Graphene-Oxide Mediated Chemodivergent Ring-Opening of Cyclobutanols

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General Methods.

^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd= doublet doublet, t = triplet, td = triple doublet, dt = double triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm).

GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense). LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer.

Chromatographic purification was done with 240-400 mesh silica gel. Other anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification. Melting points were determined with Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected.

CO_2 ≥99.5% purity, purchased from SIAD, was used in the Ni-catalyzed tandem C-C σ-bond carboxylation reaction.

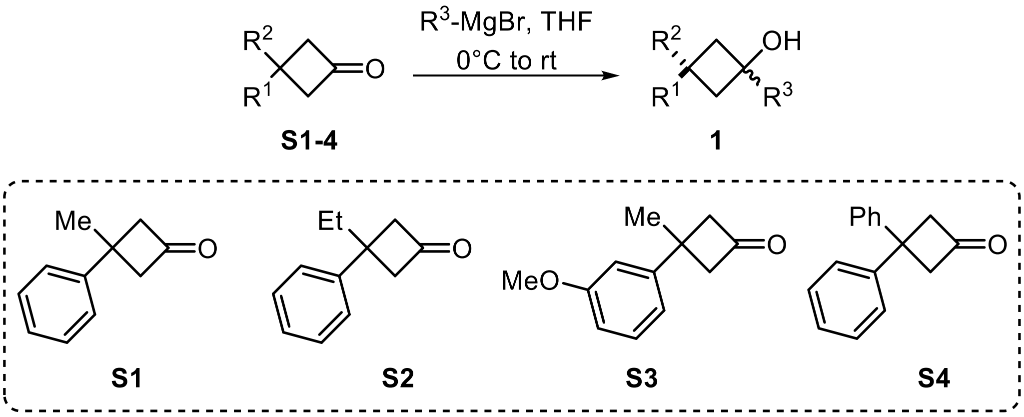
Anhydrous DMF, THF and CH_2Cl_2 were purchased from Merck and used as received. Zn dust refers to a particle size <10 μm and was purchased from Merck, having ≥98% purity. All other commercially available starting materials and (non-anhydrous) solvents were purchased from Merck, TCI chemicals, Fluorochem or Alfa Aesar and were used as such without further purification.

Starting materials **S1-4** are known compounds and were prepared following literature procedures.[1]

XPS spectra were acquired by hemispherical analyser (Phoibos 100, Specs, Germany). Non-monochromatic Mg Kα excitation was set to 125 W (XR50, Specs, Germany). Survey and high-resolution spectra were acquired in Fixed Analyser Transmission mode (FAT) on a large area of c.a. 7x3 mm^2, overall energy resolution of 0.9 eV measured on freshly sputtered Silver (Ag 3d). Spectrometer was calibrated to Au 4f$_{7/2}$ peak at 84.0 eV. Static charging effects was corrected by calibrating all spectra to C 1s 285.0 eV. Fits were performed by using CasaXPS software after Shirley background subtraction. C 1s was fitted by using asymmetric line-shape for aromatic C-sp^2 and symmetric line-shapes (pseudo-voigt) for the C-O defects.[2] The binding energies of C 1s synthetic components were: C=C sp^2 at 284.4 eV, C=C* sp^2 at 283.6 eV, C-C sp^3 285.0 eV, C-OH at 286.2 eV, C-O-C at 286.8 eV, C=O at 288.2 eV and O-C=O at 289.1 eV.

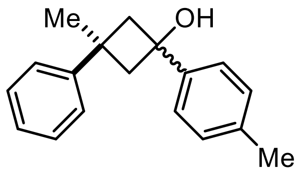
Solid-state NMR (ssNMR) experiments were recorded on a Bruker Avance III HD spectrometer operating at 850 MHz ^{1}H Larmor frequency (20 T), corresponding to 213 MHz ^{13}C Larmor frequency. The spectrometer was equipped with a 3.2 mm BVT MAS probe head in triple resonance mode. The magic angle spinning (MAS) frequency of the sample was set to 20 ± $1 \cdot 10^{-3}$ kHz through a Bruker MAS3 Unit. The tablets used for XPS were directly packed in the rotor[3] to ensure a high filling factor of the rotor. In the 1D direct excitation ^{13}C-NMR spectra, the excitation pulse duration was set to 4.15 μs, corresponding to a 90° flip angle, the spectral window was 468 ppm, and the interscan delays were set to 10 s, which is sufficient to make the experiments quantitative for the present samples. For the 2D {^{1}H}-^{13}C HETCOR experiments, cross-polarization was achieved by matching the k = 1 Hartmann–Hahn condition.[4] The 90° pulse duration on ^{13}C and ^{1}H were set to 4.15 μs and 2.5 μs, respectively. The spectral windows for ^{1}H and ^{13}C were 20 and 350 ppm, respectively. During the ^{1}H magnetization evolution under the chemical shift in the indirect dimension, the FSLG decoupling sequence[5] at 100 kHz was used to suppress ^{1}H–^{1}H dipolar couplings. In these experiments, the interscan delay was set to 1.5 s. The {^{1}H}-^{13}C HETCOR spectra were processed for denoising as recently proposed by some of us,[6] and processed applying an exponential modulation with 200 Hz line broadening in the direct dimension and a sine-squared window function on the indirect dimension.[5]

Preparation and Characterization of Starting Materials 1

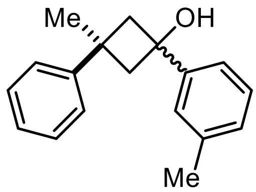


In a heat-gun dried round-bottom flask, equipped with magnetic stirrer, reflux condenser and dropping funnel, dry THF (2.0 mL), Mg (turnings, 1.5 mmol, 36 mg) and iodine (one crystal) were added under N_2. The dropping funnel was charged with dry THF (3.0 mL) and the desired aryl bromide (1.13 mmol). The mixture in the flask was heated to 50 °C and the solution of aryl bromide was added dropwise to the flask under vigorous stirring (the disappearance of the brown color of iodine indicated that the Grignard reagent started forming). After the addition was completed the resulting mixture was heated to reflux for 1 h then cooled to 0 °C. A solution of the desired cyclobutanone (**S1** for compounds **1a-h**, **S3** for **1i**, **S2** for **1j**, and **S4** for **1k-o**, 0.75 mmol in 2.0 mL of dry THF) was added dropwise through the dropping funnel and the resulting suspension was warmed to room temperature and stirred until TLC indicated full consumption of the starting material (ca. 2 h). A saturated solution of $NH_4Cl_{(aq.)}$ was then added cautiously (5 mL) followed by Et_2O (10 mL) and the biphasic mixture was transferred to a separatory funnel where the phases were separated. The aqueous phase was extracted with Et_2O (2x5 mL), the combined organic phases were washed with brine (10 mL), dried over Na_2SO_4, concentrated *in vacuo* and finally purified by Flash Chromatography (SiO_2) to give the respective cyclobutanols **1** as white solids (mixture of diastereoisomers).

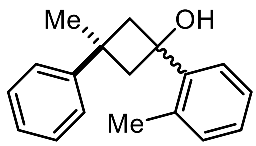
Characterization of compounds 1



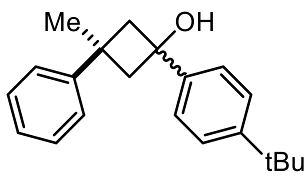
1a (1:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 79% (0.54 mmol, 498 mg, reaction run on 2.5 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47 – 7.43 (m, 2H), 7.39 – 7.26 (m, 6H), 7.25 – 7.13 (m, 8H), 7.12 – 7.08 (m, 2H), 3.03 – 2.91 (m, 4H), 2.91 – 2.83 (m, 2H), 2.65 – 2.57 (m, 2H), 2.38 (s, 3H), 2.31 (s, 3H), 2.02 (bs, 1H), 1.89 (bs, 1H) 1.72 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.8, 151.7, 144.6, 143.6, 137.1, 136.7, 129.3 (2C), 129.0 (2C), 128.3 (2C), 128.2 (2C), 125.7 (2C), 125.4, 125.3, 125.3 (2C), 125.1 (2C), 124.6 (2C), 72.8, 72.2, 48.8 (2C), 48.4 (2C), 36.0, 34.2, 32.7, 31.3, 21.1, 21.0; **Anal. Calc.** for ($C_{18}H_{20}O$: 252.15): C, 85.67; H, 7.99; found: C, 85.41; H, 8.12.



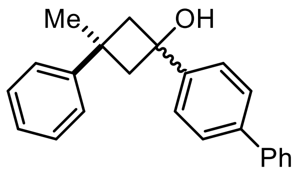
1b (1:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 82% (0.62 mmol, 155 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.39 – 7.25 (m, 9H), 7.22 – 7.09 (m, 8H), 7.04 – 6.99 (m, 1H), 3.02 – 2.92 (m, 4H), 2.90 – 2.84 (m, 2H), 2.64 – 2.56 (m, 2H), 2.40 (s, 3H), 2.30 (s, 3H), 1.97 (bs, 2H), 1.71 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.7, 151.7, 147.4, 146.3, 138.2, 138.0, 128.5, 128.3 (2C), 128.3, 128.2, 128.2 (2C), 127.8, 126.5, 125.4, 125.4, 125.3, 125.3 (2C), 125.1 (2C), 122.6, 121.7, 73.0, 72.4, 48.8 (2C), 48.3 (2C), 36.1, 34.3, 32.6, 31.4, 21.6, 21.5; **Anal. Calc.** for ($C_{18}H_{20}O$: 252.15): C, 85.67; H, 7.99; found: C, 85.75; H, 8.03.



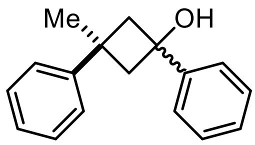
1c (1.5:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 65% (0.49 mmol, 123 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.49 – 7.45 (m, 1H minor), 7.43 – 7.38 (m, 2H major + 1H minor), 7.34 – 7.29 (m, 2H major +2H minor), 7.27 – 7.19 (m, 3H major + 3H minor), 7.19 – 7.12 (m, 2H major + 2H minor), 3.15 – 3.03 (m, 2H major + 2H minor), 3.02 – 2.96 (m, 2H minor), 2.80 – 2.69 (m, 2H major), 2.49 (s, 3H minor), 2.47 (s, 3H major), 1.97 (bs, 1H major + 1H minor), 1.79 (s, 3H major), 1.33 (s, 3H minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 152.3 (major), 151.4 (minor), 144.0 (major), 143.0 (minor), 137.3 (minor), 136.6 (major), 132.0 (minor), 131.7 (major), 128.4 (2C minor), 128.2 (2C major), 127.8 (minor), 127.7 (major), 125.6 (minor), 125.6 (major), 125.5 (minor), 125.5 (minor), 125.5 (2C minor), 125.3 (major), 125.3 (major), 125.0 (2C major), 74.3 (major), 73.6 (minor), 48.9 (2C minor), 47.7 (2C major), 36.8 (major), 35.3 (minor), 32.4 (minor), 31.9 (major), 20.4 (minor), 20.1 (major); **Anal. Calc.** for ($C_{18}H_{20}O$: 252.15): C, 85.67; H, 7.99; found: C, 85.71; H, 7.84.



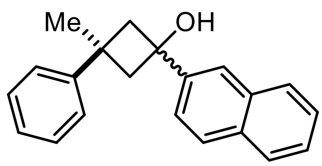
1d (1:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 78% (0.59 mmol, 173 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 – 7.41 (m, 3H), 7.38 – 7.22 (m, 12H), 7.22 – 7.10 (m, 3H), 3.05 – 2.91 (m, 4H), 2.91 – 2.84 (m, 2H), 2.67 – 2.57 (m, 2H), 1.94 (bs, 2H), 1.72 (s, 3H), 1.36 – 1.33 (s, 9H), 1.30 – 1.25 (s, 3H + 9H overlapped); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.8, 151.7, 150.3, 149.9, 144.6, 143.4, 128.3 (2C), 128.2 (2C), 125.5 (2C), 125.4, 125.4 (2C), 125.3 (2C), 125.3, 125.2 (2C), 125.1 (2C), 124.4 (2C), 72.8, 72.2, 48.8 (2C), 48.4 (2C), 36.0, 34.4, 34.3, 32.7, 31.5, 31.5, 31.4 (3C), 31.3 (3C); **Anal. Calc.** for ($C_{21}H_{26}O$: 294.19): C, 85.67; H, 8.90; found: C, 85.88; H, 9.02.



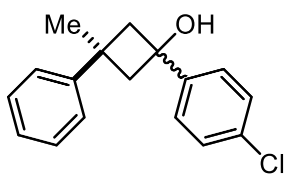
1e (1:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 69% (0.52 mmol, 162 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.69 – 7.60 (m, 6H), 7.58 – 7.50 (m, 4H), 7.49 – 7.28 (m, 14H), 7.26 – 7.13 (m, 4H), 3.08 – 2.97 (m, 4H), 2.97 – 2.89 (m, 2H), 2.70 – 2.61 (m, 2H), 2.04 (bs, 2H), 1.75 (s, 3H), 1.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.6, 151.6, 146.5, 145.4, 140.7, 140.7, 140.4, 140.0, 128.8 (2C), 128.8 (2C), 128.4 (2C), 128.3 (2C), 127.4, 127.3 (2C), 127.3, 127.1 (4C), 127.1 (2C), 126.2 (2C), 125.5, 125.4, 125.3 (2C), 125.2 (2C), 125.1 (2C), 72.8, 72.3, 48.9 (2C), 48.6 (2C), 36.0, 34.4, 32.8, 31.5; **Anal. Calc.** for ($C_{23}H_{22}O$: 314.17): C, 87.86; H, 7.05; found: C, 87.99; H, 7.35.



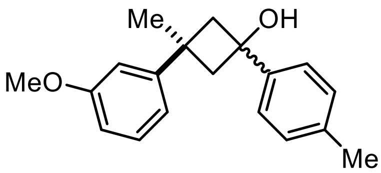
1f (1:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 72% (0.54 mmol, 126 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.59 – 7.52 (m, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.25 (m, 11H), 7.22 – 7.12 (m, 5H), 3.03 – 2.93 (m, 4H), 2.91 – 2.85 (m, 2H), 2.65 – 2.58 (m, 2H), 1.99 (bs, 1H) partially overlapped with 1.86 (bs, 1H), 1.72 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.6, 151.6, 147.4, 146.4, 128.6 (2C), 128.3 (2C), 128.3 (2C), 128.2 (2C), 127.4, 127.0, 125.7 (2C), 125.5, 125.3, 125.3 (2C), 125.1 (2C), 124.7 (2C), 73.0, 72.5, 48.8 (2C), 48.4 (2C), 36.0, 34.3, 32.7, 31.4; **Anal. Calc.** for ($C_{17}H_{18}O$: 238.14): C, 85.67; H, 7.61; found: C, 85.75; H, 7.79.



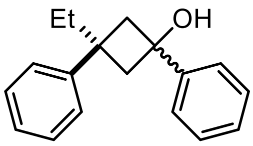
1g (1.2:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 81% (0.62 mmol, 191 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 1.9 Hz, 1H), 7.94 – 7.84 (m, 3H), 7.82 – 7.74 (m, 4H), 7.68 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.47 – 7.41 (m, 3H), 7.41 – 7.32 (m, 5H), 7.32 – 7.28 (m, 1H), 7.26 – 7.20 (m, 3H), 7.20 – 7.14 (m, 1H), 3.15 – 3.04 (m, 4H), 3.01 – 2.93 (m, 2H), 2.73 – 2.62 (m, 2H), 2.18 (d, *J* = 3.3 Hz, 1H), 2.03 (d, *J* = 3.0 Hz, 1H), 1.77 (s, 3H), 1.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.7, 151.6, 144.5, 143.6, 133.1, 133.0, 132.7, 132.4, 128.7, 128.4, 128.4 (2C), 128.3 (2C), 128.2, 128.1, 127.6, 127.5, 126.3, 126.2, 126.2, 125.9, 125.5, 125.4, 125.3 (2C), 125.1 (2C), 124.4, 124.1, 123.6, 122.8, 73.1, 72.6, 48.7 (2C), 48.4 (2C), 36.1, 34.4, 32.8, 31.4; **Anal. Calc.** for ($C_{21}H_{20}O$: 288.15): C, 87.46; H, 6.99; found: C, 87.32; H, 6.81.



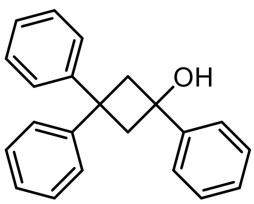
1h (1:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 77% (0.58 mmol, 157 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.44 (m, 2H), 7.40 – 7.27 (m, 9H), 7.25 – 7.20 (m, 3H overlapped with the $CHCl_3$ signal), 7.19 – 7.13 (m, 4H), 2.98 – 2.84 (m, 6H), 2.64 – 2.56 (m, 2H), 2.07 (s, 1H), 1.95 (s, 1H), 1.70 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.3, 151.3, 145.9, 144.8, 133.3, 132.8, 128.7 (2C), 128.4 (4C), 128.3 (2C), 127.2 (2C), 126.3 (2C), 125.6, 125.5, 125.2 (2C), 125.1 (2C), 72.5, 72.1, 49.0 (2C), 48.6 (2C), 35.9, 34.4, 32.8, 31.5; **Anal. Calc.** for ($C_{17}H_{17}ClO$: 272.10): C, 74.86; H, 6.28; found: C, 74.95; H, 5.99.



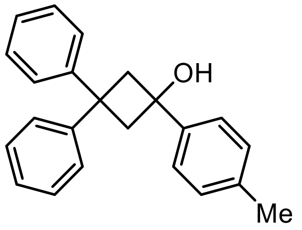
1i (1.1:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 6:1. Yield = 74% (0.56 mmol, 157 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 – 7.43 (m, 2H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.27 – 7.21 (m, 5H), 7.15 – 7.10 (m, 2H), 6.93 (ddd, *J* = 7.6, 1.7, 0.9 Hz, 1H), 6.88 (dd, *J* = 2.6, 1.7 Hz, 1H), 6.81 (ddd, *J* = 7.7, 1.8, 1.0 Hz, 1H), 6.79 – 6.70 (m, 3H), 3.84 (s, 3H), 3.80 (s, 3H), 3.01 – 2.92 (m, 4H), 2.90 – 2.85 (m, 2H), 2.64 – 2.56 (m, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 1.74 (s, 3H), 1.28 (s, 3H); the alcohol protons signals were not detected; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.6, 159.5, 153.7, 153.6, 144.7, 143.6, 137.1, 136.6, 129.4, 129.3 (3C overlapped), 129.0 (2C), 128.9, 125.8 (2C), 124.7 (2C), 124.4, 117.8, 117.7, 111.6, 111.5, 110.4, 110.3, 72.7, 72.1, 55.2, 55.2, 48.8 (2C), 48.5 (2C), 36.1, 34.3, 32.6, 31.3; **Anal. Calc.** for ($C_{19}H_{22}O_2$: 282.16): C, 80.82; H, 7.85; found: C, 80.69; H, 7.68.



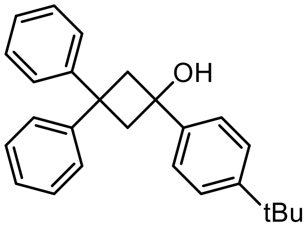
1j (1.7:1 diastereomeric mixture). White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 61% (0.46 mmol, 122 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.56 – 7.49 (m, 2H minor), 7.43 – 7.38 (m, 2H minor), 7.37 – 7.16 (m, 10H major +4H minor), 7.15 – 7.09 (m, 2H minor), 3.00 – 2.88 (m, 2H major + 2H minor), 2.86 – 2.77 (m, 2H major), 2.69 – 2.60 (m, 2H minor), 2.10 (q, *J* = 7.3 Hz, 2H minor), 2.02 (bs, 1H minor), 1.90 (bs, 1H major), 1.58 (q, *J* = 7.4 Hz, 2H major), 0.69 (t, *J* = 7.3 Hz, 3H minor), 0.55 (t, *J* = 7.3 Hz, 3H major); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 148.9 (major), 148.7 (minor), 147.6 (minor), 146.5 (major), 128.5 (2C major), 128.3 (2C minor), 128.0 (2C major), 127.8 (2C minor), 127.3 (major), 127.0 (minor), 126.4 (2C major), 126.3 (2C minor), 125.5 (2C major), 125.4 (2C minor), 125.3 (minor), 124.7 (major), 73.2 (minor), 72.9 (major), 47.4 (2C major), 47.2 (2C minor), 39.7 (minor), 38.9 (major), 36.9 (minor), 36.2 (major); **Anal. Calc.** for ($C_{18}H_{20}O$: 252.15): C, 85.67; H, 7.99; found: C, 85.41; H, 8.12.



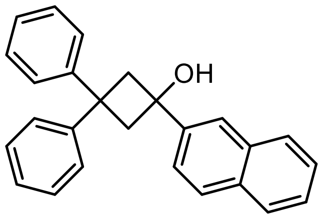
1k. White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 85% (0.64 mmol, 191 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.50 – 7.44 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.26 (m, 4H), 7.26 – 7.22 (m, 3H), 7.22 – 7.18 (m, 2H), 7.18 – 7.13 (m, 1H), 7.11 – 7.05 (m, 1H), 3.52 – 3.42 (m, 2H), 3.37 – 3.29 (m, 2H), 1.99 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 149.4, 149.3, 146.0, 128.5 (2C), 128.3 (2C), 128.3 (2C), 127.2, 126.4 (2C), 126.1 (2C), 125.7, 125.5, 125.0 (2C), 73.4, 49.9 (2C), 44.0; **Anal. Calc.** for ($C_{22}H_{20}O$: 300.15): C, 87.96; H, 6.71; found: C, 88.09; H, 6.44.



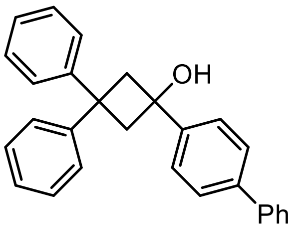
1l. White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 71% (0.53 mmol, 190 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.50 – 7.43 (m, 2H), 7.36 – 7.13 (m, 10H), 7.11 – 7.04 (m, 2H), 3.50 – 3.41 (m, 2H), 3.37 – 3.28 (m, 2H), 2.30 (s, 3H), 1.94 (d, *J* = 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 149.5, 149.4, 143.2, 136.8, 129.0 (2C), 128.5 (2C), 128.3 (2C), 126.4 (2C), 126.1 (2C), 125.7, 125.5, 124.9 (2C), 73.3, 49.9 (2C), 43.9, 21.0; **Anal. Calc.** for ($C_{23}H_{22}O$: 314.17): C, 87.86; H, 7.05; found: C, 87.64; H, 7.33.



1m. White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 71% (0.53 mmol, 190 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.45 (m, 2H), 7.36 – 7.29 (m, 6H), 7.27 – 7.19 (m, 4H), 7.18 – 7.13 (m, 1H), 7.11 – 7.06 (m, 1H), 3.49 – 3.41 (m, 2H), 3.36 – 3.28 (m, 2H), 1.98 (d, *J* = 1.8 Hz, 1H), 1.29 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 150.0, 149.6, 149.5, 143.3, 128.5 (2C), 128.3 (2C), 126.5 (2C), 126.1 (2C), 125.7, 125.5, 125.2 (2C), 124.6 (2C), 73.3, 50.0 (2C), 44.1, 34.4, 31.3 (3C); **Anal. Calc.** for ($C_{26}H_{28}O$: 356.21): C, 87.60; H, 7.92; found: C, 87.77; H, 7.79.



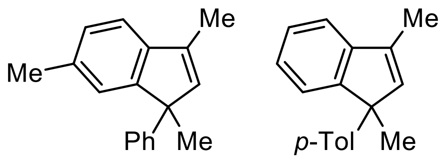
1n. White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 83% (0.62 mmol, 218 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.83 – 7.71 (m, 4H), 7.52 – 7.48 (m, 3H), 7.47 – 7.40 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 7.10 – 7.05 (m, 1H), 3.62 – 3.53 (m, 2H), 3.44 – 3.36 (m, 2H), 2.09 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 149.5, 149.3, 143.2, 133.0, 132.5, 128.6 (2C), 128.3, 128.3 (2C), 128.1, 127.5, 126.4 (2C), 126.1 (2C), 126.1, 125.9, 125.8, 125.6, 123.6, 123.4, 73.5, 49.9 (2C), 44.0; **Anal. Calc.** for ($C_{26}H_{22}O$: 350.17): C, 89.11; H, 6.33; found: C, 89.34; H, 6.50.



1o. White solid. FC eluent: *c*Hex:EtOAc: 10:1. Yield = 88% (0.66 mmol, 276 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.58 – 7.52 (m, 3H), 7.52 – 7.47 (m, 3H), 7.46 – 7.38 (m, 4H), 7.37 – 7.30 (m, 3H), 7.29 – 7.20 (m, 4H), 7.20 – 7.14 (m, 1H), 7.12 – 7.06 (m, 1H), 3.55 – 3.47 (m, 2H), 3.40 – 3.32 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 149.4, 149.3, 145.1, 140.7, 140.0, 128.7 (2C), 128.6 (2C), 128.3 (2C), 127.3, 127.0 (2C and C overlapped), 126.4 (2C), 126.1 (2C), 125.8, 125.6, 125.4 (2C), 73.3, 50.1 (2C), 44.0; **Anal. Calc.** for ($C_{28}H_{24}O$: 376.18): C, 89.33; H, 6.43; found: C, 89.30; H, 6.51.

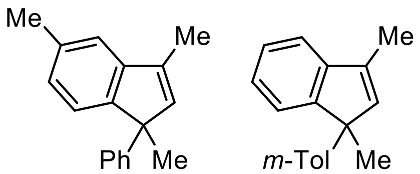
Optimized general procedure for the GO-promoted preparation of indenes 2

A screw-cap-vial was charged with reagent grade EtOAc (1.0 ml), the desired cyclobutanol **1** (0.1 mmol) and GO (100 wt% with respect to **1**). The reaction mixture was warmed at 90 °C and stirred at the same temperature overnight. Removal of the GO by filtration (Celite pad) and subsequent purification via flash chromatography led to the isolation of compounds **2** (generally as a mixture of isomers).

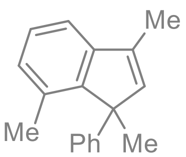


2a **2a'**

2a and **2a’** (1.2:1 ratio of regioisomers). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 55% (0.055 mmol, 12.9 mg). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.29 – 7.19 (m, 3H major + 3H minor), 7.18 – 7.10 (m, 3H major + 3H minor), 7.09 – 6.97 (m, 2H major + 2H minor), 6.19 – 6.17 (m, 1H major), 6.14 – 6.12 (m, 1H minor), 2.32 (s, 3H minor), 2.27 (s, 3H major), 2.15 (d, *J* = 1.2 Hz, 3H major), 2.13 (d, *J* = 1.2 Hz, 3H minor), 1.66 (s, 3H minor), 1.65 (s, 3H major); **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 154.1 (minor), 153.9 (major), 144.3 (major), 143.9 (minor), 141.8 (major), 141.7 (major), 140.7 (minor), 140.4 (minor), 136.8 (minor), 136.7 (major), 135.8 (major), 135.2 (minor), 128.8 (2C major), 128.2 (2C minor), 127.1 (minor), 126.4 (major), 126.1 (minor), 126.0 (2C minor), 125.8 (2C major), 125.3 (major), 123.3 (minor), 122.3 (major), 119.3 (major), 119.0 (minor), 55.1 (minor), 55.0 (major), 22.8 (minor), 22.8 (major), 21.2 (minor), 20.5 (major), 12.5 (minor), 12.4 (major); **Anal. Calc.** for ($C_{18}H_{18}$: 234.14): C, 92.26; H, 7.74; found: C, 92.11; H, 7.95.

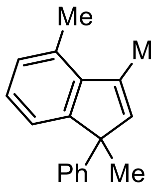


2b **2b'**

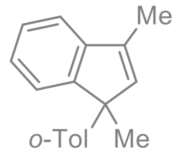


2b'' not detected

2b and **2b’** (1.2:1 ratio of regioisomers, isomer **2b’’** not detected). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 51% (0.051 mmol, 12.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 – 7.20 (m, 4H major + 4H minor), 7.19 – 7.08 (m, 3H major + 3H minor), 7.00 (d, *J* = 7.6 Hz, 1H major), 6.94 (d, *J* = 7.5 Hz, 1H minor), 6.20 (q, *J* = 1.6 Hz, 1H major), 6.04 (q, *J* = 1.6 Hz, 1H minor), 2.41 (s, 3H major), 2.15 (d, *J* = 1.5 Hz, 3H major), 2.11 (d, *J* = 1.6 Hz, 3H minor), 2.02 (s, 3H minor), 1.76 (s, 3H minor), 1.69 (s, 3H major); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.4 (minor), 151.0 (major), 145.4 (minor), 144.6 (major), 143.8 (major), 143.4 (minor), 142.2 (minor), 142.1 (major), 136.6 (minor), 136.2 (major), 135.6 (minor), 132.9 (major), 128.3 (2C major), 128.2 (2C minor), 127.6 (major), 127.1 (minor), 126.2 (minor), 126.1 (major), 126.1 (2C minor), 126.1 (minor), 126.1 (2C major), 122.3 (major), 120.2 (major), 116.9 (minor), 55.8 (minor), 55.1 (major), 23.2 (major), 21.5 (minor), 19.3 (major), 18.4 (minor), 12.8 (major), 12.8 (minor); **Anal. Calc.** for ($C_{18}H_{18}$: 234.14): C, 92.26; H, 7.74; found: C, 92.33; H, 7.61.

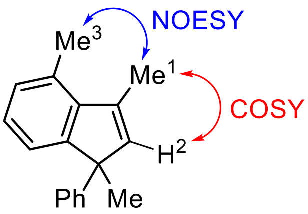


2c



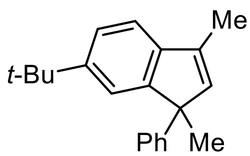
2c'
not detected

2c (isomer **2c'** not detected). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 40% (0.040 mmol, 9.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.26 – 7.10 (m, 5H), 7.07 – 6.94 (m, 3H), 6.14 (q, *J* = 1.6 Hz, 1H), 2.57 (s, 3H), 2.32 (d, *J* = 1.6 Hz, 3H), 1.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.9, 143.8, 142.8, 141.5, 138.2, 131.4, 129.3, 128.2 (2C), 126.1, 126.1 (2C), 125.5, 120.7, 54.4, 23.2, 19.8, 17.4; **Anal. Calc.** for ($C_{18}H_{18}$: 234.14): C, 92.26; H, 7.74; found: C, 92.41; H, 7.56.

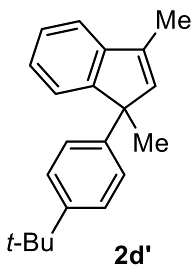


2c

The product is identified as isomer **2c** by 1D NOESY NMR experiments. Upon irradiation of the signal at 2.32 ppm, identified as Me^{1} by its multiplicity (d, coupling with H^{2}), correlation with the singlet at 2.57 ppm (identified as Me^{3} by the chemical shift typical of an aromatic Me) is observed.

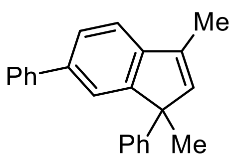


2d

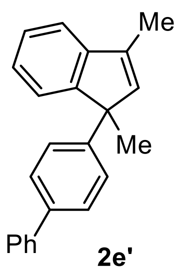


2d'

2d and **2d'** (1.0:1 ratio of regioisomers). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 66% (0.066 mmol, 18.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37 – 7.32 (m, 1H + 1H), 7.30 – 7.24 (m, 4H + 4H), 7.24 – 7.15 (m, 3H + 3H), 6.22 (q, *J* = 1.5 Hz, 1H), 6.16 (q, *J* = 1.5 Hz, 1H), 2.16 (d, *J* = 1.6 Hz, 3H), 2.14 (d, *J* = 1.6 Hz, 3H), 1.71 (s, 3H), 1.70 (s, 3H), 1.31 (s, 9H), 1.28 (s, 9H); **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 153.7, 153.4, 148.9, 148.7, 144.4, 144.0, 142.0, 141.9, 141.3, 140.4, 136.5, 136.3, 128.2, 126.5, 126.1, 126.1, 125.7, 125.3, 125.2, 123.5, 122.6, 119.8, 119.3, 118.7, 55.5, 55.1, 34.8, 34.3, 31.7, 31.3, 23.4, 23.2, 12.8, 12.8, all peaks are given without assignment; **Anal. Calc.** for ($C_{21}H_{24}$: 276.19): C, 91.25; H, 8.75; found: C, 91.05; H, 9.02.

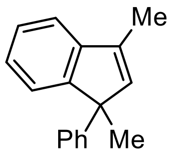


2e

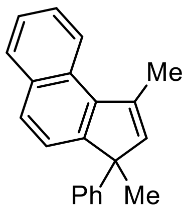


2e'

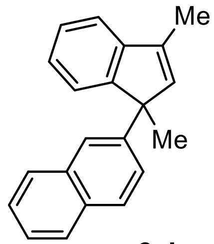
2e and **2e'** (5.0:1 ratio of regioisomers). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 54% (0.054 mmol, 18.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.56 – 7.51 (m, 3H major + 3H minor), 7.49 – 7.36 (m, 5H major + 5H minor), 7.34 – 7.27 (m, 5H major + 5H minor), 6.23 (q, *J* = 1.6 Hz, 1H major + 1H minor), 2.18 (d, *J* = 1.6 Hz, 3H minor), 2.17 (d, *J* = 1.5 Hz, 3H major), 1.74 (s, 3H minor), 1.73 (s, 3H major); **^{13}C NMR** (100 MHz, CD_2Cl_2) δ = 153.6, 144.4, 142.7, 141.7, 140.9, 139.2, 136.9, 128.7 (2C), 128.3, 127.0 (2C), 127.0 (2C), 126.7, 126.5 (2C), 125.5, 122.6, 119.4, 55.2, 23.0, 12.8, only the peaks relative to the major regioisomer are reported; **Anal. Calc.** for ($C_{23}H_{20}$: 296.16): C, 93.20; H, 6.80; found: C, 93.41; H, 6.73.



2f. Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 44% (0.044 mmol, 9.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30 – 7.27 (m, 2H), 7.26 – 7.22 (m, 3H), 7.22 – 7.15 (m, 4H), 6.21 (q, *J* = 1.6 Hz, 1H), 2.16 (d, *J* = 1.6 Hz, 3H), 1.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 153.7, 144.4, 143.5, 141.8, 136.7, 128.3, 126.6, 126.2, 126.1, 125.4, 122.6, 119.4, 55.4, 23.0, 12.8; **Anal. Calc.** for ($C_{17}H_{16}$: 220.13): C, 92.68; H, 7.32; found: C, 92.75; H, 7.45.

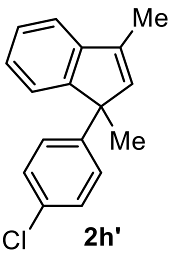


2g

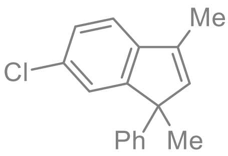


2g'

2g and **2g'** (6.7:1 **2g**:**2g'** ratio). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 59% (0.059 mmol, 16.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.92 – 7.87 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.35 (ddd, *J* = 8.2, 6.8, 1.5 Hz, 1H), 7.30 (ddd, *J* = 8.2, 6.8, 1.5 Hz, 1H), 7.23 – 7.14 (m, 3H), 7.14 – 7.08 (m, 2H), 6.28 (q, *J* = 1.6 Hz, 1H), 2.23 (d, *J* = 1.6 Hz, 3H), 1.83 (s, 3H), only the peaks relative to **2g** are reported; diagnostic peak for **2g'**: 1.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 148.3, 144.4, 142.6, 142.4, 135.6, 132.4, 129.0, 128.4, 128.2, 126.6, 126.2, 126.2, 125.8, 124.2, 124.1, 118.7, 56.4, 21.7, 13.0, only the peaks relative to **2g** are reported; **Anal. Calc.** for ($C_{21}H_{18}$: 270.19): C, 93.29; H, 6.71; found: C, 93.12; H, 6.98.

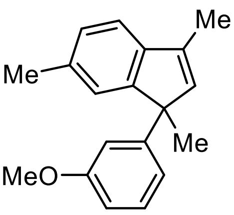


2h'

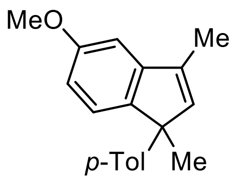


2h
not detected

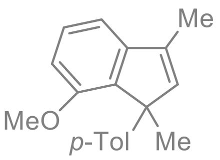
2h' (isomer **2h** not detected). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 53% (0.053 mmol, 13.5 mg; isolated as a 1:0.3:0.3 **2h'**:**3h**:**3h'** inseparable mixture, 22.4 mg, 0.088 mmol combined). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.11 (m, 8H, overlapped with **3h** and **3h'**), 6.13 (q, *J* = 1.6 Hz, 1H), 2.16 (s, 3H, overlapped with **3h** and **3h'**), 2.14 (d, *J* = 1.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 153.4, 146.1, 145.1, 144.3, 144.3, 144.0, 142.1, 141.3, 140.8, 139.3, 137.1, 134.4, 133.2, 133.2, 132.0, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.7, 127.5, 127.5, 127.5, 127.3, 127.3, 126.8, 126.5, 125.9, 125.9, 125.6, 124.6, 122.4, 119.5, 115.4, 114.9, 54.9, 45.5, 44.3, 40.9, 30.9, 27.3, 22.8, 12.7 all the peaks of the mixture are given, without assignment; **Anal. Calc.** for ($C_{17}H_{15}Cl$: 254.09): C, 80.15; H, 5.94; found: C, 80.21; H, 6.07.



2i

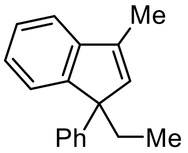


2i'

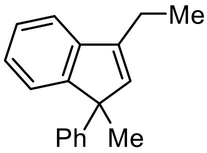


2i'' not detected

2i and **2i'** (6.4:1 **2i'**:**2i** ratio, isomer **2i''** not detected). Viscous colorless oil. FC eluent: 99:1 *n*Hex:EtOAc. Yield = 50% (0.050 mmol, 13.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.17 – 7.11 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.20 (q, *J* = 1.6 Hz, 1H), 3.83 (s, 3H), 2.28 (s, 3H), 2.11 (d, *J* = 1.6 Hz, 3H), 1.65 (s, 3H), only the peaks relative to **2i'** are reported; diagnostic peak for **2i**: 6.08 (q, *J* = 1.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.1, 146.1, 146.0, 143.3, 140.8, 136.2, 135.7, 129.0 (2C), 125.9 (2C), 123.0, 110.5, 105.4, 55.5, 54.5, 23.3, 20.9, 12.7; **Anal. Calc.** for ($C_{19}H_{20}O$: 264.15): C, 86.32; H, 7.63; found: C, 86.41; H, 7.48.

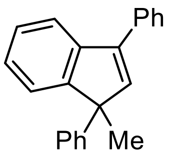


2j

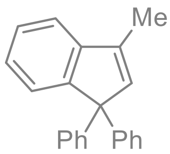


2j'

2j and **2j'** (1.7:1 **2j'**:**2j** ratio). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 45% (0.045 mmol, 10.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34 – 7.12 (m, 9H **2j'** + 9H **2j**), 6.19 (q, *J* = 1.5 Hz, 1H **2j**), 6.18 (t, *J* = 1.6 Hz, 1H **2j'**), 2.54 (tdd, *J* = 9.0, 6.6, 1.3 Hz, 2H **2j'**), 2.30 (dq, *J* = 14.6, 7.3 Hz, 1H **2j**), 2.16 (d, *J* = 1.5 Hz, 3H **2j**), 2.07 (dq, *J* = 14.6, 7.3 Hz, 1H **2j**),1.69 (s, 3H **2j'**), 1.27 (t, *J* = 7.4 Hz, 3H **2j'**), 0.69 (t, *J* = 7.3 Hz, 3H **2j**); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.0 (**2j'**), 151.6 (**2j**), 145.1 (**2j**), 143.9 (**2j'**), 143.8 (**2j**), 143.6 (**2j'**), 143.1 (**2j**), 143.0 (**2j'**), 139.8 (**2j'**), 139.1 (**2j**), 138.1 (**2j**), 128.3 (2C **2j**), 128.3 (2C **2j'**), 126.5 (**2j**), 126.5 (2C **2j**), 126.4 (**2j'**), 126.2 (**2j'**), 126.1 (2C **2j'**), 125.4 (**2j'**), 125.2 (**2j**), 122.9 (**2j**), 122.7 (**2j'**), 119.3 (**2j'**), 119.2 (**2j**), 60.0 (**2j**), 55.2 (**2j'**), 29.8 (**2j**), 23.1 (**2j'**), 20.5 (**2j'**), 12.9 (**2j**), 12.2 (**2j'**), 9.5 (**2j**); **Anal. Calc.** for ($C_{18}H_{18}$: 234.14): C, 92.26; H, 7.74; found: C, 92.33; H, 7.67.

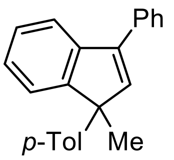


2k'

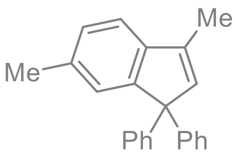


2k
not detected

2k' (isomer **2k** not detected). Viscous pale yellow oil. FC eluent: 100% *n*Hex. Yield = 55% (0.055 mmol, 15.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.68 – 7.61 (m, 2H), 7.56 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 4H), 7.23 – 7.17 (m, 2H), 6.59 (s, 1H), 1.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.4, 143.5, 142.9, 142.1, 141.8, 135.6, 128.6 (2C), 128.4 (2C), 127.7, 127.7 (2C), 126.6, 126.5, 126.2 (2C), 125.9, 123.2, 120.9, 55.6, 22.9; **Anal. Calc.** for ($C_{22}H_{18}$: 282.14): C, 93.57; H, 6.43; found: C, 93.51; H, 6.65.

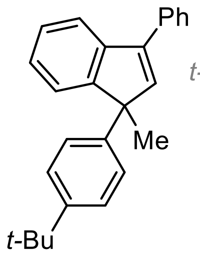


2l'

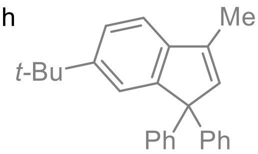


2l
not detected

2l' (isomer **2l** not detected). Viscous pale yellow oil. FC eluent: 100% *n*Hex. Yield = 56% (0.056 mmol, 16.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.67 – 7.60 (m, 2H), 7.55 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.40 – 7.33 (m, 1H), 7.32 – 7.25 (m, 2H), 7.24 – 7.18 (m, 3H), 7.10 – 7.04 (m, 2H), 6.57 (s, 1H), 2.30 (s, 3H), 1.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.5, 143.7, 142.0, 141.7, 139.8, 136.0, 135.6, 129.1, 128.6, 127.7, 127.2, 126.6, 126.1, 125.8, 123.1, 120.9, 55.3, 23.0, 20.9; **Anal. Calc.** for ($C_{23}H_{20}$: 296.16): C, 93.20; H, 6.80; found: C, 92.99; H, 6.92.

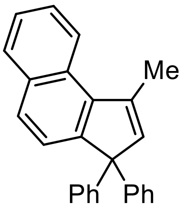


2m'

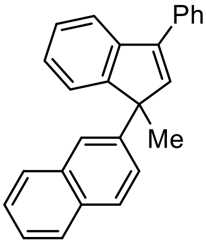


2m
not detected

2m’ (isomer **2m** not detected). Viscous pale-yellow oil. FC eluent: 100% *n*Hex. Yield = 62% (0.062 mmol, 20.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 7.1 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 8.4, 6.3 Hz, 1H), 7.33 – 7.18 (m, 7H), 6.59 (s, 1H), 1.80 (s, 3H), 1.29 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.4, 149.2, 143.7, 142.1, 141.6, 139.8, 135.7, 128.6 (2C), 127.7 (2C), 127.7, 126.6, 125.8 (2C), 125.7, 125.3 (2C), 123.2, 120.8, 55.3, 34.3, 31.3 (3C), 23.0; **Anal. Calc.** for ($C_{26}H_{26}$: 338.20): C, 92.26; H, 7.74; found: C, 92.12; H, 7.59.

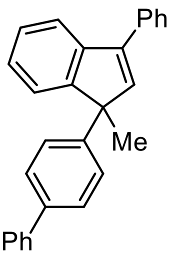


2n

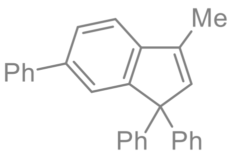


2n'

2n and **2n’** (1.76:1 **2n**:**2n’** ratio). Viscous pale yellow oil. FC eluent: 100% *n*Hex. Yield = 53% (0.053 mmol, 17.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.94 – 7.90 (m, 1H **2n** + 1H **2n’**), 7.87 (d, *J* = 8.3 Hz, 1H **2n**), 7.81 (dt, *J* = 8.2, 1.2 Hz, 1H **2n’**), 7.76 – 7.73 (m, 1H **2n’**), 7.69 – 7.62 (m, 3H **2n’**), 7.61 – 7.55 (m, 2H **2n’** + 1H **2n**), 7.49 – 7.42 (m, 2H **2n**), 7.42 – 7.36 (m, 2H **2n’**), 7.35 – 7.28 (m, 2H **2n**), 7.27 – 7.22 (m, 1H **2n** + 1H **2n’**), 7.22 – 7.11 (m, 8H **2n** + 5H **2n’**), 6.64 – 6.60 (m, 1H **2n** +1H **2n’**), 2.26 (d, *J* = 1.6 Hz, 3H **2n**), 1.91 (s, 3H **2n’**); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.4 (diagnostic for **2n’**), 146.8, 144.1, 143.4, 142.9, 142.2, 142.2, 141.0, 140.4, 136.6, 135.5, 133.5, 132.4, 132.3, 129.5, 129.0, 128.9, 128.9 (4C, diagnostic of **2n**), 128.6, 128.1 (4C, diagnostic of **2n**), 127.9, 127.8, 127.8, 127.7, 127.4, 126.7, 126.4, 126.0, 125.9, 125.8, 125.5, 125.4, 125.0, 124.3, 124.0, 123.3, 121.0, 119.0, 66.3, 55.7, 22.5, 13.0, all peaks are given, without assignment; **Anal. Calc.** for ($C_{28}H_{22}$: 358.17): C, 93.81; H, 6.19; found: C, 94.02; H, 6.10.



2o'

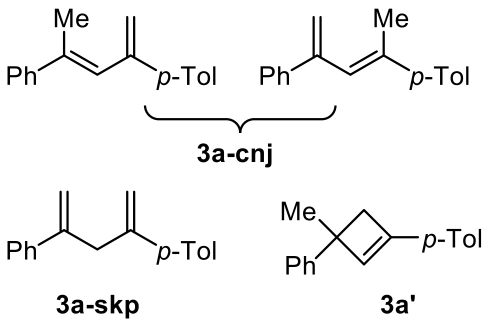


2o
not detected

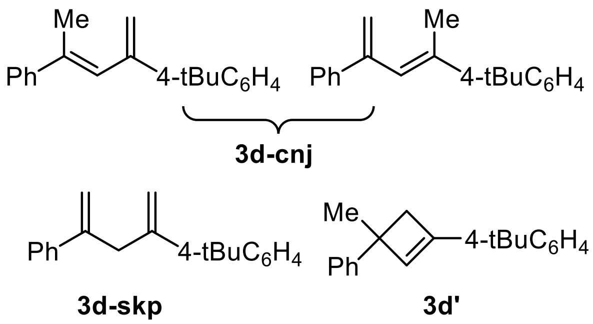
2o’ (isomer **2o** not detected). Viscous pale yellow oil. FC eluent: 100% *n*Hex. Yield = 54% (0.054 mmol, 19.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.68 – 7.63 (m, 2H), 7.58 – 7.52 (m, 4H), 7.50 – 7.41 (m, 4H), 7.41 – 7.35 (m, 4H), 7.35 – 7.27 (m, 3H), 7.26 – 7.21 (m, 1H), 6.61 (s, 1H), 1.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.3, 143.4, 142.1, 142.0, 141.9, 140.8, 139.4, 135.5, 128.7 (2C), 128.6 (2C), 127.8, 127.7 (2C), 127.1 (2C), 127.1, 127.0 (2C), 126.7, 126.6 (2C), 125.9, 123.2, 121.0, 55.4, 22.9; **Anal. Calc.** for ($C_{28}H_{22}$: 358.17): C, 93.81; H, 6.19; found: C, 94.02; H, 6.10.

Optimized general procedure for the GO-promoted preparation of dienes 3

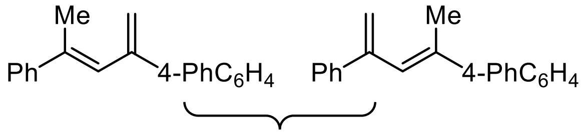
A screw-cap-vial was charged with reagent grade EtOAc (3.5 ml), the desired cyclobutanol **1** (0.1 mmol) and GO (20 wt% with respect to **1**). The reaction mixture was warmed at 90 °C and stirred at the same temperature overnight. Removal of the GO by filtration (Celite pad) and subsequent purification via flash chromatography led to the isolation of compounds **3** (generally as a mixture of isomers).



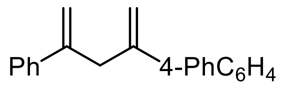
3a (and **3a'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 95% (0.095 mmol, 22.2 mg). **3a-cnj**:**3a-skp**:**3a'** = 3.1:3.8:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.52 – 7.11 (m, 9H + 9H **3a-cnj** + 9H **3a-skp** + 9H **3a'**), 6.65 (s, 1H **3a'**), 6.55 (t, *J* = 1.5 Hz, 1H **3a-cnj**), 6.53 (t, *J* = 1.4 Hz, 1H, **3a-cnj**), 5.66 (d, *J* = 1.6 Hz, 1H, **3a-cnj**), 5.64 (d, *J* = 1.6 Hz, 1H, **3a-cnj**), 5.47 (dt, *J* = 1.4, 0.7 Hz, 1H, **3a-skp**), 5.45 (dt, *J* = 1.4, 0.7 Hz, 1H, **3a-skp**), 5.23 (t, *J* = 1.5 Hz, 1H, **3a-cnj**), 5.19 (t, *J* = 1.5 Hz, 1H, **3a-cnj**), 5.12 (q, *J* = 1.4 Hz, 1H, **3a-skp**), 5.08 (q, *J* = 1.4 Hz, 1H, **3a-skp**), 3.68 – 3.62 (m, 2H **3a-skp**), 2.94 (d, *J* = 12.5 Hz, 1H **3a'**), 2.88 (d, *J* = 12.5 Hz, 1H **3a'**), 2.36 (s, 3H, **3a-cnj**), 2.35 (s, 3H, **3a-cnj**), 2.34 (s, 3H **3a-skp** + 3H **3a'**), 2.12 (d, *J* = 1.4 Hz, 3H, **3a-cnj**), 2.10 (d, *J* = 1.4 Hz, 3H, **3a-cnj**), 1.61 (s, 3H **3a'**), minor peaks corresponding to the *Z*-isomers of **3a-cnj** were detected (*E*/*Z* > 15:1). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 147.8, 145.5, 145.1, 145.1, 143.7, 143.4, 141.1, 141.1, 140.5, 138.6, 138.6, 138.0, 137.6, 137.4, 137.2, 137.0, 132.6, 132.1, 129.0, 129.0, 128.9, 128.8, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.2, 126.7, 126.6, 126.4, 126.0, 125.9, 125.9, 125.8, 125.8, 125.6, 124.5, 115.2, 114.7, 114.5, 114.0, 45.9, 44.3, 40.9, 27.6, 21.3, 21.1, 21.1, 21.0, 17.5, all expected 56 peaks are given, without assignment. **Anal. Calc.** for ($C_{18}H_{18}$: 234.14): C, 92.26; H, 7.74; found: C, 92.38; H, 7.90.



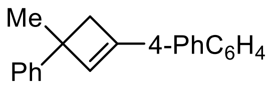
3d (and **3d'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 94% (0.094 mmol, 25.9 mg). **3d-cnj**:**3d-skp**:**3d'** = 0.8:0.9:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.54 – 7.14 (m, 9H + 9H **3d-cnj** + 9H **3d-skp** + 9H **3d'**), 6.66 (s, 1H **3d'**), 6.57 – 6.54 (m, 1H + 1H **3d-cnj**), 5.68 (d, *J* = 1.6 Hz, 1H **3d-cnj**), 5.66 (d, *J* = 1.7 Hz, 1H **3d-cnj**), 5.49 (dd, *J* = 1.5, 0.7 Hz, 1H **3d-skp**), 5.48 (dd, *J* = 1.3, 0.7 Hz, 1H **3d-skp**), 5.23 (t, *J* = 1.5 Hz, 1H **3d-cnj**), 5.19 (t, *J* = 1.5 Hz, 1H **3d-cnj**), 5.15 (q, *J* = 1.3 Hz, 1H **3d-skp**), 5.09 (q, *J* = 1.3 Hz, 1H **3d-skp**), 3.65 (dt, *J* = 1.5, 0.8 Hz, 2H **3d-skp**), 2.94 (d, *J* = 12.5 Hz, 1H **3d'**), 2.88 (d, *J* = 12.5 Hz, 1H **3d'**), 2.15 (d, *J* = 1.4 Hz, 3H **3d-cnj**), 2.11 (d, *J* = 1.4 Hz, 3H **3d-cnj**), 1.62 (s, 3H **3d'**), 1.34 (s, 3H **3d-cnj**) 1.33 (s, 9H **3d-cnj**), 1.32 (s, 9H **3d-skp**), 1.31 (s, 9H **3d'**), minor peaks corresponding to the *Z*-isomers of **3d-cnj** were detected (*E*/*Z* > 15:1). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 150.9, 150.7, 150.4, 147.8, 145.5, 144.9, 143.7, 143.4, 141.0, 140.3, 138.5, 138.4, 138.0, 137.9, 132.9, 132.0, 129.5, 128.3, 128.2, 128.0, 127.8, 127.8, 127.6, 127.5, 127.4, 127.2, 127.0, 126.8, 126.6, 126.2, 126.2, 126.0, 125.9, 125.8, 125.6, 125.6, 125.2, 125.2, 125.1, 125.0, 124.3, 115.2, 114.7, 114.5, 114.0, 45.9, 44.4, 40.8, 34.6, 34.5, 34.5, 31.3, 31.3, 31.3, 27.4, 17.5, 17.4, 57 over the expected 68 peaks (due to partial overlapping) are given, without assignment. **Anal. Calc.** for ($C_{21}H_{24}$: 276.19): C, 91.25; H, 8.75; found: C, 91.03; H, 8.99.



3e-cnj

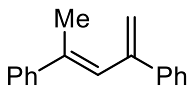


3e-skp

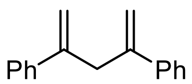


3e'

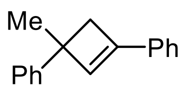
3e (and **3e'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 89% (0.089 mmol, 26.4 mg). **3e-cnj**:**3e-skp**:**3e'** = 2.2:6.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.66 – 7.26 (m, 14H + 14H **3e-cnj** + 14H **3e-skp** + 14H **3e'**), 6.76 (s, 1H **3e'**), 6.65 – 6.63 (m, 1H **3e-cnj**), 6.61 – 6.59 (m, 1H **3e-cnj**), 5.75 (d, *J* = 1.2 Hz, 1H **3e-cnj**), 5.70 (d, *J* = 1.5 Hz, 1H **3e-cnj**), 5.55 (q, *J* = 0.7 Hz, 1H **3e-skp**), 5.50 (dd, *J* = 1.4, 0.7 Hz, 1H **3e-skp**), 5.28 – 5.25 (m, 1H + 1H **3e-cnj**), 5.19 – 5.15 (m, 2H **3e-skp**), 3.71 (t, *J* = 0.7 Hz, 2H **3e-skp**), 3.01 (d, *J* = 12.5 Hz, 1H **3e'**), 2.94 (d, *J* = 12.4 Hz, 1H **3e'**), 2.17 – 2.16 (m, 3H + 3H **3e-cnj**), 1.65 (s, 3H **3e'**), minor peaks corresponding to the *Z*-isomers of **3e-cnj** were detected (*E*/*Z* > 15:1). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 147.6, 145.4, 144.9, 144.8, 143.5, 143.3, 142.2, 141.0, 141.0, 140.8, 140.7, 140.7, 140.7, 140.5, 140.5, 140.2, 140.1, 139.8, 139.8, 138.9, 138.3, 134.0, 133.7, 128.8, 128.7, 128.7, 128.3, 128.3, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 127.3, 127.3, 127.3, 127.3, 127.0, 127.0, 127.0, 127.0, 126.9, 126.8, 126.6, 126.4, 126.3, 126.0, 125.9, 125.8, 125.7, 125.0, 115.5, 115.3, 114.8, 46.1, 44.3, 40.8, 27.5, 17.6; 61 over the expected 68 peaks (due to partial overlapping) are given, without assignment. **Anal. Calc.** for ($C_{23}H_{20}$: 296.16): C, 93.20; H, 6.80; found: C, 92.99; H, 7.02.



3f-cnj

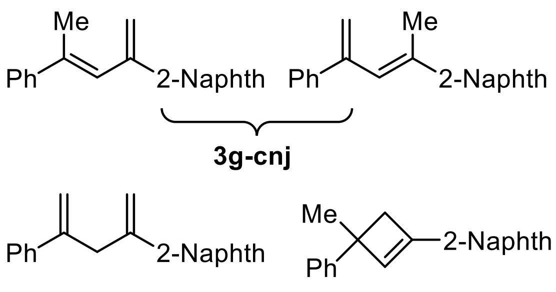


3f-skp



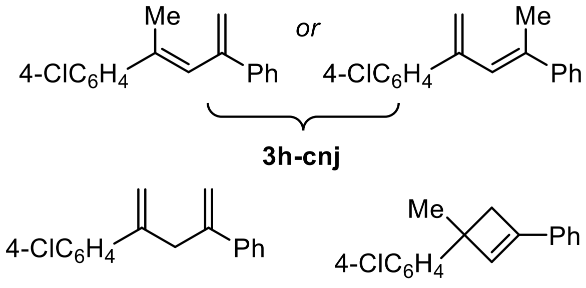
3f'

3f (and **3f'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 85% (0.085 mmol, 18.7 mg). **3f-cnj**:**3f-skp**:**3f'** = 2.6:2.8:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.55 – 7.15 (m, 10H + 10H **3f-cnj** + 10H **3f-skp** + 10H **3f'**), 6.73 (s, 1H **3f'**), 6.57 (s, 1H **3f-cnj**), 5.68 (s, 1H **3f-cnj**), 5.48 (s, 2H **3f-skp**), 5.25 (s, 1H **3f-cnj**), 5.14 (s, 2H **3f-skp**), 3.68 (s, 2H **3f-skp**), 2.98 (d, *J* = 12.0 Hz, 1H **3f'**), 2.91 (d, *J* = 12.5 Hz, 1H **3f'**), 2.13 (s, 3H **3f-cnj**), 1.63 (s, 3H **3f'**), minor peaks corresponding to the *Z*-isomers of **3f-cnj** were detected (*E*/*Z* > 15:1). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 147.7, 145.4, 145.3, 143.8, 143.4, 141.0, 140.9, 138.8, 133.7, 128.3, 128.3, 128.2, 128.1, 127.8, 127.8, 127.6, 127.5, 127.4, 127.2, 126.6, 126.0, 125.9, 125.8, 125.7, 124.6, 116.2, 115.4, 114.8, 65.8, 44.2, 40.9, 27.5, 17.6; all expected 33 peaks are given, without assignment. **Anal. Calc.** for ($C_{17}H_{16}$: 220.13): C, 92.75; H, 7.45; found: C, 92.66; H, 7.31.



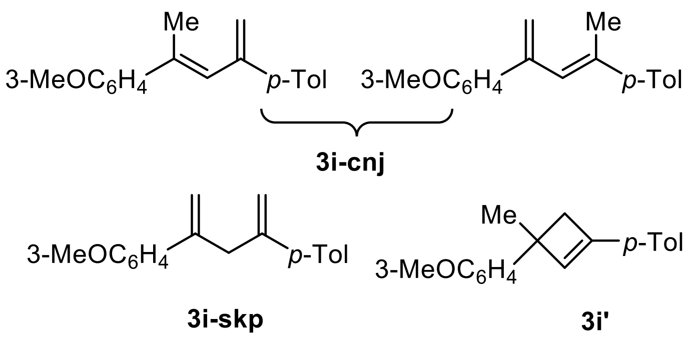
3g-cnj 3g-skp 3g'

3g (and **3g'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 96% (0.096 mmol, 25.9 mg). **3g-cnj**:**3g-skp**:**3g'** = 1.7:2.5:1. **[1]H NMR** (400 MHz, $CDCl_3$) δ = 7.91 – 7.11 (m, 12H + 12H **3a-cnj** + 12H **3a-skp** + 12H **3a'**), 6.84 (s, 1H, **3g'**), 6.73 (t, *J* = 1.5 Hz, 1H **3g-cnj**), 6.70 – 6.67 (m, 1H **3g-cnj**), 5.82 (d, *J* = 1.5 Hz, 1H **3g-cnj**), 5.72 (d, *J* = 1.6 Hz, 1H **3g-cnj**), 5.63 (d, *J* = 1.2 Hz, 1H **3g-skp**), 5.49 (dt, *J* = 1.4, 0.7 Hz, 1H **3g-skp**), 5.35 (t, *J* = 1.5 Hz, 1H **3g-cnj**), 5.30 (t, *J* = 1.5 Hz, 1H **3g-cnj**), 5.25 (q, *J* = 1.3 Hz, 1H **3g-skp**), 5.18 (q, *J* = 1.4 Hz, 3H **3g-skp**), 3.82 – 3.77 (m, 2H **3g-skp**), 3.09 (d, *J* = 12.4 Hz, 1H **3g'**), 3.02 (d, *J* = 12.4 Hz, 1H **3g'**), 2.23 (d, *J* = 1.6 Hz, 3H **3g-cnj**), 2.15 (d, *J* = 1.4 Hz, 3H **3g-cnj**), 1.67 (s, 3H **3g'**), minor peaks corresponding to the *Z*-isomers of **3g-cnj** were detected (*E*/*Z* > 15:1). **[13]C NMR** (100 MHz, $CDCl_3$) δ = 148.3, 147.7, 145.4, 145.3, 145.2, 144.4, 143.9, 143.3, 142.7, 142.4, 141.0, 139.0, 138.2, 138.1, 135.6, 134.5, 133.4, 133.4, 133.3, 133.0, 132.9, 132.8, 132.5, 132.2, 129.0, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.2, 126.2, 126.1, 126.1, 126.0, 126.0, 125.9, 125.9, 125.9, 125.8, 125.8, 125.7, 125.6, 124.7, 124.7, 124.4, 124.3, 124.2, 124.1, 123.4, 122.7, 118.7, 115.8, 115.5, 115.4, 114.9, 58.5, 56.4, 46.1, 44.3, 40.9, 27.6, 22.0, 21.7, 18.4, 17.6, 13.0, all expected 76 peaks are given, without assignment. **Anal. Calc.** for ($C_{21}H_{18}$: 270.14): C, 93.29; H, 6.71; found: C, 93.45; H, 6.66.

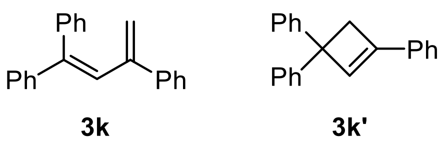


3h-cnj 3h-skp 3h'

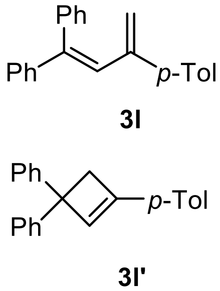
3h (and **3h'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 98% (0.098 mmol, 25.1 mg). **3h-cnj**:**3h-skp**:**3h'** = 0.4:0.6:1 (only one conjugated diene was detected). **[1]H NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.25 (m, 9H **3h-cnj** + 9H **3h-skp** + 9H **3h'**), 6.65 (s, 1H **3h'**), 6.53 (td, *J* = 1.4, 0.6 Hz, 1H **3h-cnj**), 5.67 (dd, *J* = 1.5, 0.6 Hz, 1H **3h-cnj**), 5.45 – 5.43 (m, 2H **3h-skp**), 5.23 (t, *J* = 1.5 Hz, 1H **3h-cnj**), 5.14 (q, *J* = 1.3 Hz, 1H **3h-skp**), 5.09 (q, *J* = 1.4 Hz, 1H **3h-skp**), 3.67 – 3.60 (m, 2H **3h-skp**), 2.90 (s, 2H **3h'**), 2.08 (d, *J* = 1.4 Hz, 3H **3h-cnj**), 1.59 (s, 3H **3h'**), minor peaks corresponding to the *Z*-isomer of **3h-cnj** were detected (*E*/*Z* > 15:1). **[13]C NMR** (100 MHz, $CDCl_3$) δ = [13]C NMR (101 MHz, $cdcl_3$) δ 146.1, 145.2, 145.1, 144.3, 144.0, 141.8, 140.8, 139.3, 137.6, 134.4, 133.2, 133.2, 131.4, 129.5, 129.2, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.9, 127.7, 127.5, 127.3, 127.3, 127.2, 126.5, 125.9, 124.6, 115.6, 115.4, 114.9, 58.5, 45.5, 44.3, 40.9, 27.3, 17.5; all expected 39 peaks are given, without assignment. **Anal. Calc.** for ($C_{17}H_{15}Cl$: 254.09): C, 80.15; H, 5.94; found: C, 79.95; H, 6.06.



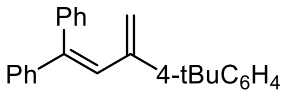
3i (and **3i'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 95% (0.095 mmol, 25.1 mg). **3i-cnj**:**3i-skp**:**3i'** = 1.4:2.2:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42 – 6.67 (m, 8H + 8H **3i-cnj** + 8H **3i-skp** + 8H **3i'**), 6.62 (s, 1H **3i'**), 6.55 (t, *J* = 1.4 Hz, 1H **3i-cnj**), 6.51 (t, *J* = 1.5 Hz, 1H **3i-cnj**), 5.65 (d, *J* = 1.6 Hz, 1H **3i-cnj**), 5.64 (d, *J* = 1.6 Hz, 1H **3i-cnj**), 5.46 (s, 1H **3i-skp**), 5.44 (s, 1H **3i-skp**), 5.22 (t, *J* = 1.5 Hz, 1H **3i-cnj**), 5.18 (t, *J* = 1.6 Hz, 1H **3i-cnj**), 5.12 (q, *J* = 1.4 Hz, 1H **3i-skp**), 5.09 (q, *J* = 1.4 Hz, 1H **3i-skp**), 3.83 (s, 3H **3i-cnj**), 3.81 (s, 3H **3i'**), 3.80 (s, 3H **3i-cnj**), 3.79 (s, 3H **3i-skp**), 3.64 – 3.62 (m, 2H **3i-skp**), 2.94 (d, *J* = 12.5 Hz, 1H **3i'**), 2.86 (d, *J* = 12.5 Hz, 1H **3i'**), 2.35 (s, 3H **3i'**), 2.35 (s, 3H **3i-cnj**), 2.33 (s, 3H **3i-skp**), 2.27 (s, 3H **3i-cnj**), 2.11 – 2.09 (m, 3H + 3H **3i-cnj**), 1.60 (s, 3H **3i'**), minor peaks corresponding to the *Z*-isomers of **3i-cnj** were detected (*E*/*Z* > 15:1). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.5, 159.5, 149.6, 145.4, 145.1, 145.1, 145.0, 143.8, 143.3, 142.7, 140.8, 140.5, 138.4, 138.0, 137.6, 137.4, 137.2, 136.2, 135.7, 132.4, 132.0, 129.2, 129.2, 129.1, 129.0, 129.0, 128.9, 128.9, 127.8, 126.6, 126.4, 125.9, 125.8, 125.8, 124.5, 123.0, 119.2, 118.6, 118.5, 118.4, 115.4, 114.9, 114.6, 114.0, 112.9, 112.7, 112.4, 112.4, 112.1, 111.9, 111.9, 110.6, 110.5, 105.4, 55.5, 55.2, 55.2, 55.2, 44.2, 41.0, 27.5, 23.3, 21.3, 21.0, 20.9, 17.6, 17.5, 12.7; all expected 68 peaks are given, without assignment. **Anal. Calc.** for ($C_{19}H_{20}O$: 264.15): C, 86.32; H, 7.63; found: C, 86.30; H, 7.42.



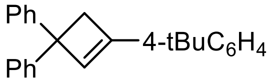
3k (and **3k'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 89% (0.089 mmol, 25.1 mg). **3k**:**3k'** = 1.9:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.48 – 7.09 (m, 15H **3k** + 15H **3k'**), 7.00 (s, 1H **3k'**), 6.75 (s, 1H **3k**), 5.40 (s, 1H **3k**), 5.04 (s, 1H **3k**), 3.43 (s, 2H **3k'**). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 146.1, 145.4, 145.3, 144.7, 143.1, 140.7, 140.1, 134.2, 131.9, 130.1, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 127.9, 127.9, 127.6, 127.4, 127.2, 127.0, 126.7, 125.9, 124.8, 117.3, 53.2, 45.1; all expected 28 peaks are given, without assignment. **Anal. Calc.** for ($C_{22}H_{18}$: 282.14): C, 93.57; H, 6.43; found: C, 93.61; H, 6.67.



3l (and **3l'**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 64% (0.064 mmol, 19.0 mg). **3l**:**3l'** = 4.0:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36 – 7.02 (m, 14H **3l** + 14H **3l'**), 6.91 (s, 1H **3l'**), 6.71 (s, 1H **3l**), 5.35 (s, 1H **3l**), 4.94 (s, 1H **3l**), 3.40 (s, 2H **3l'**), 2.34 (s, 3H **3l'**), 2.31 (s, 3H **3l**). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.9, 144.5, 143.1, 140.1, 137.9, 137.2, 130.8, 130.1, 129.1, 129.0, 128.8, 128.5, 128.5, 128.2, 128.1, 128.1, 127.9, 127.7, 127.5, 127.2, 126.9, 126.4, 126.1, 125.8, 124.7, 116.2, 53.2, 45.1, 21.3, 21.1; all expected 30 peaks are given, without assignment. **Anal. Calc.** for ($C_{23}H_{20}$: 296.16): C, 93.20; H, 6.80; found: C, 93.40; H, 6.77.

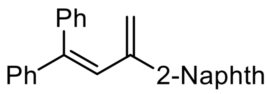


3m

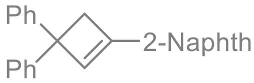


3m'

3m (and **3m’**). Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 94% (0.094 mmol, 31.8 mg). **3m**:**3m’** = 6.3:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.10 (m, 14H **3m** + 14H **3m’**), 6.93 (s, 1H **3m’**), 6.74 (s, 1H **3m**), 5.37 (s, 1H **3m**), 4.98 (s, 1H **3m**), 3.41 (s, 2H **3m’**), 1.32 (s, 9H **3m’**), 1.30 (s, 9H **3m**). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 150.4, 145.0, 144.4, 143.2, 140.1, 137.8, 130.1 (2C), 128.6, 128.1 (2C), 127.9 (2C), 127.9 (2C), 127.5, 126.9, 126.4 (2C), 125.0 (2C), 116.7, 34.5, 31.3 (3C); only the peaks of **3j** are reported. **Anal. Calc.** for ($C_{26}H_{26}$: 338.20): C, 92.26; H, 7.74; found: C, 92.52; H, 7.45.



3n



3n'

3n. Viscous colorless oil. FC eluent: 100% *n*Hex. Yield = 74% (0.074 mmol, 24.6 mg). **3k**:**3k’** > 20:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 1.8 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.53 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.38 – 7.29 (m, 5H), 7.20 – 7.09 (m, 5H), 6.84 (d, *J* = 1.3 Hz, 1H), 5.52 (d, *J* = 1.3 Hz, 1H), 5.10 (t, *J* = 1.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.1, 144.9, 143.0, 140.0, 137.9, 133.2, 132.8, 130.0 (2C), 128.3, 128.2 (2C), 128.1, 128.0 (2C), 127.9 (2C), 127.7, 127.6, 127.4, 127.0, 126.0, 125.8, 125.6, 124.7, 117.6. **Anal. Calc.** for ($C_{28}H_{22}$: 358.17): C, 93.81; H, 6.19; found: C, 93.71; H, 6.22.

Composition expressed in atomic % were obtained from survey XPS Spectra.

XPS and ssNMR tables and spectra

Sample	C 1s 285 eV	O 1s 532.6 eV	N 1s 400 eV	Cl 2p 200 eV	S 2p 168 eV	XPS O/C
Control GO	72.6	26.3	0.2	0.6	0.2	0.36
GO 100% Conditions A	78.1	21.2	0.2	0.3	0.2	0.27
GO 20% Conditions B	76.2	22.9	0.3	0.3	0.2	0.30

Table S1. XPS atomic composition (% at.) and O/C ratio from O 1s and C 1s. Errors on C 1s and O 1s are ±1.0%. Errors on N 1s, Cl 2p and S 2p are ±0.1%.

.

Sample	C=C sp^2	C-C	C-OH	C-O-C	C=O	O-C=O
GO control	41	10	18	23	7	1.3
GO 100% Conditions A	58	6	10	18	5	2.6
GO 20% Conditions B	45	8	13	24	7	2.9

Table S2 XPS C 1s fit (% on total C 1s signal). Errors on C=C sp^2, C-C and C-O-C are ±2 %, errors on COH and C=O are ±1 %; errors on O-C=O are ±0.5 %.

Sample	C=C sp^2 130 ppm	C-OH 69 ppm	C-O-C 58 ppm	C=O 193 ppm	O-C=O 162 ppm
Control GO	43.2	16.3	27.6	2.5	10.4
GO 100% Conditions A	50.7	12.5	22.9	2.9	11.3
GO 20% Conditions B	43.8	15.5	22.9	3.0	14.5

Table S3. Quantitative composition of GO in different conditions obtained by using ssNMR ^{13}C direct excitation signal. Errors on all peaks are ±1 %; errors on O-C=O are ±1.5 %.

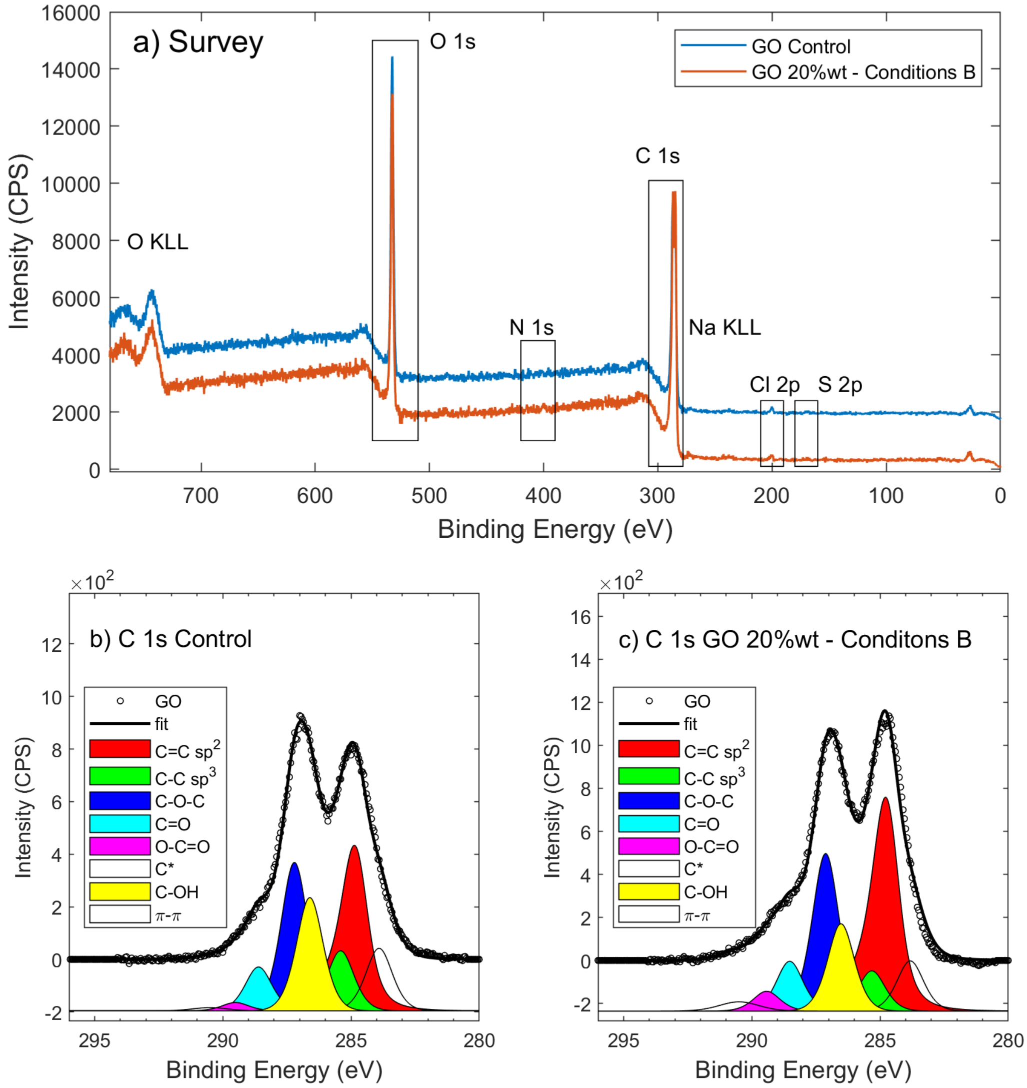


Figure S1. XPS of GO 20 %wt – Conditons B, after **3a-3a'** (a, XPS Survey; c, C1s) and control GO in AcOEt 90 °C 16 h (a, XPS Survey; b, C1s).

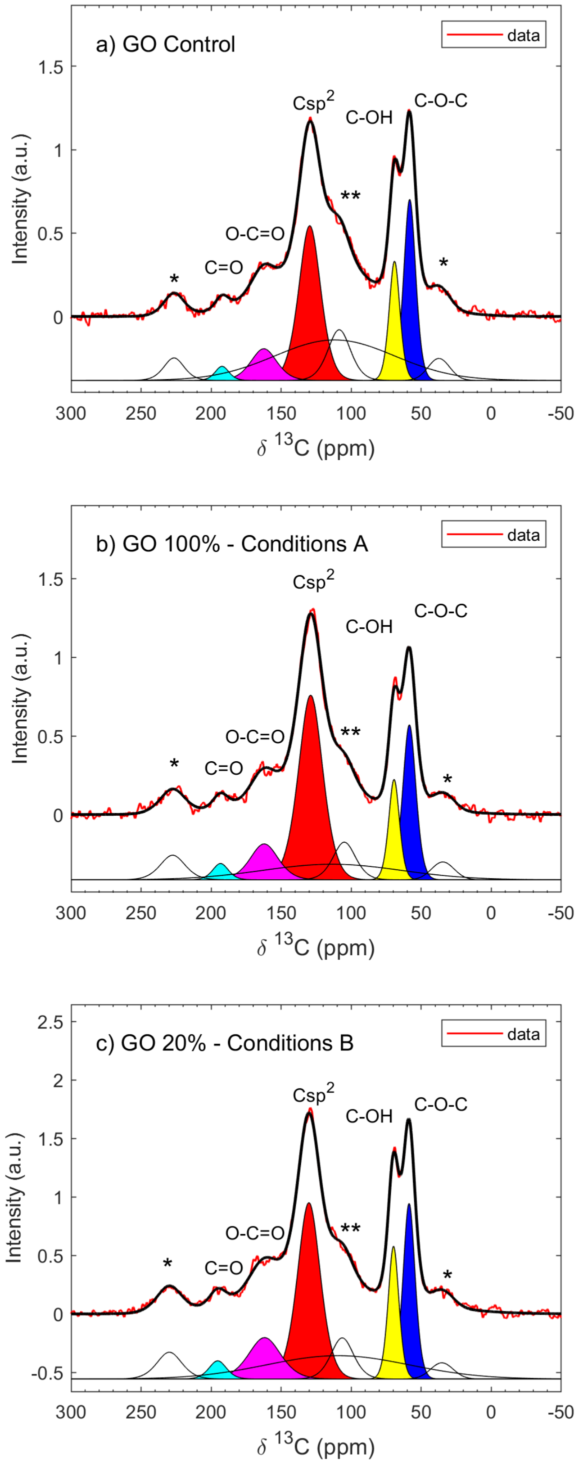


Figure S2. ^{13}C direct excitation ssNMR spectra of a) GO control; b) GO 100% wt - **Conditions A**, c) GO 20% wt – **Conditions B**. Spinning side bands are marked with *. The narrow signal at 102-103 was associated with unknown epoxy glue present in spinning probe and marked with **. The broad peak at 112 ppm, with100 ppm FWHM, was associated with resin or is indicative of paramagnetically influenced sp^2 carbon.[7]

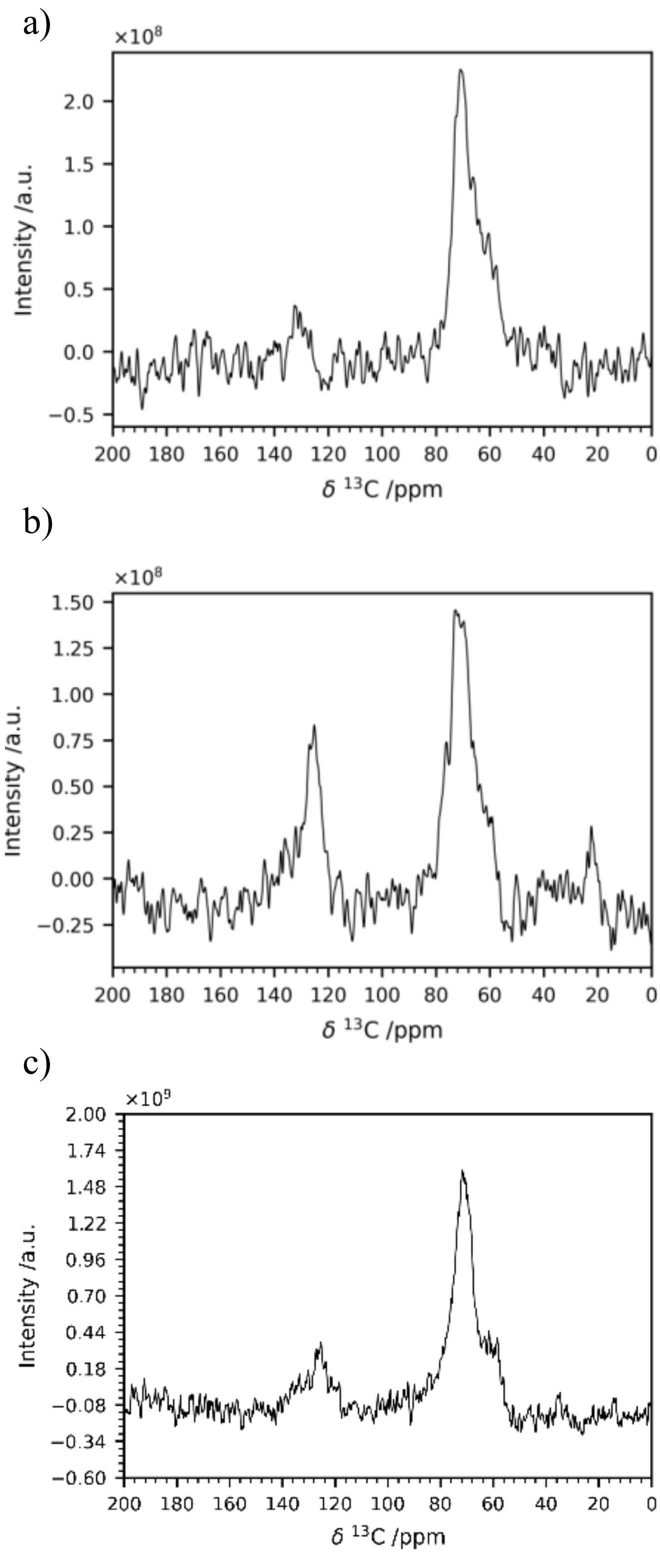
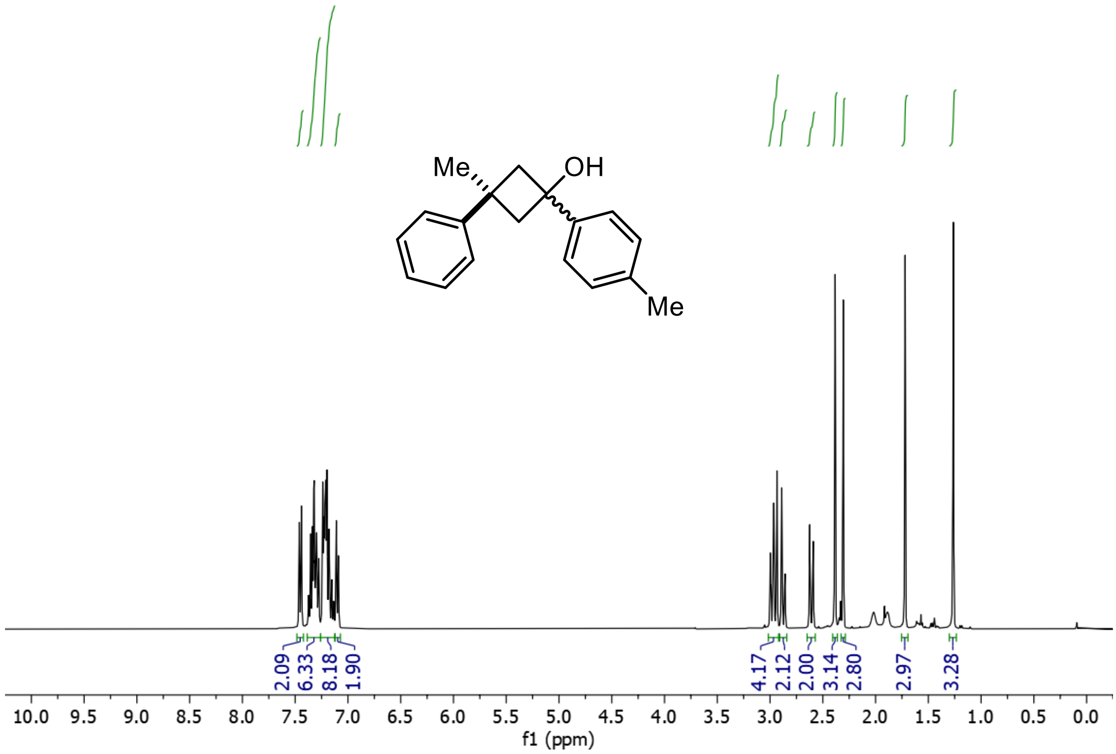


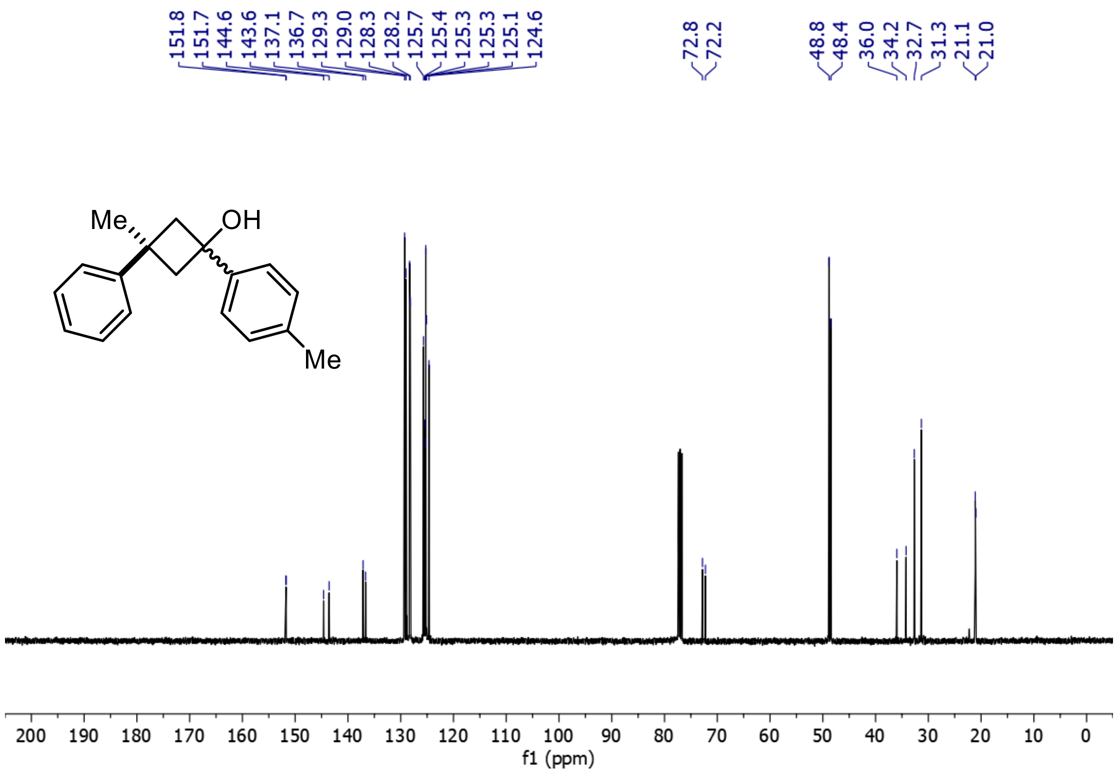
Figure S3. ^{1}H-^{13}C Cross Polarization ssNMR spectra of a) GO control; b) GO 100% wt - **Conditions A**, after **2a-2a'** synthesis; c) GO 20% wt – **Conditions** B, after **3a-3a'** synthesis.

Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

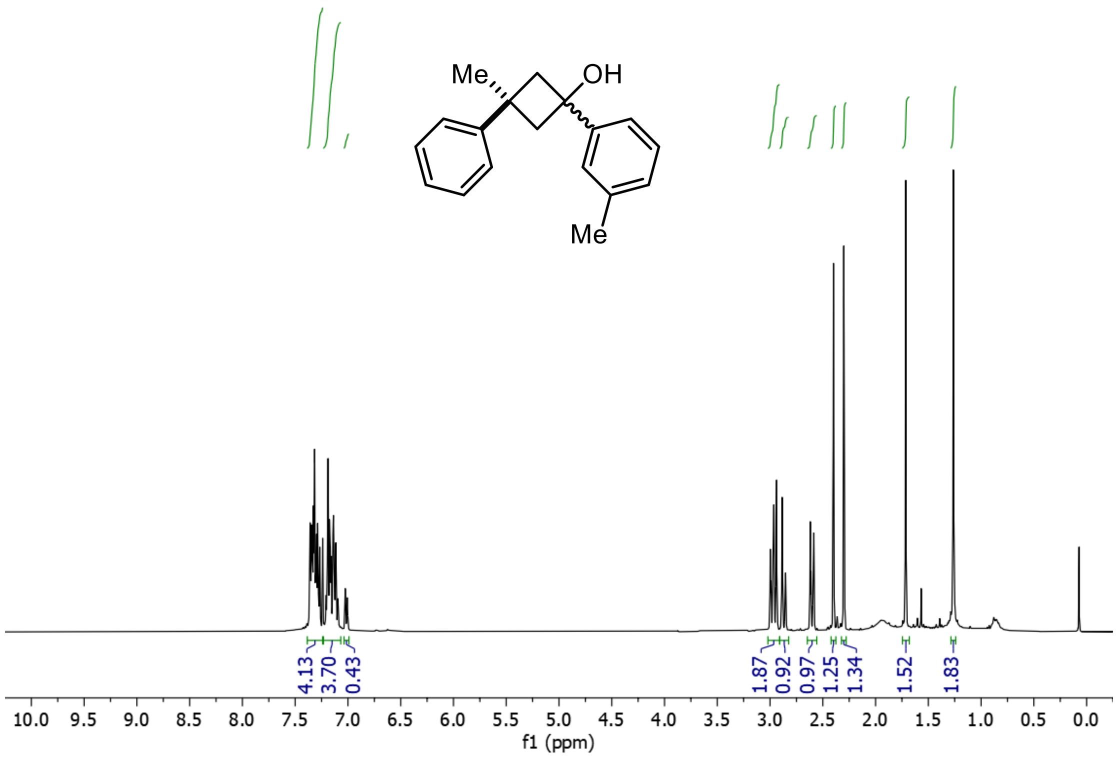
1a ^{1}H NMR (400 MHz, $CDCl_3$)



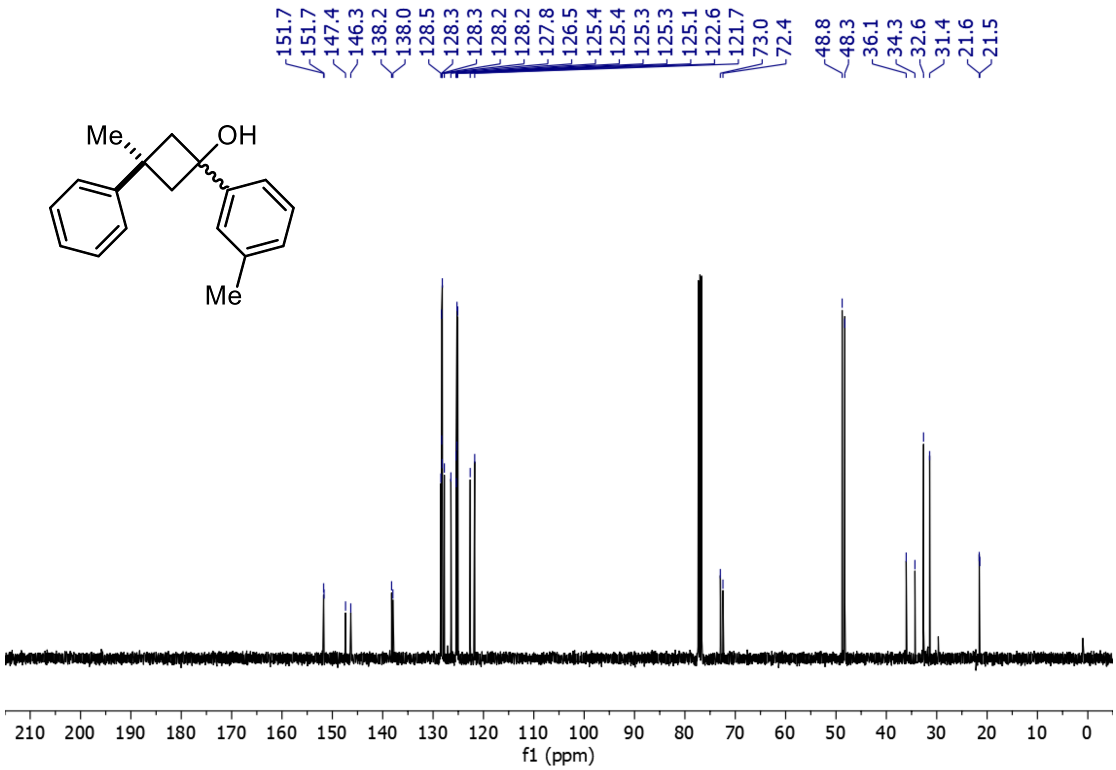
1a ^{13}C NMR (100 MHz, $CDCl_3$)



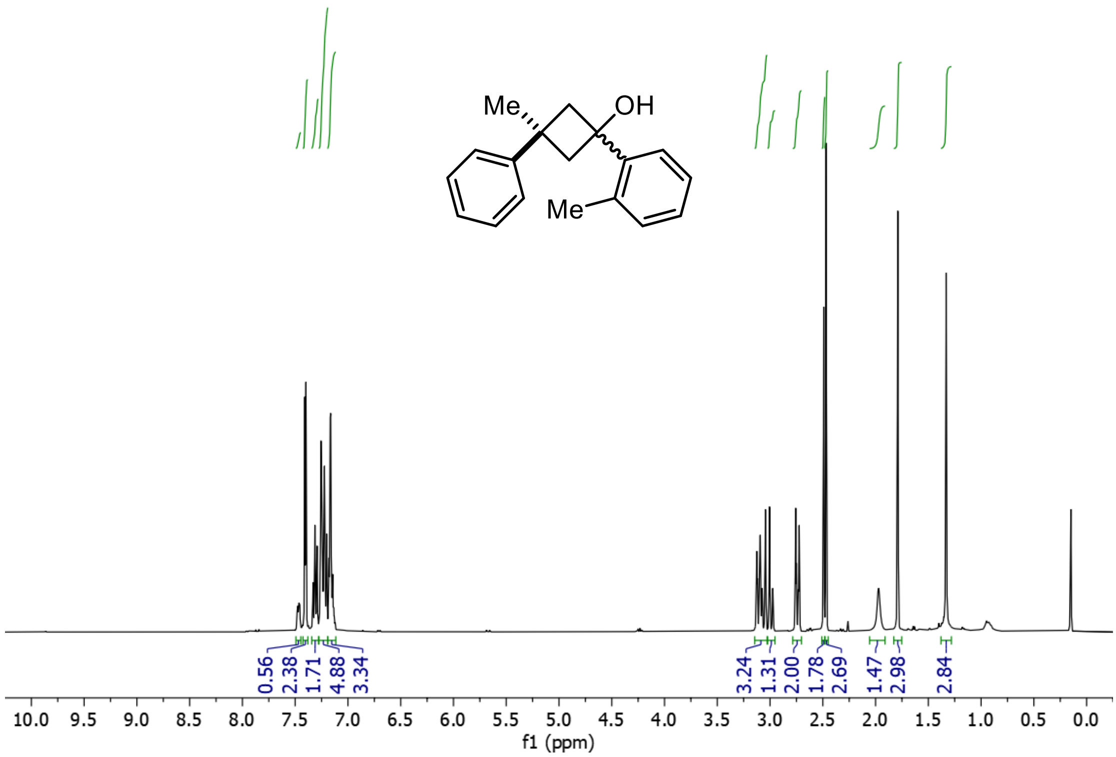
1b ^{1}H NMR (400 MHz, CDCl$_3$)



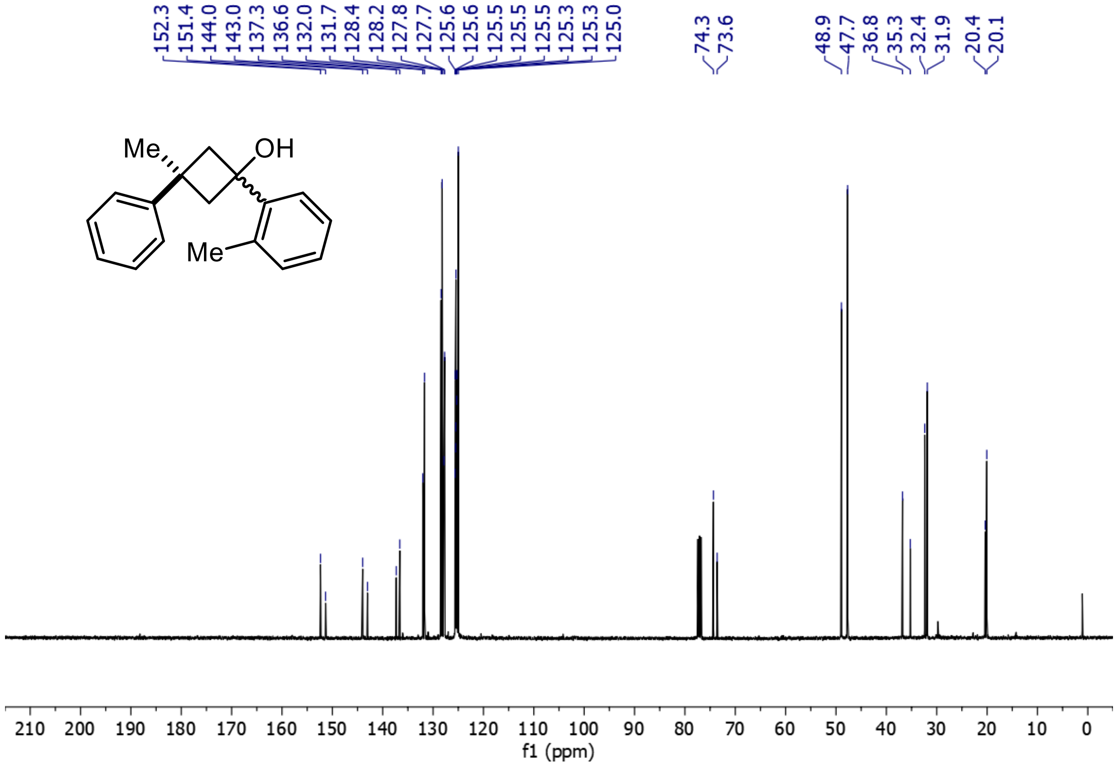
1b ^{13}C NMR (100 MHz, CDCl$_3$)



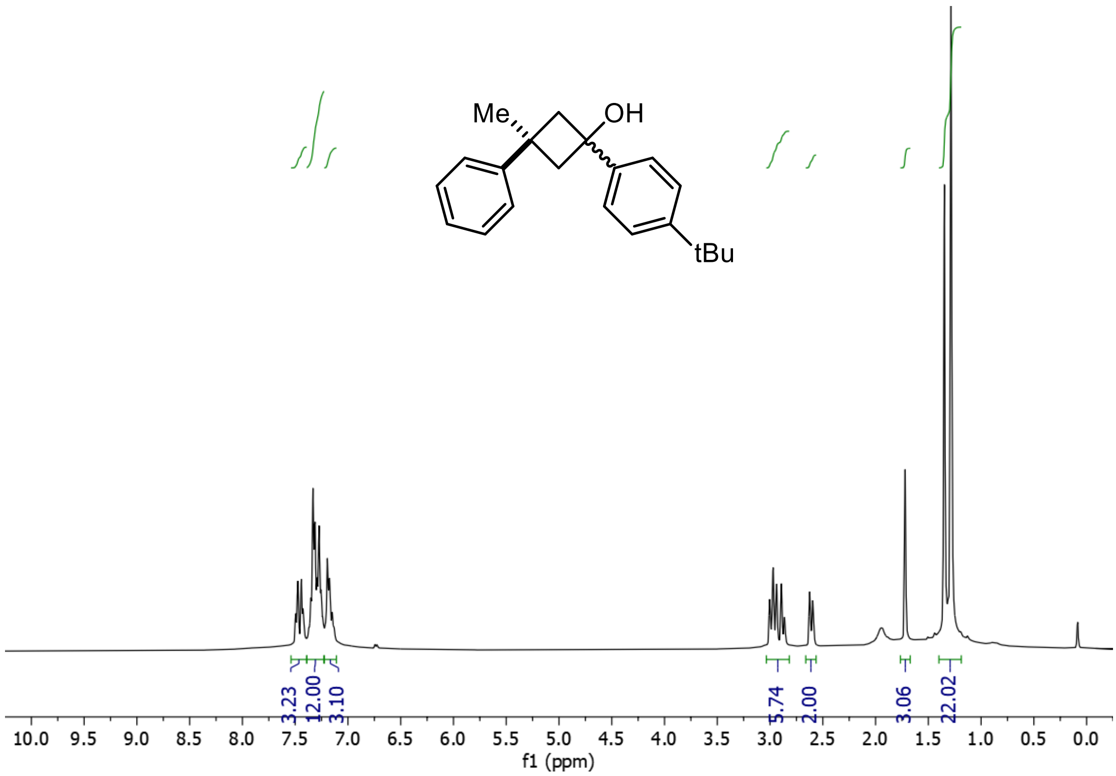
1c ^{1}H NMR (400 MHz, $CDCl_3$)



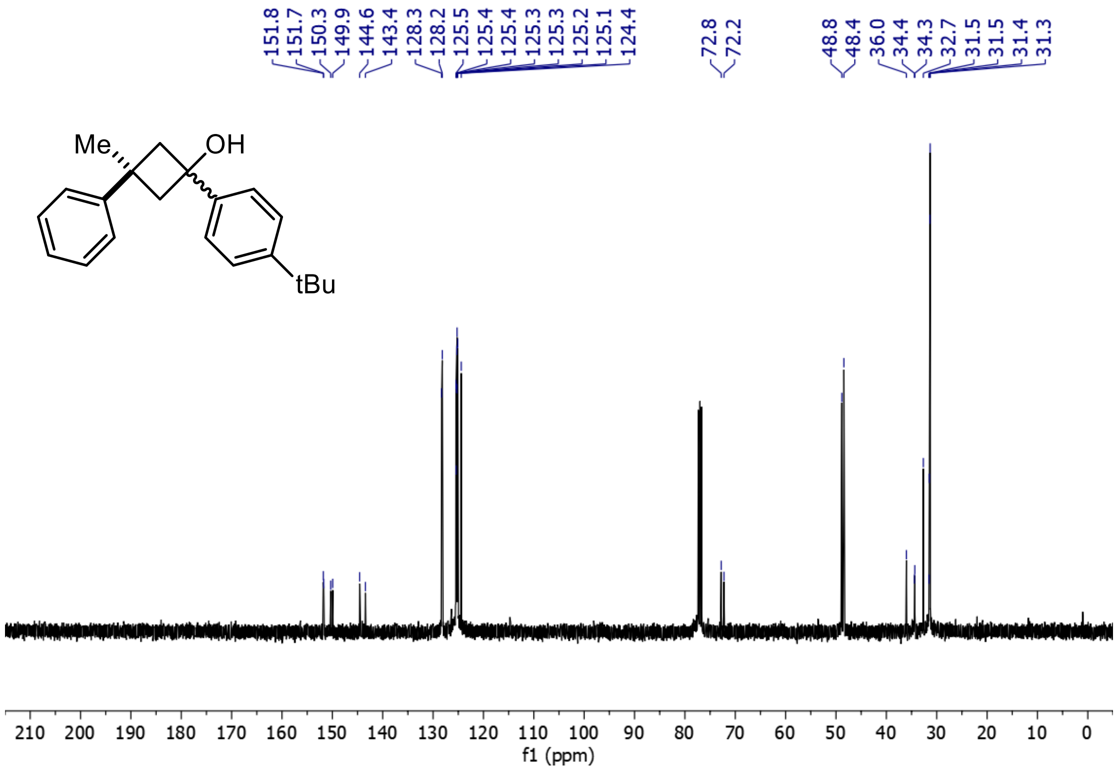
1c ^{13}C NMR (100 MHz, $CDCl_3$)



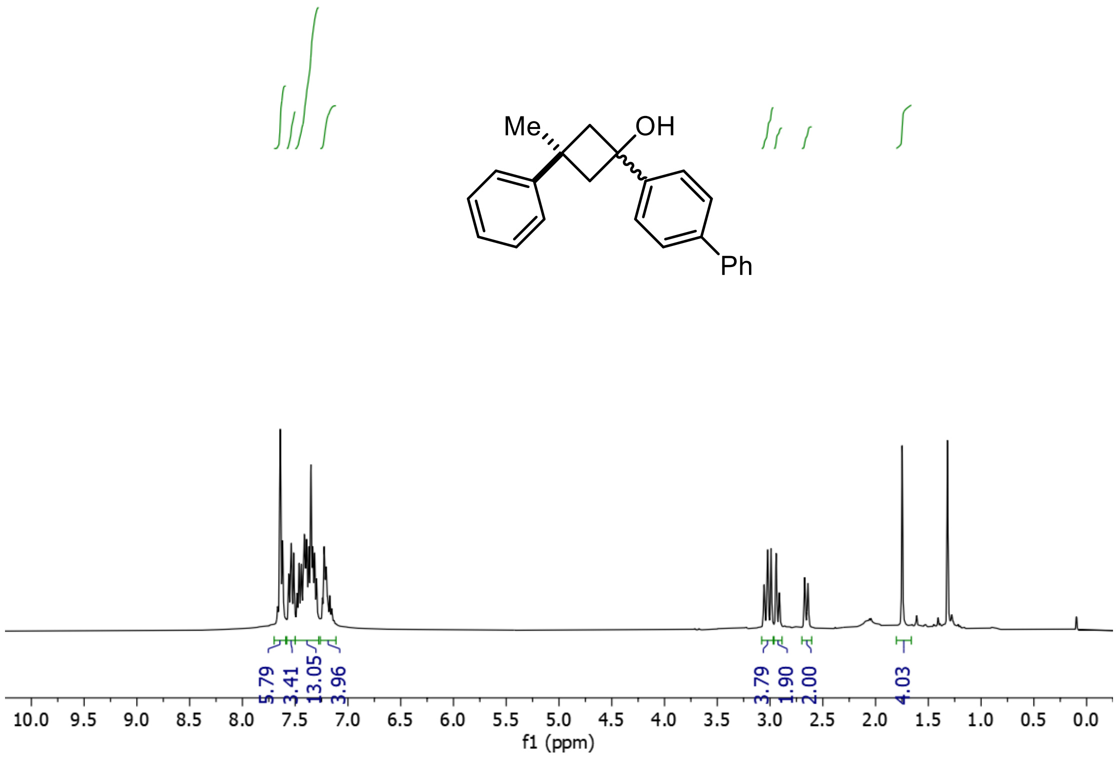
1d ^{1}H NMR (400 MHz, CDCl$_3$)



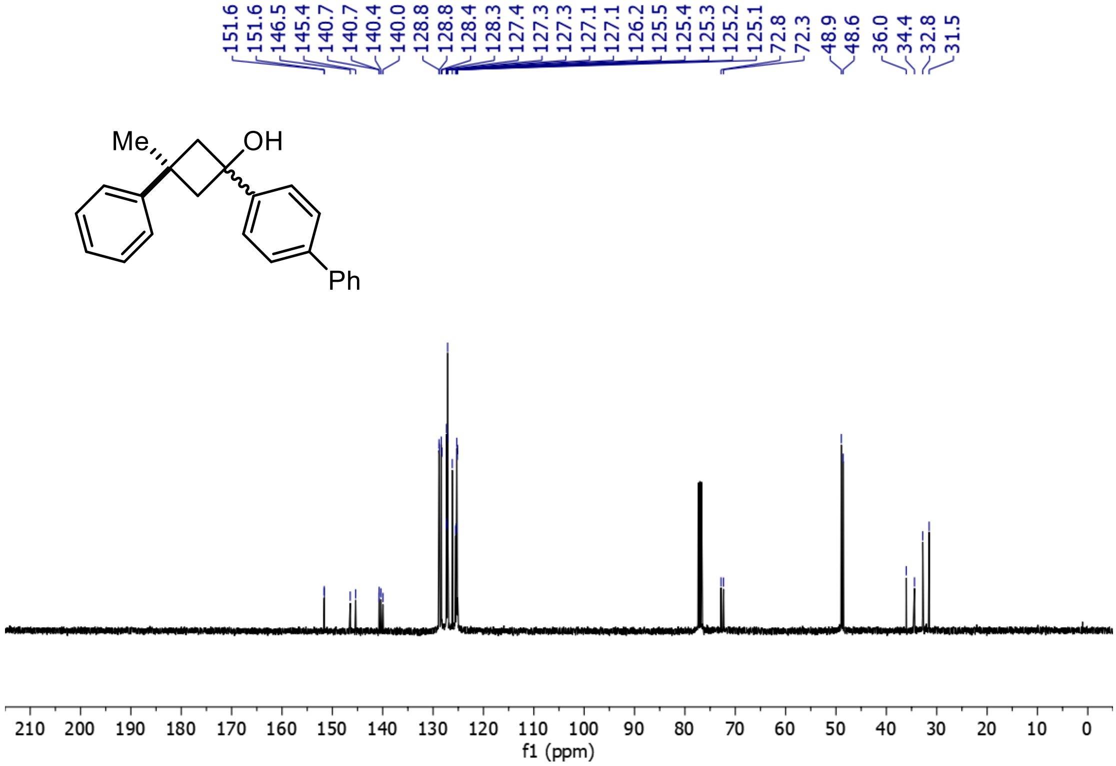
1d ^{13}C NMR (100 MHz, CDCl$_3$)



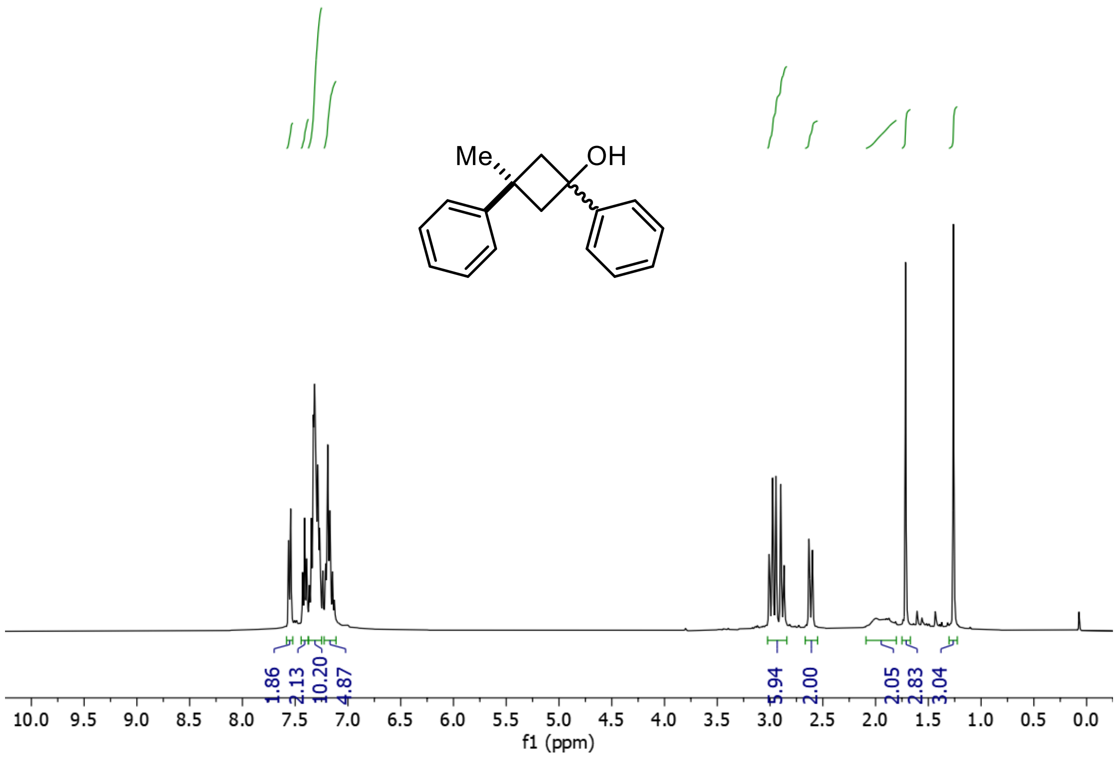
1e ^{1}H NMR (400 MHz, $CDCl_3$)



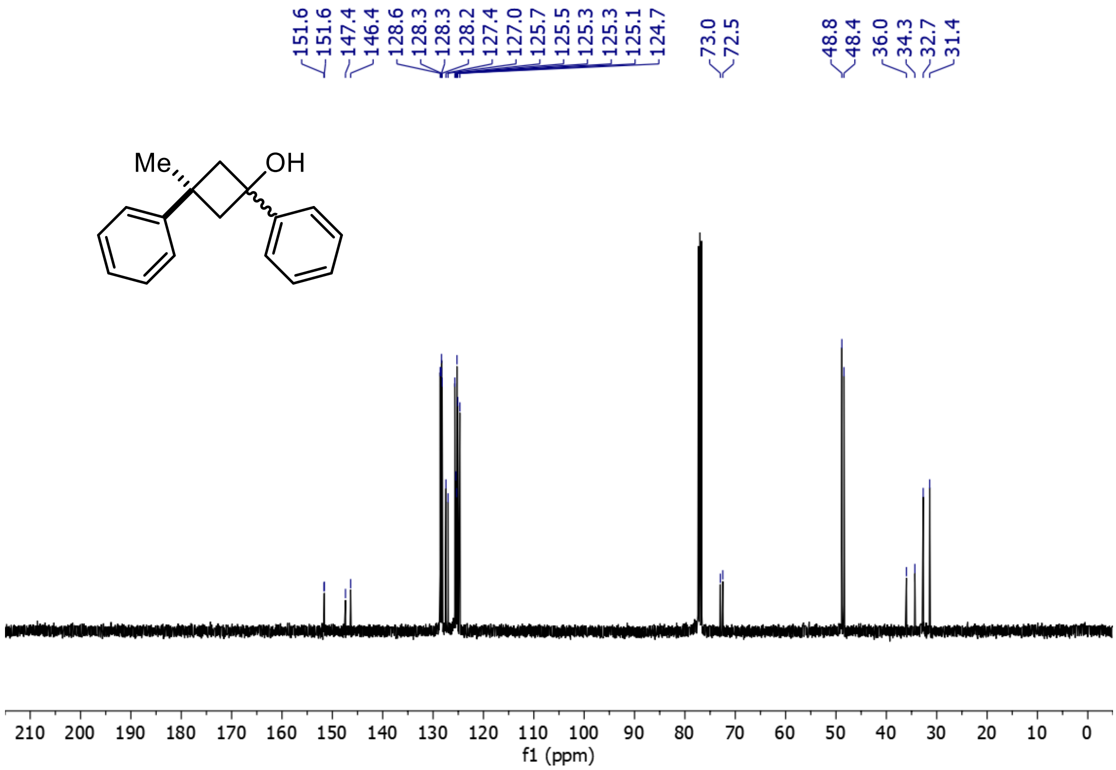
1e ^{13}C NMR (100 MHz, $CDCl_3$)



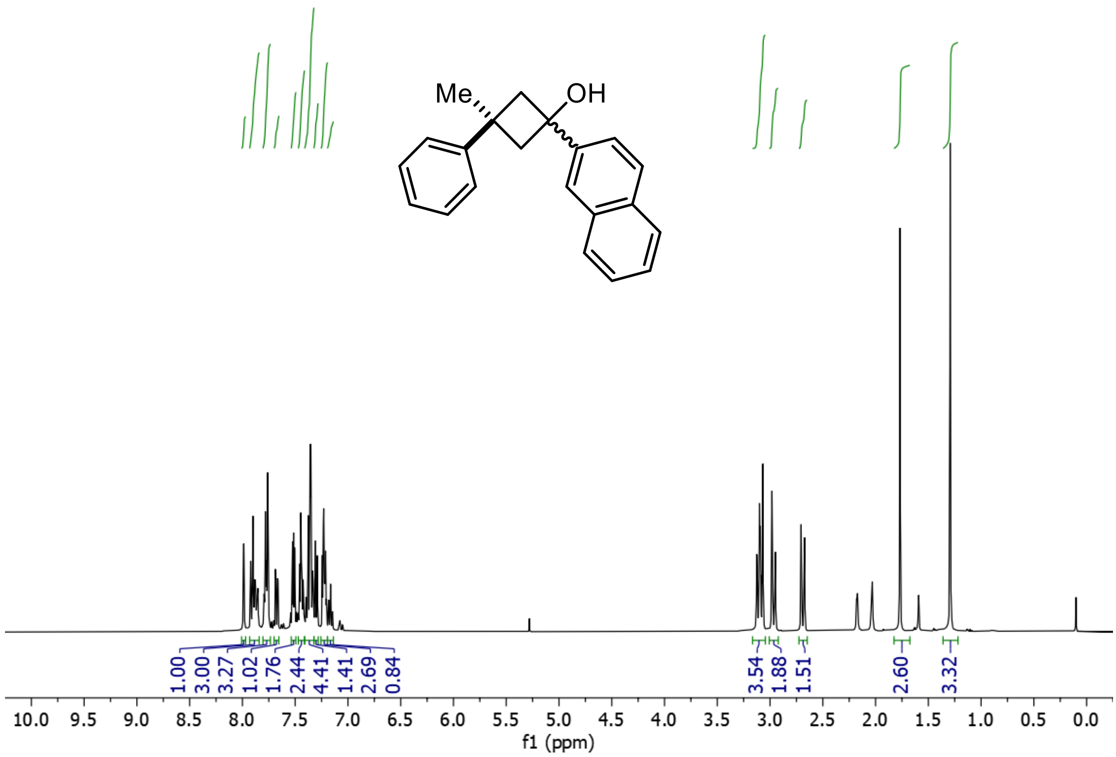
1f ^{1}H NMR (400 MHz, $CDCl_3$)



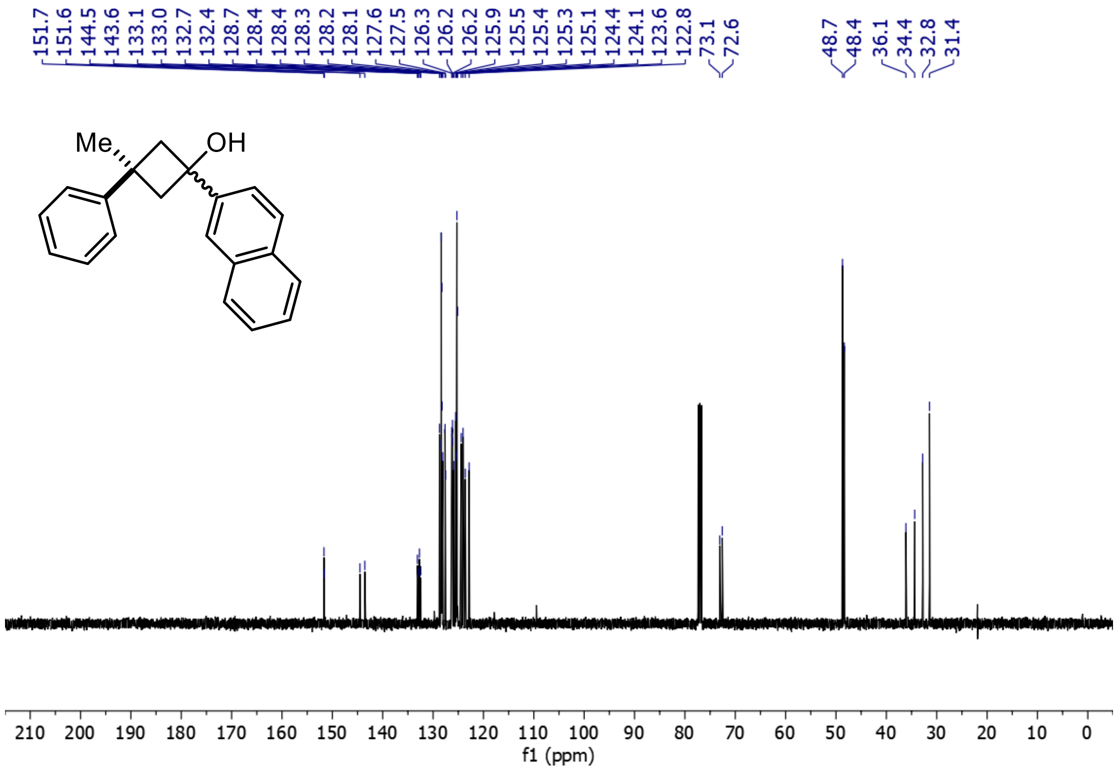
1f ^{13}C NMR (100 MHz, $CDCl_3$)



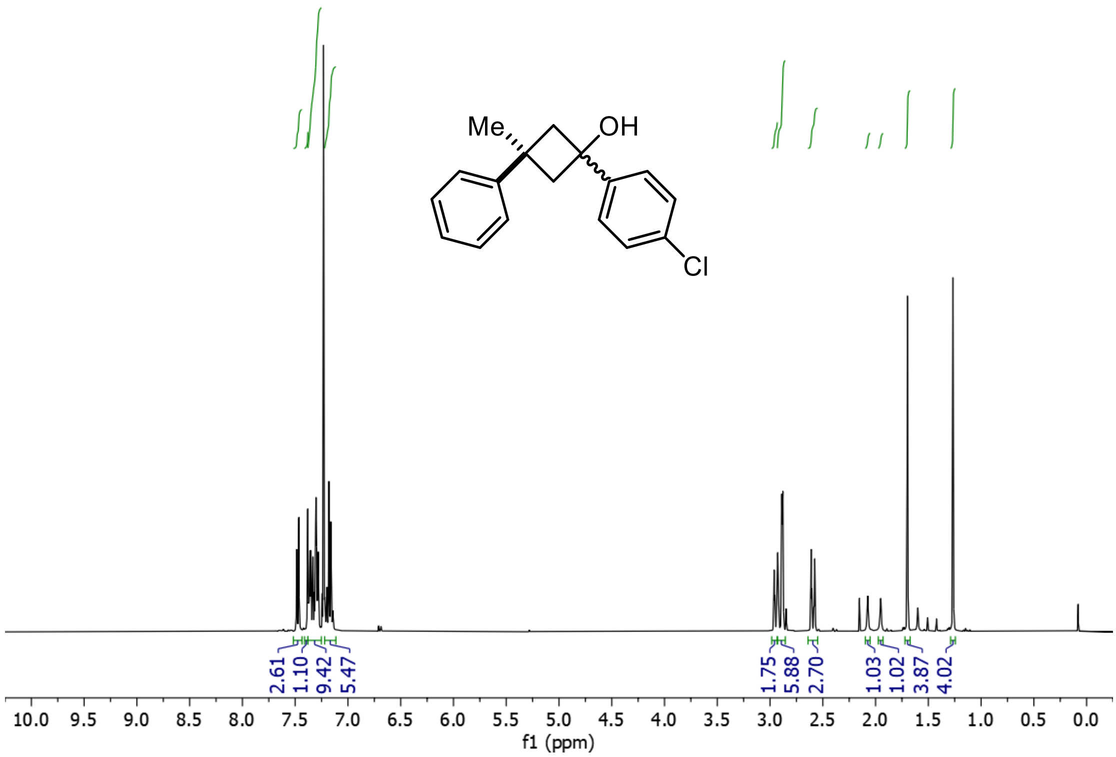
1g ^{1}H NMR (400 MHz, CDCl$_3$)



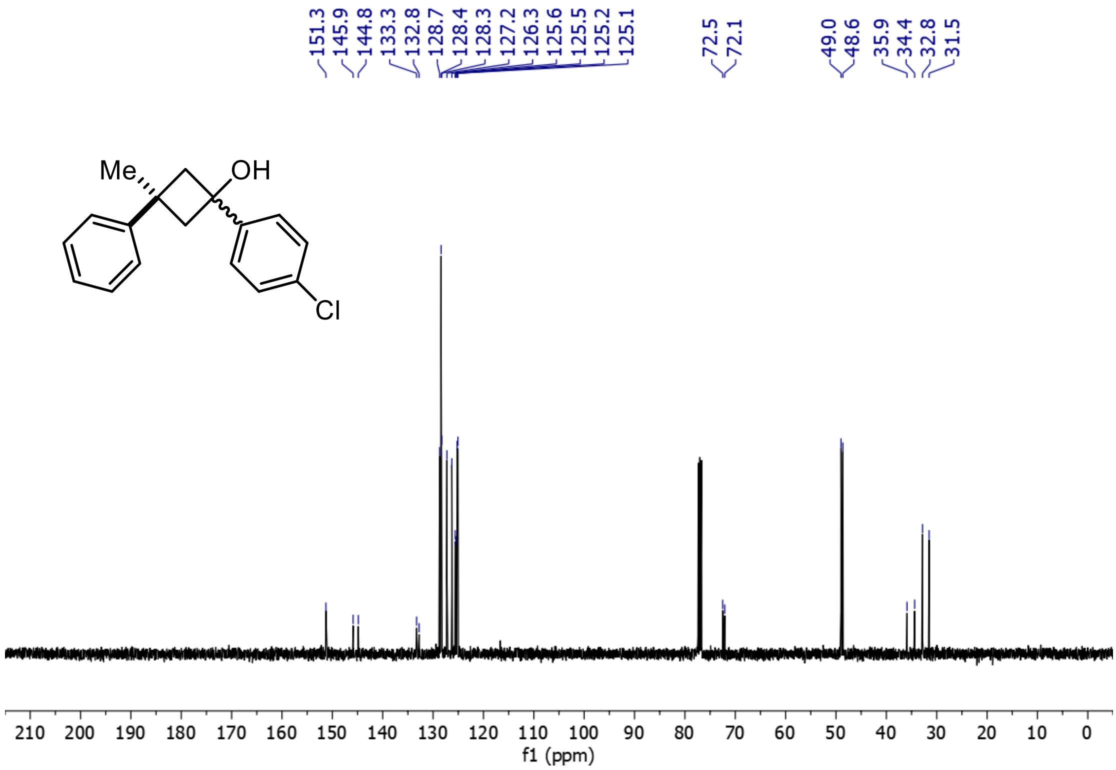
1g ^{13}C NMR (100 MHz, CDCl$_3$)



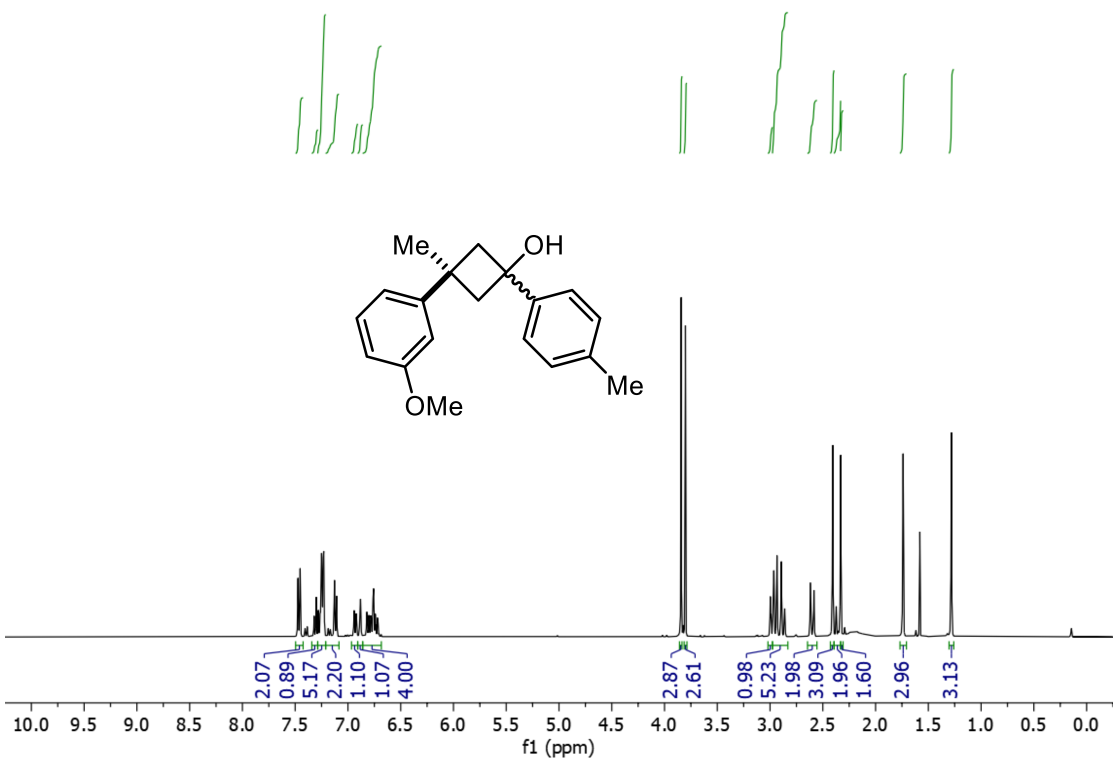
1h ^{1}H NMR (400 MHz, $CDCl_3$)



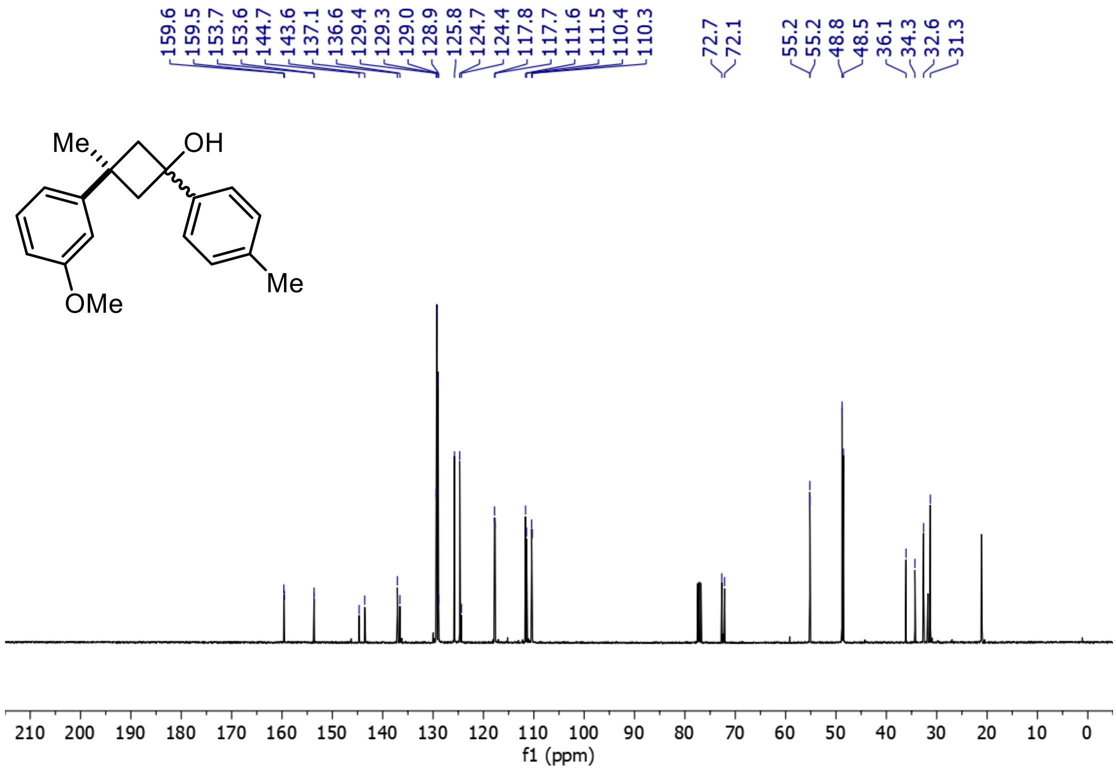
1h ^{13}C NMR (100 MHz, $CDCl_3$)



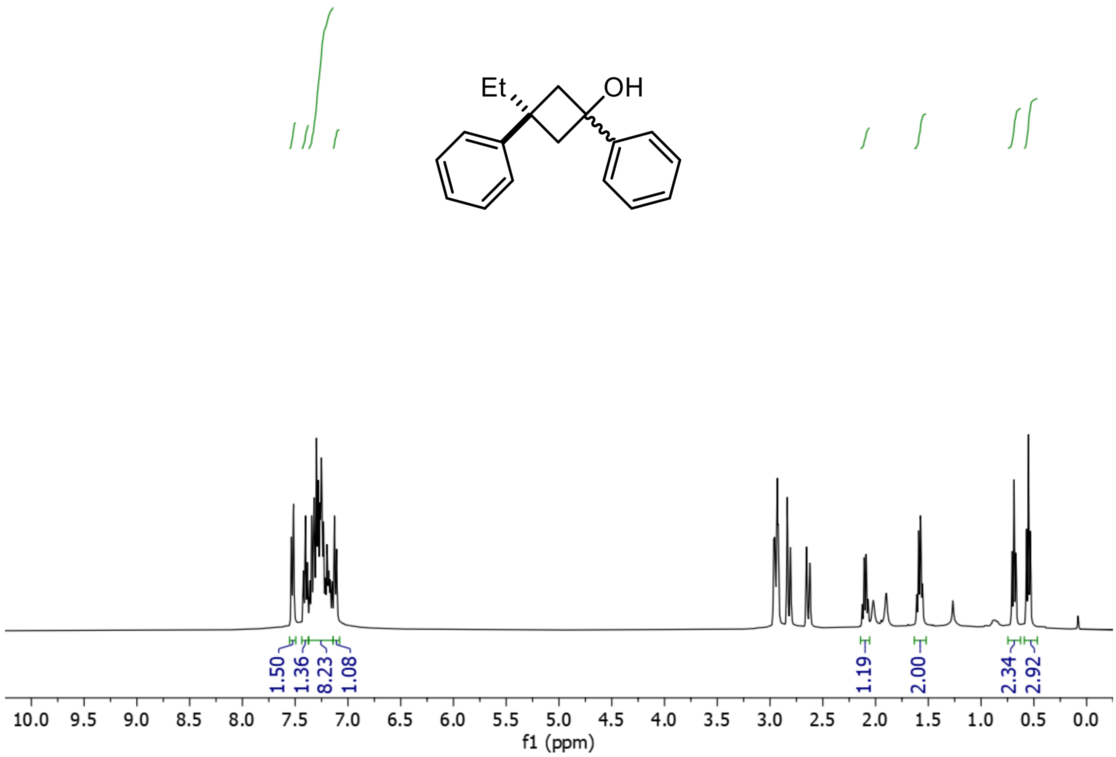
1i ^{1}H NMR (400 MHz, CDCl$_3$)



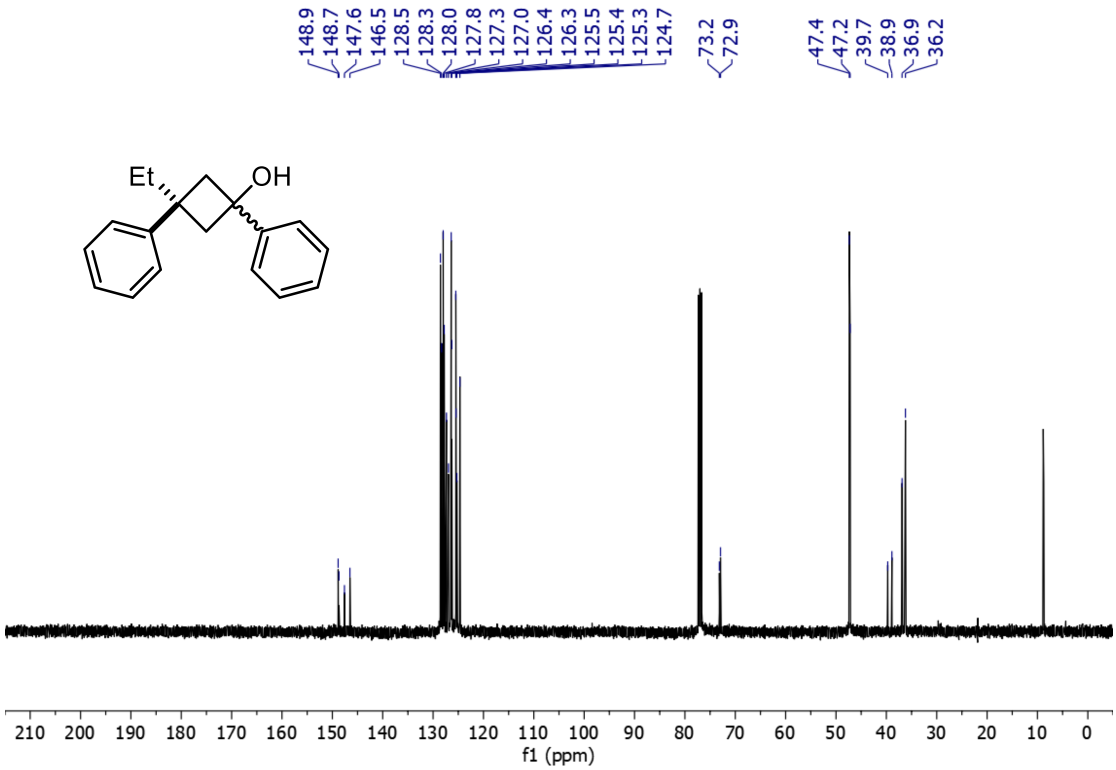
1i ^{13}C NMR (100 MHz, CDCl$_3$)



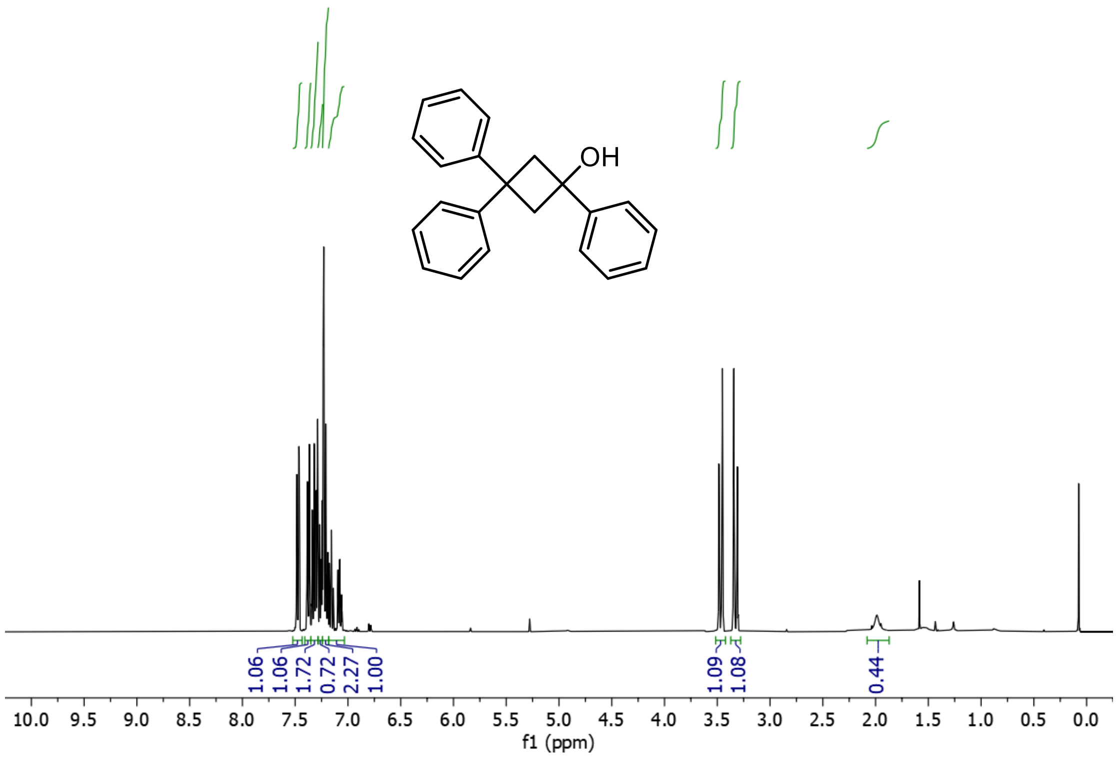
1j ^{1}H NMR (400 MHz, $CDCl_3$)



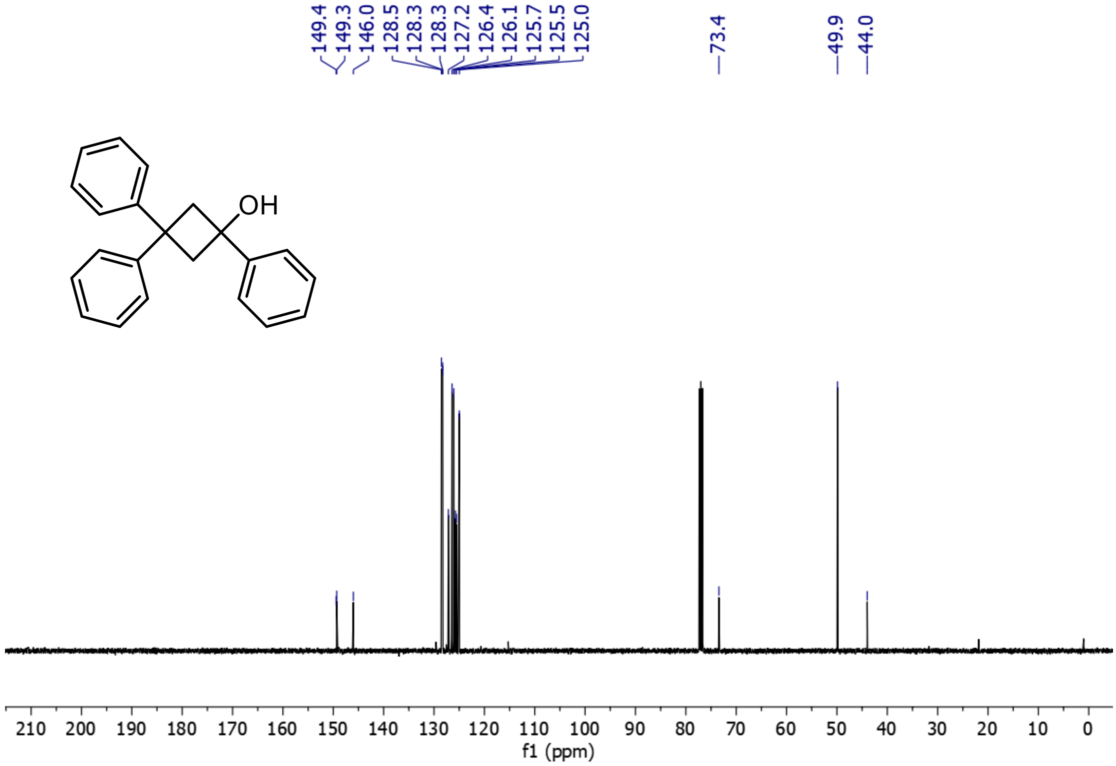
1j ^{13}C NMR (100 MHz, $CDCl_3$)



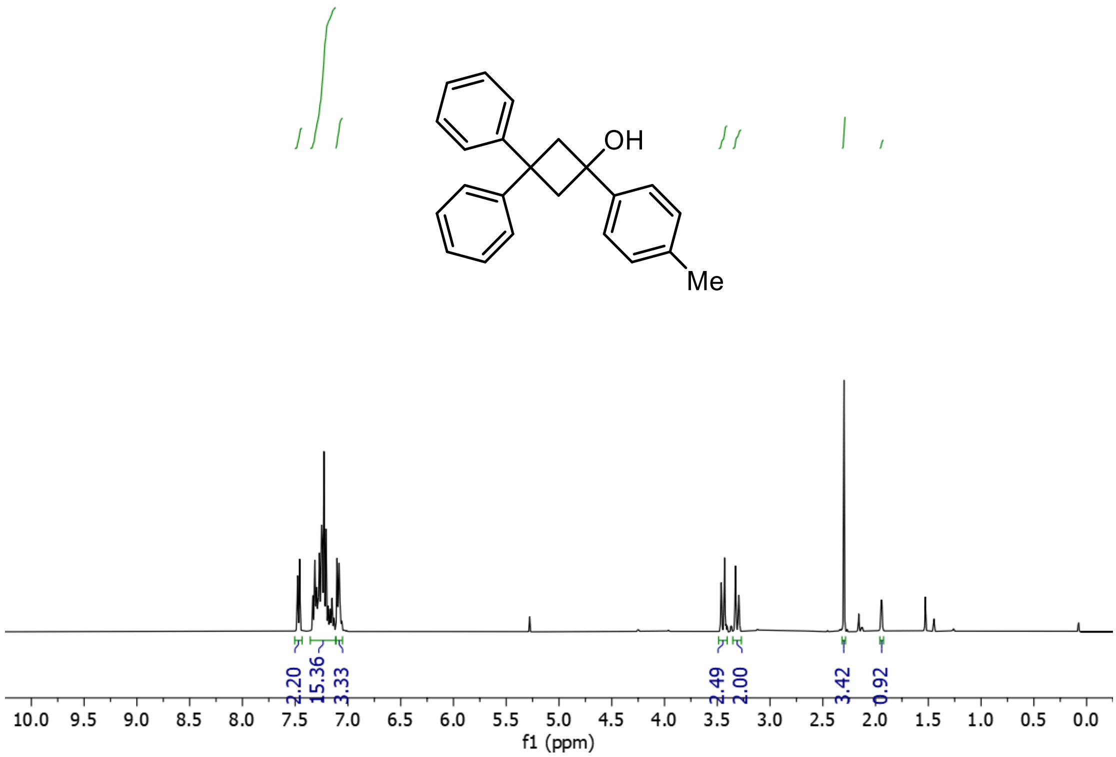
1k ^{1}H NMR (400 MHz, $CDCl_3$)



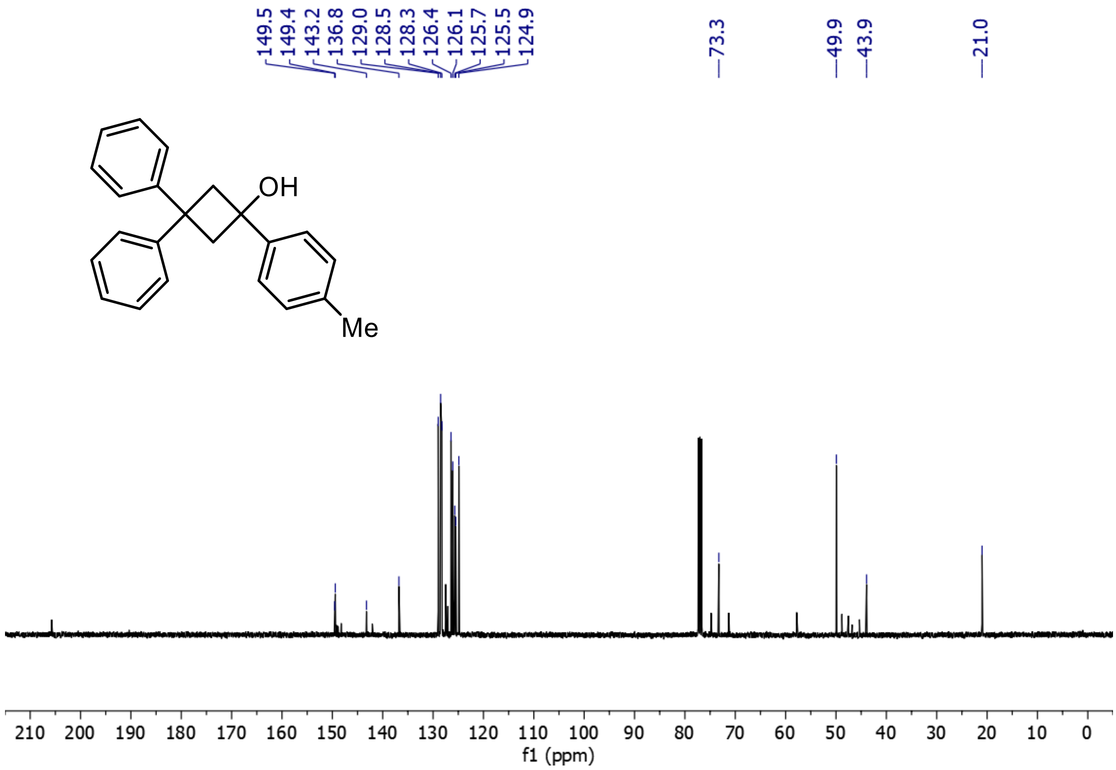
1k ^{13}C NMR (100 MHz, $CDCl_3$)



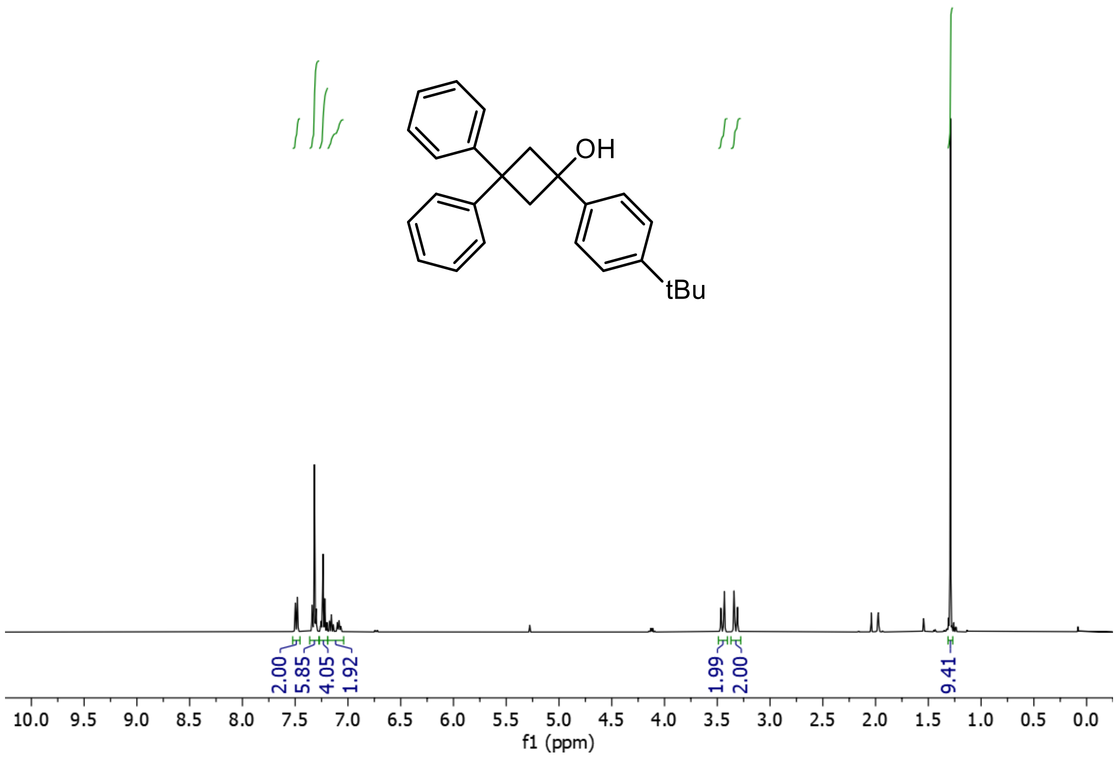
1l ^{1}H NMR (400 MHz, CDCl$_3$)



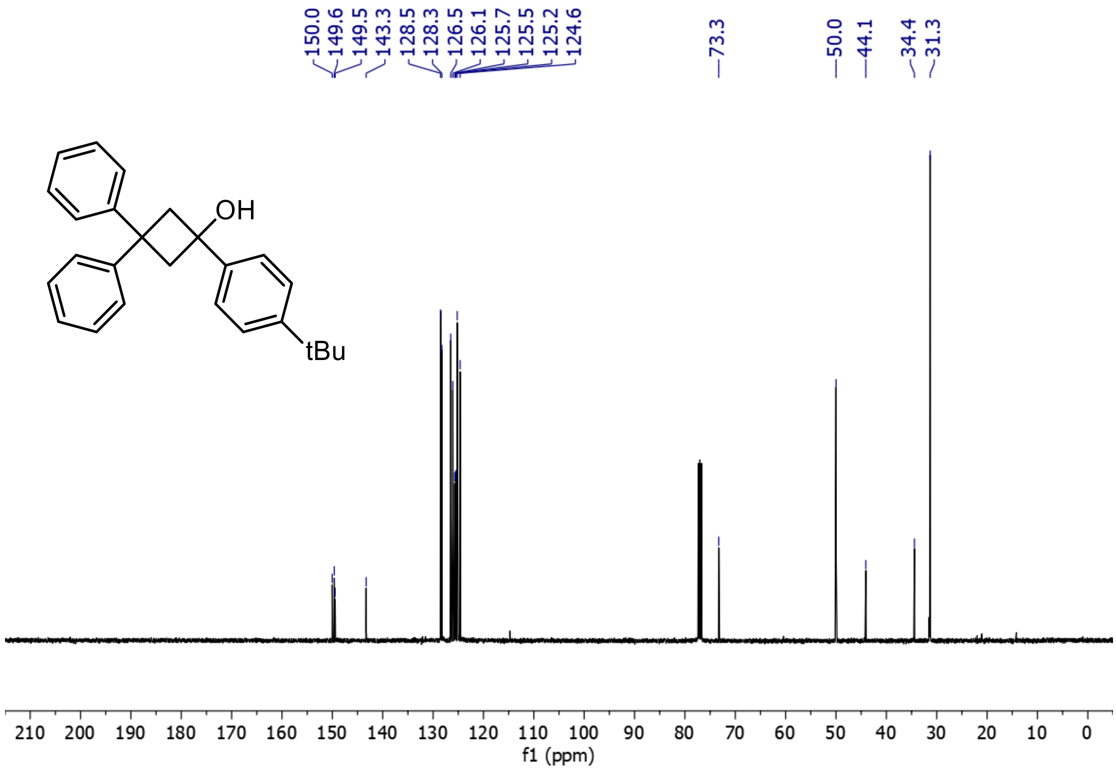
1l ^{13}C NMR (100 MHz, CDCl$_3$)



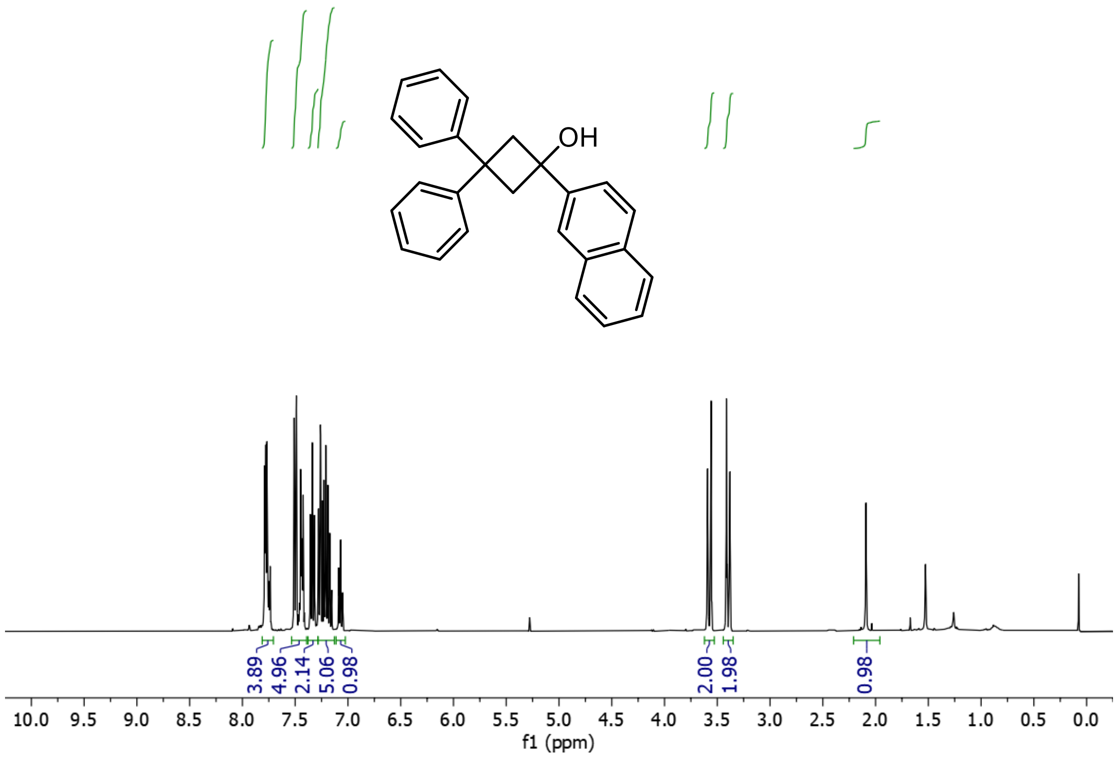
1m ^{1}H NMR (400 MHz, $CDCl_3$)



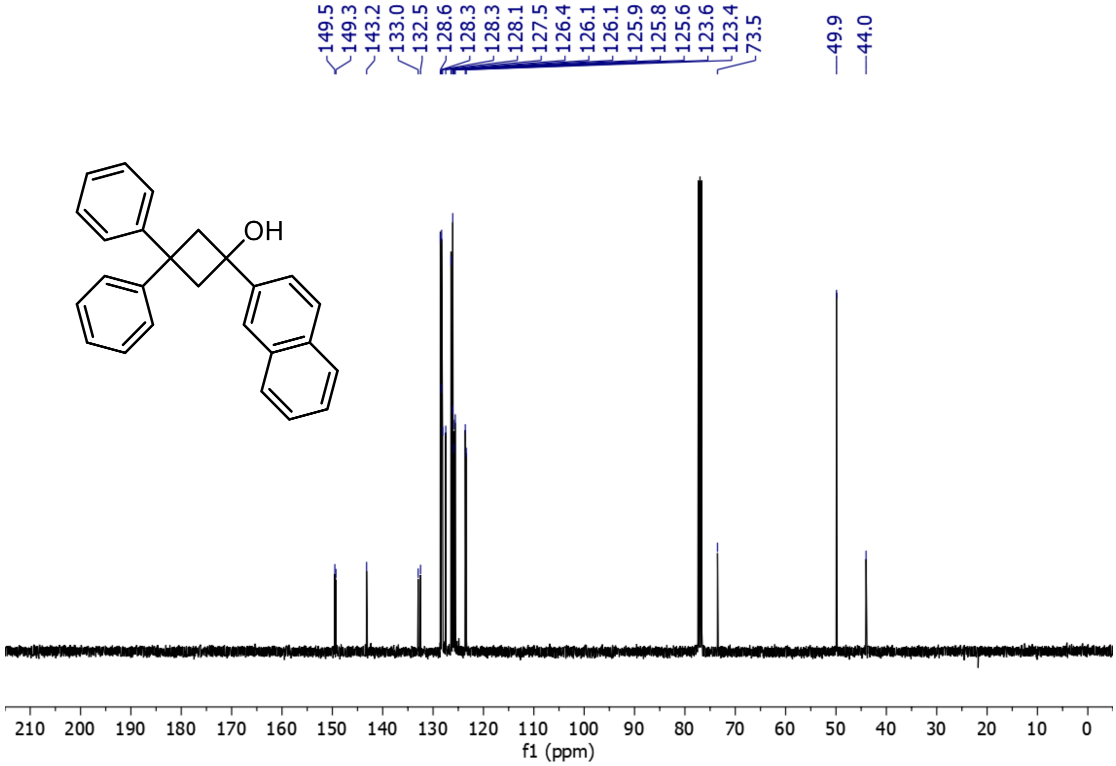
1m ^{13}C NMR (100 MHz, $CDCl_3$)



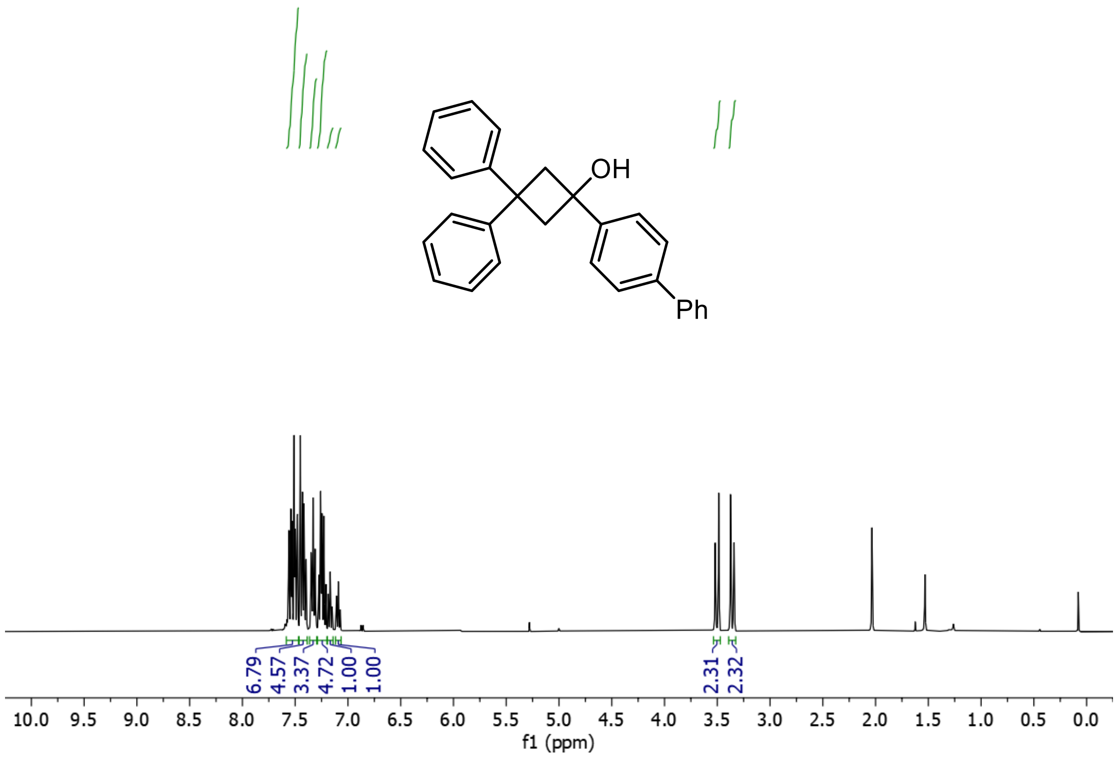
1n ^{1}H NMR (400 MHz, CDCl$_3$)



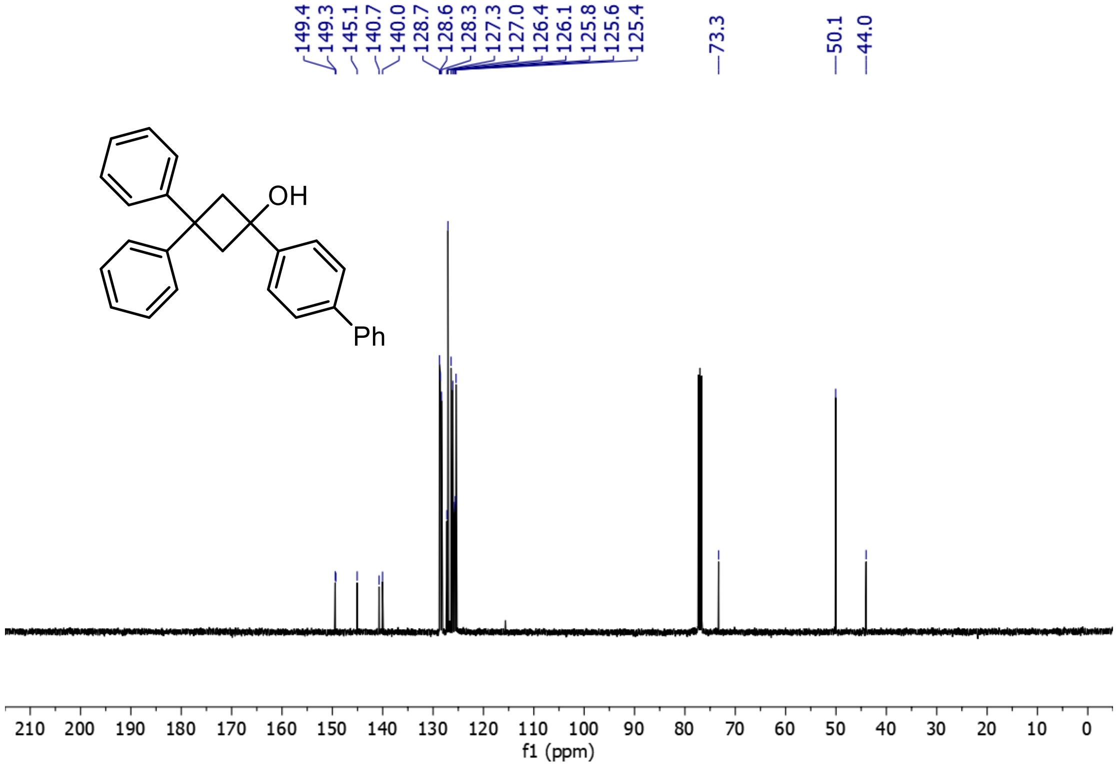
1n ^{13}C NMR (100 MHz, CDCl$_3$)



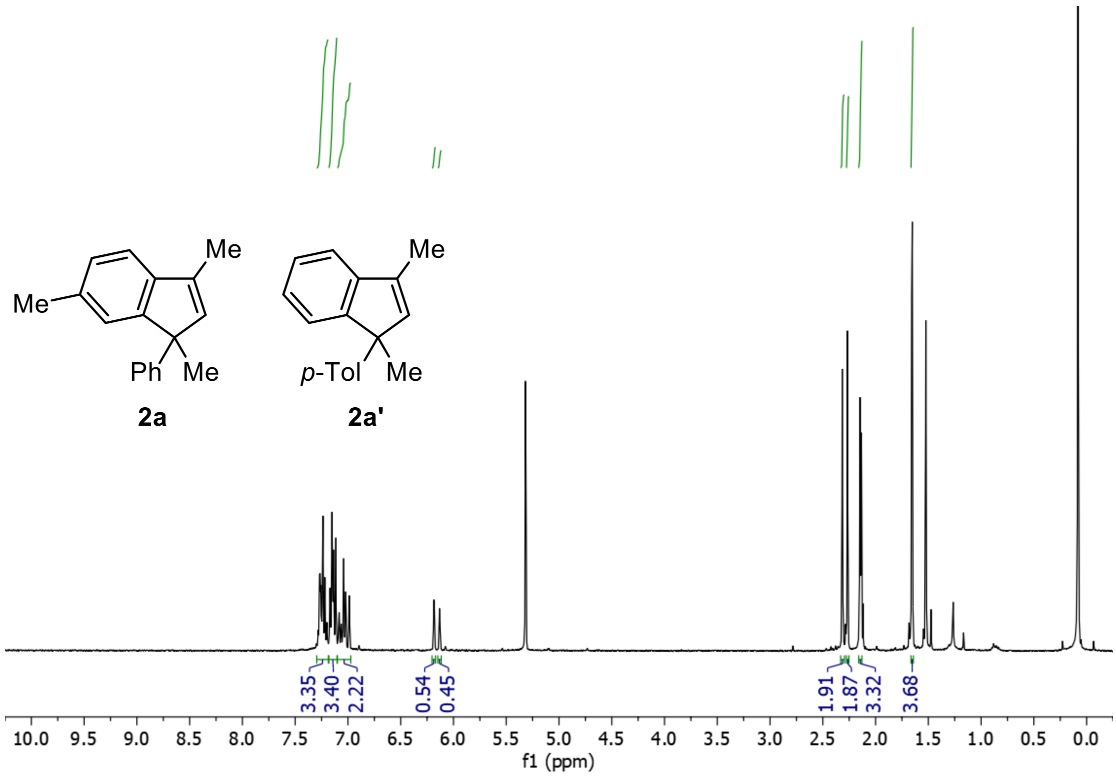
1o ^{1}H NMR (400 MHz, CDCl$_3$)



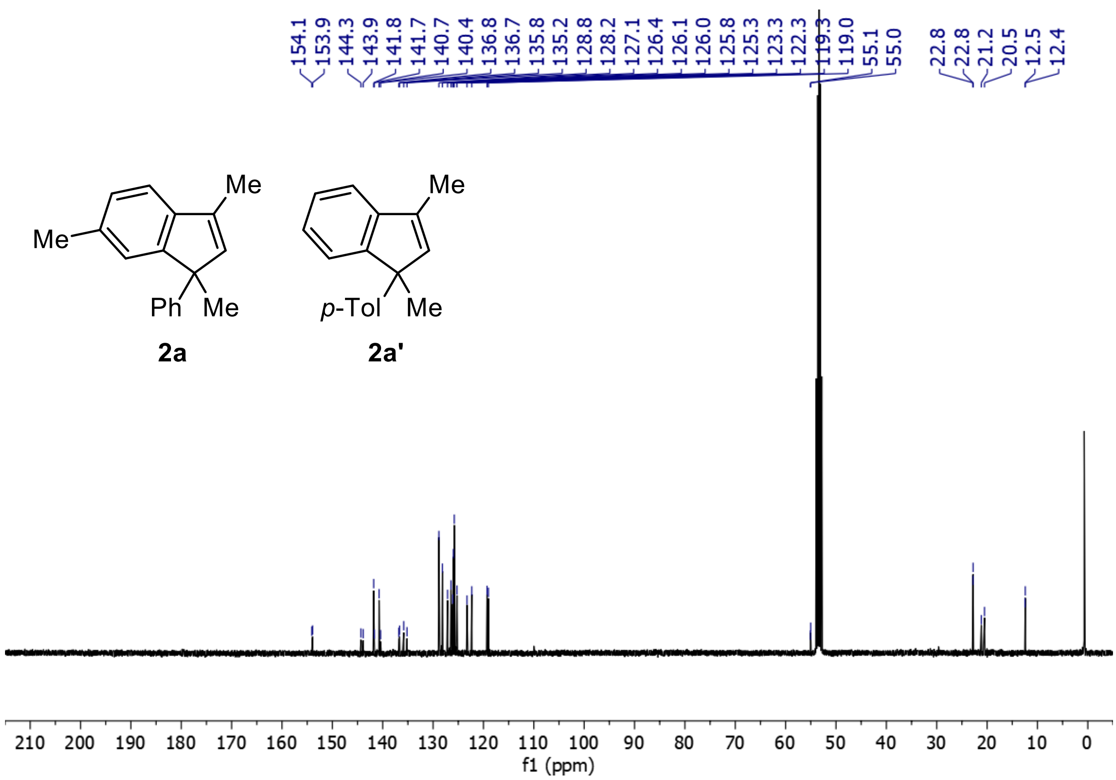
1o ^{13}C NMR (100 MHz, CDCl$_3$)



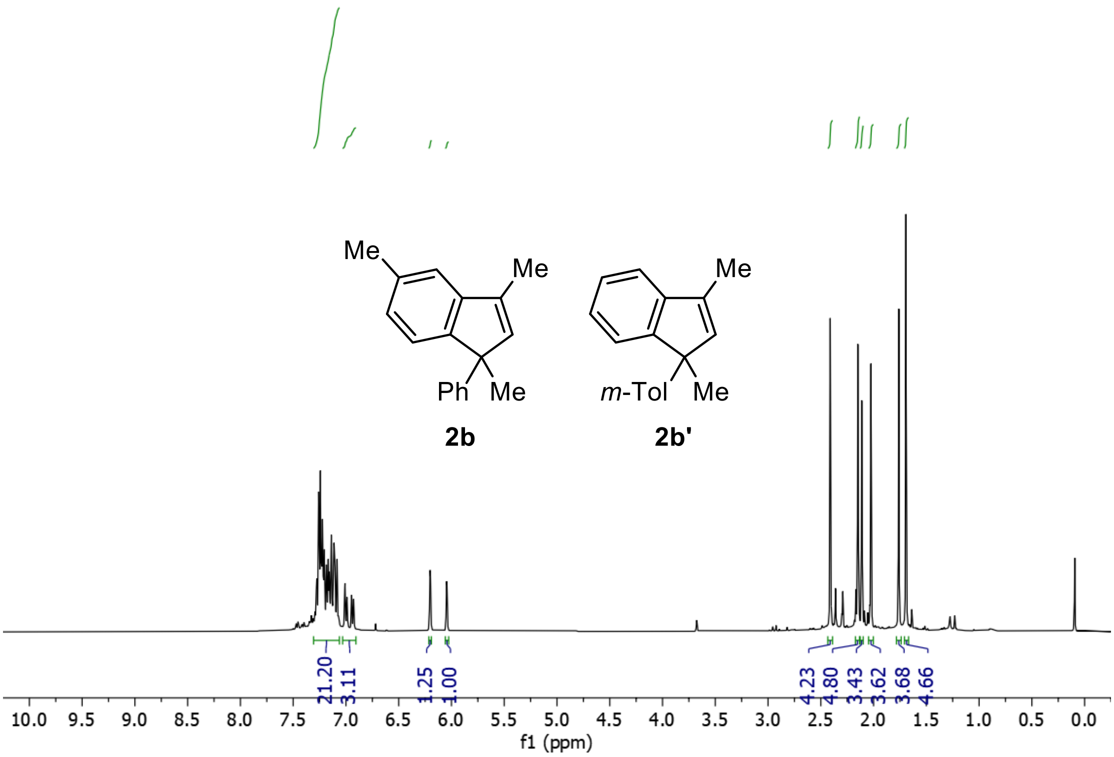
2a and 2a' ^{1}H NMR (400 MHz, CD_2Cl_2)



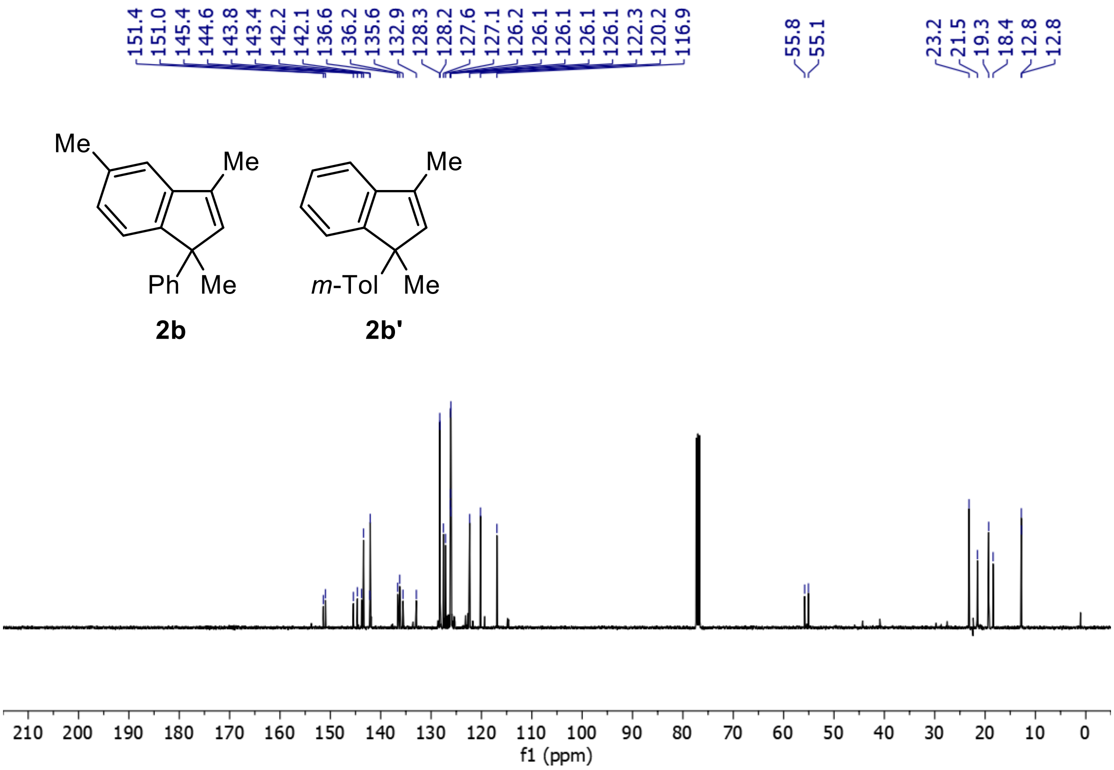
2a and 2a' ^{13}C NMR (100 MHz, CD_2Cl_2)



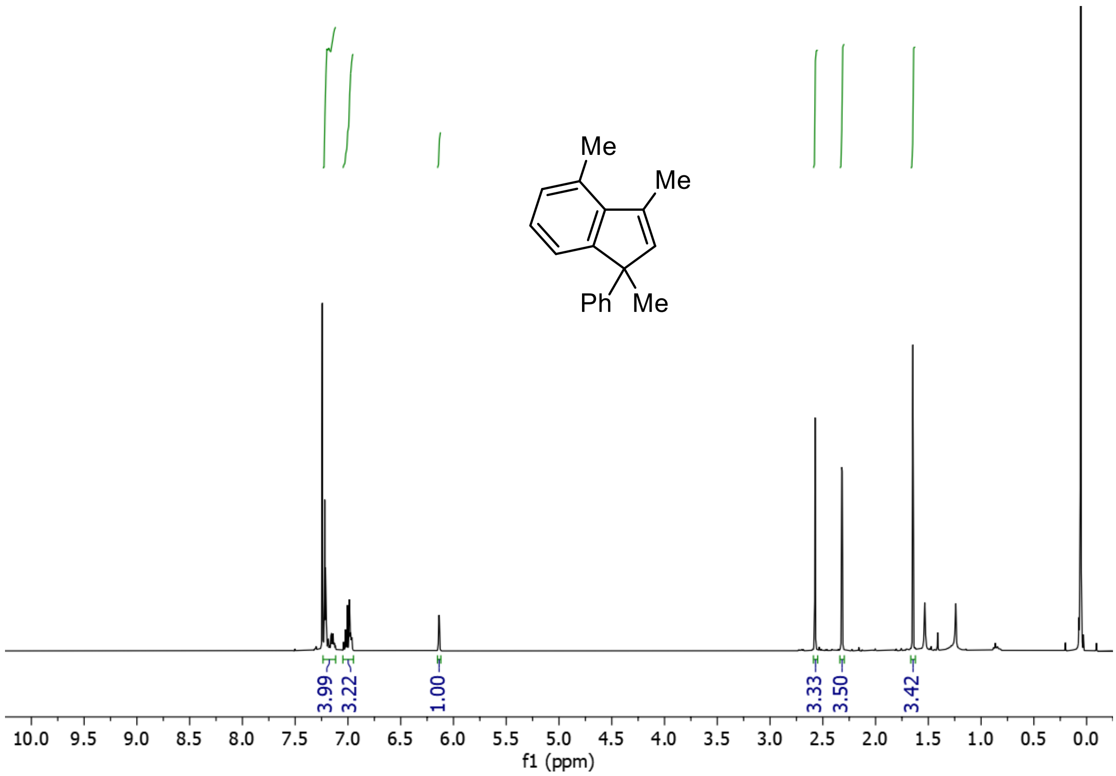
2b and 2b' ^1H NMR (400 MHz, $CDCl_3$)



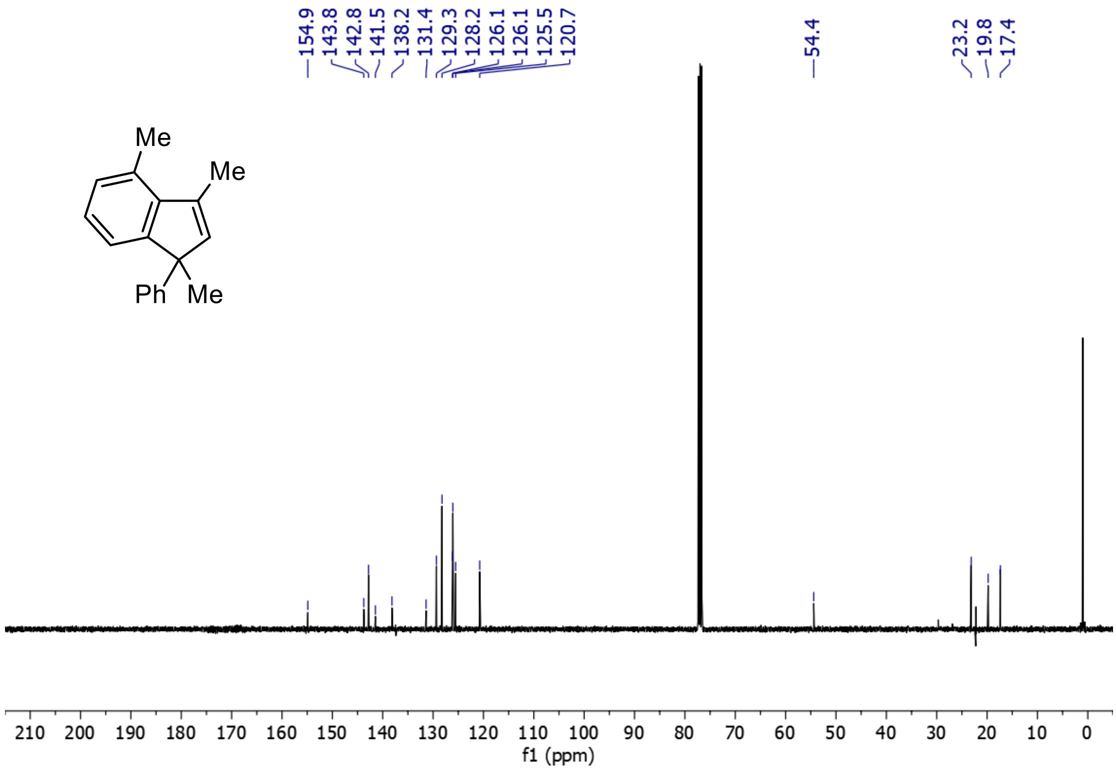
2b and 2b' ^{13}C NMR (100 MHz, $CDCl_3$)



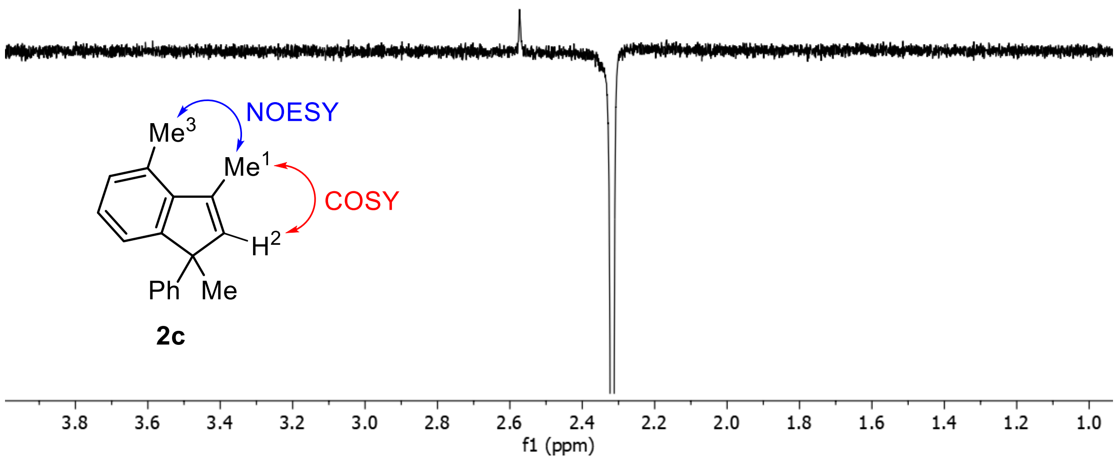
2c ^{1}H NMR (400 MHz, CDCl$_3$)



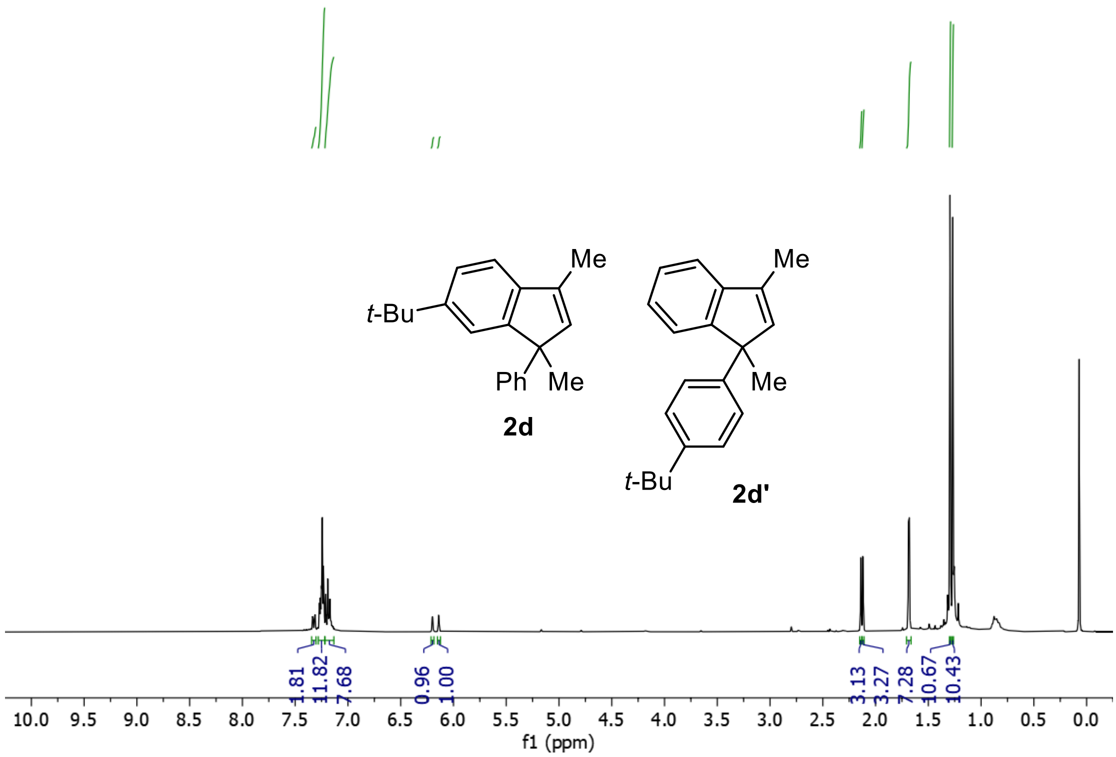
2c ^{13}C NMR (100 MHz, CDCl$_3$)



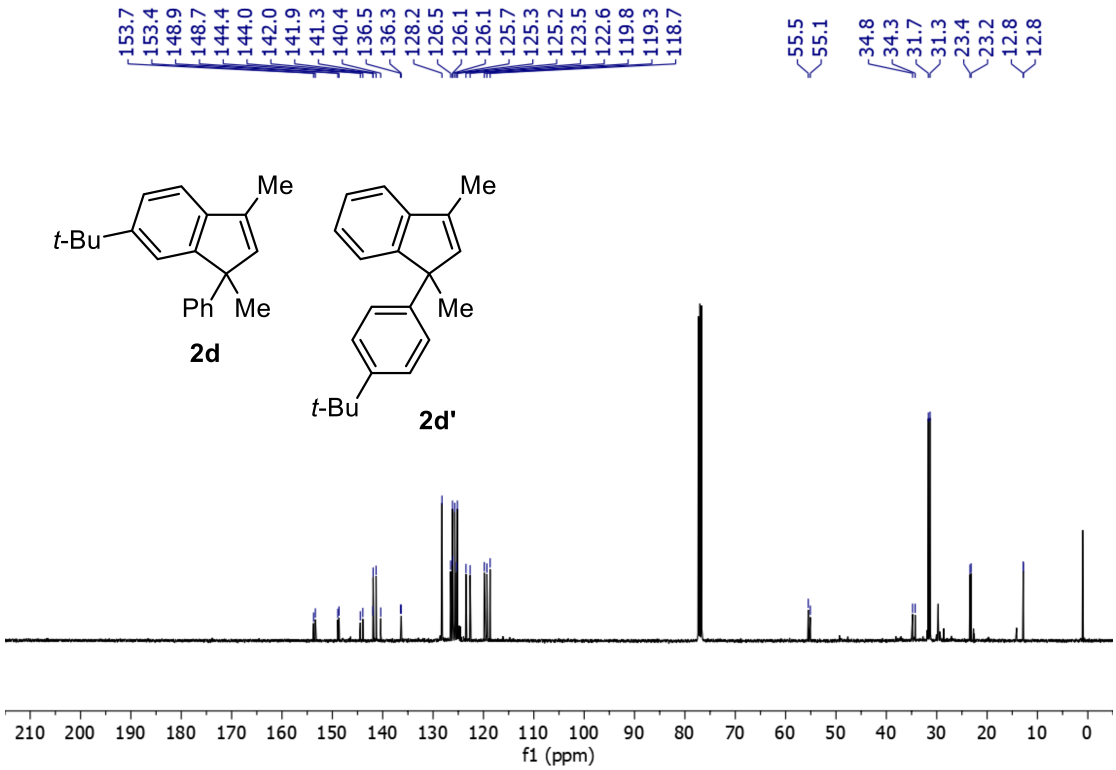
2c 1D-NOESY NMR (100 MHz, CDCl$_3$), relevant region



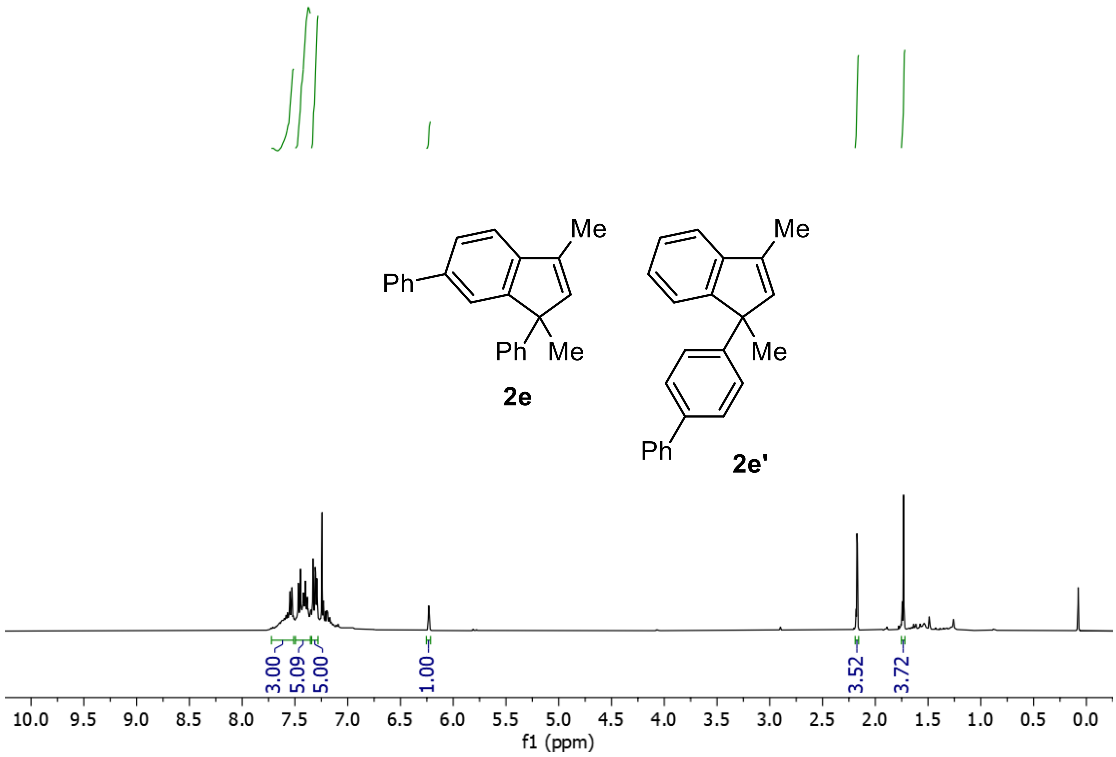
2d and 2d' ^{1}H NMR (400 MHz, $CDCl_3$)



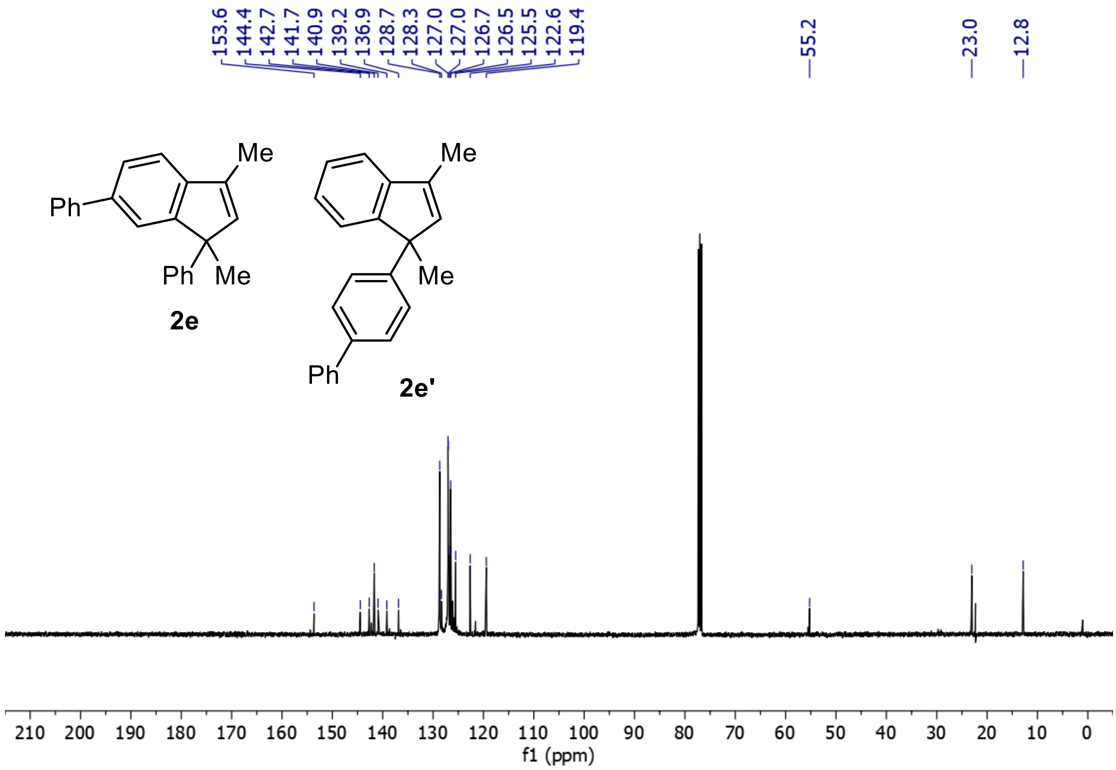
2d ^{13}C NMR (100 MHz, $CDCl_3$)



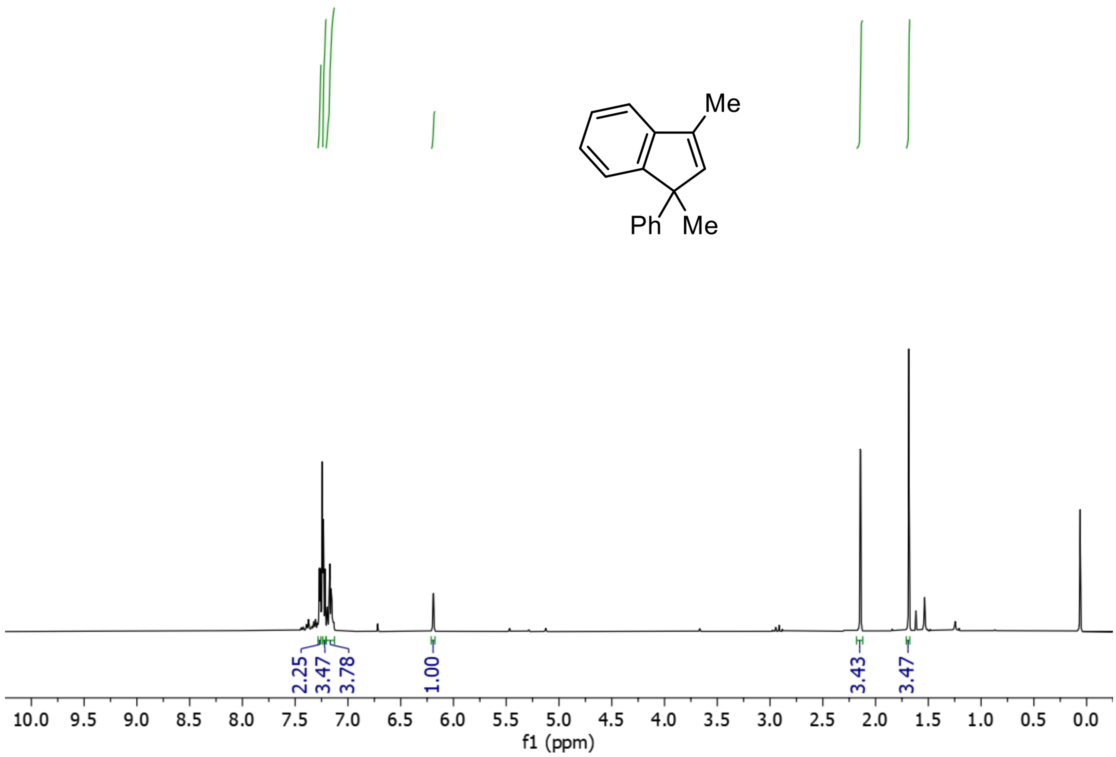
2e and 2e' ^{1}H NMR (400 MHz, $CDCl_3$)



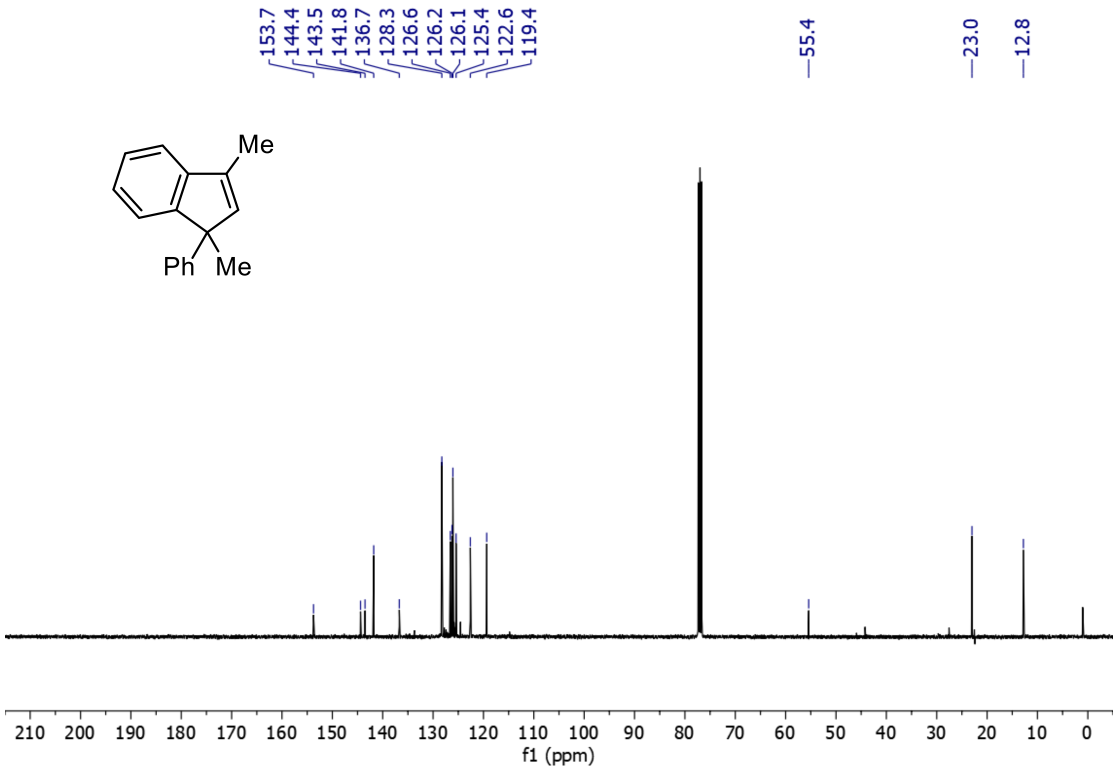
2e and 2e' ^{13}C NMR (100 MHz, $CDCl_3$)



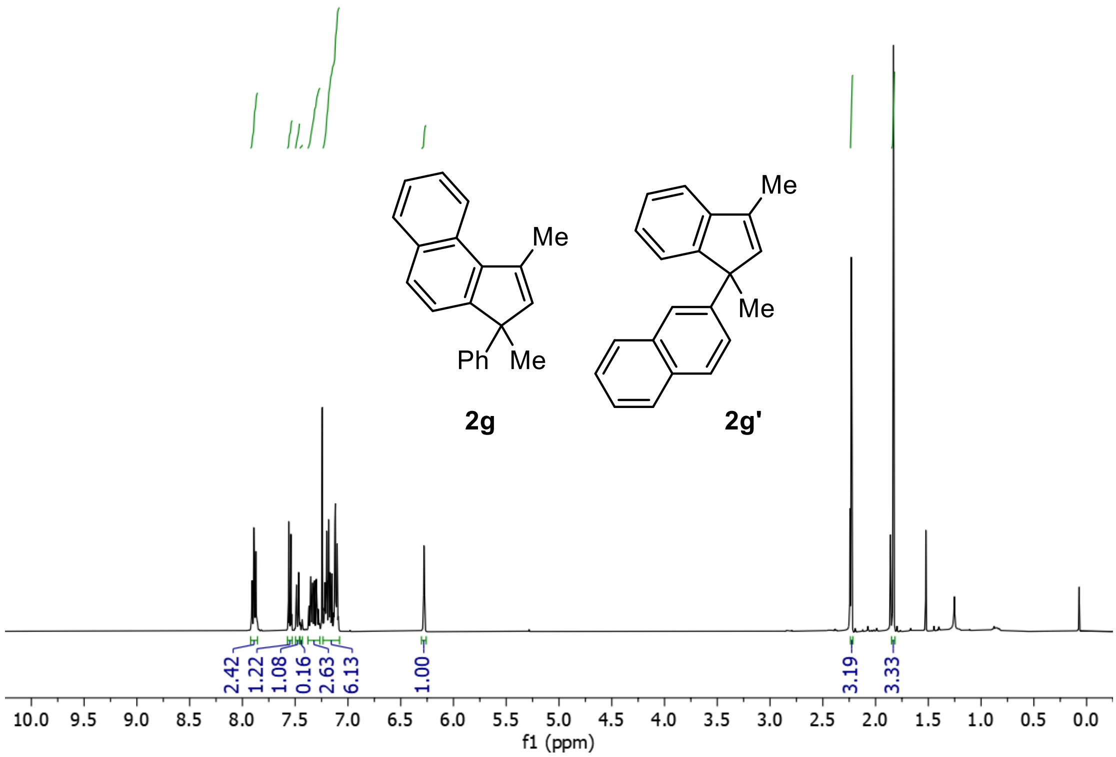
2f ^{1}H NMR (400 MHz, $CDCl_3$)



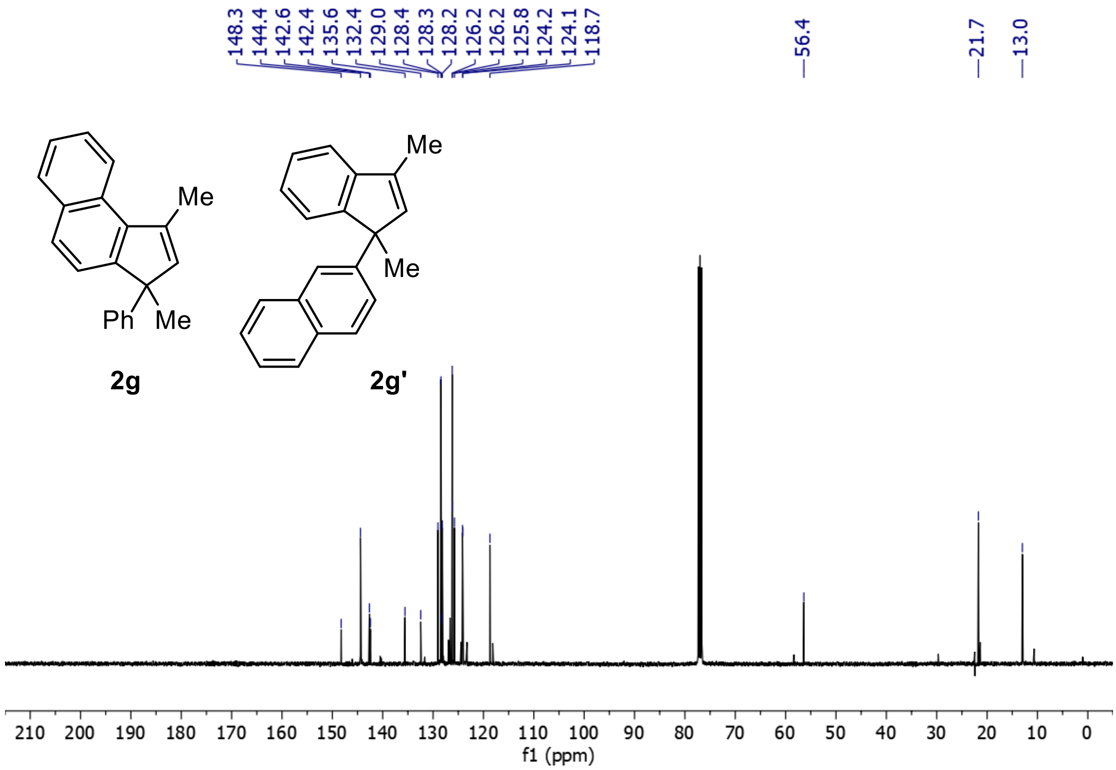
2f ^{13}C NMR (100 MHz, $CDCl_3$)



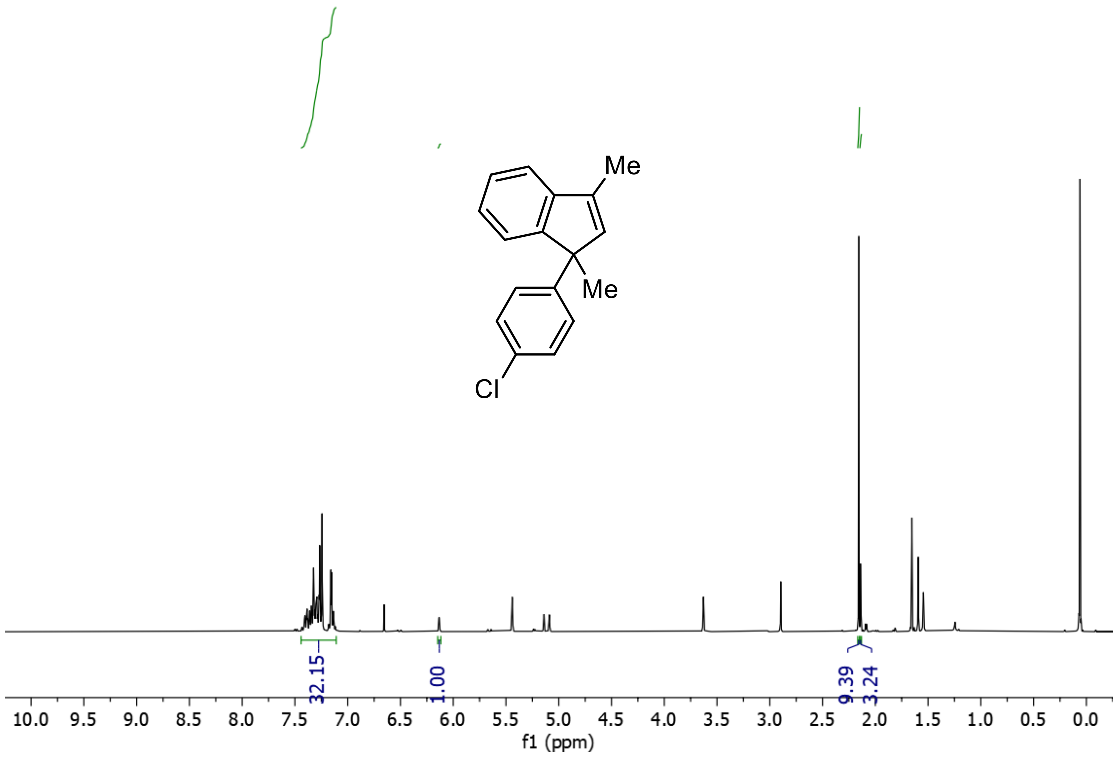
2g and 2g' ^{1}H NMR (400 MHz, CDCl$_3$)



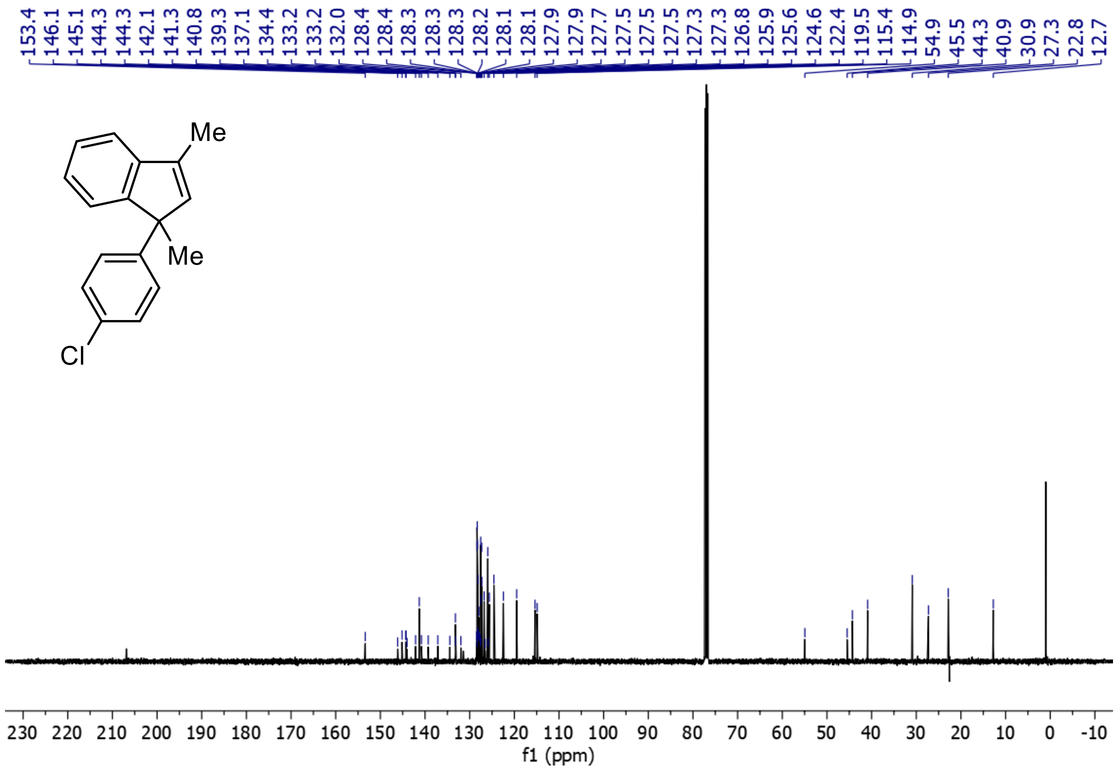
2g and 2g' ^{13}C NMR (100 MHz, CDCl$_3$)



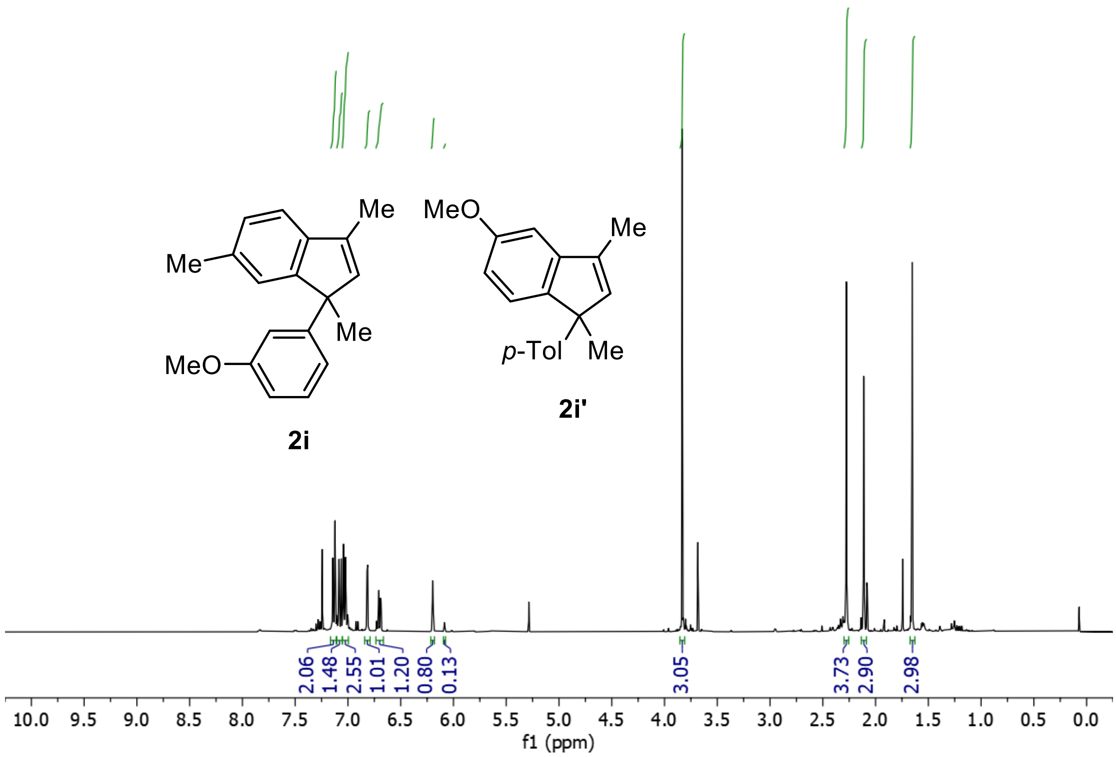
2h' (mixture with 3h and 3h') ^{1}H NMR (400 MHz, CDCl$_3$)



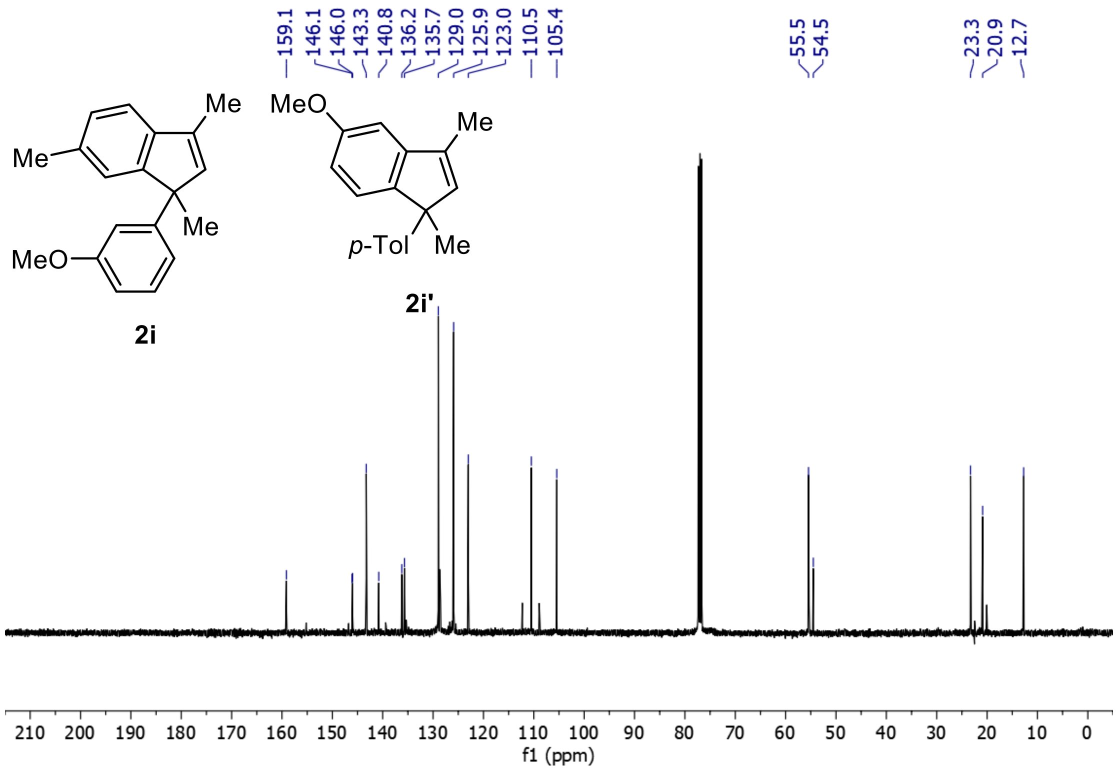
2h' (mixture with 3h and 3h') ^{13}C NMR (100 MHz, CDCl$_3$)



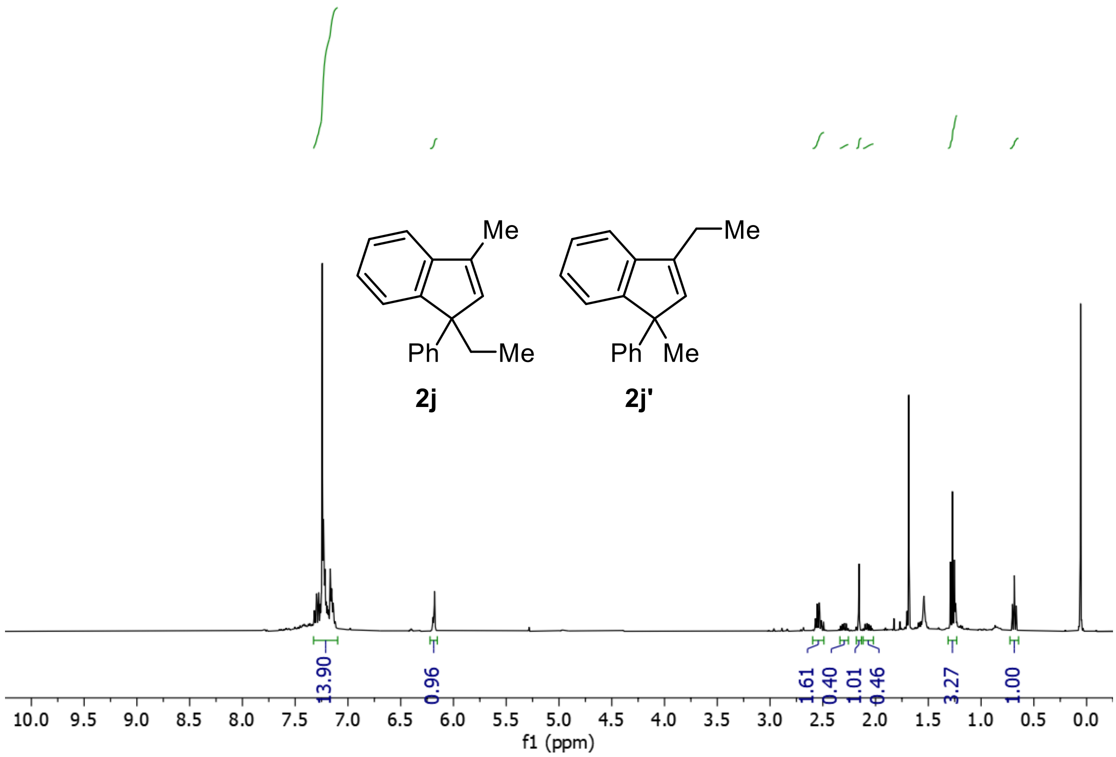
2i and 2i' ^{1}H NMR (400 MHz, $CDCl_3$)



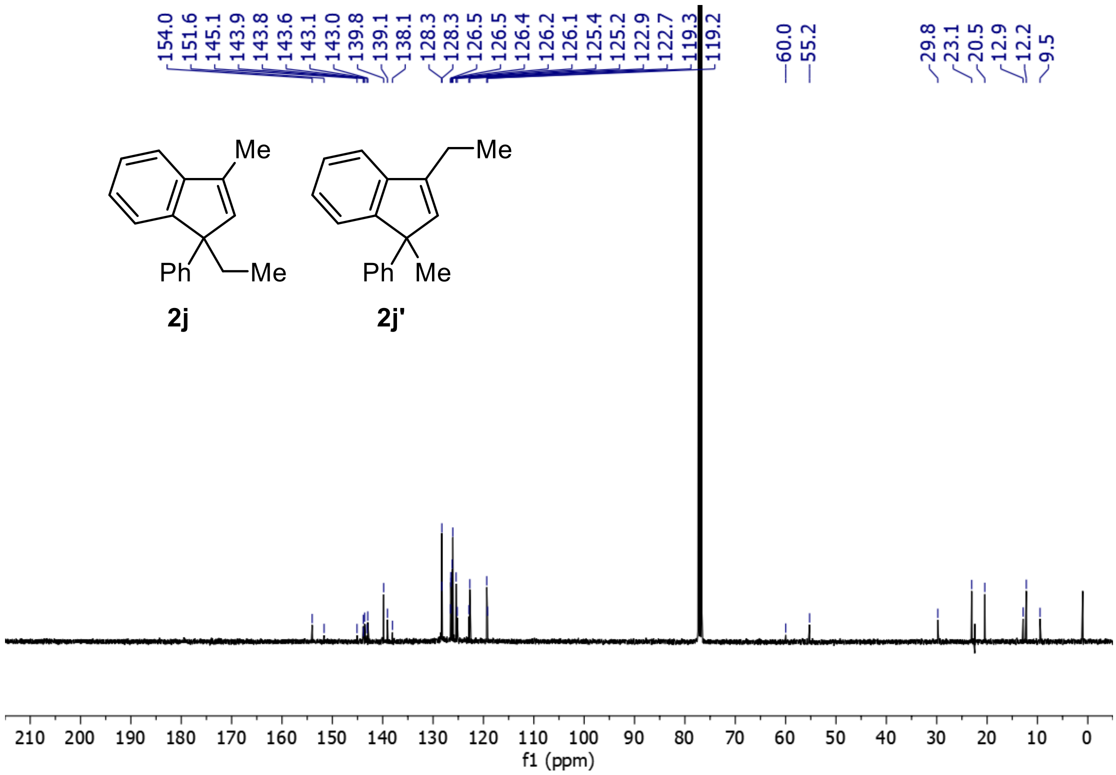
2i and 2i' ^{13}C NMR (100 MHz, $CDCl_3$)



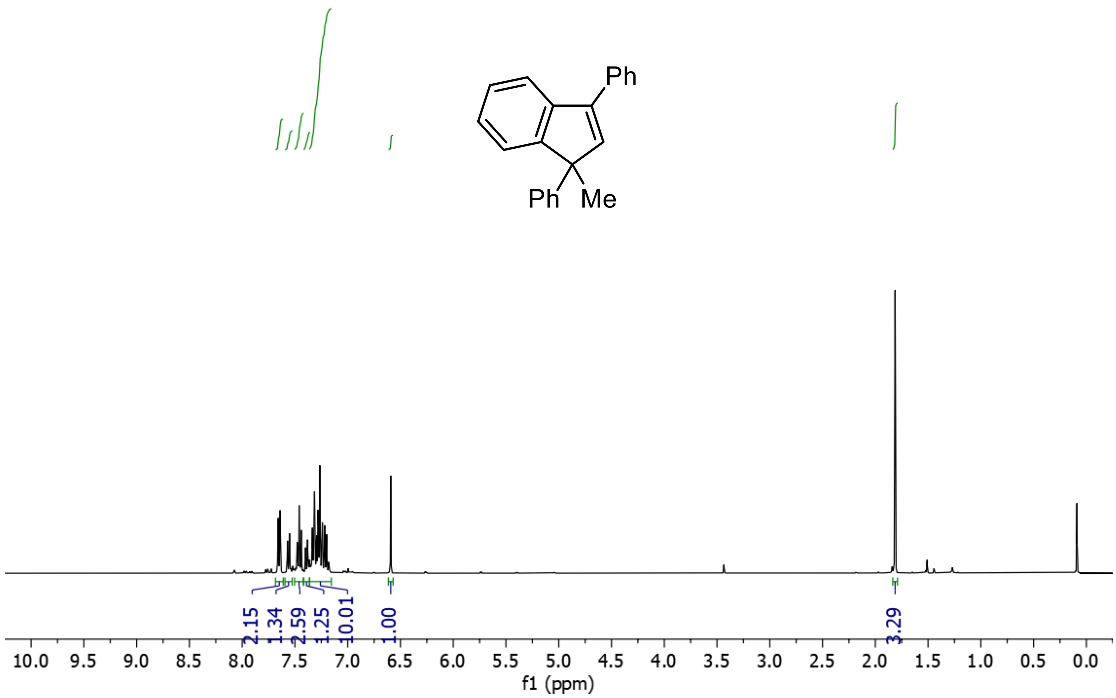
2j and 2j' ^{1}H NMR (400 MHz, $CDCl_3$)



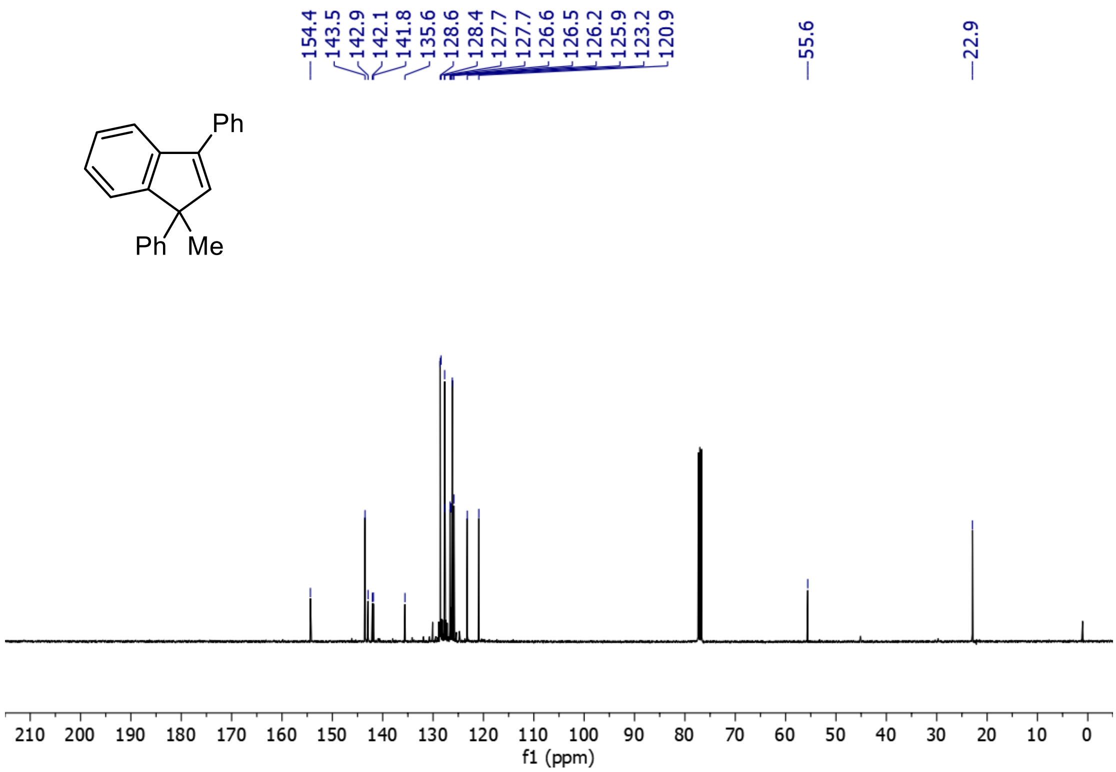
2j ^{13}C NMR (100 MHz, $CDCl_3$)



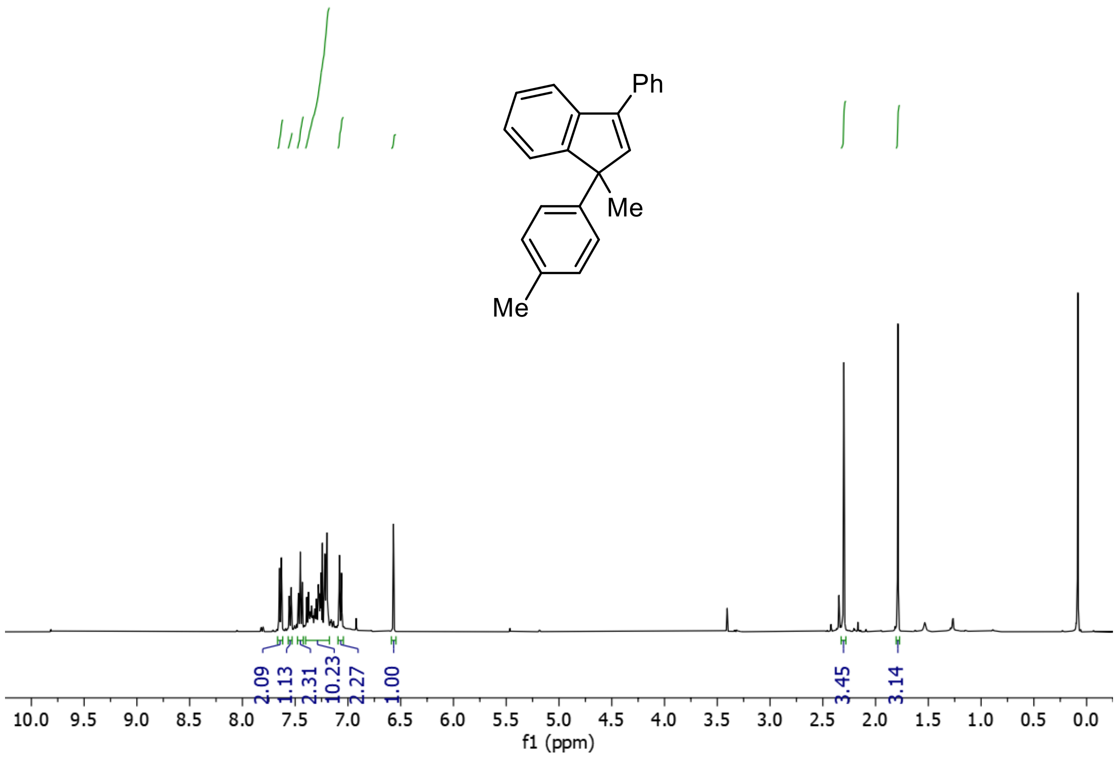
2k’ ^{1}H NMR (400 MHz, $CDCl_3$)



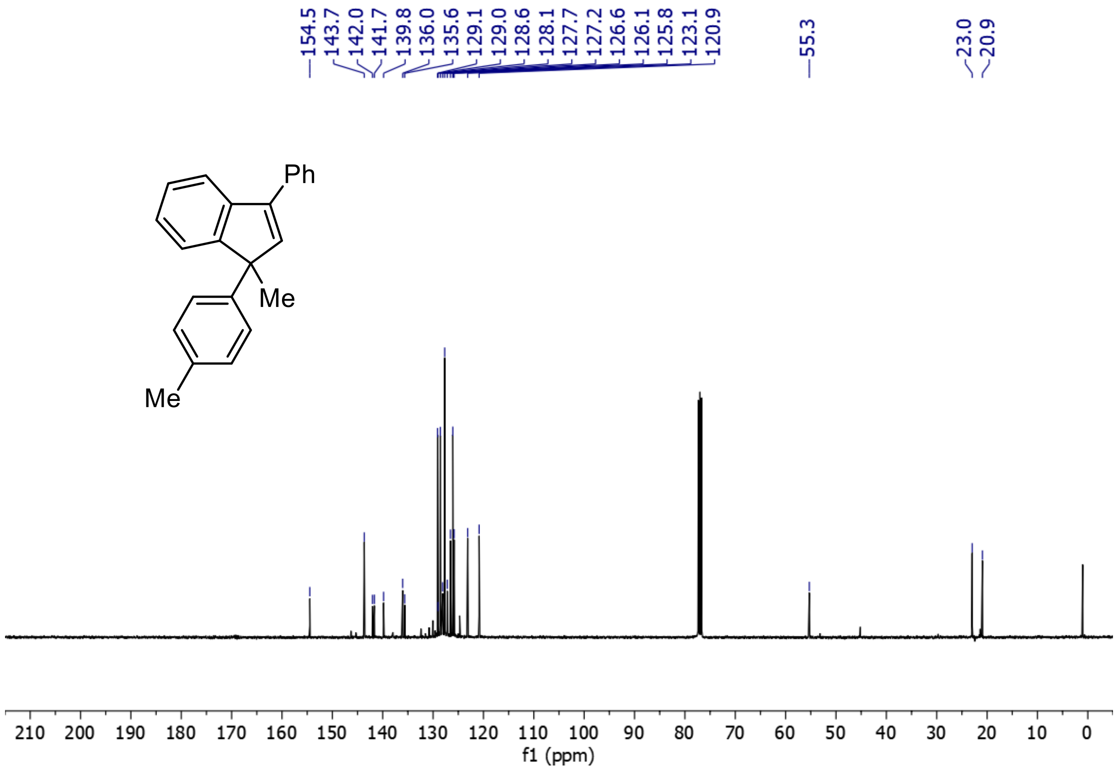
2k’ ^{13}C NMR (100 MHz, $CDCl_3$)



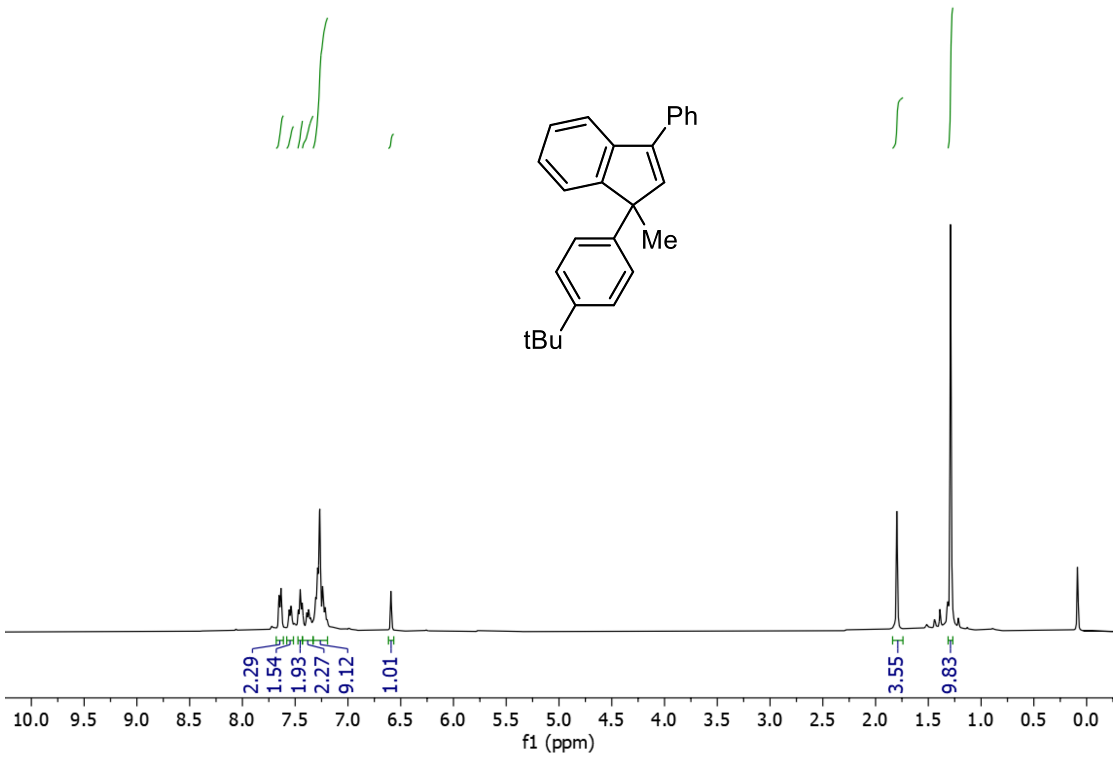
2l' ^{1}H NMR (400 MHz, CDCl$_3$)



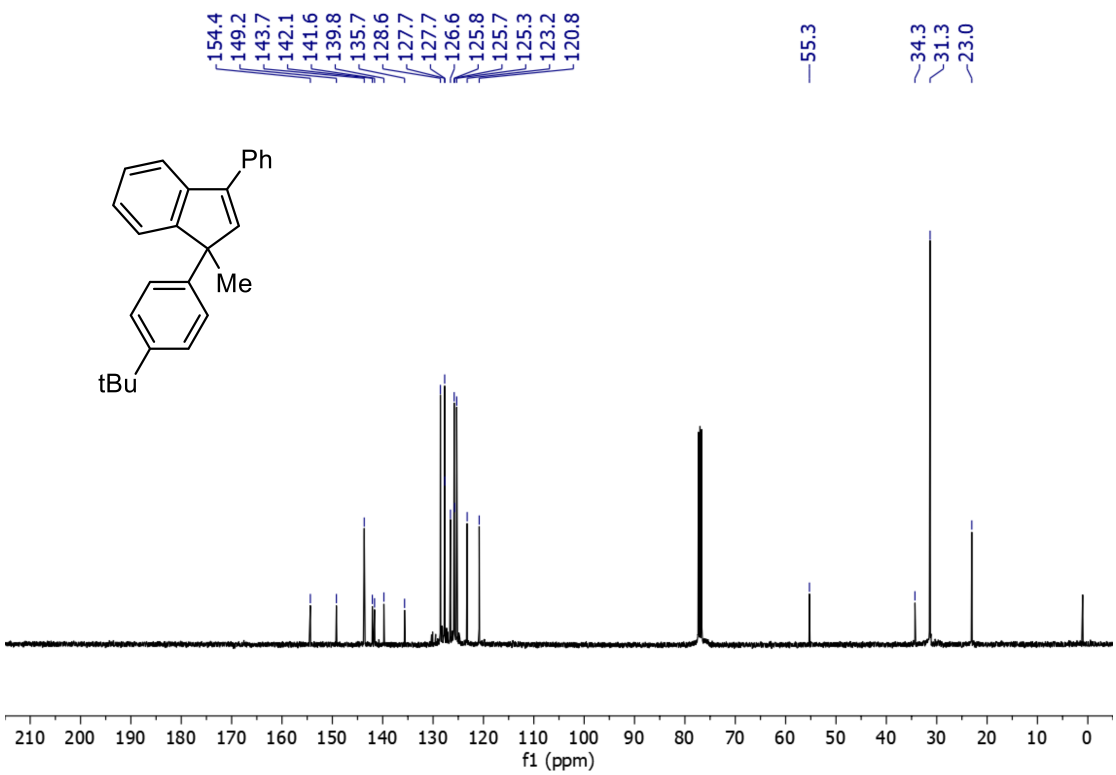
2l' ^{13}C NMR (100 MHz, CDCl$_3$)



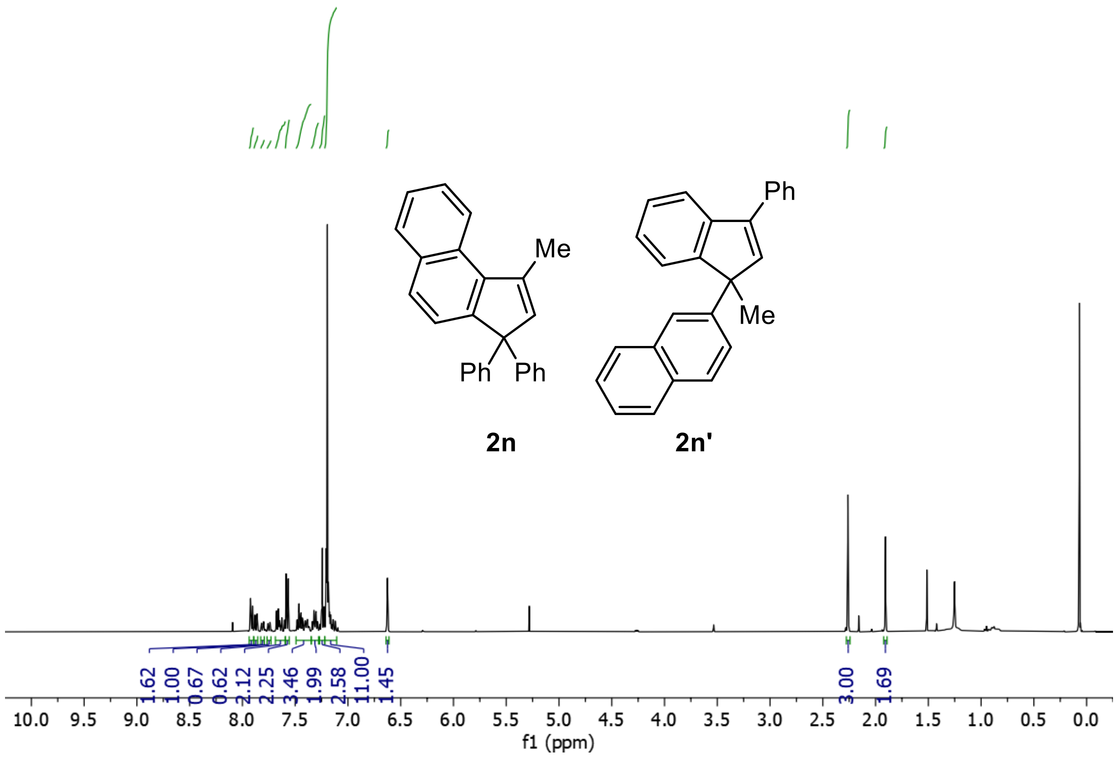
2m’ ^{1}H NMR (400 MHz, CDCl$_3$)



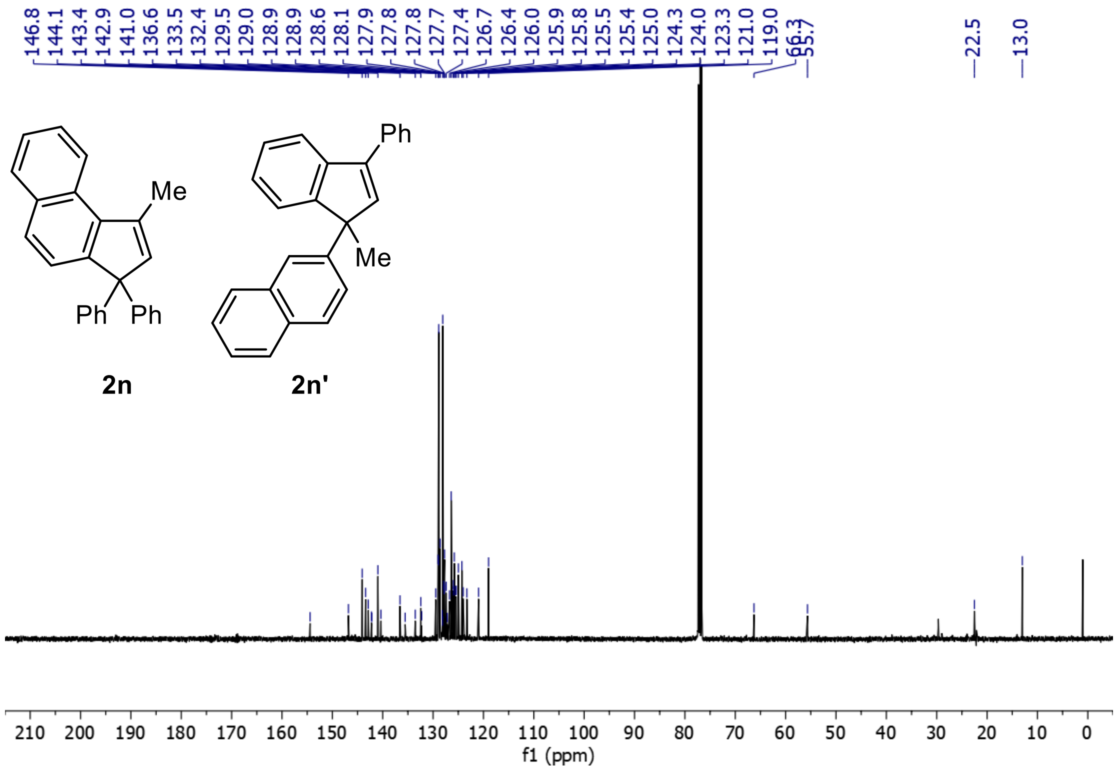
2m ^{13}C NMR (100 MHz, CDCl$_3$)



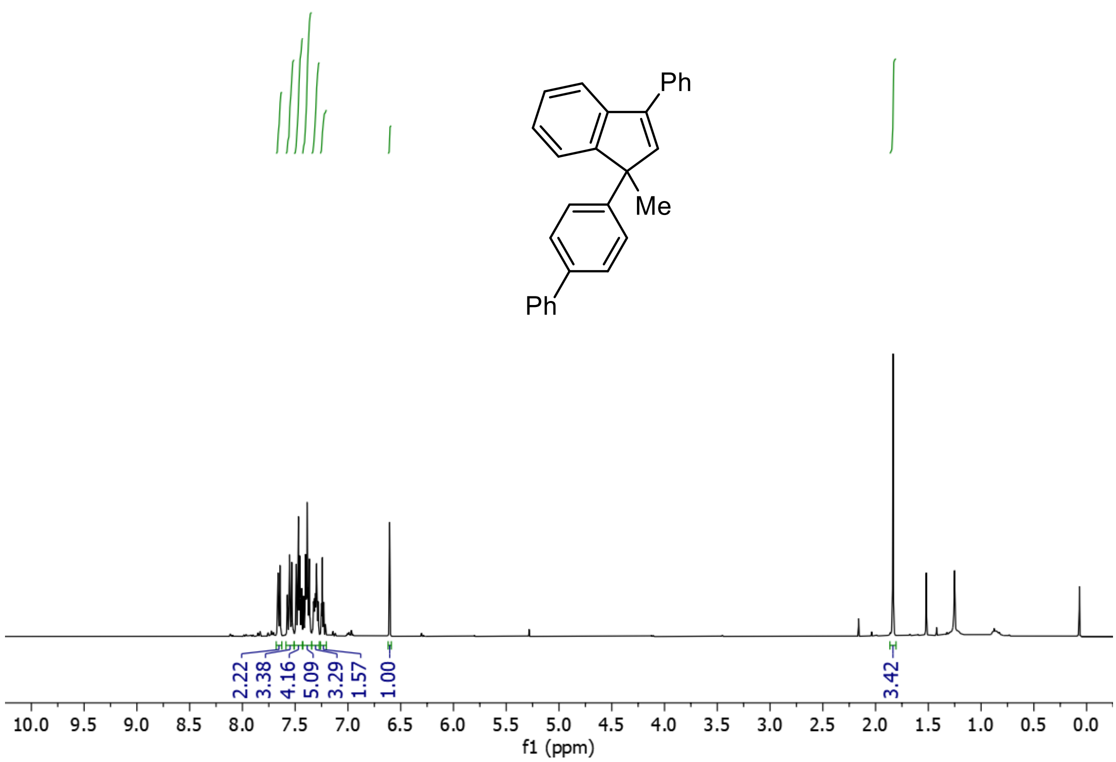
2n and 2n' ^1H NMR (400 MHz, $CDCl_3$)



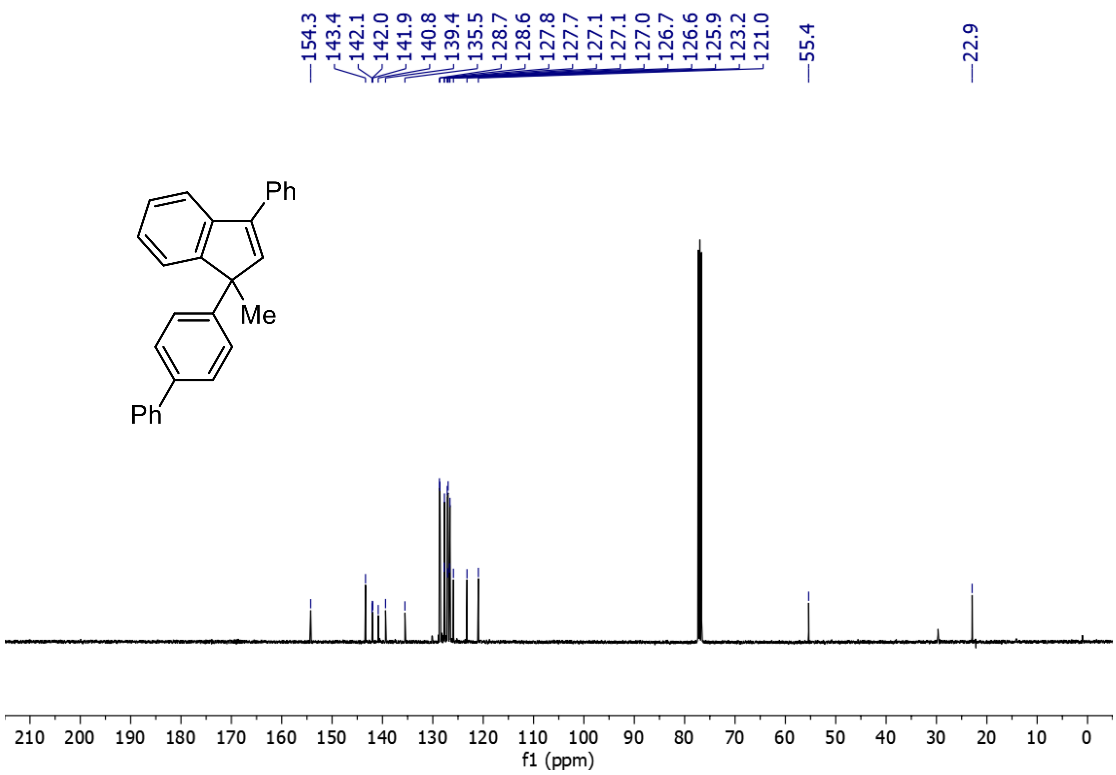
2n and 2n' ^{13}C NMR (100 MHz, $CDCl_3$)



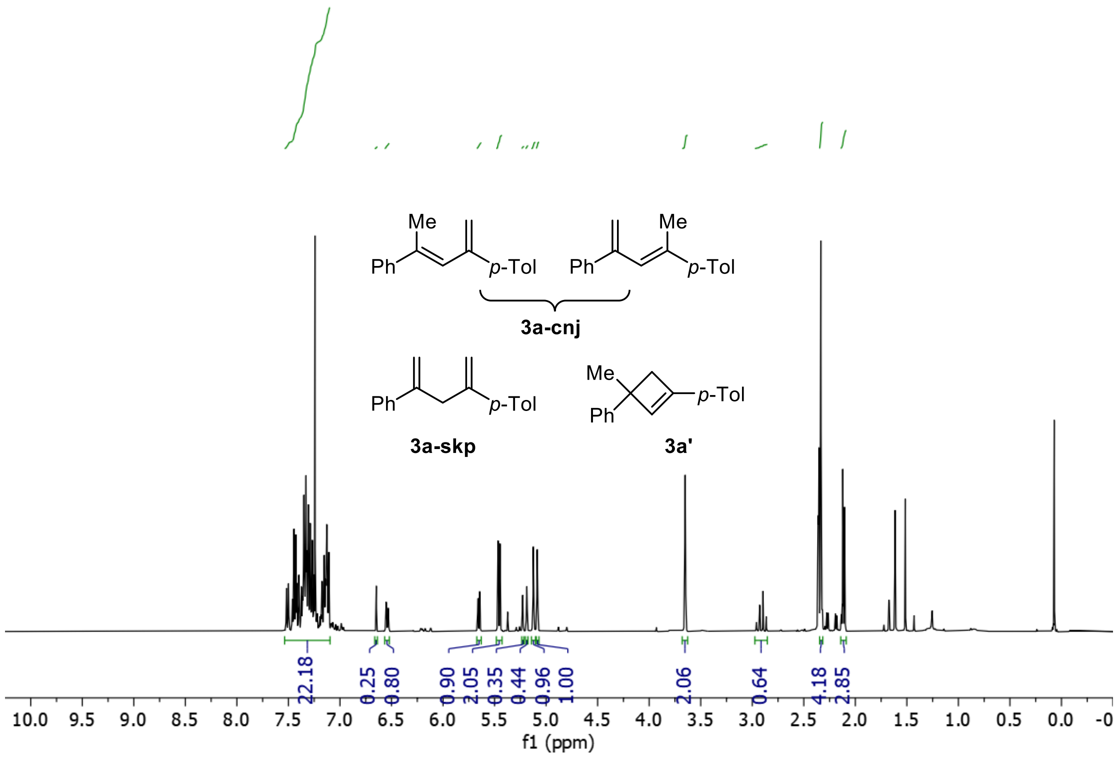
2o ^{1}H NMR (400 MHz, CDCl$_3$)



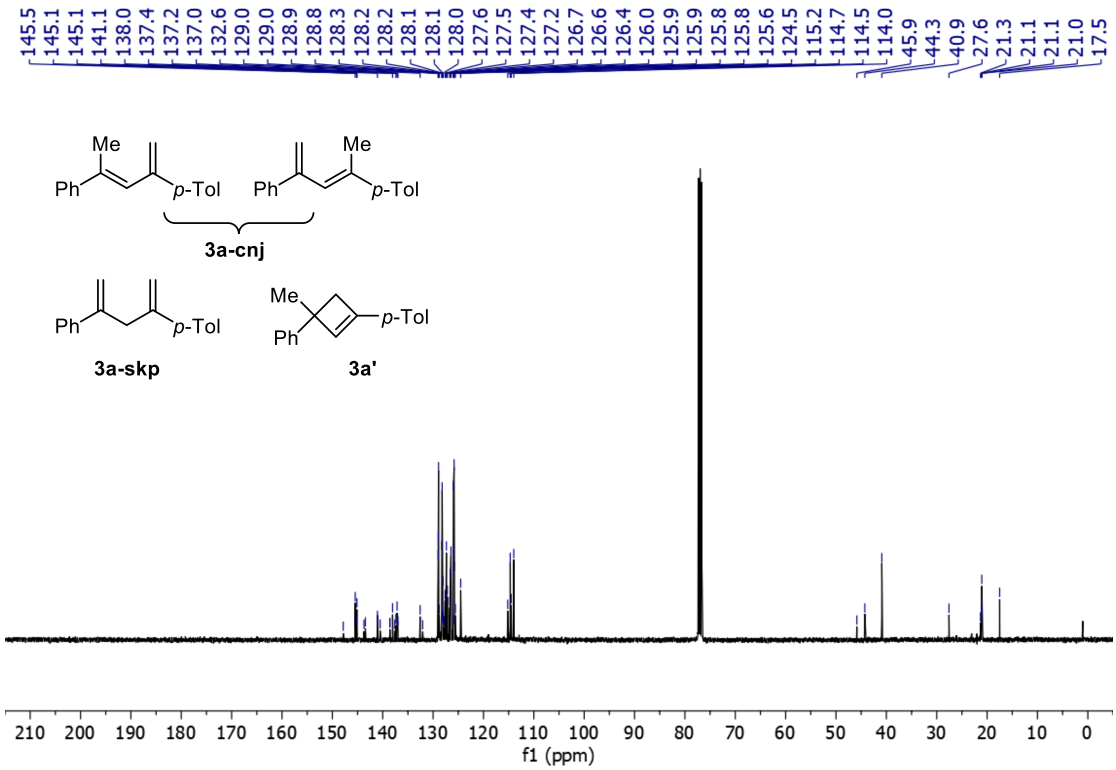
2o ^{13}C NMR (100 MHz, CDCl$_3$)



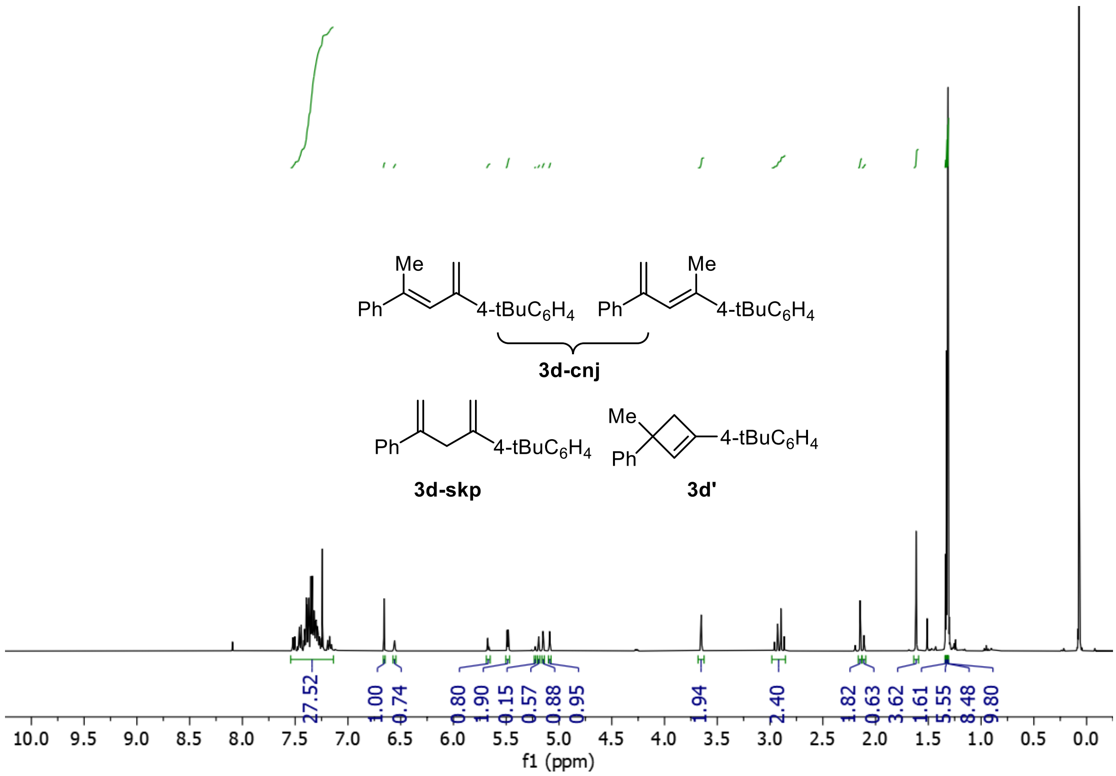
3a and 3a' ^{1}H NMR (400 MHz, $CDCl_3$)



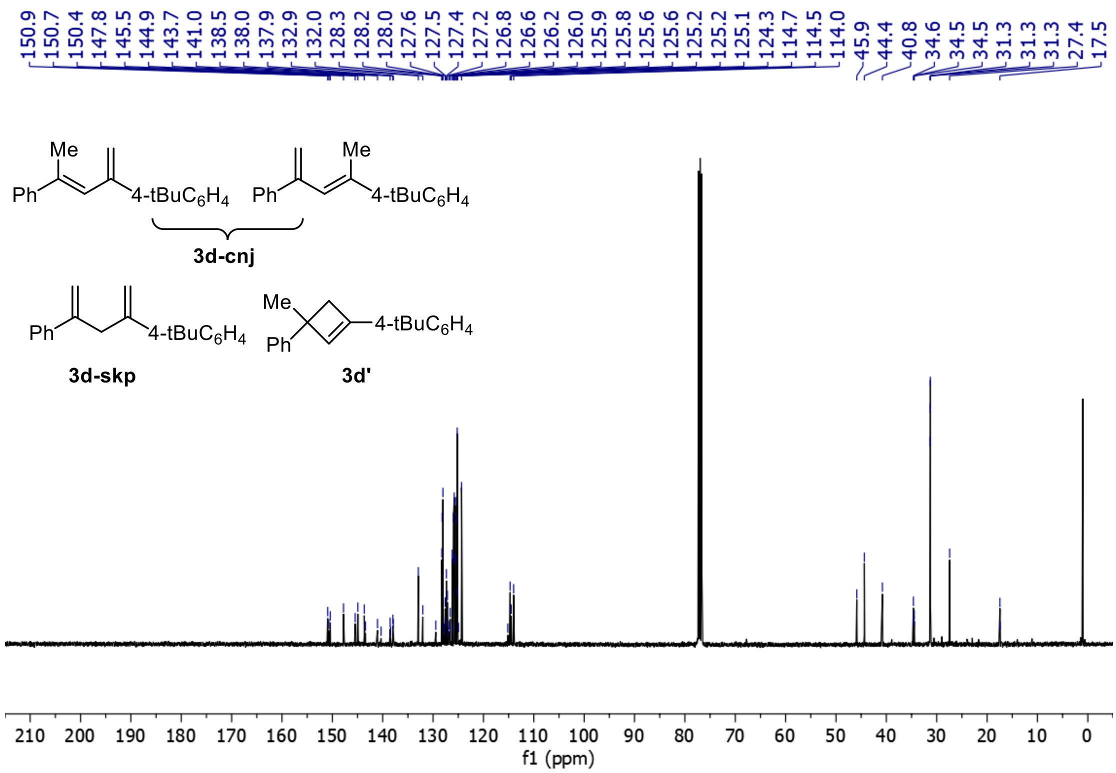
3a and 3a' ^{13}C NMR (100 MHz, $CDCl_3$)



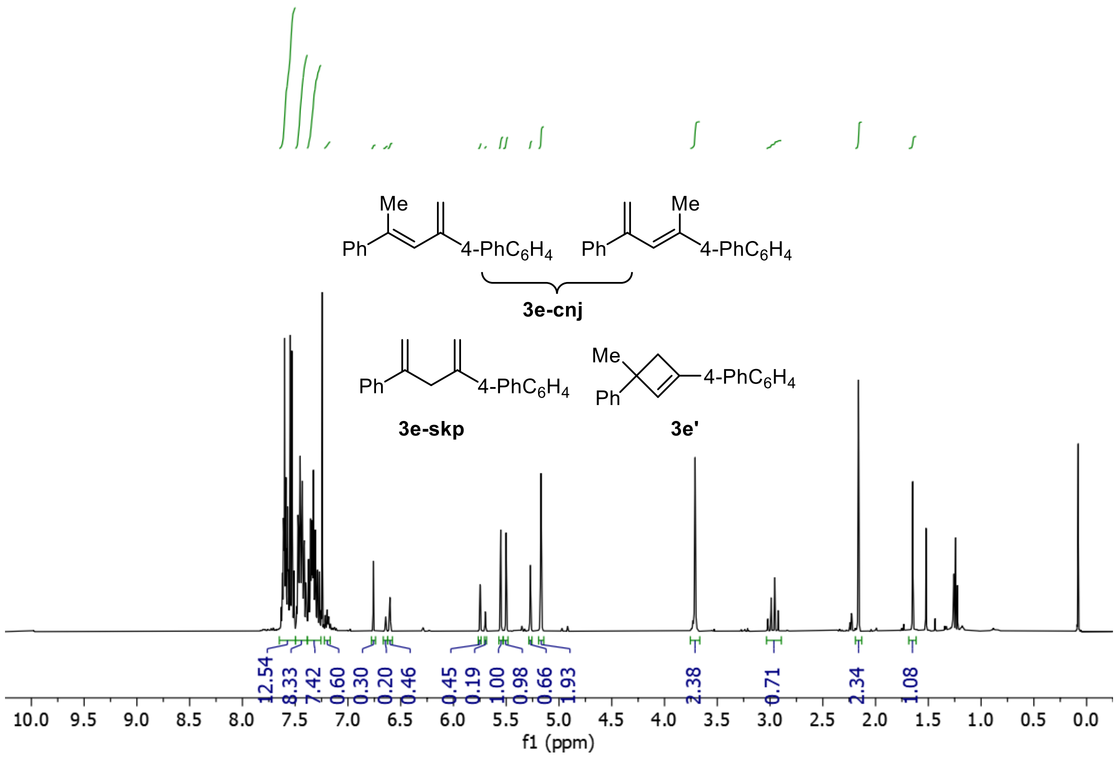
3d and 3d' ^{1}H NMR (400 MHz, $CDCl_3$)



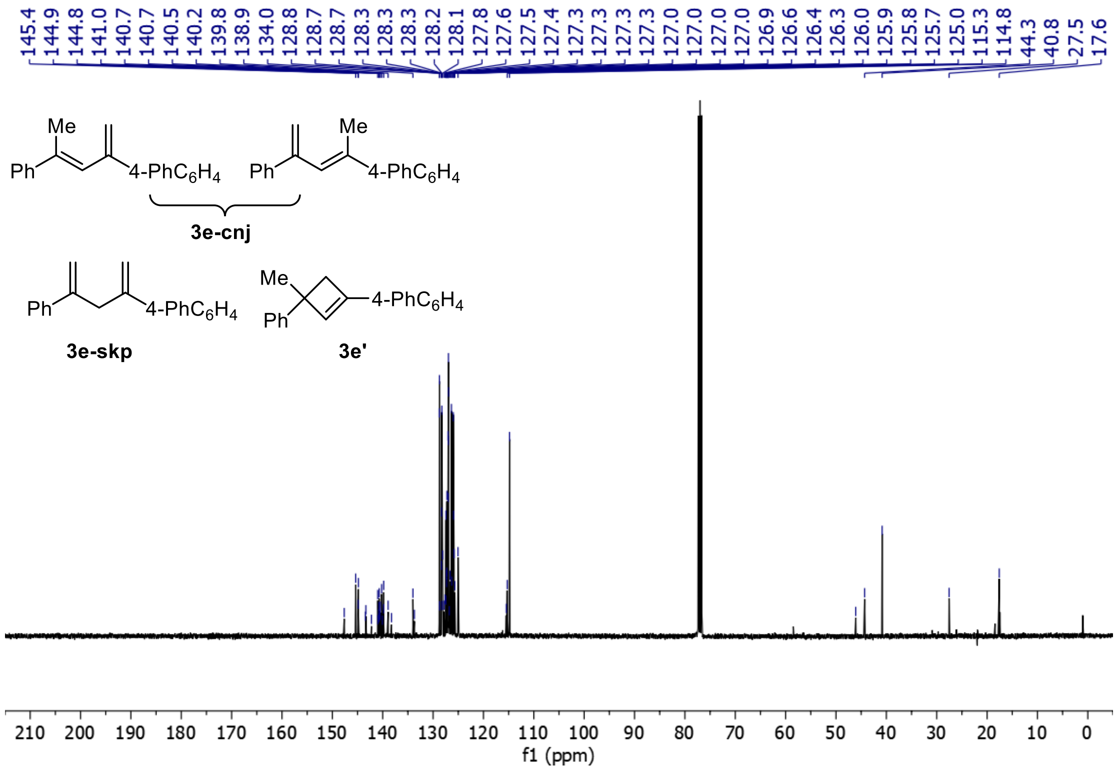
3d and 3d' ^{13}C NMR (100 MHz, $CDCl_3$)



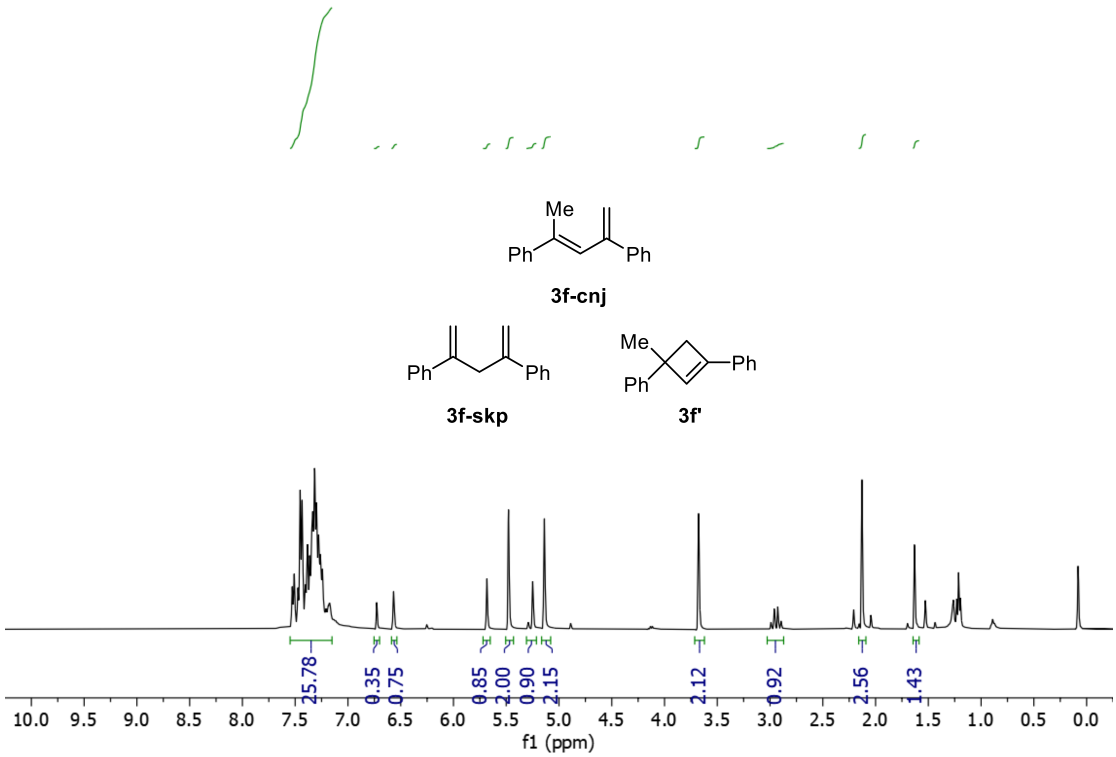
3e and 3e' ^{1}H NMR (400 MHz, $CDCl_3$)



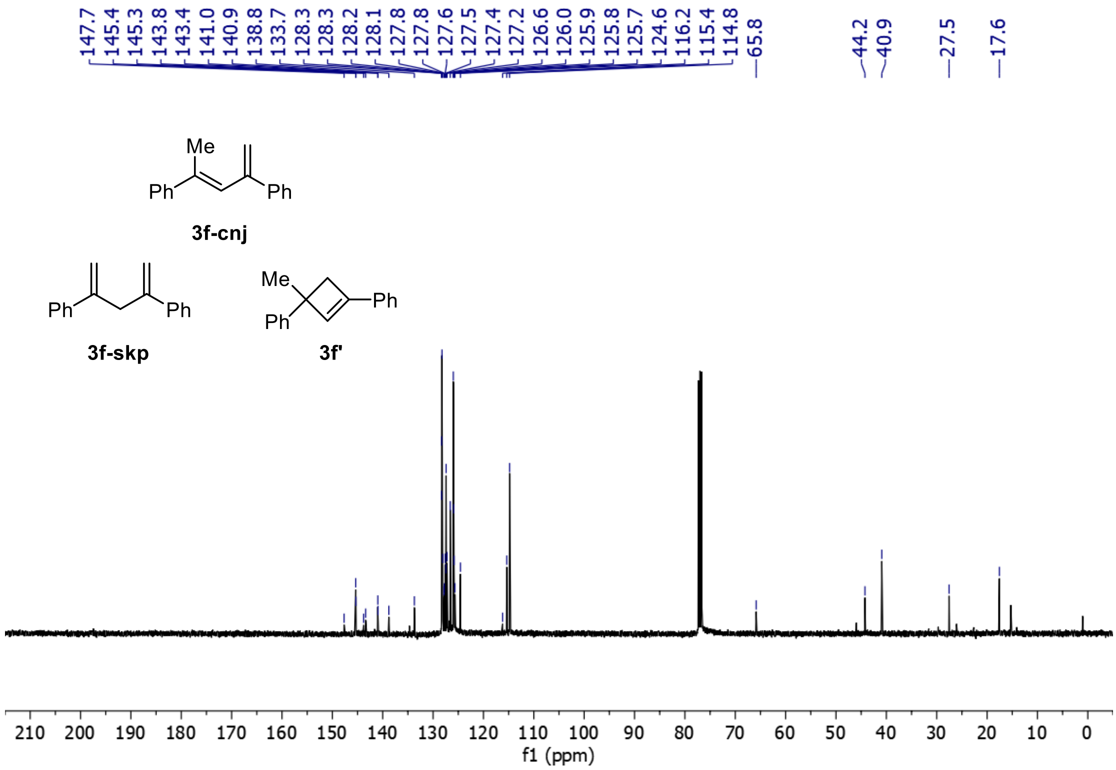
3e and 3e' ^{13}C NMR (100 MHz, $CDCl_3$)



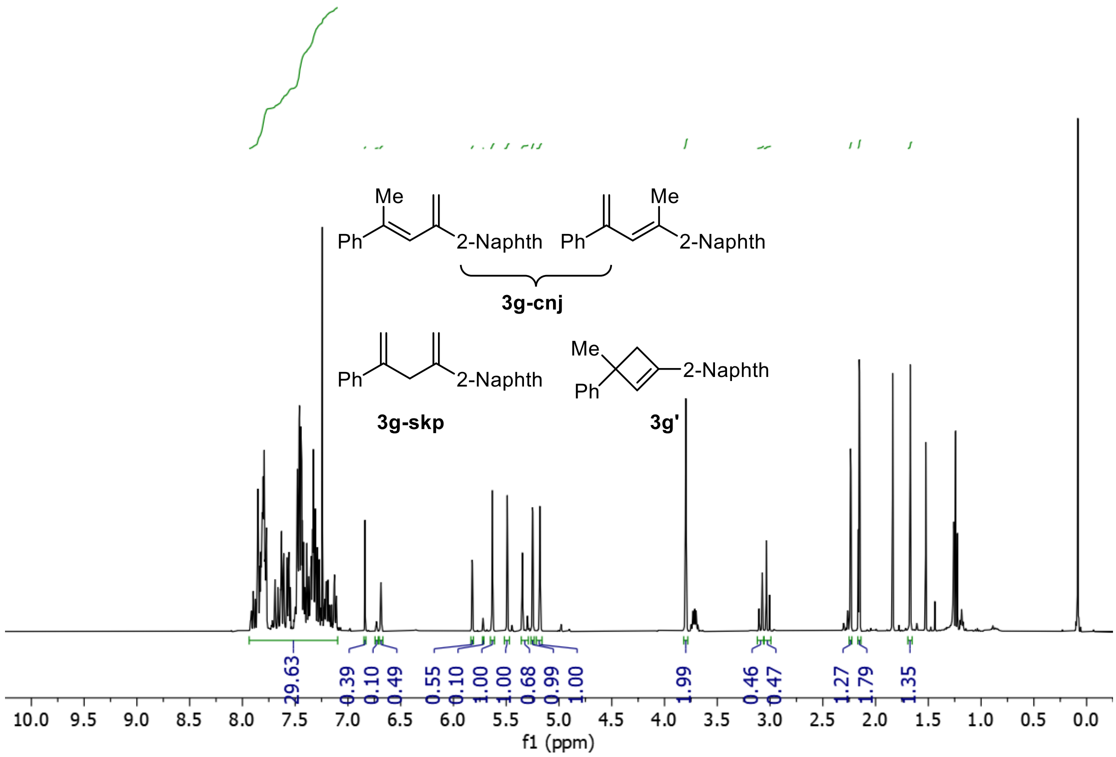
3f and 3f' ¹H NMR (400 MHz, CDCl₃)



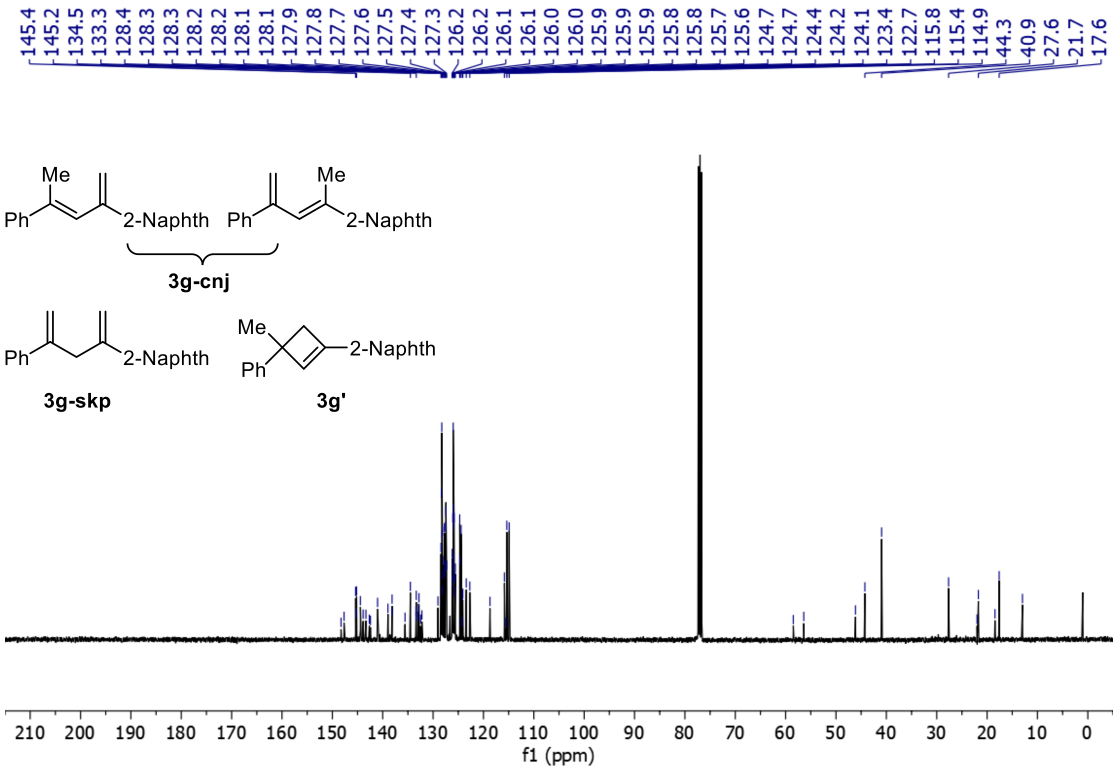
3f and 3f' ¹³C NMR (100 MHz, CDCl₃)



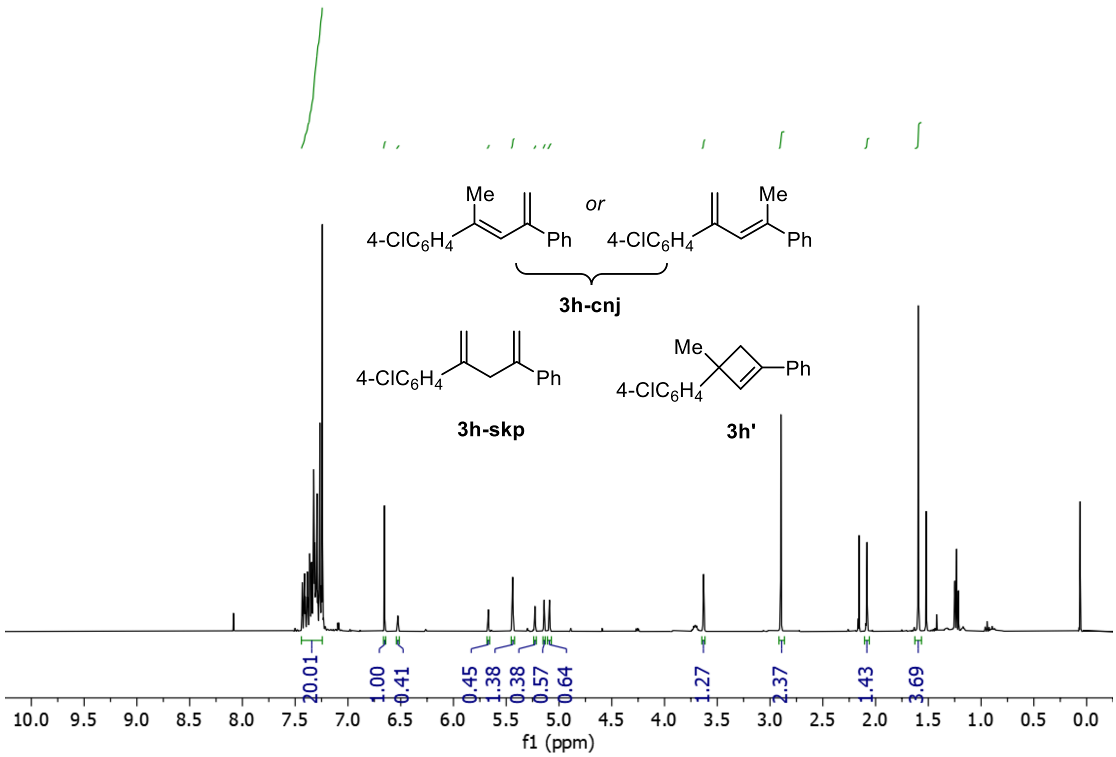
3g and 3g' ^{1}H NMR (400 MHz, $CDCl_3$)



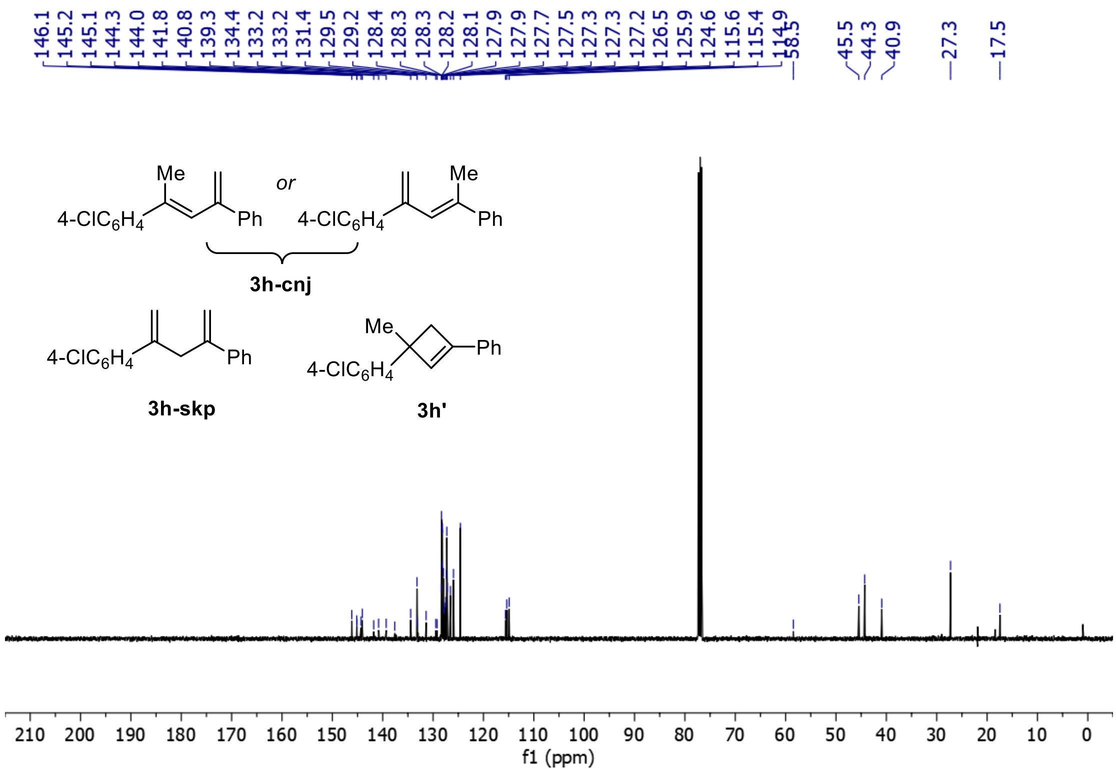
3g and 3g' ^{13}C NMR (100 MHz, $CDCl_3$)



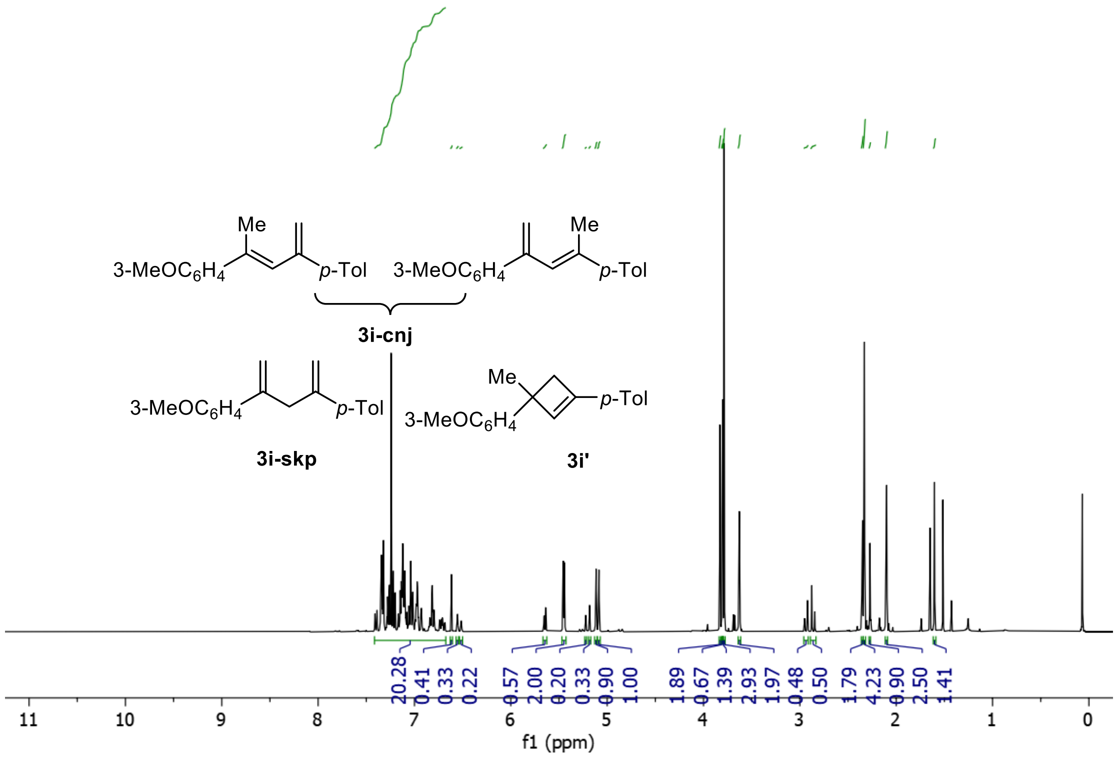
3h and 3h' ^{1}H NMR (400 MHz, CDCl$_3$)



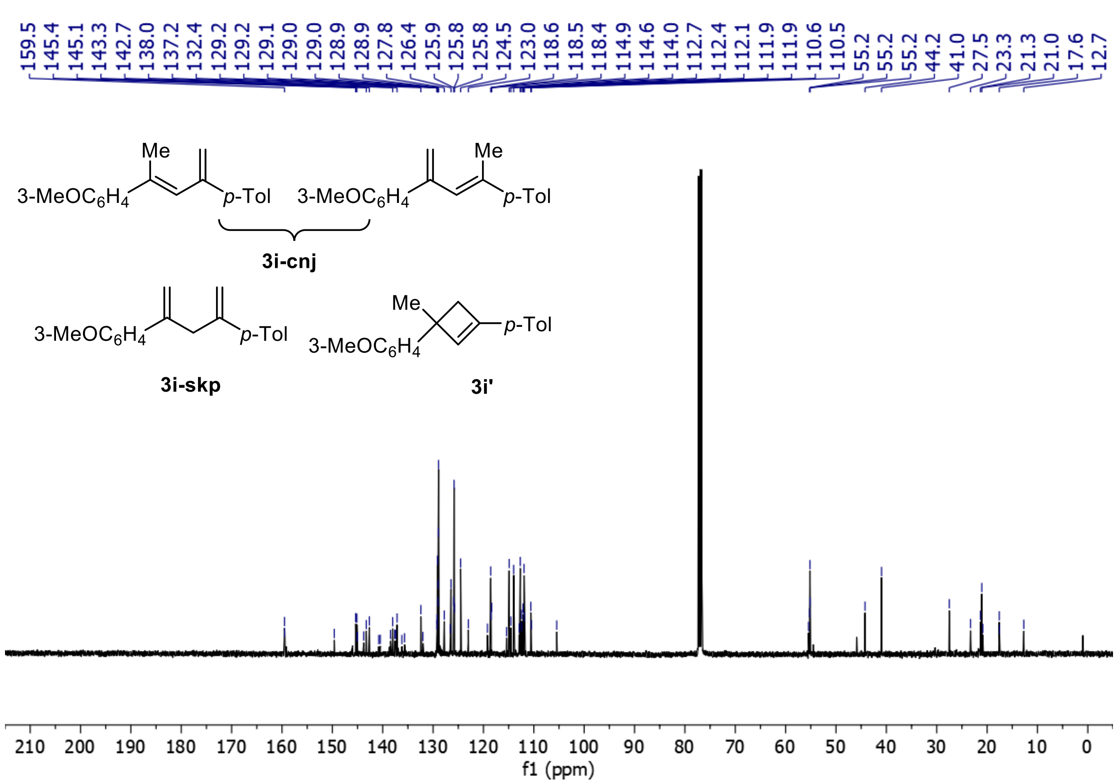
3h and 3h' ^{13}C NMR (100 MHz, CDCl$_3$)



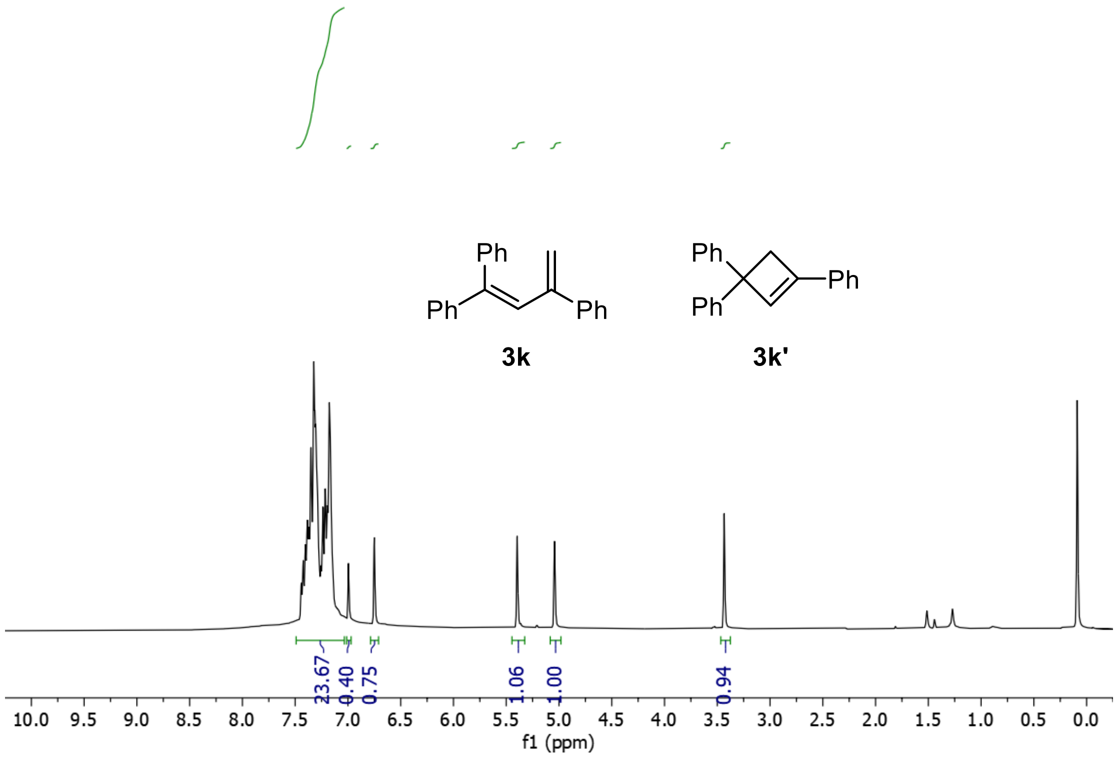
3i and 3i ^{1}H NMR (400 MHz, CDCl$_3$)



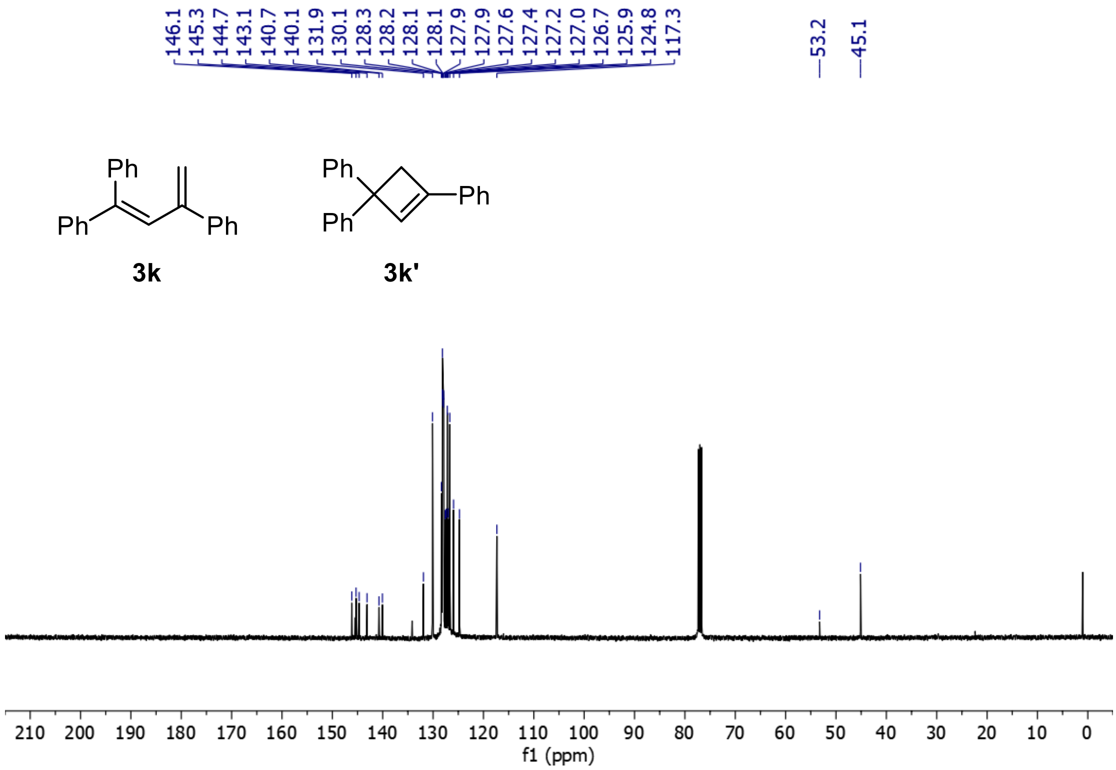
3i and 3i' ^{13}C NMR (100 MHz, CDCl$_3$)



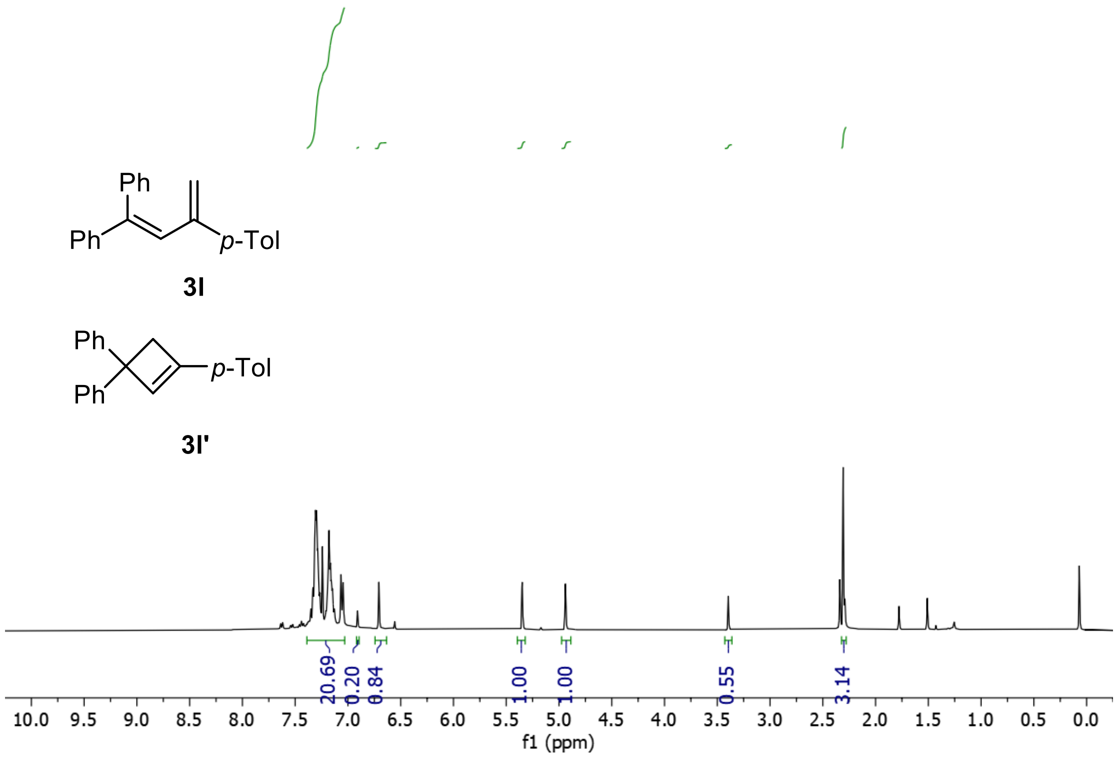
3k and 3k' ^{1}H NMR (400 MHz, $CDCl_3$)



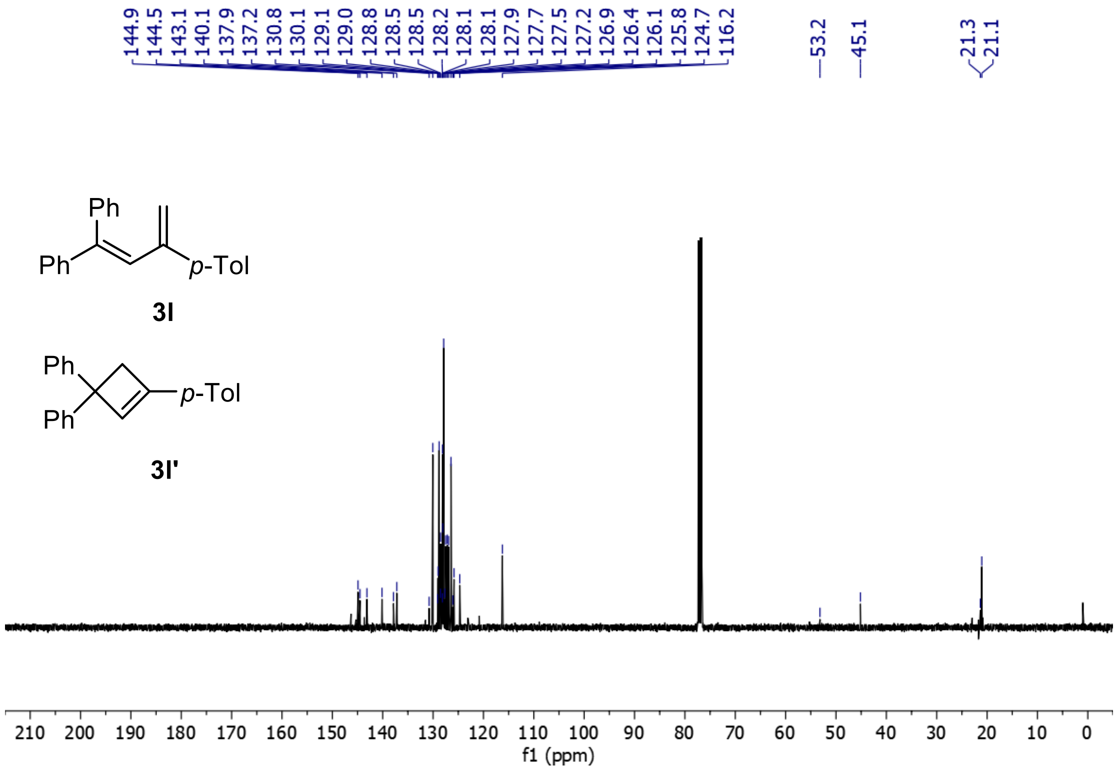
3k and 3k' ^{13}C NMR (100 MHz, $CDCl_3$)



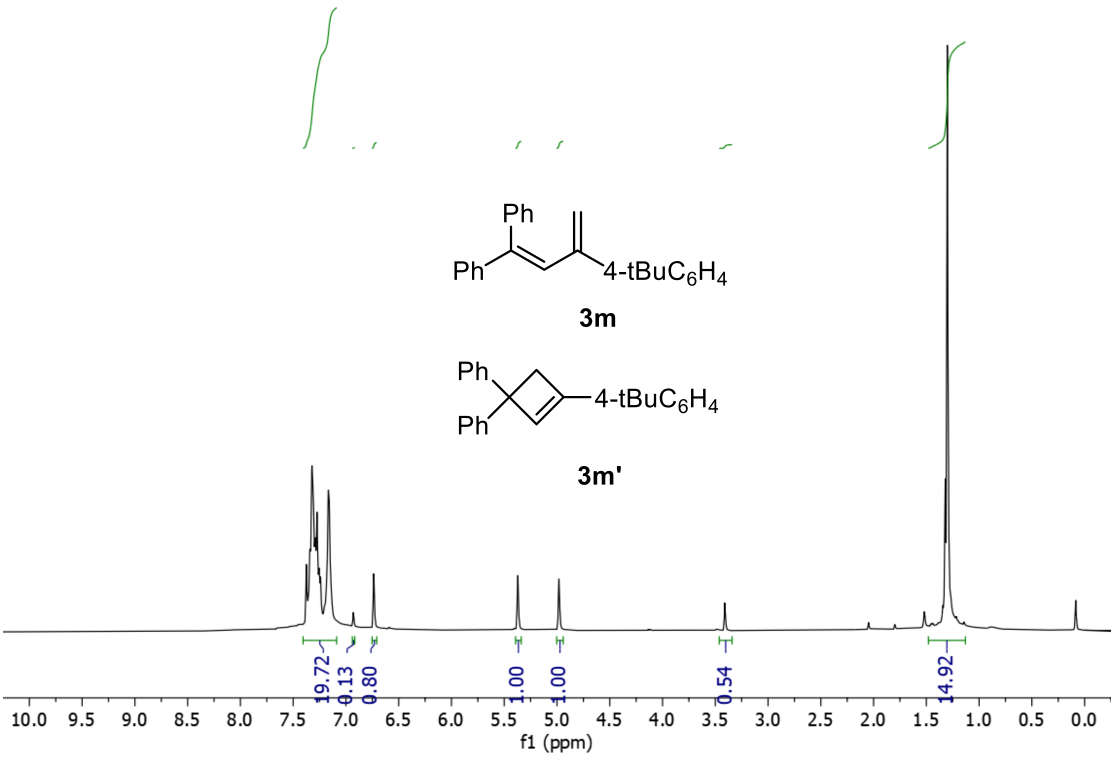
3l and 3l' ^{1}H NMR (400 MHz, $CDCl_3$)



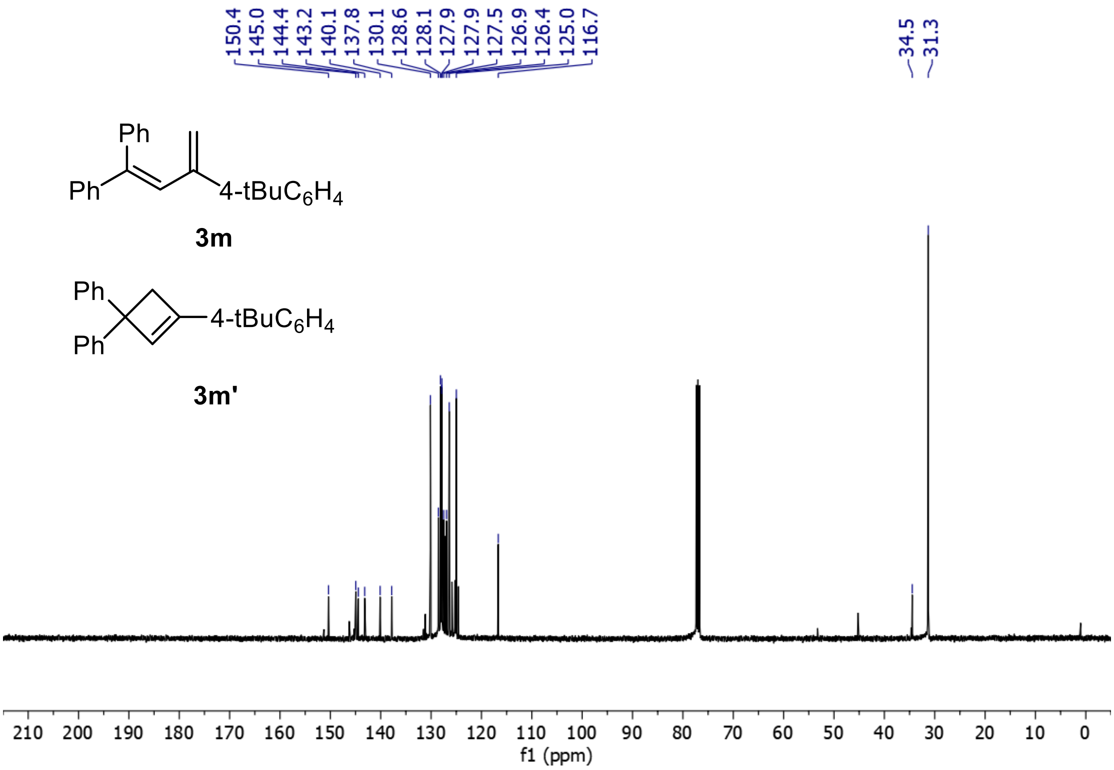
3l and 3l' ^{13}C NMR (100 MHz, $CDCl_3$)



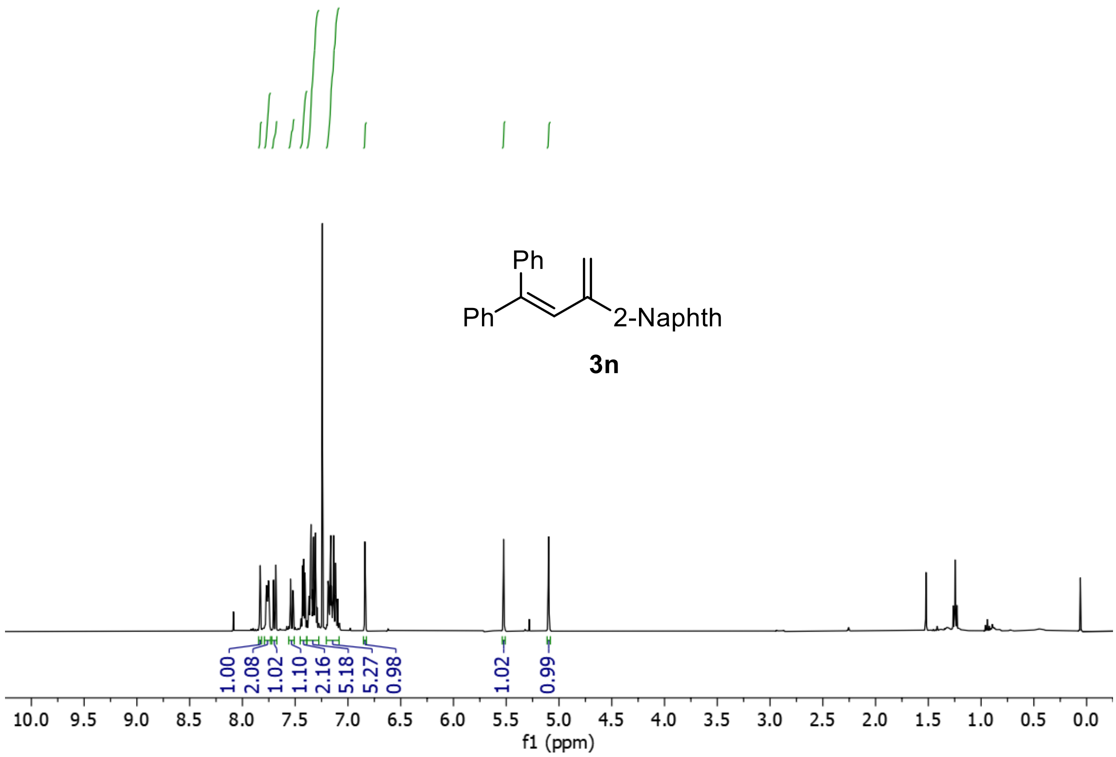
3m and 3m' ^{1}H NMR (400 MHz, $CDCl_3$)



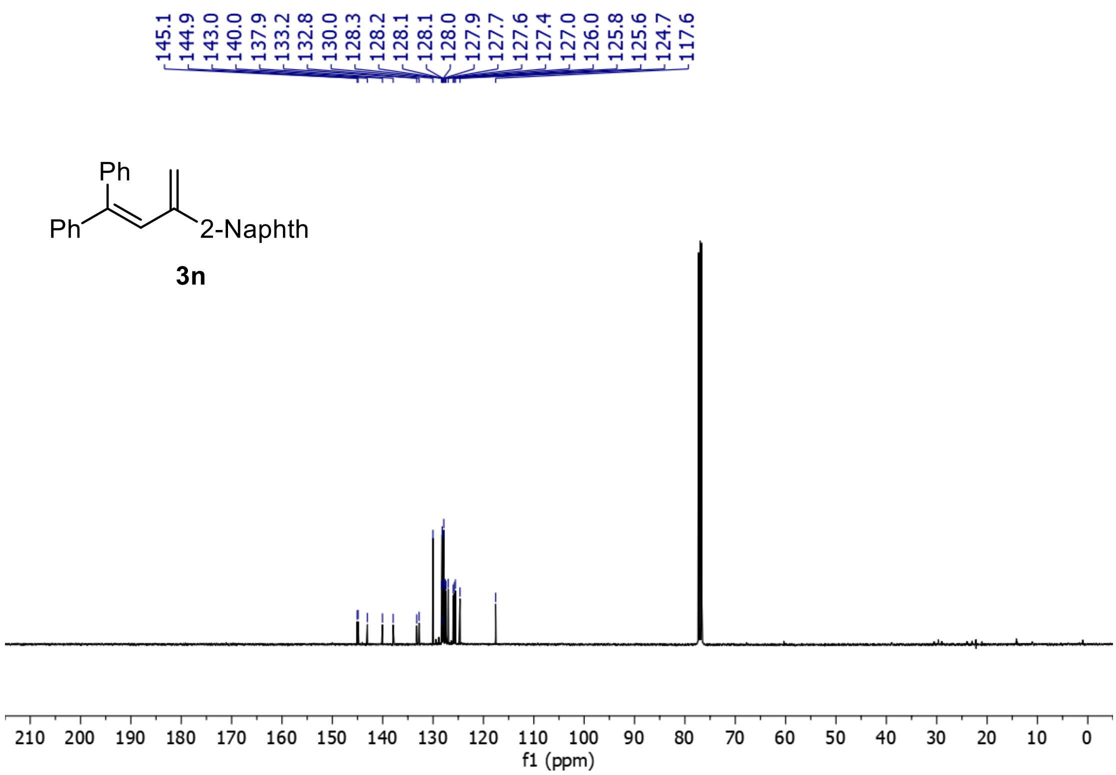
3m and 3m' ^{13}C NMR (100 MHz, $CDCl_3$)



3n ^1H NMR (400 MHz, $CDCl_3$)



3n ^{13}C NMR (100 MHz, $CDCl_3$)



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