Electronic Supplementary Material (ESI) for RSC Advances

Supporting information

Cu(I)-Catalyzed Tandem Decarboxylative/C-H activation Coupling reaction of Cyclic diketone, proline and alkyne: Synthesis of α-alkynylated pyrrolidine-oxyindoles

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General Information: All the reagents and solvents were purchased from Sigma-Aldrich or Merck chemical Co. and were used directly without any further purification. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. The progress of reaction was checked by thin-layer chromatography. The plates were visualized first with UV illumination followed by iodine. ^{1}HNMR spectra were recorded at 200 or 300 MHz using Brucker DRX-200 or 300 spectrometer and are reported in parts per million (ppm) on the δ scale relative to tetramethylsilane as an internal standard. Coupling constants (J) reported in Hz. ^{13}CNMR spectra were recorded at 50 or 75 MHz. Mass spectra were obtained using JEOL SX-102 (ESI) instrument. Elemental analysis was performed using a Perkin-Elmer autosystem XL analyzer.

Typical Procedure for the Synthesis of α-alkynylated pyrrolidine-oxyindoles (4a-n): Typical procedure for the synthesis of α-alkynylated pyrrolidine-oxyindole **4a**, CuI (0.038 mg, 20 mol %) was added to a solution of proline (**2a**, 1.5 mmol, 0.173 mg) in acetinitrile (5 mL). The mixture was stirred for 10 min under nitrogen atmosphere at room temperature, and then isatin (**1a**, 1 mmol, 0.147 mg), and alkyne (**3a**, 2 mmol, 0.204 mg) was added to the reaction mixture and reaction was heated in a oil bath at 100 ^{0}C with stirring under nitrogen atmosphere until completion of reaction monitored through TLC. Upon completion (6-8 h) of the reaction, the mixture was then cooled to room temperature and filtered on celite. The filtrate was concentrated under reduced pressure to give the crude material, which was purified by column chromatography on silica gel (eluent: EtOAc/hexane), and afforded α-substituted pyrrolidine-oxyindole **4a-n** in good to excellent yield.

Typical Procedure for the Synthesis 6a-b: CuI (0.038 mg, 20 mol %) was added to a solution of proline (**2a**, 1.5 mmol, 0.173 mg) in acetinitrile (5 mL). The mixture was stirred for 10 min under nitrogen atmosphere at room temperature, and then added acenaphthylene-1,2-dione **5a** (1 mmol, 0.182 mg), and phenyl acetylene (**3a**, 2 mmol, 0.204 mg). The reaction was then heated at 100 ^{0}C in a oil bath with stirring under nitrogen atmosphere until completion of reaction monitored through TLC. Upon completion (6-8 h) of the reaction, the mixture was then cooled to room temperature and filtered on celite.

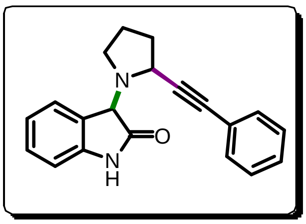
The filtrate was concentrated under reduced pressure to give the crude material, which was purified by column chromatography on silica gel (eluent: EtOAc/hexane), and afforded desired **6a-b** in good to excellent yield.

Typical Procedure for the Synthesis of 8a-c: CuI (0.038 mg, 20 mol %) was added to a solution of proline (**2a**, 1.5 mmol, 0.173 mg) in acetinitrile (5 mL). The mixture was stirred for 10 min under nitrogen atmosphere at room temperature, and then added aceanthrylene-1,2-dione **7a** (1 mmol, 0.232 mg), and phenyl acetylene (**3a**, 2 mmol, 0.204). The reaction was then heated in at 100 ^{0}C in a oil bath with stirring under nitrogen atmosphere until completion of reaction monitored through TLC. Upon completion (6-8 h) of the reaction, the mixture was then cooled to room temperature and filtered on celite. The filtrate was concentrated under reduced pressure to give the crude material, which was purified by column chromatography on silica gel (eluent: EtOAc/hexane), and afforded desired **8a-c** in good to excellent yield.

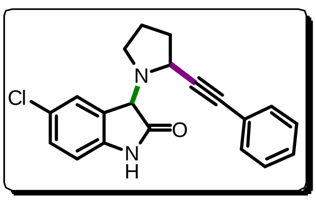
Typical Procedure for the Synthesis of 10: CuI (0.038 mg, 20 mol %) was added to a solution of proline (**2a**, 1.5 mmol, 0.173 mg) in acetinitrile (5 mL). The mixture was stirred for 10 min under nitrogen atmosphere at room temperature, and then added 1H-indene-1,2,3-trione **9a** (1 mmol, 0.160 mg), and phenyl acetylene (**3a**, 2 mmol, 0.204). The reaction was then heated in at 100 ^{0}C in a oil bath with stirring under nitrogen atmosphere until completion of reaction monitored through TLC. Upon completion (6-8 h) of the reaction, the mixture was then cooled to room temperature and filtered on celite. The filtrate was concentrated under reduced pressure to give the crude material, which was purified by column chromatography on silica gel (eluent: EtOAc/hexane), and afforded desired **10** in good to excellent yield.

Characterization Data of Synthesized compounds

3-(2-(Phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4a): Physical state: solid. **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.91-1.60 (m, 3H), 2.17-2.14 (m, 1H), 2.80 (t, *J* = 7.2 Hz, 2H), 4.80 (t, *J* = 7.1 Hz, 1H), 6.60 (s, 1H), 7.12-6.94 (m, 8H), 7.23 (d, *J* = 7.1 Hz, 1H), 9.34 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):** 26.5, 33.3, 48.5, 70.9, 79.2, 110.6, 113.6, 121.6, 125.6, 126.4, 127.1, 127.8, 129.2, 132.4, 132.8, 138.7, 139.4, 141.5, 181.1; **IR (KBr):** 3480, 2921, 3021, 2135, 1678 cm^{-1}; **ESI** MS (*m/z*): 303 $(M+H)^{+}$. Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26; Found: C, 79.48; H, 6.02; N, 9.22.

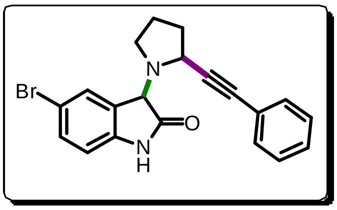


5-Chloro-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4b): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.60-150 (m, 1H), 1.86-1.82 (m, 2H), 2.11-2.04 (m, 1H), 2.69-2.64 (m, 2H), 4.66 (t, *J* = 6.9Hz, 1H), 6.52 (s, 1H), 6.87-6.81 (m, 2H), 7.08-6.96 (m, 2H), 7.15 (dd, *J* = 8.2Hz, 8.3Hz, 4H), 9.99 (s, 1H); **^{13}C**

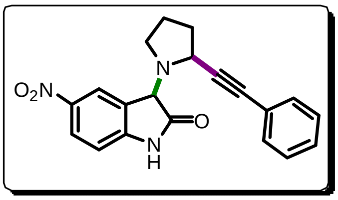


NMR (75 MHz, $CDCl_3$) δ (ppm): 28.9, 31.0, 48.2, 70.6, 111.3, 125.5, 125.7, 126.1, 127.3, 128.0, 128.4, 129.2, 132.8, 133.0, 138.5, 138.9, 141.4, 178.6; **IR (KBr):** 3440, 2910, 3034, 2201, 1680 cm^{-1}; **ESI** MS (*m/z*): 337 $(M+H)^+$. Anal. Calcd. for $C_{20}H_{17}ClN_2O$: C, 71.32; H, 5.09; N, 8.32; Found: C, 71.34; H, 5.07; N, 8.33.

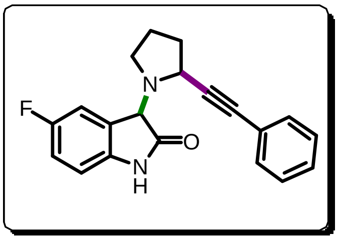
5-Bromo-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4c): Physical state: solid; **^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ* (ppm):** 0.85-0.55 (m, 2H), 1.39-1.22 (m, 4H), 3.23 (t, *J* = 7.2Hz, 1H), 5.51 (s, 1H), 5.66 (d, *J* = 8.2Hz, 1H), 5.77-5.75 (m, 1H), 5.84 (s, 1H), 5.95 (d, *J* = 5.9Hz, 3H), 6.22 (dd, *J* = 8.2Hz, 8.2Hz, 1H), 9.36 (s, 1H); **^{13}C NMR (50 MHz, DMSO-*d*$_6$) δ (ppm):** 26.1, 30.3, 47.8, 70.3, 77.6, 111.6, 112.5, 125.1, 127.1, 127.9, 128.5, 128.6, 132.0, 132.7, 133.2, 138.0, 141.6, 177.7; **IR (KBr):** 3390, 2919, 3019, 2224, 1665 cm^{-1}; **ESI** MS (*m/z*): 381 $(M+H)^+$. Anal. Calcd. for $C_{20}H_{17}BrN_2O$: C, 63.00; H, 4.49; N, 7.35; Found: C, 63.05; H, 4.43; N, 7.36.



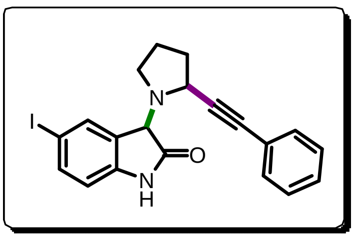
5-Nitro-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4d): Physical state: solid; **^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ* (ppm):** 0.58-0.36 (m, 3H), 0.86 (br, s, 1H), 1.65-1.60 (m, 2H), 3.29 (br, s, 1H), 5.59-5.58 (br, s, 1H), 5.77 (t, *J* = 2.6Hz, 2H), 5.96 (t, *J* = 6.4Hz, 4H), 6.51 (br, s, 1H), 7.03-6.99 (m, 1H), 10.03 (s, 1H); **^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ (ppm):** 26.6, 30.8, 48.6, 70.9, 77.8, 110.5, 121.6, 125.6, 127.2, 127.5, 127.7, 128.6, 133.0, 134.5, 138.1, 141.9, 149.3, 179.0; **IR (KBr):** 3460, 2930, 3034, 2205, 1666 cm^{-1}; **ESI** MS (*m/z*): 348 $(M+H)^+$. Anal. Calcd. for $C_{20}H_{17}N_3O_3$: C, 69.15; H, 4.93; N, 12.10; Found: C, 69.18; H, 4.89; N, 12.12.



5-Fluoro-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4e): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.96-1.88 (m, 2H), 2.22-2.12 (m, 2H), 2.78 (t, *J* = 6.6Hz, 2H), 4.77 (t, *J* = 6.7Hz, 1H), 6.60 (br, 1H), 6.76 (dd, *J* = 7.7Hz, 7.6Hz, 1H), 6.89-6.85 (m, 1H), 6.96 (dd, *J* = 8.9Hz, 8.8Hz, 1H), 7.05 (t, J = 3.3Hz, 2H), 7.16 (t, *J* = 3.6Hz, 3H), 8.82 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm):** 26.6, 31.0, 48.2, 70.7, 110.6, 110.7, 113.6, 113.9, 115.5, 115.8, 125.8, 127.2, 128.0, 128.2, 128.3, 132.8, 133.2, 138.7, 139.1, 156.0, 159.2, 178.9; **IR (KBr):** 3455, 2940, 3025, 2230, 1670 cm^{-1}; **ESI MS** (*m/z*): 321 $(M+H)^+$. Anal. Calcd. for $C_{20}H_{17}FN_2O$: C, 74.98; H, 5.35; N, 8.74; Found: C, 74.99; H, 5.38; N, 8.71.

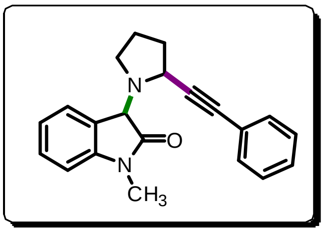


5-Iodo-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4f): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.66-1.56 (m, 2H), 1.96-1.88 (m, 1H), 2.19-2.12 (m, 1H), 2.75-2.70 (m, 2H), 4.75 (t, *J* = 7.2Hz, 1H), 6.60 (br, s, 1H), 6.75 (d, *J* = 8.2Hz, 1H), 7.03-7.00 (m, 2H), 7.17-7.15 (m, 4H), 7.57 (dd, *J* = 8.7Hz, 8.1Hz, 1H), 9.04 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm):** 27.2, 31.8,

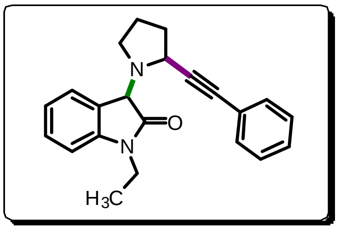


48.9, 71.6, 84.9, 113.1, 126.1, 127.8, 128.5, 129.5, 132.9, 133.2, 135.3, 138.5, 139.4, 141.5, 181.0; **IR (KBr):** 3477, 2920, 3045, 2209, 1675 cm^{-1}; **ESI MS** (*m/z*): 429 $(M+H)^{+}$. Anal. Calcd. for $C_{20}H_{17}IN_2O$: C, 56.09; H, 4.00; N, 6.54; Found: C, 56.15; H, 4.01; N, 6.52.

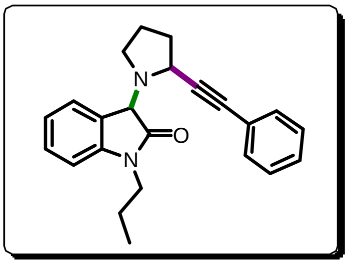
1-Methyl-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4g): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 1.61-1.54 (m, 1H), 1.81 (br, s, 2H), 2.73 (t, *J* = 7.4Hz, 2H), 3.19 (s, 3H), 4.73 (br, s, 1H), 6.44 (s, 1H), 6.81 (br, 3H), 7.02-6.87 (m, 5H), 7.27-7.20 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):** 10.5, 19.7, 26.4, 28.9, 31.0, 41.0, 48.0, 70.7, 78.3, 108.0, 121.1, 125.6, 125.8, 126.2, 126.7, 127.3, 128.7, 132.1, 132.9, 139.7, 143.3, 177.2; **IR (KBr):** 3465, 2921, 3020, 2200, 1680 cm^{-1}; **ESI MS** (*m/z*): 317 $(M+H)^{+}$. Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85; Found: C, 79.74; H, 6.33; N, 8.86.



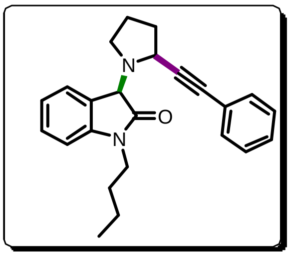
1-Ethyl-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4h): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 1.36 (t, *J* = 6.9Hz, 3H), 1.59-1.50 (m, 1H), 1.80-1.70 (m, 2H), 2.09-2.04 (m, 1H), 2.69-2.63 (m, 2H) 3.84 (q, *J* = 6.8Hz, 2H), 4.69 (t, *J* = 6.4Hz, 1H), 6.51 (br, s, 1H),6.95-6.84 (m, 5H), 7.18-7.01 (m, 4H); **IR (KBr):** 3463, 2919, 3021, 2205, 1678 cm^{-1}; **ESI MS** (*m/z*): 331 $(M+H)^{+}$. Anal. Calcd. for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48; Found: C, 79.99; H, 6.69; N, 8.49.



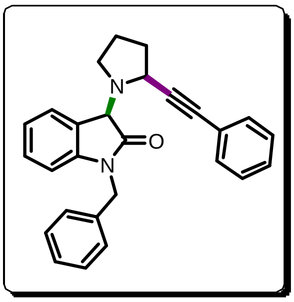
3-(2-(Phenylethynyl)pyrrolidin-1-yl)-1-propylindolin-2-one (4i): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 0.94 (t, *J* = 7.4Hz, 3H), 1.72-1.63 (m, 3H), 1.88-1.84 (m, 2H), 2.15-2.07 (m, 1H), 2.74-2.68 (m, 2H), 3.79-3.57 (m, 2H), 4.75 (t, *J* = 7.1 Hz, 1H), 6.49 (s, 1H), 6.86 (d, *J* = 8.7Hz, 1H), 6.92-6.90 (m, 2H), 7.07-6.95 (m, 5H), 7.30-7.26 (m, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):** 10.5, 19.7, 26.4, 28.9, 31.0, 41.0, 48.0, 70.7, 78.3, 108.0, 121.1, 125.6, 125.8, 126.2, 126.7, 127.3, 128.7, 132.1, 132.9, 139.7, 143.3, 177.2; **IR (KBr):** 3440, 2910, 3027, 2225, 1677 cm^{-1}; **ESI MS** (*m/z*): 345 $(M+H)^{+}$. Anal. Calcd. for $C_{23}H_{24}N_2O$: C, 80.20; H, 7.02; N, 8.13; Found: C, 80.23; H, 7.01; N, 8.12.



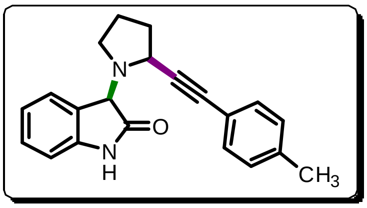
1-Butyl-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4j): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 0.88 (t, *J* = 7.3 Hz, 1H), 1.31-1.22 (m, 2H), 1.61-1.56 (m, 3H), 1.85 (d, *J* = 6.2Hz, 2H), 2.13-2.08 (m, 1H), 2.73 (br, s, 2H), 3.65-3.55 (m, 1H), 3.76-3.69 (m, 1H), 4.76 (br, s, 1H), 6.42 (br, s, 1H), 6.86-6.80 (m, 3H), 6.91 (d, *J* = 6.9Hz, 1H), 7.02-6.95 (m, 4H), 7.24-7.19 (m, 1H); **IR (KBr):** 3420, 2930, 3019, 2229, 1681 cm^{-1}; **ESI MS** (*m/z*): 359 $(M+H)^{+}$. Anal. Calcd. for $C_{24}H_{26}N_2O$: C, 80.41; H, 7.31; N, 7.81; Found: C, 80.44; H, 7.29; N, 7.82.



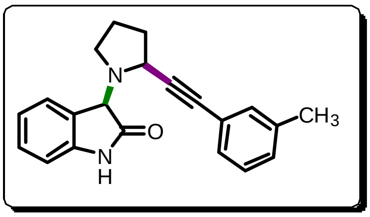
1-Benzyl-3-(2-(phenylethynyl)pyrrolidin-1-yl)indolin-2-one (4k): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.64-1.52 (m, 1H), 1.85 (br, s, 2H), 2.12-2.10 (m, 1H), 2.74 (d, *J* = 6.5Hz, 2H), 4.70 (d, *J* = 15.5Hz, 1H), 5.09 (d, *J* = 15.6Hz, 1H), 6.46 (s, 1H), 6.69 (d, *J* = 7.6Hz, 1H), 6.82 (d, *J* = 7.3Hz, 2H), 6.91 (t, *J* = 7.4Hz, 1H), 6.99-6.94 (m, 3H), 7.05 (d, *J* = 6.8Hz, 1H), 7.19-7.10 (m, 7H); **IR (KBr):** 3427, 2950, 3015, 2220, 1672 cm^{-1}; **ESI MS** (*m/z*): 393 $(M+H)^+$. Anal. Calcd. for $C_{27}H_{24}N_2O$: C, 82.62; H, 6.16; N, 7.14; Found: C, 82.64; H, 6.13; N, 7.12.



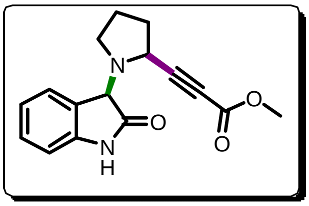
3-(2-(*p*-Tolylethynyl)pyrrolidin-1-yl)indolin-2-one (4l): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.93-1.79 (m, 4H), 2.21 (s, 3H), 2.79-2.74 (m, 2H), 4.78 (t, *J* = 8.0Hz, 1H), 6.54 (br, s, 1H), 7.00-6.91 (m, 7H), 7.25-7.20 (m, 1H), 9.07 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm):** 20.3, 26.3, 31.1, 48.2, 70.7, 78.8, 110.3, 121.3, 125.3, 126.1, 126.2, 128.3, 128.8, 129.7, 131.2, 136.6, 139.1, 141.2, 180.5; **IR (KBr):** 3455, 2960, 3054, 2264, 1676 cm^{-1}; **ESI MS** (*m/z*): 317 $(M+H)^+$. Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85; Found: C, 79.74; H, 6.34; N, 8.83.



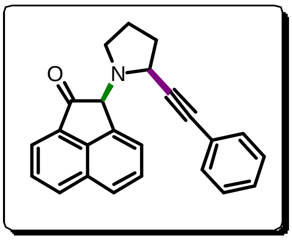
3-(2-(*m*-Tolylethynyl)pyrrolidin-1-yl)indolin-2-one (4m): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.90-1.72 (m, 4H), 2.24 (s, 3H), 2.80-2.73 (m, 2H), 4.77 (t, *J* = 8.1Hz, 1H), 6.51 (br, s, 1H), 7.03-6.94 (m, 6H), 7.28-7.19 (m, 1H), 7.75 (s, 1H), 9.09 (s, 1H); **IR (KBr):** 3458, 2970, 3025, 2245, 1679 cm^{-1}; **ESI MS** (*m/z*): 317 $(M+H)^+$. Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85; Found: C, 79.73; H, 6.34; N, 8.84.



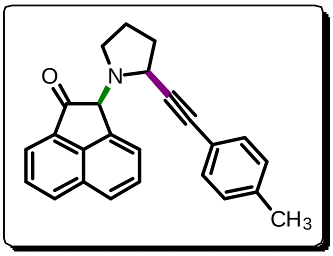
Methyl 3-(1-(2-oxoindolin-3-yl)pyrrolidin-2-yl)propiolate (4n): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 2.24-1.80 (m, 4H), 2.67 (t, *J* = 6.6Hz, 2H), 3.47 (s, 3H), 4.66 (t, *J* = 7.3Hz, 1H), 6.94-6.83 (m, 3H), 7.19-7.14 (m, 2H), 8.35 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm):** 22.0, 30.6, 31.2, 47.6, 51.0, 71.6, 110.1, 121.2, 125.2, 125.8, 129.1, 133.4, 141.5, 146.0, 161.9, 179.5; **IR (KBr):** 3480, 2967, 3025, 2325, 1723, 1680 cm^{-1}; **ESI MS** (*m/z*): 285 $(M+H)^+$. Anal. Calcd. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85; Found: C, 67.62; H, 5.69; N, 9.83.



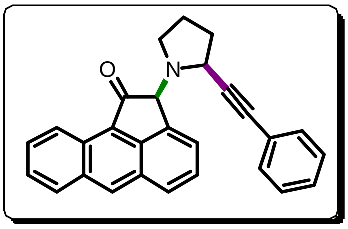
2-(2-(Phenylethynyl)pyrrolidin-1-yl)acenaphthylen-1(2*H*)-one (6a): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.78-1.61 (m, 4H), 2.46 (br, s, 1H), 2.65 (br, s, 1H), 4.76 (br, s, 1H), 6.55 (s, 1H), 6.72 (d, *J* = 7.1Hz, 1H), 6.94-6.85 (m, 3H), 7.23 (t, *J* = 6.9Hz, 1H), 7.51 (t, *J* = 8.1Hz, 1H), 7.74 (t, *J* = 7.6Hz, 1H), 7.84 (d, *J* = 8.2Hz, 1H), 8.06-8.02 (m, 2H); **IR (KBr):** 3029, 2980, 2201, 1720 cm^{-1}; **ESI MS** (*m/z*): 338 $(M+H)^+$. Anal. Calcd. for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15; Found: C, 85.46; H, 5.66; N, 4.12.



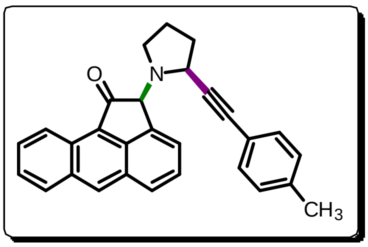
2-(2-(*p*-Tolylethynyl)pyrrolidin-1-yl)acenaphthylen-1(2*H*)-one (6b): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.81-1.67 (m, 4H), 2.12 (s, 3H), 2.46-2.35 (m, 1H), 2.66-2.61 (m, 1H), 4.77 (br, 1H), 6.58 (s, 1H), 6.68 (d, *J* = 7.8Hz, 2H), 6.76 (d, *J* = 7.8Hz, 2H), 7.29 (br, 1H), 7.58 (t, *J* = 7.3Hz, 1H), 7.79 (t, *J* = 7.6Hz, 1H), 7.89 (d, *J* = 8.4Hz, 1H), 8.14 (dd, *J* = 8.2Hz, 6.7Hz, 2H); **^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm):** 20.1, 21.8, 25.7, 28.8, 30.4, 31.1, 32.9, 49.0, 69.8, 81.8, 113.2, 122.0, 122.6, 124.5, 125.3, 127.2, 127.4, 127.9, 130.0, 130.1, 130.5, 131.4, 131.7, 135.3, 136.2, 138.4, 139.1, 141.6, 202.1; **IR (KBr):** 3030, 2970, 2265, 1718 cm^{-1}; **ESI MS** (*m/z*): 352 $(M+H)^{+}$. Anal. Calcd. for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99; Found: C, 85.48; H, 6.01; N, 3.94.



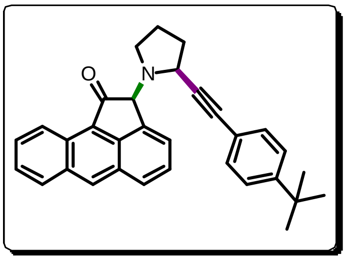
2-(2-(Phenylethynyl)pyrrolidin-1-yl)aceanthrylen-1(2*H*)-one (8a): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.82-1.60 (m, 3H), 2.15-2.08 (m, 1H), 2.45-2.40 (m, 1H), 2.69-2.61 (m, 1H), 4.79 (t, *J* = 6.6Hz, 1H), 6.61 (s, 1H), 6.91-6.76 (m, 5H), 7.47 (t, *J* = 8.4Hz, 1H), 7.61 (t, *J* = 7.5Hz, 1H), 7.72 (t, *J* = 7.5Hz, 1H), 7.93 (d, *J* = 8.6Hz, 1H), 8.13 (d, *J* = 8.4Hz, 1H), 8.65 (s, 1H), 9.21 (d, *J* = 8.6Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm):** 26.6, 31.4, 50.1, 70.9, 83.0, 123.0, 125.3, 125.6, 125.7, 126.3, 126.7, 127.3, 128.2, 128.6, 129.1, 129.4, 132.4, 133.6, 133.7, 134.0, 136.5, 140.3, 203.5; **IR (KBr):** 3031, 2975, 2260, 1721 cm^{-1}; **ESI MS** (*m/z*): 388 $(M+H)^{+}$. Anal. Calcd. for $C_{28}H_{21}NO$: C, 86.79; H, 5.46; N, 3.61; Found: C, 86.81; H, 5.44; N, 3.59.



2-(2-(*p*-Tolylethynyl)pyrrolidin-1-yl)aceanthrylen-1(2*H*)-one (8b): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.86-1.69 (m, 3H), 2.07 (s, 3H) 2.19-2.14 (m, 1H), 2.50-2.45 (m, 1H), 2.73-2.65 (m, 1H), 4.83 (t, *J* = 7.2Hz, 1H), 6.62 (s, 1H), 6.73 (t, *J* = 8.8Hz, 4H), 7.24 (d, *J* = 4.6Hz, 1H), 7.53 (t, *J* = 8.4Hz, 1H), 7.65 (t, *J* = 7.4Hz, 1H), 7.76 (t, *J* = 7.8Hz, 1H), 7.98 (d, *J* = 8.6Hz, 1H), 8.18 (d, *J* = 8.4Hz, 1H), 8.70 (s, 1H), 9.25 (d, *J* = 8.5Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm):** 20.2, 25.8, 28.9, 30.6, 49.2, 70.2, 82.2, 122.2, 124.5, 124.7, 124.9, 125.3, 125.8, 126.5, 127.8, 128.0, 128.2, 128.4, 130.3, 131.5, 131.9, 132.8, 135.8, 136.2, 139.3, 143.7, 202.8; **IR (KBr):** 3032, 2960, 2255, 1719 cm^{-1}; **ESI MS** (*m/z*): 402 $(M+H)^{+}$. Anal. Calcd. for $C_{29}H_{23}NO$: C, 86.75; H, 5.77; N, 3.49; Found: C, 86.78; H, 5.74; N, 3.48.

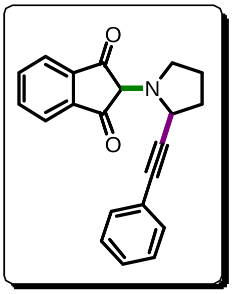


2-(2-((4-(Tert-butyl)phenyl)ethynyl)pyrrolidin-1-yl)aceanthrylen-1(2*H*)-one(8c): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) *δ* (ppm):** 1.10 (s, 9H), 1.88-1.74 (m, 3H), 2.19-2.13 (m, 1H), 2.52-2.47 (m, 1H), 2.69 (t, *J* = 8.4Hz, 1H), 4.83 (t, *J* = 7.5Hz, 1H), 6.68 (s, 1H), 6.77 (d, *J* = 8.3Hz, 2H), 6.93 (d, *J* = 8.3Hz, 2H), 7.30 (t, *J* = 6.6Hz, 1H), 7.56 (d, *J* = 6.8Hz, 1H), 7.67 (d, *J* = 7.6Hz, 1H), 7.78 (d, *J* = 7.9Hz, 1H), 8.01 (d, *J* = 8.6Hz, 1H), 8.20 (d, *J* = 8.4Hz, 1H), 8.73 (s, 1H), 9.26 (d, *J* = 8.5Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) *δ* (ppm):** 25.5, 29.9, 30.4, 33.2,



48.7, 69.8, 81.6, 121.8, 123.9, 124.2, 124.4, 124.5, 124.6, 125.5, 126.2, 127.5, 127.8, 128.0, 129.6, 131.2, 131.5, 132.4, 135.5, 138.7, 143.3, 149.1, 202.5; **IR (KBr):** 3018, 2960, 2265, 1723 cm^{-1}; **ESI MS** (*m/z*): 444 $(M+H)^+$. Anal. Calcd. for $C_{32}H_{29}NO$: C, 86.65; H, 6.59; N, 3.16; Found: C, 86.68; H, 6.58; N, 3.14.

2-(2-(Phenylethynyl)pyrrolidin-1-yl)-1*H*-indene-1,3(2*H*)-dione(10a): Physical state: solid; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 2.29-2.12 (m, 2H), 2.70 (t, *J* = 8.3Hz, 3H), 3.34-3.26 (m, 1H), 5.93 (s, 1H), 6.58 (s, 1H), 7.24-7.19 (m, 2H), 7.35 (d, *J* = 7.2Hz, 2H), 7.45 (t, *J* = 7.3Hz, 2H), 7.51 (d, *J* = 7.3Hz, 1H), 7.60 (t, *J* = 7.1Hz, 1H), 7.91 (t, *J* = 7.4Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):** 22.9, 26.5, 44.8, 99.4, 115.0, 122.4, 124.6, 125.6, 126.0, 127.7, 127.9, 128.6, 132.2, 133.4, 135.4, 138.7, 147.3, 169.5; **IR (KBr):** 3040, 2961, 2280, 1722 cm^{-1}; **ESI MS** (*m/z*): 316 $(M+H)^+$. Anal. Calcd. for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44; Found: C, 79.99; H, 5.41; N, 4.41.



Spectral data (1H NMR and 13C NMR) of all the synthesised compounds.

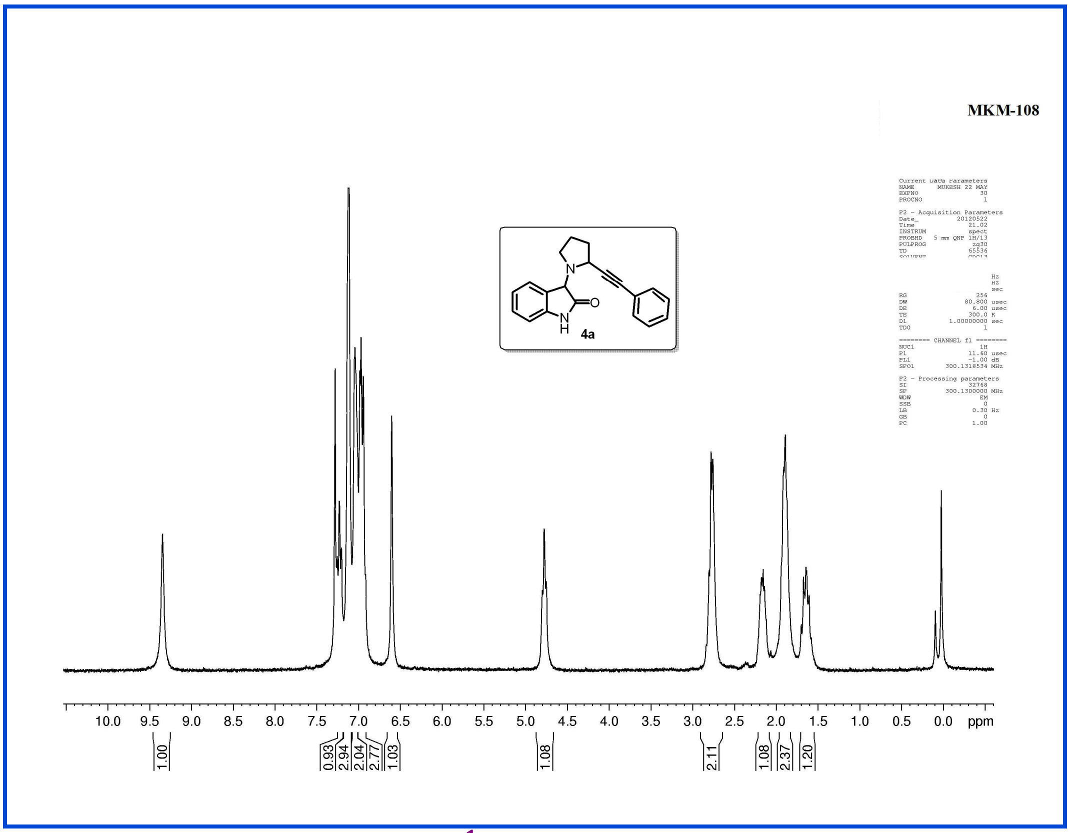


Figure 1. ^{1}H Spectrum of 4a

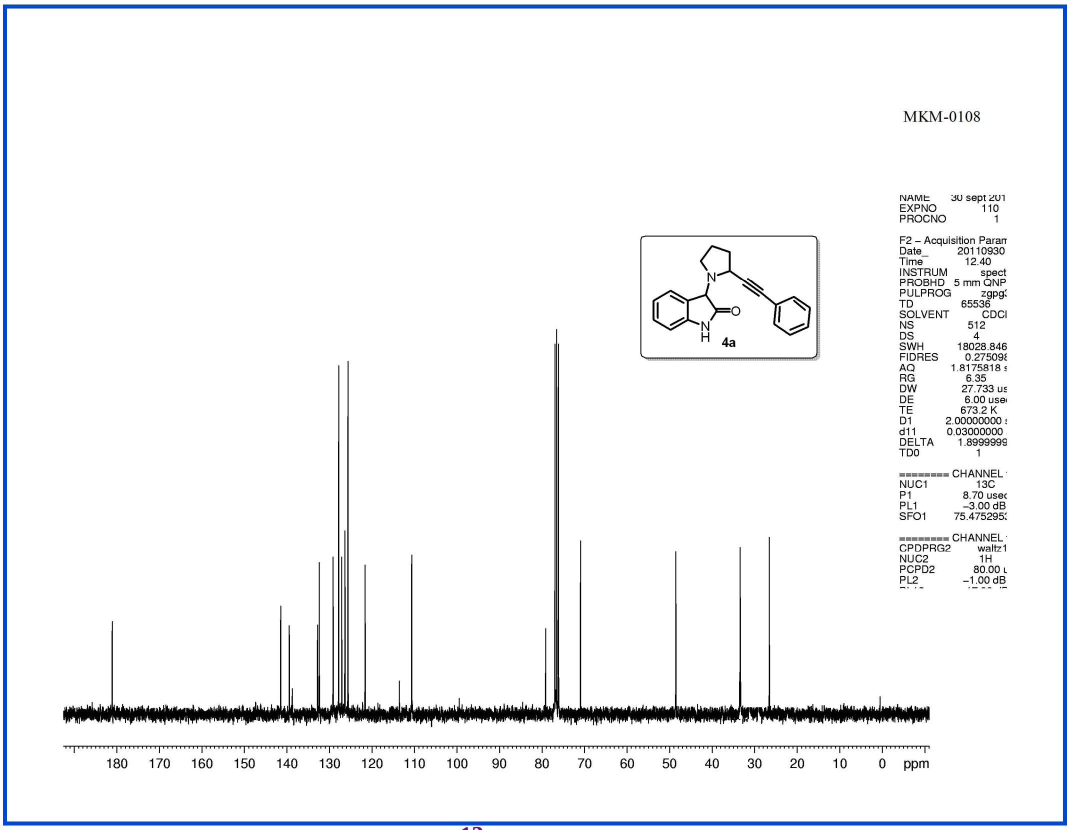


Figure 2. ^{13}C **Spectrum of 4a**

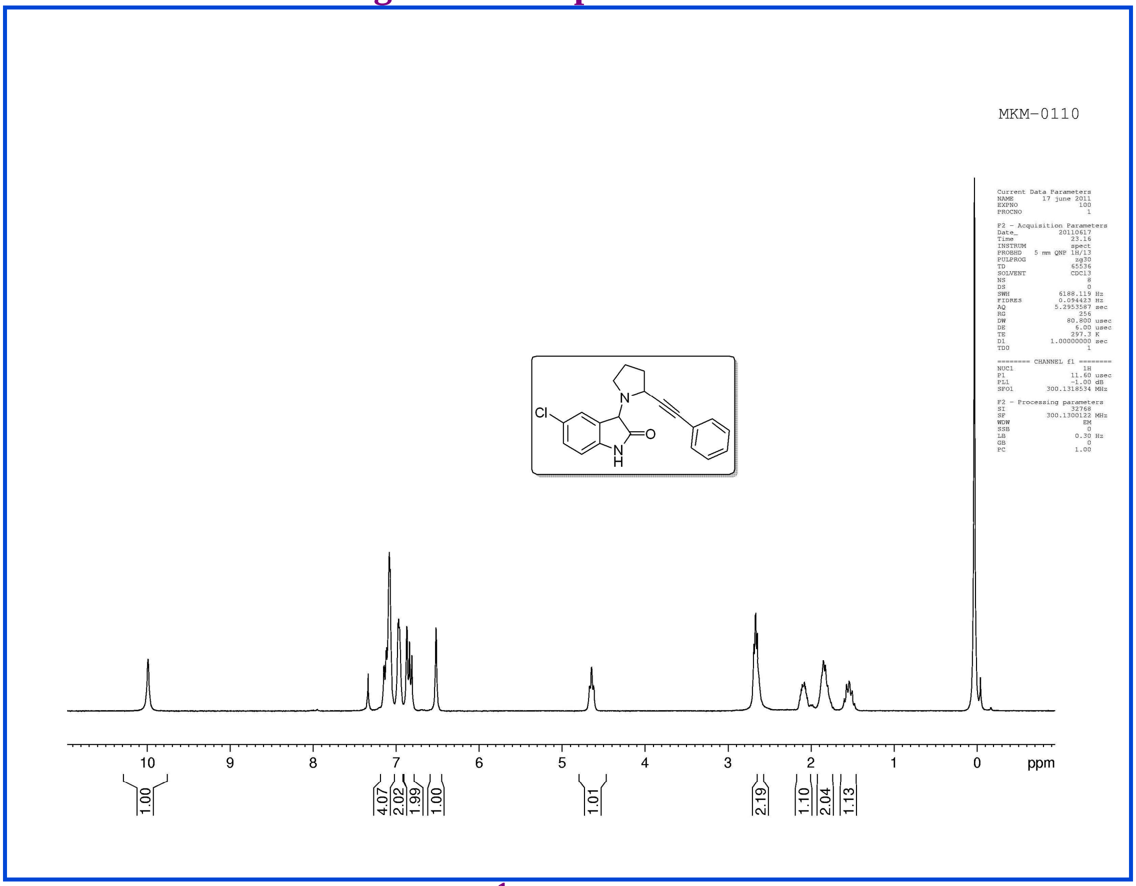


Figure 3. ^{1}H **Spectrum of 4b**

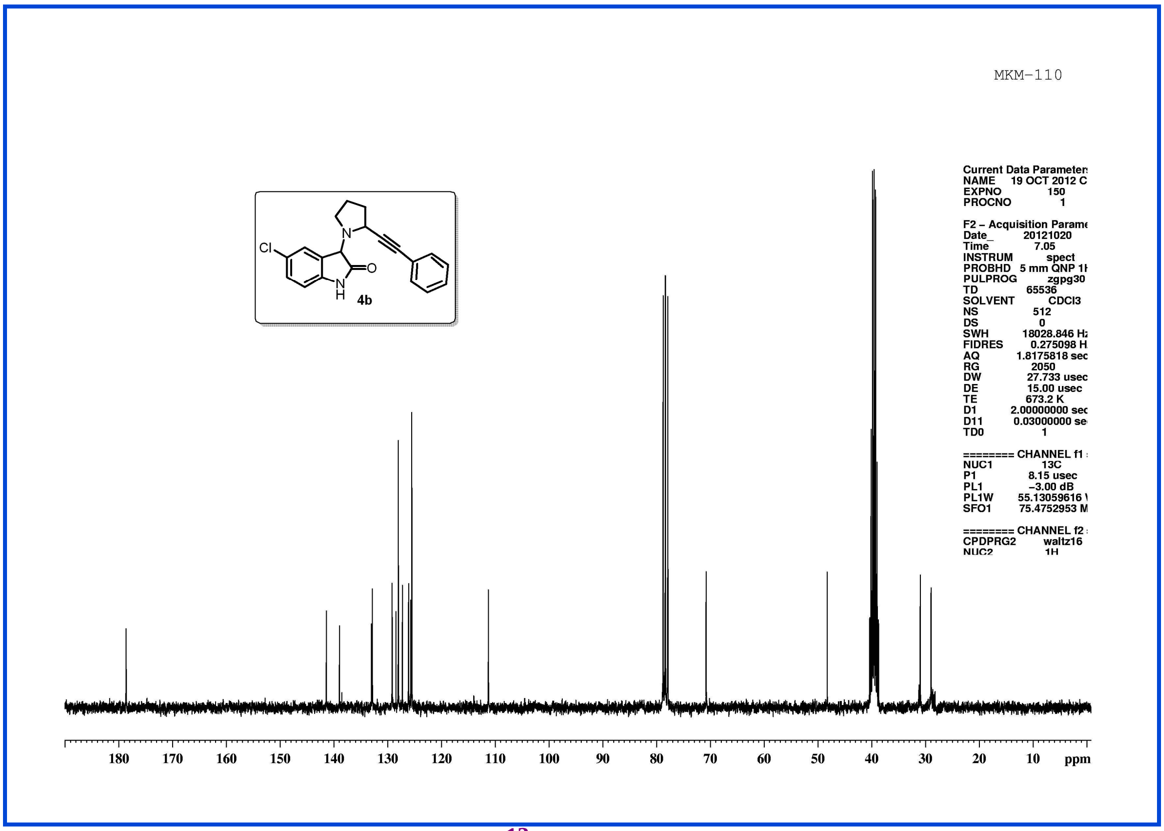


Figure 4. ^{13}C Spectrum of 4b

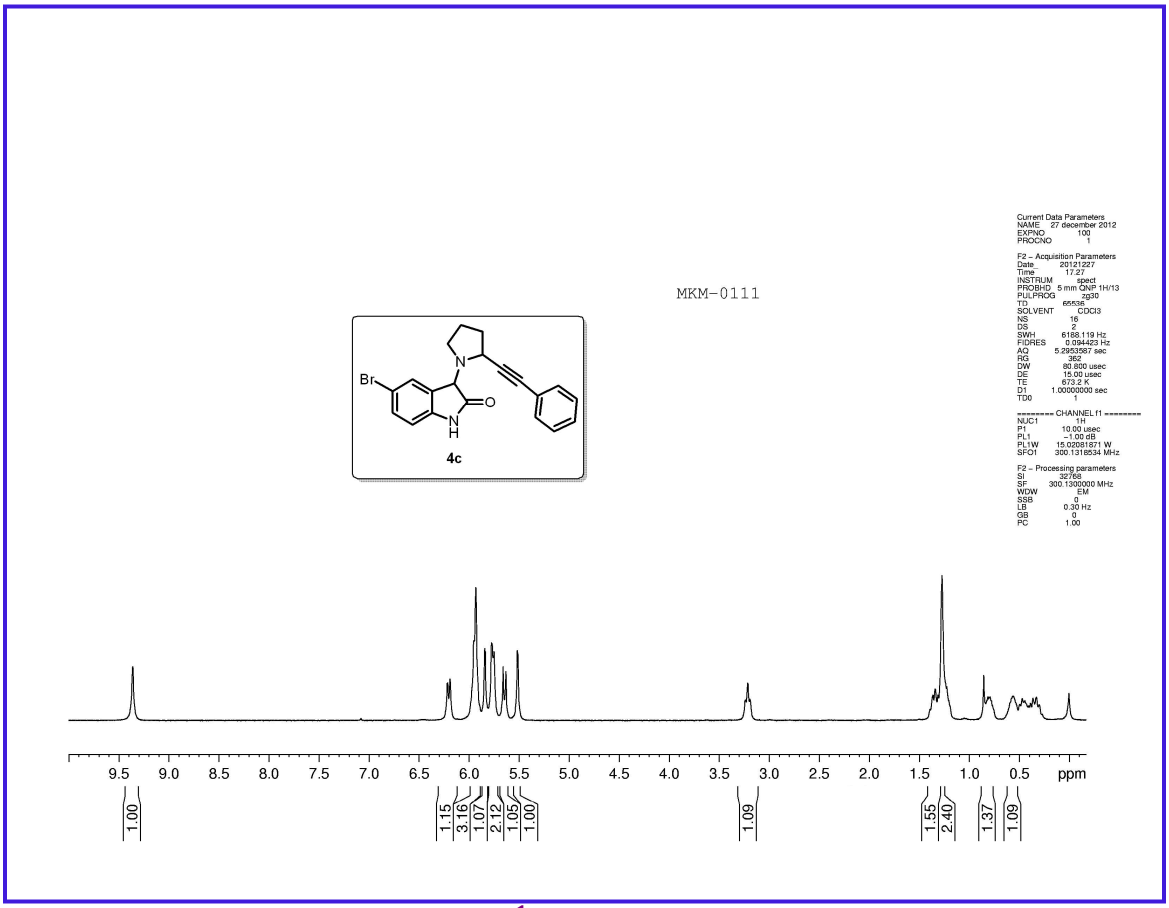


Figure 5. ^{1}H Spectrum of 4c

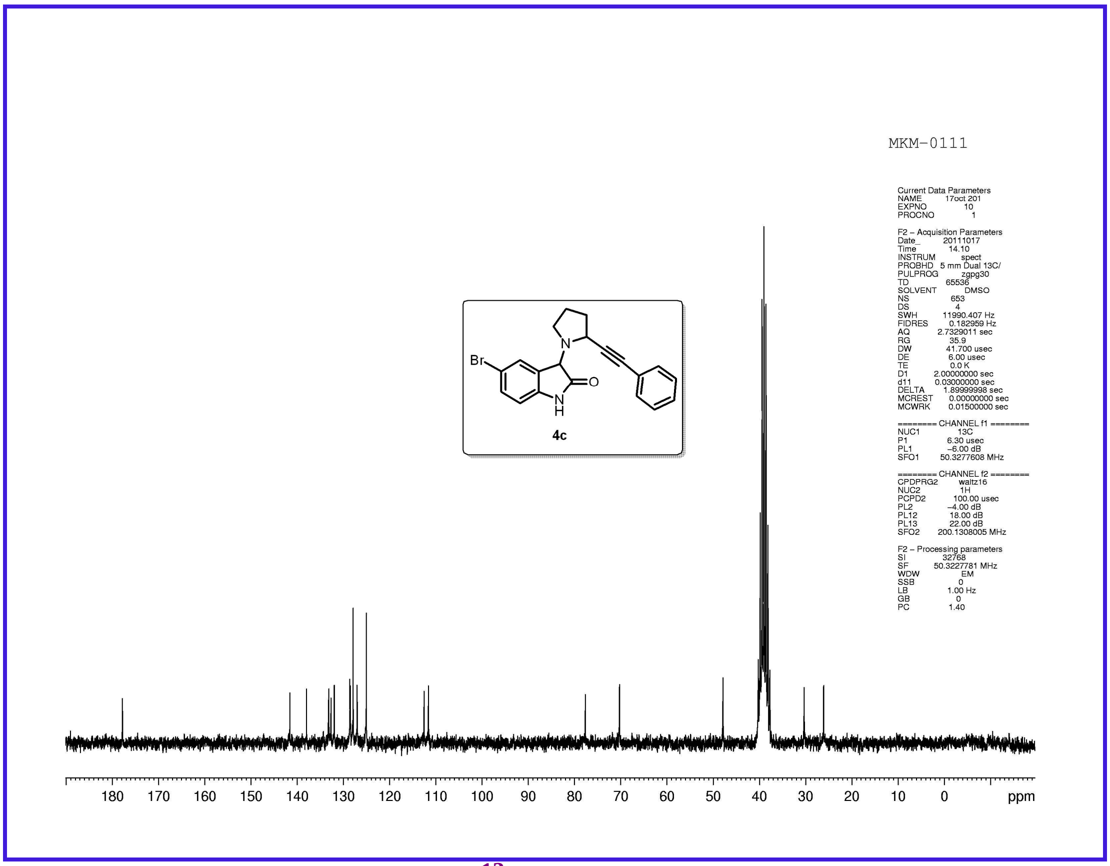


Figure 6. ^{13}C Spectrum of 4c

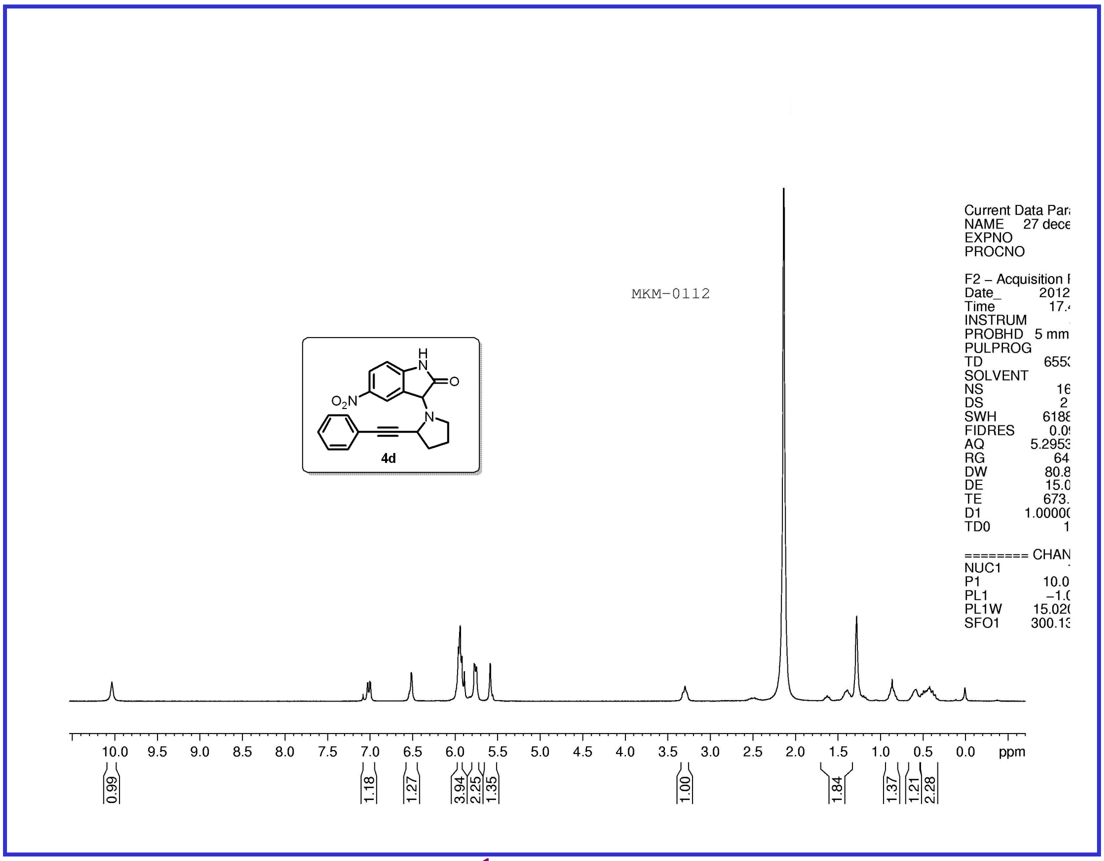


Figure 7. ^{1}H Spectrum of 4d

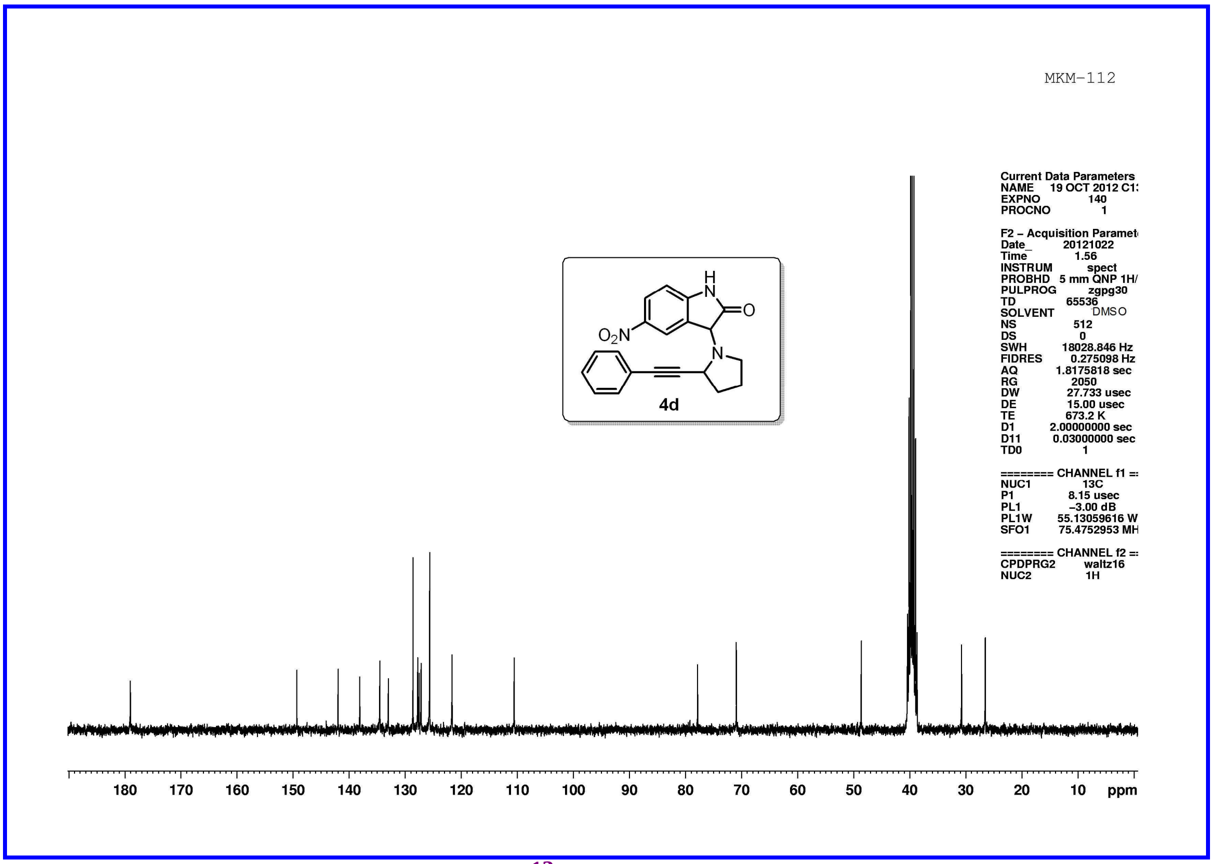


Figure 8. ^{13}**C Spectrum of 4d**

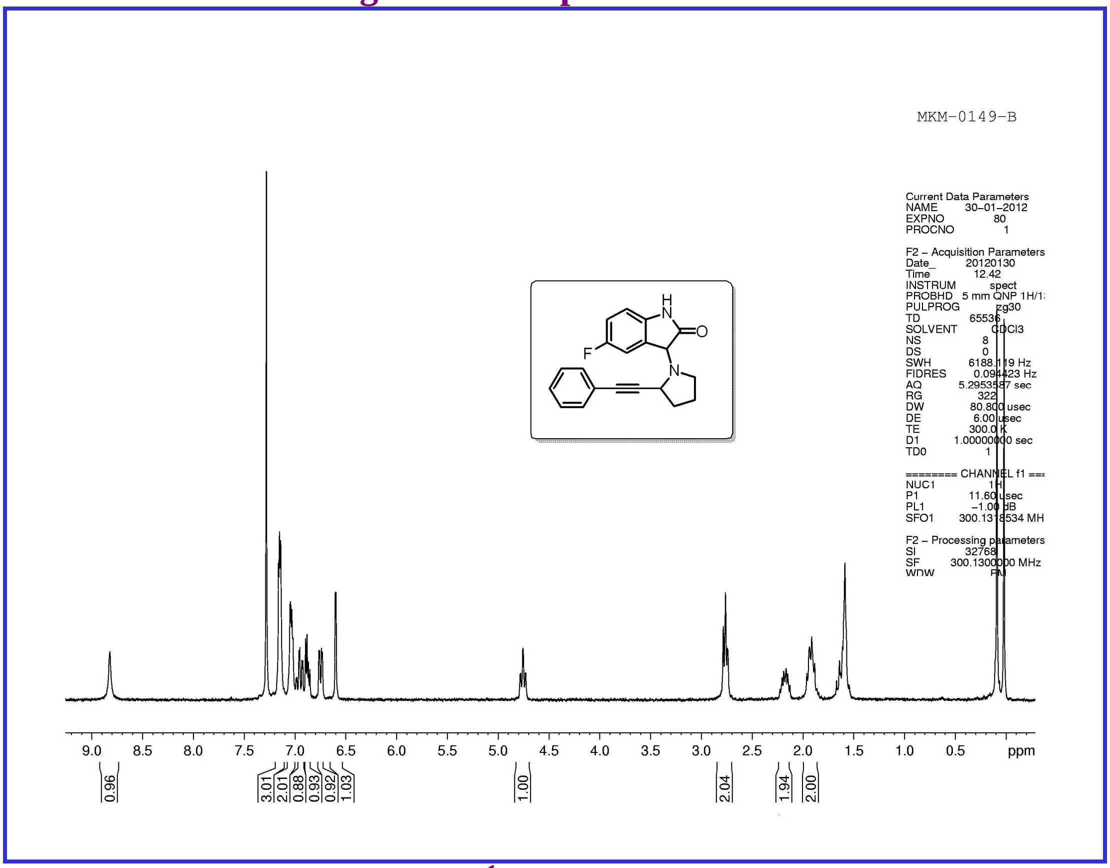


Figure 9. ^{1}**H Spectrum of 4e**

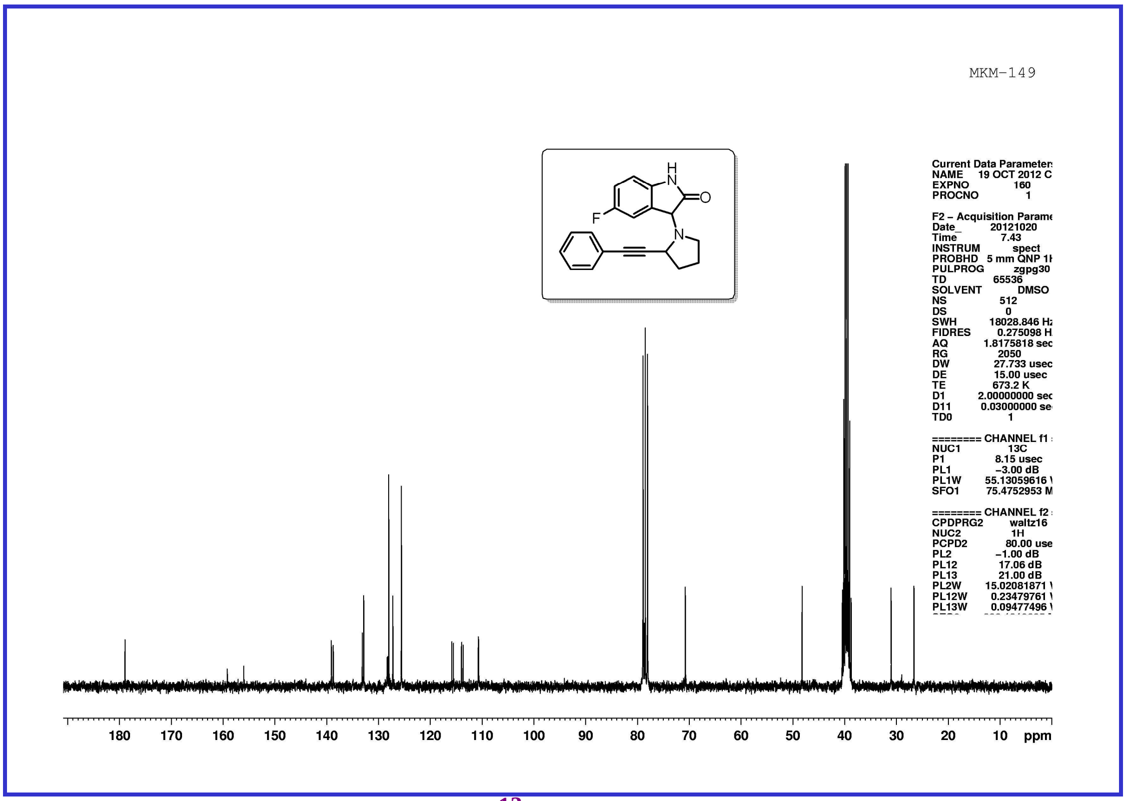


Figure 10. ^{13}C Spectrum of 4e

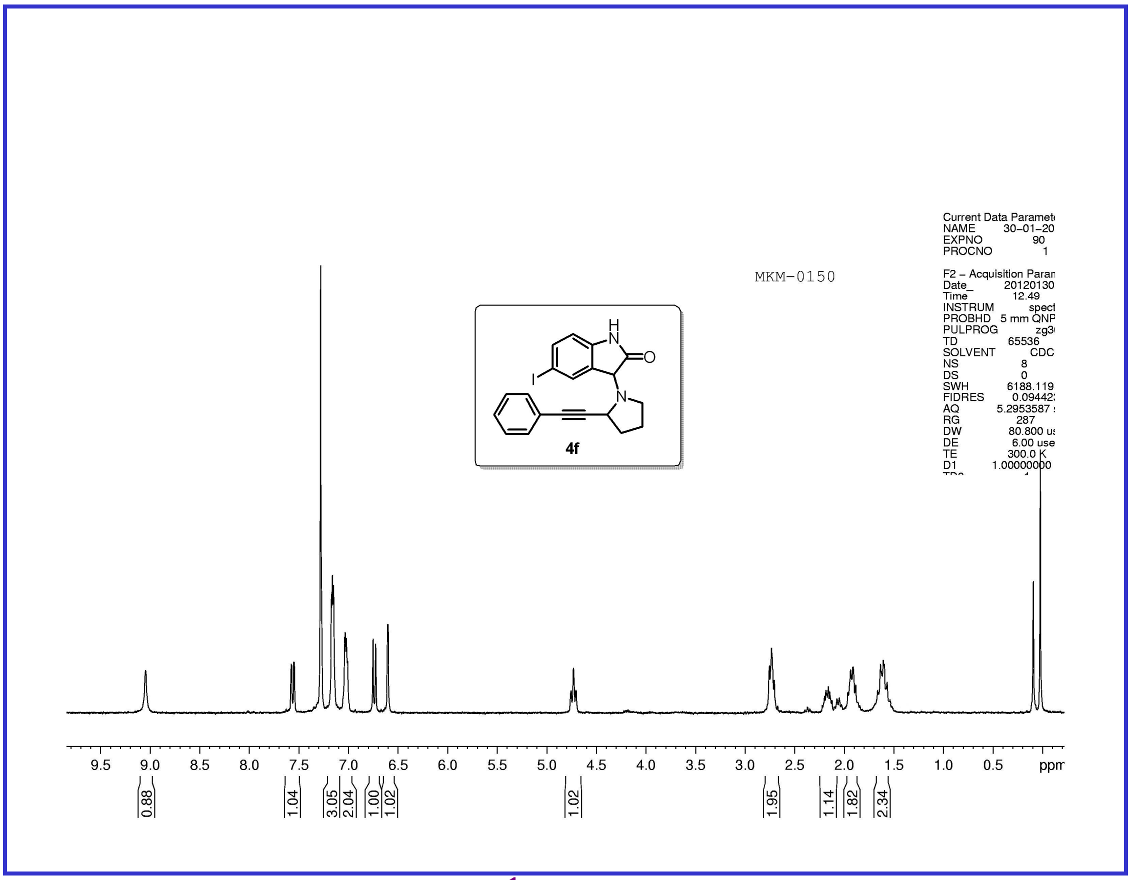


Figure 11. ^{1}H Spectrum of 4f

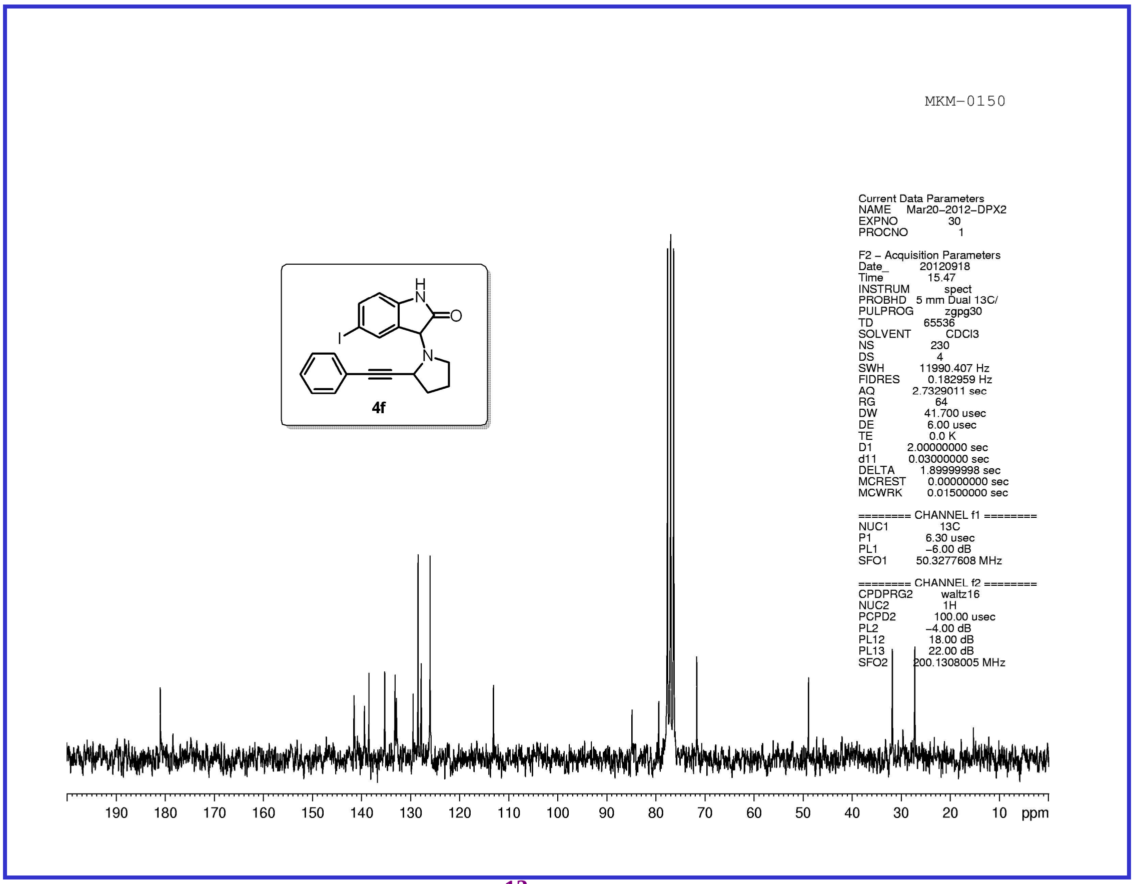


Figure 12. ^{13}C Spectrum of 4f

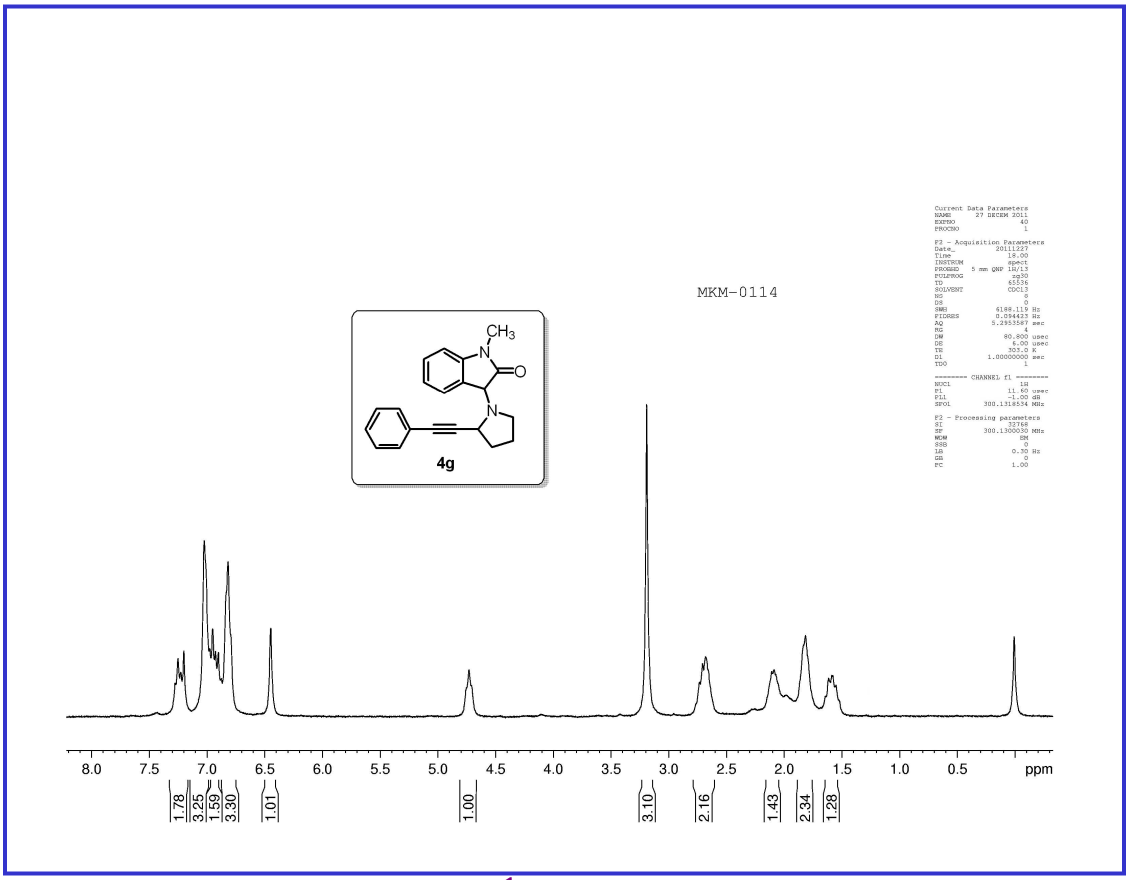


Figure 13. ^{1}H Spectrum of 4g

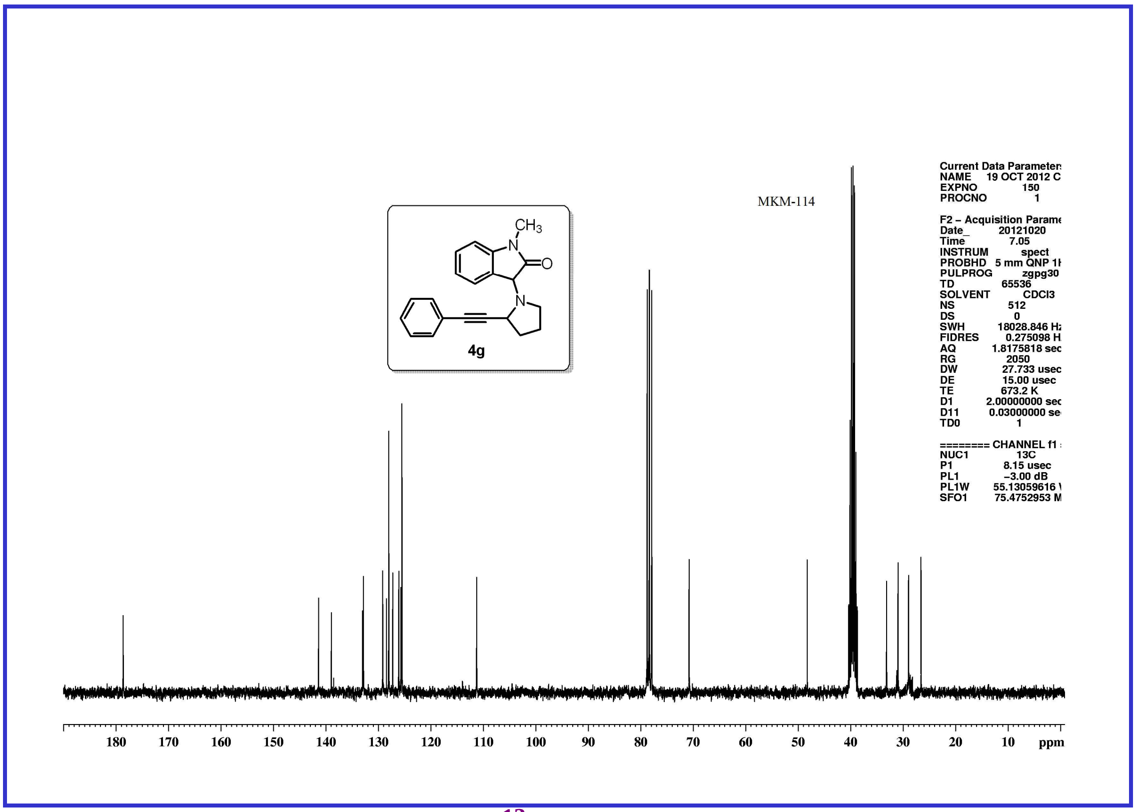


Figure 14. ^{13}C **Spectrum of 4g**

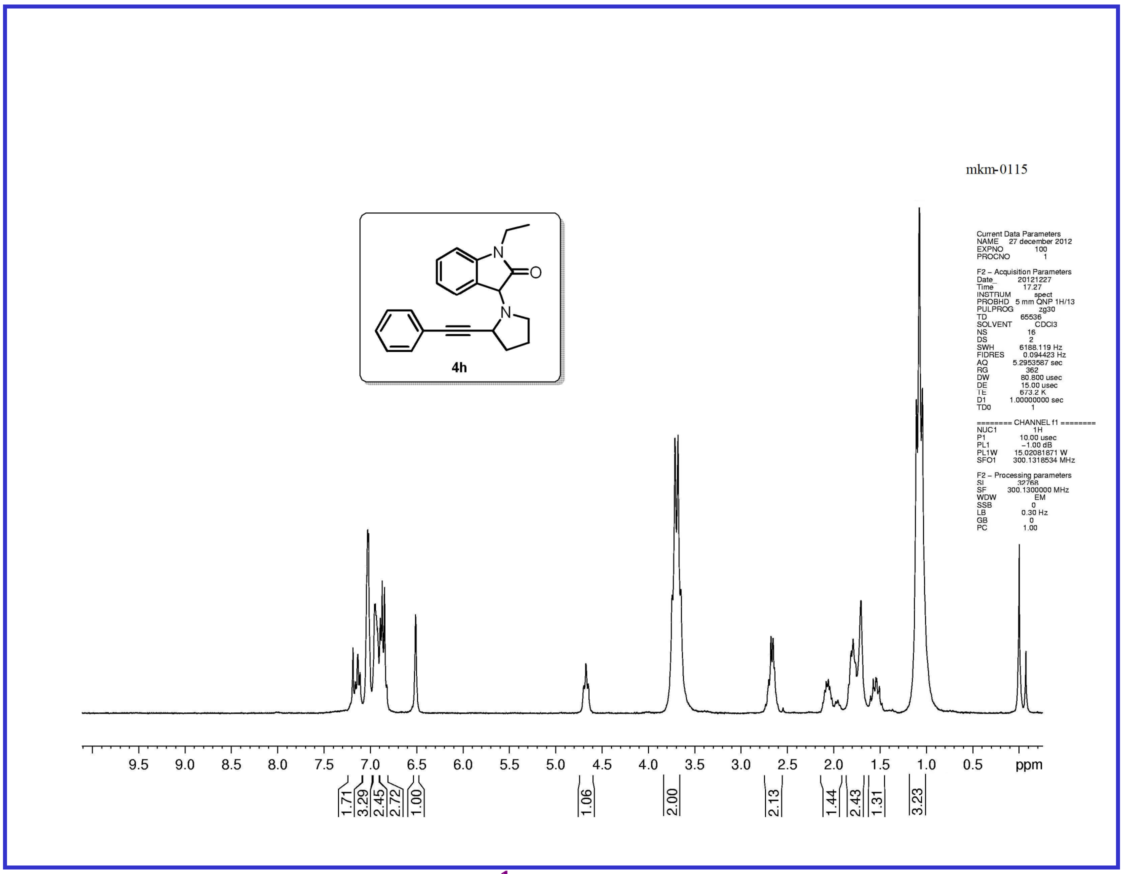


Figure 15. ^{1}H **Spectrum of 4h**

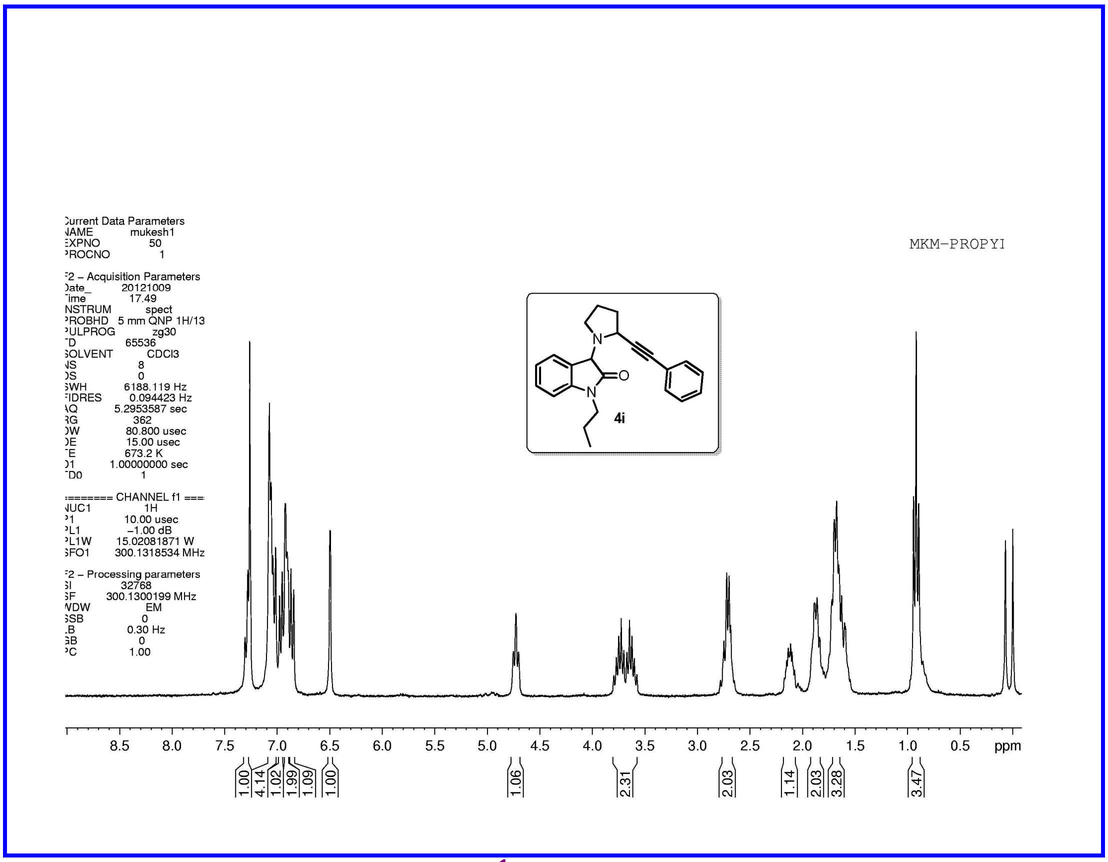


Figure 16. ^{1}H Spectrum of 4i

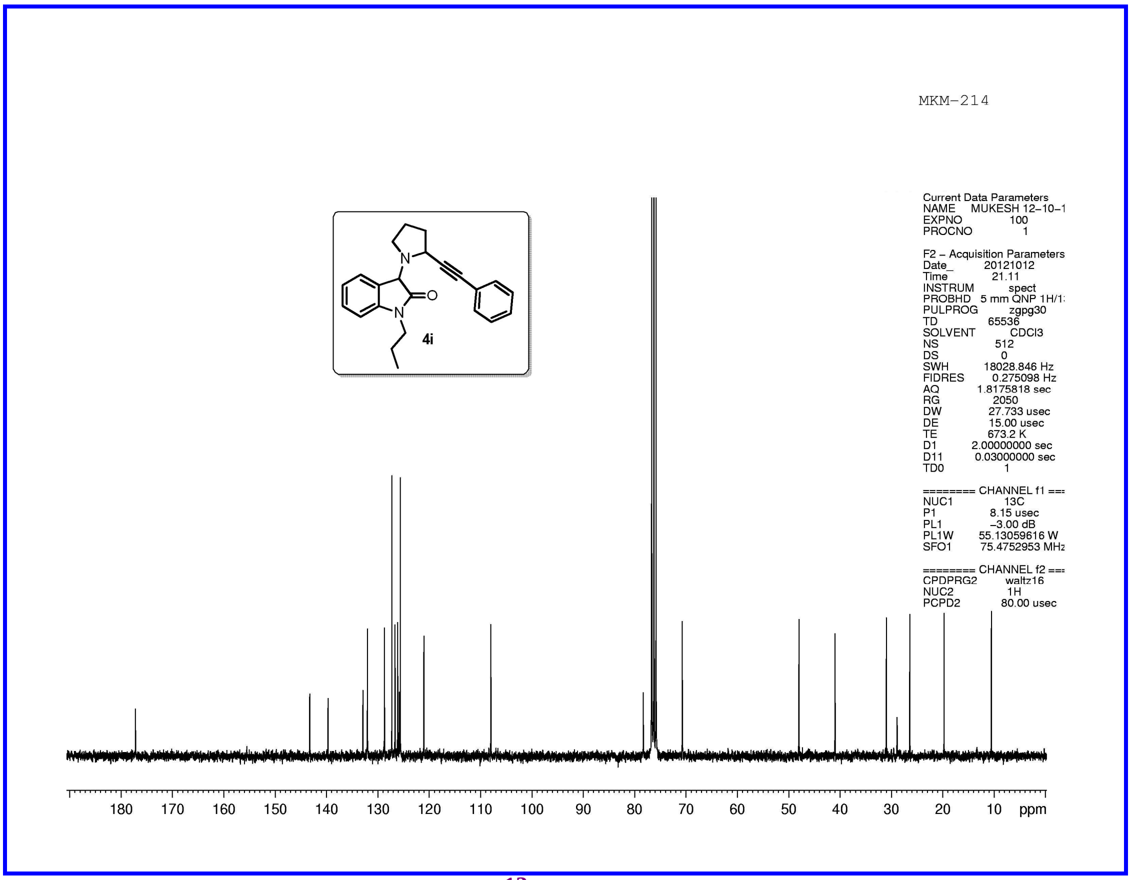


Figure 17. ^{13}C Spectrum of 4i

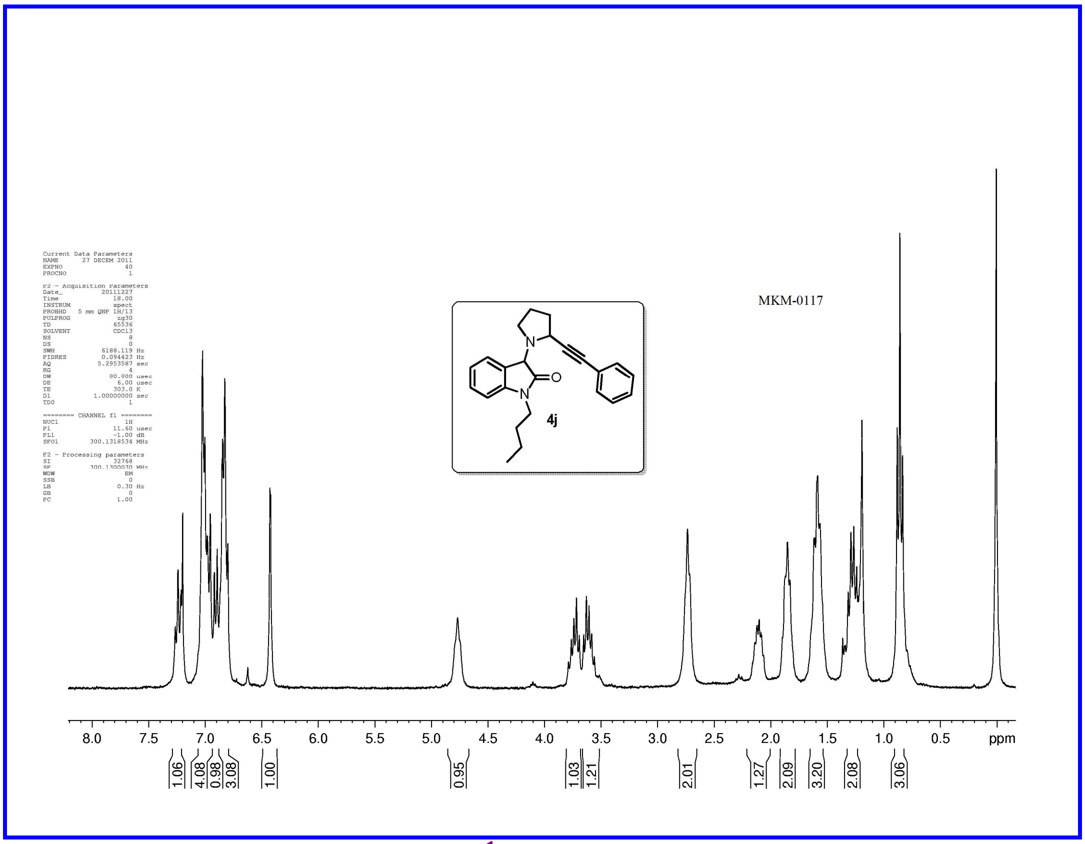


Figure 18. ^{1}H **Spectrum of 4j**

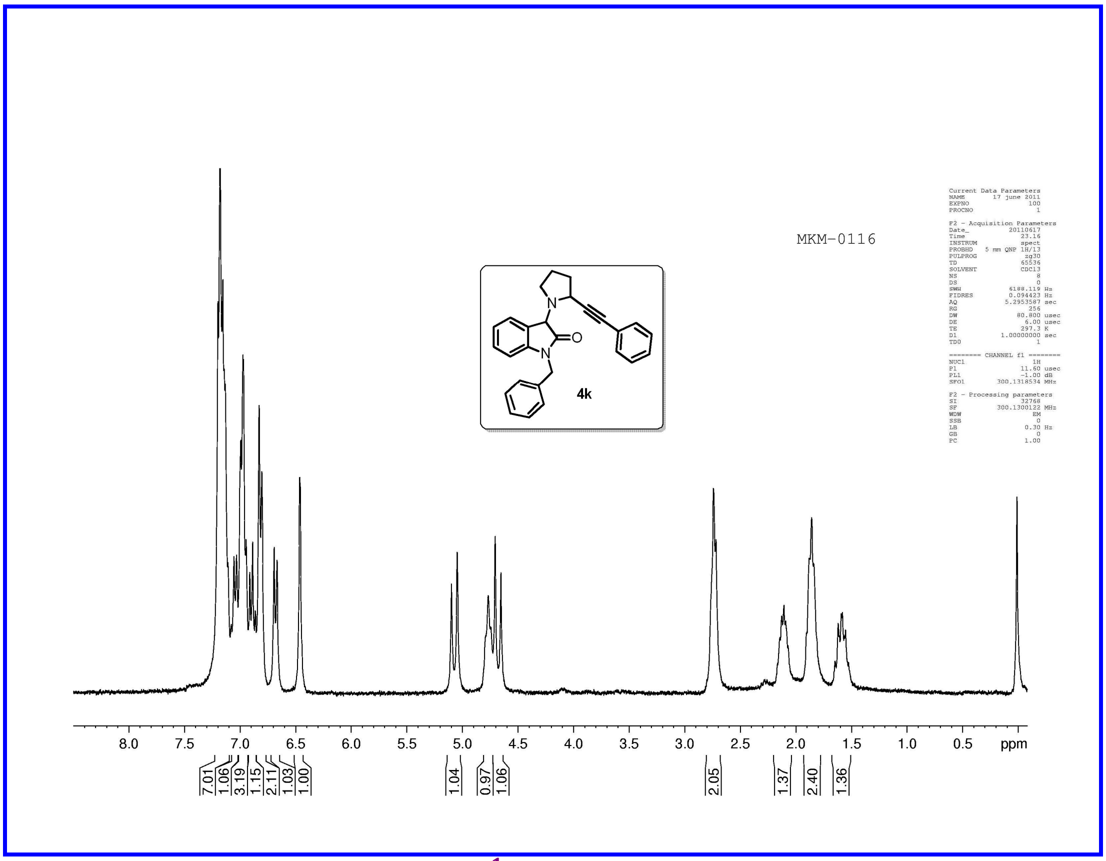


Figure 19. ^{1}H **Spectrum of 4k**

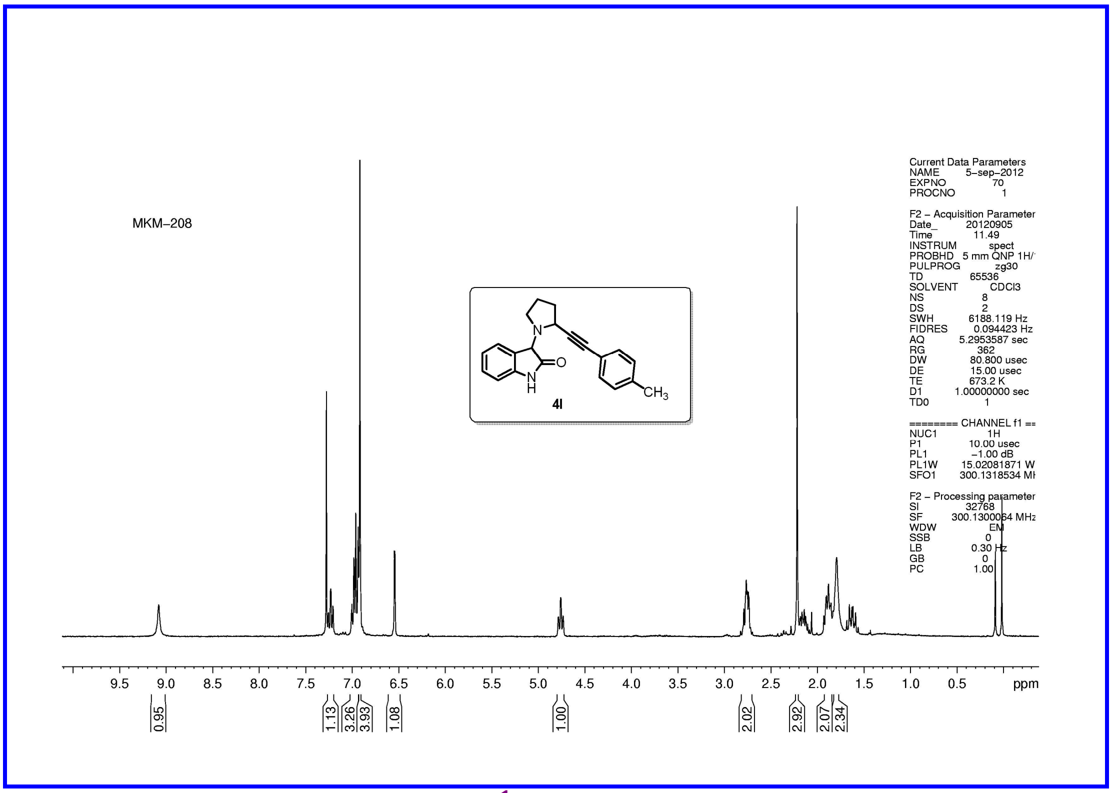


Figure 20. ^{1}H Spectrum of 4l

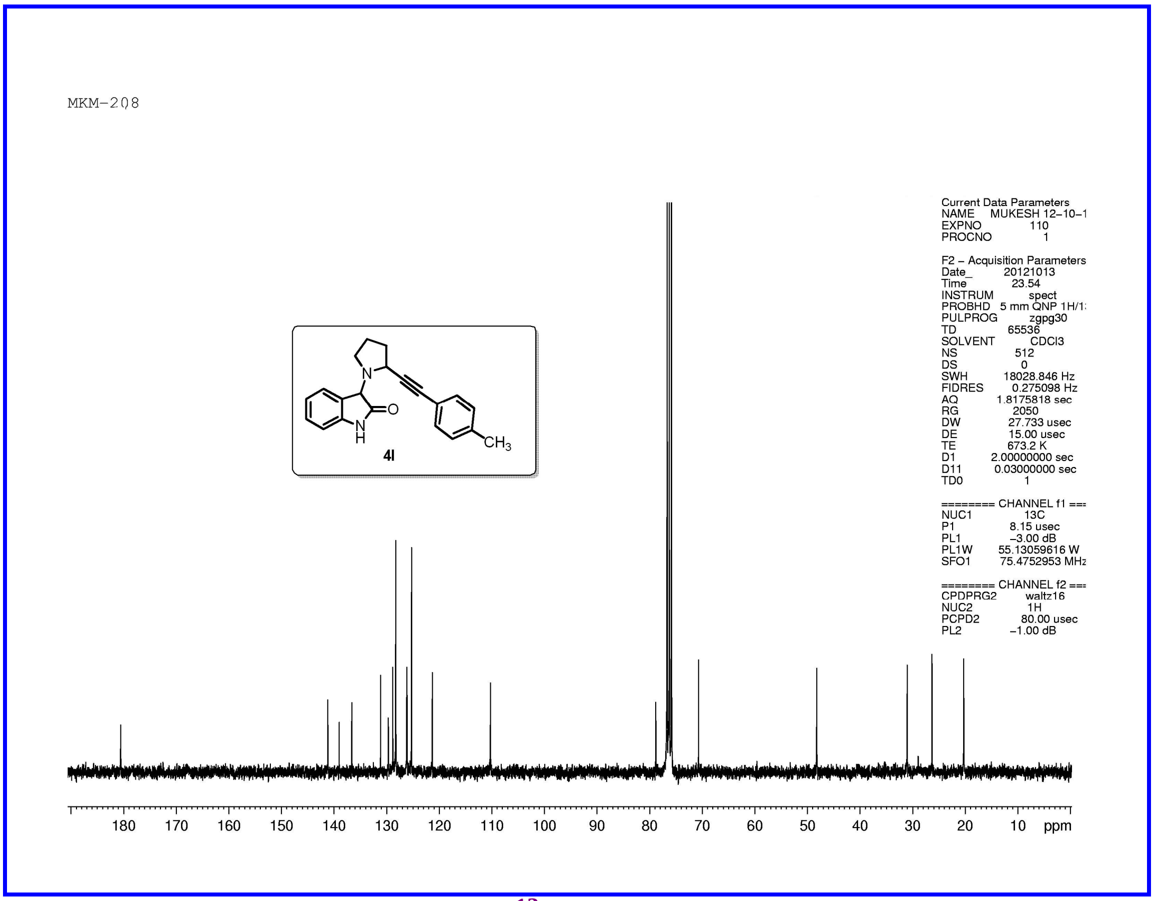


Figure 21. ^{13}C Spectrum of 4l

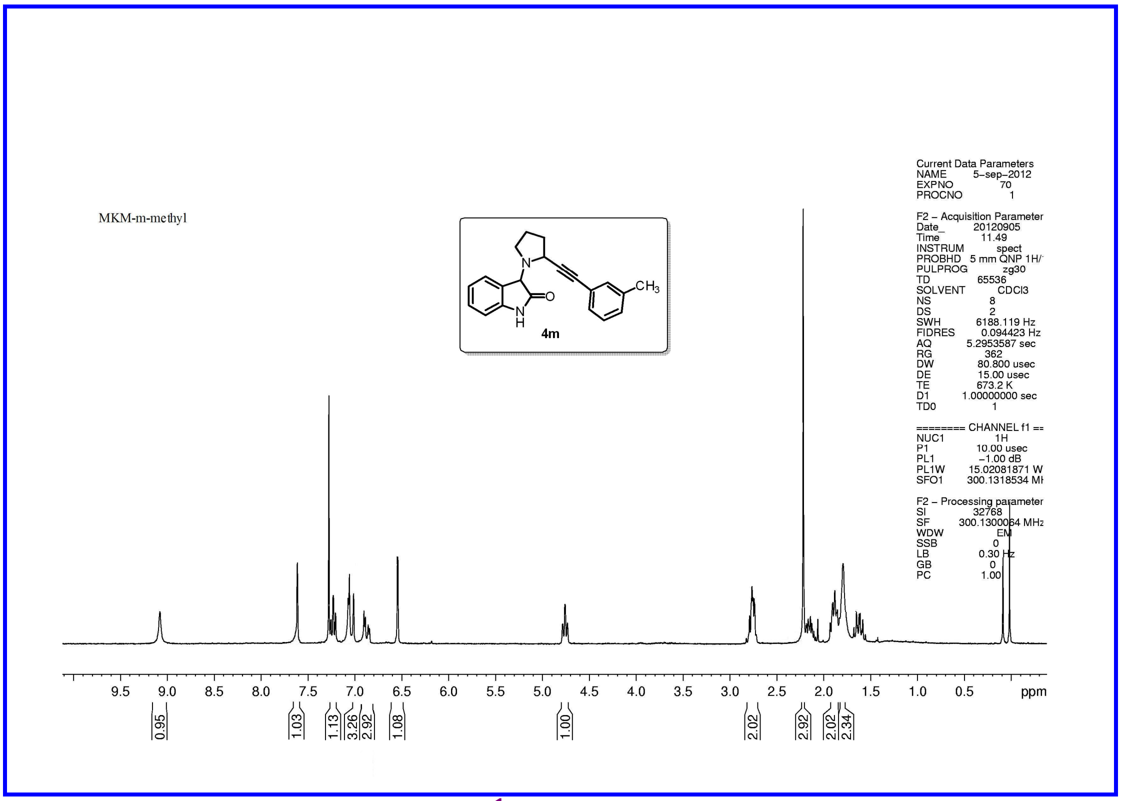


Figure 22. ^{1}H Spectrum of 4m

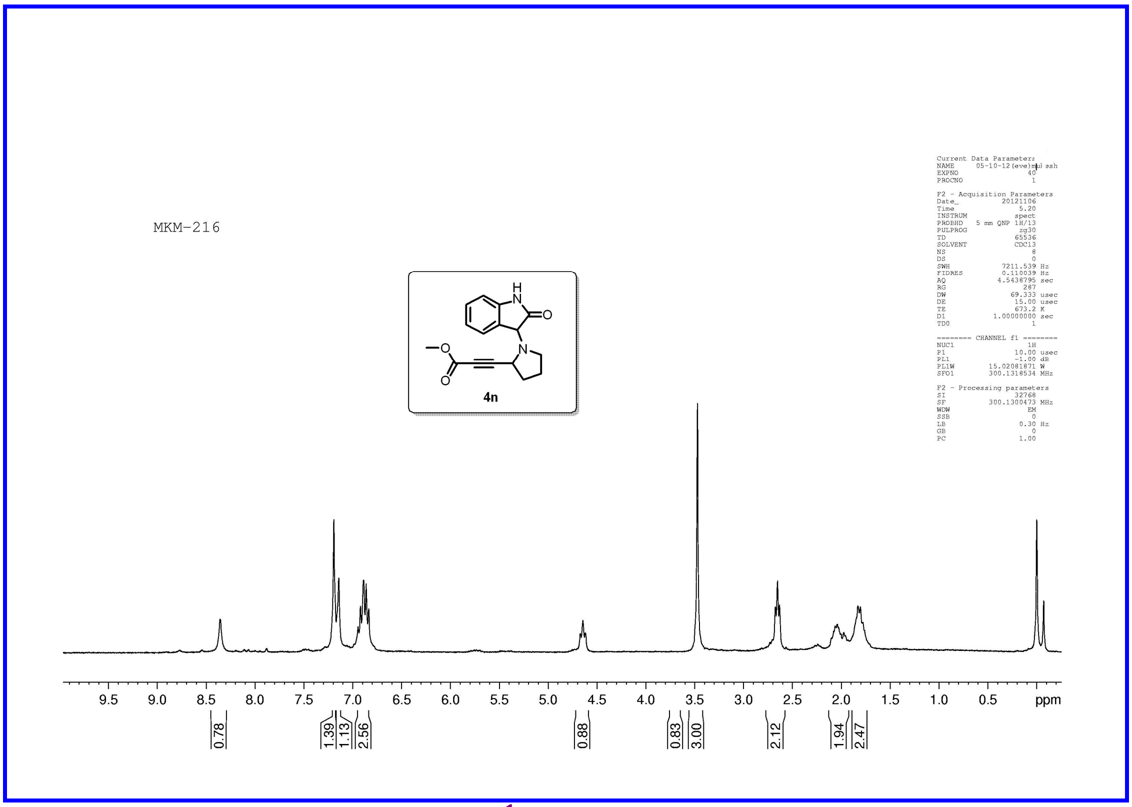


Figure 23. ^{1}H Spectrum of 4n

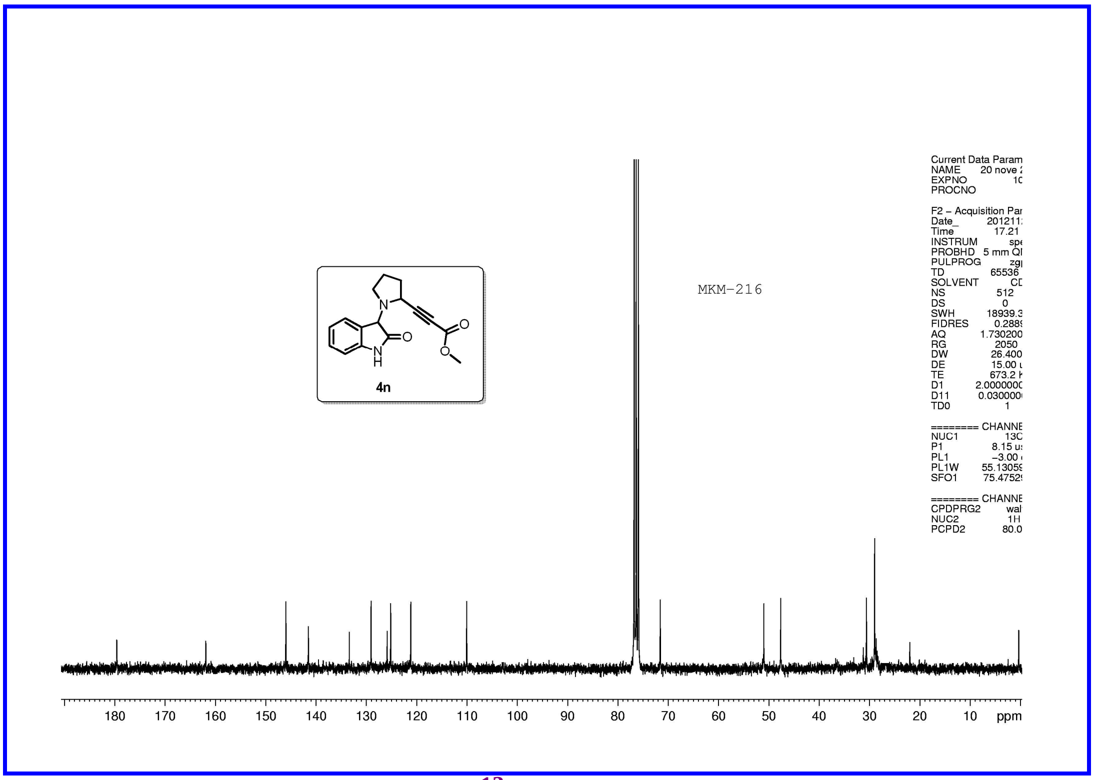


Figure 24. ^{13}C Spectrum of 4n

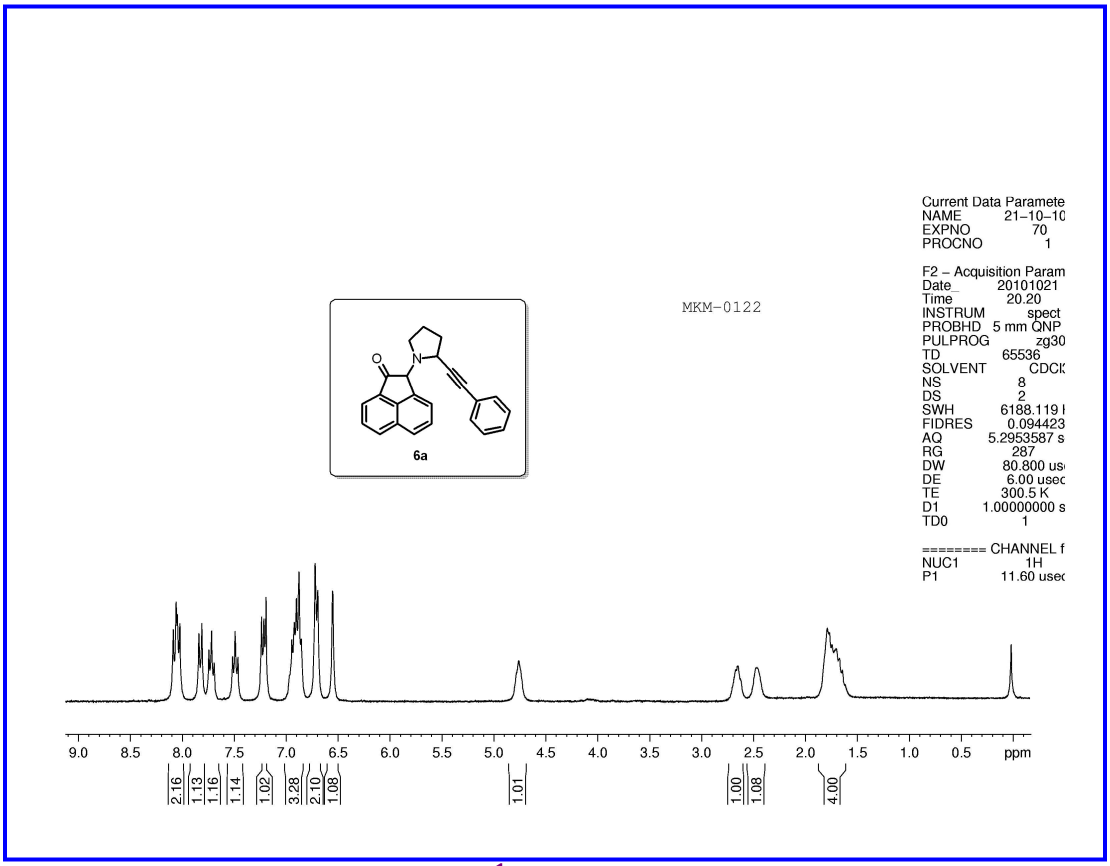


Figure 25. ^{1}H Spectrum of 6a

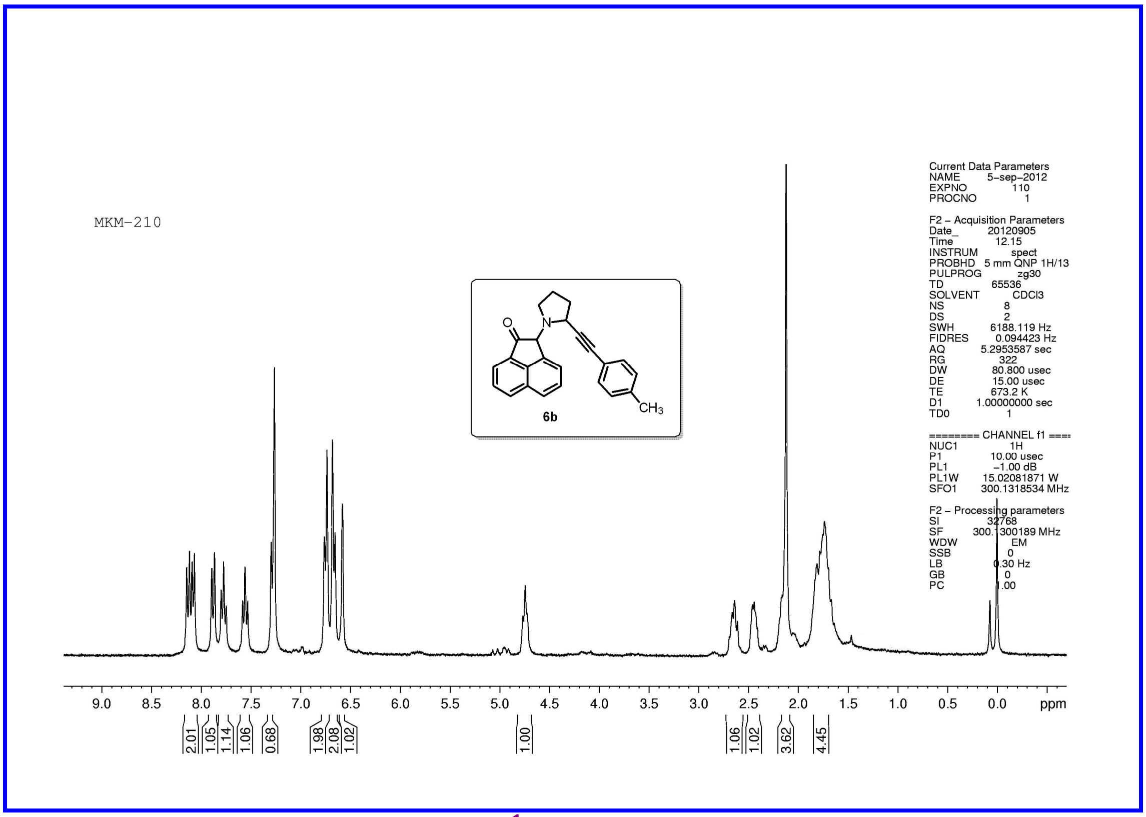


Figure 26. ¹H Spectrum of 6b

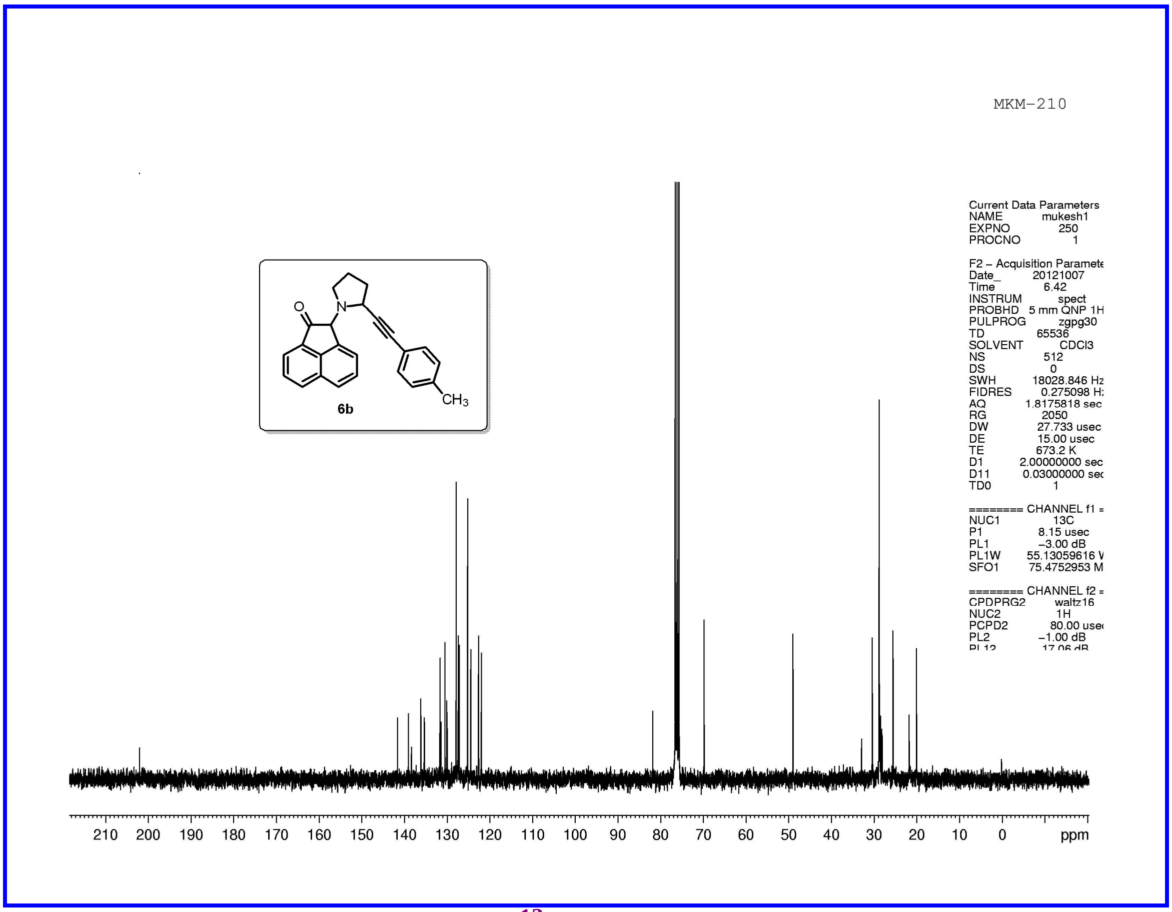


Figure 27. ¹³C Spectrum of 6b

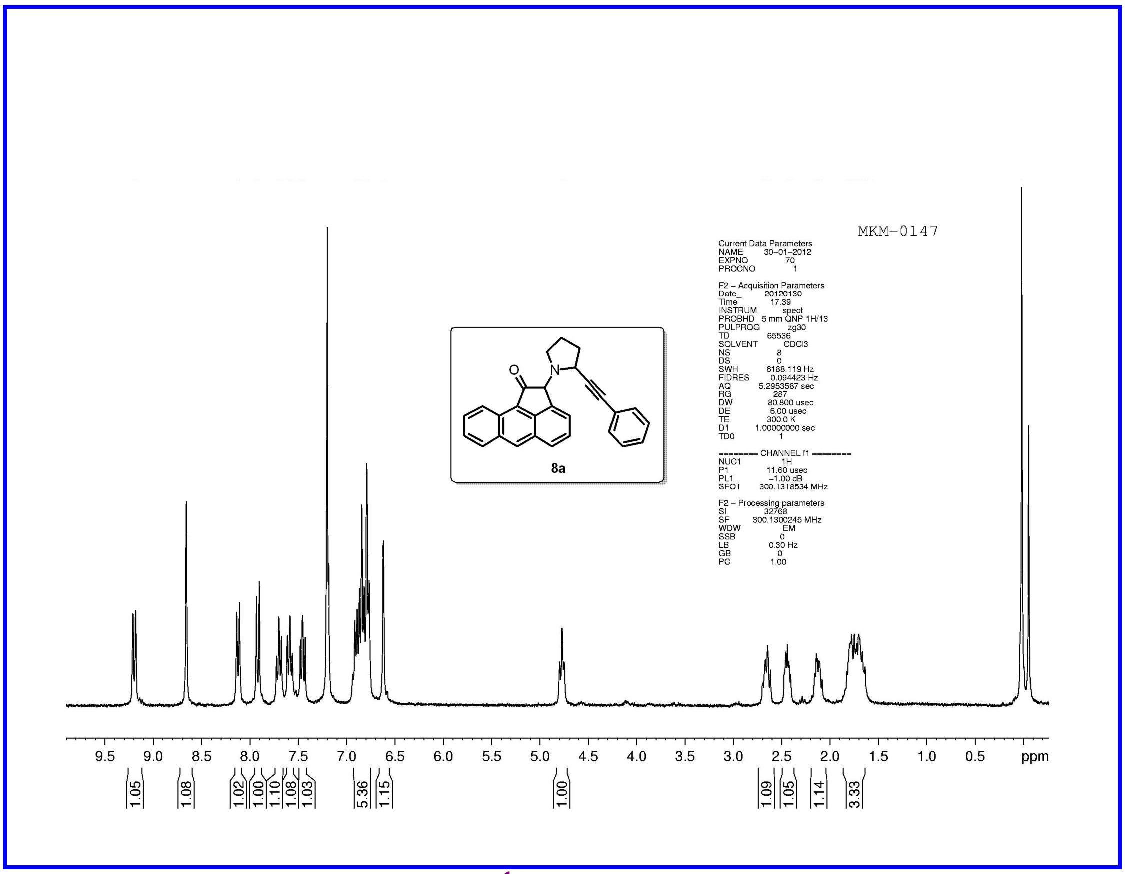


Figure 28. ¹H Spectrum of 8a

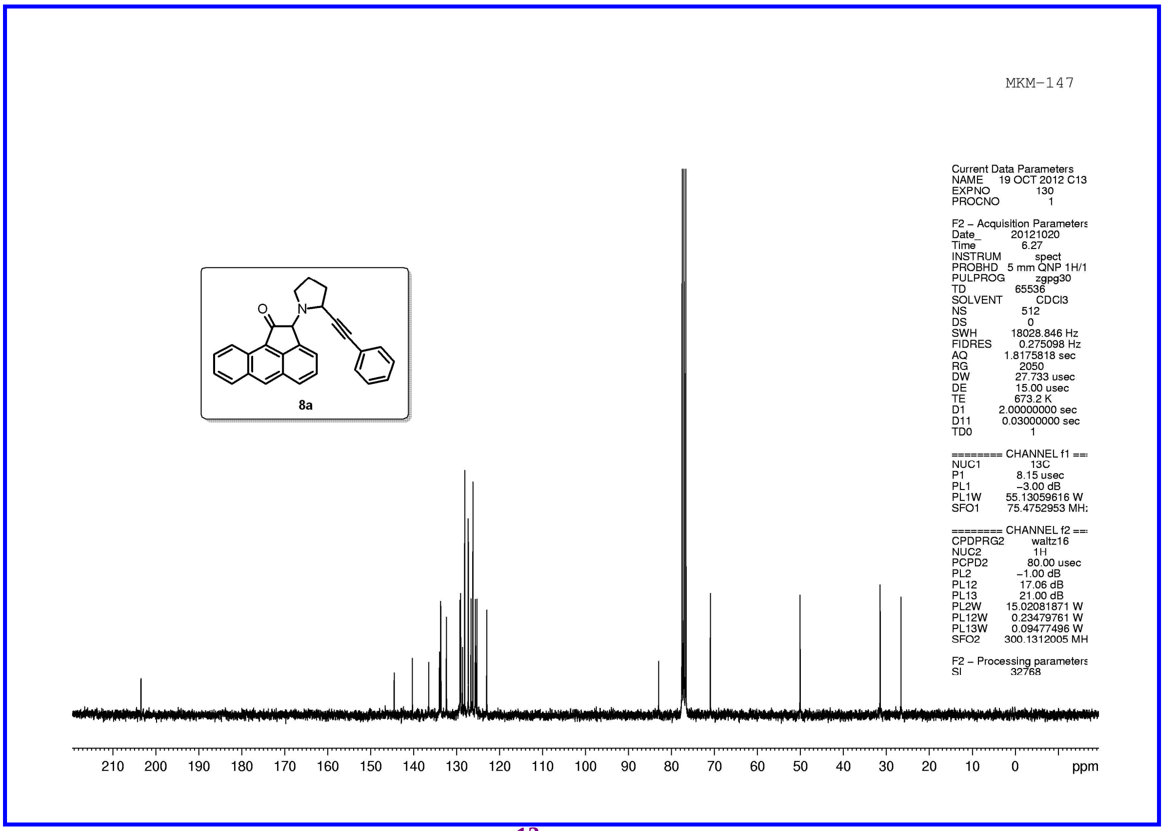


Figure 29. ¹³C Spectrum of 8a

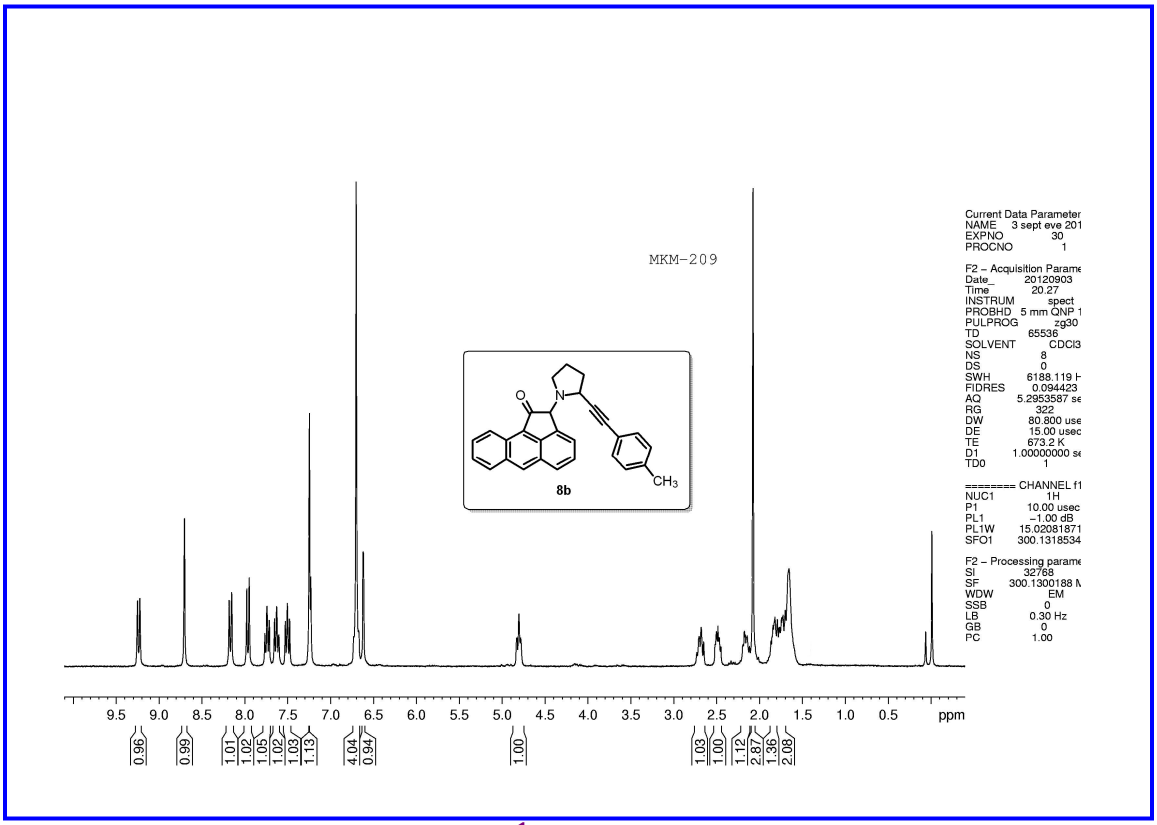


Figure 30. ^{1}H Spectrum of 8b

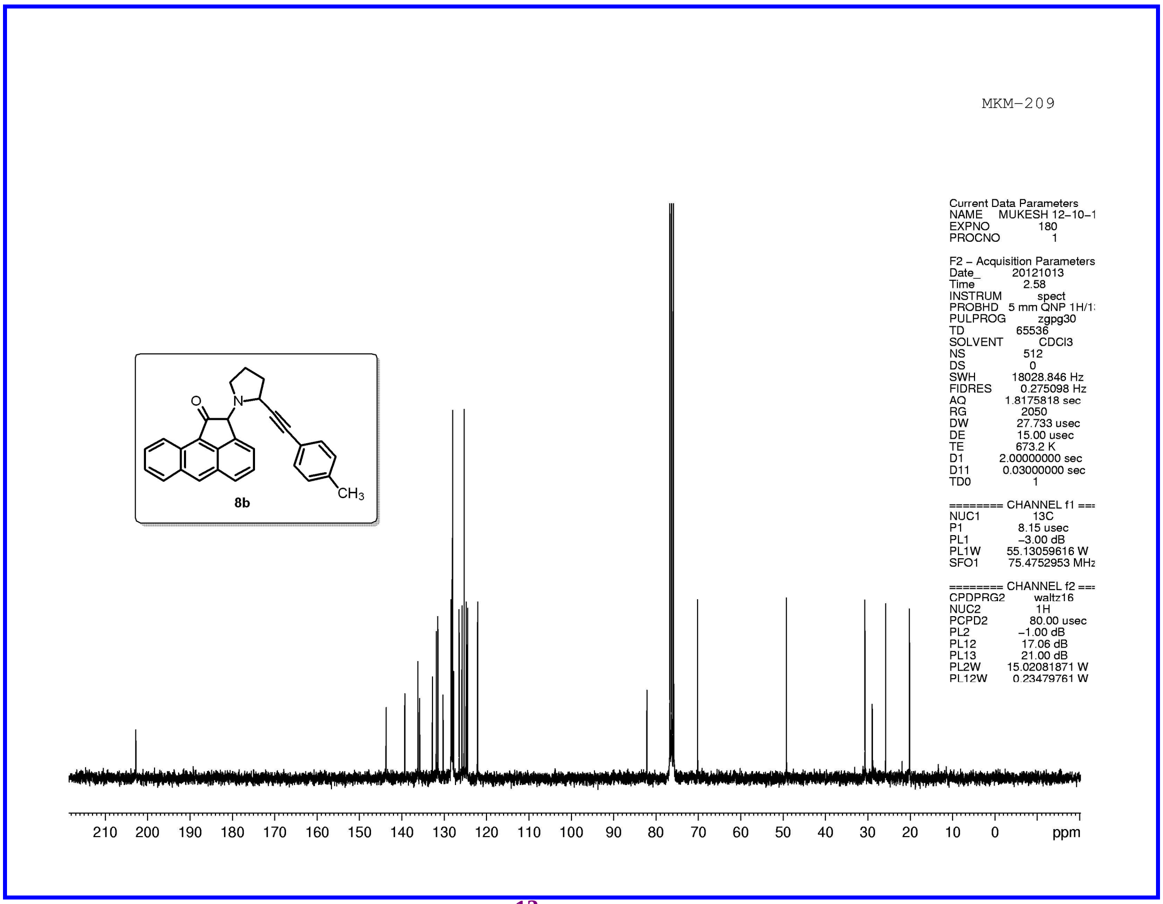


Figure 31. ^{13}C Spectrum of 8b

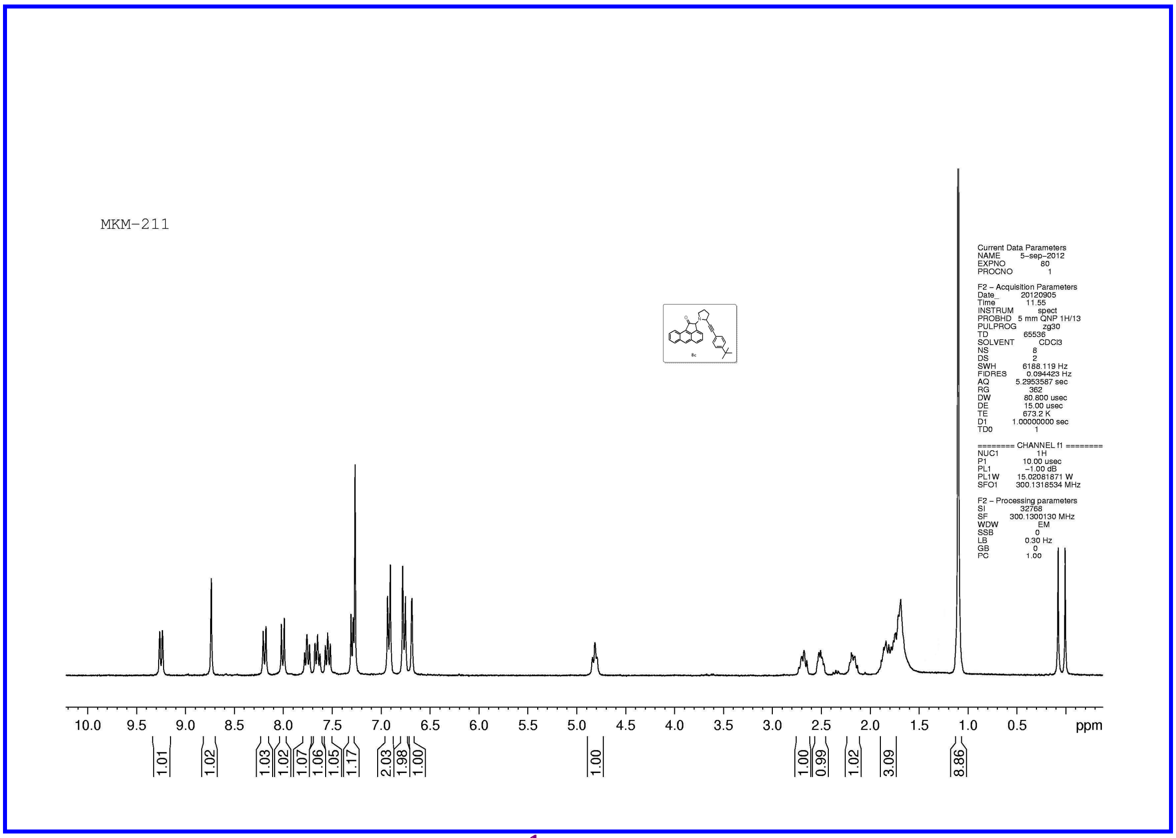


Figure 32. ^{1}H Spectrum of 8c

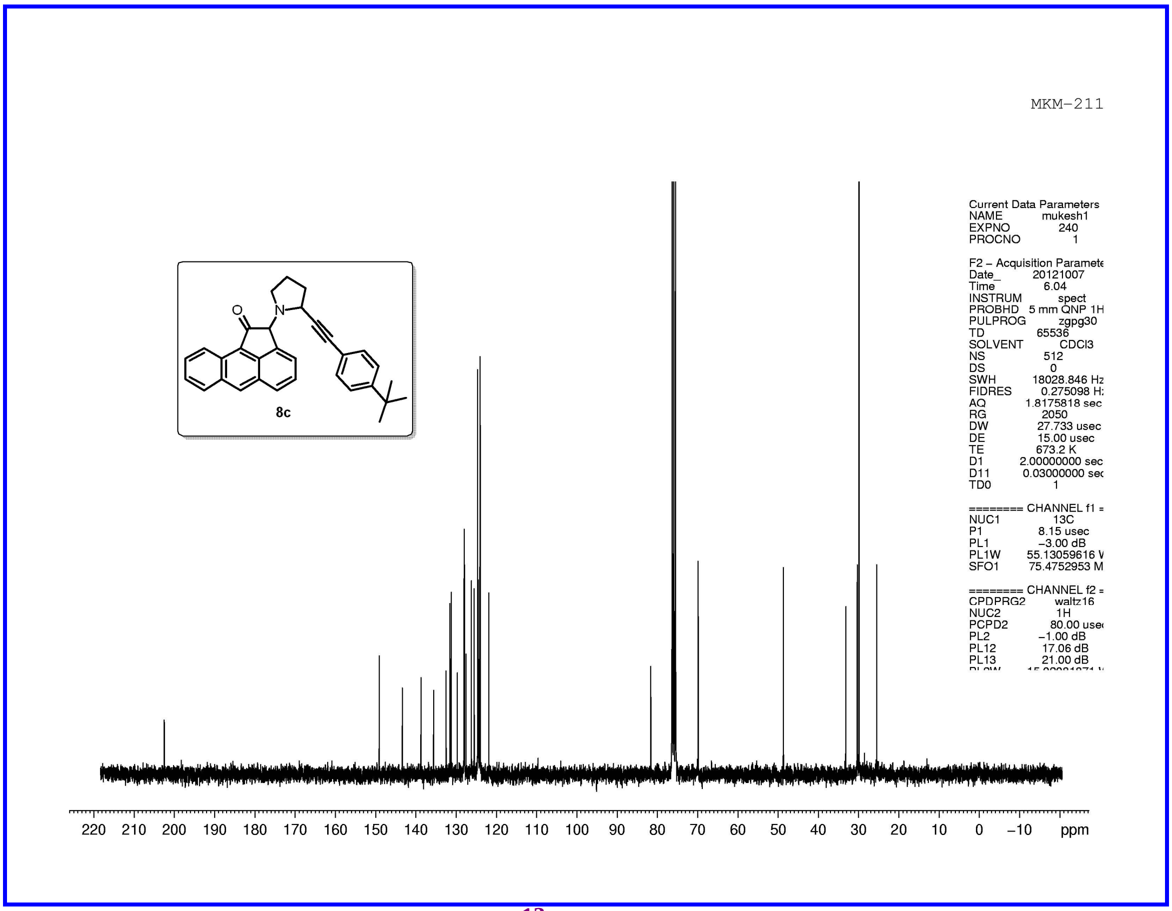


Figure 33. ^{13}C Spectrum of 8c

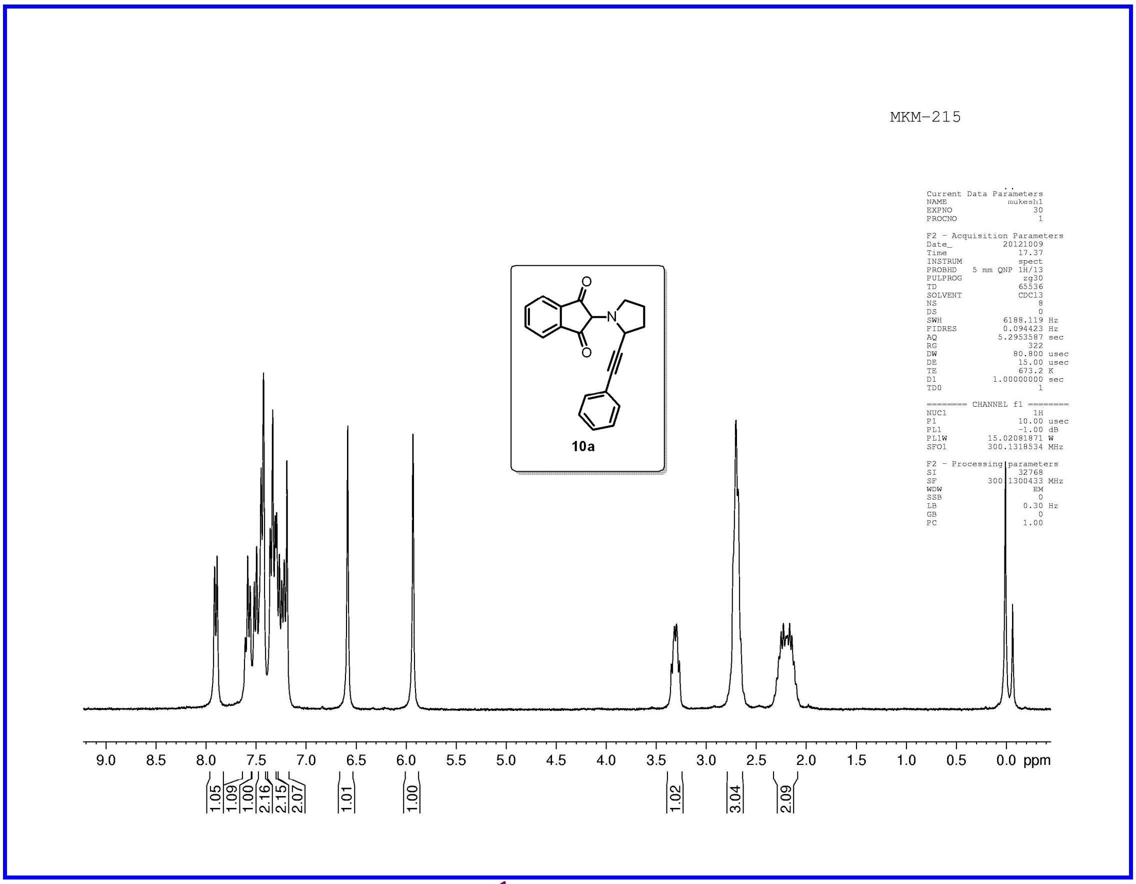


Figure 34. ^{1}H Spectrum of 10a

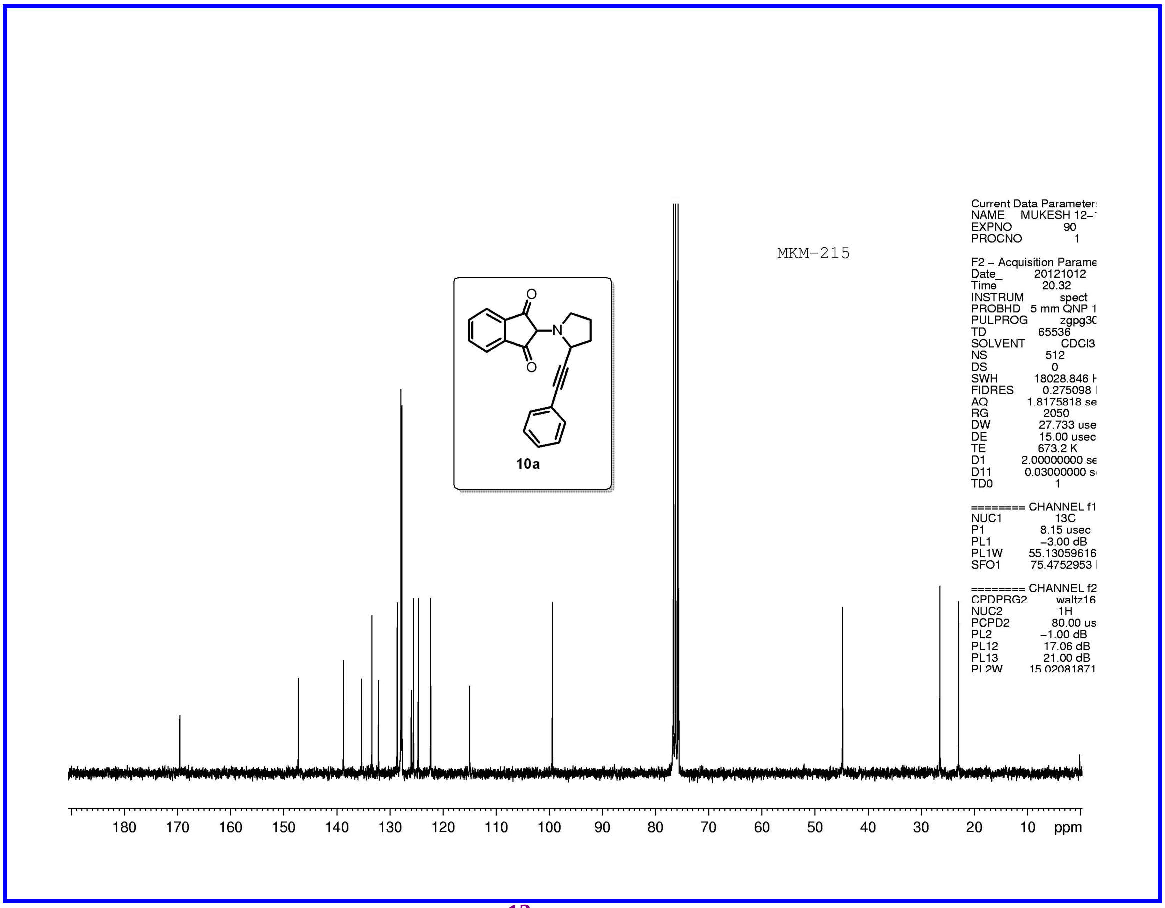


Figure 35. ^{13}C Spectrum of 10a