Supporting Information

Photochemical Organocatalytic Benzylation of Allylic C-H Bonds

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A. General Information

The NMR spectra were recorded at 300 MHz, 400 MHz and 500 MHz for ^{1}H or at 75 MHz, 101 MHz and 126 MHz for ^{13}C, 376 MHz for ^{19}F, 162 MHz for ^{31}P, respectively. The chemical shifts (δ) for ^{1}H and $^{13}C\{^{1}H\}$ are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, 77.00 ppm ^{13}C NMR). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad signal.

High-resolution mass spectra (HRMS) were obtained from the ICIQ High-Resolution Mass Spectrometry Unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization or atmospheric pressure chemical ionization. UV-vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D2 and W light sources.

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General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased. Anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using flash column chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used, using UV light as the visualizing agent and either phosphomolybdic acid in EtOH, dinitrophenylhydrazine in EtOH/H_2O, *p*-anisaldehyde or basic aqueous potassium permanganate ($KMnO_4$), and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator (*in vacuo* at 40 ºC, ~5 mbar).

Determination of Diastereomeric Ratio. The diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture through integration of diagnostic signals.

Materials: Commercial grade reagents and solvents were purchased at the highest commercial quality from Sigma Aldrich, Fluka, Acros Organics, Fluorochem, or Alfa Aesar and used as received, unless otherwise stated. Thiol catalysts **C1**, **C2** and **C3** are commercially available. The thiophosphoric acid **C4** was prepared according to a reported procedure.[1]

B. Moderately Successful and Unsuccessful Substrates

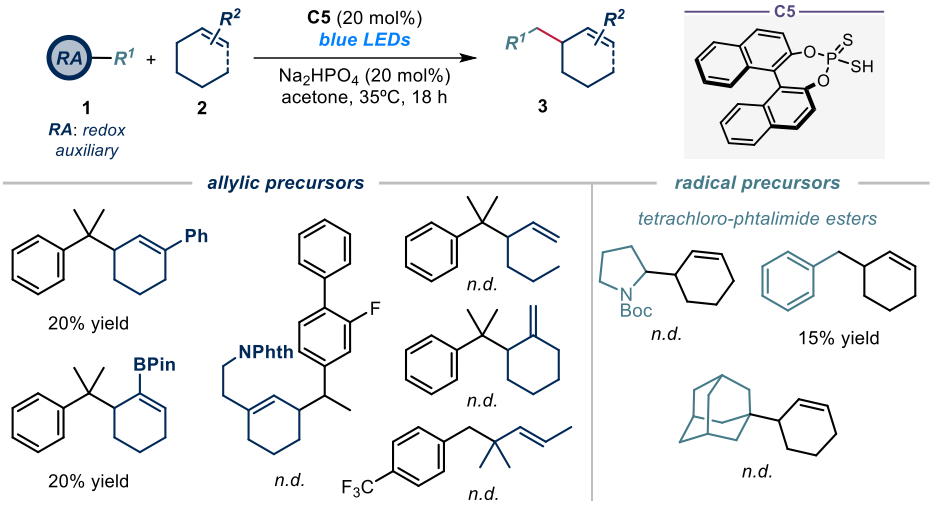
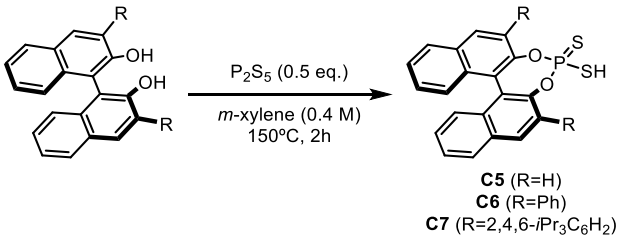


Figure S1. Moderately successful and unsuccessful substrates in the direct allylic benzylation. *n.d.*: not detected.

C. Synthesis of the Substrates

C.1 Synthesis of Catalysts C5-7

Catalysts **C5-7** were prepared following a reported procedure,[2] as described below.

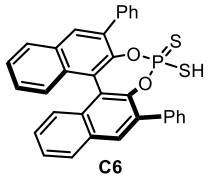


(11bS)-4-mercaptodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (C5): A flame dried flask was charged with (*S*)-1,1'-bi-2-naphtol (2.29 g, 8.0 mmol, 1.0 equiv), P_2S_5 (889 mg, 4.0 mmol, 0.5 equiv), and anhydrous *m*-xylene (20 mL). The flask was equipped with a condenser and placed in an oil-bath preheated to 150 ºC. The progress of the reaction was monitored by disappearance of the phenolic protons, as inferred by ^{1}H NMR analysis of the crude mixture. After 2 h, the reaction was completed and the mixture was cooled to ambient temperature. The solution was decanted into a flame-dried 100 mL flask and the solvent was evaporated in vacuo. The crude product was dissolved in anhydrous CH_2Cl_2 (5 mL) and treated with hexanes (50 mL). At this point, a fine precipitate was observed. The solvent was then partially evaporated until about 2 to 3 mL solvent was left. The precipitate was then collected by filtration and washed with ice-cold hexanes to afford **C5** (2.23g, 5.86 mmol, 73% yield) as a white powder that displayed spectroscopic data consistent with those reported previously.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 8.00 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.60 (dd, *J* = 8.8, 1.4 Hz, 2H), 7.54 (ddt, *J* = 8.0, 6.8, 1.1 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.36 (ddd, *J* = 8.4, 6.7, 1.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 132.4, 132.0, 131.1, 128.6, 127.2, 126.9, 126.1, 122.6, 121.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 100.24.



C6

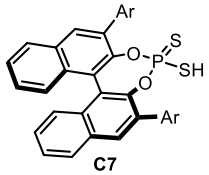
(11bS)-4-mercapto-2,6-diphenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (C6)

Prepared according to the reported procedure using (S)-3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diol.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 2H), 8.06 – 8.02 (m, 2H), 7.75 – 7.71 (m, 4H), 7.58 (dt, *J* = 7.0, 1.0 Hz, 2H), 7.52 – 7.42 (m, 8H), 7.38 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 131.4, 130.2, 129.6, 128.9, 128.6, 128.3, 127.8, 127.1, 126.7, 126.3.

^{31}P NMR (202 MHz, $CDCl_3$) δ 96.2.



C7
(Ar=2,4,6-*i*Pr$_3$C$_6$H$_2$)

(2r,11bS)-4-mercapto-2,6-bis(2,4,6-triisopropylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (C7)

Prepared according to the reported procedure using (1'S,3r)-3,3'-bis(2,4,6-triisopropylphenyl)-[1,1'-binaphthalene]-2,2'-diol.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.25 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 7.20 – 7.12 (m, 4H), 7.04 (d, *J* = 1.8 Hz, 2H), 3.18 (s, 2H), 2.87 (p, *J* = 6.9 Hz, 2H), 2.72 (p, *J* = 6.7 Hz, 2H), 1.33 (d, *J* = 6.7 Hz, 6H), 1.26 – 1.23 (m, 12H), 1.21 – 1.16 (m, 12H), 0.87 (d, *J* = 6.8 Hz, 6H).

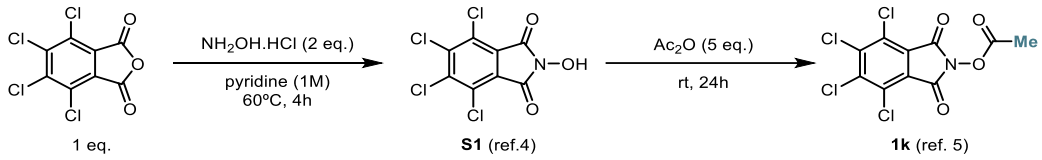
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.4, 148.1, 133.0, 132.3, 132.1, 130.6, 128.1, 127.2, 125.8, 125.1, 123.5, 121.6, 120.1, 34.2, 30.9, 30.8, 27.3, 24.9, 24.1, 24.1, 24.0, 23.6.

^{31}P NMR (202 MHz, $CDCl_3$) δ 128.0.

C.2 Synthesis of Tetrachloro-Phthalimide Esters 1

C.2.1 Synthesis of 1k

Tetrachloro-phthalimide ester **1k** was synthesized from N-hydroxytetrachlorophthalimide **S1**,[4] following reported procedures,[5] as depicted in Scheme S1.



Scheme S1. Synthesis of **S1** and **1k**.

C.2.2 General Procedure for the Synthesis of 1

Tetrachloro-phthalimide esters **1a-j**, and **1l-s** were prepared from **S1**, using a typical procedure described below. Figure S2 depicts the general synthesis of **1**, and the substrates that were previously reported. [6,7,8,9,10]

A round-bottom flask was charged with carboxylic acid (1.0 equiv), N-hydroxy-tetrachlorophthalimide **S1** (1.0 equiv.) and DMAP (0.1 equiv.). Dichloromethane was added (0.1M), and the mixture was stirred vigorously. DIC (1.1 equiv.) was then added slowly, and the mixture was allowed to stir overnight, or until the acid was fully consumed as determined by TLC. The mixture was filtered over Celite and rinsed with additional CH_2Cl_2. The solvent was removed under reduced pressure, and purification by column chromatography (and recrystallization, if necessary) afforded the corresponding tetrachloro-phthalimide esters **1**.

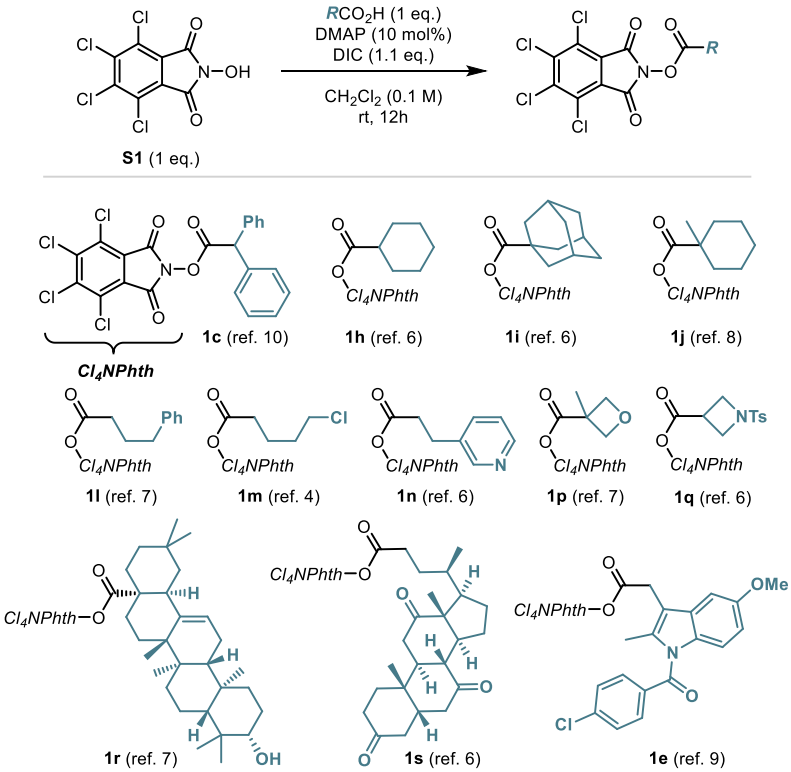
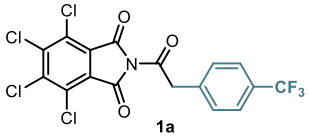


Figure S2. Previously reported tetrachloro-phthalimide esters **1**.

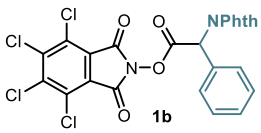


1a

4,5,6,7-tetrachloro-2-(2-(4-(trifluoromethyl)phenyl)acetyl)isoindoline-1,3-dione (1a)

Prepared according to the general procedure using 4-(Trifluoromethyl)phenylacetic acid (612 mg, 3.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 95:5 hexanes/EtOAc) to afford product **1a** as a white solid (728 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 4.06 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 157.3, 141.2, 135.1, 130.6, 129.7, 125.9 (q, *J* = 3.8 Hz), 124.6, 123.9 (q, *J* = 272.3 Hz), 37.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8.
HRMS (ESI) Calculated for $C_{18}H_{10}Cl_4F_3NNaO_5$ [M+MeOH+Na]$^+$: 539.9157, found: 539.9148.

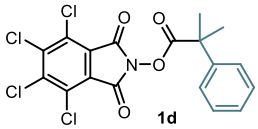


1b

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (1b)

Prepared according to the general procedure using 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetic acid (1.40 g, 5.00 mmol). The crude mixture was purified by washing with cold acetone to afford product **1b** as a white solid (1.80 g, 64% yield).

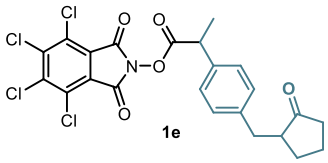
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.76 – 7.70 (m, 4H), 7.46 – 7.38 (m, 3H), 6.47 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 164.8, 134.5, 132.4, 131.6, 129.9, 129.4, 128.9, 128.6, 123.9, 123.7, 54.0.HRMS (ESI) Calculated for $C_{25}H_{14}Cl_4N_2NaO_7$ [M+MeOH+Na]$^+$: 616.9447, found: 616.9444.



4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 2-methyl-2-phenylpropanoate (1d)

Prepared according to the general procedure using 2-methyl-2-phenylpropanoic acid (500 mg, 3.05 mmol). The crude mixture was purified by column chromatography (SiO_2, 98:2 hexanes/EtOAc) to afford product **1d** as a white solid (728 mg, 54% yield).

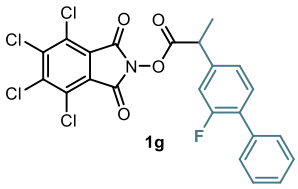
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 4H), 7.36 – 7.30 (m, 1H), 1.78 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 130.4, 128.8, 127.5, 125.7, 124.8, 46.3, 26.8.
HRMS (ESI) Calculated for $C_{19}H_{15}Cl_4NNaO_5$ [M+MeOH+Na]$^+$: 499.9597, found: 499.9598.



4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (1f)

Prepared according to the general procedure using Loxoprofen (985 mg, 4.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 98:2 hexanes/EtOAc) to afford product **1e** as a white solid (1.22 g, 58% yield).

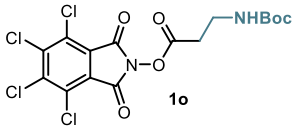
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 4.12 (q, *J* = 7.3 Hz, 1H), 3.18 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.56 (ddd, *J* = 14.0, 9.5, 1.5 Hz, 1H), 2.43 – 2.32 (m, 2H), 2.21 – hb2.09 (m, 2H), 2.00 (dddd, *J* = 12.6, 9.0, 6.4, 2.9 Hz, 1H), 1.85 – 1.72 (m, 1H), 1.68 (d, *J* = 7.2 Hz, 3H), 1.64 – 1.53 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.0, 139.8, 135.8, 130.5, 129.5, 127.6, 124.7, 50.9, 42.5, 38.2, 35.2, 29.2, 20.5, 18.9, 18.9.
HRMS (ESI) Calculated for $C_{24}H_{21}Cl_4NNaO_6$ [M+MeOH+Na]$^+$: 582.0015, found: 582.0025.



4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (1g)

Prepared according to the general procedure using Flurbiprofen (366 mg, 1.5 mmol). The crude mixture was purified by column chromatography (SiO_2, 95:5 hexanes/EtOAc) to afford product **1f** as a white solid (416 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dt, *J* = 8.2, 1.5 Hz, 2H), 7.54 – 7.45 (m, 3H), 7.44 – 7.38 (m, 1H), 7.31 – 7.20 (m, 3H), 4.18 (q, *J* = 7.0 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 141.1, 139.0, 138.9, 135.2, 131.3, 131.3, 130.5, 129.0, 129.0, 128.8, 128.5, 127.8, 124.7, 123.6, 123.5, 115.6, 115.3, 42.4, 18.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.8.
HRMS (ESI) Calculated for $C_{24}H_{16}Cl_4FNNaO_5$ [M+MeOH+Na]$^+$: 579.9659, found: 579.9668.



4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 3-((tert-butoxycarbonyl)amino)propanoate (1o)

Prepared according to the general procedure using NBoc-Alanine (568 mg, 3.00 mmol). The crude mixture was purified by washing with cold acetone to afford product **1o** as a yellow solid (841 g, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (s, 1H).3.55 (q, *J* = 6.1 Hz, 2H), 2.92 (t, *J* = 6.0 Hz, 2H), 1.45 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 155.8, 141.1, 130.6, 124.6, 36.1, 32.0, 28.4, 28.3.

HRMS (ESI) Calculated for $C_{17}H_{18}Cl_4N_2NaO_7$ $[M+MeOH+Na]^+$: 524.9760, found: 524.9755.

C.3 Synthesis of Pyridinium Salts 4

Pyridinium salts **4** were synthesized following reported procedures (Figure S3).[1112131415]

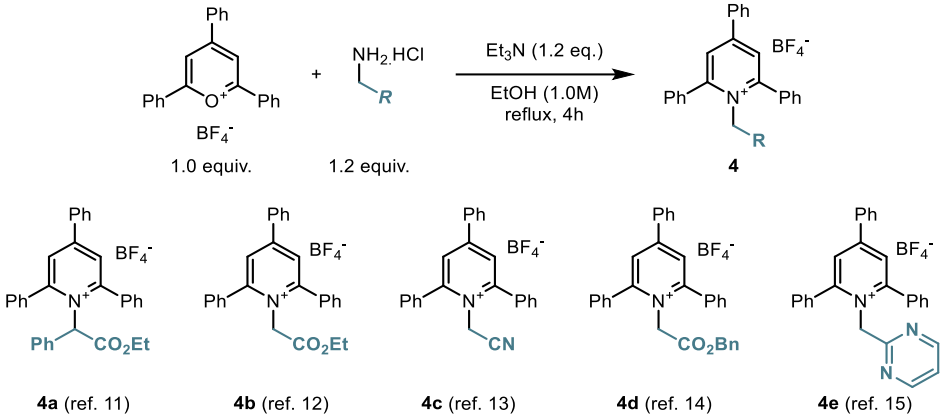
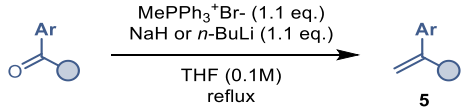


Figure S3. Pyridinium salts **4** synthetized according to reported procedures.

C.4 Synthesis of Styrene Derivatives 5

C.4.1 General Procedure for the Wittig Reaction

Alkenes **5b, 5h-i, and 5k-l** were prepared from the corresponding ketones, using Wittig reactions as detailed below. The spectroscopic data of **5b**, **5h**, **5i**, and **5k** were persistent with those reported previously (Figure S4).[16,17,18,19]



An oven-dried round-bottomed flask placed under an atmosphere of argon was charged with methyltriphenylphosphonium bromide (1.1 equiv) in dry THF (0.1 M). The suspension was cooled down to 0ºC and sodium hydride (1.1 equiv, 60% dispersion in mineral oil) or *n*-butyllithium (1.1 equiv., 2.5 M in hexanes) was added slowly. The resulting mixture was stirred at 0ºC for 30 min before adding dropwise a solution of the ketone (1.0 equiv) in dry THF. The reaction was stirred under reflux until complete conversion of the ketone was observed by TLC (typically overnight). The reaction was quenched by addition of water, and the organic phase extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to afford the crude compounds. The pure alkenes **5** were obtained by column chromatography on silica gel.

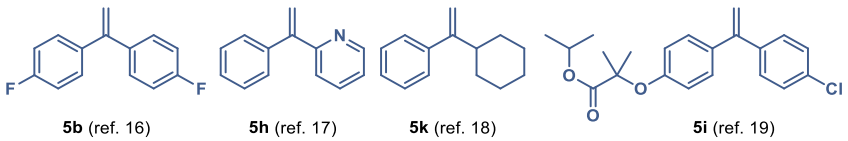
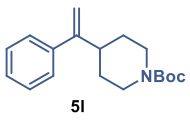


Figure S4. Previously reported alkenes **5** prepared using a Wittig reaction.



Tert-butyl 4-(1-phenylvinyl)piperidine-1-carboxylate (5l)

Prepared according to the General Procedure using tert-butyl 4-benzoylpiperidine-1-carboxylate (579 mg, 2.0 mmol), sodium hydride (88.0

mg, 2.2 mmol), and methyltriphenylphosphonium bromide (786 mg, 2.2 mmol) overnight. The crude mixture was purified by column chromatography (SiO_2, 90:10 pentane/Et_2O) to afford product **5l** as a colorless oil (246 mg, 43% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 5.19 (d, *J* = 0.9 Hz, 1H), 5.03 (t, *J* = 1.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.76 (t, *J* = 12.8 Hz, 2H), 2.58 (t, *J* = 11.8 Hz, 1H), 1.79 (d, *J* = 13.4 Hz, 2H), 1.47 (s, 9H), 1.44 – 1.33 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.84, 153.05, 142.18, 128.29, 127.31, 126.65, 111.28, 79.36, 40.81, 31.46, 28.48.

HRMS (ESI) Calculated for $C_{18}H_{25}NNaO_2$ $[M+Na]^+$: 310.1777, found: 310.1776.

C.4.2 Synthesis of Alkenes 5c-g

Alkenes **5c-g** were prepared following a reported procedure,[20] as depicted in Figure S5.

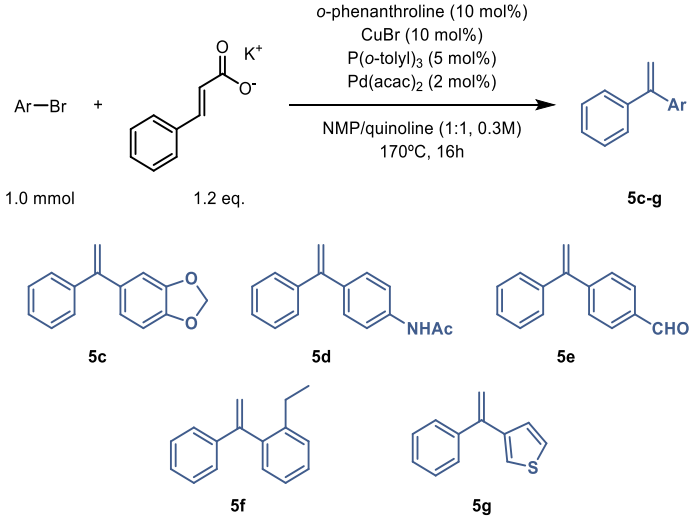
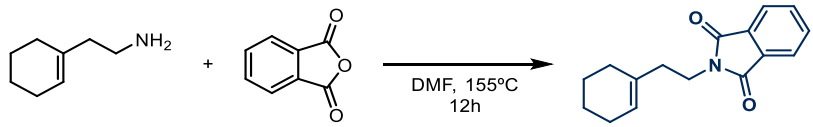


Figure S5. Alkenes **5** synthetized according to a reported procedure.

C.4.3 Synthesis of 2h

2h was synthesized adapting a procedure from the literature.[21]



Phthalic anhydride (1.78 g, 1.5 equiv.) was added to a solution of 2-(1-Cyclohexenyl)ethylamine (1.0 mL, 8.0 mmol, 1.0 equiv.) in DMF (0.5 M) and refluxed at 155° C for 12 hours. The reaction was cooled to room temperature and poured into 50 mL of 1M HCl and extracted with Et_2O. The crude mixture was purified by column chromatography (SiO2, 90:10 pentane/Et_2O) to afford product **2h** as white-off flakes (1.76 g, 86% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.73 – 7.68 (m, 2H), 5.38 (tdd, *J* = 4.8, 2.6, 1.4 Hz, 1H), 3.79 (dd, *J* = 7.5, 6.7 Hz, 2H), 2.31 (td, *J* = 7.0, 1.3 Hz, 2H), 2.05 (ddt, *J* = 8.5, 6.0, 2.1 Hz, 2H), 1.88 (ddt, *J* = 7.4, 3.6, 1.3 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.52 (ddt, *J* = 8.7, 6.2, 2.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.27, 134.25, 133.78, 132.19, 123.94, 123.07, 36.70, 36.62, 27.91, 25.30, 22.85, 22.21.

D. Photochemical Reactions

D.1 Experimental Set-up

The photoreactor used in this study consisted of a 12.5 cm diameter jar fitted with 4 standard B29 size quickfit-glass joints arranged around a central B29 size joint (Figure S6). A commercial 1-meter LED strip was wrapped around the jar, followed by a layer of aluminium foil and cotton for insulation.

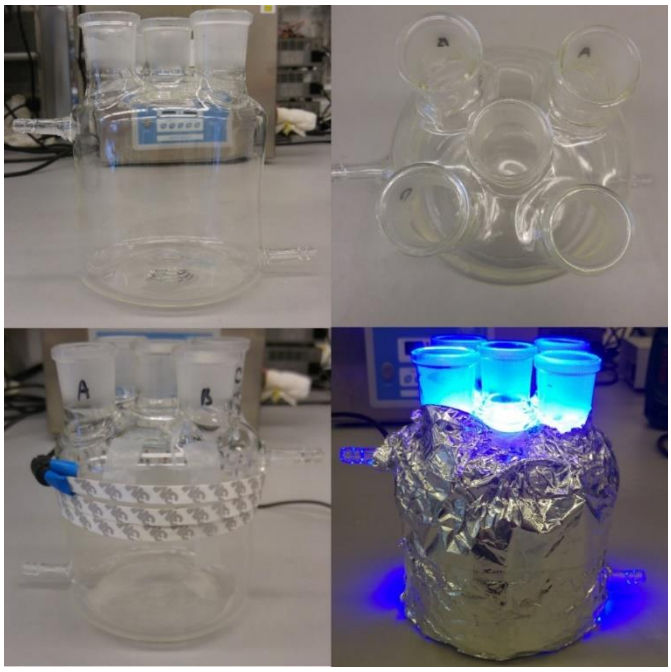


Figure S6. Photoreactor used in this study - pictures taken at different stages of the set-up assembly.

An inlet/outlet system provided circulation of liquid (ethylene glycol/water mixture) from a Huber Minichiller 300 inside the jar. This setup allowed the performance of reactions at temperatures ranging from –20 ºC to 80 ºC with accurate control of the reaction temperature (± 1ºC, **Figure S7**).

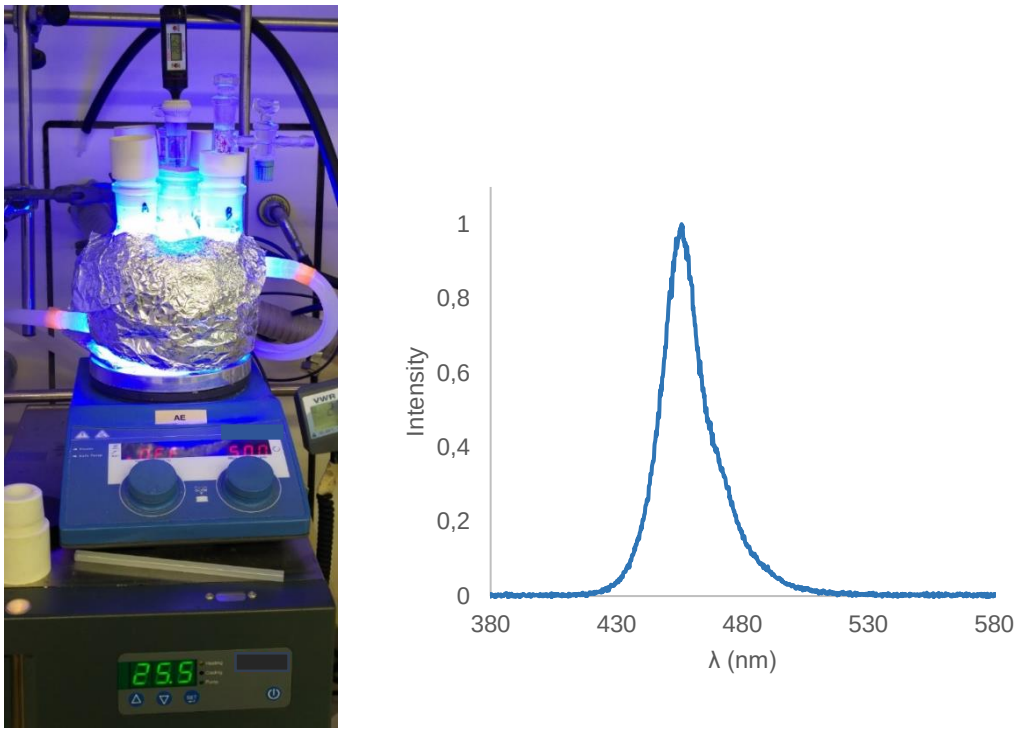
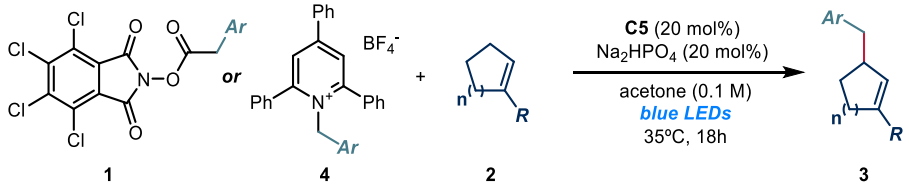


Figure S7. Fully assembled temperature-controlled photoreactor in operation (*left*)**.** Emission spectrum of the 465 nm LED strip used in this reactor (*right*).

In order to maintain consistent illumination between different experiments, only the four external positions were used to perform reactions. The central position was used to monitor the temperature using a thermometer inside an inserted Schlenk tube, ensuring that the reaction mixtures were at the desired temperature.

D.2 Direct C-H Allylic Benzylation

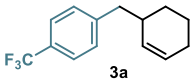
D.2.1 General Procedure A



1 4 2 3

To an argon-purged glass vial, containing the dithiophosphoric acid catalyst **C5** (0.2 equiv.), tetrachloro-phthalimide ester **1** or pyridinium salt **4** (1 equiv.), and Na_2HPO_4 (0.2 equiv.), was added the allylic precursor **2** (20 equiv.) followed by argon-sparged HPLC grade acetone (0.1M). The vial was sealed with Parafilm, and placed in the irradiation setup, maintained at a temperature of 35 ºC. The reaction was stirred for 18h, then the solvent was evaporated and the crude mixture purified by flash column chromatography on silica gel to furnish the product **3**.

D.2.2 Characterization of Products 3

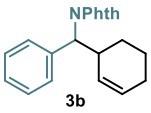


1-(cyclohex-2-en-1-ylmethyl)-4-(trifluoromethyl)benzene (3a)

Prepared according to General Procedure A using the radical precursor **1a** (97.4 mg, 0.2 mmol) and cyclohexene **2a** (406 µL, 4.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 100% pentane) to afford product **3a** as a colorless oil (19.8 mg, 41% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.71 (dtd, *J* = 9.8, 3.5, 2.2 Hz, 1H), 5.53 (dq, *J* = 10.1, 2.4 Hz, 1H), 2.69 (dd, *J* = 13.3, 7.2 Hz, 1H), 2.60 (dd, *J* = 13.3, 8.0 Hz, 1H), 2.39 (ddtq, *J* = 10.4, 7.6, 5.0, 2.7 Hz, 1H), 1.99 (dtt, *J* = 7.4, 5.2, 2.7 Hz, 2H), 1.71 (tdt, *J* = 12.6, 8.7, 4.3 Hz, 2H), 1.60 – 1.48 (m, 1H), 1.40 – 1.26 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 130.6, 129.4, 129.1 (q, *J* = 275.1 Hz), 127.9, 125.1 (q, *J* = 3.8 Hz), 42.5, 40.1, 37.0, 28.8, 26.0, 25.4, 25.3, 22.2, 21.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4.

HRMS (APCI) Calculated for $C_{14}H_{14}F_3$ $[M-H]^-$: 239.1042, found: 239.1052.



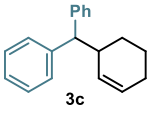
2-(cyclohex-2-en-1-yl(phenyl)methyl)isoindoline-1,3-dione (3b)

Prepared according to General Procedure A using the radical precursor **1b** (56.4 mg, 0.1 mmol), and cyclohexene **2a** (203 µL, 2.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 20:1 Hexane/EtOAc) to afford product **3b** as a white solid (7.9 mg, 25% yield, 1.1:1 dr., average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoiomers* δ 7.79 (ddd, *J* = 5.4, 3.8, 3.0 Hz, 2H), 7.67 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.63 (tt, *J* = 8.1, 1.3 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 5.78 (dtd, *J* = 9.8, 3.7, 2.0 Hz, 0.5H), 5.71 (dtd, *J* = 9.9, 3.7, 2.2 Hz, 0.5H), 5.56 – 5.50 (m, 0.5H), 5.33 – 5.26 (m, 0.5H), 5.00 (d, *J* = 12.3 Hz, 0.5H), 4.98 (d, *J* = 12.1 Hz, 0.5H), 3.83 – 3.71 (m, 0.5H), 2.05 – 1.99 (m, 2H), 1.83 – 1.68 (m, 0.5H), 1.68 – 1.48 (m, 0.5H), 1.37 – 1.27 (m, 0.5H), 1.16 (dddd, *J* = 12.9, 10.4, 7.9, 2.9 Hz, 0.5H).

^{13}C NMR (126 MHz, $CDCl_3$) *1.1:1 mixture of diastereoiomers* δ 168.4, 168.4, 138.8, 138.4, 133.9, 131.8, 131.8, 129.9, 129.4, 129.1, 129.1, 128.6, 128.0, 127.9, 127.5, 127.0, 127.0, 123.2, 123.2, 60.6, 60.0, 34.7, 34.1, 27.1, 26.6, 25.3, 25.2, 20.7, 20.5.

HRMS (ESI) Calculated for $C_{21}H_{19}NNaO_2$ $[M+Na]^+$: 340.1308, found: 340.1304

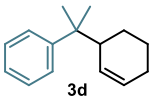


(cyclohex-2-en-1-ylmethylene)dibenzene (3c)

Prepared according to General Procedure A using the radical precursor **1c** (49.5 mg, 0.1 mmol), and cyclohexene **2a** (203 µL, 2.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 99:1 pentane/CH_2Cl_2) to afford product **3c** as a white solid (12.4 mg, 50% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.29 – 7.22 (m, 6H), 7.17 – 7.10 (m, 2H), 5.66 (dtd, *J* = 9.9, 3.5, 2.0 Hz, 1H), 5.45 (dqd, *J* = 10.3, 2.2, 1.0 Hz, 1H), 3.59 (d, *J* = 11.4 Hz, 1H), 2.98 (dddp, *J* = 10.9, 8.0, 5.4, 2.7 Hz, 1H), 1.98 (qt, *J* = 5.1, 3.1 Hz, 2H), 1.76 – 1.66 (m, 1H), 1.65 – 1.56 (m, 1H), 1.56 – 1.44 (m, 1H), 1.19 (dddd, *J* = 12.8, 11.2, 8.6, 2.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.9, 130.0, 128.5, 128.4, 128.3, 128.2, 128.0, 126.1, 126.1, 58.1, 38.9, 28.3, 25.4, 21.5. Analytical data are in agreement with the one reported in literature.[22]

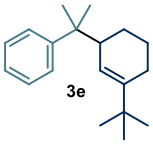


(2-(cyclohex-2-en-1-yl)propan-2-yl)benzene (3d)

Prepared according to General Procedure A using the radical precursor **1d** (89.4 mg, 0.2 mmol), and cyclohexene **2a** (406 µL, 4.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 100% pentane) to afford product **3d** as a colorless oil (18.0 mg, 45% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.20 – 7.16 (m, 1H), 5.73 – 5.66 (m, 1H), 5.49 (dp, *J* = 10.3, 2.0 Hz, 1H), 2.46 (dddt, *J* = 10.2, 8.0, 5.2, 2.6 Hz, 1H), 1.92 (dddd, *J* = 9.0, 4.4, 3.3, 2.0 Hz, 2H), 1.77 – 1.69 (m, 1H),1.50 – 1.40 (m, 1H), 1.30 (s, 3H), 1.26 (s, 3H), 1.20 (tdd, *J* = 12.7, 10.7, 2.9 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 129.0, 128.4, 127.9, 126.2, 125.4, 46.5, 40.2, 30.3 29.7, 25.3, 25.2, 25.0, 24.7, 22.8.

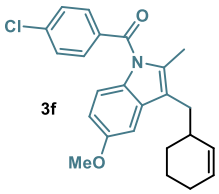
HRMS (APCI) Calculated for $C_{15}H_{21}$ $[M+H]^+$: 201.1638, found: 201.1633.



(2-(3-(tert-butyl)cyclohex-2-en-1-yl)propan-2-yl)benzene (3e)

Prepared according to General Procedure A using the radical precursor **1d** (49.7 mg, 0.1 mmol), and 1-tert-Butyl-1-cyclohexene **2b** (170 µL, 1.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 100% pentane) to afford product **3e** as a colorless oil (10 mg, single regioisomer, 39% yield, average of two runs).

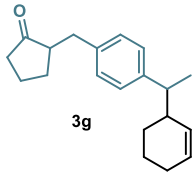
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.22 – 7.17 (m, 1H), 5.33 (tt, *J* = 2.2, 0.9 Hz, 1H), 2.43 (dddd, *J* = 10.5, 5.9, 4.0, 2.2 Hz, 1H), 2.06 – 1.98 (m, 1H), 1.91 – 1.82 (m, 1H), 1.82 – 1.73 (m, 1H), 1.54 – 1.46 (m, 1H), 1.41 – 1.33 (m, 1H), 1.31 (s, 3H), 1.27 (s, 3H), 1.09 (ddd, *J* = 12.6, 10.6, 3.2 Hz, 1H), 1.00 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 147.0, 127.8, 126.3, 125.3, 119.2, 46.7, 40.7, 35.5, 29.1, 25.3, 25.0, 24.8, 24.6, 23.5.
HRMS (APCI) Calculated for $C_{19}H_{29}$ $[M+H]^+$: 257.2264, found: 257.2256.



(4-chlorophenyl)(3-(cyclohex-2-en-1-ylmethyl)-5-methoxy-2-methyl-1H-indol-1-yl)methanone (3f)

Prepared according to General Procedure A using the radical precursor **1e** (64.1 mg, 0.1 mmol), and cyclohexene **2a** (203 µL, 2.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 98:2 hexanes/EtOAc) to afford product **3f** as a yellowish oil (12.6 mg, 32% yield, average of two runs).

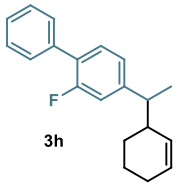
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.52 – 7.47 (m, 2H), 6.96 – 6.86 (m, 2H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.73 (td, *J* = 6.0, 2.9 Hz, 1H), 5.63 (dd, *J* = 10.1, 2.3 Hz, 1H), 3.85 (s, 3H), 2.68 (dd, *J* = 14.0, 7.3 Hz, 1H), 2.60 (dd, *J* = 14.0, 8.2 Hz, 1H), 2.47 (s, 1H), 2.34 (s, 3H), 2.03 (d, *J* = 5.7 Hz, 2H), 1.79 (dq, *J* = 10.1, 6.2, 5.4 Hz, 2H), 1.55 (s, 1H), 1.34 (td, *J* = 10.9, 8.5 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 206.9, 168.3, 155.8, 139.0, 134.7, 134.3, 131.6, 131.3, 131.1, 131.0, 129.1, 127.6, 118.6, 114.9, 110.8, 101.9, 55.8, 35.8, 30.9, 30.7, 29.3, 25.4, 21.3, 13.6.
HRMS (ESI) Calculated for $C_{24}H_{24}ClNNaO_2$ $[M+Na]^+$: 416.1388, found: 416.1399.



2-(4-(1-(cyclohex-2-en-1-yl)ethyl)benzyl)cyclopentan-1-one (3g)

Prepared according to General Procedure A using the radical precursor **1f** (52.9 mg, 0.1 mmol), and cyclohexene **2a** (203 µL, 2.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 98:2 hexanes/EtOAc) to afford product **3g** as a colorless oil (12.4 mg, 44% yield, 1.1:1 dr, average of two runs).

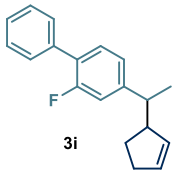
^{1}H NMR (400 MHz, $CDCl_3$) *1.1:1 mixture of diastereoiomers* δ 7.11 (s, 4H), 5.84 – 5.72 (m, 1H), 5.64 (dq, *J* = 10.1, 3.4 Hz, 0.5H), 5.38 (dd, *J* = 10.2, 2.3 Hz, 0.5H), 3.14 (dt, *J* = 13.9, 3.8 Hz, 1H), 2.68 – 2.48 (m, 2H), 2.43 – 2.32 (m, 2H), 2.30 – 2.21 (m, 1H), 2.19 – 2.06 (m, 2H), 1.97 (dtt, *J* = 8.4, 6.1, 3.3 Hz, 3H), 1.87 – 1.65 (m, 2H), 1.64 – 1.54 (m, 1H), 1.53 – 1.39 (m, 1H), 1.33 – 1.27 (m, 2H), 1.27 – 1.22 (m, 2H), 1.21 – 1.11 (m, 0.5H), 0.97 – 0.78 (m, 0.5H).
^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoiomers* δ 144.5, 144.3, 137.4, 130.8, 129.6, 128.8, 128.6, 128.2, 127.9, 127.8, 127.5, 127.5, 51.1, 44.6, 44.2, 41.9, 41.9, 41.8, 38.3, 35.2, 35.2, 29.3, 27.6, 26.5, 25.4, 25.3, 22.0, 21.4, 20.6, 18.7, 18.7, 18.5, 15.6, -18.5.
HRMS (APCI) Calculated for $C_{20}H_{27}O$ $[M+H]^+$: 283.2056, found: 283.2051.



4-(1-(cyclohex-2-en-1-yl)ethyl)-2-fluoro-1,1'-biphenyl (3h)

Prepared according to General Procedure A using the radical precursor **1g** (52.7 mg, 0.1 mmol), and cyclohexene **2a** (203 µL, 2.0 mmol). The crude mixture was purified by column chromatography (SiO_2, hexanes) to afford product **3h** as a colorless oil (13.8 mg, 49% yield, 1.1:1 dr, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) *1.1:1 mixture of diastereoiomers* δ 7.61 – 7.55 (m, 2H), 7.50 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.09 – 6.98 (m, 2H), 5.87 – 5.77 (m, 1H), 5.75 – 5.67 (m, 0.5H), 5.46 (ddd, *J* = 10.2, 2.3, 1.2 Hz, 0.5H), 2.67 (ddt, *J* = 14.5, 11.3, 7.4 Hz, 1H), 2.34 (ddddd, *J* = 18.5, 11.5, 8.1, 5.3, 2.8 Hz, 1H), 2.00 (ddt, *J* = 6.0, 4.0, 2.1 Hz, 2H), 1.91 – 1.78 (m, 1H), 1.78 – 1.68 (m, 1H), 1.62 – 1.46 (m, 1H), 1.37 – 1.28 (m, 3H), 1.28 – 1.20 (m, 0.5H), 0.96 – 0.81 (m, 0.5H).
^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoiomers* δ 160.9, 158.4, 148.5, 135.9, 130.3, 130.3, 130.2, 129.2, 129.0, 128.9, 128.6, 128.4, 128.0, 127.4, 126.3, 123.8, 123.6, 115.3, 115.1, 114.8, 44.6, 44.3, 41.8, 41.7, 27.6, 26.5, 25.4, 25.3, 21.9, 21.4, 18.6, 18.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -118.8.
HRMS (APCI) Calculated for $C_{20}H_{22}F$ $[M+H]^+$: 281.1700, found: 281.1701.

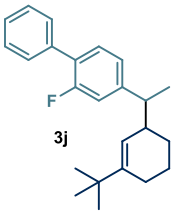


4-(1-(cyclopent-2-en-1-yl)ethyl)-2-fluoro-1,1'-biphenyl (3i)

Prepared according to General Procedure A using the radical precursor **1g** (52.7 mg, 0.1 mmol) and cyclopentene **2c** (176 µL, 2.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 30:1 hexanes/CH_2Cl_2) to afford product **3i** as a colorless oil (12.1 mg, 45% yield, 1.1:1 dr, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.56 (dt, *J* = 7.9, 1.5 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.04 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.00 (dt, *J* = 12.1, 1.8 Hz, 1H), 5.87 – 5.80 (m, 1H), 5.73 (dq, *J* = 5.8, 2.3 Hz, 0.5H), 5.45 (dq, *J* = 6.0, 2.1 Hz, 0.5H), 2.95 – 2.84 (m, 1H), 2.64 – 2.54 (m, 1H), 2.35 – 2.20 (m, 2H), 2.10 (dtd, *J* = 12.7, 8.1, 4.5 Hz, 0.5H), 1.85 (dtd, *J* = 13.4, 8.6, 5.0 Hz, 0.5H), 1.62 – 1.53 (m, 0.5H), 1.45 (ddt, *J* = 12.9, 9.0, 6.3 Hz, 0.5H), 1.31 (d, *J* = 6.9 Hz, 1.5H), 1.28 (d, *J* = 7.0 Hz, 1.5H), 1. 29 – 1.26 (m, 1H).

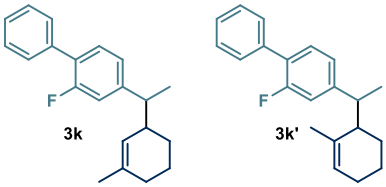
^{13}C NMR (126 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 160.6, 158.7, 148.8 (d, *J* = 7.1 Hz), 148.7 (d, *J* = 7.3 Hz), 135.9, 133.6, 132.8, 132.0, 131.2, 130.3 (d, *J* = 3.4 Hz), 130.2 (d, *J* = 3.4 Hz), 128.9 (d, *J* = 3.1 Hz), 128.4, 127.4, 126.3 (d, *J* = 4.0 Hz), 126.2 (d, *J* = 3.7 Hz), 123.6 (d, *J* = 3.3 Hz), 123.5 (d, *J* = 3.4 Hz), 115.0 (d, *J* = 4.4 Hz), 114.8 (d, *J* = 4.3 Hz), 52.8, 52.5, 45.1, 44.9, 32.3, 31.9, 28.6, 28.2, 19.8, 19.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -118.7.
HRMS (APCI) Calculated for $C_{19}H_{20}F$ $[M+H]^+$: 267.1544, found: 267.1541.



4-(1-(3-(tert-butyl)cyclohex-2-en-1-yl)ethyl)-2-fluoro-1,1'-biphenyl (3j)

Prepared according to General Procedure A using the radical precursor **1g** (52.7 mg, 0.1 mmol) and 1-tert-Butyl-1-cyclohexene **2b** (170 µL, 1.0 mmol). The crude mixture was purified by column chromatography (SiO_2, hexanes) to afford product **3j** as a colorless oil (16 mg, 48% yield, 1.1:1 dr, single regioisomer, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.62 – 7.55 (m, 2H), 7.46 (ddt, *J* = 8.2, 6.1, 0.9 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.08 – 6.98 (m, 2H), 5.60 (d, *J* = 2.6 Hz, 0.5H), 5.29 – 5.26 (m, 0.5H), 2.77 – 2.61 (m, 1H), 2.32 (dtq, *J* = 10.8, 5.5, 2.5 Hz, 1H), 2.05 (dd, *J* = 17.1, 4.7 Hz, 1H), 1.99 – 1.85 (m, 1H), 1.84 – 1.70 (m, 1H), 1.54 – 1.39 (m, 2H), 1.35 (d, *J* = 7.0 Hz, 1.5H), 1.30 – 1.28 (m, 1.5H), 1.07 (s, 4.5H), 1.00 (s, 4.5H), 0.92 (d, *J* = 3.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 160.83, 158.37, 148.68 (d, *J* = 7.2 Hz), 148.47 (d, *J* = 7.1 Hz), 136.01, 130.06 (dd, *J* = 7.9, 4.0 Hz), 128.96 (d, *J* = 3.0 Hz), 128.38, 127.35, 123.98 (d, *J* = 3.0 Hz), 123.68 (d, *J* = 3.2 Hz), 120.81, 119.56, 115.36, 115.15 (d, *J* = 3.2 Hz), 114.94, 44.87, 44.66, 42.27, 41.98, 35.53, 35.39, 29.15, 29.06, 27.37, 26.06, 24.75, 24.68, 22.77, 22.32, 18.53, 17.61.
^{19}F NMR (376 MHz, $CDCl_3$) δ -119.0.
HRMS (APCI) Calculated for $C_{20}H_{30}F$ $[M+H]^+$: 337.2326, found: 337.2324.

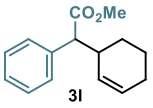


2-fluoro-4-(1-(3-methylcyclohex-2-en-1-yl)ethyl)-1,1'-biphenyl (3k)

Prepared according to General Procedure A using the radical precursor **1g** (52.7 mg, 0.1 mmol) and 1-Methyl-1-cyclohexene **2d** (237 µL, 2.0 mmol). The crude mixture was purified by column chromatography (SiO_2, hexanes) to afford product **3k** as a colorless oil (12.8 mg, 44% yield, 1.5:1 *r.r.;* major regioisomer (**3k**) 1.4:1 *d.r.*, minor regioisomer (**3k'**) 1.5:1 *d.r.*, average of two runs). Product **3k** was isolated together with an unidentified isomeric product.

^{1}H NMR (400 MHz, $CDCl_3$) *major regioisomer (**3k**)* 1.4:1 *mixture of diastereoiomers* δ 7.56 (ddddd, *J* = 7.2, 5.8, 4.3, 2.7, 1.6 Hz), 7.48 – 7.39 (m), 7.39 – 7.30 (m), 7.06 – 6.94 (m), 5.54 – 5.48 (m, 1.4H), 5.15 (dd, *J* = 2.8, 1.4 Hz, 1H), 2.59 (p, *J* = 7.2 Hz, 2.4H), 2.40 – 2.18 (m, 2.4H), 1.99 – 1.84 (m), 1.84 – 1.75 (m), 1.69 (dt, *J* = 2.3, 1.1 Hz, 3H), 1.62 (dt, *J* = 2.4, 1.2 Hz, 3H), 1.72– 1.60 (m), 1.47 (dddd, *J* = 15.0, 10.4, 5.5, 2.7 Hz), 1.32 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.37 – 1.24 (m).
^{1}H NMR (400 MHz, $CDCl_3$) *minor regioisomer (**3k'**)* 1.5:1 *mixture of diastereoiomers* δ 7.56 (ddddd, *J* = 7.2, 5.8, 4.3, 2.7, 1.6 Hz), 7.48 – 7.39 (m), 7.39 – 7.30 (m), 7.06 – 6.94 (m),5.66 (s, 1.5H), 5.58 (s, 1H), 2.79 (q, *J* = 7.2 Hz, 1H), 2.69 (qd, *J* = 7.4, 3.8 Hz, 1.5H), 1.99 – 1.84 (m), 1.84 – 1.75 (m),1.71 (s, 3H), 1.72– 1.60 (m), 1.54 (s, 4.5H), 1.47 (dddd, *J* = 15.0, 10.4, 5.5, 2.7 Hz), 1.31 (d, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 7.3 Hz, 4.5H) 1.37 – 1.24 (m).

^{13}C NMR (126 MHz, $CDCl_3$) *mixture of regioisomers and diasteroisomers* δ 160.6, 158.7, 136.0, 135.8, 135.0, 130.2, 130.2, 128.9, 128.9, 128.4, 128.4, 127.4, 127.3, 124.4, 123.8, 123.8, 123.6, 123.6, 123.2, 115.3, 115.1, 115.0, 114.8, 49.3, 47.8, 45.3, 45.0, 44.8, 44.5, 42.0, 42.0, 33.6, 31.8, 30.2, 30.1, 27.4, 26.2, 25.4, 25.1, 25.1, 24.5, 24.1, 23.9, 22.3, 21.7, 19.1, 18.7, 18.5, 15.9, 15.6, 14.1, 12.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -118.9, -119.0, -119.1, -119.4.
HRMS (APCI) Calculated for $C_{21}H_{23}F$ $[M+H]^+$: 295.1857, found: 295.1858.



methyl 2-(cyclohex-2-en-1-yl)-2-phenylacetate (3l)

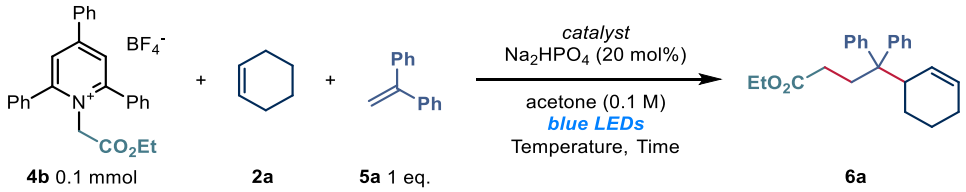
Prepared according to General Procedure A using the radical precursor **4a** (109 mg, 0.2 mmol), and cyclohexene **2a** (203 µL, 2.0 mmol). The crude mixture was purified by column chromatography (SiO_2, 50:50 hexanes/toluene) to afford product **3l** as a colorless oil (14.6 mg, 32% yield, 1.1:1 dr, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$)1.1:1 *mixture of diastereoiomers* δ 7.37 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 5.79 (dtd, *J* = 9.8, 3.7, 2.0 Hz, 0.5H), 5.67 – 5.60 (m, 1H), 5.18 – 5.13 (m, 0.5H), 3.67 (s, 3H), 3.66 (s, 3H), 3.32 (dd, *J* = 11.2, 1.1 Hz, 1H), 2.86 (dtdt, *J* = 18.8, 8.0, 5.2, 2.6 Hz, 1H), 1.98 (tt, *J* = 5.7, 4.0, 2.0 Hz, 2H), 1.93 – 1.86 (m, 1H), 1.82 – 1.71 (m, 1H), 1.67 – 1.54 (m, 1H), 1.46 (dtt, *J* = 13.3, 6.5, 3.0 Hz, 1H), 1.42 – 1.27 (m, 1H), 1.06 (dddd, *J* = 13.3, 10.7, 8.0, 2.9 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)1.1:1 *mixture of diastereoiomers* δ 174.0, 174.0, 137.6, 137.4, 129.2, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.3, 57.5, 57.4, 51.8, 51.8, 38.5, 38.4, 29.7, 27.9, 26.3, 25.3, 25.2, 21.1, 20.7.
Analytical data are in agreement with the one reported in literature.[23]

D.3 Three-component C-H Allylic Benzylation

D.3.1 Optimization Data

To an argon-purged glass vial, containing the thiol catalyst, the radical precursor **4b** (48.1 mg, 0.1 mmol), and Na_2HPO_4 (2.8 mg, 0.02 mmol, 0.2 equiv.), was added the radical trap **5a** (17.7 µL, 0.1 mmol, 1 equiv.) and cyclohexene **2a**. Then, 800 µL of argon-sparged HPLC grade acetone were added. The vial was sealed with Parafilm, and then placed in the irradiation setup, maintained at the defined temperature. The reaction was stirred for the stated amount of time, then the solvent was evaporated and the crude mixture purified by flash column chromatography on silica gel to furnish the product **6a**.



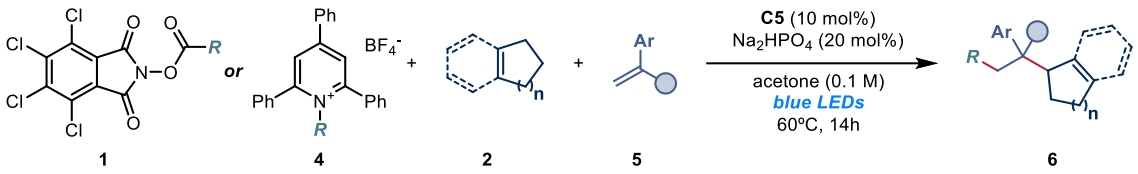
4b 0.1 mmol **2a** **5a** 1 eq. **6a**

entry	loading **2a**	catalyst (loading)	T (ºC)	time (h)	conversion (%)[a]	yield **6a** (%)[a]
1	20 equiv.	C5 (20 mol%)	35	18	75	56
2	20 equiv.	C5 (20 mol%)	35	48	100	75 (65)[c]
3	10 equiv.	C5 (20 mol%)	35	24	100	85

4	20 equiv.	C5 (10 mol%)	35	24	100	88
5	10 equiv.	C5 (10 mol%)	35	24	80	67
6	10 equiv.	C5 (10 mol%)	35	28	100	85 (78)[b]
7	**10 equiv.**	**C5 (10 mol%)**	**60**	**8**	**100**	**96 (95)[b]**
8	5 equiv.	C5 (10 mol%)	60	14	90	70
9	10 equiv.	C6 (10 mol%)	60	8	100	88
10	10 equiv.	C7 (10 mol%)	60	14	35	30
11	10 equiv.	C4 (10 mol%)	35	28	100	40
12[a]	10 equiv.	C5 (10 mol%)	60	28	-	-
13	10 equiv.	-	60	28	-	-

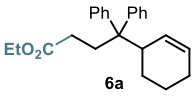
Table S1. Optimization studies for the three-component C-H allylic benzylation. [a] Yield determined by ^{1}H NMR analysis. [b] Yield of the isolated **6a**.

D.3.2 General Procedure B



To an argon-purged glass vial, containing the catalyst **C5** (3.8 mg, 0.01 mmol, 0.1 equiv.), tetrachloro-phthalimide ester **1** or pyridinium salt **4** (0.1 mmol, 1 equiv.), and Na_2HPO_4 (2.8 mg, 0.02 mmol, 0.2 equiv.), was added the alkene **5** (0.1 mmol, 1 equiv.) and the allylic precursor **2** (1 mmol, 10 equiv.). Then, 800 µL of argon-sparged HPLC grade acetone were added. The vial was sealed with Parafilm, and then placed in the irradiation setup, maintained at a temperature of 60 ºC. The reaction was stirred for 14h, then the solvent was evaporated and the crude mixture purified by flash column chromatography on silica gel to furnish the product **6**.

D.3.3 Characterization of Products 6



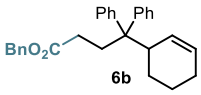
Ethyl 4-(cyclohex-2-en-1-yl)-4,4-diphenylbutanoate (6a)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 50:50 hexanes/toluene) to afford product **6a** as a colorless oil (33.0 mg, 95% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 10H), 5.81 (dt, J = 10.4, 2.1 Hz, 1H), 5.62 (dddd, J = 9.8, 5.1, 2.7, 1.3 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 3.19 (ddt, J = 9.3, 6.9, 2.4 Hz, 1H), 2.59 (ddd, J = 13.9, 11.8, 4.6 Hz, 1H), 2.48 – 2.37 (m, 1H), 2.07 (ddd, J = 16.3, 11.7, 4.6 Hz, 1H), 1.98 – 1.82 (m, 3H), 1.76 – 1.49 (m, 3H), 1.22 (t, J = 7.1 Hz, 3H), 0.94 (tdd, *J* = 12.5, 10.4, 3.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 145.2, 142.9, 129.7, 129.3, 129.0, 128.9, 127.7, 127.1, 126.0, 125.9, 60.3, 53.7, 41.6, 33.9, 30.1, 25.0, 24.7, 22.4, 14.2.

HRMS (APCI) Calculated for $C_{24}H_{29}O_2$ $[M+H]^+$: 349.2162, found: 349.2164.

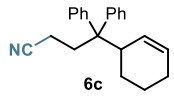


Benzyl 4-(cyclohex-2-en-1-yl)-4,4-diphenylbutanoate (6b)

Prepared according to General Procedure B using the radical precursor **4c** (54.3 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 70:30 hexanes/toluene) to afford product **6b** as a colorless oil (27.7 mg, 68% yield, average of two runs). Multiple purifications by column chromatography resulted in poor separation from several unidentified byproducts. The yield (75%, average of two runs) of **6b** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard. An analytical amount of pure compound was isolated by preparative TLC (80:20 hexanes/toluene) to obtain a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.19 (m, 15H), 5.82 (dq, J = 10.4, 2.0 Hz, 1H), 5.62 (ddt, J = 10.2, 4.9, 2.4 Hz, 1H), 5.06 (s, 2H), 3.25 – 3.16 (m, 1H), 2.63 (ddd, J = 13.9, 11.7, 4.6 Hz, 1H), 2.46 (ddd, J = 13.9, 11.6, 5.3 Hz, 1H), 2.22 – 2.10 (m, 1H), 2.02 (ddd, J = 16.5, 11.7, 5.3 Hz, 1H), 1.90 (tt, J = 15.0, 2.9 Hz, 2H), 1.77 – 1.49 (m, 3H), 0.98 (tdd, J = 12.3, 10.3, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 145.2, 142.8, 135.9, 129.7, 129.3, 129.0, 128.9, 128.5, 128.2, 128.2, 127.8, 127.7, 127.1, 127.1, 126.0, 125.9, 66.2, 53.8, 41.6, 33.9, 30.1, 25.0, 24.7, 22.4. HRMS (ESI) Calculated for $C_{29}H_{30}NaO_2$ $[M+Na]^+$: 433.2138, found: 433.2129.



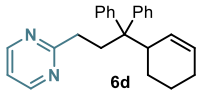
4-(cyclohex-2-en-1-yl)-4,4-diphenylbutanenitrile (6c)

Prepared according to General Procedure B using the radical precursor **4d** (43.4 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 50:50 hexanes/toluene) to afford product **6c** as a colorless oil (28.1 mg, 93% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 6H), 7.21 (ddd, J = 7.1, 3.2, 1.8 Hz, 4H), 5.76 (dt, J = 10.5, 2.0 Hz, 1H), 5.69 – 5.61 (m, 1H), 3.23 – 3.12 (m, 1H), 2.65 (ddd, J = 14.0, 11.8, 4.6 Hz, 1H), 2.47 (ddd, J = 13.9, 11.7, 5.5 Hz, 1H), 2.08 (ddd, J = 16.4, 11.7, 4.5 Hz, 1H), 1.96 – 1.82 (m, 3H), 1.75 – 1.52 (m, 3H), 0.98 (tdd, J = 12.1, 10.3, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.97, 141.62, 129.58, 129.42, 129.09, 128.23, 128.14, 127.51, 126.56, 126.52, 120.07, 53.97, 41.54, 35.09, 24.93, 24.73, 22.23, 13.25, 1.03.

HRMS (APCI) Calculated for $C_{22}H_{24}N$ $[M+H]^+$: 302.1903, found: 302.1902.



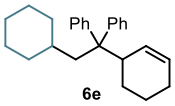
2-(3-(cyclohex-2-en-1-yl)-3,3-diphenylpropyl)pyrimidine (6d)

Prepared according to General Procedure B using the radical precursor **4e** (48.7 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 80:20 hexanes/EtOAc) to afford product **6d** as a white solid (14.5 mg, 41% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.9 Hz, 2H), 7.37 – 7.27 (m, 8H), 7.26 – 7.18 (m, 2H), 7.09 (t, *J* = 4.9 Hz, 1H), 5.88 (dt, *J* = 10.4, 2.1 Hz, 1H), 5.66 – 5.58 (m, 1H), 3.32 (ddd, *J* = 11.0, 5.5, 3.0 Hz, 1H), 2.80 – 2.67 (m, 2H), 2.66 – 2.57 (m, 2H), 1.98 (dd, *J* = 12.5, 3.7 Hz, 1H), 1.84 (s, 1H), 1.74 – 1.64 (m, 1H), 1.56 (ddt, *J* = 13.7, 10.7, 5.5 Hz, 2H), 1.04 – 0.96 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 156.9, 145.7, 143.4, 129.9, 129.4, 129.4, 128.7, 127.7, 127.0, 125.8, 125.8, 118.3, 54.2, 41.6, 37.8, 35.0, 25.0, 24.7, 22.4.

HRMS (ESI) Calculated for $C_{25}H_{26}NaN_2$ $[M+Na]^+$: 355.2169, found: 355.2175.



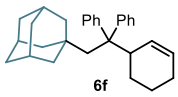
(1-(cyclohex-2-en-1-yl)-2-cyclohexylethane-1,1-diyl)dibenzene (6e)

Prepared according to General Procedure B using the radical precursor **1h** (49.3 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, pentane) to afford product **6e** as a colorless oil (24.2 mg, 70% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 10H), 5.94 – 5.88 (m, 1H), 5.60 (ddt, *J* = 10.1, 5.0, 2.5 Hz, 1H), 3.22 (ddq, *J* = 9.7, 4.7, 2.3 Hz, 1H), 2.08 (dd, *J* = 14.1, 3.9 Hz, 1H), 2.01 – 1.96 (m, 1H), 1.93 – 1.83 (m, 1H), 1.74 – 1.61 (m, 2H), 1.48 (ddd, *J* = 12.3, 8.2, 5.1 Hz, 3H), 1.17 (dtd, *J* = 14.8, 6.8, 3.8 Hz, 2H), 1.11 – 0.98 (m, 4H), 0.91 (tdd, *J* = 10.1, 5.6, 2.2 Hz, 3H), 0.85 – 0.69 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 144.7, 129.9, 129.8, 129.6, 128.6, 127.3, 126.8, 125.7, 125.6, 54.9, 46.7, 41.4, 3.5, 35.2, 33.7, 33.3, 26.6, 26.5, 26.3, 25.1, 22.5.

HRMS (APCI) Calculated for $C_{26}H_{33}$ $[M+H]^+$: 345.2577, found: 345.2578.



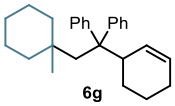
1-(2-(cyclohex-2-en-1-yl)-2,2-diphenylethyl)adamantane (6f)

Prepared according to General Procedure B using the radical precursor **1i** (55.6 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, pentane) to afford product **6f** as a colorless oil (23.0 mg, 58% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 10H), 5.89 (dt, *J* = 10.6, 2.1 Hz, 1H), 5.51 (ddt, *J* = 10.3, 5.0, 2.5 Hz, 1H), 3.46 (ddh, *J* = 9.5, 4.8, 2.5 Hz, 1H), 2.18 (d, *J* = 14.8 Hz, 1H), 2.07 (d, *J* = 15.2 Hz, 1H), 2.05 – 2.01 (m, 2H), 1.88 – 1.78 (m, 1H), 1.71 (p, *J* = 3.2 Hz, 3H), 1.67 – 1.49 (m, 7H), 1.43 (dq, *J* = 12.2, 2.1 Hz, 3H), 1.30 – 1.23 (m, 2H), 1.16 (dq, *J* = 12.3, 2.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 145.6, 130.4, 130.2, 129.7, 128.0, 127.9, 127.6, 127.1, 126.8, 126.3, 125.7, 125.5, 54.0, 52.4, 43.5, 43.1, 41.2, 36.8, 36.7, 34.7, 29.7, 28.9, 28.5, 25.4, 25.0, 22.4.

HRMS (APCI) Calculated for $C_{30}H_{36}$ $[M+H]^+$: 397.2890, found: 397.2887.



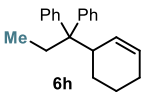
(1-(cyclohex-2-en-1-yl)-2-(1-methylcyclohexyl)ethane-1,1-diyl)dibenzene (6g)

Prepared according to General Procedure B using the radical precursor **1j** (51.0 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, pentane) to afford product **6g** as a colorless oil (21.9 mg, 58% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.31 – 7.14 (m, 8H), 5.86 (dt, *J* = 10.5, 2.0 Hz, 1H), 5.51 (ddt, *J* = 10.3, 5.1, 2.5 Hz, 1H), 3.57 – 3.38 (m, 1H), 2.31 (d, *J* = 14.8 Hz, 1H), 2.26 (d, *J* = 15.0 Hz, 1H), 2.10 – 1.97 (m, 1H), 1.82 (dt, *J* = 19.3, 3.2 Hz, 1H), 1.67 – 1.47 (m, 4H), 1.33 (tdd, *J* = 9.5, 6.8, 3.8 Hz, 3H), 1.24 – 1.05 (m, 4H), 0.96 (dd, *J* = 7.2, 3.8 Hz, 2H), 0.93 – 0.86 (m, 2H), 0.83 (t, *J* = 5.9 Hz, 2H), 0.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 145.5, 130.2, 129.6, 128.0, 127.0, 126.2, 125.6, 125.5, 54.2, 41.5, 39.8, 39.8, 34.7, 29.6, 26.2, 25.3, 25.0, 22.4, 21.9, 21.9.

HRMS (APCI) Calculated for $C_{27}H_{35}$ $[M+H]^+$: 359.2733, found: 359.2730.



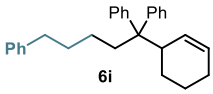
(1-(cyclohex-2-en-1-yl)propane-1,1-diyl)dibenzene (6h)

Prepared according to General Procedure B using the radical precursor **1k** (41.2 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, pentane) to afford product **6h** as a colorless oil (17.8 mg, 64% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 10H), 5.90 – 5.84 (m, 1H), 5.64 – 5.58 (m, 1H), 3.22 (ddq, J = 9.8, 4.8, 2.4 Hz, 1H), 2.22 – 2.16 (m, 2H), 1.88 (dddd, J = 14.0, 5.8, 2.7, 1.4 Hz, 2H), 1.74 – 1.62 (m, 1H), 1.03 – 0.84 (m, 3H), 0.64 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 144.2, 129.9, 129.6, 129.6, 128.5, 127.3, 126.8, 125.6, 125.4, 54.5, 40.3, 31.6, 25.0, 24.6, 22.5, 8.9.

HRMS (APCI) Calculated for $C_{21}H_{25}$ $[M+H]^+$: 277.1951, found: 277.1948.



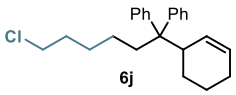
(1-(cyclohex-2-en-1-yl)pentane-1,1,5-triyl)tribenzene (6i)

Prepared according to General Procedure B using the radical precursor **1l** (53.7 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 95:5 hexanes/CH_2Cl_2) to afford product **6i** as a colorless oil (17.2 mg, 45% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 13H), 7.13 – 7.09 (m, 2H), 5.85 (dp, J = 10.5, 1.8 Hz, 1H), 5.64 – 5.58 (m, 1H), 3.21 (ddh, J = 9.3, 4.6, 2.4 Hz, 1H), 2.54 – 2.49 (m, 2H), 2.19 – 2.14 (m, 2H), 1.92 – 1.83 (m, 2H), 1.72 – 1.64 (m, 1H), 1.61 – 1.51 (m, 4H), 1.14 – 1.03 (m, 2H), 0.97 (tdd, J = 12.1, 10.3, 3.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 144.3, 142.7, 129.8, 129.5, 129.5, 128.5, 128.2, 128.2, 127.4, 126.9, 125.7, 125.5, 125.5, 54.3, 40.9, 39.1, 35.7, 32.2, 25.0, 24.7, 24.1, 22.5.

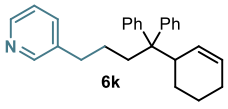
HRMS (APCI) Calculated for $C_{29}H_{33}$ $[M+H]^+$: 381.2577, found: 381.2577.



(6-chloro-1-(cyclohex-2-en-1-yl)hexane-1,1-diyl)dibenzene (6j)

Prepared according to General Procedure B using the radical precursor **1m** (50.3 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, pentane) to afford product **6i** as a colorless oil (25 mg, 71% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 4H), 7.26 – 7.19 (m, 6H), 5.84 (dd, *J* = 10.5, 2.2 Hz, 1H), 5.61 (ddt, *J* = 10.3, 5.1, 2.6 Hz, 1H), 3.44 (t, *J* = 6.7 Hz, 2H), 3.21 (ddd, *J* = 10.2, 4.7, 2.3 Hz, 1H), 2.17 – 2.09 (m, 2H), 1.92 – 1.84 (m, 2H), 1.73 – 1.63 (m, 3H), 1.57 (dt, *J* = 8.9, 3.1 Hz, 2H), 1.36 (dq, *J* = 9.4, 7.5 Hz, 2H), 1.07 – 0.92 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 144.1, 129.8, 129.4, 128.6, 127.4, 126.9, 125.8, 125.6, 54.3, 45.1, 41.1, 39.1, 32.4, 27.6, 25.1, 24.8, 23.7, 22.5.
HRMS (APCI) Calculated for $C_{24}H_{30}Cl$ $[M+H]^+$: 353.2031, found: 353.2021.



3-(4-(cyclohex-2-en-1-yl)-4,4-diphenylbutyl)pyridine (6k)

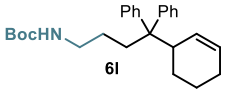
Prepared according to General Procedure B using the radical precursor **1n** (43.4 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-

diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by preparative TLC (SiO_2, 90:10 toluene/acetone) to afford product **6k** as a colorless oil (15.3 mg, 42% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.36 – 8.32 (m, 1H), 7.34 – 7.30 (m, 1H), 7.27 – 7.24 (m, 3H), 7.24 – 7.20 (m, 2H), 7.20 – 7.15 (m, 5H), 5.80 (dp, *J* = 10.5, 1.8 Hz, 1H), 5.62 – 5.56 (m, 1H), 3.22 – 3.13 (m, 1H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.22 – 2.07 (m, 2H), 1.90 – 1.77 (m, 2H), 1.72 – 1.64 (m, 2H), 1.60 – 1.46 (m, 2H), 1.41 – 1.29 (m, 2H), 0.98 – 0.89 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 147.2, 146.0, 143.8, 137.3, 135.7, 129.7, 129.4, 129.2, 128.6, 127.5, 126.9, 125.8, 125.7, 123.2, 54.2, 41.1, 38.4, 33.3, 25.6, 25.0, 24.7, 22.4.

HRMS (ESI) Calculated for $C_{27}H_{30}N$ $[M+H]^+$: 368.2373, found: 368.2374.



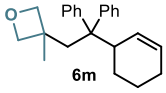
Tert-butyl (4-(cyclohex-2-en-1-yl)-4,4-diphenylbutyl)carbamate (6l)

Prepared according to General Procedure B using the radical precursor **1o** (47.2 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 80:20 hexanes/EtOAc) to afford product **6l** as a colorless oil (19.7 mg, 49% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 10H), 5.82 (dt, *J* = 10.3, 2.2 Hz, 1H), 5.65 – 5.57 (m, 1H), 4.35 (s, 1H), 3.23 – 3.16 (m, 1H), 3.02 (d, *J* = 7.1 Hz, 2H), 2.19 – 2.07 (m, 2H), 1.90 – 1.83 (m, 2H), 1.68 (dtd, *J* = 13.6, 7.5, 6.8, 4.2 Hz, 1H), 1.55 (dtt, *J* = 13.4, 7.7, 3.3 Hz, 2H), 1.44 (s, 9H), 1.20 – 1.09 (m, 2H), 1.00 – 0.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 146.0, 143.8, 129.7, 129.3, 129.2, 128.7, 127.5, 126.9, 125.8, 125.7, 54.0, 41.0, 36.3, 28.4, 25.0, 24.7, 22.4.

HRMS (ESI) Calculated for $C_{27}H_{35}NNaO_2$ $[M+Na]^+$: 428.2560, found: 428.2552.



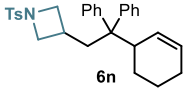
3-(2-(cyclohex-2-en-1-yl)-2,2-diphenylethyl)-3-methyloxetane (6m)

Prepared according to General Procedure B using the radical precursor **1p** (47.9 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 20:1 hexanes/Et_2O) to afford product **6m** as a white solid (28.2 mg, 85% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 10H), 5.75 (dp, *J* = 10.4, 1.8 Hz, 1H), 5.54 (ddt, *J* = 10.3, 5.0, 2.4 Hz, 1H), 3.85 (d, *J* = 5.7 Hz, 1H), 3.80 (d, *J* = 5.7 Hz, 1H), 3.65 (d, *J* = 5.7 Hz, 1H), 3.62 (d, *J* = 5.7 Hz, 1H), 3.37 – 3.27 (m, 1H), 2.69 (d, *J* = 14.6 Hz, 1H), 2.46 (d, *J* = 14.6 Hz, 1H), 1.98 – 1.89 (m, 1H), 1.88 – 1.77 (m, 1H), 1.62 (dddd, *J* = 12.8, 6.2, 4.5, 2.5 Hz, 1H), 1.58 – 1.48 (m, 2H), 1.33 (s, 3H), 0.98 – 0.81 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 142.9, 129.9, 129.7, 128.8, 128.7, 127.6, 126.7, 126.3, 126.0, 83.9, 83.3, 54.2, 46.8, 42.9, 39.7, 25.4, 25.0, 24.9, 22.3.

HRMS (APCI) Calculated for $C_{24}H_{29}O$ $[M+H]^+$: 333.2213, found: 333.2207.



3-(2-(cyclohex-2-en-1-yl)-2,2-diphenylethyl)-1-tosylazetidine (6n)

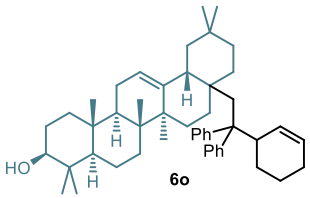
Prepared according to General Procedure B using the radical precursor **1q** (64.4 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene

5a (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 95:5 hexanes/EtOAc) to afford product **6n** as a colorless oil (28.9 mg, 61% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.19 (m, 6H), 7.05 (ddd, *J* = 7.7, 3.5, 1.6 Hz, 4H), 5.70 (dp, *J* = 10.4, 1.8 Hz, 1H), 5.56 (ddq, *J* = 10.3, 4.9, 2.4 Hz, 1H), 3.41 (t, *J* = 8.1 Hz, 1H), 3.25 (t, *J* = 8.1 Hz, 1H), 3.03 (ddt, *J* = 6.9, 4.6, 2.5 Hz, 1H), 2.83 (dd, *J* = 8.1, 7.0 Hz, 1H), 2.71 (dd, *J* = 8.1, 6.9 Hz, 1H), 2.45 (s, 3H), 2.44 – 2.34 (m, 1H), 2.21 – 2.14 (m, 2H), 2.00 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.82 (d, *J* = 17.9 Hz, 1H), 1.76 – 1.67 (m, 1H), 1.55 – 1.41 (m, 1H), 0.79 (tdd, *J* = 12.3, 10.2, 3.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 143.8, 142.7, 131.5, 129.5, 129.4, 129.2, 129.1, 128.4, 128.3, 127.9, 127.1, 126.3, 126.2, 56.4, 56.2, 53.7, 43.5, 41.3, 25.5, 24.9, 24.6, 22.3, 21.6.

HRMS (ESI) Calculated for $C_{30}H_{33}NNaO_2S$ $[M+Na]^+$: 494.2124, found: 494.2117



6o

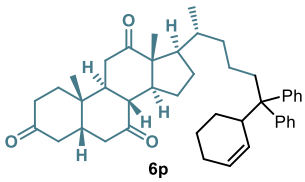
(3S,4aR,6aR,6bS,12aR,14aR,14bR)-8a-(2-(cyclohex-2-en-1-yl)-2,2-diphenylethyl)-4,4,6a,6b,11,11,14b-heptamethyl 1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydropicen-3-ol (6o)

Prepared according to General Procedure B using the radical precursor **1r** (74.0 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). Multiple purifications by column chromatography resulted in poor separation from the simple decarboxylation product. The yield (49%, 1.5:1 dr, average of two runs) of **6o** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard. An analytical amount of 86% pure compound (containing 14% of the simple decarboxylation product as estimated by ^{1}H NMR) was isolated by preparative TLC (90:10 hexanes/EtOAc) to obtain a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) *1.5:1 mixture of diastereoiomers* δ 7.46 – 7.13 (m, 10H), 5.84 (d, *J* = 10.6 Hz, 0.5H), 5.71 (d, *J* = 11.0 Hz, 0.5H), 5.55 – 5.45 (m, 1H), 5.09 – 5.05 (m, 0.5H), 4.96 (t, *J* = 3.6 Hz, 0.5H), 3.57 – 3.37 (m, 1H), 3.28 – 3.20 (m, 1H), 2.49 (d, *J* = 15.2 Hz, 0.5H), 2.43 – 2.32 (m, 1H), 2.21 (d, *J* = 11.5 Hz, 0.5H), 2.07 – 1.93 (m, 2H), 1.92 – 1.73 (m, 5H), 1.69 – 1.53 (m, 14H), 1.44 (qd, *J* = 12.5, 3.2 Hz, 5H), 1.08 (d, *J* = 4.6 Hz, 2H), 1.04 – 1.00 (m, 6H), 0.98 (d, *J* = 4.1 Hz, 4H), 0.95 – 0.89 (m, 4H), 0.81 (d, *J* = 2.3 Hz, 3H), 0.75 (d, *J* = 1.6 Hz, 4H), 0.54 (d, *J* = 6.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) *1.5:1 mixture of diastereoiomers* δ 145.4, 145.1, 129.7, 129.5, 128.3, 127.1, 127.0, 126.2, 126.1, 125.6, 125.5, 125.4, 122.2, 122.0, 79.0, 55.2, 55.1, 54.6, 54.2, 47.7, 47.6, 47.5, 46.7, 46.6, 44.9, 44.1, 43.9, 41.8, 40.9, 40.8, 39.9, 38.7, 38.5, 38.4, 37.2, 37.1, 36.9, 36.8, 35.7, 34.4, 34.3, 33.6, 33.3, 33.0, 32.3, 32.1, 31.1, 30.9, 30.6, 30.3, 30.2, 29.2, 28.0, 28.0, 27.2, 26.9, 26.9, 26.2, 26.1, 25.4, 25.0, 23.9, 23.8, 23.7, 23.6, 23.6, 22.7, 22.2, 18.3, 16.9, 16.8, 15.6, 15.5, 15.5, 15.5, 15.3.

HRMS (APCI) Calculated for $C_{49}H_{69}O$ $[M+H]^+$: 673.5343, found: 673.5337.



6p

(5S,8R,9S,10S,13R,14S,17R)-17-(6-(cyclohex-2-en-1-yl) 6,6-diphenylhexan-2-yl)-10,13-dimethyldodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (6p)

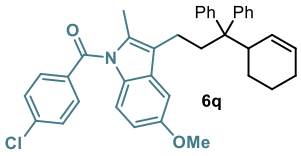
Prepared according to General Procedure B using the radical precursor **1s** (68.5 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by

column chromatography (SiO_2, 90:10 toluene/EtOAc) to afford product **6p** as a white solid (40.7 mg, 66% yield, 1.1:1 *d.r.*, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoiomers* δ 7.31 – 7.17 (m, 10H), 5.83 (t, *J* = 8.7 Hz, 1H), 5.63 – 5.55 (m, 1H), 3.20 (s, 1H), 2.96 – 2.79 (m, 3H), 2.38 – 2.21 (m, 6H), 2.17 – 2.02 (m, 5H), 2.01 – 1.79 (m, 6H), 1.71 – 1.52 (m, 5H), 1.25 (d, *J* = 24.8 Hz, 6H), 1.16 – 1.06 (m, 2H), 1.03 (d, *J* = 2.4 Hz, 3H), 0.89 – 0.74 (m, 2H), 0.66 (dd, *J* = 9.3, 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *1.1:1 mixture of diastereoiomers* δ 212.0, 209.0, 208.8, 146.4, 144.6, 144.1, 129.8, 129.8, 129.5, 129.5, 129.4, 128.5, 128.4, 127.3, 126.9, 126.8, 125.6, 125.6, 125.4, 56.9, 54.5, 54.3, 51.7, 49.0, 46.8, 46.0, 46.0, 45.5, 45.0, 42.8, 41.4, 40.7, 39.7, 39.5, 38.6, 36.5, 36.2, 36.0, 35.9, 35.8, 35.3, 29.7, 29.2, 27.7, 27.7, 25.1, 25.0, 24.8, 24.7, 22.5, 22.4, 21.9, 21.4, 21.3, 18.9, 11.8.

HRMS (ESI) Calculated for $C_{43}H_{54}NaO_3$ $[M+Na]^+$: 641.3965, found: 641.3964.



6q

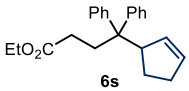
(4-chlorophenyl)(3-(3-(cyclohex-2-en-1-yl)-3,3-diphenylpropyl)-5-methoxy-2-methyl-1H-indol-1-yl)methanone (6q)

Prepared according to General Procedure B using the radical precursor **1e** (64.1 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), 1,1-diphenylethylene **5a** (35.3 µL, 0.2 mmol), and catalyst **C5** (7.6 mg, 0.2 mmol). The crude mixture was purified by column chromatography (SiO_2, 98:2 hexanes/EtOAc) to afford product **6q** as a yellowish oil (20.8 mg, 36% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 2H), 7.49 – 7.45 (m, 2H), 7.38 – 7.29 (m, 8H), 7.28 – 7.22 (m, 2H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.63 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 5.95 (d, *J* = 10.4 Hz, 1H), 5.67 (ddd, *J* = 10.4, 4.8, 2.5 Hz, 1H), 3.78 (s, 3H), 3.38 (s, 1H), 2.45 – 2.37 (m, 1H), 2.36 – 2.25 (m, 3H), 2.18 (s, 3H), 2.01 – 1.87 (m, 2H), 1.77 – 1.66 (m, 1H), 1.34 (d, *J* = 24.8 Hz, 1H), 1.15 – 1.03 (m, 1H), 0.96 – 0.84 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 155.8, 146.2, 144.0, 138.9, 134.3, 133.5, 131.0, 131.0, 130.9, 129.9, 129.6, 129.1, 129.0, 129.0, 127.7, 127.1, 126.0, 125.9, 120.2, 115.1, 111.4, 100.6, 55.7, 54.5, 40.3, 39.3, 25.1, 24.9, 22.5, 18.9, 13.1.

HRMS (ESI) Calculated for $C_{38}H_{36}ClNNaO_2$ $[M+Na]^+$: 596.2327, found: 596.2336.



6s

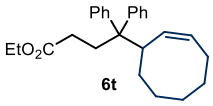
Ethyl 4-(cyclopent-2-en-1-yl)-4,4-diphenylbutanoate (6s)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclopentene **2c** (110 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 70:30 hexanes/toluene) to afford product **6s** as a colorless oil (25.0 mg, 75% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 10H), 5.83 (dq, *J* = 6.0, 2.0 Hz, 1H), 5.64 (dq, *J* = 5.8, 2.3 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.76 (ddt, *J* = 8.5, 6.0, 2.5 Hz, 1H), 2.53 (ddd, *J* = 13.9, 11.7, 4.8 Hz, 1H), 2.39 (ddd, *J* = 13.8, 11.6, 5.2 Hz, 1H), 2.12 (ddd, *J* = 16.4, 11.7, 4.8 Hz, 1H), 2.07 – 1.98 (m, 3H), 1.54 – 1.46 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.94 – 0.84 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 145.9, 144.1, 133.3, 131.8, 129.8, 129.2, 127.4, 127.2, 125.9, 125.8, 60.3, 53.5, 51.3, 34.8, 31.6, 30.0, 25.7, 14.1.

HRMS (ESI) Calculated for $C_{23}H_{26}NaO_2$ $[M+Na]^+$: 357.1825, found: 357.1818.



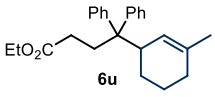
Ethyl (Z)-4-(cyclooct-2-en-1-yl)-4,4-diphenylbutanoate (6t)

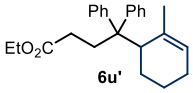
Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), Z-cyclooctene **2e** (130 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). Multiple purifications by column chromatography resulted in poor separation from several unidentified byproducts. The yield (39%, average of two runs) of **6t** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard. An analytical amount of pure compound was isolated by preparative TLC (50:50 hexanes/toluene) to obtain a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 4H), 7.25 – 7.18 (m, 6H), 5.66 (td, *J* = 9.6, 7.0 Hz, 1H), 5.27 (ddd, *J* = 10.8, 9.5, 1.4 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.50 – 3.40 (m, 1H), 2.38 (dd, *J* = 9.0, 7.7 Hz, 2H), 2.14 (ddd, *J* = 13.4, 7.3, 3.7 Hz, 1H), 1.93 (td, *J* = 7.9, 6.3 Hz, 2H), 1.90 – 1.81 (m, 1H), 1.74 (ddd, *J* = 13.6, 7.5, 3.7 Hz, 1H), 1.66 – 1.46 (m, 4H), 1.45 – 1.29 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.76 (tt, *J* = 12.7, 5.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 145.3, 144.0, 130.6, 130.3, 129.5, 127.6, 127.1, 126.1, 125.9, 60.2, 53.1, 39.6, 35.7, 31.1, 29.8, 29.6, 26.7, 26.7, 25.9, 14.1.

HRMS (ESI) Calculated for $C_{26}H_{32}NaO_2$ $[M+Na]^+$: 399.22875 found: 399.2287.





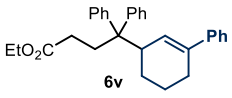
Ethyl 4-(3-methylcyclohex-2-en-1-yl)-4,4-diphenylbutanoate (6u)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), 1-methylcyclohexene **2d** (118 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 70:30 hexanes/toluene) to afford product **6u** as a colorless oil (24.3 mg, 67% yield, 5:1 *r.r.*, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) *5:1 mixture of regioisomers* δ 7.33 – 7.15 (m, 12H), 5.47 (brs, 1H), 5.46 – 5.42 (m, 0.2H), 4.09 – 3.99 (m, 2.4H), 3.19 – 3.08 (m, 1.2H), 2.55 (ddd, *J* = 13.9, 11.8, 4.5 Hz, 1H), 2.48 – 2.41 (m, 0.2H), 2.36 (ddd, *J* = 14.0, 11.8, 5.3 Hz, 1H), 2.24 (td, *J* = 15.3, 14.6, 3.2 Hz, 0.2H), 2.06 – 1.98 (m, 1.2H), 1.96 – 1.90 (m, 1H), 1.90 – 1.85 (m, 0.2H), 1.86 – 1.76 (m, 1.2H), 1.70 (dd, *J* = 15.9, 5.5 Hz, 1.2H), 1.57 (s, 0.8H), 1.52 (dd, *J* = 2.3, 1.3 Hz, 3H), 1.23 – 1.15 (m, 3.6H), 0.85 – 0.79 (m, 1.2H).

^{13}C NMR (101 MHz, $CDCl_3$) *major regioisomer* δ 173.9, 145.5, 143.0, 135.8, 129.7, 129.3, 127.6, 127.6, 126.9, 125.8, 125.8, 123.0, 60.2, 53.9, 41.7, 33.9, 30.1, 29.8, 24.4, 23.9, 22.5, 14.1.

HRMS (ESI) Calculated for $C_{25}H_{30}NaO_2$ $[M+Na]^+$: 385.2138 found: 385.2139.

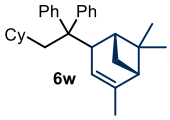


Ethyl 4,4-diphenyl-4-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)butanoate (6v)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), 1-phenylcyclohexene **2f** (160 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 70:30 hexanes/toluene) to afford product **6v** as a colorless oil (22.0 mg, 52% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 5H), 7.28 – 7.17 (m, 9H), 6.17 (dt, *J* = 2.6, 1.4 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.37 (d, *J* = 9.5 Hz, 1H), 2.62 (ddd, *J* = 14.0, 11.6, 4.8 Hz, 1H), 2.49 (ddd, *J* = 14.0, 11.5, 5.6 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.12 – 1.93 (m, 5H), 1.81 – 1.74 (m, 1H), 1.72 – 1.64 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.03 (tdd, *J* = 12.7, 10.2, 3.3 Hz, 1H).

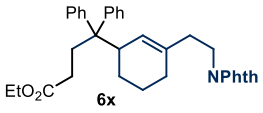
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 145.1, 142.9, 142.8, 138.4, 129.7, 129.3, 128.1, 127.8, 126.7, 126.6, 126.1, 126.0, 125.3, 60.3, 54.2, 42.1, 34.1, 30.1, 27.4, 24.2, 22.7, 14.1.
HRMS (ESI) Calculated for $C_{30}H_{32}NaO_2$ $[M+Na]^+$: 447.2295 found: 447.2293.

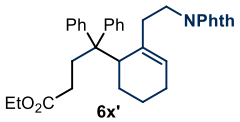


(1S,5R)-4-(2-cyclohexyl-1,1-diphenylethyl)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (6w)

Prepared according to General Procedure B using the radical precursor **1h** (49.3 mg, 0.12 mmol), α-pinene **2g** (158 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, cyclohexane) to afford product **6w** as a colorless oil (19.4 mg, 49% yield, >10:1 *d.r.*, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 10H), 5.49 (p, *J* = 1.8 Hz, 1H), 3.33 (q, *J* = 2.3 Hz, 1H), 2.21 (tt, *J* = 5.8, 1.9 Hz, 1H), 2.14 (dd, *J* = 14.1, 3.5 Hz, 1H), 1.87 (dd, *J* = 14.1, 5.2 Hz, 1H), 1.66 (td, *J* = 5.4, 1.3 Hz, 1H), 1.59 (dd, *J* = 2.5, 1.6 Hz, 3H), 1.55 – 1.41 (m, 6H), 1.23 (s, 3H), 1.03 (td, *J* = 11.3, 4.4 Hz, 3H), 0.97 (s, 3H), 0.95 – 0.84 (m, 3H), 0.72 – 0.63 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 145.5, 129.6, 129.4, 127.2, 126.9, 125.5, 125.4, 116.8, 54.0, 46.9, 46.2, 44.8, 42.0, 41.3, 35.6, 35.1, 33.6, 26.6, 26.4, 26.3, 25.4, 23.2, 20.7.
HRMS (APCI) Calculated for $C_{30}H_{39}$ $[M+H]^+$: 399.3046 found: 399.3036.

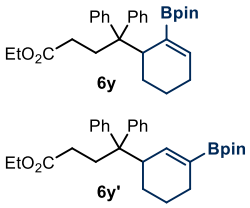




ethyl 4-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)cyclohex-2-en-1-yl)-4,4-diphenylbutanoate (6x)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), 2-(2-(cyclohex-1-en-1-yl)ethyl)isoindoline-1,3-dione **2h** (128 mg, 5.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 90:10 hexanes/EtOAc) to afford product **6x** as a colorless oil (32.3 mg, 62% yield, 5:1 *r.r.*, average of two runs). When using catalyst **C7**, **6x** was obtained as a colorless oil (25 mg, 48% yield, 10:1 *r.r.*).

^{1}H NMR (500 MHz, $CDCl_3$) *5:1 mixture of regioisomers* δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.79 (td, *J* = 5.4, 2.3 Hz, 2H), 7.22 – 7.11 (m, 6H), 7.11 – 7.06 (m, 2H), 7.03 – 6.98 (m, 2H), 5.47 (s, 1H), 5.26 (m, 0.2H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.70 – 3.63 (m, 1H), 3.60 (ddd, *J* = 13.4, 7.8, 5.3 Hz, 1H), 3.02 (d, *J* = 9.2 Hz, 1H), 2.46 (ddd, *J* = 14.0, 11.2, 5.2 Hz, 1H), 2.35 (ddd, *J* = 13.9, 11.1, 5.9 Hz, 1H), 2.20 (dt, *J* = 15.0, 7.6 Hz, 1H), 2.13 (dt, *J* = 12.8, 6.2 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.86 (dt, *J* = 13.5, 4.1 Hz, 2H), 1.70 – 1.61 (m, 2H), 1.58 – 1.49 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.90 – 0.81 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) *major regioisomer* δ 173.8, 168.1, 145.1, 142.8, 135.9, 133.8, 132.2, 129.7, 129.1, 127.6, 126.9, 126.0, 125.9, 125.8, 123.1, 60.2, 53.7, 41.3, 36.9, 36.4, 33.9, 29.9, 27.6, 24.2, 22.5, 14.1.
HRMS (ESI) Calculated for $C_{34}H_{35}NNaO_4$ $[M+Na]^+$: 544.2458 found: 544.2469.



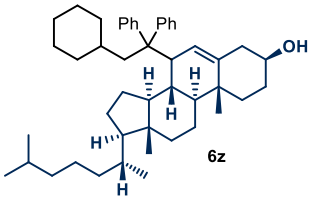
ethyl 4,4-diphenyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-2-en-1-yl)butanoate (6y)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2i** (110 µL, 0.5 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 50:50 hexanes/toluene) to afford product **6y** as a colorless oil (21.3 mg, 45% yield, 1.2:1 *r.r.*, average of two runs). When using catalyst **C6**, the yield (50% yield, 1:4 *r.r.*) of **6y'** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

^{1}H NMR (500 MHz, $CDCl_3$) *1.2:1 mixture of regioisomers* δ 7.43 – 7.39 (m, 1H), 7.36 – 7.29 (m, 3H), 7.27 – 7.20 (m, 6H), 6.68 (d, *J* = 2.6 Hz, 0.5H), 6.61 (ddd, *J* = 4.9, 3.4, 1.2 Hz, 0.5H), 4.06 (q, *J* = 7.1 Hz, H), 3.99 (qd, *J* = 7.1, 0.9 Hz, 1H), 3.60 – 3.55 (m, 1H), 2.56 – 2.44 (m, 1H), 2.43 – 2.32 (m, 1H), 2.20 (ddd, *J* = 15.1, 11.6, 5.3 Hz, 1H), 1.98 (dd, *J* = 9.3, 7.4 Hz, 1H), 1.75 (qd, *J* = 6.1, 3.0 Hz, 1H), 1.70 – 1.63 (m, 1H), 1.28 (d, *J* = 2.2 Hz, 1H), 1.26 (s, 4H), 1.24 (s, 3H), 1.21 (d, *J* = 2.0 Hz, 3H), 1.20 – 1.19 (m, 3H), 1.17 (d, *J* = 7.1 Hz, 1H), 1.07 – 0.99 (m, 1H), 0.95 – 0.82 (m, 2H), 0.73 – 0.64 (m, 0.5H).

^{13}C NMR (101 MHz, $CDCl_3$) *1.2:1 mixture of regioisomers* δ 174.0, 173.9, 146.9, 143.8, 143.3, 143.0, 130.6, 130.4, 129.8, 129.4, 127.8, 127.4, 127.0, 126.0, 125.9, 83.2, 82.9, 60.3, 60.0, 56.7, 53.9, 41.9, 40.1, 36.3, 33.9, 30.7, 30.0, 26.3, 25.1, 25.0, 24.9, 24.4, 24.3, 22.5, 19.4, 14.1.

HRMS (ESI) Calculated for $C_{30}H_{39}NaO_4{}^{10}B$ $[M+Na]^+$: 496.2870 found: 496.2864.



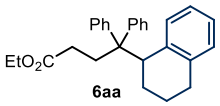
(3S,8S,9S,10R,13R,14S,17R)-7-(2-cyclohexyl-1,1-diphenylethyl)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (6z)

Prepared according to General Procedure B using the radical precursor **1h** (49.3 mg, 0.12 mmol), cholesterol **2j** (193 mL, 0.5 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 95:5 hexanesEtOAc) to afford product **6y** as a white solid. The yield (48% yield, 5:1 *d.r.*, average of two runs) of **6z** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

^{1}H NMR (500 MHz, $CDCl_3$) *5:1 mixture of diastereoisomers* δ 7.63 – 6.97 (m, 10H), 5.61 – 5.35 (m, 1H), 3.58 – 3.40 (m, 1H), 3.25 (d, *J* = 71.6 Hz, 1H), 2.37 (d, *J* = 14.0 Hz, 1H), 2.25 – 2.14 (m, 1H), 2.02 – 1.95 (m, 1H), 1.90 (td, *J* = 11.5, 7.5 Hz, 2H), 1.86 – 1.74 (m, 3H), 1.72 (d, *J* = 3.5 Hz, 2H), 1.64 – 1.49 (m, 7H), 1.39 (ddt, *J* = 33.2, 17.5, 7.1 Hz, 9H), 1.25 – 1.12 (m, 10H), 1.11 – 0.99 (m, 4H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.90 (dt, *J* = 6.6, 2.6 Hz, 7H), 0.74 – 0.58 (m, 1H), 0.16 (q, *J* = 12.0, 10.8 Hz, 1H), -0.21 (d, *J* = 12.5 Hz, 1H), -0.57 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) *5:1 mixture of diastereoisomers* δ 146.9, 142.2, 140.9, 129.1, 126.1, 126.1, 125.6, 125.4, 71.1, 60.4, 59.0, 56.7, 56.4, 49.7, 46.3, 44.8, 43.1, 42.3, 41.8, 39.5, 38.5, 37.6, 37.4, 36.2, 36.1, 34.8, 34.7, 34.3, 31.6, 28.8, 28.1, 28.0, 26.8, 26.4, 26.0, 24.1, 24.0, 22.8, 22.6, 19.1, 19.0, 15.5, 13.2, 11.1.

HRMS (APCI) Calculated for $C_{47}H_{69}O$ $[M+H]^+$: 649.5186, found: 649.5180.



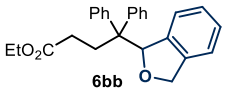
Ethyl 4,4-diphenyl-4-(1,2,3,4-tetrahydronaphthalen-1-yl)butanoate (6aa)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), tetralin **2k** (136 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). Multiple purifications by column chromatography resulted in poor separation from several unidentified byproducts. The yield (60%, average of two runs) of **6aa** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard. An analytical amount of pure compound was isolated by preparative TLC (50:50 hexanes/toluene) to obtain a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 7H), 7.16 – 7.10 (m, 3H), 7.09 – 7.02 (m, 4H), 6.81 (d, J = 7.3 Hz, 1H), 4.06 (qd, J = 7.2, 3.0 Hz, 2H), 2.67 (ddd, J = 14.0, 11.6, 4.1 Hz, 1H), 2.37 (ddd, J = 14.1, 12.1, 5.3 Hz, 1H), 2.28 – 2.20 (m, 1H), 2.16 (ddd, J = 16.1, 12.1, 4.0 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.88 (ddt, J = 14.3, 11.8, 5.9 Hz, 1H), 1.67 (ddd, J = 16.1, 11.7, 5.3 Hz, 1H), 1.57 – 1.50 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H), 1.15 (dddd, J = 16.7, 10.3, 6.1, 3.0 Hz, 1H), 0.80 – 0.70 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 143.5, 137.0, 130.8, 130.3, 130.2, 128.5, 127.8, 127.8, 127.4, 127.2, 126.3, 126.0, 125.9, 124.7, 60.2, 57.4, 44.2, 35.5, 30.7, 29.1, 25.1, 23.2, 14.2, 14.2.

HRMS (ESI) Calculated for $C_{28}H_{30}NaO_2$ $[M+Na]^+$: 421.2138, found: 421.2138.



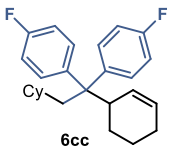
Ethyl 4-(1,3-dihydroisobenzofuran-1-yl)-4,4-diphenylbutanoate (6bb)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), 1,3-dihydrobenzofuran **2l** (109 µL, 1.0 mmol), and 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 60:40 hexanes/toluene) to afford product **6bb** as a colorless oil (21.4 mg, 55% yield, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.27 – 7.13 (m, 9H), 7.08 – 6.97 (m, 2H), 6.44 (d, *J* = 7.7 Hz, 1H), 6.20 (d, *J* = 3.0 Hz, 1H), 4.88 (d, *J* = 12.1 Hz, 1H), 4.48 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.78 (ddd, *J* = 14.0, 11.5, 4.9 Hz, 1H), 2.45 (ddd, *J* = 14.0, 11.4, 5.7 Hz, 1H), 2.28 – 2.13 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 144.1, 142.8, 140.8, 138.6, 129.7, 129.5, 127.6, 127.5, 126.4, 126.3, 126.2, 123.6, 120.4, 88.9, 72.9, 60.2, 56.3, 31.6, 30.5, 14.1, 1.0.

HRMS (ESI) Calculated for $C_{26}H_{26}NaO_3$ $[M+Na]^+$: 409.1774 found: 409.1776.

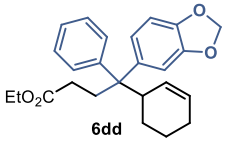


4,4'-(1-(cyclohex-2-en-1-yl)-2-cyclohexylethane-1,1-diyl)bis(fluorobenzene) (6cc)

Prepared according to General Procedure B using the radical precursor **1h** (49.3 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), and 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) **5b** (21.6 mg, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, pentane) to afford product **6cc** as a colorless oil (25.8 mg, 68% yield, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (pd, *J* = 6.6, 6.2, 3.1 Hz, 4H), 6.96 (td, *J* = 8.8, 6.3 Hz, 4H), 5.81 (dt, *J* = 10.4, 2.2 Hz, 1H), 5.62 (ddt, *J* = 10.3, 5.1, 2.6 Hz, 1H), 3.15 (ddq, *J* = 9.6, 4.7, 2.3 Hz, 1H), 2.03 – 1.82 (m, 4H), 1.66 (dddd, *J* = 19.4, 8.8, 4.4, 2.2 Hz, 1H), 1.52 – 1.47 (m, 3H), 1.11 (tt, *J* = 7.5, 3.4 Hz, 1H), 1.07 – 0.96 (m, 5H), 0.93 – 0.86 (m, 2H), 0.85 – 0.74 (m, 3H).

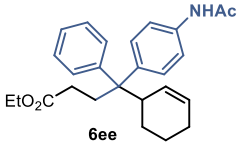
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 16.2 Hz), 160.0 (d, *J* = 16.3 Hz), 141.7 (d, *J* = 3.4 Hz), 140.1 (d, *J* = 3.3 Hz), 131.2 (d, *J* = 7.5 Hz), 131.0 (d, *J* = 7.6 Hz), δ 129.2, 128.8, 114.1 (d, *J* = 20.8 Hz), 113.5 (d, *J* = 20.6 Hz), 54.0, 46.9, 41.4, 35.4, 35.2, 33.7, 26.5 (d, *J* = 8.6 Hz), 26.2, 25.0 (d, *J* = 3.9 Hz), 22.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.7
HRMS (APCI) Calculated for $C_{26}H_{31}F_2$ $[M+H]^+$: 381.2388, found: 381.2380.



Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-4-(cyclohex-2-en-1-yl)-4-phenylbutanoate (6dd)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), 5-(1-phenylvinyl)benzo[d][1,3]dioxole **5c** (22.4 mg, 0.1 mmol), and catalyst **C5** (7.6 mg, 0.02 mmol). The crude mixture was purified by column chromatography (SiO_2, 60:40 hexanes/toluene) to afford product **6dd** as a colorless oil (29.5 mg, 73% yield, 1.1:1 dr, average of two runs).

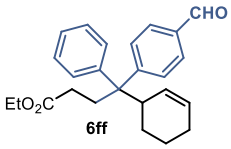
^{1}H NMR (400 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.32 – 7.19 (m, 5H), 6.79 – 6.66 (m, 3H), 5.98 – 5.94 (m, 2H), 5.85 – 5.73 (m, 1H), 5.67 – 5.61 (m, 1H), 4.07 (dq, *J* = 9.3, 7.1 Hz, 2H), 3.13 (d, *J* = 8.5 Hz, 1H), 2.50 (ddd, *J* = 13.8, 11.8, 4.7 Hz, 1H), 2.36 (ddd, *J* = 11.6, 7.8, 5.8 Hz, 1H), 2.04 (ddd, *J* = 16.3, 11.6, 4.7 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.90 (d, *J* = 5.2 Hz, 2H), 1.80 – 1.68 (m, 1H), 1.58 – 1.48 (m, 1H), 1.23 (q, *J* = 7.0 Hz, 3H), 1.07 – 0.95 (m, 1H), 0.93 – 0.84 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 173.9, 173.8, 147.3, 146.7, 145.6, 145.3, 143.0, 139.3, 137.0, 129.7, 129.3, 129.1, 129.0, 129.0, 127.8, 127.2, 126.0, 126.0, 122.7, 122.4, 110.6, 110.0, 107.3, 106.8, 100.9, 100.8, 60.3, 53.6, 42.0, 41.7, 34.3, 34.1, 30.2, 30.1, 25.1, 25.0, 24.8, 24.7, 22.4, 14.2.
HRMS (ESI) Calculated for $C_{25}H_{28}NaO_4$ $[M+Na]^+$: 415.1880, found: 415.1882.



Ethyl 4-(4-acetamidophenyl)-4-(cyclohex-2-en-1-yl)-4-phenylbutanoate (6ee)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), N-(4-(1-phenylvinyl)phenyl)acetamide **5d** (23.7 mg, 0.1 mmol), and catalyst **C5** (7.6 mg, 0.02 mmol). Multiple purifications by column chromatography resulted in poor separation from several unidentified byproducts. The yield (83%,1.1:1 dr, average of two runs) of **6ee** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard. An analytical amount of the pure compound was isolated by preparative TLC (90:10 hexanes/EtOAc) to obtain a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.14 (m, 6H), 5.77 (d, *J* = 10.8 Hz, 1H), 5.60 (d, *J* = 10.8 Hz, 1H), 4.06 (qd, *J* = 7.2, 2.2 Hz, 2H), 3.15 (s, 1H), 2.54 (ddd, *J* = 13.9, 11.7, 4.5 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.20 (s, 3H), 2.10 – 1.99 (m, 1H), 1.97 – 1.82 (m, 3H), 1.61 (s, 4H), 1.22 (td, *J* = 7.1, 1.3 Hz, 3H), 0.95 (dd, *J* = 24.8, 12.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 173.8, 168.1, 145.1, 138.9, 135.8, 130.3, 129.9, 129.6, 129.2, 129.0, 128.9, 127.7, 127.1, 126.0, 125.9, 119.0, 118.4, 60.3, 53.4, 41.6, 34.0, 30.0, 25.0, 24.6, 22.3, 14.1, 1.0.
HRMS (ESI) Calculated for $C_{26}H_{31}NaNO_3$ $[M+Na]^+$: 428.2196, found: 428.2184.



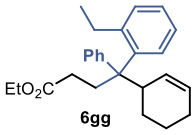
4-(1-(cyclohex-2-en-1-yl)-2-cyclohexyl-1-phenylethyl)benzaldehyde (6ff)

Prepared according to General Procedure B using the radical precursor **1h** (49.3 mg, 0.12 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), 4-(1-phenylvinyl)benzaldehyde **5e** (20.8 mg, 0.1 mmol), and catalyst **C5** (7.6 mg, 0.02 mmol). The crude mixture was purified by column chromatography (SiO_2, 95:5 hexanes/CH_2Cl_2) to afford product **6ff** as a colorless oil (23 mg, 62% yield,1.1:1 dr, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 10.02 (d, *J* = 3.3 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.44 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.31 – 7.18 (m, 5H), 5.89 (dq, *J* = 10.3, 2.0 Hz, 0.5H), 5.82 (dp, *J* = 10.4, 1.8 Hz, 0.5H), 5.62 (ddt, *J* = 10.3, 4.9, 2.5 Hz, 1H), 3.32 – 3.22 (m, 1H), 2.09 (ddd, *J* = 14.0, 8.0, 3.9 Hz, 1H), 2.03 (ddd, *J* = 14.2, 4.9, 2.7 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.87 (d, *J* = 17.3 Hz, 1H), 1.56 (qdd, *J* = 10.6, 4.6, 2.5 Hz, 3H), 1.51 – 1.44 (m, 3H), 1.13 (tt, *J* = 7.0, 3.9 Hz, 1H), 1.08 – 0.94 (m, 5H), 0.88 (dddd, *J* = 11.1, 7.4, 5.4, 1.9 Hz, 1H), 0.84 – 0.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 192.2, 192.1, 154.1, 152.4, 145.3, 143.7, 134.1, 134.0, 130.5, 130.4, 129.7, 129.5, 129.3, 129.2, 128.8, 128.7, 128.2, 127.6, 127.0, 126.0, 126.0, 55.6, 46.5, 41.4, 41.2, 35.4, 35.4, 35.2, 35.2, 33.7, 33.6, 26.5, 26.5, 26.4, 26.2, 26.1, 25.0, 25.0, 22.4, 22.3.

HRMS (ESI) Calculated for $C_{27}H_{32}NaO$ $[M+Na]^+$: 395.2345, found: 395.2348.



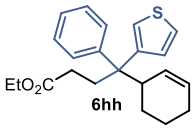
Ethyl 4-(cyclohex-2-en-1-yl)-4-(2-ethylphenyl)-4-phenylbutanoate (6gg)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), 1-ethyl-2-(1-phenylvinyl)benzene **5f** (20.8 mg, 0.1 mmol), and catalyst **C5** (7.6 mg, 0.02 mmol). Multiple purifications by column chromatography resulted in poor separation from several unidentified byproducts. The yield (76%, 1.5:1 *d.r.*, average of two runs) of **6gg** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard. An analytical amount of the pure compound was isolated by preparative TLC (20:80 hexanes/toluene) to obtain a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *Major diastereoisomer* δ 7.48 (t, *J* = 7.0 Hz,), 7.32 – 7.01 (m), 5.97 (d, *J* = 10.5 Hz, 1H), 5.77 (dq, *J* = 10.3, 3.4 Hz, 1H), 4.11 – 4.04 (q, 2H), 3.13 (m, *J* = 2.8 Hz, 1H), 2.87 (ddd, *J* = 20.8, 11.6, 5.2 Hz), 2.47 – 2.22 (m), 2.09 (ddt, *J* = 26.8, 14.7, 7.3 Hz), 1.92 – 1.74 (m), 1.71 – 1.61 (m), 1.22 (t, *J* = 7.1, 3H), 1.18 – 1.00 (m), 0.87 (t, *J* = 7.5 Hz, 3H). *Minor diastereoisomer* δ 7.48 (t, *J* = 7.0 Hz,), 7.32 – 7.01 (m), 5.86 (s, 1H), 5.54 (dd, *J* = 10.4, 3.5 Hz, 1H), 4.11 – 4.04 (q, 2H), 3.24 (s, 1H), 2.87 (ddd, *J* = 20.8, 11.6, 5.2 Hz), 2.47 – 2.22 (m), 2.09 (ddt, *J* = 26.8, 14.7, 7.3 Hz), 1.92 – 1.74 (m), 1.71 – 1.61 (m), 1.22 (t, *J* = 7.1, 3H), 1.18 – 1.00 (m), 0.87 (t, *J* = 7.5, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *1.5:1 mixture of diastereoisomers* δ 173.9, 144.3, 141.9, 141.8, 131.6, 131.3, 130.0, 129.4, 129.0, 128.7, 128.5, 127.6, 127.3, 127.0, 126.4, 125.6, 125.6, 124.6, 124.5, 60.3, 60.2, 52.8, 52.5, 30.9, 30.5, 30.1, 30.0, 29.7, 26.7, 26.2, 25.9, 25.1, 25.0, 24.0, 22.9, 21.5, 15.3, 15.1, 14.1, 1.0.

HRMS (ESI) Calculated for $C_{26}H_{32}NaO_2$ $[M+Na]^+$: 399.2295, found: 399.2281.



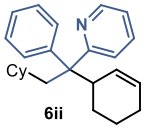
Ethyl 4-(cyclohex-2-en-1-yl)-4-phenyl-4-(thiophen-3-yl)butanoate (6hh)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), 3-(1-phenylvinyl)thiophene **5g** (18.6 mg, 0.1 mmol), and catalyst **C5** (7.6 mg, 0.02 mmol). Multiple purifications by column chromatography resulted in poor separation from several unidentified byproducts. The yield (69%, 1.1:1 dr, average of two runs) of **6hh** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard. An analytical amount of the pure compound was isolated by preparative TLC (70:30 hexanes/toluene) to obtain a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.32 – 7.19 (m, 6H), 7.13 (dd, *J* = 2.9, 1.4 Hz, 0.5H), 6.99 (dd, *J* = 3.0, 1.4 Hz, 0.5H), 6.87 (dt, *J* = 5.1, 1.1 Hz, 1H), 5.79 (d, *J* = 10.5 Hz, 0.5H), 5.72 (d, *J* = 10.4 Hz, 0.5H), 5.62 (tq, *J* = 7.7, 2.4 Hz, 1H), 4.12 – 4.04 (m, 2H), 3.16 – 3.00 (m, 1H), 2.56 (dddd, *J* = 14.3, 11.8, 10.0, 4.6 Hz, 1H), 2.43 – 2.32 (m, 1H), 2.19 – 2.05 (m, 1H), 2.03 – 1.84 (m, 3H), 1.79 – 1.46 (m, 3H), 1.23 (td, *J* = 7.1, 4.1 Hz, 3H), 1.11 – 0.96 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 173.8, 146.5, 144.8, 144.4, 142.5, 129.7, 129.2, 129.1, 128.9, 128.9, 128.8, 128.7, 128.5, 127.9, 127.2, 126.1, 126.1, 124.5, 123.4, 122.4, 122.4, 60.3, 52.0, 51.9, 43.3, 42.5, 34.9, 33.7, 30.2, 30.2, 29.7, 25.0, 25.0, 24.6, 24.6, 22.3, 22.2, 14.1.

HRMS (ESI) Calculated for $C_{22}H_{26}NaO_2S$ $[M+Na]^+$: 377.1546, found: 377.1547.



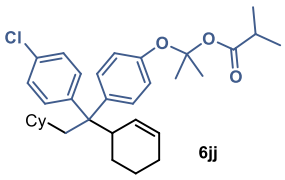
2-(1-(cyclohex-2-en-1-yl)-2-cyclohexyl-1-phenylethyl)pyridine (6ii)

Prepared according to General Procedure B using the radical precursor **1h** (41.1 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), 2-(1-phenylvinyl)pyridine **5h** (21.7 mg, 0.12 mmol), and sodium hydrogen phosphate (14.2 mg, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 98:2 hexanes/EtOAc) to afford product **6ii** as a pale-yellow oil (21.7 mg, 63% yield, 1.3:1 *d.r.*, average of two runs).

^{1}H NMR (400 MHz, $CDCl_3$) *Major diastereoisomer* δ 8.66 (ddd, *J* = 4.8, 2.0, 0.9 Hz, 1H), 7.50 (td, *J* = 7.7, 1.9 Hz), 7.32 – 7.18 (m), 7.14 – 7.10 (m), 7.06 (ddt, *J* = 15.3, 8.1, 1.1 Hz), 5.78 (dt, *J* = 10.4, 2.0 Hz, 1H), 5.58 (dddt, *J* = 15.2, 10.3, 5.2, 2.5 Hz), 3.65 – 3.55 (m, 1H), 2.13 – 2.09 (m, 2H), 2.00 – 1.81 (m, 4H), 1.67 – 1.42 (m, 12H), 1.23 (tt, *J* = 11.1, 3.9 Hz, 1H), 1.17 – 1.09 (m, 2H), 1.01 (tdd, *J* = 14.0, 9.6, 6.0 Hz), 0.92 – 0.83 (m), 0.76 (td, *J* = 11.8, 5.6 Hz). *Minor diastereoisomer* δ 8.63 (ddd, *J* = 4.8, 2.0, 0.9 Hz, 1H), 7.50 (td, *J* = 7.7, 1.9 Hz), 7.32 – 7.18 (m), 7.14 – 7.10 (m), 7.06 (ddt, *J* = 15.3, 8.1, 1.1 Hz), 5.93 (dp, *J* = 10.4, 1.8 Hz, 1H), 5.58 (dddt, *J* = 15.2, 10.3, 5.2, 2.5 Hz), 3.43 – 3.34 (m, 1H), 2.20 (d, *J* = 4.4 Hz), 2.00 – 1.81 (m), 1.67 – 1.42 (m), 1.23 (tt, *J* = 11.1, 3.9 Hz), 1.17 – 1.09 (m), 1.01 (tdd, *J* = 14.0, 9.6, 6.0 Hz), 0.92 – 0.83 (m), 0.76 (td, *J* = 11.8, 5.6 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) *1.3:1 mixture of diastereoiomers* δ 166.1, 164.7, 147.9, 147.4, 145.5, 143.6, 135.0, 134.3, 130.2, 129.8, 129.5, 129.4, 128.6, 128.1, 127.3, 126.8, 125.9, 125.7, 125.5, 125.4, 120.8, 120.7, 57.1, 57.0, 45.9, 45.8, 41.7, 40.9, 35.3, 35.3, 35.1, 35.0, 33.7, 33.4, 26.7, 26.6, 26.4, 26.3, 26.2, 25.1, 25.1, 24.9, 24.7, 22.5, 22.4.

HRMS (APCI) Calculated for $C_{25}H_{32}N$ $[M+H]^+$: 346.2529 found: 346.2530.



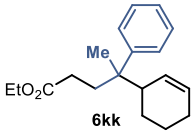
2-(4-(1-(4-Chlorophenyl)-1-(cyclohex-2-en-1-yl)-2-cyclohexylethyl)phenoxy)propan-2-yl isobutyrate (6jj)

Prepared according to General Procedure B using the radical precursor **1h** (61.7 mg, 0.15 mmol), cyclohexene **2a** (101 µL, 2.0 mmol), and 2-(4-(1-(4-chlorophenyl)vinyl)phenoxy)propan-2-yl isobutyrate **5i** (35.9 mg, 0.1 mmol). The crude mixture was purified by column chromatography (SiO_2, 80:1 hexanes/EtOAc) to afford product **6jj** as a colorless oil (38.2 mg, 73% yield,1.1:1 dr, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diasteroisomers* δ 7.22 – 7.18 (m, 2H), 7.16 – 7.11 (m, 2H), 7.04 – 7.01 (m, 2H), 6.76 – 6.69 (m, 2H), 5.76 (dd, *J* = 20.8, 10.5 Hz, 1H), 5.58 – 5.52 (m, 1H), 5.08 (dtd, *J* = 12.5, 6.3, 2.3 Hz, 2H), 3.15 – 3.03 (m, 1H), 1.95 (ddd, *J* = 14.1, 6.4, 3.8 Hz, 1H), 1.90 – 1.78 (m, 3H), 1.59 (s, 3H), 1.56 (s, 3H), 1.52 – 1.39 (m, 5H), 1.22 (dd, *J* = 6.3, 0.9 Hz, 3H), 1.20 (dd, *J* = 6.2, 1.9 Hz, 3H), 1.05 (d, *J* = 12.6 Hz, 2H), 1.02 – 0.91 (m, 4H), 0.87 – 0.80 (m, 1H), 0.80 – 0.64 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) *1.1:1 mixture of diasteroisomers* δ 173.9, 173.8, 153.5, 153.3, 144.9, 143.2, 139.3, 137.4, 131.4, 131.3, 131.1, 131.1, 130.3, 130.1, 129.1, 129.0, 129.0, 128.9, 128.5, 128.3, 128.0, 127.7, 127.3, 126.8, 118.5, 118.3, 118.2, 117.1, 79.0, 78.9, 68.8, 68.8, 54.1, 54.0, 46.7, 46.6, 41.4, 41.3, 35.5, 35.4, 35.2, 35.2, 33.7, 33.6, 33.3, 26.6, 26.5, 26.5, 26.2, 26.2, 25.4, 25.3, 25.3, 25.2, 25.1, 25.0, 25.0, 25.0, 22.4, 22.3, 21.6, 21.5.

HRMS (ESI) Calculated for $C_{33}H_{43}ClNaO_3$ $[M+Na]^+$: 545.2793, found: 545.2787.



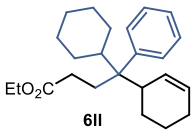
Ethyl 4-(cyclohex-2-en-1-yl)-4-phenylpentanoate (6kk)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (202 µL, 2.0 mmol), α-methyl styrene **5j** (15.6 µL, 0.12 mmol), sodium hydrogen phosphate (14.2 mg, 0.1 mmol.), and catalyst **C5** (7.6 mg, 0.02 mmol). The crude mixture was purified by column chromatography (SiO_2, 75:25 hexanes/toluene) to afford product **6kk** as a colorless oil (13.7 mg, 42% yield, 1.1:1 *d.r.*, average of two runs).

^{f1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.30 (dt, *J* = 6.9, 4.5 Hz, 3H), 7.27 – 7.24 (m, 1H), 7.20 – 7.16 (m, 1H), 5.78 (s, 1H), 5.65 – 5.59 (m, 0.5H), 5.14 (dp, *J* = 10.4, 2.0 Hz, 0.5H), 4.05 (qdd, *J* = 6.9, 4.1, 2.4 Hz, 2H), 2.52 (dq, *J* = 8.4, 2.7 Hz, 0.5H), 2.46 (ddd, *J* = 8.8, 6.7, 4.7 Hz, 0.5H), 2.20 – 2.10 (m, 2H), 2.10 – 2.04 (m, 1H), 2.03 – 1.95 (m, 0.5H), 1.95 – 1.77 (m, 3H), 1.64 (ddd, *J* = 12.3, 6.0, 3.0 Hz, 0.5H), 1.50 (dddd, *J* = 19.9, 12.9, 7.9, 2.7 Hz, 0.5H), 1.45 – 1.30 (m, 1.5H), 1.29 – 1.22 (m, 2H), 1.25 (s, 3H) 1.22 – 1.17 (m, 3H), 1.07 (tdd, *J* = 13.1, 10.7, 3.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 174.2, 146.3, 146.0, 129.1, 128.9, 128.6, 128.3, 128.1, 126.9, 126.6, 125.7, 125.6, 60.2, 46.8, 46.7, 43.3, 34.6, 34.5, 29.9, 29.9, 29.7, 25.3, 25.3, 24.8, 24.3, 22.8, 22.7, 18.6, 14.2.

HRMS (ESI) Calculated for $C_{19}H_{26}NaO_2$ $[M+Na]^+$: 309.1825, found: 309.1829.



Ethyl 4-(cyclohex-2-en-1-yl)-4-cyclohexyl-4-phenylbutanoate (6ll)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (202 µL, 2.0 mmol), (1-cyclohexylvinyl)benzene **5k** (18.6 mg, 0.1 mmol), sodium hydrogen phosphate (14.2 mg, 0.1 mmol.), and catalyst **C5** (7.6 mg, 0.02 mmol). The crude mixture was purified by

preparative TLC (SiO_2, 50:50 hexanes/toluene) to afford product **6ll** as a colorless oil (16.7 mg, 47% yield, 1.1:1 *d.r.*, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.34 – 7.24 (m, 4H), 7.21 – 7.16 (m, 1H), 5.85 (d, *J* = 10.4 Hz, 0.5H), 5.69 – 5.64 (m, 0.5H), 5.51 – 5.44 (m, 0.5H), 5.34 (d, *J* = 10.5 Hz, 0.5H), 4.17 – 4.10 (m, 2H), 3.22 – 3.13 (m, 0.5H), 3.09 – 2.98 (m, 0.5H), 2.62 (t, *J* = 13.9 Hz, 0.5H), 2.59 – 2.48 (m, 1H), 2.44 – 2.39 (m, 0.5H), 2.39 – 2.25 (m, 1H), 2.21 – 2.07 (m, 1H), 2.04 – 1.94 (m, 2H), 1.94 – 1.87 (m, 1H), 1.86 – 1.79 (m, 2H), 1.79 – 1.45 (m, 4H), 1.31 – 1.23 (m, 3H), 1.04 – 0.91 (m, 2H), 0.91 – 0.80 (m, 2H), 0.80 – 0.69 (m, 1H), 0.57 – 0.46 (m, 0.5H), 0.28 (q, *J* = 12.3 Hz, 0.5H).

^{13}C NMR (126 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 174.5, 174.4, 143.6, 132.1, 129.8, 128.8, 128.0, 127.5, 127.4, 126.3, 125.5, 125.4, 60.3, 60.2, 49.2, 48.1, 45.6, 42.2, 40.3, 38.6, 30.9, 30.6, 30.3, 29.7, 28.6, 28.5, 28.3, 28.1, 28.0, 27.5, 27.4, 27.3, 26.6, 26.4, 25.6, 25.5, 25.4, 24.1, 23.5, 23.3, 14.3.

HRMS (ESI) Calculated for $C_{24}H_{34}NaO_2$ $[M+Na]^+$: 377.2451, found: 377.2455.

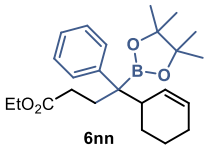
Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-4-(cyclohex-2-en-1-yl)-4-phenylbutanoate (6mm)

Prepared according to General Procedure B using the radical precursor **4b** (72.2 mg, 0.15 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), tert-butyl 4-(1-phenylvinyl)piperidine-1-carboxylate **5l** (28.7 mg, 0.1 mmol), sodium hydrogen phosphate (14.2 mg, 0.1 mmol.), and catalyst **C5** (7.6 mg, 0.02 mmol). The crude mixture was purified by column chromatography (SiO_2, 90:10 hexanes/Et_2O) to afford product **6mm** as a colorless oil (20.0 mg, 44% yield, 1.1:1 *d.r.*, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.36 – 7.29 (m, 3H), 7.27 – 7.20 (m, 2H), 5.86 (d, *J* = 10.6 Hz, 0.5H), 5.73 (dd, *J* = 10.5, 3.4 Hz, 0.5H), 5.52 (dd, *J* = 10.4, 3.4 Hz, 0.5H), 5.34 (d, *J* = 11.1 Hz, 0.5H), 4.20 – 4.01 (m, 4H), 3.11 (d, *J* = 51.5 Hz, 1H), 2.68 – 2.52 (m, 4H), 2.37 (td, J = 14.8, 14.1, 10.2 Hz, 1H), 2.23 – 2.13 (m, 1H), 2.08 – 1.90 (m, 5H), 1.75 (dd, *J* = 9.9, 5.6 Hz, 3H), 1.40 (d, *J* = 10.8 Hz, 9H), 1.31 – 1.27 (m, 4H), 0.91 – 0.84 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 174.3, 174.1, 154.7, 154.6, 142.6, 140.0, 131.6, 129.1, 128.7, 128.2, 127.9, 127.8, 127.7, 126.7, 125.9, 125.7, 79.2, 79.2, 60.4, 60.3, 48.6, 47.6, 44.2, 41.2, 40.0, 38.5, 31.5, 30.6, 30.5, 28.4, 28.3, 28.3, 27.9, 25.6, 25.4, 25.4, 24.1, 23.4, 23.2, 22.6, 14.2, 14.1.

HRMS (ESI) Calculated for $C_{28}H_{41}NNaO_4$ $[M+Na]^+$: 478.2928, found: 478.2927.



Ethyl 4-(cyclohex-2-en-1-yl)-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (6nn)

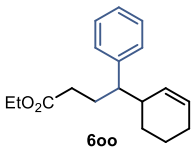
Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (101 µL, 1.0 mmol), 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane **5m** (23.0 mg, 0.1 mmol), and catalyst **C5** (7.6 mg, 0.02 mmol). The crude mixture was purified by two successive separations on column chromatography (SiO_2, 90:10 hexanes:CH_2Cl_2 and then 50:50 hexanes/toluene) to afford product **6nn** as a colorless oil (19.8 mg, 50% yield, 1.1:1 dr, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.37 – 7.33 (m, 4H), 7.31 – 7.27 (m, 4H), 7.20 – 7.15 (m, 2H), 5.81 (dp, *J* = 10.3, 1.7 Hz, 1H), 5.74 – 5.68 (m, 1H), 5.66 – 5.59

(m, 2H), 4.08 (qd, *J* = 7.1, 1.1 Hz, 4H), 2.82 – 2.74 (m, 1H), 2.70 – 2.62 (m, 1H), 2.45 (ddd, *J* = 14.6, 12.5, 4.7 Hz, 1H), 2.40 – 2.27 (m, 2H), 2.25 – 2.17 (m, 1H), 2.17 – 2.08 (m, 2H), 2.06 – 1.98 (m, 2H), 1.97 – 1.88 (m, 4H), 1.77 (dd, *J* = 4.6, 2.5 Hz, 1H), 1.74 – 1.65 (m, 2H), 1.58 – 1.46 (m, 1H), 1.45 – 1.38 (m, 2H), 1.30 (s, 12H), 1.27 (d, *J* = 3.7 Hz, 12H), 1.23 (td, *J* = 7.1, 2.1 Hz, 6H), 0.93 – 0.82 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 174.4, 143.8, 143.1, 130.7, 129.5, 128.8, 128.7, 128.6, 128.0, 127.9, 127.3, 125.4, 125.4, 83.5, 83.4, 60.1, 60.0, 43.9, 42.5, 31.5, 31.1, 30.6, 29.1, 26.0, 25.4, 25.3, 25.3, 25.0, 25.0, 24.8, 24.8, 24.6, 23.0, 22.8, 14.2.

HRMS (ESI) Calculated for $C_{24}H_{35}NaBO_4$ $[M+Na]^+$: 420.2557, found: 420.2551.



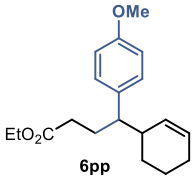
Ethyl 4-(cyclohex-2-en-1-yl)-4-phenylbutanoate (6oo)

Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (202 µL, 2.0 mmol), styrene **5n** (14 µL, 0.12 mmol), sodium hydrogen phosphate (14.2 mg, 0.1 mmol.), and catalyst **C5** (7.6 mg, 0.02 mmol). The crude mixture was purified by column chromatography (SiO_2, 75:25 hexanes/toluene) to afford product **6oo** as a colorless oil (12.6 mg, 42% yield, 1.1:1 *d.r.*, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$)) *1.1:1 mixture of diastereoisomers* δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.13 (td, *J* = 8.0, 7.6, 1.3 Hz, 2H), 5.89 (dd, *J* = 10.3, 2.5 Hz, 0.5H), 5.78 – 5.71 (m, 0.5H), 5.66 – 5.58 (m, 0.5H), 5.35 (d, *J* = 10.2 Hz, 0.5H), 4.09 – 4.03 (m, 2H), 2.45 – 2.33 (m, 1H), 2.27 (dtd, *J* = 16.8, 8.1, 3.5 Hz, 1H), 2.21 – 2.13 (m, 0.5H), 2.09 – 2.04 (m, 2H), 1.97 – 1.83 (m, 3H), 1.77 – 1.68 (m, 0.5H), 1.62 (dq, *J* = 11.2, 4.3, 3.7 Hz, 0.5H), 1.53 – 1.37 (m, 1H), 1.36 – 1.27 (m, 1H), 1.20 (td, *J* = 7.0, 1.8 Hz, 3H), 1.14 – 1.06 (m, 0.5H).

^{13}C NMR (126 MHz, $CDCl_3$) 1.1:1 *mixture of diastereoisomers* δ 173.8, 173.7, 143.2, 143.1, 130.2, 129.6, 128.5, 128.4, 128.3, 128.3, 128.3, 127.9, 127.5, 126.2, 60.1, 50.8, 50.7, 41.1, 40.6, 32.8, 32.6, 28.0, 27.6, 27.3, 27.0, 25.4, 25.3, 21.9, 21.1, 14.2.

HRMS (ESI) Calculated for $C_{18}H_{24}NaO_2$ $[M+Na]^+$: 295.1669, found: 295.1672.



Ethyl 4-(cyclohex-2-en-1-yl)-4-(4-methoxyphenyl)butanoate (6pp)

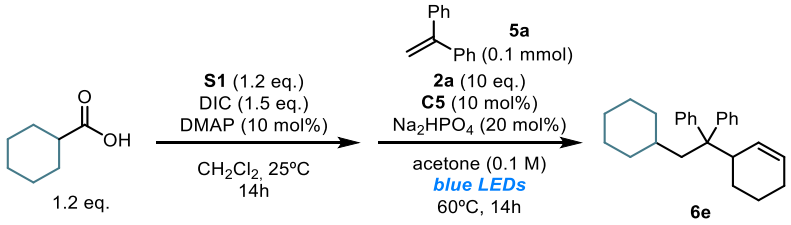
Prepared according to General Procedure B using the radical precursor **4b** (48.1 mg, 0.1 mmol), cyclohexene **2a** (202 µL, 2.0 mmol), 1-methoxy-4-vinylbenzene **5o** (16.2 µL, 0.12 mmol), sodium hydrogen phosphate (14.2 mg, 0.1 mmol.), and catalyst **C5** (7.6 mg, 0.02 mmol). The crude mixture was purified by column chromatography (SiO_2, 33:66 hexanes/toluene) to afford product **6pp** as a colorless oil (11.8 mg, 40% yield, 1.1:1 *d.r.*, average of two runs).

^{1}H NMR (500 MHz, $CDCl_3$) *1.1:1 mixture of diastereoisomers* δ 7.06 – 7.01 (m, 2H), 6.85 – 6.80 (m, 2H), 5.86 (dd, *J* = 10.2, 2.5 Hz, 0.5H), 5.77 – 5.69 (m, 0.5H), 5.62 (dq, *J* = 10.0, 3.3, 2.9 Hz, 0.5H), 5.36 (ddd, *J* = 10.3, 2.3, 1.2 Hz, 0.5H), 4.06 (qd, *J* = 7.2, 1.5 Hz, 2H), 3.79 (s, 6H), 2.39 – 2.29 (m, 1H), 2.24 (dddd, *J* = 13.1, 8.9, 7.2, 3.7 Hz, 1H), 2.17 – 2.09 (m, 0.5H), 2.09 – 2.03 (m, 2H), 1.93 (dp, *J* = 7.4, 1.7 Hz, 2H), 1.88 – 1.78 (m, 1H), 1.71 (dq, *J* = 9.0, 4.6 Hz, 0.5H), 1.67 – 1.55 (m, 2H), 1.54 – 1.45 (m, 0.5H), 1.41 (tdd, *J* = 11.7, 6.1, 2.9 Hz, 1H), 1.34 – 1.24 (m, 3H), 1.20 (td, *J* = 7.1, 1.7 Hz, 3H), 1.10 (dddd, *J* = 13.1, 10.4, 7.6, 2.5 Hz, 0.5H), 0.91 – 0.79 (m, 0.5H).

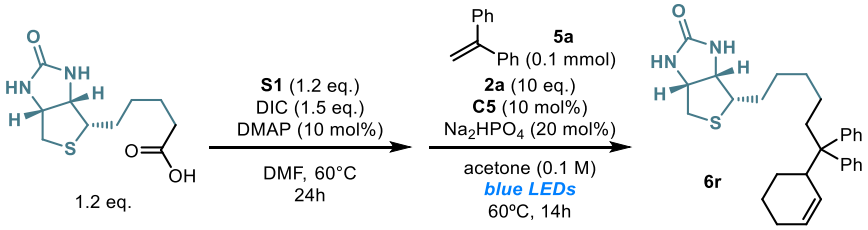
^{13}C NMR (126 MHz, $CDCl_3$) 1.1:1 *mixture of diastereoisomers* δ 173.9, 173.8, 158.0, 158.0, 135.2, 135.1, 130.2, 129.8, 129.4, 129.3, 129.1, 128.3, 127.8, 113.8, 113.6, 113.6, 60.1, 55.2, 49.9, 49.8, 41.2, 40.7, 32.8, 32.6, 29.7, 28.2, 27.7, 27.2, 27.1, 25.4, 25.3, 21.9, 21.1, 14.2.

HRMS (ESI) Calculated for $C_{19}H_{29}NaO_3$ $[M+Na]^+$: 325.1774, found: 325.1778.

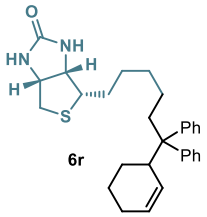
D.3.3 Telescoped Three-component C-H Allylic benzylation



An oven-dried glass vial, was charged with cyclohexanecarboxylic acid (15.4 mg, 1.2 equiv.), **S1** (36.1 mg, 1.2 equiv.), and DMAP (1.2 mg, 0.1 equiv.). The vial was purged with argon before adding 1 mL of degassed acetone, followed by dropwise addition of DIC (23.5 µL, 1.5 equiv.). The vial was sealed with parafilm and the reaction stirred at 25ºC for 14 h. CH_2Cl_2 was evaporated under reduced pressure. **C5** (3.8 mg, 0.01 mmol, 0.1 equiv.) and Na_2HPO_4 (2.8 mg, 0.02 mmol, 0.2 equiv.) were sequentially added and the vial purged with argon. 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol) and cyclohexene **2a** (101 µL, 1 mmol, 10 equiv.) were finally added, followed by 800 µL of argon-sparged HPLC grade acetone. The vial was sealed with Parafilm, and then placed in the irradiation setup, maintained at a temperature of 60 ºC. The reaction was stirred for 14 h, then the solvent was evaporated and the crude mixture purified by column chromatography (SiO_2, pentane) to afford product **6e** as a colorless oil (19.3 mg, 56% yield).



An oven-dried glass vial, was charged with D-biotin (29.3 mg, 1.2 equiv.), **S1** (36.1 mg, 1.2 equiv.), and DMAP (1.2 mg, 0.1 equiv.). The vial was purged with argon before adding 1 mL degassed DMF, followed by dropwise addition of DIC (23.5 µL, 1.5 equiv.). The vial was sealed with parafilm and the reaction stirred at 60ºC for 24h. DMF was then removed at 60ºC under high vacuum. **C5** (3.8 mg, 0.01 mmol, 0.1 equiv.), and Na_2HPO_4 (2.8 mg, 0.02 mmol, 0.2 equiv.), were added and the vial purged with argon again. 1,1-diphenylethylene **5a** (17.7 µL, 0.1 mmol) and cyclohexene **2a** (101 µL, 1 mmol, 10 equiv.) were finally added, followed by 800 µL of argon-sparged HPLC grade acetone. The vial was sealed with Parafilm, and then placed in the irradiation setup, maintained at a temperature of 60 ºC. The reaction was stirred for 14h, then the solvent was evaporated and the crude mixture purified by flash column chromatography. Multiple purifications by column chromatography resulted in poor separation from several unidentified byproducts. The yield (37%, average of two runs, 1.1:1 *d.r.*) of **6r** was inferred by ^{1}H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard. An analytical amount of the pure compound was isolated by preparative TLC (70:30 hexanes/toluene) to obtain a colorless oil.



(3aS,4S,6aR)-4-(6-(cyclohex-2-en-1-yl)-6,6-diphenylhexyl)tetrahydro-1H-thieno[3,4-d]imidazol-2(3H)-one (6r)

^{1}H NMR (400 MHz, MeOD) δ 7.36 – 7.29 (m, 6H), 7.26 (dd, *J* = 7.9, 4.1 Hz, 4H), 5.88 (d, *J* = 10.6 Hz, 1H), 5.67 – 5.56 (m, 1H), 4.53 (ddd, *J* = 7.9, 5.0, 1.0 Hz, 1H), 4.30 (dd, *J* = 7.9, 4.5 Hz, 1H), 3.30 (s, 1H), 3.18 (dt, *J* = 8.7, 5.3 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.76 (d, *J* = 12.7 Hz, 1H), 2.19 (dd, *J* = 10.7, 5.9 Hz, 1H), 1.94 (t, *J* = 18.0 Hz, 2H), 1.74 – 1.59 (m, 4H), 1.57 – 1.48 (m, 1H), 1.35 (d, *J* = 15.3 Hz, 6H), 1.15 – 0.95 (m, 4H).

^{13}C NMR (101 MHz, MeOD) δ 163.2, 144.7, 142.6, 128.1, 127.8, 127.7, 126.3, 125.5, 125.0, 123.9, 123.8, 60.4, 58.7, 54.2, 52.6, 39.4, 39.3, 38.1, 37.5, 28.2, 27.8, 27.2, 26.7, 26.6, 23.2, 23.0, 22.4, 20.6.

HRMS (ESI) Calculated for $C_{29}H_{36}N_2NaOS$ $[M+Na]^+$: 483.2441, found: 483.2433.

E. Mechanistic Studies

E.1 UV-Vis Measurements

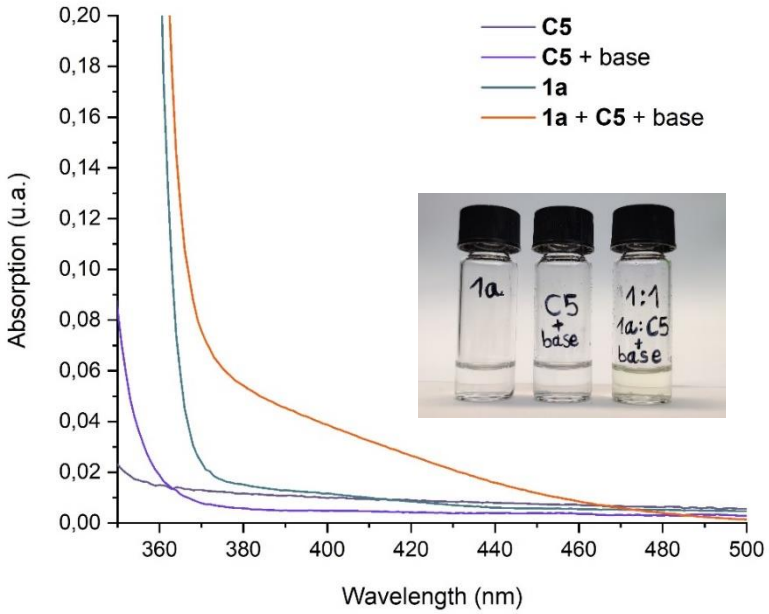


Figure S8. Optical absorption spectra, recorded in acetone in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer, and visual appearance of the separate reaction components and of the colored EDA complex between catalyst **C5** and **1a**. [**1a**] = 0.10 M, [**C5**] = 0.02 M, [Na_2HPO_4] = 0.02 M.

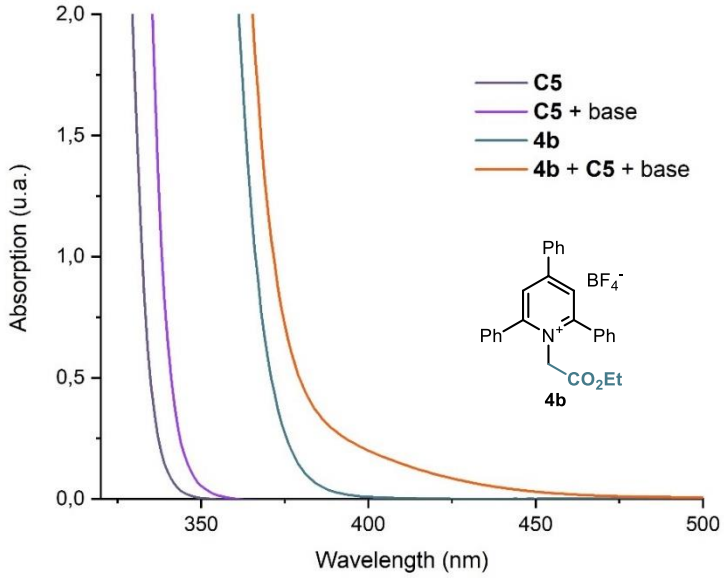


Figure S9. Optical absorption spectra, recorded in acetone in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer of the colored EDA complex between catalyst **C5** and **4b**. [**4b**] = 0.10 M, [**C5**] = 0.01 M, [Na_2HPO_4] = 0.02 M.

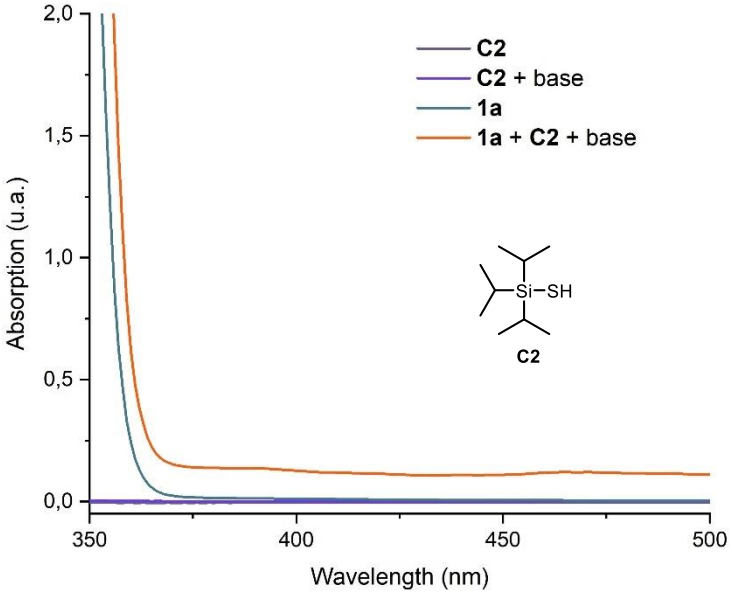


Figure S10. Optical absorption spectra, recorded in acetone in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer of the colored EDA complex between catalyst **C2** and **1a**. [**1a**] = 0.10 M, [**C2**] = 0.02 M, [Na_2HPO_4] = 0.02 M.

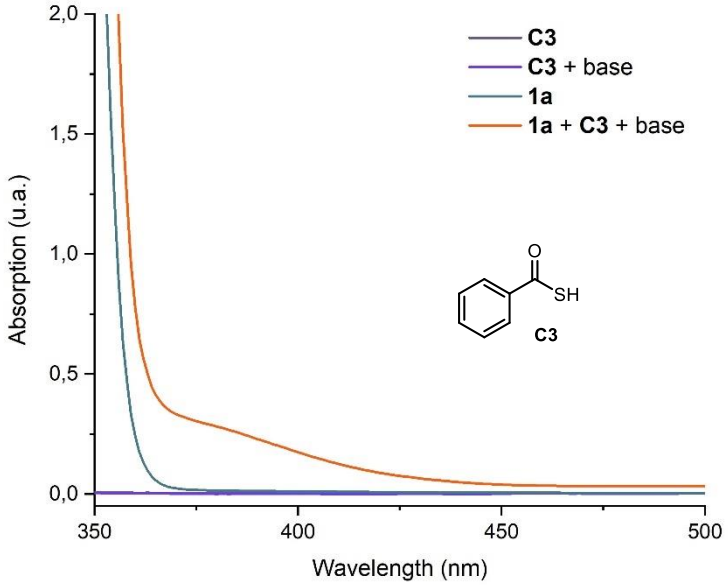


Figure S11. Optical absorption spectra, recorded in acetone in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer of the colored EDA complex between catalyst **C3** and **1a**. [**1a**] = 0.10 M, [**C3**] = 0.02 M, [Na_2HPO_4] = 0.02 M.

E.2 Cyclic Voltammetry Measurements

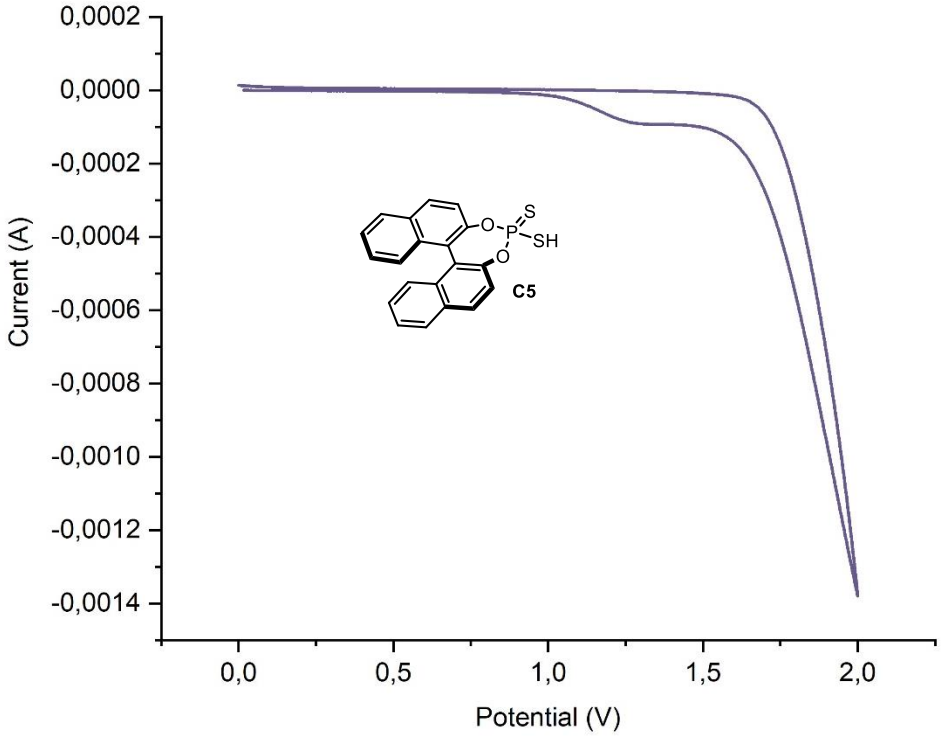
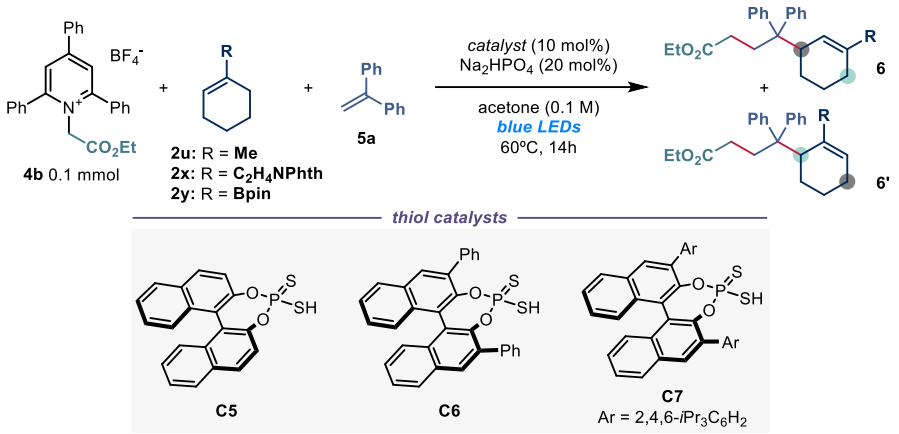


Figure S12. Cyclic voltammogram for catalyst **C5** [0.02M] in [0.1 M] $TBAPF_6$ in CH_3CN. Measurement started by oxidation from 0 to +2.0 V and finishing at 0 V. Platinum disk working electrode, Ag/AgCl (NaCl 3 M) reference electrode, Pt wire auxiliary electrode. Sweep rate: 500 mV/s. One irreversible oxidation observed at +1.28 V.

E.3 Regioselectivity Study

Non-symmetrical cyclohexene derivatives **2d**, **2h** and **2i** were submitted to the reaction conditions following the General Procedure B, using thiol catalysts with different steric hindrance: catalysts **C5**, **C6**, and **C7** were tested. The yields of products and ratio of regioisomers for each combination are reported in Table S2.



entry	R	catalyst	yield **6** + **6'** (%)	**6** : **6'** [b]
1	Me (**2d**)	**C5**	67	5:1 (**6u**:**6u'**)
2		**C6**	37	5:1 (**6u**:**6u'**)
3		**C7**	26[a]	4:1 (**6u**:**6u'**)
4	C_2H_4NPhth (**2h**)	**C5**	62	6:1 (**6x**:**6x'**)
5		**C6**	54	7:1 (**6x**:**6x'**)
6		**C7**	**48**	**10:1** (**6x**:**6x'**)
7	Bpin (**2i**)	**C5**	45	1:1.2 (**6y'**:**6y**)
8		**C6**	**50[a]**	**4:1** (**6y'**:**6y**)
9		**C7**	19[a]	4:1 (**6y'**:**6y**)

Table S2. Regioselectivity studies using non-symmetrical cyclohexene derivatives. [a] Yield determined by ^{1}H NMR analysis. [b] Regioisomers ratio determined by ^{1}H NMR analysis.

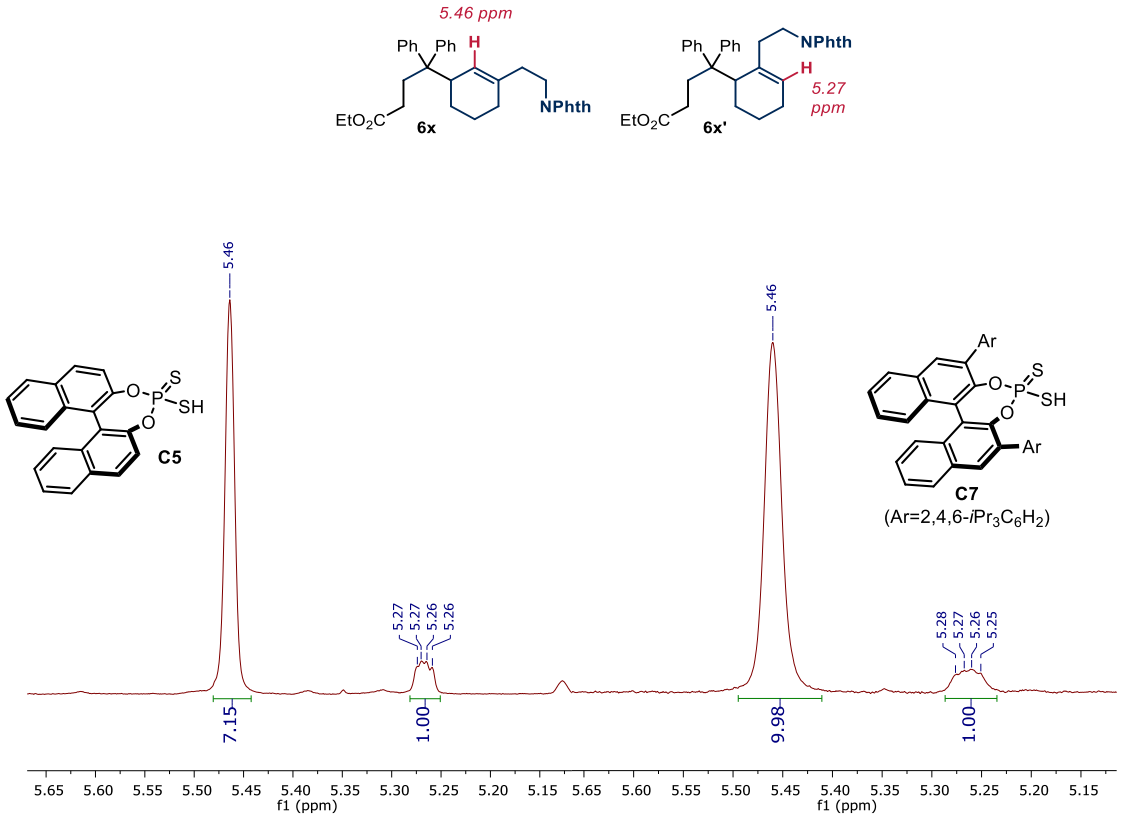


Figure S13. Regioselectivity study of **6x** and **6x'** using catalysts **C5** and **C7.**

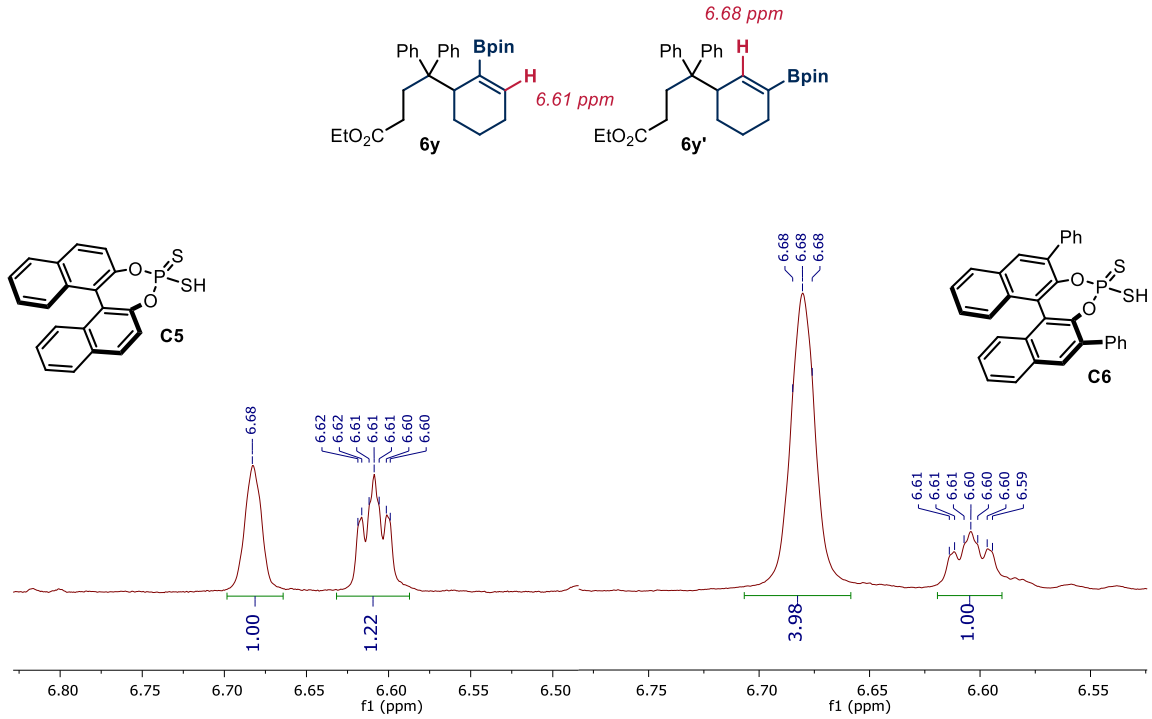


Figure S14. Regioselectivity study of **6y** and **6y'** using catalysts **C5** and **C6.**

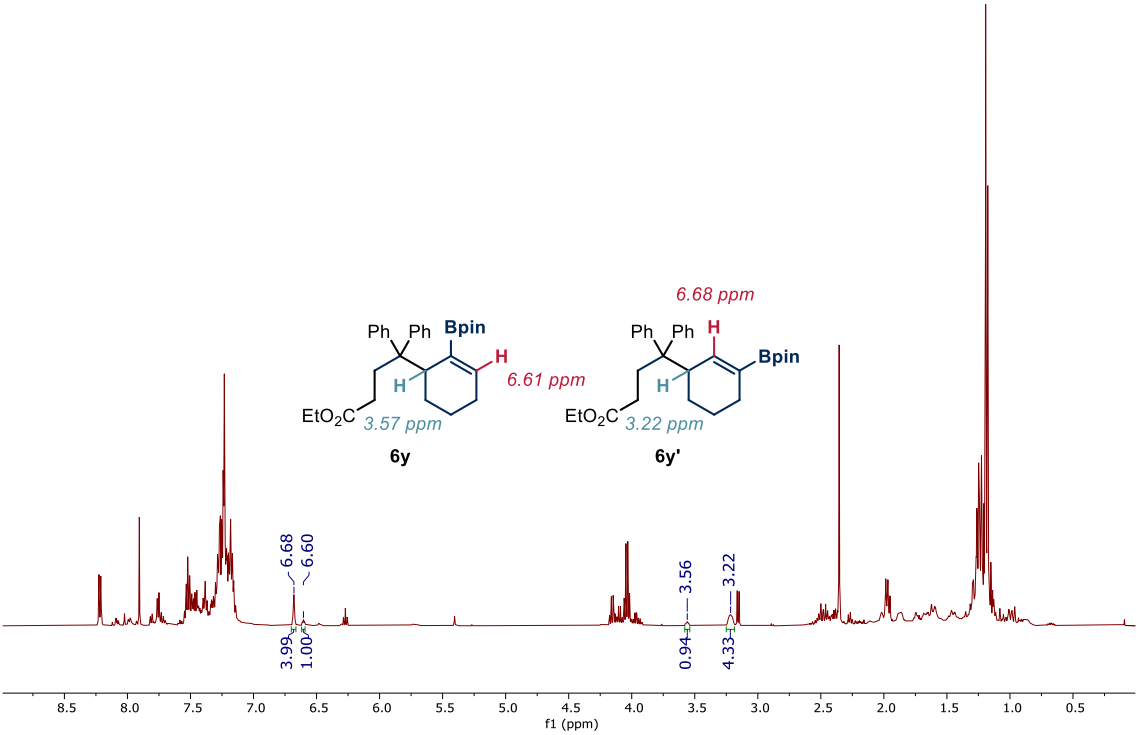


Figure S15. NMR spectrum of purified **6y**/**6y'**, after column chromatography; reaction performed with catalyst **C6**.

E.4 DFT calculations

Computational Methods

Calculations were performed using the Gaussian 09 suite of programs.[24] DFT was applied using B3LYP functional.[25] The 6-31G(d,p) basis set[26] was employed for all atoms (C, H, O, S and P). Full geometry optimizations were carried out in acetone, through an implicit solvent SMD.[27] The stationary points were characterized by vibrational analysis. Minima were identified by the presence of a full set of real frequencies. Reported energies are potential energies (E), enthalpies (H) and free energies (G) in solution, computed at 298 K and 1 atm. Homolytic bond dissociation enthalpies (BDE) were also calculated at the same level of theory.

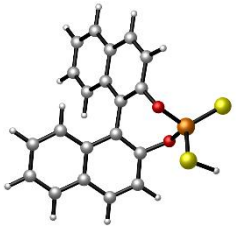
Bond Dissociation Enthalpies

BDE (S-H): 83.3 kcal·mol^{-1} BDE (C-H): 82.2 kcal·mol^{-1}

Figure S15. Bond dissociation enthalpies (BDE) calculated for **C5** and **2a.** DFT Method: B3LYP/6-31G(d,p).

Computed Structures and Energies

C5



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H = -2160.934966 Hartrees
G = -2161.003202 Hartrees

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C	-6.83161200	6.35628700	-2.12936100
C	-6.84319300	7.21508400	-3.26227300
C	-6.10978900	6.91202300	-4.38641700
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H	-4.68096300	3.98736100	-3.38161400
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C	-7.54804000	6.69538900	-0.95044100
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C	-7.48390000	5.89340200	0.16188400
C	-6.73477700	4.70141200	0.10501500
H	-8.12880300	7.61270400	-0.93183300
H	-7.99723300	6.14608900	1.08293400
C	-5.36678400	2.95333900	-1.01878000
C	-5.63083800	1.91649600	-1.98106000
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C	-6.66188200	2.01791600	-2.95668800
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C	-5.09555500	-0.30729800	-2.90626500
C	-3.87176800	0.53537200	-0.93051600
H	-2.95724100	1.37511400	0.83044200
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O	-4.19106000	3.64340000	0.96887800
P	-5.32693900	3.81594700	2.13834500
S	-5.48240800	2.45239400	3.50841800
S	-4.73147800	5.76338200	2.70105200
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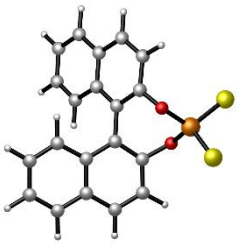
II



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G = -2160.348175 Hartrees

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C	-6.12396700	6.91810400	-4.41280900
H	-4.75935600	5.50764600	-5.33613800
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C	-3.67555700	1.52041700	0.02631900
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C	-3.86945000	0.54776000	-0.92400400
H	-2.95136800	1.40823600	0.82543500
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S	-5.43592700	2.44224500	3.47018600
S	-4.86621600	5.54444700	3.12372000

Hydrogen

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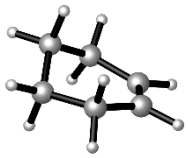
G = -0.535532 Hartrees

H	0.00000000	0.00000000	0.00000000

2a



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H	1.15857900	0.38860900	0.51068900
H	-0.33903600	-1.76736900	0.83306600
H	-0.15282400	-1.24433700	-0.82617900
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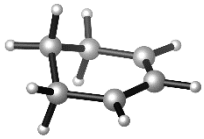
H	-3.77527000	-0.02410800	1.19208700

IV



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H	-3.73847200	0.11003800	1.13455600.

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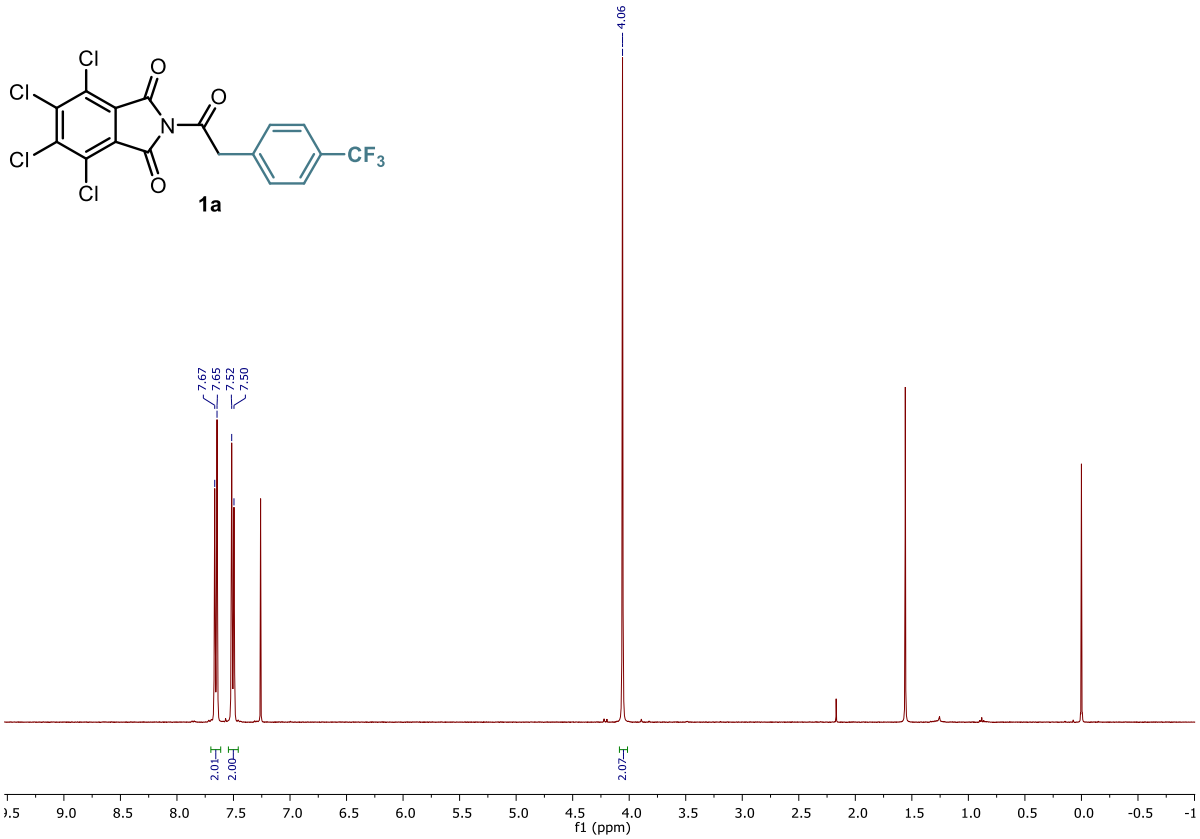
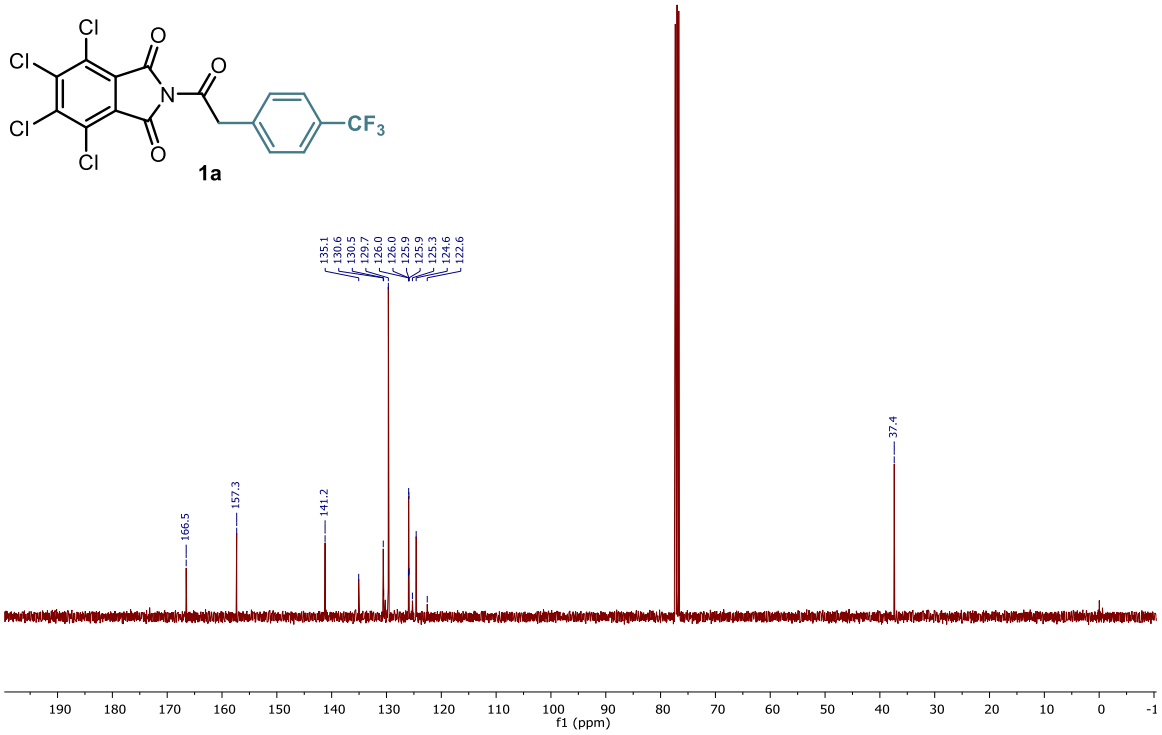
G. NMR Spectra

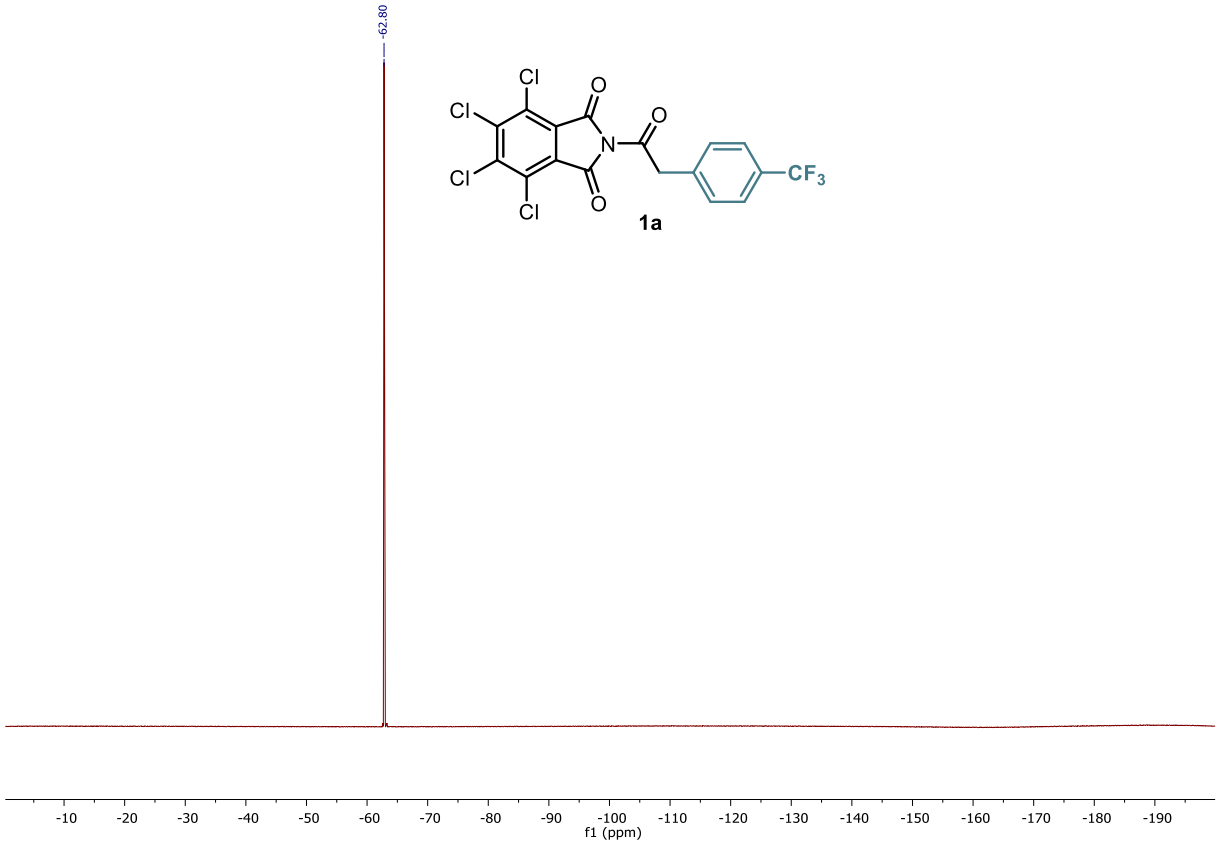
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



^{13}C NMR (101 MHz, $CDCl_3$) of **1a**



^{19}F NMR (376 MHz, $CDCl_3$) of **1a**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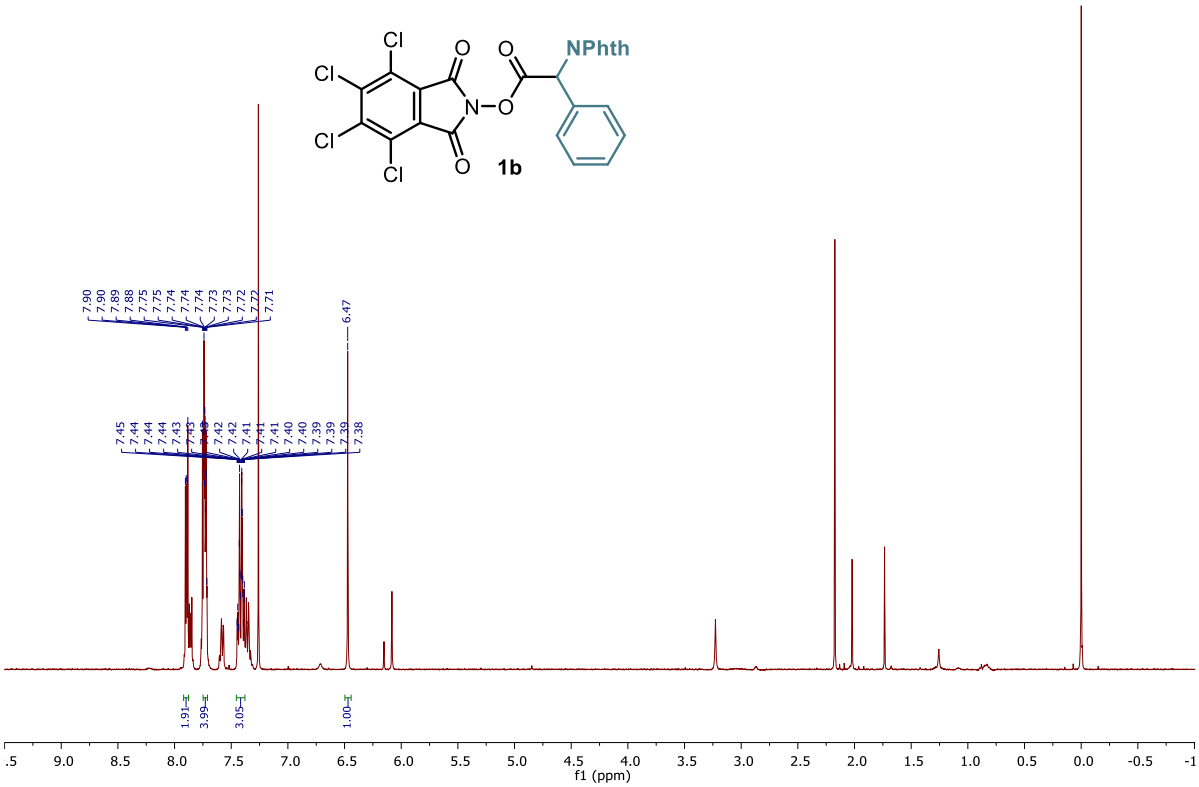
Cl
Cl
O
O
O
N
CF3
1a
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

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



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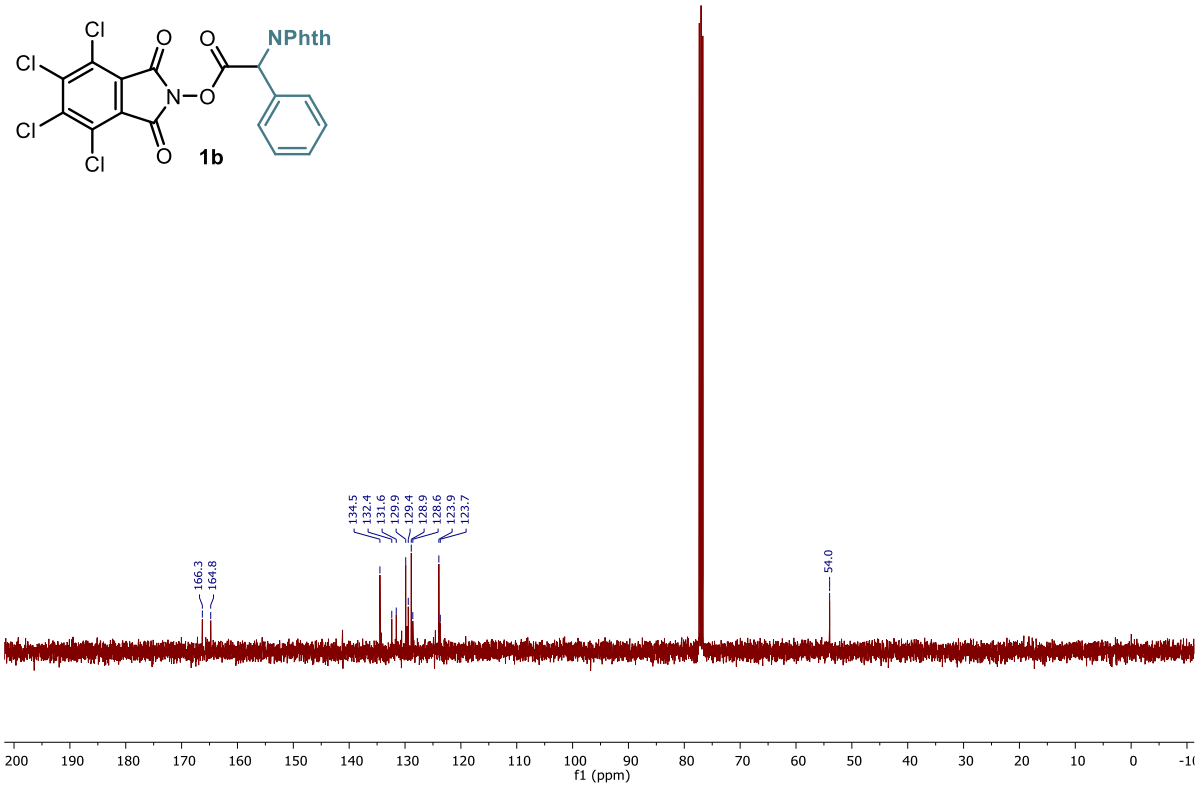

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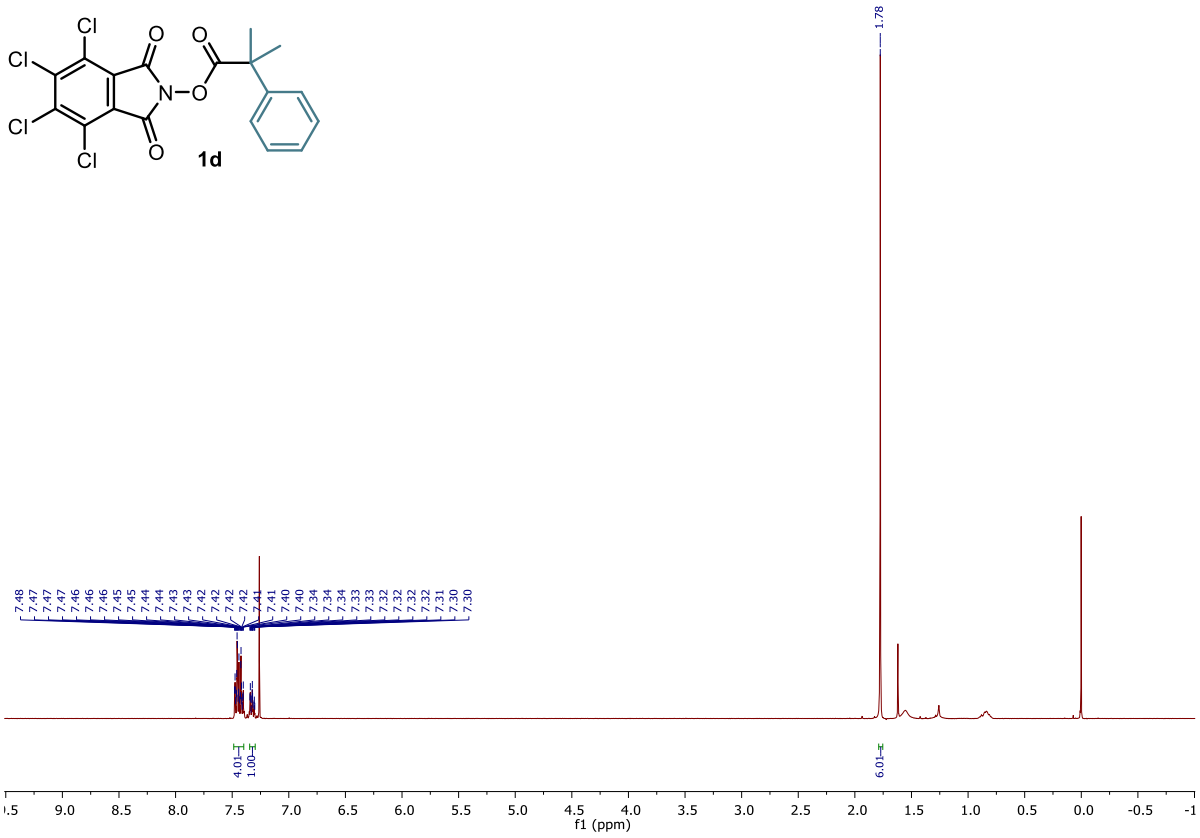

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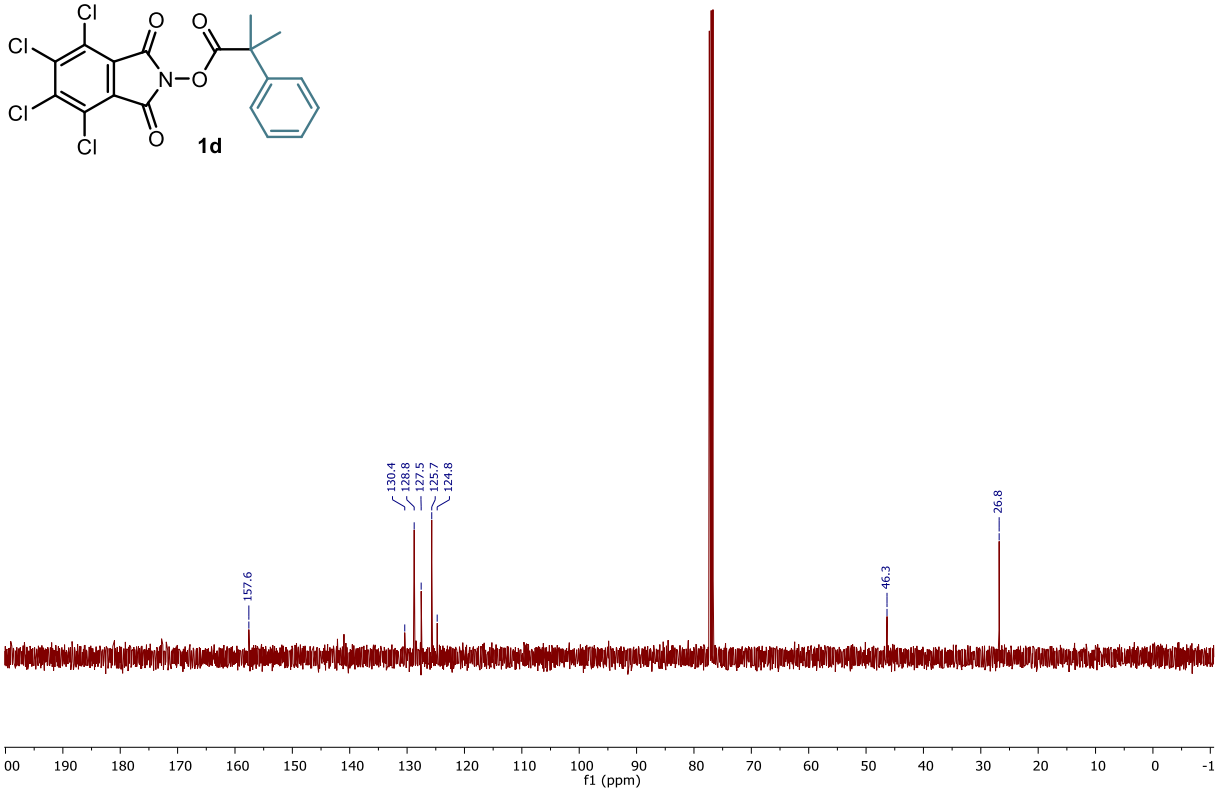

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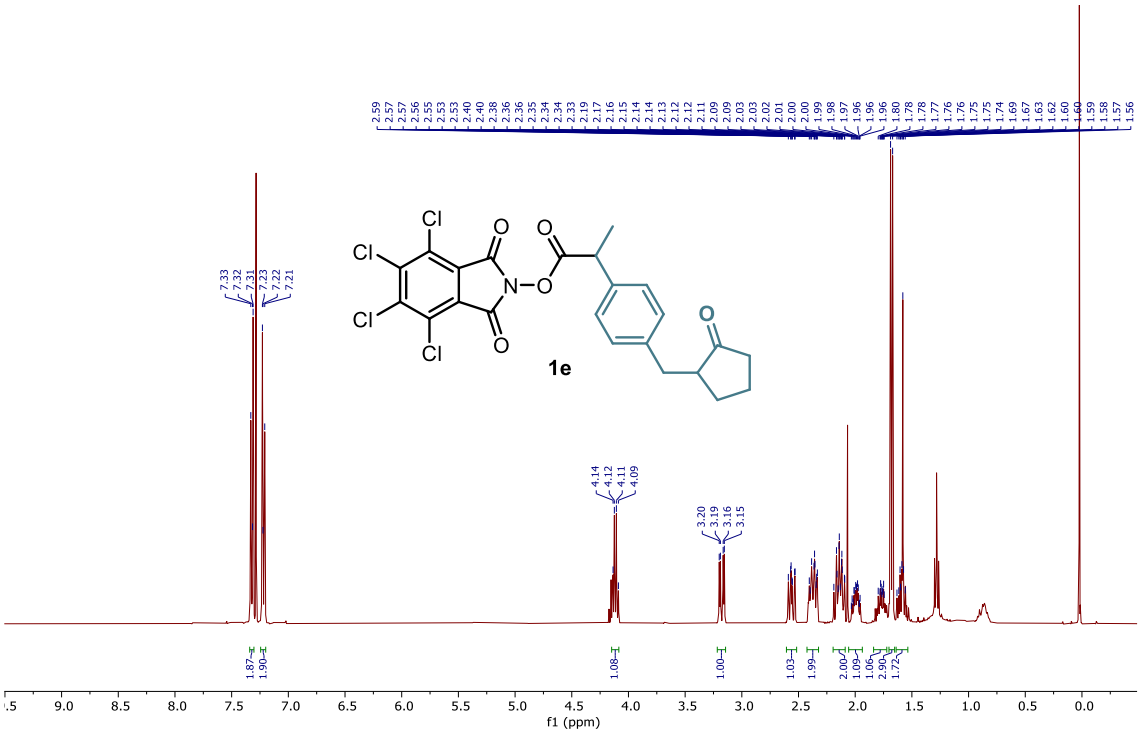
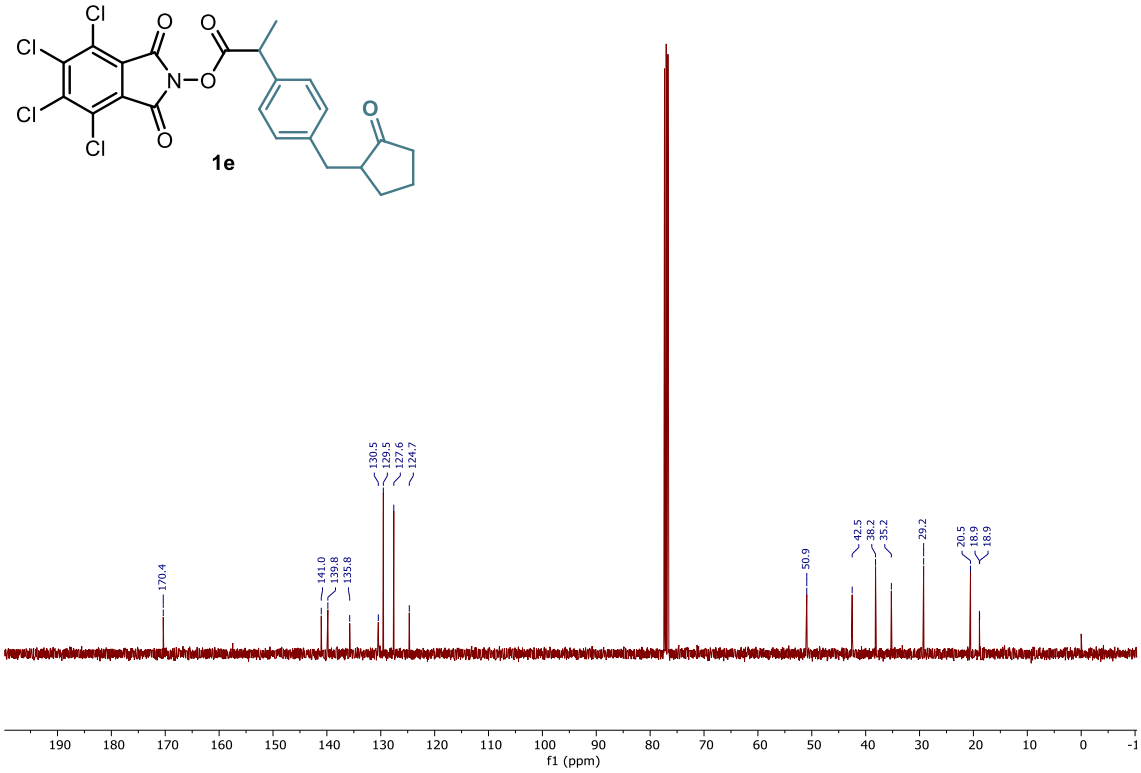


^{13}C NMR (101 MHz, $CDCl_3$) of **1e**



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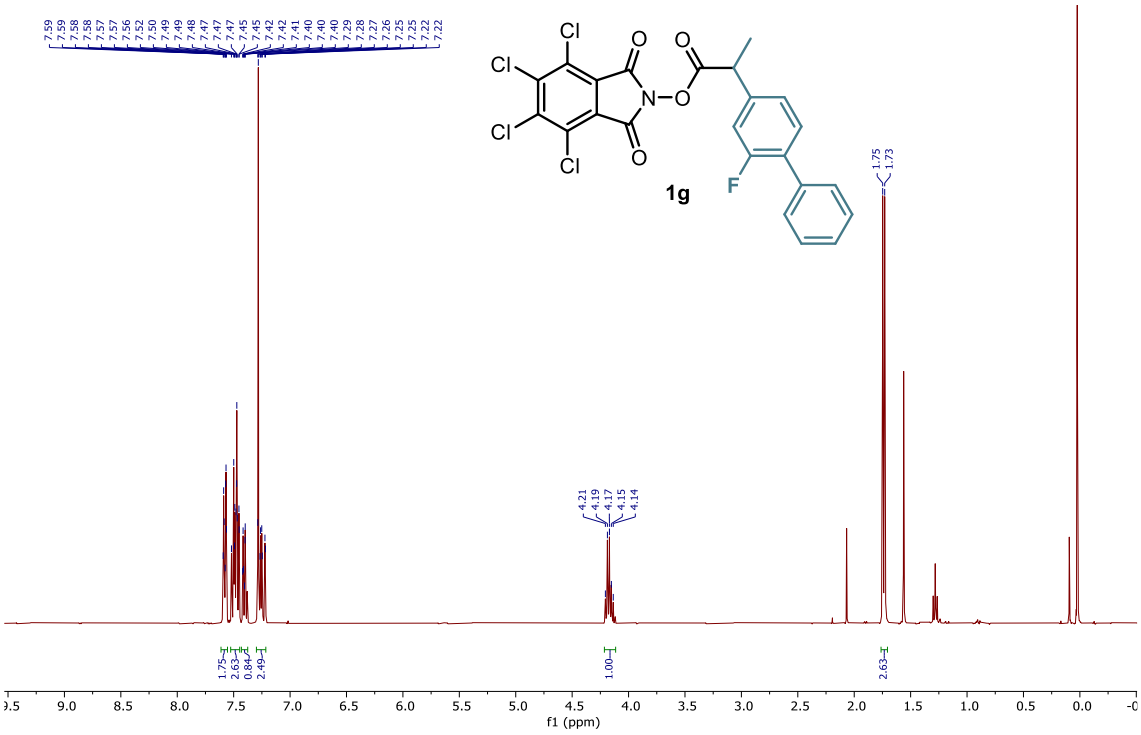

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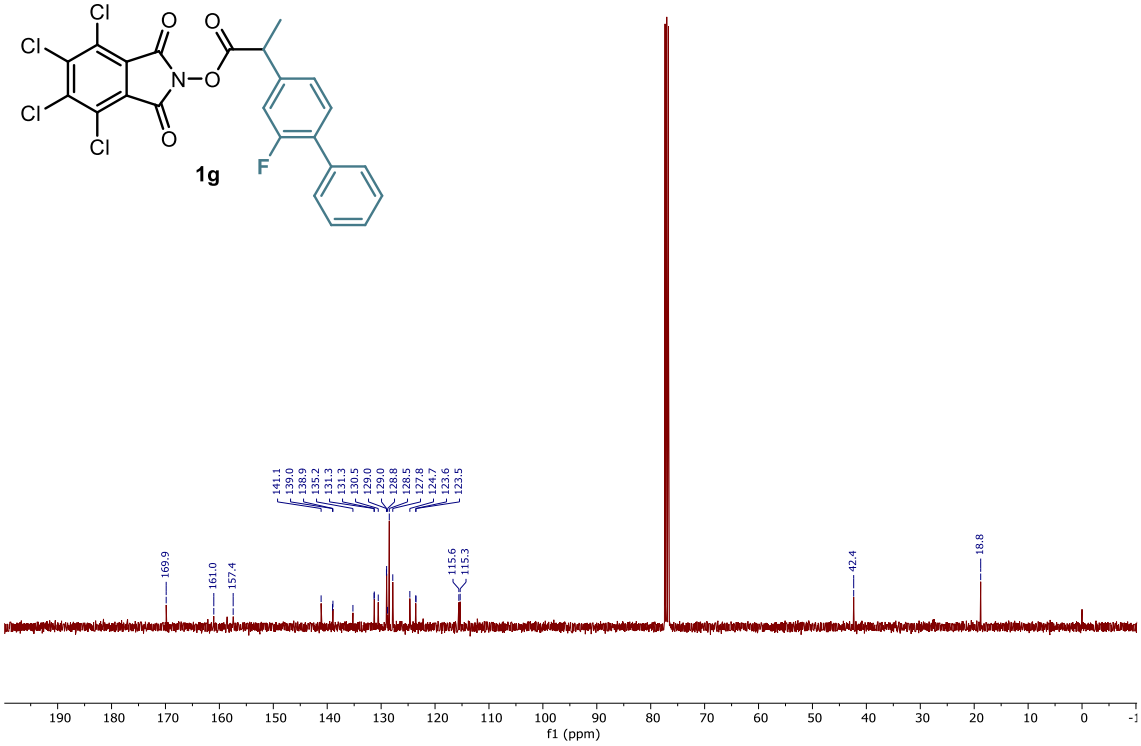
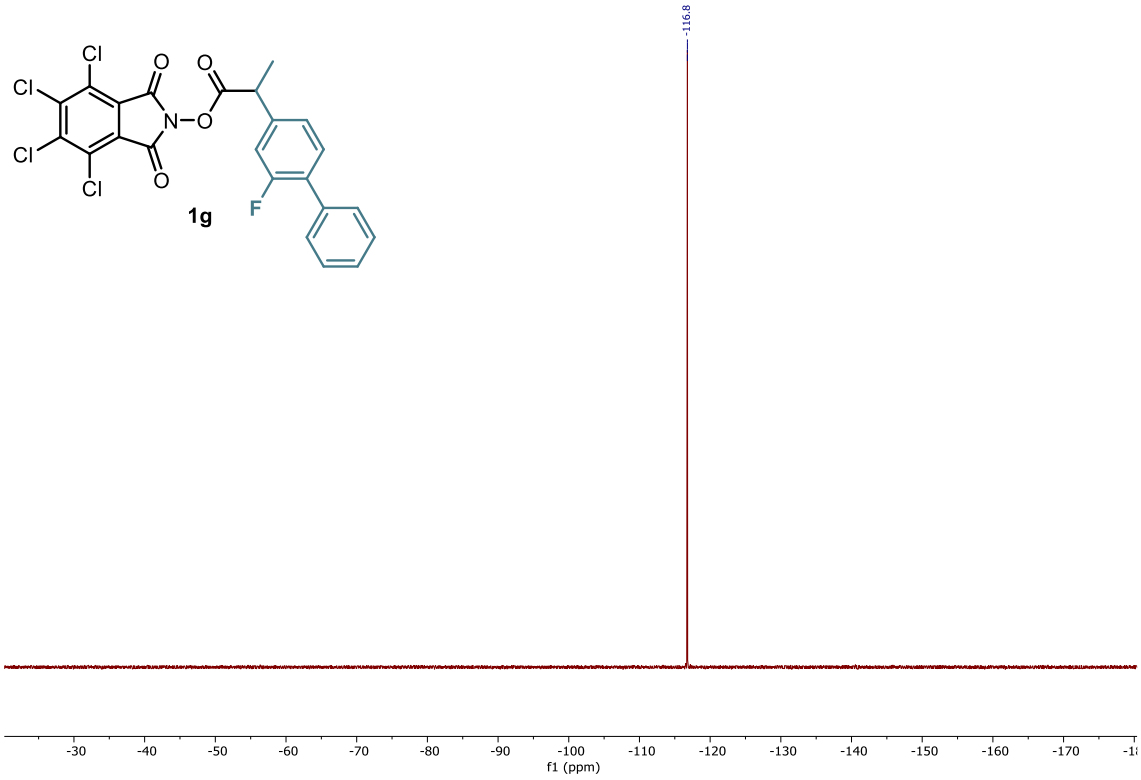


^{19}F NMR (376 MHz, $CDCl_3$) of **1g**



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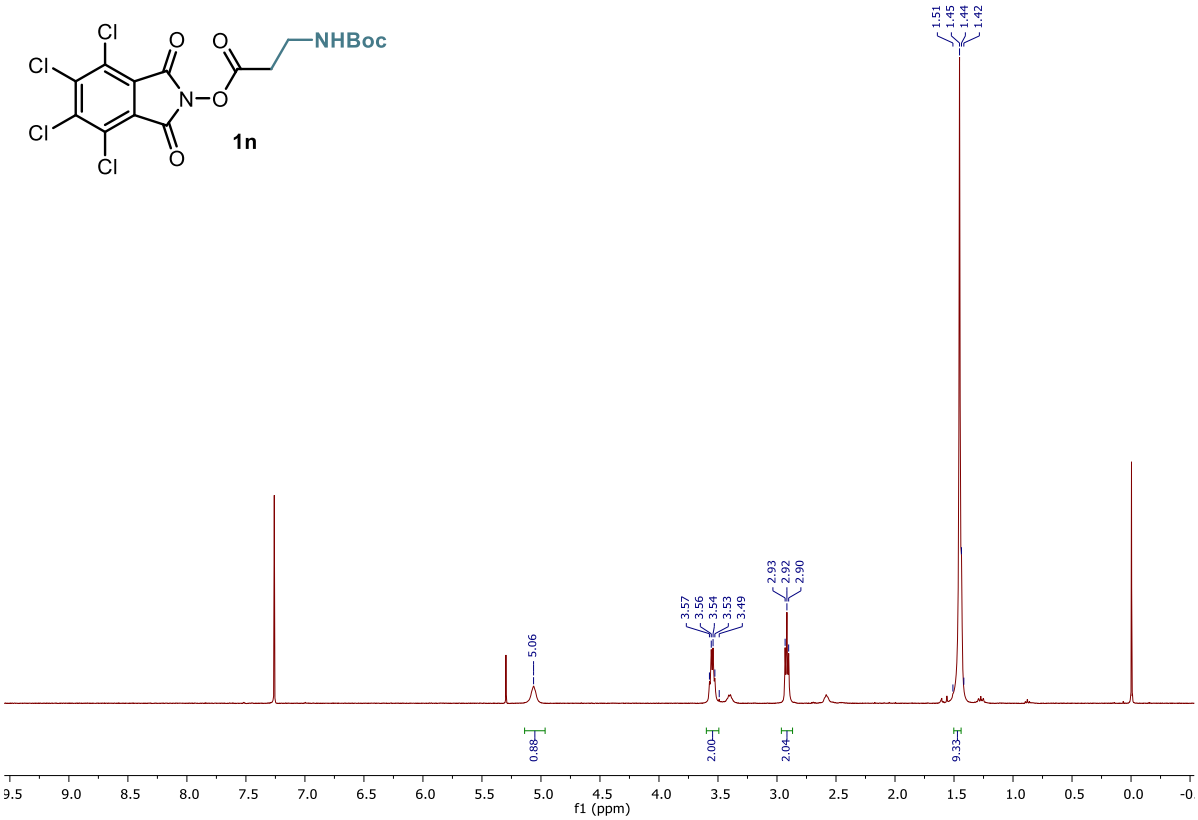

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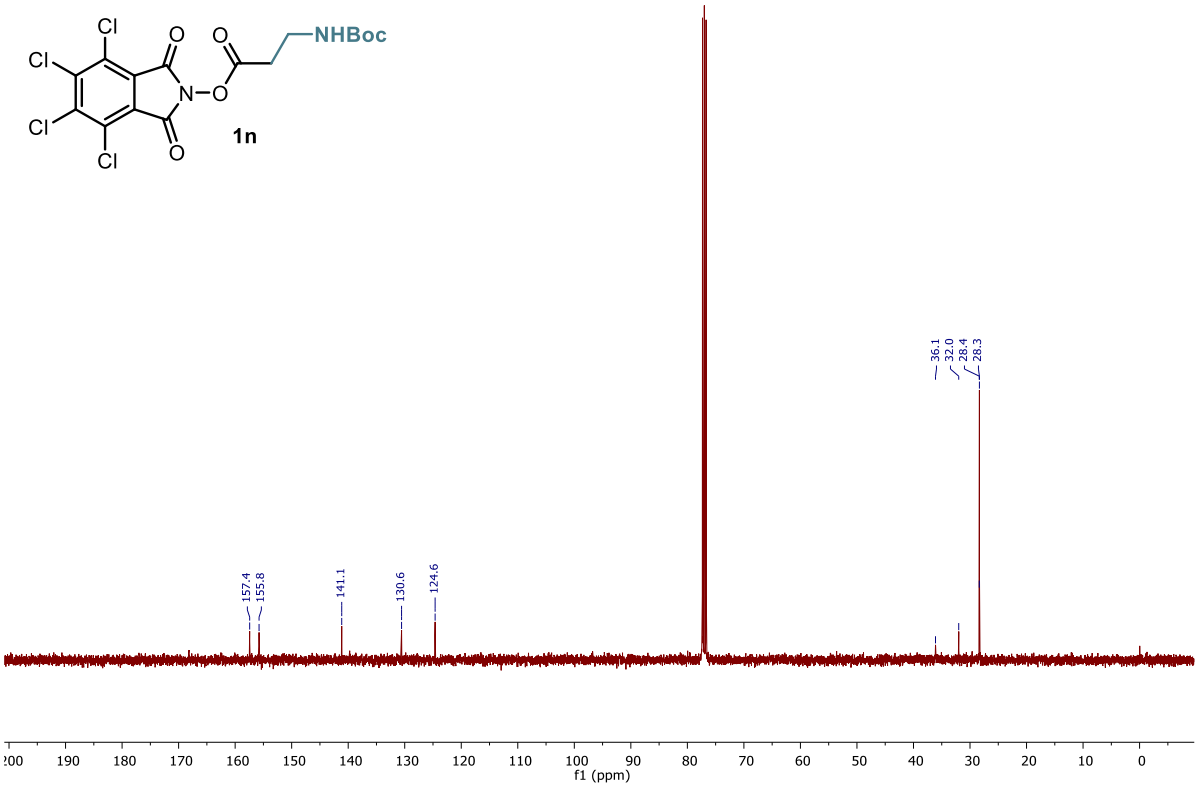

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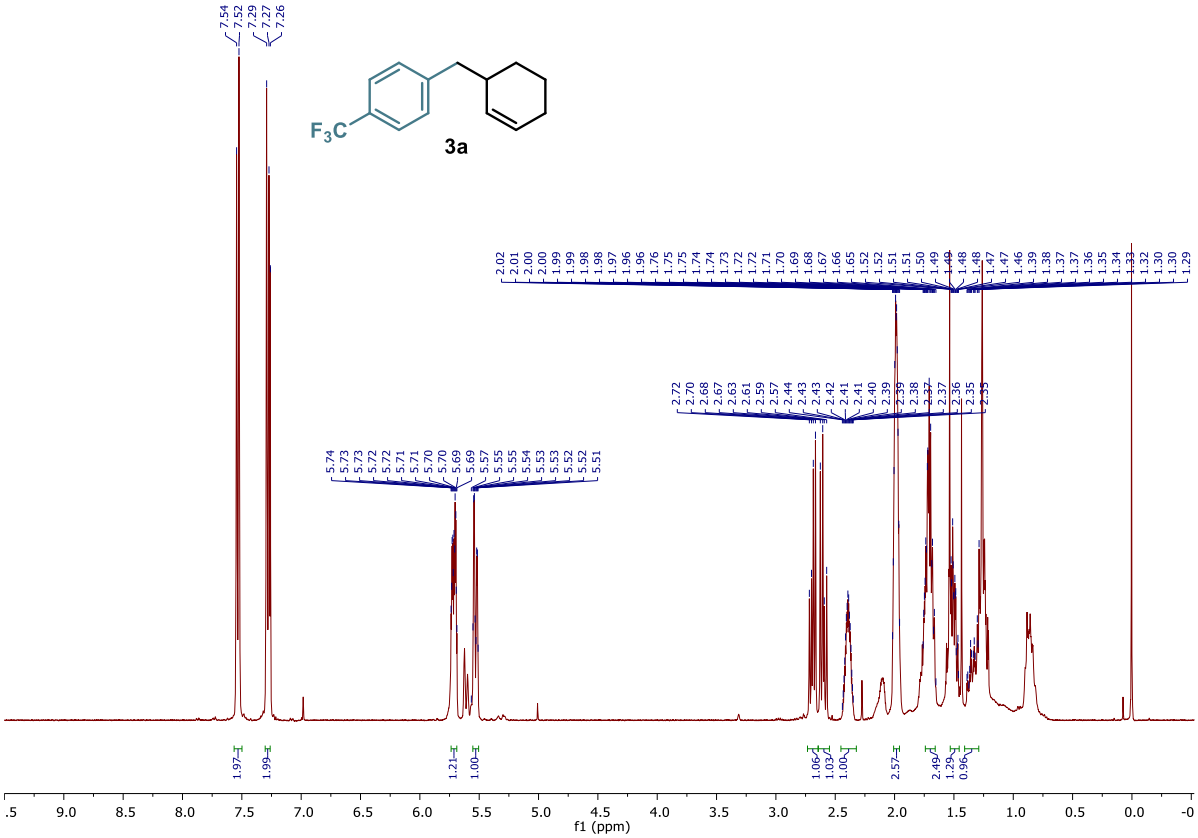
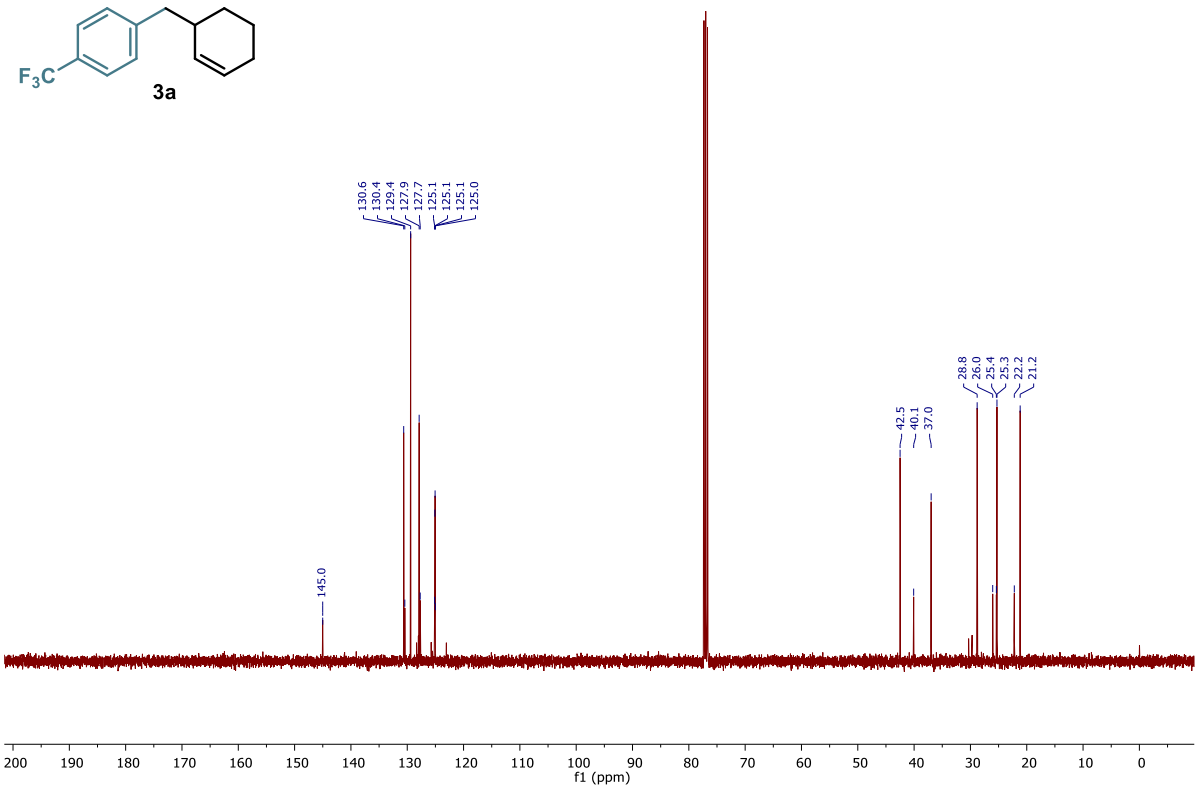
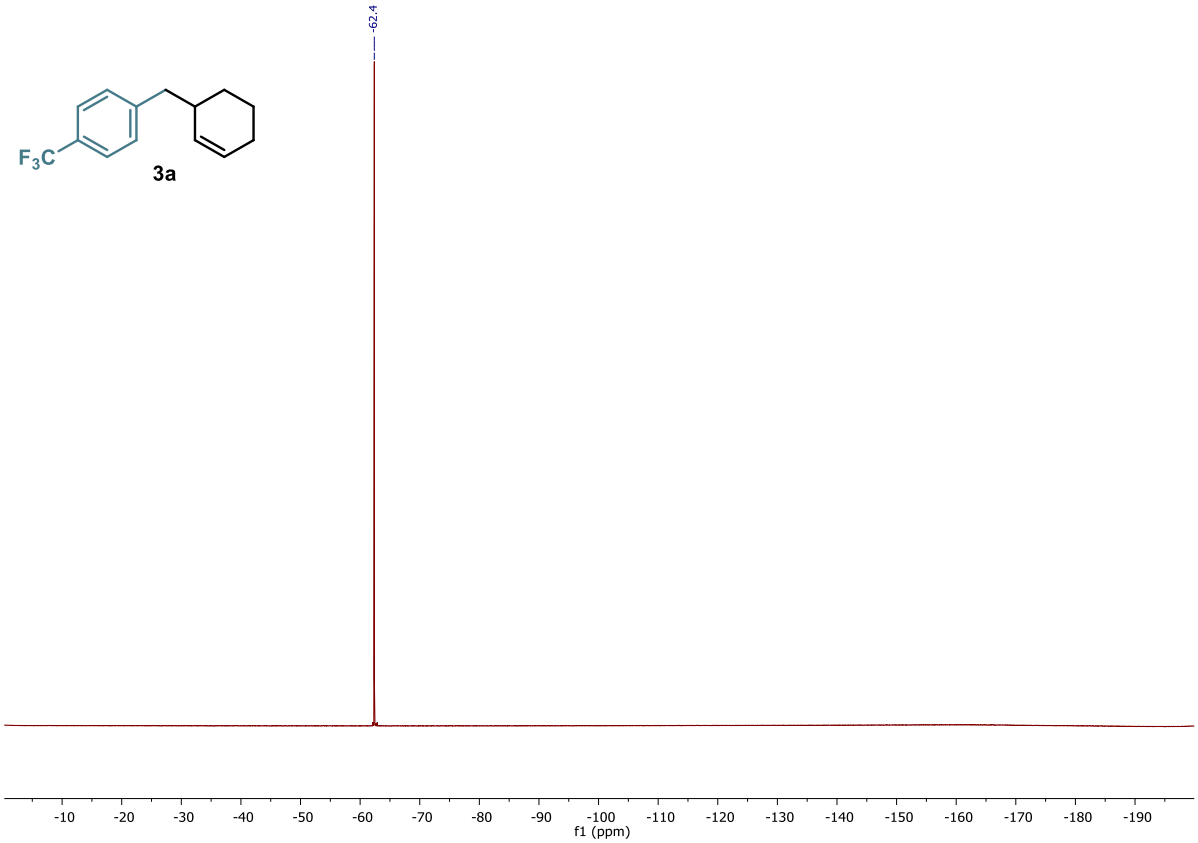


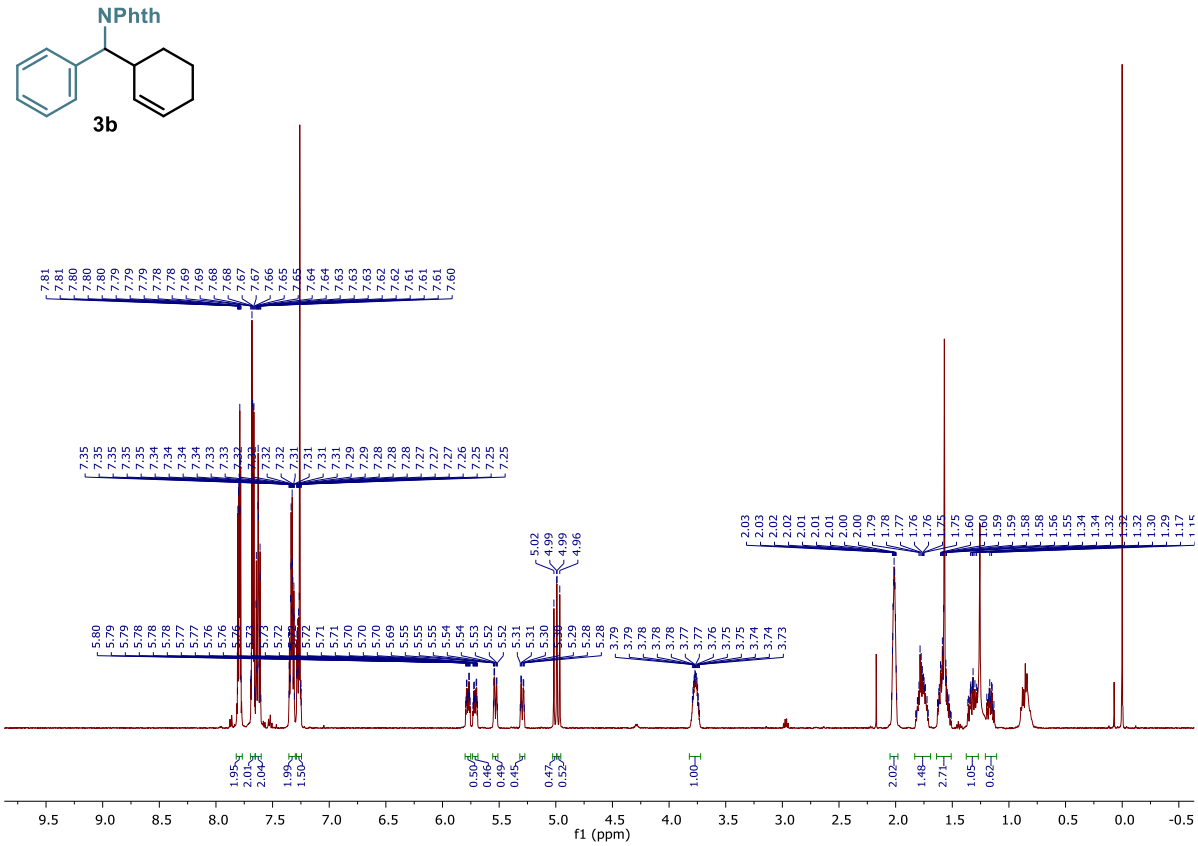
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



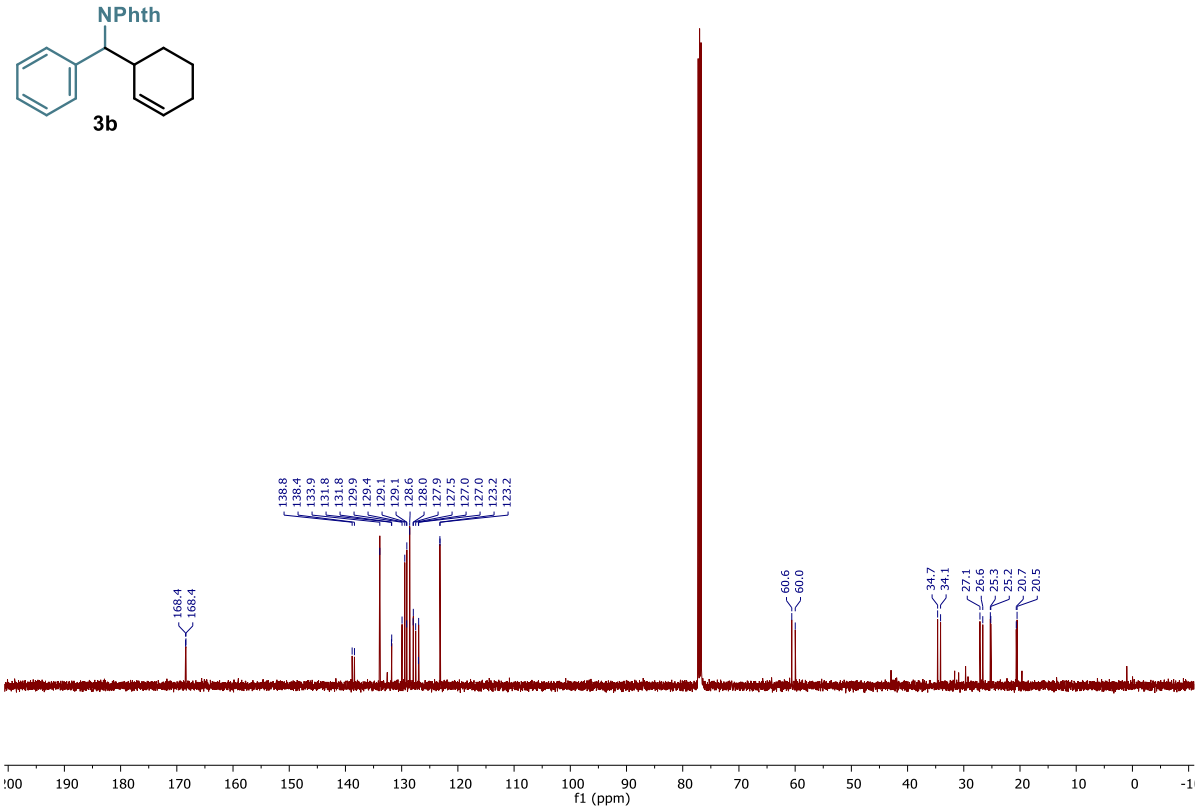
^{19}F NMR (376 MHz, $CDCl_3$) of **3a**



^{1}H NMR (500 MHz, $CDCl_3$) of **3b**



^{13}C NMR (126 MHz, $CDCl_3$) of **3b**



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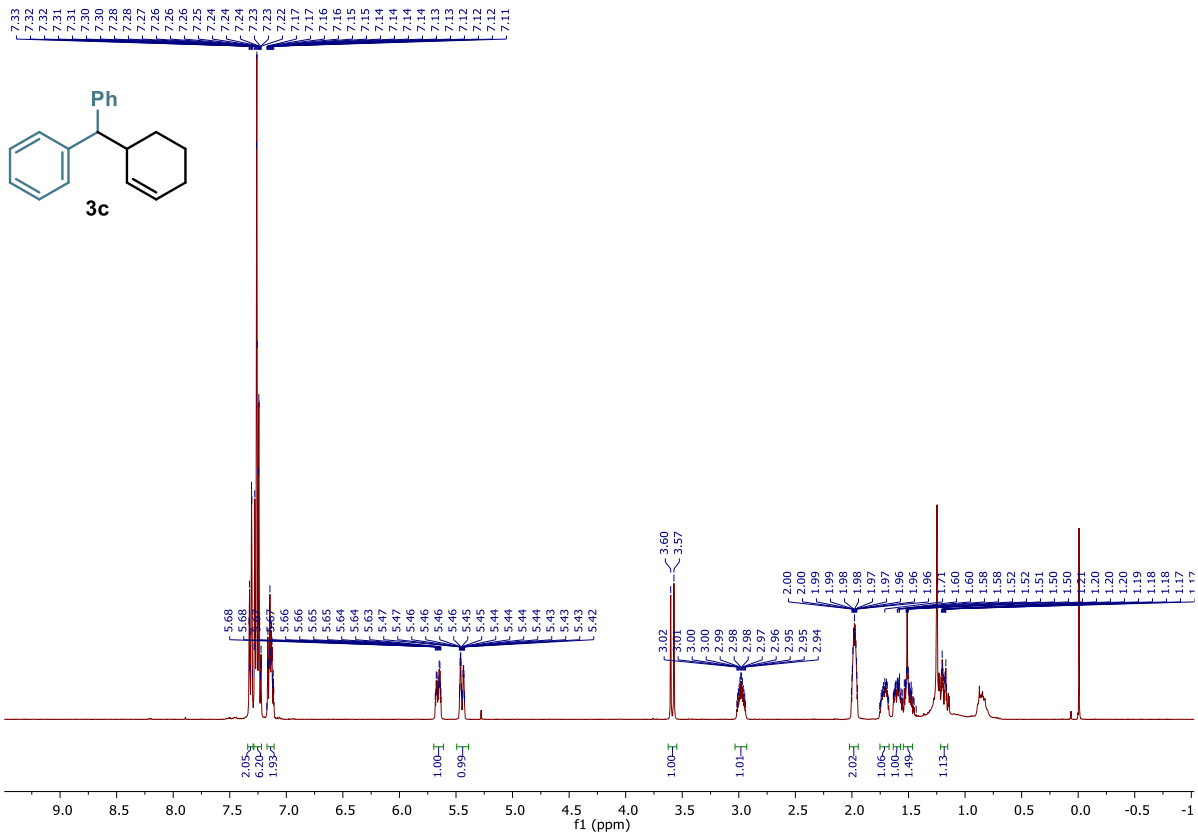

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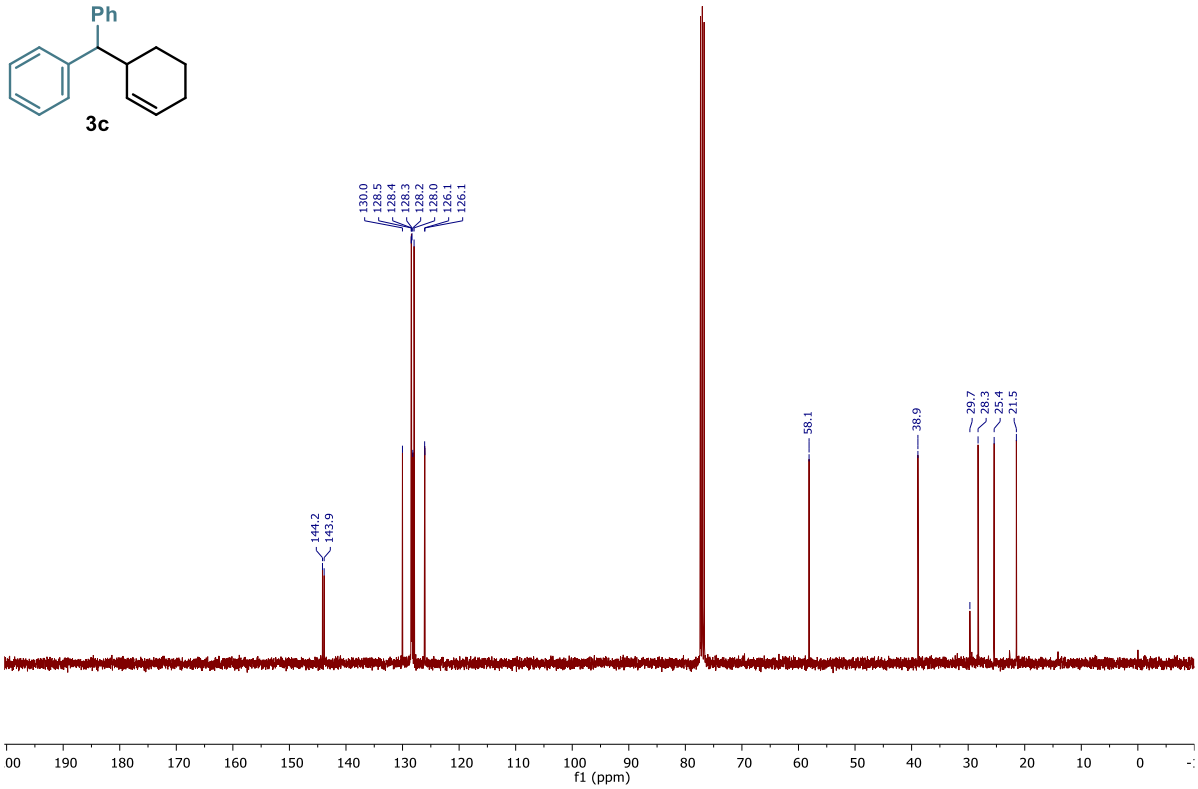

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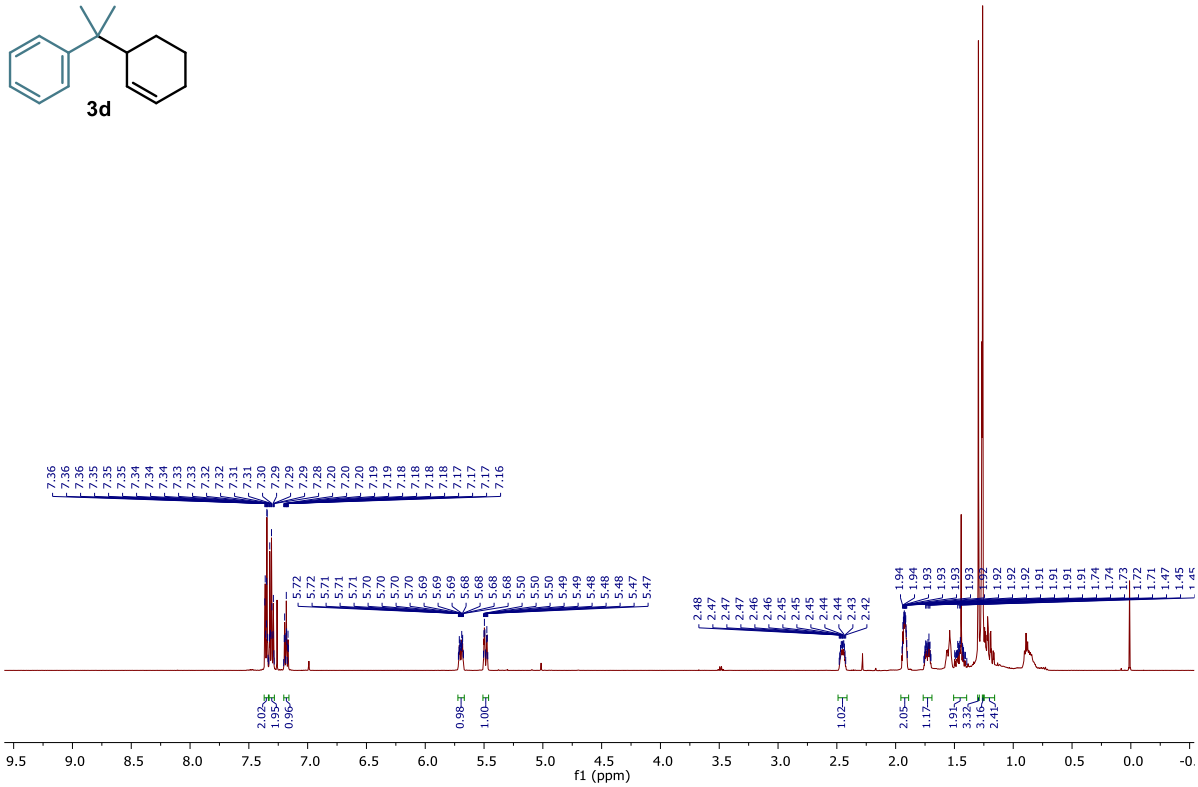

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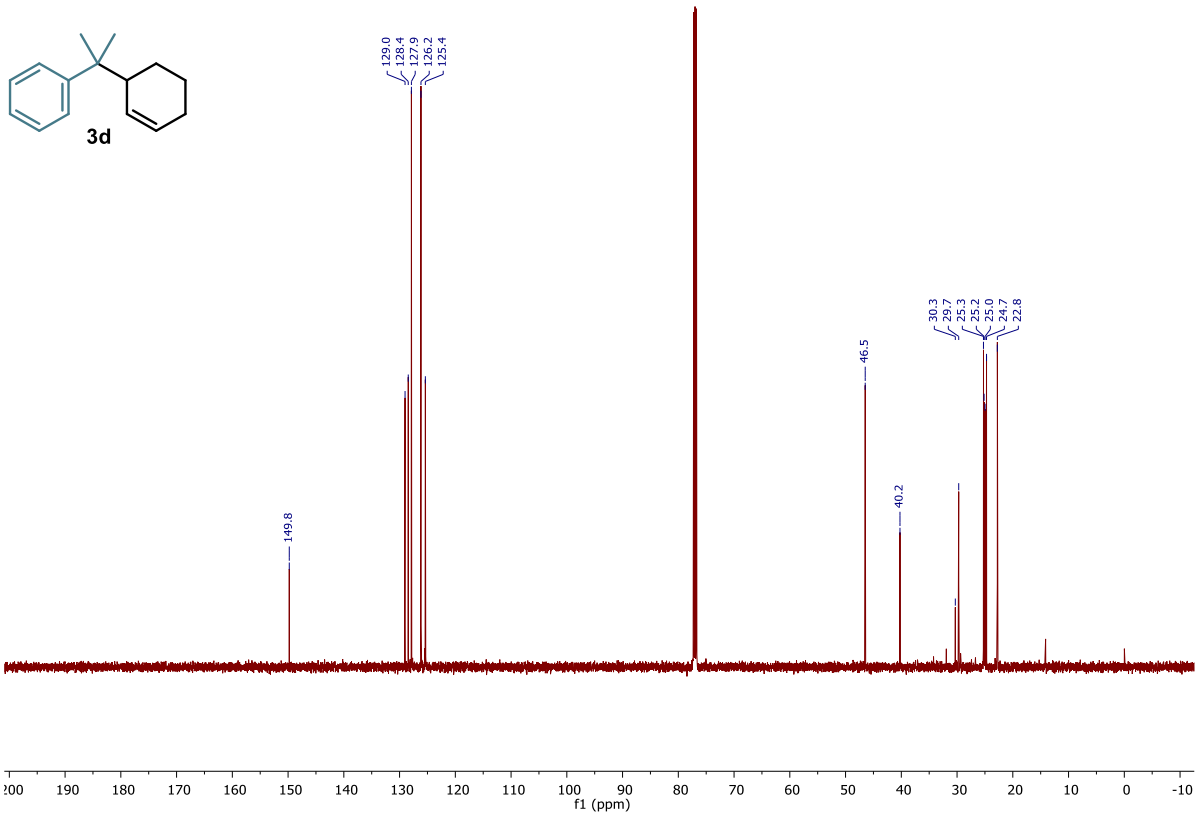

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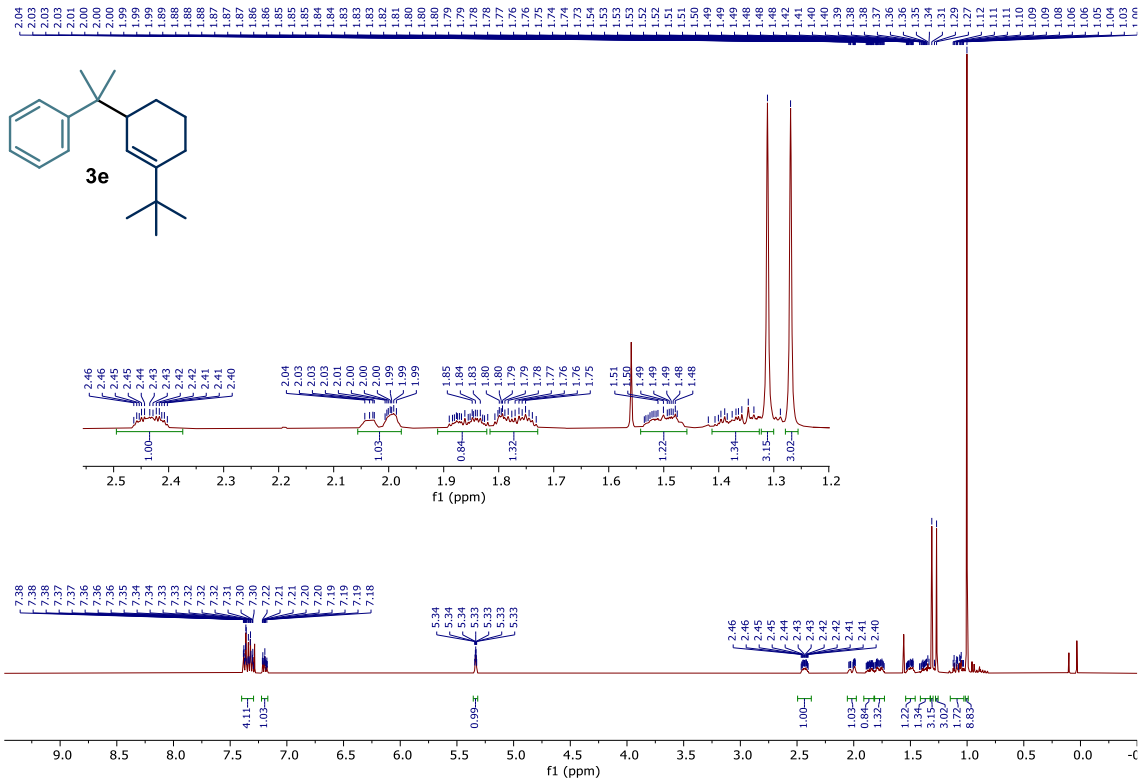

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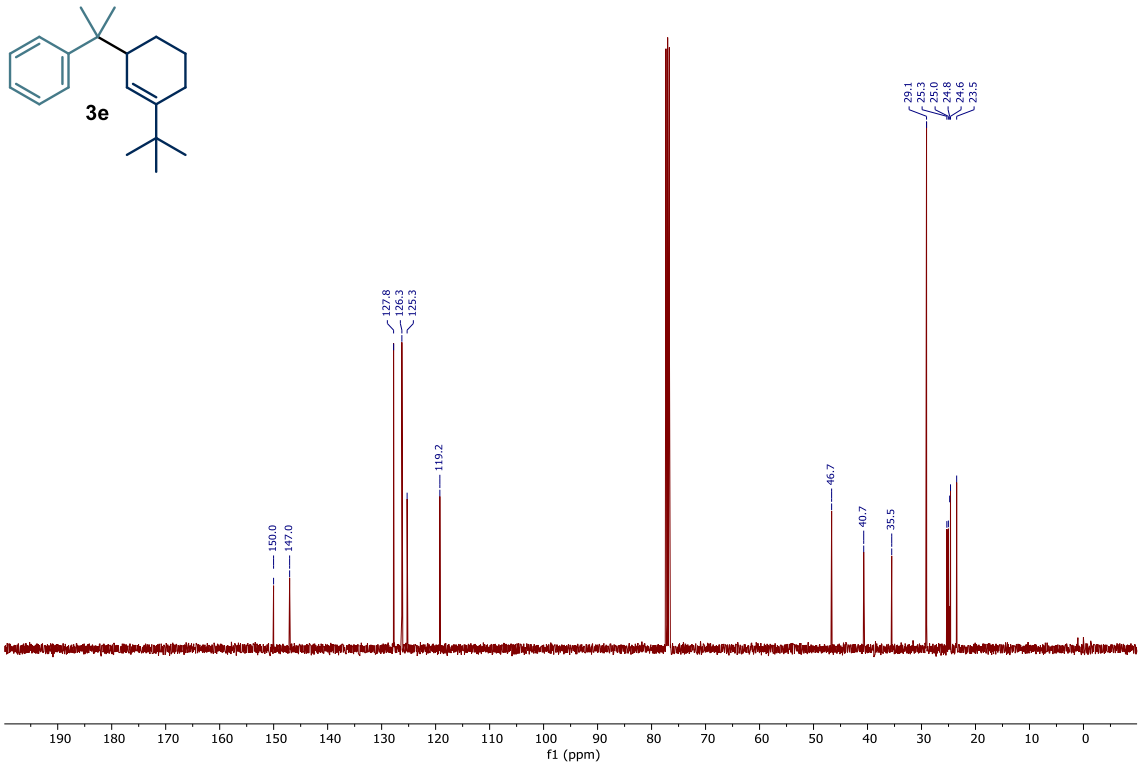

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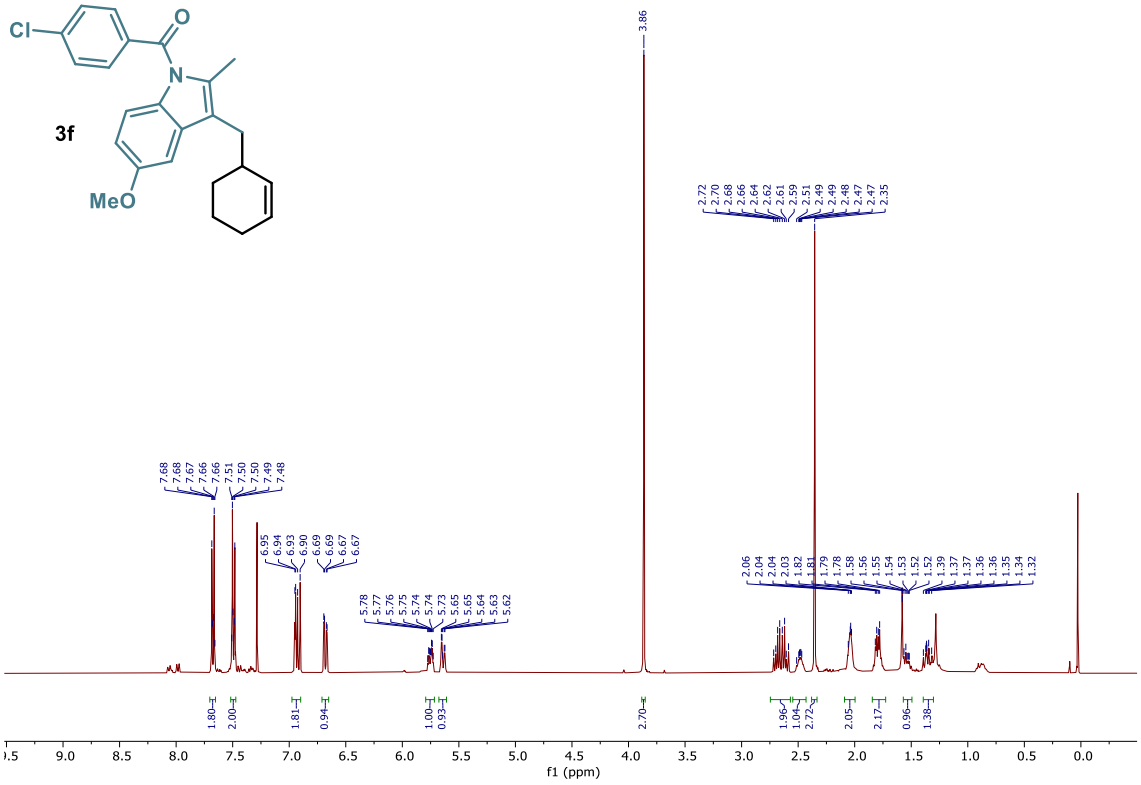

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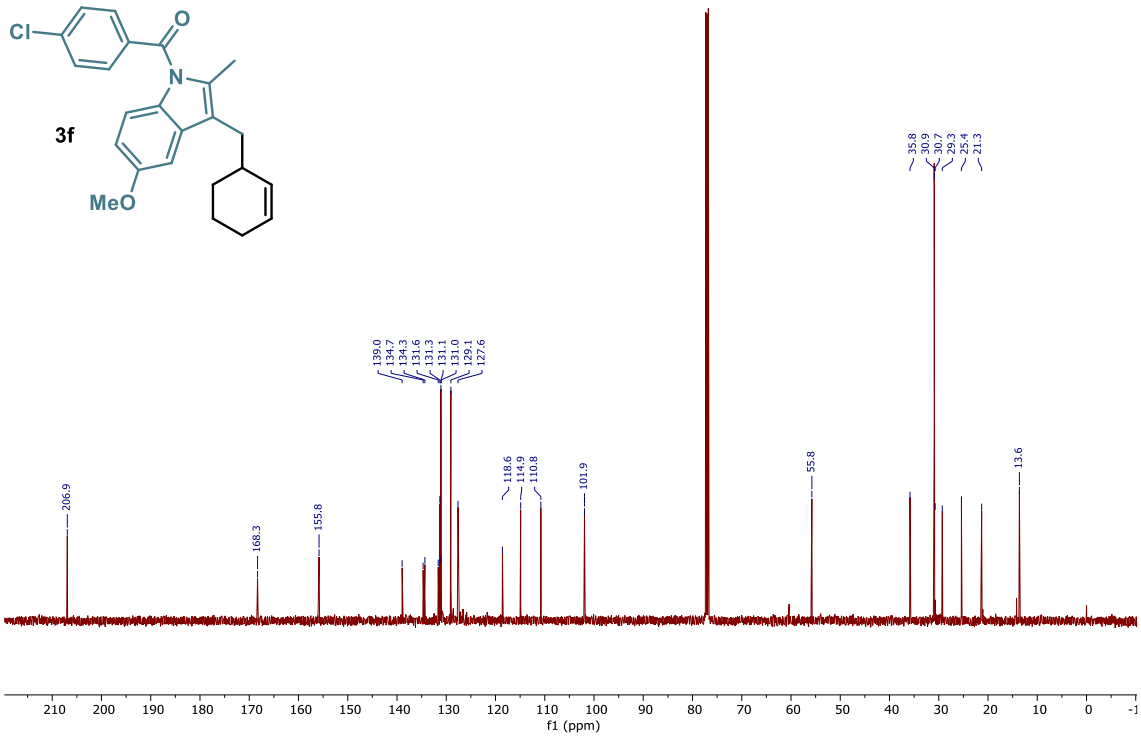

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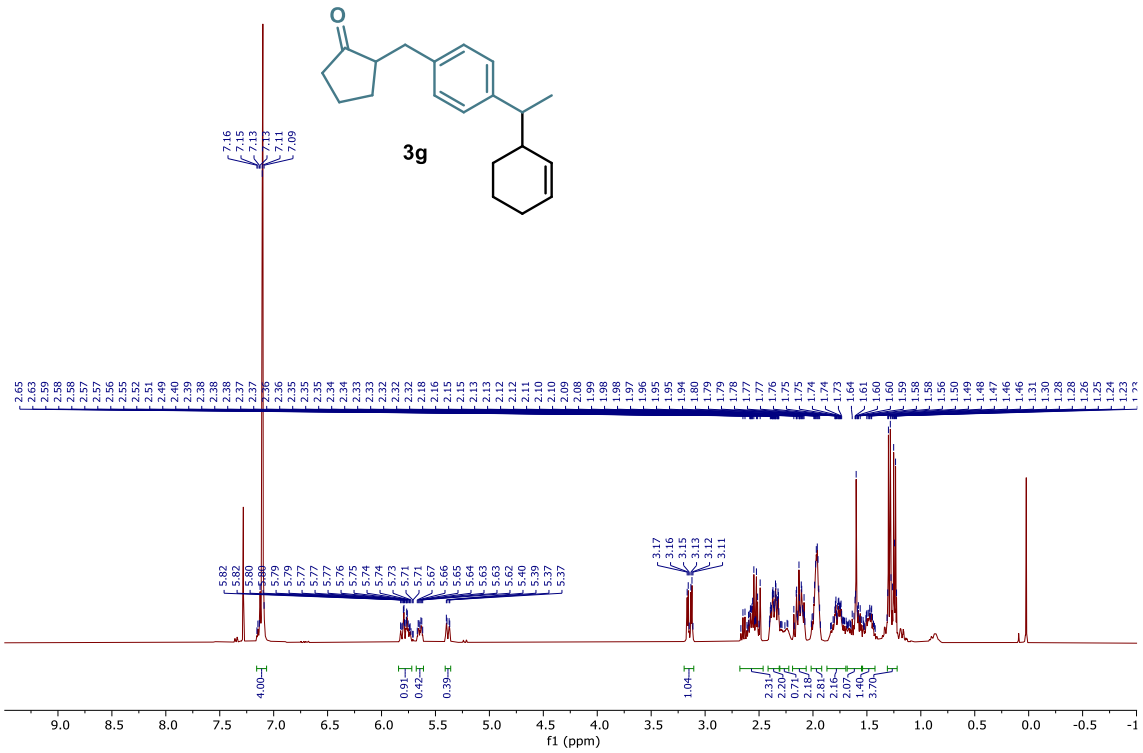

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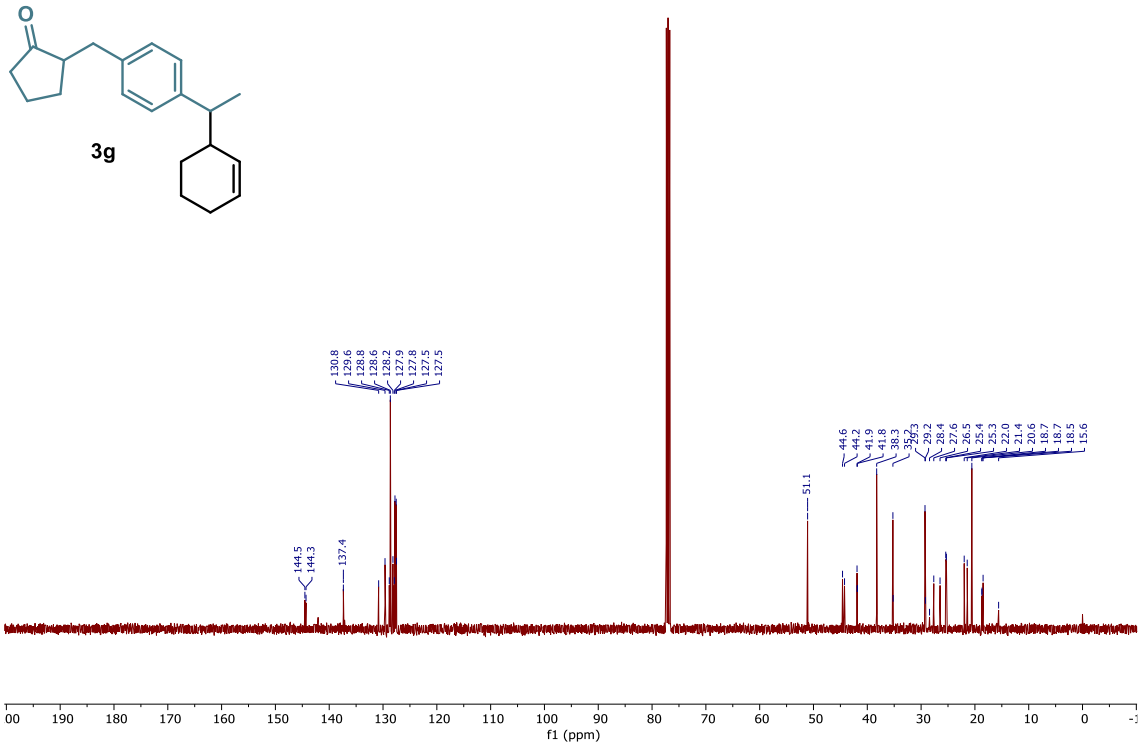

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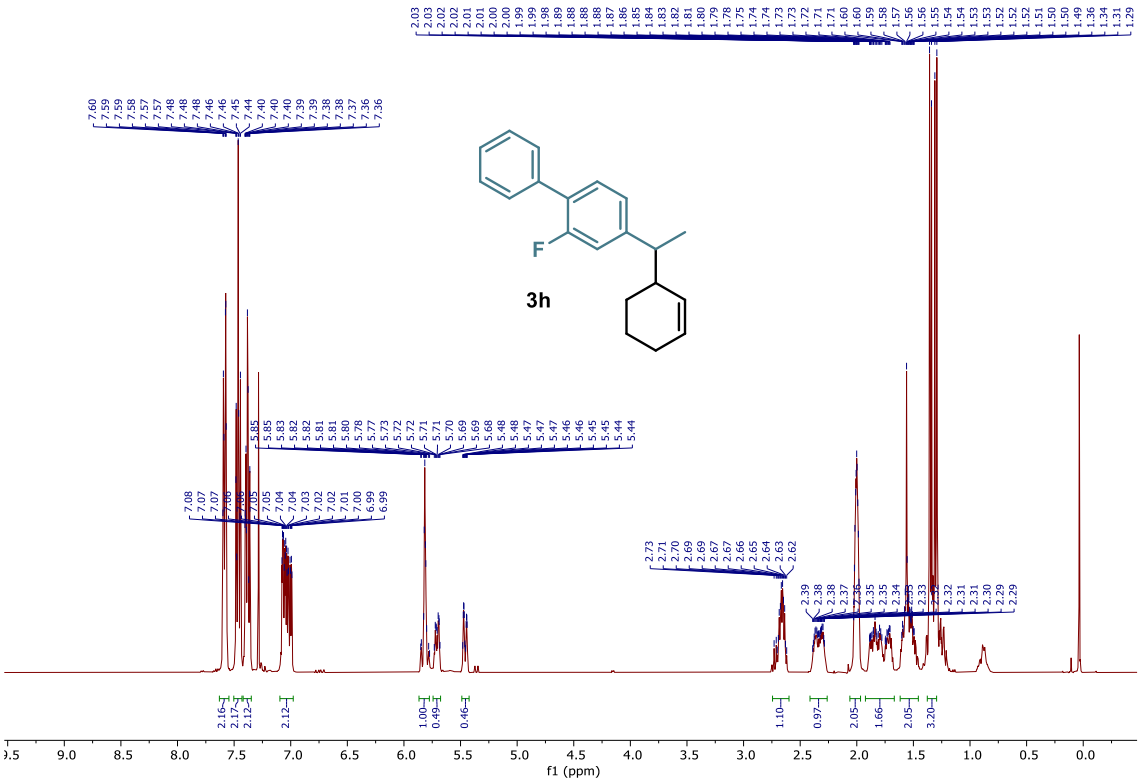
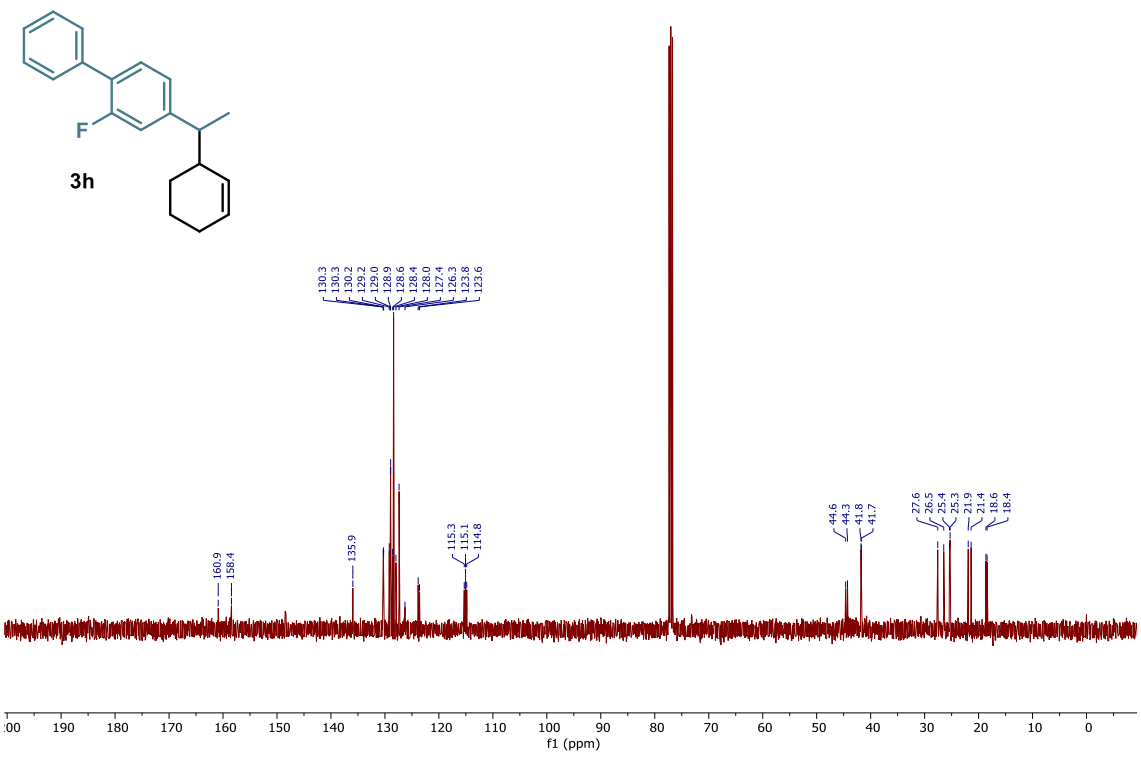
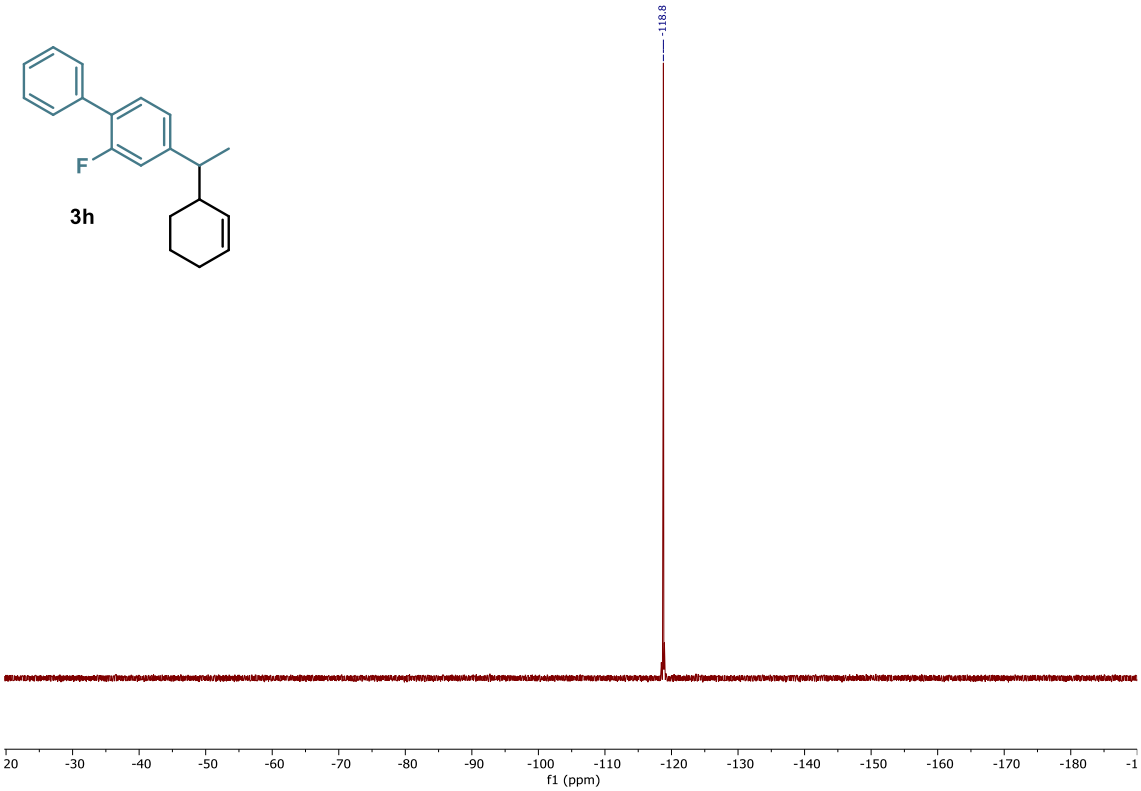


^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



^{19}F NMR (376 MHz, $CDCl_3$) of **3h**



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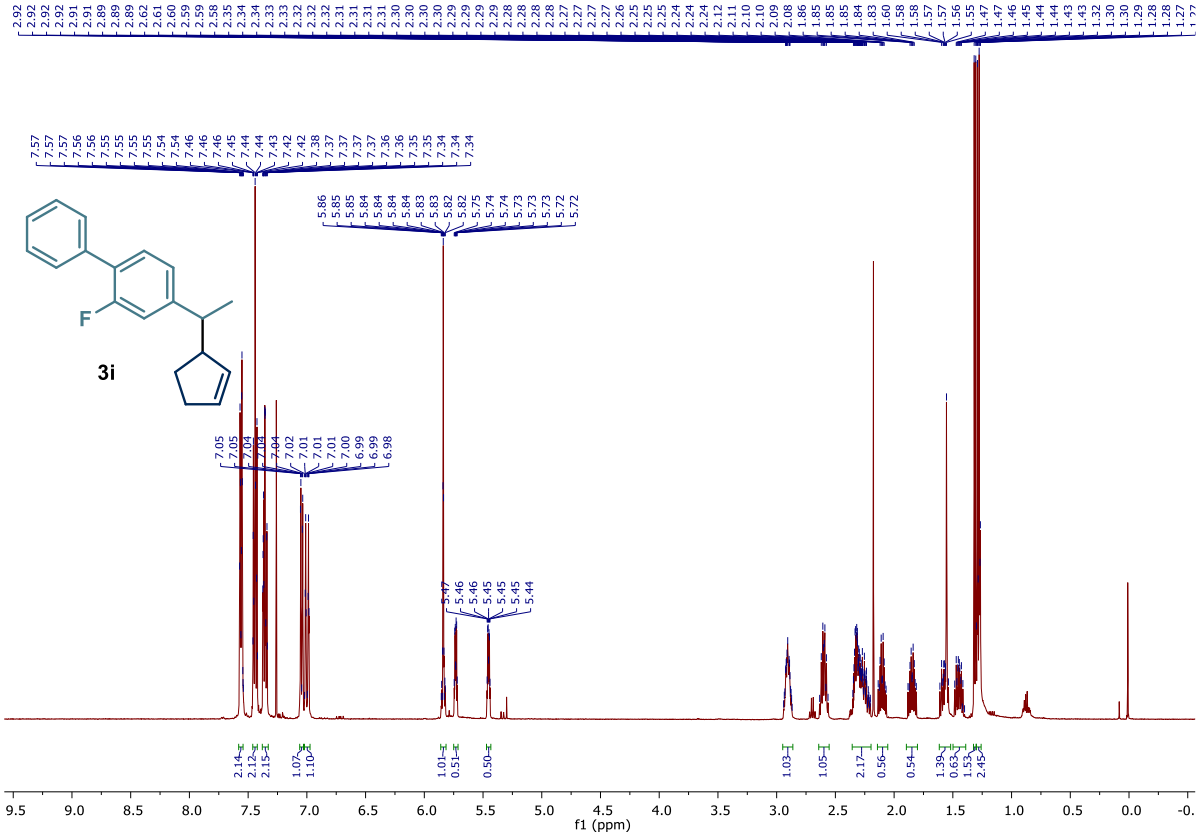

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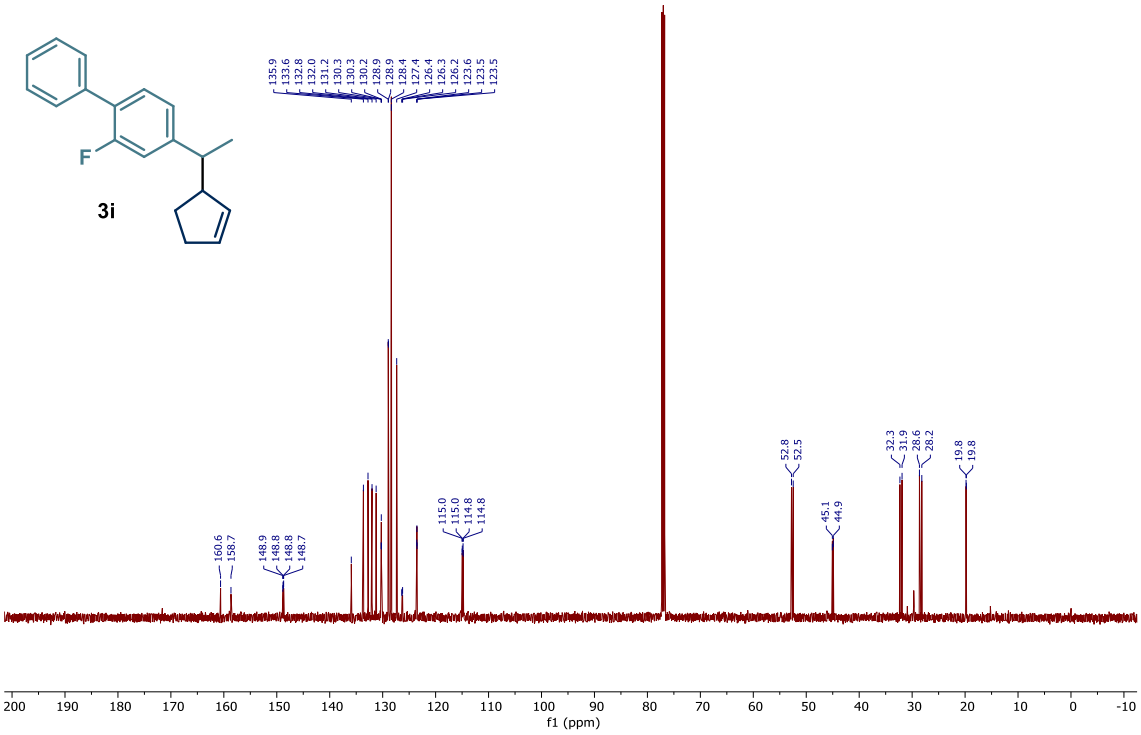

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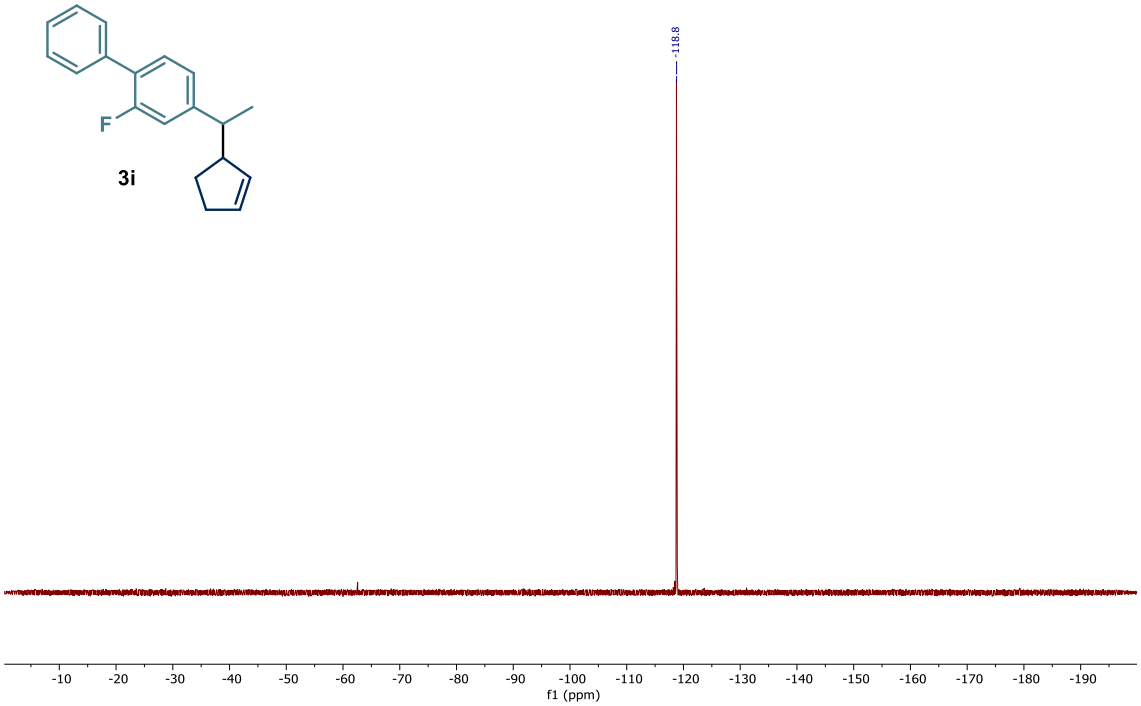

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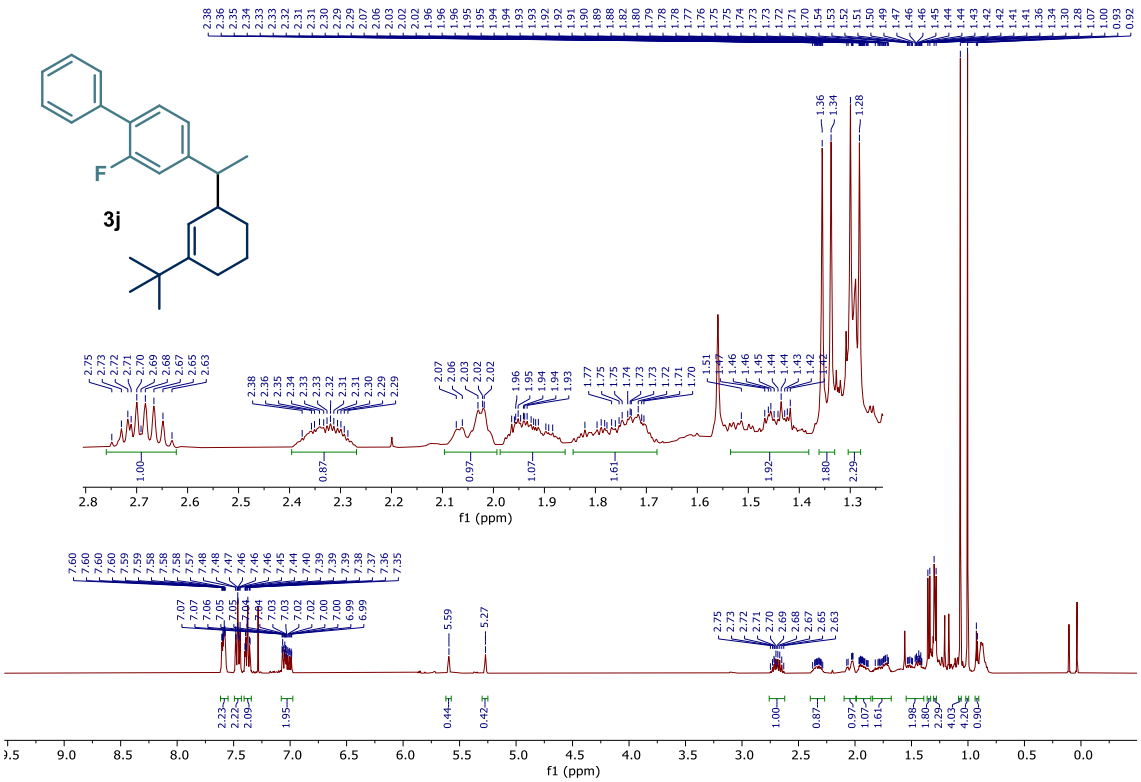

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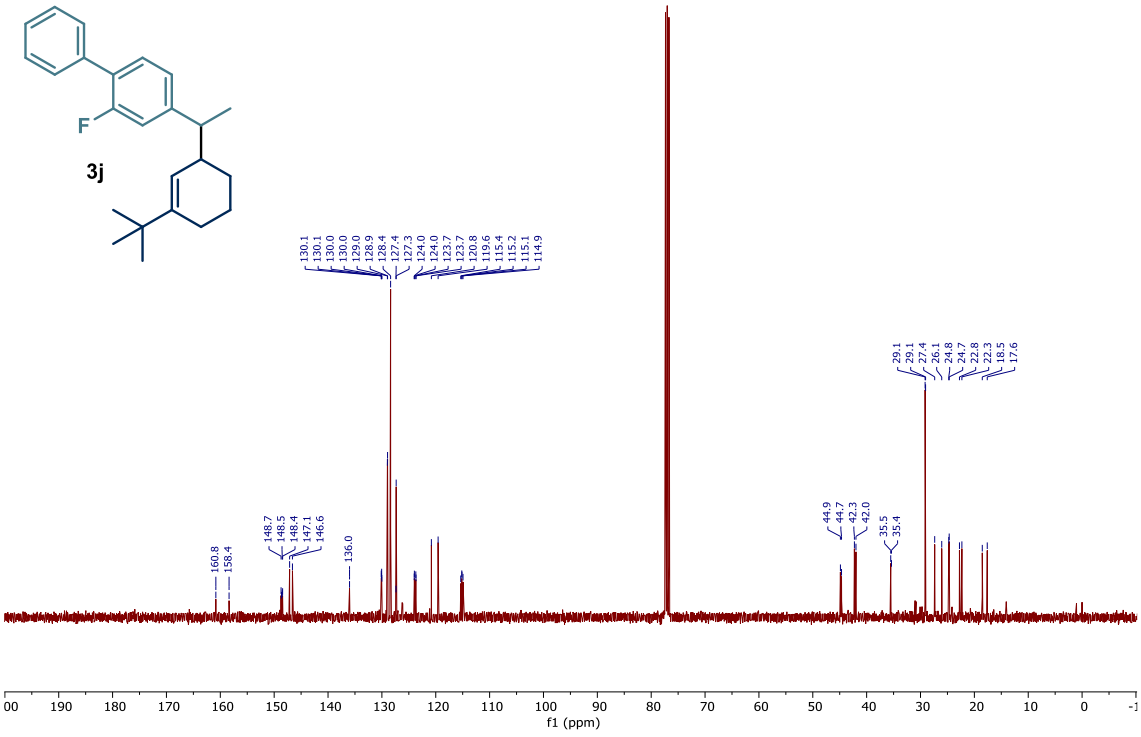

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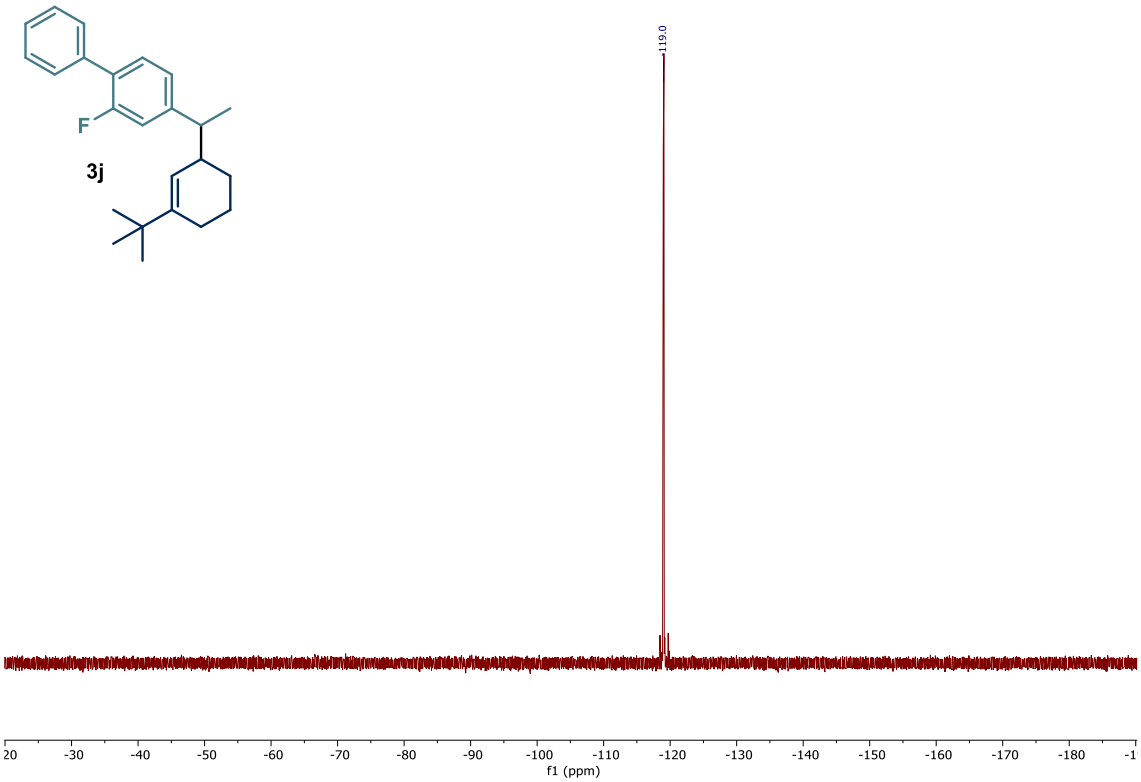

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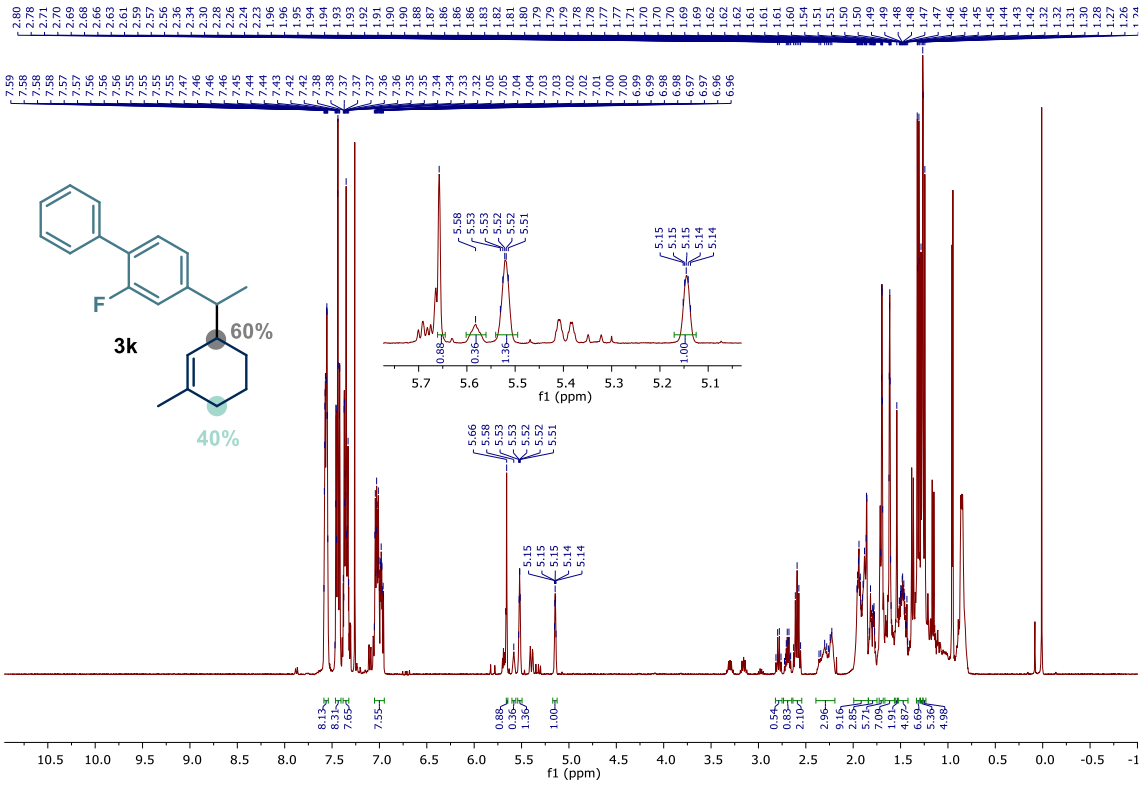

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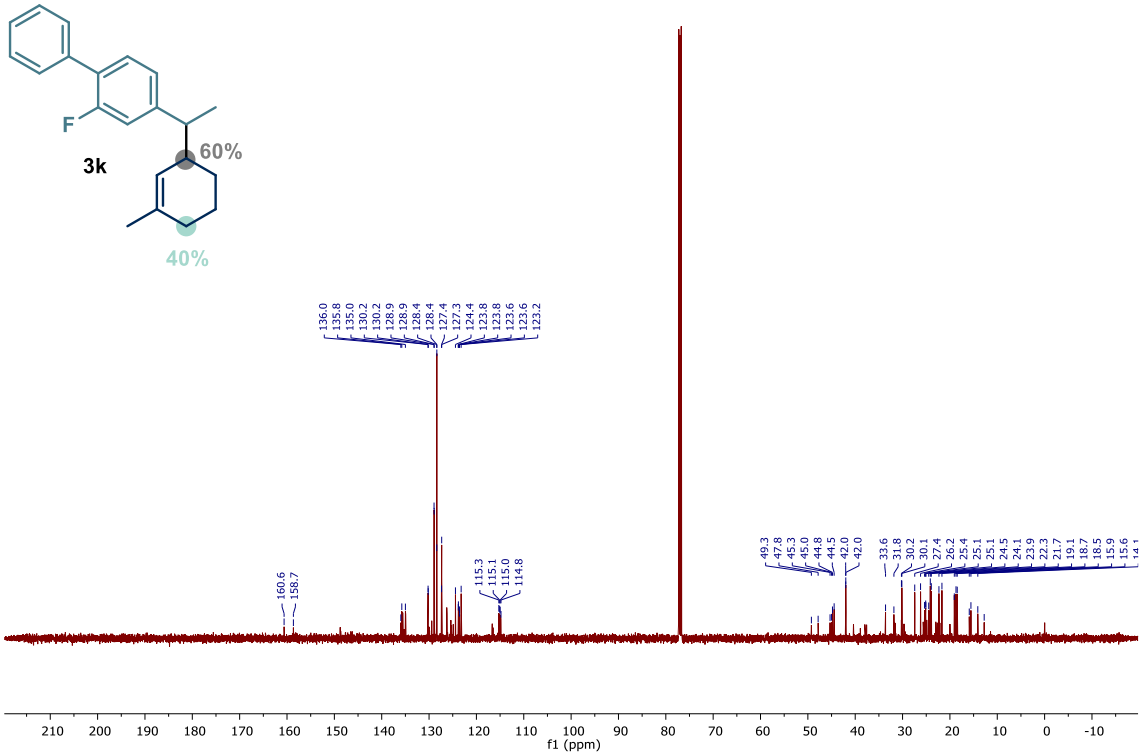

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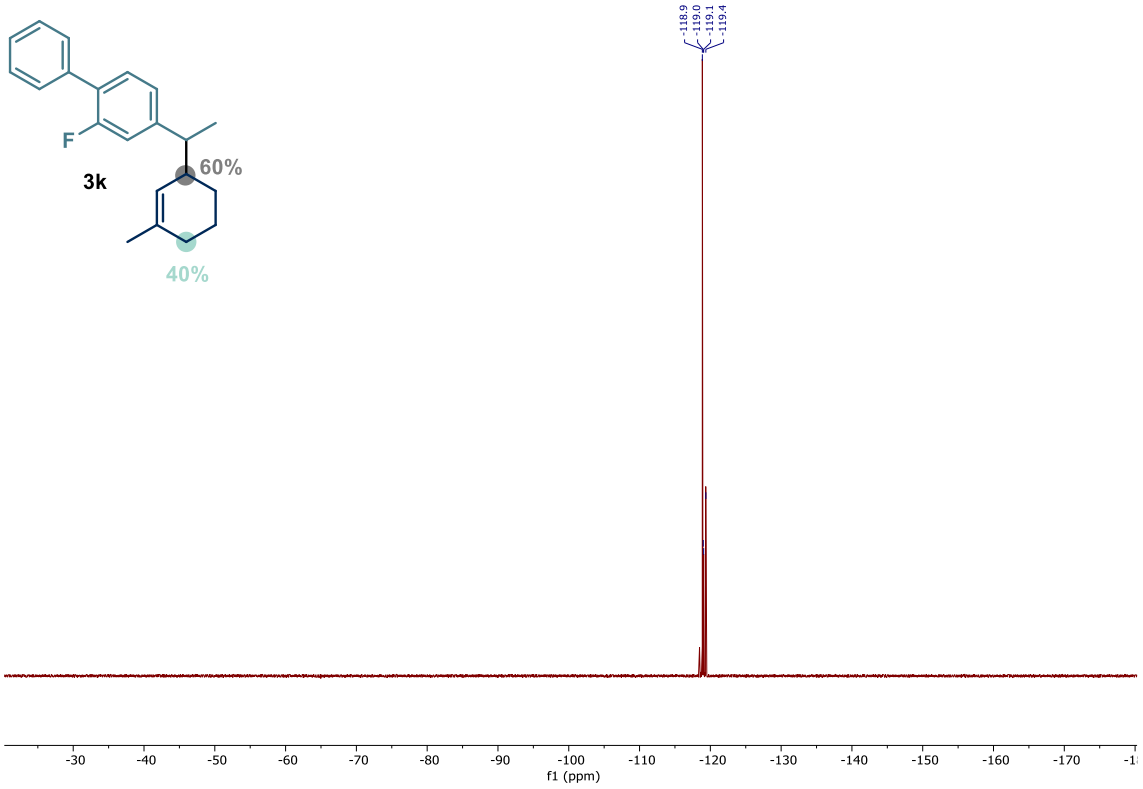

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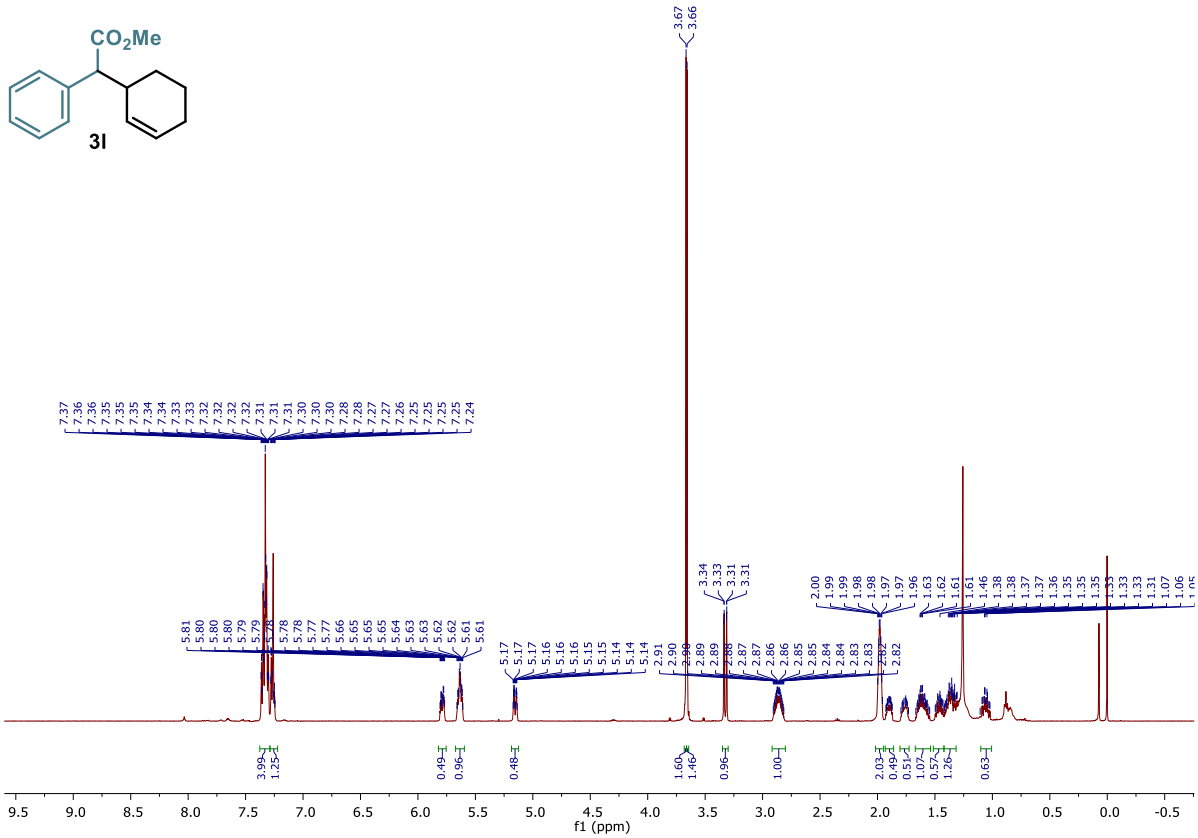

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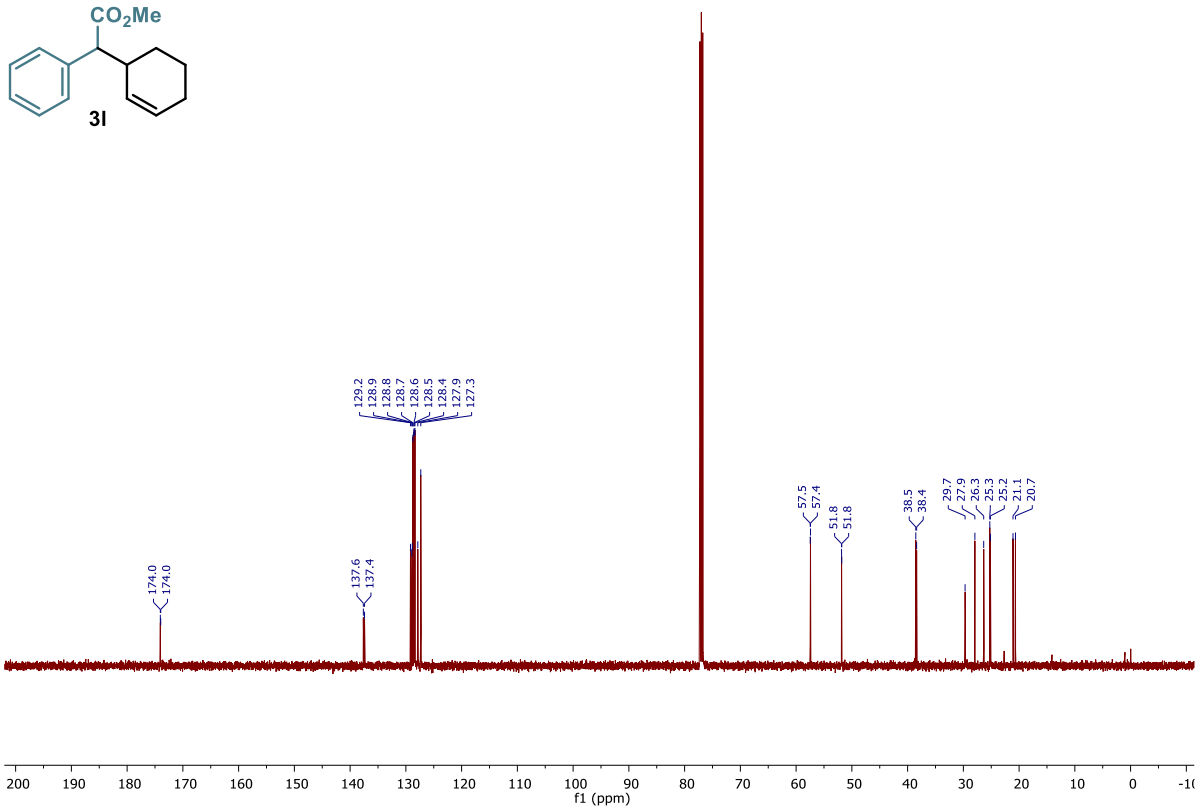

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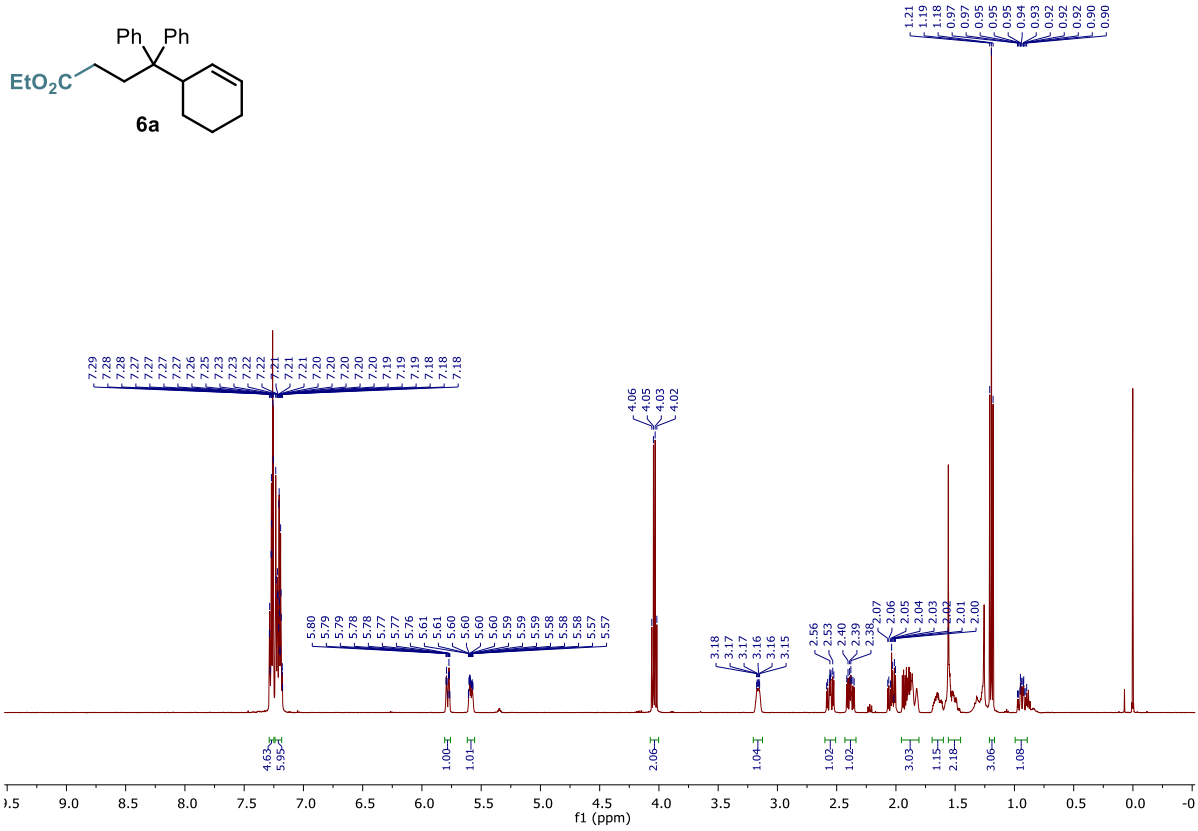

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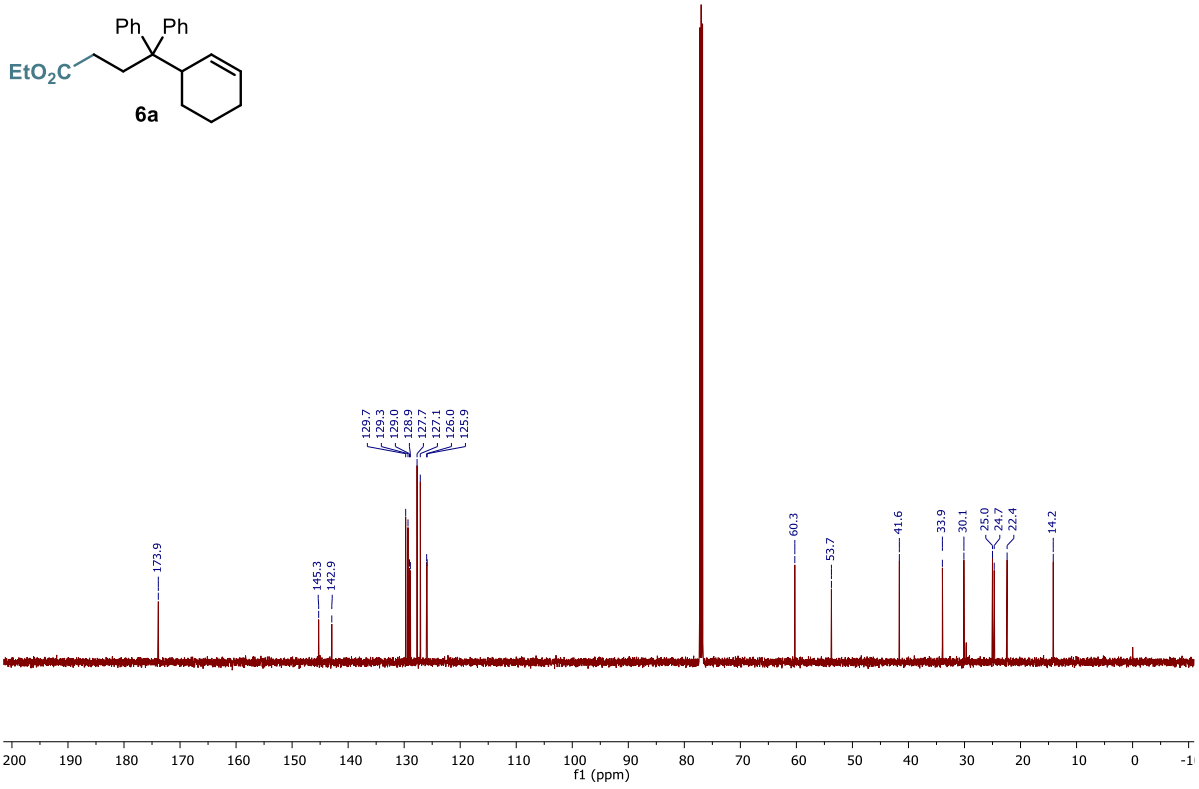

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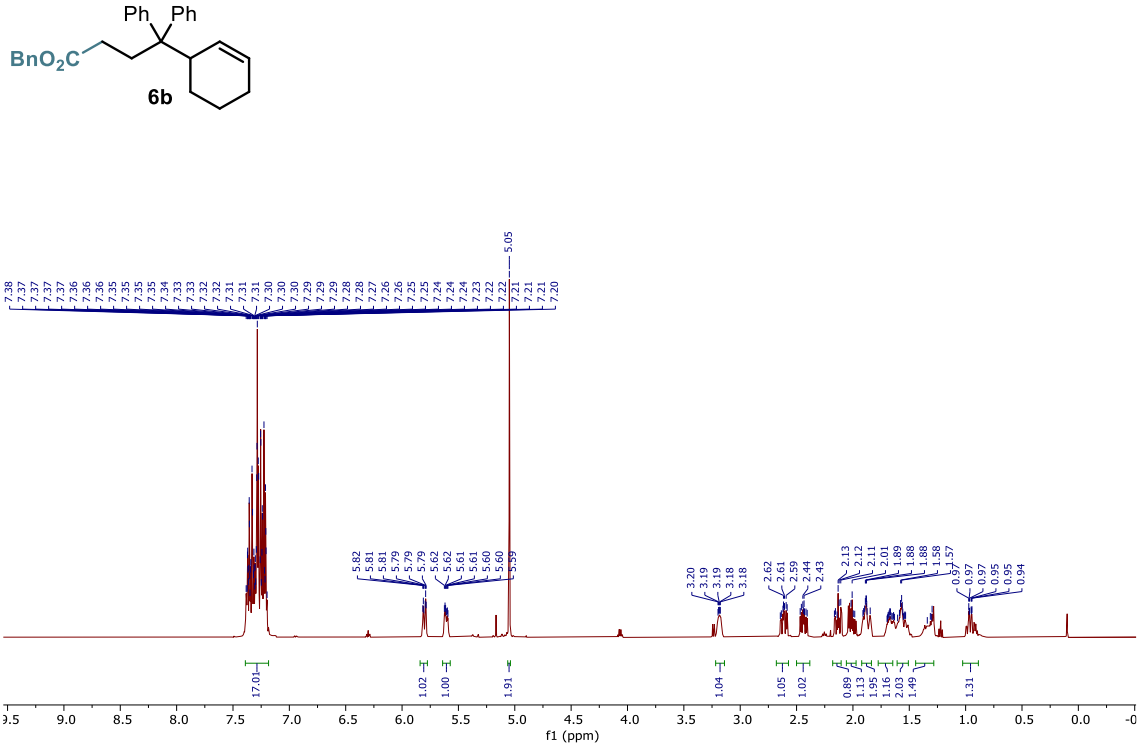
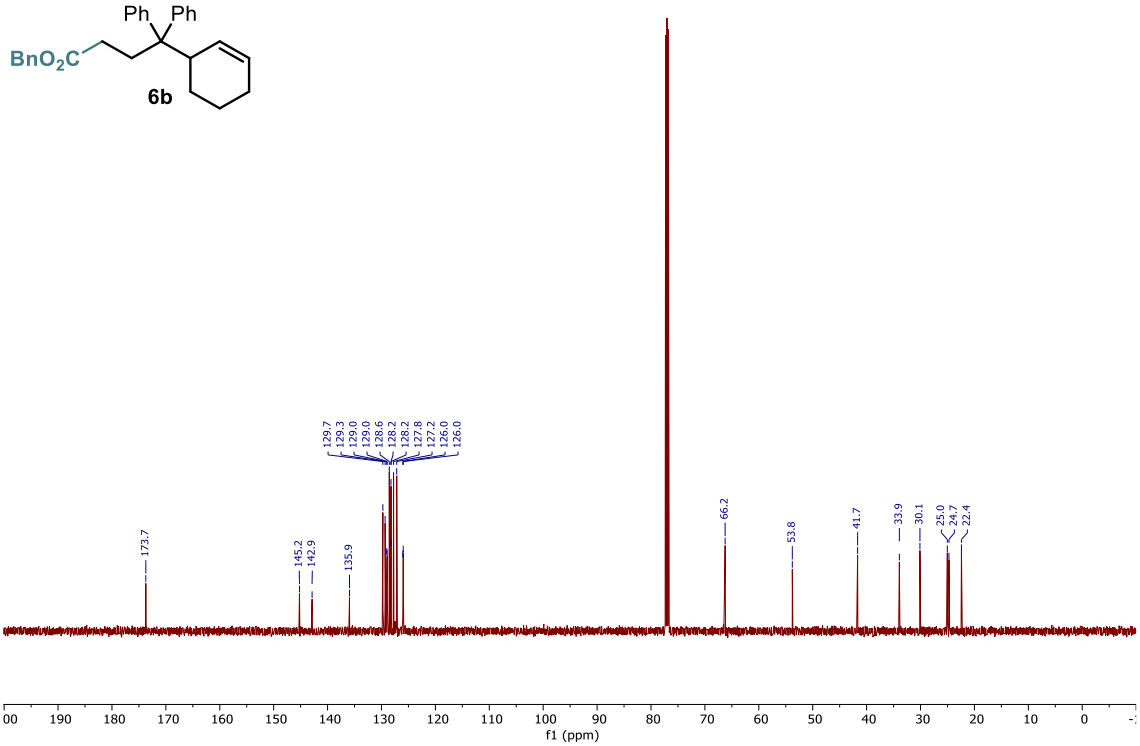
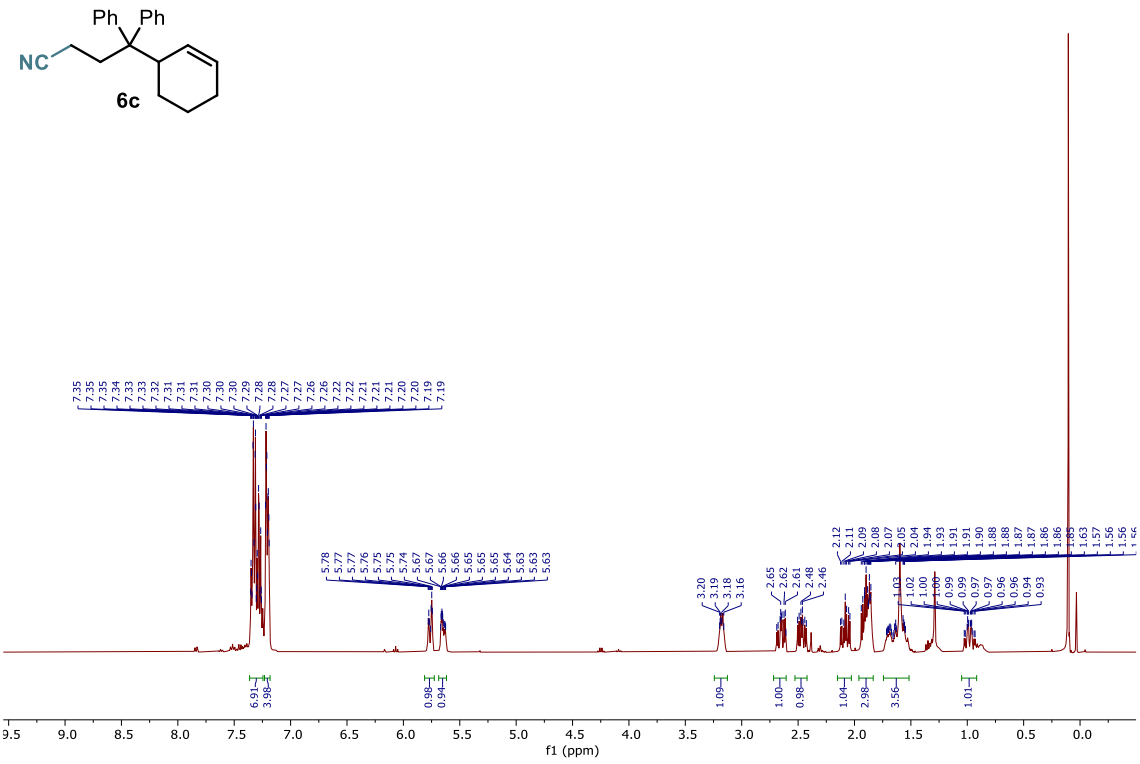


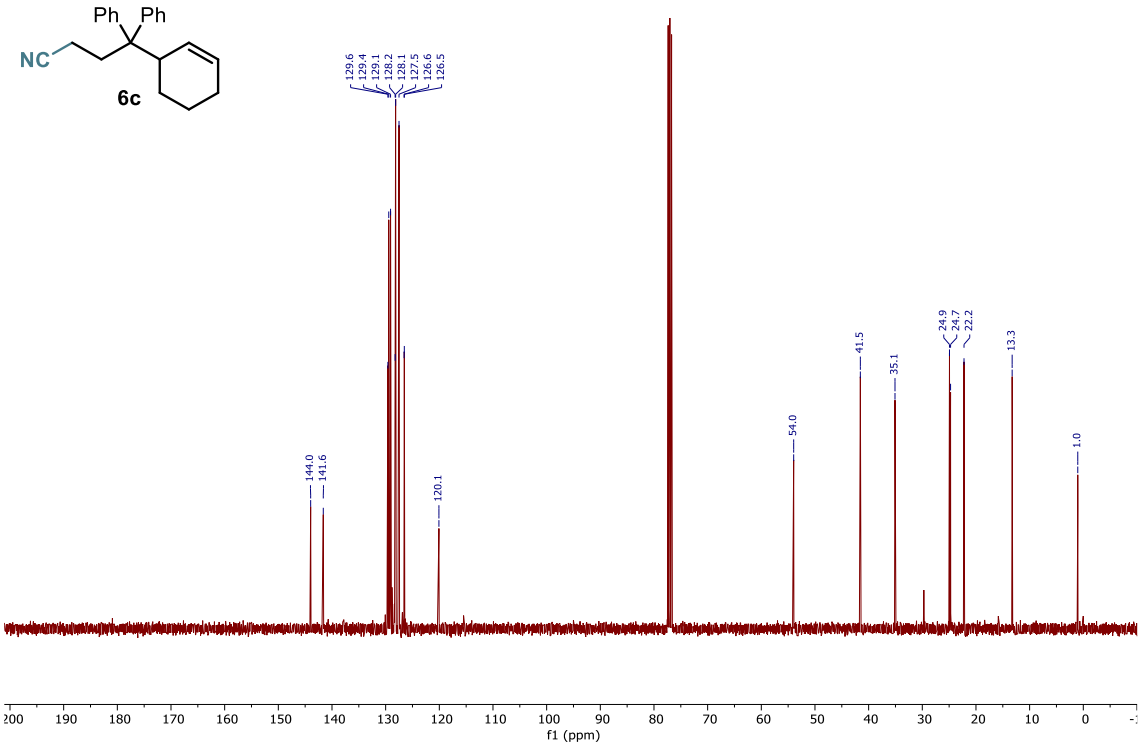
^{13}C NMR (126 MHz, $CDCl_3$) of **6b**



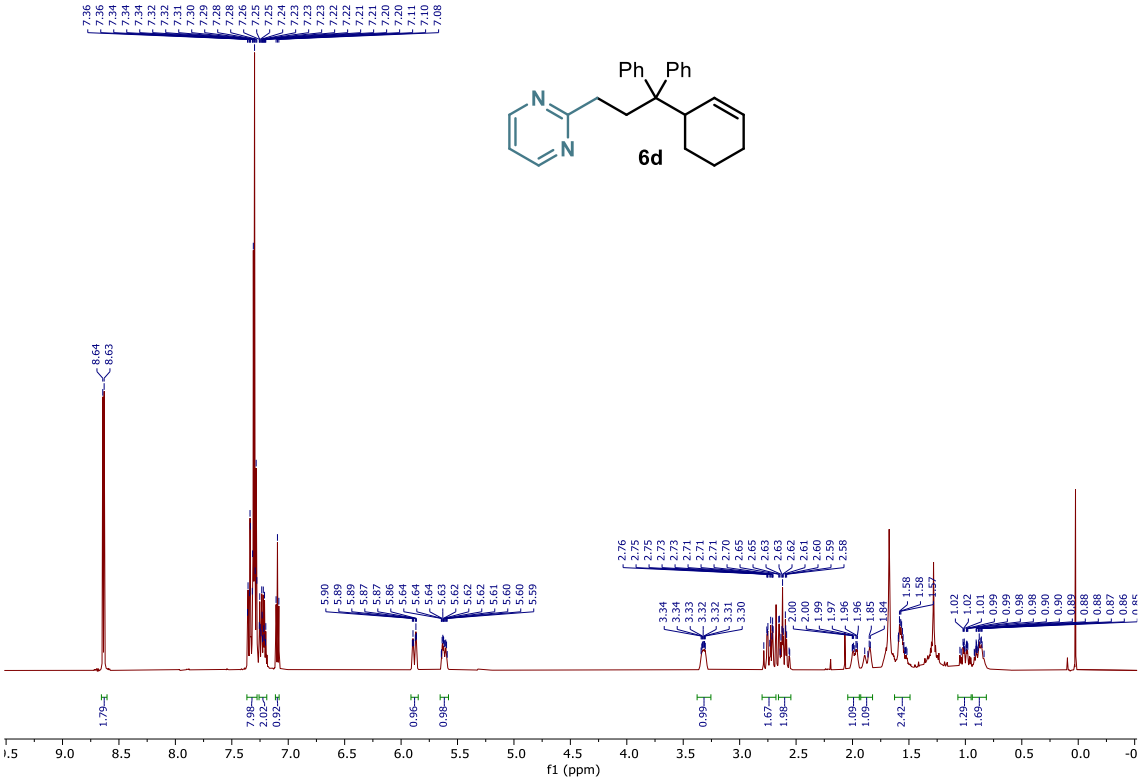
^{1}H NMR (400 MHz, $CDCl_3$) of **6c**



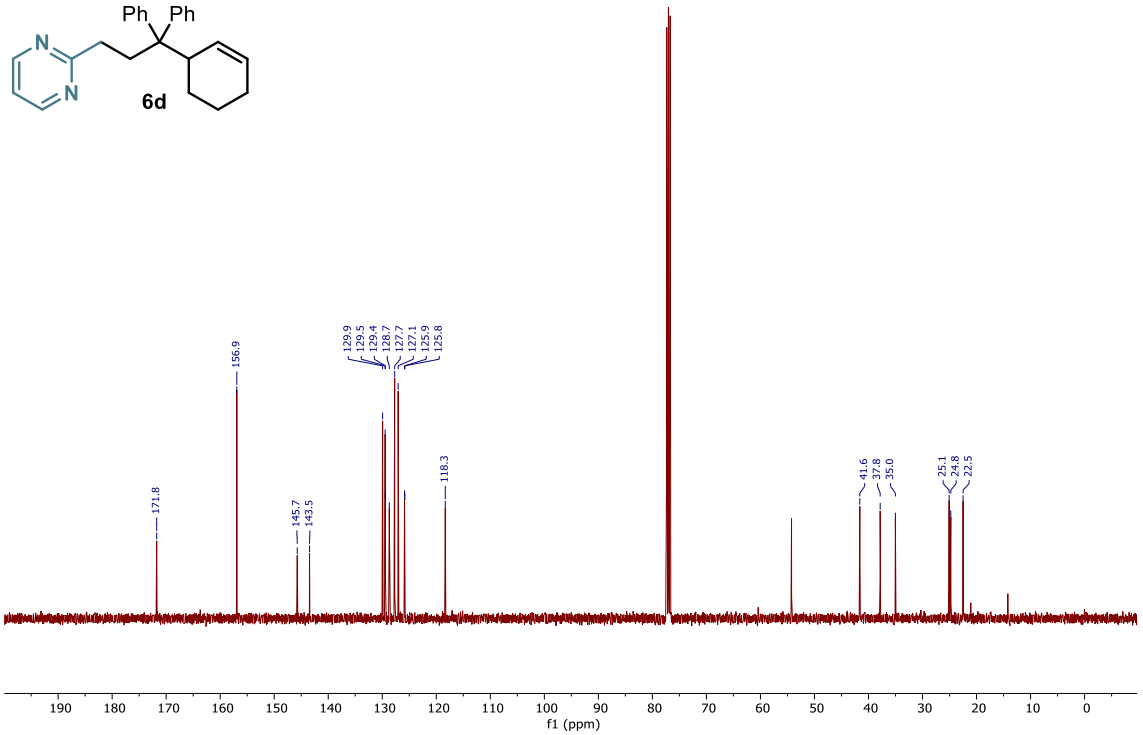
^{13}C NMR (101 MHz, $CDCl_3$) of **6c**



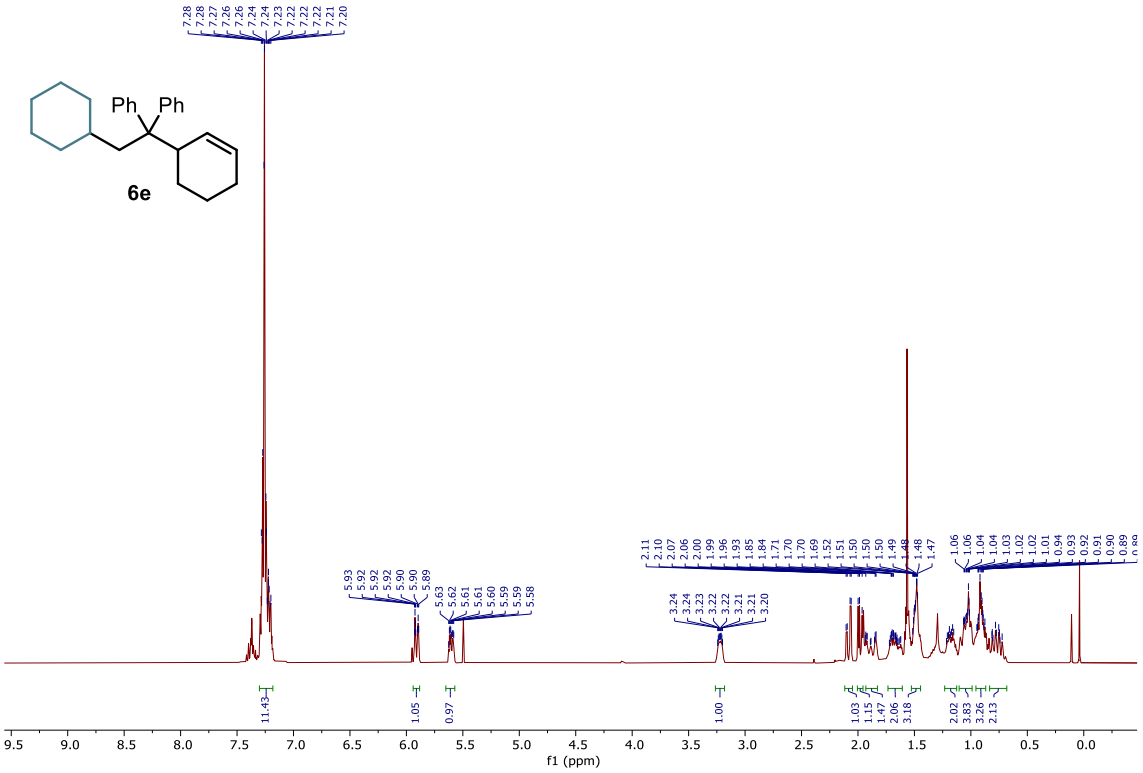
^{1}H NMR (400 MHz, $CDCl_3$) of **6d**



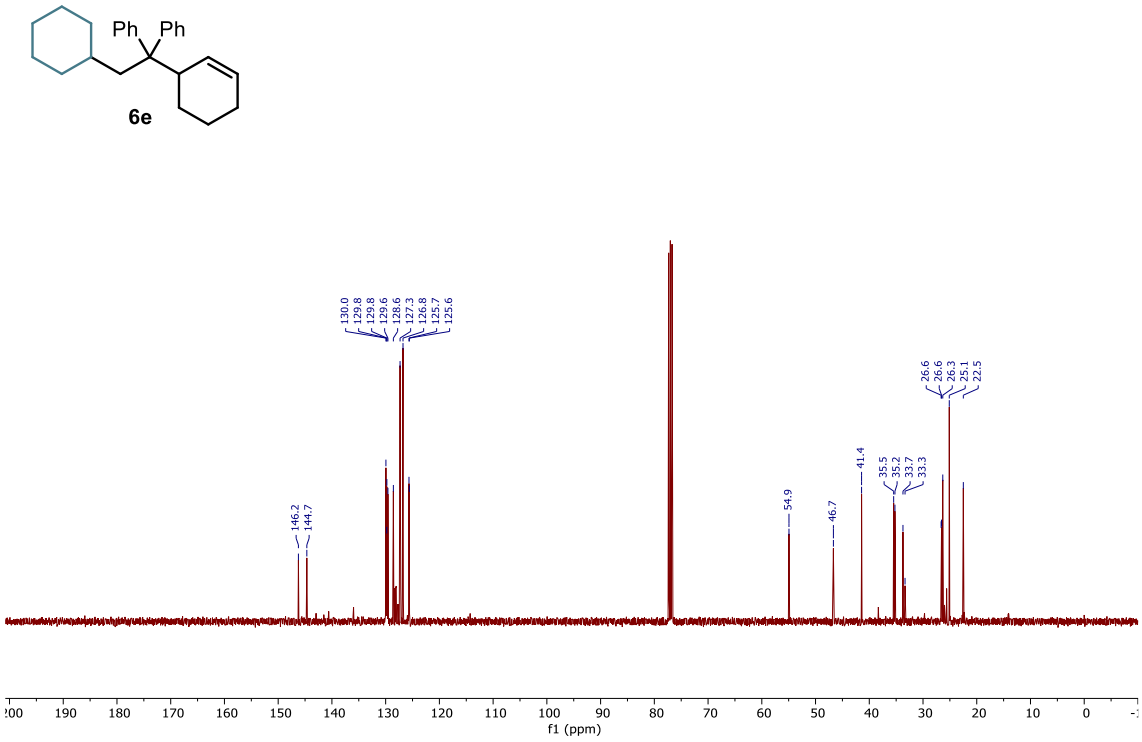
^{13}C NMR (101 MHz, $CDCl_3$) of **6d**



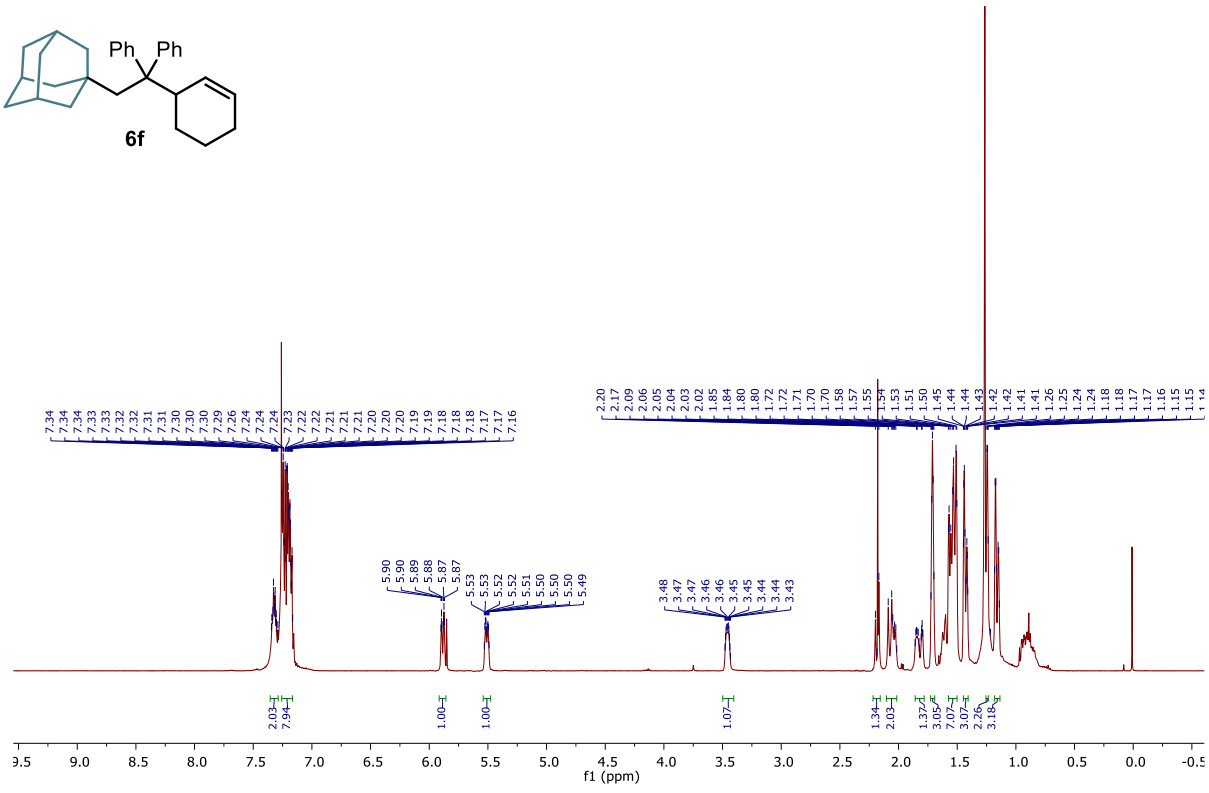
^{1}H NMR (400 MHz, $CDCl_3$) of **6e**



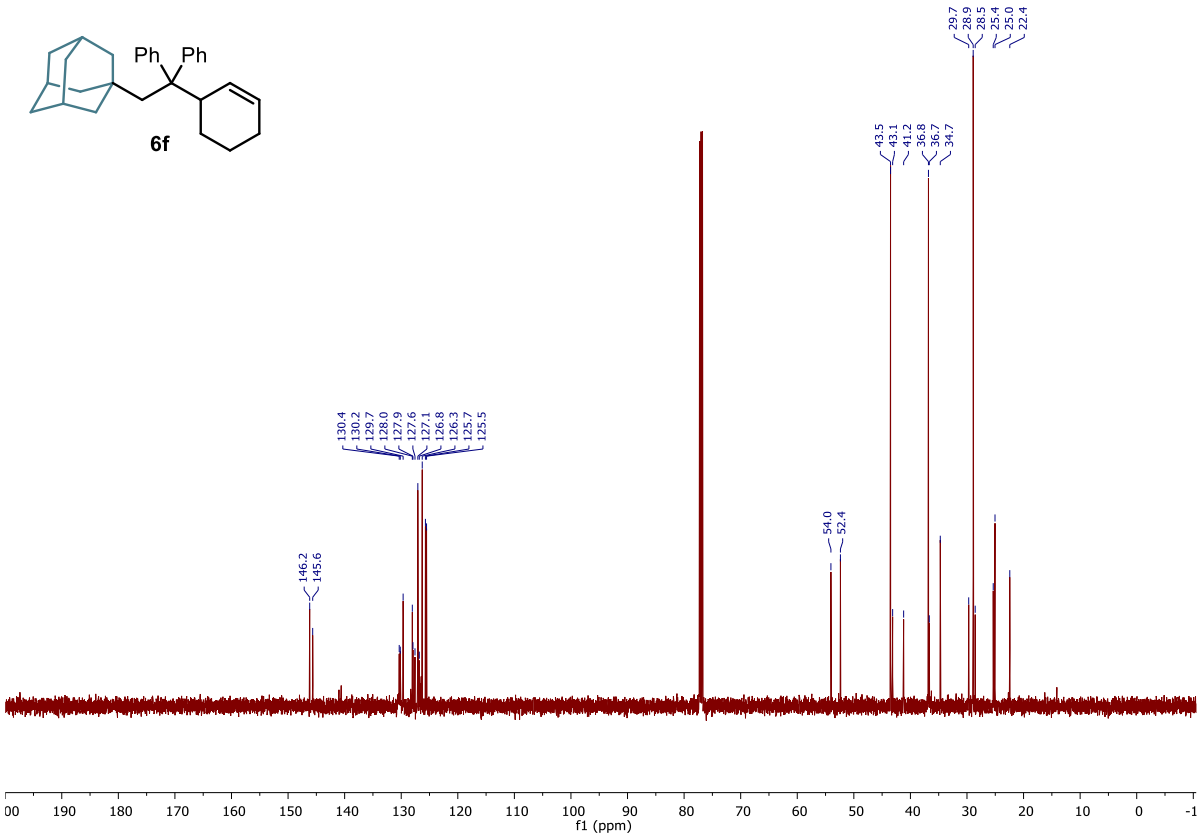
^{13}C NMR (101 MHz, $CDCl_3$) of **6e**



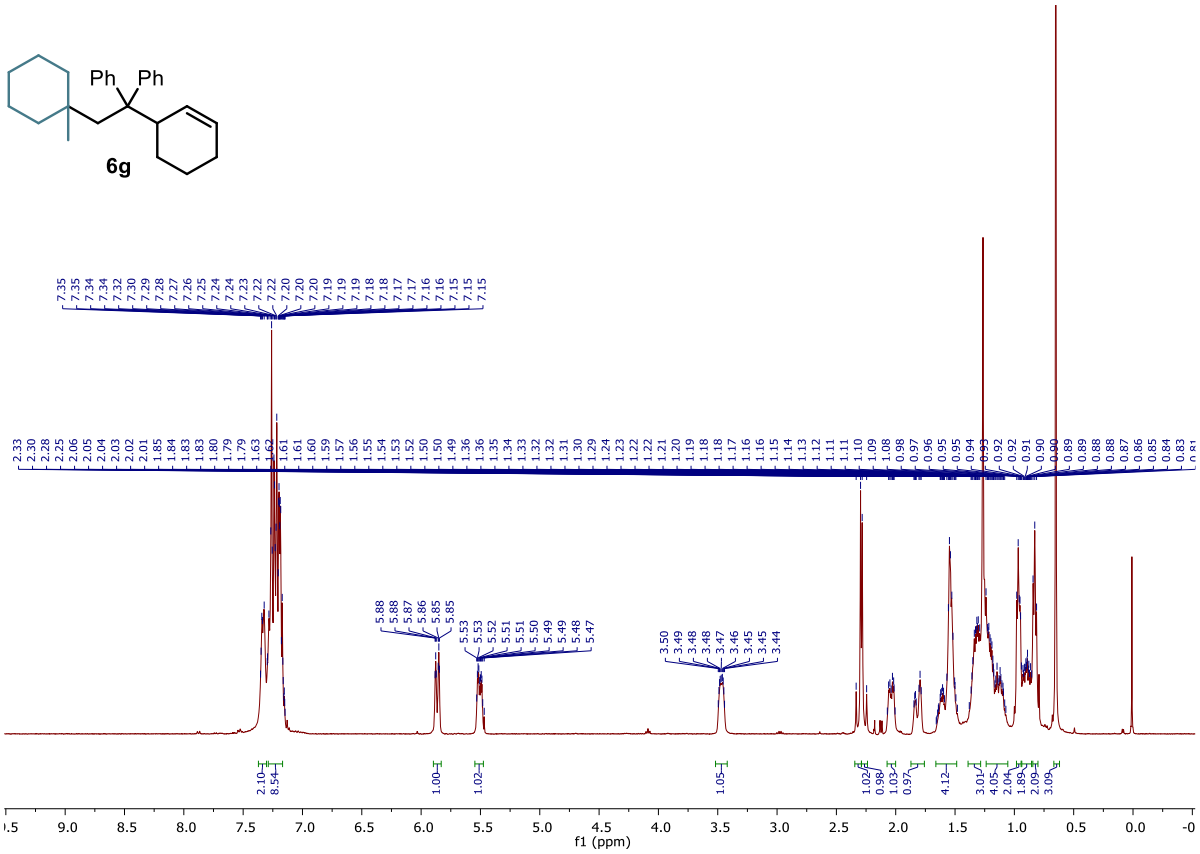
^{1}H NMR (500 MHz, $CDCl_3$) of **6f**



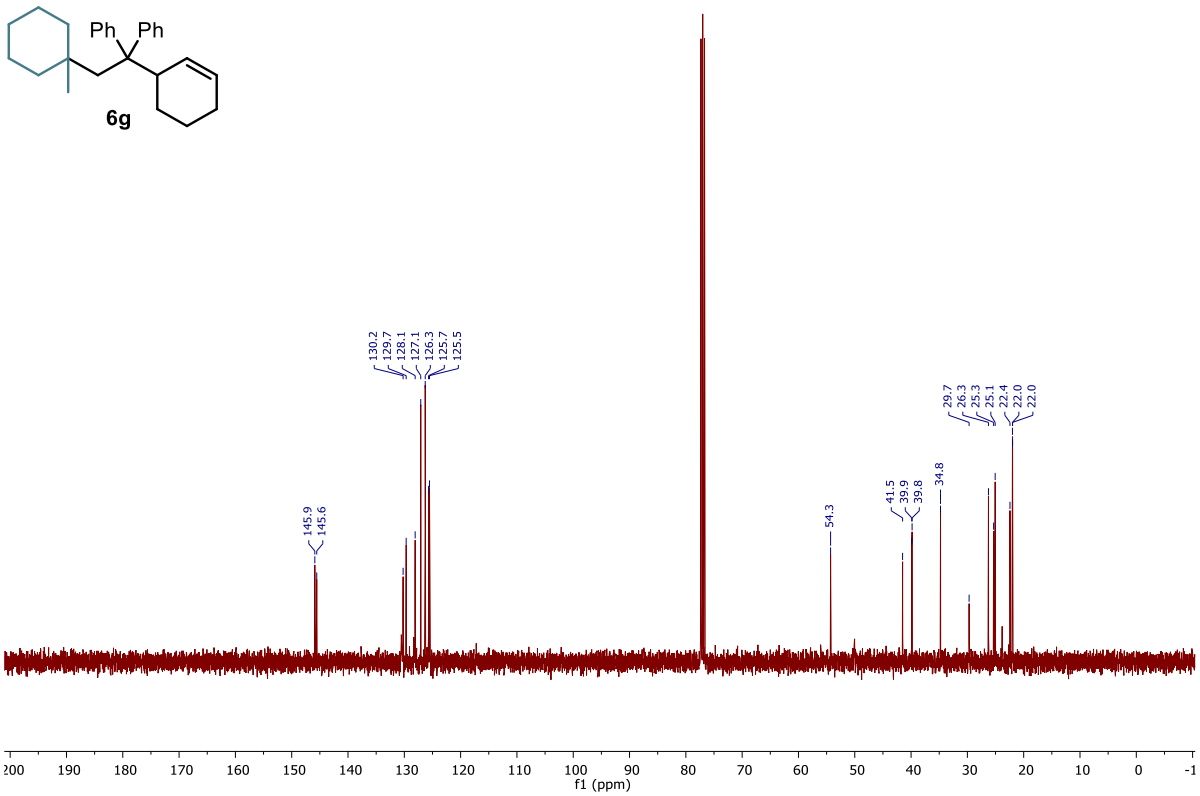
^{13}C NMR (126 MHz, $CDCl_3$) of **6f**



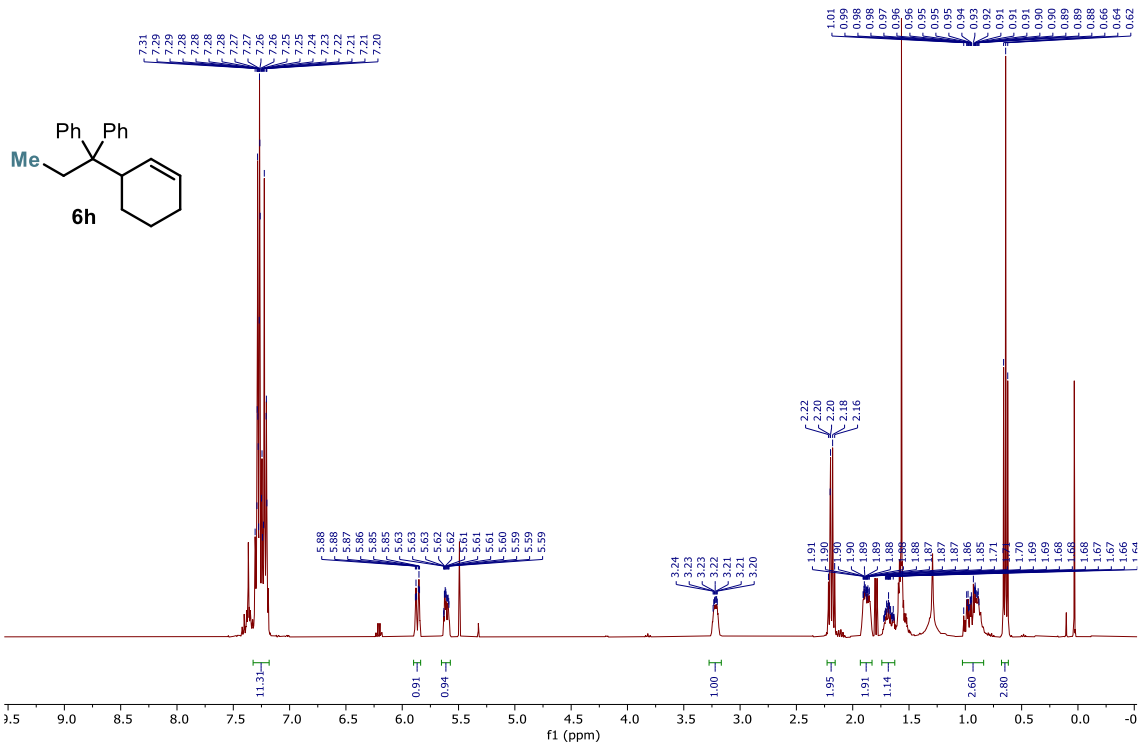
^{1}H NMR (400 MHz, $CDCl_3$) of **6g**



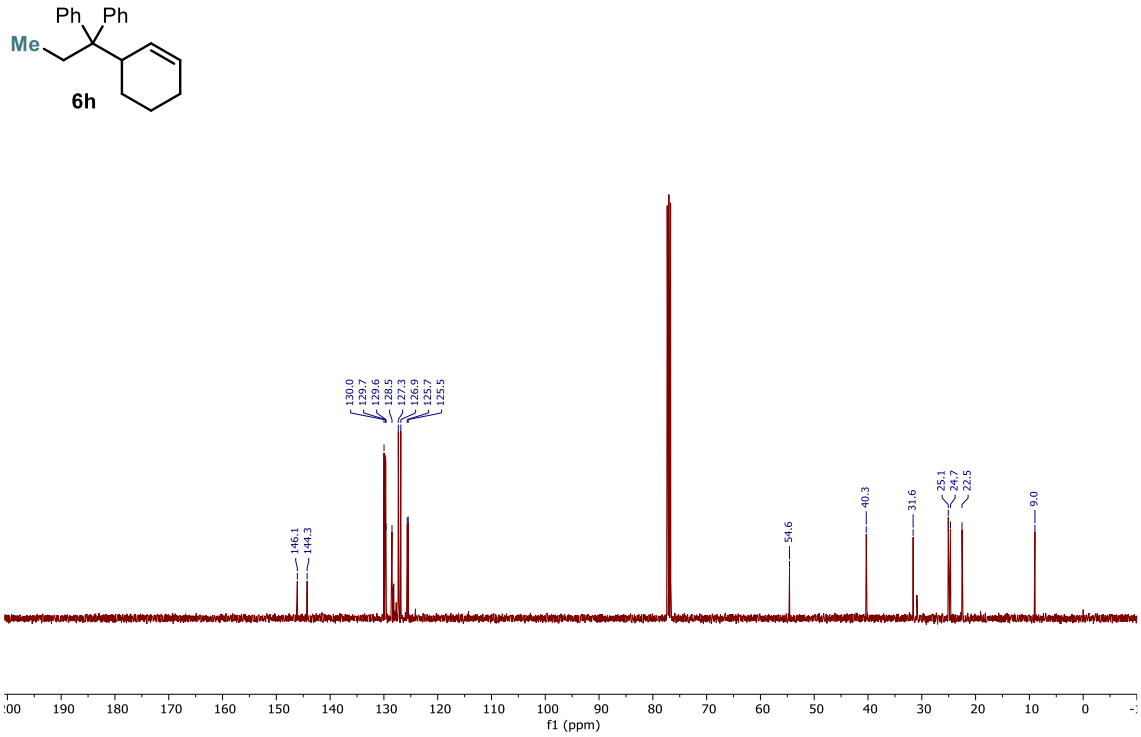
^{13}C NMR (101 MHz, $CDCl_3$) of **6g**



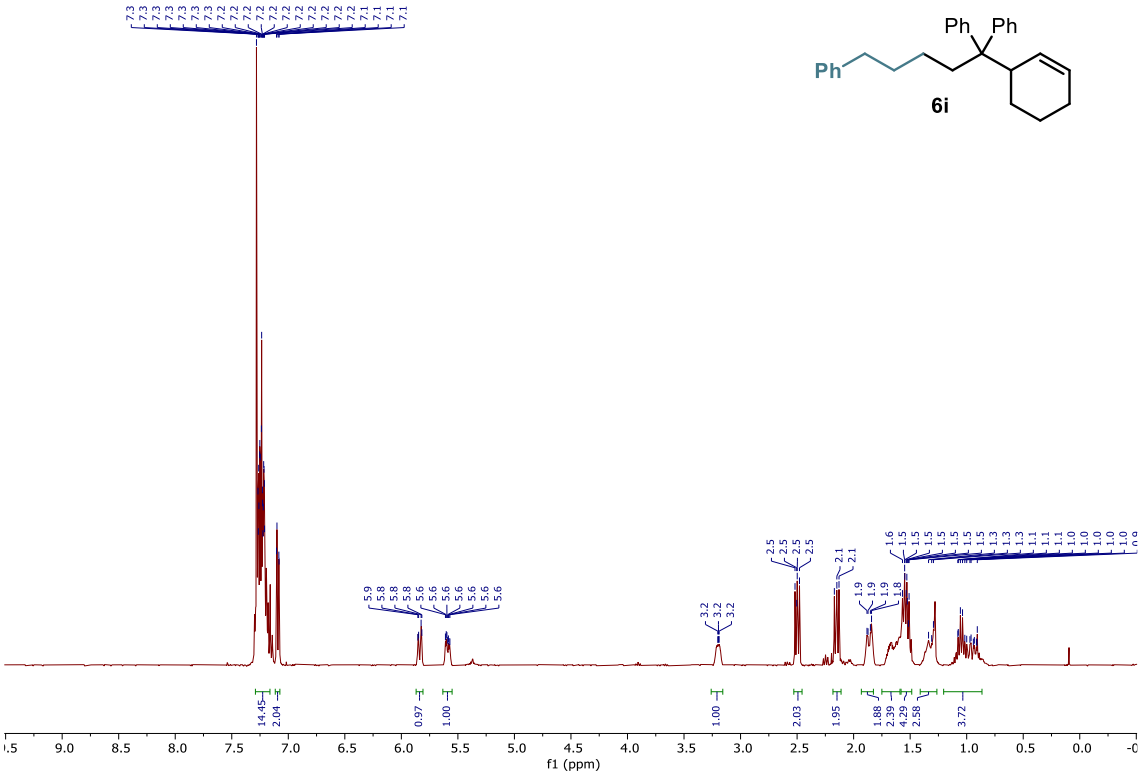
^{1}H NMR (400 MHz, $CDCl_3$) of **6h**



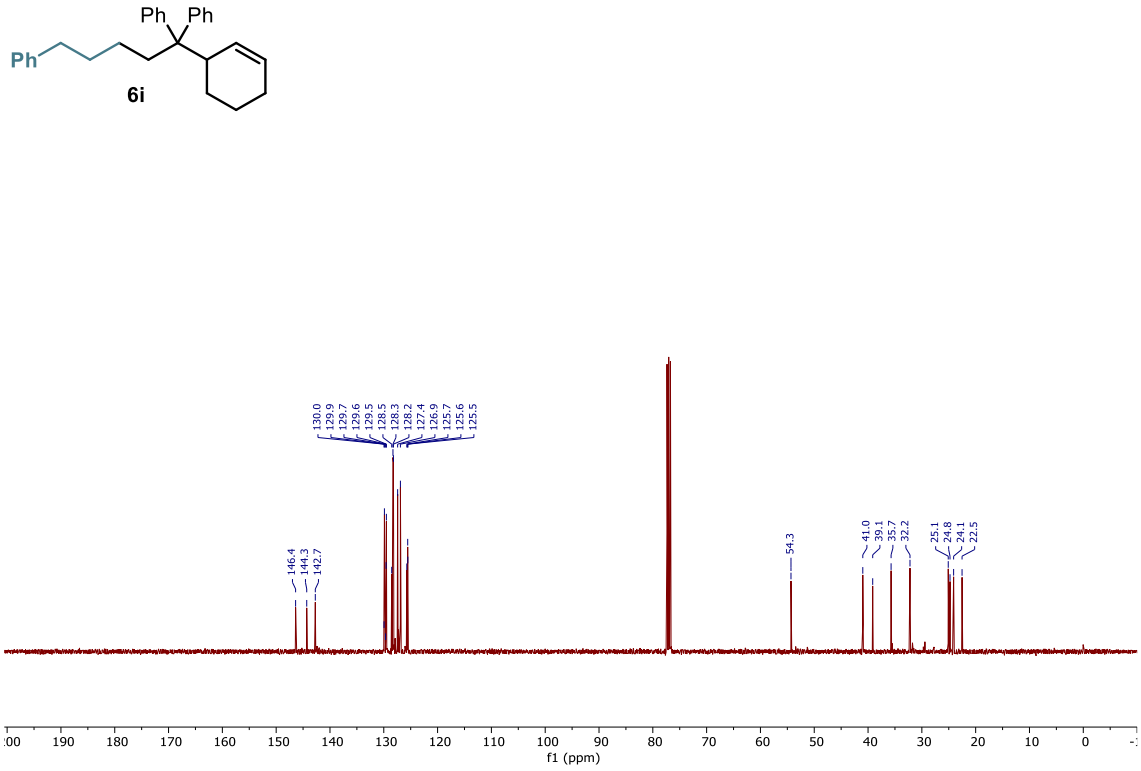
^{13}C NMR (101 MHz, $CDCl_3$) of **6h**



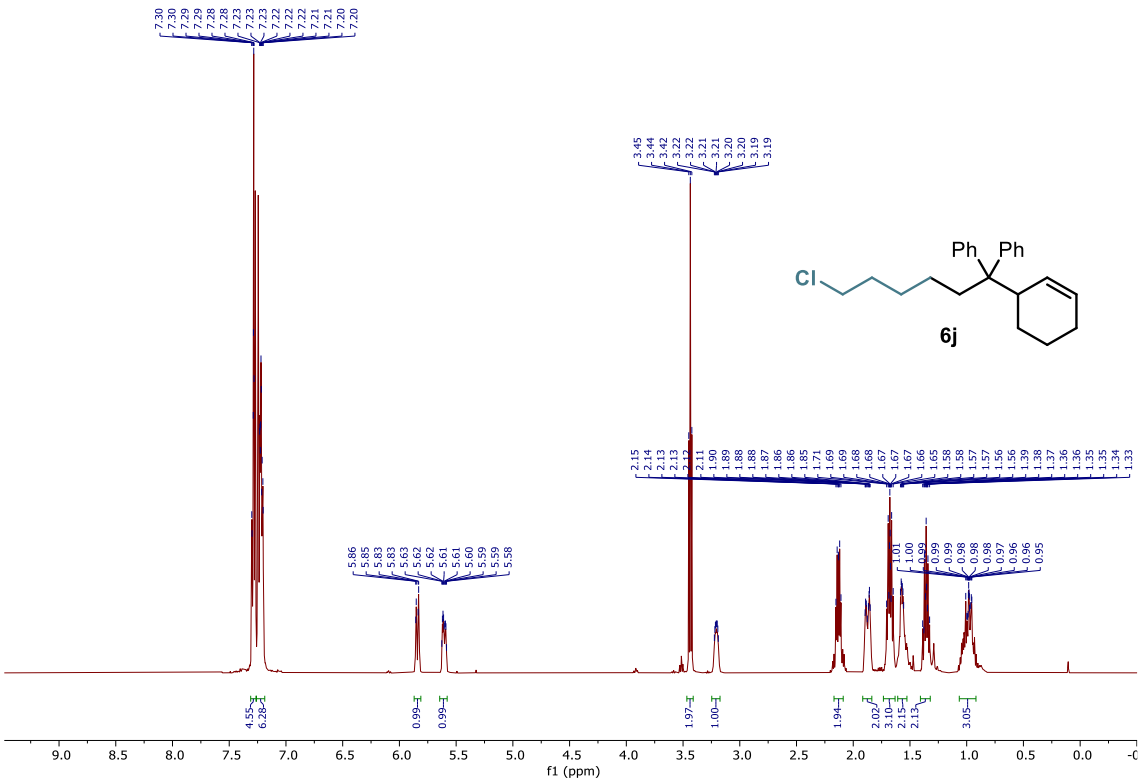
^{1}H NMR (500 MHz, $CDCl_3$) of **6i**



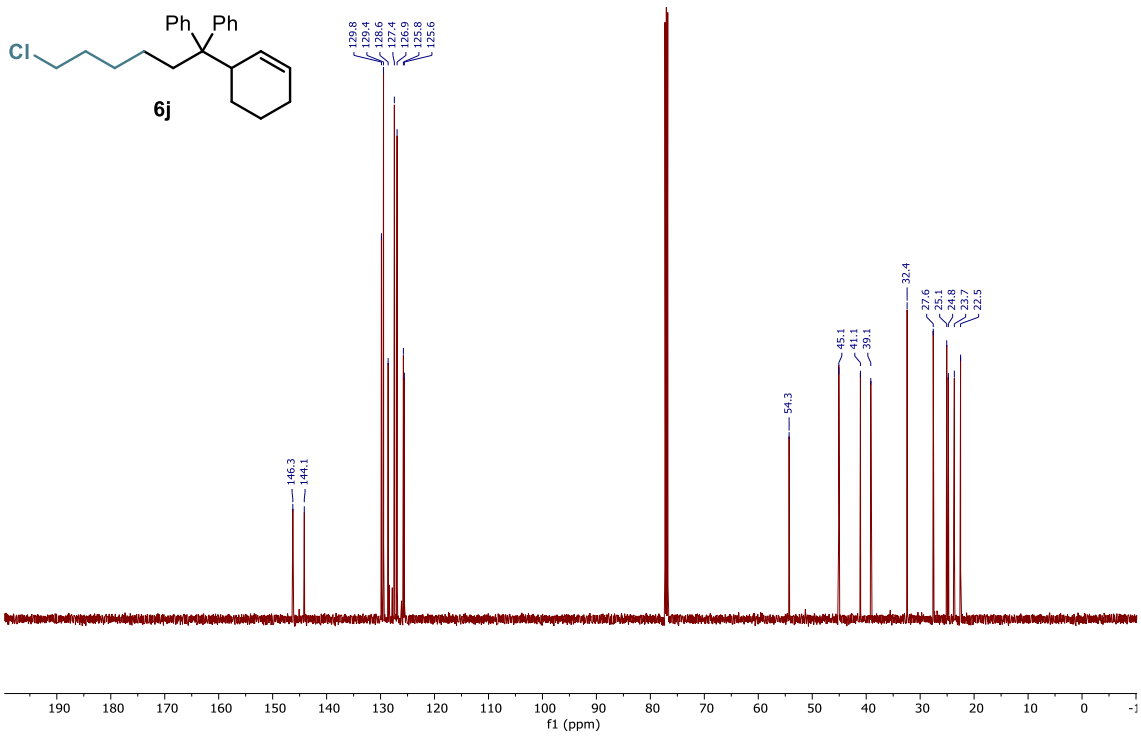
^{13}C NMR (101 MHz, $CDCl_3$) of **6i**



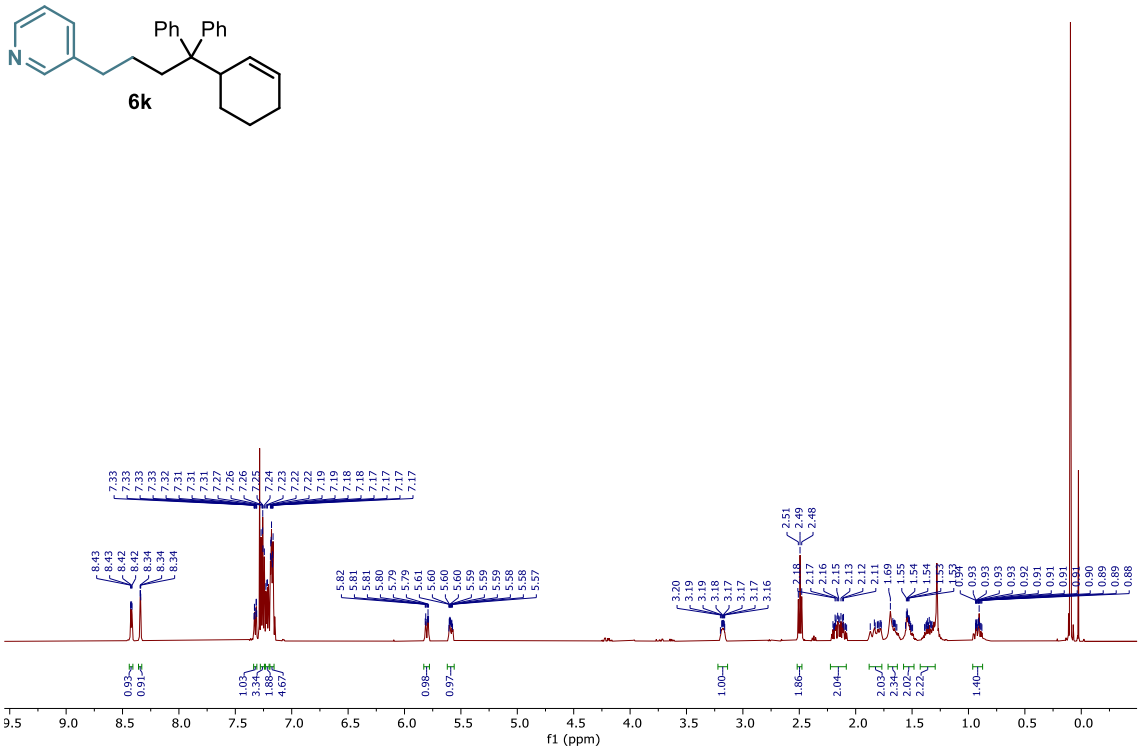
^{1}H NMR (500 MHz, $CDCl_3$) of **6j**



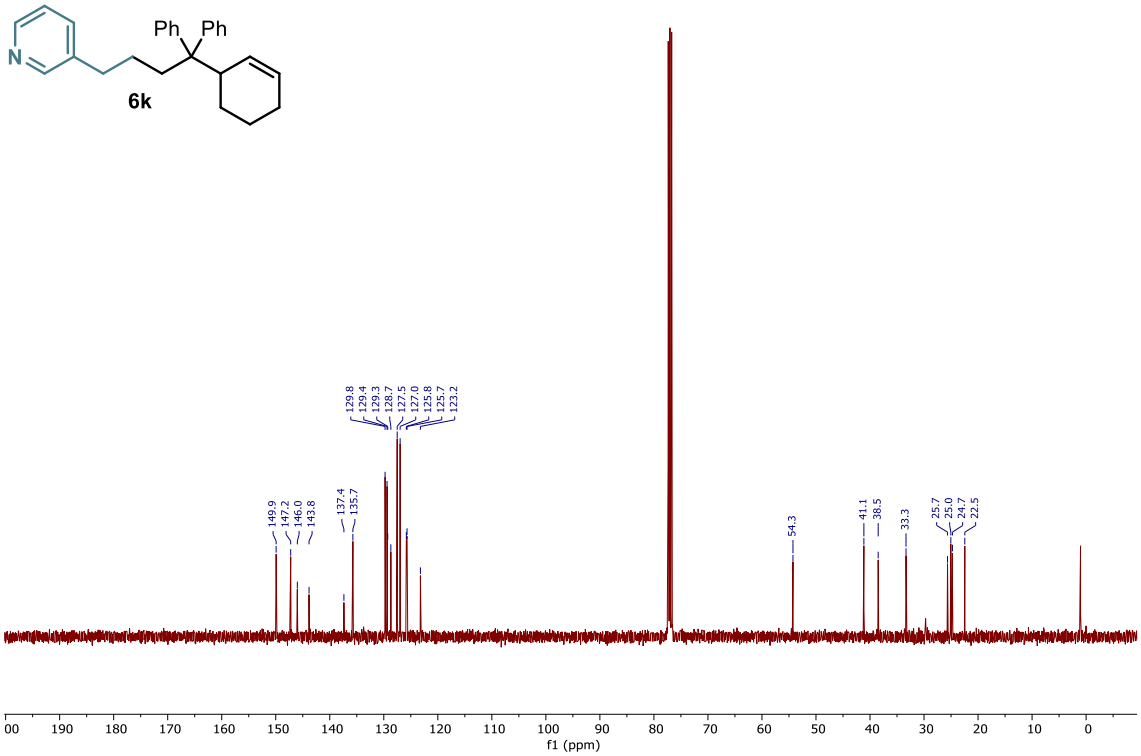
^{13}C NMR (126 MHz, $CDCl_3$) of **6j**



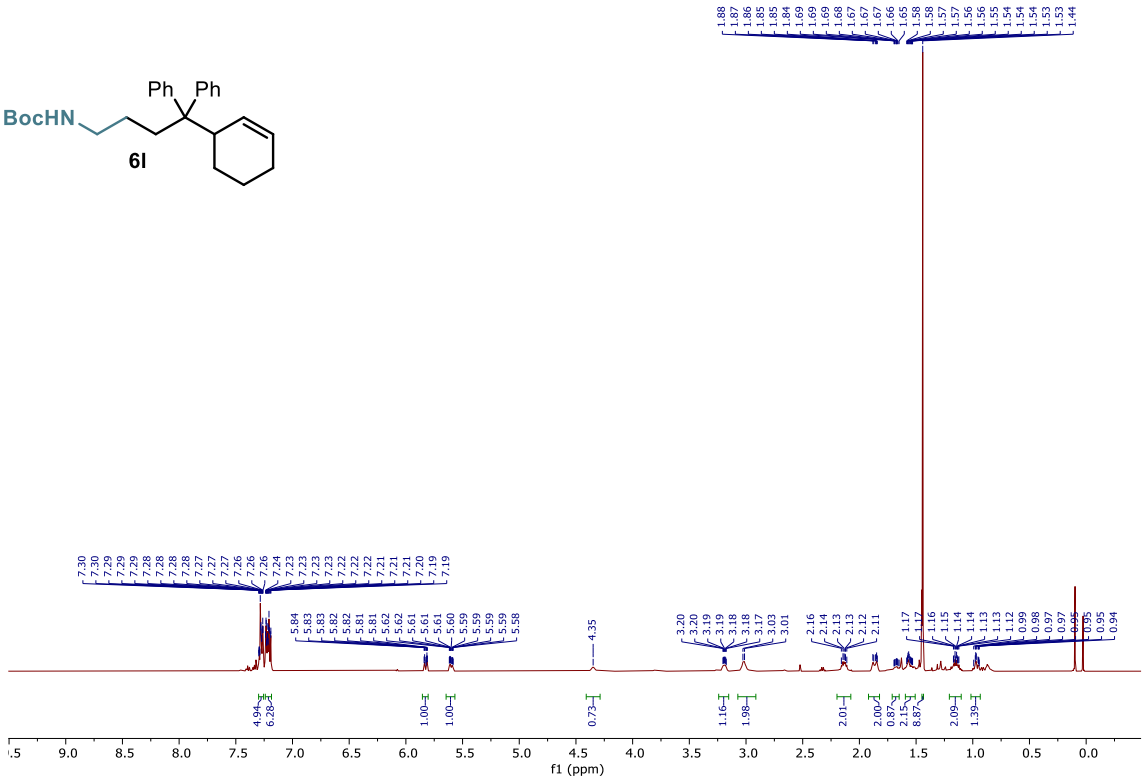
^{1}H NMR (500 MHz, $CDCl_3$) of **6k**



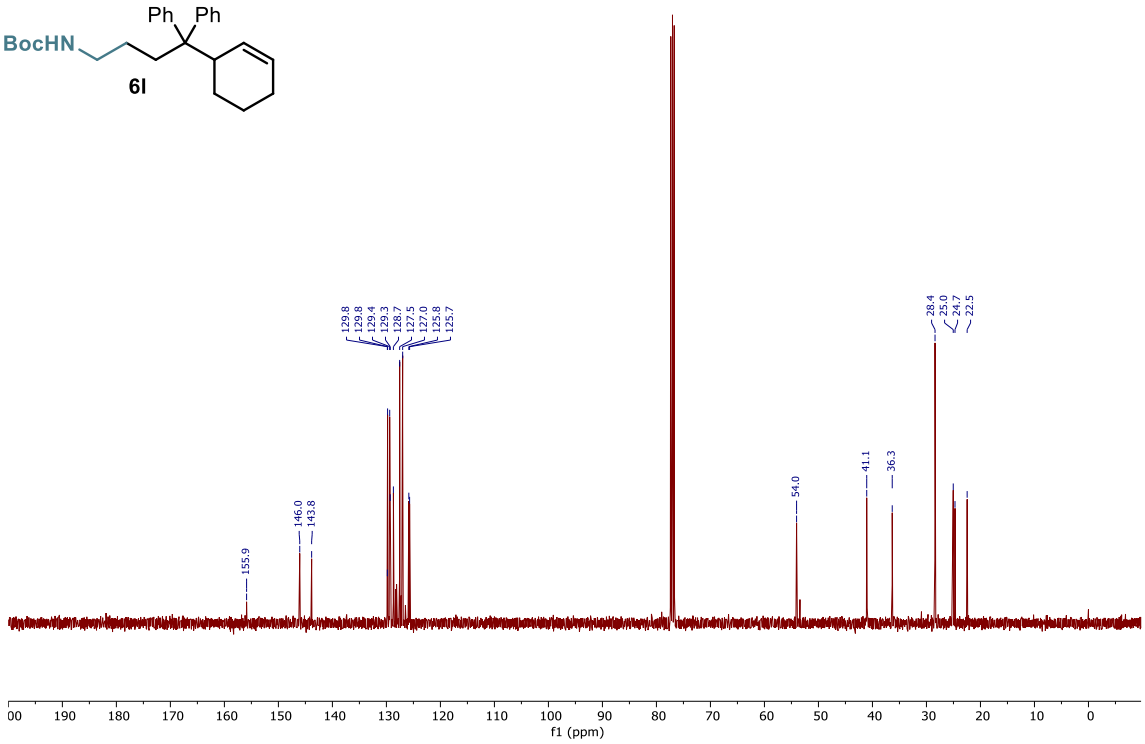
^{13}C NMR (101 MHz, $CDCl_3$) of **6j**



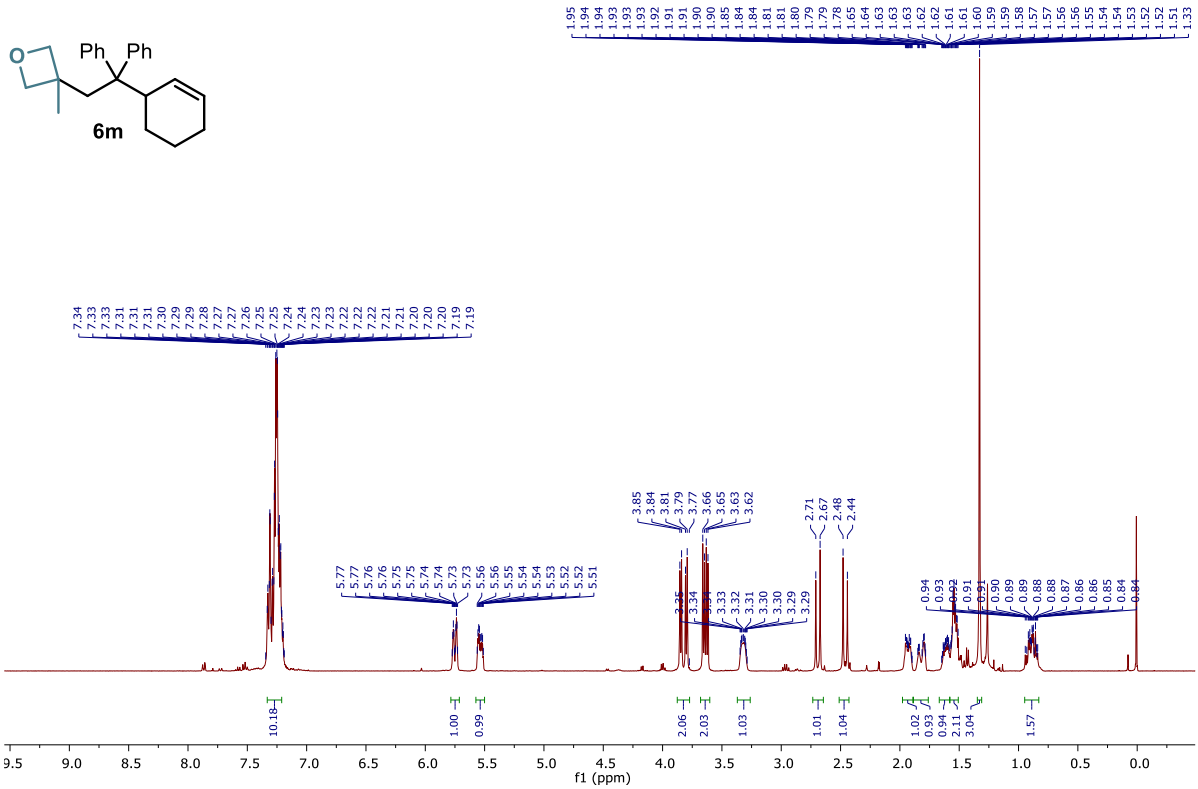
^{1}H NMR (500 MHz, $CDCl_3$) of **6l**



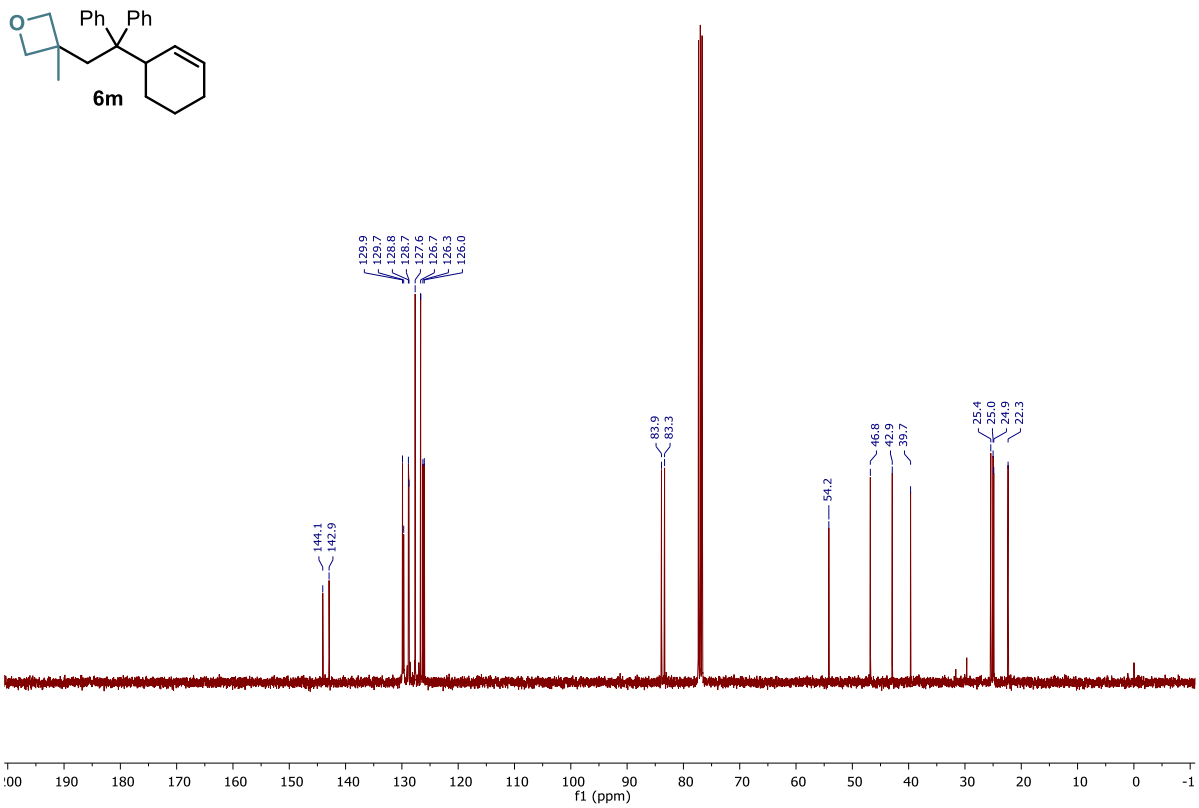
^{13}C NMR (101 MHz, $CDCl_3$) of **6l**



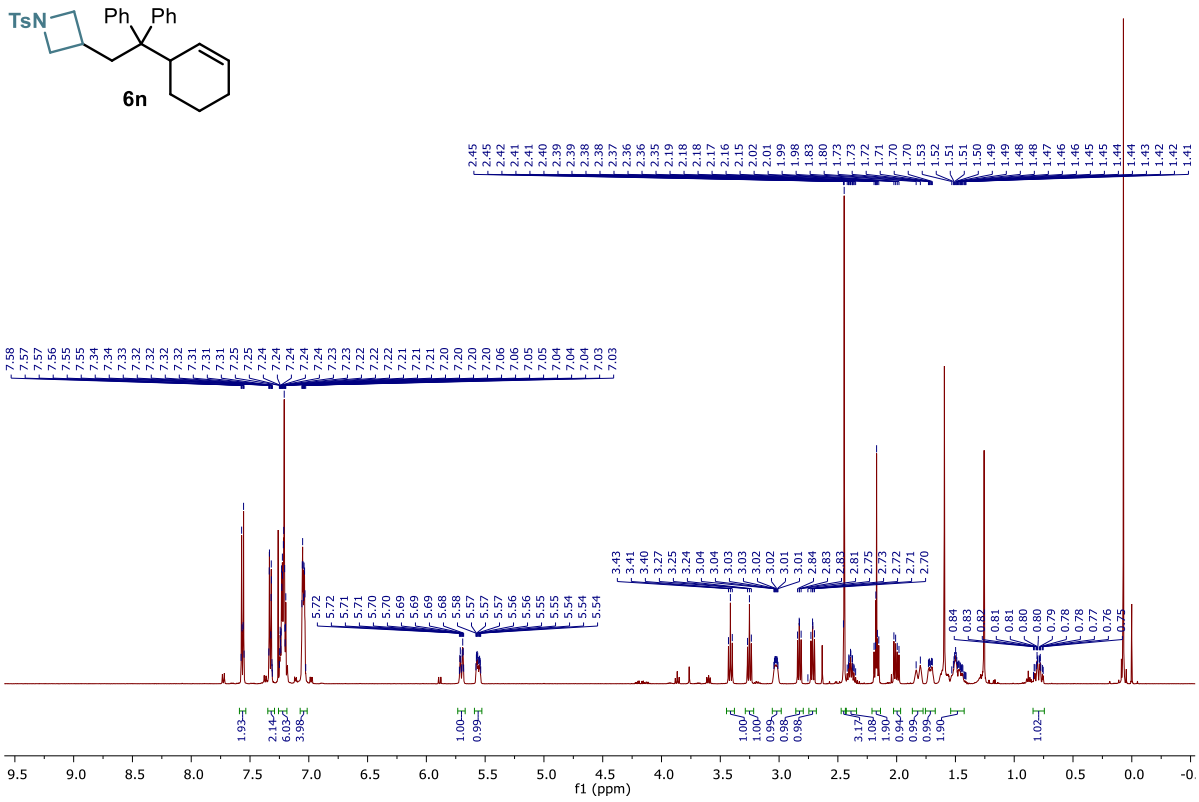
^{1}H NMR (400 MHz, $CDCl_3$) of **6m**



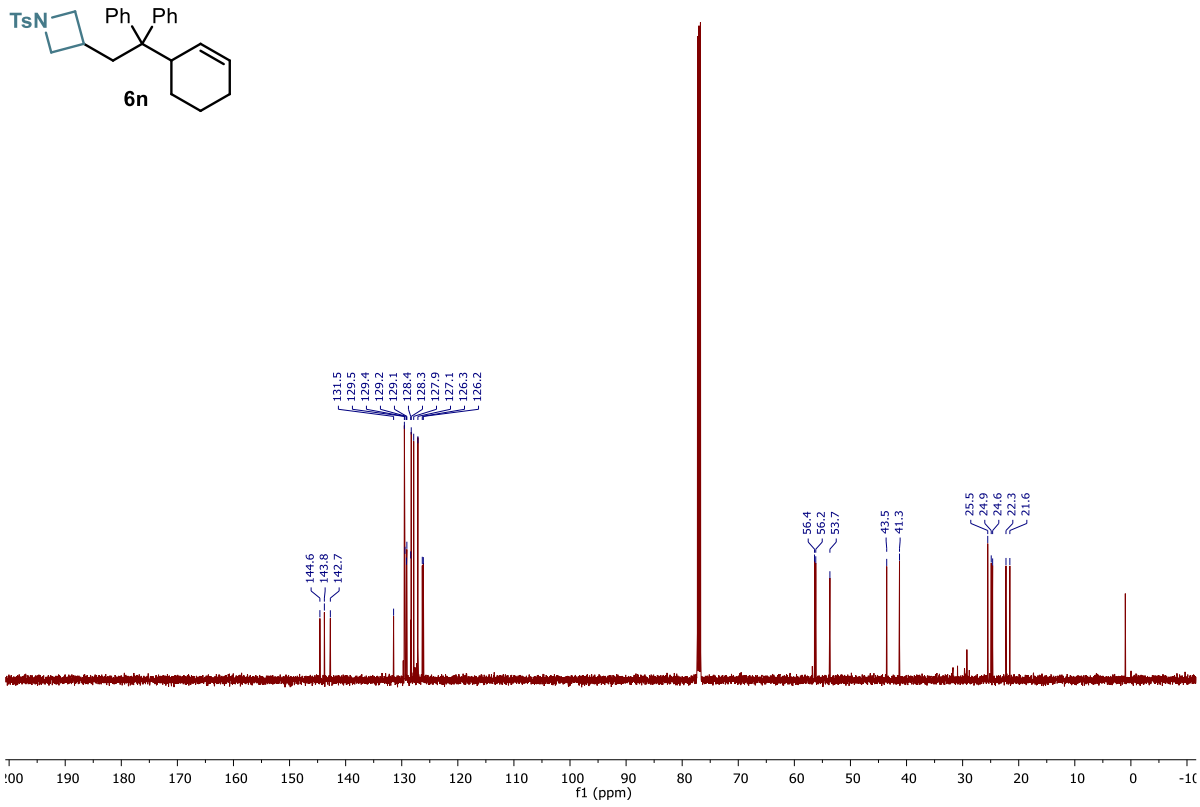
^{13}C NMR (101 MHz, $CDCl_3$) of **6m**



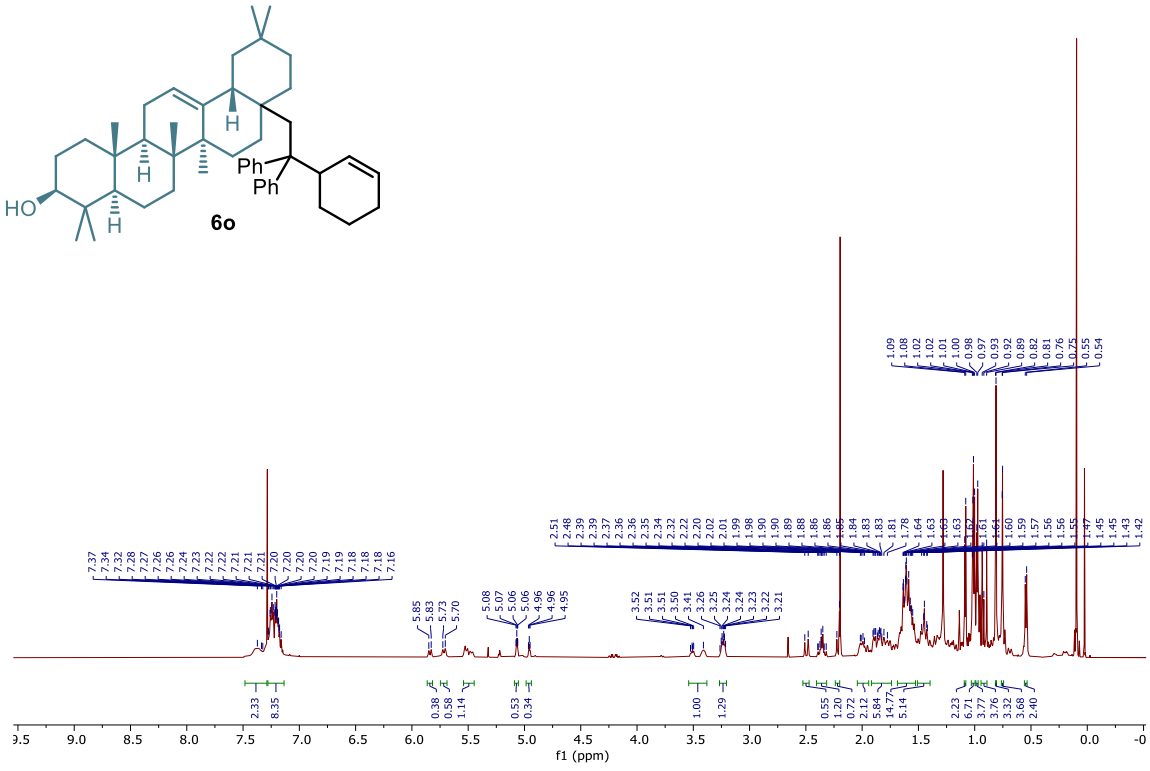
^{1}H NMR (500 MHz, $CDCl_3$) of **6n**



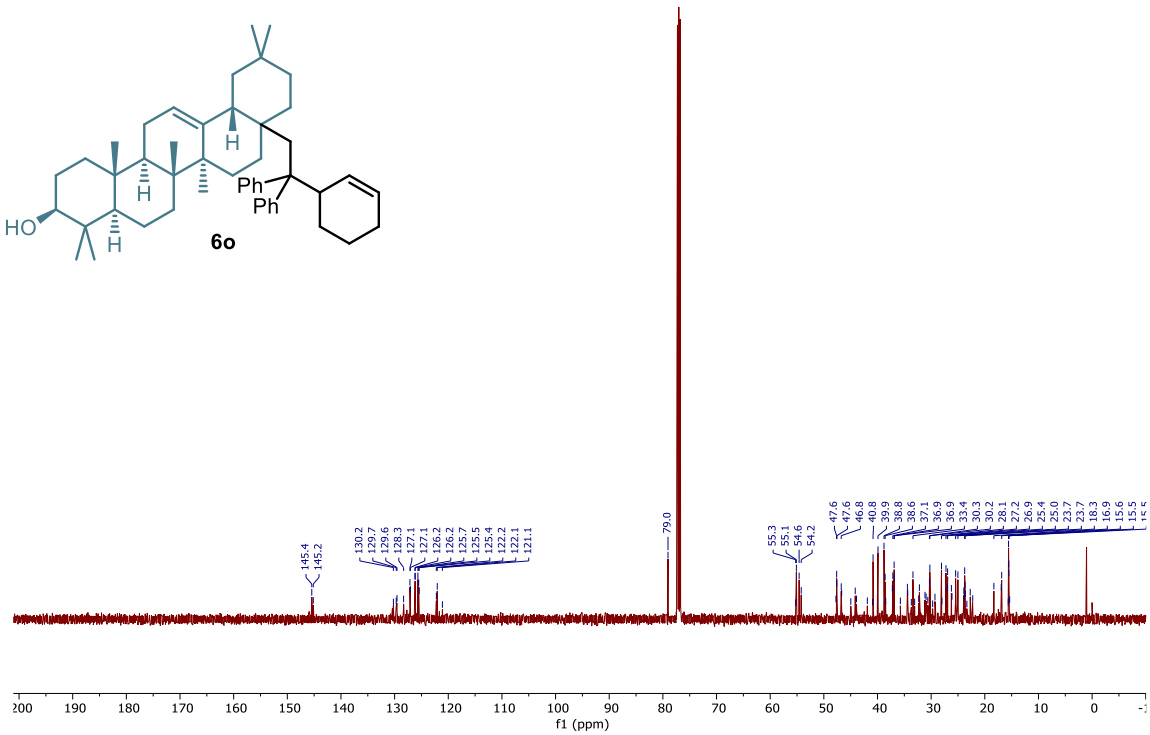
^{13}C NMR (126 MHz, $CDCl_3$) of **6n**



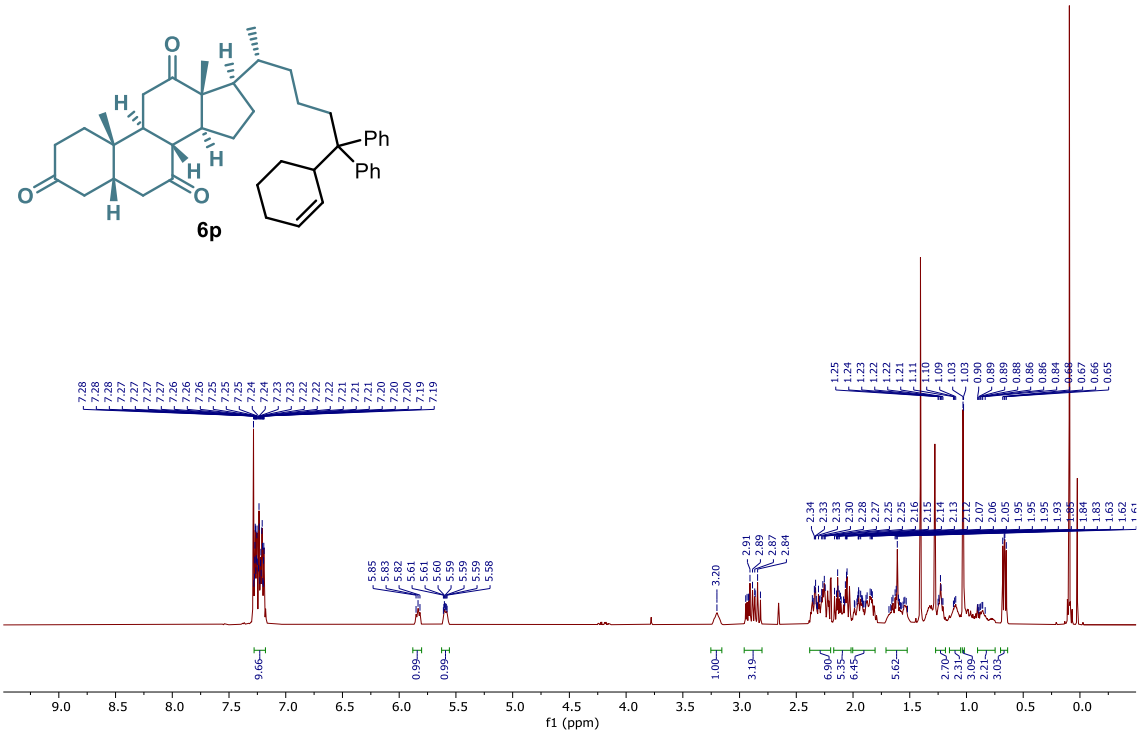
^{1}H NMR (500 MHz, $CDCl_3$) of **6o**



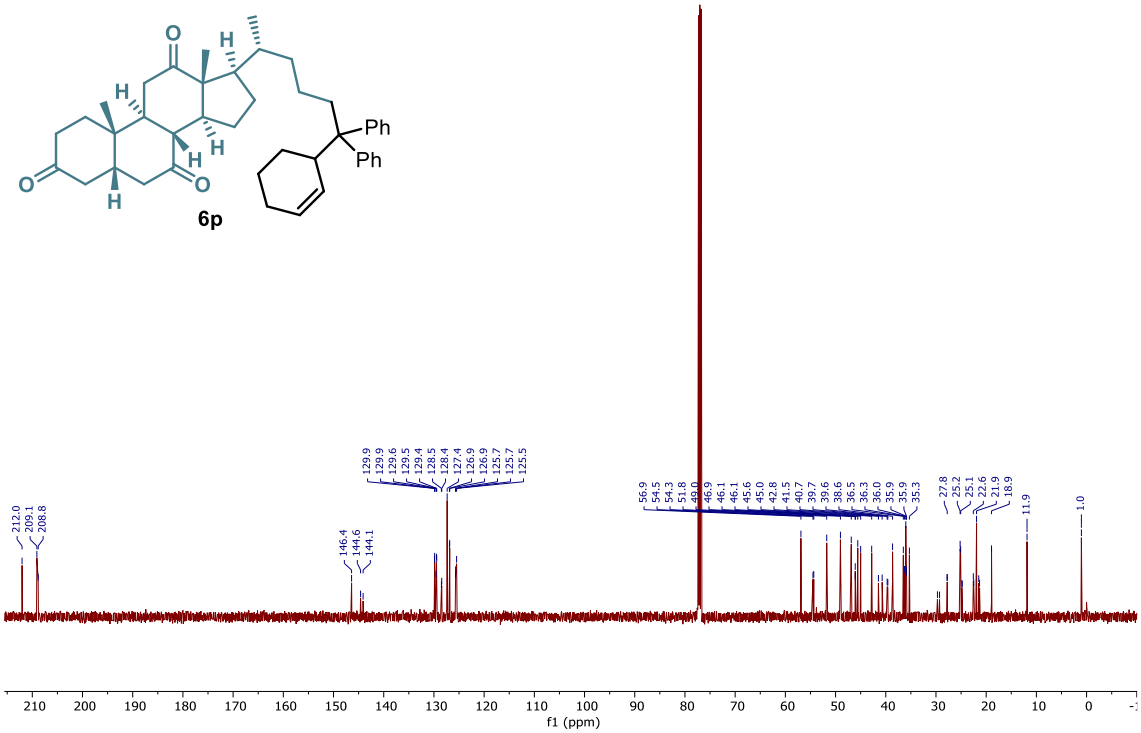
^{13}C NMR (126 MHz, $CDCl_3$) of **6o**



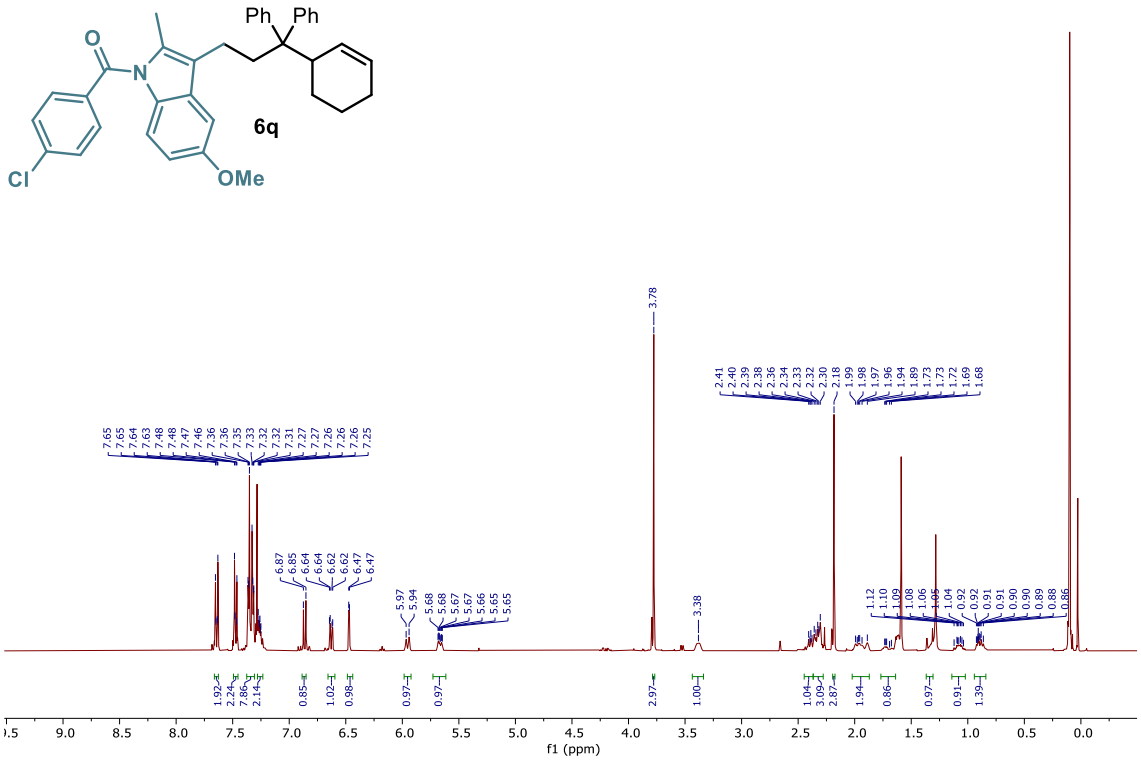
^{1}H NMR (500 MHz, $CDCl_3$) of **6p**



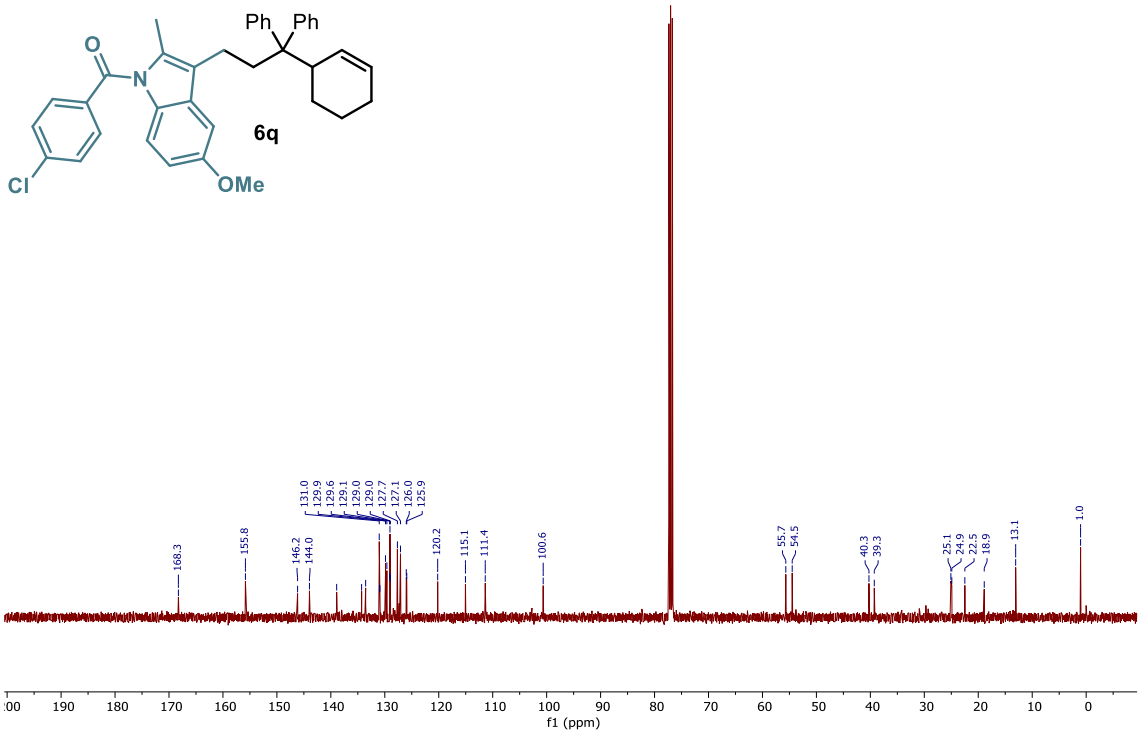
^{13}C NMR (126 MHz, $CDCl_3$) of **6p**


O
H
H
H
H
O
O
H
Ph
Ph
6p
212.0
209.1
208.8
146.4
144.6
144.1
129.9
129.9
129.6
129.5
129.4
128.5
128.4
127.4
126.9
126.9
125.7
125.7
125.5
56.9
54.5
54.3
51.8
49.0
46.9
46.1
45.6
45.0
42.8
41.5
40.7
39.7
39.6
38.6
36.5
36.3
36.0
35.9
35.9
35.3
27.8
25.2
25.1
22.6
21.9
18.9
11.9
1.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

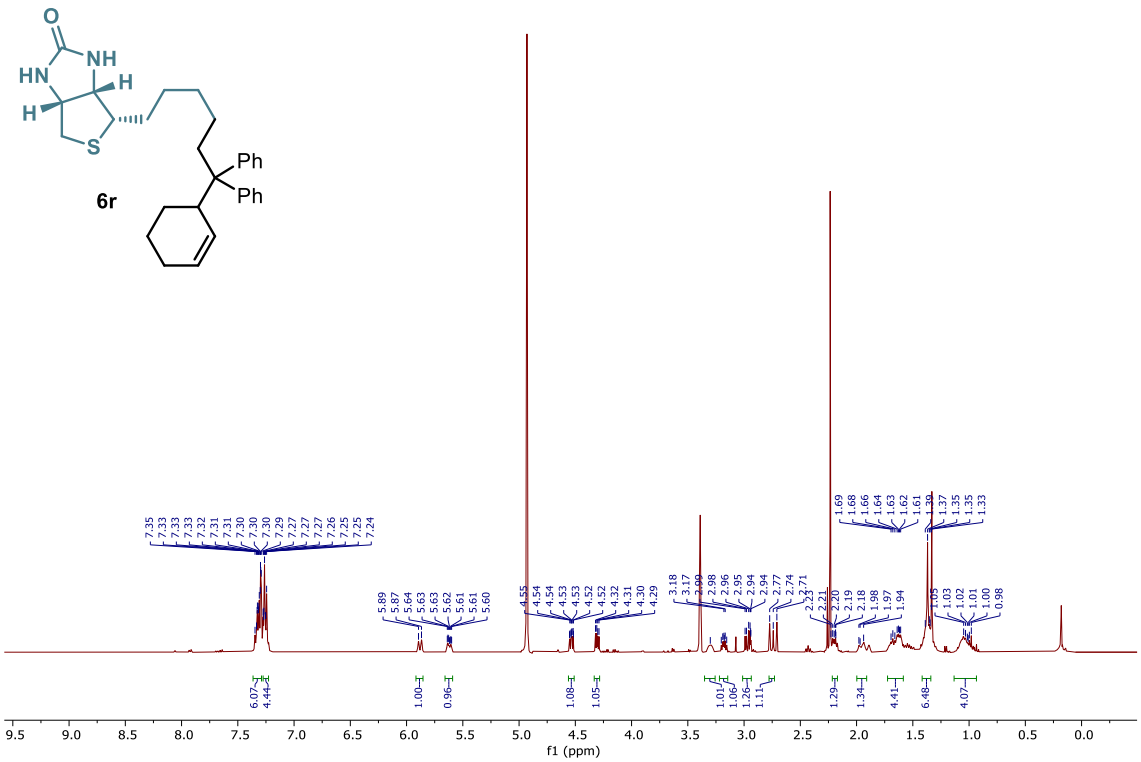
^{1}H NMR (500 MHz, $CDCl_3$) of **6q**



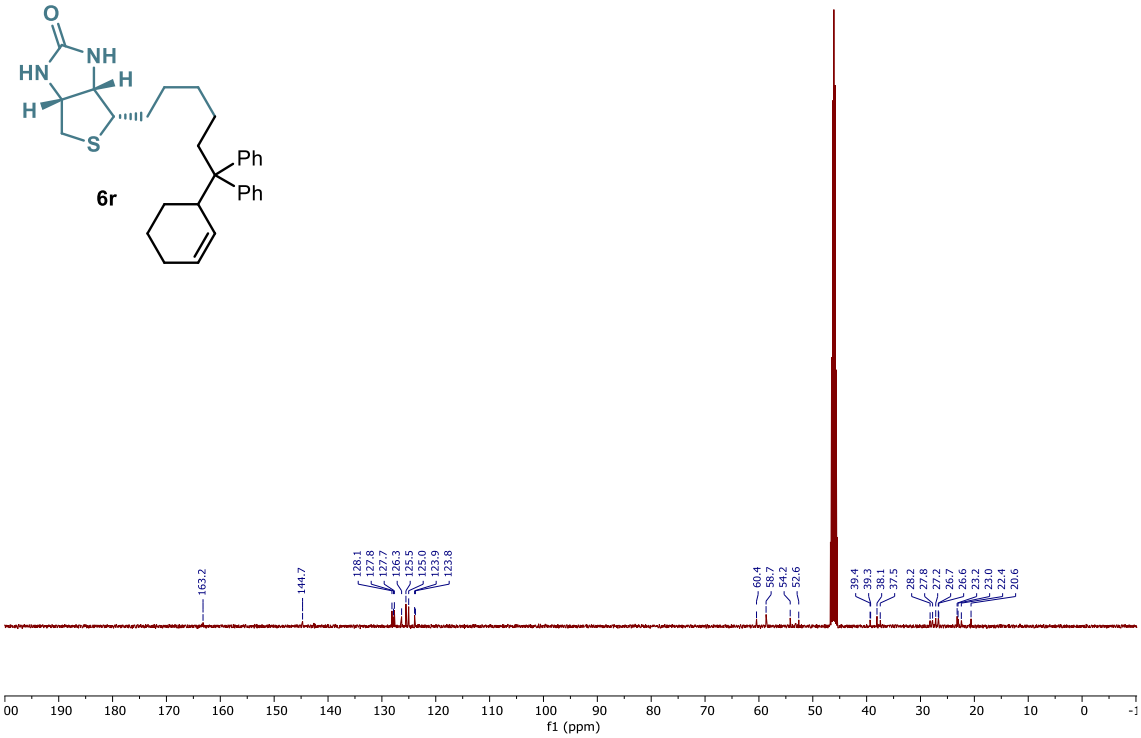
^{13}C NMR (101 MHz, $CDCl_3$) of **6q**



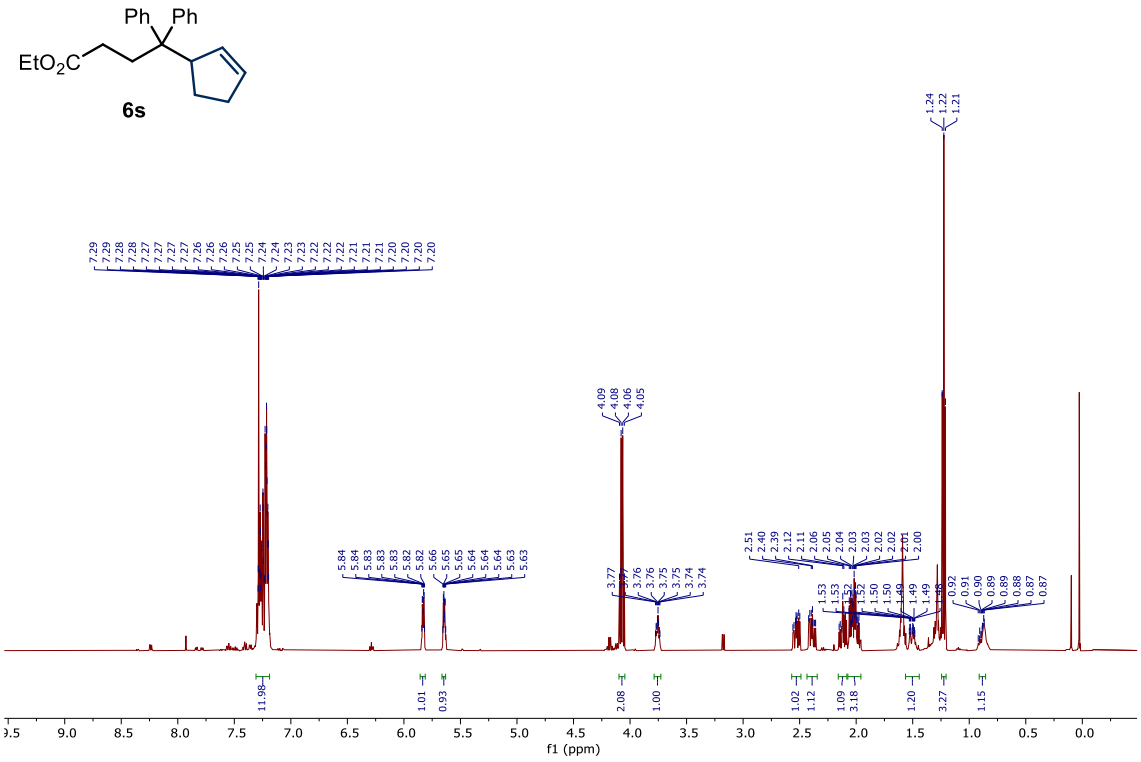
^{1}H NMR (400 MHz, $CDCl_3$) of **6r**



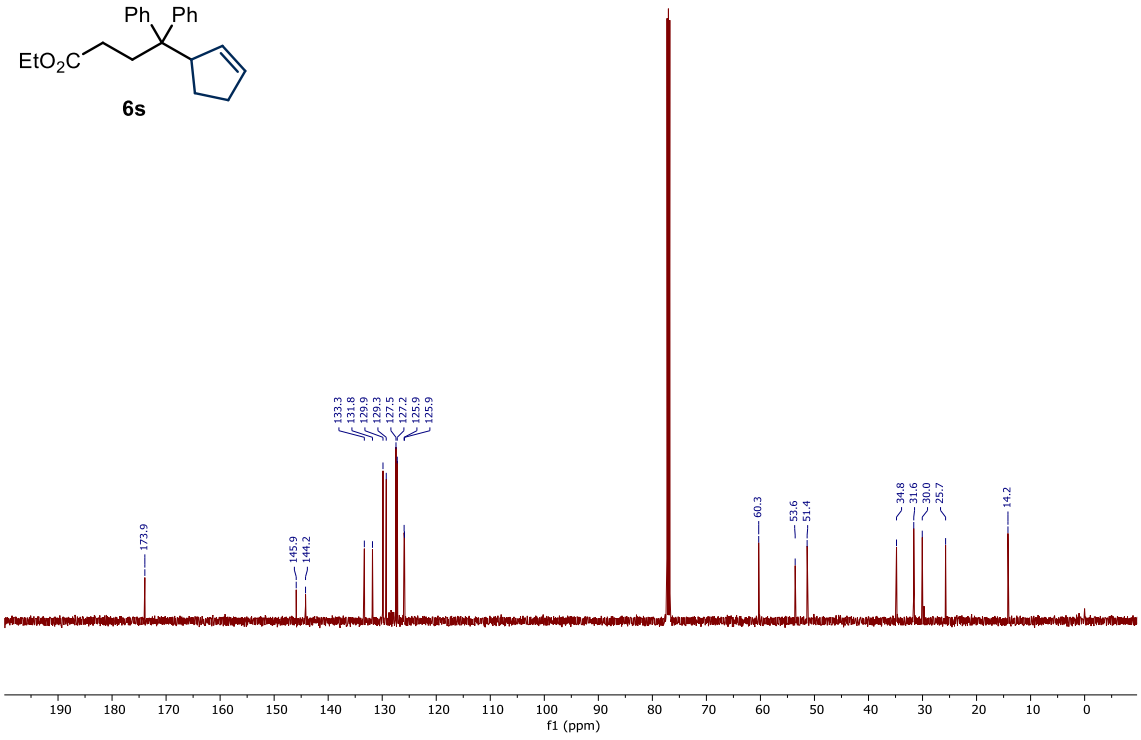
^{13}C NMR (101 MHz, $CDCl_3$) of **6r**



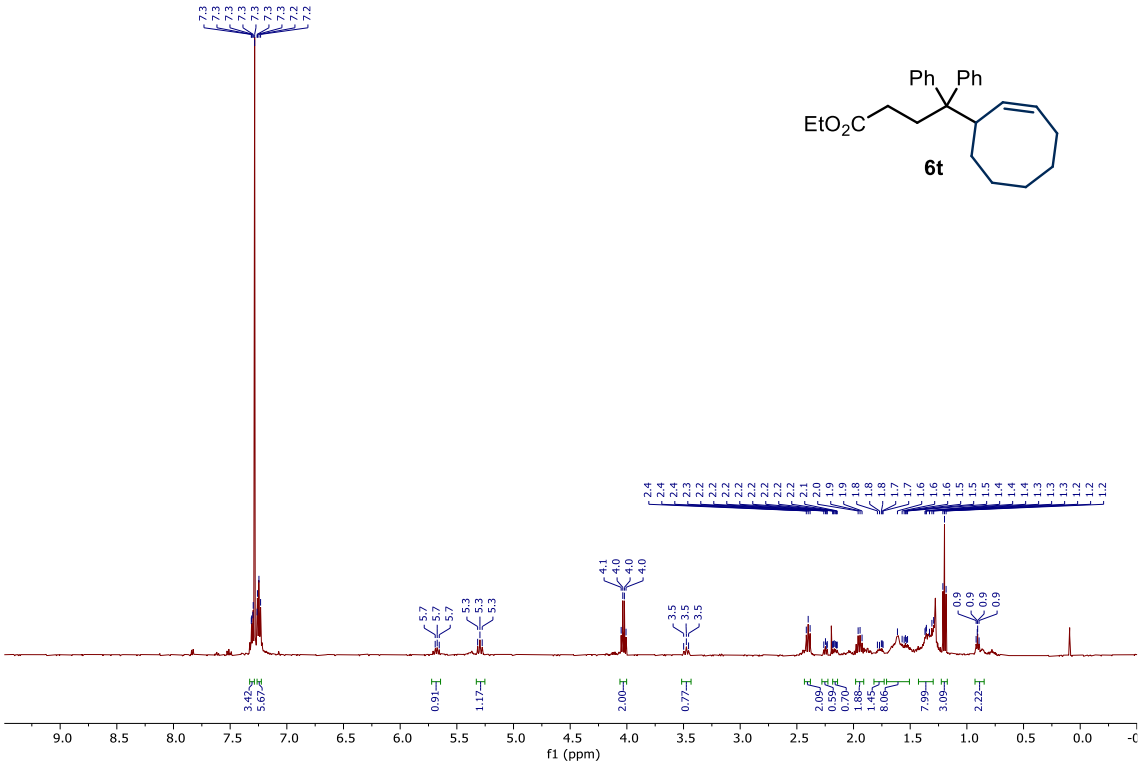
^{1}H NMR (500 MHz, $CDCl_3$) of **6s**



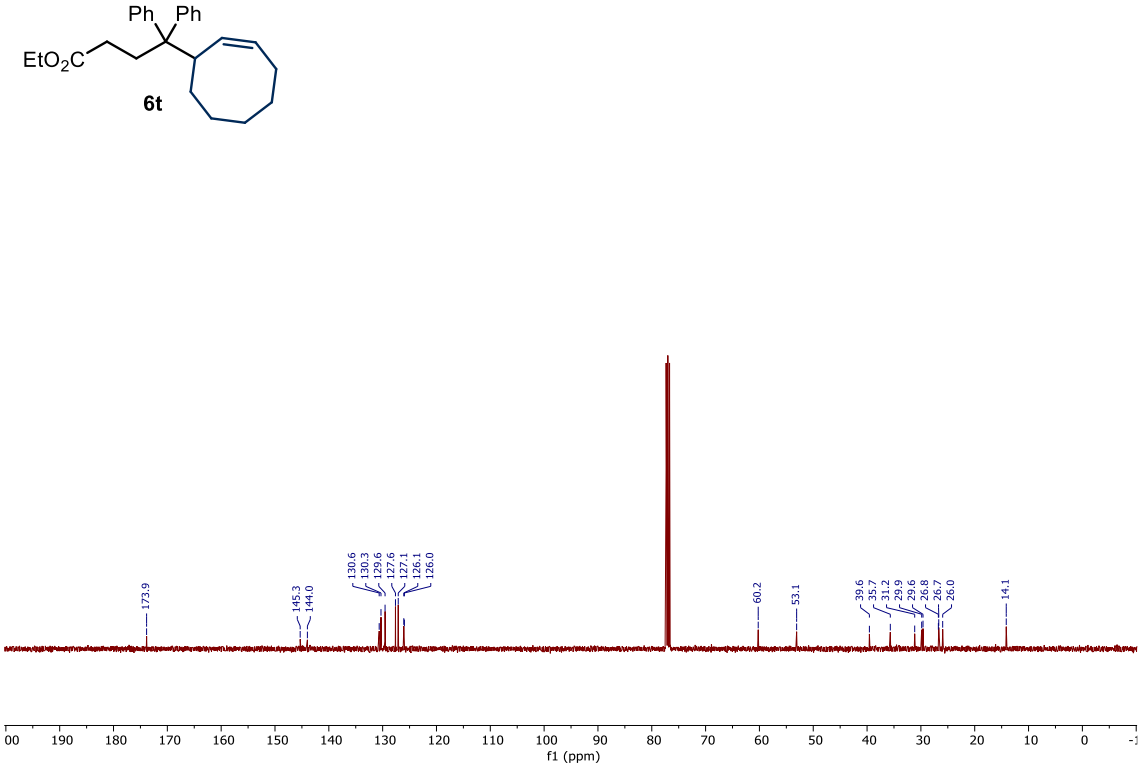
^{13}C NMR (126 MHz, $CDCl_3$) of **6s**



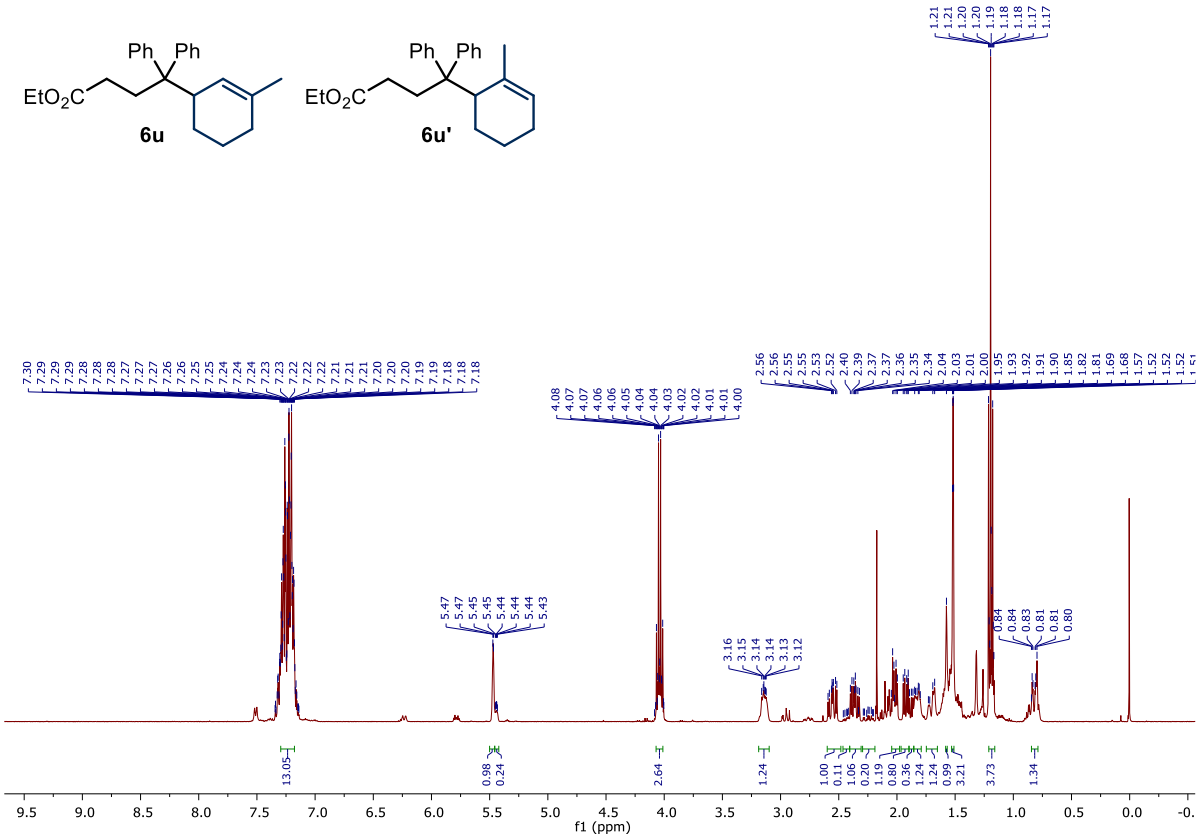
^{1}H NMR (400 MHz, $CDCl_3$) of **6t**



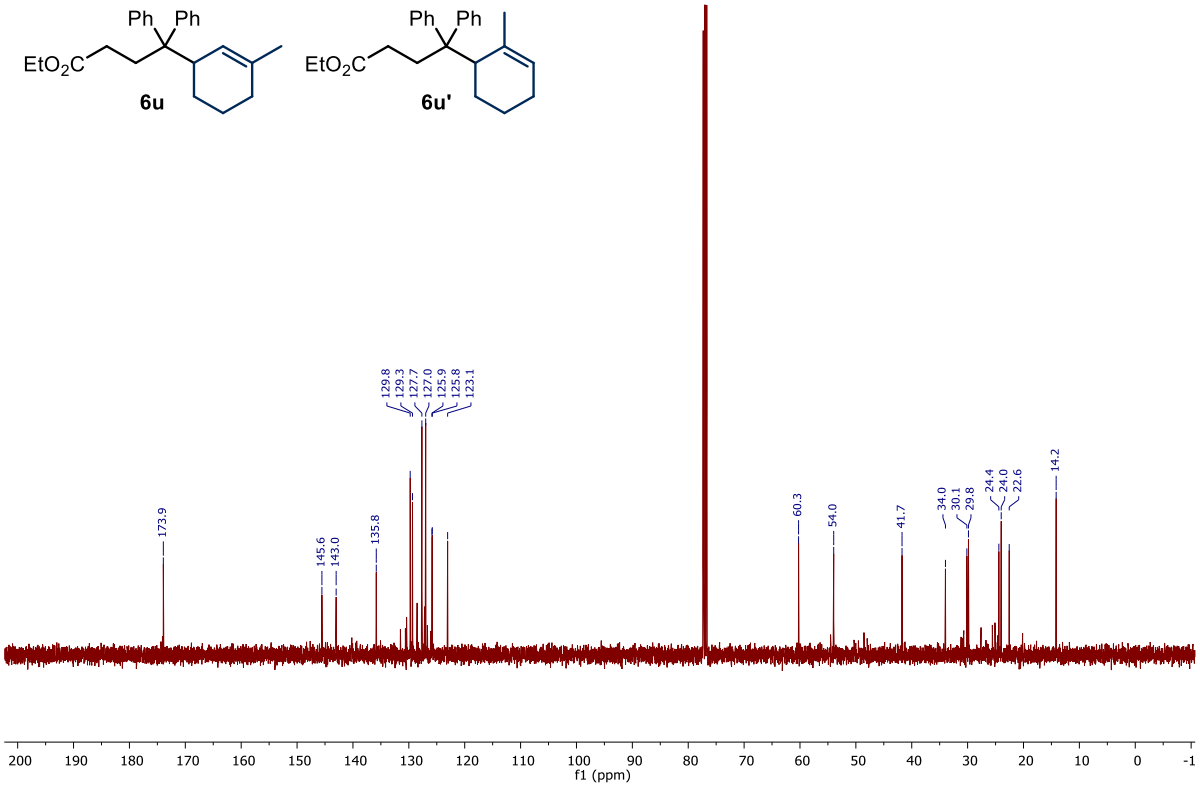
^{13}C NMR (101 MHz, $CDCl_3$) of **6t**



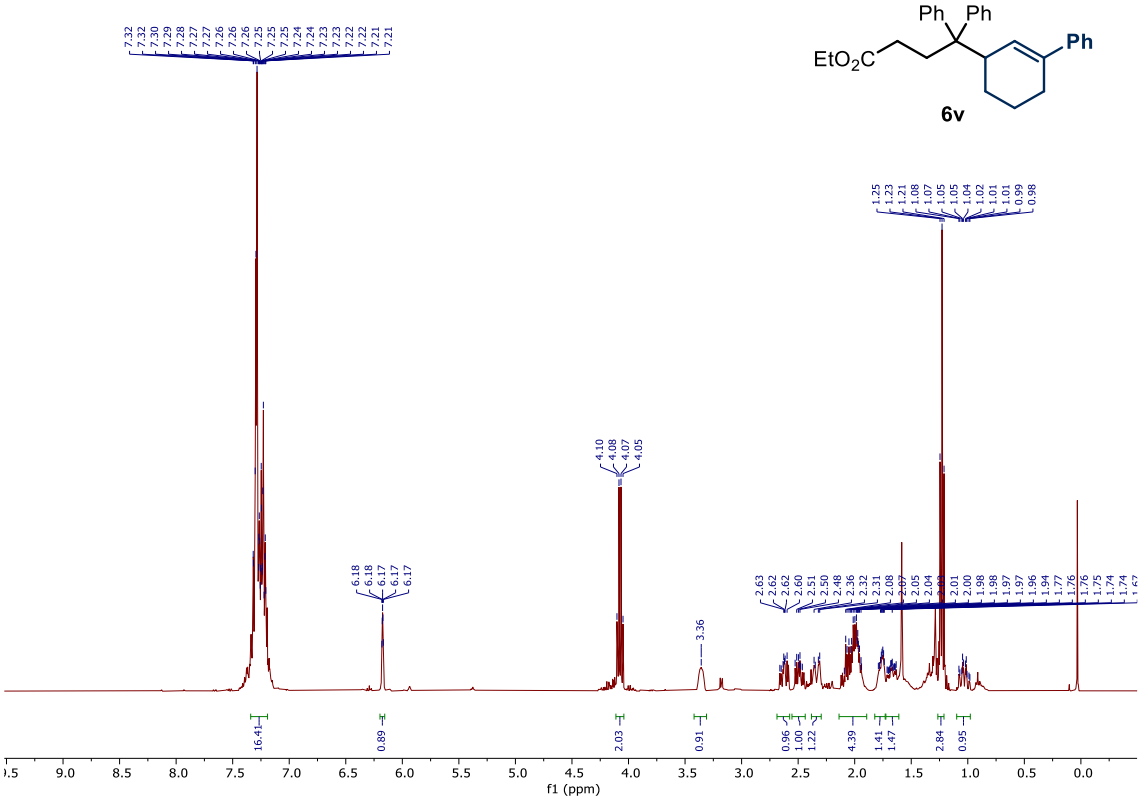
^{1}H NMR (400 MHz, $CDCl_3$) of **6u**



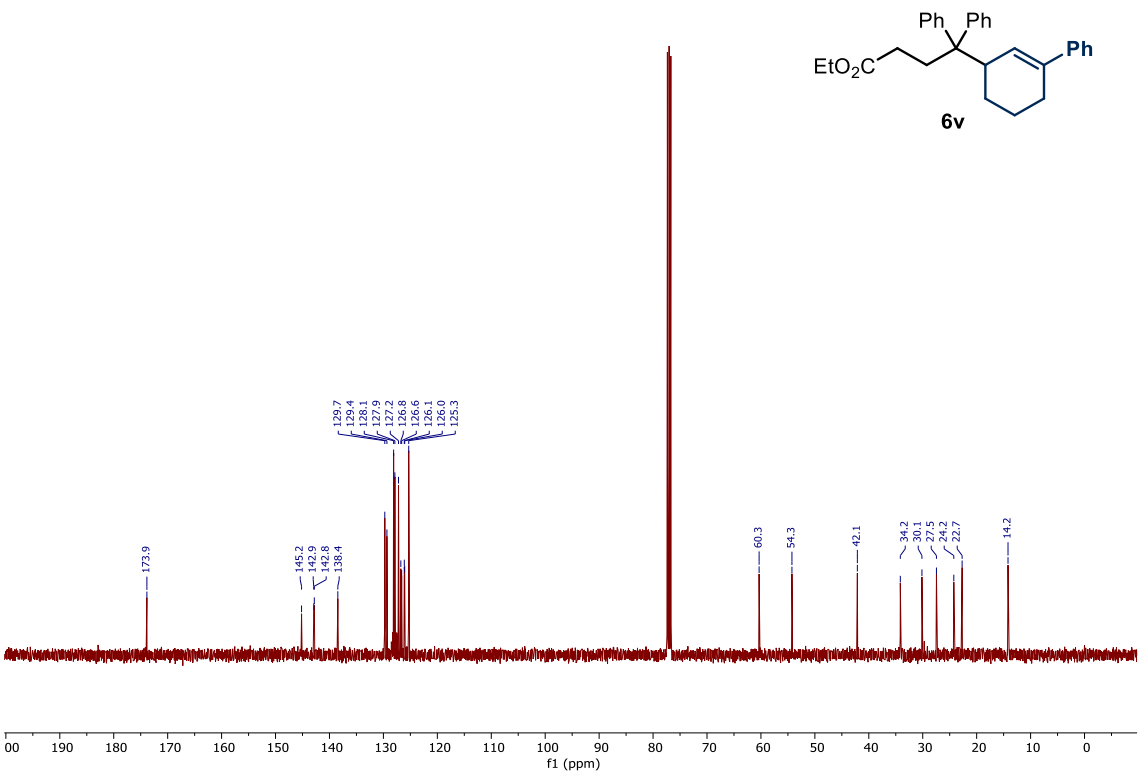
^{13}C NMR (101 MHz, $CDCl_3$) of **6u**



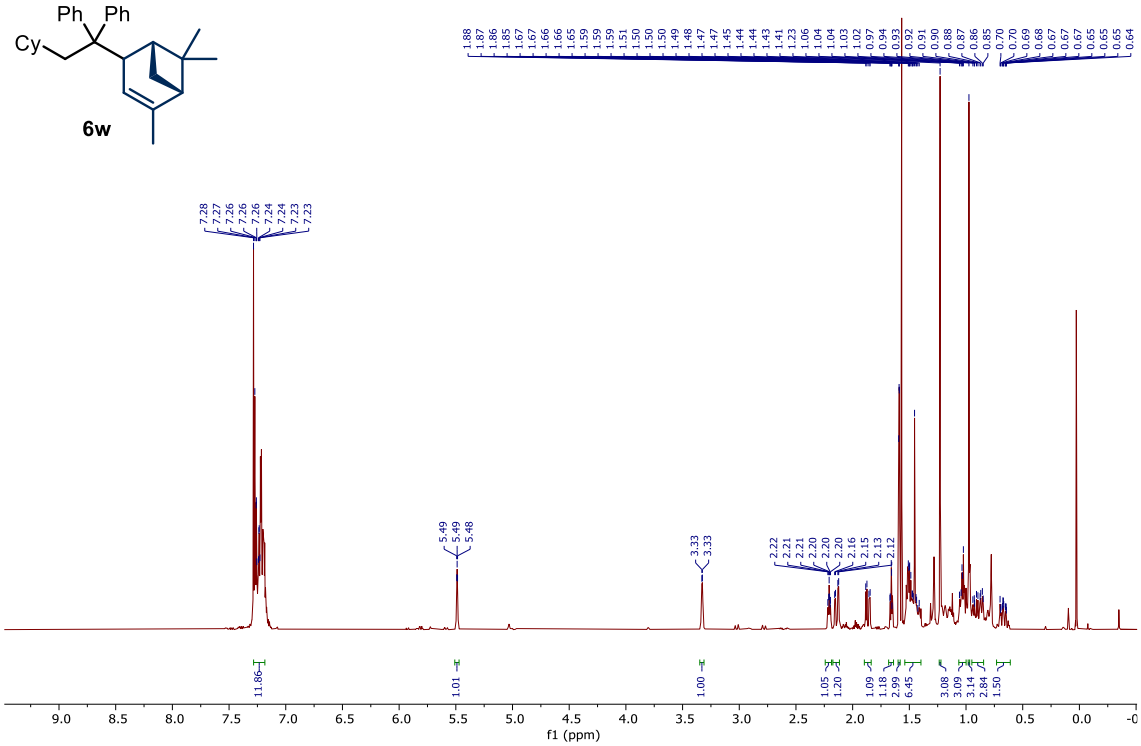
^{1}H NMR (400 MHz, $CDCl_3$) of **6v**



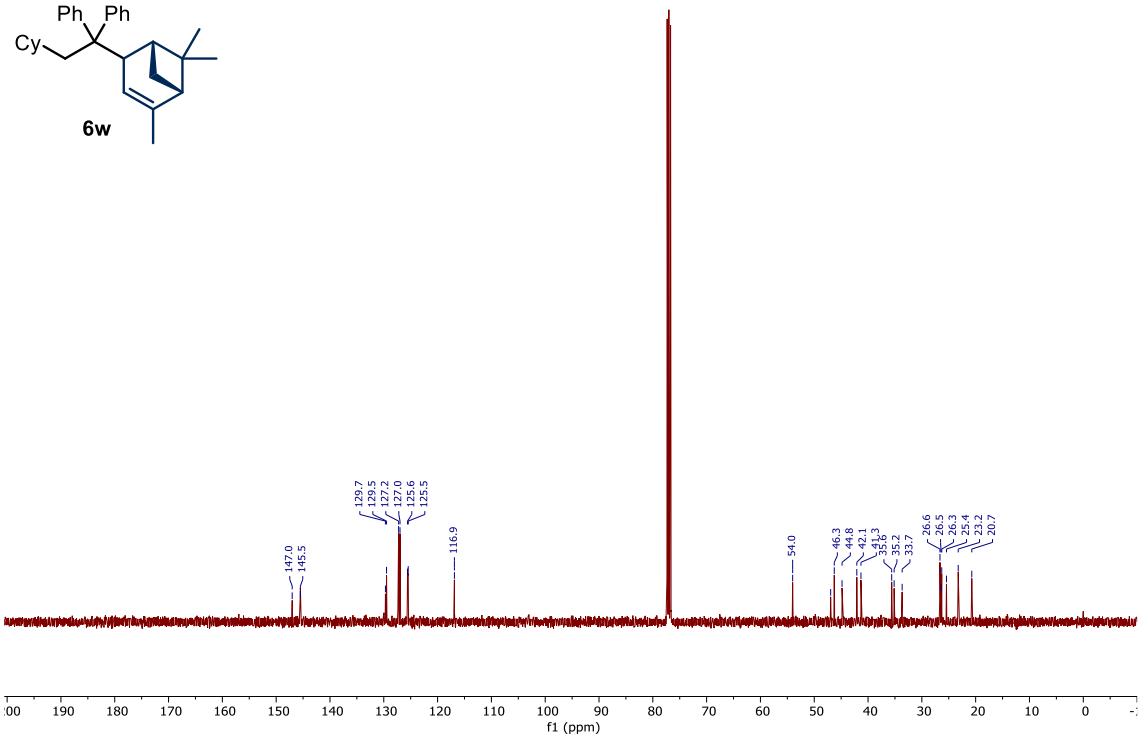
^{13}C NMR (101 MHz, $CDCl_3$) of **6v**



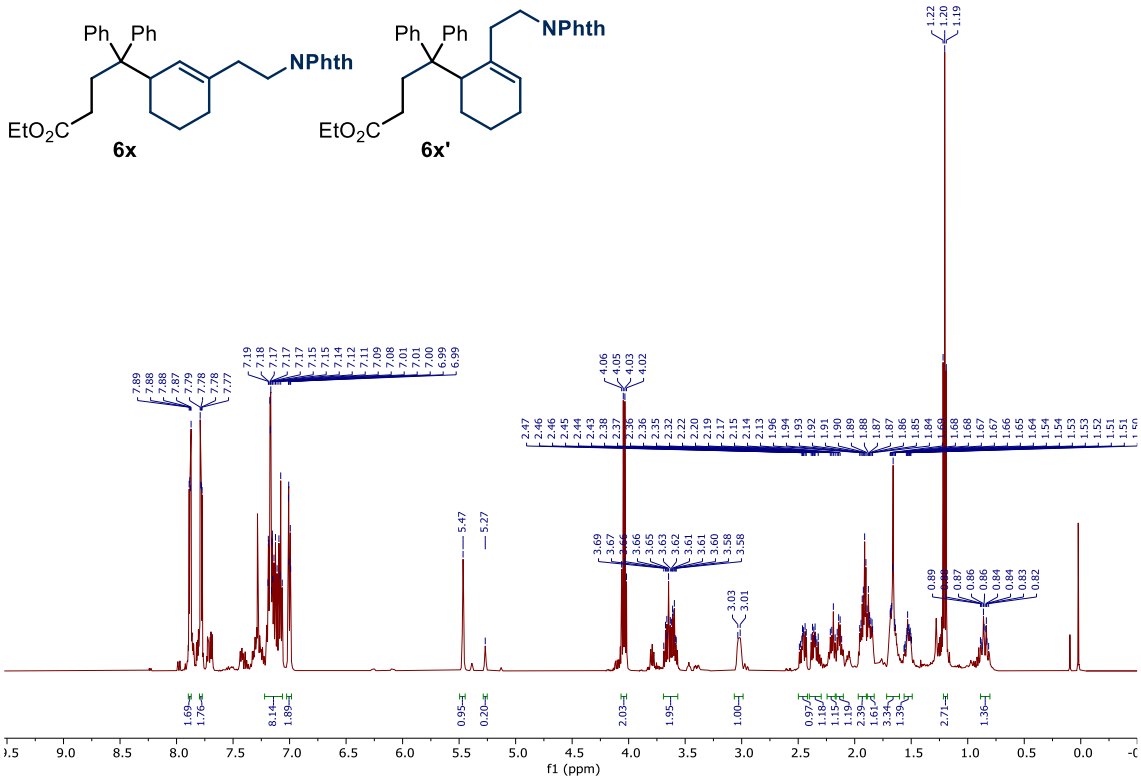
^{1}H NMR (**5**00 MHz, $CDCl_3$) of **6w**



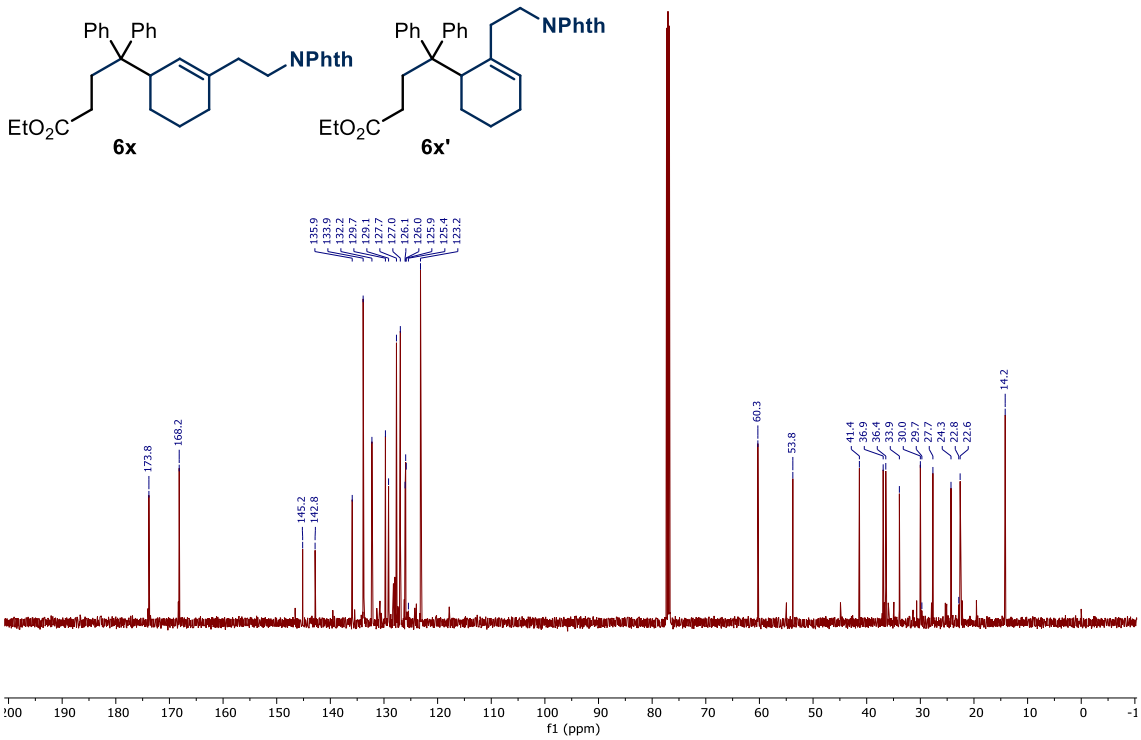
^{13}C NMR (101 MHz, $CDCl_3$) of **6w**



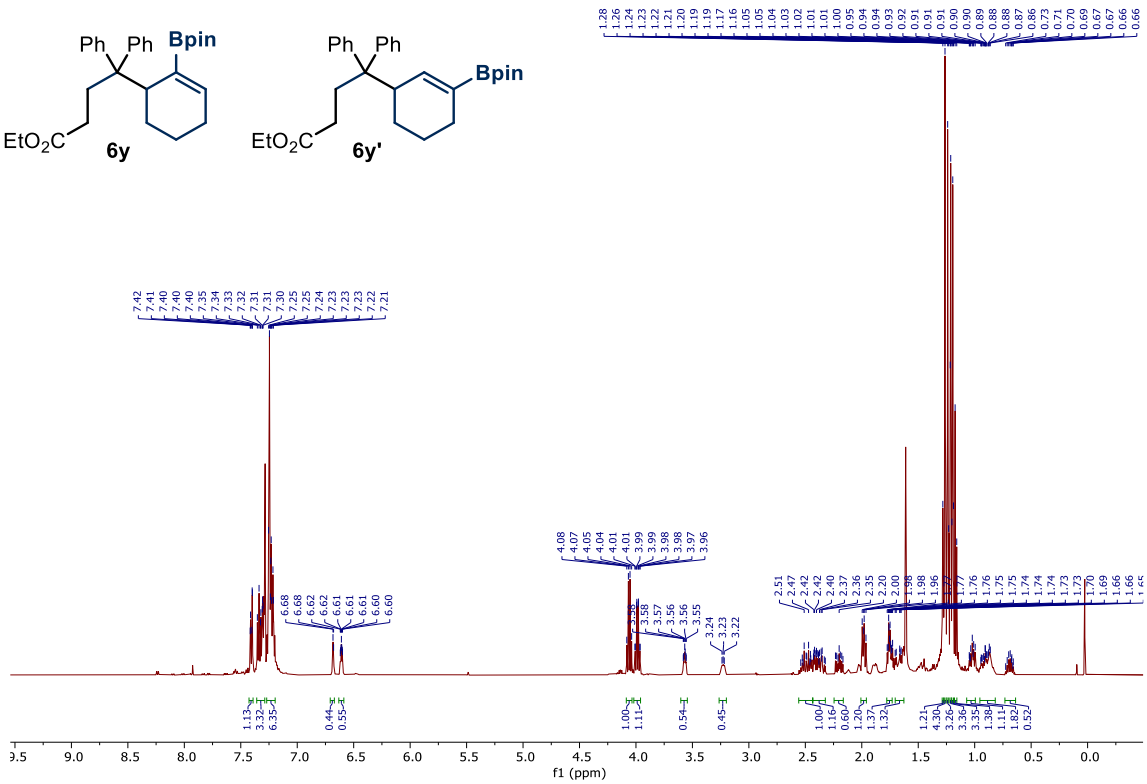
^{1}H NMR (500 MHz, $CDCl_3$) of **6x**



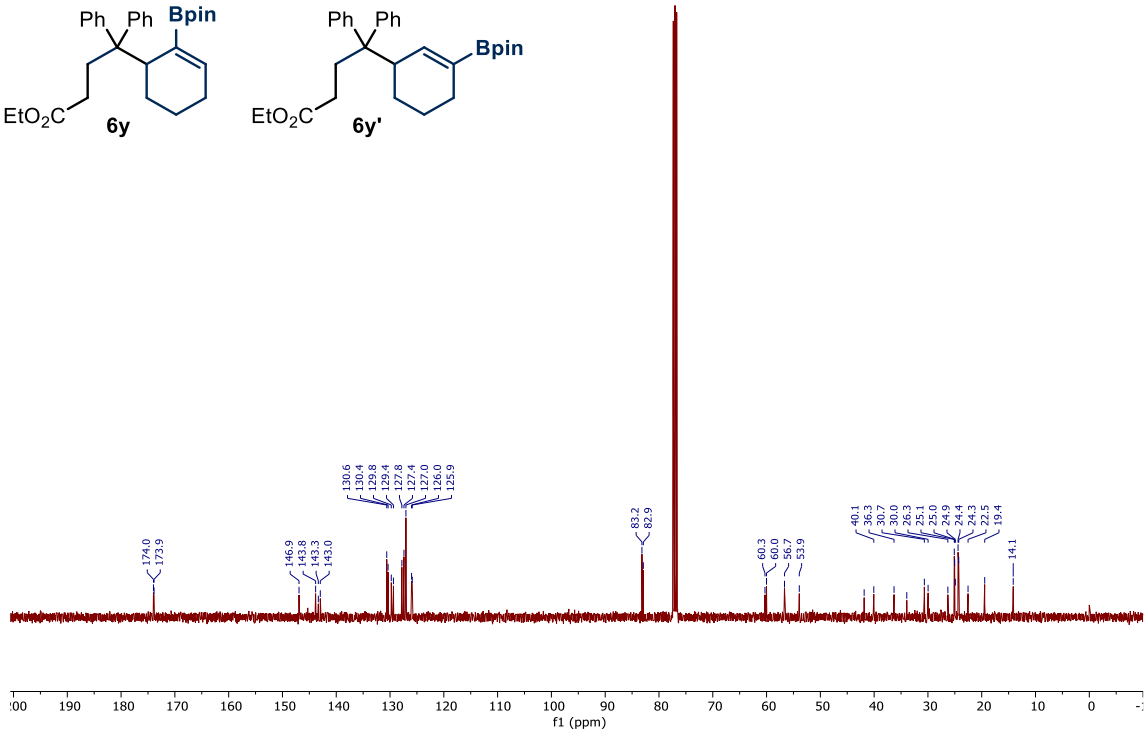
^{13}C NMR (126 MHz, $CDCl_3$) of **6x**



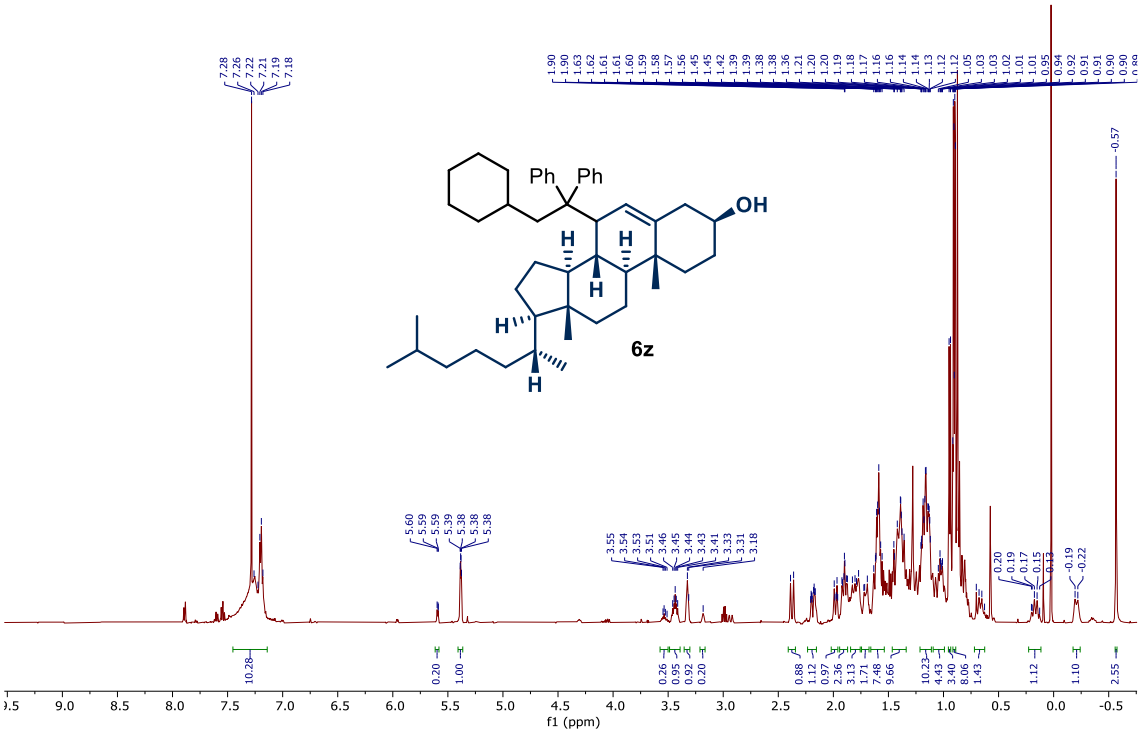
^{1}H NMR (500 MHz, $CDCl_3$) of **6y**



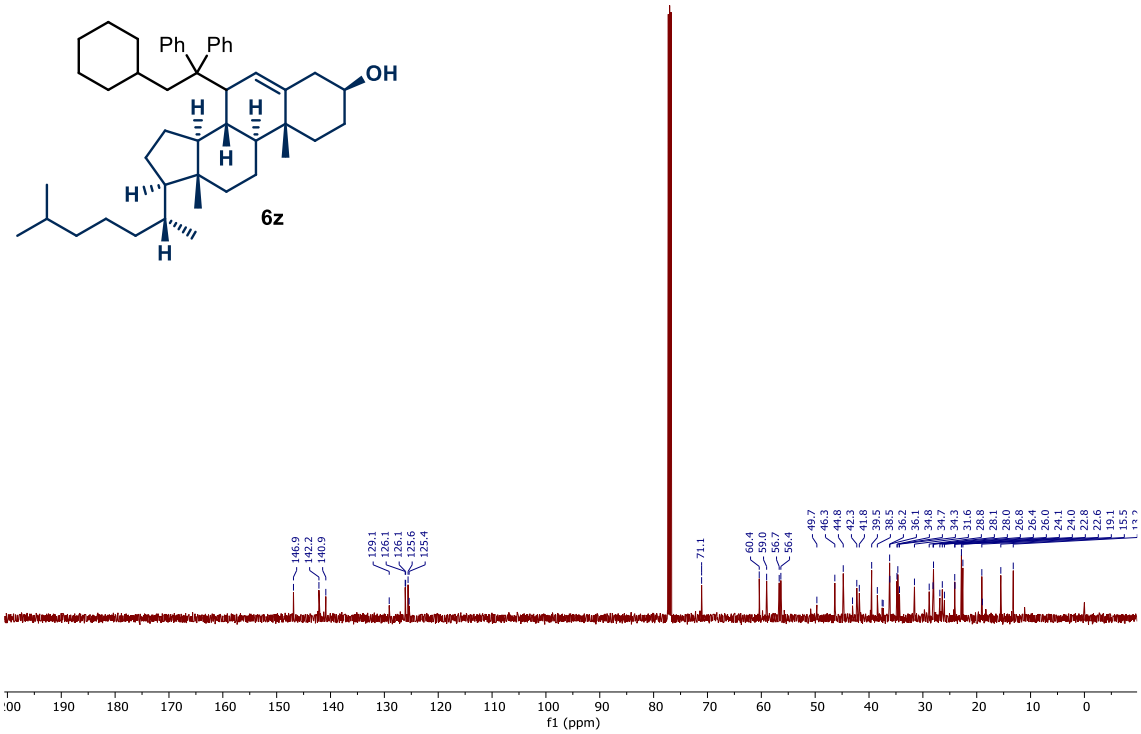
^{13}C NMR (101 MHz, $CDCl_3$) of **6y**



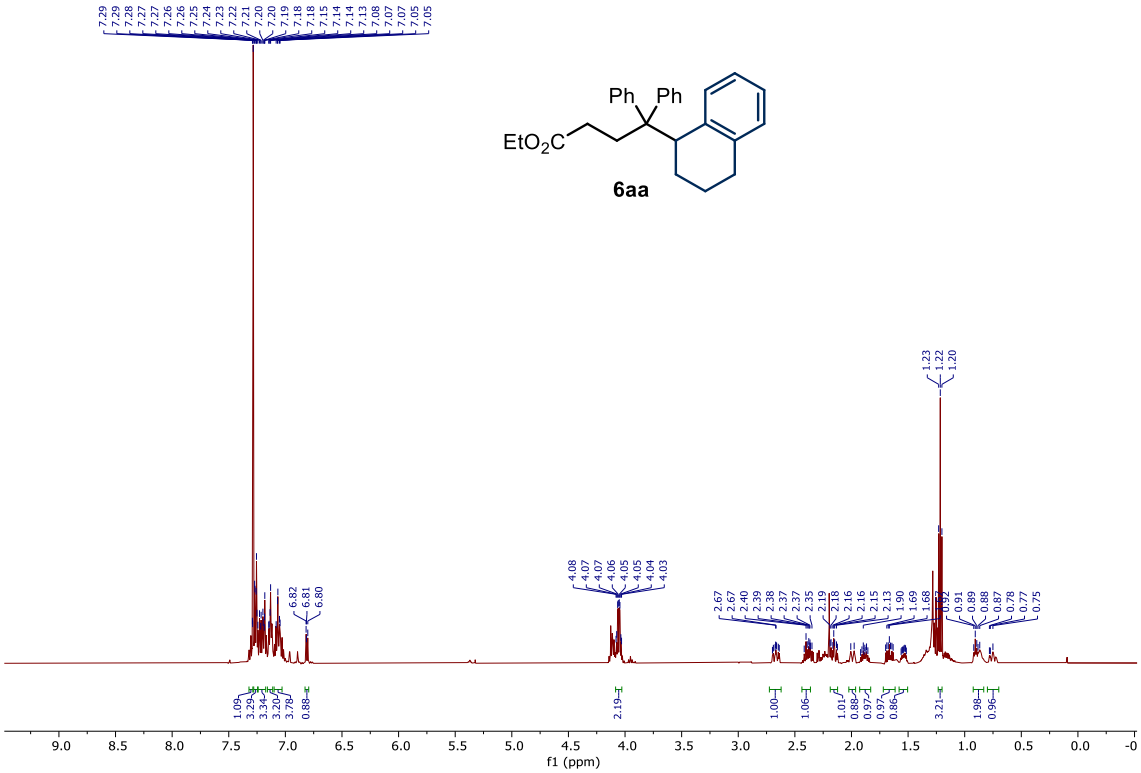
^{1}H NMR (500 MHz, $CDCl_3$) of **6z**



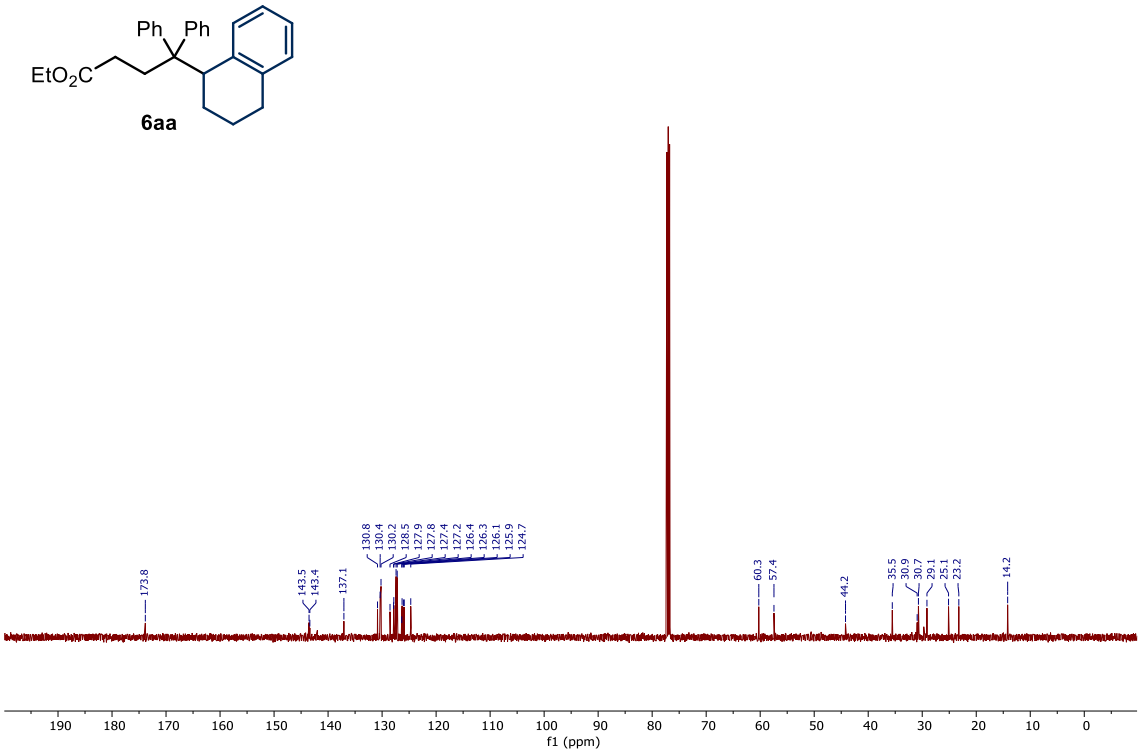
^{13}C NMR (126 MHz, $CDCl_3$) of **6z**



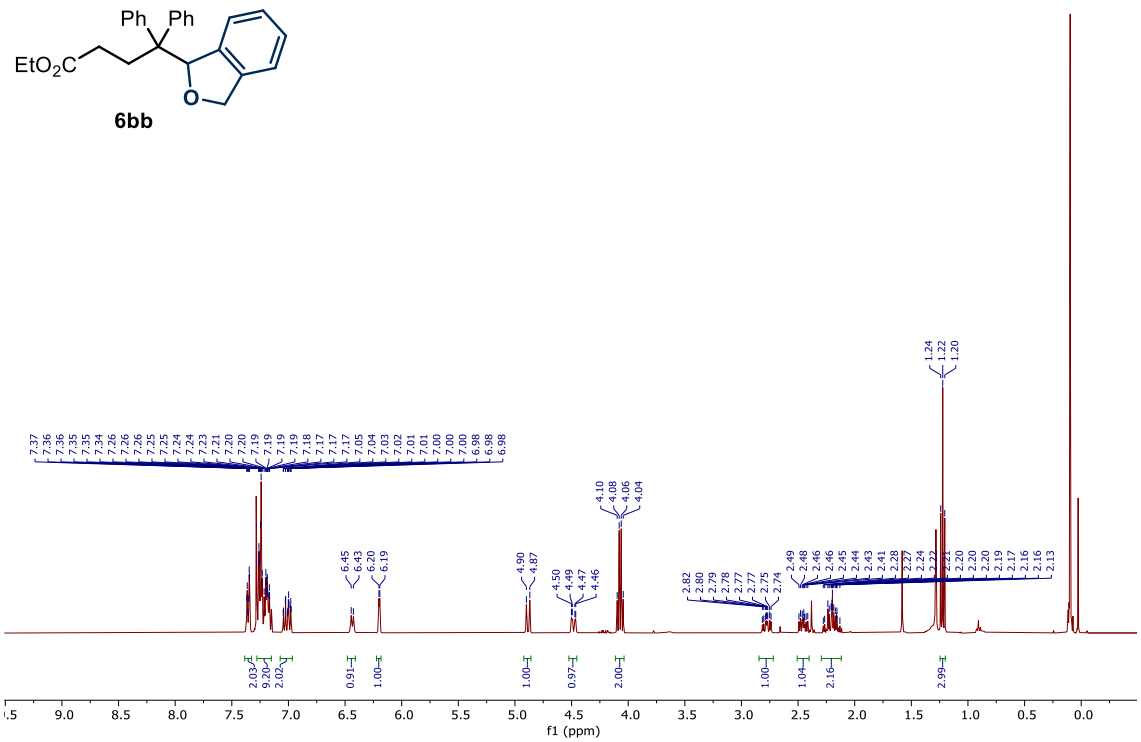
^{1}H NMR (500 MHz, $CDCl_3$) of **6aa**



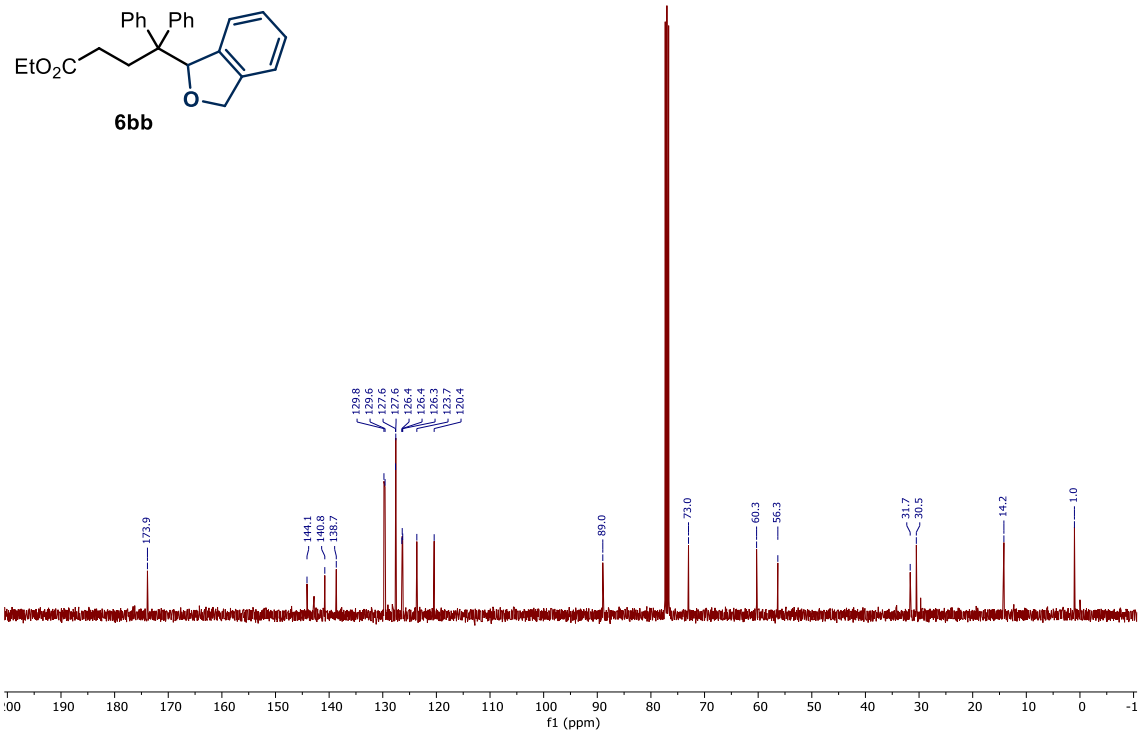
^{13}C NMR (126 MHz, $CDCl_3$) of **6aa**



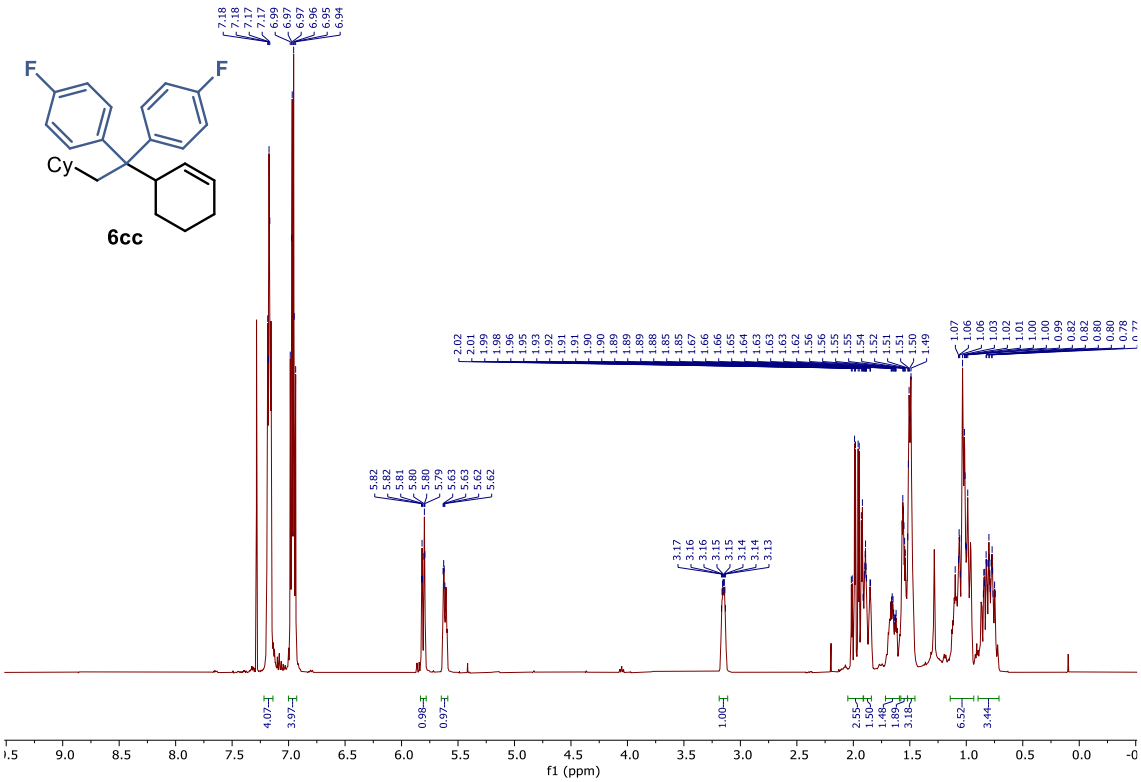
^{1}H NMR (**4**00 MHz, $CDCl_3$) of **6bb**



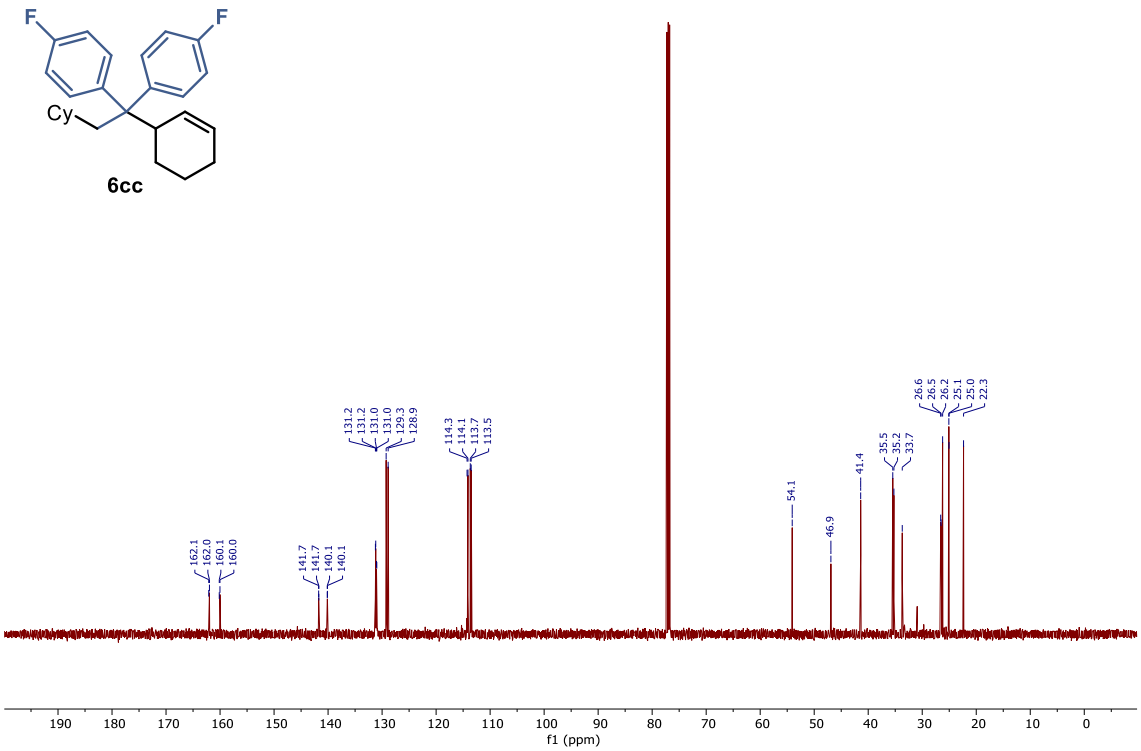
^{13}C NMR (101 MHz, $CDCl_3$) of **6bb**



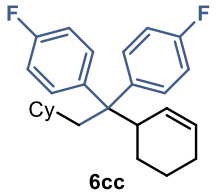
^{1}H NMR (**5**00 MHz, $CDCl_3$) of **6cc**



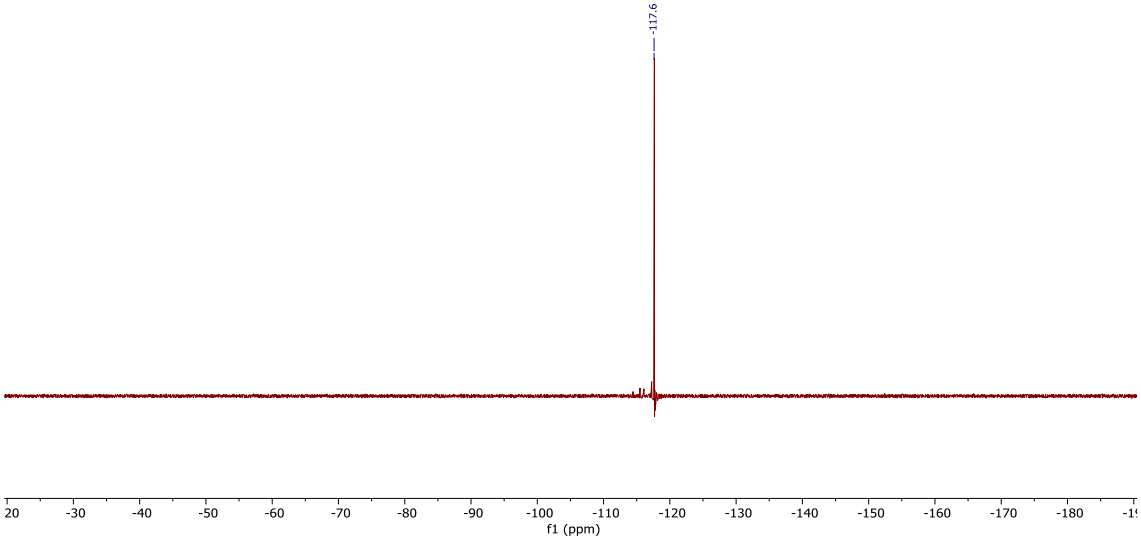
^{13}C NMR (126 MHz, $CDCl_3$) of **6cc**



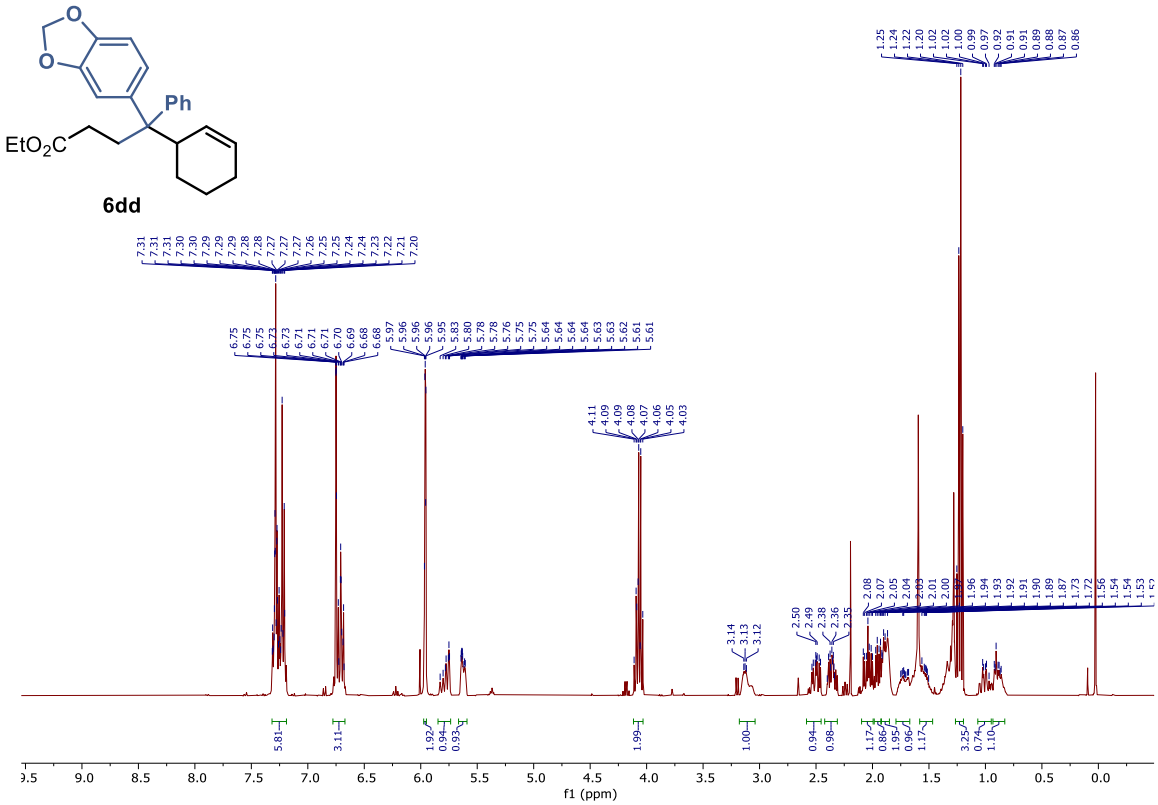
^{19}F NMR (376 MHz, $CDCl_3$) of **6cc**



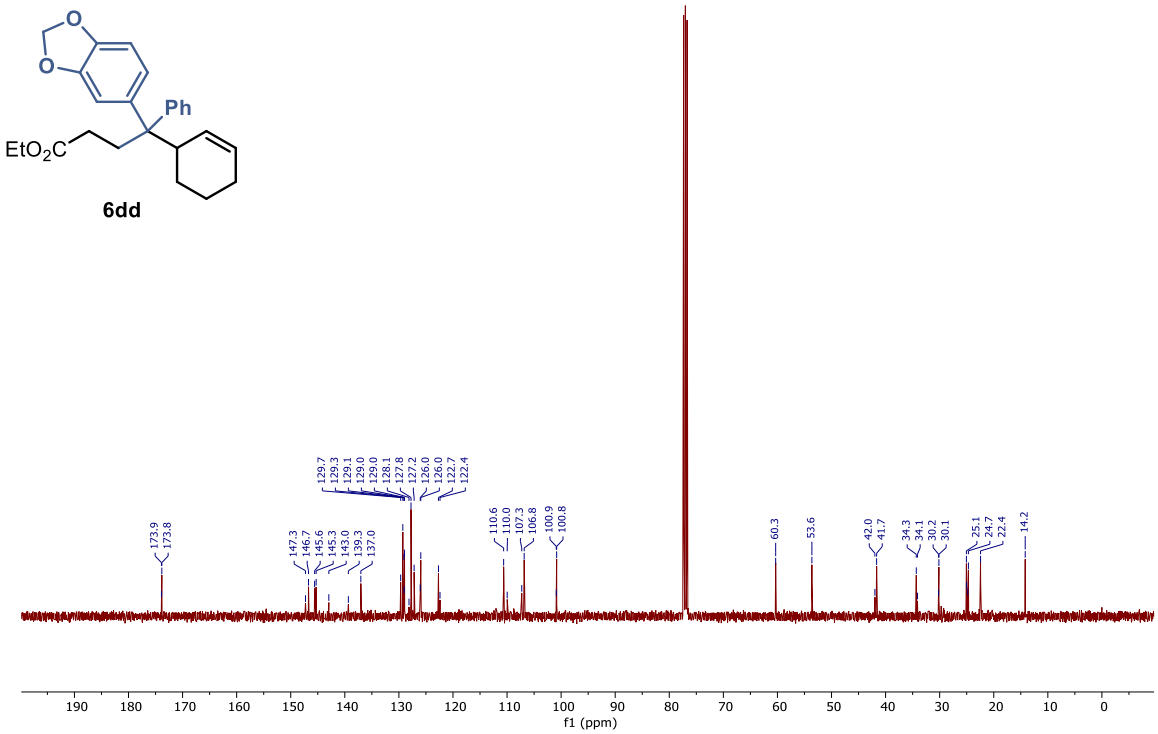
6cc



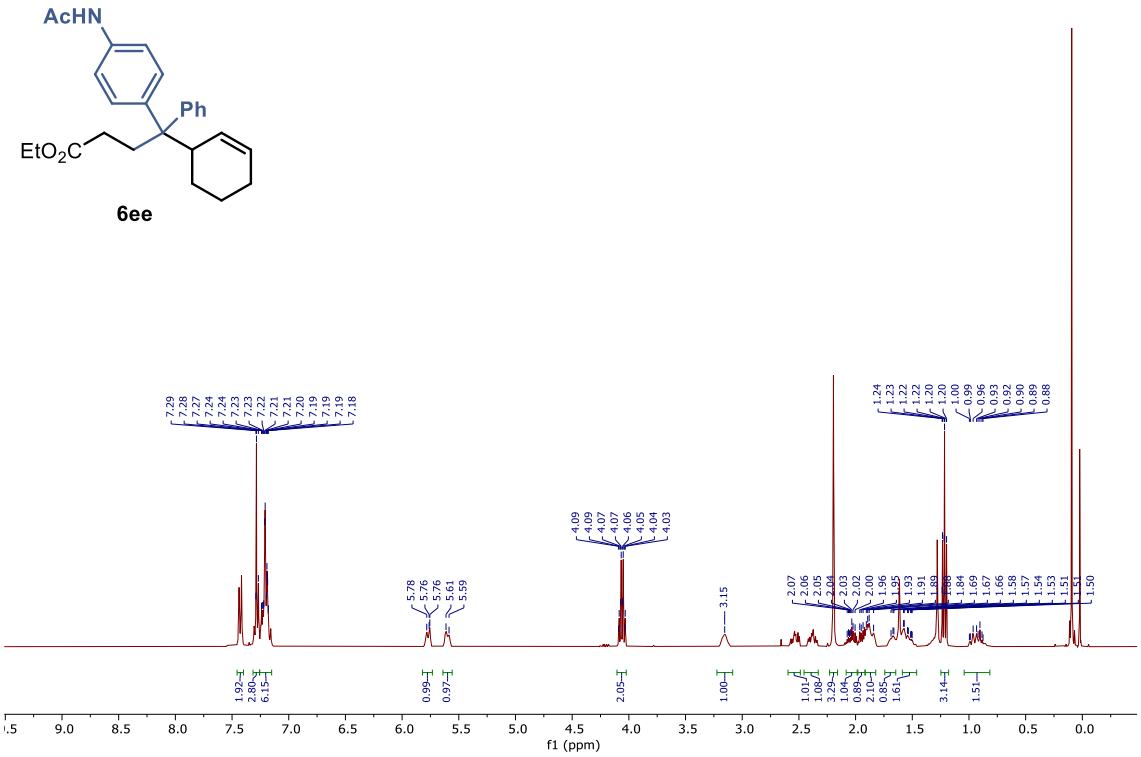
^{1}H NMR (400 MHz, $CDCl_3$) of **6dd**



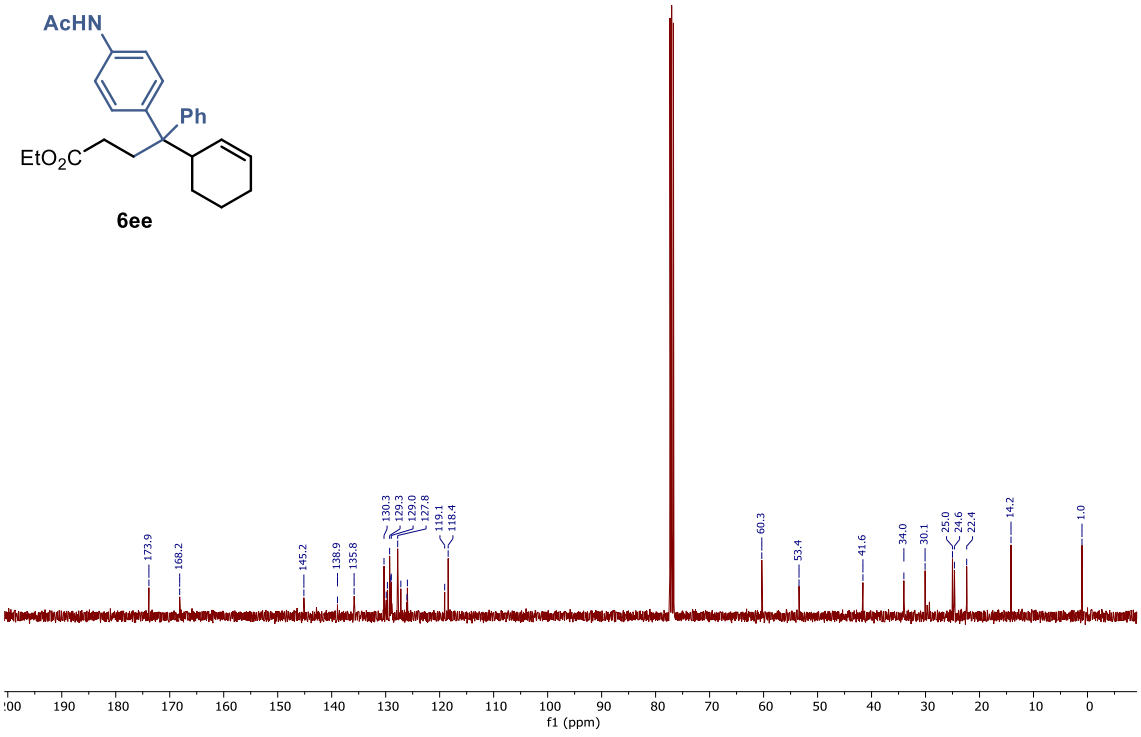
^{13}C NMR (101 MHz, $CDCl_3$) of **6dd**



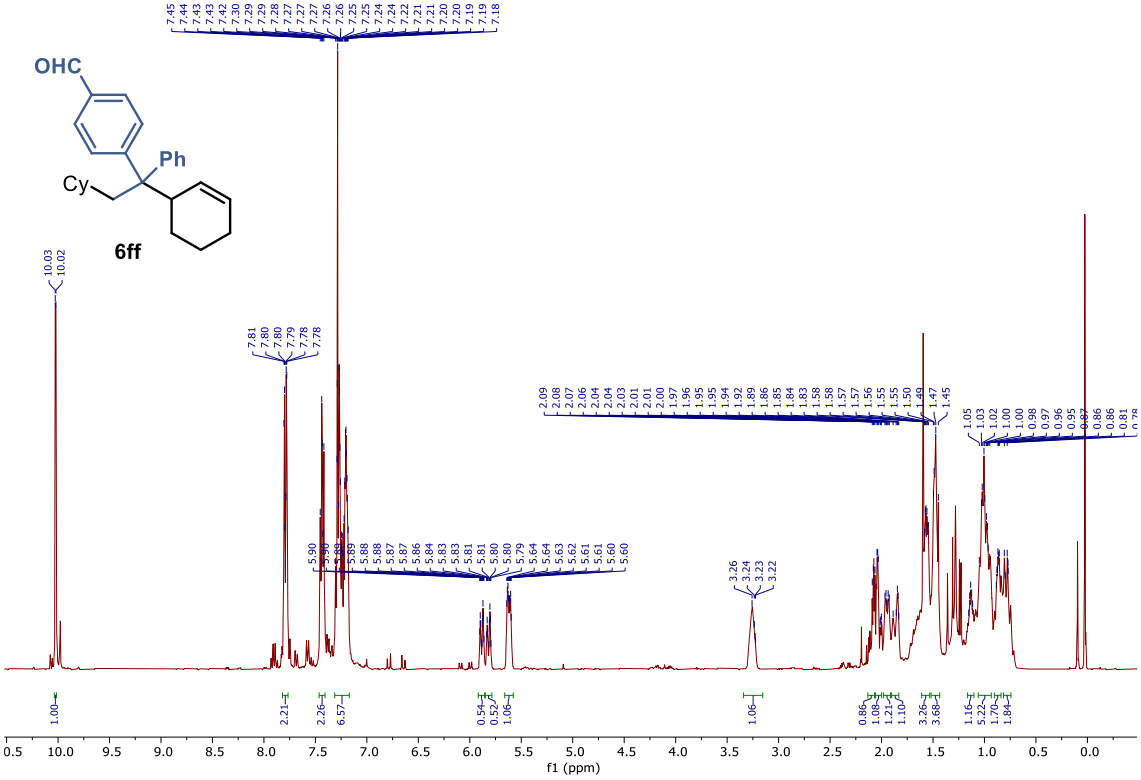
^{1}H NMR (400 MHz, $CDCl_3$) of **6ee**



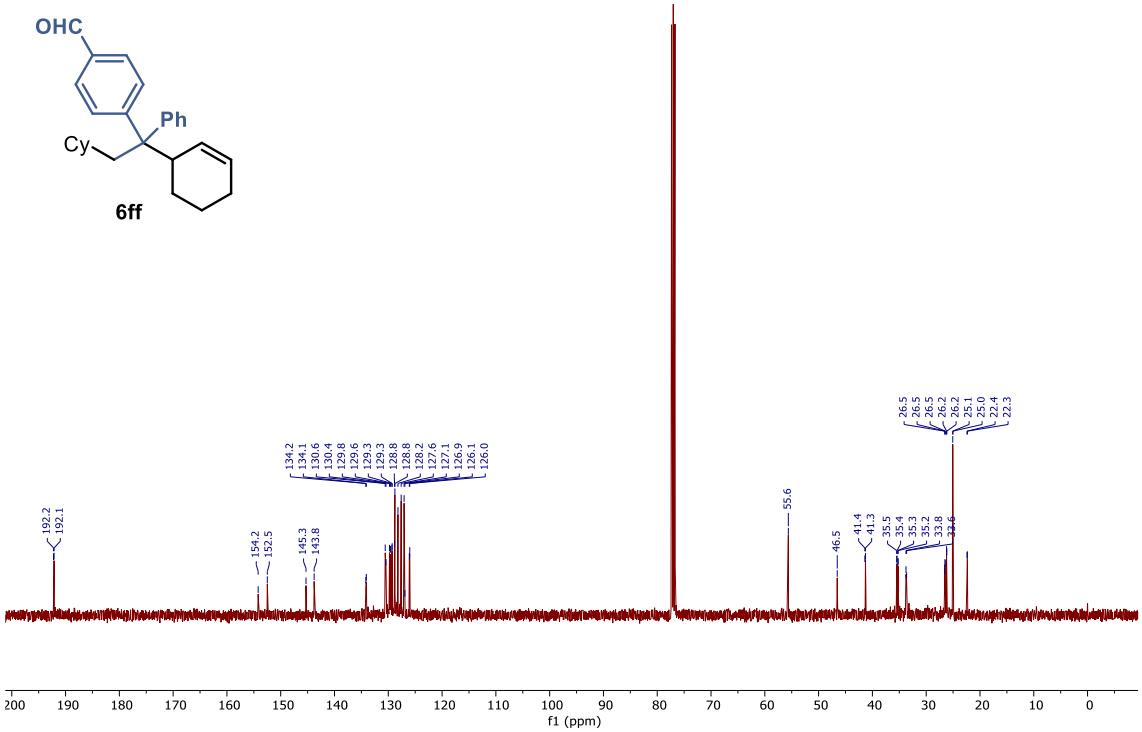
^{13}C NMR (101 MHz, $CDCl_3$) of **6ee**



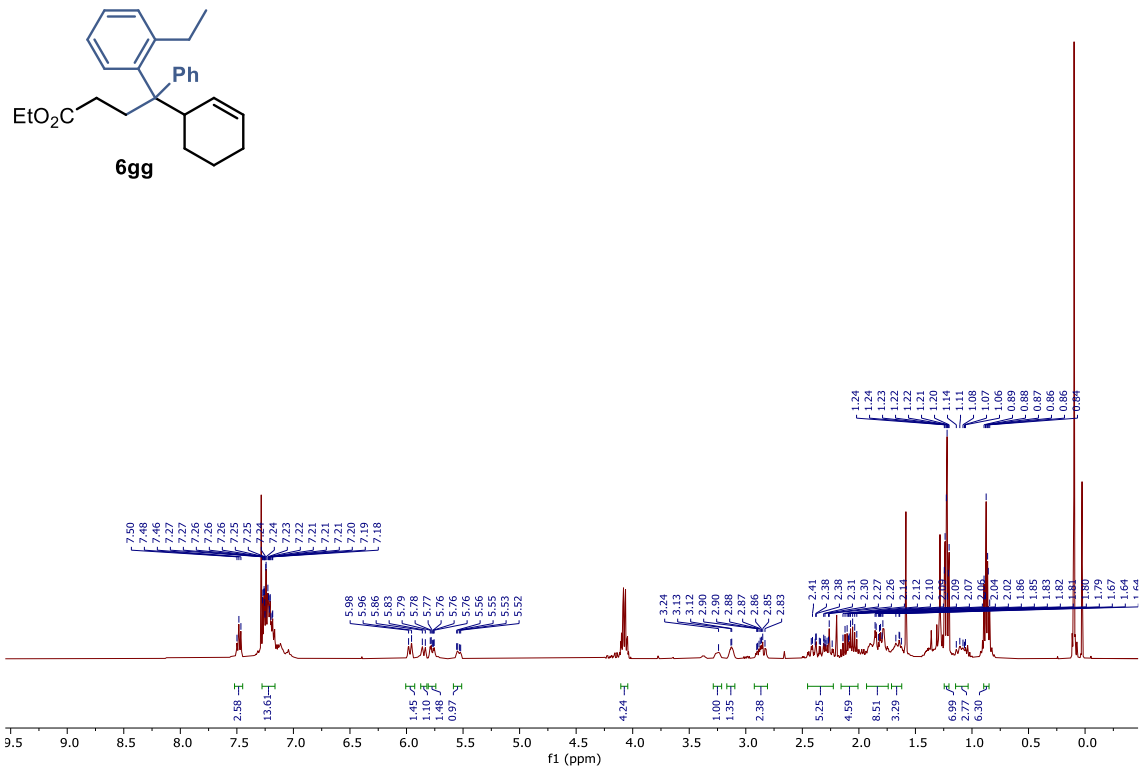
^{1}H NMR (500 MHz, $CDCl_3$) of **6ff**



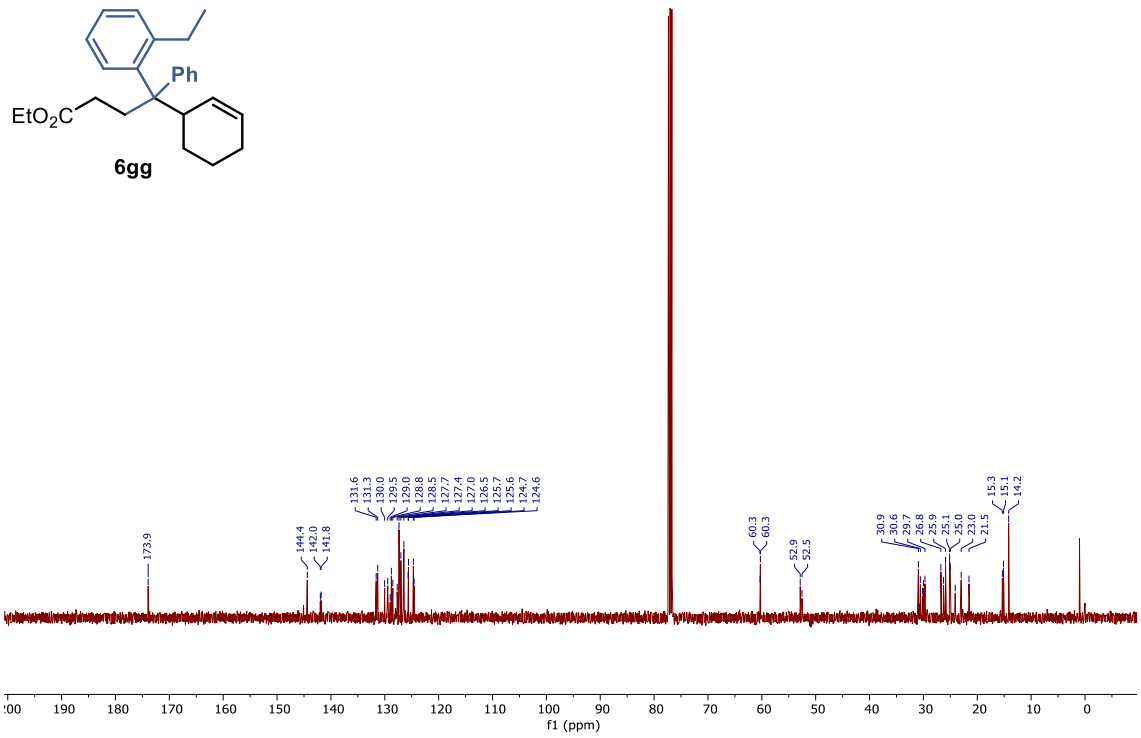
^{13}C NMR (101 MHz, $CDCl_3$) of **6ff**



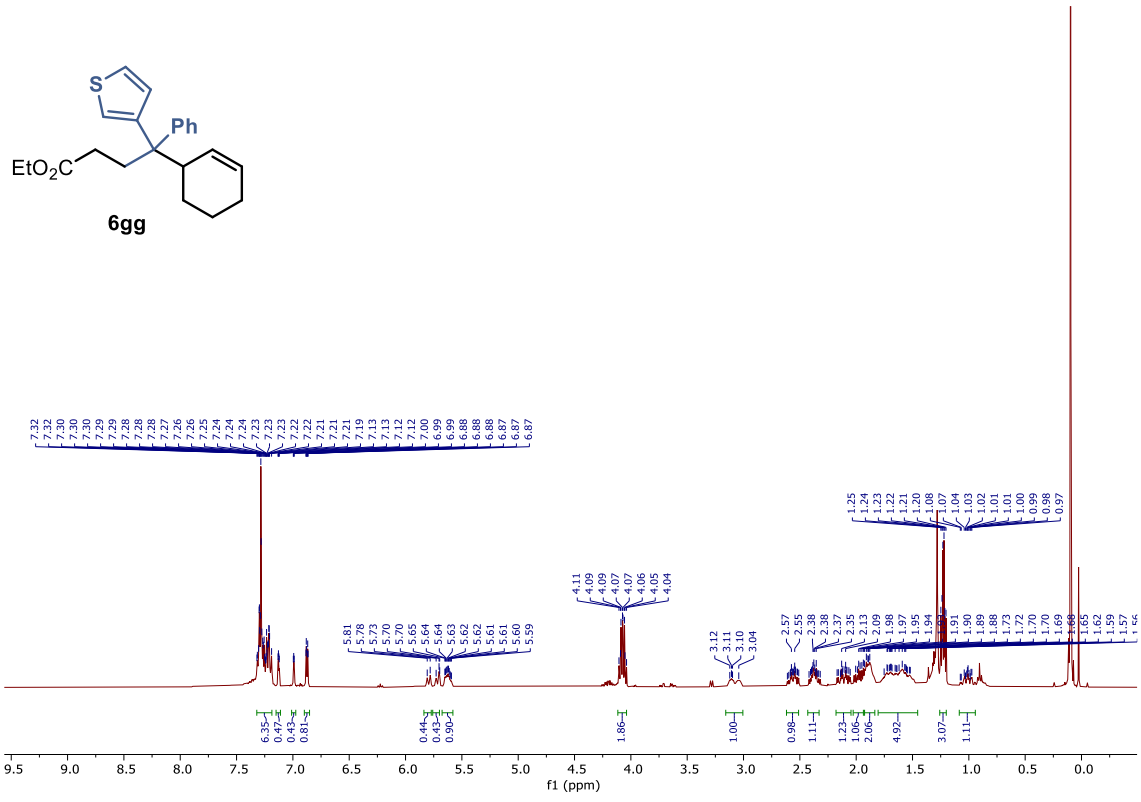
^{1}H NMR (400 MHz, $CDCl_3$) of **6gg**



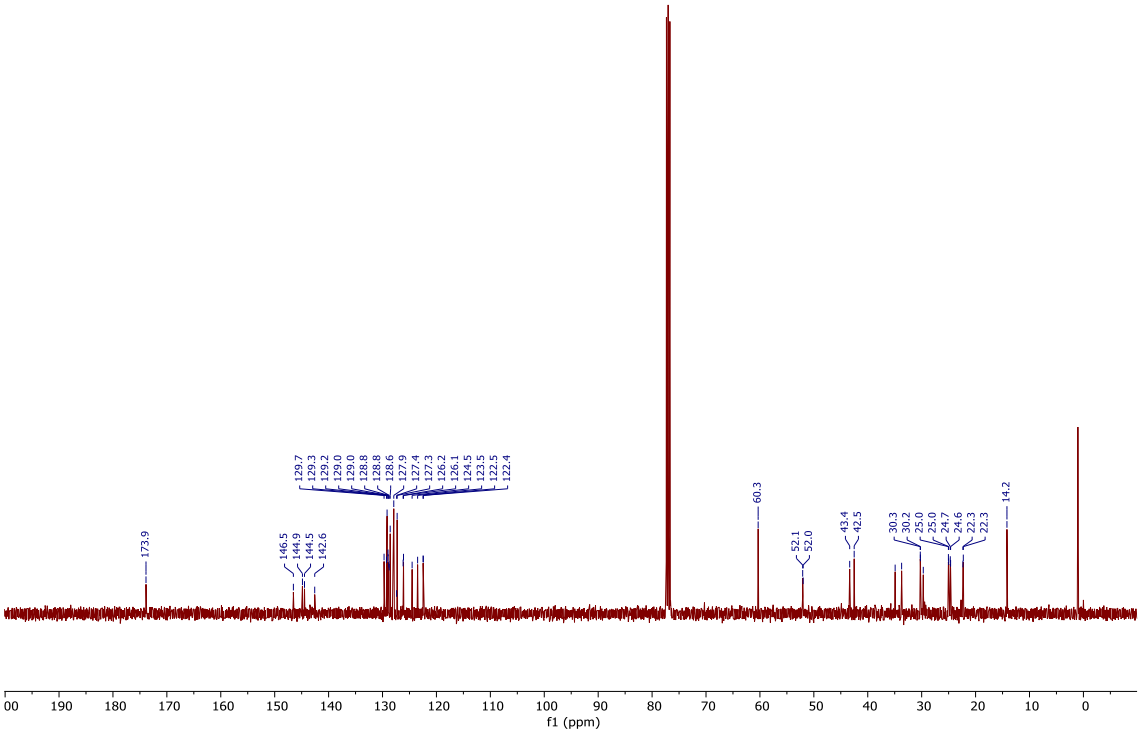
^{13}C NMR (101 MHz, $CDCl_3$) of **6gg**



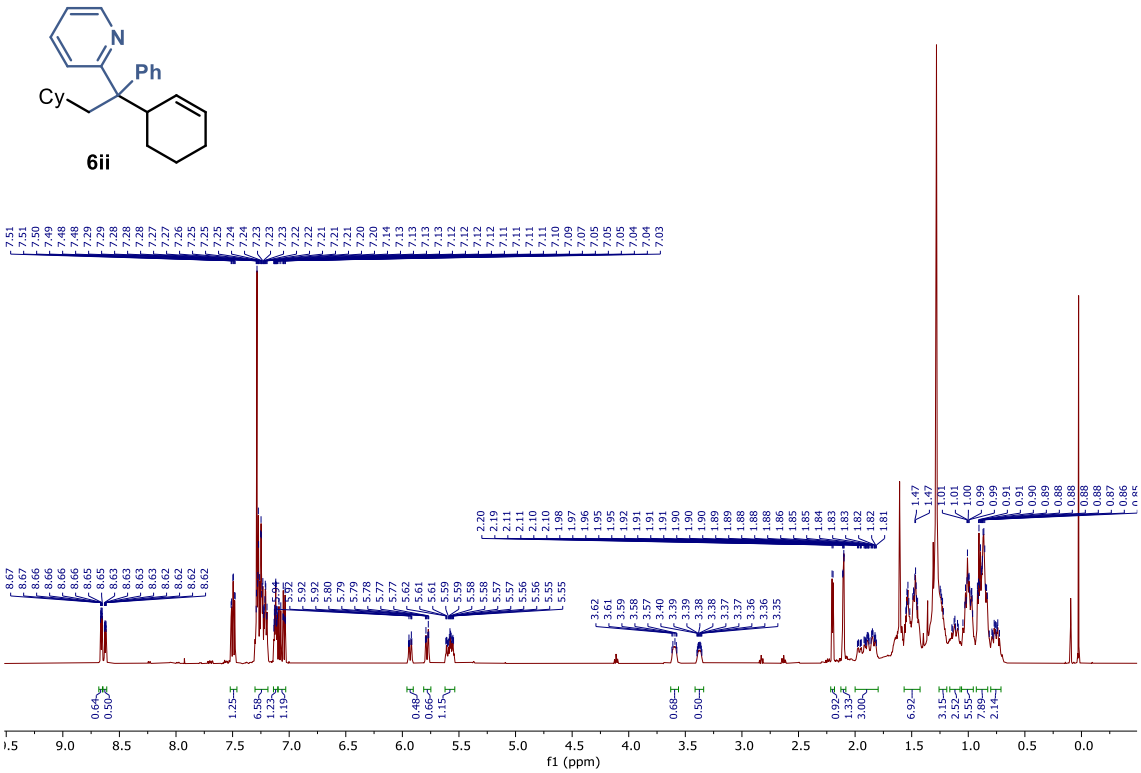
^{1}H NMR (400 MHz, $CDCl_3$) of **6hh**



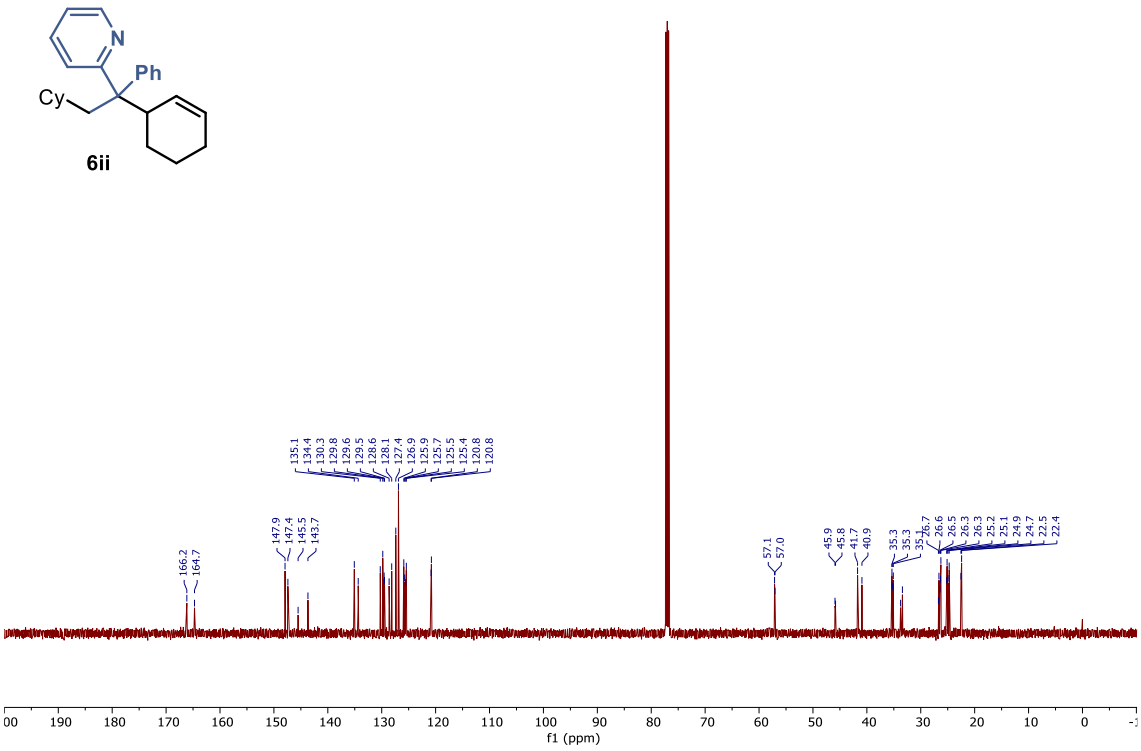
^{13}C NMR (101 MHz, $CDCl_3$) of **6hh**



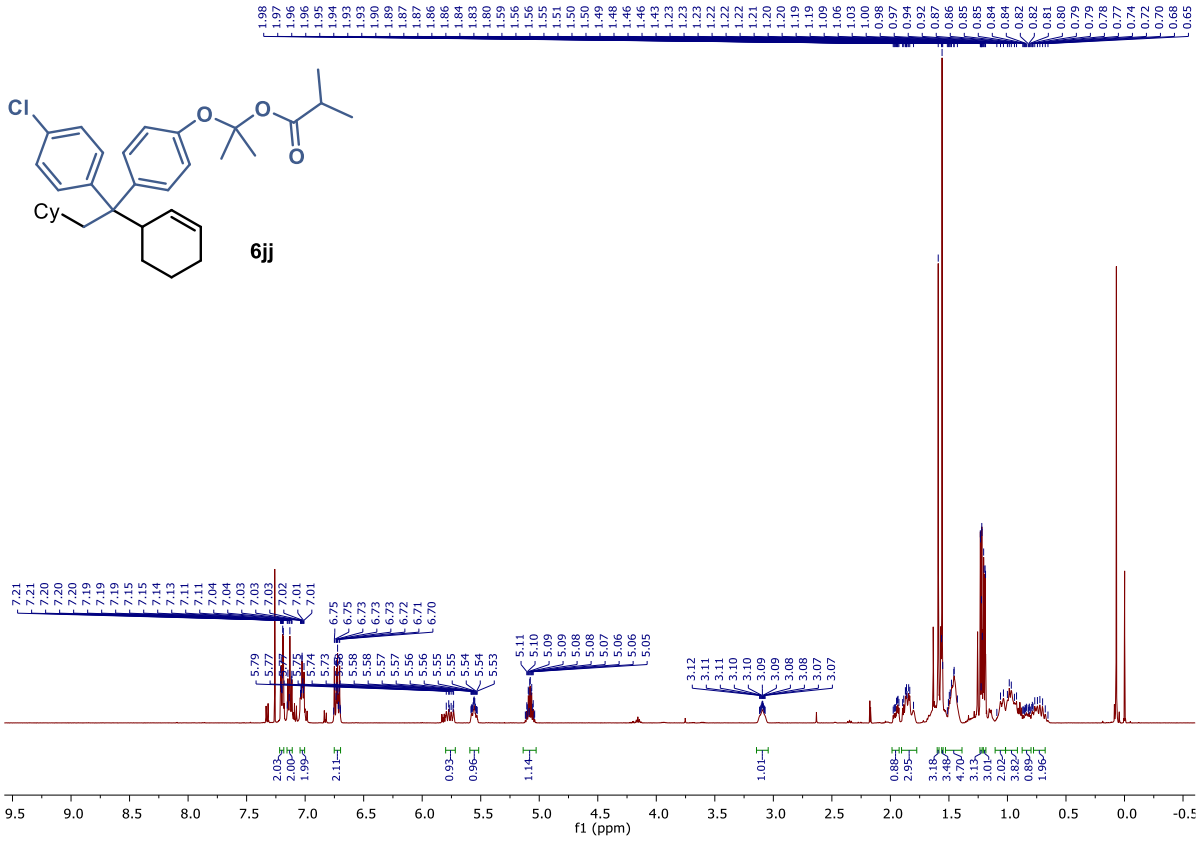
^{1}H NMR (**5**00 MHz, $CDCl_3$) of **6ii**



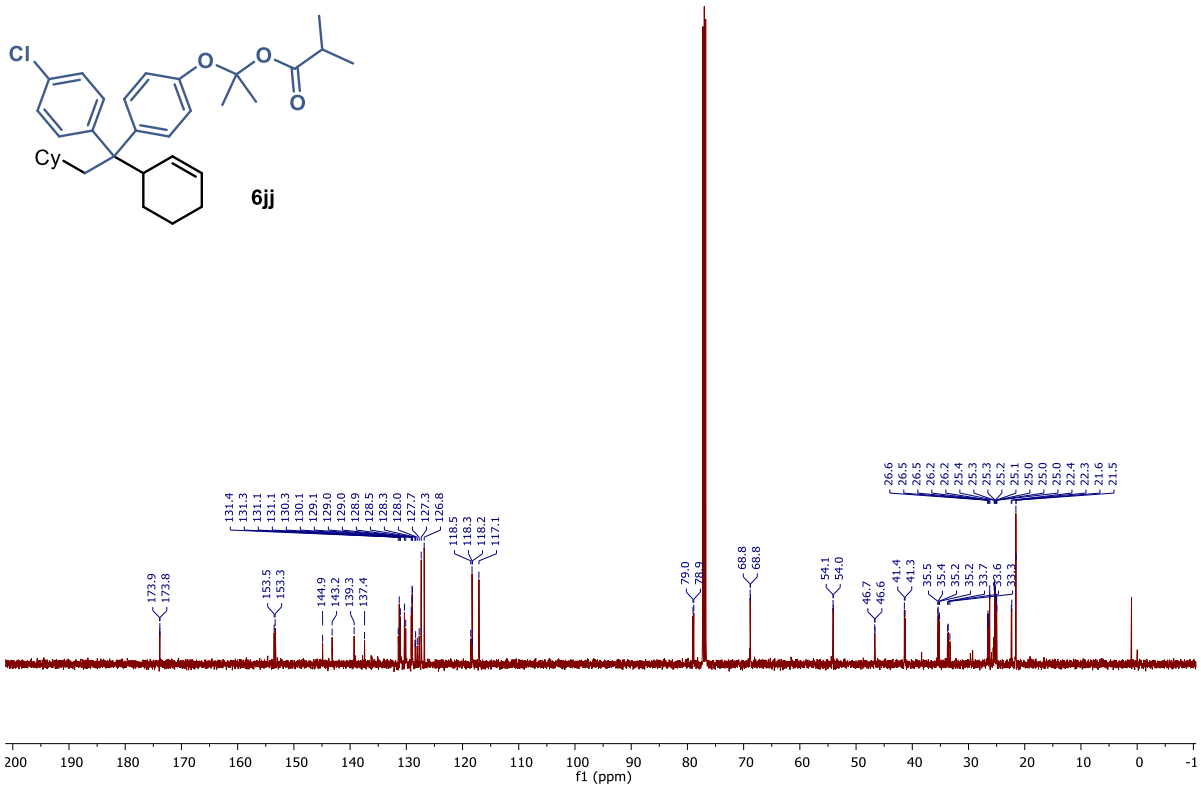
^{13}C NMR (126 MHz, $CDCl_3$) of **6ii**



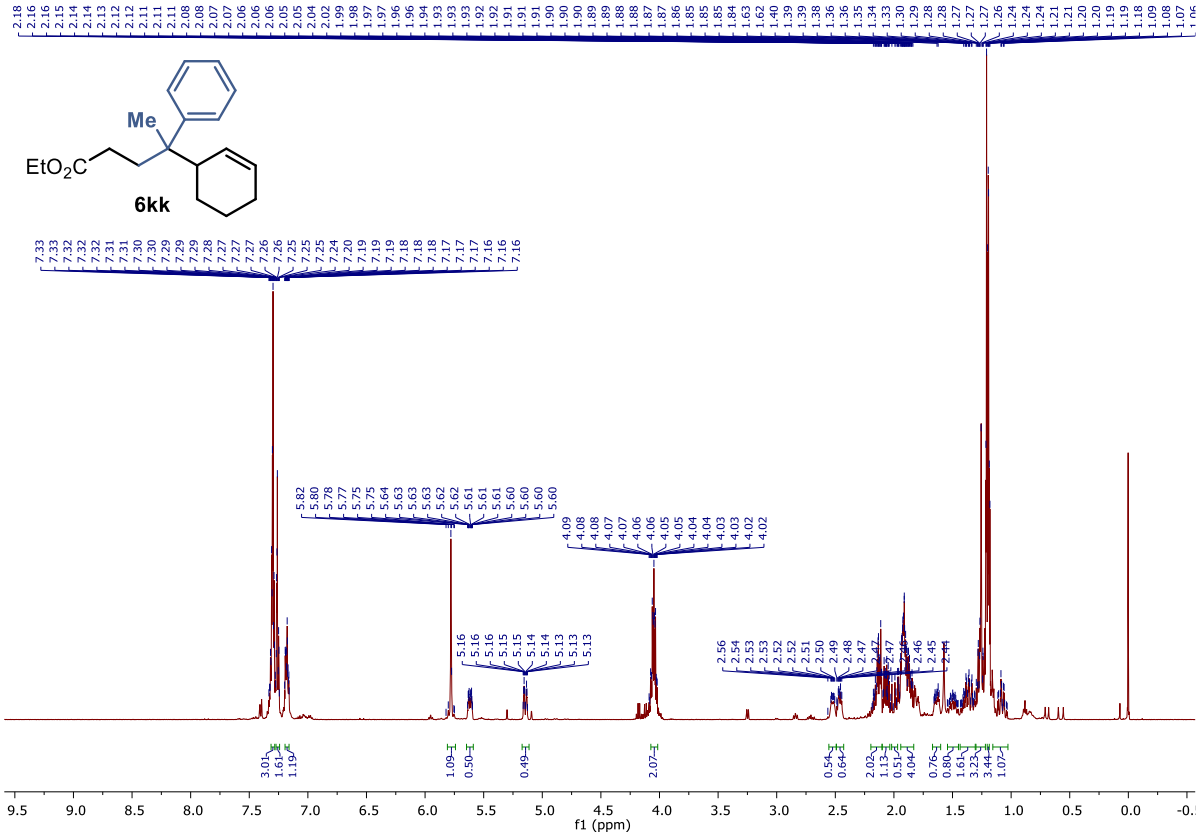
^{1}H NMR (500 MHz, $CDCl_3$) of **6jj**



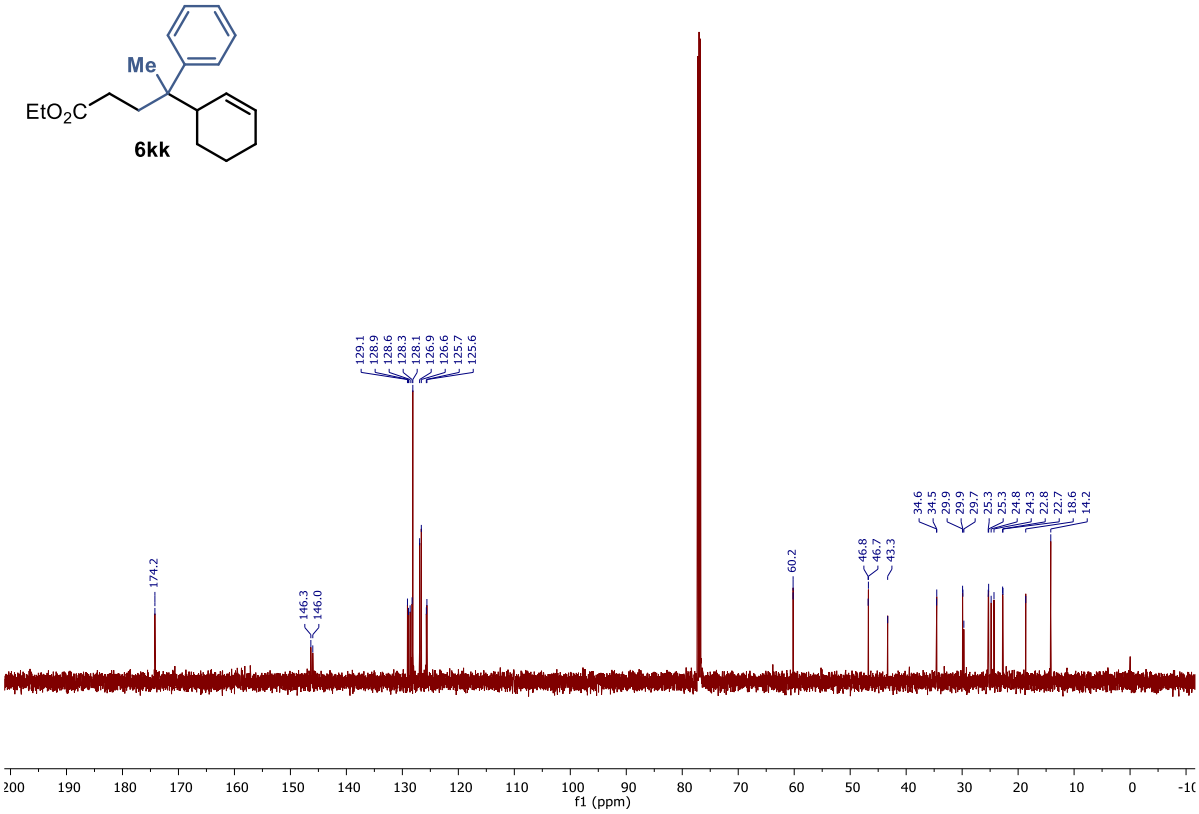
^{13}C NMR (126 MHz, $CDCl_3$) of **6jj**



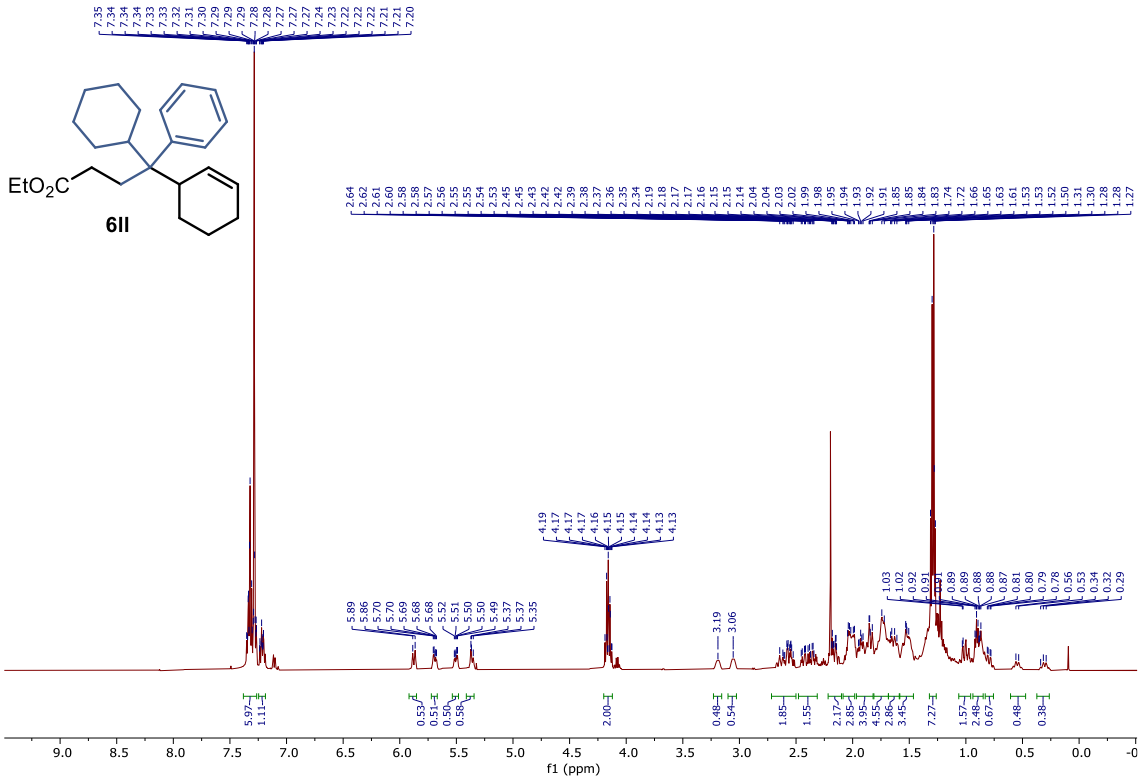
^{1}H NMR (500 MHz, $CDCl_3$) of **6kk**



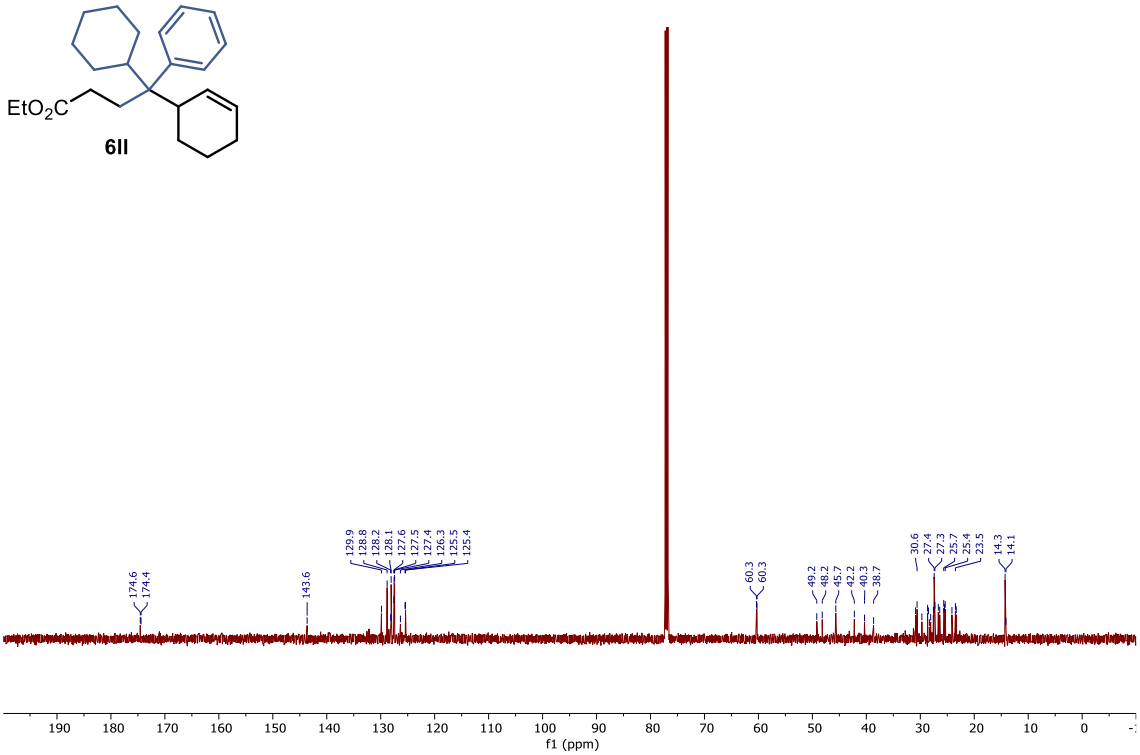
^{13}C NMR (126 MHz, $CDCl_3$) of **6kk**



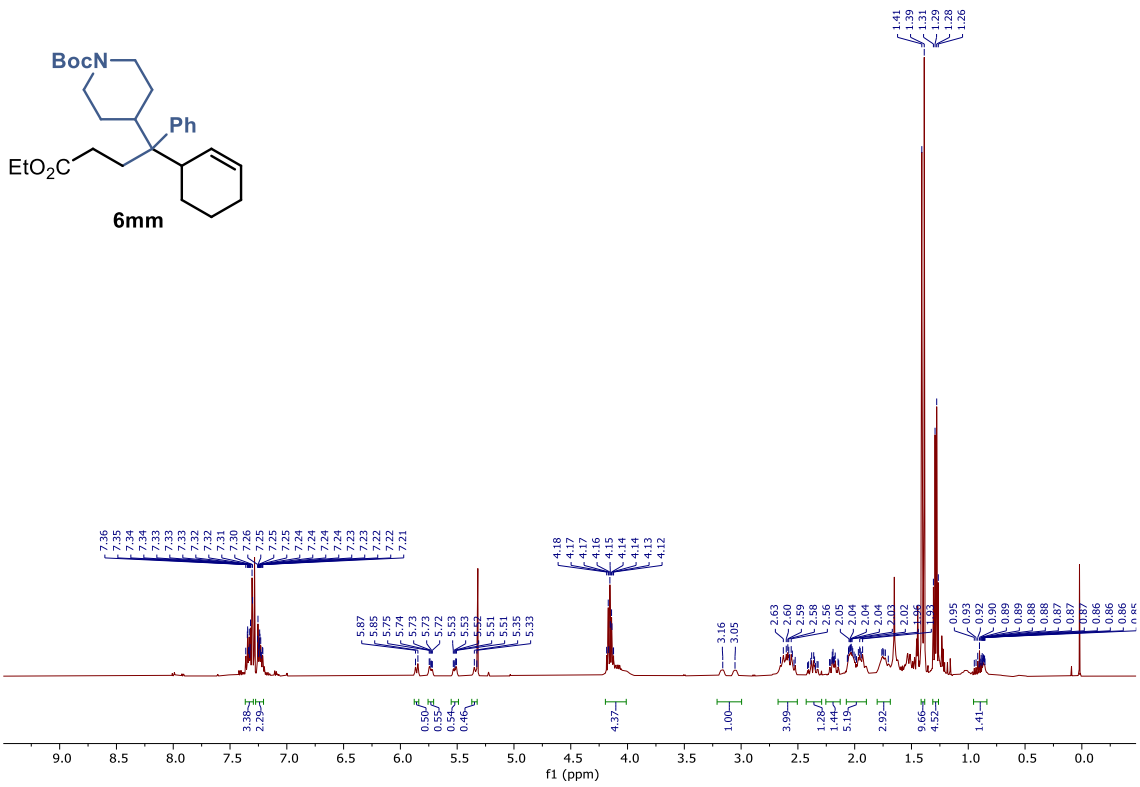
^{1}H NMR (500 MHz, $CDCl_3$) of **6ll**



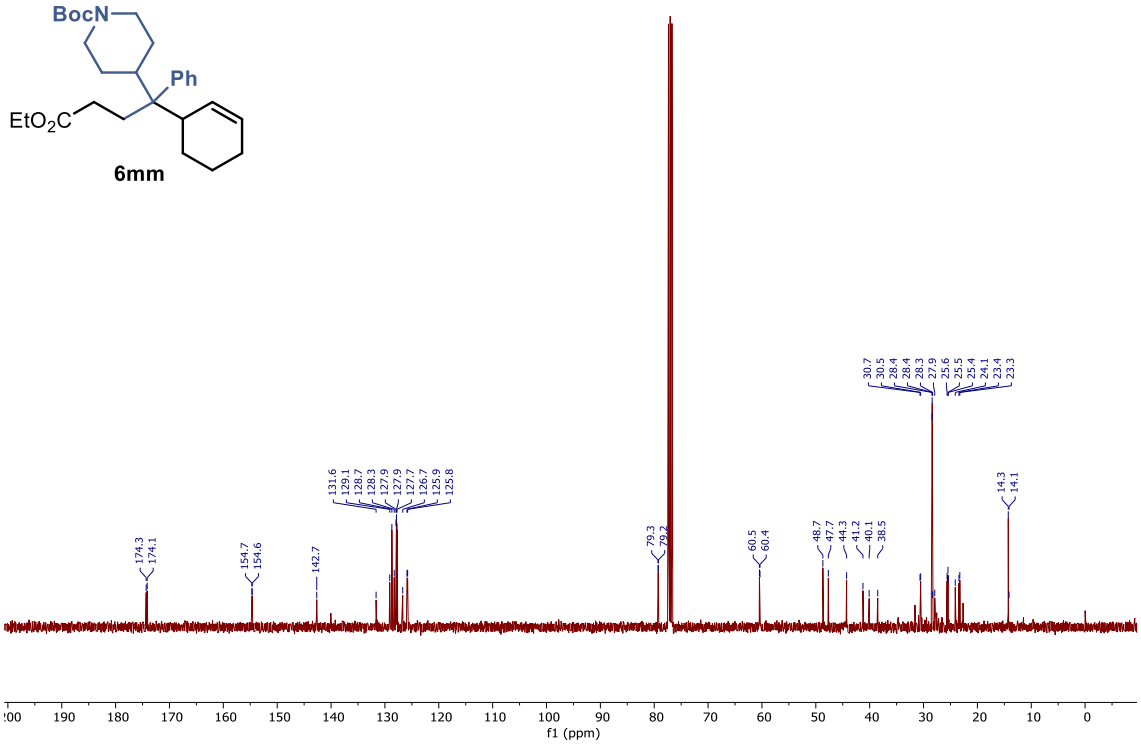
^{13}C NMR (126 MHz, $CDCl_3$) of **6ll**



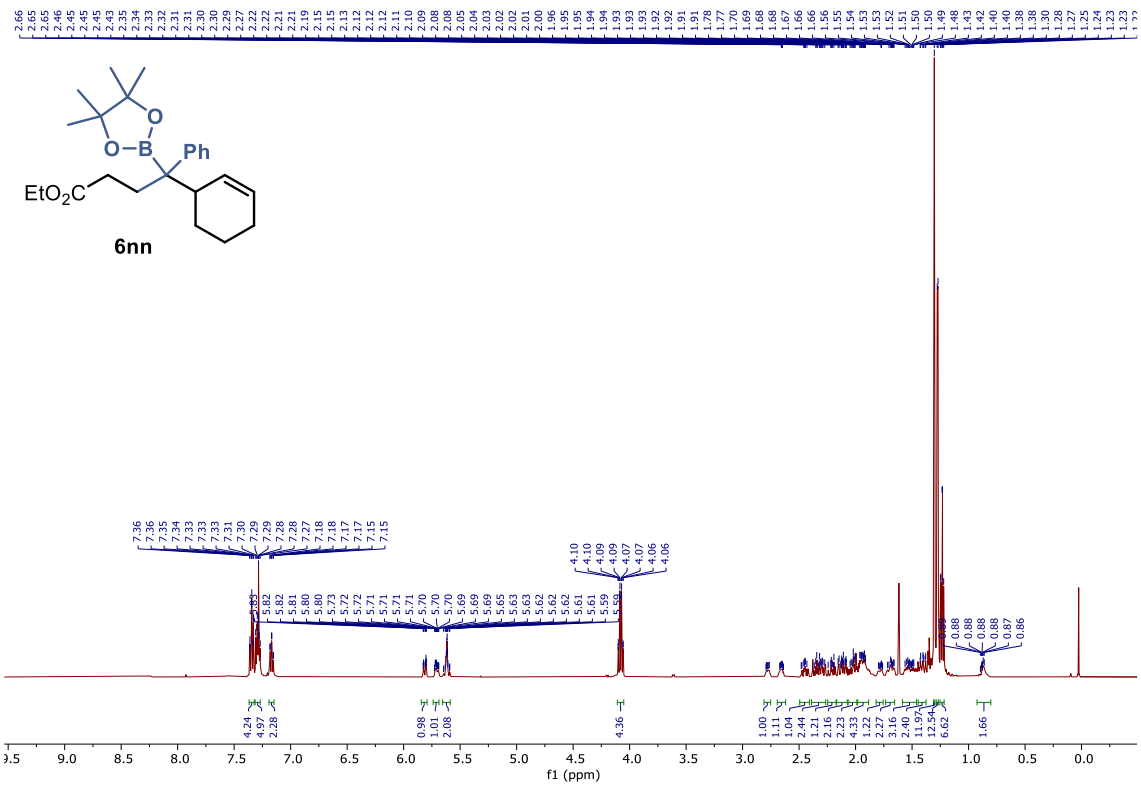
^{1}H NMR (500 MHz, $CDCl_3$) of **6mm**



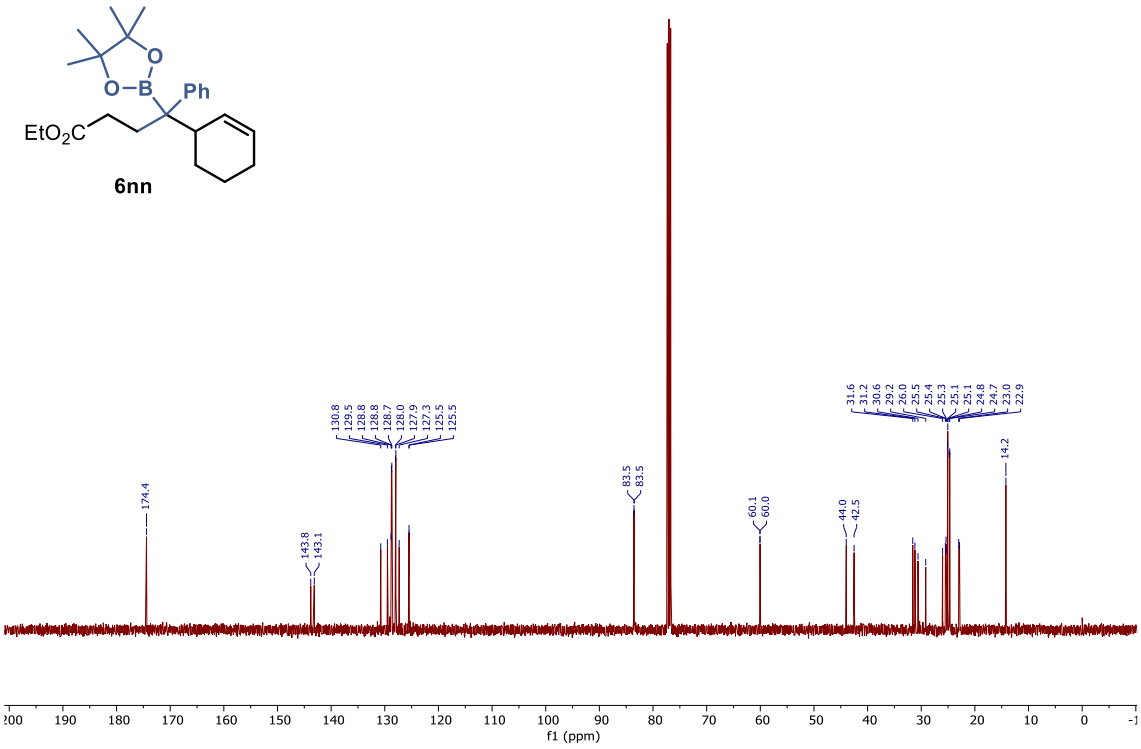
^{13}C NMR (101 MHz, $CDCl_3$) of **6mm**



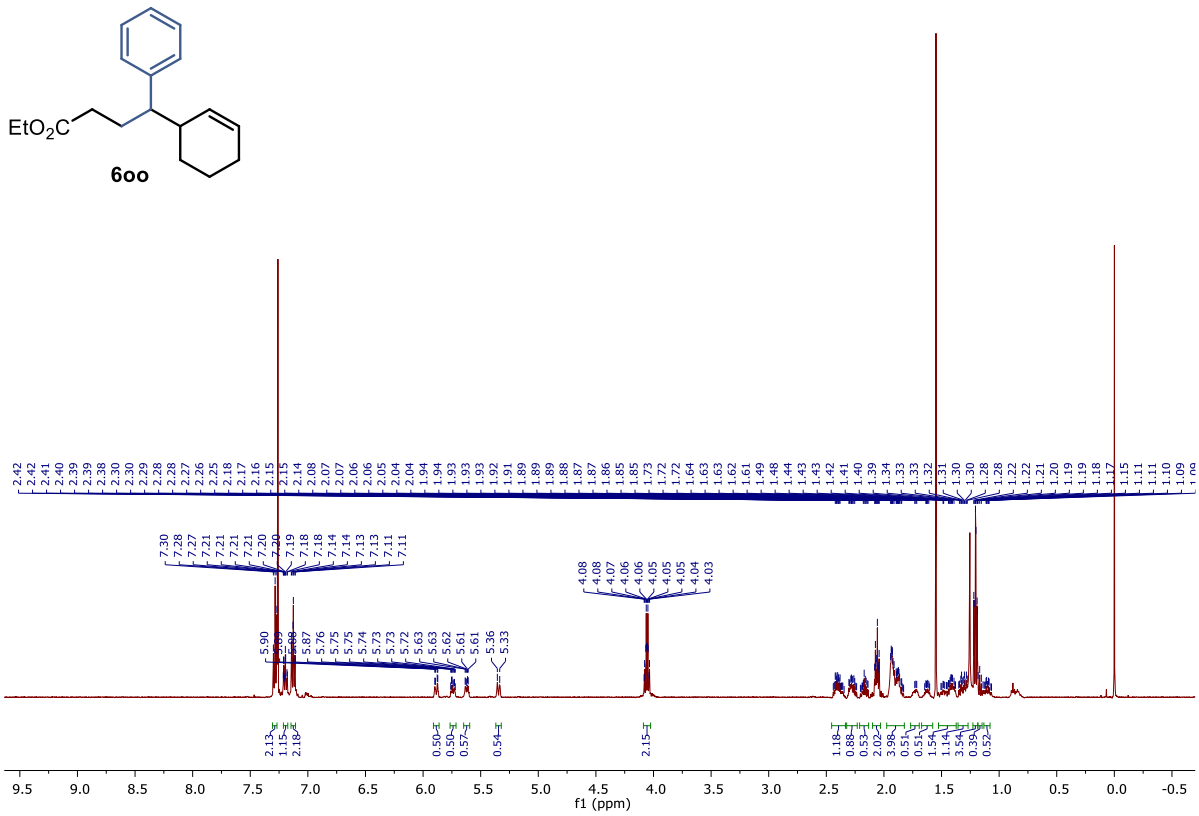
^{1}H NMR (**5**00 MHz, $CDCl_3$) of **6nn**



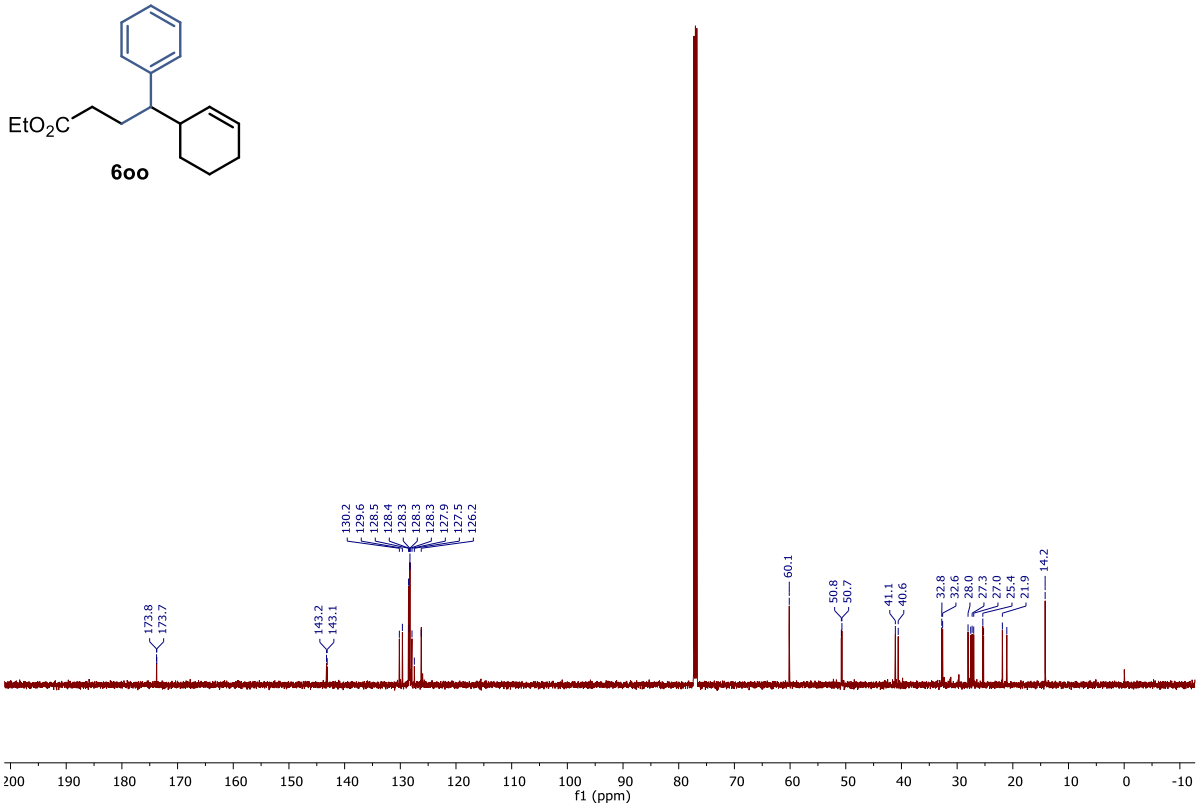
^{13}C NMR (101 MHz, $CDCl_3$) of **6nn**



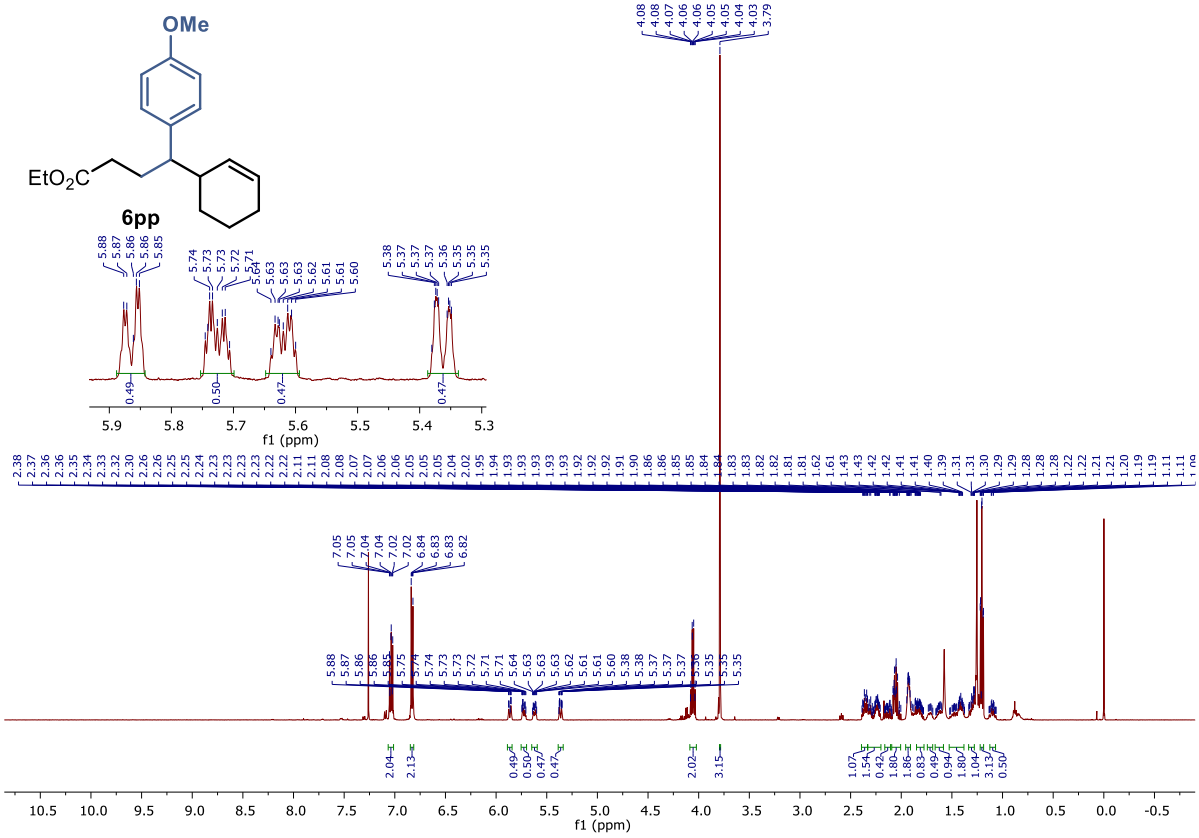
^{1}H NMR (**5**00 MHz, $CDCl_3$) of **6oo**



^{13}C NMR (126 MHz, $CDCl_3$) of **6oo**



^{1}H NMR (500 MHz, $CDCl_3$) of **6pp**



^{13}C NMR (126 MHz, $CDCl_3$) of **6pp**