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A Novel Ultra Small Pd NPs on SOS Spheres: a New Catalyst for Domino Intramolecular Heck and Intermolecular Sonogashira Couplings

Bhairi Lakshminarayana, T. Vinod kumar, G. Satyanarayana* and Ch. Subrahmanyam*

*Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, 502285, Telangana, India. Ph. No: +91(40) 23016054, E-mail: csubbu@iith.ac.in

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Experimental Procedure for the Synthesis of Dihydrobenzofurans 3:

In an oven-dried Schlenk tube, 1-iodo-2-((2-methylallyl)oxy)benzene **1a** (0.25 mmol), Alkyne **2** (0.5 mmol), K_2CO_3 base (0.5 mmol), Pd/SOS spheres catalyst (0.3 mol% of Pd), solvent (DMF) (1.0 mL) were added. The resulting reaction mixture was stirred at 100 °C temperature for 1-24 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with ethyl acetate (5 mL) and neutral NH_4Cl solution (5 mL) was added fallowed by extraction with ethyl acetate (2 × 4 mL). The organic layers were dried with Na_2SO_4 and concentrated in reduced vacuum. Purification of the residue by silica gel column chromatography using distilled petroleum ether (Hexane) as the eluent furnished the dihydrobenzofurans **3**.

Experimental Procedure for the Synthesis of Oxindoles 5:

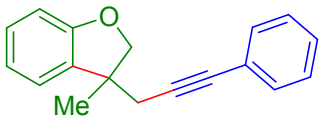
In an oven-dried Schlenk tube, *N*-(2-iodophenyl)-*N*-alkylmethacrylamide **4** (0.25 mmol), Alkyne **2** (0.5 mmol), K_2CO_3 base (0.5 mmol), Pd/SOS spheres catalyst (0.3 mol% of Pd), solvent (DMF) (1.0 mL) were added. The resulting reaction mixture was stirred at 100 °C temperature for 12-24 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with ethyl acetate (5 mL) and neutral NH_4Cl solution (5 mL) was added fallowed by extraction with ethyl acetate (2 × 4 mL). The organic layers were dried with Na_2SO_4 and concentrated in reduced vacuum. Purification of the residue by silica gel column chromatography using distilled petroleum ether/ethyl acetate as the eluent furnished the dihydrobenzofurans **5**.

Instruments used for characterization

X-ray powder diffraction was performed on a PANalytical, X'pertPRO instrument with Cu Kα-radiation of wavelength 1.5406 Å. The augmented voltage and current used for this instrument were 40 kV and 30 mA respectively. The step size used for the scan is 0.017° per step in the 2θ angle range of 10°-100°. HRTEM was performed by depositing samples on a carbon covered Cu grid on a 200 kV FEI model TECNAIG2 S-Twin TEM instrument connected with a moderate output CCD camera. The catalysts were portrayed by X-ray photoelectron spectra (XPS) with

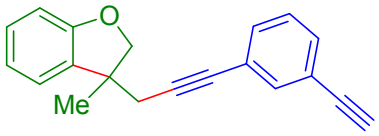
omicron gear utilizing Al Kα radiation (1486.6 eV). The instrument was precalibrated with a reference of C (1s) peak at 284.5 eV. IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. Every beginning material were synthesized and gotten from suppliers and used as received. Solvents were sanitized by standard methodology. Experiments were carried out under closed environment. ^{1}H NMR spectra were recorded at 400 MHz utilizing Bruker AVANCE instrument at 278 K. Chemical shift (δ) in ppm downfield from tetramethylsilane with the dissolvable as the interior reference ($CDCl_3$: δ 7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = expansive, m = multiplet), coupling constants (Hz), and integration. $^{13}CNMR$ spectra were recorded on either a Bruker AVANCE 100 MHz with complete proton decoupling.

The assignment of signals was confirmed by ^{1}H, ^{13}C and DEPT spectra. All small-scale dry reactions were carried out using the standard technique. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Acme's silica gel (60–120 mesh) was used for column chromatography.



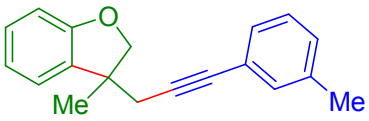
3aa (99%, 1h)

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.41 - 7.36 (m, 2 H), 7.32 - 7.26 (m, 3 H), 7.25 - 7.22 (m, 1 H), 7.16 (dt, *J* = 1.5, 7.8 Hz, 1 H), 6.93 - 6.88 (m, 1 H), 6.82 (d, *J* = 8.3 Hz, 1 H), 4.55 (d, *J* = 8.8 Hz, 1 H), 4.24 (d, *J* = 8.8 Hz, 1 H), 2.68 (s, 2 H), 1.54 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.0, 131.6, 128.5, 128.2, 127.8, 123.5, 123.0, 120.6, 109.8, 86.7, 82.5, 82.3, 45.3, 31.5, 24.2



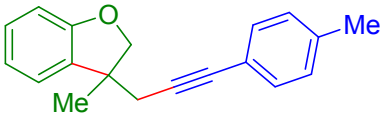
3ab

^{1}H NMR (400MHz ,CHLOROFORM-d) δ = 7.42 (s, 1 H), 7.31 (d, *J* = 7.3 Hz, 1 H), 7.25 (s, 1 H), 7.13 (d, *J* = 7.3 Hz, 1 H), 7.16 (d, *J* = 7.8 Hz, 1 H), 7.11 - 7.05 (m, 1 H), 6.82 (t, *J* = 7.3 Hz, 1 H), 6.74 (d, *J* = 7.8 Hz, 1 H), 4.45 (d, *J* = 8.8 Hz, 1 H), 4.14 (d, *J* = 8.8 Hz, 1 H), 2.99 (s, 1 H), 2.59 (s, 2 H), 1.44 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 135.1, 133.9, 131.9, 131.4, 128.6, 128.3, 123.8, 122.9, 122.3, 120.6, 109.8, 87.5, 82.8, 82.2, 81.5, 77.7, 45.2, 31.5, 24.2



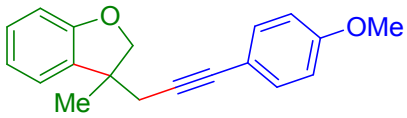
3ac

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.20 - 7.02 (m, 5 H), 6.99 (d, *J* = 7.3 Hz, 1 H), 6.80 (dt, *J* = 1.7, 7.2 Hz, 1 H), 6.72 (d, *J* = 7.8 Hz, 1 H), 4.44 (td, *J* = 1.7, 8.8 Hz, 1 H), 4.21 - 4.00 (m, 1 H), 2.57 (s, 2 H), 2.21 (s, 3 H), 1.43 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 137.8, 134.0, 132.1, 128.7, 128.6, 128.5, 128.1, 123.2, 122.9, 120.5, 109.8, 86.2, 82.6, 82.2, 45.2, 31.5, 24.2, 21.1



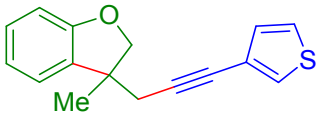
3ad

^{1}H NMR (400MHz, CHLOROFORM-d) δ = 7.23 - 7.12 (m, 3 H), 7.12 - 6.98 (m, 3 H), 6.81 (t, *J* = 7.1 Hz, 1 H), 6.74 (d, *J* = 7.8 Hz, 1 H), 4.46 (d, *J* = 8.8 Hz, 1 H), 4.15 (d, *J* = 8.8 Hz, 1 H), 2.59 (s, 2 H), 2.25 (s, 3 H), 1.45 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 137.9, 134.1, 131.4, 129.0, 128.5, 123.0, 120.5, 120.4, 109.8, 85.8, 82.5, 82.3, 45.3, 31.5, 24.2, 21.4



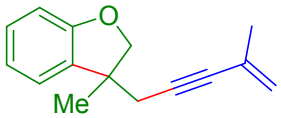
3ae

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.32 - 7.26 (m, 2 H), 7.19 (dd, *J* = 1.5, 7.3 Hz, 1 H), 7.15 - 7.09 (m, 1 H), 6.86 (dt, *J* = 1.0, 7.6 Hz, 1 H), 6.81 - 6.77 (m, 3 H), 4.51 (d, *J* = 8.8 Hz, 1 H), 4.19 (d, *J* = 8.8 Hz, 1 H), 3.75 (s, 3 H), 2.63 (s, 2 H), 1.49 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 159.2, 134.1, 134.0, 132.9, 128.5, 122.9, 120.5, 115.6, 114.1, 113.8, 109.7, 85.0, 82.3, 82.2, 55.2, 45.3, 31.5, 24.2



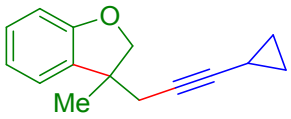
3af

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.35 (dd, *J* = 1.0, 2.9 Hz, 1 H), 7.25 - 7.19 (m, 2 H), 7.15 (dt, *J* = 1.5, 7.8 Hz, 1 H), 7.05 (dd, *J* = 1.2, 5.1 Hz, 1 H), 6.92 - 6.87 (m, 1 H), 6.81 (d, *J* = 8.3 Hz, 1 H), 4.53 (d, *J* = 8.8 Hz, 1 H), 4.22 (d, *J* = 9.3 Hz, 1 H), 2.65 (s, 2 H), 1.52 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.0, 129.9, 128.5, 128.0, 125.1, 122.9, 122.4, 120.5, 109.8, 86.2, 82.2, 77.5, 45.2, 31.5, 24.2



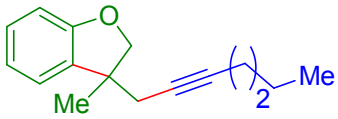
3ag

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.25 - 7.11 (m, 2 H), 6.90 (dt, *J* = 1.0, 7.3 Hz, 1 H), 6.82 (d, *J* = 7.8 Hz, 1 H), 5.24 (s, 1 H), 5.21 - 5.15 (m, 1 H), 4.50 (d, *J* = 8.8 Hz, 1 H), 4.21 (d, *J* = 8.8 Hz, 1 H), 2.59 (s, 2 H), 1.88 (s, 3 H), 1.50 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.0, 128.5, 126.9, 122.9, 120.9, 120.5, 109.8, 85.7, 83.7, 82.2, 45.2, 31.4, 24.1, 23.6



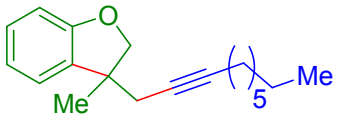
3ah

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.08 - 7.01 (m, 2 H), 6.78 (dt, *J* = 1.0, 7.3 Hz, 1 H), 6.73 - 6.66 (m, 1 H), 4.36 (d, *J* = 8.8 Hz, 1 H), 4.07 (d, *J* = 8.8 Hz, 1 H), 2.30 (d, *J* = 2.0 Hz, 2 H), 1.34 (s, 3 H), 1.11 (tt, *J* = 3.2, 5.1 Hz, 1 H), 0.67 - 0.58 (m, 2 H), 0.54 - 0.45 (m, 2 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.2, 128.3, 122.8, 120.4, 109.6, 85.4, 82.2, 71.9, 45.1, 30.9, 24.2, 8.0, -0.5



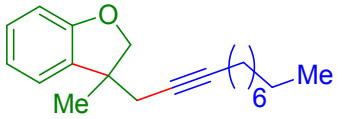
3ai

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.21 - 7.12 (m, 2 H), 6.93 - 6.86 (m, 1 H), 6.81 (d, *J* = 7.8 Hz, 1 H), 4.51 (d, *J* = 8.8 Hz, 1 H), 4.20 (d, *J* = 8.8 Hz, 1 H), 2.45 (s, 2 H), 2.18 (t, *J* = 2.4, 6.8 Hz, 2 H), 1.49 - 1.34 (m, 7 H), 0.93 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.3, 128.3, 122.8, 120.4, 109.7, 82.3, 82.2, 76.5, 45.1, 31.0, 30.9, 24.3, 21.8, 18.3, 13.6



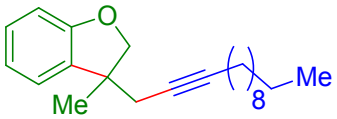
3aj

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.21 - 7.11 (m, 2 H), 6.89 (dt, *J* = 1.0, 7.3 Hz, 1 H), 6.81 (d, *J* = 7.8 Hz, 1 H), 4.50 (d, *J* = 8.8 Hz, 1 H), 4.19 (d, *J* = 8.8 Hz, 1 H), 2.45 (t, *J* = 2.0 Hz, 2 H), 2.21 - 2.12 (m, 2 H), 1.47 (s, 3 H), 1.44 - 1.22 (m, 10 H), 0.94 - 0.88 (m, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.3, 128.3, 122.8, 120.4, 109.7, 82.4, 82.2, 76.5, 45.1, 31.8, 30.9, 29.0, 28.9, 28.8, 28.8, 24.3, 22.6, 18.6, 14.1



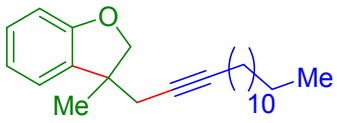
3ak

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.21 - 7.11 (m, 2 H), 6.92 - 6.85 (m, 1 H), 6.81 (d, *J* = 7.8 Hz, 1 H), 4.50 (d, *J* = 8.8 Hz, 1 H), 4.19 (d, *J* = 8.8 Hz, 1 H), 2.45 (t, *J* = 2.2 Hz, 2 H), 2.17 (tt, *J* = 2.4, 7.1 Hz, 2 H), 1.47 (s, 4 H), 1.40 - 1.35 (m, 2 H), 1.34 - 1.25 (m, 10 H), 0.91 (t, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.3, 128.3, 122.8, 120.4, 109.7, 82.4, 82.2, 76.5, 45.1, 31.8, 30.9, 29.2, 29.1, 29.0, 28.8, 24.3, 22.6, 18.7, 14.1



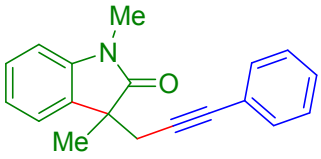
3al

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.21 - 7.12 (m, 2 H), 6.89 (dt, *J* = 1.0, 7.3 Hz, 1 H), 6.81 (d, *J* = 7.8 Hz, 1 H), 4.51 (d, *J* = 8.8 Hz, 1 H), 4.20 (d, *J* = 8.8 Hz, 1 H), 2.45 (t, *J* = 2.2 Hz, 2 H), 2.22 - 2.12 (m, 2 H), 1.48 (s, 3 H), 1.35 - 1.17 (m, 16 H), 0.92 (t, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.3, 128.3, 122.8, 120.4, 109.7, 82.4, 82.2, 76.5, 45.1, 31.9, 30.9, 29.6, 29.5, 29.3, 29.1, 29.0, 28.8, 24.3, 22.7, 18.6, 14.1



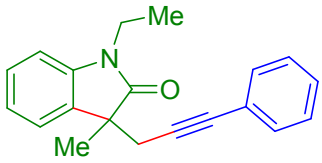
3am

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.21 - 7.12 (m, 2 H), 6.89 (dt, *J* = 1.0, 7.3 Hz, 1 H), 6.81 (d, *J* = 7.8 Hz, 1 H), 4.51 (d, *J* = 8.8 Hz, 1 H), 4.20 (d, *J* = 8.8 Hz, 1 H), 2.49 - 2.41 (m, 2 H), 2.17 (tt, *J* = 2.3, 7.0 Hz, 2 H), 1.47 (s, 3 H), 1.33 - 1.26 (m, 20 H), 0.91 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 159.4, 134.3, 128.3, 122.8, 120.4, 109.7, 82.4, 82.2, 76.5, 45.1, 31.9, 30.9, 29.7, 29.6, 29.6, 29.3, 29.1, 29.0, 28.8, 24.3, 22.7, 18.6, 14.1



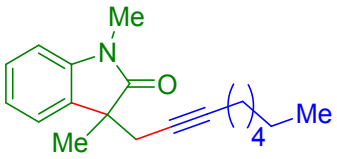
5aa

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.51 - 7.44 (m, 1 H), 7.37 - 7.20 (m, 6 H), 7.12 - 7.06 (m, 1 H), 6.87 (d, *J* = 7.8 Hz, 1 H), 3.23 (s, 3 H), 2.91 (d, *J* = 16.6 Hz, 1 H), 2.68 (d, *J* = 16.6 Hz, 1 H), 1.52 (s, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.5, 143.1, 133.3, 131.5, 128.2, 128.1, 127.8, 123.4, 123.3, 122.6, 107.9, 85.4, 82.8, 47.2, 28.9, 26.3, 21.7



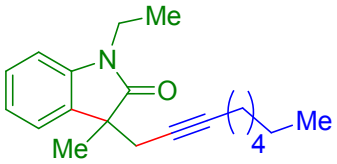
5ba

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.47 (d, *J* = 6.8 Hz, 1 H), 7.39 - 7.14 (m, 6 H), 7.12 - 7.04 (m, 1 H), 6.89 (d, *J* = 7.8 Hz, 1 H), 3.84 (qd, *J* = 7.2, 14.2 Hz, 1 H), 3.72 (qd, *J* = 7.2, 14.2 Hz, 1 H), 2.91 (d, *J* = 16.6 Hz, 1 H), 2.73 (d, *J* = 16.6 Hz, 1 H), 1.51 (s, 3 H), 1.23 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.1, 142.2, 133.5, 131.5, 128.1, 128.1, 127.8, 123.4, 123.3, 122.3, 108.1, 85.4, 82.7, 47.1, 34.6, 28.9, 21.8, 12.7



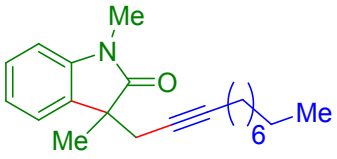
5an

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.41 (dd, *J* = 1.0, 7.3 Hz, 1 H), 7.33 - 7.24 (m, 1 H), 7.12 - 7.03 (m, 1 H), 6.85 (d, *J* = 7.3 Hz, 1 H), 3.22 (s, 3 H), 2.71 - 2.59 (m, 1 H), 2.52 - 2.40 (m, 1 H), 2.12 - 2.03 (m, 2 H), 1.44 (s, 3 H), 1.30 - 1.20 (m, 8 H), 0.90 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.8, 143.1, 133.5, 127.9, 123.1, 122.4, 107.8, 82.7, 75.2, 47.2, 31.7, 28.8, 28.8, 28.6, 28.2, 26.1, 22.6, 21.7, 18.6, 14.0



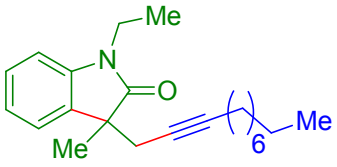
5bn

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.39 (dd, *J* = 1.0, 7.3 Hz, 1 H), 7.31 - 7.22 (m, 1 H), 7.09 - 7.01 (m, 1 H), 6.86 (d, *J* = 7.8 Hz, 1 H), 3.88 - 3.66 (m, 2 H), 2.64 (td, *J* = 2.4, 16.6 Hz, 1 H), 2.48 (td, *J* = 2.4, 16.3 Hz, 1 H), 2.04 (tt, *J* = 2.4, 6.8 Hz, 2 H), 1.41 (s, 3 H), 1.30 - 1.19 (m, 12 H), 0.88 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.3, 142.2, 133.7, 127.8, 123.3, 122.1, 107.9, 82.5, 75.2, 47.1, 34.5, 31.7, 28.8, 28.6, 28.3, 22.6, 21.8, 18.6, 14.0, 12.7



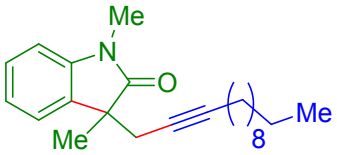
5ak

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.40 (d, *J* = 7.3 Hz, 1 H), 7.28 (dt, *J* = 1.2, 7.7 Hz, 1 H), 7.10 - 7.03 (m, 1 H), 6.84 (d, *J* = 7.8 Hz, 1 H), 3.22 (s, 3 H), 2.65 (td, *J* = 2.4, 16.1 Hz, 1 H), 2.46 (td, *J* = 2.4, 16.1 Hz, 1 H), 2.11 - 2.02 (m, 2 H), 1.43 (s, 3 H), 1.34 - 1.05 (m, 12 H), 0.89 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.7, 143.1, 133.5, 127.9, 123.1, 122.4, 107.8, 82.7, 75.2, 47.2, 31.8, 29.1, 29.1, 28.8, 28.7, 28.2, 26.1, 22.6, 21.7, 18.6, 14.0



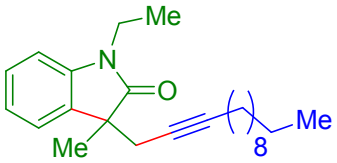
5bk

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.43 - 7.35 (m, 1 H), 7.31 - 7.24 (m, 1 H), 7.09 - 7.02 (m, 1 H), 6.87 (d, *J* = 7.8 Hz, 1 H), 3.87 - 3.67 (m, 2 H), 2.65 (td, *J* = 2.4, 16.1 Hz, 1 H), 2.48 (td, *J* = 2.4, 16.3 Hz, 1 H), 2.05 (tt, *J* = 2.3, 7.0 Hz, 2 H), 1.42 (s, 3 H), 1.31 - 1.16 (m, 15 H), 0.89 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.3, 142.2, 133.7, 127.8, 123.3, 122.1, 107.9, 82.5, 75.2, 47.1, 34.5, 31.8, 29.1, 29.1, 28.8, 28.7, 28.3, 22.6, 21.8, 18.6, 14.1, 12.7



5al

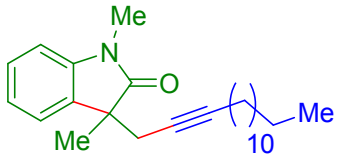
^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.41 (dd, *J* = 1.0, 7.3 Hz, 1 H), 7.32 - 7.24 (m, 1 H), 7.11 - 7.03 (m, 1 H), 6.84 (d, *J* = 7.8 Hz, 1 H), 3.22 (s, 3 H), 2.65 (td, *J* = 2.4, 16.1 Hz, 1 H), 2.46 (td, *J* = 2.4, 16.1 Hz, 1 H), 2.11 - 2.03 (m, 2 H), 1.43 (s, 3 H), 1.32 - 1.18 (m, 16 H), 0.92 - 0.86 (m, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.7, 143.1, 133.5, 127.9, 123.1, 122.3, 107.8, 82.7, 75.2, 47.2, 31.9, 29.6, 29.5, 29.3, 29.1, 28.8, 28.7, 28.2, 26.1, 22.6, 21.7, 18.6, 14.1



5bl

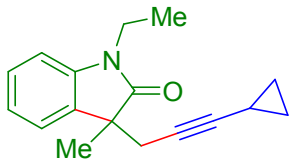
^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.39 (dd, *J* = 1.0, 7.3 Hz, 1 H), 7.31 - 7.23 (m, 1 H), 7.09 - 7.01 (m, 1 H), 6.86 (d, *J* = 7.8 Hz, 1 H), 3.88 - 3.67 (m, 2 H), 2.64 (td, *J* = 2.4, 16.1 Hz, 1 H), 2.48 (td, *J* = 2.4, 16.3 Hz, 1 H), 2.04 (tt, *J* = 2.4, 6.8 Hz, 2 H), 1.42 (s, 3 H), 1.30 - 1.18 (m, 20 H), 0.92 - 0.85 (m, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.3, 142.2,

133.7, 127.8, 123.3, 122.1, 107.9, 82.5, 75.2, 47.1, 34.5, 31.9, 29.6, 29.5, 29.3, 29.1, 28.8, 28.7, 28.3, 22.6, 21.8, 18.6, 14.1, 12.7



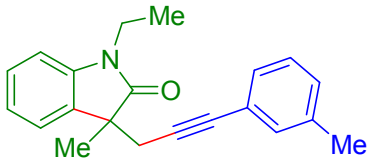
5am

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.41 (d, *J* = 7.3 Hz, 1 H), 7.28 (dt, *J* = 1.2, 7.7 Hz, 1 H), 7.11 - 7.04 (m, 1 H), 6.84 (d, *J* = 7.8 Hz, 1 H), 3.22 (s, 3 H), 2.65 (td, *J* = 2.4, 16.1 Hz, 1 H), 2.46 (td, *J* = 2.4, 16.1 Hz, 1 H), 2.11 - 2.03 (m, 2 H), 1.43 (s, 3 H), 1.30 - 1.20 (m, 21 H), 0.91 - 0.86 (m, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.7, 143.1, 133.5, 127.9, 123.1, 122.4, 107.8, 82.7, 75.2, 47.2, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.1, 28.8, 28.7, 28.2, 26.1, 22.7, 21.7, 18.6, 14.1



5bh

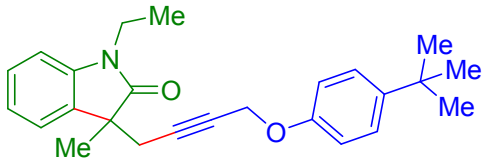
^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.37 (d, *J* = 7.3 Hz, 1 H), 7.28 (dt, *J* = 1.2, 7.7 Hz, 1 H), 7.10 - 7.02 (m, 1 H), 6.87 (d, *J* = 7.8 Hz, 1 H), 3.83 (qd, *J* = 7.2, 14.2 Hz, 1 H), 3.71 (qd, *J* = 7.2, 14.2 Hz, 1 H), 2.61 (dd, *J* = 2.0, 16.6 Hz, 1 H), 2.44 (dd, *J* = 2.0, 16.1 Hz, 1 H), 1.40 (s, 3 H), 1.27 (t, *J* = 7.3 Hz, 4 H), 1.14 - 1.04 (m, 1 H), 0.68 - 0.59 (m, 2 H), 0.50 - 0.40 (m, 2 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.3, 142.2, 133.7, 127.8, 123.3, 122.1, 107.9, 85.6, 70.5, 47.1, 34.6, 28.3, 21.6, 12.7, 7.9, 7.8, -0.6



5bc

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.53 - 7.44 (m, 1 H), 7.31 (dt, *J* = 1.2, 7.7 Hz, 1 H), 7.18 - 7.05 (m, 5 H), 6.90 (d, *J* = 7.8 Hz, 1 H), 3.85 (qd, *J* = 7.2, 14.2 Hz, 1 H), 3.74 (qd, *J* = 7.2, 14.2 Hz, 1 H), 2.92 (d, *J* = 16.1 Hz, 1 H), 2.72 (d, *J* = 16.6 Hz, 1 H), 2.30 (s, 3 H), 1.52 (s, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 179.1, 142.1, 137.8,

133.5, 132.1, 128.7, 128.5, 128.0, 123.4, 123.1, 122.3, 108.1, 85.0, 82.8, 47.1, 34.6, 28.9, 21.7, 21.1, 12.7



5bo

^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.31 - 7.22 (m, 4 H), 7.01 - 6.93 (m, 1 H), 6.89 - 6.73 (m, 3 H), 4.63 - 4.51 (m, 2 H), 3.81 - 3.61 (m, 2 H), 2.72 (td, *J* = 2.0, 16.5 Hz, 1 H), 2.52 (td, *J* = 2.2, 16.6 Hz, 1 H), 1.39 (s, 3 H), 1.30 (s, 9 H), 1.23 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, CHLOROFORM-d) δ = 178.9, 155.4, 143.8, 142.0, 133.2, 128.0, 126.2, 123.4, 122.3, 114.3, 108.1, 83.1, 77.5, 56.0, 46.7, 34.6, 34.0, 31.5, 28.2, 21.7, 12.6

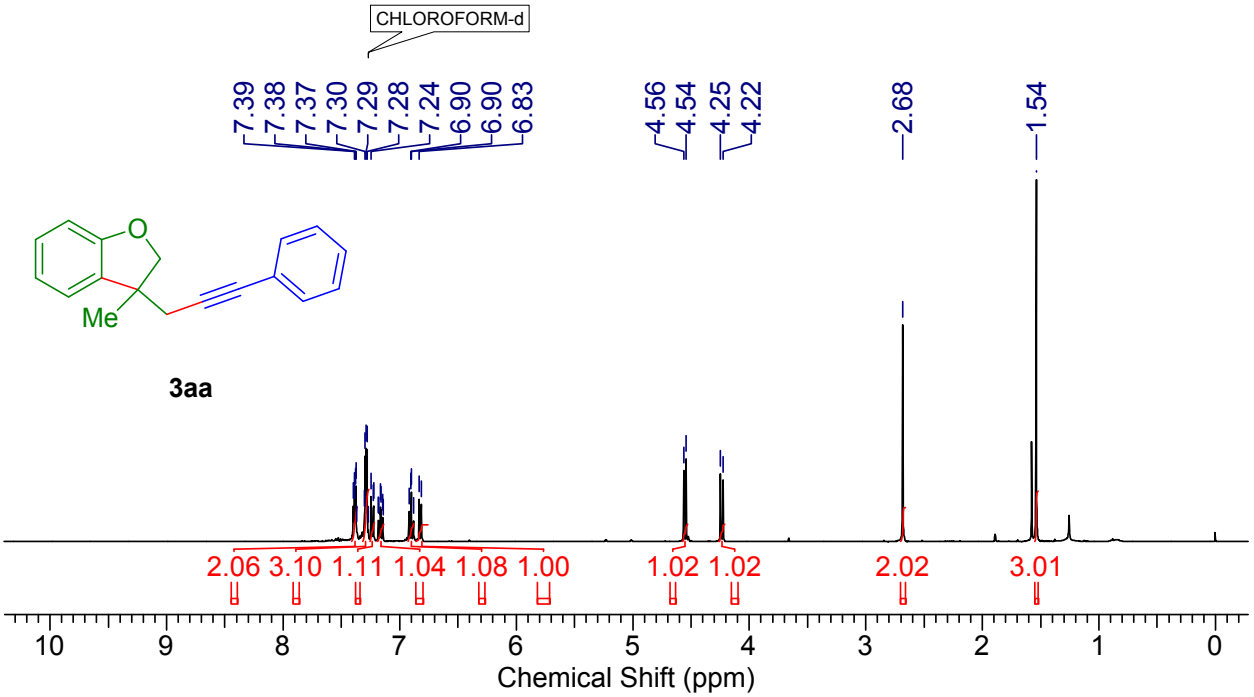


Figure S1A: ^{1}H NMR (400 MHz) spectrum of **3aa** in $CDCl_3$

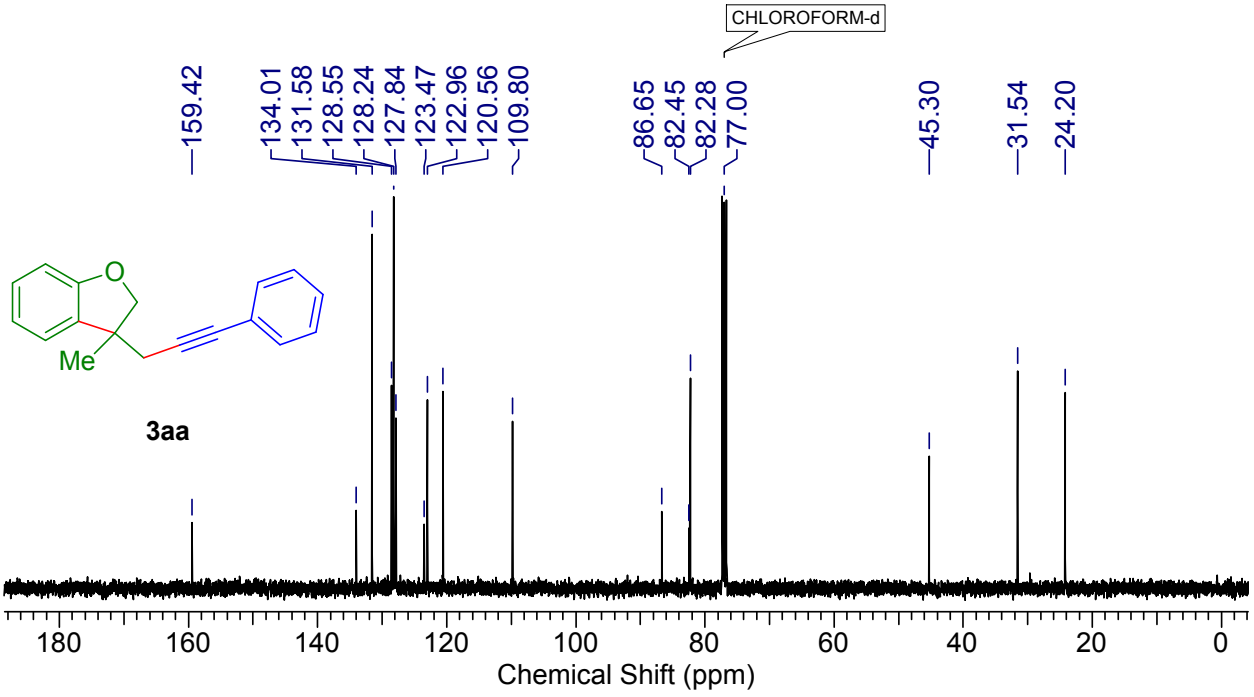


Figure S1B: ^{13}C NMR (400 MHz) spectrum of **3aa** in $CDCl_3$

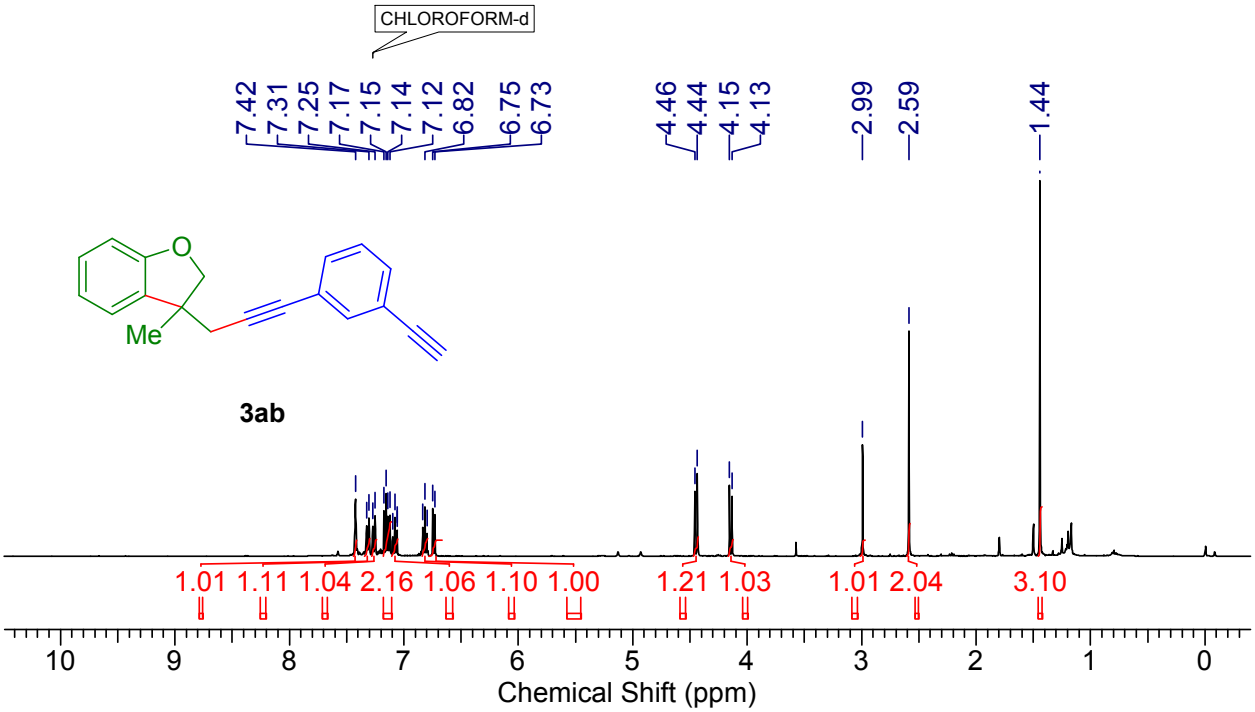


Figure S2A: ^{1}H NMR (400 MHz) spectrum of **3ab** in $CDCl_3$

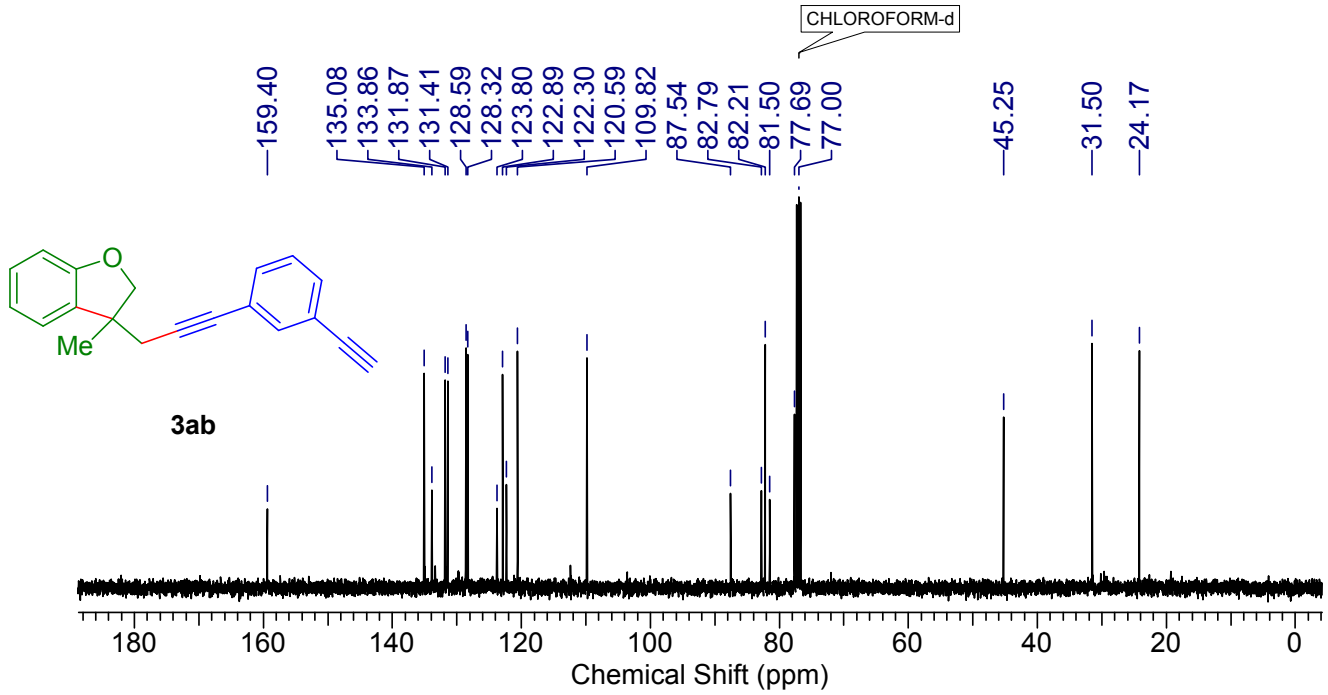


Figure S2B: ^{13}C NMR (400 MHz) spectrum of **3ab** in $CDCl_3$

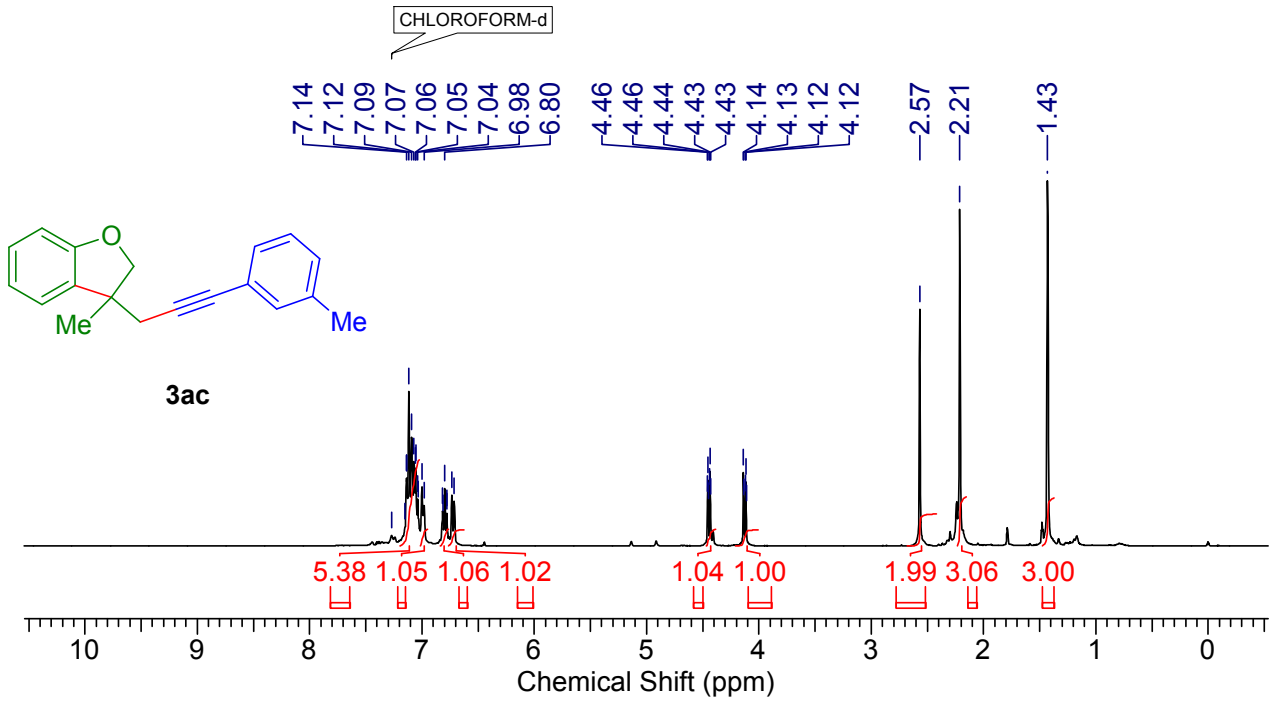


Figure S3A: ^{1}H NMR (400 MHz) spectrum of **3ac** in $CDCl_3$

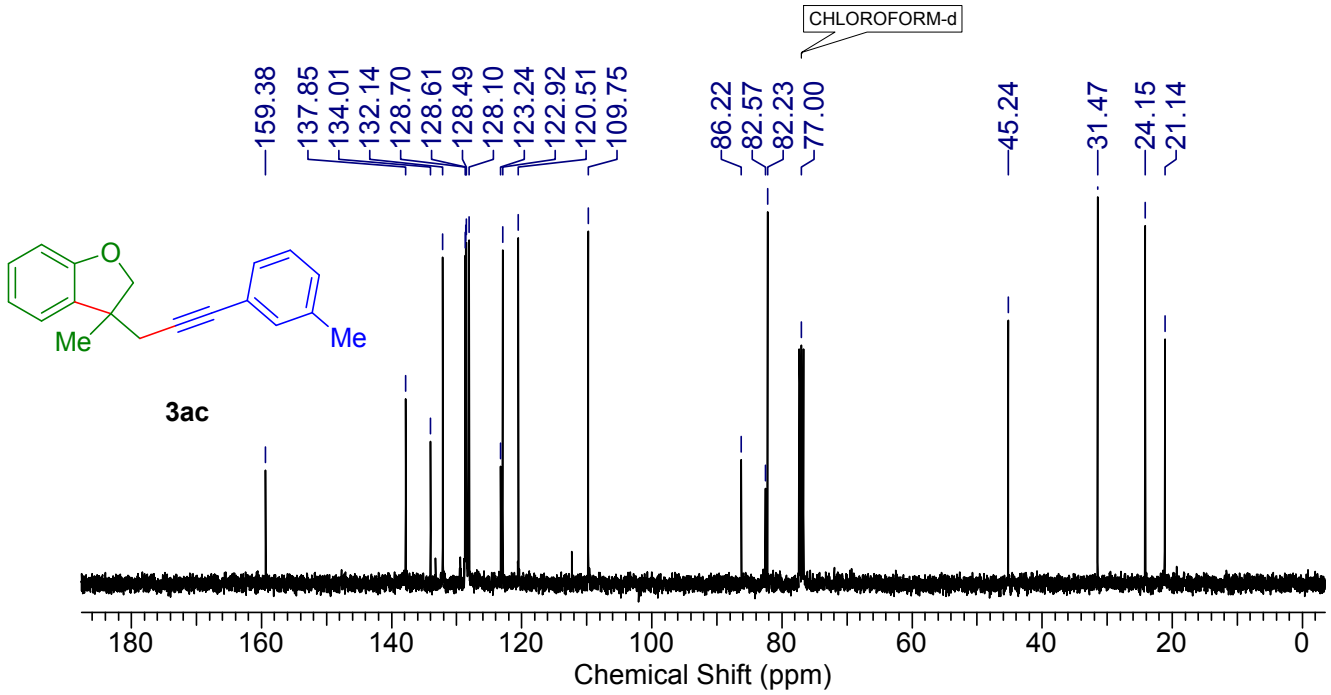


Figure S3B: ^{13}C NMR (400 MHz) spectrum of **3ac** in $CDCl_3$

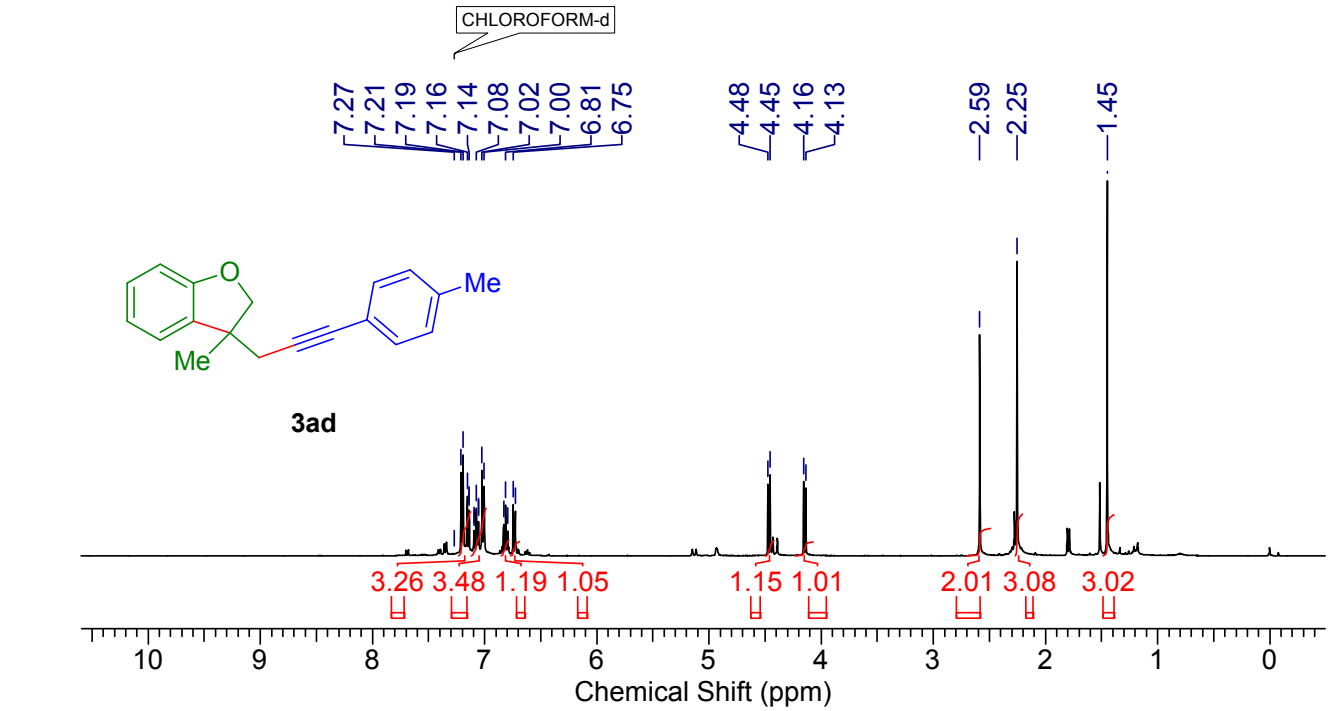


Figure S4A: ^{1}H NMR (400 MHz) spectrum of **3ad** in $CDCl_3$

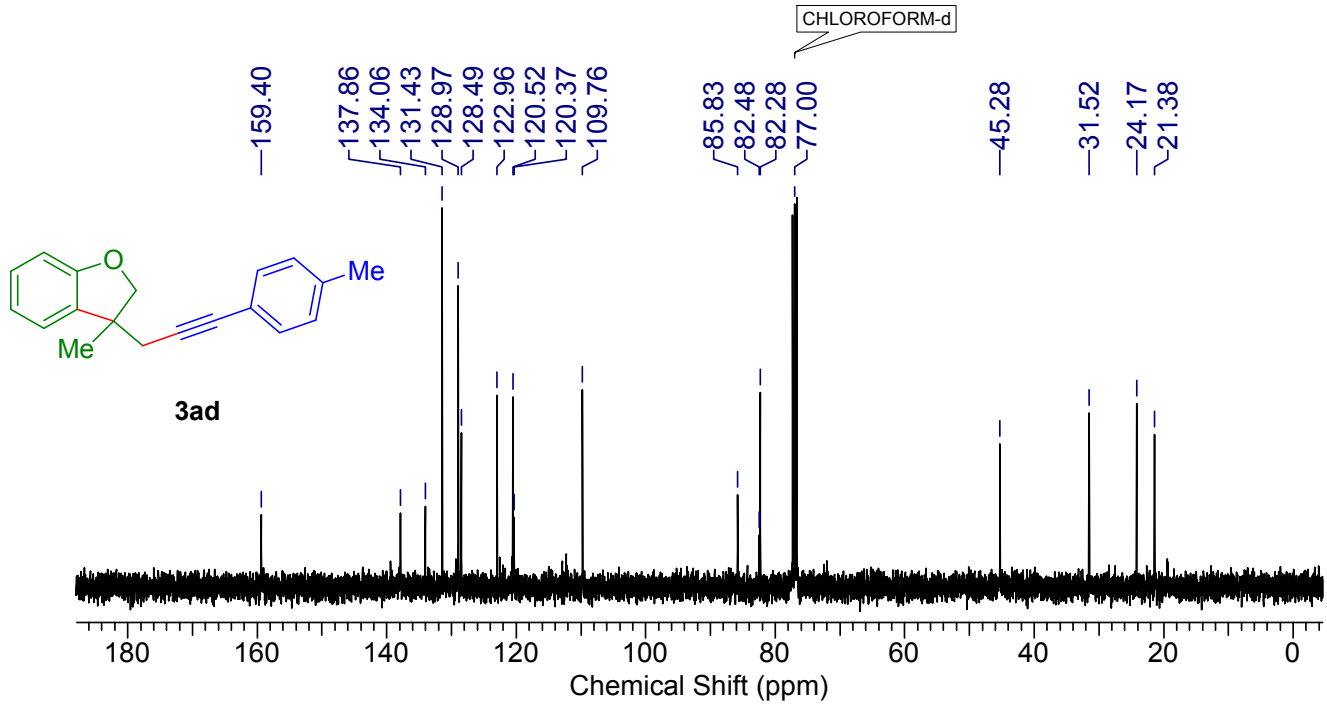


Figure S4B: ^{13}C NMR (400 MHz) spectrum of **3ad** in $CDCl_3$

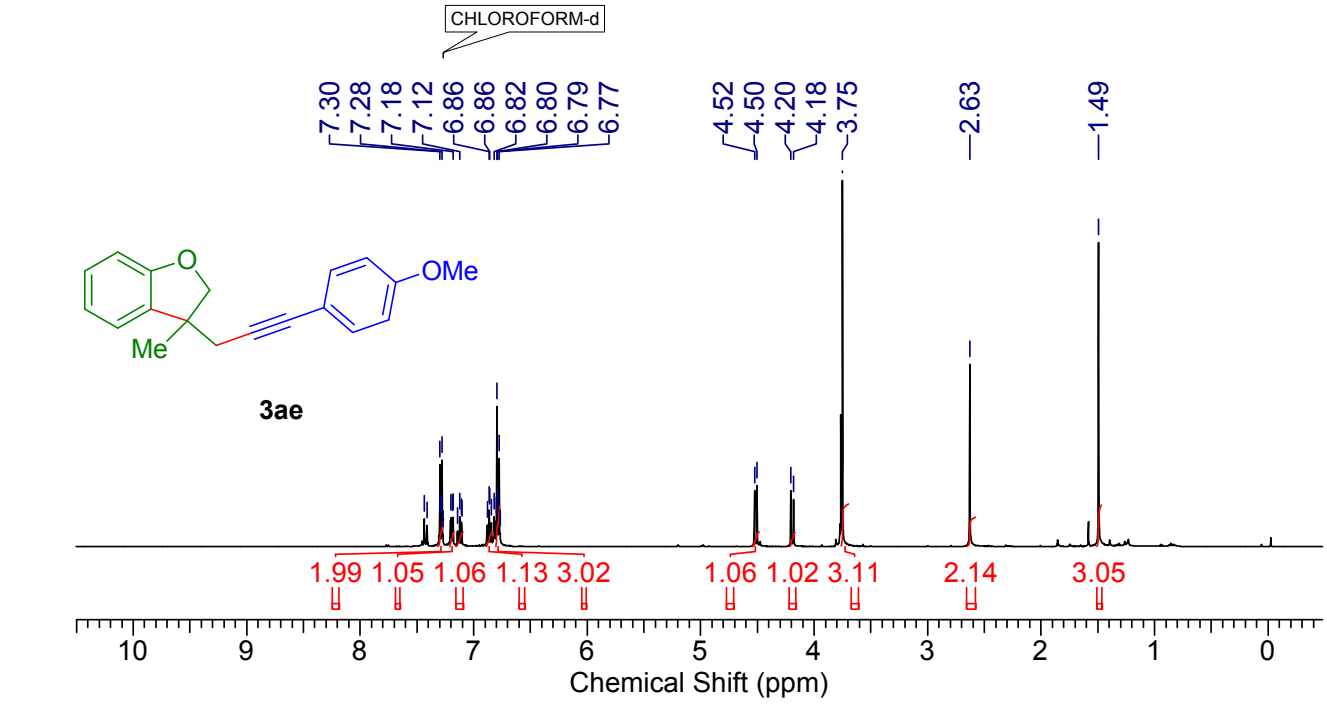


Figure S5A: ^{1}H NMR (400 MHz) spectrum of **3ae** in $CDCl_3$

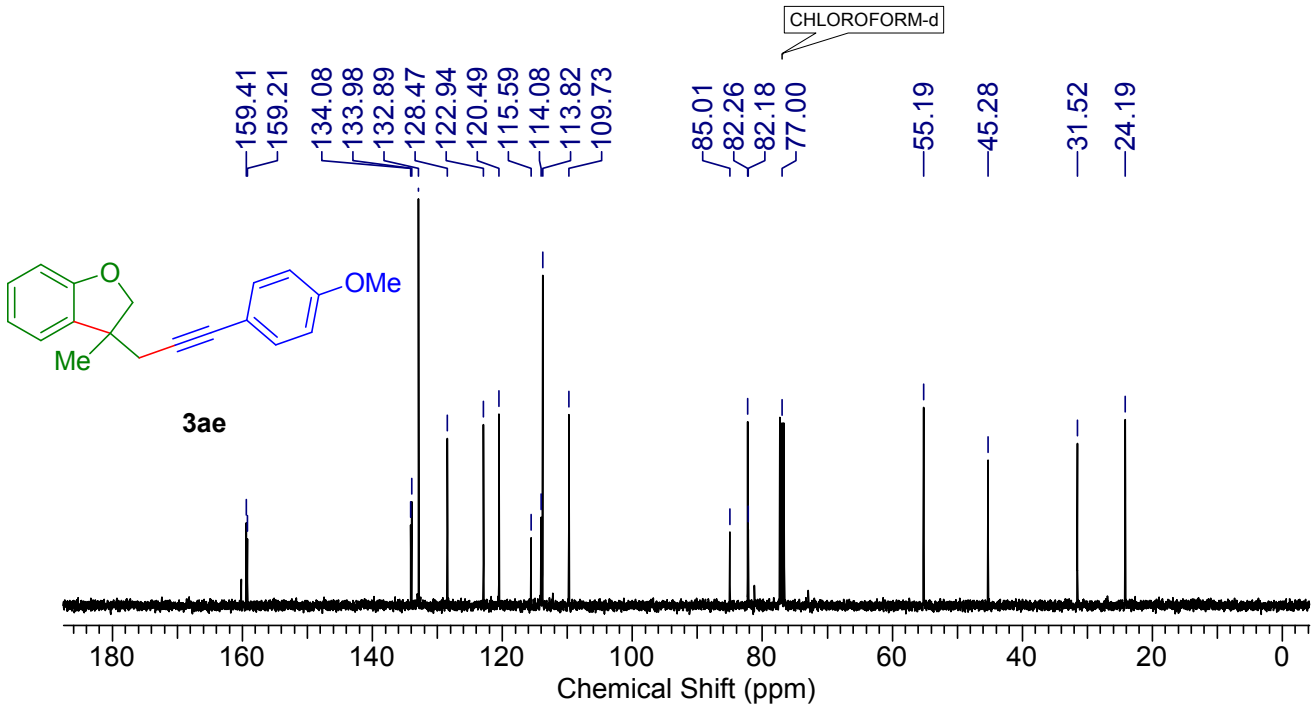


Figure S5B: ^{13}C NMR (400 MHz) spectrum of **3ae** in $CDCl_3$

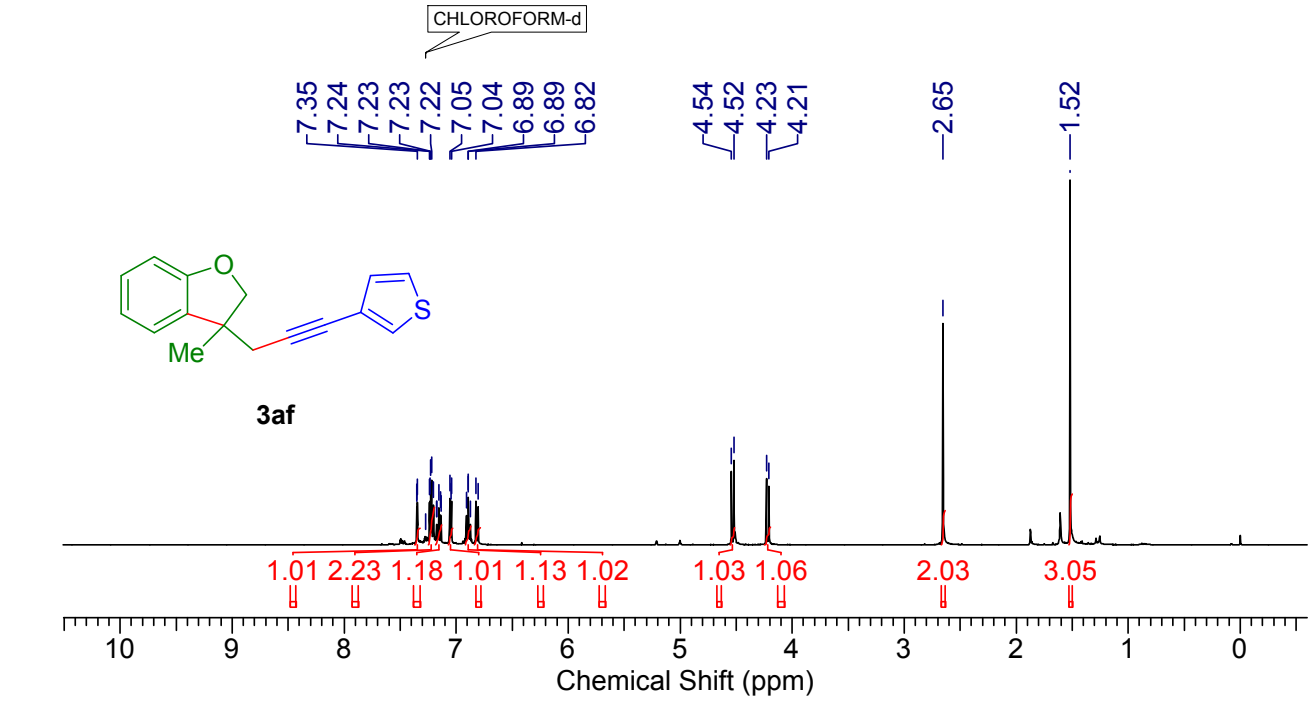


Figure S6A: ^{1}H NMR (400 MHz) spectrum of **3af** in $CDCl_3$

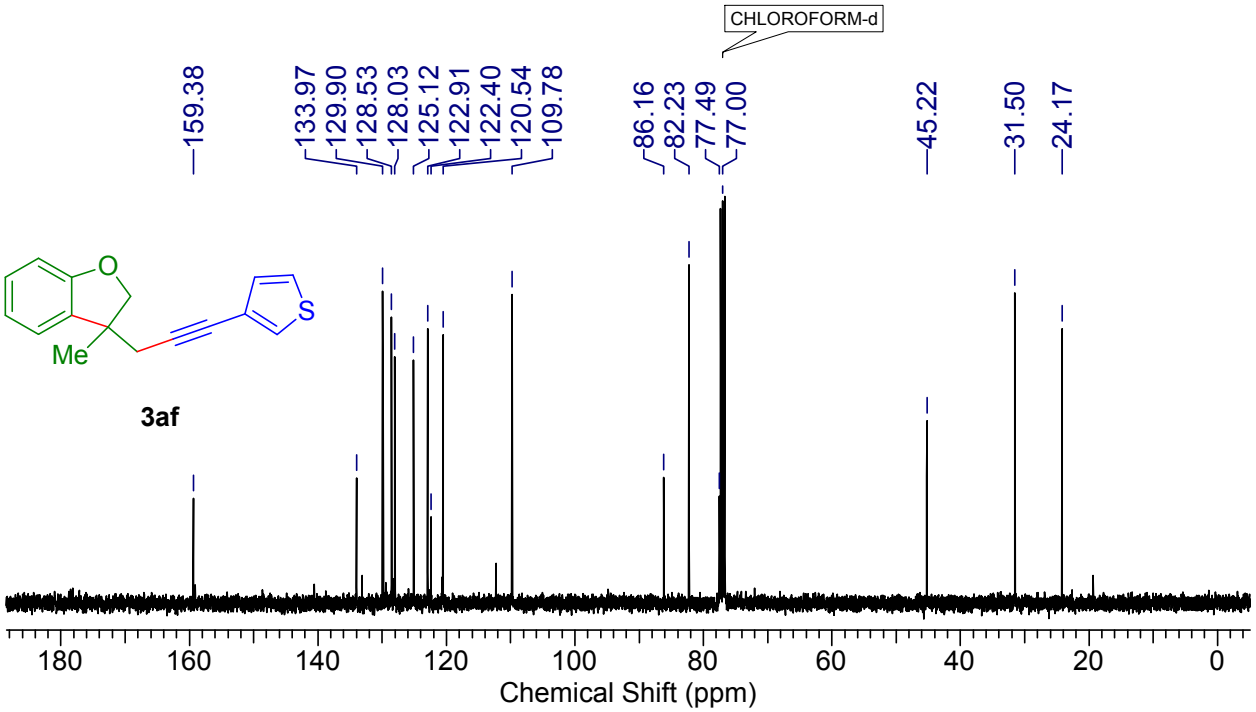


Figure S6B: ^{13}C NMR (400 MHz) spectrum of **3af** in $CDCl_3$

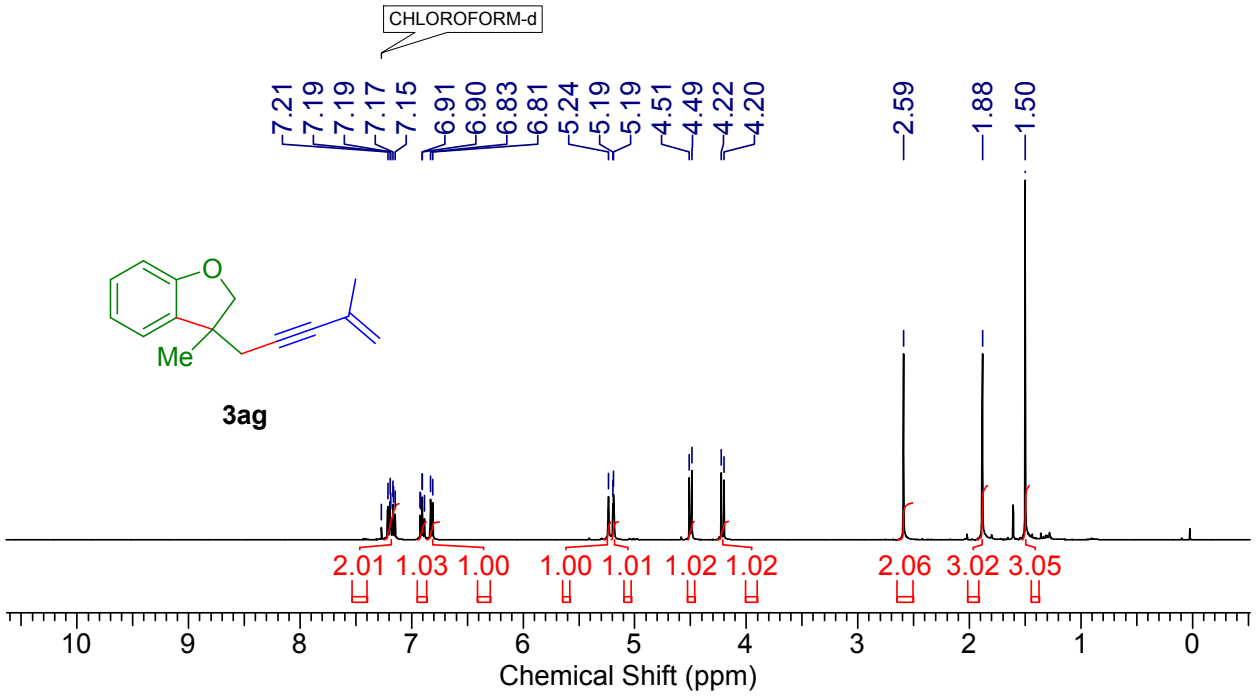


Figure S7A: ^{1}H NMR (400 MHz) spectrum of **3ag** in $CDCl_3$

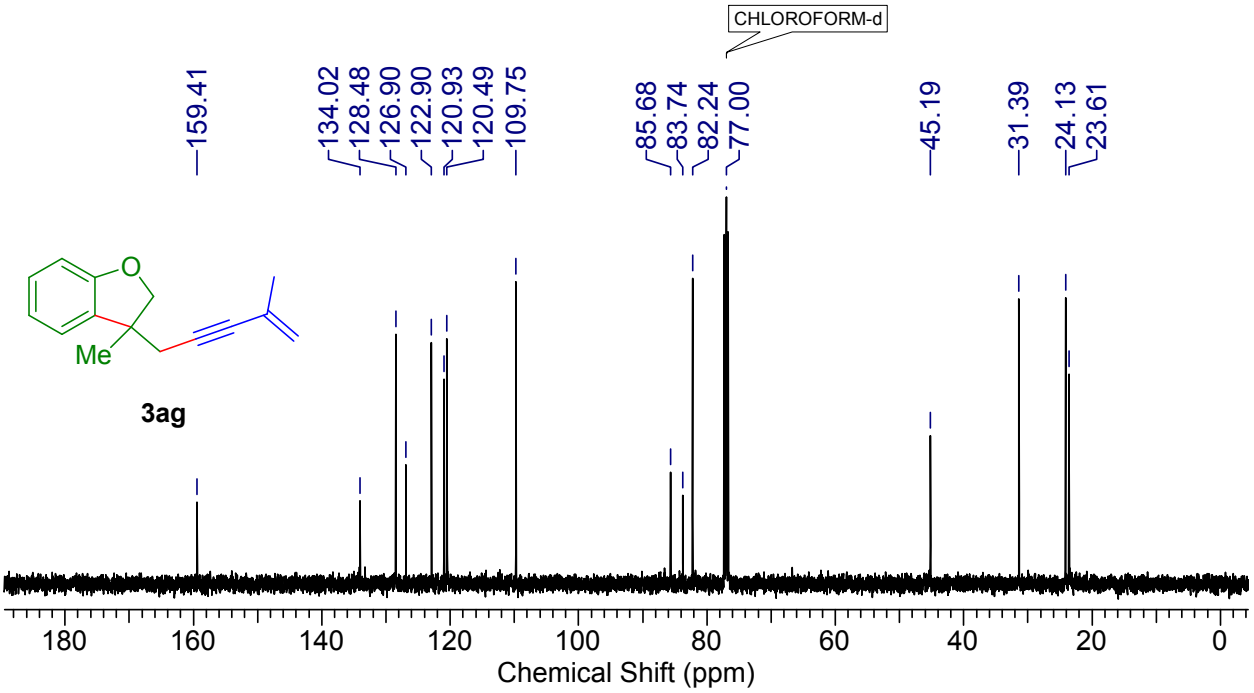


Figure S7B: ^{13}C NMR (400 MHz) spectrum of **3ag** in $CDCl_3$

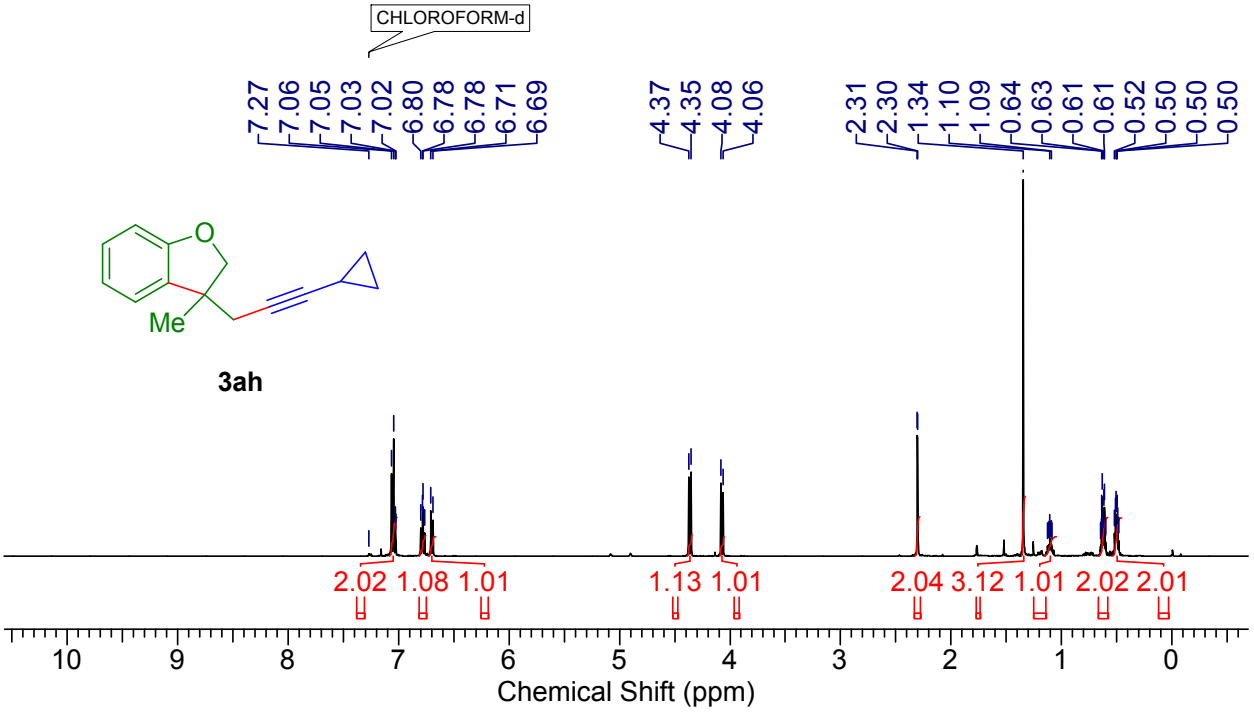


Figure S8A: ^{1}H NMR (400 MHz) spectrum of **3ah** in $CDCl_3$

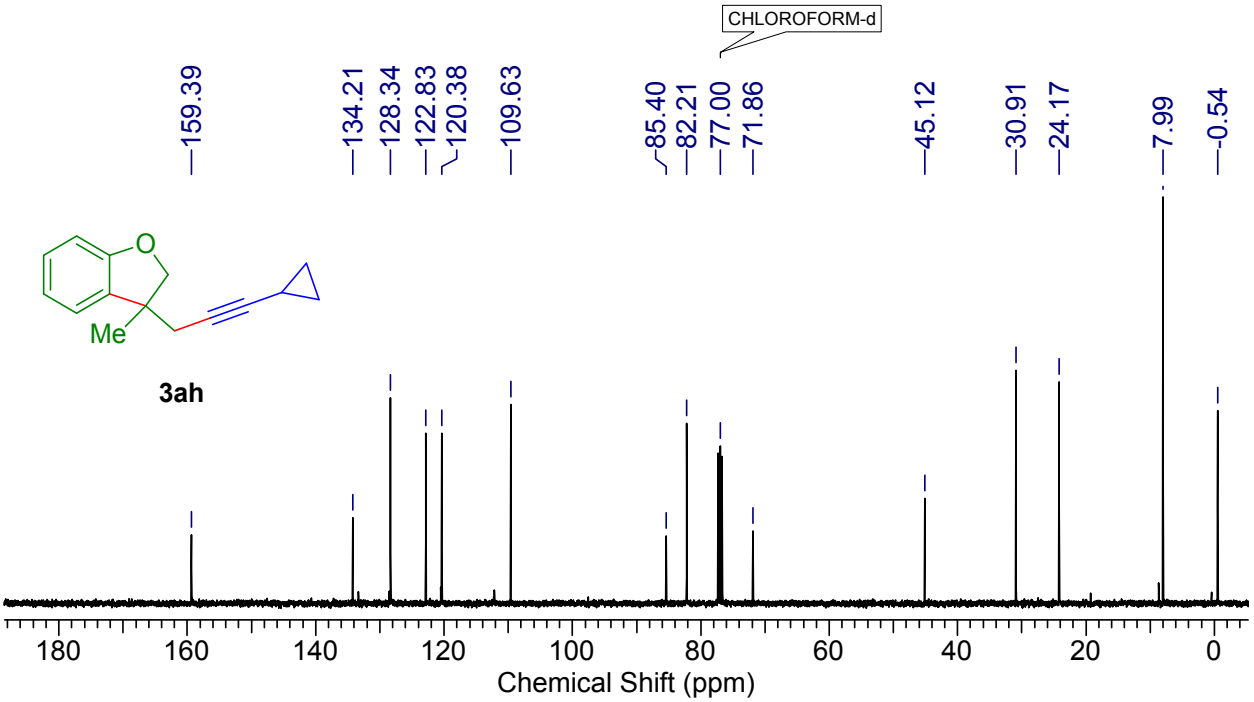


Figure S8B: ^{13}C NMR (400 MHz) spectrum of **3ah** in $CDCl_3$

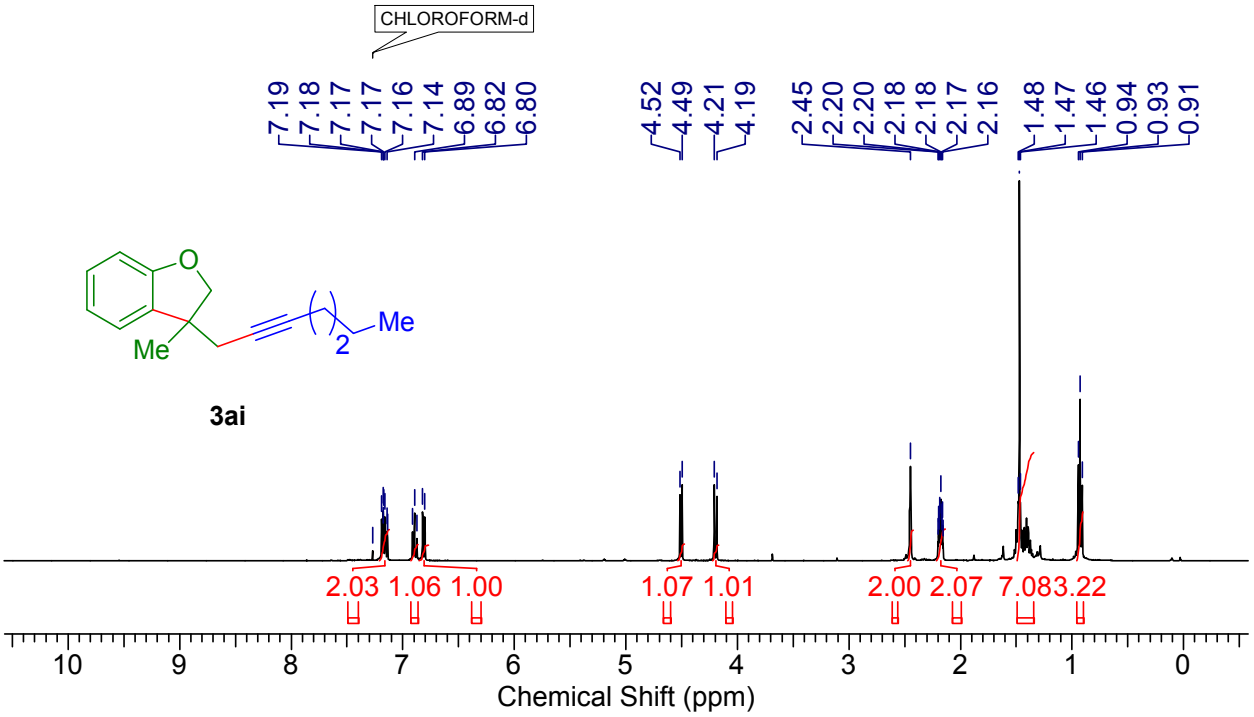


Figure S9A: ^{1}H NMR (400 MHz) spectrum of **3ai** in $CDCl_3$

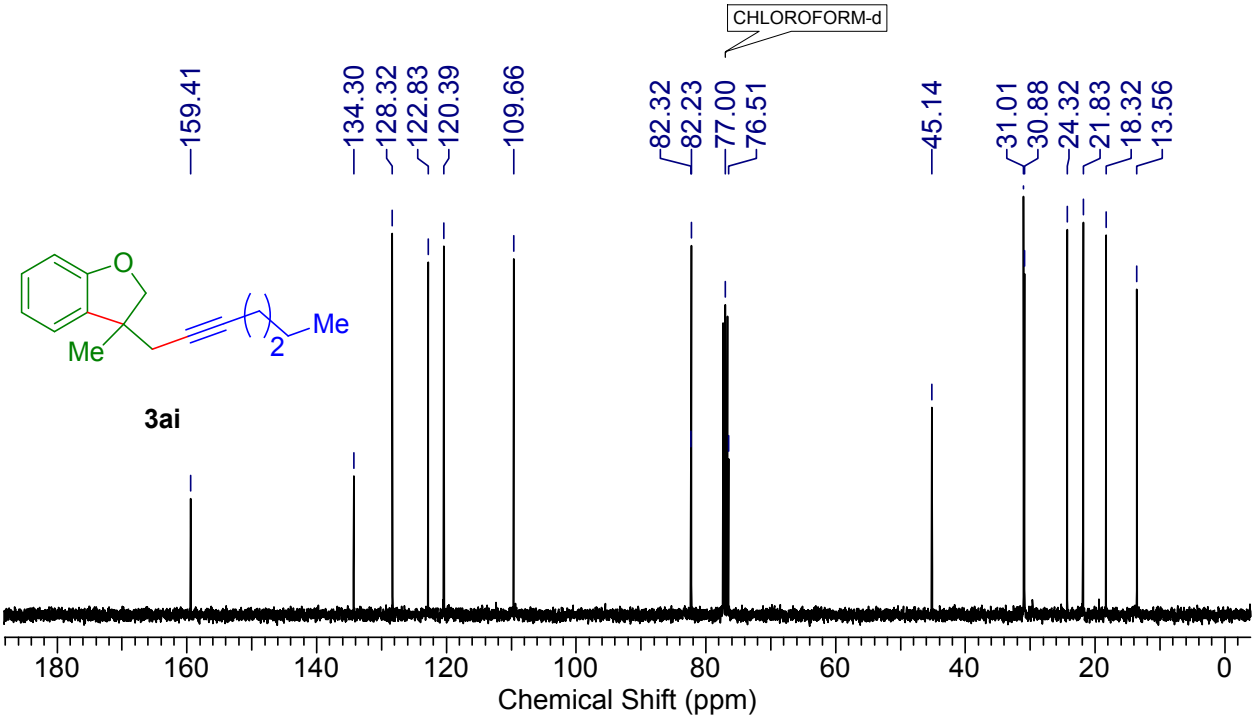


Figure S9B: ^{13}C NMR (400 MHz) spectrum of **3ai** in $CDCl_3$

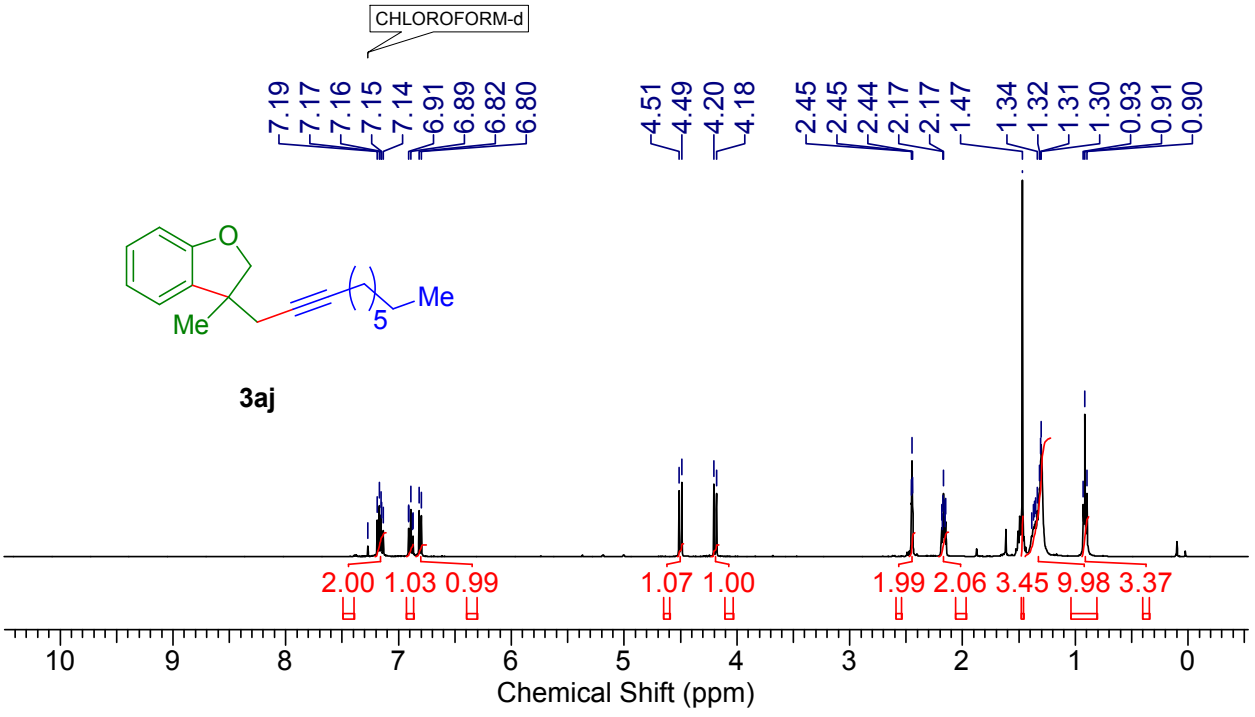


Figure S10A: ^{1}H NMR (400 MHz) spectrum of **3aj** in $CDCl_3$

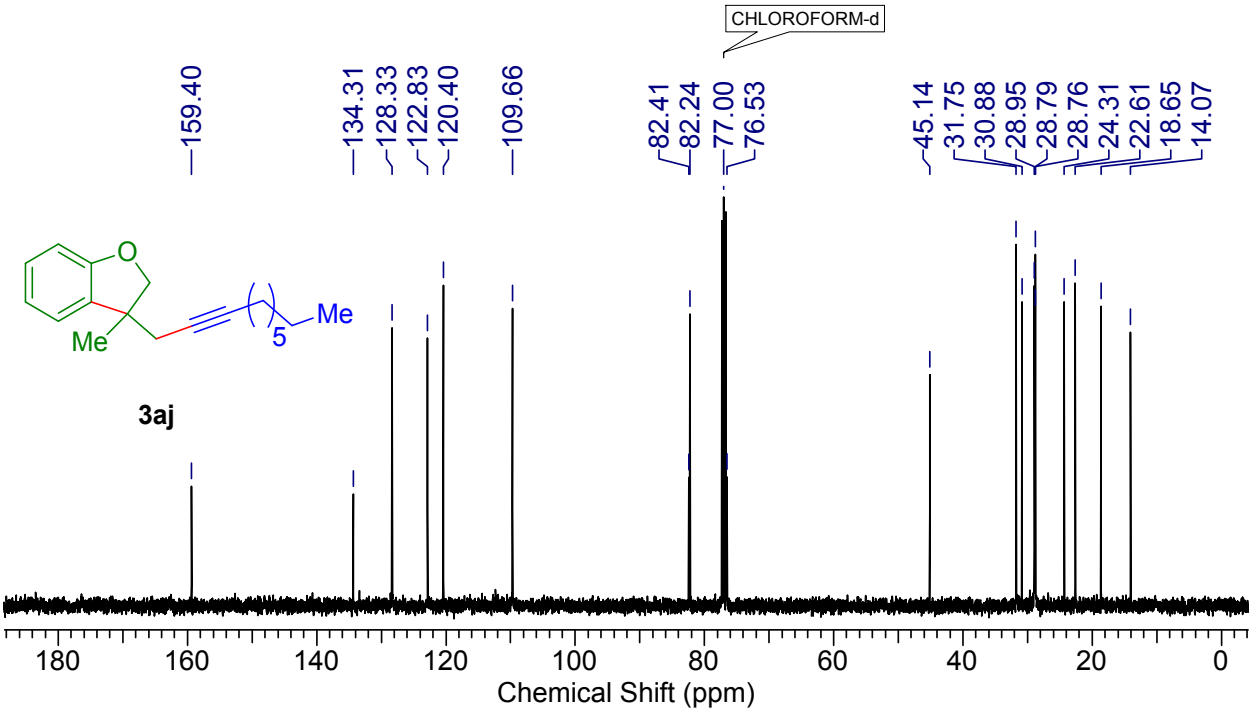


Figure S10B: ^{13}C NMR (400 MHz) spectrum of **3aj** in $CDCl_3$

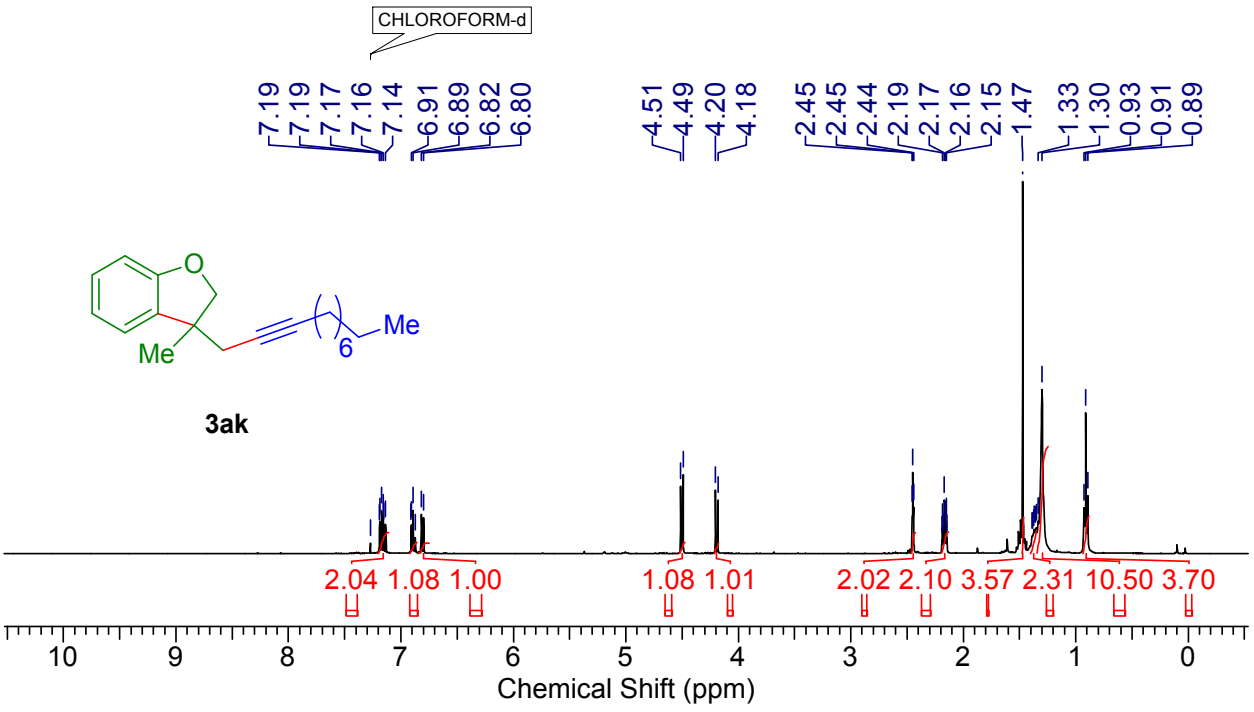


Figure S11A: ^{1}H NMR (400 MHz) spectrum of **3ak** in $CDCl_3$

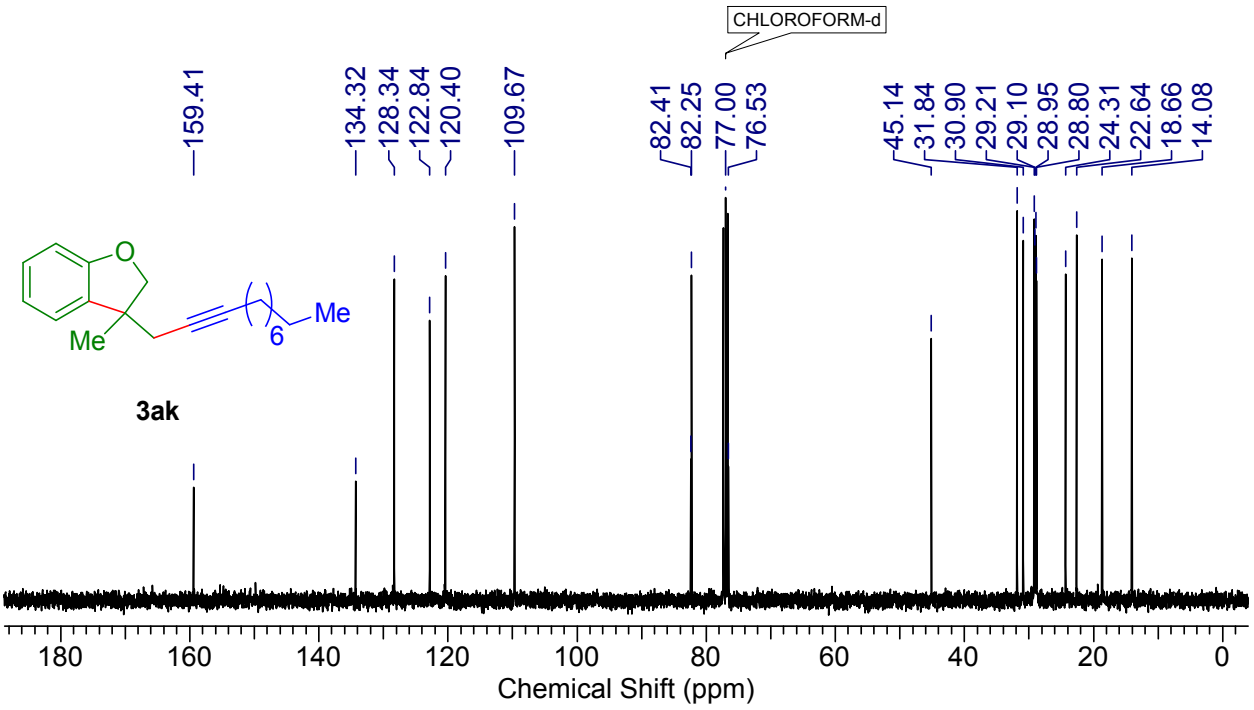


Figure S11B: ^{13}C NMR (400 MHz) spectrum of **3ak** in $CDCl_3$

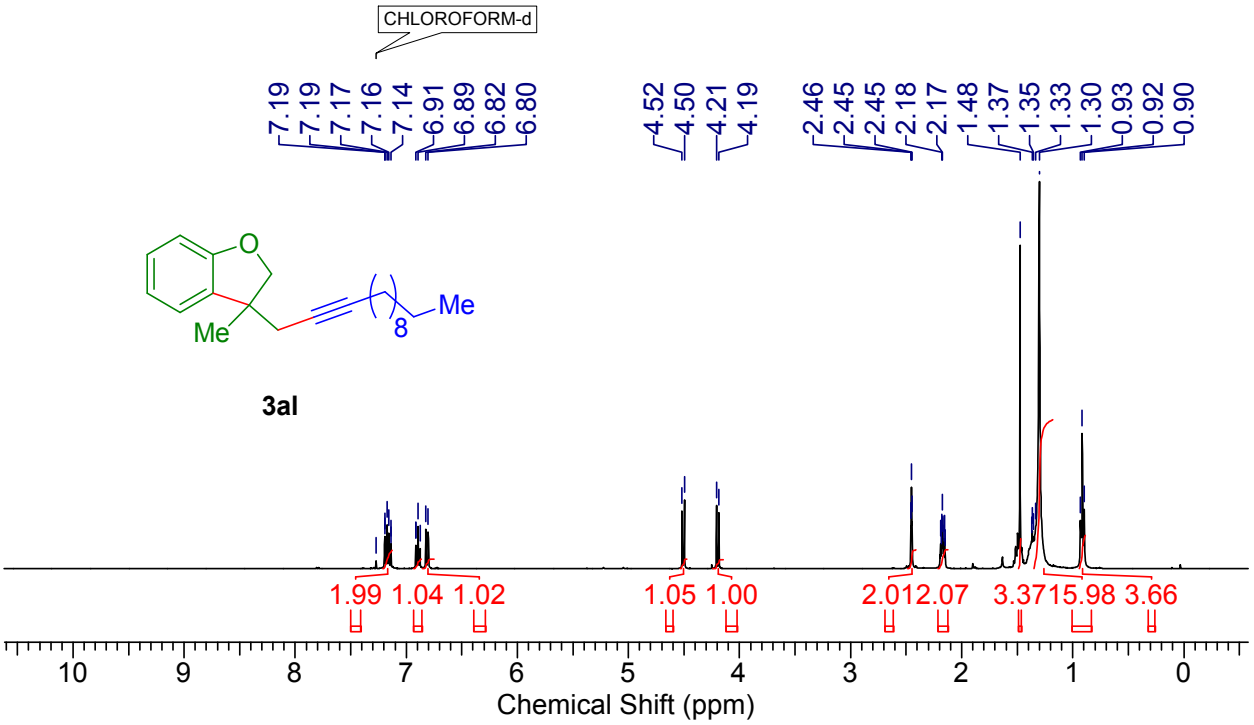


Figure S12A: ^{1}H NMR (400 MHz) spectrum of **3al** in $CDCl_3$

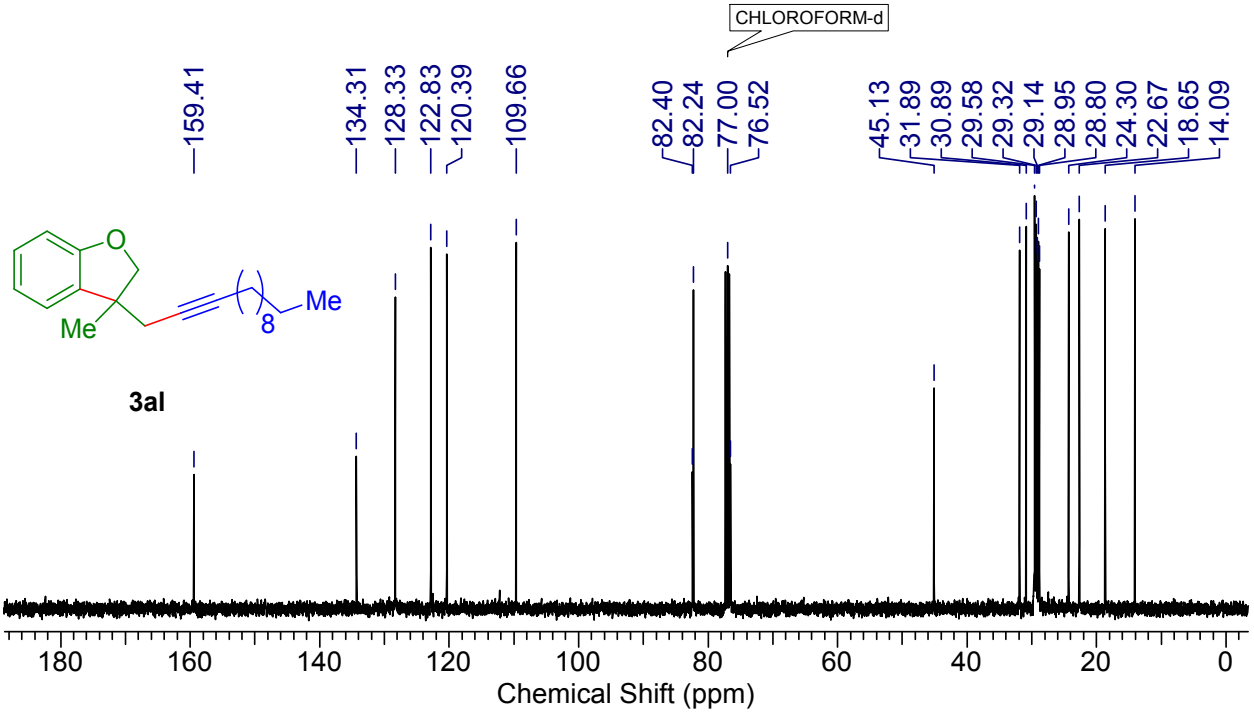


Figure S12B: ^{13}C NMR (400 MHz) spectrum of **3al** in $CDCl_3$

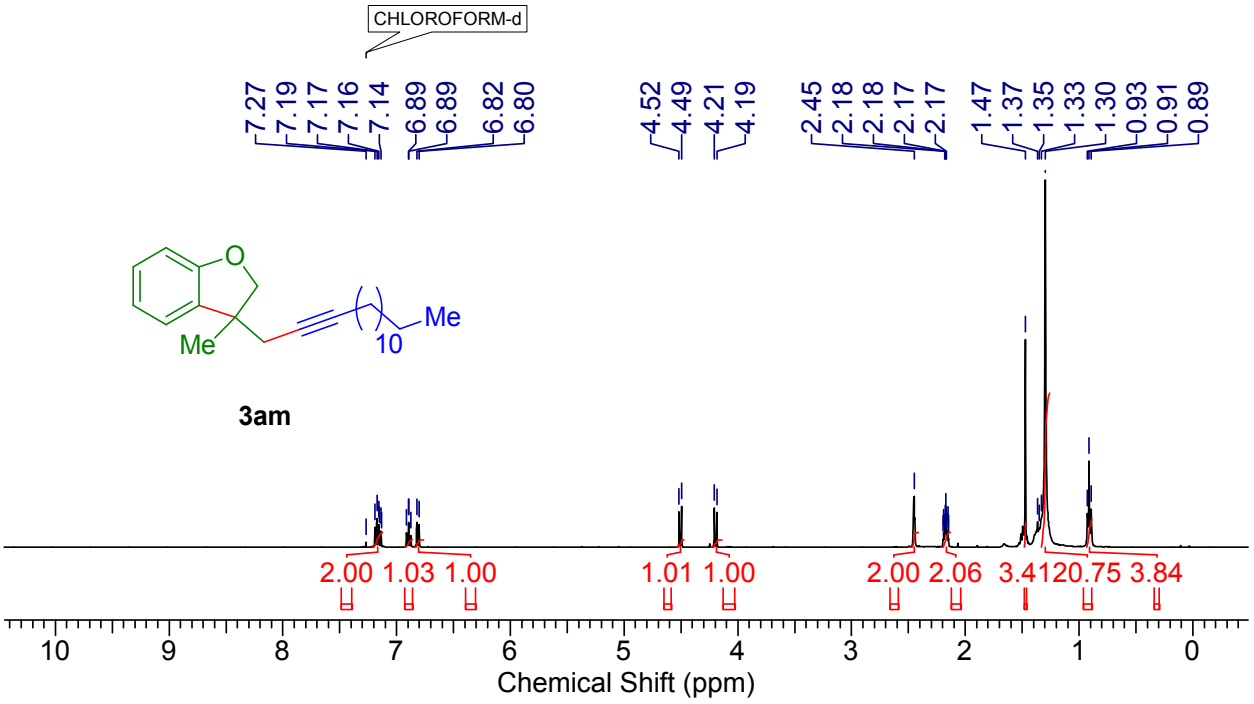


Figure S13A: ^{1}H NMR (400 MHz) spectrum of **3am** in $CDCl_3$

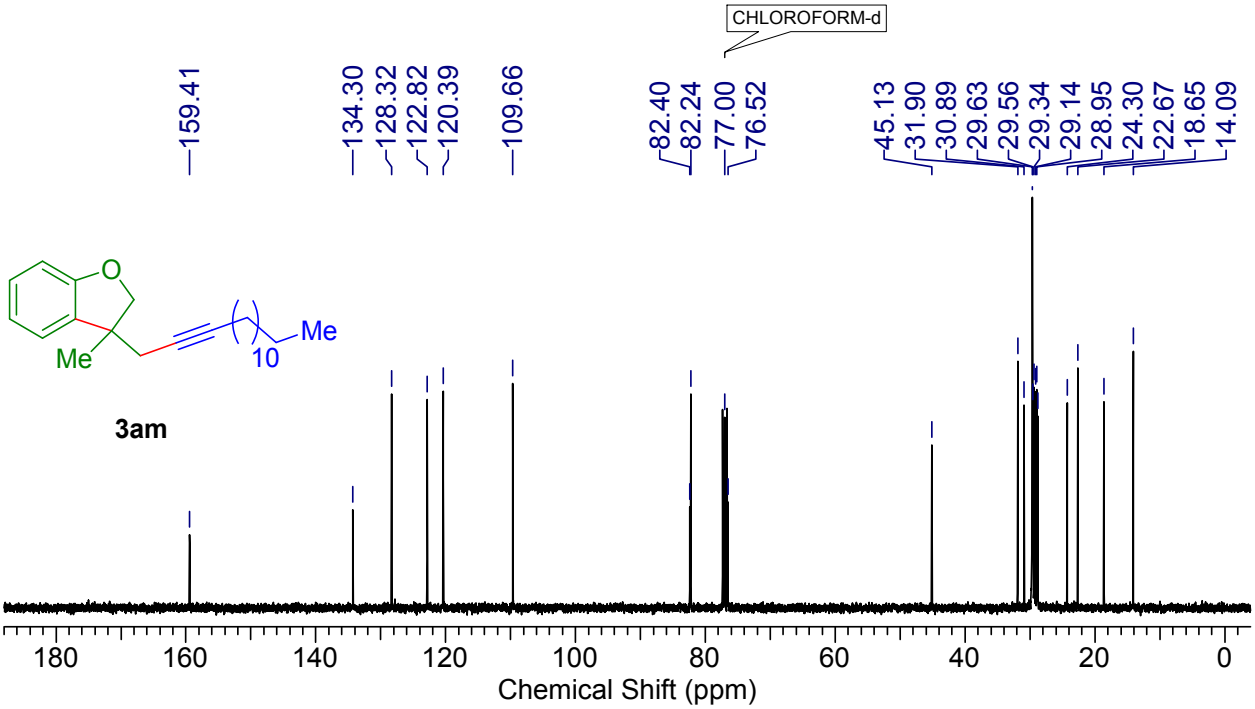


Figure S13B: ^{13}C NMR (400 MHz) spectrum of **3am** in $CDCl_3$

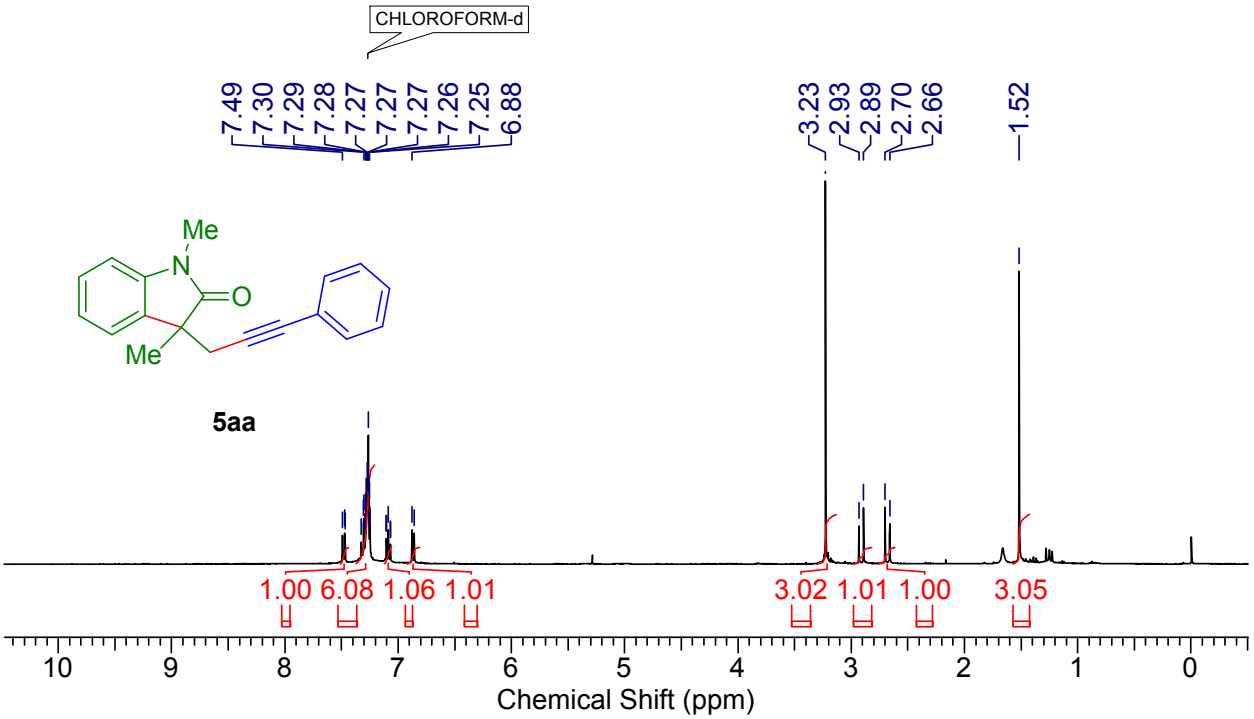


Figure S14A: ^{1}H NMR (400 MHz) spectrum of **5aa** in $CDCl_3$

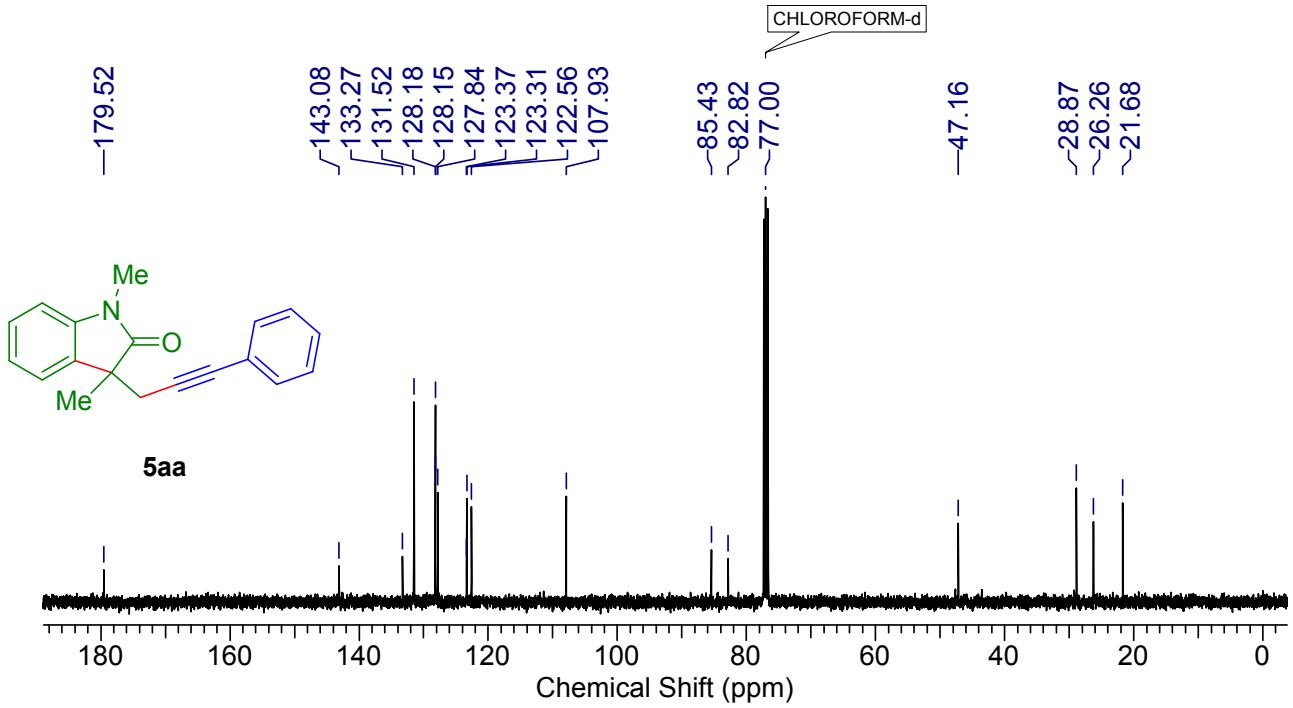


Figure S14B: ^{13}C NMR (400 MHz) spectrum of **5aa** in $CDCl_3$

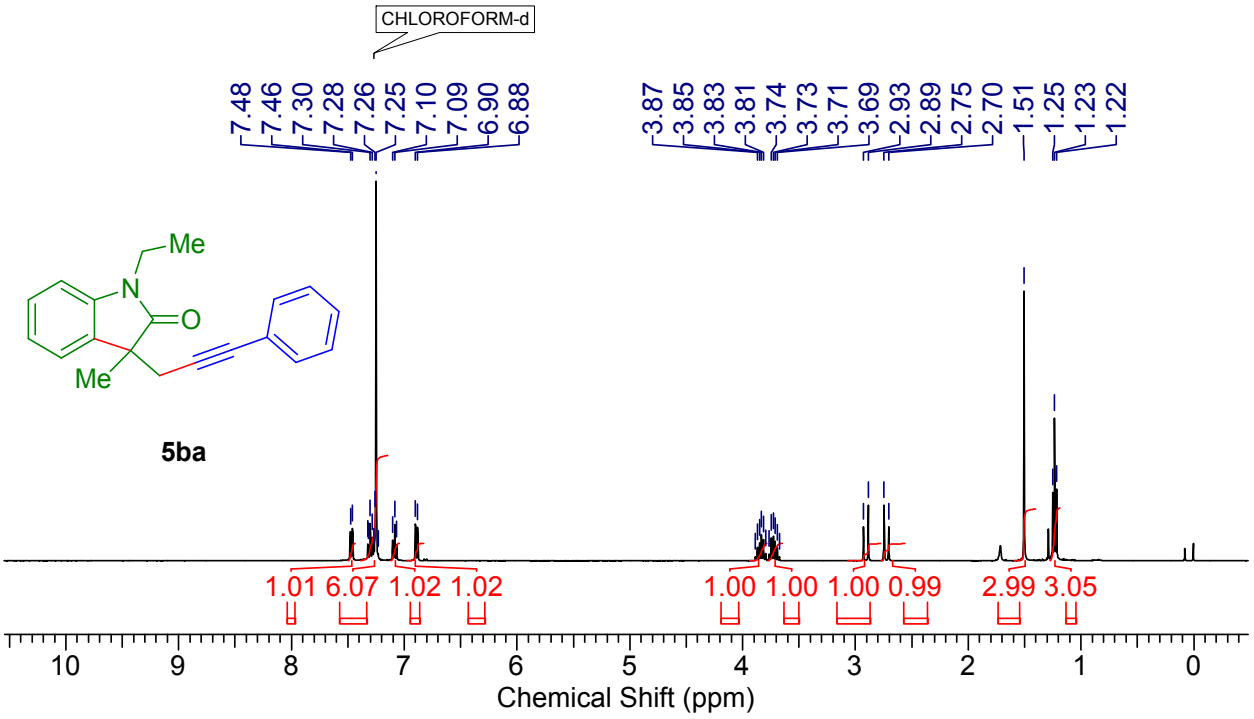


Figure S15A: ^{1}H NMR (400 MHz) spectrum of **5ba** in $CDCl_3$

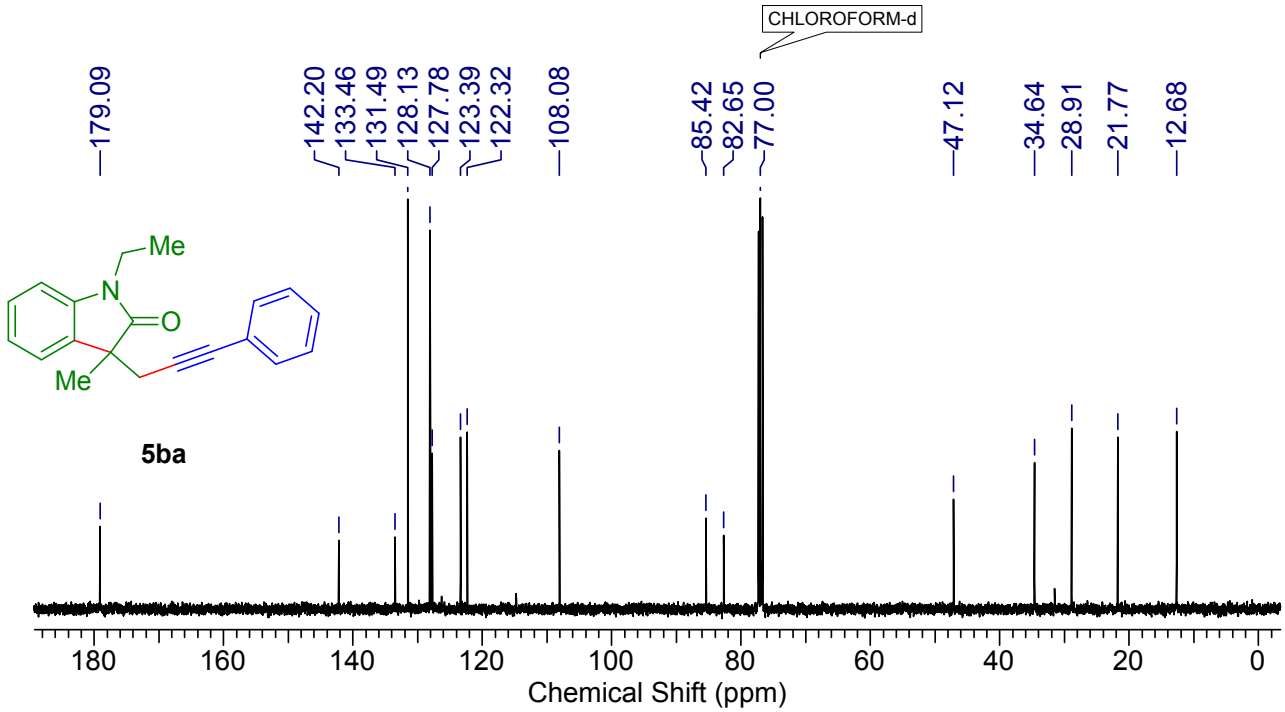


Figure S15B: ^{13}C NMR (400 MHz) spectrum of **5ba** in $CDCl_3$

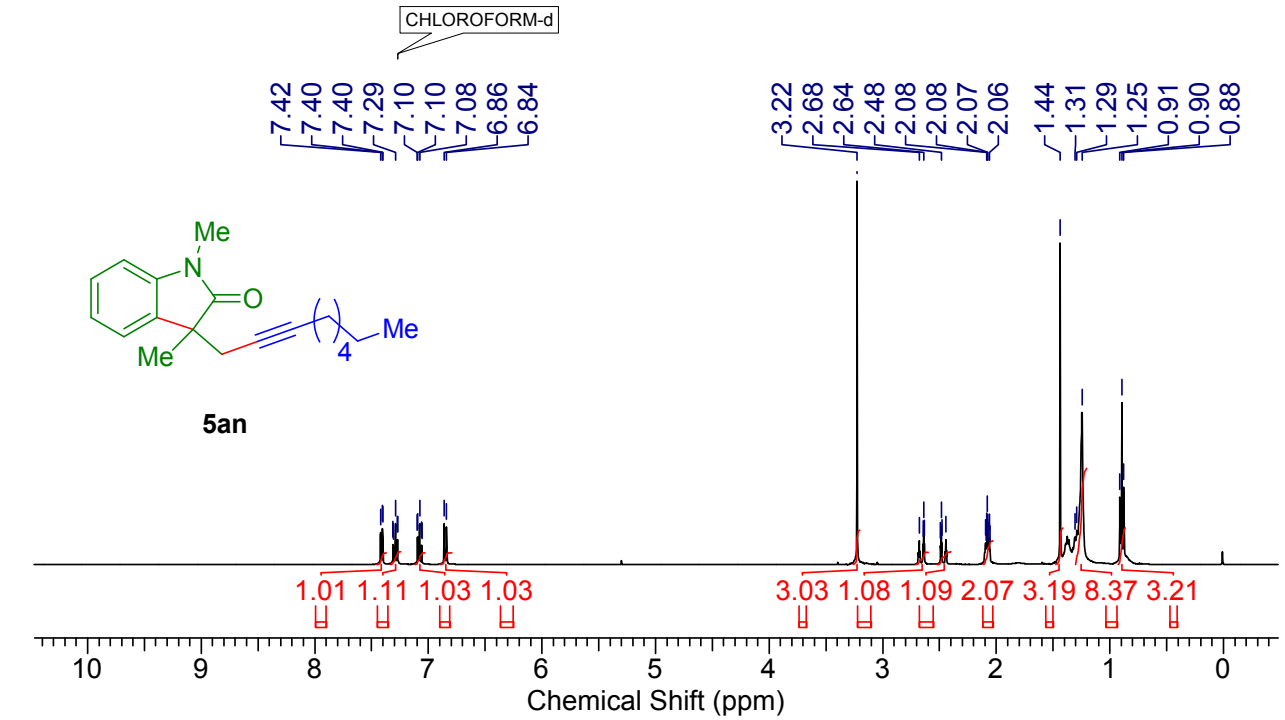


Figure S16A: ^{1}H NMR (400 MHz) spectrum of **5an** in $CDCl_3$

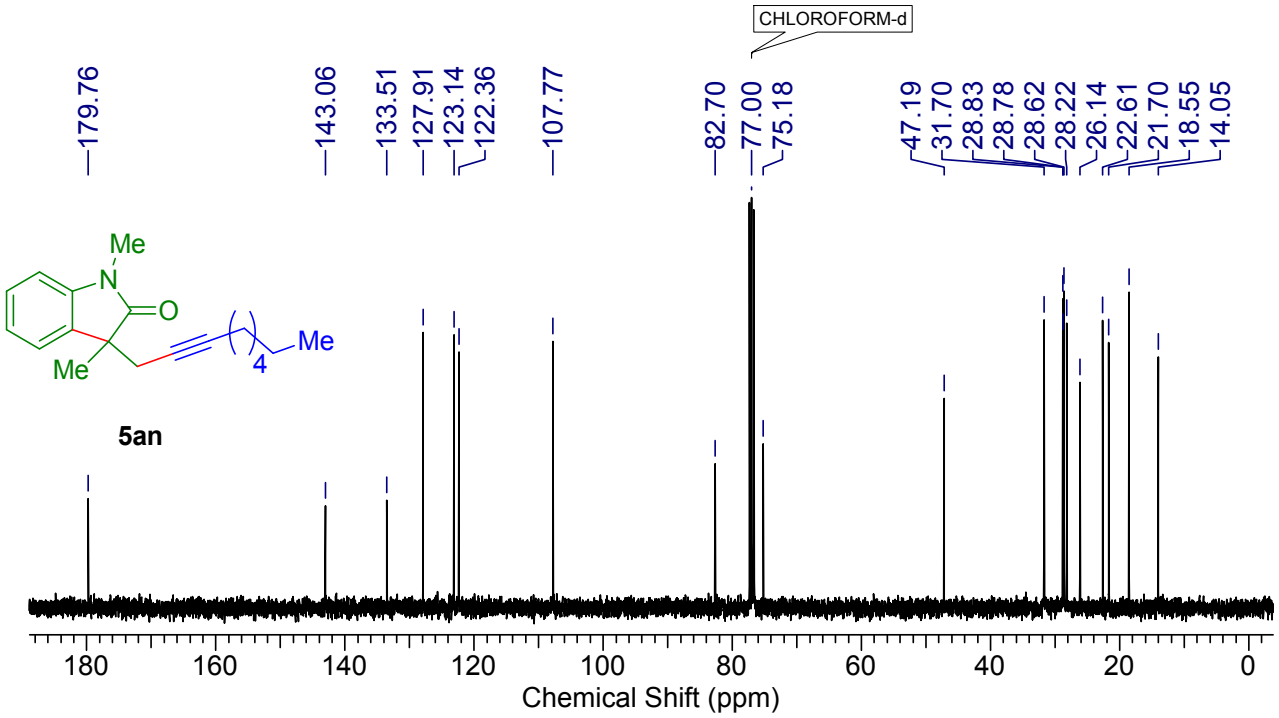


Figure S16B: ^{13}C NMR (400 MHz) spectrum of **5an** in $CDCl_3$

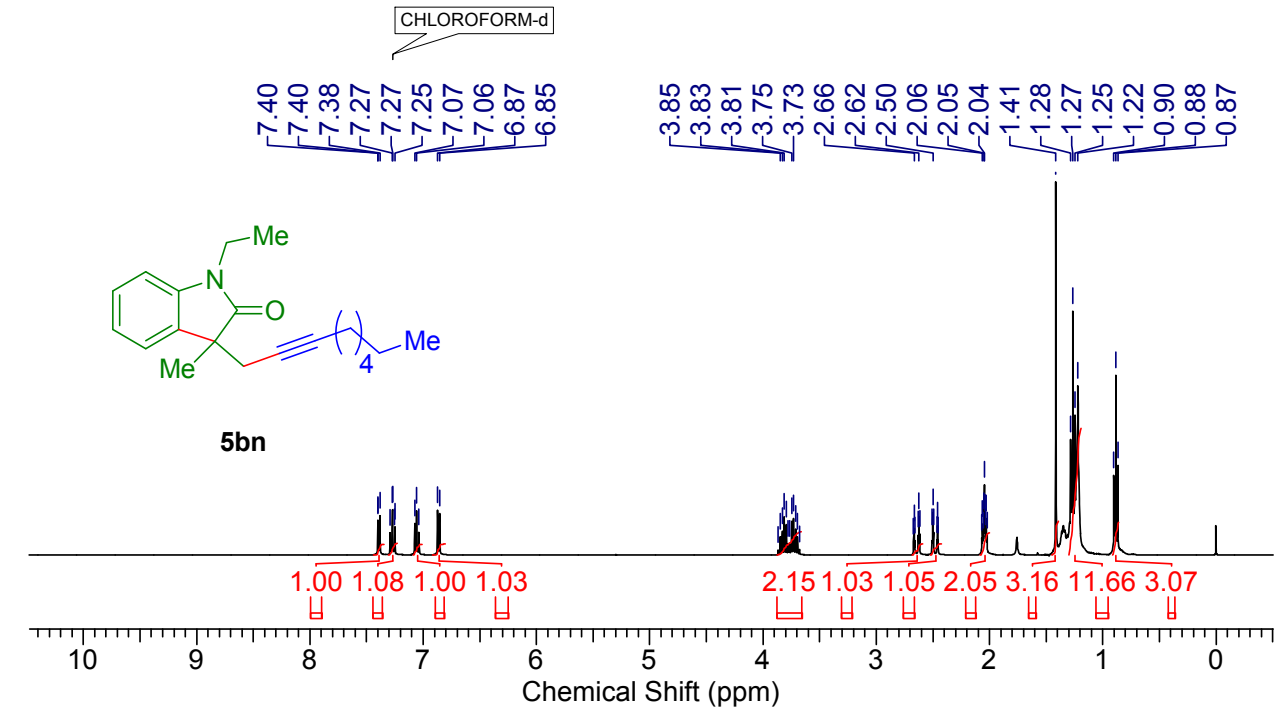


Figure S17A: ^{1}H NMR (400 MHz) spectrum of **5bn** in $CDCl_3$

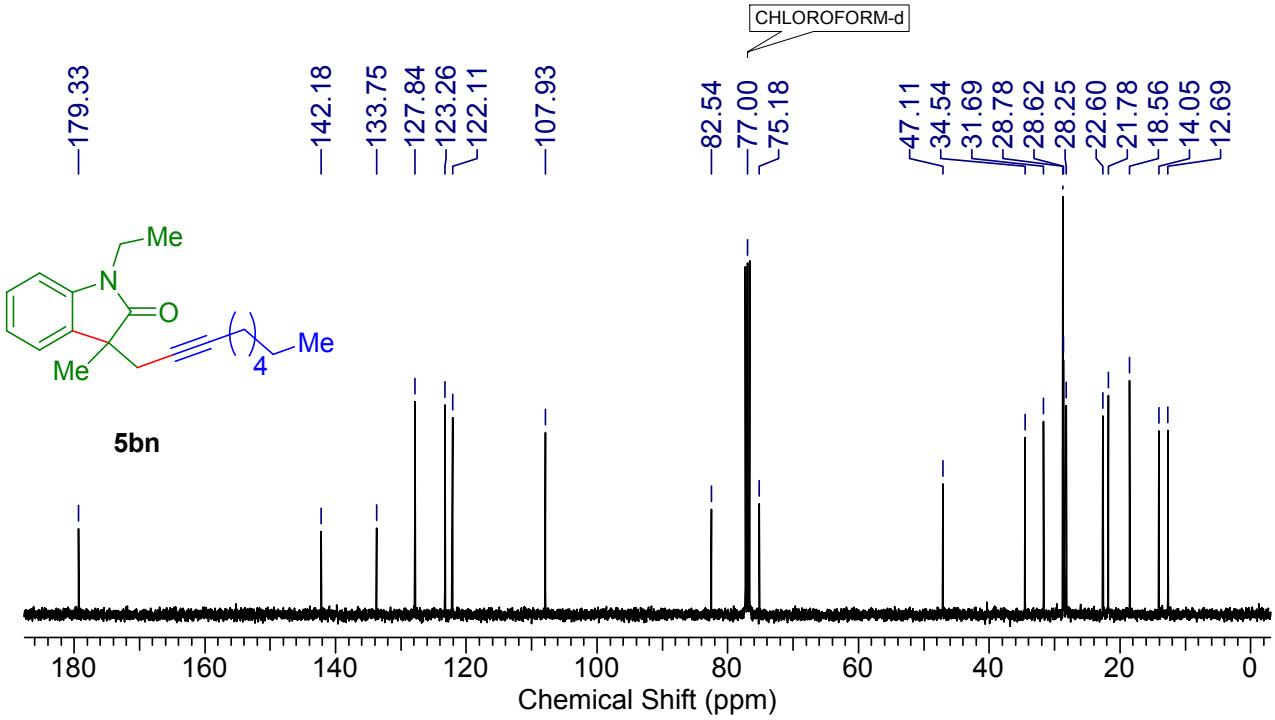


Figure S17B: ^{13}C NMR (400 MHz) spectrum of **5bn** in $CDCl_3$

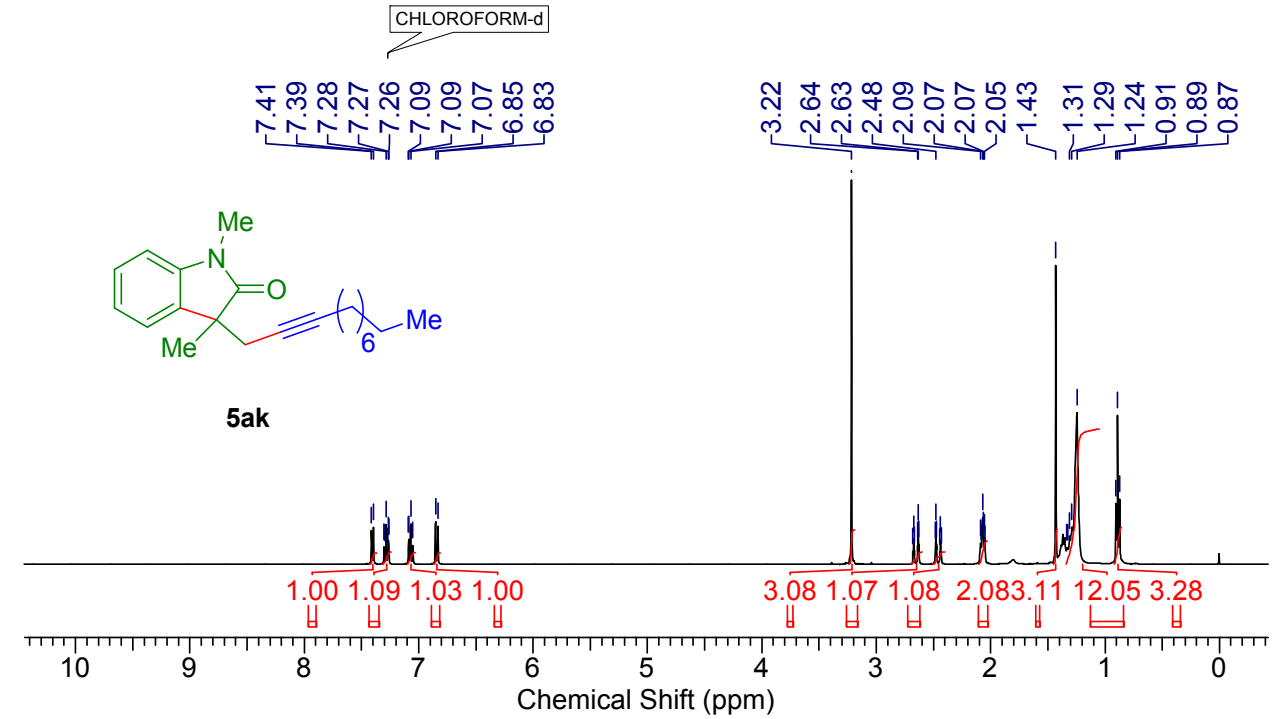


Figure S18A: ^{1}H NMR (400 MHz) spectrum of **5ak** in $CDCl_3$

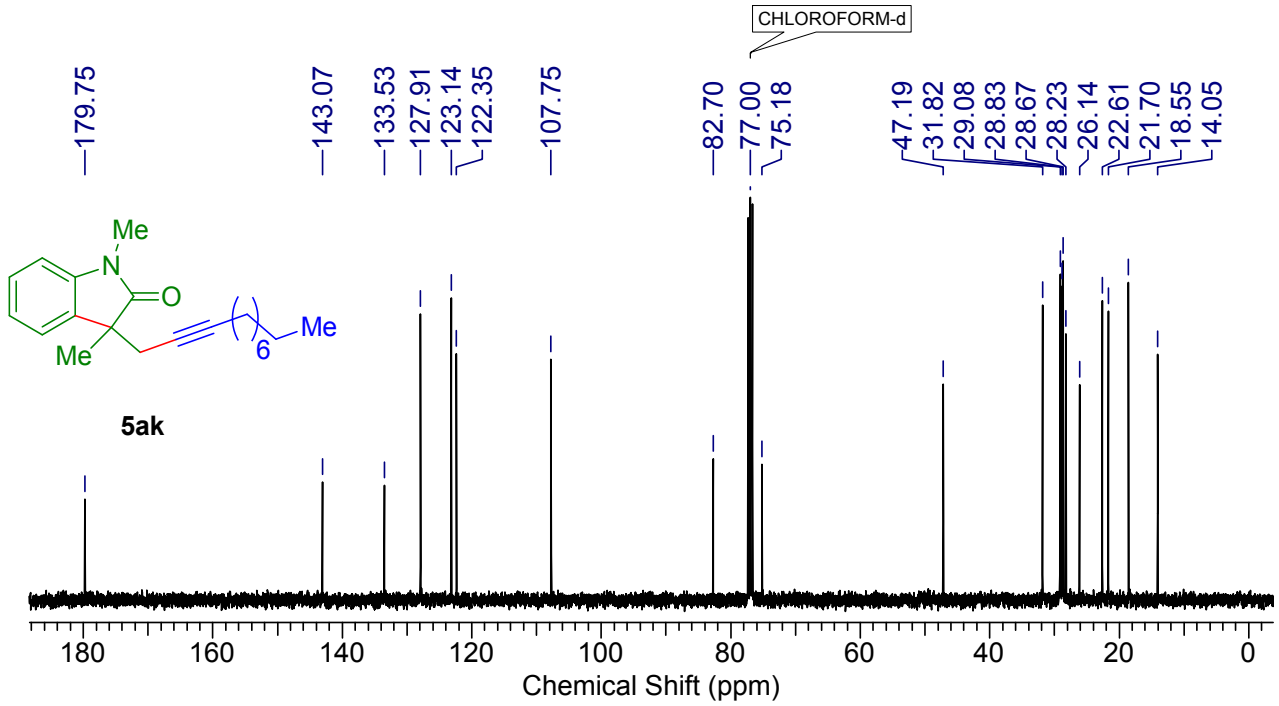


Figure S18B: ^{13}C NMR (400 MHz) spectrum of **5ak** in $CDCl_3$

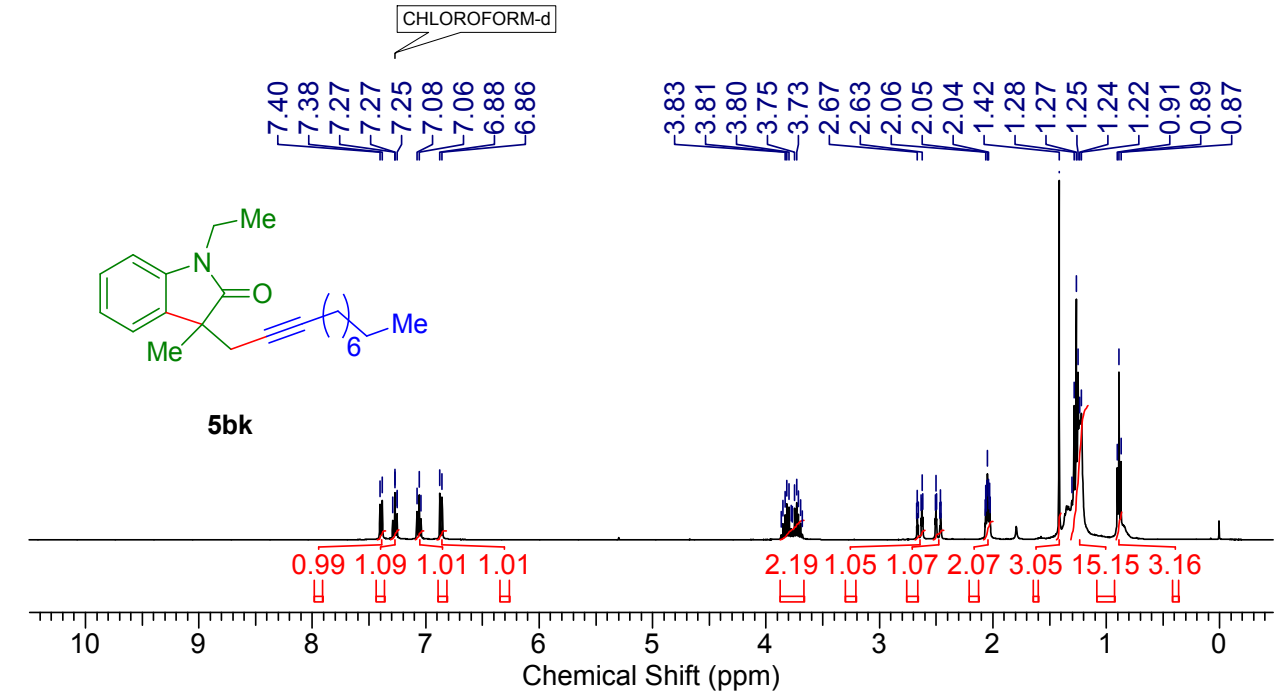


Figure S19A: ^{1}H NMR (400 MHz) spectrum of **5bk** in $CDCl_3$

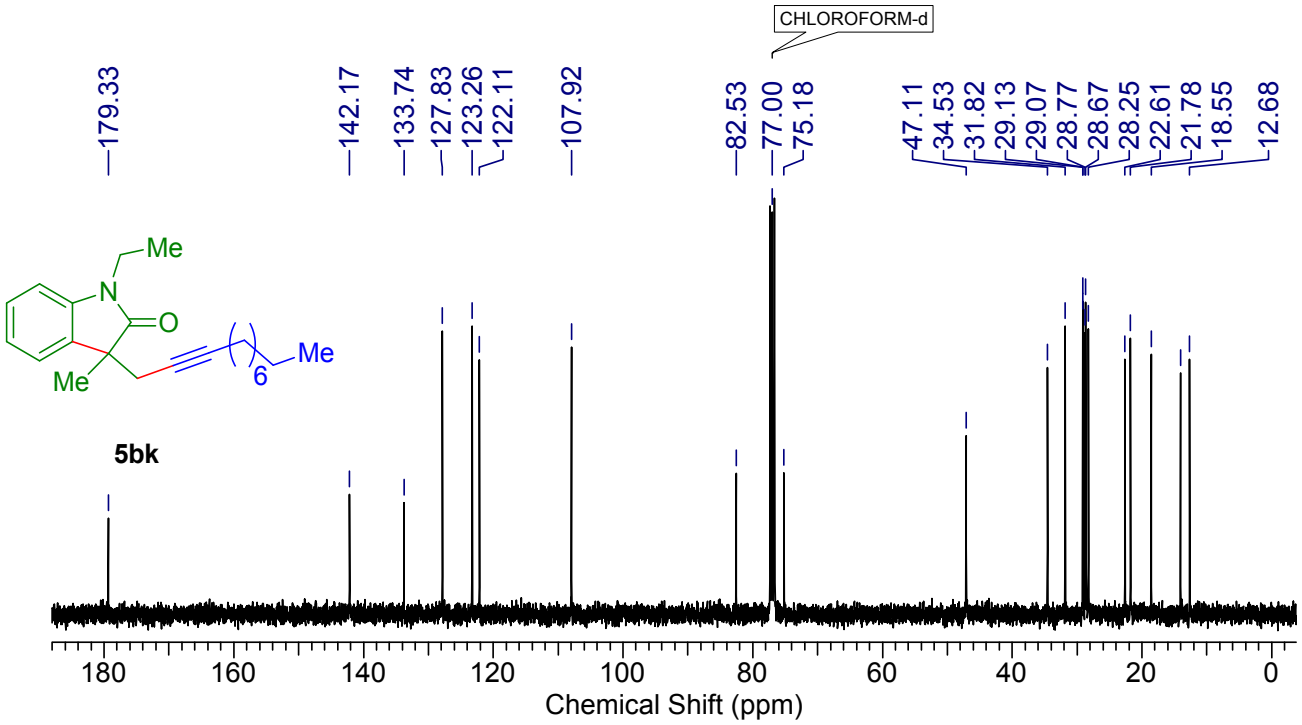


Figure S19B: ^{13}C NMR (400 MHz) spectrum of **5bk** in $CDCl_3$

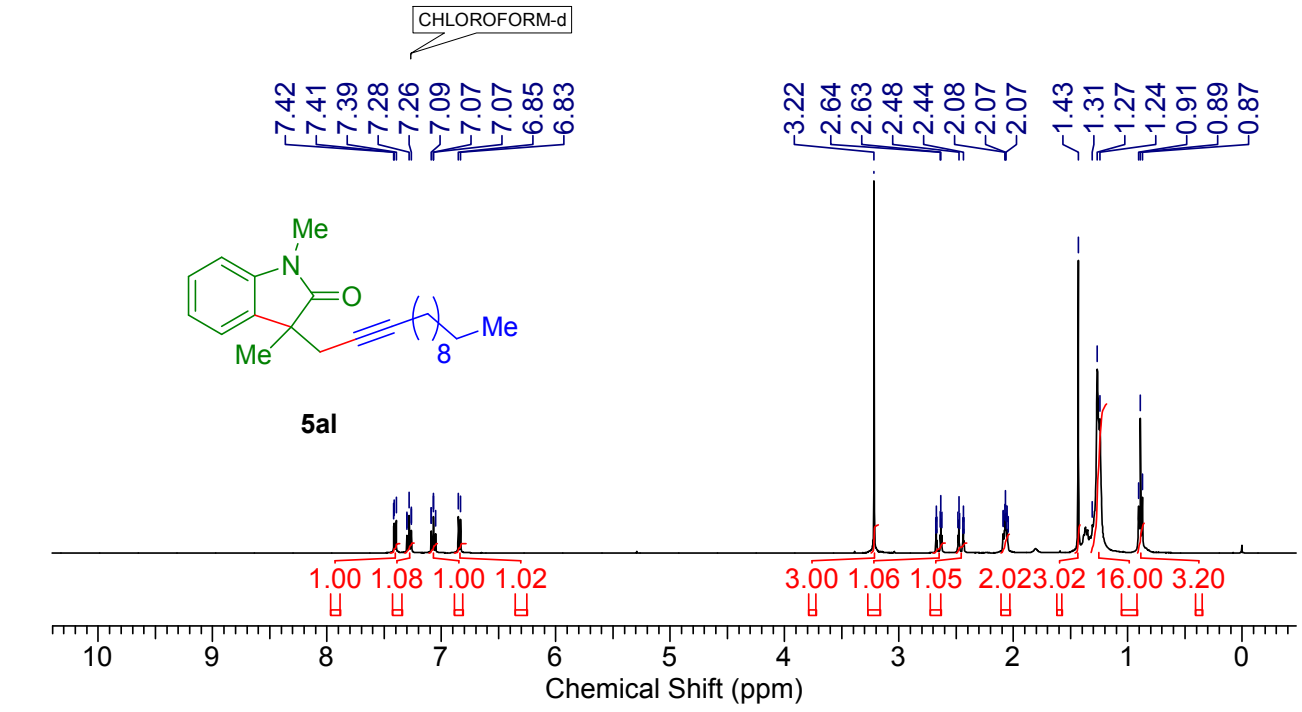


Figure S20A: ^{1}H NMR (400 MHz) spectrum of **5al** in $CDCl_3$

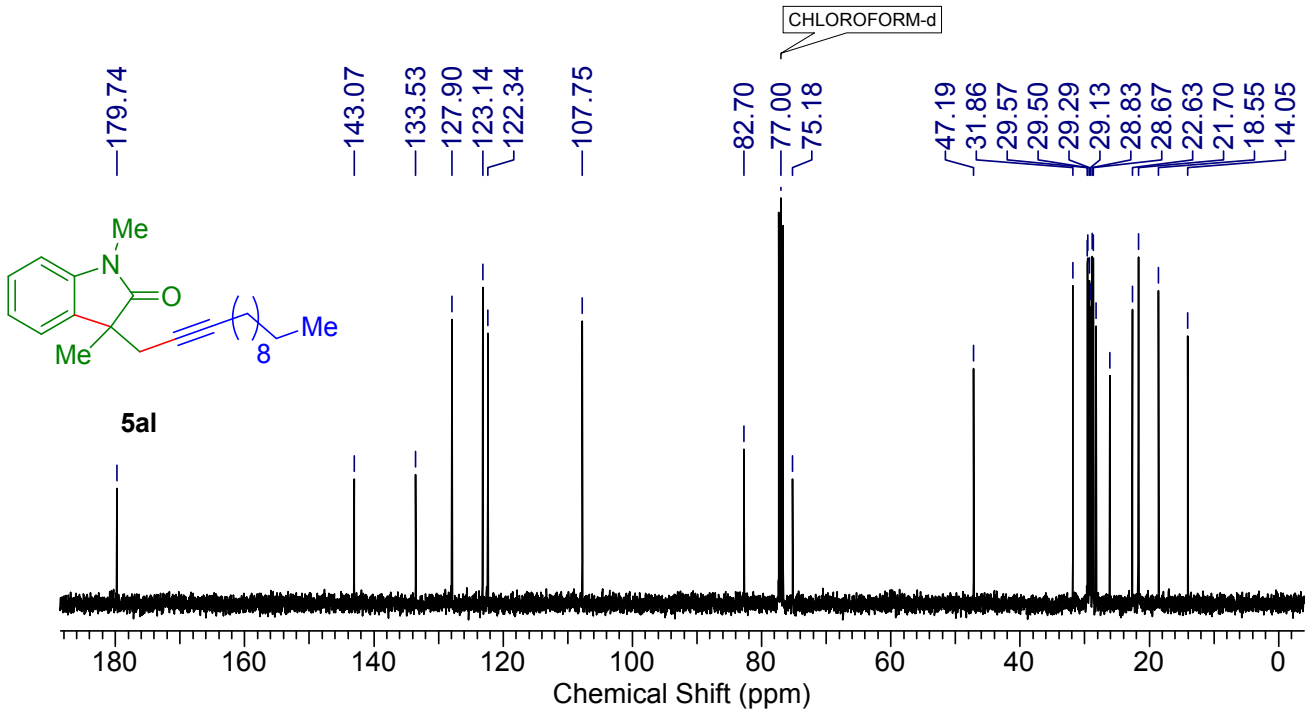


Figure S20B: ^{13}C NMR (400 MHz) spectrum of **5al** in $CDCl_3$

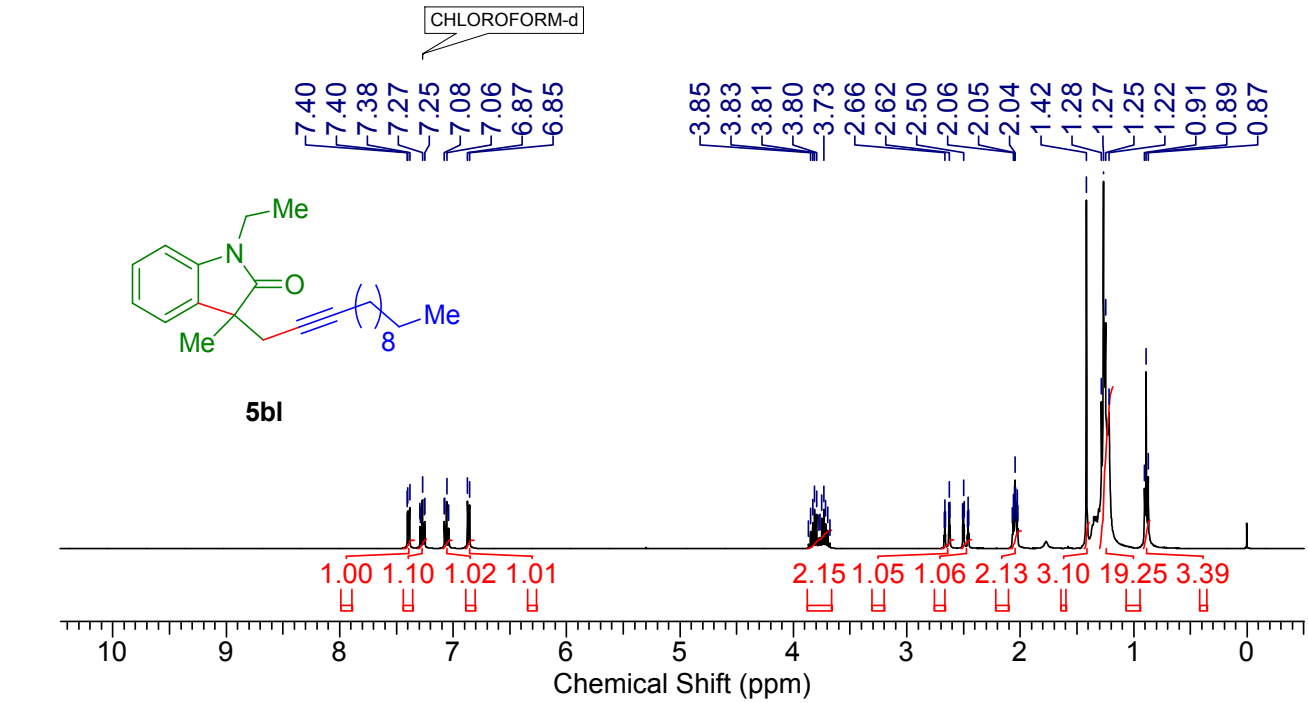


Figure S21A: ^{1}H NMR (400 MHz) spectrum of **5bl** in $CDCl_3$

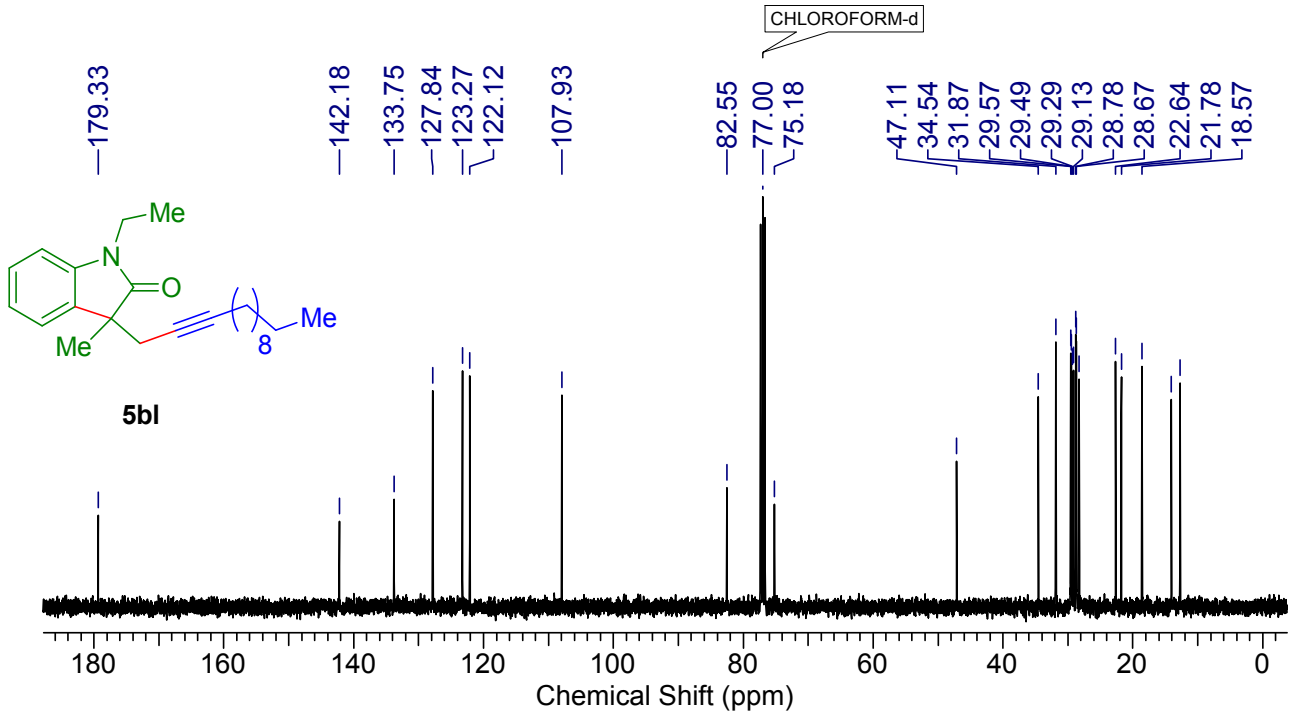


Figure S21B: ^{13}C NMR (400 MHz) spectrum of **5bl** in $CDCl_3$

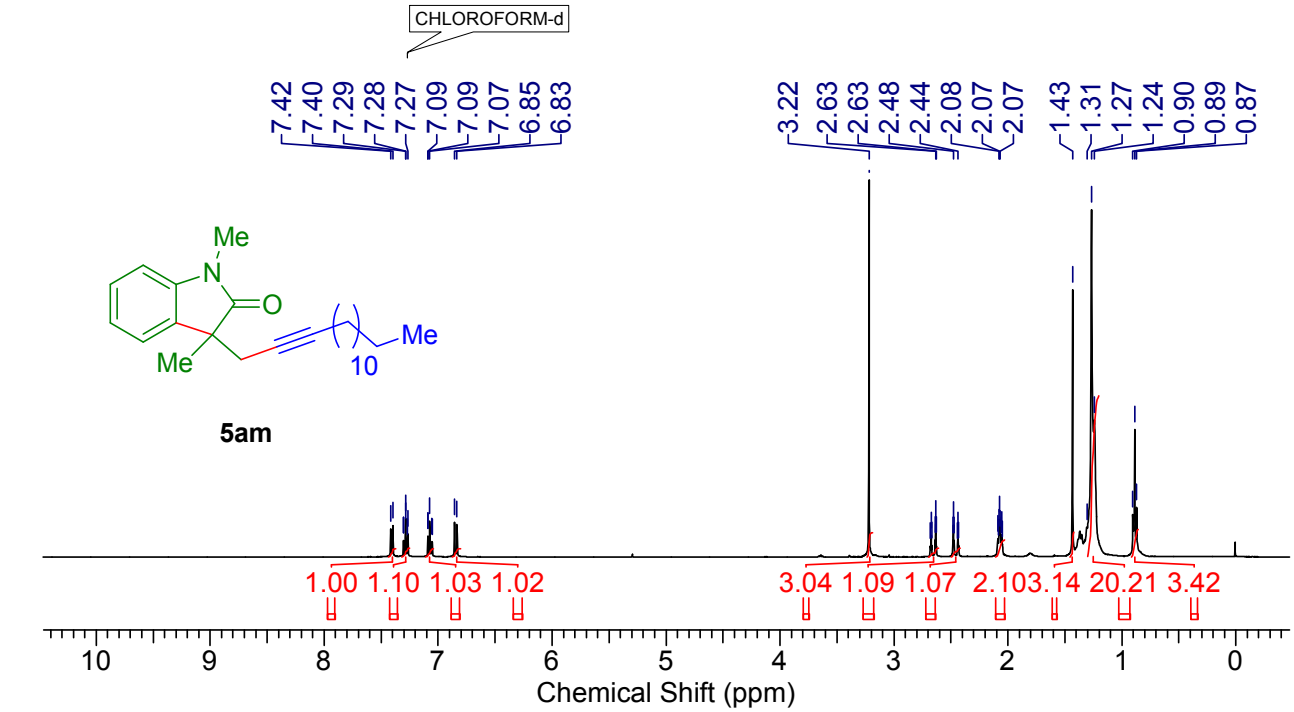


Figure S22A: ^{1}H NMR (400 MHz) spectrum of **5am** in $CDCl_3$

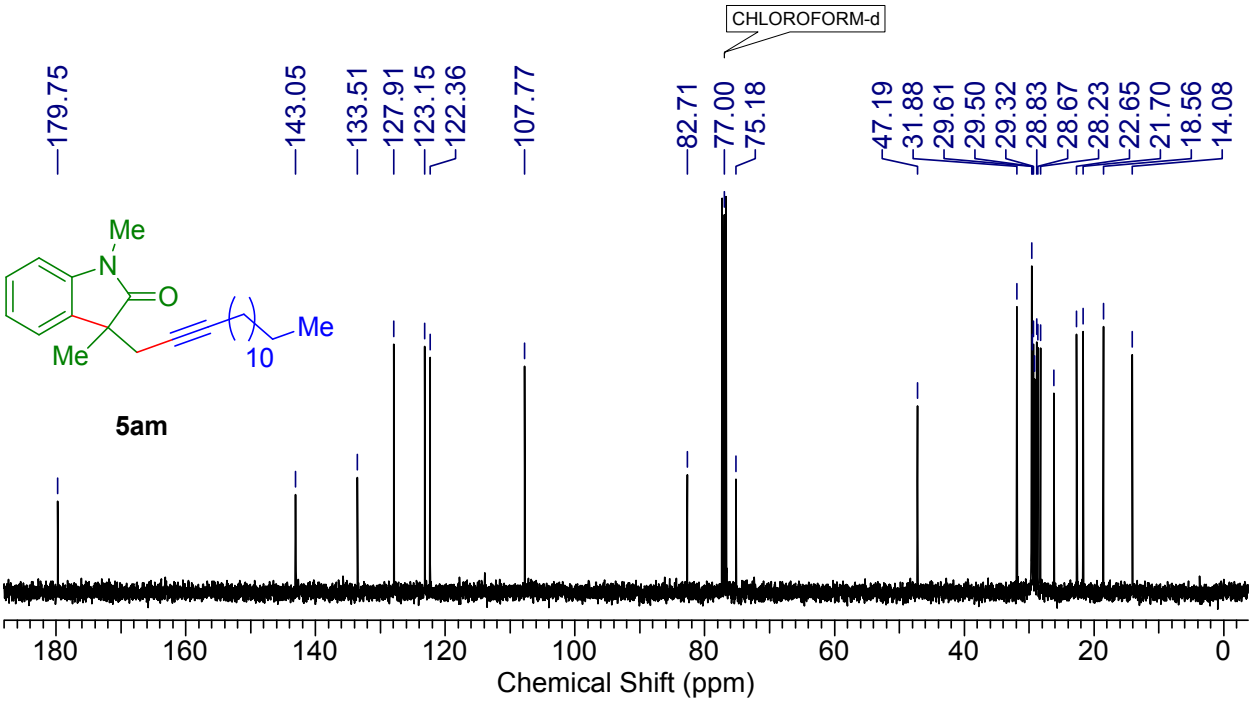


Figure S22B: ^{13}C NMR (400 MHz) spectrum of **5am** in $CDCl_3$

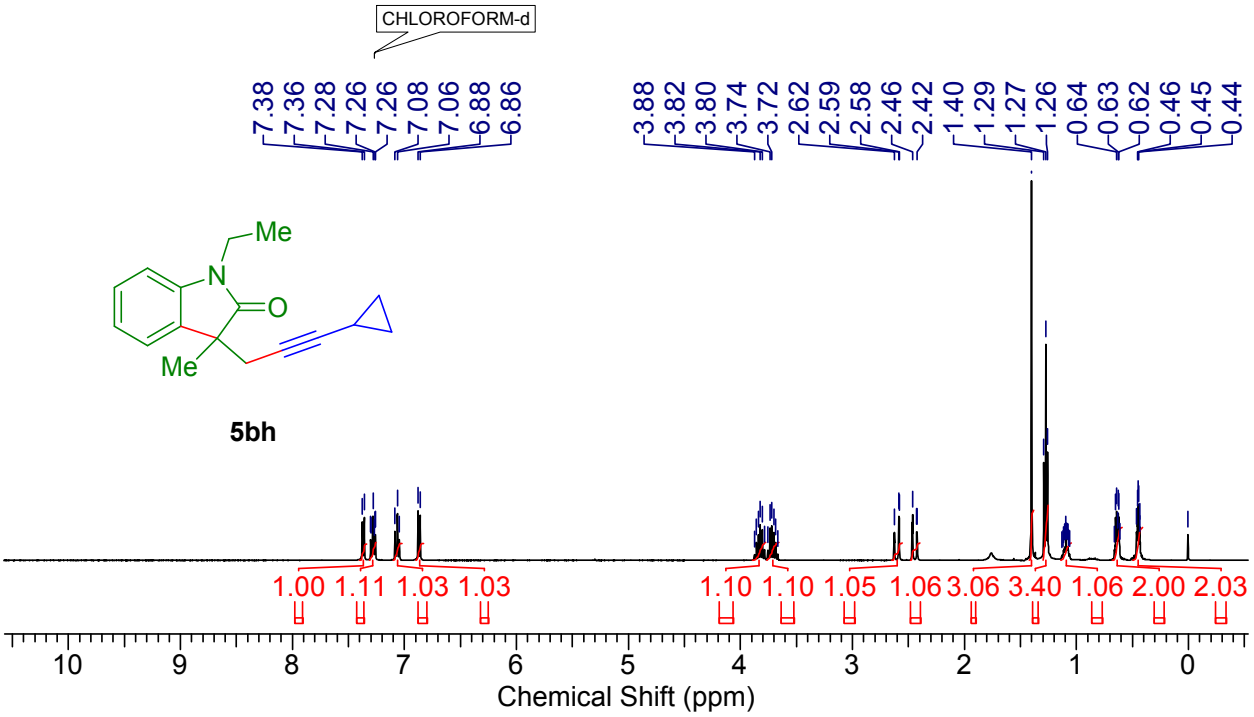


Figure S23A: ^{1}H NMR (400 MHz) spectrum of **5bh** in $CDCl_3$

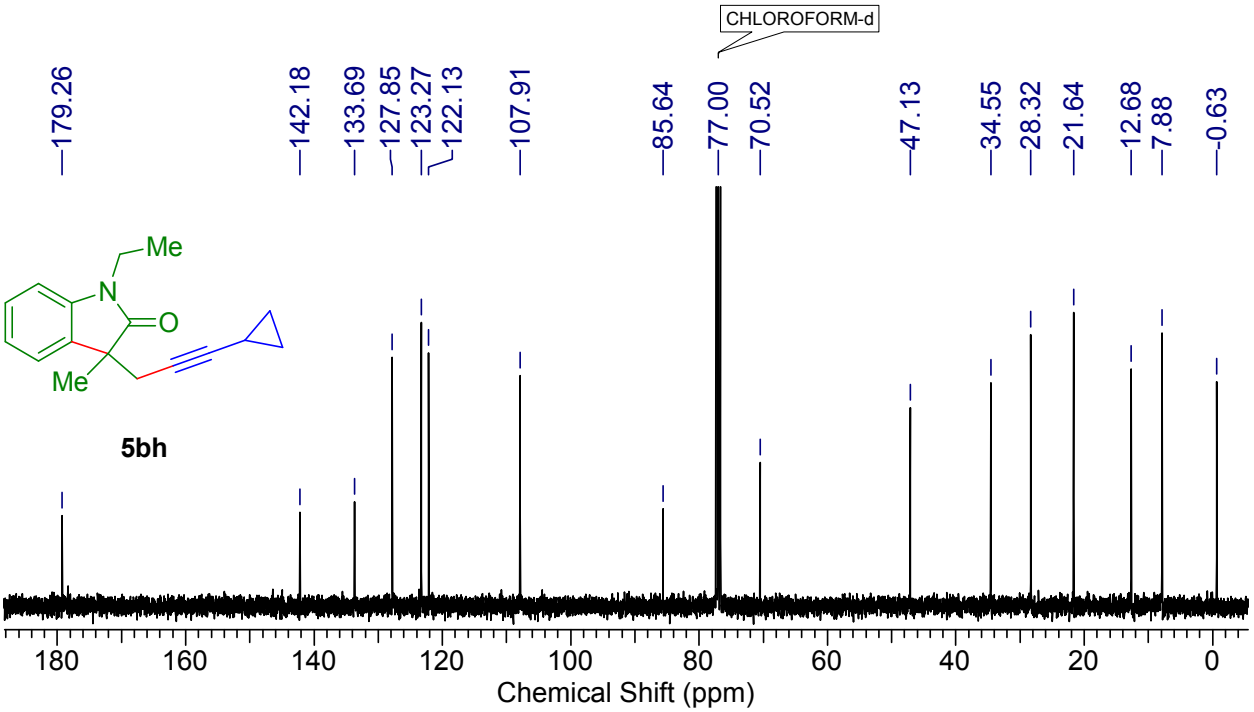


Figure S23B: ^{13}C NMR (400 MHz) spectrum of **5bh** in $CDCl_3$

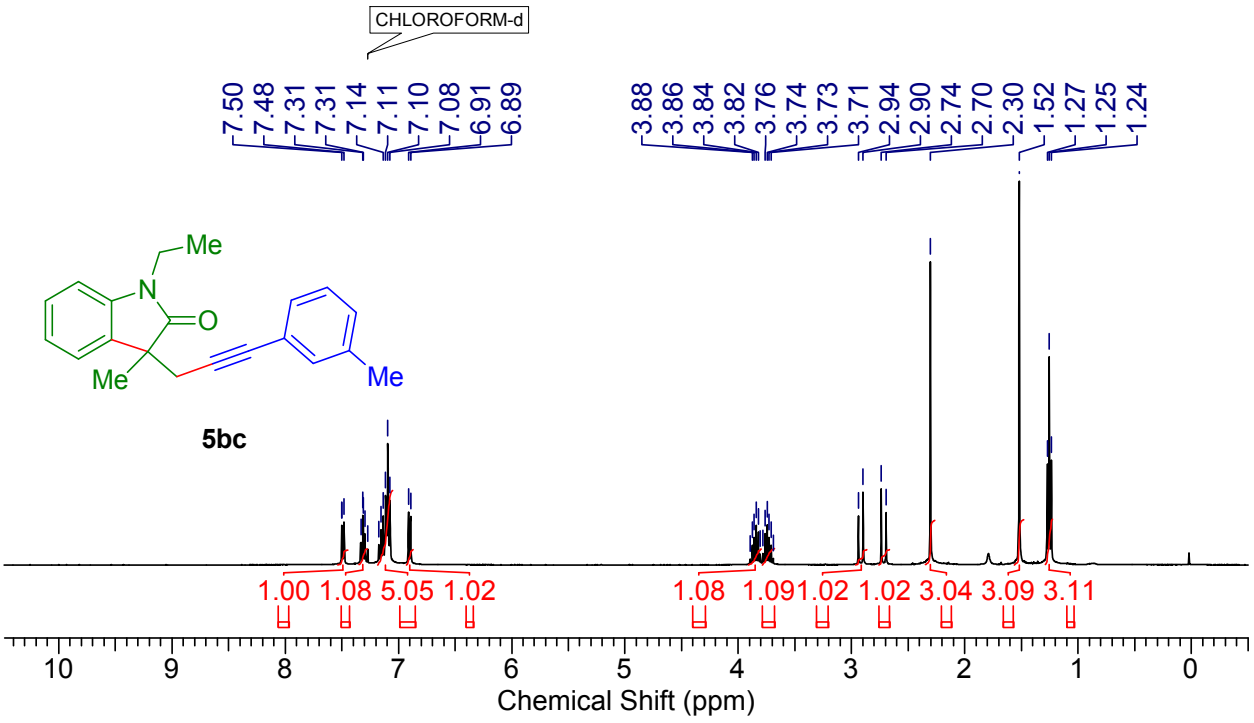


Figure S24A: ^{1}H NMR (400 MHz) spectrum of **5bc** in $CDCl_3$

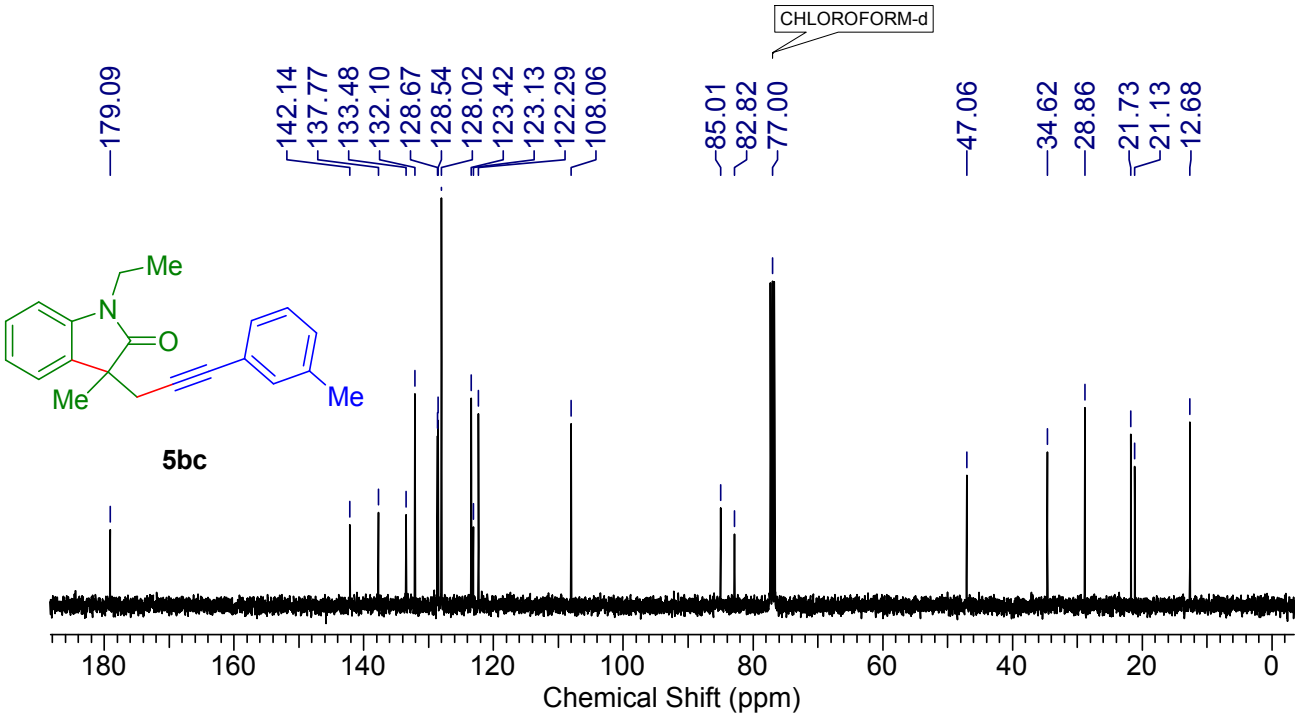


Figure S24B: ^{13}C NMR (400 MHz) spectrum of **5bc** in $CDCl_3$

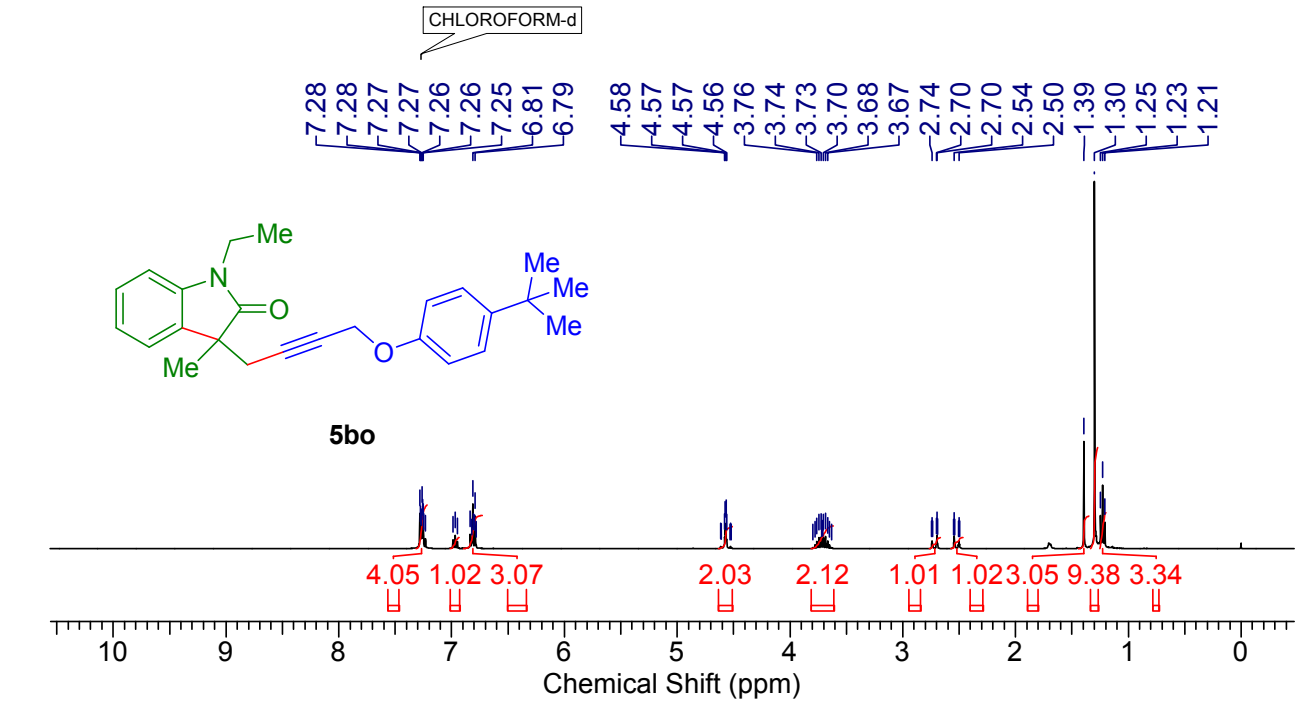


Figure S25A: ^{1}H NMR (400 MHz) spectrum of **5bo** in $CDCl_3$

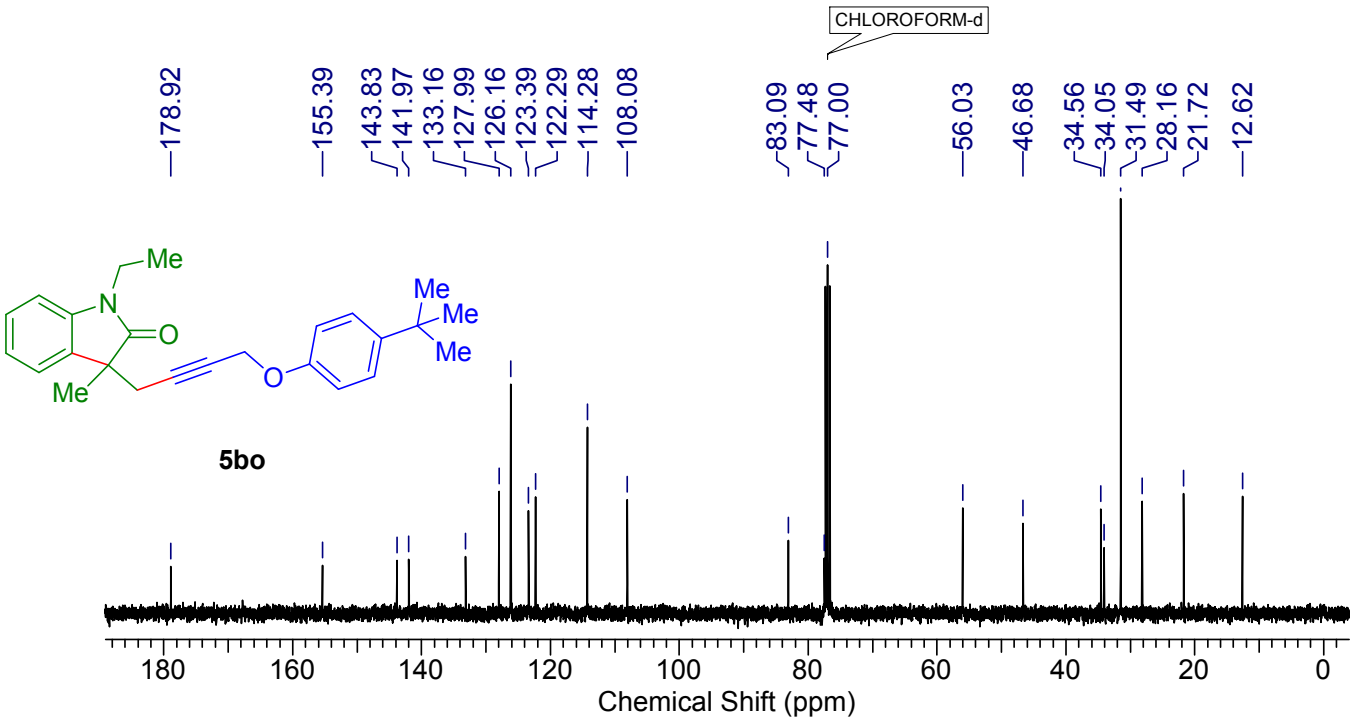


Figure S25B: ^{13}C NMR (400 MHz) spectrum of **5bo** in $CDCl_3$