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Supplementary information

Photocatalytic phosphine-mediated water activation for radical hydrogenation

Photocatalytic phosphine-mediated water activation for radical hydrogenation

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Supplementary Information

Content

1. General information

Chemicals: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware using standard Schlenk techniques at ambient room temperature, unless otherwise specified. All commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI Chemicals, Acros Organics or ABCR in the highest purity grade and used without further purification. The following solvents (ACROS ExtraDry solvents with ACROSeal® cap) were purchased from ACROS Organics, stored under 3 or 4 Å activated molecular sieves and collected under positive argon pressure: acetonitrile (CH_3CN), dimethylformamide (DMF), dimethylacetamide (DMA), chloroform ($CHCl_3$) and methanol (CH_3OH). Anhydrous tetrahydrofuran (THF) was refluxed over sodium and freshly distilled from potassium prior to use. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates and visualized by fluorescence quenching under UV light. Column chromatography was performed on Merck or Fluka silica gel 60 (40-63 μm).

NMR Spectroscopy: ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded using a Bruker DPX 300, Bruker AV 300, Bruker AV 400, Agilent DD2 500 or Agilent DD2 600 spectrometer at 299 K or 300 K. ^{1}H-NMR chemical shifts are given relative to TMS and residual monoprotic solvent peaks were used as an internal reference for ^{1}H-NMR ($CDCl_3$: $\delta = 7.26$ ppm; DMSO: $\delta = 2.50$ ppm) and ^{13}C-NMR spectra ($CDCl_3$: $\delta = 77.16$ ppm; DMSO: $\delta = 39.52$ ppm). ^{31}P-NMR spectra are referenced according to the proton signal as the primary reference for the unified chemical shift scale. Coupling constants (J) are quoted to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used to describe ^{1}H-, ^{13}C and ^{31}P-NMR multiplicities: s = singlet, broad singlet = brs, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet.

Mass Spectrometry: High-resolution (HRMS) ESI (m/z) spectra were measured on a Bruker MicroTof or ThermoFisher Scientific LTQ XL Orbitrap. High-resolution APCI (m/z) spectra were measured on a Thermo-Fisher Scientific Orbitrap LTQ XL. High-resolution EI (m/z) spectra were measured on a Thermo-Fischer Scientific Exactive GC Orbitrap GC-MS System. MassLinx 4.0 of Water-Micromass was used for data analysis.
GC-FID: GC-FID was conducted on an Agilent GC 6890 equipped with a flame ionization detector (FID) and an Agilent HP-5, Methyl Siloxan (Model No: 19091Z-413) column using H_2 as carrier gas with a flow rate of 1.5 mL min^{-1}. The method used starts with the injection temperature T_0, the column is heated to temperature T_1 (ramp) and this temperature is held for an additional time t ($T_0 = 50$ °C, $T_1 = 300$ °C, ramp = 10 °C min^{-1}, $t = 15$ min).

Light Sources: Photochemical reactions were performed with one LED light (5 W, 455 nm) as light source. The reaction temperature was kept at 20 °C using a circulating water system.

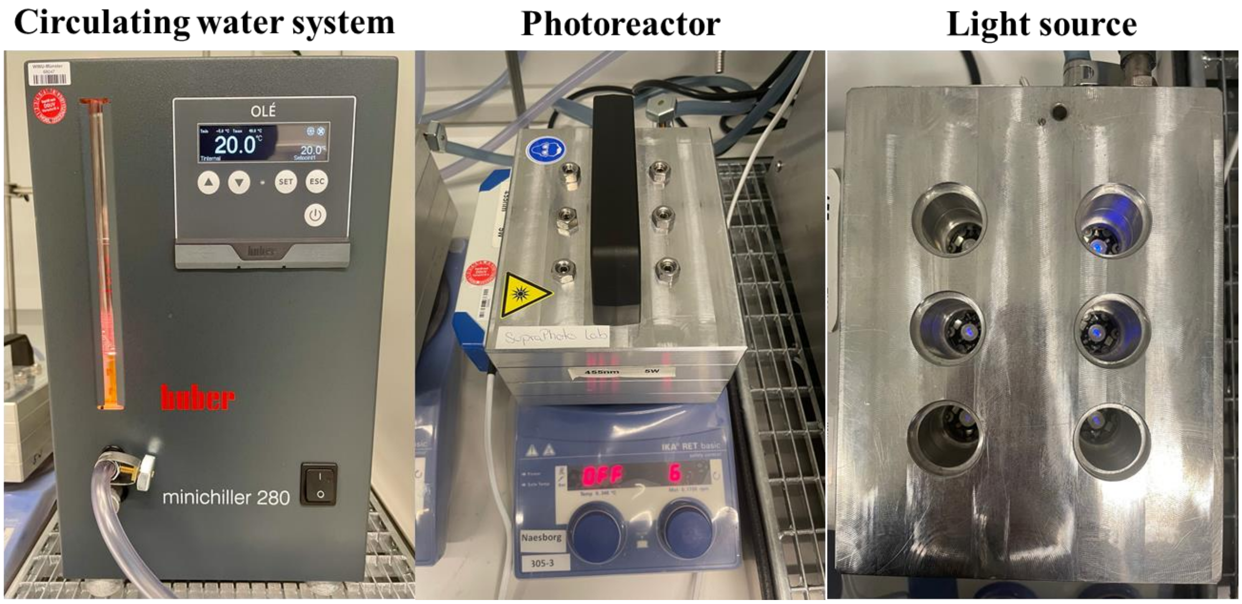


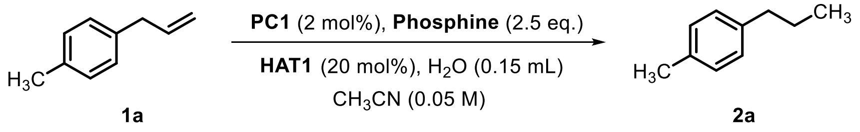
Figure S1. Photoreactors used in this work (455 nm, 5 W or 445 nm, 10 W).

2. Reaction optimization

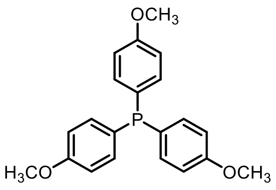
Investigation of commonly used phosphines for reduction of the alkene **1a**:

To an oven dried Schlenk tube with a magnetic stirring bar, the phosphine (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the alkene **1a** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped, then the crude yield of **2a** was determined by GC with tetradecane as the internal standard.

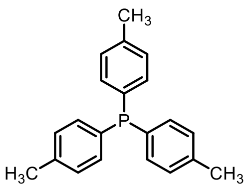
Table S1. Investigation of commonly used phosphines for reduction of the alkene **1a**.



Phosphine	Yield (**2a**)
P1	92%
P2	9%
P3	6%
P4	50%
P5	7%
P6	< 5%
P7	< 5%



P1



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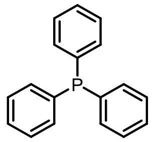

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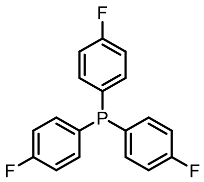
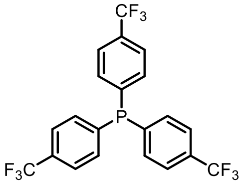
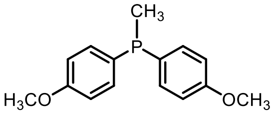


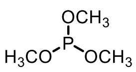
P4



P5



P6

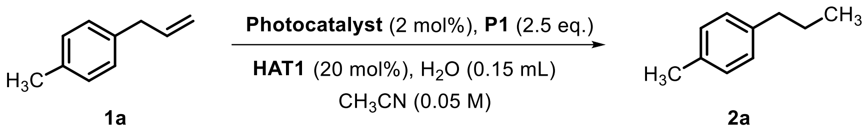


P7

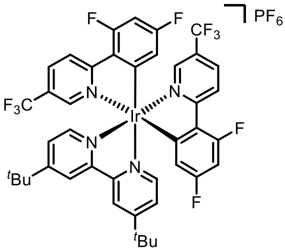
Investigation of commonly used photocatalysts for reduction of the alkene **1a**:

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), the photocatalyst (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the alkene **1a** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped, then the crude yield of **2a** was determined by GC with tetradecane as the internal standard.

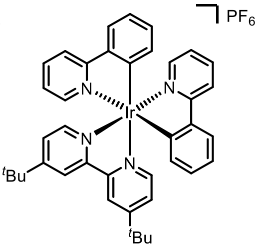
Table S2. Investigation of commonly used photocatalysts for reduction of the alkene **1a**.



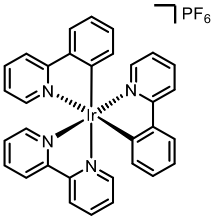
Photocatalyst	Yield (**2a**)
PC1	92%
PC2	32%
PC3	< 5%
PC4	0
PC5	0



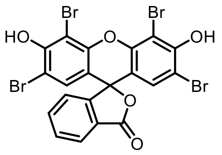
PC1



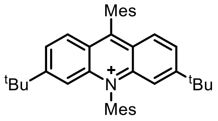
PC2



PC3



PC4

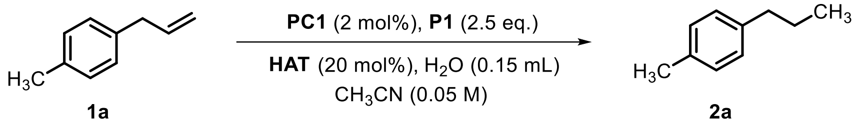


PC5

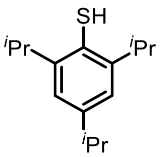
Investigation of commonly used HAT catalysts for reduction of the alkene **1a**:

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the alkene **1a** (0.2 mmol, 1.0 equiv.) and the HAT catalyst (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ºC using the standard set-up. After 72 hours, the irradiation was stopped, then the crude yield of **2a** was determined by GC with tetradecane as the internal standard.

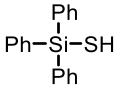
Table S3. Investigation of commonly used HAT catalysts for reduction of the alkene **1a**.



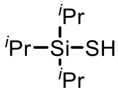
Photocatalyst	Yield (**2a**)
HAT1	92%
HAT2	0
HAT3	0
HAT4	0



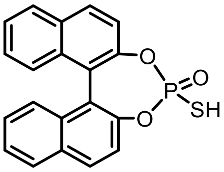
HAT1



HAT2



HAT3

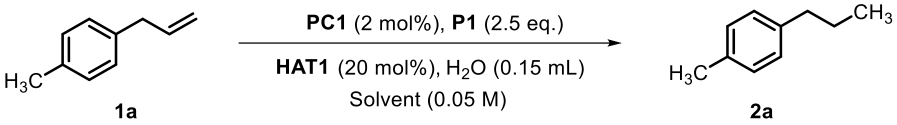


HAT4

Investigation of commonly used solvents for reduction of the alkene **1a**:

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and the solvent (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the alkene **1a** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ºC using the standard set-up. After 72 hours, the irradiation was stopped, then the crude yield of **2a** was determined by GC with tetradecane as the internal standard.

Table S4. Investigation of commonly used solvents for reduction of the alkene **1a**.

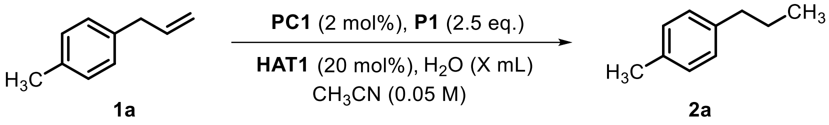


Photocatalyst	Yield (**2a**)
CH_3CN	92%
DMF	62%
DMSO	60%
THF	30%
Toluene	0
EtOAc	0

Investigation of the water amount for reduction of the alkene **1a**:

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (X mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the alkene **1a** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped, then the crude yield of **2a** was determined by GC with tetradecane as the internal standard.

Table S5. Investigation of the water amount for reduction of the alkene **1a**.

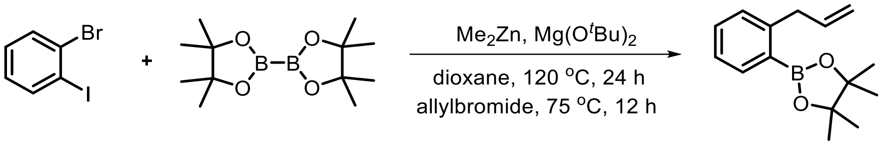


Water	Yield (**2a**)
0.4 mL	42%
0.3 mL	62%
0.2 mL	80%
0.15 mL	92%
0.1 mL	78%

3. The synthesis of starting materials

Most substrates used in this work are commercially available unless otherwise specified. Substrates **5q**,[1] **5s**[2] and **5u**[3] were synthesized through the reported methods. Substrates **1g**, **1h**, **1i**, **1l**, **1n**, **1q**, **1t**, **1w**, **1x**, **1y**, **1z**, **3j**, **5h**, **5r**, **5t** and **15** were synthesized using the following procedures:

The synthesis of **1g**:



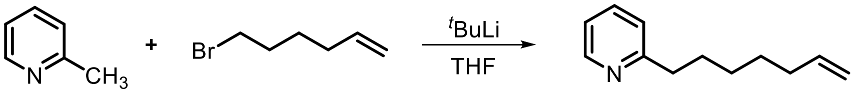
Bis(pinacolato)diboron (254 mg, 1.00 mmol) and magnesium *tert*-butoxide (171 mg, 1.00 mmol) were charged in a dried Schlenk tube under argon atmosphere, and dissolved in dry 1,4-dioxane (2 mL). To the mixture dimethylzinc (1.5 mL, 1.50 mmol; 1.0 M hexane solution) was added at 0 ºC, and the solution was stirred for 30 min at room temperature. To the mixture the 2-bromoiodobenzene (142 mg, 0.50 mmol) was added at room temperature. The mixture was stirred for 24 h at 120 ºC. After cooling to room temperature, to the mixture was added allyl bromide (3.0 equiv.) at the room temperature, and the solution was allowed to warm to 75 ºC, and stirred for 12 h. After cooling again to room temperature, the reaction was quenched by aqueous NH_4Cl (10 mL), and extracted with EtOAc (3 × 15 mL). The combined EtOAc layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification of the resulting crude residue via silica gel flash chromatography (pentane/EtOAc 10/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 1H), 7.48 – 7.35 (m, 1H), 7.31 – 7.13 (m, 2H), 6.20 – 5.87 (m, 1H), 5.15 – 4.92 (m, 2H), 3.76 (d, *J* = 6.6 Hz, 2H), 1.43 – 1.34 (m, 12H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 146.8, 139.2, 136.1, 131.1, 129.2, 125.4, 114.8, 83.5, 39.8, 24.9.

The NMR data were in agreement with those reported in the literature.[4]

The synthesis of **1h**:



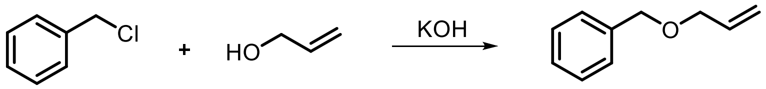
A round bottom flask equipped with a magnetic stir bar was flame dried and back filled with argon. THF (25 mL) and 2-methylpyridine (0.49 mL, 5.0 mmol, 1.0 equiv.) were added. The reaction mixture was cooled to -78 °C and *tert*-butyllithium (3.2 mL, 1.7 M in pentane, 5.5 mmol, 1.1 equiv.) was added dropwise. After completing addition, the reaction mixture was left to stir for 20 minutes, then 6-bromo-1-hexene (0.67 mL, 5.0 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature then left to stir for 1 h at room temperature. The reaction mixture was cooled to 0 °C and quenched with aqueous NH_4Cl (10 mL). Brine was added, the layers were separated, and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the crude residue. Purification of the resulting crude residue via silica gel flash chromatography (pentane/EtOAc 10/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.56 (tt, *J* = 7.7, 1.6 Hz, 1H), 7.21 – 6.98 (m, 2H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.22 – 4.65 (m, 2H), 2.93 – 2.60 (m, 2H), 2.04 (qd, *J* = 7.5, 3.3 Hz, 2H), 1.87 – 1.60 (m, 2H), 1.56 – 1.30 (m, 4H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 162.4, 149.2, 139.0, 136.2, 122.7, 120.9, 114.3, 38.4, 33.7, 29.8, 28.9, 28.8.

The NMR data were in agreement with those reported in the literature.[5]

The synthesis of **1i**:



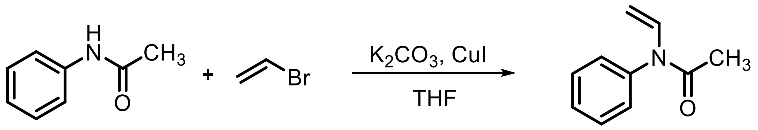
KOH (850 mg, 12.8 mmol) was suspended in allyl alcohol (2.2 mL, 32.4 mmol) and the mixture was stirred until all KOH had dissolved. The mixture was cooled with a water bath around 10 °C and benzyl chloride (0.74 mL, 12.8 mmol) was added slowly. The water bath was removed and the reaction mixture heated to 60 °C for 3 h. The reaction mixture was filtered and purification of the resulting crude residue via silica gel flash chromatography (pentane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.25 (m, 5H), 6.12 – 5.86 (m, 1H), 5.43 – 5.29 (m, 1H), 5.25 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.57 (d, *J* = 1.7 Hz, 2H), 4.17 – 3.97 (m, 2H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 138.3, 134.8, 128.4, 127.8, 127.6, 117.2, 72.1, 71.2.

The NMR data were in agreement with those reported in the literature.[6]

The synthesis of **1l**:



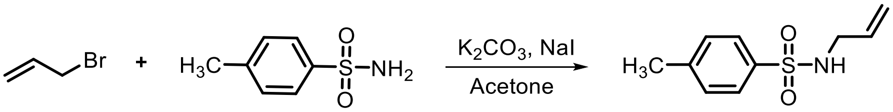
To an oven-dried screw-cap vial fitted with a magnetic stirring bar amide (1.0 equiv.), vinyl bromide (1.0 M solution in THF, 2.0 equiv.), CuI (0.050 equiv.), *N,N'*-dimethylethylenediamine (0.10 equiv.), and K_2CO_3 (2.0 equiv.) were added. The vial was tightly sealed using Teflon tape and heated to 80 °C while stirring overnight. Upon completion of the reaction, the mixture was filtered through a pad of celite, rinsing with EtOAc, and solvent was removed in vacuo to afford the crude product. Purification of the resulting crude residue via silica gel flash chromatography (pentane/EtOAc 3/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 15.9, 9.2 Hz, 1H), 7.49 (ddt, *J* = 12.9, 8.3, 4.3 Hz, 3H), 7.19 (dd, *J* = 7.1, 1.8 Hz, 2H), 4.38 (d, *J* = 9.0 Hz, 1H), 3.86 (d, *J* = 15.9 Hz, 1H), 1.87 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 168.8, 139.2, 133.7, 130.0, 128.9, 128.7, 96.3, 23.3.

The NMR data were in agreement with those reported in the literature.[7]

The synthesis of **1n**:



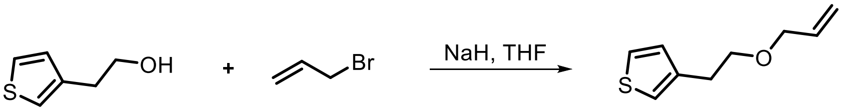
p-Toluenesulfonamide (1.5 equiv.), K_2CO_3 (2.0 equiv.) and NaI (10 mol%) were dissolved in reagent grade acetone (1.0 M). The allyl bromide (1.0 equiv.) was added and the reaction mixture was heated to reflux for 12 h. The reaction mixture was cooled, then poured onto H_2O and extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. Purification of the resulting crude residue via silica gel flash chromatography (pentane/EtOAc 2/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.85 – 5.57 (m, 1H), 5.23 – 5.05 (m, 2H), 4.93 (t, *J* = 6.3 Hz, 1H), 3.58 (tt, *J* = 6.2, 1.5 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 143.5, 136.9, 133.0, 129.7, 127.2, 117.6, 45.8, 21.6.

The NMR data were in agreement with those reported in the literature.[8]

The synthesis of **1q**:



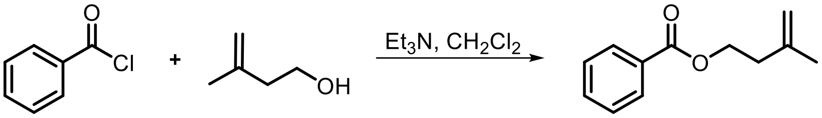
A round-bottomed flask (250 mL) was equipped with a magnetic stirring bar, and flame dried under argon. The 2-(thiophen-2-yl)ethanol (846 mg, 6.6 mmol) was weighed in the flask and dissolved in dry THF (70 mL). Sodium hydride (60%) (13.2 mmol, 2 equiv.) was added to the flask. The resulting dispersion was heated to 50 °C using a silicone oil bath for one hour. The mixture was cooled to 0 °C (ice/water bath) and allyl bromide (13.2 mmol, 2 equiv.) was added through a syringe needle. The new mixture was stirred at 0 °C for five minutes, then warmed to room temperature and stirred overnight. The reaction was quenched by careful addition of a saturated ammonium chloride solution (50 mL) and transferred to a separatory funnel (250 mL) with EtOAc (50 mL). The biphasic mixture was shaken, separated and the aqueous layer extracted twice with EtOAc (2 × 50 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$ and the solvent removed in vacuo, to give a dry residue. Purification was achieved employing flash column chromatography on silica gel (eluted with pentane/EtOAc 9:1) to afford the title product as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 1H), 7.09 – 7.04 (m, 1H), 7.02 (dd, *J* = 4.9, 1.4 Hz, 1H), 6.08 – 5.84 (m, 1H), 5.30 (ddd, *J* = 17.2, 2.4, 1.2 Hz, 1H), 5.21 (dt, *J* = 10.9, 1.7 Hz, 1H), 4.04 (dd, *J* = 5.6, 1.4 Hz, 2H), 3.69 (t, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 139.2, 134.8, 128.5, 125.3, 121.2, 117.0, 71.9, 70.5, 30.8.

The NMR data were in agreement with those reported in the literature.[9]

The synthesis of **1t**:



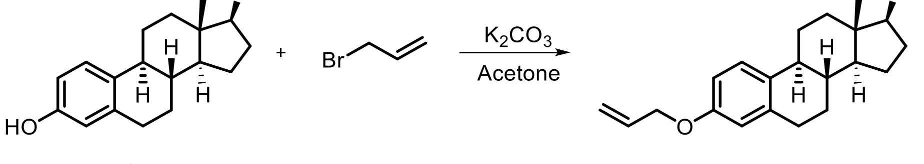
Into a 100-mL round-bottomed flask, equipped with a dropping funnel and charged with argon, 20 mL of dichloromethane, 3-buten-1-ol (2.0 g, 28 mmol) and triethylamine (5.7 g, 56 mmol) were added. To this solution cooled in an ice-water bath, benzoyl chloride (3.6 g, 26 mmol) was added dropwise over 10 minutes. Reaction mixture was stirred for an additional 50 minutes at 0 °C and at room temperature for 3 h. The mixture was poured into 1 M HCl (50 mL), and extracted with diethyl ether (3 × 30 mL). The separated organic layer was washed with aqueous $NaHCO_3$ (50 mL), and dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, components of the residue were separated by column chromatography on silica gel (pentane/EtOAc 20/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.24 (m, 5H), 5.06 (dd, *J* = 2.2, 1.1 Hz, 1H), 5.01 – 4.89 (m, 1H), 4.54 (s, 2H), 3.98 (s, 2H), 1.82 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 142.2, 138.5, 128.4, 127.7, 127.6, 112.4, 74.2, 71.8, 19.6.

The NMR data were in agreement with those reported in the literature.[10]

The synthesis of **1w**:



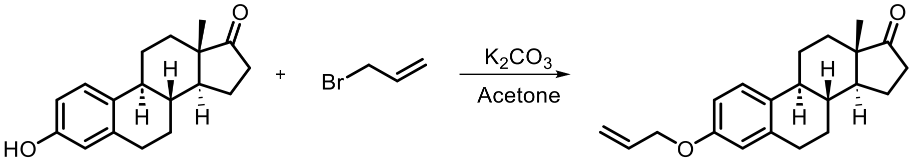
To a flame dried Schlenk flask, *β*-estradiol (136.2 mg, 0.5 mmol, 1.0 equiv.), 3-bromopropene (86 µL, 1.0 mmol, 2.0 equiv.), K_2CO_3 (207 mg, 1.5 mmol, 3.0 equiv.) and acetone (7.5 mL) were added. The resulting mixture was stirred at 50 ºC for 40 h. After complete consumption of the starting phenol, the reaction mixture was concentrated and the resulting residue was extracted with CH_2Cl_2 for three times. The combined organic layer was dried over $MgSO_4$, concentrated under vacuum. The residue was separated by column chromatography on silica gel (pentane/EtOAc 6/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 1H), 6.75 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.68 (d, *J* = 2.7 Hz, 1H), 6.08 (ddt, *J* = 17.4, 10.5, 5.3 Hz, 1H), 5.50 – 5.37 (m, 1H), 5.30 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.65 – 4.42 (m, 2H), 3.74 (d, *J* = 11.0 Hz, 1H), 2.97 – 2.74 (m, 2H), 2.33 (dt, *J* = 12.5, 3.7 Hz, 1H), 2.29 – 2.05 (m, 2H), 2.04 – 1.82 (m, 2H), 1.72 (tdd, *J* = 10.0, 7.3, 4.0 Hz, 1H), 1.61 – 1.13 (m, 9H), 0.81 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 156.5, 138.0, 133.6, 132.8, 126.3, 117.5, 114.8, 112.2, 81.9, 68.8, 50.1, 44.0, 43.3, 38.8, 36.7, 30.6, 29.8, 27.3, 26.3, 23.2, 11.1.

The NMR data were in agreement with those reported in the literature.[11]

The synthesis of **1x**:



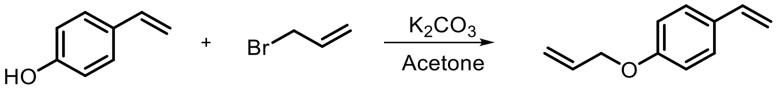
To a flame dried Schlenk flask, estrone (135.2 mg, 0.5 mmol, 1.0 equiv.), 3-bromopropene (86 µL, 1.0 mmol, 2.0 equiv.), K_2CO_3 (207 mg, 1.5 mmol, 3.0 equiv.) and acetone (7.5 mL) were added. The resulting mixture was stirred at 50 ºC for 40 h. After complete consumption of the starting phenol, the reaction mixture was concentrated and the resulting residue was extracted with CH_2Cl_2 for three times. The combined organic layer was dried over $MgSO_4$, concentrated under vacuum. The residue was separated by column chromatography on silica gel (pentane/EtOAc 5/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.74 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.67 (s, 1H), 6.06 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.41 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.28 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.51 (dt, *J* = 5.1, 1.4 Hz, 2H), 2.90 (dt, *J* = 8.5, 3.8 Hz, 2H), 2.57 – 2.45 (m, 1H), 2.40 (ddt, *J* = 12.0, 4.2, 2.1 Hz, 1H), 2.32 – 2.20 (m, 1H), 2.18 – 1.89 (m, 4H), 1.69 – 1.35 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 221.0, 156.6, 137.8, 133.5, 132.2, 126.3, 117.5, 114.8, 112.3, 68.8, 50.4, 48.0, 44.0, 38.4, 35.9, 31.6, 29.7, 26.6, 25.9, 21.6, 13.9.

The NMR data were in agreement with those reported in the literature.[12]

The synthesis of **1y**:

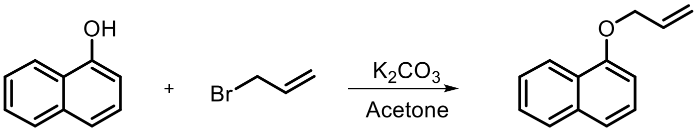


To a flame dried Schlenk flask, 4-vinylphenol (600 mg, 5.0 mmol, 1.0 equiv.), 3-bromopropene (860 µL, 10.0 mmol, 2.0 equiv.), K_2CO_3 (15.0 mmol, 3.0 equiv.) and acetone (50 mL) were added. The resulting mixture was stirred at 50 ºC for 40 h. After complete consumption of the starting phenol, the reaction mixture was concentrated and the resulting residue was extracted with CH_2Cl_2 for three times. The combined organic layer was dried over $MgSO_4$, concentrated under vacuum. The residue was separated by column chromatography on silica gel (pentane/EtOAc 20/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.58 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.98 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.53 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.33 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.21 (dd, *J* = 10.5, 1.4 Hz, 1H), 5.05 (dd, *J* = 10.9, 1.0 Hz, 1H), 4.46 (dt, *J* = 5.3, 1.5 Hz, 2H).

The NMR data were in agreement with those reported in the literature.[13]

The synthesis of **1z**:

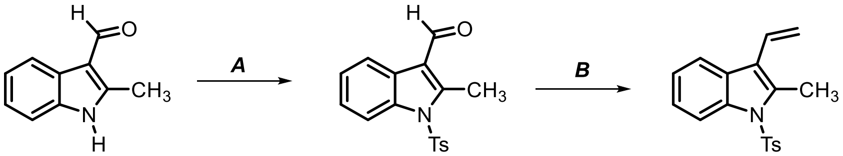


To a flame dried Schlenk flask, naphthalen-1-ol (720 mg, 5.0 mmol, 1.0 equiv.), 3-bromopropene (860 µL, 10.0 mmol, 2.0 equiv.), K_2CO_3 (15.0 mmol, 3.0 equiv.) and acetone (50 mL) were added. The resulting mixture was stirred at 50 ºC for 40 h. After complete consumption of the starting phenol, the reaction mixture was concentrated and the resulting residue was extracted with CH_2Cl_2 for three times. The combined organic layer was dried over $MgSO_4$, concentrated under vacuum. The residue was separated by column chromatography on silica gel (pentane/EtOAc 20/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 – 8.32 (m, 1H), 7.93 – 7.78 (m, 1H), 7.60 – 7.35 (m, 4H), 6.86 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.23 (ddt, *J* = 17.3, 10.4, 5.1 Hz, 1H), 5.58 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.39 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.77 (dt, *J* = 5.1, 1.6 Hz, 2H).

The NMR data were in agreement with those reported in the literature.[14]

The synthesis of **3l**:



***Procedure A**:* Diisopropylethylamine (3.93 mL, 22.6 mmol) was added to a solution of 2-methyl 1H-indole-3-carbaldehyde (3.0 g, 18.8 mmol) and *p*-toluenesulfonyl chloride (3.94 g, 20.7 mmol) in acetonitrile (50 mL). After 18 h, the reaction mixture was poured into aqueous hydrochloric acid (1 M, 500 mL). The aqueous layer was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were washed with brine (25 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography to afford 2-methyl-1-tosyl-1H-indole-3-carbaldehyde as a yellow solid.

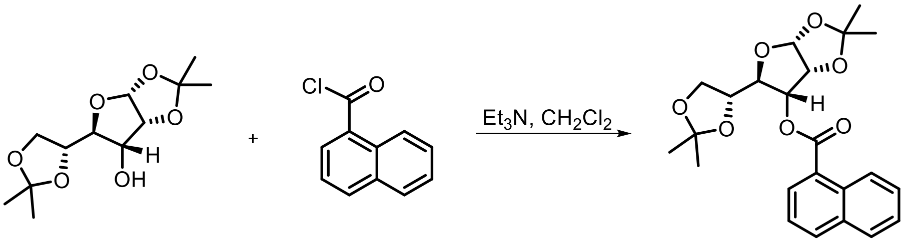
Procedure B: n-Butyllithium (2.5 M solution in hexanes, 1.0 mL, 2.5 mmol) was added over 5 minutes to a suspension of the methyltriphenylphosphonium bromide (1.1 g, 3.0 mmol) in anhydrous tetrahydrofuran (25 mL) maintained at 0 °C under an atmosphere of dry nitrogen. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The resulting orange colored solution, containing a small amount of unreacted solid phosphonium salt, was cooled to -15 °C. 2-Methyl-1-tosyl-1H-indole-3-carbaldehyde (0.63 g, 2.0 mmol) was added and the reaction mixture was allowed to warm to -5 °C over a period of 1 h. The reaction was quenched with water (25 mL) and extracted with ethyl acetate (3 × 10 mL). The organic extract was washed with brine (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude product was purified using silica gel column chromatography (pentane/EtOAc 5/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.0 Hz, 1H), 7.59 (dd, *J* = 13.9, 8.4 Hz, 3H), 7.26 – 7.14 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.65 (dd, *J* = 17.8, 11.6 Hz, 1H), 5.61 (d, *J* = 17.8 Hz, 1H), 5.35 (d, *J* = 11.5 Hz, 1H), 2.54 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 144.8, 136.5, 136.3, 134.6, 129.9, 128.6, 127.7, 126.4, 124.2, 123.7, 119.5, 118.5, 116.8, 114.6, 21.6, 13.1.

The NMR data were in agreement with those reported in the literature.[15]

The synthesis of **5h**:



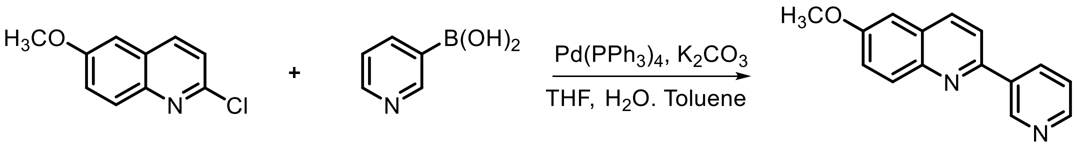
Into a 100-mL round-bottomed flask, equipped with a dropping funnel and charged with argon, 20 mL of dichloromethane, 1,2:5,6-di-O-isopropyliden-α-D-allofuranos (1.0 g, 3.8 mmol) and triethylamine (1.0 g, 10 mmol) were added. To this solution cooled in an ice-water bath, 1-naphthoyl chloride (722 mg, 3.8 mmol) was added dropwise over 10 min. Reaction mixture was stirred for additional 50 min at 0 °C and at room temperature for 3 h. The mixture was poured into 1 M HCl (50 mL), and extracted with diethyl ether (3 × 30 mL). The separated organic layer was washed with aqueous $NaHCO_3$ (50 mL), and dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, components of the residue were separated by column chromatography on silica gel (pentane/EtOAc 5/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (d, *J* = 8.6 Hz, 1H), 8.29 – 8.13 (m, 1H), 8.11 – 7.98 (m, 1H), 7.89 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.67 – 7.46 (m, 3H), 5.94 (d, *J* = 3.7 Hz, 1H), 5.27 – 5.14 (m, 1H), 5.07 (dd, *J* = 5.1, 3.8 Hz, 1H), 4.49 – 4.34 (m, 2H), 4.12 (ddd, *J* = 8.0, 4.5, 1.5 Hz, 1H), 4.05 – 3.92 (m, 1H), 1.59 (s, 3H), 1.43 (s, 3H), 1.35 (d, *J* = 3.3 Hz, 6H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 166.6, 133.8, 133.7, 131.4, 130.5, 128.6, 127.8, 126.5, 126.3, 125.9, 124.5, 113.2, 110.1, 104.3, 77.9, 77.8, 75.3, 73.5, 65.9, 26.8, 26.7, 26.4, 25.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{26}O_7Na$ 437.1571; found 437.1571.

The synthesis of **5r**:



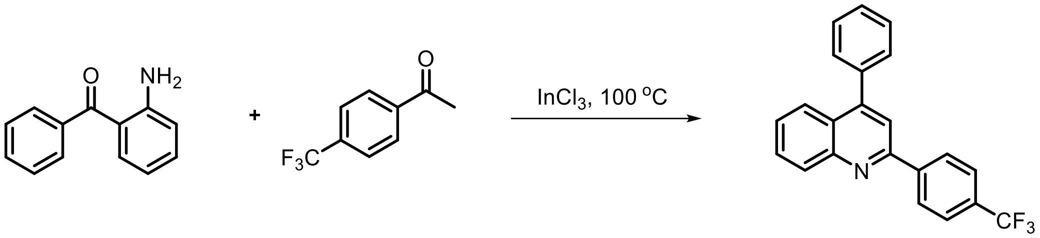
Under nitrogen atmosphere a two neck round bottom flask was charged with boronic acid (1.0 mmol), 2-chloro-6-methoxyquinoline (1 mmol), $Pd(PPh_3)_4$ (5 mol%) and potassium carbonate (3.0 mmol). The flask was protected against light. Degassed water (2.5 ml), degassed THF (2.5 ml), toluene (5 ml) were added via syringe. The mixture was heated at 80 °C for 40 h and then diluted with CH_2Cl_2. The aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. After removal of solvent the crude product was purified by column chromatography on silica gel (pentane/EtOAc 8/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.30 (d, *J* = 1.5 Hz, 1H), 8.64 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.42 (ddd, *J* = 8.0, 2.3, 1.6 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.04 (d, *J* = 2.8 Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 158.0, 152.1, 149.9, 148.6, 144.5, 135.8, 135.2, 134.6, 131.2, 128.4, 123.6, 122.8, 118.7, 104.9, 55.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O$ 237.1022; found 237.1022.

The synthesis of **5t**:



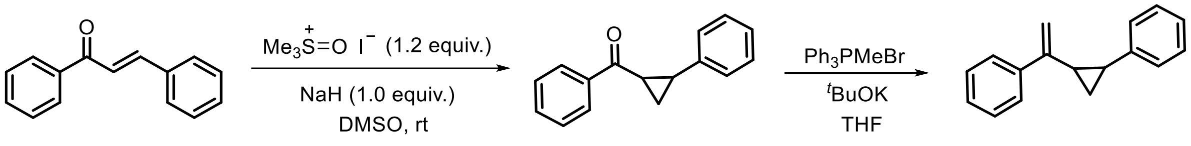
A mixture of 2-aminobenzophenone (10.0 mmol), acetophenone (12.0 mmol), and $InCl_3$ (2.0 mmol) under solvent-free conditions was heated at 100 °C in a 25 mL round-bottomed flask. After completion of the reaction (monitored by TLC), water (15 mL) was added and the reaction mixture was extracted with EtOAc (3 × 10 mL). The combined organic extract was washed with brine and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (pentane/ EtOAc 20/1).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.32 (d, *J* = 8.1 Hz, 2H), 8.26 (d, *J* = 8.1 Hz, 1H), 7.98 – 7.89 (m, 1H), 7.86 – 7.74 (m, 4H), 7.62 – 7.46 (m, 6H).

^{19}F NMR (282 MHz, CDCl$_3$) δ -62.50.

The NMR data were in agreement with those reported in the literature.[16]

The synthesis of **15**:



***Procedure A**:* To a two-necked round flask, sodium hydride (60% in mineral oil, 1.0 equiv.) was added. Then, dry DMSO and trimethylsulfoxonium iodide (1.2 equiv.) were added to the flask at room temperature under an Ar atmosphere. After hydrogen evolution ceased, the reaction mixture was stirred for additional 15 minutes, during which time the solution became clear. Chalcone (1.0 equiv.) was then added in one portion to the clear solution. The reaction solution was stirred at room temperature for 5 h. After completion of the reaction as detected by TLC, the reaction was quenched with ice cold water and extracted with diethyl ether (3 × 30 mL). The combined organic layer was washed with brine, dried over Na$_2$SO$_4$. The product was purified by flash silica gel column chromatography using (petroleum ether/ethyl acetate) as eluent to afford the cyclopropyl ketone product.

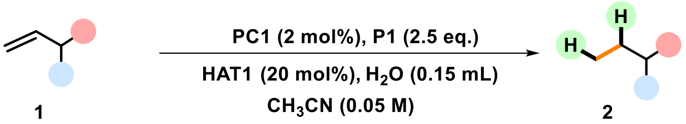
***Procedure B**:* Then, to an oven dried flask, methyl triphenylphosphonium bromide (12 mmol, 1.2 equiv.) and THF (30 mL) were added. The suspension was cooled to 0 ^{o}C, *t*-BuOK (12 mmol, 1.2 equiv.) was added and the resulting yellow suspension was stirred at 0 ^{o}C for 1 hour. To this suspension, a solution of the cyclopropyl ketone (10 mmol, 1.0 equiv.) in THF (10 mL) was added slowly and the resulting mixture was warmed gradually to room temperature and stirred at room temperature for 18 hours. The reaction mixture was concentrated under reduced pressure and filtered over celite. The filtrate was concentrated under reduced pressure and the crude product was purified using silica gel column chromatography (pentane/EtOAc 5/1).

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.58 – 7.41 (m, 2H), 7.38 – 7.02 (m, 8H), 5.36 (s, 1H), 5.03 (s, 1H), 2.08 – 1.89 (m, 2H), 1.43 – 1.36 (m, 1H), 1.30 – 1.27 (m, 1H).

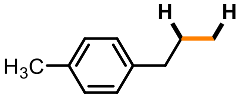
The NMR data were in agreement with those reported in the literature.[17]

4. Synthesis and characterization of products

4.1 Synthesis and characterization of products 2



General procedure (GP1) for the reduction of unactivated alkenes: To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the alkene **1** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane, pentane/EtOAc or pentane/Et_2O mixtures, as detailed in the individual entries), to afford the corresponding product **2**.



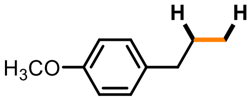
2a, 81%

1-Methyl-4-propylbenzene **2a**. According to the **GP1**, using the alkene **1a** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2a** (21.7 mg, 0.16 mmol, 81%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 6.99 (m, 4H), 2.68 – 2.51 (m, 2H), 2.36 (s, 3H), 1.67 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 139.7, 135.0, 128.9, 128.4, 37.7, 24.8, 21.0, 13.9.

The NMR data were in agreement with those reported in the literature.[18]



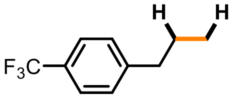
2b, 89%

1-Methoxy-4-propylbenzene **2b**. According to the **GP1**, using the alkene **1b** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2b** (26.7 mg, 0.18 mmol, 89%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 – 7.05 (m, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.53 (dd, *J* = 8.5, 6.8 Hz, 2H), 1.67 – 1.55 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 157.7, 134.8, 129.3, 113.6, 55.3, 37.2, 24.8, 13.8.

The NMR data were in agreement with those reported in the literature.[19]

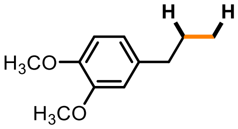


2c, 76%

1-Propyl-4-(trifluoromethyl)benzene **2c**. According to the **GP1**, using the alkene **1c** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2c** (28.58 mg, 0.152 mmol, 76%) as a colorless liquid along with the unreacted alkene **1c** and 2,4,6-triisopropylbenzenethiol.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.57 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

The NMR data were in agreement with those reported in the literature.[20]



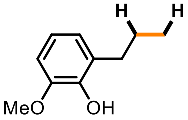
2d, 91%

1,2-Dimethoxy-4-propylbenzene **2d**. According to the **GP1**, using the alkene **1d** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **2d** (32.8 mg, 0.18 mmol, 91%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 6.0, 2.1 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.73 – 2.38 (m, 2H), 1.72 – 1.49 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 147.1, 135.4, 120.2, 111.9, 111.2, 55.9, 55.8, 37.7, 24.8, 13.8.

The NMR data were in agreement with those reported in the literature.[21]



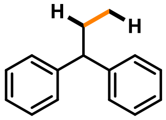
2e, 90%

2-Methoxy-6-propylphenol **2e**. According to the **GP1**, using the alkene **1e** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 5/1 to 3/1) to give **2e** (29.9 mg, 0.18 mmol, 90%) as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 – 6.64 (m, 3H), 5.68 (s, 1H), 3.89 (s, 3H), 2.72 – 2.54 (m, 2H), 1.75 – 1.56 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 146.3, 143.5, 128.5, 122.4, 119.1, 108.2, 56.0, 31.8, 22.9, 14.1.

The NMR data were in agreement with those reported in the literature.[21]



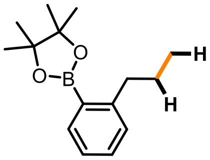
2f, 68%

Propane-1,1-diyldibenzene **2f**. According to the **GP1**, using the alkene **1f** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2f** (26.6$_5$ mg, 0.14 mmol, 68%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 8H), 7.25 (tdd, *J* = 7.1, 3.3, 1.7 Hz, 2H), 3.88 (t, *J* = 7.8 Hz, 1H), 2.16 (p, *J* = 7.4 Hz, 2H), 1.07 – 0.87 (m, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 145.2, 128.4, 128.0, 126.1, 53.3, 28.7, 12.9.

The NMR data were in agreement with those reported in the literature.[22]



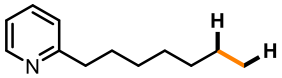
2g, 82%

4,4,5,5-Tetramethyl-2-(2-propylphenyl)-1,3,2-dioxaborolane **2g**. According to the **GP1**, using the alkene **1g** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2g** (40.3 mg, 0.16 mmol, 82%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.09 (ddd, *J* = 8.2, 5.3, 1.6 Hz, 2H), 2.83 – 2.71 (m, 2H), 1.49 (t, *J* = 7.6 Hz, 2H), 1.26 (s, 12H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 149.8, 136.0, 130.7, 129.2, 124.9, 83.4, 37.9, 26.6, 24.9, 14.1.

The NMR data were in agreement with those reported in the literature.[23]



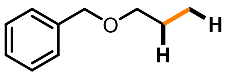
2h, 58%

2-Heptylpyridine **2h**. According to the **GP1**, using the alkene **1h** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2h** (20.5 mg, 0.12 mmol, 58%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.45 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.50 (td, *J* = 7.7, 1.9 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.04 – 6.98 (m, 1H), 2.81 – 2.54 (m, 2H), 1.65 (pd, *J* = 7.3, 3.6 Hz, 2H), 1.40 – 1.09 (m, 8H), 0.95 – 0.64 (m, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 162.6, 149.2, 136.2, 122.7, 120.8, 38.5, 31.8, 29.9, 29.4, 29.2, 22.6, 14.1.

The NMR data were in agreement with those reported in the literature.[24]



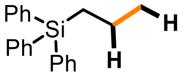
2i, 80%

(Propoxymethyl)benzene **2i**. According to the **GP1**, using the alkene **1i** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2i** (24.0 mg, 0.16 mmol, 80%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50 – 7.24 (m, 5H), 4.55 (s, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 1.69 (h, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 138.7, 128.4, 127.7, 127.5, 72.9, 72.2, 23.0, 10.7.

The NMR data were in agreement with those reported in the literature.[25]



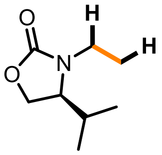
2j, 87%

Triphenyl(propyl)silane **2j**. According to the **GP1**, using the alkene **1j** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2j** (52.5 mg, 0.17 mmol, 87%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.42 (m, 6H), 7.31 – 7.24 (m, 9H), 1.48 – 1.37 (m, 2H), 1.32 – 1.25 (m, 2H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 135.7, 135.5, 129.4, 127.9, 18.6, 17.7, 16.0.

The NMR data were in agreement with those reported in the literature.[26]



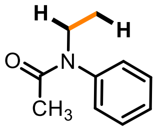
2k, 89%

(S)-3-Ethyl-4-isopropyloxazolidin-2-one **2k**. According to the **GP1**, using the alkene **1k** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 5/1) to give **2k** (27.9 mg, 0.18 mmol, 89%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 4.19 (t, *J* = 9.0 Hz, 1H), 4.04 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.76 (ddd, *J* = 9.2, 5.7, 3.6 Hz, 1H), 3.56 (dq, *J* = 14.7, 7.4 Hz, 1H), 3.03 (dq, *J* = 14.2, 7.0 Hz, 1H), 2.04 (ddq, *J* = 10.5, 6.9, 3.5 Hz, 1H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 158.3, 62.7, 58.7, 36.7, 27.6, 17.7, 14.3, 12.4.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_{15}NO_2Na$ 180.0995; found 180.0995.



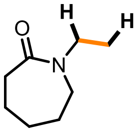
2l, 88%

N-Ethyl-N-phenylacetamide **2l**. According to the **GP1**, using the alkene **1l** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 5/1) to give **2l** (28.7 mg, 0.18 mmol, 88%) as a colorless solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.41 – 7.22 (m, 3H), 7.15 – 7.01 (m, 2H), 3.68 (q, *J* = 7.2 Hz, 2H), 1.76 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 170.3, 142.8, 129.7, 128.2, 127.9, 43.9, 22.8, 13.0.

The NMR data were in agreement with those reported in the literature.[27]



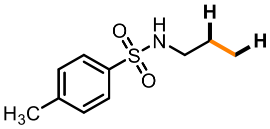
2m, 90%

1-Ethylazepan-2-one **2m**. According to the **GP1**, using the alkene **1m** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 5/1) to give **2m** (25.4 mg, 0.18 mmol, 90%) as a colorless solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 3.37 (q, *J* = 6.5 Hz, 2H), 3.34 – 3.25 (m, 2H), 2.54 – 2.40 (m, 2H), 1.73 – 1.52 (m, 6H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 175.8, 49.2, 43.0, 37.1, 30.0, 28.7, 23.3, 13.2.

The NMR data were in agreement with those reported in the literature.[28]

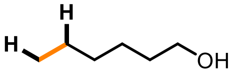


2n, 30%

4-Methyl-N-propylbenzenesulfonamide **2n**. According to the **GP1**, using the alkene **1n** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **2n** (12.8 mg, 0.06 mmol, 30%) as a colorless liquid along with the inseparably unreacted alkene **1n**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, 3H), 7.26 (d, *J* = 1.0 Hz, 2H), 4.60 (s, 1H), 2.89 (q, *J* = 6.8 Hz, 2H), 1.47 (h, *J* = 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

The NMR data were in agreement with those reported in the literature.[29]



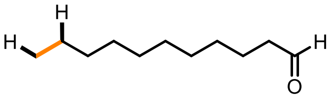
2o, 78%

Hexan-1-ol **2o**. According to the **GP1**, using the alkene **1o** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 20/1) to give **2o** (15.9 mg, 0.16 mmol, 78%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 – 3.55 (m, 2H), 1.59 (td, *J* = 15.2, 8.2 Hz, 3H), 1.45 – 1.19 (m, 6H), 1.07 – 0.77 (m, 3H).

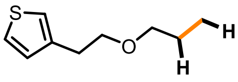
^{13}C NMR (76 MHz, $CDCl_3$) δ 63.0, 63.0, 32.8, 31.6, 25.4, 22.6, 14.0.

The NMR data were in agreement with those reported in the literature.[30]



2p, 71%

Undecanal **2p**. According to the **GP1**, using the alkene **1p** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The yield was determined by the GC with tetradecane as the internal standard (71%).



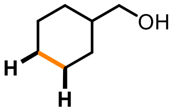
2q, 73%

3-(2-Propoxyethyl)thiophene **2q**. According to the **GP1**, using the alkene **1q** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **2q** (24.8 mg, 0.15 mmol, 73%) as a yellow liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.26 – 7.22 (m, 1H), 7.07 – 6.92 (m, 2H), 3.64 (t, *J* = 7.1 Hz, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 2.92 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.56 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 139.4, 128.6, 125.2, 121.1, 72.7, 71.0, 30.8, 22.9, 10.6.

The NMR data were in agreement with those reported in the literature.[31]



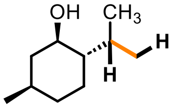
2r, 65%

Cyclohexylmethanol **2r**. According to the **GP1**, using the alkene **1r** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 20/1) to give **2r** (14.8 mg, 0.13 mmol, 65%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 3.43 (d, *J* = 6.3 Hz, 2H), 1.86 – 1.62 (m, 6H), 1.59 – 1.38 (m, 1H), 1.37 – 1.03 (m, 3H), 0.93 (qd, *J* = 12.4, 3.6 Hz, 2H).

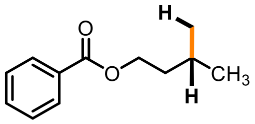
^{13}C NMR (76 MHz, CDCl$_3$) δ 68.7, 40.5, 29.6, 26.6, 25.8.

The NMR data were in agreement with those reported in the literature.[32]



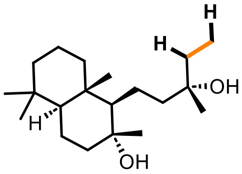
2s, 42%

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexan-1-ol **2s**. According to the **GP1**, using the alkene **1s** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The yield was determined by the GC with tetradecane as the internal standard (42%).



2t, 41%

Isopentyl benzoate **2t**. According to the **GP1**, using the alkene **1t** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The yield was determined by the GC with tetradecane as the internal standard (41%).



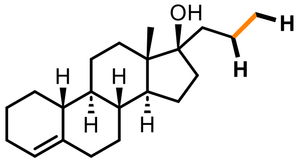
2u, 81%

(1R,2R,4aS,8aS)-1-((S)-3-Hydroxy-3-methylpentyl)-2,5,5,8a-tetramethyldecahydronaphthalen-2-ol **2u**. According to the **GP1**, using the alkene **1u** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **2u** (50.2 mg, 0.16 mmol, 81%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 2.34 (s, 2H), 1.83 (dt, *J* = 11.9, 3.1 Hz, 1H), 1.60 (tdd, *J* = 13.9, 7.3, 4.3 Hz, 4H), 1.52 – 1.35 (m, 6H), 1.35 – 1.20 (m, 3H), 1.14 (d, *J* = 7.6 Hz, 8H), 0.94 (t, *J* = 2.9 Hz, 1H), 0.89 (d, *J* = 7.4 Hz, 3H), 0.85 (d, *J* = 2.3 Hz, 4H), 0.78 (s, 3H), 0.77 (s, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 74.7, 73.4, 62.1, 56.1, 44.2, 44.1, 42.0, 39.7, 39.2, 35.8, 33.4, 33.2, 25.4, 24.3, 21.5, 20.5, 18.9, 18.5, 15.4, 8.3.

The NMR data were in agreement with those reported in the literature.[33]



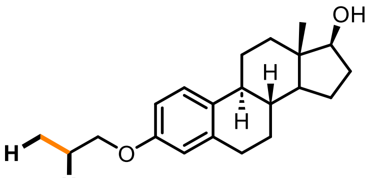
2v, 56%

(8R,9S,10R,13S,14S,17S)-13-Methyl-17-propyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-ol **2v.** According to the **GP1**, using the alkene **1v** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **2v** (33.8 mg, 0.11 mmol, 56%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 5.38 (s, 1H), 2.26 – 2.13 (m, 1H), 2.08 – 1.87 (m, 5H), 1.79 (td, *J* = 8.7, 2.2 Hz, 2H), 1.74 – 1.61 (m, 3H), 1.60 – 1.41 (m, 5H), 1.41 – 1.30 (m, 4H), 1.28 – 1.17 (m, 2H), 1.16 (d, *J* = 3.7 Hz, 1H), 1.13 – 1.00 (m, 3H), 0.99 – 0.87 (m, 7H).

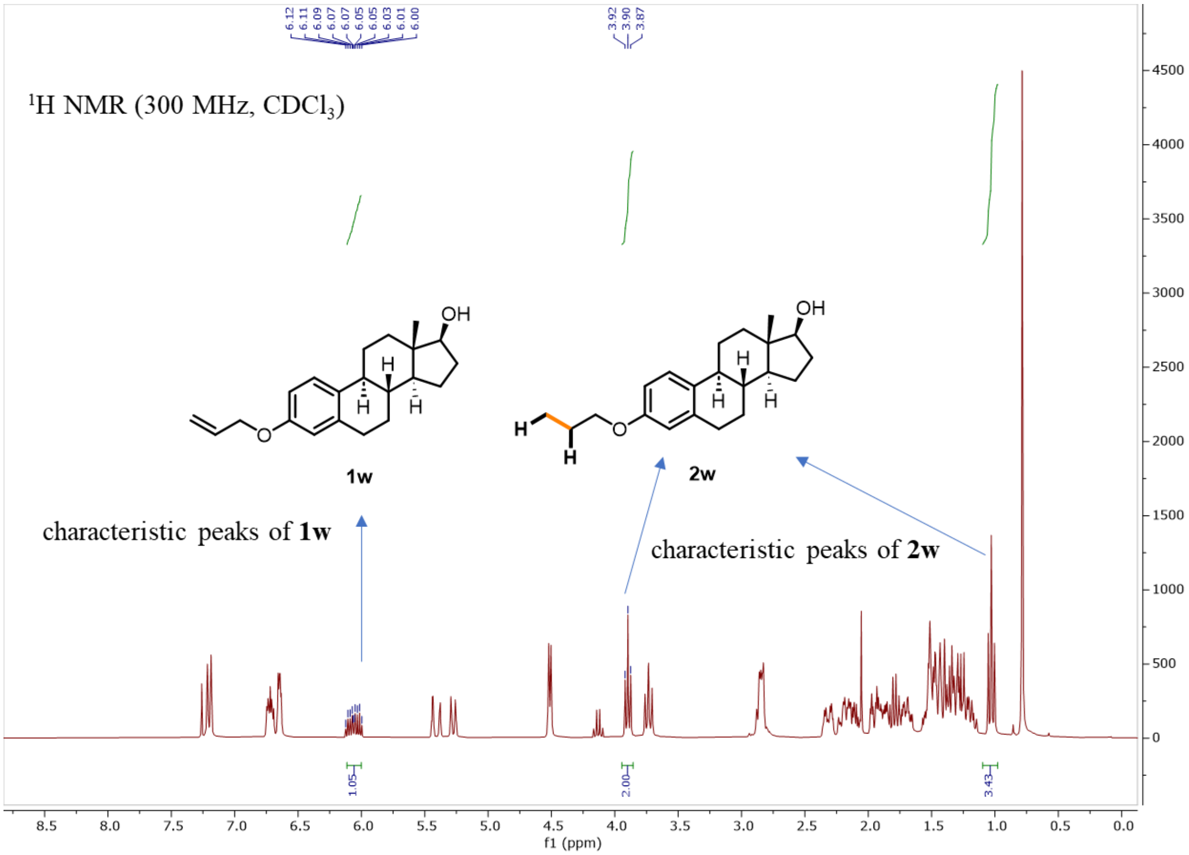
^{13}C NMR (76 MHz, $CDCl_3$) δ 140.7, 119.9, 86.6, 47.8, 46.9, 42.4, 42.3, 39.8, 37.1, 36.0, 34.8, 32.6, 30.3, 28.4, 26.6, 25.5, 22.0, 21.3, 17.2, 16.3, 15.0.

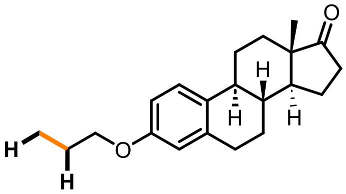
HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{34}ONa$ 325.2502; found 325.2502.



2w, 50%

(8R,9S,13S,17S)-13-Methyl-3-propoxy-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthre17ol **2w**. According to the **GP1**, using the alkene **1w** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The yield was determined by the ^{1}H NMR spectrum (50%, ^{1}H NMR yield) along with a small amount of inseparable alkene **1w**.





2x, 76%

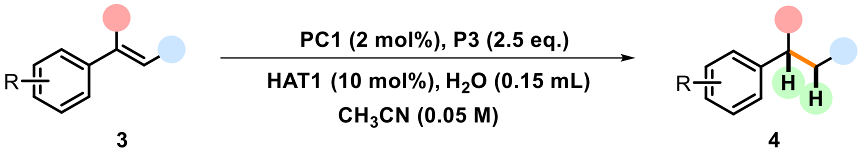
(8R,9S,13S,14S)-13-Methyl-3-propoxy-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one **2x**. According to the **GP1**, using the alkene **1x** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 5/1) to give **2x** (47.2 mg, 0.15 mmol, 76%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 3.90 (t, *J* = 6.6 Hz, 2H), 2.90 (dt, *J* = 8.4, 4.3 Hz, 2H), 2.58 – 2.46 (m, 1H), 2.40 (dp, *J* = 9.3, 2.6 Hz, 1H), 2.25 (t, *J* = 11.2 Hz, 1H), 2.18 – 1.92 (m, 4H), 1.87 – 1.73 (m, 2H), 1.69 – 1.36 (m, 6H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.92 (s, 3H).

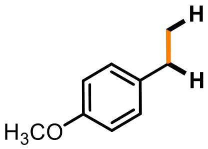
^{13}C NMR (76 MHz, $CDCl_3$) δ 221.0, 157.2, 137.7, 131.8, 126.3, 114.6, 112.1, 69.4, 50.4, 48.0, 44.0, 38.4, 35.9, 31.6, 29.7, 26.6, 26.0, 22.7, 21.6, 13.9, 10.6.

The NMR data were in agreement with those reported in the literature.[11]

4.2 Synthesis and characterization of products 4



General procedure (GP2) for the reduction of styrene derivates: To an oven dried Schlenk tube with a magnetic stirring bar, **P3** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the alkene **3** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.03 mmol, 0.15 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ºC using the standard set-up. After 48-72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane, pentane/EtOAc or pentane/Et_2O mixtures, as detailed in the individual entries), to afford the corresponding product **4**.



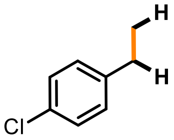
4a, 72%

1-Ethyl-4-methoxybenzene **4a**. According to the **GP2**, using the alkene **3a** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 48 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **4a** (19.6 mg, 0.14 mmol, 72%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.81 (d, *J* = 1.1 Hz, 3H), 2.62 (q, *J* = 7.7 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H).

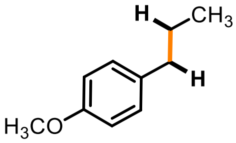
^{13}C NMR (76 MHz, CDCl$_3$) δ 157.7, 136.4, 128.7, 113.8, 55.3, 28.0, 16.0.

The NMR data were in agreement with those reported in the literature.[11]



4b, 72%

1-Chloro-4-ethylbenzene **4b**. According to the **GP2**, using the alkene **3b** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The yield was determined by the GC with tetradecane as the internal standard (72%).



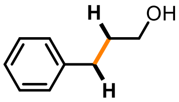
4c, 86%

1-Methoxy-4-propylbenzene **4c**. According to the **GP2**, using the alkene **3c** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 48 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **4c** (25.8 mg, 0.17 mmol, 86%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.12 – 7.05 (m, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.53 (dd, *J* = 8.5, 6.8 Hz, 2H), 1.67 – 1.55 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 157.7, 134.8, 129.3, 113.6, 55.3, 37.2, 24.8, 13.8.

The NMR data were in agreement with those reported in the literature.[11]



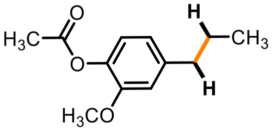
4d, 85%

3-Phenylpropan-1-ol **4d**. According to the **GP2**, using the alkene **3d** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 48 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **4d** (23.1 mg, 0.17 mmol, 85%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.16 – 7.08 (m, 3H), 3.61 (t, J = 6.4 Hz, 2H), 2.71 – 2.55 (m, 2H), 1.91 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 128.4, 128.4, 125.9, 62.3, 34.2, 32.1.

The NMR data were in agreement with those reported in the literature.[34]



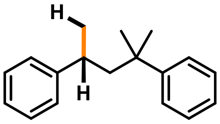
4e, 82%

2-Methoxy-4-propylphenyl acetate **4e**. According to the **GP2**, using the alkene **3e** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **4e** (34.1 mg, 0.16 mmol, 82%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (d, J = 8.0 Hz, 1H), 6.74 – 6.63 (m, 2H), 3.74 (s, 3H), 2.56 – 2.41 (m, 2H), 2.23 (s, 3H), 1.63 – 1.48 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 169.3, 150.7, 141.7, 137.6, 122.3, 120.5, 112.6, 55.8, 38.0, 24.6, 20.7, 13.9.

The NMR data were in agreement with those reported in the literature.[35]

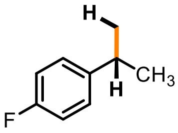


4f, 47%

(2-Methylpentane-2,4-diyl)dibenzene **4f**. According to the **GP2**, using the alkene **3f** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **4f** (22.37 mg, 0.094 mmol, 47%) as a colorless liquid along with the inseparable alkene **3f**.

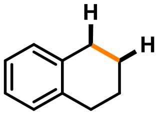
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 5H), 7.15 – 7.07 (m, 3H), 7.03 (dd, J = 8.2, 1.5 Hz, 2H), 2.55 (td, J = 7.1, 5.2 Hz, 1H), 2.07 (dd, J = 14.1, 7.0 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.26 (s, 3H), 1.16 (s, 3H), 1.04 (d, J = 7.1 Hz, 3H).

The NMR data were in agreement with those reported in the literature.[36]



4g, 77%

1-Fluoro-4-isopropylbenzene **4g**. According to the **GP2**, using the alkene **3g** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The yield was determined by the GC with tetradecane as the internal standard (77%).



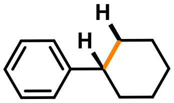
4h, 52%

1,2,3,4-Tetrahydronaphthalene **4h**. According to the **GP2**, using the alkene **3h** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 48 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **4h** (13.7 mg, 0.10 mmol, 52%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.15 (d, *J* = 2.0 Hz, 4H), 2.96 – 2.70 (m, 4H), 1.88 (dd, *J* = 4.9, 2.3 Hz, 4H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 137.2, 129.2, 125.5, 29.4, 23.3.

The NMR data were in agreement with those reported in the literature.[37]



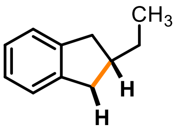
4i, 88%

Cyclohexylbenzene **4i**. According to the **GP2**, using the alkene **3i** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 48 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **4i** (28.2 mg, 0.18 mmol, 88%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.18 (m, 3H), 2.55 (td, *J* = 8.0, 3.9 Hz, 1H), 1.92 (qd, *J* = 9.8, 6.3 Hz, 4H), 1.85 – 1.75 (m, 1H), 1.47 (dq, *J* = 16.0, 11.9 Hz, 4H), 1.32 (td, *J* = 9.5, 4.8 Hz, 1H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 148.1, 128.3, 126.9, 125.8, 44.7, 34.5, 27.0, 26.2.

The NMR data were in agreement with those reported in the literature.[38]

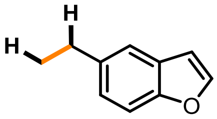


4j, 88%

2-Ethyl-2,3-dihydro-1H-indene **4j**. According to the **GP2**, using the alkene **3j** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 48 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **4j** (25.7 mg, 0.176 mmol, 88%) as a colorless liquid along with the inseparable 2,4,6-triisopropylbenzenethiol.

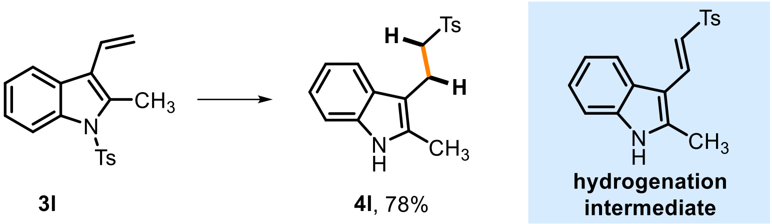
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 7.13 (dt, *J* = 5.0, 3.6 Hz, 2H), 3.05 (dd, *J* = 15.3, 7.9 Hz, 2H), 2.59 (dd, *J* = 15.5, 8.1 Hz, 2H), 2.37 (ddd, *J* = 15.4, 8.3, 7.3 Hz, 1H), 1.59 – 1.47 (m, 2H), 0.98 (d, *J* = 7.4 Hz, 4H).

The NMR data were in agreement with those reported in the literature.[39]



4k, 78%

5-Ethylbenzofuran **4k**. According to the **GP1**, using the alkene **3k** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The yield was determined by the GC with tetradecane as the internal standard (41%).



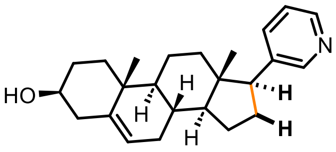
2-Methyl-3-(2-tosylethyl)-1H-indole **4l**. According to the **GP1**, using the alkene **3l** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1 to 1:1) to give **4l** (48.8 mg, 0.156 mmol, 78%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.68 (m, 3H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.13 – 6.99 (m, 2H), 3.39 – 3.23 (m, 2H), 3.23 – 3.04 (m, 2H), 2.45 (s, 3H), 2.32 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 144.6, 136.2, 135.2, 131.6, 129.9, 128.0, 127.7, 121.4, 119.5, 117.3, 110.4, 107.3, 56.3, 21.7, 17.7, 11.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{19}NO_2SNa$ 336.1029; found 336.1029.

Comment: The product was obtained through the hydrogenation of the photoisomerized intermediate of **3l**.[40,41]



4m, 93%, dr > 20 : 1

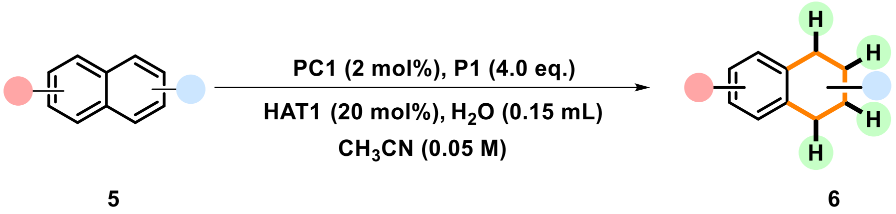
(3S,8S,9S,10R,13S,14S,17S)-10,13-Dimethyl-17-(pyridin-3-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol **4m**. According to the **GP2**, using the alkene **3m** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **4m** (65.3 mg, 0.19 mmol, 93%) as a colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.47 – 8.32 (m, 2H), 7.51 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.19 (dd, *J* = 7.9, 4.8 Hz, 1H), 5.45 – 5.22 (m, 1H), 3.67 – 3.39 (m, 1H), 2.65 (t, *J* = 9.8 Hz, 1H), 2.54 (s, 1H), 2.38 – 2.14 (m, 2H), 2.13 – 1.90 (m, 3H), 1.92 – 1.73 (m, 3H), 1.70 – 1.43 (m, 5H), 1.42 – 1.15 (m, 4H), 1.15 – 0.99 (m, 2H), 0.98 (s, 3H), 0.47 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 150.2, 147.3, 141.1, 136.4, 135.7, 122.8, 121.3, 71.5, 56.5, 54.4, 50.3, 44.3, 42.3, 37.4, 37.3, 36.6, 32.3, 31.9, 31.6, 25.9, 24.5, 20.7, 19.4, 12.6.

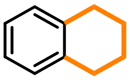
The NMR data were in agreement with those reported in the literature.[42]

4.3 Synthesis and characterization of products 6

Synthesis and characterization of products 6a-p



General procedure (GP3) for the reduction of naphthalene derivates: To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.8 mmol, 4.0 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the naphthalene **5** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane, pentane/EtOAc or pentane/Et_2O mixtures, as detailed in the individual entries), to afford the corresponding product **6**.



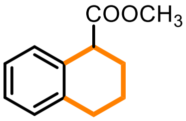
6a, 89%

1,2,3,4-Tetrahydronaphthalene **6a**. According to the **GP3**, using the alkene **5a** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **6a** (23.5 mg, 0.18 mmol, 89%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 2.0 Hz, 4H), 2.96 – 2.70 (m, 4H), 1.88 (dd, *J* = 4.9, 2.3 Hz, 4H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 137.2, 129.2, 125.5, 29.4, 23.3.

The NMR data were in agreement with those reported in the literature.[37]



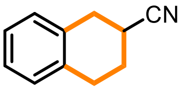
6b, 82%

Methyl 1,2,3,4-tetrahydronaphthalene-1-carboxylate **6b**. According to the **GP3**, using the alkene **5b** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 20/1) to give **6b** (31.2 mg, 0.16 mmol, 82%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.06 (m, 4H), 3.89 – 3.82 (m, 1H), 3.72 (s, 3H), 2.92 – 2.71 (m, 2H), 2.21 – 2.09 (m, 1H), 2.06 – 1.94 (m, 2H), 1.84 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 137.2, 133.3, 129.4, 129.3, 126.9, 125.8, 52.0, 44.8, 29.1, 26.7, 20.6.

The NMR data were in agreement with those reported in the literature.[43]



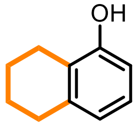
6c, 86%

1,2,3,4-Tetrahydronaphthalene-2-carbonitrile **6c**. According to the **GP3**, using the alkene **5c** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 20/1) to give **6c** (27.0 mg, 0.17 mmol, 86%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 6.94 (m, 4H), 3.04 (td, *J* = 16.7, 6.8 Hz, 2H), 2.96 – 2.86 (m, 2H), 2.77 (ddd, *J* = 17.4, 9.0, 6.1 Hz, 1H), 2.12 (dtdd, *J* = 11.9, 6.0, 3.2, 1.1 Hz, 1H), 2.08 – 1.88 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 132.3, 129.1, 129.0, 126.7, 126.3, 122.1, 32.4, 27.1, 26.3, 25.6.

The NMR data were in agreement with those reported in the literature.[44]



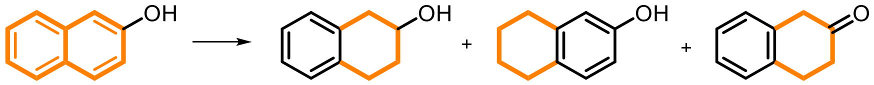
6d, 78%

5,6,7,8-Tetrahydronaphthalen-1-ol **6d**. According to the **GP3**, using the alkene **5d** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 5/1) to give **6d** (23.1 mg, 0.156 mmol, 78%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.10 – 6.95 (m, 1H), 6.74 (t, *J* = 6.2 Hz, 1H), 6.65 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.76 (s, 1H), 2.80 (t, *J* = 5.8 Hz, 2H), 2.67 (t, *J* = 5.9 Hz, 2H), 1.86 (tt, *J* = 10.6, 4.6 Hz, 4H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 153.4, 139.0, 126.0, 123.3, 121.6, 111.8, 29.6, 22.8, 22.8, 22.7.

The NMR data were in agreement with those reported in the literature.[45]



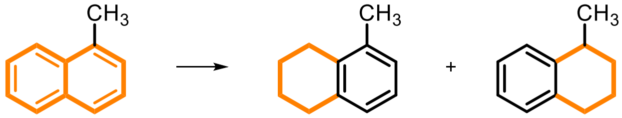
6e, 45% **6e'**, 20% **6e''**, 11%

1,2,3,4-Tetrahydronaphthalen-2-ol **6e**; 5,6,7,8-tetrahydronaphthalen-2-ol **6e'**; 3,4-dihydronaphthalen-2(1H)-one **6e''**. According to the **GP3**, using the alkene **5e** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **6e** (13.3 mg, 0.09 mmol, 45%) as a colorless liquid; **6e'** (5.9 mg, 0.040 mmol, 20%) as a colorless liquid; **6e''** (3.2 mg, 0.022 mmol, 11%) as a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$, **6e**) δ 7.11 (q, *J* = 3.1 Hz, 4H), 4.16 (dd, *J* = 9.4, 5.5 Hz, 1H), 3.17 – 3.05 (m, 1H), 3.03 – 2.84 (m, 2H), 2.78 (dd, *J* = 16.3, 7.7 Hz, 1H), 2.13 – 1.99 (m, 1H), 1.92 – 1.75 (m, 1H).

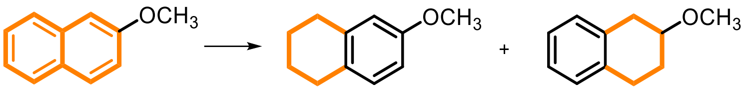
^{13}C NMR (101 MHz, CDCl$_3$, **6e**) δ 135.7, 134.2, 129.5, 128.6, 126.0, 125.9, 67.3, 38.4, 31.5, 27.0.

The NMR data were in agreement with those reported in the literature.[46]



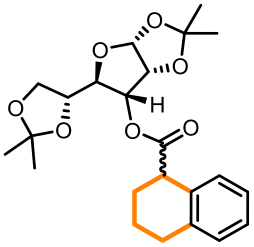
6f, 47% **6f'**, 23%

5-Methyl-1,2,3,4-tetrahydronaphthalene **6f**; 1-methyl-1,2,3,4-tetrahydronaphthalene **6f'**. According to the **GP3**, using the alkene **5f** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **6f** (13.7 mg, 0.094 mmol, 47%) as a colorless liquid; **6f'** (6.7 mg, 0.046 mmol, 23%) as a colorless liquid.



6g, 38% **6g'**, 24%

6-Methoxy-1,2,3,4-tetrahydronaphthalene **6g**; 2-methoxy-1,2,3,4-tetrahydronaphthalene **6g'**; According to the **GP3**, using the alkene **5g** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **6g** (12.3 mg, 0.076 mmol, 38%) as a colorless liquid; **6g'** (7.8 mg, 0.048 mmol, 24%) as a colorless liquid.



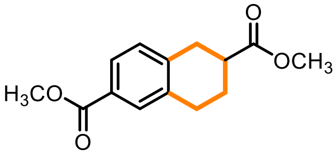
6h, 92%, dr 1:1

(3aR,5R,6R,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 1,2,3,4-tetrahydronaphthalene-1-carboxylate **6h**. According to the **GP3**, using the alkene **5h** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 5/1) to give **6h** (76.9 mg, 0.18 mmol, 92%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$, both diastereoisomers) δ 7.25 – 7.18 (m, 1H), 7.18 – 7.07 (m, 3H), 5.83 (dd, *J* = 3.8, 1.8 Hz, 1H), 4.88 (ddd, *J* = 5.9, 3.0, 1.3 Hz, 1H), 4.84 – 4.78 (m, 1H), 4.29 (td, *J* = 6.4, 4.0 Hz, 1H), 4.11 (dt, *J* = 8.5, 3.9 Hz, 1H), 4.03 – 3.95 (m, 1H), 3.89 (q, *J* = 5.6 Hz, 1H), 3.79 – 3.65 (m, 1H), 2.91 – 2.69 (m, 2H), 2.27 – 2.12 (m, 1H), 2.11 – 1.91 (m, 2H), 1.85 – 1.68 (m, 1H), 1.51 (d, *J* = 7.1 Hz, 3H), 1.38 (d, *J* = 7.3 Hz, 3H), 1.34 (d, *J* = 5.2 Hz, 6H).

^{13}C NMR (76 MHz, $CDCl_3$, both diastereoisomers) δ 174.1, 174.0, 137.2, 137.2, 132.9, 132.9, 130.0, 129.5, 129.4, 129.3, 126.9, 126.9, 125.8, 125.6, 112.9, 112.9, 110.0, 110.0, 104.3, 104.2, 77.7, 77.6, 77.5, 75.0, 74.8, 73.0, 72.8, 65.6, 65.4, 44.8, 44.7, 29.1, 29.1, 26.8, 26.8, 26.7, 26.6, 26.6, 26.2, 26.2, 25.1, 25.0, 20.6, 20.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{30}O_7Na$ 441.1884; found 441.1884.

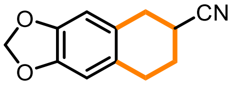


6i, 66%

Dimethyl 1,2,3,4-tetrahydronaphthalene-2,6-dicarboxylate **6i**. According to the **GP3**, using the alkene **5i** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6i** (32.7 mg, 0.13 mmol, 66%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.7 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H), 3.05 (d, *J* = 7.9 Hz, 2H), 2.89 (dt, *J* = 11.0, 5.7 Hz, 2H), 2.83 – 2.69 (m, 1H), 2.28 – 2.15 (m, 1H), 1.88 (qd, *J* = 10.7, 6.2 Hz, 1H).

The NMR data were in agreement with those reported in the literature.[47]



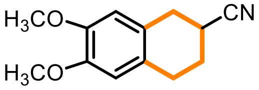
6j, 84%

5,6,7,8-Tetrahydronaphtho[2,3-d][1,3]dioxole-6-carbonitrile **6j**. According to the **GP3**, using the alkene **5j** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6j** (33.8 mg, 0.17 mmol, 84%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.55 (s, 1H), 6.52 (s, 1H), 5.89 (s, 2H), 3.05 – 2.81 (m, 4H), 2.81 – 2.66 (m, 1H), 2.13 (dtd, *J* = 11.8, 6.1, 2.9 Hz, 1H), 2.07 – 1.95 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 146.5, 146.2, 127.5, 125.0, 122.0, 108.7, 108.5, 100.9, 32.4, 27.1, 26.2, 25.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{11}NO_2Na$ 224.0682; found 224.0682.



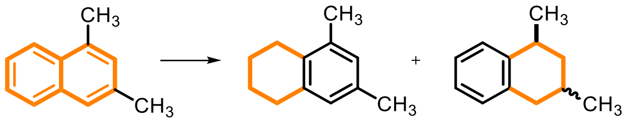
6k, 89%

6,7-Dimethoxy-1,2,3,4-tetrahydronaphthalene-2-carbonitrile **6k**. According to the **GP3**, using the alkene **5k** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6k** (38.6 mg, 0.18 mmol, 89%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (s, 1H), 6.54 (s, 1H), 3.84 (s, 6H), 3.06 – 2.84 (m, 4H), 2.85 – 2.71 (m, 1H), 2.21 – 2.09 (m, 1H), 2.10 – 1.94 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 147.9, 147.6, 126.4, 124.0, 122.1, 111.6, 111.5, 56.0, 55.9, 32.0, 26.6, 26.3, 25.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{15}NO_2Na$ 240.0995; found 240.0995.

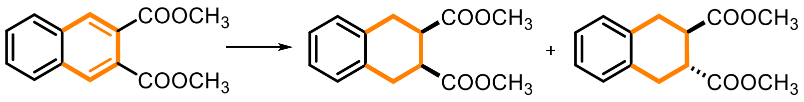


6l, 56% **6l'**, 26%, cis:trans 2:1

5,7-Dimethyl-1,2,3,4-tetrahydronaphthalene **6l**; 1,3-dimethyl-1,2,3,4-tetrahydronaphthalene **6l'**. According to the **GP3**, using the alkene **5l** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 120 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6l** (17.9 mg, 0.11 mmol, 56%) as a colorless liquid; give **6l'** (8.3 mg, 0.052 mmol, 26%) as a colorless liquid along with a small amount of inseparably unreacted **5l** and 2,4,6-triisopropylbenzenethiol.

^{1}H NMR (300 MHz, $CDCl_3$, **6l**) δ 6.84 (s, 1H), 6.79 (s, 1H), 2.76 (t, *J* = 6.1 Hz, 2H), 2.61 (t, *J* = 6.3 Hz, 2H), 2.28 (s, 3H), 2.21 (s, 3H), 1.82 (ddddd, *J* = 13.9, 12.3, 7.9, 4.8, 2.8 Hz, 4H).

The NMR data were in agreement with those reported in the literature.[48]



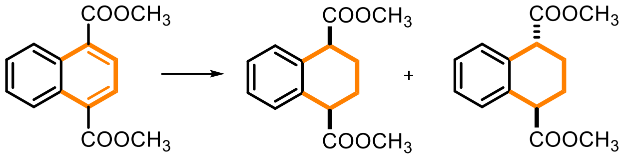
6m, 85% cis:trans 10:1

2-(λ^3-Methyl) 3-methyl 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate ***cis*-6m**; dimethyl 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate ***trans*-6m**. According to the **GP3**, using the alkene **5m** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6m** (42.2 mg, 0.17 mmol, 85%) as a colorless solid with inseparable 10:1 cis: trans mixture.

^{1}H NMR (300 MHz, $CDCl_3$, ***cis*-6m**) δ 7.12 (s, 4H), 3.69 (s, 6H), 3.36 – 3.19 (m, 4H), 3.18 – 3.02 (m, 2H).

^{13}C NMR (76 MHz, $CDCl_3$, ***cis*-6m**) δ 173.4, 133.8, 129.0, 126.1, 52.0, 40.5, 29.5.

The NMR data were in agreement with those reported in the literature.[49]



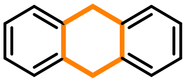
6n, 91% cis:trans 2:1

Dimethyl 1,2,3,4-tetrahydronaphthalene-1,4-dicarboxylate ***cis*-6n**; dimethyl (1R)-1,2,3,4-tetrahydronaphthalene-1,4-dicarboxylate ***trans*-6n**. According to the **GP3**, using the alkene **5n** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6n** (45.1 mg, 0.17 mmol, 91%) as a colorless solid with inseparable 2:1 cis: trans mixture.

^{1}H NMR (300 MHz, CDCl$_3$, ***cis*-6n** and ***trans*-6n**) δ 7.19 – 7.10 (m, 4H), 3.83 – 3.78 (m, 1H), 3.75 (t, *J* = 6.1 Hz, 1H), 3.64 (s, 6H), 2.33 – 2.19 (m, 1H), 2.19 – 2.09 (m, 1H), 2.05 (ddq, *J* = 9.1, 7.3, 2.3 Hz, 1H), 1.96 – 1.84 (m, 1H).

^{13}C NMR (76 MHz, CDCl$_3$, ***cis*-6n** and ***trans*-6n**) δ 174.9, 174.6, 133.4, 133.4, 129.8, 129.7, 127.2, 127.2, 52.2, 52.1, 44.7, 43.9, 24.1, 23.4.

HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{16}O_4Na$ 271.0941; found 271.0941.



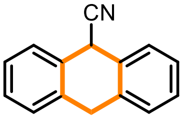
6o, 70%

9,10-Dihydroanthracene **6o**. According to the **GP3**, using the alkene **5o** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **6o** (25.2 mg, 0.14 mmol, 70%) as a colorless solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.43 – 7.31 (m, 4H), 7.32 – 7.15 (m, 4H), 4.00 (s, 4H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 136.7, 127.4, 126.1, 36.2.

The NMR data were in agreement with those reported in the literature.[50]



6p, 69%

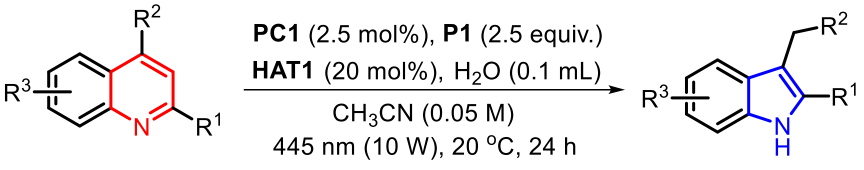
9,10-Dihydroanthracene-9-carbonitrile **6p**. According to the **GP3**, using the alkene **5p** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED irradiation. The crude residue was purified by chromatography (pentane) to give **6p** (28.3 mg, 0.14 mmol, 69%) as a colorless solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (ddd, *J* = 4.5, 3.7, 1.6 Hz, 2H), 7.40 – 7.30 (m, 6H), 5.04 (dd, *J* = 2.4, 1.1 Hz, 1H), 4.10 (d, *J* = 17.9 Hz, 1H), 3.93 (dd, *J* = 17.9, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 136.1, 130.8, 128.3, 128.0, 127.1, 126.6, 118.3, 37.1, 35.6.

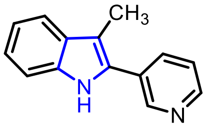
The NMR data were in agreement with those reported in the literature.[51]

Synthesis and characterization of products 6q-u



5q-u **6q-u**

General procedure (GP4) for the skeletal editing of quinoline derivates: To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.005 mmol, 2.5 mol%), deionized water (0.10 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the quinoline **5q-u** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 10 W 445 nm LED at 20 °C using the standard set-up. After 24 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane, pentane/EtOAc or pentane/Et_2O mixtures, as detailed in the individual entries), to afford the corresponding product **6q-u**.



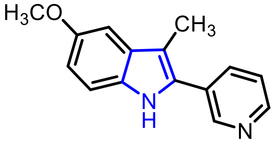
6q, 61%

3-Methyl-2-(pyridin-3-yl)-1*H*-indole **6q**. According to the **GP4**, using the alkene **5q** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 24 h under 10 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 1/1 to EtOAc) to give **6q** (25.4 mg, 0.12 mmol, 61%) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.3 Hz, 1H), 8.58 – 8.45 (m, 2H), 7.84 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.57 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.23 – 7.18 (m, 1H), 7.17 – 7.08 (m, 1H), 2.42 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 148.6, 148.0, 136.3, 134.9, 130.6, 129.7, 129.5, 123.7, 122.9, 119.8, 119.2, 111.0, 110.3, 9.6.

The NMR data were in agreement with those reported in the literature.[52]



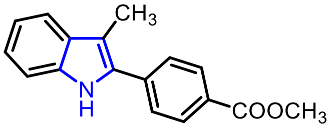
6r, 46%

5-Methoxy-3-methyl-2-(pyridin-3-yl)-1*H*-indole **6r**. According to the **GP4**, using the alkene **5r** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 10 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 1/1 to EtOAc) to give **6r** (21.9 mg, 0.09 mmol, 46%) as a white solid along with a small amount of inseparable unidentified byproduct.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.85 (d, *J* = 2.3 Hz, 1H), 8.58 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.20 (s, 1H), 7.87 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.40 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.90 (dt, *J* = 8.9, 2.5 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 154.3, 148.6, 148.1, 146.3, 134.8, 131.5, 130.2, 129.5, 123.6, 113.2, 111.7, 110.1, 100.8, 55.9, 9.7.

HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{15}N_2O$ 239.1179; found 239.1179.



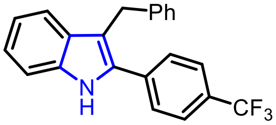
6s

Methyl 4-(3-methyl-1*H*-indol-2-yl)benzoate **6s**. According to the **GP4**, using the alkene **5s** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 24 h under 10 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6s** (27.0 mg, 0.10 mmol, 51%) as a white solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.19 – 8.08 (m, 3H), 7.69 – 7.60 (m, 3H), 7.39 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.20 – 7.12 (m, 1H), 3.96 (s, 3H), 2.51 (s, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 166.9, 137.8, 136.2, 132.8, 130.1, 130.0, 128.5, 127.2, 123.1, 119.8, 119.3, 110.9, 110.6, 52.2, 9.9.

The NMR data were in agreement with those reported in the literature.[53]



6t, 52%

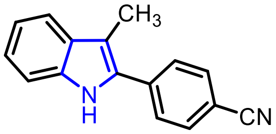
3-Benzyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indole **6t**. According to the **GP4**, using the alkene **5t** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 72 h under 5 W blue LED (455 nm) irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6t** (36.5 mg, 0.10 mmol, 52%) as a yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.08 (m, 6H), 7.02 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 4.20 (s, 2H).

^{19}F NMR (376 MHz, CDCl$_3$) δ -62.49.

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.0, 136.4, 136.4, 136.3, 133.7, 129.5, 128.6, 128.1, 127.9, 126.0, 125.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.1 Hz), 123.2, 120.2, 119.9, 112.7, 111.0, 30.4.

HRMS (ESI) m/z: [M - H]$^-$ Calcd for $C_{22}H_{15}F_3N$ 350.1162; found 350.1162.



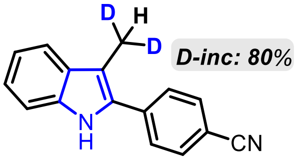
6u, 36%

4-(3-Methyl-1*H*-indol-2-yl)benzonitrile **6u**. According to the **GP4**, using the alkene **5u** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 24 h under 10 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6u** (16.7 mg, 0.07 mmol, 36%) as a white solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.07 (s, 1H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.63 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.40 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.18 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 2.50 (s, 3H).

^{13}C NMR (76 MHz, CDCl$_3$) δ 137.8, 136.4, 132.6, 131.8, 129.9, 127.8, 123.6, 120.1, 119.5, 118.9, 111.5, 111.0, 110.4, 10.0.

The NMR data were in agreement with those reported in the literature.[54]

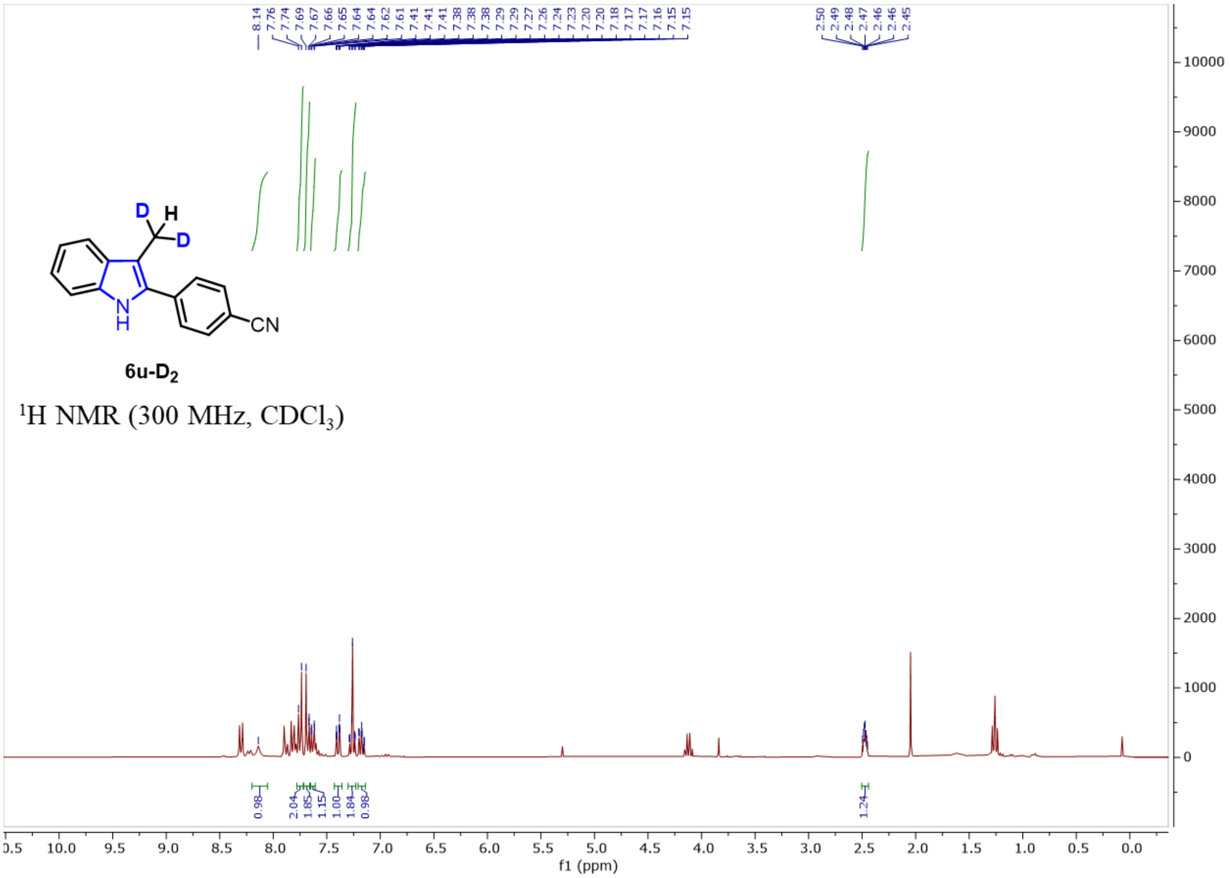


6u-D$_2$, 20%

4-(3-(Methyl-*d*$_2$)-1*H*-indol-2-yl)benzonitrile **6u-D$_2$**. According to the **GP4**, using the alkene **5u** (0.2 mmol, 1.0 equiv.) and stirring at room temperature for 24 h under 10 W blue LED irradiation. The crude residue was purified by chromatography (pentane/EtOAc 10/1) to give **6u-D$_2$** (9.4 mg, 0.04 mmol, 20%) as a white solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.14 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.39 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.17 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 2.47 (tt, *J* = 4.4, 2.4 Hz, 1H, 2D).

HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{10}D_2N_2Na$ 257.1018; found 257.1018.



6u-D$_2$

^{1}H NMR (300 MHz, CDCl$_3$)

The amount of D-incorporation was determined by HR-MS (ESI) analysis:

WWU
MÜNSTER

Organisch-Chemisches Institut
Abteilung Massenspektrometrie
Corrensstraße 40
48149 Münster

0251-83-33 299

LabelChecker Results

Formula:	C16 H12 N2 Na
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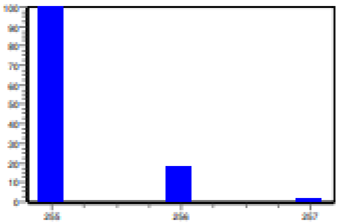

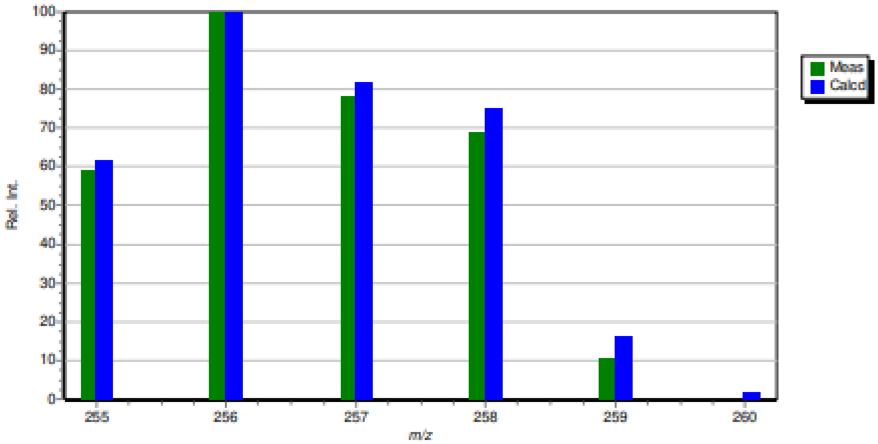

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Deuterium: 4-fold [%]: 4,89 1,54
Deuterium: 5-fold [%]: 0,00 0,00
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Label Atom Sum: 1,50 (12,48%)

Isotope list used for fitting data:

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257,10  3662020
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258,11  290223
258,28  3217597
259,08  239612
259,11  55004
259,28  498750
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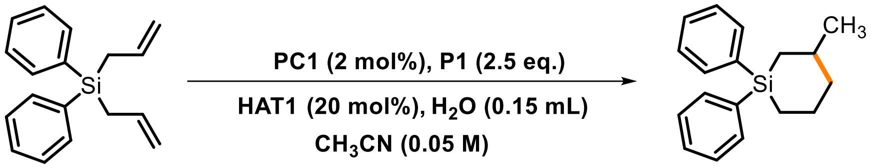
Citation of UMC software in scientific publications: The computer software UMC (Universal Mass Calculator) was used to (e.g. simulate isotope patterns, evaluate the degree of deuteration/labeling, evaluate elemental compositions). UMC Version 3.11.0.71, Dr. Matthias C. Letzel, WWU Münster, Org.-Chem. Institut, Germany. https://www.uni-muenster.de/Chemie.oc/ms/downloads.html

5. Radical cyclization and ring-opening experiments

5.1 Radical cyclization experiments



7

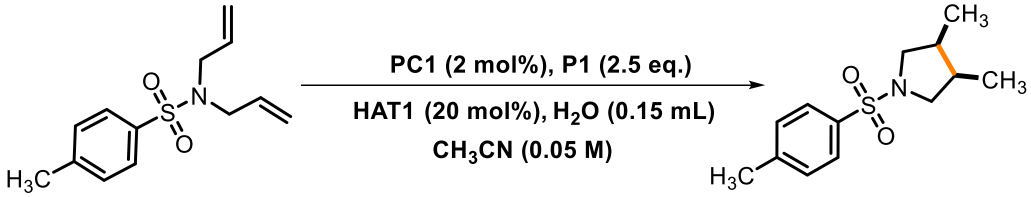
8, 91%

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **7** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane) to afford the product **8** (48.4 mg, 0.18 mmol, 91%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.48 – 7.43 (m, 2H), 7.43 – 7.37 (m, 3H), 7.35 – 7.29 (m, 3H), 2.15 – 2.03 (m, 1H), 1.71 (tdt, *J* = 13.5, 6.2, 2.9 Hz, 2H), 1.58 – 1.48 (m, 1H), 1.48 – 1.35 (m, 2H), 1.05 (d, *J* = 6.4 Hz, 4H), 0.90 (td, *J* = 14.4, 5.3 Hz, 1H), 0.74 (dd, *J* = 14.5, 12.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 135.8, 134.8, 134.3, 129.2, 129.1, 128.0, 127.8, 38.4, 31.5, 27.7, 23.7, 20.9, 10.7.

The NMR data were in agreement with those reported in the literature.[55]



9

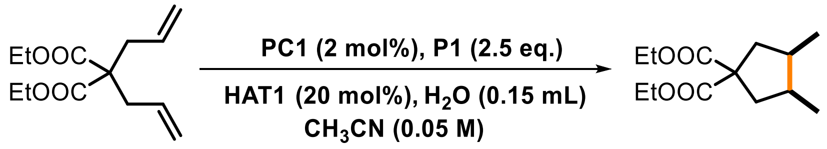
10, 62%, cis:trans 12:1

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **9** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane/EtOAc 5/1) to afford the product **10** (31.4 mg, 0.12 mmol, 62%) as a colorless solid with inseparable 12:1 cis: trans mixture.

^{1}H NMR (400 MHz, $CDCl_3$, ***cis*-10**) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.37 (dd, *J* = 9.7, 6.7 Hz, 2H), 2.95 (dd, *J* = 9.7, 5.7 Hz, 2H), 2.43 (s, 3H), 2.19 – 2.05 (m, 2H), 0.76 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, ***cis*-10**) δ 143.2, 134.3, 129.5, 127.4, 53.9, 36.2, 21.5, 12.9.

The NMR data were in agreement with those reported in the literature.[56]



11

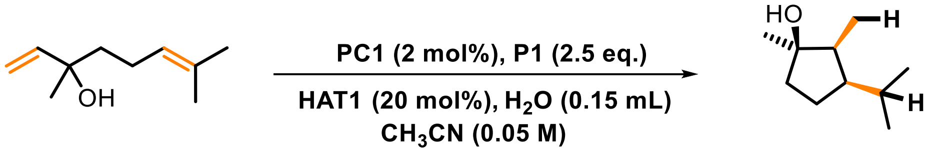
12, 87%, cis:trans 9:1

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **11** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane/EtOAc 50/1) to afford the product **12** (42.1 mg, 0.17 mmol, 87%) as a colorless liquid with inseparable 9:1 cis: trans mixture.

^{1}H NMR (300 MHz, $CDCl_3$, ***cis*-12**) δ 4.15 (qd, *J* = 7.1, 1.3 Hz, 4H), 2.37 (dd, *J* = 13.3, 6.8 Hz, 2H), 2.14 – 2.00 (m, 2H), 1.93 (dd, *J* = 13.5, 6.9 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 6H), 0.85 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (76 MHz, $CDCl_3$, ***cis*-12**) δ 173.1, 172.9, 61.2, 61.2, 59.2, 41.0, 36.8, 14.9, 14.0.

The NMR spectra data were in agreement with those reported in the literature.[57]



13

14, 43%, all cis

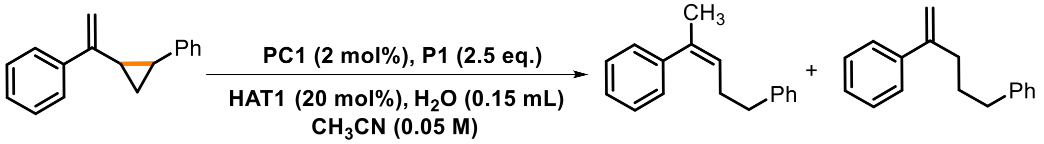
To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **13** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 120 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane/EtOAc 50/1) to afford the product **14** (13.4 mg, 0.086 mmol, 43%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 – 1.70 (m, 2H), 1.70 – 1.64 (m, 2H), 1.62 – 1.52 (m, 2H), 1.51 – 1.34 (m, 2H), 1.32 (s, 3H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.85 (dd, *J* = 6.8, 1.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 80.4, 49.2, 45.2, 37.8, 30.0, 29.8, 25.6, 21.9, 21.4, 8.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{20}ONa$ 179.1406; found 179.1406.

5.2 Cycle-opening experiment

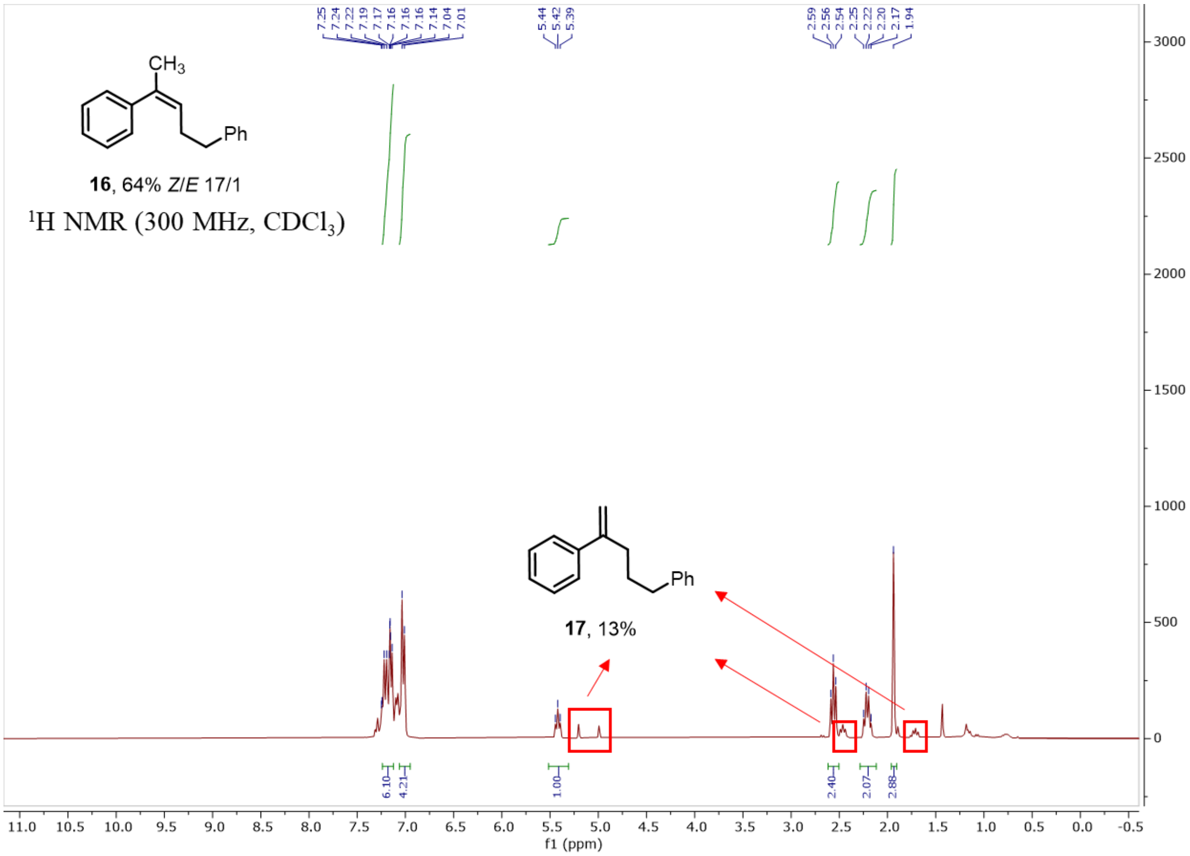


15 **16**, 64% *Z*/*E* 17/1 **17**, 13%

To an oven dried Schlenk tube with a magnetic stirring bar, **P3** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **15** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.02 mmol, 0.1 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane to pentane/EtOAc 50/1) to afford the product **16** (28.4 mg, 0.13 mmol, 64%) as a colorless liquid along with a small amount of **17**[58] (13% yield, inseparable).

^{1}H NMR (300 MHz, $CDCl_3$, ***Z*-16**) δ 7.24 – 7.12 (m, 6H), 7.02 (d, *J* = 7.6 Hz, 4H), 5.42 (t, *J* = 7.4 Hz, 1H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.21 (q, *J* = 7.7 Hz, 2H), 1.94 (s, 3H).

The NMR spectra data were in agreement with those reported in the literature.[59]

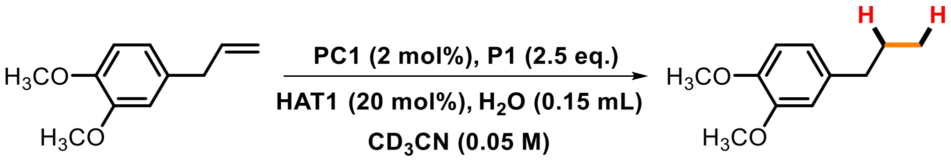


16, 64% *Z*/*E* 17/1

^{1}H NMR (300 MHz, CDCl$_3$)

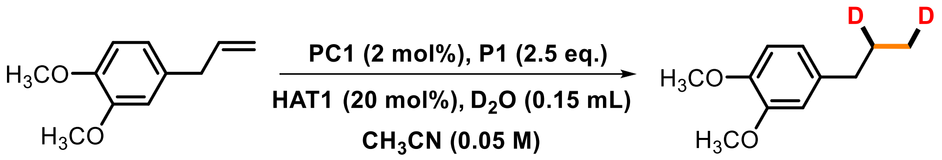
17, 13%

6. Deuteration experiments with CD_3CN and D_2O as hydrogen source



1d **2d**, 90%

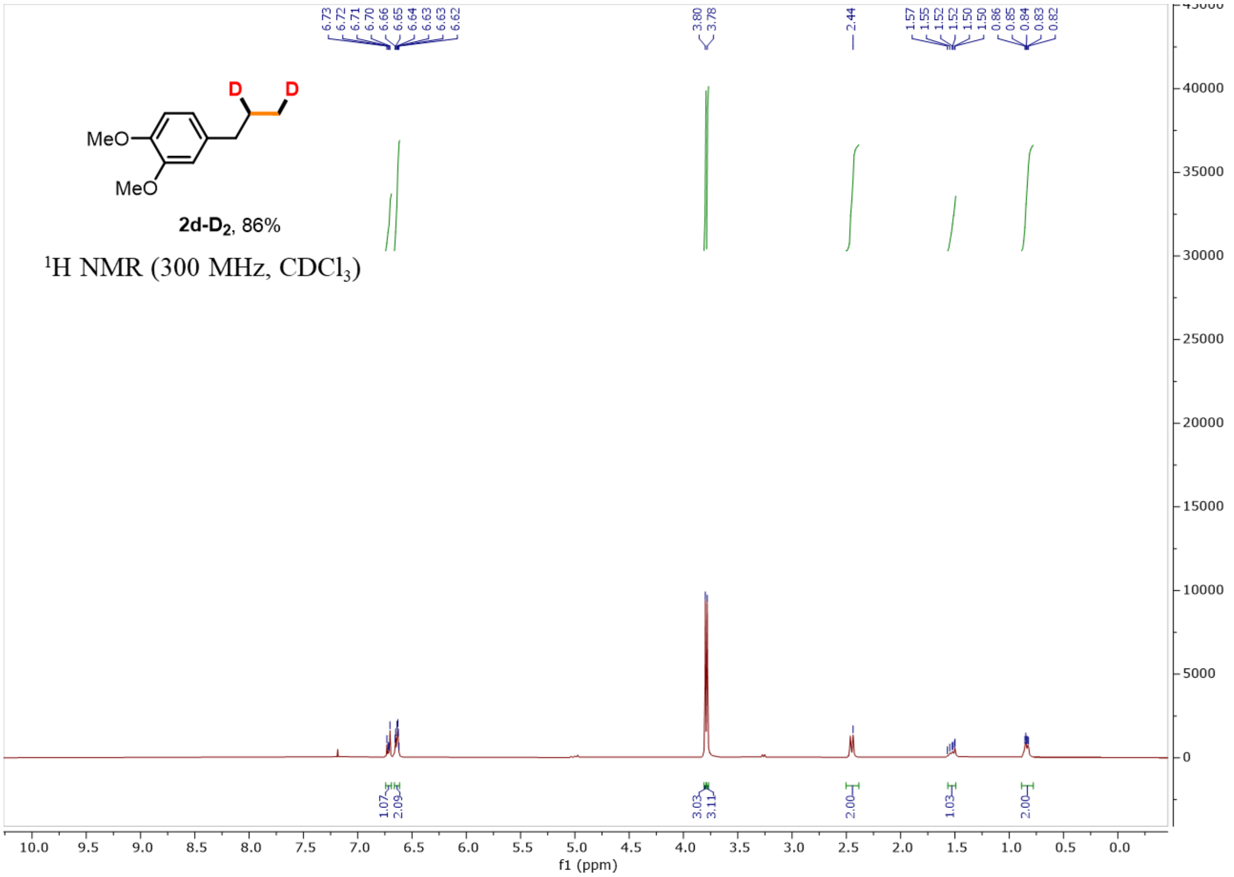
To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), deionized water (0.15 mL) and CD_3CN (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **1d** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane to pentane/EtOAc 10/1) to afford the product **2d** (32.4 mg, 0.18 mmol, 90%) as a colorless liquid.



1d **2d-D^2**, 86%

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), D_2O (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **1d** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 120 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane to pentane/EtOAc 10/1) to afford the product **2d-D^2** (31.3 mg, 0.17 mmol, 86%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (d, J = 8.6 Hz, 1H), 6.64 (dq, J = 3.1, 1.9 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.44 (s, 2H), 1.58 – 1.49 (m, 1H, 1D), 0.89 – 0.77 (m, 2H, 1D).



The amount of D-incorporation was determined by HR-MS (ESI) analysis:

Organisch-Chemisches Institut
Abteilung Massenspektrometrie
Corrensstraße 40
48149 Münster

0251-83-33 299

LabelChecker Results

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Difference Value: 0,000115
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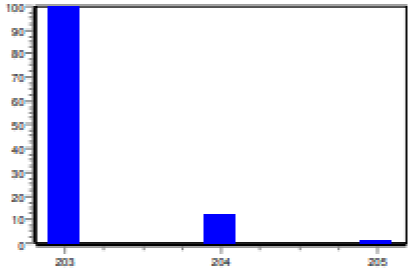

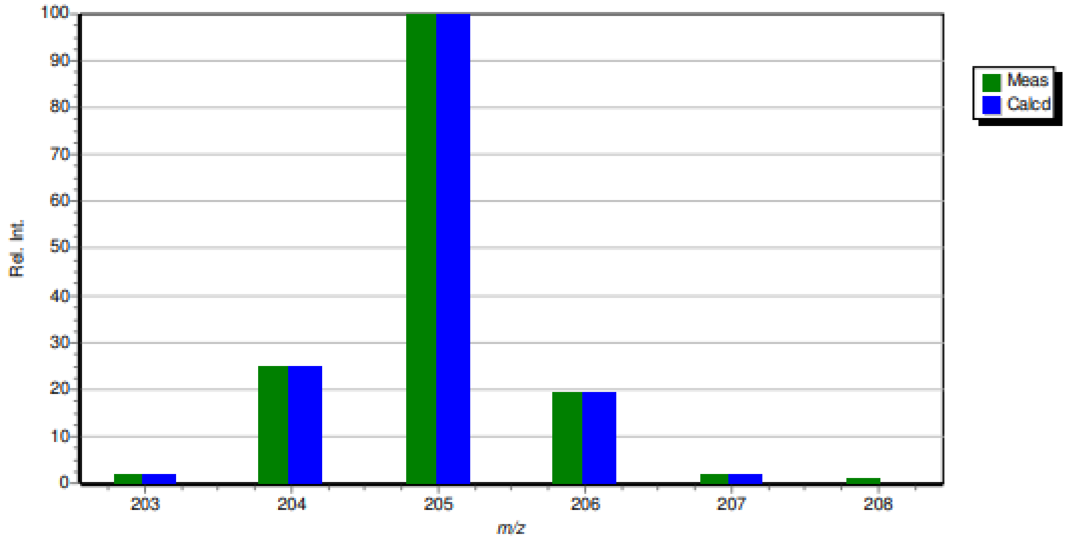

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205,12	781893591
205,19	61842
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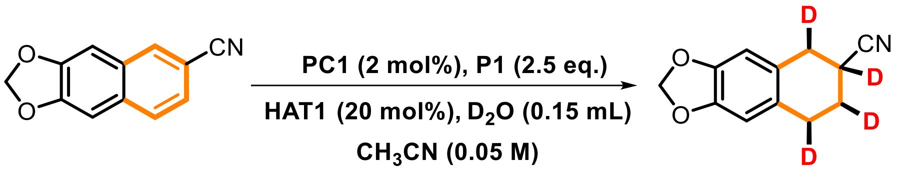
207,13	13015988
208,13	9254309

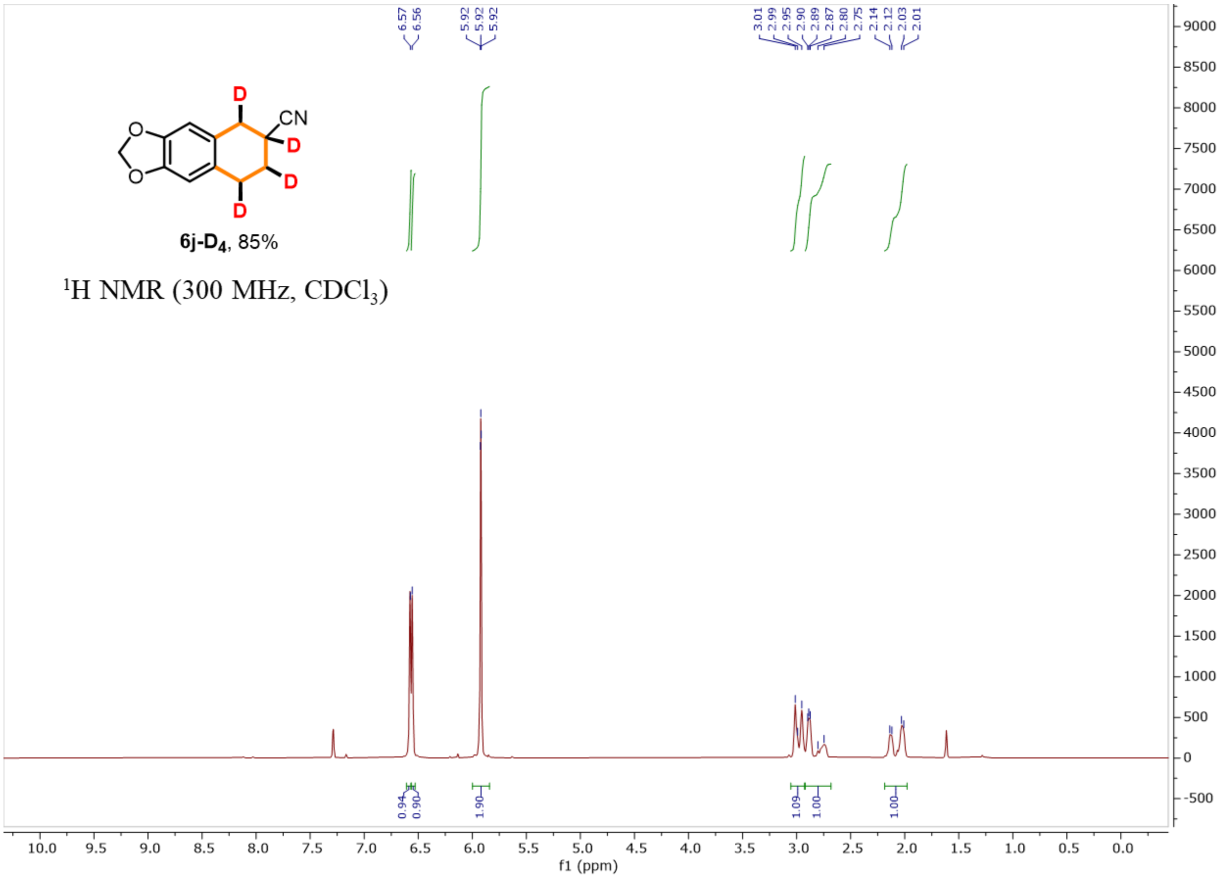
Citation of UMC software in scientific publications: The computer software UMC (Universal Mass Calculator) was used to (e.g. simulate isotope patterns, evaluate the degree of deuteration/labelling, evaluate elemental compositions). UMC Version 3.11.0.71, Dr. Matthias C. Letzel, WWU Münster, Org.-Chem. Institut, Germany. https://www.uni-muenster.de/Chemie.oc/ms/downloads.html



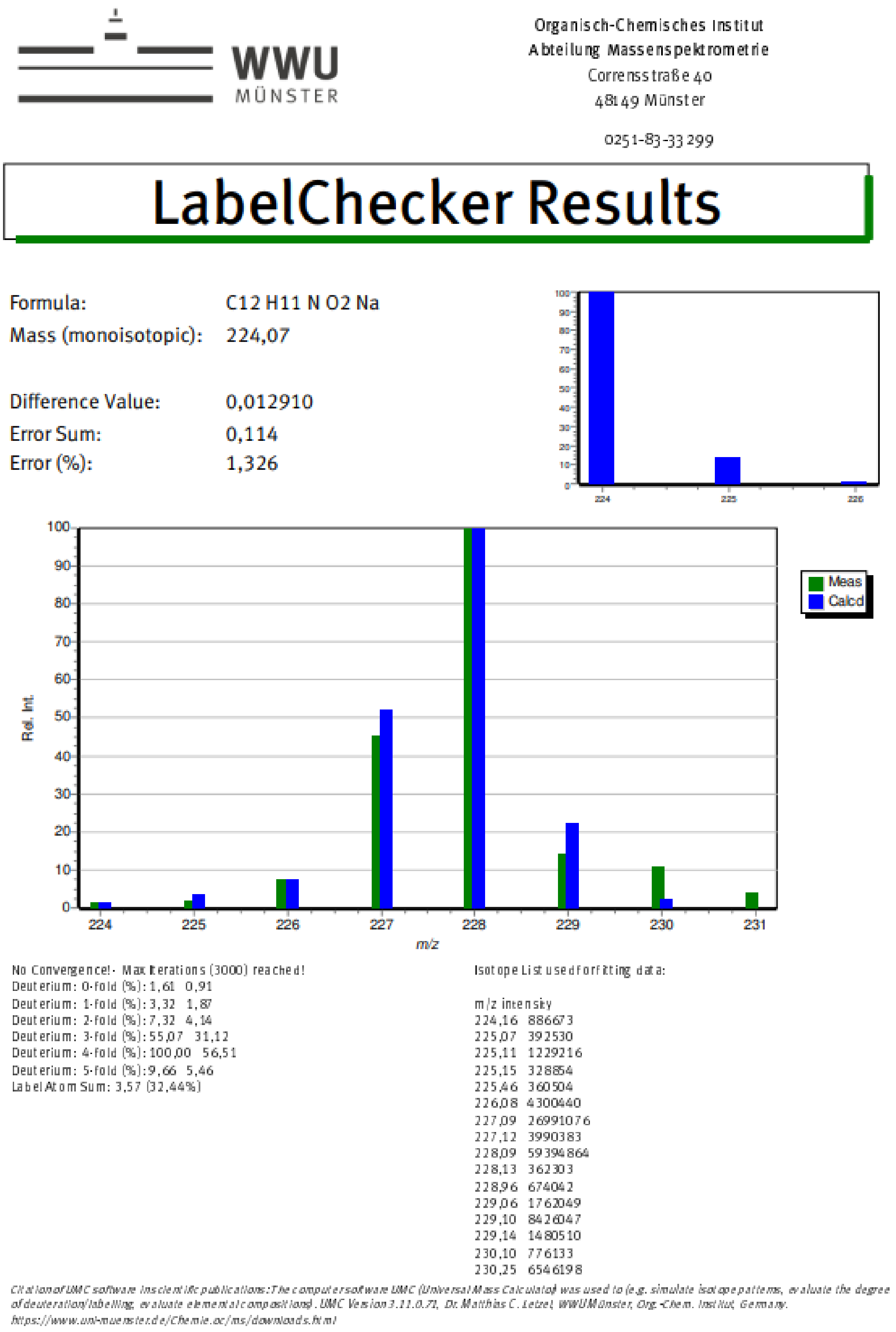
5j **6j-D$_4$**, 85%

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), D_2O (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **5j** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ºC using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane to pentane/EtOAc 10/1) to afford the product **6j-D$_4$** (34.9 mg, 0.17 mmol, 85%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (s, 1H), 6.46 (s, 1H), 5.82 (s, 2H), 2.97 – 2.87 (m, 1H, 1D), 2.86 – 2.77 (m, 1H, 1D), 2.06 – 1.92 (m, 1H, 1D).



The amount of D-incorporation was determined by HR-MS (ESI) analysis:



Organisch-Chemisches Institut
Abteilung Massenspektrometrie
Corrensstraße 40
48149 Münster

0251-83-33 299

LabelChecker Results

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Error (%):	1,326

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Deuterium: 5-fold (%): 9,66  5,46
Label Atom Sum: 3,57 (32,44%)
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Isotope List used for fitting data:

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227,12  3990383
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228,13  362303
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229,06  1762049
229,10  8426047
229,14  1480510
230,10  776133
230,25  6546198
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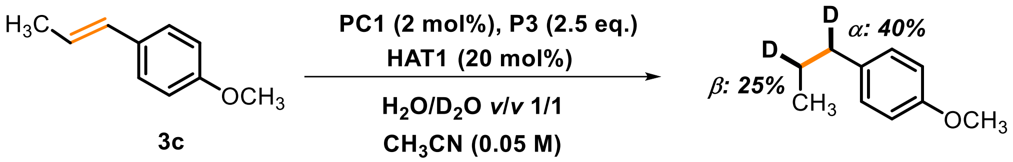
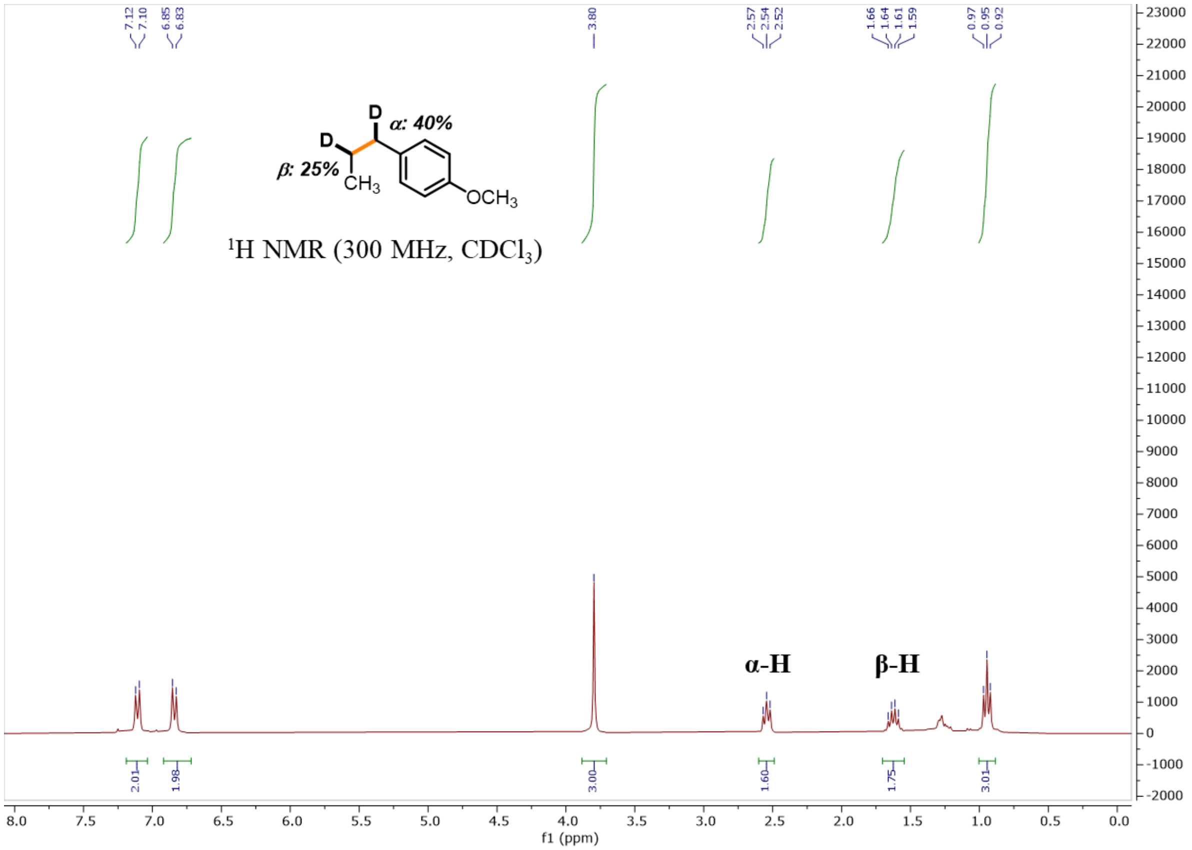
Citation of UMC software in scientific publications: The computer software UMC (Universal Mass Calculator) was used to (e.g. simulate isotope patterns, evaluate the degree of deuteration/labelling, evaluate elemental compositions). UMC Version 3.11.0.71, Dr. Matthias C. Letzel, WWU Münster, Org.-Chem. Institut, Germany. https://www.uni-muenster.de/Chemie.oc/ms/downloads.html

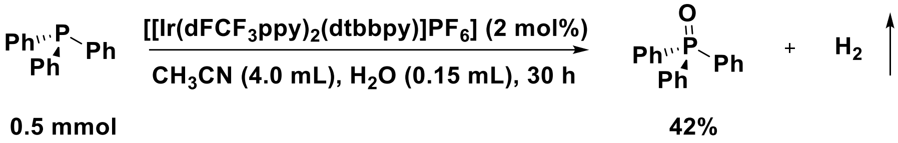


To an oven dried Schlenk tube with a magnetic stirring bar, **P3** (0.5 mmol, 2.5 equiv.), **PC1** (0.004 mmol, 2 mol%), D_2O (0.10 mL), H_2O (0.10 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **3c** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 72 hours, the irradiation was stopped. The volatiles were removed in vacuo, then the crude residue was purified by flash column chromatography on silica (pentane to pentane/EtOAc 10/1) to afford the product **3c-D$_2$** (26.7 mg, 0.18 mmol, 89%) as a colorless liquid. The deuterium ratio of *α*- and *β*-positions of the product **3c-D$_2$** was analyzed by ^{1}H NMR spectrum.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 3.80 (s, 3H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.63 (q, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).



7. Detection of hydrogen gas H_2



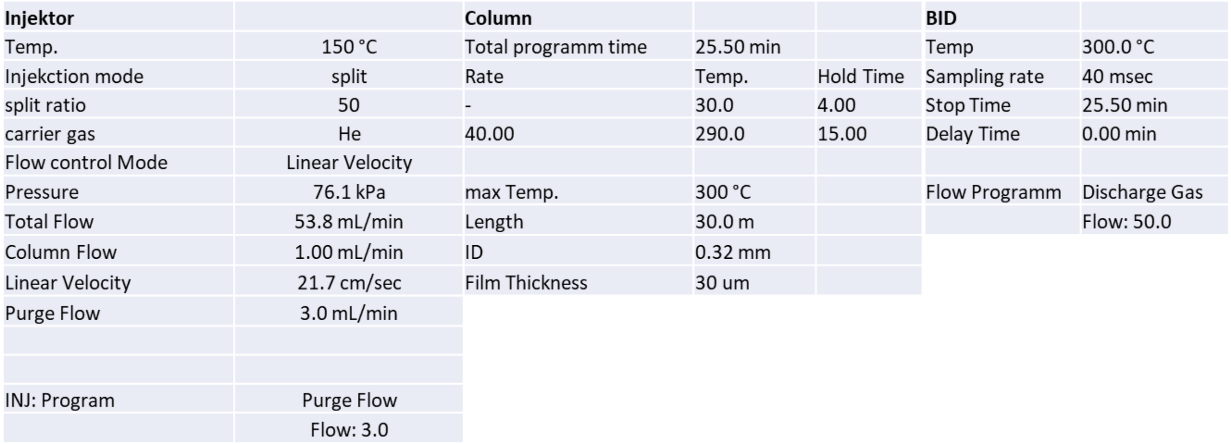
To an oven dried Schlenk tube with a magnetic stirring bar, triphenyl phosphine PPh_3 (0.5 mmol), **PC1** (0.01 mmol, 2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ^{o}C using the standard set-up. After 30 hours, the irradiation was stopped. The mixture was analyzed by GC (0.014 ± 0.00045 mmol of hydrogen gas in the gas phase). Then, 10 mL of $CDCl_3$ was added and the mixture was continued to be analyzed by ^{1}H NMR and ^{31}P NMR (0.21 mmol).

Comments: No hydrogen gas was detected without either PPh_3 or H_2O, indicating that both components were involved in generation of hydrogen gas.

Detected by GC:

1) Method

Table S6. The method for detection of hydrogen gas H_2.



Injektor		**Column**			**BID**	
Temp.	150 °C	Total programm time	25.50 min		Temp	300.0 °C
Injekction mode	split	Rate	Temp.	Hold Time	Sampling rate	40 msec
split ratio	50	-	30.0	4.00	Stop Time	25.50 min
carrier gas	He	40.00	290.0	15.00	Delay Time	0.00 min
Flow control Mode	Linear Velocity					
Pressure	76.1 kPa	max Temp.	300 °C		Flow Programm	Discharge Gas
Total Flow	53.8 mL/min	Length	30.0 m			Flow: 50.0
Column Flow	1.00 mL/min	ID	0.32 mm			
Linear Velocity	21.7 cm/sec	Film Thickness	30 um			
Purge Flow	3.0 mL/min					
INJ: Program	Purge Flow					
	Flow: 3.0					

2) GC spectrum

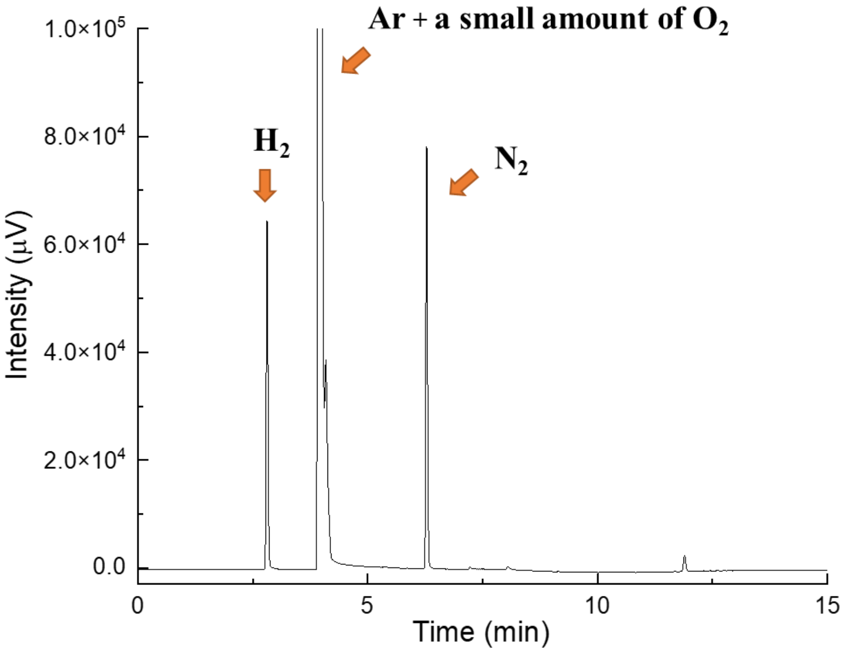
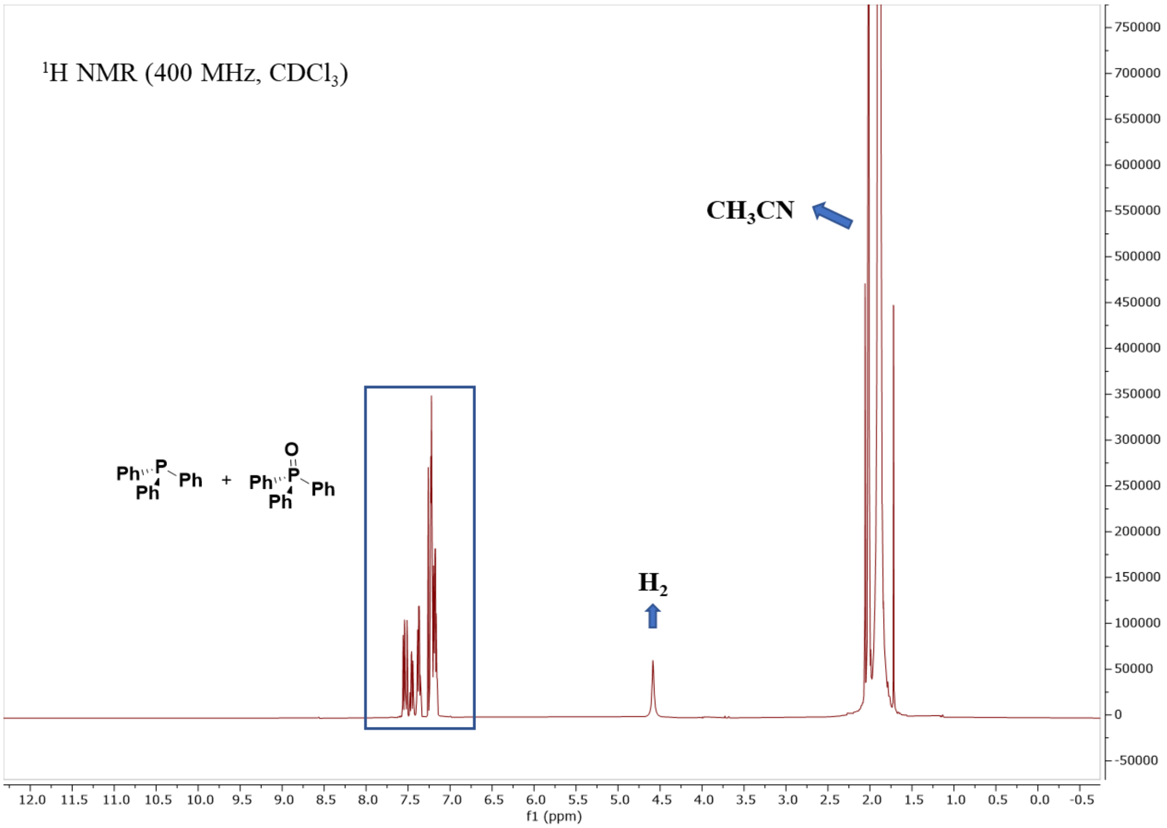


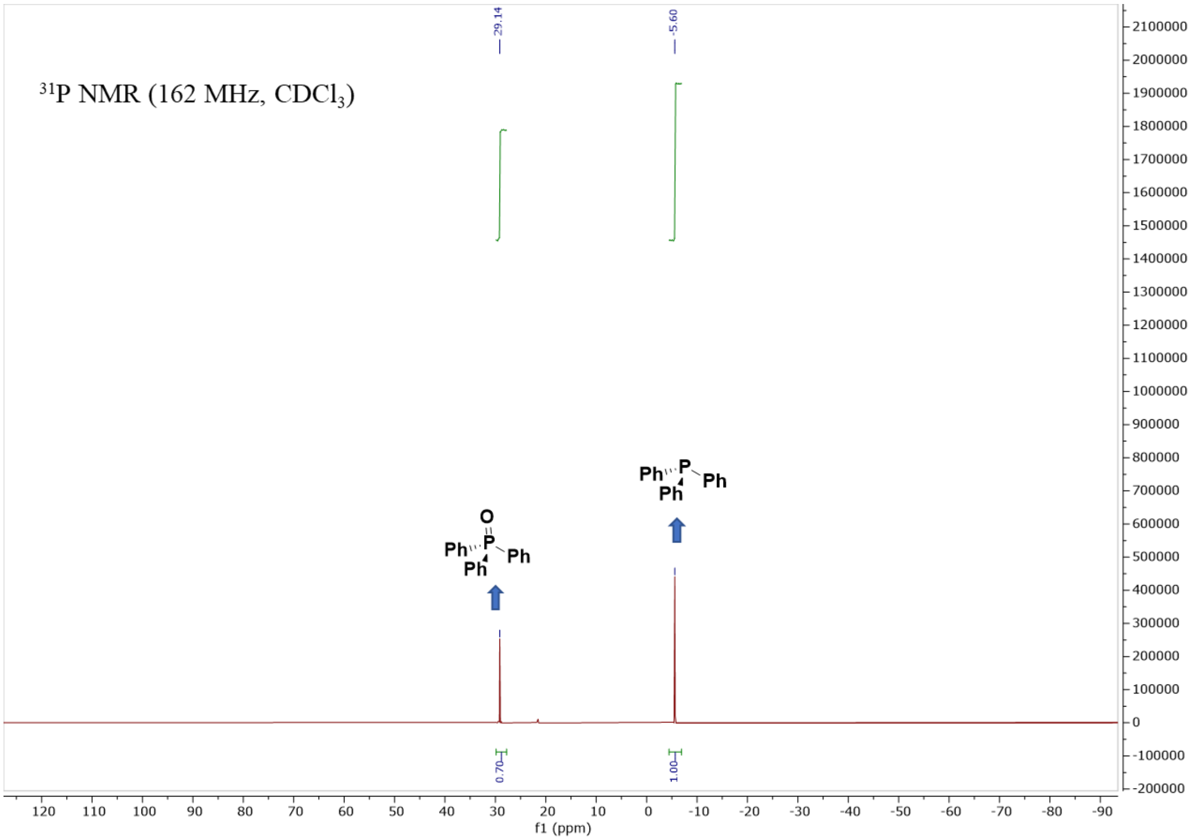
Figure S2. The GC sprctrum for detection of hydrogen gas H_2.

Detected by NMR:

1) ^{1}H NMR



2) ^{31}P NMR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1.00
O
P
Ph
Ph
Ph
P
Ph
Ph
Ph
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2000000
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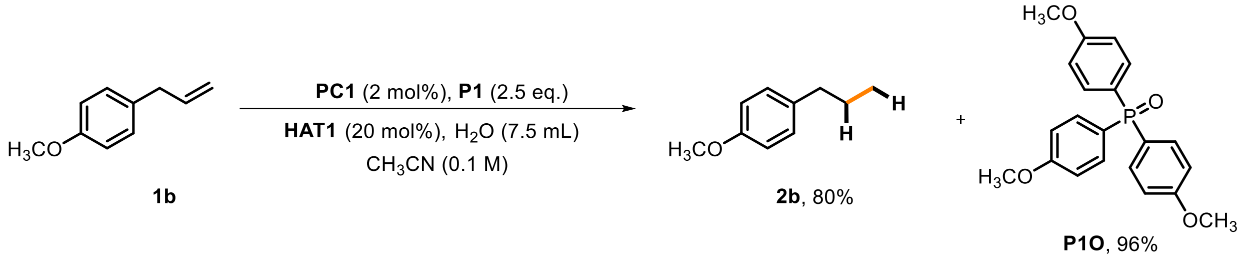
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

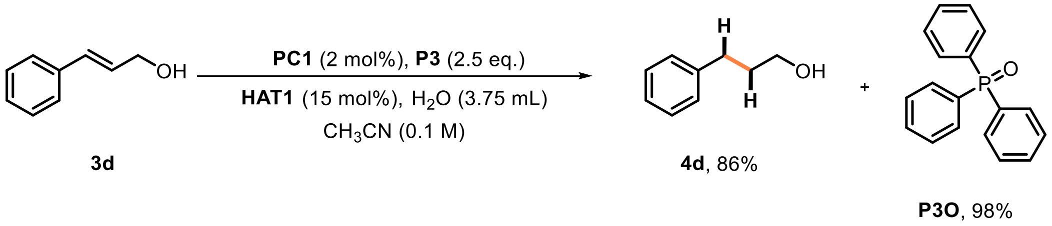
8. Gram-scale experiments and recycle of phosphine oxides

2b:



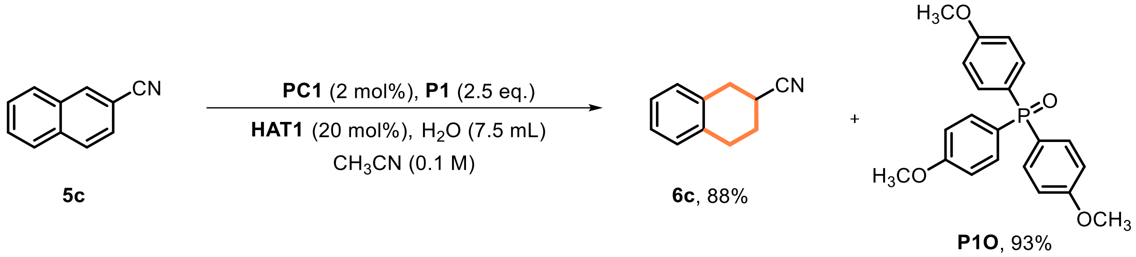
To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (2.5 equiv.), **PC1** (2 mol%), deionized water (7.5 mL) and acetonitrile (100.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **1b** (10.0 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (2.0 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with two Kessil PR160L (40 W, 456 nm) lights at 20 ºC using the standard set-up. After 72 hours, the irradiation was stopped. Hydrogen peroxide was added to oxide the remaining **P1** to the corresponding phosphine oxide. Then poured onto H_2O and extracted with EtOAc (3 × 100 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. Purification of the resulting crude residue via silica gel flash chromatography (pentane) to afford the product **2b** (1.20 g, 80%) and phosphine oxide (**P1O**, 8.81 g, 96%).

4d:



To an oven dried Schlenk tube with a magnetic stirring bar, **P3** (2.5 equiv.), **PC1** (2 mol%), deionized water (3.75 mL) and acetonitrile (50.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **3d** (5.0 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.75 mmol, 0.15 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with two Kessil PR160L (40 W, 456 nm) lights at 20 ºC using the standard set-up. After 72 hours, the irradiation was stopped. Hydrogen peroxide was added to oxide the remaining **P1** to the corresponding phosphine oxide. Then poured onto H_2O and extracted with EtOAc (3 × 100 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. Purification of the resulting crude residue via silica gel flash chromatography (pentane/EtOAc 10/1) to afford the product **4d** (0.58 g, 86%) and phosphine oxide (**P3O**, 3.27 g, 98%).

6c:



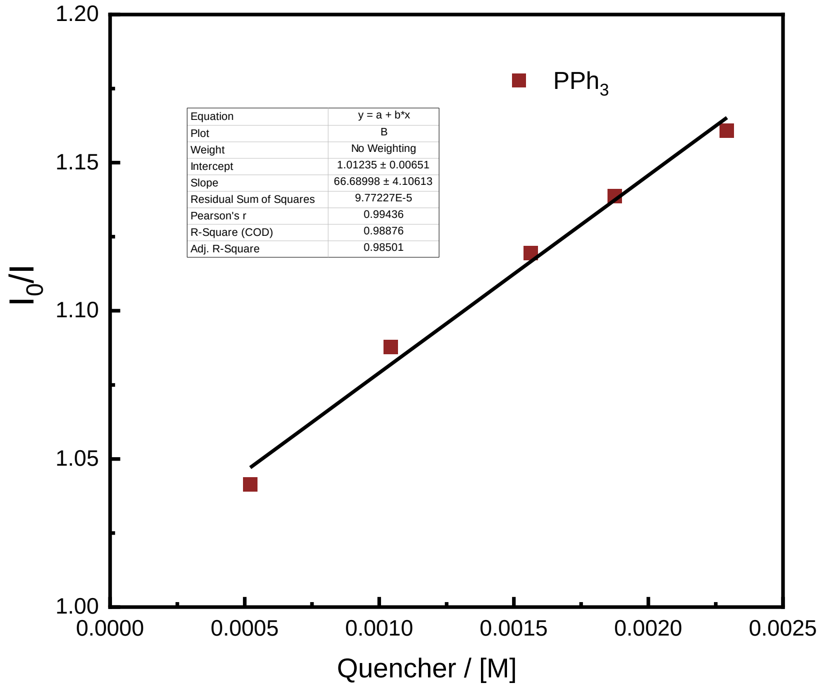
To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (2.5 equiv.), **PC1** (2 mol%), deionized water (7.5 mL) and acetonitrile (100.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **5c** (10.0 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (2.0 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with two Kessil PR160L (40 W, 456 nm) lights at 20 ºC using the standard set-up. After 72 hours, the irradiation was stopped. Hydrogen peroxide was added to oxide the remaining **P1** to the corresponding phosphine oxide. Then poured onto H_2O and extracted with EtOAc (3 × 100 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. Purification of the resulting crude residue via silica gel flash chromatography (pentane) to afford the product **6c** (1.38 g, 88%) and phosphine oxide (**P1O**, 8.53 g, 93%).

9. Stern-Volmer quenching experiment and quantum yield measurment

Stern-Volmer quenching experiment

Stern-Volmer luminescence quenching analysis was conducted using a Jasco FP8300 spectrofluorometer at 25 °C. The following parameters were employed: Excitation bandwidth = 5 nm, data interval = 0.2 nm, scan speed = 500 nm/min, response time = 0.2 sec. The samples were measured in Hellma fluorescence QS quartz cuvettes (chamber volume = 1.4 mL, H × W × D = 46 mm × 12.5 mm, 12.5 mm) fitted with a PTFE stopper. Samples were prepared in 1.4 mL quartz cuvettes equipped with PTFE stoppers inside an argon filled glove bag. The CH_3CN solution of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.5×10^{-5} M) were excited at λ_{ex} = 380 nm and the emission was recorded at 475 nm. For each quenching experiment, 10 µl of the quenching reagent were titrated to a solution (1.4 mL) of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 in a screw-top 10.0 mm quartz cuvette I_0 is the luminescence intensity without the quencher, I is the intensity in the presence of the quencher. The results are listed below:

Entry	[PPh_3] / M	I_o/I	[**1a**] / M	I_o/I
1	0	1	0	1
2	0.000521	1.04138	0.00102	0.9996
3	0.00104	1.08782	0.00204	0.9994
4	0.00156	1.11944	0.00408	0.9990
5	0.00188	1.13866	0.00816	0.9990
6	0.00229	1.16079	0.0163	0.9989



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	1.01235 ± 0.00651
Slope	66.68998 ± 4.10613
Residual Sum of Squares	9.77227E-5
Pearson's r	0.99436
R-Square (COD)	0.98876
Adj. R-Square	0.98501

Figure S3. Stern-Volmer quenching experiment.

Determination of the light intensity of 5 W-455 nm LEDs

Standard ferrioxalate actinometry[60,61] was used to determine the photon flux of 5 W-455 nm LEDs. A solution of ferrioxalate (0.15 M) was prepared by dissolving potassium ferrioxalate trihydrate (737 mg, 1.50 mmol) in 10.0 mL of 0.20 M aqueous H_2SO_4. A buffered solution of 1,10-phenanthroline (0.15 M) was prepared by dissolving NaOAc (1.23 g, 15.0 mmol) and 1,10-phenanthroline (541 mg, 3.00 mmol) in 20 mL of 0.20 M aqueous H_2SO_4. To a 10-mL borosilicate vial equipped with a stir bar was added 1.0 mL of the ferrioxalate solution. The vial was sealed with a Teflon cap and placed in the 5 W-455 nm LEDs. After being irradiated for 20 seconds, 0.5 mL of the reaction mixture was taken out immediately and injected into a 4-mL borosilicate vial containing 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution. The resulting mixture was then allowed to rest for 1 hour to allow the formed ferrous ions to react completely with 1,10-phenanthroline. An aliquot (25 µL) of the resulting solution was diluted with 3.0 mL of 0.20 M aqueous sulfuric acid, and the absorbance in a cuvette (l = 1.0 cm) at 510 nm was measured by UV-Vis spectrometer. The above procedure was repeated four more times, and the average absorption was used for the calculation of photon flux. A nonirradiated sample was also prepared and the absorbance at 510 nm was measured. The photon flux was calculated as follows:

$$\textbf{mol Fe}^{2+} = \frac{V \times \Delta A\ (510\ \text{nm})}{l \times \varepsilon}$$

where V is the total volume (0.96 L) of the solution that was analyzed, ΔA (0.23) is the difference between the average absorption of irradiated and non-irradiated solutions at 510 nm, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11100 L mol^{-1} cm^{-1}).

The photon flux was calculated as follows:

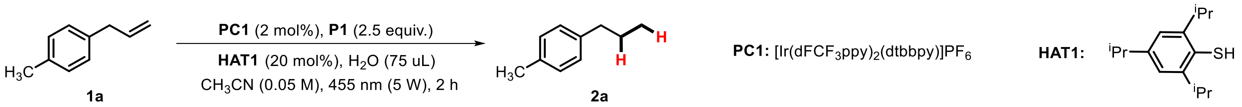
$$\textbf{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \times t \times f}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.9),[62,63] t is the irradiation time (20 s), and f is the fraction of light absorbed at λ = 455 nm by the ferrioxalate actinometer. This value is calculated using the following equation where A(455 nm) is the absorption of the ferrioxalate solution at 455 nm. An absorption spectrum gave an A(455) value of 1.84, indicating that the fraction of absorbed light (f) is 0.986.

$$f = 1 - 10^{-A(455\ nm)}$$

The average photon flux was thus calculated to be 1.12×10^{-6} einsteins s^{-1}.

Determination of quantum yield



To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.25 mmol, 2.5 equiv.), **PC1** (0.002 mmol, 2 mol%) and CH_3CN (2.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, alkene **1a** (0.1 mmol, 1.0 equiv.) and **HAT1** (0.02 mmol, 0.2 equiv.) were added under argon. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ^{o}C using the standard set-up. After one hour, the irradiation was stopped. The yield of product **2a** (6% yield) was determined by gas chromatography with tetradecane as internal standard. The quantum yield was calculated as follows:

$$\boldsymbol{\Phi = \frac{\text{mol product}}{\text{photo flux x } t \text{ x } f}}$$

where mol product is the amount of product **2a** (1.2×10^{-5} mol), photon flux is determined by above ferrioxalate actinometry (1.12×10^{-6} einsteins s^{-1}), t is the reaction time (7200 s), and f is the fraction of light absorbed by the reaction mixture at 455 nm. This value is calculated using the following equation where A(455 nm) is the absorption of the non-irradiated reaction mixture (3.22) at 455 nm. (Note: the reaction mixture was pre-stirred for 30 min without irradiation, and the resulting solution was filtered through a syringe filter before measuring the absorption spectrum). The fraction of light absorbed at 455 nm was calculated:

$$\boldsymbol{f = 1 - 10^{-A(455\,nm)}}$$

Thus, the quantum yield was calculated as $\Phi = 0.0019$.

Comment: The relatively low quantum yield indicates that there are several possible pathways for energy besides the pathway generating the corresponding product and also shows that a chain reaction is not operative. Hence, the Ir-catalyst is a true catalyst and not an initiator in this transformation.

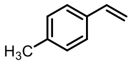
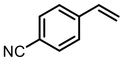
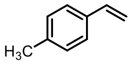
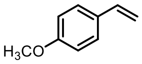
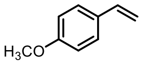
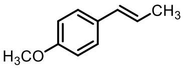
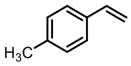
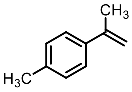
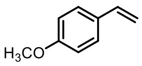
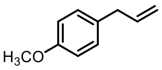
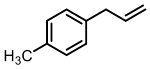
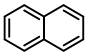
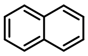
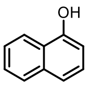
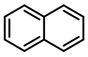
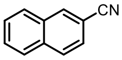
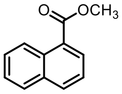
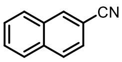
10. Chemoselective hydrogenation experiments

Competition experiments

To an oven dried Schlenk tube with a magnetic stirring bar, **P** (**P1** or **P3**, 4.0 equiv.), **PC1** (2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, **substrate-1** (0.2 mmol, 1.0 equiv.), **substrate-2** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 °C using the standard set-up. After 16 hours, the irradiation was stopped. The yield ratio was determined by the GC with tetradecane as the internal standard.

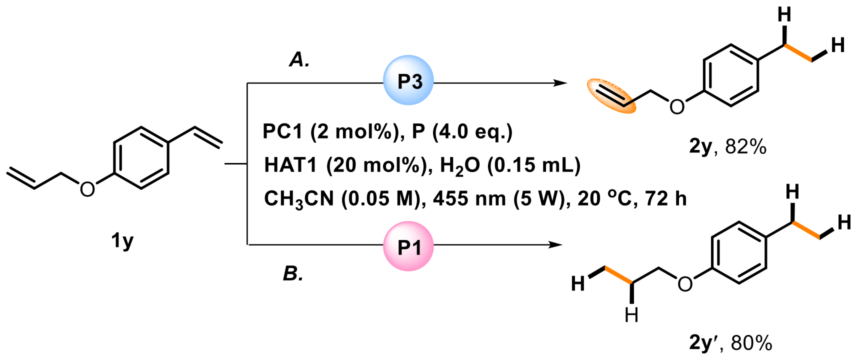
Table S7. Competition experiments for chemoselective hydrogenation.

$$\underset{0.2\ \text{mmol}}{\textbf{substrate-1}} + \underset{0.2\ \text{mmol}}{\textbf{substrate-2}} \xrightarrow[\substack{\textbf{HAT1 (20 mol\%), } \mathbf{H_2O} \textbf{ (0.15 mL)} \\ \mathbf{CH_3CN} \textbf{ (0.05 M)}}]{\textbf{PC1 (2 mol\%), P (4.0 eq.)}} \textbf{product-1} + \textbf{product-2}$$

Entry	**substrate-1**	**substrate-2**	**P**	Time	Yield (**product-1**/**product-2**)
1			**P3**	16 h	15% / **21%**
2			**P3**	16 h	10% / **20%**
3			**P3**	16 h	**16%** / 7%
4			**P3**	16 h	**19%** / 9%
5			**P3**	16 h	**14%** / 0%
6			**P1**	16 h	**32%** / 0%
7			**P1**	16 h	14% / **25%**
8			**P1**	16 h	0 / **41%**
9			**P1**	16 h	5% / **18%**

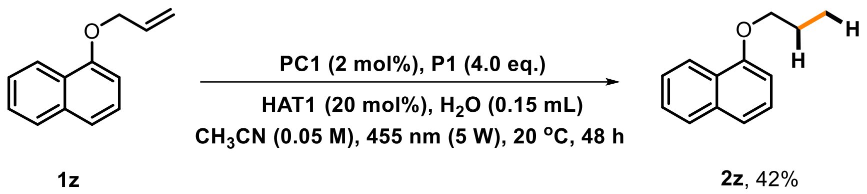
Comment: Considering styrene pairs that slightly differ in their electronics by variation of their para-substituents, low selectivity was noted using the milder PPh_3-derived H-donor (Me vs. CN = 1:1.4; Me vs. MeO = 1:2). Steric effects play a role as *α*-methyl (trans) and also *β*-methyl-substituted styrenes are less reactive than their corresponding unsubstituted styrenes (around 2:1). Comparing an activated alkene with an unactivated alkene, we found excellent chemoselectivity for the hydrogenation with the milder **P3** as mediator. The same outcome was noted for the hydrogenation pair of unactivated alkene and naphthalene with more reactive **P1** as mediator. Considering HAT to naphthalenes, we ran a series of competition experiments. Only in the case of 2-cyanonaphthalene versus naphthalene, complete chemoselectivity for the hydrogenation of cyanonaphthalene was obtained. 1-Naphthol was around 1.8 times more reactive than naphthalene. 2-Cyanonaphthalene was 3.6 times more reactive than 1-methoxycarbonylnapthalene.

Chemoselective hydrogenation

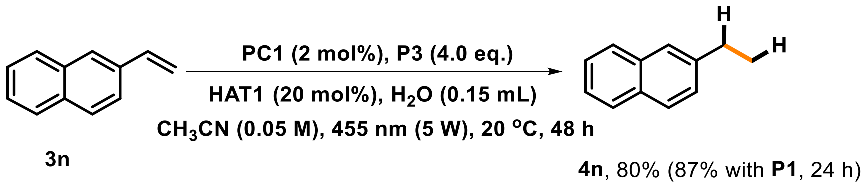


Process A: To an oven dried Schlenk tube with a magnetic stirring bar, **P3** (4.0 equiv.), **PC1** (2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, **1y** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ºC using the standard set-up. After 72 hours, the irradiation was stopped. The yield was determined by the GC with tetradecane as the internal standard. The product analysis showed that only activated alkene of **1y** was reduced to give **2y** with 82% yield.

Process B: To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (4.0 equiv.), **PC1** (2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, **1y** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ºC using the standard set-up. After 72 hours, the irradiation was stopped. The yield was determined by the GC with tetradecane as the internal standard. The product analysis showed that **1y** was fully reduced to give **2y'** with 80% yield.

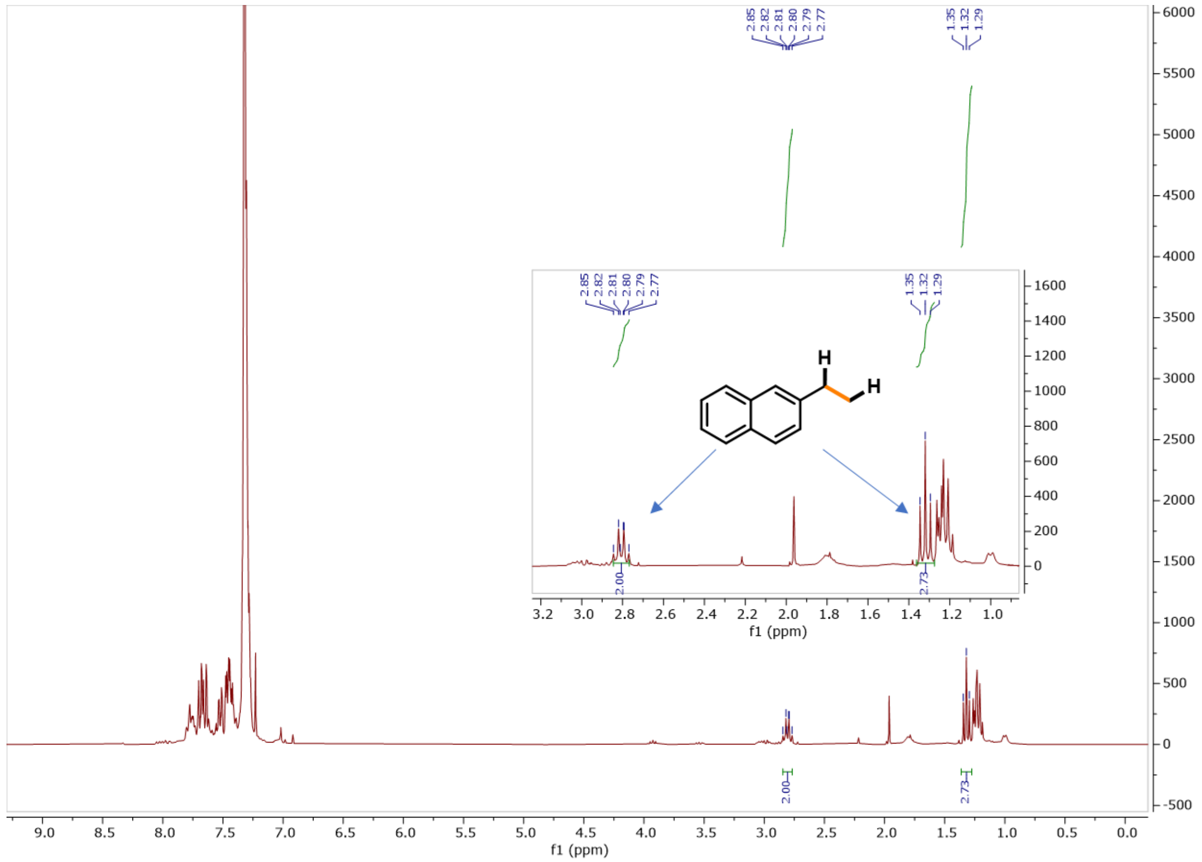


To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (4.0 equiv.), **PC1** (2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, **1z** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ^{o}C using the standard set-up. After 48 hours, the irradiation was stopped. The yield was determined by the GC with tetradecane as the internal standard. The product analysis showed that only alkene of **1z** was reduced to give **2z** with 42% yield.



To an oven dried Schlenk tube with a magnetic stirring bar, **P3** (4.0 equiv.), **PC1** (2 mol%), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, **3n** (0.2 mmol, 1.0 equiv.) and the HAT catalyst **HAT1** (0.04 mmol, 0.2 equiv.) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ^{o}C using the standard set-up. After 48 hours, the irradiation was stopped. The yield was determined by the GC with tetradecane as the internal standard. The product analysis showed that only alkene of **3n** was reduced to give **4n** with 80% yield.

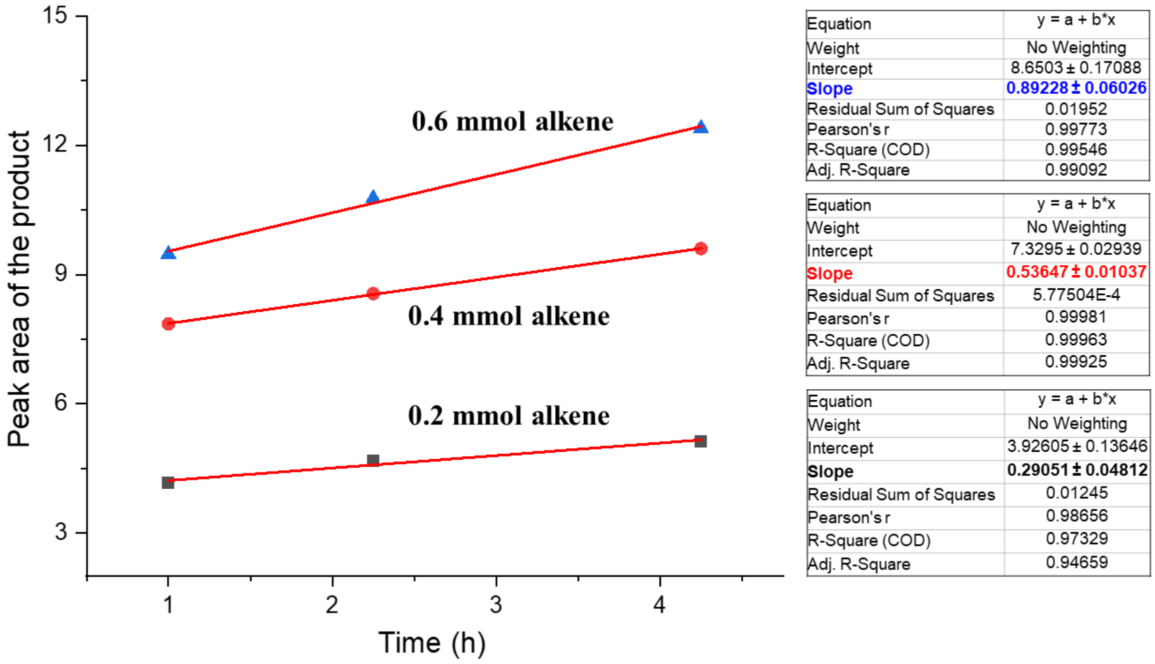
The ^{1}H NMR spectrum of the reaction mixture:


2.85
2.82
2.81
2.80
2.79
2.77
1.35
1.32
1.29
H
H
2.00
2.73
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
1600
1400
1200
1000
800
600
400
200
0
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

11. Kinetic experiments

11.1 The reaction order of alkenes in our conditions

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol), **PC1** (0.01 mmol), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **1a** (0.2 mmol, 0.4 mmol and 0.6 mmol for three different Schlenk tubes, respectively), the HAT catalyst **HAT1** (0.04 mmol) and tetradecane (internal standard, 0.1 mmol) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ºC using the standard set-up. At each indicated time an aliquot (60 μL) of the reaction mixture was taken under positive argon pressure, which was diluted and analyzed by GC.



Equation	y = a + b*x
Weight	No Weighting
Intercept	8.6503 ± 0.17088
Slope	**0.89228 ± 0.06026**
Residual Sum of Squares	0.01952
Pearson's r	0.99773
R-Square (COD)	0.99546
Adj. R-Square	0.99092

Equation	y = a + b*x
Weight	No Weighting
Intercept	7.3295 ± 0.02939
Slope	**0.53647 ± 0.01037**
Residual Sum of Squares	5.77504E-4
Pearson's r	0.99981
R-Square (COD)	0.99963
Adj. R-Square	0.99925

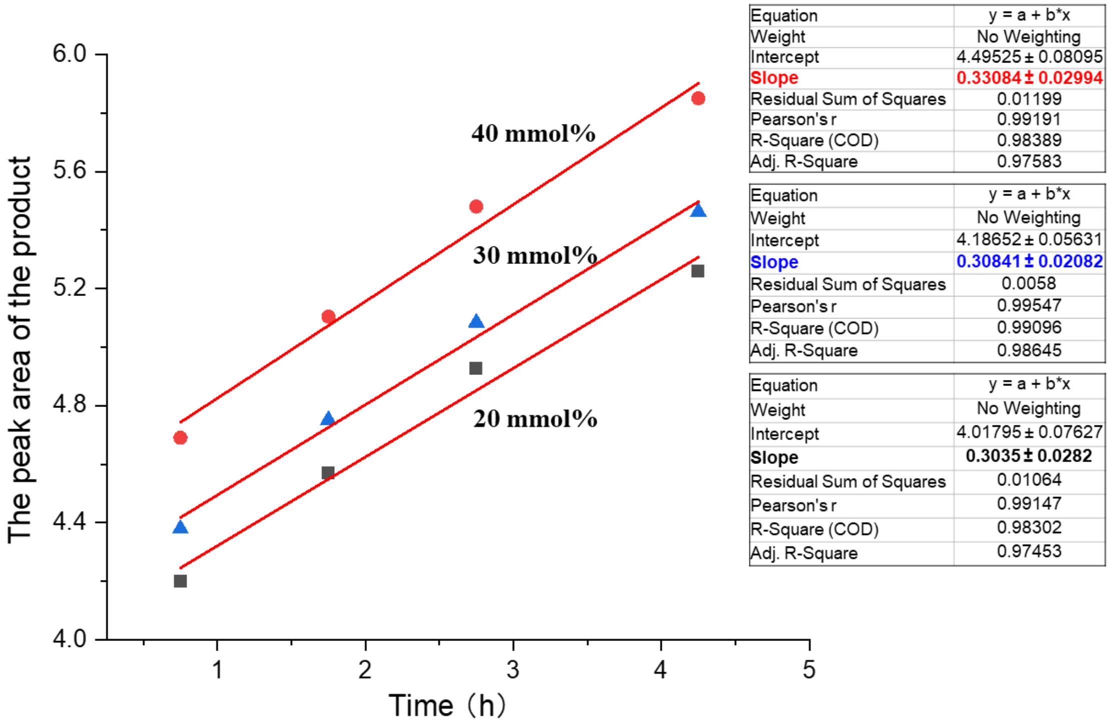
Equation	y = a + b*x
Weight	No Weighting
Intercept	3.92605 ± 0.13646
Slope	**0.29051 ± 0.04812**
Residual Sum of Squares	0.01245
Pearson's r	0.98656
R-Square (COD)	0.97329
Adj. R-Square	0.94659

Figure S4. The measutrement of reaction order of alkenes in our conditions.

Comment: The reaction is first order in the alkene, indicating that the reaction step where the alkene is involved is involved in the rate-determining step.

11.2 The reaction order of the HAT catalyst in our conditions

To an oven dried Schlenk tube with a magnetic stirring bar, **P1** (0.5 mmol), **PC1** (0.01 mmol), deionized water (0.15 mL) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **1j** (0.2 mmol), the HAT catalyst **HAT1** (0.02 mmol, 0.04 mmol and 0.06 mmol for three different Schlenk tubes, respectively) and tetradecane (internal standard, 0.2 mmol) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ºC using the standard set-up. At each indicated time an aliquot (60 μL) of the reaction mixture was taken under positive argon pressure, which was diluted and analyzed by GC.



Equation	y = a + b*x
Weight	No Weighting
Intercept	4.49525 ± 0.08095
Slope	0.33084 ± 0.02994
Residual Sum of Squares	0.01199
Pearson's r	0.99191
R-Square (COD)	0.98389
Adj. R-Square	0.97583

Equation	y = a + b*x
Weight	No Weighting
Intercept	4.18652 ± 0.05631
Slope	0.30841 ± 0.02082
Residual Sum of Squares	0.0058
Pearson's r	0.99547
R-Square (COD)	0.99096
Adj. R-Square	0.98645

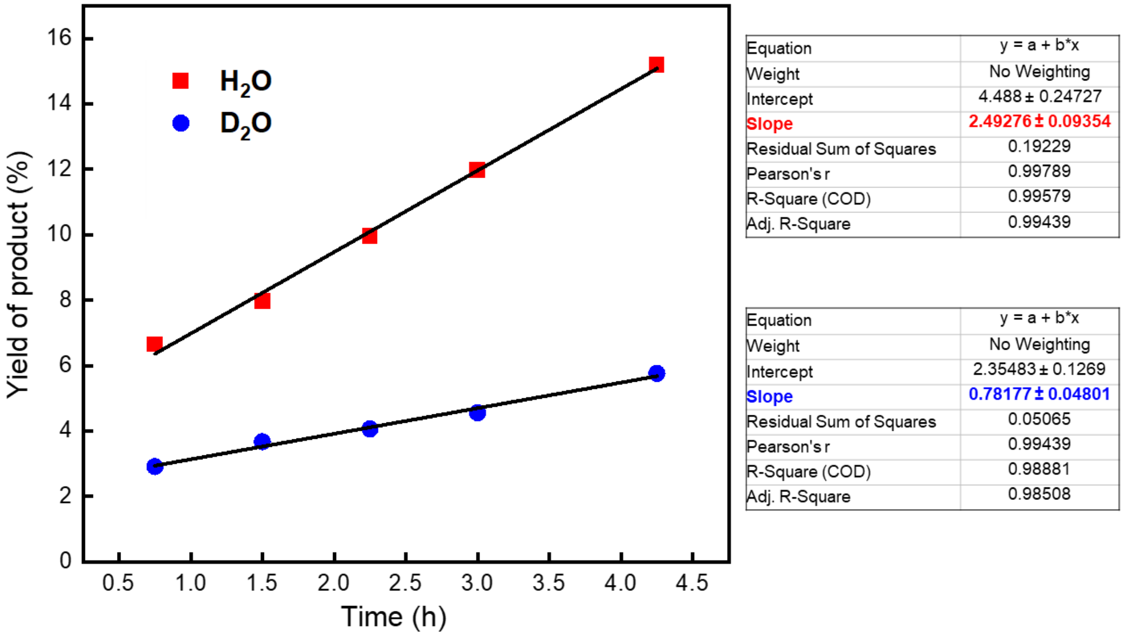
Equation	y = a + b*x
Weight	No Weighting
Intercept	4.01795 ± 0.07627
Slope	**0.3035 ± 0.0282**
Residual Sum of Squares	0.01064
Pearson's r	0.99147
R-Square (COD)	0.98302
Adj. R-Square	0.97453

Figure S5. The measurement of reaction order of the HAT catalyst in our conditions.

Comment: The reaction is zero order in the HAT catalyst, indicating the reaction step where the thiol is involved is not the rate-determining step.

11.3 The KIE measurement

To an oven dried Schlenk tube with a magnetic stirring bar, **P3** (0.5 mmol), **PC1** (0.01 mmol), H_2O or D_2O (0.15 mL for two different Schlenk tubes, respectively) and acetonitrile (4.0 mL) were added under argon atmosphere using standard Schlenk techniques at ambient temperature. Then, the substrate **3a** (0.2 mmol), the HAT catalyst **HAT1** (0.03 mmol) and tetradecane (internal standard, 0.2 mmol) were added under argon atmosphere. The tube was sealed and placed in the photoreactor, and then irradiated with a 5 W 455 nm LED at 20 ^{o}C using the standard set-up. At each indicated time an aliquot (60 μL) of the reaction mixture was taken under positive argon pressure, which was diluted and analyzed by GC.



Equation	y = a + b*x
Weight	No Weighting
Intercept	4.488 ± 0.24727
Slope	**2.49276 ± 0.09354**
Residual Sum of Squares	0.19229
Pearson's r	0.99789
R-Square (COD)	0.99579
Adj. R-Square	0.99439

Equation	y = a + b*x
Weight	No Weighting
Intercept	2.35483 ± 0.1269
Slope	**0.78177 ± 0.04801**
Residual Sum of Squares	0.05065
Pearson's r	0.99439
R-Square (COD)	0.98881
Adj. R-Square	0.98508

Figure S6. The rate constants for the reactions using H_2O or D_2O as hydrogen source.

Comment: The KIE value of the reaction is 3.2, indicating that the cleavage of the O-H bond is involved in the rate-determining step.

12. DFT calculations

12.1 Methods

All structures were optimized without geometry constraints using the PBE0 hybrid functional[64,65] and an atom-pairwise dispersion correction (D3).[66,67] A flexible triple zeta basis set (def2-TZVP)[68] was used in all calculations. The nature of the optimized stationary points was proven by the presence of either 0 (minimum) or 1 (transition structure) imaginary vibrational frequency. For the determination of the enthalpy and free enthalpy contributions at 298 K (H^{RRHO}, G^{RRHO}), the rigid-rotor-harmonic-oscillator model and a rotor approximation for vibrational modes with wave numbers below 100 cm^{-1} was applied.[69] Electronic energies of the structures optimized with PBE0-D3 were recalculated with the double hybrid functional PWPB95(-D3)[70] using the def2-TZVP basis set and the frozen core option for the perturbation theory part of the correlation energy. Solvation free energies (G_{solv}) for T = 298.15 K in acetonitrile were obtained with COSMO-RS.[71,72] Relative values of free enthalpy in solution ($\Delta G^{\mathrm{s}}_{298}$), *i.e.* the activation free energies of HAT for **P3**-OH were obtained using the sum of the differences in PWPB95-D3 electronic energies, G^{RRHO}(298K), and G_{solv} as

$$\Delta G^{\mathrm{s}}_{298} = \Delta E(\mathrm{PWPB95\text{-}D3}) + \Delta G^{\mathrm{RRHO}}(298\mathrm{K}) + \Delta G_{\mathrm{solv}} \qquad (1)$$

Bond dissociation energies for the H-atom donors (Table S9) were calculated as enthalpies for the reaction R-H → R + $\mathrm{H}^{\bullet}$:

$$\mathrm{BDE} = \Delta H^{\mathrm{o}}(298\mathrm{K}) = \Delta E(\mathrm{PWPB95\text{-}D3}) + \Delta H^{\mathrm{RRHO}}(298\mathrm{K}) \qquad (2)$$

Spin density isosurfaces of **P3**-OH and the transition structures of H-atom transfer were calculated with PBE0/def2-TZVP (Figure S7).

All PBE0 calculations were performed with the TURBOMOLE program.[73,74] For the PWPB95-D3 double hybrid energy calculations, ORCA was used.

12.2 DFT calculated energies

Table S8. DFT-calculates energies and thermostatistical contributions of all molecular species.

Structure	E(PBE0-D3) [E_h]	$G^{RRHO}_{298\ K}$ [kcal/mol]	$H^{RRHO}_{298\ K}$ [kcal/mol]	E(PWPB95-D3)[a] [E_h]	$G_{solv}(CH_3CN)$ COSMO-RS [kcal/mol]
P1-OH	-1454.733077	209.257	258.268	-1455.231938	-17.823
P1=O	-1454.211067	204.716	252.999	-1454.719451	-18.334
P2-OH	-1229.245314	200.478	246.869	-1229.635654	-13.629
P2=O	-1228.717969	195.187	241.470	-1229.117739	-14.150
P3-OH	-1111.390124	153.047	191.906	-1111.748784	-13.046
P3=O	-1110.861463	148.256	186.528	-1111.229267	-13.071
P3-Hortho	-1111.412034	153.466	192.331	-1111.771294	-12.751
P3-TS-STYR	-1420.791573	229.998	278.875	-1421.258076	-14.574
P3-TS-PROP	-1229.184121	197.381	242.603	-1229.573328	-11.071
P4-OH	-1408.968422	135.829	178.183	-1409.475076	-13.024
P4=O	-1408.442921	131.196	172.833	-1408.959484	-12.743
P5-OH	-2122.041959	153.338	208.033	-2122.885518	-15.234
P5=O	-2121.506149	147.796	202.543	-2122.359449	-13.177
CH4	-40.475114	16.387	30.463	-40.485495	4.050
CH3	-39.799762	7.348	21.206	-39.808846	3.689
PROPENE	-117.800541	34.347	53.182	-117.840296	2.593
STYRENE	-309.390352	64.434	88.691	-309.506185	-1.553
H.	-0.501037	-6.271	1.481	-0.498413	

[a] calculated using the structures optimized with PBE0-D3

Table S9. DFT-calculated BDE(O-H) for PR_3O-H radicals from values in Table S8 using Eqn. (2).

Radical	Ar	BDE = ΔH^o(298K)
P1-OH	(p-OMe)Ph	5.04
P2-OH	(p-Me)Ph	8.32
P3-OH	Ph	9.35
P4-OH	(p-F)Ph	6.91
P5-OH	(p-CF_3)Ph	13.35

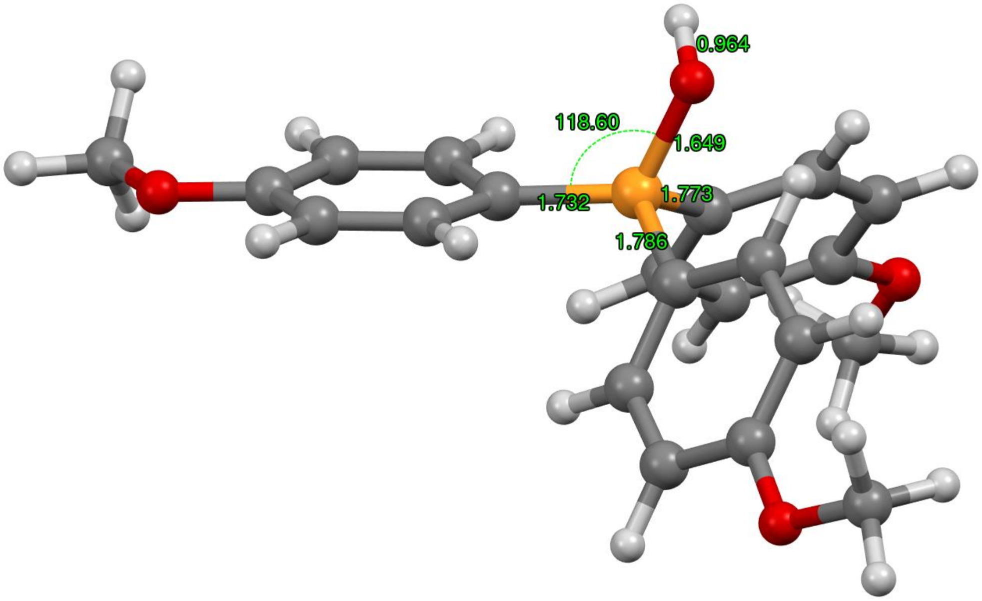
Table S10. DFT-calculates energies and thermostatistical contributions of HAT from **P1**-OH to naphthalenes **5b**, **5c** and **5f**.

Structure	***E*(PBE0-D3)**	**G^{RRHO}_{298}**	***E*(PWPB95-D3)**[a]	**G_{solv} (CH_3CN) COSMO-RS**
	[E_h]	**[kcal/mol]**	**[E_h]**	**[kcal/mol]**
5f	-424.863736	89.528	-425.019969	-3.233
5f-TS2	-1879.606497	311.722	-1880.257285	-20.940
5f-TS3	-1879.608540	312.471	-1880.260030	-21.115
5f-TS4	-1879.613187	312.273	-1880.263211	-21.117
5f-TS5	-1879.611789	311.882	-1880.262396	-21.080
5f-TS6	-1879.607436	312.232	-1880.259216	-21.084
5f-TS7	-1879.607591	312.218	-1880.258516	-20.987
5f-TS8	-1879.612416	312.012	-1880.262561	-20.669
5f-H2	-425.414915	94.206	-425.562460	-3.234
5f-H3	-425.414505	94.781	-425.562268	-3.116
5f-H4	-425.422786	94.648	-425.570332	-3.034
5f-H5	-425.421808	94.576	-425.569316	-3.077
5f-H6	-425.413159	94.428	-425.560763	-3.188
5f-H7	-425.414626	94.588	-425.562282	-3.192
5f-H8	-425.422555	94.531	-425.570002	-3.156
5b	-613.306849	96.800	-613.552730	-5.942
5b-H2	-613.864470	102.295	-614.102063	-5.999
5b-H3	-613.856106	101.877	-614.093572	-6.318
5b-H4	-613.869797	102.144	-614.107187	-6.114
5b-H5	-613.865539	101.855	-614.102569	-5.963
5b-H6	-613.856921	101.829	-614.094027	-5.983
5b-H7	-613.859557	101.868	-614.096676	-5.820
5b-H8	-613.866840	101.901	-614.104200	-5.413
5c	-477.753151	70.916	-477.949053	-6.627
5c-H1	-478.318361	76.300	-478.504863	-6.791
5c-H3	-478.306941	76.039	-478.493554	-6.677
5c-H4	-478.311148	75.968	-478.498033	-6.683
5c-H5	-478.311995	75.996	-478.499030	-6.615
5c-H6	-478.306605	76.080	-478.493584	-7.084
5c-H7	-478.304331	75.942	-478.491302	-6.697
5c-H8	-478.313416	76.068	-478.500225	-6.786

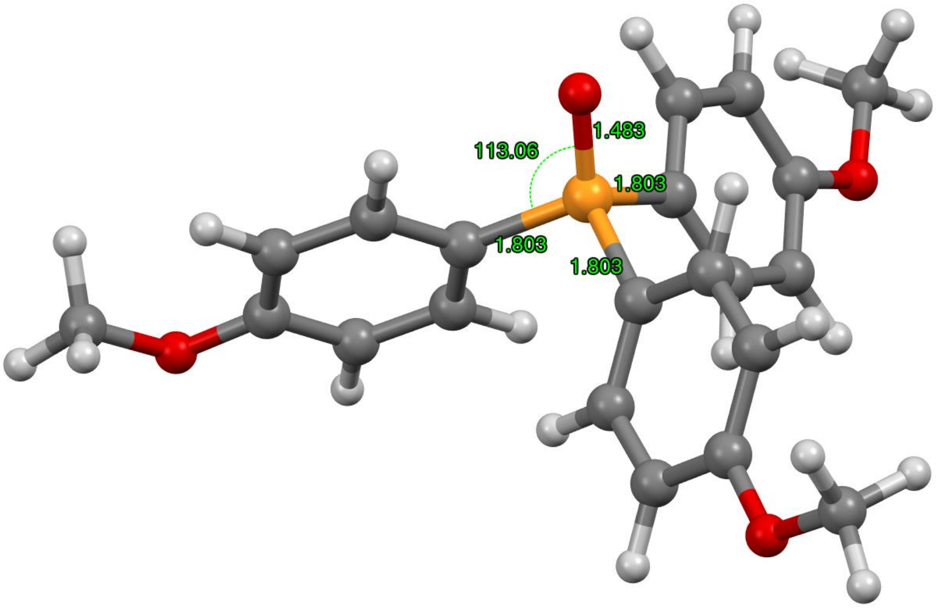
[a] calculated using the structures optimized with PBE0-D3

12.3 Optimized molecular structures

Figure S7. Molecular structures of all intermediates and transition structures optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P), green (F).

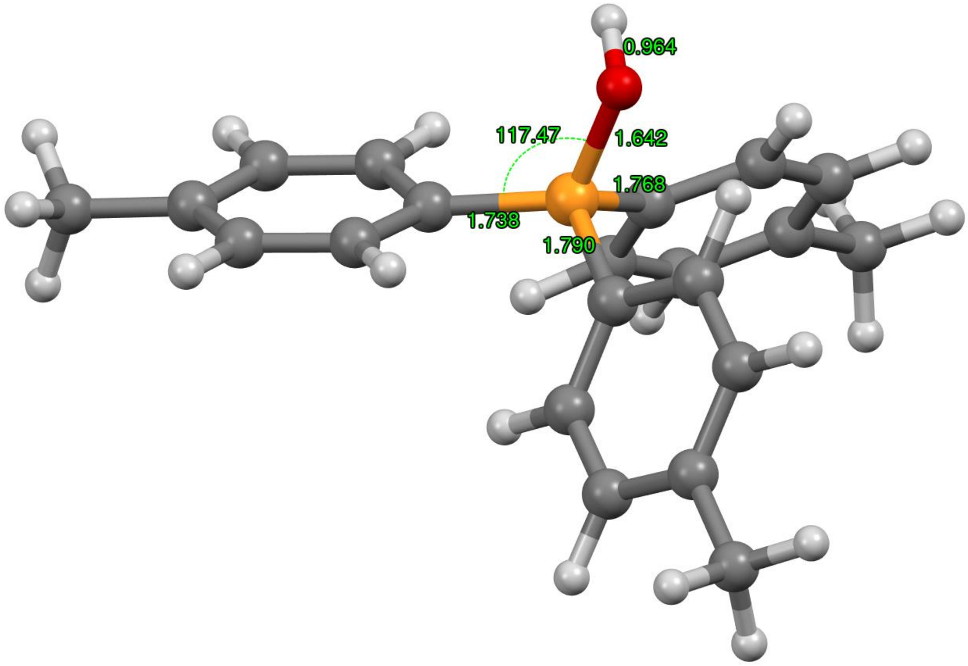


P1-OH

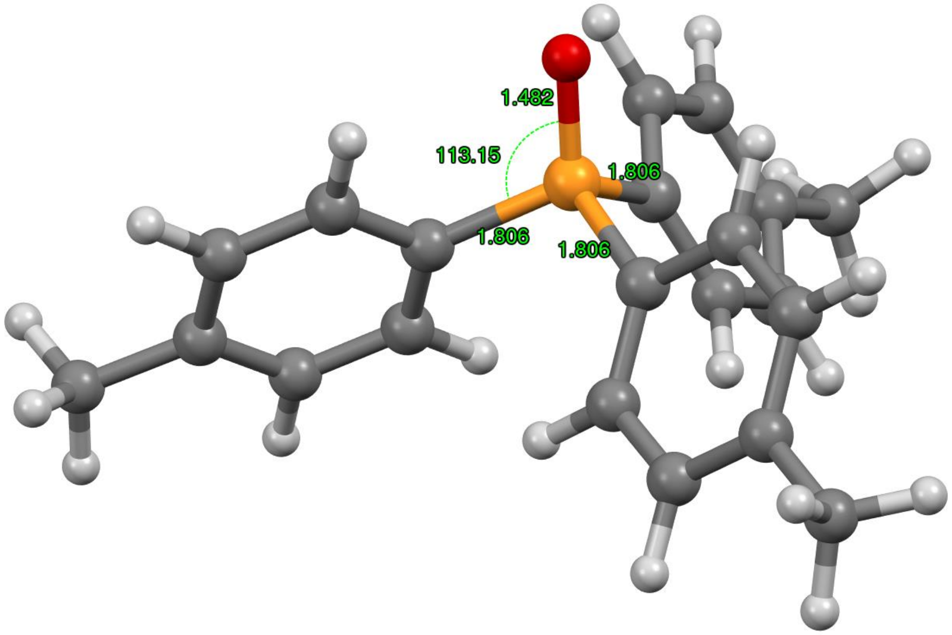


P1=O

Figure S7 (continued). Molecular structures of all intermediates and transition structures optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P), green (F).

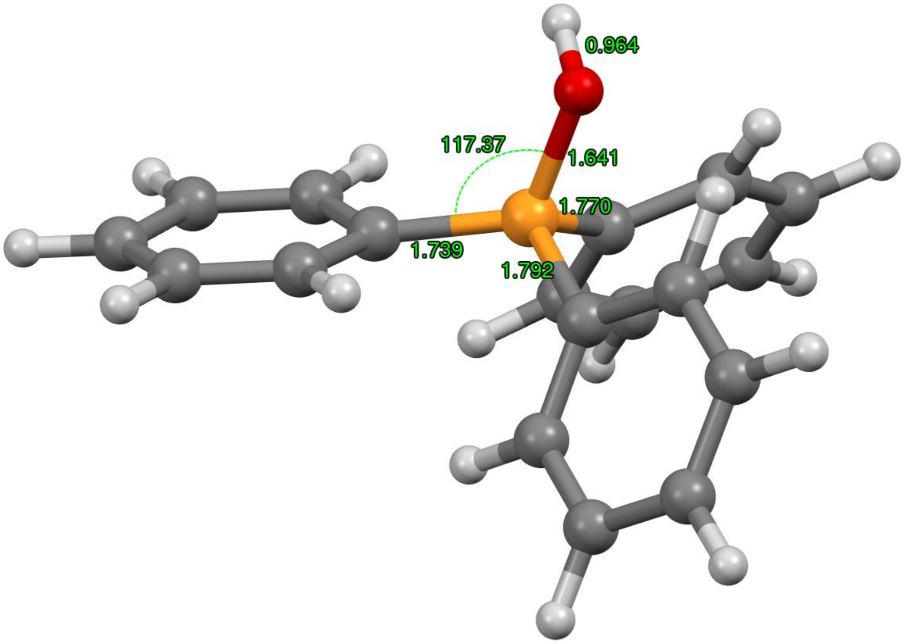


P2-OH

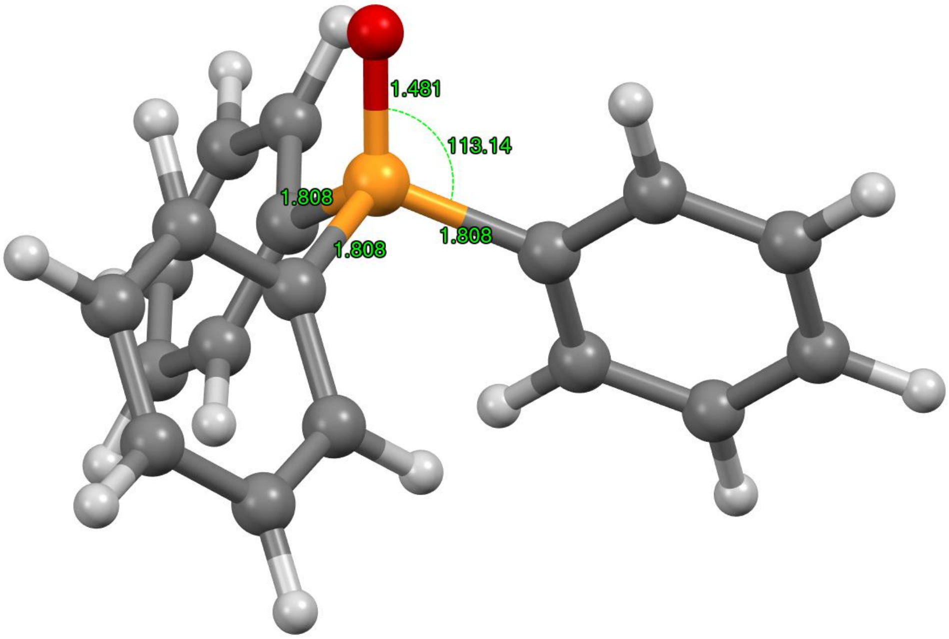


P2=O

Figure S7 (continued). Molecular structures of all intermediates and transition structures optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P), green (F).

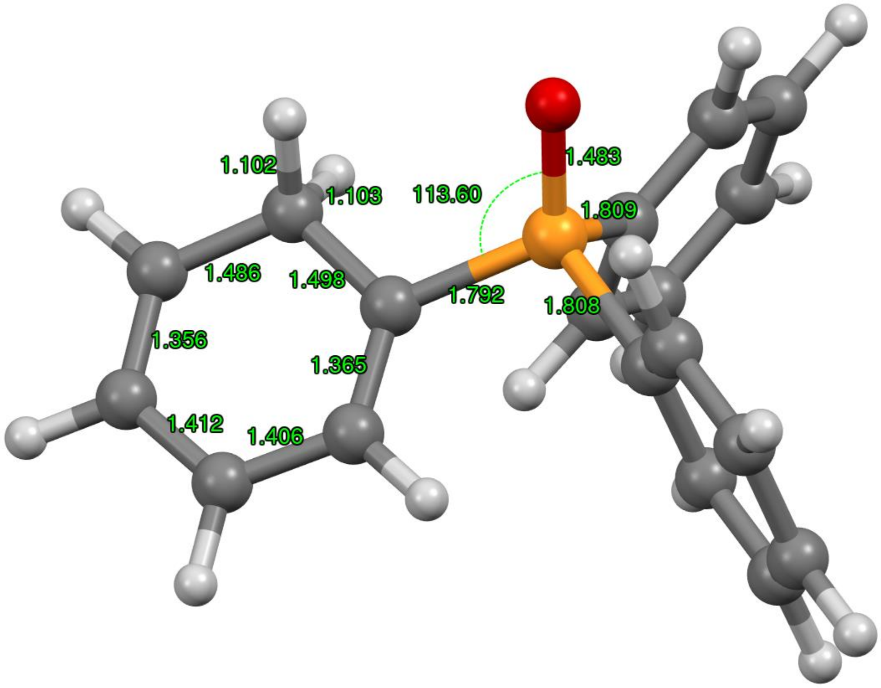


P3-OH



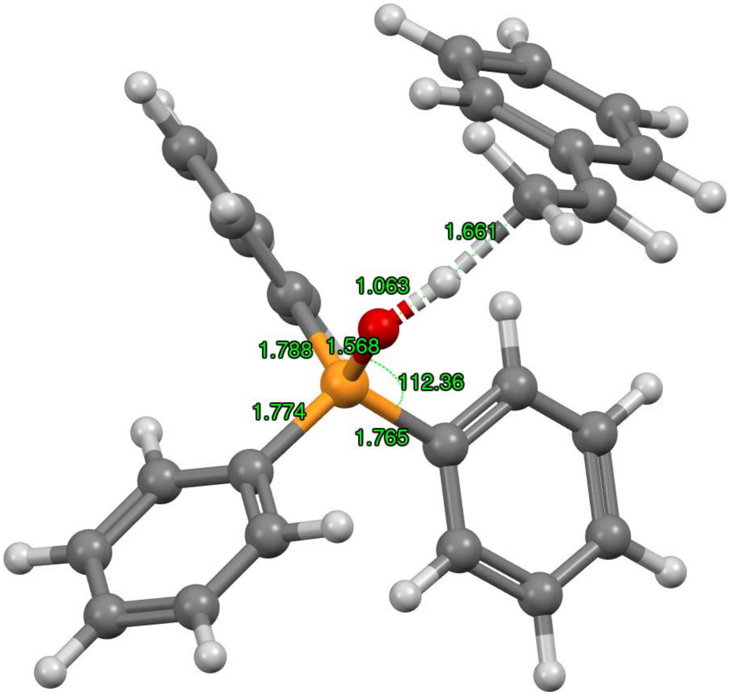
P3=O

Figure S7 (continued). Molecular structures of all intermediates and transition structures optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P), green (F).

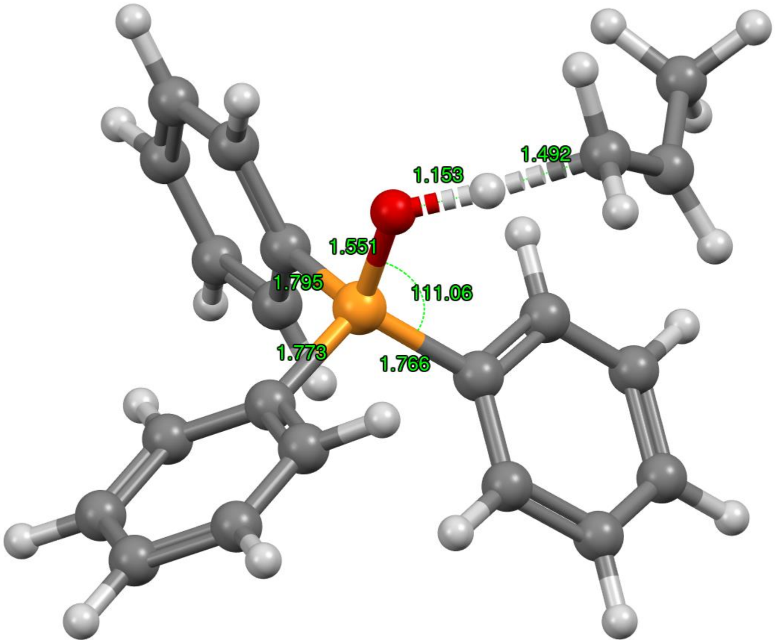


P3-H_{ortho}

Figure S7 (continued). Molecular structures of all intermediates and transition structures optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P), green (F).

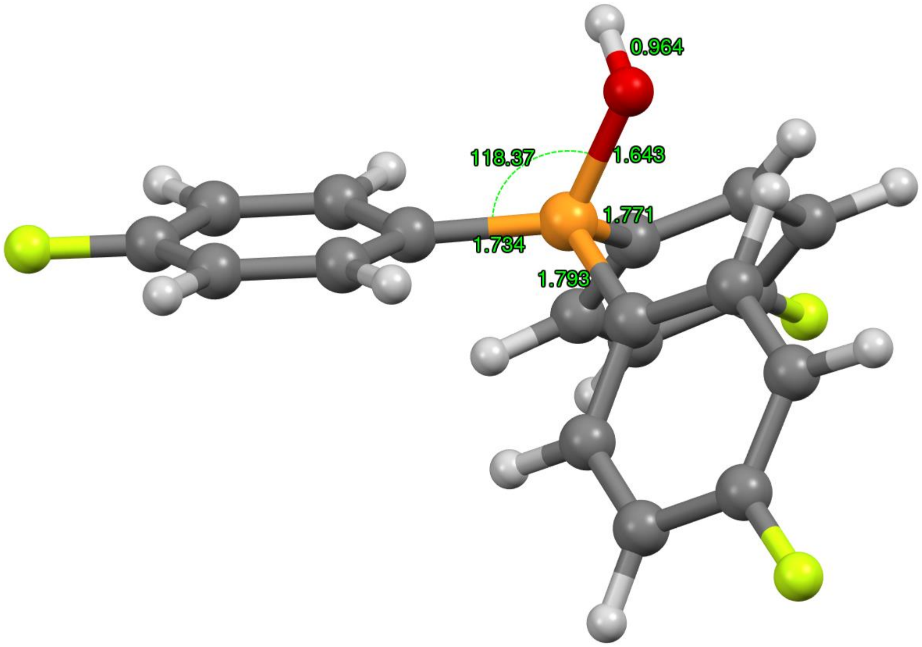


P3-TS-STYR

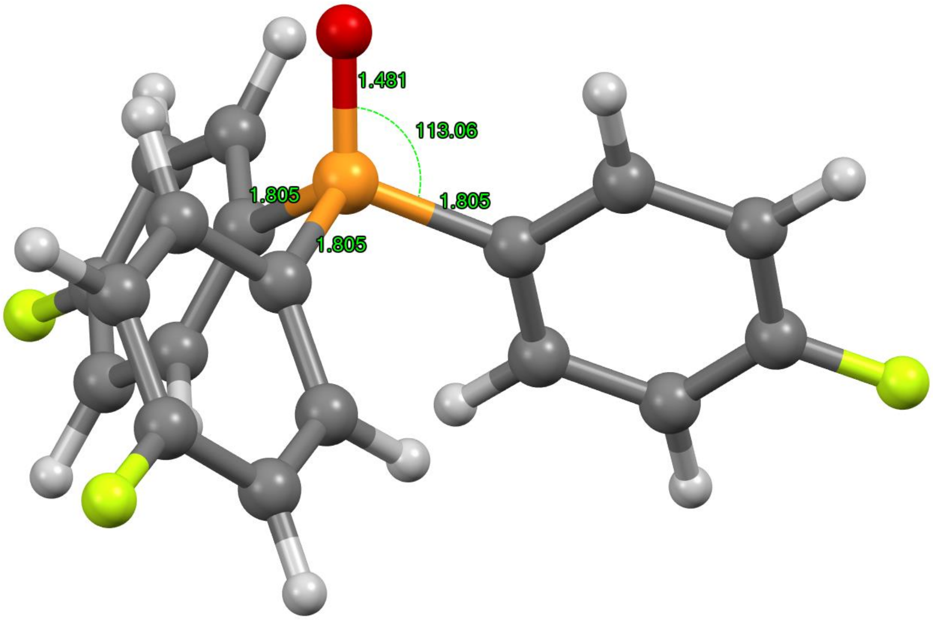


P3-TS-PROP

Figure S7 (continued). Molecular structures of all intermediates and transition structures optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P), green (F).

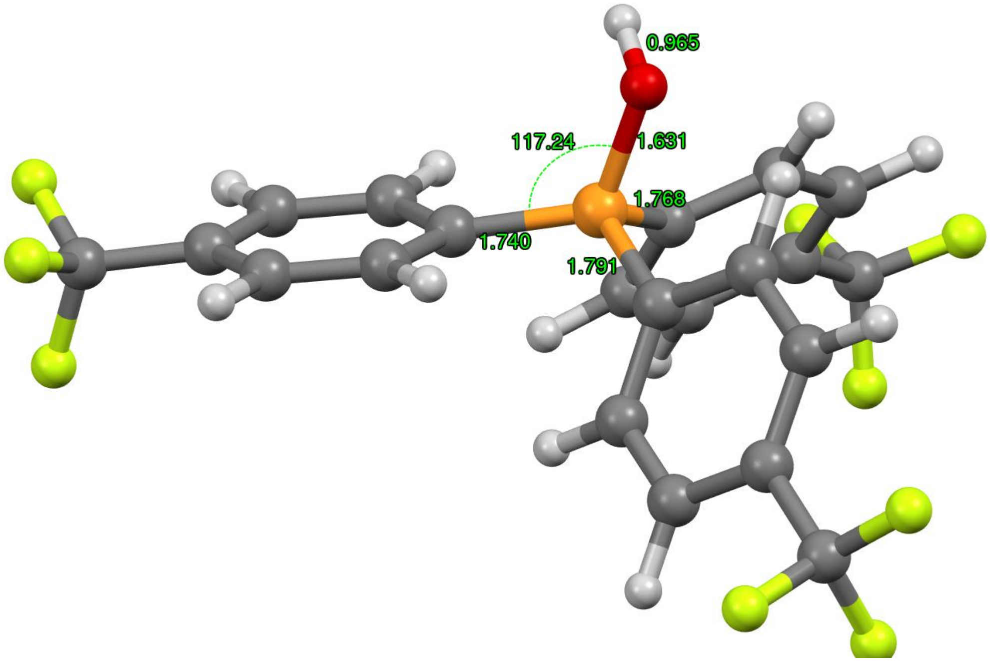


P4-OH

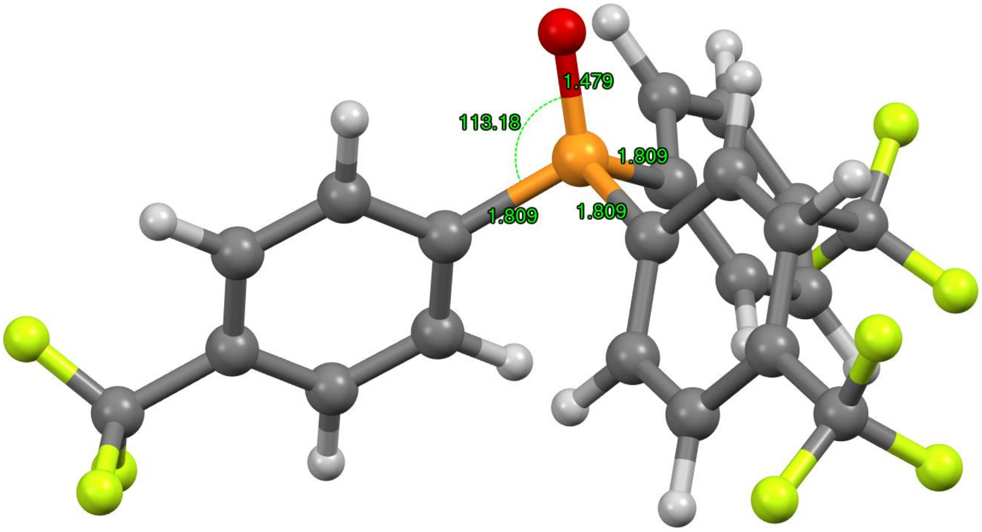


P4=O

Figure S7 (continued). Molecular structures of all intermediates and transition structures optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P), green (F).

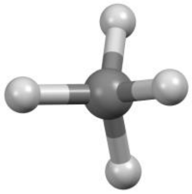


P5-OH

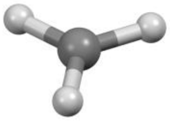


P5=O

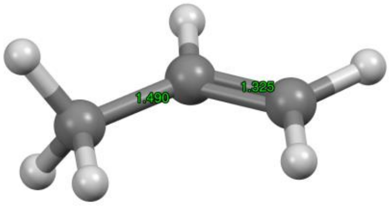
Figure S7 (continued). Molecular structures of all intermediates and transition structures optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P), green (F).



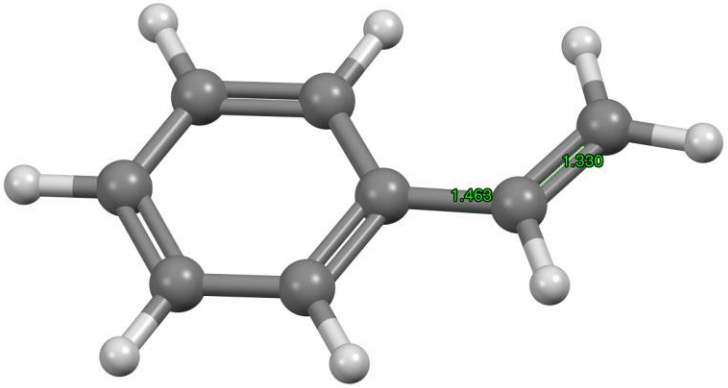
CH_4



$CH_3^{\cdot}$

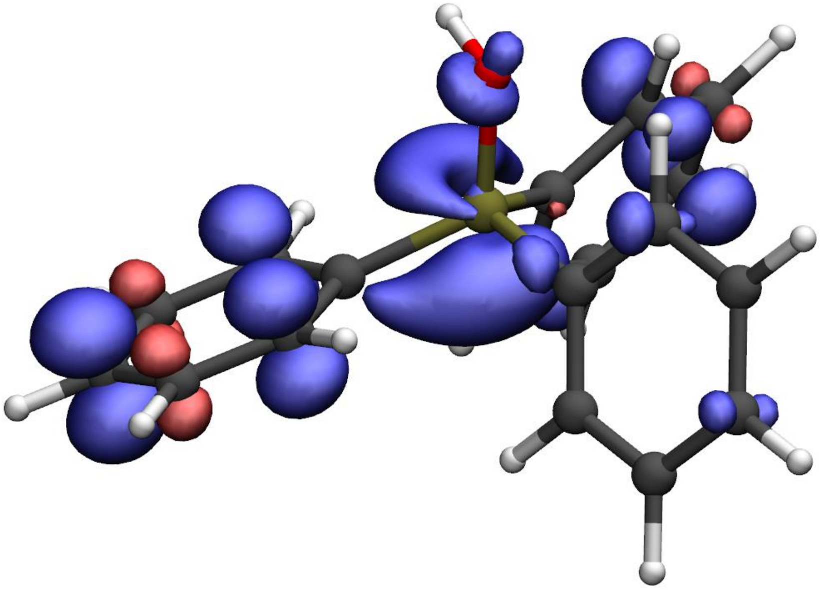


PROPENE

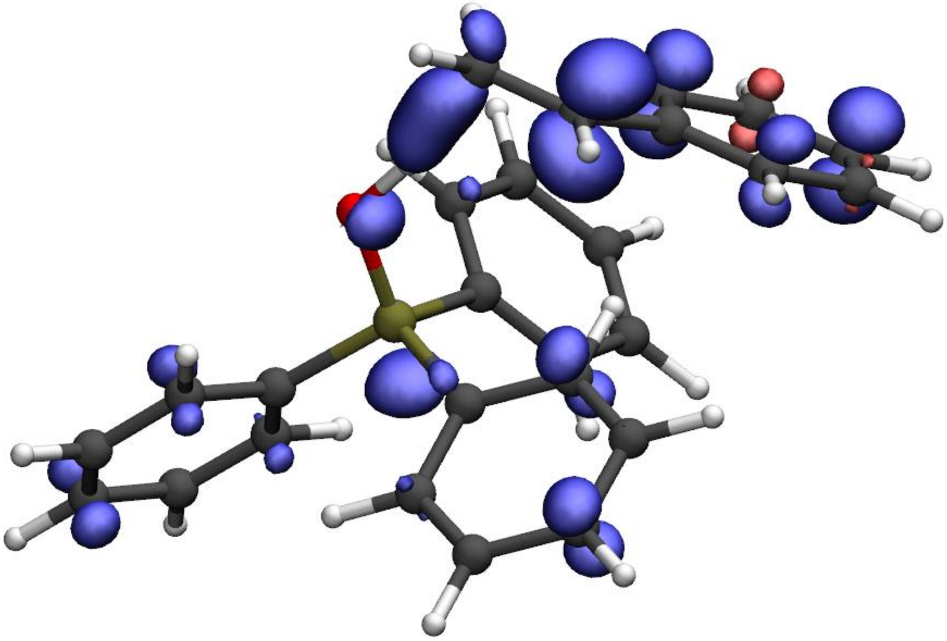


STYRENE

Figure S8. Spin density isosurfaces ($\rho_{SD} = \rho_{\alpha}-\rho_{\beta}$, ρ_{SD}^{iso} = 0.005 a.u., PBE0-D3/def2-TZVP).

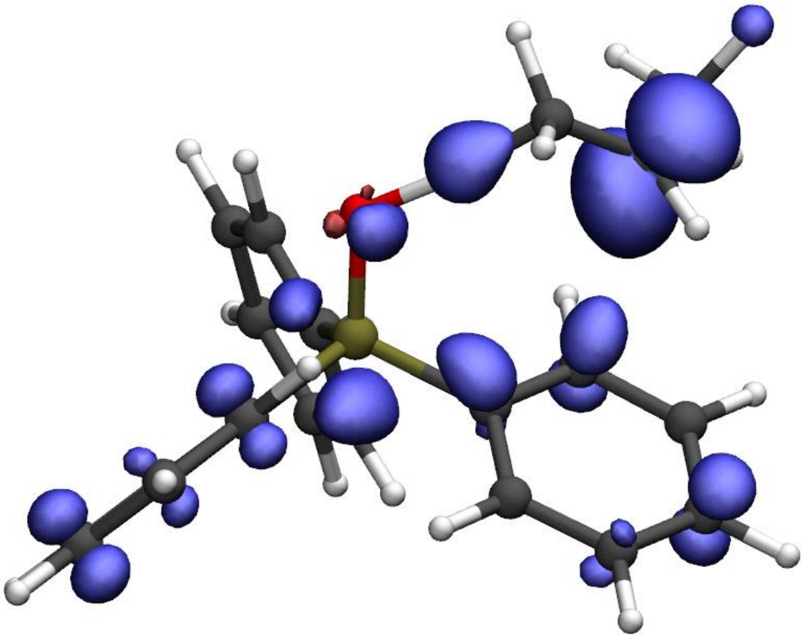


P3-OH



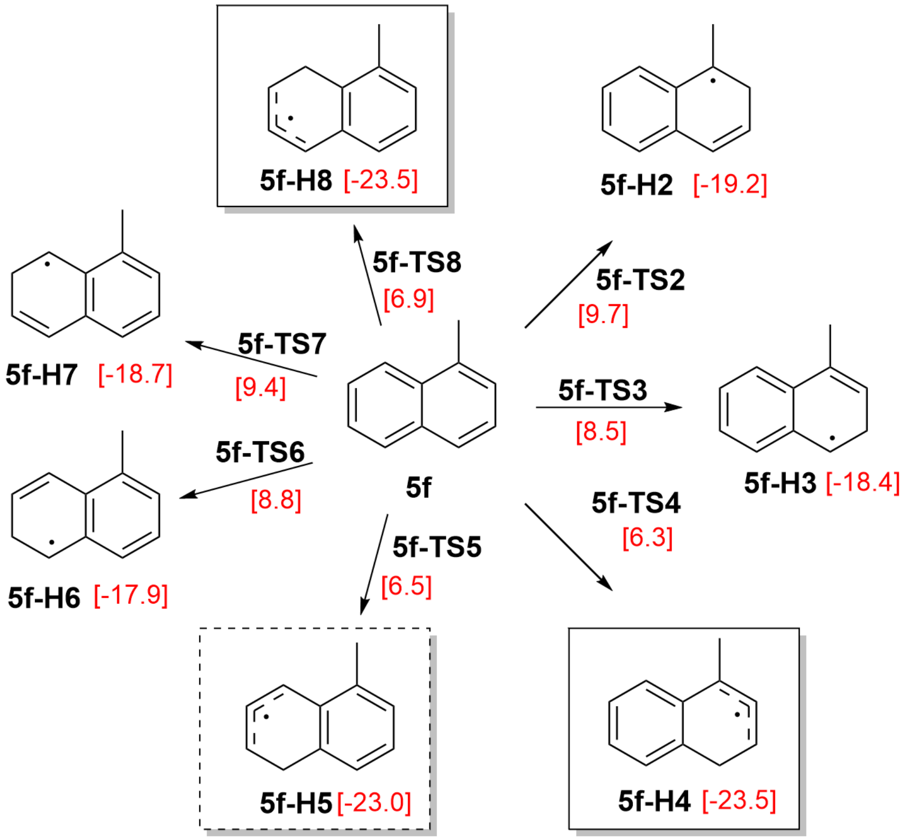
P3-TS-STYR

Figure S8 (continued). Spin density isosurfaces ($\rho_{SD} = \rho_{\alpha}-\rho_{\beta,}$ ρ_{SD}^{iso} = 0.005 a.u., PBE0-D3/def2-TZVP).



P3-TS-PROP

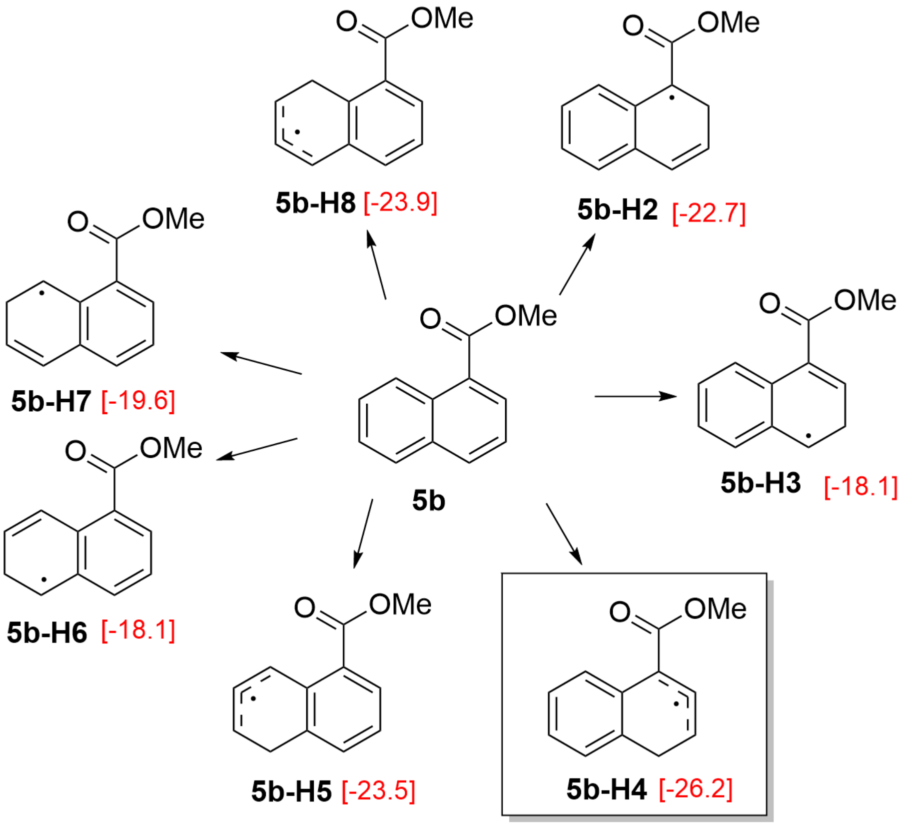
Figure S9. Gibbs free energies of the HAT from radical **P1**-OH to positions 2-8 of 1-methyl-naphthalene (**5f**). Transition state free energies (**5f-TS*n***) correspond to free energy barriers with respect to the separated **P1**-OH radical and **5f**.



$[\Delta G^{s}_{298}$ / kcal mol$^{-1}]$

PWPB95-D3/def2-TZVP//PBE0-D3/def2-TZVP + COSMO-RS(CH_3CN)

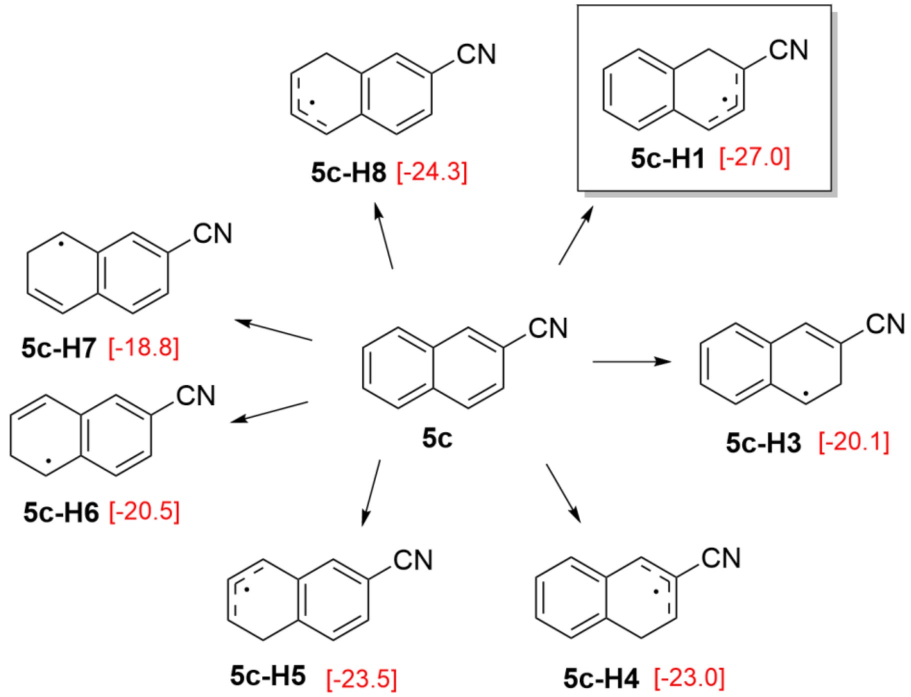
Figure S10. Gibbs free energies of the HAT from radical **P1**-OH to positions 2-8 of naphthalene-1-methylester (**5b**).



[ΔG^{s}_{298} / kcal mol^{-1}]

PWPB95-D3/def2-TZVP//PBE0-D3/def2-TZVP + COSMO-RS(CH_3CN)

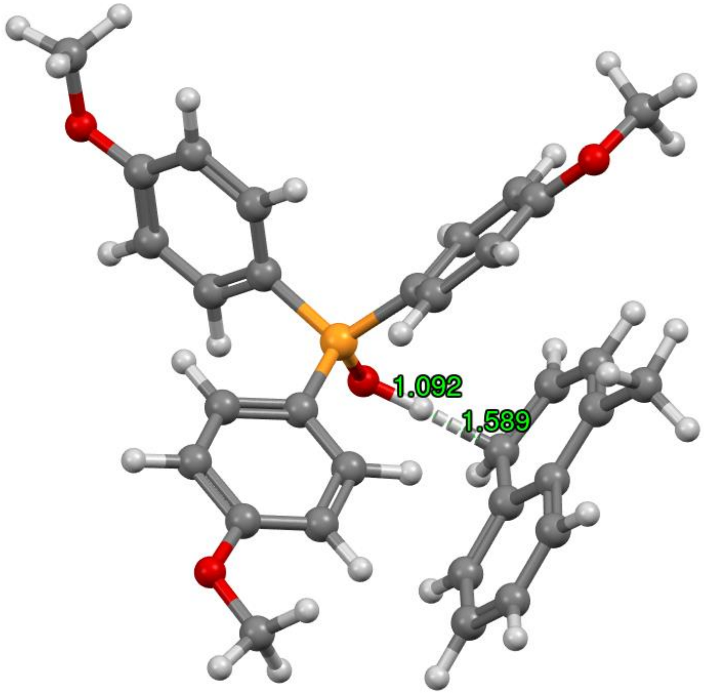
Figure S11. Gibbs free energies of the HAT from radical **P1**-OH to positions 1 and 3-8 of 2-cyano-naphthalene (**5c**).



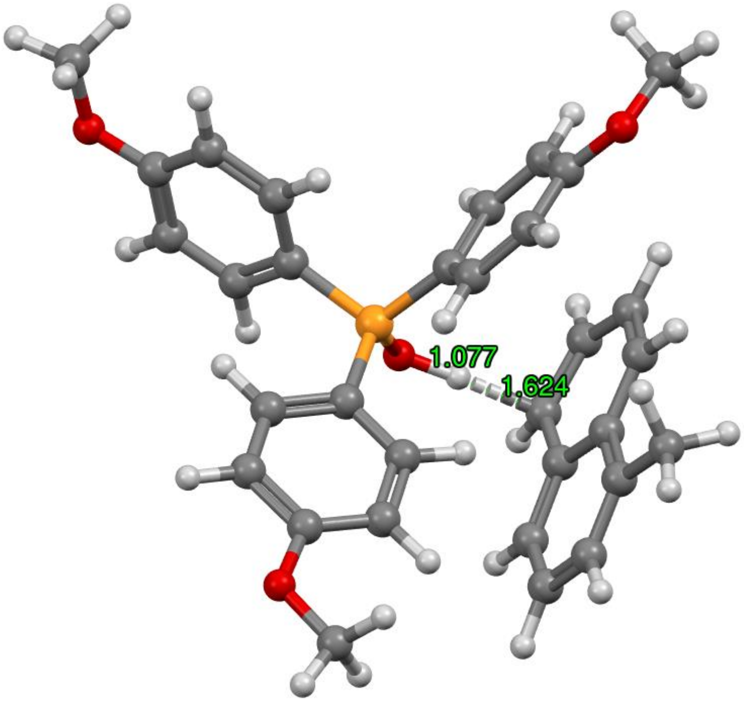
[ΔG^{s}_{298} / kcal mol^{-1}]

PWPB95-D3/def2-TZVP//PBE0-D3/def2-TZVP + COSMO-RS(CH_3CN)

Figure S12. Molecular structures of the two most favorable transition structures of HAT from **P1**-OH to **5f**, optimized with PBE0-D3/def2-TZVP. Distances are given in Å. Element colors are gray (C), white (H), red (O), orange (P).



5f-TS4



5f-TS5

12.4 DFT optimized (PBE0-D3/def2-TZVP) cartesian coordinates

P1-OH

E(PBE0-D3/def2-TZVP) = -1454.733077432 (conv)

Lowest Freq. = 19.71 cm^-1

48

P1-OH (053c1/opt)

P	1.1233471	-0.1298920	-0.0521003
C	0.6645890	1.3349228	0.8354575
C	1.3680507	2.5357125	0.6193588
H	2.2672142	2.5279084	0.0154303
C	0.9282979	3.7256067	1.1604557
H	1.4713309	4.6480365	0.9922369
C	-0.2209362	3.7634128	1.9449895
C	-0.9422345	2.5846293	2.1583676
H	-1.8502661	2.5869638	2.7462089
C	-0.5121527	1.4011672	1.5932485
H	-1.1071920	0.5066239	1.7316081
C	0.5718853	-1.5558852	0.7619883
C	0.4049334	-2.7750481	0.0459028
H	0.5771062	-2.7957180	-1.0231922
C	0.0228477	-3.9267345	0.6829465
H	-0.1164494	-4.8453277	0.1248758
C	-0.1818657	-3.9503146	2.0680686
C	0.0407002	-2.7847556	2.8040330
H	-0.0691305	-2.7796313	3.8807199
C	0.4268799	-1.6211256	2.1713895
H	0.6247854	-0.7432045	2.7739963
C	0.6402549	-0.1646770	-1.7714144
C	-0.6633938	-0.5674793	-2.0932578
H	-1.3053701	-0.9604109	-1.3127018
C	-1.1385332	-0.4715990	-3.3788508
H	-2.1404889	-0.7948638	-3.6332245
C	-0.3325499	0.0695961	-4.3867834
C	0.9536935	0.4959517	-4.0819752
H	1.5953745	0.9184926	-4.8433115

C	1.4346527	0.3696027	-2.7844289
H	2.4454275	0.6833817	-2.5609553
O	2.7429152	0.0632263	-0.2969020
H	3.1995150	0.1333396	0.5492185
O	-0.5668503	4.9708008	2.4465449
O	-0.5579554	-5.1422260	2.5991094
O	-0.8915142	0.1390161	-5.6132032
C	-1.7296198	5.0475789	3.2330362
H	-1.8242091	6.0889160	3.5356441
H	-1.6530076	4.4187376	4.1268423
H	-2.6195170	4.7560825	2.6646436
C	-0.7471349	-5.2027754	3.9878812
H	0.1770736	-4.9755179	4.5319180
H	-1.0508546	-6.2240457	4.2124840
H	-1.5327293	-4.5134254	4.3188849
C	-0.1215705	0.6839402	-6.6569453
H	0.1567431	1.7225609	-6.4488104
H	-0.7482646	0.6513761	-7.5462124
H	0.7861726	0.0970736	-6.8332200

P1=O

E(PBE0-D3/def2-TZVP) = -1454.211067460 (conv)

Lowest Freq. = 18.41 cm^-1

47

P1=O (061c1/opt)

P	1.2429435	-0.0611013	-0.0226846
C	0.6222379	1.3537838	0.9058321
C	-0.5721451	2.0115511	0.6098263
H	-1.1642811	1.6997901	-0.2434777
C	-1.0034651	3.0710057	1.3806161
H	-1.9264430	3.5919004	1.1565128
C	-0.2405927	3.5019003	2.4659699
C	0.9606423	2.8633114	2.7638224
H	1.5747943	3.1896393	3.5920523
C	1.3801113	1.7976013	1.9827392
H	2.3225748	1.3069344	2.1994461

C	0.4767874	-1.5094781	0.7284925
C	1.1366254	-2.7254800	0.5983432
H	2.0933926	-2.7517289	0.0886332
C	0.6021337	-3.8911045	1.1252790
H	1.1417064	-4.8216416	1.0130839
C	-0.6168879	-3.8450306	1.7970510
C	-1.2820071	-2.6275451	1.9425414
H	-2.2208666	-2.6111620	2.4826651
C	-0.7366448	-1.4749929	1.4165278
H	-1.2534332	-0.5317378	1.5549249
C	0.5152823	0.0776541	-1.6660274
C	-0.7394147	-0.4310118	-2.0034763
H	-1.3179231	-0.9770215	-1.2665169
C	-1.2493078	-0.2644865	-3.2742345
H	-2.2200274	-0.6596434	-3.5481370
C	-0.5067858	0.4118434	-4.2422189
C	0.7530018	0.9121578	-3.9227250
H	1.3516243	1.4276435	-4.6613417
C	1.2513672	0.7407949	-2.6404654
H	2.2385376	1.1133006	-2.3901253
O	2.7239488	-0.1350566	-0.0476119
O	-0.7388376	4.5452466	3.1608142
O	-1.2231638	-4.9181153	2.3452568
O	-1.0832732	0.5244790	-5.4565439
C	0.0009387	5.0205098	4.2601834
H	-0.5699090	5.8495618	4.6739519
H	0.9885093	5.3800005	3.9528621
H	0.1213991	4.2472395	5.0260953
C	-0.5842351	-6.1674162	2.2320729
H	-0.4611761	-6.4607088	1.1842739
H	-1.2316579	-6.8852924	2.7319909
H	0.3950006	-6.1620624	2.7219948
C	-0.3666651	1.1903869	-6.4688727
H	-0.1606250	2.2305247	-6.1956221
H	-1.0014245	1.1705071	-7.3526759
H	0.5776334	0.6825498	-6.6910980

P2-OH

E(PBE0-D3/def2-TZVP) = -1229.245313825 (conv)

Lowest Freq. = 25.83 cm^-1

45

P2-OH (018c1/opt)

P	1.0308729	-0.0979339	0.1756812
C	0.4967698	1.3576553	1.0258113
C	1.2304321	2.5480227	0.8806777
H	2.1819358	2.5333285	0.3627454
C	0.7471258	3.7413716	1.3907760
H	1.3341450	4.6456294	1.2646694
C	-0.4651820	3.8067301	2.0667794
C	-1.2037438	2.6214268	2.1924334
H	-2.1653697	2.6456825	2.6954674
C	-0.7511835	1.4317131	1.6711835
H	-1.3688599	0.5452017	1.7449707
C	0.3637336	-1.5359280	0.8871070
C	0.2825687	-2.7346610	0.1346358
H	0.5809620	-2.7364832	-0.9066045
C	-0.1727475	-3.8994487	0.7120058
H	-0.2341223	-4.7964300	0.1032570
C	-0.5424157	-3.9636150	2.0578702
C	-0.4026946	-2.7939317	2.8178883
H	-0.6428852	-2.8185927	3.8764965
C	0.0509472	-1.6191530	2.2677345
H	0.1788841	-0.7507571	2.9024226
C	0.7475843	-0.0847943	-1.5913540
C	-0.5124489	-0.4598445	-2.0688206
H	-1.2470084	-0.8575056	-1.3772746
C	-0.8258955	-0.3253764	-3.4048875
H	-1.8047590	-0.6346215	-3.7567264
C	0.0891633	0.2196917	-4.3104390
C	1.3295595	0.6142588	-3.8260336
H	2.0547927	1.0439062	-4.5094978
C	1.6658757	0.4613054	-2.4890081

H	2.6461494	0.7570391	-2.1399249
O	2.6670954	0.0353908	0.1291109
H	3.0216340	0.1078296	1.0228362
C	-0.9778101	5.0898318	2.6390686
H	-1.9874046	5.3099300	2.2804875
H	-0.3346137	5.9290848	2.3706672
H	-1.0298042	5.0442917	3.7314947
C	-1.0654114	-5.2246890	2.6669340
H	-0.7463512	-6.1020156	2.1007250
H	-2.1612564	-5.2339009	2.6912403
H	-0.7216826	-5.3437232	3.6974968
C	-0.2624275	0.3583927	-5.7583585
H	-0.2804537	-0.6184237	-6.2515521
H	0.4597640	0.9833685	-6.2851890
H	-1.2534637	0.8007462	-5.8850040

P2=O

E(PBE0-D3/def2-TZVP) = -1228.717968701 (conv)

Lowest Freq. = 16.83 cm^-1

44

P2=O (058c1/opt)

P	1.4220512	-0.0316862	0.1241210
C	0.6695207	1.3901371	0.9443001
C	-0.4958001	2.0052577	0.5005559
H	-0.9831246	1.6555755	-0.4028805
C	-1.0315814	3.0751118	1.2006552
H	-1.9411998	3.5469002	0.8435776
C	-0.4165504	3.5604441	2.3502584
C	0.7560357	2.9428858	2.7822863
H	1.2537806	3.3103964	3.6739185
C	1.2962150	1.8736816	2.0910468
H	2.2176738	1.4090732	2.4238989
C	0.6155099	-1.4830309	0.8337408
C	1.3075249	-2.6914695	0.7786006
H	2.3038538	-2.7092633	0.3511201
C	0.7346705	-3.8460554	1.2794691

H	1.2841252	-4.7807622	1.2311990
C	-0.5370848	-3.8291246	1.8505257
C	-1.2171560	-2.6171669	1.9077962
H	-2.2046481	-2.5813323	2.3561024
C	-0.6493314	-1.4543387	1.4098544
H	-1.1911797	-0.5177510	1.4818226
C	0.8596453	0.0448135	-1.5900329
C	-0.3309694	-0.5191478	-2.0340116
H	-0.9604643	-1.0699672	-1.3438518
C	-0.7116400	-0.3934218	-3.3612927
H	-1.6428508	-0.8389401	-3.6956823
C	0.0860728	0.2874883	-4.2749864
C	1.2826272	0.8415400	-3.8223297
H	1.9219896	1.3712866	-4.5212404
C	1.6688294	0.7227504	-2.4998476
H	2.6089293	1.1418327	-2.1587409
O	2.8980947	-0.0643171	0.2520786
C	-0.9776932	4.7359105	3.0886694
H	-0.8965076	4.6012222	4.1691554
H	-2.0275384	4.8981279	2.8406220
H	-0.4323903	5.6497754	2.8339874
C	-1.1376306	-5.0802869	2.4125689
H	-0.6741068	-5.3374615	3.3696647
H	-0.9854013	-5.9286229	1.7418230
H	-2.2089261	-4.9662022	2.5831641
C	-0.3101678	0.3993757	-5.7145682
H	0.2708585	-0.2923108	-6.3318738
H	-0.1284440	1.4054941	-6.0984594
H	-1.3656214	0.1635789	-5.8567852

P3-OH

E(PBE0-D3/def2-TZVP) = -1111.390124009 (conv)

Lowest Freq. = 28.03 cm^-1

36

P3-OH (011c1/opt)

P	0.7925257	-0.0821743	0.1355014

C	0.2564541	1.3804597	0.9758534
C	1.0034611	2.5639750	0.8272342
H	1.9569806	2.5355975	0.3137643
C	0.5292254	3.7622365	1.3318500
H	1.1202611	4.6626418	1.2075859
C	-0.6862331	3.8162863	1.9987199
H	-1.0502263	4.7546960	2.3988817
C	-1.4429444	2.6521331	2.1350366
H	-2.4029718	2.6857978	2.6373362
C	-0.9933108	1.4569443	1.6160496
H	-1.6129871	0.5719446	1.6886548
C	0.1195730	-1.5189909	0.8472190
C	0.0454172	-2.7159789	0.0894753
H	0.3438671	-2.7111702	-0.9517093
C	-0.4074960	-3.8835327	0.6636354
H	-0.4683227	-4.7802965	0.0569247
C	-0.7747535	-3.9282726	2.0075096
H	-1.1233222	-4.8516681	2.4525390
C	-0.6520349	-2.7708743	2.7795400
H	-0.9029426	-2.7958810	3.8342027
C	-0.1994740	-1.5948820	2.2271080
H	-0.0801052	-0.7214912	2.8563495
C	0.5086026	-0.0620174	-1.6335111
C	-0.7528390	-0.4343170	-2.1078041
H	-1.4854622	-0.8338357	-1.4154378
C	-1.0668055	-0.2951085	-3.4459567
H	-2.0428327	-0.6016845	-3.8033958
C	-0.1396577	0.2519718	-4.3278275
H	-0.3917638	0.3735703	-5.3747321
C	1.1048469	0.6444187	-3.8615191
H	1.8305871	1.0708723	-4.5445230
C	1.4358673	0.4848330	-2.5241021
H	2.4160418	0.7716597	-2.1677371
O	2.4277328	0.0429806	0.0916878
H	2.7850414	0.0991568	0.9855967

P3=O

E(PBE0-D3/def2-TZVP) = -1110.861463254 (conv)

Lowest Freq. = 24.75 cm^-1

35

P3=O (029c1/opt)

P	1.1406598	0.1260966	0.2030661
C	0.1402176	1.4425207	0.9340121
C	0.7288316	2.7011937	1.0341135
H	1.7552481	2.8298593	0.7093991
C	0.0123442	3.7626857	1.5624274
H	0.4748272	4.7396232	1.6420395
C	-1.2929407	3.5733214	1.9953259
H	-1.8515365	4.4040249	2.4111490
C	-1.8794982	2.3192868	1.9077396
H	-2.8936823	2.1674238	2.2585693
C	-1.1642878	1.2542210	1.3810233
H	-1.6173676	0.2703924	1.3319265
C	0.4678034	-1.4174401	0.8611687
C	-0.5995616	-2.0958127	0.2801165
H	-1.0474865	-1.7206907	-0.6332585
C	-1.0788989	-3.2624595	0.8567485
H	-1.9075467	-3.7899773	0.3987203
C	-0.4906769	-3.7583519	2.0110846
H	-0.8635256	-4.6725875	2.4584859
C	0.5823539	-3.0918487	2.5867850
H	1.0496622	-3.4857240	3.4818368
C	1.0624085	-1.9252404	2.0141435
H	1.9114773	-1.4041871	2.4420123
C	0.7286652	0.1231681	-1.5572301
C	-0.4784558	0.5982086	-2.0614313
H	-1.2137690	1.0291552	-1.3911464
C	-0.7347728	0.5391795	-3.4231000
H	-1.6743847	0.9139870	-3.8121442
C	0.2149265	0.0114800	-4.2856385
H	0.0150289	-0.0304205	-5.3502025
C	1.4254108	-0.4517481	-3.7884683

H	2.1722337	-0.8529667	-4.4636863
C	1.6838033	-0.3957036	-2.4285699
H	2.6319669	-0.7364734	-2.0280831
O	2.5905226	0.2858047	0.4610656

P3-Hortho

E(PBE0-D3/def2-TZVP) = -1111.412034368 (conv)

Lowest Freq. = 24.50 cm^-1

36

P3-Hortho (017c1/opt)

P	1.0922943	0.2354984	-0.0190488
C	0.0929899	1.5068525	0.7927115
C	0.6442240	2.7785585	0.9218837
H	1.6525164	2.9515004	0.5627374
C	-0.0860721	3.7940427	1.5187534
H	0.3460099	4.7829710	1.6191169
C	-1.3658337	3.5433023	1.9940682
H	-1.9342877	4.3377662	2.4638715
C	-1.9147502	2.2739388	1.8796036
H	-2.9088258	2.0745234	2.2628363
C	-1.1864981	1.2567928	1.2818410
H	-1.6067066	0.2588518	1.2074753
C	0.5956798	-1.2972720	0.7645161
C	-0.1013080	-2.2824310	0.1257835
H	-0.4019396	-2.1380478	-0.9064185
C	-0.4406074	-3.4840439	0.7720465
H	-0.9954463	-4.2453532	0.2388746
C	-0.0553429	-3.6929613	2.1143258
H	-0.3267092	-4.6216202	2.6044207
C	0.6493349	-2.7557608	2.7959280
H	0.9414655	-2.9339104	3.8250751
C	1.0564069	-1.4660277	2.1794693
H	0.6983002	-0.6239029	2.7957482
C	0.5114057	0.1547513	-1.7287637
C	-0.8166809	0.3485293	-2.0989183
H	-1.5608367	0.5883512	-1.3479502

C	-1.1883616	0.2508874	-3.4303437
H	-2.2225277	0.4060053	-3.7151685
C	-0.2350093	-0.0349873	-4.3981071
H	-0.5268167	-0.1074166	-5.4395772
C	1.0914495	-0.2176156	-4.0351405
H	1.8376506	-0.4309950	-4.7916678
C	1.4659178	-0.1220019	-2.7036368
H	2.4997111	-0.2459830	-2.4016448
O	2.5471806	0.5080691	0.0781905
H	2.1520237	-1.3508616	2.2171087

P3-TS-Styr

E(PBE0-D3/def2-TZVP) = -1420.791573061 (conv)

Lowest Freq. = -902.17 cm^-1

52

P3-TS-Styr (023TSc3/opt)

P	-1.0124655	0.6443415	0.5182938
C	-2.7358228	1.0341306	0.6760940
C	-3.2192813	1.5082601	1.9027880
H	-2.5302648	1.6824239	2.7209593
C	-4.5677036	1.7757293	2.0585280
H	-4.9343343	2.1413042	3.0106782
C	-5.4458161	1.5942059	0.9978293
H	-6.4997043	1.8128923	1.1216510
C	-4.9668412	1.1407575	-0.2266585
H	-5.6471357	1.0033603	-1.0589308
C	-3.6234133	0.8572713	-0.3891120
H	-3.2557401	0.4981643	-1.3430251
C	-0.6363582	-0.8732254	1.3372150
C	0.5911762	-1.5015593	1.0689066
H	1.2793231	-1.0805307	0.3488306
C	0.9203789	-2.6792046	1.7198255
H	1.8688976	-3.1547436	1.4982151
C	0.0509966	-3.2404274	2.6417251
H	0.3151895	-4.1602627	3.1498678
C	-1.1712346	-2.6206066	2.9097666

H	-1.8588551	-3.0611992	3.6221109
C	-1.5150292	-1.4505327	2.2664496
H	-2.4718575	-0.9843917	2.4681654
C	-0.6057046	0.5106015	-1.2175985
C	-0.5488703	-0.7180767	-1.8725934
H	-0.6980313	-1.6338210	-1.3137763
C	-0.2891951	-0.7657390	-3.2312839
H	-0.2312582	-1.7234416	-3.7340975
C	-0.0975534	0.4105697	-3.9448199
H	0.1083612	0.3702042	-5.0081453
C	-0.1648263	1.6367323	-3.2989826
H	-0.0132741	2.5539877	-3.8557662
C	-0.4152994	1.6910173	-1.9379429
H	-0.4495803	2.6439033	-1.4228661
O	-0.2433114	1.8623335	1.1366165
H	0.8003625	1.7917334	1.3269920
H	4.1496624	-1.7766574	-3.1299196
C	3.9271628	-1.2526262	-2.2082793
C	4.2632119	-1.8135423	-0.9766207
C	3.3032739	-0.0106214	-2.2348242
C	3.0141291	0.6616836	-1.0631154
C	3.9754142	-1.1475853	0.1963245
C	3.3388097	0.1093966	0.1928942
H	3.0280432	0.4357900	-3.1840141
H	4.7551603	-2.7793673	-0.9380471
H	2.5099459	1.6188643	-1.1126424
H	4.2361620	-1.5950035	1.1505817
C	2.9964073	0.7482728	1.4289517
C	2.4294915	1.9949219	1.5769618
H	3.1714557	0.1560688	2.3237366
H	2.4626870	2.7121917	0.7610296
H	2.3530595	2.4220519	2.5710734

P3-TS-Prop

E(PBE0-D3/def2-TZVP) = -1229.184121491 (conv)

Lowest Freq. = -1787.47 cm^-1

45

P3-TS-Prop (033TSc1/opt)

P	-0.3739772	0.5967447	-0.0544471
C	-2.0761663	0.9578774	0.2841329
C	-2.4072955	1.4533766	1.5540774
H	-1.6243958	1.6292009	2.2833551
C	-3.7241547	1.7373885	1.8683273
H	-3.9693965	2.1164764	2.8537819
C	-4.7261537	1.5542818	0.9240517
H	-5.7554238	1.7853890	1.1709380
C	-4.4001201	1.0844334	-0.3446229
H	-5.1763768	0.9482056	-1.0886567
C	-3.0893237	0.7854980	-0.6649195
H	-2.8446436	0.4181068	-1.6542779
C	0.1299938	-0.8633361	0.8009514
C	1.3507582	-1.4609842	0.4258322
H	1.9483467	-1.0258242	-0.3656964
C	1.7408416	-2.6603574	1.0100796
H	2.6650148	-3.1315564	0.6937676
C	0.9735237	-3.2416176	2.0014997
H	1.2920042	-4.1690796	2.4624345
C	-0.2243104	-2.6340109	2.4023931
H	-0.8321627	-3.0891719	3.1752888
C	-0.6457491	-1.4685429	1.8005724
H	-1.5913725	-1.0242571	2.0880240
C	-0.1945530	0.2921908	-1.8146382
C	-0.5130507	-0.9488966	-2.3625828
H	-0.8241310	-1.7582199	-1.7116063
C	-0.4219637	-1.1457090	-3.7310896
H	-0.6718304	-2.1109159	-4.1555993
C	-0.0027049	-0.1091897	-4.5542871
H	0.0712498	-0.2657849	-5.6243576
C	0.3299762	1.1230849	-4.0108267
H	0.6645479	1.9286257	-4.6538281
C	0.2350987	1.3258572	-2.6422208
H	0.4975567	2.2807097	-2.2023570

O	0.5172421	1.8056283	0.3333669
H	1.4348335	1.6013267	1.0006765
C	3.2487127	0.3178187	1.7385061
C	2.6203290	1.5398729	1.9041567
H	2.9957491	-0.5037008	2.3989584
H	3.0846635	2.4196368	1.4574919
H	2.0899204	1.7256581	2.8353446
C	4.3243302	0.0870747	0.7395476
H	4.3487670	-0.9468937	0.3867547
H	5.3144024	0.2977176	1.1685140
H	4.2113937	0.7458678	-0.1268107

P4-OH

E(PBE0-D3/def2-TZVP) = -1408.968422356 (conv)

Lowest Freq. = 25.46 cm^-1

36

P4-OH (037c1/opt)

P	0.8127821	-0.0700909	0.1371956
C	0.2680092	1.3853068	0.9858968
C	1.0085673	2.5741680	0.8555332
H	1.9675279	2.5574758	0.3528417
C	0.5273579	3.7710428	1.3600131
H	1.0920390	4.6900587	1.2634263
C	-0.6911229	3.7823260	2.0062895
C	-1.4588882	2.6321085	2.1406826
H	-2.4206614	2.6850191	2.6352782
C	-0.9880867	1.4498500	1.6142420
H	-1.6035210	0.5610481	1.6745379
C	0.1485480	-1.5067407	0.8452952
C	0.0661241	-2.7037400	0.0829439
H	0.3719374	-2.7024649	-0.9556451
C	-0.4051547	-3.8708867	0.6429254
H	-0.4818770	-4.7788122	0.0571232
C	-0.7735457	-3.8860553	1.9790137
C	-0.6465283	-2.7557686	2.7780443
H	-0.9043872	-2.8125154	3.8285372

C	-0.1735643	-1.5883234	2.2269620
H	-0.0417754	-0.7229675	2.8642819
C	0.5235982	-0.0583644	-1.6320890
C	-0.7502377	-0.4051666	-2.0916291
H	-1.4882572	-0.7734692	-1.3878884
C	-1.0802699	-0.2857647	-3.4267309
H	-2.0585641	-0.5636083	-3.7976773
C	-0.1307496	0.2197771	-4.3006652
C	1.1288505	0.5925782	-3.8798669
H	1.8400096	0.9832283	-4.5968781
C	1.4576245	0.4441759	-2.5407953
H	2.4486177	0.7099999	-2.1993995
O	2.4474008	0.0852118	0.0737342
H	2.8208748	0.1025630	0.9624777
F	-1.1572817	4.9320237	2.5078912
F	-1.2245955	-5.0259244	2.5252143
F	-0.4508006	0.3527017	-5.5911167

P4=O

E(PBE0-D3/def2-TZVP) = -1408.442921322 (conv)

Lowest Freq. = 24.36 cm^-1

35

P4=O (059c1/opt)

P	1.1583542	-0.0715982	0.1278489
C	0.4497878	1.4046684	0.8879480
C	1.2436304	2.5502181	0.9090242
H	2.2496198	2.5025405	0.5078646
C	0.7647881	3.7286972	1.4540330
H	1.3664195	4.6283590	1.4847768
C	-0.5151569	3.7421075	1.9771919
C	-1.3232377	2.6212688	1.9822841
H	-2.3129934	2.6749827	2.4178376
C	-0.8292635	1.4478847	1.4351581
H	-1.4441056	0.5551672	1.4502143
C	0.2805423	-1.4667935	0.8638550
C	-0.9205805	-1.9661417	0.3685112

H	-1.3596820	-1.5374900	-0.5251743
C	-1.5572539	-3.0243632	0.9970908
H	-2.4892217	-3.4311963	0.6254508
C	-0.9689932	-3.5742462	2.1201057
C	0.2302918	-3.1106973	2.6290049
H	0.6601135	-3.5824889	3.5036197
C	0.8532435	-2.0516936	1.9920328
H	1.8034575	-1.6773188	2.3554945
C	0.6398754	-0.0250746	-1.6007182
C	1.4315294	-0.7132142	-2.5186518
H	2.3290672	-1.2123537	-2.1714858
C	1.0912449	-0.7417721	-3.8597345
H	1.6947725	-1.2658986	-4.5900204
C	-0.0480820	-0.0718798	-4.2662945
C	-0.8482436	0.6284886	-3.3838722
H	-1.7223567	1.1514416	-3.7508135
C	-0.4935517	0.6500436	-2.0444855
H	-1.0999176	1.2125281	-1.3436495
O	2.6276790	-0.1599519	0.2901042
F	-0.9839723	4.8756815	2.5052514
F	-1.5759024	-4.5960174	2.7294630
F	-0.3819019	-0.0938876	-5.5592655

P5-OH

E(PBE0-D3/def2-TZVP) = -2122.041959222 (conv)

Lowest Freq. = 7.66 cm^-1

45

P5-OH (048c1/opt)

P	1.0525254	-0.0982433	0.1885241
C	0.4943039	1.3589905	1.0195604
C	1.2313075	2.5472659	0.8709735
H	2.1873978	2.5297848	0.3625459
C	0.7477064	3.7425648	1.3695396
H	1.3262707	4.6497486	1.2514392
C	-0.4732328	3.7818071	2.0260645
C	-1.2262200	2.6120645	2.1620026

H	-2.1908739	2.6461800	2.6541643
C	-0.7614789	1.4235559	1.6509311
H	-1.3766000	0.5357215	1.7218190
C	0.3784178	-1.5384863	0.8948926
C	0.3184040	-2.7328597	0.1350636
H	0.6259560	-2.7288356	-0.9031163
C	-0.1310071	-3.9034697	0.7004228
H	-0.1818466	-4.8031504	0.0999735
C	-0.5038585	-3.9458065	2.0433326
C	-0.3971939	-2.7888087	2.8223107
H	-0.6520977	-2.8242918	3.8745184
C	0.0510435	-1.6140675	2.2716536
H	0.1609095	-0.7419971	2.9039086
C	0.7628374	-0.0777272	-1.5793198
C	-0.5018389	-0.4486596	-2.0484639
H	-1.2374759	-0.8420234	-1.3564133
C	-0.8167228	-0.3172429	-3.3835277
H	-1.7911346	-0.6225657	-3.7452645
C	0.1177470	0.2202054	-4.2668720
C	1.3639996	0.6125663	-3.8097280
H	2.0872207	1.0267133	-4.5001579
C	1.6910946	0.4602617	-2.4709336
H	2.6736471	0.7451354	-2.1203858
O	2.6782365	0.0240177	0.1506249
H	3.0494876	0.0639703	1.0398616
C	-1.0037334	5.0549075	2.6052080
C	-1.0390493	-5.2000786	2.6479204
C	-0.2634045	0.3723771	-5.7098462
F	-2.3867039	-5.2139197	2.6712849
F	-0.6405928	-5.3559936	3.9199463
F	-0.6582553	-6.2924826	1.9730449
F	-1.0361781	5.0119935	3.9488529
F	-2.2617476	5.2966777	2.2045351
F	-0.2665225	6.1169217	2.2646424
F	-0.6556172	-0.7964877	-6.2384921
F	-1.2891596	1.2242800	-5.8586752

F	0.7440330	0.8294862	-6.4583657

P5=O

E(PBE0-D3/def2-TZVP) = -2121.506149093 (conv)

Lowest Freq. = 2.37 cm^-1

44

P5=O (060c1/opt)

P	1.4215354	-0.1328199	0.0707467
C	0.7939180	1.3548329	0.8866367
C	1.5200639	1.8257715	1.9779619
H	2.4313060	1.3156010	2.2680923
C	1.0911365	2.9470160	2.6652187
H	1.6577985	3.3199836	3.5093478
C	-0.0635028	3.6036468	2.2599874
C	-0.7856334	3.1486624	1.1670659
H	-1.6738500	3.6779122	0.8464107
C	-0.3537306	2.0264366	0.4790436
H	-0.9064776	1.6867401	-0.3891687
C	0.5421773	-1.5137244	0.8406888
C	1.1796071	-2.7511307	0.8227453
H	2.1685125	-2.8314544	0.3864254
C	0.5636291	-3.8587953	1.3798367
H	1.0603405	-4.8206379	1.3736092
C	-0.6895487	-3.7289003	1.9613913
C	-1.3270684	-2.4964382	1.9938324
H	-2.2961928	-2.4003722	2.4673922
C	-0.7094678	-1.3898553	1.4365238
H	-1.1984867	-0.4237995	1.4848406
C	0.8049610	-0.0476954	-1.6277487
C	-0.4463045	-0.5160413	-2.0145780
H	-1.0976767	-0.9951276	-1.2927614
C	-0.8595008	-0.3930515	-3.3311594
H	-1.8295502	-0.7643404	-3.6363220
C	-0.0160935	0.1926369	-4.2635143
C	1.2404723	0.6496241	-3.8886746
H	1.8989259	1.0894271	-4.6273481

C	1.6508128	0.5273697	-2.5731430
H	2.6369748	0.8591727	-2.2695473
O	2.8925580	-0.2637124	0.1500997
C	-0.5489620	4.7928826	3.0396849
C	-1.3859557	-4.9327313	2.5307401
C	-0.4759798	0.3719650	-5.6828688
F	-2.2297370	-5.4723308	1.6367728
F	-2.1114489	-4.6224712	3.6115113
F	-0.5254947	-5.8912750	2.8857190
F	-1.2781907	4.4114986	4.1002977
F	-1.3219853	5.5964221	2.3020759
F	0.4646660	5.5288559	3.5081348
F	-1.4002131	-0.5300913	-6.0290004
F	-1.0232499	1.5842143	-5.8651801
F	0.5349061	0.2661242	-6.5518185

CH4

E(PBE0-D3/def2-TZVP) = -40.47511350880 (conv)

Lowest Freq. = 1326.81 cm^-1

5

CH4 (CH4/opt)

H	0.0000000	0.0000000	-1.0887801
C	-0.0000000	0.0000000	0.0007861
H	-0.5136301	-0.8896334	0.3639731
H	-0.5136301	0.8896334	0.3639731
H	1.0272601	0.0000000	0.3639731

CH3

E(PBE0-D3/def2-TZVP) = -39.79976187783 (conv)

Lowest Freq. = 526.63 cm^-1

4

CH3 (CH3/opt)

C	0.0000000	0.0000000	0.0076124
H	-0.5400054	-0.9353167	0.0081699
H	-0.5400054	0.9353167	0.0081699
H	1.0800107	0.0000000	0.0081699

PROP

E(PBE0-D3/def2-TZVP) = -117.8005413712 (conv)

Lowest Freq. = 208.44 cm^-1

9

PROP (PROP/opt)

H	0.4631268	-0.9542626	-1.2205238
C	0.4121970	0.1222078	-1.0469924
H	-0.2191363	0.5661093	-1.8231063
H	1.4145821	0.5402320	-1.1829146
C	-0.1152576	0.4308312	0.3115215
C	-0.4816472	-0.4720072	1.2100400
H	-0.1982450	1.4858321	0.5661920
H	-0.8586980	-0.1832182	2.1840626
H	-0.4169217	-1.5357243	1.0017211

STYR

E(PBE0-D3/def2-TZVP) = -309.3903523134 (conv)

Lowest Freq. = 33.82 cm^-1

16

STYR (STYR/opt)

H	1.3309472	-3.1770125	-0.2468929
C	0.9641187	-2.1598721	-0.1746390
C	1.8451441	-1.0924654	-0.2394718
C	-0.3950291	-1.9164617	-0.0162321
C	-0.8675150	-0.6208111	0.0763594
C	1.3686427	0.2055883	-0.1464407
C	0.0074105	0.4667099	0.0129691
H	-1.0906268	-2.7462781	0.0352256
H	2.9073302	-1.2695702	-0.3629131
H	-1.9306523	-0.4513214	0.1993354
H	2.0613162	1.0393606	-0.1976199
C	-0.4392666	1.8570800	0.1059296
C	-1.6861334	2.2938742	0.2612986
H	0.3581260	2.5936456	0.0375760
H	-1.8990889	3.3539212	0.3177317

H	-2.5347238	1.6236127	0.3377841

5f

E(PBE0-D3/def2-TZVP) = -424.8637356965 (conv)

Lowest Freq. = 133.67 cm^-1

21

5f (094c1/opt)

C	2.5961481	1.2108281	-0.0729700
C	2.6031426	-0.1950986	-0.0828146
C	1.4262236	-0.8936268	-0.0507032
C	0.1811369	-0.2272194	-0.0071285
C	0.1778572	1.1958826	0.0024965
C	1.4082790	1.8870580	-0.0312489
C	-1.0531621	1.8866181	0.0453429
C	-2.2294778	1.1951248	0.0774079
C	-2.2247116	-0.2120131	0.0681978
C	-1.0568573	-0.9301205	0.0270289
H	3.5331319	1.7549127	-0.0985556
H	3.5468278	-0.7272817	-0.1160389
H	1.4482450	-1.9763437	-0.0588539
H	1.3931170	2.9718791	-0.0234278
H	-1.0453022	2.9712124	0.0521809
H	-3.1745868	1.7247762	0.1102356
H	-3.1701822	-0.7435977	0.0943113
C	-1.0847119	-2.4264163	0.0179736
H	-0.5521849	-2.8434301	0.8776002
H	-0.6114971	-2.8315472	-0.8811519
H	-2.1114353	-2.7915971	0.0501178

5f-TS2

E(PBE0-D3/def2-TZVP) = -1879.606496561 (conv)

Lowest Freq. = -1104.64 cm^-1

69

5f-TS2 (105TSc1/opt)

P	-0.1491301	-0.4502966	-1.1652548
C	0.0499028	1.1963437	-0.5348252

C	0.9274996	2.0646255	-1.1956864
H	1.5025965	1.7103477	-2.0423647
C	1.0819140	3.3596157	-0.7570534
H	1.7720600	4.0379806	-1.2430031
C	0.3839778	3.8086359	0.3638144
C	-0.5125679	2.9620474	1.0134562
H	-1.0594973	3.2890951	1.8857729
C	-0.6702353	1.6656174	0.5598774
H	-1.3576570	1.0081302	1.0764849
C	-1.0232737	-1.4171416	0.0373673
C	-2.1327782	-2.1965023	-0.3067970
H	-2.5119925	-2.1775212	-1.3218166
C	-2.7526037	-2.9858660	0.6344119
H	-3.6132746	-3.5923635	0.3812453
C	-2.2749947	-3.0158972	1.9492105
C	-1.1784264	-2.2370129	2.3058129
H	-0.7997487	-2.2311661	3.3188377
C	-0.5572116	-1.4450042	1.3530774
H	0.2979079	-0.8462532	1.6447235
C	-1.1258938	-0.3831311	-2.6563569
C	-2.1145673	0.5892664	-2.8280859
H	-2.2655769	1.3438111	-2.0643601
C	-2.8914693	0.6038153	-3.9641913
H	-3.6586209	1.3538759	-4.1118043
C	-2.6955265	-0.3568098	-4.9598656
C	-1.7078505	-1.3258632	-4.8026153
H	-1.5319073	-2.0713401	-5.5658324
C	-0.9298001	-1.3307377	-3.6549987
H	-0.1504143	-2.0743219	-3.5375431
O	1.2057886	-1.0797491	-1.5668921
H	2.1033588	-1.0959341	-0.8984239
O	0.6428354	5.0699880	0.7513280
O	-2.9426582	-3.8194659	2.7975937
O	-3.5006565	-0.2620135	-6.0334972
C	0.0399053	5.5332607	1.9388437
H	0.4301148	6.5354933	2.1042099

H	0.3012956	4.8939919	2.7872452
H	-1.0495241	5.5822928	1.8407562
C	-2.4899417	-3.8959495	4.1300318
H	-1.4600294	-4.2634844	4.1800748
H	-3.1491342	-4.6002339	4.6334322
H	-2.5507131	-2.9232229	4.6285049
C	-3.3379798	-1.2013068	-7.0714153
H	-2.3365768	-1.1419520	-7.5095321
H	-4.0770905	-0.9463653	-7.8280471
H	-3.5191135	-2.2215632	-6.7182317
C	1.8183143	1.0690087	4.0218323
C	2.1685066	2.3044060	3.4862186
C	2.7817294	2.3527460	2.2372276
C	3.0298181	1.1981152	1.5005328
C	2.6559885	-0.0837112	2.0344050
C	2.0639569	-0.0996255	3.3260981
C	2.8893669	-1.2527889	1.2825645
C	3.4036482	-1.1435756	-0.0473776
C	3.8871525	0.1166062	-0.4960687
C	3.6829137	1.2487085	0.2257790
H	1.3591877	1.0174905	5.0038318
H	1.9937918	3.2147948	4.0482842
H	3.0827357	3.3072795	1.8167381
H	1.8092807	-1.0503568	3.7799040
H	3.8043159	-2.0420101	-0.5126118
H	4.3836276	0.1719381	-1.4602295
H	4.0153326	2.2115453	-0.1462581
C	2.6655290	-2.6121312	1.8635265
H	3.4144227	-2.8427801	2.6326911
H	2.7436154	-3.3778365	1.0894530
H	1.6860455	-2.7275883	2.3358406

5f-TS3

E(PBE0-D3/def2-TZVP) = -1879.608539787 (conv)

Lowest Freq. = -1077.89 cm^-1

69

5f-TS3 (106TSc1/opt)

P	-0.2443678	-0.7764191	-1.0225724
C	-0.0269074	0.8640663	-0.3816300
C	0.7901697	1.7485502	-1.0964690
H	1.3185050	1.4049562	-1.9779356
C	0.9327189	3.0512901	-0.6783244
H	1.5557479	3.7511892	-1.2202719
C	0.2923590	3.4894095	0.4824390
C	-0.5320076	2.6222778	1.1937637
H	-1.0295714	2.9396556	2.0984569
C	-0.6890257	1.3193125	0.7533624
H	-1.3316804	0.6502659	1.3106713
C	-1.1136050	-1.7656883	0.1663871
C	-2.2165802	-2.5458301	-0.1996554
H	-2.5925583	-2.5060128	-1.2152000
C	-2.8336786	-3.3624522	0.7190700
H	-3.6889319	-3.9686975	0.4477148
C	-2.3601807	-3.4218179	2.0348083
C	-1.2682283	-2.6475178	2.4131690
H	-0.8913221	-2.6688313	3.4267458
C	-0.6501194	-1.8258071	1.4829380
H	0.1959087	-1.2242825	1.7898031
C	-1.2421631	-0.6775654	-2.4996897
C	-2.2821853	0.2498051	-2.6034293
H	-2.4634597	0.9485404	-1.7943799
C	-3.0717900	0.2913576	-3.7298479
H	-3.8792830	1.0067072	-3.8254022
C	-2.8355217	-0.5947211	-4.7843936
C	-1.7960297	-1.5167123	-4.6949858
H	-1.5891021	-2.2036721	-5.5039350
C	-1.0070544	-1.5506760	-3.5548680
H	-0.1895445	-2.2585738	-3.4870271
O	1.1050185	-1.3965805	-1.4526426
H	2.0046759	-1.3651180	-0.7794312
O	0.5322878	4.7626620	0.8385067
O	-3.0283808	-4.2481614	2.8611389

O	-3.6562927	-0.4777203	-5.8438211
C	-0.0291124	5.2283858	2.0455766
H	0.3353458	6.2455037	2.1749061
H	0.2930966	4.6128110	2.8901941
H	-1.1229485	5.2402521	1.9971991
C	-2.5857232	-4.3501672	4.1949459
H	-1.5554620	-4.7165668	4.2461599
H	-3.2470213	-5.0657640	4.6793125
H	-2.6527445	-3.3876750	4.7123055
C	-3.4554490	-1.3416607	-6.9389944
H	-2.4635593	-1.2018242	-7.3803969
H	-4.2154497	-1.0809503	-7.6726088
H	-3.5781420	-2.3898354	-6.6479635
C	1.6739714	1.0908888	4.0293215
C	2.1854179	2.2723228	3.4989184
C	2.8664865	2.2408894	2.2838092
C	3.0394881	1.0563205	1.5709084
C	2.5137265	-0.1669551	2.1123058
C	1.8359726	-0.1028906	3.3584998
C	2.6797285	-1.3666598	1.4111561
C	3.2604391	-1.3816810	0.1134997
C	3.8579128	-0.1755864	-0.3505691
C	3.7512466	1.0099901	0.3144634
H	1.1542329	1.1055449	4.9818450
H	2.0790109	3.2057522	4.0398941
H	3.2684581	3.1628551	1.8810553
H	1.4627349	-1.0255355	3.7932836
H	2.3280265	-2.2914116	1.8563514
H	3.6256920	-2.3238236	-0.2895954
H	4.3993963	-0.1971200	-1.2928942
C	4.3909457	2.2501029	-0.2181139
H	3.6617339	3.0536453	-0.3681556
H	4.8795284	2.0534394	-1.1739027
H	5.1452003	2.6402151	0.4742203

5f-TS4

E(PBE0-D3/def2-TZVP) = -1879.613187414 (conv)

Lowest Freq. = -884.80 cm^-1

69

5f-TS4 (107TSc1/opt)

P	-0.3300766	1.1515157	0.2313778
C	-1.6782670	2.1730545	0.7979270
C	-1.5545595	3.5659335	0.7803509
H	-0.6167413	4.0151653	0.4760163
C	-2.6098307	4.3653947	1.1595599
H	-2.5272252	5.4452792	1.1542638
C	-3.8138789	3.7899882	1.5706676
C	-3.9446273	2.4029616	1.6004350
H	-4.8646819	1.9361738	1.9238836
C	-2.8777291	1.6077839	1.2133577
H	-2.9804666	0.5288731	1.2429444
C	-0.4320652	-0.4300245	1.0156311
C	-0.8286066	-1.5827974	0.3271595
H	-1.0149918	-1.5345740	-0.7386257
C	-0.9801049	-2.7762313	0.9904605
H	-1.2738026	-3.6780902	0.4685442
C	-0.7356383	-2.8455816	2.3687758
C	-0.3600775	-1.7055118	3.0678051
H	-0.1639163	-1.7433013	4.1304503
C	-0.1993145	-0.5049491	2.3917737
H	0.1130803	0.3766734	2.9381707
C	-0.4743281	0.9531245	-1.5254196
C	-1.4944490	1.5678144	-2.2591663
H	-2.2387137	2.1698944	-1.7517161
C	-1.5634908	1.4124668	-3.6249866
H	-2.3484658	1.8820450	-4.2048319
C	-0.6083048	0.6392409	-4.2914004
C	0.4090070	0.0204785	-3.5707966
H	1.1673208	-0.5784324	-4.0547761
C	0.4733618	0.1812585	-2.1976103
H	1.2783564	-0.3047099	-1.6584686

O	0.9653321	1.9059066	0.6351542
H	1.9065346	1.3636460	0.7459247
O	-4.7862210	4.6499054	1.9241040
O	-0.8870504	-4.0631211	2.9256434
O	-0.7511023	0.5490773	-5.6265413
C	-6.0204461	4.1199973	2.3503181
H	-6.6519888	4.9749337	2.5826836
H	-5.9016243	3.5038544	3.2473025
H	-6.4928646	3.5251816	1.5620052
C	-0.5980003	-4.2029137	4.2962088
H	0.4404556	-3.9319845	4.5132631
H	-0.7529643	-5.2535555	4.5335333
H	-1.2663943	-3.5910307	4.9111154
C	0.1995611	-0.2083197	-6.3410175
H	1.2084732	0.1962942	-6.2131897
H	-0.0870023	-0.1419804	-7.3886334
H	0.1903176	-1.2570206	-6.0276234
C	3.9426977	-0.0582428	-2.6891174
C	3.6415280	-1.4141409	-2.7155583
C	3.2676892	-2.0647261	-1.5491496
C	3.1931673	-1.3857544	-0.3172542
C	3.4863722	0.0141819	-0.2989599
C	3.8547641	0.6428630	-1.4952592
C	3.3559798	0.7405177	0.9349382
C	3.1604245	0.0179454	2.1352394
C	2.8917027	-1.3346426	2.0983958
C	2.8625603	-2.0518173	0.9031761
H	4.2394083	0.4549559	-3.5969676
H	3.7080879	-1.9704238	-3.6445918
H	3.0435969	-3.1239252	-1.5814428
H	4.0806571	1.7042392	-1.4733747
H	3.8033189	1.7310584	0.9815870
H	3.1909107	0.5391155	3.0858061
H	2.6967876	-1.8639246	3.0256524
C	2.5500405	-3.5098195	0.8995637
H	1.6601838	-3.7353596	0.2983278

H	2.3570290	-3.8659257	1.9131018
H	3.3713058	-4.1059607	0.4838795

5f-TS5

E(PBE0-D3/def2-TZVP) = -1879.611788731 (conv)

Lowest Freq. = -779.44 cm^-1

69

5f-TS5 (101TSc1/opt)

P	-0.3383649	1.1695856	0.3160732
C	-1.6885813	2.1765493	0.9006683
C	-1.5737960	3.5705944	0.8995117
H	-0.6399858	4.0297322	0.5977545
C	-2.6329756	4.3584989	1.2915494
H	-2.5572386	5.4388728	1.2988929
C	-3.8319946	3.7705848	1.6997711
C	-3.9538331	2.3824121	1.7131173
H	-4.8700014	1.9058782	2.0333705
C	-2.8834307	1.5988198	1.3127479
H	-2.9799237	0.5190546	1.3285712
C	-0.4307168	-0.4259085	1.0727891
C	-0.8063045	-1.5725965	0.3607990
H	-0.9935384	-1.5072710	-0.7037683
C	-0.9302338	-2.7814812	0.9991395
H	-1.2038920	-3.6785502	0.4580921
C	-0.6788109	-2.8761776	2.3738328
C	-0.3359113	-1.7401186	3.0982575
H	-0.1401241	-1.7948809	4.1601541
C	-0.2041548	-0.5241629	2.4479691
H	0.0907257	0.3519330	3.0129830
C	-0.4782752	0.9998865	-1.4424160
C	-1.4911262	1.6351849	-2.1695536
H	-2.2323312	2.2348040	-1.6547465
C	-1.5570866	1.5022492	-3.5375355
H	-2.3367784	1.9869729	-4.1120219
C	-0.6056492	0.7322393	-4.2136993
C	0.4042475	0.0937758	-3.5001312

H	1.1590854	-0.5039483	-3.9910795
C	0.4653395	0.2305182	-2.1242077
H	1.2649181	-0.2705204	-1.5907214
O	0.9527508	1.9295261	0.7356465
H	1.8943345	1.4126516	0.8166086
O	-4.8084476	4.6198959	2.0669596
O	-0.8042173	-4.1067793	2.9068800
O	-0.7455441	0.6646810	-5.5505814
C	-6.0381582	4.0770925	2.4901023
H	-6.6742020	4.9251589	2.7350008
H	-5.9128545	3.4505538	3.3789562
H	-6.5092578	3.4893148	1.6957567
C	-0.5162642	-4.2669064	4.2759388
H	0.5149985	-3.9771118	4.5018375
H	-0.6484708	-5.3252479	4.4917384
H	-1.2007830	-3.6828145	4.8999785
C	0.2011712	-0.0884940	-6.2745750
H	1.2127266	0.3067068	-6.1383764
H	-0.0824676	-0.0039352	-7.3216765
H	0.1836585	-1.1418146	-5.9774192
C	3.8502150	-0.2792640	-2.5854120
C	3.4802847	-1.6170655	-2.4984084
C	3.1089386	-2.1863572	-1.2878054
C	3.1159257	-1.3960658	-0.1102945
C	3.4612056	-0.0108761	-0.2067513
C	3.8250634	0.5167135	-1.4514132
C	3.3909114	0.8036850	0.9769421
C	3.2211330	0.1872841	2.2379330
C	2.9141756	-1.1546576	2.3184014
C	2.8216757	-1.9364243	1.1677147
H	4.1458516	0.1426715	-3.5394386
H	3.4912486	-2.2386791	-3.3889631
H	4.0965465	1.5655396	-1.5143038
H	3.8377110	1.7940933	0.9291106
H	3.2959008	0.7859739	3.1393004
H	2.7440495	-1.6101210	3.2875945

H	2.5656207	-2.9840404	1.2557080
C	2.7270137	-3.6308826	-1.2168396
H	2.7364877	-4.0841447	-2.2093923
H	1.7265242	-3.7635024	-0.7915151
H	3.4152864	-4.1988883	-0.5811061

5f-TS6

E(PBE0-D3/def2-TZVP) = -1879.607435551 (conv)

Lowest Freq. = -1099.27 cm^-1

69

5f-TS6 (102TSc1/opt)

P	-0.2179906	-0.8365319	-1.1135467
C	-0.0089841	0.8053261	-0.4719914
C	0.8297719	1.6825726	-1.1690078
H	1.3757412	1.3333344	-2.0372419
C	0.9786792	2.9825139	-0.7466741
H	1.6293353	3.6712171	-1.2709179
C	0.3189652	3.4270846	0.3999879
C	-0.5231403	2.5649402	1.0980815
H	-1.0326048	2.8862760	1.9948110
C	-0.6853104	1.2652794	0.6534383
H	-1.3421755	0.6010153	1.1998758
C	-1.0837607	-1.8301242	0.0724724
C	-2.1631455	-2.6388593	-0.3027948
H	-2.5259966	-2.6147420	-1.3236435
C	-2.7732349	-3.4635015	0.6130448
H	-3.6101788	-4.0916488	0.3345727
C	-2.3159779	-3.5030065	1.9357417
C	-1.2485358	-2.7001805	2.3235246
H	-0.8855409	-2.7057509	3.3424031
C	-0.6374050	-1.8695542	1.3961942
H	0.1887423	-1.2448572	1.7103710
C	-1.2104877	-0.7439685	-2.5945443
C	-2.2547670	0.1780626	-2.7027680
H	-2.4426493	0.8765069	-1.8949721
C	-3.0406047	0.2148525	-3.8319663

H	-3.8513469	0.9260622	-3.9308968
C	-2.7963365	-0.6709496	-4.8849061
C	-1.7526089	-1.5877032	-4.7910909
H	-1.5394856	-2.2743190	-5.5987272
C	-0.9672696	-1.6166379	-3.6483261
H	-0.1463188	-2.3202347	-3.5772132
O	1.1385204	-1.4461358	-1.5390335
H	2.0325196	-1.4111284	-0.8617902
O	0.5584150	4.6995165	0.7582640
O	-2.9757413	-4.3398166	2.7584753
O	-3.6140594	-0.5589205	-5.9472367
C	0.0040443	5.1614044	1.9699938
H	0.3796927	6.1734882	2.1066835
H	0.3218646	4.5352805	2.8085776
H	-1.0896801	5.1858474	1.9237909
C	-2.5481712	-4.4236326	4.0983787
H	-1.5101019	-4.7646868	4.1649909
H	-3.1982604	-5.1522589	4.5784950
H	-2.6450149	-3.4601408	4.6091487
C	-3.4053005	-1.4229121	-7.0408752
H	-2.4126322	-1.2786450	-7.4791015
H	-4.1641088	-1.1666541	-7.7772884
H	-3.5238238	-2.4713912	-6.7492161
C	1.6986008	1.1120473	3.9321940
C	2.2641278	2.2704040	3.4057362
C	2.9647399	2.2394337	2.1991122
C	3.0808025	1.0325442	1.4950668
C	2.5185191	-0.1725583	2.0373838
C	1.8274110	-0.0902503	3.2728973
C	2.6744347	-1.3836873	1.3478704
C	3.2755098	-1.4335322	0.0565231
C	3.8943361	-0.2450404	-0.4191293
C	3.7832765	0.9379177	0.2460237
H	1.1675738	1.1551372	4.8775516
H	2.1887514	3.2051003	3.9519964
H	1.4221358	-0.9992192	3.7073237

H	2.3028632	-2.2961287	1.8019512
H	3.6273182	-2.3900547	-0.3240517
H	4.4391778	-0.2788157	-1.3579881
H	4.2375520	1.8280264	-0.1706349
C	3.6217326	3.4873577	1.6925442
H	3.2965582	3.7452537	0.6812461
H	4.7109599	3.3797453	1.6609210
H	3.3900784	4.3346312	2.3399155

5f-TS7

E(PBE0-D3/def2-TZVP) = -1879.607591181 (conv)

Lowest Freq. = -1114.00 cm^-1

69

5f-TS7 (103TSc1/opt)

P	-0.1119367	-0.5742905	-1.2271775
C	0.0819993	1.0725734	-0.5947377
C	0.8935889	1.9695081	-1.3006360
H	1.4319438	1.6355717	-2.1794919
C	1.0266234	3.2698655	-0.8719104
H	1.6643668	3.9709968	-1.3957034
C	0.3741503	3.6971948	0.2844003
C	-0.4532211	2.8201134	0.9832583
H	-0.9609029	3.1289427	1.8853881
C	-0.5916675	1.5186864	0.5386162
H	-1.2287821	0.8397337	1.0905584
C	-1.0154109	-1.5407390	-0.0470852
C	-2.1807485	-2.2313834	-0.4002572
H	-2.5636255	-2.1603468	-1.4113862
C	-2.8508212	-2.9967258	0.5251507
H	-3.7538041	-3.5338328	0.2627273
C	-2.3720049	-3.0890413	1.8365888
C	-1.2139112	-2.4094962	2.2002366
H	-0.8299869	-2.4640727	3.2094184
C	-0.5380292	-1.6435155	1.2627305
H	0.3640664	-1.1175297	1.5556459
C	-1.0668997	-0.4890202	-2.7325682

C	-2.0727143	0.4672159	-2.8947158
H	-2.2494119	1.1997810	-2.1152067
C	-2.8348255	0.4932145	-4.0406839
H	-3.6155635	1.2305530	-4.1809995
C	-2.6047990	-0.4382958	-5.0564230
C	-1.5989129	-1.3900342	-4.9090049
H	-1.3971246	-2.1128904	-5.6874102
C	-0.8376967	-1.4077283	-3.7501909
H	-0.0461180	-2.1391071	-3.6378806
O	1.2451038	-1.2109101	-1.6081759
H	2.1621580	-1.1450974	-0.9669176
O	0.6054684	4.9692164	0.6539823
O	-3.0983500	-3.8526205	2.6750152
O	-3.3972281	-0.3342109	-6.1384637
C	0.0388984	5.4188264	1.8645572
H	0.3979089	6.4362714	2.0060550
H	0.3616027	4.7963904	2.7040879
H	-1.0548925	5.4260032	1.8144220
C	-2.6500698	-3.9848199	4.0042552
H	-1.6541864	-4.4373817	4.0462261
H	-3.3641632	-4.6387072	4.5007869
H	-2.6281298	-3.0173986	4.5163940
C	-3.2004177	-1.2438262	-7.1968234
H	-2.1947457	-1.1523371	-7.6192955
H	-3.9346377	-0.9858101	-7.9571546
H	-3.3643003	-2.2761041	-6.8713317
C	1.9654376	1.1283898	3.9244683
C	2.2736922	2.3656534	3.3610408
C	2.8563206	2.4150234	2.1021847
C	3.1028568	1.2504797	1.3802688
C	2.7628693	-0.0268203	1.9430121
C	2.2133444	-0.0593240	3.2620011
C	2.9941543	-1.1859130	1.1896580
C	3.4742031	-1.1173392	-0.1510142
C	3.9282634	0.1457095	-0.6264471
C	3.7218987	1.2836145	0.0870994

H	1.5409750	1.0887278	4.9236820
H	2.0900817	3.2764561	3.9197162
H	3.1278423	3.3688910	1.6610045
H	2.7734887	-2.1563205	1.6169037
H	3.8792023	-2.0183576	-0.6059566
H	4.4039552	0.1998040	-1.6010845
H	4.0294743	2.2453622	-0.3091209
C	1.9761715	-1.3706813	3.9384437
H	2.9203773	-1.8996911	4.1133156
H	1.3605232	-2.0485748	3.3381417
H	1.4870288	-1.2284749	4.9038129

5f-TS8

E(PBE0-D3/def2-TZVP) = -1879.612415674 (conv)

Lowest Freq. = -823.65 cm^-1

69

5f-TS8 (104TSc1/opt)

P	-0.4096945	0.8711940	0.3487133
C	-1.7600014	1.8877491	0.9169473
C	-1.6383312	3.2811876	0.9134693
H	-0.7000509	3.7349992	0.6175180
C	-2.6962279	4.0753626	1.2963974
H	-2.6150984	5.1553621	1.3016449
C	-3.9005175	3.4944140	1.6988809
C	-4.0290207	2.1068859	1.7153182
H	-4.9492551	1.6356229	2.0317012
C	-2.9602359	1.3170488	1.3231994
H	-3.0621398	0.2377959	1.3415532
C	-0.5084697	-0.7177461	1.1187641
C	-0.9272536	-1.8623038	0.4285468
H	-1.1381438	-1.8036485	-0.6320250
C	-1.0667230	-3.0610665	1.0833427
H	-1.3743921	-3.9566827	0.5586272
C	-0.7894009	-3.1464203	2.4537114
C	-0.3969727	-2.0129185	3.1560943
H	-0.1773844	-2.0610858	4.2136609

C	-0.2477374	-0.8079078	2.4883401
H	0.0826646	0.0665256	3.0358278
C	-0.5367188	0.6905244	-1.4096273
C	-1.5027672	1.3780399	-2.1534458
H	-2.2208184	2.0146467	-1.6503727
C	-1.5522639	1.2502493	-3.5223846
H	-2.2955302	1.7757198	-4.1091732
C	-0.6303619	0.4324756	-4.1834825
C	0.3302776	-0.2606348	-3.4536903
H	1.0609842	-0.8960964	-3.9332340
C	0.3754960	-0.1286171	-2.0764628
H	1.1382516	-0.6723074	-1.5307396
O	0.8820000	1.6270610	0.7745736
H	1.8200724	1.0916456	0.8551913
O	-4.8750389	4.3494542	2.0581579
O	-0.9383765	-4.3666423	3.0045082
O	-0.7480592	0.3760536	-5.5229684
C	-6.1094612	3.8135471	2.4762394
H	-6.7428089	4.6652086	2.7156070
H	-5.9917602	3.1887498	3.3673674
H	-6.5791885	3.2258663	1.6809980
C	-0.6294936	-4.5178893	4.3699002
H	0.4140118	-4.2563211	4.5730579
H	-0.7889188	-5.5689786	4.6022120
H	-1.2843563	-3.9055786	4.9987166
C	0.1742456	-0.4207388	-6.2316943
H	1.2015254	-0.0790064	-6.0706758
H	-0.0817303	-0.3155955	-7.2840461
H	0.0961668	-1.4734665	-5.9422883
C	3.7590842	-0.4619147	-2.6030641
C	3.4837957	-1.8243238	-2.5744911
C	3.1451466	-2.4349959	-1.3812359
C	3.0965111	-1.7017054	-0.1814098
C	3.3763738	-0.3002214	-0.2160109
C	3.6918620	0.3102737	-1.4474661
C	3.2875397	0.4461869	1.0120013

C	3.1214861	-0.2442063	2.2383418
C	2.8518772	-1.5978190	2.2491920
C	2.8021533	-2.3193444	1.0624204
H	4.0178200	0.0183379	-3.5413911
H	3.5407818	-2.4086427	-3.4868564
H	2.9339877	-3.4988792	-1.3490344
H	3.7311694	1.4373984	1.0390014
H	3.1777241	0.3081342	3.1700697
H	2.6809542	-2.1051003	3.1922159
H	2.5860552	-3.3817989	1.0751868
C	3.9488179	1.7824834	-1.5078562
H	4.1537836	2.0993718	-2.5314295
H	4.8043855	2.0718077	-0.8878449
H	3.0876985	2.3532210	-1.1428163

5f-H2

E(PBE0-D3/def2-TZVP) = -425.4149146717 (conv)

Lowest Freq. = 61.46 cm^-1

22

5f-H2 (118c1/opt)

C	2.7290840	1.2223825	-0.1021585
C	2.7402769	-0.1728417	-0.1085290
C	1.5609897	-0.8821545	-0.0652573
C	0.3072403	-0.2246691	-0.0133113
C	0.3112035	1.2056406	-0.0078889
C	1.5158013	1.8934231	-0.0519966
C	-0.9493398	1.9091875	0.0439701
C	-2.1197656	1.2684754	0.0875200
C	-2.2115427	-0.2156804	0.0864400
C	-0.9050334	-0.9285978	0.0317301
H	3.6590071	1.7768749	-0.1362069
H	3.6843898	-0.7044017	-0.1478533
H	1.5917560	-1.9646807	-0.0708866
H	1.4964158	2.9785903	-0.0467384
H	-0.9197951	2.9944400	0.0464362
H	-3.0482483	1.8286240	0.1256991

H	-2.8465400	-0.5472786	-0.7541044
C	-0.9468249	-2.4190453	0.0281678
H	-0.4146727	-2.8450897	0.8861413
H	-0.4817925	-2.8392014	-0.8706928
H	-1.9754857	-2.7813580	0.0662878
H	-2.7771236	-0.5526394	0.9732314

5f-H3

E(PBE0-D3/def2-TZVP) = -425.4145047024 (conv)

Lowest Freq. = 92.60 cm^-1

22

5f-H3 (119c1/opt)

C	2.7345206	1.1355311	-0.0958470
C	2.7311886	-0.2606303	-0.1155419
C	1.5261295	-0.9497443	-0.0764071
C	0.3084695	-0.2835963	-0.0171090
C	0.3040229	1.1483748	0.0042273
C	1.5479634	1.8256554	-0.0373573
C	-0.8969628	1.8477545	0.0645866
C	-2.2115310	1.1704893	0.1107762
C	-2.1177480	-0.3134225	0.0827449
C	-0.9643198	-0.9944649	0.0241414
H	3.6740873	1.6753255	-0.1265714
H	3.6654071	-0.8071844	-0.1613370
H	1.5404504	-2.0326415	-0.0925898
H	1.5450118	2.9104049	-0.0215662
H	-0.8731088	2.9322770	0.0796828
H	-2.8481628	1.5167599	-0.7213850
H	-3.0533782	-0.8643967	0.1125854
C	-0.9620013	-2.4909107	0.0000252
H	-0.4124924	-2.9025701	0.8516973
H	-0.4840044	-2.8742069	-0.9062498
H	-1.9807159	-2.8774645	0.0353146
H	-2.7728254	1.4886606	1.0061797

5f-H4

E(PBE0-D3/def2-TZVP) = -425.4227859471 (conv)

Lowest Freq. = 77.21 cm^-1

22

5f-H4 (120c1/opt)

C	2.6786404	1.0793747	-0.0756857
C	2.6733225	-0.3096350	-0.0993038
C	1.4752435	-0.9942775	-0.0683907
C	0.2450574	-0.3177234	-0.0127333
C	0.2604393	1.0935698	0.0116203
C	1.4744054	1.7634508	-0.0206907
C	-1.0156556	1.8839855	0.0734269
C	-2.2478277	1.0570889	0.0921123
C	-2.2027612	-0.3044552	0.0665187
C	-1.0050115	-1.0324523	0.0171808
H	3.6143667	1.6252752	-0.1001402
H	3.6074467	-0.8577995	-0.1422608
H	1.4837707	-2.0770186	-0.0878598
H	1.4747433	2.8492389	-0.0021555
H	-1.0509914	2.5850695	-0.7742237
H	-3.2028377	1.5685808	0.1299868
H	-3.1356892	-0.8602239	0.0844934
C	-1.0293125	-2.5222964	-0.0075965
H	-0.4928653	-2.9526309	0.8454560
H	-0.5548074	-2.9222980	-0.9107188
H	-2.0545501	-2.8927313	0.0221191
H	-0.9951263	2.5379081	0.9588453

5f-H5

E(PBE0-D3/def2-TZVP) = -425.4218075840 (conv)

Lowest Freq. = 78.80 cm^-1

22

5f-H5 (114c1/opt)

C	2.6027238	1.0561522	-0.0535326
C	2.5585639	-0.3050240	-0.0808644
C	1.3465965	-1.0047185	-0.0561766

C	0.0952812	-0.3182056	-0.0073926
C	0.0833044	1.0931057	0.0205408
C	1.3668197	1.8769156	0.0077604
C	-1.1257736	1.7703207	0.0623182
C	-2.3246324	1.0791665	0.0787838
C	-2.3180668	-0.3107110	0.0539774
C	-1.1330104	-1.0227022	0.0111814
H	3.5548668	1.5742159	-0.0732692
H	3.4857369	-0.8667985	-0.1233163
H	1.3590741	-2.0858589	-0.0782783
H	1.3510481	2.5841643	-0.8355093
H	-1.1254799	2.8557742	0.0824462
H	-3.2646615	1.6173855	0.1111405
H	-3.2580779	-0.8522897	0.0677751
C	-1.1588135	-2.5195517	-0.0155836
H	-0.6308683	-2.9469617	0.8418502
H	-0.6808775	-2.9148371	-0.9166964
H	-2.1853314	-2.8863638	0.0068439
H	1.4015777	2.5268221	0.8960017

5f-H6

E(PBE0-D3/def2-TZVP) = -425.4131591360 (conv)

Lowest Freq. = 102.42 cm^-1

22

5f-H6 (115c1/opt)

C	2.5662686	1.1718256	-0.0288847
C	2.4735922	-0.3134049	-0.0447038
C	1.3049764	-0.9647990	-0.0337035
C	0.0291535	-0.2843534	-0.0044661
C	0.0372696	1.1464173	0.0123516
C	1.2444028	1.8413074	-0.0000059
C	-1.2024027	1.8303507	0.0416634
C	-2.3833264	1.1330415	0.0541558
C	-2.3770678	-0.2642083	0.0375249
C	-1.1847378	-0.9801783	0.0081290
H	3.1512166	1.5163085	-0.8990520

H	3.4029575	-0.8731464	-0.0663387
H	1.3077789	-2.0483712	-0.0467334
H	1.2202751	2.9259727	0.0124228
H	-1.1996581	2.9148980	0.0544591
H	-3.3278931	1.6645840	0.0770856
H	-3.3171100	-0.8046934	0.0476255
C	-1.2221769	-2.4793907	-0.0093314
H	-0.7099381	-2.9069304	0.8570151
H	-0.7400308	-2.8851335	-0.9030227
H	-2.2522540	-2.8365193	0.0038835
H	3.1787046	1.4964232	0.8299260

5f-H7

E(PBE0-D3/def2-TZVP) = -425.4146258173 (conv)

Lowest Freq. = 102.48 cm^-1

22

5f-H7 (116c1/opt)

C	2.4680933	1.2815602	-0.0424504
C	2.5734718	-0.2027839	-0.0392616
C	1.2618337	-0.8967120	-0.0185048
C	0.0426204	-0.2262221	-0.0002458
C	0.0296566	1.2058728	-0.0027076
C	1.2899096	1.9117985	-0.0250873
C	-1.1768725	1.8901412	0.0155686
C	-2.3792913	1.2025994	0.0361281
C	-2.3780420	-0.1941652	0.0382481
C	-1.2063170	-0.9206006	0.0205759
H	3.3908973	1.8519665	-0.0592547
H	3.1629327	-0.5347582	-0.9108647
H	1.2757482	-1.9796359	-0.0172067
H	1.2541026	2.9969700	-0.0279118
H	-1.1668647	2.9751623	0.0134364
H	-3.3183076	1.7426359	0.0504518
H	-3.3237019	-0.7262178	0.0544128
C	-1.2412394	-2.4148052	0.0236475
H	-0.7242188	-2.8270168	0.8958002

H	-0.7521192	-2.8299683	-0.8630723
H	-2.2695750	-2.7767807	0.0405686
H	3.1872832	-0.5290401	0.8177295

5f-H8

E(PBE0-D3/def2-TZVP) = -425.4225552921 (conv)

Lowest Freq. = 107.07 cm^-1

22

5f-H8 (117c1/opt)

C	2.5504677	1.2682227	-0.0727577
C	2.6038102	-0.0946066	-0.0672411
C	1.3767534	-0.9320487	-0.0282464
C	0.0834007	-0.1687476	-0.0005860
C	0.0920741	1.2418089	-0.0078682
C	1.3318733	1.9500790	-0.0432359
C	-1.1283856	1.9340773	0.0192867
C	-2.3229887	1.2493863	0.0524387
C	-2.3229456	-0.1400941	0.0592696
C	-1.1303962	-0.8575675	0.0330490
H	3.4734865	1.8375219	-0.1008406
H	3.5602035	-0.6045619	-0.0908496
H	1.3774591	-1.6232063	-0.8863989
H	1.3101110	3.0333593	-0.0479643
H	-1.1152422	3.0187095	0.0135852
H	-3.2617864	1.7907741	0.0731893
H	-3.2632949	-0.6801577	0.0854625
C	-1.1568563	-2.3549666	0.0408155
H	-0.6228465	-2.7626244	0.9046232
H	-0.6764890	-2.7705036	-0.8503653
H	-2.1811183	-2.7268324	0.0736932
H	1.4227103	-1.6080216	0.8409412

5b

E(PBE0-D3/def2-TZVP) = -613.3068493583 (conv)

Lowest Freq. = 31.23 cm^-1

24

5b (092c1/opt)

C	2.9099920	1.9886057	-0.3314012
C	2.9898518	0.5924064	-0.1935903
C	1.8623563	-0.1691801	-0.0425398
C	0.5802515	0.4281776	-0.0232913
C	0.5034274	1.8445575	-0.1702892
C	1.6881777	2.5981411	-0.3200110
C	-0.7529382	2.4854102	-0.1685536
C	-1.9067490	1.7662903	-0.0389344
C	-1.8457280	0.3730132	0.0951389
C	-0.6433732	-0.2980779	0.1122828
H	3.8139908	2.5748634	-0.4476813
H	3.9598258	0.1086176	-0.2054215
H	1.9398151	-1.2390426	0.0747377
H	1.6048938	3.6741792	-0.4289027
H	-0.7835338	3.5647877	-0.2742264
H	-2.8693483	2.2631498	-0.0380213
H	-2.7611152	-0.1933724	0.1965697
C	-0.6607344	-1.7721939	0.3003264
O	0.2711102	-2.4595430	0.6366115
O	-1.8753195	-2.2935335	0.0618382
C	-1.9785011	-3.6963640	0.2656342
H	-1.2956243	-4.2323541	-0.3948252
H	-3.0101406	-3.9535658	0.0361039
H	-1.7405869	-3.9549724	1.2984461

5b-H2

E(PBE0-D3/def2-TZVP) = -613.8644699240 (conv)

Lowest Freq. = 41.15 cm^-1

25

5b-H2 (110c1/opt)

C	3.0150532	1.9782061	-0.2861187

C	3.1051394	0.5913460	-0.1749699
C	1.9721962	-0.1818435	-0.0638081
C	0.6826814	0.4030785	-0.0598751
C	0.6052043	1.8266258	-0.1754275
C	1.7695240	2.5789930	-0.2848260
C	-0.6788311	2.4858064	-0.1790541
C	-1.8206242	1.8046703	-0.0799721
C	-1.8506736	0.3292525	0.0414542
C	-0.5178175	-0.3447822	0.0502102
H	3.9114871	2.5807175	-0.3728286
H	4.0769382	0.1113786	-0.1755349
H	2.0502448	-1.2544497	0.0226257
H	1.6843023	3.6571107	-0.3705637
H	-0.6871543	3.5674225	-0.2668562
H	-2.7735409	2.3229251	-0.0859132
H	-2.4694403	-0.0945023	-0.7641970
C	-0.5308830	-1.8026002	0.1776365
O	0.4189394	-2.5539516	0.2159151
O	-1.7974725	-2.2704114	0.2559254
C	-1.9090718	-3.6795540	0.3834921
H	-1.4615640	-4.1829157	-0.4749959
H	-2.9754171	-3.8898196	0.4338159
H	-1.4088188	-4.0274262	1.2886380
H	-2.4104012	0.0447233	0.9452280

5b-H3

E(PBE0-D3/def2-TZVP) = -613.8561060737 (conv)

Lowest Freq. = 41.76 cm^-1

25

5b-H3 (109c1/opt)

C	3.0205693	1.8734248	-0.3890334
C	3.0791110	0.4841634	-0.2670065
C	1.9170733	-0.2526181	-0.0854873
C	0.6731297	0.3651815	-0.0232742
C	0.6018725	1.7904397	-0.1573340
C	1.8074409	2.5131444	-0.3352456

C	-0.6201041	2.4558923	-0.1210643
C	-1.9098151	1.7507881	0.0409902
C	-1.7666295	0.2799864	0.1600662
C	-0.5854554	-0.3608647	0.1405032
H	3.9304520	2.4463167	-0.5267917
H	4.0337528	-0.0261220	-0.3093310
H	1.9777442	-1.3249498	0.0269955
H	1.7495916	3.5919364	-0.4326362
H	-0.6314203	3.5357024	-0.2213971
H	-2.5892801	1.9792644	-0.7981296
H	-2.6736252	-0.2993938	0.2799008
C	-0.5929918	-1.8363363	0.3483335
O	0.3039757	-2.4836720	0.8249640
O	-1.7497221	-2.3950762	-0.0402532
C	-1.8521185	-3.7929308	0.2004094
H	-1.0709441	-4.3332147	-0.3357979
H	-2.8348010	-4.0845559	-0.1633848
H	-1.7585429	-4.0093841	1.2656042
H	-2.4592630	2.1328779	0.9184000

5b-H4

E(PBE0-D3/def2-TZVP) = -613.8697969114 (conv)

Lowest Freq. = 23.83 cm^-1

25

5b-H4 (108c1/opt)

C	2.9770723	1.8579030	-0.2844908
C	3.0515110	0.4742642	-0.1808598
C	1.9034304	-0.2789992	-0.0583398
C	0.6319693	0.3254437	-0.0350862
C	0.5676239	1.7332699	-0.1441991
C	1.7376999	2.4704605	-0.2655792
C	-0.7371476	2.4698373	-0.1326267
C	-1.9303669	1.6037415	-0.0474077
C	-1.8384052	0.2561062	0.0495112
C	-0.6003244	-0.4276102	0.0759547
H	3.8778587	2.4527875	-0.3805948

H	4.0149623	-0.0218547	-0.1961267
H	1.9658660	-1.3526641	0.0265797
H	1.6682216	3.5507616	-0.3482022
H	-0.8059544	3.1075640	-1.0262515
H	-2.9055682	2.0778563	-0.0555887
H	-2.7422972	-0.3328722	0.1181019
C	-0.6171429	-1.8910566	0.2246989
O	0.3381456	-2.6151461	0.3907580
O	-1.8692194	-2.3908592	0.1647180
C	-1.9598159	-3.7984952	0.3216083
H	-1.3982167	-4.3122702	-0.4601195
H	-3.0187252	-4.0372690	0.2480188
H	-1.5660368	-4.1064111	1.2915308
H	-0.7451404	3.1855122	0.7039922

5b-H5

E(PBE0-D3/def2-TZVP) = -613.8655389537 (conv)

Lowest Freq. = 28.24 cm^-1

25

5b-H5 (129c1/opt)

C	2.9159762	1.8287565	-0.3084749
C	2.9449461	0.4749016	-0.1843614
C	1.7817670	-0.2901239	-0.0268931
C	0.4913539	0.3197939	-0.0051807
C	0.4034523	1.7270697	-0.1426170
C	1.6366810	2.5770475	-0.2803817
C	-0.8312798	2.3513691	-0.1482447
C	-2.0060703	1.6265906	-0.0273821
C	-1.9427229	0.2507853	0.1009736
C	-0.7215246	-0.4133798	0.1211087
H	3.8338072	2.3934616	-0.4258207
H	3.8989134	-0.0411785	-0.2052346
H	1.8517963	-1.3599470	0.0830295
H	1.5490440	3.1955075	-1.1860260
H	-0.8726413	3.4316400	-0.2508614
H	-2.9650965	2.1299565	-0.0327259

H	-2.8518002	-0.3261590	0.1957088
C	-0.7316248	-1.8873807	0.2971237
O	0.2050455	-2.5818670	0.6070701
O	-1.9519992	-2.4085654	0.0795874
C	-2.0478400	-3.8134545	0.2669568
H	-1.3801364	-4.3399570	-0.4164198
H	-3.0842854	-4.0698521	0.0586335
H	-1.7849436	-4.0859424	1.2901548
H	1.6591821	3.3109275	0.5402774

5b-H6

E(PBE0-D3/def2-TZVP) = -613.8569212226 (conv)

Lowest Freq. = 35.25 cm^-1

25

5b-H6 (130c1/opt)

C	2.8744426	1.9298754	-0.2901132
C	2.8575864	0.4505813	-0.1585670
C	1.7353388	-0.2649548	-0.0211055
C	0.4232234	0.3480166	0.0023726
C	0.3569646	1.7732238	-0.1505067
C	1.5209083	2.5250587	-0.2895617
C	-0.9094236	2.4046673	-0.1569539
C	-2.0655244	1.6758989	-0.0312799
C	-2.0046977	0.2926972	0.1070178
C	-0.7752568	-0.3708336	0.1342084
H	3.4201872	2.2171256	-1.2047800
H	3.8140222	-0.0619926	-0.1732692
H	1.7922498	-1.3375651	0.0859848
H	1.4312278	3.6006491	-0.3994330
H	-0.9474940	3.4833110	-0.2656718
H	-3.0281222	2.1734394	-0.0382006
H	-2.9134438	-0.2834404	0.2053117
C	-0.7855418	-1.8451664	0.3325362
O	0.1267684	-2.5207061	0.7388116
O	-1.9763696	-2.3796666	0.0165751
C	-2.0809124	-3.7817539	0.2241055

H	-1.3525827	-4.3167237	-0.3868260
H	-3.0935037	-4.0497796	-0.0690951
H	-1.9072937	-4.0306228	1.2720268
H	3.4872470	2.3686614	0.5164129

5b-H7

E(PBE0-D3/def2-TZVP) = -613.8595573476 (conv)

Lowest Freq. = 23.94 cm^-1

25

5b-H7 (131c1/opt)

C	2.7853460	2.0499506	-0.2466604
C	2.9707849	0.5839086	-0.1107367
C	1.7121576	-0.1906082	-0.0059156
C	0.4503165	0.3923170	-0.0334015
C	0.3580054	1.8208323	-0.1718806
C	1.5700496	2.6014240	-0.2727170
C	-0.8754117	2.4463669	-0.2094667
C	-2.0524108	1.7163856	-0.1179857
C	-1.9925222	0.3363792	0.0135997
C	-0.7822936	-0.3416825	0.0608151
H	3.6709030	2.6716217	-0.3256122
H	3.5684878	0.2017199	-0.9556532
H	1.7882804	-1.2619987	0.0994780
H	1.4591165	3.6765840	-0.3734884
H	-0.9105884	3.5260148	-0.3129789
H	-3.0125703	2.2162765	-0.1479119
H	-2.9080041	-0.2336537	0.0857144
C	-0.8044559	-1.8125607	0.2167006
O	0.1525539	-2.5359336	0.3618983
O	-2.0558002	-2.3080881	0.1850086
C	-2.1490052	-3.7155786	0.3454336
H	-1.6076511	-4.2322491	-0.4484700
H	-3.2103248	-3.9495059	0.2960013
H	-1.7350908	-4.0239586	1.3066922
H	3.6101277	0.3660365	0.7615371

5b-H8

E(PBE0-D3/def2-TZVP) = -613.8668399424 (conv)

Lowest Freq. = 22.67 cm^-1

25

5b-H8 (132c1/opt)

C	2.8573846	2.0129772	-0.3147258
C	2.9797235	0.6637019	-0.1729488
C	1.8092996	-0.2303558	0.0102571
C	0.4669074	0.4460834	-0.0224168
C	0.4062564	1.8523916	-0.1712021
C	1.6017806	2.6214248	-0.3080320
C	-0.8406679	2.4942485	-0.1906093
C	-2.0134603	1.7806113	-0.0762109
C	-1.9635576	0.4039828	0.0557443
C	-0.7368397	-0.2654825	0.0854694
H	3.7440070	2.6258345	-0.4356163
H	3.9589676	0.1986764	-0.1790550
H	1.8340945	-1.0378271	-0.7329060
H	1.5108471	3.6953509	-0.4187810
H	-0.8650641	3.5733490	-0.3002257
H	-2.9693819	2.2903246	-0.0916663
H	-2.8751805	-0.1696346	0.1412497
C	-0.7422067	-1.7426489	0.2426565
O	0.2243107	-2.4383421	0.4353405
O	-1.9783829	-2.2583089	0.1487721
C	-2.0566377	-3.6682409	0.3071478
H	-1.4664801	-4.1752855	-0.4574289
H	-3.1098208	-3.9197319	0.2038227
H	-1.6869785	-3.9673997	1.2889624
H	1.9110797	-0.7856991	0.9524026

5c

E(PBE0-D3/def2-TZVP) = -477.7531509349 (conv)

Lowest Freq. = 87.67 cm^-1

19

5c (093c1/opt)

C	2.6770596	0.8098079	0.0000000
C	2.6759297	-0.5985601	0.0000000
C	1.4952304	-1.2871457	0.0000000
C	0.2618764	-0.5985749	0.0000000
C	0.2627819	0.8236820	0.0000000
C	1.4985096	1.5040610	0.0000000
C	-0.9728254	1.5094831	0.0000000
C	-2.1553328	0.8306980	0.0000000
C	-2.1541945	-0.5854391	0.0000000
C	-0.9687103	-1.2820260	0.0000000
H	3.6202530	1.3433726	0.0000000
H	3.6174490	-1.1347737	0.0000000
H	1.4884136	-2.3715720	0.0000000
H	1.4980973	2.5885539	0.0000000
H	-0.9687881	2.5937742	0.0000000
H	-3.1010641	1.3574127	0.0000000
H	-0.9780337	-2.3656861	0.0000000
C	-3.3950981	-1.2883343	0.0000000
N	-4.4015533	-1.8487334	0.0000000

5c-H1

E(PBE0-D3/def2-TZVP) = -478.3183610339 (conv)

Lowest Freq. = 49.16 cm^-1

20

5c-H1 (111c1/opt)

C	2.7544748	0.8997523	-0.0284483
C	2.7620065	-0.4909698	0.0011770
C	1.5647604	-1.1891673	0.0222513
C	0.3479636	-0.5239104	0.0141155
C	0.3348667	0.8830447	-0.0167988
C	1.5531680	1.5766111	-0.0373481
C	-0.9131486	1.5839690	-0.0295679
C	-2.1201083	0.9106881	-0.0171071
C	-2.1725760	-0.4711082	0.0130944
C	-0.9322245	-1.3069420	0.0399994
H	3.6882224	1.4490606	-0.0448882

H	3.7016670	-1.0303683	0.0076875
H	1.5757579	-2.2742622	0.0454377
H	1.5364955	2.6609455	-0.0611719
H	-0.9002812	2.6670744	-0.0531232
H	-3.0494388	1.4676713	-0.0322157
H	-0.9515512	-2.0095118	-0.8042264
C	-3.4123979	-1.1389165	0.0216966
N	-4.4162188	-1.7138715	0.0283733
H	-0.9514375	-1.9497888	0.9310628

5c-H3

E(PBE0-D3/def2-TZVP) = -478.3069408201 (conv)

Lowest Freq. = 76.04 cm^-1

20

5c-H3 (112c1/opt)

C	2.8256945	0.7463717	-0.0212861
C	2.8122396	-0.6539451	-0.0434049
C	1.6037599	-1.3292335	-0.0405250
C	0.3974375	-0.6371978	-0.0155351
C	0.3980552	0.7936431	0.0076159
C	1.6507107	1.4563856	0.0034880
C	-0.8050792	1.4884943	0.0332720
C	-2.1299862	0.8236668	0.0395110
C	-2.0392675	-0.6732890	0.0128591
C	-0.8603054	-1.3262180	-0.0123056
H	3.7727139	1.2735181	-0.0237558
H	3.7438005	-1.2057944	-0.0627961
H	1.5863011	-2.4138686	-0.0577994
H	1.6652863	2.5406232	0.0205953
H	-0.7866741	2.5726845	0.0504107
H	-2.7369174	1.1678191	-0.8127158
H	-0.8524706	-2.4107947	-0.0307655
C	-3.2602887	-1.3976932	0.0154878
N	-4.2712786	-1.9534391	0.0186687
H	-2.7137316	1.1382669	0.9189809

5c-H4

E(PBE0-D3/def2-TZVP) = -478.3111482965 (conv)

Lowest Freq. = 57.07 cm^-1

20

5c-H4 (113c1/opt)

C	2.7627174	0.6881564	0.0013631
C	2.7473203	-0.7029876	-0.0328926
C	1.5438334	-1.3741188	-0.0418694
C	0.3261058	-0.6746934	-0.0166574
C	0.3475619	0.7346291	0.0189608
C	1.5682394	1.3915801	0.0269855
C	-0.9321085	1.5216794	0.0490607
C	-2.1695977	0.7057309	0.0275419
C	-2.1288115	-0.6650419	-0.0080199
C	-0.9156132	-1.3721458	-0.0287401
H	3.7051731	1.2225753	0.0080323
H	3.6780892	-1.2572781	-0.0528300
H	1.5219881	-2.4581521	-0.0692340
H	1.5851454	2.4766615	0.0538711
H	-0.9501799	2.2284036	-0.7942956
H	-3.1256066	1.2140367	0.0423295
H	-0.9237980	-2.4539579	-0.0567389
C	-3.3557409	-1.3999171	-0.0253945
N	-4.3408623	-1.9958690	-0.0395489
H	-0.9438553	2.1707088	0.9380763

5c-H5

E(PBE0-D3/def2-TZVP) = -478.3119951054 (conv)

Lowest Freq. = 79.42 cm^-1

20

5c-H5 (133c1/opt)

C	2.6710945	0.6686445	0.0209545
C	2.6213256	-0.6945085	-0.0106234
C	1.4070118	-1.3848874	-0.0262230
C	0.1656399	-0.6785805	-0.0136664
C	0.1548726	0.7321008	0.0192665

C	1.4423634	1.5047197	0.0448064
C	-1.0592786	1.4040243	0.0290839
C	-2.2627752	0.7242627	0.0077450
C	-2.2572102	-0.6736018	-0.0244854
C	-1.0549966	-1.3640084	-0.0349795
H	3.6268327	1.1795776	0.0319067
H	3.5468397	-1.2595726	-0.0245969
H	1.3904383	-2.4675644	-0.0507318
H	1.4579182	2.2104437	-0.7993973
H	-1.0634795	2.4889013	0.0540548
H	-3.2040365	1.2584305	0.0155349
H	-1.0590410	-2.4473714	-0.0602368
C	-3.4909334	-1.3900319	-0.0467620
N	-4.4883912	-1.9657861	-0.0646591
H	1.4558055	2.1548081	0.9330088

5c-H6

E(PBE0-D3/def2-TZVP) = -478.3066046684 (conv)

Lowest Freq. = 78.17 cm^-1

20

5c-H6 (134c1/opt)

C	2.6241942	0.7842501	0.0439245
C	2.5264806	-0.7008862	0.0275947
C	1.3555531	-1.3445252	0.0051195
C	0.0927154	-0.6425526	-0.0054399
C	0.1043669	0.7906796	0.0082386
C	1.3116042	1.4712281	0.0319549
C	-1.1419148	1.4710249	-0.0028965
C	-2.3255759	0.7862555	-0.0254030
C	-2.3248723	-0.6222528	-0.0378664
C	-1.1126983	-1.3175784	-0.0279066
H	3.2362032	1.1252128	-0.8078519
H	3.4542395	-1.2628319	0.0348054
H	1.3287145	-2.4292884	-0.0058943
H	1.3021433	2.5560714	0.0425643
H	-1.1426738	2.5552097	0.0069617

H	-3.2706351	1.3146432	-0.0335210
H	-1.1219069	-2.4014681	-0.0377568
C	-3.5536127	-1.3326914	-0.0596298
N	-4.5535273	-1.9081956	-0.0768149
H	3.2112021	1.1076952	0.9198176

5c-H7

E(PBE0-D3/def2-TZVP) = -478.3043308636 (conv)

Lowest Freq. = 87.02 cm^-1

20

5c-H7 (135c1/opt)

C	2.5300080	0.8989205	0.0182798
C	2.6262366	-0.5866695	0.0391003
C	1.3108633	-1.2695494	0.0310167
C	0.1020392	-0.5776332	0.0082782
C	0.0953561	0.8526636	-0.0093507
C	1.3608285	1.5472044	-0.0037020
C	-1.1143586	1.5346872	-0.0315363
C	-2.3226621	0.8612904	-0.0374609
C	-2.3268576	-0.5434779	-0.0209556
C	-1.1392182	-1.2509990	0.0015331
H	3.4590839	1.4590211	0.0216240
H	3.2376739	-0.9291890	-0.8125816
H	1.2946784	-2.3539130	0.0436162
H	1.3398336	2.6321737	-0.0179576
H	-1.1058951	2.6191860	-0.0444189
H	-3.2613019	1.3992052	-0.0546159
H	-1.1580990	-2.3342863	0.0142795
C	-3.5690578	-1.2449174	-0.0275684
N	-4.5743473	-1.8075249	-0.0329308
H	3.2151961	-0.9061925	0.9153510

5c-H8

E(PBE0-D3/def2-TZVP) = -478.3134158042 (conv)

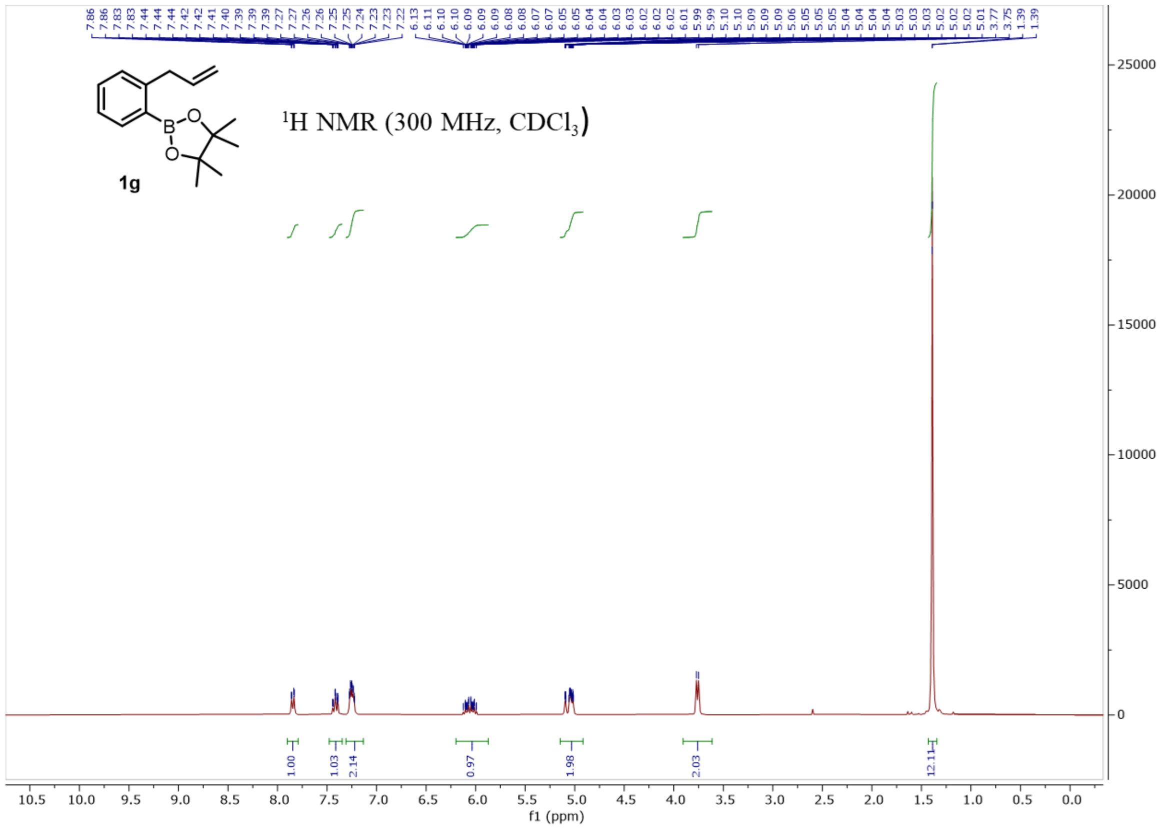
Lowest Freq. = 63.99 cm^-1

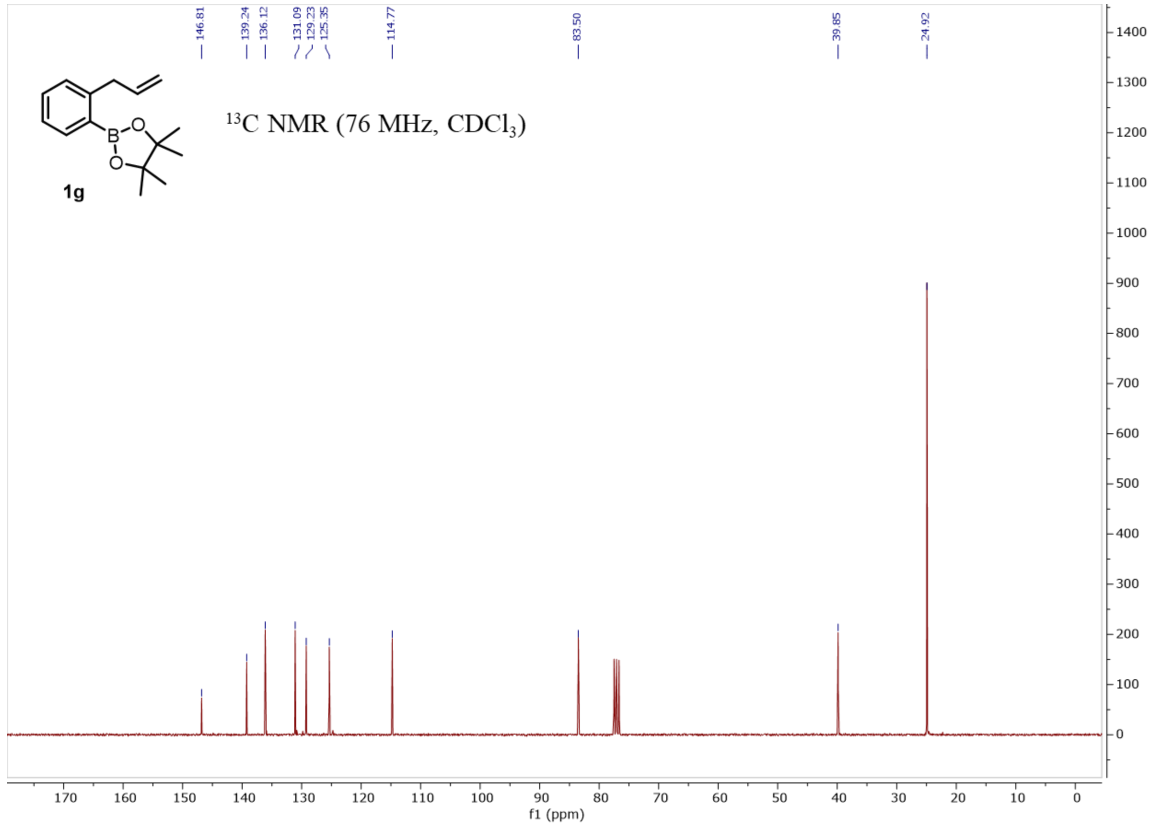
20

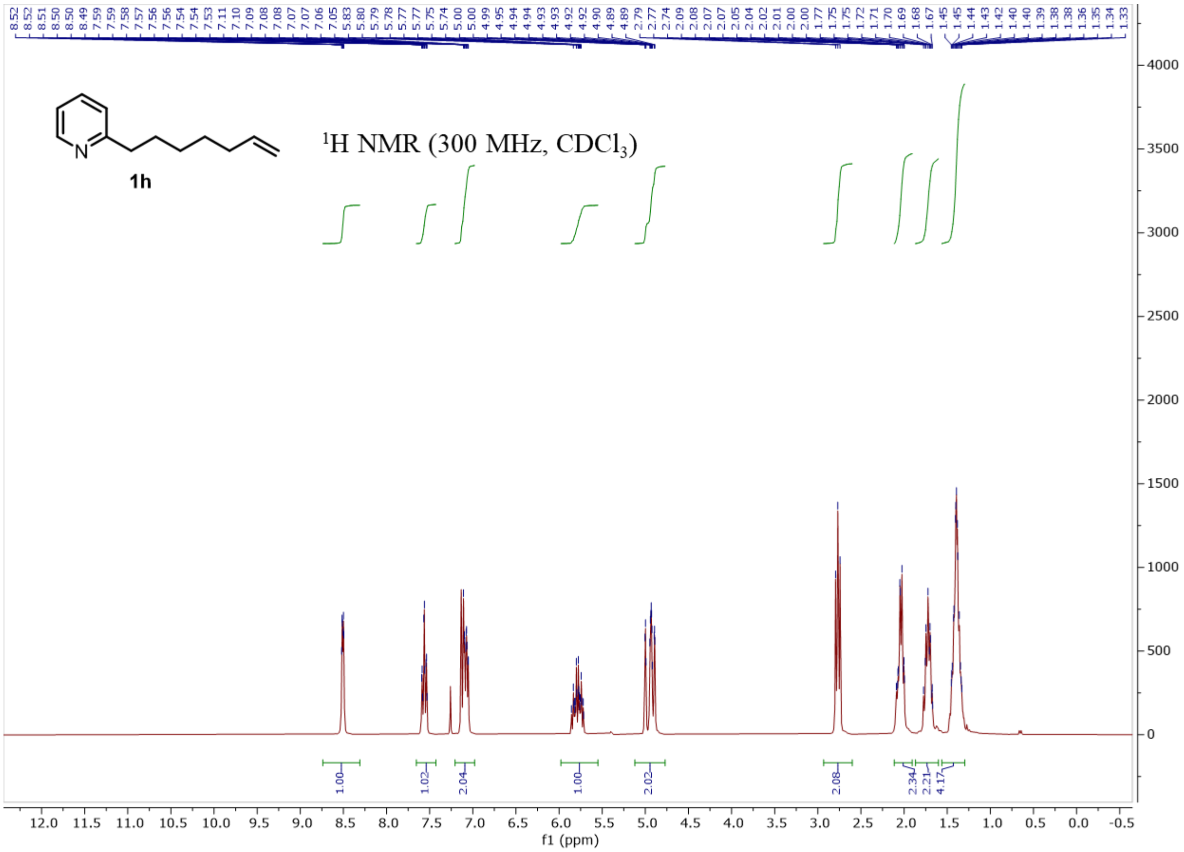
5c-H8 (136c1/opt)

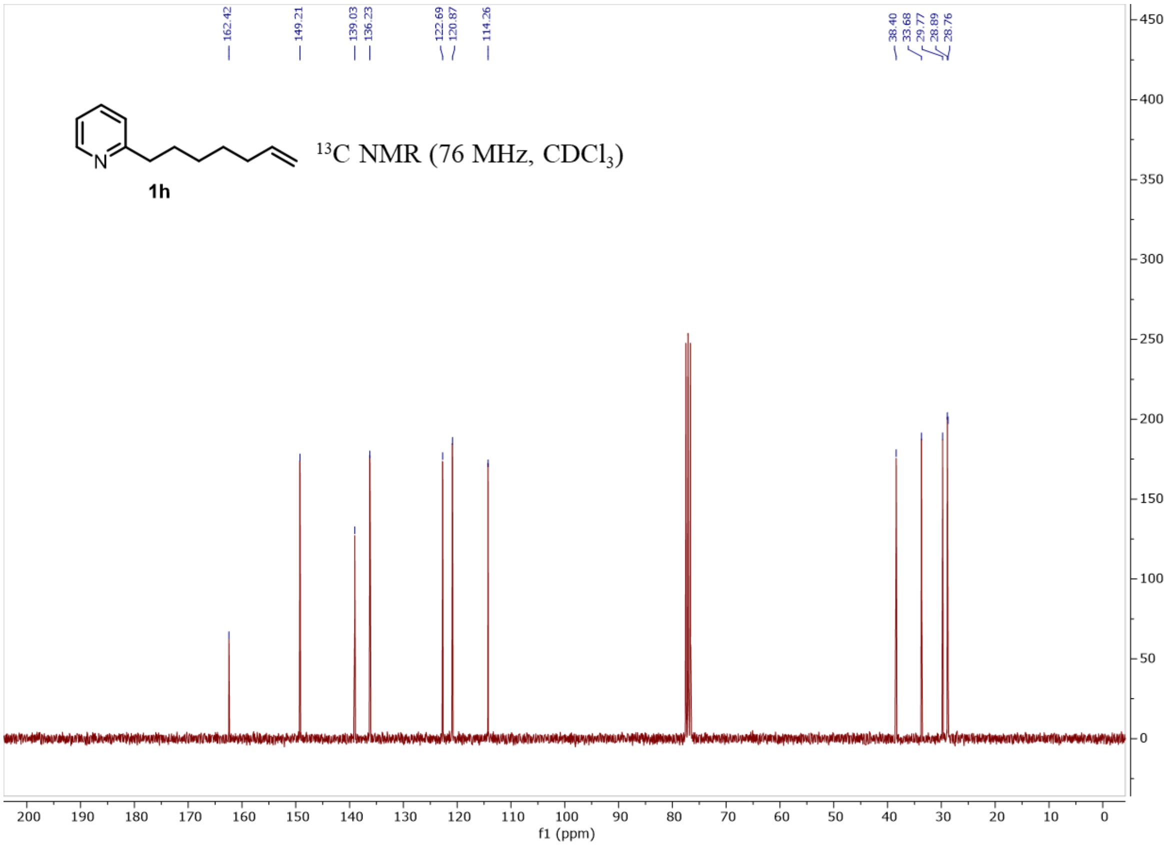
C	2.6227845	0.8981801	-0.0047861
C	2.6701897	-0.4632262	0.0188705
C	1.4408055	-1.2975828	0.0347141
C	0.1541735	-0.5211706	0.0119617
C	0.1670351	0.8919826	-0.0122580
C	1.4061263	1.5905289	-0.0184214
C	-1.0583107	1.5820061	-0.0315503
C	-2.2568050	0.9113532	-0.0282364
C	-2.2632673	-0.4883346	-0.0049424
C	-1.0556188	-1.1875943	0.0152859
H	3.5484931	1.4629744	-0.0136607
H	3.6250411	-0.9760110	0.0286568
H	1.4604213	-1.9964864	-0.8146413
H	1.3935699	2.6736172	-0.0364455
H	-1.0464468	2.6660690	-0.0502404
H	-3.1955329	1.4504783	-0.0439299
H	-1.0760060	-2.2718345	0.0336232
C	-3.4963267	-1.1981659	-0.0021523
N	-4.4953969	-1.7735495	-0.0001743
H	1.4550711	-1.9532340	0.9183268

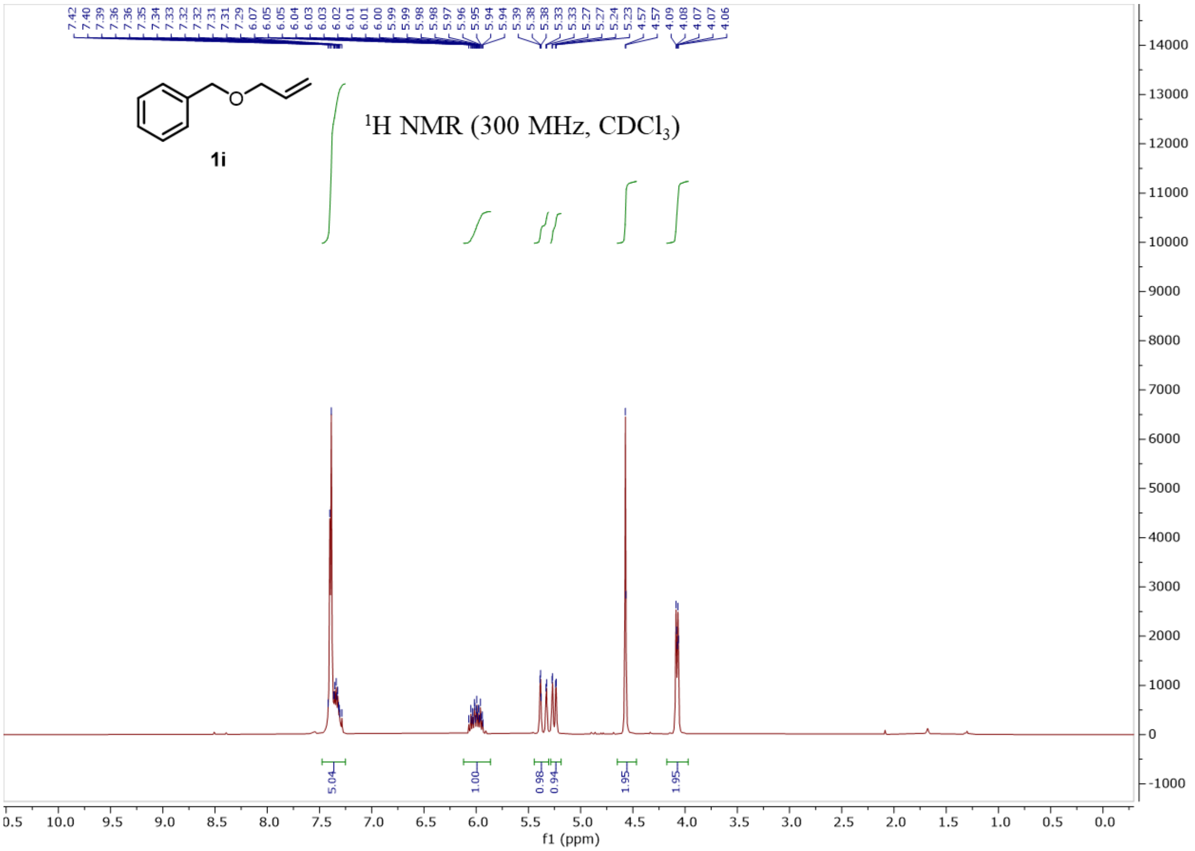
13. NMR spectra

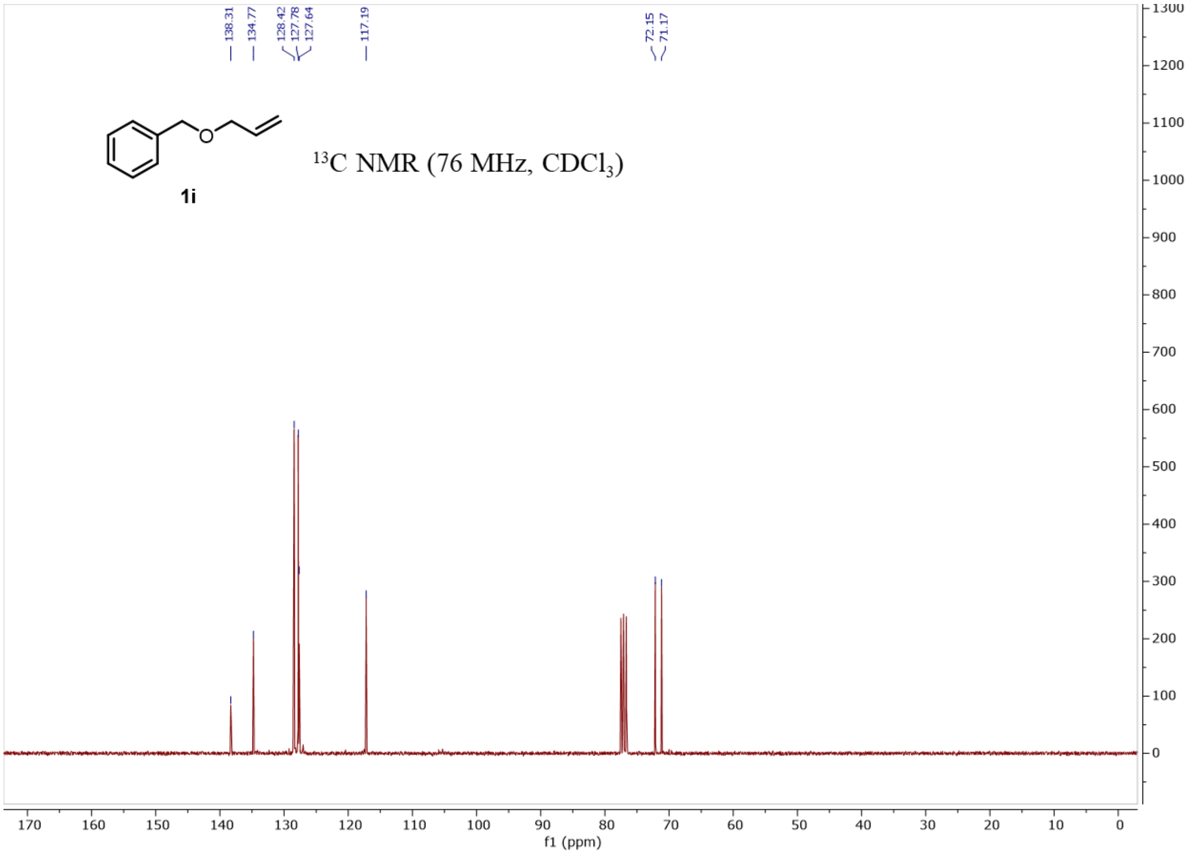


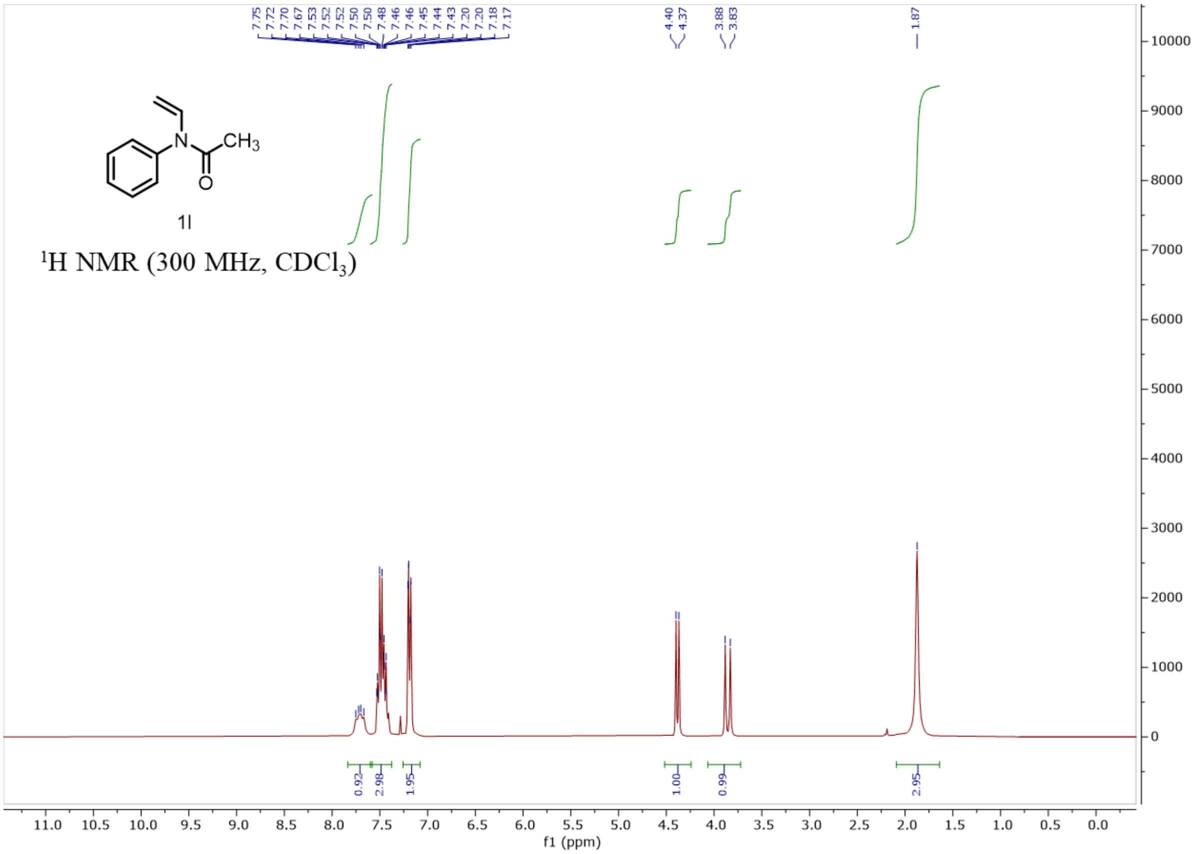



1h
^{1}H NMR (300 MHz, CDCl$_3$)
8.52 8.52 8.51 8.50 8.50 8.49 7.59 7.59 7.58 7.57 7.56 7.56 7.54 7.54 7.53 7.11 7.10 7.09 7.08 7.08 7.07 7.07 7.06 7.05 5.83 5.80 5.79 5.78 5.77 5.77 5.75 5.74 5.00 5.00 4.99 4.95 4.94 4.94 4.93 4.93 4.92 4.92 4.90 4.89 4.89 2.79 2.77 2.74 2.09 2.08 2.07 2.07 2.05 2.04 2.02 2.01 2.00 2.00 1.77 1.75 1.75 1.72 1.71 1.70 1.69 1.68 1.67 1.45 1.45 1.44 1.43 1.42 1.40 1.40 1.39 1.38 1.38 1.36 1.35 1.34 1.33
1.00 1.02 2.04 1.00 2.02 2.08 2.34 2.21 4.17
f1 (ppm)

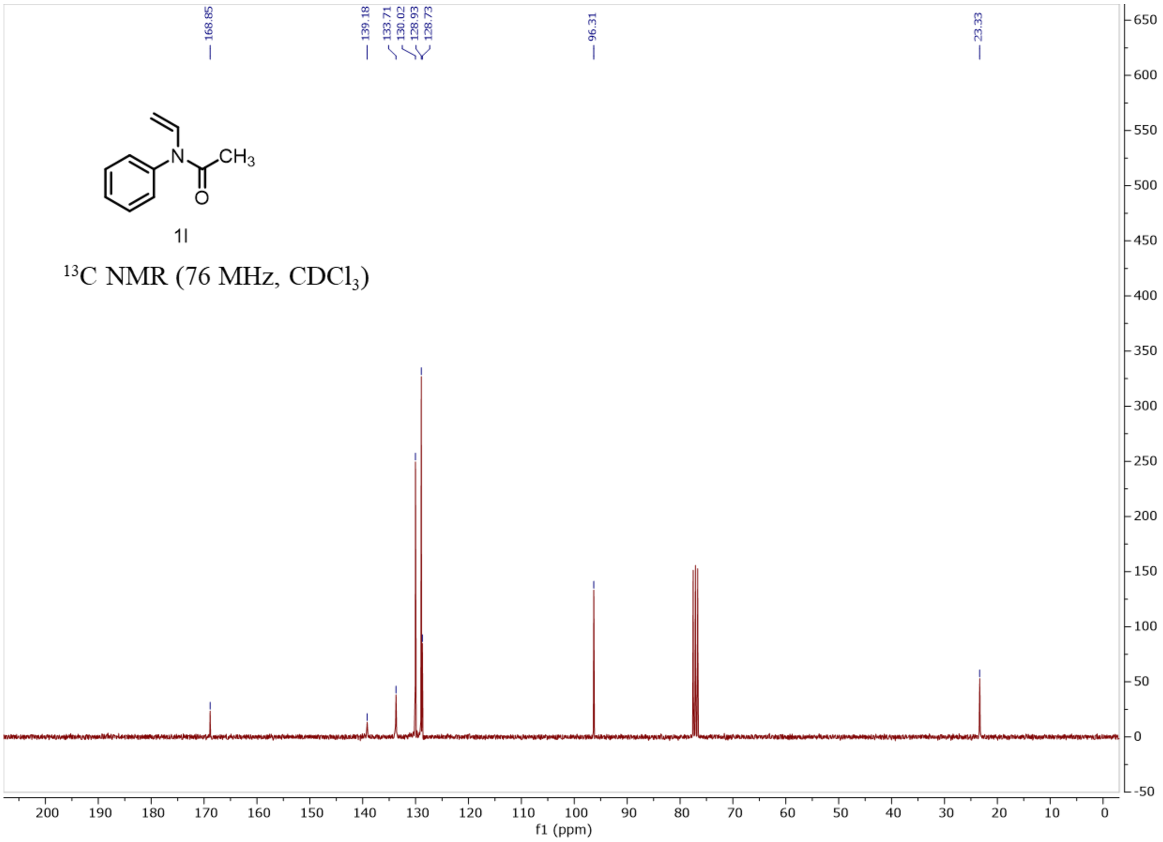

1h
^{13}C NMR (76 MHz, CDCl$_3$)
162.42 149.21 139.03 136.23 122.69 120.87 114.26 38.40 33.68 29.77 28.89 28.76
f1 (ppm)


7.42 7.40 7.39 7.36 7.36 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.29 6.07 6.05 6.05 6.04 6.03 6.03 6.02 6.01 6.01 6.00 5.99 5.99 5.98 5.98 5.97 5.96 5.95 5.94 5.94 5.39 5.38 5.38 5.33 5.33 5.27 5.27 5.24 5.23 4.57 4.57 4.09 4.08 4.07 4.07 4.06
O
1i
^{1}H NMR (300 MHz, CDCl$_3$)
5.04
1.00
0.98
0.94
1.95
1.95
f1 (ppm)

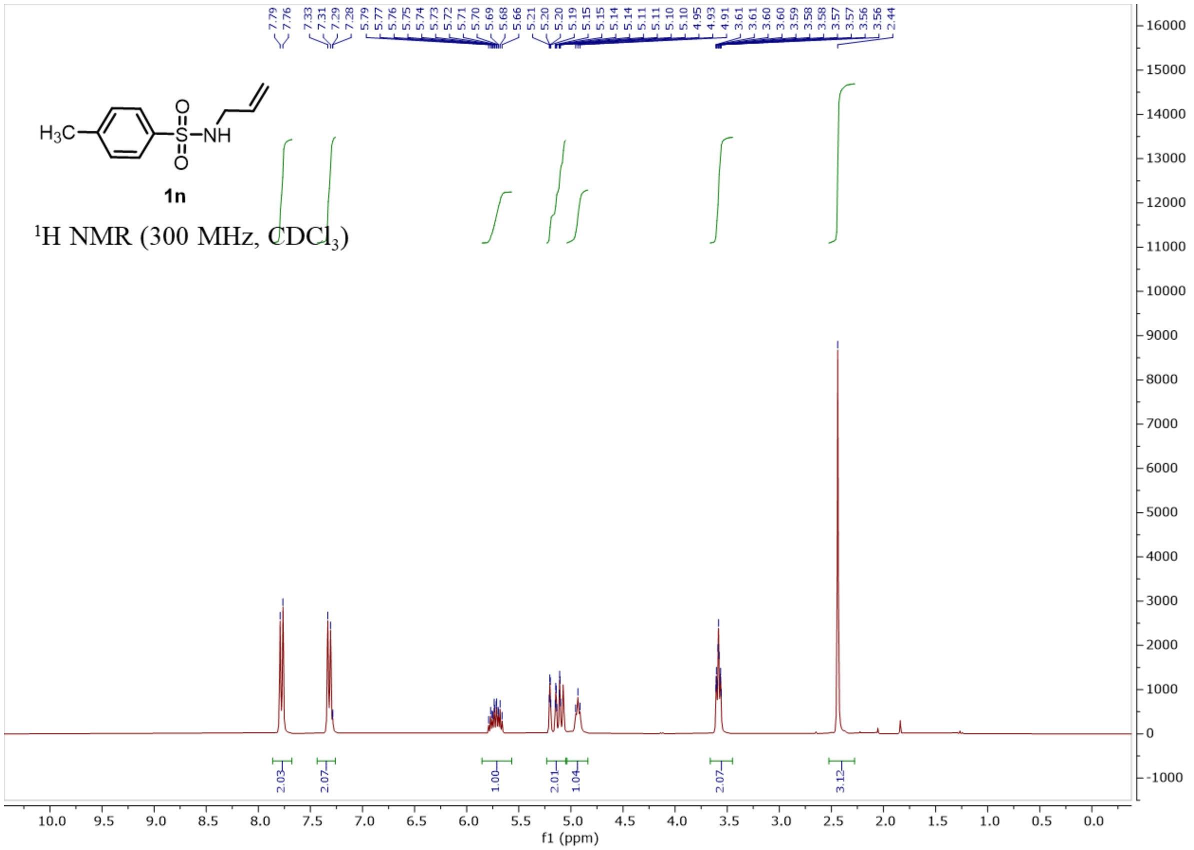

138.31
134.77
128.42
127.78
127.64
117.19
72.15
71.17
O
1i
^{13}C NMR (76 MHz, CDCl$_3$)
f1 (ppm)


1l

^{1}H NMR (300 MHz, $CDCl_3$)

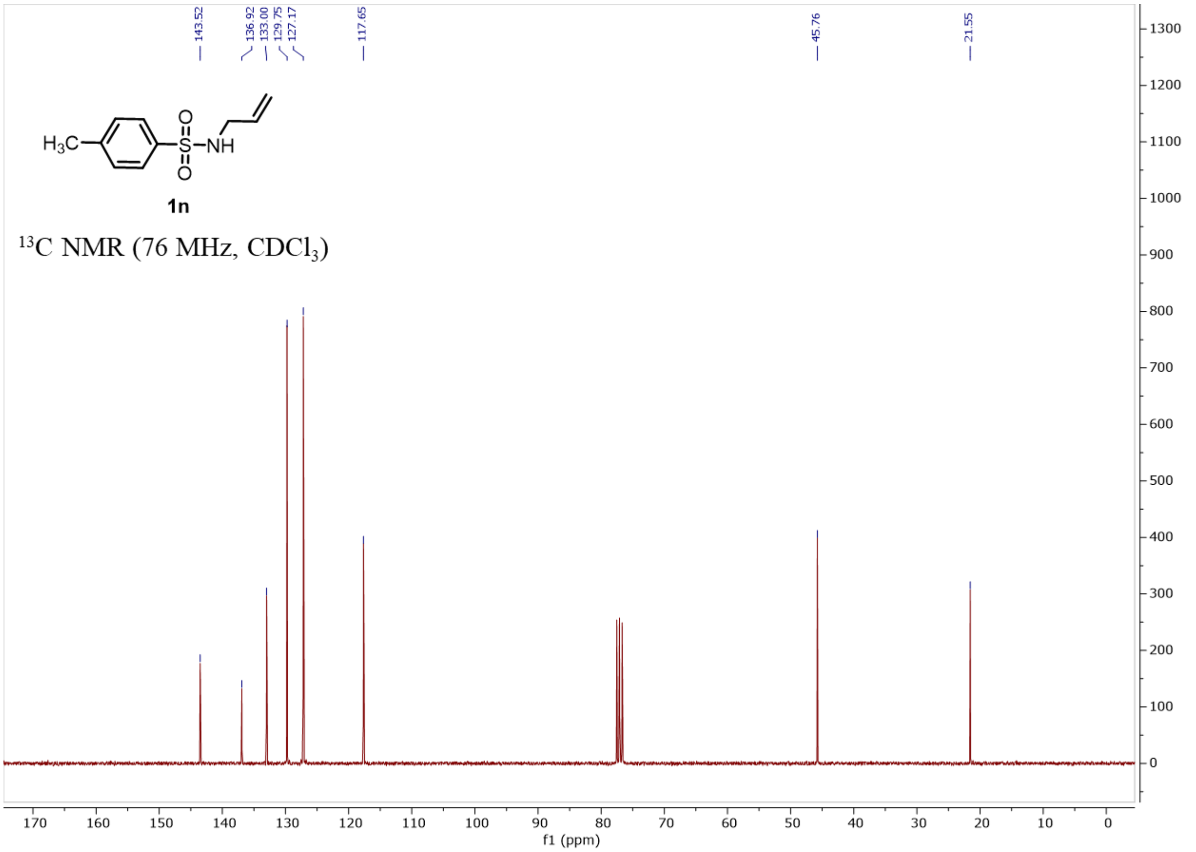

1l

^{13}C NMR (76 MHz, $CDCl_3$)



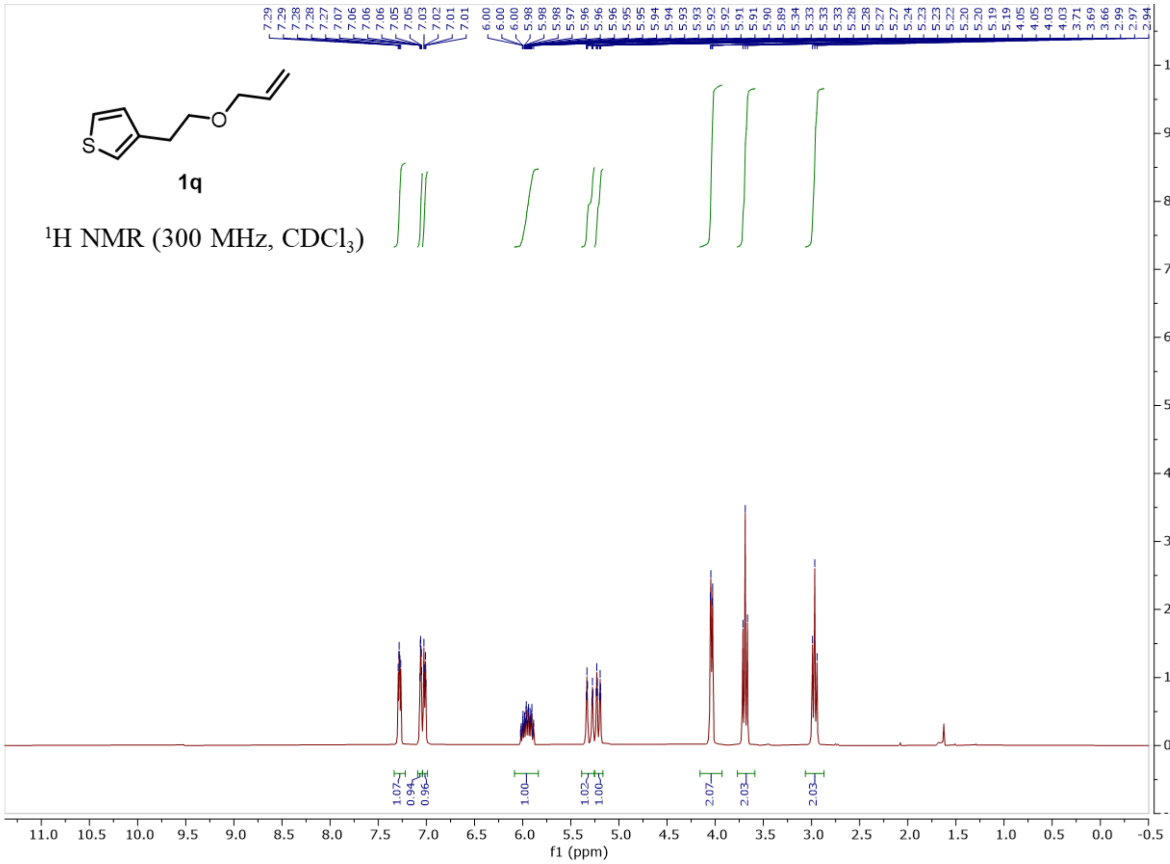
1n

^{1}H NMR (300 MHz, CDCl$_3$)



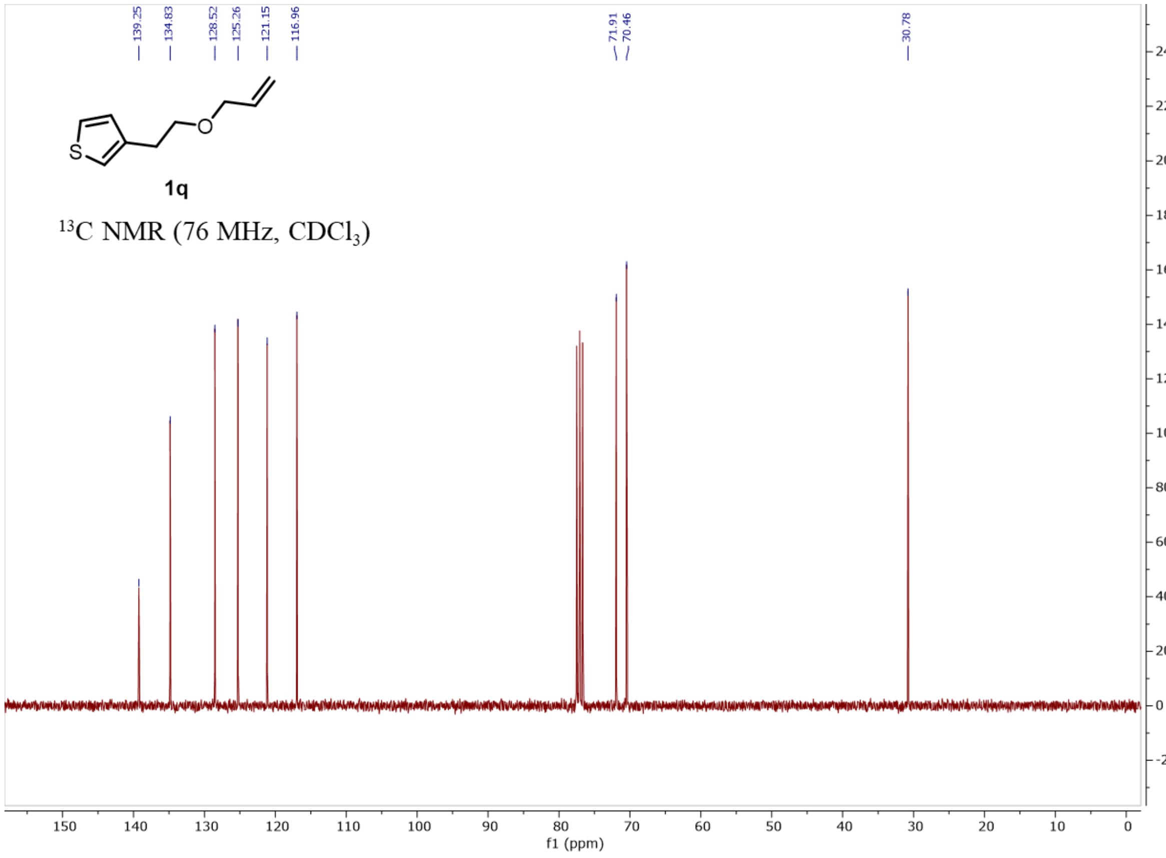
1n

^{13}C NMR (76 MHz, CDCl$_3$)



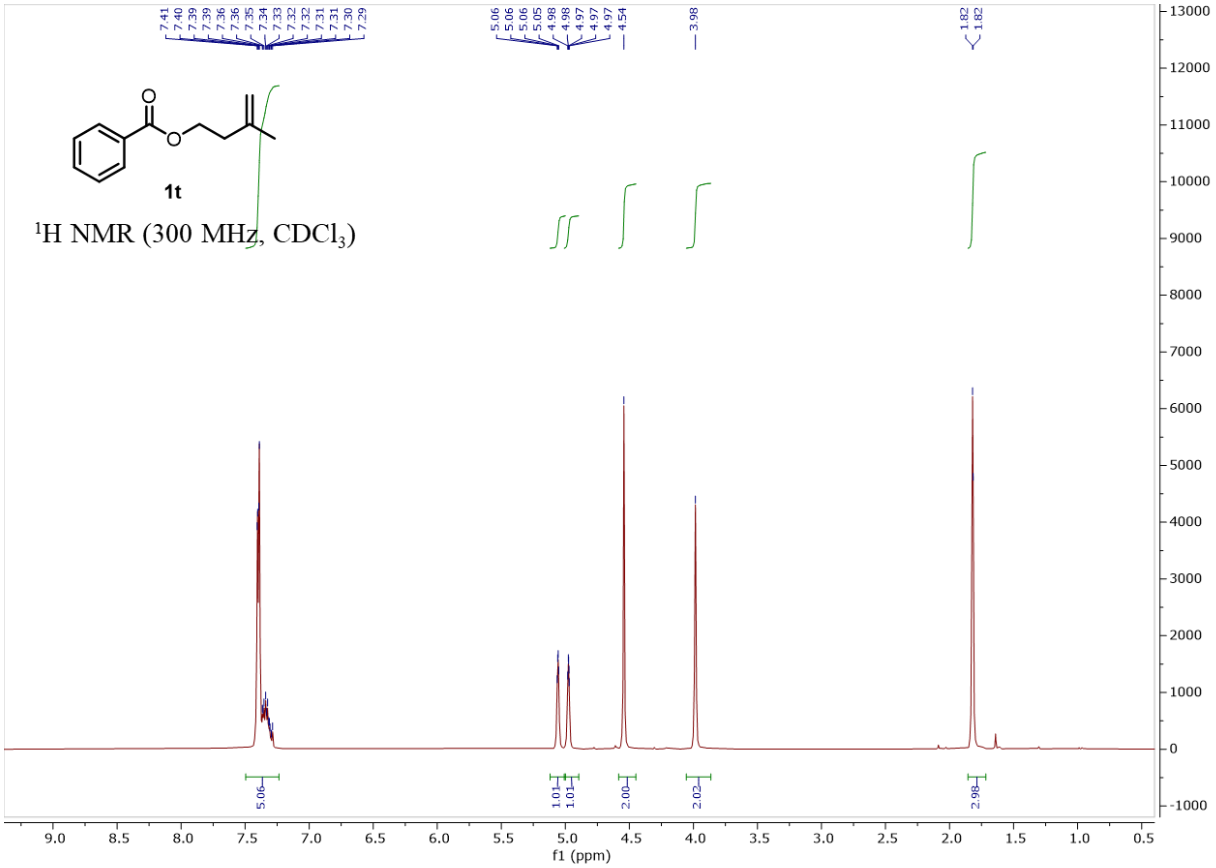
1q

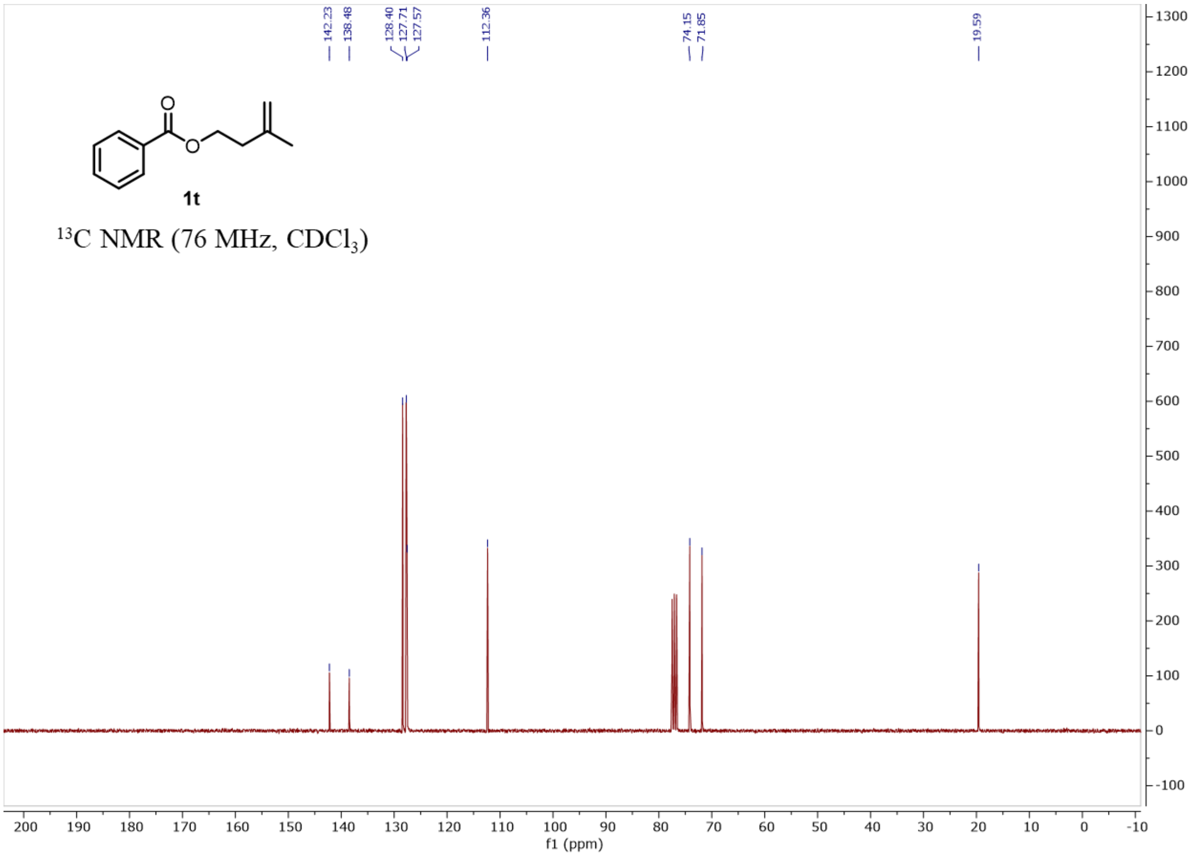
^{1}H NMR (300 MHz, CDCl$_3$)

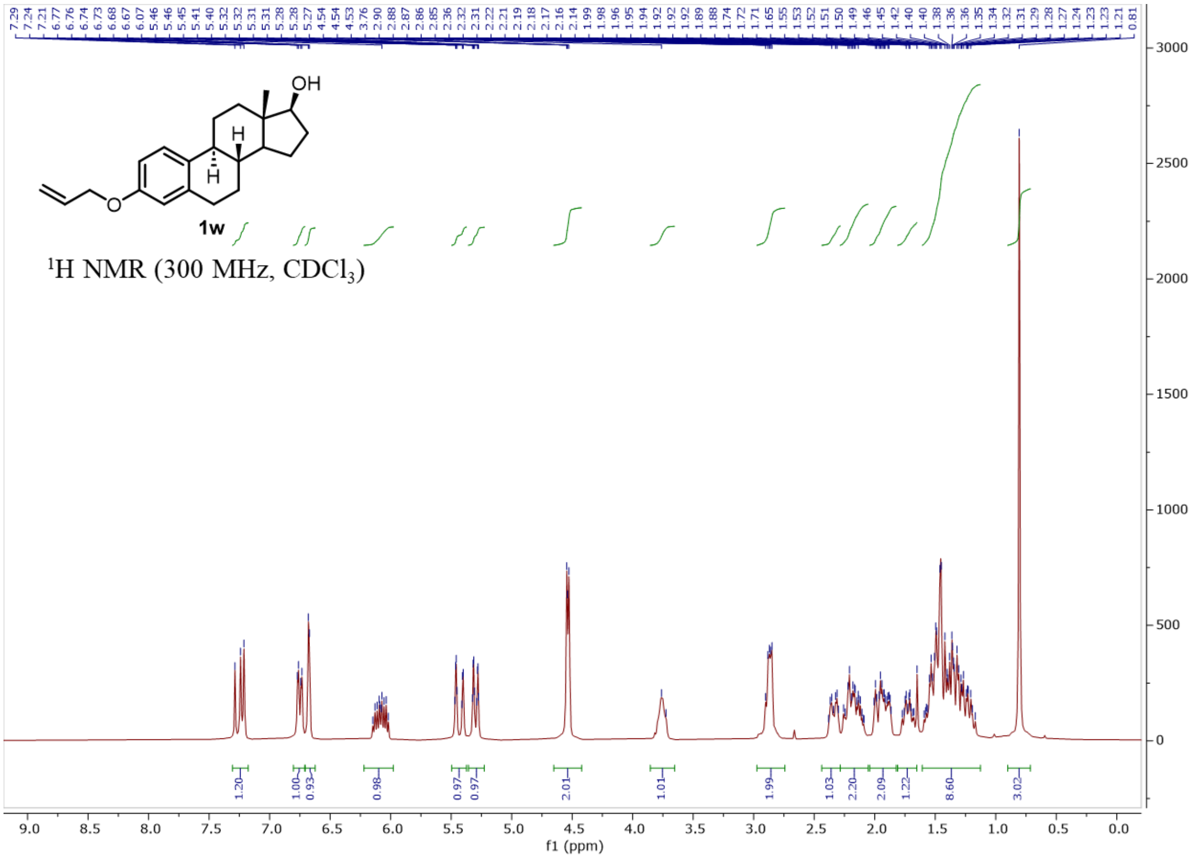


1q

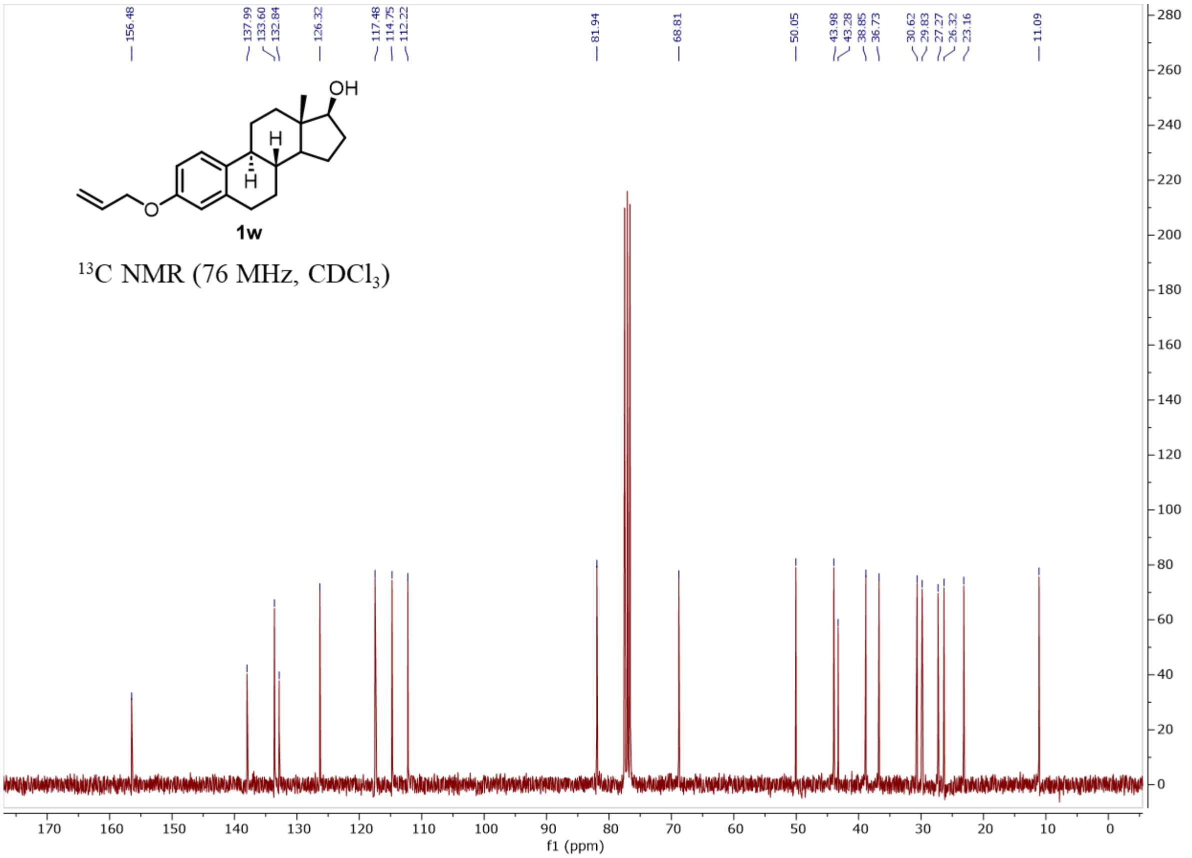
^{13}C NMR (76 MHz, CDCl$_3$)


1t
^{1}H NMR (300 MHz, CDCl$_3$)
7.41 7.40 7.39 7.39 7.36 7.36 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29
5.06 5.06 5.06 5.05 4.98 4.98 4.97 4.97 4.97 4.54
3.98
1.82 1.82
5.06
1.01 1.01
2.00
2.02
2.98
f1 (ppm)

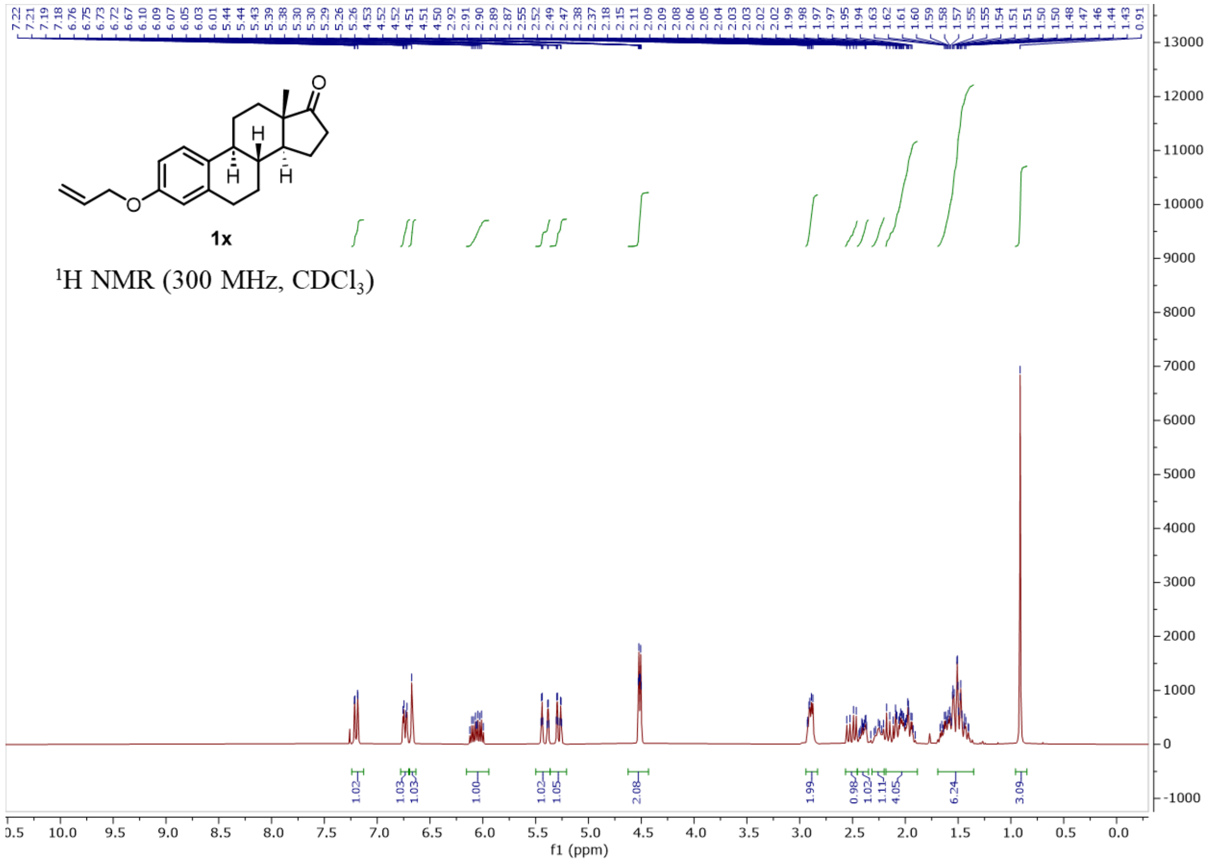

1t
^{13}C NMR (76 MHz, CDCl$_3$)
142.23
138.48
128.40 127.71 127.57
112.36
74.15 71.85
19.59
f1 (ppm)

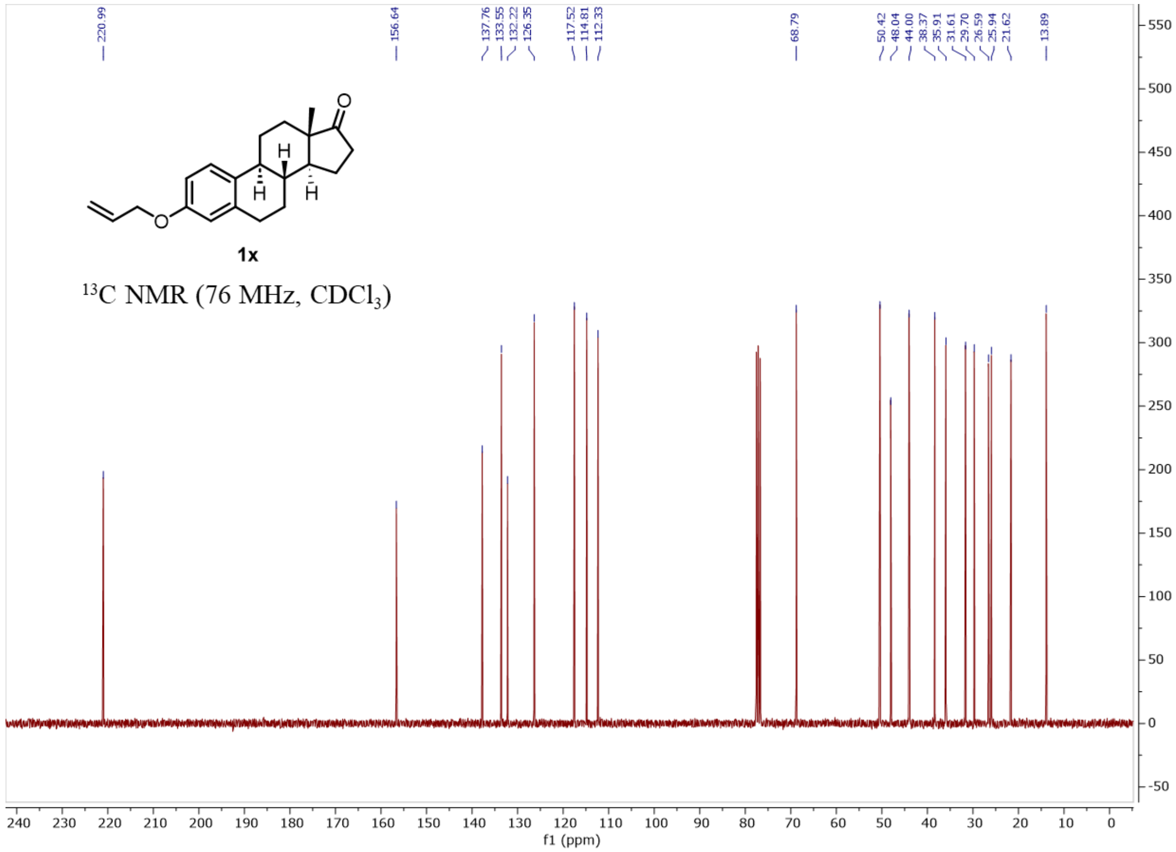

1w

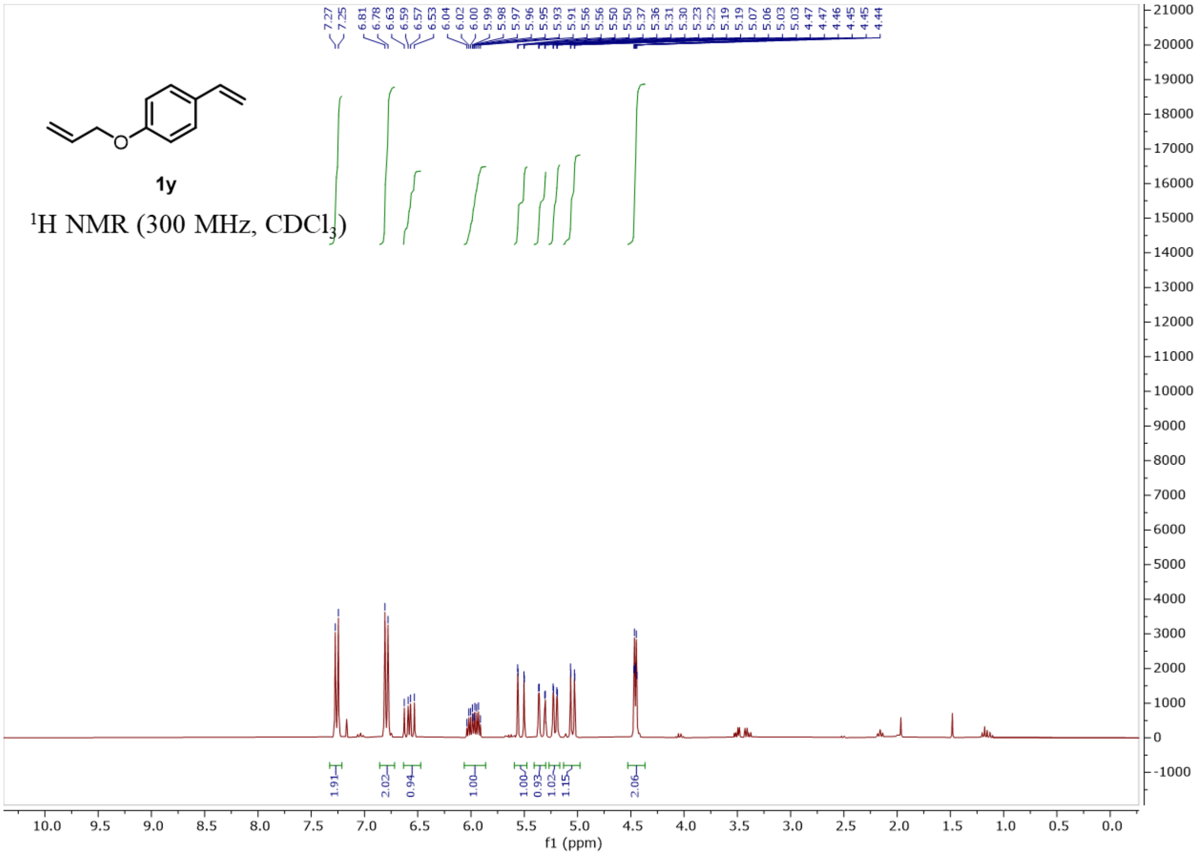
^{1}H NMR (300 MHz, $CDCl_3$)


1w

^{13}C NMR (76 MHz, $CDCl_3$)

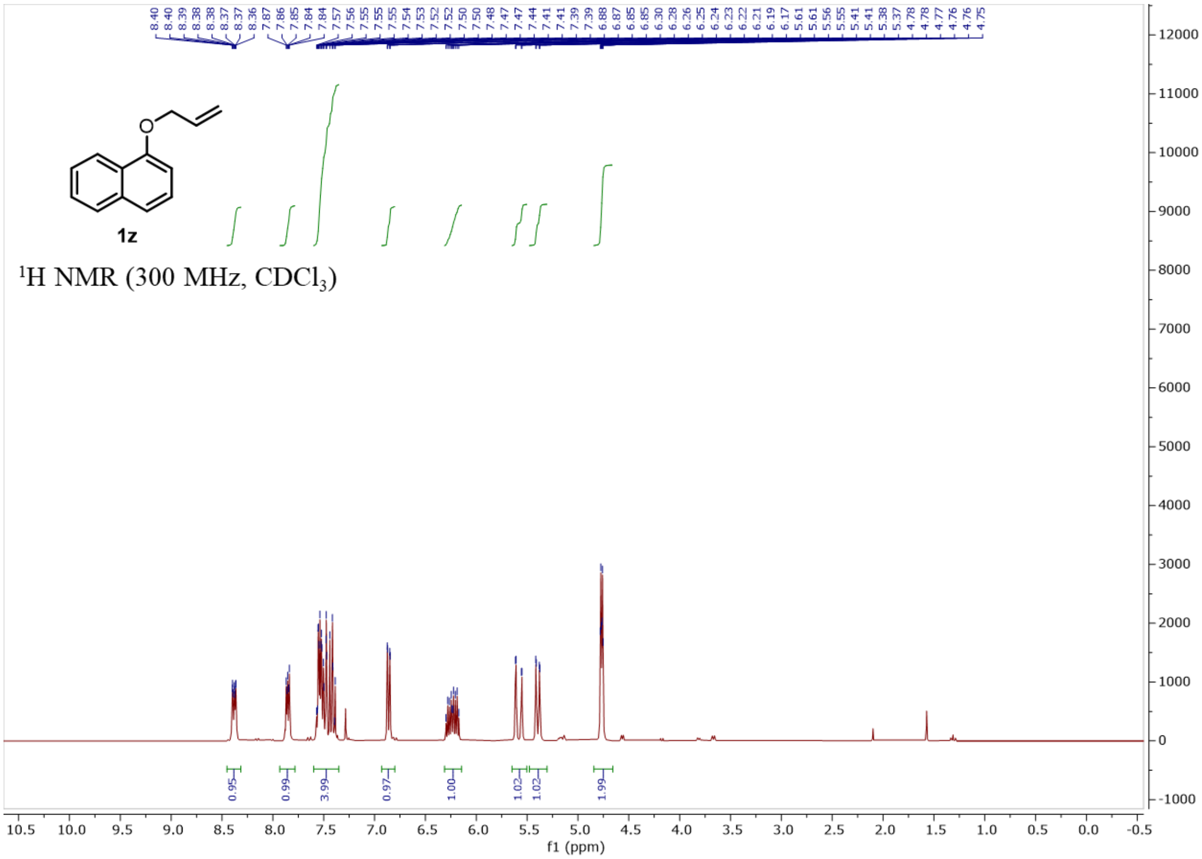

7.22 7.21 7.19 7.18 6.76 6.75 6.73 6.72 6.67 6.10 6.09 6.07 6.05 6.03 6.01 5.44 5.44 5.43 5.39 5.38 5.30 5.30 5.29 5.26 5.26 4.53 4.52 4.52 4.51 4.51 4.50 2.92 2.91 2.90 2.89 2.87 2.55 2.52 2.49 2.47 2.38 2.37 2.18 2.15 2.11 2.09 2.09 2.08 2.06 2.05 2.04 2.03 2.03 2.02 2.02 1.99 1.98 1.97 1.97 1.95 1.94 1.63 1.62 1.61 1.60 1.59 1.58 1.57 1.55 1.55 1.54 1.51 1.51 1.50 1.50 1.48 1.47 1.46 1.44 1.43 0.91
H
H
H
O
O
1x
¹H NMR (300 MHz, CDCl₃)
1.02 1.03 1.03 1.00 1.02 1.05 2.08 1.99 0.98 1.02 1.11 4.05 6.24 3.09
13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


220.99
156.64
137.76 133.55 132.22 126.35
117.52 114.81 112.33
68.79
50.42 48.04 44.00 38.37 35.91 31.61 29.70 26.59 25.94 21.62
13.89
H
H
H
O
O
1x
¹³C NMR (76 MHz, CDCl₃)
550 500 450 400 350 300 250 200 150 100 50 0 -50
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



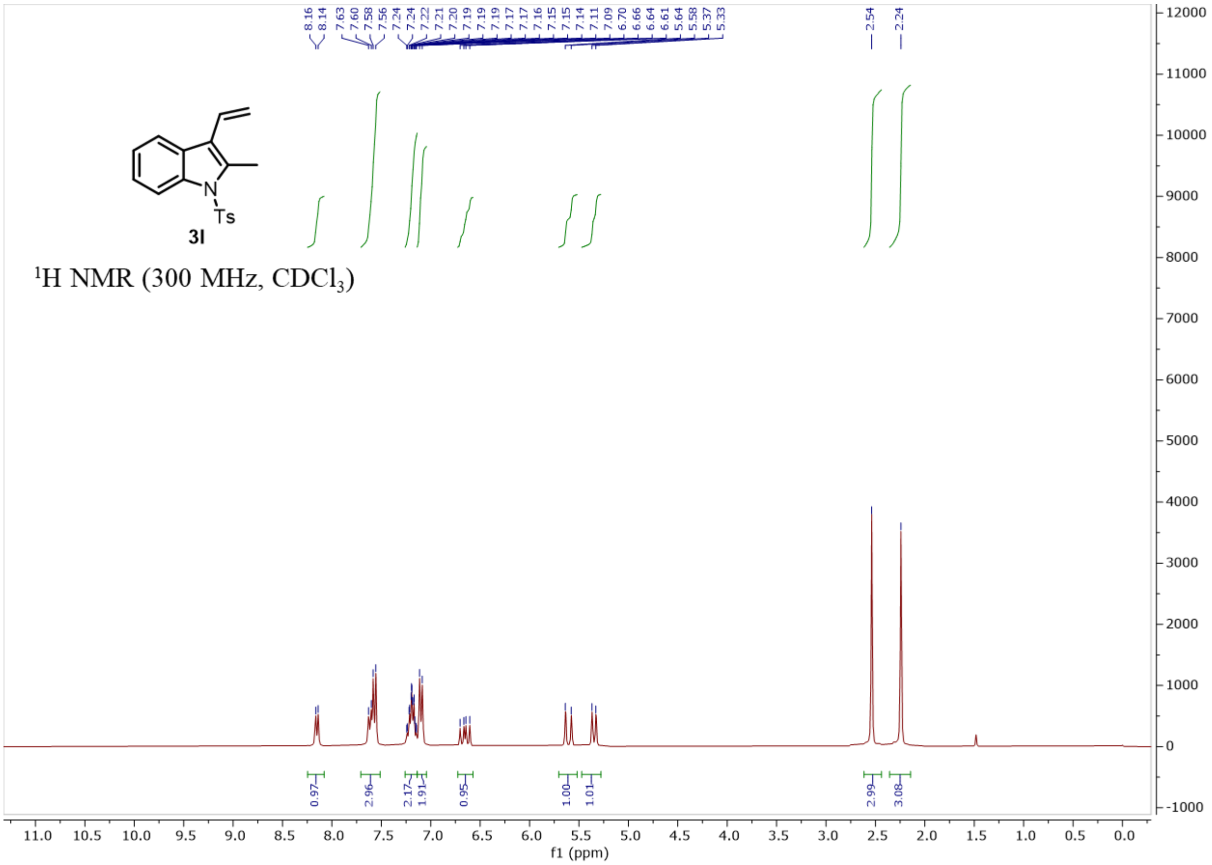
1y

^{1}H NMR (300 MHz, CDCl$_3$)



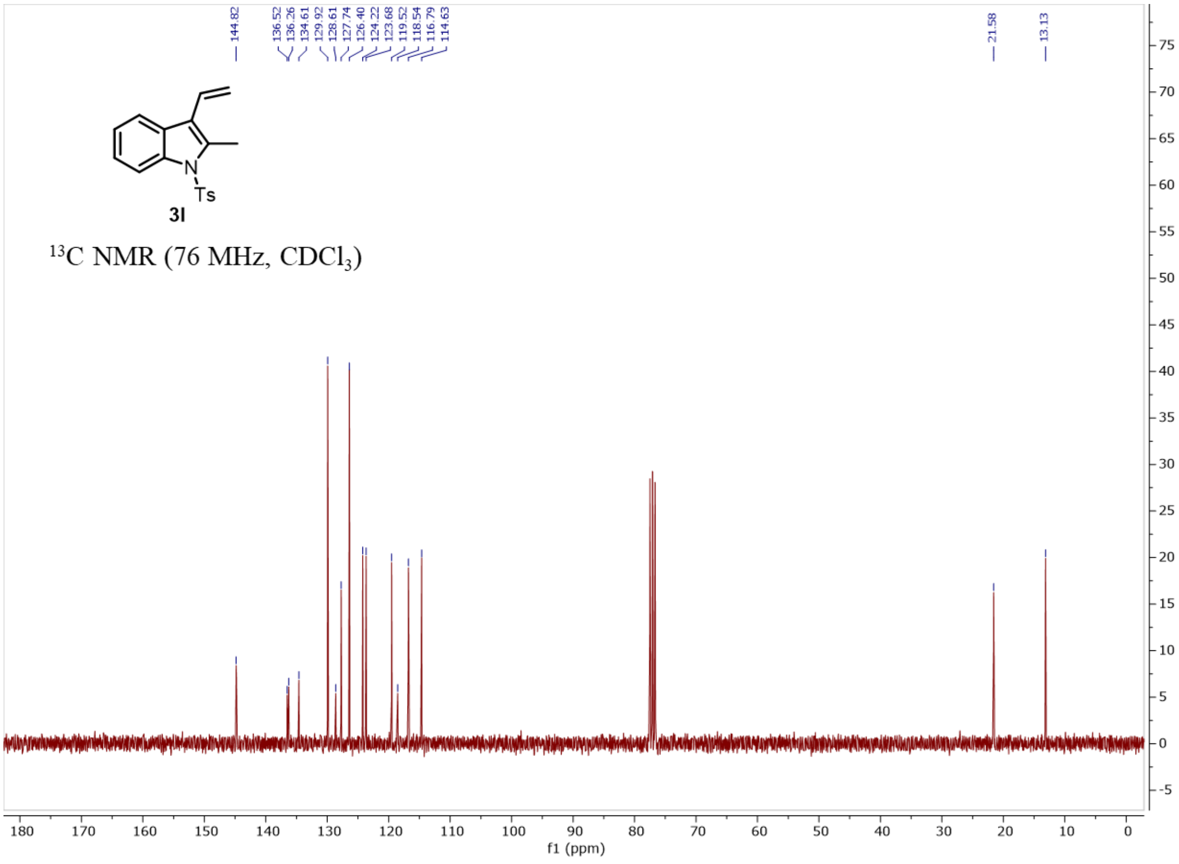
1z

^{1}H NMR (300 MHz, CDCl$_3$)



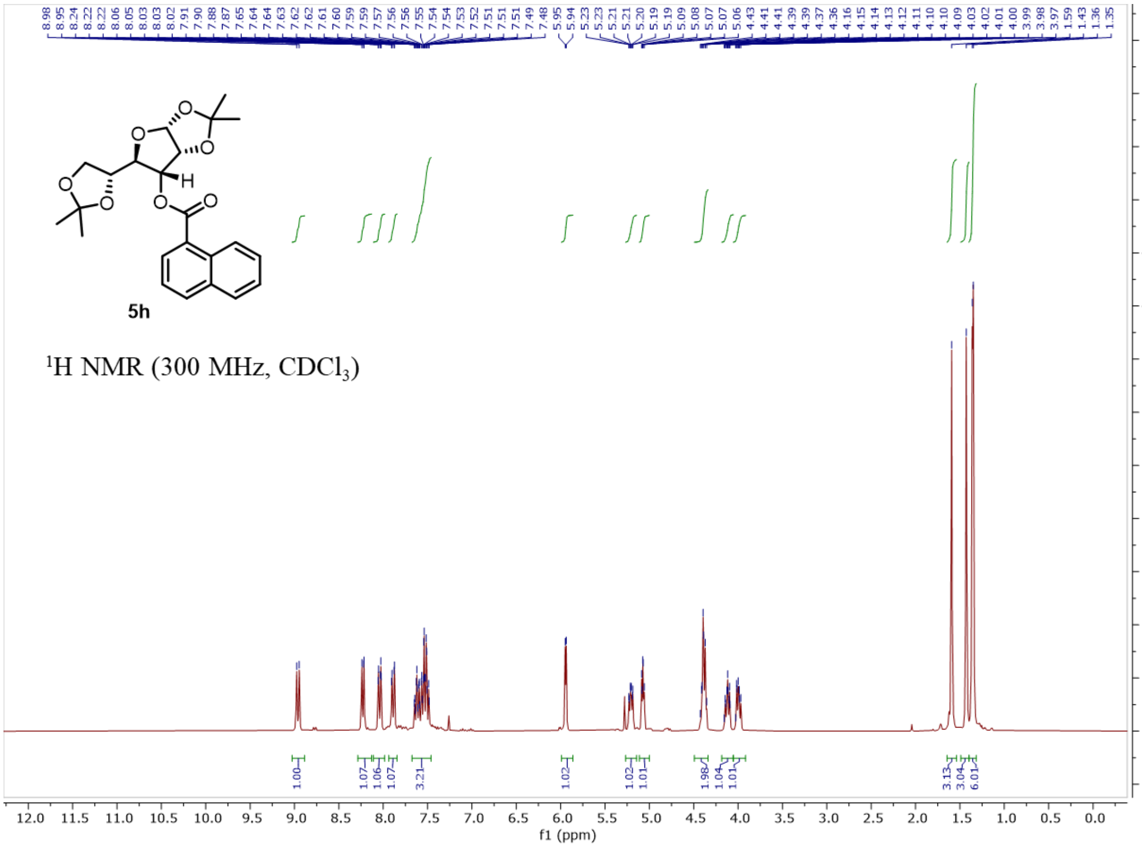
3l

^{1}H NMR (300 MHz, $CDCl_3$)



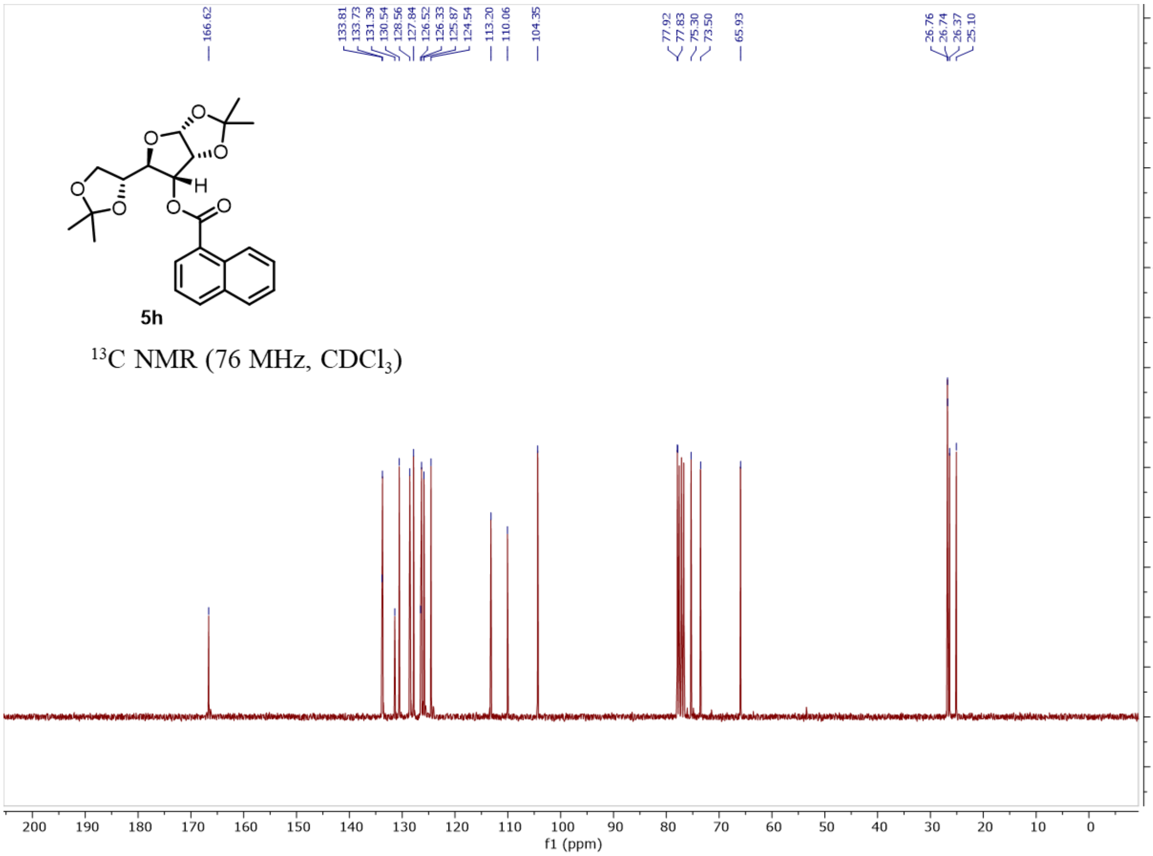
3l

^{13}C NMR (76 MHz, $CDCl_3$)



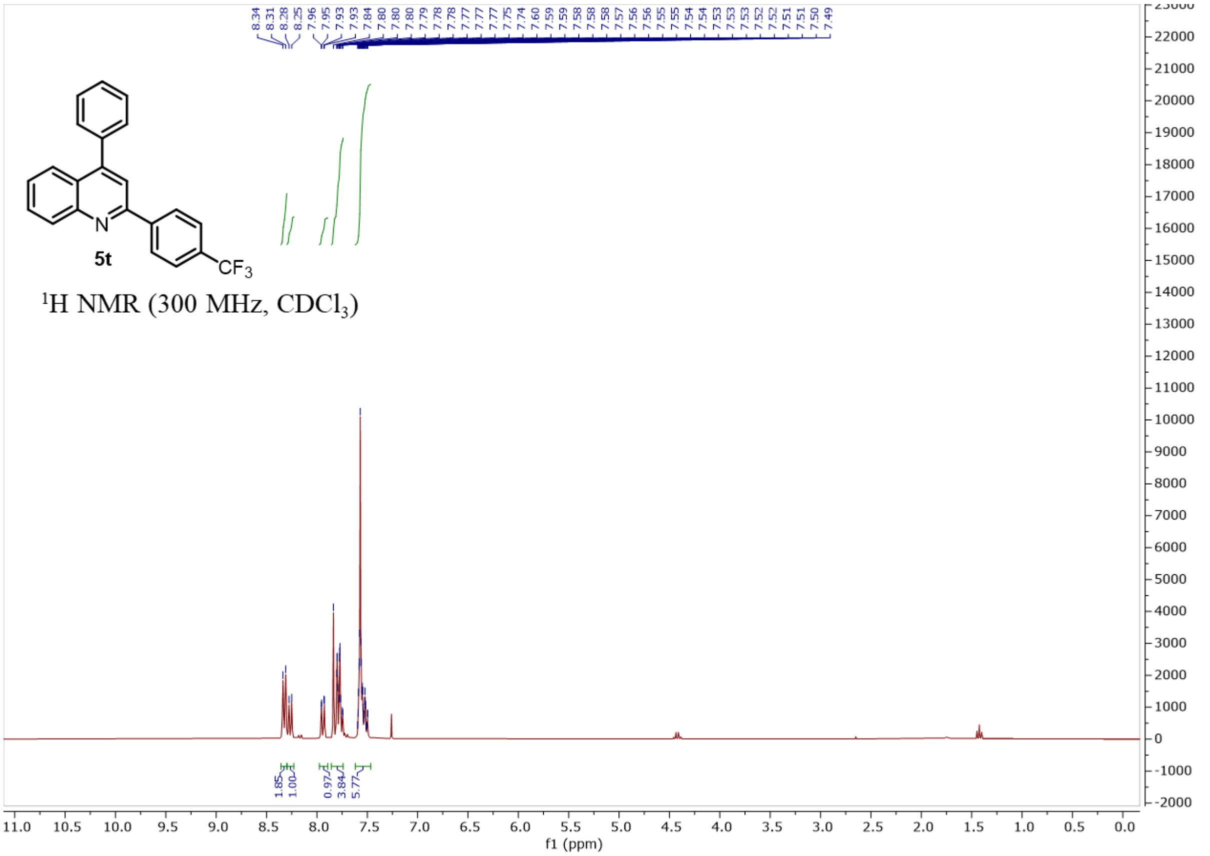
5h

^{1}H NMR (300 MHz, CDCl$_3$)

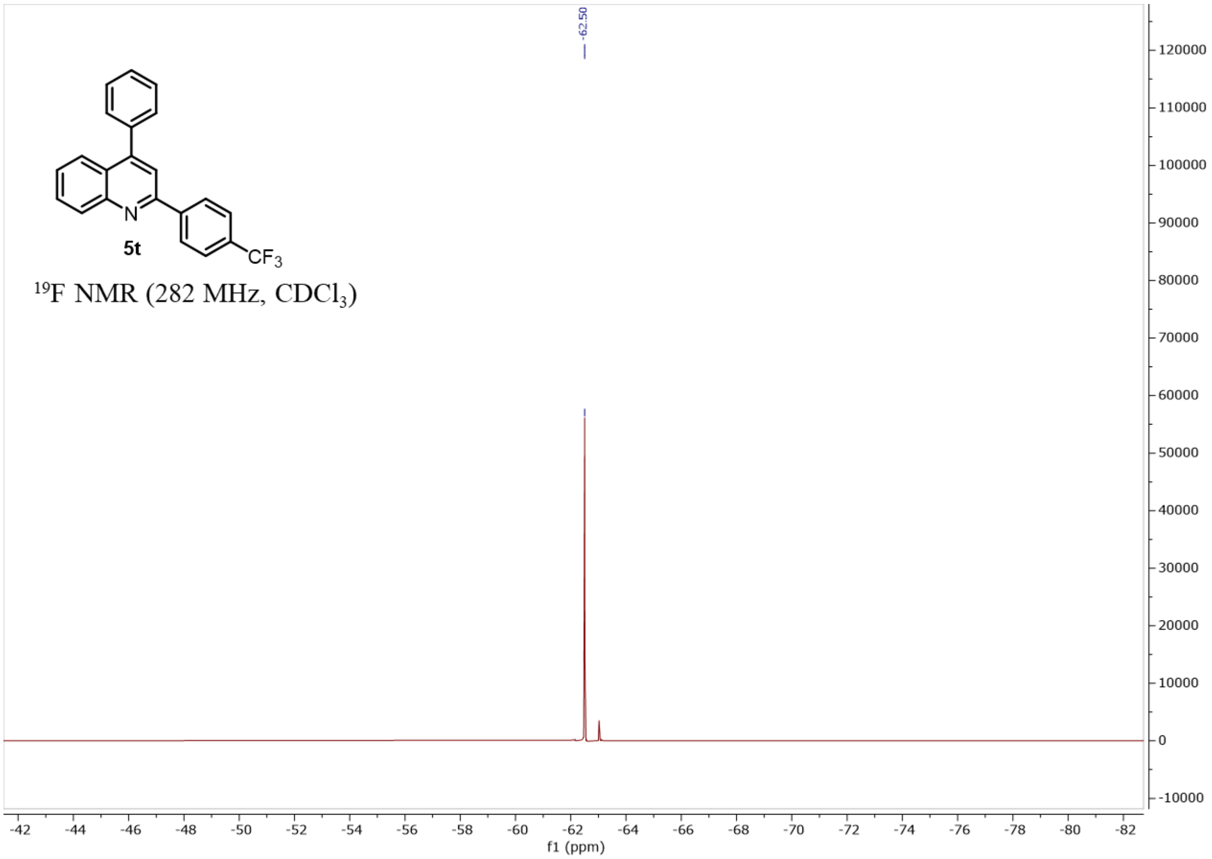


5h

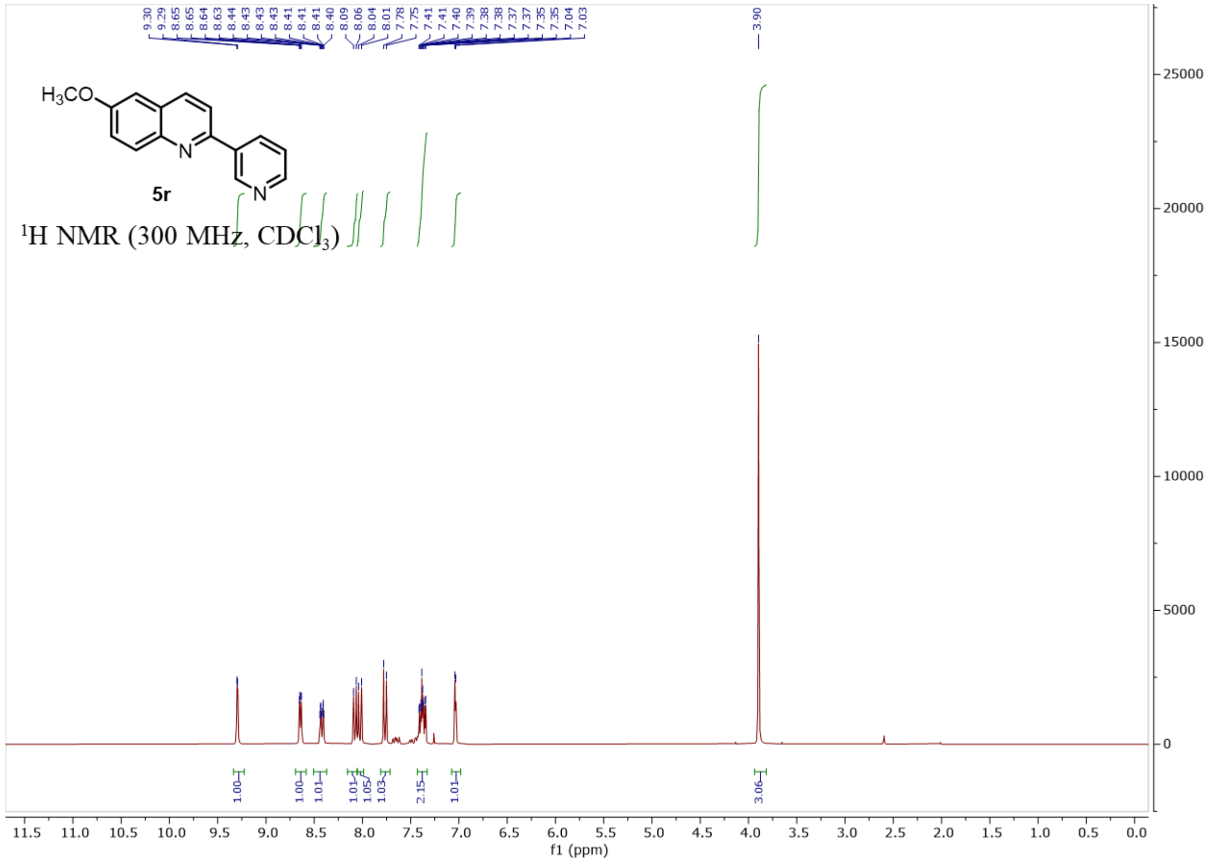
^{13}C NMR (76 MHz, CDCl$_3$)



8.34
8.31
8.28
8.25
7.96
7.95
7.93
7.93
7.84
7.80
7.80
7.80
7.79
7.78
7.78
7.78
7.77
7.77
7.75
7.74
7.60
7.59
7.59
7.58
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.49
N
5t
CF3
1H NMR (300 MHz, CDCl3)
1.85
1.00
0.97
3.84
5.77
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

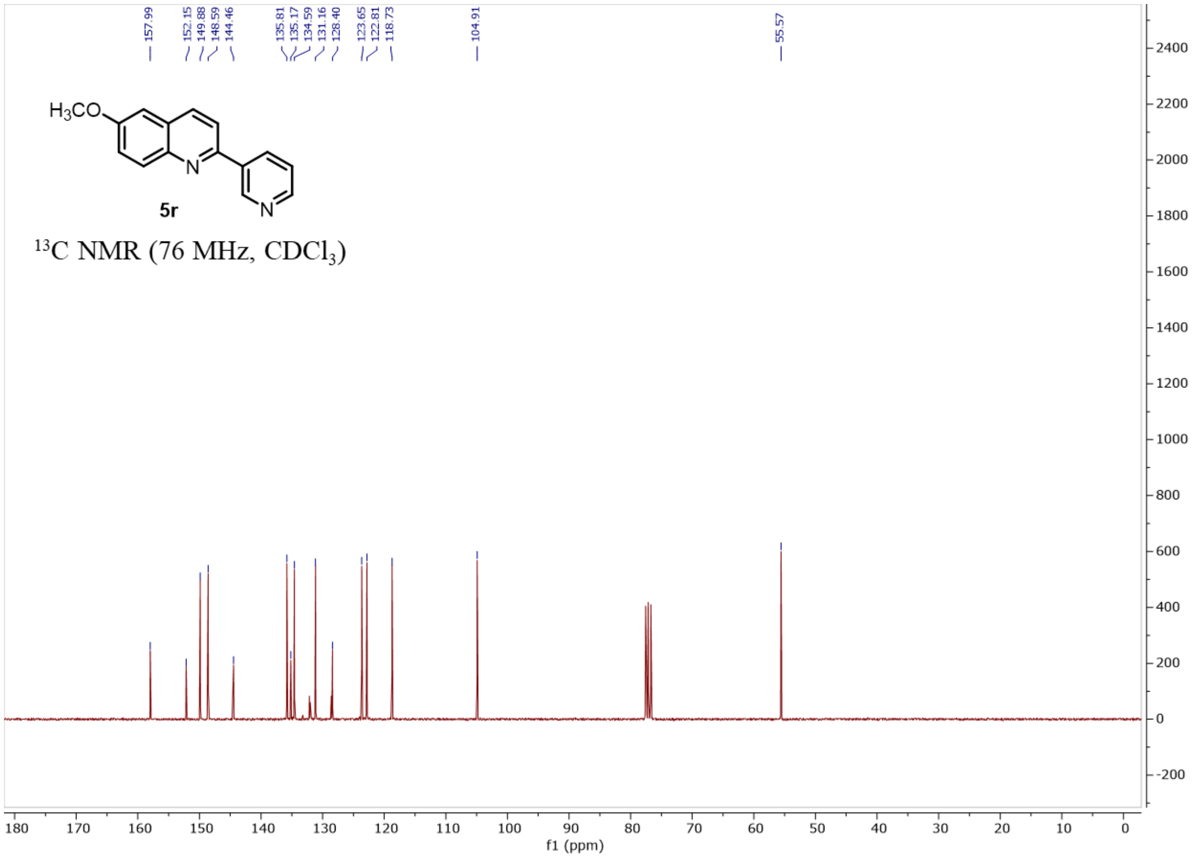


-62.50
N
5t
CF3
19F NMR (282 MHz, CDCl3)
f1 (ppm)
-42
-44
-46
-48
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000



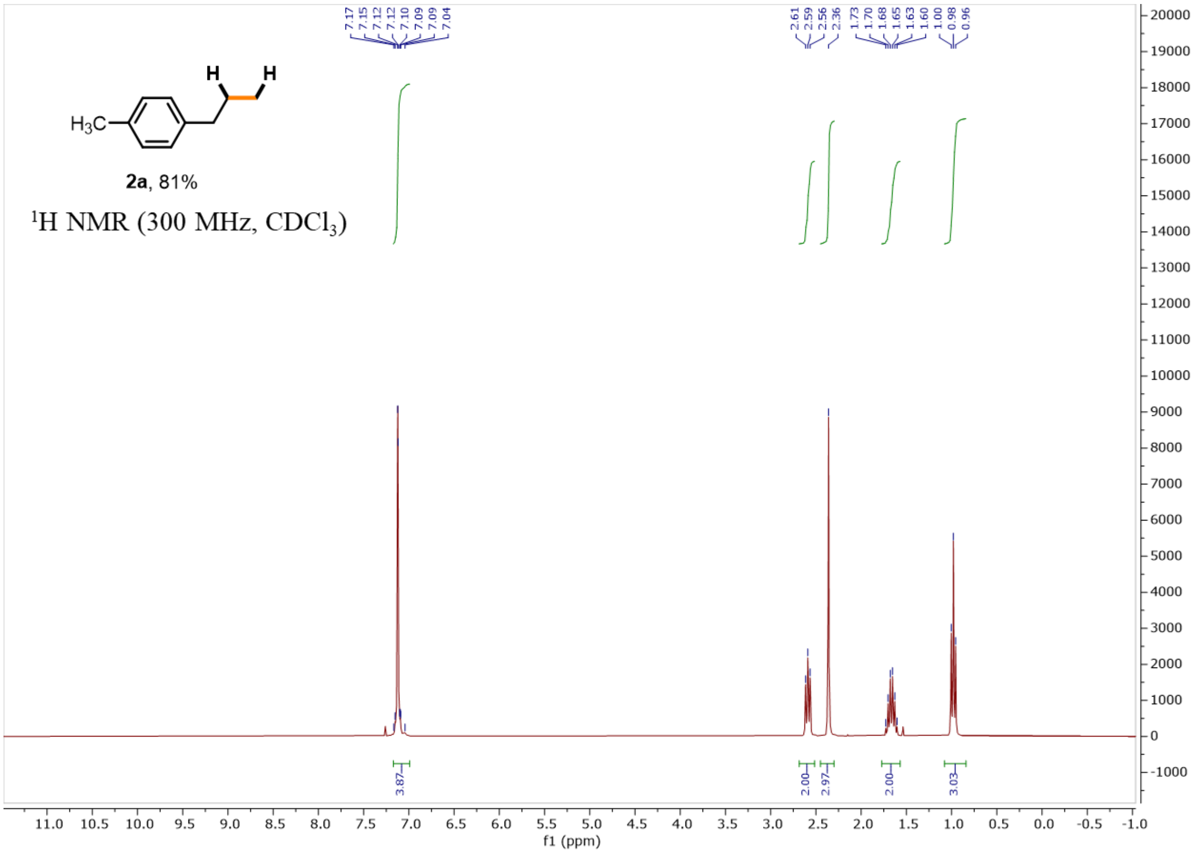
5r

^{1}H NMR (300 MHz, $CDCl_3$)

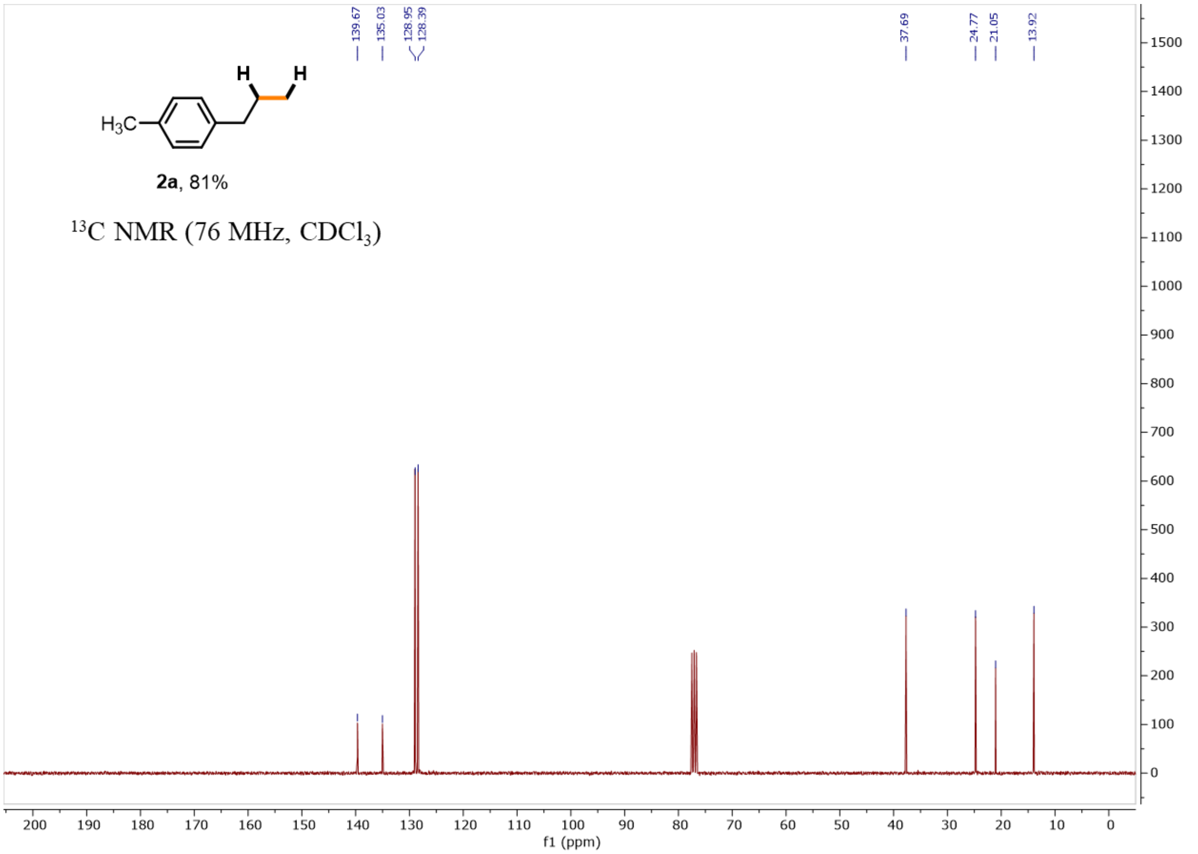


5r

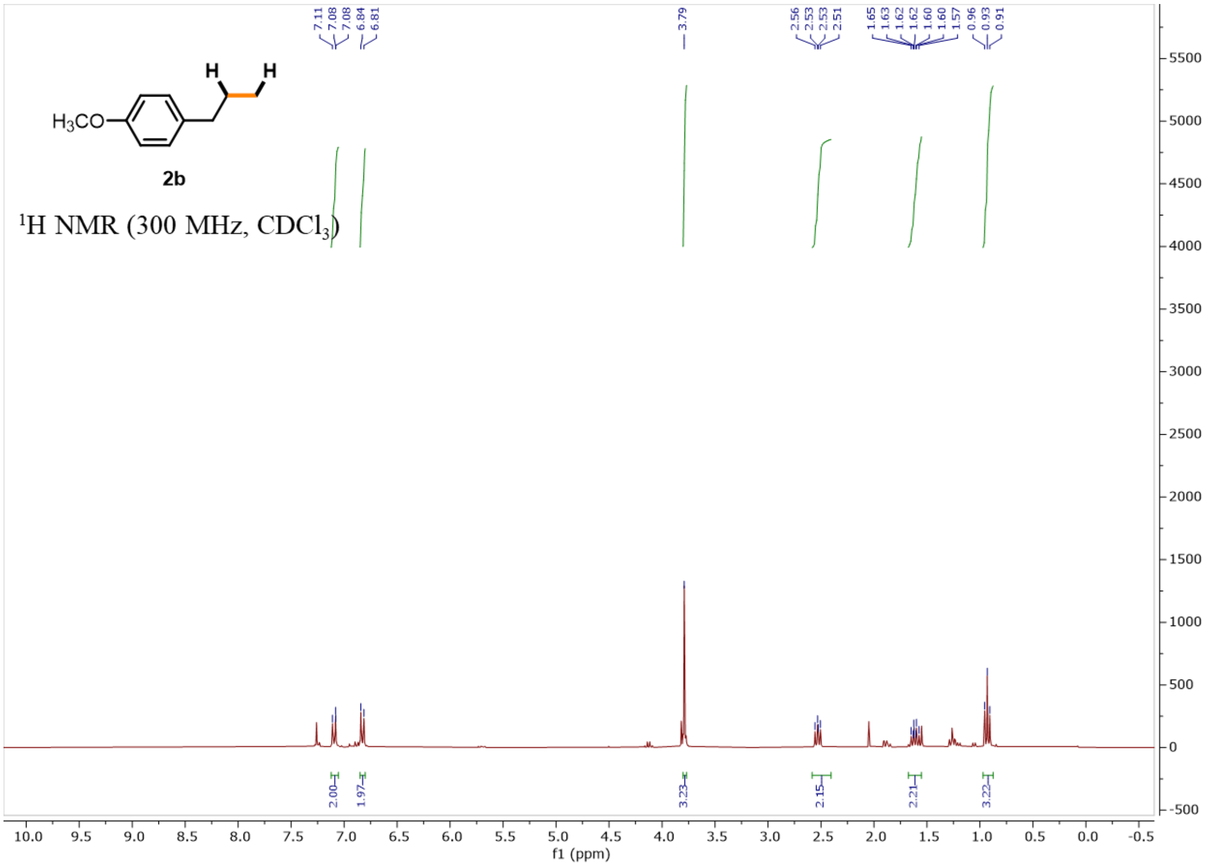
^{13}C NMR (76 MHz, $CDCl_3$)

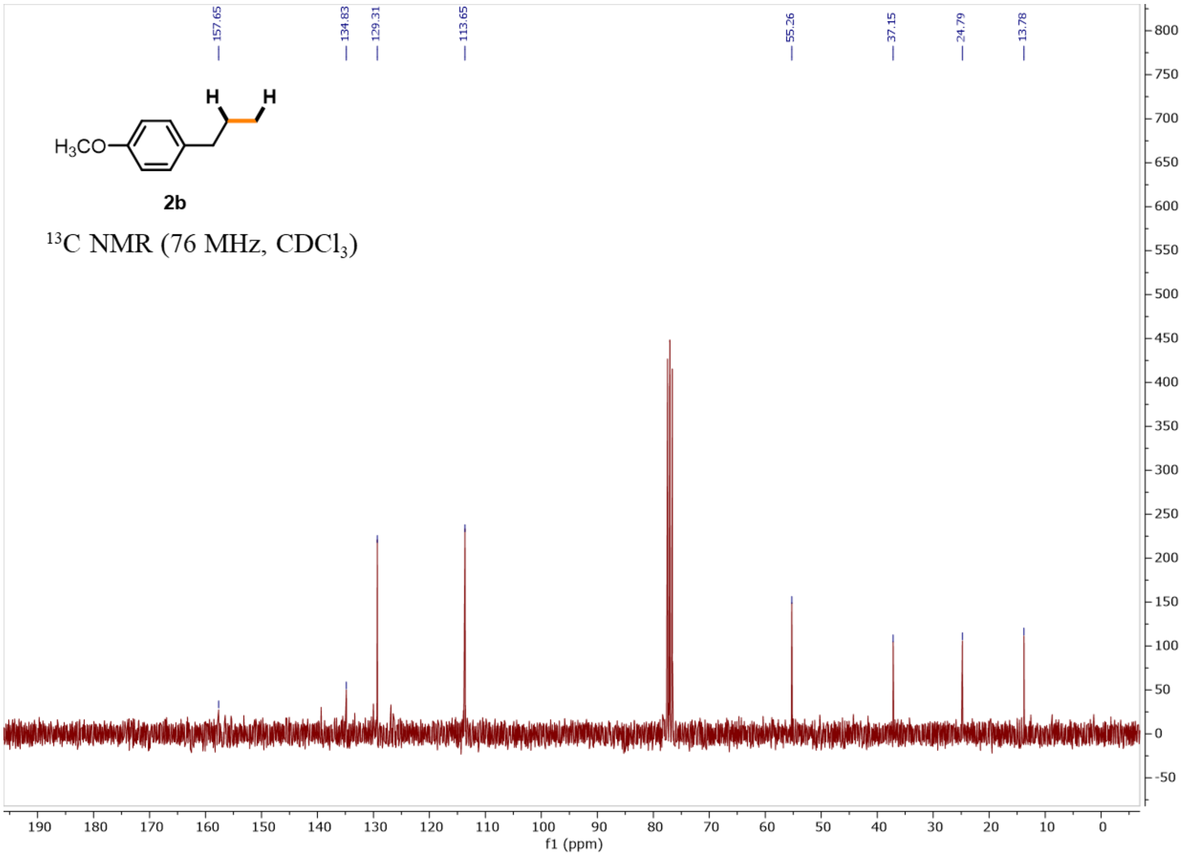

2a, 81%

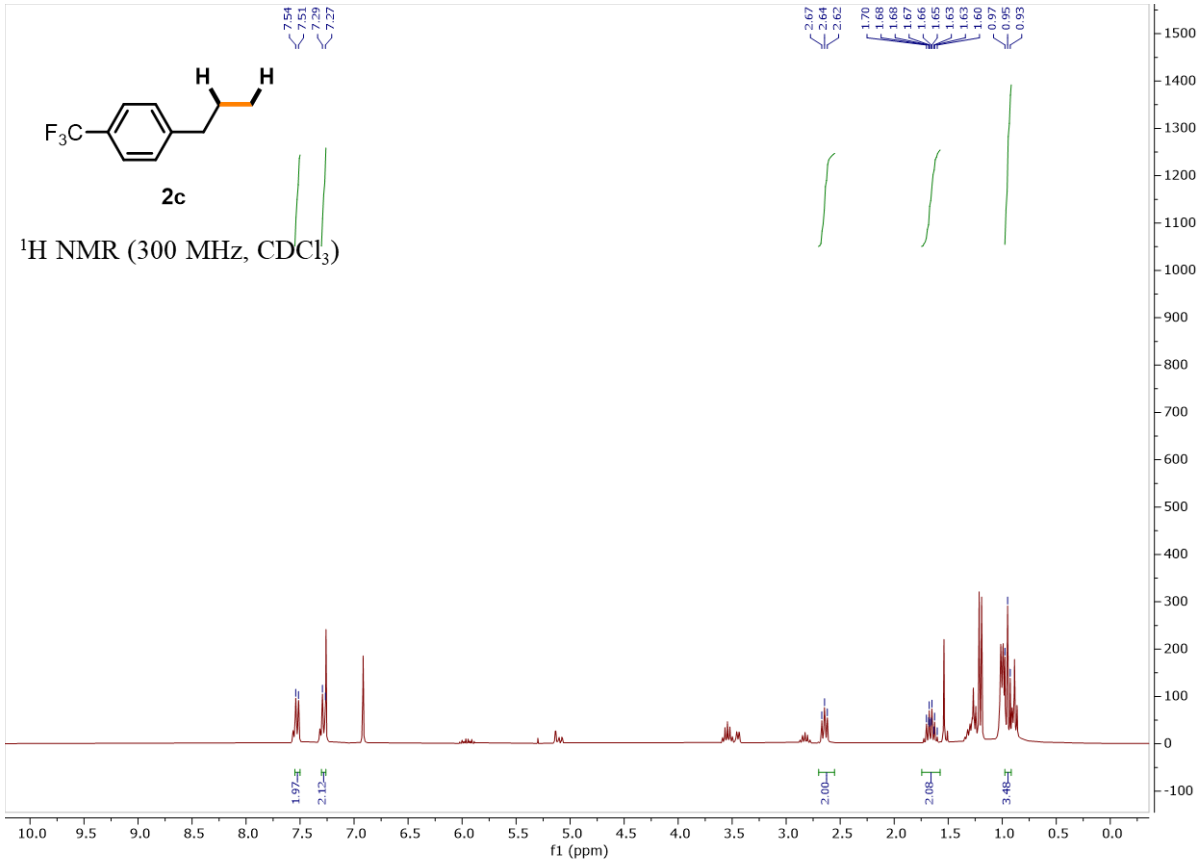
^{1}H NMR (300 MHz, $CDCl_3$)


2a, 81%

^{13}C NMR (76 MHz, $CDCl_3$)

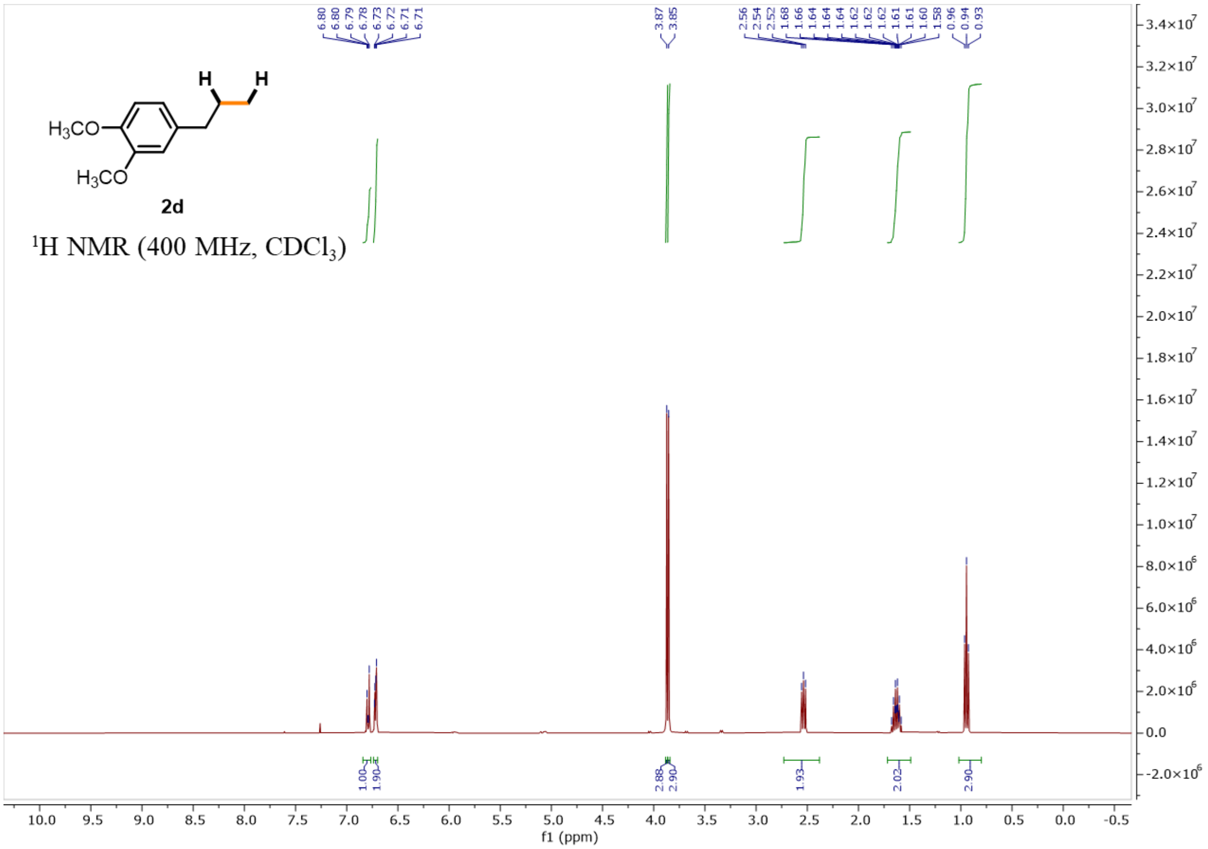

7.11
7.08
7.08
6.84
6.81
3.79
2.56
2.53
2.53
2.51
1.65
1.63
1.62
1.62
1.60
1.60
1.57
0.96
0.93
0.91
H
H
H_3CO
2b
^1H NMR (300 MHz, $CDCl_3$)
2.00
1.97
3.23
2.15
2.21
3.22
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

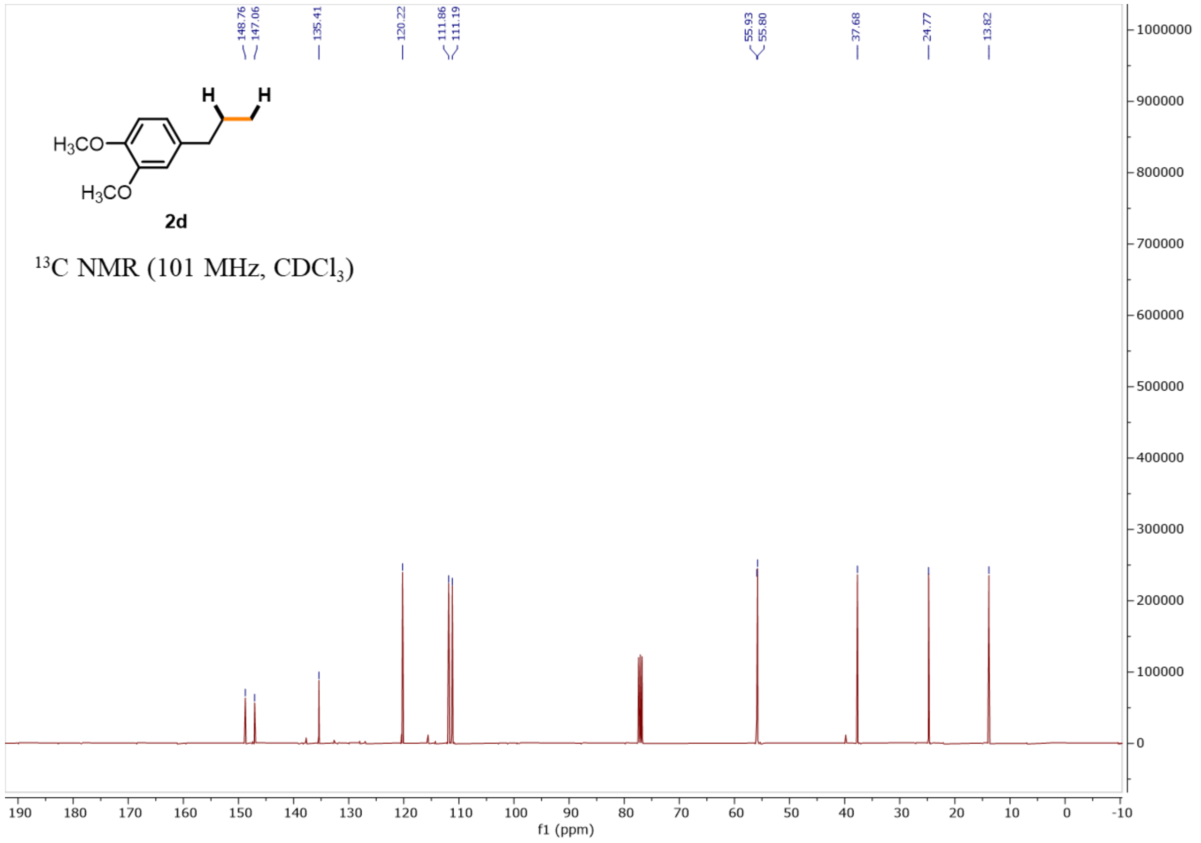

157.65
134.83
129.31
113.65
55.26
37.15
24.79
13.78
H
H
H_3CO
2b
^{13}C NMR (76 MHz, $CDCl_3$)
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

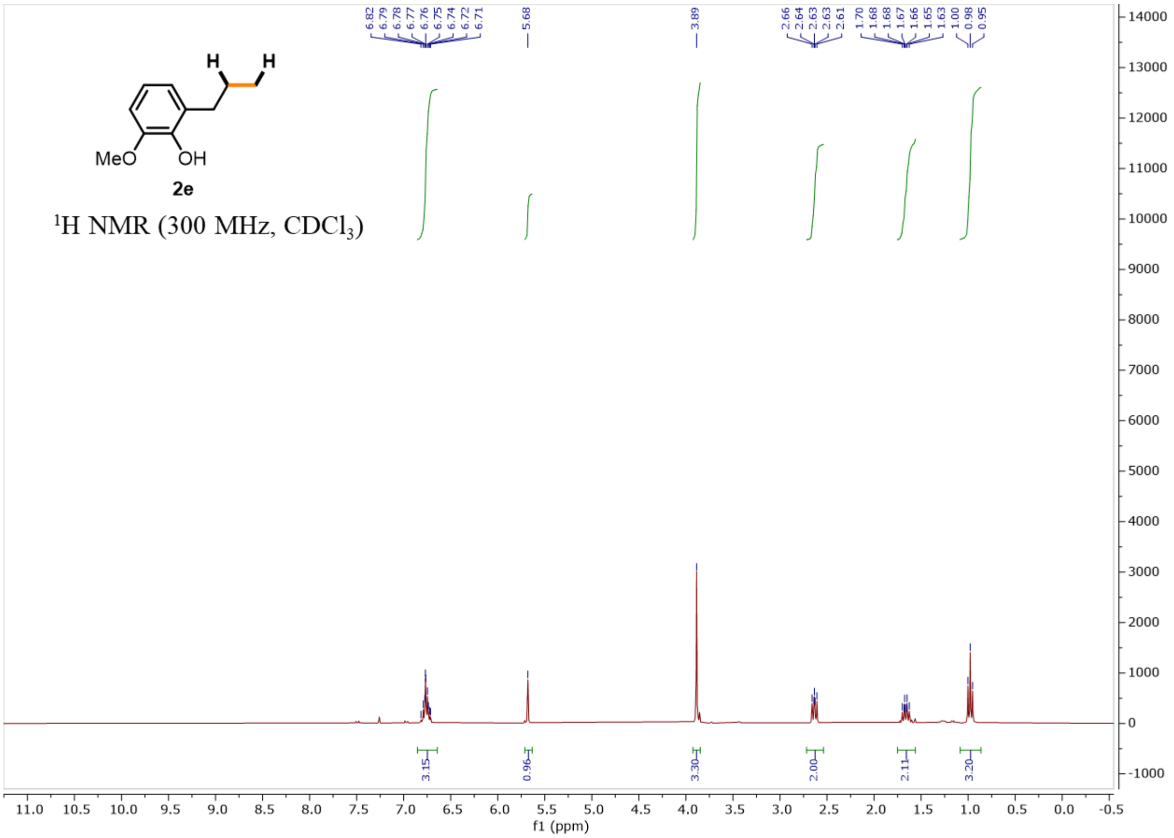


2c

^{1}H NMR (300 MHz, $CDCl_3$)

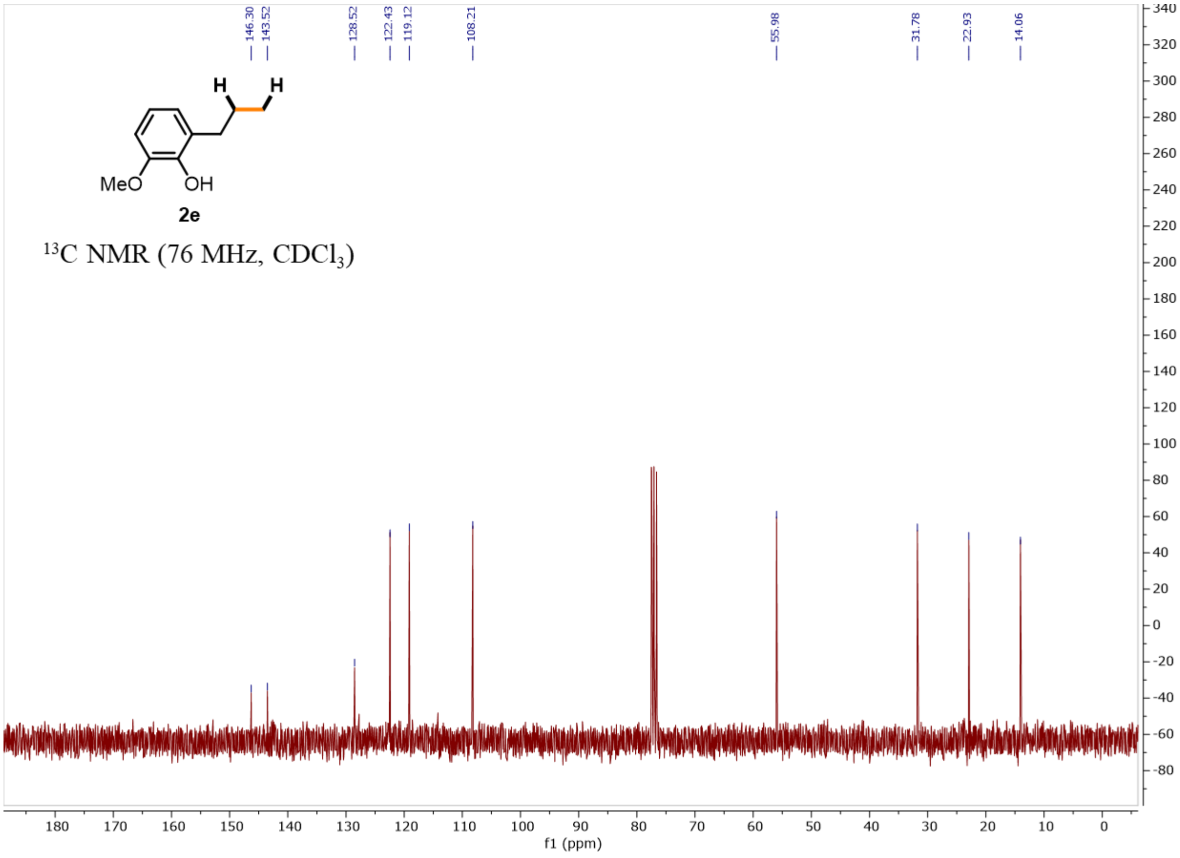

H
H
H_3CO
H_3CO
2d
^1H NMR (400 MHz, $CDCl_3$)
6.80
6.80
6.79
6.78
6.73
6.72
6.71
6.71
3.87
3.85
2.56
2.54
2.52
1.68
1.66
1.64
1.64
1.64
1.62
1.62
1.62
1.61
1.61
1.60
1.58
0.96
0.94
0.93
1.00
1.90
2.88
2.90
1.93
2.02
2.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
3.4×10^7
3.2×10^7
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6


H
H
H_3CO
H_3CO
2d
^{13}C NMR (101 MHz, $CDCl_3$)
148.76
147.06
135.41
120.22
111.86
111.19
55.93
55.80
37.68
24.77
13.82
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0



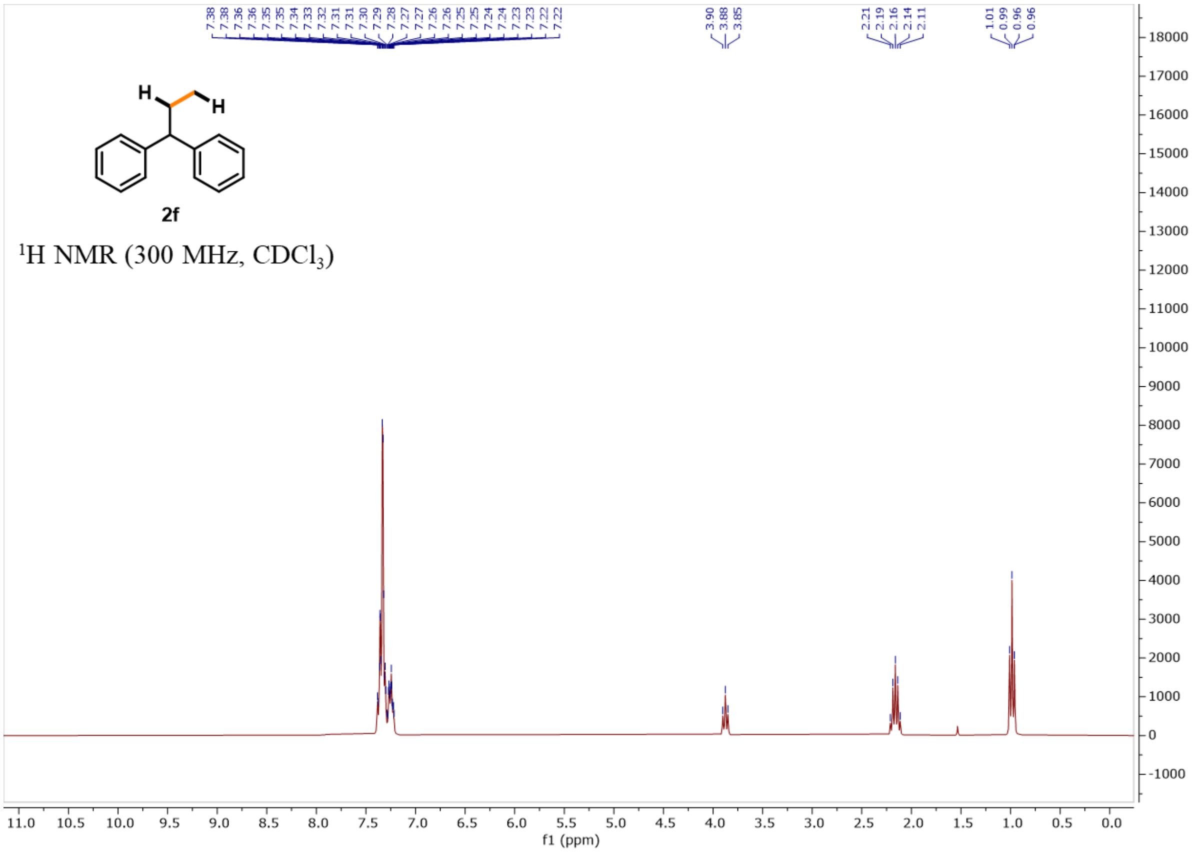
2e

^{1}H NMR (300 MHz, CDCl$_3$)

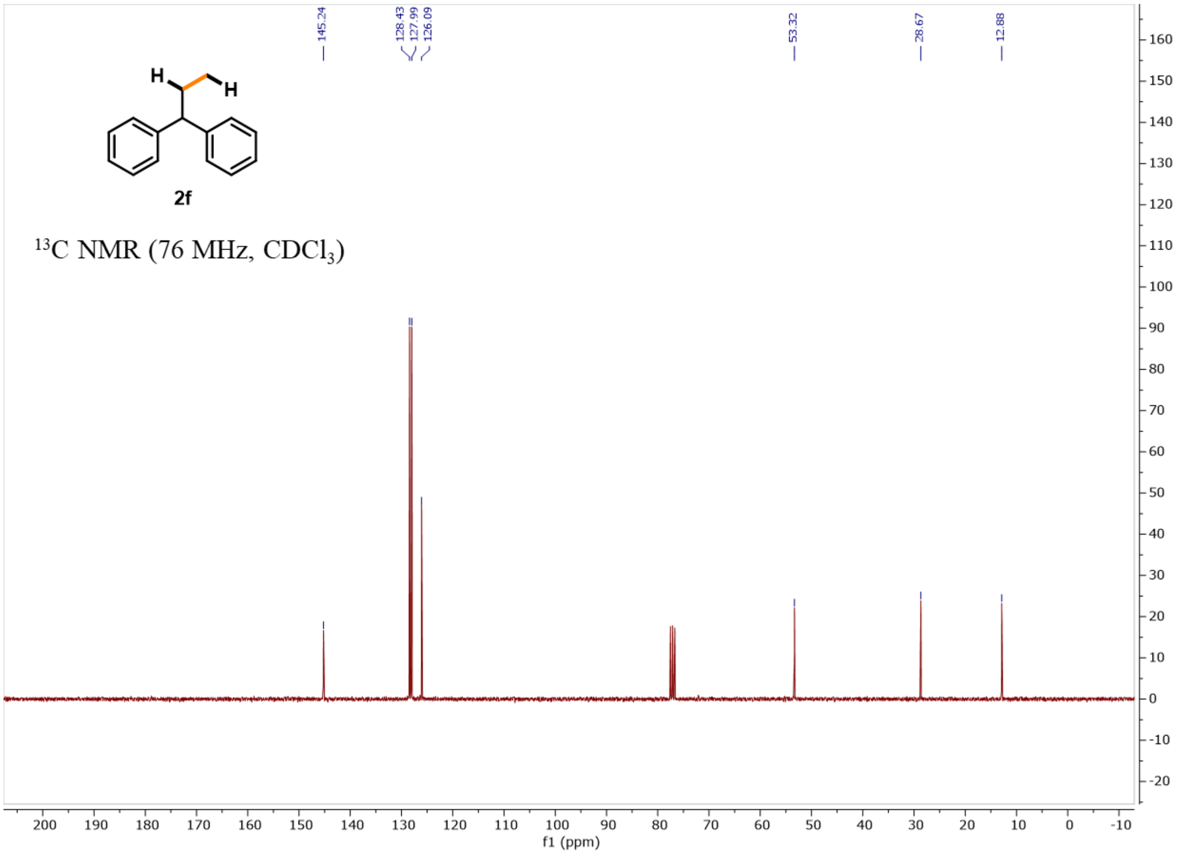


2e

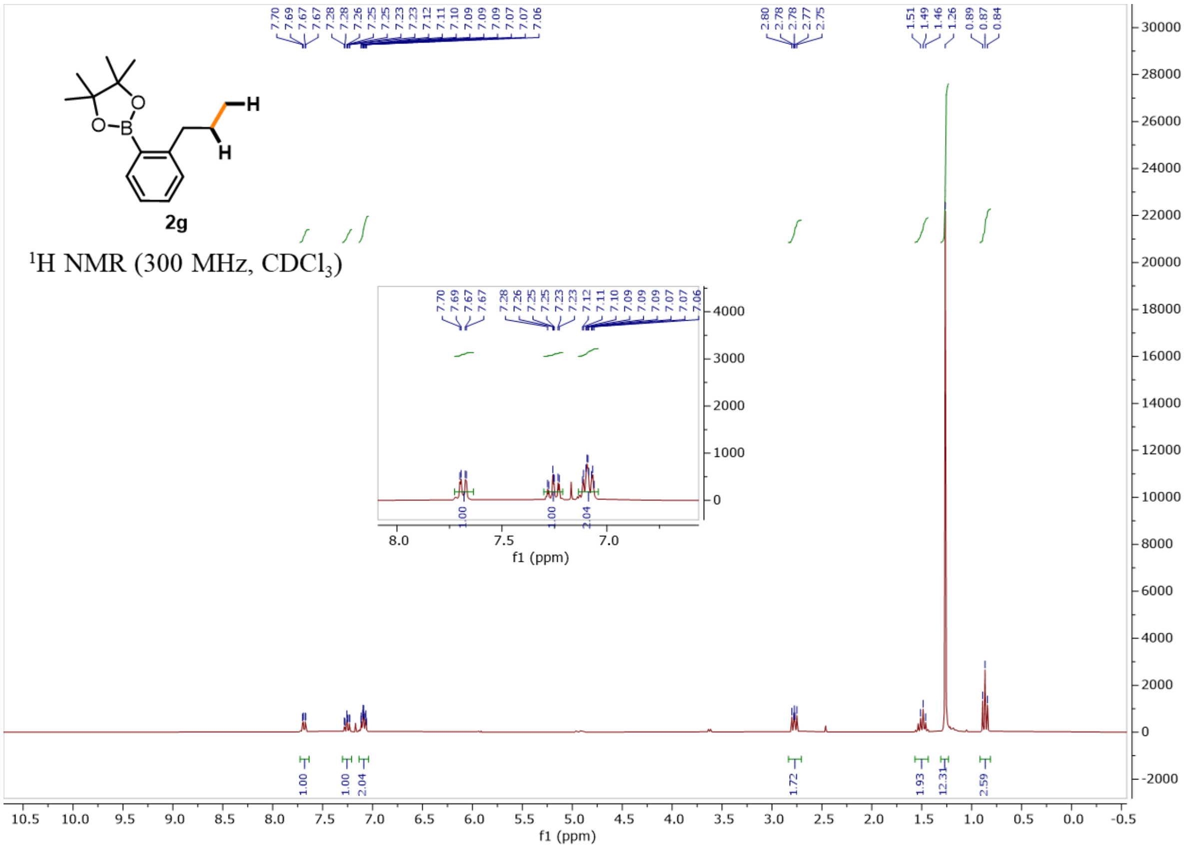
^{13}C NMR (76 MHz, CDCl$_3$)

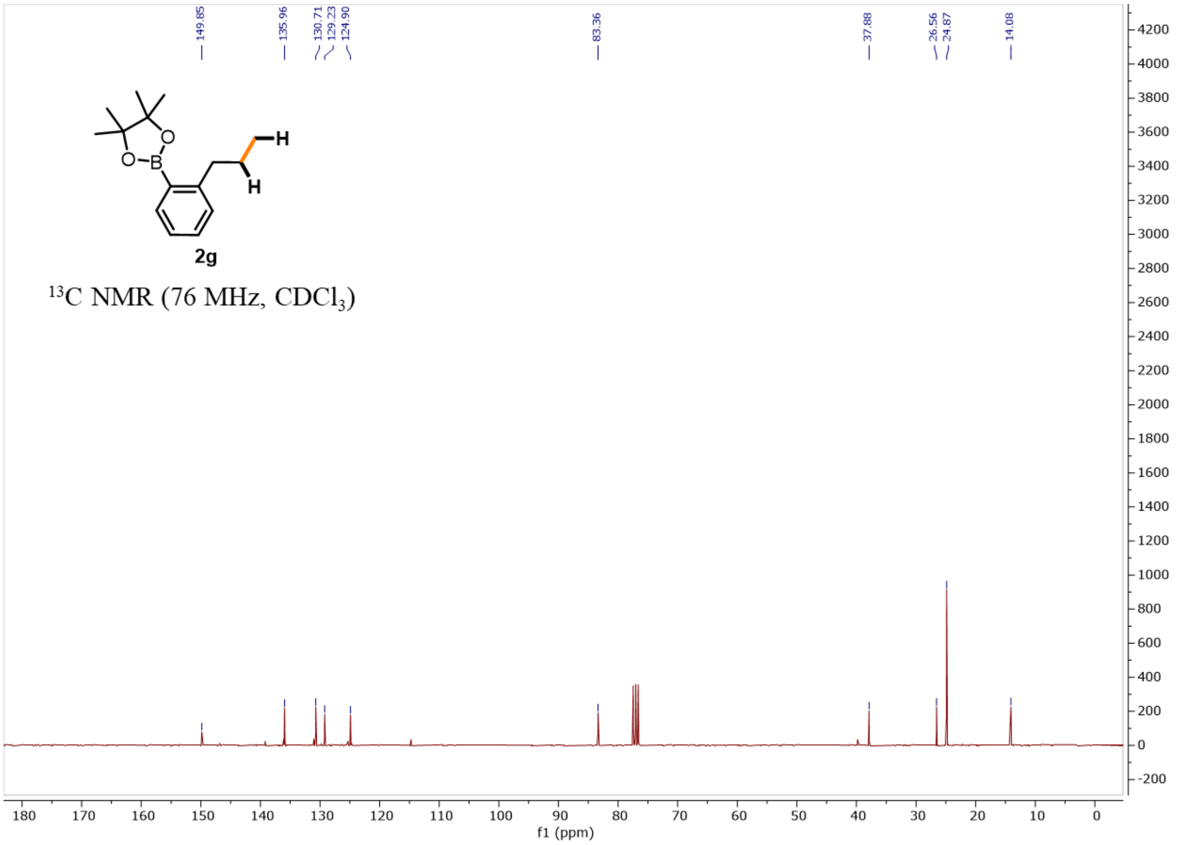


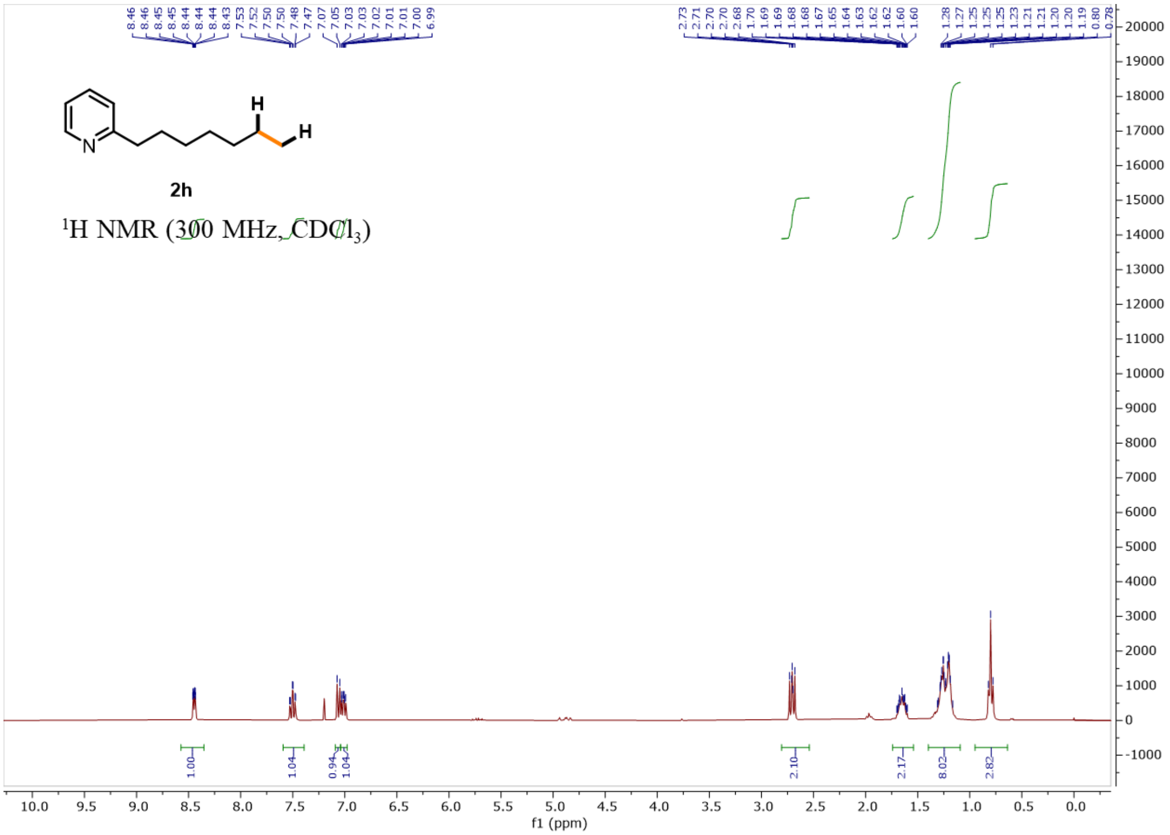
^{1}H NMR (300 MHz, CDCl$_3$)



^{13}C NMR (76 MHz, CDCl$_3$)

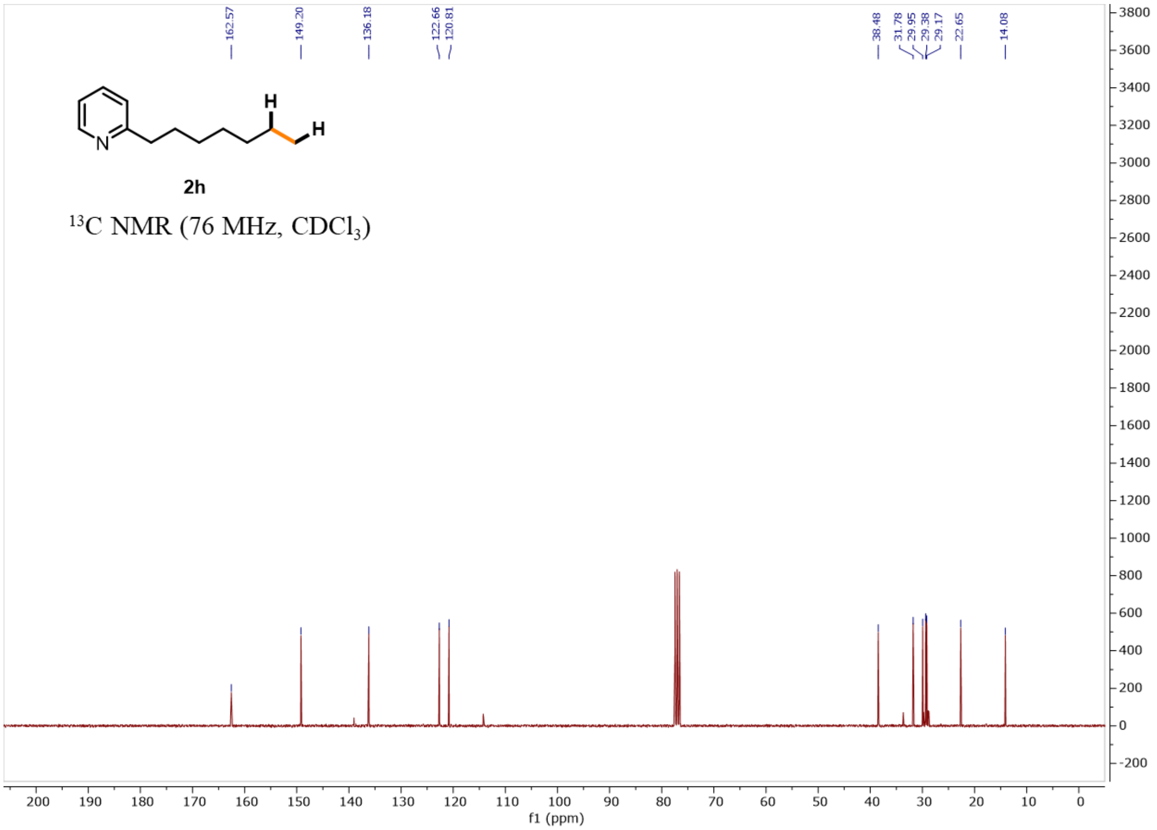

2g
^{1}H NMR (300 MHz, CDCl$_3$)
7.70 7.69 7.67 7.67 7.28 7.28 7.26 7.25 7.25 7.23 7.23 7.12 7.11 7.10 7.09 7.09 7.09 7.07 7.07 7.06
2.80 2.78 2.78 2.77 2.75
1.51 1.49 1.46 1.26
0.89 0.87 0.84
1.00 1.00 2.04 1.72 1.93 12.31 2.59
f1 (ppm)


2g
^{13}C NMR (76 MHz, CDCl$_3$)
149.85
135.96
130.71 129.23 124.90
83.36
37.88
26.56 24.87
14.08
f1 (ppm)



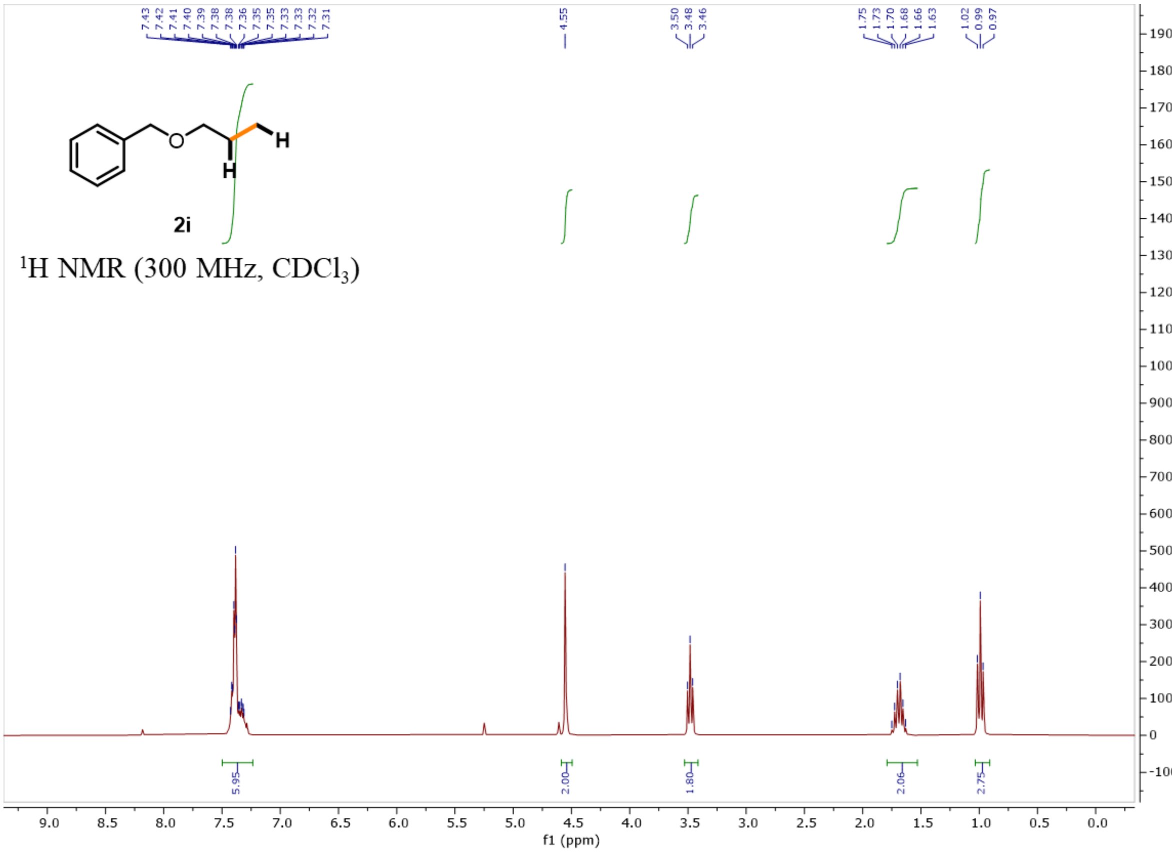
2h

^{1}H NMR (300 MHz, CDCl$_3$)



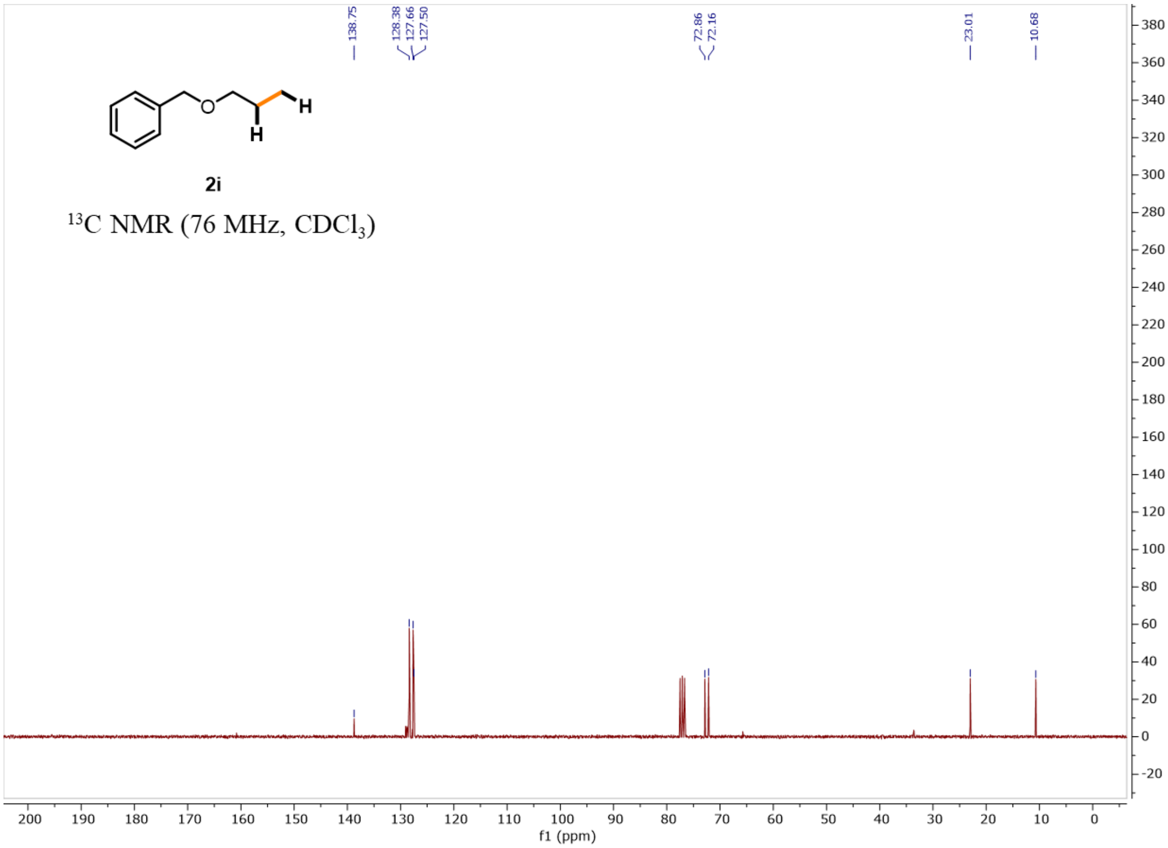
2h

^{13}C NMR (76 MHz, CDCl$_3$)



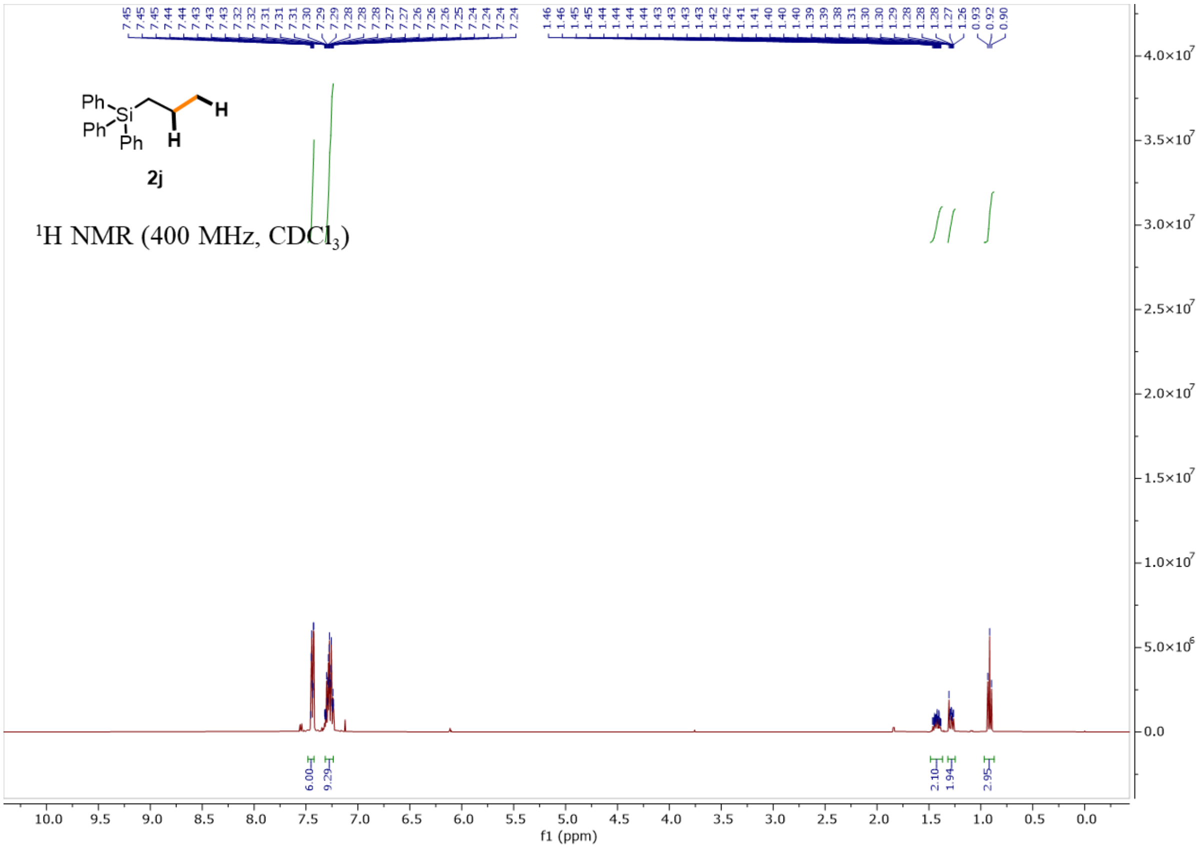
2i

^{1}H NMR (300 MHz, $CDCl_3$)



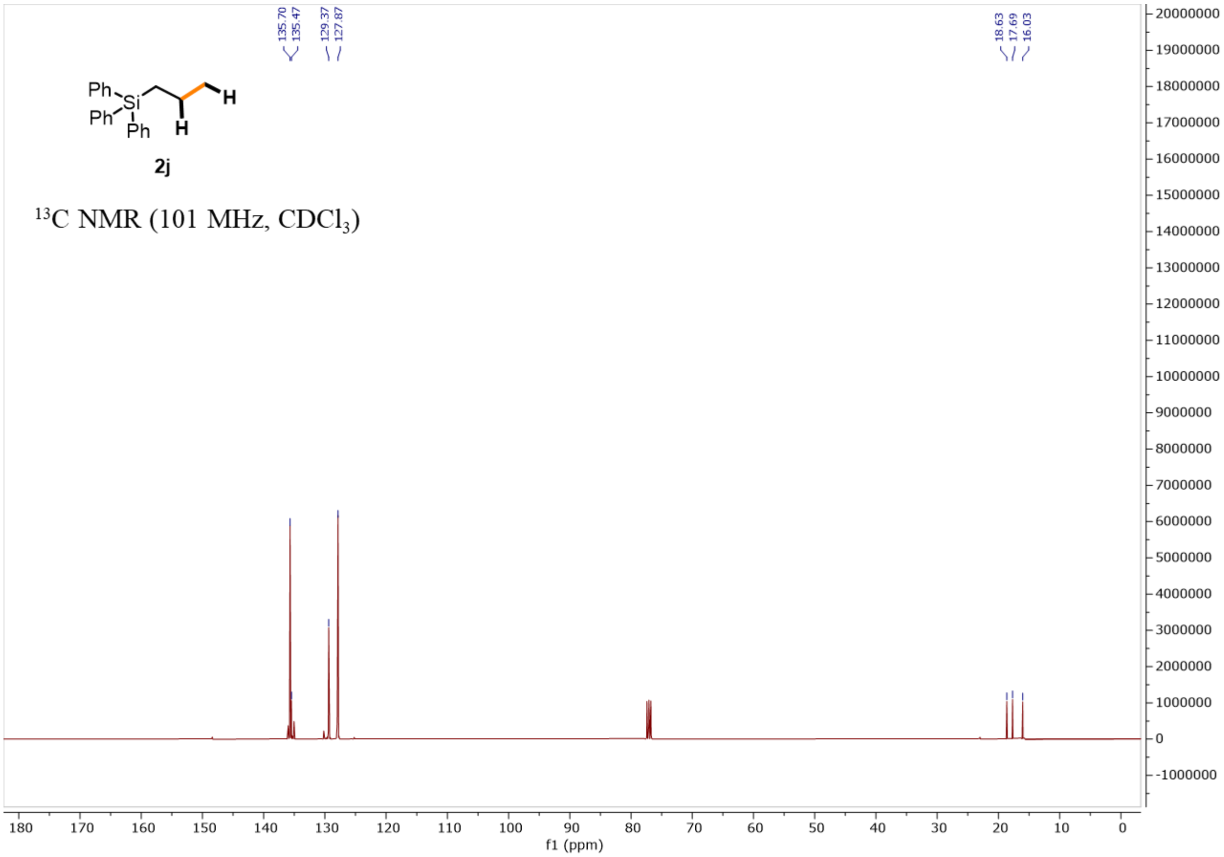
2i

^{13}C NMR (76 MHz, $CDCl_3$)



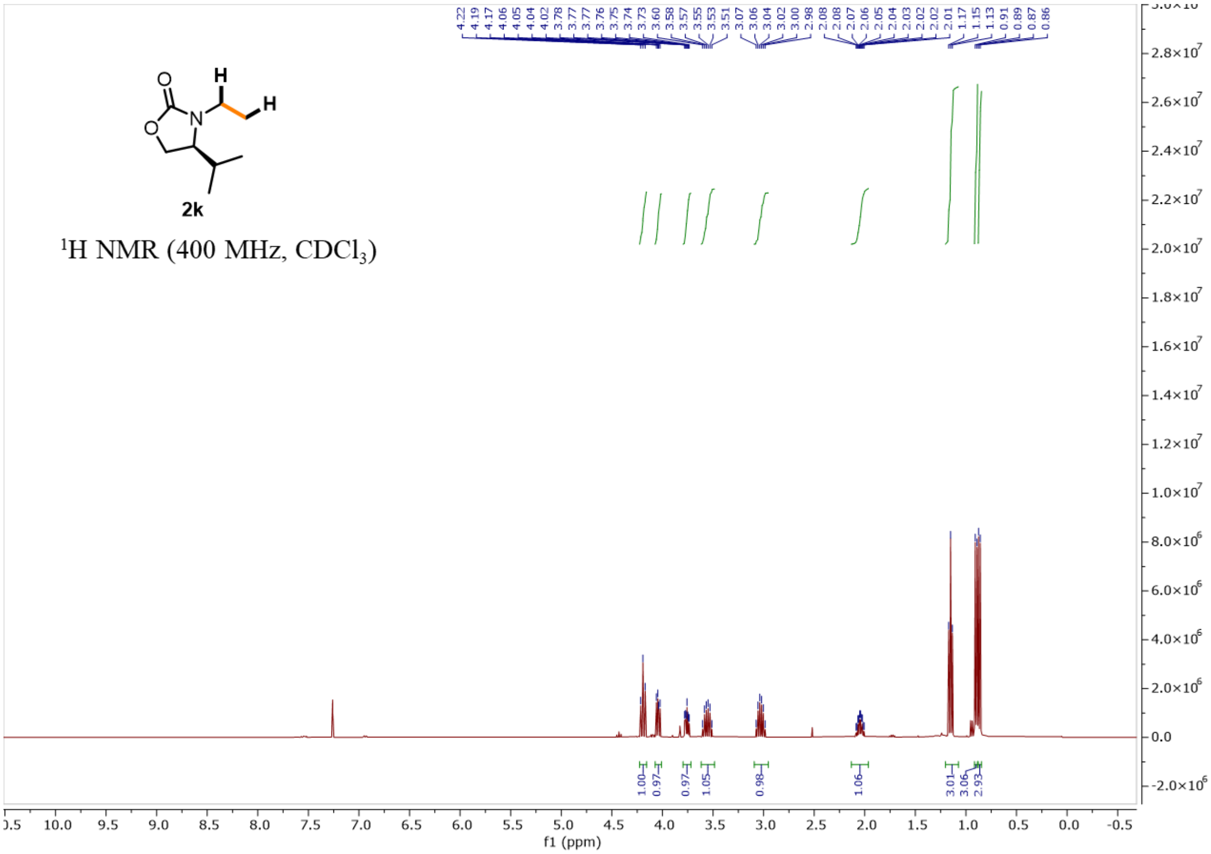
2j

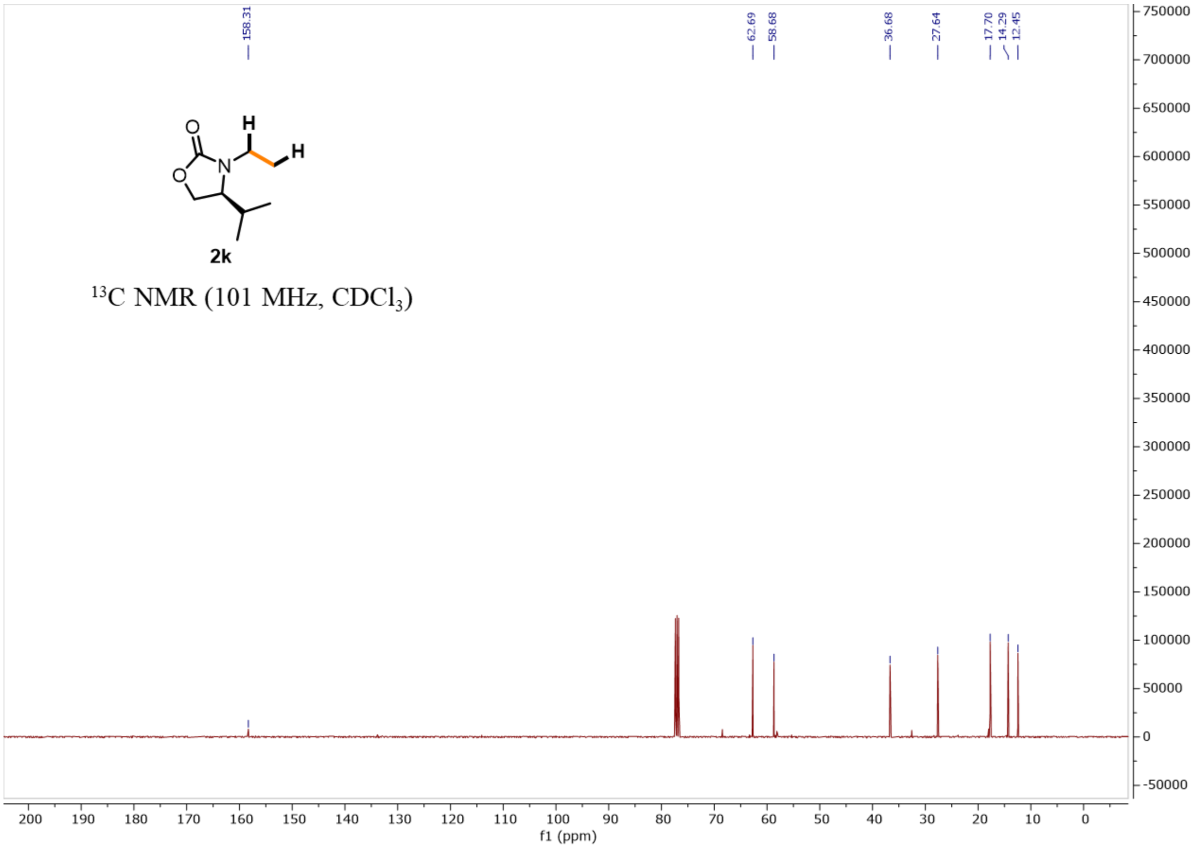
^{1}H NMR (400 MHz, CDCl$_3$)

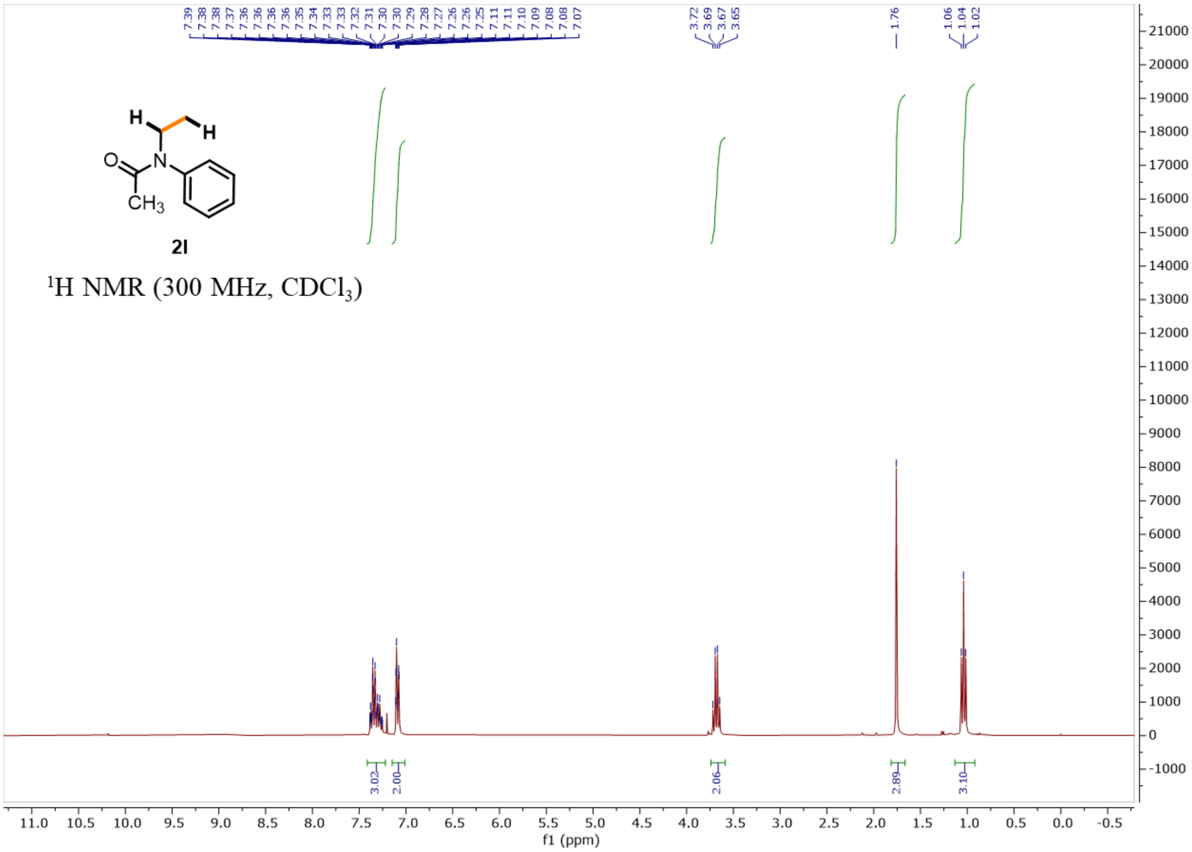


2j

^{13}C NMR (101 MHz, CDCl$_3$)

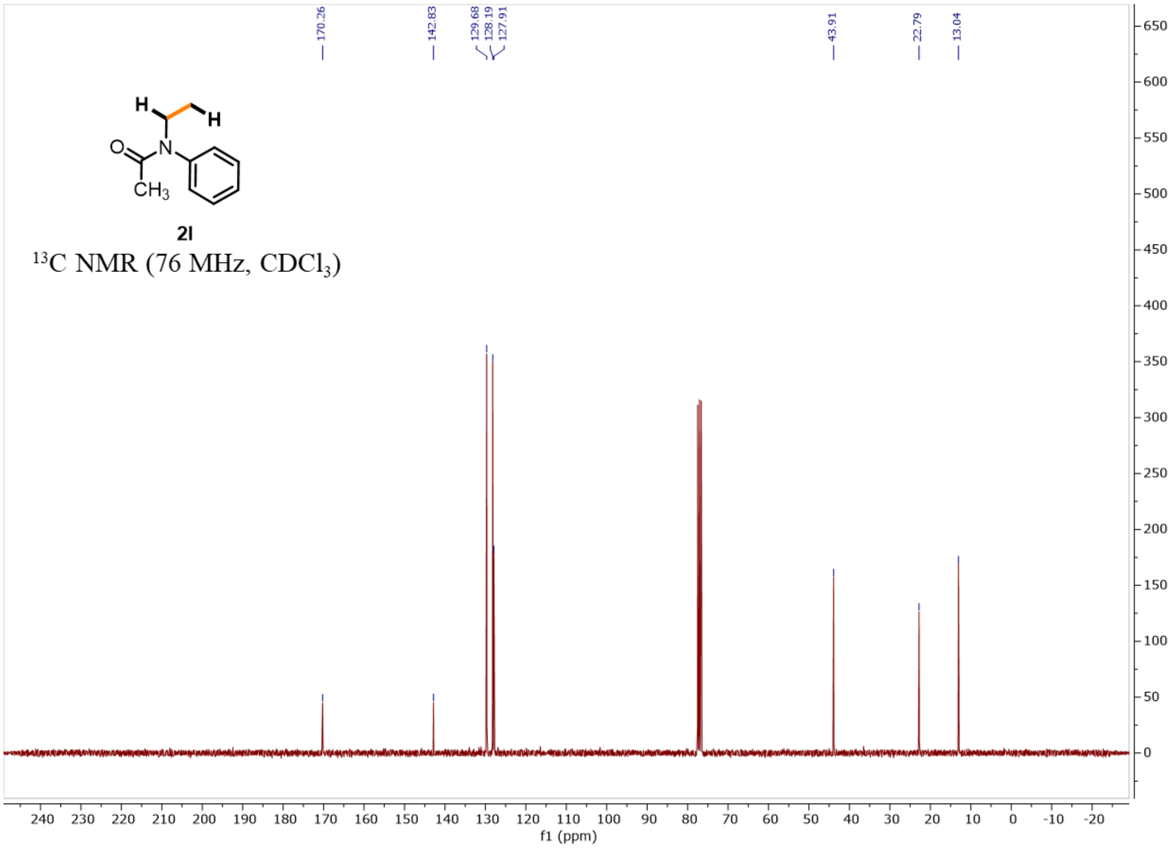

2k
^{1}H NMR (400 MHz, CDCl$_3$)
4.22
4.19
4.17
4.06
4.05
4.04
4.02
3.78
3.77
3.77
3.76
3.75
3.74
3.73
3.60
3.58
3.57
3.55
3.53
3.51
3.07
3.06
3.04
3.02
3.00
2.98
2.08
2.08
2.07
2.06
2.05
2.04
2.03
2.02
2.02
2.01
1.17
1.15
1.13
0.91
0.89
0.87
0.86
1.00
0.97
0.97
1.05
0.98
1.06
3.01
3.06
2.93
f1 (ppm)


2k
^{13}C NMR (101 MHz, CDCl$_3$)
158.31
62.69
58.68
36.68
27.64
17.70
14.29
12.45
f1 (ppm)



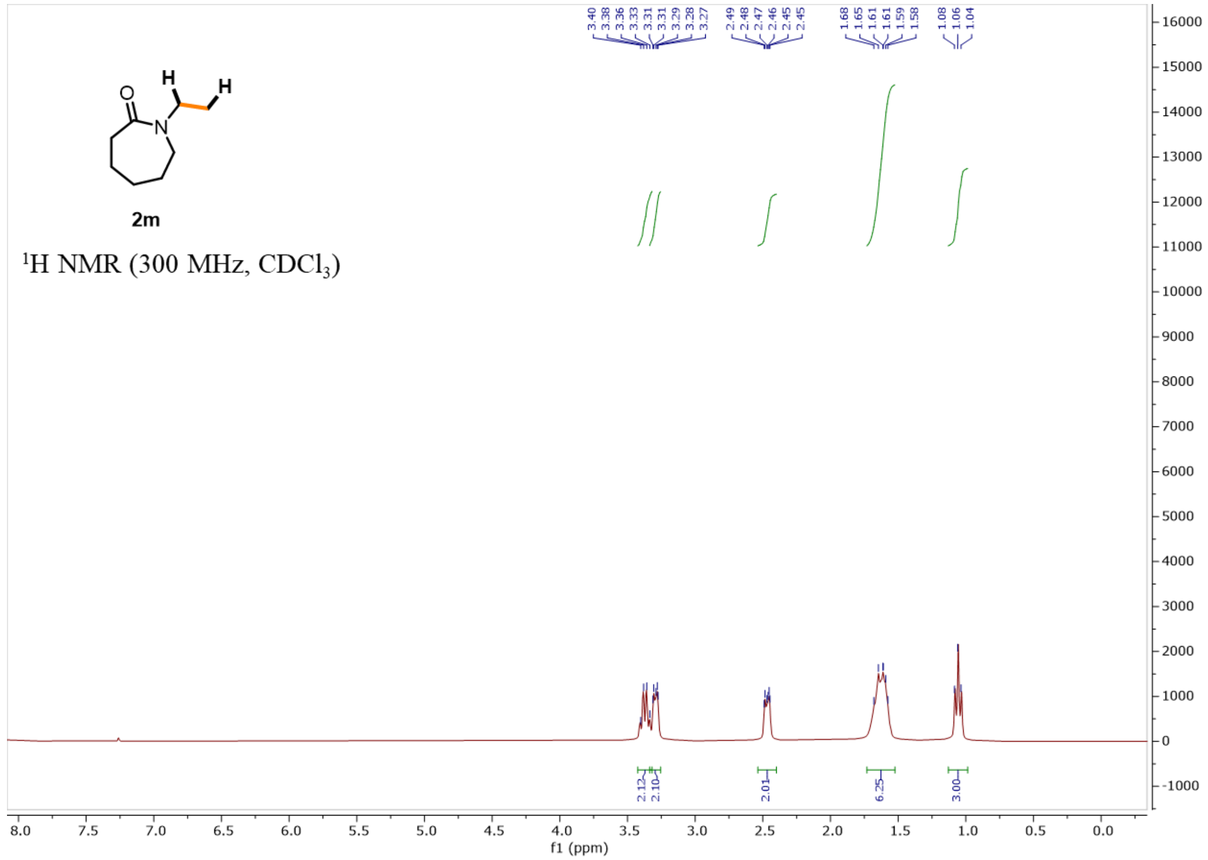
2l

^{1}H NMR (300 MHz, $CDCl_3$)

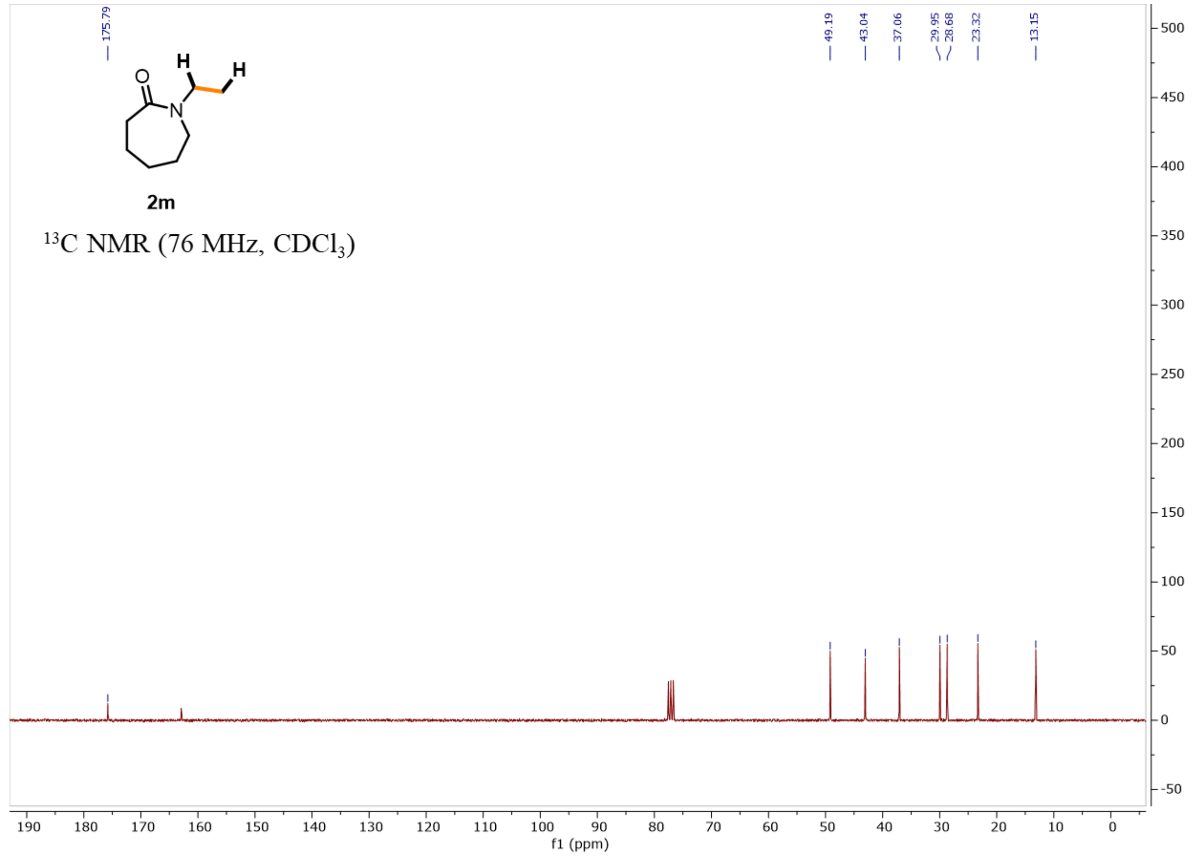


2l

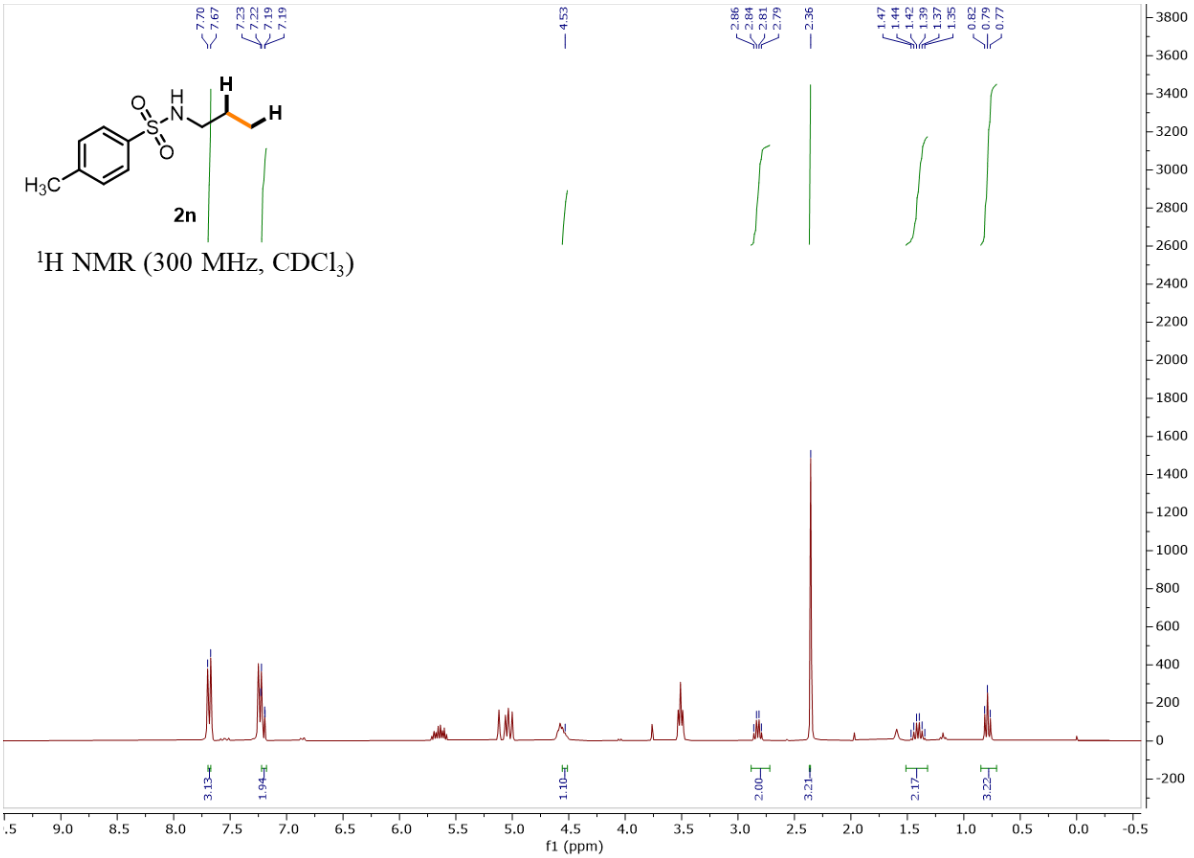
^{13}C NMR (76 MHz, $CDCl_3$)


2m

^{1}H NMR (300 MHz, CDCl$_3$)

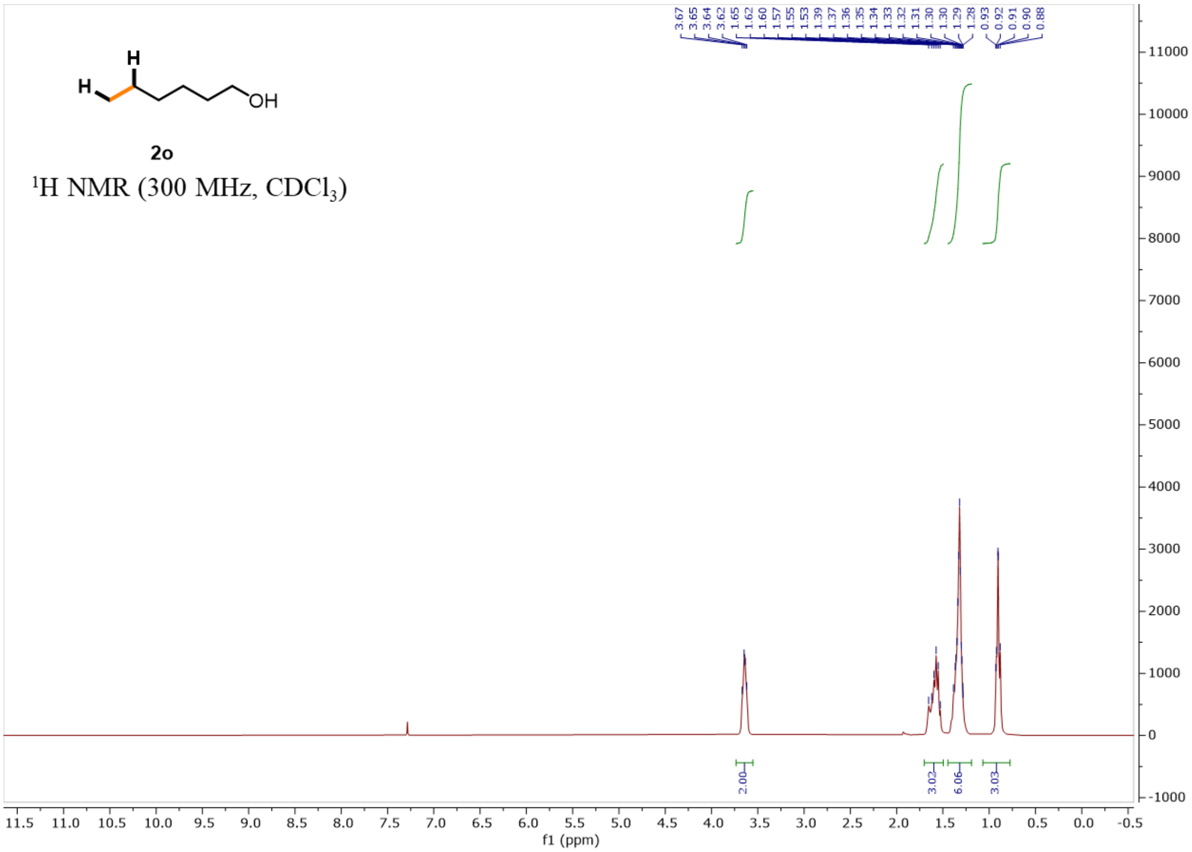

2m

^{13}C NMR (76 MHz, CDCl$_3$)



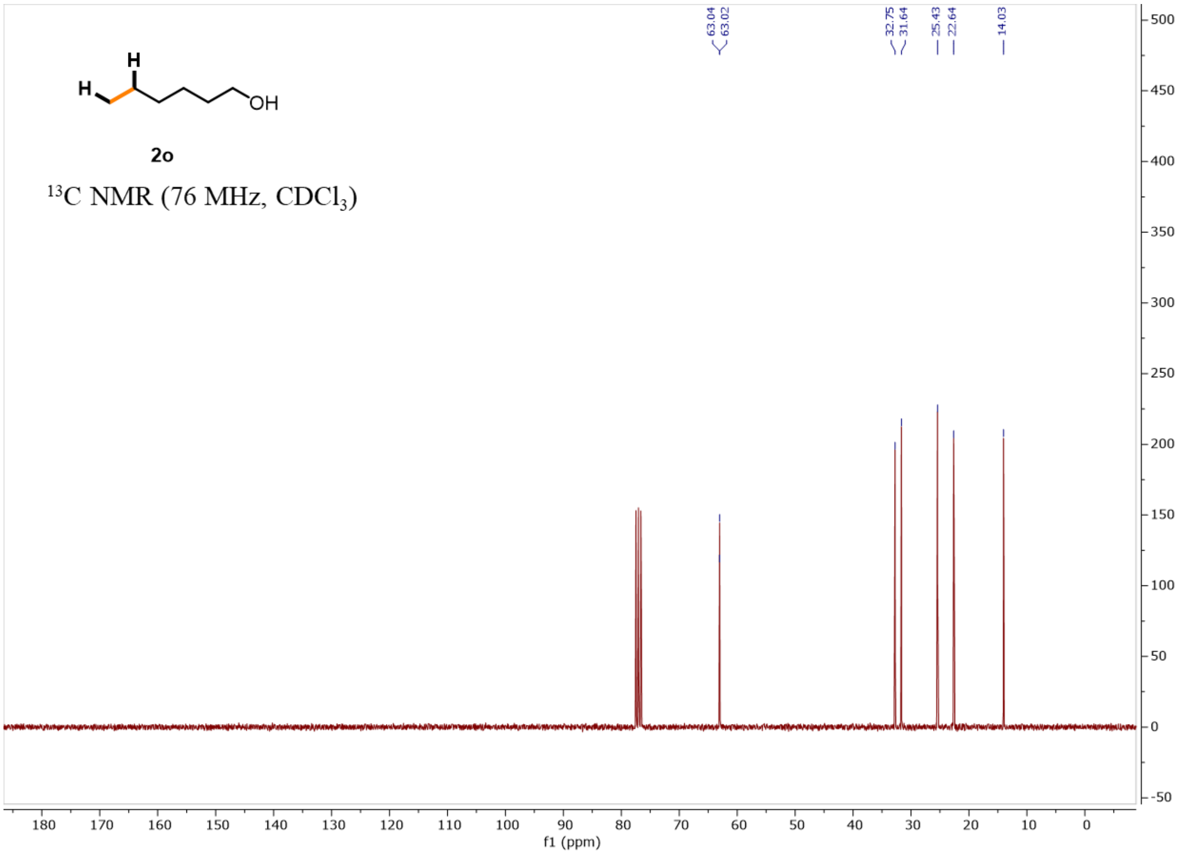
2n

^{1}H NMR (300 MHz, CDCl$_3$)



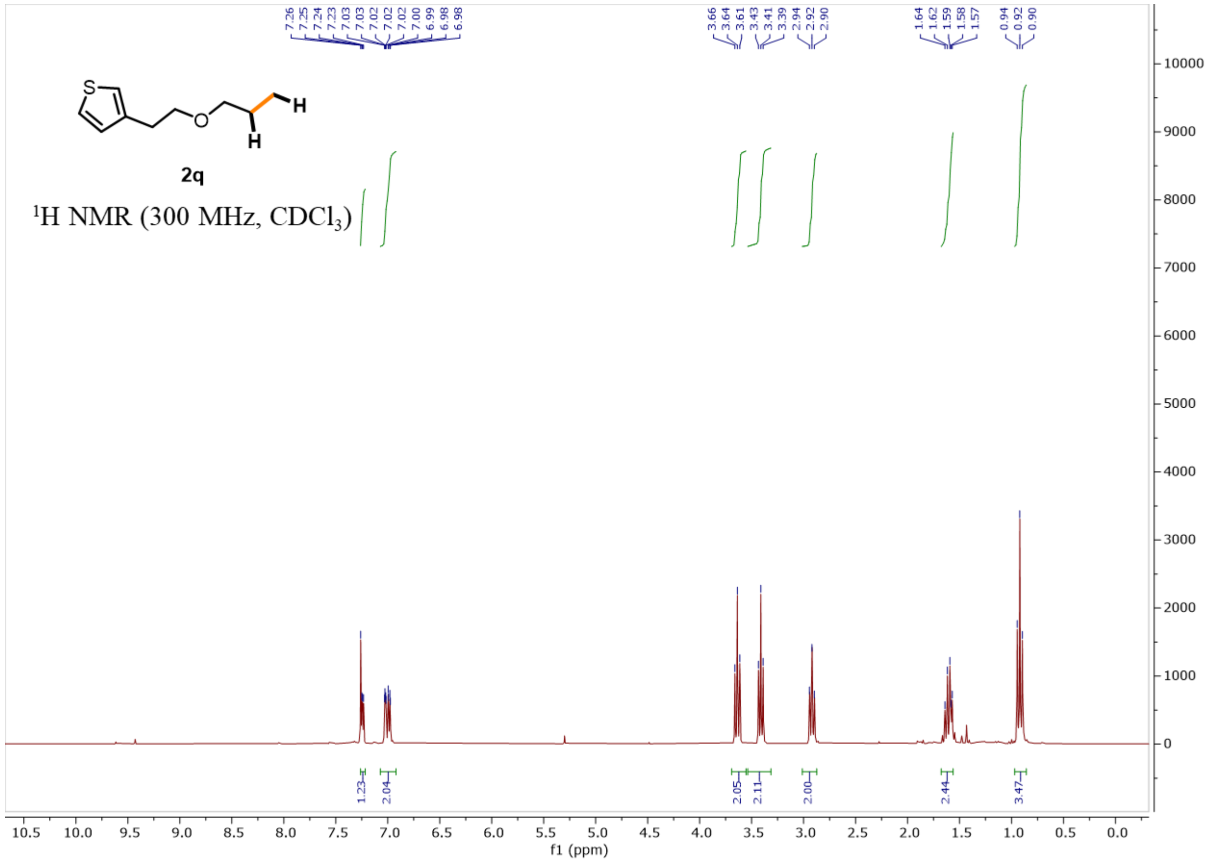
2o

^{1}H NMR (300 MHz, $CDCl_3$)



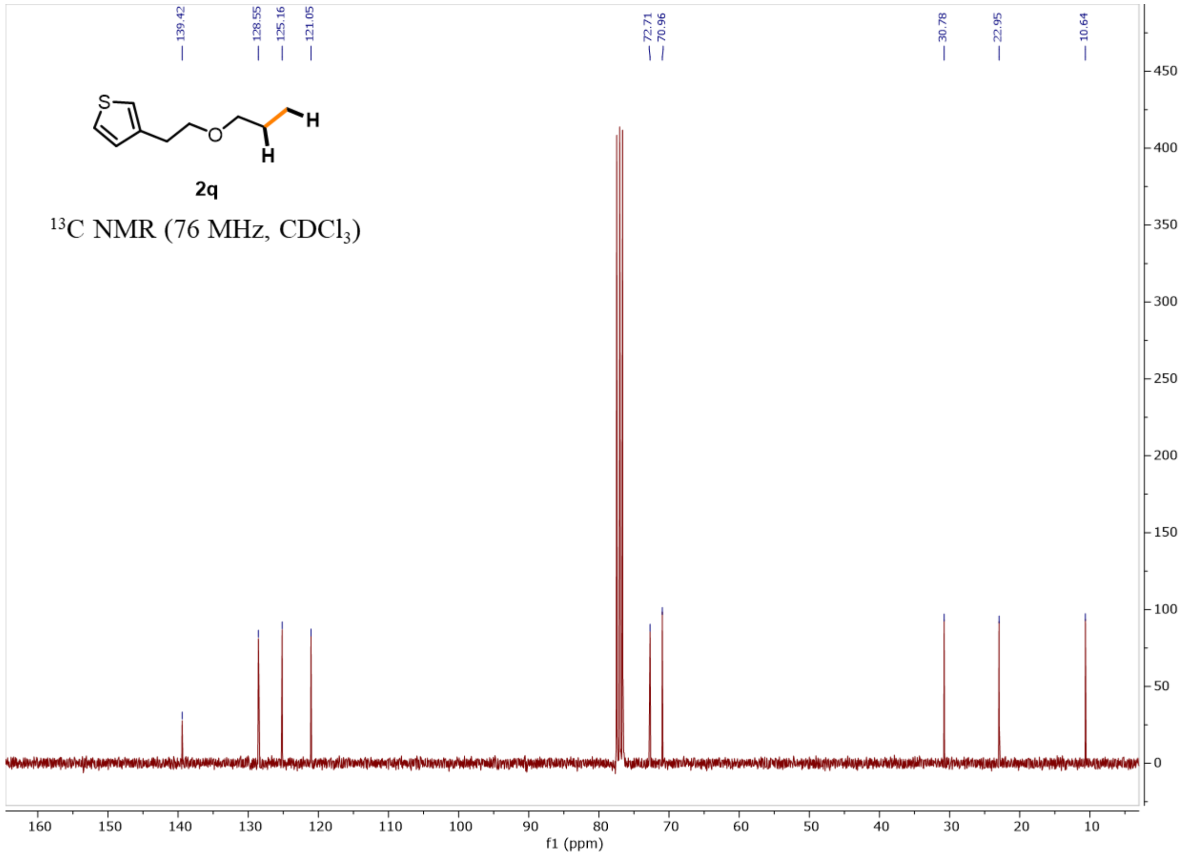
2o

^{13}C NMR (76 MHz, $CDCl_3$)



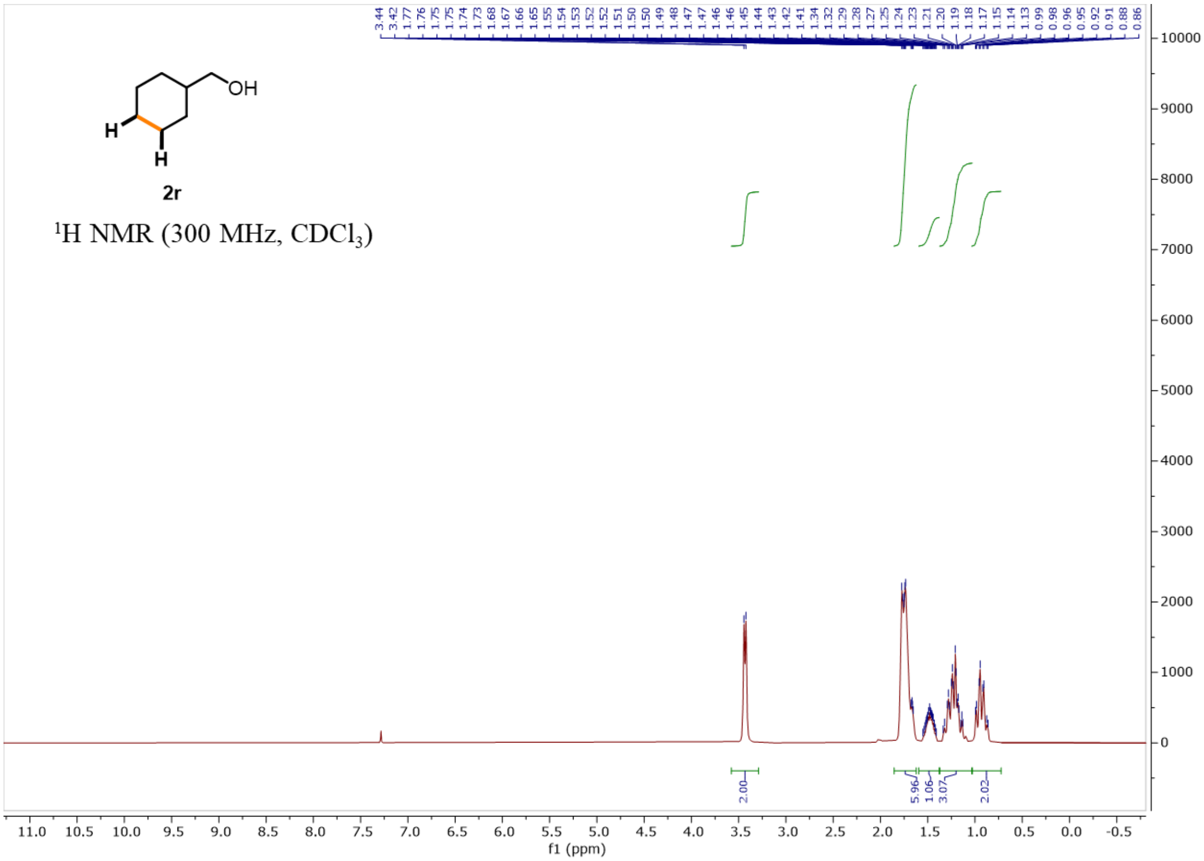
2q

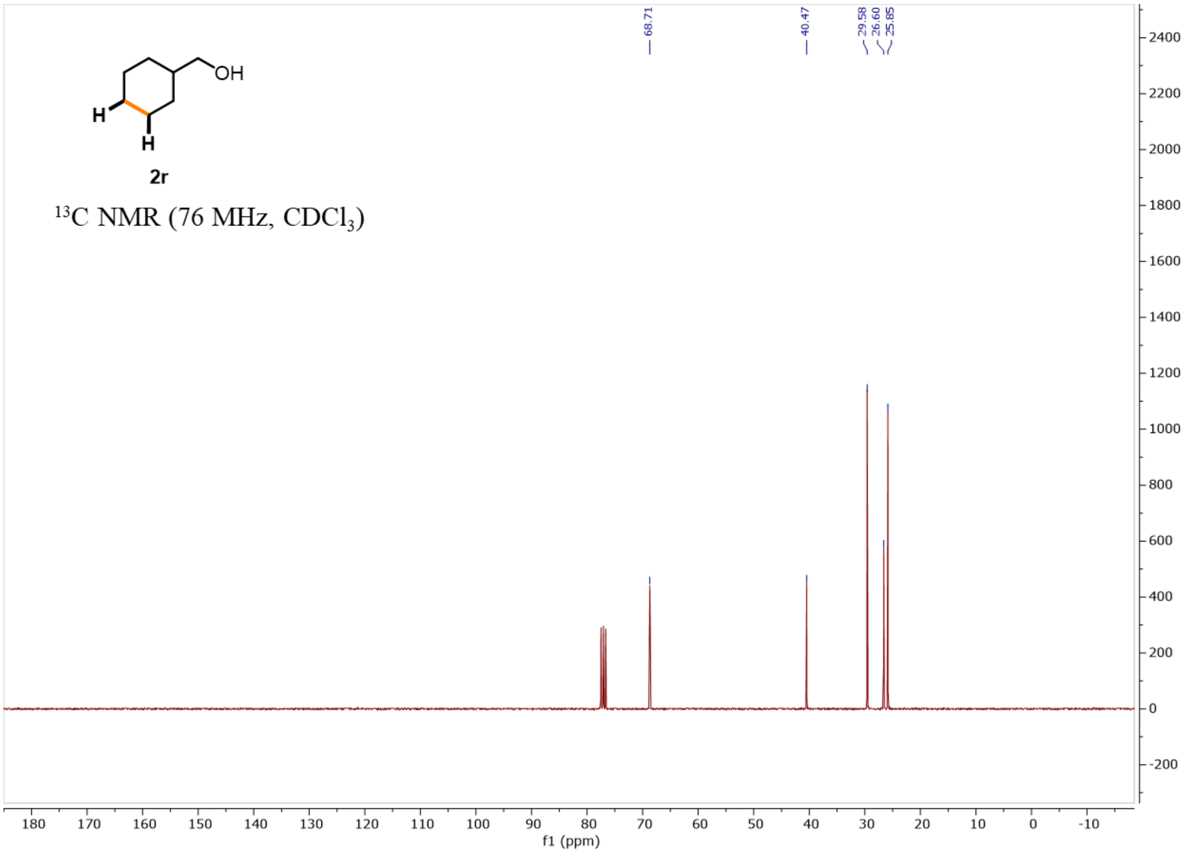
^{1}H NMR (300 MHz, CDCl$_3$)

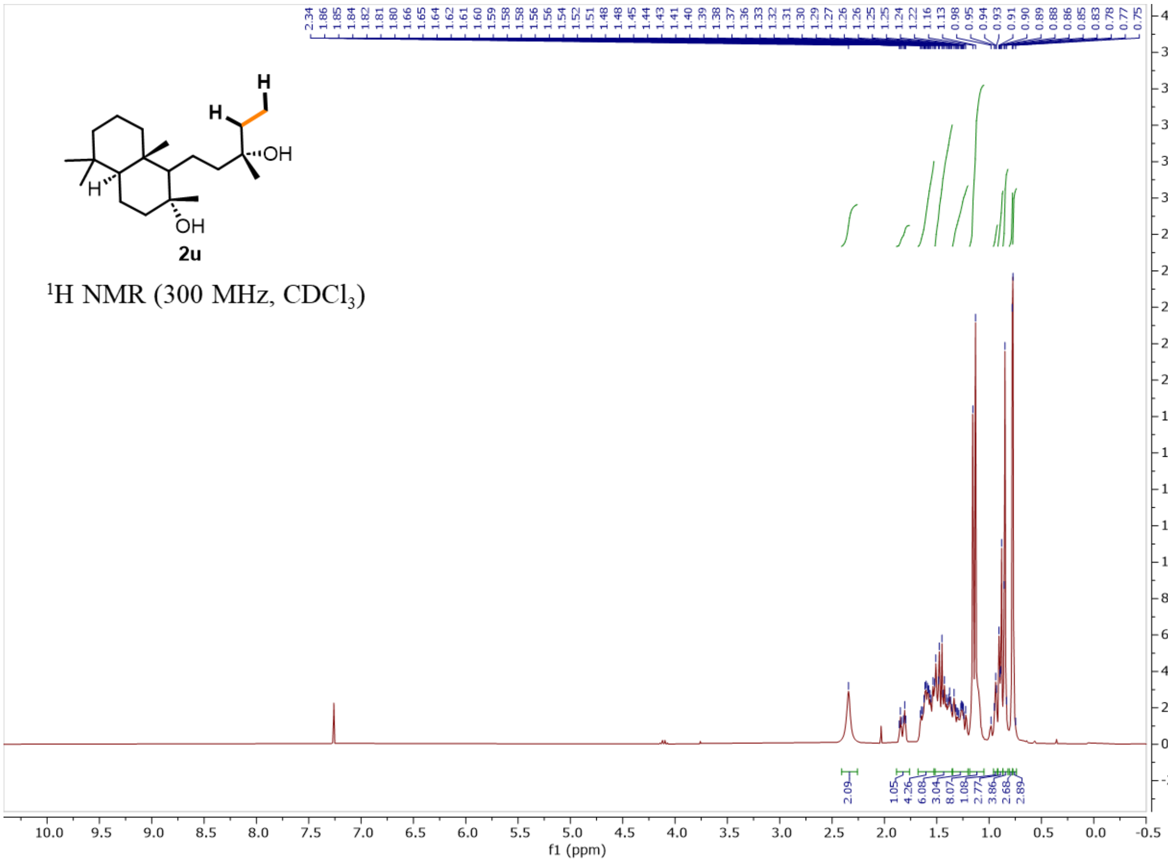


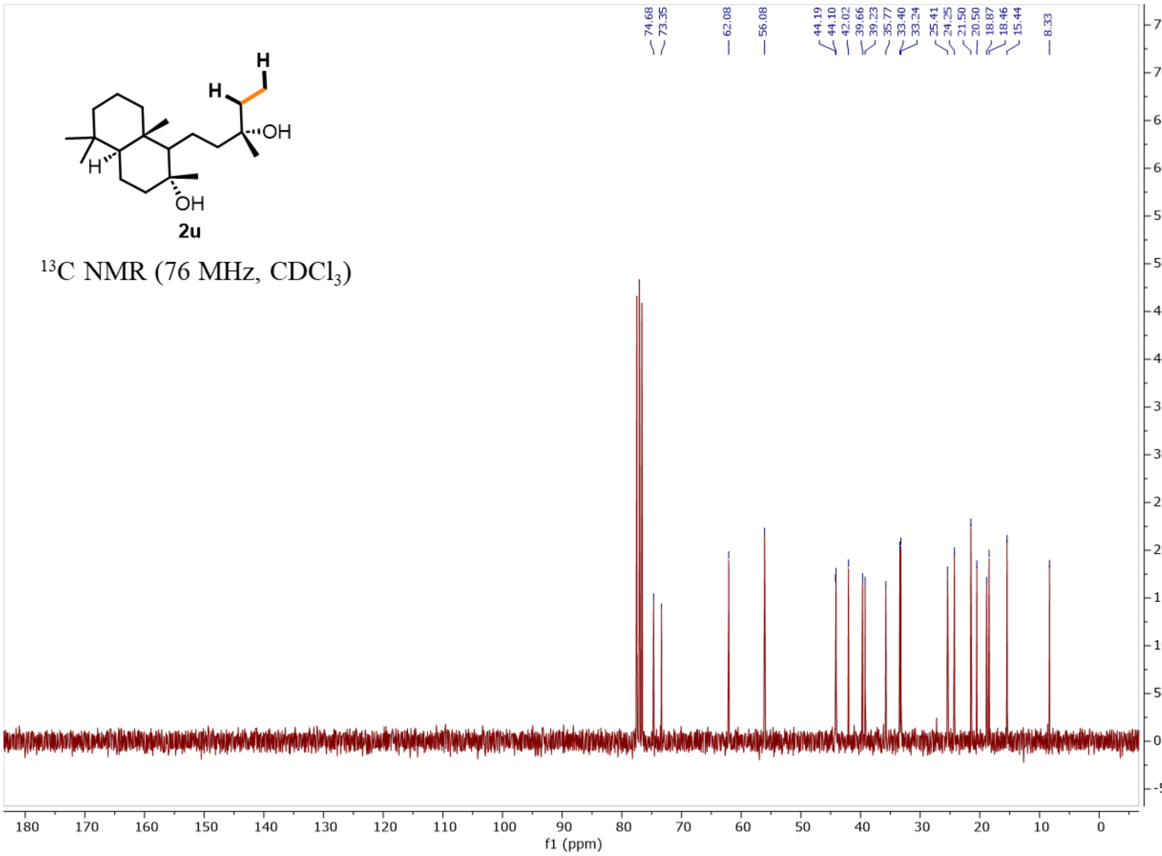
2q

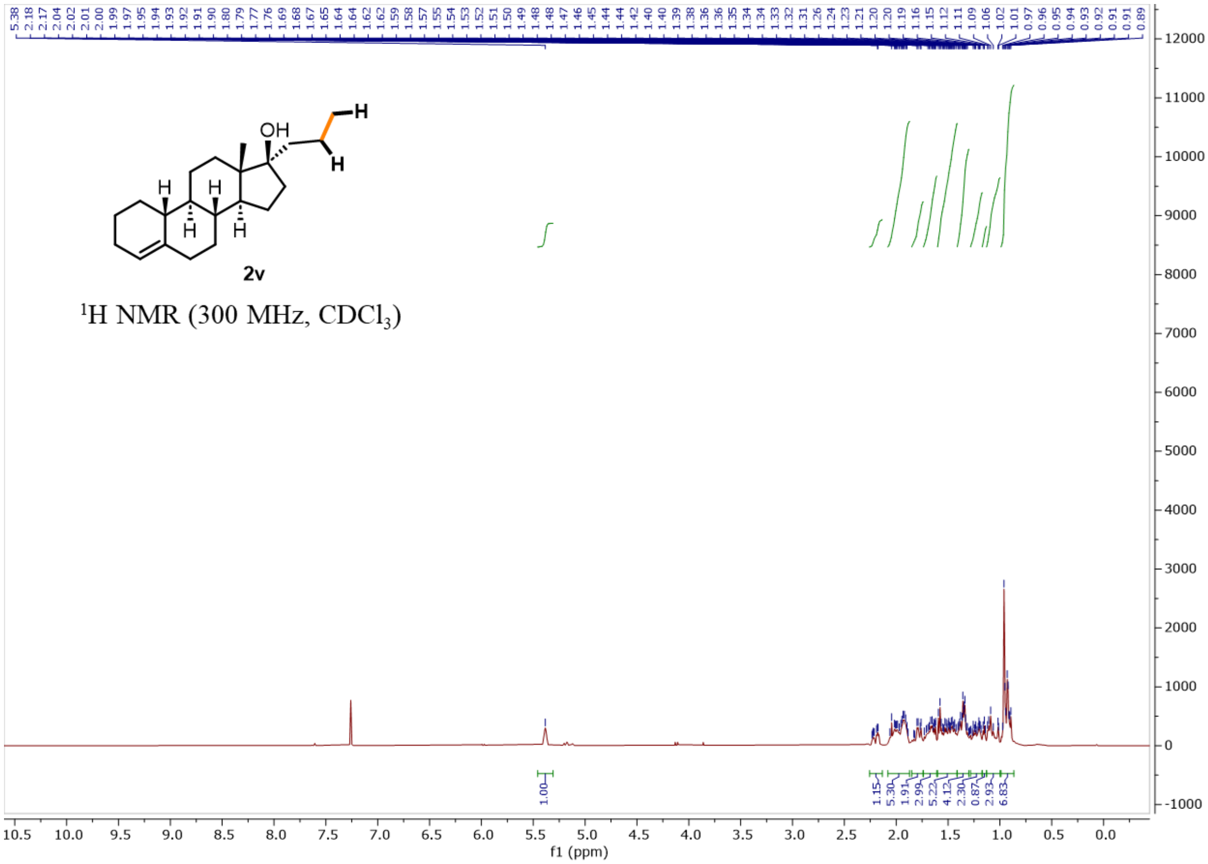
^{13}C NMR (76 MHz, CDCl$_3$)


OH
H
H
2r
¹H NMR (300 MHz, CDCl₃)
3.44 3.42 1.77 1.76 1.75 1.75 1.74 1.73 1.68 1.67 1.66 1.65 1.55 1.54 1.53 1.52 1.52 1.51 1.50 1.50 1.49 1.48 1.47 1.47 1.46 1.46 1.45 1.44 1.43 1.42 1.41 1.34 1.32 1.29 1.28 1.27 1.25 1.24 1.23 1.21 1.20 1.19 1.18 1.17 1.15 1.14 1.13 0.99 0.98 0.96 0.95 0.92 0.91 0.88 0.86
2.00
5.96
1.06
3.07
2.02
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


OH
H
H
2r
¹³C NMR (76 MHz, CDCl₃)
68.71
40.47
29.58
26.60
25.85
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

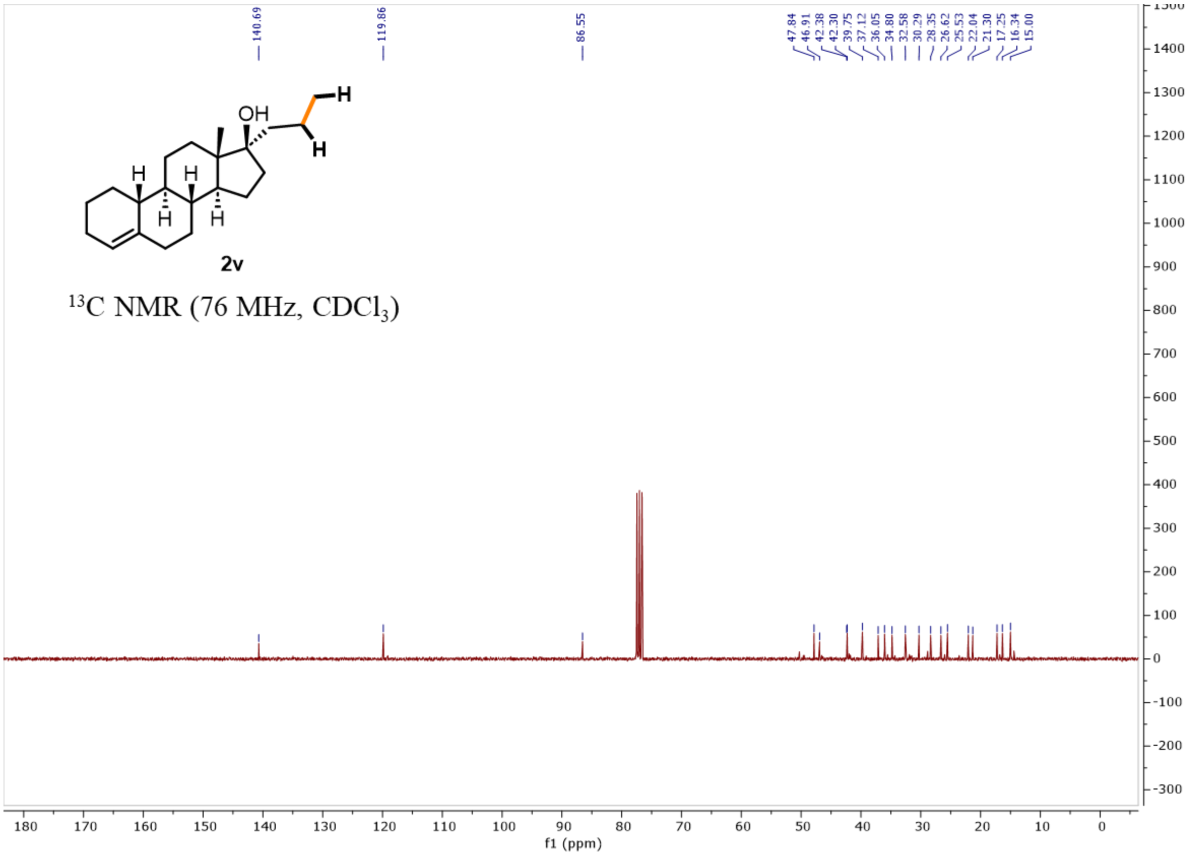

2u
¹H NMR (300 MHz, CDCl₃)
2.34 1.86 1.85 1.84 1.82 1.81 1.80 1.66 1.65 1.64 1.62 1.61 1.60 1.59 1.58 1.58 1.56 1.56 1.54 1.52 1.51 1.48 1.48 1.45 1.44 1.43 1.41 1.40 1.39 1.38 1.37 1.36 1.33 1.32 1.31 1.30 1.29 1.27 1.26 1.26 1.25 1.25 1.24 1.22 1.16 1.13 0.98 0.95 0.94 0.93 0.91 0.90 0.89 0.88 0.86 0.85 0.83 0.78 0.77 0.75
2.09 1.05 4.26 6.08 3.04 8.07 1.08 2.77 3.86 2.68 2.89
f1 (ppm)


2u
¹³C NMR (76 MHz, CDCl₃)
74.68 73.35 62.08 56.08 44.19 44.10 42.02 39.66 39.23 35.77 33.40 33.24 25.41 24.25 21.50 20.50 18.87 18.46 15.44 8.33
f1 (ppm)



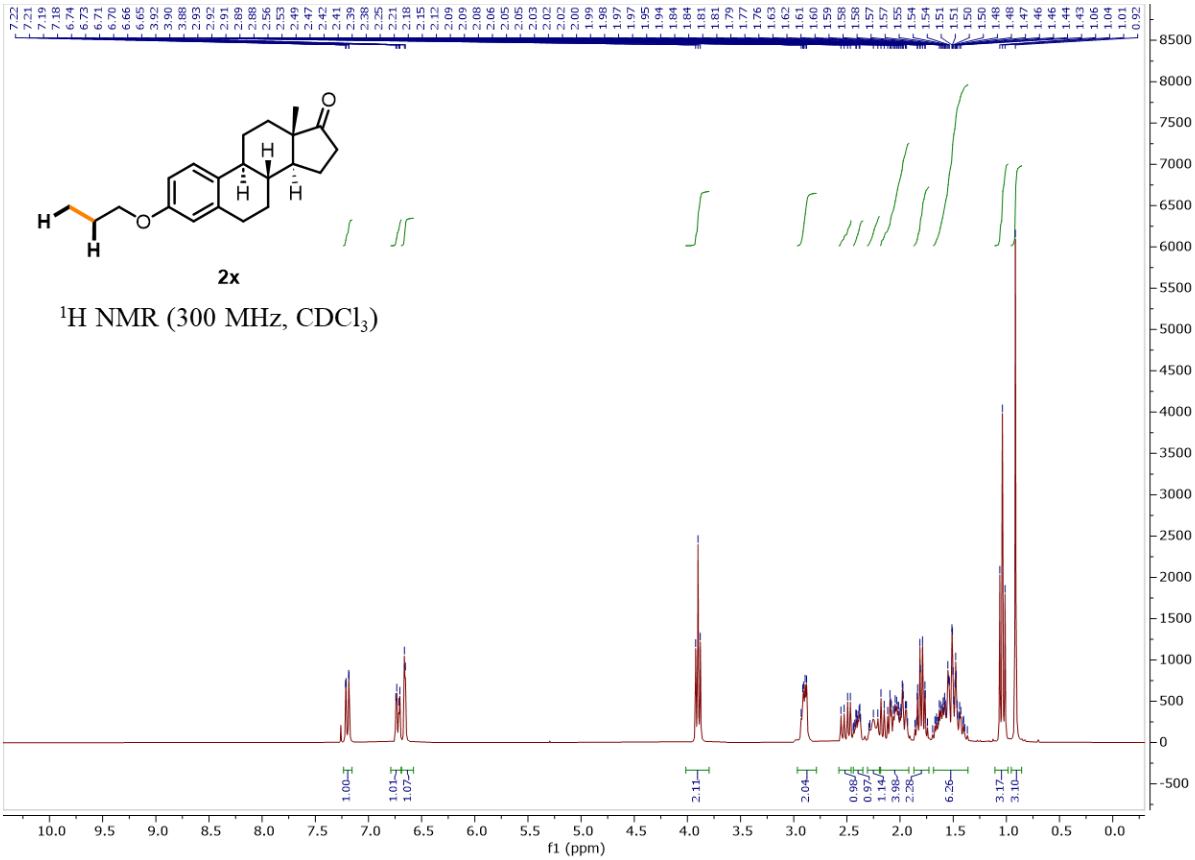
2v

^1H NMR (300 MHz, $CDCl_3$)



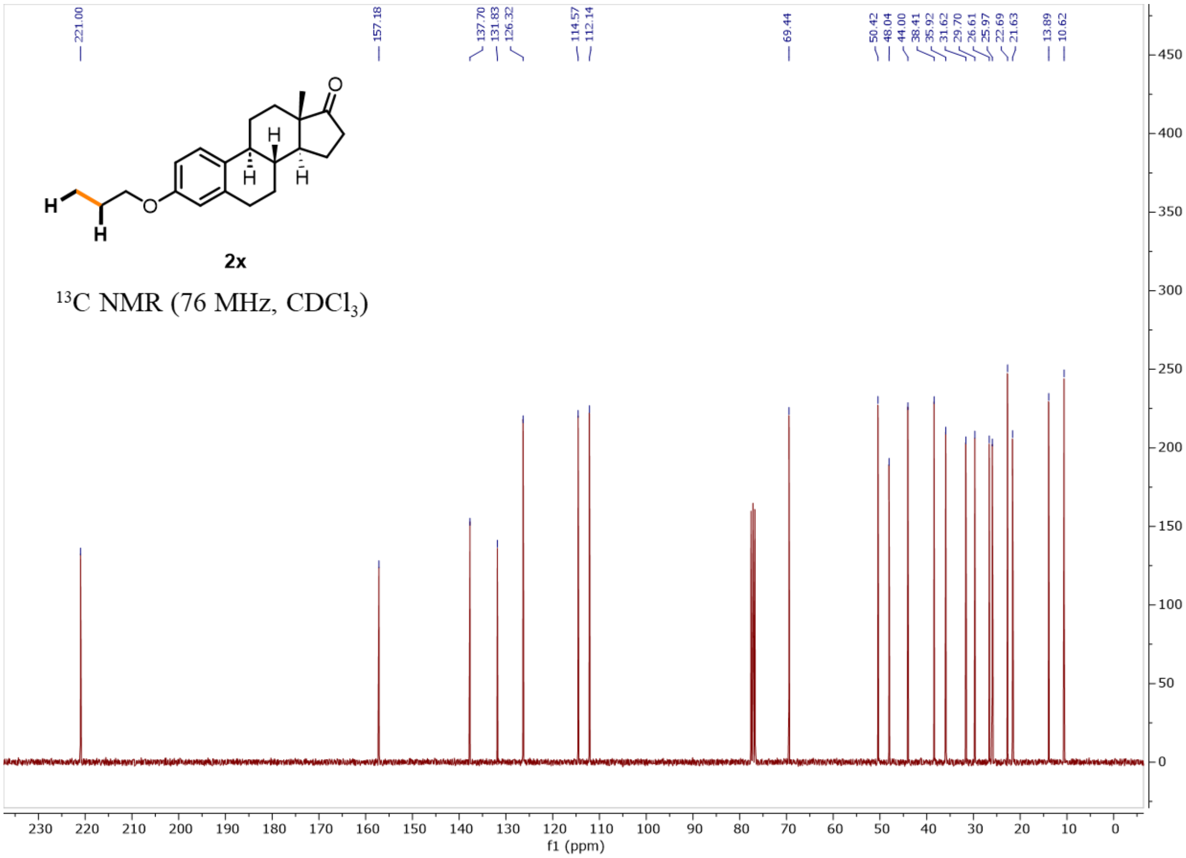
2v

^{13}C NMR (76 MHz, $CDCl_3$)



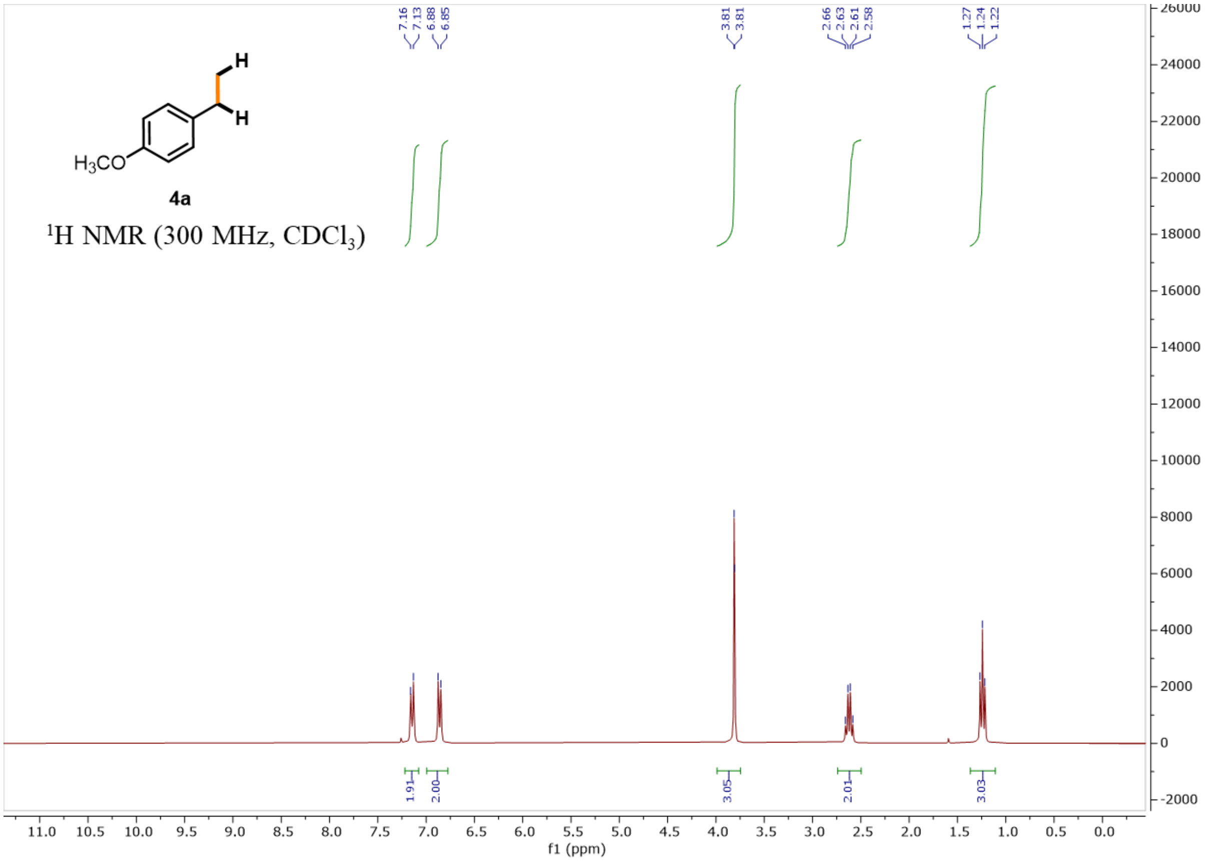
2x

^{1}H NMR (300 MHz, $CDCl_3$)



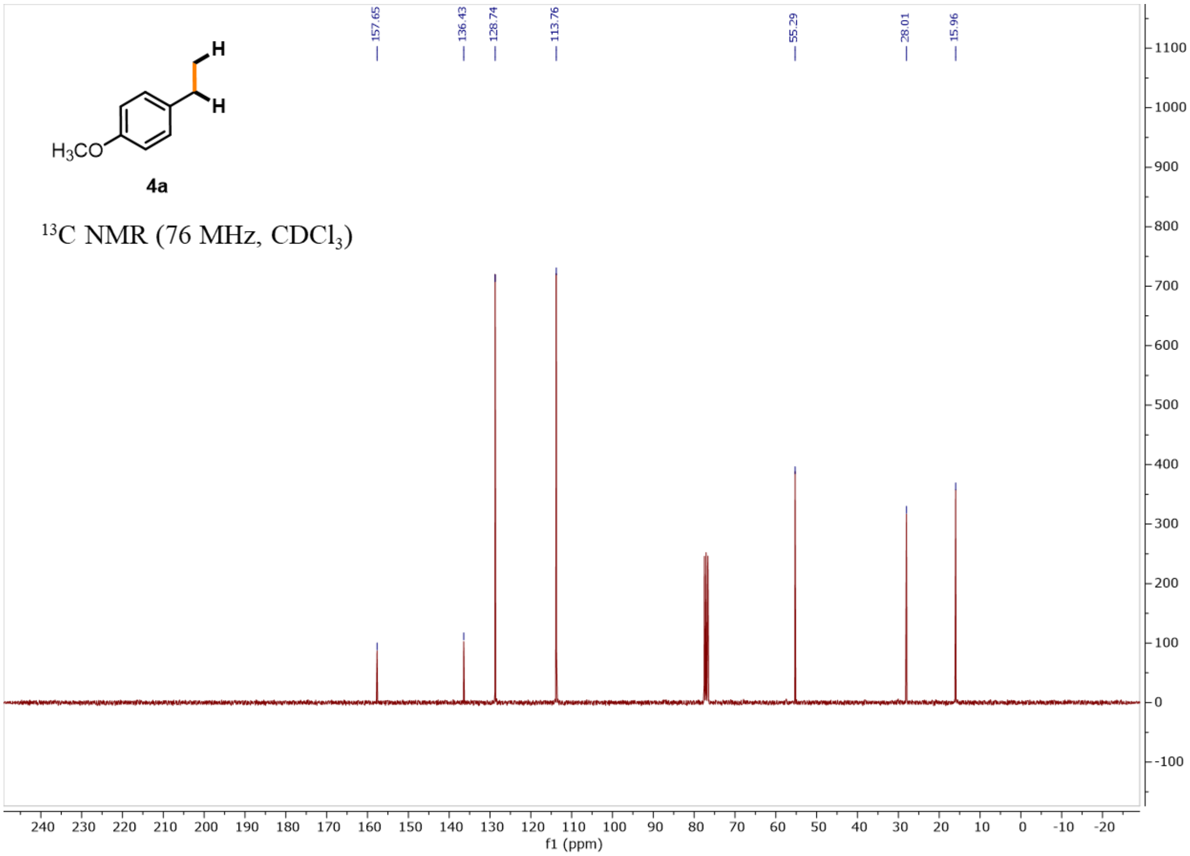
2x

^{13}C NMR (76 MHz, $CDCl_3$)



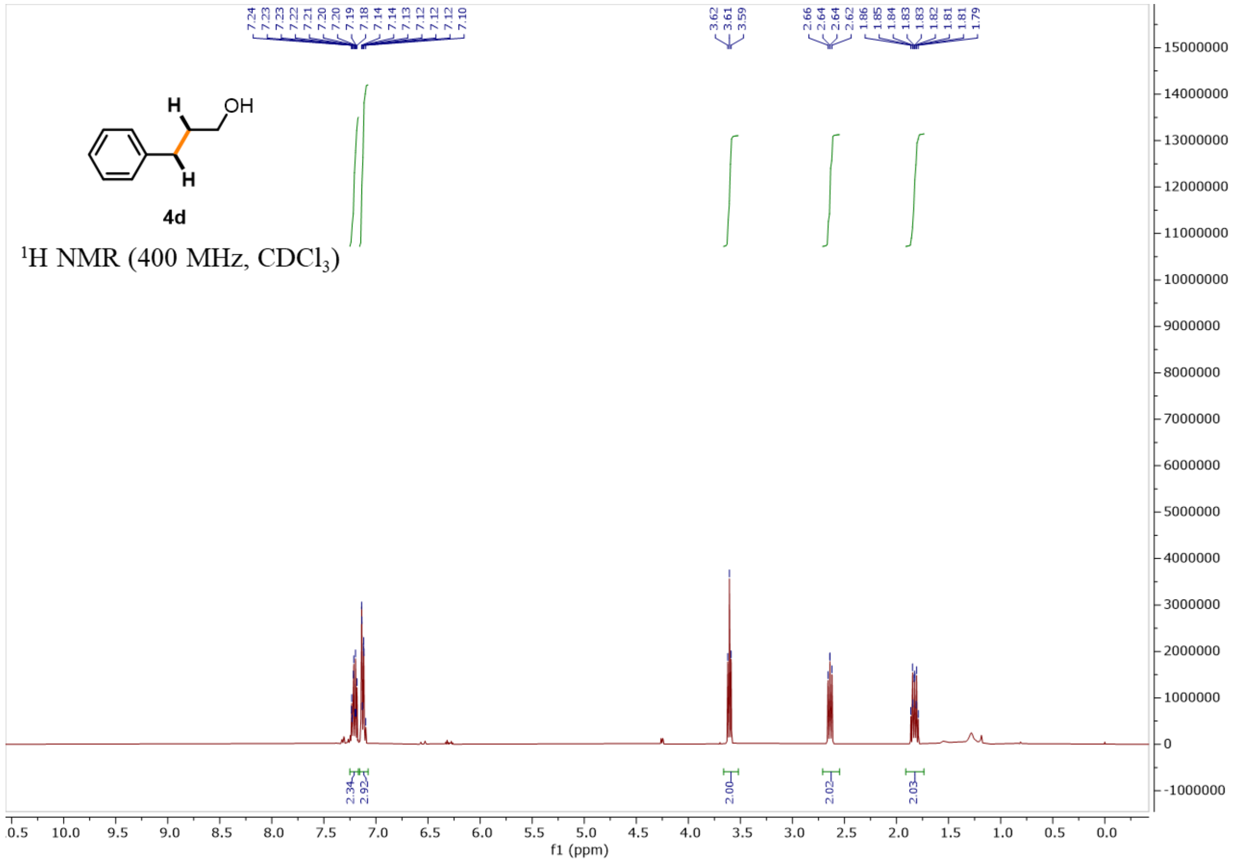
4a

^{1}H NMR (300 MHz, CDCl$_3$)

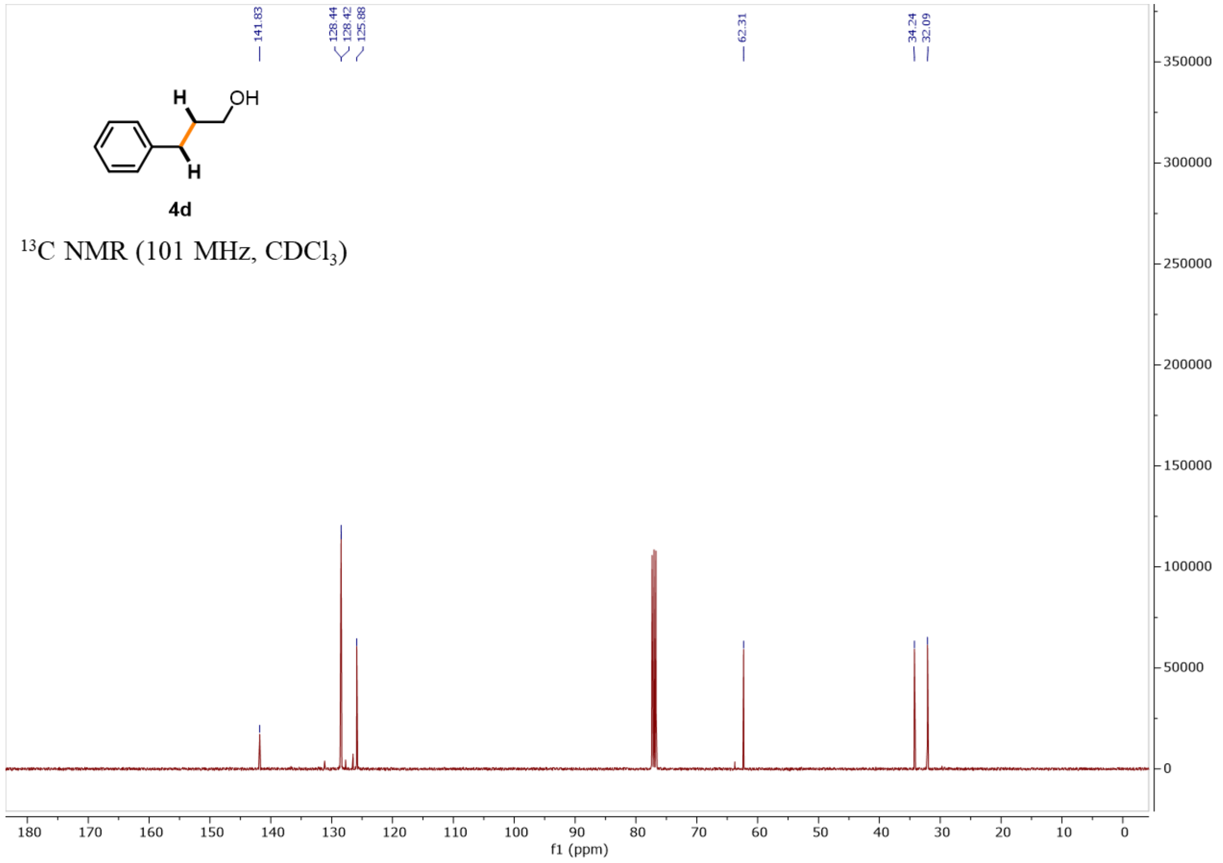


4a

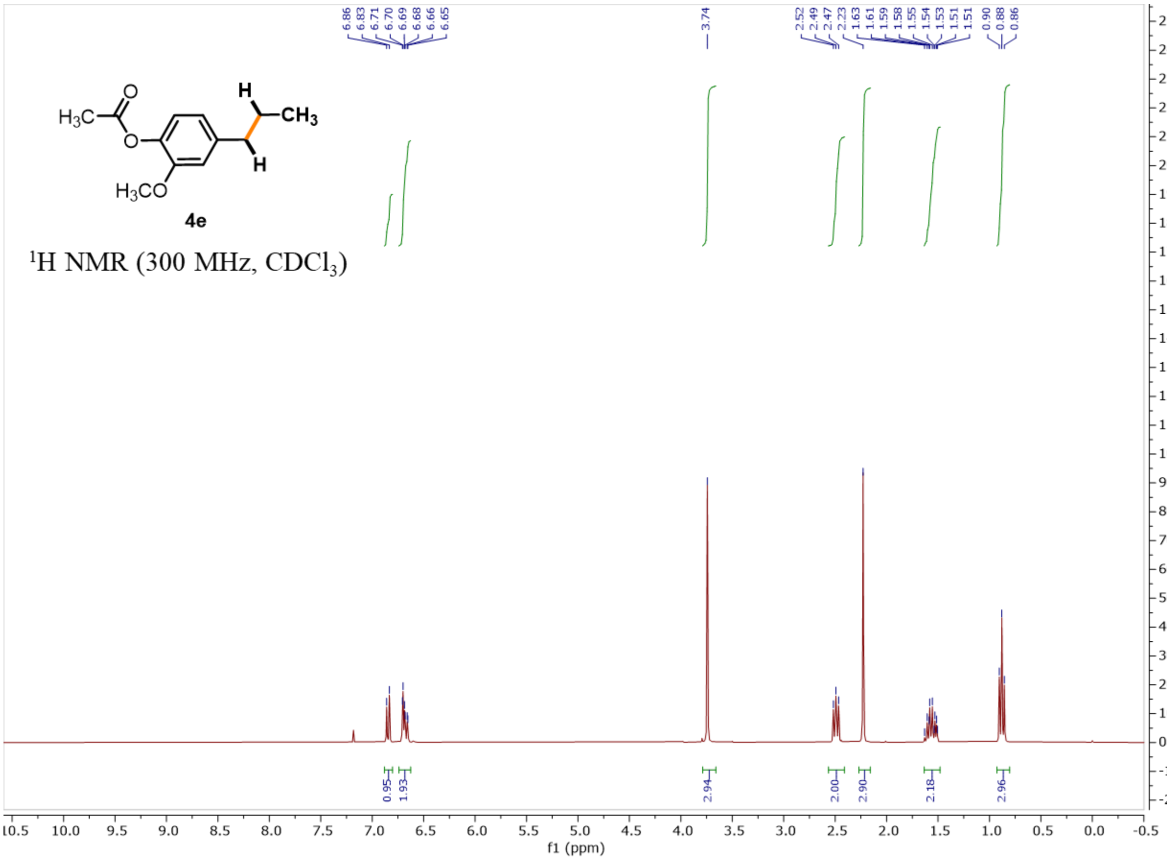
^{13}C NMR (76 MHz, CDCl$_3$)



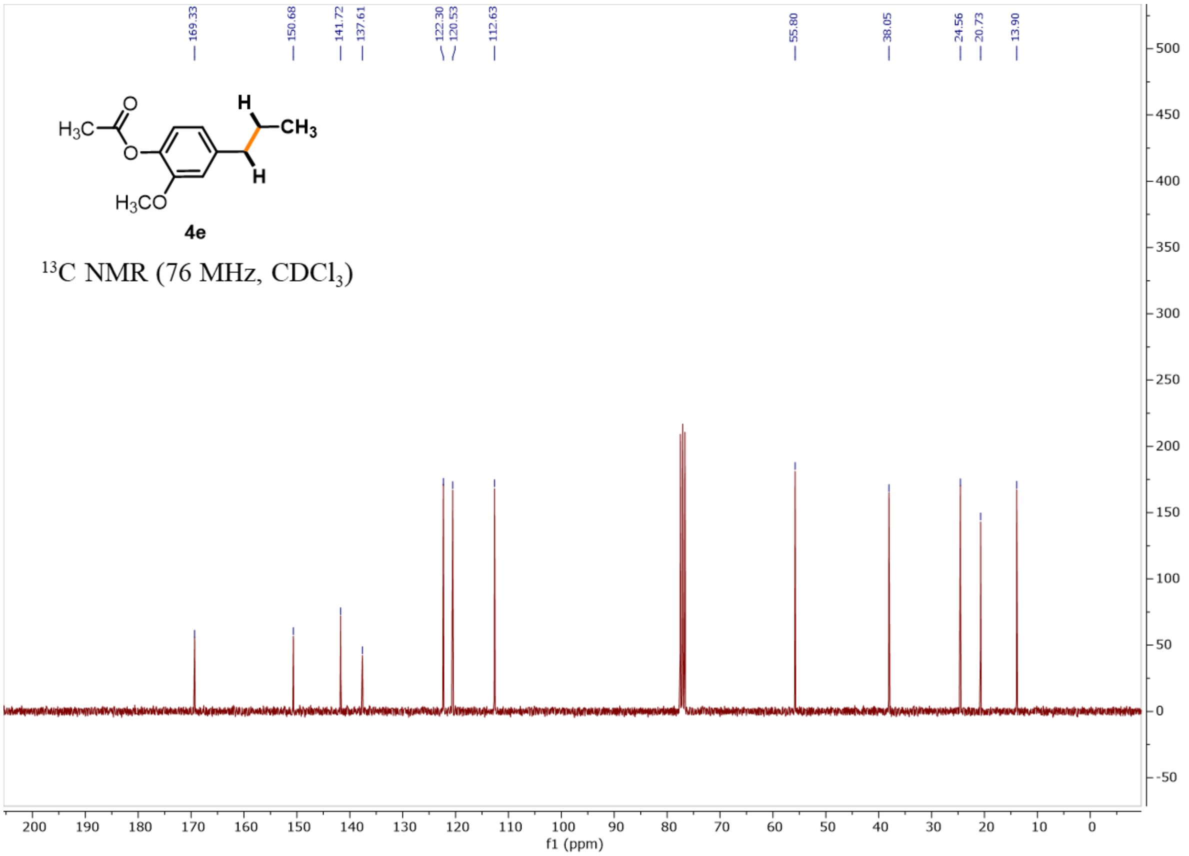
7.24 7.23 7.23 7.22 7.21 7.20 7.20 7.19 7.18 7.14 7.14 7.13 7.12 7.12 7.12 7.10
3.62 3.61 3.59
2.66 2.64 2.64 2.62 1.86 1.85 1.84 1.83 1.83 1.82 1.81 1.81 1.79
H
OH
H
4d
^{1}H NMR (400 MHz, CDCl$_3$)
2.34
2.92
2.00
2.02
2.03
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



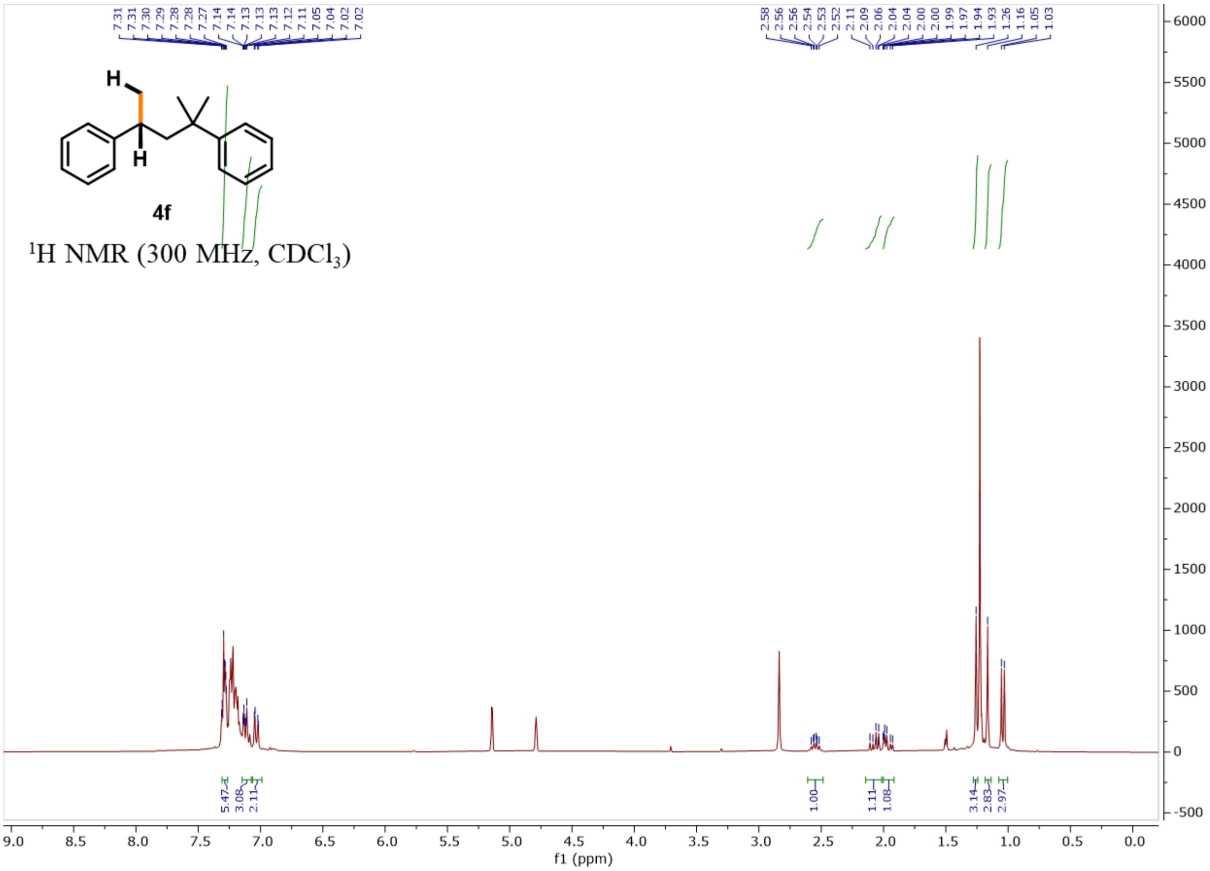
141.83
128.44 128.42 125.88
62.31
34.24 32.09
H
OH
H
4d
^{13}C NMR (101 MHz, CDCl$_3$)
350000
300000
250000
200000
150000
100000
50000
0
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



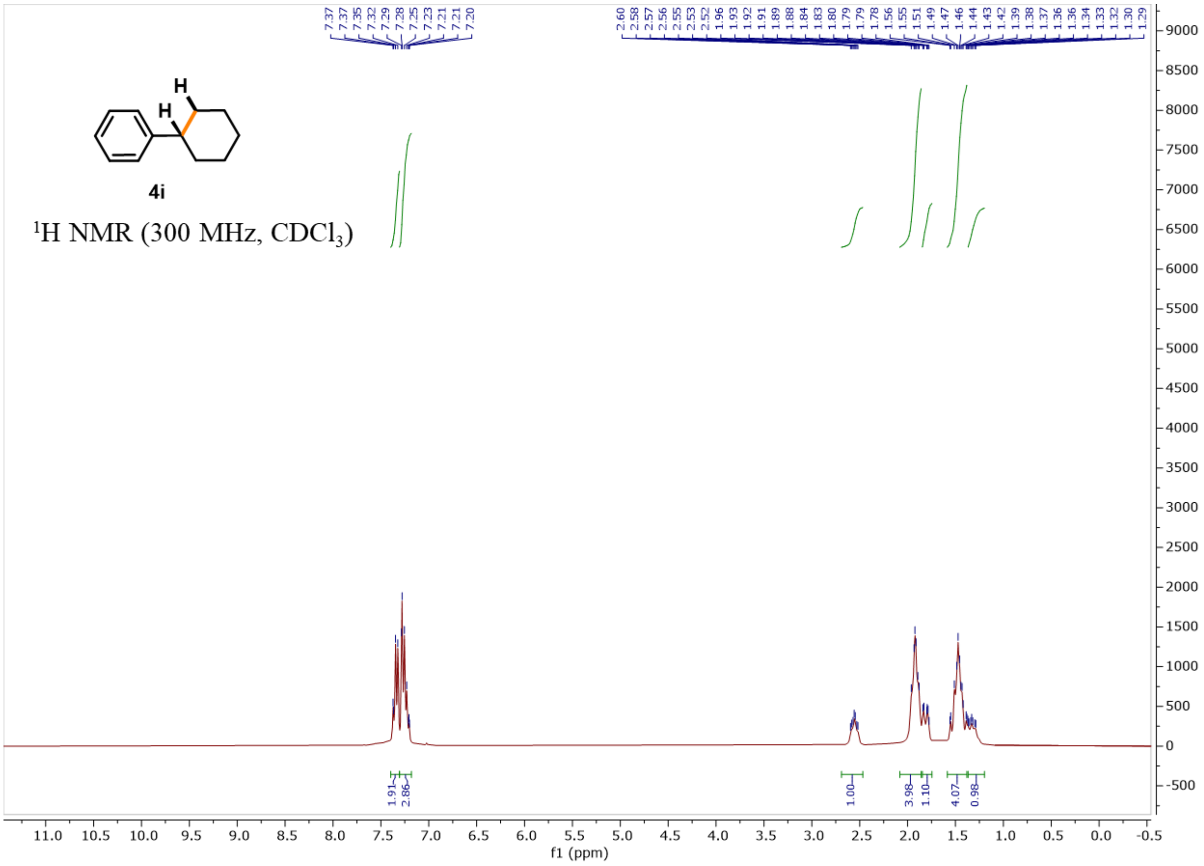
^{1}H NMR (300 MHz, CDCl$_3$)



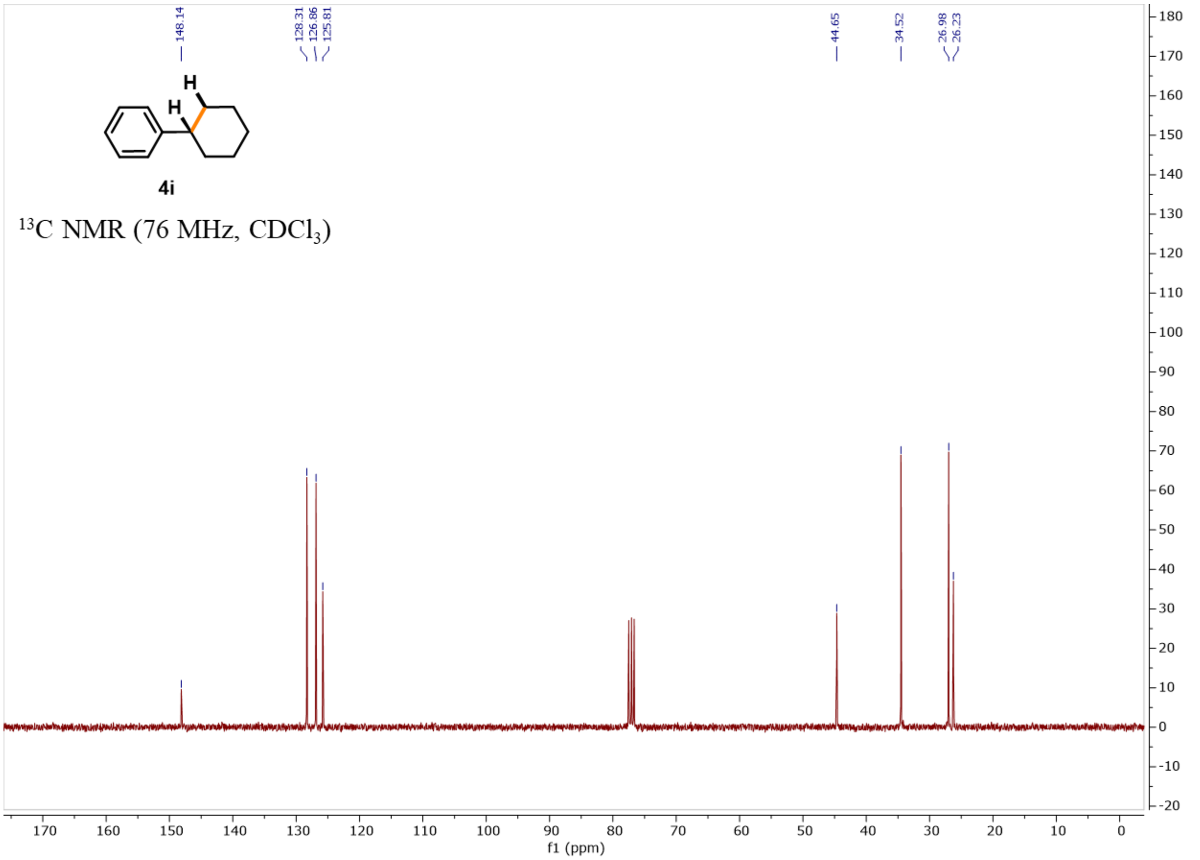
^{13}C NMR (76 MHz, CDCl$_3$)


4f

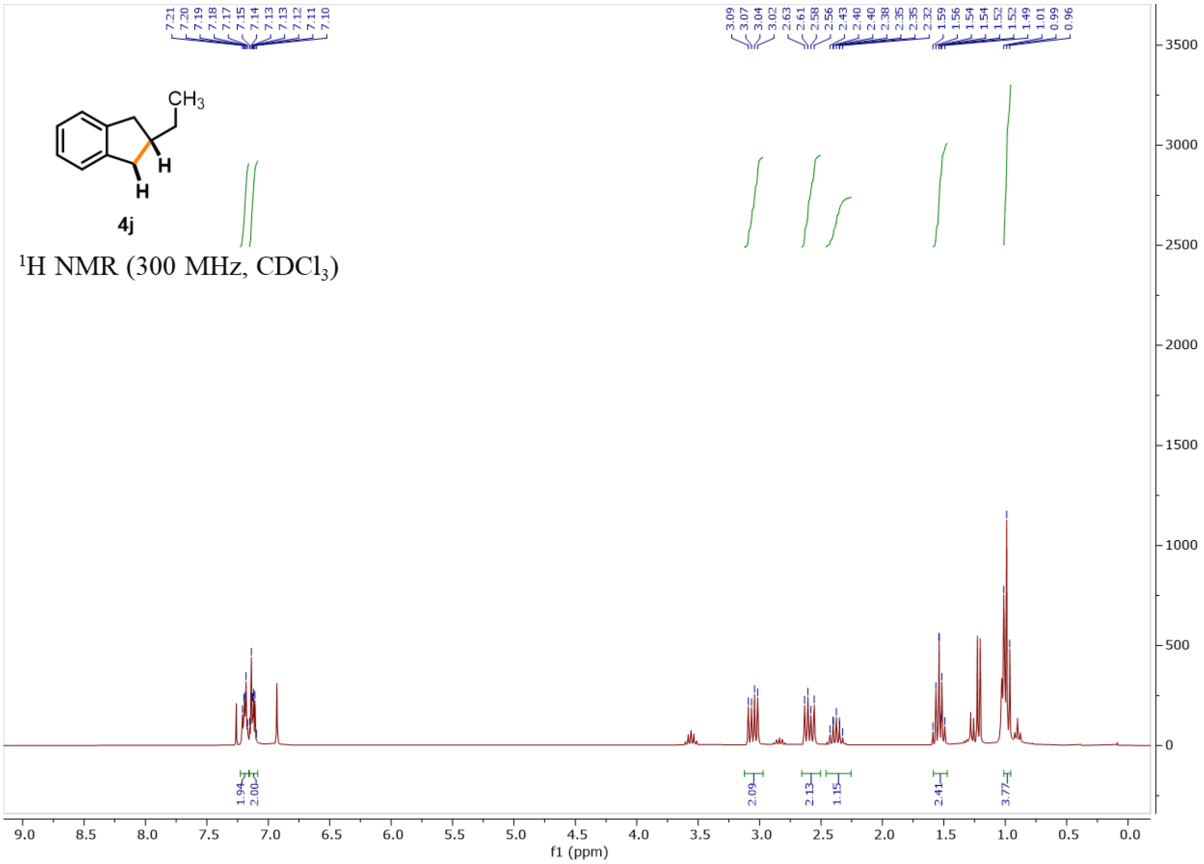
^{1}H NMR (300 MHz, CDCl$_3$)


4i

^{1}H NMR (300 MHz, CDCl$_3$)

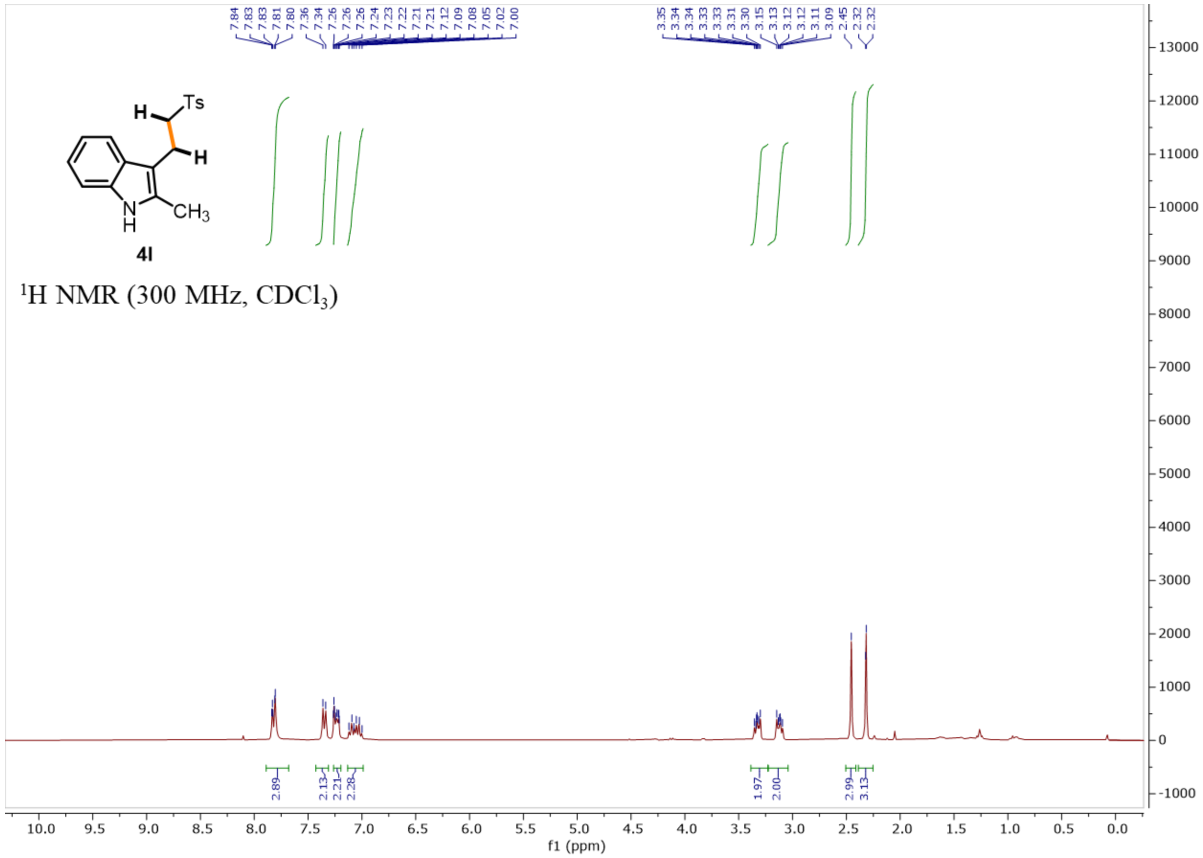

4i

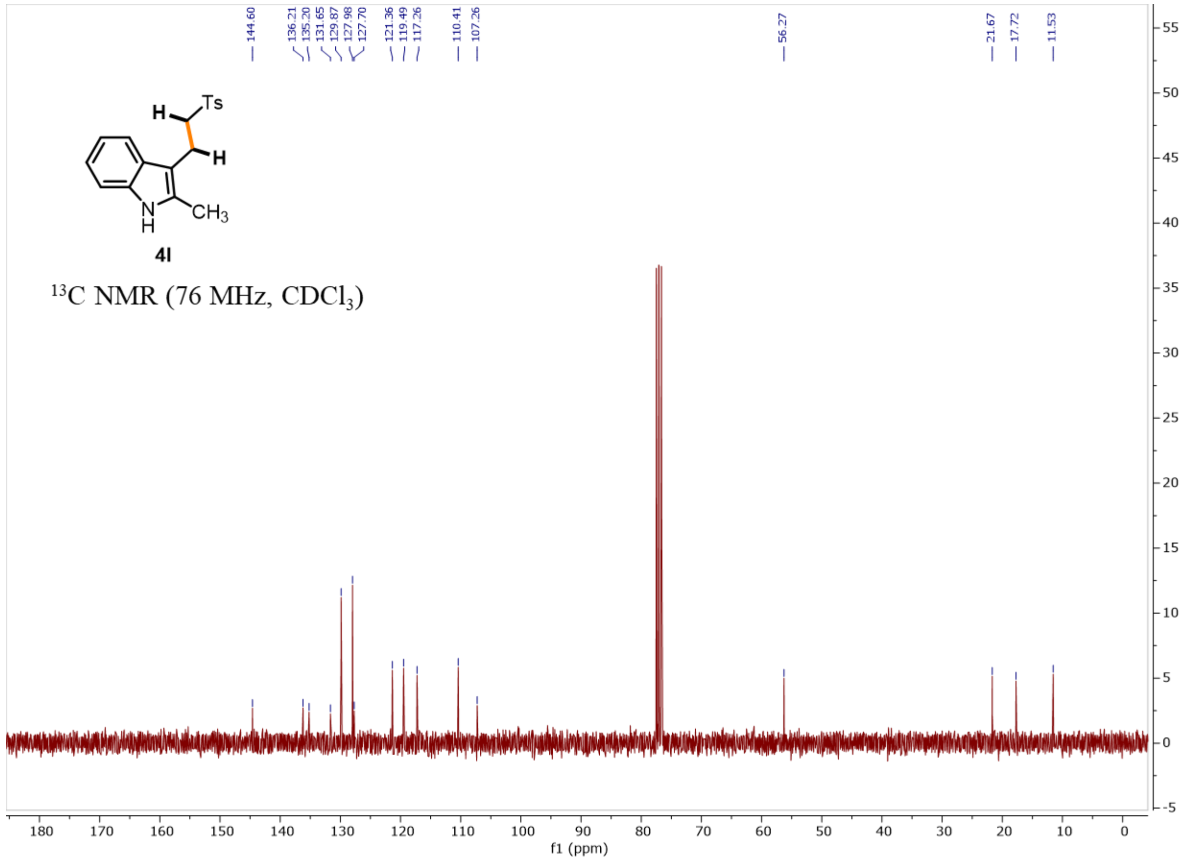
^{13}C NMR (76 MHz, CDCl$_3$)

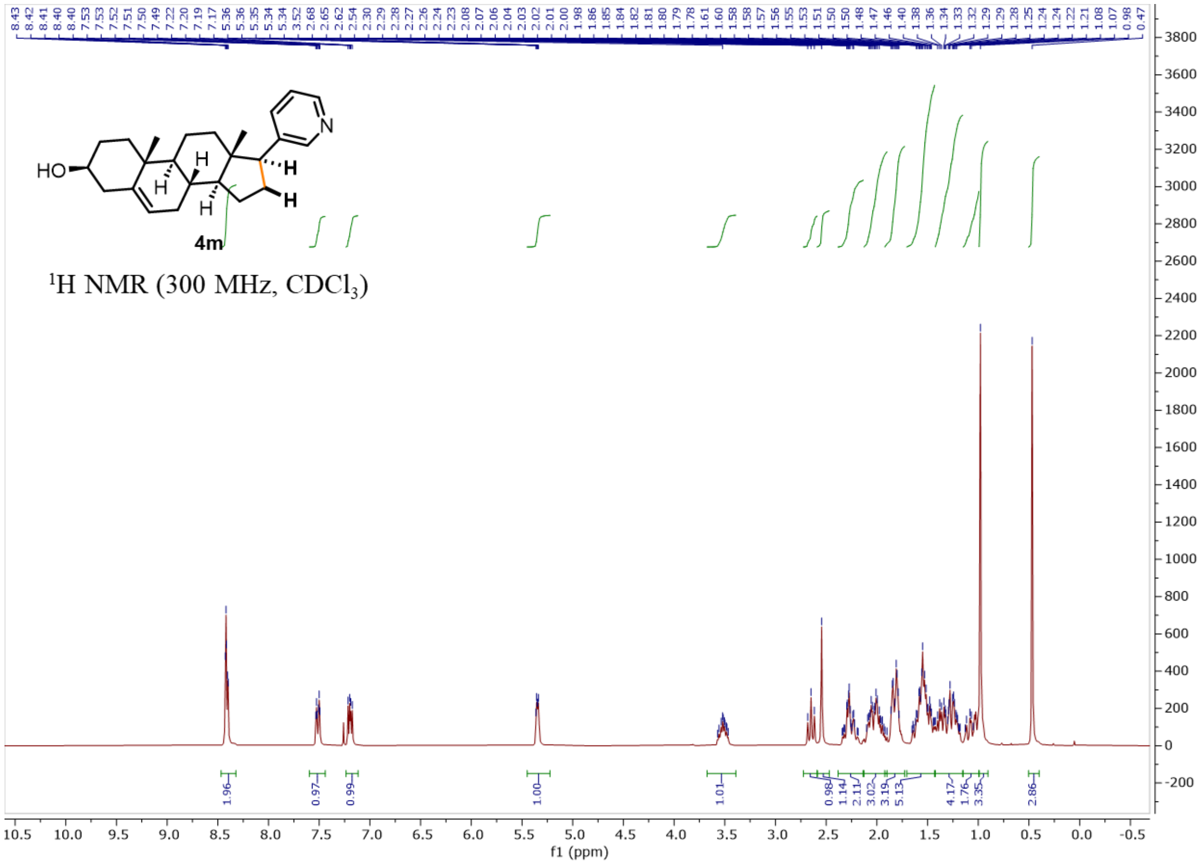


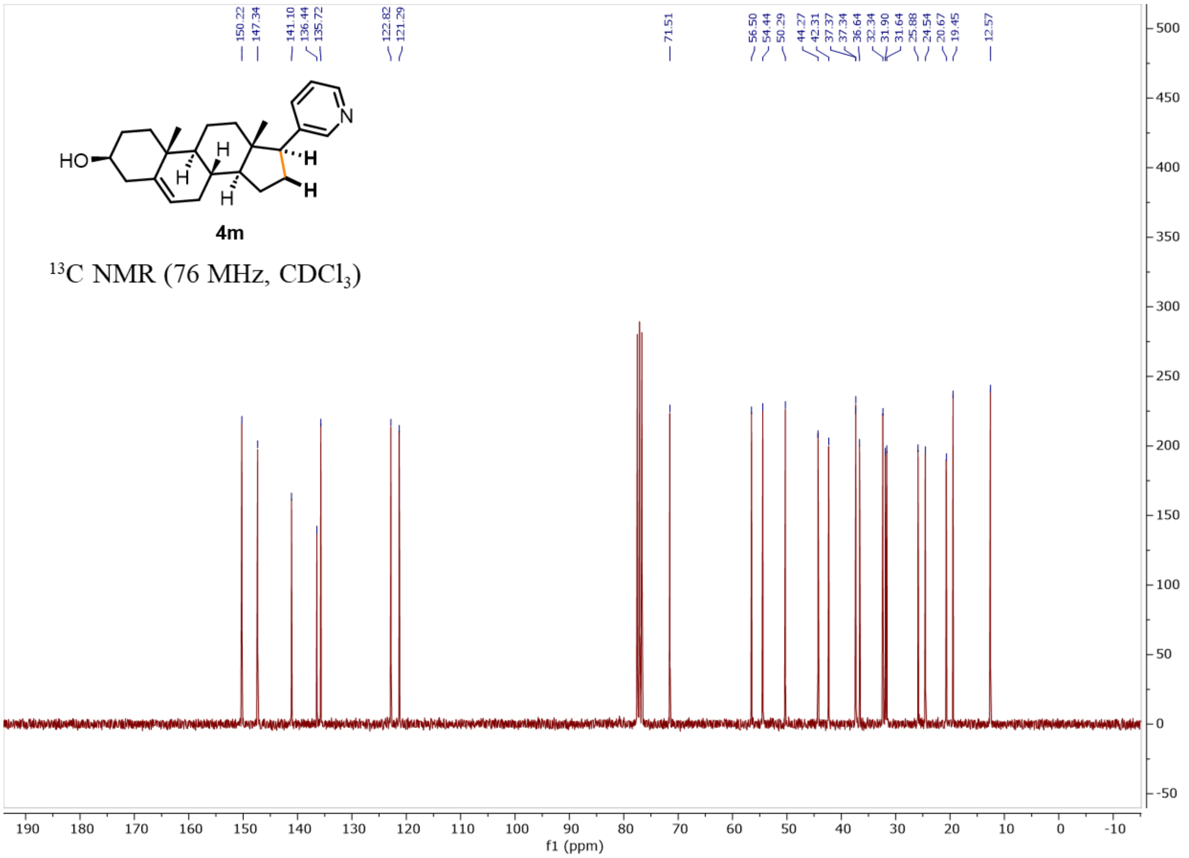
4j

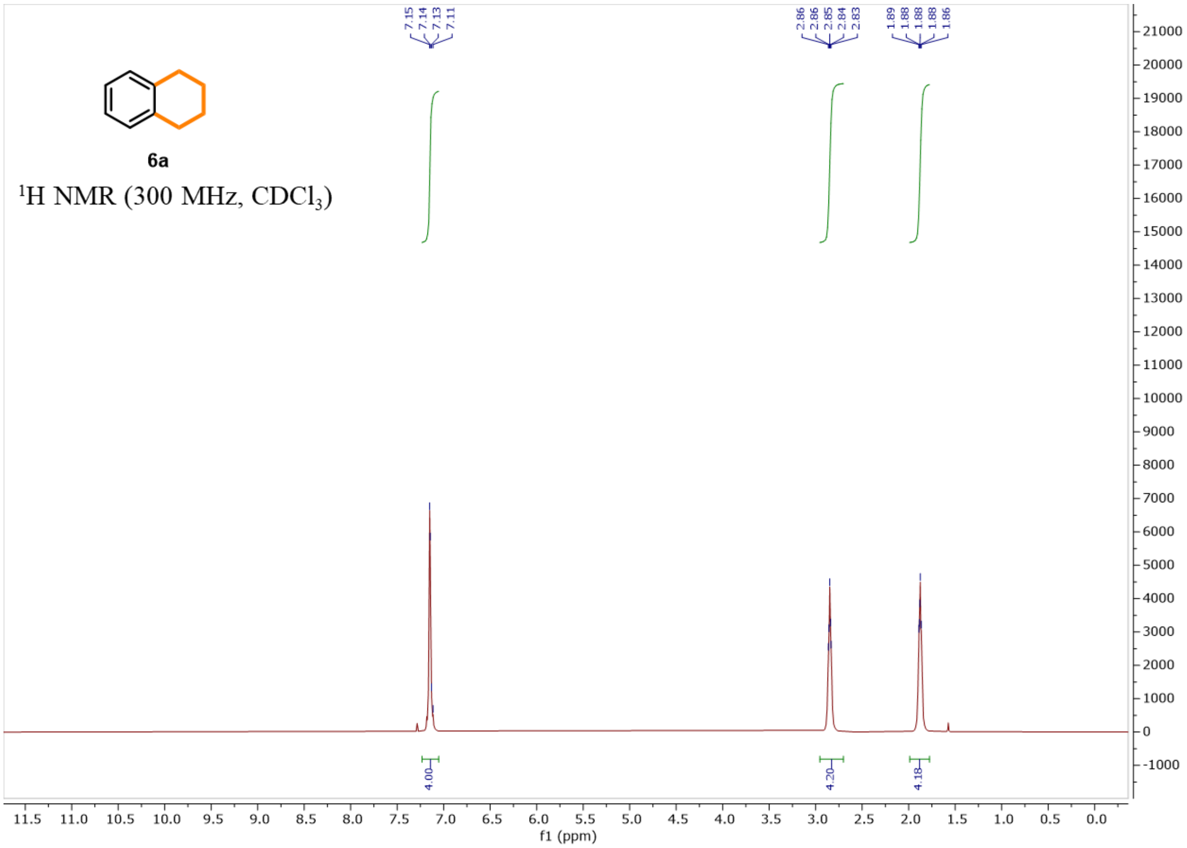
^{1}H NMR (300 MHz, $CDCl_3$)


7.84
7.83
7.83
7.81
7.80
7.36
7.34
7.26
7.26
7.26
7.24
7.23
7.22
7.21
7.21
7.12
7.09
7.08
7.05
7.02
7.00
3.35
3.34
3.34
3.33
3.33
3.31
3.30
3.15
3.13
3.12
3.12
3.11
3.09
2.45
2.32
2.32
Ts
H
H
N
H
CH3
4l
1H NMR (300 MHz, CDCl3)
2.89
2.13
2.21
2.28
1.97
2.00
2.99
3.13
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

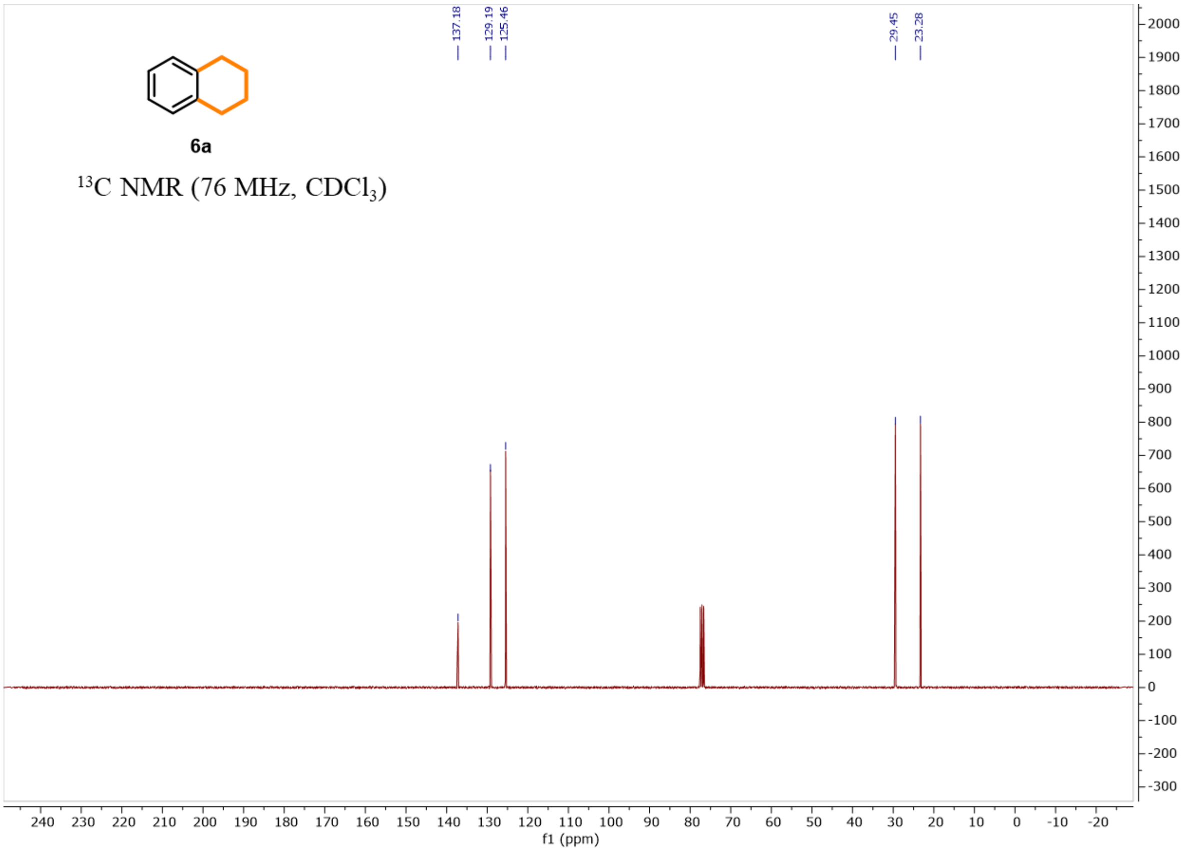

144.60
136.21
135.20
131.65
129.87
127.98
127.70
121.36
119.49
117.26
110.41
107.26
56.27
21.67
17.72
11.53
Ts
H
H
N
H
CH3
4l
13C NMR (76 MHz, CDCl3)
55
50
45
40
35
30
25
20
15
10
5
0
-5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.43 8.42 8.41 8.40 8.40 7.53 7.53 7.52 7.51 7.50 7.49 7.22 7.20 7.19 7.17 5.36 5.36 5.35 5.34 5.34 3.52 2.68 2.65 2.62 2.54 2.30 2.29 2.28 2.27 2.26 2.24 2.23 2.08 2.07 2.06 2.04 2.03 2.02 2.01 2.00 1.98 1.86 1.85 1.84 1.82 1.81 1.80 1.79 1.78 1.61 1.60 1.58 1.58 1.57 1.56 1.55 1.53 1.51 1.50 1.50 1.48 1.47 1.46 1.40 1.38 1.36 1.34 1.33 1.32 1.29 1.29 1.28 1.25 1.24 1.24 1.22 1.21 1.08 1.07 0.98 0.47
HO
H
H
H
N
H
H
4m
^{1}H NMR (300 MHz, CDCl$_3$)
1.96
0.97
0.99
1.00
1.01
0.98
1.14
2.11
3.02
3.19
5.13
4.17
1.76
3.35
2.86
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

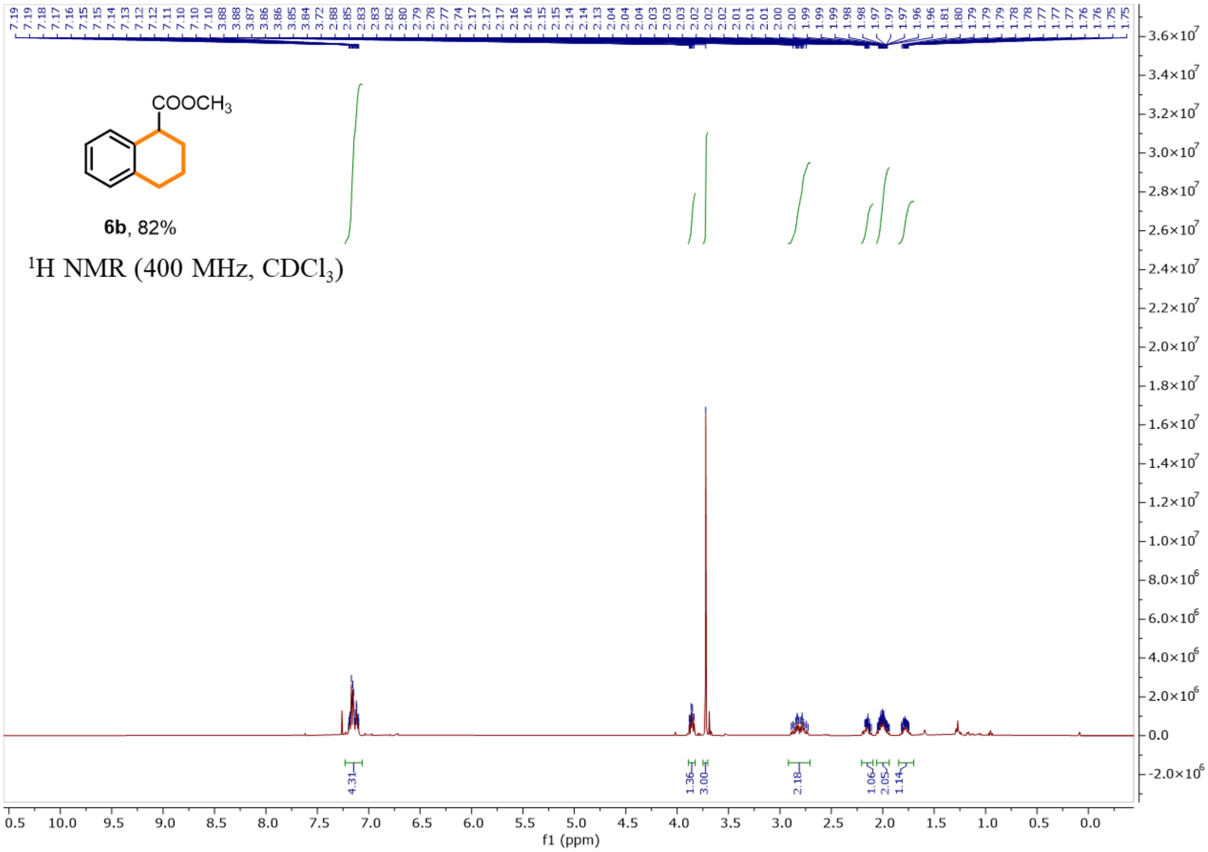

150.22 147.34 141.10 136.44 135.72 122.82 121.29 71.51 56.50 54.44 50.29 44.27 42.31 37.37 37.34 36.64 32.34 31.90 31.64 25.88 24.54 20.67 19.45 12.57
HO
H
H
H
N
H
H
4m
^{13}C NMR (76 MHz, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
500 450 400 350 300 250 200 150 100 50 0 -50

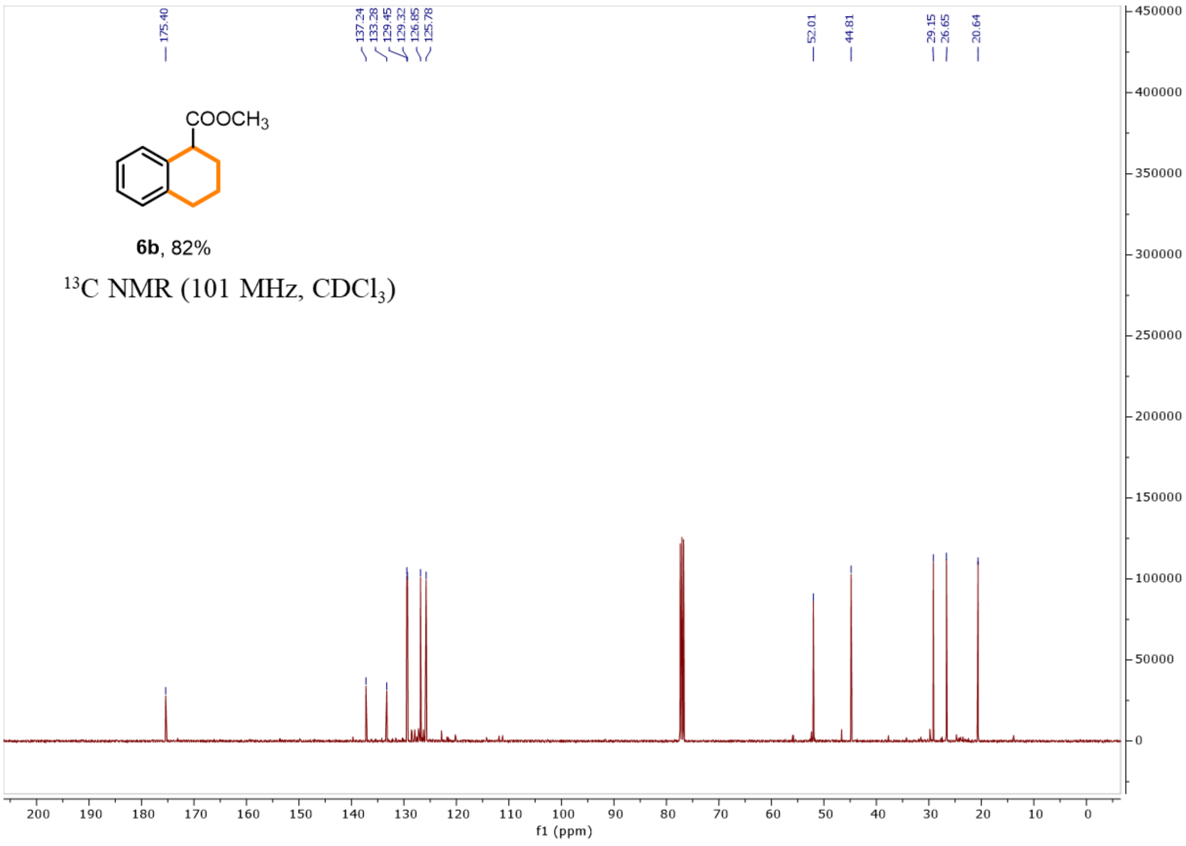

6a

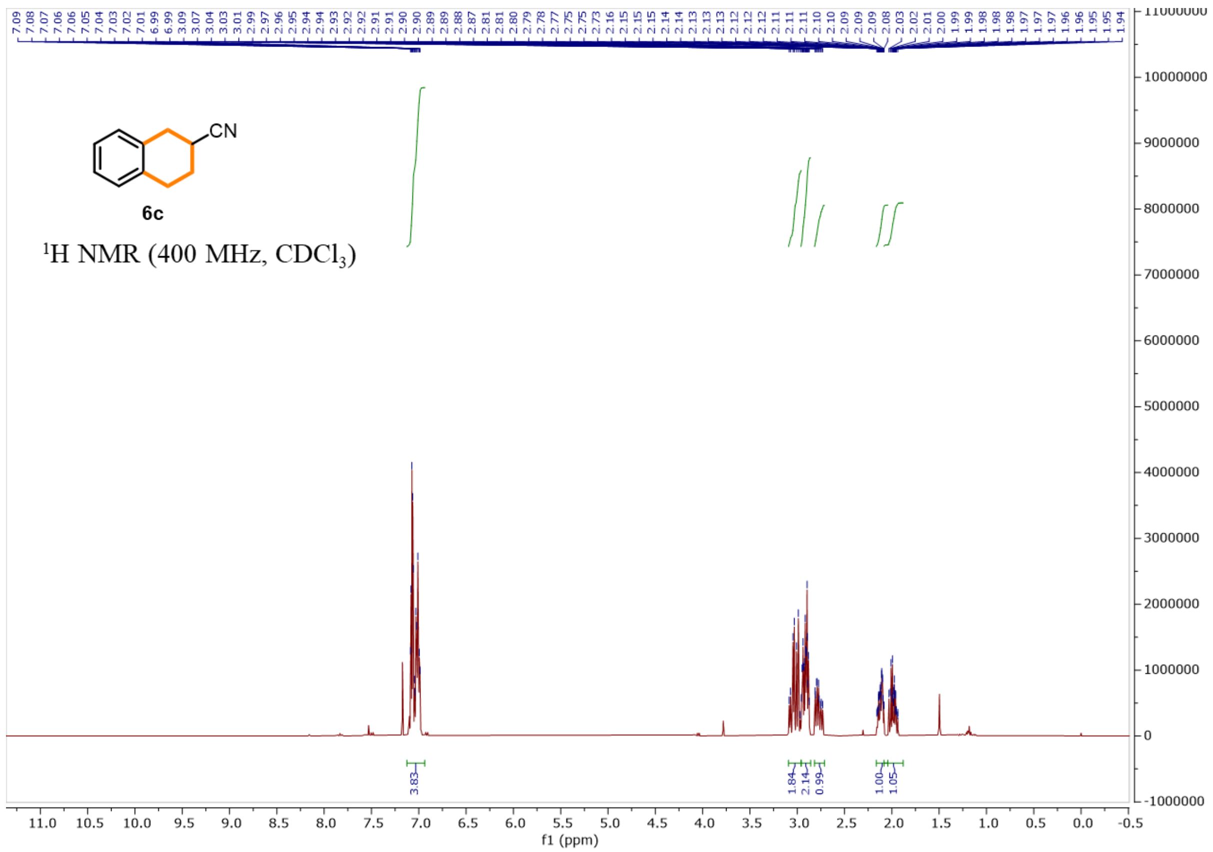
^{1}H NMR (300 MHz, CDCl$_3$)


6a

^{13}C NMR (76 MHz, CDCl$_3$)

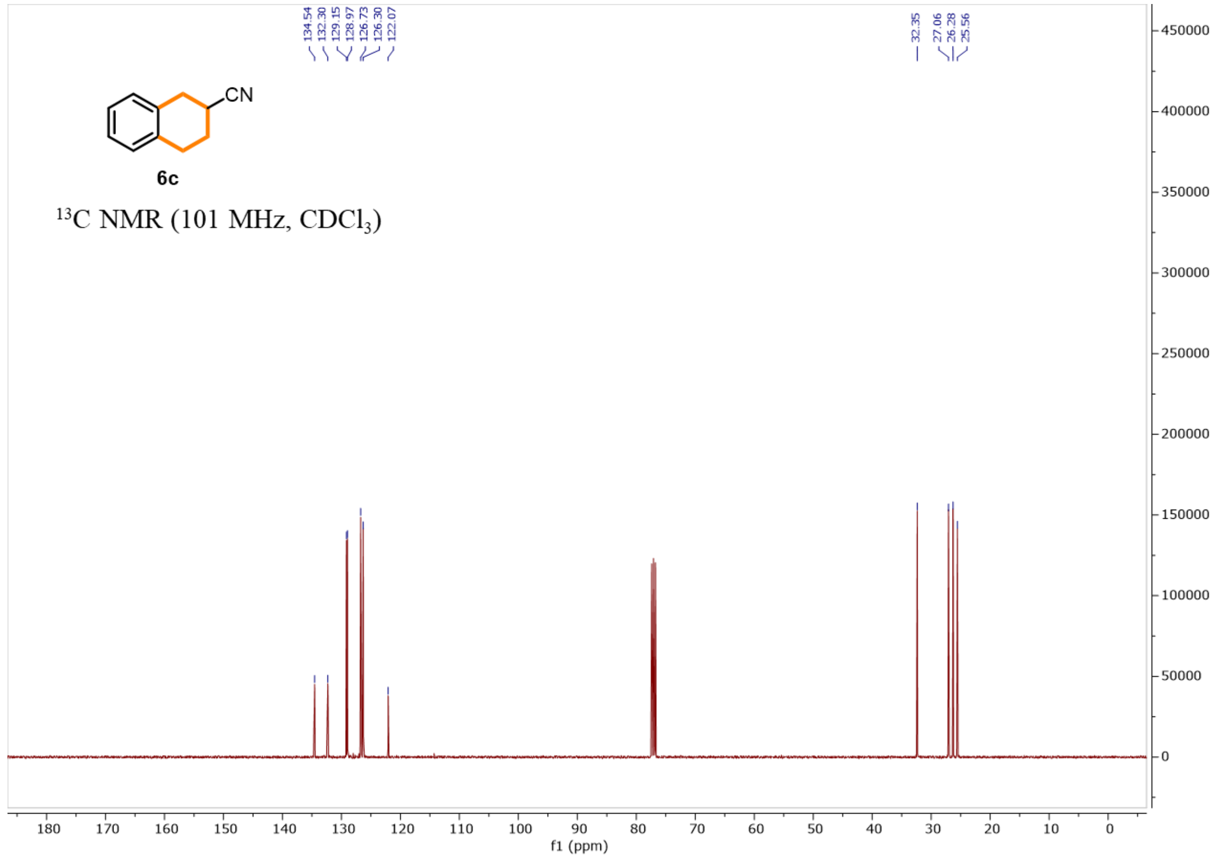

7.19 7.19 7.18 7.17 7.16 7.15 7.15 7.14 7.13 7.12 7.12 7.11 7.10 7.10 7.10 3.88 3.88 3.87 3.86 3.86 3.85 3.84 3.72 2.88 2.85 2.83 2.83 2.82 2.80 2.79 2.78 2.77 2.74 2.17 2.17 2.17 2.16 2.16 2.15 2.15 2.14 2.14 2.13 2.04 2.04 2.04 2.03 2.03 2.03 2.02 2.02 2.02 2.01 2.01 2.01 2.00 2.00 1.99 1.99 1.99 1.98 1.98 1.97 1.97 1.97 1.97 1.96 1.96 1.81 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.77 1.76 1.76 1.75 1.75
COOCH3
6b, 82%
1H NMR (400 MHz, CDCl3)
4.31
1.36
3.00
2.18
1.06
2.05
1.14
f1 (ppm)


175.40
137.24 133.28 129.45 129.32 126.85 125.78
52.01
44.81
29.15 26.65
20.64
COOCH3
6b, 82%
13C NMR (101 MHz, CDCl3)
f1 (ppm)



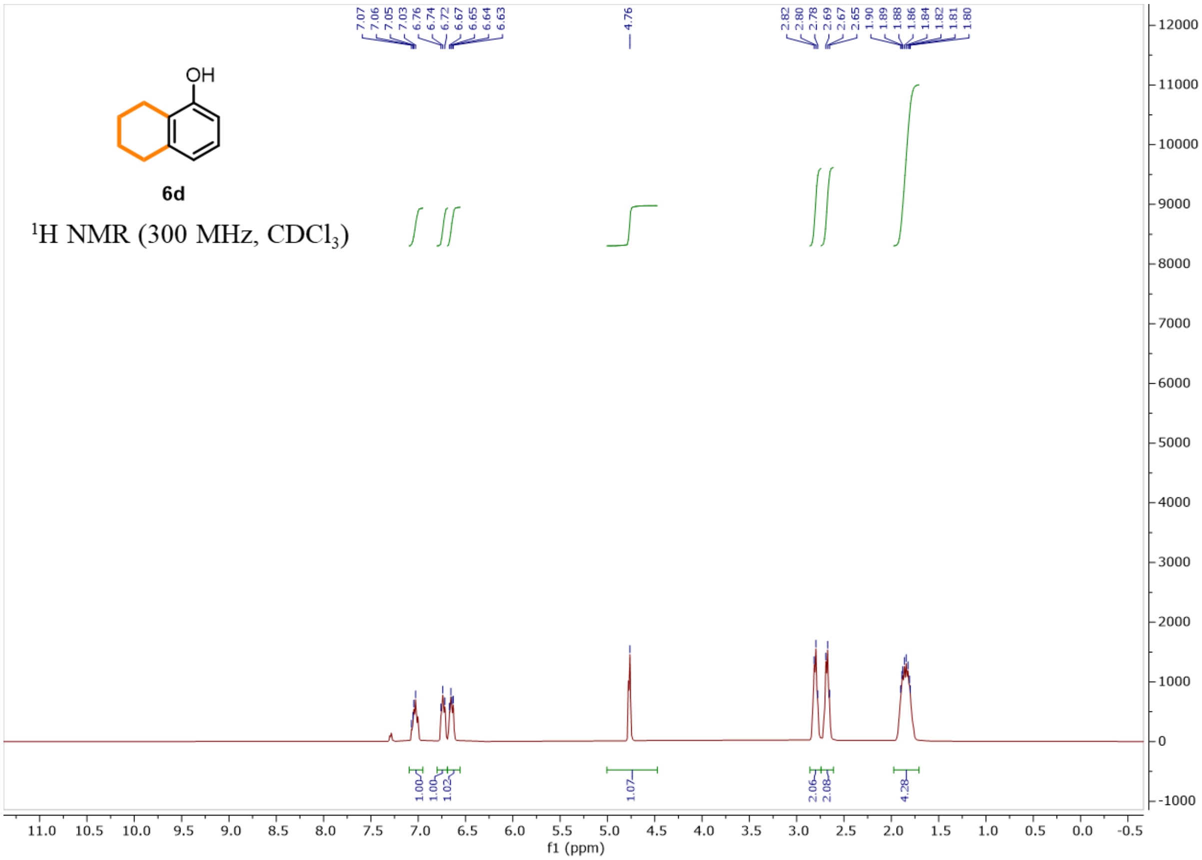
6c

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



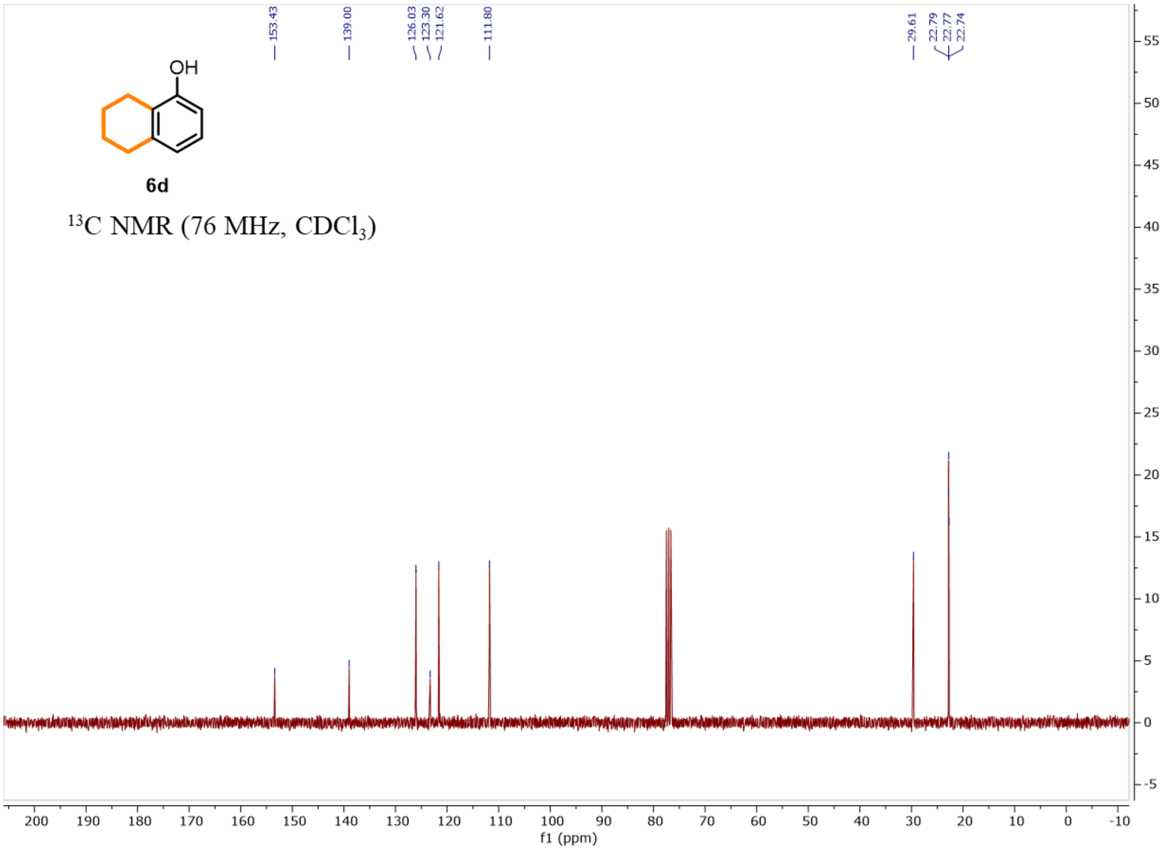
6c

^{13}C NMR (101 MHz, CDCl$_3$)



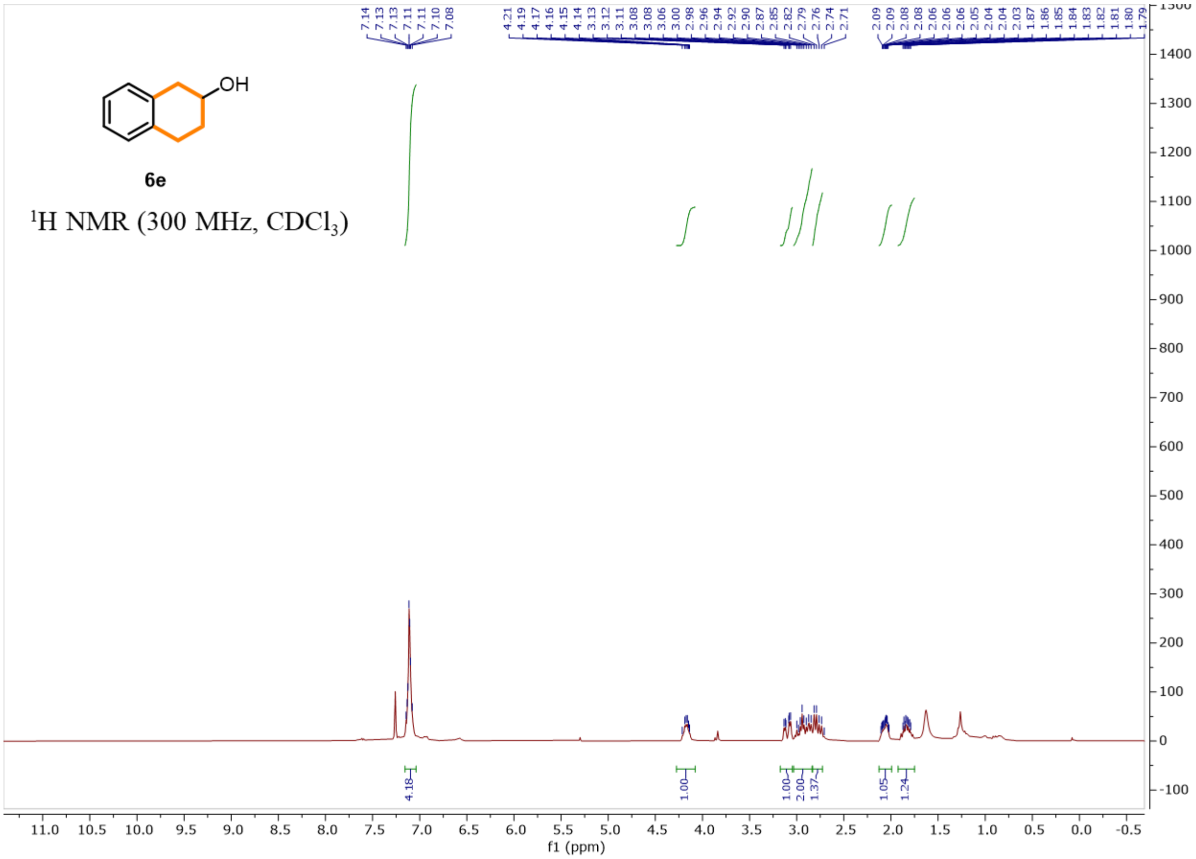
6d

^{1}H NMR (300 MHz, $CDCl_3$)



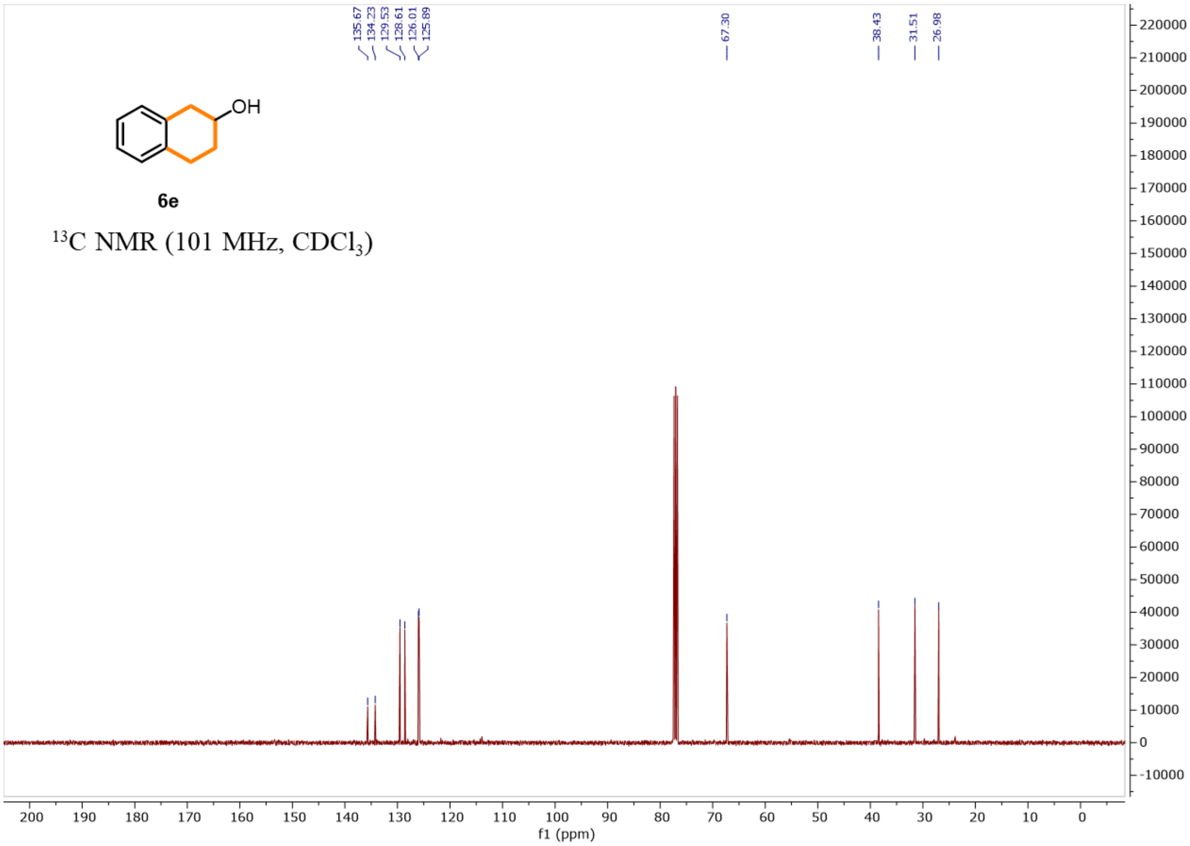
6d

^{13}C NMR (76 MHz, $CDCl_3$)



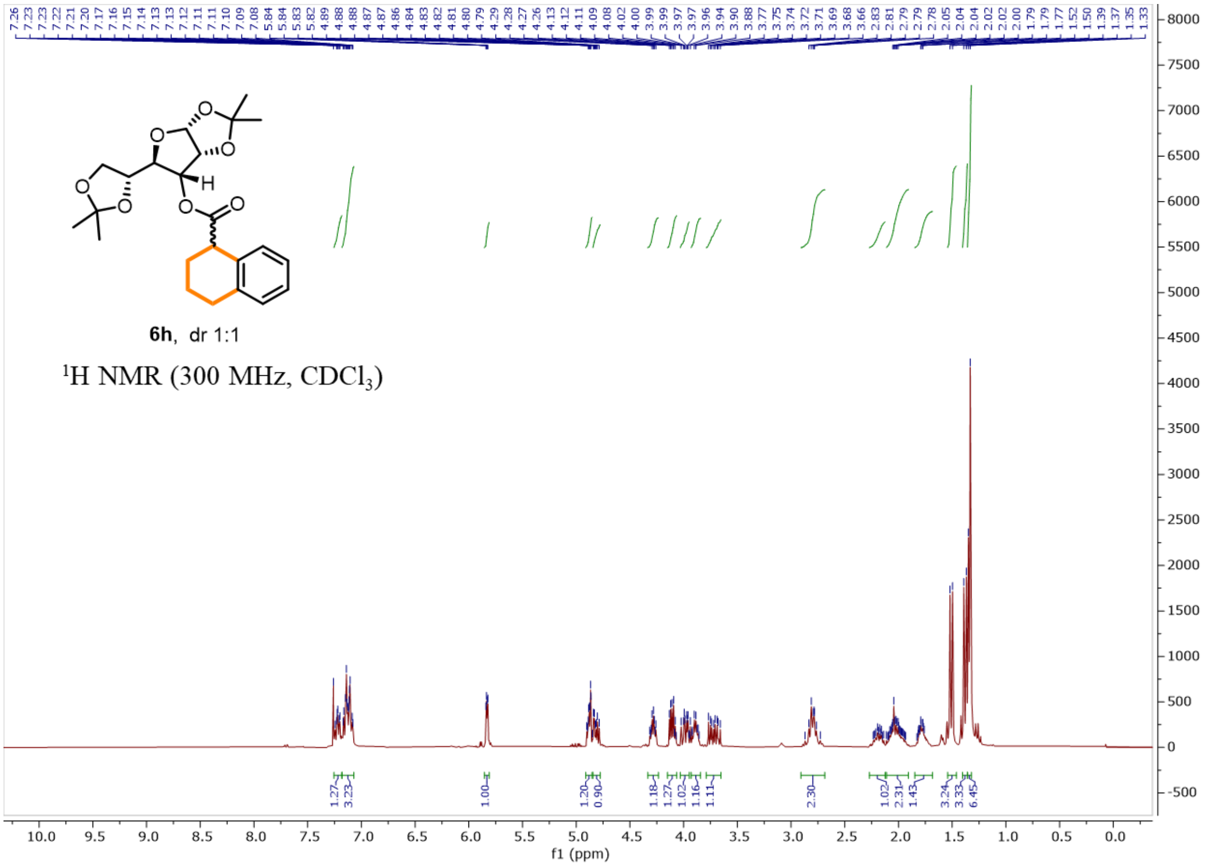
6e

^{1}H NMR (300 MHz, CDCl$_3$)

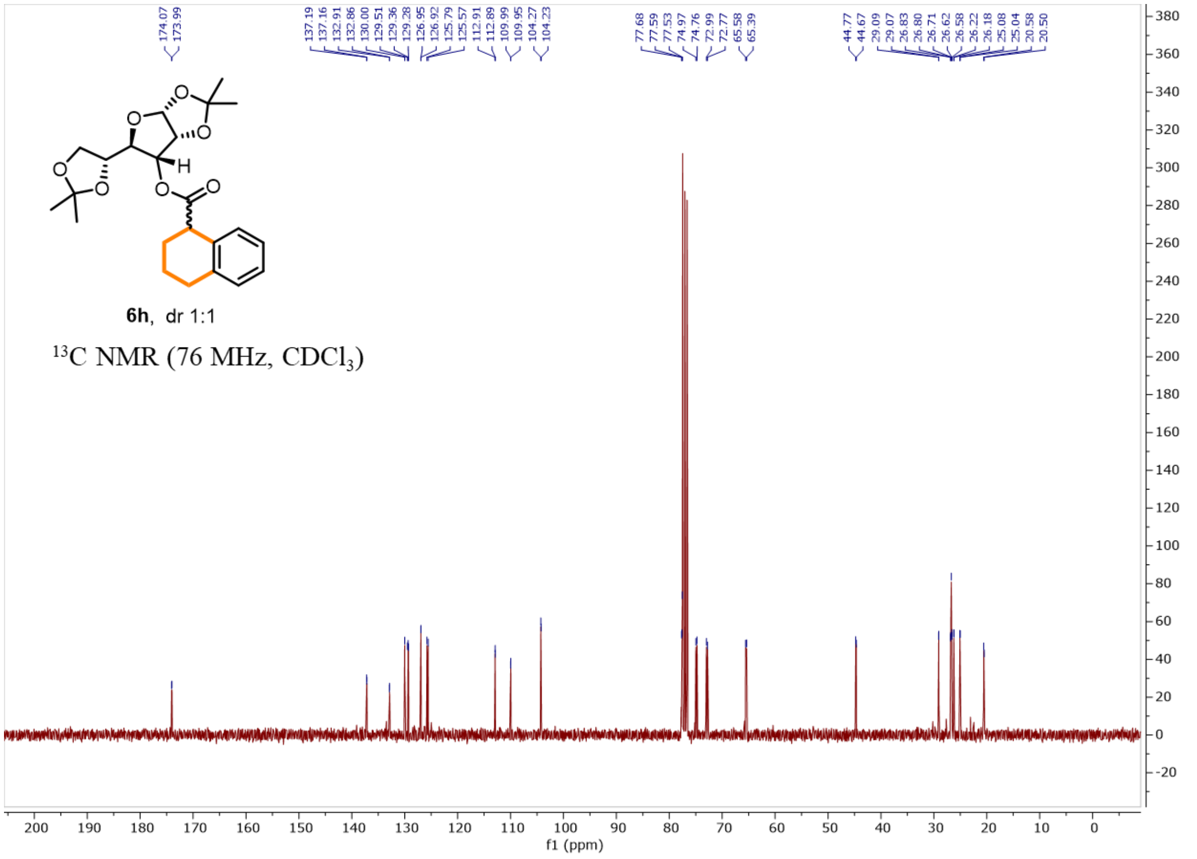


6e

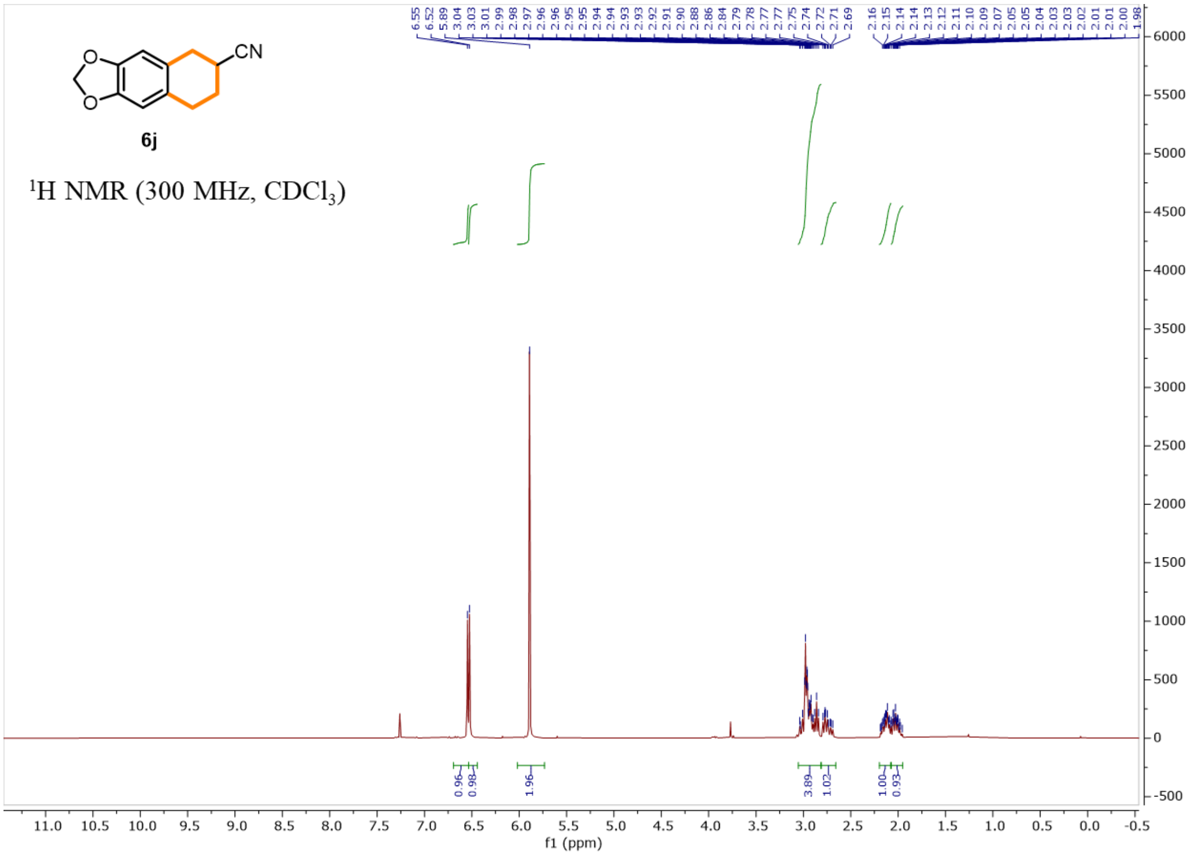
^{13}C NMR (101 MHz, CDCl$_3$)



7.26 7.23 7.23 7.22 7.21 7.20 7.17 7.16 7.15 7.14 7.13 7.13 7.12 7.11 7.11 7.10 7.09 7.08 5.84 5.84 5.83 5.82 4.89 4.88 4.88 4.87 4.87 4.86 4.84 4.83 4.82 4.81 4.80 4.79 4.29 4.28 4.27 4.26 4.13 4.12 4.11 4.09 4.08 4.02 4.00 3.99 3.99 3.97 3.97 3.96 3.94 3.90 3.88 3.77 3.75 3.74 3.72 3.71 3.69 3.68 3.66 2.83 2.81 2.79 2.78 2.05 2.04 2.04 2.02 2.02 2.00 1.79 1.77 1.52 1.50 1.39 1.37 1.35 1.33
H
O
6h, dr 1:1
^{1}H NMR (300 MHz, CDCl$_3$)
1.27 3.23 1.00 1.20 0.90 1.18 1.27 1.02 1.16 1.11 2.30 1.02 2.31 1.43 3.24 3.33 6.45
8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

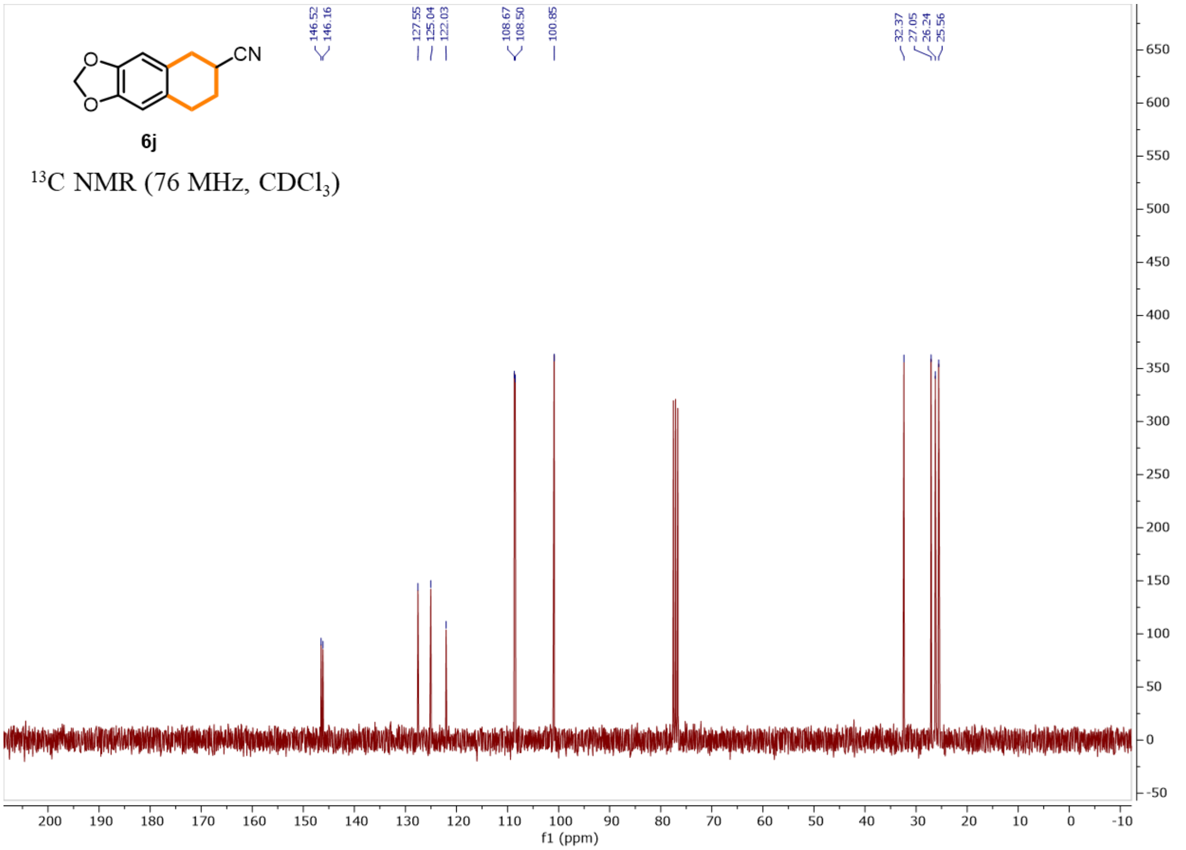


174.07 173.99 137.19 137.16 132.91 132.86 130.00 129.51 129.36 129.28 126.95 126.92 125.79 125.57 112.91 112.89 109.99 109.95 104.27 104.23 77.68 77.59 77.53 74.97 74.76 72.99 72.77 65.58 65.39 44.77 44.67 29.09 29.07 26.83 26.80 26.71 26.62 26.58 26.22 26.18 25.08 25.04 20.58 20.50
H
O
6h, dr 1:1
^{13}C NMR (76 MHz, CDCl$_3$)
380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



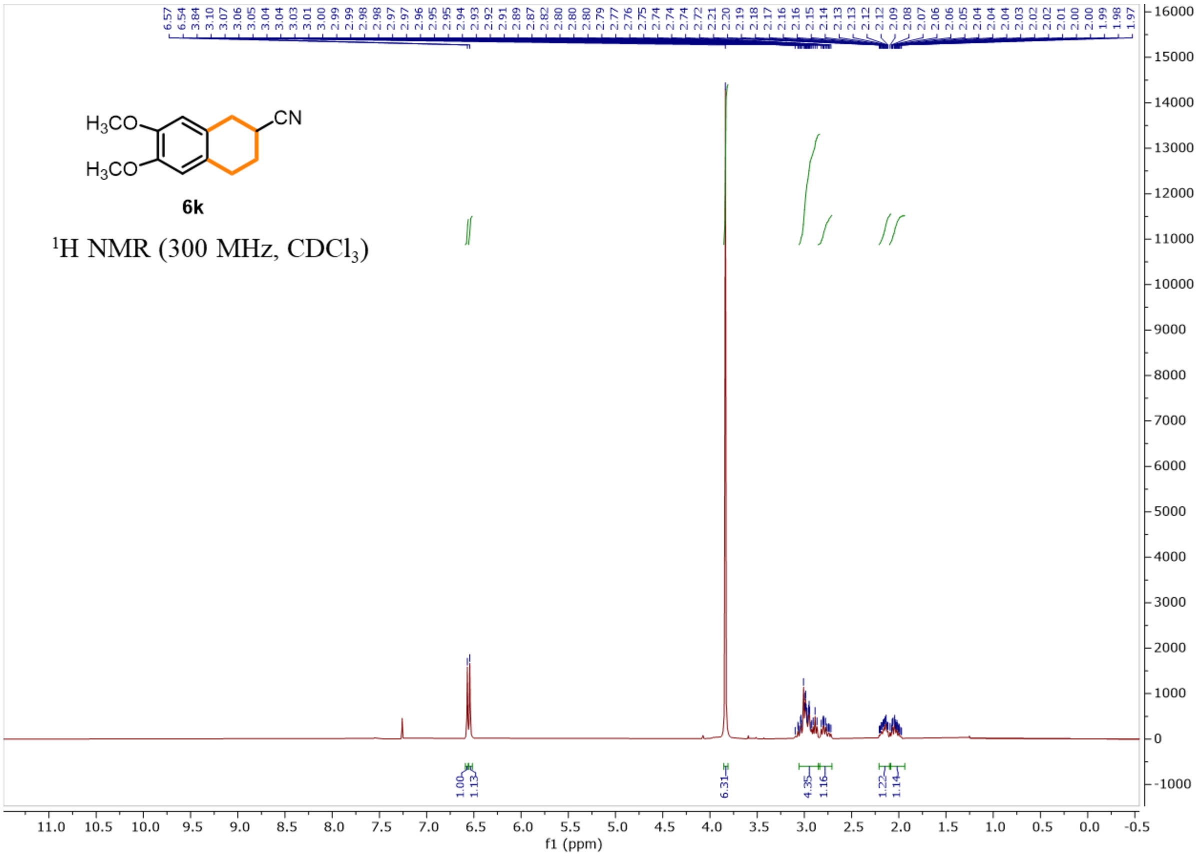
6j

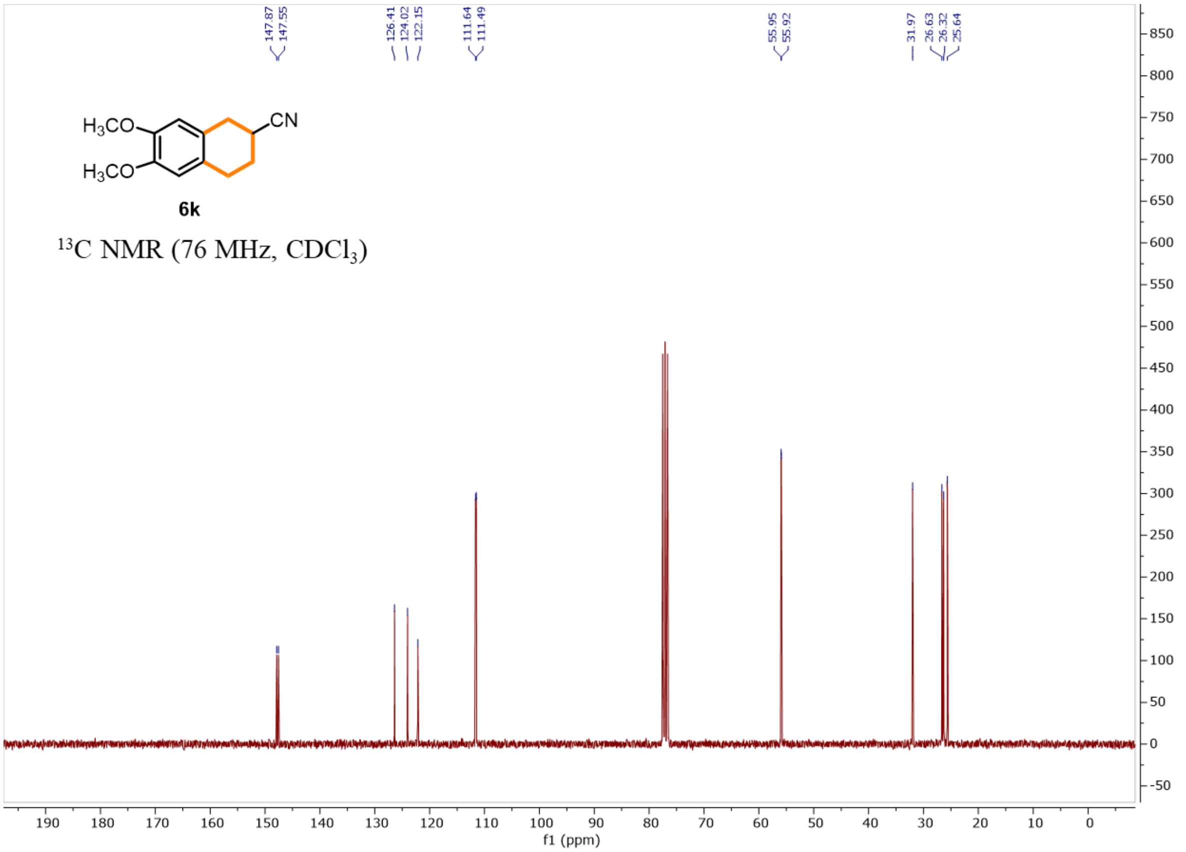
^{1}H NMR (300 MHz, CDCl$_3$)

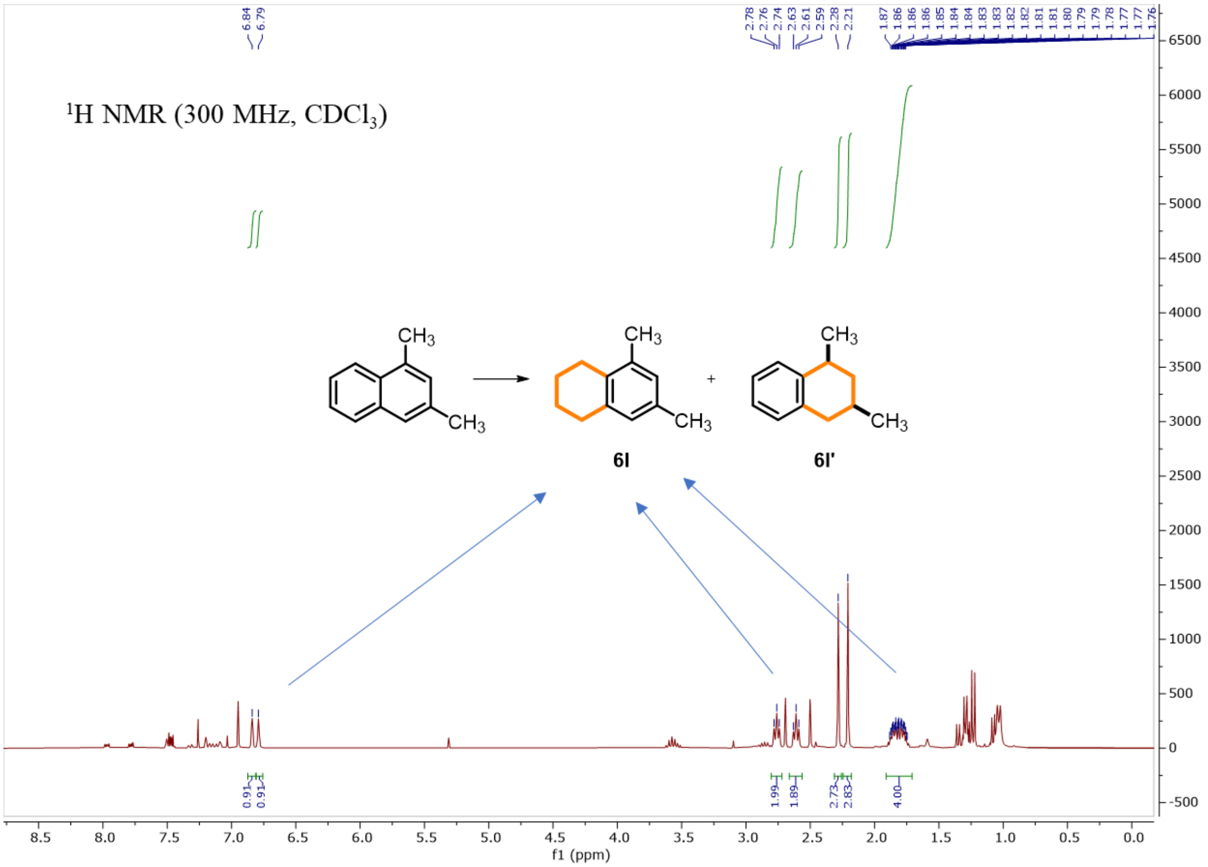


6j

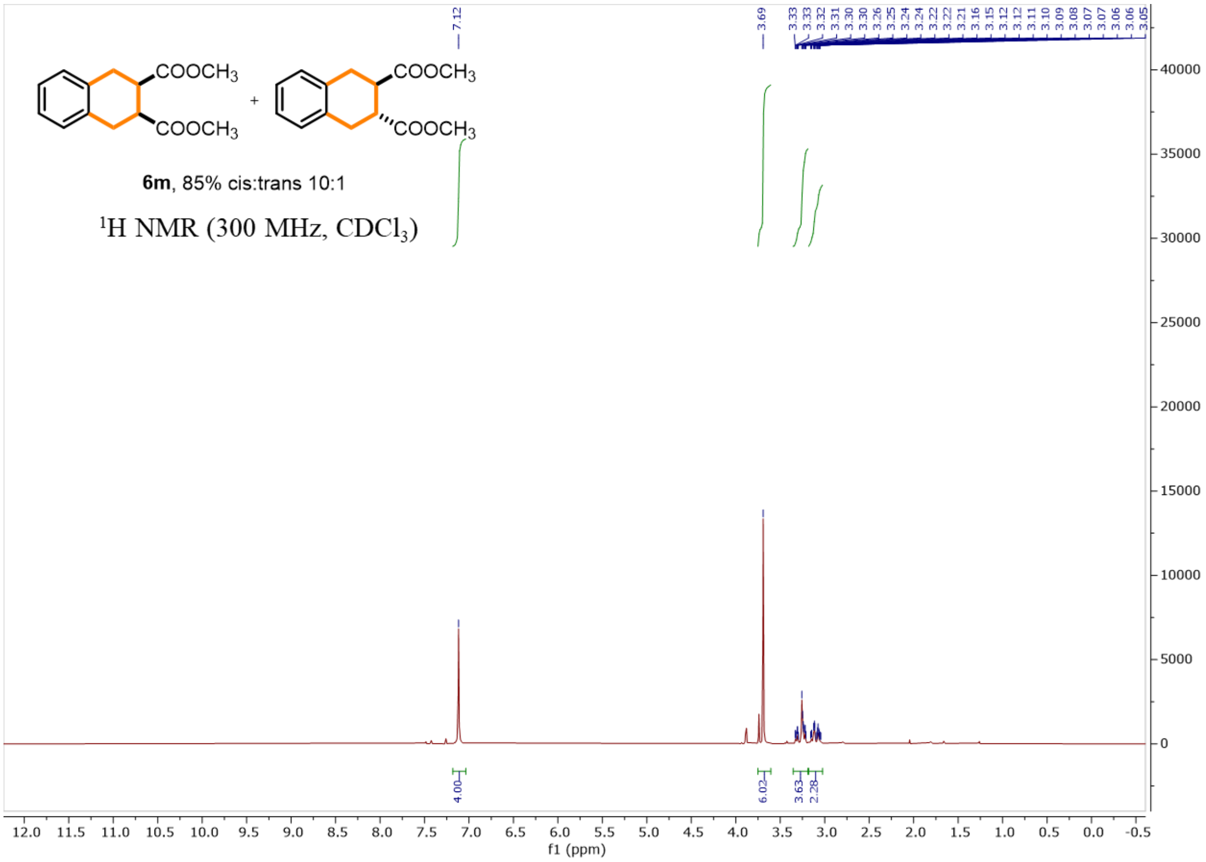
^{13}C NMR (76 MHz, CDCl$_3$)


H$_3$CO
H$_3$CO
CN
6k
^{1}H NMR (300 MHz, CDCl$_3$)
6.57 6.54 3.84 3.10 3.07 3.06 3.05 3.04 3.04 3.03 3.01 3.00 2.99 2.99 2.98 2.98 2.97 2.97 2.96 2.95 2.95 2.94 2.93 2.92 2.91 2.89 2.87 2.82 2.80 2.80 2.79 2.77 2.76 2.75 2.74 2.74 2.74 2.72 2.21 2.20 2.19 2.18 2.17 2.16 2.16 2.15 2.14 2.13 2.13 2.12 2.12 2.09 2.08 2.07 2.06 2.06 2.05 2.04 2.04 2.04 2.03 2.02 2.02 2.01 2.00 2.00 1.99 1.98 1.97
1.00
1.13
6.31
4.35
1.16
1.22
1.14
f1 (ppm)


H$_3$CO
H$_3$CO
CN
6k
^{13}C NMR (76 MHz, CDCl$_3$)
147.87 147.55 126.41 124.02 122.15 111.64 111.49 55.95 55.92 31.97 26.63 26.32 25.64
f1 (ppm)

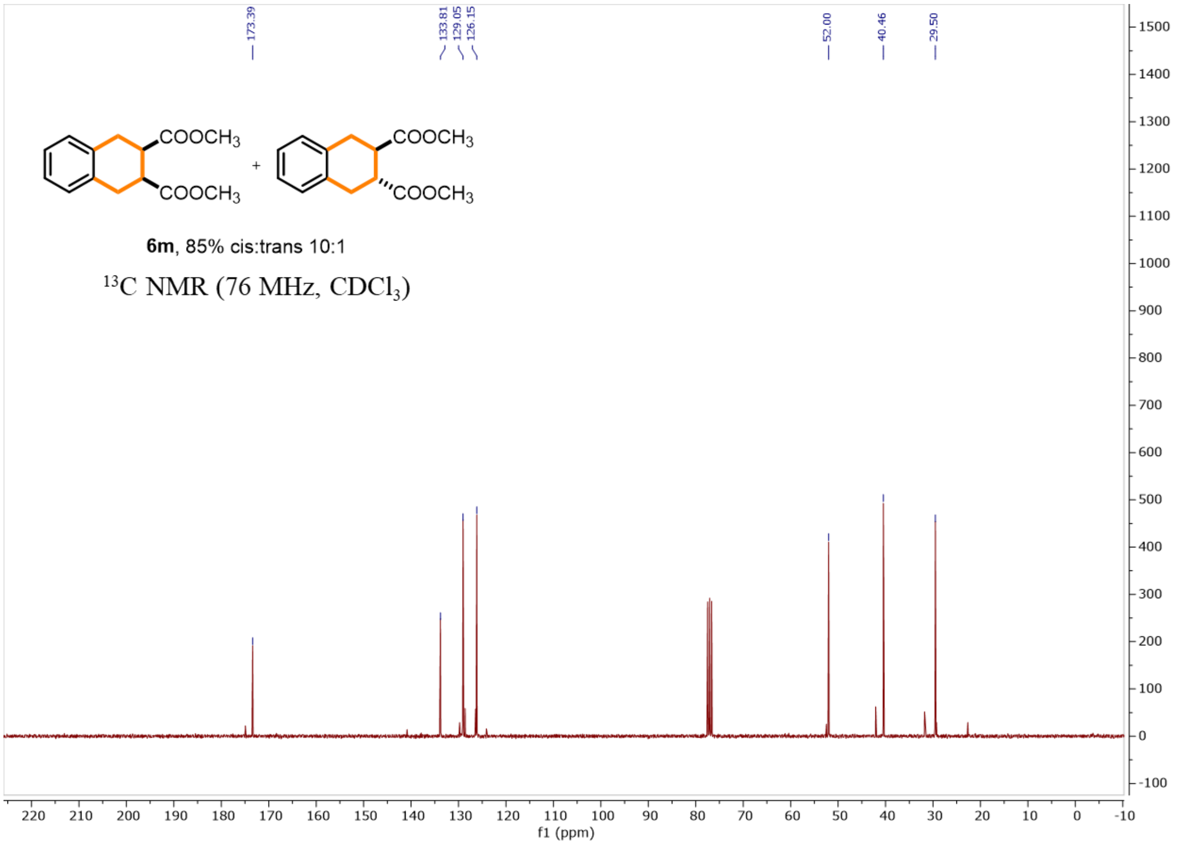

^{1}H NMR (300 MHz, $CDCl_3$)

6l **6l'**



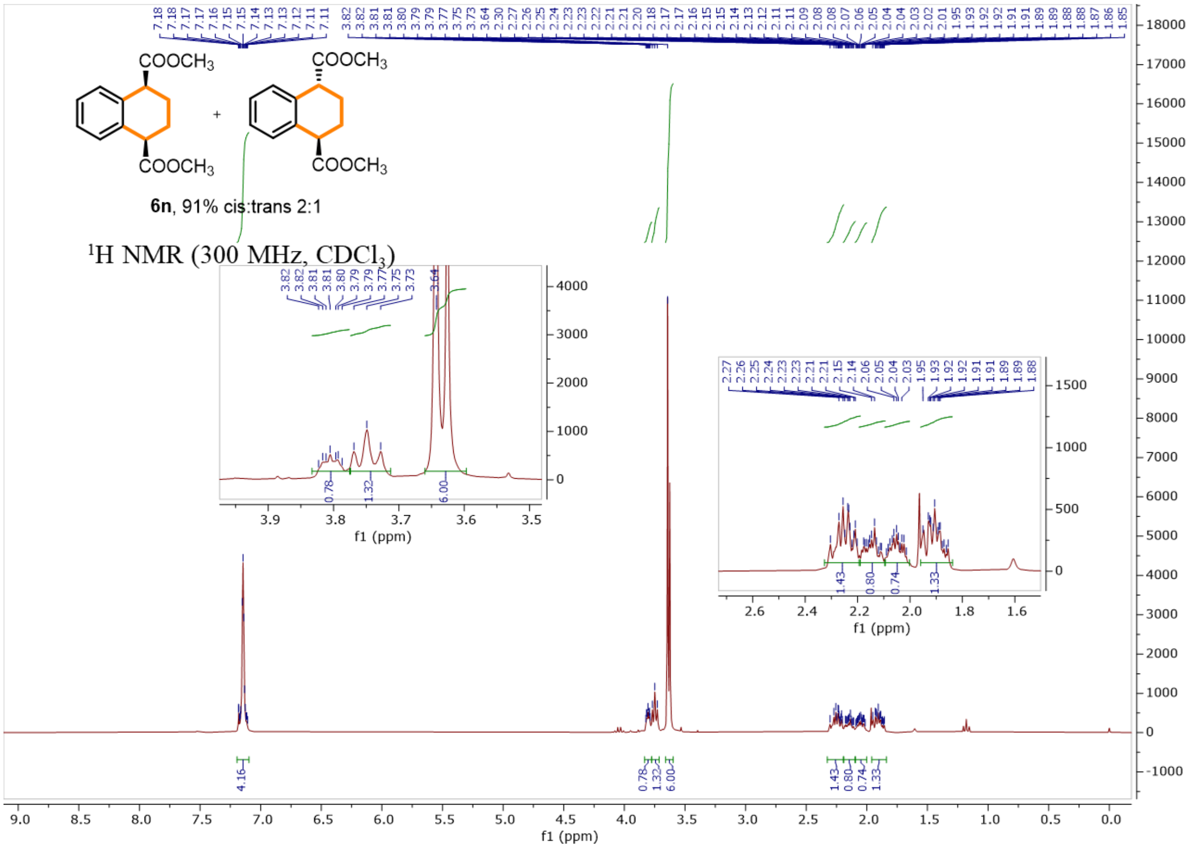
6m, 85% cis:trans 10:1

^{1}H NMR (300 MHz, $CDCl_3$)

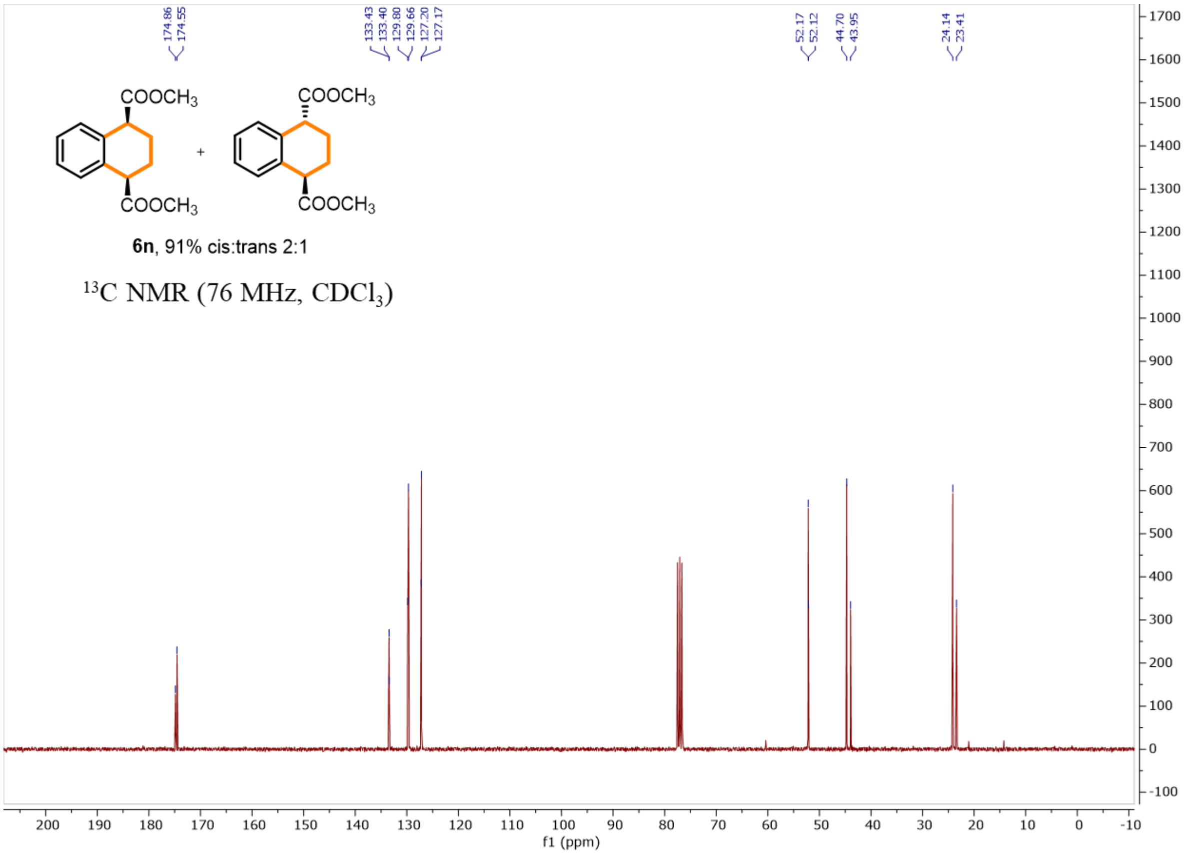


6m, 85% cis:trans 10:1

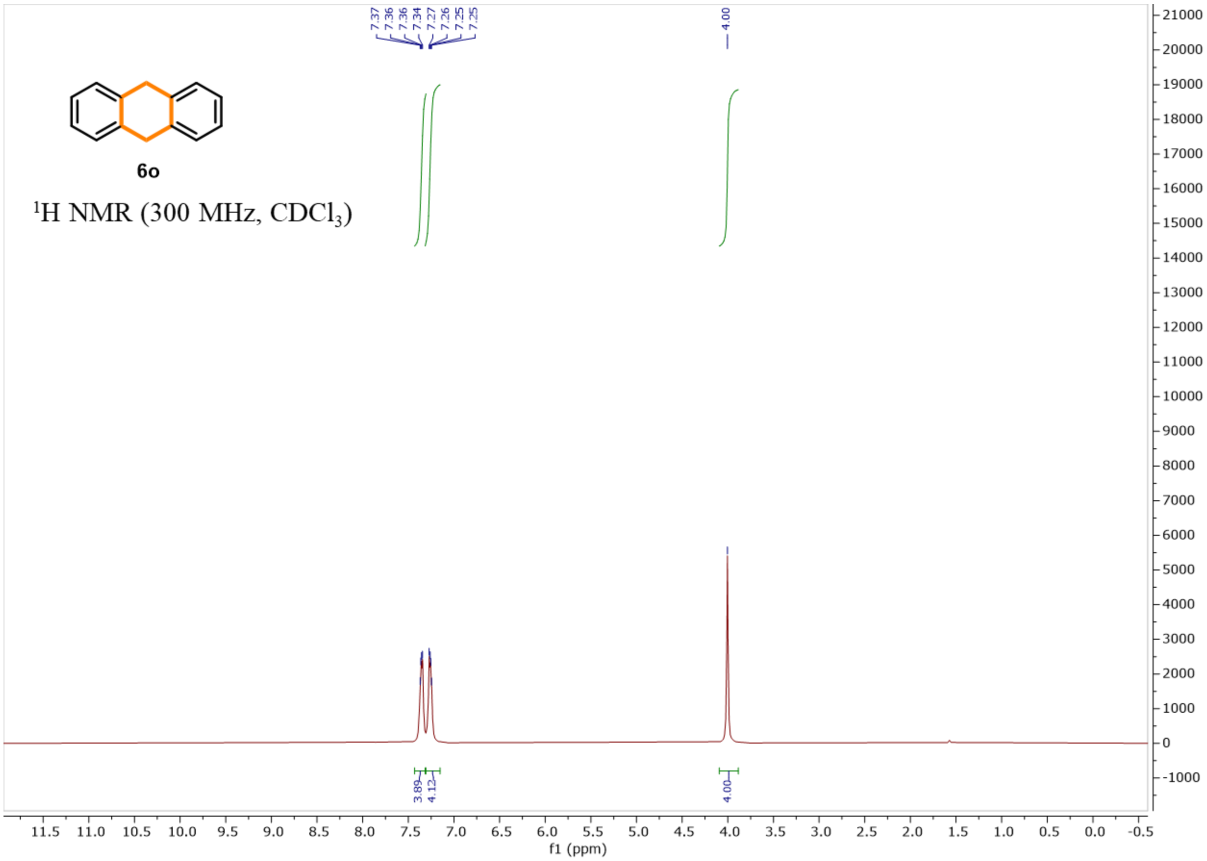
^{13}C NMR (76 MHz, $CDCl_3$)


6n, 91% cis:trans 2:1

^{1}H NMR (300 MHz, $CDCl_3$)

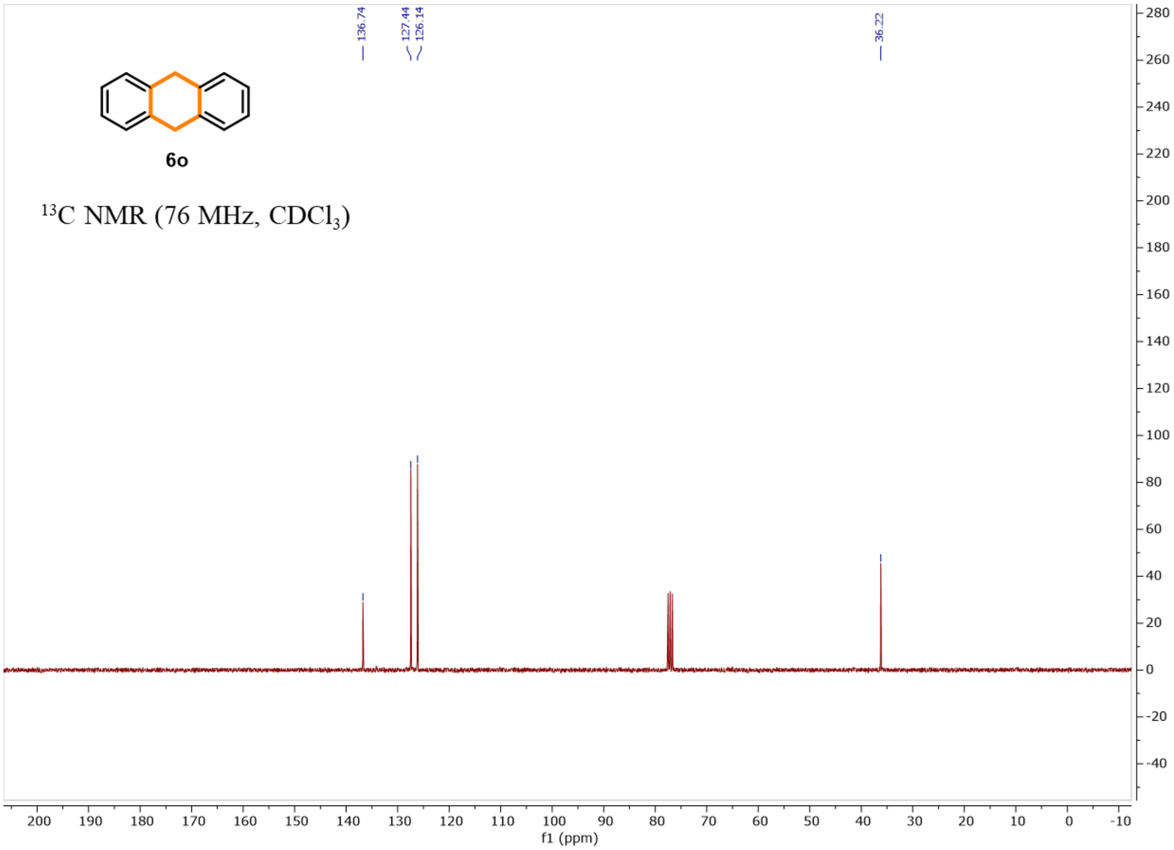

6n, 91% cis:trans 2:1

^{13}C NMR (76 MHz, $CDCl_3$)



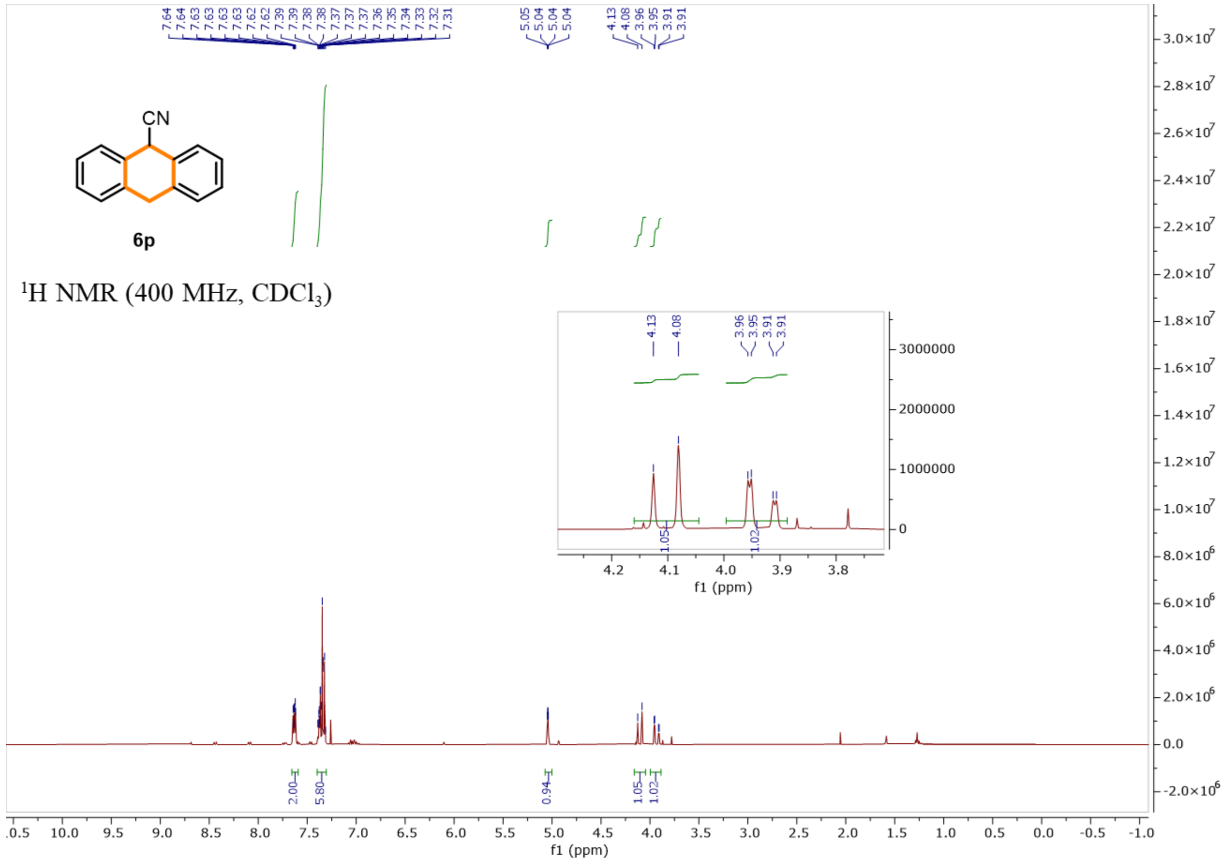
6o

^{1}H NMR (300 MHz, CDCl$_3$)

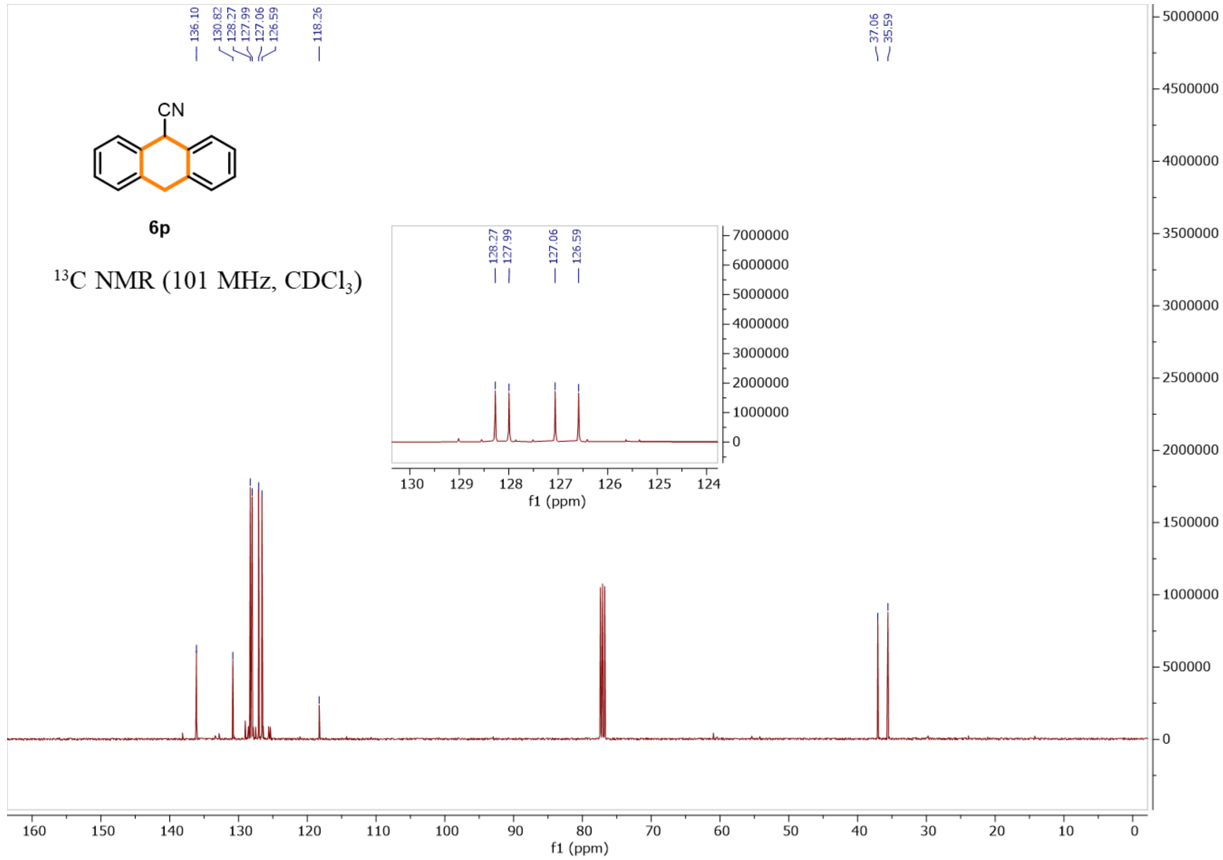


6o

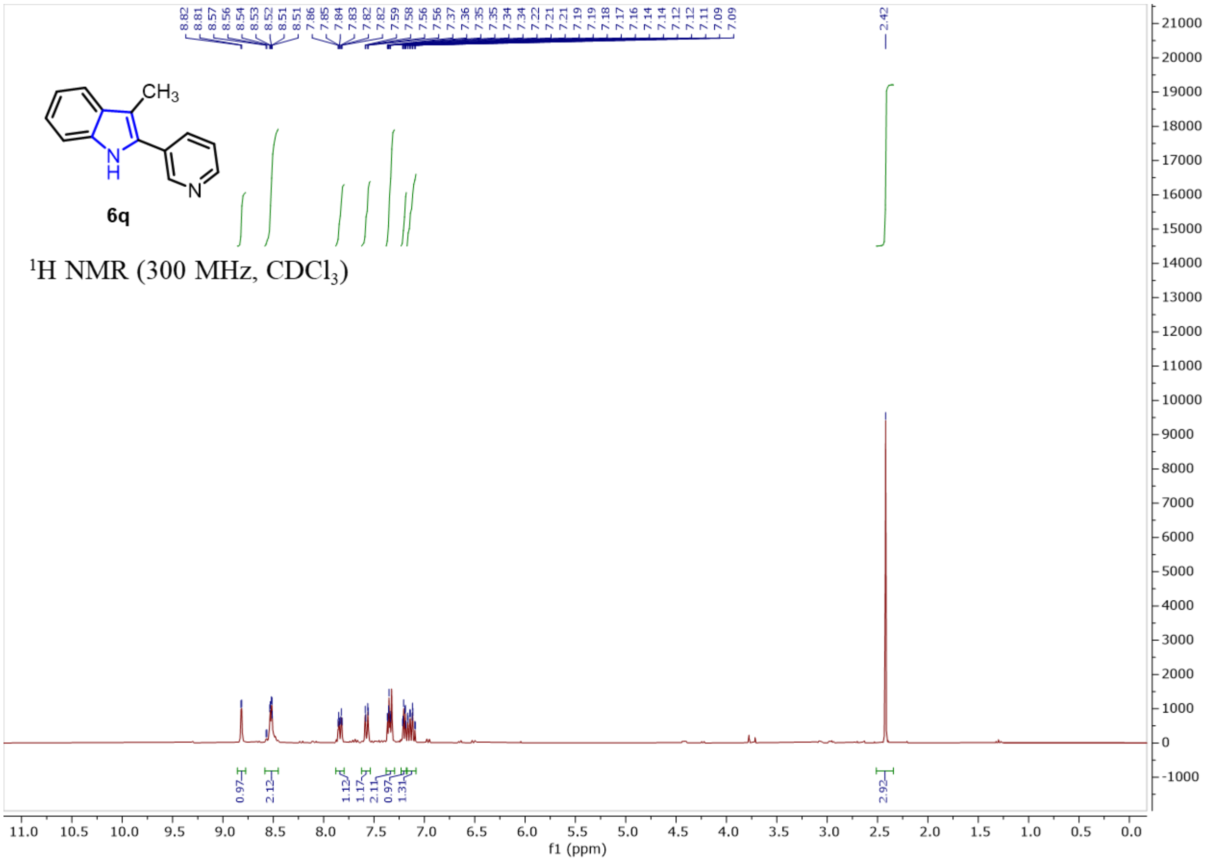
^{13}C NMR (76 MHz, CDCl$_3$)


6p

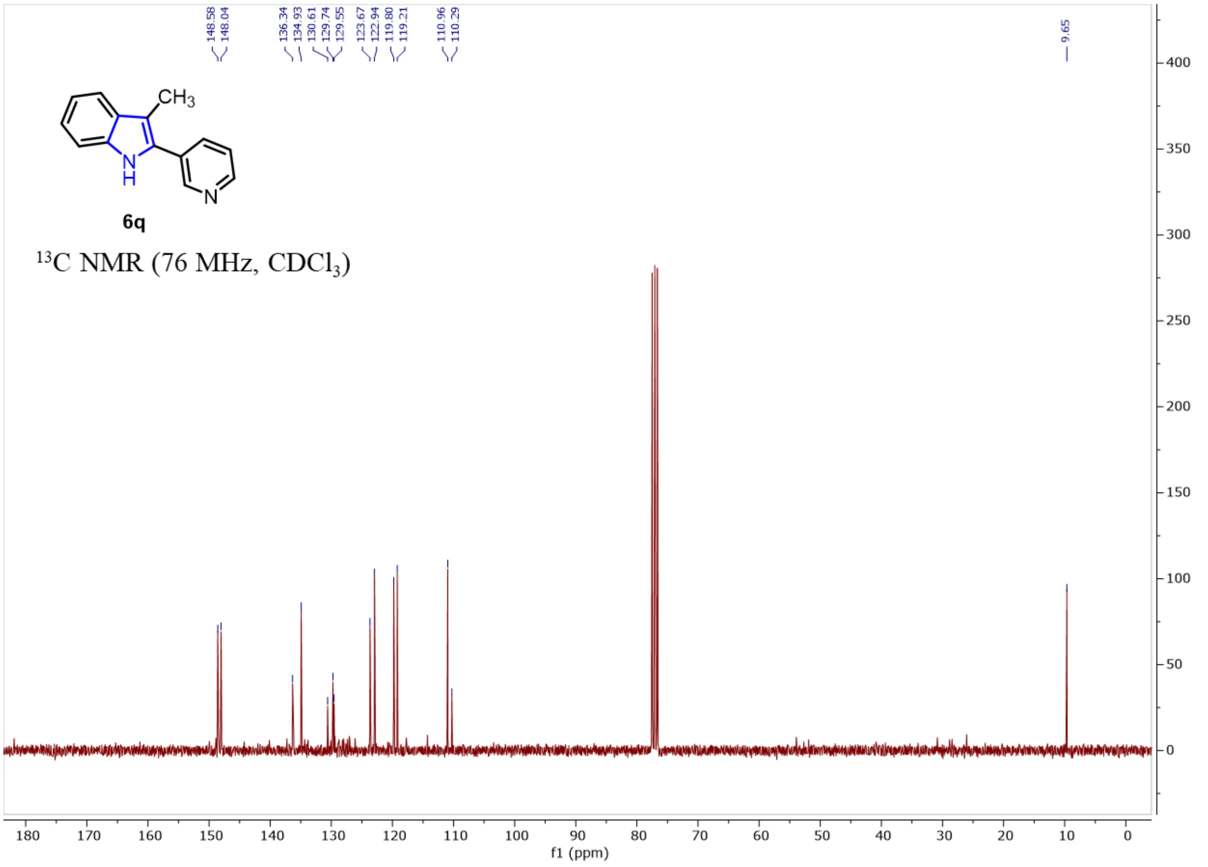
^{1}H NMR (400 MHz, CDCl$_3$)


6p

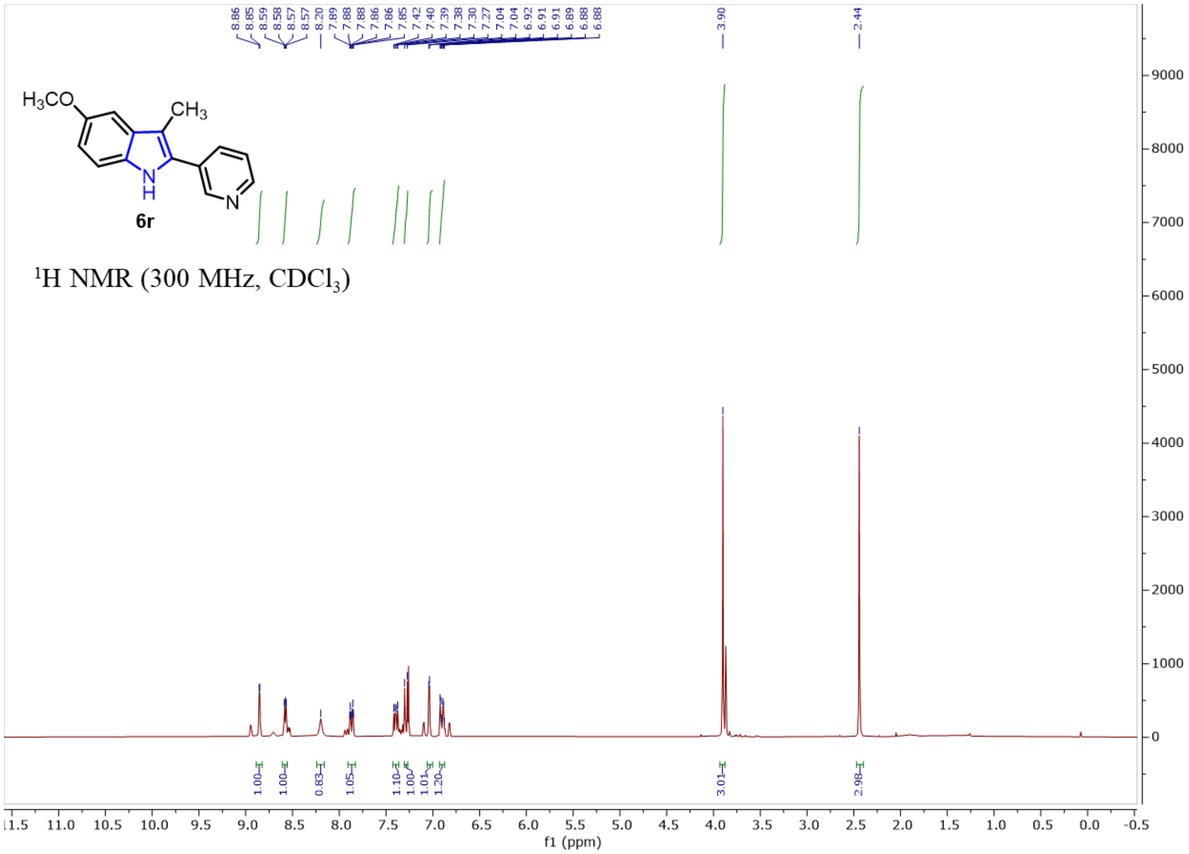
^{13}C NMR (101 MHz, CDCl$_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

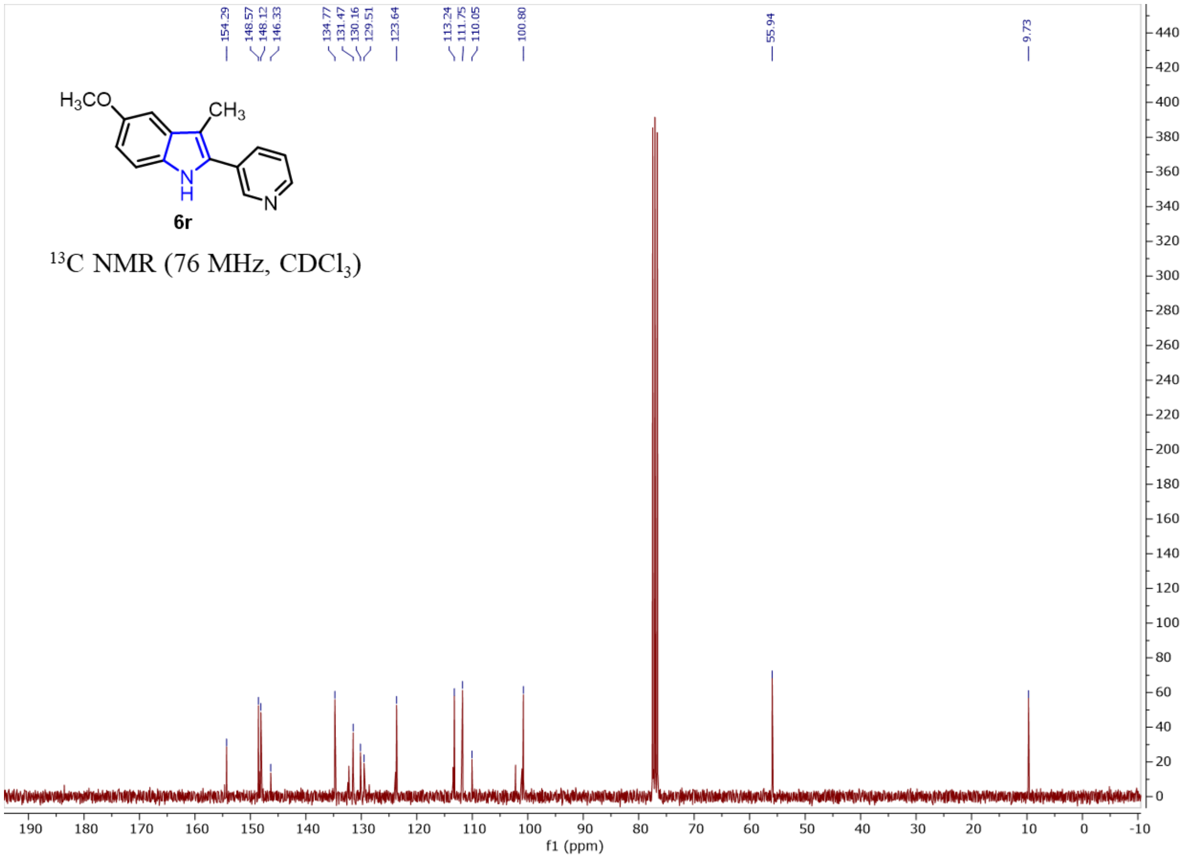


^{13}C NMR (76 MHz, $CDCl_3$)



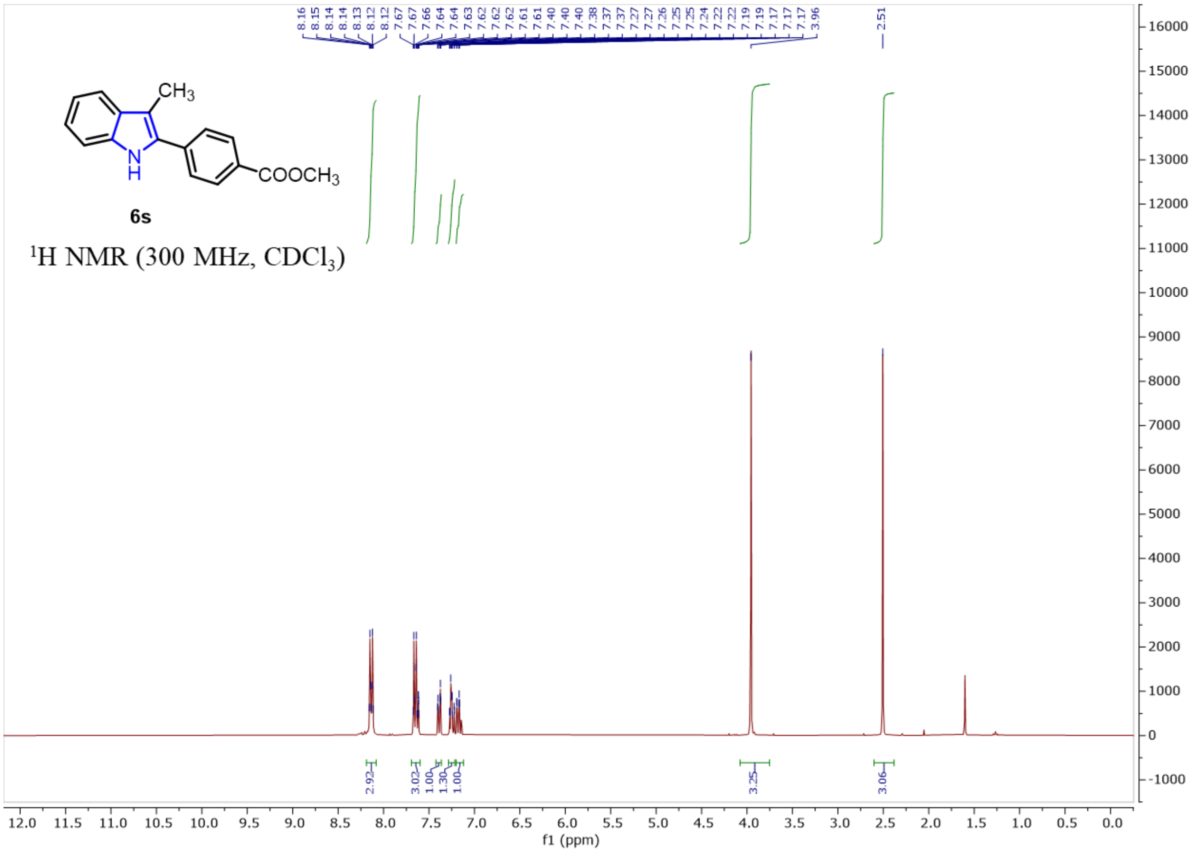
6r

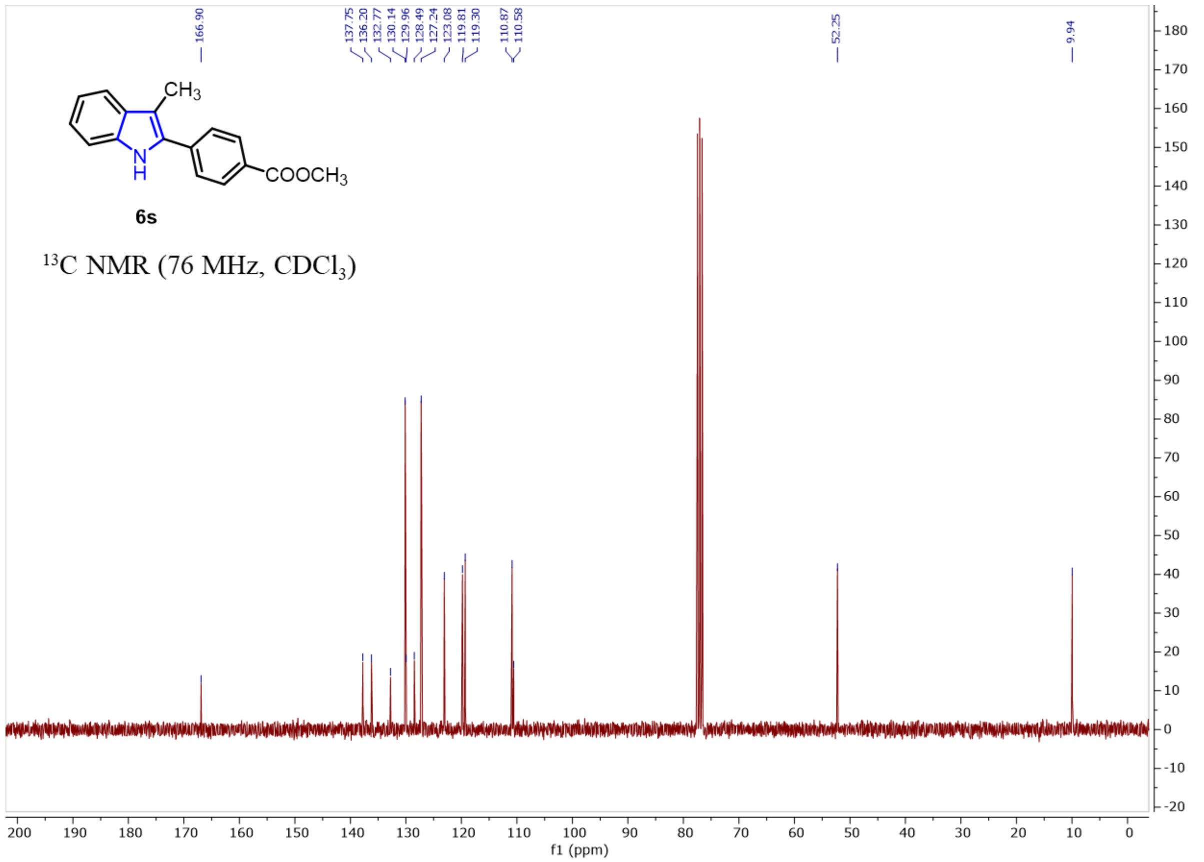
^{1}H NMR (300 MHz, $CDCl_3$)

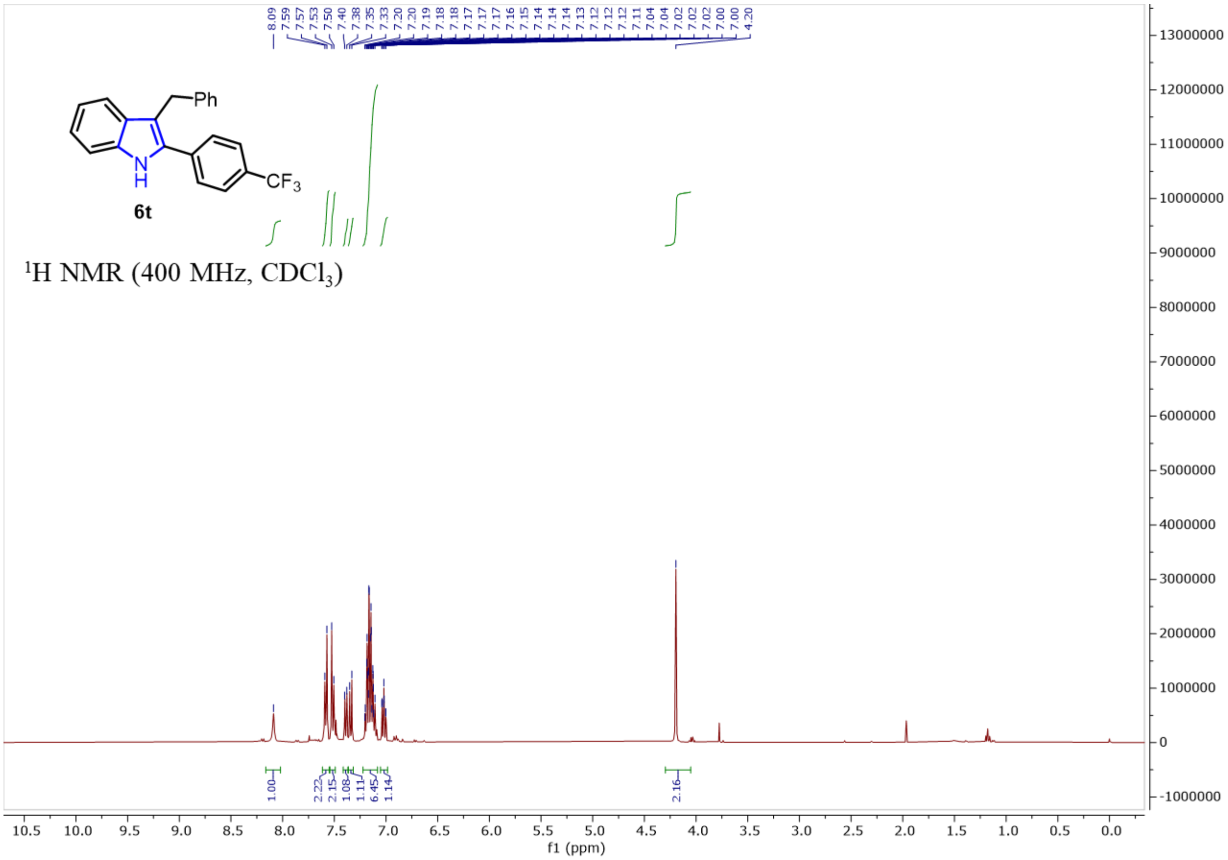


6r

^{13}C NMR (76 MHz, $CDCl_3$)

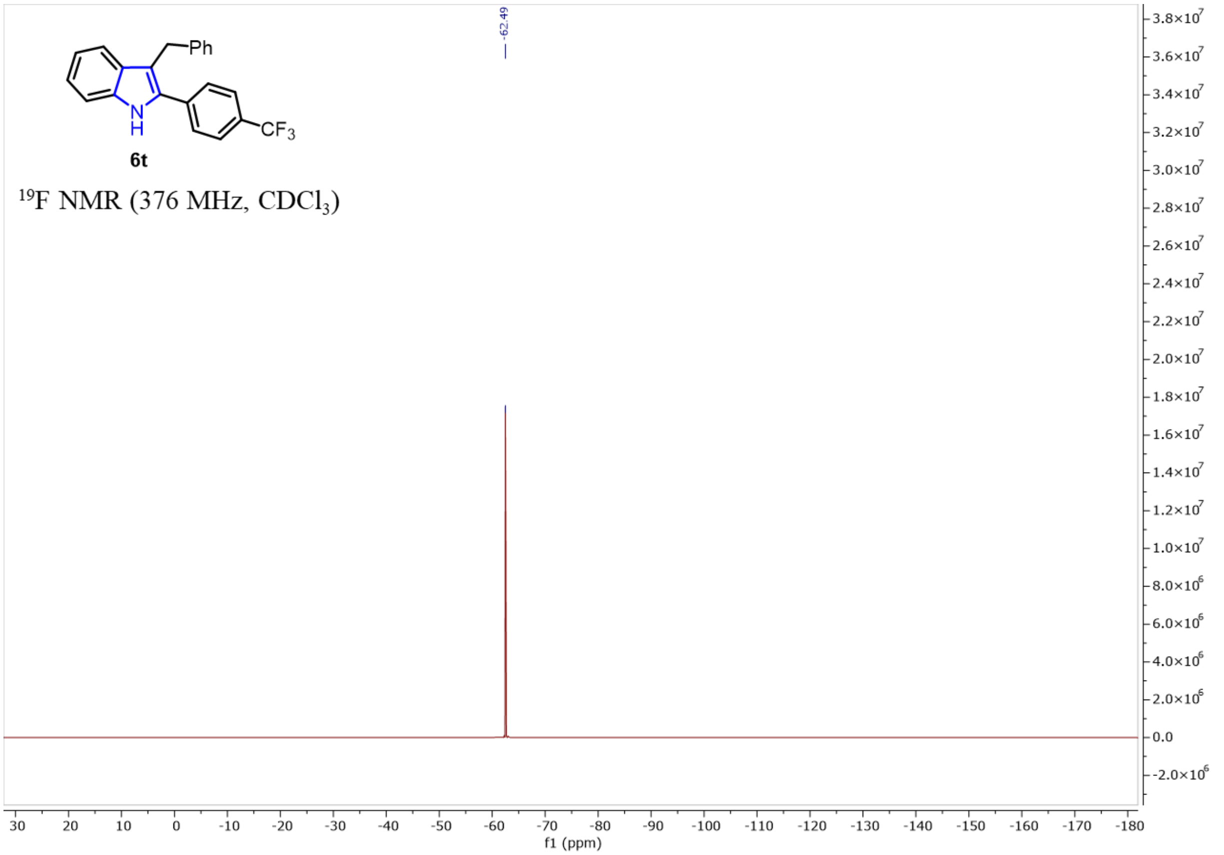

6s
^{1}H NMR (300 MHz, CDCl$_3$)
8.16 8.15 8.14 8.14 8.13 8.12 8.12 7.67 7.67 7.66 7.64 7.64 7.63 7.62 7.62 7.62 7.61 7.61 7.40 7.40 7.40 7.38 7.37 7.37 7.27 7.27 7.26 7.25 7.25 7.24 7.22 7.22 7.19 7.19 7.17 7.17 7.17 3.96
2.51
2.92 3.02 1.00 1.30 1.00 3.25 3.06
f1 (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
CH3
N
H
COOCH3


6s
^{13}C NMR (76 MHz, CDCl$_3$)
166.90
137.75 136.20 132.77 130.14 129.96 128.49 127.24 123.08 119.81 119.30 110.87 110.58
52.25
9.94
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
CH3
N
H
COOCH3



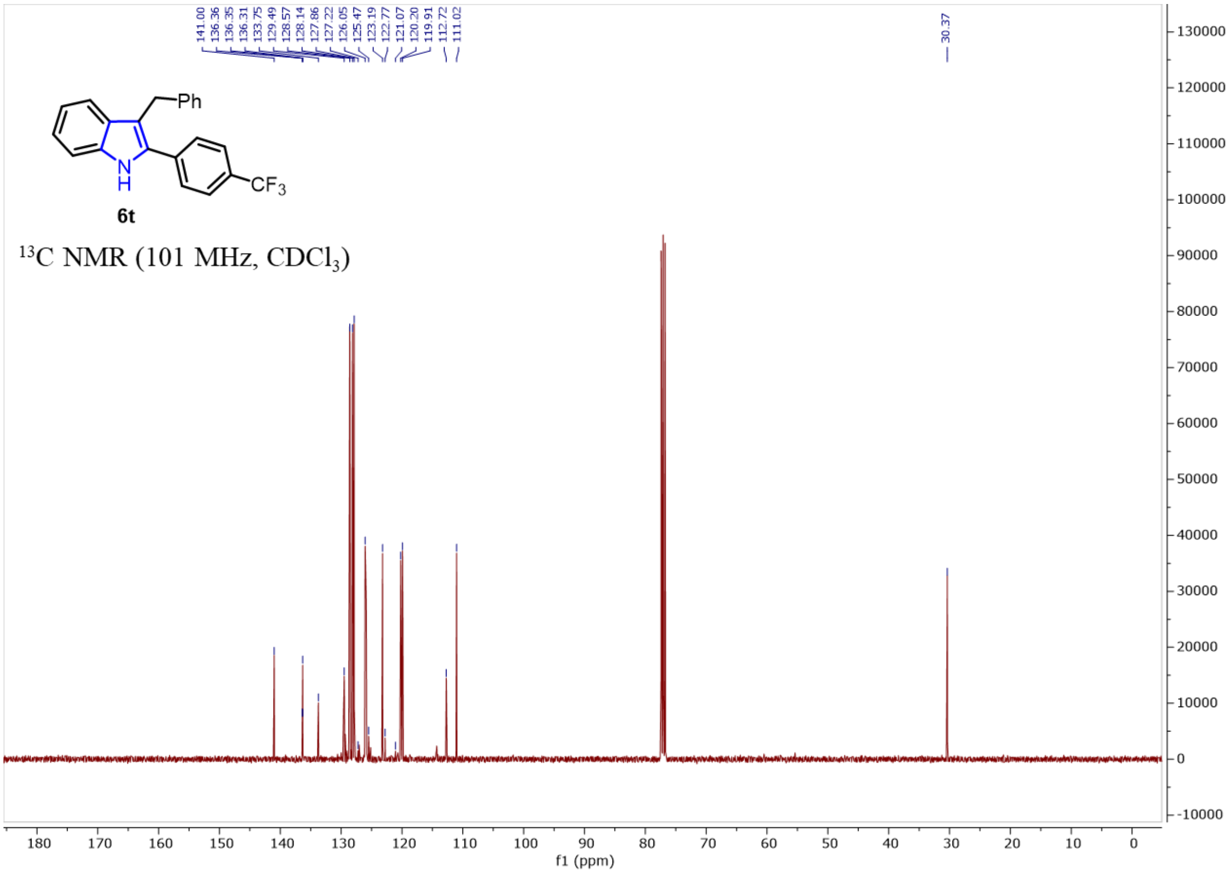
6t

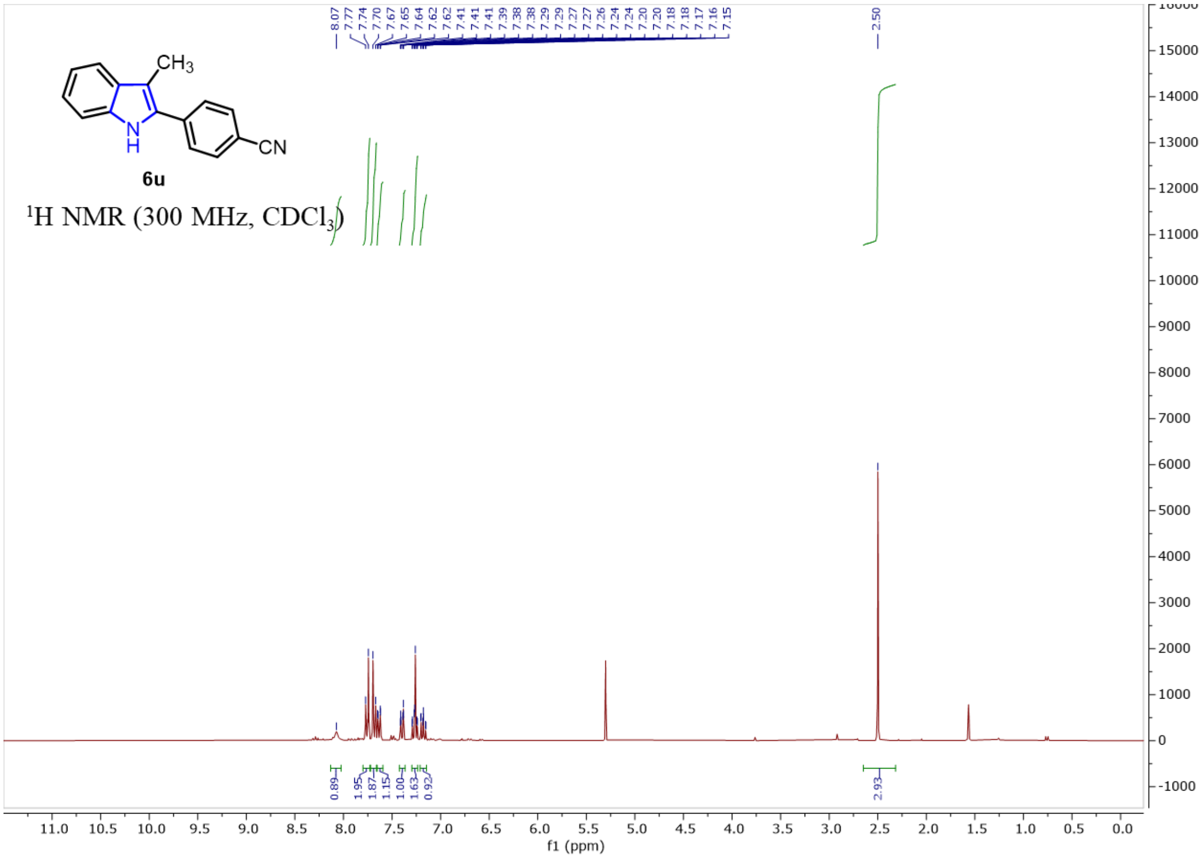
^{1}H NMR (400 MHz, CDCl$_3$)

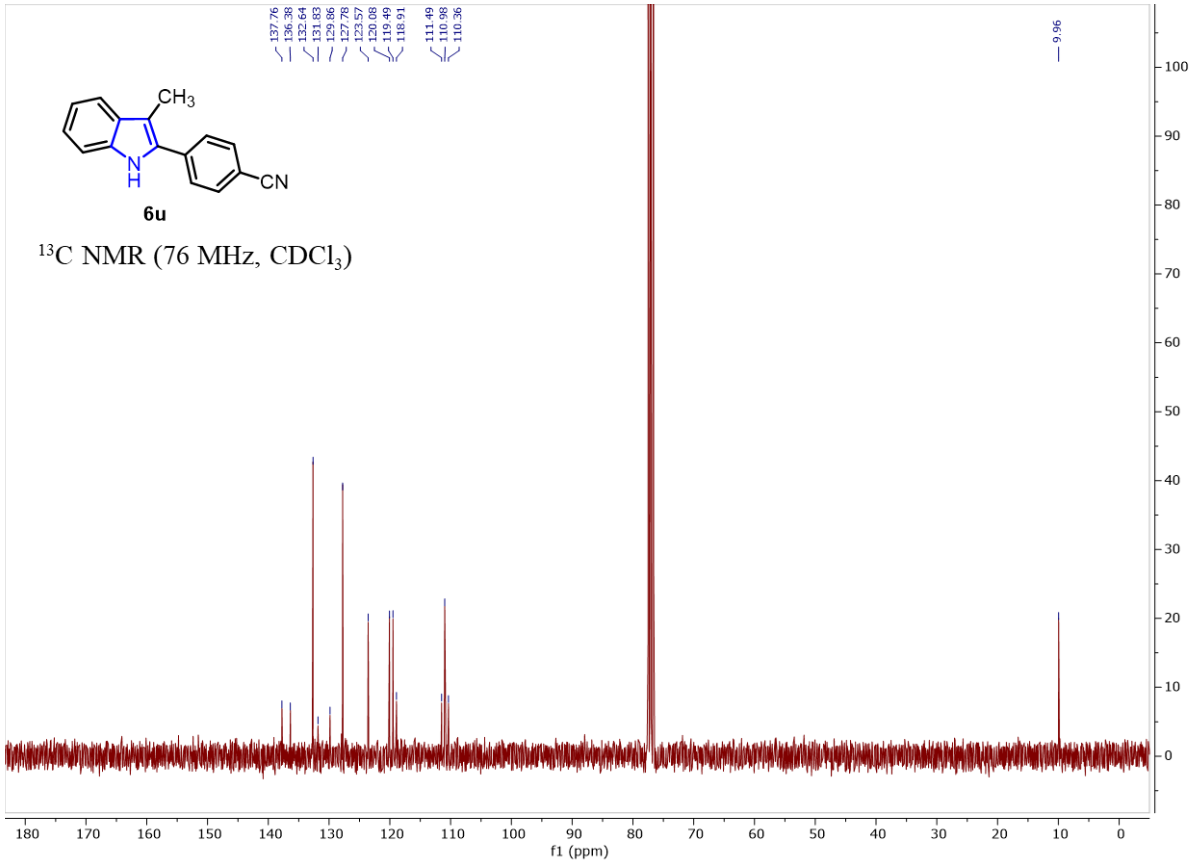


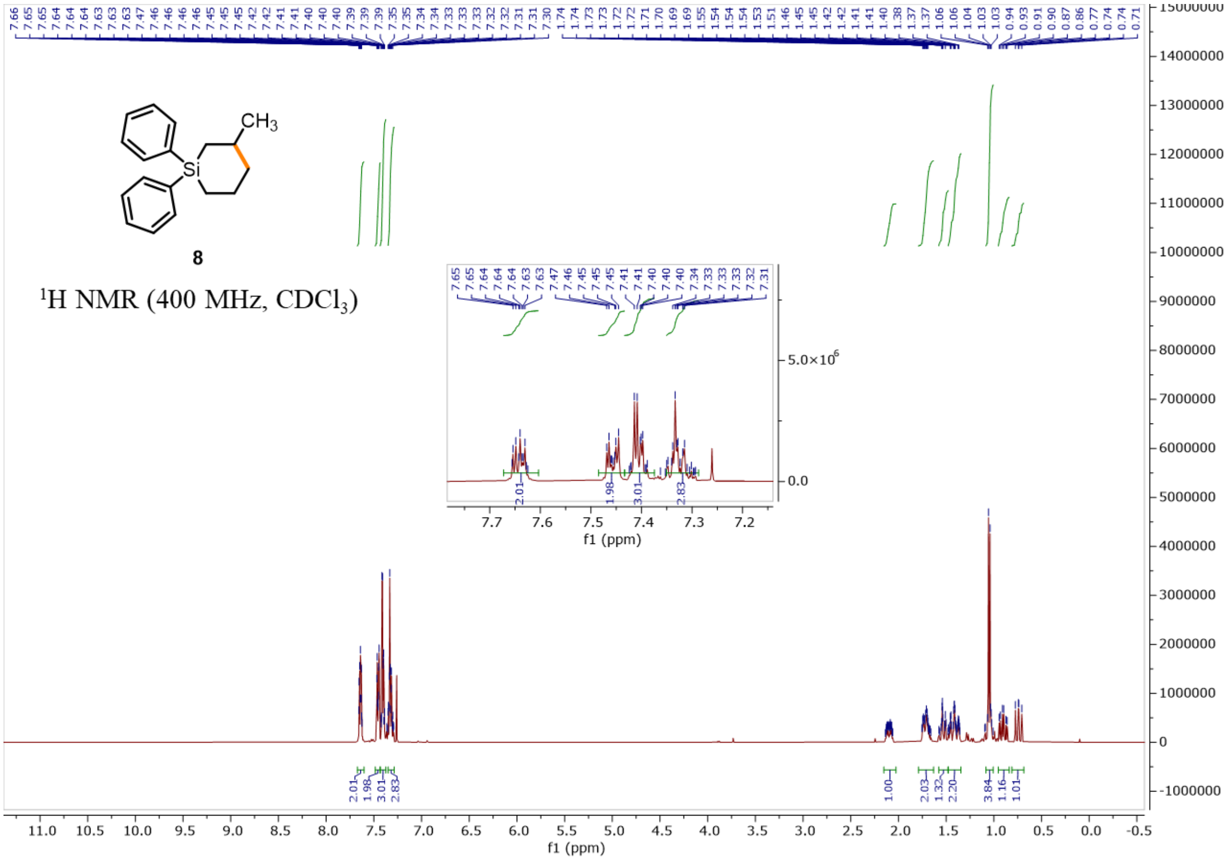
6t

^{19}F NMR (376 MHz, CDCl$_3$)


141.00
136.36
136.35
136.31
133.75
129.49
128.57
128.14
127.86
127.22
126.05
125.47
123.19
122.77
121.07
120.20
119.91
112.72
111.02
30.37
Ph
N
H
CF$_3$
6t
^{13}C NMR (101 MHz, CDCl$_3$)
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

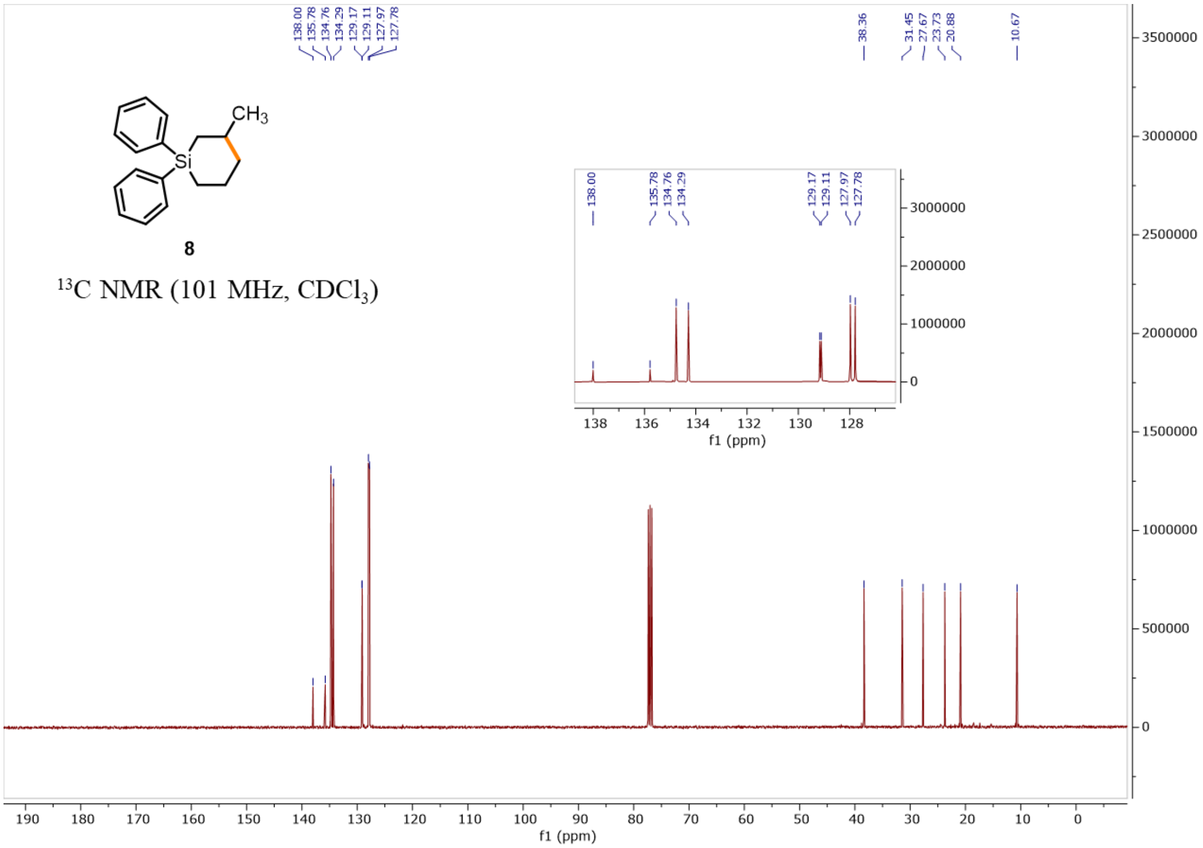

CH3
N
H
CN
6u
1H NMR (300 MHz, CDCl3)
8.07
7.77
7.74
7.70
7.67
7.65
7.64
7.62
7.62
7.41
7.41
7.41
7.39
7.38
7.38
7.29
7.29
7.27
7.27
7.26
7.24
7.24
7.20
7.20
7.18
7.18
7.17
7.16
7.15
2.50
0.89
1.95
1.87
1.15
1.00
1.63
0.92
2.93
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


137.76
136.38
132.64
131.83
129.86
127.78
123.57
120.08
119.49
118.91
111.49
110.98
110.36
9.96
CH3
N
H
CN
6u
13C NMR (76 MHz, CDCl3)
100
90
80
70
60
50
40
30
20
10
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



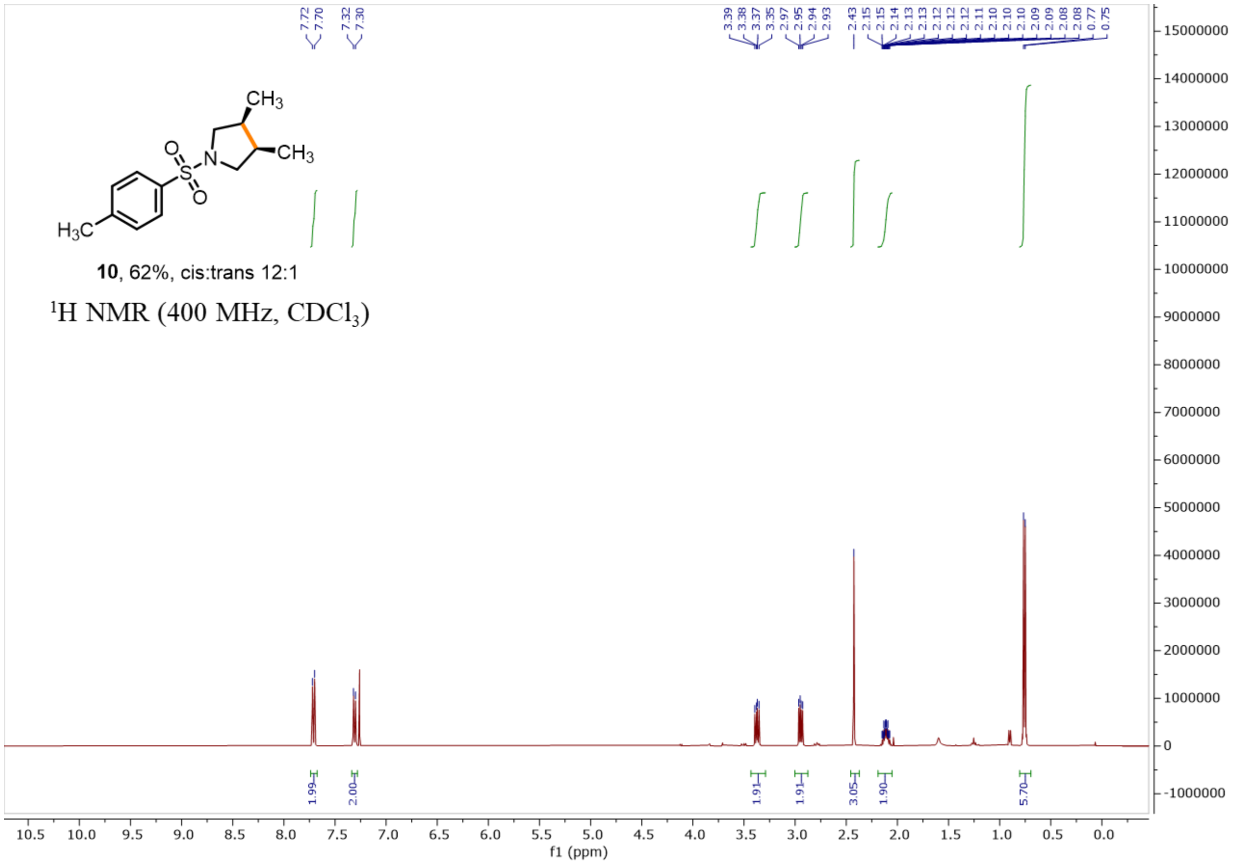
8

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



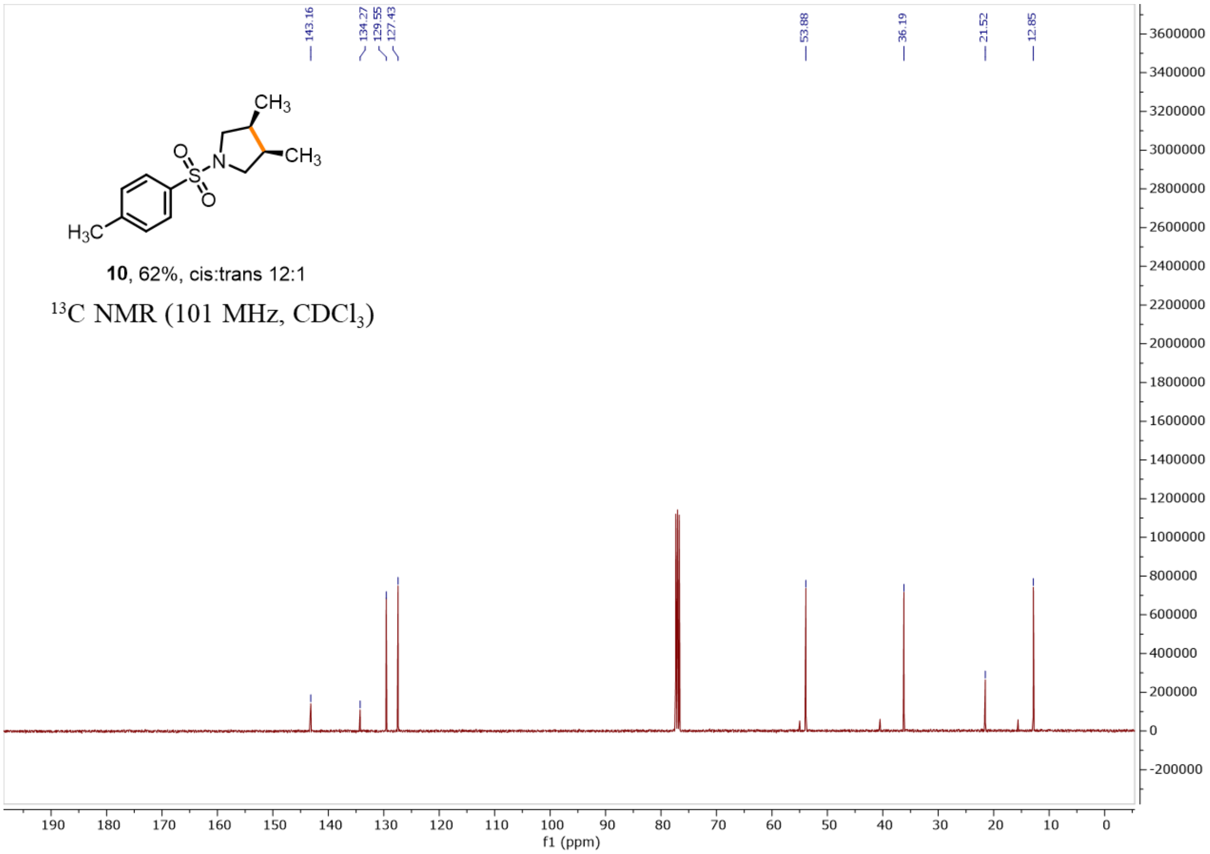
8

^{13}C NMR (101 MHz, CDCl$_3$)



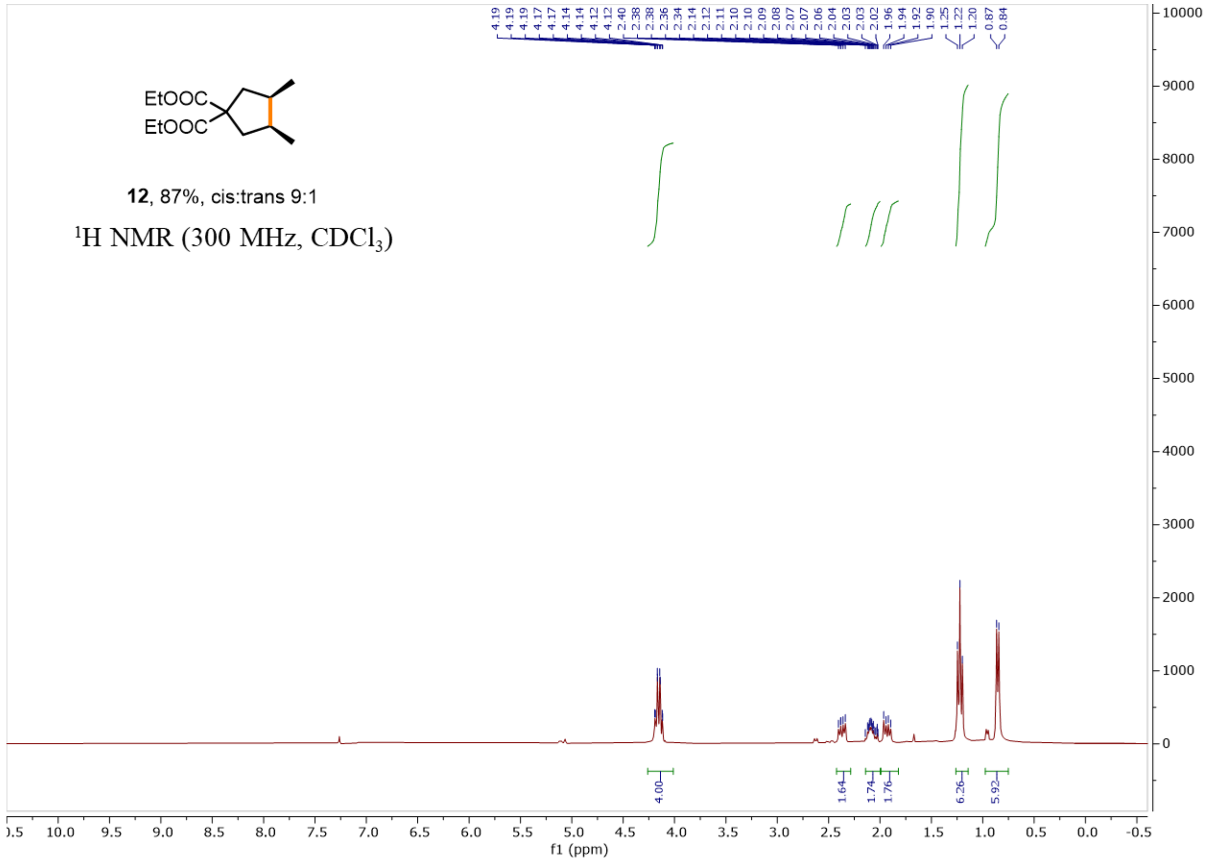
10, 62%, cis:trans 12:1

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



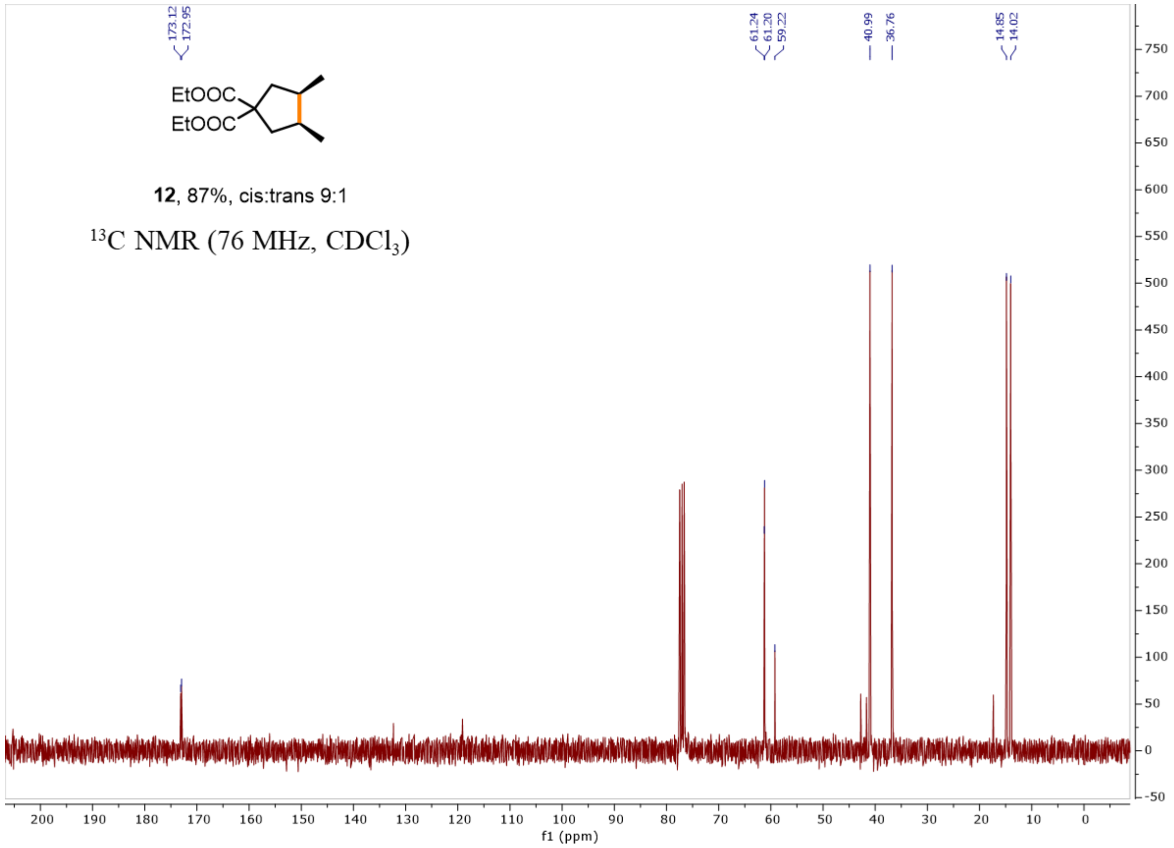
10, 62%, cis:trans 12:1

^{13}C NMR (101 MHz, $CDCl_3$)



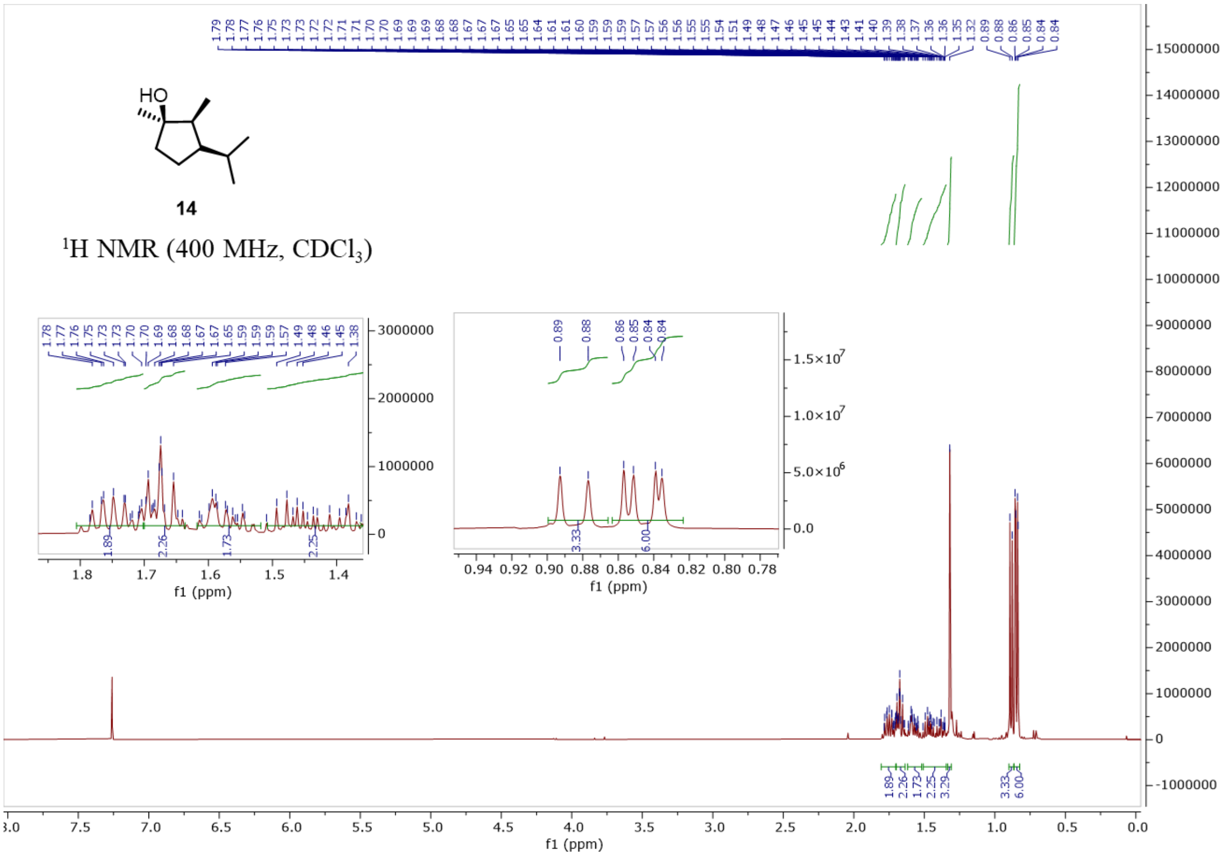
12, 87%, cis:trans 9:1

^{1}H NMR (300 MHz, $CDCl_3$)

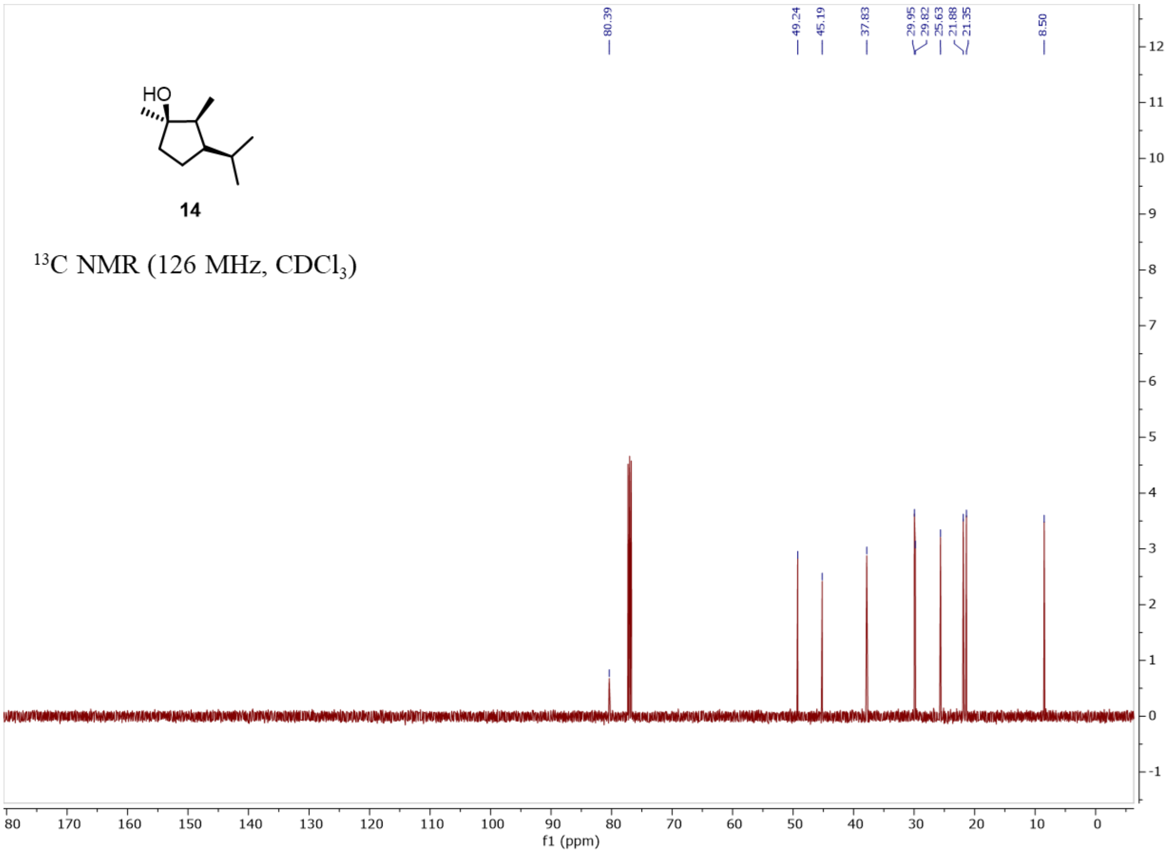


12, 87%, cis:trans 9:1

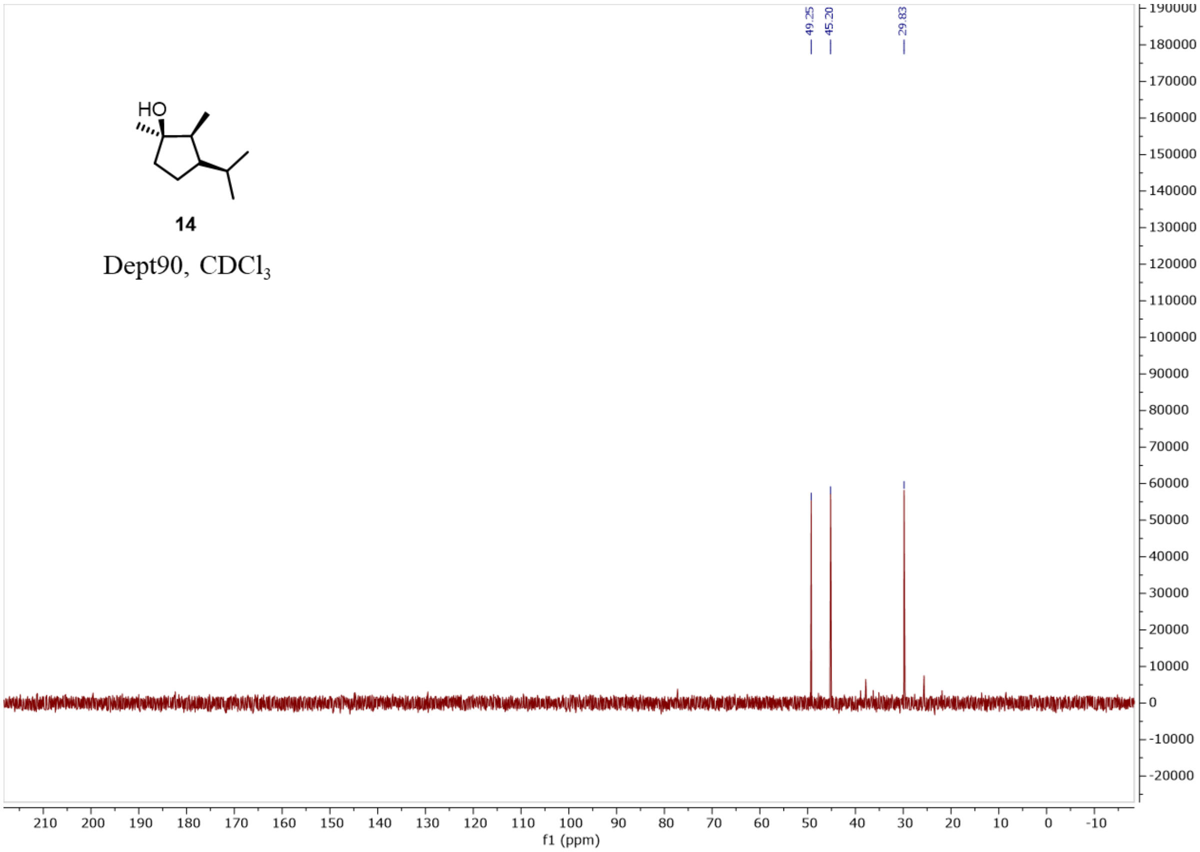
^{13}C NMR (76 MHz, $CDCl_3$)


14

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

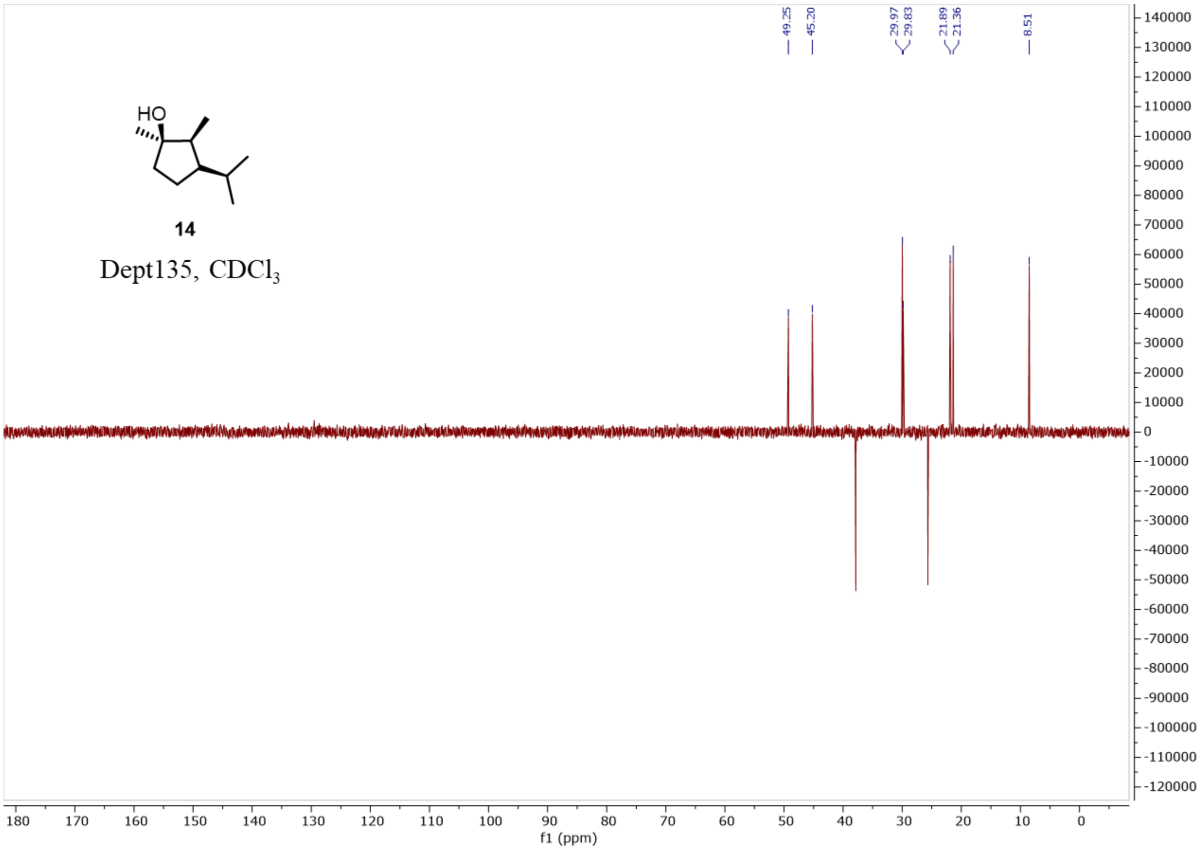

14

^{13}C NMR (126 MHz, CDCl$_3$)



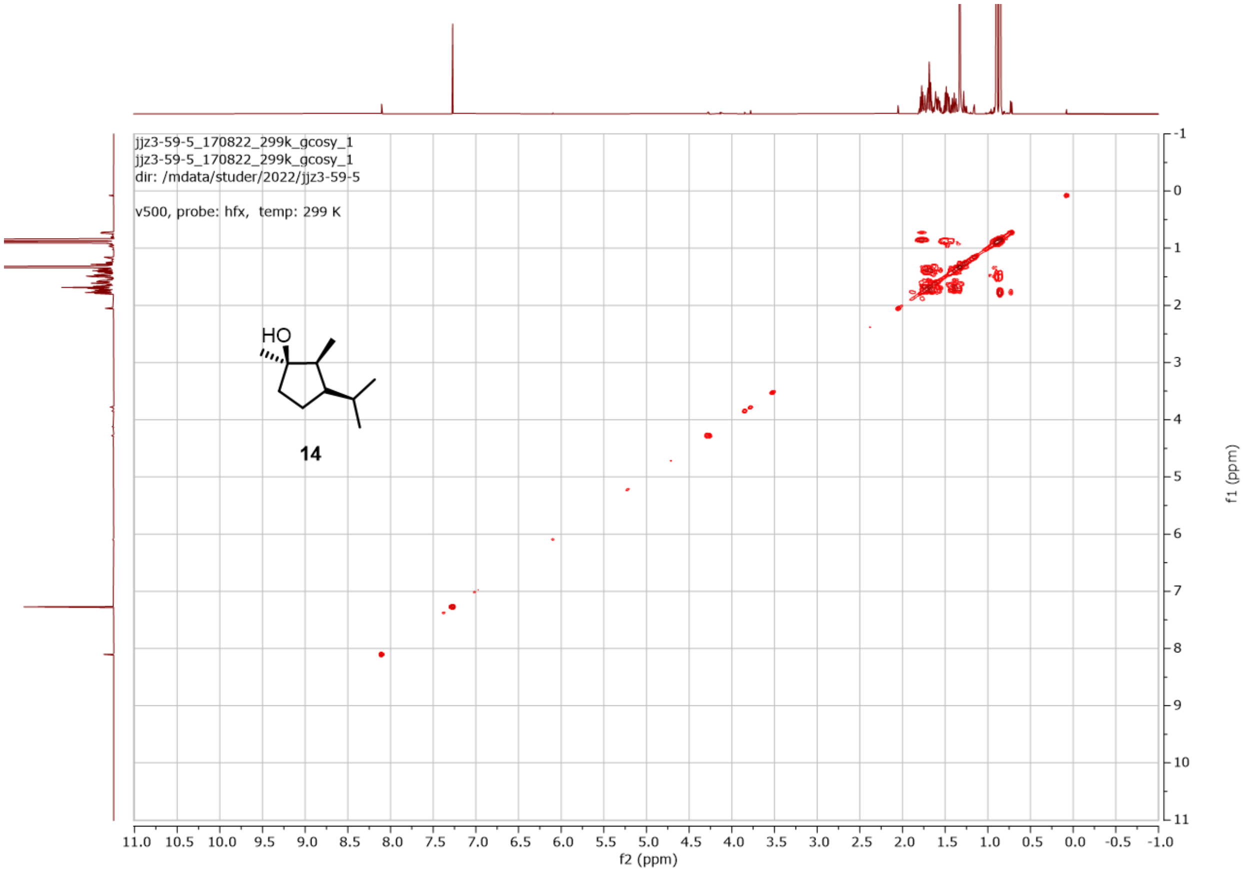
14

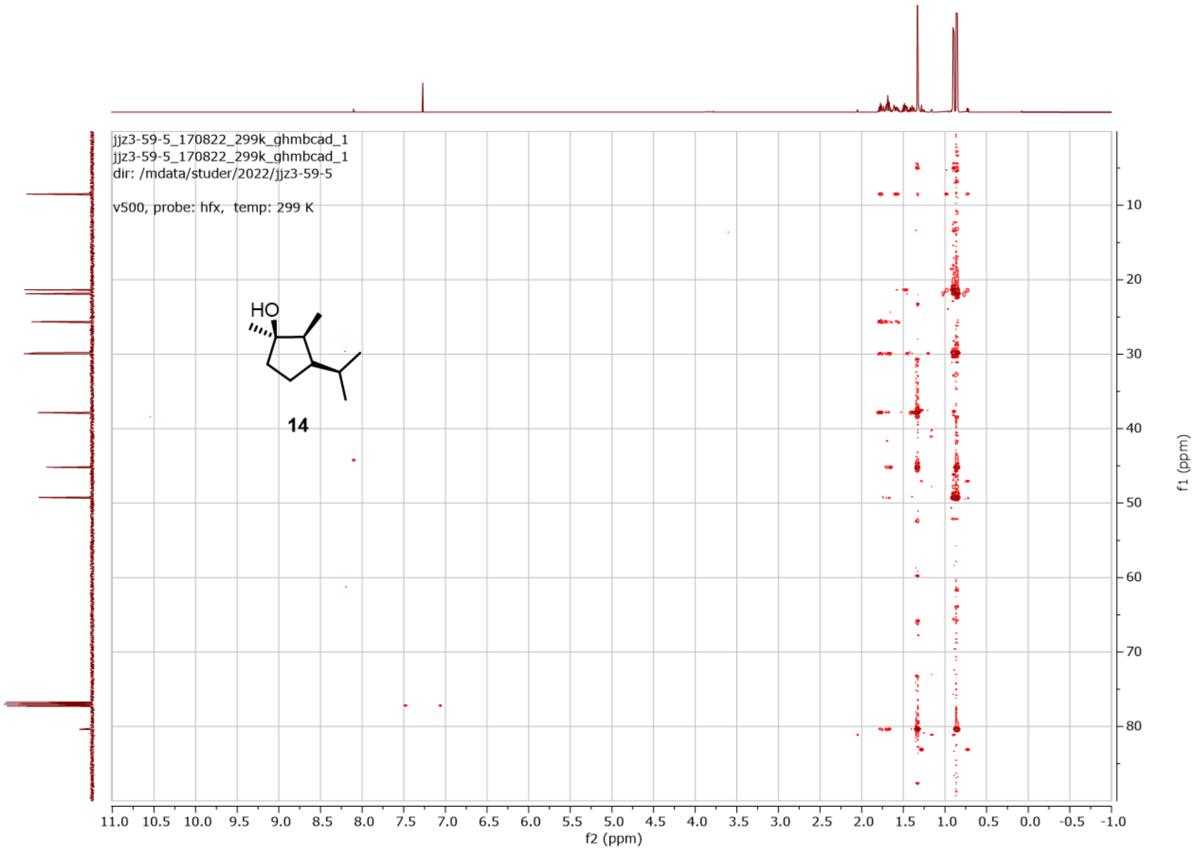
Dept90, CDCl$_3$

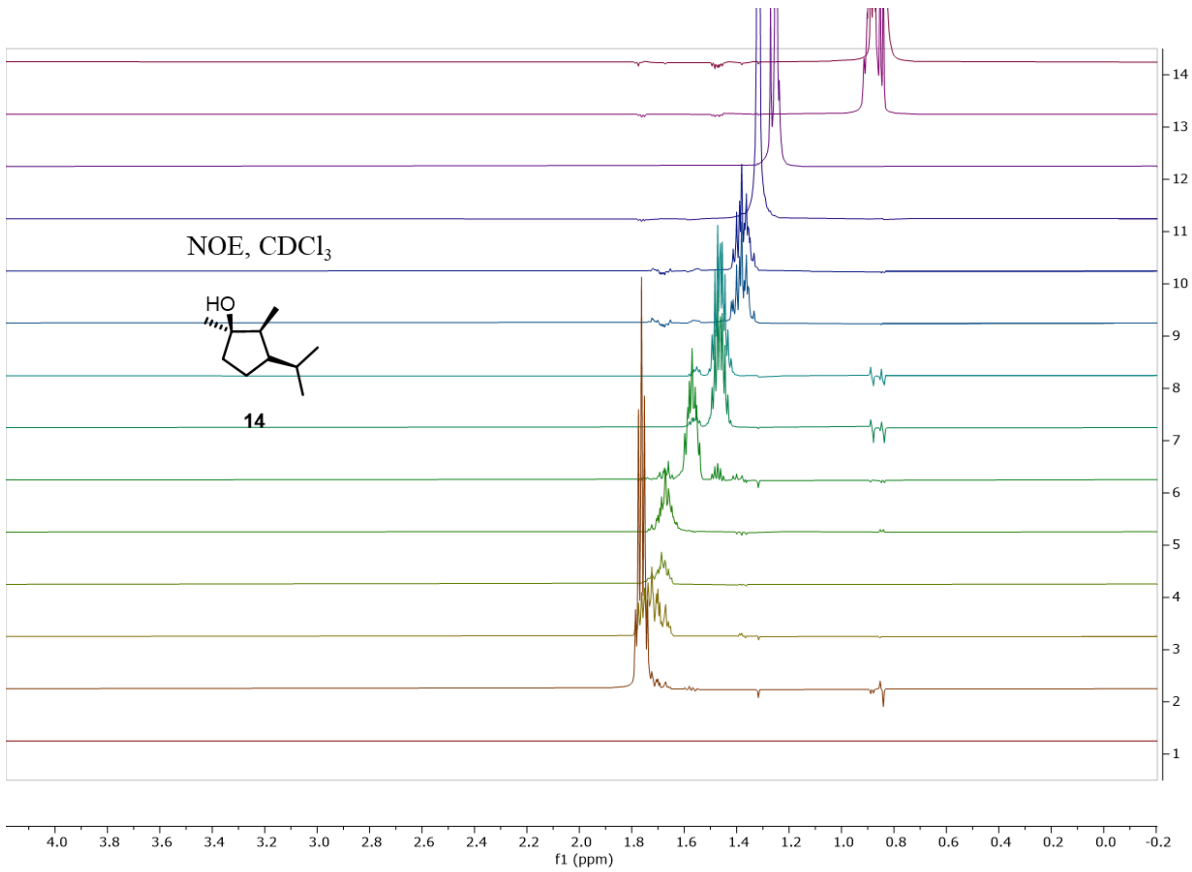


14

Dept135, CDCl$_3$


jjz3-59-5_170822_299k_gcosy_1
jjz3-59-5_170822_299k_gcosy_1
dir: /mdata/studer/2022/jjz3-59-5
v500, probe: hfx, temp: 299 K
HO
14
f2 (ppm)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
-1 0 1 2 3 4 5 6 7 8 9 10 11


jjz3-59-5_170822_299k_ghmbcad_1
jjz3-59-5_170822_299k_ghmbcad_1
dir: /mdata/studer/2022/jjz3-59-5
v500, probe: hfx, temp: 299 K
HO
14
f2 (ppm)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
10 20 30 40 50 60 70 80


NOE, $CDCl_3$
HO
14
14
13
12
11
10
9
8
7
6
5
4
3
2
1
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
f1 (ppm)

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