Cobalt-Catalyzed Intramolecular Oxidative C(sp^3)-H/N-H Carbonylation of Aliphatic Amides

Li Zeng,[†,§] Shan Tang,[†,§] Dan Wang,[†] Yi Deng,[†] Jeng-Lung Chen,[⊥] Jyh-Fu Lee,[⊥] and Aiwen Lei*[,†,‡]

†College of Chemistry and Molecular Sciences, the Institute for Advanced Studies (IAS), Wuhan University, Wuhan 430072, P. R. China; ‡State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China; ⊥National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan; * Email: aiwenlei@whu.edu.cn

Contents

General information

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. Aliphatic amides were synthesized according to literature procedures.[1] Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). X-ray absorption measurements were acquired in transmission mode at beamline 17C1[2] at National Synchrotron Radiation Research Center (NSSRC) in Taiwan. A pure Co foil spectrum (edge energy 7709 eV) was acquired simultaneously with each measurement for energy calibration. Multiple scans were taken to reduce the noise. ^{1}H, and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.

Experimental procedure

General procedure for the oxidative C(sp^3)-H/N-H carbonylation of aliphatic amides: In an oven-dried Schlenk tube equipped with a stir bar, aliphatic amides (0.3 mmol), $Co(acac)_2$ (11.6 mg, 0.045 mmol), NH_4OAc (23.1 mg, 0.30 mmol) and Ag_2CO_3 (207.0 mg, 0.75 mmol), a balloon filled CO (1 atm) was connected to the Schlenk tube by the side tube and purged three times. Then PhCl (1.0 mL) were added to the tube through a syringe. The Schlenk tube was heated at 120 °C for 24 h and then cooled to room temperature. After the balloon gas was released carefully, the reaction was quenched by saturated potassium carbonate solution and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel (petroleum: ethyl ether = 1:2).

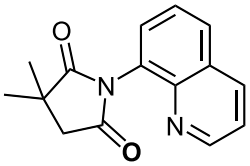
Experimental details of XAS study: All solution samples were placed in a sample holder (the XAS solution cell) made of PEEK (polyether ether ketone) equipped with a screw top and O-ring fitting to prevent exposure to air and water.[3] For solution samples, the Co concentration was adjusted to be

0.05 - 0.1 M with a path length of 3.5 mm. The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point of the edge. The data procedures were carried out using the Athena software package using standard methods.[4] Standard procedures based on Artemis software (Demeter 0.9.20) were used to extract the extended X-ray absorption fine structure (EXAFS) data. The coordination parameters were obtained by a least square fit in R-space of the nearest neighbor, k^2 weighted Fourier transform data. XAFS spectrum was measured at -110 ^{o}C.

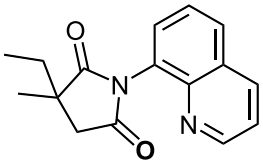
Experimental procedure for removing the directing group: In an oven-dried Teflon septum screw-capped tube equipped with a stir bar, 2**m** (44.1 mg, 0.15 mmol) or 2**n** (46.2 mg, 0.15 mmol), trifluoroacetic acid (1.0 mL) and conc. HCl (1.0 mL) were combined and sealed. The reaction mixture was stirred at 120 ^{o}C for 36 h. After cooling to room temperature, the reaction mixture was concentered under reduced pressure to remove trifluoroacetic acid. The residue was diluted with 3M HCl (2.0 mL) and extracted with EtOAc (10 mL x 3). The combined organic layers were evaporated in vacuo to afford crude product. The crude product was added a solution of 2 M NaOH (10 mL), then the mixture was washed with EtOAc (10 mL x 3), the pH of the water layers was adjusted to 2 with 3 M HCl. The water layers were extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and then evaporated in vacuo to afford the carboxylic acid **3m** or **3n**.

Procedure for the synthesis of 1a on 1.0 mmol scale: In an oven-dried Schlenk tube equipped with a stir bar, **1a** (1.0 mmol), $Co(acac)_2$ (38.5 mg, 0.15 mmol), NH_4OAc (77.1 mg, 1.0 mmol) and Ag_2CO_3 (689.3 mg, 2.5 mmol), a balloon filled CO (1 atm) was connected to the Schlenk tube by the side tube and purged three times. Then PhCl (3.0 mL) were added to the tube through a syringe. The Schlenk tube was heated at 120 ^{o}C for 24 h and then cooled to room temperature. After the balloon gas was released carefully, the reaction was quenched by saturated potassium carbonate solution and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum. Yellow oil was obtained with 78% isolated yield (198.1 mg) after purification by flash chromatography on silica gel (petroleum: ethyl ether = 1:2).

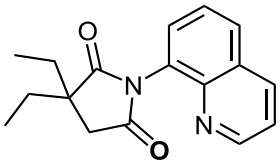
Detail descriptions for products



3,3-Dimethyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2a):[5] yellow oil was obtained with 82% isolated yield (62.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 3.1 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.98 – 7.87 (m, 1H), 7.62 (d, *J* = 4.6 Hz, 2H), 7.48 – 7.38 (m, 1H), 2.95 (d, *J* = 18.0 Hz, 1H), 2.82 (d, *J* = 18.0 Hz, 1H), 1.61 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.00, 175.75, 150.97, 143.58, 136.02, 130.24, 129.62, 129.34, 129.16, 126.01, 121.92, 44.16, 40.97, 26.21, 25.43.

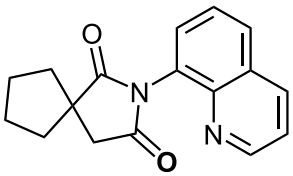


3-Ethyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2b):[5] yellow oil was obtained with 65% isolated yield (52.2 mg, a mixture of diastereomers, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.92 – 8.84 (m, 1H), 8.25 – 8.16 (m, 1H), 7.98 – 7.90 (m, 1H), 7.70 – 7.60 (m, 2H), 7.48 – 7.40 (m, 1H), 3.06 (d, *J* = 17.2 Hz, 0.5H), 2.93 (d, *J* = 18.3 Hz, 0.5H), 2.86 (d, *J* = 17.0 Hz, 0.5H), 2.71 (d, *J* = 19.3 Hz, 0.5H), 2.11 – 2.00 (m, 0.5H), 2.00 – 1.91 (m, 0.5H), 1.90 – 1.73 (m, 1H), 1.61 (s, 1.5H), 1.50 (s, 1.5H), 1.20 (t, *J* = 7.0 Hz, 1.5H), 1.09 (t, *J* = 7.0 Hz, 1.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.62, 182.50, 176.06, 175.99, 150.96, 150.80, 143.54, 143.50, 136.01, 135.95, 130.33, 130.23, 129.60, 129.55, 129.33, 129.27, 129.13, 129.11, 125.97, 125.95, 121.89, 121.86, 44.98, 44.91, 40.97, 40.94, 31.29, 31.10, 24.42, 24.01, 8.87, 8.80.

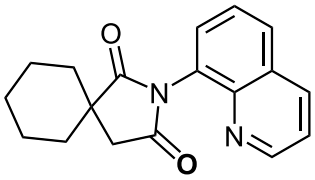


3,3-Diethyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2c):[5] yellow oil was obtained with 50% isolated yield (42.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.94 (d, *J* = 18.4 Hz, 1H), 2.75 (d, *J* = 18.4 Hz, 1H), 2.05 – 1.86 (m, 2H), 1.78 (m, 2H), 1.17 (t, *J* = 7.5 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 181.98, 176.38, 150.86,

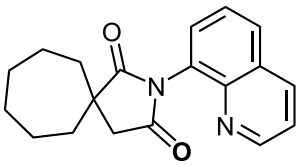
143.55, 135.96, 130.43, 129.58, 129.29, 129.14, 125.98, 121.89, 49.27, 37.80, 30.07, 30.00, 8.69.



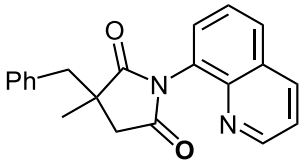
2-(Quinolin-8-yl)-2-azaspiro[4.4]nonane-1,3-dione (2d):[5] yellow oil was obtained with 72% isolated yield (60.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.81 (m, 1H), 8.18 – 8.11 (m, 1H), 7.88 (dd, *J* = 7.2, 2.3 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.99 (d, *J* = 18.0 Hz, 1H), 2.84 (d, *J* = 18.0 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.35 – 2.24 (m, 1H), 2.03 – 1.89 (m, 3H), 1.87 – 1.74 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.94, 176.01, 150.86, 143.45, 135.98, 130.31, 129.48, 129.28, 129.06, 125.92, 121.81, 50.95, 44.09, 38.83, 38.08, 25.30, 25.24.



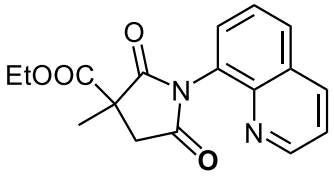
2-(Quinolin-8-yl)-2-azaspiro[4.5]decane-1,3-dione (2e):[5] yellow oil was obtained with 73% isolated yield (64.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.9 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.65 – 7.57 (m, 2H), 7.40 (dd, *J* = 8.2, 4.1 Hz, 1H), 2.97 (d, *J* = 18.1 Hz, 1H), 2.80 (d, *J* = 18.1 Hz, 1H), 1.97 (m, 3H), 1.86 (m, 2H), 1.74 (m, 2H), 1.43 (m , 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.71, 176.13, 150.93, 143.51, 136.02, 130.18, 129.56, 129.37, 129.14, 125.99, 121.88, 45.73, 40.55, 33.64, 33.43, 25.00, 22.25, 22.09.



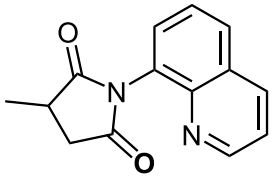
2-(Quinolin-8-yl)-2-azaspiro[4.6]undecane-1,3-dione (2f):[5] yellow oil was obtained with 68% isolated yield (62.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 – 8.82 (m, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 6.3, 2.5 Hz, 1H), 7.70 – 7.58 (m, 2H), 7.51 – 7.39 (m, 1H), 3.00 (dd, *J* = 18.0, 1.4 Hz, 1H), 2.84 (dd, *J* = 18.0, 1.3 Hz, 1H), 2.34 – 2.17 (m, 2H), 2.12 (m, 1H), 1.90 (m, 3H), 1.76 – 1.54 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 183.53, 176.12, 150.92, 143.61, 136.01, 130.14, 129.53, 129.35, 129.13, 125.98, 121.87, 48.13, 42.56, 37.49, 37.27, 28.81, 23.70, 23.59.



3-Benzyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2g):[5] colorless oil was obtained with 73% isolated yield (72.3 mg, a mixture of diastereomers, 2.3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.2, 1.6 Hz, 0.7H), 8.77 (dd, *J* = 4.1, 1.6 Hz, 0.3H), 8.18 – 8.11 (m, 1H), 7.93 – 7.88 (m, 0.3H), 7.85 (dd, *J* = 8.3, 1.1 Hz, 0.7H), 7.64 – 7.59 (m, 0.6H), 7.55 – 7.49 (m, 0.7H), 7.42 – 7.23 (m, 6H), 7.13 (dd, *J* = 7.3, 1.2 Hz, 0.7H), 3.40 (d, *J* = 13.7 Hz, 0.3H), 3.33 (d, *J* = 13.3 Hz, 0.7H), 3.17 (d, *J* = 18.1 Hz, 0.3H), 3.06 – 2.97 (m, 1H), 2.85 – 2.75 (m, 1.4H), 2.55 (d, *J* = 18.1 Hz, 0.3H), 1.69 (s, 2.1H), 1.50 (s, 0.9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.23, 181.82, 175.59, 175.40, 150.95, 150.75, 143.50, 143.45, 136.33, 136.29, 135.99, 135.91, 130.55, 130.12, 129.98, 129.60, 129.52, 129.23, 129.19, 129.09, 129.01, 128.65, 128.37, 127.32, 126.89, 125.95, 121.87, 121.83, 46.04, 45.66, 43.93, 43.08, 40.53, 40.15, 25.56, 24.69.

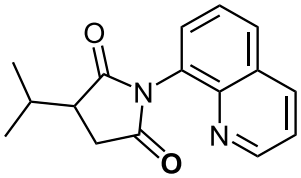


Ethyl 3-methyl-2,5-dioxo-1-(quinolin-8-yl)pyrrolidine-3-carboxylate (2h):[5] colorless oil was obtained with 40% isolated yield (37.4 mg, a mixture of diastereomers, 2.4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.83 (m, 1H), 8.23 – 8.17 (m, 1H), 7.98 – 7.90 (m, 1H), 7.68 – 7.60 (m, 2H), 7.48 – 7.40 (m, 1H), 4.37 – 4.26 (m, 2H), 3.67 (d, *J* = 18.1 Hz, 0.3H), 3.42 (d, *J* = 18.0 Hz, 0.7H), 2.99 (d, *J* = 18.0 Hz, 0.7H), 2.81 (d, *J* = 18.0 Hz, 0.3H), 1.85 (s, 2.1H), 1.76 (s, 0.9H), 1.38 – 1.31 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.17, 175.86, 174.67, 174.44, 170.30, 169.85, 151.06, 150.88, 143.55, 143.40, 136.17, 135.98, 129.89, 129.86, 129.37, 129.20, 126.09, 125.93, 122.03, 121.99, 62.45, 51.49, 51.39, 41.47, 41.17, 21.36, 20.79, 14.04.

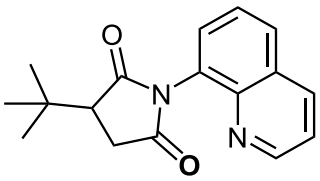


3-Methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2i): yellow solid was obtained with 89% isolated yield (64.1 mg, a mixture of diastereomers, 1.1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 –

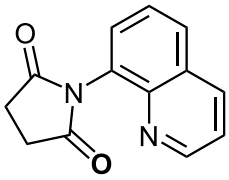
8.80 (m, 1H), 8.19 – 8.13 (m, 1H), 7.93 – 7.86 (m, 1H), 7.64 – 7.56 (m, 2H), 7.44 – 7.38 (m, 1H), 3.35 – 3.24 (m, 1H), 3.20 – 3.08 (m, 1H), 2.81 – 2.69 (m, 0.5H), 2.64 – 2.54 (m, 0.5H), 1.57 (d, *J* = 7.0 Hz, 1.5H), 1.48 (d, *J* = 6.8 Hz, 1.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.33, 180.23, 176.30, 176.07, 150.91, 150.78, 143.35, 143.30, 136.27, 136.07, 130.12, 129.99, 129.62, 129.59, 129.43, 129.33, 129.16, 129.08, 126.01, 125.98, 121.87, 121.86 , 37.03, 36.94, 35.50, 35.28, 17.04, 16.70. HRMS (ESI) calcd for $C_{14}H_12N_2O_2$ $[M+H]^+$: 241.0972; found: 241.0982.



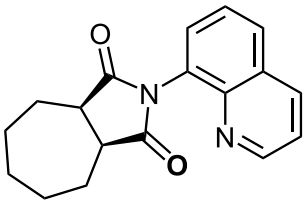
3-Isopropyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2j): yellow solid was obtained with 84% isolated yield (67.5 mg, a mixture of diastereomers, 1.1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 – 8.78 (m, 1H), 8.22 – 8.11 (m, 1H), 7.94 – 7.86 (m, 1H), 7.67 – 7.52 (m, 2H), 7.46 – 7.35 (m, 1H), 3.27 – 3.19 (m, 0.5H), 3.14 – 3.02 (m, 1H), 2.98 – 2.81 (m, 1H), 2.71 (dd, *J* = 18.3, 4.4 Hz, 0.5H), 2.58 – 2.42 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 1.4H), 1.13 (d, *J* = 6.9 Hz, 1.4H), 1.10 (d, *J* = 6.9 Hz, 1.6H), 1.05 (d, *J* = 6.8 Hz, 1.6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.21, 179.00, 176.71, 176.60, 150.85, 150.76, 143.39, 143.37, 136.22, 135.90, 130.28, 130.04, 129.66, 129.52, 129.37, 129.22, 129.17, 129.04, 126.02, 125.95, 121.90, 121.84, 46.48, 46.24, 30.86, 30.57, 28.93, 28.90, 20.50, 20.06, 17.35, 17.33. HRMS (ESI) calcd for $C_{16}H_{16}N_2O_2$ $[M+H]^+$: 269.1285; found: 269.1278.



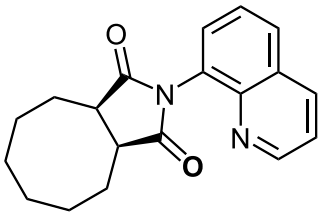
3-(Tert-butyl)-1-(quinolin-8-yl)pyrrolidine-2,5-dione (2k): yellow solid was obtained with 61% isolated yield (51.6 mg, a mixture of diastereomers, 1.2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.79 (m, 1H), 8.22 – 8.12 (m, 1H), 7.94 – 7.86 (m, 1H), 7.64 – 7.53 (m, 2H), 7.48 – 7.36 (m, 1H), 3.20 – 3.02 (m, 1H), 2.99 – 2.76 (m, 2H), 1.22 (s, 4H), 1.16 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.13, 178.02, 176.34, 176.31, 150.89, 150.72, 143.42, 143.35, 136.32, 135.88, 130.31, 130.11, 129.67, 129.49, 129.45, 129.21, 129.19, 129.04, 126.05, 125.93, 121.89, 121.82, 50.48, 50.33, 33.76, 33.58, 32.33, 32.31, 27.46, 27.40, 27.21. HRMS (ESI) calcd for $C_{17}H_{18}N_2O_2$ $[M+H]^+$: 283.1441; found: 283.1432.



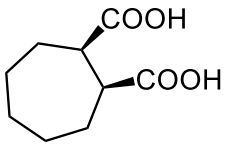
1-(Quinolin-8-yl)pyrrolidine-2,5-dione(2l):[6] yellow solid was obtained with 82% isolated yield (55.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.93 (dd, *J* = 6.5, 3.2 Hz, 1H), 7.69 – 7.56 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.22 – 3.08 (m, 2H), 3.02 – 2.89 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.94, 150.90, 143.35, 136.28, 130.00, 129.74, 129.47, 129.20, 126.10, 121.97, 28.90.



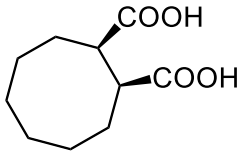
Cis-2-(quinolin-8-yl)hexahydrocyclohepta[c]pyrrole-1,3(2H,3aH)-dione (2m): yellow solid was obtained with 67% isolated yield (59.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 – 8.82 (m, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.96 – 7.88 (m, 1H), 7.62 (d, *J* = 5.9 Hz, 2H), 7.43 (dd, *J* = 7.9, 4.0 Hz, 1H), 3.23 – 3.14 (m, 1H), 3.02 – 2.89 (m, 1H), 2.55 – 2.40 (m, 2H), 1.88 – 1.74 (m, 4H), 1.74 – 1.57 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.60, 178.45, 150.83, 143.48, 136.11, 130.28, 129.45, 129.30, 129.16, 126.03, 121.83, 46.88, 46.67, 27.94, 27.87, 27.25, 27.20, 25.23. HRMS (ESI) calcd for $C_{18}H_{18}N_2O_2$ $[M+H]^+$: 295.1441; found: 295.1439.



Cis-2-(quinolin-8-yl)octahydro-1H-cycloocta[c]pyrrole-1,3(2H)-dione (2n): yellow solid was obtained with 70% isolated yield (64.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.95 – 7.86 (m, 1H), 7.64 – 7.56 (m, 2H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.17 – 3.10 (m, 1H), 3.00 – 2.90 (m, 1H), 2.55 – 2.39 (m, 2H), 1.98 – 1.77 (m, 5H), 1.69 – 1.48 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.52, 179.45, 150.88, 143.40, 136.07, 130.32, 129.50, 129.30, 129.15, 126.00, 121.84, 46.28, 46.06, 30.40, 30.38, 27.00, 26.90, 24.79, 24.70. HRMS (ESI) calcd for $C_{19}H_{20}N_2O_2$ $[M+H]^+$: 309.1598; found: 309.1589.



Cis-cycloheptane-1,2-dicarboxylic acid (3m):[7] pale yellow solid was obtained with 71% isolated yield (19.8 mg). ^{1}H NMR (400 MHz, DMSO) δ 12.16 (s, 2H), 2.87 – 2.59 (m, 2H), 2.03 – 1.71 (m, 3H), 1.66 – 1.34 (m, 7H). ^{13}C NMR (101 MHz, DMSO) δ 176.69, 46.24, 29.18, 28.30, 26.06. IR(KBr): υ (COOH) 3700-2400cm^{-1}, υ (CO) 1702 cm^{-1}.



Cis-cyclooctane-1,2-dicarboxylic acid (3n):[8] pale yellow solid was obtained with 66% isolated yield (19.8 mg). ^{1}H NMR (400 MHz, DMSO) δ 12.14 (s, 2H), 2.90 – 2.65 (m, 2H), 1.94 – 1.32 (m, 12H). ^{13}C NMR (101 MHz, DMSO) δ 176.88, 44.28, 26.60, 26.53, 25.31. IR(KBr): υ (COOH) 3700-2400cm^{-1}, υ (CO) 1705 cm^{-1}.

References

(1) Wu, X.; Yang, K.; Zhao, Y.; Sun, H.; Li, G.; Ge, H. *Nat. Commun.* **2015**, *6*, 6462.

(2) K. L. Tsang, C. H. Lee, Y. C. Jean, T. E. Dann, J. R. Chen, K. L. D`Amico, T. Oversluizen, Rev. Sci. Instrum. 1995, 66, 1812.

(3) Nelson, R. C.; Miller, J. T. Catal. Sci. Technol. 2012, 2, 461.

(4) Ravel, B.; Newville, M. J. Synchrotron Radiat. 2005, 12, 537.

(5) Wu, X.; Zhao, Y.; Ge, H. *J. Am. Chem. Soc.* **2015**, *137*, 4924.

(6) Martyn, D. C.; Abell, A. D. *Aust. J. Chem.* **2004**, *57*, 1073.

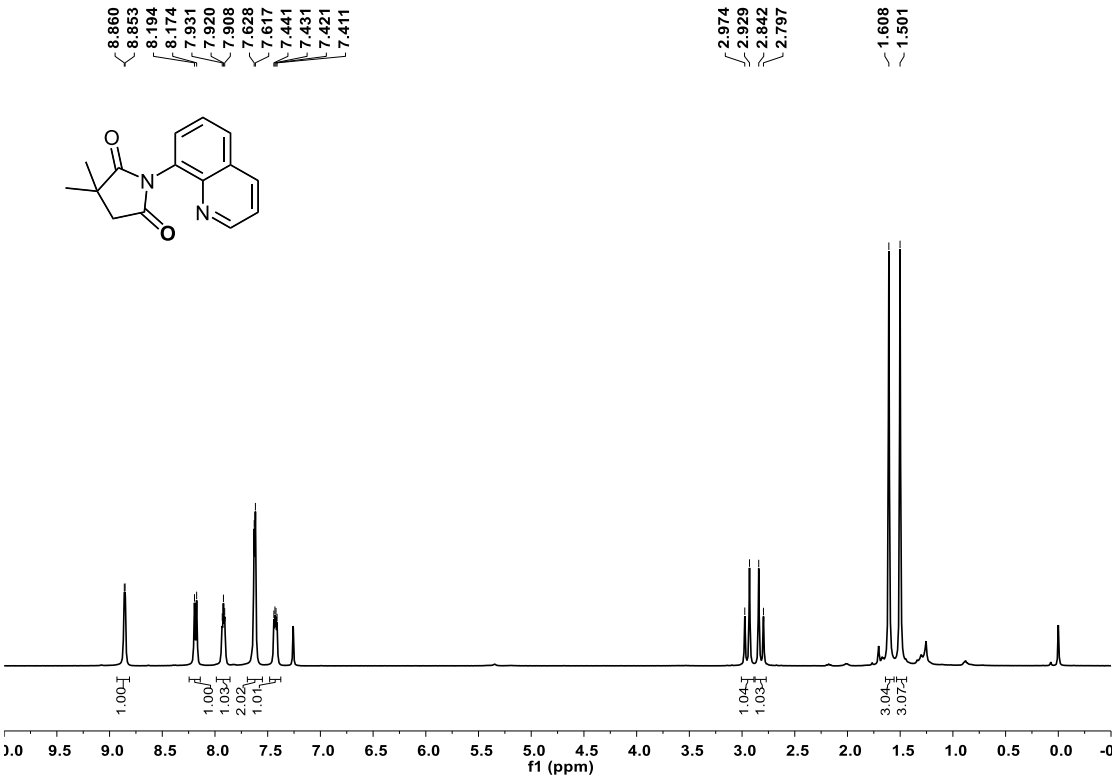
(7) Sicher, J.; Sipos, F.; Jonas, J. *Collect. Czech. Chem. Commun.* **1961**, *26*, 262.

(8) Hoberg, H.; Ballesteros, A. *J. Organomet. Chem.* **1991**, *411*, C11.

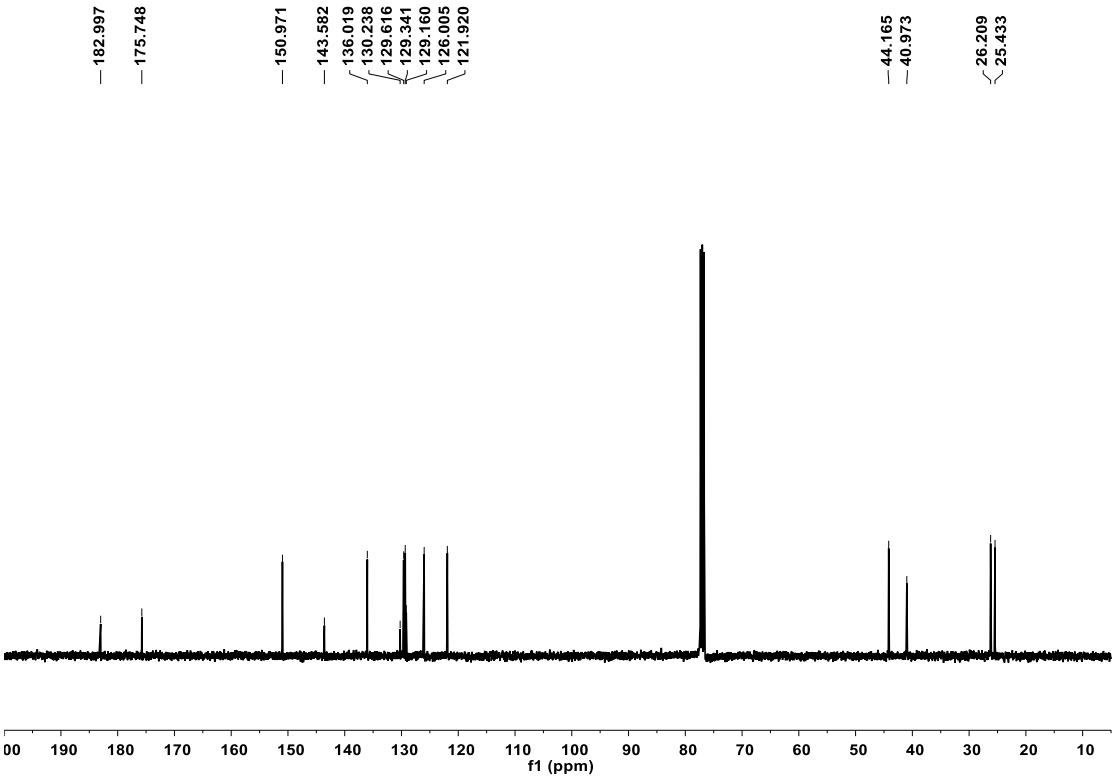
Copies of product NMR Spectra

2a

^{1}H NMR

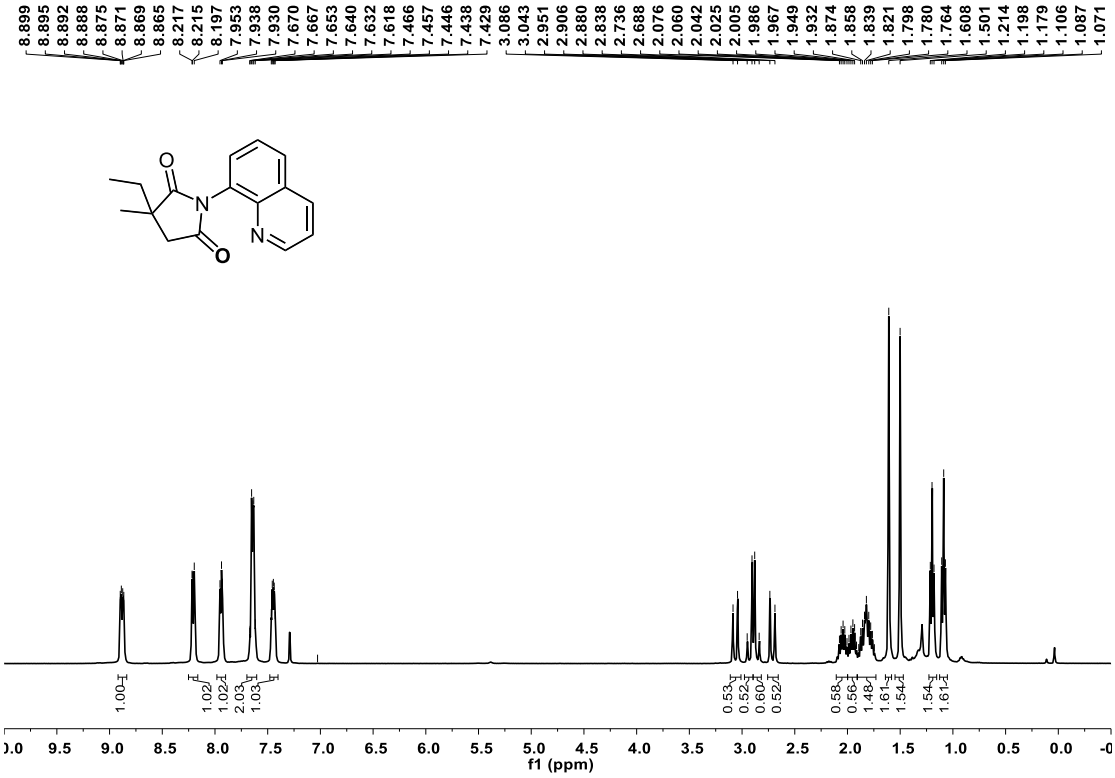


^{13}C NMR

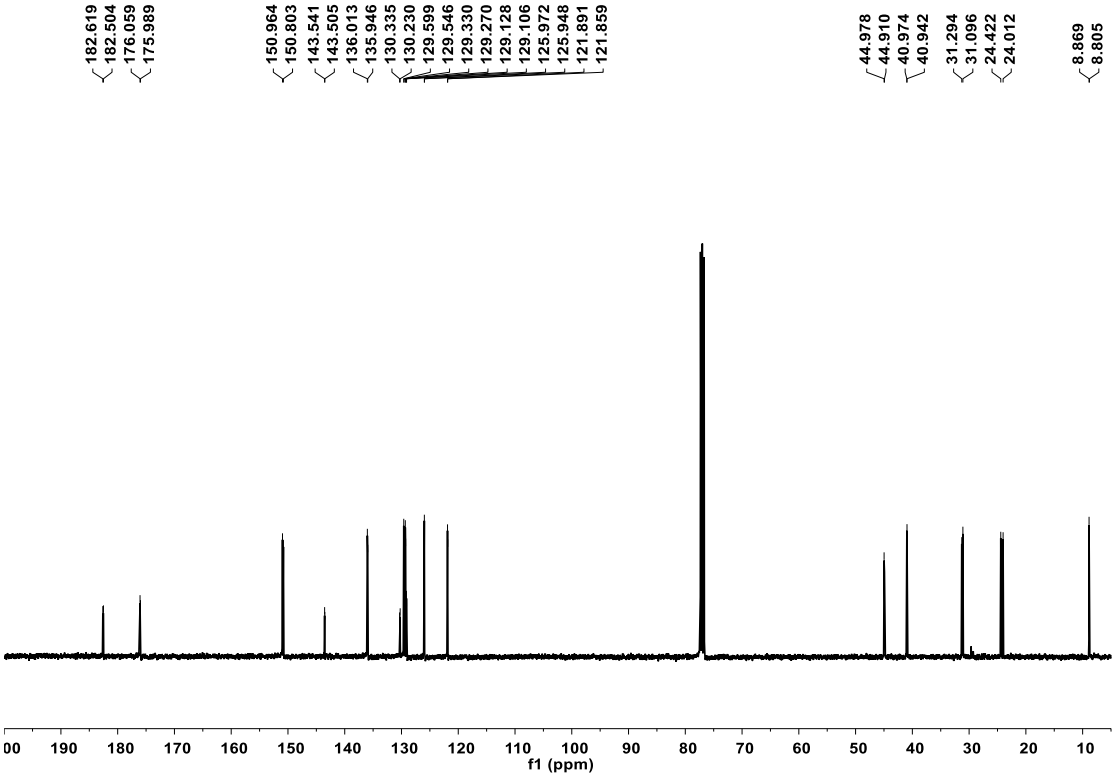


2b

^{1}H NMR

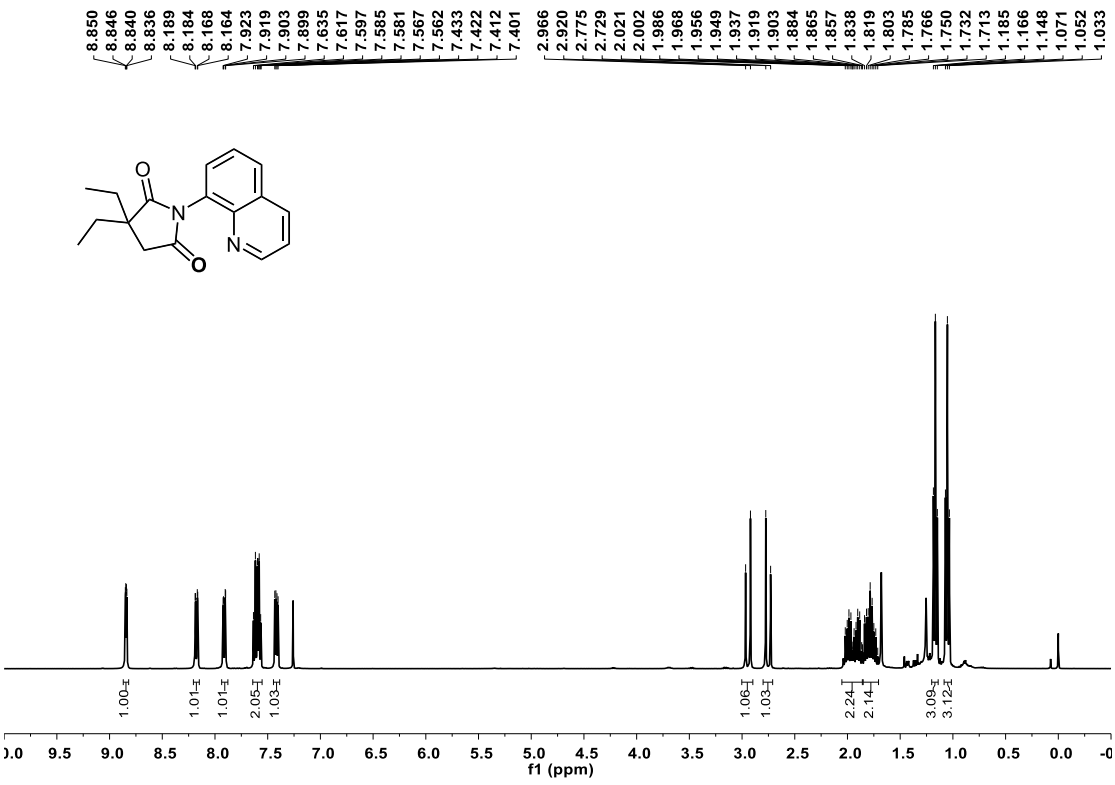


^{13}C NMR

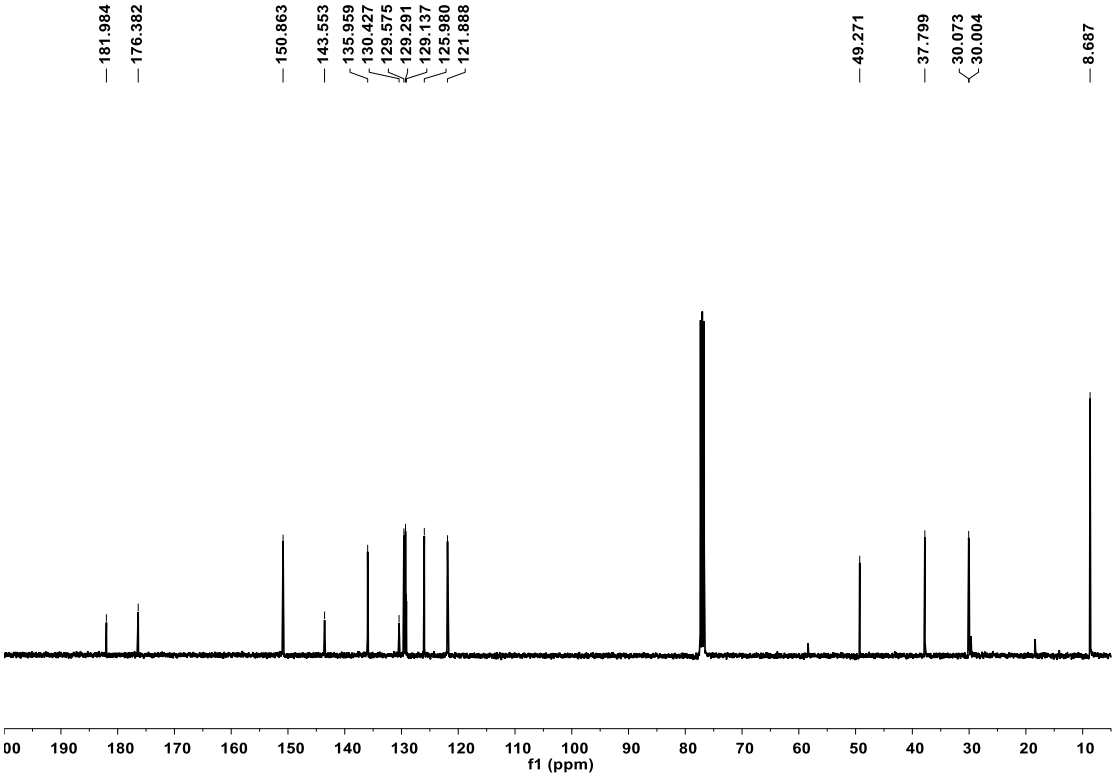


2c

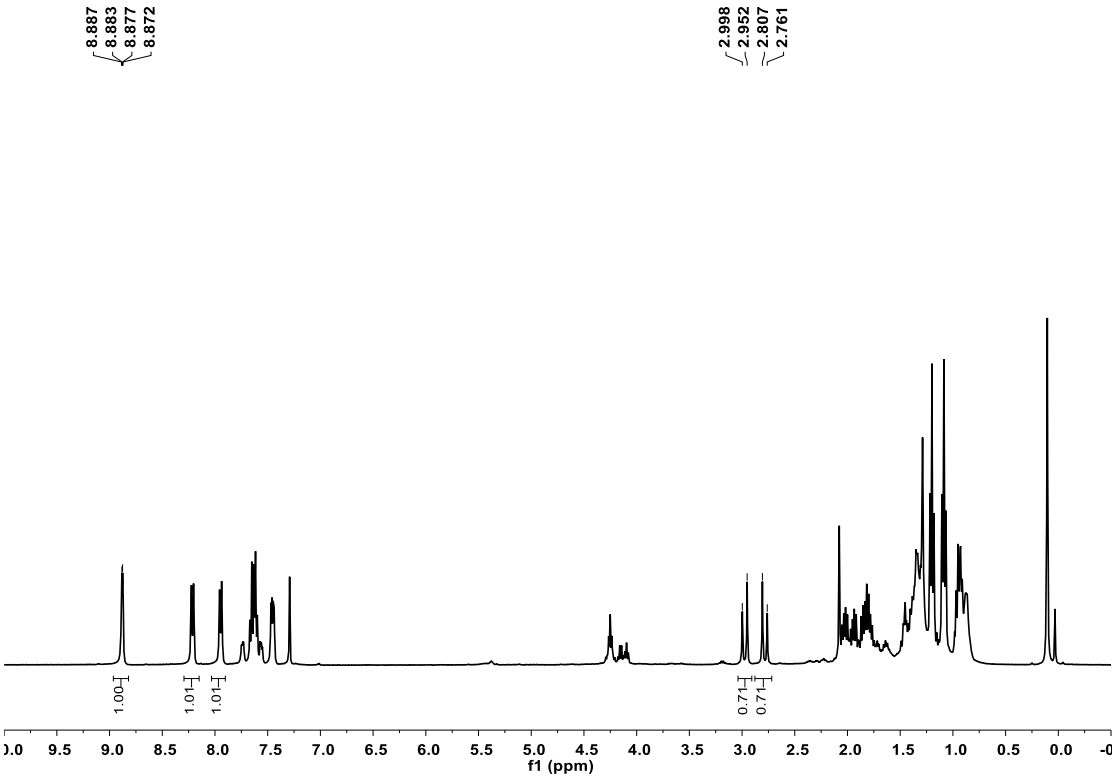
^{1}H NMR



^{13}C NMR

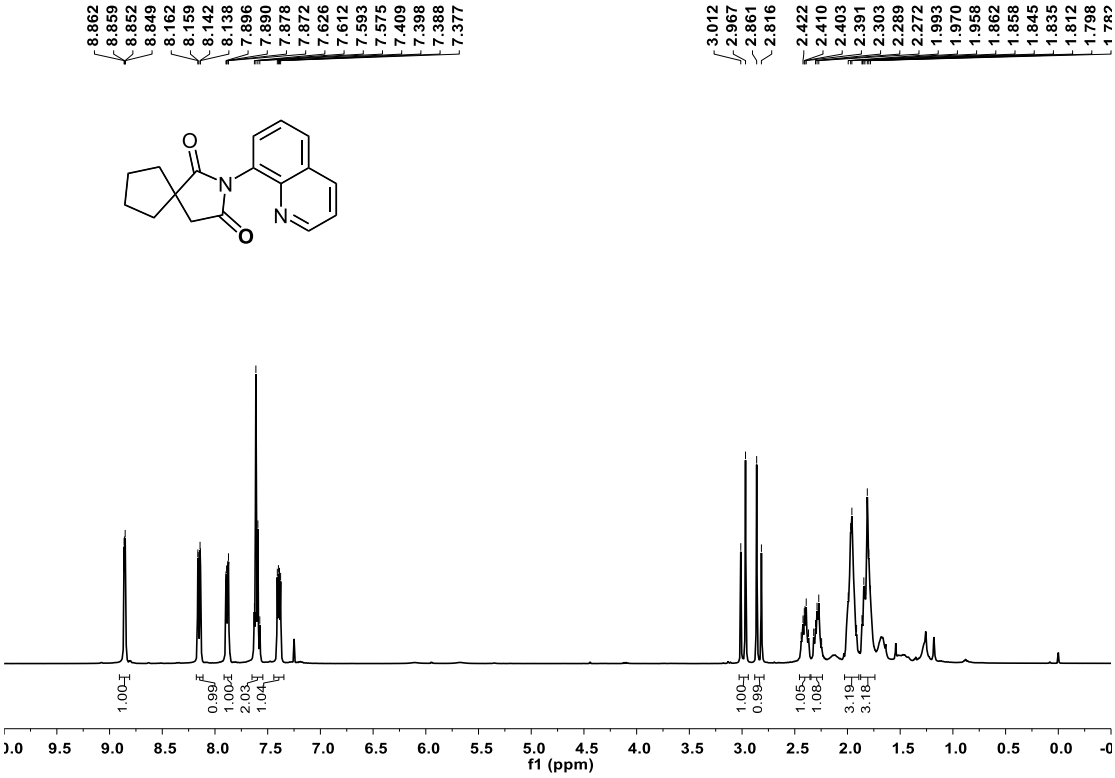


2c & [D_2]-2c

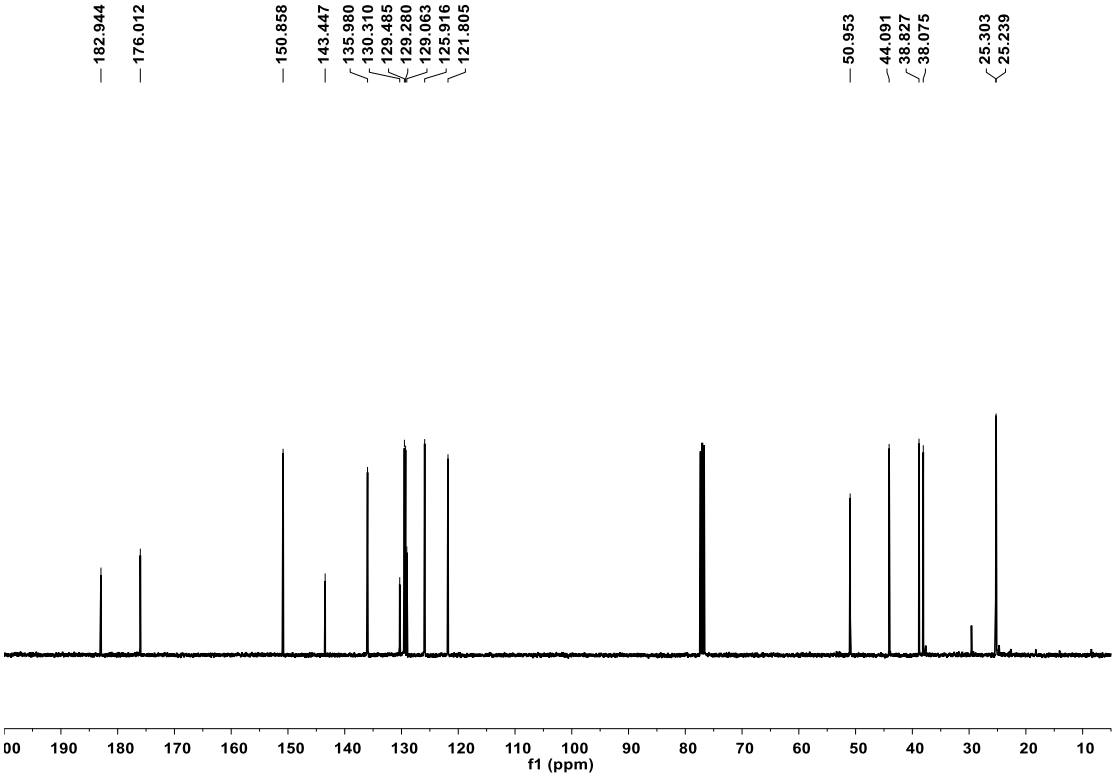

8.887
8.883
8.877
8.872
2.998
2.952
2.807
2.761
1.00
1.01
1.01
0.71
0.71
f1 (ppm)

2d

^{1}H NMR

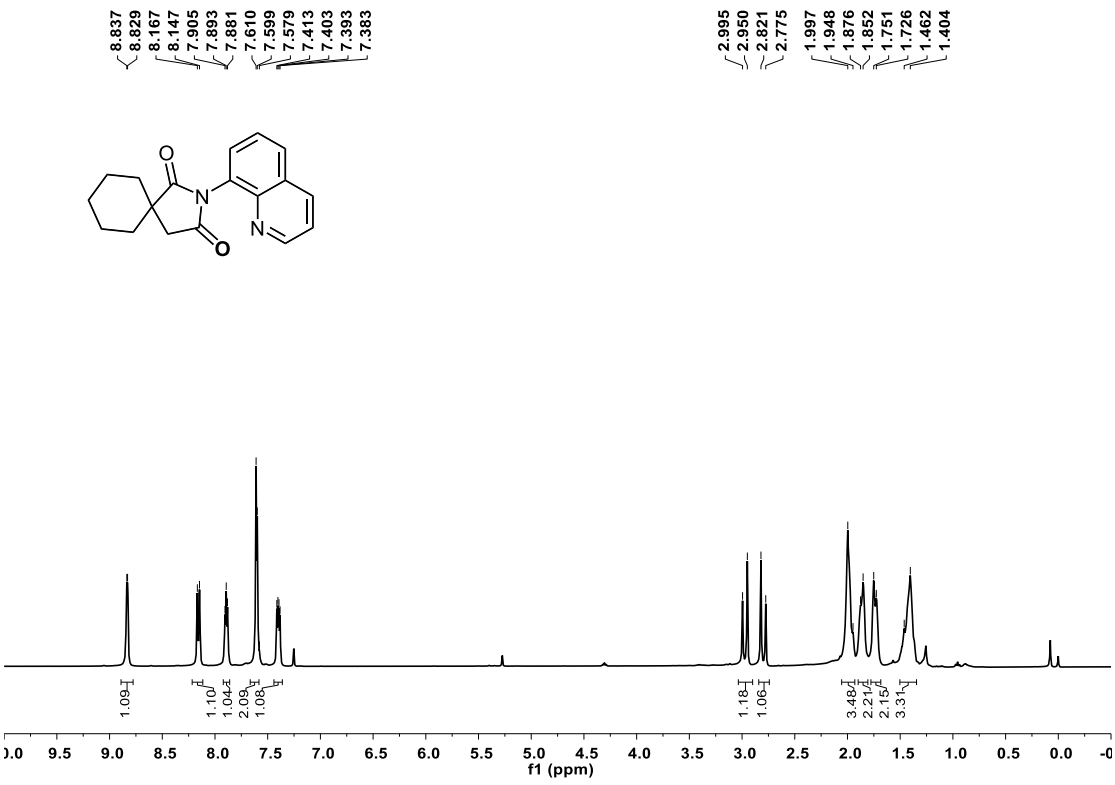


^{13}C NMR

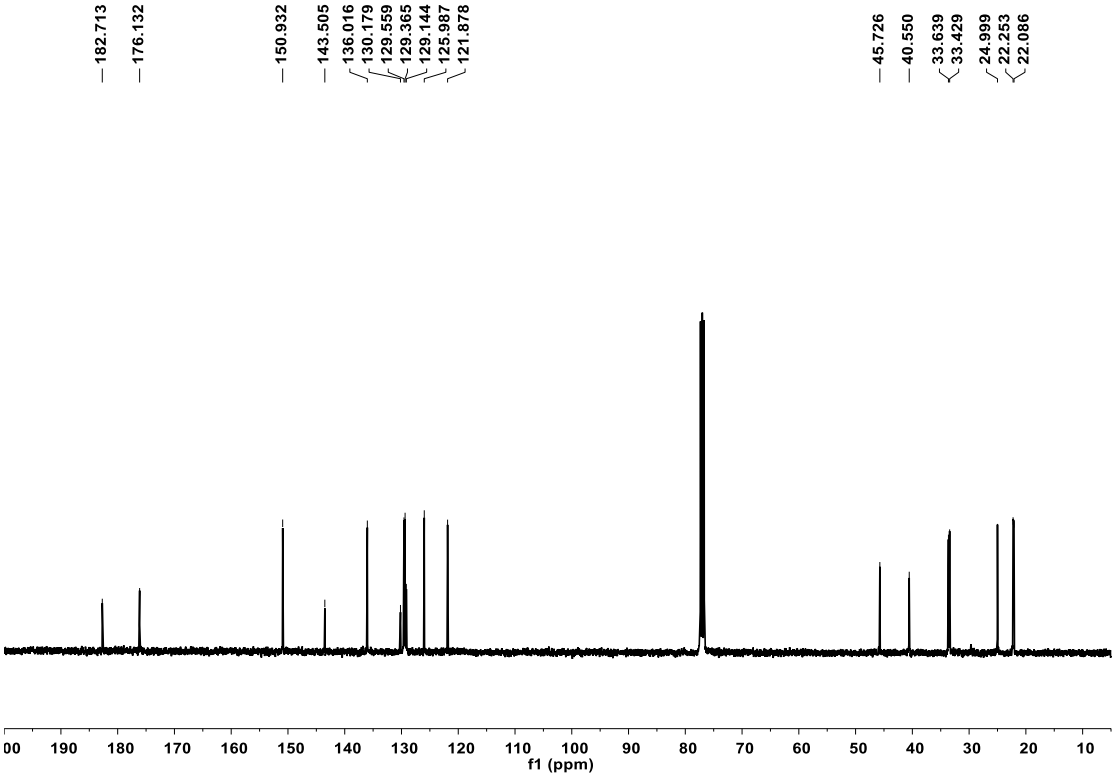


2e

^{1}H NMR

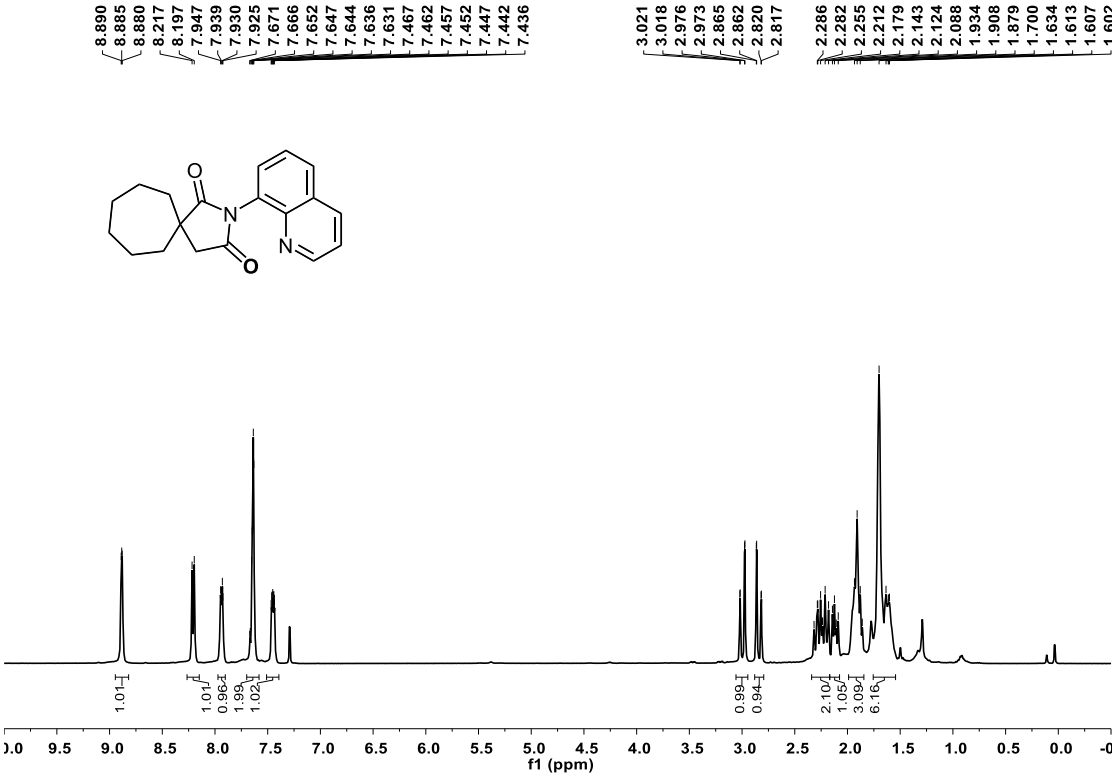


^{13}C NMR

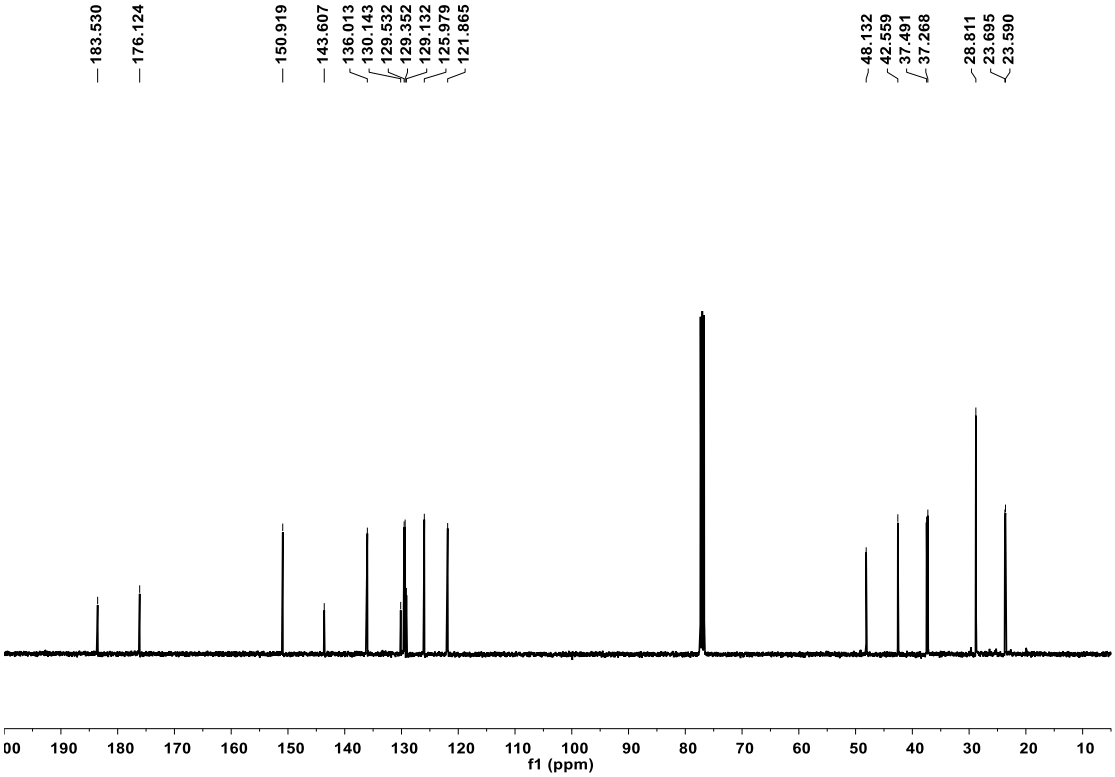


2f

^{1}H NMR

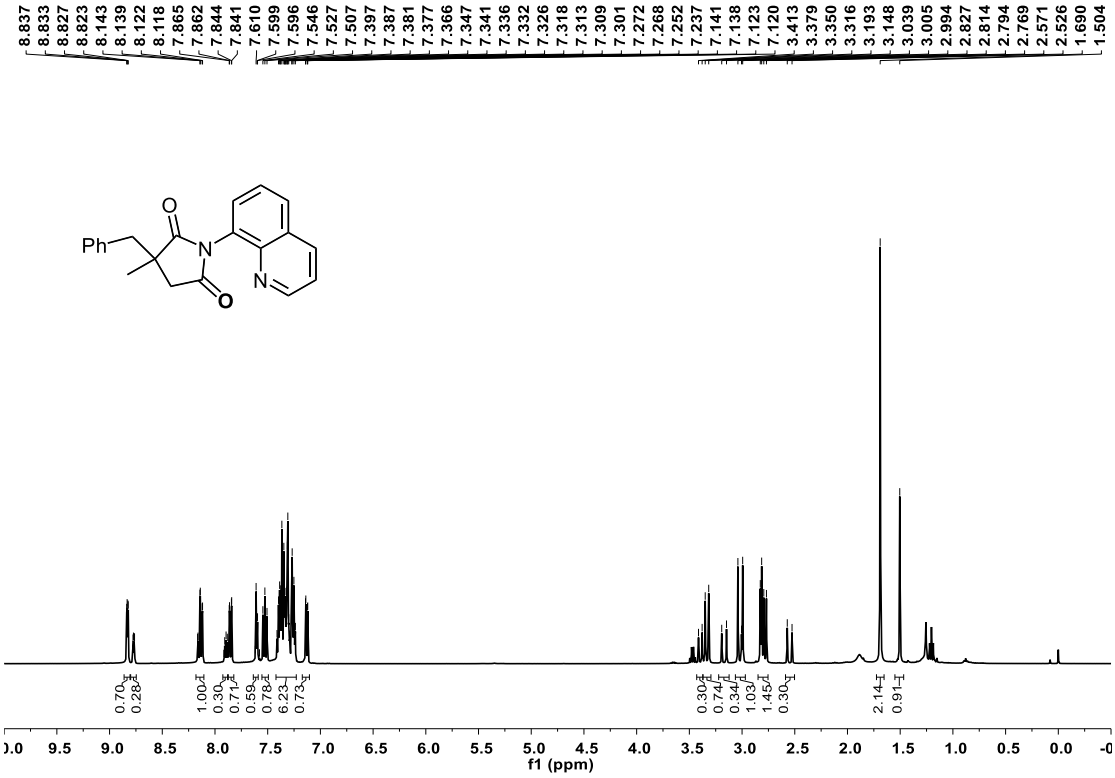


^{13}C NMR

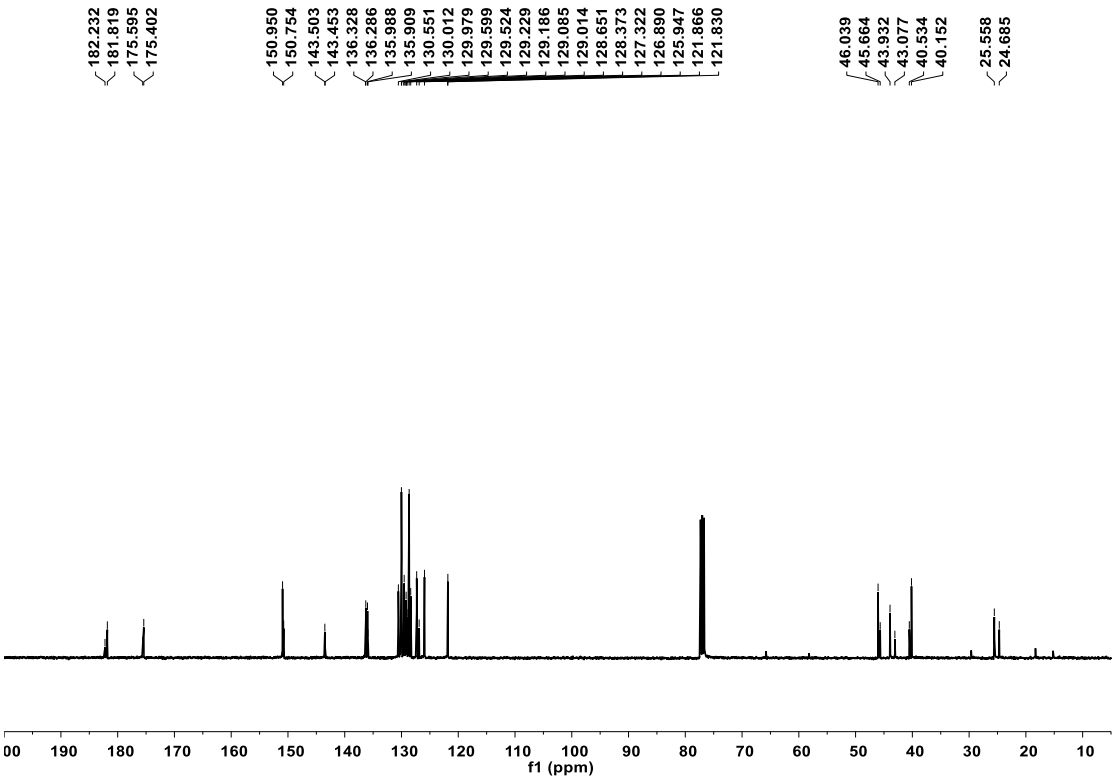


2g

^{1}H NMR

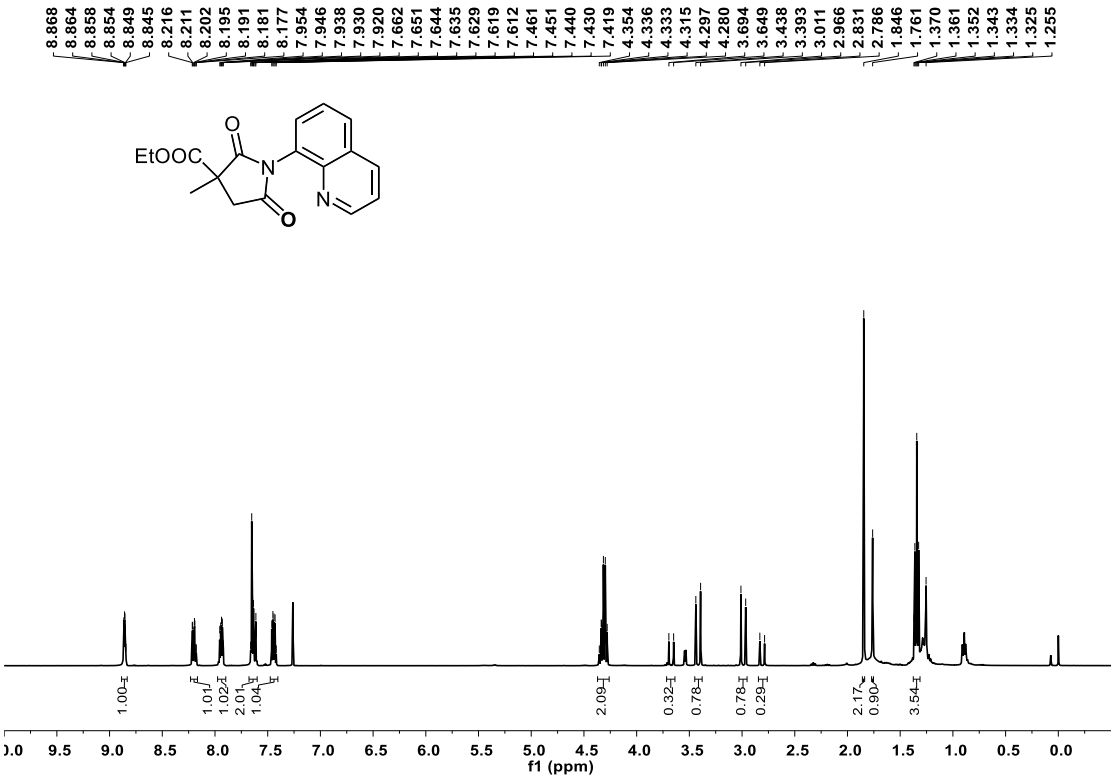


^{13}C NMR

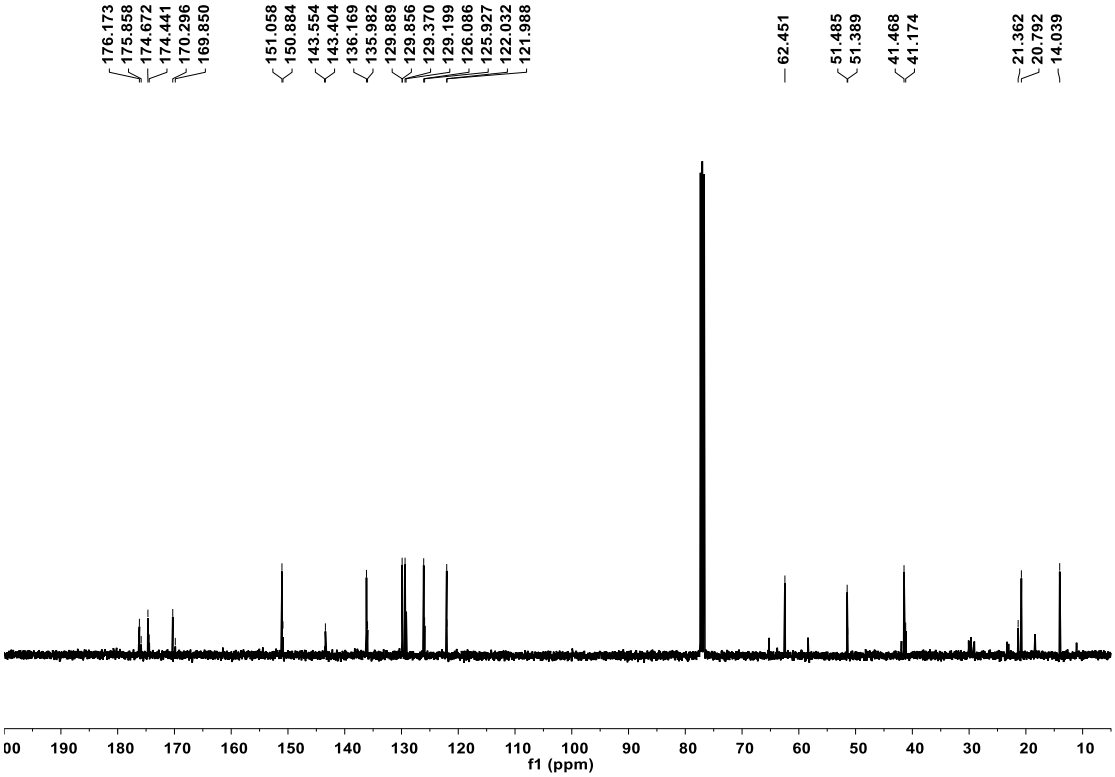


2h

^{1}H NMR

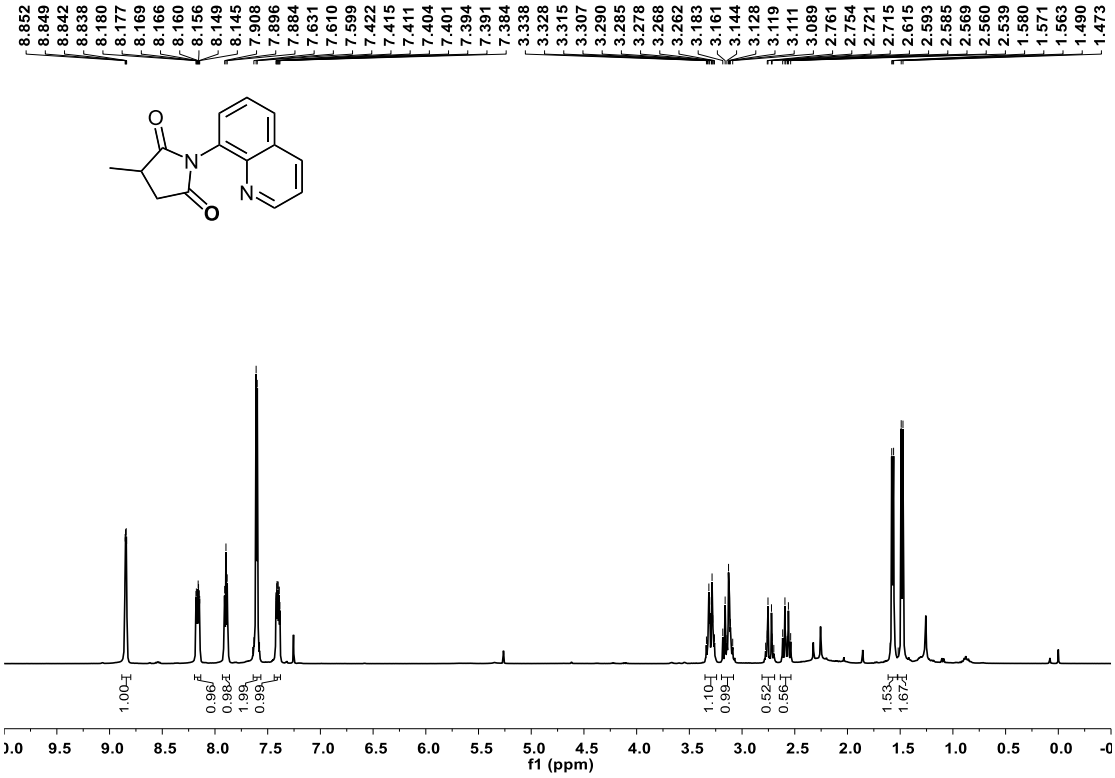


^{13}C NMR

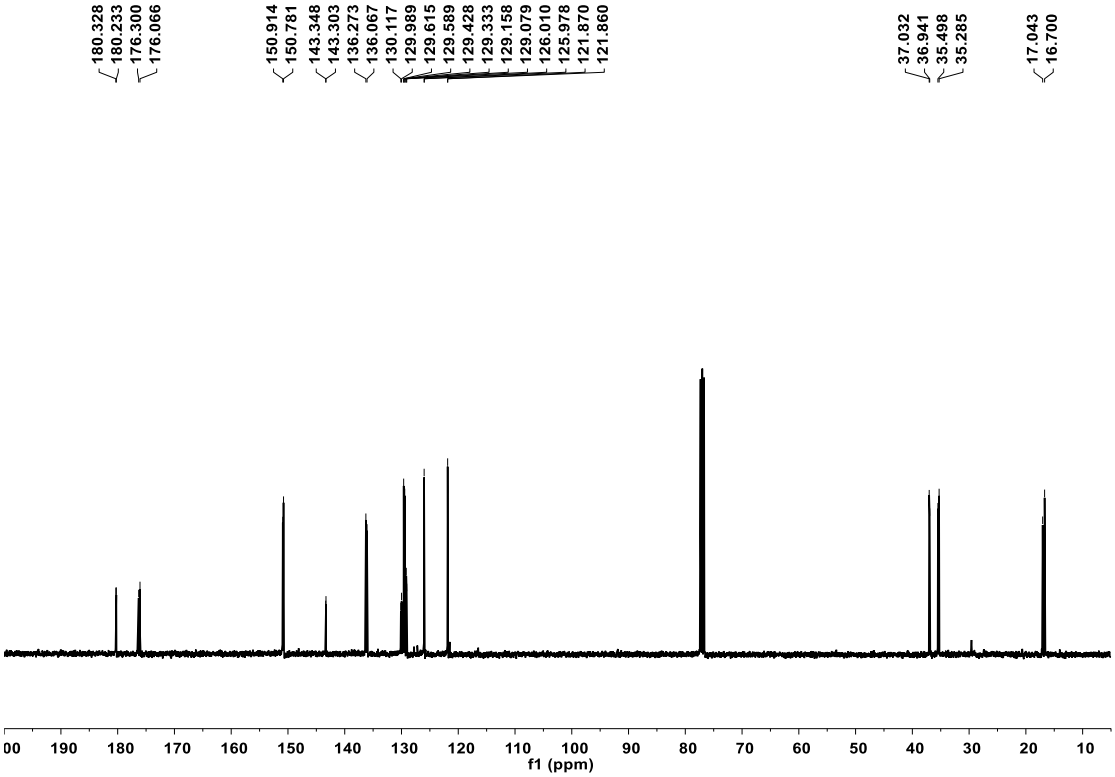


2i

H NMR

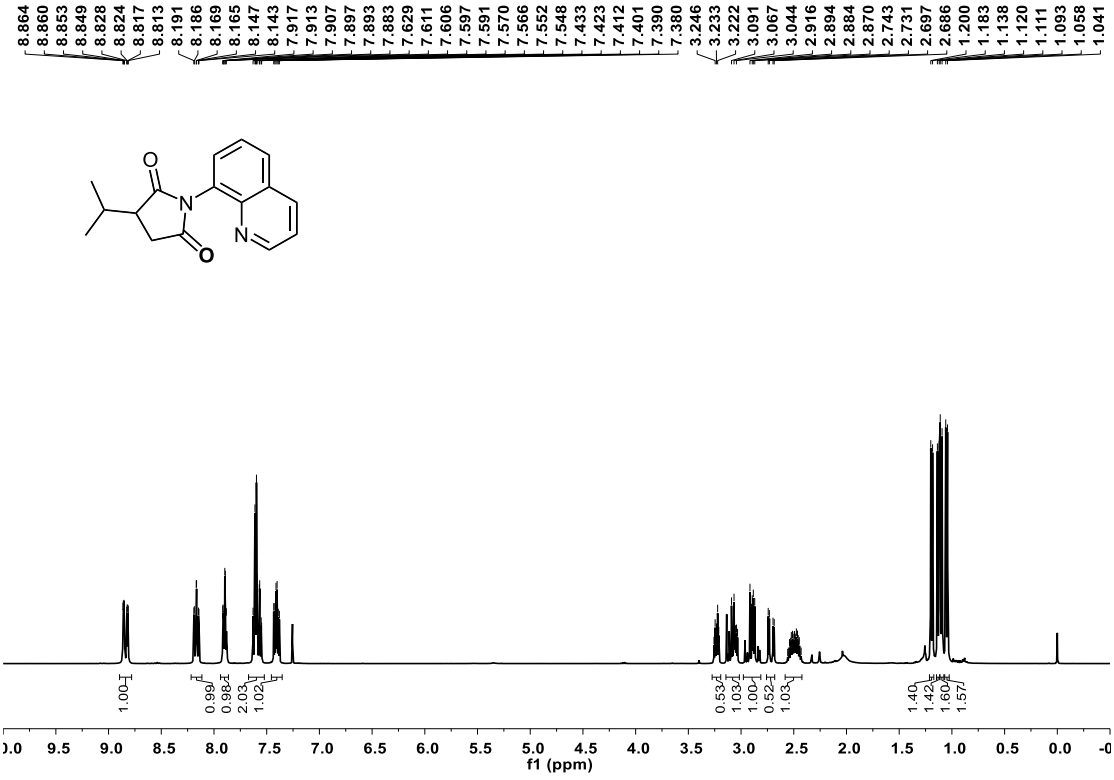


^{13}C NMR



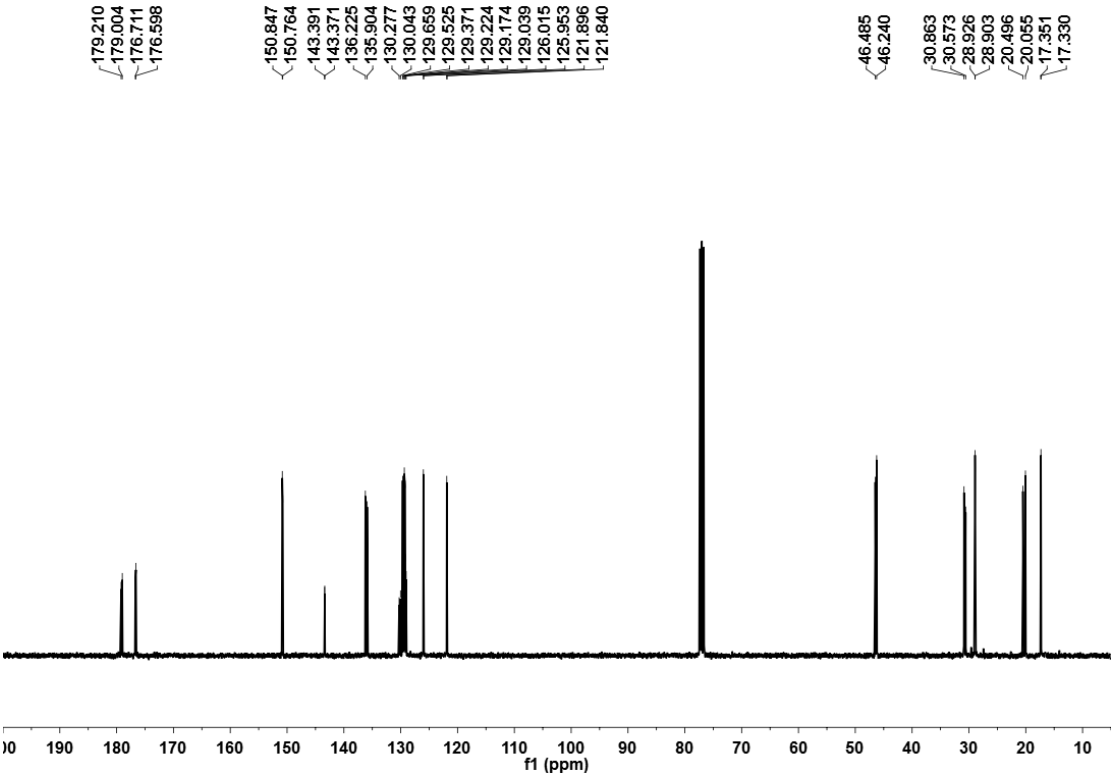
2j

^{1}H NMR



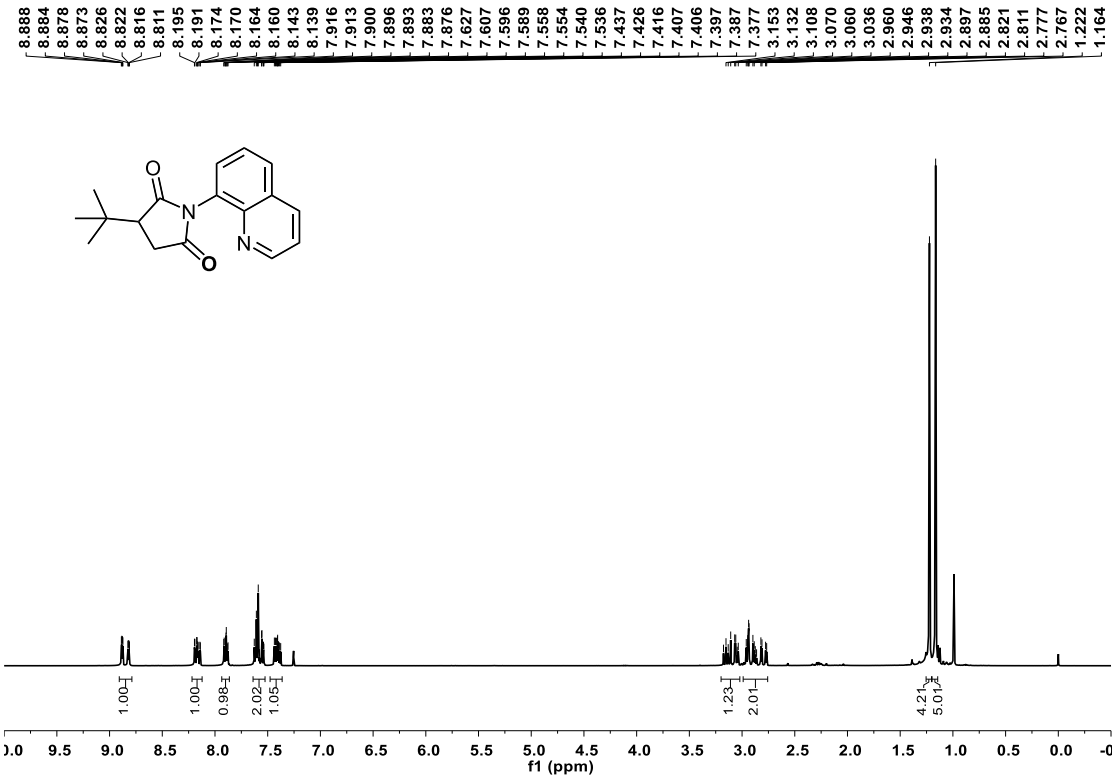
1: 1) 1

^{13}C NMR

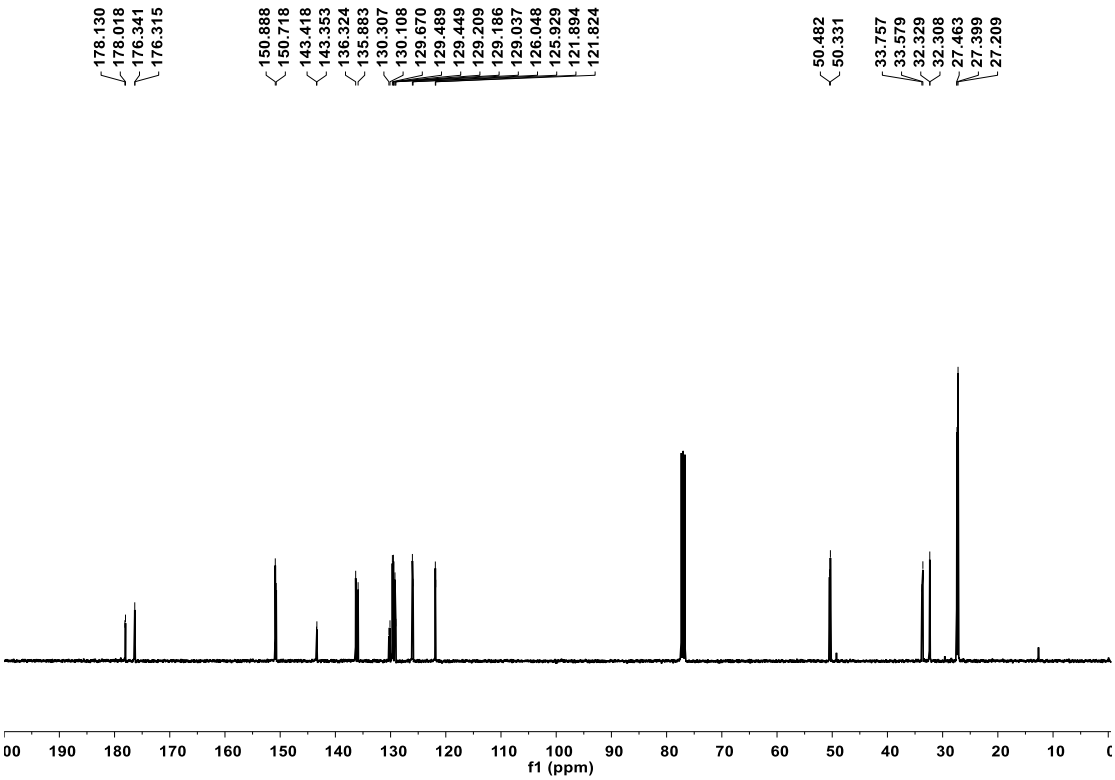


2k

^{1}H NMR

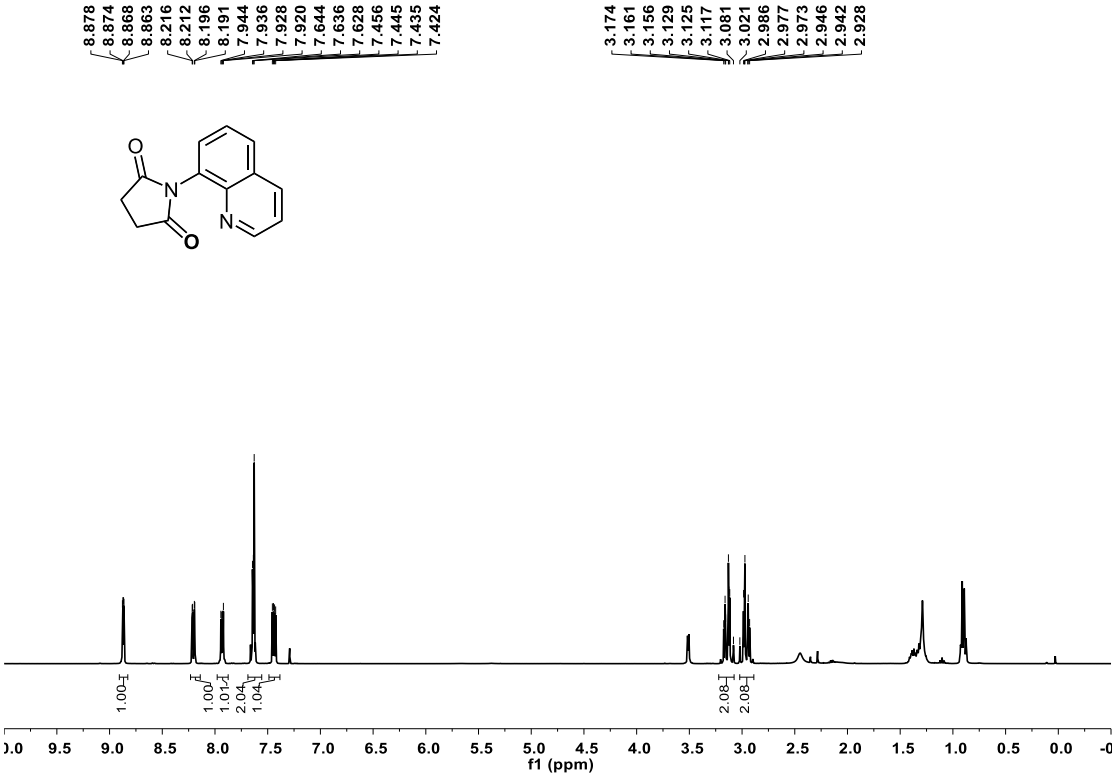


^{13}C NMR

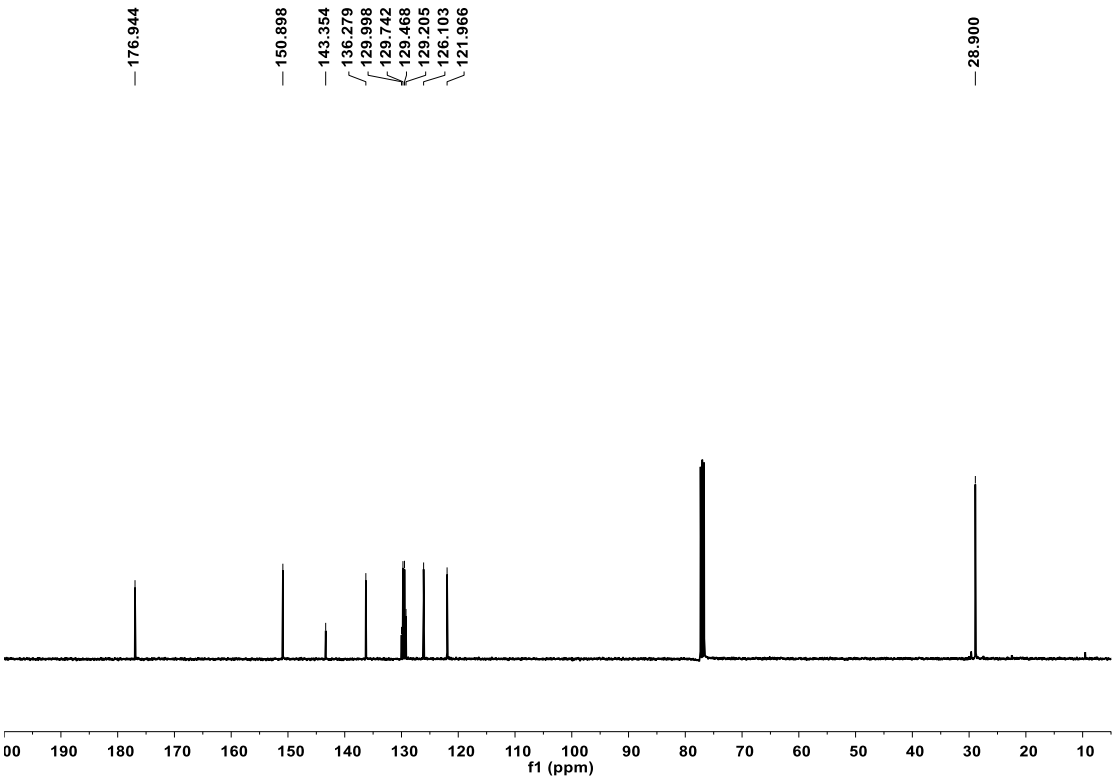


2l

^{1}H NMR

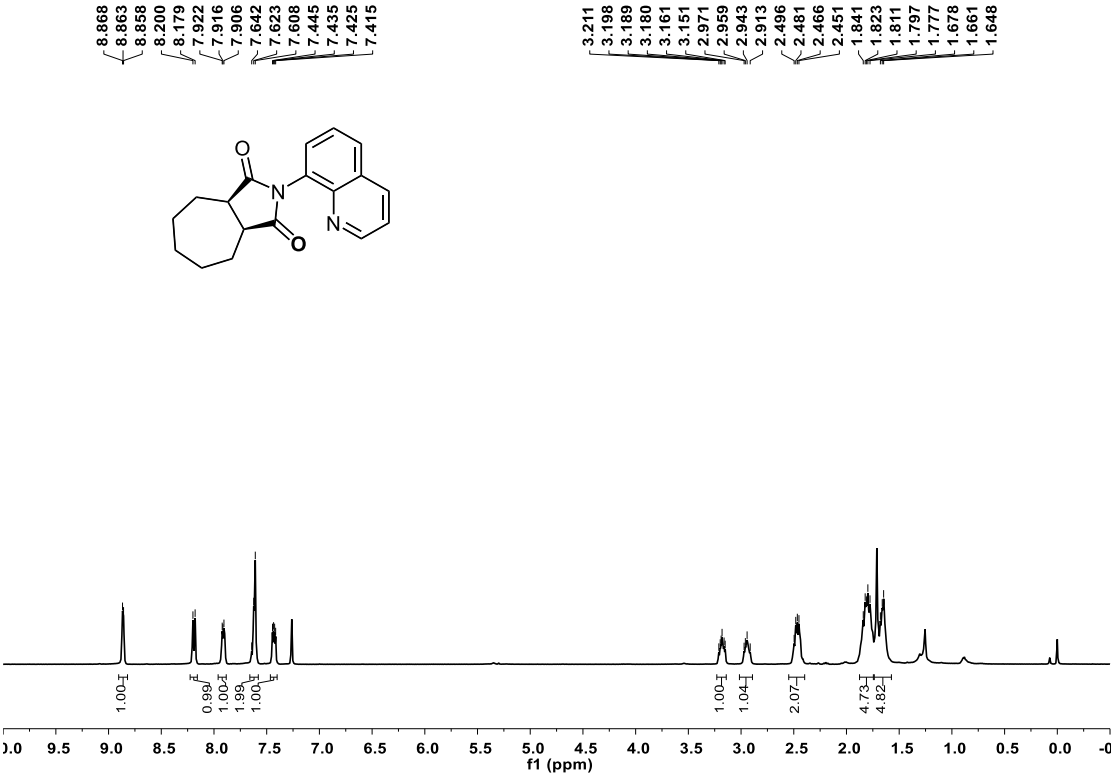


^{13}C NMR

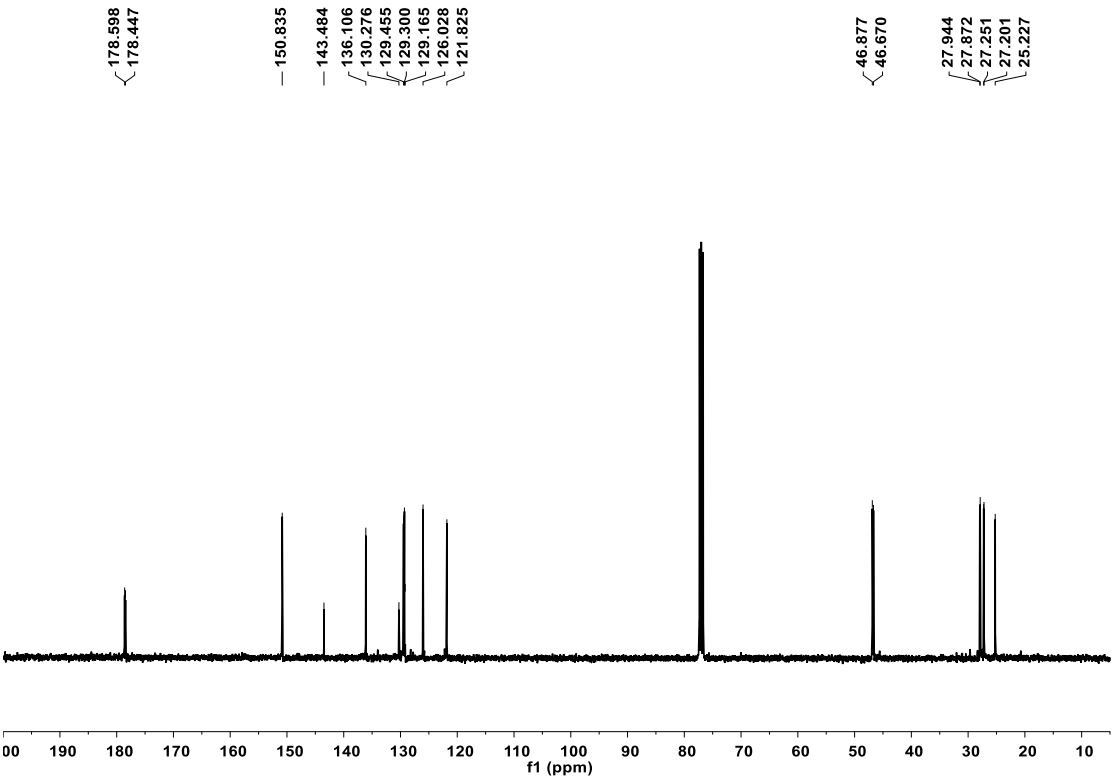


2m

^{1}H NMR

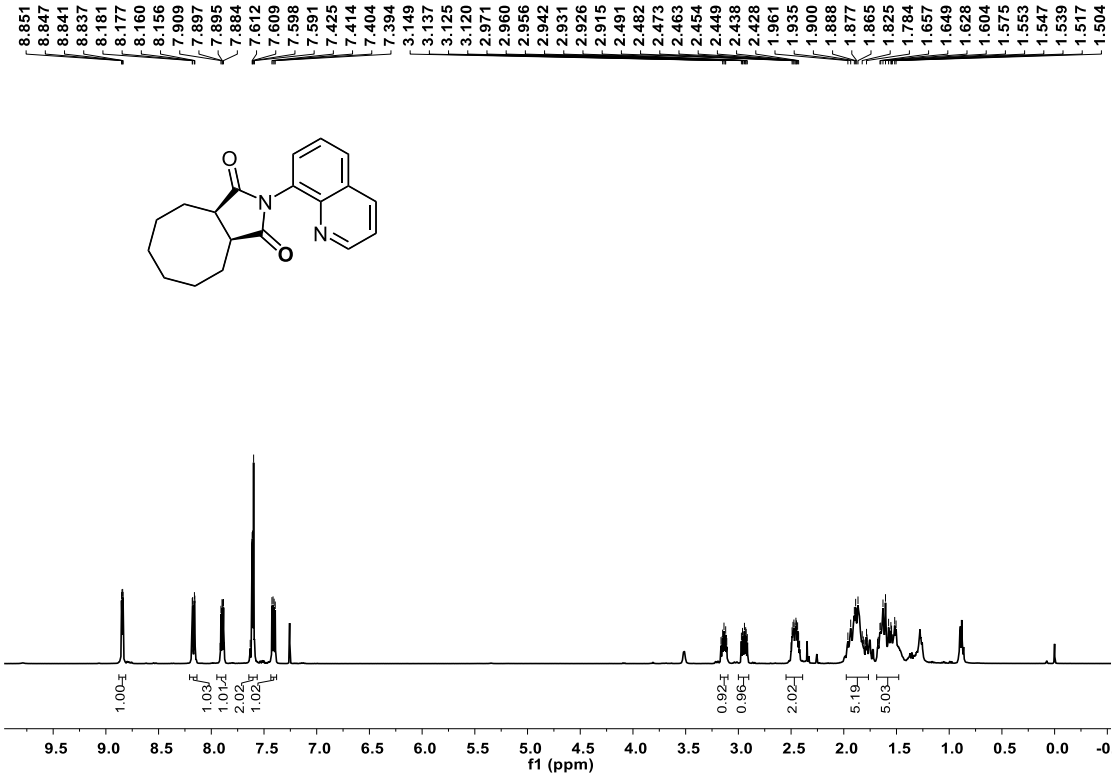


^{13}C NMR

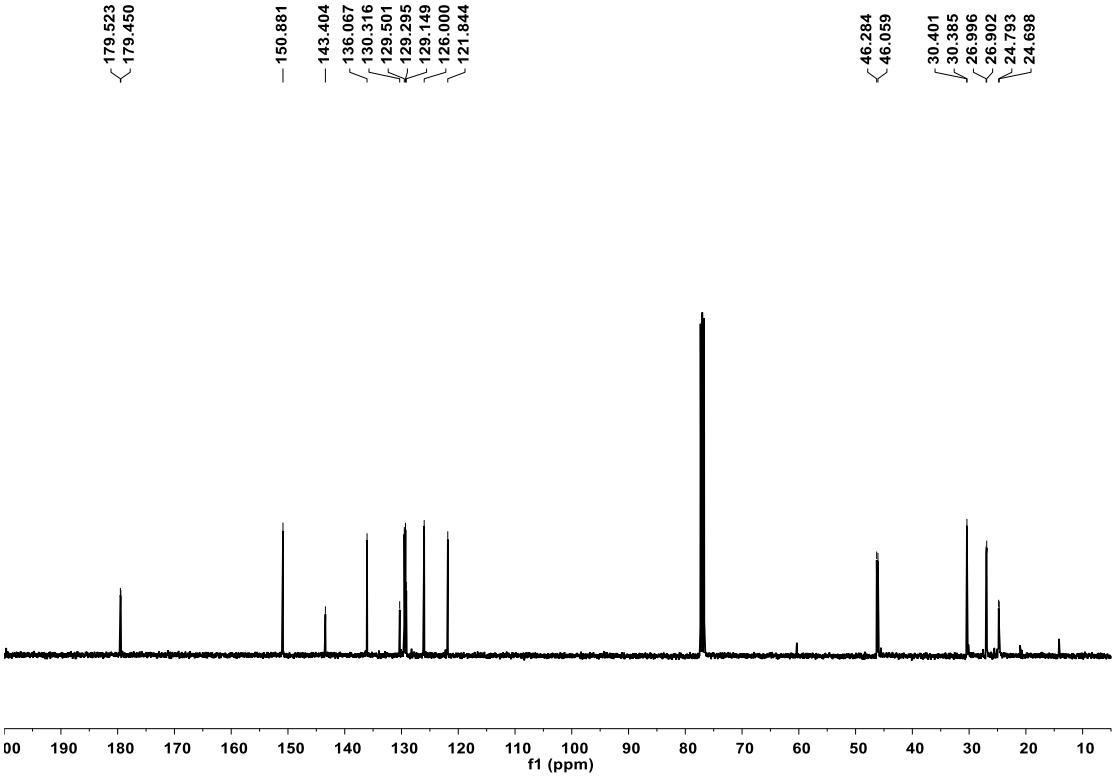


2n

^{1}H NMR

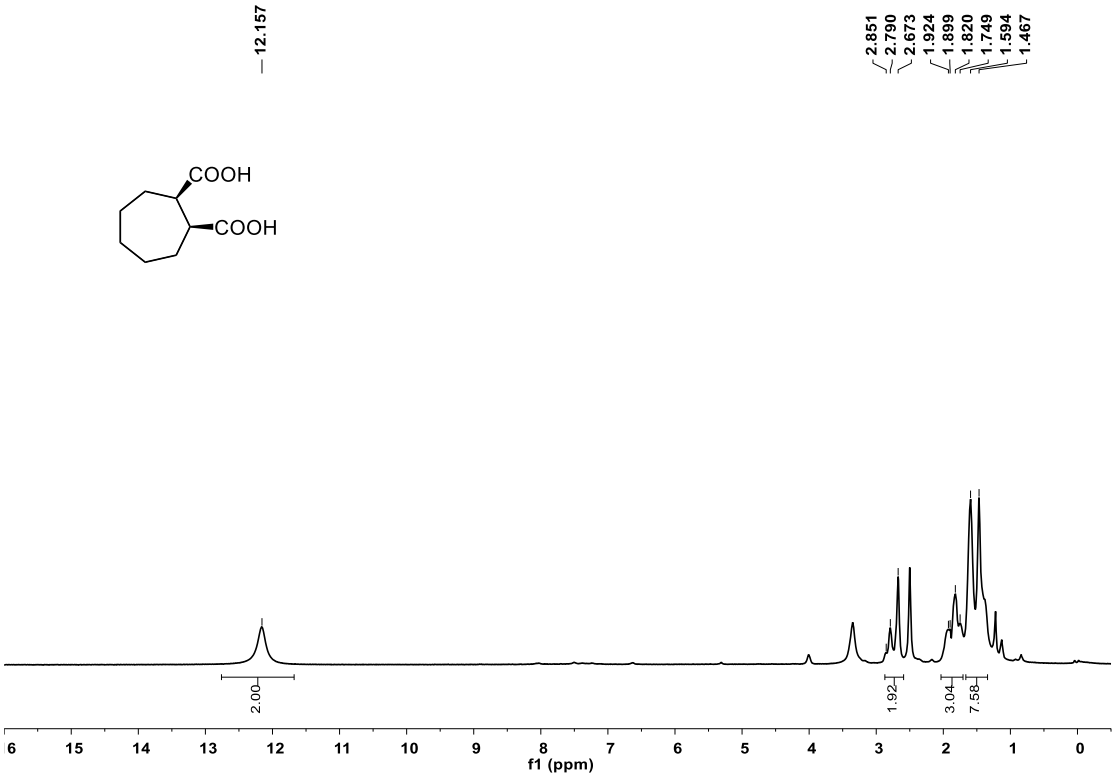


^{13}C NMR

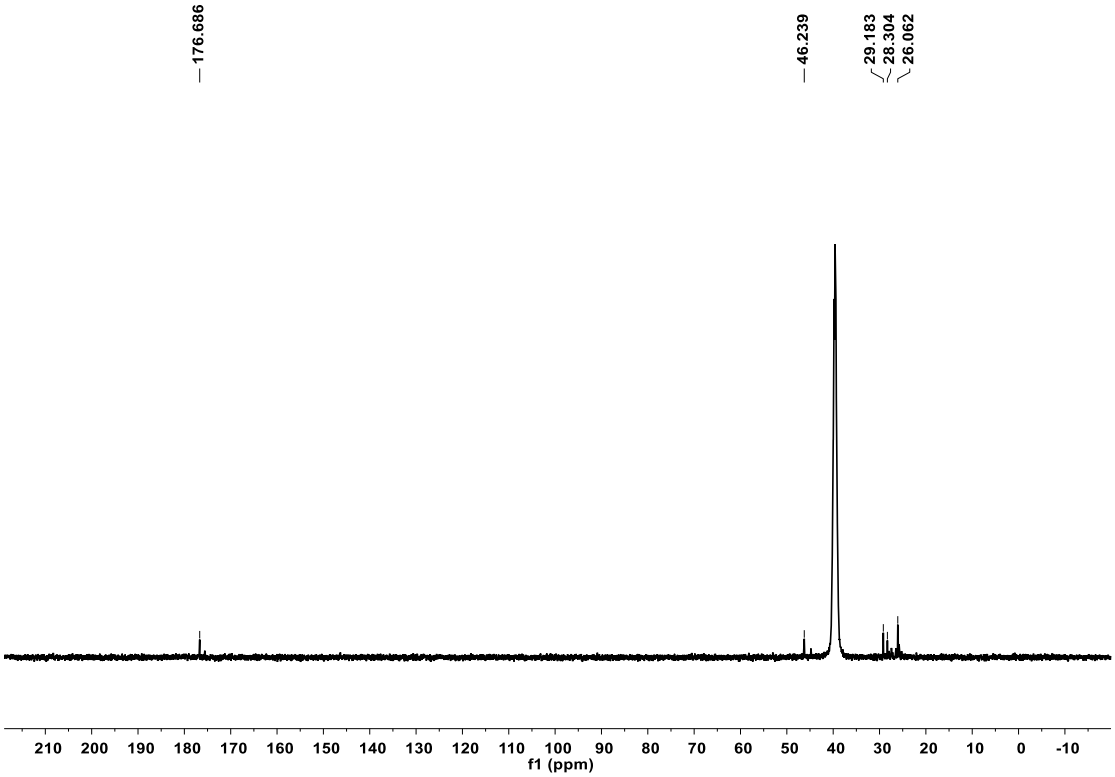


3m

^{1}H NMR

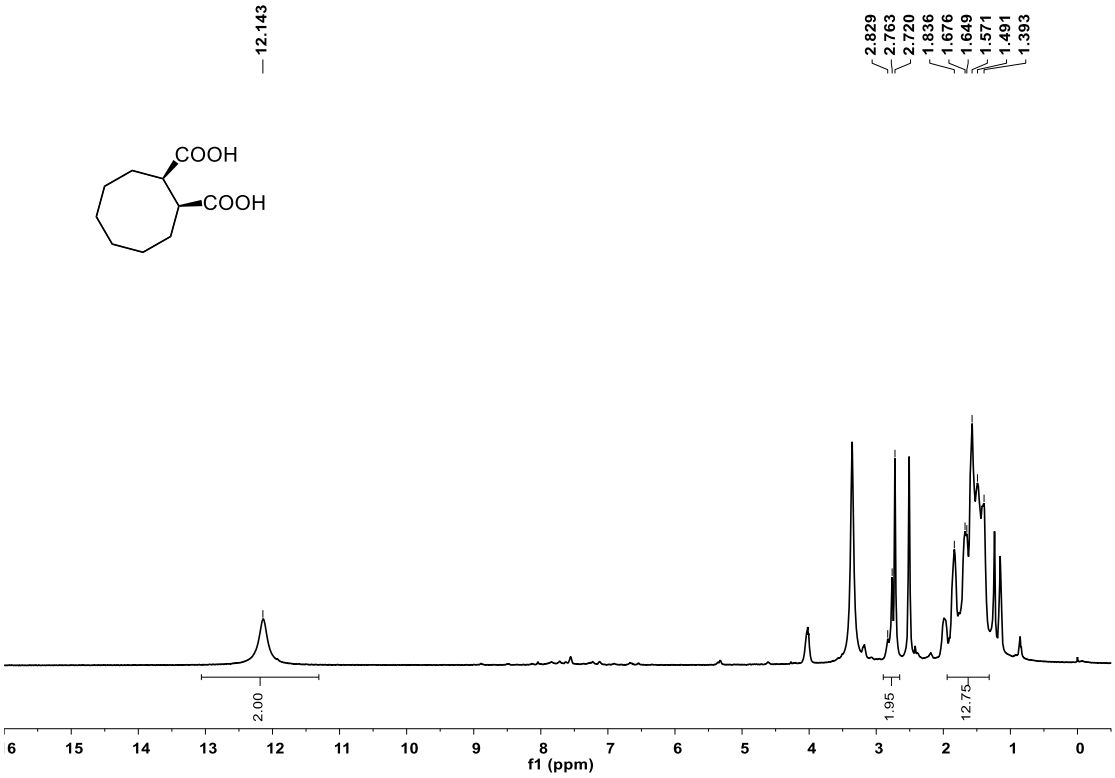


^{13}C NMR



3n

^{1}H NMR



^{13}C NMR