure B -- synthesis of ketone tethered pyridotriazoles



Pyridotriazole **8** was known and prepared according to literature report[2].

To a stirred solution of compound **8** (20 mmol, 1.0 equiv) in THF was added dropwise *n*-BuLi (2.5 M, 8 mL, 1.0 equiv.) at -78 °C under argon. After addition, the solution was allowed to stir for 30 min at the same temperature. Then, TIPSCl (24 mmol, 1.2 equiv.) was added dropwise and the solution was allowed to warm to room temperature. After stirring for 1 h, the reaction was quenched with saturated aqueous NH_4Cl and the aqueous layer was extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford compound **9**.

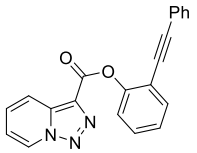
To a stirred solution of compound **9** (1.0 mmol, 1.0 equiv) in THF was added dropwise *n*-BuLi (2.5 M, 0.44 mL, 1.1 equiv.) at -78 °C under argon. After addition, the solution was allowed to stir for 1 h at the same temperature. Then, 2-(alkynyl)benzaldehyde (1.2 mmol, 1.2 equiv) was added dropwise and the solution was allowed to warm to room temperature then stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl and the aqueous layer was extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford compound **10**.

To a DCM solution of compound **10** was added pyridinium chlorochromate (PCC, 1.2 equiv). The resulting mixture was allowed to react for 1 h at room temperature. Upon completion, the reaction mixture was filtered through a short path of silica gel, concentrated under reduced pressure, and purified by column chromatography to afford compound **11**.

To a THF solution of compound **11** was added TBAF (1.1 equiv, 1M solution in THF), and the reaction mixture was stirred at room temperature for 1 h. Upon completion, the mixture was

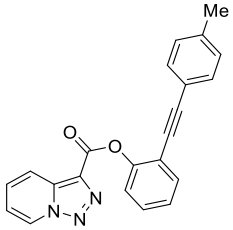
concentrated under reduced pressure, and the crude product was purified by column chromatography to afford the corresponding alkynyl pyridotriazole substrate **1**.

2-(phenylethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1aa



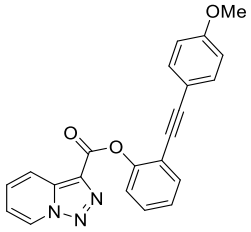
Compound **1aa** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.88 (d, *J*=6.97 Hz, 1 H), 8.41 (d, *J*=8.80 Hz, 1 H), 7.64 (d, *J*=7.34 Hz, 1 H), 7.53 - 7.50 (m, 1 H), 7.45 - 7.40 (m, 2 H), 7.30 (t, *J*=7.34 Hz, 1 H), 7.23 – 7.14 (m, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.10, 151.14, 132.98, 131.40, 129.81, 129.46, 128.33, 128.11, 126.11, 122.71, 122.55, 119.49, 117.40, 116.59, 94.58, 84.40. HRMS (ESI) calculated for $C_{21}H_{14}N_3O_2$ $[M+H]^+$: 340.1086, found: 340.1080. Overlapping signals in ^{13}C spectrum due to highly aromatic structure.

2-(p-tolylethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ab



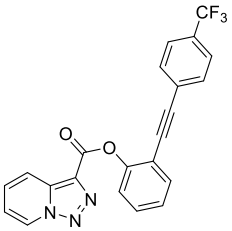
Compound **1ab** was prepared according to the **General Procedure A.** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.87 (d, *J*=6.72 Hz, 1 H), 8.39 (d, *J*=9.06 Hz, 1 H), 7.62 (d, *J*=7.60 Hz, 1 H), 7.53 – 7.49 (m, 1 H), 7.41 – 7.38 (m, 2 H), 7.29 – 7.28 (m, 1 H), 7.18 (t, *J*=6.72 Hz, 1 H), 7.10 (d, *J*=7.89 Hz, 2H), 6.95 (d, *J*=7.89 Hz, 2 H), 2.25 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.98, 150.97, 138.50, 135.38, 132.84, 131.22, 129.81, 129.22, 128.83, 128.48, 126.06, 126.00, 122.44, 119.52, 117.50, 116.59, 94.76, 83.68, 21.35. HRMS (ESI) calculated for $C_{22}H_{16}N_3O_2$ $[M+H]^+$: 354.1243, found: 354.1238.

2-((4-methoxyphenyl)ethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ac



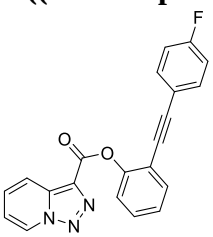
Compound **1ac** was prepared according to the **General Procedure A.** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.87 (d, *J*=6.72 Hz, 1 H), 8.40 (d, *J*=8.77 Hz, 1 H), 7.61 (d, *J*=7.60 Hz, 1 H), 7.52 (t, *J*=7.89 Hz, 1 H), 7.40 – 7.39 (m, 2 H), 7.30 – 7.28 (m, 1 H), 7.20 – 7.13 (m, 3 H), 6.67 (d, *J*=8.48 Hz, 2 H), 3.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.57, 159.01, 150.92, 135.42, 132.84, 132.74, 129.79, 129.06, 128.55, 126.06, 126.01, 122.44, 119.41, 117.66, 116.61, 114.73, 113.72, 94.67, 83.10, 55.17. HRMS (ESI) calculated for $C_{22}H_{16}N_3O_3$ $[M+H]^+$: 370.1192, found: 370.1183.

2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ad



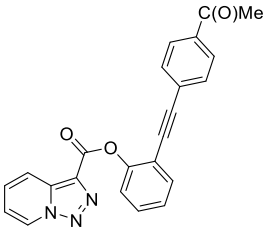
Compound **1ad** was prepared according to the **General Procedure A.** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.90 (d, *J*=6.72 Hz, 1 H), 8.37 (d, *J*=8.77 Hz, 1 H), 7.65 (d, *J*=7.60 Hz, 1 H), 7.58 – 7.54 (m, 1 H), 7.49 – 7.39 (m, 4 H), 7.33 – 7.30 (m, 3 H), 7.21 (t, *J*=6.58 Hz, 1 H), ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.03, 151.25, 135.54, 133.00, 131.57, 130.09, 129.97, 129.69, 127.39 (q, *J*=183 Hz), 126.23, 126.15, 125.03 (q, *J*=5 Hz), 122.64, 122.34, 119.22, 116.75, 116.71, 92.99, 86.67. HRMS (ESI) calculated for $C_{22}H_{13}F_3N_3O_2$ $[M+H]^+$: 408.0960, found: 408.0960. Overlapping signals in ^{13}C spectrum due to highly aromatic structure.

2-((4-fluorophenyl)ethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ae



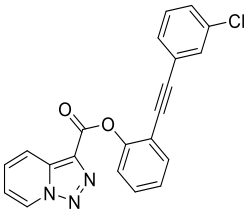
Compound **1ae** was prepared according to the **General Procedure A.** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.89 (d, *J*=7.02 Hz, 1 H), 8.38 (d, *J*=8.77 Hz, 1 H), 7.61 (d, *J*=7.02 Hz, 1 H), 7.56 – 7.52 (m, 1 H), 7.45 – 7.37 (m, 2 H), 7.29 (t, *J*=7.45 Hz, 1 H), 7.21 – 7.18 (m, 3 H), 6.85 (t, *J*=8.62 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.42 (d, *J*=250.7 Hz), 159.01, 151.12, 135.49, 133.29 (d, *J*=6.3 Hz), 132.84, 129.83, 129.50, 128.46, 126.12, 126.09, 122.55, 119.30, 118.80 (d, *J*=3.8 Hz), 117.25, 116.62, 115.42 (d, *J*=21.4 Hz), 93.47, 84.09. HRMS (ESI) calculated for $C_{21}H_{13}FN_3O_2$ $[M+H]^+$: 358.0992, found: 358.0982.

2-((4-acetylphenyl)ethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1af



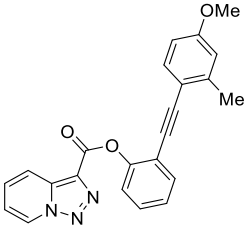
Compound **1af** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.90 (d, *J*=6.24 Hz, 1 H), 8.38 (d, *J*=8.44 Hz, 1 H), 7.75 (d, *J*=7.70 Hz, 2 H), 7.65 (d, *J*=7.34 Hz, 1 H), 7.56 (t, *J*=7.52 Hz, 1 H), 7.48 -7.46 (m, 1 H), 7.41 – 7.40 (m, 1 H), 7.33 – 7.29 (m, 3 H), 7.22 – 7.20 (m, 1 H), 2.53 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 197.23, 159.03, 151.26, 136.15, 135.55, 133.05, 131.49, 130.09, 129.96, 128.37, 128.04, 127.55, 126.23, 126.18, 122.67, 119.30, 116.89, 116.69, 93.66, 87.62, 26.56. HRMS (ESI) calculated for $C_{23}H_{16}N_3O_3$ $[M+H]^+$: 382.1192, found: 382.1189.

2-((3-chlorophenyl)ethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ag



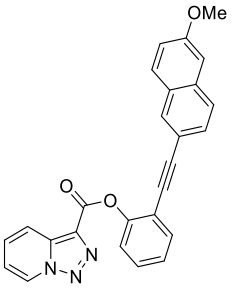
Compound **1ag** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.90 (d, *J*=5.87 Hz, 1 H), 8.39 (d, *J*=8.07 Hz, 1 H), 7.62 (d, *J*=6.60 Hz, 1 H), 7.57 – 7.54 (m, 1 H), 7.45 – 7.39 (m, 2 H), 7.31 – 7.30 (m, 1 H), 7.20 – 7.16 (m, 2 H), 7.10 – 7.08 (m, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.01, 151.33, 147.11, 135.53, 133.86, 132.92, 131.15, 129.96, 129.86, 129.45, 129.37, 128.53, 128.40, 126.17, 124.39, 122.64, 119.27, 116.93, 116.64, 93.06, 85.63. HRMS (ESI) calculated for $C_{21}H_{13}ClN_3O_2$ $[M+H]^+$: 374.0696, found: 374.0689.

2-((4-methoxy-2-methylphenyl)ethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ah



Compound **1ah** was prepared according to the **General Procedure A.** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.87 (d, *J*=7.02 Hz, 1 H), 8.38 (d, *J*=9.06 Hz, 1 H), 7.64 – 7.62 (m, 1 H), 7.54 – 7.51 (m, 1 H), 7.42 – 7.35 (m, 2 H), 7.31 – 7.27 (m, 1 H), 7.20 – 7.13 (m, 2 H), 6.59 – 6.58 (m, 1 H), 6.53 (dd, *J*=8.48, 2.34 Hz, 1 H), 3.72 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.60, 159.10, 150.67, 141.88, 135.52, 133.19, 132.97, 129.74, 128.99, 126.13, 126.04, 122.53, 119.43, 118.15, 116.56, 114.83, 111.07, 93.57, 86.82, 55.12, 20.66. HRMS (ESI) calculated for $C_{23}H_{18}N_3O_3$ $[M+H]^+$: 384.1348, found: 384.1343. Overlapping signals in ^{13}C spectrum due to highly aromatic structure.

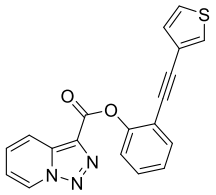
2-((6-methoxynaphthalen-2-yl)ethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ai



Compound **1ai** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.83 (d, *J*=6.97 Hz, 1 H), 8.38 (d, *J*=8.80 Hz, 1 H), 7.65 (d, *J*=7.34 Hz, 1 H), 7.58 (s, 1 H), 7.48 – 7.41 (m, 5 H), 7.31 – 7.29 (m, 1 H), 7.20 (dd, *J*=8.44, 1.47 Hz, 1 H), 7.11 (td, *J*=6.88, 1.28 Hz, 1 H), 7.05 (dd, *J*=8.99, 2.38 Hz, 1 H), 6.97 (d, *J*=2.20 Hz, 1 H), 3.84 (s, 3 H). ^{13}C NMR (126

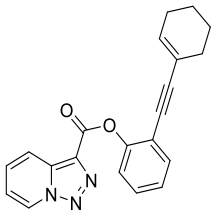
MHz, $CDCl_3$) δ ppm 159.01, 158.23, 151.17, 135.39, 133.98, 132.74, 131.15, 129.77, 129.24, 129.06, 128.52, 128.46, 128.05, 126.52, 126.08, 125.93, 122.47, 119.28, 119.24, 117.50, 117.43, 116.53, 105.59, 95.30, 84.07, 55.19. HRMS (ESI) calculated for $C_{26}H_{18}N_3O_3$ $[M+H]^+$: 420.1348, found: 420.1340.

2-(thiophen-3-ylethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1aj



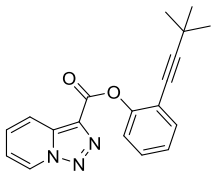
Compound **1aj** was prepared according to the **General Procedure A.** ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.87 (d, *J*=5.87 Hz, 1 H), 8.38 (d, *J*=8.44 Hz, 1 H), 7.60 (d, *J*=6.97 Hz, 1 H), 7.53 – 7.50 (m, 1 H), 7.42 – 7.39 (m, 2 H), 7.28 – 7.11 (m, 4 H), 6.85 (s, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.96, 151.05, 135.40, 132.76, 129.81, 129.49, 129.33, 128.81, 128.49, 126.05, 125.18, 122.49, 121.71, 119.31, 117.30, 116.62, 89.74, 83.91. HRMS (ESI) calculated for $C_{19}H_{12}N_3O_2S$ $[M+H]^+$: 346.0650, found: 346.0645. Overlapping signals in ^{13}C spectrum due to highly aromatic structure.

2-(cyclohex-1-en-1-ylethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ak



Compound **1ak** was prepared according to the **General Procedure A.** ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.87 (d, *J*=6.60 Hz, 1 H), 8.37 (d, *J*=8.44 Hz, 1 H), 7.57 (t, *J*=7.70 Hz, 1 H), 7.48 (d, *J*=7.34 Hz, 1 H), 7.35 – 7.30 (m, 2 H), 7.21 – 7.19 (m, 2 H), 5.86 (m, 1 H), 1.90 – 1.83 (m, 4 H), 1.43 – 1.36 (m, 4 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.86, 150.83, 135.52, 135.30, 132.65, 129.68, 128.75, 128.55, 125.98, 125.92, 122.28, 120.24, 119.39, 117.83, 116.58, 96.59, 81.65, 28.57, 25.45, 21.92, 21.13. HRMS (ESI) calculated for $C_{21}H_{18}N_3O_2$ $[M+H]^+$: 344.1399, found: 344.1389.

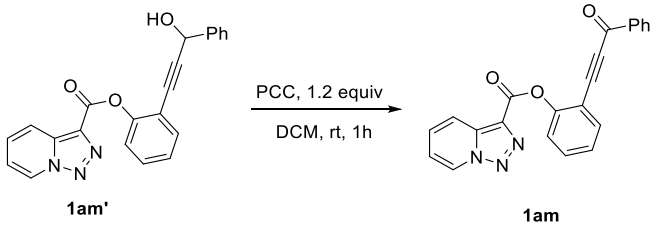
2-(3,3-dimethylbut-1-yn-1-yl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1al



Compound **1al** was prepared according to the **General Procedure A.** ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.90 (d, *J*=7.02 Hz, 1 H), 8.38 (d, *J*=8.77 Hz, 1 H), 7.60 (dd, *J*=8.33, 7.16 Hz, 1 H), 7.48 (dd, *J*=7.75, 1.32 Hz, 1 H), 7.36 – 7.32 (m, 1 H), 7.28 – 7.26 (m, 1 H), 7.23 – 7.20 (m, 2 H), 0.98 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.92, 151.16, 135.36, 132.77, 129.72, 128.67,

128.59, 126.09, 125.97, 122.20, 119.41, 118.15, 116.59, 104.01, 73.92, 30.46, 27.82. HRMS (ESI) calculated for $C_{19}H_{18}N_3O_2$ $[M+H]^+$: 320.1399, found: 320.1397.

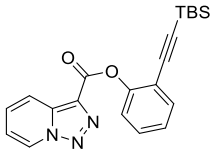
2-(3-oxo-3-phenylprop-1-yn-1-yl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1am



1am' **1am**

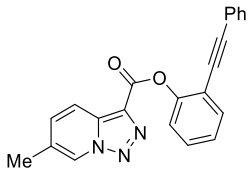
Compound **1am'** was prepared according to the **General Procedure A**, followed by oxidation using PCC to afford compound **1am**. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.88 (d, *J*=7.02 Hz, 1 H), 8.35 (d, *J*=9.06 Hz, 1 H), 8.03 (d, *J*=7.60 Hz, 2 H), 7.80 (d, *J*=6.72 Hz, 1 H), 7.61 – 7.55 (m, 2 H), 7.48 – 7.35 (m, 3 H), 7.24 – 7.17 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 177.58, 158.85, 152.26, 136.42, 135.70, 134.84, 133.91, 132.14, 130.18, 129.40, 128.29, 126.40, 126.06, 123.00, 119.30, 116.75, 114.57, 91.24, 87.64. HRMS (ESI) calculated for $C_{22}H_{14}N_3O_3$ $[M+H]^+$: 368.1035, found: 368.1030.

2-((tert-butyldimethylsilyl)ethynyl)phenyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1an



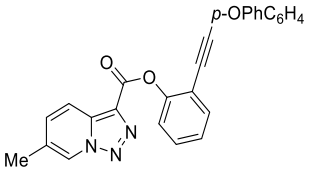
Compound **1an** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.90 (d, *J*=6.97 Hz, 1 H), 8.37 (d, *J*=8.80 Hz, 1 H), 7.61 – 7.57 (m, 2 H), 7.42 – 7.39 (m, 1 H), 7.30 – 7.20 (m, 3 H), 0.67 (s, 9 H), -0.12 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.93, 151.58, 141.62, 135.56, 133.48, 129.67, 128.64, 126.06, 122.49, 119.56, 117.67, 116.52, 100.13, 98.38. 25.70, 16.26, -5.04. HRMS (ESI) calculated for $C_{21}H_{24}N_3O_2Si$ $[M+H]^+$: 378.1638, found: 378.1632.

2-(phenylethynyl)phenyl 6-methyl-[1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ao



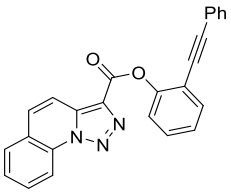
Compound **1ao** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.65 (s, 1 H), 8.26 (d, *J*=9.17 Hz, 1 H), 7.63 (dd, *J*=7.89, 1.28 Hz, 1 H), 7.44 – 7.34 (m, 3 H), 7.30 – 7.27 (m, 1 H), 7.22 – 7.19 (m, 3 H), 7.17 – 7.14 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.13, 151.23, 134.23, 132.98, 132.95, 131.45, 129.48, 128.33, 128.13, 127.23, 126.10, 123.77, 122.80, 122.61, 118.48, 117.49, 94.59, 84.48, 18.22. HRMS (ESI) calculated for $C_{22}H_{16}N_3O_2$ $[M+H]^+$: 354.1243, found: 354.1239.

2-((4-phenoxyphenyl)ethynyl)phenyl 6-methyl-[1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ap



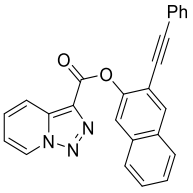
Compound **1ap** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.65 (s, 1 H), 8.27 (d, *J*=8.80 Hz, 1 H), 7.62 (d, *J*=7.34 Hz, 1 H), 7.43 – 7.26 (m, 6 H), 7.17 (d, *J*=8.44 Hz, 2 H), 7.11 (t, *J*=7.15 Hz, 1 H), 6.95 (d, *J*=7.70 Hz, 2 H), 6.77 (d, *J*=8.44 Hz, 2 H), 2.46 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.16, 157.66, 156.26, 151.16, 134.26, 133.08, 132.95, 132.85, 129.85, 129.32, 128.33, 127.24, 126.11, 123.88, 123.80, 122.60, 119.39, 118.48, 118.11, 117.61, 117.33, 94.26, 83.89, 18.23. HRMS (ESI) calculated for $C_{28}H_{20}N_3O_3$ $[M+H]^+$: 446.1505, found: 446.1495.

2-(phenylethynyl)phenyl [1,2,3]triazolo[1,5-a]quinoline-3-carboxylate 1aq



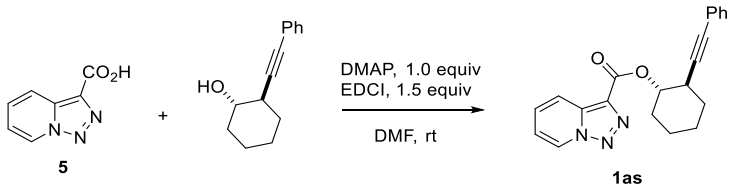
Compound **1aq** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.88 (d, *J*=8.07 Hz, 1 H), 8.21 (d, *J*=9.54 Hz, 1 H), 7.91 (d, *J*=8.07 Hz, 1 H), 7.85 (t, *J*=7.70 Hz, 1 H), 7.75 (d, *J*=9.17 Hz, 1 H), 7.70 – 7.64 (m, 2 H), 7.46 – 7.41 (m, 2 H), 7.32 – 7.29 (m, 1 H), 7.25 – 7.24 (m, 2 H), 7.18 – 7.10 (m, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.21, 151.14, 139.52, 134.06, 132.98, 131.40, 131.02, 130.90, 130.40, 129.45, 128.73, 128.28, 128.08, 127.87, 126.12, 123.96, 122.70, 122.56, 117.43, 116.50, 115.40, 94.63, 84.40. HRMS (ESI) calculated for $C_{25}H_{16}N_3O_2$ $[M+H]^+$: 390.1243, found: 390.1233.

3-(phenylethynyl)naphthalen-2-yl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1ar



Compound **1ar** was prepared according to the **General Procedure A.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.86 (d, *J*=6.97 Hz, 1 H), 8.40 (d, *J*=8.80 Hz, 1 H), 8.15 (s, 1 H), 7.84 – 7.81 (m, 3 H), 7.53 – 7.47 (m, 3 H), 7.23 – 7.13 (m, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.36, 147.67, 135.48, 133.20, 131.37, 131.21, 129.80, 128.55, 128.33, 128.09, 127.61, 127.58, 127.34, 128.45, 126.00, 122.68, 119.86, 119.36, 116.56, 116.39, 94.33, 84.90. HRMS (ESI) calculated for $C_{25}H_{16}N_3O_2$ $[M+H]^+$: 390.1243, found: 390.1234.

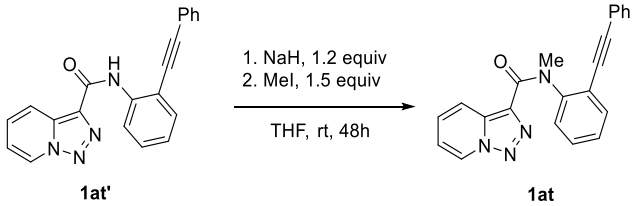
2-(phenylethynyl)cyclohexyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1as



To a stirred suspension of carboxylic acid **5** (1.0 equiv), 2-(phenylethynyl)cyclohexan-1-ol (1.2 equiv) and 4-(dimethylamino)pyridine (DMAP, 1.0 equiv) in DMF was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 1.5 equiv). The mixture was stirred at room temperature for 2 h (until a clear solution is formed). After water was added, the mixture was extracted with ethyl acetate, and the organic layer was washed with 1 M HCl, water, saturated aqueous Na_2CO_3, and brine, and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude product was purified by column chromatography to afford compound **1as**.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.77 (d, *J*=6.72 Hz, 1 H), 8.25 (d, *J*=9.06 Hz, 1 H), 7.47 (dd, *J*=8.33, 7.16 Hz, 1 H), 7.24 – 7.21 (m, 2 H), 7.14 – 7.07 (m, 4 H), 5.24 (td, *J*=9.06, 3.80 Hz, 1 H), 2.95 (td, *J*=9.35, 4.09 Hz, 1 H), 2.26 – 2.13 (m, 2 H), 1.83 – 1.75 (m, 2 H), 1.70 – 1.58 (m, 2 H), 1.53 – 1.45 (m, 1 H), 1.40 – 1.31 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.49, 134.78, 131.30, 129.38, 128.99, 127.86, 127.48, 125.71, 123.23, 119.16, 116.18, 90.03, 82.08, 75.17, 35.20, 30.48, 30.39, 23.84, 23.34. HRMS (ESI) calculated for $C_{21}H_{20}N_3O_2$ $[M+H]^+$: 346.1556, found: 346.1553.

N-methyl-N-(2-(phenylethynyl)phenyl)-[1,2,3]triazolo[1,5-a]pyridine-3-carboxamide 1at

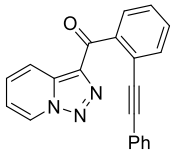


Compound **1at'** was prepared according to the **General Procedure A,** followed by methylation to form compound **1at**.

To a THF solution of **1at'** (1.0 equiv) was added NaH (95%, 1.2 equiv) under argon atmosphere at room temperature. After 2 h, MeI (1.5 equiv) was added and the reaction mixture was allowed to react until completion. Then, the mixture was concentrated under reduced pressure and the crude product was purified by column chromatography to afford compound **1at**.

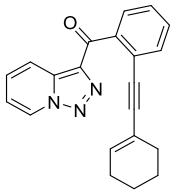
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.54 (d, *J*=6.24 Hz, 1 H), 8.23 (d, *J*=8.44 Hz, 1 H), 7.49 – 7.40 (m, 5 H), 7.28 – 7.22 (m, 5 H), 6.92 (t, *J*=6.05 Hz, 1 H), 3.57 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.68, 146.30, 135.15, 132.84, 132.34, 131.43, 129.42, 128.46, 128.36, 128.17, 127.45, 127.34, 125.05, 122.72, 122.06, 119.87, 115.78, 93.63, 85.84, 37.54. HRMS (ESI) calculated for $C_{22}H_{17}N_4O$ $[M+H]^+$: 353.1402, found: 353.1396.

[1,2,3]triazolo[1,5-a]pyridin-3-yl(2-(phenylethynyl)phenyl)methanone 1ba



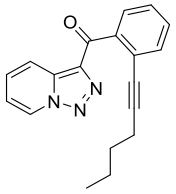
Compound **1ba** was prepared according to the **General Procedure B**. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.83 (d, *J*=7.02 Hz, 1 H), 8.52 (d, *J*=8.77 Hz, 1 H), 7.92 – 7.90 (m, 1 H), 7.69 (dd, *J*=7.60, 0.88 Hz, 1 H), 7.61 (dd, *J*=8.48, 7.31 Hz, 1 H), 7.54 – 7.46 (m, 2 H), 7.25 – 7.16 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 188.16, 140.64, 135.19, 133.16, 131.35, 130.62, 130.22, 129.55, 128.17, 128.05, 127.82, 125.72, 122.97, 122.19, 120.12, 116.89, 109.46, 93.47, 87.89. HRMS (ESI) calculated for $C_{21}H_{14}N_3O$ $[M+H]^+$: 324.1137, found: 324.1133.

[1,2,3]triazolo[1,5-a]pyridin-3-yl(2-(cyclohex-1-en-1-ylethynyl)phenyl)methanone 1bb



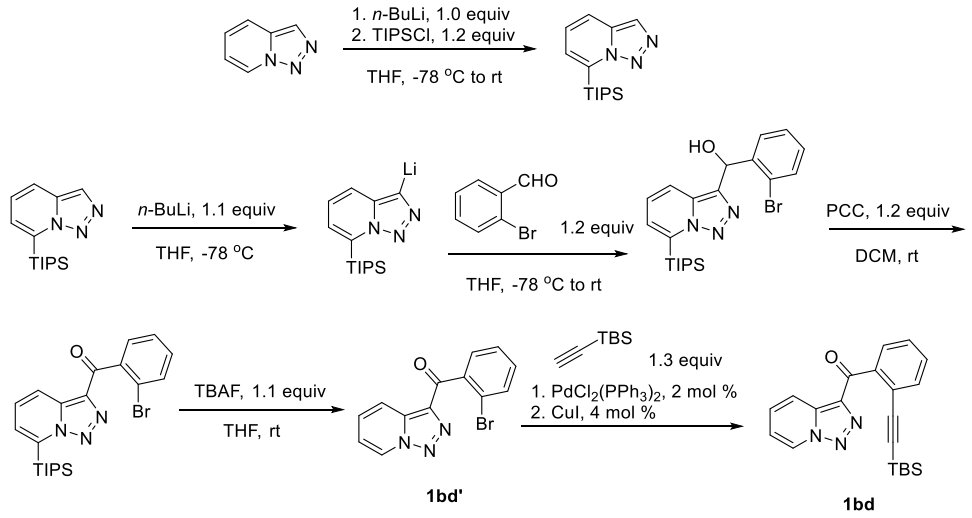
Compound **1bb** was prepared according to the **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (d, *J*=6.97 Hz, 1 H), 8.49 (d, *J*=8.80 Hz, 1 H), 7.82 (d, *J*=7.34 Hz, 1 H), 7.62 – 7.55 (m, 2 H), 7.47 – 7.39 (m, 2 H), 7.19 (t, *J*=6.79 Hz, 1 H), 5.90 (br, 1 H), 1.98 (br, 2 H), 1.87 (br, 2 H), 1.49 - 1.48 (m, 4 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 188.44, 140.48, 137.26, 135.33, 135.14, 132.95, 130.52, 130.03, 129.33, 127.28, 125.68, 122.77, 120.50, 120.18, 116.80, 95.65, 85.29, 28.52, 25.58, 22.08, 21.29. HRMS (ESI) calculated for $C_{21}H_{18}N_3O$ $[M+H]^+$: 328.1450, found: 328.1447.

[1,2,3]triazolo[1,5-a]pyridin-3-yl(2-(hex-1-yn-1-yl)phenyl)methanone 1bc



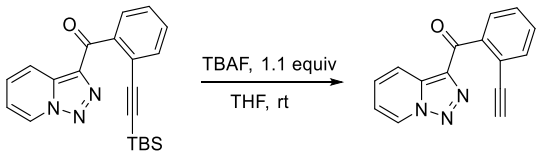
Compound **1bc** was prepared according to the **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.86 (d, *J*=6.60 Hz, 1 H), 8.51 (d, *J*=8.44 Hz, 1 H), 7.75 (d, *J*=6.97 Hz, 1 H), 7.62 (t, *J*=7.52 Hz, 1 H), 7.54 (d, *J*=7.34 Hz, 1 H), 7.46 – 7.40 (m, 2 H), 7.20 (t, *J*=6.60 Hz, 1 H), 2.21 (t, *J*=6.60 Hz, 2 H), 1.27 – 1.16 (m, 4 H), 0.72 (t, *J*=6.97 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 188.91, 140.84, 137.26, 135.14, 133.23, 130.37, 130.06, 128.92, 127.08, 125.74, 122.89, 120.24, 116.81, 95.05, 78.88, 30.33, 21.63, 19.10, 13.45. HRMS (ESI) calculated for $C_{19}H_{18}N_3O$ $[M+H]^+$: 304.1450, found: 304.1450.

[1,2,3]triazolo[1,5-a]pyridin-3-yl(2-((tert-butyldimethylsilyl)ethynyl)phenyl)methanone 1bd



Compound **1bd'** was prepared according to the **General Procedure B**, followed by Sonogashira cross-coupling reaction to form **1bd.** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.83 (d, *J*=6.97 Hz, 1 H), 8.45 (d, *J*=8.80 Hz, 1 H), 7.72 – 7.70 (m, 1 H), 7.62 – 7.59 (m, 2 H), 7.45 – 7.43 (m, 2 H), 7.18 (t, *J*=6.60 Hz, 1 H), 0.67 (s, 9 H), -0.12 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 188.83, 141.80, 137.17, 134.89, 133.24, 130.17, 128.27, 128.15, 125.68, 121.78, 119.97, 116.86, 103.41, 97.50, 25.66, 16.26, -5.14. HRMS (ESI) calculated for $C_{12}H_{24}N_3OSi$ $[M+H]^+$: 362.1689, found: 362.1681.

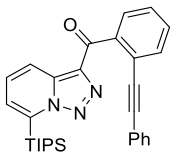
[1,2,3]triazolo[1,5-a]pyridin-3-yl(2-ethynylphenyl)methanone 1be



To a THF solution of compound **1bd** was added TBAF (1.1 equiv, 1M solution in THF), and the reaction mixture was stirred at room temperature for 1 h. Upon completion, the mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography to afford compound **1be**.

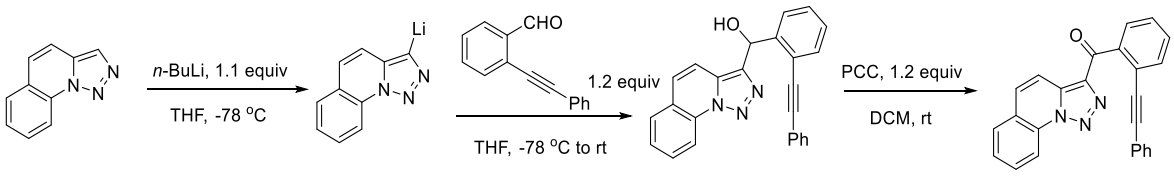
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.87 (d, *J*=6.60 Hz, 1 H), 8.56 (d, *J*=8.80 Hz, 1 H), 7.94 – 7.92 (m, 1 H), 7.69 – 7.62 (m, 2 H), 7.51 – 7.49 (m, 2 H), 7.22 (t, *J*=6.79 Hz, 1 H), 3.14 (s, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 187.75, 140.92, 136.93, 135.49, 134.27, 130.65, 130.39, 129.89, 128.27, 125.83, 121.06, 120.39, 117.03, 81.81, 81.24. HRMS (ESI) calculated for $C_{15}H_{10}N_3O$ $[M+H]^+$: 248.0824, found: 248.0818.

(2-(phenylethynyl)phenyl)(7-(triisopropylsilyl)-[1,2,3]triazolo[1,5-a]pyridin-3-yl)methanone 1bf



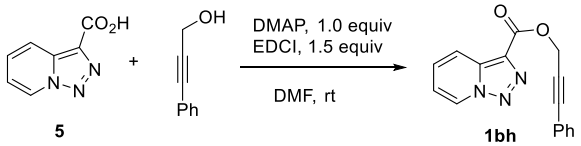
Compound **1bf** was prepared according to the **General Procedure B**. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.57 (d, *J*=8.44 Hz, 1 H), 7.91 (d, *J*=7.34 Hz, 1 H), 7.68 (d, *J*=7.34 Hz, 1 H), 7.58 (t, *J*=7.70 Hz, 1 H), 7.53 – 7.47 (m, 2 H), 7.32 (d, *J*=6.60 Hz, 1 H), 7.20 – 7.16 (m, 5 H), 1.77 (quin, *J*=7.43 Hz, 3 H), 1.09 (d, *J*=7.70 Hz, 18 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 188.58, 141.12, 139.99, 136.65, 135.20, 133.03, 131.39, 130.40, 129.40, 129.03, 128.09, 128.02, 127.89, 125.73, 123.08, 122.22, 120.21, 93.52, 88.06, 18.60, 11.48. HRMS (ESI) calculated for $C_{30}H_{34}N_3OSi$ $[M+H]^+$: 480.2471, found: 480.2467.

[1,2,3]triazolo[1,5-a]quinolin-3-yl(2-(phenylethynyl)phenyl)methanone 1bg



Compound **1bg** was prepared according to the **General Procedure B**. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.79 (d, *J*=8.48 Hz, 1 H), 8.30 (d, *J*=9.06 Hz, 1 H), 7.97 (d, *J*=7.02 Hz, 1 H), 7.89 (d, *J*=8.18 Hz, 1 H), 7.84 – 7.78 (m, 2 H), 7.71 (d, *J*=7.31 Hz, 1 H), 7.66 – 7.62 (m, 1 H), 7.56 – 7.48 (m, 2 H), 7.26 – 7.25 (m, 2 H), 7.18 – 7.13 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 188.49, 140.59, 138.72, 133.68, 133.21, 131.35, 131.20, 131.14, 130.88, 130.72, 129.75, 128.56, 128.12, 127.99, 127.79, 127.70, 124.21, 122.94, 122.31, 116.37, 116.11, 93.57, 87.96. HRMS (ESI) calculated for $C_{25}H_{16}N_3O$ $[M+H]^+$: 374.1293, found: 374.1287.

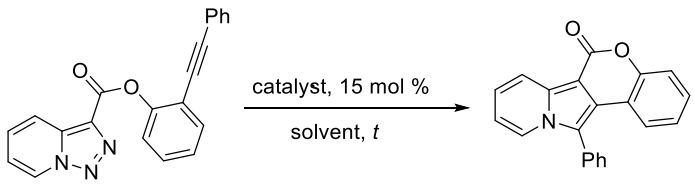
3-phenylprop-2-yn-1-yl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 1bh



Compound **1bh** was prepared according to the **General Procedure A**. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.83 (d, *J*=6.60 Hz, 1 H), 8.28 (d, *J*=8.44 Hz, 1 H), 7.56 (t, *J*=7.52 Hz, 1 H), 7.44 (d, *J*=5.87 Hz, 2 H), 7.29 – 7.28 (m, 3 H), 7.16 (t, *J*=6.42 Hz, 1 H), 5.27 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.49, 135.15, 131.80, 129.49, 128.68, 128.18, 125.92, 122.00, 119.20, 116.46, 86.75, 82.69, 53.17. HRMS (ESI) calculated for $C_{16}H_{12}N_3O_2$ $[M+H]^+$: 278.0930, found: 278.0929.

Part II. Cu-Catalyzed Intramolecular Transannulation Reaction

1. Optimization of the Cu-catalyzed Transannulation Reaction Conditions

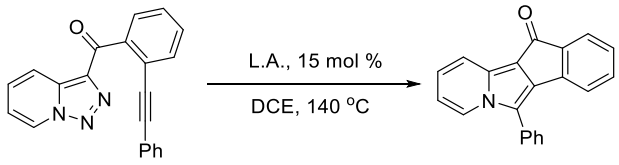


1aa **2aa**

Entry	Catalyst	Loading	Solvent	Temperature/^{o}C	GC Yield/%
1	**CuBr SMe_2**	**15 mol %**	**DCE**	**140**	**85**
2	$Cu(MeCN)_4PF_6$	15 mol %	DCE	140	48
3	CuOAc	15 mol %	DCE	140	56
4	CuCl	15 mol %	DCE	140	73
5	CuBr	15 mol %	DCE	140	67
6	$[Cu(OTf)]_2$ Bz	15 mol %	DCE	140	26
7	$CuBr_2$	15 mol %	DCE	140	43
8	CuBr SMe_2	15 mol %	PhCl	140	75
9	CuBr SMe_2	15 mol %	$PhCF_3$	140	74
10	CuBr SMe_2	15 mol %	PhMe	140	63
11	CuBr SMe_2	15 mol %	DCE	130	81
12	CuBr SMe_2	15 mol %	DCE	150	86
13	CuBr SMe_2	10 mol %	DCE	140	78
14	$In(OTf)_3$	15 mol %	DCE	140	10
15	none	--	DCE	140	0

1aa (0.05 mmol) and catalyst (15 mol %) were dissolved in solvent (0.5 mL) and heated at the indicated temperature

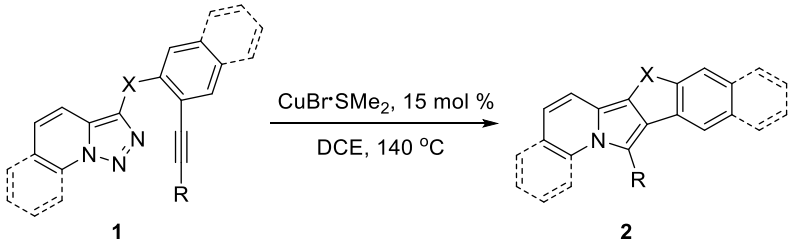
2. Employment of Lewis Acid in the Transannulation Reaction



1ba **2ba**

Entry	Catalyst, 15 mol %	GC Yield/%
1	**TIPSOTf**	**30**
2	$AlCl_3$	decompose
3	$HfCl_4$	decompose
4	$ZnCl_2$	<10, decompose
5	BF_3 Et_2O	decompose
6	$Eu(OTf)_3$	48
7	**$In(OTf)_3$**	**64**
8	$Sm(OTf)_3$	57
9	$La(OTf)_3$	39
10	$Y(OTf)_3$	<20
11	$Sc(OTf)_3$	decompose
12	$Yb(OTf)_3$	20
13	$Zn(OTf)_2$	<20

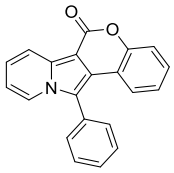
3. Cu-Catalyzed Intramolecular Transannulation Reaction



1 2

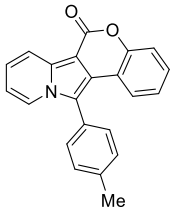
General Procedure: An oven-dried 3.0 mL V-vial equipped with a stirring bar was charged with CuBr•SMe_2 (15 mol %), alkynylpyridotriazole **1** (0.2 mmol) and DCE (2 mL) under N_2 atmosphere. The reaction vessel was capped with Mininert syringe valve and the reaction mixture was stirred at 140 °C. Upon completion the reaction mixture was cooled to room temperature, concentrated under reduced pressure, and the crude product was purified by column chromatography to afford the corresponding transannulation product.

12-phenyl-6H-chromeno[3,4-a]indolizin-6-one 2aa



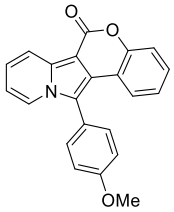
Was prepared according to the general procedure in 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.37 (d, *J*=8.80 Hz, 1 H), 7.94 (d, *J*=6.60 Hz, 1 H), 7.66 – 7.60 (m, 3 H), 7.57 – 7.56 (m, 2 H), 7.36 – 7.34 (m, 2 H), 7.31 – 7.28 (m, 1 H), 7.21 (t, *J*=7.70 Hz, 1 H), 6.98 (t, *J*=7.52 Hz, 1 H), 6.87 (t, *J*=6.79 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.92, 152.43, 134.40, 131.45, 130.06, 129.89, 129.77, 128.58, 123.74, 123.46, 123.31, 122.52, 119.46, 118.95, 117.62, 116.67, 114.64, 96.85. HRMS (ESI) calculated for $C_{21}H_{13}NO_2$ $[M+H]^+$: 312.1025, found: 312.1016. Overlapping signals in ^{13}C spectrum due to highly aromatic structure.

12-(p-tolyl)-6H-chromeno[3,4-a]indolizin-6-one 2ab



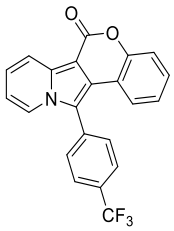
Was prepared according to the general procedure in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.37 (d, *J*=8.77 Hz, 1 H), 7.95 (d, *J*=7.02 Hz, 1 H), 7.46 - 7.27 (m, 7 H), 7.23 - 7.19 (m, 1 H), 6.99 (t, *J*=7.31 Hz, 1 H), 6.86 (t, *J*=6.72 Hz, 1 H), 2.52 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.00, 152.39, 139.82, 134.35, 131.23, 130.60, 128.49, 126.89, 123.79, 123.42, 123.38, 122.41, 119.42, 119.07, 117.59, 116.78, 114.54, 96.72, 21.52. HRMS (ESI) calculated for $C_{22}H_{15}NO_2$ $[M+H]^+$: 326.1181, found: 326.1174.

12-(4-methoxyphenyl)-6H-chromeno[3,4-a]indolizin-6-one 2ac



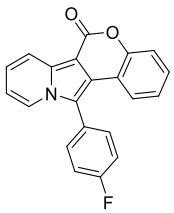
Was prepared according to the general procedure in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.34 (d, *J*=8.77 Hz, 1 H), 7.93 (d, *J*=7.02 Hz, 1 H), 7.47 – 7.44 (m, 2 H), 7.38 – 7.27 (m, 3 H), 7.22 – 7.14 (m, 3 H), 7.01 – 6.97 (m, 1 H), 6.86 (td, *J*=6.87, 1.17 Hz, 1 H), 3.94 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 160.55, 158.97, 152.39, 134.28, 132.75, 128.46, 123.74, 123.36, 123.33, 122.51, 121.78, 119.38, 118.82, 117.57, 116.81, 115.30, 114.53, 96.63, 55.39. HRMS (ESI) calculated for $C_{22}H_{15}NO_3$ $[M+H]^+$: 342.1130, found: 342.1124.

12-(4-(trifluoromethyl)phenyl)-6H-chromeno[3,4-a]indolizin-6-one 2ad



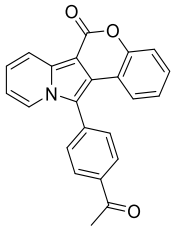
Was prepared according to the general procedure in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.35 (d, *J*=8.44 Hz, 1 H), 7.96 – 7.88 (m, 3 H), 7.77 – 7.76 (m, 2 H), 7.33 – 7.29 (m, 3 H), 7.24 – 7.21 (m, 1 H), 7.04 – 6.98 (m, 1 H), 6.93 – 6.87 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.64, 152.46, 134.77, 134.11, 132.09, 131.76 (q, *J*=34.0 Hz), 129.00, 126.89 (q, *J*=3.78 Hz), 123.90, 123.82 (q, *J*=272.2 Hz), 123.62, 123.14, 122.97, 119.64, 117.84, 117.03, 116.19, 115.06, 97.24. HRMS (ESI) calculated for $C_{22}H_{12}F_3NO_2$ $[M+H]^+$: 380.0898, found: 380.0893. Overlapping signals in ^{13}C spectrum due to highly aromatic structure.

12-(4-fluorophenyl)-6H-chromeno[3,4-a]indolizin-6-one 2ae



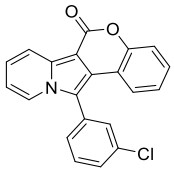
Was prepared according to the general procedure in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.34 (d, *J*=8.80 Hz, 1 H), 7.90 (d, *J*=6.97 Hz, 1 H), 7.58 – 7.55 (m, 2 H), 7.37 – 7.28 (m, 5 H), 7.21 (t, *J*=7.70 Hz, 1 H), 7.00 (t, *J*=7.15 Hz, 1 H), 6.88 (t, *J*=6.60 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.47 (d, *J*=249.5 Hz), 158.79, 152.43, 134.45, 133.62, 133.55, 128.73, 126.04 (d, *J*=3.78 Hz), 123.68, 123.50, 123.15, 122.86, 119.49, 117.71, 117.62, 117.20 (d, *J*=21.4 Hz), 116.50, 114.80, 96.85. HRMS (ESI) calculated for $C_{21}H_{12}FNO_2$ $[M+H]^+$: 330.0930, found: 330.0929.

2-(4-acetylphenyl)-6H-chromeno[3,4-a]indolizin-6-one 2af



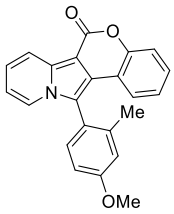
Was prepared according to the general procedure in 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.38 (d, *J*=8.80 Hz, 1 H), 8.23 (d, *J*=8.07 Hz, 2 H), 7.97 (d, *J*=6.97 Hz, 1 H), 7.73 (d, *J*=8.07 Hz, 2 H), 7.35 – 7.31 (m, 3 H), 7.27 – 7.24 (m, 1 H), 6.99 (t, *J*=7.52 Hz, 1 H), 6.91 (t, *J*=6.79 Hz, 1 H), 2.74 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 197.35, 158.71, 152.49, 137.84, 135.02, 134.83, 131.80, 129.70, 128.98, 123.92, 123.59, 123.06, 119.70, 117.84, 117.55, 116.30, 115.03, 97.33, 26.76. HRMS (ESI) calculated for $C_{23}H_{15}NO_3$ $[M+H]^+$: 354.1130, found: 354.1126.

12-(3-chlorophenyl)-6H-chromeno[3,4-a]indolizin-6-one 2ag



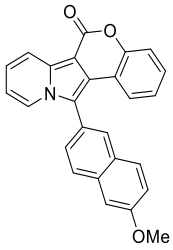
Was prepared according to the general procedure in 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.39 (d, *J*=8.48 Hz, 1 H), 7.94 (d, *J*=6.72 Hz, 1 H), 7.60 – 7.59 (m, 3 H), 7.49 (br, 1 H), 7.38 – 7.33 (m, 3 H), 7.28 – 7.24 (m, 1 H), 7.03 (t, *J*=6.87 Hz, 1 H), 6.92 (t, *J*=6.72 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.79, 152.46, 135.71, 134.60, 131.95, 131.48, 131.25, 130.06, 129.82, 128.89, 123.82, 123.64, 123.61, 123.17, 122.97, 119.60, 117.79, 117.16, 116.30, 114.97, 97.03. HRMS (ESI) calculated for $C_{21}H_{12}ClNO_2$ $[M+H]^+$: 346.0635, found: 346.0630.

12-(4-methoxy-2-methylphenyl)-6H-chromeno[3,4-a]indolizin-6-one 2ah



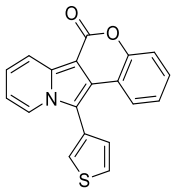
Was prepared according to the general procedure in 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.40 (d, *J*=8.80 Hz, 1 H), 7.71 (d, *J*=6.60 Hz, 1 H), 7.38 – 7.36 (m, 1 H), 7.32 – 7.29 (m, 2 H), 7.27 – 7.24 (m, 1 H), 7.19 (d, *J*=7.70 Hz, 1 H), 7.03 – 6.96 (m, 3 H), 6.89 (t, *J*=6.60 Hz, 1 H), 3.93 (s, 3 H), 2.00 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.90, 159.05, 152.45, 141.26, 134.37, 133.20, 128.46, 123.67, 123.55, 123.33, 123.27, 122.84, 121.11, 119.49, 118.09, 117.52, 116.97, 116.47, 114.64, 112.59, 96.60, 55.31, 19.49. HRMS (ESI) calculated for $C_{23}H_{17}NO_3$ $[M+H]^+$: 356.1287, found: 356.1279.

12-(6-methoxynaphthalen-2-yl)-6H-chromeno[3,4-a]indolizin-6-one 2ai



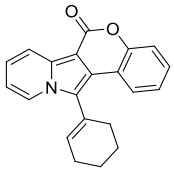
Was prepared according to the general procedure in 81% yield. ^{1}H NMR (500 MHz, DMSO-*d*6) δ ppm 8.25 (d, *J*=8.44 Hz, 1 H), 8.18 – 8.16 (m, 2 H), 8.12 (d, *J*=8.44 Hz, 1 H), 7.94 (d, *J*=8.80 Hz, 1 H), 7.64 (d, *J*=8.07 Hz, 1 H), 7.51 (s, 1 H), 7.45 (t, *J*=7.52 Hz, 1 H), 7.38 – 7.35 (m, 2 H), 7.28 – 7.26 (m, 2 H), 7.09 (t, *J*=6.42 Hz, 1 H), 7.01 (t, *J*=6.60 Hz, 1 H), 3.94 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-*d*6) δ ppm 158.91, 158.04, 152.36, 135.27, 134.25, 131.41, 130.36, 129.49, 129.35, 129.07, 129.01, 125.35, 124.88, 124.54, 124.32, 123.74, 122.02, 119.96, 119.74, 118.70, 117.88, 116.76, 115.95, 106.62, 96.07, 55.90. HRMS (ESI) calculated for $C_{26}H_{17}NO_3$ $[M+H]^+$: 392.1287, found: 292.1277.

12-(thiophen-3-yl)-6H-chromeno[3,4-a]indolizin-6-one 2aj



Was prepared according to the general procedure in 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.34 (d, *J*=8.44 Hz, 1 H), 7.98 (d, *J*=5.87 Hz, 1 H), 7.67 (br, 2 H), 7.43 (d, *J*=6.97 Hz, 1 H), 7.33 – 7.29 (m, 3 H), 7.21 – 7.19 (m, 1 H), 7.05 – 7.02 (m, 1 H), 6.90 – 6.87 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.86, 152.45, 134.64, 129.81, 129.18, 128.70, 128.15, 127.89, 123.77, 123.67, 123.58, 123.55, 123.40, 119.43, 117.64, 116.65, 114.71, 113.58, 96.85. HRMS (ESI) calculated for $C_{19}H_{11}NO_2S$ $[M+H]^+$: 318.0589, found: 318.0584.

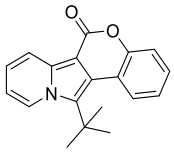
12-(cyclohex-1-en-1-yl)-6H-chromeno[3,4-a]indolizin-6-one 2ak



Was prepared according to the general procedure in 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.31 (d, *J*=8.77 Hz, 1 H), 8.08 (d, *J*=7.02 Hz, 1 H), 7.95 (d, *J*=7.60 Hz, 1 H), 7.37 – 7.35 (m, 2 H), 7.24 – 7.18 (m, 2 H), 6.94 (td, *J*=6.87, 0.88 Hz, 1 H), 6.21 – 6.19 (m, 1 H), 2.38 – 2.37 (m, 2 H), 2.29 -2.28 (m, 2 H), 1.95 – 1.85 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.03, 152.33,

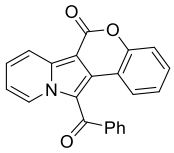
135.71, 133.94, 128.27, 128.20, 123.83, 123.67, 123.29, 122.91, 121.13, 120.96, 119.49, 117.60, 117.08, 114.42, 96.25, 27.96, 25.85, 22.86, 21.85. HRMS (ESI) calculated for $C_{21}H_{17}NO_2$ $[M+H]^+$: 316.1338, found: 316.1330.

12-(tert-butyl)-6H-chromeno[3,4-a]indolizin-6-one



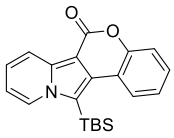
Was prepared according to the general procedure in 41% yield. ^{1}H NMR (500 MHz, acetone-*d*6) δ ppm 8.97 (d, *J*=7.34 Hz, 1 H), 8.37 (d, *J*=8.80 Hz, 1 H), 8.19 – 8.17 (m, 1 H), 7.44 – 7.41 (m, 1 H), 7.34 – 7.30 (m, 3 H), 7.06 – 7.03 (m, 1 H), 1.83 (s, 9 H). ^{13}C NMR (126 MHz, acetone-*d*6) δ ppm 157.84, 152.28, 135.05, 129.63, 128.66, 128.23, 127.86, 125.74, 124.55, 122.82, 119.02, 117.74, 117.45, 113.76, 97.95, 34.07, 28.94. HRMS (ESI) calculated for $C_{19}H_{17}NO_2$ $[M+H]^+$: 292.1338, found: 292.1338.

12-benzoyl-6H-chromeno[3,4-a]indolizin-6-one 2am



Was prepared according to the general procedure in 50% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.25 (d, *J*=6.97 Hz, 1 H), 8.56 (d, *J*=8.80 Hz, 1 H), 7.85 (d, *J*=7.70 Hz, 2 H), 7.59 – 7.56 (m, 1 H), 7.52 (t, *J*=7.70 Hz, 1 H), 7.44 – 7.41 (m, 2 H), 7.35 – 7.33 (m, 1 H), 7.30 – 7.28 (m, 1 H), 7.13 (t, *J*=6.79 Hz, 1 H), 6.97 (d, *J*=8.07 Hz, 1 H), 6.75 (t, *J*=7.52 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 187.69, 158.23, 153.11, 139.06, 137.30, 133.48, 130.40, 129.87, 129.83, 129.17, 127.92, 127.70, 127.56, 123.14, 119.50, 117.72, 117.36, 116.53, 114.89, 96.06. HRMS (ESI) calculated for $C_{22}H_{13}NO_3$ $[M+H]^+$: 340.0974, found: 340.0970.

12-(tert-butyldimethylsilyl)-6H-chromeno[3,4-a]indolizin-6-one 2an

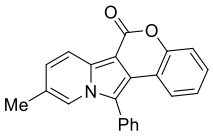


An oven-dried 3.0 mL V-vial equipped with a stirring bar was charged with $[Rh^*CpCl_2]_2$ (5 mol %), alkynylpyridotriazole **1** (0.2 mmol) and mesitylene (2 mL) under N_2 atmosphere. The reaction vessel was capped with Mininert syringe valve and the reaction mixture was stirred at 140 °C. Upon completion the reaction mixture was cooled to room temperature, concentrated under reduced pressure, and the crude product was purified by column chromatography to afford the transannulation products in 67% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.54 (d, *J*=6.97 Hz, 1 H), 8.49 (d, *J*=8.80 Hz, 1 H), 8.11 (d, *J*=8.07 Hz, 1 H), 7.41 (d, *J*=3.67 Hz, 2 H), 7.33 – 7.30 (m, 1 H), 7.25 – 7.22 (m, 1 H), 6.95 (t,

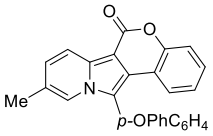
J=6.79 Hz, 1 H), 1.20 (s, 9 H), 0.55 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.93, 152.39, 139.11, 136.30, 128.93, 128.59, 126.89, 124.27, 122.46, 119.90, 117.81, 117.37, 117.15, 114.14, 99.96, 27.58, 20.35, -1.37. HRMS (ESI) calculated for $C_{21}H_{23}NO_2Si$ $[M+H]^+$: 350.1576, found: 350.1570.

9-methyl-12-phenyl-6H-chromeno[3,4-a]indolizin-6-one 2ao



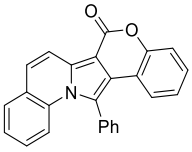
Was prepared according to the general procedure in 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.27 (d, *J*=9.17 Hz, 1 H), 7.71 (s, 1 H), 7.68 – 7.61 (m, 3 H), 7.56 (d, *J*=6.24 Hz, 2 H), 7.36 – 7.27 (m, 3 H), 7.08 (d, *J*=9.17 Hz, 1 H), 6.97 (t, *J*=7.52 Hz, 1 H), 2.28 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.03, 152.45, 133.19, 131.57, 130.36, 129.92, 129.73, 128.42, 126.61, 124.67, 123.70, 123.44, 121.21, 118.88, 118.63, 117.67, 116.91, 109.58, 96.61, 18.63. HRMS (ESI) calculated for $C_{22}H_{16}NO_2$ $[M+H]^+$: 326.1181, found: 326.1177.

9-methyl-12-(4-phenoxyphenyl)-6H-chromeno[3,4-a]indolizin-6-one 2ap



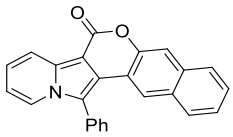
Was prepared according to the general procedure in 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.24 (d, *J*=9.17 Hz, 1 H), 7.73 (s, 1 H), 7.50 (d, *J*=8.44 Hz, 2 H), 7.47 – 7.44 (m, 2 H), 7.38 – 7.28 (m, 3 H), 7.25 – 7.20 (m, 5 H), 7.06 – 7.00 (m, 2 H), 2.29 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.00, 155.91, 152.44, 133.16, 133.11, 130.08, 128.42, 126.58, 124.66, 124.41, 124.30, 123.66, 123.46, 122.57, 121.20, 120.07, 119.10, 118.83, 118.04, 117.68, 116.95, 96.52, 18.66. HRMS (ESI) calculated for $C_{28}H_{20}NO_3$ $[M+H]^+$: 418.1443, found: 418.1441.

14-phenyl-6H-chromeno[3',4':3,4]pyrrolo[1,2-a]quinolin-6-one 2aq



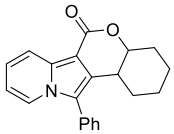
PhCl was used as solvent and heated at 180 ºC to afford the product in 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.45 (d, *J*=9.17 Hz, 1 H), 7.79 (d, *J*=7.70 Hz, 1 H), 7.71 – 7.69 (m, 3 H), 7.63 – 7.62 (m, 2 H), 7.54 (d, *J*=9.17 Hz, 1 H), 7.39 – 7.35 (m, 3 H), 7.28 – 7.27 (m, 1 H), 7.19 (t, *J*=7.70 Hz, 1 H), 6.92 – 6.92 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.21, 152.23, 134.37, 134.08, 133.80, 131.58, 130.18, 130.08, 129.33, 128.24, 128.06, 126.05, 125.21, 124.98, 123.61, 123.43, 122.00, 117.92, 117.68, 117.62, 116.99, 99.56. HRMS (ESI) calculated for $C_{25}H_{15}NO_2$ $[M+H]^+$: 362.1181, found: 362.1181.

13-phenyl-7H-benzo[6,7]chromeno[3,4-a]indolizin-7-one 2ar



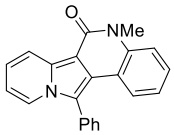
Was prepared according to the general procedure in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.39 (d, *J*=9.06 Hz, 1 H), 7.98 (d, *J*=7.02 Hz, 1 H), 7.82 (s, 1 H), 7.77 (d, *J*=8.18 Hz, 1 H), 7.73 – 7.68 (m, 4 H), 7.65 – 7.63 (m, 2 H), 7.50 (d, *J*=8.18 Hz, 1 H), 7.43 – 7.40 (m, 1 H), 7.33 – 7.30 (m, 1 H), 7.25 – 7.21 (m, 1 H), 6.88 (td, *J*=6.87, 1.17 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.91, 150.46, 134.78, 133.05, 131.49, 130.07, 130.00, 129.96, 129.71, 127.87, 127.14, 126.60, 124.97, 123.70, 123.39, 123.02, 122.22, 119.61, 119.52, 117.00, 114.67, 113.30, 96.88. HRMS (ESI) calculated for $C_{25}H_{15}NO_2$ $[M+H]^+$: 362.1181, found: 362.1168.

12-phenyl-1,2,3,4,4a,12b-hexahydro-6H-chromeno[3,4-a]indolizin-6-one 2as



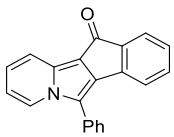
Was prepared according to the general procedure in 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.18 (d, *J*=8.80 Hz, 1 H), 7.76 (d, *J*=6.97 Hz, 1 H), 7.52 – 7.48 (m, 3 H), 7.38 (br, 2 H), 7.12 – 7.09 (m, 1 H), 6.67 (t, *J*=6.60 Hz, 1 H), 4.13 (td, *J*=11.19, 4.03 Hz, 1 H), 2.99 (td, *J*=11.46, 3.48 Hz, 1 H), 1.71 (qd, *J*=12.29, 3.85 Hz, 1 H), 1.58 – 1.56 (m, 1 H), 1.36 – 1.18 (m, 2 H), 1.00 (qd, *J*=12.78, 3.12 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.23, 135.11, 131.31, 130.55, 129.52, 129.00, 123.43, 123.24, 120.53, 119.02, 113.02, 99.38, 83.32, 38.66, 31.67, 27.86, 25.17, 24.30. HRMS (ESI) calculated for $C_{21}H_{19}NO_2$ $[M+H]^+$: 318.1494, found: 318.1489.

5-methyl-12-phenylindolizino[1,2-c]quinolin-6(5H)-one 2at



Was prepared according to the general procedure in 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.63 (d, *J*=8.80 Hz, 1 H), 7.91 (d, *J*=6.97 Hz, 1 H), 7.66 – 7.55 (m, 6 H), 7.39 – 7.39 (m, 2 H), 7.17 – 7.14 (m, 1 H), 6.95 (dt, *J*=7.89, 4.13 Hz, 1 H), 6.82 (t, *J*=6.42 Hz, 1 H), 3.81 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.27, 139.01, 132.23, 131.73, 131.51, 129.87, 129.37, 127.78, 124.40, 122.40, 122.30, 121.30, 120.97, 120.05, 117.77, 117.61, 115.06, 114.03, 102.72, 28.67. HRMS (ESI) calculated for $C_{22}H_{16}N_2O$ $[M+H]^+$: 325.1341, found: 325.1332.

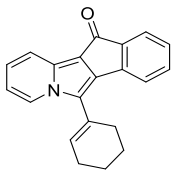
6-phenyl-11H-indeno[2,1-a]indolizin-11-one 2ba



Was prepared according to the general procedure in 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.98 (d, *J*=6.97 Hz, 1 H), 7.70 (d, *J*=8.80 Hz, 1 H), 7.62 – 7.48 (m, 6 H), 7.18 – 7.15 (m, 3

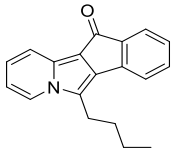
H), 7.04 (t, *J*=7.52 Hz, 1 H), 6.56 (t, *J*=6.60 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 185.16, 142.48, 138.76, 135.48, 132.43, 132.21, 129.59, 129.42, 129.36, 128.92, 128.03, 125.55, 124.93, 123.49, 120.65, 120.50, 118.96, 113.56, 112.83. HRMS (ESI) calculated for $C_{21}H_{13}NO$ $[M+H]^+$: 296.1075, found: 296.1074.

6-(cyclohex-1-en-1-yl)-11H-indeno[2,1-a]indolizin-11-one 2bb



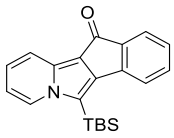
Was prepared according to the general procedure in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.78 (d, *J*=7.02 Hz, 1 H), 7.64 (d, *J*=8.77 Hz, 1 H), 7.53 (d, *J*=7.31 Hz, 1 H), 7.29 – 7.22 (m, 2 H), 7.16 – 7.13 (m, 1 H), 7.01 – 6.97 (m, 1 H), 6.57 (t, *J*=6.43 Hz, 1 H), 6.14 (br, 1 H), 2.34 – 2.32 (m, 4 H), 1,91 – 1.80 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 185.04, 142.66, 139.11, 133.96, 133.36, 132.08, 132.01, 127.61, 127.42, 125.68, 124.97, 123.39, 122.98, 120.93, 118.85, 112.84, 112.40, 28.03, 25.63, 22.73, 21.96. HRMS (ESI) calculated for $C_{21}H_{17}NO$ $[M+H]^+$: 300.1388, found: 300.1386.

6-butyl-11H-indeno[2,1-a]indolizin-11-one 2bc



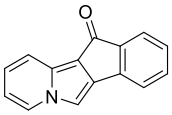
Was prepared according to the general procedure in 73% yield. ^{1}H NMR (500 MHz, acetone-*d*6) δ ppm 8.12 (d, *J*=6.97 Hz, 1 H), 7.56 (d, *J*=8.80 Hz, 1 H), 7.48 (d, *J*=7.34 Hz, 1 H), 7.43 (d, *J*=7.34 Hz, 1 H), 7.36 (t, *J*=7.34 Hz, 1 H), 7.19 (t, *J*=7.52 Hz, 1 H), 7.15 – 7.12 (m, 1 H), 6.77 (t, *J*=6.42 Hz, 1 H), 3.11 (t, *J*=7.52 Hz, 2 H), 1.73 – 1.67 (m, 2 H), 1.50 – 1.42 (m, 2 H), 0.94 (t, *J*=7.34 Hz, 3 H). ^{13}C NMR (126 MHz, acetone-*d*6) δ ppm 183.62, 142.61, 139.38, 133.91, 132.30, 131.72, 127.44, 125.61, 124.96, 122.82, 121.17, 117.98, 112.65, 29.63, 24.19, 22.16, 13.26. HRMS (ESI) calculated for $C_{19}H_{17}NO$ $[M+H]^+$: 276.1388, found: 276.1391.

6-(tert-butyldimethylsilyl)-11H-indeno[2,1-a]indolizin-11-one 2bd



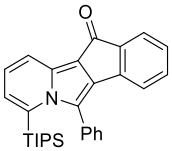
Was prepared according to the general procedure in 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.12 (d, *J*=7.34 Hz, 1 H), 7.72 (d, *J*=8.44 Hz, 1 H), 7.55 (d, *J*=7.34 Hz, 1 H), 7.48 (d, *J*=7.70 Hz, 1 H), 7.30 – 7.27 (m, 1 H), 7.17 (t, *J*=7.34 Hz, 1 H), 7.05 (t, *J*=7.52 Hz, 1 H), 6.57 (t, *J*=6.60 Hz, 1 H), 1.03 (s, 9 H), 0.57 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 185.07, 148.57, 142.70, 139.74, 135.28, 132.03, 129.36, 127.80, 125.68, 123.25, 122.89, 119.59, 118.72, 115.86, 112.50, 26.50, 19.45, -2.63. HRMS (ESI) calculated for $C_{21}H_{23}NOSi$ $[M+H]^+$: 334.1627, found: 334.1624.

11H-indeno[2,1-a]indolizin-11-one 2be



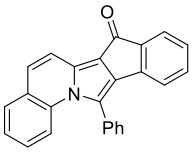
Was prepared according to the general procedure in 23% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.83 (d, *J*=6.97 Hz, 1 H), 7.67 (d, *J*=9.17 Hz, 1 H), 7.54 (d, *J*=7.34 Hz, 1 H), 7.32 – 7.27 (m, 2 H), 7.18 (t, *J*=7.34 Hz, 1 H), 7.09 (s, 1 H), 7.05 – 7.01 (m, 1 H), 6.60 (t, *J*=6.79 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 185.14, 142.43, 138.49, 137.86, 132.37, 128.11, 127.62, 125.48, 123.52, 121.22, 118.93, 113.93, 112.89, 107.22. HRMS (ESI) calculated for $C_{15}H_9NO$ $[M+H]^+$: 220.0762, found: 220.0765.

6-phenyl-4-(triisopropylsilyl)-11H-indeno[2,1-a]indolizin-11-one 2bf



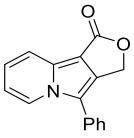
Was prepared according to the general procedure in 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.78 (d, *J*=8.07 Hz, 1 H), 7.53 – 7.47 (m, 6 H), 7.11 – 7.09 (m, 2 H), 7.01 – 6.98 (m, 2 H), 6.84 – 6.83 (m, 1 H), 0.96 (d, *J*=7.34 Hz, 18 H), 0.76 (dt, *J*=14.76, 7.47 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 185.48, 142.39, 141.12, 139.14, 137.81, 135.14, 132.58, 132.17, 130.81, 129.03, 128.59, 127.84, 126.92, 125.05, 123.43, 123.30, 120.00, 119.87, 114.37, 19.30, 13.16. HRMS (ESI) calculated for $C_{30}H_{33}NOSi$ $[M+H]^+$: 452.2410, found: 452.2400.

12-phenyl-7H-indeno[2',1':3,4]pyrrolo[1,2-a]quinolin-7-one 2bg



Was prepared according to the general procedure in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.72 (d, *J*=9.17 Hz, 1 H), 7.66 – 7.57 (m, 7 H), 7.37 (d, *J*=9.17 Hz, 1 H), 7.32 (d, *J*=8.80 Hz, 1 H), 7.28 – 7.26 (m, 1 H), 7.18 – 7.12 (m, 3 H), 6.90 (d, *J*=6.97 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 186.43, 142.00, 139.36, 135.25, 134.83, 133.47, 132.72, 131.36, 130.05, 129.20, 129.11, 128.38, 127.74, 126.80, 125.39, 124.24, 124.21, 123.77, 120.43, 117.67, 117.33, 116.24. HRMS (ESI) calculated for $C_{25}H_{15}NO$ $[M+H]^+$: 346.1232, found: 346.1228.

4-phenyl-1H,3H-furo[3,4-a]indolizin-1-one 2bh



Was prepared according to the general procedure in 40% yield.

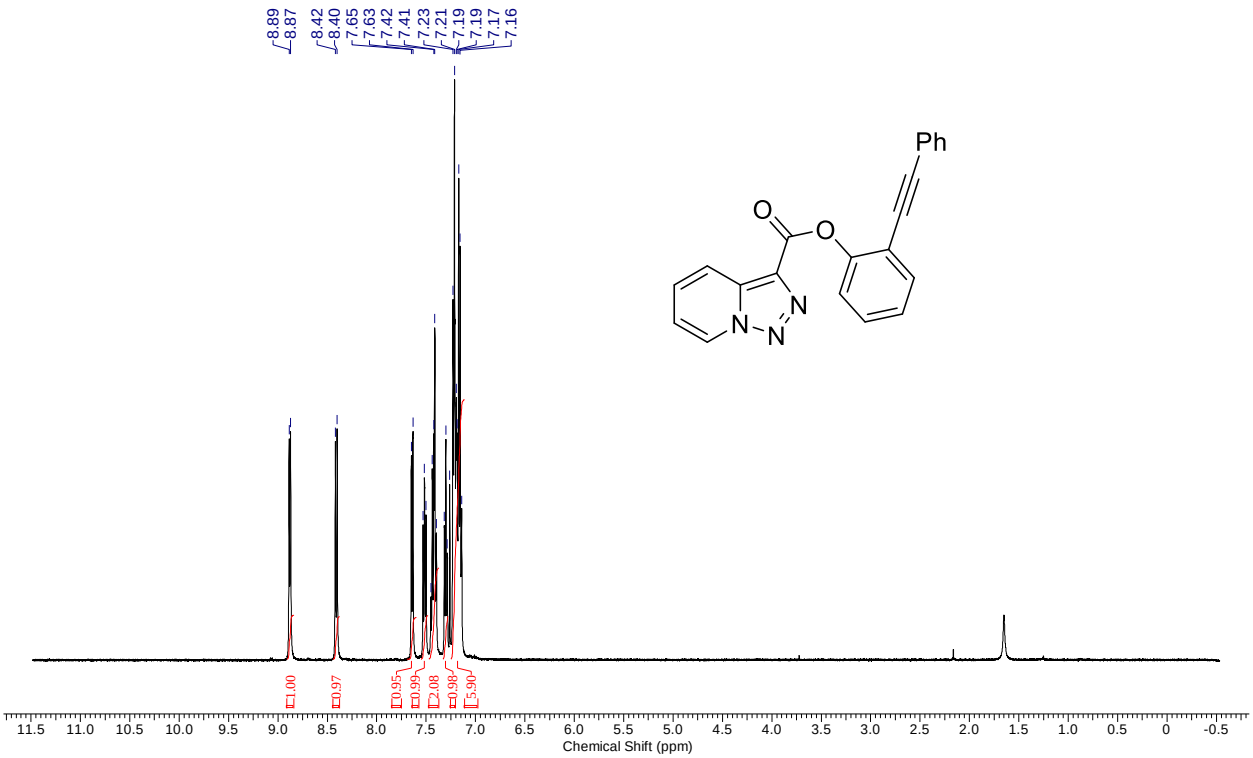
Rh condition: An oven-dried 3.0 mL V-vial equipped with a stirring bar was charged with $Rh(esp)_2$ (1.0 mol %), alkynylpyridotriazole **1** (0.2 mmol) and PhMe (2 mL) under N_2 atmosphere. The reaction vessel was capped with Mininert syringe valve and the reaction mixture was stirred at 120 °C. Upon completion the reaction mixture was cooled to room temperature, concentrated under reduced pressure, and the crude product was purified by column chromatography to afford **2bh** in 84% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.40 (d, *J*=6.97 Hz, 1 H), 7.87 (d, *J*=8.80 Hz, 1 H), 7.54 – 7.48 (m, 4 H), 7.42 – 7.40 (m, 1 H), 7.15 – 7.12 (m, 1 H), 6.84 (t, *J*=6.60 Hz, 1 H), 5.35 (s, 2 H). ^{13}C NMR (126 MHz, DMSO-*d6*) δ ppm 166.50, 138.50, 129.88, 129.82, 129.44, 128.38, 127.98, 125.14, 123.85, 117.93, 116.66, 114.79, 103.57, 66.25. HRMS (ESI) calculated for $C_{16}H_{11}NO_2$ $[M+H]^+$: 250.0868, found: 250.0871.

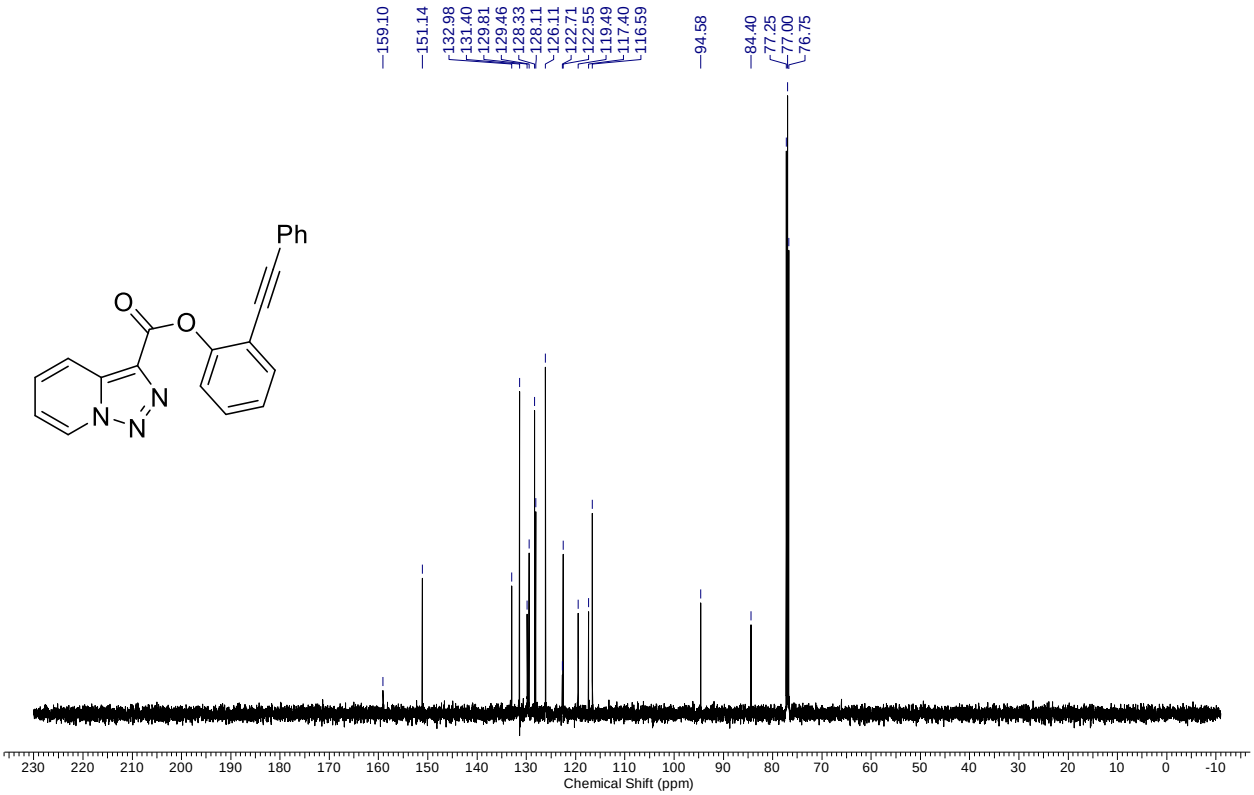
References:

1. Y. Shi, A. V. Gulevich, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2014**, *53*, 14191-14195; *Angew. Chem*. **2014**, *126*, 14415–14419;
2. V. Helan, A. V. Gulevich, V. Gevorgyan, *Chem. Sci*., **2015**, *6*, 1928-1931.

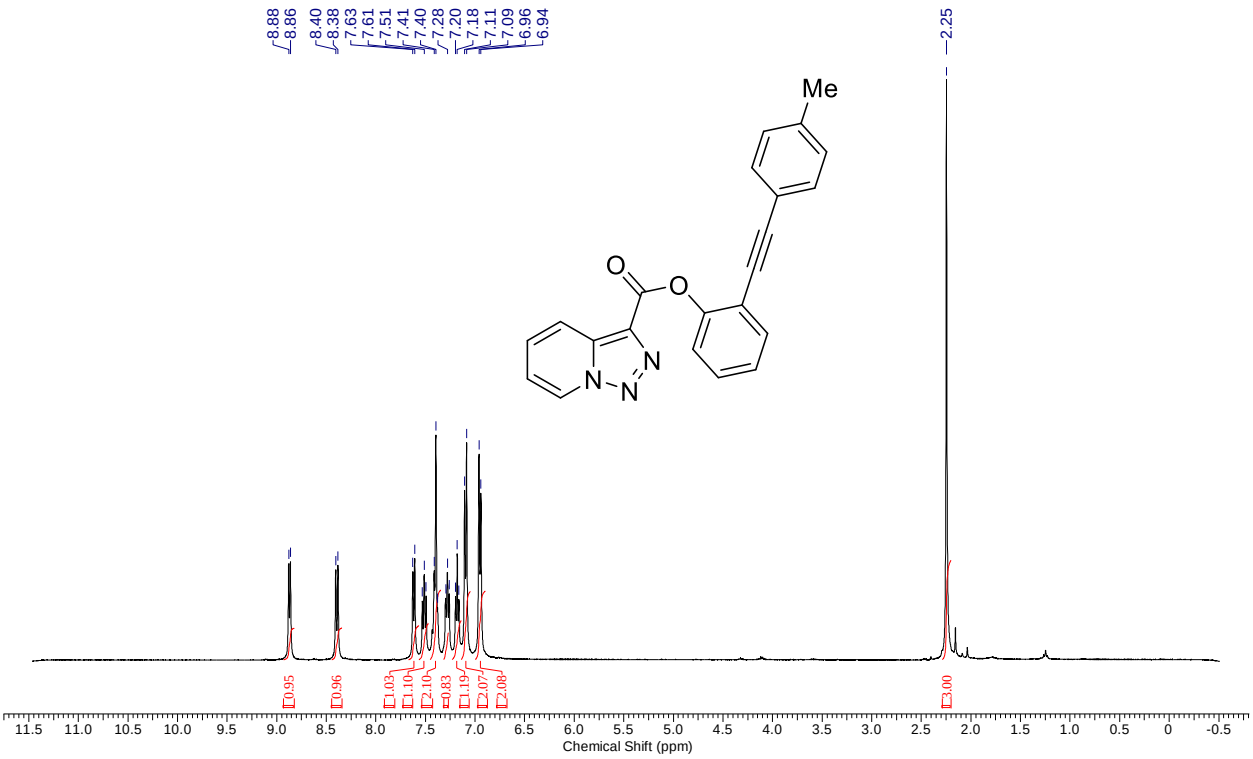
^{1}H NMR Spectrum of **1aa**



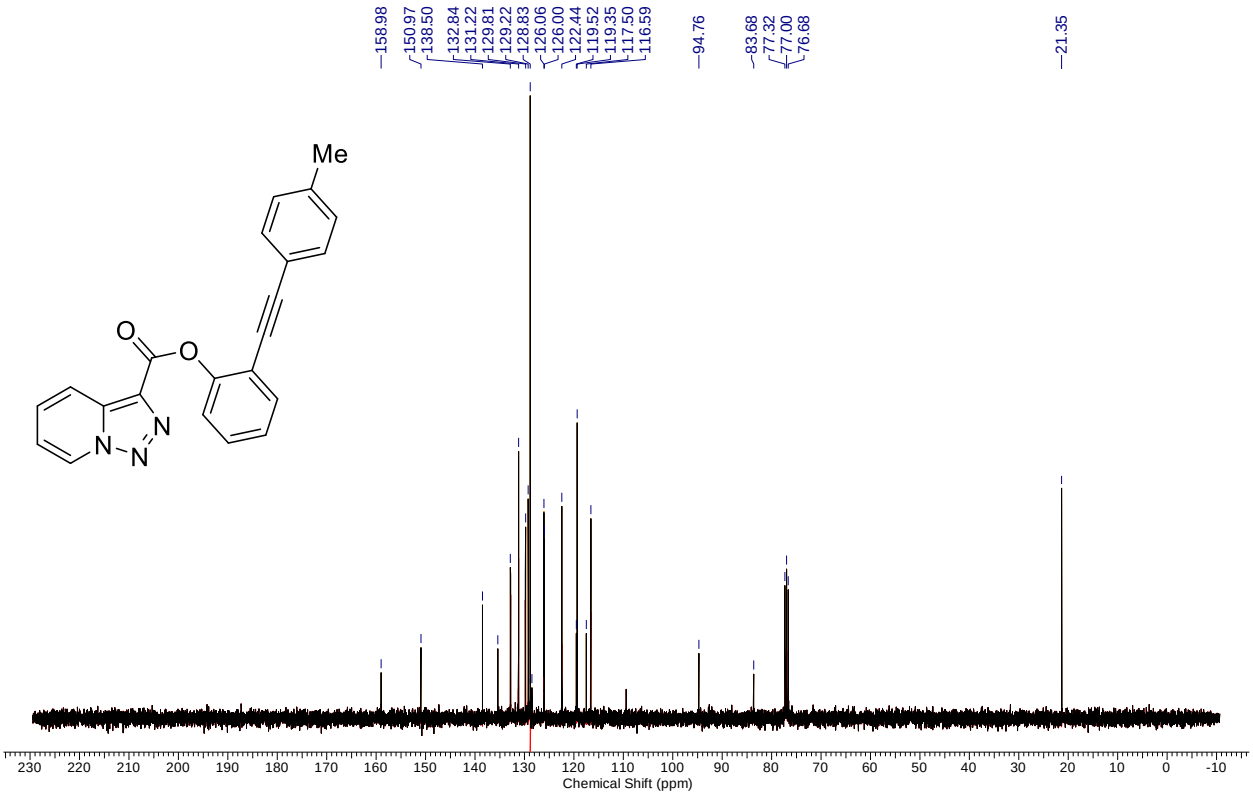
[13] NMR Spectrum of **1aa**



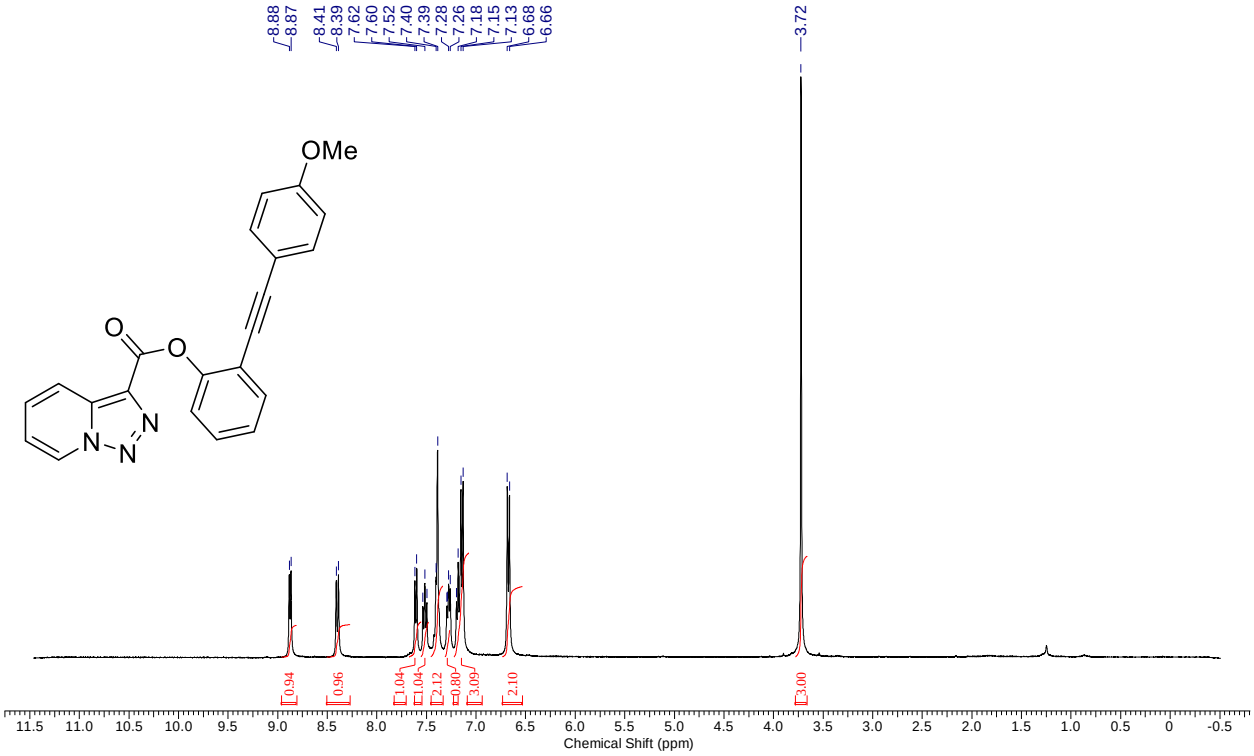
[1]H NMR Spectrum of **1ab**



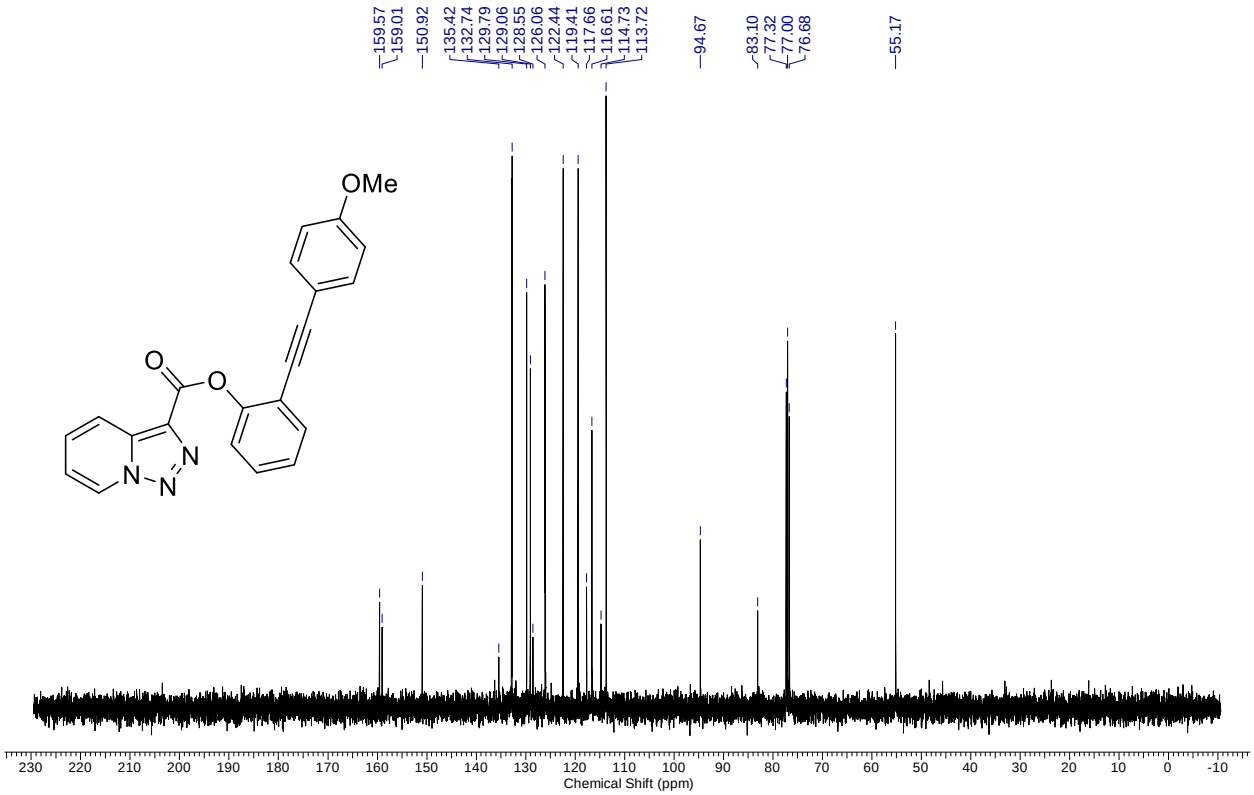
^{13}C NMR Spectrum of **1ab**



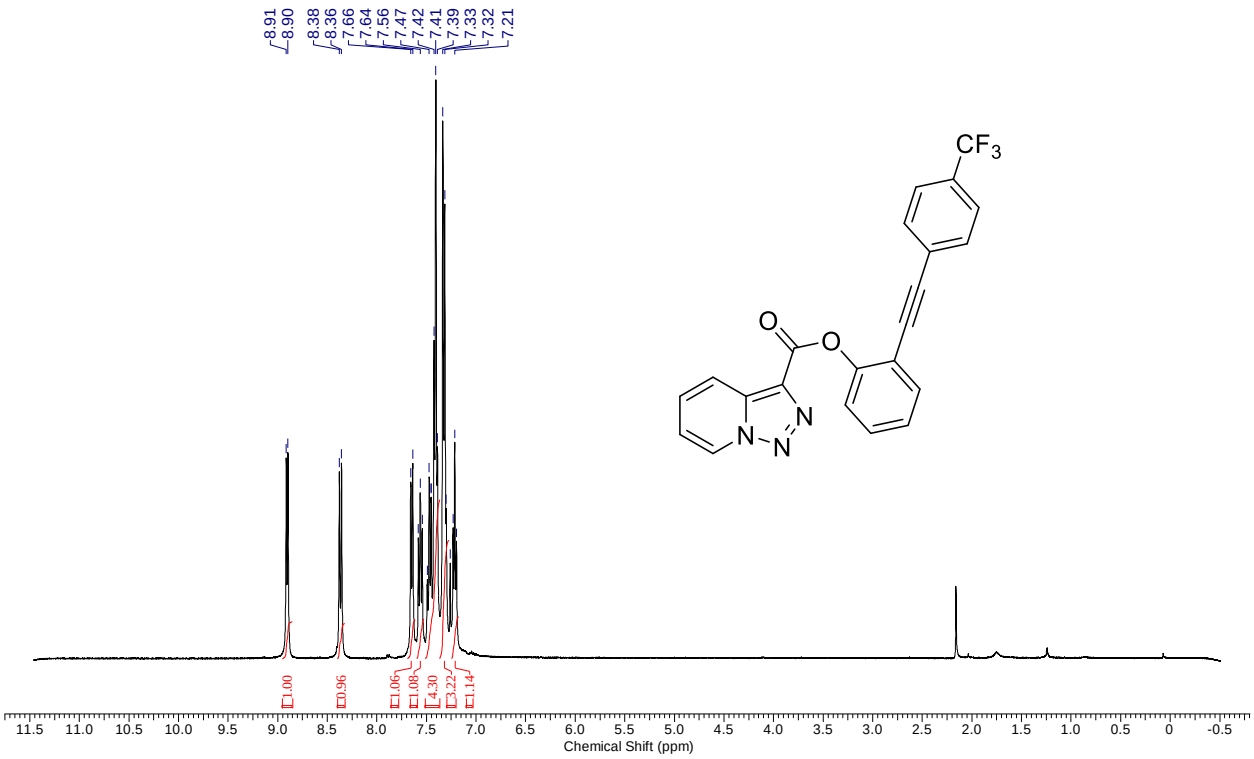
^{1}H NMR Spectrum of **1ac**



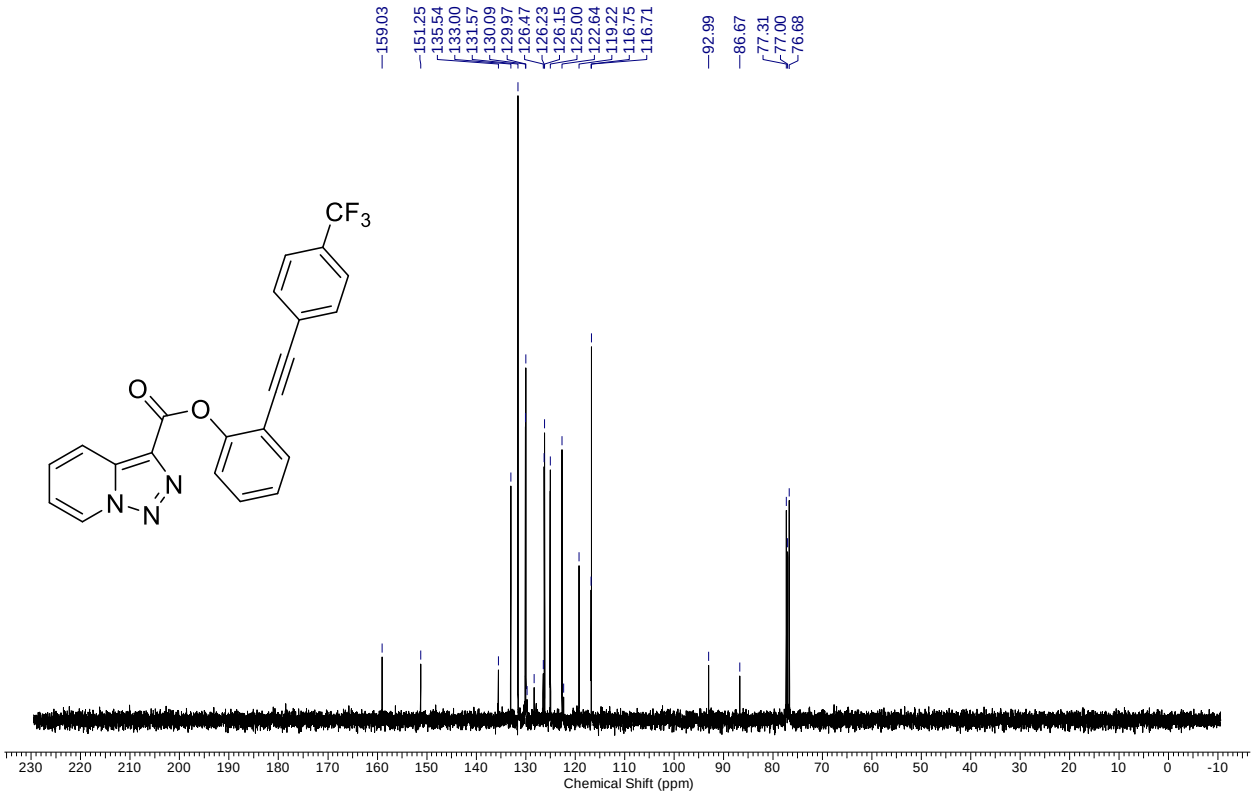
^{13}C NMR Spectrum of **1ac**



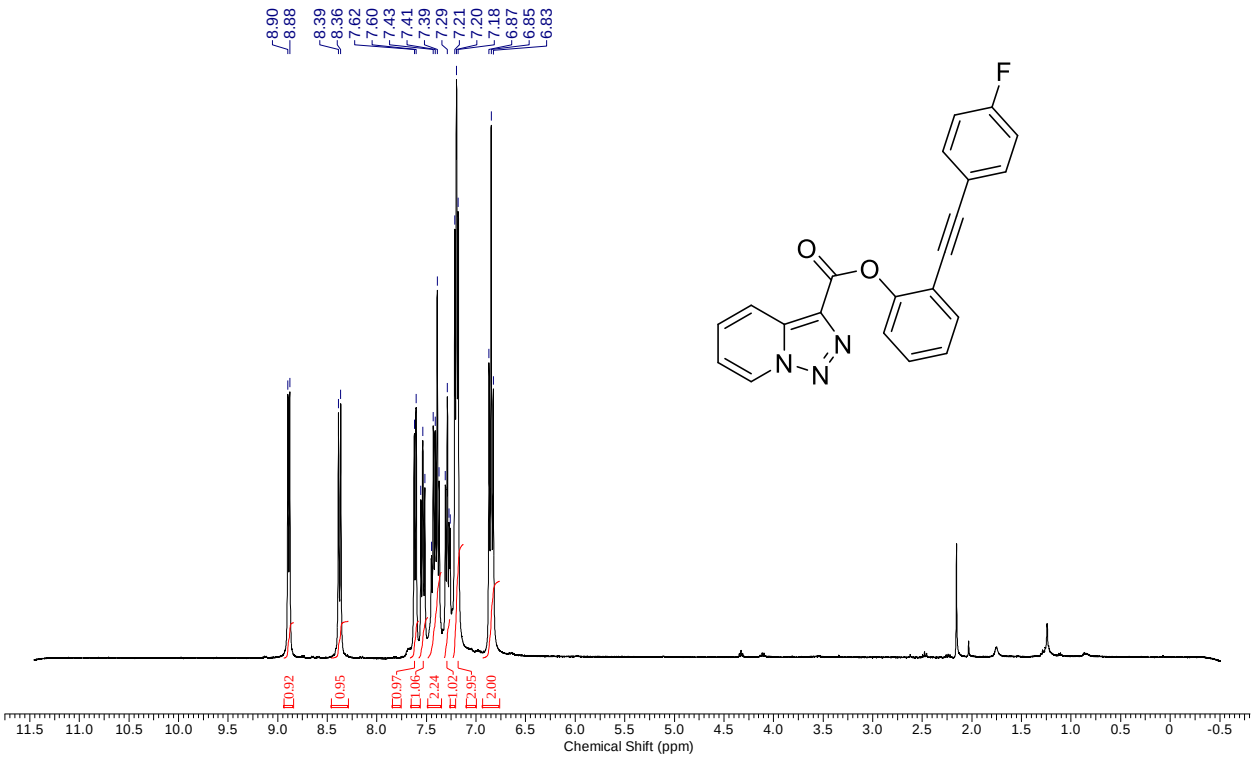
^{1}H NMR Spectrum of **1ad**



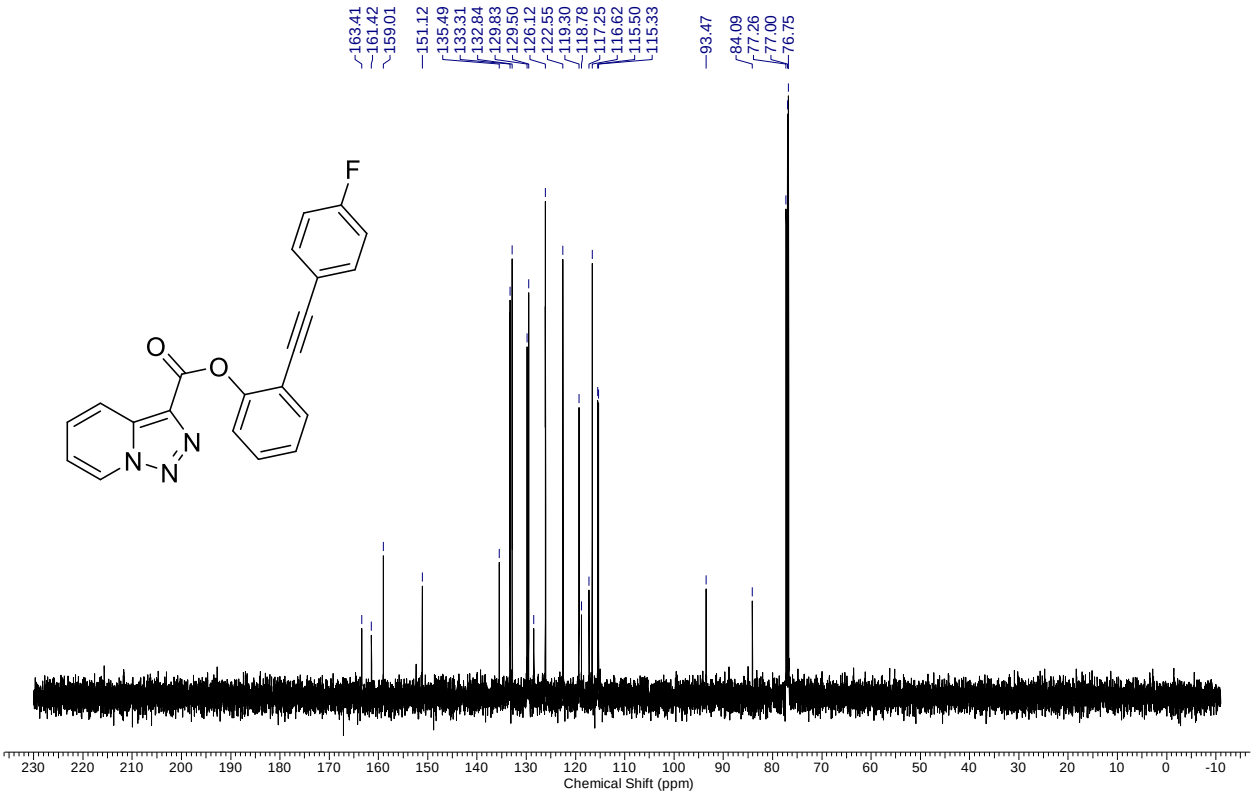
^{13}C NMR Spectrum of **1ad**



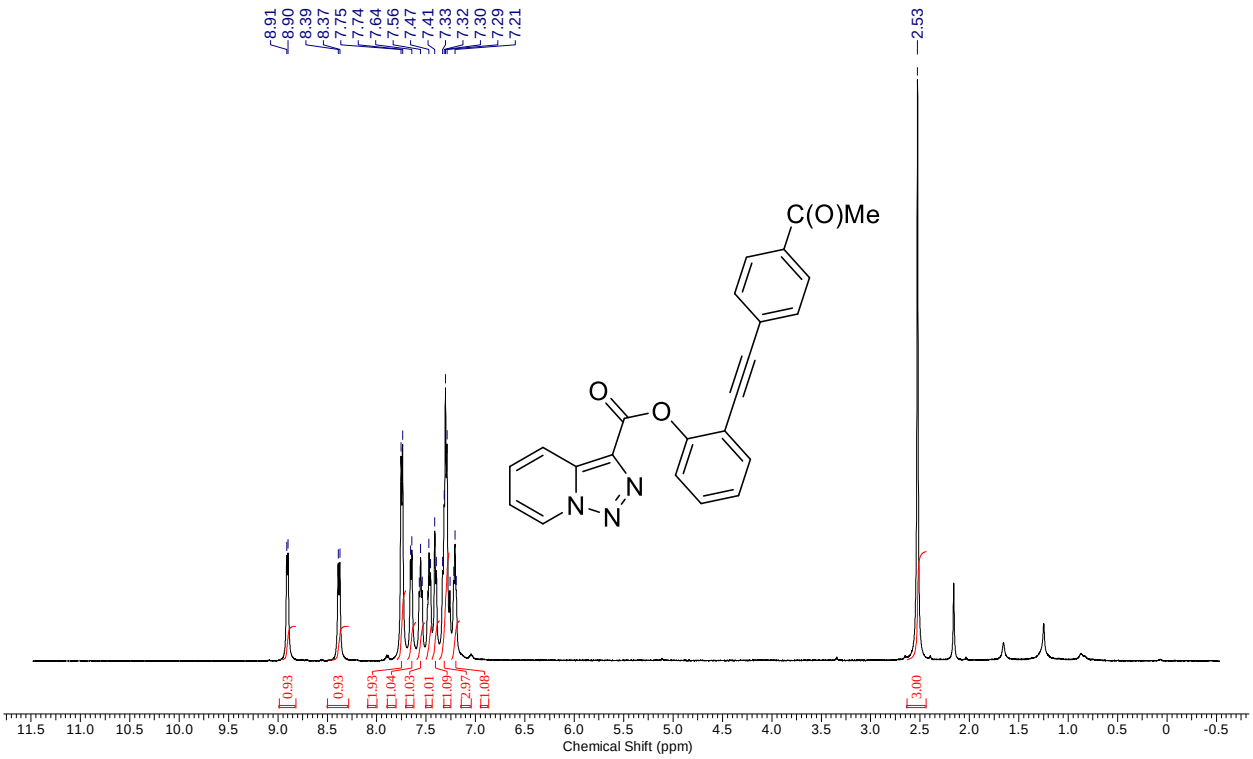
^{1}H NMR Spectrum of **1ae**



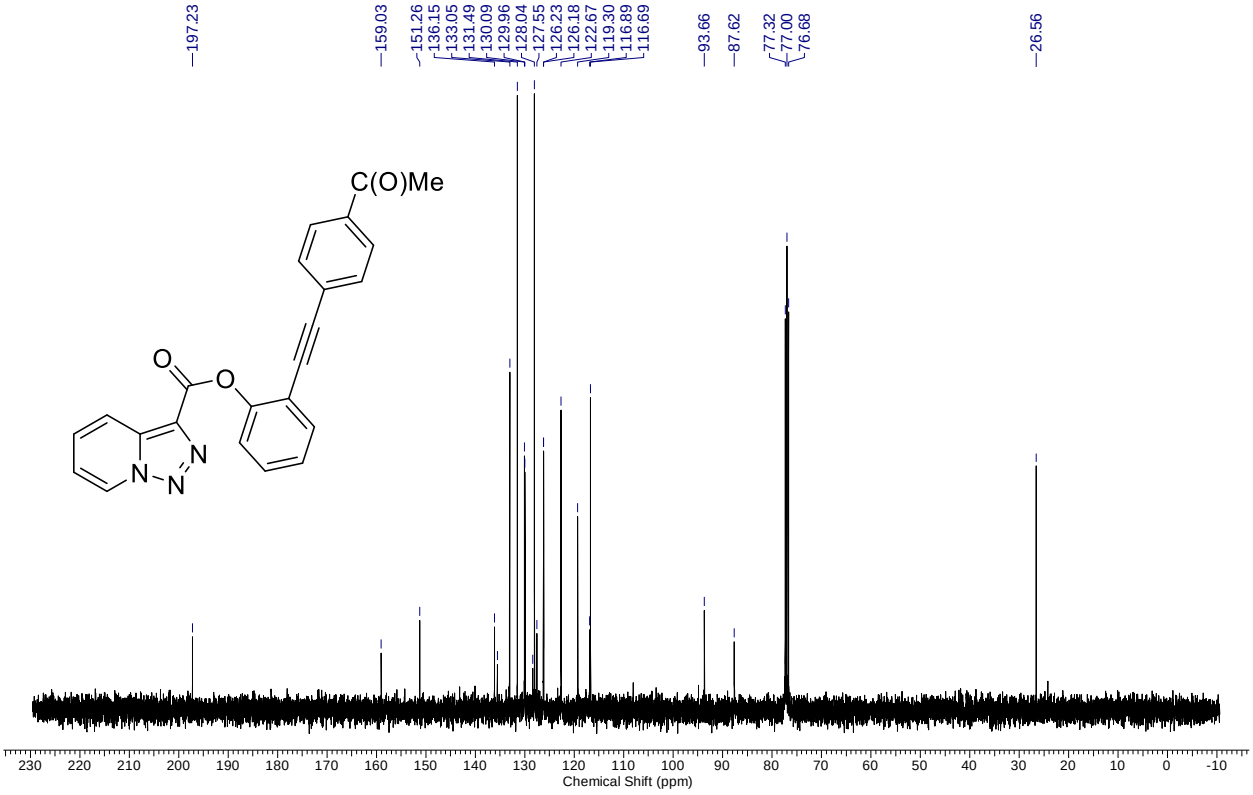
^{13}C NMR Spectrum of **1ae**



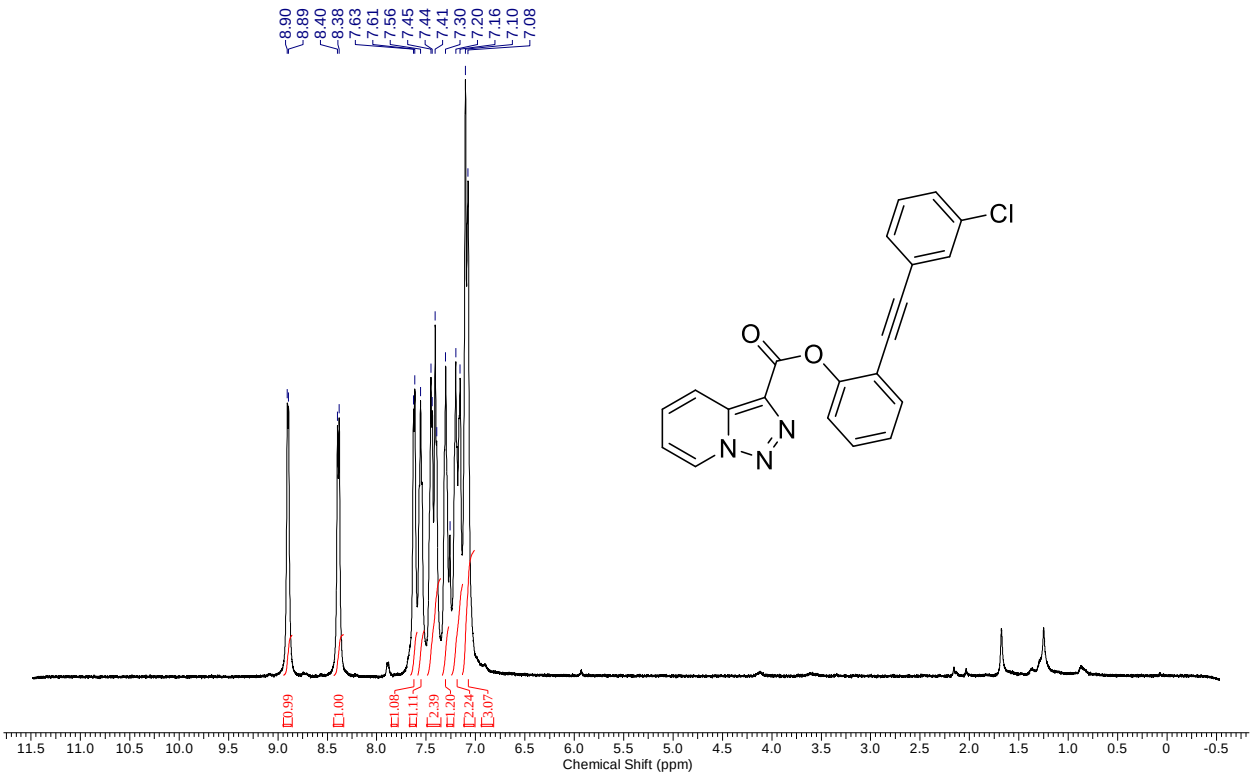
^{1}H NMR Spectrum of **1af**



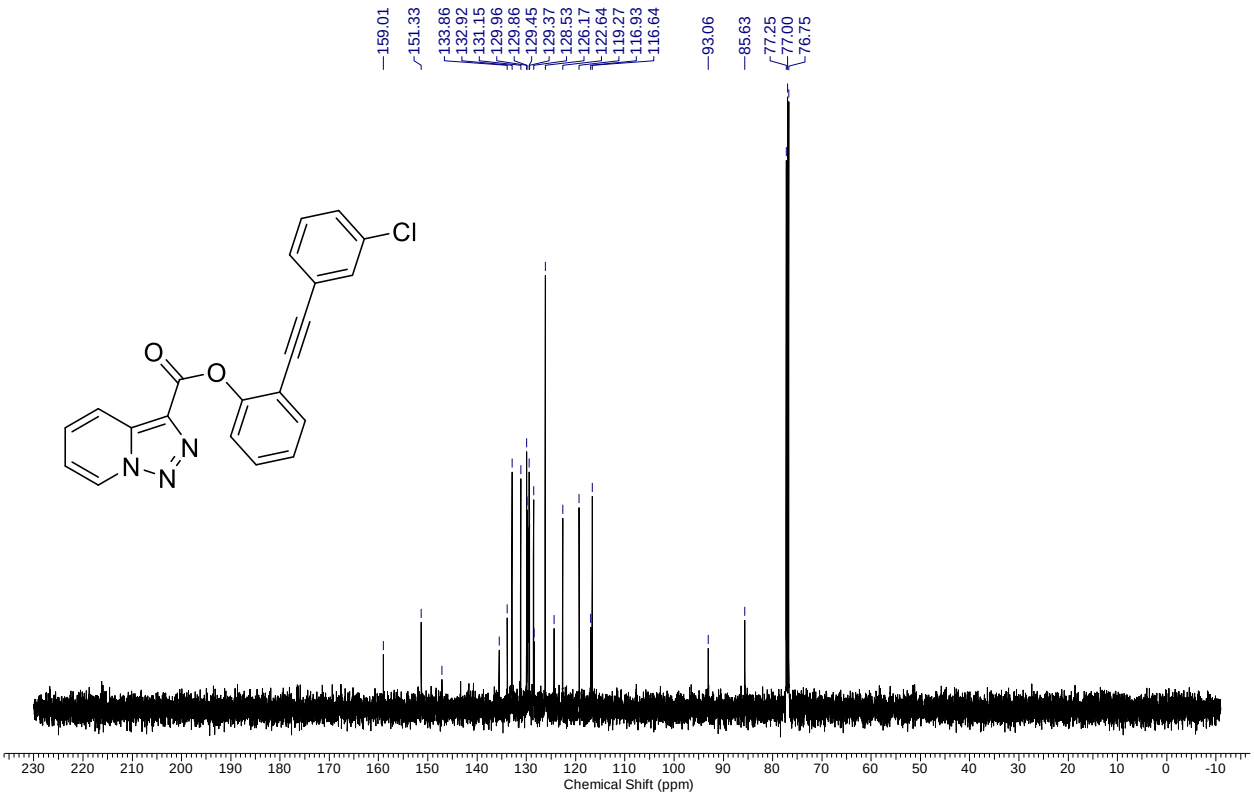
^{13}C NMR Spectrum of **1af**



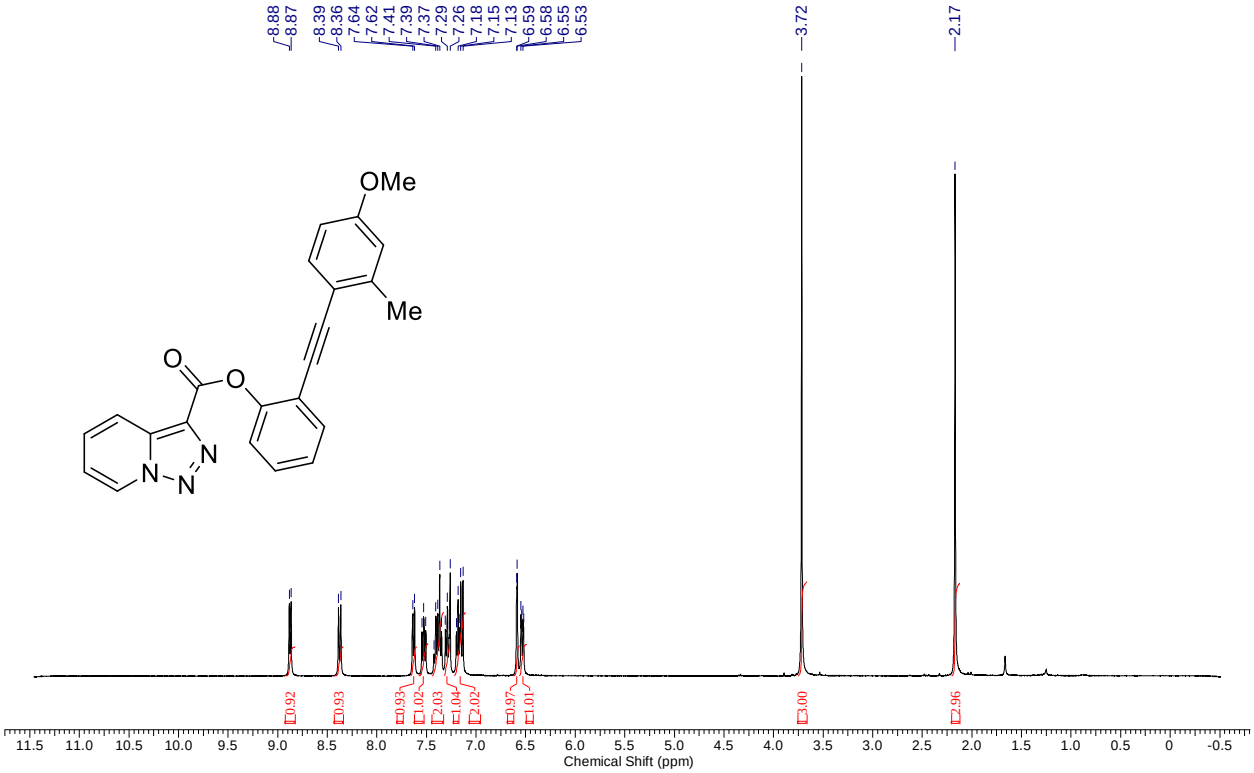
^{1}H NMR Spectrum of **1ag**



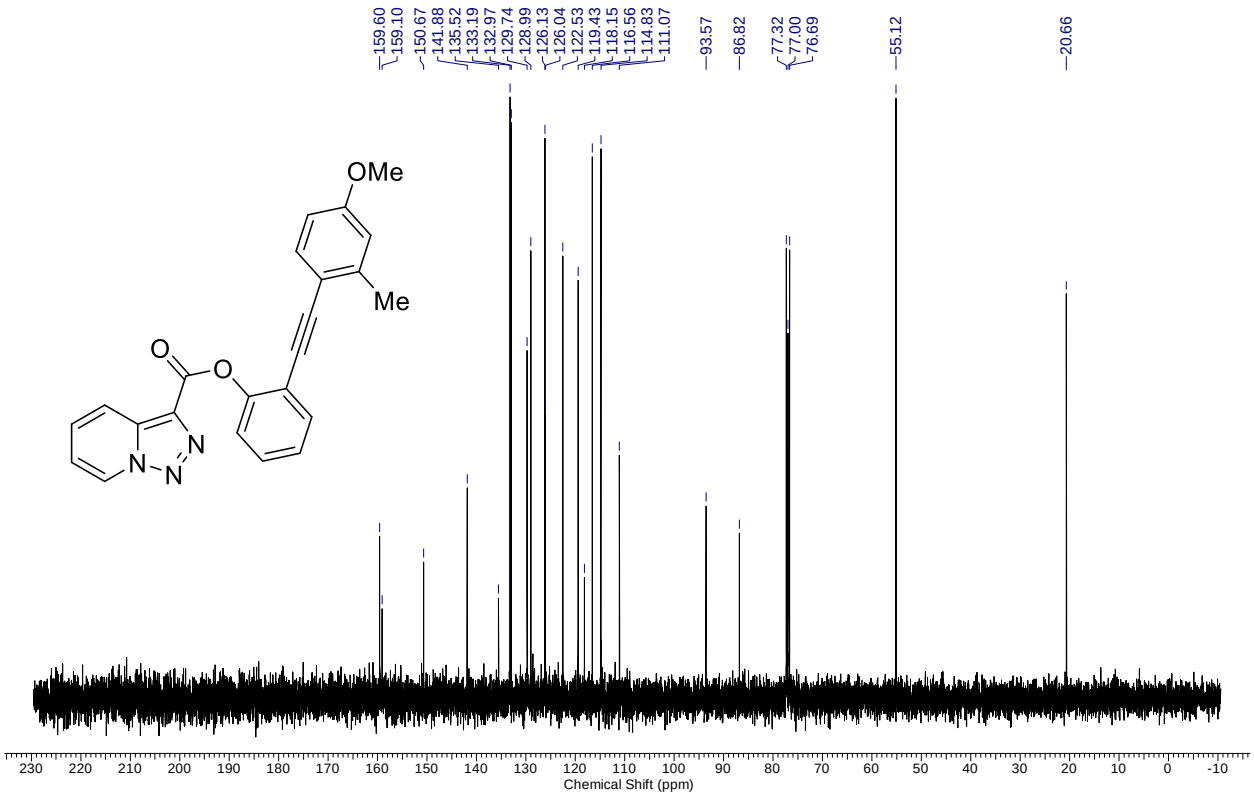
^{13}C NMR Spectrum of **1ag**



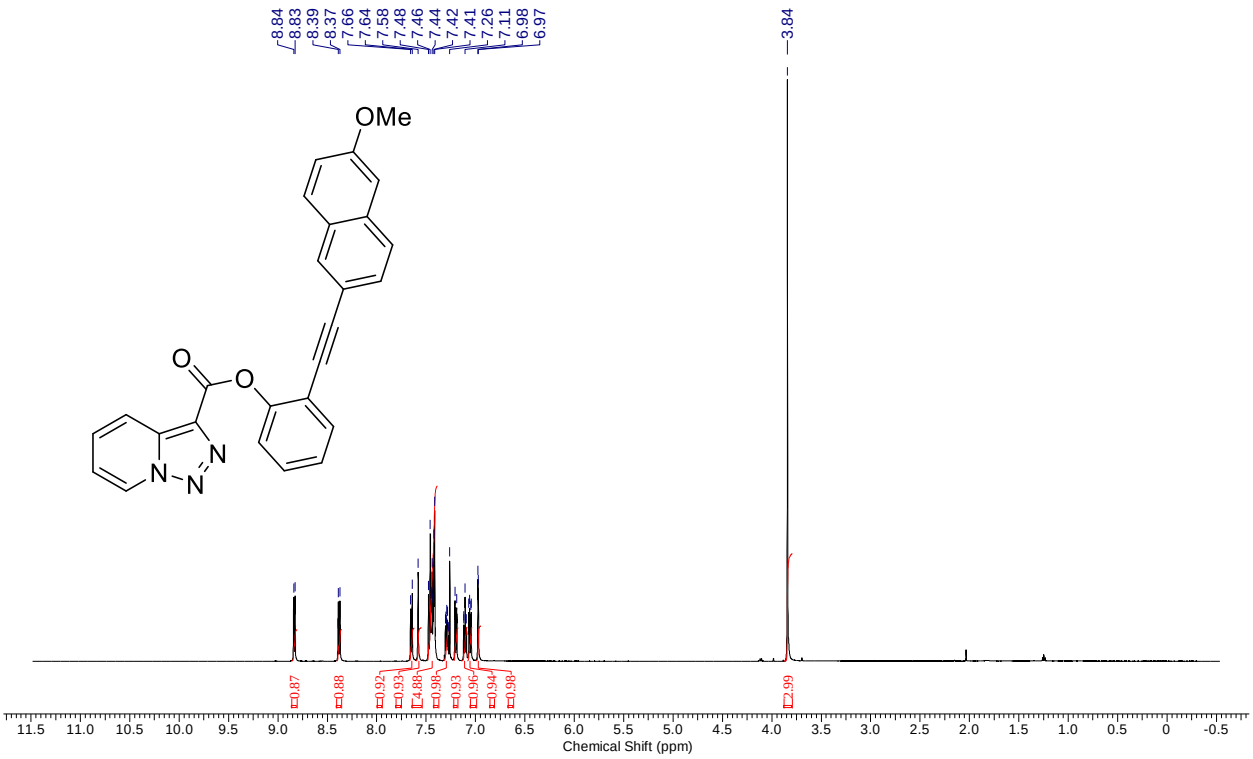
^{1}H NMR Spectrum of **1ah**



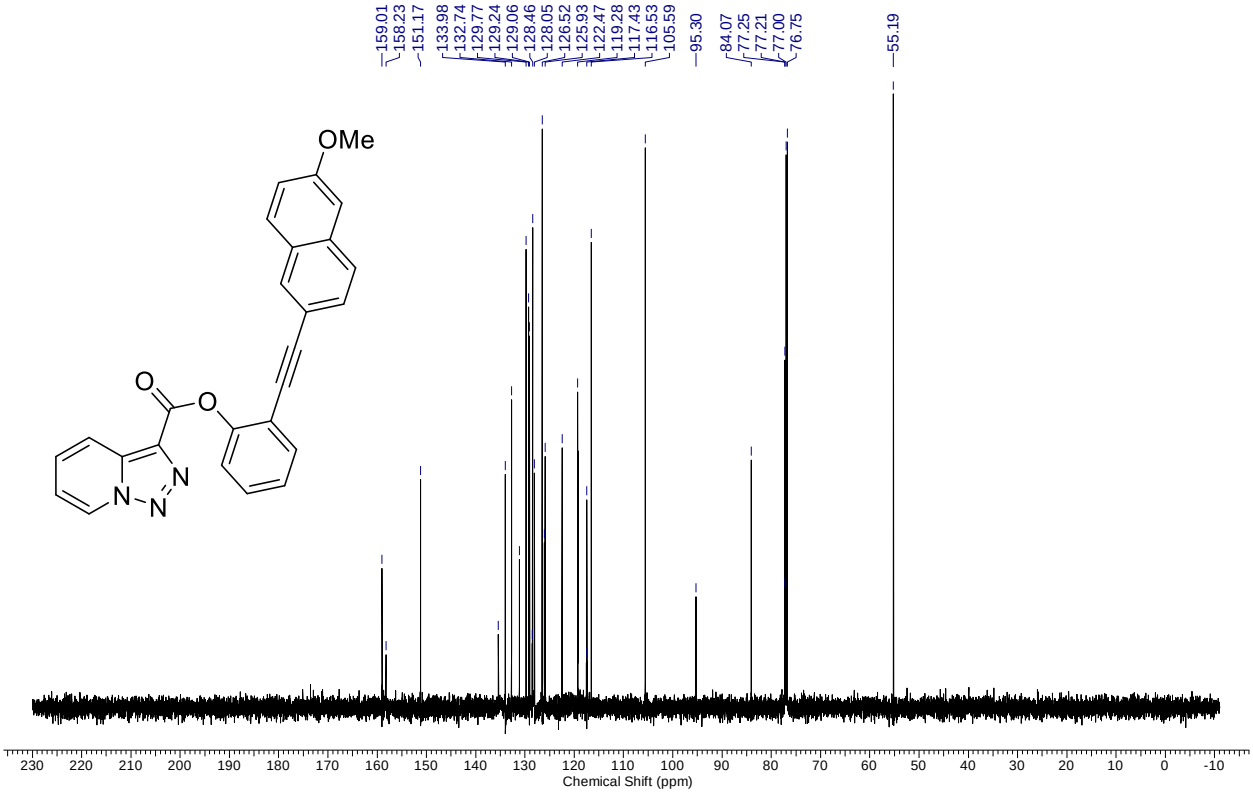
^{13}C NMR Spectrum of **1ah**



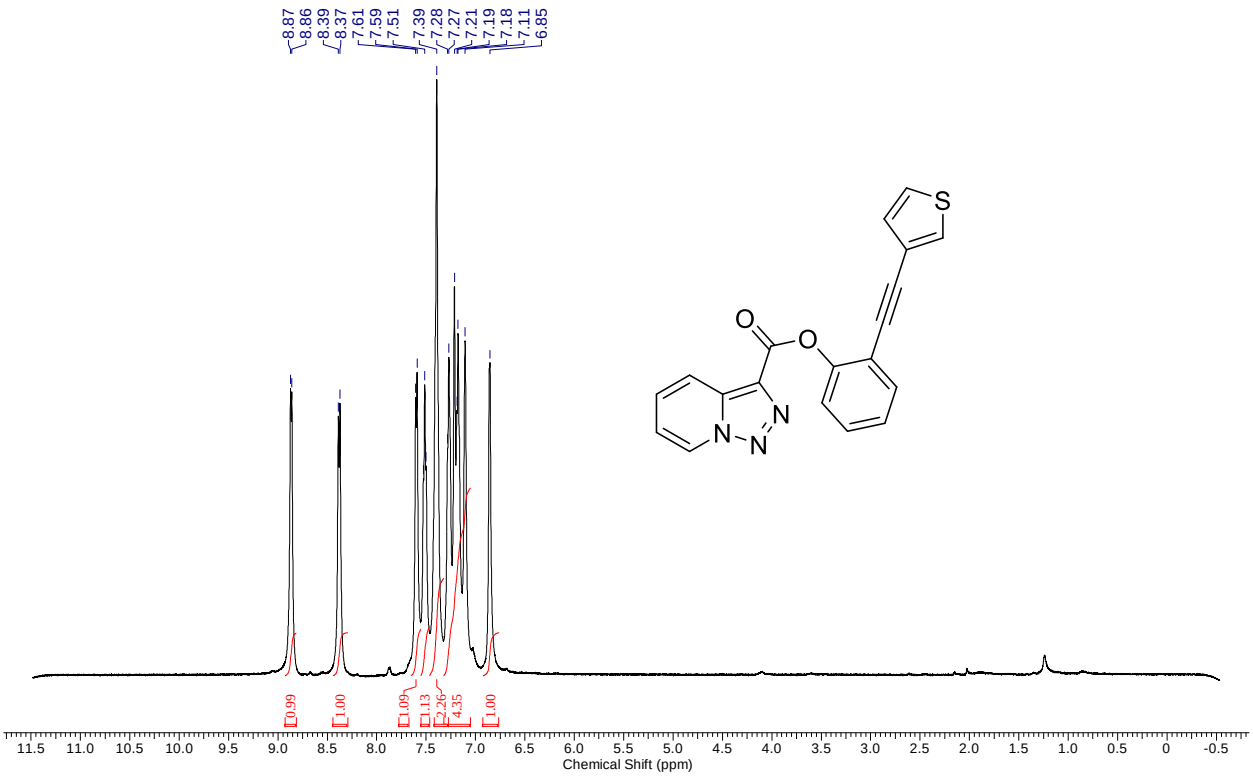
^{1}H NMR Spectrum of **1ai**



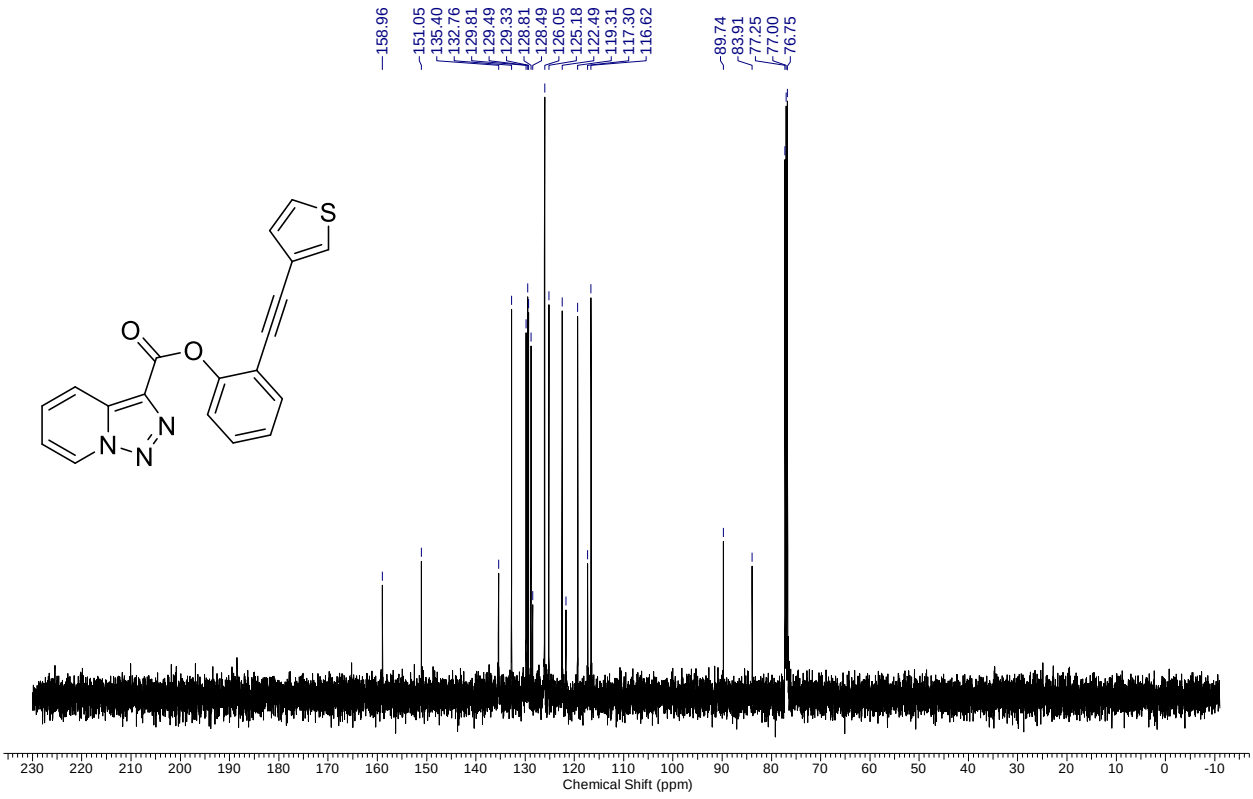
^{13}C NMR Spectrum of **1ai**



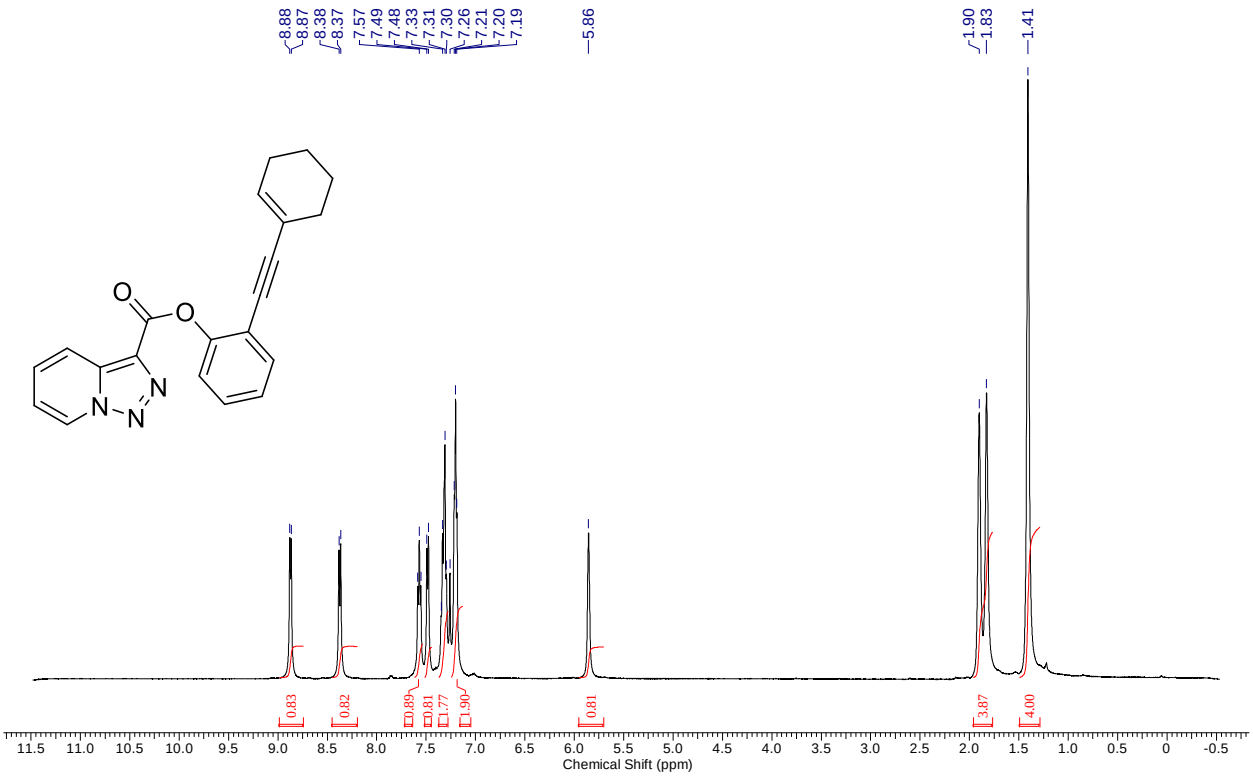
^{1}H NMR Spectrum of **1aj**



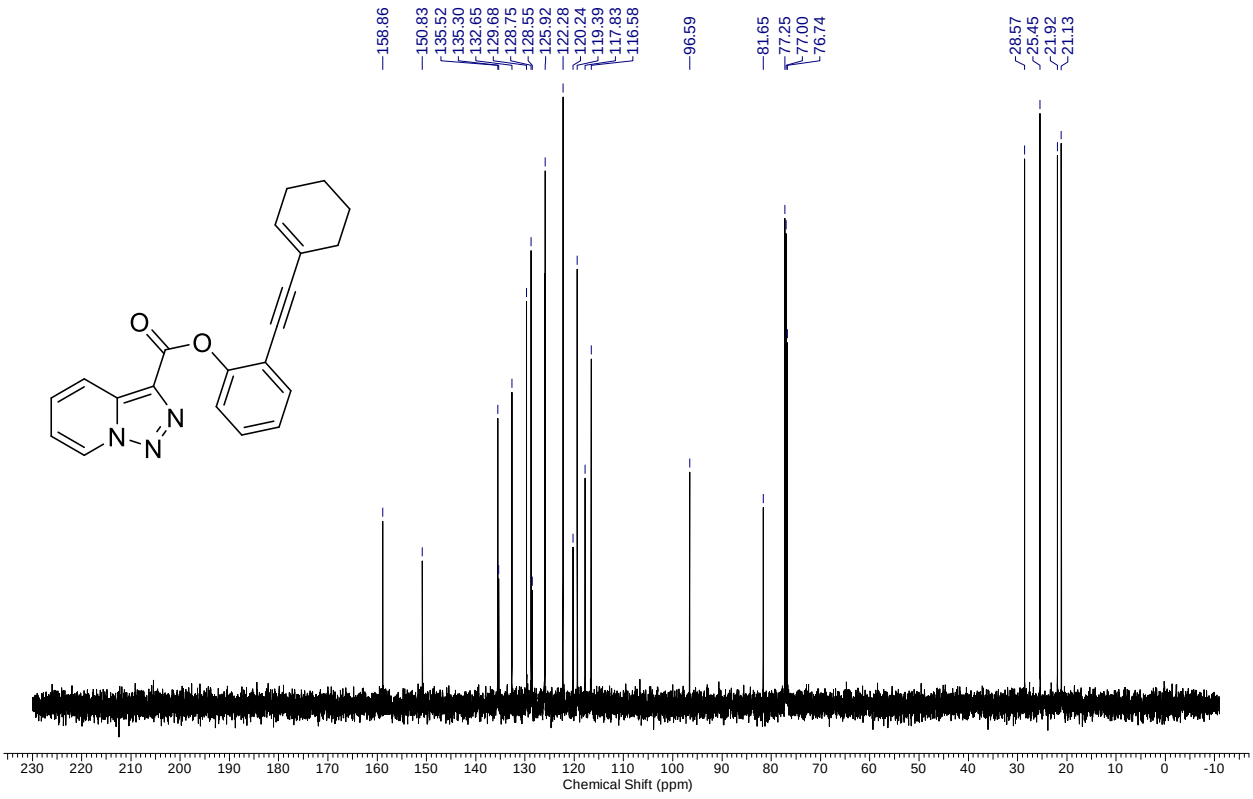
^{13}C NMR Spectrum of **1aj**



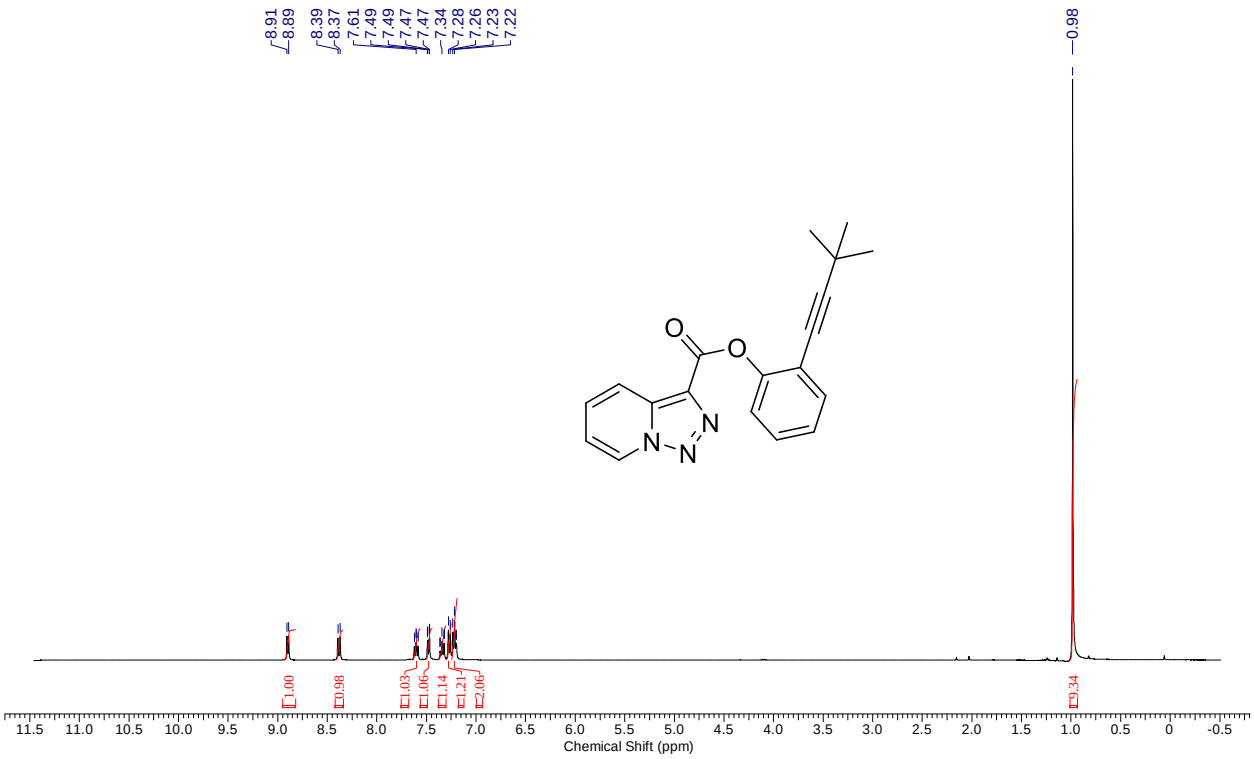
^{1}H NMR Spectrum of **1ak**



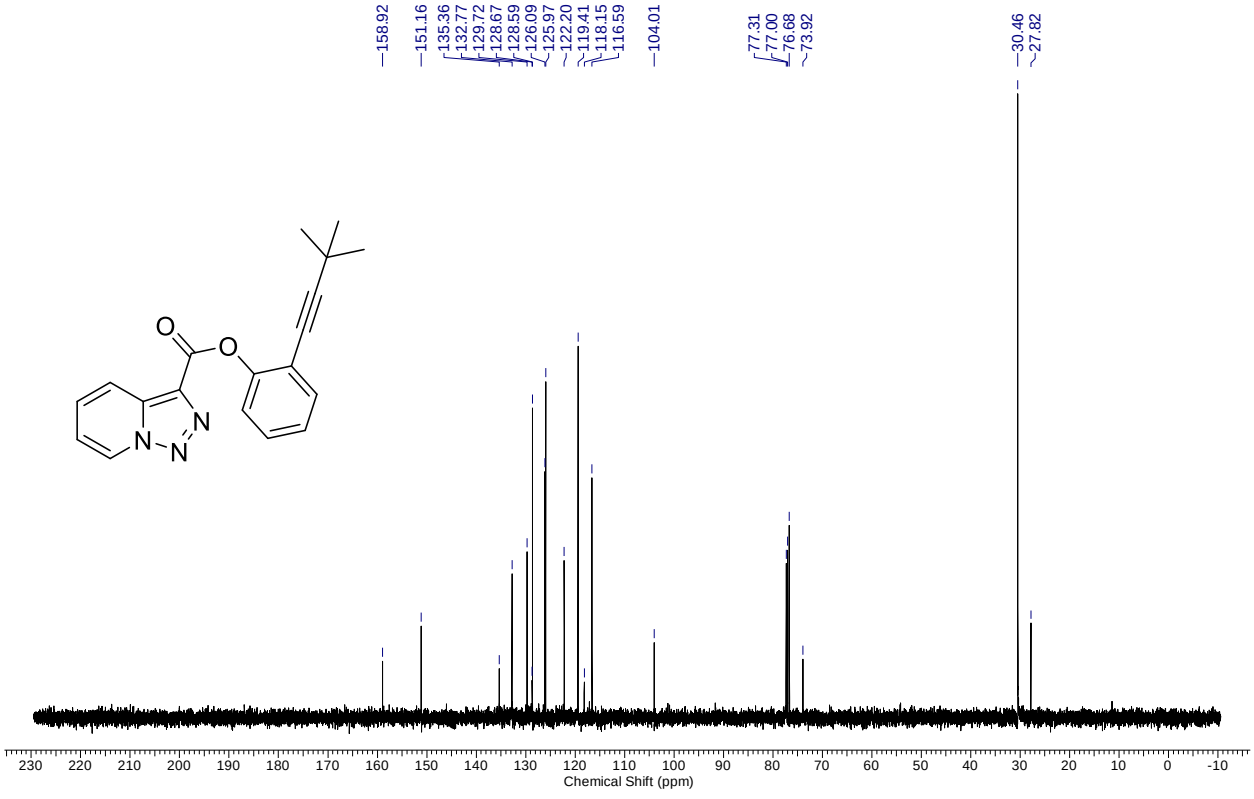
^{13}C NMR Spectrum of **1ak**



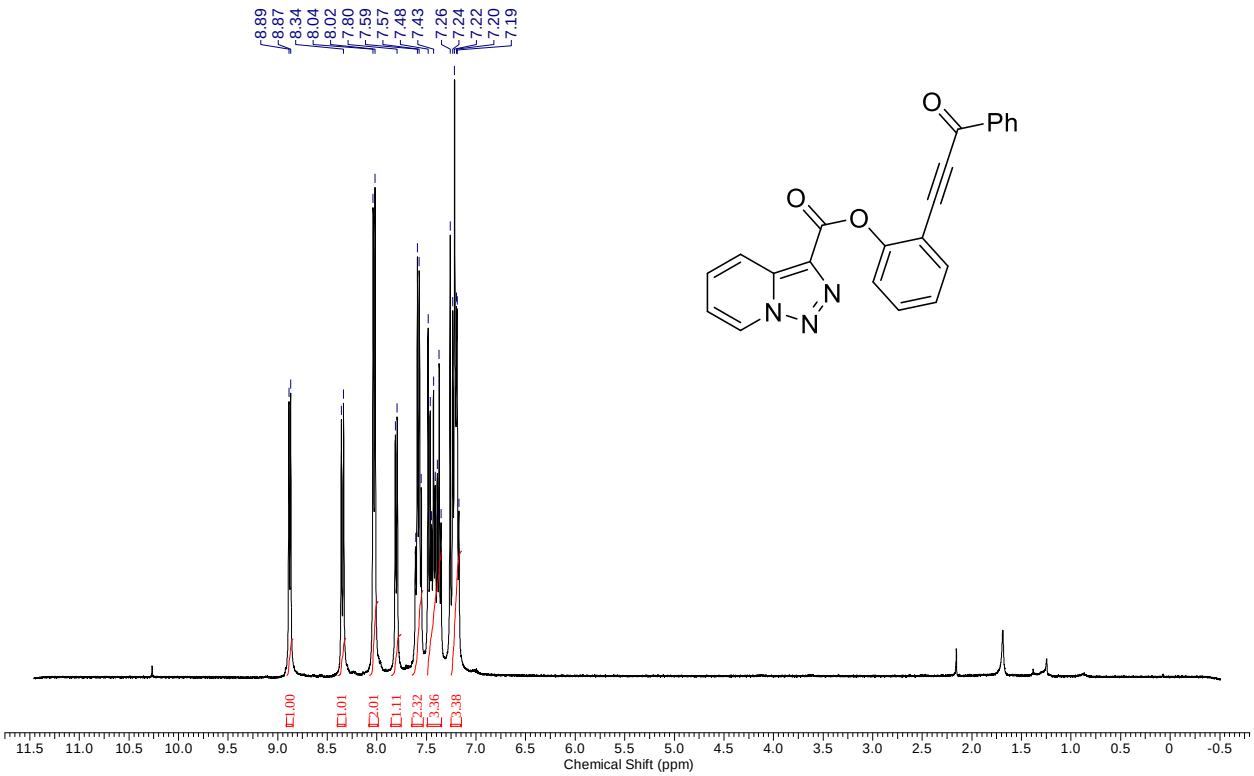
^{1}H NMR Spectrum of **1al**



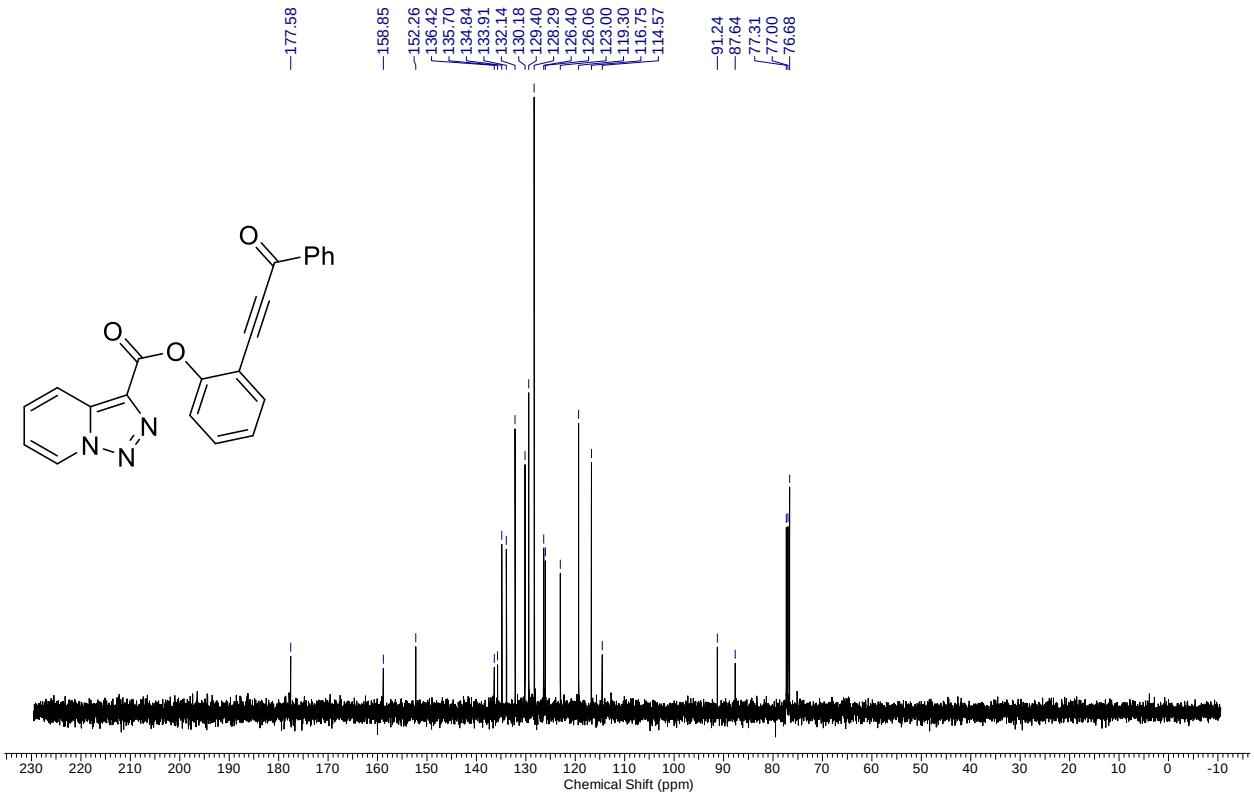
^{13}C NMR Spectrum of **1al**



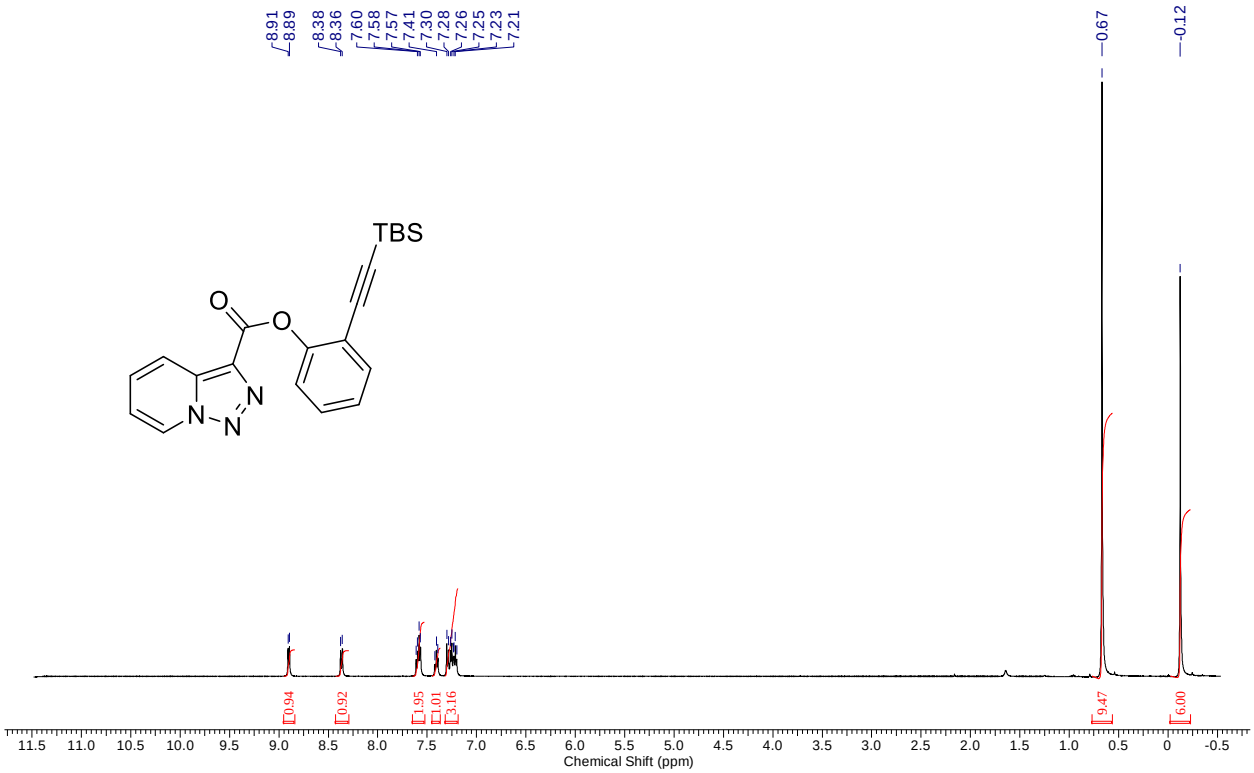
^{1}H NMR Spectrum of **1am**



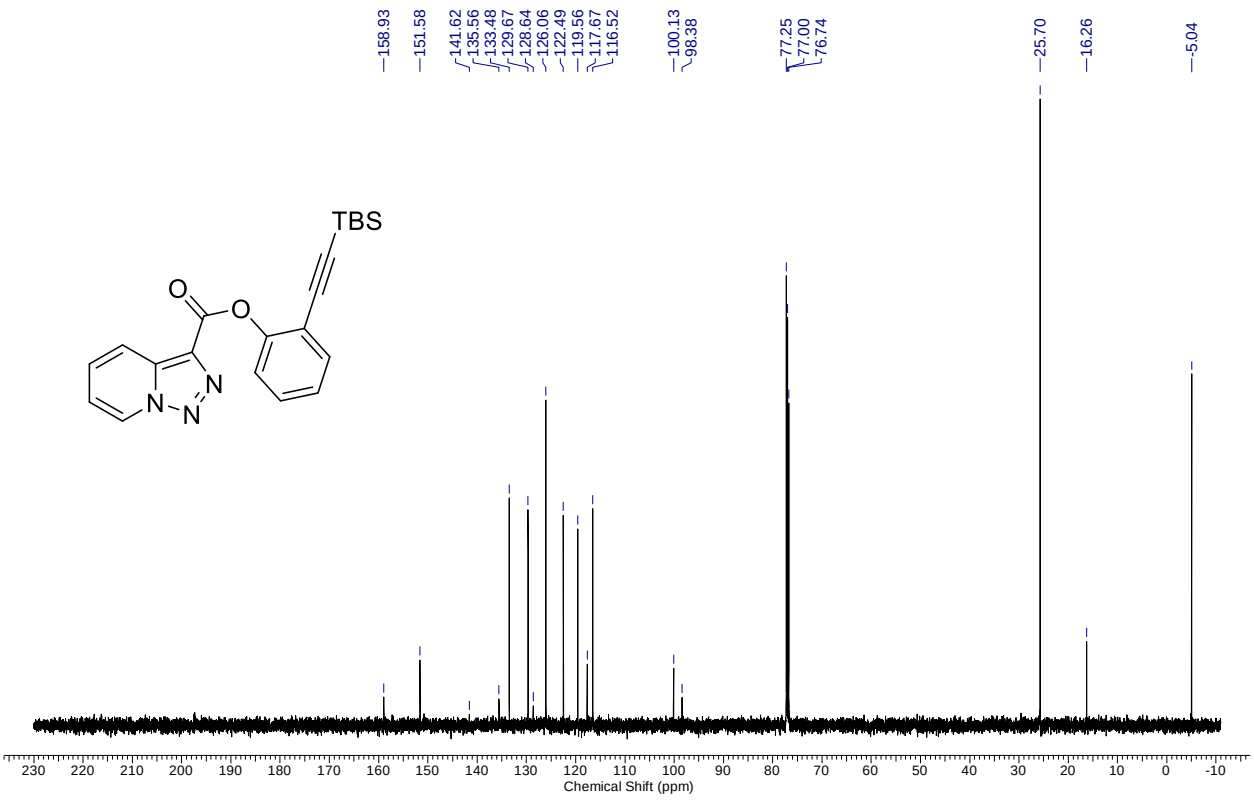
^{13}C NMR Spectrum of **1am**



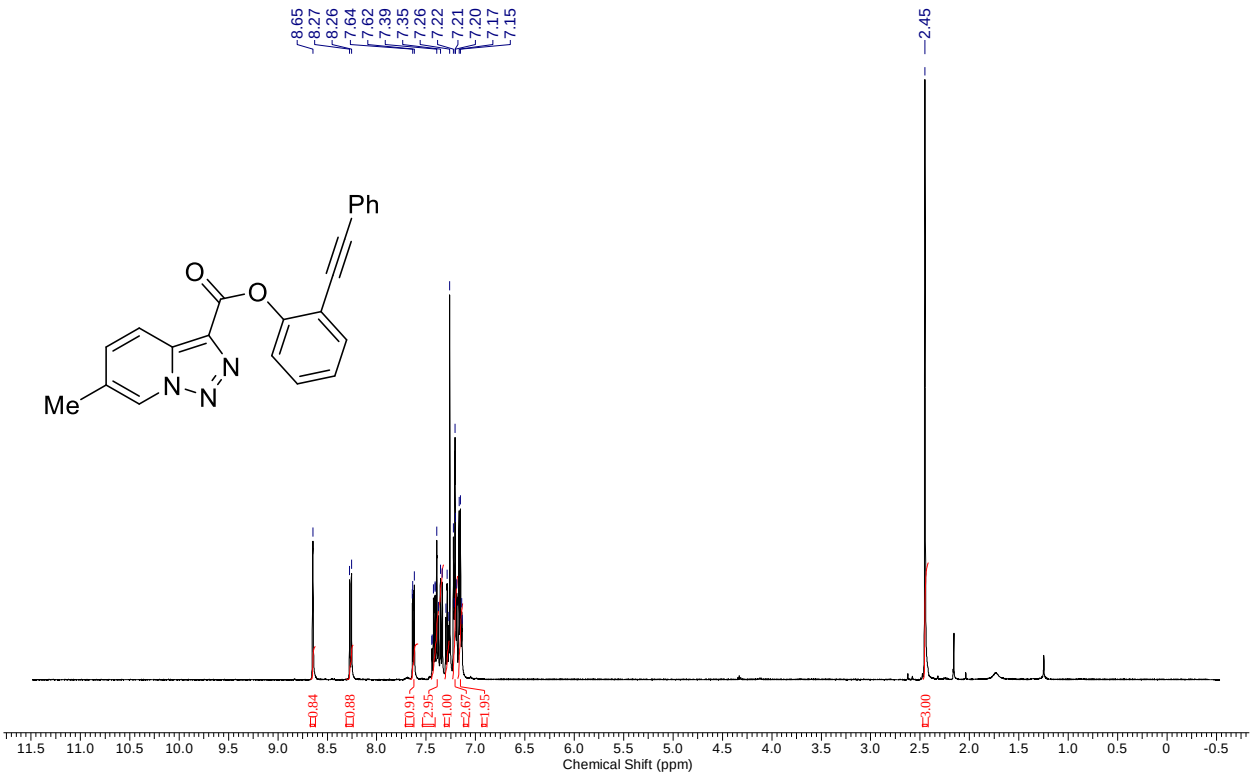
^{1}H NMR Spectrum of **1an**



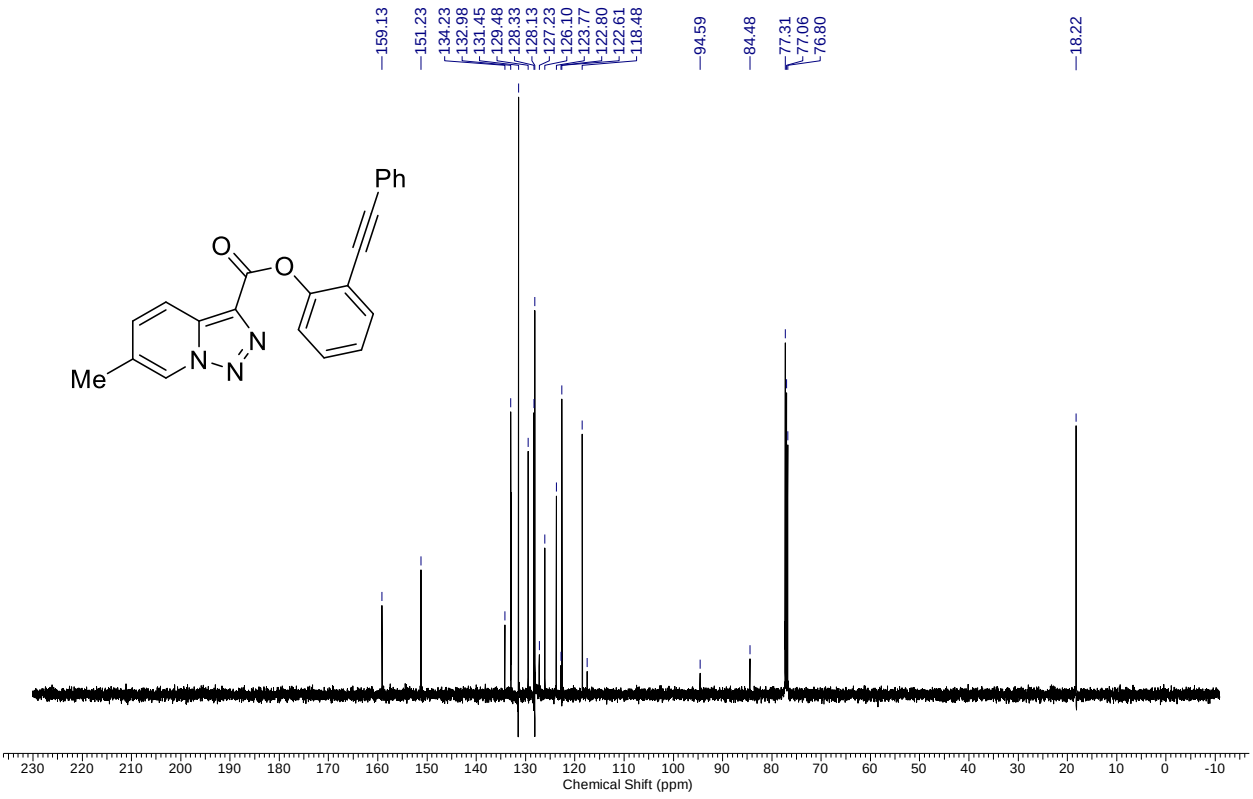
^{13}C NMR Spectrum of **1an**



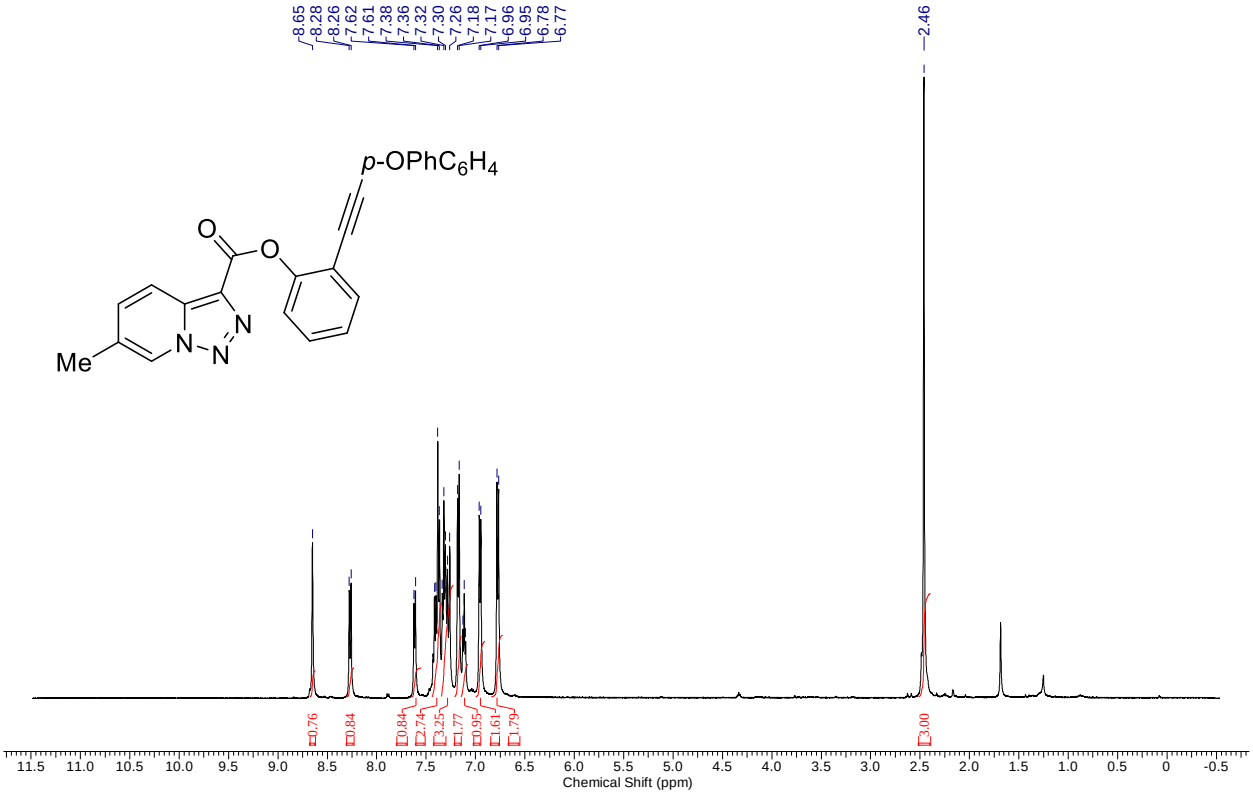
^{1}H NMR Spectrum of **1ao**



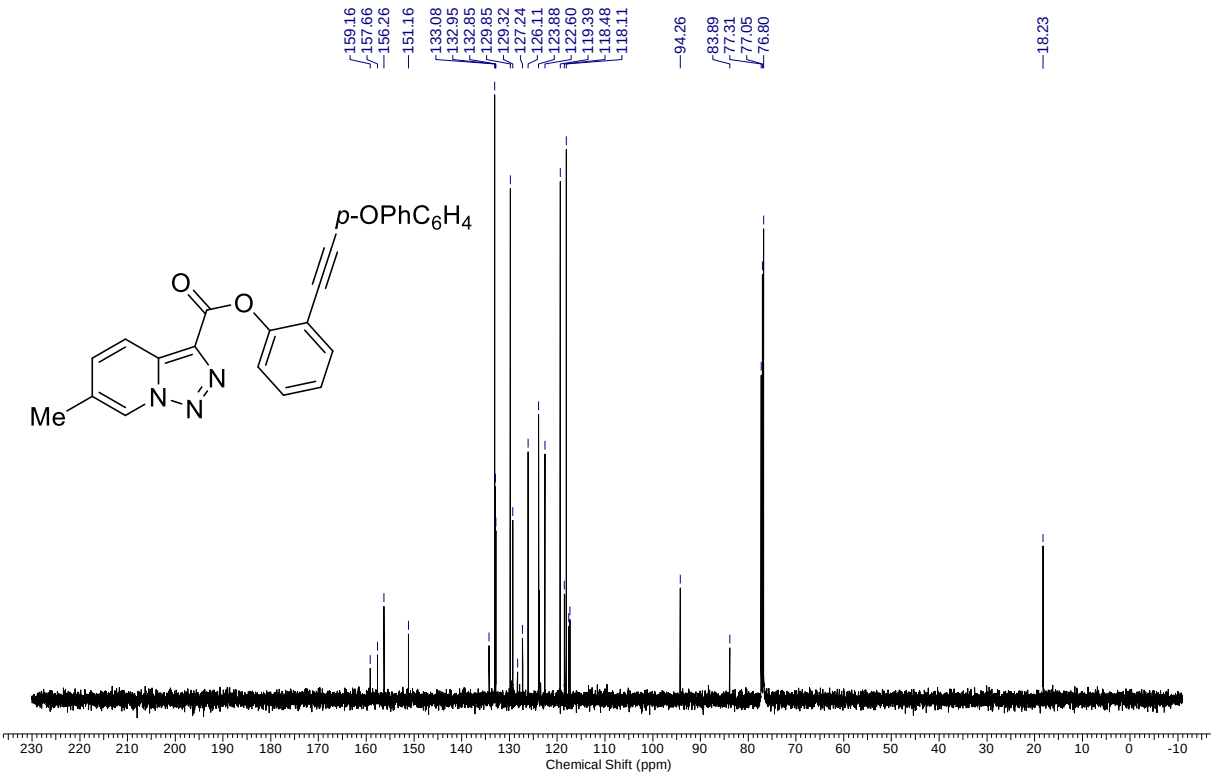
^{13}C NMR Spectrum of **1ao**



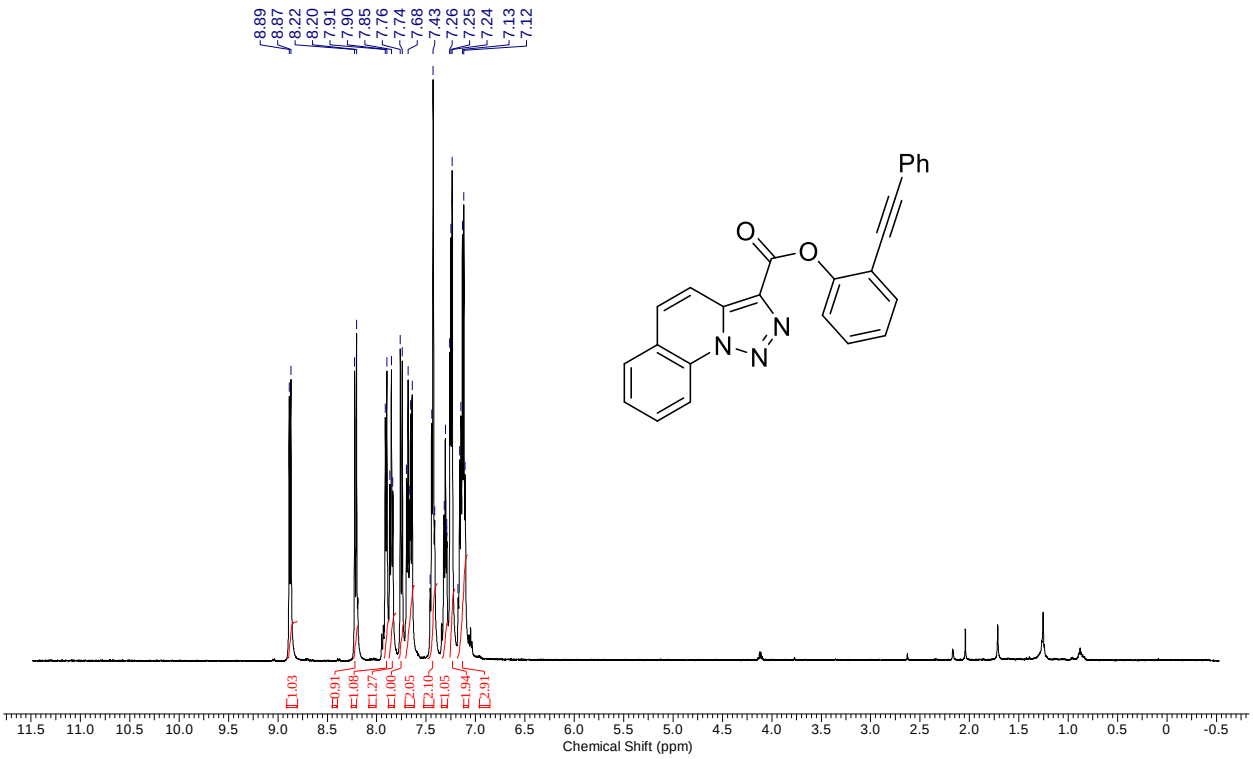
^{1}H NMR Spectrum of **1ap**



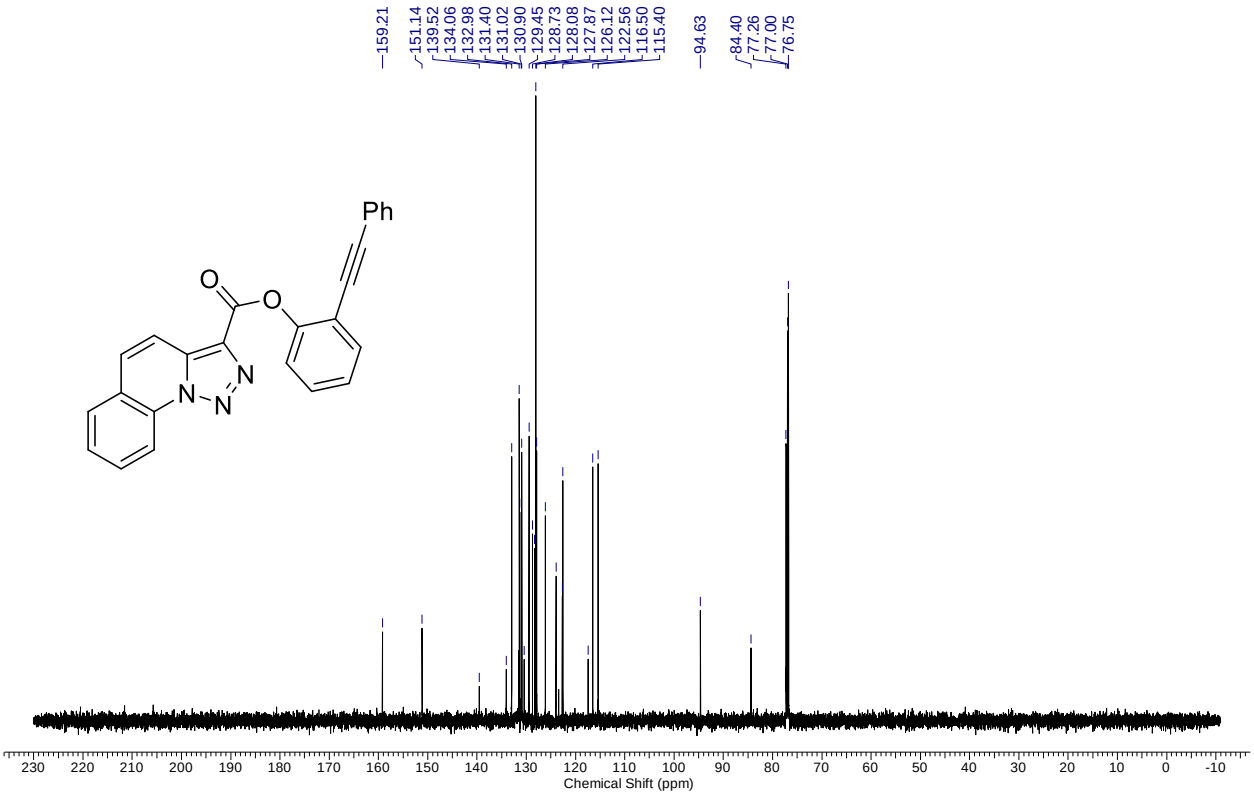
^{13}C NMR Spectrum of **1ap**



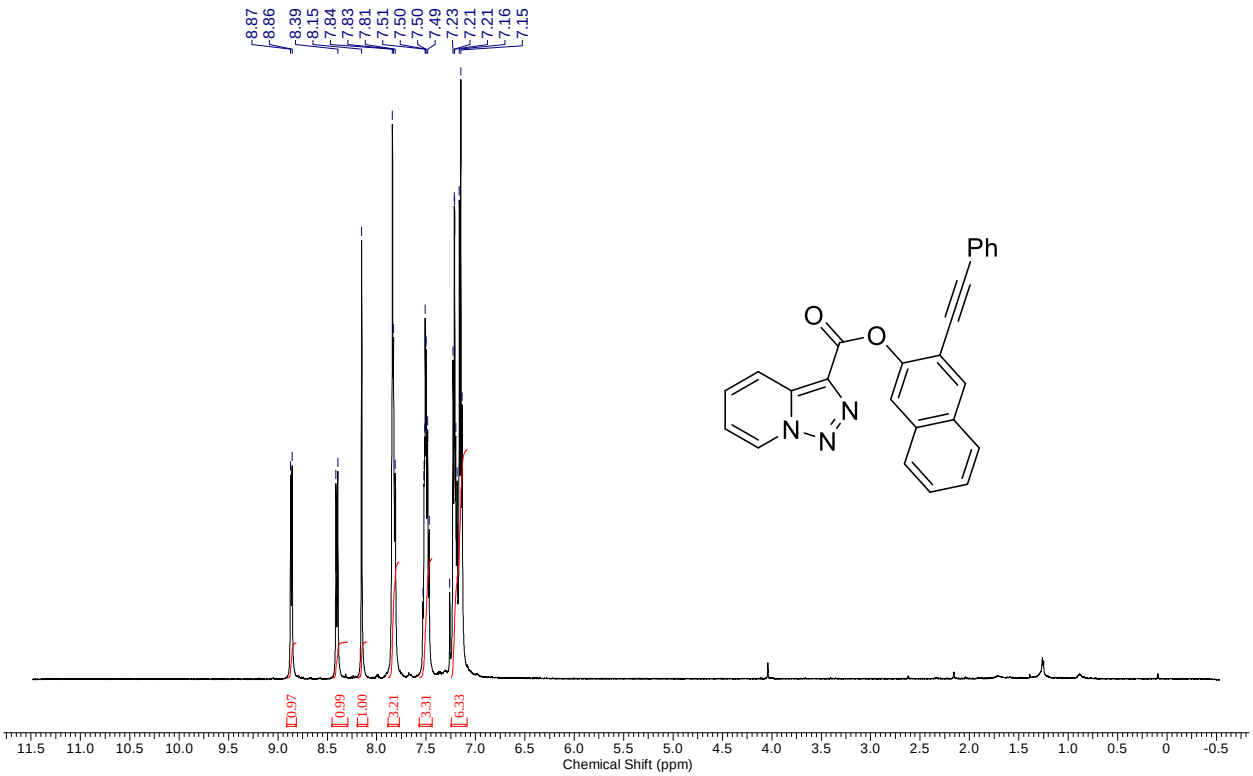
^{1}H NMR Spectrum of **1aq**



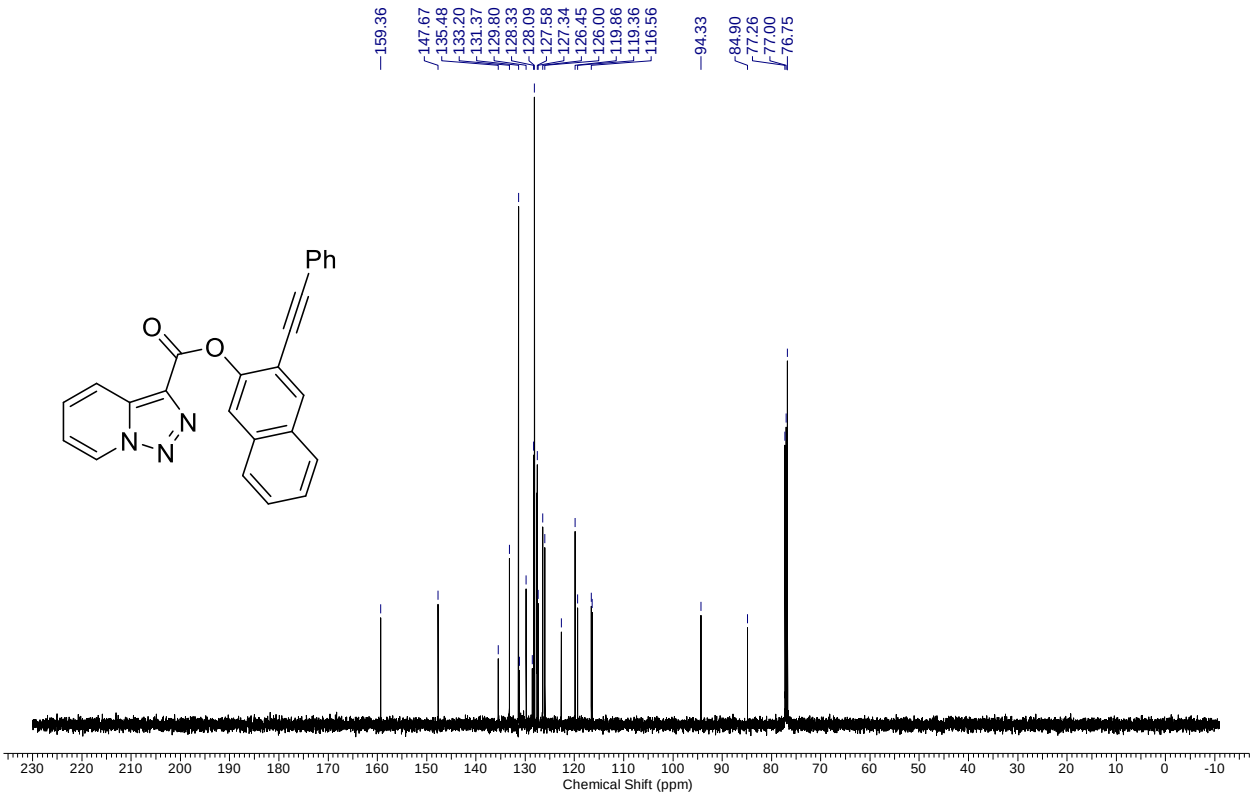
^{13}C NMR Spectrum of **1aq**



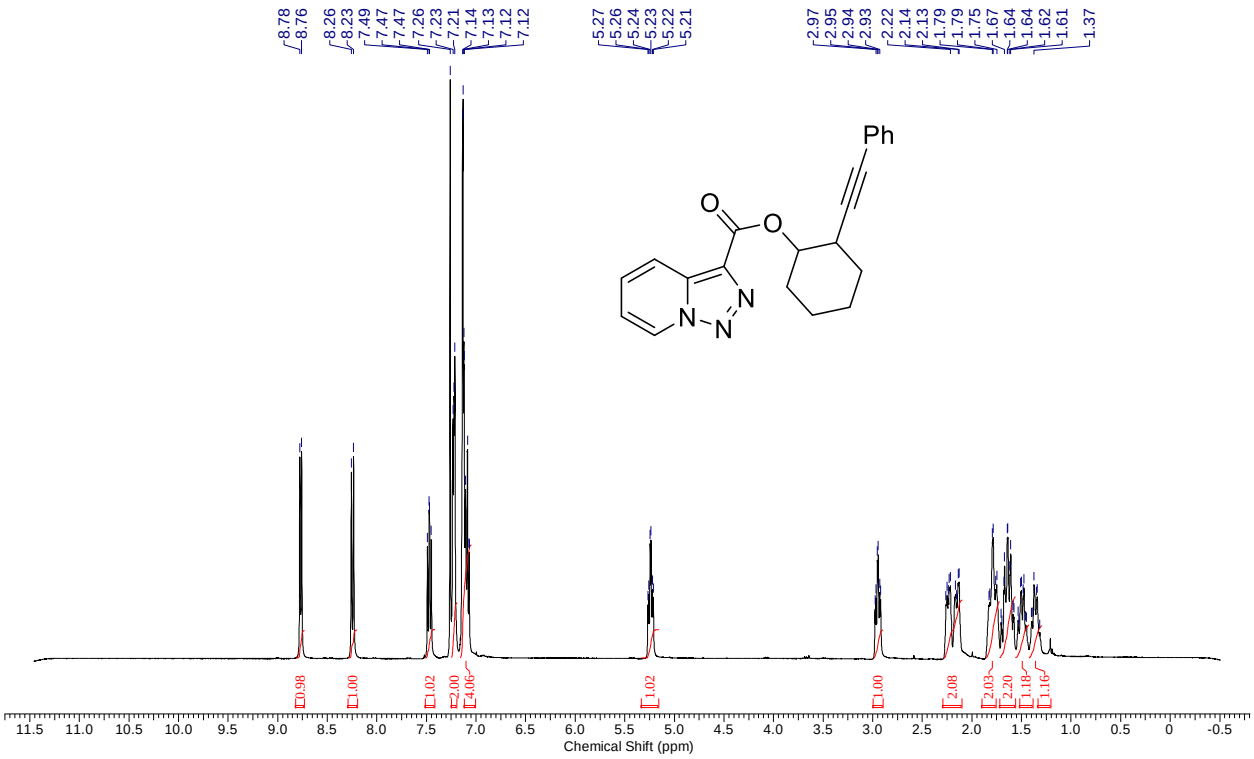
^{1}H NMR Spectrum of **1ar**



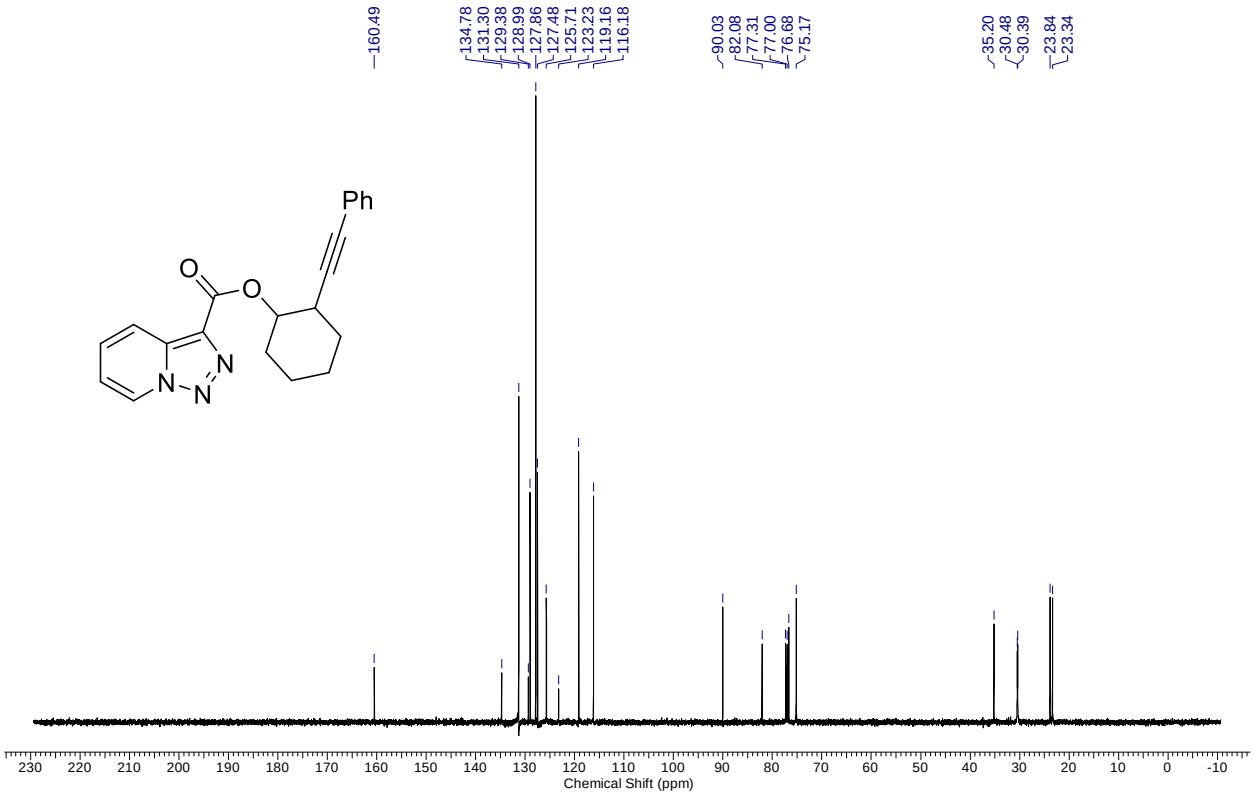
^{13}C NMR Spectrum of **1ar**



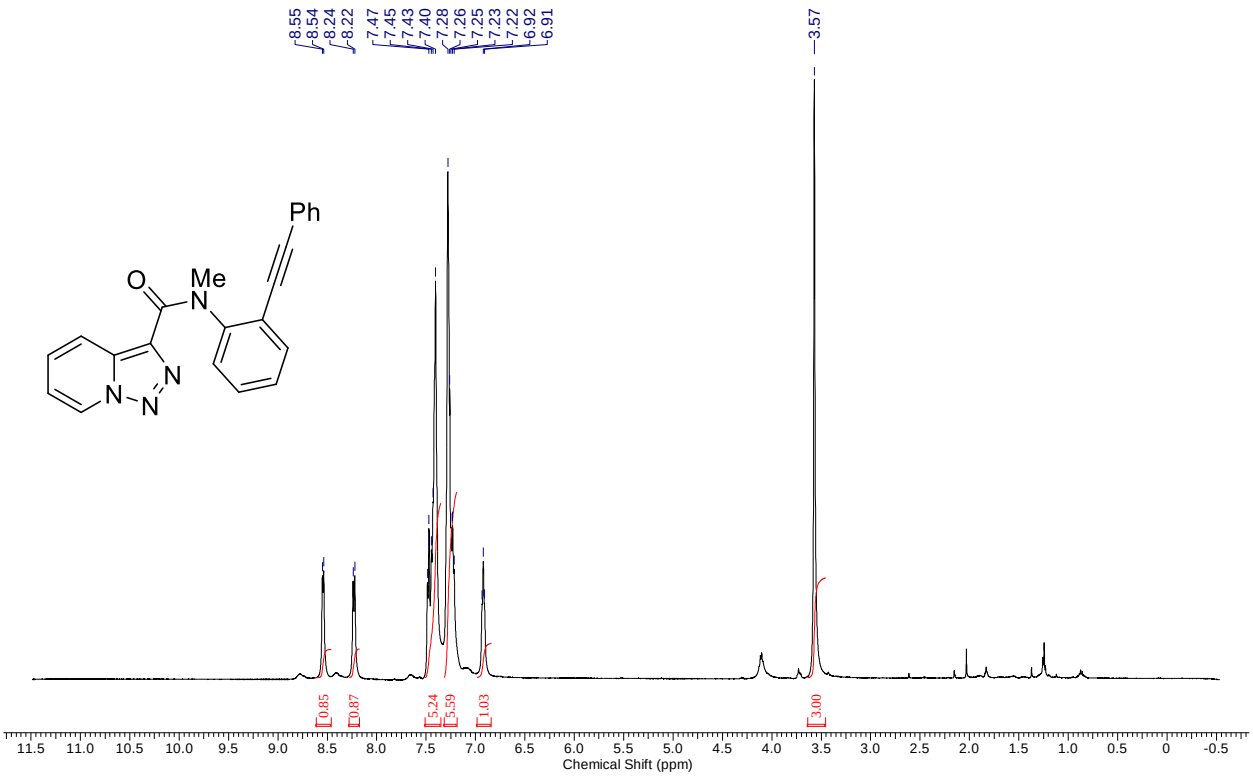
^{1}H NMR Spectrum of **1as**



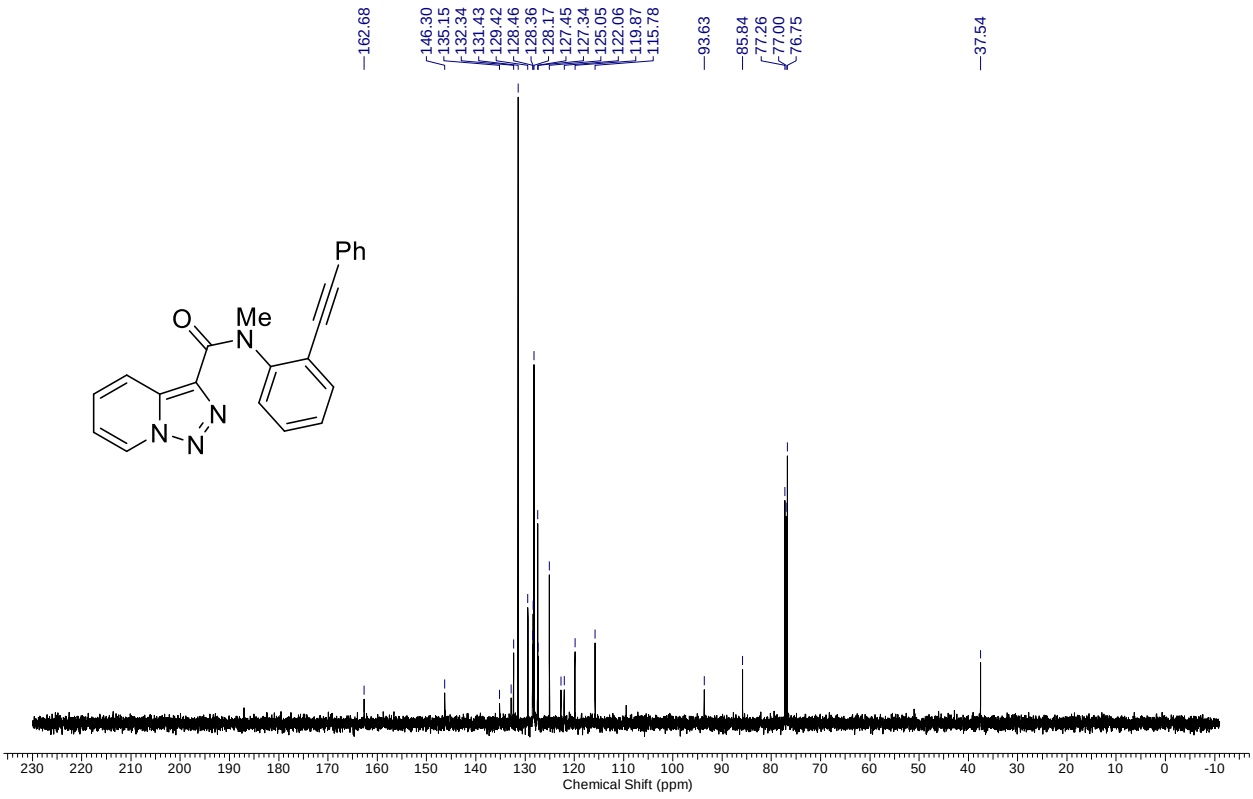
^{13}C NMR Spectrum of **1as**



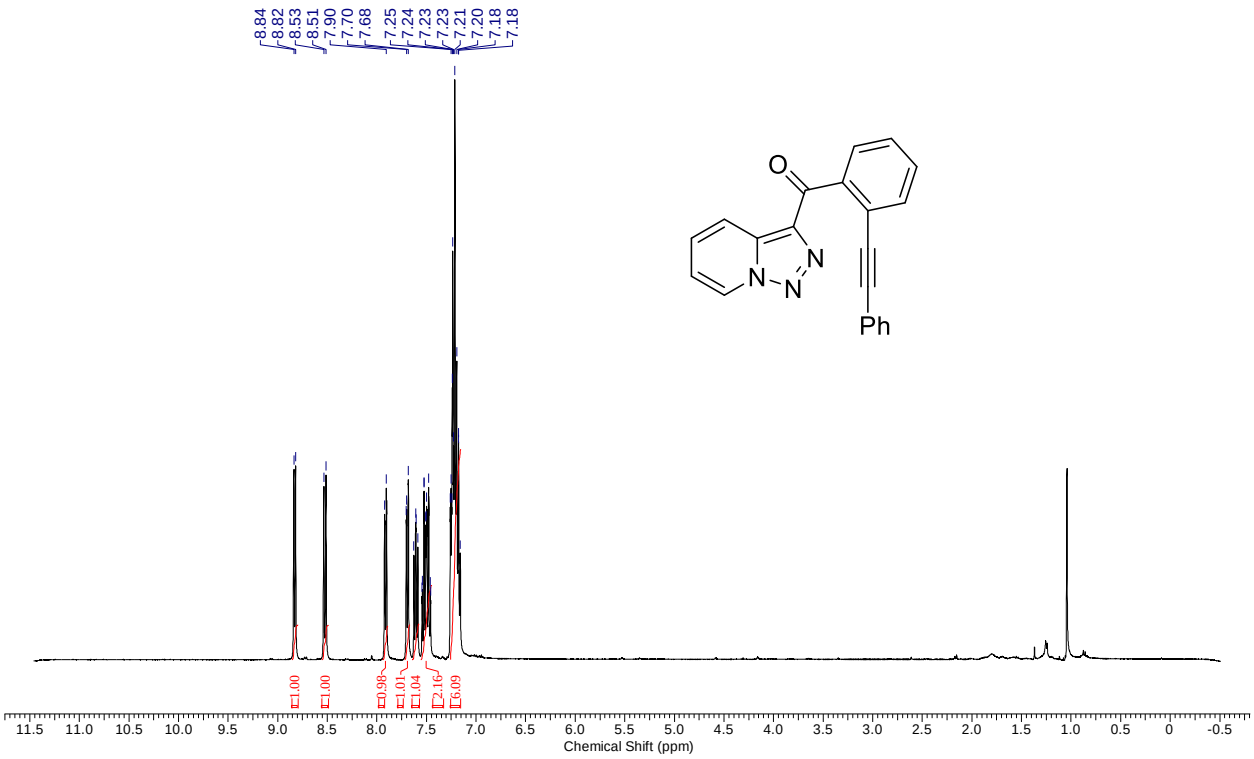
^{1}H NMR Spectrum of **1at**



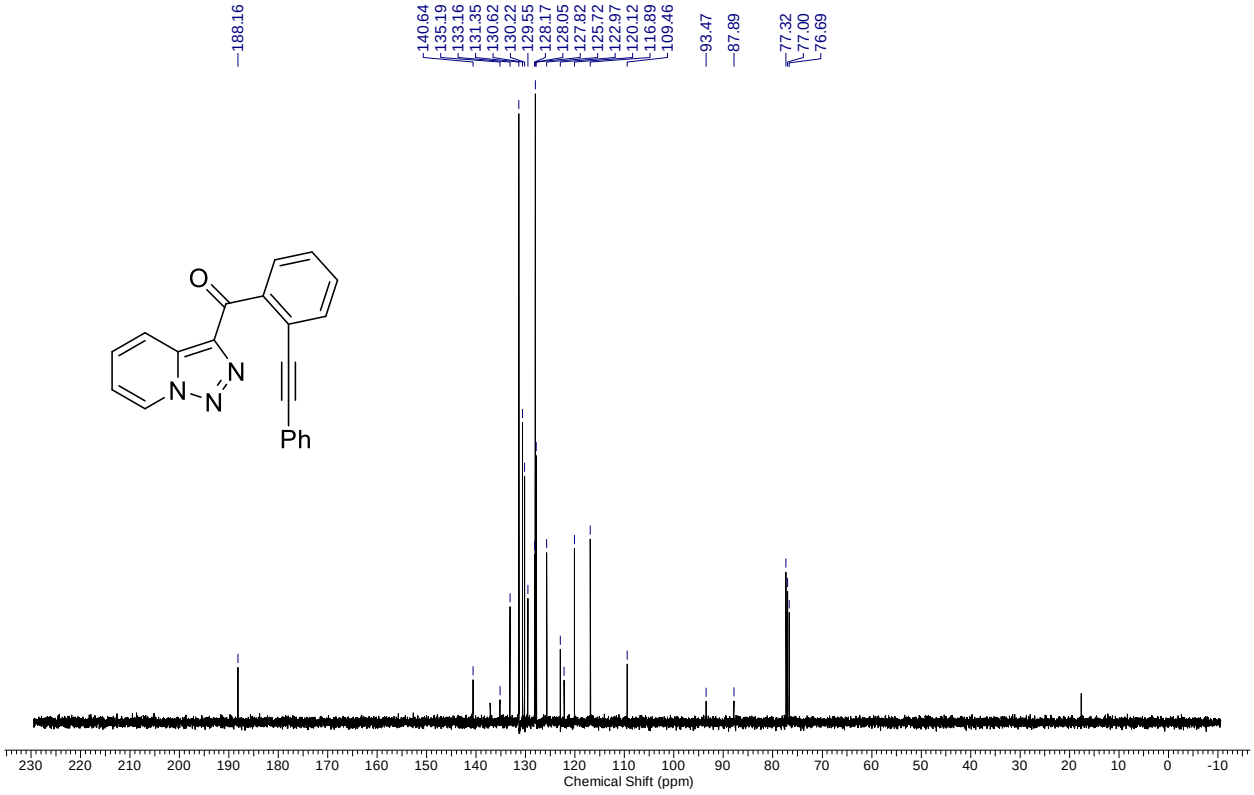
^{13}C NMR Spectrum of **1at**



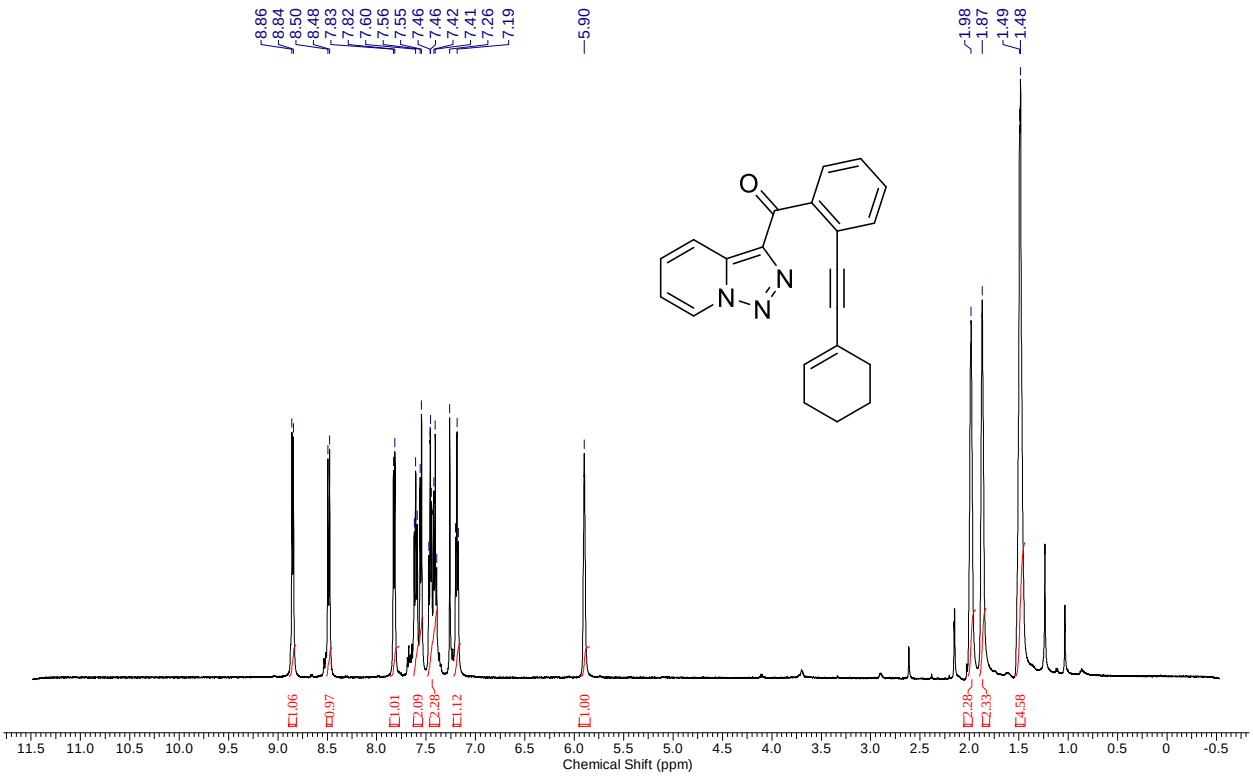
^{1}H NMR Spectrum of **1ba**



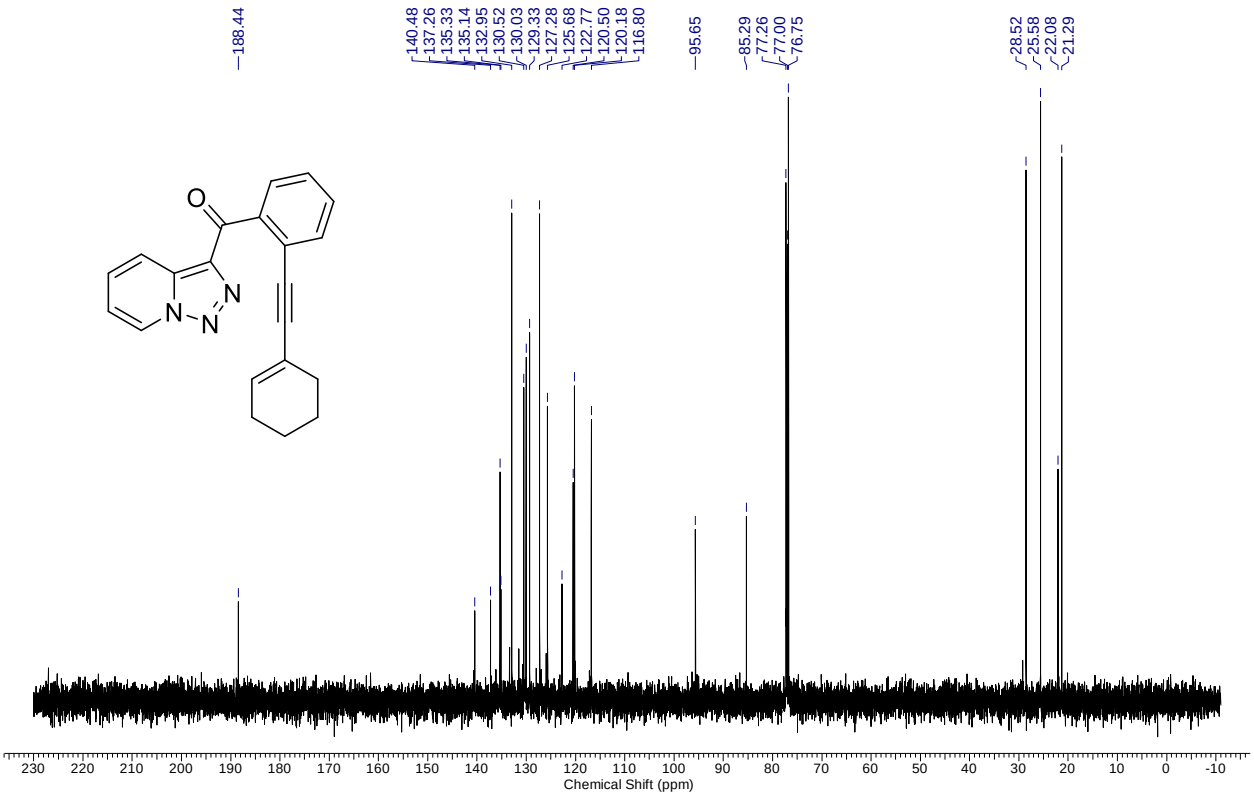
^{13}C NMR Spectrum of **1ba**



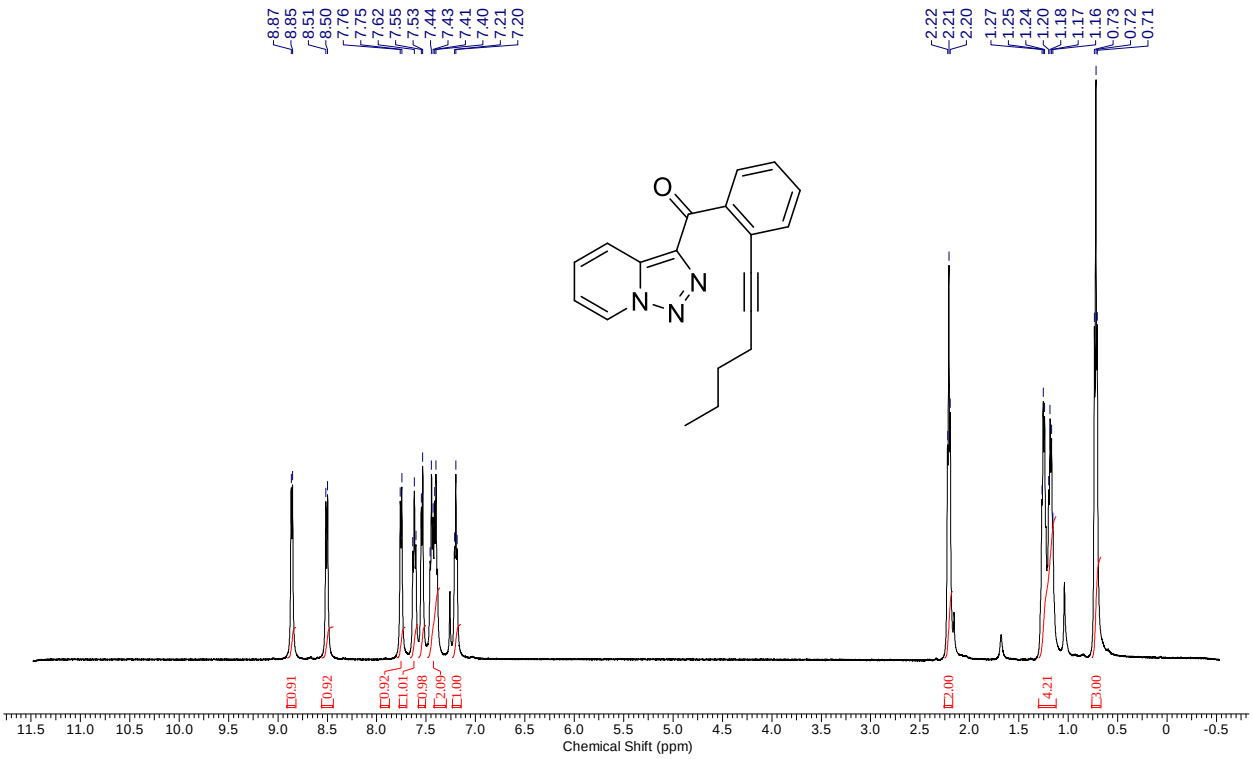
^{1}H NMR Spectrum of **1bb**



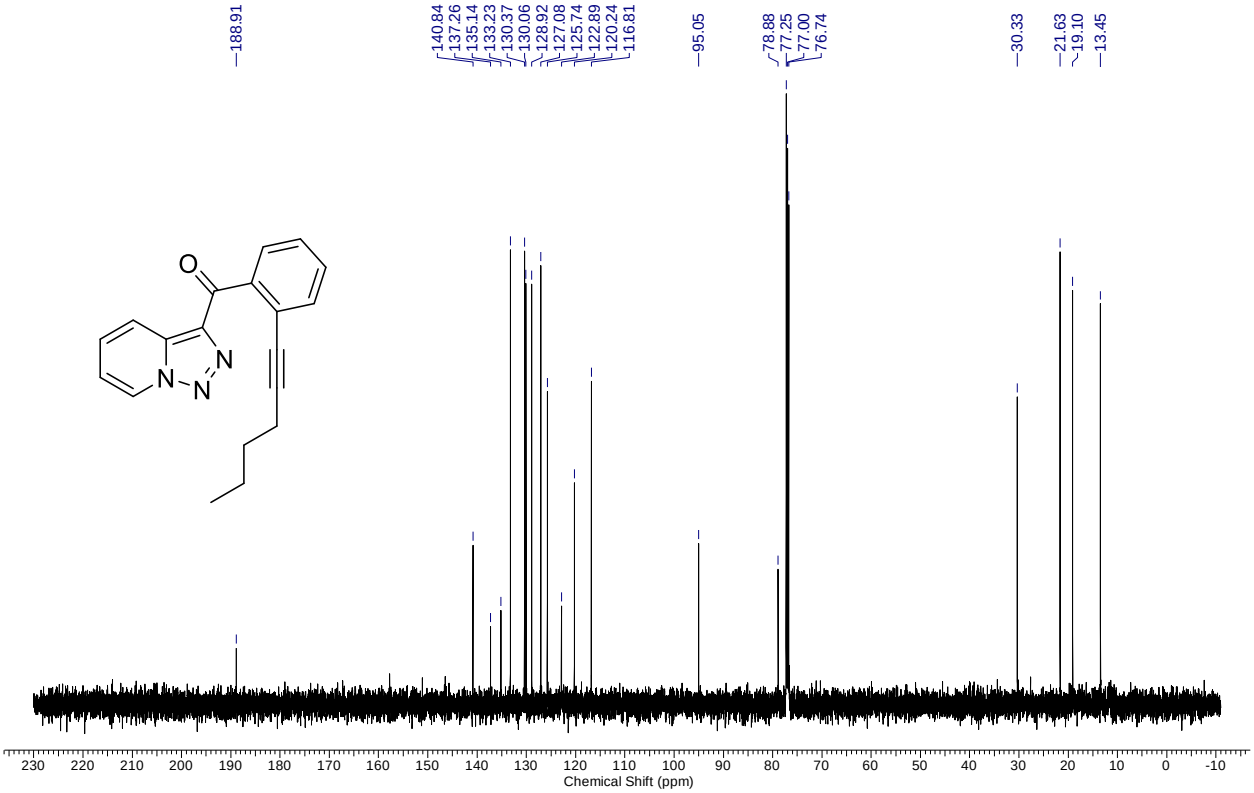
^{13}C NMR Spectrum of **1bb**



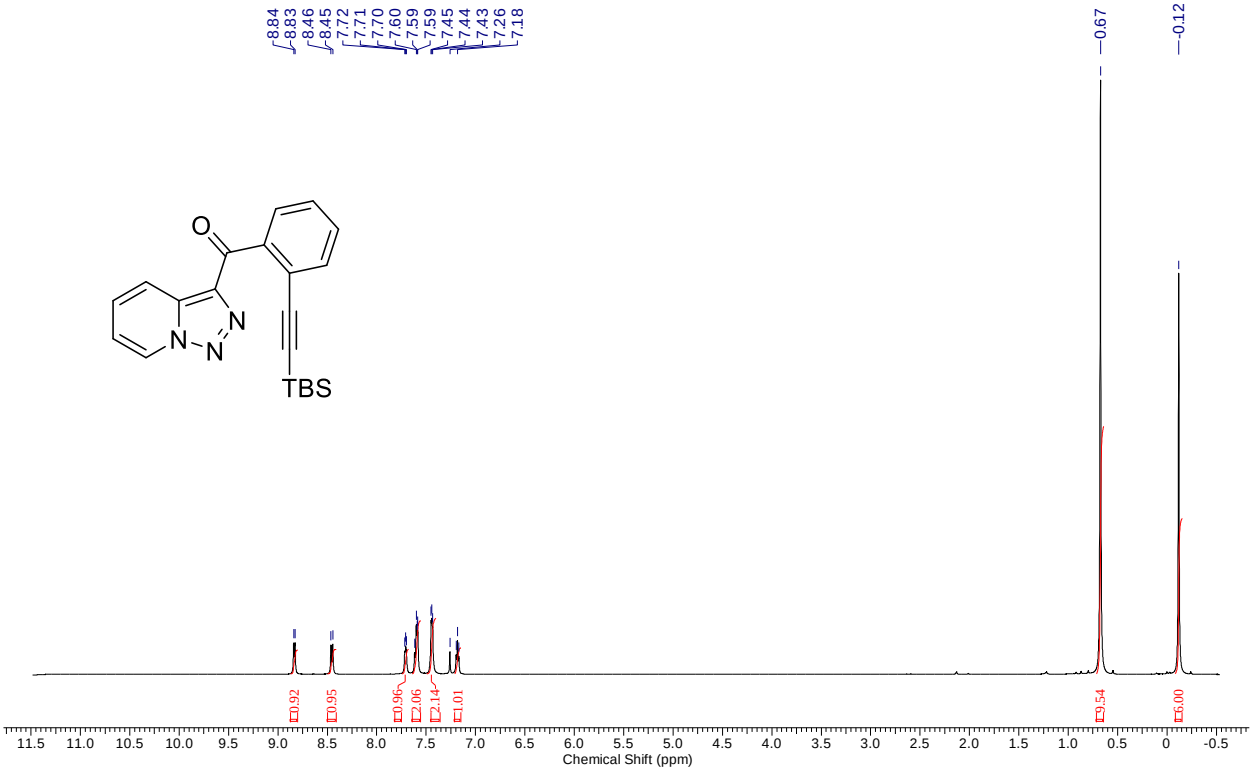
^{1}H NMR Spectrum of **1bc**



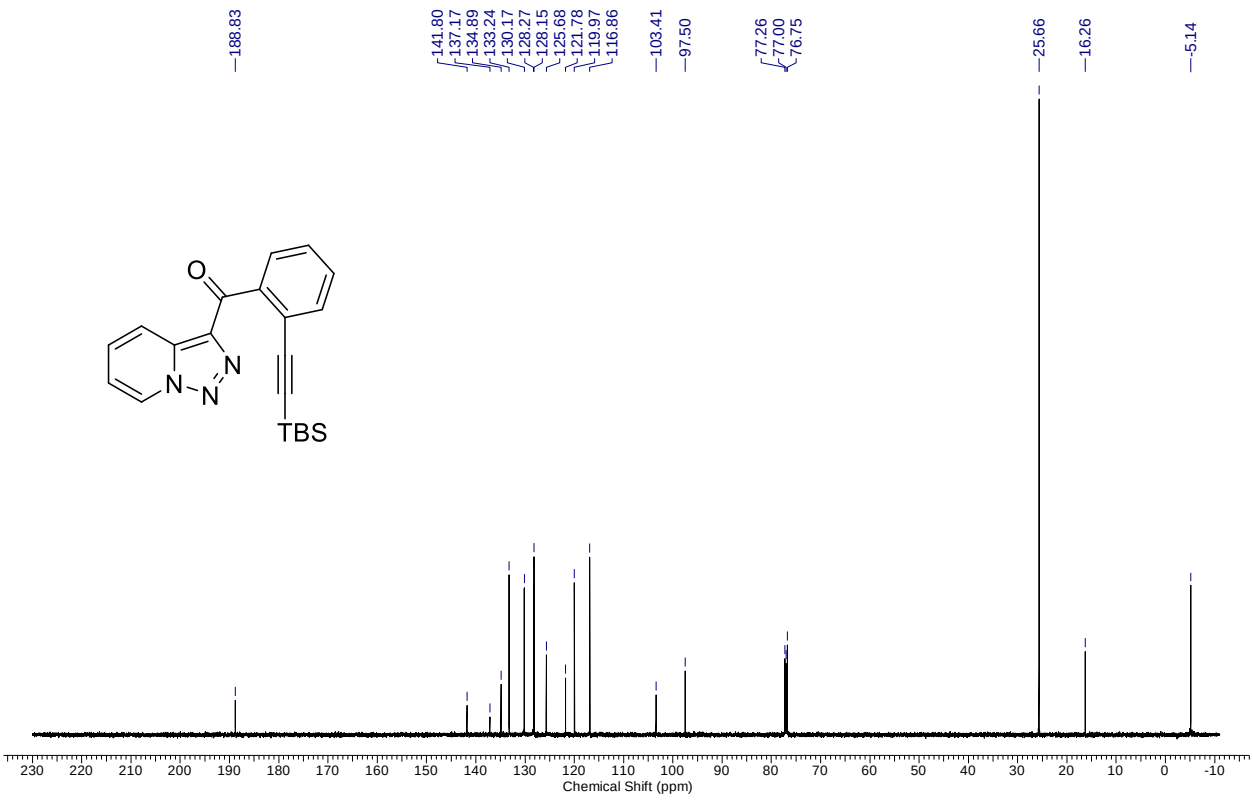
^{13}C NMR Spectrum of **1bc**



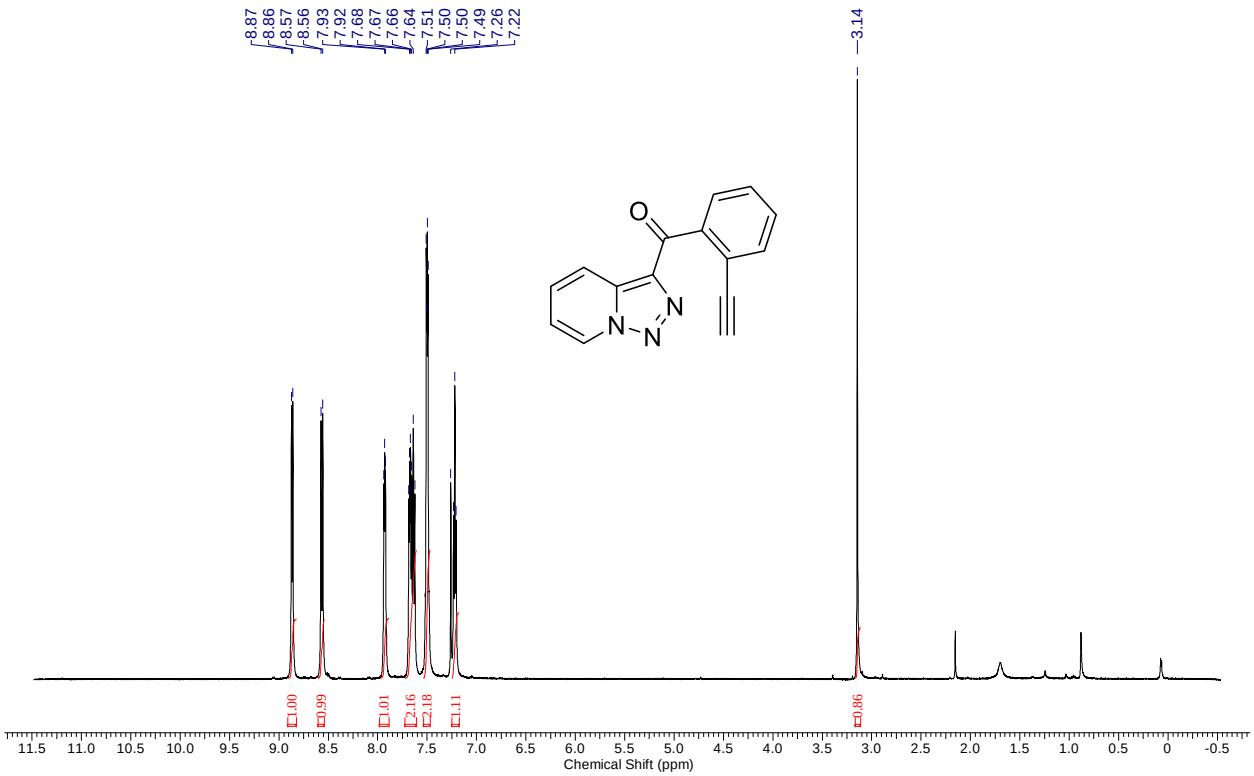
^{1}H NMR Spectrum of **1bd**



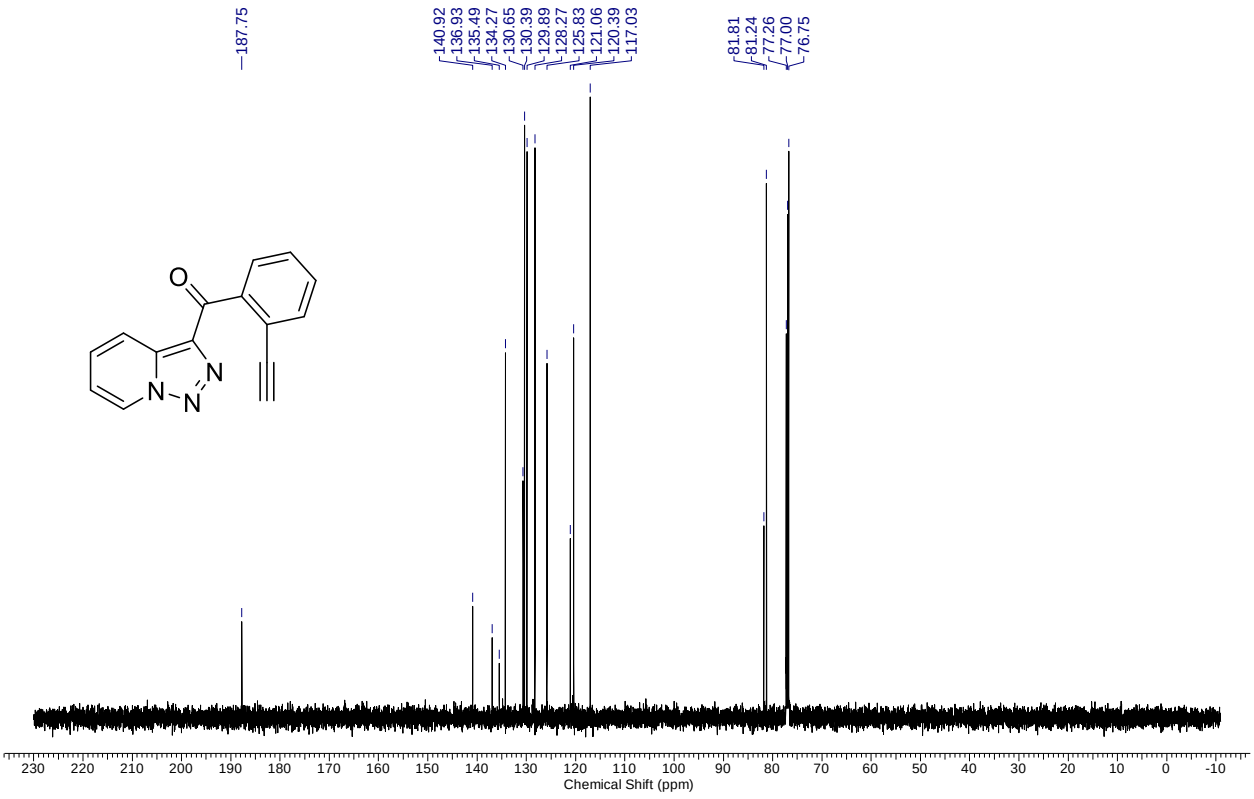
^{13}C NMR Spectrum of **1bd**



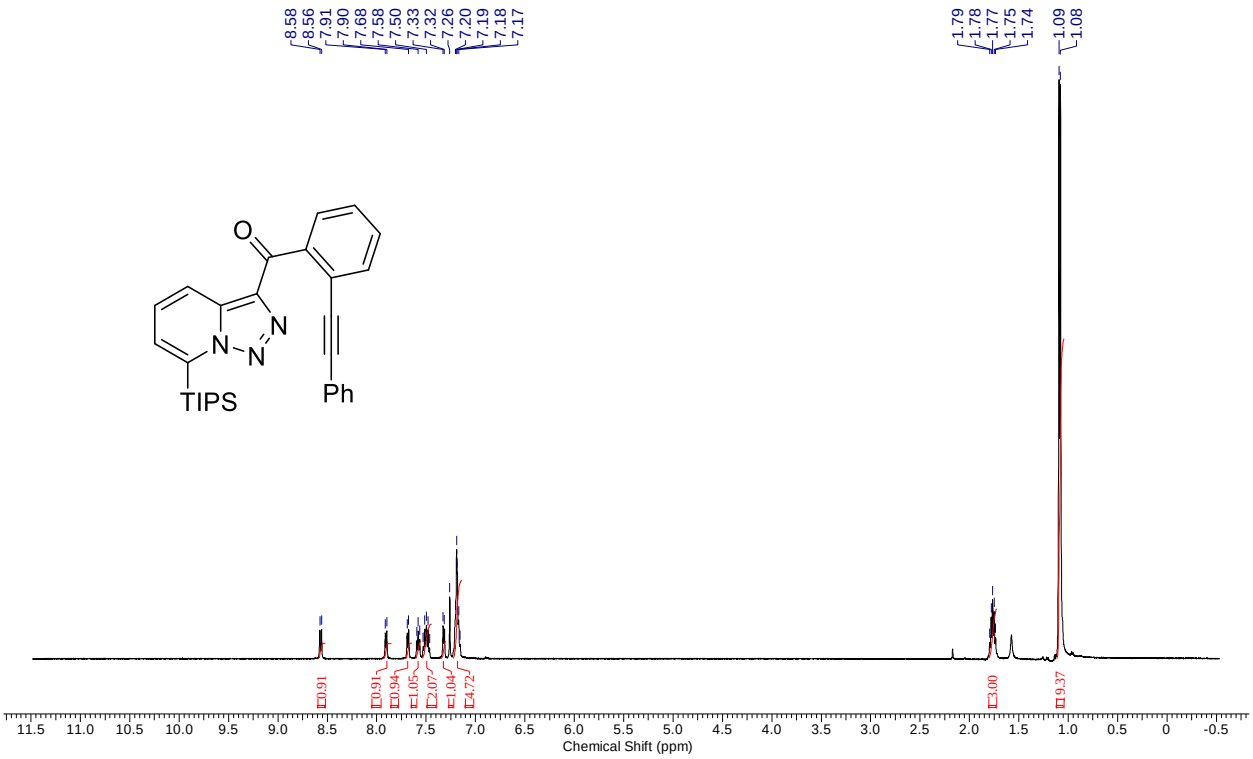
^{1}H NMR Spectrum of **1be**



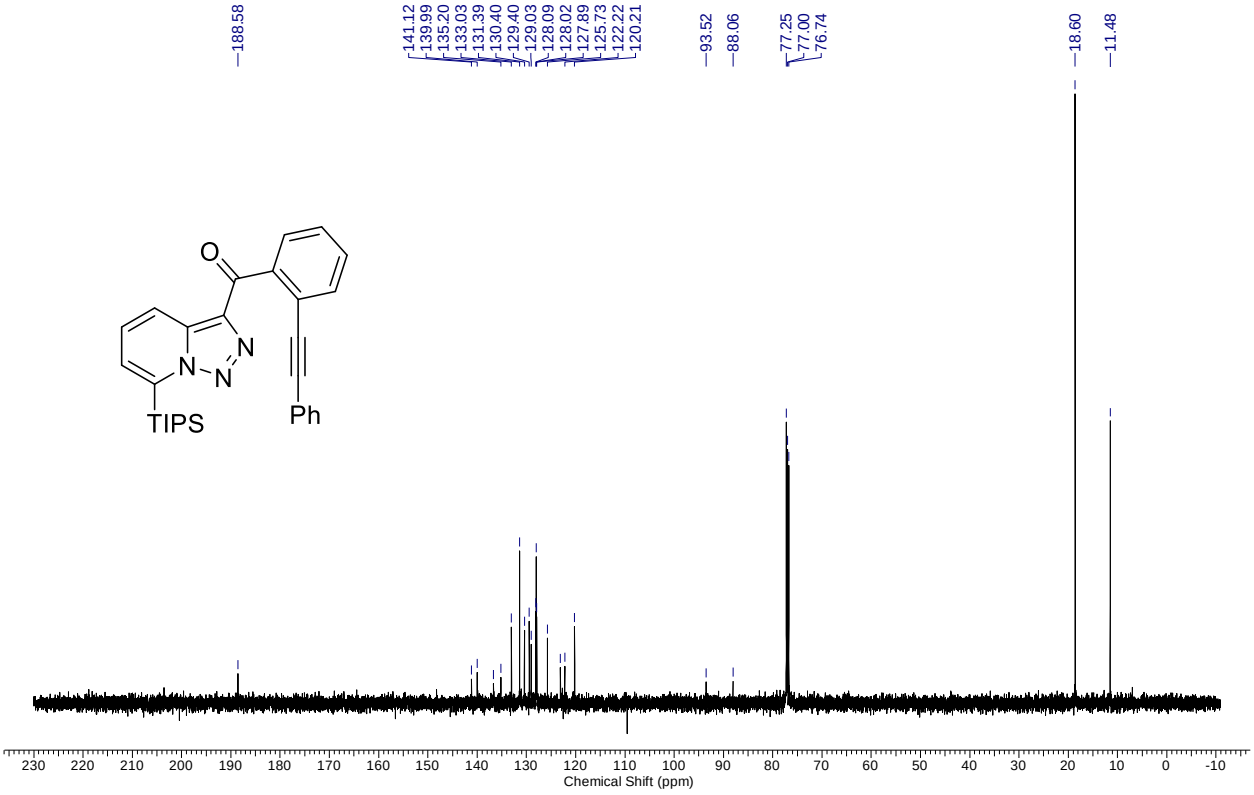
^{13}C NMR Spectrum of **1be**



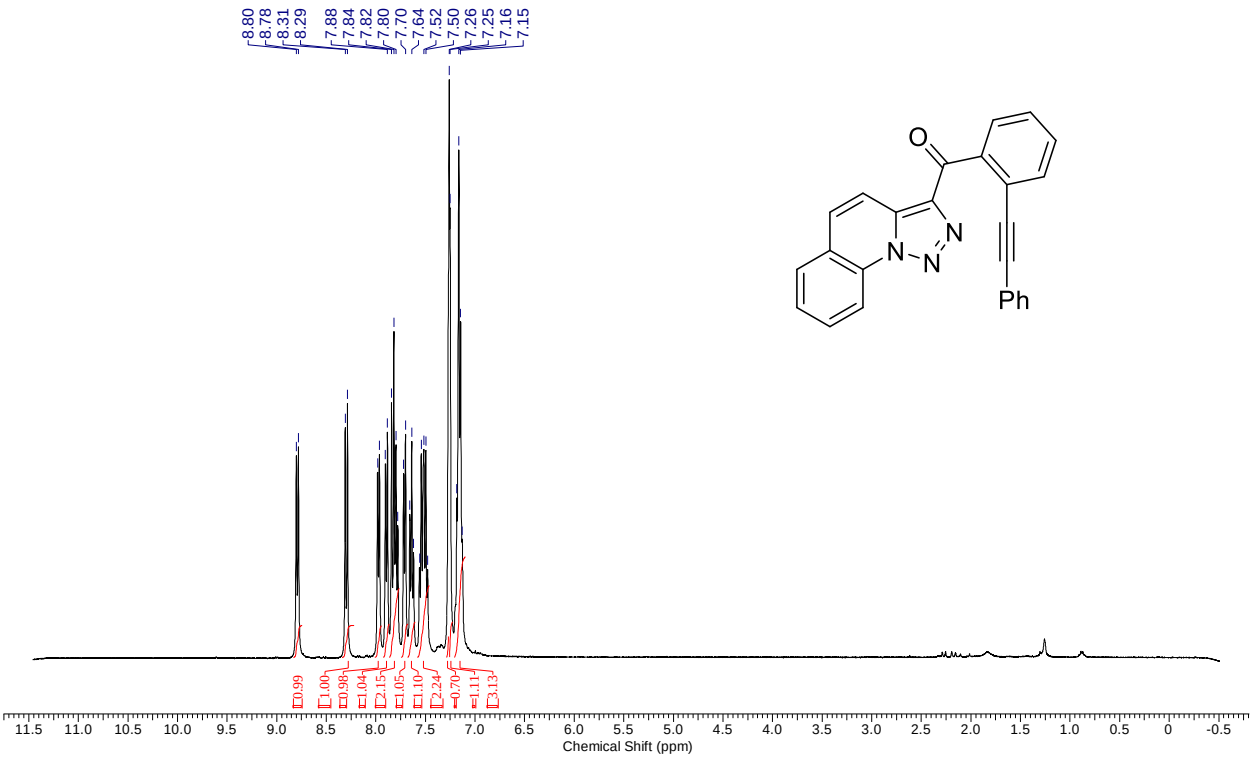
^{1}H NMR Spectrum of **1bf**



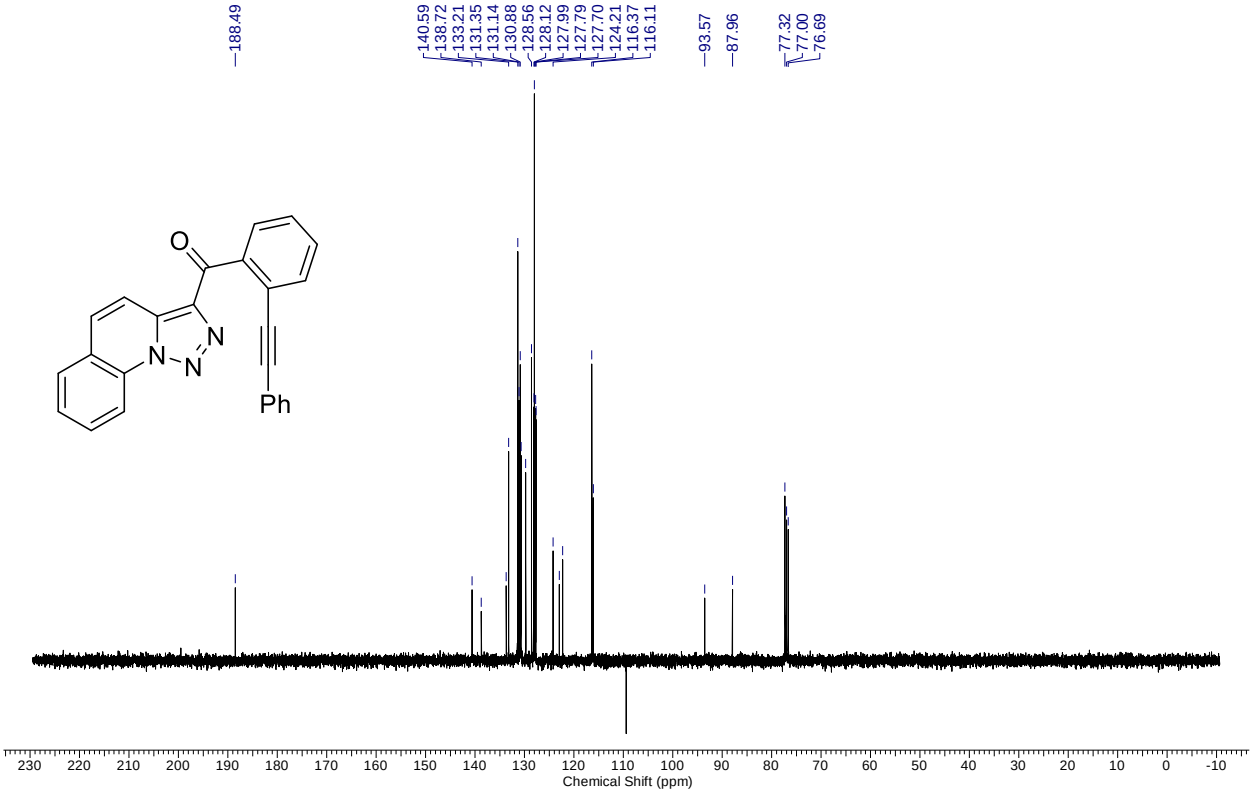
^{13}C NMR Spectrum of **1bf**



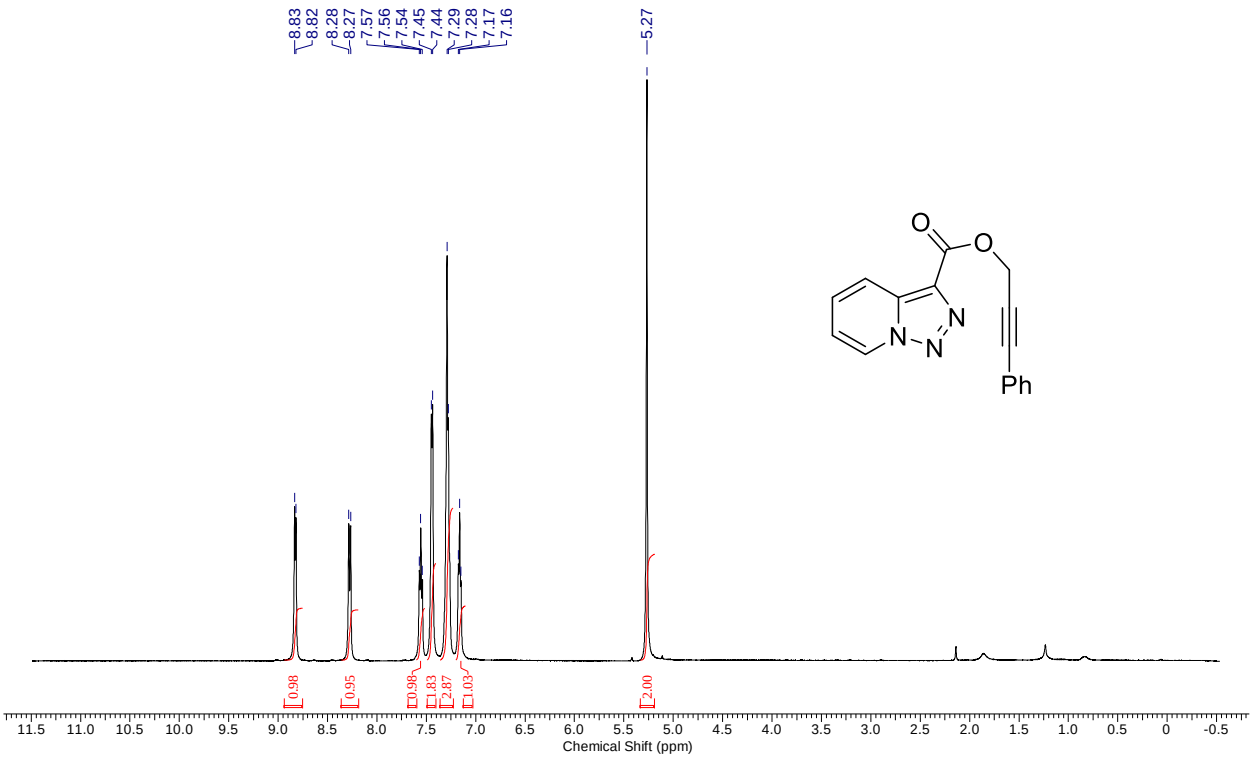
^{1}H NMR Spectrum of **1bg**



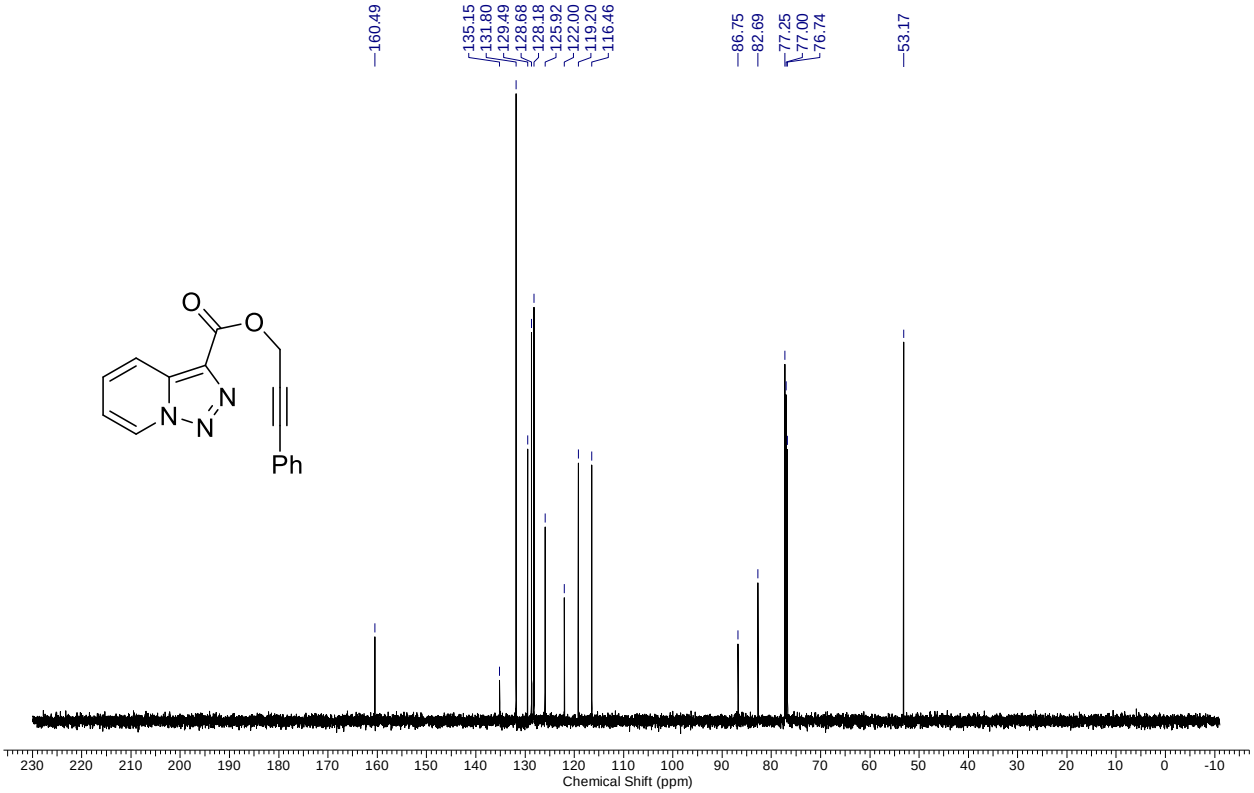
^{13}C NMR Spectrum of **1bg**



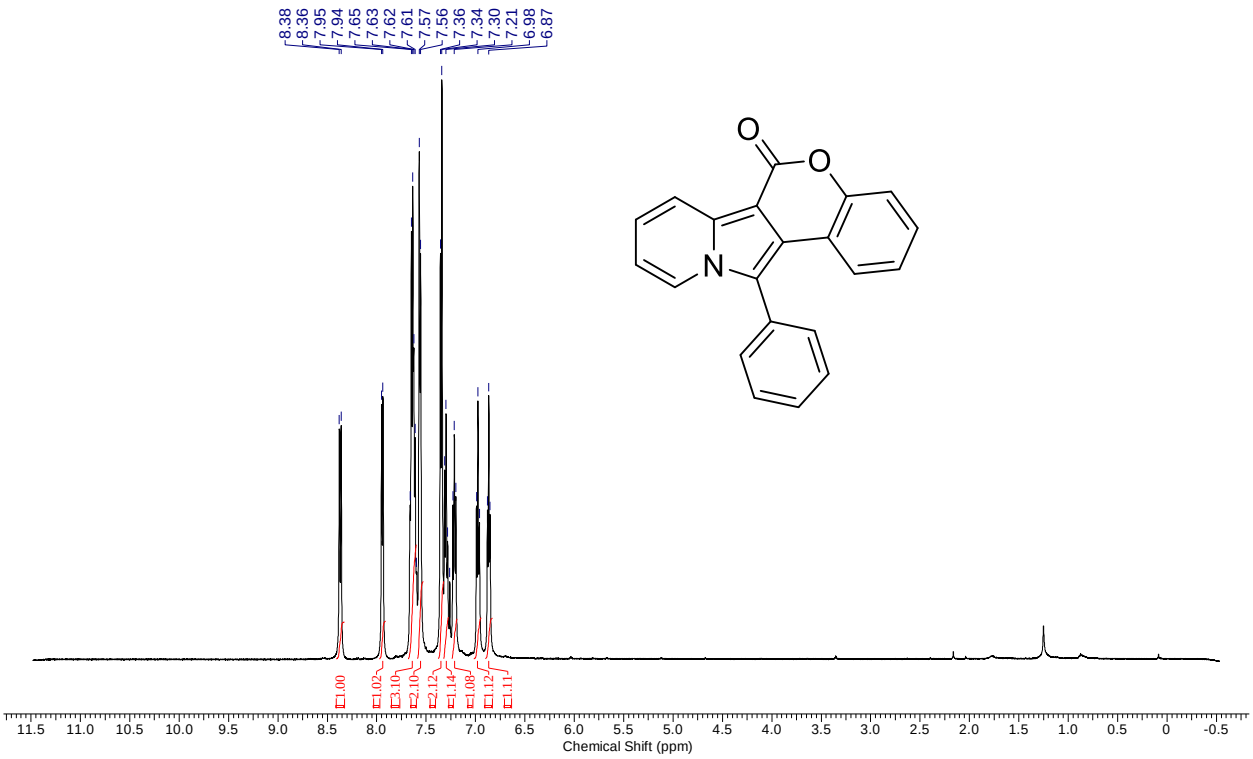
^{1}H NMR Spectrum of **1bh**



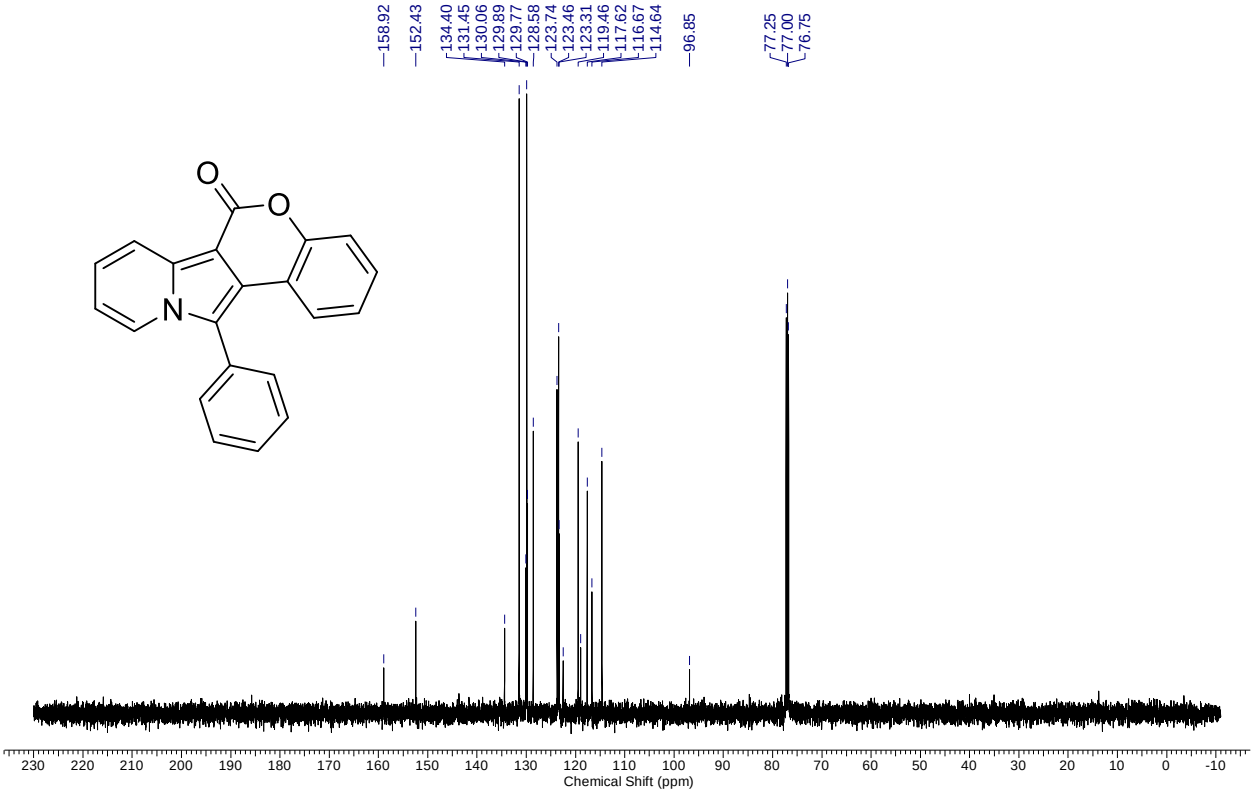
^{13}C NMR Spectrum of **1bh**



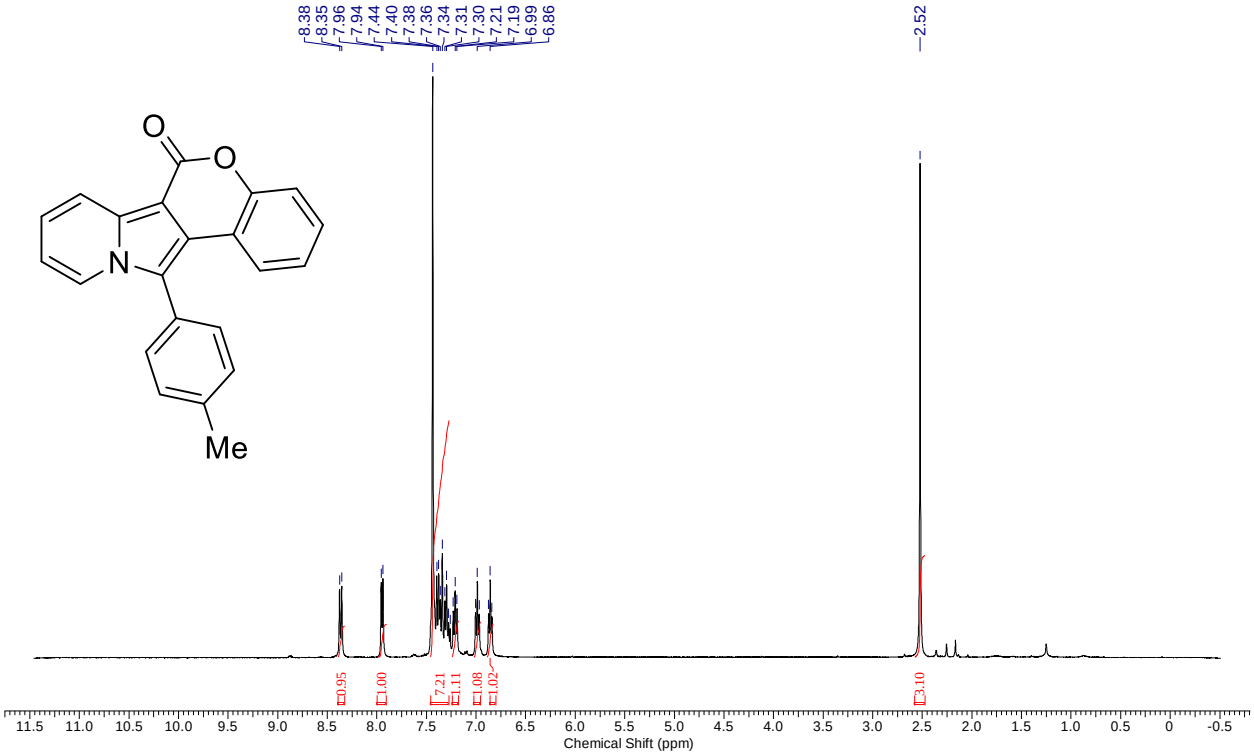
^{1}H NMR Spectrum of **2aa**



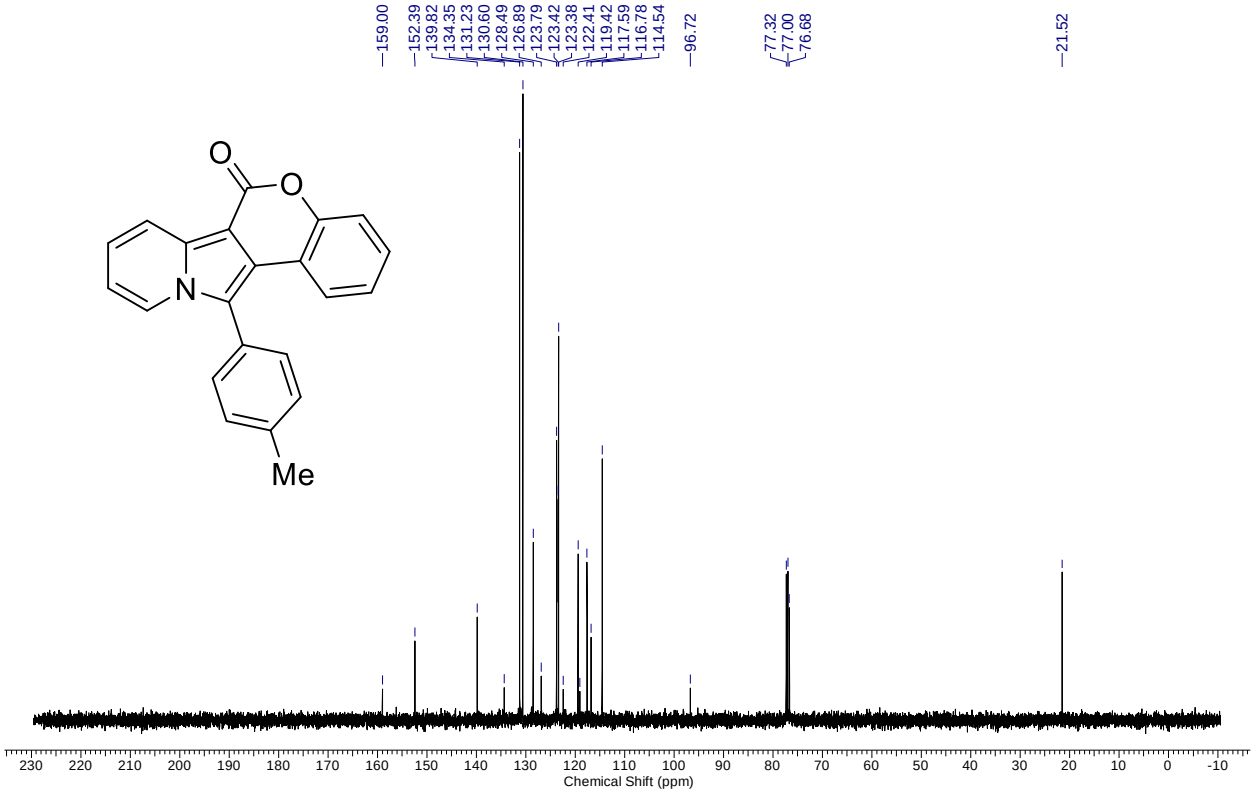
^{13}C NMR Spectrum of **2aa**



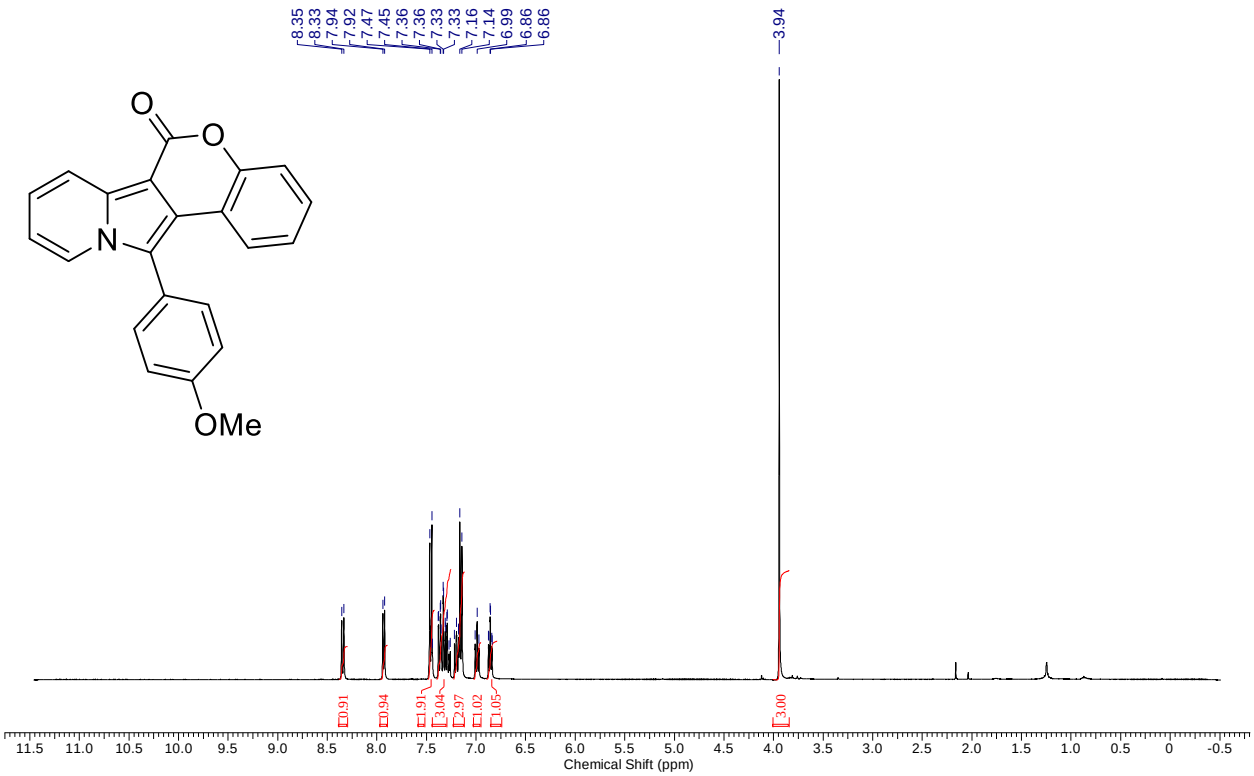
^{1}H NMR Spectrum of **2ab**



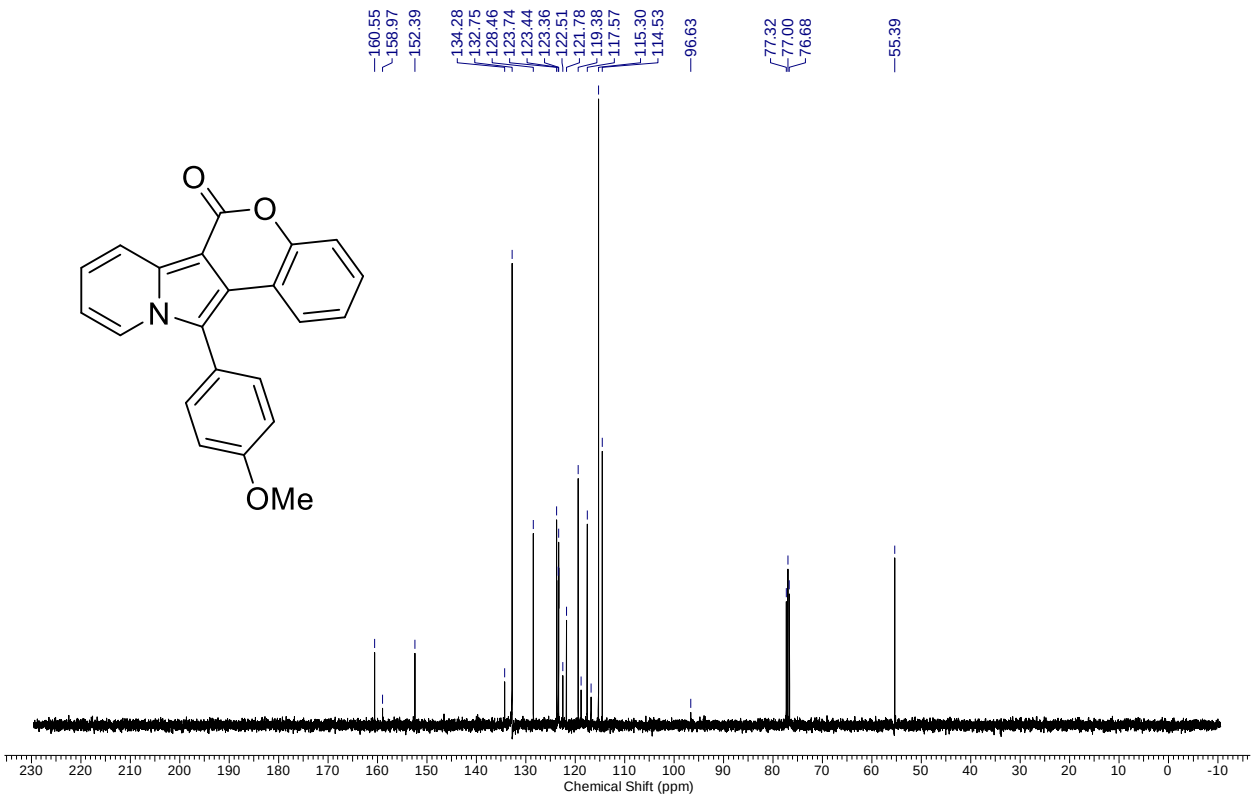
^{13}C NMR Spectrum of **2ab**



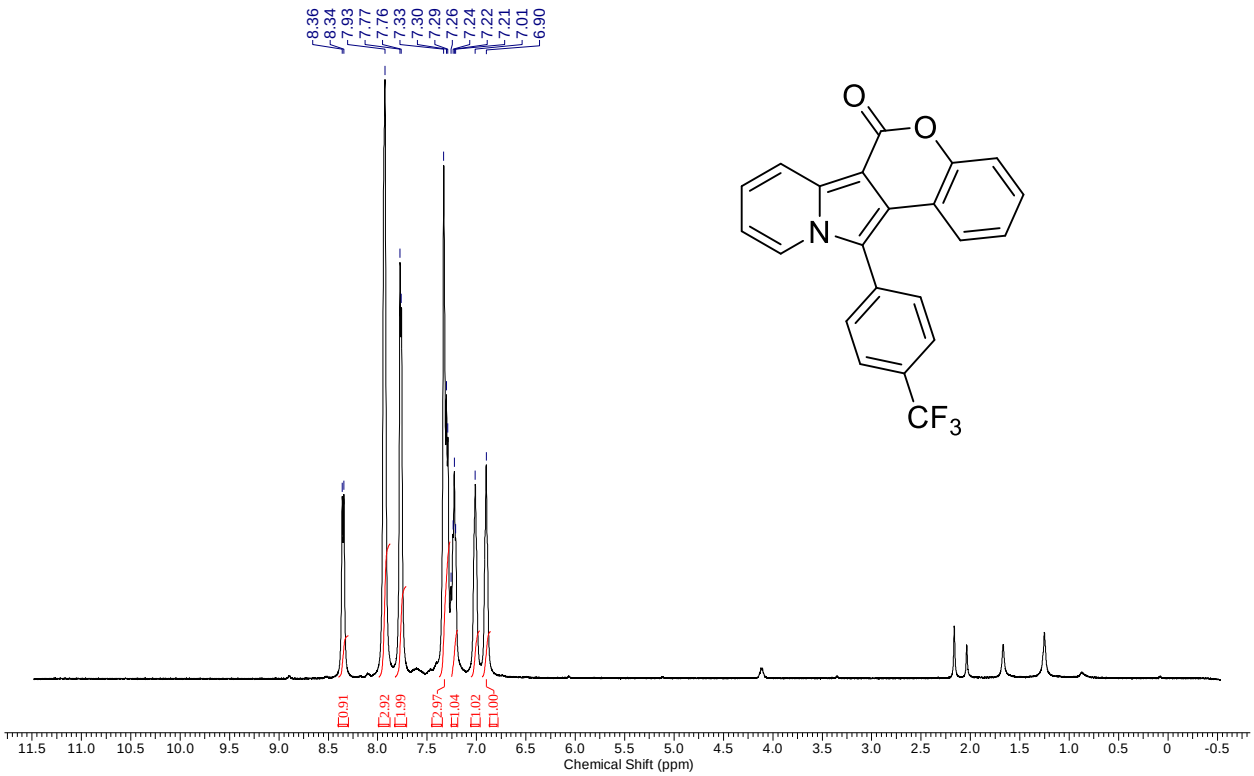
^{1}H NMR Spectrum of **2ac**



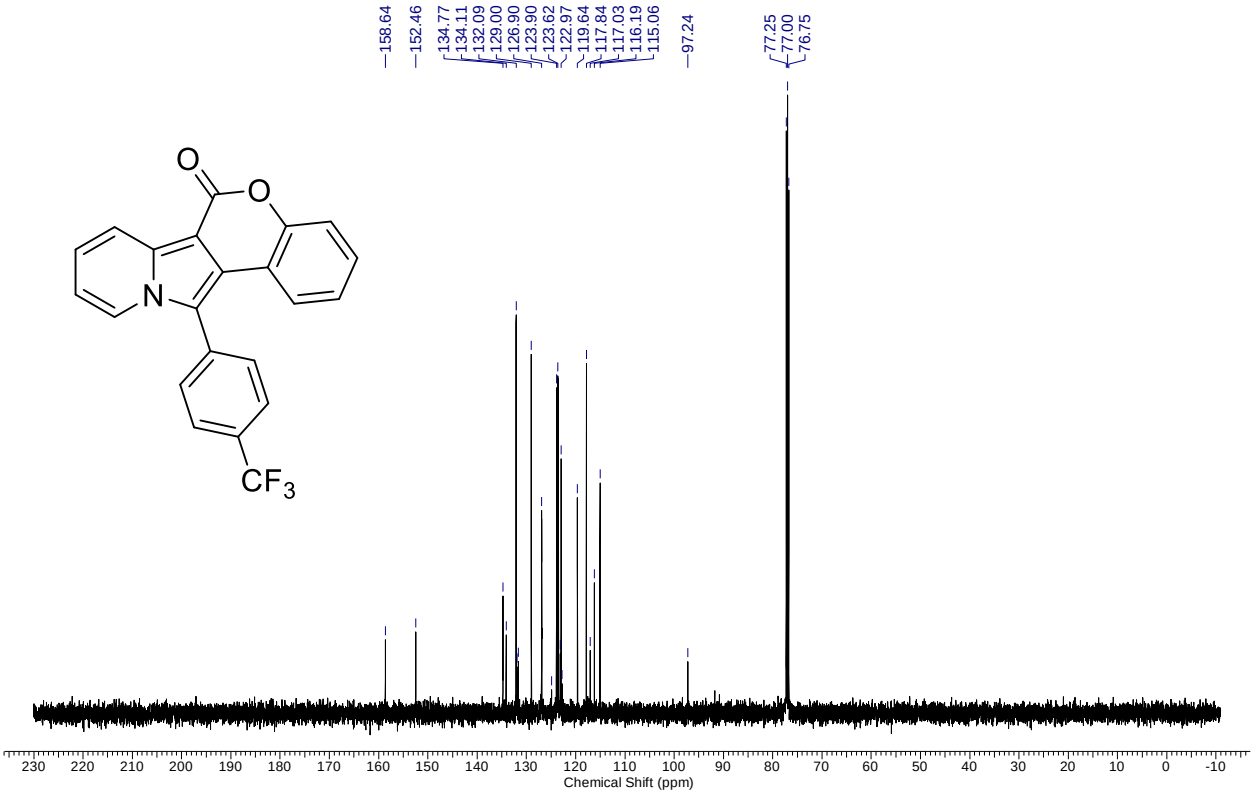
^{13}C NMR Spectrum of **2ac**



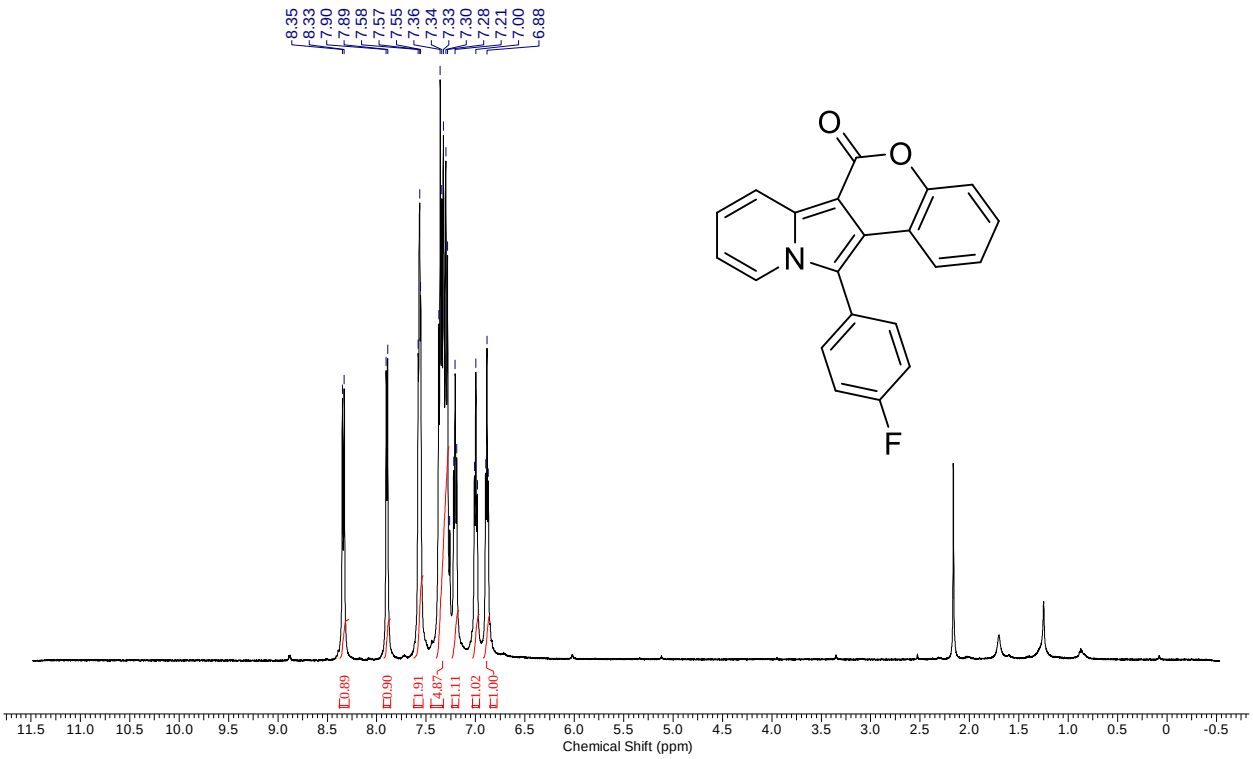
^{1}H NMR Spectrum of **2ad**



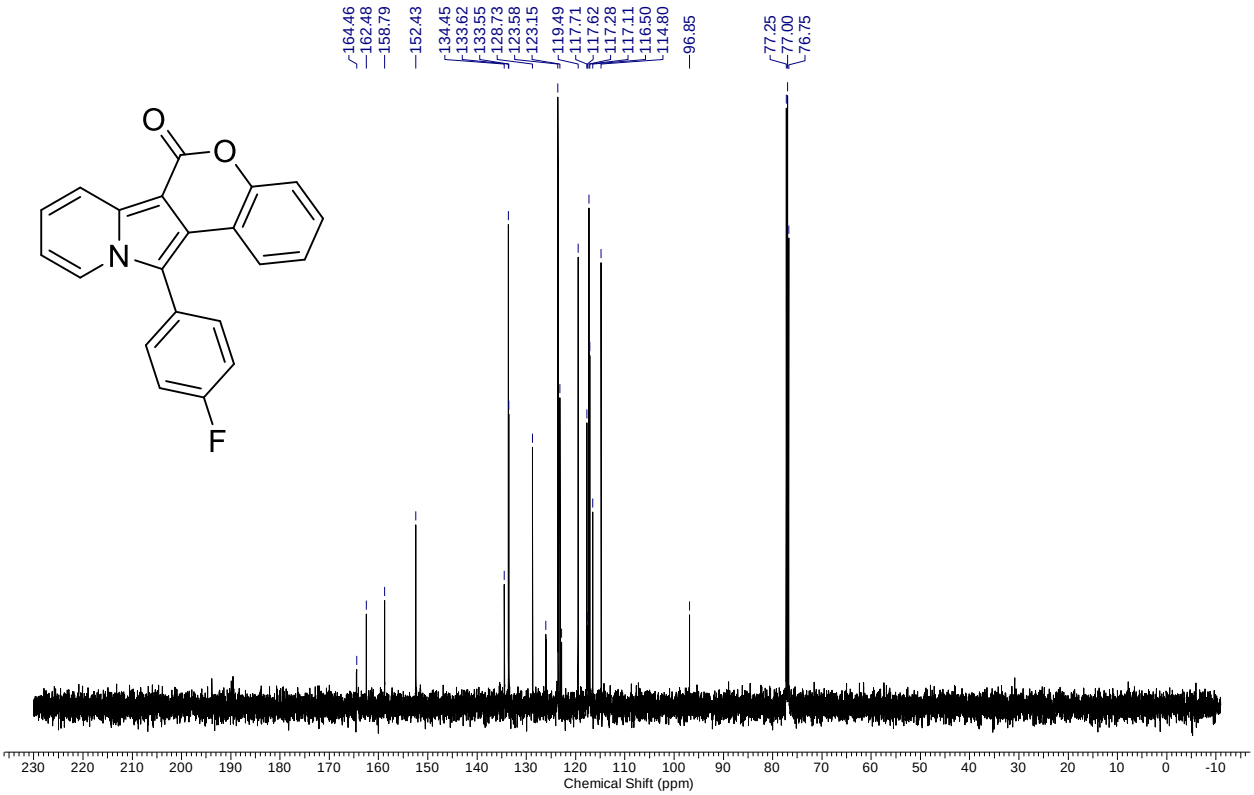
^{13}C NMR Spectrum of **2ad**



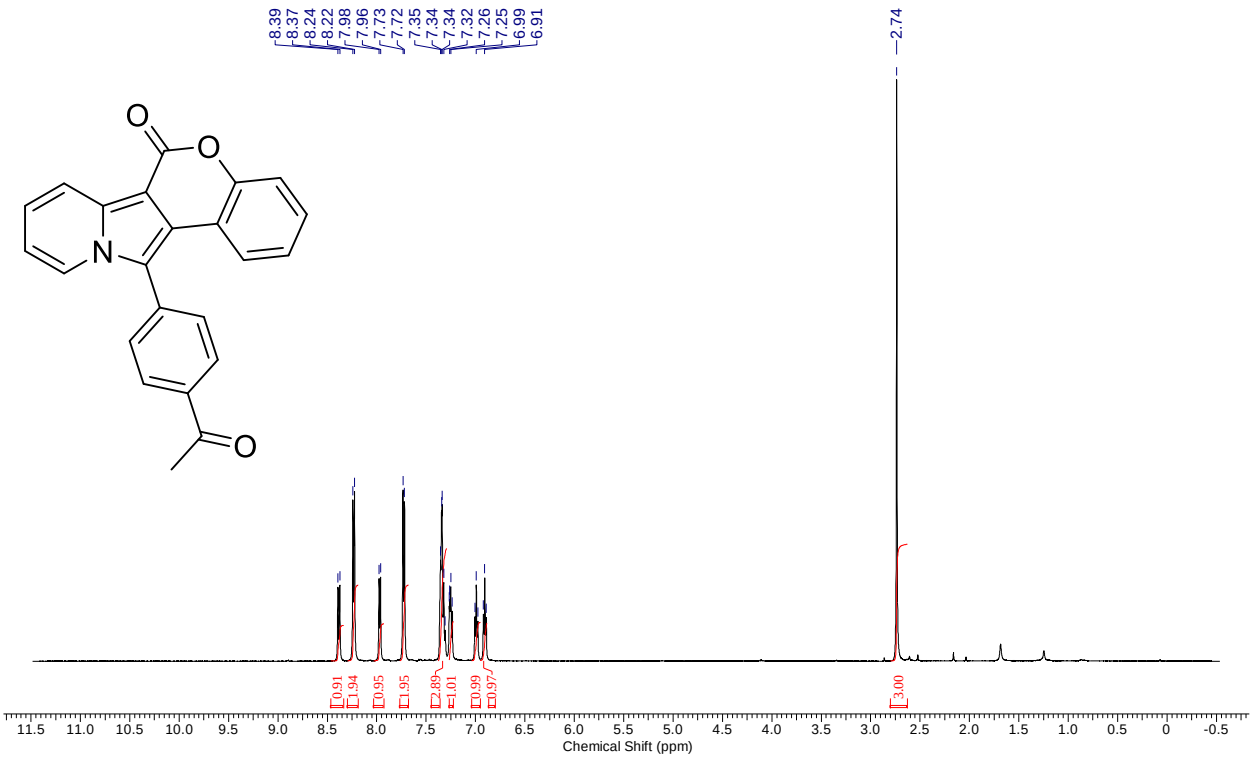
^{1}H NMR Spectrum of **2ae**



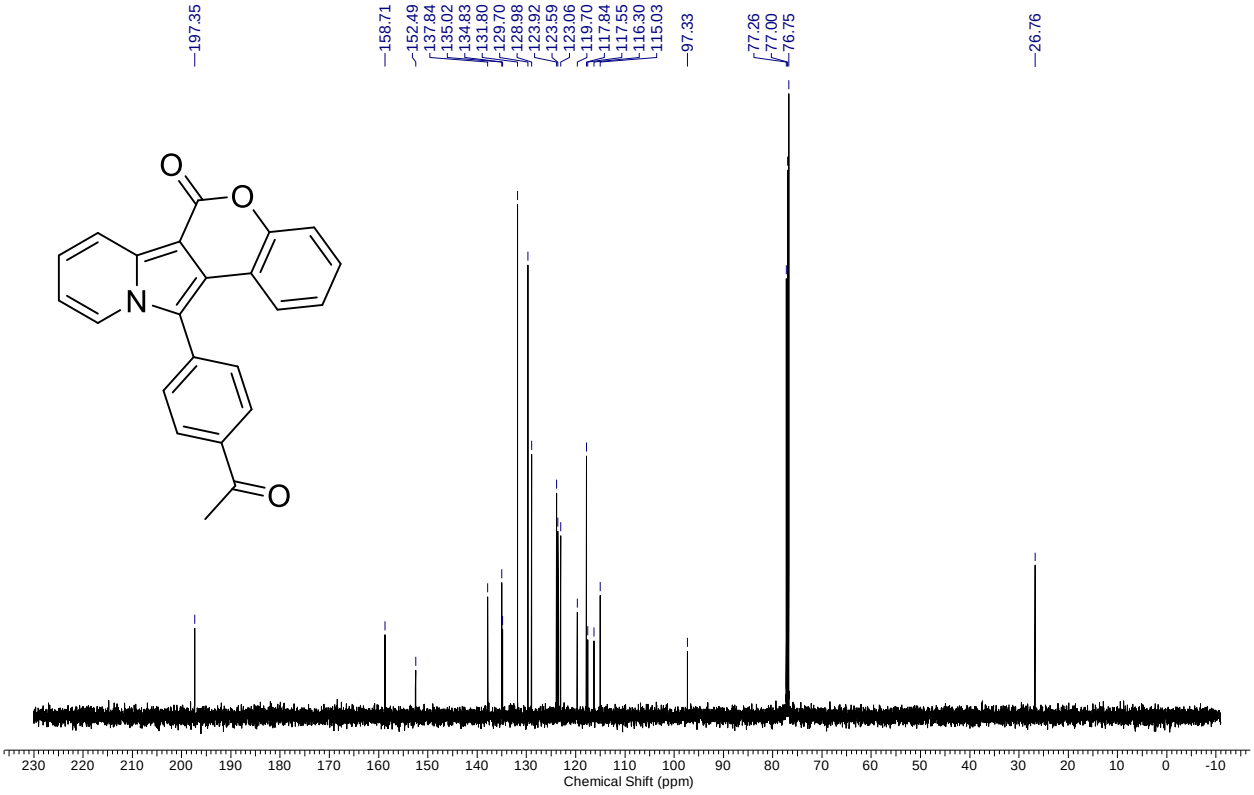
^{13}C NMR Spectrum of **2ae**



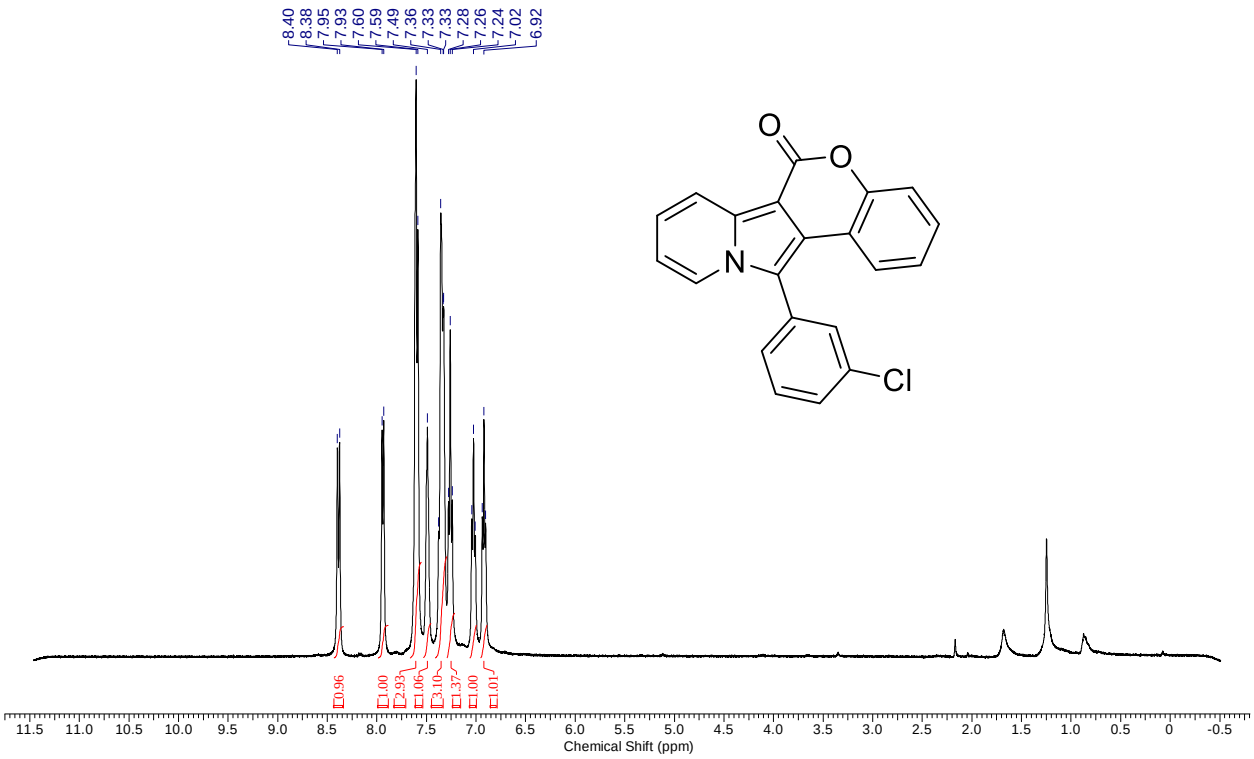
^{1}H NMR Spectrum of **2af**



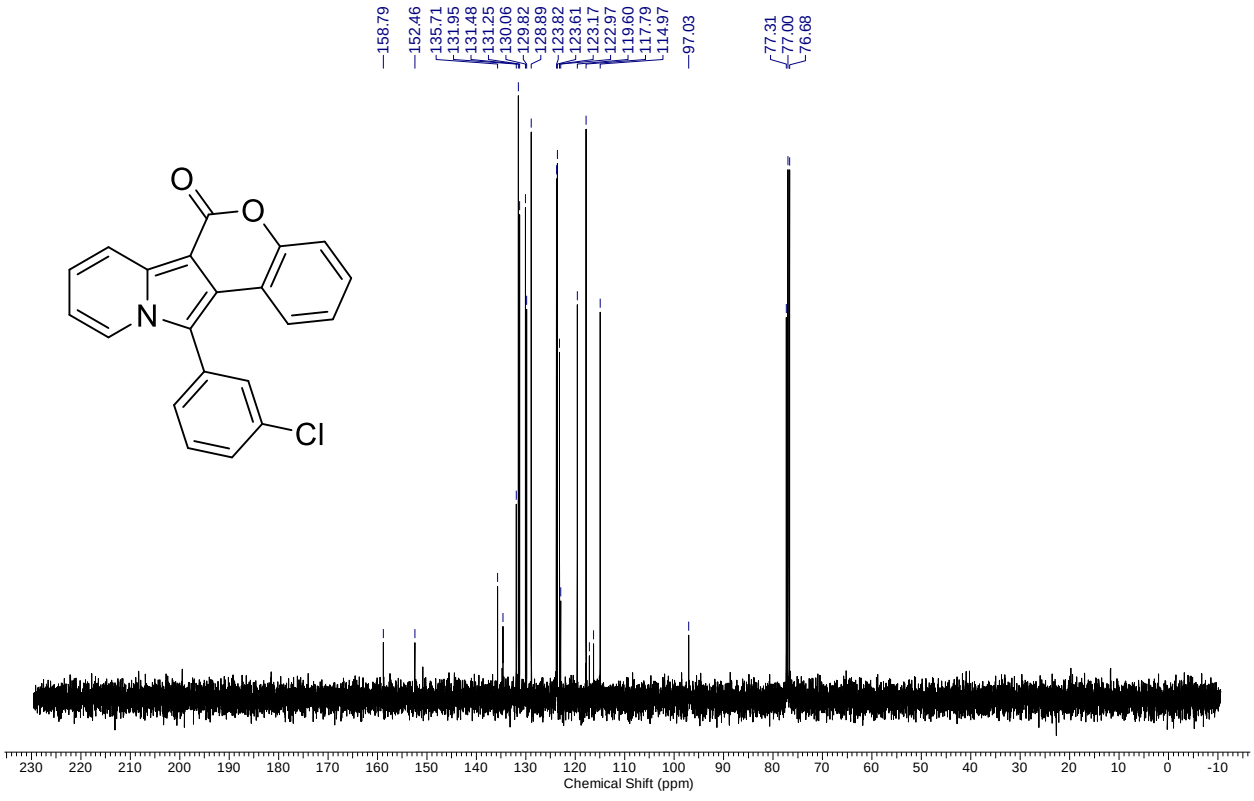
^{13}C NMR Spectrum of **2af**



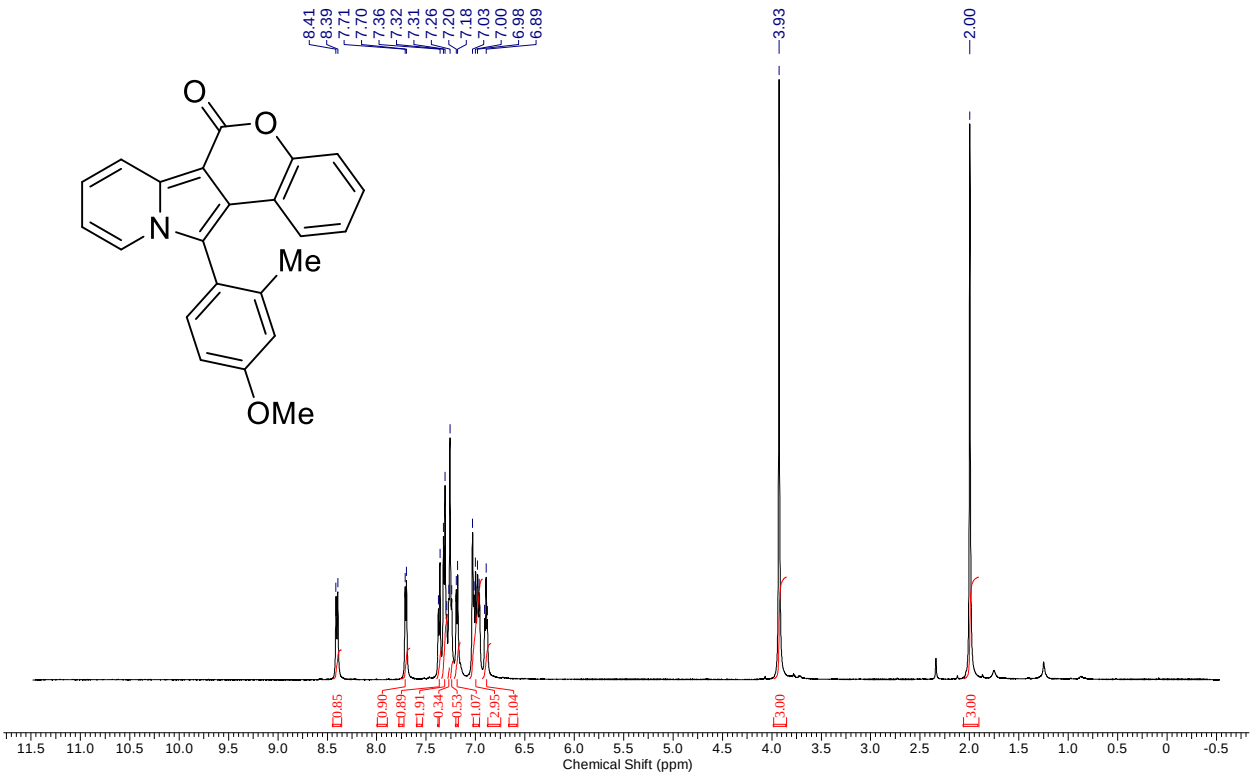
^{1}H NMR Spectrum of **2ag**



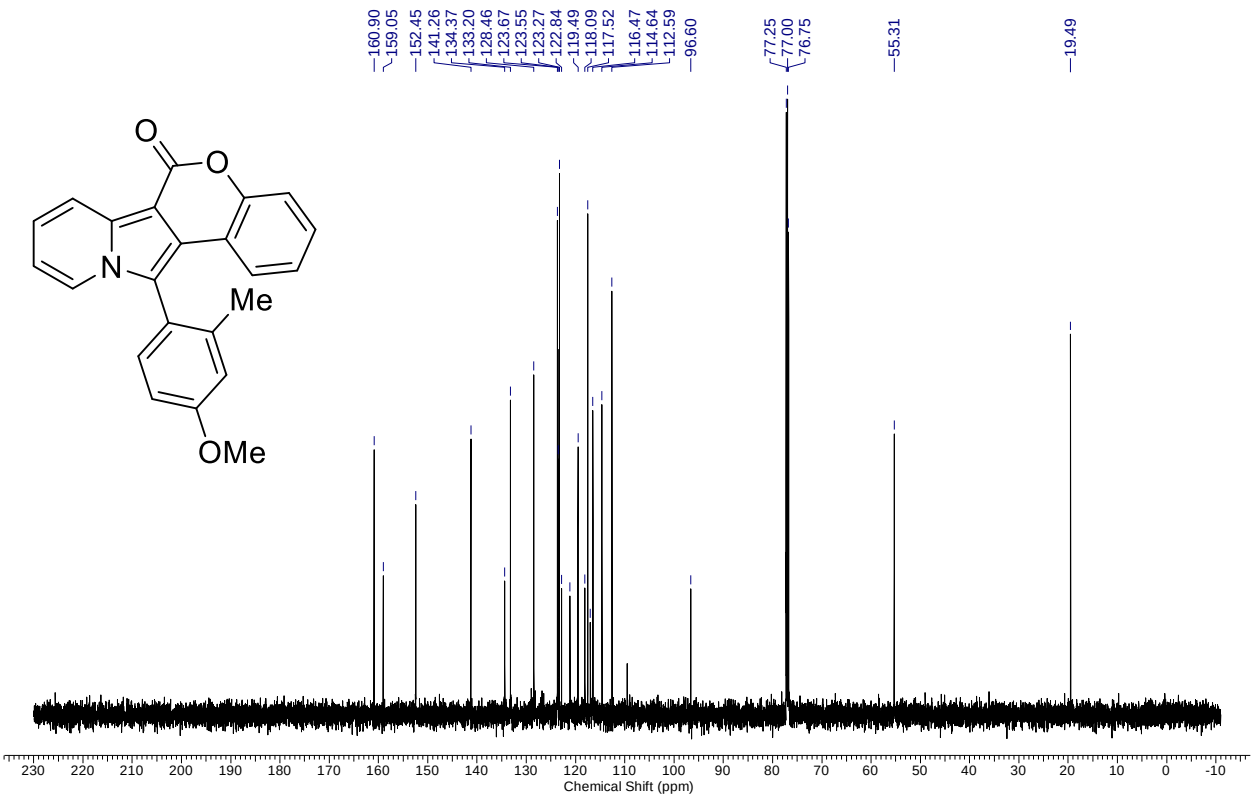
^{13}C NMR Spectrum of **2ag**



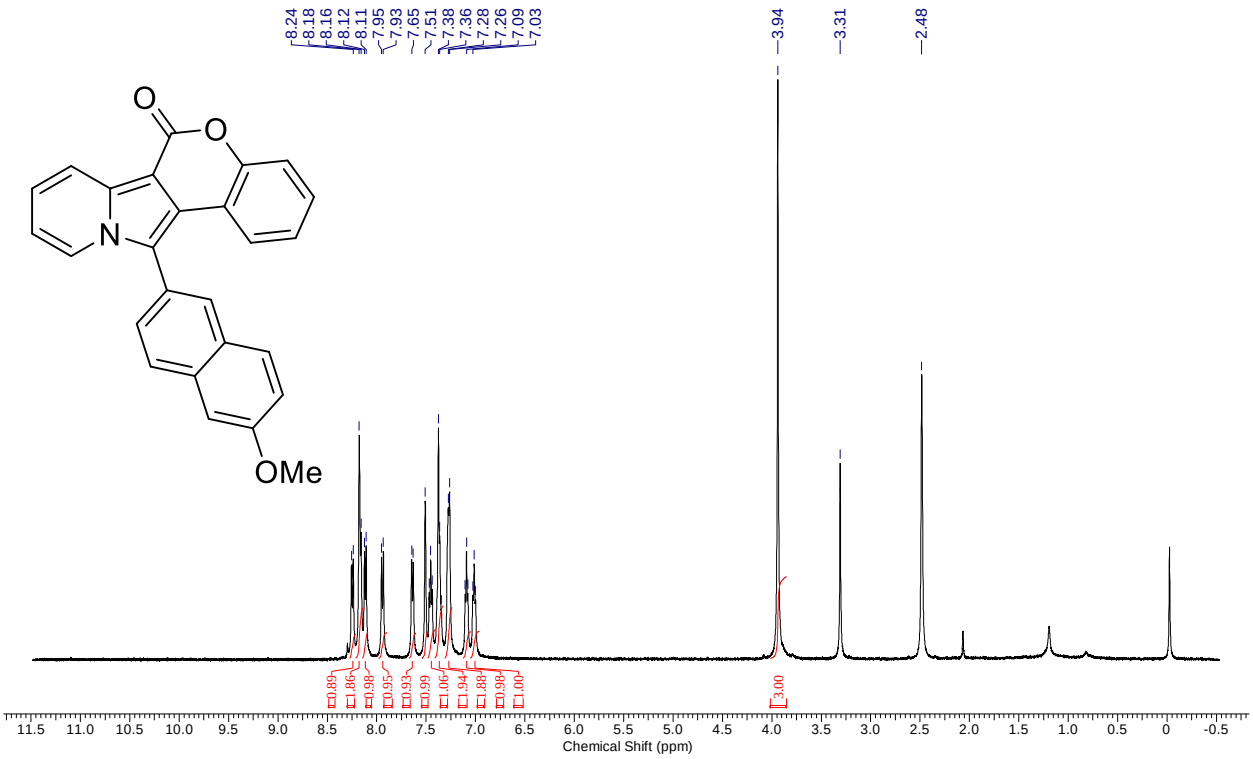
^{1}H NMR Spectrum of **2ah**



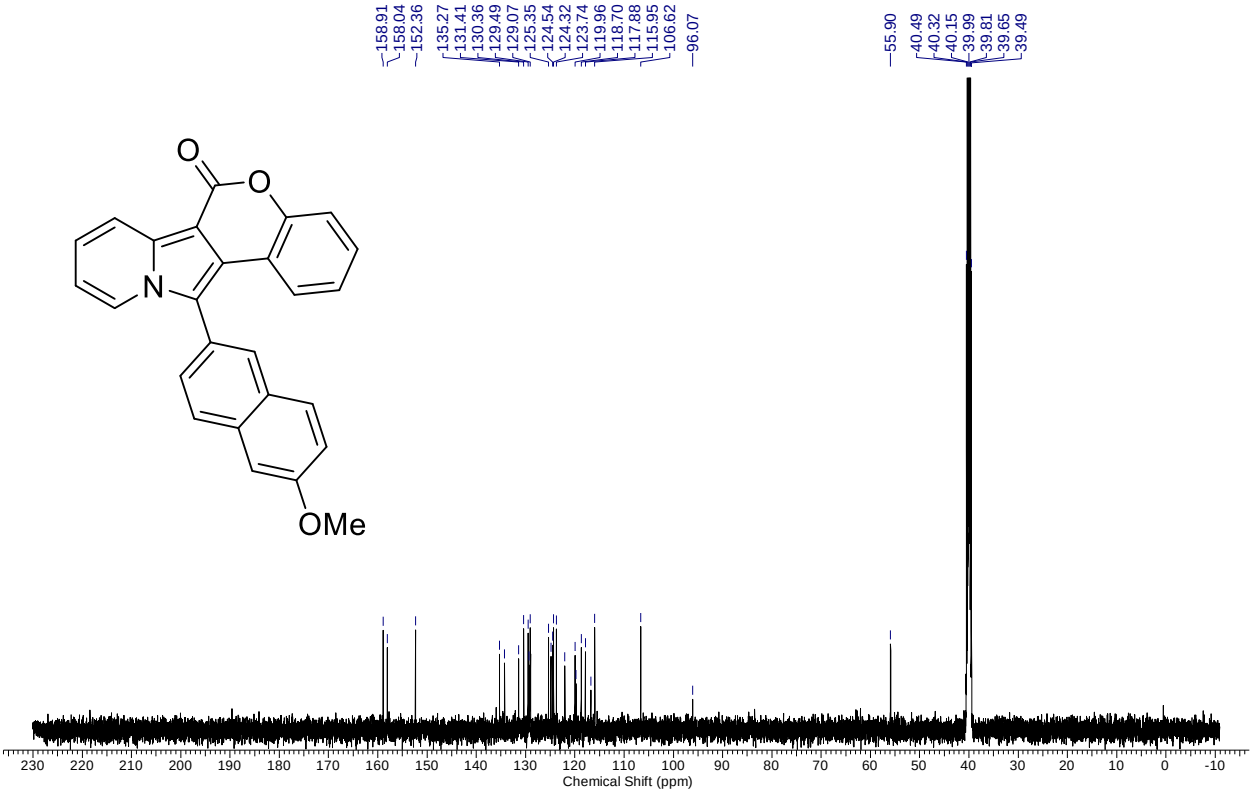
^{13}C NMR Spectrum of **2ah**



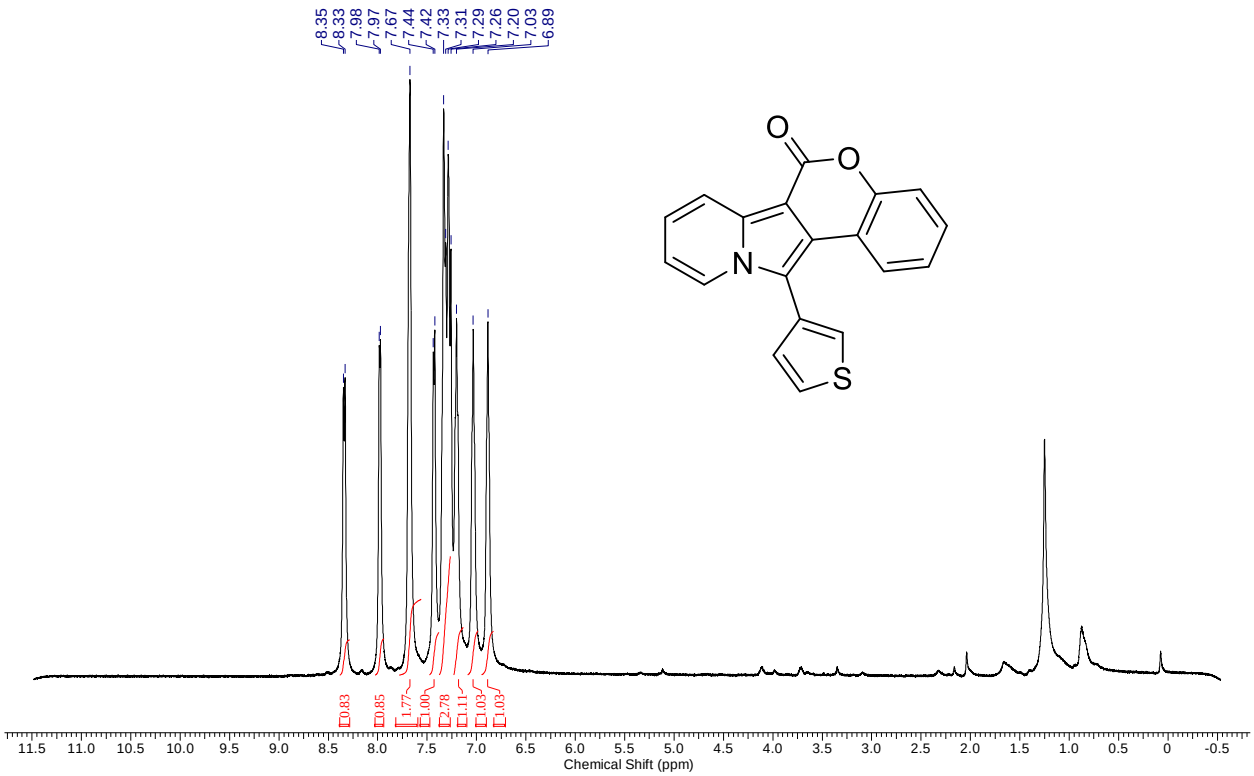
^{1}H NMR Spectrum of **2ai**



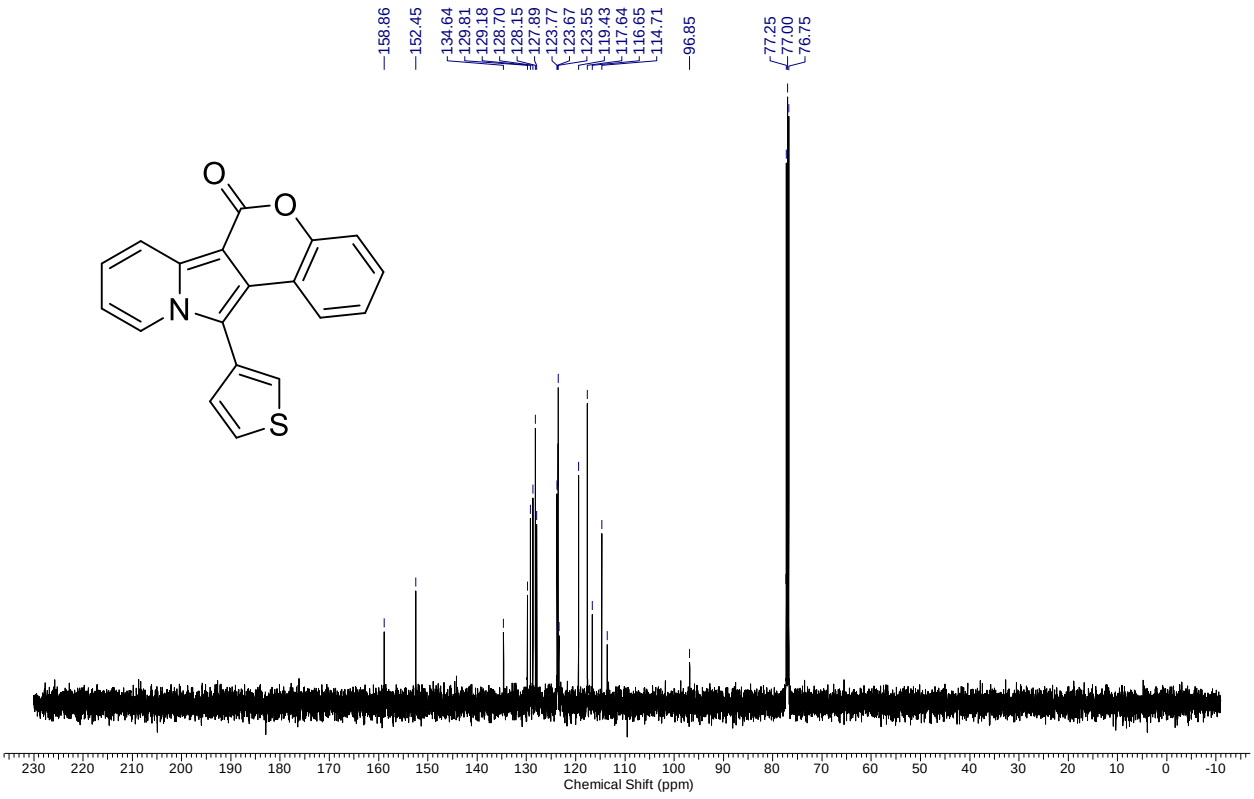
^{13}C NMR Spectrum of **2ai**



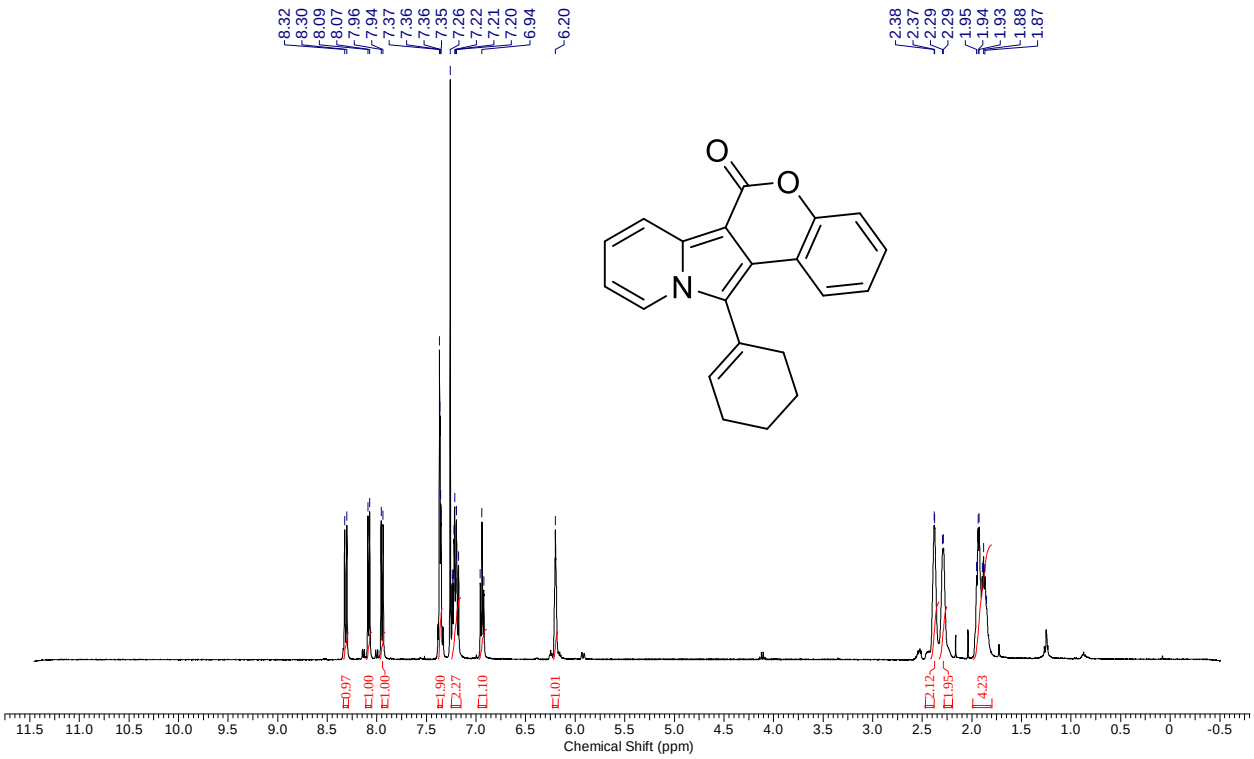
^{1}H NMR Spectrum of **2aj**



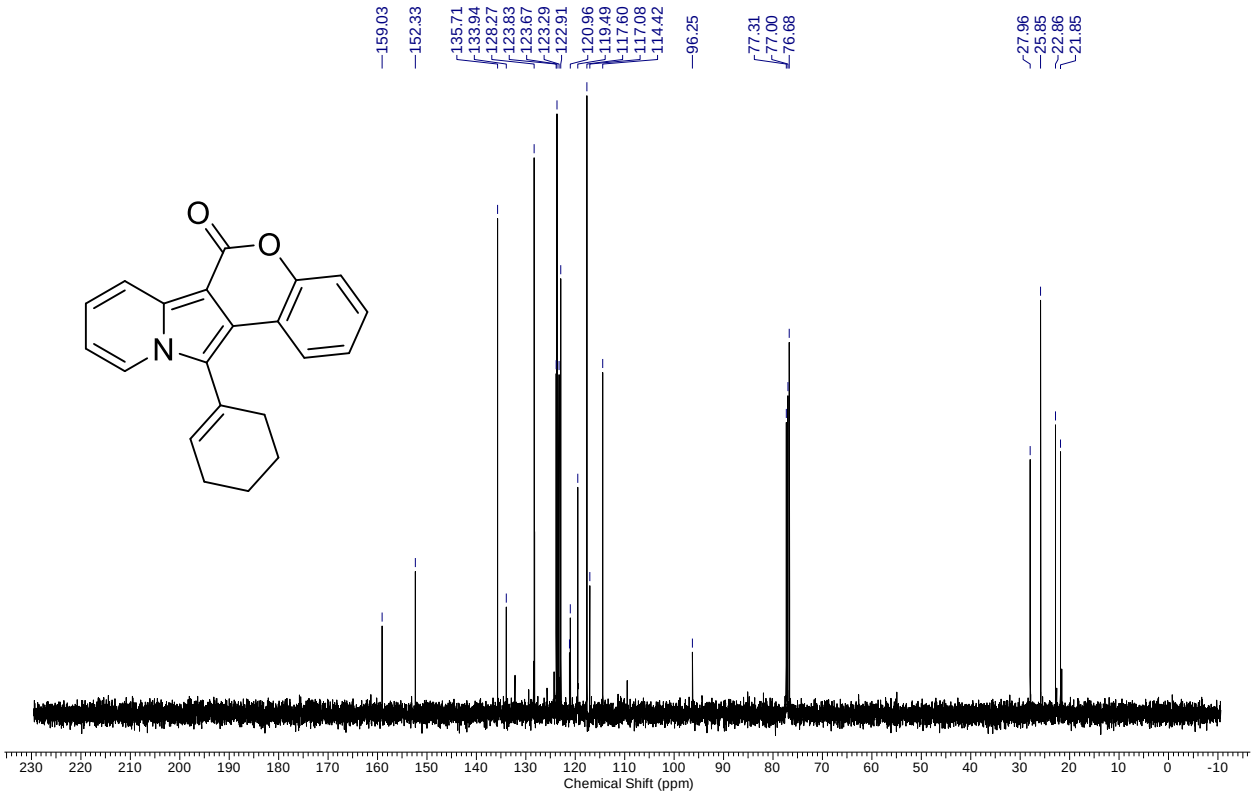
^{13}C NMR Spectrum of **2aj**



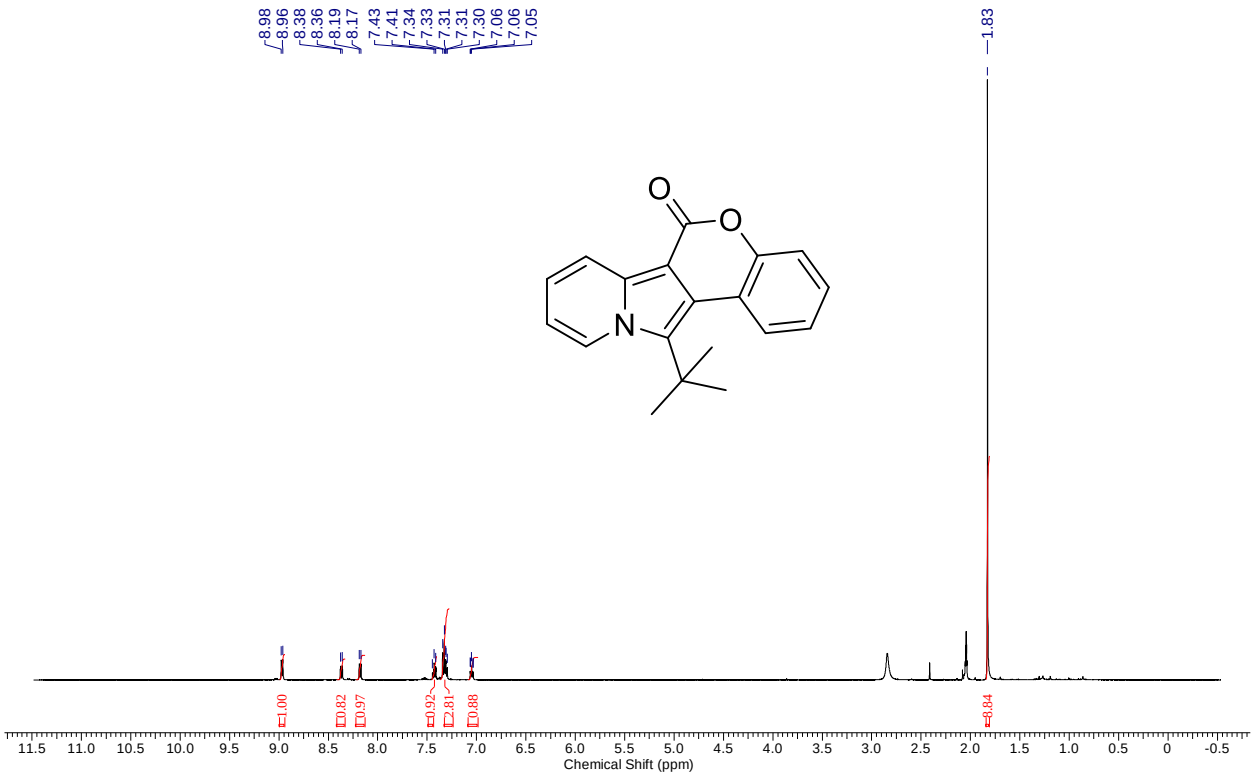
^{1}H NMR Spectrum of **2ak**



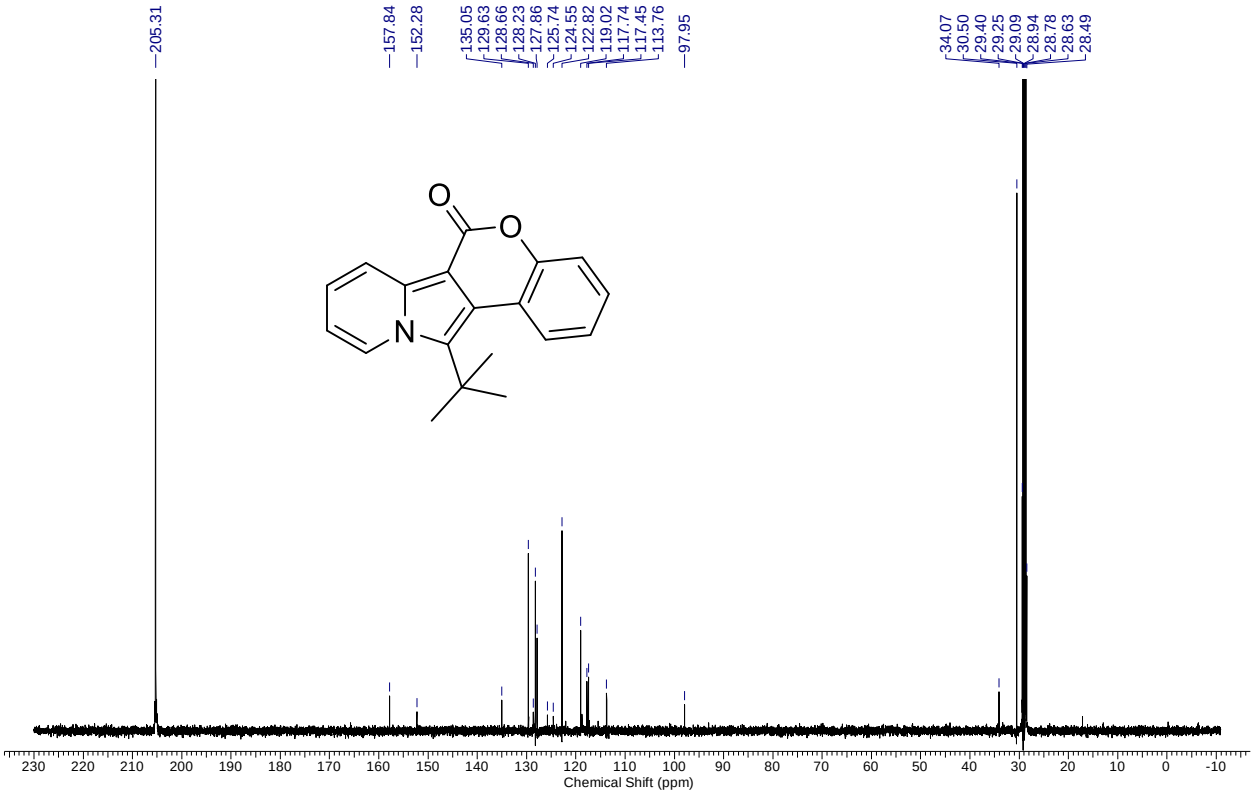
^{13}C NMR Spectrum of **2ak**



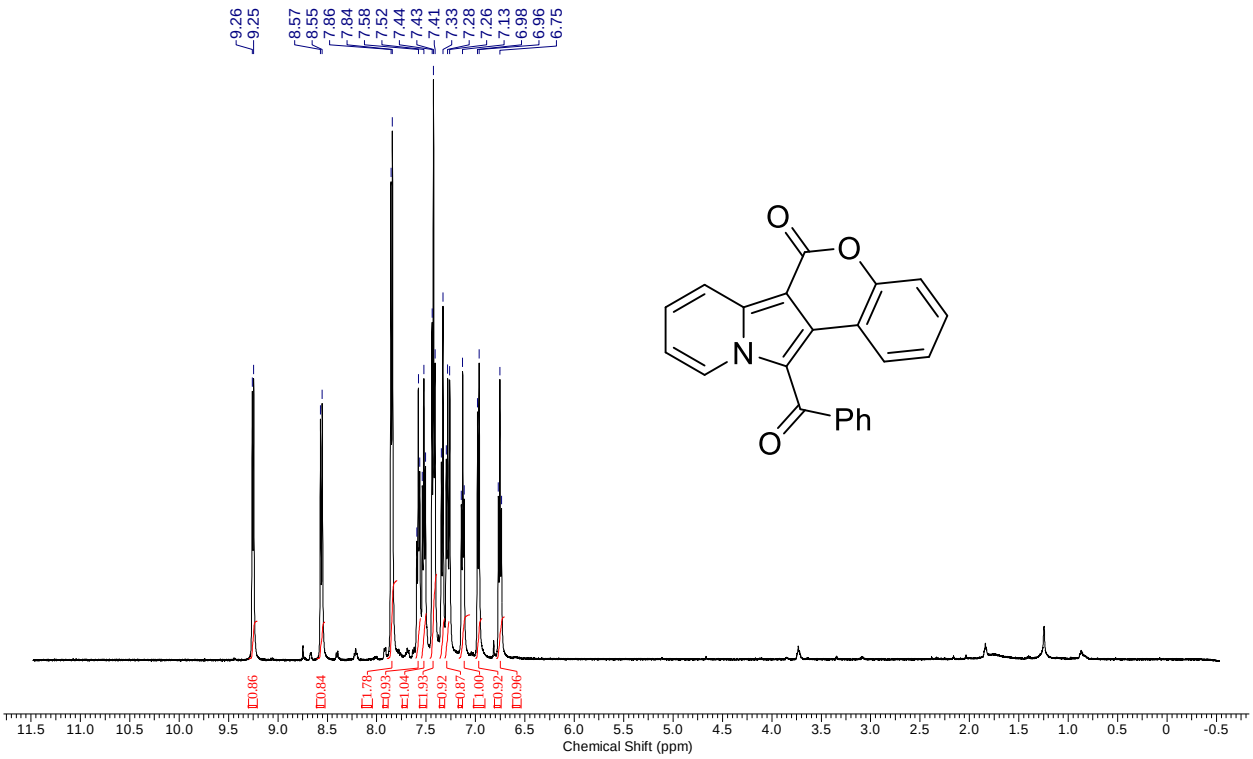
^{1}H NMR Spectrum of **2al**



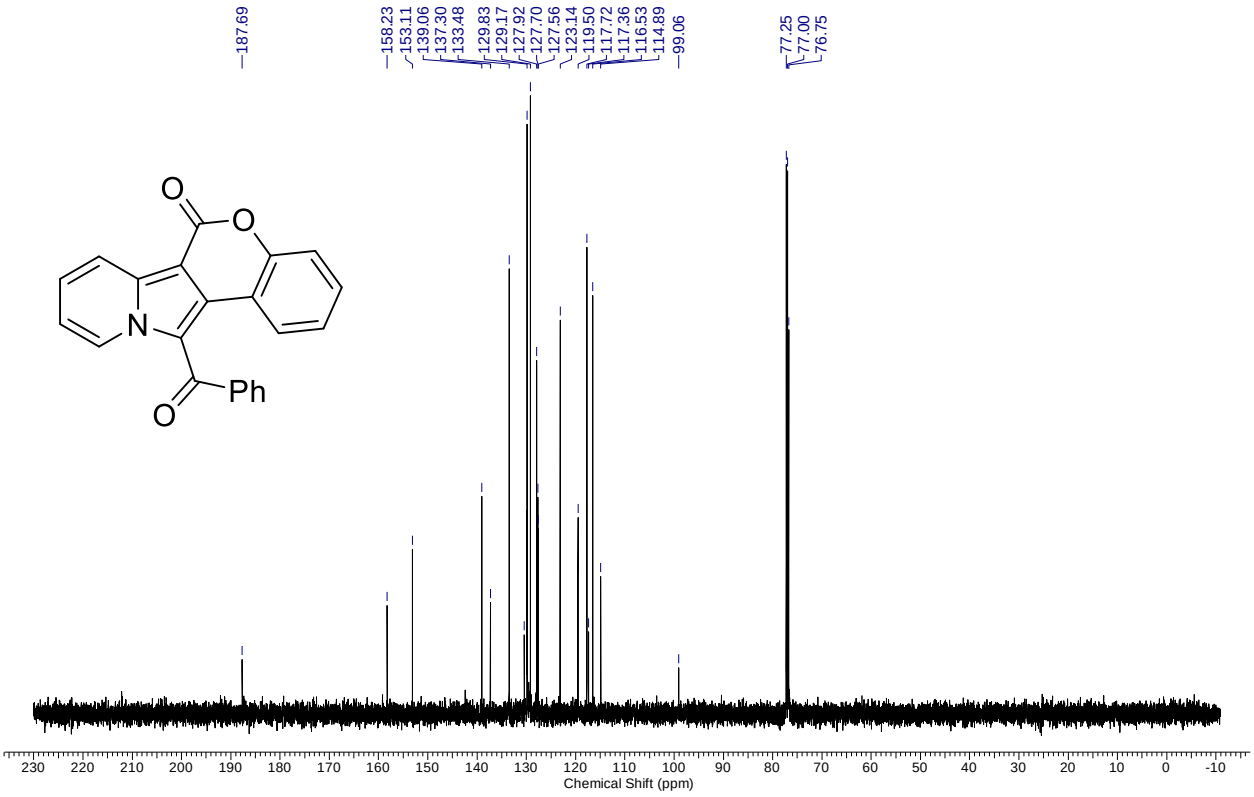
^{13}C NMR Spectrum of **2al**



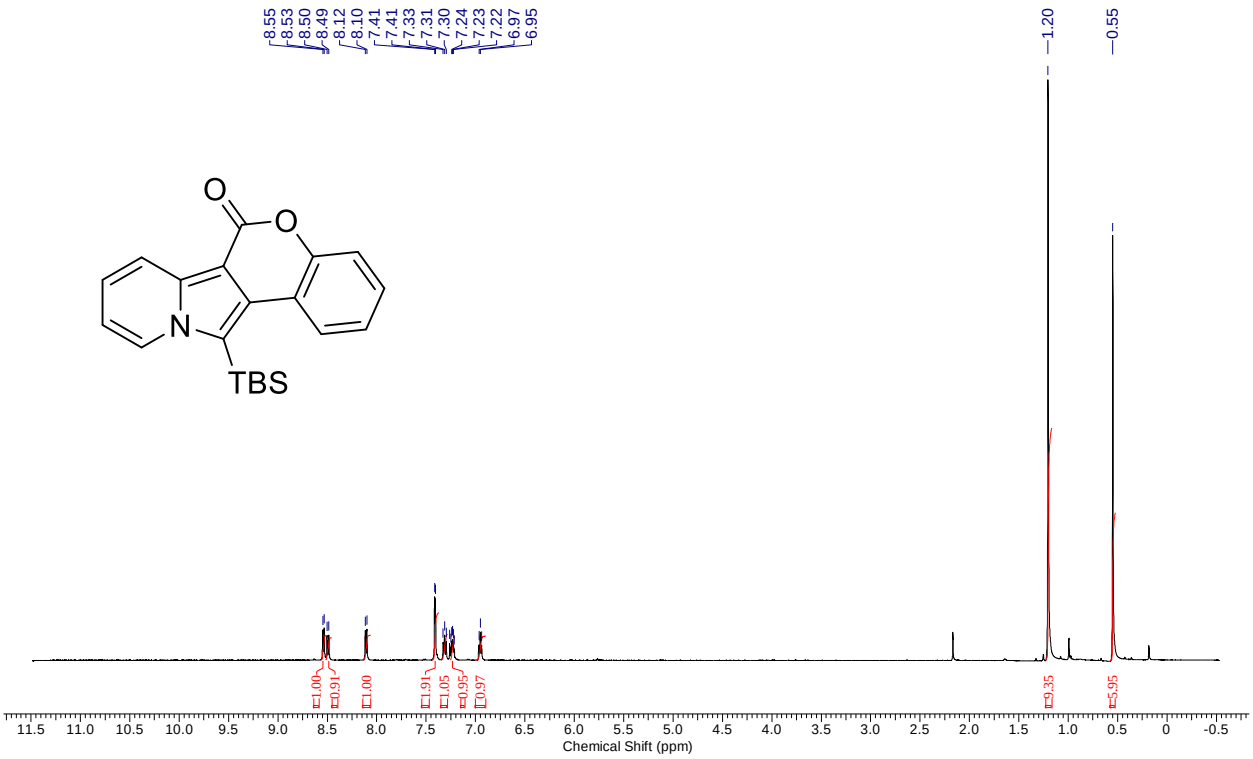
^{1}H NMR Spectrum of **2am**



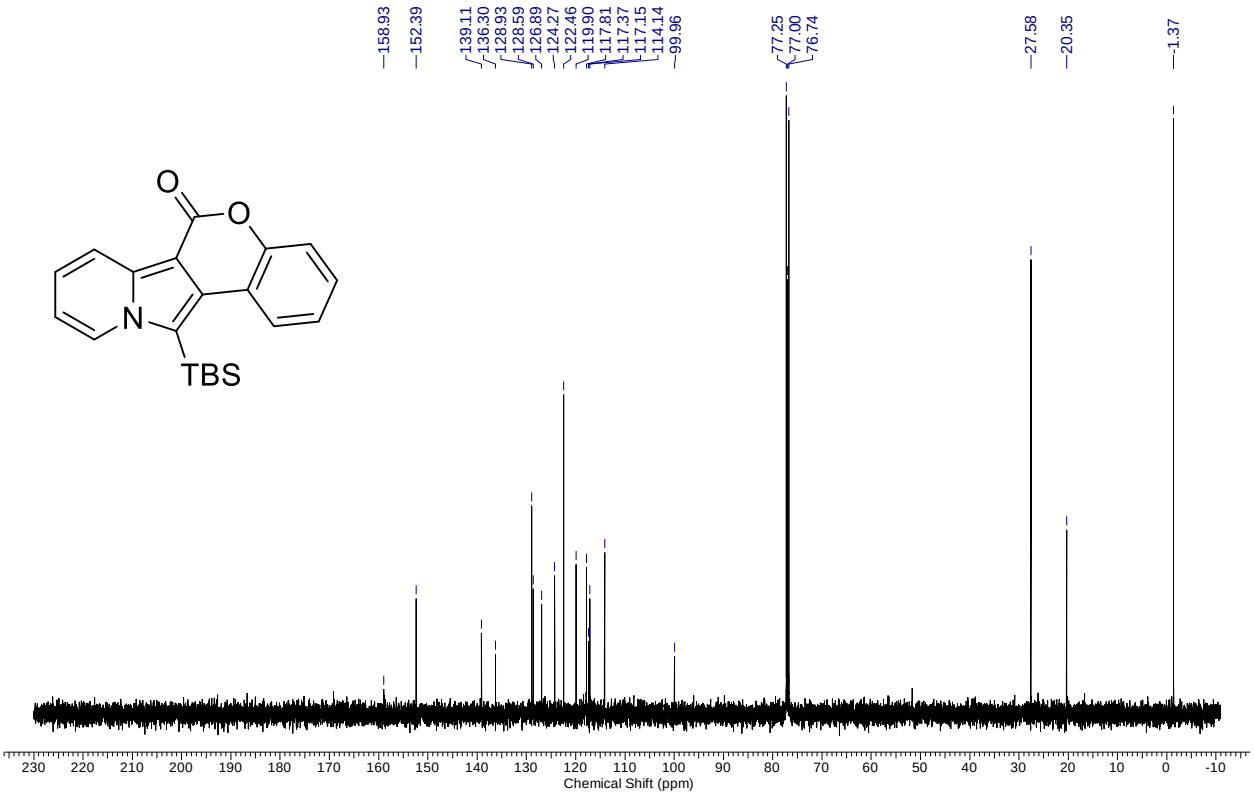
^{13}C NMR Spectrum of **2am**



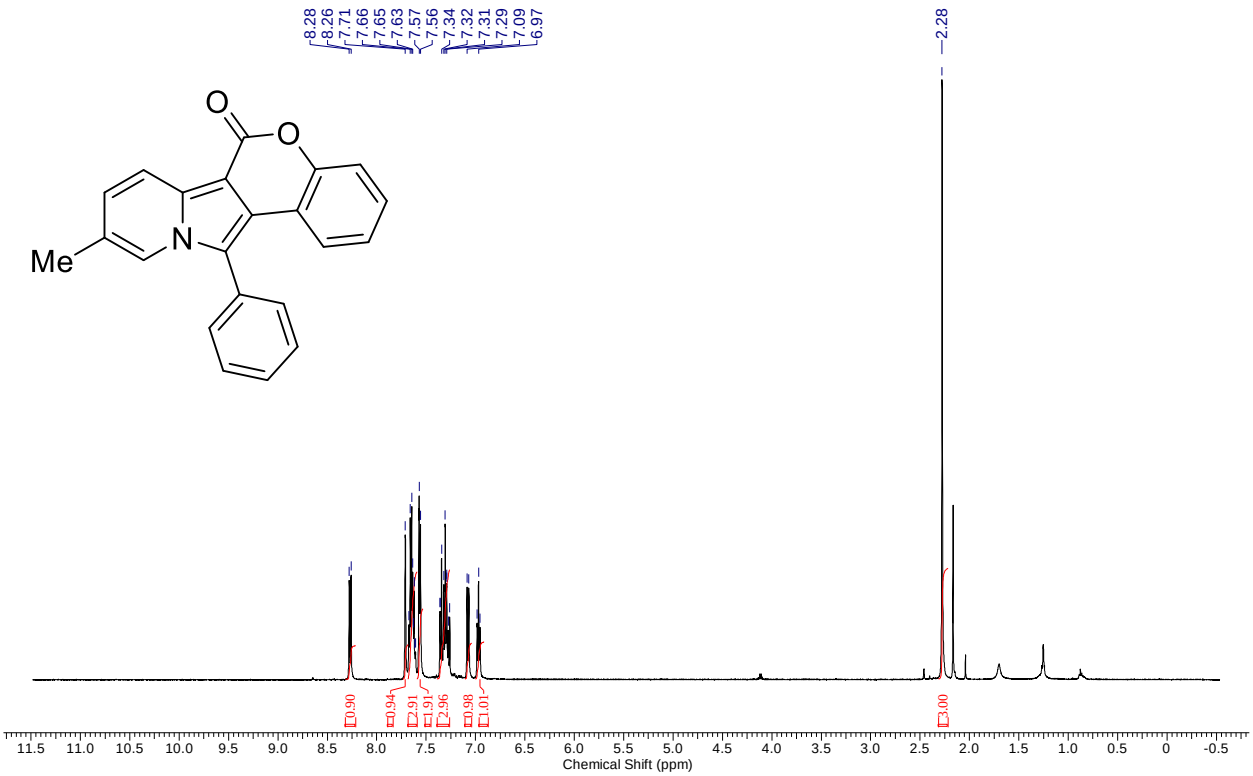
^{1}H NMR Spectrum of **2an**



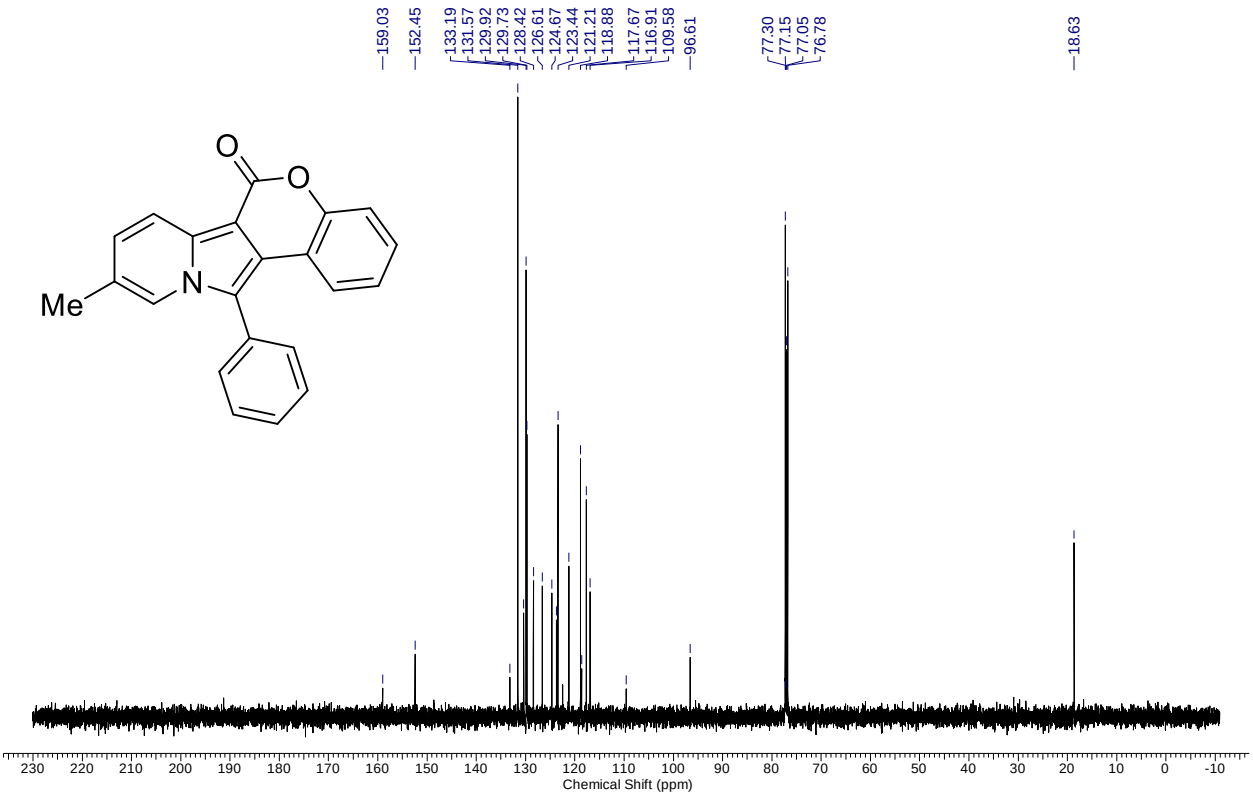
^{13}C NMR Spectrum of **2an**



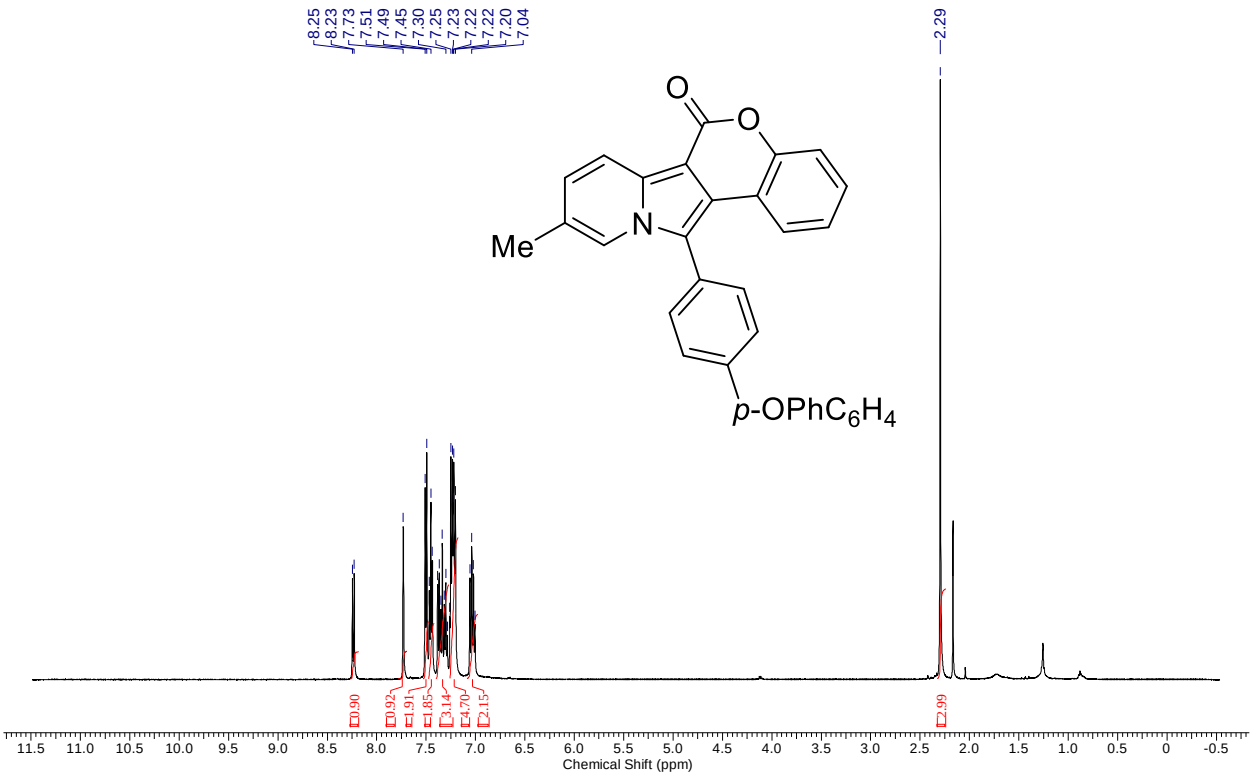
^{1}H NMR Spectrum of **2ao**



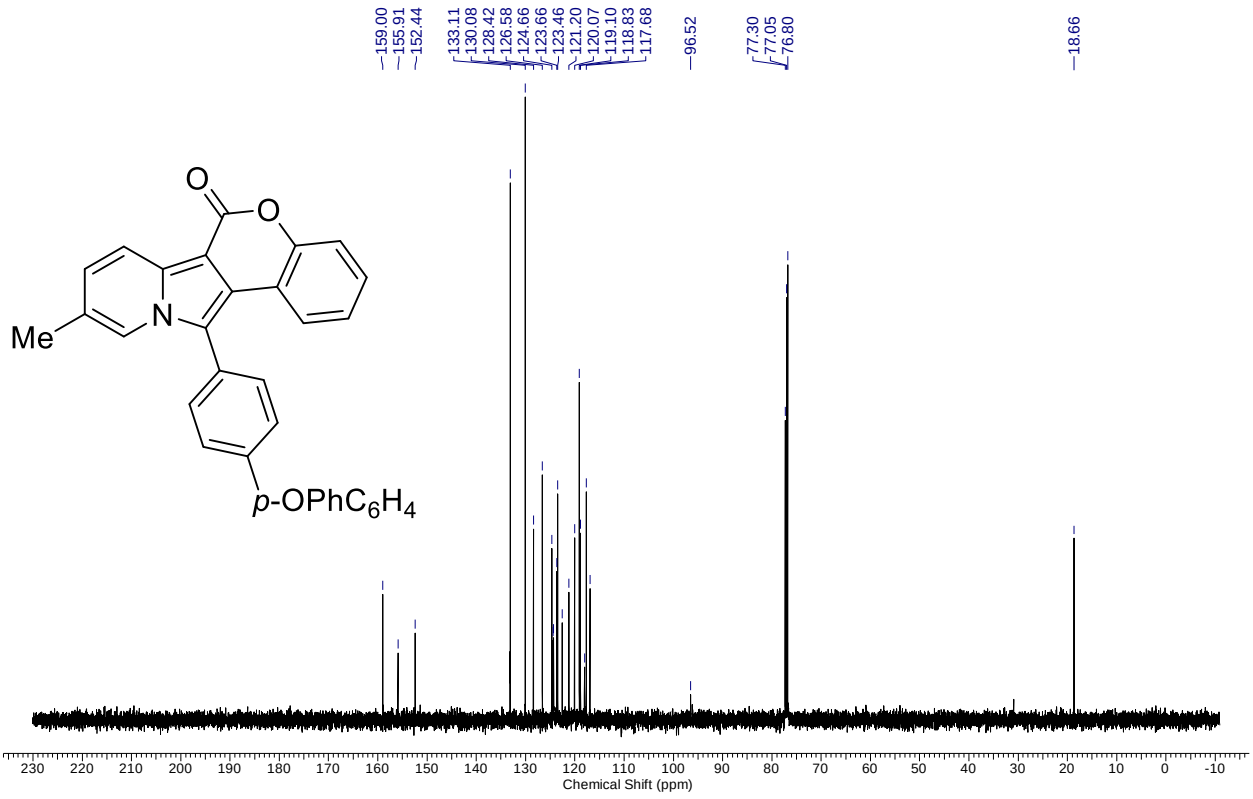
^{13}C NMR Spectrum of **2ao**



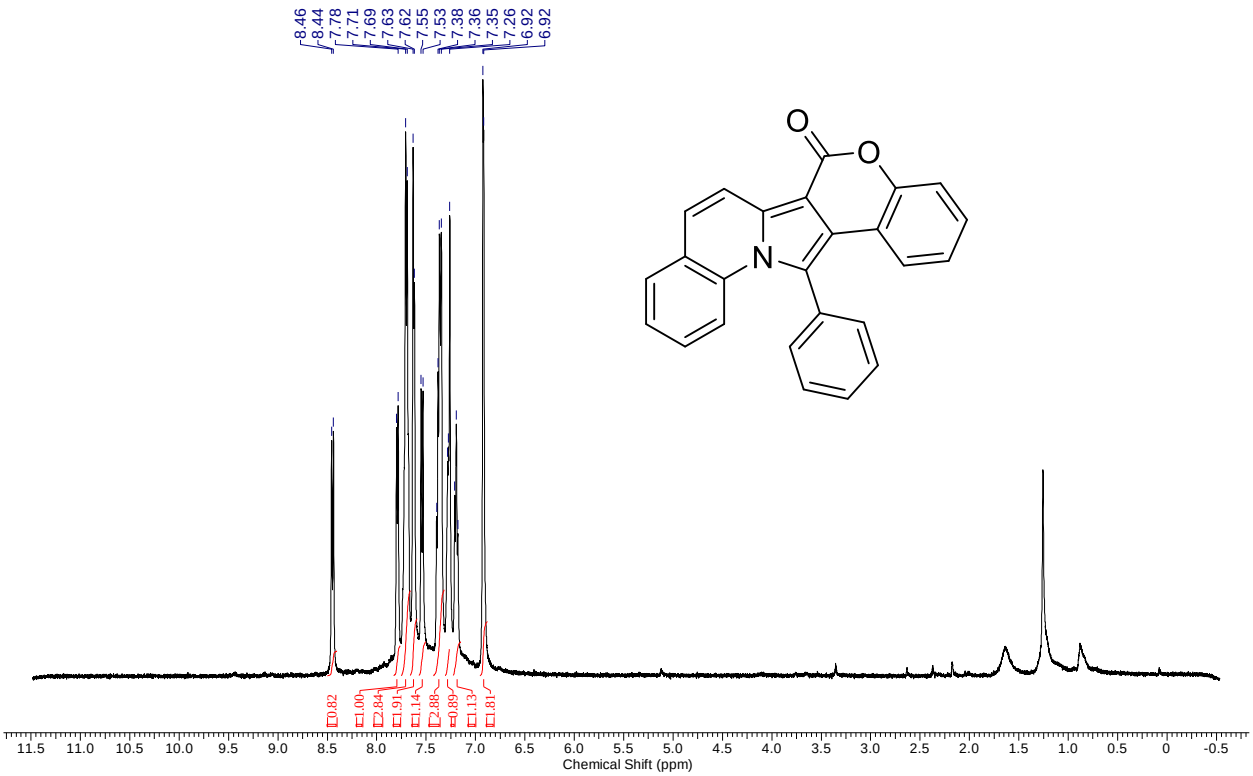
^{1}H NMR Spectrum of **2ap**



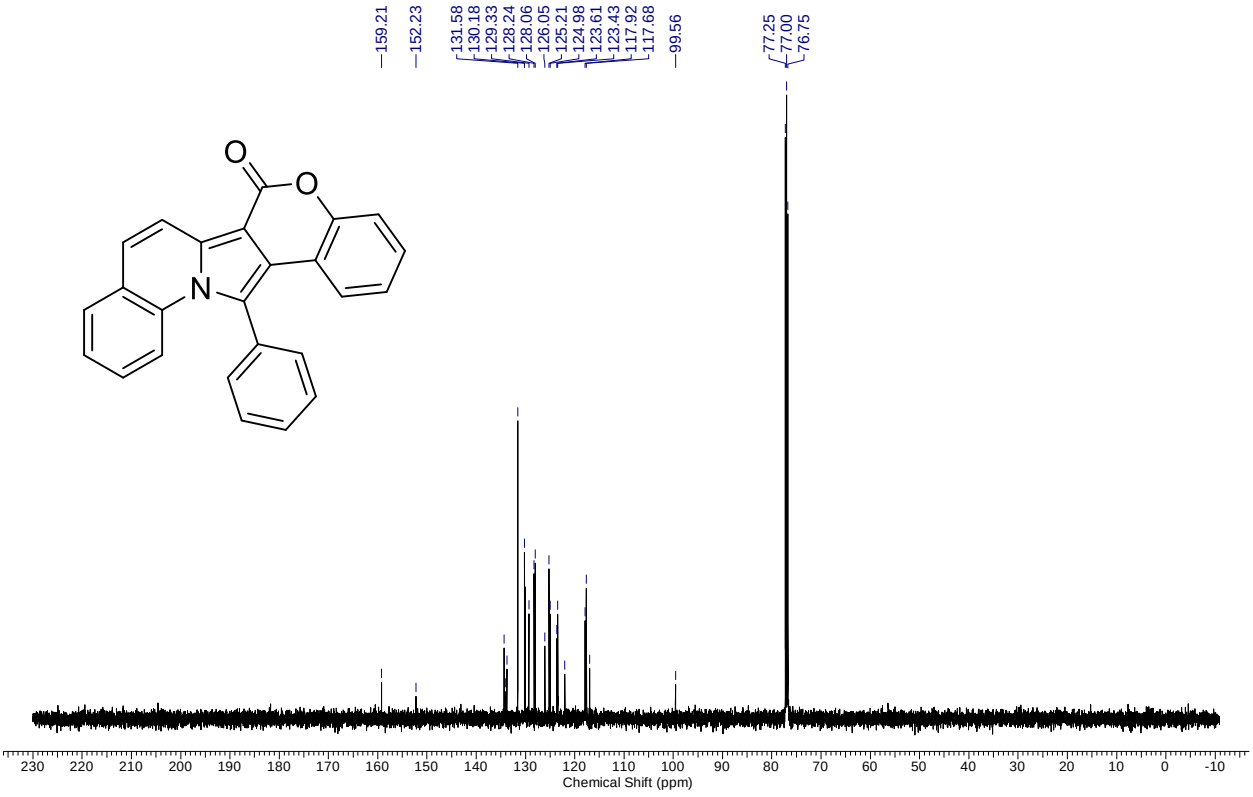
^{13}C NMR Spectrum of **2ap**



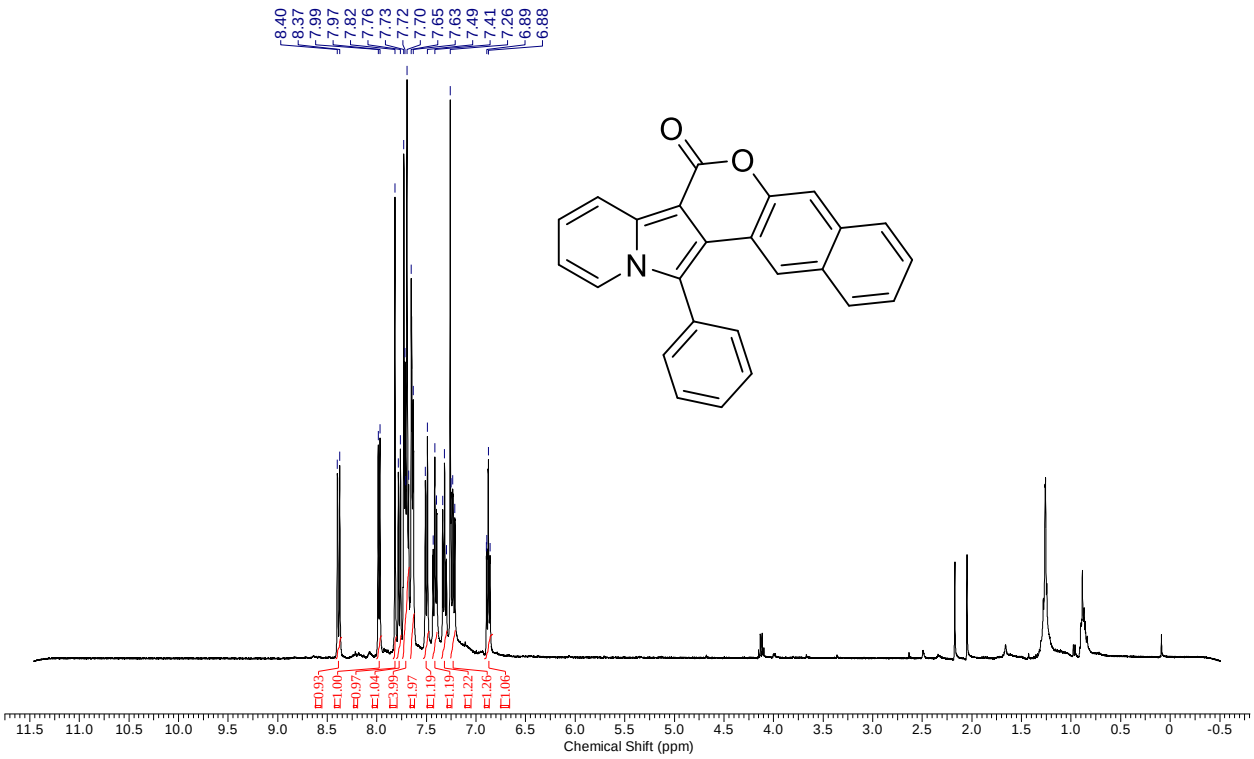
^{1}H NMR Spectrum of **2aq**



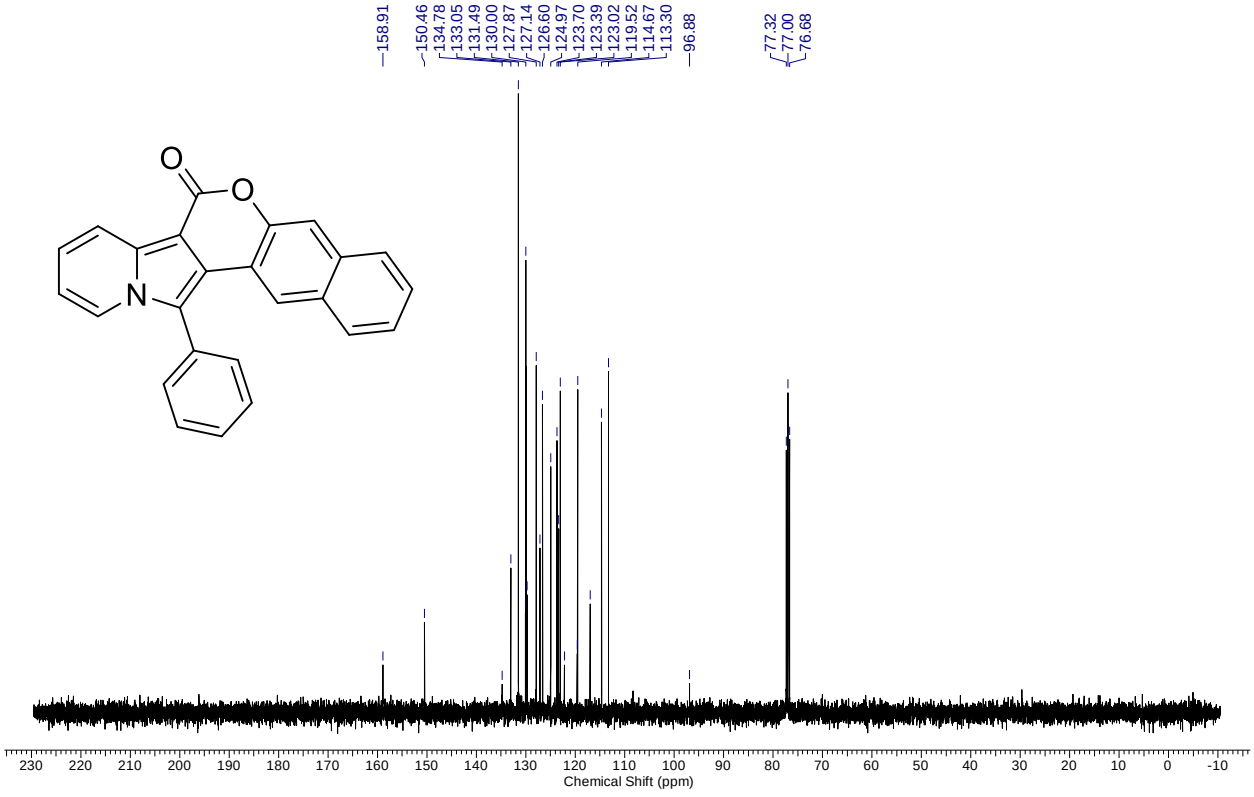
^{13}C NMR Spectrum of **2aq**



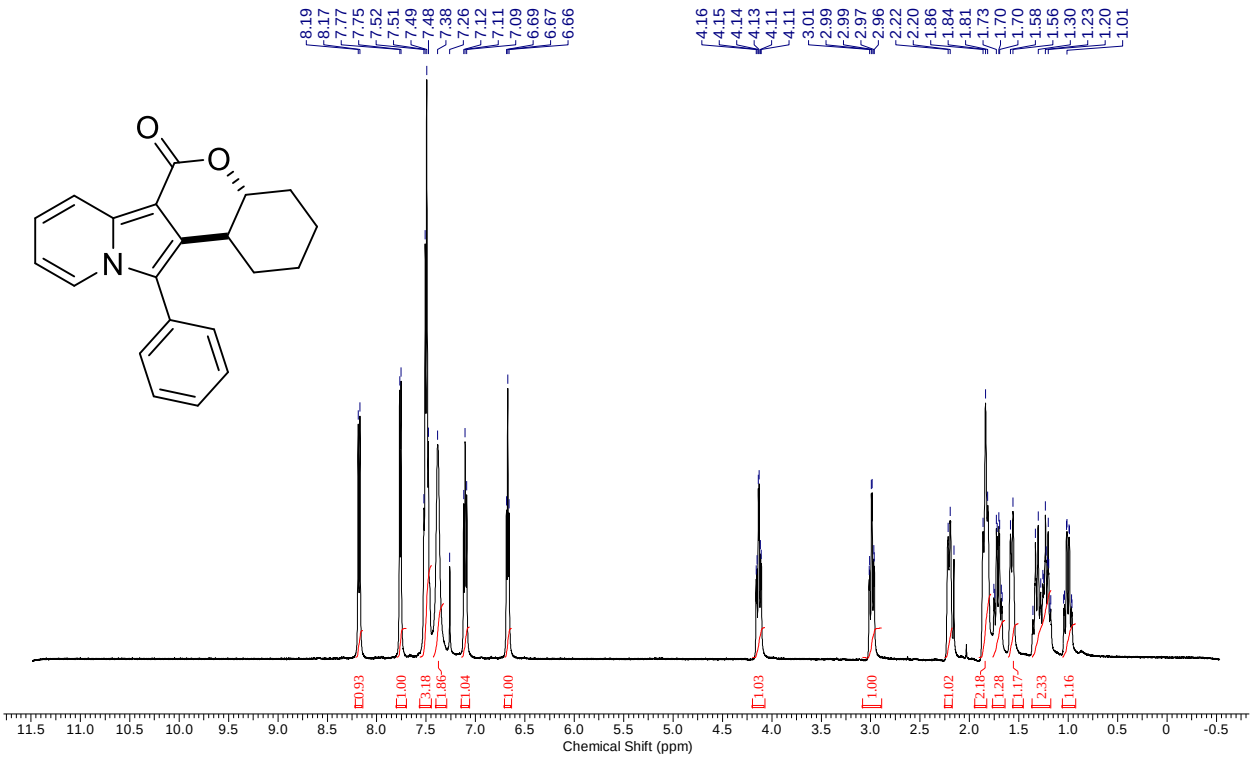
^{1}H NMR Spectrum of **2ar**



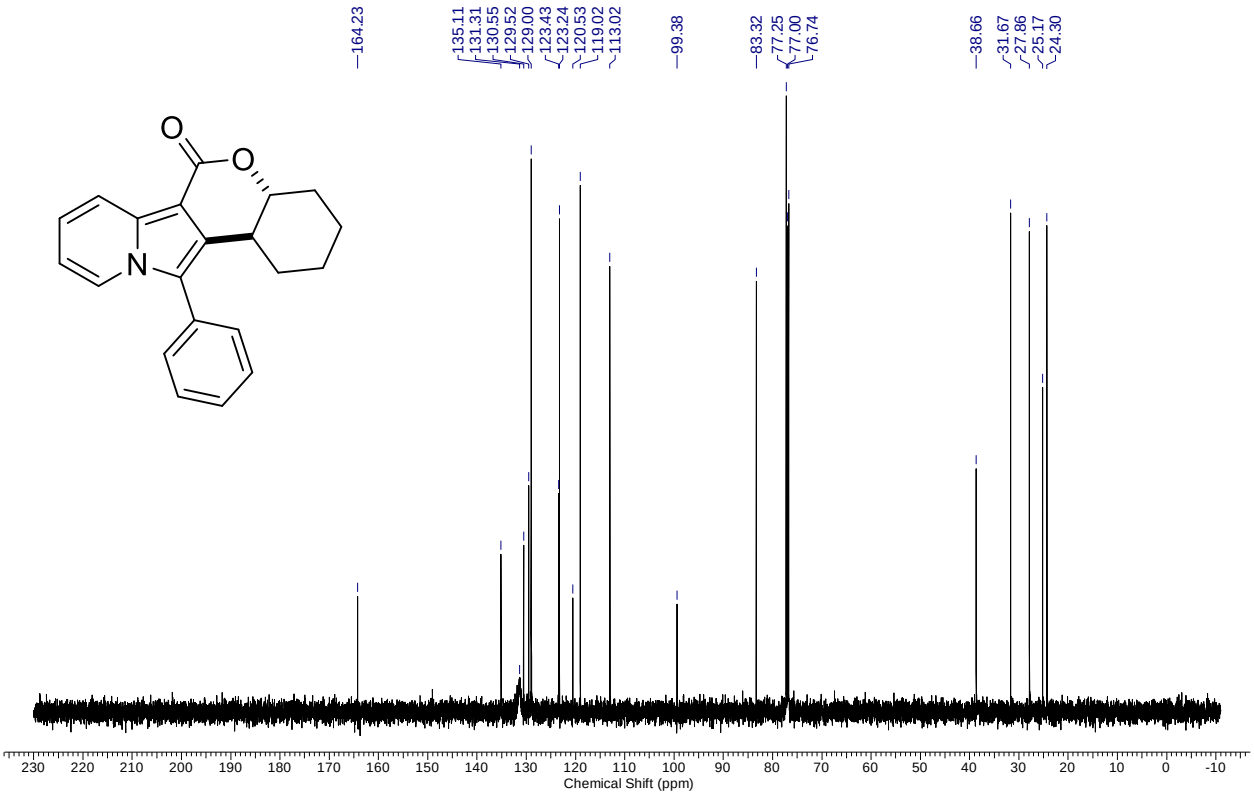
^{13}C NMR Spectrum of **2ar**



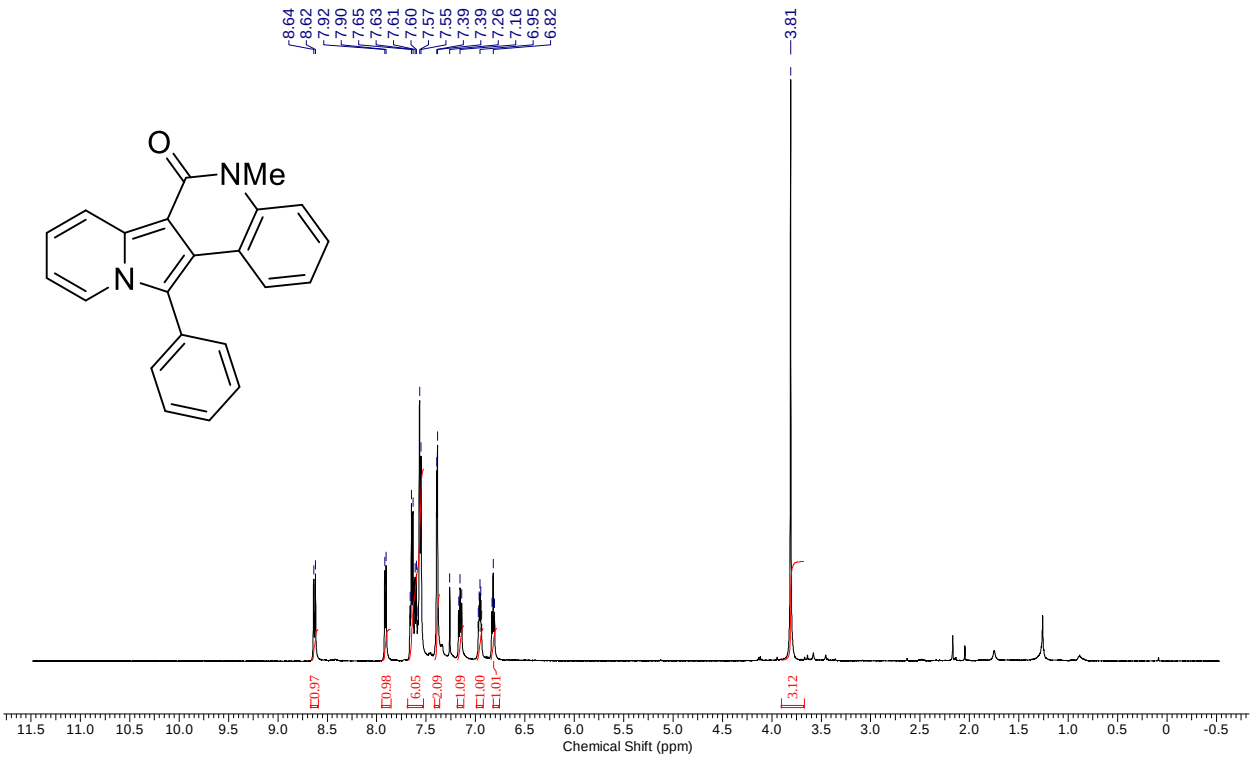
^{1}H NMR Spectrum of **2as**



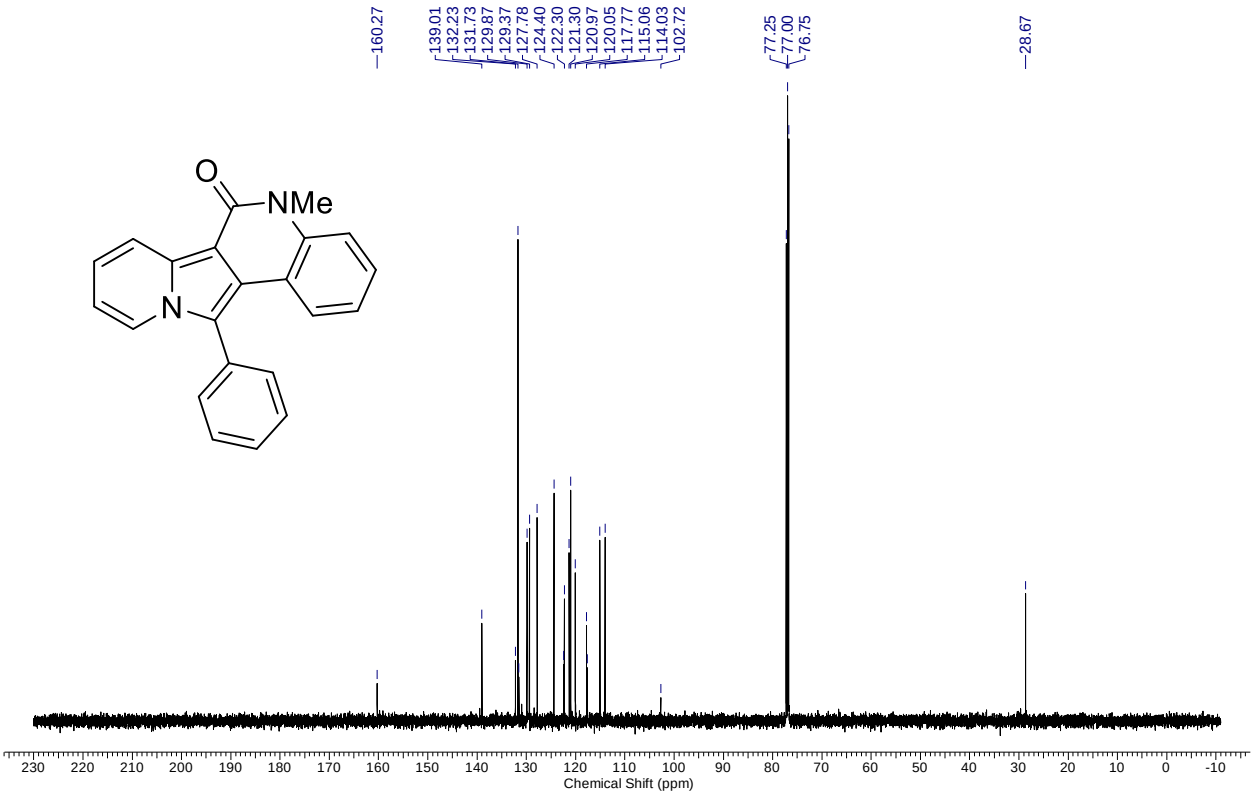
^{13}C NMR Spectrum of **2as**



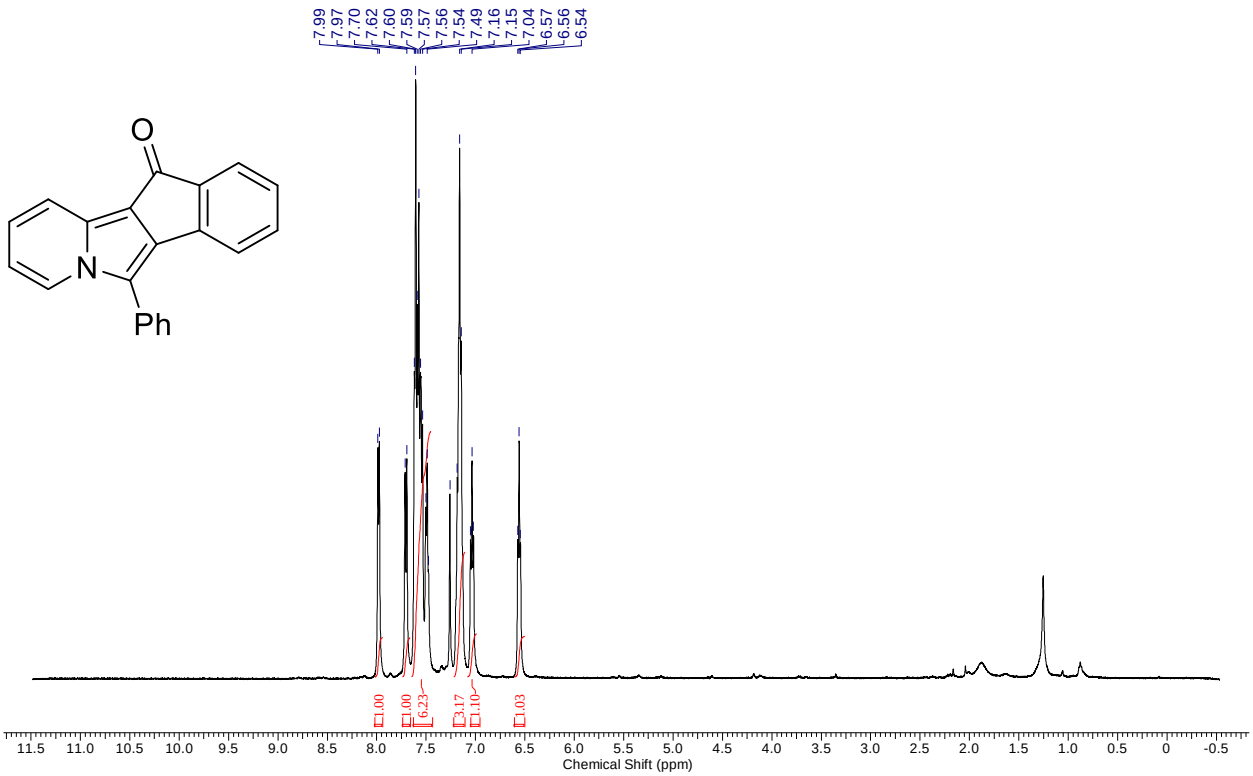
^{1}H NMR Spectrum of **2at**



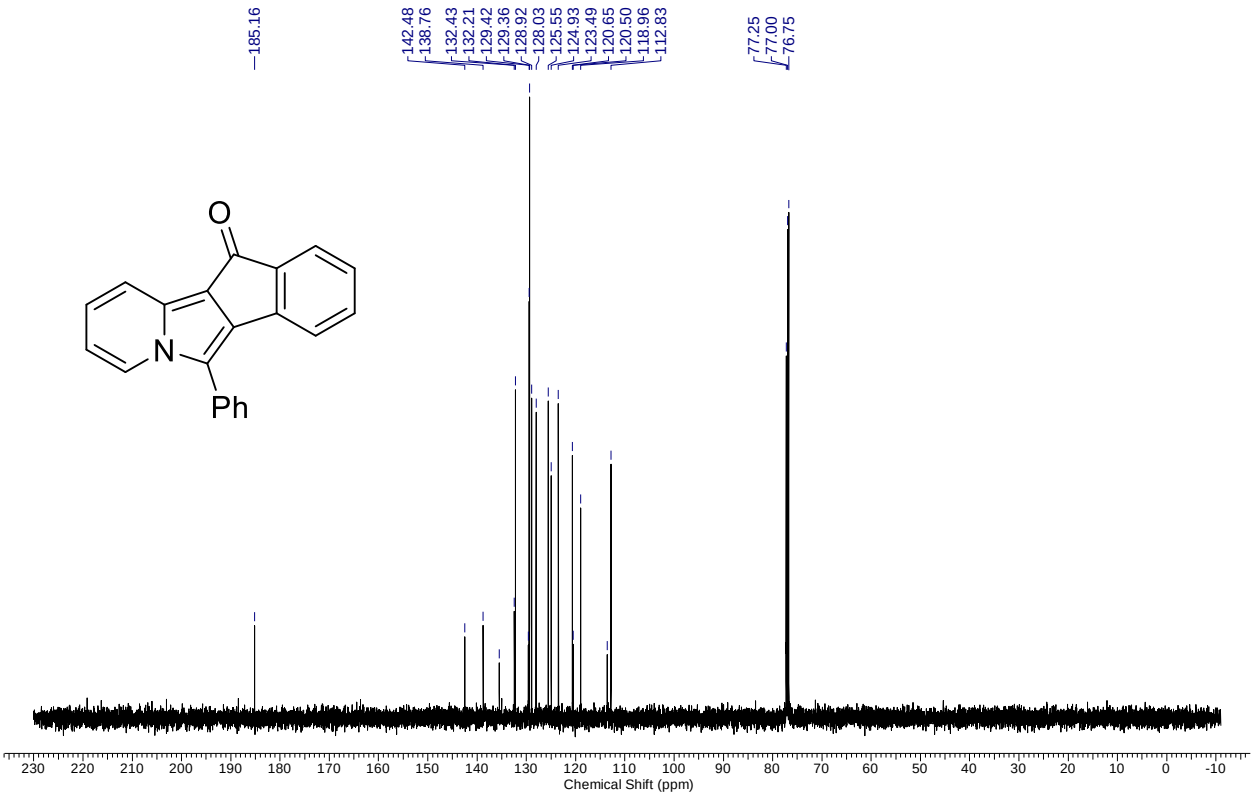
^{13}C NMR Spectrum of **2at**



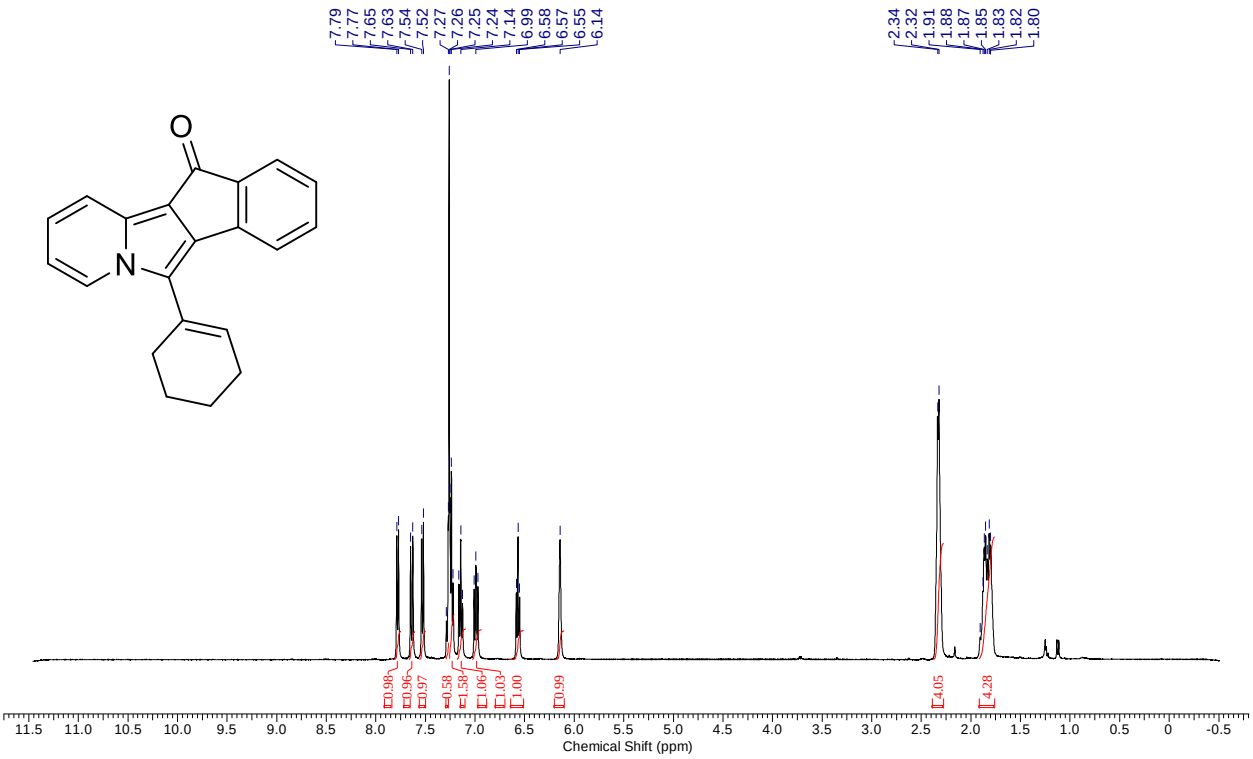
^{1}H NMR Spectrum of **2ba**



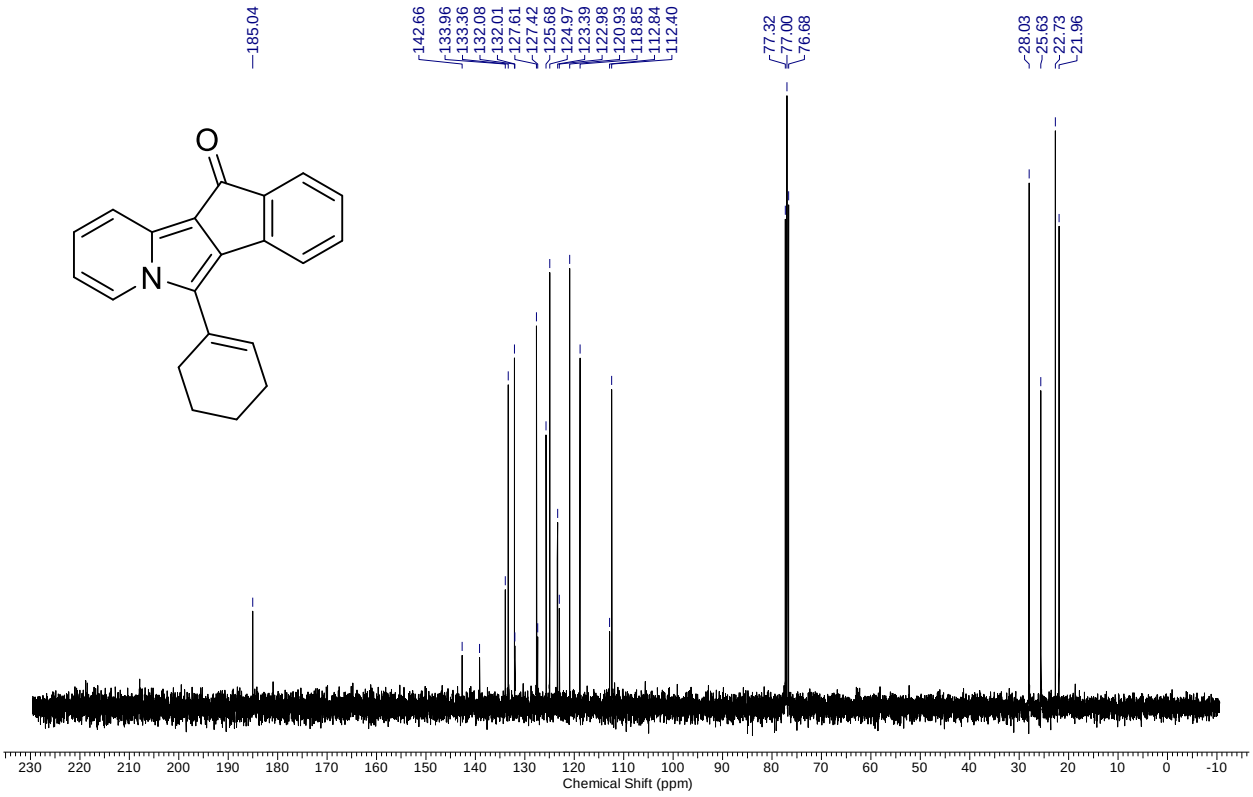
^{13}C NMR Spectrum of **2ba**



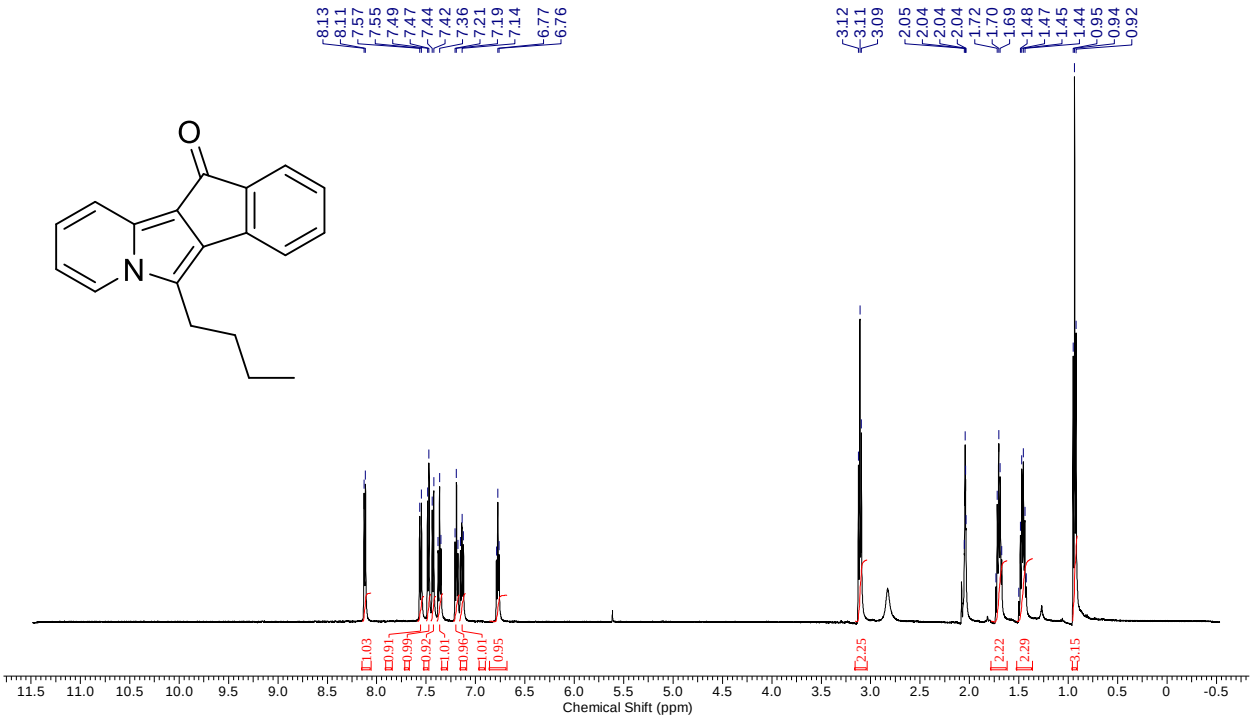
^{1}H NMR Spectrum of **2bb**



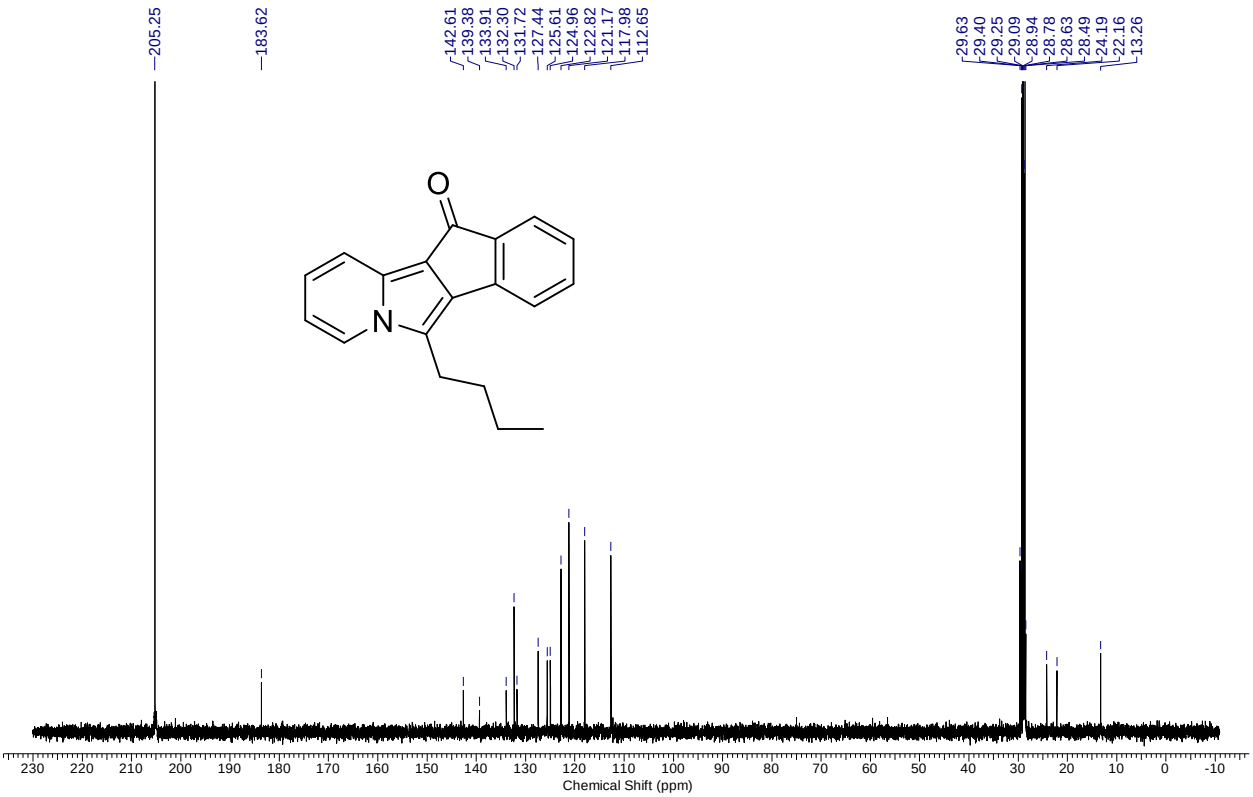
^{13}C NMR Spectrum of **2bb**



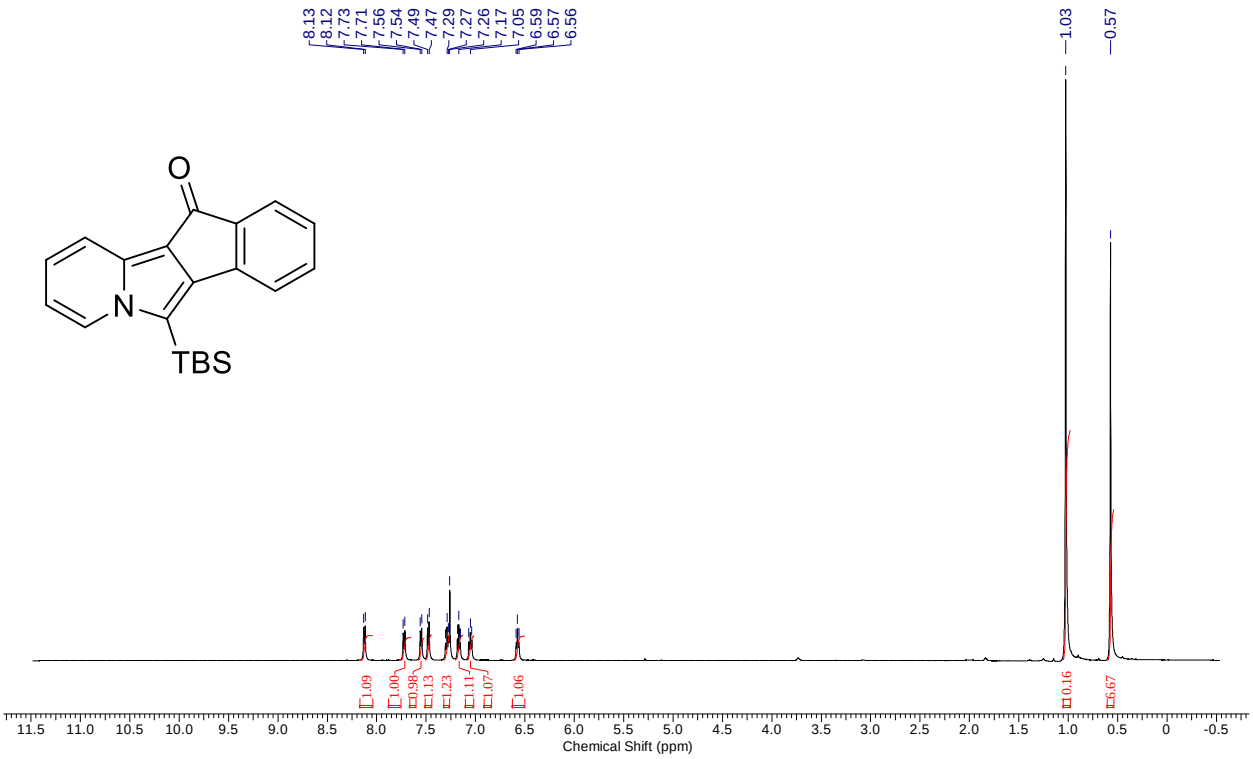
^{1}H NMR Spectrum of **2bc**



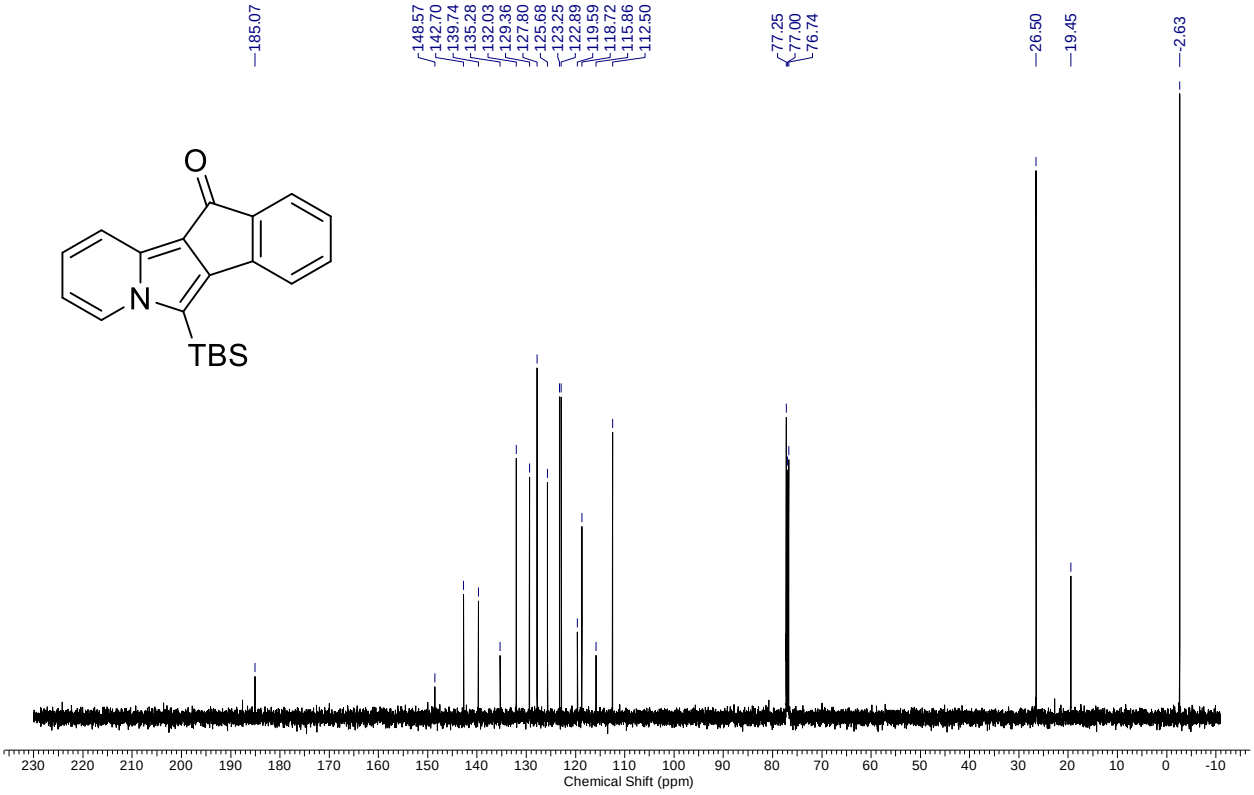
^{13}C NMR Spectrum of **2bc**



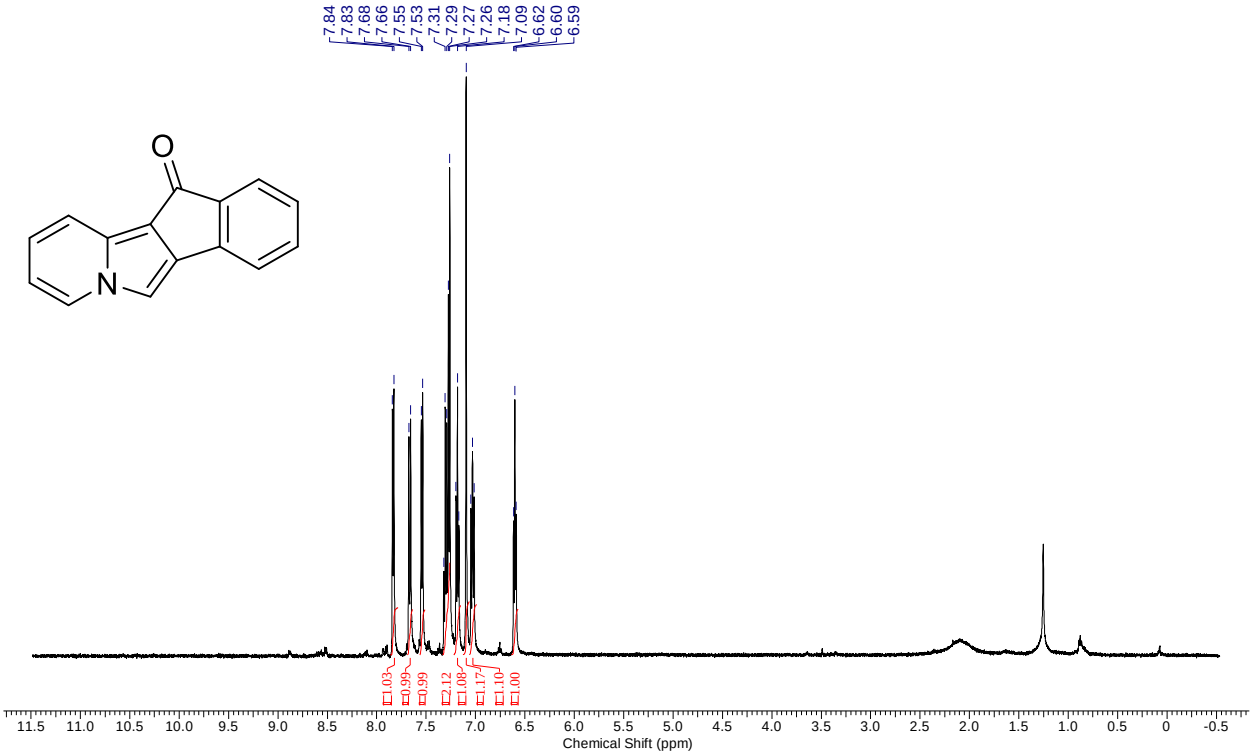
^{1}H NMR Spectrum of **2bd**



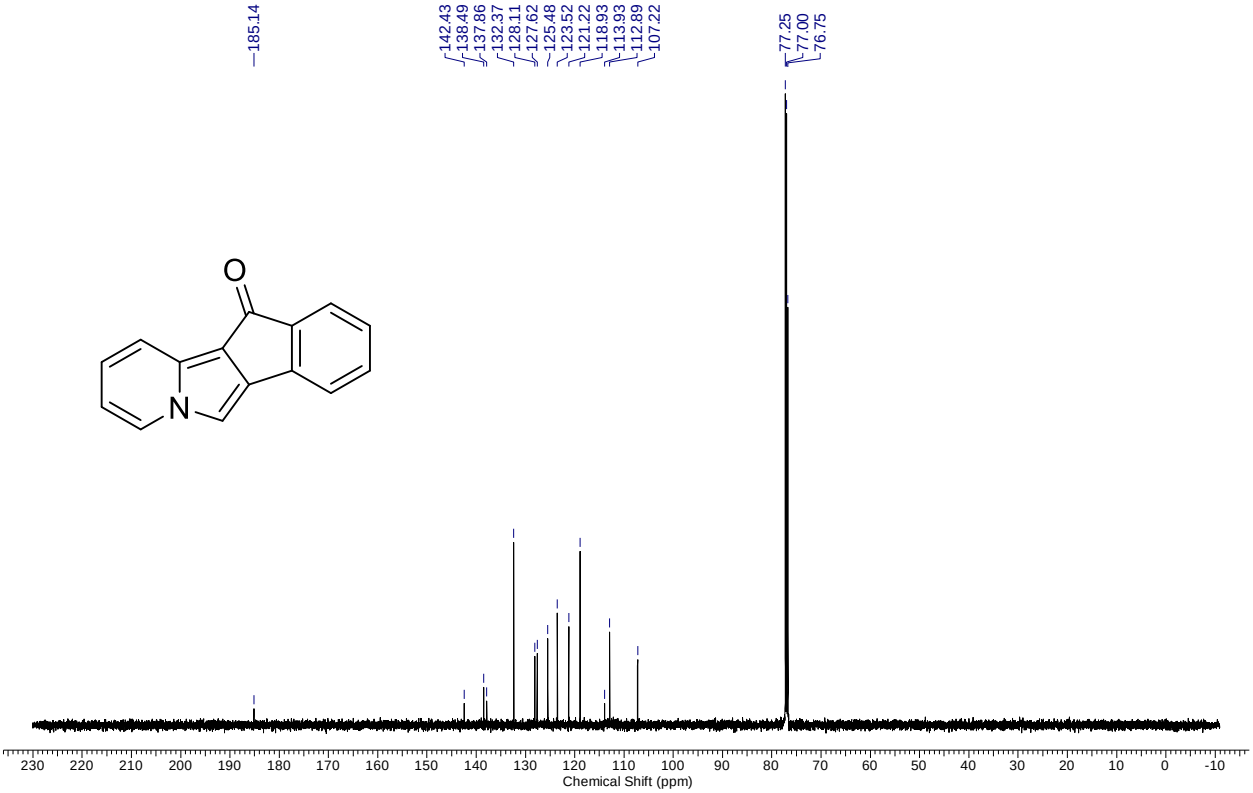
^{13}C NMR Spectrum of **2bd**



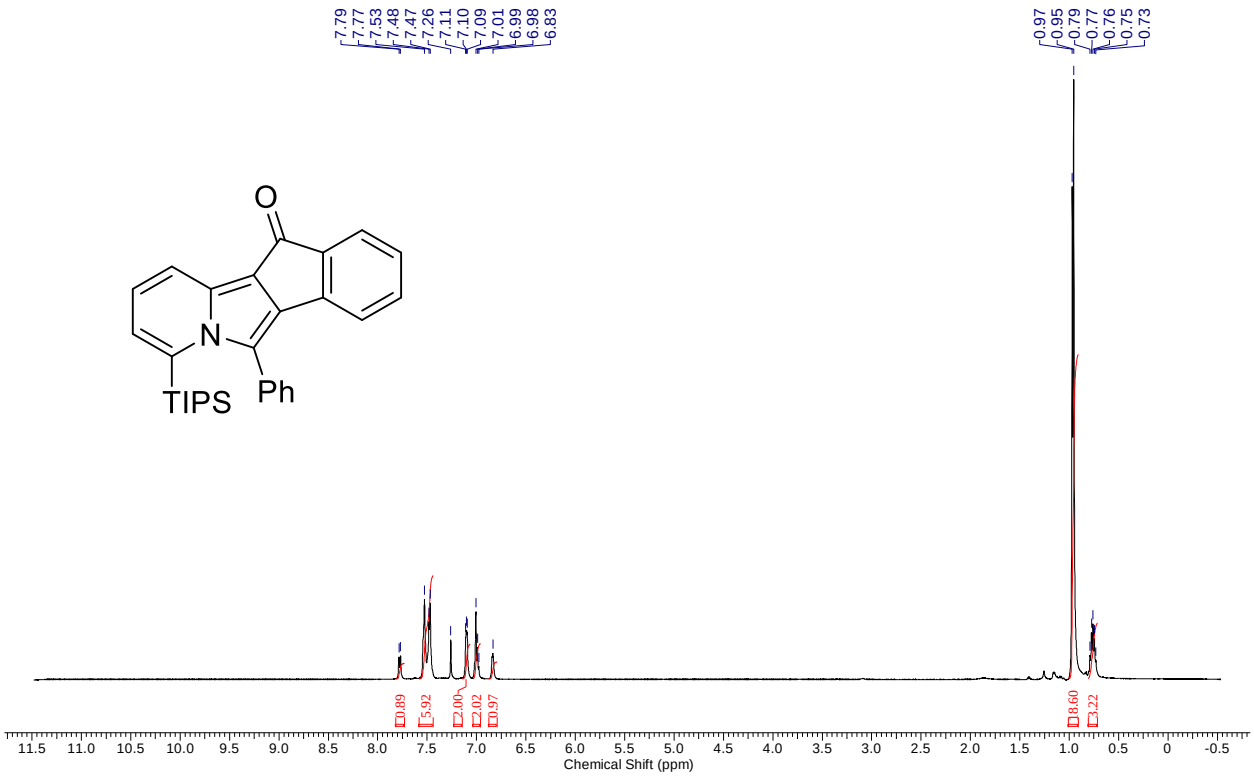
^{1}H NMR Spectrum of **2be**



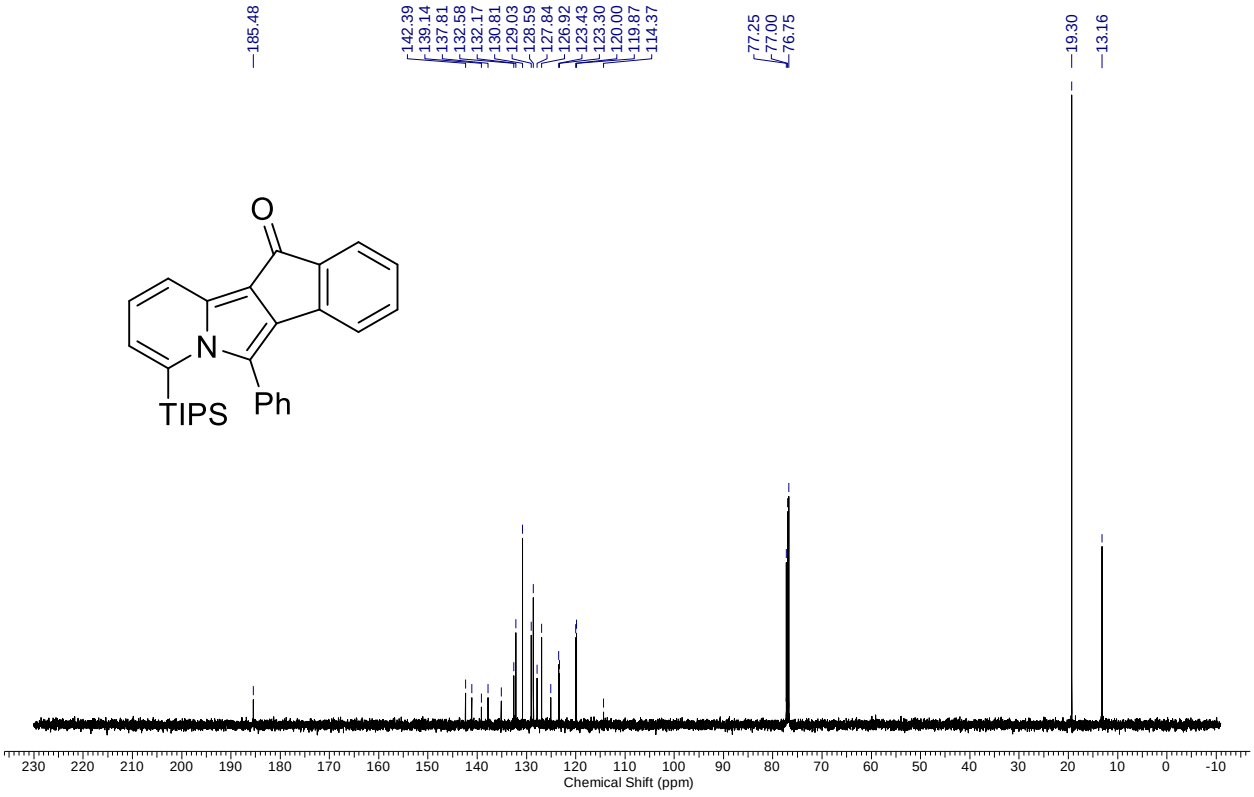
^{13}C NMR Spectrum of **2be**



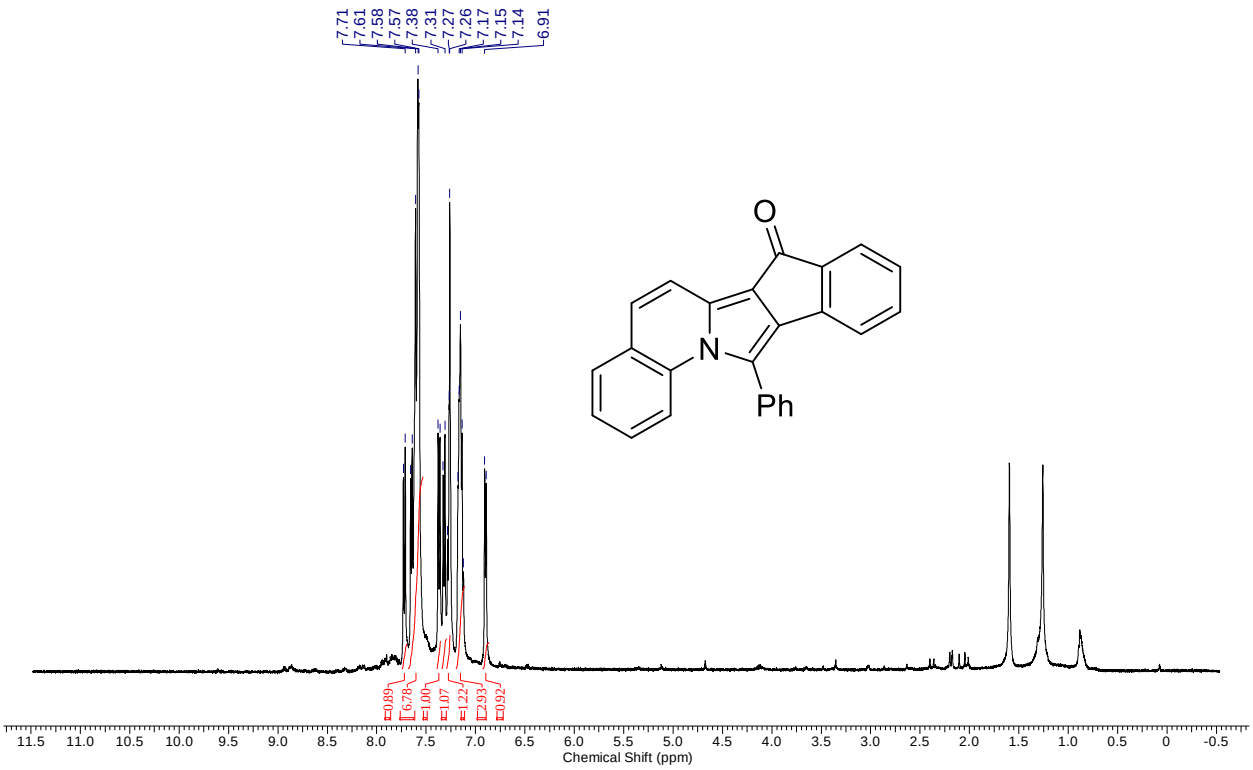
^{1}H NMR Spectrum of **2bf**



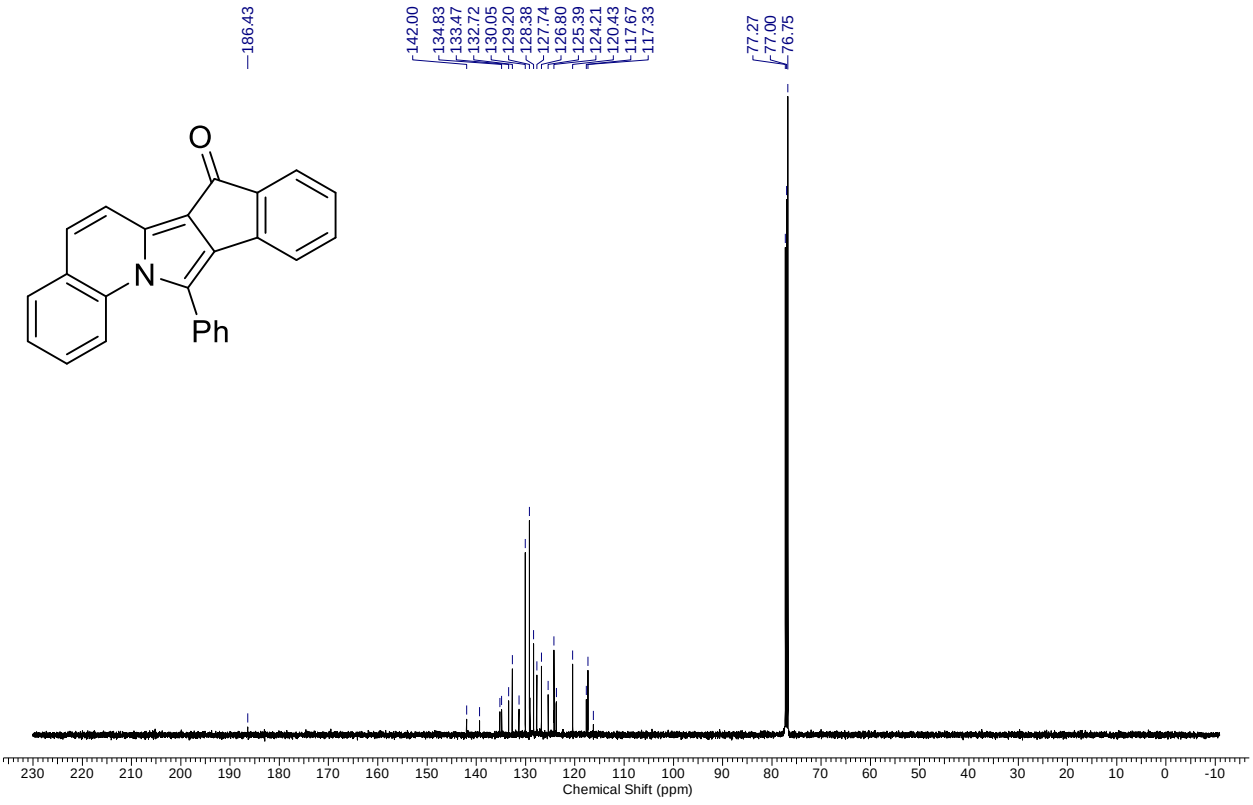
^{13}C NMR Spectrum of **2bf**



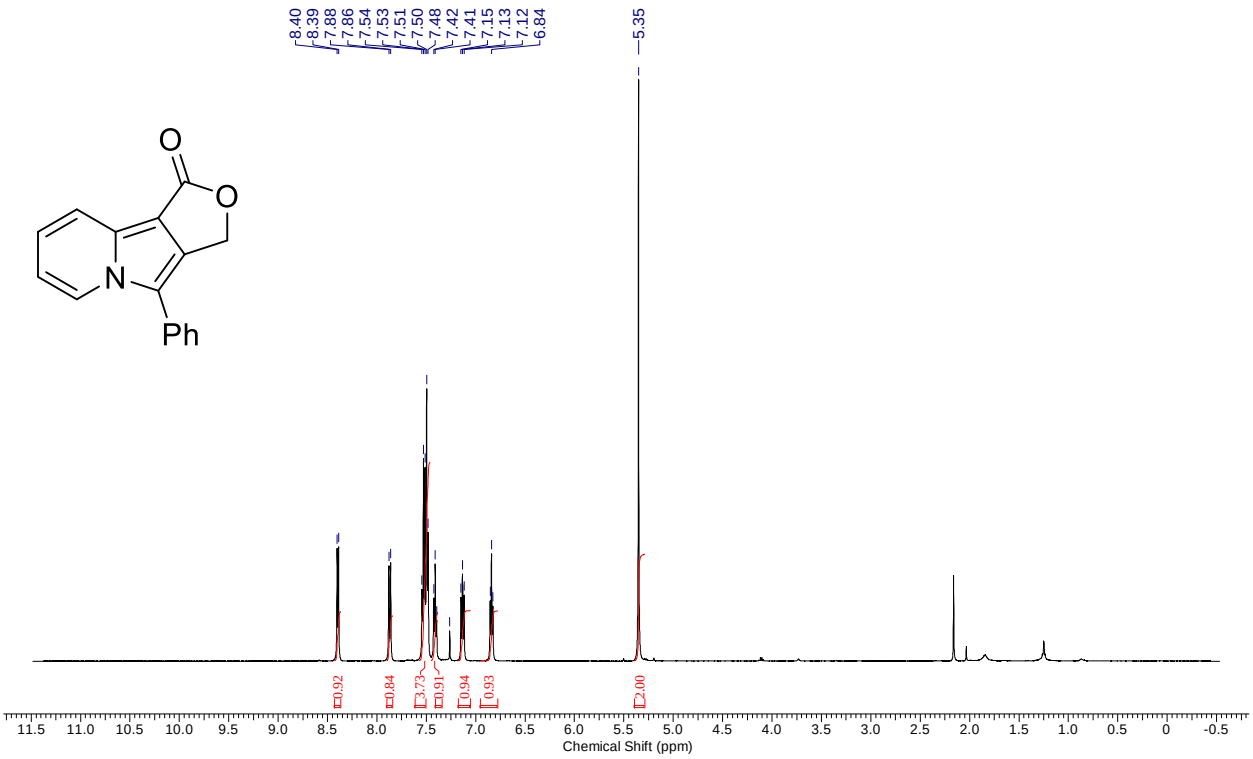
^{1}H NMR Spectrum of **2bg**



^{13}C NMR Spectrum of **2bg**



^{1}H NMR Spectrum of **2bh**



^{13}C NMR Spectrum of **2bh**