Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Iron-catalyzed Cross-Coupling of Propargyl Carboxylates and Grignard Reagents: Synthesis of Substituted Allenes

*Simon N. Kessler and Jan-E. Bäckvall**

anie_201511139_sm_miscellaneous_information.pdf

Supporting Information

Content:

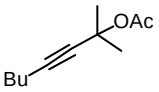
General Information

Unless otherwise noted: All reagents and solvents were obtained from either Sigma-Aldrich , Acros, Alfa, VWR, or TCI and were used as received unless otherwise stated. Dry solvents were obtained from commercial sources, from a VAC™ drying system or dried over molecular sieve. $Fe(acac)_3$ was purchased from Sigma-Aldrich (Prod. Nr.: 517003, Lot Nr.: MKBS7930V with an Cu-content of 0.5 ppm). Grignard reagents were titrated before use.[1] All reactions were conducted in dry flasks under argon atmosphere. Room temperature is ca. 22 °C. Reactions were monitored using Merck silica gel 60 F254 plates (TLC analysis). TLC plates were visualized with UV light (254 nm), iodine or $KMnO_4$. Flash column chromatography was carried out with 60Å (particle size 35 - 70 μm) silica gel. GC samples were run on GC Varian 3900 equipped with an auto sampler and a FID detector. HPLC samples were run on HPLC Waters 2695 equipped with an auto sampler and a UV detector. ^{1}H- and ^{13}C-NMR Experiments were performed on a Bruker NMR (400/100.6 MHz) at 25 °C. Chemical shifts (δ) are reported in parts per million (ppm) relative to the $CDCl_3$ peak (δ(H)=7.26 and δ(C)=77.16 ppm). Coupling constants (*J*) are reported in Hertz (Hz). LRMS was conducted via GC-MS from ThermoQuest. HRMS were recorded on a Bruker MicroTOF spectrometer equipped with an ESI or APCI ion source.

1 Synthesis of Substrates

The substrates from Table 2 entry 5[2], 10[3], Table 3, entry 6[4] and 14[5] and Table 4 entry 4[6] were synthesized according to literature, by esterification form the corresponding alcohols purchased from Sigma-Aldrich.

1.1 2-Methyloct-3-yn-2-yl acetate[7]

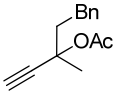


To anhydrous THF (60 mL) was added *n*-BuLi (12.2 mL, 30.4 mmol, 2.5M in hexane, 1.25 equiv.) under an argon atmosphere and the flask was cooled to –78 °C. Then, hexyne (2.00 g, 24.4 mmol, 1.00 equiv.) was added dropwise. After 30 minutes at –78 C, acetone (1.84 g, 2.32 mL, 31.7 mmol, 1.30 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was cooled to 0 °C and acetic anhydride (3.36 g, 3.11 mL, 32.9 mmol, 1.35 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. After completion, sat. aq. NH_4Cl (15 mL) was added and the mixture was extracted with pentane (2 × 25 mL) washed with sat. $NaHCO_3$ (10 mL), H_2O (10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (75 g; ethyl acetate/pentane 2.5 – 5%) to afford the product as a colorles oil (4.22 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (t, *J* = 7.0 Hz, 2H), 2.00 (s, 3H), 1.63 (s, 6H), 1.53 – 1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.39, 84.63, 81.37, 72.62, 30.67, 29.31, 22.11, 21.89, 18.38, 13.60.

1.2 3-Methyl-5-phenylpent-1-yn-3-yl acetate[8]

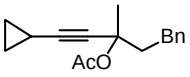


To a solution of 4-phenylbutan-2-one (3.00 g, 20.2 mmol, 1.00 equiv.) in THF (50 mL) was added ethynylmagnesium bromide (44.5 mL, 22.3 mmol, 0.5M in THF, 1.10 equiv.) at 0 °C. The reaction mixture was stirred for 10 min and allowed to warm to room temperature. After stirring for 1.5 h, acetic anhydride (2.58 g, 23.9 mmol, 1.25 equiv.) and DMAP (247 mg, 2.02 mmol, 0.10 equiv.) were added and the reaction mixture was allowed to stir overnight. After completion, the reaction was quenched with H_2O (20 mL) and the mixture was extracted with pentane (50 mL), washed with sat. $NaHCO_3$ (20 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (100 g; ethyl acetate/petroleum ether 0 – 10%) to obtain the product (2.93 g, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.10 (m, 5H), 2.92 – 2.73 (m, 2H), 2.62 (s, 1H), 2.36 – 2.22 (m, 1H), 2.17 – 2.06 (m, 1H), 2.03 (s, 3H), 1.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.49, 141.49, 128.56, 126.10, 83.69, 74.69, 73.77, 43.37, 30.72, 26.65, 21.99.

1.3 1-(Cyclopropylethynyl)cyclohexyl acetate



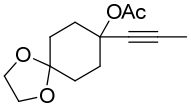
To anhydrous THF (40 mL) was added *n*-BuLi (7.56 mL, 18.9 mmol, 2.5M in hexane, 1.25 equiv.) under an argon atmosphere and the flask was cooled to –78 °C. Then, ethynylcyclopropane (1.00 g, 15.1 mmol, 1 equiv.) was added dropwise. After 30 minutes at –78 C, 4-phenylbutan-2-one (2.91 g, 3.68 mL, 19.7 mmol, 1.30 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was cooled to 0 °C and acetic anhydride (2.08 g, 1.93 mL, 20.4 mmol, 1.35 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and stired for 1.5 h. After completion, H_2O (10 mL) was added and the mixture was extracted with pentane (40 mL) washed with sat. $NaHCO_3$ (10 mL), H_2O (10 mL), brine (10 mL) and dried over $NaSO_4$. The crude product was purified by column chromatography on silica gel (50 g; ethyl acetate/pentane 5%) to afford the product as a colorles oil (2.36 g, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 5H), 2.87 – 2.73 (m, 2H), 2.30 – 2.19 (m, 1H), 2.14 – 1.98 (m, 4H), 1.70 (s, 3H), 1.36 – 1.23 (m, 1H), 0.85 – 0.63 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.39, 141.78, 128.49, 128.45, 125.92, 89.34, 75.57, 75.34, 43.65, 30.91, 26.93, 22.12, 8.57, 8.54, -0.38.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_2Na$ 279.1356; Found 279.1369.

1.4 8-(Prop-1-yn-1-yl)-1,4-dioxaspiro[4.5]decan-8-yl acetate



To a solution of 1,4-dioxaspiro[4.5]decan-8-one (1.25 g, 8.43 mmol, 1.00 equiv.) in THF (20 mL) was added prop-1-yn-1-ylmagnesium bromide (18.6 mL, 9.28 mmol, 0.5M in THF, 1.10 equiv.) at 0 °C. The reaction mixture was stirred for 10 min and allowed to warm to room temperature. After stirring for 1.5 h, acetic anhydride (1.08 g, 1.00 mL, 10.5 mmol, 1.25 equiv.) and DMAP (103 mg, 843 µmol, 0.10 equiv.) were added and the reaction mixture was allowed to stir overnight. After completion, the reaction was quenched with H_2O (10 mL) and the mixture was extracted with pentane (20 mL) washed with sat. $NaHCO_3$ (10 mL) and dried over Na_2SO_4. The crude product was purified by column

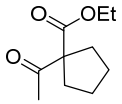
chromatography on silica gel (50 g; ethyl ether/petroleum ether 35%) to obtain the product (916 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 4H), 2.28 – 2.08 (m, 4H), 2.03 (s, 3H), 1.86 (s, 3H), 1.84 – 1.69 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43, 107.69, 82.18, 78.35, 74.35, 64.38, 64.32, 34.61, 31.13, 21.96, 3.74.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}O_4Na$ 261.1097; Found 261.1102.

1.5 Ethyl 1-acetylcyclopentane-1-carboxylate[9]

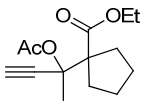


To a stirred solution of ethyl acetoacetate (4.10 mL, 4.22 g, 32.4 mmol, 1.00 equiv.) and potassium carbonate (11.2 g, 81.1 mmol, 2.50 equiv.) in dimethyl sulfoxide (8 mL) at room temperature, was added dropwise 1,4-dibromobutane (3.87 mL, 32.4 mmol, 1.00 equiv.). After three days of stirring, the reaction mixture was filtered and the residue was washed with Et_2O (3 × 25 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude reaction mixture was purified by column chromatography on silica gel (50 g; hexane/ethyl acetate 9:1) to give product as a colorless oil (4.06 g, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (q, J = 7.1 Hz, 2H), 2.15 (s, 3H), 2.13 – 2.05 (m, 4H), 1.74 – 1.54 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.13, 173.63, 67.03, 61.47, 33.14, 26.56, 25.81, 14.19.

1.6 Ethyl 1-(2-acetoxybut-3-yn-2-yl)cyclopentane-1-carboxylate



To a solution of ethyl 1-acetylcyclopentane-1-carboxylate (2.25 g, 12.2 mmol, 1.00 equiv.) in THF (30 mL) was added ethynylmagnesium bromide (26.9 mL, 13.4 mmol, 0.5M in THF, 1.10 equiv.) at 0 °C. The reaction mixture was stirred for 10 min and allowed to warm to room temperature. After stirring for 1.5 h, acetic anhydride (1.44 mL, 1.56 g, 15.3 mmol, 1.25 equiv.) and DMAP (149 mg, 1.22 mmol, 0.10 equiv.) were added and the reaction mixture was allowed to stir overnight. After completion, the reaction was quenched with H_2O (15 mL) and the mixture was extracted with pentane (30 mL), washed with sat. $NaHCO_3$ (15 mL) and dried over Na_2SO_4. The crude product was purified by column

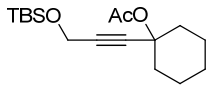
chromatography on silica gel (50 g; ethyl acetate/petroleum ether 0 – 10%) to obtain the product (2.12 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 – 4.02 (m, 2H), 2.53 (s, 1H), 2.35 – 2.15 (m, 2H), 2.03 – 1.80 (m, 5H), 1.73 (s, 3H), 1.71 – 1.44 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.01, 168.79, 82.14, 78.53, 74.50, 63.00, 60.95, 33.04, 32.54, 25.53, 25.24, 23.65, 21.89, 14.19.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}O_4Na$ 275.1254; Found 275.1260.

1.7 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclohexyl acetate



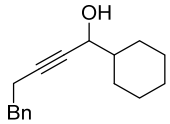
To a suspension of NaH (1.11 g, 27.9 mmol, 60% in mineral oil, 1.25 equiv.) in THF (50 mL) was added propargyl alcohol (1.25 g, 22.3 mmol, 1.00 equiv.) at 0 °C and the reaction was stirred for 15 min before adding TBSCl (3.70 g, 24.5 mmol, 1.10 equiv.). The reaction was allowed to stir for 1.5 h at room temperature. Then, it was cooled to –78 °C and *n*-BuLi (11.2 mL, 27.9 mmol, 2.5M in hexane, 1.25 equiv.) was added dropwise. After stirring for 30 min, cyclohexanone (3.83 g, 39.0 mmol, 1.75 equiv.) was added and 10 min later the reaction was allowed to warm to room temperature. The reaction mixture was cooled to 0 °C, acetic anhydride (3.69 mL, 3.98 g, 39.0 mmol, 1.75 equiv.) was added and stirred overnight. The reaction was quenched with H_2O (20 mL), extracted with pentane (50 mL), and washed with sat. $NaHCO_3$ solution and dried over Na_2SO_4. The evaporated crude mixture was purified by column chromatography on silica gel (75 g; ether/pentane 2 – 10%) to obtain the product as a colourless oil (5.56 g, 80%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (s, 2H), 2.15 – 1.97 (m, 5H), 1.94 – 1.77 (m, 2H), 1.67 – 1.54 (m, 4H), 1.54 – 1.43 (m, 1H), 1.40 – 1.27 (m, 1H), 0.90 (s, 9H), 0.12 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.30, 84.87, 84.80, 75.55, 52.00, 37.07, 25.93, 25.31, 22.64, 22.11, 18.39, -4.95.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{30}O_3SiNa$ 333.1856; Found 333.1856.

1.8 1-Cyclohexyl-5-phenylpent-2-yn-1-ol[10]

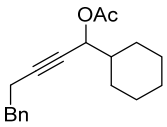


A dry flask was charged with (*R*)-BINOL (286 mg, 1.00 mmol, 0.10 equiv.) and $InBr_3$ (355 mg, 1.00 mmol, 0.10 equiv.) under Ar. To the flask was added dry distilled CH_2Cl_2 (50 mL) and then freshly

distilled cyclohexanecarboxaldehyde (1.21 g, 10.0 mmol, 1.00 equiv.) at room temperature. The resulting solution was stirred for 15 minutes, and dicyclohexylmethylamine (1.07 mL, 977 mg, 5.00 mmol, 0.50 equiv.) was added. After stirring again for 10 minutes, but-3-yn-1-ylbenzene (2.60 g, 20.0 mmol, 2.00 equiv.) was added. The mixture was stirred for 7 d at 40 °C. After cooling, the reaction was quenched with aqueous NH_4Cl (10 mL) and a small amount of 1M HCl (1 mL), extracted with diethyl ether (1 × 50 mL, 2 × 25 mL), and dried over Na_2SO_4. The organic solvent was extracted and the resulting crude mixture was purified by flash column chromatography on silica gel (50 g, ethyl acetate/pentane 10%) to give product as a colorless oil (1.780 g, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.09 (m, 5H), 4.21 – 4.02 (m, 1H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.53 (td, *J* = 7.5, 1.9 Hz, 2H), 1.83 – 1.59 (m, 6H), 1.54 – 1.39 (m, 1H), 1.36 – 0.87 (m, 5H).

1.9 1-Cyclohexyl-5-phenylpent-2-yn-1-yl acetate



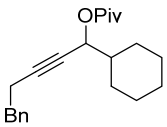
To a mixture of 1-cyclohexyl-5-phenylpent-2-yn-1-ol (850 mg, 3.51 mmol, 1.00 equiv.), acetic anhydride (414 µl, 448 mg, 4.38 mmol, 1.25 equiv.) and DMAP (21.4 mg, 175 µmol, 0.05 equiv.) in DCM (10 mL) was added Et_3N (856 µl, 6.14 mmol, 1.75 equiv.) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then, the reaction was quenched with 10% citric acid, (5 mL) extracted with pentane (10 mL) and washed with H_2O (5 mL), sat. $NaHCO_3$ (5 mL), H_2O (5 mL), brine (3 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (25 g; ethyl acetate/pentane 5%) to obtain the product (962.6 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.12 (m, 5H), 5.18 (dt, *J* = 6.2, 2.0 Hz, 1H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.52 (td, *J* = 7.4, 2.0 Hz, 2H), 2.07 (s, 3H), 1.80 – 1.52 (m, 7H), 1.31 – 0.93 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.32, 140.65, 128.64, 128.46, 126.40, 85.96, 68.84, 42.08, 35.03, 28.66, 28.15, 26.33, 25.92, 25.87, 21.22, 21.04.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_2Na$ 307.1669; Found 307.1679.

1.10 1-Cyclohexyl-5-phenylpent-2-yn-1-yl pivalate



To a mixture of 1-cyclohexyl-5-phenylpent-2-yn-1-ol (850 mg, 3.51 mmol, 1.00 equiv.), pivaloyl chloride (518 µl, 507 mg, 4.21 mmol, 1.20 equiv.), and DMAP (21.4 mg, 175 µmol, 0.05 equiv.) in

DCM (10 mL) was added Et_3N (856 µl, 6.14 mmol, 1.75 equiv.) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then, the reaction was quenched with 10% citric acid, (5 mL) extracted with pentane (10 mL) and washed with H_2O (5 mL), sat. $NaHCO_3$ (5 mL), H_2O (5 mL), brine (3 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (25 g; ethyl acetate/pentane 5%) to obtain the product (1.14 g, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.12 (m, 5H), 5.19 – 5.09 (m, 1H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.51 (td, *J* = 7.4, 2.0 Hz, 2H), 1.82 – 1.53 (m, 6H), 1.27 – 0.96 (m, 14H).

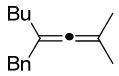
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.59, 140.71, 128.64, 128.44, 126.36, 85.44, 77.76, 68.50, 42.25, 38.99, 35.09, 28.54, 28.40, 27.26, 26.40, 25.96, 21.02.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{30}O_2Na$ 349.2138; Found 349.2155.

2 Iron-Catalyzed Synthesis of Allenes

General procedure: In a dry 20 or 5 mL microwave flask under argon was added catalyst $Fe(acac)_3$ (1 - 5 mol%) and diethyl ether (5 mL/mmol) to obtain an orange solution. The solution was cooled to –20 °C and propargyl carboxylate (1.00 equiv.) was added followed by the drop wise addition of Grignard reagent (1.25 equiv.) for 5 min. The reaction mixture was stirred for another 30 min, quenched with aq. 1 - 10% citric acid solution (1 mL/mmol), extracted with pentane or diethyl ether (3 × 2 mL/mmol) and the combined organic phase was carefully evaporated. The crude product was purified by column chromatography over SiO_2 (20 g/mmol, diethyl ether/pentane) to obtain the product.

2.1 (2-(2-Methylprop-1-en-1-ylidene)hexyl)benzene



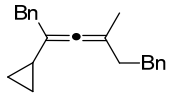
According to the general procedure catalyst (14.1 mg, 40 µmol, 5.00 mol%), 2-methyloct-3-yn-2-yl acetate (146 mg, 800 µmol, 1.00 equiv.) and benzylmagnesium chloride (1.00 mL, 1.00 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 161 mg of product (94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.11 (m, 5H), 3.25 (s, 2H), 1.86 (t, *J* = 7.2 Hz, 2H), 1.65 (s, 6H), 1.41 – 1.24 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.11, 140.81, 129.03, 128.15, 125.92, 101.49, 95.35, 77.48, 77.16, 76.84, 40.59, 31.85, 29.99, 22.44, 20.98, 14.18.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{23}$ 215.1794; Found 215.1794.

2.2 (2-Cyclopropyl-4-methylhexa-2,3-diene-1,6-diyl)dibenzene



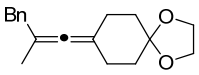
According to the general procedure catalyst (26.5 mg, 75 µmol, 5.00 mol%), 1-cyclopropyl-3-methyl-5-phenylpent-1-yn-3-yl acetate (384 mg, 1.50 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.88 mL, 1.88 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1%) to yield 372.1 mg of product (86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.13 (m, 10H), 3.38 (d, *J* = 2.9 Hz, 2H), 2.62 (t, *J* = 8.1 Hz, 2H), 2.32 – 2.09 (m, 2H), 1.70 (s, 3H), 1.18 – 1.04 (m, 1H), 0.69 – 0.52 (m, 2H), 0.43 – 0.25 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.13, 142.63, 140.73, 129.29, 128.56, 128.47, 128.24, 126.06, 125.91, 107.40, 101.65, 40.69, 36.43, 34.42, 19.78, 12.76, 7.26, 7.02.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{24}Na$ 311.1770; Found 311.1770.

2.3 8-(2-Methyl-3-phenylprop-1-en-1-ylidene)-1,4-dioxaspiro[4.5]decane



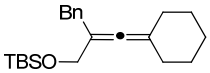
According to the general procedure catalyst (17.7 mg, 50 μmol, 5.00 mol%), 8-(prop-1-yn-1-yl)-1,4-dioxaspiro[4.5]decan-8-yl acetate (238 mg, 1.00 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.25 mL, 1.25 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was quenched with aq. 1% citric acid, extracted and purified over SiO_2 (ethyl ether/pentane 5%) to yield 232.8 mg of product (86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.13 (m, 5H), 3.93 (s, 4H), 3.24 (s, 2H), 2.28 – 2.04 (m, 4H), 1.73 – 1.60 (m, 5H), 1.50 – 1.39 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.33, 140.51, 129.23, 128.31, 126.20, 108.72, 99.70, 98.01, 64.51, 64.48, 41.91, 35.68, 29.07, 19.49.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{22}O_2Na$ 293.1512; Found 293.1524.

2.4 ((2-Benzyl-3-cyclohexylideneallyl)oxy)(tert-butyl)dimethylsilane



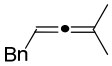
According to the general procedure catalyst (26.5 mg, 75 μmol, 5.00 mol%), 8 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclohexyl acetate (466 mg, 1.50 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.88 mL, 1.88 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was quenched with aq. 2.5 % citric acid, extracted and purified over SiO_2 (ethyl ether/pentane 1 – 2%) to yield 397.7 mg of product (77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.12 (m, 5H), 4.09 (s, 2H), 3.32 (s, 2H), 2.08 – 1.93 (m, 4H), 1.61 – 1.19 (m, 6H), 0.92 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.44, 140.53, 129.37, 128.24, 125.99, 104.26, 102.53, 64.68, 36.85, 31.79, 27.63, 26.37, 26.20, 18.62, -4.92.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{34}OSiNa$ 365.2271; Found 365.2278.

2.5 (4-Methylpenta-2,3-dien-1-yl)benzene[11]

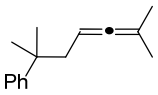


According to the general procedure catalyst (35.3 mg, 100 µmol, 5.00 mol%), 2-methylbut-3-yn-2-yl acetate (252 mg, 2.00 mmol, 1.00 equiv.) and benzylmagnesium chloride (2.50 mL, 2.50 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 290.5 mg of product (92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.14 (m, 5H), 5.18 – 5.04 (m, 1H), 3.31 (d, *J* = 7.1 Hz, 2H), 1.70 (d, *J* = 2.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.41, 141.03, 128.46, 128.26, 125.93, 95.40, 88.26, 36.23, 20.64.

2.6 (2,6-Dimethylhepta-4,5-dien-2-yl)benzene



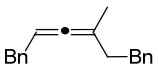
According to the general procedure catalyst (26.5 mg, 75 µmol, 5.00 mol%), 8 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclohexyl acetate (252 mg, 2.00 mmol, 1.00 equiv.) and (2-methyl-2-phenylpropyl)magnesium chloride (5.21 mL, 1.25 mmol, 0.48 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 397.7 mg of product (99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 4H), 7.21 – 7.13 (m, 1H), 4.77 – 4.60 (m, 1H), 2.29 (d, *J* = 7.7 Hz, 2H), 1.58 (d, *J* = 2.9 Hz, 6H), 1.35 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.50, 149.26, 128.10, 126.08, 125.56, 93.78, 85.30, 44.71, 38.27, 28.62, 20.62.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{20}Na$ 223.1457; Found 223.1456.

2.7 (4-Methylhexa-2,3-diene-1,6-diyl)dibenzene



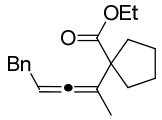
According to the general procedure catalyst (26.5 mg,75.0 µmol, 5.00 mol%), 3-methyl-5-phenylpent-1-yn-3-yl acetate (324 mg, 1.50 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.88 mL, 1.88 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 0.75%) to yield 361.5 mg of product (97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.14 (m, 10H), 5.36 – 5.17 (m, 1H), 3.33 (d, *J* = 7.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.36 – 2.23 (m, 2H), 1.79 (d, *J* = 2.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.27, 142.49, 141.16, 128.75, 128.62, 128.51, 128.48, 126.20, 125.96, 99.76, 90.60, 36.41, 36.01, 34.25, 19.55.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}$ 249.1638; Found 249.1635.

2.8 Ethyl 1-(5-phenylpenta-2,3-dien-2-yl)cyclopentanecarboxylate



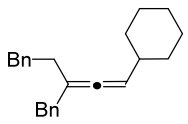
According to the general procedure catalyst (26.5 mg,75.0 μmol, 5.00 mol%), ethyl 1-(2-acetoxybut-3-yn-2-yl)cyclopentane-1-carboxylate (324 mg, 1.50 mmol, 1.00 equiv.) and benzylmagnesium bromide (1.88 mL, 1.88 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was quenched with aq. 2.5% citric acid, extracted and purified over SiO_2 (ethyl ether/pentane 5%) to yield 272.1 mg of product (64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 5H), 5.34 (tq, *J* = 6.9, 2.7 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.35 (d, *J* = 6.9 Hz, 2H), 2.16 – 2.00 (m, 2H), 1.87 – 1.73 (m, 1H), 1.73 – 1.64 (m, 4H), 1.65 – 1.49 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.00, 176.16, 140.65, 128.69, 128.42, 126.17, 103.09, 92.01, 60.73, 57.22, 36.07, 35.02, 24.34, 24.31, 16.58, 14.35.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}O_2Na$ 307.1669; Found 307.1671.

2.9 (2-(2-Cyclohexylvinylidene)butane-1,4-diyl)dibenzene



From acetate (R=Ac): According to the general procedure catalyst (8.83 mg,25.0 μmol, 5.00 mol%), 1-cyclohexyl-5-phenylpent-2-yn-1-yl acetate (142 mg, 500 μmol, 1.00 equiv.) and benzylmagnesium chloride (625 μL, 1.25 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (2.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 0.8%) to yield allene 125.5 mg of product (79%). By-product was not isolated.

From pivalate (R=Piv): According to the general procedure catalyst (8.83 mg,25.0 μmol, 5.00 mol%), 1-cyclohexyl-5-phenylpent-2-yn-1-yl pivalate (163 mg, 500 μmol, 1.00 equiv.) and benzylmagnesium chloride (625 μL, 1.25 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (2.5 mL) were reacted. The reaction mixture was extracted and purified by thin layer chromatography (TLC) on slica gel (ethyl ether/pentane 1%) to yield allene 105.4 mg of product (67%) and acetylene 20.7 mg (13%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.03 (m, 10H), 5.22 – 5.04 (m, 1H), 3.34 (d, *J* = 2.5 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.33 – 2.14 (m, 2H), 1.96 – 1.83 (m, 1H), 1.77 – 1.58 (m, 5H), 1.35 – 0.91 (m, 5H).

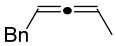
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.81, 142.45, 140.04, 129.19, 128.55, 128.34, 128.27, 126.17, 125.82, 104.25, 98.69, 40.69, 37.87, 34.31, 33.69, 33.37, 33.22, 26.36, 26.26.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{28}Na$ 339.2083; Found 339.2083.

Acetylene side product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.10 (m, 10H), 2.87 – 2.62 (m, 4H), 2.53 – 2.36 (m, 3H), 1.86 – 1.58 (m, 5H), 1.36 – 1.08 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.20, 140.78, 129.31, 128.66, 128.38, 128.20, 126.22, 126.08, 82.50, 40.85, 40.47, 39.16, 35.70, 31.86, 28.67, 26.61, 26.41, 21.07.

2.10 Penta-2,3-dien-1-ylbenzene



According to the general procedure catalyst (35.3 mg,100 μmol, 5.00 mol%), but-3-yn-2-yl pivalate (339 mg, 2.00 mmol, 1.00 equiv.) and benzylmagnesium chloride (2.50 mL, 2.50 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 95.4 mg of product (33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.14 (m, 5H), 5.30 – 5.18 (m, 1H), 5.18 – 5.06 (m, 1H), 3.35 (dd, *J* = 7.2, 2.6 Hz, 2H), 1.68 (dd, *J* = 7.0, 3.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.47, 140.79, 128.58, 128.46, 126.21, 89.88, 86.09, 35.94, 14.61.

LRMS (EI) m/z (%): 144.1 (M^+ ,5), 129.0 (100).

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}$ 145.1012; Found 145.1012.

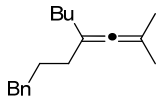
2.11 Buta-2,3-dien-1-ylbenzene[12]

According to the general procedure catalyst (35.3 mg,100 μmol, 5.00 mol%), propargyl acetate (196 mg, 2.00 mmol, 1.00 equiv.) and benzylmagnesium chloride (2.50 mL, 2.55 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 35.9 mg of product (14%).

^{1}H NMR (400 MHz, CDCl3) δ 7.37 – 7.17 (m, 5H), 5.29 (tt, *J* = 7.4, 6.6 Hz, 1H), 4.73 (dt, *J* = 6.6, 2.9 Hz, 2H), 3.37 (dt, *J* = 7.4, 2.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.13, 140.42, 128.56, 128.52, 126.35, 89.68, 75.22, 35.25.

2.12 (4-(2-Methylprop-1-en-1-ylidene)octyl)benzene



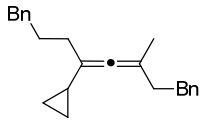
According to the general procedure catalyst (5.30 mg, 15 μmol, 1.00 mol%), 2-methyloct-3-yn-2-yl acetate (273 mg, 1.50 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (2.34 mL, 1.88 mmol, 0.80 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 336.8 mg of product (93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 3H), 2.64 (t, *J* = 7.7 Hz, 2H), 1.94 (dt, *J* = 15.7, 7.1 Hz, 4H), 1.79 – 1.63 (m, 8H), 1.45 – 1.26 (m, 4H), 0.92 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.72, 143.12, 128.62, 128.37, 125.70, 101.60, 95.64, 35.72, 33.02, 32.64, 30.10, 29.79, 22.52, 21.18, 14.21.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{27}$ 243.2107; Found 243.2105.

2.13 (5-Cyclopropyl-3-methylocta-3,4-diene-1,8-diyl)dibenzene



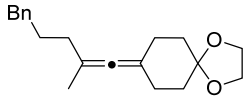
According to the general procedure catalyst (3.53 mg, 10 μmol, 1.00 mol%), 1-cyclopropyl-3-methyl-5-phenylpent-1-yn-3-yl acetate (256 mg, 1.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (1.39 mL, 1.25 mmol, 0.90 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 0.75%) to yield 213.8 mg of product (68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.13 (m, 10H), 2.74 – 2.59 (m, 4H), 2.32 – 2.19 (m, 2H), 2.13 – 1.99 (m, 2H), 1.80 – 1.68 (m, 5H), 1.13 – 1.02 (m, 1H), 0.68 – 0.55 (m, 2H), 0.37 – 0.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.82, 142.97, 142.50, 128.61, 128.48, 128.38, 128.37, 125.80, 125.73, 107.21, 101.55, 36.40, 35.79, 34.43, 32.97, 29.97, 19.95, 13.06, 6.88, 6.67.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{28}Na$ 339.2083; Found 339.2091.

2.14 8-(2-Methyl-5-phenylpent-1-en-1-ylidene)-1,4-dioxaspiro[4.5]decane



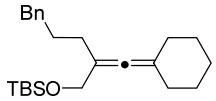
According to the general procedure catalyst (3.53 mg, 10 µmol, 1.00 mol%), 8-(prop-1-yn-1-yl)-1,4-dioxaspiro[4.5]decan-8-yl acetate (238 mg, 1.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (1.39 mL, 1.25 mmol, 0.90 M in diethyl ether, 1.25 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was quenched with aq. 1% citric acid, extracted and purified over SiO_2 (ethyl ether/pentane 5%) to yield 191.5 mg of product (64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.24 – 7.13 (m, 3H), 3.97 (s, 4H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.34 – 2.21 (m, 4H), 1.96 (t, *J* = 7.2 Hz, 2H), 1.80 – 1.70 (m, 6H), 1.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.77, 142.67, 128.47, 128.25, 125.61, 108.58, 99.31, 97.04, 64.31, 64.29, 35.77, 35.28, 33.63, 29.20, 29.05, 19.85.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}O_2Na$ 321.1825; Found 321.1825.

2.15 tert-Butyl((2-(cyclohexylidenemethylene)-5-phenylpentyl)oxy)dimethylsilane



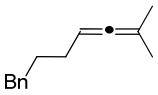
According to the general procedure catalyst (26.5 mg, 75 µmol, 1.00 mol%), 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclohexyl acetate (465.8 mg, 1.50 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (2.08 mL, 1.88 mmol, 0.90 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was quenched with aq. 2.5% citric acid, extracted and purified over SiO_2 (ethyl ether/pentane 1 – 2%) to yield 414.5 mg of product (75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.09 (m, 5H), 4.10 (s, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.17 – 2.08 (m, 4H), 2.02 (t, *J* = 7.2 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.65 – 1.47 (m, 6H), 0.90 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.93, 142.84, 128.49, 128.21, 125.55, 104.10, 101.76, 65.41, 35.46, 31.83, 29.34, 28.72, 27.72, 26.26, 25.97, 18.40, -5.16.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{38}OSiNa$ 393.2584; Found 393.2587.

2.16 (6-Methylhepta-4,5-dien-1-yl)benzene



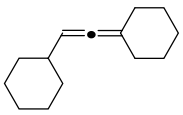
According to the general procedure catalyst (7.06 mg, 20 µmol, 1.00 mol%), 2-methylbut-3-yn-2-yl acetate (252 mg,2.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (2.78 mL, 2.00 mmol, 0.90 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 291.3 mg of product (78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 2H), 7.25 – 7.08 (m, 3H), 5.06 – 4.91 (m, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.01 (q, *J* = 7.0 Hz, 2H), 1.82 – 1.62 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.00, 142.83, 128.63, 128.39, 125.76, 95.21, 88.58, 35.42, 31.08, 28.82, 20.94.

LRMS (EI) m/z (%): 186.1 (M^+ ,6), 143.2 (100).

2.17 (2-Cyclohexylidenevinyl)cyclohexane



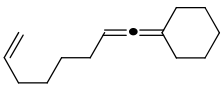
According to the general procedure catalyst (7.06 mg, 20 µmol, 1.00 mol%), 1-ethynylcyclohexyl acetate (332 mg,2.00 mmol, 1.00 equiv.) and cyclohexylmagnesium chloride (2.50 mL, 2.00 mmol, 1.00 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 271 mg of product (71%).

1H NMR (400 MHz, $CDCl_3$) δ 5.08 – 4.83 (m, 1H), 2.26 – 2.00 (m, 4H), 1.99 – 1.83 (m, 1H), 1.80 – 1.40 (m, 11H), 1.36 – 0.98 (m, 5H).

^{13}C NMR (101 MHz, CDCl3) δ 197.23, 103.43, 95.07, 37.64, 33.34, 32.16, 27.80, 26.47, 26.43, 26.21.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{23}$ 191.1794; Found 191.1796.

2.18 Octa-1,7-dien-1-ylidenecyclohexane



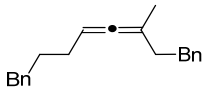
According to the general procedure catalyst (7.06 mg, 20 µmol, 1.00 mol%), 1-ethynylcyclohexyl acetate (332 mg,2.00 mmol, 1.00 equiv.) and hex-5-en-1-ylmagnesium bromide (1.92 mL, 2.50 mmol, 1.30 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 240.9 mg of product (63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 – 5.73 (m, 1H), 5.12 – 4.88 (m, 3H), 2.18 – 1.94 (m, 8H), 1.70 – 1.37 (m, 10H).

^{13}C NMR (101 MHz, CDCl3) δ 198.29, 139.11, 114.15, 102.38, 88.49, 33.68, 31.83, 29.13, 28.58, 28.24, 27.53, 26.23.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{23}$ 191.1794; Found 191.1795.

2.19 (3-Methylocta-3,4-diene-1,8-diyl)dibenzene



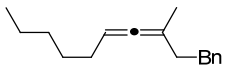
According to the general procedure catalyst (5.30 mg, 15 μmol, 1.00 mol%), 3-methyl-5-phenylpent-1-yn-3-yl acetate (324 mg, 1.50 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (2.08 mL, 1.88 mmol, 0.90 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 371.9 mg of product (90%).

1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.03 (m, 10H), 5.23 – 5.04 (m, 1H), 2.81 (t, J = 7.8 Hz, 2H), 2.71 (t, J = 7.7 Hz, 2H), 2.33 (t, J = 7.7 Hz, 2H), 2.12 – 1.96 (m, 2H), 1.88 – 1.67 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.52, 142.65, 142.32, 128.52, 128.44, 128.31, 128.27, 125.74, 125.69, 99.12, 90.57, 35.84, 35.42, 34.11, 31.04, 28.83, 19.55.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}$ 277.1951; Found 277.1958.

2.20 (3-Methyldeca-3,4-dien-1-yl)benzene



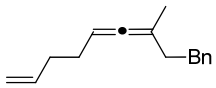
According to the general procedure catalyst (5.30 mg, 15 μmol, 1.00 mol%), 3-methyl-5-phenylpent-1-yn-3-yl acetate (324 mg, 1.50 mmol, 1.00 equiv.) and pentylmagnesium bromide (938 μL, 1.88 mmol, 2.00 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 238.6 mg of product (70%).

1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.06 (m, 5H), 5.13 – 4.94 (m, 1H), 2.73 (d, J = 8.0 Hz, 2H), 2.33 – 2.19 (m, 2H), 1.92 (q, J = 6.7 Hz, 2H), 1.72 (d, J = 2.8 Hz, 3H), 1.46 – 1.17 (m, 6H), 0.90 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 201.26, 142.40, 128.39, 128.21, 125.66, 98.75, 90.97, 35.83, 34.10, 31.36, 29.27, 28.98, 22.54, 19.49, 14.11.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{24}$ 229.1951; Found 229.1954.

2.21 (3-Methylnona-3,4,8-trien-1-yl)benzene



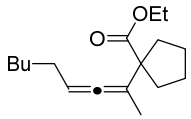
According to the general procedure catalyst (5.30 mg, 15 µmol, 1.00 mol%), 3-methyl-5-phenylpent-1-yn-3-yl acetate (324 mg, 1.50 mmol, 1.00 equiv.) and but-3-en-1-ylmagnesium bromide (2.08 mL, 1.88 mmol, 0.90 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 193.8 mg of product (61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.11 (m, 5H), 5.94 – 5.77 (m, 1H), 5.16 – 4.93 (m, 3H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.37 – 2.21 (m, 2H), 2.20 – 1.95 (m, 4H), 1.75 (d, *J* = 2.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.40, 142.31, 138.46, 128.39, 128.23, 125.70, 114.60, 99.28, 90.24, 35.76, 34.04, 33.35, 28.66, 19.47.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}$ 213.1638; Found 213.1629.

2.22 Ethyl 1-(7-phenylhepta-2,3-dien-2-yl)cyclopentanecarboxylate



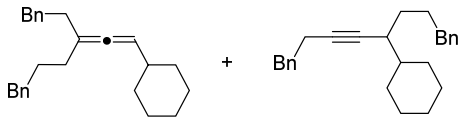
According to the general procedure catalyst (5.30 mg,15.0 µmol, 1.00 mol%), ethyl 1-(2-acetoxybut-3-yn-2-yl)cyclopentane-1-carboxylate (324 mg, 1.50 mmol, 1.00 equiv.) and pentylmagnesium bromide (938 µL, 1.88 mmol, 2 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was quenched with aq. 2.5 % citric acid, extracted and purified over SiO_2 (ethyl ether/pentane 5%) to yield 242.4 mg of product (61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (td, *J* = 6.4, 3.0 Hz, 1H), 4.20 – 4.05 (m, 2H), 2.16 – 1.89 (m, 4H), 1.88 – 1.74 (m, 2H), 1.70 – 1.52 (m, 7H), 1.49 – 1.28 (m, 6H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.31, 176.39, 102.23, 92.64, 60.68, 57.26, 35.17, 34.91, 31.55, 29.18, 28.88, 24.38, 24.35, 22.66, 16.63, 14.35, 14.22.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{28}O_2Na$ 287.1982; Found 258.1976.

2.23 (3-(2-Cyclohexylvinylidene)hexane-1,6-diyl)dibenzene and (5-Cyclohexyloct-3-yne-1,8-diyl)-dibenzene



From pivalate (R=Piv): According to the general procedure catalyst (0.9 mg,2.50 μmol, 5.00 mol%), 1-cyclohexyl-5-phenylpent-2-yn-1-yl pivalate (81.6 mg, 250 μmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (391 μL, 1.25 mmol, 0.8 M in diethyl ether, 1.25 equiv.) in diethyl ether (1.25 mL) were reacted. The reaction mixture was extracted and purified by thin layer chromatography (TLC) on slica gel (ethyl ether/pentane 1%) to yield 26.5 mg (31%) of allene product and acetylene product 38 mg (44%).

From acetate (R=Ac): According to the general procedure catalyst (8.83 mg,25.0 μmol, 5.00 mol%), 1-cyclohexyl-5-phenylpent-2-yn-1-yl acetate (142 mg, 500 μmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (694 μL, 1.25 mmol, 0.9 M in diethyl ether, 1.25 equiv.) in diethyl ether (2.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 0.5%) to yield 41.7 mg (24%) of allene product and acetylene product 59.4 mg (34%).

Allene: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 – 7.13 (m, 10H), 5.13 (dt, J = 6.0, 3.0 Hz, 1H), 2.71 (t, J = 8.1 Hz, 2H), 2.64 (dd, J = 8.6, 6.8 Hz, 2H), 2.23 (dt, J = 7.4, 4.0 Hz, 2H), 1.95 (ddd, J = 42.3, 5.5, 3.0 Hz, 3H), 1.80 – 1.65 (m, 6H), 1.33 – 0.96 (m, 6H).

13C NMR (101 MHz, CDCl3) δ 199.56, 142.79, 142.60, 128.62, 128.54, 128.39, 128.37, 125.82, 125.77, 104.47, 99.18, 38.01, 35.74, 34.80, 34.34, 33.52, 33.47, 32.59, 29.56, 26.37, 26.32, 26.30.

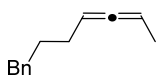
HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{26}H_{32}Na$ 367.2396; Found 367.2408.

Acetylene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.07 (m, 10H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.68 – 2.53 (m, 2H), 2.53 – 2.44 (m, 2H), 2.21 – 2.11 (m, 1H), 1.89 – 1.56 (m, 7H), 1.43 (q, *J* = 7.8 Hz, 2H), 1.32 – 0.97 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.83, 141.19, 128.67, 128.56, 128.37, 126.21, 125.74, 83.14, 81.59, 41.67, 38.13, 35.96, 35.83, 32.25, 31.59, 29.66, 29.29, 26.68, 26.65, 26.53, 21.11.

HRMS (APCI-TOF) m/z: [M + H]+ Calcd for $C_{26}H_{33}$ 345.2577; Found 345.2567.

2.24 Hepta-4,5-dien-1-ylbenzene



According to the general procedure catalyst (5.30 mg, 15 μmol, 1.00 mol%), but-3-yn-2-yl pivalate (339 mg, 2.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (3.57 mL, 2.50 mmol, 0.70 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 134.5 mg of product (39%).

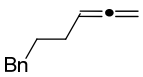
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.13 (m, 5H), 5.15 – 5.01 (m, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.08 – 1.97 (m, 2H), 1.81 – 1.70 (m, 2H), 1.70 – 1.61 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.87, 142.53, 128.49, 128.26, 125.66, 89.94, 85.73, 35.26, 30.84, 28.30, 14.64.

LRMS (EI) m/z (%): 172.1 (M^+ ,2), 143.2 (100).

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}$ 173.1325; Found 173.1321.

2.25 Hexa-4,5-dien-1-ylbenzene[13]

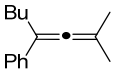


According to the general procedure catalyst (7.06 mg, 20 μmol, 1.00 mol%), but-3-yn-2-yl pivalate (280 mg, 2.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (3.57 mL, 2.50 mmol, 0.70 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 74.8 mg of product (24%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.14 (m, 5H), 5.21 – 5.10 (m, 1H), 4.77 – 4.66 (m, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.14 – 2.01 (m, 2H), 1.85 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.77, 142.49, 128.62, 128.42, 125.84, 89.85, 75.03, 35.40, 30.91, 27.80.

2.26 (2-Methylocta-2,3-dien-4-yl)benzene[14]

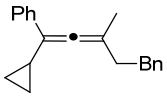


According to the general procedure catalyst (26.5 mg, 75 μmol, 5.00 mol%), 2-methyloct-3-yn-2-yl acetate (273 mg, μmol, 1.50 equiv.) and phenylmagnesium chloride (625 μL, 1.88 mmol, 3.00 M in ethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 276.8 mg of product (92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.12 (m, 5H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.83 (s, 6H), 1.59 – 1.36 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.95, 138.70, 128.32, 126.15, 103.48, 98.18, 30.30, 30.03, 22.61, 20.57, 14.22.

2.27 (1-Cyclopropyl-3-methylpenta-1,2-diene-1,5-diyl)dibenzene



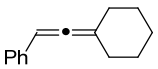
According to the general procedure catalyst (26.5 mg, 75 µmol, 5.00 mol%), 1-cyclopropyl-3-methyl-5-phenylpent-1-yn-3-yl acetate (385 mg, 1.50 mmol, 1.00 equiv.) and phenylmagnesium bromide (625 µL, 1.88 mmol, 3.00 M in diethyl ether, 1.25 equiv.) in diethyl ether (7.5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1%) to yield 329.2 mg of product (84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 6.98 (m, 10H), 2.91 – 2.66 (m, 2H), 2.54 – 2.30 (m, 2H), 1.83 (d, J = 5.5 Hz, 3H), 1.64 – 1.48 (m, 1H), 0.95 – 0.67 (m, 2H), 0.58 – 0.30 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.17, 142.00, 138.48, 128.39, 128.32, 128.16, 126.29, 126.16, 125.79, 108.77, 103.67, 36.08, 34.01, 19.14, 11.26, 7.02, 6.86.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}Na$ 297.1614; Found 297.1616.

2.28 (2-Cyclohexylidenevinyl)benzene[15]

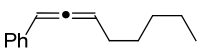


According to the general procedure catalyst (35.3 mg, 100 µmol, 5.00 mol%), 1-ethynylcyclohexyl acetate (332 mg, 2.00 mmol, 1.00 equiv.) and phenylmagnesium bromide (833 µL, 2.50 mmol, 3.00 M in diethyl ether, 1.25 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 207.1 mg of product (56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.10 (m, 5H), 6.04 – 5.96 (m, 1H), 2.34 – 2.14 (m, 4H), 1.78 – 1.49 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.81, 136.30, 128.63, 126.64, 126.42, 106.61, 92.51, 31.48, 27.85, 26.28.

2.29 Octa-1,2-dien-1-ylbenzene[15]



According to the general procedure catalyst (35.3 mg, 100 µmol, 5.00 mol%), oct-1-yn-3-yl pivalate (421 mg, 2.00 mmol, 1.00 equiv.) and phenylmagnesium bromide (833 µL, 2.50 mmol, 3.00 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (pentane) to yield 152.9 mg of product (41%).

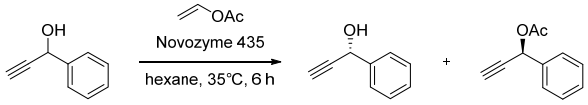
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.13 (m, 5H), 6.17 – 6.09 (m, 1H), 5.62 – 5.52 (m, 1H), 2.21 – 2.07 (m, 2H), 1.55 – 1.44 (m, 2H), 1.42 – 1.26 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.15, 135.18, 128.53, 126.59, 126.57, 95.11, 94.54, 31.41, 28.86, 28.74, 22.48, 14.08.

3 Experiments for the Transfer of Chirality

3.1 Synthesis of Substrates

3.1.1 Kinetic resolution of 1-Phenylprop-2-yn-1-ol[16,17]

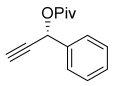


To a 50mL Erlenmeyer flask containing hexane (10 mL), vinyl acetate (2.00 mL, 21.8 mmol, 2.65 equiv.) and Novozyme 435 (300 mg) was added 1-phenylprop-2-yn-1-ol (1.00 mL, 8.25 mmol, 1 equiv.). The reaction mixture was stirred at 35 °C for 6 h. After that, the mixture was filtered and the solvent evaporated. The residue was purified by column chromatography on silica gel (25g, ether/pentane 20%) to obtain the acetate (682 mg, 47%) and the alcohol (433 mg, 40%)

Acetate: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 2H), 7.45 – 7.32 (m, 3H), 6.46 (d, *J* = 2.3 Hz, 1H), 2.66 (d, *J* = 2.3 Hz, 1H), 2.12 (s, 3H).

Alcohol: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 2H), 7.46 – 7.31 (m, 3H), 5.46 (dd, *J* = 6.3, 2.3 Hz, 1H), 2.68 (d, *J* = 2.3 Hz, 1H), 2.46 – 2.38 (m, 1H).

3.1.2 (*S*)-1-phenylprop-2-yn-1-yl pivalate ((*S*)-**1**)[18]



To a mixture of (*S*)-1-phenylprop-2-yn-1-ol (790 mg, 5.98 mmol, 1.00 equiv.), pivaloyl chloride (883 µl, 865 mg, 7.17 mmol, 1.20 equiv.), and DMAP (36.5 mg, 299 µmol, 0.05 equiv.) in DCM (15 mL) was added Et_3N (1.46 mL, 10.5 mmol, 1.75 equiv.) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then, the reaction was quenched with water (5 mL) extracted with pentane (15 mL) and washed with H_2O (5 mL), brine (3 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (25 g; ether/pentane 5%) to obtain the product (1.26 g, 98%; 99.3 *ee*).

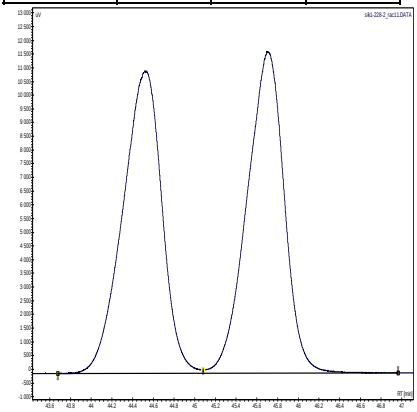
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.46 (m, 2H), 7.44 – 7.31 (m, 3H), 6.43 (d, *J* = 2.2 Hz, 1H), 2.62 (d, *J* = 2.2 Hz, 1H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.25, 136.95, 128.95, 128.77, 127.42, 80.61, 75.20, 65.20, 38.89, 27.11.

GC-FID: gradient: 95 °C, 0.1 °C/min to 102, 20ºC/min to 200ºC, 1 min; column: IVADEX-1 (25 m × 0.25 mm × 0.25 µm); carrier gas: H_2; flow: 1.8 mL/min.

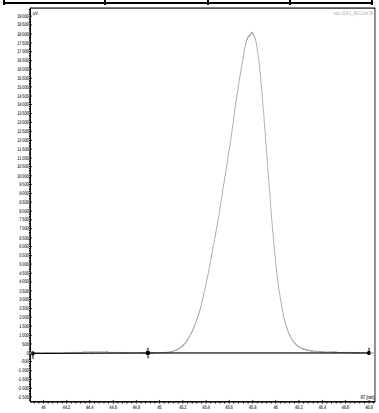
Racemate

Ret. Time	Area	% Area	Height
44.53	4832.5	49.80	11042.6
45.71	4871.7	50.20	11724.9



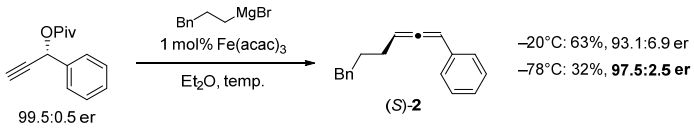
Enantiomer

Ret. Time	Area	% Area	Height
44.44	69.1	0.33	26.5
45.79	18115.5	99.67	7911.6



3.2 Iron-Catalyzed Synthesis of Allenes

3.2.1 (*S*)-Hexa-1,2-diene-1,6-diyldibenzene ((*S*)-**2**).



In a dry 20 or 5 mL microwave flask under argon was added catalyst $Fe(acac)_3$ (8.83 mg, 25.0 µmol, 5.00 mol %) and diethylether (2.5 mL) to obtain an orange solution. The solution was cooled to −20 °C/−78 °C and (S)-1-phenylprop-2-yn-1-yl pivalate (108 mg, 500 µmol, 1.25 equiv) was added followed by the drop wise addition of (3-phenylpropyl)magnesium bromide (1.25 mL, 625 µmol, 0.50 M in diethyl ether, 1.25 equiv) for 5 min. The reaction mixture was stirred for another 30 min, quenched by aq. Citric acid solution (0.5 mL), extracted with pentane (3 x 1 mL) and the combined organic phase was carefully evaporated. The crude product was purified by column chromatography over SiO_2 (25 g, ether/pentane 0.7%) to obtain 74 mg (63%) product at −20 °C and 37 mg (32 %) at −78 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 6H), 7.25 – 7.14 (m, 4H), 6.25 – 6.13 (m, 1H), 5.63 (q, *J* = 6.6 Hz, 1H), 2.72 (dd, *J* = 8.6, 6.9 Hz, 2H), 2.28 – 2.14 (m, 2H), 1.94 – 1.77 (m, 2H).

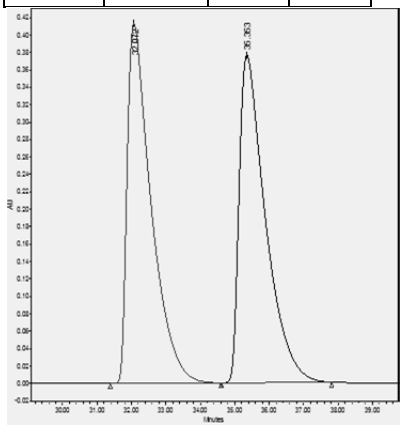
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.41, 142.38, 135.12, 128.71, 128.62, 128.45, 126.84, 126.75, 125.89, 95.03, 94.84, 35.53, 30.97, 28.37.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{30}O_2Na$ 257.1301; Found 257.1298.

HPLC: CHIRALCEL®-IB, *iso*-hexane, 30 °C, 0.3 mL/min.

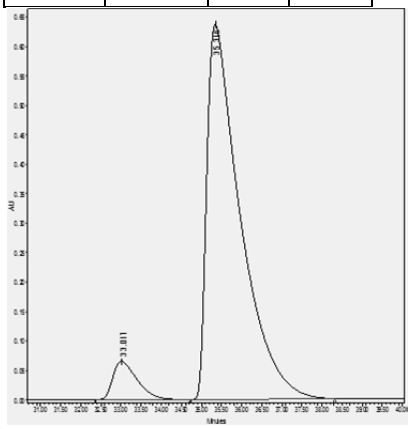
Racemic Substrate

Ret. Time	Area	% Area	Height
32.072	19920427	50.04	413105
35.353	19886382	49.96	376091



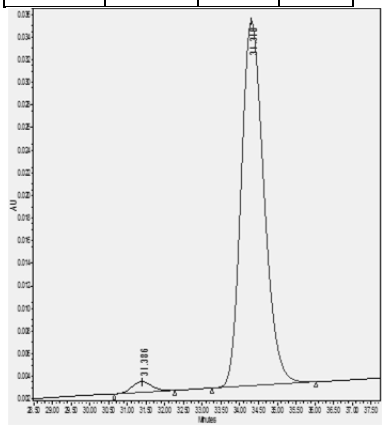
Reaction at −20 °C

Ret. Time	Area	% Area	Height
33.017	2714290	6.89	64761
35.346	36698361	93.11	637267



Reaction at −78 °C

Ret. Time	Area	% Area	Height
31.386	35070	2.52	957
34.310	1358414	97.48	32246



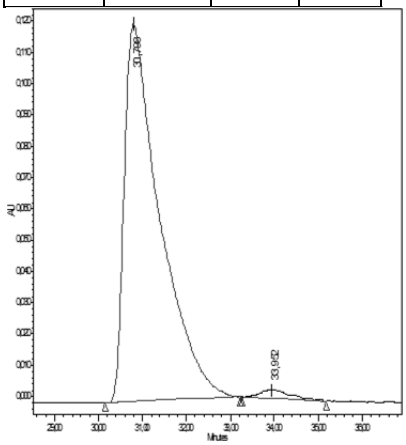
Samples with known Configuration:

The samples of known configuration for the comparison via HPLC were synthesized by a zinc and α,α-Diphenyl-*L*-prolinol mediated condensation reaction[19] (resulting in *R*-configuration) or synthesized according to literature procedures[20,21] by copper-mediated coupling of Grignard reagent with propargyl pivalate.

From Zn mediated condensation

Excess of ***R*-Isomer**

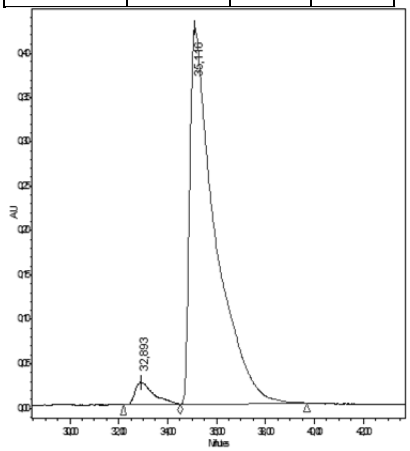
Ret. Time	Area	% Area	Height
30,798	6773346	98,03	120650
33,952	135933	1,97	2783



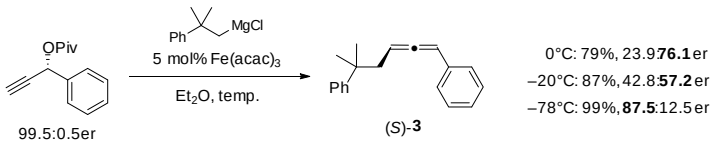
From Cu mediated coupling

Excess of ***S*-Isomer**

Ret. Time	Area	% Area	Height
32,893	1330555	4,19	25550
35,116	30448964	95,81	423733



3.2.2 (*S*)-(5-Methylhexa-1,2-diene-1,5-diyl)dibenzene ((*S*)-**3**).



In a dry 20 or 5 mL microwave flask under argon was added catalyst $Fe(acac)_3$ (8.83 mg, 25.0 µmol, 5.00 mol %) and diethylether (2.5 mL) to obtain a orange solution. The solution was cooled to 0 °C/−20 °C/−78 °C and (S)-1-phenylprop-2-yn-1-yl pivalate (108 mg, 500 µmol, 1.25 equiv) was added followed by the drop wise addition of (2-methyl-2-phenylpropyl)magnesium chloride (1.25 mL, 625 µmol, 0.50 M in diethyl ether, 1.25 equiv) for 5 min. The reaction mixture was stirred for another 30 min, quenched by aq. Citric acid solution (0.5 mL), extracted with pentane (3 x 1 mL) and the combined organic phase was carefully evaporated. The crude product was purified by column chromatography over SiO_2 (25 g, ether/pentane 0.9%) to obtain 99 mg (79%) of product at 0 °C, 109 mg (87%) at −20 °C and 123mg (99%) at −78 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.13 (m, 10H), 6.10 – 6.04 (m, 1H), 5.34 (q, *J* = 7.6 Hz, 1H), 2.57 – 2.50 (m, 2H), 1.47 (s, 6H).

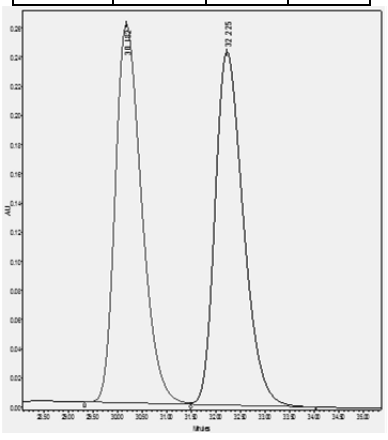
^{13}C NMR (101 MHz, $CDCl_3$) δ 206.40, 148.64, 135.00, 128.61, 128.34, 126.76, 126.67, 126.08, 125.85, 93.69, 91.58, 44.29, 38.27, 29.15, 28.40.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{30}O_2Na$ 271.1457; Found 271.1456.

HPLC: CHIRALCEL®-IB, *iso*-hexane, 30 °C, 0.3 mL/min.

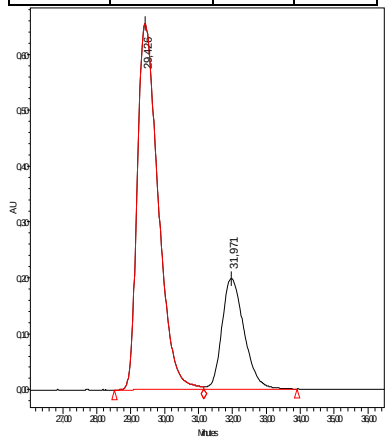
Racemic Substrate

Ret. Time	Area	% Area	Height
32.225	9637456	49.93	242230
30.182	9663224	50.07	259585



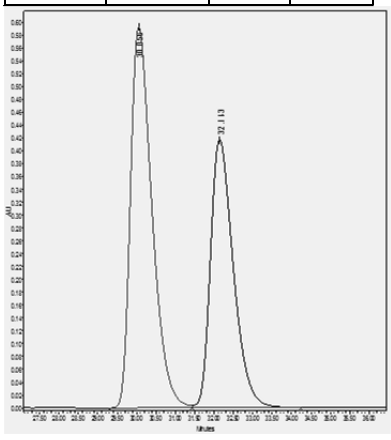
0 °C

Ret. Time	Area	% Area	Height
29,426	28155660	75,68	655053
31,971	9047414	24,32	198323



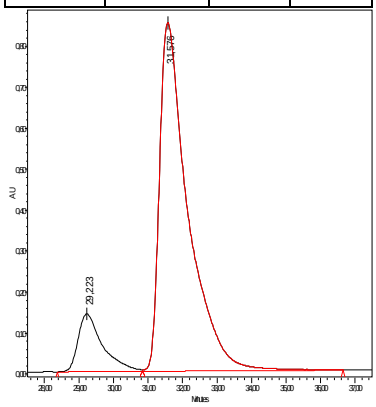
Reaction at −20 °C

Ret. Time	Area	% Area	Height
30.056	22765420	57.20	592809
32.143	17036985	42.80	417070



Reaction at −78 °C

Ret. Time	Area	% Area	Height
29,223	6980564	12,51	141422
31,576	48817937	87,49	850561



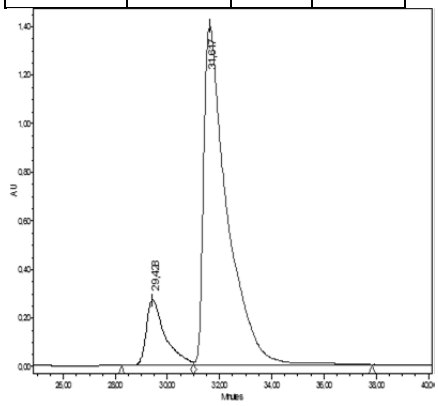
Samples with known Configuration:

The sample of known configuration for the comparison via HPLC was synthesized according to literature procedures[20,21] by copper-mediated coupling of Grignard reagent with propargyl pivalate.

From Cu mediated coupling

Excess of ***S*-Isomer**

Ret. Time	Area	% Area	Height
29,428	13383911	13,38	268200
31,617	86625814	86,62	1395200



4 Control Experiments

The $Fe(acac)_3$ obtained from Sigma-Aldrich had an Cu content of 0.5 ppm. To rule out that copper is responsible for the reaction catalyzed by the commercial $Fe(acac)_3$, the reaction from Table 1 with $PhCH_2MgCl$ (also Table 2, entry 5) was run without $Fe(acac)_3$ but with small amounts of a copper salt (CuI). The amount of CuI used corresponds to a copper impurity of 100 ppm (which is 200 times higher than the copper amount in the iron catalyst). The reaction led to <1% NMR-yield after 30 min.

The corresponding iron-catalyzed reaction was finished in less than 5 min subsequent to addition of the Grignard reagent. The control experiment was carried out as follows:

A solution of copper(I) iodide in acetonitrile (2.8 µl of a 10 mM solution, 5.3 µg CuI, 0.0028 mol%) was added to a dried 20 ml microwave vial and evaporated under high vacuum. Subsequently, 2-methylbut-3-yn-2-yl acetate (126 mg, 1.00 mmol, 1.00 equiv.) and diethyl ether (5 mL) were added. The mixture was cooled to –20 °C, benzylmagnesium chloride (0.63 mL, 1.25 mmol, 2 M in tetrahydrofuran, 1.25 equiv.) was added for 5 min and the reaction was stirred for 30 min. The yield determined by ^{1}H NMR was <1%.

Furthermore, a different batch of $Fe(acac)_3$ led to a reproducible NMR-yield of 93%.

References

[1] A. Krasovskiy, P. Knochel, *Synthesis* **2006**, *2006*, 0890–0891.

[2] D. Vasu, S. K. Pawar, R.-S. Liu, *Beilstein J. Org. Chem.* **2013**, *9*, 1751–1756.

[3] G. S. Sheppard, J. Wang, M. Kawai, S. D. Fidanze, N. Y. BaMaung, S. A. Erickson, D. M. Barnes, J. S. Tedrow, L. Kolaczkowski, A. Vasudevan, et al., *J. Med. Chem.* **2006**, *49*, 3832–3849.

[4] T. S. N. Zhao, Y. Yang, T. Lessing, K. J. Szabó, *J. Am. Chem. Soc.* **2014**, *136*, 7563–7566.

[5] T. Achard, A. Lepronier, Y. Gimbert, H. Clavier, L. Giordano, A. Tenaglia, G. Buono, *Angew. Chem. Int. Ed.* **2011**, *50*, 3552–3556.

[6] M. J. Ardolino, M. S. Eno, J. P. Morken, *Adv. Synth. Catal.* **2013**, *355*, 3413–3419.

[7] S. Wang, L. Zhang, *J. Am. Chem. Soc.* **2006**, *128*, 8414–8415.

[8] D. O'Hagan, N. A. Zaidi, *Tetrahedron Asymmetry* **1994**, *5*, 1111–1118.

[9] G. Bose, E. Ullah, P. Langer, *Chem. – Eur. J.* **2004**, *10*, 6015–6028.

[10] R. Takita, K. Yakura, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* **2005**, *127*, 13760–13761.

[11] M. Tang, C.-A. Fan, F.-M. Zhang, Y.-Q. Tu, W.-X. Zhang, A.-X. Wang, *Org. Lett.* **2008**, *10*, 5585–5588.

[12] *Org. Synth.* **2013**, *90*, 327.

[13] G. Song, B. Wang, M. Nishiura, Z. Hou, *Chem. – Eur. J.* **2015**, *21*, 8394–8398.

[14] S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2008**, *130*, 5048–5049.

[15] B. Bolte, Y. Odabachian, F. Gagosz, *J. Am. Chem. Soc.* **2010**, *132*, 7294–7296.

[16] D. Xu, Z. Li, S. Ma, *Tetrahedron Lett.* **2003**, *44*, 6343–6346.

[17] C. Raminelli, J. V. Comasseto, L. H. Andrade, A. L. M. Porto, *Tetrahedron Asymmetry* **2004**, *15*, 3117–3122.

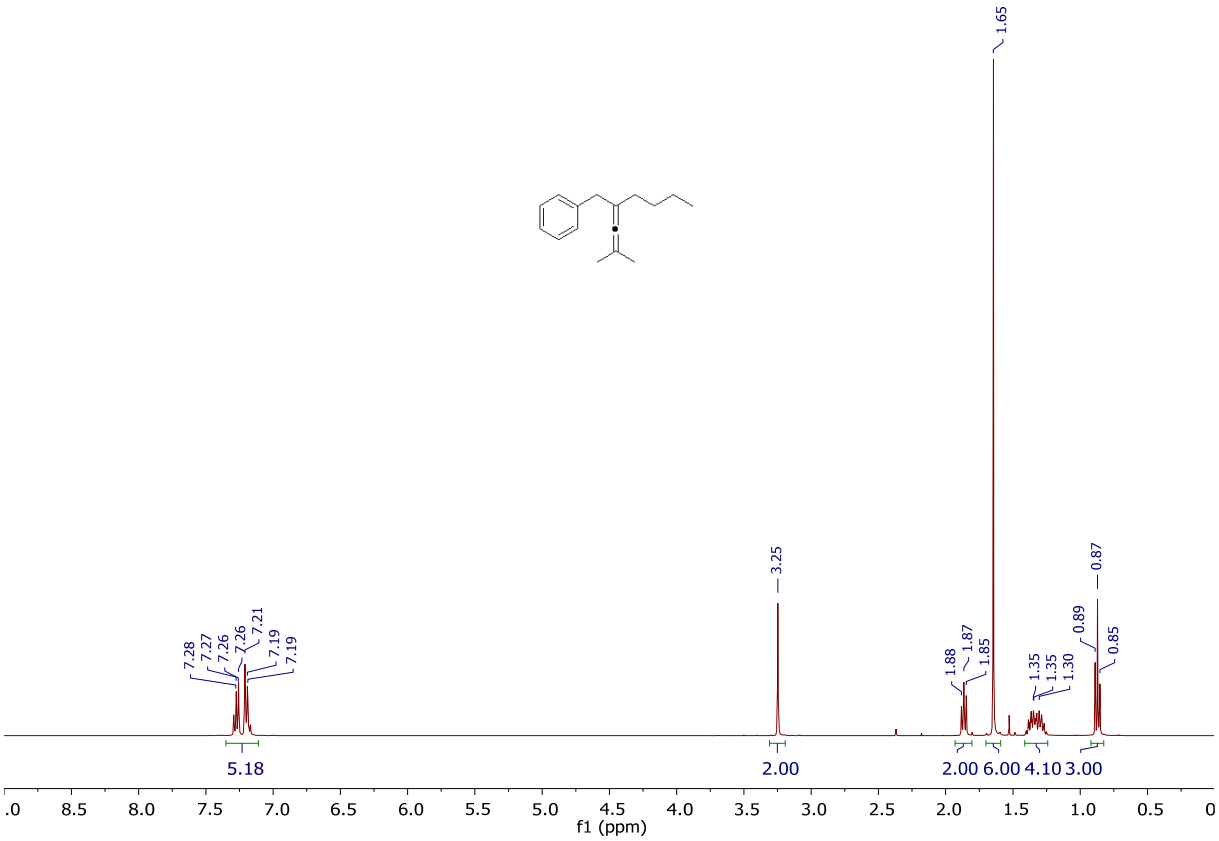
[18] C. A. Witham, P. Mauleón, N. D. Shapiro, B. D. Sherry, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 5838–5839.

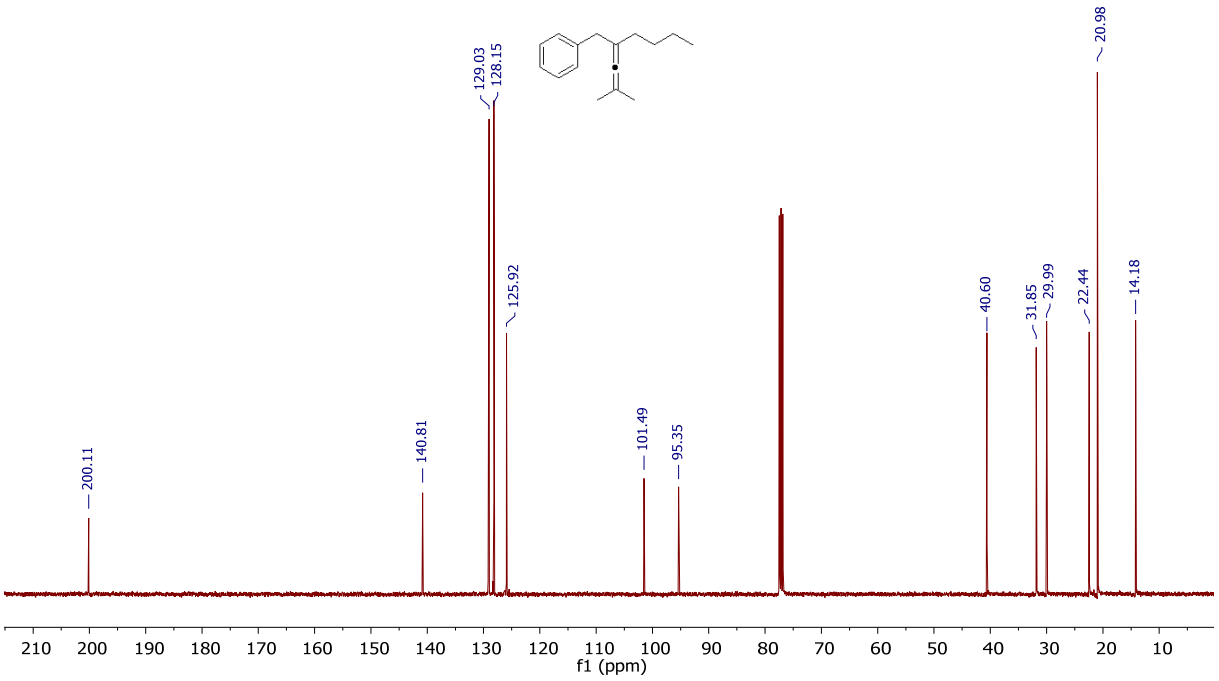
[19] M. Periasamy, N. Sanjeevakumar, M. Dalai, R. Gurubrahamam, P. O. Reddy, *Org. Lett.* **2012**, *14*, 2932–2935.

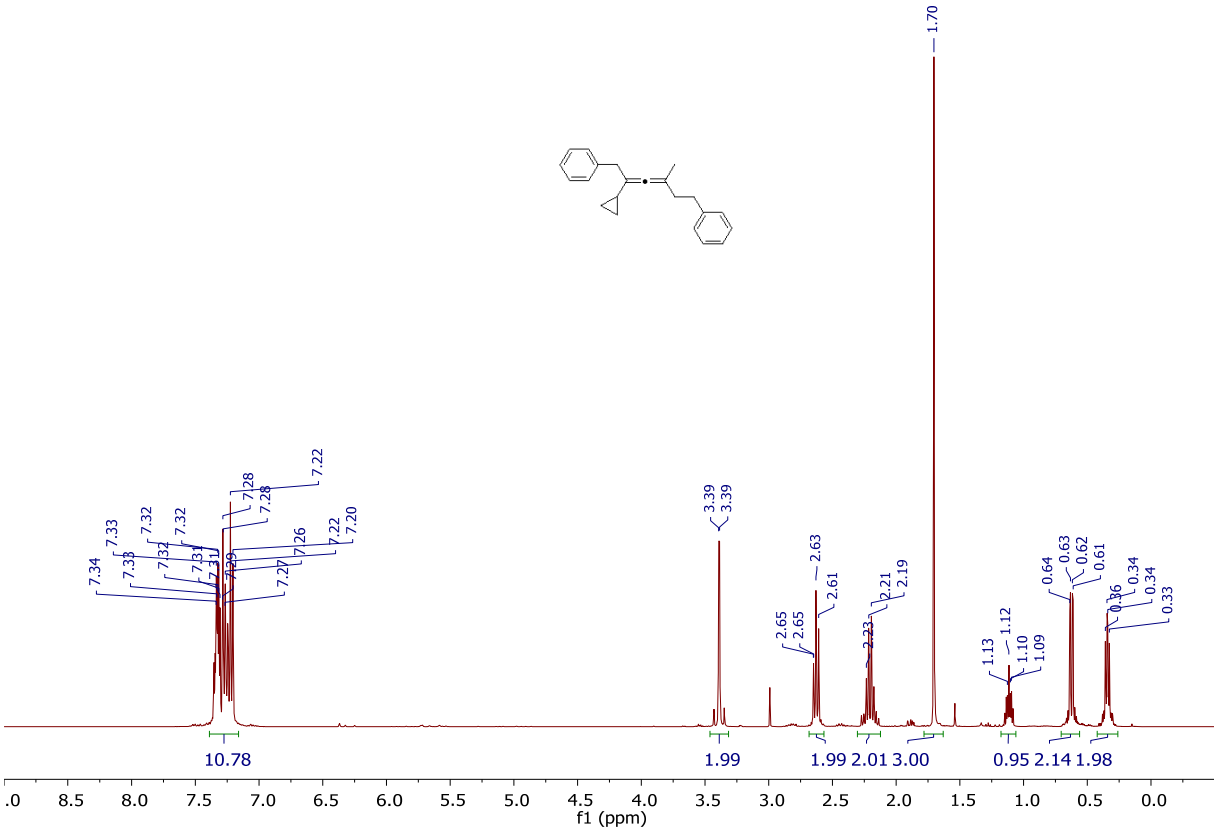
[20] J. Z. Stemple, D. G. Peters, *J. Org. Chem.* **1989**, *54*, 5318–5323.

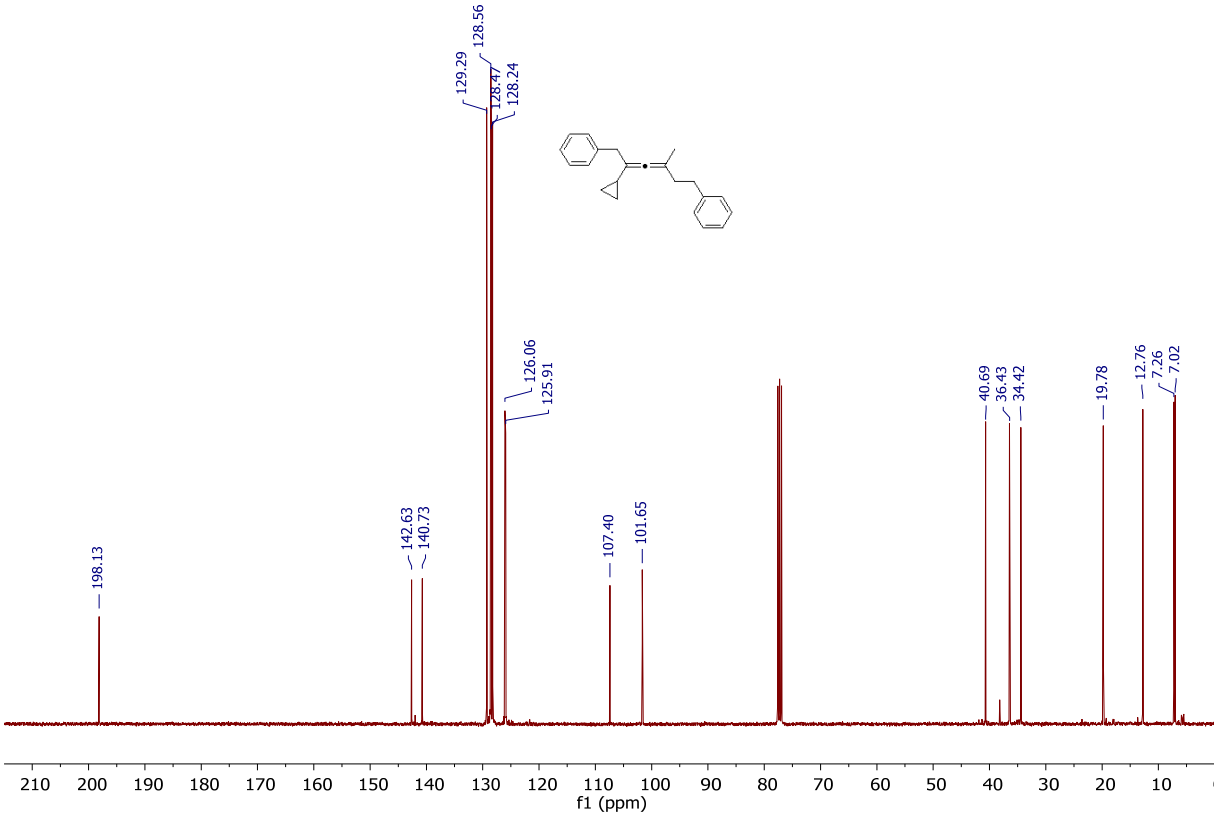
[21] C. E. Janßen, N. Krause, *Eur. J. Org. Chem.* **2005**, *2005*, 2322–2329.

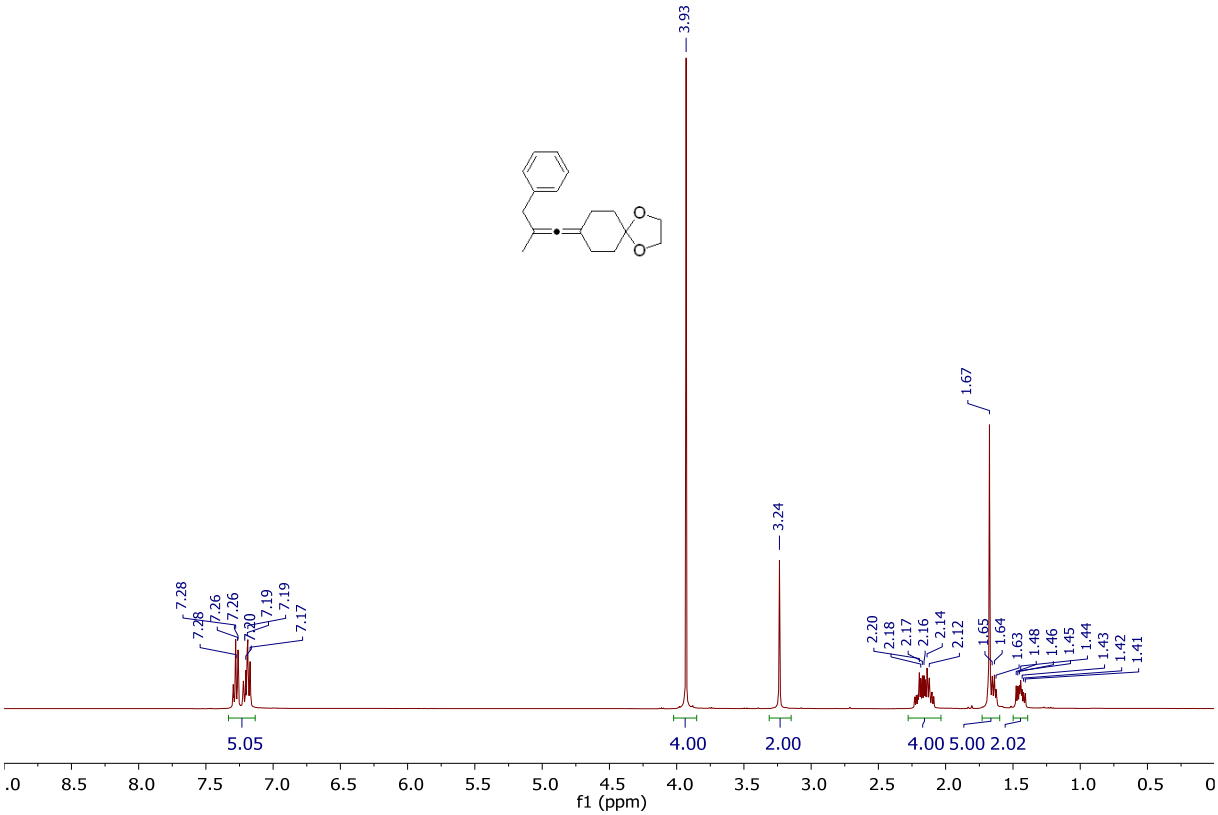
5 ^{1}H and ^{13}C NMR Spectra

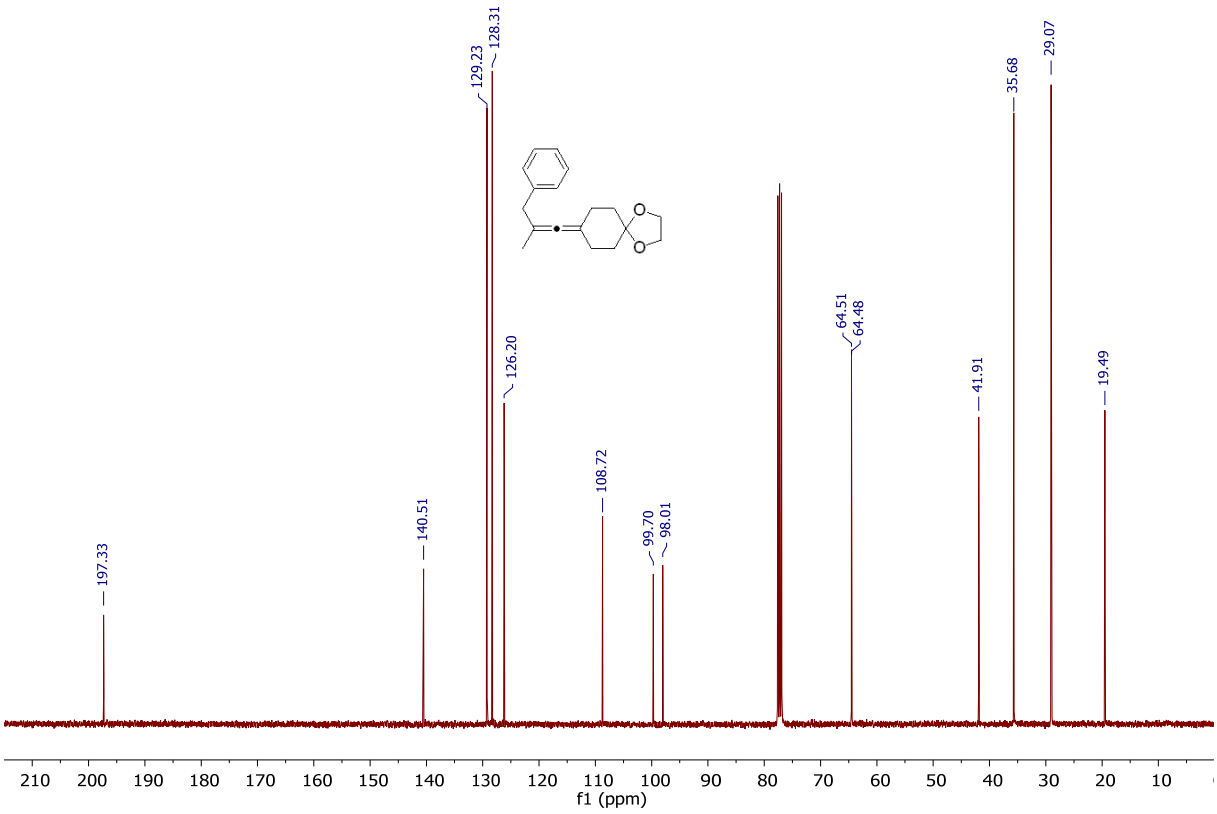


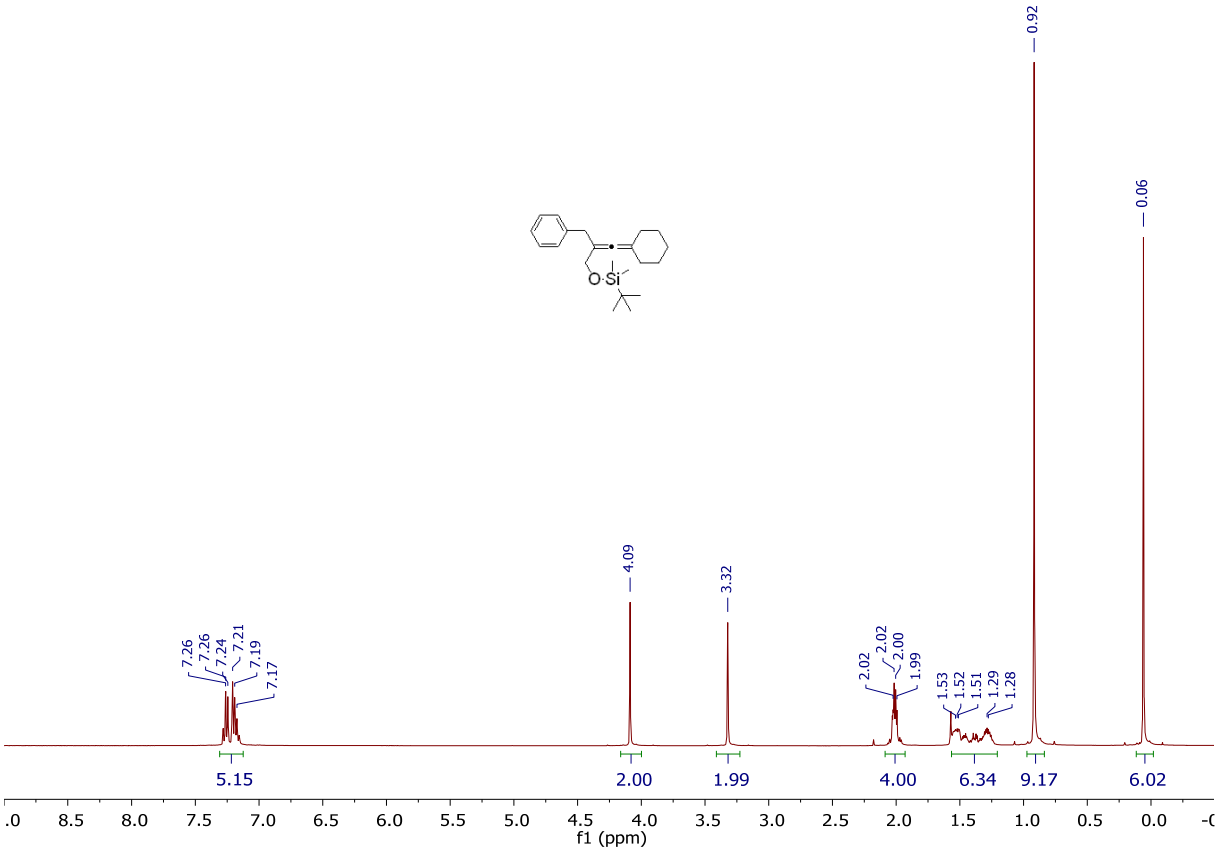


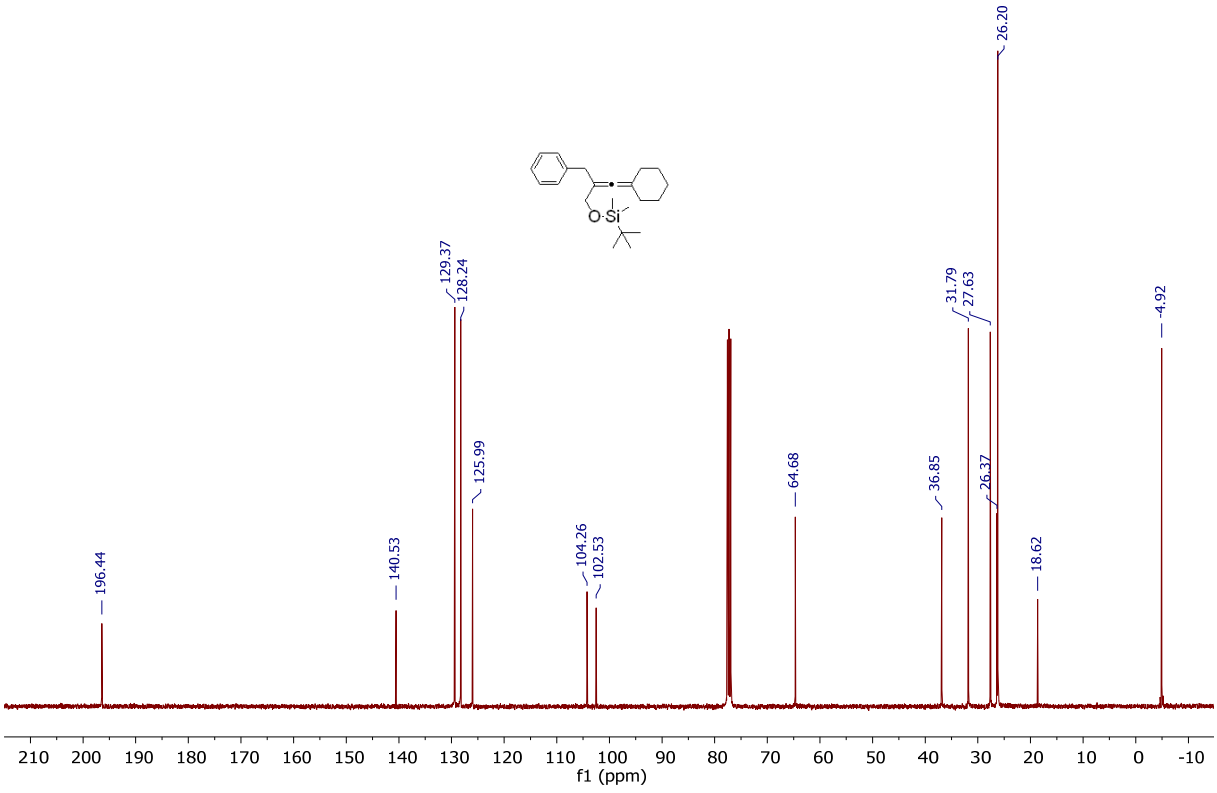

1.70
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.29
7.28
7.28
7.27
7.26
7.22
7.22
7.20
3.39
3.39
2.65
2.65
2.63
2.61
2.23
2.21
2.19
1.13
1.12
1.10
1.09
0.64
0.63
0.62
0.61
0.36
0.34
0.34
0.33
10.78
1.99
1.99
2.01
3.00
0.95
2.14
1.98
f1 (ppm)

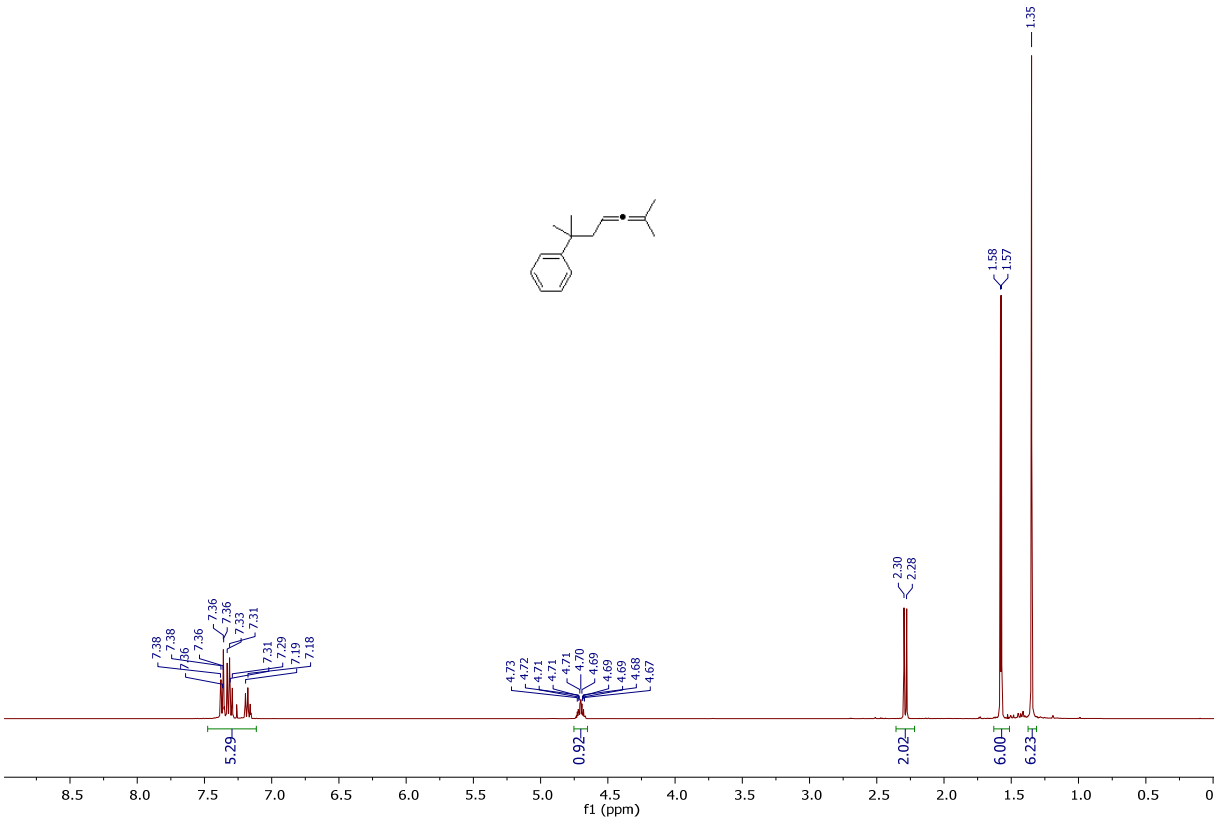

198.13
142.63
140.73
129.29
128.56
128.47
128.24
126.06
125.91
107.40
101.65
40.69
36.43
34.42
19.78
12.76
7.26
7.02
f1 (ppm)

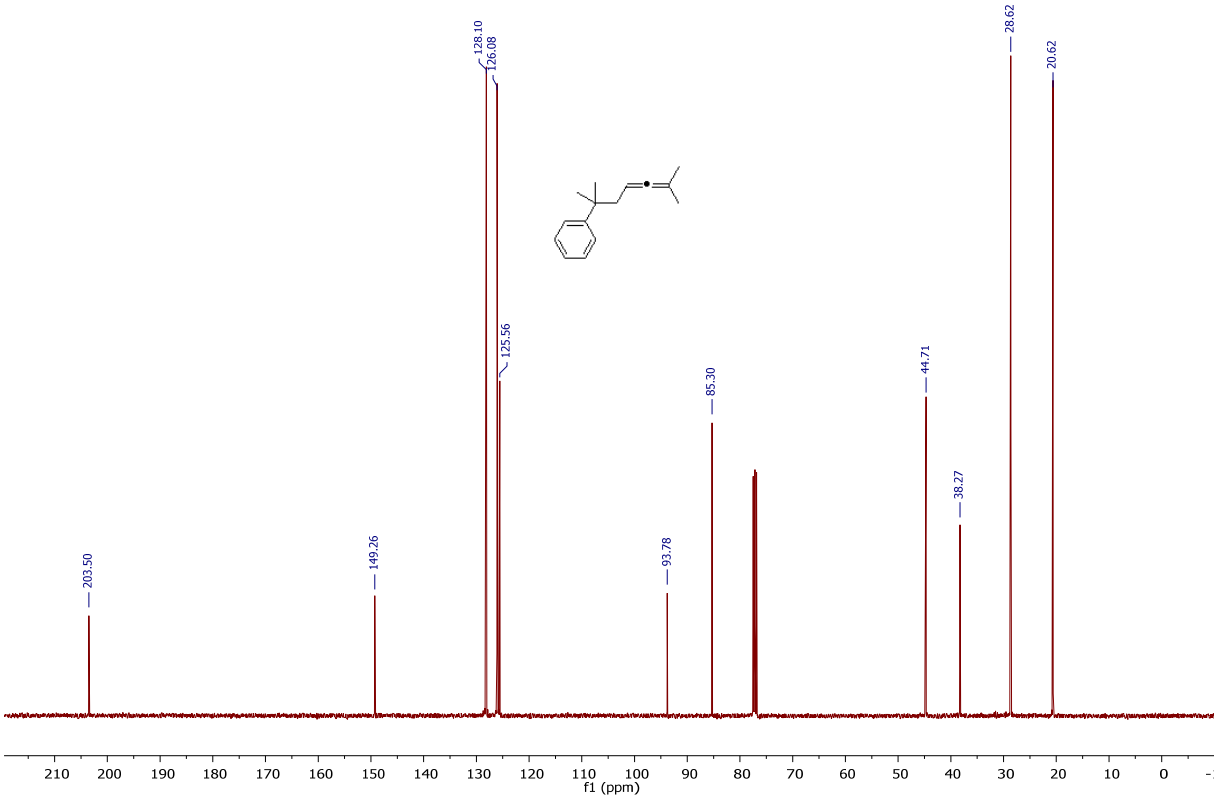

3.93
3.24
1.67
7.28
7.26
7.19
7.17
2.20
2.18
2.17
2.16
2.14
2.12
1.65
1.64
1.63
1.48
1.46
1.45
1.44
1.43
1.42
1.41
5.05
4.00
2.00
4.00
5.00
2.02
f1 (ppm)

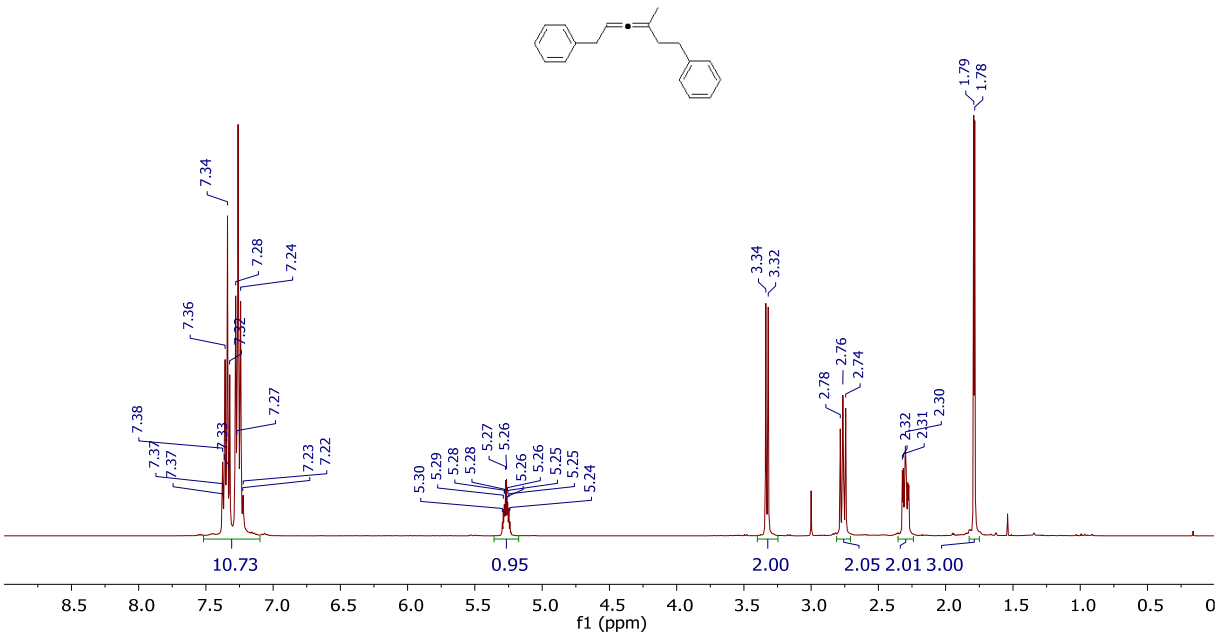

129.23
128.31
126.20
140.51
108.72
99.70
98.01
197.33
64.51
64.48
41.91
35.68
29.07
19.49
f1 (ppm)

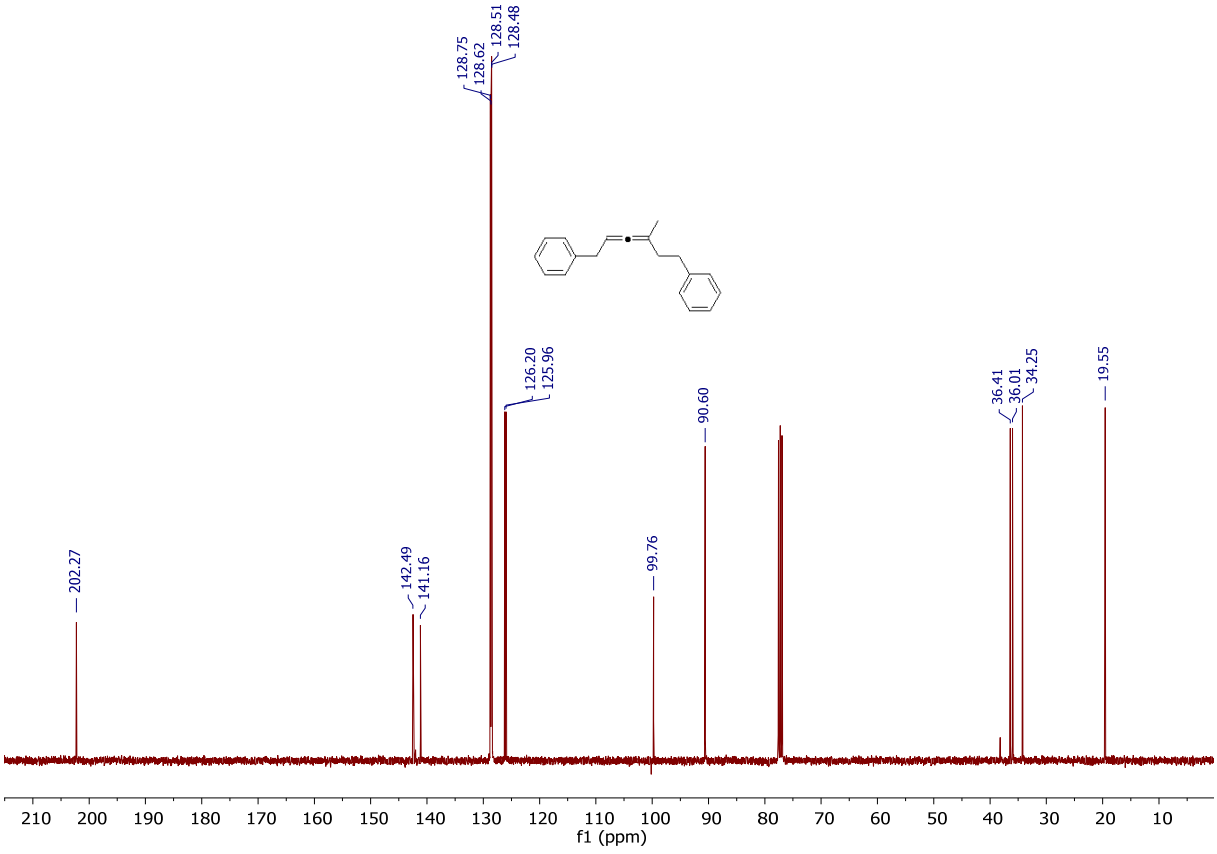

0.92
0.06
4.09
3.32
7.26
7.26
7.24
7.21
7.19
7.17
2.02
2.02
2.00
1.99
1.53
1.52
1.51
1.29
1.28
5.15
2.00
1.99
4.00
6.34
9.17
6.02
f1 (ppm)

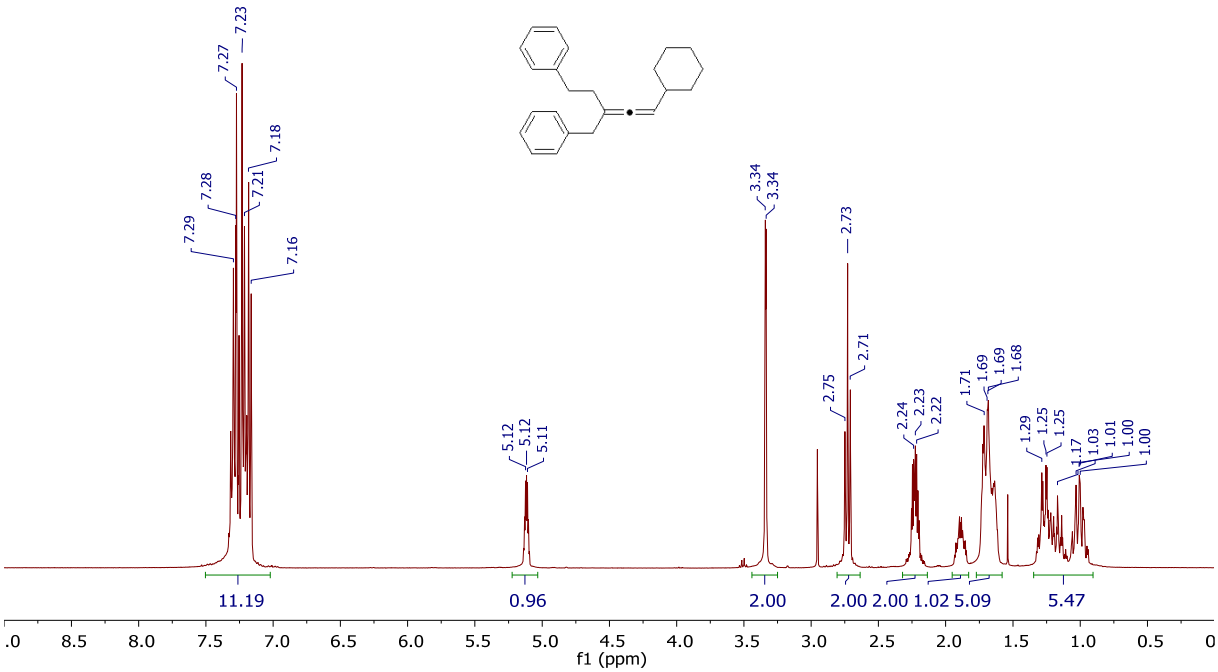

26.20
129.37
128.24
31.79
27.63
-4.92
125.99
64.68
36.85
26.37
196.44
140.53
104.26
102.53
18.62
f1 (ppm)

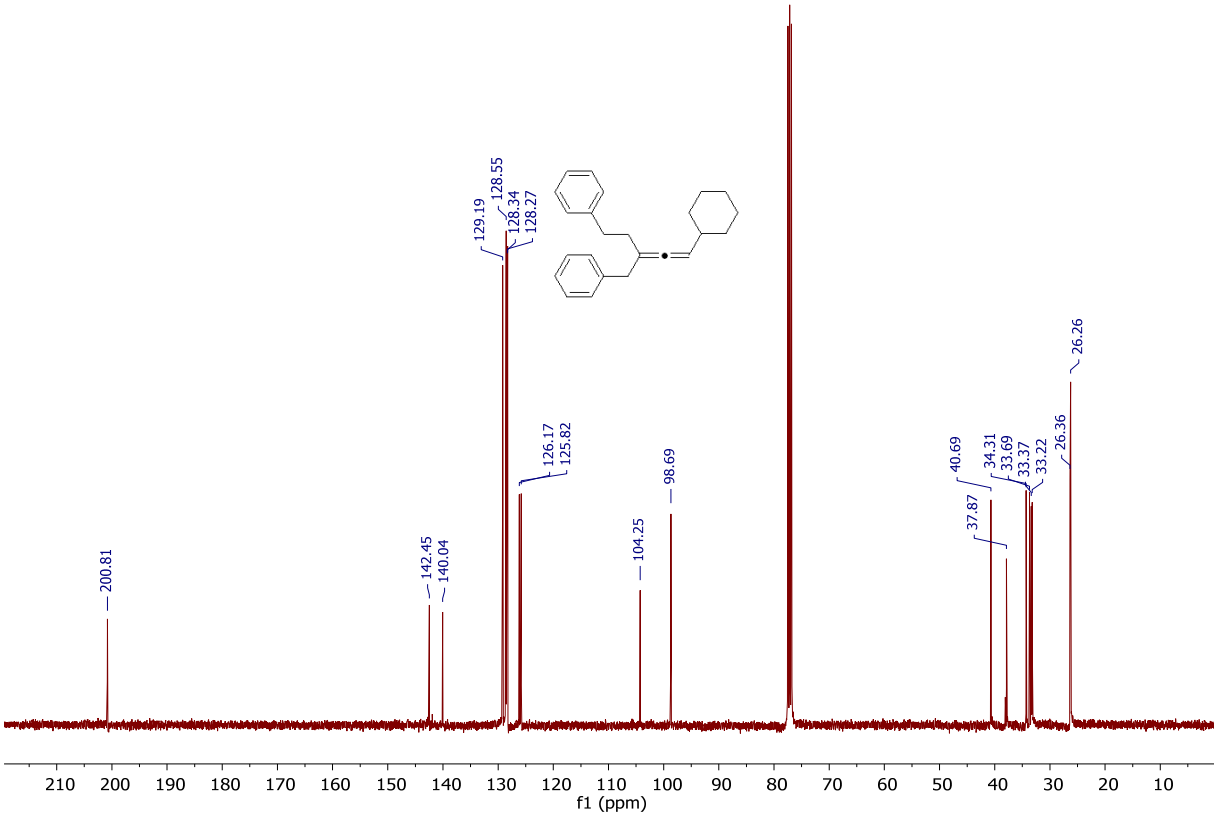

7.38
7.38
7.36
7.36
7.36
7.33
7.31
7.31
7.29
7.19
7.18
4.73
4.72
4.71
4.71
4.71
4.70
4.69
4.69
4.69
4.68
4.67
2.30
2.28
1.58
1.57
1.35
5.29
0.92
2.02
6.00
6.23
f1 (ppm)

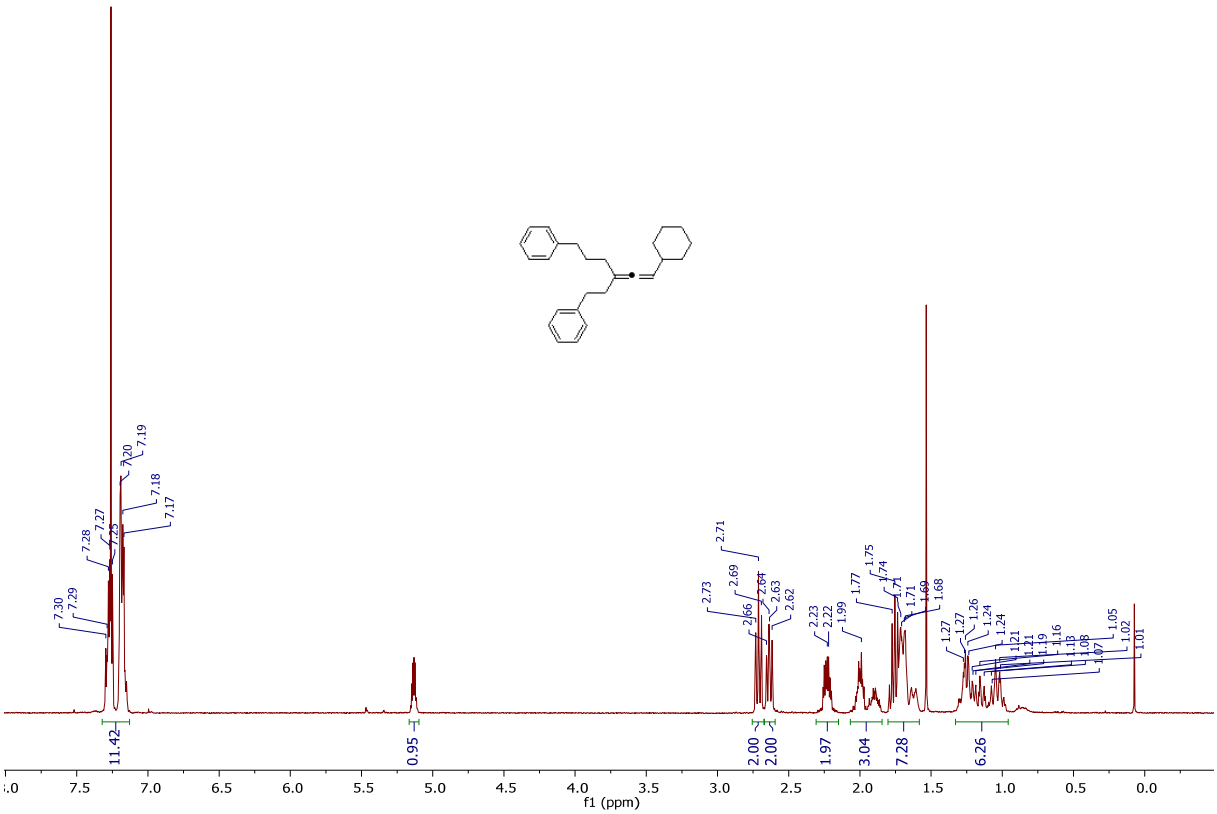

203.50
149.26
128.10
126.08
125.56
93.78
85.30
44.71
38.27
28.62
20.62
f1 (ppm)

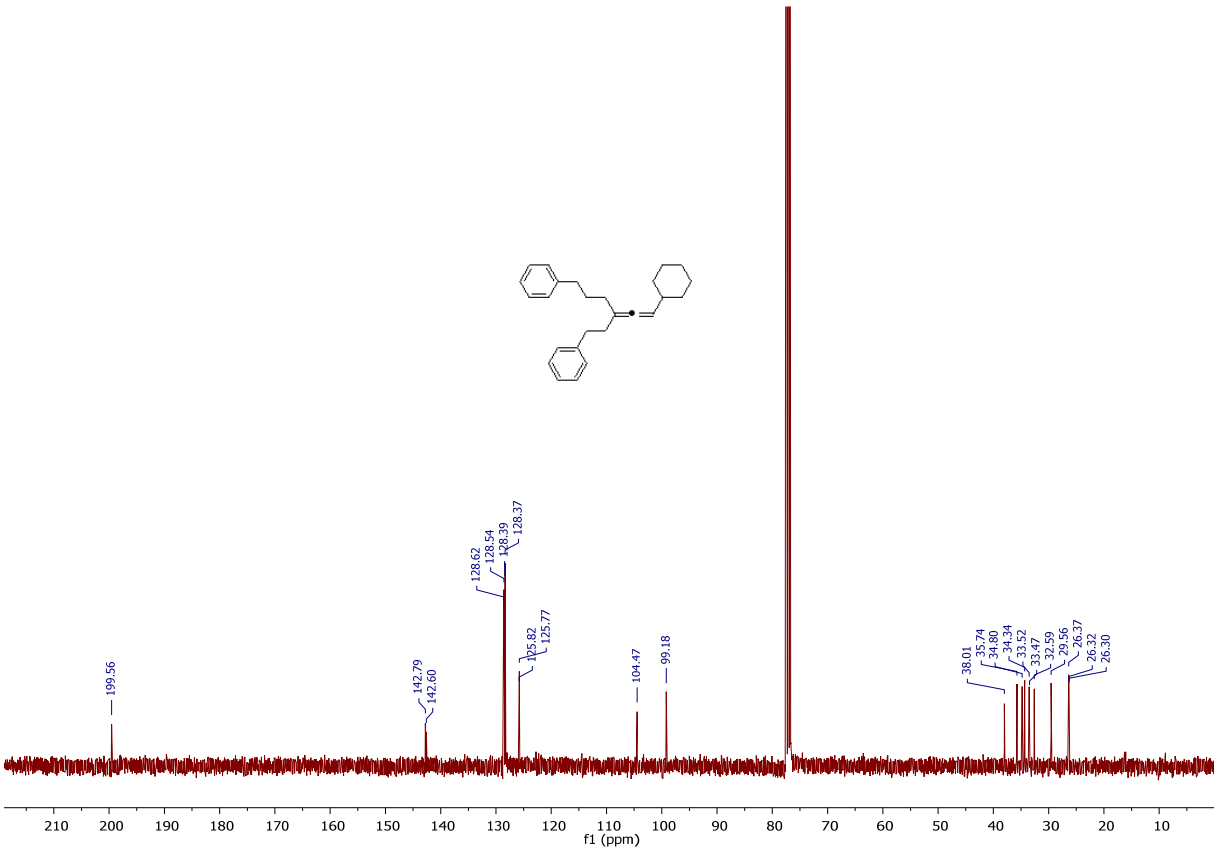

7.34
7.36
7.38
7.37
7.37
7.33
7.32
7.28
7.24
7.27
7.23
7.22
5.30
5.29
5.28
5.28
5.27
5.26
5.26
5.26
5.25
5.25
5.24
3.34
3.32
2.78
2.76
2.74
2.32
2.31
2.30
1.79
1.78
10.73
0.95
2.00
2.05
2.01
3.00
f1 (ppm)

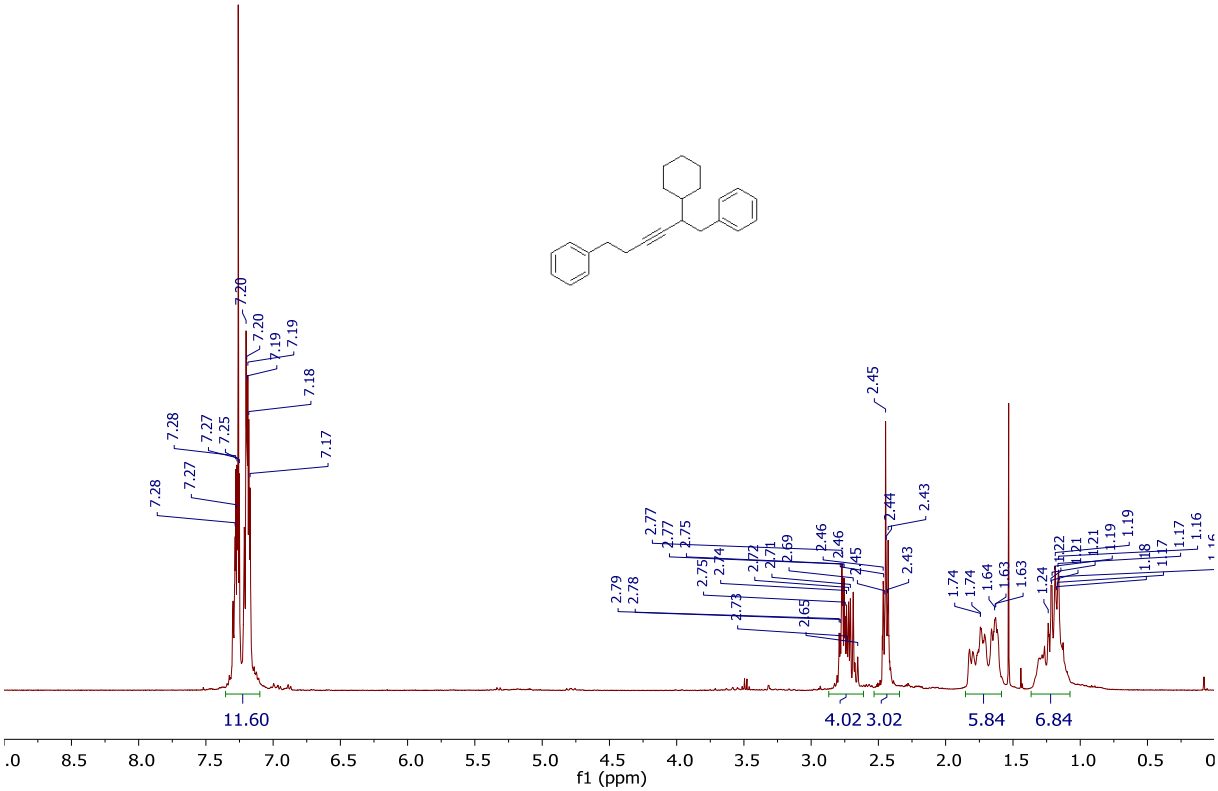

128.75
128.62
128.51
128.48
126.20
125.96
90.60
36.41
36.01
34.25
19.55
202.27
142.49
141.16
99.76
f1 (ppm)

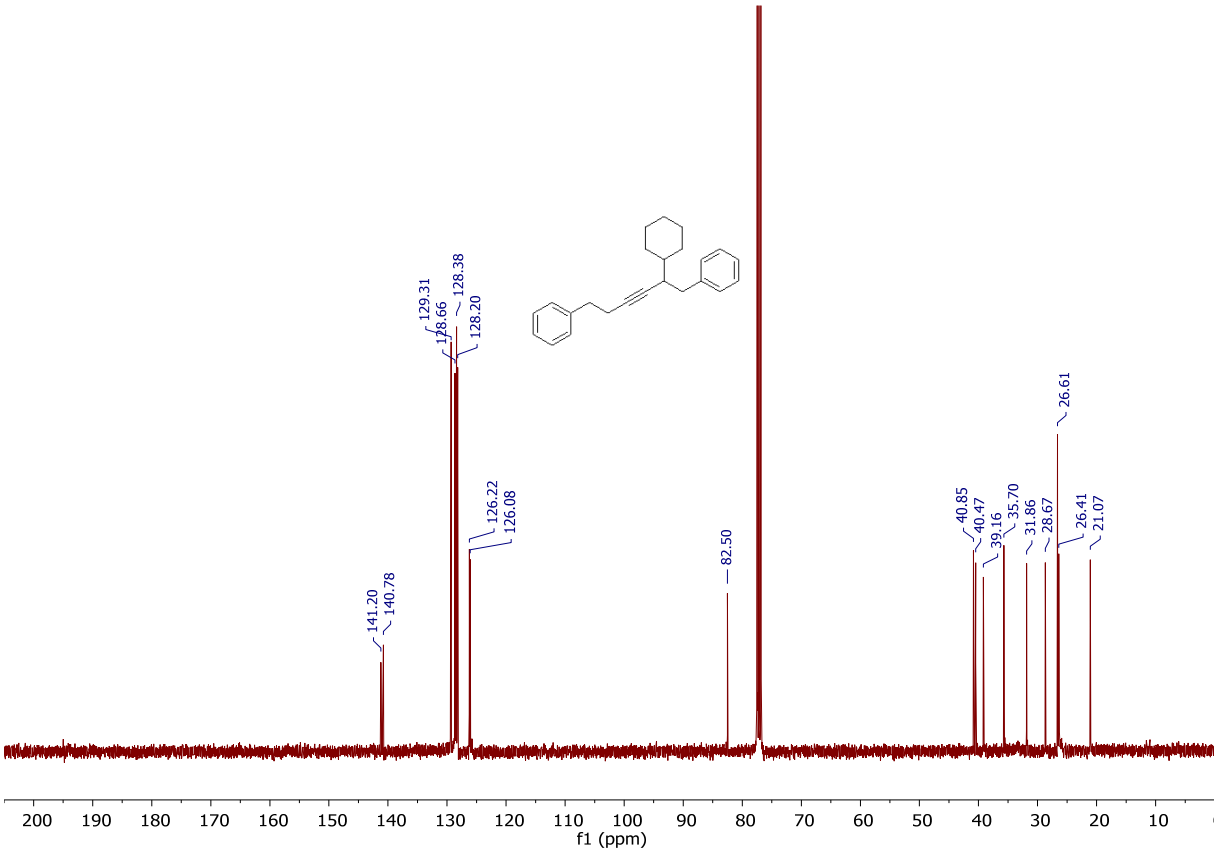

7.29
7.28
7.27
7.23
7.21
7.18
7.16
5.12
5.12
5.11
3.34
3.34
2.75
2.73
2.71
2.24
2.23
2.22
1.71
1.69
1.69
1.68
1.29
1.25
1.25
1.17
1.03
1.01
1.00
1.00
11.19
0.96
2.00
2.00 2.00 1.02 5.09
5.47
f1 (ppm)

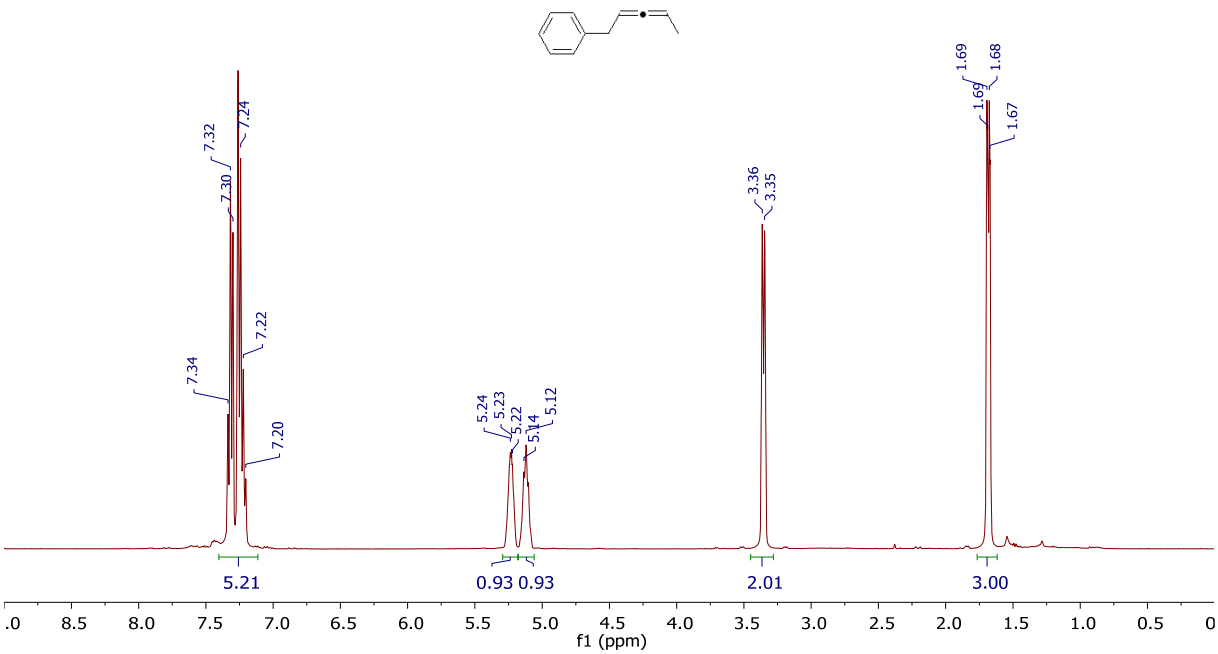

200.81
142.45
140.04
129.19
128.55
128.34
128.27
126.17
125.82
104.25
98.69
40.69
37.87
34.31
33.69
33.37
33.22
26.36
26.26
f1 (ppm)

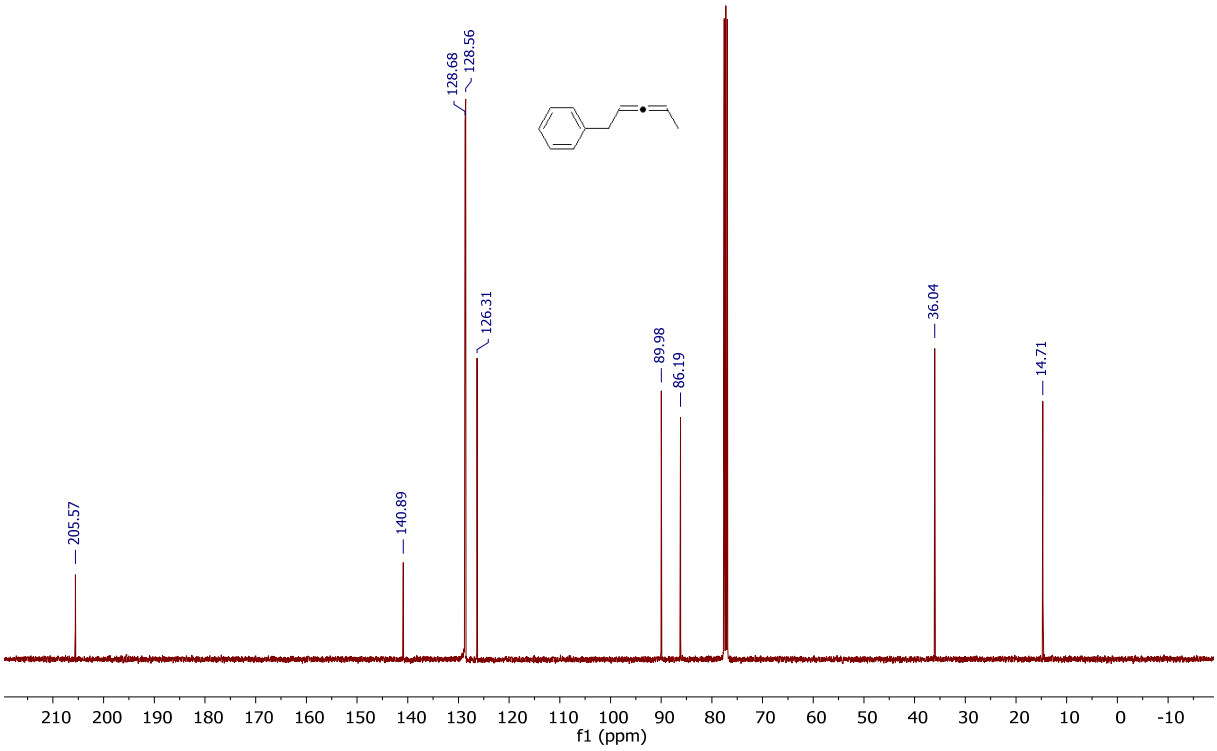

7.30
7.29
7.28
7.27
7.25
7.20
7.19
7.18
7.17
2.73
2.71
2.69
2.66
2.64
2.63
2.62
2.23
2.22
2.20
1.99
1.77
1.75
1.74
1.71
1.69
1.68
1.27
1.26
1.24
1.24
1.21
1.19
1.16
1.08
1.07
1.05
1.02
1.01
11.42
0.95
2.00
2.00
1.97
3.04
7.28
6.26
f1 (ppm)

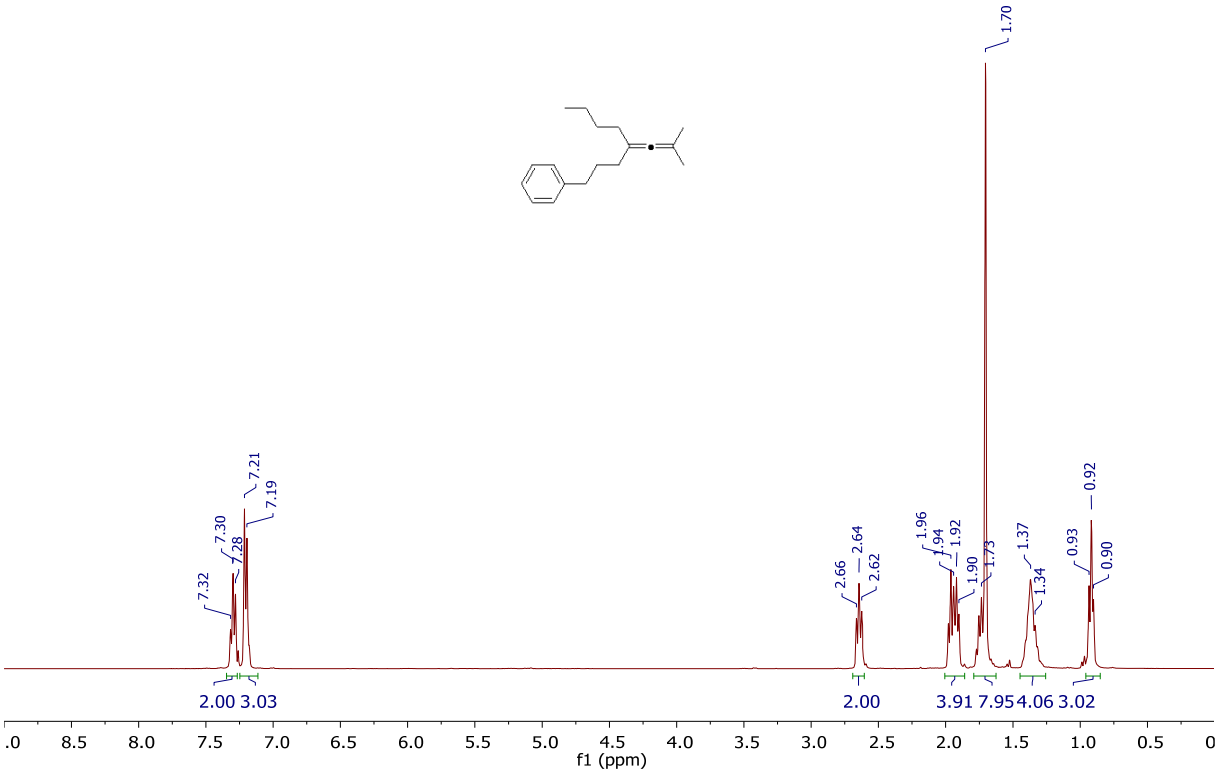

199.56
142.79
142.60
128.62
128.54
128.39
128.37
125.82
125.77
104.47
99.18
38.01
35.74
34.80
34.34
33.52
33.47
32.59
29.56
26.37
26.32
26.30
f1 (ppm)

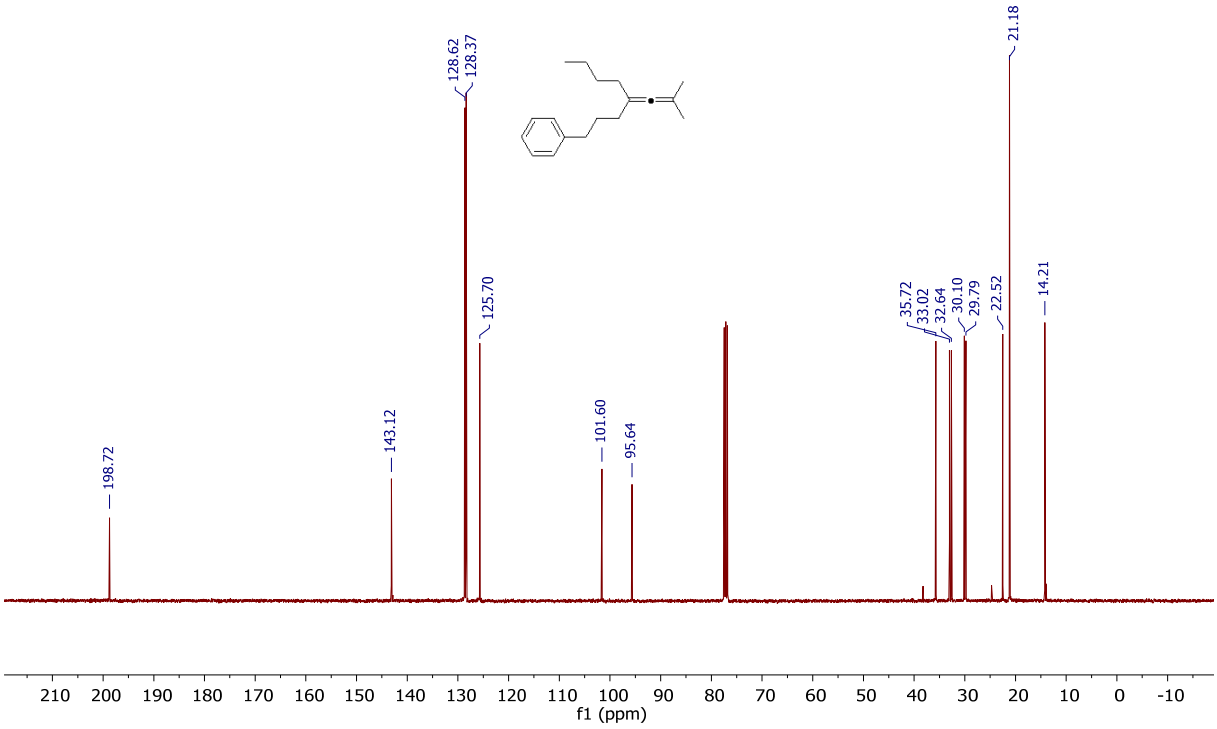

7.28
7.27
7.25
7.20
7.20
7.19
7.19
7.18
7.17
2.45
2.44
2.43
11.60
4.02
3.02
5.84
6.84
f1 (ppm)

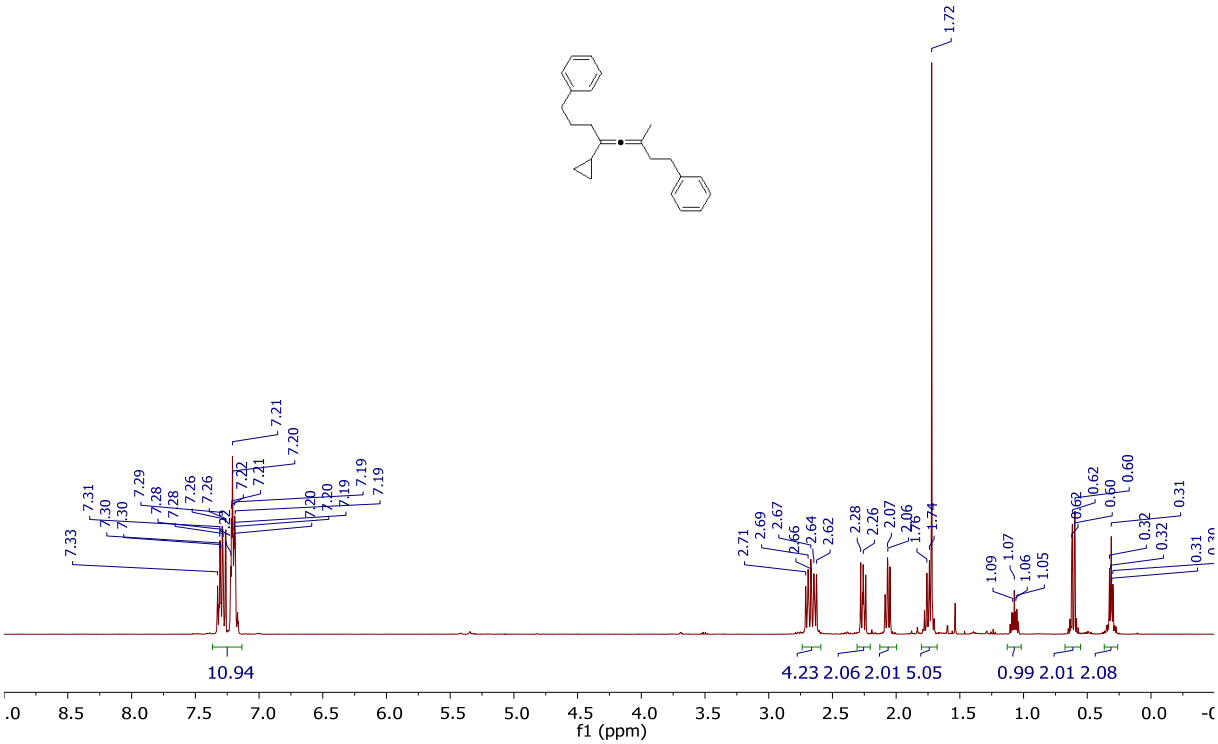

129.31
128.66
128.38
128.20
126.22
126.08
141.20
140.78
82.50
40.85
40.47
39.16
35.70
31.86
28.67
26.61
26.41
21.07
f1 (ppm)

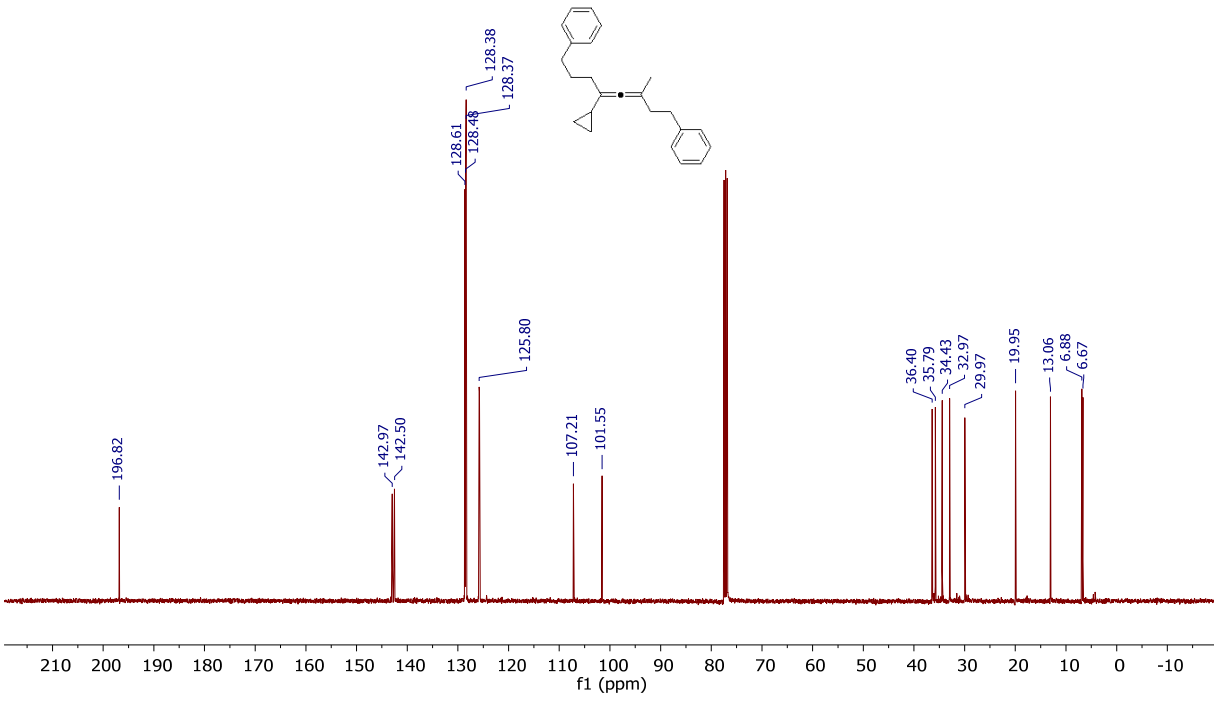

7.34
7.32
7.30
7.24
7.22
7.20
5.24
5.23
5.22
5.14
5.12
3.36
3.35
1.69
1.69
1.68
1.67
5.21
0.93 0.93
2.01
3.00
f1 (ppm)

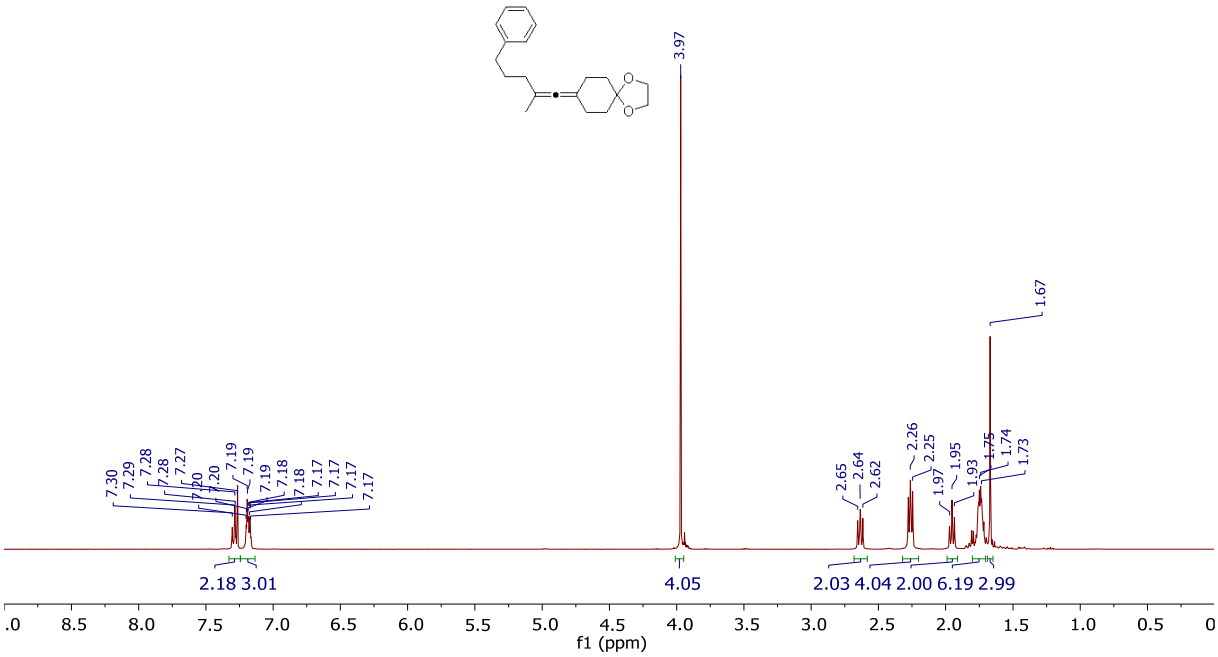

205.57
140.89
128.68
128.56
126.31
89.98
86.19
36.04
14.71
f1 (ppm)

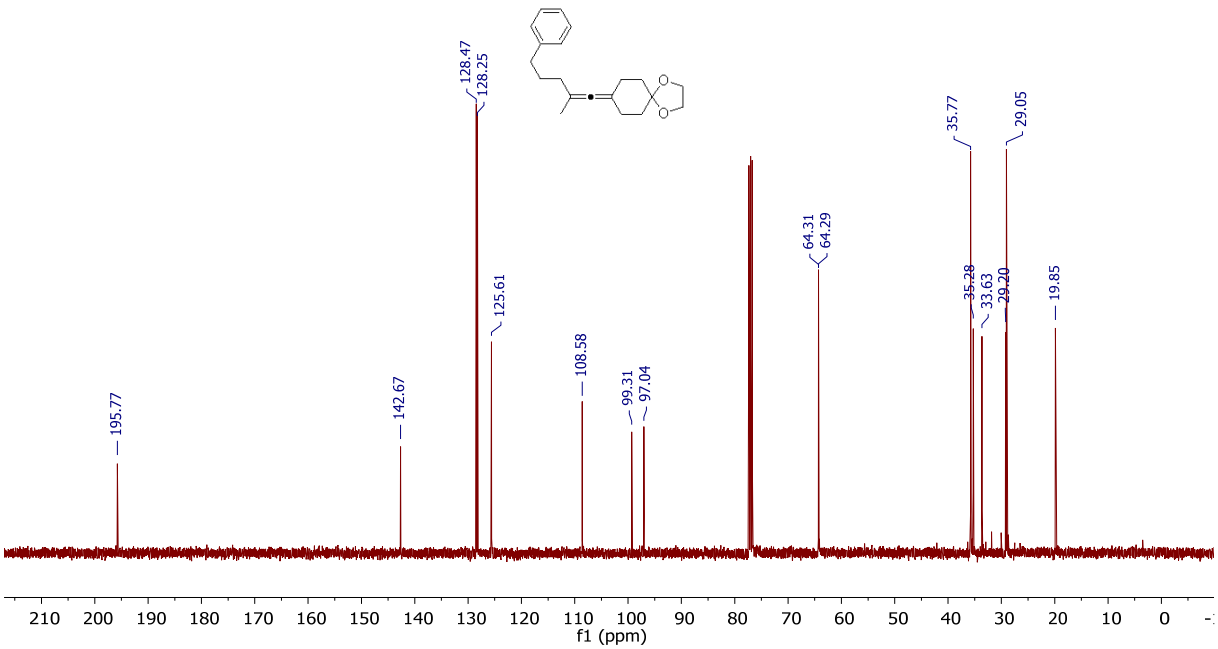

1.70
7.32
7.30
7.28
7.21
7.19
2.66
2.64
2.62
1.96
1.94
1.92
1.90
1.73
1.37
1.34
0.93
0.92
0.90
2.00 3.03
2.00
3.91 7.95 4.06 3.02
f1 (ppm)

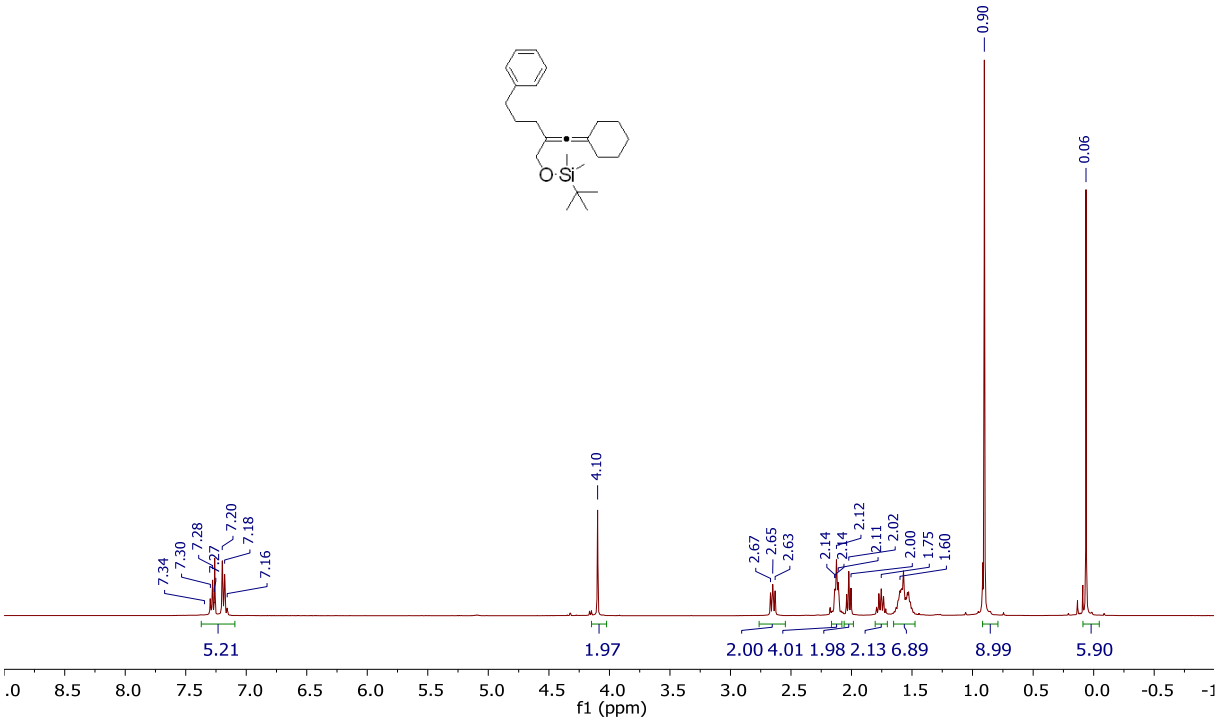

128.62
128.37
21.18
125.70
35.72
33.02
32.64
30.10
29.79
22.52
14.21
143.12
101.60
95.64
198.72
f1 (ppm)

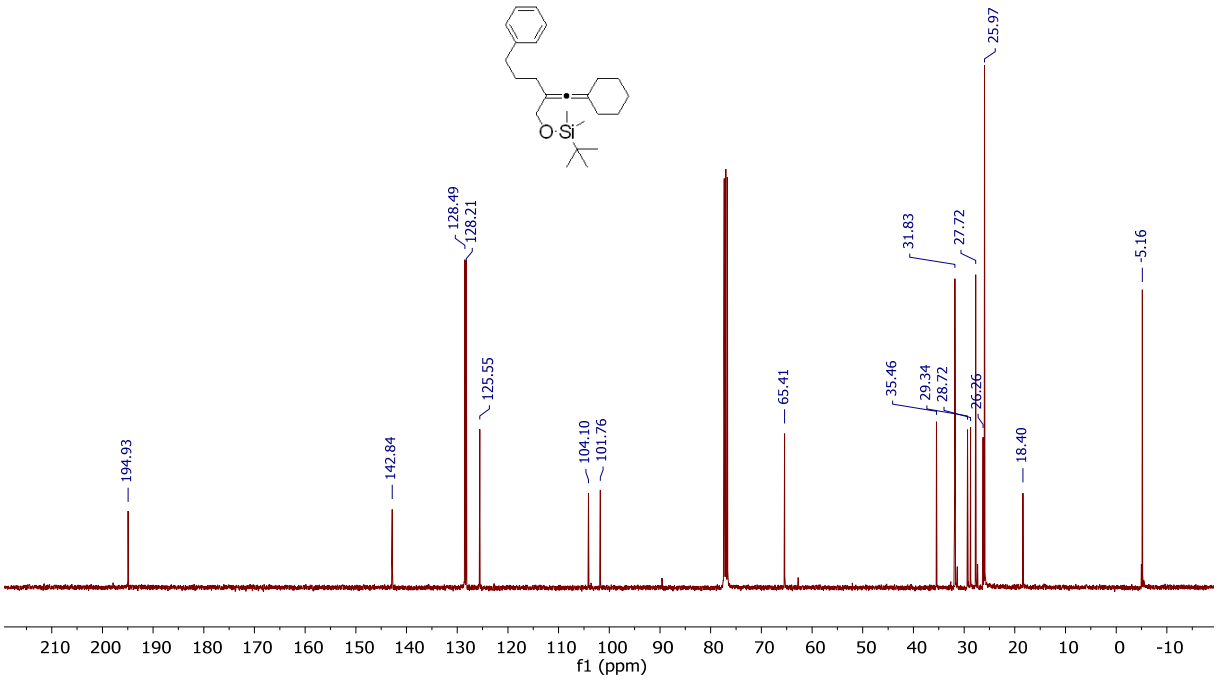

1.72
7.33
7.31
7.30
7.30
7.29
7.28
7.28
7.26
7.26
7.22
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.19
2.71
2.69
2.67
2.66
2.64
2.62
2.28
2.26
2.07
2.06
1.76
1.74
1.09
1.07
1.06
1.05
0.63
0.62
0.60
0.60
0.32
0.32
0.31
0.31
10.94
4.23 2.06 2.01 5.05
0.99 2.01 2.08
f1 (ppm)

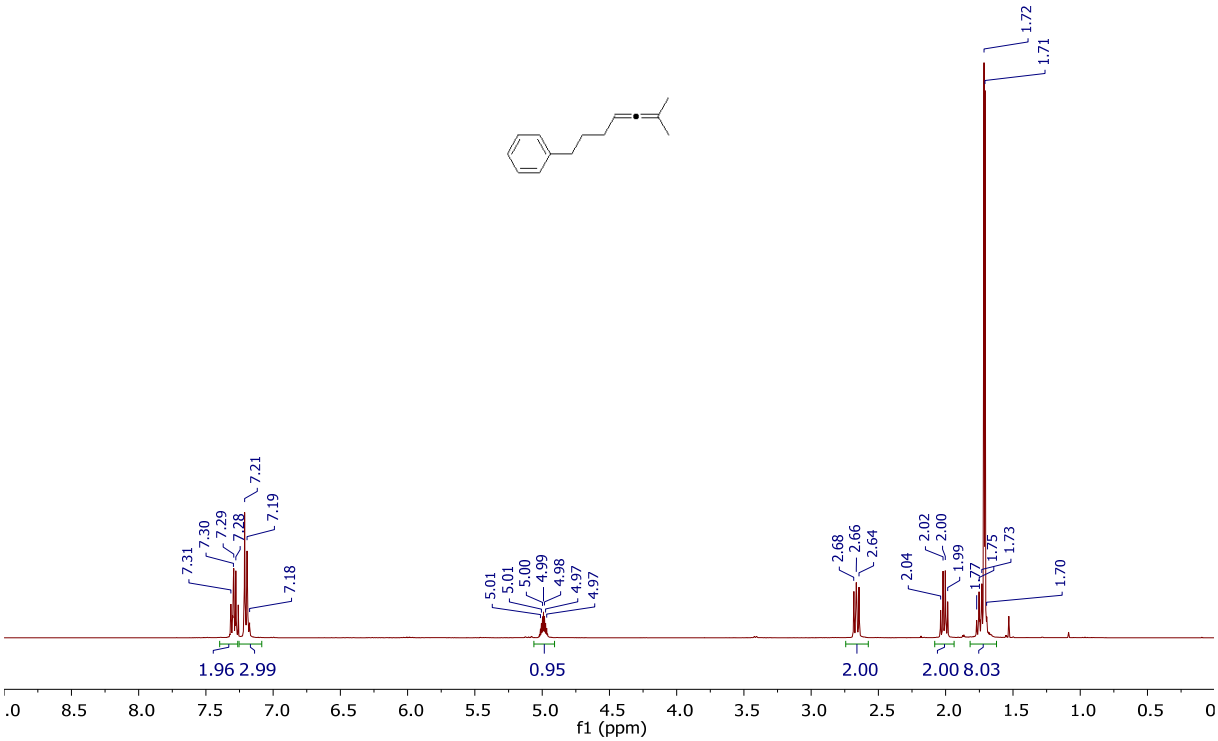

196.82
142.97
142.50
128.61
128.48
128.38
128.37
125.80
107.21
101.55
36.40
35.79
34.43
32.97
29.97
19.95
13.06
6.88
6.67
f1 (ppm)

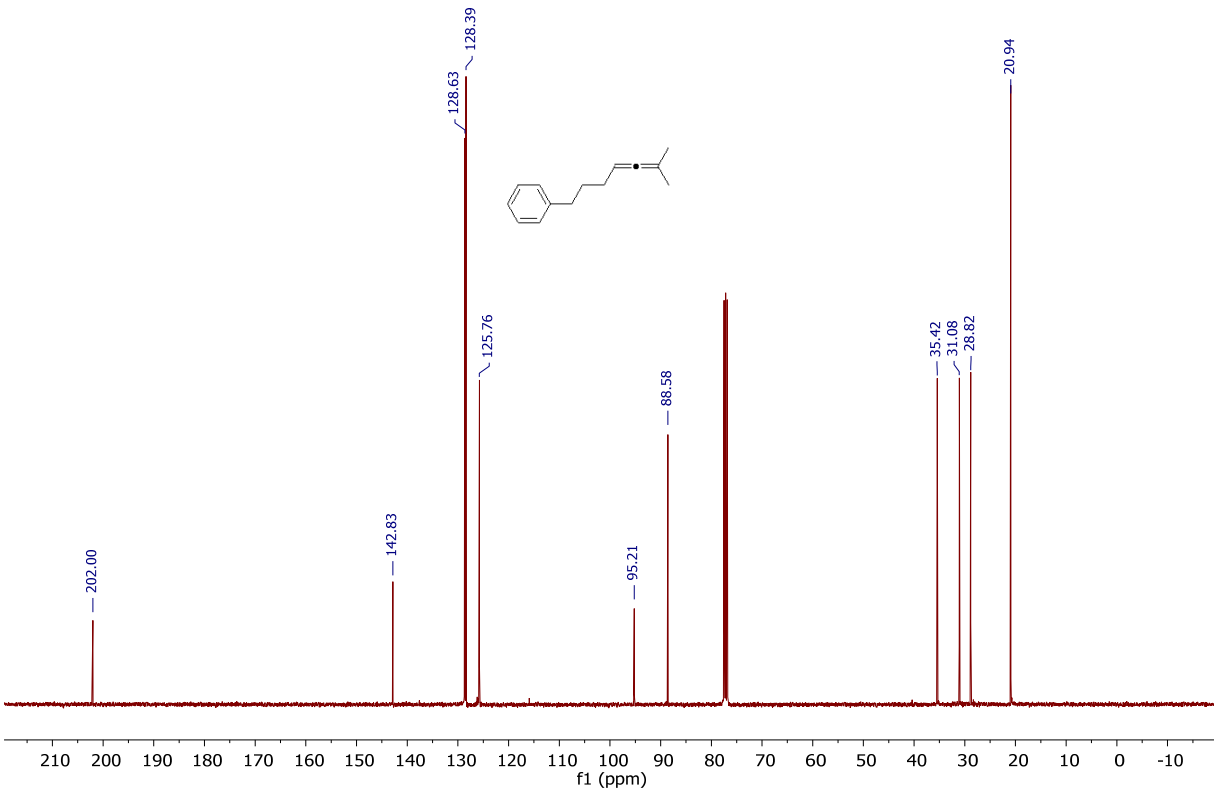

3.97
1.67
7.30
7.29
7.28
7.28
7.27
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.17
7.17
7.17
7.17
2.65
2.64
2.62
2.26
2.25
1.97
1.95
1.93
1.75
1.74
1.73
2.18 3.01
4.05
2.03 4.04 2.00 6.19 2.99
f1 (ppm)

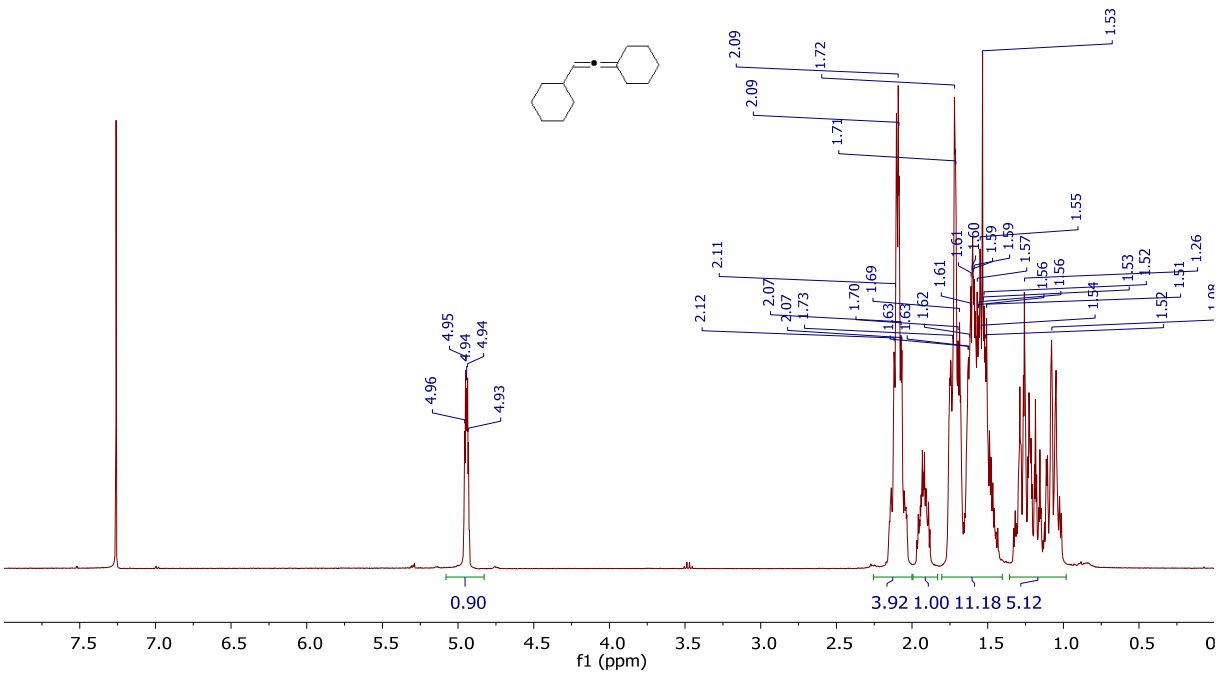

128.47
128.25
125.61
108.58
99.31
97.04
142.67
195.77
64.31
64.29
35.77
35.28
33.63
29.20
29.05
19.85
f1 (ppm)

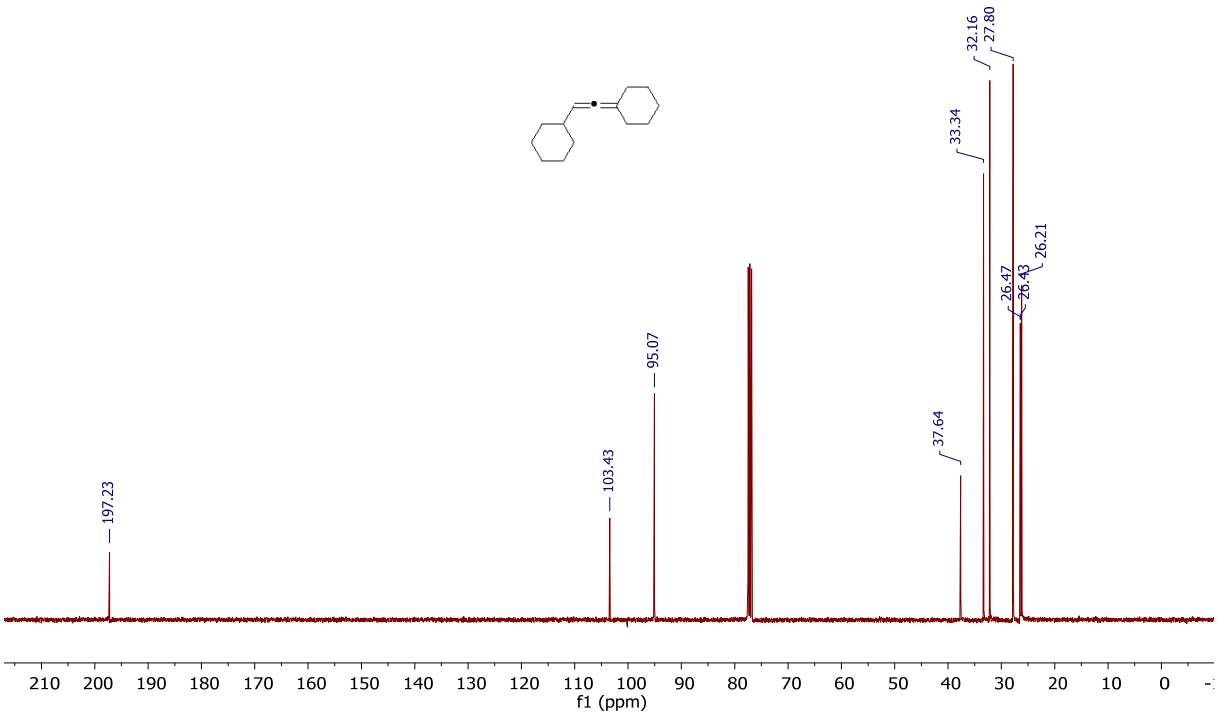

0.90
0.06
4.10
7.34
7.30
7.28
7.27
7.20
7.18
7.16
2.67
2.65
2.63
2.14
2.14
2.12
2.11
2.02
2.00
1.75
1.60
5.21
1.97
2.00 4.01 1.98 2.13 6.89
8.99
5.90
f1 (ppm)

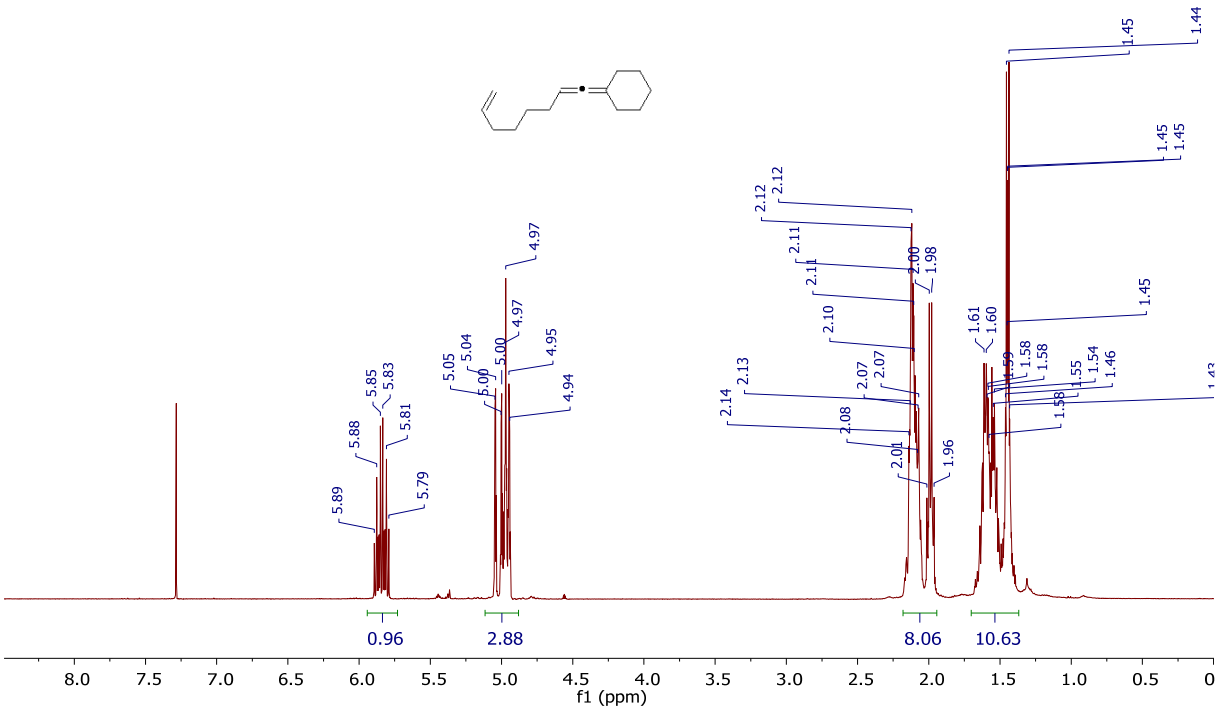

25.97
128.49
128.21
31.83
27.72
-5.16
125.55
65.41
35.46
29.34
28.72
26.26
194.93
142.84
104.10
101.76
18.40
f1 (ppm)

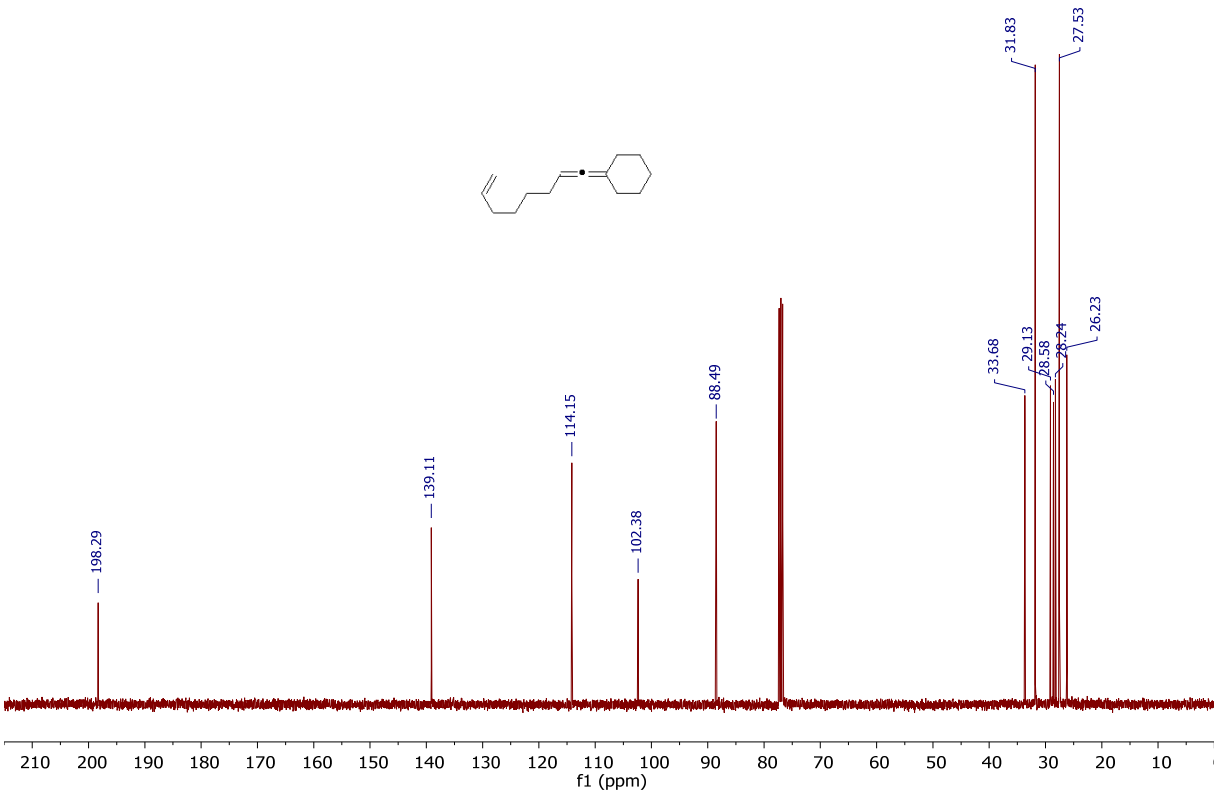

1.72
1.71
7.31
7.30
7.29
7.28
7.21
7.19
7.18
5.01
5.01
5.00
4.99
4.98
4.97
4.97
2.68
2.66
2.64
2.04
2.02
2.00
1.99
1.77
1.75
1.73
1.70
1.96 2.99
0.95
2.00
2.00 8.03
f1 (ppm)

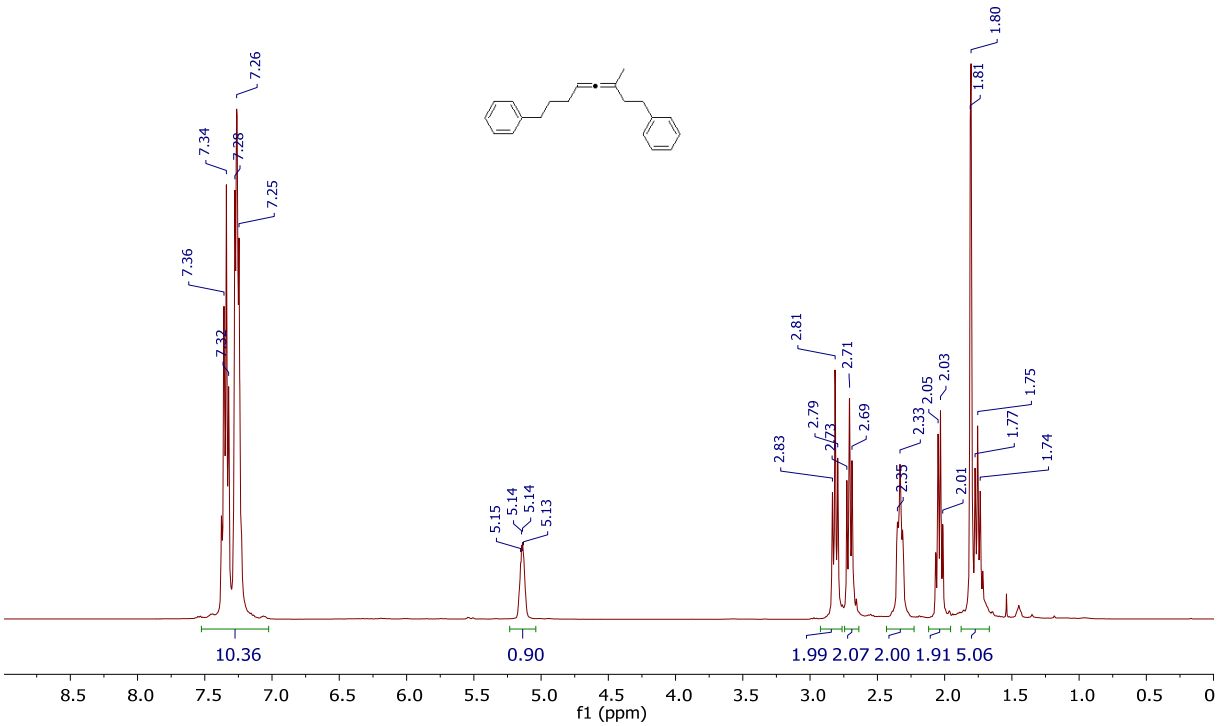

128.39
128.63
20.94
125.76
35.42
31.08
28.82
88.58
202.00
142.83
95.21
f1 (ppm)

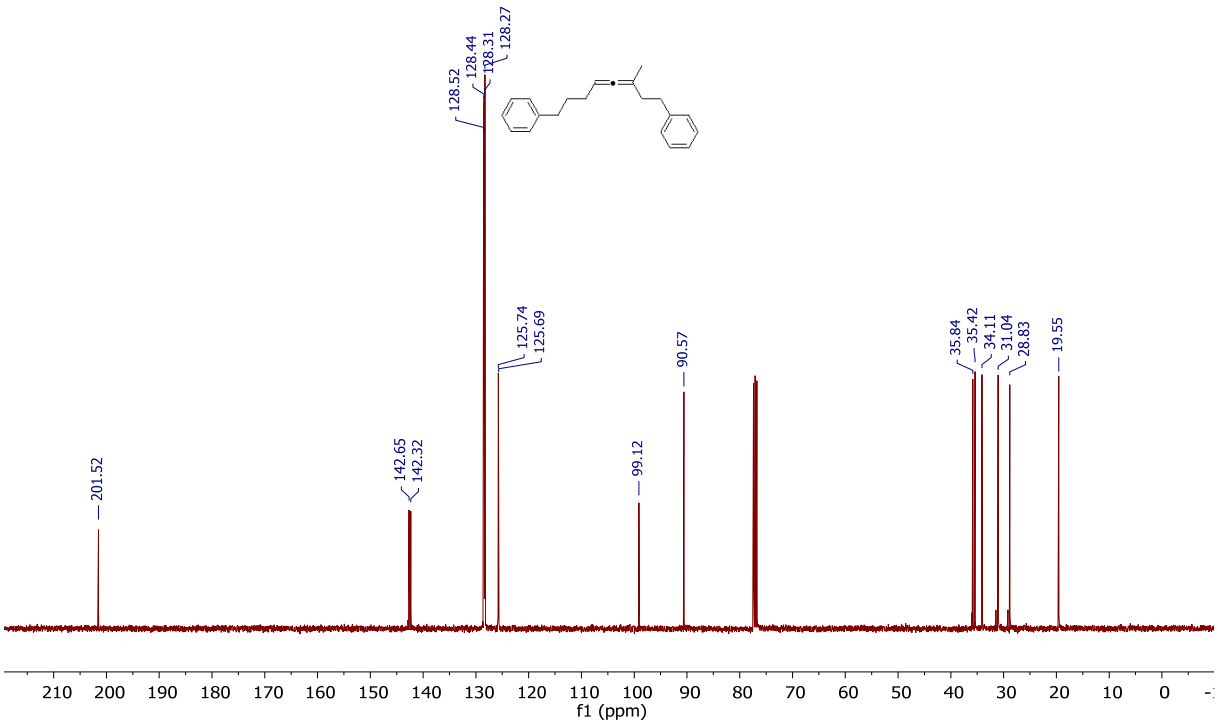

4.96
4.95
4.94
4.94
4.93
2.12
2.11
2.09
2.09
2.07
2.07
1.73
1.72
1.71
1.70
1.69
1.63
1.63
1.62
1.61
1.61
1.60
1.59
1.59
1.57
1.56
1.56
1.55
1.54
1.53
1.53
1.52
1.52
1.51
1.26
0.90
3.92 1.00 11.18 5.12
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

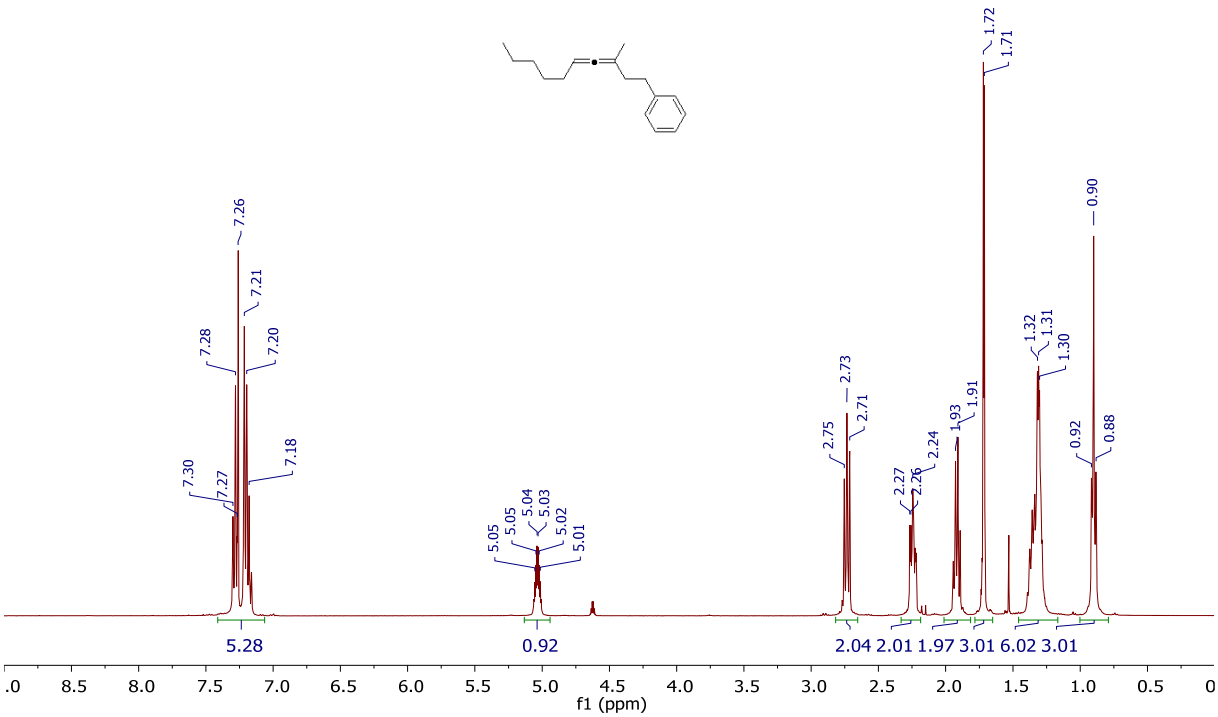

197.23
103.43
95.07
37.64
33.34
32.16
27.80
26.47
26.43
26.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

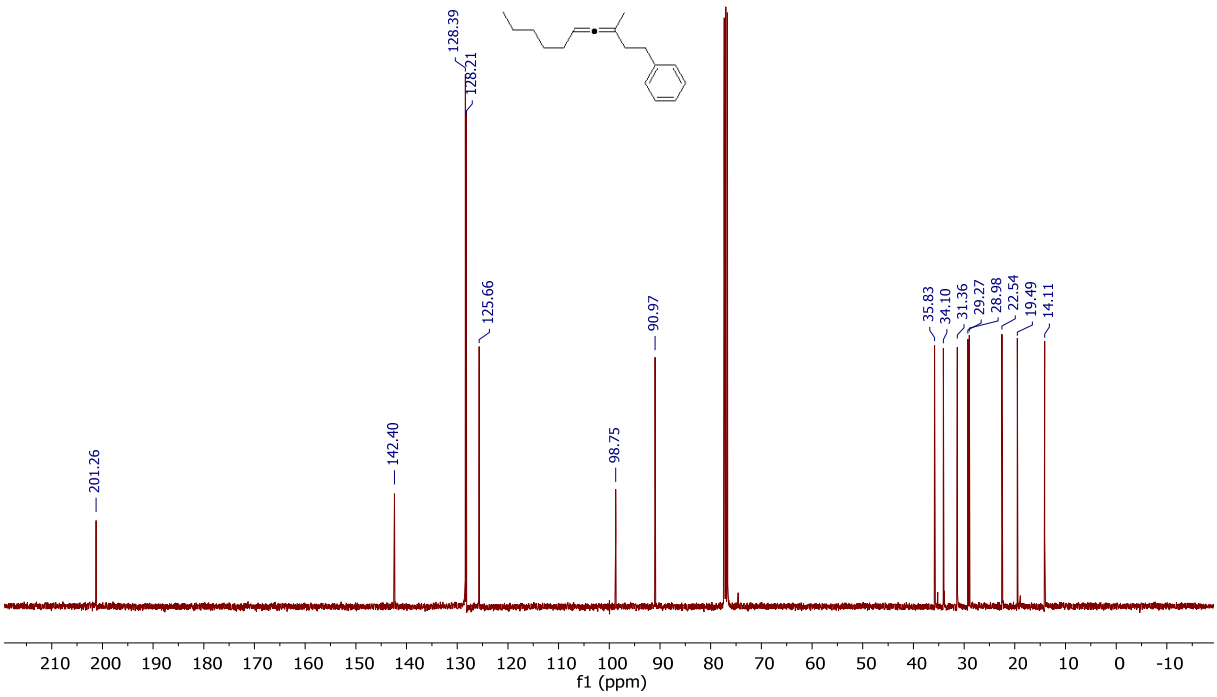

5.89
5.88
5.85
5.83
5.81
5.79
5.05
5.04
5.00
4.97
4.95
4.94
2.14
2.13
2.12
2.11
2.10
2.08
2.07
2.01
1.98
1.96
1.61
1.60
1.59
1.58
1.55
1.54
1.46
1.45
1.44
0.96
2.88
8.06
10.63
f1 (ppm)

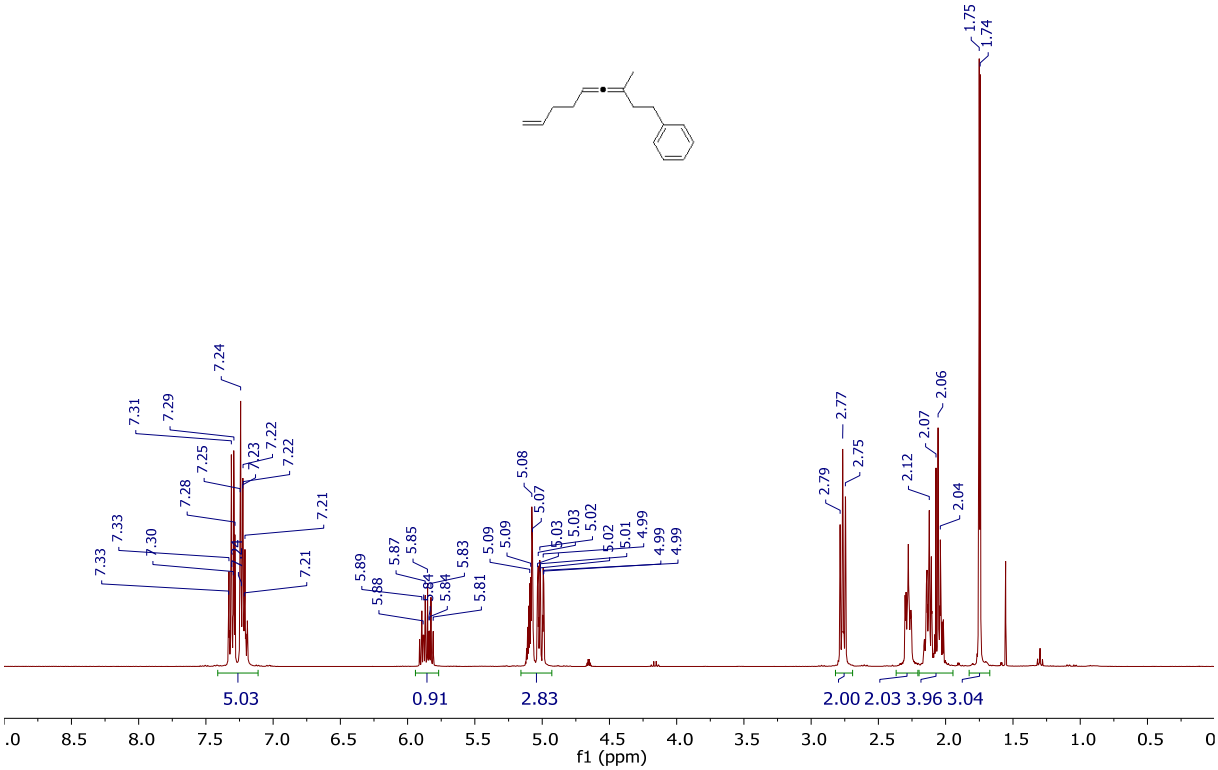

198.29
139.11
114.15
102.38
88.49
33.68
31.83
29.13
28.58
28.24
27.53
26.23
f1 (ppm)

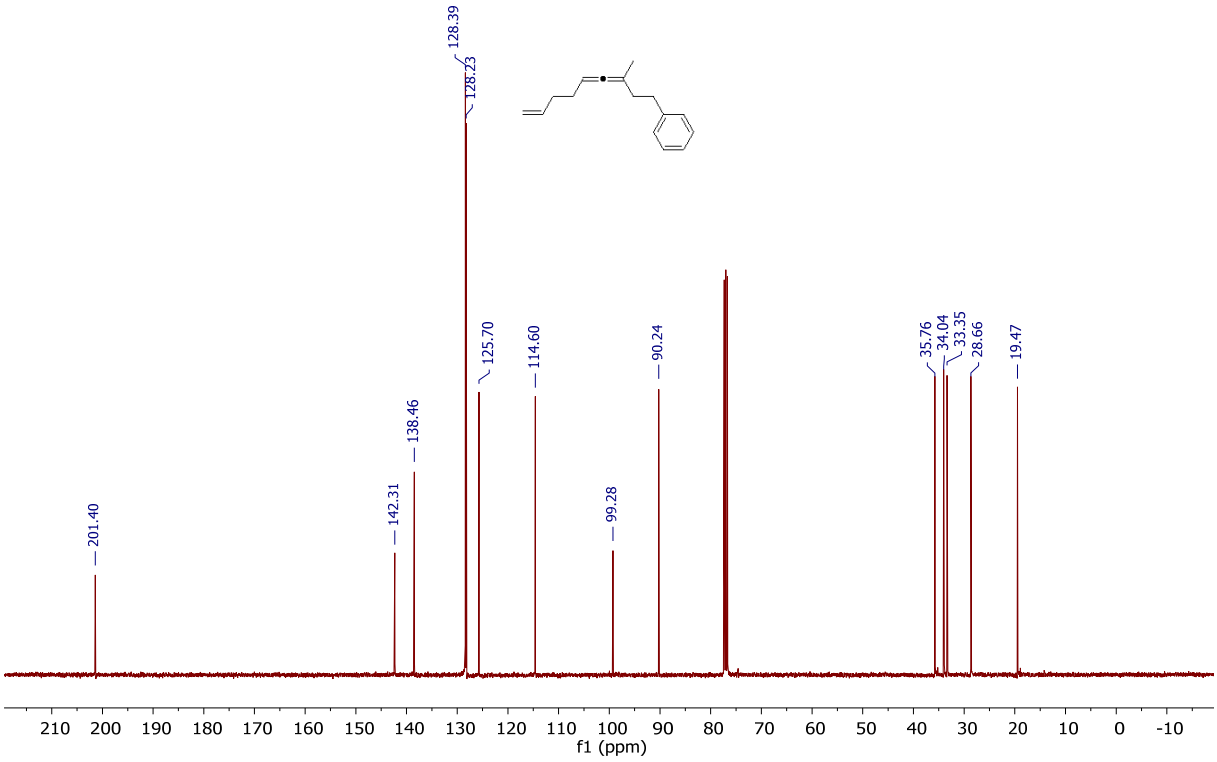

7.26
7.34
7.28
7.25
7.36
7.32
1.80
1.81
2.81
2.71
2.03
2.79
2.73
2.69
2.05
2.33
1.75
1.77
2.83
2.35
2.01
1.74
5.15
5.14
5.14
5.13
10.36
0.90
1.99 2.07 2.00 1.91 5.06
f1 (ppm)

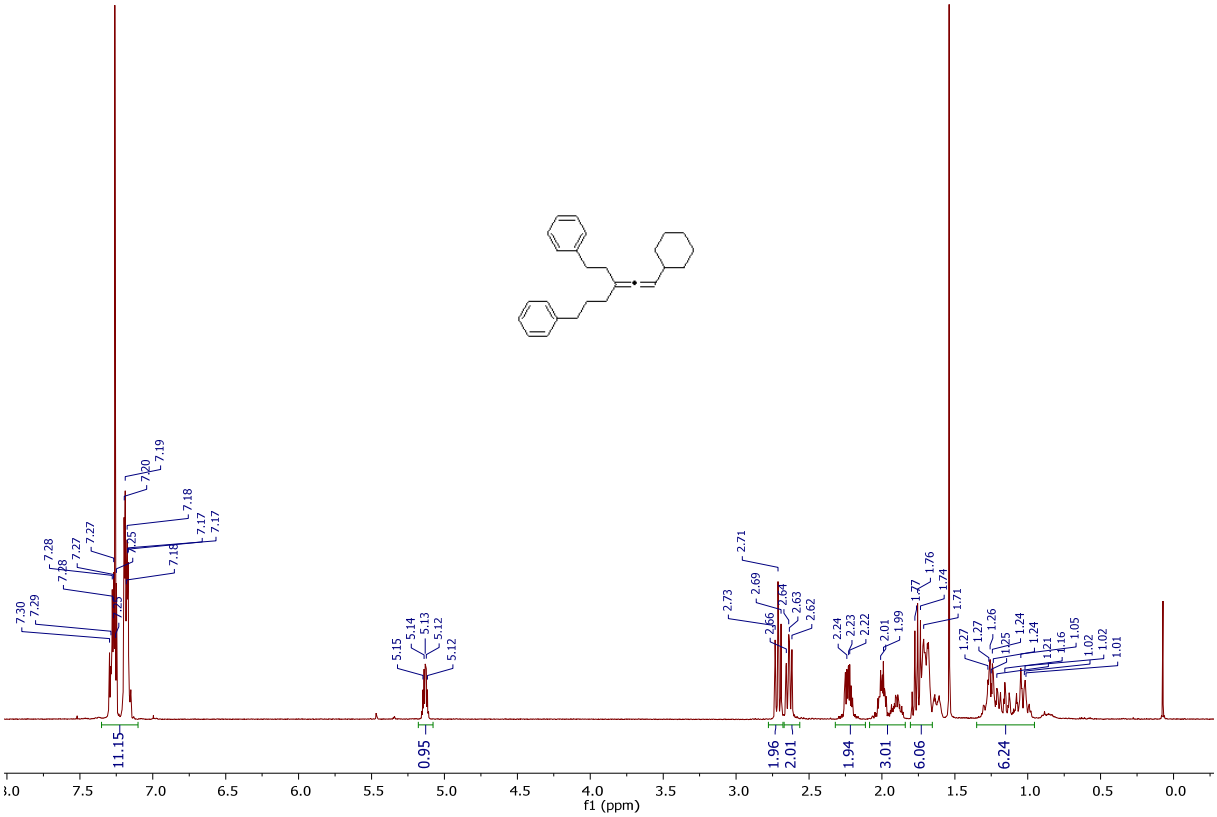

128.52
128.44
128.31
128.27
125.74
125.69
90.57
35.84
35.42
34.11
31.04
28.83
19.55
201.52
142.65
142.32
99.12
f1 (ppm)

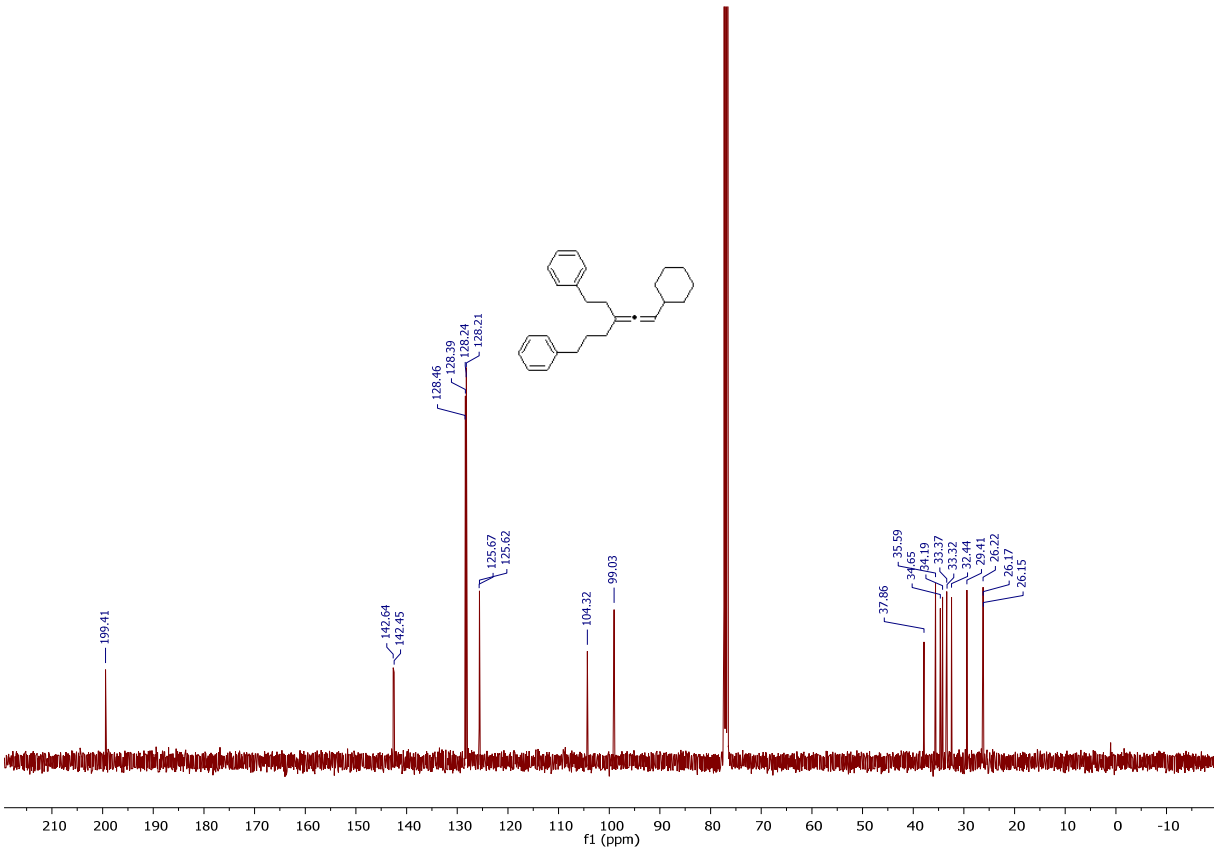

7.26
7.28
7.21
7.20
7.30
7.27
7.18
5.05
5.05
5.04
5.03
5.02
5.01
2.75
2.73
2.71
2.27
2.26
2.24
1.93
1.91
1.72
1.71
1.32
1.31
1.30
0.92
0.90
0.88
5.28
0.92
2.04 2.01 1.97 3.01 6.02 3.01
f1 (ppm)

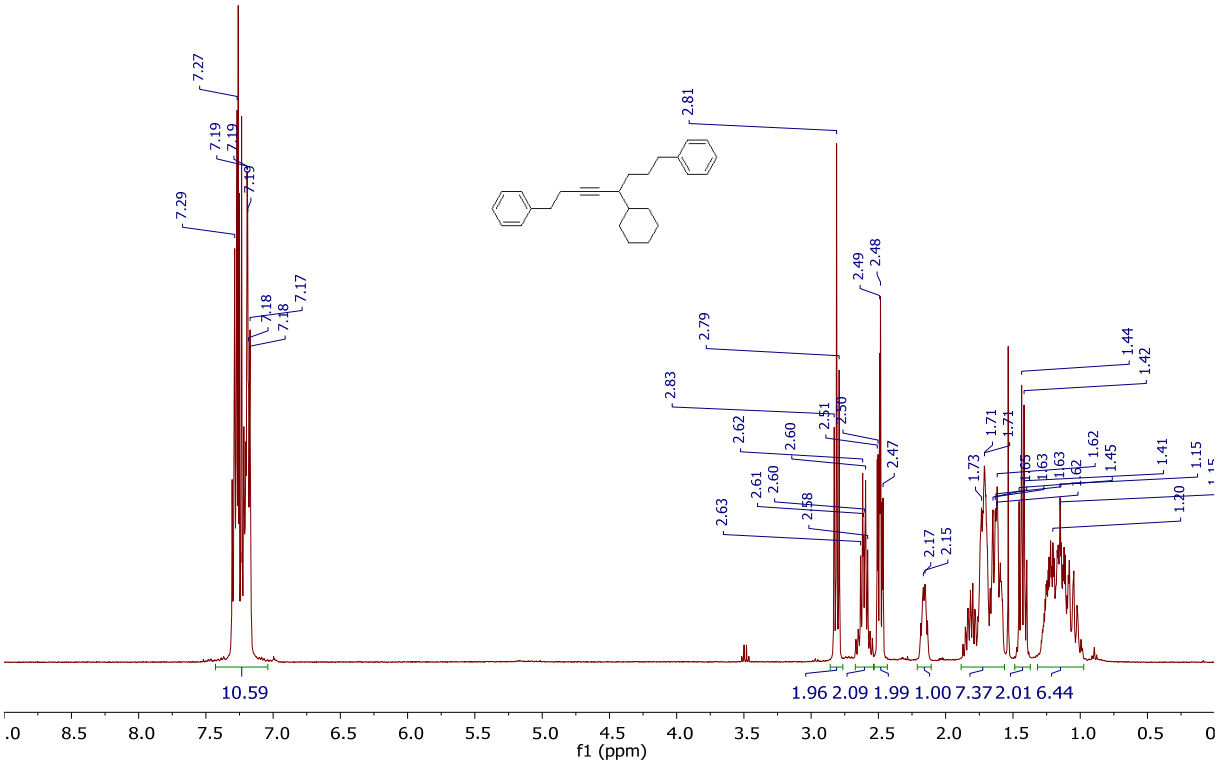

128.39
128.21
125.66
90.97
142.40
98.75
201.26
35.83
34.10
31.36
29.27
28.98
22.54
19.49
14.11
f1 (ppm)

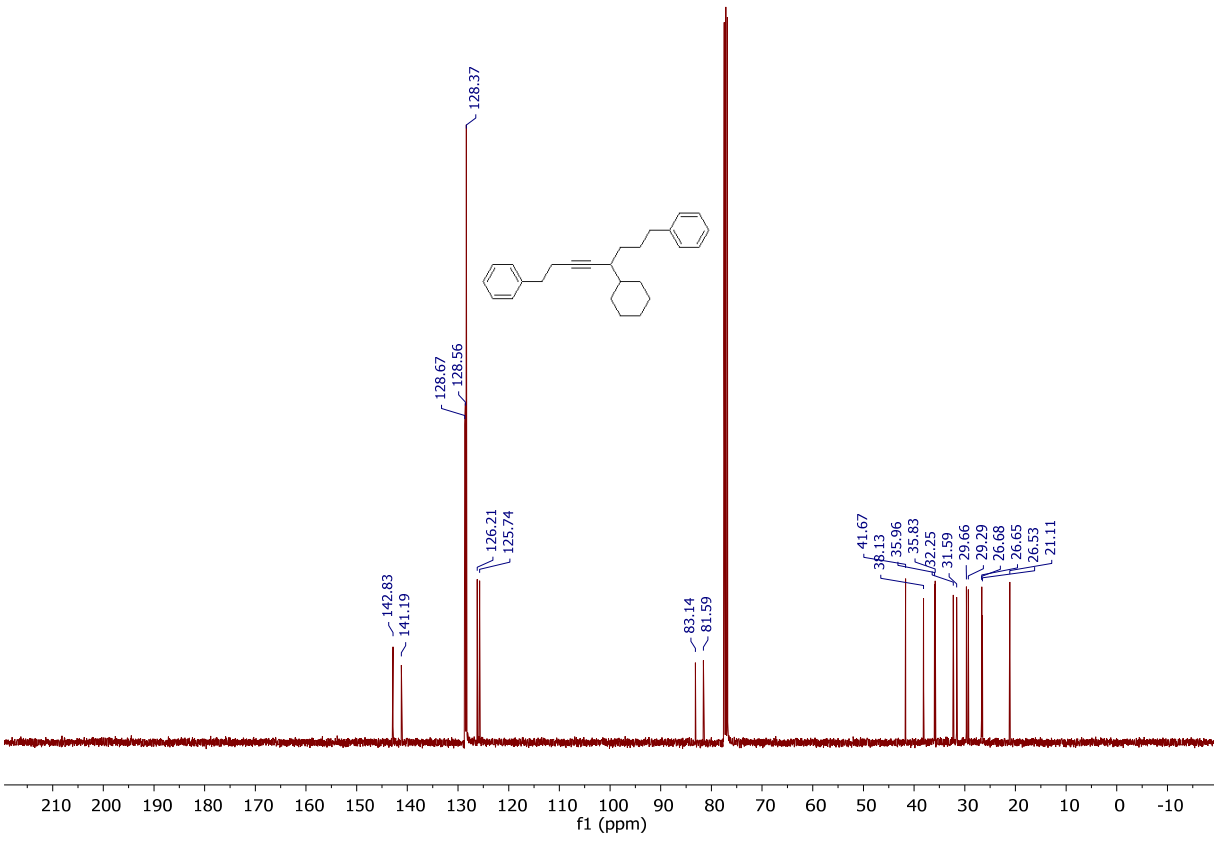

1.75
1.74
7.24
7.31
7.29
7.23
7.22
7.25
7.28
7.21
7.33
7.30
5.89
5.87
5.85
5.83
5.88
5.84
5.81
5.09
5.08
5.07
5.03
5.02
5.01
4.99
2.77
2.75
2.79
2.12
2.07
2.06
2.04
5.03
0.91
2.83
2.00 2.03 3.96 3.04
f1 (ppm)

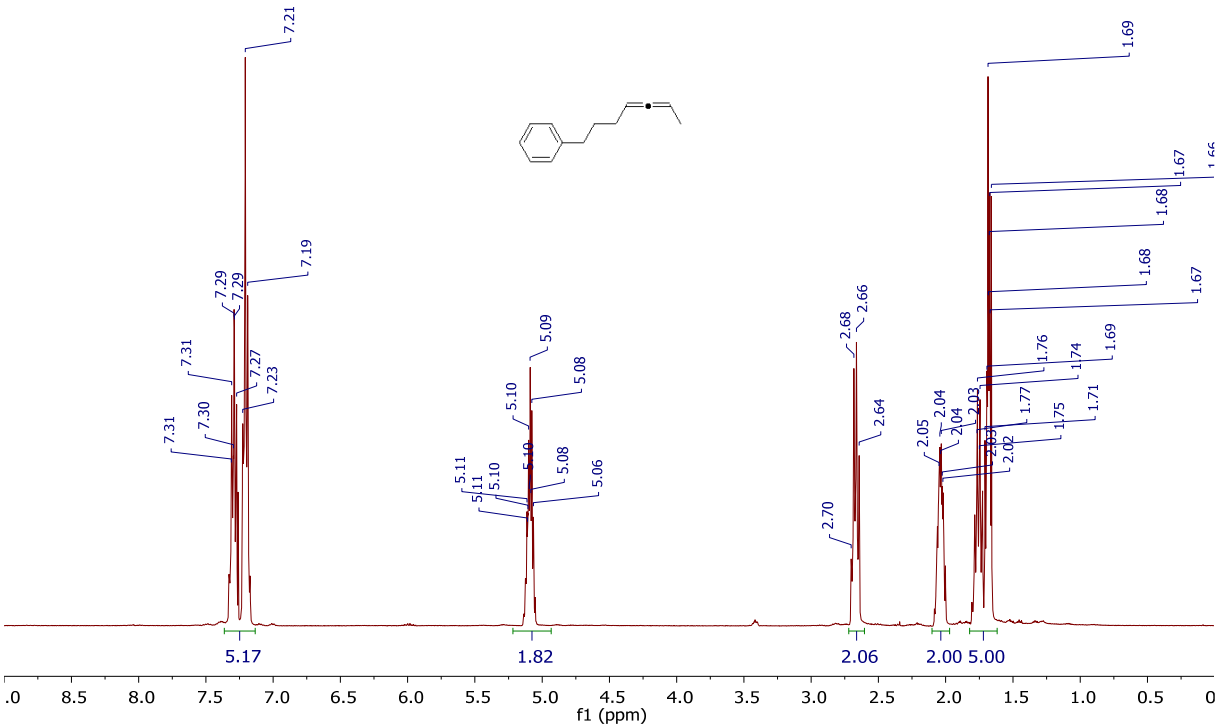

128.39
128.23
125.70
114.60
90.24
138.46
142.31
99.28
201.40
35.76
34.04
33.35
28.66
19.47
f1 (ppm)

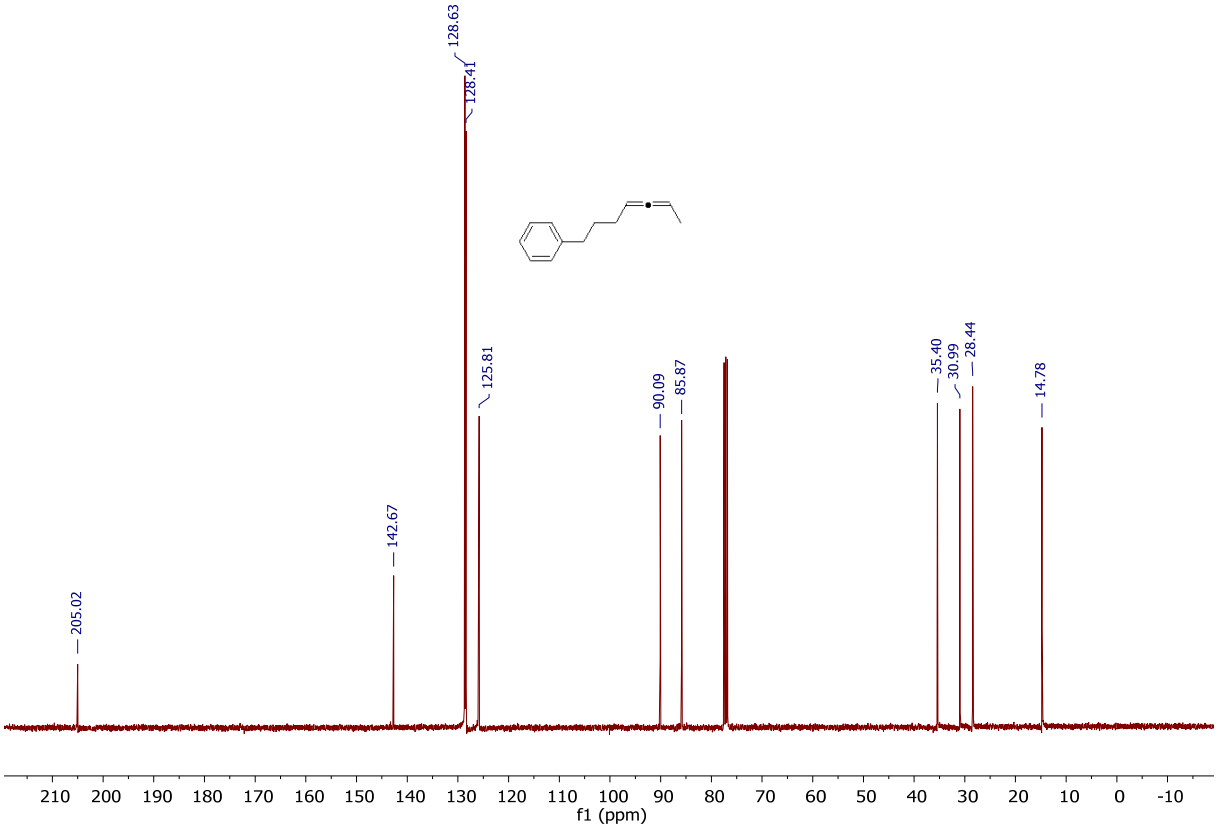

7.30
7.29
7.28
7.28
7.27
7.27
7.25
7.25
7.20
7.19
7.18
7.18
7.17
7.17
5.15
5.14
5.13
5.12
5.12
2.73
2.71
2.69
2.66
2.64
2.63
2.62
2.24
2.23
2.22
2.01
1.99
1.77
1.76
1.74
1.71
1.27
1.27
1.26
1.25
1.24
1.24
1.21
1.16
1.05
1.02
1.02
1.01
11.15
0.95
1.96
2.01
1.94
3.01
6.06
6.24
f1 (ppm)

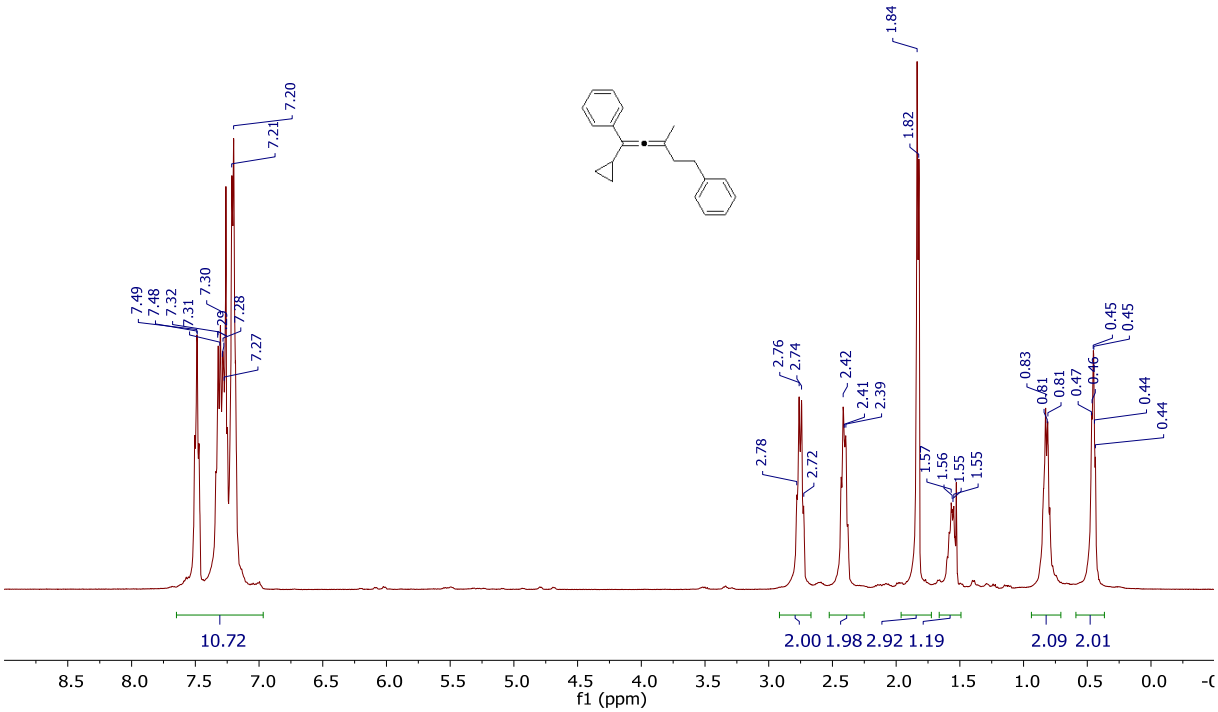

199.41
142.64
142.45
128.46
128.39
128.24
128.21
125.67
125.62
104.32
99.03
37.86
35.59
34.65
34.19
33.37
33.32
32.44
29.41
26.22
26.17
26.15
f1 (ppm)

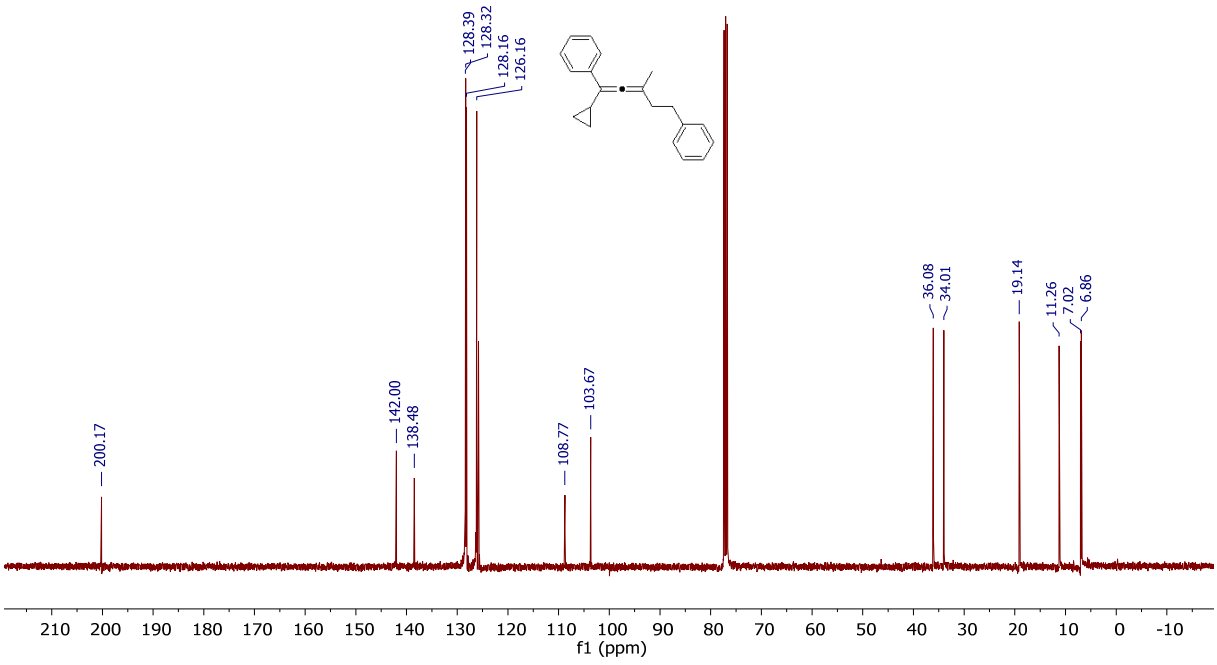

7.27
7.19
7.19
7.19
7.29
7.18
7.18
7.17
2.81
2.49
2.48
2.79
1.44
1.42
2.83
2.62
2.60
2.51
2.50
1.71
1.71
2.47
2.61
2.60
2.58
2.63
1.73
1.62
1.45
1.41
1.15
1.20
2.17
2.15
10.59
1.96 2.09 1.99 1.00 7.37 2.01 6.44
f1 (ppm)

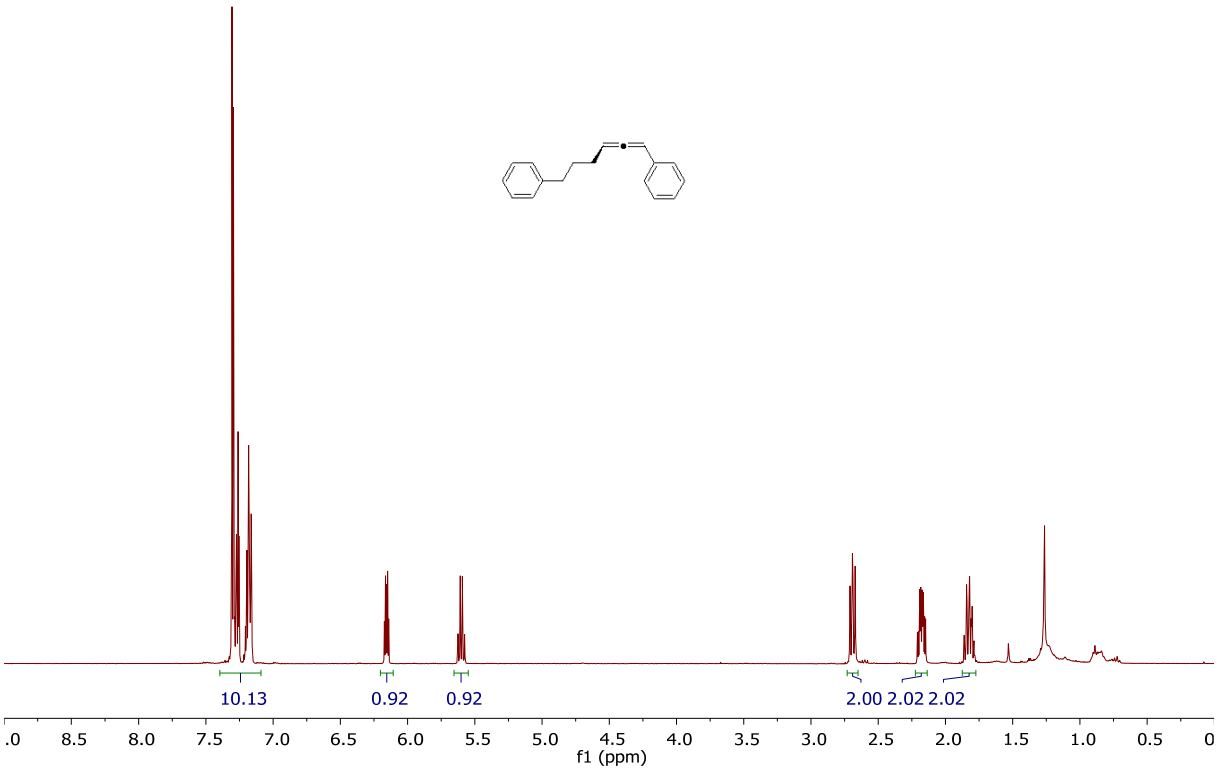

128.37
128.67
128.56
126.21
125.74
142.83
141.19
83.14
81.59
41.67
38.13
35.96
35.83
32.25
31.59
29.66
29.29
26.68
26.65
26.53
21.11
f1 (ppm)

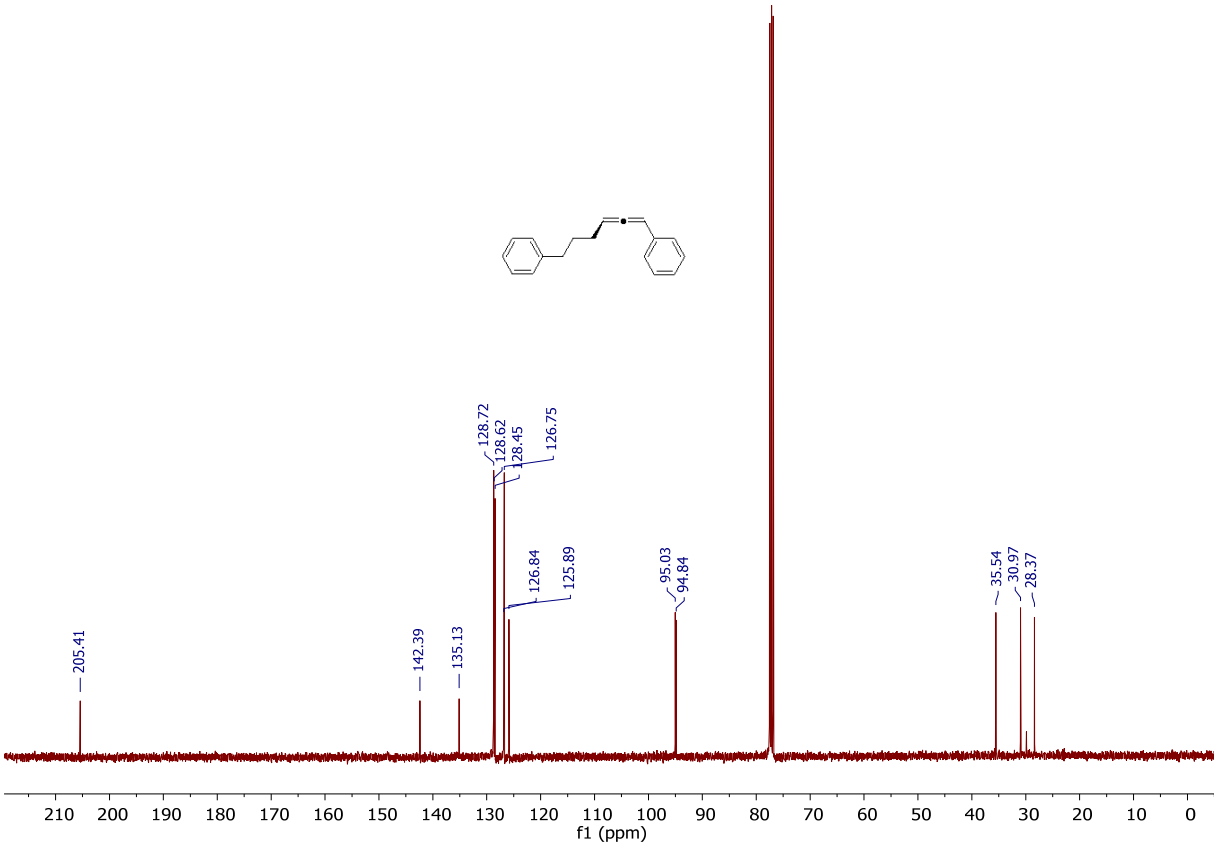

7.21
7.19
7.31
7.30
7.29
7.29
7.27
7.23
5.09
5.08
5.10
5.11
5.10
5.08
5.06
2.68
2.66
2.64
2.70
1.69
1.67
1.68
1.68
1.67
1.76
1.74
1.69
1.77
1.75
1.71
2.05
2.04
2.04
2.03
2.02
5.17
1.82
2.06
2.00 5.00
f1 (ppm)

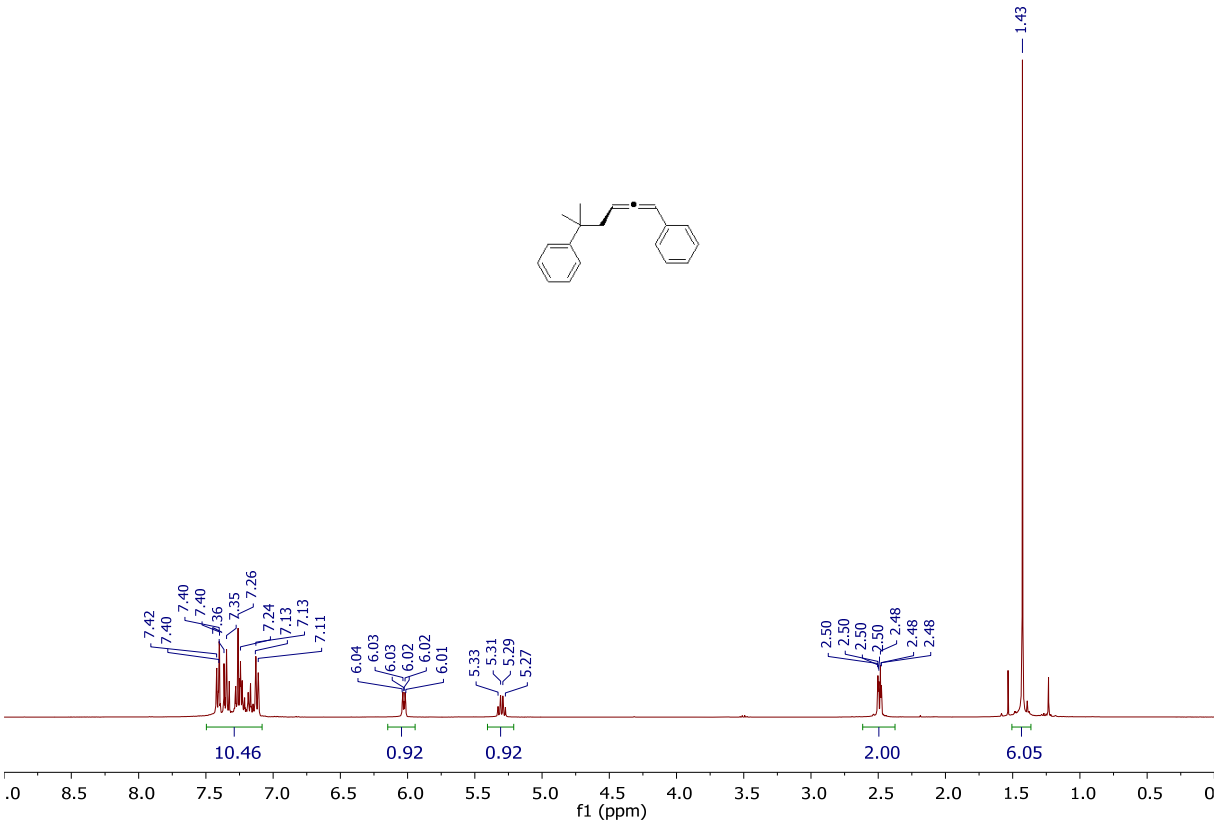

128.63
128.41
125.81
142.67
205.02
90.09
85.87
35.40
30.99
28.44
14.78
f1 (ppm)

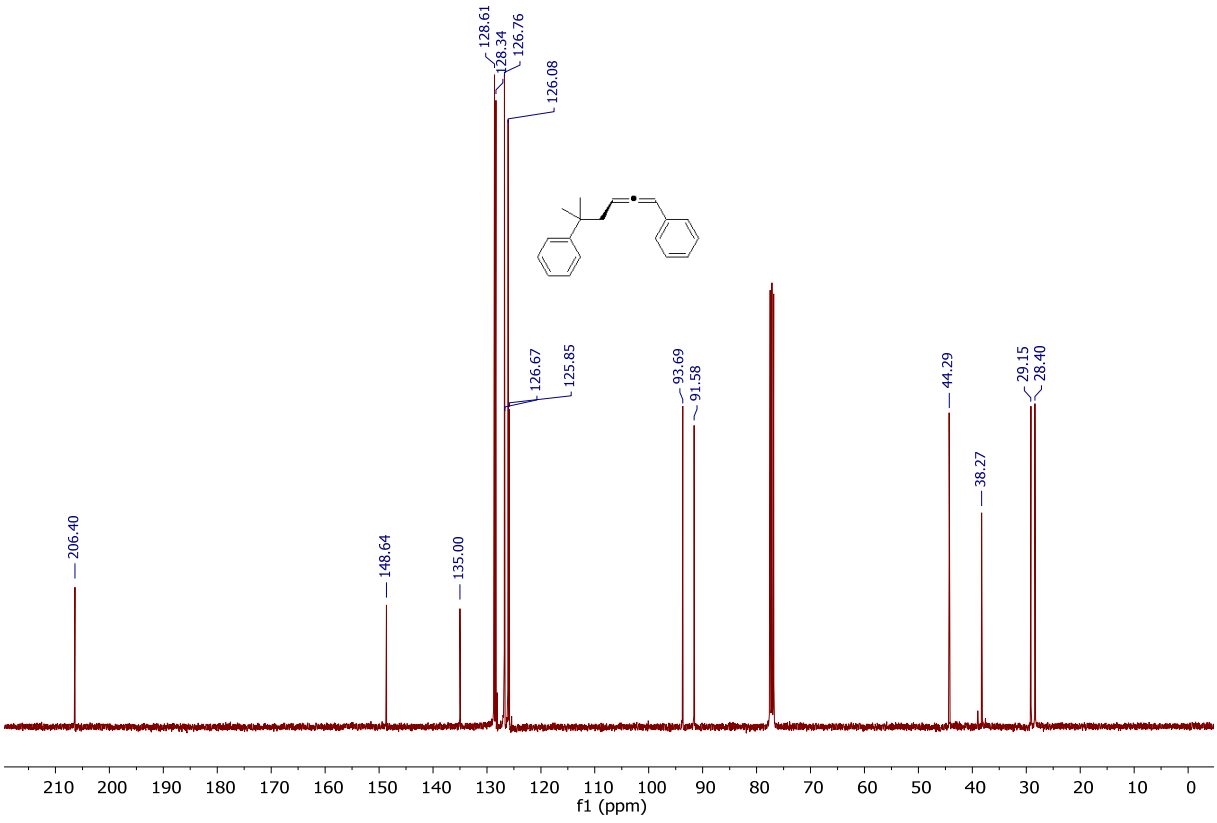

7.49
7.48
7.32
7.31
7.30
7.29
7.28
7.27
7.21
7.20
2.78
2.76
2.74
2.72
2.42
2.41
2.39
1.84
1.82
1.57
1.56
1.55
1.55
0.83
0.81
0.81
0.47
0.46
0.45
0.45
0.44
0.44
10.72
2.00 1.98 2.92 1.19
2.09 2.01
f1 (ppm)


200.17
142.00
138.48
128.39
128.32
128.16
126.16
108.77
103.67
36.08
34.01
19.14
11.26
7.02
6.86
f1 (ppm)


10.13
0.92
0.92
2.00
2.02
2.02
f1 (ppm)


205.41
142.39
135.13
128.72
128.62
128.45
126.75
126.84
125.89
95.03
94.84
35.54
30.97
28.37
f1 (ppm)


1.43
7.42
7.40
7.40
7.40
7.36
7.35
7.26
7.24
7.13
7.13
7.11
6.04
6.03
6.03
6.02
6.02
6.01
5.33
5.31
5.29
5.27
2.50
2.50
2.50
2.50
2.48
2.48
2.48
10.46
0.92
0.92
2.00
6.05
f1 (ppm)


128.61
128.34
126.76
126.08
126.67
125.85
93.69
91.58
44.29
29.15
28.40
38.27
206.40
148.64
135.00
f1 (ppm)