Supporting Information

A Synthesis of Substituted α-Allenols via Iron-Catalyzed Cross-Coupling of Propargyl Carboxylates with Grignard Reagents

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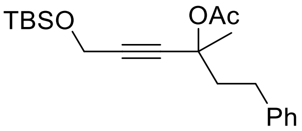
General Information

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) or $KMnO_4$. Flash column chromatography was carried out with 60Å (particle size 35 - 70 µm) silica gel. ^{1}H- and ^{13}C-NMR Experiments were performed on a Bruker NMR (400/100.6 MHz) or (500/125 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). HRMS were recorded on a Bruker MicroTOF spectrometer equipped with an ESI or APCI ion source.

1 Synthesis of Substrates

1.1 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (1a)



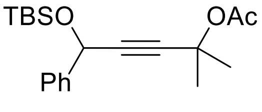
To a suspension of NaH (0.88 g, 22.0 mmol, 60% in mineral oil, 1.10 equiv.) in THF (50 mL) was added propargyl alcohol (1.12 g, 20.0 mmol, 1.00 equiv.) at 0 °C and the reaction was stirred for 15 min before adding TBSCl (3.17 g, 21.0 mmol, 1.05 equiv.). The reaction was allowed to stir for 1.5 h at room temperature. Then, it was cooled to –78 °C and n-BuLi (8.44 mL, 21.0 mmol, 2.5 M in hexane, 1.05 equiv.) was added dropwise. After stirring for 30 min, benzylacetone (3.71 ml, 25.0 mmol, 1.25 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 (3.31 mL, 35.0 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 4%) to obtain the product as a colorless oil (4.5 g, 62%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 5H), 4.39 (s, 2H), 2.84 – 2.79 (m, 2H), 2.26 – 2.11 (m, 2H), 2.00 (s, 3H), 1.72 (s, 3H), 0.91 (s, 9H), 0.14 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.41, 141.69, 128.59, 128.55, 126.05, 84.67, 84.36, 75.15, 51.93, 43.40, 30.84, 26.68, 25.94 (4C), 22.06, -4.94 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{32}O_3SiNa$ 383.2013; Found 383.2009.

1.2 5-((tert-butyldimethylsilyl)oxy)-2-methyl-5-phenylpent-3-yn-2-yl acetate (1b)



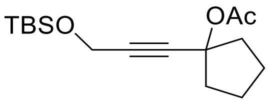
To a suspension of NaH (0.88 g, 22.0 mmol, 60% in mineral oil, 1.10 equiv.) in THF (50 mL) was added 1-phenylprop-2-yn-1-ol (2.64 g, 20.0 mmol, 1.00 equiv.) at 0 °C and the reaction was stirred for 15 min before adding TBSCl (3.17 g, 21.0 mmol, 1.05 equiv.). The reaction was allowed to stir for 1.5 h at room temperature. Then, it was cooled to –78 °C and n-BuLi (8.44 mL, 21.0 mmol, 2.5 M in hexane, 1.05 equiv.) was added dropwise. After stirring for 30 min, acetone (2.20 ml, 30.0 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 (3.31 mL, 35.0 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 4%) to obtain the product as a yellowish oil (4.08 g, 59%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.25 (m, 5H), 5.56 (s, 1H), 2.01 (s, 3H), 1.67 (d, *J* = 3.36 Hz, 6H), 0.95 (s, 9H), 0.18 (d, *J* = 2.21 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36, 141.53, 128.32 (2C), 127.67, 126.38 (2C), 86.87, 84.78, 72.16, 64.79, 29.02, 29.00, 25.99 (3C), 22.07, 18.49, -4.28, -4.74.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{30}O_3SiNa$ 369.1856; Found 369.1854.

1.3 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclopentyl acetate (1c)



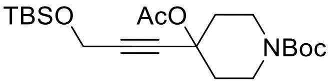
To a suspension of NaH (2.32 g, 58.0 mmol, 60% in mineral oil, 1.25 equiv.) in THF (150 mL) was added propargyl alcohol (2.60 g, 46.4 mmol, 1.00 equiv.) at 0 °C and the reaction was stirred for 15 min before adding TBSCl (7.69 g, 51.0 mmol, 1.10 equiv.). The reaction was allowed to stir for 1.5 h at room temperature. Then, it was cooled to –78 °C and n-BuLi (23.2 mL, 58.0 mmol, 2.5 M in hexane, 1.25 equiv.) was added dropwise. After stirring for 1 h, cyclopentanone (6.83 g, 81.2 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, treated with acetic anhydride (3.31 mL, 3.57 g, 35.0 mmol, 1.75 equiv.), allowed to warm to r.t. and stirred overnight. The reaction was quenched with half-sat. $NaHCO_3$ (20 mL), extracted with pentane (100 mL), washed with brine and dried over Na_2SO_4. The evaporated crude mixture was purified by column chromatography on silica gel (75 g; ether/pentane 2 – 5%) to obtain the product as a colorless oil (10.2 g, 74%)

^{1} H NMR (400 MHz, $CDCl_3$) δ 4.32 (s, 2H), 2.18 – 2.08 (m, 4H), 1.98 (s, 3H), 1.72 – 1.69 (m, 4H), 0.87 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.55, 85.28, 83.43, 80.58, 51.95, 40.29 (2C), 25.90 (3C), 23.35 (2C), 21.82, 18.33, -4.98 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{28}O_3SiNa$ 319.1700; Found 319,1689.

1.4 tert-butyl 4-acetoxy-4-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)piperidine-1-carboxylate (1d)



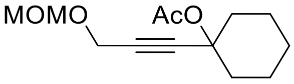
To a suspension of NaH (0.44 g, 11.0 mmol, 60% in mineral oil, 1.10 equiv.) in THF (25 mL) was added propargyl alcohol (0.56 g, 10.0 mmol, 1.00 equiv.) at 0 °C and the reaction was stirred for 15 min before adding TBSCl (1.59 g, 10.5 mmol, 1.05 equiv.). The reaction was allowed to stir for 1.5 h at room temperature. Then, it was cooled to –78 °C and n-BuLi (4.42 mL, 10.5 mmol, 2.5 M in hexane, 1.05 equiv.) was added dropwise. After stirring for 30 min, 1-boc-4-piperidone (2.09 g, 10.5 mmol, 1.05 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 (1.65 mL, 1.79 g, 17.5 mmol, 1.75 equiv.) was added and stirred overnight. The reaction was quenched with H_2O (10 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 10 – 20%) to obtain the product as a colorless oil (2.82 g, 68%)

^{1} H NMR (400 MHz, $CDCl_3$) δ 4.37 (s, 2H), 3.66 (br, 2H), 3.38-3.31 (m, 2H), 2.15-2.11 (m, 2H), 2.04 (s, 3H), 1.96-1.92 (m, 2H), 1.45 (s, 9H), 0.89 (s, 9H), 0.11 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.22, 154.74, 86.02, 83.03, 79.93, 73.41, 51.86, 40.04 (br, 2C), 36.42 (2C), 28.55, 25.90 (3C), 21.96 (3C), 18.37, -4.97 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{37}NO_5SiNa$ 434.2333; Found 434.2323.

1.5 1-(3-(methoxymethoxy)prop-1-yn-1-yl)cyclohexyl acetate (1e)



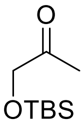
To a suspension of NaH (1.00 g, 25.0 mmol, 60% in mineral oil, 1.25 equiv.) in THF (50 mL) was added propargyl alcohol (1.12 g, 20.0 mmol, 1.00 equiv.) at 0 °C and the reaction was stirred for 15 min before adding MOMCl (2.75 g, 22.0 mmol, 1.10 equiv.). The reaction was allowed to stir for 1.5 h at room temperature. Then, it was cooled to –78 °C and n-BuLi (10.05 mL, 25.2 mmol, 2.5 M in hexane, 1.25 equiv.) was added dropwise. After stirring for 30 min, cyclohexanone (3.44 g, 35.0 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 (3.31 mL, 3.57 g, 35.0 mmol, 1.75 equiv.) was added and stirred overnight. The reaction was quenched with H_2O (10 mL), extracted with ether (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 10 – 20%) to obtain the product as a colorless oil (2.57 g, 54%)

^{1} H NMR (400 MHz, $CDCl_3$) δ 4.72 (s, 2H), 4.28 (s, 2H), 3.38 (s, 3H), 2.13 – 2.07 (m, 2H), 2.03 (s, 3H), 1.88-1.83 (m, 2H), 1.66 – 1.48 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.33, 94.77, 86.43, 81.81, 75.41, 55.75, 54.55, 37.09 (2C), 25.29, 22.69 (2C), 22.11.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_4Na$ 263.1254; Found 263.1256.

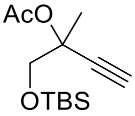
1.6 1-(tert-Butyldimethylsilyloxy)propan-2-one[2]



To a DCM (50 mL) solution of 1-hydroxypropan-2-one (3.50 g, 47.3 mmol, 1.00 equiv.), DMAP (289 mg, 2.36 mmol, 0.05 equiv.) and Et_3N (7.91 mL, 59.1 mmol, 1.25 equiv.) was added TBSCl (7.83 g, 52.0 mmol, 1.1 equiv) at 0 °C under nitrogen atmosphere. The mixture was stirred at r.t. for 2 h. Then the reaction mixture was quenched with half-sat. $NaHCO_3$ (20 ml), extracted with pentane (50 ml), washed with brine, and dried over Na_2SO_4. The evaporated crude mixture was purified by column chromatography on silica gel (75 g; ether/pentane 10%) to obtain the product (7.867 g, 88%).

^{1} H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 2H), 2.15 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H).

1.7 1-((tert-Butyldimethylsilyl)oxy)-2-methylbut-3-yn-2-yl acetate[3] (3a)



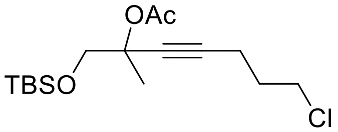
To a solution of 1-(tert-butyldimethylsilyloxy)propan-2-one (3.00 g, 15.9 mmol, 1.00 equiv.) in THF (50 mL) was added ethynylmagnesium bromide (35.0 mL, 17.5 mmol, 0.5M in THF, 1.10 equiv.) at 0 °C. The reaction mixture was stirred for 10 min and allowed to warm to room temperature. After stirring for 2 h, acetic anhydride (1.08 mL, 23.9 mmol, 1.25 equiv.) and DMAP (195 mg, 1.59 mmol, 0.10 equiv.) were added and the reaction mixture was allowed to stir overnight. After completion, the reaction was quenched with half-sat. $NaHCO_3$ (15 ml) and the mixture was extracted with pentane (50 mL), washed with brine and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (ethyl ether/pentane 5 %) to obtain the product (3.63 g, 89 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (d, *J* = 10.3 Hz, 1H), 3.70 (d, *J* = 10.3 Hz, 1H), 2.53 (s, 1H), 2.03 (s, 3H), 1.65 (s, 3H), 0.90 (s, 9H), 0.07 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.45, 82.53, 74.80, 74.02, 68.38, 25.92 (3C), 23.41, 21.94, 18.44, -5.19 (2C).

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{13}H_{24}O_3SiNa$ 279.1387; Found 279.1395.

1.8 1-((tert-Butyldimethylsilyl)oxy)-7-chloro-2-methylhept-3-yn-2-yl acetate[6] (3b)



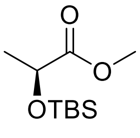
To anhydrous THF (15 mL) was added n-BuLi (2.66 mL, 6.65 mmol, 2.5 M in hexane, 1.15 equiv.) under an argon atmosphere and the flask was cooled to –78 °C. Then, 5-chloro-1-pentyne (0.59 g, 5.72 mmol, 1.00 equiv.) was added dropwise. After 30 minutes at –78 °C, 1-(tert-butyldimethylsilyloxy)propan-2-one (1.40 g, 7.43 mmol, 1.30 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. The reaction mixture was cooled to 0 °C and acetic anhydride (0.73 g, 0.68 mL, 7.15 mmol, 1.25 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), H2O (10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (75 g; ethyl ether/petroleum ether 5%) to afford the product as a colorless oil (1.40 g, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (d, J = 10.3 Hz, 1H), 3.66 – 3.63 (m, 3H), 2.40 (t, J = 6.7 Hz, 2H), 2.01 (s, 3H), 1.94 (tt, J = 6.7, J = 6.6 Hz, 2H), 1.60 (s, 3H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.63, 84.43, 79.89, 75.23, 68.46, 43.87, 31.18, 25.88 (3C), 23.57, 22.18, 18.41, 16.27, -5.19 (2C).

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{29}ClO_3SiNa$ 355.1467; Found 355.1457.

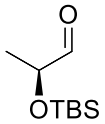
1.9 Methyl (S)-2-((tert-butyldimethylsilyl)oxy)propanoate[4]



To a solution of (-)-methyl lactate (2.08 g, 20 mmol, 1.00 equiv.) in dry CH_2Cl_2 (40 mL) was added triethylamine (4.2 mL, 30 mmol, 1.5 equiv.) and 4-dimethylamino pyridine (0.24 g, 2.0 mmol, 0.10 equiv.). The resulting solution was cooled to 0 ℃ and then tertbutyldimethylsilyl chloride (TBSCl, 3.3 g, 22 mmol, 1.10 equiv.) was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched by addition of water (20 mL). The organic fractions were collected and the aqueous phase was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic fractions were washed with 1 M citric acid (20 mL), saturated $NaHCO_3$ (20 mL) and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (75 g; ether/pentane 5 – 10%) to obtain the product (3.30 g, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.33 (q, *J* = 6.9 Hz, 1H), 3.72 (s, 3H), 1.40 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H).

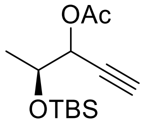
1.10 (S)-2-((tert-Butyldimethylsilyl)oxy)propanal[5]



To a cooled (–78 °C) stirred solution of methyl (S)-2-((tert-butyldimethylsilyl)oxy)propanoate (3.2 g, 14.65 mmol, 1.00 equiv.) in dry DCM (65 mL) was added slowly DIBAL-H (1.0 M in hexane, 14.65 mL, 14.65 mmol, 1.00 equiv) and stirred for 0.5 h. After completion, the reaction was quenched with saturated sodium potassium tartrate (40 mL), stirred for 0.5 h, and extracted with DCM (3 × 50 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ether/petrol ether 10 – 20%) to give the aldehyde (1.72 g, 62%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 4.09 (m, 1H), 1.28 (d, *J* = 4.8 Hz, 3H), 0.92 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H).

1.11 (4S)-4-((tert-Butyldimethylsilyl)oxy)pent-1-yn-3-yl acetate (3c)



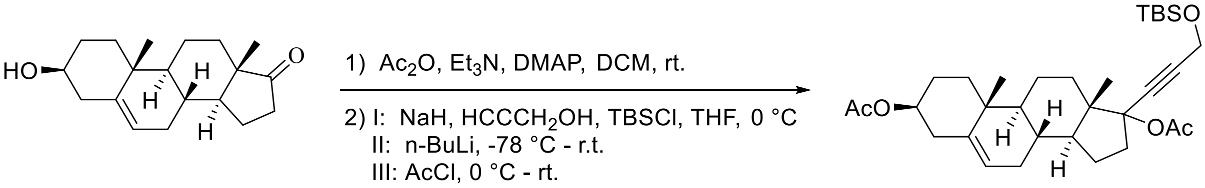
To a solution of (S)-2-((tert-butyldimethylsilyl)oxy)propanal (1.72 g, 9.13 mmol, 1.00 equiv.) in THF (25 mL) was added ethynylmagnesium bromide (20.2 mL, 10.1 mmol, 0.5 M in THF, 1.10 equiv.) at 0 °C. The reaction mixture was stirred for 10 min and allowed to warm to room temperature. After stirring for 1.5 h, acetic anhydride (1.08 mL, 1.17 g, 11.4 mmol, 1.25 equiv.) and DMAP (55.8 mg,0.46 mmol, 0.05 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. $NaHCO_3$ (10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (ethyl ether/petroleum ether 5%) to obtain the product (1.52 g, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 – 5.19 (m, 1H), 4.03 – 3.93 (m, 1H), 2.43 – 2.41 (m, 1H), 2.10 (s, 3H), 1.28 – 1.23 (m, 3H), 0.89 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.12, 79.02, 74.58, 69.28, 68.10, 25.81 (3C), 21.19, 19.32, 18.21, -4.57, -4.72.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{24}O_3SiNa$ 279.1387; Found 279.1376.

1.12 (3S,8R,9S,10R,13S,14S)-17-(3-((tert-Butyldimethylsilyl)oxy)prop-1-yn-1-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-3,17-diyl diacetate (5)



To a stirred solution of dihydroandrosterone (2.00 g, 6.93 mmol, 1.00 equiv.), Et_3N (1.93 ml, 13.9 mmol, 2.00 equiv.), and DMAP (42.4 mg, 347 µmol, 5 mol%), in DCM (50 ml) was added Ac_2O (819 µl, 8.67 mmol, 1.25 equiv.). The reaction was stirred for 1 h before quenching with H_2O (10 ml), extracted with pentane (50 ml) and washed with 10% citric acid (10 ml), sat. $NaHCO_3$ (10 ml) and brine (10 ml). The organic phase was dried over Na_2SO_4 and concentrated to obtain 2.243 g of crude product (98%). To a suspension of NaH (218 mg, 5.45 mmol, 60% in mineral oil, 1.20 equiv.) in THF (25 ml) was added propargyl alcohol (280 mg, 5.00 mmol, 1.10 equiv.) at 0°C and the reaction was stirred for 15 min before adding TBSCl (753 mg, 4.99 mmol, 1.10 equiv.). The reaction was allowed to stir for 1.5 h at r.t. Then it was cooled to –78°C and n-BuLi (1.91 mL, 4.77 mmol, 2.5 M in hexane, 1.05 equiv.) was added dropwise and stirred for 1 h and acetyl-dehydroandrosterone (1.50 g, 4.54 mmol, 1.00 equiv.) was added. After 2 h the reaction mixture was allowed to warm to 0 °C and AcCl (484 µl, 6.81 mmol, 1.5 equiv.) was added and the reaction was stirred for overnight. The reaction was quenched with sat. $NaHCO_3$ (10 ml), extracted with pentane (25 ml), and washed with H_2O (10 ml) and brine (10 ml) and dried over Na_2SO_4. The evaporated crude mixture was purified by column chromatography on silica gel (SiO_2 75g; Ether/pentane 3-5%) to yield 1.450 g of product (59%).

^1H NMR (400 MHz, , $CDCl_3$) δ 5.40 – 5.34 (m, 1H), 4.67 – 4.56 (m, 1H), 4.36 (s, 2H), 2.75 – 2.63 (m, 1H), 2.39 – 2.27 (m, 2H), 2.07 – 1.93 (m, 8H), 1.93 – 1.78 (m, 3H), 1.78 – 1.36 (m, 8H), 1.36 – 1.23 (m, 1H), 1.23 – 0.82 (m, 17H), 0.11 (d, $J = 1.5$ Hz, 6H).

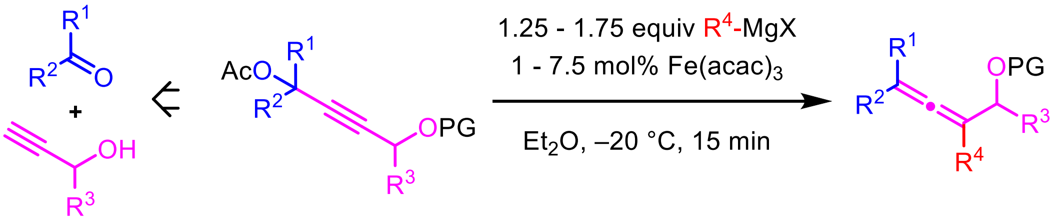
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.67, 169.59, 139.79, 122.36, 85.49, 84.87, 84.44, 74.00, 52.04, 49.73, 49.09, 47.74, 38.23, 37.28, 37.13, 36.74, 33.09, 32.42, 31.62, 27.88, 25.92 (3C), 23.87, 21.62, 21.59, 20.78, 19.49, 18.40, 13.53, -4.93, -4.96.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{50}ONa$ 565.3320; Found 565.3315.

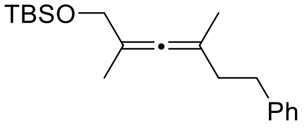
2 Iron-Catalyzed Synthesis of Substituted Allenols

General procedure: In a dry 20 or 5 mL microwave flask under argon was added catalyst Fe(acac)$_3$ (1 – 7.5 mol%) and diethyl ether (10 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 dropwise addition of Grignard reagent (1.25 – 2.00 equiv.) for 5 min. The reaction mixture was stirred for another 10 min, quenched with aq. 2.5% citric acid solution (2 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 Preparation of α-allenols from propargyl substrates with acetate and protected hydroxyl on opposite sides of the alkyne



2.1.1 tert-Butyl((2,4-dimethyl-6-phenylhexa-2,3-dien-1-yl)oxy)dimethylsilane (**2a**)



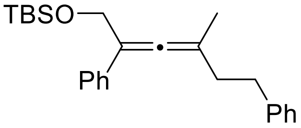
According to the general procedure catalyst (8.83 mg, 25 µmol, 5 mol%), 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (180.3 mg, 0.50 mmol, 1.00 equiv.) and methylmagnesium bromide (0.25 mL, 0.750 mmol, 3 M in diethyl ether, 1.5 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO$_2$ (ethyl ether/pentane 1.5 – 2%) to yield 132.1 mg of product (83%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.23 (m, 5H), 4.09 – 4.02 (m, 2H), 2.80 – 2.76 (m, 2H), 2.34 – 2.30 (m, 2H), 1.77 (s, 3H), 1.67 (s, 3H), 0.97 (s, 9H), 0.13 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 198.54, 142.44, 128.53 (2C), 128.34 (2C), 125.78, 99.39, 98.86, 65.84, 36.10, 34.18, 26.06 (3C), 19.37, 18.50, 15.98, -5.06 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{32}OSiNa$ 339.2115; Found 339.2126.

2.1.2 tert-Butyldimethyl((4-methyl-2,6-diphenylhexa-2,3-dien-1-yl)oxy)silane (**2b**)



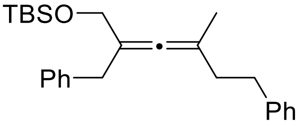
According to the general procedure catalyst (13.25 mg, 37.5 µmol, 7.50 mol%), 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (180.3 mg, 0.50 mmol, 1.00 equiv.) and phenylmagnesium bromide (0.292 mL, 0.875 mmol, 3 M in diethyl ether, 1.75 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1.5 – 2%) to yield 153 mg of product (81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.23 (m, 10H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.50 (d, *J* = 12.2 Hz, 1H), 2.89 – 2.85 (m, 2H), 2.49 (t, *J* = 8.5 Hz, 2H), 1.92 (s, 3H), 0.96 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.64, 142.05, 136.47, 128.53(2C), 128.45(2C), 128.26 (C2), 126.50 (2C), 126.41, 125.94, 105.74, 102.73, 63.40, 36.12, 34.06, 26.00 (3C), 18.85, 18.40, -5.01 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{34}OSiNa$ 401.2271; Found 401.2264.

2.1.3 ((2-Benzyl-4-methyl-6-phenylhexa-2,3-dien-1-yl)oxy)(tert-butyl)dimethylsilane (**2c**)



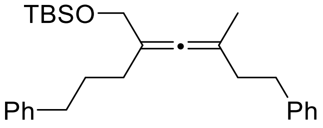
According to the general procedure catalyst (8.83 mg, 25 µmol, 5 mol%), 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (180.3 mg, 0.50 mmol, 1.00 equiv.) and benzylmagnesium chloride (0.875 mL, 0.875 mmol, 1 M in diethyl ether, 1.75 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1.5 – 2%) to yield 160.7 mg of product (82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34- 7.19 (m, 10H), 4.09 – 4.02 (m, 2H), 3.40 – 3.31 (m, 2H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.27 – 2.21 (m, 2H), 1.73 (s, 3H), 0.97 (s, 9H), 0.11 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.34, 142.43, 140.26, 129.21 (2C), 128.48 (2C), 128.36 (2C), 128.16 (2C), 125.98, 125.82, 103.99, 100.48, 63.95, 36.55, 36.18, 34.21, 26.07 (3C), 19.18, 18.47, -5.07 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{36}OSiNa$ 415.2428; Found 415.2418.

2.1.4 tert-Butyldimethyl((4-methyl-6-phenyl-2-(3-phenylpropyl)hexa-2,3-dien-1-yl)oxy)silane (**2d**)



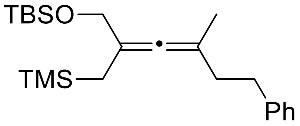
According to the general procedure catalyst (1.76 mg, 5 µmol, 1 mol%), 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (180.3 mg, 0.50 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (0.780 mL, 0.625 mmol, 0.8 M in diethyl ether, 1.25 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1 – 2%) to yield 172.1 mg of product (82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.15 (m, 10H), 4.07 – 3.97 (m, 2H), 2.76 – 2.69 (m, 2H), 2.66 – 2.57 (m, 2H), 2.32 – 2.25 (m, 2H), 2.06 – 1.93 (m, 2H), 1.74 (s, 3H), 1.71 – 1.63 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.20, 142.93, 142.40, 128.62 (2C), 128.52 (2C), 128.38 (2C), 128.37 (2C), 125.83, 125.74, 104.05, 100.54, 65.06, 36.23, 35.88, 34.31, 29.69, 29.05, 26.07 (3C), 19.48, 18.50, -5.03, -5.05.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{40}OSiNa$ 443.2741; Found 443.2738.

2.1.5 tert-Butyldimethyl((4-methyl-6-phenyl-2-((trimethylsilyl)methyl)hexa-2,3-dien-1-yl)oxy)silane (**2e**)



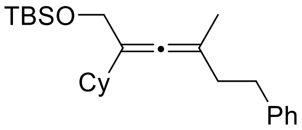
According to the general procedure catalyst (8.83 mg, 25 µmol, 5 mol%), 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (180.3 mg, 0.50 mmol, 1.00 equiv.) and (trimethylsilyl)methylmagnesium chloride (0.750 mL, 0.750 mmol, 1.0 M in diethyl ether, 1.50 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1 %) to yield 134 mg of product (69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 5H), 4.00 – 3.90 (m, 2H), 2.73 (t, J = 7.9 Hz, 2H), 2.33 – 2.18 (m, 2H), 1.72 (s, 3H), 1.28 (s, 2H), 0.92 (s, 9H), 0.07 (d, J = 0.6 Hz, 6H), 0.04 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.67, 142.60, 128.53 (2C), 128.37 (2C), 125.79, 101.23, 99.33, 66.24, 36.69, 34.36, 26.09 (3C), 19.61, 18.52, 17.78, -1.02 (3C), -5.02, -5.03.

HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{23}H_{40}OSi_2Na$ 411.2510; Found 411.2521.

2.1.6 tert-Butyl((2-cyclohexyl-4-methyl-6-phenylhexa-2,3-dien-1-yl)oxy)dimethylsilane (**2f**)



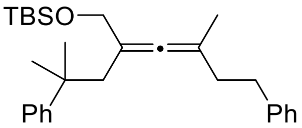
According to the general procedure catalyst (1.76 mg, 5 µmol, 1 mol%), 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (180.3 mg, 0.50 mmol, 1.00 equiv.) and cyclohexylmagnesium chloride (0.313 mL, 0.625 mmol, 2.0 M in diethyl ether, 1.25 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (toluene/pentane 5 – 10%) to yield 118.3 mg of product (62%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 4.09 (q, *J* = 12.1 Hz, 2H), 2.77 – 2.73 (m, 2H), 2.31 – 2.27 (m, 2H), 1.96 – 1.87 (m, 1H), 1.86 – 1.63 (m, 8H), 1.30 – 1.02 (m, 5H), 0.94 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.83, 142.58, 128.52 (2C), 128.37 (2C), 125.81, 110.08, 101.12, 63.61, 37.77, 36.28, 34.38, 32.84, 32.69, 26.76, 26.74, 26.54, 26.07 (3C), 19.58, 18.48, -5.03 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{40}OSiNa$ 407.2741; Found 407.2735.

2.1.7 tert-Butyldimethyl((4-methyl-2-(2-methyl-2-phenylpropyl)-6-phenylhexa-2,3-dien-1-yl)oxy)silane (**2g**)



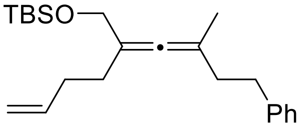
According to the general procedure catalyst (8.83 mg, 25 µmol, 5 mol%), 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (180.3 mg, 0.50 mmol, 1.00 equiv.) and (2-methyl-2-phenylpropyl)magnesium chloride (1.5 mL, 0.750 mmol, 0.5 M in diethyl ether, 1.5 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1.5 – 2%) to yield 191.9 mg of product (88%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 10H), 3.77 – 3.69 (m, 2H), 2.58 – 2.49 (m, 2H), 2.38 (s, 2H), 2.07 (t, *J* = 8.0 Hz, 2H), 1.52 (s, 3H), 1.39 (s, 6H), 0.93 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.45, 149.54, 142.59, 128.49 (2C), 128.31 (2C), 127.99 (2C), 126.04 (2C), 125.74, 125.41, 100.91, 99.53, 65.84, 43.33, 38.05, 36.06, 33.95, 29.84, 29.59, 26.06 (3C), 18.98, 18.45, -5.09 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{42}OSiNa$ 457.2897; Found 457.2891.

2.1.8 ((2-(But-3-en-1-yl)-4-methyl-6-phenylhexa-2,3-dien-1-yl)oxy)(tert-butyl)dimethylsilane (**2h**)



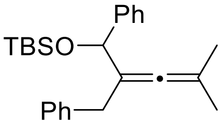
According to the general procedure catalyst (1.76 mg, 5 µmol, 1 mol%), 6-((tert-butyldimethylsilyl)oxy)-3-methyl-1-phenylhex-4-yn-3-yl acetate (180.3 mg, 0.50 mmol, 1.00 equiv.) and but-3-en-1-ylmagnesium bromide (1.04 mL, 0.625 mmol, 0.6 M in diethyl ether, 1.25 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2%) to yield 116 mg of product and byproduct (65%).

^1H NMR (400 MHz, , $CDCl_3$) δ 7.35 – 7.08 (m, 6H), 5.91 – 5.74 (m, 1H), 5.07 – 4.87 (m, 2H), 4.11 – 3.93 (m, 2H), 2.76 – 2.66 (m, 2H), 2.31 – 2.21 (m, 2H), 2.16 – 1.95 (m, 4H), 1.71 (s, 3H), 0.90 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.27, 142.42, 139.05, 128.51 (2C), 128.37 (2C), 125.84, 114.38, 103.79, 100.70, 65.03, 36.18, 34.27, 32.08, 28.86, 26.07 (3C), 19.43, 18.49, -5.04, -5.06.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{36}OSiNa$ 379.2428; Found 379.2422.

2.1.9 ((2-Benzyl-4-methyl-1-phenylpenta-2,3-dien-1-yl)oxy)(tert-butyl)dimethylsilane (**2i**)



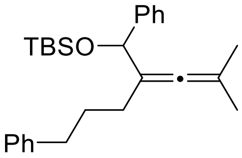
According to the general procedure catalyst (13.25 mg, 37.5 µmol, 7.50 mol%), 5-((tert-butyldimethylsilyl)oxy)-2-methyl-5-phenylpent-3-yn-2-yl acetate (173.3 mg, 0.50 mmol, 1.00 equiv.) and benzylmagnesium chloride (0.875 mL, 0.875 mmol, 1 M in diethyl ether, 1.75 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1.5 – 2%) to yield 130.1 mg of product (69%).

^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.27 – 7.17 (m, 3H), 7.15 – 7.10 (m, 1H), 7.04 (d, *J* = 6.8 Hz, 2H), 5.31 (s, 1H), 3.27 (d, *J* = 15.5 Hz, 1H), 2.95 (d, *J* = 15.5 Hz, 1H), 1.59 (s, 3H), 1.56 (s, 3H), 0.96 (s, 9H), 0.10 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.72, 143.98, 140.62, 129.27 (2C), 127.97 (2C), 127.82 (2C), 126.82, 126.16 (2C), 125.59, 106.42, 97.47, 76.22, 33.69, 26.04 (3C), 20.61, 20.07, 18.50, -4.59, -4.97.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{34}OSiNa$ 401.2271; Found 401.2259.

2.1.10 tert-Butyldimethyl((4-methyl-1-phenyl-2-(3-phenylpropyl)penta-2,3-dien-1-yl)oxy)silane (**2j**)



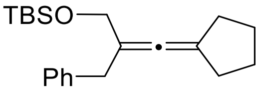
According to the general procedure catalyst (1.76 mg, 5 μmol, 1.00 mol%), 5-((tert-butyldimethylsilyl)oxy)-2-methyl-5-phenylpent-3-yn-2-yl acetate (173.3 mg, 0.50 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (0.780 mL, 0.625 mmol, 0.8 M in diethyl ether, 1.25 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/petrolether 1.5 - 2%) to yield 141.8 mg of product. (70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 5.27 (s, 1H), 2.54 – 2.44 (m, 2H), 1.98 (dt, *J* = 15.1, 7.2 Hz, 1H), 1.75 (d, 6H), 1.71 – 1.66 (m, 1H), 1.64 – 1.54 (m, 2H), 0.94 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.42, 144.54, 143.40, 128.80 (2C), 128.55 (2C), 128.16 (2C), 126.94, 126.26 (2C), 125.86, 106.03, 97.22, 77.10, 36.00, 30.01, 26.29 (3C), 26.05, 21.39, 20.84, 18.74, -4.34, -4.73.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{38}OSiNa$ 429.2584; Found 429.2570.

2.1.11 ((2-Benzyl-3-cyclopentylideneallyl)oxy)(tert-butyl)dimethylsilane (**2k**)



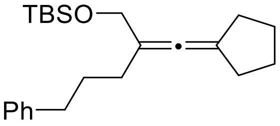
According to the general procedure catalyst (17.7 mg, 50 μmol, 5.00 mol%), 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclopentyl acetate (296.5 mg, 1.00 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.25 mL, 1.25 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2.5%) to yield 190 mg of product (58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 5H), 4.13 (s, 2H), 3.39 (s, 2H), 2.36 – 2.24 (m, 4H), 1.67 – 1.60 (m, 4H), 0.96 (s, 9H), 0.10 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.36, 140.36, 129.17 (2C), 128.11 (2C), 125.93, 105.41, 104.79, 64.19, 36.79, 31.13 (2C), 27.07 (2C), 26.07 (3C), 18.51, -5.08 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{32}OSiNa$ 351.2115; Found 351.2108.

2.1.12 tert-Butyl((2-(cyclopentylidenemethylene)-5-phenylpentyl)oxy)dimethylsilane (**2l**)



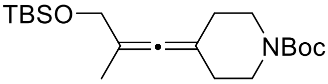
According to the general procedure catalyst (3.53 mg, 10 μmol, 1.00 mol%), 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclopentyl acetate (296.5 mg, 1.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (1.98 mL, 1.25 mmol, 0.63 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2.5%) to yield 271.1 mg of product (76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 5H), 4.18 (s, 2H), 2.71 (t, *J* = 7.44 Hz, 2H), 2.44 – 2.40 (m, 4H), 2.10 (t, *J* = 7.15 Hz, 2H), 1.85 – 1.79 (m, 2H), 1.76 – 1.72 (m, 4H), 0.97 (s, 9H), 0.13 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.00, 143.02, 128.62 (2C), 128.37 (2C), 125.71, 105.53, 104.76, 65.27, 35.76, 31.33 (2C), 29.64, 29.09, 27.20 (2C), 26.07 (3C), 18.53, -5.06 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{36}OSiNa$ 379.2428; Found 379.2424.

2.1.13 tert-Butyl 4-(3-((tert-butyldimethylsilyl)oxy)-2-methylprop-1-en-1-ylidene)piperidine-1-carboxylatecarboxylate (**2m**)



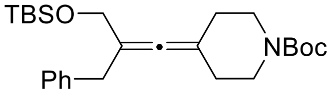
According to the general procedure catalyst (13.25 mg, 37.5 μmol, 7.50 mol%), tert-butyl 4-acetoxy-4-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)piperidine-1-carboxylate (205.8 mg, 0.50 mmol, 1.00 equiv.) and methylmagnesium bromide (0.290 mL, 0.875 mmol, 3 M in diethyl ether, 1.75 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 7.5 - 10%) to yield 120.2 mg of product (65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 2H), 3.45 – 3.42 (m, 4H), 2.14 – 2.11 (m, 4H), 1.66 (s, 3H), 1.45 (s, 9H), 0.88 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.88, 154.85, 98.90, 98.80, 79.60, 65.80, 45.04 (br, 2C), 31.07 (2C), 28.58 (3C), 26.04 (3C), 18.50, 16.26, -5.07 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{37}NO_3Na$ 390.2435; Found 390.2432.

2.1.14 tert-Butyl 4-(2-benzyl-3-((tert-butyldimethylsilyl)oxy)prop-1-en-1-ylidene)piperidine-1-carboxylate (**2n**)



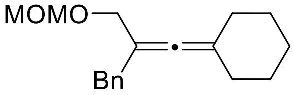
According to the general procedure catalyst (13.25 mg, 37.5 µmol, 7.50 mol%), tert-butyl 4-acetoxy-4-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)piperidine-1-carboxylate (205.8 mg, 0.50 mmol, 1.00 equiv.) and benzylmagnesium chloride (0.875 mL, 0.875 mmol, 1 M in diethyl ether, 1.75 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO$_2$ (ethyl ether/pentane 10%) to yield 173.1 mg of product (78%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.11 (m, 5H), 4.12 (s, 2H), 3.58 (s, 2H), 3.31 (s, 2H), 2.87 – 2.74 (m, 2H), 2.10 – 1.93 (m, 4H), 1.44 (s, 9H), 0.91 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (101 MHz, CDCl3) δ 196.84, 154.76, 140.01, 129.28 (2C), 128.23 (2C), 126.14, 104.66, 100.87, 79.60, 64.30, 44.62 (2C), 36.54, 30.94 (2C), 28.58 (3C), 26.05 (3C), 18.50, -5.02 (2C).

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{41}NO_3SiNa$ 466.2748; Found 466.2752.

2.1.15 (3-Cyclohexylidene-2-((methoxymethoxy)methyl)allyl)benzene (**2o**)



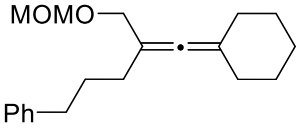
According to the general procedure catalyst (13.25 mg, 37.5 µmol, 7.5 mol%), 1-(3-(methoxymethoxy)prop-1-yn-1-yl)cyclohexyl acetate (120.2 mg, 0.50 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.0 mL, 1.0 mmol, 1 M in diethyl ether, 2.0 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO$_2$ (ethyl ether/pentane 7.5%) to yield 45 mg of product (33%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.21 (m, 5H), 4.69 (s, 2H), 4.05 (s, 2H), 3.42 (s, 3H), 3.39 (s, 2H), 2.09 – 2.06 (m, 4H), 1.61 – 1.31 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 198.18, 140.16, 129.22 (2C), 128.24 (2C), 126.04, 103.86, 98.79, 95.22, 68.42, 55.48, 37.32, 31.71 (2C), 27.49 (2C), 26.19.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{24}O_2Na$ 295.1669; Found 295.1675.

2.1.16 (5-Cyclohexylidene-4-((methoxymethoxy)methyl)pent-4-en-1-yl)benzene (**2p**)



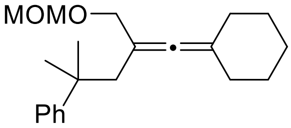
According to the general procedure catalyst (17.66 mg, 50 μmol, 5 mol%), 1-(3-(methoxymethoxy)prop-1-yn-1-yl)cyclohexyl acetate (240.3 mg, 1.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (2.18 mL, 1.75 mmol, 0.8 M in diethyl ether, 1.75 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/petrolether 5- 10%) to yield 103.5 mg of product (34%).

^1H NMR (400 MHz, , $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.23 – 7.12 (m, 3H), 4.63 (s, 2H), 4.01 (s, 2H), 3.36 (s, 3H), 2.70 – 2.61 (t, *J* = 7.3 Hz, 2H), 2.16 – 2.08 (m, 4H), 2.05 (t, *J* = 7.3 Hz, 2H), 1.81 – 1.72 (m, 2H), 1.63 – 1.49 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.94, 142.82, 128.61 (2C), 128.38 (2C), 125.75, 103.96, 98.27, 95.15, 69.41, 55.43, 35.55, 31.98, 29.54 (2C), 29.47, 27.82 (2C), 26.34.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{28}O_2Na$ 323.1982; Found 323.1982.

2.1.17 (5-Cyclohexylidene-4-((methoxymethoxy)methyl)-2-methylpent-4-en-2-yl)benzene (**2q**)



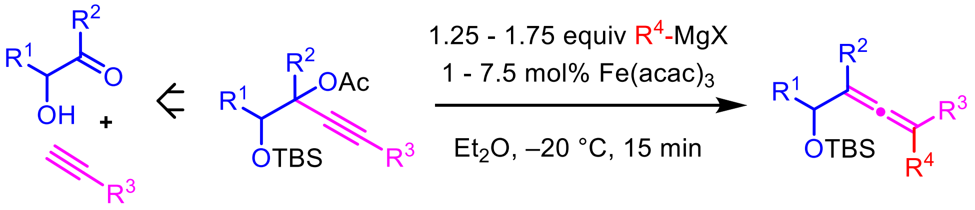
According to the general procedure catalyst (26.49 mg, 75 μmol, 7.5 mol%), 1-(3-(methoxymethoxy)prop-1-yn-1-yl)cyclohexyl acetate (240.3 mg, 1.00 mmol, 1.00 equiv.) and (2-methyl-2-phenylpropyl)magnesium chloride (3.5 mL, 1.750 mmol, 0.5 M in diethyl ether, 1.75 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 7.5%) to yield 253.7 mg of product (81%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.15 (m, 5H), 4.54 (s, 2H), 3.69 (s, 2H), 3.35 (s, 3H), 2.41 (s, 2H), 1.94 – 1.84 (m, 4H), 1.45 (br, 6H), 1.39 (s, 6H).

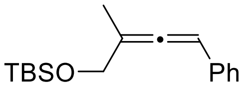
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.41, 149.27, 128.00 (2C), 125.97 (2C), 125.43, 102.11, 95.03, 94.95, 70.32, 55.40, 43.73, 38.18, 31.40 (2C), 29.54 (2C), 27.15 (2C), 26.16.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{30}O_2Na$ 337.2138; Found 337.2147.

2.2 Allenols from propargyl substrates with acetate and protected hydroxyl on the same side of the alkyne



2.2.1 tert-Butyldimethyl((2-methyl-4-phenylbuta-2,3-dien-1-yl)oxy)silane (**4a**)



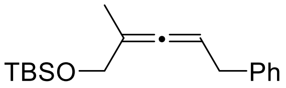
According to the general procedure catalyst (13.2 mg, 37.5 µmol, 7.50 mol%), 1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-yn-2-yl acetate (128.2 mg, 0.50 mmol, 1.00 equiv.) and phenylmagnesium bromide (0.292 mL, 0.875 mmol, 3.0 M in diethyl ether, 1.75 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2.5%) to yield 101.4 mg of product (74%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.14 (m, 5H), 6.17 – 6.10 (m, 1H), 4.23 (d, *J* = 2.3 Hz, 2H), 1.84 (d, *J* = 2.9 Hz, 3H), 0.90 (s, 9H), 0.07 (d, *J* = 8.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.35, 135.33, 128.51 (2C), 126.80 (2C), 126.67, 103.85, 94.80, 65.01, 25.92 (3C), 18.42, 15.40, -5.19, -5.26.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{26}OSiNa$ 297.1645; Found 297.1637.

2.2.2 tert-Butyldimethyl((2-methyl-5-phenylpenta-2,3-dien-1-yl)oxy)silane (**4b**)



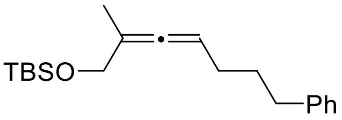
According to the general procedure catalyst (17.7 mg, 50.0 µmol, 5.00 mol%), 1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-yn-2-yl acetate (256 mg, 1.00 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.25 mL, 1.25 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2.5%) to yield 226.7 mg of product (79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 5H), 5.29 – 5.25 (m, 1H), 4.12 (s, 2H), 3.36 (d, *J* = 7.2 Hz, 2H), 1.73 (d, *J* = 2.9 Hz, 3H), 0.93 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.67, 140.82, 128.59 (2C), 128.46 (2C), 126.18, 100.12, 90.63, 65.53, 36.01, 26.08 (3C), 18.56, 15.84, -5.07 (2C).

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{28}OSiNa$ 311.1802; Found 311.1808.

2.2.3 tert-Butyldimethyl((2-methyl-7-phenylhepta-2,3-dien-1-yl)oxy)silane (**4c**)



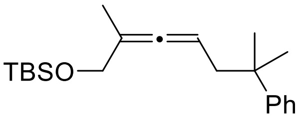
According to the general procedure catalyst (3.53 mg, 10.0 μmol, 1.00 mol%), 1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-yn-2-yl acetate (256 mg, 1.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (1.98 mL, 1.25 mmol, 0.63 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2.5%) to yield 209.5 mg of product (66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 5H), 5.20 – 5.16 (m, 1H), 4.17 (d, *J* = 2.3 Hz, 2H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.10 (q, *J* = 7.3 Hz, 2H), 1.83 – 1.76 (m, 5H), 0.97 (s, 9H), 0.14 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.26, 142.67, 128.63 (2C), 128.40 (2C), 125.79, 99.80, 90.85, 65.73, 35.44, 31.19, 28.64, 26.07 (3C), 18.55, 15.95, -5.07 (2C).

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{32}OSiNa$ 339.2115; Found 339.2113.

2.2.4 tert-Butyl((2,6-dimethyl-6-phenylhepta-2,3-dien-1-yl)oxy)dimethylsilane (**4d**)



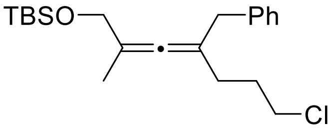
According to the general procedure catalyst (8.83 mg, 25.0 μmol, 5.00 mol%), 1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-yn-2-yl acetate (128.2 mg, 0.50 mmol, 1.00 equiv.) and (2-methyl-2-phenylpropyl)magnesium chloride (1.5 mL, 0.750 mmol, 0.5 M in diethyl ether, 1.5 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2.5%) to yield 143.7 mg of product (87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 5H), 4.83 – 4.77 (m, 1H), 3.99 – 3.91 (m, 2H), 2.29 (d, *J* = 7.7 Hz, 2H), 1.57 (d, *J* = 2.8 Hz, 3H) 1.33 (s, 6H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.53, 148.89, 127.98 (2C), 125.92 (2C), 125.49, 98.23, 87.18, 65.52, 44.17, 38.10, 28.53, 28.39, 25.93 (3C), 18.39, 15.51, -5.19, -5.22.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{34}OSiNa$ 353.2271; Found 353.2280.

2.2.5 ((4-Benzyl-7-chloro-2-methylhepta-2,3-dien-1-yl)oxy)(tert-butyl)dimethylsilane (**4e**)



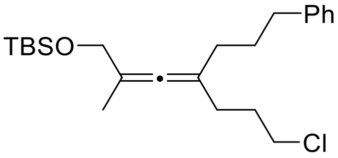
According to the general procedure catalyst (17.66 mg, 50.0 µmol, 5.00 mol%), 1-((tert-butyldimethylsilyl)oxy)-7-chloro-2-methylhept-3-yn-2-yl acetate (332.9 mg, 1.00 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.25 mL, 1.25 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1 - 2%) to yield 269.6 mg of product (74%).

1H NMR (400 MHz, CDCl3) δ 7.34 – 7.22 (m, 5H), 4.13 – 4.06 (m, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 3.39 – 3.30 (m, 2H), 2.08 – 2.05 (m, 2H), 1.93 – 1.88 (m, 2H), 1.72 (s, 3H), 0.96 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 198.81, 139.90, 129.00 (2C), 128.33 (2C), 126.24, 102.68, 101.23, 65.38, 44.72, 40.51, 30.84, 29.05, 26.05 (3C), 18.51, 16.00, -5.12 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{33}ClOSiNa$ 387.1881; Found 387.1883.

2.2.6 tert-Butyl((7-chloro-2-methyl-4-(3-phenylpropyl)hepta-2,3-dien-1-yl)oxy)dimethylsilane (**4f**)



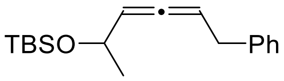
According to the general procedure catalyst (3.53 mg, 10.0 µmol, 1.00 mol%), 1-((tert-butyldimethylsilyl)oxy)-7-chloro-2-methylhept-3-yn-2-yl acetate (332.9 mg, 1.00 mmol, 1.00 equiv.) and (3-phenylpropyl)magnesium bromide (1.98 mL, 1.25 mmol, 0.63 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 1 - 2%) to yield 217.2 mg of product (55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 5H), 4.09 (s, 2H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.67 – 2.61 (m, 2H), 2.13 – 2.04 (m, 2H), 2.04 – 1.94 (m, 2H), 1.93 – 1.86 (m, 2H), 1.79 – 1.68 (m, 5H), 0.91 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.52, 142.61, 128.47 (2C), 128.27 (2C), 125.65, 102.77, 101.48, 65.42, 44.71, 35.51, 32.53, 30.73, 29.92, 29.58, 25.90 (3C), 18.35, 16.02, -5.26 (2C).

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{37}ClOSiNa$ 415.2194; Found 415.2184.

2.2.7 tert-Butyldimethyl((6-phenylhexa-3,4-dien-2-yl)oxy)silane (**4g**)



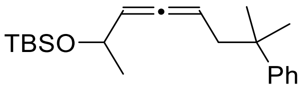
According to the general procedure catalyst (17.66 mg, 50.0 µmol, 5.00 mol%), (4S)-4-((tert-butyldimethylsilyl)oxy)pent-1-yn-3-yl acetate (256 mg, 1.00 mmol, 1.00 equiv.) and benzylmagnesium chloride (1.25 mL, 1.25 mmol, 1 M in diethyl ether, 1.25 equiv.) in diethyl ether (10 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2.5%) to yield 97.9 mg of product (31%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 5H), 5.36 – 5.30 (m, 1H), 5.24 – 5.20 (m, 1H), 4.38 – 4.36 (m, 1H), 3.39 – 3.35 (m, 2H), 1.26 (d, *J* = 6.2 Hz, 3H), 0.91 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.73, 140.43, 128.60 (2C), 128.52 (2C), 126.32, 97.62, 92.25, 67.63, 35.67, 26.06 (3C), 24.64, 18.44, -4.33, -4.63.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{28}OSiNa$ 311.1802; Found 311.1790.

2.2.8 tert-Butyldimethyl((7-methyl-7-phenylocta-3,4-dien-2-yl)oxy)silane (**4h**)



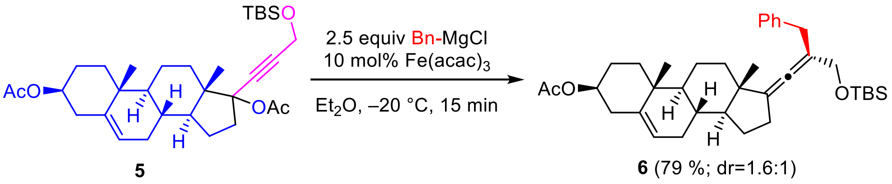
According to the general procedure catalyst (8.83 mg, 25.0 µmol, 5.00 mol%), (4S)-4-((tert-butyldimethylsilyl)oxy)pent-1-yn-3-yl acetate (128.2 mg, 0.50 mmol, 1.00 equiv.) and (2-methyl-2-phenylpropyl)magnesium chloride (2.0 mL, 1.00 mmol, 0.5 M in diethyl ether, 2.0 equiv.) in diethyl ether (5 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (ethyl ether/pentane 2 - 2.5%) to yield 96.1 mg of product (58%) and 52.6 mg of educt (59% conversion).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.16 (m, 5H), 5.09 – 5.00 (m, 1H), 4.93 – 4.85 (m, 1H), 4.32 – 4.14 (m, 1H), 2.38 – 2.31 (m, 2H), 1.35 (s, 6H), 1.22 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.65, 203.34, 149.41, 148.88, 128.22, 128.19, 128.14, 128.07, 126.11, 126.05, 126.01, 125.77, 125.73, 125.42, 96.22, 96.03, 89.30, 88.91, 68.11, 67.75, 44.31, 44.13, 38.99, 38.37, 38.20, 37.56, 29.21, 29.02, 28.60, 28.19, 26.07, 26.05, 24.83, 24.65, 18.43, 18.40, -4.29, -4.32, -4.60, -4.67.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{34}OSiNa$ 353.2271; Found 353.2280.

2.3 Functionalization of steroidal compound



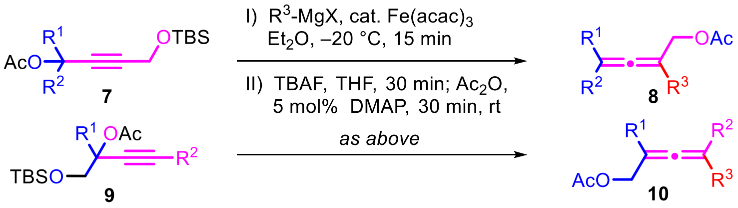
According to the general procedure catalyst (7.06 mg, 20.0 µmol, 10.0 mol%), steroidal substrate (108.57 mg, 200 µmol, 1.00 equiv.) and benzylmagnesium chloride (500 µL, 500 µmol, 1 M in diethyl ether, 2.5 equiv.) in diethyl ether (2 mL) were reacted. The reaction mixture was extracted and purified over SiO_2 (25 g; ethyl ether/pentane 5 - 10%) to yield 91 mg of product (79%).

^{1}H NMR (400 MHz, , $CDCl_3$) δ 7.34 – 7.09 (m, 5H), 5.37 (d, *J* = 4.9 Hz, 1H), 4.68 – 4.52 (m, 1H), 4.08 (s, 2H), 3.44 – 3.26 (m, 2H), 2.54 – 2.17 (m, 4H), 2.07 – 1.95 (m, 4H), 1.90 – 1.82 (m, 2H), 1.75 – 1.35 (m, 7H), 1.27 – 0.80 (m, 18H), 0.59 (s, 2H), 0.05 (d, *J* = 2.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.54, 193.51, 170.64, 140.47, 140.25, 139.92, 129.43, 129.34, 128.08, 128.04, 125.93, 125.88, 122.54, 114.83, 114.73, 107.39, 107.08, 74.03, 64.63, 64.50, 55.59, 55.13, 50.38, 50.29, 44.55, 38.26, 37.16, 37.09, 36.86, 36.84, 36.76, 36.40, 35.88, 31.92, 31.87, 27.91, 27.36, 27.23, 26.11, 24.97, 24.87, 21.58, 21.13, 21.10, 19.47, 18.52, 18.50, 18.15, -4.96, -5.00, -5.04.

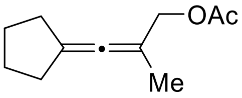
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{54}O_3SiNa$ 597.3734; Found 597.3735.

2.4 Gram-scale synthesis of allenyl acetaes from propargyl susbstrates



General procedure: In a dry 20 mL microwave flask under argon was added catalyst $Fe(acac)_3$ (1 – 10 mol%) and diethyl ether (10 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 dropwise addition of Grignard reagent (1.25 – 2.50 equiv.) for 5 min. The reaction mixture was stirred for another 10 min, quenched with aq. 5% citric acid solution. The reaction mixture was separated, filtered over a pad of Celite (5 cm) covered with Na_2SO_4 and evaporated to obtain crude product. To the crude product was added THF together with TBAF (1 M in THF, 1.05 equiv.). After 30 min Ac_2O (2.00 equiv.) and DMAP (5mol%) were added and stirred for another 30 min. The reaction was quenched with sat. $NaHCO_3$ and extracted with etherextracted with pentane or diethyl ether and the combined organic phase was dried over Na_2SO_4 and carefully evaporated. The crude product was purified by column chromatography over SiO_2 (diethyl ether/pentane) to obtain the product.

2.4.1 3-Cyclopentylidene-2-methylallyl acetate (**10a**)



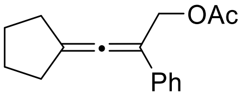
According to the general procedure 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclopentyl acetate (2.25 g, 7.59 mmol, 1.00 equiv.), $Fe(acac)_3$ (134 mg, 379 µmol, 5 mol%) and MeMgBr (3.79 ml, 11.4 mmol, 3 M in diethyl ether, 1.5 equiv.) in Et_2O (75 ml) were reacted, quenched with 5% citric acid (10 ml), separated and filtered. The crude product was dissolved in THF (40 ml) reacted with TBAF (7.97 ml, 7.97 mmol, 1 M in THF, 1.05 equiv.) and subsequently with Ac_2O (1.43 ml, 15.2 mmol, 2.00 equiv.) and DMAP (46.4 mg, 379 µmol, 5mol%). The reaction was quenched with sat. $NaHCO_3$ (10 ml) and extracted with ether (2 x 50 ml). The crude product was purified over SiO_2 (75 g, ether/pentane 2.5%) to obtain 836mg of product (61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (s, 2H), 2.39 – 2.23 (m, 4H), 2.05 (s, 3H), 1.68 (s, 3H), 1.67 – 1.61 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.74, 170.95, 104.78, 95.51, 66.87, 31.19, 27.13, 21.13, 16.56.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}O_2Na$ 203.1043; Found 203.1047.

2.4.2 3-Cyclopentylidene-2-phenylallyl acetate (**10b**)



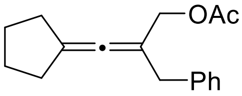
According to the general procedure 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclopentyl acetate (1.50 g, 5.06 mmol, 1.00 equiv.), Fe(acac)$_3$ (134 mg, 379 µmol, 7.5 mol%) and PhMgBr (2.95 ml, 8.85 mmol, 3 M in diethyl ether, 1.75 equiv.) in Et$_2$O (50 ml) were reacted, quenched with 5% citric acid (10 ml), separated and filtered. The crude product was dissolved in THF (40 ml) reacted with TBAF (5.31 ml, 5.31 mmol, 1 M in THF, 1.05 equiv.) and subsequently with Ac$_2$O (957 µl, 10.1 mmol, 2.00 equiv.) and DMAP (30.9 mg, 253 µmol, 5mol%) The reaction was quenched with sat. NaHCO$_3$ (10 ml) and extracted with ether (2 x 25 ml). The crude product was purified over SiO$_2$ (75 g, ether/pentane 5%) to obtain 905 mg of product (74%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.31 (m, 4H), 7.25 – 7.20 (m, 1H), 5.02 (s, 2H), 2.61 – 2.45 (m, 4H), 2.09 (s, 3H), 1.83 – 1.74 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 199.07, 171.06, 135.84, 128.58, 126.75, 126.09, 108.21, 101.87, 64.18, 31.23, 27.35, 21.27.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{18}O_2Na$ 265.1199; Found 265.1207

2.4.3 2-Benzyl-3-cyclopentylideneallyl acetate (**10c**)



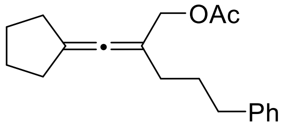
According to the general procedure 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclopentyl acetate (2.00 g, 6.75 mmol, 1.00 equiv.), Fe(acac)$_3$ (119 mg, 337 µmol, 5 mol%) and BnMgCl (10.1 ml, 10.1 mmol, 1 M in diethyl ether, 1.50 equiv.) in Et$_2$O (65 ml) were reacted, quenched with 5% citric acid (10 ml), separated and filtered. The crude product was dissolved in THF (40 ml) reacted with TBAF (7.09 ml, 7.09 mmol, 1 M in THF, 1.05 equiv.) and subsequently with Ac$_2$O (1.28 ml, 13.5 mmol, 2.00 equiv.) and DMAP (41.2 mg, 338 µmol, 5mol%). The reaction was quenched with sat. NaHCO$_3$ (10 ml) and extracted with ether (2 x 50 ml). The crude product was purified over SiO$_2$ (75 g, ether/pentane 2.5%) to obtain 1.391 g of product (80%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22 – 7.03 (m, 5H), 4.39 (s, 2H), 3.23 (s, 2H), 2.30 – 2.08 (m, 4H), 1.92 (s, 3H), 1.58 – 1.42 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.81, 170.80, 139.50, 128.89, 128.57, 128.26, 128.15, 126.08, 106.03, 99.91, 65.16, 37.36, 31.04, 26.95, 21.00.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{17}H_{20}O_2Na$ 279.1356; Found 279.1362

2.4.4 2-(Cyclopentylidenemethylene)-5-phenylpentyl acetate (**10d**)



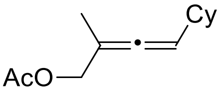
According to the general procedure 1-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)cyclopentyl acetate (2.00 g, 6.75 mmol, 1.00 equiv.), Fe(acac)$_3$ (23.8 mg, 67.5 µmol, 1 mol%) and Bn(CH$_2$)$_2$MgBr (8.88 ml, 8.43 mmol, 0.95 M in diethyl ether, 1.25 equiv.) in Et$_2$O (65 ml) were reacted, quenched with 5% citric acid (10 ml), separated and filtered. The crude product was dissolved in THF (40 ml) reacted with TBAF (7.09 ml, 7.09 mmol, 1 M in THF, 1.05 equiv.) and subsequently with Ac$_2$O (1.28 ml, 13.5 mmol, 2.00 equiv.) and DMAP (41.2 mg, 338 µmol, 5mol%). The reaction was quenched with sat. NaHCO$_3$ (10 ml) and extracted with ether (2 x 50 ml). The crude product was purified over SiO$_2$ (75 g, ether/pentane 2.5%) to obtain 1.118 g of product (58%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.14 (m, 5H), 4.52 (s, 2H), 2.69 – 2.58 (m, 2H), 2.40 – 2.31 (m, 4H), 2.04 (d, *J* = 12.7 Hz, 5H), 1.79 – 1.70 (m, 2H), 1.72 – 1.63 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 195.51, 171.00, 142.70, 128.60, 128.41, 125.81, 106.48, 100.17, 100.13, 66.18, 35.53, 31.32, 29.55, 29.46, 27.20, 21.20.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{24}O_2Na$ 307.1669; Found 307.1670.

2.4.5 4-Cyclohexyl-2-methylbuta-2,3-dien-1-yl acetate (**8a**)



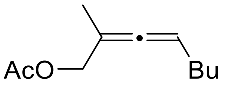
According to the general procedure 1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-yn-2-yl acetate (1.25 g, 4.87 mmol, 1.00 equiv.), Fe(acac)$_3$ (17.22 mg, 48.8 µmol, 1 mol%) and CyMgCl (3.05 ml, 6.09 mmol, 2 M in diethyl ether, 1.25 equiv.) in Et$_2$O (50 ml) were reacted, quenching with 5% citric acid (6 ml), separated and filtered. The crude product was dissolved in THF (20 ml) reacted with TBAF (5.1 ml, 5.11 mmol, 1 M in THF, 1.05 equiv.) and subsequently with Ac$_2$O (920 µl, 9.74 mmol, 2.00 equiv.) and DMAP (30 mg, 24.4 µmol, 5mol%). The reaction was quenched with sat. NaHCO$_3$ (5 ml) and extracted with ether (2 x 25 ml). The crude product was purified over SiO$_2$ (75 g, ether/pentane 2.5%) to obtain 561 mg of product (55%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 5.21 – 5.11 (m, 1H), 4.52 (d, *J* = 2.1 Hz, 2H), 2.09 (s, 3H), 2.02 – 1.95 (m, 1H), 1.79 – 1.63 (m, 8H), 1.33 – 1.03 (m, 5H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 201.29, 170.97, 98.19, 96.26, 66.38, 37.42, 33.20, 33.12, 26.29, 26.11 (2C), 21.13, 16.50.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{13}H_{20}O_2Na$ 231.1356; Found 231.1354.

2.4.6 2-Methylocta-2,3-dien-1-yl acetate (**8b**)



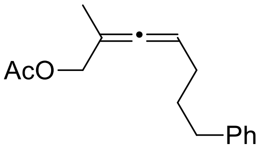
According to the general procedure 1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-yn-2-yl acetate (1.50 g, 4.87 mmol, 1.00 equiv.), Fe(acac)$_3$ (17.22 mg, 48.8 µmol, 1 mol%) and BuMgCl (3.66 ml, 7.31 mmol, 2.0 M in diethyl ether, 1.25 equiv.) in Et$_2$O (50 ml) were reacted, quenching with 5% citric acid (8 ml), separated and filtered. The crude product was dissolved in THF (25 ml) reacted with TBAF (5.11 ml, 5.11 mmol, 1.0 M in THF, 1.05 equiv.) and subsequently with Ac$_2$O (920 µl, 9.74 mmol, 2.00 equiv.) and DMAP (29.7 mg, 244 µmol, 5 mol%). The reaction was quenched with sat. NaHCO$_3$ (7.5 ml) and extracted with ether (2 x 35 ml). The crude product was purified over SiO$_2$ (75 g, ether/pentane 2.5 %) to obtain 328 mg of product (31%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 5.19 – 5.08 (m, 1H), 4.49 (d, *J* = 2.2 Hz, 2H), 2.06 (s, 3H), 2.01 – 1.93 (m, 2H), 1.70 (d, *J* = 2.9 Hz, 3H), 1.39 – 1.29 (m, 4H), 0.92 – 0.86 (m, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 202.47, 170.96, 95.28, 92.04, 66.41, 31.35, 28.56, 22.20, 21.08, 16.40, 14.01.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{11}H_{18}O_2Na$ 205.1199; Found 205.1202.

2.4.7 2-Methyl-7-phenylhepta-2,3-dien-1-yl acetate (**8c**)



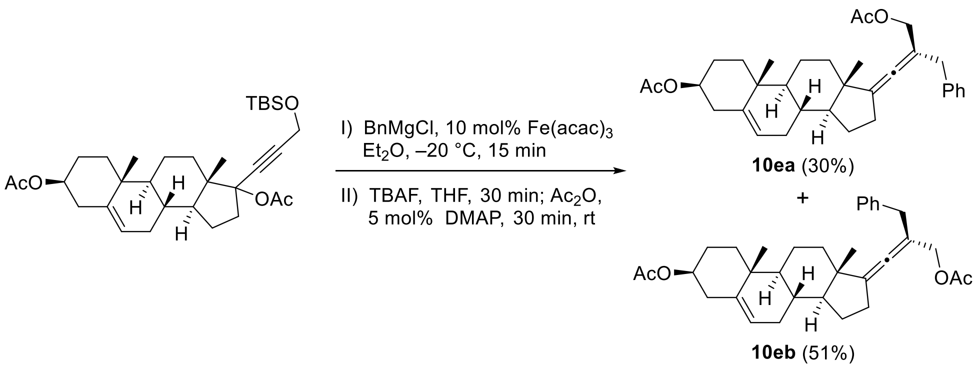
According to the general procedure 1-((tert-butyldimethylsilyl)oxy)-2-methylbut-3-yn-2-yl acetate (850 mg, 3.31 mmol, 1.00 equiv.), Fe(acac)$_3$ (11.7 mg, 33.2 µmol, 1 mol%) and Bn(CH$_2$)$_2$MgBr (4.36 ml, 4.14 mmol, 0.95 M in diethyl ether, 1.25 equiv.) in Et$_2$O (35 ml) were reacted, quenching with 5% citric acid (5 ml), separated and filtered. The crude product was dissolved in THF (20 ml) reacted with TBAF (3.48 ml, 3.48 mmol, 1 M in THF, 1.05 equiv.) and subsequently with Ac$_2$O (626 µl, 6.62 mmol, 2.00 equiv.) and DMAP (20.2 mg, 166 µmol, 5mol%). The reaction was quenched with sat. NaHCO$_3$ (5 ml) and extracted with ether (2 x 20 ml). The crude product was purified over SiO$_2$ (50 g, ether/pentane 5%) to obtain 442 mg of product (55%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.14 (m, 5H), 5.28 – 5.11 (m, 1H), 4.52 (d, *J* = 2.2 Hz, 2H), 2.69 – 2.61 (t, *J*=7.8 Hz, 2H), 2.08 – 2.00 (m, 5H), 1.77 – 1.68 (m, 5H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 202.47, 170.83, 142.36, 128.46, 128.29, 125.71, 95.56, 91.57, 66.21, 35.22, 30.72, 28.17, 20.96, 16.32.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{20}O_2Na$ 267.1356; Found 267.1363.

2.4.8 (R)-3-((3S,8R,9S,10R,13S,14S)-3-Acetoxy-10,13-dimethyl-1,2,3,4,7,8,9,10,11,12,13,14,15,16-tetradecahydro-17H-cyclopenta[a]phenanthren-17-ylidene)-2-benzylallyl acetate (**10e**)



According to the general procedure steroidal substrate (650 mg, 1.20 mmol, 1.00 equiv.), Fe(acac)$_3$ (42.3 mg, 120 µmol, 10 mol%) and BnMgCl (2.99 ml, 2.99 mmol, 1 M in diethyl ether, 2.50 equiv.) in Et$_2$O (12 ml) were reacted, quenching with 5% citric acid (2 ml), separated and filtered. . The crude product was dissolved in THF (10 ml) reacted with TBAF (1.26 ml, 1.26 mmol, 1 M in THF, 1.05 equiv.) and subsequently with Ac$_2$O (227 µl, 2.4 mmol, 2.00 equiv.) and DMAP (7.33 mg, 60.0 µmol, 5mol%). The reaction was quenched with sat. NaHCO$_3$ (2 ml) and extracted with ether (2 x 10 ml). The crude product was purified over SiO$_2$ (75 g, ether/pentane 2.5%) to obtain separated diastereomers 10ea 178 mg (30%) and 10eb 307 mg (51%) to give a combined yield of 81%.

10ea: ^{1}H NMR (500 MHz, , CDCl$_3$) δ 7.29 – 7.15 (m, 5H), 5.37 (d, *J* = 5.1 Hz, 1H), 4.65 – 4.57 (m, 1H), 4.55 – 4.41 (m, 2H), 3.33 (q, *J* = 15.0 Hz, 2H), 2.51 (ddd, *J* = 16.6, 9.9, 1.7 Hz, 1H), 2.37 – 2.21 (m, 3H), 2.11 – 1.90 (m, 7H), 1.90 – 1.82 (m, 2H), 1.72 – 1.51 (m, 5H), 1.50 – 1.38 (m, 2H), 1.30 – 0.99 (m, 7H), 0.96 – 0.86 (m, 2H), 0.84 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.02, 170.91, 170.69, 139.96, 139.50, 129.24, 128.28, 126.27, 122.48, 115.75, 102.44, 74.03, 65.26, 55.23, 50.29, 44.86, 38.27, 37.85, 37.17, 36.86, 35.89, 31.93, 31.89, 27.92, 27.36, 24.93, 21.59, 21.19, 21.10, 19.48, 18.48.

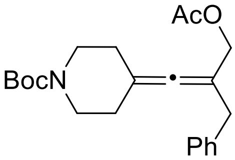
HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{33}H_{42}O_4Na$ 525.2975; Found 525.2972.

10eb: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 – 7.11 (m, 5H), 5.37 (d, *J* = 4.7 Hz, 1H), 4.65 – 4.54 (m, 1H), 4.51 (q, 2H), 3.32 (q, 2H), 2.45 (dd, *J* = 16.8, 8.6 Hz, 1H), 2.38 – 2.25 (m, 3H), 2.09 – 1.95 (m, 7H), 1.91 – 1.81 (m, 2H), 1.76 – 1.69 (m, 1H), 1.67 – 1.56 (m, 4H), 1.52 – 1.37 (m, 2H), 1.32 – 0.87 (m, 9H), 0.63 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.08, 170.77, 170.52, 139.79, 139.54, 129.04, 128.14, 126.08, 122.33, 115.53, 102.59, 73.87, 65.42, 55.55, 50.17, 44.63, 38.10, 37.38, 36.98, 36.72, 36.04, 31.79, 31.77, 27.75, 27.13, 24.81, 21.44, 21.08, 20.96, 19.33, 18.01.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{33}H_{42}O_4Na$ 525.2975; Found 525.2978.

2.4.9 tert-Butyl 4-(3-acetoxy-2-benzylprop-1-en-1-ylidene)piperidine-1-carboxylate (**10f**)



According to the general procedure tert-butyl 4-acetoxy-4-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)piperidine-1-carboxylate (1.23g, 3.00 mmol, 1.00 equiv.), Fe(acac)$_3$ (74.2 mg, 210 µmol, 7.5 mol%) and BnMgCl (5.25 ml, 5.25 mmol, 1.0 M in diethyl ether, 1.75 equiv.) in Et$_2$O (30 ml) were reacted, quenching with H$_2$O (5 ml), separated, dried over Na$_2$SO$_4$ and purified over SiO$_2$ (50 g, ether/pentane 5 - 10%) to obtain 1.098g of intermediate (82 %). The intermediate (1.00 g, 2.25 mmol, was dissolved in THF (10 ml) reacted with TBAF (2.81 ml, 2.81 mmol, 1 M in THF, 1.25 equiv.) subsequently with Ac$_2$O (532 µl, 5.63 mmol, 2.50 equiv.) and DMAP (13.7 mg, 113 µmol, 5 mol%). The reaction was quenched with sat. NaHCO$_3$ (5 ml) and extracted with ether (3 x 10 ml). The crude product was purified over SiO$_2$ (50 g, ether/pentane 25%) to obtain 831 mg of product (99%; 81% over 2 steps).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34 – 7.12 (m, 5H), 4.53 (s, 2H), 3.52 (s, 2H), 3.32 (s, 2H), 2.95 (ddd, J = 12.7, 8.4, 4.0 Hz, 2H), 2.18 – 1.92 (m, 7H), 1.45 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 198.29, 170.82, 154.70, 139.28, 129.14 (2C), 128.38 (2C), 126.42, 101.67, 99.88, 79.69, 65.08, 44.93 (2C), 37.16, 30.73 (br, 2C), 28.56 (3C), 21.12.

HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{22}H_{29}NO_4Na$ 394.1989; Found 394.1995.

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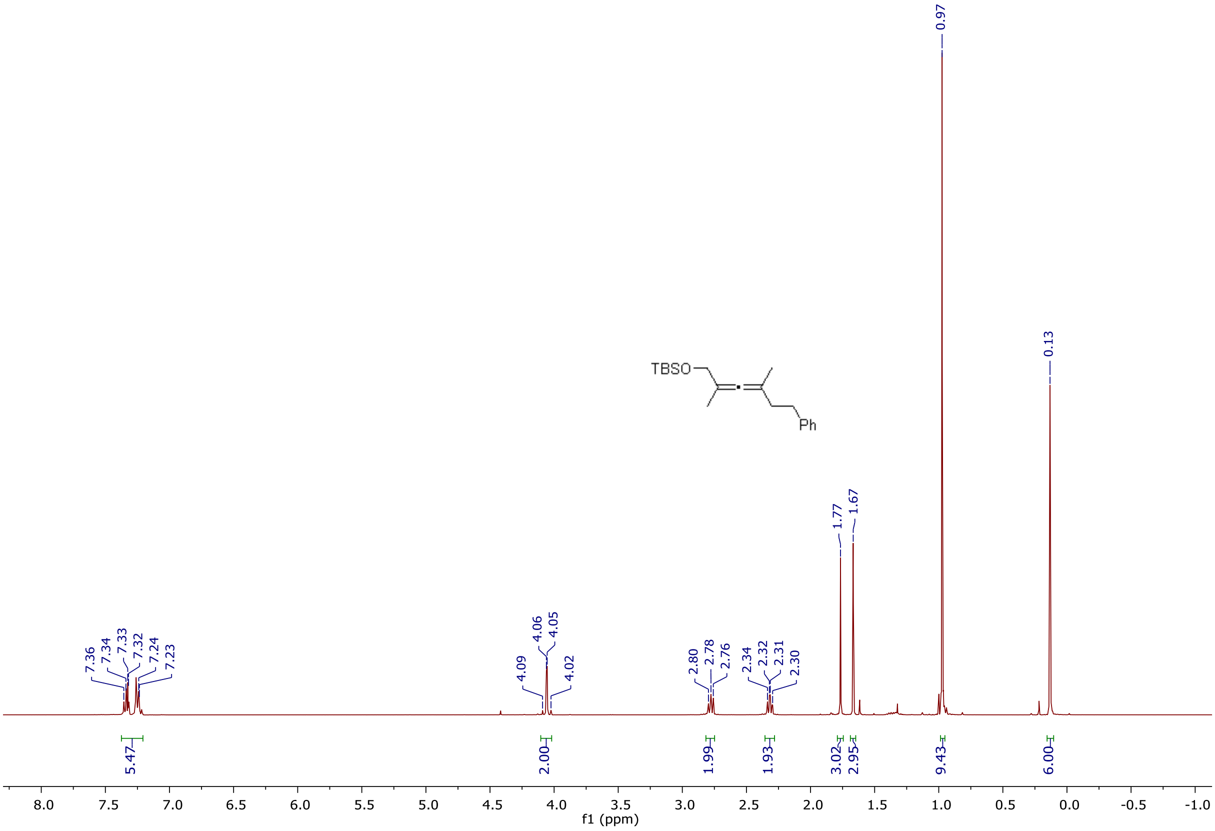
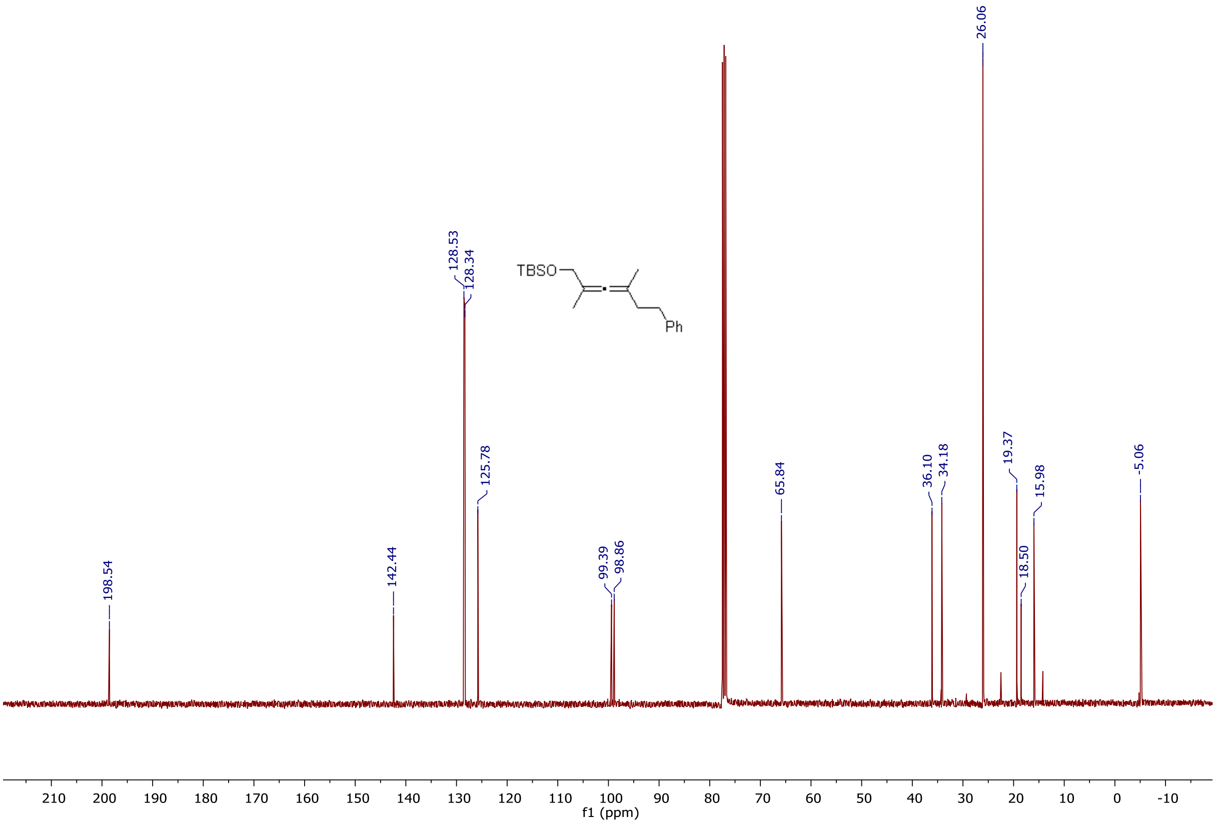
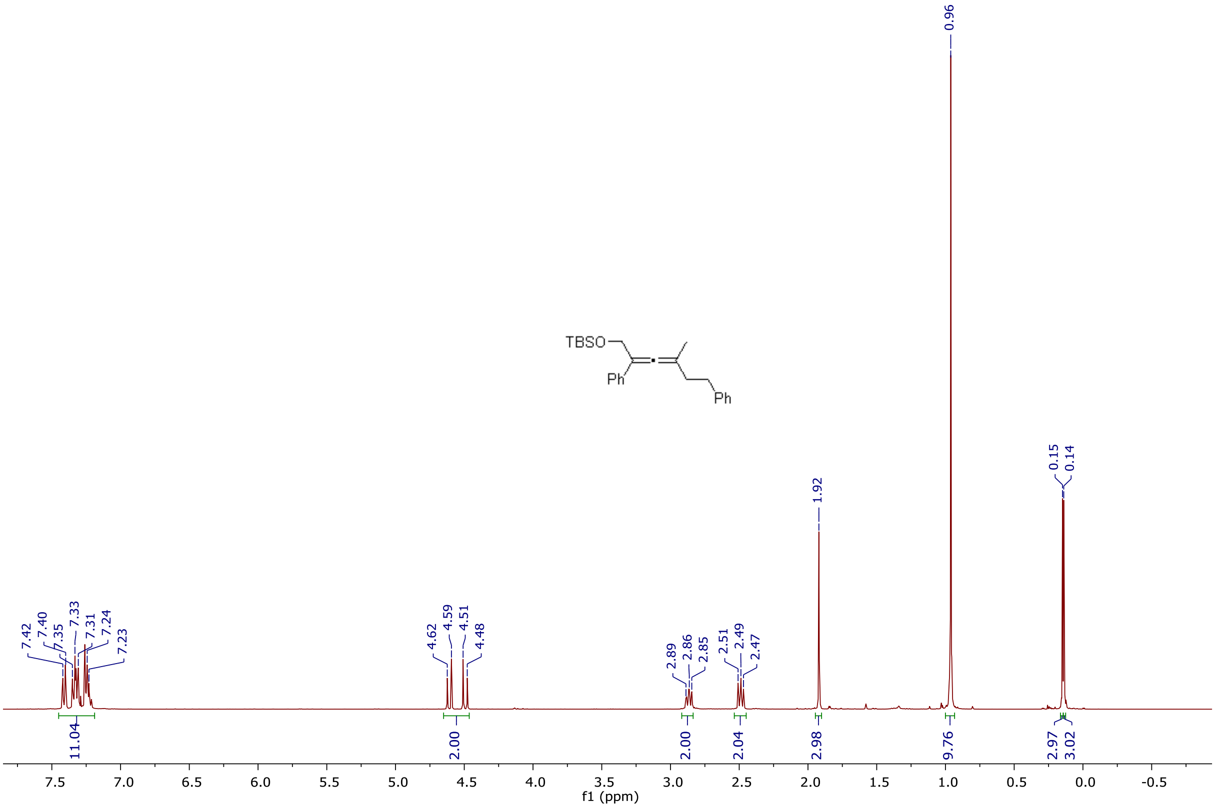
4 ^{1}H and ^{13}C NMR Spectra






TBSO
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2.89
2.86
2.85
2.51
2.49
2.47
1.92
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0.14
11.04
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2.00
2.04
2.98
9.76
2.97
3.02
7.5
7.0
6.5
6.0
5.5
5.0
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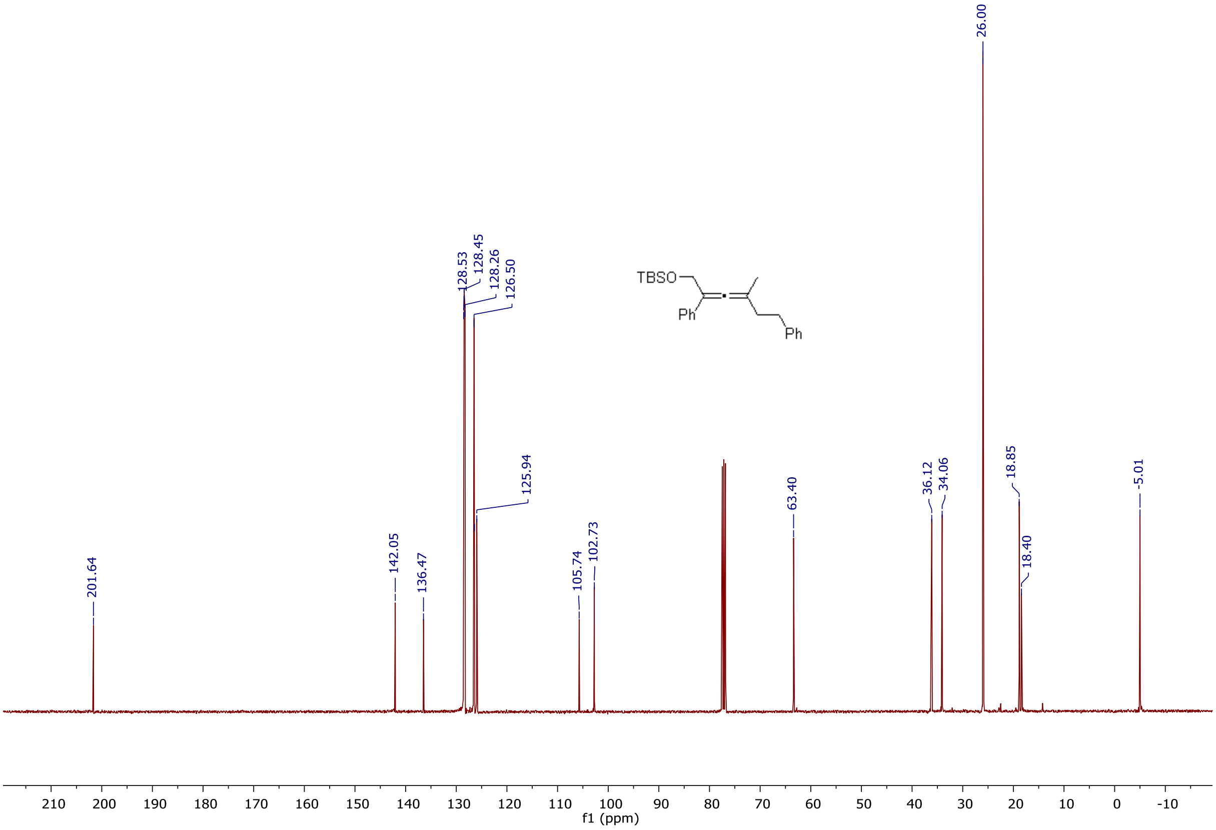
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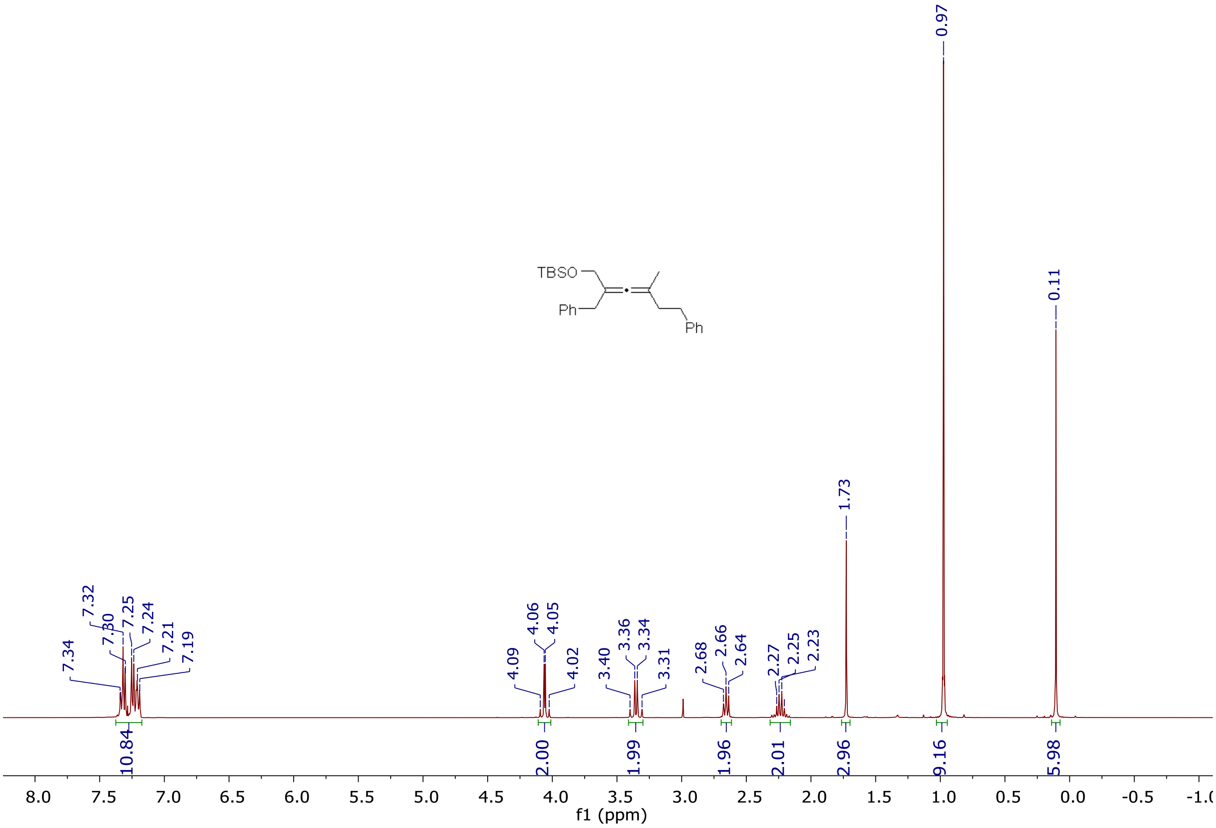
f1 (ppm)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4.02
3.40
3.36
3.34
3.31
2.68
2.66
2.64
2.27
2.25
2.23
1.73
0.97
0.11
10.84
2.00
1.99
1.96
2.01
2.96
9.16
5.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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0.5
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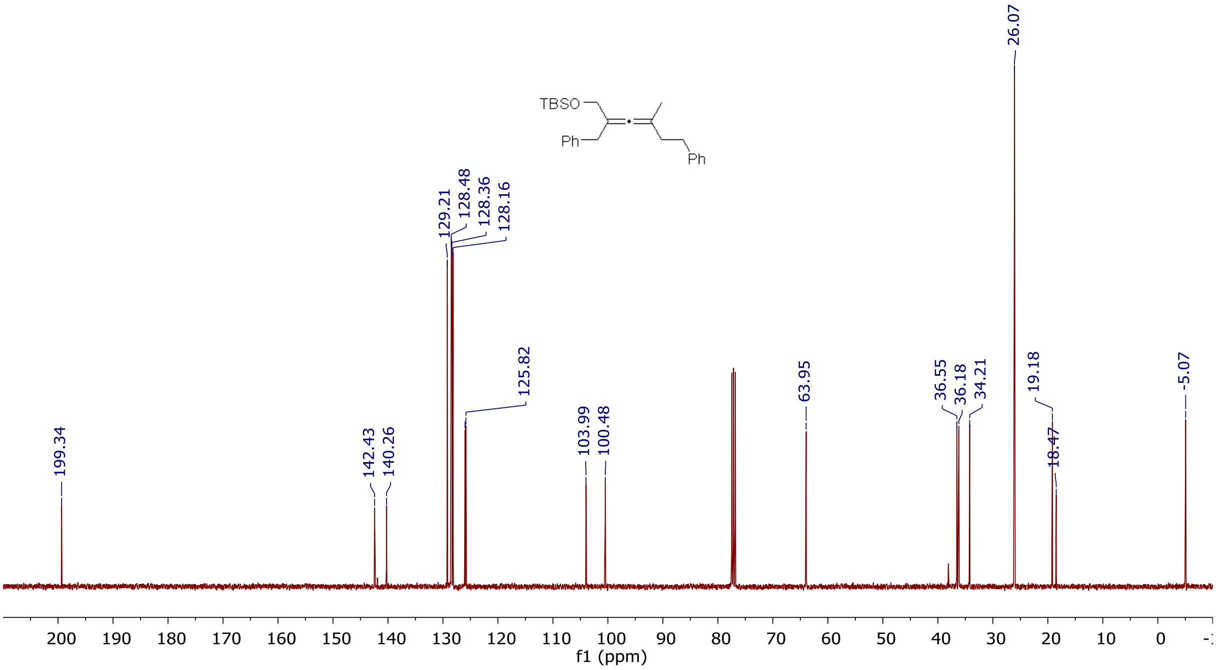
-0.5
f1 (ppm)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Ph
Ph
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129.21
128.48
128.36
128.16
125.82
103.99
100.48
63.95
36.55
36.18
34.21
26.07
19.18
18.47
-5.07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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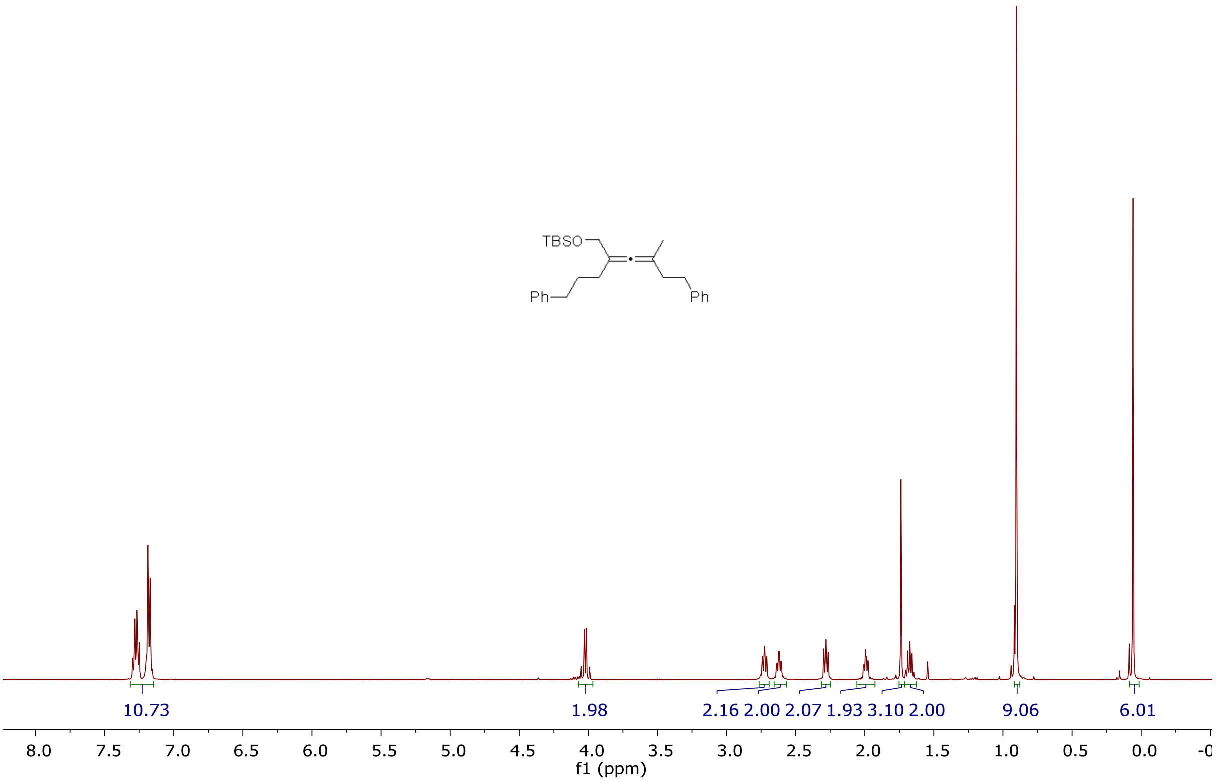
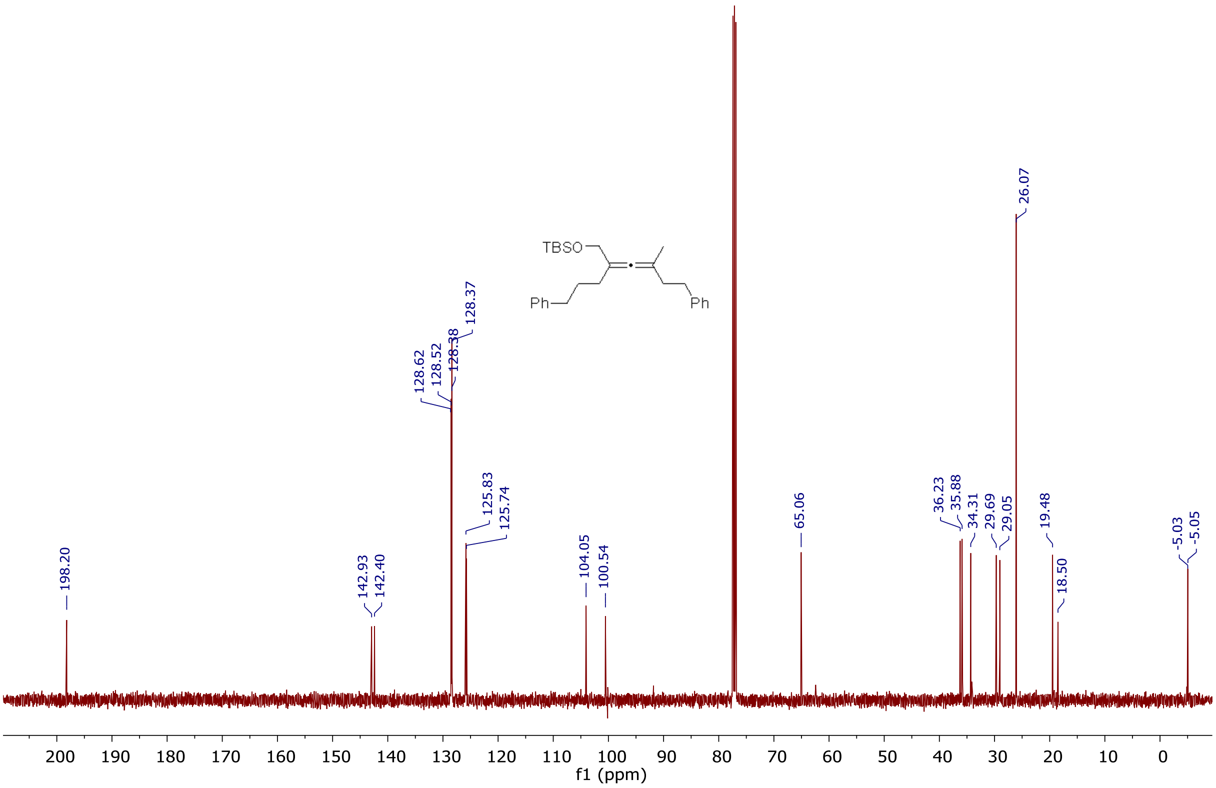
10
0
f1 (ppm)


TBSO
Ph
Ph
10.73
1.98
2.16 2.00 2.07 1.93 3.10 2.00
9.06
6.01
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
f1 (ppm)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Ph
Ph
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142.40
128.62
128.52
128.38
128.37
125.83
125.74
104.05
100.54
65.06
36.23
35.88
34.31
29.69
29.05
26.07
19.48
18.50
-5.03
-5.05
200
190
180
170
160
150
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120
110
100
90
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70
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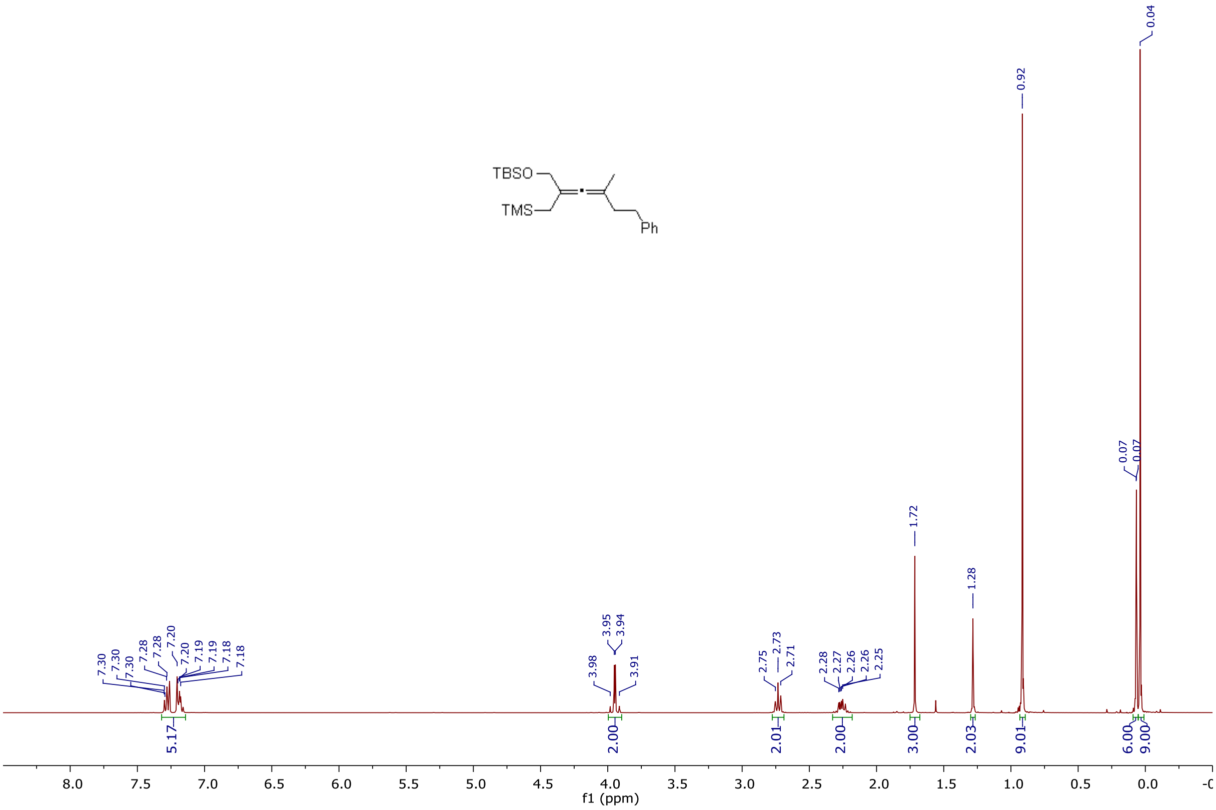
50
40
30
20
10
0
f1 (ppm)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TMS
Ph
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7.30
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7.28
7.20
7.20
7.19
7.19
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7.18
3.98
3.95
3.94
3.91
2.75
2.73
2.71
2.28
2.27
2.26
2.26
2.25
1.72
1.28
0.92
0.07
0.07
0.04
5.17
2.00
2.01
2.00
3.00
2.03
9.01
6.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
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1.0
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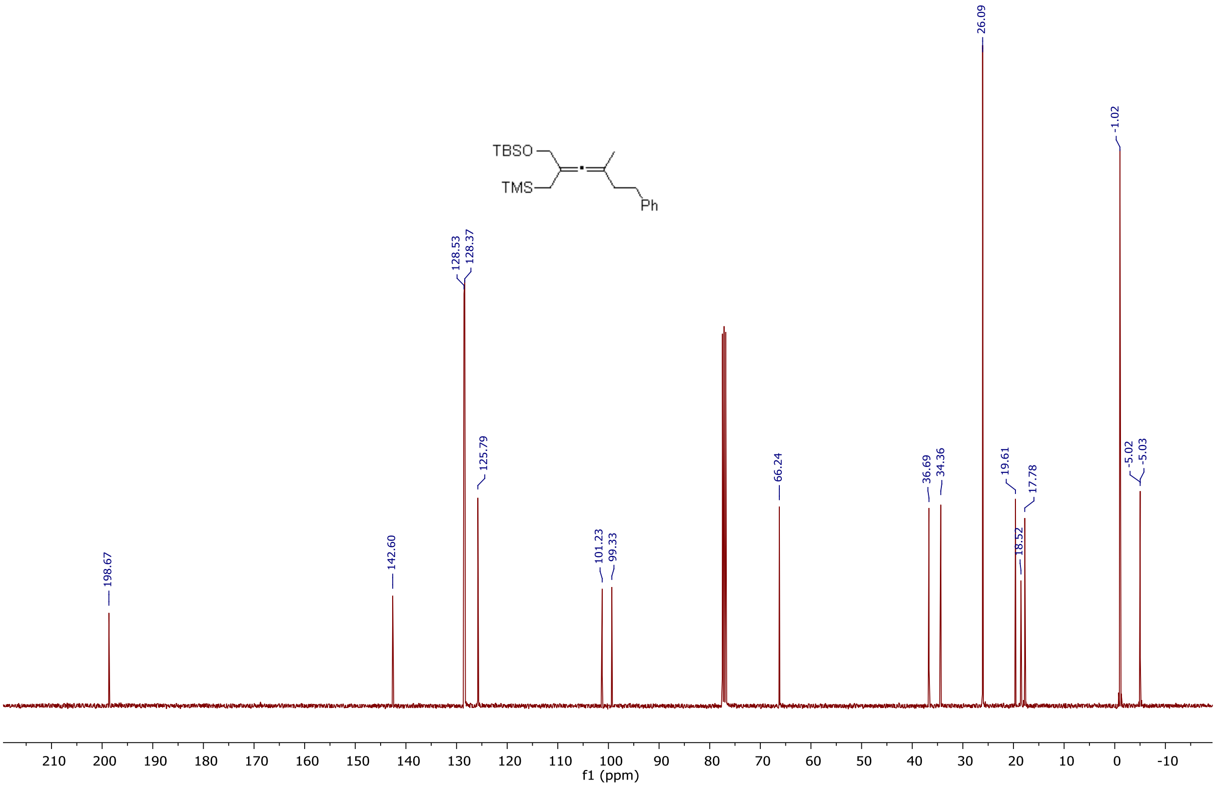
0.0
f1 (ppm)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TMS
Ph
198.67
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128.37
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101.23
99.33
66.24
36.69
34.36
26.09
19.61
18.52
17.78
-1.02
-5.02
-5.03
210
200
190
180
170
160
150
140
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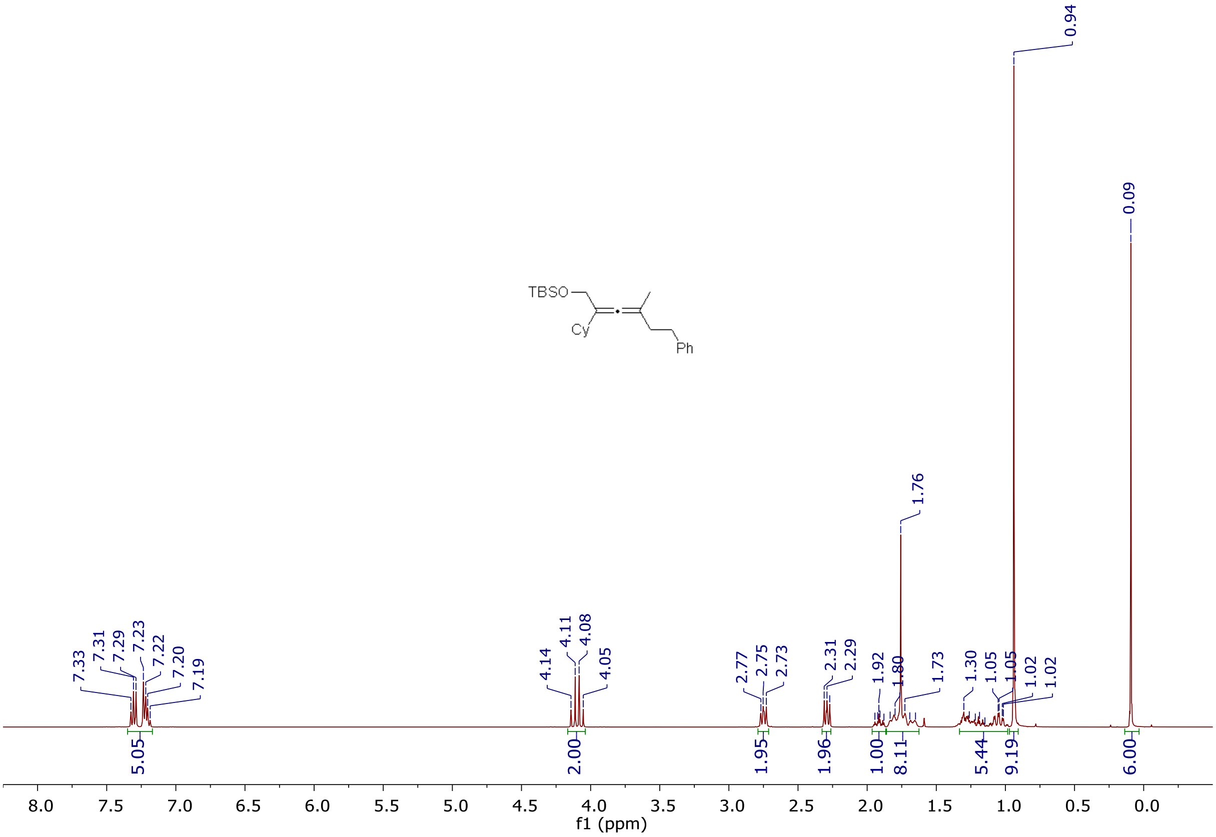
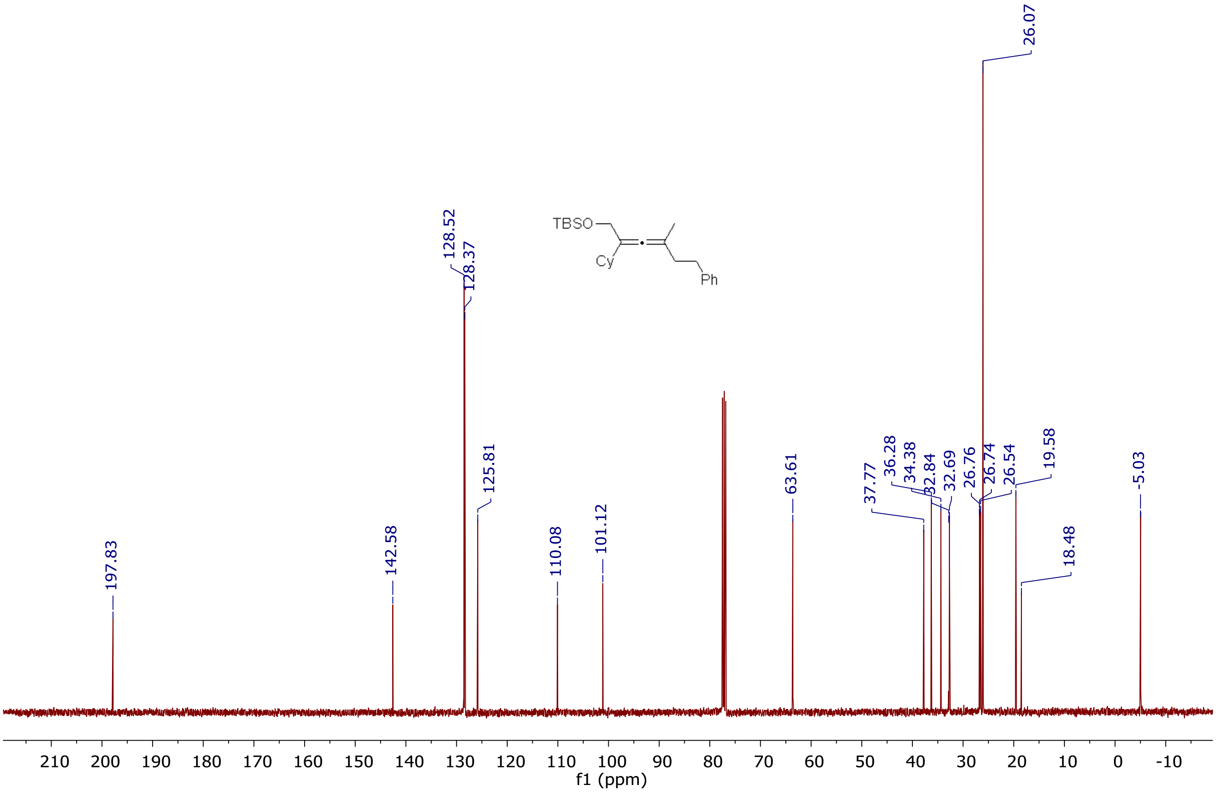
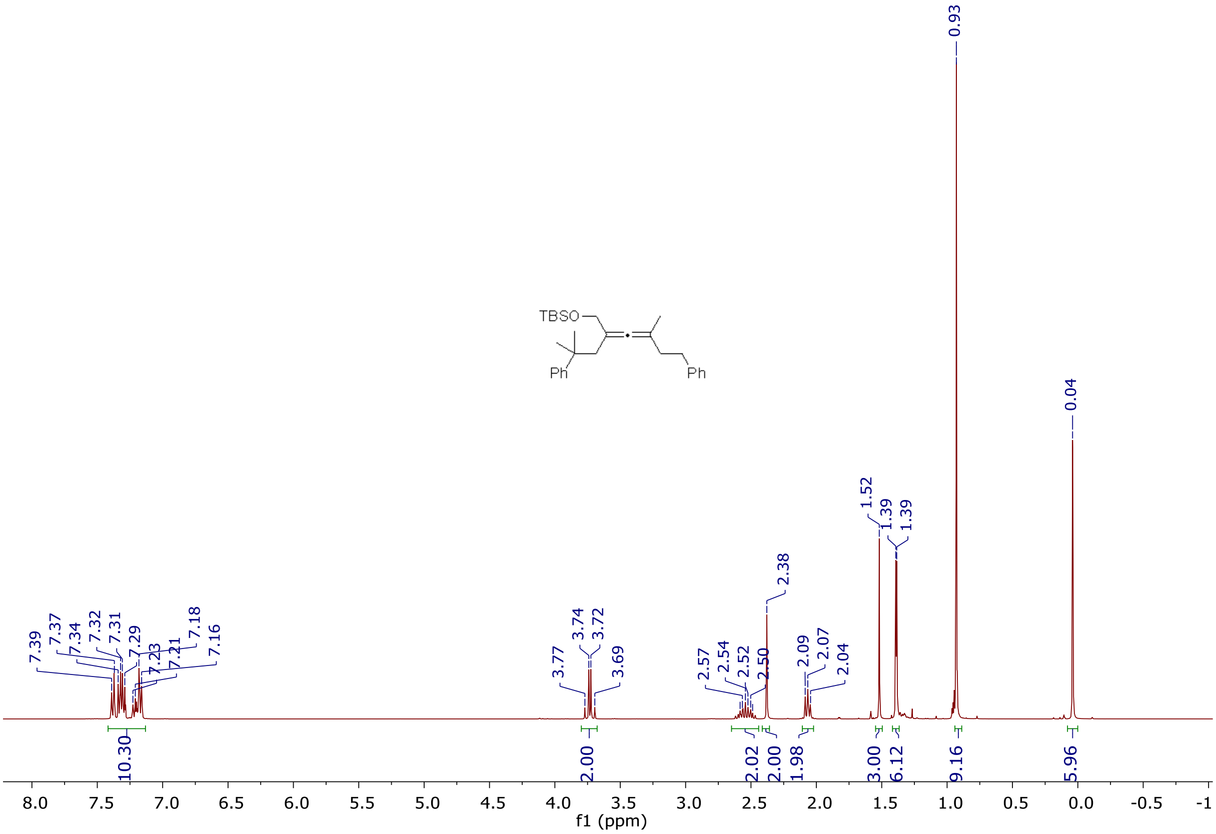
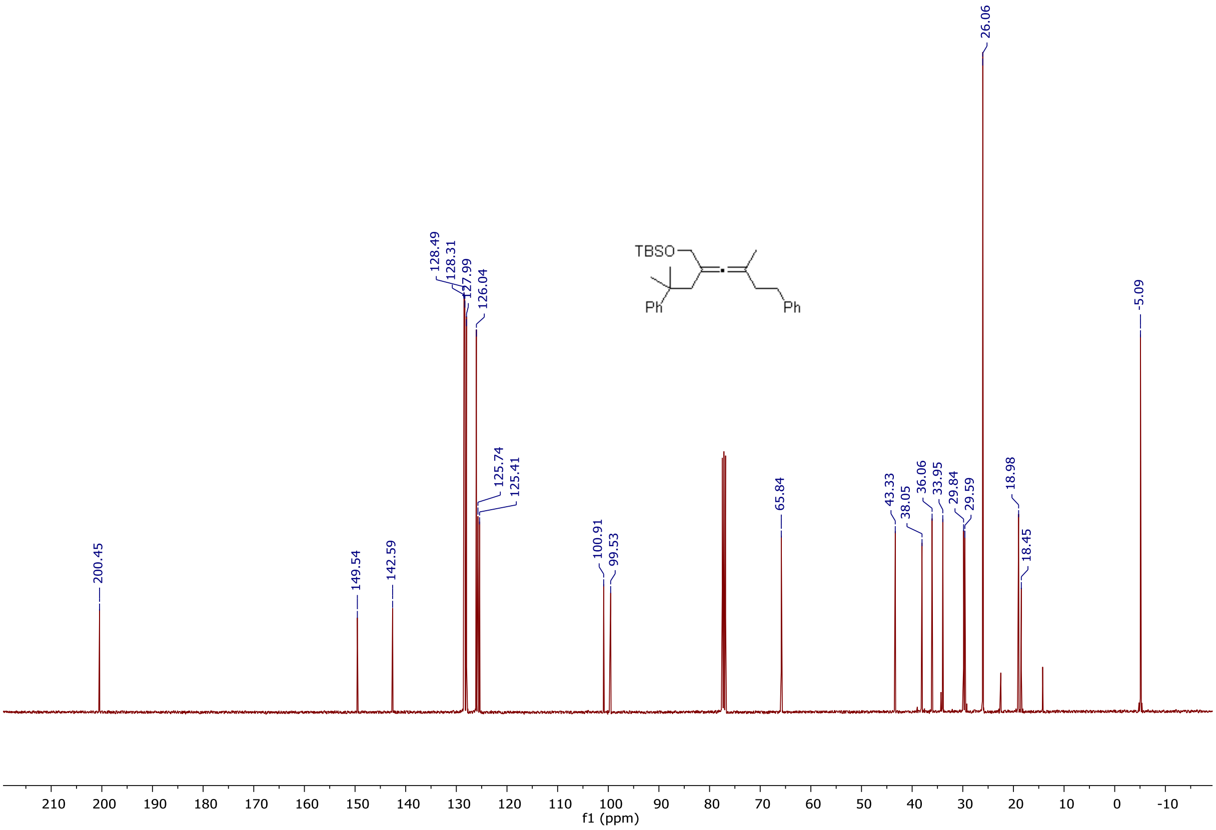
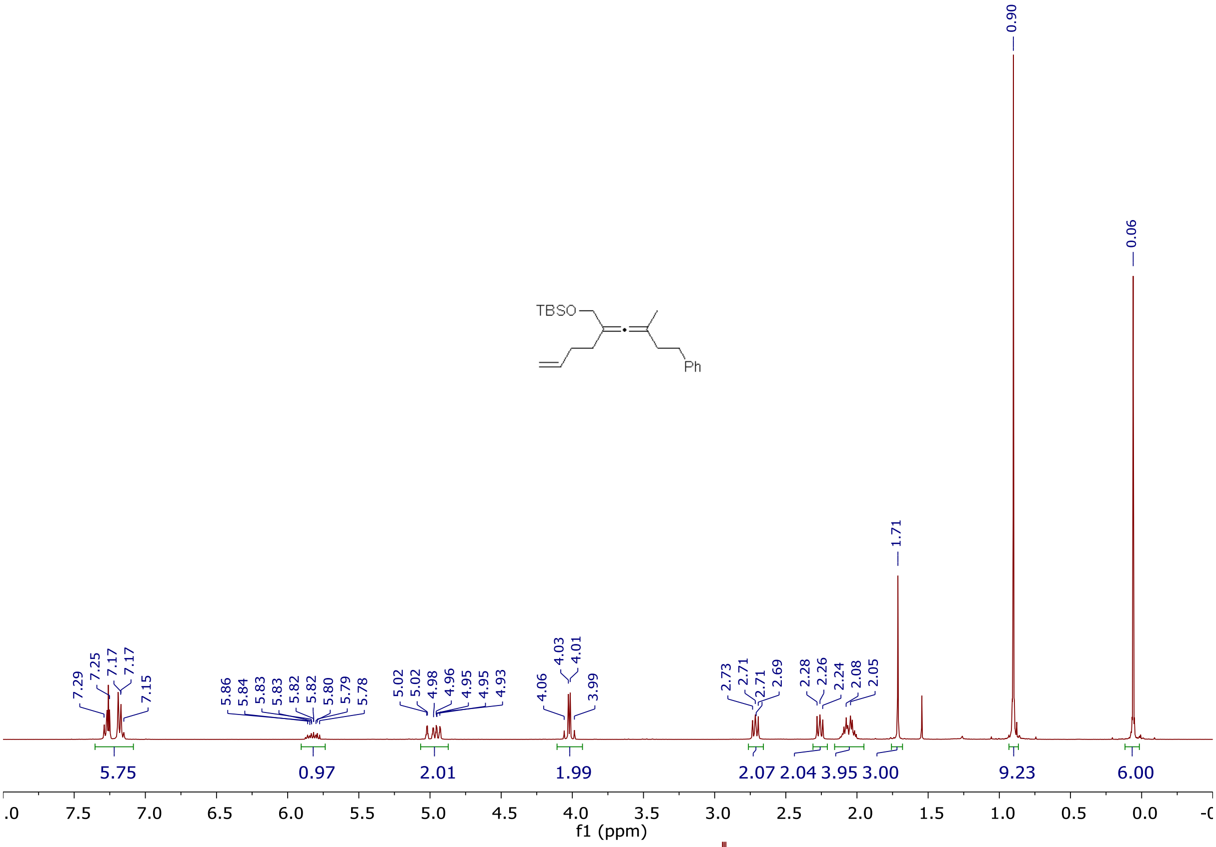
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

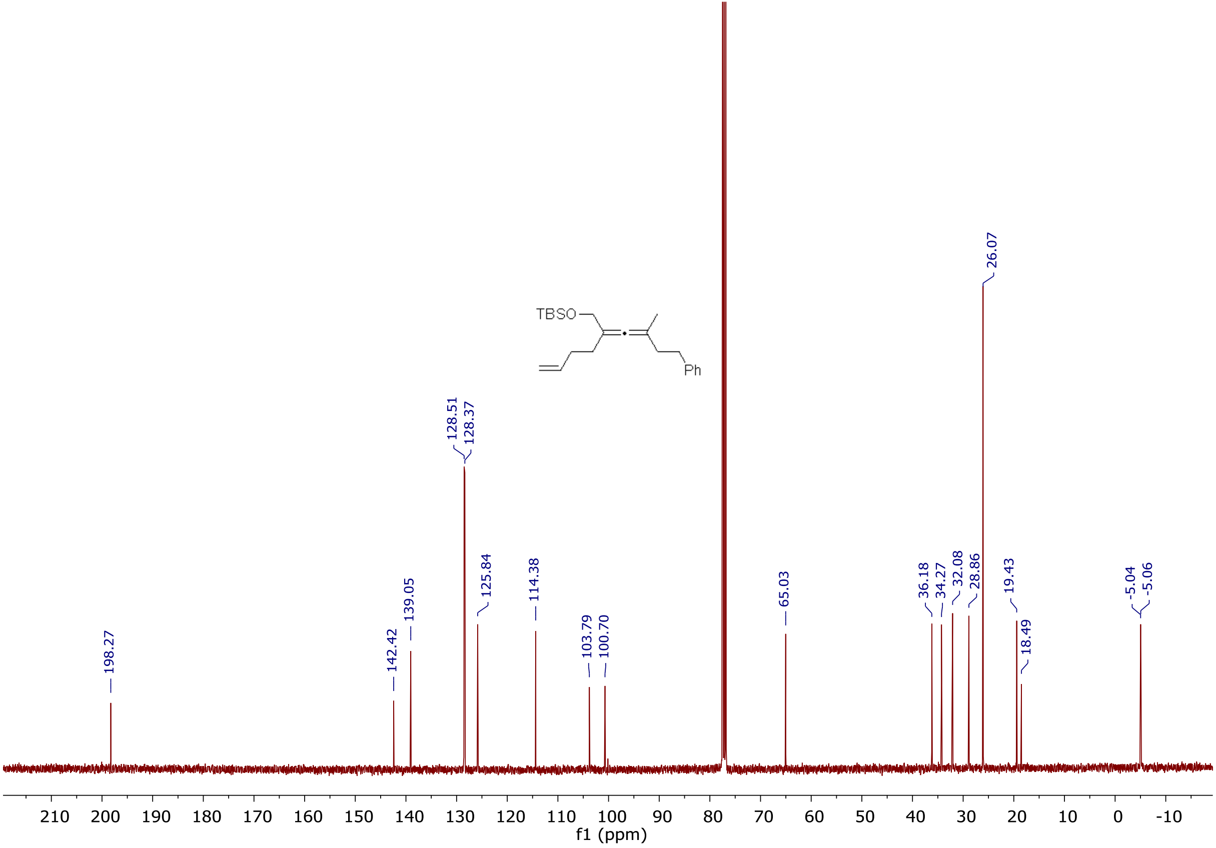

7.33
7.31
7.29
7.23
7.22
7.20
7.19
4.14
4.11
4.08
4.05
2.77
2.75
2.73
2.31
2.29
1.92
1.80
1.76
1.73
1.30
1.05
1.05
1.02
1.02
0.94
0.09
5.05
2.00
1.95
1.96
1.00
8.11
5.44
9.19
6.00
TBSO
Cy
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

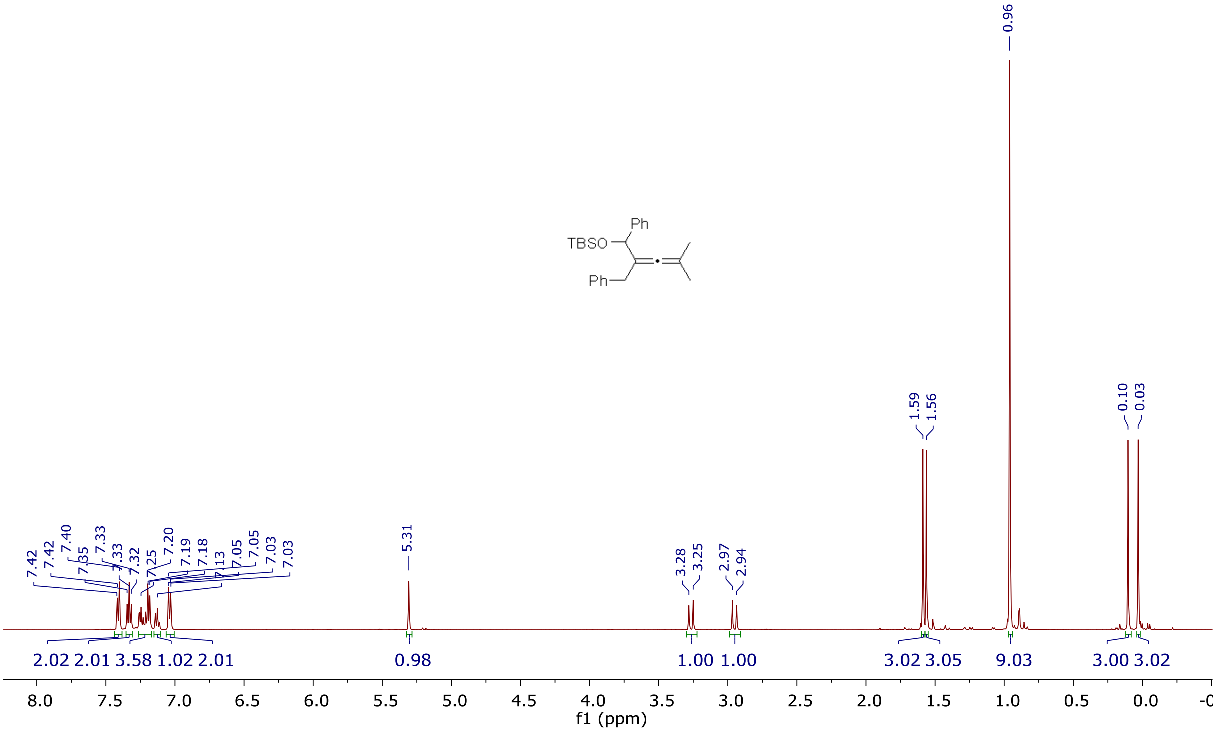

197.83
142.58
128.52
128.37
125.81
110.08
101.12
63.61
37.77
36.28
34.38
32.84
32.69
26.76
26.74
26.54
26.07
19.58
18.48
-5.03
TBSO
Cy
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

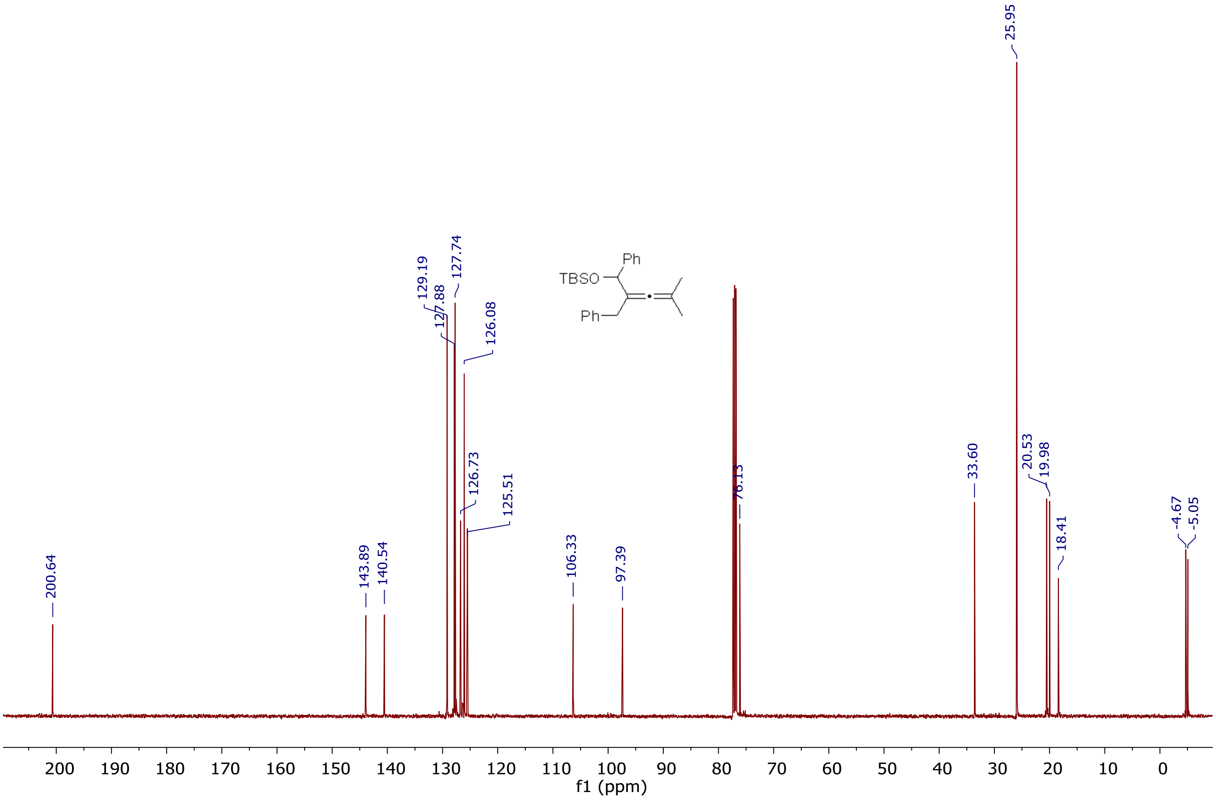

TBSO
Ph
Ph
7.39
7.37
7.34
7.32
7.31
7.29
7.23
7.21
7.18
7.16
3.77
3.74
3.72
3.69
2.57
2.54
2.52
2.50
2.38
2.09
2.07
2.04
1.52
1.39
1.39
0.93
0.04
10.30
2.00
2.02
2.00
1.98
3.00
6.12
9.16
5.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


TBSO
Ph
Ph
200.45
149.54
142.59
128.49
128.31
127.99
126.04
125.74
125.41
100.91
99.53
65.84
43.33
38.05
36.06
33.95
29.84
29.59
26.06
18.98
18.45
-5.09
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)


TBSO
Ph
7.29
7.25
7.17
7.17
7.15
5.86
5.84
5.83
5.83
5.82
5.82
5.80
5.79
5.78
5.02
5.02
4.98
4.96
4.95
4.95
4.93
4.06
4.03
4.01
3.99
2.73
2.71
2.71
2.69
2.28
2.26
2.24
2.08
2.05
1.71
0.90
0.06
5.75
0.97
2.01
1.99
2.07
2.04
3.95
3.00
9.23
6.00
f1 (ppm)


TBSO
Ph
198.27
142.42
139.05
128.51
128.37
125.84
114.38
103.79
100.70
65.03
36.18
34.27
32.08
28.86
26.07
19.43
18.49
-5.04
-5.06
f1 (ppm)


TBSO
Ph
Ph
7.42
7.42
7.40
7.35
7.33
7.33
7.32
7.25
7.20
7.19
7.18
7.13
7.05
7.05
7.03
7.03
5.31
3.28
3.25
2.97
2.94
1.59
1.56
0.96
0.10
0.03
2.02
2.01
3.58
1.02
2.01
0.98
1.00
1.00
3.02
3.05
9.03
3.00
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TBSO
Ph
Ph
200.64
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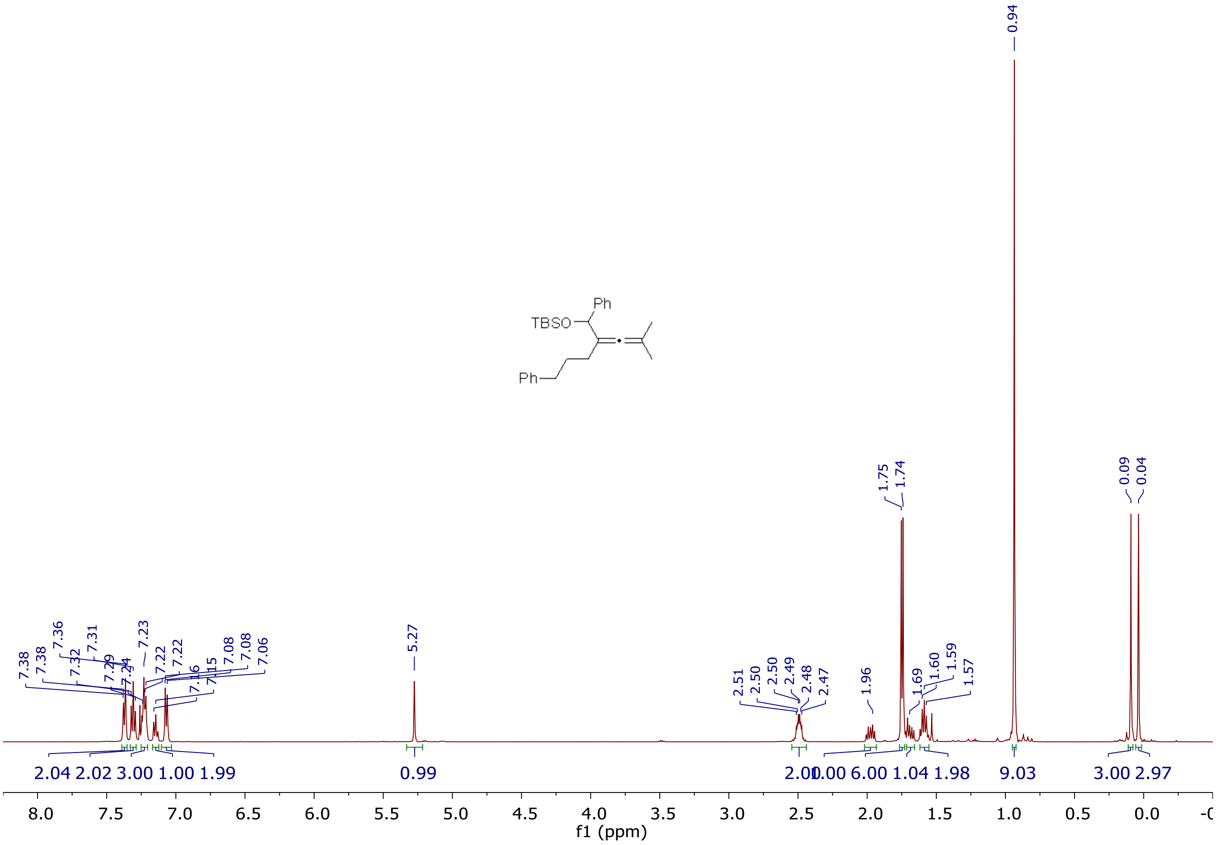
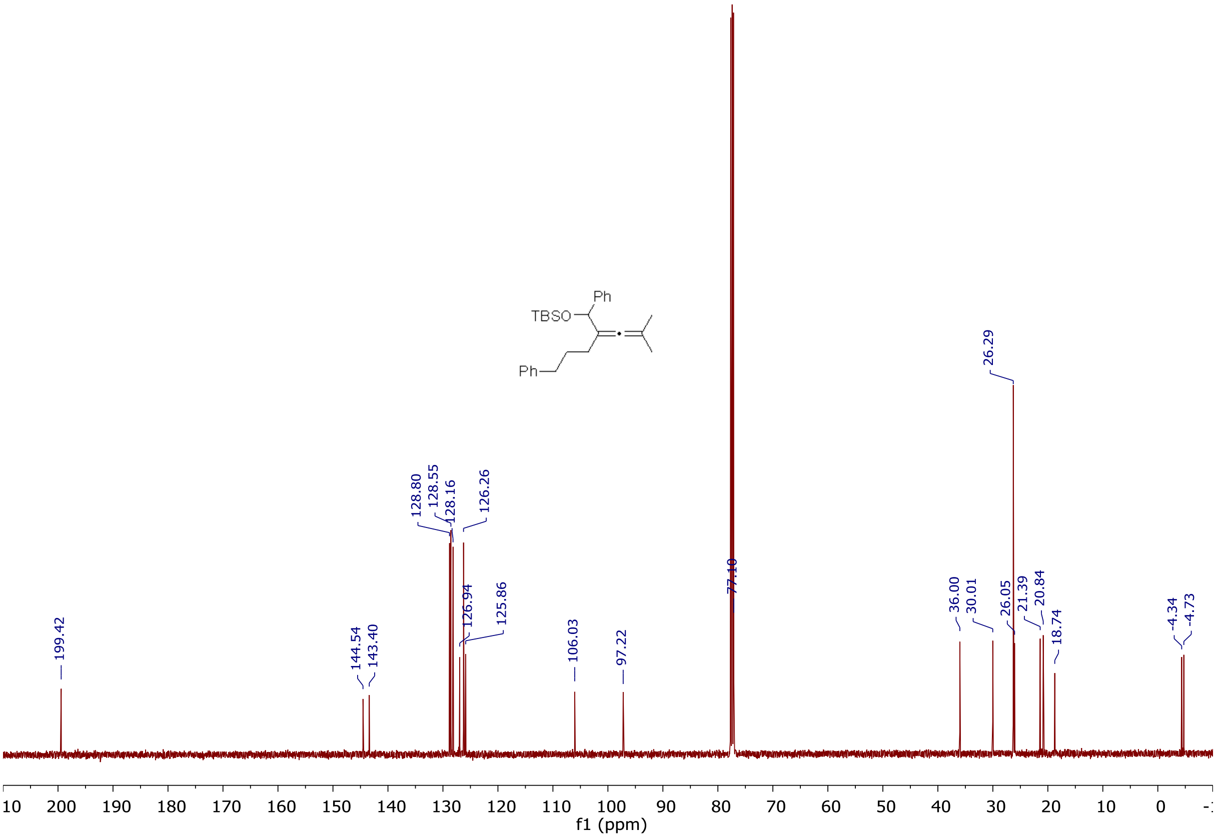
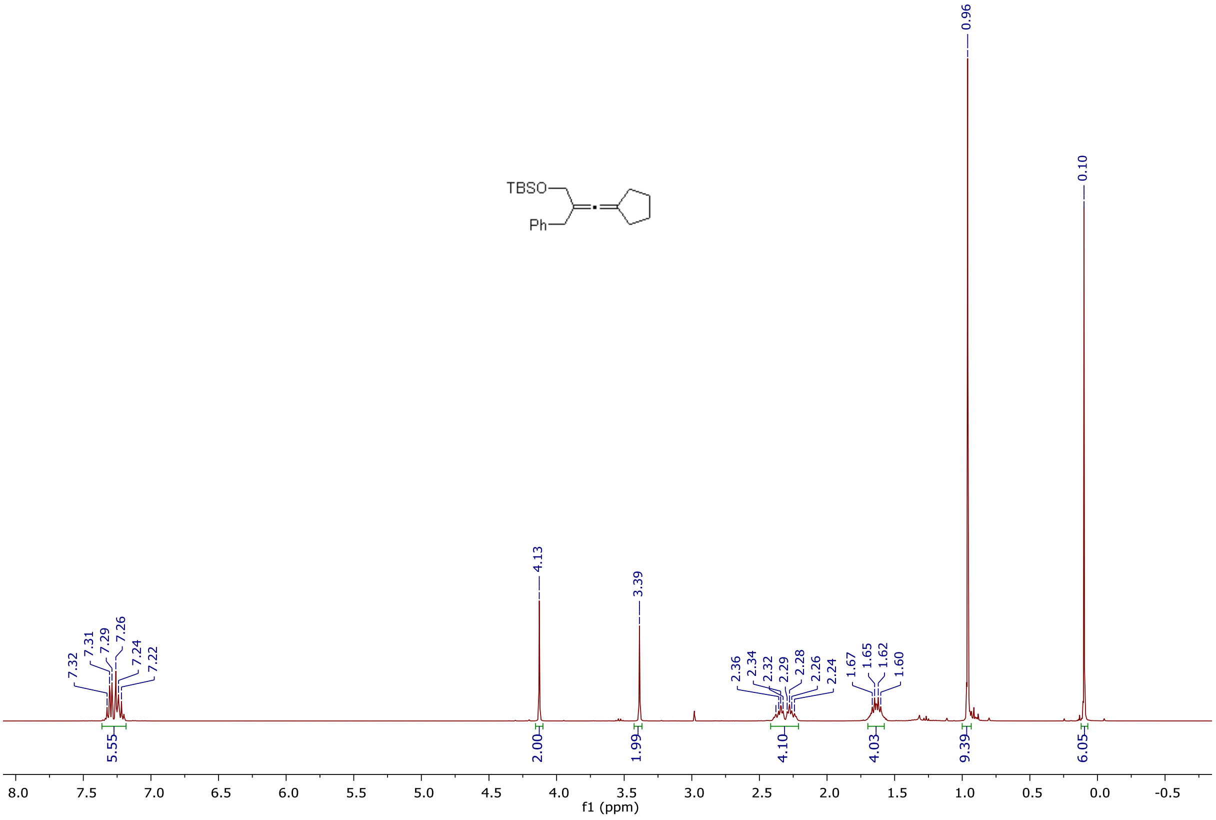
140.54
129.19
127.88
127.74
126.08
126.73
125.51
106.33
97.39
76.13
33.60
25.95
20.53
19.98
18.41
-4.67
-5.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



TBSO
Ph
Ph
7.38
7.38
7.36
7.32
7.31
7.29
7.24
7.23
7.22
7.22
7.16
7.15
7.08
7.08
7.06
5.27
2.51
2.50
2.50
2.49
2.48
2.47
1.96
1.75
1.74
1.69
1.60
1.59
1.57
0.94
0.09
0.04
2.04
2.02
3.00
1.00
1.99
0.99
2.00
1.00
6.00
1.04
1.98
9.03
3.00
2.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



TBSO
Ph
Ph
199.42
144.54
143.40
128.80
128.55
128.16
126.94
126.26
125.86
106.03
97.22
77.10
36.00
30.01
26.29
26.05
21.39
20.84
18.74
-4.34
-4.73
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TBSO
Ph
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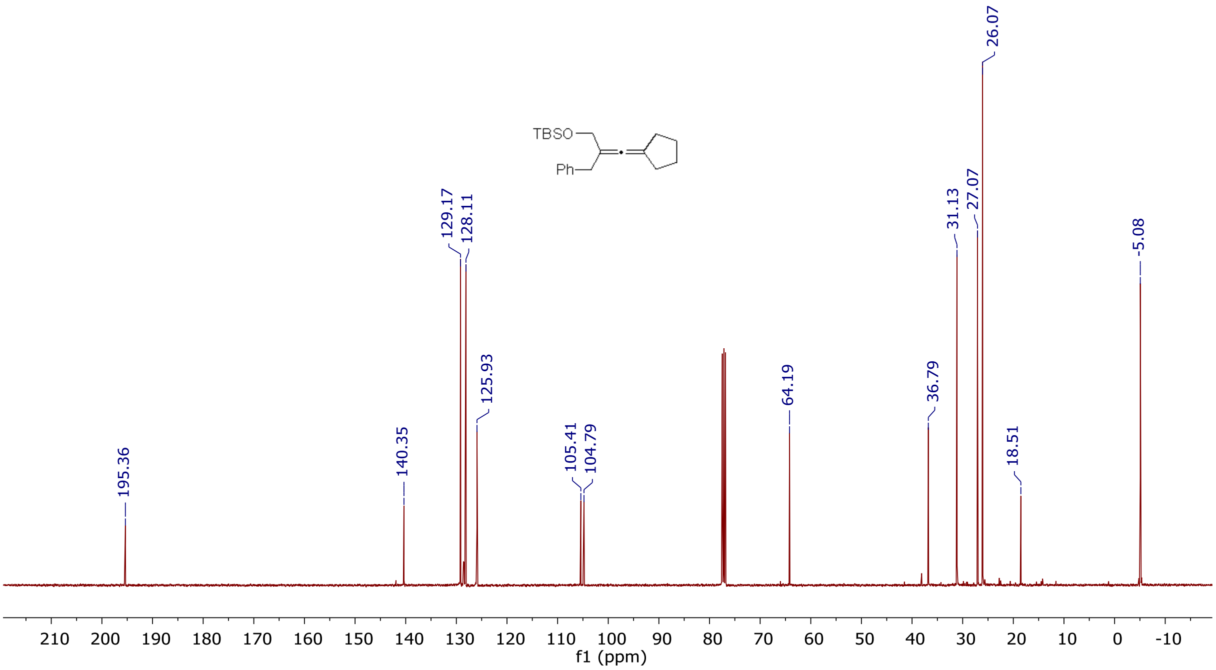
7.31
7.29
7.26
7.24
7.22
4.13
3.39
2.36
2.34
2.32
2.29
2.28
2.26
2.24
1.67
1.65
1.62
1.60
0.96
0.10
5.55
2.00
1.99
4.10
4.03
9.39
6.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


TBSO
Ph
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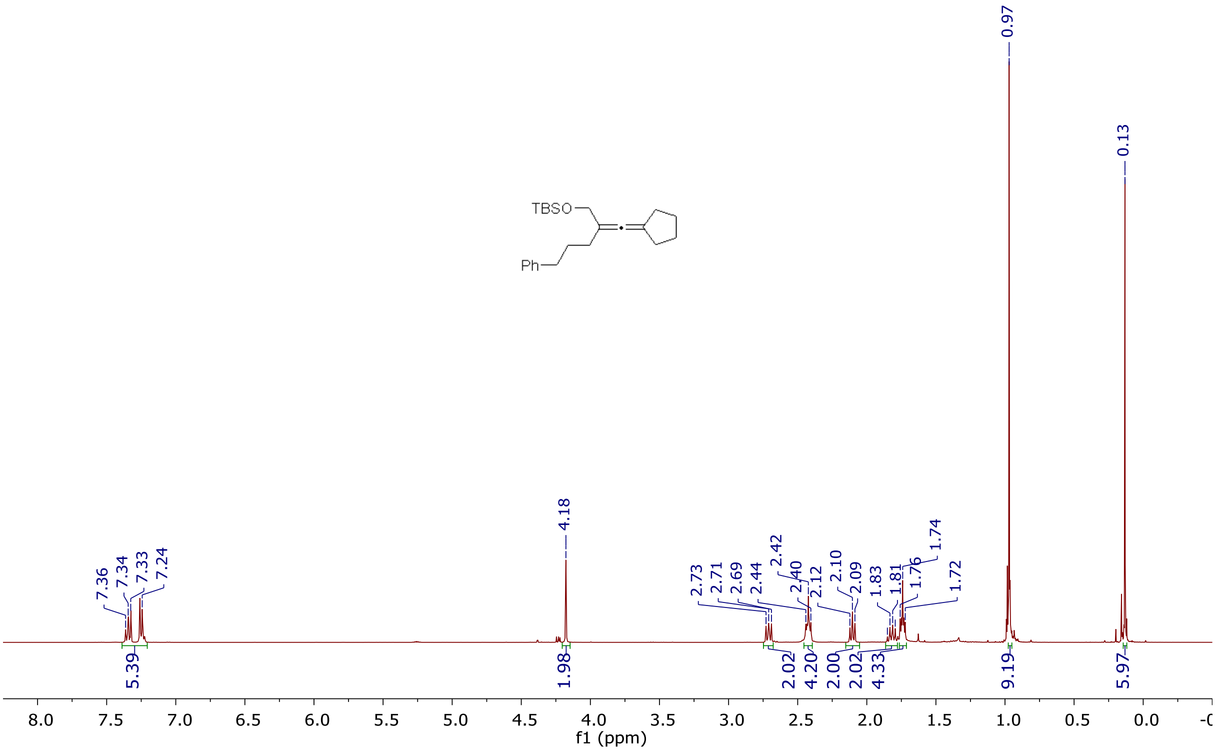
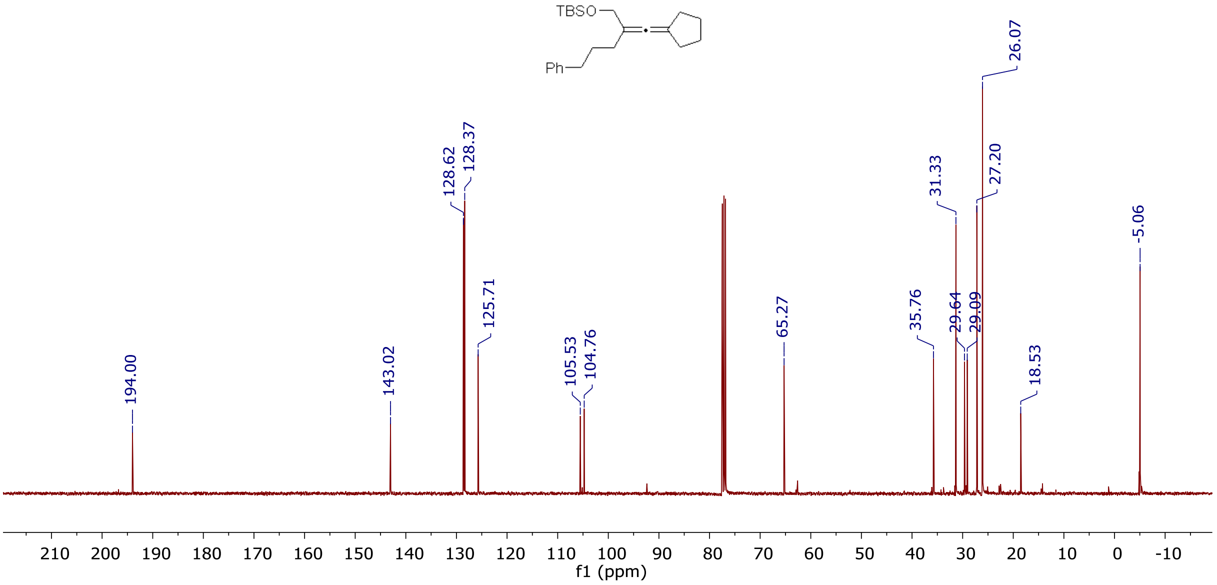
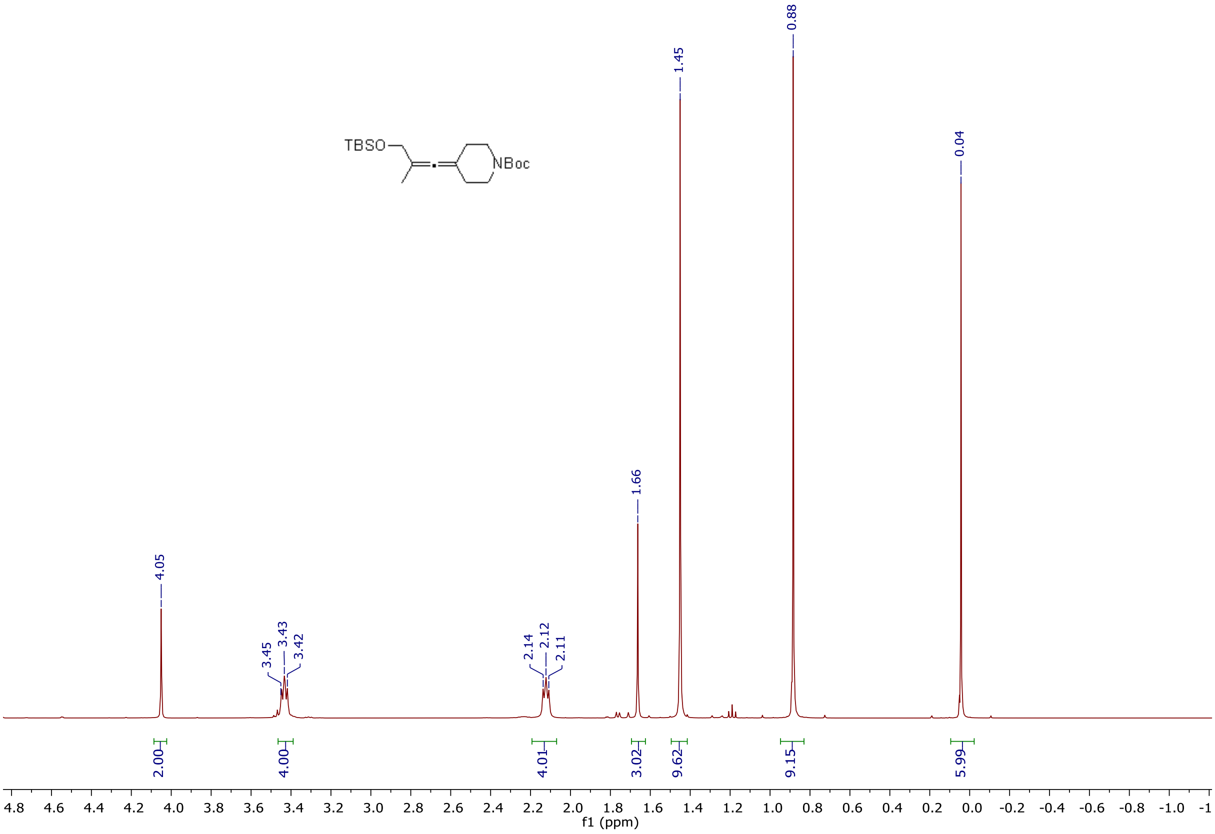
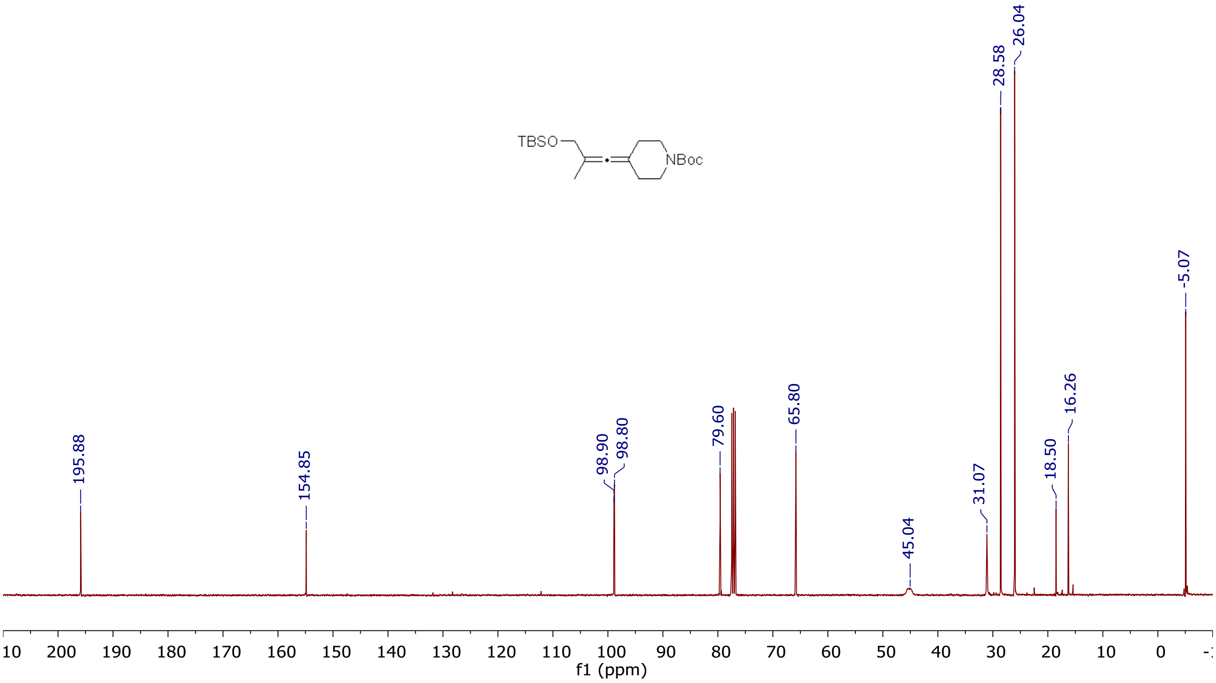
128.11
125.93
105.41
104.79
64.19
36.79
31.13
27.07
26.07
18.51
-5.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


TBSO
Ph
7.36
7.34
7.33
7.24
4.18
2.73
2.71
2.69
2.44
2.42
2.40
2.12
2.10
2.09
1.83
1.81
1.76
1.74
1.72
0.97
0.13
5.39
1.98
2.02
4.20
2.00
2.02
4.33
9.19
5.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TBSO
Ph
194.00
143.02
128.62
128.37
125.71
105.53
104.76
65.27
35.76
31.33
29.64
29.09
27.20
26.07
18.53
-5.06
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)


TBSO
NBoc
4.05
3.45
3.43
3.42
2.14
2.12
2.11
1.66
1.45
0.88
0.04
2.00
4.00
4.01
3.02
9.62
9.15
5.99
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4 -0.6 -0.8 -1.0 -1
f1 (ppm)


TBSO
NBoc
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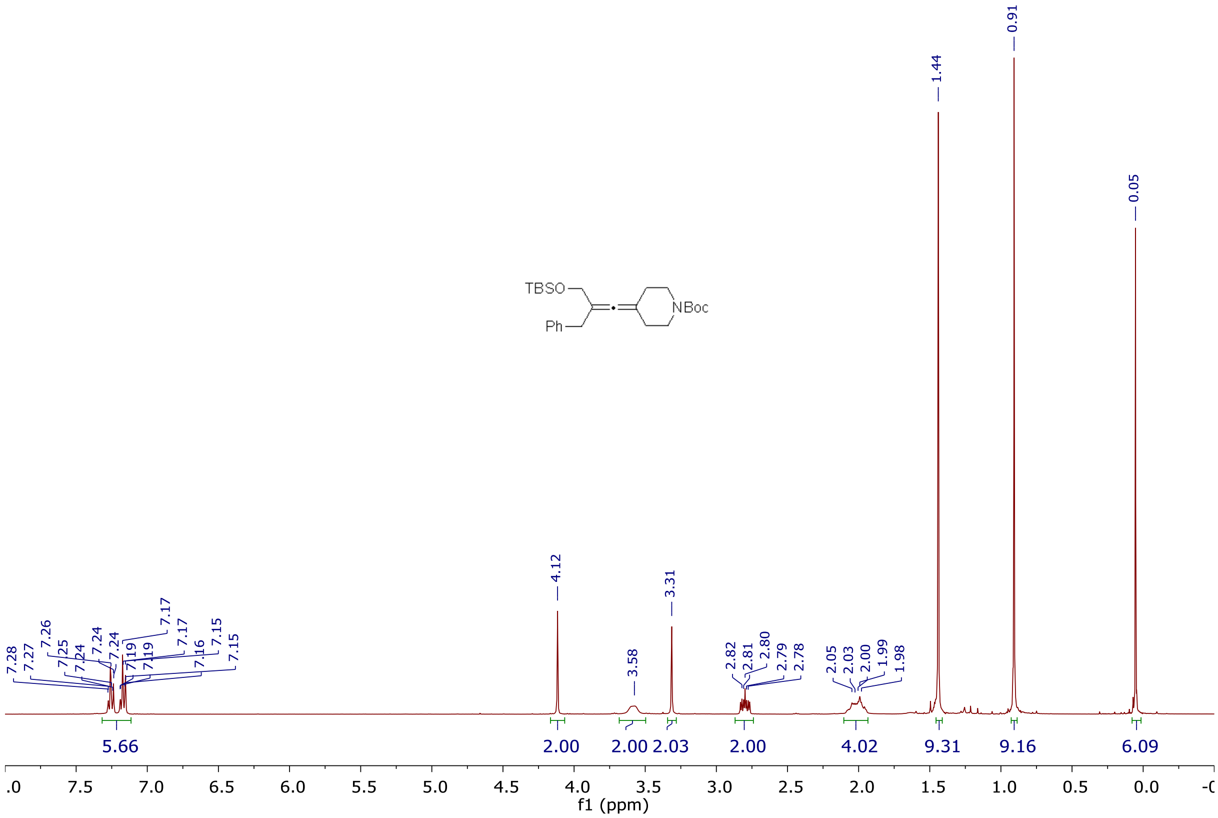
154.85
98.90
98.80
79.60
65.80
45.04
31.07
28.58
26.04
18.50
16.26
-5.07
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)


TBSO
Ph
NBoc
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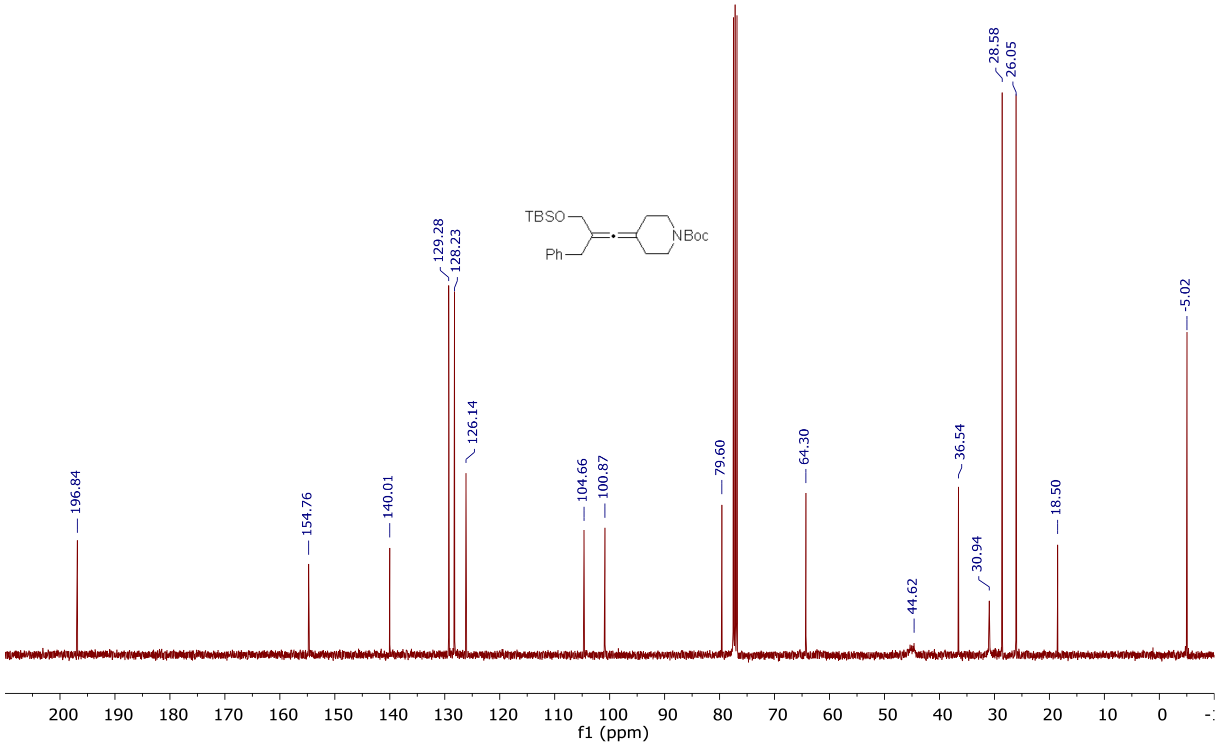
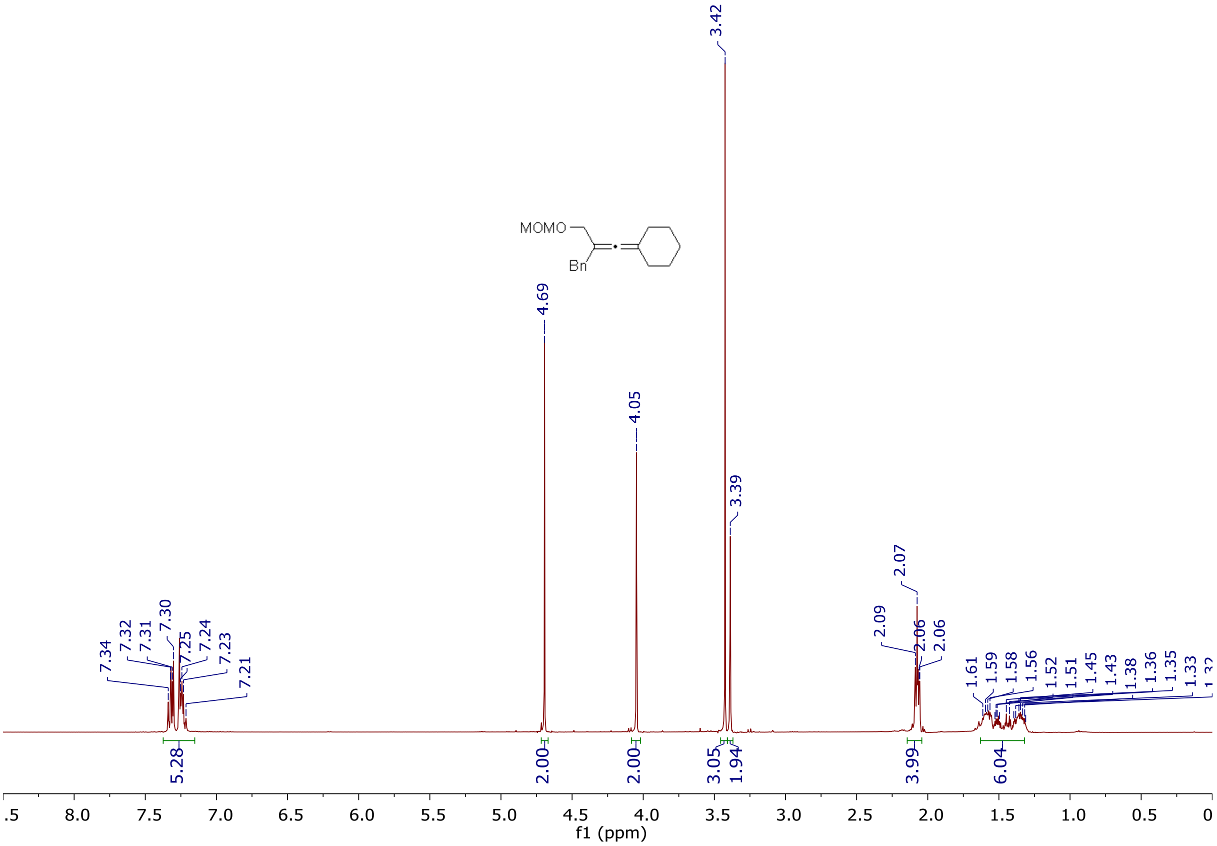
7.27
7.26
7.25
7.24
7.24
7.24
7.19
7.19
7.17
7.17
7.16
7.15
7.15
4.12
3.58
3.31
2.82
2.81
2.80
2.79
2.78
2.05
2.03
2.00
1.99
1.98
1.44
0.91
0.05
5.66
2.00
2.00
2.03
2.00
4.02
9.31
9.16
6.09
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)


TBSO
Ph
NBoc
196.84
154.76
140.01
129.28
128.23
126.14
104.66
100.87
79.60
64.30
44.62
36.54
30.94
28.58
26.05
18.50
-5.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-:
f1 (ppm)


MOMO
Bn
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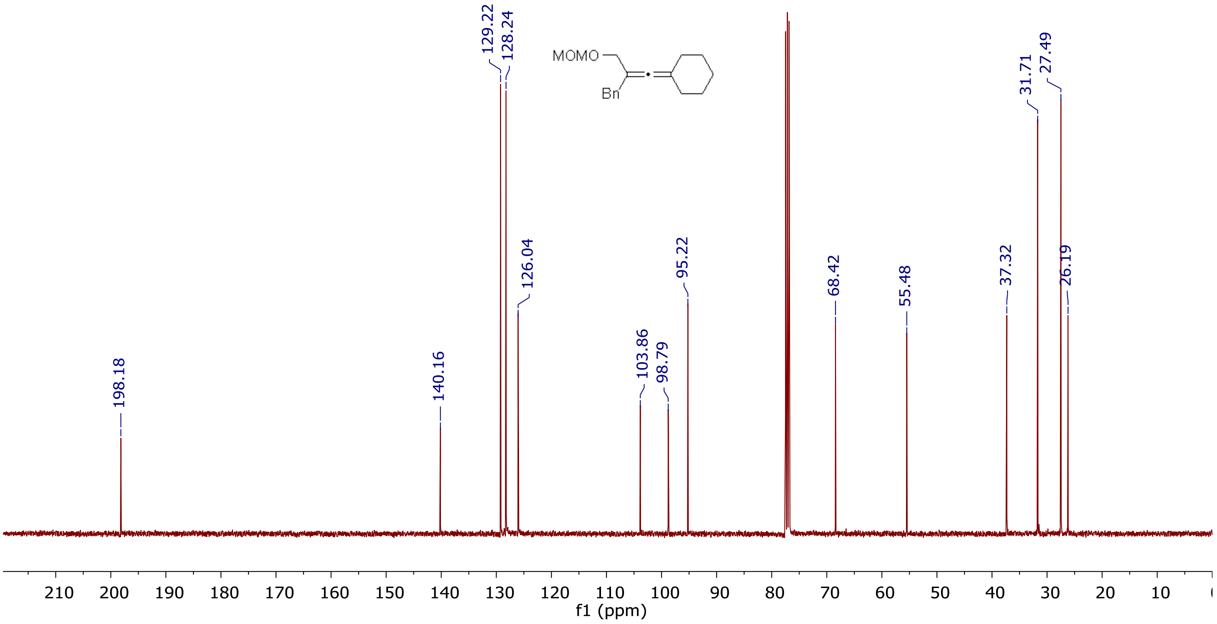
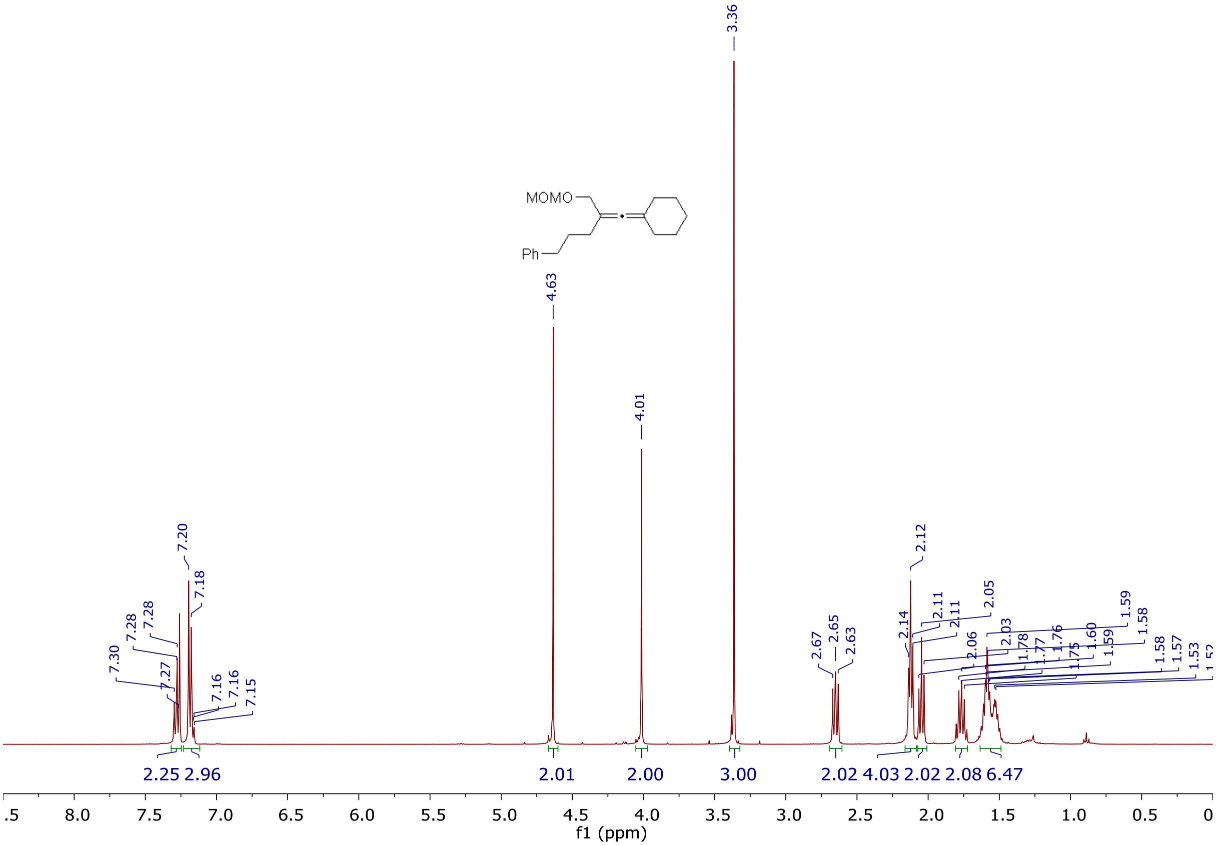
7.32
7.31
7.30
7.25
7.24
7.23
7.21
4.69
4.05
3.42
3.39
2.09
2.07
2.06
2.06
1.61
1.59
1.58
1.56
1.52
1.51
1.45
1.43
1.38
1.36
1.35
1.33
5.28
2.00
2.00
3.05
1.94
3.99
6.04
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


MOMO
Bn
198.18
140.16
129.22
128.24
126.04
103.86
98.79
95.22
68.42
55.48
37.32
31.71
27.49
26.19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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Ph
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7.30
7.28
7.28
7.27
7.20
7.18
7.16
7.16
7.15
2.67
2.65
2.63
2.14
2.12
2.11
2.11
2.06
2.05
2.03
1.78
1.77
1.76
1.75
1.60
1.59
1.59
1.58
1.58
1.57
1.53
1.5
2.25
2.96
2.01
2.00
3.00
2.02
4.03
2.02
2.08
6.47
.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
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1.5
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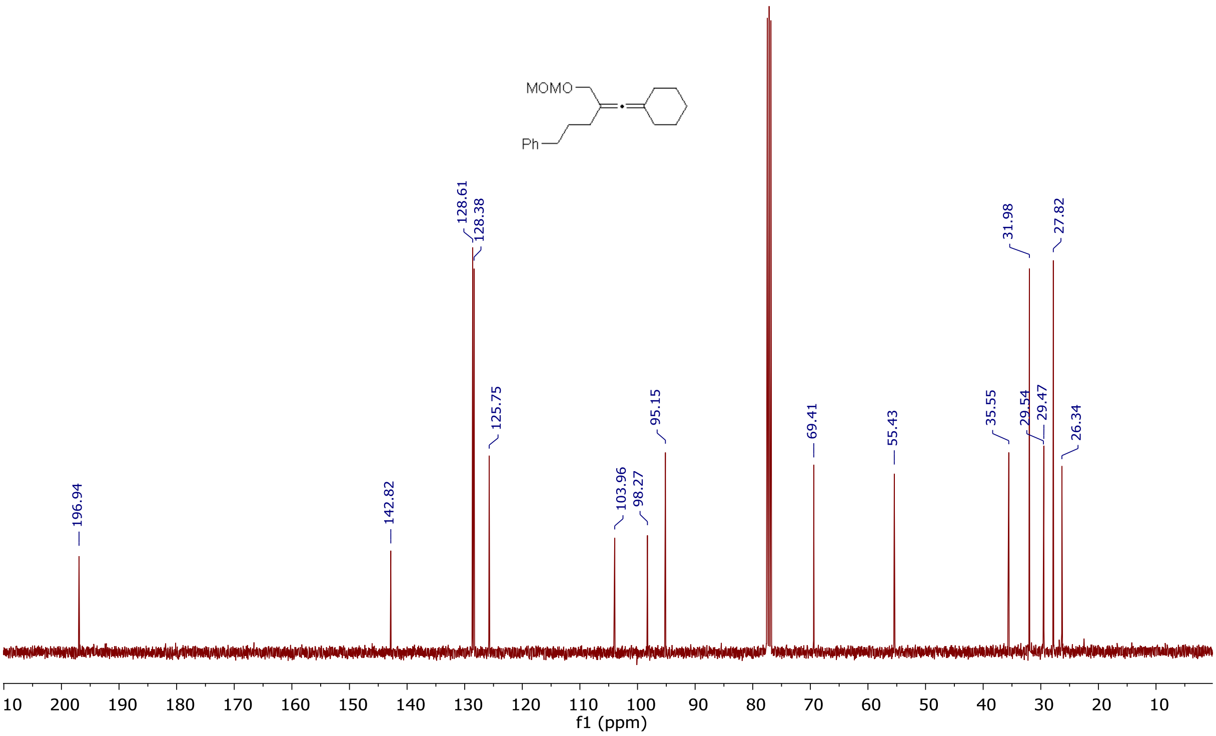
0
f1 (ppm)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Ph
196.94
142.82
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128.38
125.75
103.96
98.27
95.15
69.41
55.43
35.55
31.98
29.54
29.47
27.82
26.34
10
200
190
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120
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100
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80
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60
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20
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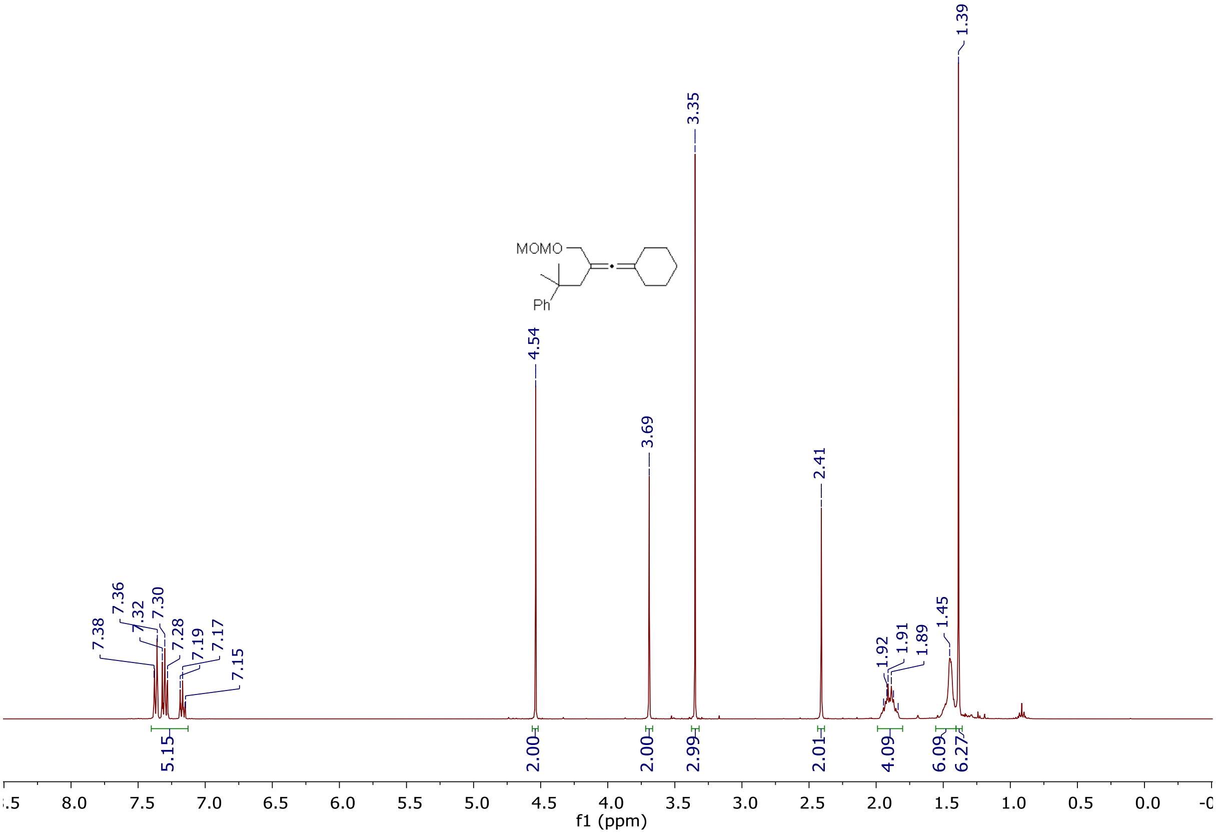
f1 (ppm)


MOMO
Ph
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3.35
2.41
1.92
1.91
1.89
1.45
1.39
5.15
2.00
2.00
2.99
2.01
4.09
6.09
6.27
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
1.5
1.0
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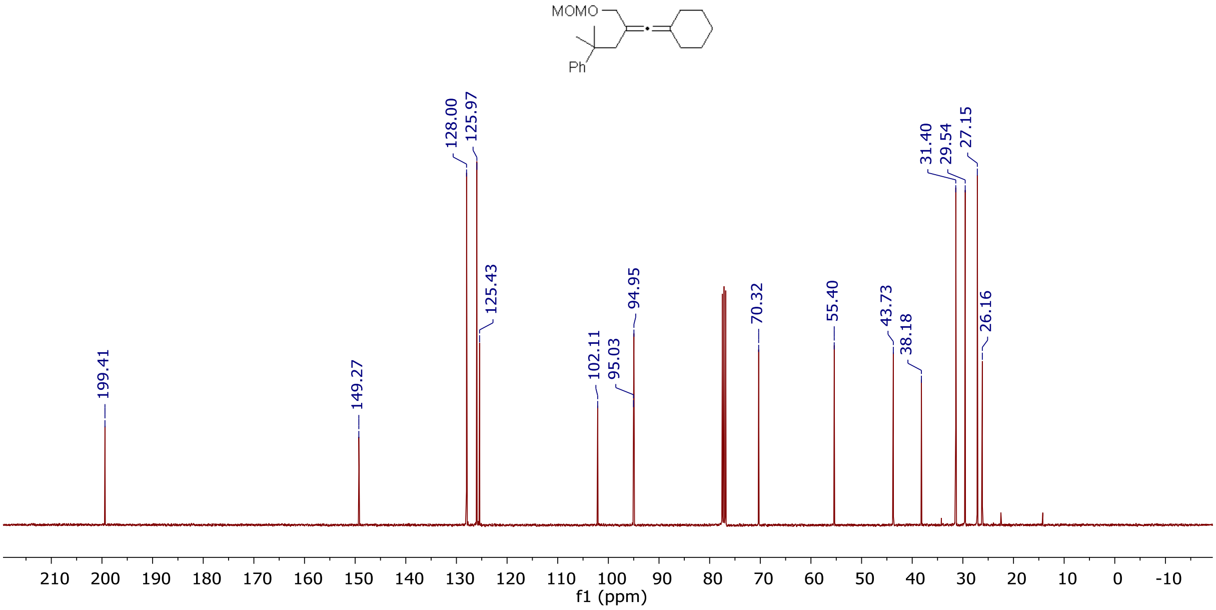
f1 (ppm)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70.32
55.40
43.73
38.18
31.40
29.54
27.15
26.16
210
200
190
180
170
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100
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80
70
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30
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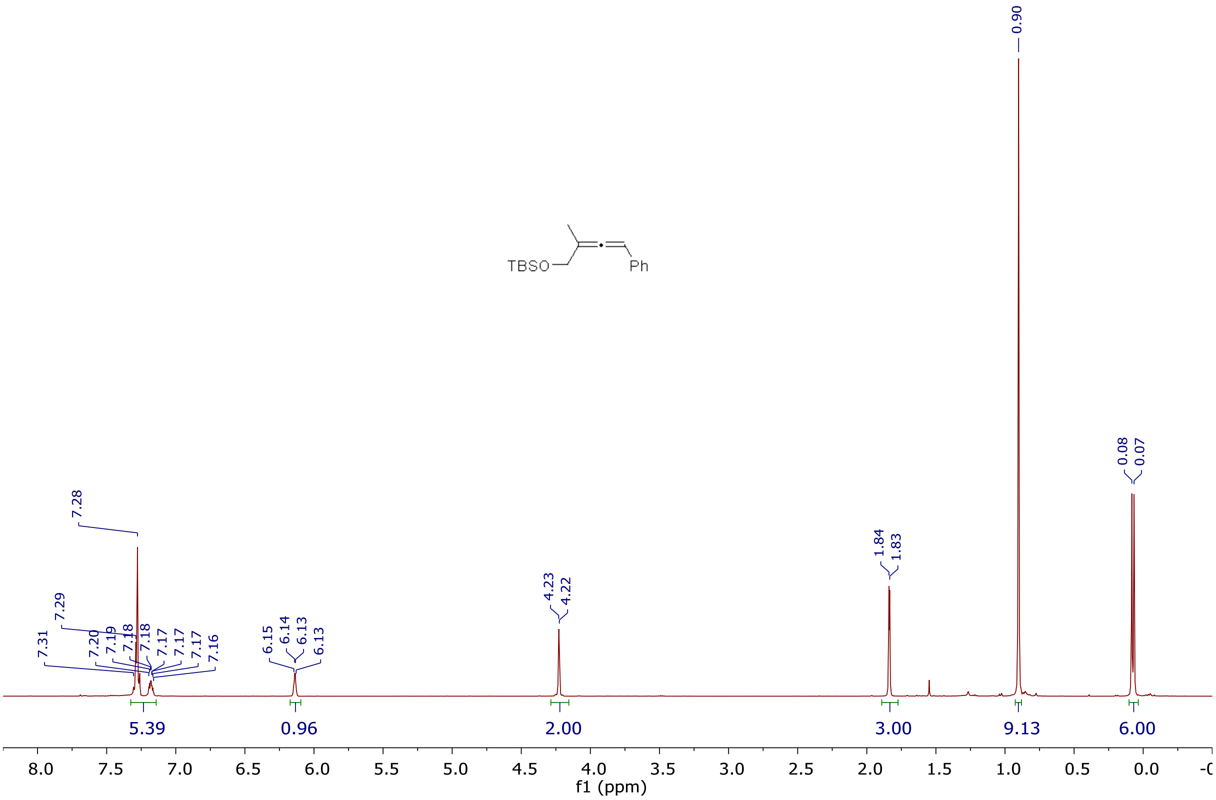
f1 (ppm)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Ph
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7.16
6.15
6.14
6.13
6.13
4.23
4.22
1.84
1.83
0.90
0.08
0.07
5.39
0.96
2.00
3.00
9.13
6.00
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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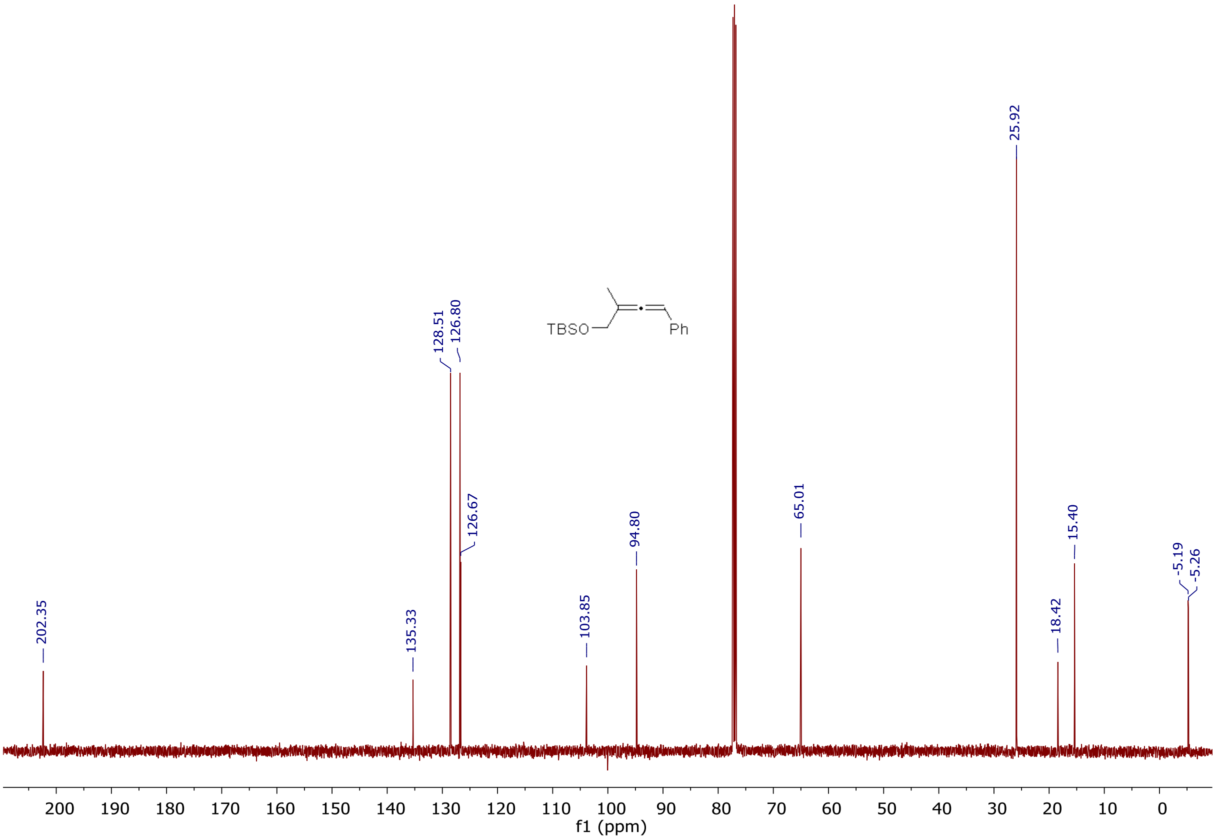
0.0
f1 (ppm)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126.80
126.67
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25.92
18.42
15.40
-5.19
-5.26
200
190
180
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150
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130
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110
100
90
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40
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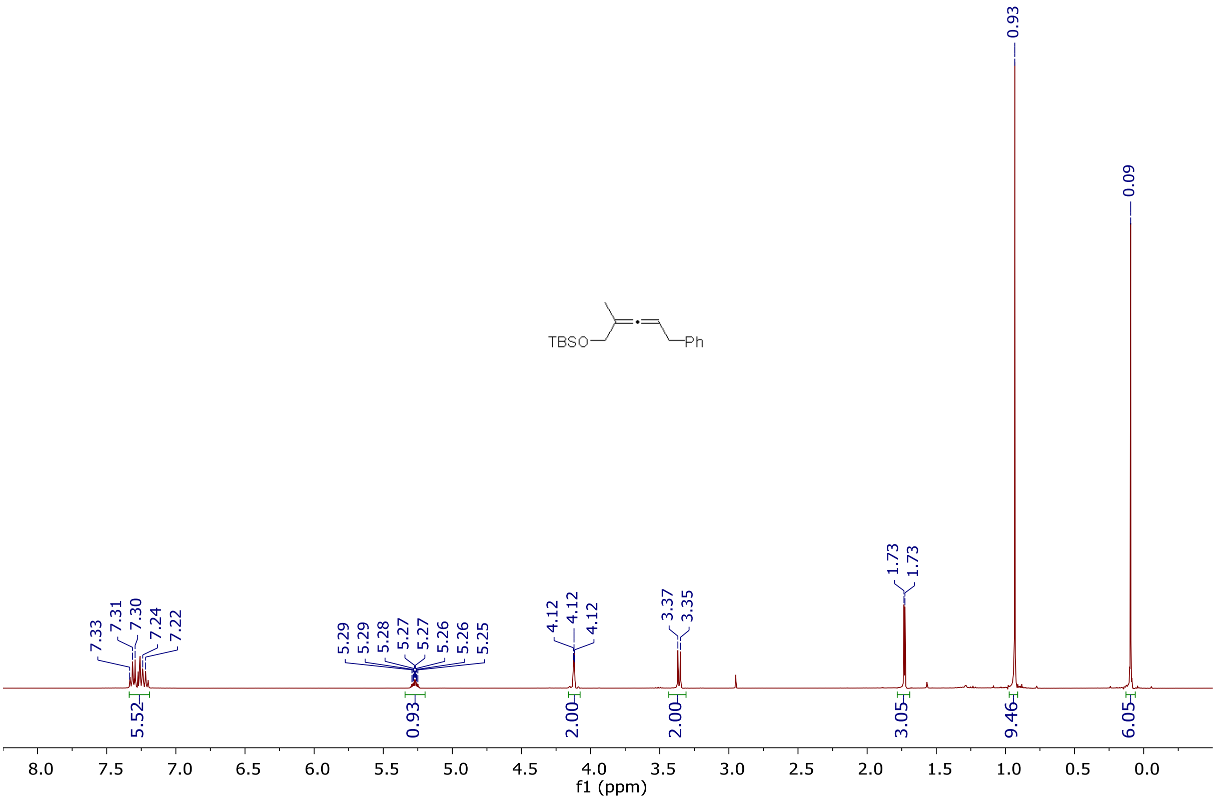
10
0
f1 (ppm)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5.25
4.12
4.12
4.12
3.37
3.35
1.73
1.73
0.93
0.09
TBSO
Ph
5.52
0.93
2.00
2.00
3.05
9.46
6.05
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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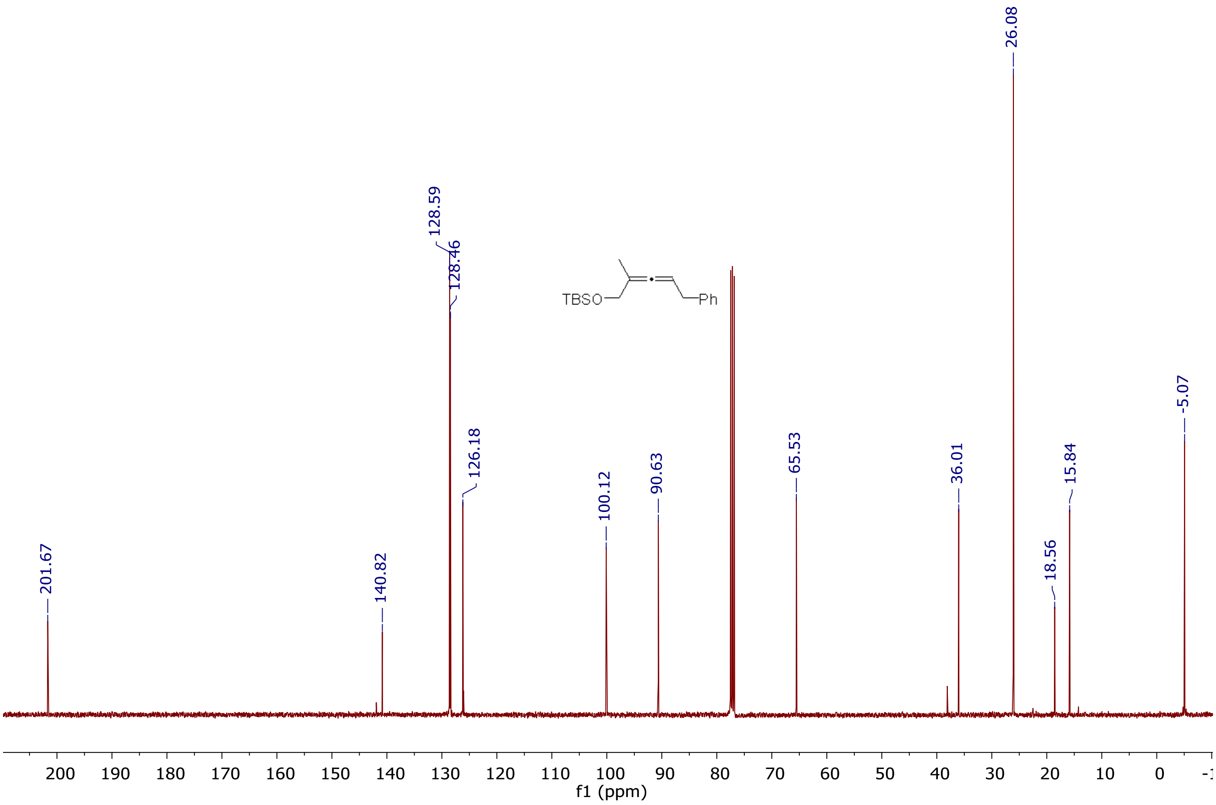
0.0
f1 (ppm)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128.46
126.18
100.12
90.63
65.53
36.01
26.08
18.56
15.84
-5.07
TBSO
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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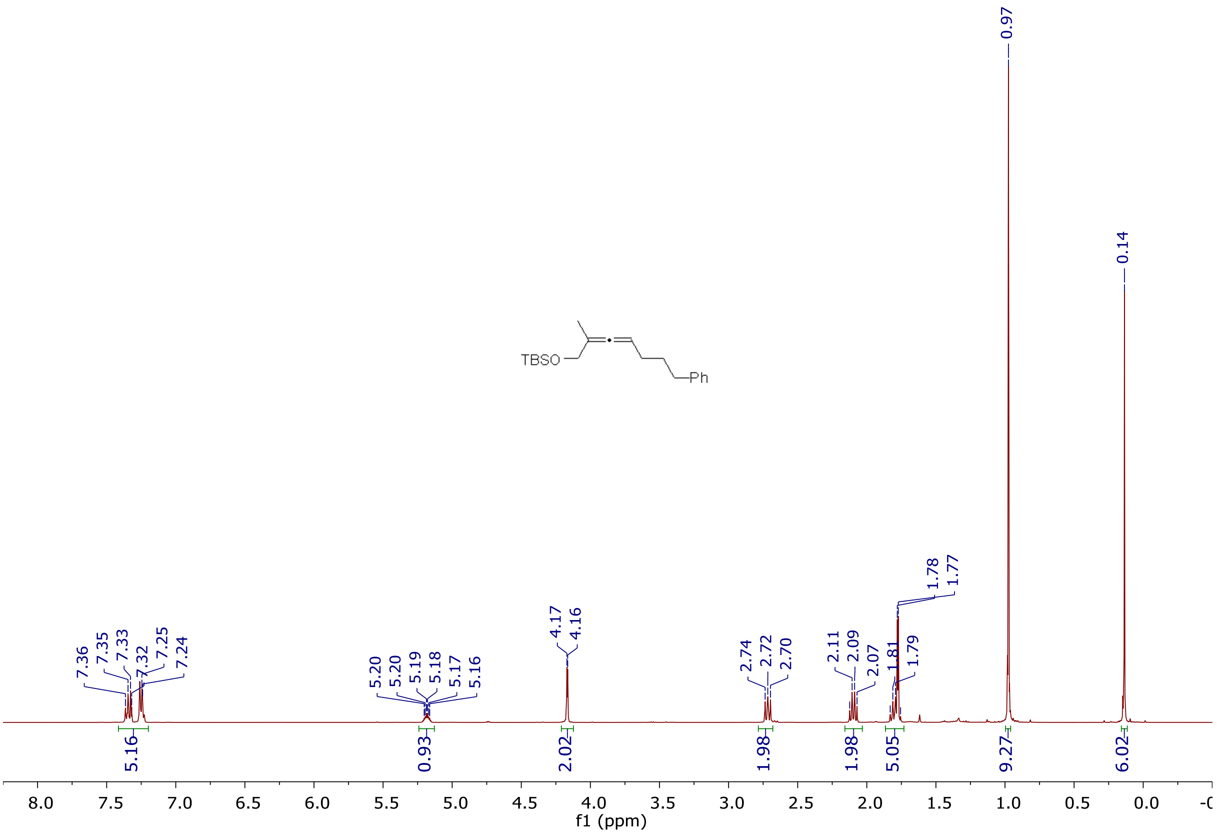
50
40
30
20
10
0
f1 (ppm)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7.24
5.20
5.20
5.19
5.18
5.17
5.16
4.17
4.16
2.74
2.72
2.70
2.11
2.09
2.07
1.81
1.79
1.78
1.77
0.97
0.14
TBSO
Ph
5.16
0.93
2.02
1.98
1.98
5.05
9.27
6.02
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7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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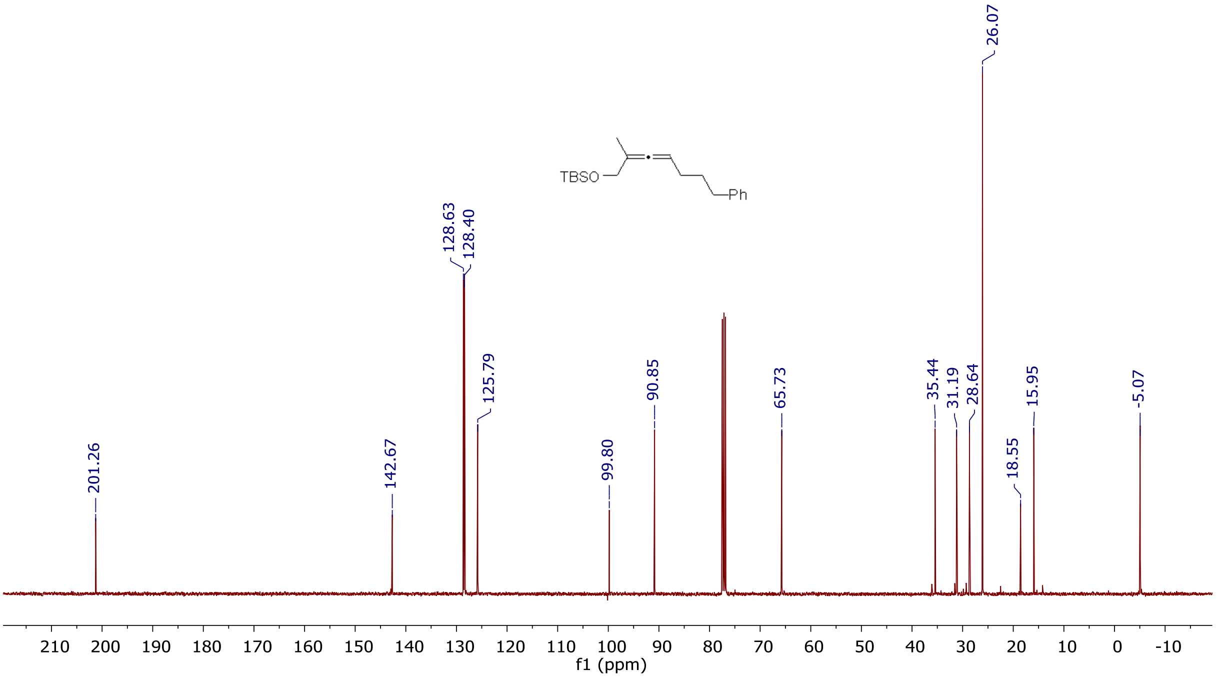
0.0
f1 (ppm)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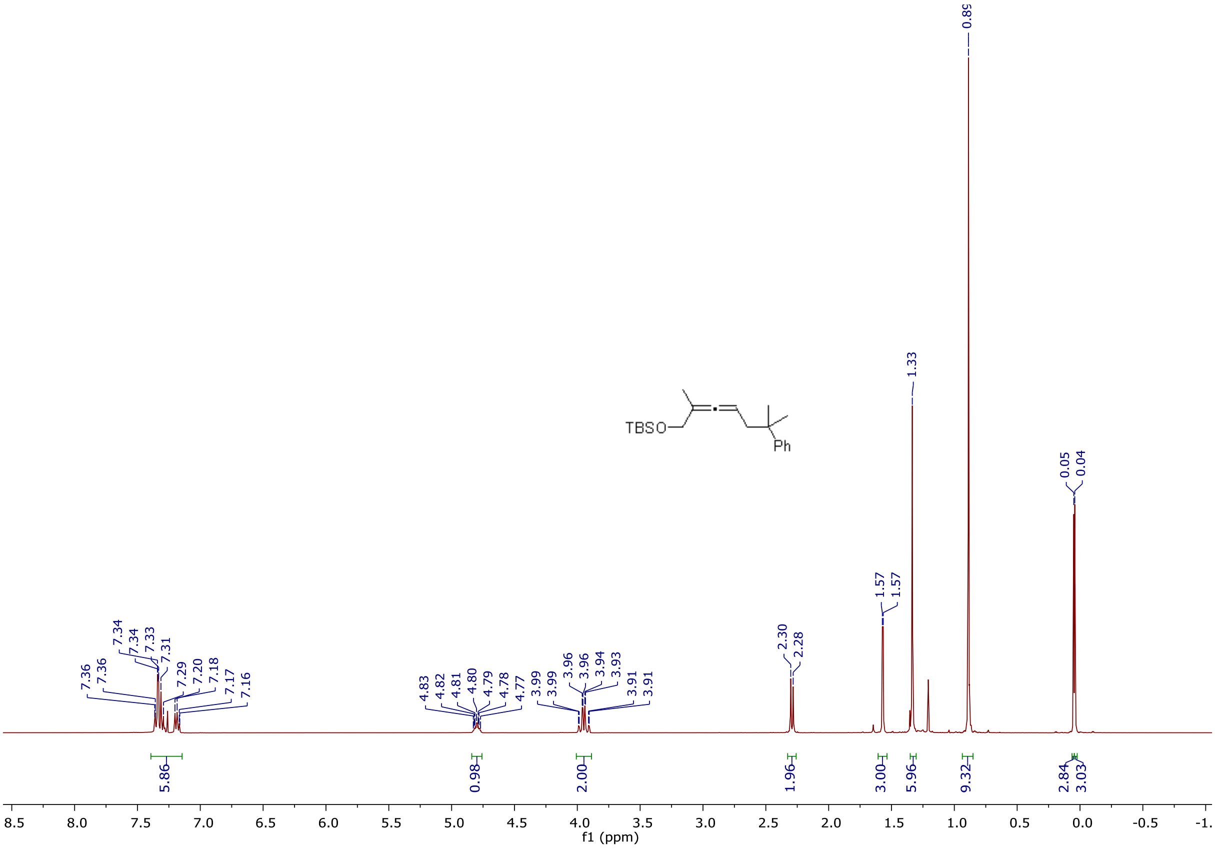
99.80
90.85
65.73
35.44
31.19
28.64
26.07
18.55
15.95
-5.07
TBSO
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
Ph
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7.33
7.31
7.29
7.20
7.18
7.17
7.16
4.83
4.82
4.81
4.80
4.79
4.78
4.77
3.99
3.99
3.96
3.96
3.94
3.93
3.91
3.91
2.30
2.28
1.57
1.57
1.33
0.89
0.05
0.04
5.86
0.98
2.00
1.96
3.00
5.96
9.32
2.84
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
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1.0
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0.0
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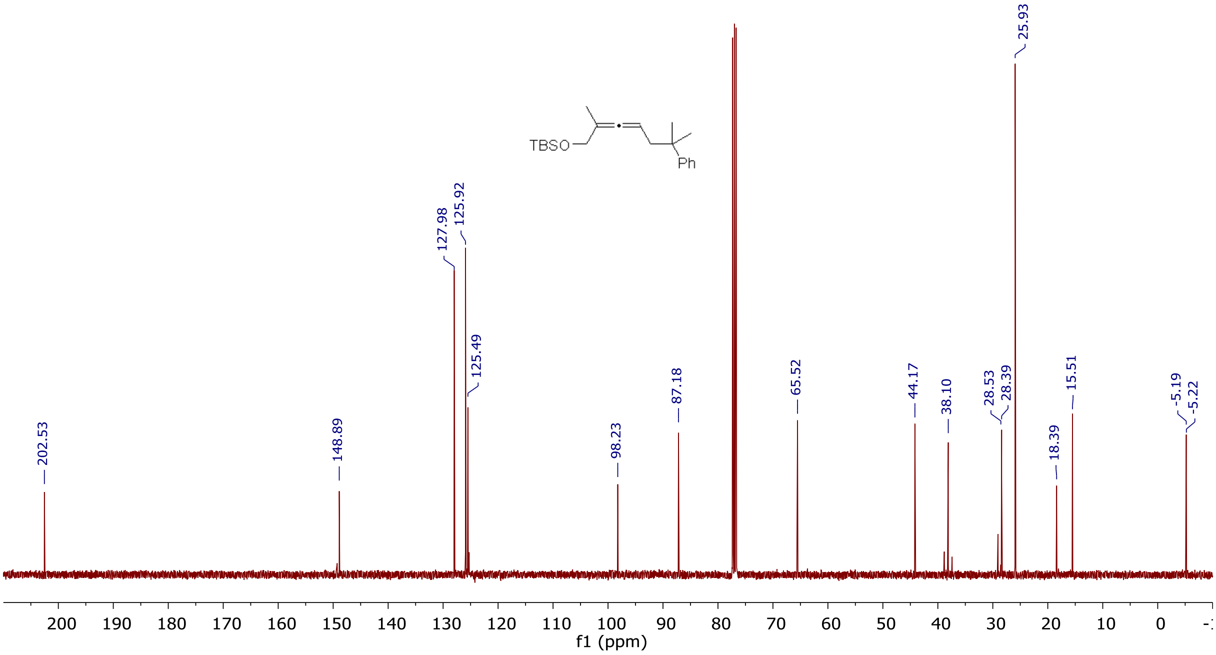
-1.
f1 (ppm)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Ph
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44.17
38.10
28.53
28.39
25.93
18.39
15.51
-5.19
-5.22
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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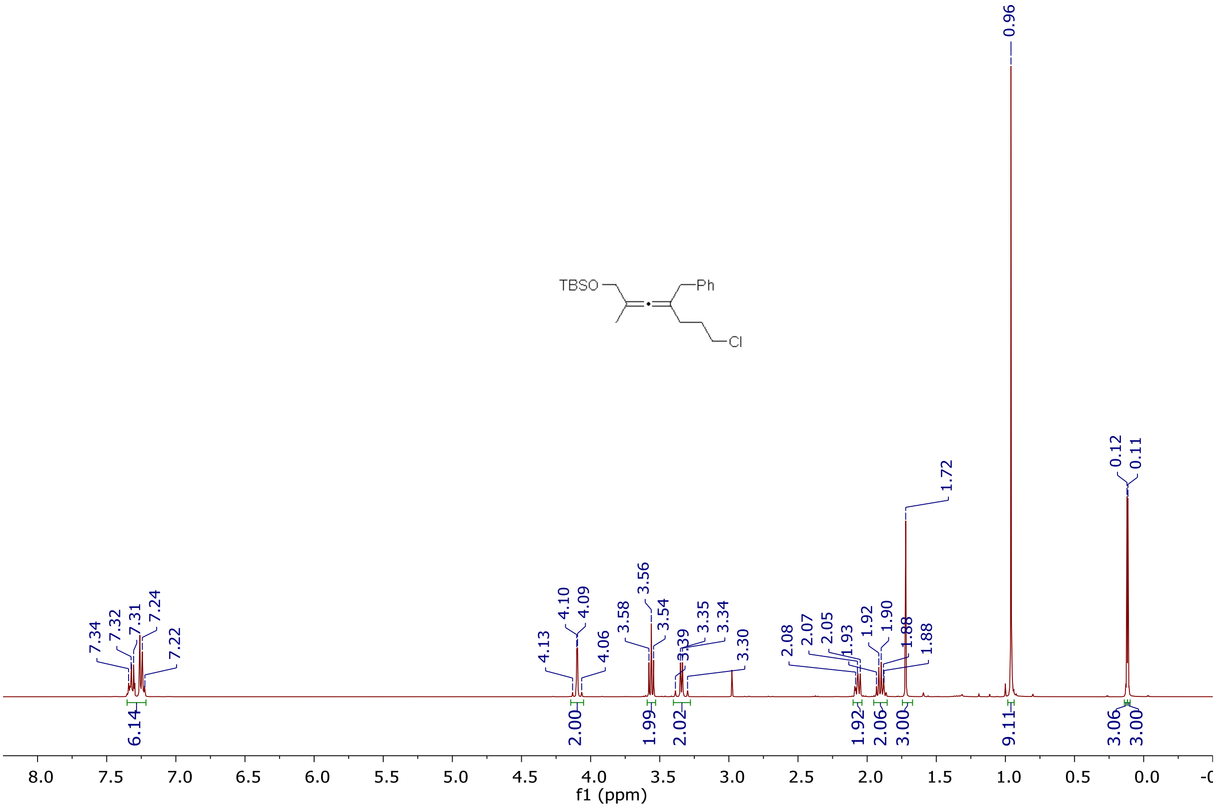
0
-
f1 (ppm)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Ph
Cl
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4.09
4.06
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3.35
3.34
3.30
2.08
2.07
2.05
1.93
1.92
1.90
1.88
1.88
1.72
0.96
0.12
0.11
6.14
2.00
1.99
2.02
1.92
2.06
3.00
9.11
3.06
3.00
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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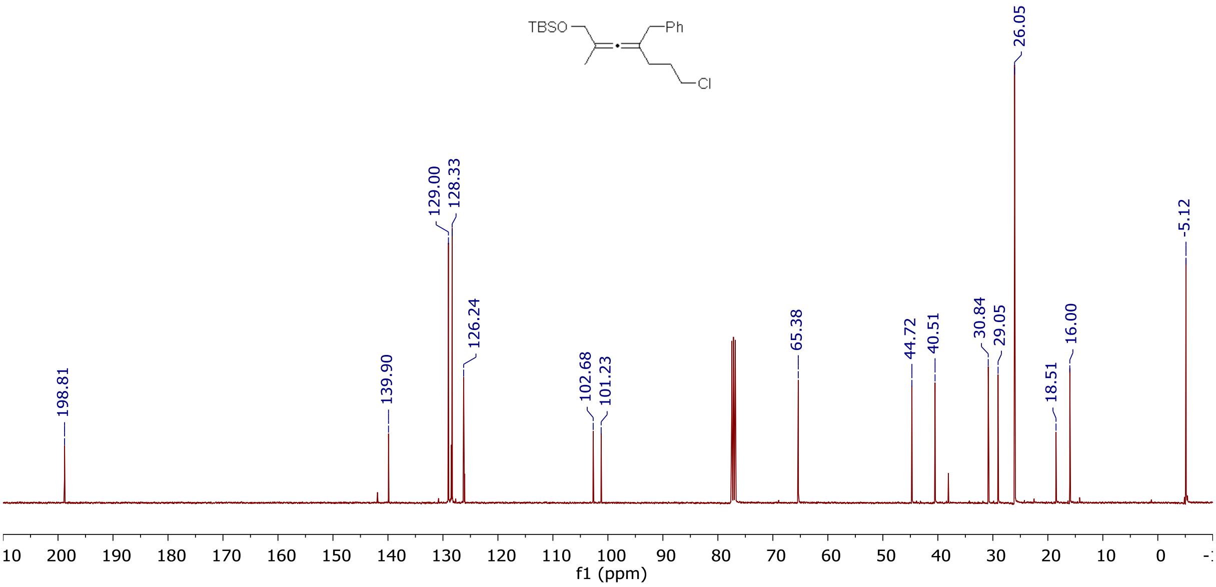
f1 (ppm)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Ph
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40.51
30.84
29.05
26.05
18.51
16.00
-5.12
10
200
190
180
170
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150
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130
120
110
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90
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50
40
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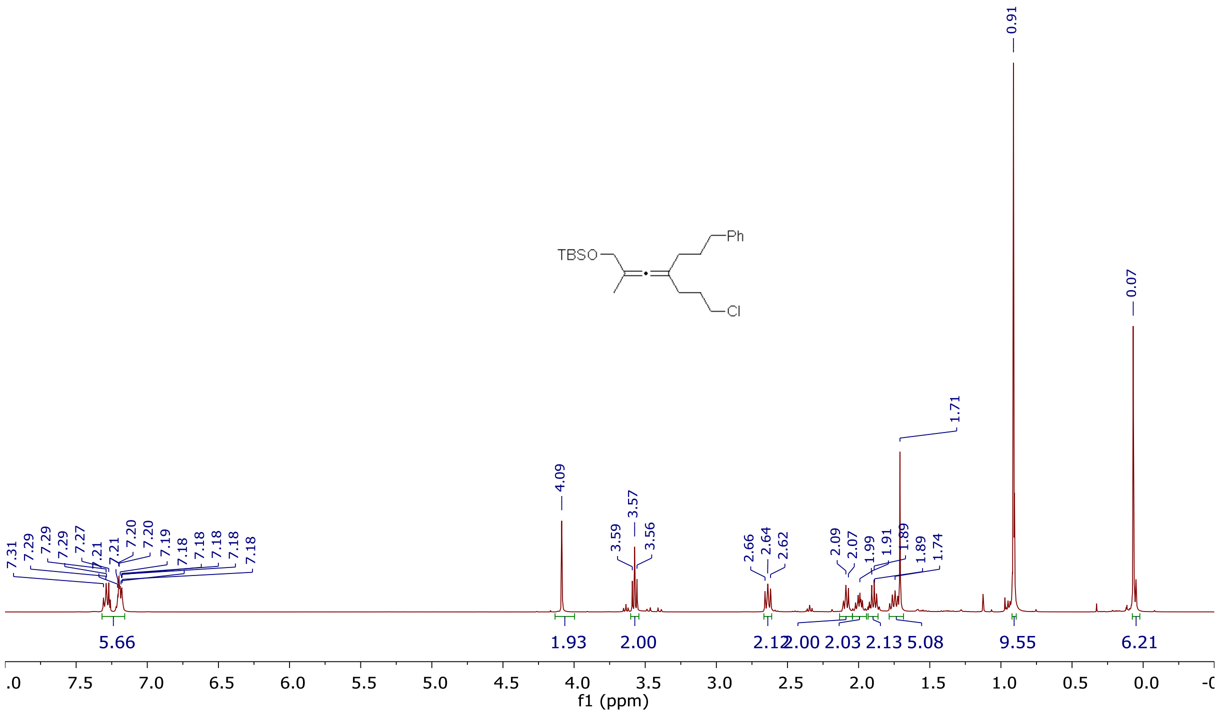
10
0
f1 (ppm)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Ph
Cl
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7.18
7.18
7.18
7.18
4.09
3.59
3.57
3.56
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2.64
2.62
2.09
2.07
1.99
1.91
1.89
1.89
1.74
1.71
0.91
0.07
5.66
1.93
2.00
2.12
2.00
2.03
2.13
5.08
9.55
6.21
.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
1.5
1.0
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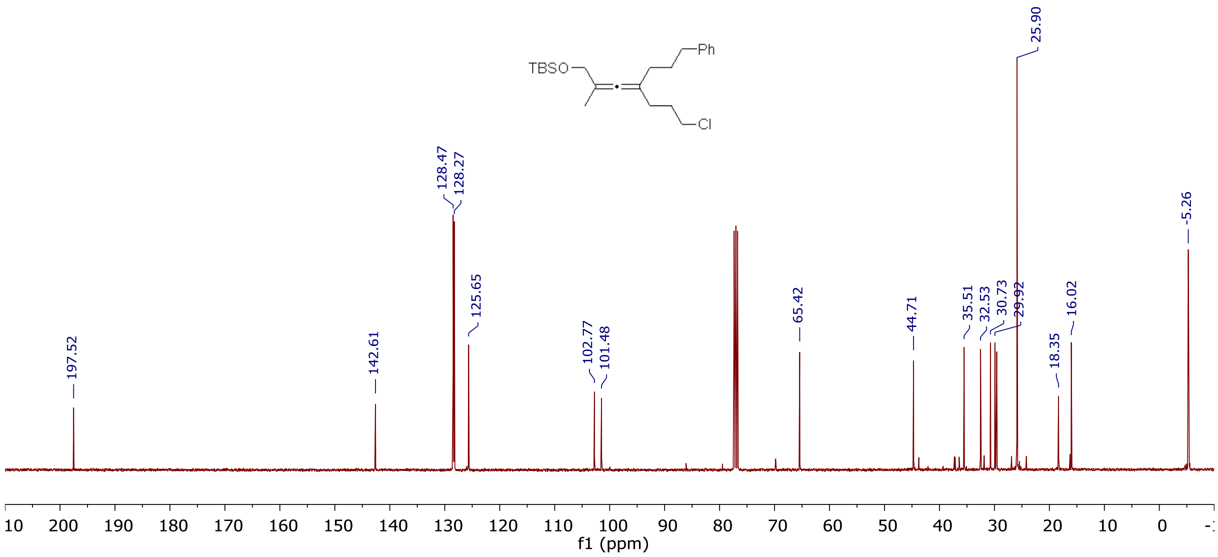
f1 (ppm)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Ph
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32.53
30.73
29.92
25.90
18.35
16.02
-5.26
10
200
190
180
170
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140
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120
110
100
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80
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30
20
10
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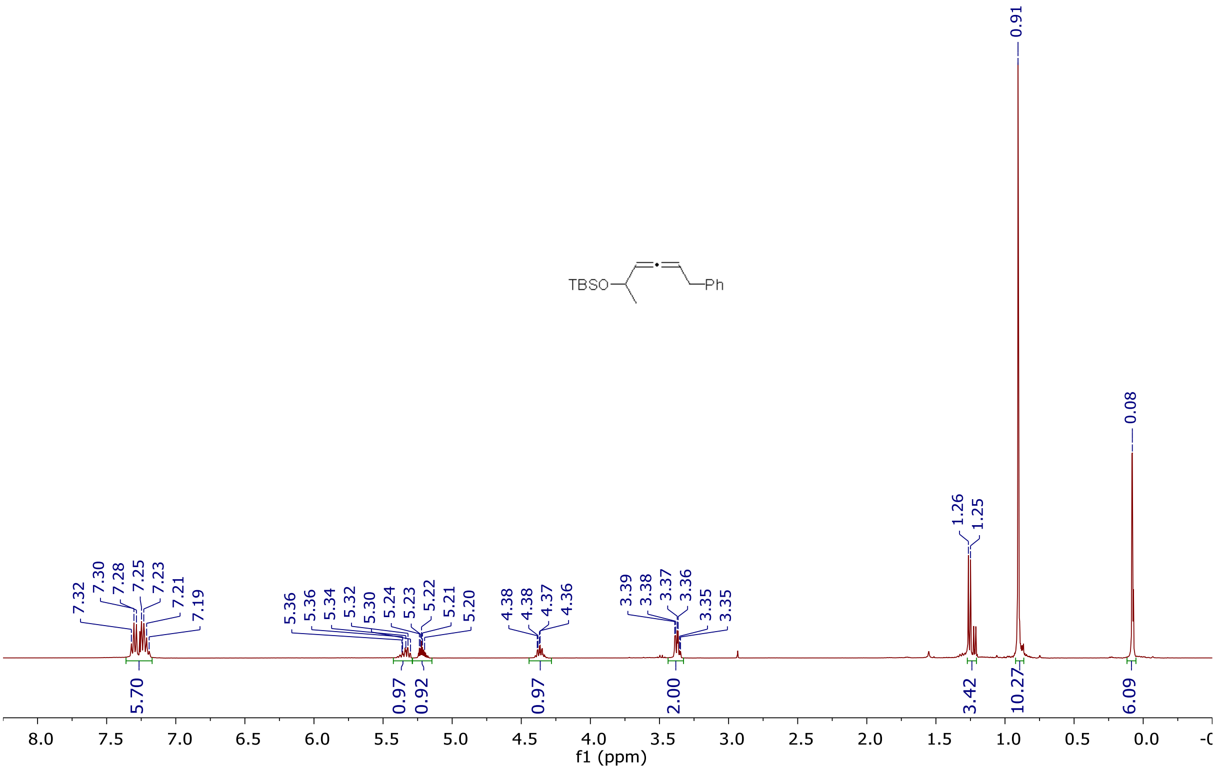
-:
f1 (ppm)


TBSO
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5.21
5.20
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4.38
4.37
4.36
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3.38
3.37
3.36
3.35
3.35
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1.25
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2.00
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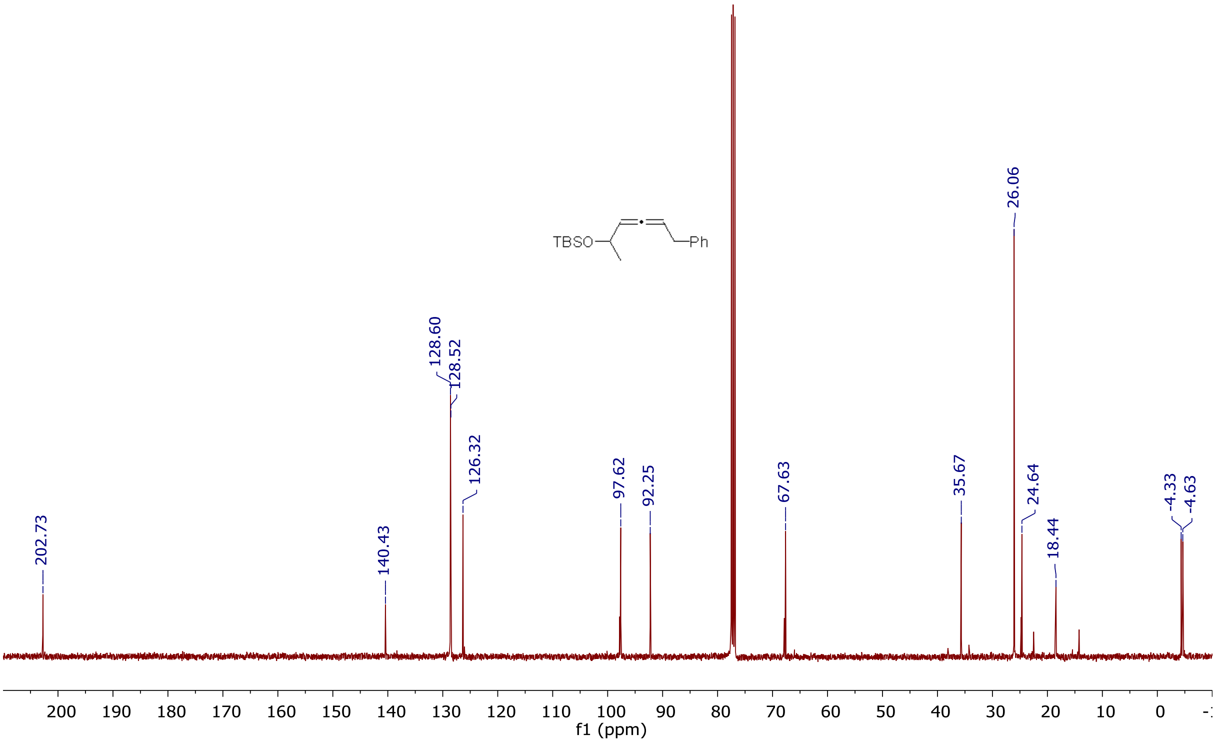
f1 (ppm)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35.67
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24.64
18.44
-4.33
-4.63
200
190
180
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100
90
80
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50
40
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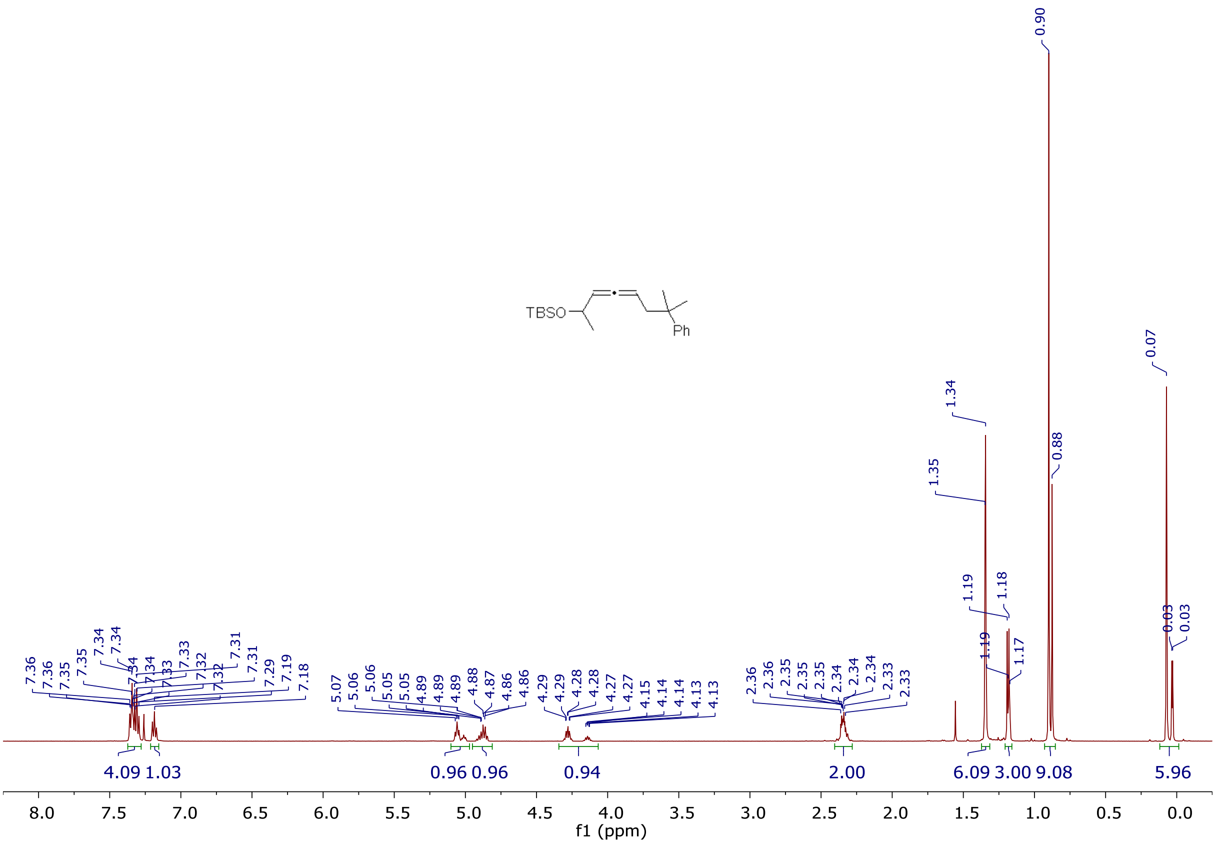
20
10
0
f1 (ppm)


TBSO
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5.05
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4.89
4.89
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4.86
4.86
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4.29
4.28
4.28
4.27
4.27
4.15
4.14
4.14
4.13
4.13
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1.19
1.19
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1.17
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0.88
0.07
0.03
0.03
4.09
1.03
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0.96
0.94
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6.09
3.00
9.08
5.96
8.0
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7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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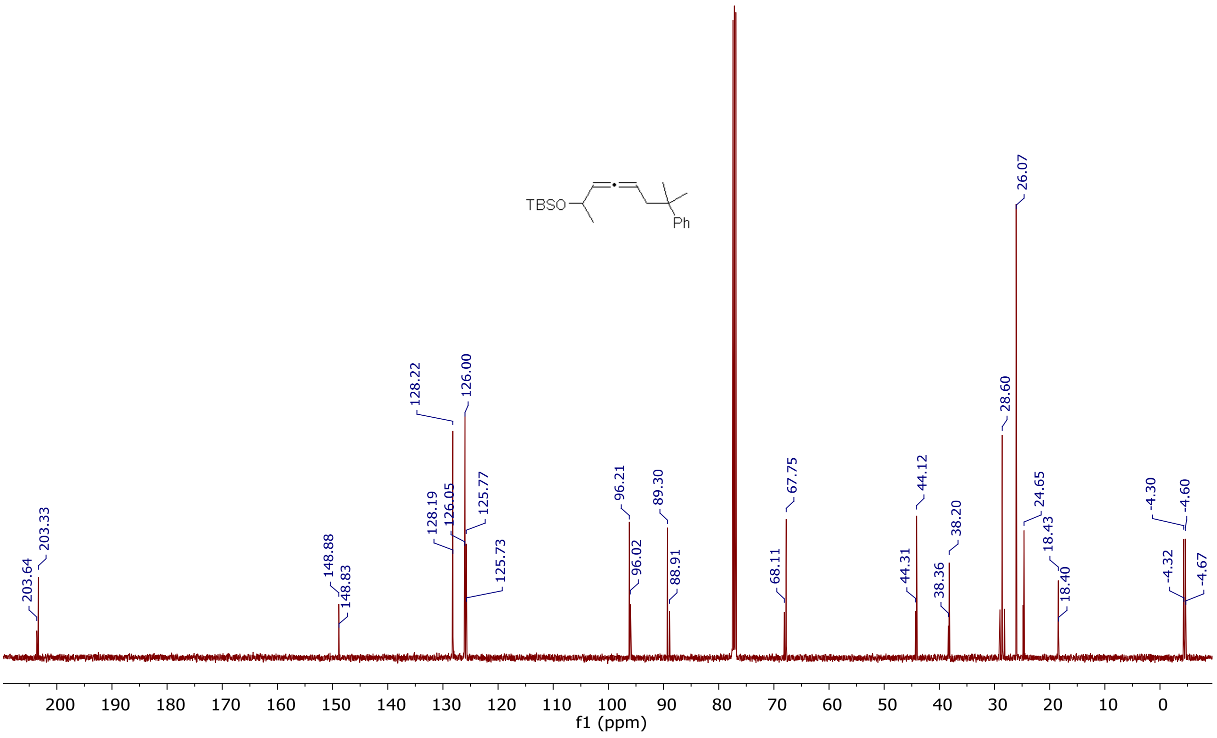
0.0
f1 (ppm)


TBSO
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126.00
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125.73
96.21
96.02
89.30
88.91
68.11
67.75
44.31
44.12
38.36
38.20
28.60
26.07
24.65
18.43
18.40
-4.30
-4.32
-4.60
-4.67
200
190
180
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130
120
110
100
90
80
70
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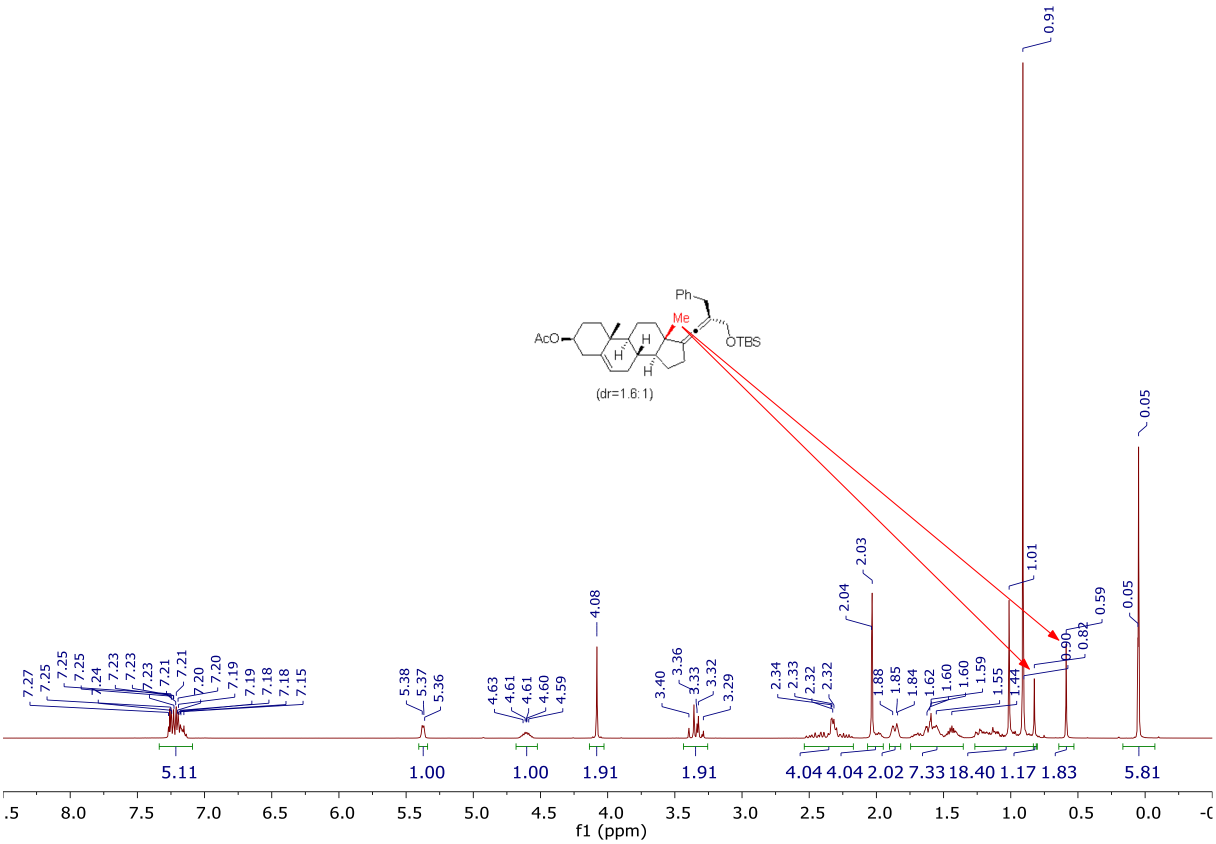
50
40
30
20
10
0
f1 (ppm)



AcO
H
H
H
Me
Ph
OTBS
(dr=1.6:1)
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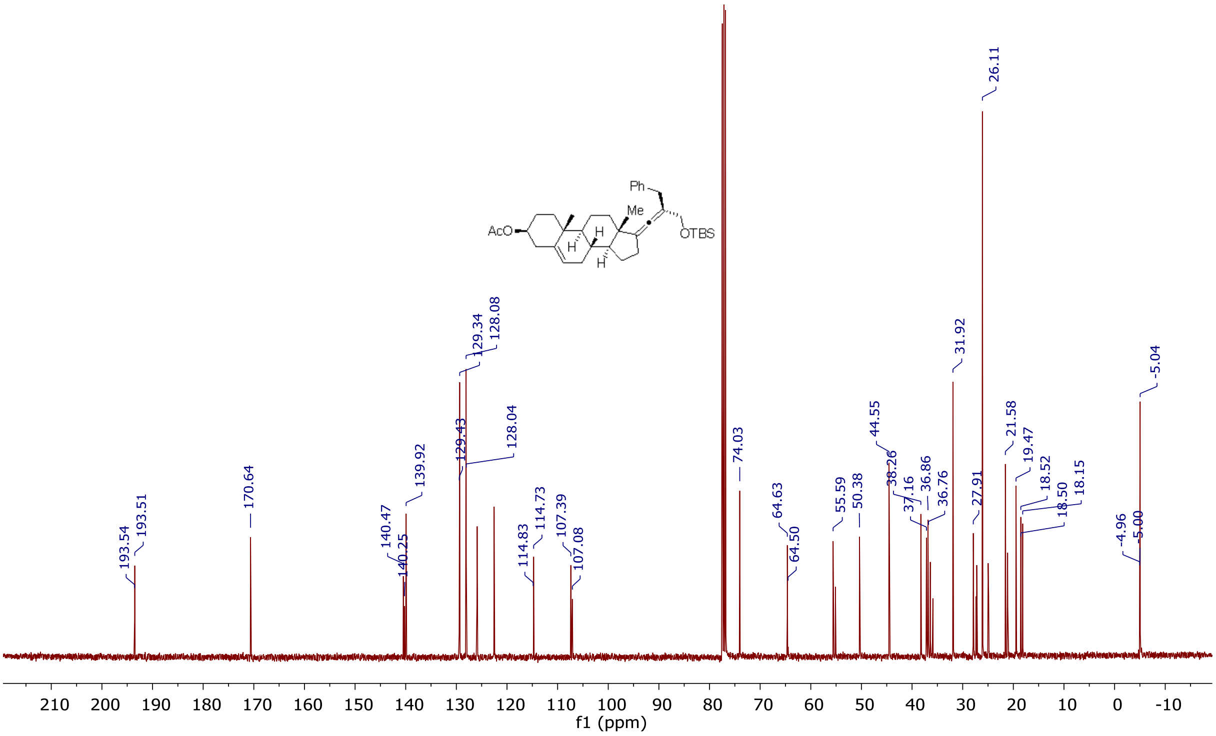
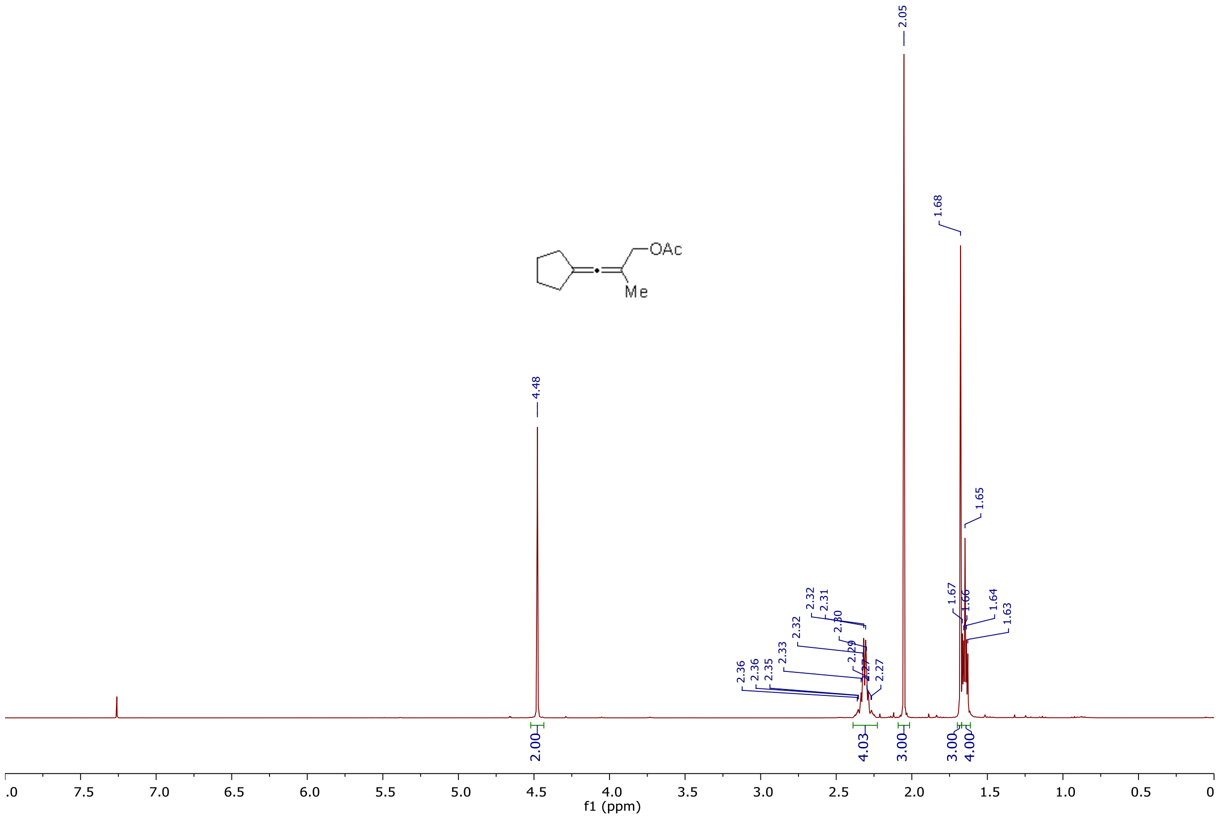
5.38 5.37 5.36
4.63 4.61 4.61 4.60 4.59
4.08
3.40 3.36 3.33 3.32 3.29
2.34 2.33 2.32 2.32
2.04 2.03
1.88 1.85 1.84 1.62 1.60 1.60 1.59 1.55 1.44
1.01 0.91 0.90 0.82 0.59 0.05 0.05
5.11 1.00 1.00 1.91 1.91 4.04 4.04 2.02 7.33 18.40 1.17 1.83 5.81
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)



AcO
H
H
Me
Ph
OTBS
193.54 193.51
170.64
140.47 140.25 139.92
129.43 129.34 128.08 128.04
114.83 114.73 107.39 107.08
74.03
64.63 64.50
55.59 50.38 44.55
38.26 37.16 36.86 36.76
31.92 27.91 26.11
21.58 19.47 18.52 18.50 18.15
-4.96 -5.00 -5.04
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)


OAc
Me
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2.32
2.32
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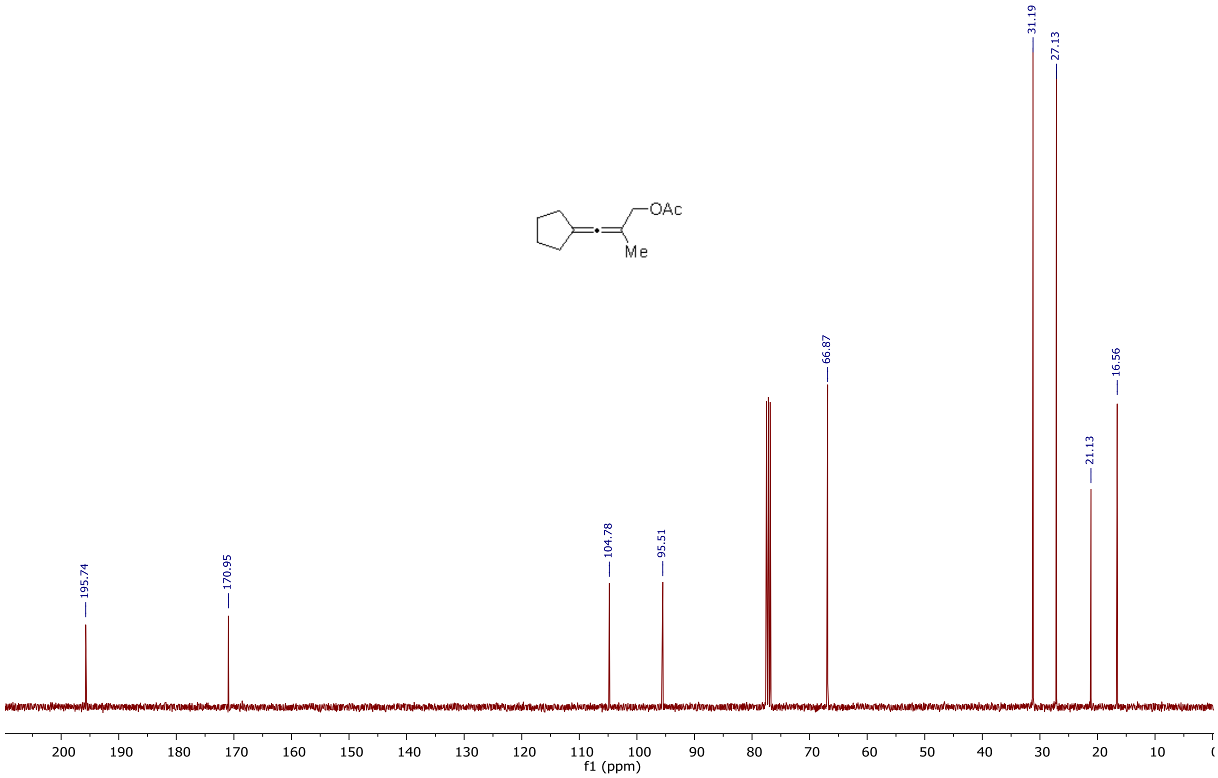
2.30
2.29
2.27
2.27
2.05
1.68
1.67
1.66
1.65
1.64
1.63
2.00
4.03
3.00
3.00
4.00
f1 (ppm)


OAc
Me
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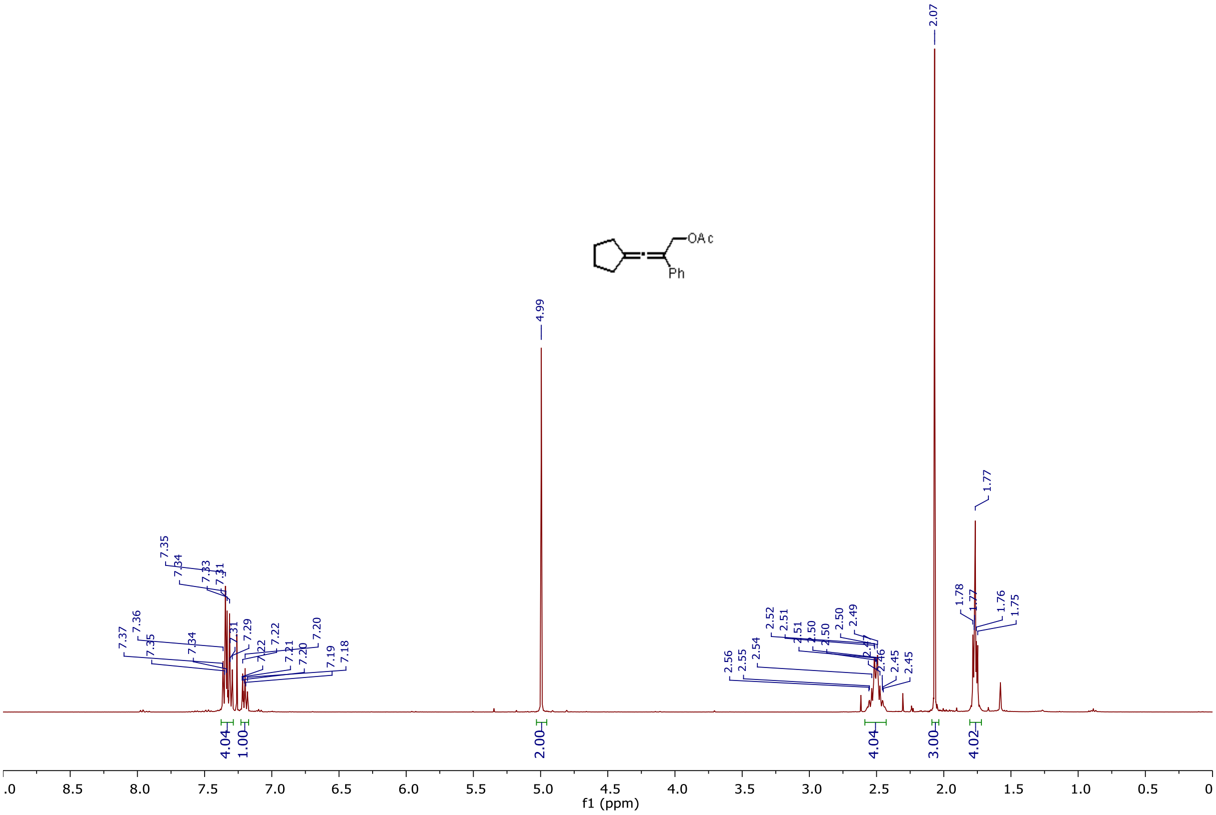
21.13
16.56
f1 (ppm)



OAc
Ph
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7.33
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7.31
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7.22
7.21
7.20
7.20
7.19
7.18
4.99
2.56
2.55
2.54
2.52
2.51
2.51
2.50
2.50
2.50
2.49
2.47
2.46
2.45
2.45
2.07
1.78
1.77
1.77
1.76
1.75
4.04
1.00
2.00
4.04
3.00
4.02
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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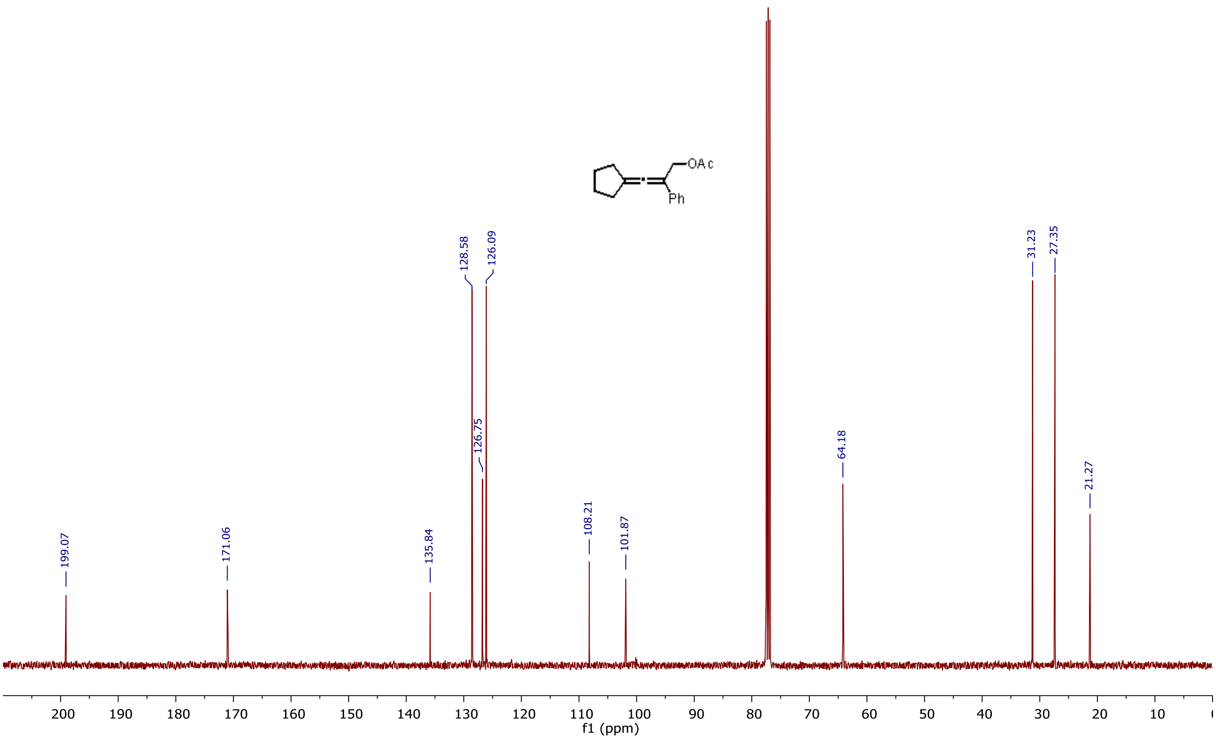
f1 (ppm)



OAc
Ph
199.07
171.06
135.84
128.58
126.75
126.09
108.21
101.87
64.18
31.23
27.35
21.27
200
190
180
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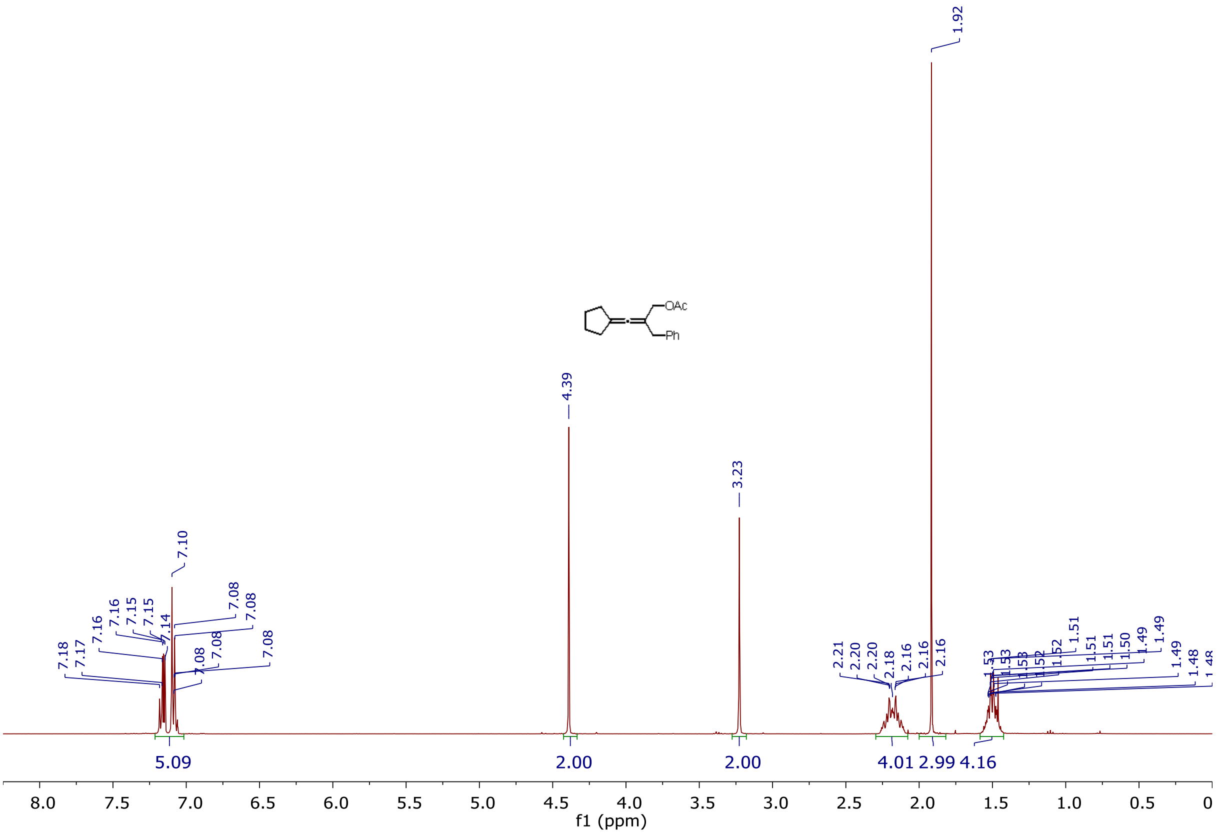
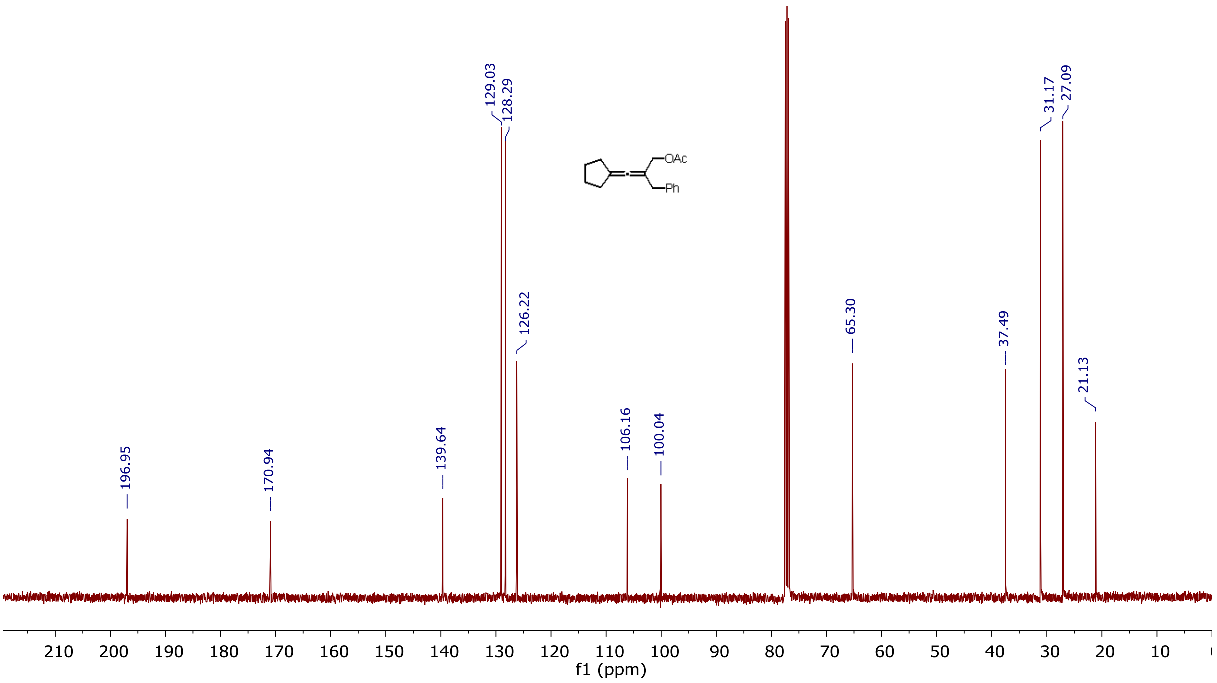
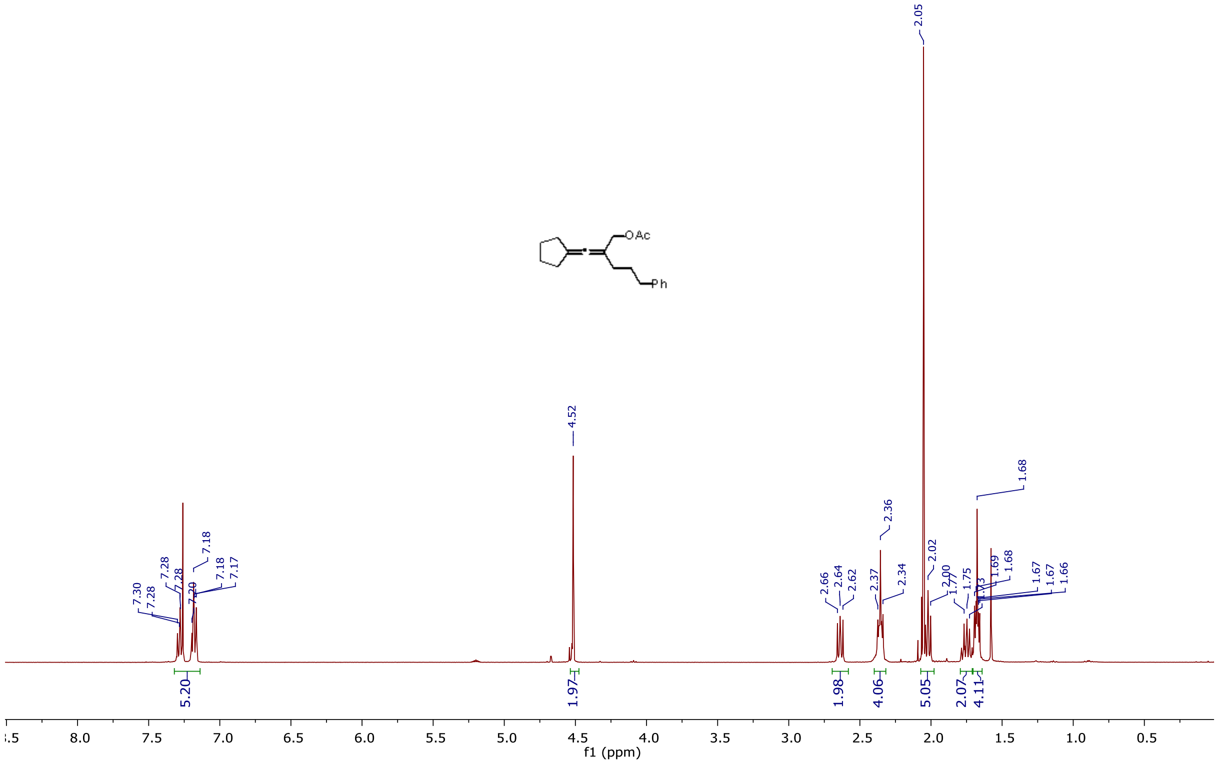
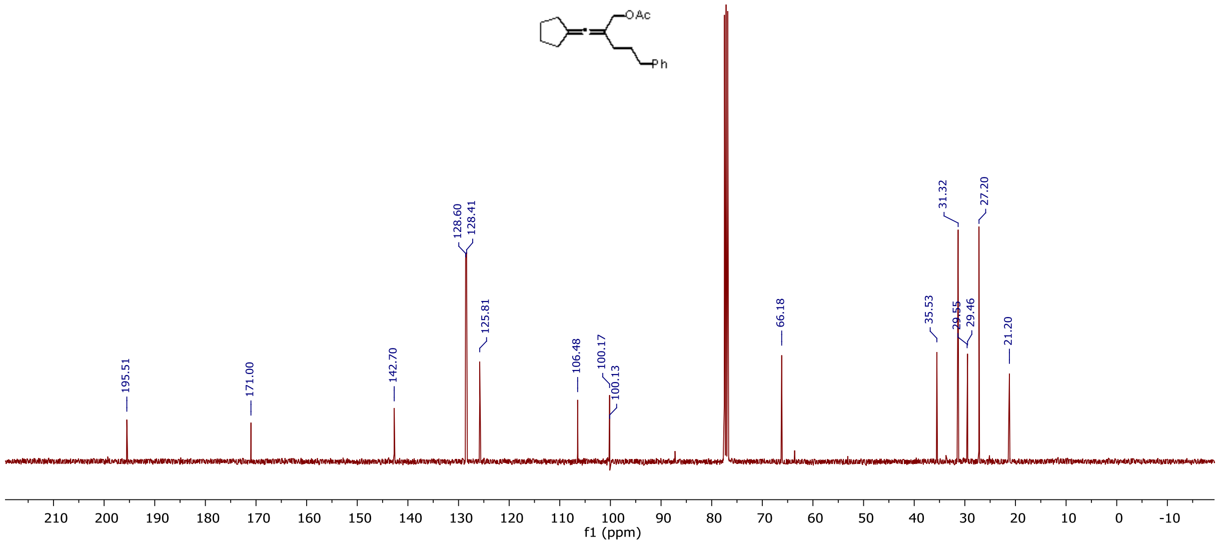
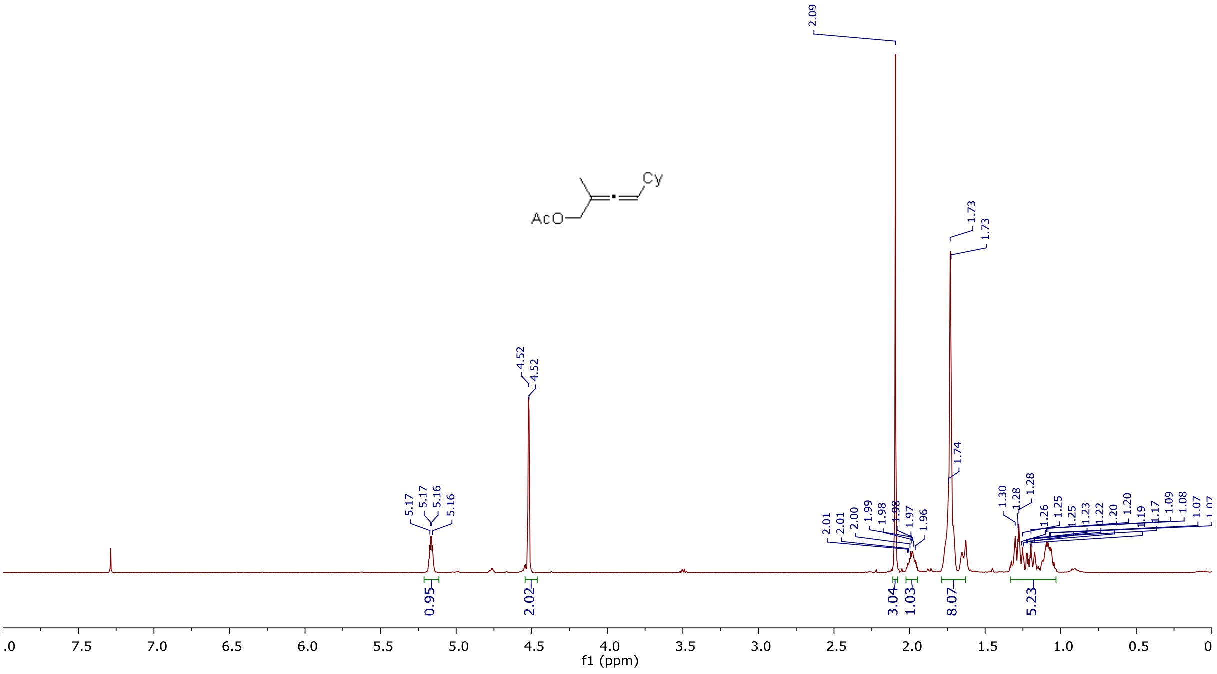
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

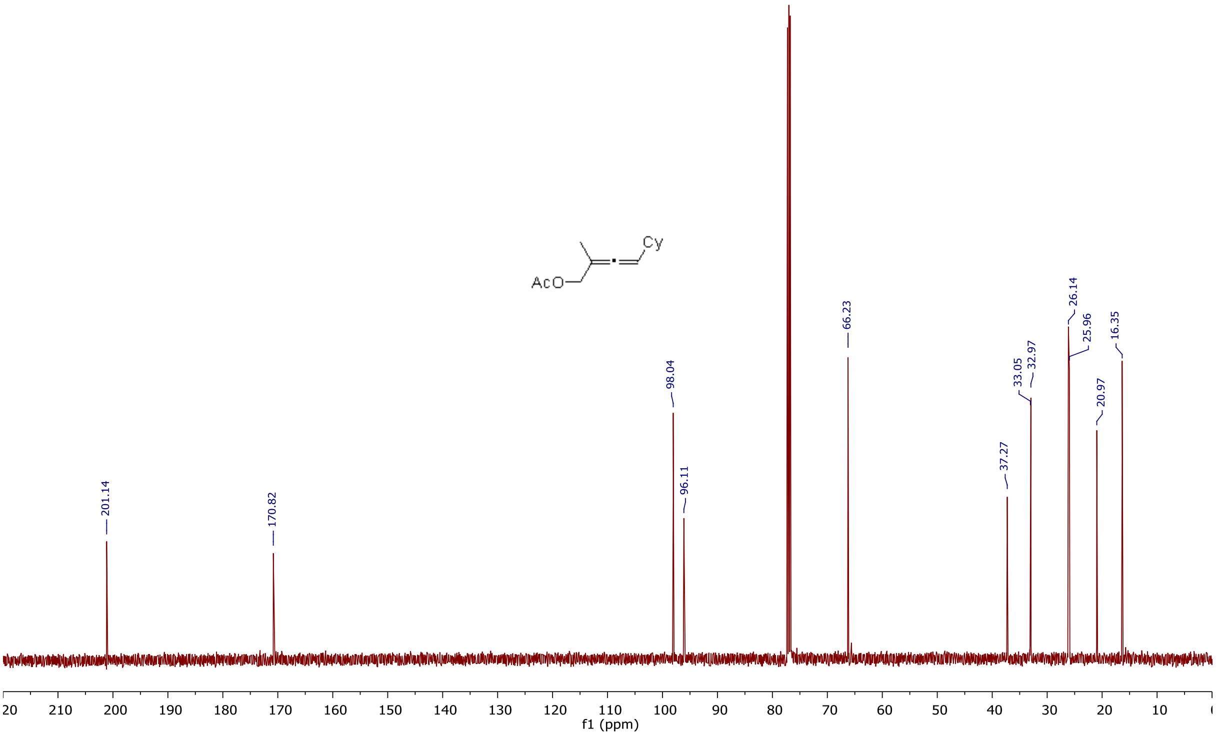

OAc
Ph
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.10
7.08
7.08
7.08
7.08
4.39
3.23
2.21
2.20
2.20
2.18
2.16
2.16
2.16
1.92
1.53
1.53
1.53
1.52
1.52
1.51
1.51
1.51
1.50
1.49
1.49
1.49
1.48
1.48
5.09
2.00
2.00
4.01
2.99
4.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

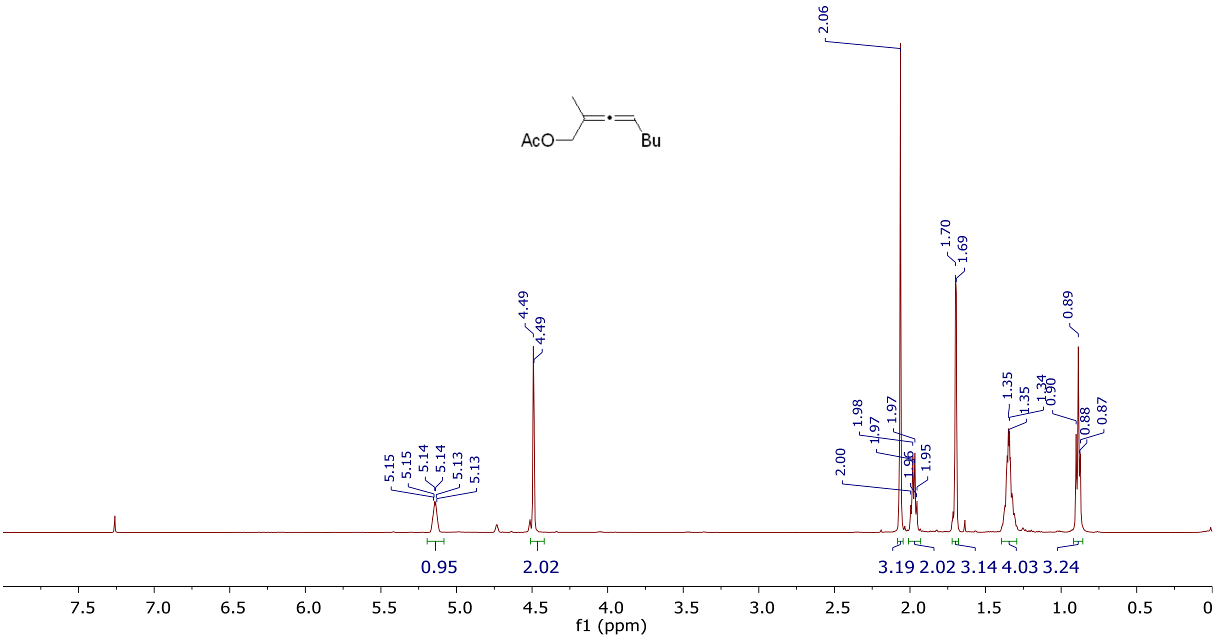

OAc
Ph
196.95
170.94
139.64
129.03
128.29
126.22
106.16
100.04
65.30
37.49
31.17
27.09
21.13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

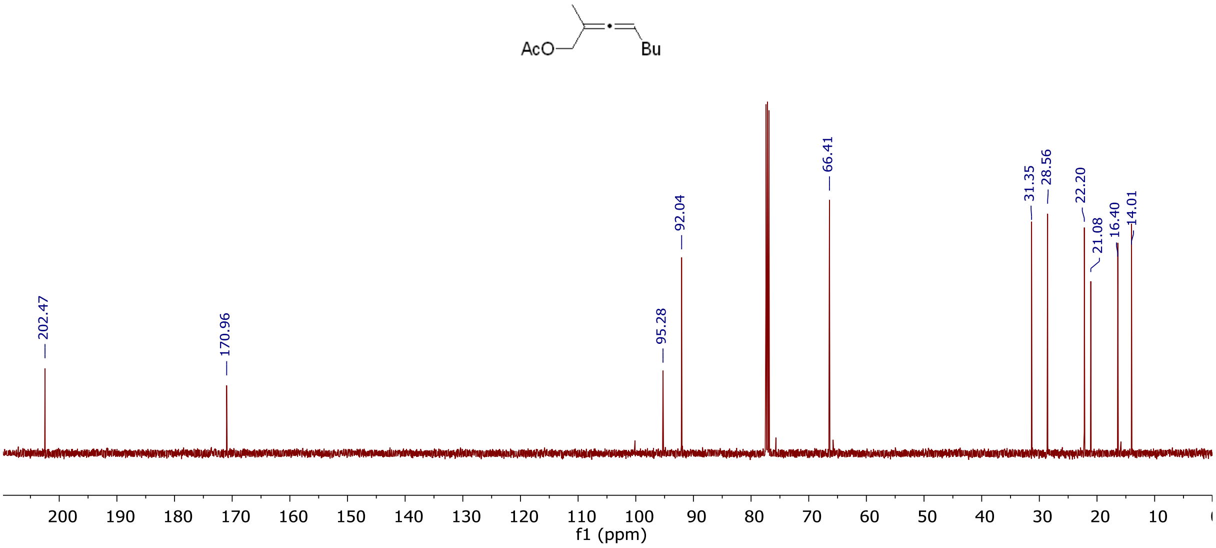

OAc
Ph
7.30
7.28
7.28
7.28
7.20
7.18
7.18
7.17
4.52
2.66
2.64
2.62
2.37
2.36
2.34
2.05
2.02
2.00
1.77
1.75
1.73
1.69
1.68
1.68
1.67
1.67
1.66
5.20
1.97
1.98
4.06
5.05
2.07
4.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

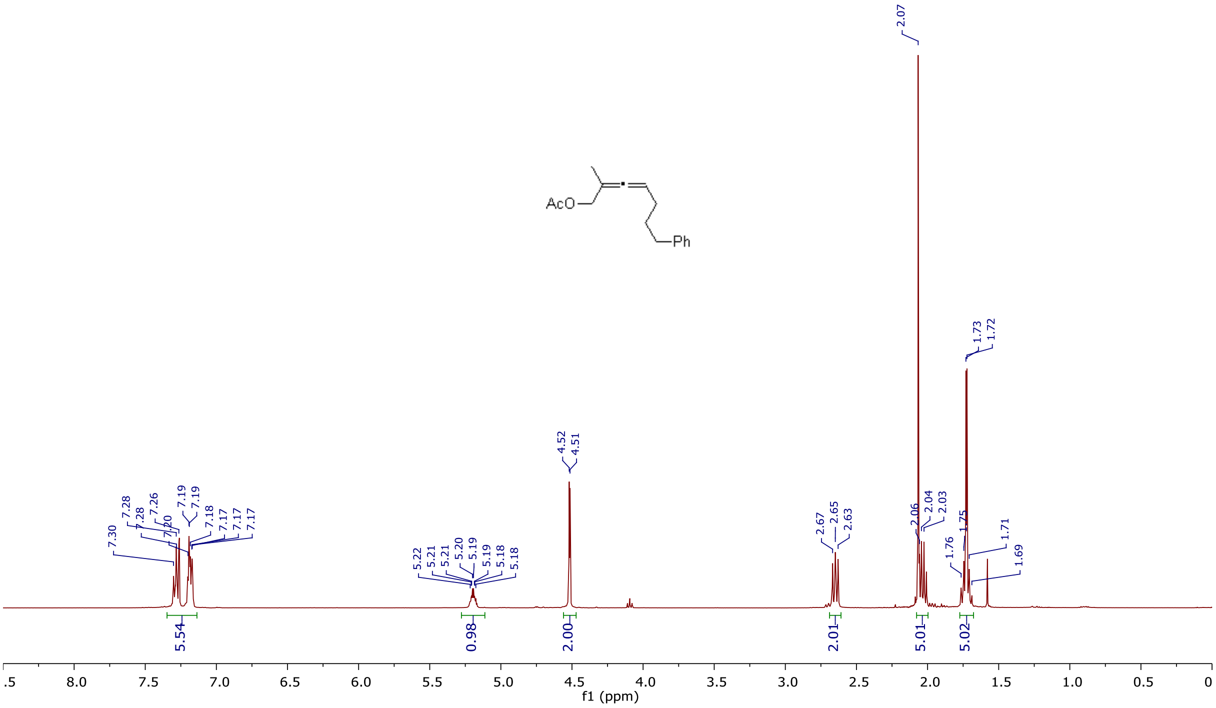

OAc
Ph
195.51
171.00
142.70
128.60
128.41
125.81
106.48
100.17
100.13
66.18
35.53
31.32
29.55
29.46
27.20
21.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

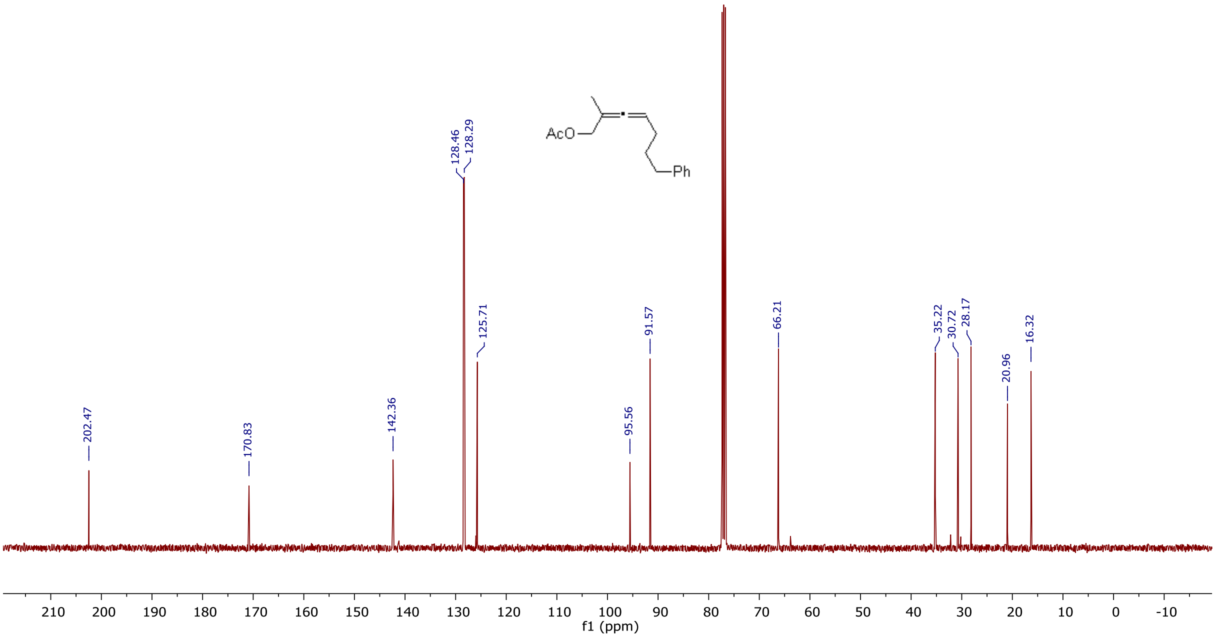

AcO
Cy
2.09
1.73
1.73
4.52
4.52
1.74
5.17
5.17
5.16
5.16
2.01
2.01
2.00
1.99
1.98
1.98
1.97
1.96
1.30
1.28
1.28
1.26
1.25
1.25
1.23
1.22
1.20
1.20
1.19
1.17
1.09
1.08
1.07
1.07
0.95
2.02
3.04
1.03
8.07
5.23
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

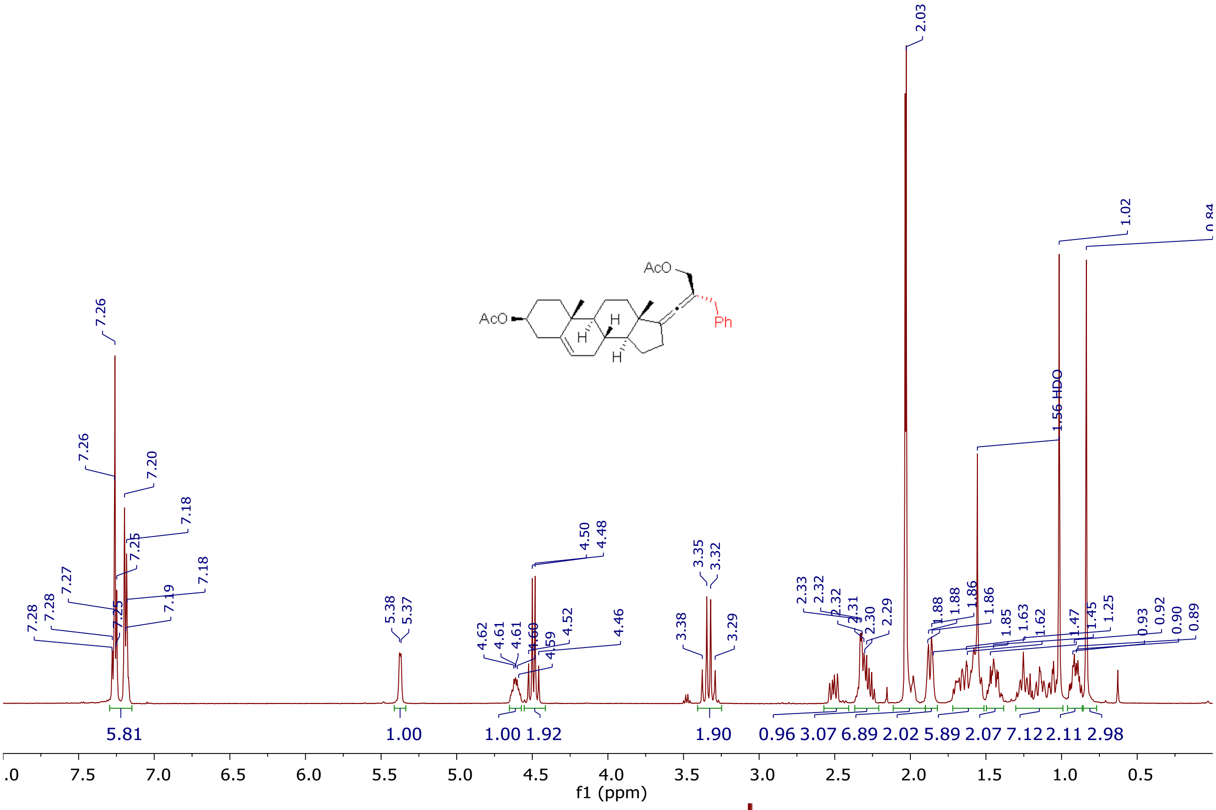

AcO
Cy
201.14
170.82
98.04
96.11
66.23
37.27
33.05
32.97
26.14
25.96
20.97
16.35
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

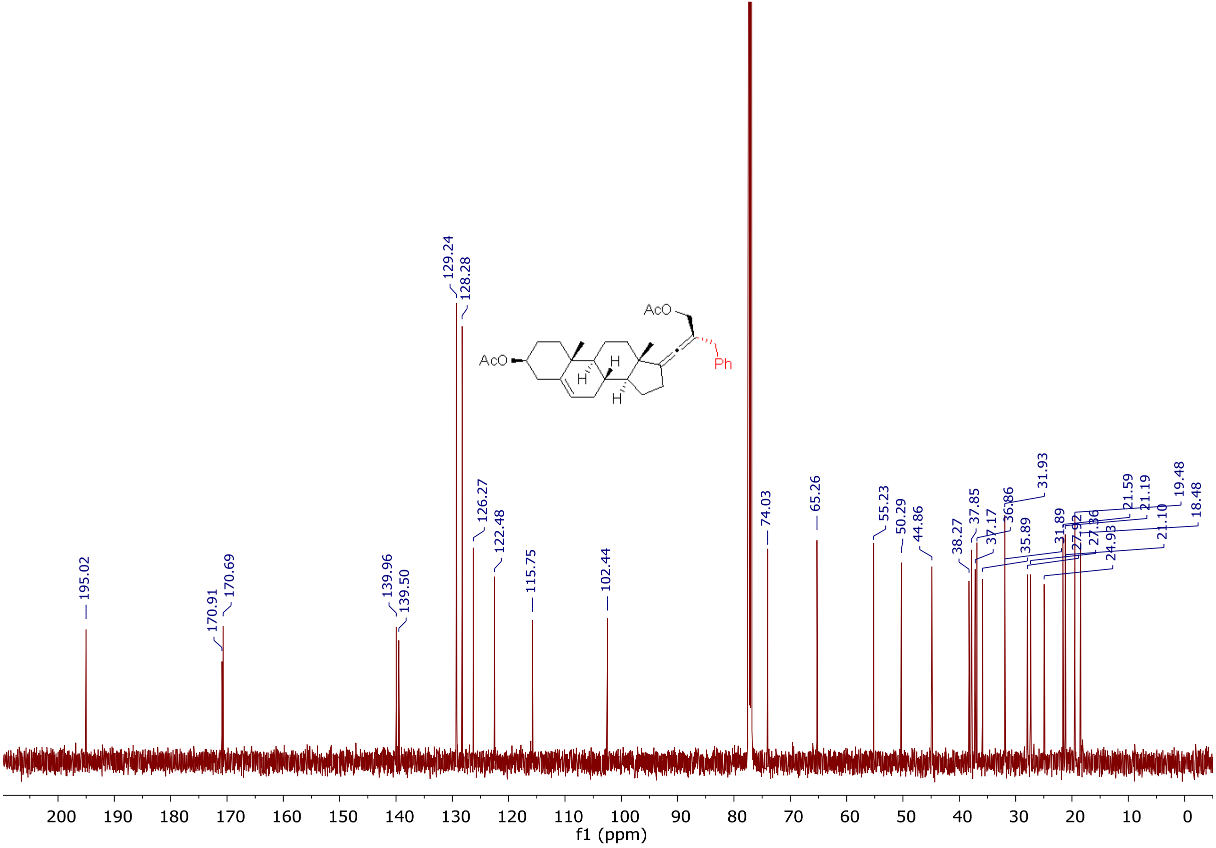

AcO
Bu
2.06
1.70
1.69
4.49
4.49
0.89
1.35
1.35
1.34
0.90
1.98
1.97
1.97
0.88
0.87
2.00
1.96
1.95
5.15
5.15
5.14
5.14
5.13
5.13
0.95
2.02
3.19
2.02
3.14
4.03
3.24
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

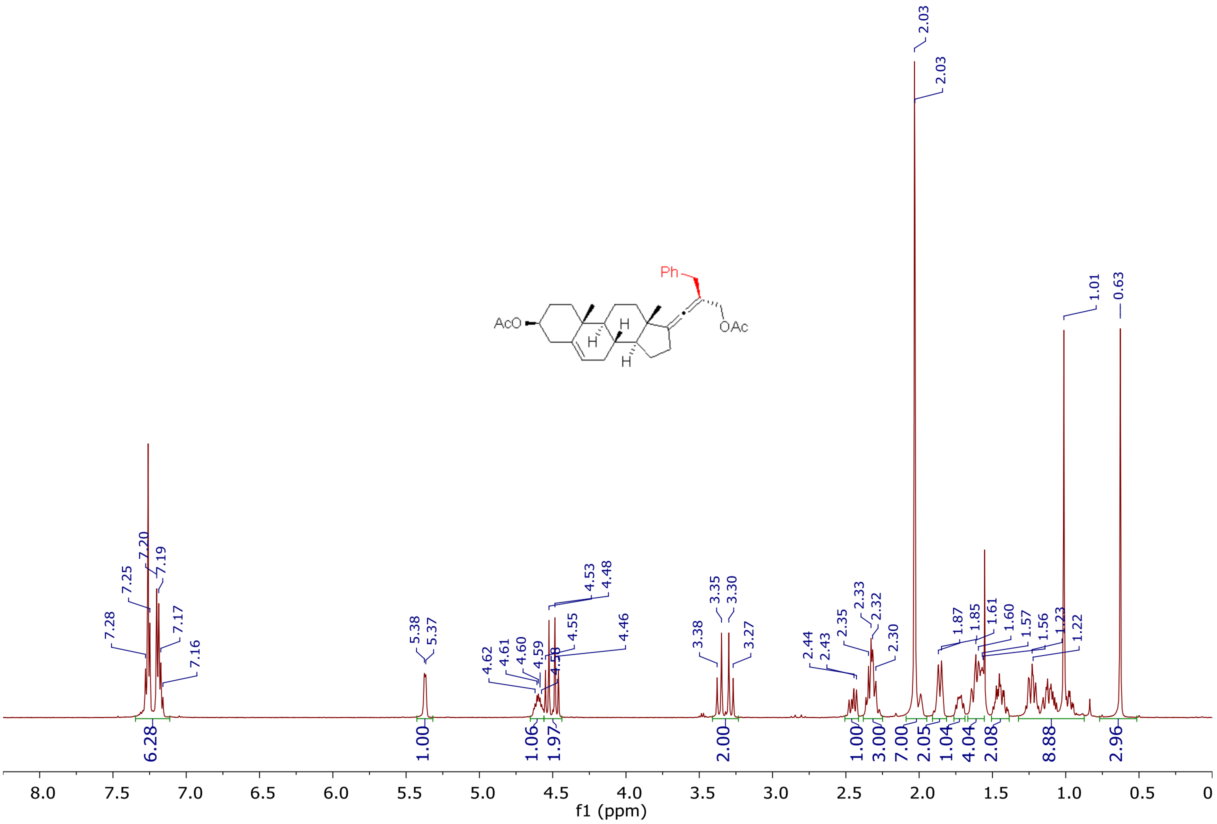

AcO
Bu
202.47
170.96
95.28
92.04
66.41
31.35
28.56
22.20
21.08
16.40
14.01
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

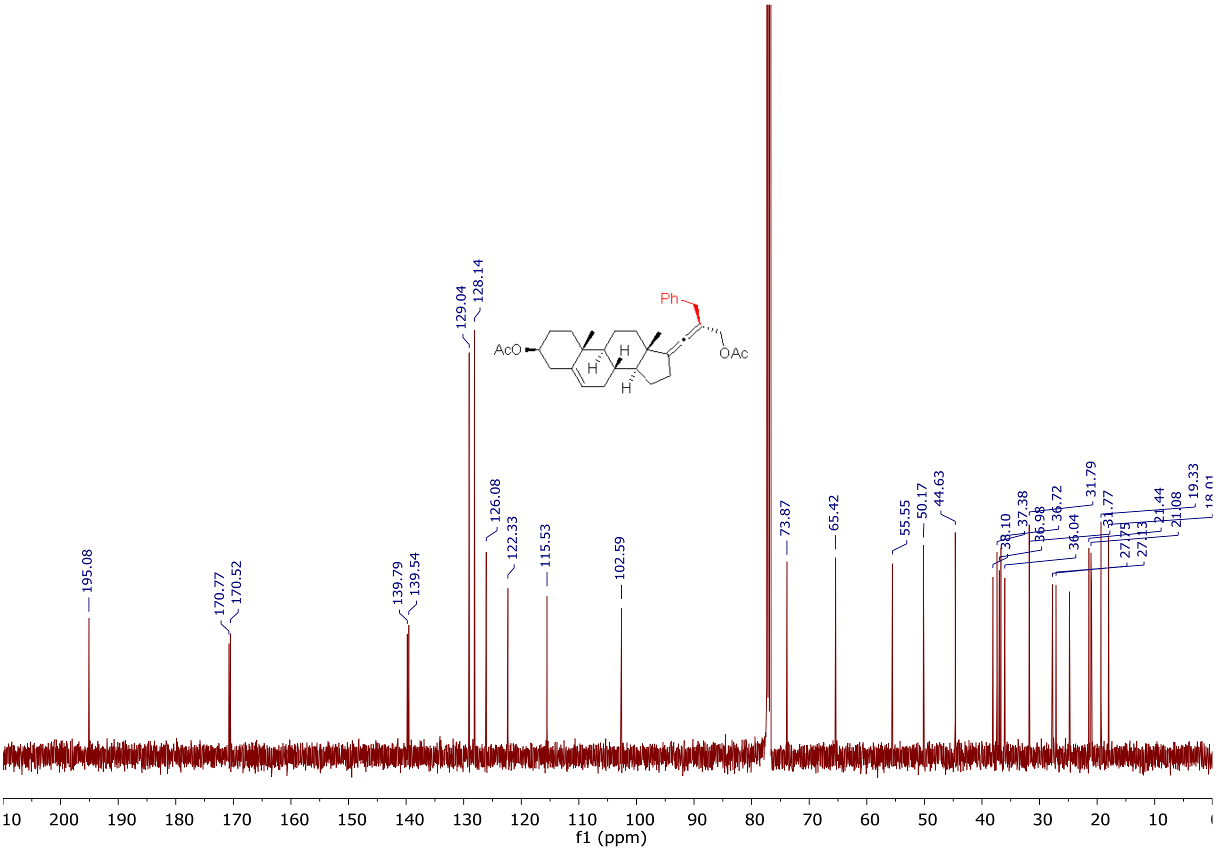

AcO
Ph
2.07
1.73
1.72
4.52
4.51
7.30
7.28
7.28
7.26
7.20
7.19
7.19
7.18
7.17
7.17
7.17
5.22
5.21
5.21
5.20
5.19
5.19
5.18
5.18
2.67
2.65
2.63
2.06
2.04
2.03
1.76
1.75
1.71
1.69
5.54
0.98
2.00
2.01
5.01
5.02
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


AcO
Ph
202.47
170.83
142.36
128.46
128.29
125.71
95.56
91.57
66.21
35.22
30.72
28.17
20.96
16.32
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)


AcO
AcO
H
H
H
Ph
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.20
7.19
7.18
7.18
5.38
5.37
4.62
4.61
4.61
4.60
4.59
4.52
4.50
4.48
4.46
3.38
3.35
3.32
3.29
2.33
2.32
2.32
2.31
2.30
2.29
1.88
1.88
1.86
1.86
1.85
1.63
1.62
1.56 HDO
1.47
1.45
1.25
1.02
0.93
0.92
0.90
0.89
0.84
5.81
1.00
1.00
1.92
1.90
0.96
3.07
6.89
2.02
5.89
2.07
7.12
2.11
2.98
.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
f1 (ppm)


AcO
AcO
H
H
H
Ph
195.02
170.91
170.69
139.96
139.50
129.24
128.28
126.27
122.48
115.75
102.44
74.03
65.26
55.23
50.29
44.86
38.27
37.85
37.17
36.86
35.89
31.93
31.89
27.92
27.36
24.93
21.59
21.19
21.10
19.48
18.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
AcO
H
H
H
OAc
7.28
7.25
7.20
7.19
7.17
7.16
5.38
5.37
4.62
4.61
4.60
4.59
4.58
4.55
4.53
4.48
4.46
3.38
3.35
3.30
3.27
2.44
2.43
2.35
2.33
2.32
2.30
2.03
2.03
1.87
1.85
1.61
1.60
1.57
1.56
1.23
1.22
1.01
0.63
6.28
1.00
1.06
1.97
2.00
1.00
3.00
7.00
2.05
1.04
4.04
2.08
8.88
2.96
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
f1 (ppm)


Ph
AcO
H
H
OAc
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170.52
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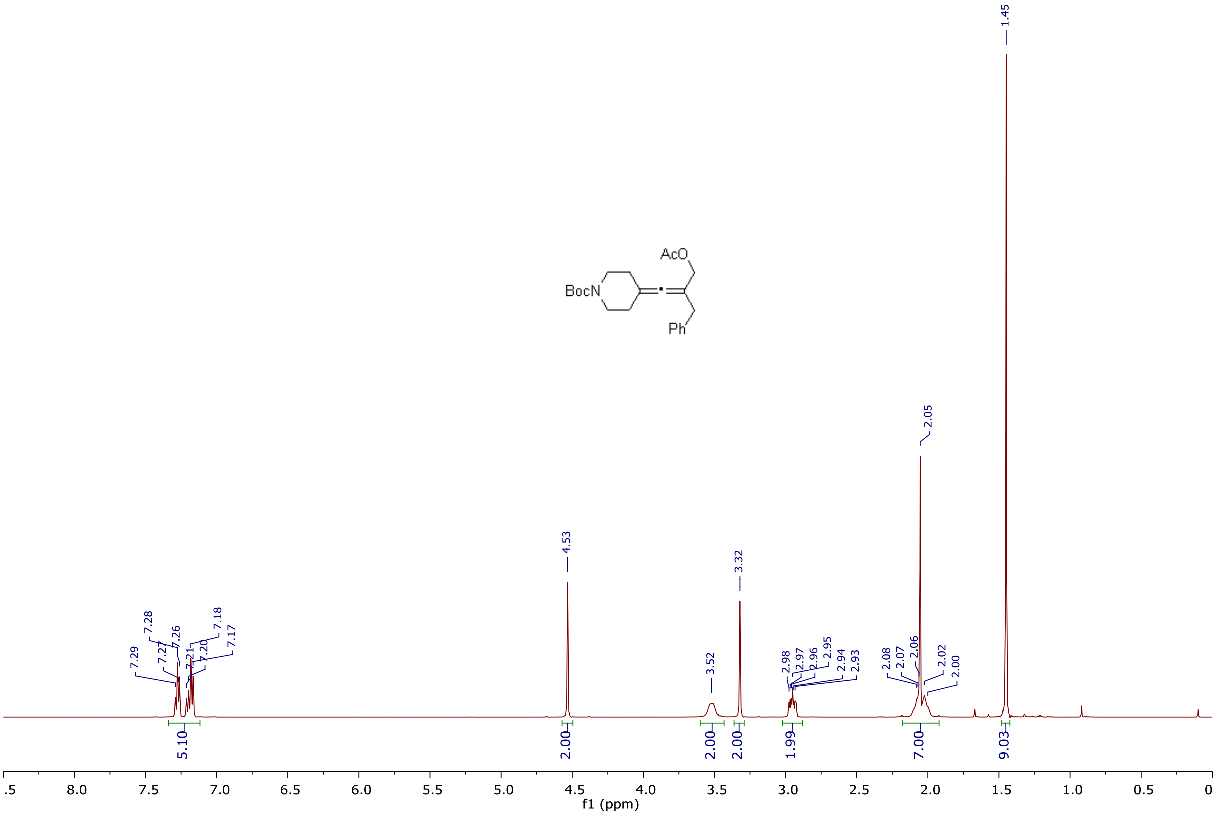
139.54
129.04
128.14
126.08
122.33
115.53
102.59
73.87
65.42
55.55
50.17
44.63
38.10
37.38
36.98
36.72
36.04
31.79
31.77
27.75
27.13
21.44
21.08
19.33
18.01
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


AcO
BocN
Ph
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7.28
7.27
7.26
7.21
7.20
7.18
7.17
4.53
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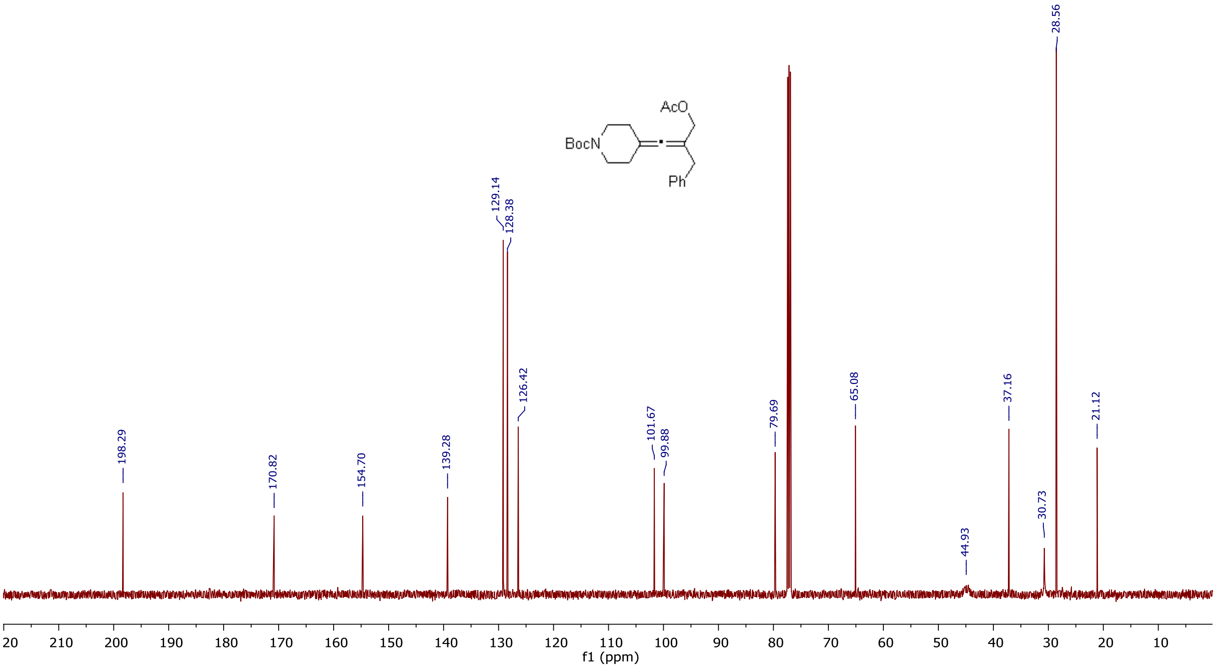
3.32
2.98
2.97
2.96
2.95
2.94
2.93
2.08
2.07
2.06
2.05
2.02
2.00
1.45
5.10
2.00
2.00
2.00
1.99
7.00
9.03
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


AcO
BocN
Ph
198.29
170.82
154.70
139.28
129.14
128.38
126.42
101.67
99.88
79.69
65.08
44.93
37.16
30.73
28.56
21.12
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)