Supplementary Information

Hydride-Free Reduction of Propargyl Electrophiles: A Nickel-Catalyzed Photoredox Strategy for Allene Synthesis.

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1. General remarks

Methods: All reactions were performed under an inert atmosphere of argon. Reaction glassware was oven-dried prior to use. ^{1}H, and ^{13}C spectra were recorded on Bruker Avance 300 or 400 spectrometers at 298 K. Chemical shifts (δ) are expressed in parts per million. ^{1}H and $^{19}F\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$ (δ_H with reference to the solvent resonance at 7.26 ppm). NMR yields were determined by adding fluorobenzene (^{19}F NMR) as an internal standard to the crude reaction mixtures and by integration of crude NMR spectra. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. GC-MS analyses were performed using Shimadzu GC-2010 Gas Chromatograph coupled to a GCMS-QP2010S mass spectrometer using helium as the carrier gas at a flow rate of 1.19 mL/min and an initial oven temperature of 70 °C. The column used was a Zebron 5ms (30 m length, 0.25 mm diameter and 0.25 μm thickness). The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 70 °C, temperature was increased with a 9 °C/min ramp after 70 °C hold for 1 min to a final temperature of 240 °C, then hold at 240 °C for 8 min (split mode of injection, total run time of 27.89 min). Enantiomeric ratios (e.r.) were obtained by high performance liquid chromatography (HPLC) on a Shimadzu system with a chiral stationary phase (Lux-cell-1 or Lux-cell-2) and *n*-heptane/*i*PrOH as mobile phase (flow rate: 1 $mL.min^{-1}$). Flash chromatographies were performed using normal phase 40–63 μm silica gel columns. TLC analyses were carried out on pre-coated TLC-sheets ALUGRAM Xtra SIL G/UV_{254}. The plates were visualized using a 254 nm ultraviolet lamp.

2. Reagents, catalysts, and starting materials.

Reagents:

Commercially available chemicals, including nickel salts and ligands, were purchased and used without additional purification. Anhydrous solvents (on molecular sieves except for acetone) were purchased at the highest grade and used as received unless noted otherwise.

Photocatalysts:

$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ [S1] and 4-CzIPN [S2] were prepared according to reported procedures.

9,10-Diphenylanthracene (DPA, **3a**) has been purchased from TCI and used as received.

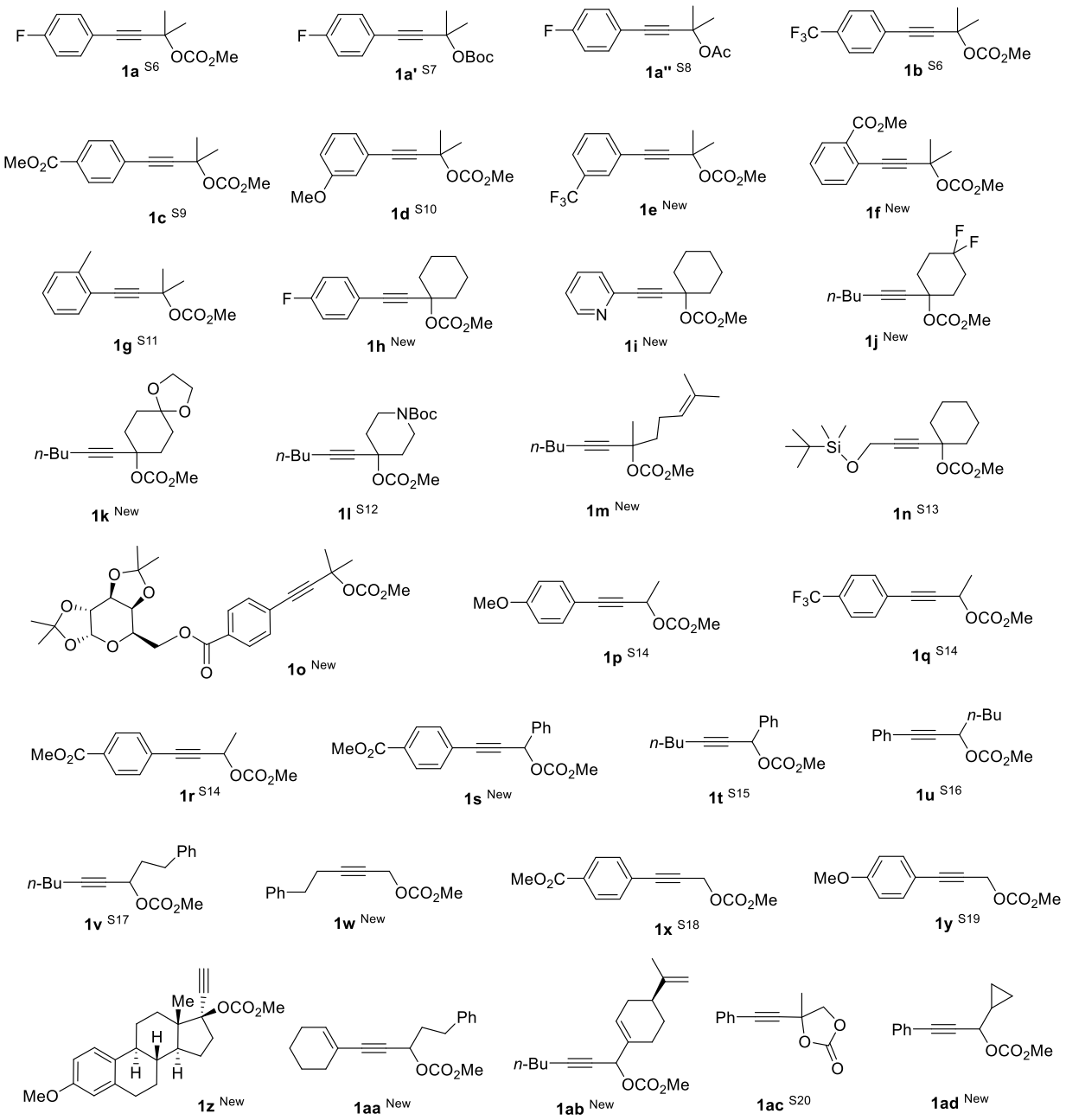
Other functionalized DPA derivatives (**3b-d**) were prepared by (modified) literature protocols: [S3,S4]

9-(4-Methoxyphenyl)-10-phenylanthracene (DPA-OMe, **3b**): In a 8 mL Biotage microwave vial were successively added 9-bromo-10-phenylanthracene (333.2 mg, 1 mmol, 1 equiv), 4-(methoxy)-phenylboronic acid (227.9 mg, 1.5 mmol, 1.5 equiv), $PdCl_2$(dppf) (14.6 mg, 0.02 mmol, 0.02 equiv), and potassium carbonate (415 mg, 3 mmol, 3 equiv). Deionized water (1 mL) and dioxane (3 mL) were then added, and the vial was flushed with argon and capped. The reaction mixture was heated via microwave irradiation on a Biotage system at 120 °C for 8 h, after which time control TLC analysis showed full consumption of the bromide. The reaction mixture was diluted with ethyl acetate (20 mL), washed with water (30 mL), and dried over $MgSO_4$. Purification by flash chromatography (appropriate mixture of petroleum ether and ethyl acetate as eluent) provided DPA-OMe as a yellow solid (272.7 mg, 76%). The analytical data were consistent with the literature. [S3]

9-(4-Methoxycarbonylphenyl)-10-phenylanthracene (DPA-CO_2Me, **3c**): In a 8 mL Biotage microwave vial were successively added 9-bromo-10-phenylanthracene (333.2 mg 1 mmol, 1 equiv), 4-(methoxycarbonyl)-phenylboronic acid (270 mg, 1.5 mmol, 1.5 equiv), $PdCl_2$(dppf) (14.6 mg, 0.02 mmol, 0.02 equiv), and potassium carbonate (415 mg, 3 mmol, 3 equiv). Deionized water (1 mL) and dioxane (3 mL) were then added, and the vial was flushed with argon and capped. The reaction mixture was heated via microwave irradiation on a Biotage system at 120 °C for 20 minutes, after which time control TLC analysis showed full consumption of the bromide. The reaction mixture was diluted with ethyl acetate (20 mL), washed with water (30 mL), and dried over $MgSO_4$. Purification by flash chromatography (appropriate mixture of petroleum ether and ethyl acetate as eluent) provided DPA-CO_2Me as a yellow solid (373 mg, 96%). The analytical data were consistent with the literature. [S4]

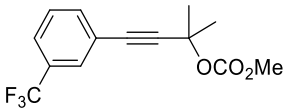
Propargyl electrophiles: Propargyl electrophiles used in this study **(**Table S1) were prepared using literature methods. [S5- S20]

Table S1. Propargyl electrophiles used in Table 2



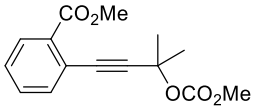
Preparation of unpublished propargyl carbonates: [S5]

Preparation of propargyl carbonates **1e** and **1f**



Methyl (2-methyl-4-(3-(trifluoromethyl)phenyl)but-3-yn-2-yl) carbonate (1e):

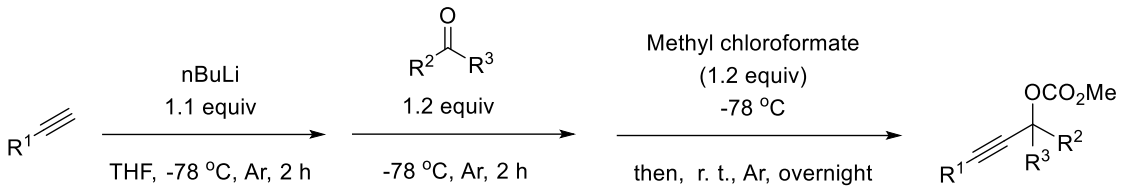
To a cooled (-78 °C) solution of the propargyl alcohol precursor, 2-methyl-4-(3-(trifluoromethyl)phenyl)but-3-yn-2-ol [S21] (1.0 g, 4.4 mmol, 1.0 equiv), in dry THF (15 mL) was added *n*-BuLi (1.94 mL, 4.84 mmol, 1.1 equiv, 2.5 M in hexane) dropwise under argon, and the resulting solution was stirred for 2 h while maintaining the cooling. Then, methyl chloroformate (0.41 mL, 5.28 mmol, 1.2 equiv) was added, and the reaction mixture was allowed to warm to room temperature, and stirred overnight. The reaction medium was then quenched with an aqueous NH_4Cl solution, extracted with ethyl acetate (10 mL × 4), washed with brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude residue was purified by flash chromatography on silica gel (20:1 of petroleum ether/ethyl acetate as eluent) to give 1.2 g (95% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.76 – 7.69 (m, 1H), 7.65 – 7.54 (m, 2H), 7.48 – 7.40 (m, 1H), 3.81 (s, 3H), 1.82 (s, 6H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -63.0. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.49, 134.9 (q, *J* = 1.5 Hz), 130.9 (q, *J* = 32.3 Hz), 128.71, 128.6 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 270.8 Hz), 123.3, 91.0, 82.9, 74.3, 54.3, 28.7. **GC-MS** = 286 *m/z*.



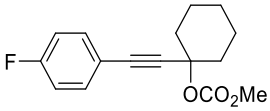
Methyl 2-(3-((methoxycarbonyl)oxy)-3-methylbut-1-yn-1-yl)benzoate (1f):

To a cooled (-78 °C) solution of the propargyl alcohol precursor, methyl 2-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate [S22] (1.0 g, 4.6 mmol, 1.0 equiv), in dry THF (15 mL) was added LDA (2.53 mL, 5.06 mmol, 1.1 equiv, 2 M in THF/heptane/ethyl benzene) dropwise under argon, and the resulting solution was stirred for 2 h while maintaining the cooling. Then, methyl chloroformate (0.43 mL, 5.52 mmol, 1.2 equiv) was added, and the reaction mixture was allowed to warm to room temperature, and stirred overnight. The reaction medium was then quenched with an aqueous NH_4Cl solution, extracted with ethyl acetate (4 x 10 mL), washed with brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude residue was purified by flash chromatography on silica gel (50:1 of petroleum ether/ethyl acetate as eluent) to give 0.5 g (40% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.95 – 7.89 (m, 1H), 7.57 – 7.52 (m, 1H), 7.45 (td, *J* = 6.0, 1.5 Hz, 1H), 7.36 (td, *J* = 9.0, 1.5 Hz, 1H), 3.92 (s, 3H), 3.78 (s, 3H), 1.82 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.6, 153.4, 134.1, 132.1, 131.5, 130.3, 128.1, 122.6, 94.1, 83.2, 74.7, 54.2, 52.0, 28.7. **GC-MS** = 276 *m/z*.

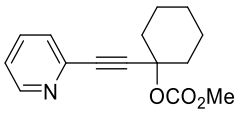
Preparation of propargyl carbonates **1h**, **1i**, **1j**, **1k**, and **1m** according to the following reaction sequence:



General conditions: To a cooled (-78 °C) solution of the selected alkyne (1.0 equiv) in dry THF (0.3 M) was added *n*-BuLi (1.1 equiv, 2.5 M in hexane) dropwise under argon, and the resulting solution was stirred for 2 h while maintaining the cooling. Then, the selected ketone (1.2 equiv) was added, and the resulting solution was stirred for an additional 2 h at -78 °C. Then, methyl chloroformate (1.2 equiv) was added; the reaction mixture was warmed to room temperature and stirred overnight, after which time it was quenched with an aqueous NH_4Cl solution, extracted with ethyl acetate (10 mL × 4), washed with brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by flash chromatography on silica gel (appropriate mixture of petroleum ether and ethyl acetate as eluent) to afford the corresponding propargyl carbonate.

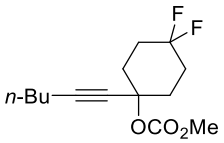


1-((4-Fluorophenyl)ethynyl)cyclohexyl methyl carbonate (1h): Obtained according to general conditions (6 mmol scale). The crude product was purified by flash chromatography (30:1 of petroleum ether/ethyl acetate as eluent) to give 1.0 g (60% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 – 7.39 (m, 2H), 7.04 – 6.94 (m, 2H), 3.77 (s, 3H), 2.32 – 2.18 (m, 2H), 2.01 – 1.87 (m, 2H), 1.77 – 1.51 (m, 5H), 1.42 – 1.27 (m, 1H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -110.8. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.6 (d, *J* = 250.5 Hz), 153.33, 133.8 (d, *J* = 8.1 Hz), 118.6 (d, *J* = 4.0 Hz), 115.4 (d, *J* = 22.2 Hz), 88.1, 85.6, 78.1, 54.3, 37.0, 25.0, 22.8. **GC-MS** = 276 *m/z*.

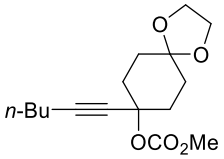


Methyl (1-(pyridin-2-ylethynyl)cyclohexyl) carbonate (1i): Obtained according to general conditions (10 mmol scale). The crude product was purified by flash chromatography (1:1 of petroleum ether/ethyl acetate as eluent) to give 780.9 mg (30% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.58 (ddd, *J* = 2.7, 1.8, 0.9 Hz, 1H), 7.63 (td, *J* = 7.8, 1.8 Hz, 1H), 7.46 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.22 (ddd, *J* = 6.0, 4.8, 1.2 Hz, 1H), 3.78 (s, 3H), 2.34 – 2.24 (m, 2H), 2.03 – 1.92 (m,

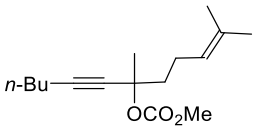
2H), 1.75 – 1.66 (m, 4H), 1.62 – 1.49 (m, 1H), 1.45 – 1.32 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.3, 149.9, 142.9, 136.0, 127.5, 123.0, 88.4, 85.9, 54.3, 36.8, 25.0, 22.6. **GC-MS** = 259 *m/z*.



4,4-Difluoro-1-(hex-1-yn-1-yl)cyclohexyl methyl carbonate (1j): Obtained according to general conditions (6 mmol scale). The crude product was purified by flash chromatography (30:1 of petroleum ether/ethyl acetate as eluent) to give 1.12 g (68% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 3.77 (s, 3H), 2.28 – 2.18 (m, 6H), 2.11 – 1.96 (m, 4H), 1.56 – 1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -98.3 (d, $J_{F\text{-}F}$ = 253.8 Hz, 1F), -99.3 (d, $J_{F\text{-}F}$ = 253.8 Hz, 1F). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.3, 122.1 (t, *J* = 240 Hz), 88.2, 75.5, 54.4, 33.5 (t, *J* = 4.5 Hz), 30.5, 30.3 (t, *J* = 22.5 Hz), 21.9, 21.9, 18.4, 13.5. **GC-MS** = 274 *m/z*.

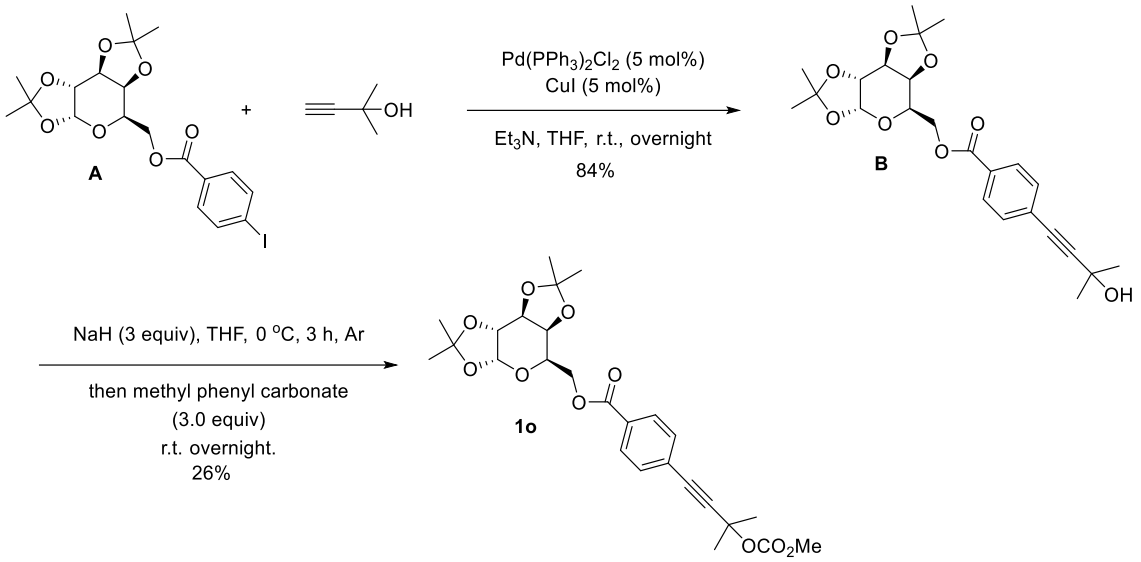


8-(Hex-1-yn-1-yl)-1,4-dioxaspiro[4.5]decan-8-yl methyl carbonate (1k): Obtained according to general conditions (6 mmol scale). The crude product was purified by flash chromatography (20:1 of petroleum ether/ethyl acetate as eluent) to give 1.54 g (86% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 3.93 (s, 4H), 3.75 (s, 3H), 2.26 – 2.13 (m, 6H), 1.86 – 1.68 (m, 4H), 1.55 – 1.32 (m, 4H), 0.89 (t, *J* = 6.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.4, 107.5, 87.3, 78.5, 64.3, 64.2, 54.2, 34.5, 31.1, 30.5, 21.8, 18.3, 13.5. **GC-MS** = 296 *m/z*.



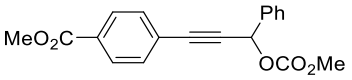
2,6-Dimethyldodec-2-en-7-yn-6-yl methyl carbonate (1m): Obtained according to general conditions (7.2 mmol scale). The crude product was purified by flash chromatography (30:1 of petroleum ether/ethyl acetate as eluent) to give 0.96 g (60% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.16 – 5.06 (m, 1H), 3.74 (s, 3H), 2.26 – 2.12 (m, 4H), 2.03 – 1.90 (m, 1H), 1.84 – 1.74 (m, 1H), 1.68 (s, 6H), 1.62 (s, 3H), 1.53 – 1.35 (m, 4H), 0.90 (t, *J* = 6.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.5, 132.1, 123.3, 86.4, 79.6, 77.9, 54.1, 41.6, 30.6, 26.6, 25.6, 23.1, 21.8, 18.3, 17.5, 13.5. **GC-MS** = 266 *m/z*.

Preparation of propargyl carbonate **1o** according to the following reaction sequence:



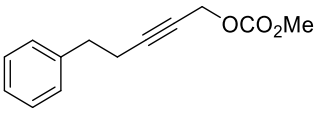
((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(3-((methoxycarbonyl)oxy)-3-methylbut-1-yn-1-yl)-benzoate (1o). Iodoaryl compound **A** [S23] (2.37g, 4.8 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (168.5 mg, 0.24 mmol, 0.05 equiv), CuI (45.7 mg, 0.24 mmol, 0.05 equiv), THF (10 mL), triethylamine (15 mL), and 2-methyl-3-butyn-2-ol (0.51 mL, 5.28 mmol, 1.1 equiv) were added to a 50 mL Schlenk flask with a stir bar under an atmosphere of argon. The reaction mixture was stirred at room temperature overnight, then filtered through celite® and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (5:1 of petroleum ether and ethyl acetate as eluent) to afford 1.88 g (84% yield) of pure propargyl alcohol (**B**) as a solid [^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.49 – 7.43 (m, 2H), 5.57 (d, *J* = 3.0 Hz, 1H), 4.66 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.53 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.42 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.37 – 4.29 (m, 2H), 4.21 – 4.14 (m, 1H), 1.63 (s, 6H), 1.51 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H)]. To a cooled (0 °C) suspension of NaH (64 mg of sodium hydride dry 90%, 2.67 mmol, 3.0 equiv) in dry THF (5 mL) was added a solution of propargyl alcohol **B** (397.4 mg, 0.89 mmol) in dry THF (10 mL) dropwise under argon. The reaction mixture was then stirred for 3 h at room temperature. Then, the reaction medium was cooled again to 0 °C, and methyl phenyl carbonate (0.27 mL, 2.67 mmol, 3.0 equiv) was added. The resulting reaction mixture was stirred overnight at room temperature. The reaction medium was quenched with an aqueous NH_4Cl solution, extracted with ethyl acetate (10 mL × 4), washed with brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by flash chromatography on silica gel (10:1 of petroleum ether/ethyl acetate as eluent) to give 117 mg (26% yield) of pure carbonate **1o** as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01 – 7.94 (m, 2H), 7.52 – 7.44 (m, 2H), 5.56 (d, *J* = 6.0 Hz, 1H), 4.65 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.52 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.42 (dd, *J* = 12.0, 9.0 Hz, 1H), 4.36 – 4.29 (m, 2H), 4.20 – 4.13 (m, 1H), 3.78 (s, 3H), 1.79 (s, 6H), 1.50 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.9, 153.5, 131.7, 129.7, 129.5, 127.2, 109.7, 108.8, 96.0, 92.3, 83.8, 74.5, 71.1, 70.7, 70.5, 66.1, 64.1, 54.4, 28.8, 25.99, 25.95, 25.0, 24.5, 23.8. **HRMS** (ESI) calcd for $C_{26}H_{32}NaO_{10}$ *m/z* : 527.1888 [M+Na], Found: 527.1883.

Preparation of propargyl carbonate **1s:**



Methyl 4-(3-((methoxycarbonyl)oxy)-3-phenylprop-1-yn-1-yl)benzoate (1s). *Preparation of the propargyl alcohol precursor:* Methyl 4-iodobenzoate (3.42 g, 13.0 mmol, 11.15 equiv), $Pd(PPh_3)_2Cl_2$ (220 mg, 0.3 mmol, 0.03 equiv), CuI (60 mg, 0.3 mmol, 0.03 equiv), diisopropylamine (50 mL), and 1-phenyl-2-propyn-1-ol (1.4 mL, 11.35 mmol, 1.0 equiv) were added to a 100 mL Schlenk flask with a stir bar under an atmosphere of argon. The reaction mixture was stirred at room temperature overnight, then filtered through celite® and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (5:1 of petroleum ether and ethyl acetate as eluent) to afford 3.0 g (99% yield) of pure methyl 4-(3-hydroxy-3-phenylprop-1-yn-1-yl)benzoate as a solid. The analytical data were consistent with the literature.[S24] *Propargyl carbonate*: To a solution of the propargyl alcohol precursor (1.1 g, 4.13 mmol, 1 equiv) in dichloromethane (20 mL) were successively added DMAP (50.5 mg, 0.13 mmol, 0.1 equiv), pyridine (1.67 mL, 20.6 mmol, 5.0 equiv), and methyl chloroformate (1.0 mL, 12.9 mmol, 3.0 equiv) under an atmosphere of argon. The reaction mixture was stirred at room temperature overnight, then concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (20:1 of petroleum ether/ethyl acetate as eluent) to give 1.2 g (90% yield) of pure carbonate as a solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.02 – 7.96 (m, 2H), 7.64 – 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.47 – 7.3 (m, 3H), 6.53 (s, 1H), 3.92 (s, 3H), 3.83 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.3, 154.8, 136.1, 131.8, 130.1, 129.4, 129.3, 128.8, 127.7, 126.5, 87.6, 87.0, 70.0, 55.1, 52.2. **GC-MS** = 324 *m/z*.

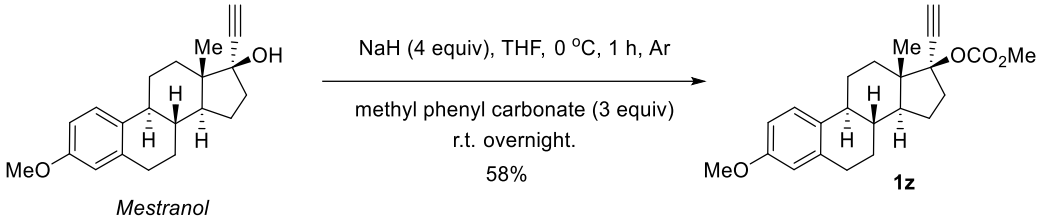
Preparation of propargyl carbonate **1w:**



Methyl (5-phenylpent-2-yn-1-yl) carbonate (1w): To a solution of the propargyl alcohol precursor, 5-phenylpent-2-yn-1-ol [S25] (1.15 g, 7.16 mmol, 1 equiv), in dichloromethane (20 mL) were successively added DMAP (52.2 mg, 0.43 mmol, 0.06 equiv), pyridine (5.8 mL, 71.6 mmol, 10.0 equiv), and methyl chloroformate (1.22 mL, 15.8 mmol, 2.2 equiv) under an atmosphere of argon. The reaction mixture was then stirred at room temperature overnight, then concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (30:1 of petroleum ether/ethyl acetate as eluent) to give 1.41 g (90% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.33 –

7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 4.71 (t, *J* = 2.1 Hz, 2H), 3.81 (s, 3H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.57 – 2.47 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.3, 140.4, 128.4, 126.3, 87.6, 74.1, 56.1, 55.0, 34.7, 20.9. **GC-MS** = 218 *m/z*.

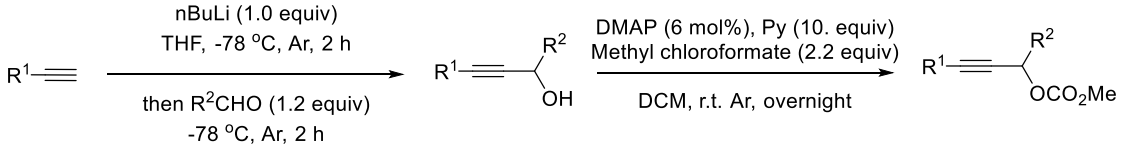
Preparation of propargyl carbonate **1z**:



Mestranol

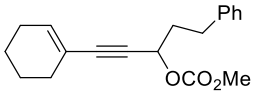
(8R,9S,13S,14S,17R)-17-Ethynyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl-methyl carbonate (1z). (*N.B.: Methyl phenyl carbonate proved more effective than methyl chloroformate in the conversion of Mestranol to carbonate* ***1z****. Procedure adapted from the literature* [S26]): To a cooled (0 °C) suspension of NaH (76.8 mg of sodium hydride dry 90%, 3.2 mmol, 4.0 equiv) in dry THF (5 mL) was added a solution of commercially available mestranol (248.4 mg, 0.8 mmol) in dry THF (10 mL) dropwise under argon, and the mixture was stirred for 1 h at room temperature. Then, methyl phenyl carbonate (0.24 mL, 2.4 mmol, 3.0 equiv) was added at 0 °C. The resulting mixture was stirred overnight at room temperature. The reaction medium was then quenched with an aqueous NH_4Cl solution, extracted with ethyl acetate (10 mL × 4), washed with NaOH (1 M) and brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by flash chromatography on silica gel (100:1 of petroleum ether/ethyl acetate as eluent) to give 170.3 mg (58% yield) of pure carbonate **1z** as a solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.21 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.63 (d, *J* = 2.7 Hz, 1H), 3.78 (d, *J* = 3.3 Hz, 6H), 2.90 – 2.71 (m, 3H), 2.68 (s, 1H), 2.42 – 1.97 (m, 4H), 1.93 – 1.70 (m, 4H), 1.53 – 1.33 (m, 4H), 0.94 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 157.5, 154.4, 137.8, 132.3, 126.4, 113.8, 111.5, 86.7, 83.0, 75.6, 55.2, 54.5, 48.1 (d, *J* = 6.8 Hz), 43.4, 39.1, 37.4, 33.1, 29.8, 27.3, 26.3, 23.1, 13.3. **HRMS** (ESI) calcd for $C_{23}H_{28}NaO_4$ *m/z* : 391.1880 [M+Na], Found 391.1882.

Preparation of propargyl carbonates **1aa, 1ab,** and **1ad** according to the following reaction sequence:

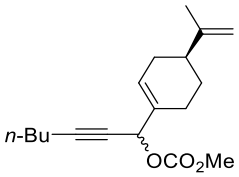


Preparation of propargyl alcohols: To a cooled (-78 °C) solution of the selected alkyne (1.0 equiv) in dry THF (0.3 M) was added *n*-BuLi (1.0 equiv, 2.5 M in hexane) dropwise under argon. The solution was then stirred for 2 h while maintaining the cooling, after which time the selected aldehyde (1.2 equiv) was added, and the mixture was stirred for an additional 2 h at -78 °C. The reaction medium was then quenched with an aqueous NH_4Cl solution, extracted with ethyl acetate (10 mL × 4), washed with brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by flash chromatography on silica gel (appropriate mixture of petroleum ether and ethyl acetate as eluent) to afford the corresponding propargyl alcohol.

Preparation of propargyl carbonates: To a solution of the propargyl alcohol (1 equiv) in dichloromethane (0.3 M) were added DMAP (0.06 equiv), pyridine (10.0 equiv), and methyl chloroformate (2.2 equiv) under an atmosphere of argon. The reaction mixture was then stirred at room temperature overnight. The solvent was removed under vacuum, and the crude product was purified by flash chromatography on silica gel (appropriate mixture of petroleum ether and ethyl acetate as eluent) to afford the propargyl carbonates.

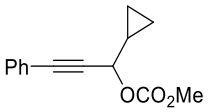


1-(Cyclohex-1-en-1-yl)-5-phenylpent-1-yn-3-yl methyl carbonate (1aa):
The propargyl alcohol precursor was prepared on 6 mmol scale from 1-ethynylcyclohexene and 3-phenyl propyl aldehyde. The crude product was purified by flash chromatography (10:1 of petroleum ether/ethyl acetate as eluent) to give 1.33 g (92% yield) of pure propargyl alcohol as an oil. Spectral data are in accordance with the literature.[S27] The propargyl carbonate was prepared on 5.53 mmol scale. The crude product was purified by flash chromatography (50:1 of petroleum ether/ethyl acetate as eluent) to give 1.32 g (80% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.33 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 6.19 – 6.11 (m, 1H), 5.35 (t, *J* = 6.3 Hz, 1H), 3.80 (s, 3H), 2.84 – 2.76 (m, 2H), 2.20 – 2.06 (m, 6H), 1.67 – 1.54 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.0, 140.7, 136.2, 128.5, 128.4, 126.1, 119.8, 88.5, 82.7, 68.3, 54.8, 36.6, 31.2, 29.0, 25.6, 22.2, 21.4. **GC-MS** = 298 *m/z.*



Methyl (1-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hept-2-yn-1-yl) carbonate (1ab): The propargyl alcohol precursor was prepared on 15 mmol scale from 1-hexyne and (S)-perillaldehyde. The crude product was purified by flash chromatography (10:1 of petroleum ether/ethyl acetate as eluent) to give 2.86 g (82% yield) of pure propargylic alcohol as an oil [^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 – 5.84 (m, 1H), 4.78 – 4.68 (m, 3H), 2.38 – 2.11 (m, 6H), 2.06 – 1.84 (m, 2H), 1.74 (t, *J* =

1.2 Hz, 3H), 1.55 – 1.36 (m, 5H), 0.91 (t, *J* = 7.2 Hz, 3H)]. The propargyl carbonate was prepared on 11.96 mmol scale. The crude product was purified by flash chromatography (50:1 of petroleum ether/ethyl acetate as eluent) to give 725.3 mg (42% yield, d.r. = 2:1) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.58 (br. s, 0.66H, CH $_{\text{major isomer}}$), 5.45 (br. s, 0.33H, CH $_{\text{minor isomer}}$), 5.22 – 5.09 (m, 1H), 4.74 – 4.67 (m, 2H), 3.79 (s, 1H, $CH_{3\ \text{minor isomer}}$), 3.76 (s, 2H, $CH_{3\ \text{major isomer}}$), 3.19 – 3.08 (m, 0.33H, CH $_{\text{minor isomer}}$), 2.94 – 2.83 (m, 0.66H, CH $_{\text{major isomer}}$), 2.57 – 1.81 (m, 5H), 2.15 (s, 3H, CH_3), 1.70 (t, *J* = 0.9 Hz, 3H, CH_3), 1.62 – 1.20 (m, 7H), 0.91 (t, *J* = 7.2 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 154.9, 148.6, 148.2, 147.8, 146.8, 109.6, 109.3, 108.7, 100.6, 95.8, 94.4, 78.6, 54.8, 54.6, 43.6, 38.9, 38.5, 37.0, 31.6, 31.5, 31.0, 30.9, 30.8, 29.7, 26.9, 22.0, 20.8, 20.6, 19.2, 13.6. **GC-MS** = 290 *m/z*.



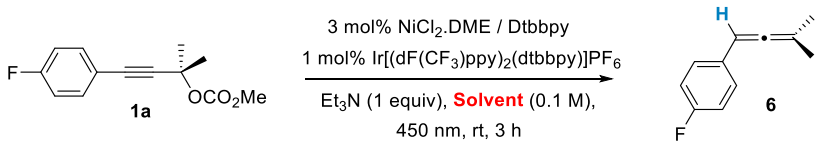
1-Cyclopropyl-3-phenylprop-2-yn-1-yl methyl carbonate (1ad): The propargyl alcohol precursor was prepared on 6 mmol scale from phenylacetylene and cyclopropanecarbaldehyde. The crude product was purified by flash chromatography (10:1 of petroleum ether/ethyl acetate as eluent) to give 1.01 g (98% yield) of pure propargyl alcohol as an oil. Spectral data are in accordance with the literature.[S28] The propargyl carbonate was prepared on 5.85 mmol scale. The crude product was purified by flash chromatography (100:1 of petroleum ether/ethyl acetate as eluent) to give 1.24 g (98% yield) of pure carbonate as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.47 – 7.40 (m, 2H), 7.34 – 7.27 (m, 3H), 5.34 (d, *J* = 9.0 Hz, 1H), 3.83 (s, 3H), 1.48 – 1.35 (m, 1H), 0.70 – 0.56 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.1, 131.9, 128.7, 128.2, 122.0, 86.3, 83.7, 72.3, 54.9, 14.5, 3.7, 2.3. **GC-MS** = 230 *m/z*.

3. Selected optimization experiments.

Lighting set-up: The reactions were run using the EvoluChem™ photobox device (on a stirrer plate), under the irradiation of a 405 nm purple LED lamp (18 W, Hepatochem HCK1012-01-010) or a 450 nm blue LED lamp (30 W, Hepatochem HCK1012-01-008) with the built-in fan switched ON.

General screening (benchtop) procedure: A 8 mL vial equipped with a magnetic stir bar was charged with the selected nickel catalyst, ligand and photocatalyst, the vial was flushed under argon for 1 min. Then solvent (2.5 mL), Et_3N (34.8 µl, 0.25 mmol, 1.0 equiv), and 4-(4-fluorophenyl)-2-methylbut-3-yn-2-yl methyl carbonate (**1a**) (59.1 mg, 0.25 mmol, 1.0 equiv) were added under argon. The vial was then capped, and the reaction mixture was stirred at room temperature under purple or blue light irradiation. The crude mixture was analyzed by ^{19}F NMR (internal standard: fluorobenzene, 23.5 µl, 0.25 mmol) to determine the crude yield.

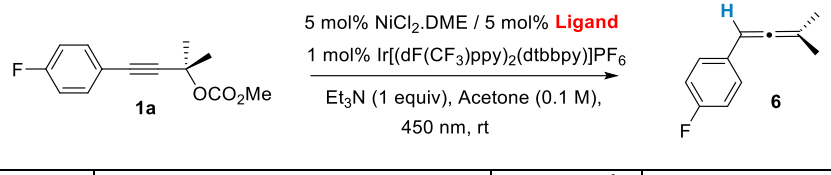
Table S2. Screening of solvents [a]



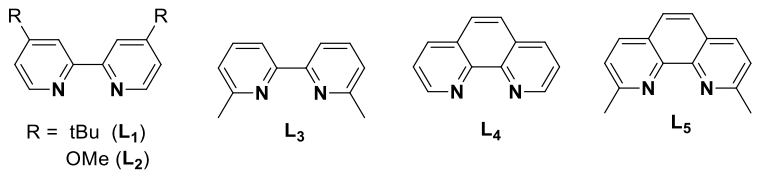
Entry	Solvent	Yield (%)
1	MeCN	75
2	Acetone	73
3	AcOEt	43
4	1,4-Dioxane	37
5	MeOH	41

[a] Reactions were performed on a 0.25 mmol scale. Yields were determined by ^{19}F NMR using fluorobenzene as internal standard.

Table S3. Screening of nickel ligands [a]

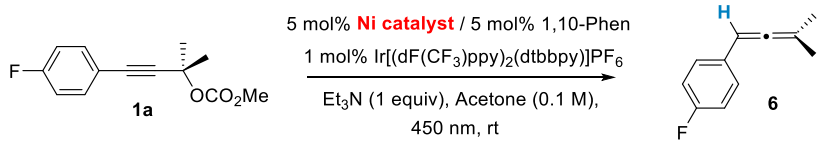


Entry	Ligand	Time (h) [b]	Yield (%)
1	**L_1**	3	90
2	**L_2**	3	56
3	**L_3**	3	82
4	**L_4**	4	99
5	**L_5**	6	72



[a] Reactions were performed on a 0.25 mmol scale. Yields were determined by ^{19}F NMR using fluorobenzene as internal standard. [b] Time refers to completed conversion of starting material.

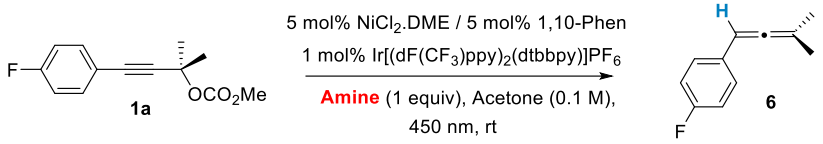
Table S4. Screening of nickel sources [a]



Entry	Ni Catalyst	Time (h) [b]	Yield (%)
1	$NiCl_2$.DME	4	99
2	$Ni(OAc)_2.4H_2O$	5	95
3	$Ni(NO_3)_2.6H_2O$	3	90
4	$Ni(acac)_2$	24	68

[a] Reactions were performed on a 0.25 mmol scale. Yields were determined by ^{19}F NMR using fluorobenzene as internal standard. [b] Time refers to completed conversion of starting material.

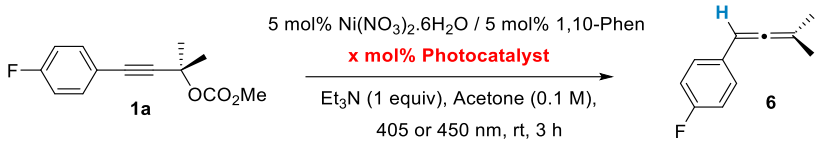
Table S5. Screening of amines [a]



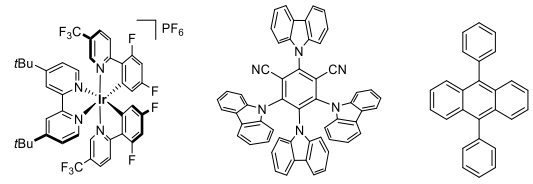
Entry	Amine	Time (h)	Yield (%)
1	Et_3N	3	99
2	*N*-Ethylpiperidine	3	37
3	Et_2NH	24	82
4	Quinuclidine	24	0

[a] Reactions were performed on a 0.25 mmol scale. Yields were determined by ^{19}F NMR using fluorobenzene as internal standard.

Table S6. Screening of photocatalysts [a]



Entry	Photocatalyst	Mol%	Yield (%)
1	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ at 405 nm	1	66
2	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ at 450 nm	1	90
3	4-CzIPN at 405 nm	2	53
4	4-CzIPN at 450 nm	2	68
5	DPA at 405 nm	5	99
6	DPA at 450 nm	5	0



$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ 4-CzIPN DPA

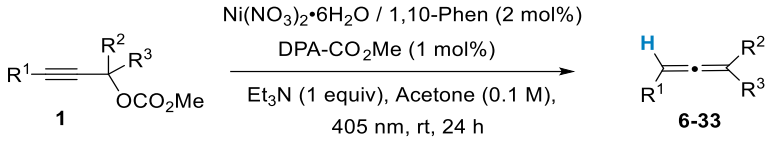
[a] Reactions were performed on a 0.25 mmol scale. Yields were determined by ^{19}F NMR using fluorobenzene as internal standard.

Note: *4-CzIPN and $Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ showed remarkable photocatalytic activity in this reaction, especially when irradiated at 450 nm. However, their observed propensity to photo-degrade the allenyl compound, possibly due to their higher triplet energy with respect to DPA, precluded their use when prolonged reaction times proved necessary. For instance, ^{19}F NMR monitoring of the reaction from entry 2 showed a dramatic decrease of the yield overtime, dropping from 90% after 3h to 6% after 24 h. This trend was not observed with DPA, even at a higher loading (5 mol%) of photocatalyst and higher energy (405 nm) wavelenght.*

4. Synthesis and characterization of allenes.

Synthetic procedure:

The reactions were run using the EvoluChem™ photobox device (on a stirrer plate), under the irradiation of a 405 nm purple LED lamp (18 W, Hepatochem HCK1012-01-010) with the built-in fan switched ON.

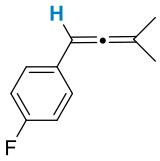


Stock solutions of the nickel catalyst, ligand, and photocatalyst were prepared and kept under argon:

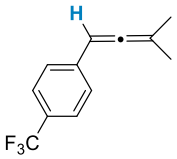
Stock solution A: 10 mL vial charged with $Ni(NO_3)_2•6H_2O$ (100 mg, 0.344 mmol) dissolved in 5 mL of dry acetone under argon (0.0688 M).
Stock solution B: 10 mL vial charged with 1,10-phen (100 mg, 0.55 mmol) dissolved in 5 mL of dry acetone under argon (0.11 M).
Stock solution C: 10 mL vial charged with DPA-CO_2Me (42 mg, 0.11 mmol) dissolved in 8 mL of dry acetone under argon (0.01375 M).

General (benchtop) procedure: A 8 mL vial equipped with a magnetic stir bar was charged with the selected propargyl carbonate **1** (0.4 mmol, 1 equiv) and flushed with argon for 1 min. Then, acetone (2 mL), $Ni(NO_3)_2•6H_2O$ (116 µL of stock solution A, 0.008 mmol, 0.02 equiv), 1,10-phen (73 µL of stock solution B, 0.008 mmol, 0.02 equiv), DPA-CO_2Me (291 µL of stock solution C, 0.004 mmol, 0.01 equiv), and Et_3N (56 µL, 0.4 mmol, 1.0 equiv) were added under argon. Another portion of acetone (2 mL) was finally added, and the vial was capped. The reaction mixture was stirred at room temperature under purple light irradiation for 24 h, after which time it was concentrated under vacuum and the crude product was purified by flash chromatography on silica gel (appropriate mixture of petroleum ether and ethyl acetate as eluent) to afford the corresponding allene.

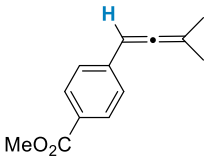
Characterization of pure allenes:



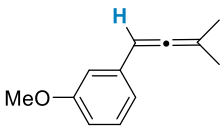
1-Fluoro-4-(3-methylbuta-1,2-dien-1-yl)benzene (6): Obtained according to general conditions. The crude product was purified by flash chromatography (100:0 of petroleum ether/ethyl acetate as eluent) to give 54.5 mg (84% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.25 – 7.18 (m, 2H), 7.03 – 6.92 (m, 2H), 6.00 – 5.92 (m, 1H), 1.83 (d, *J* = 2.7 Hz, 6H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -116.4. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 202.9 (d, *J* = 2.3 Hz), 161.6 (d, *J* = 243.5 Hz), 131.9 (d, *J* = 3.8 Hz), 127.9 (d, *J* = 7.5 Hz), 115.3 (d, *J* = 21.8 Hz), 99.4, 91.6, 20.2. **GC-MS** = 162 *m/z*. Spectral data are in accordance with the literature. [S29]



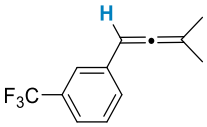
1-(3-Methylbuta-1,2-dien-1-yl)-4-(trifluoromethyl)benzene (7): Obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 64.2 mg (78% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 6.11-5.98 (m, 1H), 1.87 (d, *J* = 3.0 Hz, 6H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -62.32. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.2, 140.0, 128.2 (q, *J* = 32.3 Hz), 126.7, 125.4 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270 Hz), 99.9, 91.8, 20.0. **GC-MS** = 212 *m/z*. Spectral data are in accordance with the literature. [S30]



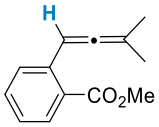
Methyl 4-(3-methylbuta-1,2-dien-1-yl)benzoate (8): Obtained according to general conditions. The crude product was purified by flash chromatography (50:1 of petroleum ether/ethyl acetate as eluent) to give 70.6 mg (87% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.99 – 7.91 (m, 2H), 7.33 – 7.28 (m, 2H), 6.06 – 5.97 (m, 1H), 3.90 (s, 3H), 1.84 (d, *J* = 3.0 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.5, 167.1, 141.2, 129.9, 127.9, 126.4, 99.7, 92.2, 52.0, 20.1. **GC-MS** = 202 *m/z*. Spectral data are in accordance with the literature. [S31]



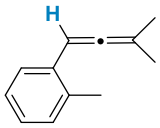
1-Methoxy-3-(3-methylbuta-1,2-dien-1-yl)benzene (9): Obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 40.9 mg (59% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.21 (t, *J* = 7.8 Hz, 1H), 6.93 – 6.79 (m, 2H), 6.78 – 6.69 (m, 1H), 6.02 – 5.91 (m, 1H), 3.81 (s, 3H), 1.83 (d, *J* = 3.0 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 203.2, 159.8, 137.6, 129.4, 119.3, 112.1, 111.9, 99.2, 92.5, 55.2, 20.2. **GC-MS** = 174 *m/z*. Spectral data are in accordance with the literature. [S31]



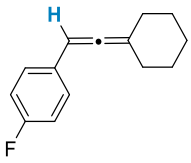
1-(3-Methylbuta-1,2-dien-1-yl)-3-(trifluoromethyl)benzene (10): Unknown compound, obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 50.9 mg (60% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 (s, 1H), 7.46 – 7.34 (m, 3H), 6.06 – 5.97 (m, 1H), 1.85 (d, *J* = 3.0 Hz, 6H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -62.7. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 203.6, 137.1, 130.9 (q, *J* = 32.3 Hz), 129.7 (d, *J* = 0.75 Hz), 128.8, 124.2 (q, *J* = 270.8 Hz), 123.2 (q, *J* = 3.8 Hz), 122.9 (q, *J* = 3.8 Hz), 100.1, 91.8, 20.1. **HRMS** (APCI) calcd for $C_{12}H_{12}F_3$ *m/z* 213.0890 [M+H], Found 213.0886.



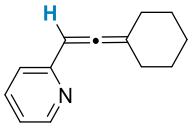
Methyl 2-(3-methylbuta-1,2-dien-1-yl)benzoate (11): Unknown compound, obtained according to general conditions. The crude product was purified by flash chromatography (50:1 of petroleum ether/ethyl acetate as eluent) to give 58.2 mg (72% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.86 – 7.81 (m, 1H), 7.55 – 7.49 (m, 1H), 7.45 – 7.37 (m, 1H), 7.23 – 7.15 (m, 1H), 6.99 – 6.92 (m, 1H), 3.90 (s, 3H), 1.83 (d, *J* = 3.0 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.6, 168.0, 137.1, 131.6, 130.5, 128.4, 127.7, 125.9, 98.6, 90.3, 51.9, 20.0. **HRMS** (ESI) calcd for $C_{13}H_{14}NaO_2$ *m/z* 225.0886 [M+Na], Found 225.0884.



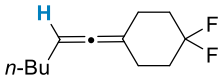
1-Methyl-2-(3-methylbuta-1,2-dien-1-yl)benzene (12): Unknown compound, obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 51.3 mg (81% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.35 – 7.29 (m, 1H), 7.19 – 7.05 (m, 3H), 6.21 – 6.13 (m, 1H), 2.36 (s, 3H), 1.83 (d, *J* = 3.0 Hz, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.0, 134.8, 134.0, 130.4, 127.3, 126.3, 125.9, 97.9, 90.0, 20.4, 19.8. **HRMS** (ESI) calcd for $C_{12}H_{15}$ *m/z* 159.1174 [M+H], Found 159.1168.



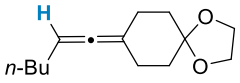
1-(2-Cyclohexylidenevinyl)-4-fluorobenzene (13): Unknown compound, obtained according to general conditions, The crude product was purified by flash chromatography (petroleum ether as eluent) to give 68.8 mg (85% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.19 – 7.11 (m, 2H), 6.95 – 6.85 (m, 2H), 5.92 – 5.84 (m, 1H), 2.25 – 2.05 (m, 4H), 1.70 – 1.48 (m, 6H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -116.5. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 199.4 (d, *J* = 2.3 Hz), 161.4 (d, *J* = 247.5 Hz), 132.1 (d, *J* = 3.8 Hz), 127.8 (d, *J* = 7.5 Hz), 115.3 (d, *J* = 21.8 Hz), 106.7, 91.4, 31.3, 27.7, 26.1. **HRMS** (ESI) calcd for $C_{14}H_{15}F$ *m/z* 202.1152 [M^+], Found 202.1151.



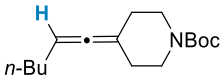
2-(2-Cyclohexylidenevinyl)pyridine (14): Obtained according to general conditions. The crude product was purified by flash chromatography (20:1 of petroleum ether/ethyl acetate as eluent) to give 43.7 mg (59% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.52 – 8.45 (m, 1H), 7.57 (td, *J* = 7.5, 1.8 Hz, 1H), 7.38 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.25 – 6.13 (m, 1H), 2.34 – 2.17 (m, 4H), 1.74 – 1.54 (m, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 201.7, 156.3, 149.3, 136.0, 120.9, 120.8, 106.9, 94.2, 31.0, 27.5, 26.0. **GC-MS** = 185 *m/z.* Spectral data are in accordance with the literature. [S32]



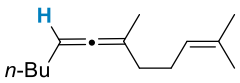
1,1-Difluoro-4-(hex-1-en-1-ylidene)cyclohexane (15): Unknown compound, obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 46.5 mg (58% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.11 – 5.00 (m, 1H), 2.29 (td, *J* = 6.3, 2.4 Hz, 4H), 2.07 – 1.90 (m, 6H), 1.45 – 1.29 (m, 4H), 0.97 – 0.83 (m, 3H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -96.8 (d, $J_{F,F}$ = 236.9 Hz, 1F), -97.6 (d, $J_{F,F}$ = 236.9 Hz, 1F). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 199.0 (t, *J* = 0.8 Hz), 123.1 (t, *J* = 240.0 Hz), 97.7 (t, *J* = 1.5 Hz), 90.0, 34.5 (t, *J* = 23.3 Hz), 31.2, 28.7, 27.6 (t, *J* = 5.3 Hz), 22.0, 13.9. **HRMS** (APCI) calcd for $C_{12}H_{19}F_2$ *m/z* 201.1449 [M+H], Found 201.1449.



8-(Hex-1-en-1-ylidene)-1,4-dioxaspiro[4.5]decane (16): Unknown compound, obtained according to general conditions. The crude product was purified by flash chromatography (50:1 of petroleum ether/ethyl acetate as eluent) to give 66.7 mg (75% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.05 – 4.92 (m, 1H), 3.96 (s, 4H), 2.33 – 2.19 (m, 4H), 2.02 – 1.89 (m, 2H), 1.79 – 1.67 (m, 4H), 1.44 – 1.22 (m, 4H), 0.94 – 0.82 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 198.5, 108.4, 99.7, 89.2, 64.3, 35.4, 31.1, 28.8, 28.7, 22.0, 13.9. **HRMS** (ESI) calcd for $C_{14}H_{23}O_2$ *m/z* 223.1698 [M+H], Found 223.1693.

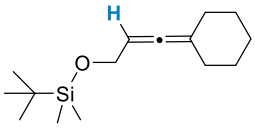


tert-Butyl 4-(hex-1-en-1-ylidene)piperidine-1-carboxylate (17): Obtained according to general conditions. The crude product was purified by flash chromatography (20:1 of petroleum ether/ethyl acetate as eluent) to give 79.6 mg (75% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.09 – 4.98 (m, 1H), 3.54 – 3.34 (m, 4H), 2.20 – 2.07 (m, 4H), 2.01 – 1.91 (m, 2H), 1.46 (s, 9H), 1.40 – 1.29 (m, 4H), 0.93 – 0.84 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 198.9, 154.7, 98.3, 90.1, 79.5, 45.1, 31.1, 31.0, 28.8, 28.4, 22.0, 13.9. **GC-MS** = 265 *m/z.* Spectral data are in accordance with the literature. [S18]

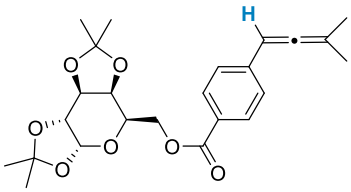


2,6-Dimethyldodeca-2,6,7-triene (18): Unknown compound, obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 56.2 mg (73% yield) of pure allenes as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.18 – 5.09 (m, 1H),

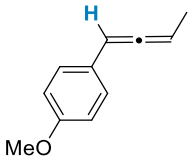
5.06 – 4.95 (m, 1H), 2.16 – 2.04 (m, 2H), 2.03 – 1.87 (m, 4H), 1.73 – 1.65 (m, 6H), 1.61 (d, *J* = 1.5 Hz, 3H), 1.43 – 1.29 (m, 4H), 0.95 – 0.84 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 201.2, 131.4, 124.4, 99.0, 90.4, 34.3, 31.5, 29.1, 26.3, 25.7, 22.2, 19.3, 17.7, 13.9. **HRMS** (APCI) calcd for $C_{14}H_{25}$ *m/z* 193.1949 [M+H], Found 193.1951.



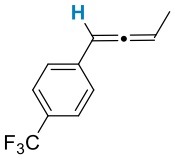
tert-Butyl((3-cyclohexylideneallyl)oxy)dimethylsilane (19): Obtained according to general conditions (0.2 mmol scale, $Ni(NO_3)_2$•$6H_2O$ (0.05 equiv), 1,10-phen (0.05 equiv), DPA-CO_2Me (0.025 equiv)). The crude product was purified by flash chromatography (petroleum ether as eluent) to give 37.0 mg (73% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.16 – 5.01 (m, 1H), 4.14 (d, *J* = 6.0 Hz, 2H), 2.16 – 2.05 (m, 4H), 1.64 – 1.46 (m, 6H), 0.90 (s, 9H), 0.08 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 197.9, 103.6, 89.6, 62.7, 31.3, 27.3, 26.1, 26.0, 18.4, -5.0. **GC-MS** = 252 *m/z*. Spectral data are in accordance with the literature.[S33]



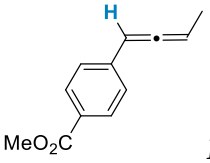
((3aR,5R,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(3-methylbuta-1,2-dien-1-yl)benzoate (20): Unknown compound, obtained according to general conditions (0.1 mmol scale, $Ni(NO_3)_2$•$6H_2O$ (0.05 equiv), 1,10-phen (0.05 equiv), DPA-CO_2Me (0.025 equiv)). The crude product was purified by flash chromatography (30:1 of petroleum ether/ethyl acetate as eluent) to give 17.0 mg (39% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.99 – 7.93 (m, 2H), 7.33 – 7.27 (m, 2H), 6.05 – 5.97 (m, 1H), 5.57 (d, *J* = 3.0 Hz, 1H), 4.65 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.52 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.45 – 4.29 (m, 3H), 4.22 – 4.13 (m, 1H), 1.84 (d, *J* = 3.0 Hz, 6H), 1.51 (s, 3H), 1.48 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.5, 166.3, 141.2, 130.0, 127.8, 126.4, 109.7, 108.8, 99.7, 96.3, 92.3, 71.2, 70.8, 70.6, 66.2, 63.7, 29.7, 26.02, 25.97, 25.0, 24.5, 20.0. **HRMS** (APCI) calcd for $C_{24}H_{31}O_7$ *m/z* 431.2064 [M+H], Found 431.2064.



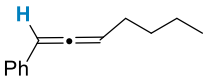
1-(Buta-1,2-dien-1-yl)-4-methoxybenzene (21): Obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 41.0 mg (64% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.24 – 7.18 (m, 2H), 6.88 – 6.81 (m, 2H), 6.10 – 6.01 (m, 1H), 5.57 – 5.44 (m, 1H), 3.80 (s, 3H), 1.78 (dd, *J* = 6.0, 3.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 205.3, 158.5, 127.7, 127.3, 114.0, 93.3, 89.5, 55.3, 14.3. **GC-MS** = 160 *m/z*. Spectral data are in accordance with the literature.[S34]



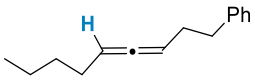
1-(Buta-1,2-dien-1-yl)-4-(trifluoromethyl)benzene (22): Obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 56.4 mg (71% yield) of pure allenes as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 6.0 Hz, 2H), 6.19 – 6.04 (m, 1H), 5.70 – 5.53 (m, 1H), 1.81 (dd, *J* = 6.0, 3.0 Hz, 3H). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -62.4. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 206.9, 139.0, 128.5 (q, *J* = 32.3 Hz), 126.71, 125.4 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270 Hz), 93.2, 90.2, 13.8. **GC-MS** = 198 *m/z.* Spectral data are in accordance with the literature. [S34]



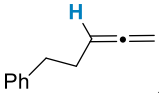
Methyl 4-(buta-1,2-dien-1-yl)benzoate (23): Obtained according to general conditions. The crude product was purified by flash chromatography (50:1 of petroleum ether/ethyl acetate as eluent) to give 45.2 mg (60% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.00 – 7.92 (m, 2H), 7.36 – 7.29 (m, 2H), 6.18 – 6.06 (m, 1H), 5.65 – 5.51 (m, 1H), 3.90 (s, 3H), 1.81 (dd, *J* = 6.0, 3.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 207.1, 166.9, 140.1, 129.8, 128.1, 126.4, 93.6, 90.0, 52.0, 13.8. **GC-MS** = 188 *m/z.* Spectral data are in accordance with the literature. [S34]



Hepta-1,2-dien-1-ylbenzene (25): Obtained according to general conditions from propargyl carbonates **1t** or **1u**. The crude products were purified by flash chromatography (petroleum ether as eluent) to give 23.5 mg (34% yield) or 52.4 mg (76% yield) of the pure allene, respectively, as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.33- 7.28 (m, 4H), 7.23 – 7.15 (m, 1H), 6.16 – 6.10 (m, 1H), 5.58 (q, *J* = 6.0 Hz, 1H), 2.21 – 2.08 (m, 2H), 1.55 – 1.32 (m, 4H), 0.92 (t, *J* = 6.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 205.2, 135.2, 128.5, 126.58, 126.56, 95.1, 94.5, 31.3, 28.4, 22.3, 13.9. **GC-MS** = 172 *m/z.* Spectral data are in accordance with the literature. [S35]

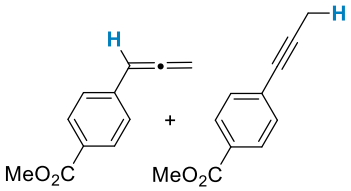


Nona-3,4-dien-1-ylbenzene (26): Obtained according to general conditions. The crude product was purified by flash chromatography (petroleum ether as eluent) to give 58.5 mg (73% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.24 – 7.16 (m, 2H), 7.16 – 7.05 (m, 3H), 5.12 – 4.94 (m, 2H), 2.64 (t, *J* = 9.0, 2H), 2.29 – 2.17 (m, 2H), 1.94 – 1.80 (m, 2H), 1.32 – 1.19 (m, 4H), 0.87 – 0.75 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.0, 141.9, 128.5, 128.2, 125.8, 91.5, 90.2, 35.5, 31.3, 30.7, 28.6, 22.1, 13.9. **GC-MS** = 200 *m/z.* Spectral data are in accordance with the literature. [S18]

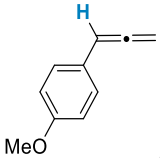


Penta-3,4-dien-1-ylbenzene (27): Obtained according to general conditions ($Ni(NO_3)_2$•$6H_2O$ (0.03 equiv), 1,10-phen (0.03 equiv), DPA-CO_2Me (0.015 equiv)). The crude product was purified by flash chromatography (100:0 of petroleum ether/ethyl acetate as eluent) to give 34.3 mg (59% yield) of

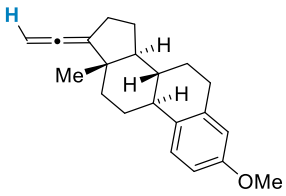
pure allenes as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.25 – 7.16 (m, 2H), 7.16 – 7.06 (m, 3H), 5.16 – 4.99 (m, 1H), 4.66 – 4.51 (m, 2H), 2.65 (dd, *J* = 12.0, 9.0 Hz, 2H), 2.30 – 2.17 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 208.6, 141.8, 128.5, 128.3, 125.9, 89.5, 75.2, 35.4, 30.0. **GC-MS** = 144 *m/z*. Spectral data are in accordance with the literature. [S36]



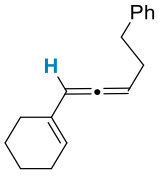
Methyl 4-(propa-1,2-dien-1-yl)benzoate (28a): Obtained according to general conditions. The crude product (4:1 mixture of inseparable allene **28a** and alkyne **28b**) was purified by flash chromatography (50:1 of petroleum ether/ethyl acetate as eluent) to give 48.0 mg (69% yield) of the mixture of isomers as an oil. **28a**: **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.99 – 7.95 (m, 2H), 7.38 – 7.31 (m, 2H), 6.20 (t, *J* = 6.0 Hz, 1H), 5.21 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 210.6, 166.9, 139.0, 130.0, 126.5, 93.6, 79.2, 52.0. **GC-MS** = 174 *m/z*. **28b**: **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.95 – 7.92 (m, 2H), 7.46 – 7.41 (m, 2H), 3.91 (s, 3H), 2.07 (s, 3H). Spectral data for **28a** [S36] and **28b** [S37] are in accordance with the literature.



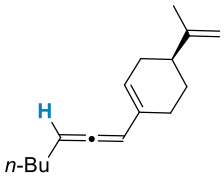
1-Methoxy-4-(propa-1,2-dien-1-yl)benzene (29a): Obtained according to general conditions ($Ni(NO_3)_2$•$6H_2O$ (0.03 equiv), 1,10-phen (0.03 equiv), DPA-CO_2Me (0.015 equiv), 72 h). The crude product (13:1 mixture of allene **29a** and alkyne **29b**) was purified by flash chromatography (petroleum ether as eluent) to give 30.7 mg (53% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.26 – 7.20 (m, 2H), 6.90 – 6.83 (m, 2H), 6.14 (t, *J* = 6.0 Hz, 1H), 5.13 (dd, *J* = 6.0, 0.6 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 209.4, 158.7, 127.7, 126.1, 114.2, 93.3, 78.7, 55.3. **GC-MS** = 146 *m/z*. Spectral data are in accordance with the literature. [S36]



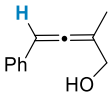
(8S,9S,13S,14S)-3-Methoxy-13-methyl-17-vinylidene-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (30): Obtained according to general conditions (0.1 mmol scale, $Ni(NO_3)_2$•$6H_2O$ (0.05 equiv), 1,10-phen (0.05 equiv), DPA-CO_2Me (0.025 equiv)). The crude product was purified by flash chromatography (100:1 of petroleum ether/ethyl acetate as eluent) to give 17.4 mg (59% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.23 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.72 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.65 (d, *J* = 3.0 Hz, 1H), 4.83 – 4.64 (m, 2H), 3.79 (s, 3H), 2.94 – 2.81 (m, 2H), 2.69 – 2.54 (m, 1H), 2.52 – 2.20 (m, 3H), 2.00 – 1.82 (m, 3H), 1.58 – 1.34 (m, 6H), 0.91 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 200.5, 157.5, 137.9, 132.7, 126.3, 113.8, 112.0, 111.5, 55.2, 54.5, 44.4, 44.0, 38.8, 36.1, 29.9, 27.8, 27.3, 26.7, 24.6, 18.4. **GC-MS** = 294 *m/z*. Spectral data are in accordance with the literature. [S38]



(5-(Cyclohex-1-en-1-yl)penta-3,4-dien-1-yl)benzene (31): Obtained according to general conditions (0.2 mmol scale, $Ni(NO_3)_2$•$6H_2O$ (0.05 equiv), 1,10-phen (0.05 equiv), DPA-CO_2Me (0.025 equiv)). The crude product was purified by flash chromatography (petroleum ether as eluent) to give 27.5 mg (61% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.24 – 7.16 (m, 2H), 7.15 – 7.05 (m, 3H), 5.82 – 5.68 (m, 1H), 5.61 – 5.51 (m, 1H), 5.40 – 5.24 (m, 1H), 2.74 – 2.57 (m, 2H), 2.35 – 2.19 (m, 2H), 2.07 – 1.96 (m, 2H), 1.94 – 1.68 (m, 2H), 1.58 – 1.45 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.3, 141.8, 132.4, 128.5, 128.3, 125.8, 125.6, 98.2, 93.4, 35.4, 30.9, 25.8, 25.61, 22.59, 22.5. **GC-MS** = 224 *m/z.* Spectral data are in accordance with the literature. [S39]



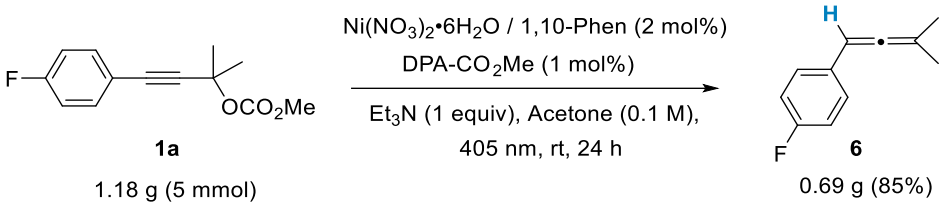
(4S)-1-(Hepta-1,2-dien-1-yl)-4-(prop-1-en-2-yl)cyclohex-1-ene (32): Unknown compound, obtained according to general conditions (0.2 mmol scale, $Ni(NO_3)_2$•$6H_2O$ (0.05 equiv), 1,10-phen (0.05 equiv), DPA-CO_2Me (0.025 equiv)). The crude product was purified by flash chromatography (petroleum ether as eluent) to give 26.2 mg (61% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.87 – 5.79 (m, 1H), 5.70 – 5.60 (m, 1H), 5.43 – 5.29 (m, 1H), 4.78 – 4.67 (m, 2H), 2.27 – 1.97 (m, 7H), 1.90 – 1.80 (m, 1H), 1.74 (t, *J* = 3.0 Hz, 3H), 1.52 – 1.29 (m, 5H), 0.94 – 0.86 (m, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.4, 204.3, 149.91, 149.88, 132.3, 124.6, 108.6, 97.22, 97.19, 94.14, 94.12, 41.3, 41.2, 31.4, 31.33, 31.30, 28.9, 28.8, 27.6, 26.3, 26.1, 22.3, 22.2, 20.8, 13.9. **HRMS** (APCI) calcd for $C_{16}H_{25}$ *m/z* 217.1950 [M+H], Found 217.1951.



2-Methyl-4-phenylbuta-2,3-dien-1-ol (33): Obtained according to general conditions ($Ni(NO_3)_2$•$6H_2O$ (0.03 equiv), 1,10-phen (0.03 equiv), DPA-CO_2Me (0.015 equiv)). The crude product was purified by flash chromatography (1.5:1 of petroleum ether/dichloromethane as eluent) to give 53.8 mg (84% yield) of pure allene as an oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 4H), 7.24 – 7.17 (m, 1H), 6.32 – 6.24 (m, 1H), 4.24 – 4.07 (m, 2H), 1.86 (d, *J* = 3.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 200.9, 134.8, 128.6, 127.1, 126.8, 104.7, 97.1, 63.9, 15.4. **GC-MS** = 160 *m/z.* Spectral data are in accordance with the literature. [S40]

Scale-up experiment (Non-optimized)

The reaction was performed on 1.18 g (5 mmol) of **1a** using a 100 mL Schlenk tube exposed to LED lighting from a single 405 nm EvoluChem™ 18 W purple LED lamp (P206-18-1 405 nm) placed 5 cm away, and an external cooling fan that maintained the temperature below 35 °C (Fig S1).



A 100 mL Schlenk tube equipped with a magnetic stir bar was charged with $Ni(NO_3)_2$•$6H_2O$ (29.1 mg, 0.1 mmol, 0.02 equiv), 1,10-phen (18.0 mg, 0.1 mmol, 0.02 equiv), and DPA-CO_2Me (19.4 mg, 0.05 mmol, 0.01 equiv). The vessel was evacuated and backfilled three times with argon. Acetone (40 mL), propargyl carbonate **1a** (1.18 g, 5 mmol, 1 equiv, dissolved in acetone (10 mL)), and Et_3N (0.7 mL, 5 mmol, 1.0 equiv) were added under argon. The reaction mixture was stirred at room temperature under 405 nm purple LED irradiation for 24 h, after which time the reaction medium was concentrated under vacuum and the crude product was purified by flash chromatography on silica gel (petroleum ether as eluent) to afford 0.69 g (85%) of pure allene **6**.

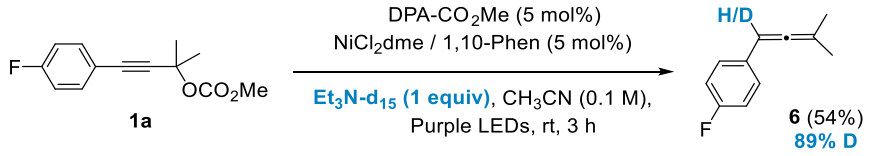
Figure S1. Reaction set-up for scale-up experiment.

5. Mechanistic experiments

5.1. Deuterium labelling studies

In order to avoid the presence of undesired water in these experiments, the nickel catalyst $NiCl_2$.glyme was preferred to the hydrated complex $Ni(NO_3)_2.6H_2O$. Acetonitrile was also preferred as the solvent. Fully deuterated triethylamine and methanol were purchased and used as received without further drying.

- Deuteration with Et_3N-d_{15} *:*



In a glove-box, a 8 mL vial equipped with a magnetic stir bar was charged with $NiCl_2$•dme (2.2 mg, 0.01 mmol, 0.05 equiv), 1,10-phen (1.8 mg, 0.01 mmol, 0.05 equiv), DPA-CO_2Me (3.9 mg, 0.01 mmol, 0.05 equiv), CH_3CN (2 mL), Et_3N-d_{15} (23.3 mg, 0.2 mmol, 1.0 equiv), and propargyl carbonate **1a** (47.2 mg, 0.2 mmol, 1.0 equiv). The vial was then capped, and the reaction mixture was stirred at room temperature outside the glove-box under purple light irradiation for 3 h. When the reaction was completed, the solvent was removed under vacuum, and the crude product was purified by flash chromatography on silica gel (petroleum ether as eluent) to afford deuterated allene **6** (17.5 mg, 54% yield, 89% of deuterium incorporation) (Fig S2).

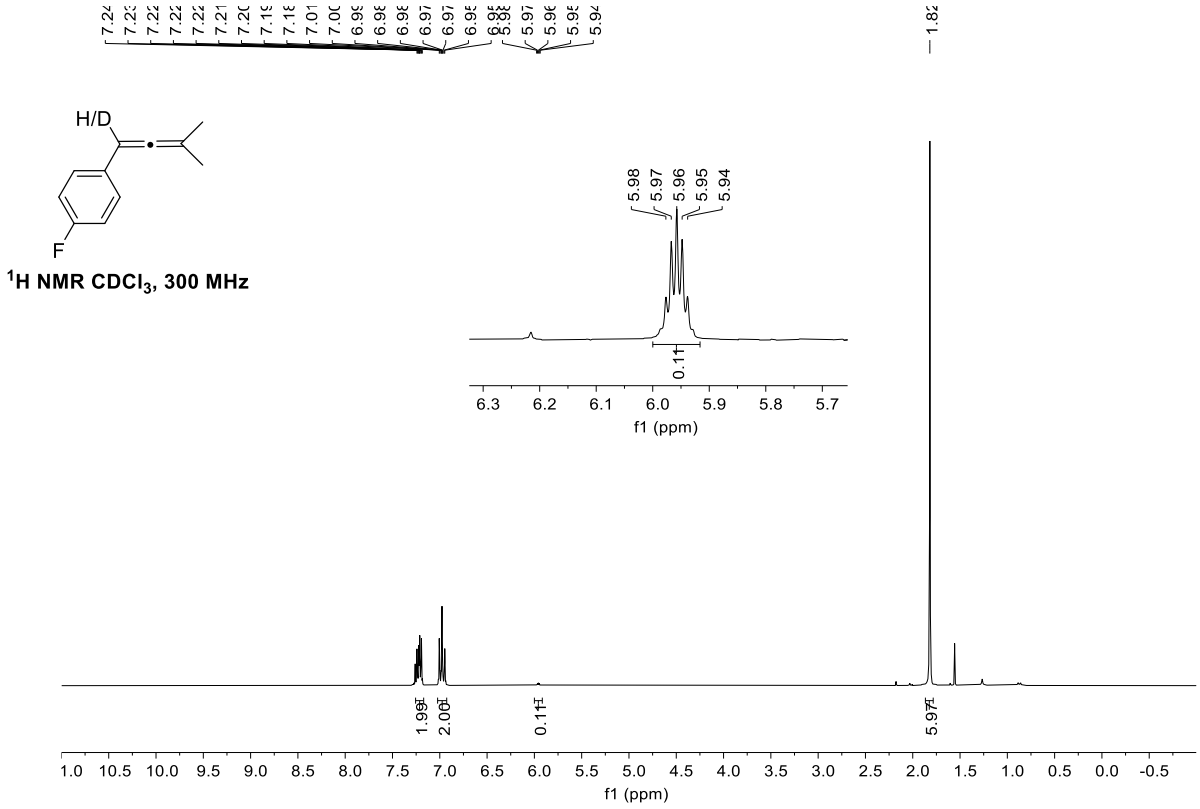
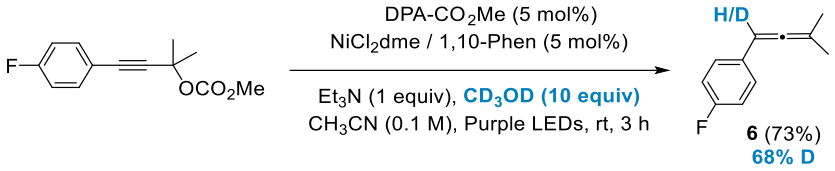


Figure S2. ^{1}H NMR spectrum of allene **6** obtained with Et_3N-d_{15}.

- Deuteration with MeOH-d_4:



In a glove-box, a 8 mL vial equipped with a magnetic stir bar was charged with $NiCl_2$•dme (2.2 mg, 0.01 mmol, 0.05 equiv), 1,10-phen (1.8 mg, 0.01 mmol, 0.05 equiv), DPA-CO_2Me (3.9 mg, 0.01 mmol, 0.05 equiv), CH_3CN (2 mL), Et_3N (28 μL, 0.2 mmol, 1.0 equiv), CD_3OD (81.2 μL, 2.0 mmol, 10.0 equiv), and propargyl carbonates **1** (47.2 mg, 0.2 mmol, 1.0 equiv). The vial was then capped, and the reaction mixture was stirred at room temperature outside the glove-box under purple light irradiation for 3 h. When the reaction was completed, the solvent was removed under vacuum, and the crude product was purified by flash chromatography on silica gel (petroleum ether as eluent) to afford deuterated allene **6** (23.8 mg, 73% yield, 68% of deuterium incorporation) (Fig S3).

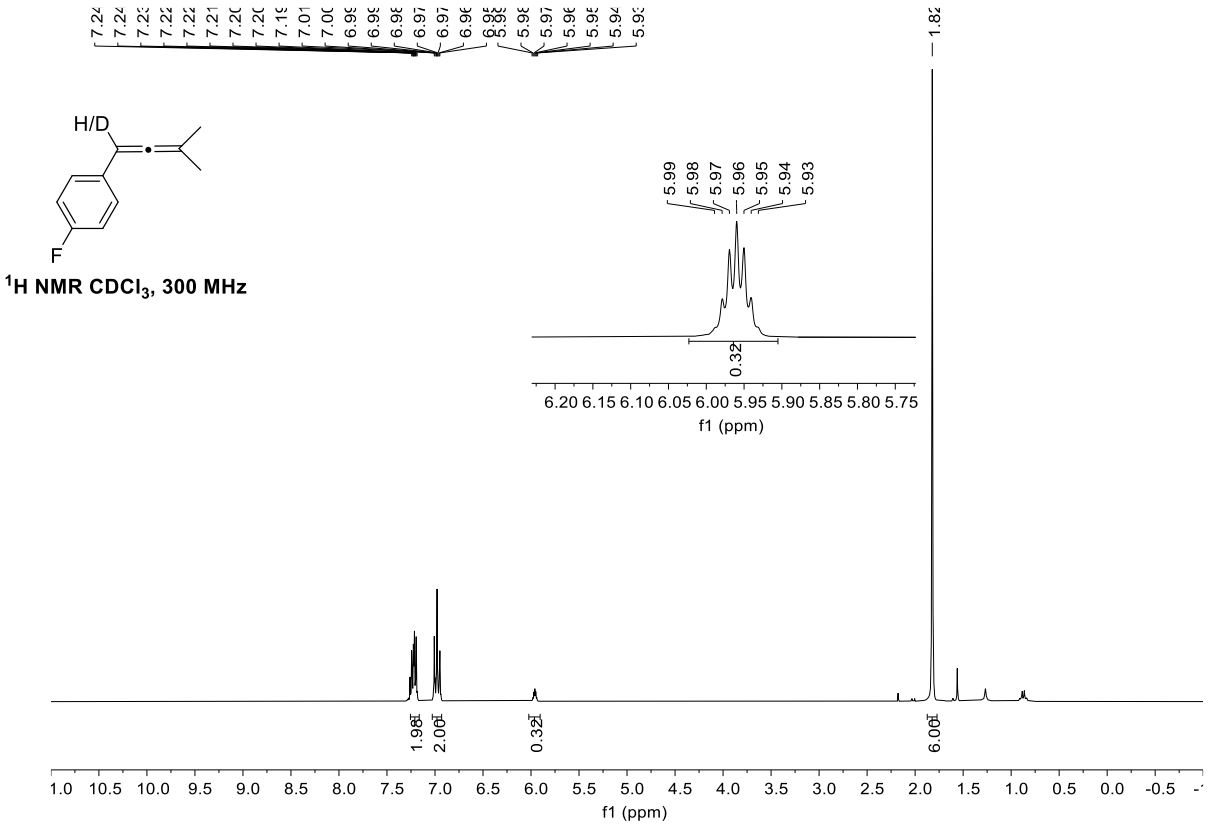
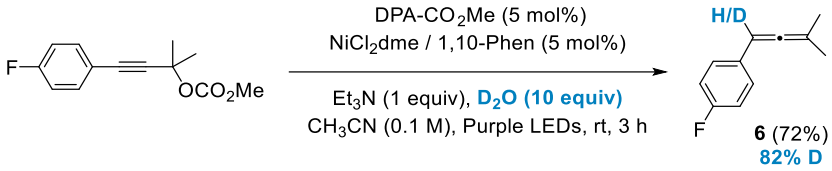


Figure S3. ^{1}H NMR spectrum of allene **6** obtained with Et_3N & CD_3OD.

- Deuteration with D_2O*:*



In a glove-box, A 8 mL vial equipped with a magnetic stir bar was charged with the $NiCl_2$•dme (2.2 mg, 0.01 mmol, 0.05 equiv), 1,10-phen (1.8 mg, 0.01 mmol, 0.05 equiv), DPA-CO_2Me (3.9 mg, 0.01 mmol, 0.05 equiv), CH_3CN (2 mL), Et_3N (28 µL, 0.2 mmol, 1.0 equiv), and propargyl carbonates **1** (47.2 mg, 0.2 mmol, 1.0 equiv). The vial was then capped and transferred out of the glovebox. D_2O (36.2 µl, 2.0 mmol, 10.0 equiv) was added under argon atmosphere. Then the reaction mixture was stirred at room temperature under purple light irradiation for 3 h. When the reaction was completed, the solvent was removed under vacuum, and the crude product was purified by flash chromatography on silica (petroleum ether as eluent) to afford the deuterated allene **2** (23.5 mg, 72% yield, 82% of deuterium incorporation) (Fig S4).

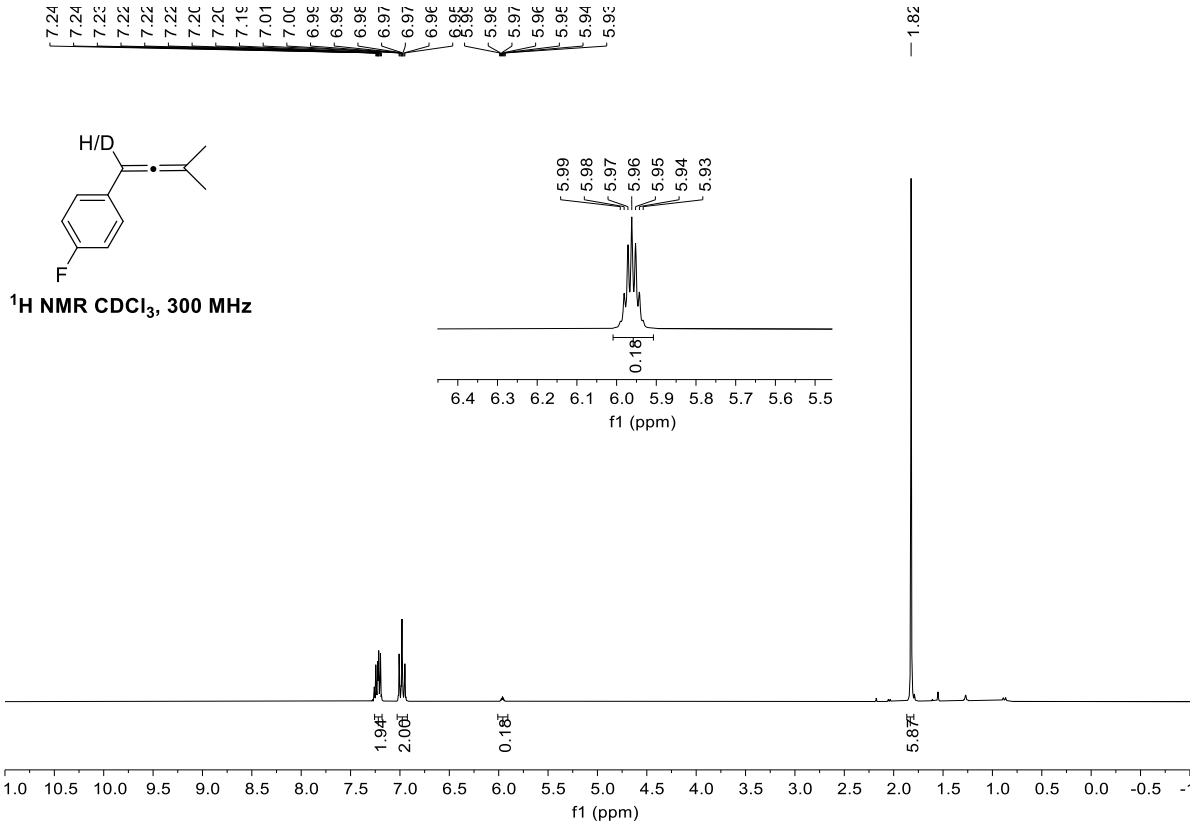
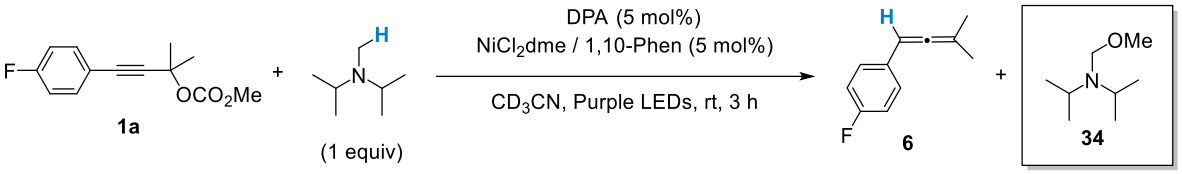


Figure S4: ^1H NMR spectrum of allene **6** obtained with Et_3N & D_2O.

5.2. Trialkylamine reaction outcome.

*In order to probe the formation of an hemiaminal ether co-product, the reduction of propargyl carbonate **1a** was performed using diisopropylmethylamine as both reductive quencher and proton source, which was expected to produce the relatively stable, known N-methoxymethylamine **34**:* [S41]



In a glove-box, a J-Young NMR tube was charged with $NiCl_2$•dme (0.66 mg, 0.003 mmol, 0.05 equiv), 1,10-phen (0.54 mg, 0.003 mmol, 0.05 equiv), DPA (0.99 mg, 0.003 mmol, 0.05 equiv), propargyl carbonate **1a** (11.8 mg, 0.06 mmol, 1.0 equiv), *N*,*N*-diisopropylmethylamine (9.2 μL, 0.06 mmol, 1.0 equiv), and CD_3CN (0.5 mL). The tube was then sealed and irradiated with purple light outside the glove-box at room temperature until full conversion of **1a** was observed (3 h, ^{19}F NMR). Direct spectroscopic analysis of the crude reaction mixture by ^1H NMR confirmed the presence of hemiaminal ether **34** (Fig S5). Data from crude spectrum: **^{1}H NMR (CD_3CN, 300 MHz)** δ 4.15 (s, 2H, C$\underline{H}_2$OMe), 3.16 – 3.08 (m, 2H, C$\underline{H}$CH$_3$), 3.10 (s, 3H, OMe), 1.05 (d, *J* = 6.6 Hz, 12H, CHC$\underline{H}_3$). The product was also detected by mass spectroscopy: **LRMS (ESI+)**: *m/z* Calcd for [($C_8H_{19}NO$) + H^+]: 146.1539, found: 146.2 (Fig S6).

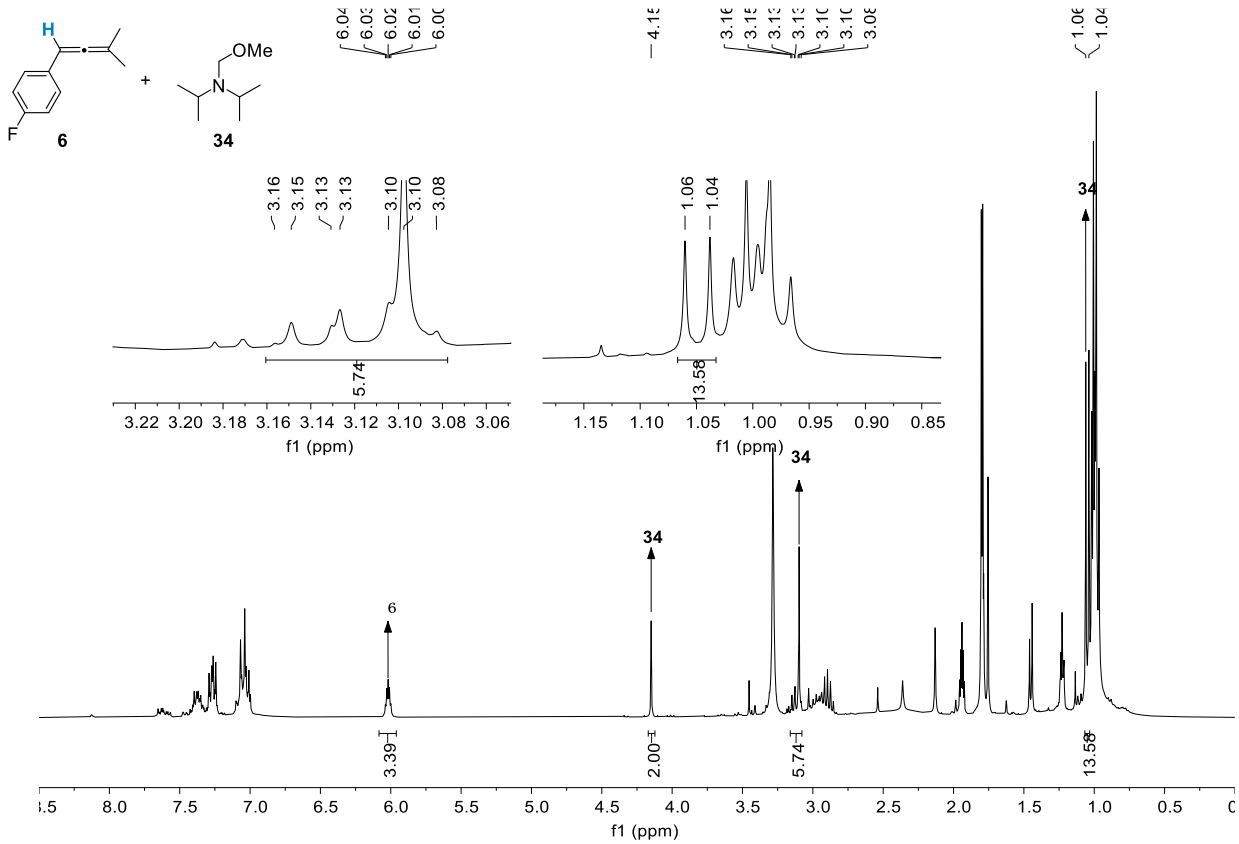


Figure S5. Crude ^1H NMR spectrum (CD_3CN, 300 MHz) showing allene **6** and hemiaminal ether **34.**

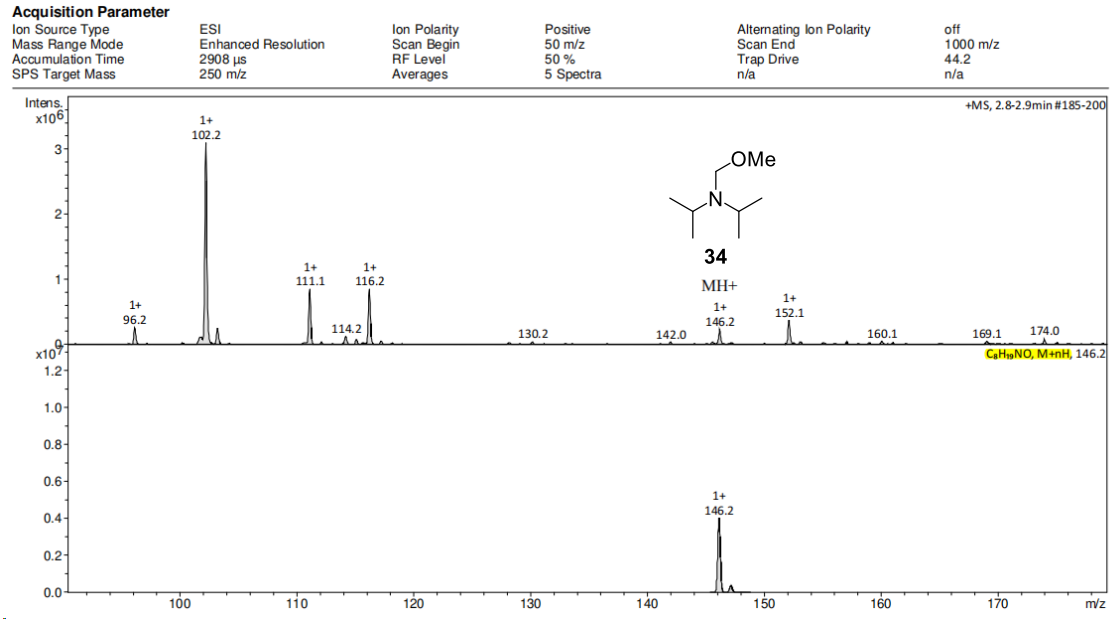
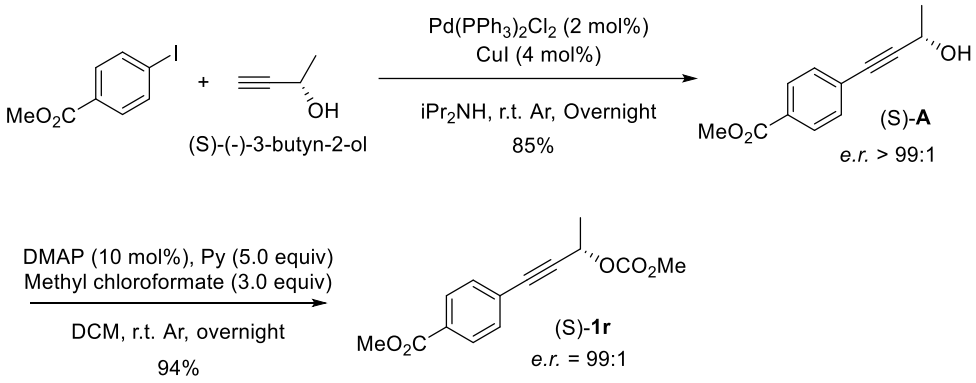


Figure S6. Detection of hemiaminal ether **34** by LRMS (ESI+)

5.3 Stereospecificity

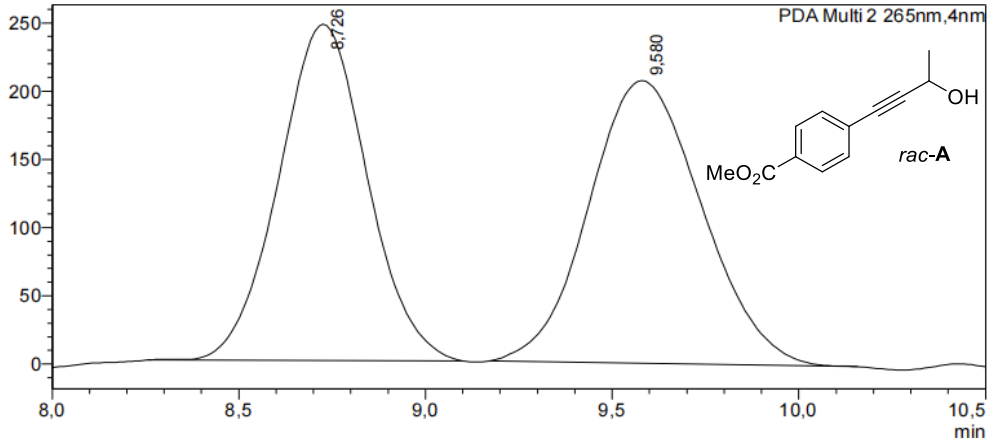
Preparation of enantiopure propargyl carbonate (S)-**1r** from commercially available (S)-(-)-3-butyn-2-ol:



Methyl 4-iodobenzoate (2.13 g, 8.13 mmol, 1.15 equiv), $Pd(PPh_3)_2Cl_2$ (120 mg, 0.17 mmol, 0.024 equiv), CuI (30 mg, 0.15 mmol, 0.022 equiv), diisopropylamine (30 mL), and (*S*)-(-)-3-butyn-2-ol (500 mg, 7.13 mmol, 1 equiv) were added to a 50 mL Schlenk flask with a stir bar under an atmosphere of argon. The reaction mixture was then stirred at room temperature overnight, after which time it was filtered through

celite® and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (5:1 petroleum ether and ethyl acetate as eluent) to afford 1.25 g (85%, *e.r.* > 99:1) of propargyl alcohol (S)-**A** (Fig S7-8).

To a solution of propargyl alcohol (S)-**A** (1 g, 5 mmol, 1 equiv) in dichloromethane (15 mL) were added DMAP (60 mg, 0.5 mmol, 0.1 equiv), pyridine (2 mL), and methyl chloroformate (1.2 mL, 15 mmol, 3.0 equiv) under an atmosphere of argon. The reaction mixture was then stirred at room temperature overnight, concentrated under vacuum, and the crude product was purified by flash chromatography on silica gel (20:1 mixture of petroleum ether and ethyl acetate as eluent) to afford 1.2 g (94%, *e.r.* = 99:1) of propargyl carbonate (S)-**1r** (Fig S9-10).

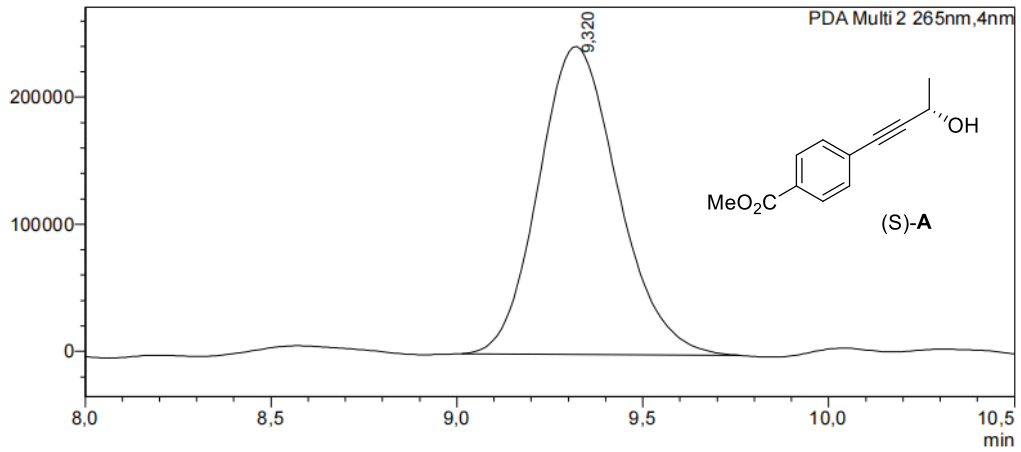


<Peak Table>

PDA Ch2 265nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8,726	4053762	246405	48,219		M	
2	9,580	4353258	207031	51,781		M	
Total		8407020	453437				

Figure S7. HPLC spectrum for racemic methyl 4-(3-hydroxybut-1-yn-1-yl)benzoate (*rac*-**A**) [Lux-cell-3 column, Hept/iPrOH = 95:5, Flow rate: 1 mL.min^{-1}, Detection*:* UV at 265 nm]

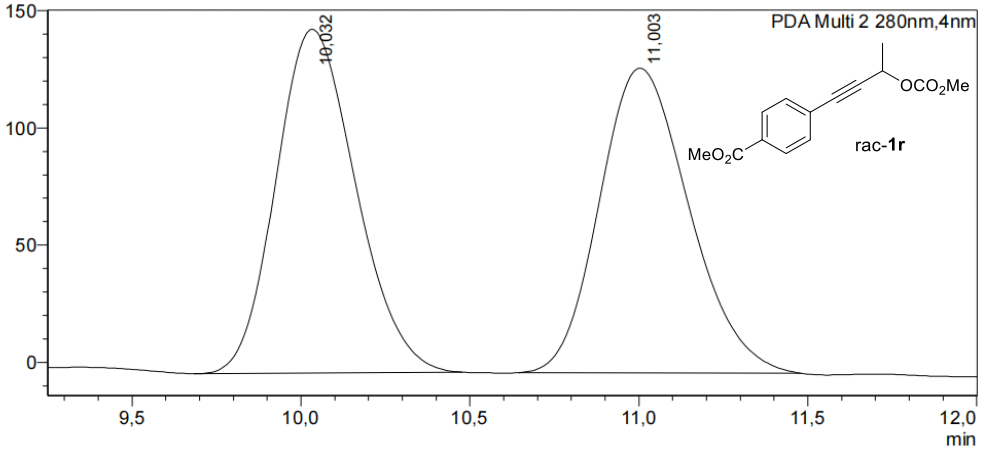


<Peak Table>

PDA Ch2 265nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9,320	3606493	242229	100,000		M	
Total		3606493	242229				

Figure S8. HPLC spectrum for enantiopure methyl 4-(3-hydroxybut-1-yn-1-yl)benzoate ((S)-**A**) [Lux-cell-3 column, Hept/iPrOH = 95:5, Flow rate: 1 mL.min^{-1}, Detection*:* UV at 265 nm]

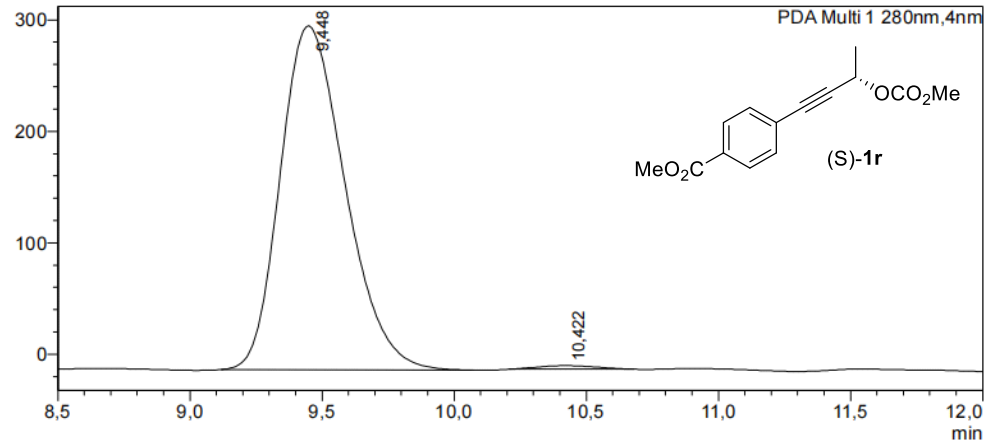


<Peak Table>

PDA Ch2 280nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10,032	2401306	146285	50,075		M	
2	11,003	2394121	129817	49,925		M	
Total		4795427	276102				

Figure S9. HPLC spectrum for racemic methyl 4-(3-((methoxycarbonyl)oxy)but-1-yn-1-yl)benzoate (*rac*-**1r**) [Lux-cell-3 column, Hept/iPrOH = 99:1, Flow rate: 1 mL.min^{-1}, Detection*:* UV at 280 nm]



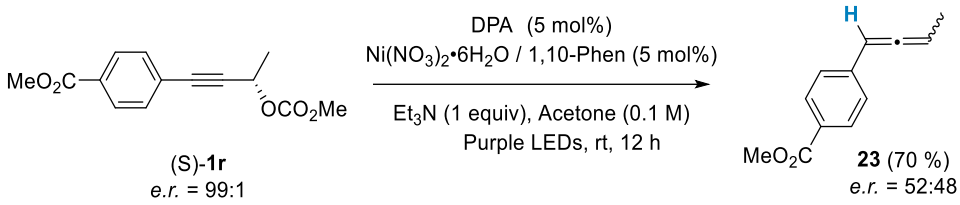
<Peak Table>

PDA Ch1 280nm

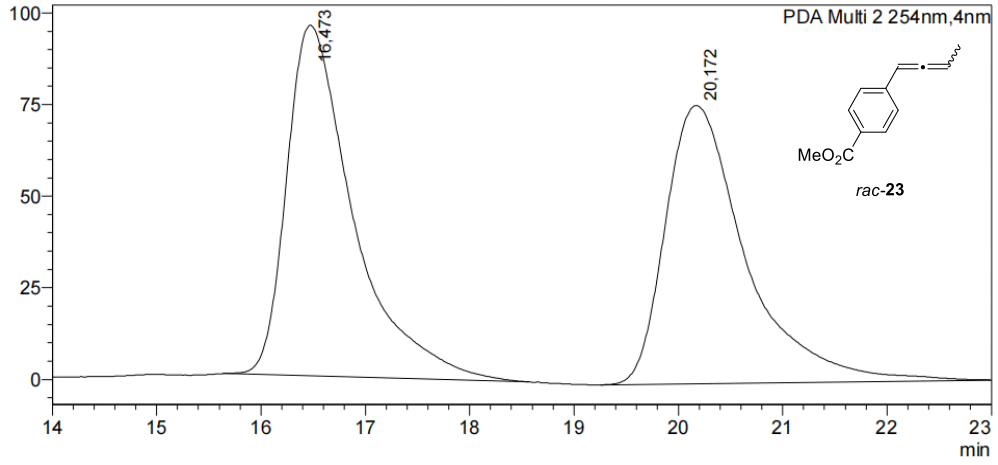
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9,448	5272374	308627	99,047		M	
2	10,422	50751	3235	0,953		M	
Total		5323125	311862				

Figure S10. HPLC spectrum for enantiopure methyl 4-(3-((methoxycarbonyl)oxy)but-1-yn-1-yl)benzoate ((S)-**1r**) [Lux-cell-3 column, Hept/iPrOH = 95:5, Flow rate: 1 mL.min^{-1}, Detection: UV at 280 nm]

Reduction of enantiopure methyl 4-(3-((methoxycarbonyl)oxy)but-1-yn-1-yl)benzoate ((S)-**1r**):



In a 8 mL vial equipped with a magnetic stir bar, $Ni(NO_3)_2$•$6H_2O$ (7.26 mg, 0.025 mmol, 0.05 equiv), 1,10-phen (4.5 mg, 0.025 mmol, 0.05 equiv), DPA (8.2 mg, 0.025 mmol, 0.05 equiv), and Et_3N (69 µl, 0.5 mmol, 1.0 equiv) were added to a solution of propargyl carbonate (S)-**1r** (131 mg, 0.5 mmol, 1 equiv) in acetone (5 mL). The vial was flushed with argon for 1 min and capped, and the reaction mixture was stirred at room temperature under 405 nm purple light irradiation for 12 h. When the reaction was completed, the reaction medium was concentrated under vacuum, and the crude product was purified by flash chromatography on silica gel (petroleum ether as eluent) to afford 0.13 g (70%, *e.r.* = 52:48) of allene **23** (Fig S11-12).

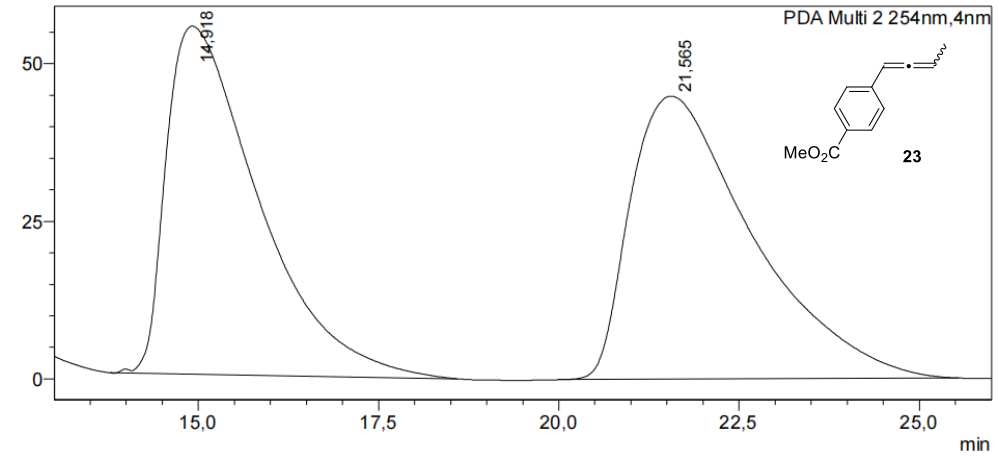


<Peak Table>

PDA Ch2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16,473	4254469	95685	51,129		M	
2	20,172	4066546	75901	48,871		M	
Total		8321015	171586				

Figure S11. HPLC spectrum for racemic methyl 4-(buta-1,2-dien-1-yl)benzoate (*rac*-**23**) [Lux-cell-2 column, Hept/iPrOH = 99.9:0.1, Flow rate: 1 mL.min^{-1}, Detection*:* UV at 254 nm]



<Peak Table>

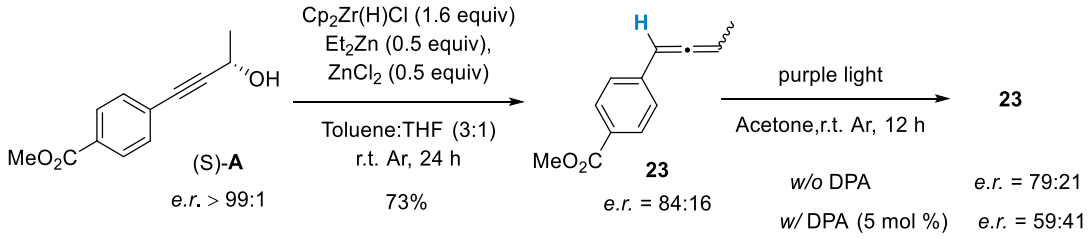
PDA Ch2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14,918	4926364	55207	48,141		M	
2	21,565	5306813	44890	51,859		M	
Total		10233178	100097				

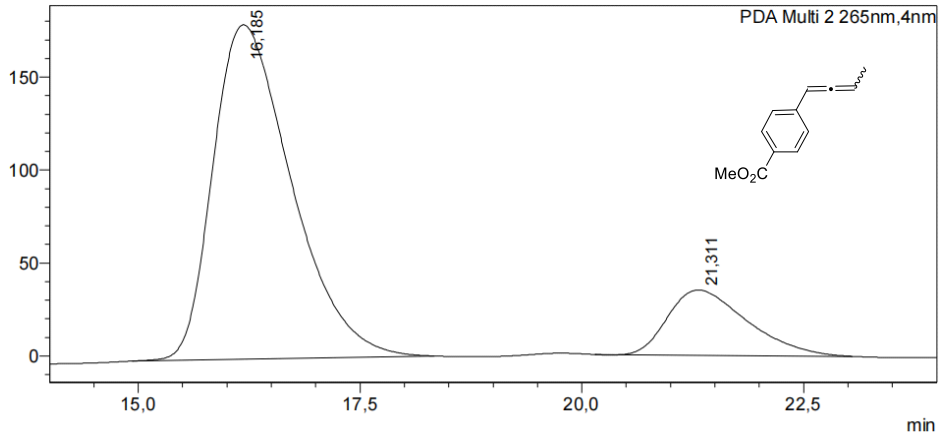
Figure S12. HPLC spectrum for allene **23** obtained from reduction of propargyl carbonate (S)-**1r** [Lux-cell-2 column, Hept/iPrOH = 99.9:0.1, Flow rate: 1 mL.min^{-1}, Detection*:* UV at 254 nm]

Influence of light and photocatalyst on stereospecificity:

In order to probe a possible photo-induced post-reaction erosion of allene chirality as documented by Morrison, [S42] *a sample of enantioenriched allene **23** was prepared by reduction of propargyl alcohol (S)-**A** with Schwartz reagent according to the procedure described by Ready.* [S43] *Solutions of this sample in acetone were subjected to standard reaction conditions in the absence of both nickel catalyst and triethylamine. The experiments showed a slight erosion of chirality when only light irradiation was applied, whereas significant erosion was observed in the presence of the photocatalyst* (Fig S13-15).



*Procedure for the preparation of enantioenriched **23**:* In a glove-box, a 5 mL microwave vial equipped with a magnetic stir bar was charged with enantiopure 4-(3-hydroxybut-1-yn-1-yl)benzoate (S)-**A** (40.8 mg, 0.2 mmol, 1 equiv), $ZnCl_2$ (13.6 mg, 0.1 mmol, 0.5 equiv), $Cp_2Zr(H)Cl$ (82.5 mg, 0.32 mmol, 1.6 equiv), toluene (0.96 mL) and THF (30 µL). The vial was then capped and transferred outside the glovebox. Then, Et_2Zn (0.1 mL, 0.1 mmol, 0.5 equiv, 1 M in hexane) was added under argon, and the reaction mixture was stirred at room temperature for 24 h. The reaction medium was then concentrated under vacuum and the crude product was purified by flash chromatography on silica gel (petroleum ether as eluent) to afford 27.6 mg (73 %, *e.r.* = 84:16) of pure allene **23**.

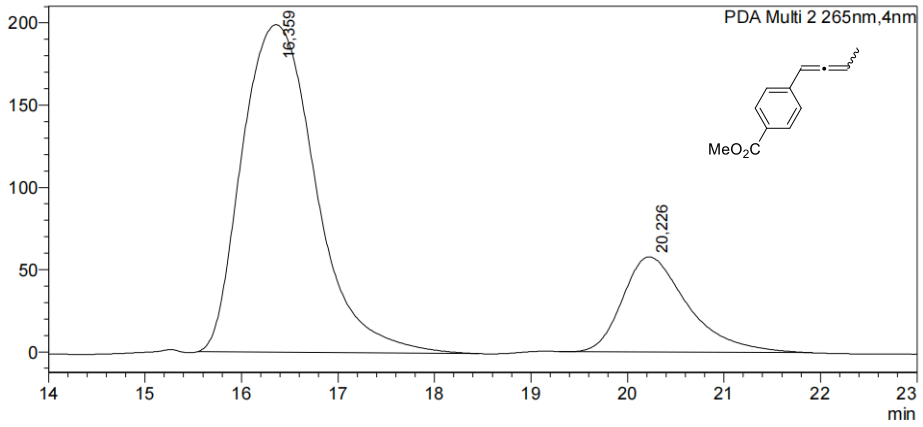


<Peak Table>

PDA Ch2 265nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16,185	11078464	179844	83,551			
2	21,311	2181032	35084	16,449		M	
Total		13259497	214927				

Figure S13. HPLC spectrum for prepared enantioenriched allene **23** [Lux-cell-2 column, Hept/iPrOH = 99.9:0.1, Flow rate: 1 mL.min^{-1}, Detection*:* UV at 265 nm]

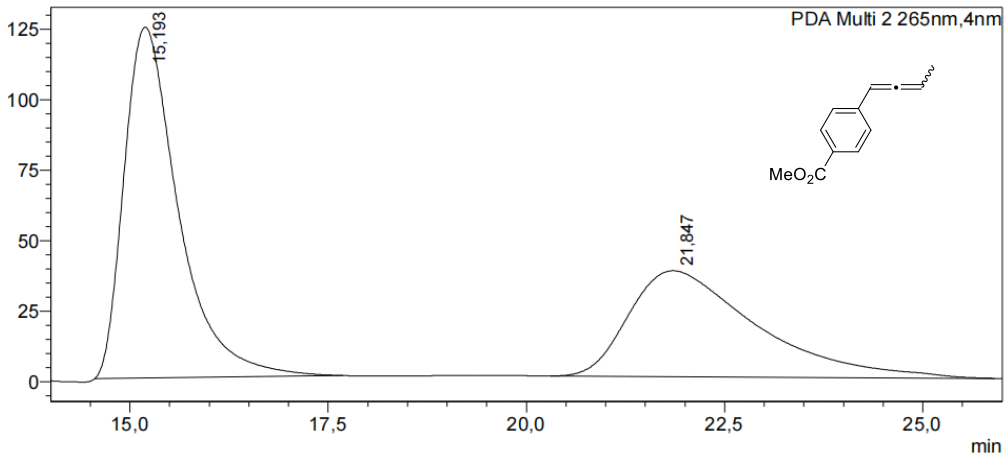


<Peak Table>

PDA Ch2 265nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16,359	10546667	198987	79,454		M	
2	20,226	2727193	57864	20,546		M	
Total		13273859	256851				

Figure S14. HPLC spectrum after light irradiation of enantioenriched allene **23** [Lux-cell-2 column, Hept/iPrOH = 99.9:0.1, Flow rate: 1 mL.min^{-1}, Detection*:* UV at 265 nm]



<Peak Table>

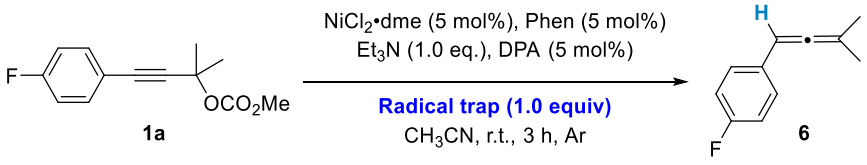
PDA Ch2 265nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15,193	5935799	124427	58,522		M	
2	21,847	4207020	37611	41,478		M	
Total		10142819	162038				

Figure S15. HPLC spectrum after irradiation of enantioenriched allene **23** in the presence of DPA [Lux-cell-2 column, Hept/iPrOH = 99.9:0.1, Flow rate: 1 mL.min^{-1}, Detection*:* UV at 265 nm]

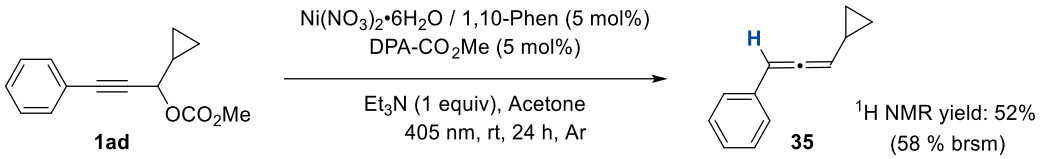
5.4. Influence of radical trapping agents

To probe the eventual involvement of free radical in the mechanism, the reaction was performed in the presence of two different radical trapping agents: TEMPO and BHT.



In a glove-box, a 8 mL vial equipped with a magnetic stir bar was charged with the $NiCl_2$•dme (2.2 mg, 0.01 mmol, 0.05 equiv), phen (1.8 mg, 0.01 mmol, 0.05 equiv), DPA (3.3 mg, 0.01 mmol, 0.05 equiv), the radical trap 2,2,6,6-tetramethylpiperidin-1-yl)oxy (31.3 mg, 0.2 mmol, 1.0 equiv) or butylated hydroxytoluene (44.1 mg, 0.2 mmol, 1.0 equiv), CH_3CN (2 mL), Et_3N (28 µl, 0.2 mmol, 1.0 equiv), and propargyl carbonates **1a** (47.2 mg, 0.2 mmol, 1.0 equiv). The vial was then capped, and the reaction mixture was stirred at room temperature outside the glove-box under purple light irradiation for 3 h. When the reaction was completed, The crude mixture was analyzed by ^{19}F NMR (internal standard: Fluorobenzene) and GC/MS.

5.5. Radical clock experiment



A 8 mL vial equipped with a magnetic stir bar was charged with the $Ni(NO_3)_2$•$6H_2O$ (5.8 mg, 0.02 mmol, 0.05 equiv), 1,10-phen (3.6 mg, 0.02 mmol, 0.05 equiv), DPA-CO_2Me (3.9 mg, 0.02 mmol, 0.05 equiv), and propargyl carbonates **1ad** (92.1 mg, 0.4 mmol, 1 equiv), the vial was flushed under argon for 1 min. Then acetone (2 mL), Et_3N (56 µl, 0.4 mmol, 1.0 equiv), and acetone (2 mL) were added under argon. The vial was then capped, and the reaction mixture was stirred at room temperature under purple light irradiation for 24 h. When the reaction was completed, the crude mixture was analyzed by ^{1}H NMR (Fig S16, CH_2Br_2 (0.5 equiv) as internal standard), showing the formation of allene **35** as major product (52 % yield; 58% based on unreacted starting material). **^{1}H NMR** (**$CDCl_3$, 300 MHz,** selected data from crude spectrum in accordance with the literature [S44]): δ 6.22 (d, *J* = 6.0 Hz, 1H), 5.46 (t, *J* = 9.0 Hz, 1H), 1.42 – 1.32 (m, 1H), 0.82 – 0.73 (m, 2H), 0.52 – 0.42 (m, 2H). **GC-MS** = 156 *m/z*.

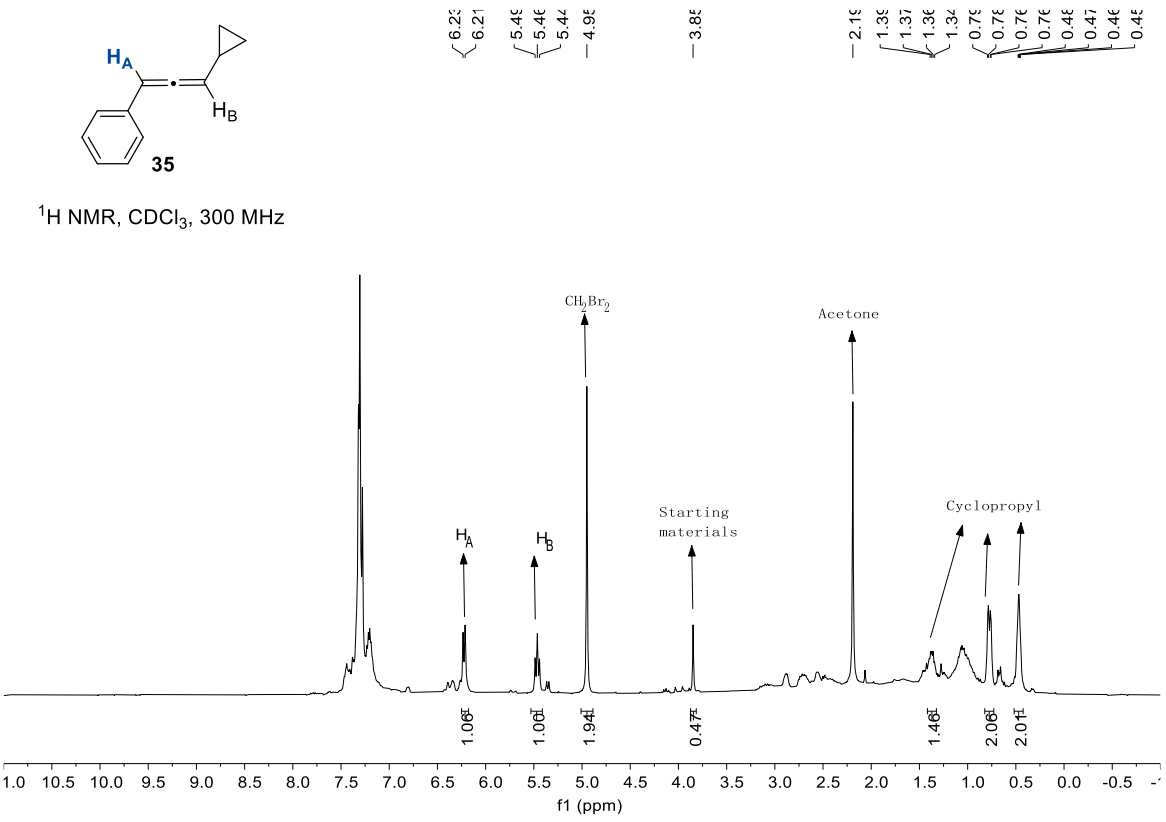


Figure S16: ^{1}H NMR ($CDCl_3$, 300 MHz) crude spectrum of allene **35**.

*Despite the fact that the reaction also yielded minor side-products that proved inseparable from **35** by conventional column chromatography and could not be identified, this result argues against the formation of free allenyl radical intermediate as a main pathway.*

5.6. Cyclic voltammetry

Electrochemical measurements were performed using an OrigaFlex - OGF500 all-in-one potentiostat, using a standard three-electrode setup with a glassy carbon electrode (working electrode, diameter = 3 mm), platinum wire auxiliary electrode and a non-aqueous Ag/Ag^+ (0.01 M $AgNO_3$ + 0.1 M $^nBu_4NClO_4$) system in acetonitrile as the reference electrode (Fig. 17). The Origasoft software was used for cyclic voltammetry experiments. All solutions under the study were 0.1 M in the supporting electrolyte $^nBu_4NPF_6$ (Fluka puriss electrochemical grade) with the voltage scan rate of 0.1 V s^{-1}. MeCN was obtained from Fisher Scientific. Solutions (10 mL) were thoroughly bubbled with dry argon for 15 minutes to remove oxygen before any experiment and kept under positive pressure of argon. Under these experimental conditions the ferrocene/ferrocenium couple, used as external reference for potential measurements, was located at $E_{1/2}$ = + 0.07 V (+ 0.39 V *vs* SCE) in MeCN. E (V *vs* SCE) = E (Ag/Ag^+ 0.01 M) + 0.32. [S45]

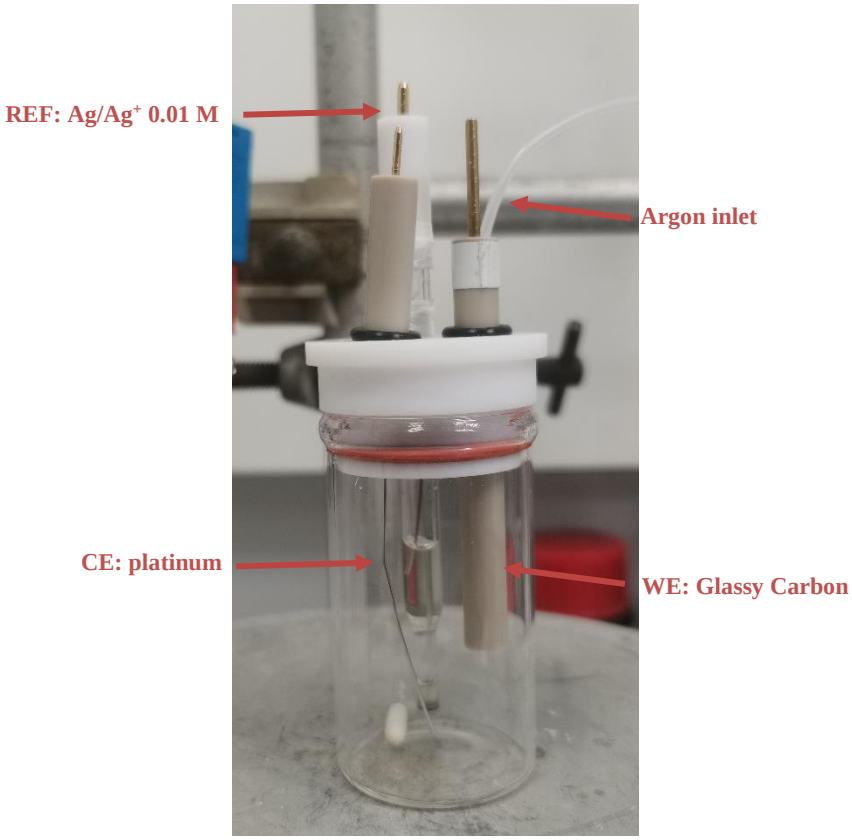
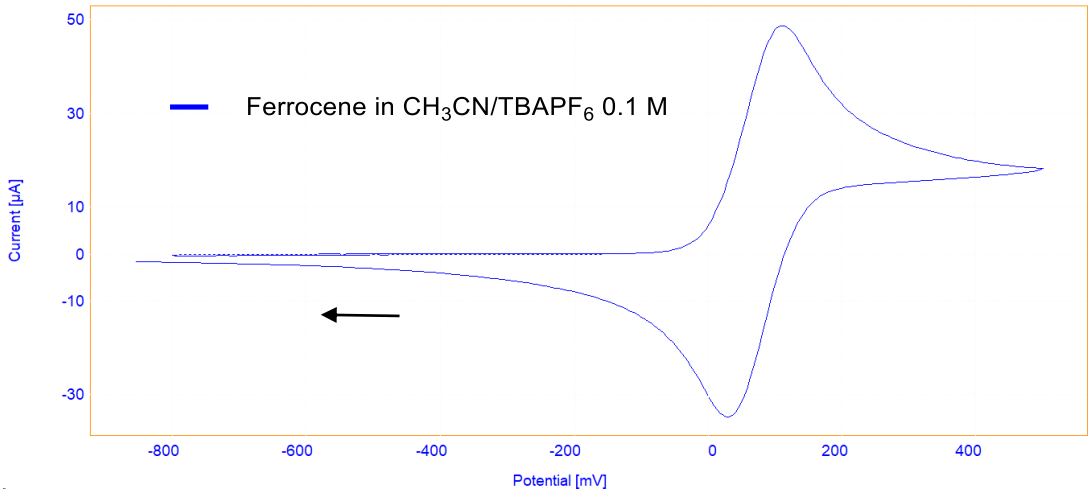


Figure S17. Gas-tight cell (20 mL) used for cyclic voltammetry.



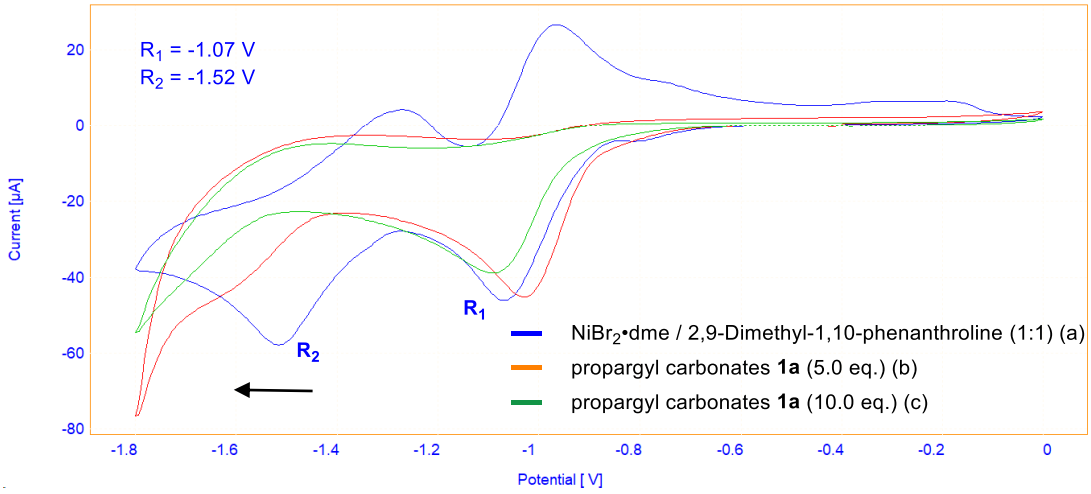


Figure S18. (a) CV of $NiBr_2$•dme 2 mM and 2,9-dimethyl-1,10-phenanthroline 2 mM (Ni/L = 1:1). (b) CV of $NiBr_2$•dme 2 mM and 2,9-dimethyl-1,10-phenanthroline 2 mM (Ni/L = 1:1) in the presence of propargyl carbonate **1a** 10 mM. (c) CV of $NiBr_2$•dme 2 mM and 2,9-dimethyl-1,10-phenanthroline 2 mM (Ni/L = 1:1) in the presence of propargyl carbonate **1a** 20 mM. Glassy carbon electrode (3 mm); CH_3CN + $TBAPF_6$ 0.1 M at 0.1 Vs^{-1}.

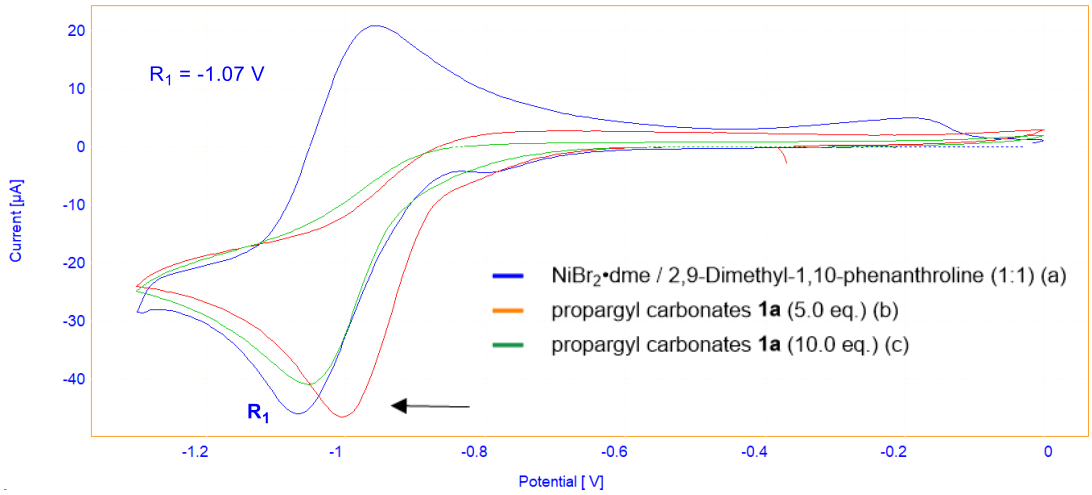


Figure S19. CV of the redox window from 0 V to -1.30 V. (a) CV of $NiBr_2$•dme 2 mM and 2,9-dimethyl-1,10-phenanthroline 2 mM (Ni/L = 1:1). (b) CV of $NiBr_2$•dme 2 mM and 2,9-dimethyl-1,10-phenanthroline 2 mM (Ni/L = 1:1) in the presence of propargyl carbonate **1a** 10 mM. (c) CV of $NiBr_2$•dme 2 mM and 2,9-dimethyl-1,10-phenanthroline 2 mM (Ni/L = 1:1) in the presence of propargyl carbonate **1a** 20 mM. Glassy carbon electrode (3 mm); CH_3CN + $TBAPF_6$ 0.1 M at 0.1 Vs^{-1}.

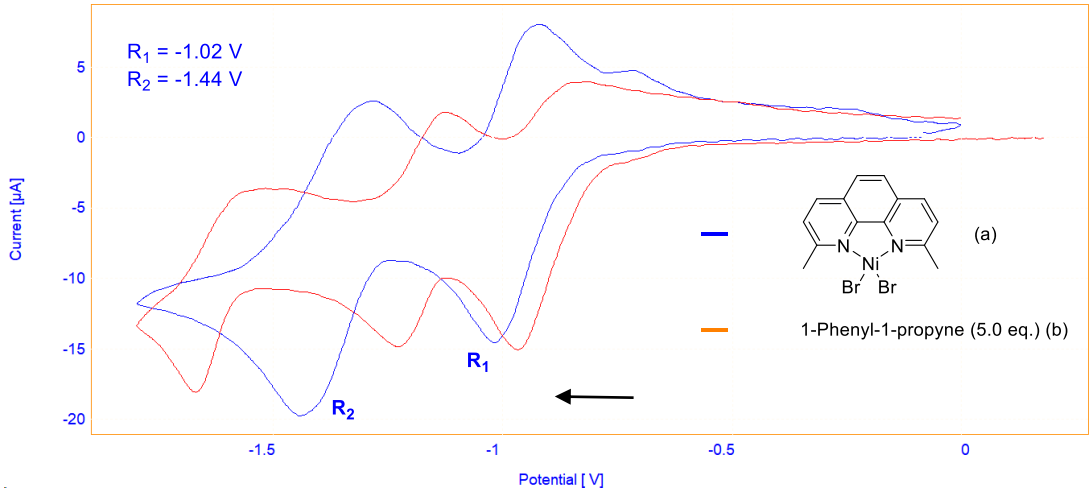
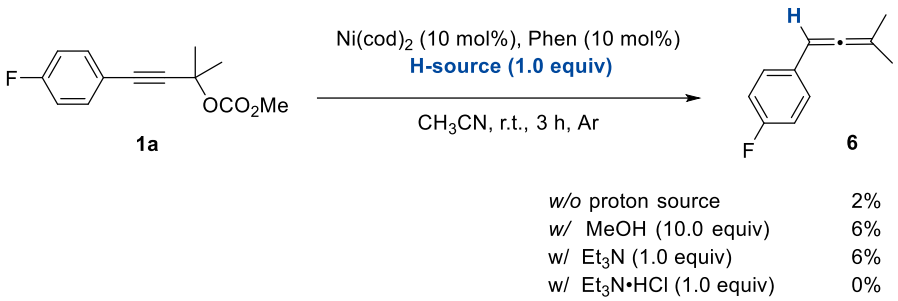


Figure S20. (a) CV of Ni complex (**I**) 1 mM. (b) CV of Ni complex (**I**) 1 mM in the presence of 1-phenyl-1-propyne 5 mM. Glassy carbon electrode (3 mm); CH_3CN + $TBAPF_6$ 0.1 M at 0.1 Vs^{-1}.

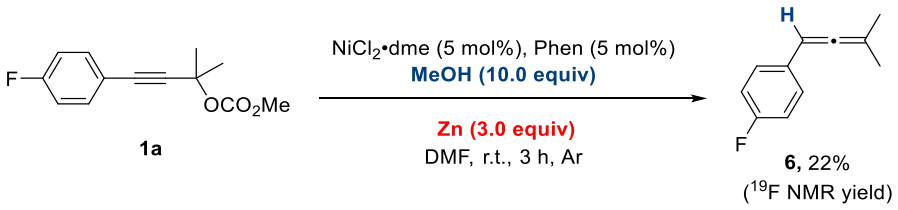
5.7. Comparison with alternative non-photochemical catalytic protocols:

Alternative protocol using Ni(0):



In a glove-box, a 8 mL vial equipped with a magnetic stir bar was charged with the $Ni(cod)_2$ (5.5 mg, 0.02 mmol, 0.1 equiv), phen (3.6 mg, 0.02 mmol, 0.1 equiv), and CH_3CN (2 mL), and the reaction mixture was stirred in the glove-box for 20 mins. Then propargyl carbonates **1a** (47.2 mg, 0.2 mmol, 1.0 equiv), and proton source MeOH (81.0 µl, 2 mmol, 10.0 equiv), Et_3N (28 µl, 0.2 mmol, 1.0 equiv), or Et_3N•HCl (27.5 mg, 0.2 mmol, 1.0 equiv) was added immediately, respectively. The vial was then capped, and the reaction mixture was stirred at room temperature outside the glove-box for 3 h. When the reaction was completed, The crude mixture was analyzed by ^{19}F NMR (internal standard: Fluorobenzene) and GC/MS.

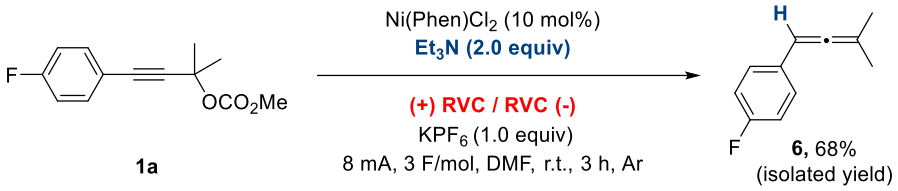
Alternative protocol using Ni(II) / Zn(0):



In a glove-box, a 8 mL vial equipped with a magnetic stir bar was charged with the $NiCl_2$•dme (2.2 mg, 0.01 mmol, 0.05 equiv), phen (1.8 mg, 0.01 mmol, 0.05 equiv), Zn (39.2 mg, 0.6 mmol, 3.0 equiv), DMF (2 mL), MeOH (81.0 µl, 2 mmol, 10.0 equiv), and propargyl carbonates **1a** (47.2 mg, 0.2 mmol, 1.0 equiv). The vial was then capped, and the reaction mixture was stirred at room temperature outside the glove-box for 3 h. When the reaction was completed, The crude mixture was analyzed by ^{19}F NMR (internal standard: Fluorobenzene) and GC/MS.

Alternative electrochemical protocol :

Electrochemical experiments were conducted using an ElectraSyn 2.0. Information and details can be found at https://www.ika.com/en/Products-Lab-Eq/Electrochemistry-Kit-csp-516/ElectraSyn-20-Package-cpdt-20008980/.
Reticulated Vitreous Carbon (RVC) electrodes (Dimensions: W x H x D = 6 x 36 x 5 mm) were purchased on the IKA website: (https://www.ika.com/en/Products-Lab-Eq/Electrochemistry-Kit-Accessories-cspacc-516/).



Preparation of $Ni(Phen)Cl_2$: In a 100 mL Schlenk flask equipped with a magnetic stir bar, 1,10-phenanthroline (540 mg, 3.0 mmol, 1.0 equiv), $NiCl_2•6H_2O$ (713.1 mg, 3.0 mmol, 1.0 equiv), and THF (30 mL) were added under an argon atmosphere, and the mixture was heated at 70 °C overnight. After cooling the reaction mixture to room temperature, the precipitate was isolated by vacuum filtration, washed with ethanol (x 2) and diethyl ether (x 2), and then dried under vacuum overnight using phosphorus pentoxide to obtain the Ni-phenanthroline complex as a green powder (541.5 mg, 58%).

Procedure for the electrosynthesis of allene 6: In a glove-box, a 5 mL ElectraSyn vial equipped with a magnetic stir bar was charged with the propargyl carbonates **1a** (70.9 mg, 0.3 mmol, 1.0 equiv), KPF_6 (55.2 mg, 0.3 mmol, 1.0 equiv), $Ni(Phen)Cl_2$ (11.5 mg, 0.03 mmol, 0.1 equiv), DMF (3 mL), and Et_3N (83.4 µl, 0.6 mmol, 2.0 equiv). The ElectraSyn vial was then sealed with a cap equipped with anode (RVC) and cathode (RVC). The reaction mixture was electrolyzed under a constant current of 8 mA until 3 F/mol were delivered. When the reaction was completed, the crude product was purified by flash chromatography on silica gel (petroleum ether as eluent) to give 33.2 mg (68% yield) of pure allene **6**.

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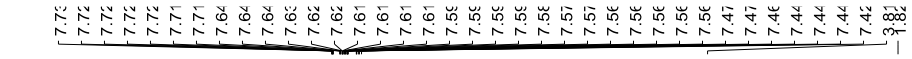
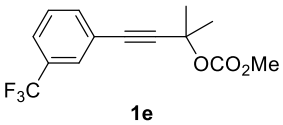
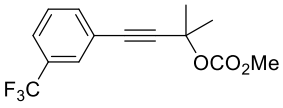
7. NMR spectra of propargyl carbonates and allenes.





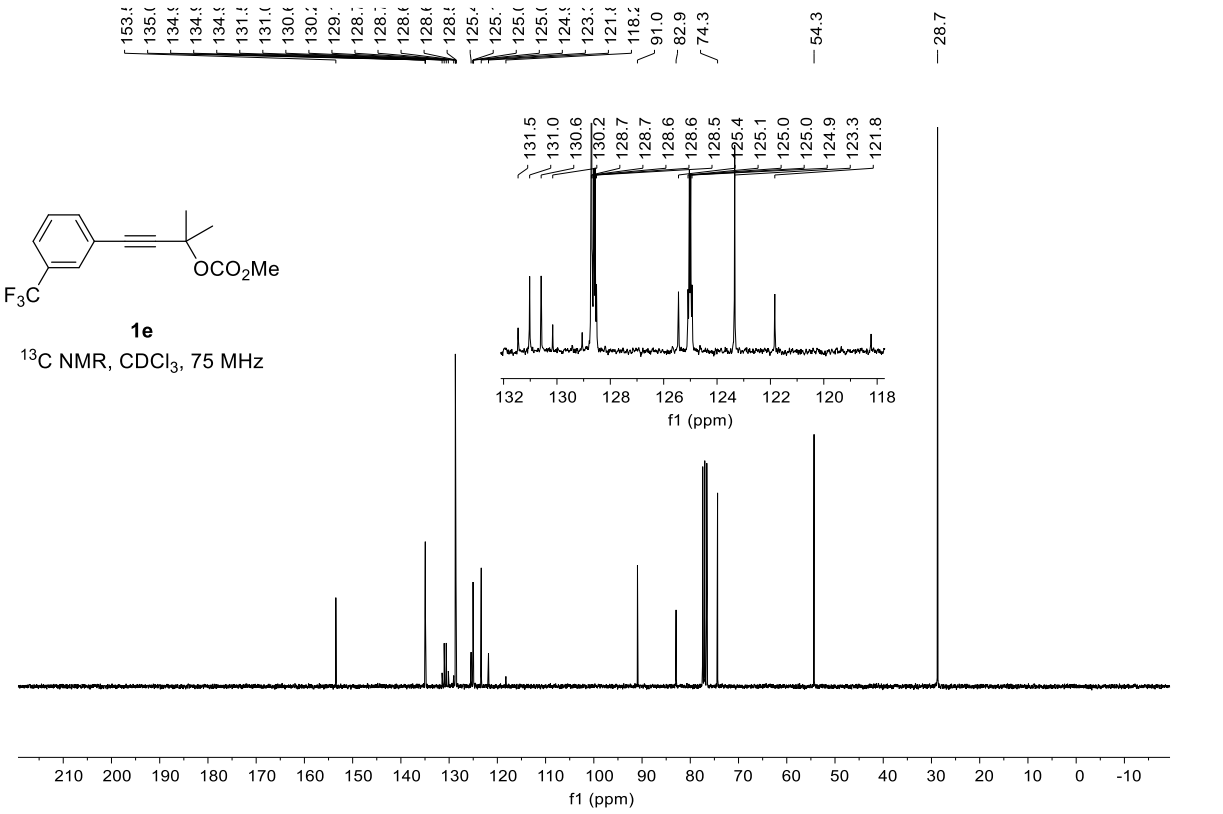
1e

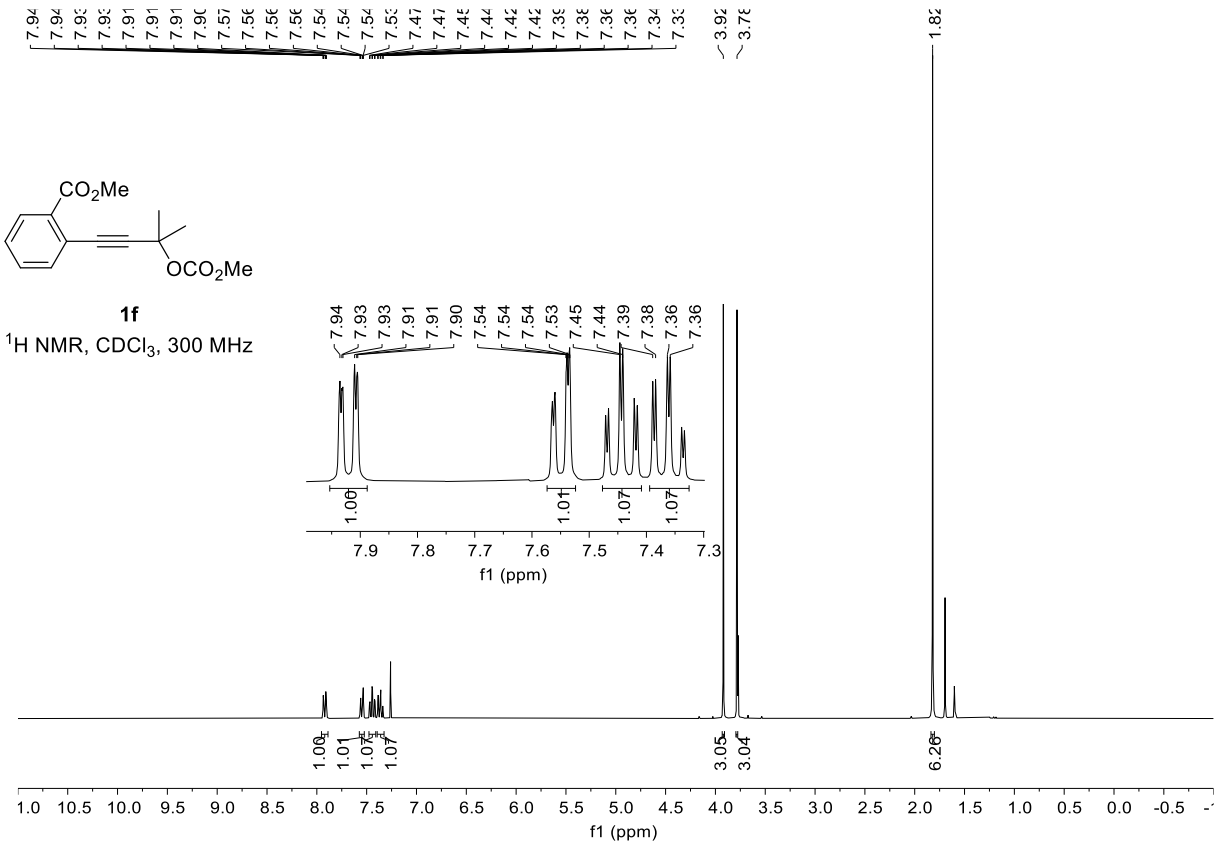
^{1}H NMR, $CDCl_3$, 300 MHz

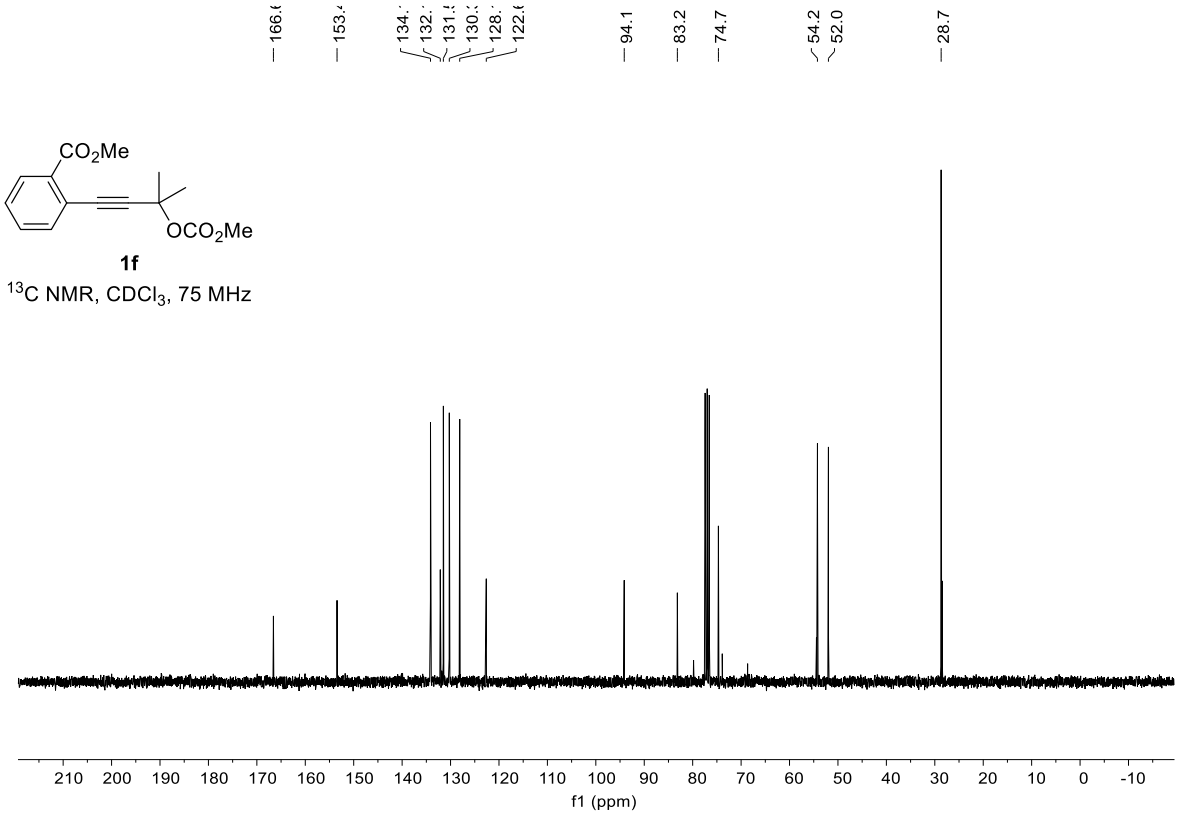


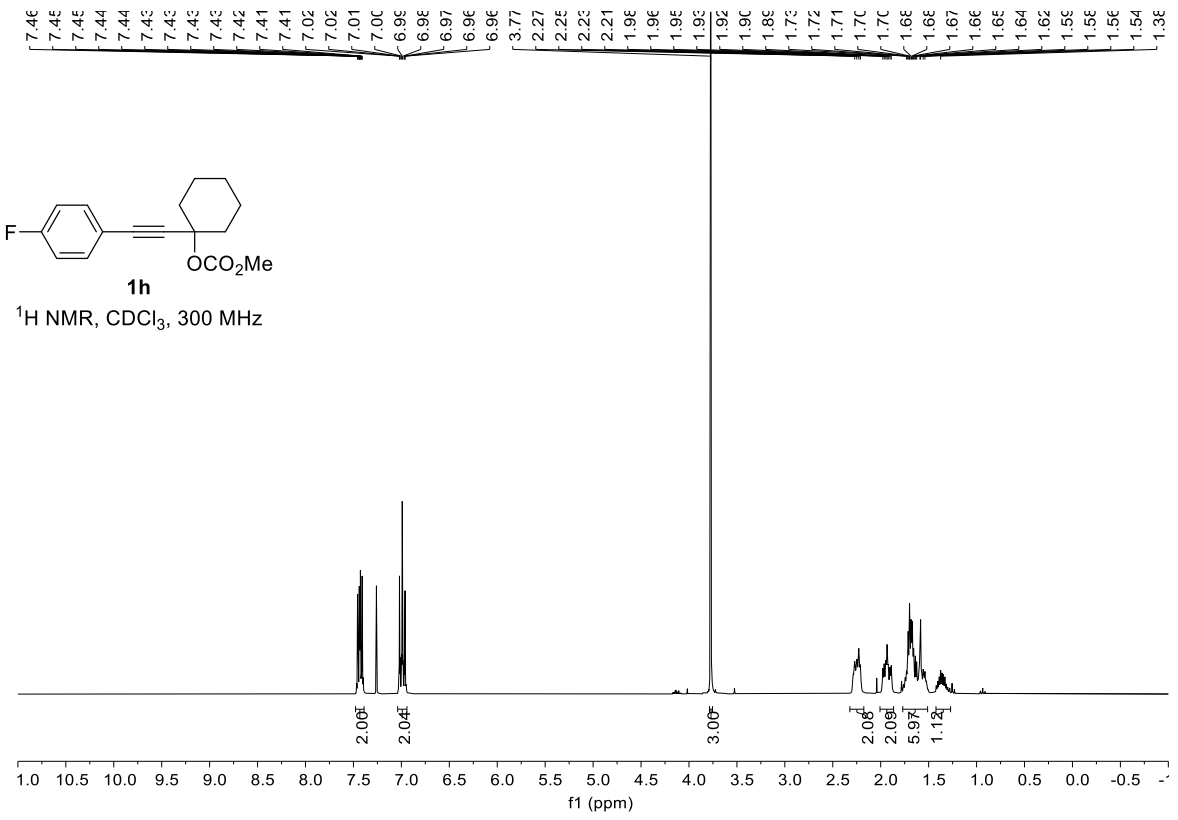
1e

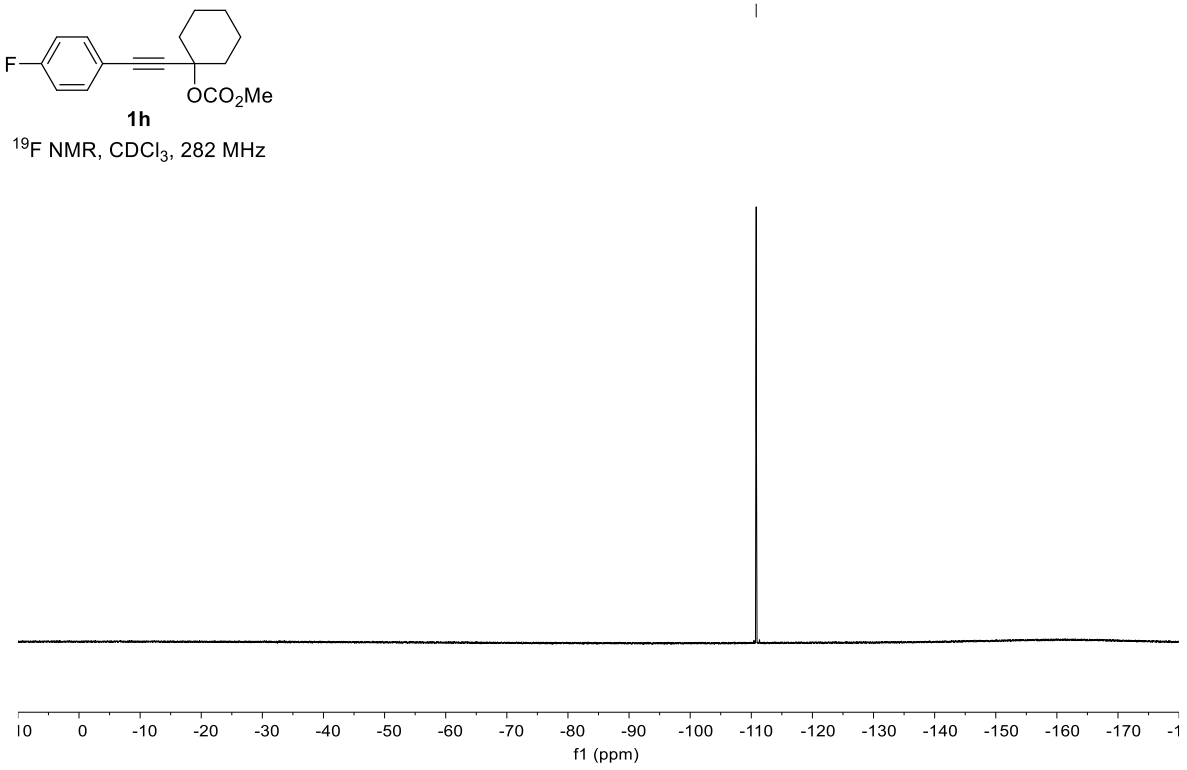
^{19}F NMR, $CDCl_3$, 282 MHz

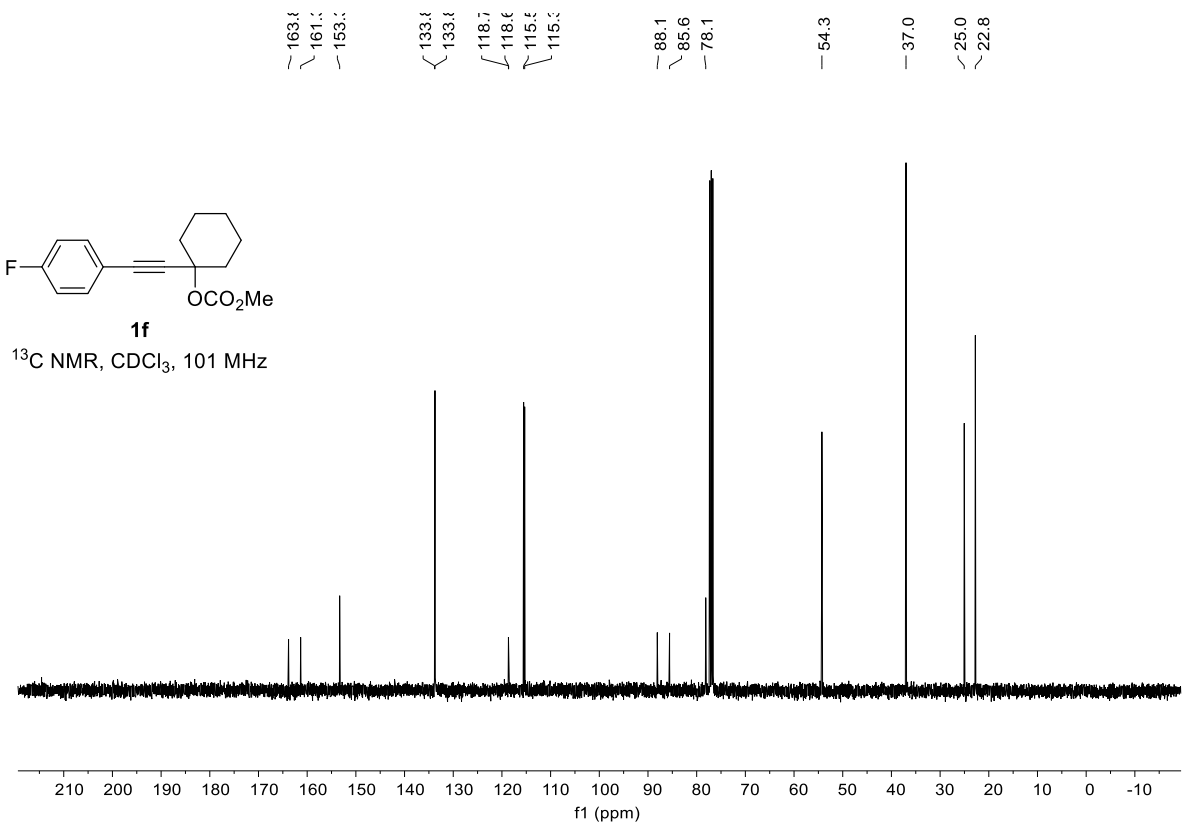

OCO2Me
F3C
1e
13C NMR, CDCl3, 75 MHz
f1 (ppm)

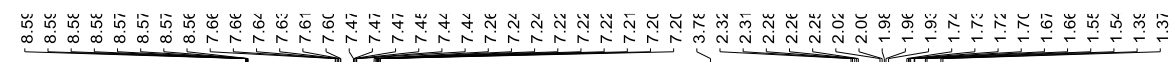

CO2Me
OCO2Me
1f
1H NMR, CDCl3, 300 MHz
f1 (ppm)

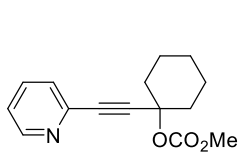

CO2Me
OCO2Me
1f
13C NMR, CDCl3, 75 MHz
166.
153.
134.
132.
131.
130.
128.
122.
94.1
83.2
74.7
54.2
52.0
28.7
f1 (ppm)


F
OCO2Me
1h
1H NMR, CDCl3, 300 MHz
2.00
2.04
3.00
2.08
2.09
5.97
1.12
f1 (ppm)


F
OCO2Me
1h
19F NMR, CDCl3, 282 MHz
-110.8
f1 (ppm)

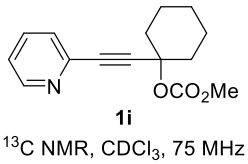

163.8
161.4
153.3
133.8
133.8
118.7
118.6
115.8
115.5
88.1
85.6
78.1
54.3
37.0
25.0
22.8
F
OCO2Me
1f
13C NMR, CDCl3, 101 MHz
f1 (ppm)





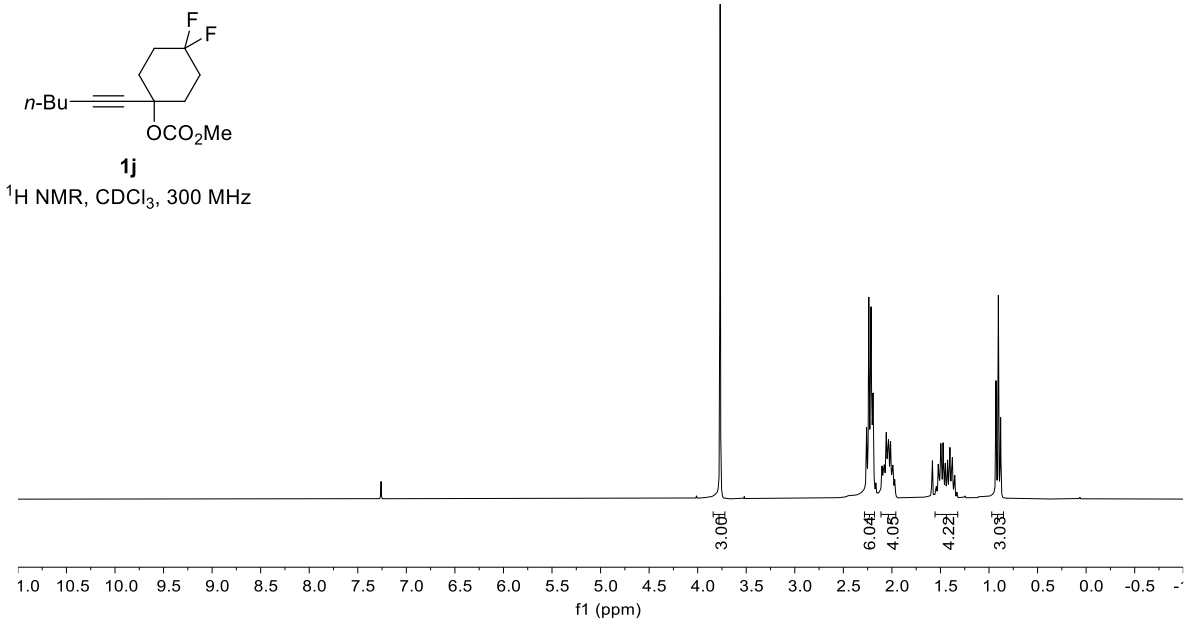
1i

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



1i

^{13}C NMR, $CDCl_3$, 75 MHz

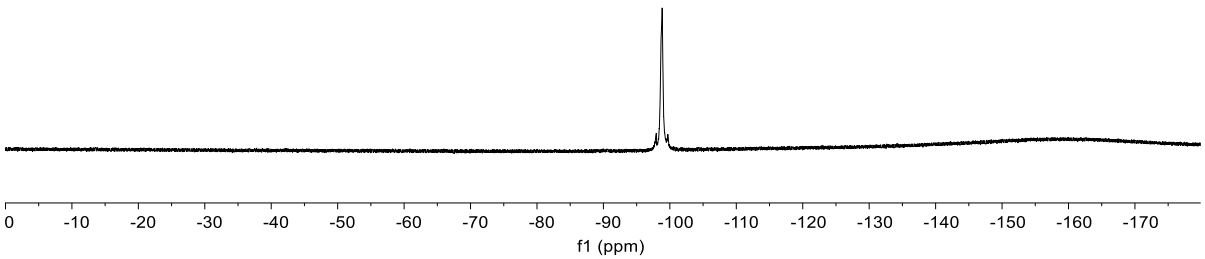


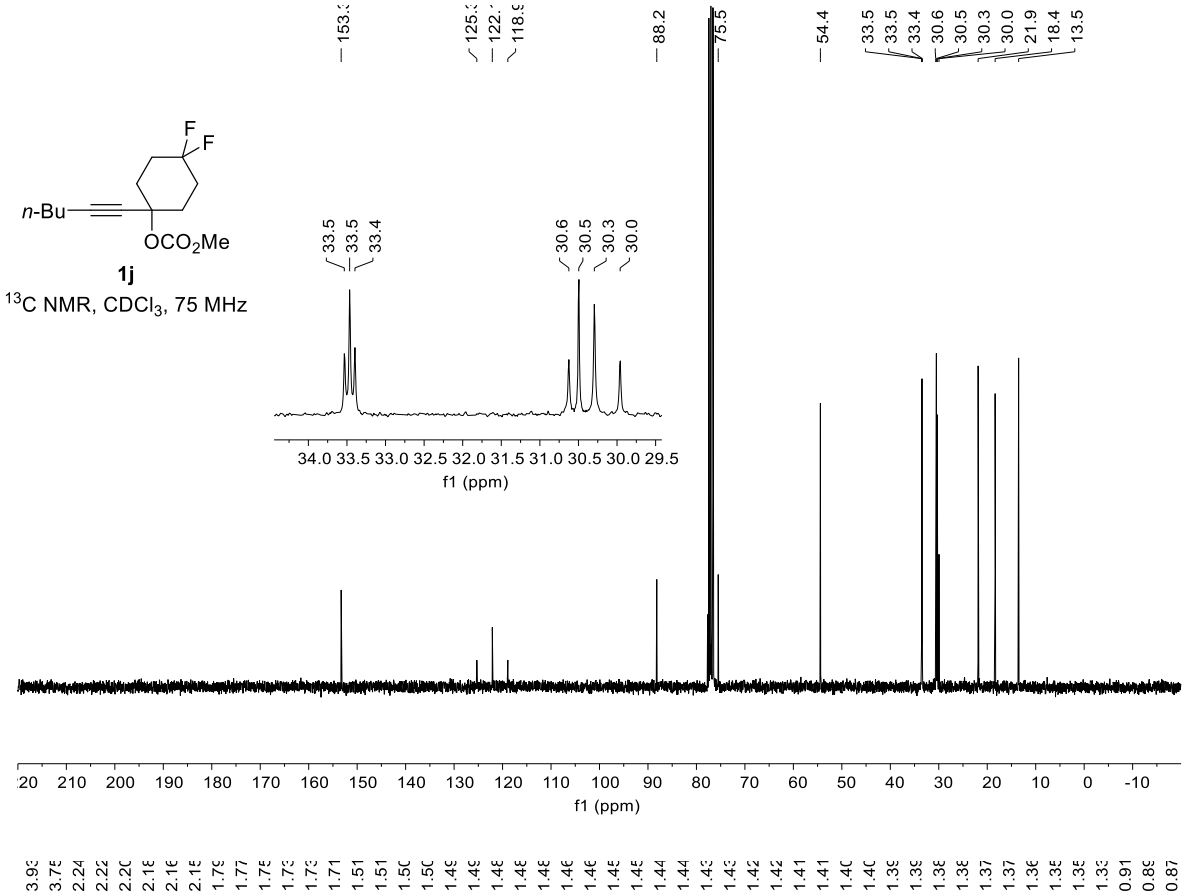
1j

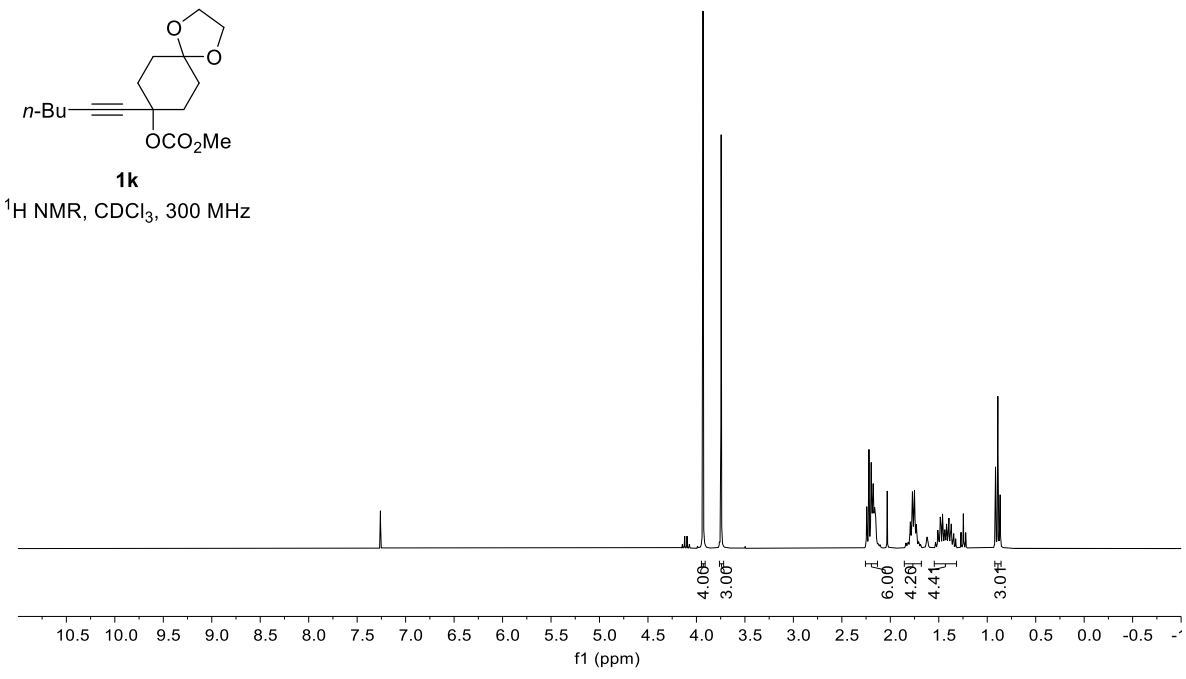
^{1}H NMR, $CDCl_3$, 300 MHz

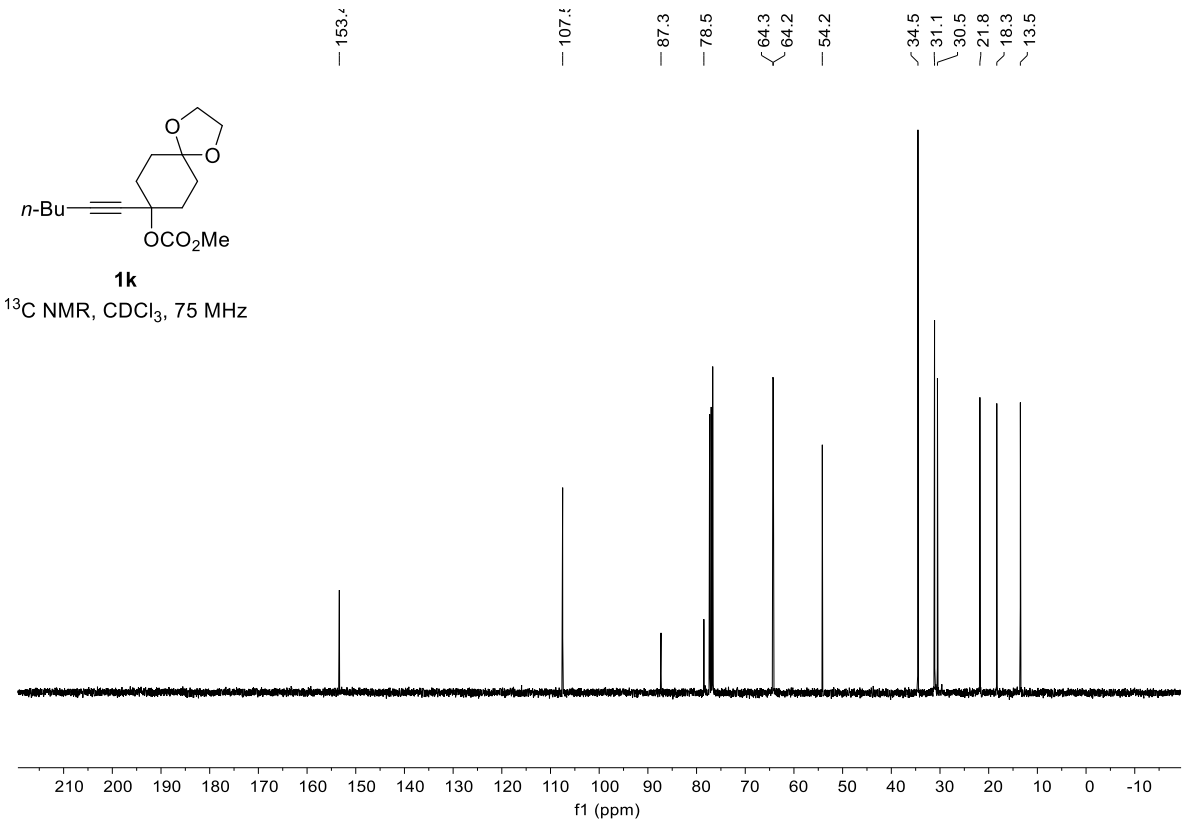
1j

^{19}F NMR, $CDCl_3$, 282 MHz



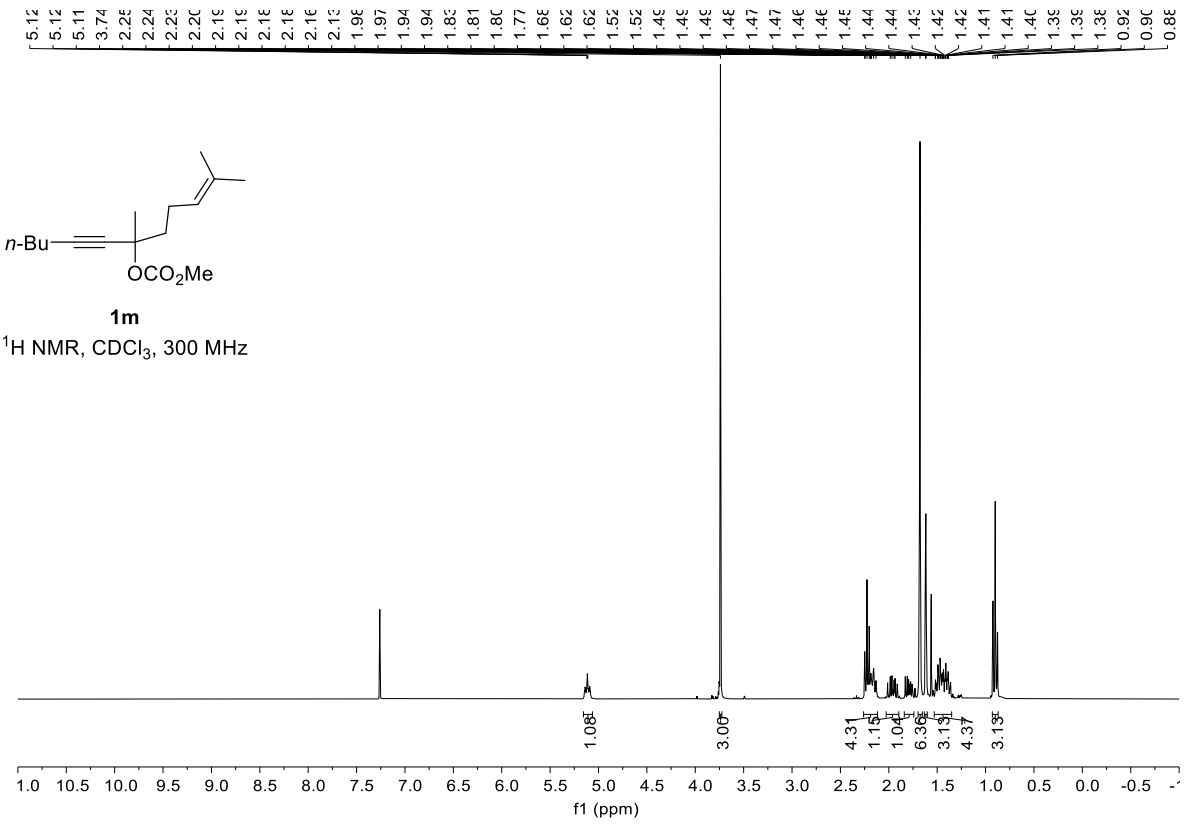

F
F
n-Bu
OCO2Me
1j
13C NMR, CDCl3, 75 MHz
153.
125.
122.
118.
88.2
75.5
54.4
33.5
33.5
33.4
30.6
30.5
30.3
30.0
21.9
18.4
13.5
34.0 33.5 33.0 32.5 32.0 31.5 31.0 30.5 30.0 29.5
f1 (ppm)
f1 (ppm)


O
O
n-Bu
OCO2Me
1k
1H NMR, CDCl3, 300 MHz
4.00
3.00
6.00
4.26
4.41
3.01
f1 (ppm)



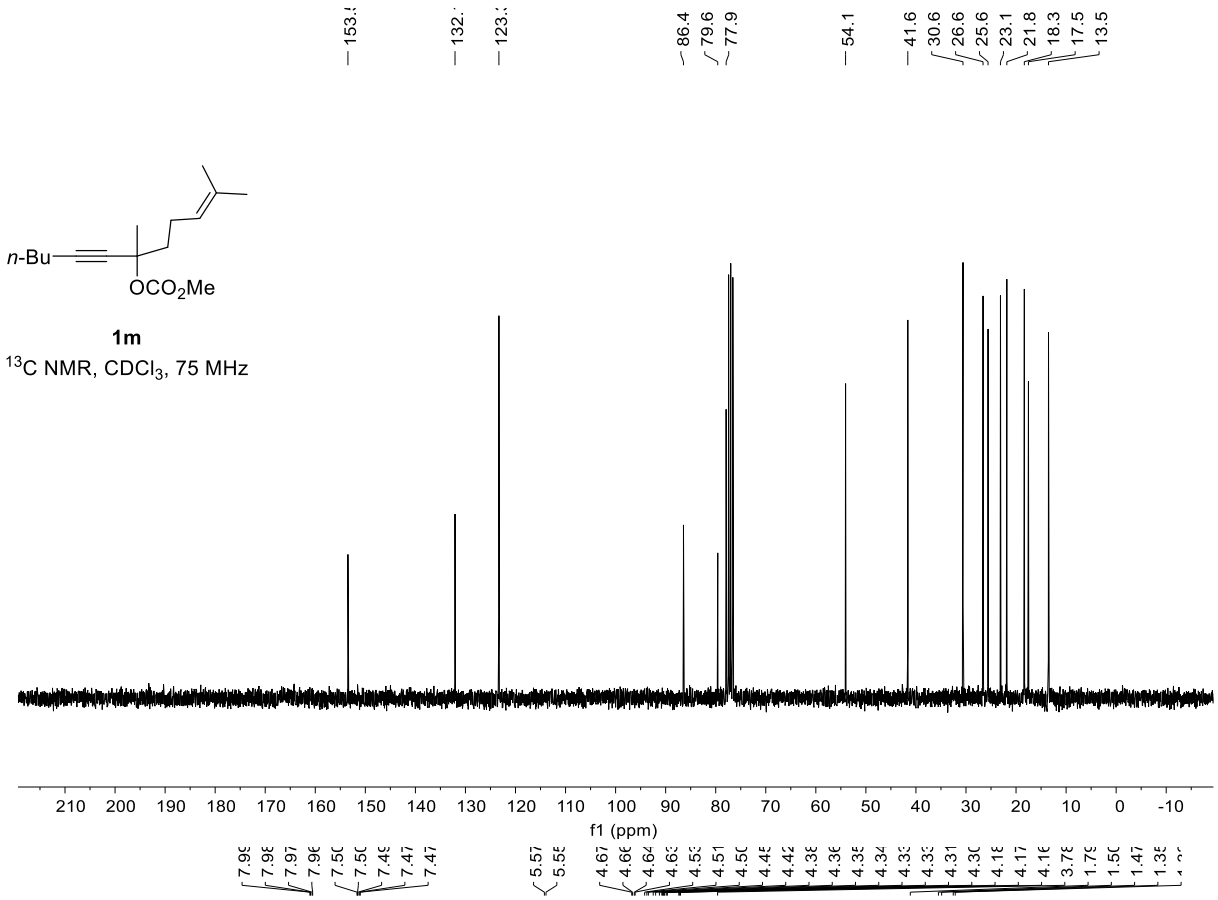
1k

^{13}C NMR, $CDCl_3$, 75 MHz



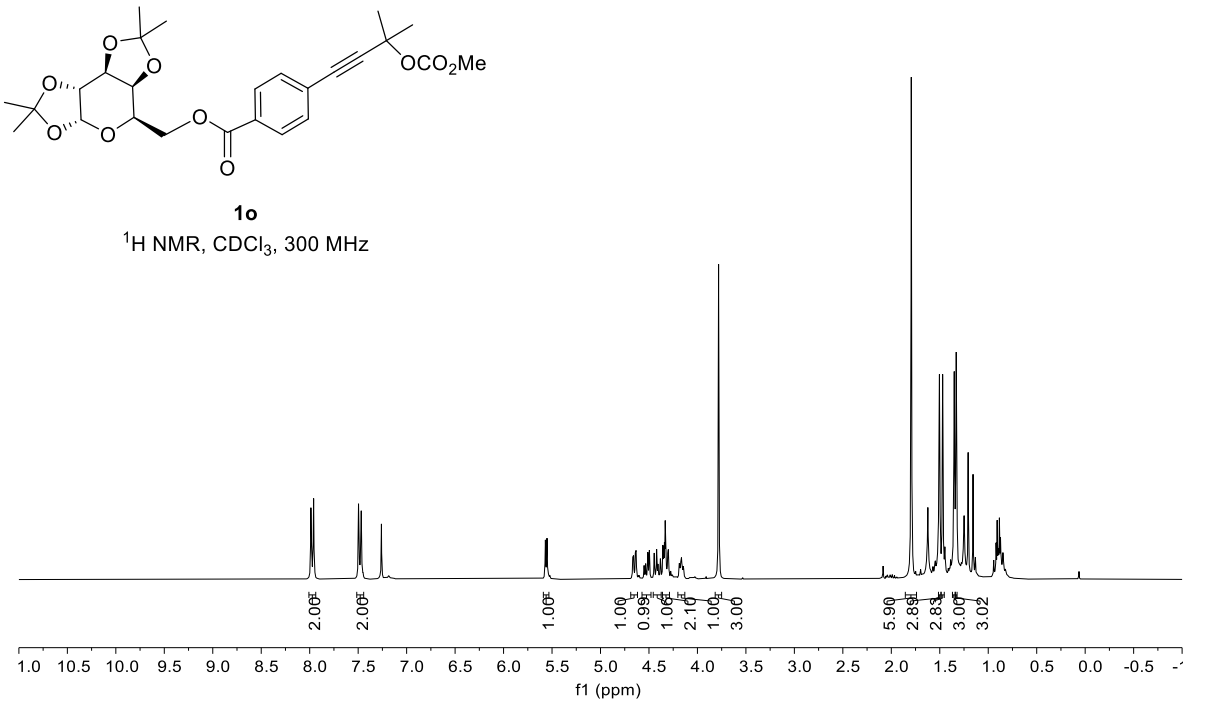
1m

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



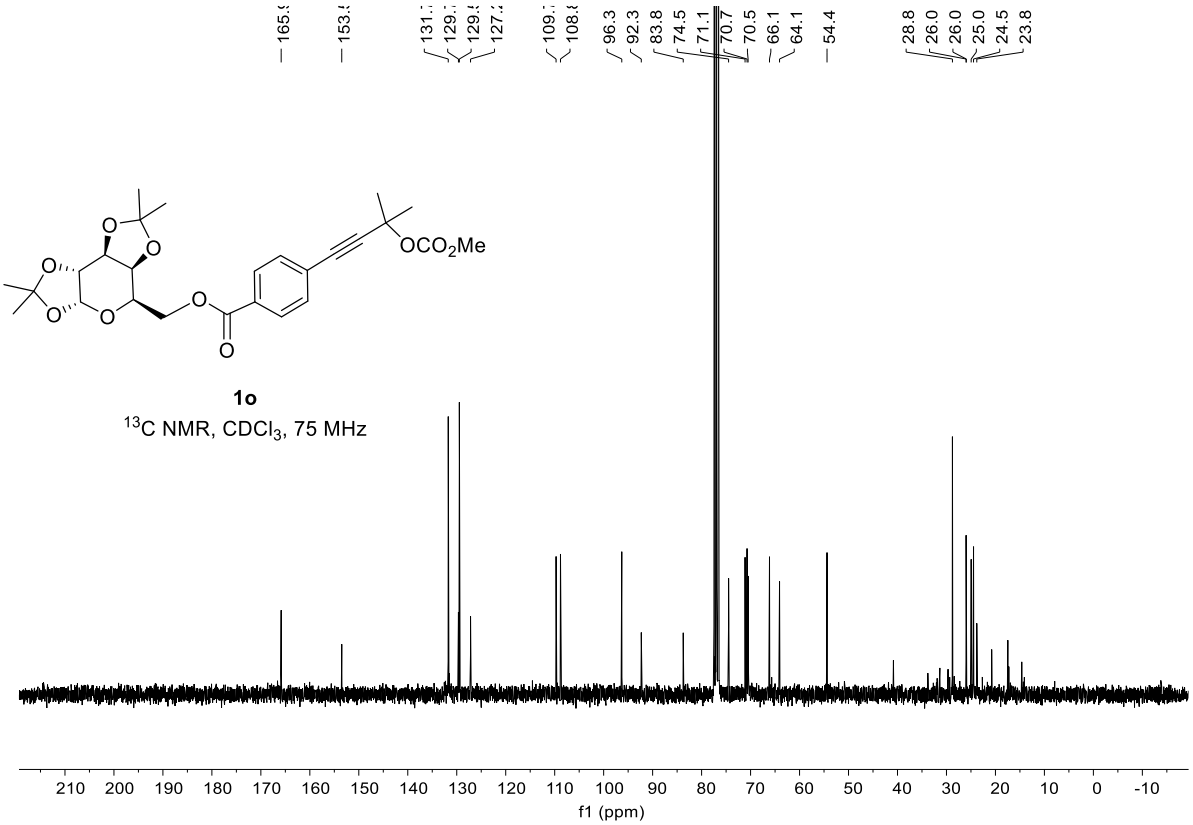
1m

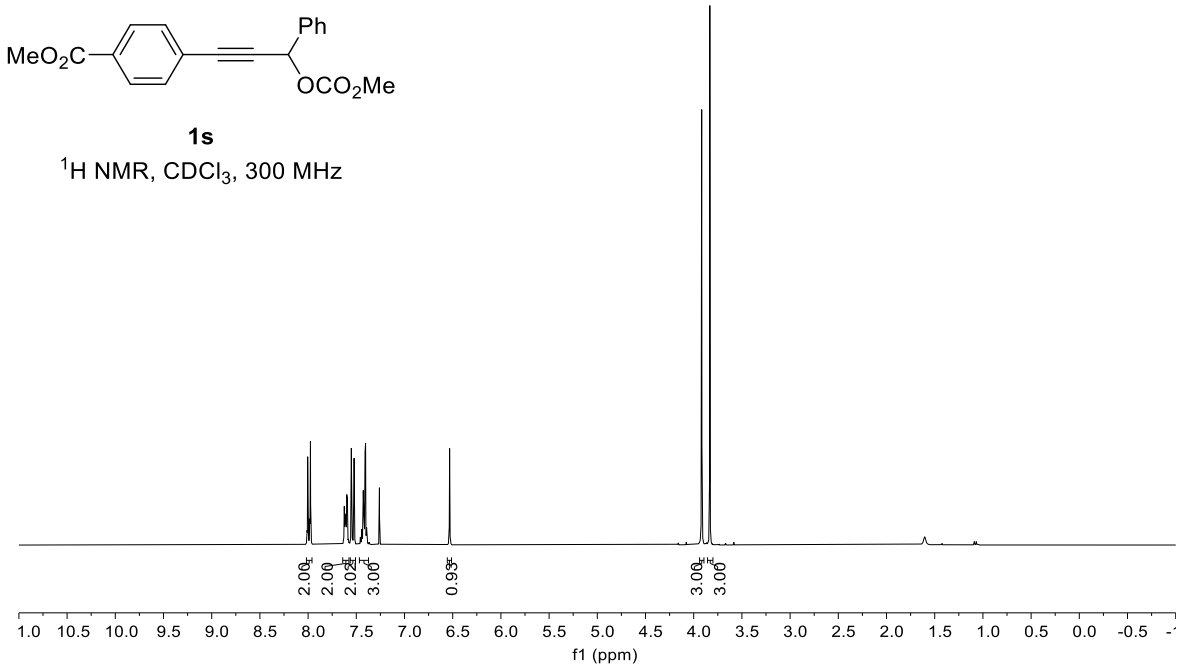
^{13}C NMR, $CDCl_3$, 75 MHz

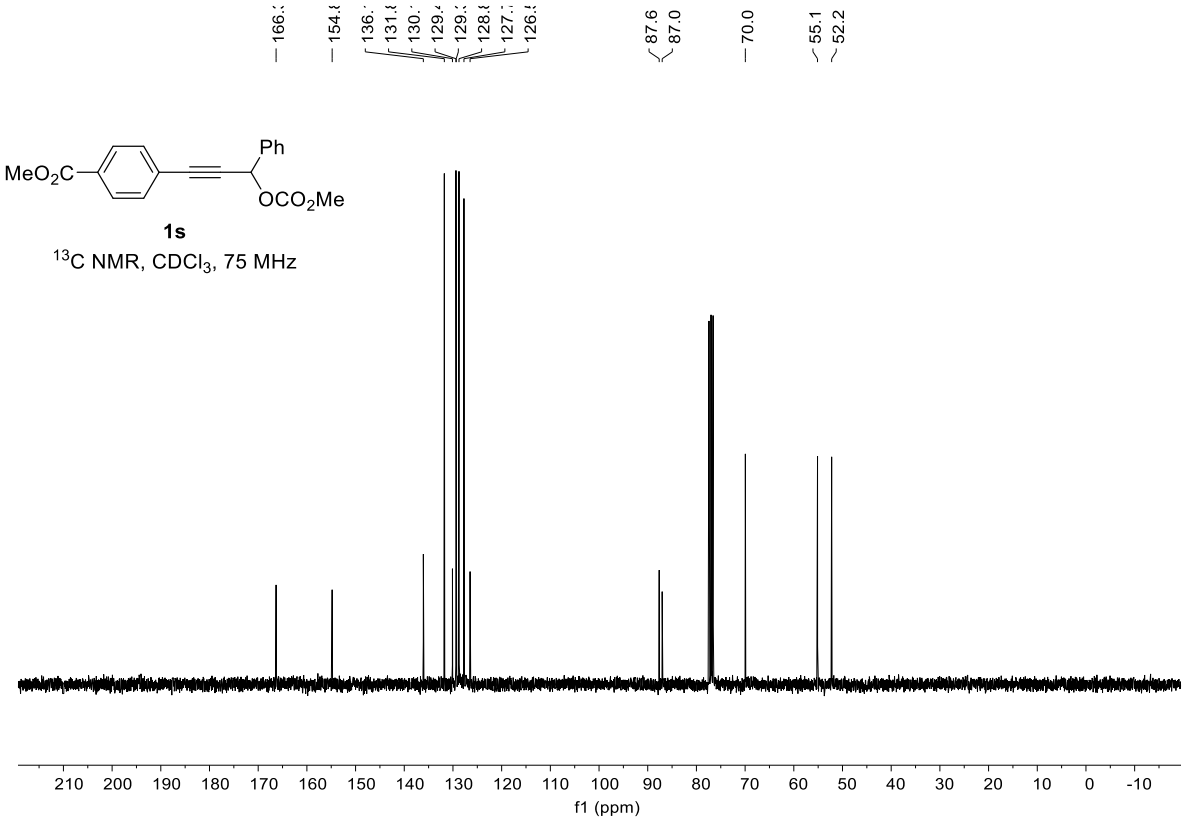


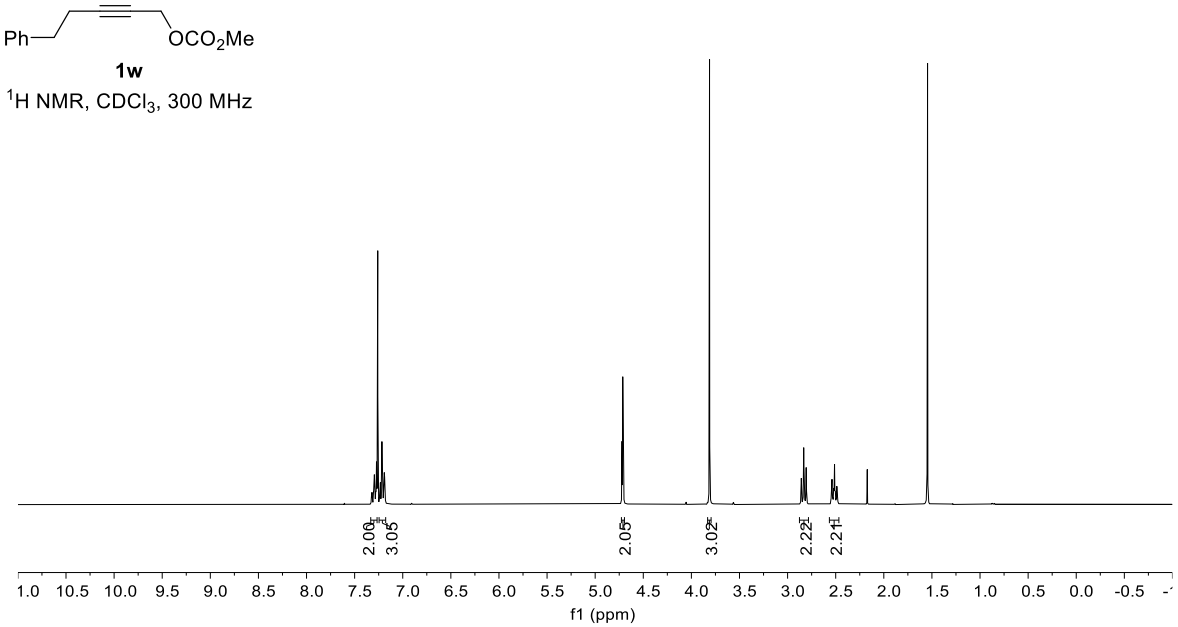
1o

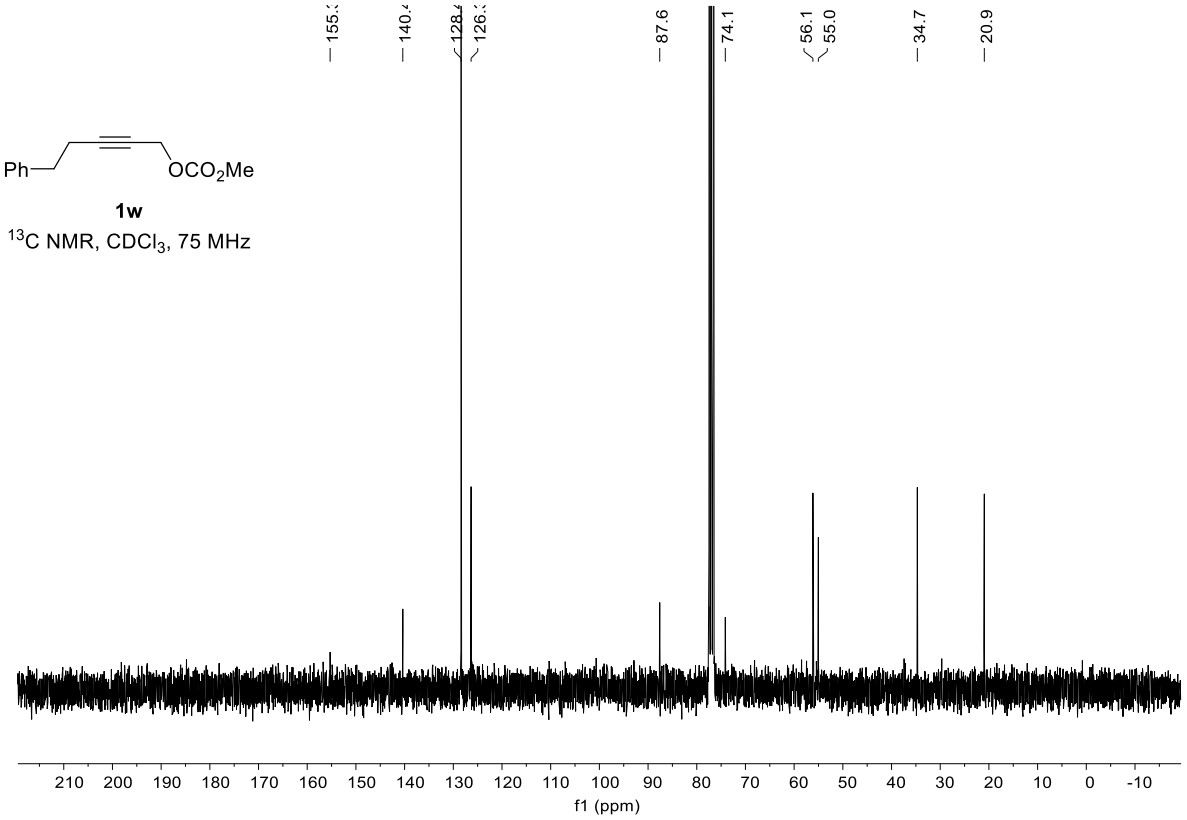
^{1}H NMR, $CDCl_3$, 300 MHz

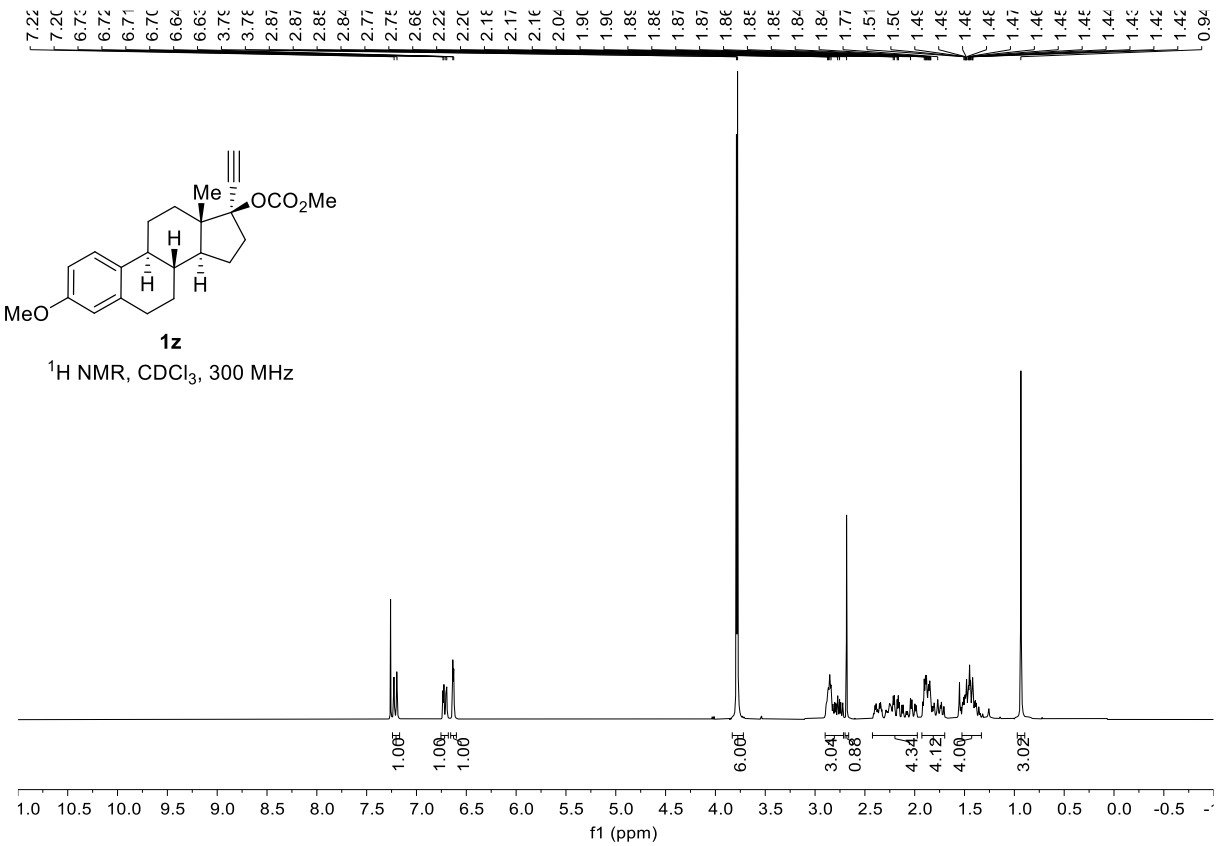

OCO2Me
1o
13C NMR, CDCl3, 75 MHz
f1 (ppm)

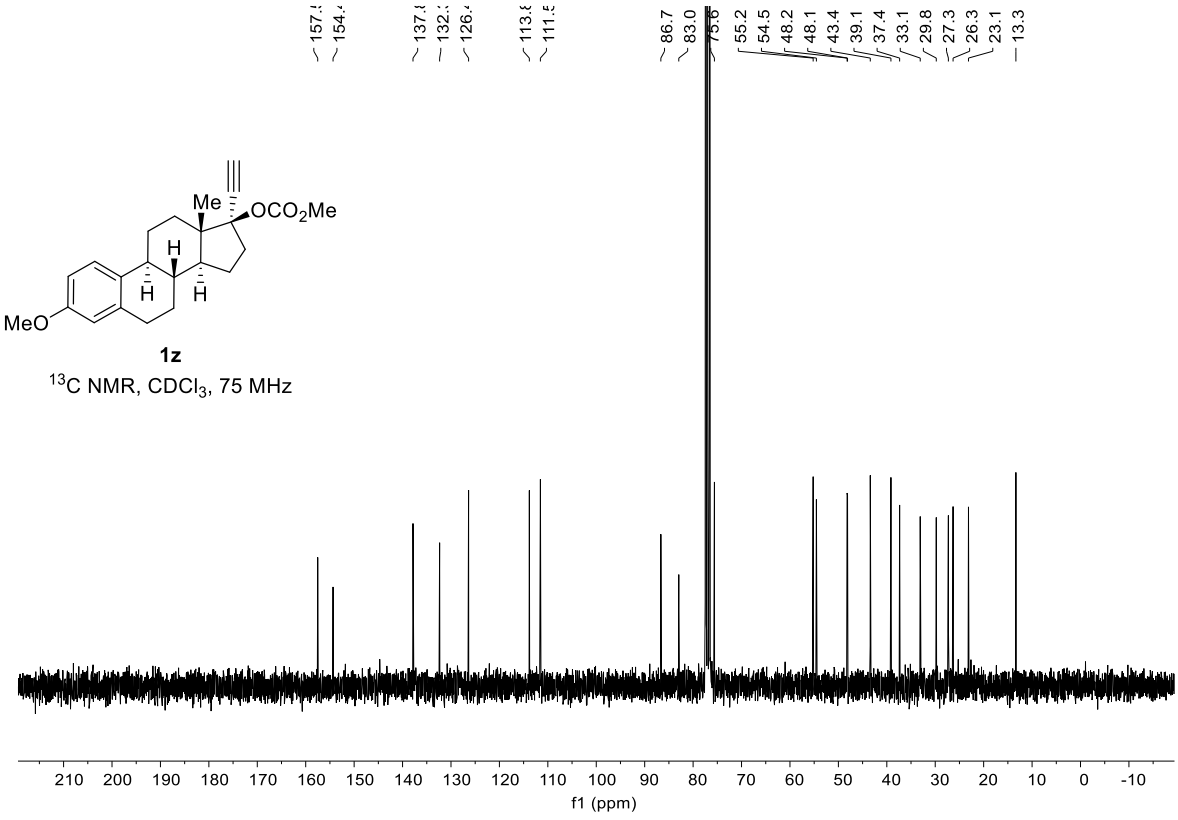

MeO2C
Ph
OCO2Me
1s
1H NMR, CDCl3, 300 MHz
f1 (ppm)


MeO2C
Ph
OCO2Me
1s
13C NMR, CDCl3, 75 MHz
f1 (ppm)


Ph
OCO2Me
1w
1H NMR, CDCl3, 300 MHz
f1 (ppm)

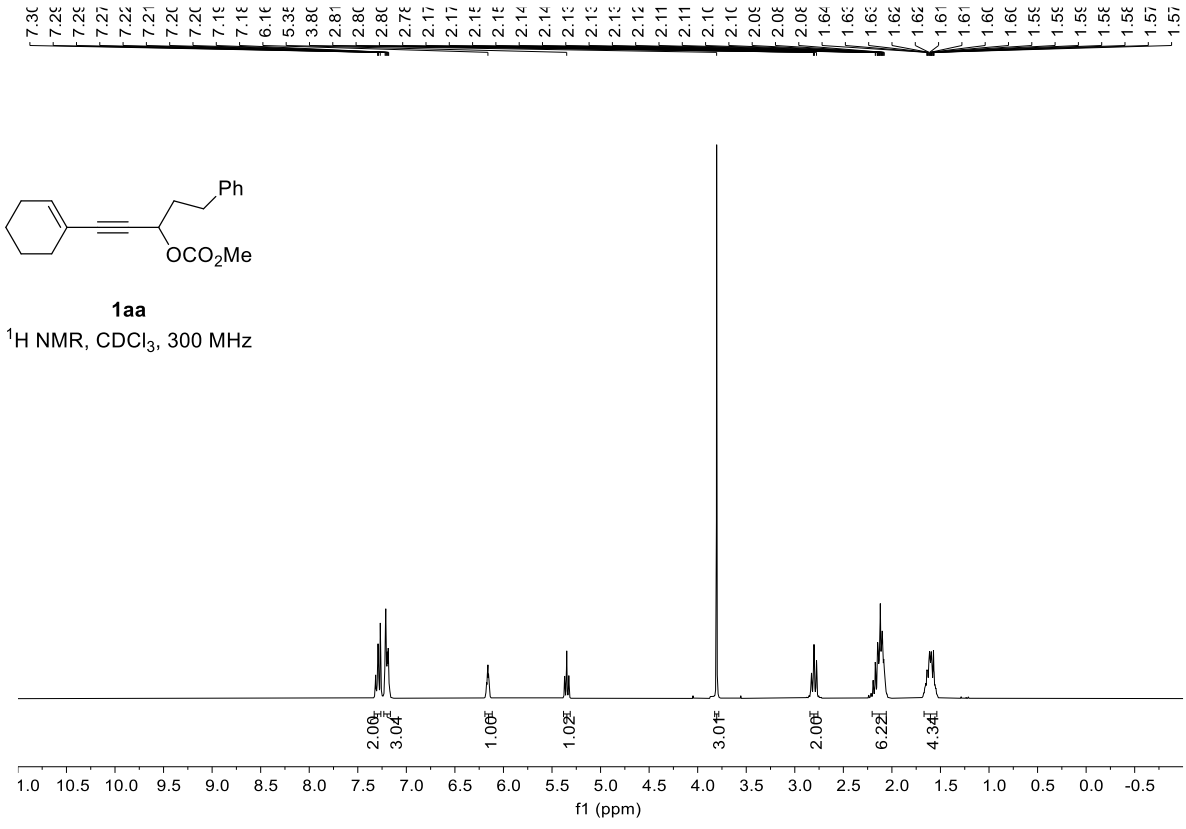

155.3
140.4
128.4
126.3
87.6
74.1
56.1
55.0
34.7
20.9
Ph
OCO2Me
1w
13C NMR, CDCl3, 75 MHz
f1 (ppm)


Me
OCO2Me
H
H
H
MeO
1z
1H NMR, CDCl3, 300 MHz
1.00
1.00
1.00
6.00
3.04
0.88
4.34
4.12
4.00
3.02
f1 (ppm)



1z

^{13}C NMR, $CDCl_3$, 75 MHz



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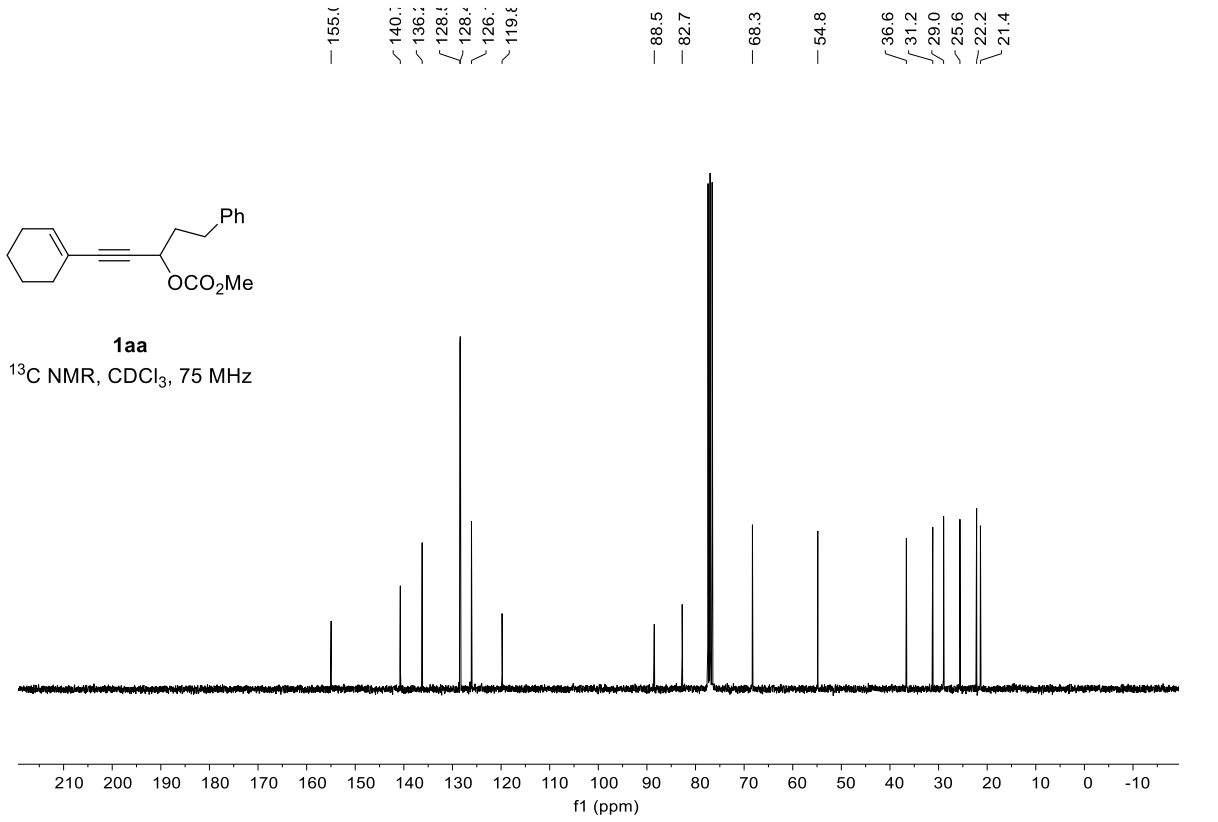

1aa

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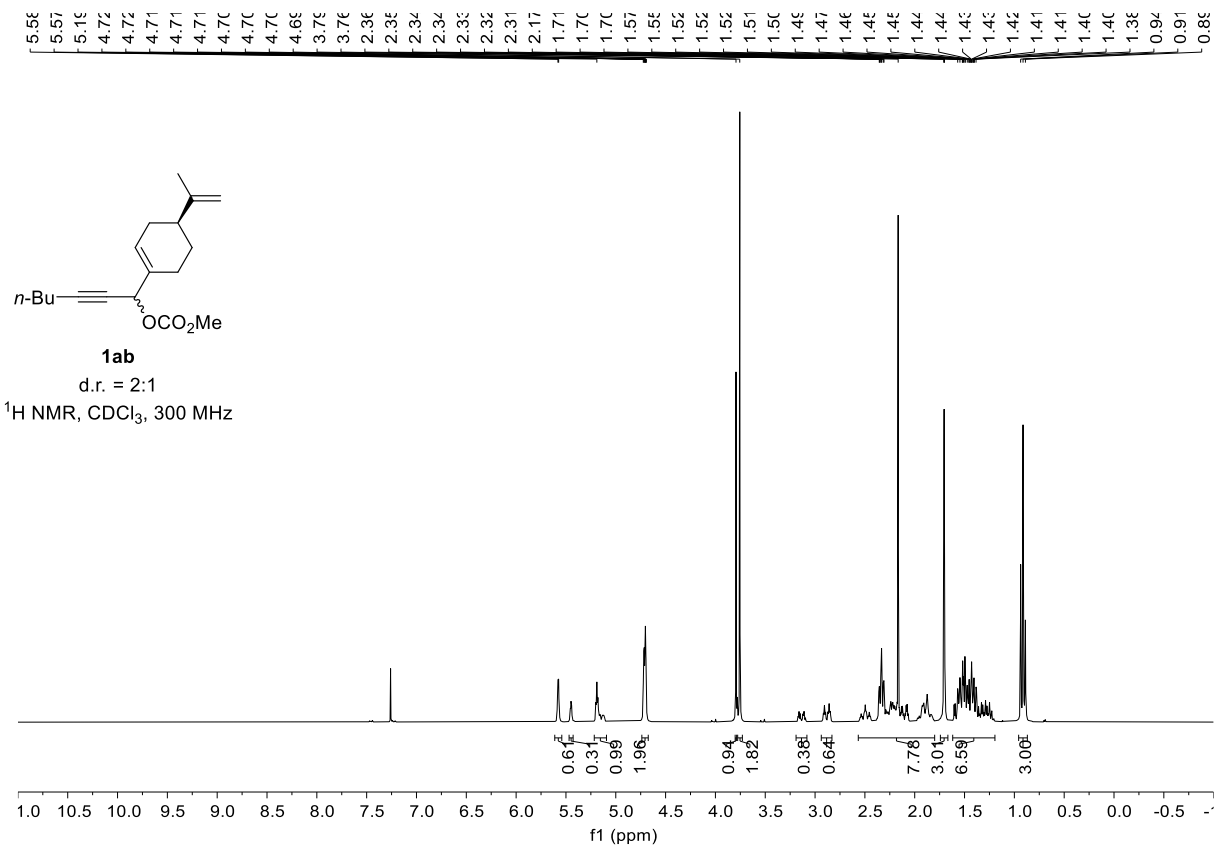

1ab

d.r. = 2:1

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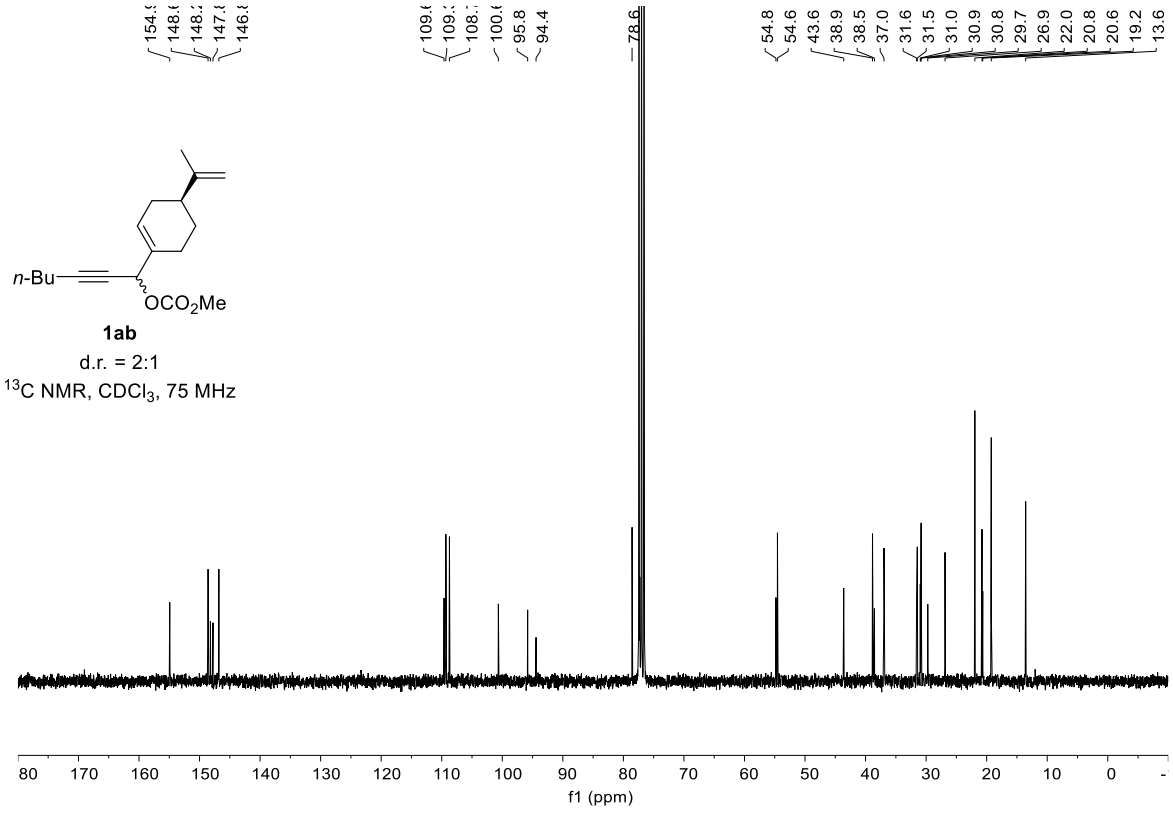

1ab

d.r. = 2:1

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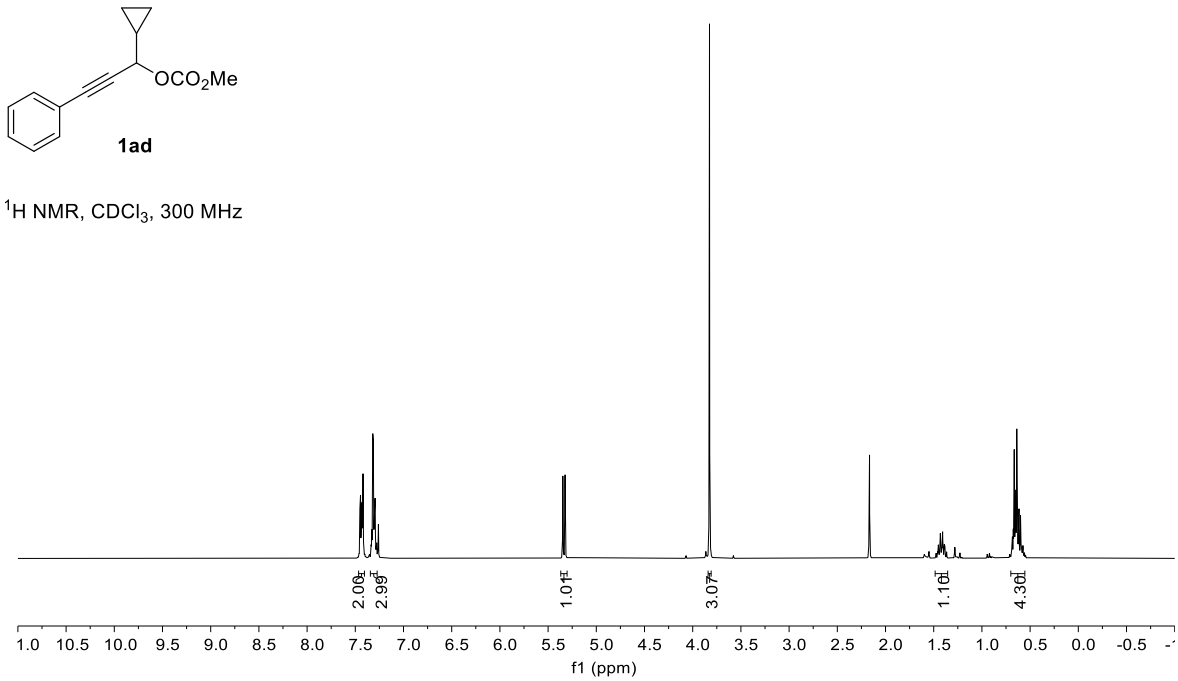
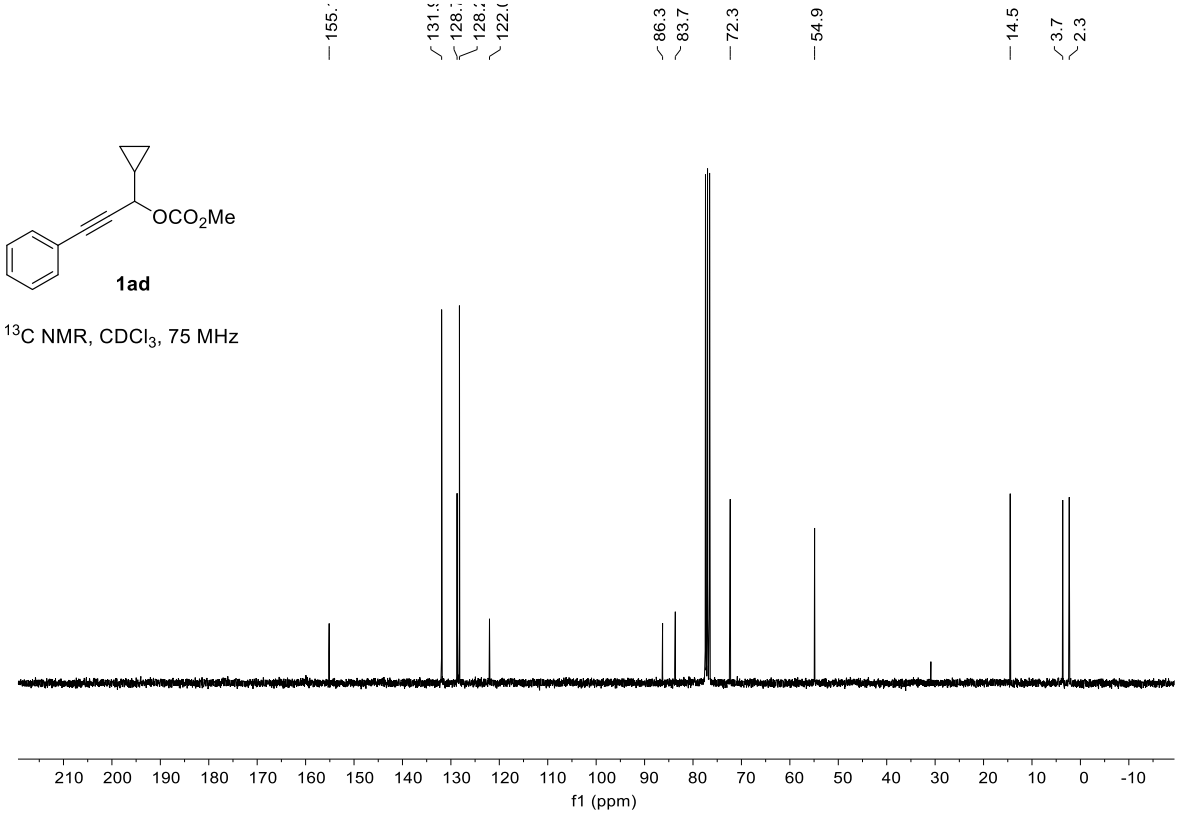
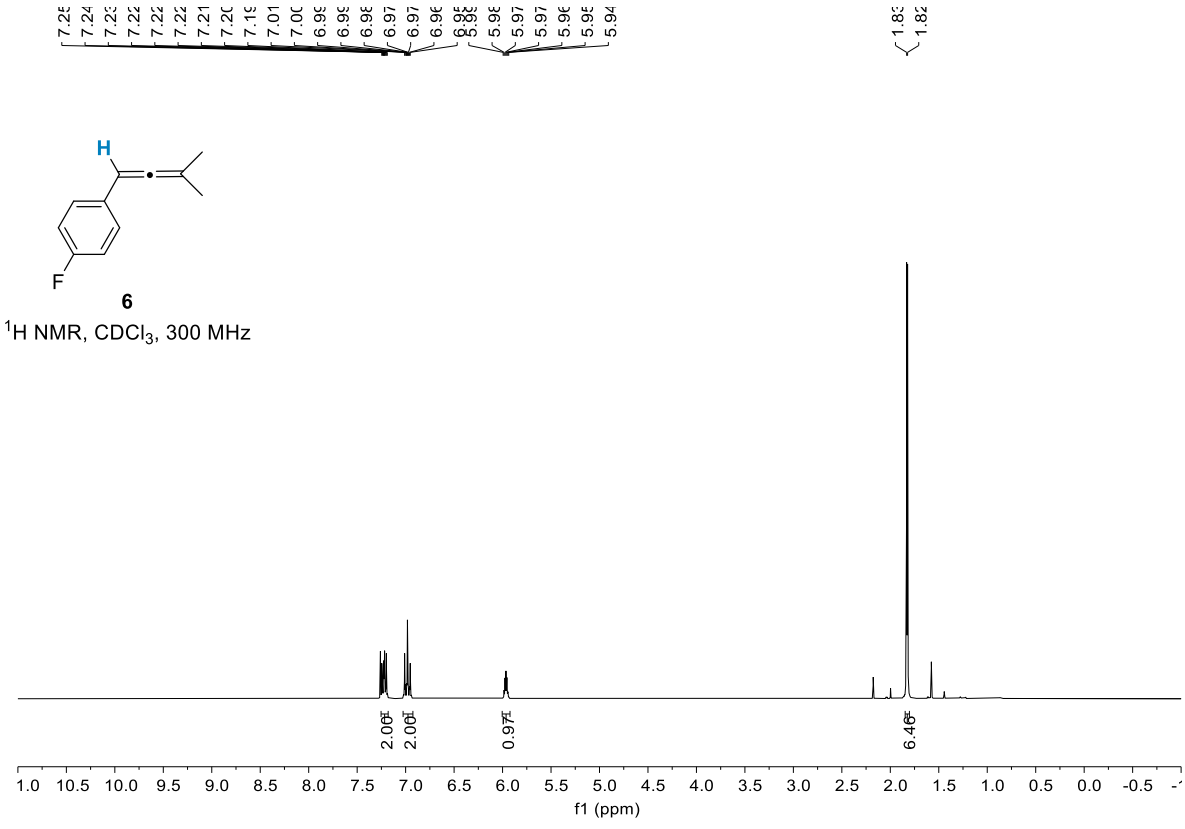
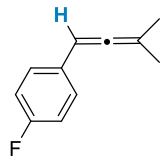


1ad

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

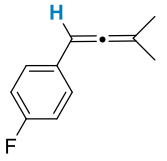

OCO2Me
1ad
13C NMR, CDCl3, 75 MHz
155.
131.
128.
128.
122.
86.3
83.7
72.3
54.9
14.5
3.7
2.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
F
6
1H NMR, CDCl3, 300 MHz
2.00
2.00
0.97
6.46
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



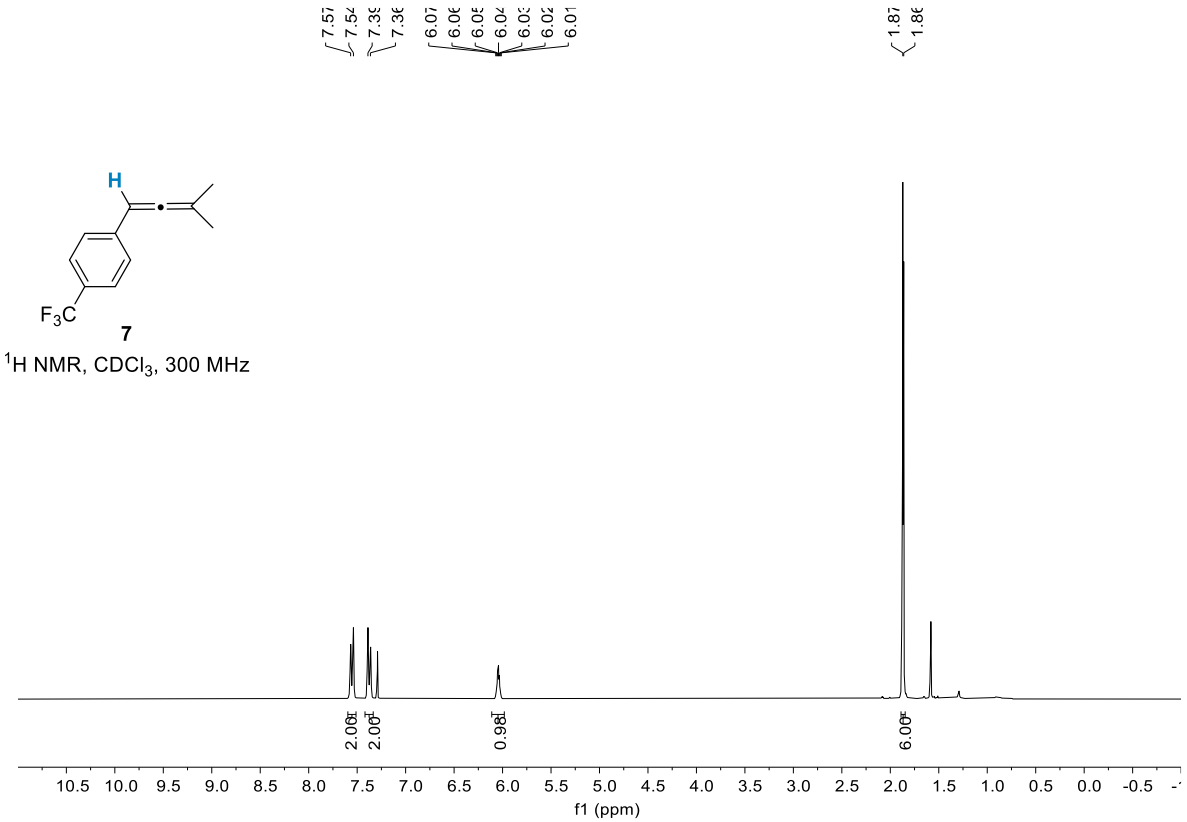
6

^{19}F NMR, $CDCl_3$, 282 MHz



6

^{13}C NMR, $CDCl_3$, 75 MHz



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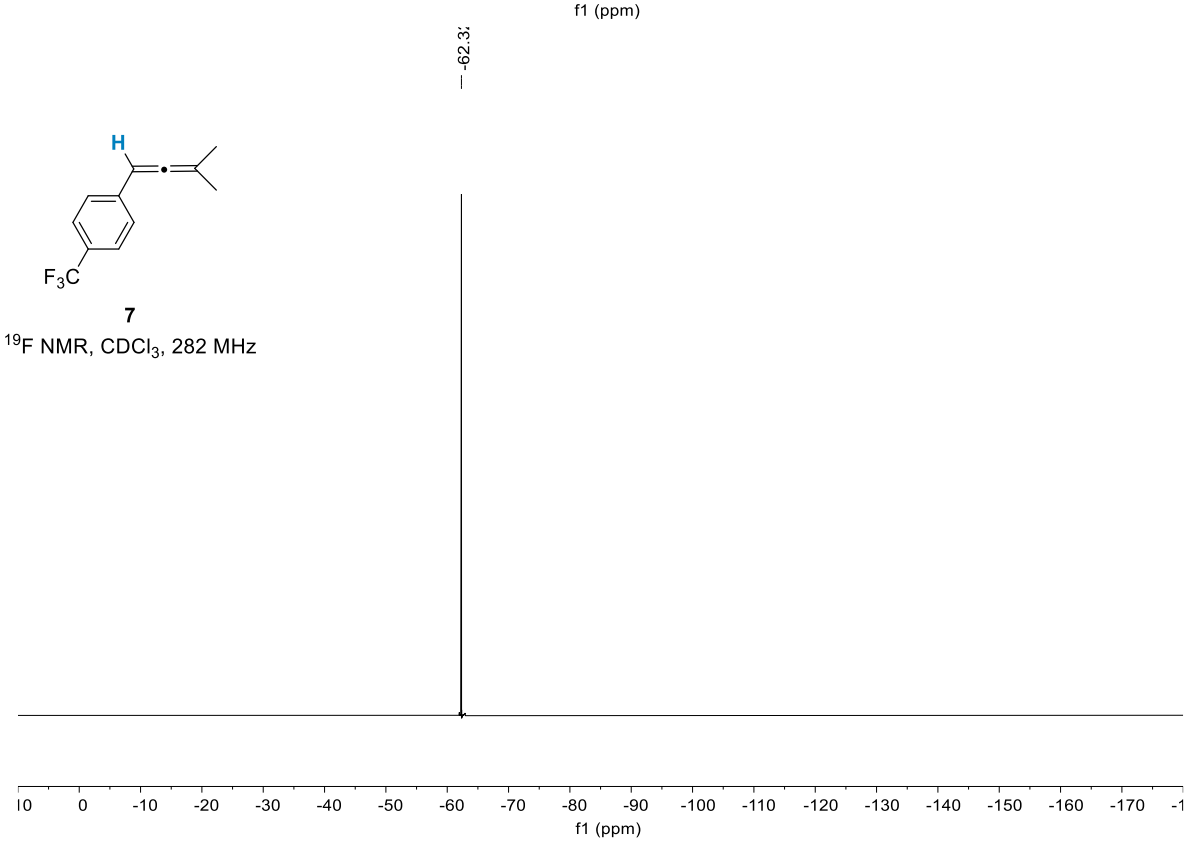
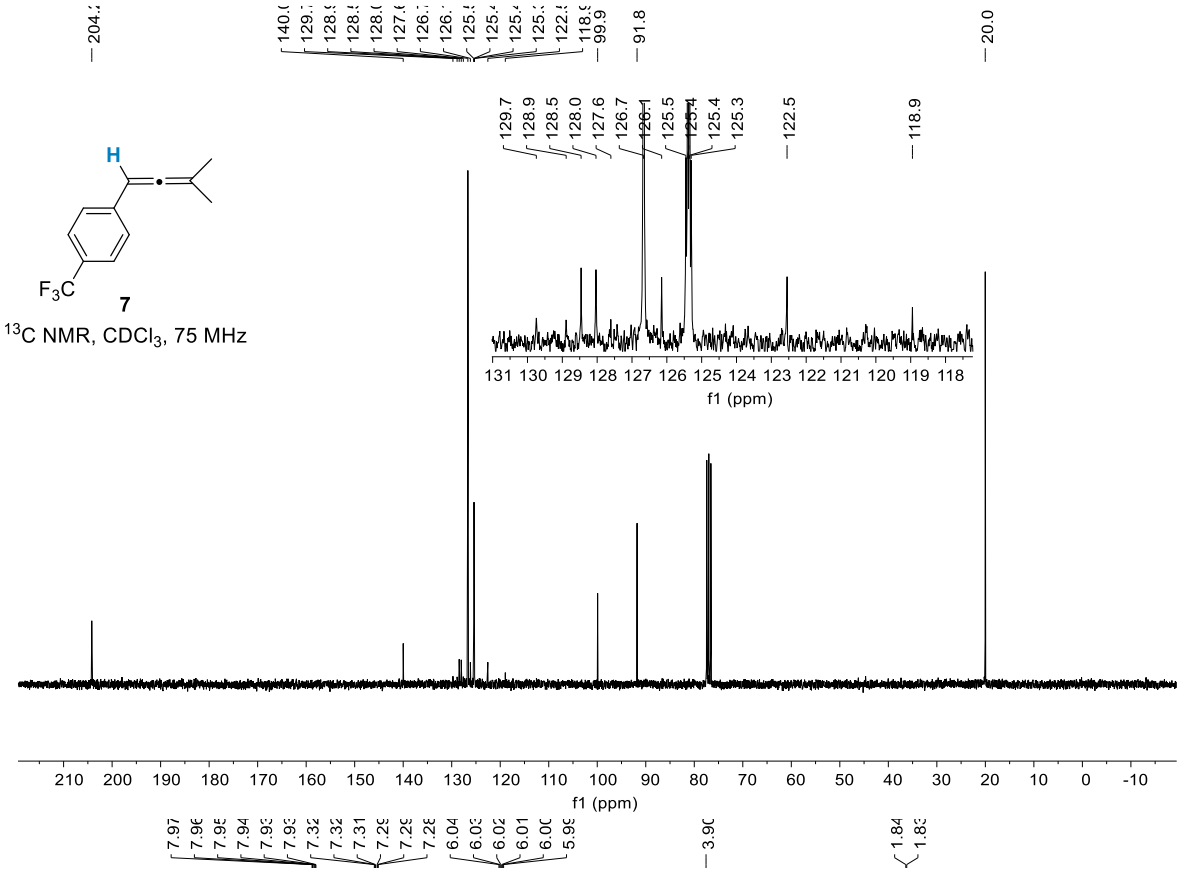
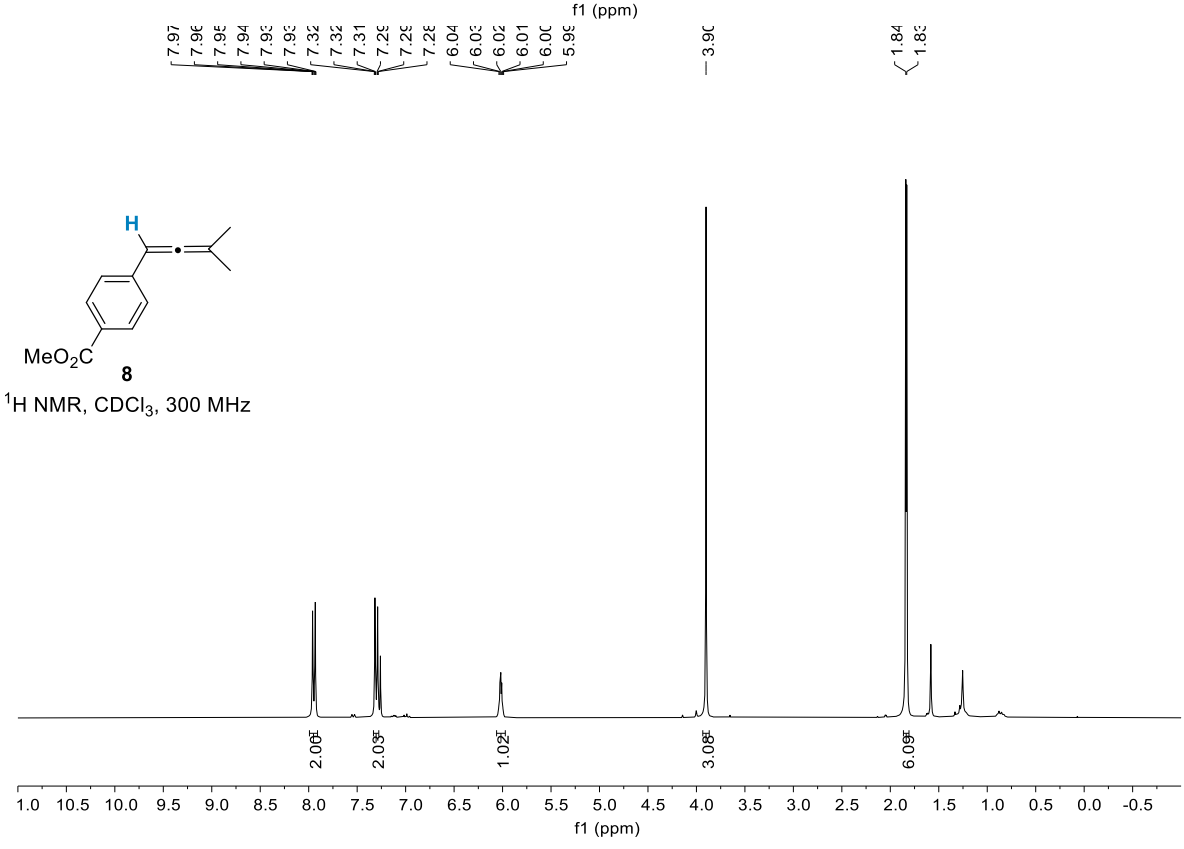
^{1}H NMR, $CDCl_3$, 300 MHz

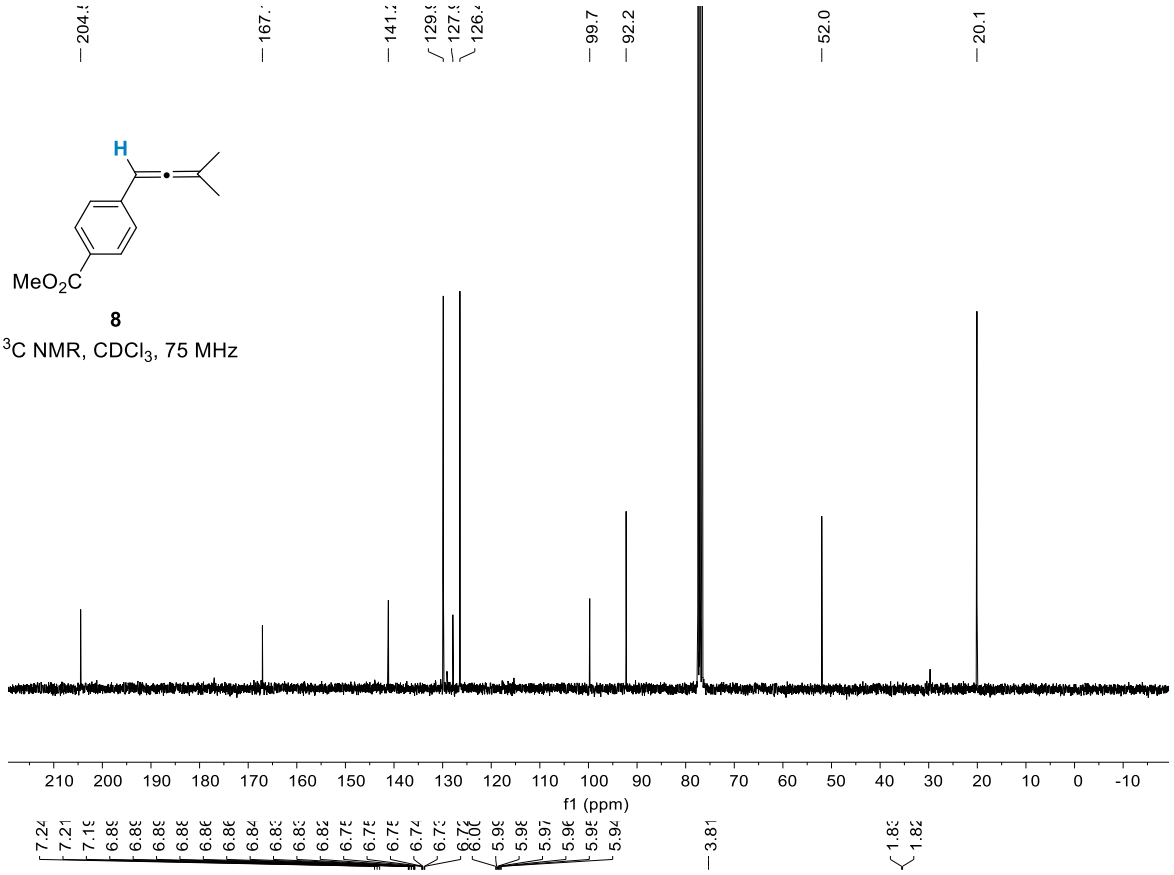


7

^{19}F NMR, $CDCl_3$, 282 MHz

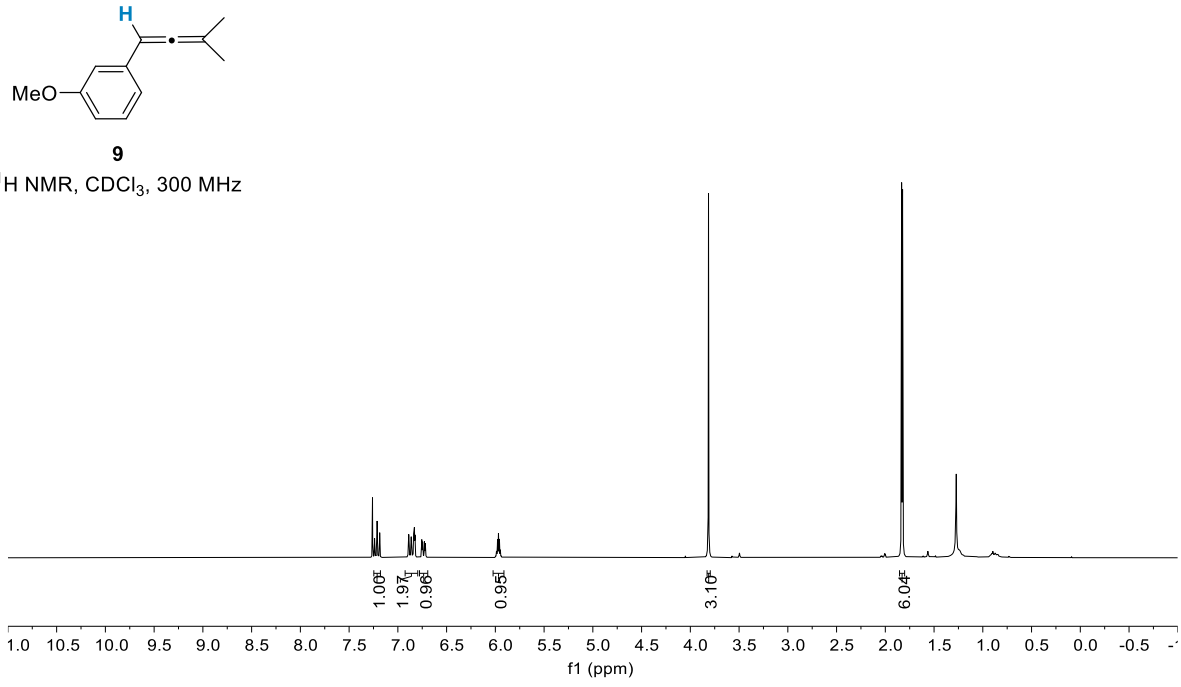

H
F3C
7
13C NMR, CDCl3, 75 MHz
f1 (ppm)


H
MeO2C
8
1H NMR, CDCl3, 300 MHz
f1 (ppm)



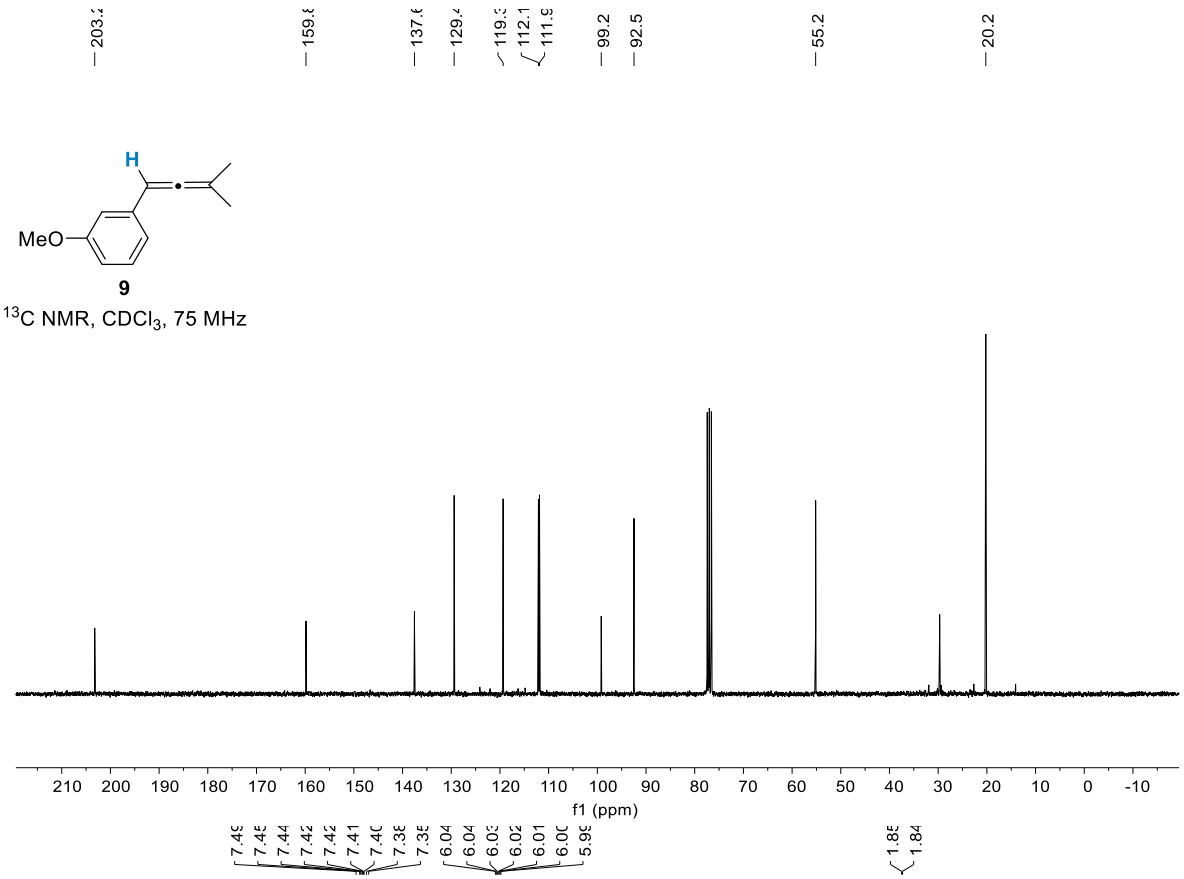
8

^{13}C NMR, $CDCl_3$, 75 MHz



9

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


203.4
159.8
137.6
129.4
119.3
112.1
111.9
99.2
92.5
55.2
20.2
H
MeO
9
13C NMR, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
7.45
7.45
7.44
7.43
7.42
7.41
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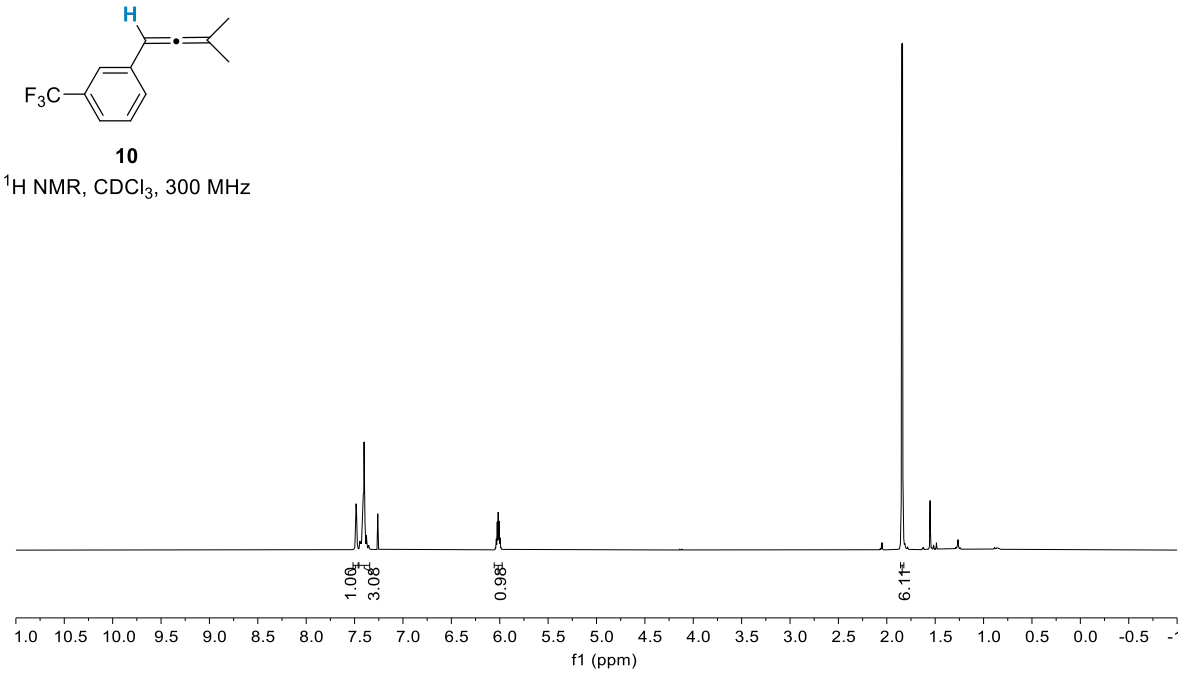
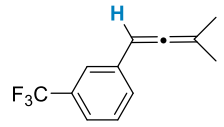
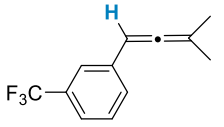
6.02
6.01
6.00
5.99
1.85
1.84


H
F3C
10
1H NMR, CDCl3, 300 MHz
1.00
3.08
0.98
6.11
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



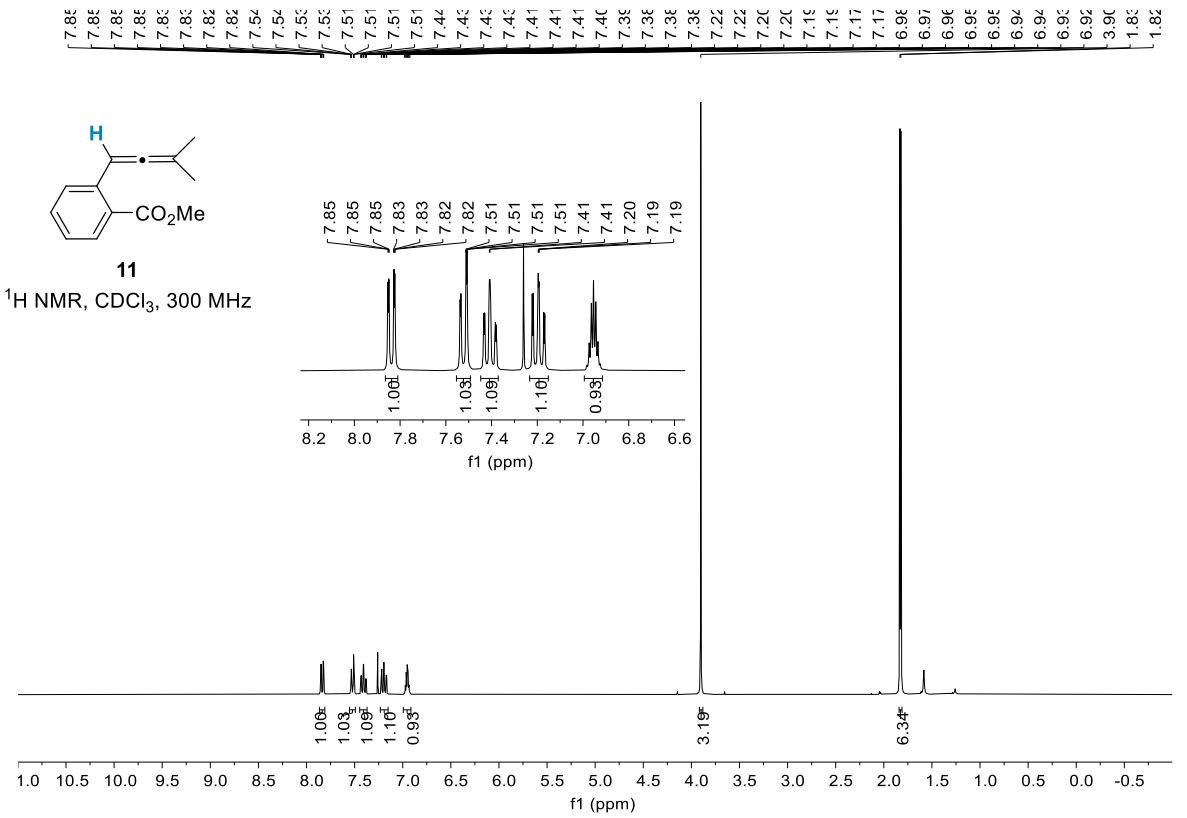
10

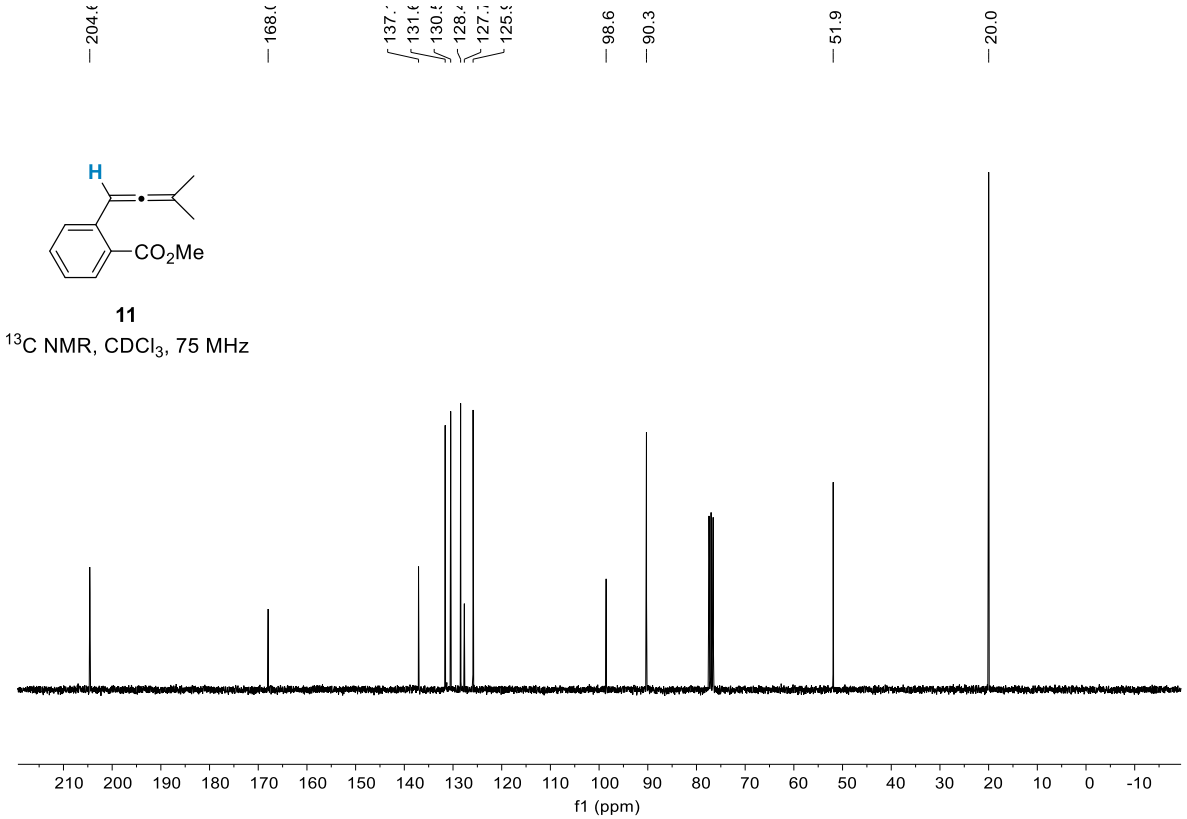
^{19}F NMR, $CDCl_3$, 282 MHz

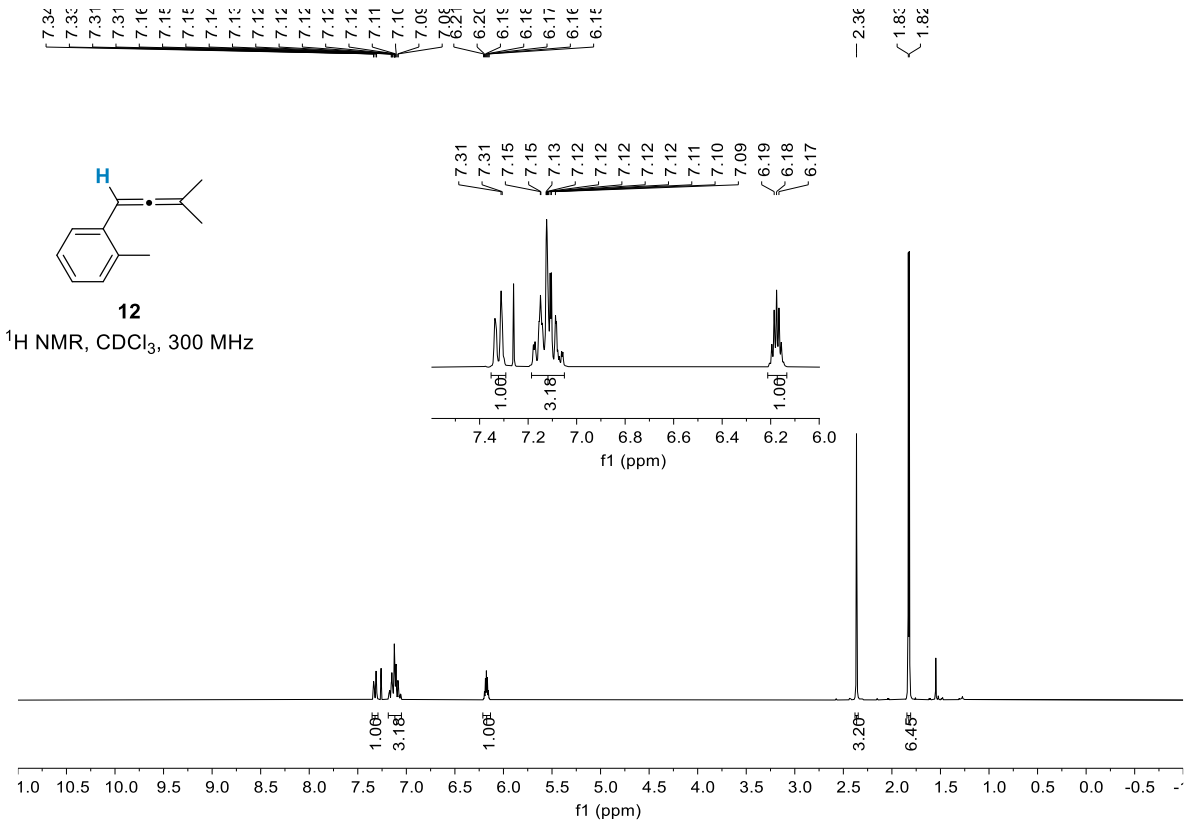


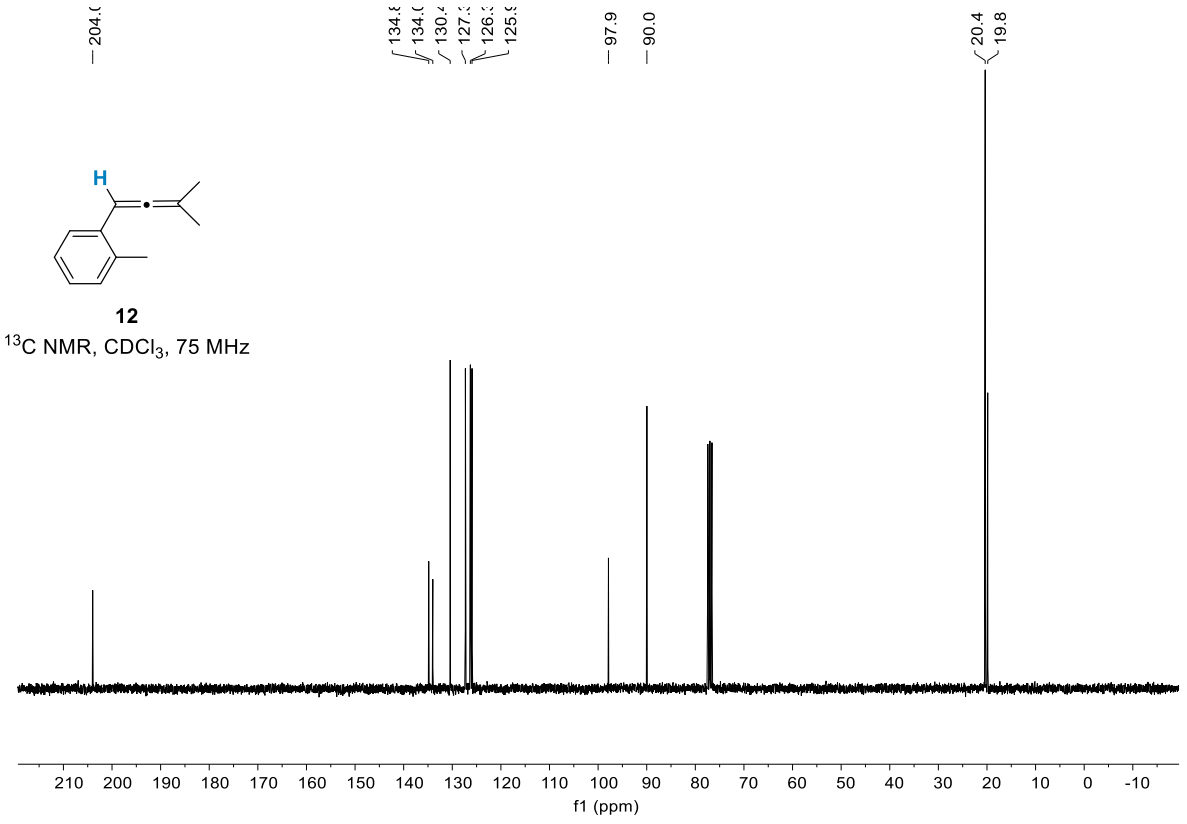
10

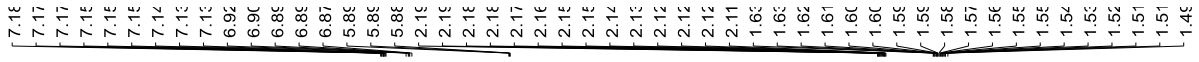
^{13}C NMR, $CDCl_3$, 75 MHz

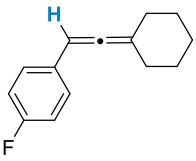

H
CO2Me
11
1H NMR, CDCl3, 300 MHz
f1 (ppm)


H
CO2Me
11
13C NMR, CDCl3, 75 MHz
f1 (ppm)


H
12
1H NMR, CDCl3, 300 MHz
f1 (ppm)

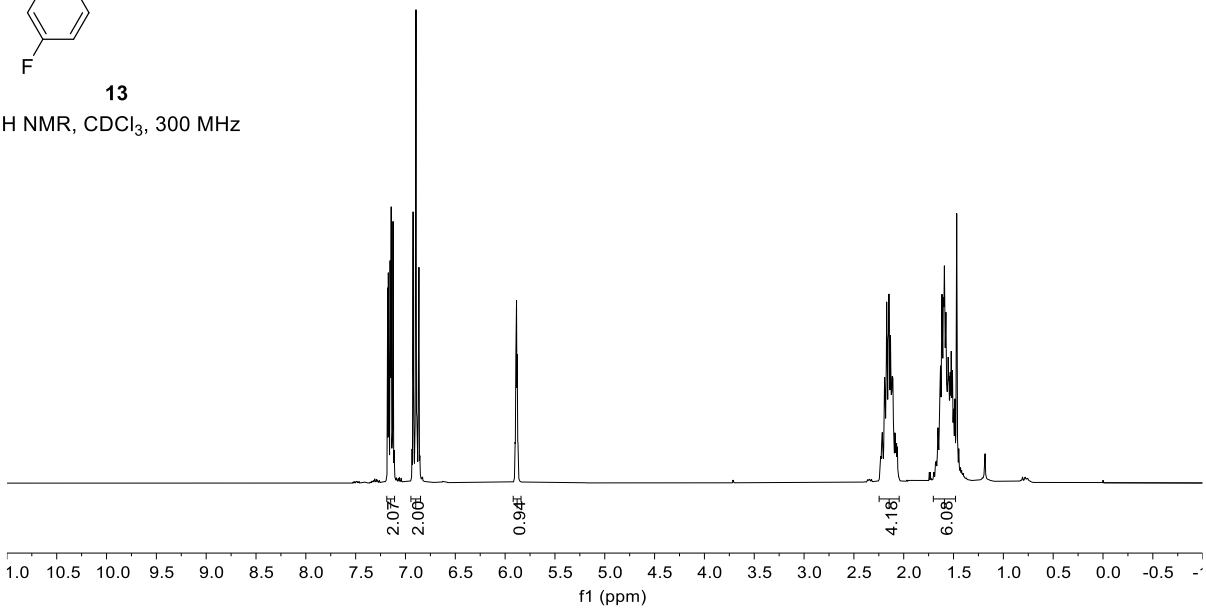

H
12
13C NMR, CDCl3, 75 MHz
f1 (ppm)

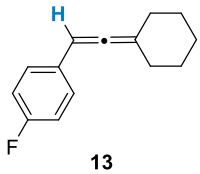




13

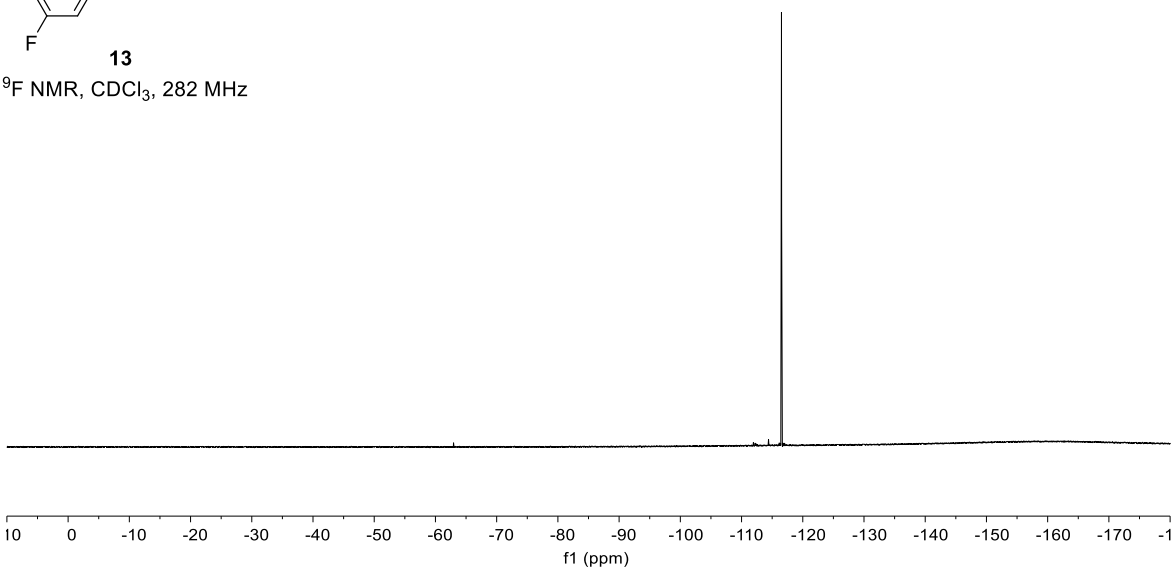
^{1}H NMR, $CDCl_3$, 300 MHz

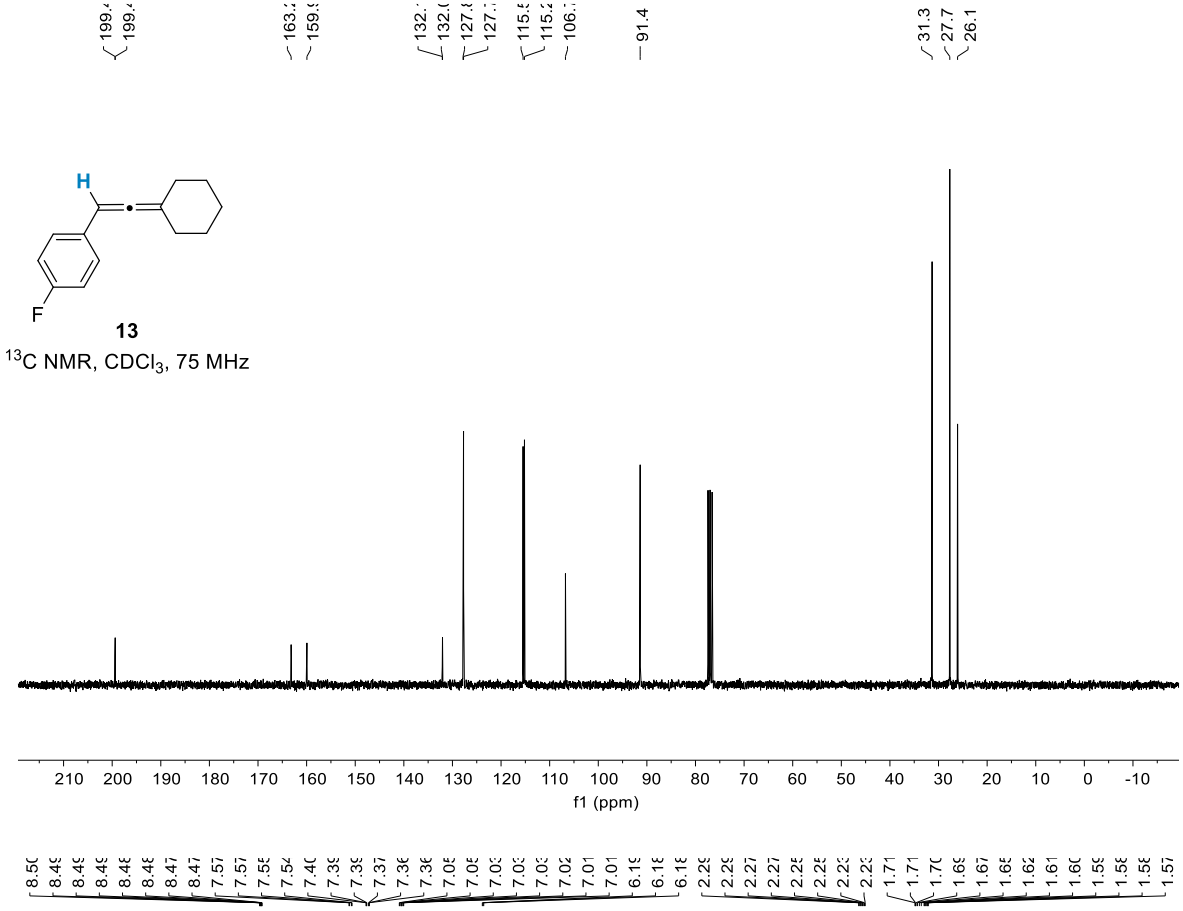


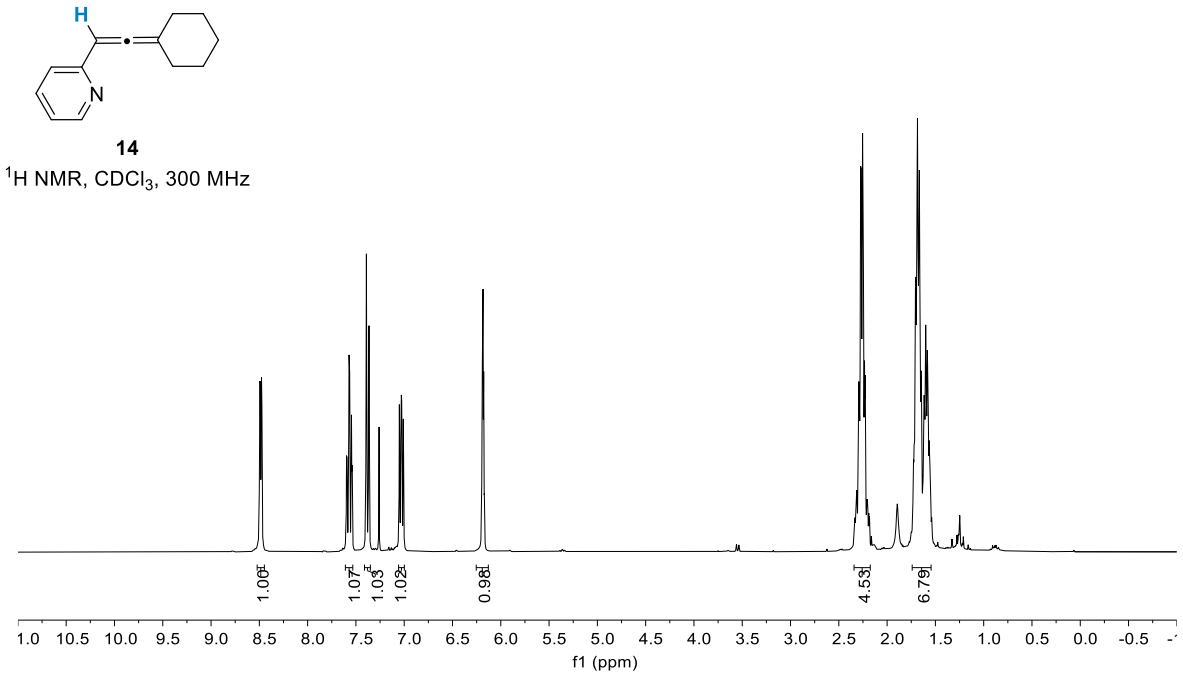


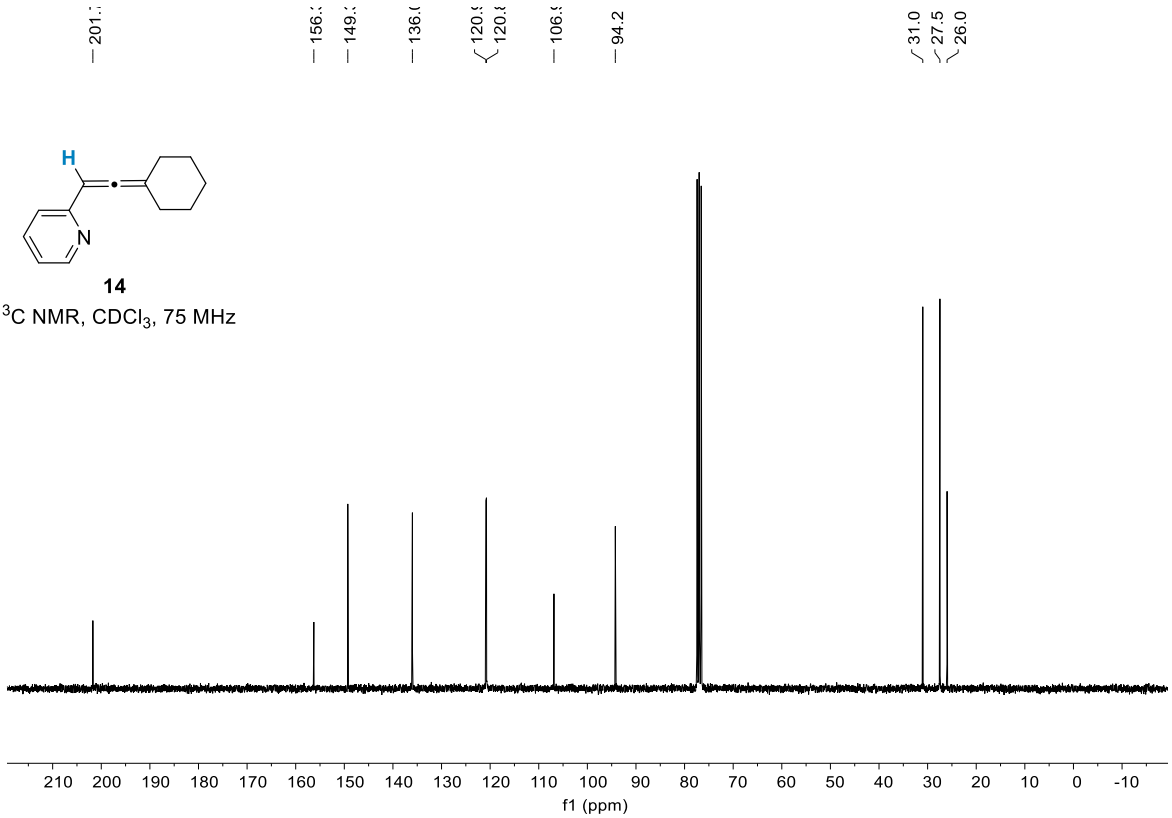
13

^{19}F NMR, $CDCl_3$, 282 MHz



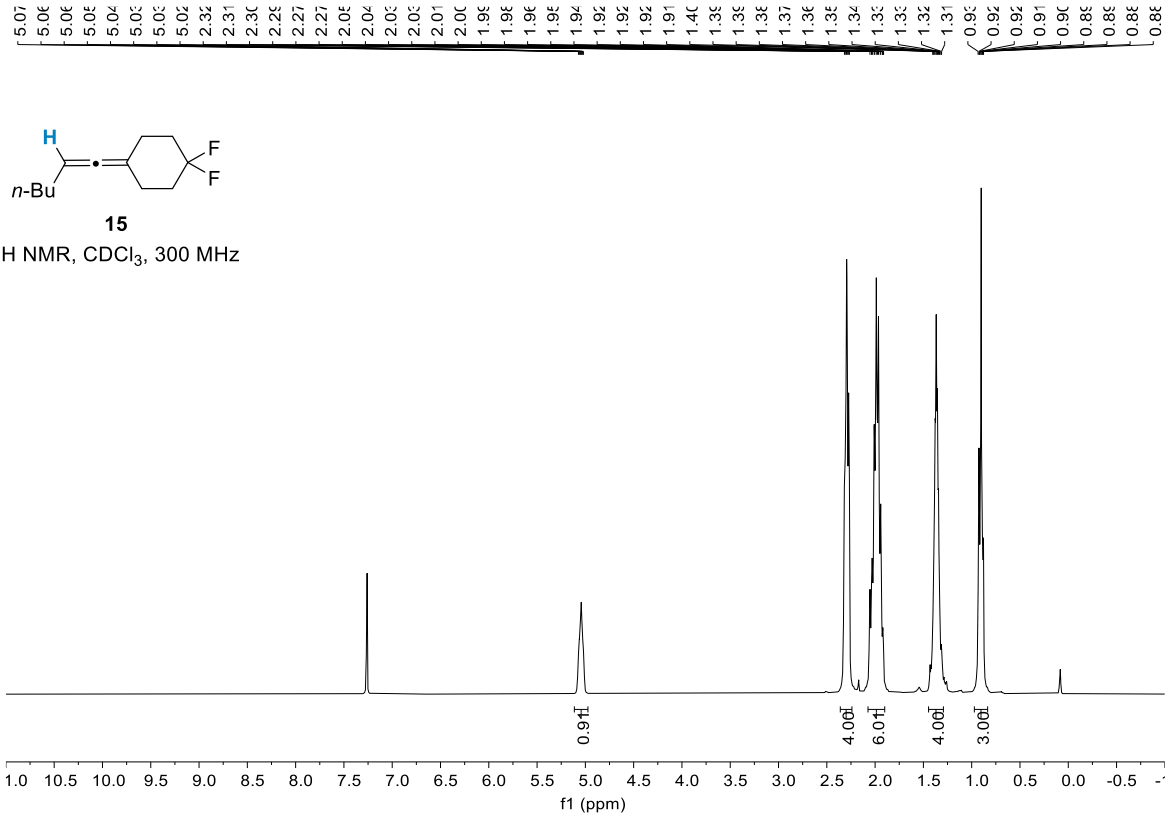

H
F
13
^{13}C NMR, CDCl$_3$, 75 MHz
f1 (ppm)


H
N
14
^{1}H NMR, CDCl$_3$, 300 MHz
f1 (ppm)



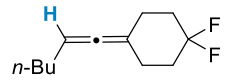
14

^{13}C NMR, $CDCl_3$, 75 MHz



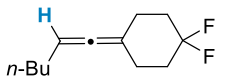
15

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



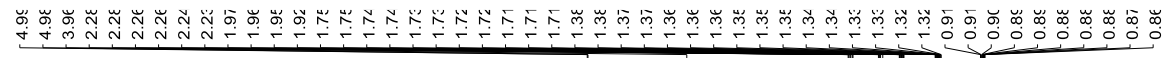
15

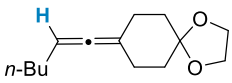
^{19}F NMR, $CDCl_3$, 282 MHz



15

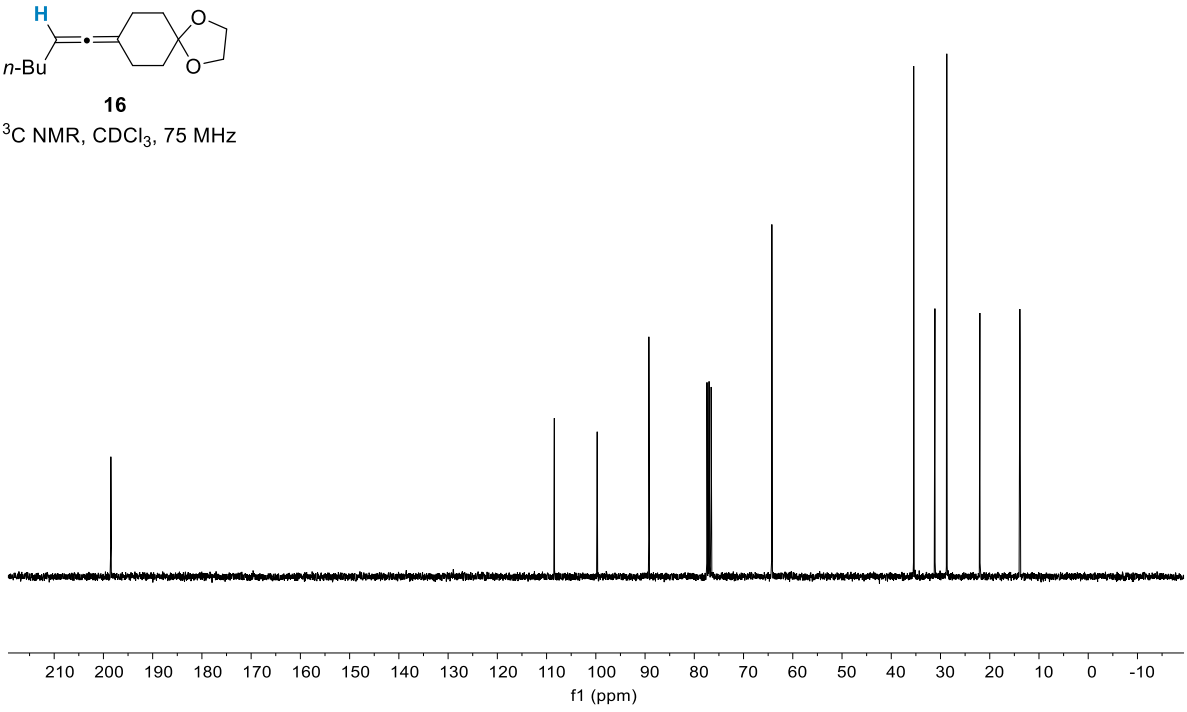
^{13}C NMR, $CDCl_3$, 75 MHz





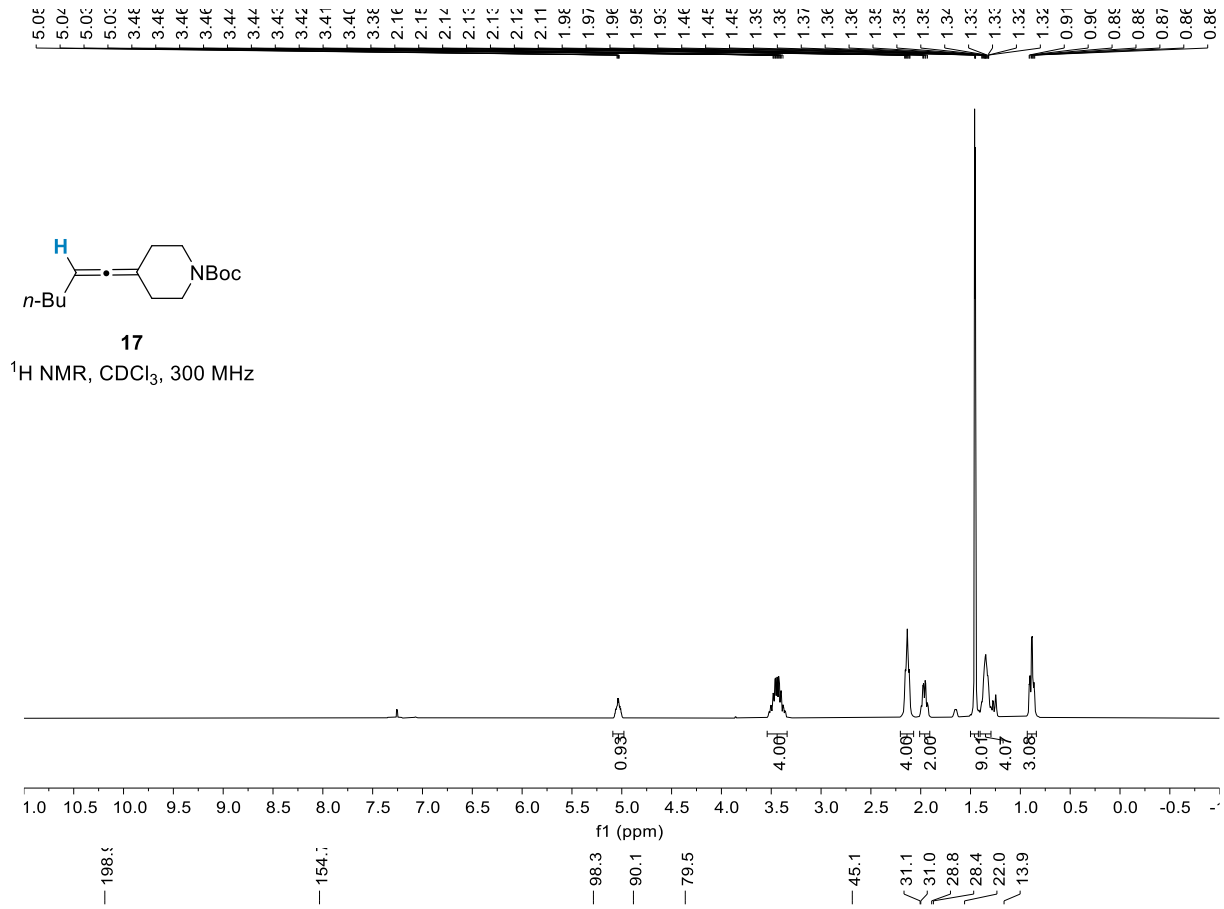
16

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



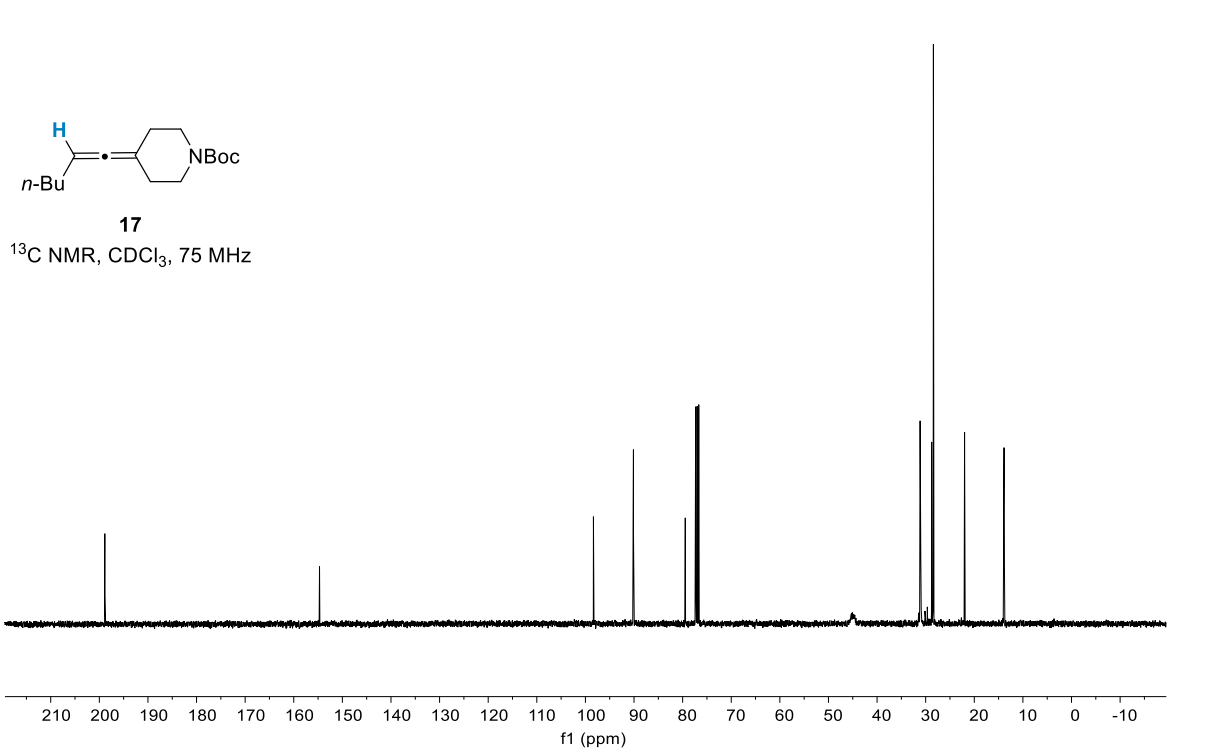
16

^{13}C NMR, $CDCl_3$, 75 MHz



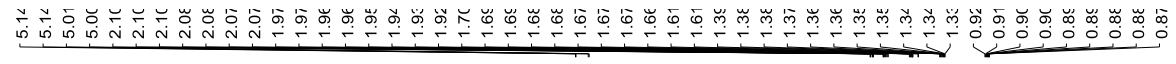
17

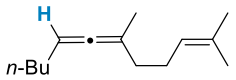
^{1}H NMR, $CDCl_3$, 300 MHz



17

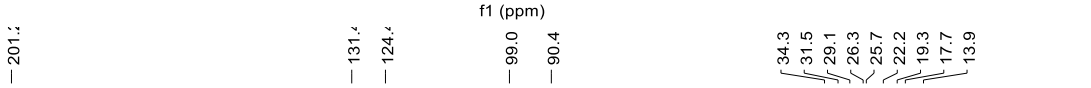
^{13}C NMR, $CDCl_3$, 75 MHz

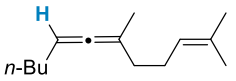




18

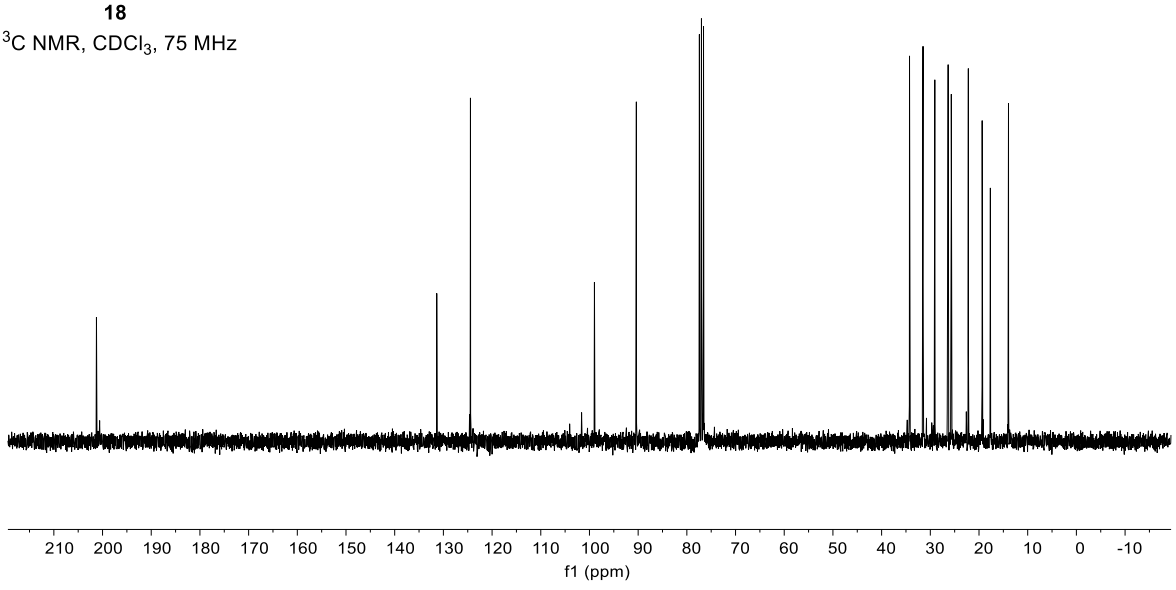
^{1}H NMR, $CDCl_3$, 300 MHz

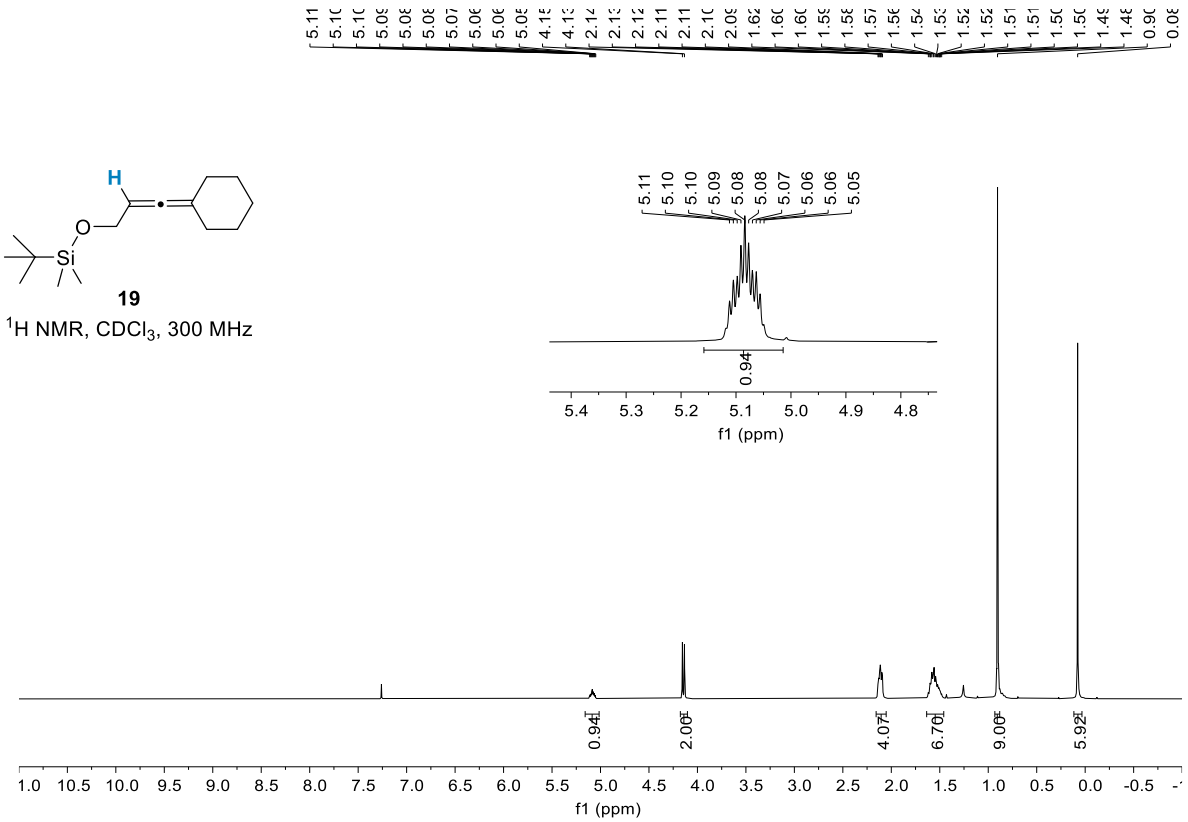


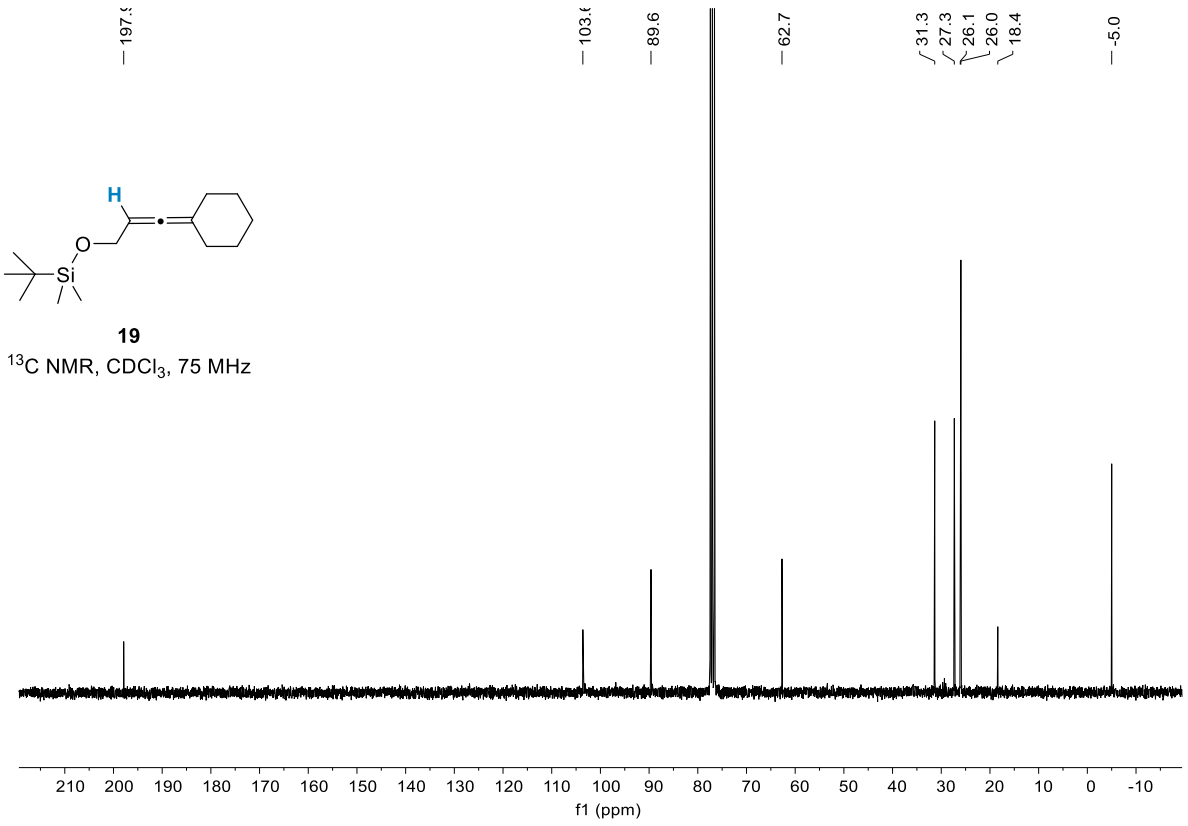


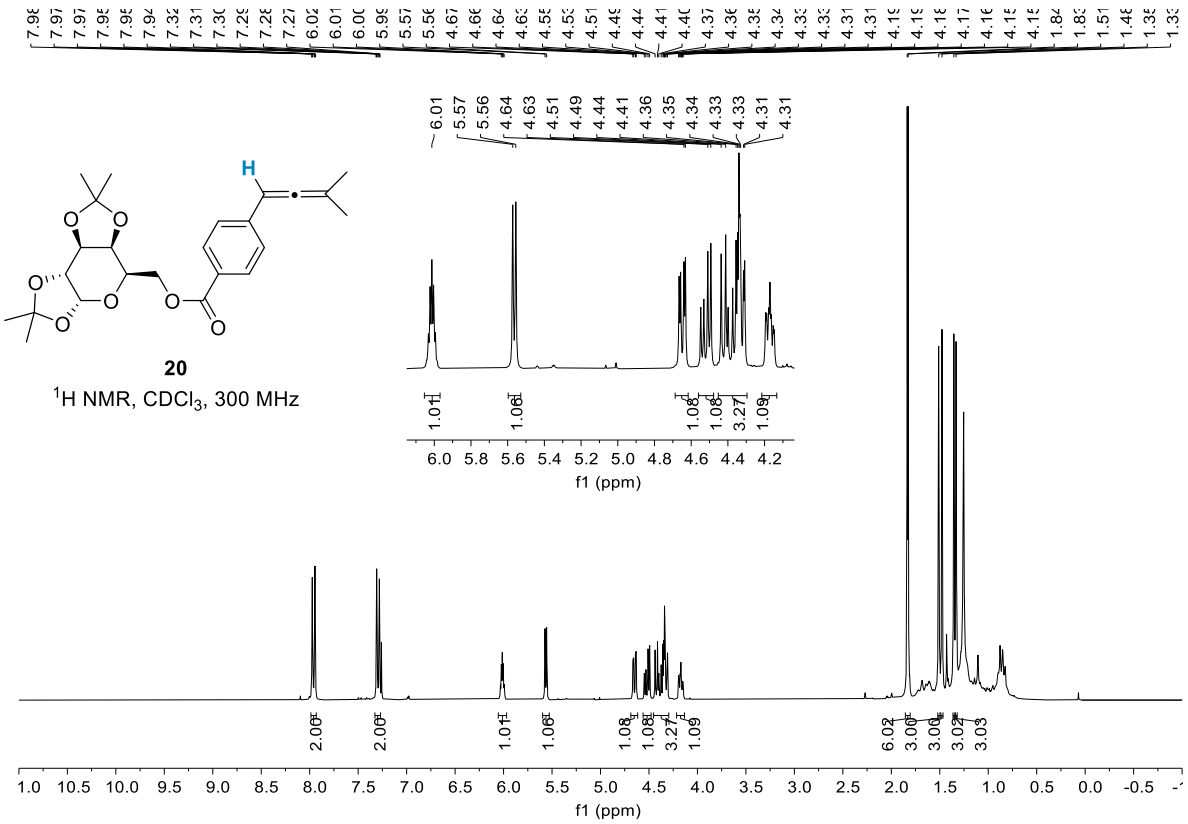
18

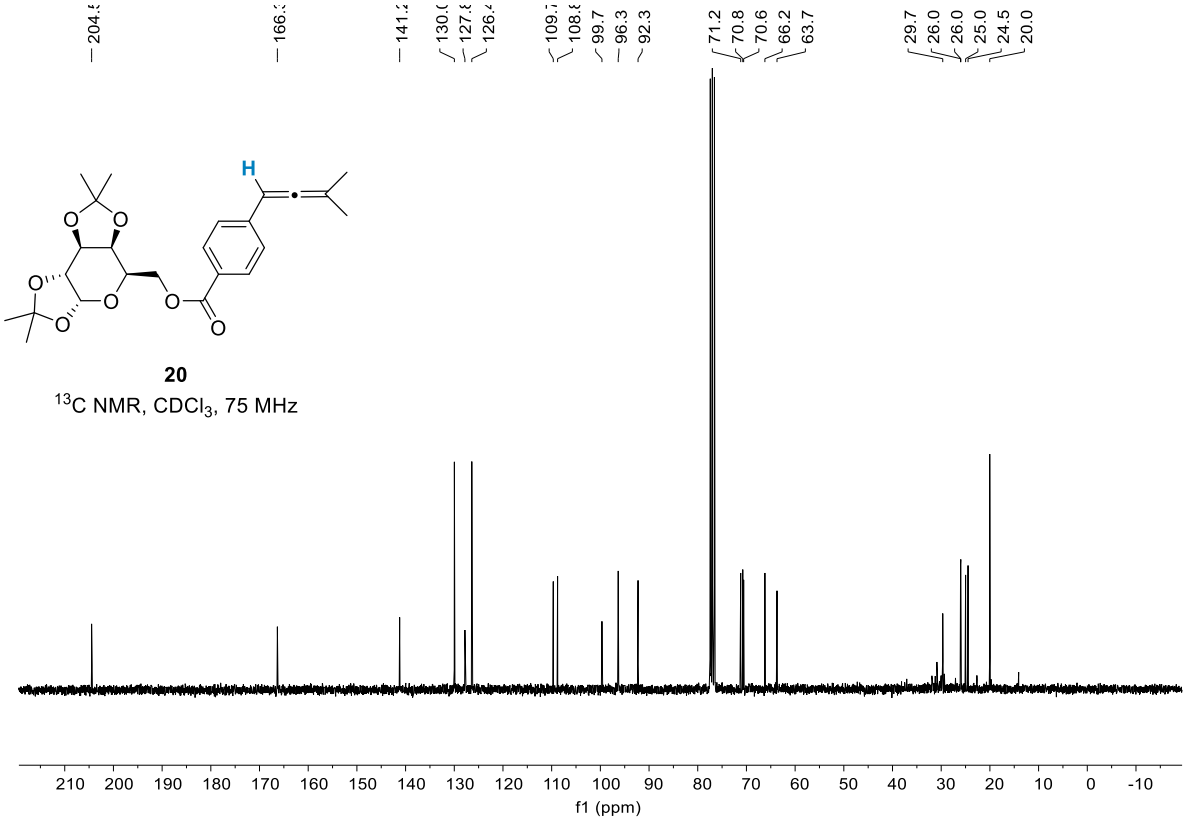
^{13}C NMR, $CDCl_3$, 75 MHz

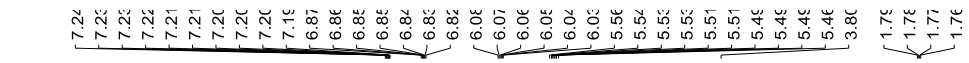


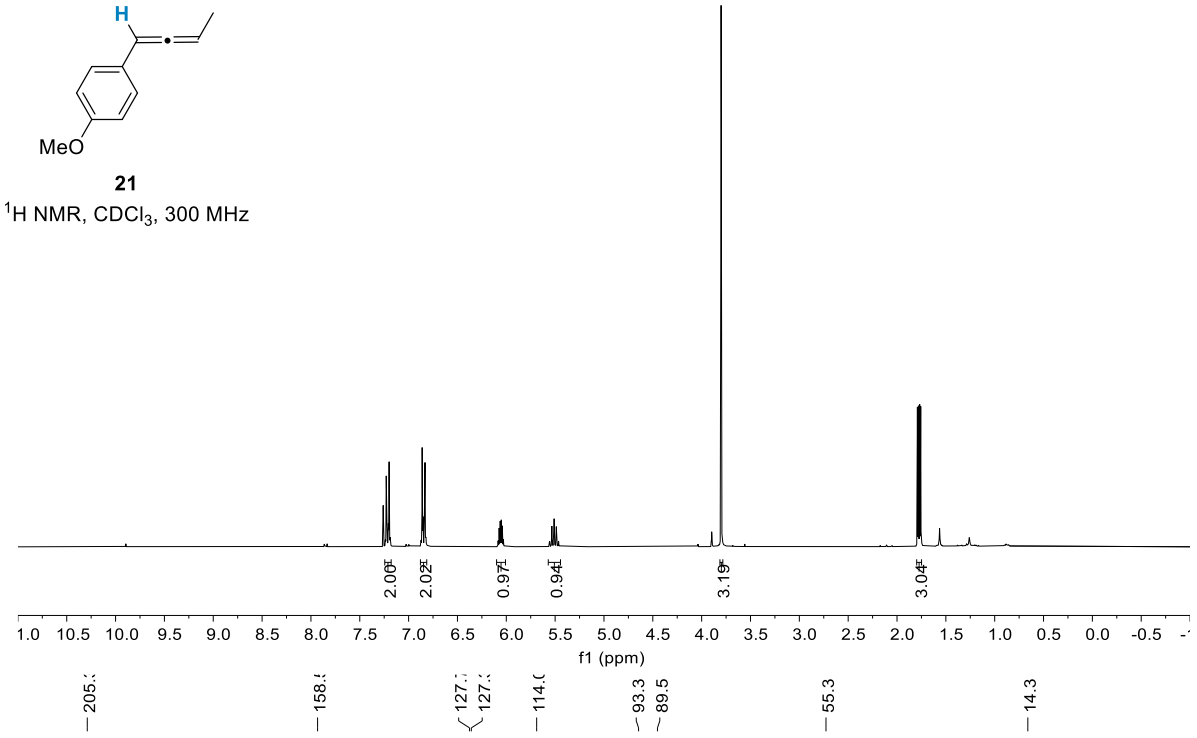

H
O
Si
19
1H NMR, CDCl3, 300 MHz
f1 (ppm)


H
O
Si
19
13C NMR, CDCl3, 75 MHz
f1 (ppm)


H
O
O
O
O
O
O
O
20
1H NMR, CDCl3, 300 MHz
f1 (ppm)

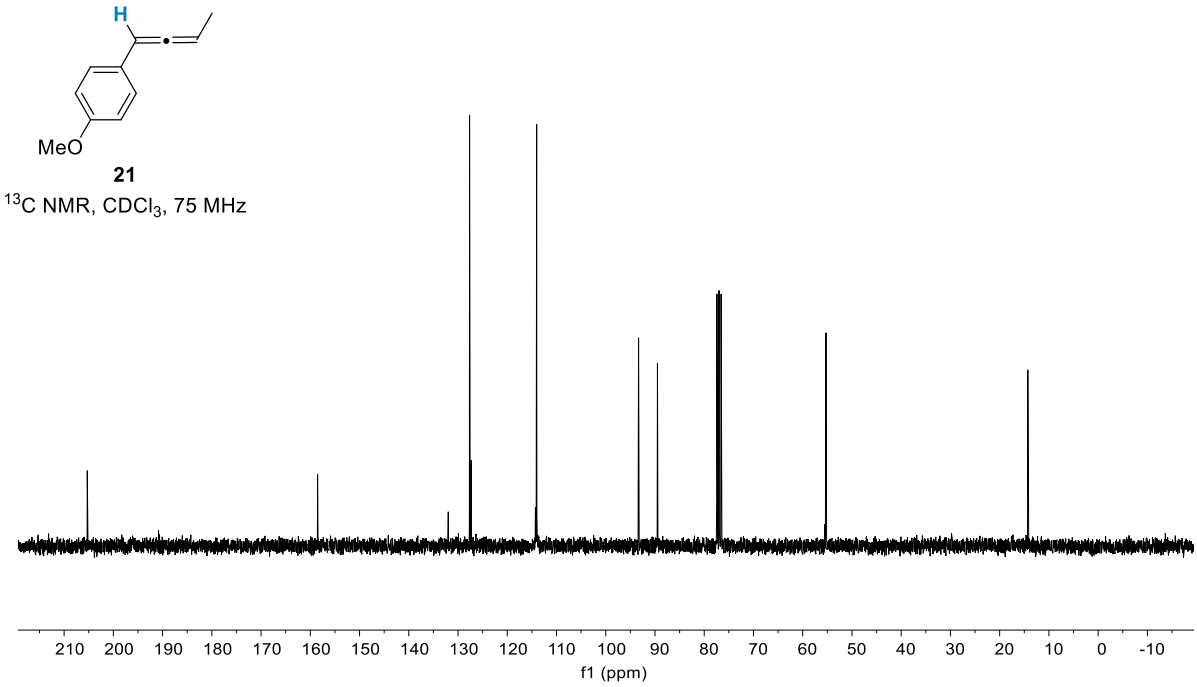

H
O
O
O
O
O
O
O
20
13C NMR, CDCl3, 75 MHz
f1 (ppm)





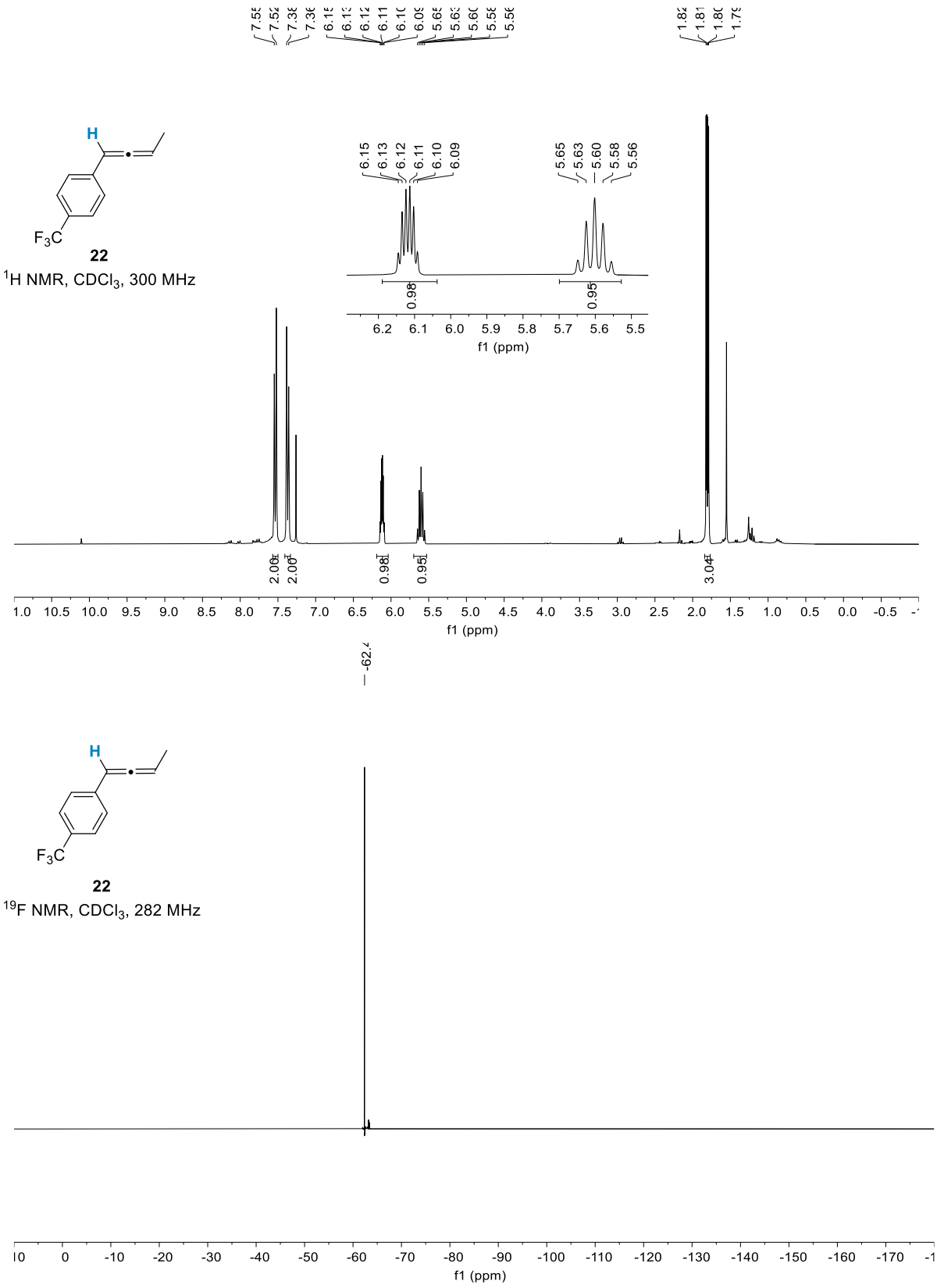
21

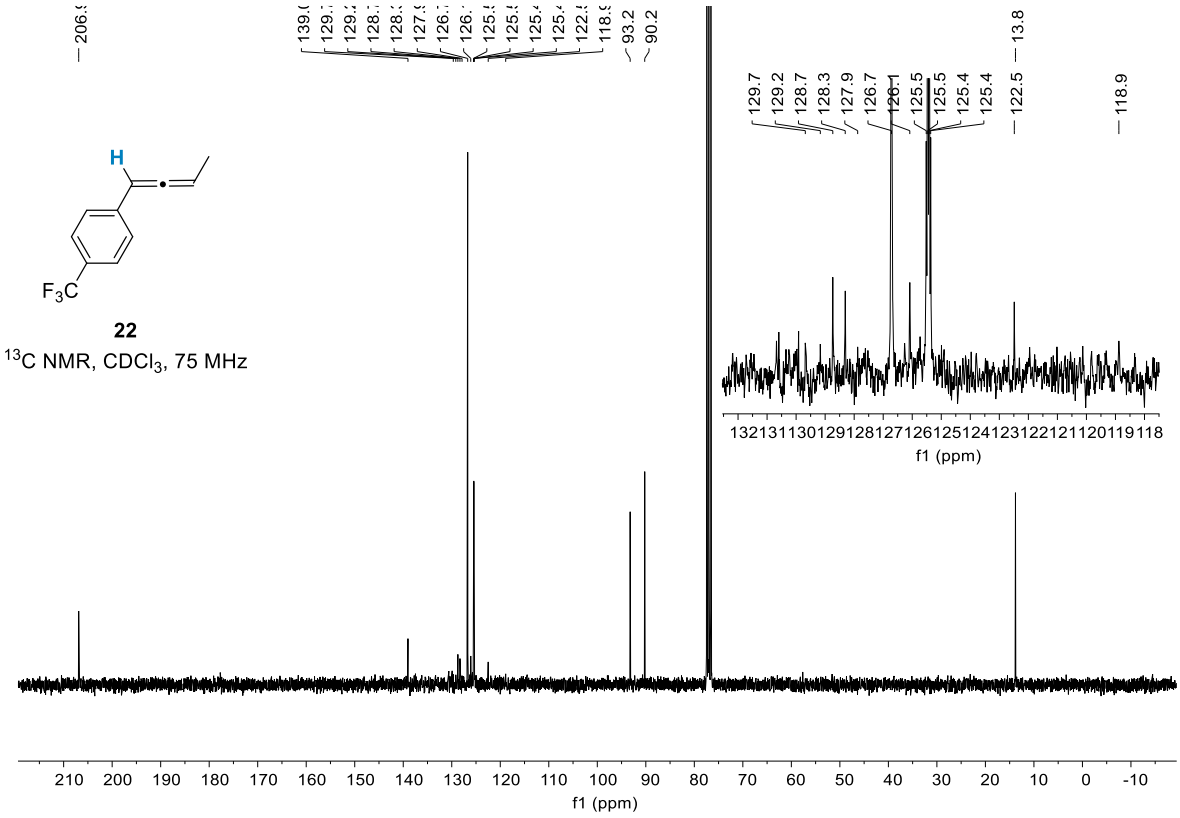
^{1}H NMR, $CDCl_3$, 300 MHz

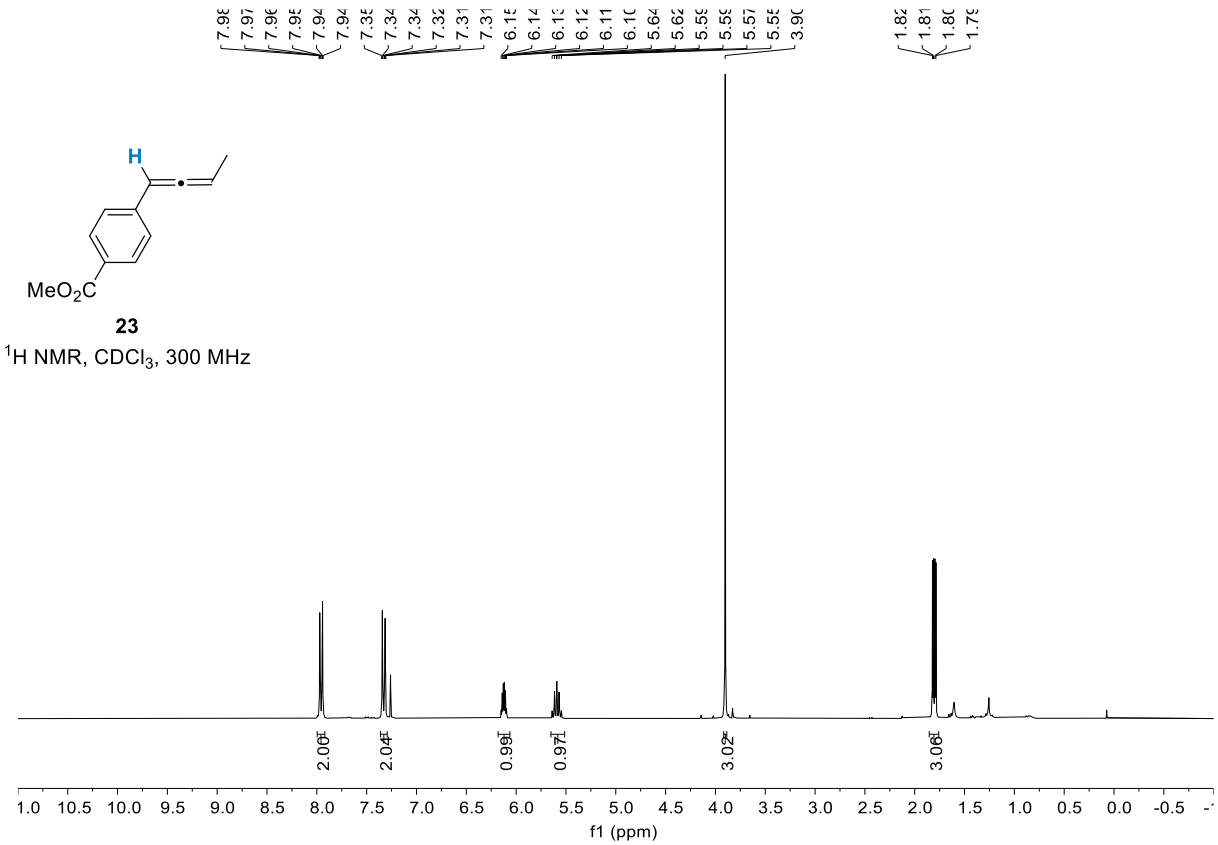


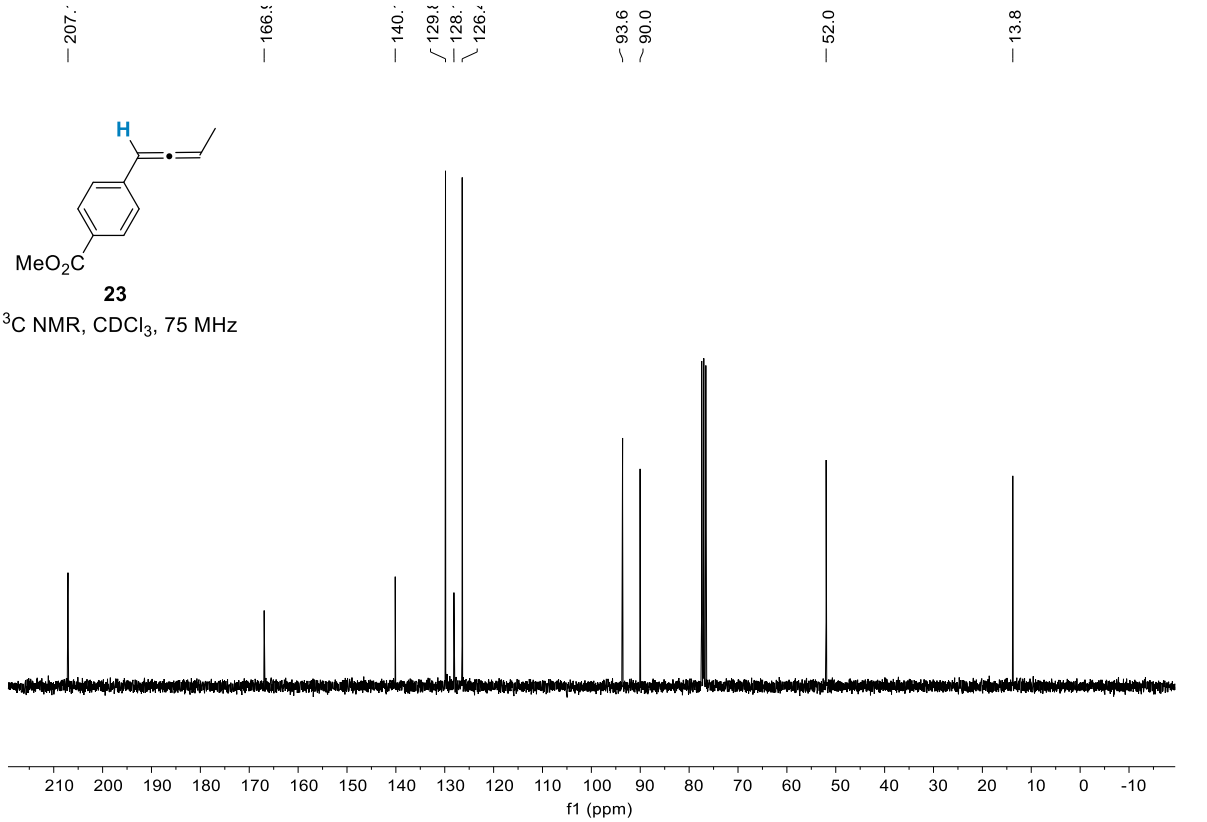
21

^{13}C NMR, $CDCl_3$, 75 MHz


22
1H NMR, CDCl3, 300 MHz
f1 (ppm)
22
19F NMR, CDCl3, 282 MHz
f1 (ppm)

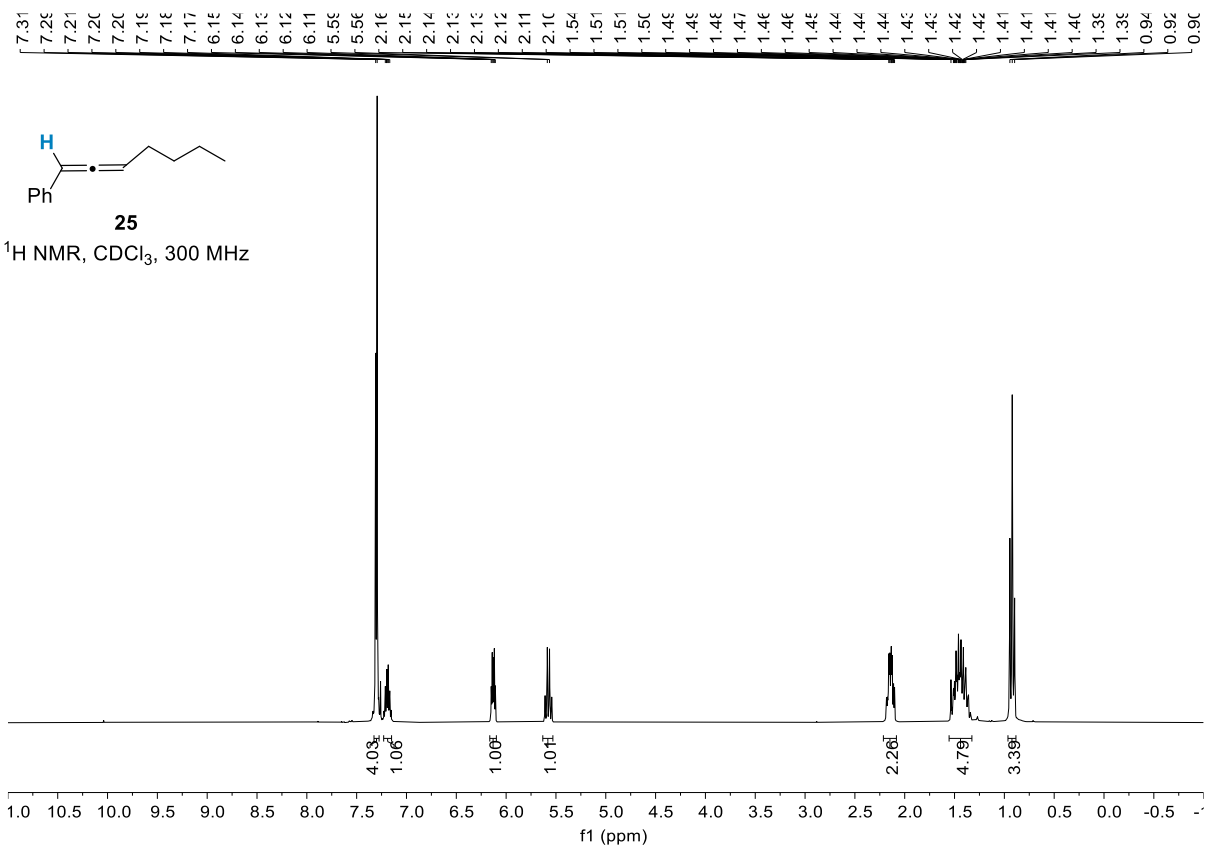

H
F3C
22
13C NMR, CDCl3, 75 MHz
f1 (ppm)


H
MeO2C
23
1H NMR, CDCl3, 300 MHz
2.00
2.04
0.99
0.97
3.02
3.06
f1 (ppm)



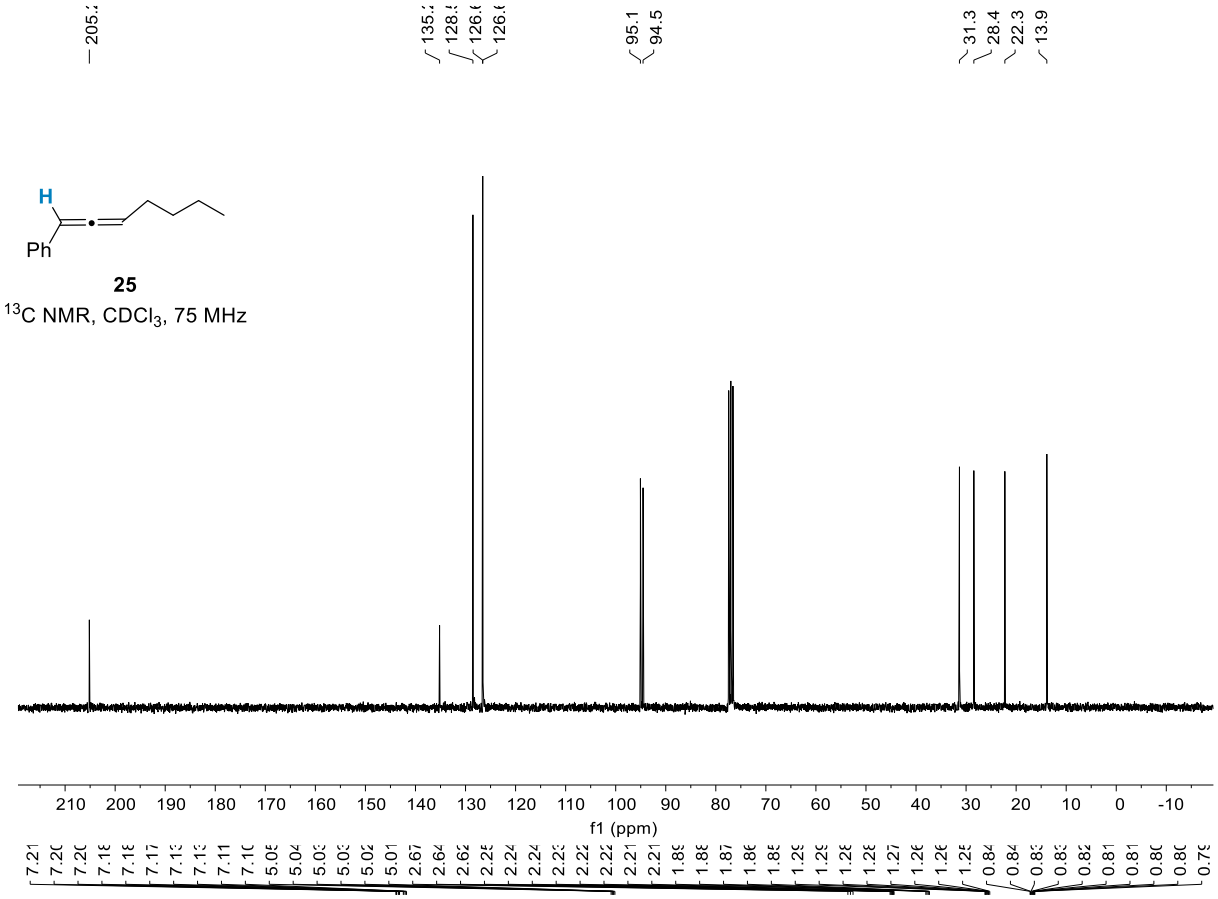
23

^{13}C NMR, $CDCl_3$, 75 MHz



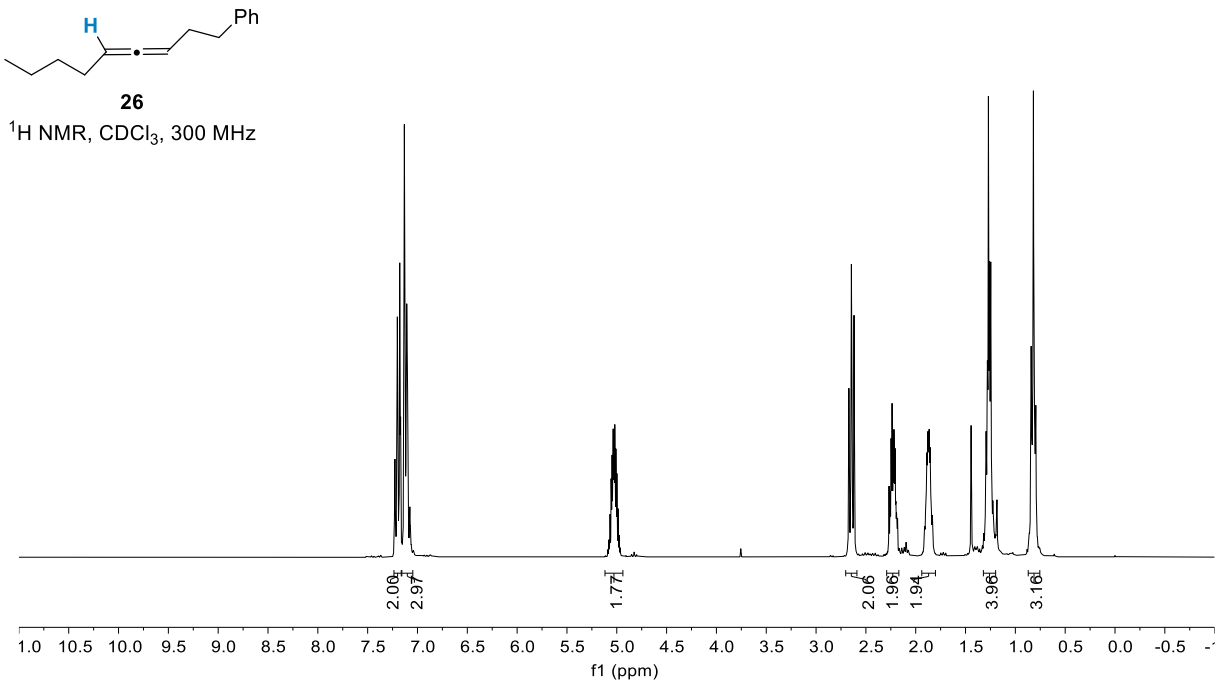
25

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



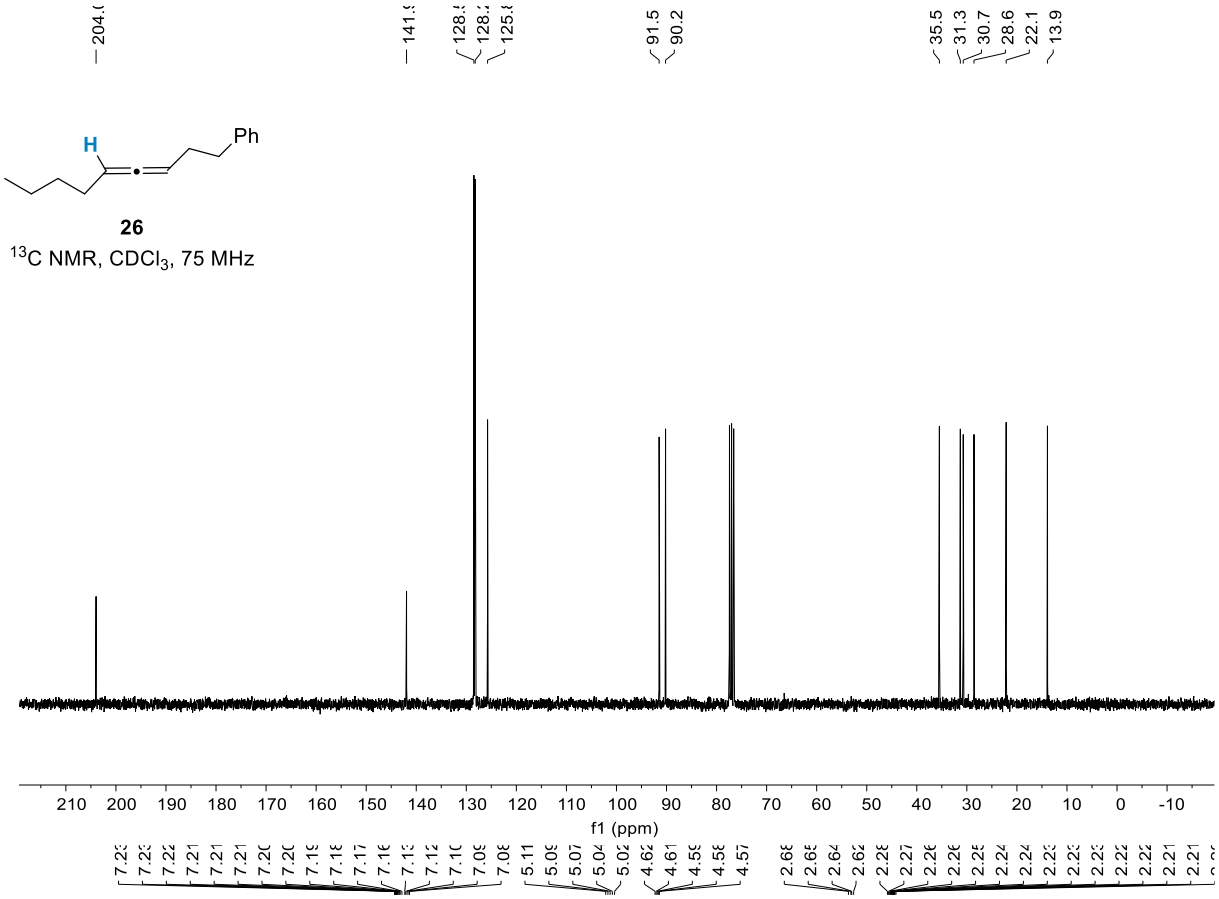
25

^{13}C NMR, $CDCl_3$, 75 MHz



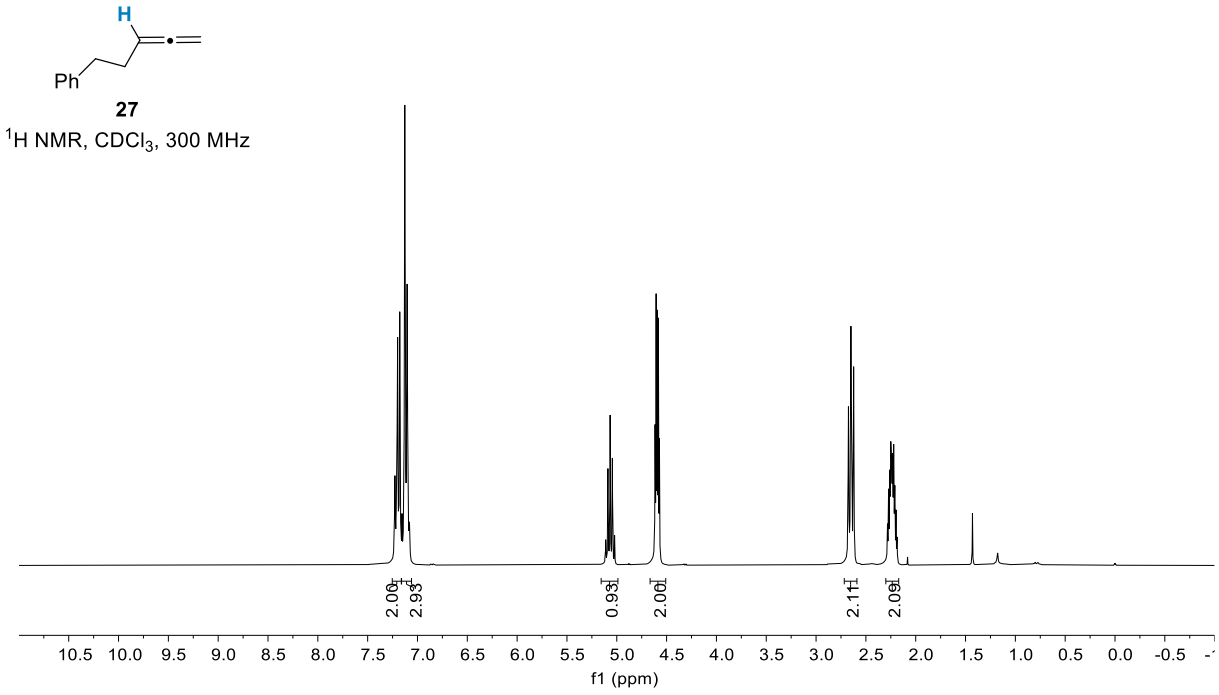
26

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



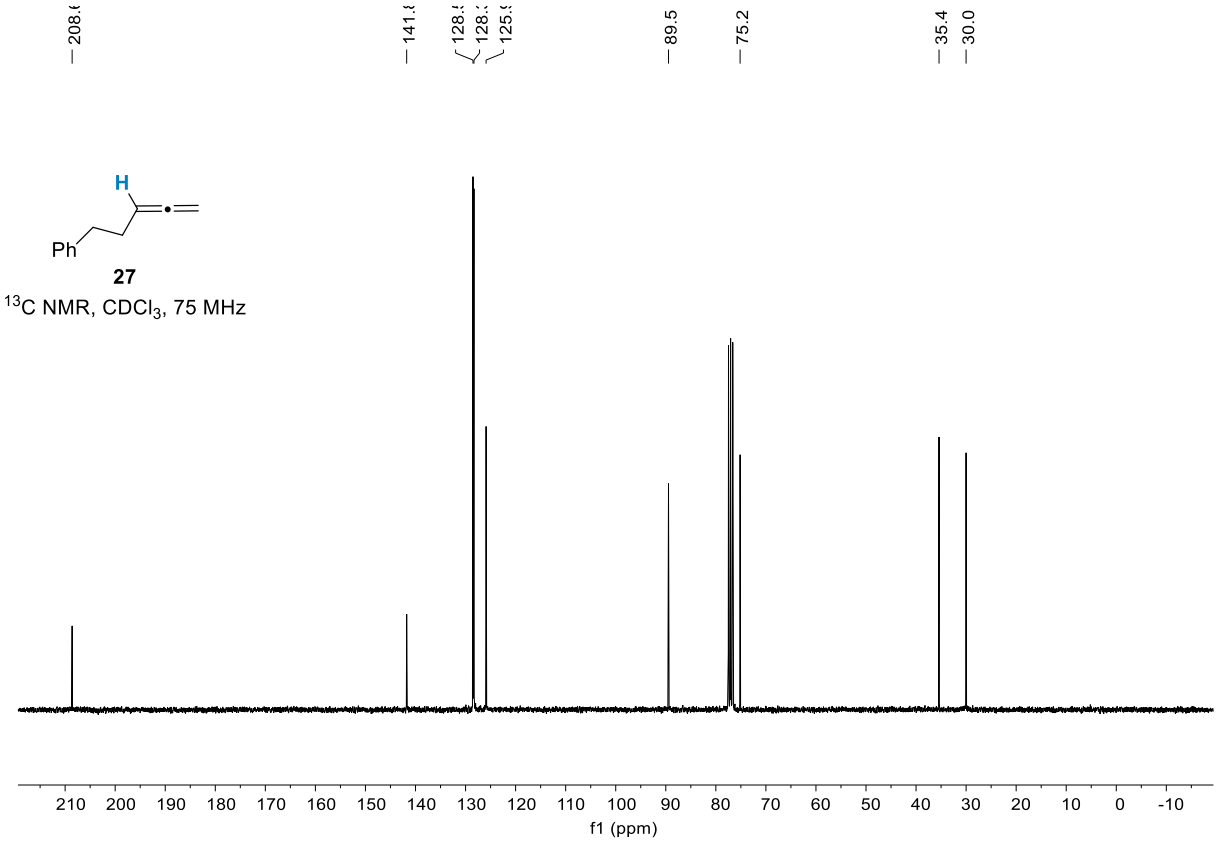
26

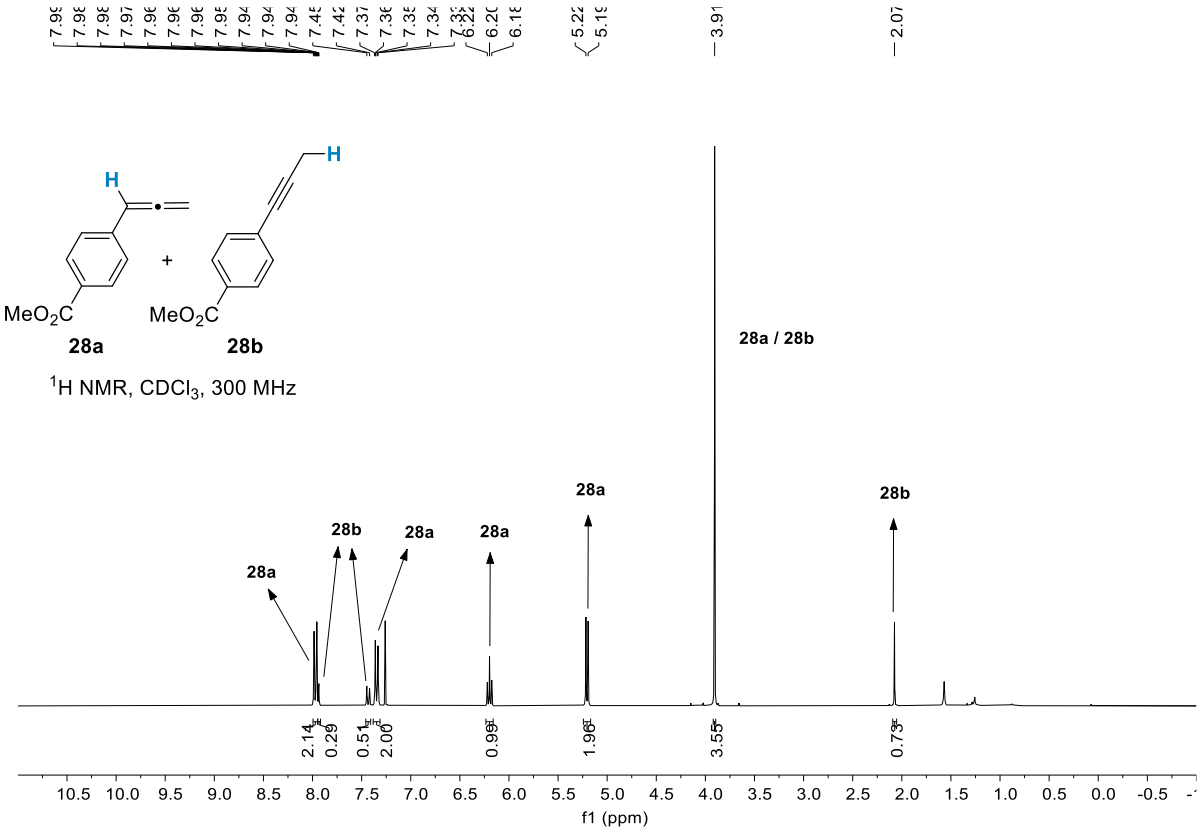
^{13}C NMR, $CDCl_3$, 75 MHz

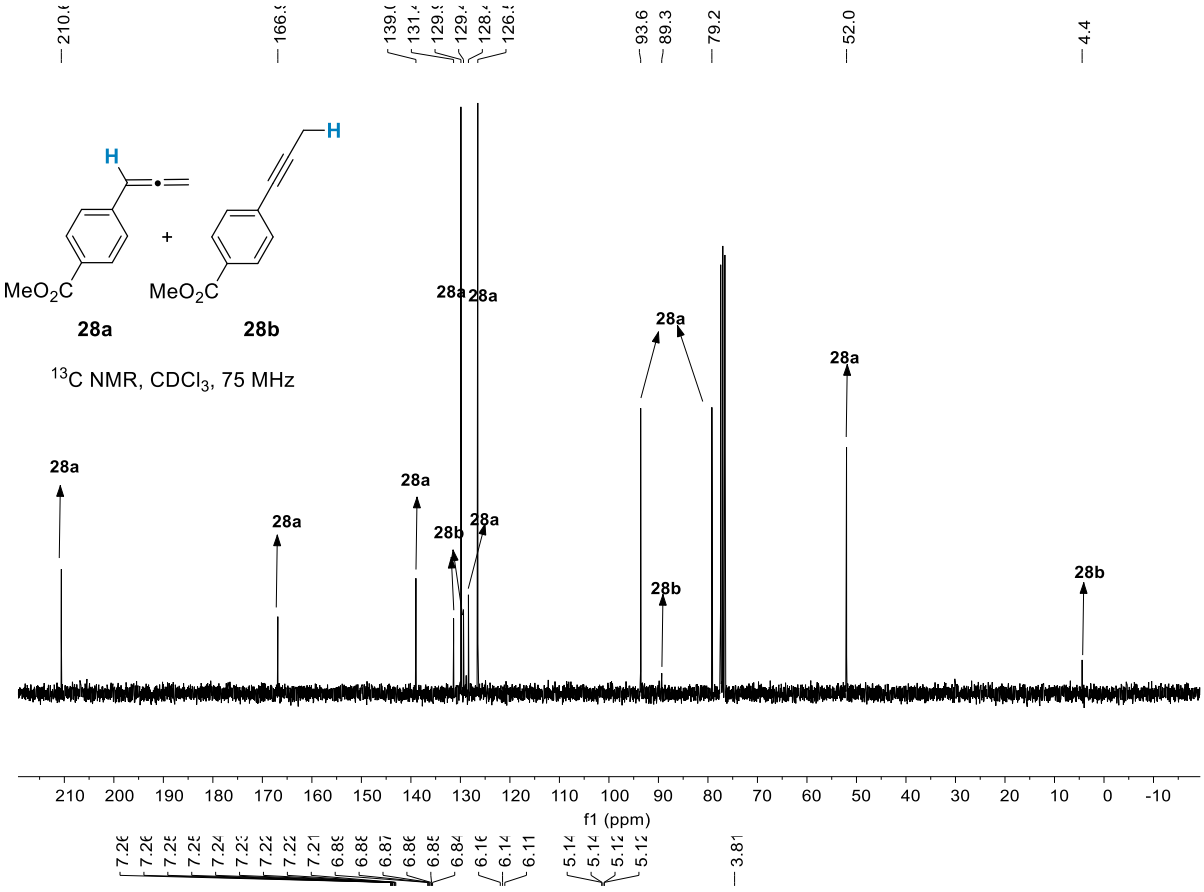


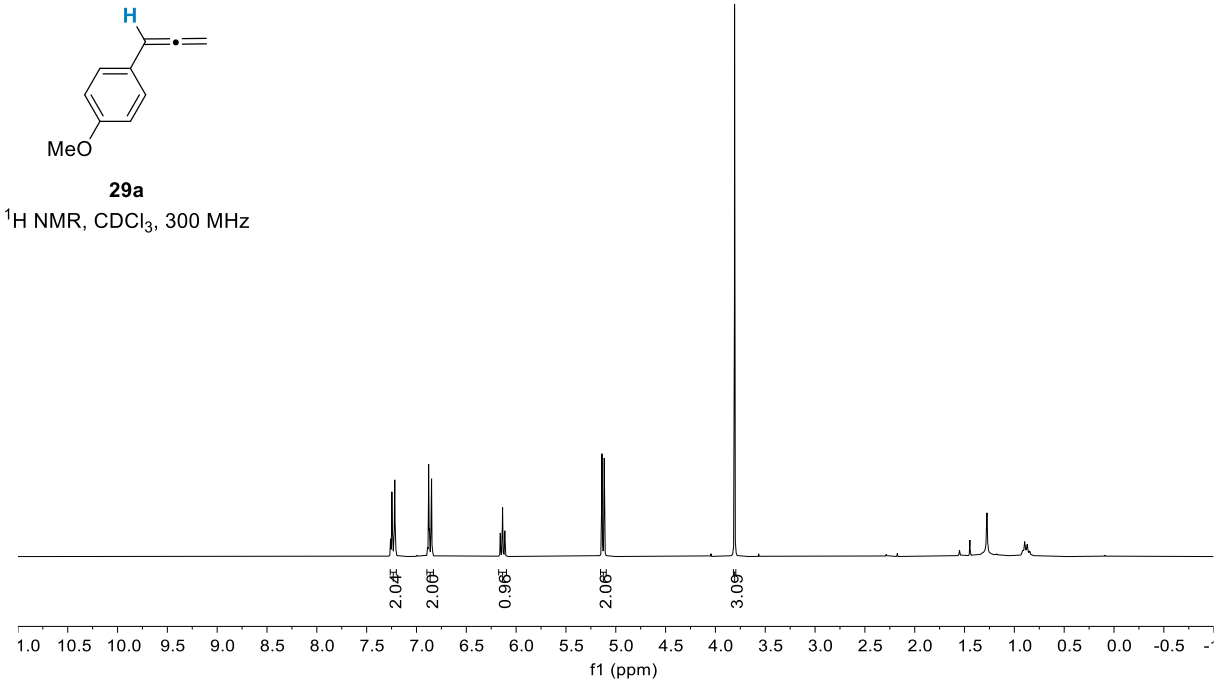
27

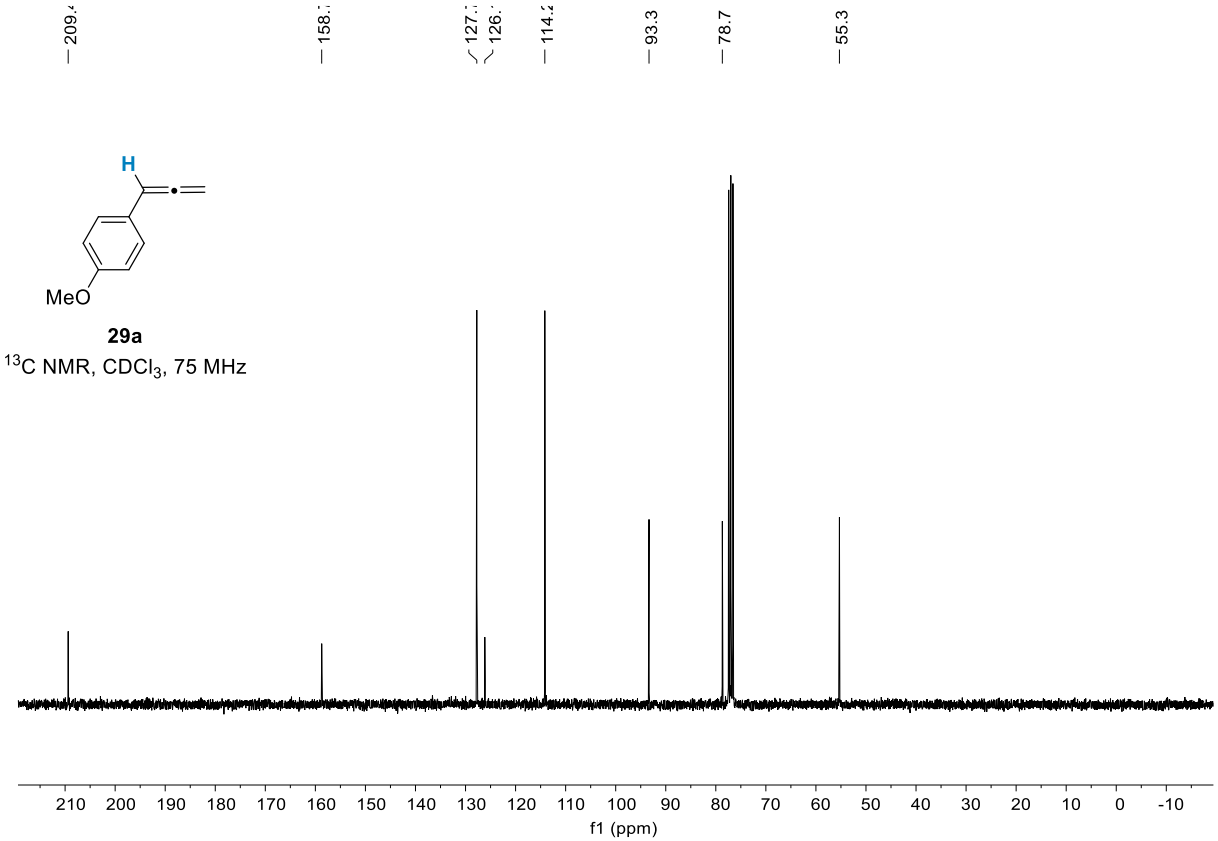
^{1}H NMR, $CDCl_3$, 300 MHz


H
Ph
27
13C NMR, CDCl3, 75 MHz
f1 (ppm)


H
MeO2C
28a
28b
1H NMR, CDCl3, 300 MHz
28a / 28b
f1 (ppm)

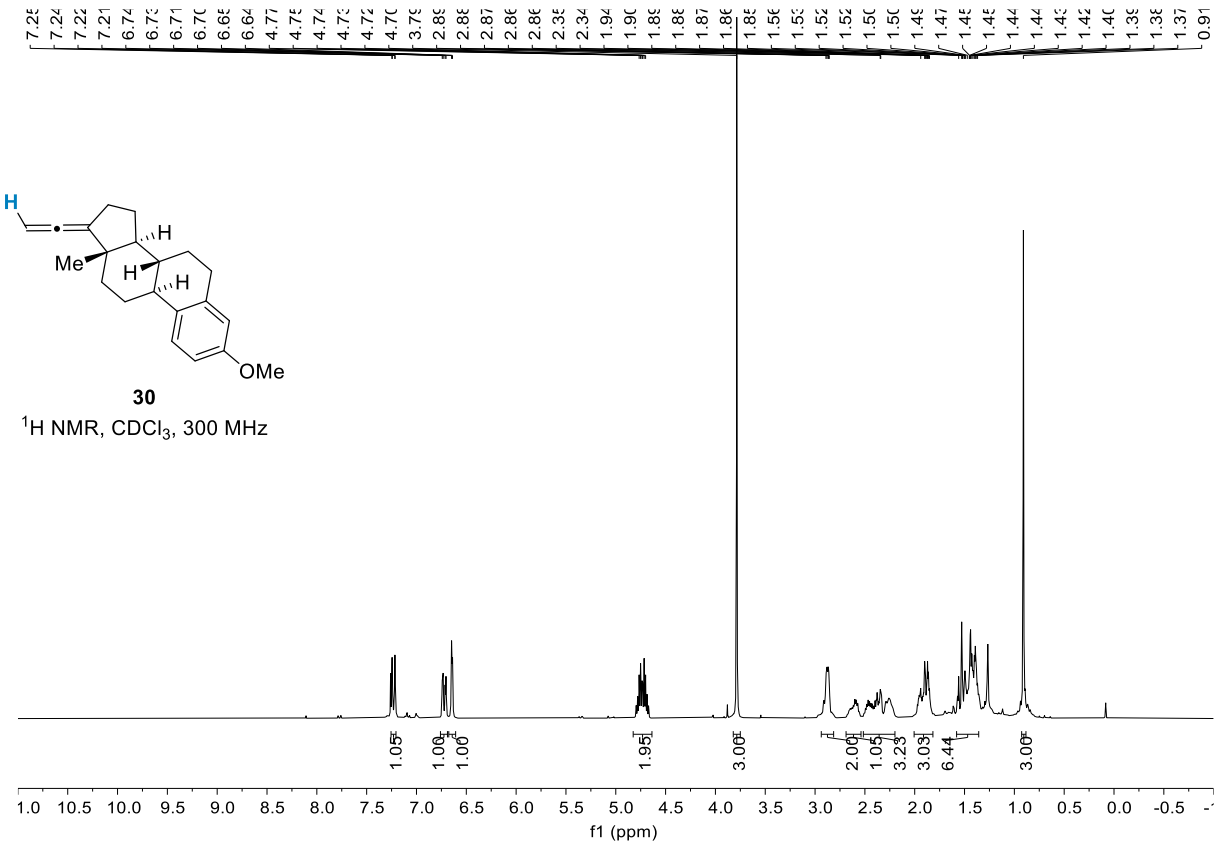

210.
166.
139.
131.
129.
129.
128.
126.
93.6
89.3
79.2
52.0
4.4
H
MeO2C
+
H
MeO2C
28a
28b
28a
28a
28a
28a
28a
28a
28b
28a
28b
28a
28b
13C NMR, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.21
6.85
6.88
6.87
6.86
6.85
6.84
6.16
6.14
6.11
5.14
5.14
5.12
5.12
3.81


H
MeO
29a
1H NMR, CDCl3, 300 MHz
2.04
2.00
0.96
2.06
3.09
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



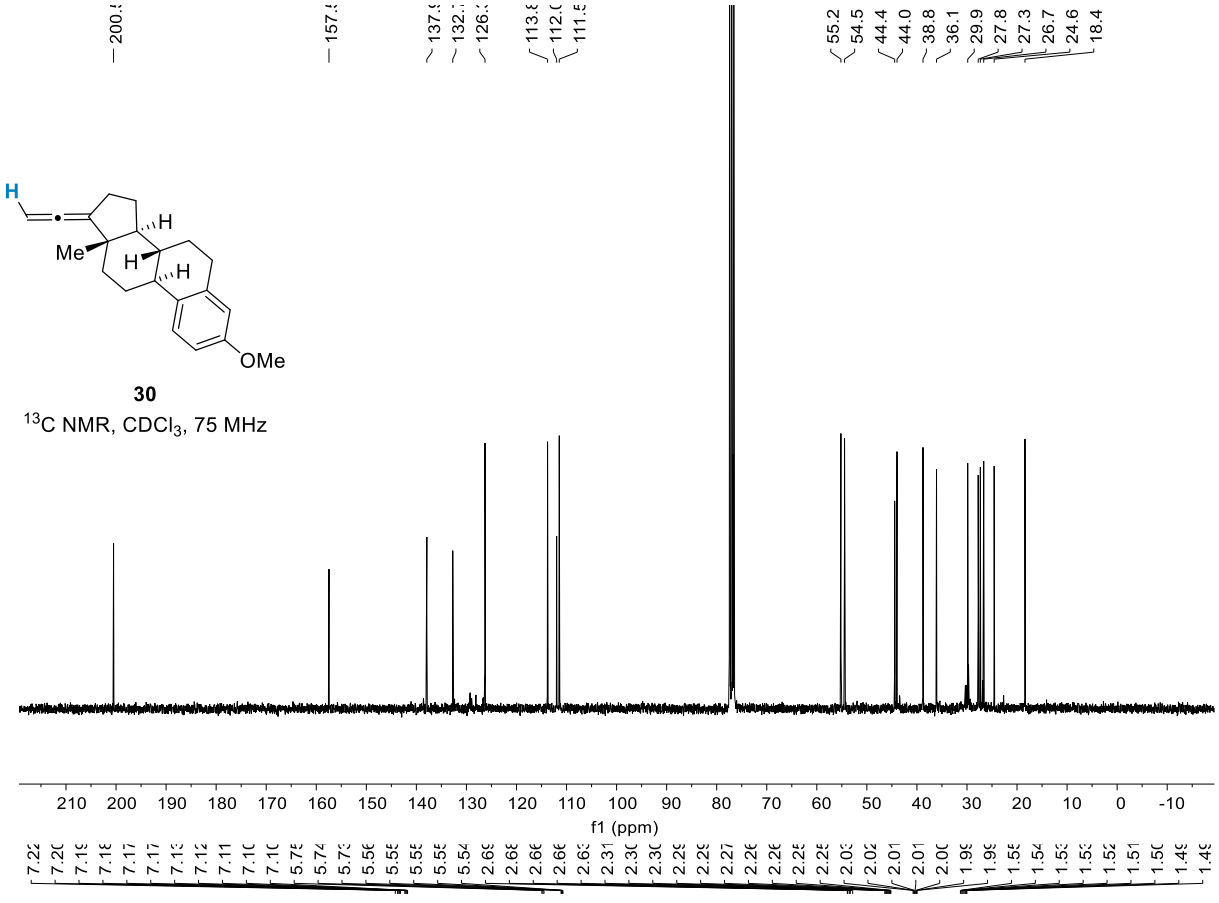
29a

^{13}C NMR, $CDCl_3$, 75 MHz



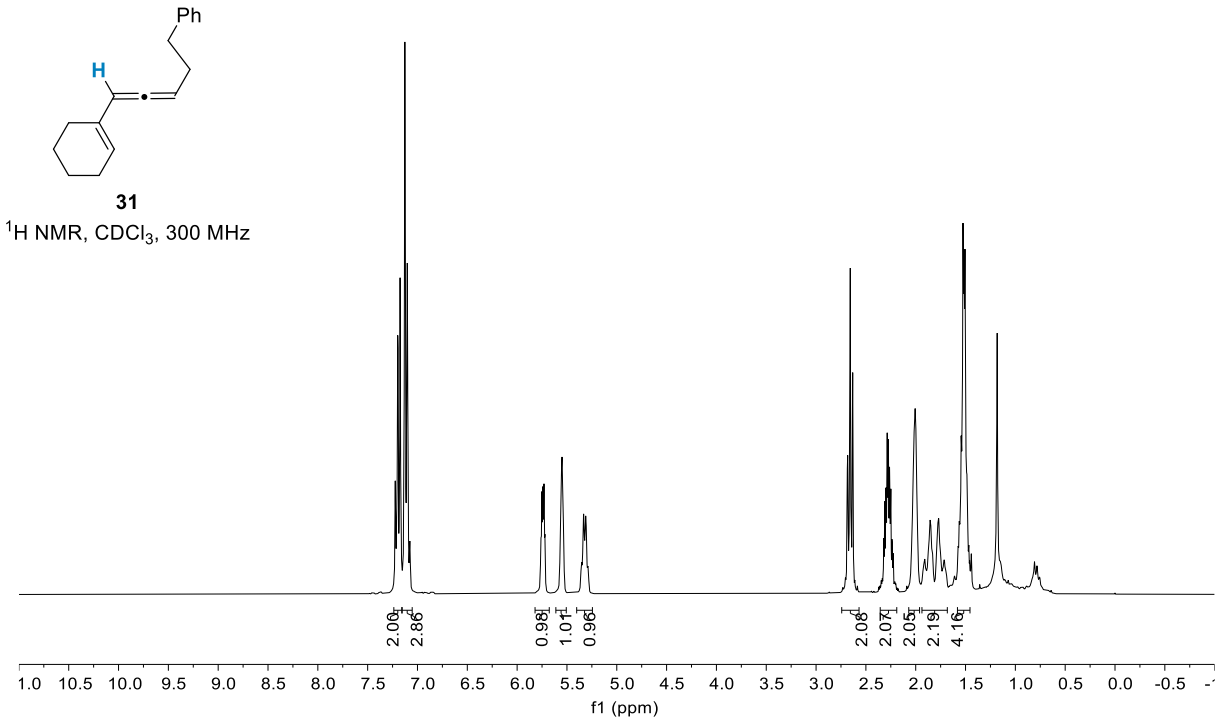
30

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



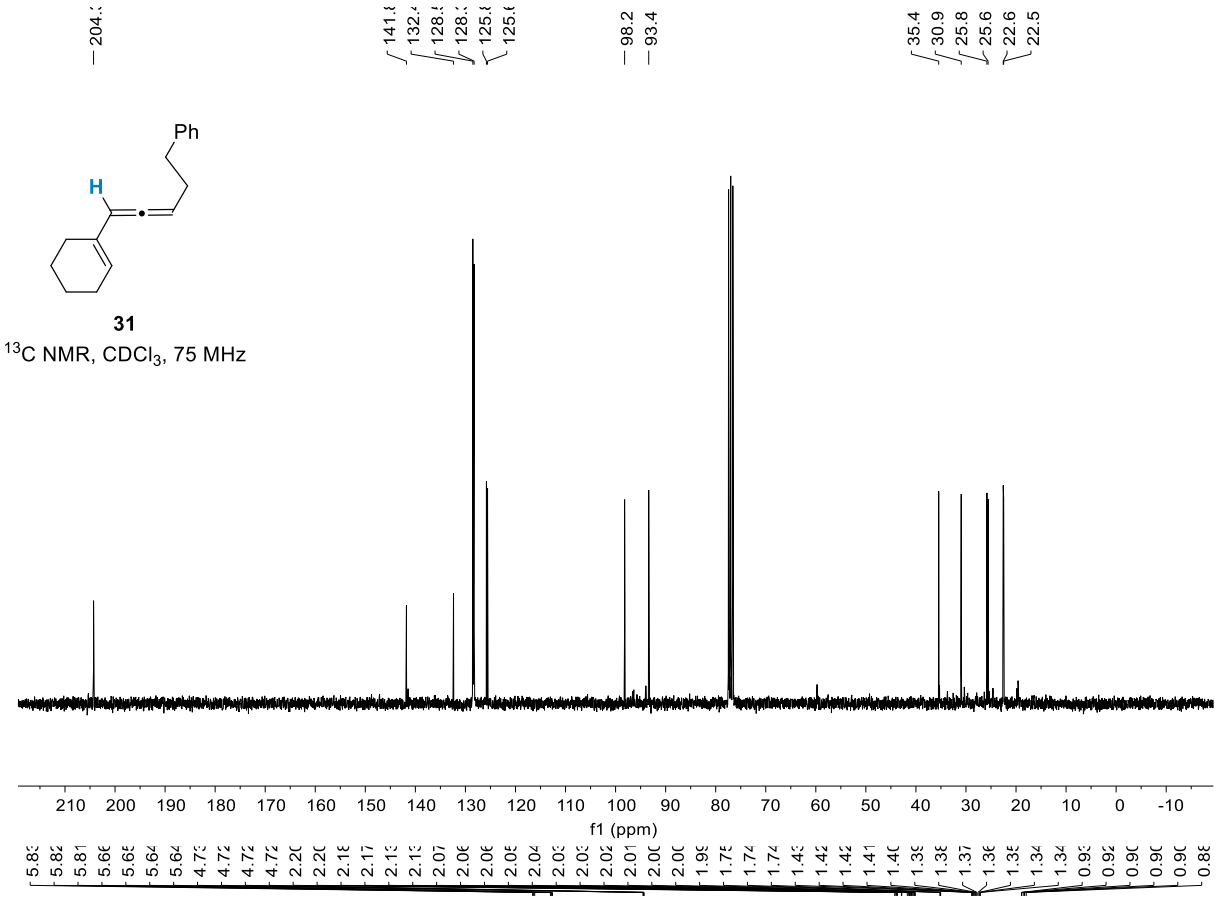
30

^{13}C NMR, $CDCl_3$, 75 MHz



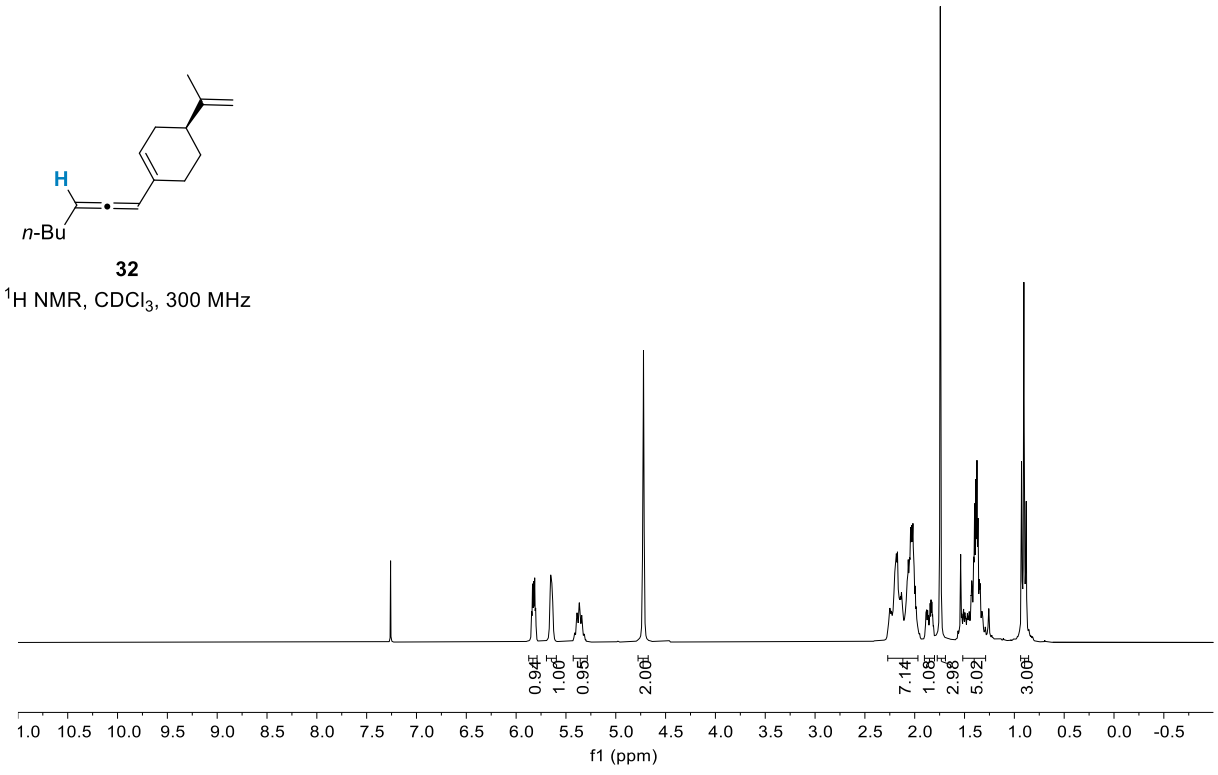
31

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



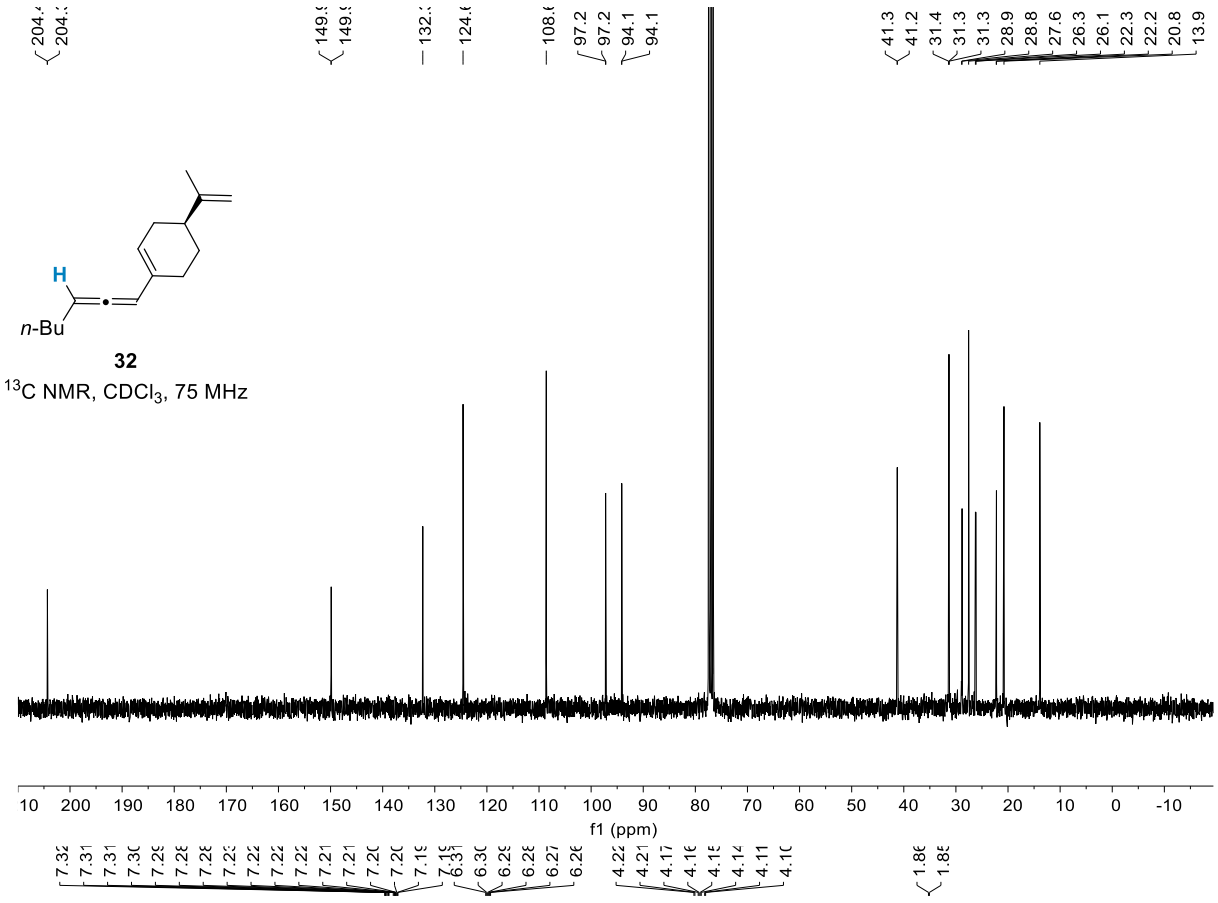
31

^{13}C NMR, $CDCl_3$, 75 MHz



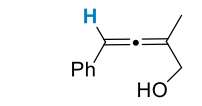
32

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



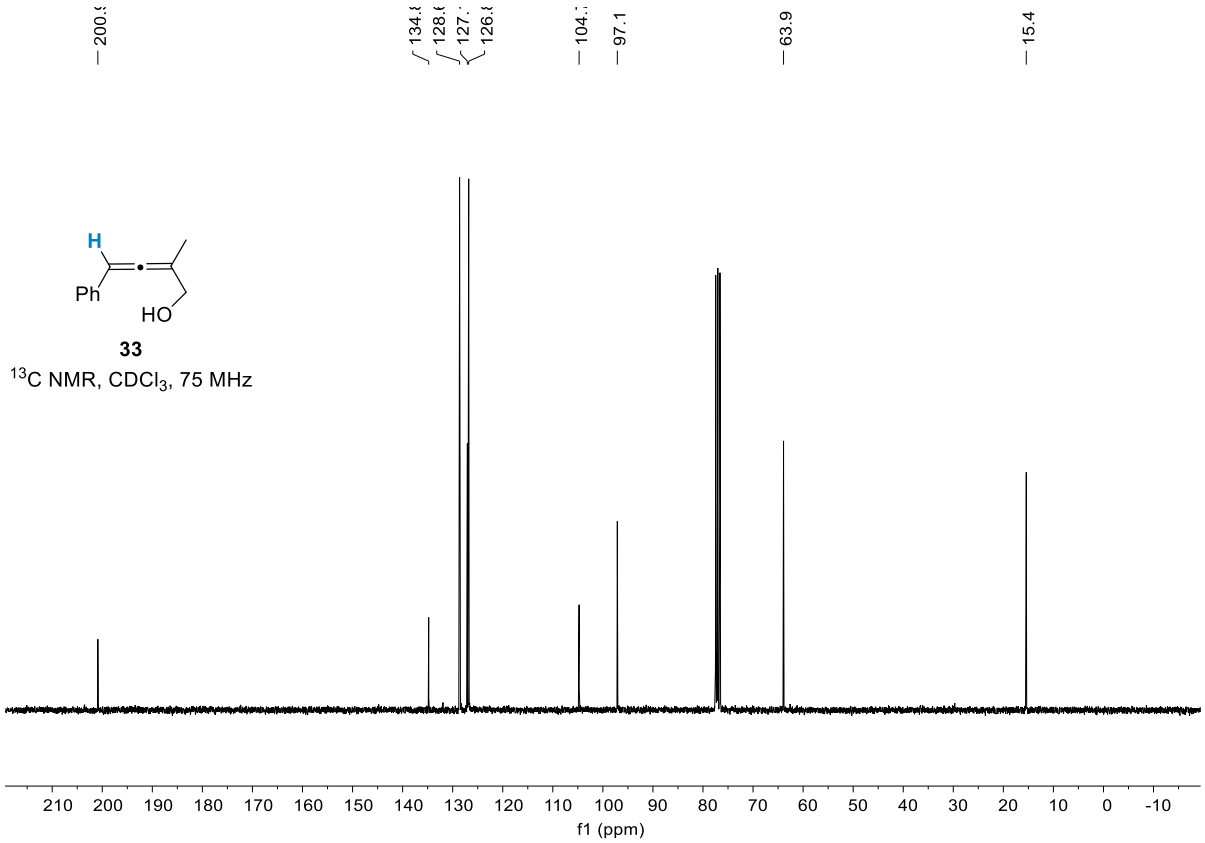
32

^{13}C NMR, $CDCl_3$, 75 MHz



33

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


— 200.
134.
128.
127.
126.
— 104.
— 97.1
— 63.9
— 15.4
H
Ph
HO
33
13C NMR, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)