Supplementary data for the article:

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Cyclization reactions of oxyallyl cation. A method for cyclopentane ring formation

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Supporting Information

Table of Contents

General experimental details

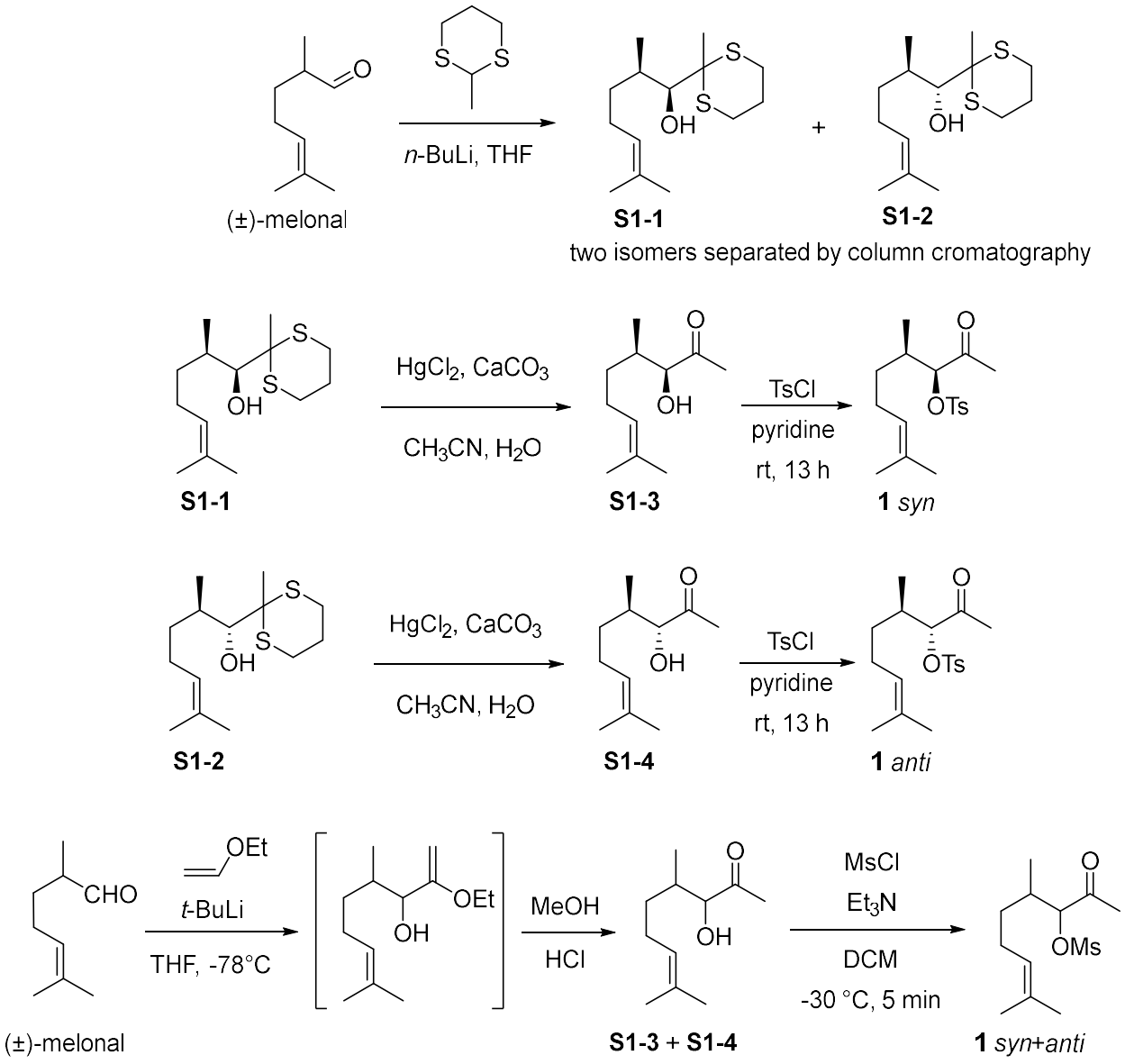
All chromatographic separations[1] were performed on Silica, 10-18, 60Å, ICN Biomedicals and Merck Silica gel 60 (0.063-0.200 mm) (70-230 mesh ASTM). Standard techniques were used for the purification of reagents and solvents.[2] Petroleum-ether refers to the fraction boiling at 70–72 °C. For all reactions that required heating, oil bath was used as the heat source. NMR spectra were recorded on a Varian Gemini 200, (^{1}H NMR at 200 MHz, ^{13}C NMR at 50 MHz, and on a Bruker Avance III 500 (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz). Chemical shifts are expressed in ppm (δ) using tetramethylsilane as internal standard, coupling constants (*J)* are in Hz. Gas chromatography (GC) and gas chromatography coupled to low resolution mass spectrometry (GC–MS) analysis were performed on two different instruments. Agilent Technologies 7890A instrument, using HP-5MSI capillary column (length: 30 m; diam. 0.25 mm; film: 0.25 μ) and using He gas as carrier. GC was equipped with an FID detector. GC–MS was performed on Agilent Technologies 5975C Inert XL EI/CI MSD quadrupole detector. Shimadzu GCMS-QP2010 Ultra instrument, a comprehensive two dimensional gas chromatograph – quadrupole mass spectrometer (GC×GC-qMS) with ZX2 thermal modulation system, using RtxR-1 (first column: RESTEK, CrossbondR 100% dimethyl polysiloxane, 30 m, 0.25 mm ID, df=0.25 μm) and a BPX50 (SGE Analytical Science, 1 m, 0.1 mm ID, df=0.1 μm) columns (columns were connected through the GC×GC modulator as the first and second capillary columns, and samples were analysed without modulation). IR spectra were recorded on a Nicolet 6700 FT instrument, and are expressed in cm^{-1}. Mass spectra were obtained on Agilent technologies 6210 TOF LC/MS instrument (LC: series 1200) and LTQ Orbitrap XL hybrid FTMS (Thermo Scientific). Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

[1] For description of the technique of dry-flash chromatography, see: a) Harwood, L. M. *Aldrichimica Acta* **1985**, *18*, 25; b) *Vogel's Textbook of Practical Organic Chemistry*, Longman Scientific&Technical, 5th edition, London, 1989, p. 220; c) A recent account which includes some improvements of the separation technique: Pedersen, D. S.; Rosenbohm, C. *Synthesis* **2001**, 2431.

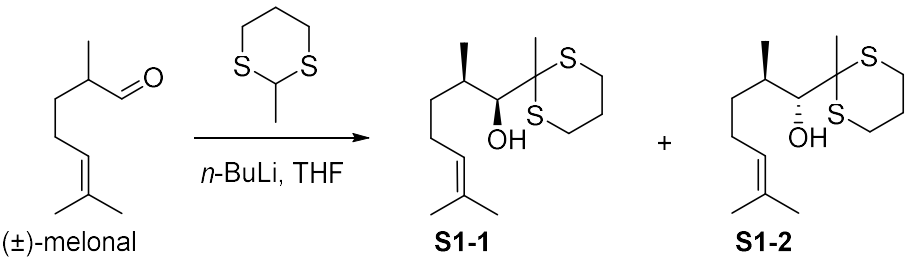
[2] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd edition, Pergamon Press, **1988**.

1. Preparation of precursors

Scheme S1: Preparation of precursor 1



2,6-Dimethyl-1-(2-methyl-1,3-dithian-2-yl)hept-5-en-1-ol, *syn* and *anti* (S1-1 and S1-2)[3]



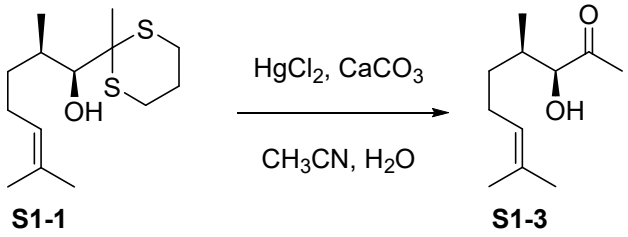
To a solution of 1,3-dithiane[3] (0.4 mL, 3.34 mmol, 1 eq) in THF (6.7 mL) was added *n*-BuLi in hexane (2.15 M, 1.8 mL, 3.87 mmol, 1.16 eq), with stirring at –78 °C, under an argon atmosphere. The mixture was allowed to warm to 0 °C within 1 h, cooled down to –78 °C again, and 2,6-dimethyl-5-heptenal (0.7 mL, 4.25 mmol, 1.27 eq) was added dropwise. The reaction mixture was allowed to warm to room temperature within 3 h and then quenched by the addition of water. The aqueous layer was extracted with CH_2Cl_2. The combined organic extract was washed with water, KOH (7%) and water, dried over anh. $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by dry flash chromatography (petroleum-ether/ethyl acetate = 95/5) followed by column chromatography (petroleum-ether/ethyl acetate = 95/5) to afford 503 mg (55%) of 2,6-dimethyl-1-(2-methyl-1,3-dithian-2-yl)hept-5-en-1-ol (**S1-1**) and 216 mg (23%) of 2,6-dimethyl-1-(2-methyl-1,3-dithian-2-yl)hept-5-en-1-ol (**S1-2**), both as pale yellow oils.

S1-1:
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 – 5.11 (m, 1H), 3.89 (t, J = 1.8 Hz, 1H), 3.01 – 2.92 (m, 2H), 2.69 – 2.62 (m, 2H), 2.56 (dd, J = 2.1, 1.1 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.13 – 1.98 (m, 3H), 1.92 – 1.82 (m, 1H), 1.69 (d, J = 1.0 Hz, 3H), 1.62 (s, 3H), 1.56 – 1.48 (m, 1H), 1.47 (s, 3H), 1.46 – 1.39 (m, 1H), 0.96 (d, J = 6.8 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 131.5, 124.5, 73.5, 55.0, 38.1, 32.5, 26.3, 25.9, 25.8, 25.7, 24.4, 23.0, 17.1, 14.6.
IR (ATR) ν_{max}: 3480, 2967, 2916, 2856, 1448, 1381, 1252.
HRMS (ESI) calcd. for $C_{14}H_{27}OS_2^+$ $[M+H]^+$: 275.1498, found: 275.1493.

S1-2:
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.16 – 5.09 (m, 1H), 3.81 (t, J = 2.1 Hz, 1H), 3.01 – 2.92 (m, 2H), 2.68 – 2.59 (m, 2H), 2.61 (dd, J = 1.9, 0.9 Hz, 1H), 2.13 – 2.03 (m, 3H), 1.97– 1.79 (m, 2H), 1.68 (d, J = 2.1, 3H), 1.67 – 1.61 (m, 1H), 1.61 (s, 3H), 1.45 (s, 3H), 1.28 – 1.19 (m, 1H), 1.14 (d, J = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 131.4, 124.8, 75.4, 55.0, 32.8, 32.7, 26.4, 26.1, 25.8, 25.7, 24.4, 22.6, 21.0, 17.6.
IR (ATR) ν_{max}: 3484, 2961, 2914, 1447, 1377, 1271.
HRMS (ESI) calcd. for $C_{14}H_{27}OS_2^+$ $[M+H]^+$: 275.1498, found: 275.1493.

[3] Dickschat, J. S., Wickel, S., Bolten, C. J., Nawrath, T., Schulz, S., Wittmann, C., *Eur. J. Org. Chem.* **2010**, 2687–2695.

3-Hydroxy-4,8-dimethylnon-7-en-2-one (S1-3)[4]

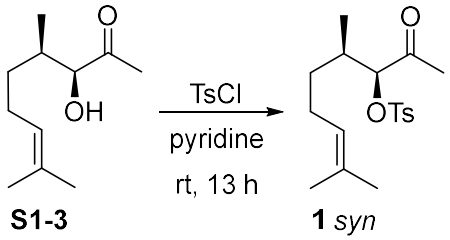


S1-1 **S1-3**

To a solution of **S1-1** (163 mg, 0.59 mmol, 1 eq) in acetonitrile/water (4:1, 12 mL) were added mercury(II) chloride (478 mg, 1.76 mmol, 3 eq) and calcium carbonate (239 mg, 2.39 mmol, 4 eq). The reaction mixture was heated to 65 ºC for 45 min, then cooled to rt. After addition of diethyl ether (20 mL), reaction mixture was filtered through Celite. The filtrate was washed with water and brine, dried over anh. $MgSO_4$ and concentrated *in vacuo*. Dry flash chromatography (petroleum-ether/ethyl acetate = 925/75) afforded 76 mg (70%) of compound **S1-3** as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 – 5.10 (m, 1H), 4.19 (dd, J = 4.8, 2.2 Hz, 1H), 3.37 (d, J = 4.8 Hz, 1H), 2.18 (s, 3H), 2.15 – 2.04 (m, 2H), 2.03 – 1.95 (m, 1H), 1.71 (d, J = 1.0 Hz, 3H), 1.65 – 1.57 (m, 1H), 1.63 (s, 3H), 1.47 – 1.37 (m, 1H), 0.70 (d, J = 6.8 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.1, 131.9, 124.0, 79.2, 35.1, 33.8, 25.7, 25.6, 25.2, 17.7, 12.7.
IR (ATR) ν_{max}: 3480, 2961, 2925, 2856, 1712, 1458, 1379, 1265.
HRMS (ESI) calcd. for $C_{11}H_{24}O_2N^+$ $[M+NH_4]^+$: 202.1802, found: 202.1801.

4,8-Dimethyl-2-oxonon-7-en-3-yl 4-methylbenzenesulfonate (1 *syn*)



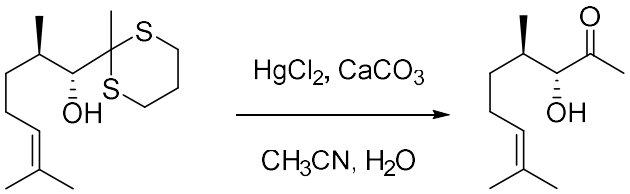
S1-3 **1** *syn*

Tosyl chloride (168 mg, 0.88 mmol, 4 eq) was added to a solution of **S1-3** (41.6 mg, 0.22 mmol, 1 eq) in pyridine (1.1 mL) and the reaction mixture was stirred at room temperature for 13 h. The reaction mixture was then diluted with CH_2Cl_2, washed with sat. $CuSO_4$ solution, water, brine, dried over anh. $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (petroleum-ether/ethyl acetate = 9/1) afforded 60 mg (82%) of compound **1 *syn*** as a colorless oil.

[4] Love, B.; Jones, E. *J. Org. Chem.* **1999**, 3755–3756.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.39 – 7.35 (m, 2H), 4.93 – 4.87 (m, 1H), 4.62 (d, J = 3.9 Hz, 1H), 2.47 (s, 3H), 2.20 (s, 3H), 2.03 – 1.95 (m, 1H), 1.91 (dt, J = 14.7, 7.2 Hz, 1H), 1.79 (dt, J = 14.8, 7.4 Hz, 1H), 1.67 (d, J = 1.1 Hz, 3H), 1.56 (s, 3H), 1.24 – 1.15 (m, 1H), 1.15 – 1.06 (m, 1H), 0.85 (d, J = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 145.2, 133.0, 132.1, 129.8, 128.0, 123.4, 87.2, 35.1, 32.5, 27.1, 25.6, 24.9, 21.6, 17.6, 14.0.
IR (ATR) ν_{max}: 2969, 2927, 1720, 1597, 1452, 1370.
HRMS (ESI) calcd. for $C_{18}H_{30}O_4SN^+$ $[M+NH_4]^+$: 356.1890, found: 356.1889.

3-Hydroxy-4,8-dimethylnon-7-en-2-one (S1-4)[4]

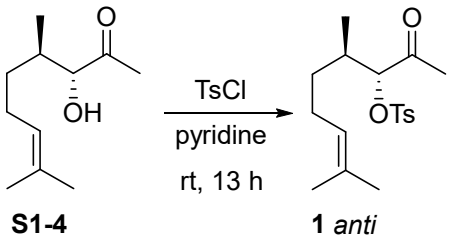


S1-2 **S1-4**

To a solution of **S1-2** (35 mg, 0.127 mmol, 1 eq) in acetonitrile/water (4:1, 2.6 mL) were added mercury(II) chloride (104 mg, 0.38 mmol, 3 eq) and calcium carbonate (51 mg, 0.51 mmol, 4 eq). The reaction mixture was heated to 65 ºC for 45 min, then cooled to rt. After addition of diethyl ether (5 mL), reaction mixture was filtered through Celite. The filtrate was washed with water and brine, dried over anh. $MgSO_4$ and concentrated *in vacuo*. Dry flash chromatography (petroleum-ether/ethyl acetate = 9/1) afforded 11.8 mg (50%) of compound **S1-4**, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07-5.00 (m, 1H), 4.09 (dd, J = 4.7, 2.5 Hz, 1H), 3.40 (d, J = 4.7 Hz, 1H), 2.19 (s, 3H), 2.08 – 1.96 (m, 2H), 1.94 – 1.84 (m, 1H), 1.68 (d, J = 0.7 Hz, 3H), 1.59 (s, 3H), 1.29 – 1.20 (m, 1H), 1.12 (d, J = 6.9 Hz, 3H), 1.07 – 0.98 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.9, 132.2, 123.9, 81.8, 35.5, 29.7, 25.7, 25.6, 25.4, 17.7, 16.9.
IR (ATR) ν_{max}: 3480, 3054, 2968, 2928, 1710, 1453, 1358, 1265.
HRMS (ESI) calcd. for $C_{11}H_{24}O_2N^+$ $[M+NH_4]^+$: 202.1802, found: 202.1800.

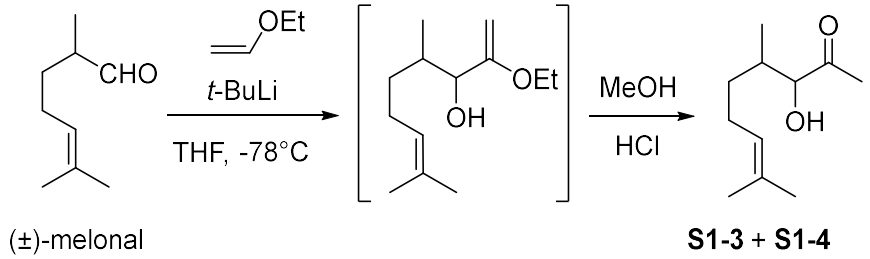
4,8-Dimethyl-2-oxonon-7-en-3-yl 4-methylbenzenesulfonate (1 *anti*)



Tosyl chloride (65 mg, 0.34 mmol, 4 eq) was added to a solution of **S1-4** (15.8 mg, 0.085 mmol, 1 eq) in pyridine (0.4 mL) and the reaction mixture was stirred at room temperature for 13 h. The reaction mixture was then diluted with CH_2Cl_2, washed with sat. $CuSO_4$ solution, water, brine, dried over anh. $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (petroleum-ether/ethyl acetate = 95/5) afforded 16.2 mg (56%) of **1 *anti***, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.37 – 7.33 (m, 2H), 4.97 – 4.91 (m, 1H), 4.48 (d, J = 5.3 Hz, 1H), 2.46 (s, 3H), 2.18 (s, 3H), 2.01 – 1.78 (m, 3H), 1.65 (d, J = 0.8 Hz, 3H), 1.55 (s, 3H), 1.38 – 1.28 (m, 1H), 1.20 – 1.10 (m, 1H), 0.80 (d, J = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 145.3, 133.0, 132.2, 129.9, 128.0, 123.4, 88.5, 35.2, 31.1, 27.1, 25.6, 24.9, 21.7, 17.6, 15.2.
IR (ATR) ν_{max}: 2970, 2927, 1721, 1598, 1455, 1369.
HRMS (ESI) calcd. for $C_{18}H_{26}O_4SK^+$ $[M+K]^+$: 377.1183, found: 377.1184.

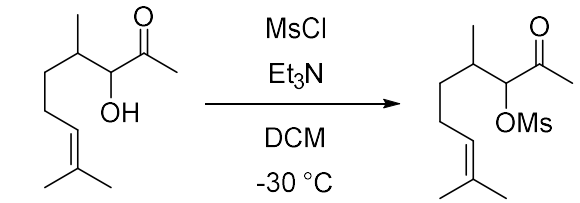
For a gram scale preparation of **S1-3** and **S1-4** mixture, a shorter and higher yielding procedure was used:



To a solution of methyl vinyl ether (10.98 mL, 0.114 M, 8 eq), in THF (130 mL), at –78 °C, *t*-BuLi (1.6 M, 35 mL, 4 eq) was added dropwise over a period of 15 minutes, under an argon atmosphere. A yellow precipitate appeared and the mixture was stirred for additional 15 minutes at –78 °C. The yellow suspension was then warmed to 0 °C and stirred for 20 minutes to give a colorless solution. The reaction mixture was cooled to –78 °C and 2,6-dimethylhept-5-enal (2 g, 0.0143 M) in THF (5 mL) was added dropwise. The reaction mixture was stirred at –78 °C for 1h, then warmed up to room temperature. The reaction was quenched with water and the mixture was

extracted with Et_2O (2 × 25 mL). The combined organic extract was washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was stirred with aqueous methanolic HCl (0.05 M, 45 mL) for 20 min. The reaction mixture was concentrated *in vacuo*, diluted with water, extracted with Et_2O (2 x 30 mL), dried over anh. $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (petroleum-ether/ethyl acetate = 95/5) afforded 2.1 g (77%) 3-hydroxy-4,8-dimethylnon-7-en-2-one (**S1-3** + **S1-4**), as a colorless oil.

General procedure 1. (G.P.1.): mesylation of hydroxy ketones
4,8-Dimethyl-2-oxonon-7-en-3-yl methanesulfonate (1 *syn* + *anti*)

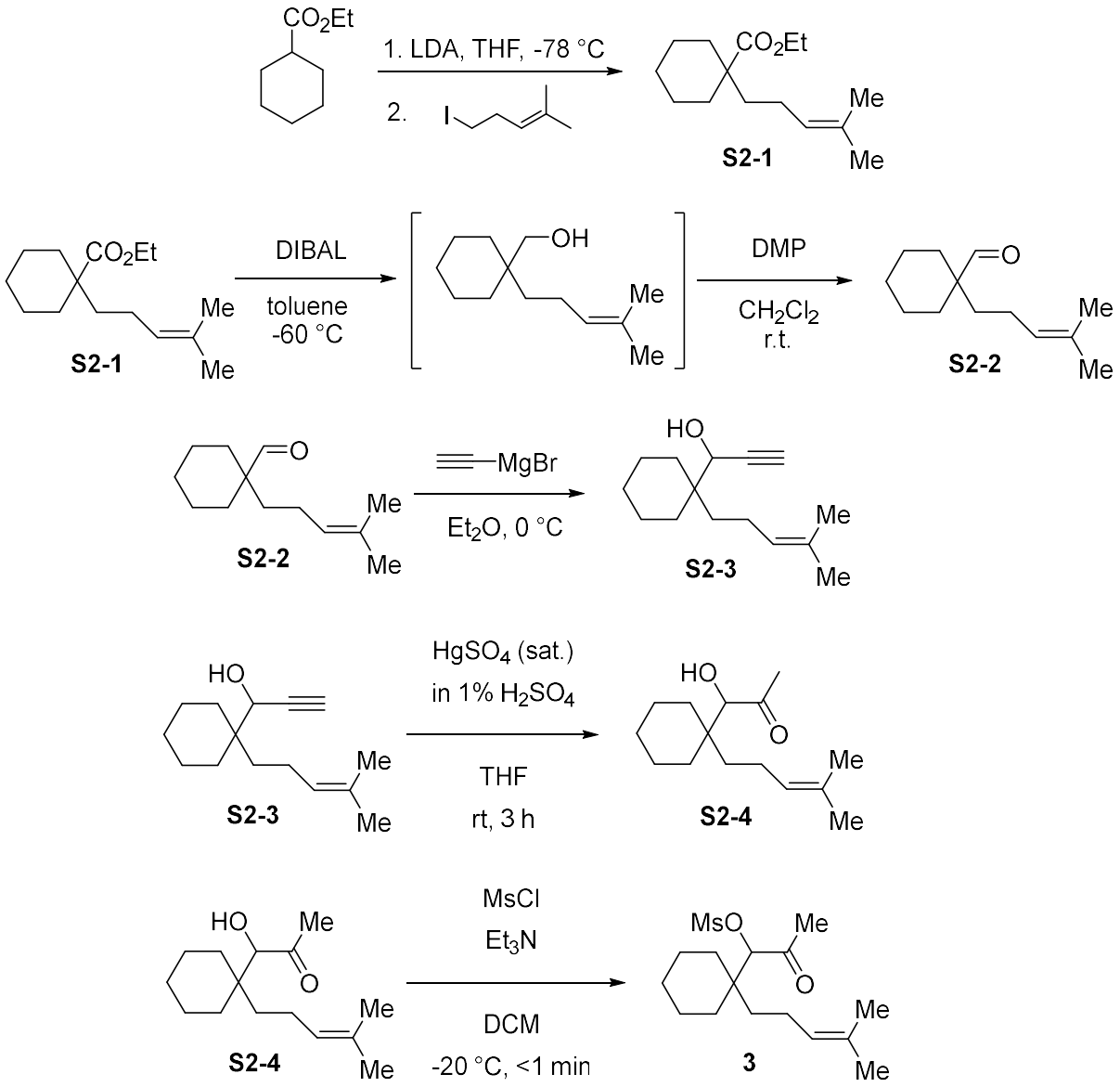


S1-3 + S1-4 **1** *syn+anti*

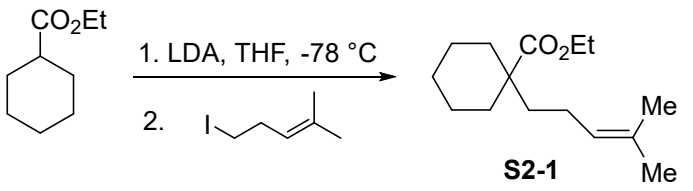
Mesyl chloride (0.044 mmol, 3.4 µL, 2 eq) was added to a solution of **S1-3 + S1-4** (4.1 mg, 0.022 mmol, 1 eq), triethylamine (9 µL, 0.067 mmol, 3 eq) and a few crystals of DMAP in CH_2Cl_2 (0.17 mL) at -30 °C and the reaction was completed almost immediately. The reaction mixture was concentrated in *vacuo* and the residue was purified by column chromatography (petroleum-ether/ethyl acetate = 8/2) to afford 3.6 mg (62%) of **1 *syn* + *anti*** as a colorless oil (mixture of isomers in a relative ratio 1.5:1, as determined by ^{1}H NMR).

Spectral data for a mixture of isomers, where H: H' are isomers in the ratio 1.5:1
^{1}H NMR (500 MHz, $CDCl_3$) 5.12 – 5.06 (m, 1H), 5.12 – 5.06 (m, 1H'), 4.96 (d, J = 3.1 Hz, 1H), 4.82 (d, J = 4.1 Hz, 1H'), 3.14 (s, 3H), 3.12 (s, 3H'), 2.24 (s, 3H'), 2.22 (s, 3H), 2.20 – 2.12 (m, 1H+1H'), 2.12 – 2.02 (m, 2H+1H'), 1.97 – 1.88 (m, 1H'), 1.70 (d, J = 1.0 Hz, 3H), 1.68 (d, J = 0.9 Hz, 3H'), 1.63 (s, 3H), 1.60 (s, 3H'), 1.58 – 1.49 (m, 1H), 1.44 – 1.24 (m, 1H+2H'), 1.07 (d, J = 6.9 Hz, 3H'), 0.90 (d, J = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 204.2, 204.2, 132.6, 123.3, 123.2, 88.5, 86.9, 38.9, 38.7, 34.6, 34.4, 33.0, 30.7, 27.0, 26.8, 25.7 (2×C), 25.2, 25.1, 17.7 (2×C), 15.9, 13.7.
IR (ATR) ν_{max}: 2970, 2934, 1728, 1456, 1358.
HRMS (ESI) calcd. for $C_{11}H_{22}O_4SNa^+$ $[M+Na]^+$: 285.1131, found: 285.1123.

Scheme S2: Preparation of precursor 3



Ethyl 1-(4-methylpent-3-en-1-yl)cyclohexane-1-carboxylate (S2-1)

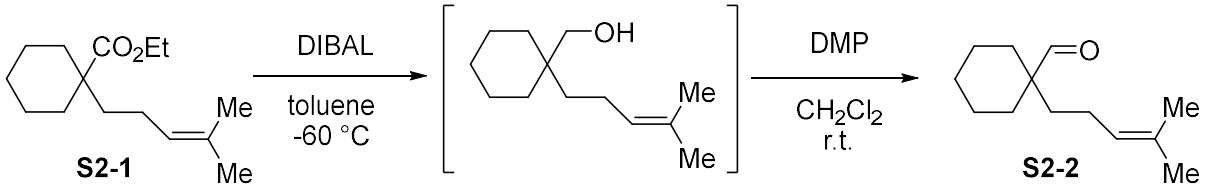


To a cold (0 °C) solution of diisopropylamine (1.80 g; 17.8 mmol; 1.1 eq) in dry THF (15.0 mL), butyllithium was added (14.85 mL of the 1.2 M solution in hexane; 17.8 mmol, 1.1 eq), under an

argon atmosphere. The solution was stirred for 10 min at that temperature, cooled to –78 °C, and then ethyl cyclohexanecarboxylate (2.50 g; 16.0 mmol) was added dropwise, over 15 min. After the addition was complete, the reaction mixture was stirred for 1 hour at –78 °C, when a solution of 5-iodo-2-methylpent-2-ene (3.70 g; 17.8 mmol; 1.1 eq) in DMSO (3.0 mL) was added dropwise. The reaction mixture was stirred at –78 °C for 30 min, warmed to room temperature and stirred overnight. The reaction mixture was quenched with 1.5 M HCl and the organic phase was washed with water and brine, dried over anh. $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by dry-flash chromatography (SiO_2, eluent petroleum-ether/ethyl acetate = 975/25) to provide 3.0 g (78%) of ethyl 1-(4-methylpent-3-enyl)cyclohexanecarboxylate (**S2-1**), as a colorless oil. NMR spectra consistent with literature.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05 – 5.02 (m, 1H), 4.13 (q, J = 7.0 Hz, 2H), 2.06 (bd, J = 13.0 Hz, 2H), 1.88 – 1.83 (m, 2H), 1.65 (s, 3H), 1.58 – 1.51 (m, 3H), 1.56 (s, 3H), 1.49 – 1.46 (m, 2H), 1.38 – 1.28 (m, 2H), 1.25 (t, J = 7.0 Hz, 3H), 1.23 – 1.16 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 131.7, 124.3, 60.0, 46.8, 40.6, 34.2 (2 x C), 26.1, 25.8, 23.4 (2 x C), 22.9, 17.6, 14.5.
IR (ATR) ν_{max} 2930, 2857, 1696, 1453, 1244, 1199 cm^{-1}.
HRMS (ESI) calcd. for $C_{15}H_{27}O_2^+$ $[M+H]^+$: 239.2006, found: 239.2006.

1-(4-Methylpent-3-en-1-yl)cyclohexane-1-carbaldehyde (S2-2)



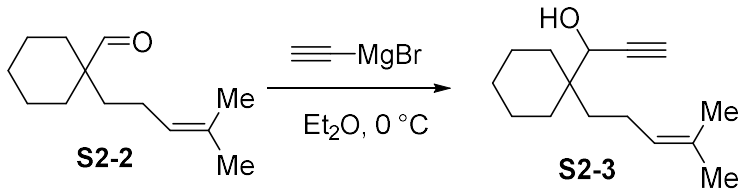
Solution of ethyl 1-(4-methylpent-3-en-1-yl)cyclohexane-1-carboxylate **S2-1** (300 mg, 1.26 mmol) in toluene (10 mL) was cooled to –60°C and a 1.0 M solution of DIBAL-H in toluene (2.52 mL; 2.52 mmol) was added. The solution was stirred for 30 min at –78 °C and then warmed to the room temperature. The reaction was diluted with EtOAc (50 mL) and quenched by successive addition of MeOH (2 mL) and a saturated aqueous solution of potassium sodium tartrate. The mixture was stirred for 30 min, the organic layer was separated, filtered through a short pad of silica gel and concentrated *in vacuo*. The residue (used immediately in the next step, without further purification) was dissolved in CH_2Cl_2 (25 mL) and Dess-Martin periodinane (1.06 g, 2.52 mmol) was added. The reaction mixture was stirred at room temperature for 30 min, after which time it was quenched with 20% aq. $Na_2S_2O_3$ (10 mL) and a saturated aqueous solution $NaHCO_3$ (8 mL). The mixture was stirred until the aqueous layer was clear. The aqueous layer was extracted

[5] Compound **S2-1** was prepared according to the procedure: M. Trajkovic, Z. Ferjancic, R. N. Saicic, F. Bihelovic. *Chem. Eur. J.* **2019**, *25*, 4340-4344

with CH_2Cl_2 (3×10 mL). The combined organic extract was dried over anh. $MgSO_4$ and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum-ether/ethyl acetate = 95:5) to give 162 mg, (66%) of 1-(4-methylpent-3-en-1-yl)cyclohexane-1-carbaldehyde (**S2-2**), as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 5.02 (t, J = 7.1 Hz, 1H), 1.91 – 1.81 (m, 4H), 1.65 (s, 3H), 1.61 – 1.50 (m, 3H), 1.55 (s, 3H), 1.47 – 1.41 (m, 2H), 1.34 – 1.26 (m, 6H).
9.44 (s, 1H), 5.09 – 4.99 (m, 1H), 1.94 –1.84 (m, 4H), 1.67 (s, 3H), 1.62 – 1.53 (m, 3H), 1.57 (s, 3H), 1.49 – 1.44 (m, 2H), 1.34 – 1.26 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 132.3, 124.0, 49.8, 36.7, 31.1 (2 x C), 26.0, 25.8, 22.7 (2 x C), 22.4, 17.7.
IR (ATR) ν_{max} 3391, 2932, 2858, 1699, 1452, 1380, 1260, 1131, 1072, 901.

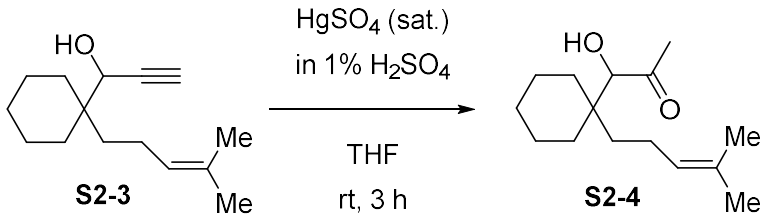
1-(1-(4-Methylpent-3-en-1-yl)cyclohexyl)prop-2-yn-1-ol (S2-3)



A solution of ethynylmagnesium bromide (0.5 M in THF, 4 mL, 2 mmol) was added to a solution of aldehyde **S2-2** (221 mg, 1.0 mmol) in Et_2O (15 mL), at 0 °C, and then warmed to room temperature, under an argon atmosphere. After 20 min, 2% aqueous solution of HCl was added, and the mixture was extracted with EtOAc (2 × 25 mL). The combined organic extract was washed with H_2O and brine, dried over anh. $MgSO_4$, filtered and concentrated. The residue was purified by dry-flash chromatography (SiO_2; eluent: petroleum-ether/ethyl acetate = 9:1) to give 1-(1-(4-methylpent-3-en-1-yl)cyclohexyl)prop-2-yn-1-ol (**S2-3**; 155 mg, 62%), as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 – 5.10 (m, 1H), 4.32 (d, J = 4.1 Hz, 1H), 2.47 (d, J = 2.2 Hz, 1H), 1.95 (dd, J^1 = 16.2, J^2 = 8.0 Hz, 2H), 1.69 (s, 3H), 1.62 (s, 3H), 1.58 – 1.41 (m, 12H), 1.29 – 1.24 (m, 1H).
5.17 – 5.10 (m, 1H), 4.32 (d, J = 2.3 Hz, 1H), 2.47 (d, J = 2.3, Hz, 1H), 1.99 – 1.91 (m, 2H), 1.69 (s, 3H), 1.62 (s, 3H), 1.57 – 1.41 (m, 10H), 1.35 – 1.20 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 131.6, 125.1, 83.6, 74.6, 68.4, 40.1, 32.3, 30.8, 30.1, 26.2, 25.8, 22.0, 21.5, 21.4, 17.7.
IR (ATR) ν_{max} 3424, 3307, 2929, 2860, 1670, 1454, 1039.
HRMS (ESI) calcd. for $C_{15}H_{25}O^+$ $[M+H]^+$: 221.1900, found: 221.1903.

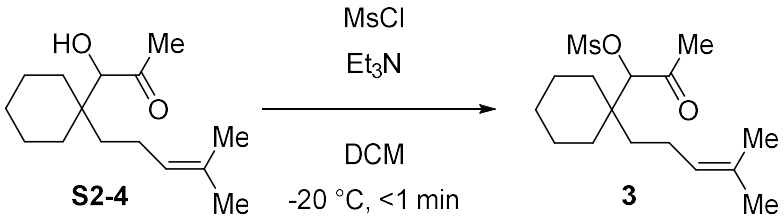
1-Hydroxy-1-(1-(4-methylpent-3-en-1-yl)cyclohexyl)propan-2-one (S2-4)



Propargylic alcohol **S2-3** (200 mg, 0.91 mmol) was added to a solution containing of THF (1.8 ml), water, (0.2 ml) and $HgSO_4$ (2.0 ml of a saturated solution in 1% H_2SO_4). The reaction mixture was stirred at room temperature for 3 h. The progress of the reaction was monitored by TLC. On completion of the reaction, the mixture was diluted with water, neutralized with saturated aqueous solution of $NaHCO_3$, and extracted with diethyl ether. The extracts were dried over anh. $MgSO_4$ and concentrated under reduced pressure. The residue was purified by dry-flash chromatography (eluent: petroleum-ether/ethyl acetate = 9/1) to give 1-hydroxy-1-(1-(4-methylpent-3-en-1-yl)cyclohexyl)propan-2-one (**S2-4**; 126 mg, 58%), as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.06 (dddd, J^1 = 7.1, J^2 = 5.9, J^3 = 2.7, J^4 = 1.4 Hz, 1H), 4.15 (d, J = 5.3 Hz, 1H), 3.19 (d, J = 6.0 Hz, 1H), 2.26 (s, 3H), 1.99 – 1.84 (m, 2H), 1.66 (d, J = 0.7 Hz, 3H), 1.59 (s, 3H), 1.57 – 1.37 (m, 10H), 1.29 (ddd, J^1 = 14.4, J^2 = 12.0, J^3 = 5.2 Hz, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 211.9, 131.6, 124.7, 81.6, 41.1, 32.8, 31.93, 31.8, 29.8 26.1, 25.8, 22.2, 21.5, 21.5, 17.7.
IR (ATR) ν_{max}: 3470, 2928, 1701, 1610, 1455, 1354, 1072.
HRMS (ESI) calcd. for $C_{15}H_{27}O_2^+$ $[M+H]^+$: 239.2006, found: 239.2008

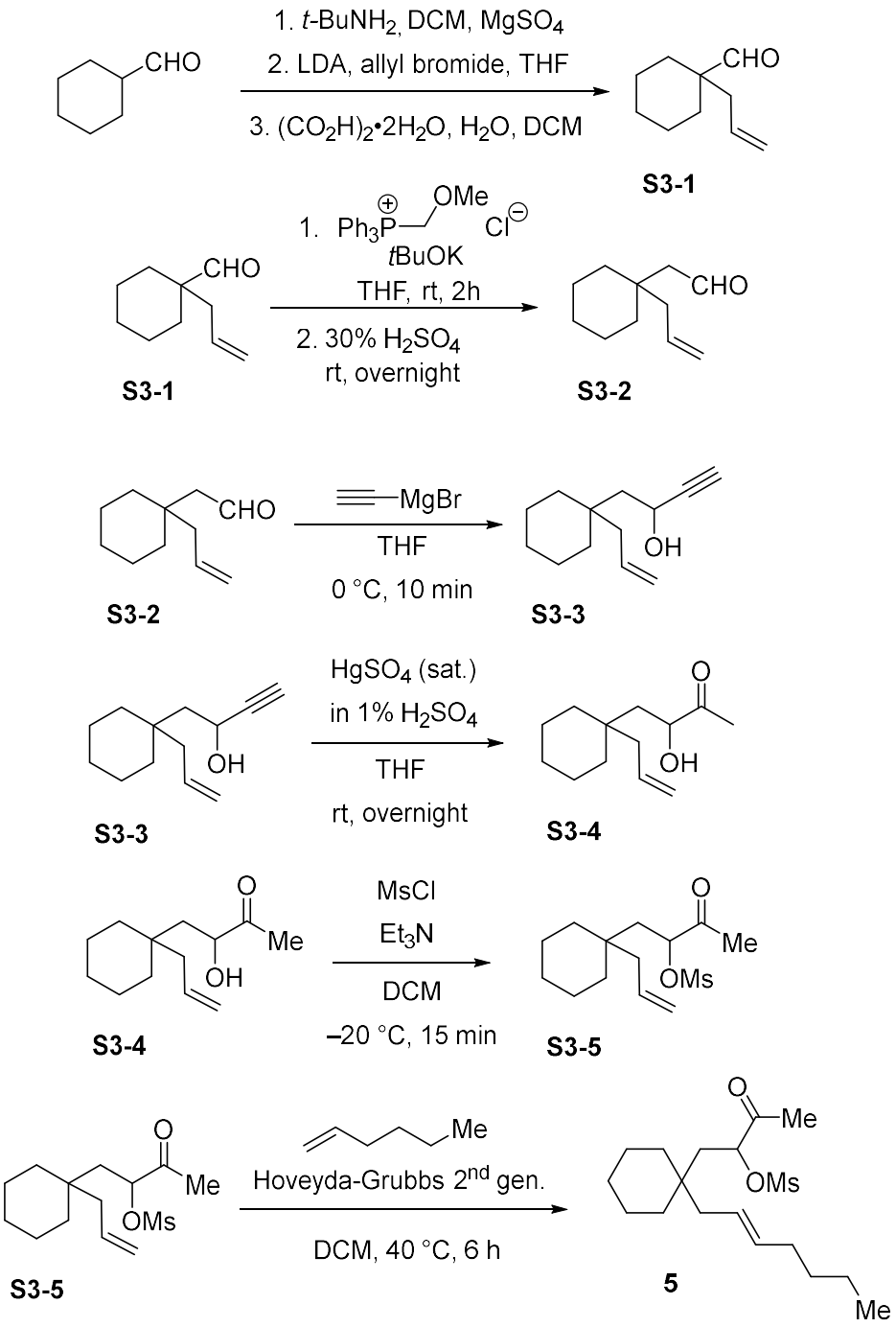
1-(1-(4-Methylpent-3-en-1-yl)ciclohexyl)-2-oxopropyl methanesulfonate (3)



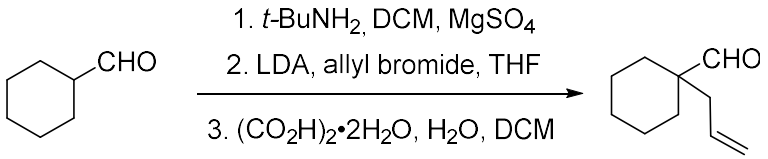
Mesyl chloride (66.5 µL, 0.86 mmol) was added to a solution of hydroxy ketone **S2-4** (102 mg, 0.43 mmol), triethylamine (180 µL, 1.29 mmol) and a few crystals of DMAP in CH_2Cl_2 (3 mL) at –30 °C and the reaction was completed almost immediately. The reaction mixture was diluted with CH_2Cl_2 (20 mL), filtered through a pad of silica gel and concentrated *in vacuo*. Since mesylate **3**

was prone to decomposition, the crude product was used immediately in the cyclization step, without further purification.

Scheme S3: Preparation of precursor 5



1-Allylcyclohexanecarbaldehyde (S3-1)[6]



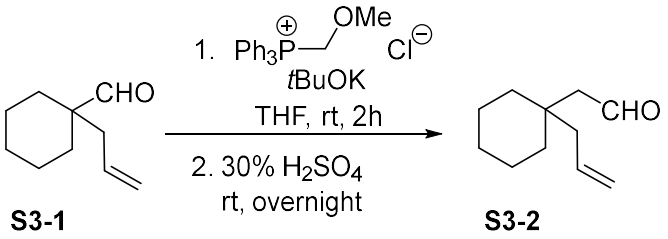
S3-1

A suspension of anh. $MgSO_4$ (10 g, 83 mmol), cyclohexane carbaldehyde (6 mL, 50 mmol) and *t*-$BuNH_2$ (5.6 mL, 53 mmol) in dry CH_2Cl_2 (50 mL) was refluxed for 1 h, then cooled to room temperature, filtered under reduced pressure, and concentrated at rotavap to give 7.1 g (86%) of the crude aldimine that was used immediately in the next step.
To an ice cold solution of diisopropylamine (8.1 mL, 58 mmol) in THF (60 mL) under argon, *n*-BuLi (35 mL, 1.49 M, 52 mmol) was added dropwise, and after 15 min of stirring at that temperature a solution of crude aldimine (7.1 g, 42 mmol) in THF (10 mL) was added. After 3.5 h of stirring at 0 °C, a solution of allyl bromide (4.6 mL, 53 mmol) in THF (10 mL) was added, and stirring continued overnight, allowing the reaction mixture to warm up to room temperature. After quenching with H_2O (10 mL), reaction mixture was poured in H_2O (240 mL) and extracted with Et_2O (3×120 mL). The combined organic extract was dried over K_2CO_3, filtered and concentrated at rotavap to give 8.8 g of the crude allylated aldimine.
A solution of crude allylated aldimine (8.8 g) and $(COOH)_2•H_2O$ (6.3 g) in CH_2Cl_2 (100 mL) and H_2O (60 mL) was vigorously stirred under reflux for 1 h. The organic layer was separated, the water layer was extracted with CH_2Cl_2 (2×20 mL), and the combined organic extract was dried over anh. $MgSO_4$ and concentrated *in vacuo*. The residue was distilled under reduced pressure to give 3.7 g (50% overall) of 1-allylcyclohexanecarbaldehyde (**S3-1**) as a clear colorless liquid (bp. 90-100 °C/7 mm Hg). NMR spectra consistent with literature.[7]

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.43 (s, 1H), 5.80 – 5.50 (m, 1H), 5.12 – 4.90 (m, 2H), 2.16 (dt, J^1 = 7.4, J^2 = 1.0 Hz, 2H), 1.94 – 1.76 (m, 2H), 1.66 – 1.43 (m, 2H), 1.41 – 1.14 (m, 6H).
^{13}C NMR (50 MHz, $CDCl_3$) δ 207.1, 132.1, 118.4, 49.7, 40.9, 30.8, 25.7, 22.5.

[6] (a) According to the published procedure: De Kimpe, N; De Smaele, D; Hofkens, A; Dejaegher, Y; Kesteleyn, B. *Tetrahedron*, **1997**, *53*, 10803-10816. (b) A published procedure that did not work in our hands: Ibrahem, I; Cordova, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 1952-1956.
[7] Cozzi, P. G.; Benfatti, F.; Capdevila, M. G.; Mignogna, A. *Chem Comm.*. **2008**, 3317-3318.

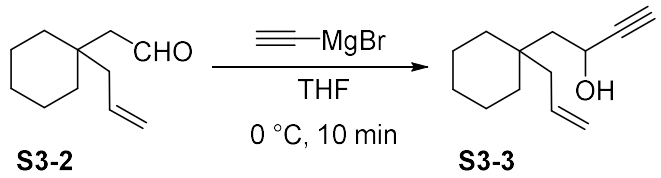
2-(1-Allylcyclohexyl)acetaldehyde (S3-2)[8]



A solution of *t*-BuOK (344 mg, 3.1 mmol) in THF (5 mL) was added dropwise, with stirring, to an ice-cold suspension of (methoxymethyl)triphenylphosphonium chloride (1.05 g, 3.1 mmol) in dry THF (4 mL), under an argon atmosphere. The resulting cherry-red solution was stirred at 0 °C for 1 h, when a solution of 1-allylcyclohexanecarbaldehyde **S3-1** (310 mg, 2.0 mmol) in dry THF (2 mL) was added at 0 °C, and stirring was continued at room temperature for 2 h. Water (2.3 mL) was added, the reaction mixture was concentrated under reduced pressure to approximately 5 mL, when 30% H_2SO_4 (1 mL) was added and the mixture was stirred overnight at room temperature. Saturated $NaHCO_3$ solution (2.8 mL) was added to reaction mixture, followed by extraction with diethyl ether (3×5 mL). The combined organic extract was washed with water (5 mL), dried over anh. $MgSO_4$ and carefully concentrated at rotavap (ca. 20 mm Hg/34 °C bath temperature). The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 95/5) to afford 262 mg (77%) of 2-(1-allylcyclohexyl)acetaldehyde (**S3-2**) as a clear liquid.[9]

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.86 (td, J^1 = 3.1, J^2 = 0.6 Hz, 1H), 5.97 – 5.66 (m, 1H), 5.22 – 4.95 (m, 2H), 2.34 (d, J = 3.1 Hz, 2H), 2.22 (d, J = 7.5 Hz, 2H), 1.46 (s, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ 203.9, 134.1, 118.4, 50.7, 42.7, 36.9, 36.0, 26.1, 21.6.

1-(1-Allylcyclohexyl)but-3-yn-2-ol (S3-3)



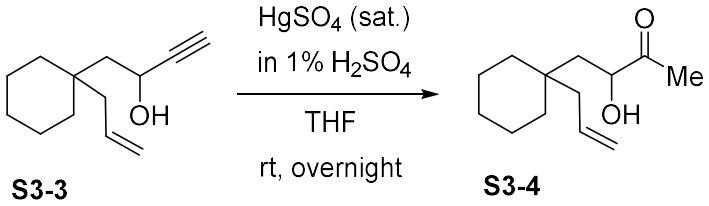
To an ice-cold solution of 2-(1-allylcyclohexyl)acetaldehyde **S3-2** (262 mg, 1.57 mmol) in THF (10 mL), ethynylmagnesium bromide solution (7 mL, 0.5 M in THF, 3.5 mmol) was added dropwise via syringe, under an argon atmosphere. After 10 min of stirring TLC indicated complete consumption of the starting material. The reaction was quenched by addition of NH_4Cl $_{(sat.)}$ (42

[8] Following the procedure from: Clavette, C; Rocan, J-F. V; Beauchemin, A. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 12705–12708.
[9] Known compound: Bai, Y.; Davis, D. C.; Dai, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 6519–6522.

mL) and extracted with EtOAc (3×30 mL). Combined organic extract was washed with brine (30 mL), dried over anh. $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 8/1) to afford 249 mg (82%) of 1-(1-allylcyclohexyl)but-3-yn-2-ol (**S3-3**), as a pale yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.83 (ddt, J^1 = 15.0, J^2 = 11.6, J^3 = 7.4 Hz, 1H), 5.12 – 4.96 (m, 2H), 4.51 (qd, J^1 = 6.3, J^2 = 2.1 Hz, 1H), 2.48 (d, J = 2.1 Hz, 1H), 2.17 (d, J = 7.4 Hz, 2H), 1.92-1.83 (m, 1H), 1.77 (dd, J^1 = 6.4, J^2 = 1.6 Hz, 2H), 1.51-1.32 (m, 10H).
^{13}C NMR (50 MHz, $CDCl_3$) δ 135.1, 117.5, 86.5, 72.9, 72.8, 59.2, 45.3, 42.0, 36.1, 35.7, 35.4, 26.3, 21.7.
IR (ATR) ν_{max}: 3306, 2927, 2856, 1639, 1455, 1006, 914.

4-(1-Allylcyclohexyl)-3-hydroxybutan-2-one (S3-4)

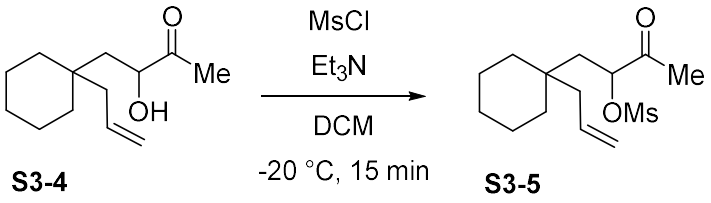


S3-3 **S3-4**

Water (11.6 mL) was added to a solution of 1-(1-allylcyclohexyl)but-3-yn-2-ol **S3-3** (246 mg, 1.28 mmol) in THF (27.6 mL), followed by dropwise addition of saturated $HgSO_4$ solution in 1% H_2SO_4 (2.77 mL). After 16 h of stirring at room temperature, the reaction mixture was poured into brine (130 mL) and extracted with Et_2O (3×40 mL). The combined organic extract was dried over anh. $MgSO_4$ and concentrated at rotavap. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 6/1) to afford 213 mg (79%) of hydroxy ketone **S3-4,** as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 – 5.80 (m, 1H), 5.13 – 5.03 (m, 2H), 4.27 (ddd, J^1 = 9.9, J^2 = 5.3, J^3 = 1.7 Hz, 1H), 3.40 (d, J = 5.3 Hz, 1H), 2.32 (dd, J^1 = 14.1, J^2 = 6.6 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.19 (s, 3H) 1.65 (dd, J^1 = 14.7, J^2 = 1.7 Hz, 1H), 1.51 – 1.31 (m, 11H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 210.8, 135.2, 117.5, 74.8, 41.8, 41.2, 36.1, 36.0 (2×C), 26. 3, 25.3, 21.8 (2×C).
IR (ATR) ν_{max}: 3471, 2927, 2857, 1714, 1639, 1454, 1358, 1097.

1-(1-Allylcyclohexyl)-3-oxobutan-2-yl methanesulfonate (S3-5)

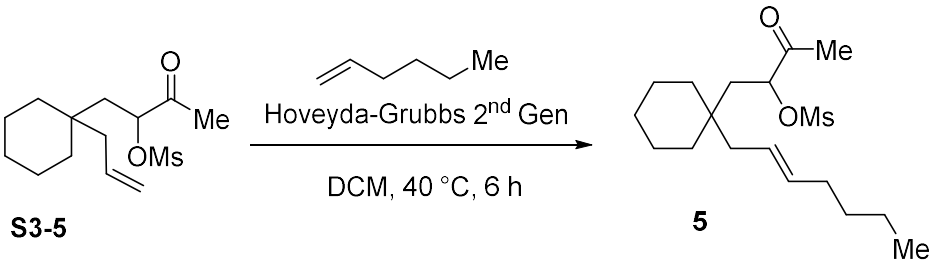


S3-4 **S3-5**

According to G.P.1: MsCl (25 µL, 0.323 mmol) was added to a cold (–20 °C) solution of 4-(1-allylcyclohexyl)-3-hydroxybutan-2-one **S3-4** (38 mg, 0.120 mmol), DMAP (1 mg, 0.008 mmol) and Et_3N (70 µL, 0.502 mmol). After 10 min TLC indicated complete conversion. SiO_2 (200 mg) was added to the reaction mixture and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 9/1) to afford 36.8 mg (71 %) of 1-(1-allylcyclohexyl)-3-oxobutan-2-yl methanesulfonate (**S3-5**), as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 – 5.74 (m, 1H), 5.21 – 5.03 (m, 3H), 3.12 (s, 3H), 2.26 (dd, J^1 = 14.4, J^2 = 6.7 Hz, 1H), 2.22 (s, 3H), 2.17 (dd, J^1 = 14.9, J^2 = 8.7 Hz, 1H), 1.77 (dd, J^1 = 5.6, J^2 = 9.6 Hz, 1H), 1.59 (dd, J^1 = 15.8, J^2 = 1.7 Hz, 2H), 1.52 – 1.33 (m, 10H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.4, 134.1, 118.4, 81.4, 41.4, 39.4, 37.6, 35.8 (2×C), 35.7, 26.1, 25.9, 21.6 (2×C).
IR (ATR) ν_{max}: 2928, 2857, 1733, 1638, 1352, 1175, 951, 914, 882, 795.
HRMS (ESI) calcd. for $C_{14}H_{28}O_4SN^+$ $[M + NH4]^+$: 306.1734; found: 306.1727.

(*E*)-1-(1-(Hept-2-enyl)cyclohexyl)-3-oxobutan-2-yl methanesulfonate (5)



S3-5 **5**

A solution of 1-(1-allylcyclohexyl)-3-oxobutan-2-yl methanesulfonate **S3-5** (28.6 mg, 0.1 mmol), 1-hexene (25 µL, 0.2 mmol) and and Hoveyda-Grubbs 2nd generation catalyst (2.0 mg, 0.003 mmol) in dry CH_2Cl_2 (1 mL) was stirred overnight at room temperature under an argon atmosphere. TLC showed slow reaction, and more Hoveyda-Grubbs 2nd generation catalyst (2.0 mg, 0.033 mmol) and 1-hexene (25 µL, 0.2 mmol) were added, and the reaction mixture was heated to reflux. After 3 h of reflux, one more portion of Hoveyda-Grubbs 2nd generation catalyst (2.0 mg, 0.033 mmol) and 1-hexene (25 µL, 0.2 mmol) was added and the reflux was continued for 3

h more. SiO_2 (120 mg) was added to the reaction mixture and volatiles were removed under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 9/1) to afford 18.5 mg (54 %) of (*E*)-1-(1-(hept-2-enyl)cyclohexyl)-3-oxobutan-2-yl methanesulfonate (**5**), as a yellow oil. Mixture of *E* and *Z* isomers in a relative ratio 6.7:1, according to ^{1}H NMR spectrum integration of [-C**H**OMs-] signals at 5.11 (dd, J^1 = 9.5, J^2 = 2.0 Hz, $1H_{major}$) and 5.07 (dd, J^1 = 9.6, J^2 = 2.0 Hz, $1H_{minor}$).

NMR data for the major (*E*)-isomer

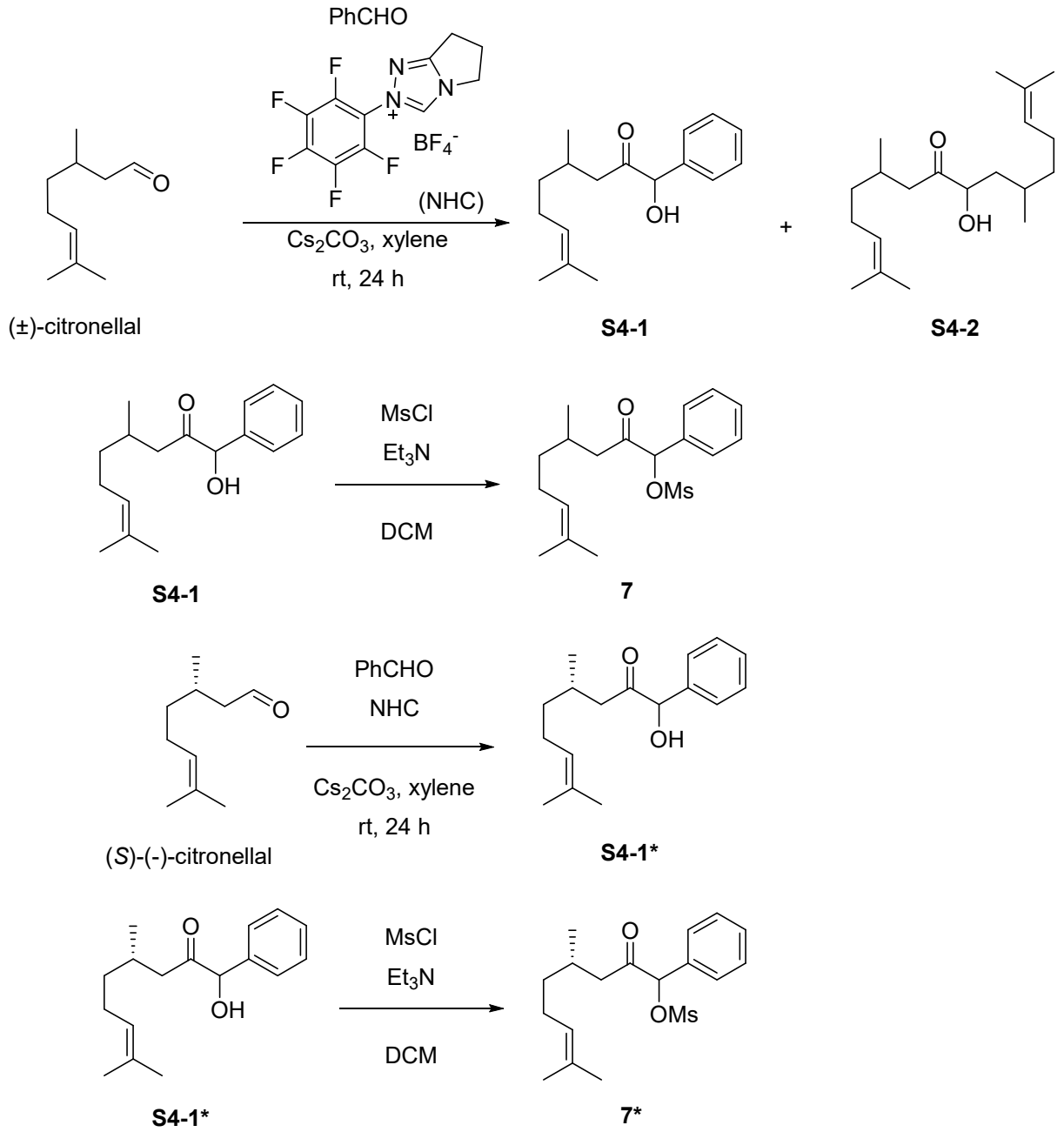
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 – 5.46 (m, 1H), 5.41 – 5.33 (m, 1H), 5.11 (dd, J^1 = 9.5, J^2 = 2.0 Hz, 1H), 3.11 (s, 3H), 2.20 (s, 3H), 2.17 (dd, J^1 = 14.6, J^2 = 6.7 Hz, 1H), 2.08 (dd, J^1 = 14.5, J^2 = 7.8 Hz, 1H), 2.01 (q, J = 6.6 Hz, 2H), 1.75 (dd, J^1 = 15.5, J^2 = 9.6 Hz, 1H), 1.57 (dd, J^1 = 15.5, J^2 = 2.0 Hz, 1H), 1.52 – 1.27 (m, 14H), 0.88 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.4, 134.6, 125.0, 81. 6, 40.0, 39.3, 37.6 35.9, 35.8, 35.6, 32.6, 31.8, 26.1, 25.8, 22.3, 21.7, 21.6, 14.0.

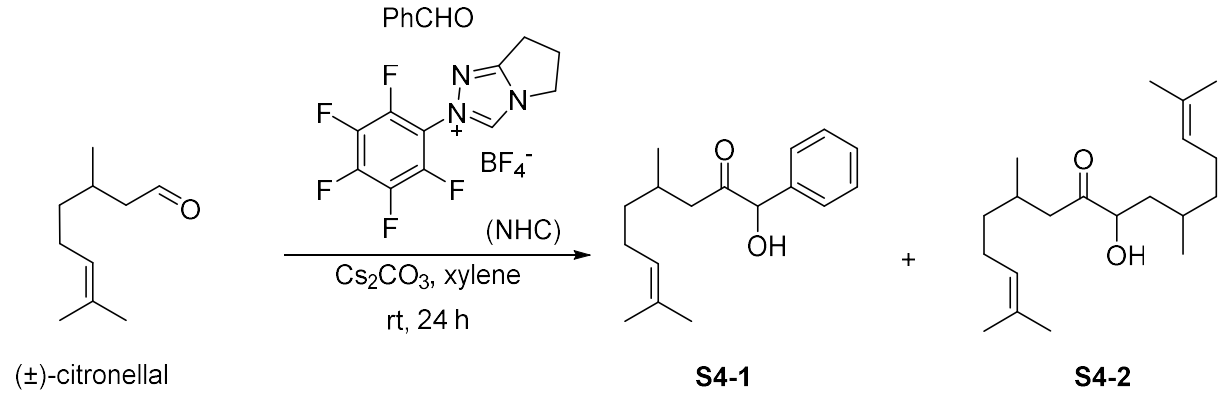
IR (ATR) ν_{max}: 2928, 2857, 1733, 1456, 1355, 1177, 972, 944.

HRMS (ESI) calcd. for $C_{18}H_{36}O_4SN^+$ $[M + NH_4]^+$: 362.2360; found: 362.2358.

Scheme S4: Preparation of precursor 7



General procedure 2. (G.P.2.) – cross-acyloin condensation
1-Hydroxy-4,8-dimethyl-1-phenylnon-7-en-2-one (S4-1) and 9-hydroxy-2,6,11,15-tetramethylhexadeca-2,14-dien-8-one (S4-2) [10]



A suspension of anhydrous Cs_2CO_3 (16 mg, 0.049 mmol, 0.1 eq), benzaldehyde (50 µL, 0.49 mmol, 1 eq), 3,7-dimethyloct-6-enal (0.322 mL, 2.45 mmol, 5 eq) and *N*-heterocyclic carbene precatalyst NHC (17.8 mg, 0.049 mmol, 0.1 eq) in dry xylene (1 mL) was stirred at room temperature for 24 h. The reaction mixture was then quenched with distilled water and extracted with ethyl acetate. The combined organic extract was washed with brine, dried over anh. $MgSO_4$ and concentrated *in vacuo*. Dry flash chromatography of the residue (petroleum-ether/ethyl acetate = 95/5), followed by column chromatography (benzene/ethyl acetate = 95/5) afforded 40.4 mg (33%) of hydroxy ketone **S4-1**, as a colorless oil (mixture of two diastereoisomers in a relative ratio 1.5:1, as determined by ^{1}H NMR), and 64.0 mg (16%) of citronellal dimer **S4-2** as a colorless oil (mixture of diastereoisomers, ratio not determined).

S4-1
Spectral data for a mixture of isomers, where H and H' correspond to the isomers in a ratio 1.5:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H+5H'), 5.08 – 5.01 (m, 1H+2H'), 4.97 – 4.91 (m, 1H), 4.39 (d, J = 4.3 Hz, 1H), 4.39 (d, J = 4.5 Hz, 1H'), 2.37 (dd, J = 16.3, 5.4 Hz, 1H'), 2.26 (dd, J = 16.4, 6.0 Hz, 1H), 2.20 (dd, J = 16.4, 7.7 Hz, 1H), 2.13 (dd, J = 16.3, 8.3 Hz, 1H'), 2.05 – 1.75 (m, 3H+3H'), 1.67 (d, J = 1.0 Hz, 3H'), 1.67 (d, J = 1 Hz, 3H), 1.57 (s, 3H'), 1.52 (s, 3H), 1.28 – 1.20 (m, 1H'), 1.19 – 1.10 (m, 1H+1H'), 1.08 – 0.99 (m, 1H), 0.86 (d, J = 6.7 Hz, 3H), 0.69 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.3, 209.2, 138.0, 137.9, 128.9, 128.6, 127.5, 124.0, 80.2, 79.8, 45.1, 45.0, 36.8, 36.6, 29.0, 28.9, 25.6, 25.4, 19.6, 19.4, 17.6, 17.6.
IR (ATR) ν_{max}: 3462, 2963, 2921, 2854, 1714, 1454, 1379.
HRMS (ESI) calcd. for $C_{17}H_{24}O_2Na^+$ $[M+Na]^+$: 283.1668, found: 283.1679.

[10] Jin, M. Y., Kim, S. M., Mao, H., Ryu, D. H., Song C. E., Yang, J. W., *Org. Biomol. Chem.*, **2014**, *12*, 1547–1550.

S4-2

Spectral data for a mixture of isomers

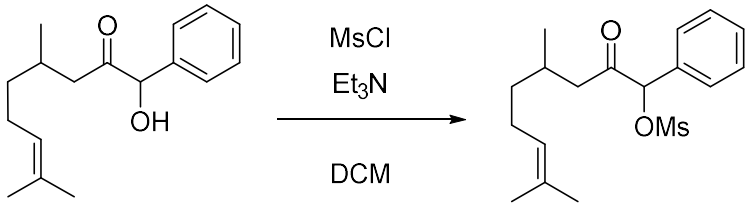
^{1}H NMR (500 MHz, $CDCl_3$) 5.15 – 5.05 (m, 2H), 4.20 – 4.11 (m, 1H), 3.46 – 3.39 (m, 1H), 2.48 – 2.39 (m, 1H), 2.33 – 2.22 (m, 1H), 2.13 – 1.90 (m, 5H), 1.86 – 1.76 (m, 1H), 1.72 – 1.66 (m, 6H), 1.63 – 1.58 (m, 6H), 1.46 – 1.39 (m, 1H), 1.36 – 1.12 (m, 5H), 1.02 – 0.94 (m, 3H), 0.93 – 0.89 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7 (2×C), 212.6, 131.7, 131.4, 124.6, 124.5, 124.1 (2×C), 75.7, 75.3, 75.1, 74.8, 45.3 (2×C), 45.2, 41.3, 41.2, 41.1, 41.0, 38.0, 36.9, 35.7, 29.5, 29.1, 29.0 (2×C), 28.9, 25.7, 25.5, 25.4 (2×C), 25.3, 20.4, 19.9, 19.7, 18.5, 17.7.

IR (ATR) ν_{max}: 3481, 2962, 2922, 2854, 1709, 1454, 1378.

HRMS (ESI) calcd. for $C_{20}H_{36}O_2Na^+$ $[M+Na]^+$: 331.2607, found: 331.2604.

4,8-Dimethyl-2-oxo-1-phenylnon-7-enyl methanesulfonate (7)



S4-1 **7**

Prepared according **G.P.1**, using **S4-1** (8.3 mg, 0.032 mmol, 1 eq), mesyl chloride (7.4 µL, 0.095 mmol, 3 eq), triethylamine (22 µL, 0.159 mmol, 5 eq), a few crystals of DMAP, and CH_2Cl_2 (0.2 mL). Column chromatography (petroleum-ether/ethyl acetate = 85/15) afforded 8.7 mg (81%) of mesylate **7**, as a colorless oil (mixture of isomers in a relative ratio 1.5:1, as determined by ^{1}H NMR).

Spectral data for a mixture of isomers, where H and H' correspond to the isomers in a ratio H/H'= 1.5: 1

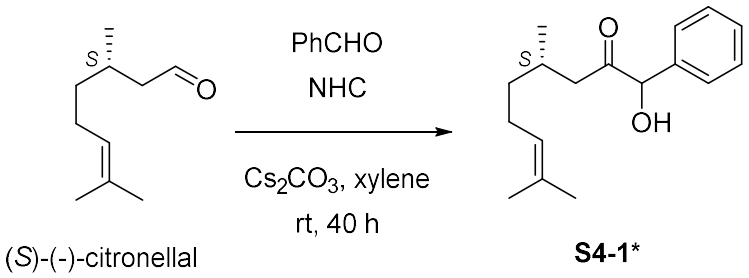
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 5H+5H'), 5.90 (s, 1H'), 5.88 (s, 1H), 5.06 – 4.96 (m, 1H+1H'), 3.04 (s, 3H+3H'), 2.46 (dd, J^l = 17.0, 5.2 Hz, 1H'), 2.38 (dd, J = 17.0, 5.8 Hz, 1H), 2.30 (dd, J = 17.0, 7.7 Hz, 1H), 2.23 (dd, J = 17.0, 8.4 Hz, 1H'), 2.07 – 1.80 (m, 3H+3H'), 1.67 (d, J = 1.0 Hz, 3H'), 1.65 (d, J = 1.0 Hz, 3H), 1.56 (s, 3H'), 1.54 (s, 3H), 1.29 – 1.04 (m, 2H+2H'), 0.85 (d, J = 6.7 Hz, 3H), 0.76 (d, J = 6.6 Hz, 3H').

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 202.6, 132.2, 132.1, 131.7, 131.6, 130.1, 130.0, 129.3, 128.2, 128.1, 124.0, 85.7, 85.5, 45.9, 39.4, 36.7, 36.5, 28.4, 28.3, 25.7, 25.3, 25.2, 19.5, 19.4, 17.6.

IR (ATR) ν_{max}: 2958, 2917, 2852, 1732, 1455, 1367.

HRMS (ESI) calcd. for $C_{18}H_{26}O_4SK$ $[M+K]^+$: 377.1183, found: 377.1174.

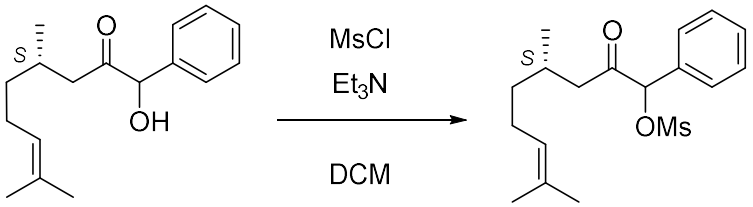
(1*S*,4*S*)-1-Hydroxy-4,8-dimethyl-1-phenylnon-7-en-2-one and (1*R*,4*S*)-1-hydroxy-4,8-dimethyl-1-phenylnon-7-en-2-one (S4-1*)



Prepared by **G.P.2**, using (*S*)-3,7-dimethyloct-6-enal (1.01 g, 6.5 mmol, 10 eq), benzaldehyde (66 µL, 0.65 mmol, 1 eq), **NHC** (23.6 mg, 0.065 mmol, 0.1 eq), cesium carbonate (21 mg, 0.065 mmol, 0.1 eq) and xylene (1.3 mL), during 40 h. Purification by dry-flash chromatography (petroleum-ether/ethyl acetate = 95/5) and two consecutive column chromatographies (benzene/ethyl acetate = 95/5 and petroleum-ether/ethyl acetate = 9/1) afforded 76.3 mg (45%) of a mixture of isomers **S4-1* (**ratio 1:1 as determined by ^{1}H NMR), as a colorless oil.

Spectral data for a mixture of isomers in a ratio H:H'=2:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H+5H'), 5.08 – 5.01 (m, 1H+2H'), 4.97 – 4.91 (m, 1H), 4.39 (d, J = 4.3 Hz, 1H), 4.39 (d, J = 4.5 Hz, 1H'), 2.37 (dd, J = 16.3, 5.4 Hz, 1H'), 2.26 (dd, J = 16.4, 6.0 Hz, 1H), 2.20 (dd, J = 16.4, 7.7 Hz, 1H), 2.13 (dd, J = 16.3, 8.3 Hz, 1H'), 2.05 – 1.75 (m, 3H+3H'), 1.67 (d, J = 1.0 Hz, 3H'), 1.67 (d, J = 1 Hz, 3H), 1.57 (s, 3H'), 1.52 (s, 3H), 1.28 – 1.20 (m, 1H'), 1.19 – 1.10 (m, 1H+1H'), 1.08 – 0.99 (m, 1H), 0.86 (d, J = 6.7 Hz, 3H), 0.69 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.3, 209.2, 138.0, 131.6, 128.9, 128.7, 127.5, 124.0, 80.2, 79.8, 45.1, 45.0, 36.8, 36.6, 29.0, 28.9, 25.7, 25.6, 25.4, 25.2, 19.6, 19.4, 17.6, 17.6.
IR (ATR) ν_{max}: 3460, 3062, 3030, 2963, 2919, 2729, 1712, 1600, 1493, 1453, 1378, 1287.
HRMS (ESI) calcd. for $C_{17}H_{24}O_2Na^+$ $[M+Na]^+$: 283.1668, found: 283.1679.

(1*S*,4*S*)-4,8-Dimethyl-2-oxo-1-phenylnon-7-enyl methanesulfonate and (1*R*,4*S*)-4,8-dimethyl-2-oxo-1-phenylnon-7-enyl methanesulfonate (7*)

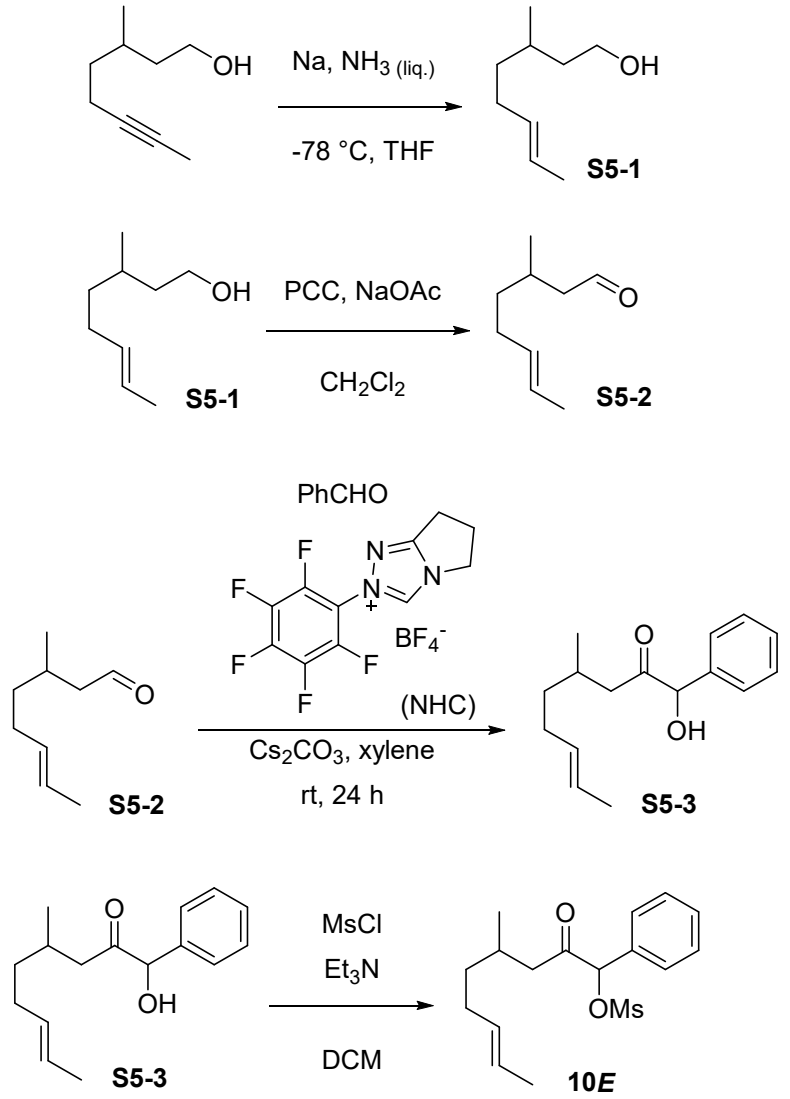


S4-1* **7***

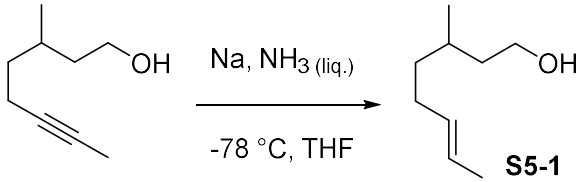
Prepared by **G.P.1**, using **S4-1*** (57 mg, 0.22 mmol, 1 eq), mesyl chloride (34 µL, 0.44 mmol, 2 eq), triethylamine (92 µL, 0.66 mmol, 3 eq), DMAP (2.7 mg. 0.022 mmol, 0.1 eq) and CH_2Cl_2 (1.1 mL). Column chromatography (petroleum-ether/acetone = 85/15) afforded 65.9 mg (88%) of **7***, as a colorless oil (mixture of two isomers in a relative ratio 1:1).

Spectral data for mixture, where H and H' correspond to isomers in a relative ratio 1:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 5H+5H'), 5.90 (s, 1H'), 5.88 (s, 1H), 5.05 – 4.96 (m, 1H+1H'), 3.04 (s, 3H+3H'), 2.46 (dd, J = 16.9, 5.2 Hz, 1H'), 2.38 (dd, J = 17.0, 5.8 Hz, 1H), 2.30 (dd, J = 17.0, 7.7 Hz, 1H), 2.23 (dd, J = 17.0, 8.4 Hz, 1H'), 2.06 – 1.80 (m, 3H+3H'), 1.66 (d, J = 0.7 Hz, 3H'), 1.65 (s, 3H), 1.56 (s, 3H'), 1.54 (s, 3H), 1.29 – 1.04 (m, 2H+2H'), 0.85 (d, J = 6.7 Hz, 3H), 0.76 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 202.6, 132.3, 132.2, 131.7, 131.6, 130.1, 130.1, 129.3, 128.2, 128.1, 124.1, 85.7, 85.5, 45.9, 39.5, 39.5, 36.7, 36.6, 28.5, 28.3, 25.7, 25.4, 25.3, 19.6, 19.4, 17.6.
IR (ATR) ν_{max}: 3032, 2963, 2921, 1732, 1495, 1454, 1409, 1361.
HRMS (ESI) calcd. for $C_{18}H_{26}O_4SNa^+$ $[M+Na]^+$: 361.1444, found: 361.1432.

Scheme S5: Preparation of precursor 10*E*



(*E*)-3-Methyloct-6-en-1-ol (S5-1)



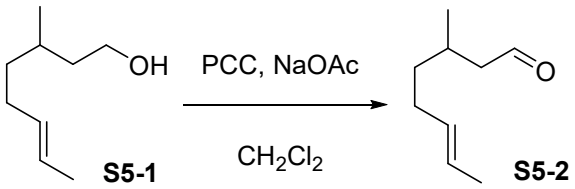
Sodium (5.3 g, 0.23 mol, 10.7 eq) was dissolved in liquid ammonia (350 mL) at –78 °C and 3-methyloct-6-yn-1-ol[11] (3g, 0.0214 mol, 1 eq) in THF (10 mL) was added to the resulting blue

[11] Gao, P., Xu, P. F.,Zhai, H., *J. Org. Chem.* **2009**, *74*, 2592–2593.

solution. The reaction mixture was stirred at –78 °C for 6 h, then warmed to room temperature and stirred until all ammonia has evaporated. The residual solid was carefully quenched with sat. NH_4Cl solution, extracted with ethyl acetate, washed with water, dried over anh. $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by dry-flash chromatography (petroleum-ether/ethyl acetate = 8/2), followed by column chromatography (the same eluent) afforded 704 mg (23%) of alkene **S5-1**, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) 5.46 – 5.36 (m, 2H), 3.71 – 3.60 (m, 2H), 2.07 – 1.90 (m, 3H), 1.66 – 1.53 (m, 5H), 1.42 – 1.33 (m, 2H), 1.24 – 1.15 (m, 1H), 0.89 (d, J = 6.6 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 131.4, 124.6, 60.9, 39.7, 36.9, 29.9, 28.9, 19.4, 17.8.
IR (ATR) ν_{max}: 3348, 3020, 2924, 1730, 1455, 1376, 1176.
HRMS (ESI) calcd. for $C_9H_{19}O^+$ $[M+H]^+$: 143.1430, found: 143.1425.

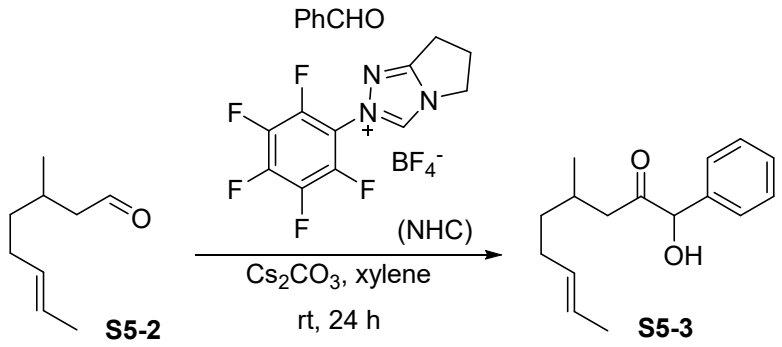
(*E*)-3-Methyloct-6-enal (S5-2)



Alcohol **S5-1** (608 mg, 4.27 mmol, 1 eq) was added to the suspension of anhydrous sodium acetate (111 mg, 1.345 mmol, 0.315 eq) and PCC (1.47 g, 6.84 mmol, 1.6 eq) in dry CH_2Cl_2 (6 mL), and the mixture was stirred for 1.5 h. Diethyl ether (70 mL) was added to the reaction mixture and the suspension was filtered through Celite. The resulting filtrate was washed with sat. $NaHCO_3$ solution, brine, dried over anh. $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by dry flash chromatography (petroleum-ether/ethyl acetate = 975/25), followed by column chromatography (with the same eluent) afforded 315 mg (53%) of aldehyde **S5-2**, as a volatile colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) 9.76 – 9.74 (m, 1H), 5.48 – 5.35 (m, 2H), 2.40 (ddd, J^1 = 16.1, J^2 = 5.6, J^3 = 2.0 Hz, 1H), 2.23 (ddd, J^1 = 16.1, J^2 = 7.9, J^3 = 2.6 Hz, 1H), 2.12 – 1.93 (m, 3H), 1.66 – 1.62 (m, 3H), 1.43 – 1.32 (m, 1H), 1.33 – 1.25 (m, 1H), 0.96 (d, J = 6.7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 131.5, 125.9, 51.6, 37.4, 30.6, 28.3, 20.5, 18.6.
IR (ATR) ν_{max}: 3020, 2959, 2880, 2853, 2715, 1726, 1456, 1410, 1380.
HRMS (ESI) calcd. for $C_{16}H_{26}O_3^+$ $[M+Na]^+$: 289.1774, found: 289.1774.

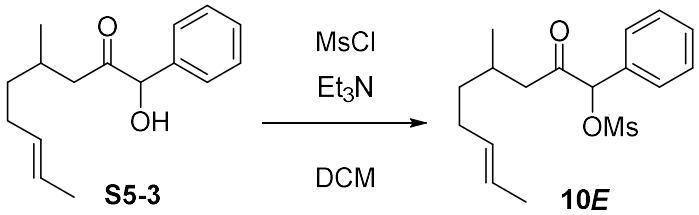
(*E*)-1-Hydroxy-4-methyl-1-phenylnon-7-en-2-one (S5-3)



Prepared by **G.P.2** using **S5-2** (250 mg, 1.78 mmol, 4 eq), benzaldehyde (45 µL, 0.445 mmol, 1 eq), NHC (23 mg, 0.063 mmol, 0.14 eq), cesium carbonate (21.5 mg, 0.066 mmol, 0.15 eq) and xylene (1 mL) during 64 h; dry-flash chromatography (petroleum-ether/ethyl acetate = 95/5) followed by column chromatography (petroleum-ether/ethyl acetate 9/1) afforded 36.5 mg (33%) of hydroxy ketone **S5-3**, as a colorless oil (mixture of isomers in a relative ratio 1.1:1, as determined by ^{1}H NMR),

Spectral data for a mixture of isomers in a ratio of H:H'= 1.1:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H+5H'), 5.43 – 5.23 (m, 2H+2H'), 5.05 (d, J = 4.4 Hz, 1H), 5.02 (d, J = 4.3 Hz, 1H'), 4.41 (d, J = 4.3 Hz, 1H), 4.40 (d, J = 4.5 Hz, 1H'), 2.36 (dd, J = 16.3, 5.5 Hz, 1H'), 2.26 (dd, J = 16.4, 6.0 Hz, 1H), 2.19 (dd, J = 16.4, 7.7 Hz, 1H), 2.12 (dd, J = 16.3, 8.3 Hz, 1H'), 2.05 – 1.75 (m, 3H+3H'), 1.65 – 1.61 (m, 3H'), 1.61 – 1.58 (m, 3H), 1.30 – 1.22 (m, 1H'), 1.22 – 1.12 (m, 1H'+1H), 1.09 – 1.00 (m, 1H), 0.85 (d, J = 6.7 Hz, 3H), 0.68 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 209.4, 138.2 (2×C), 131.0 (2×C), 129.2, 128.9, 127.7, 125.3, 125.2, 80.5, 80.0, 45.3, 45.2, 36.8, 36.5, 29.9, 29.0, 19.8, 19.6, 18.1 (2×C).
IR (ATR) ν_{max}: 3464, 3063, 3026, 2928, 2853, 1717, 1600, 1494, 1455, 1362.
HRMS (ESI) calcd. for $C_{16}H_{23}O_2^+$ $[M+H]^+$: 247.1693, found: 247.1687.

(*E*)-4-Methyl-2-oxo-1-phenylnon-7-enyl methanesulfonate (10*E*)

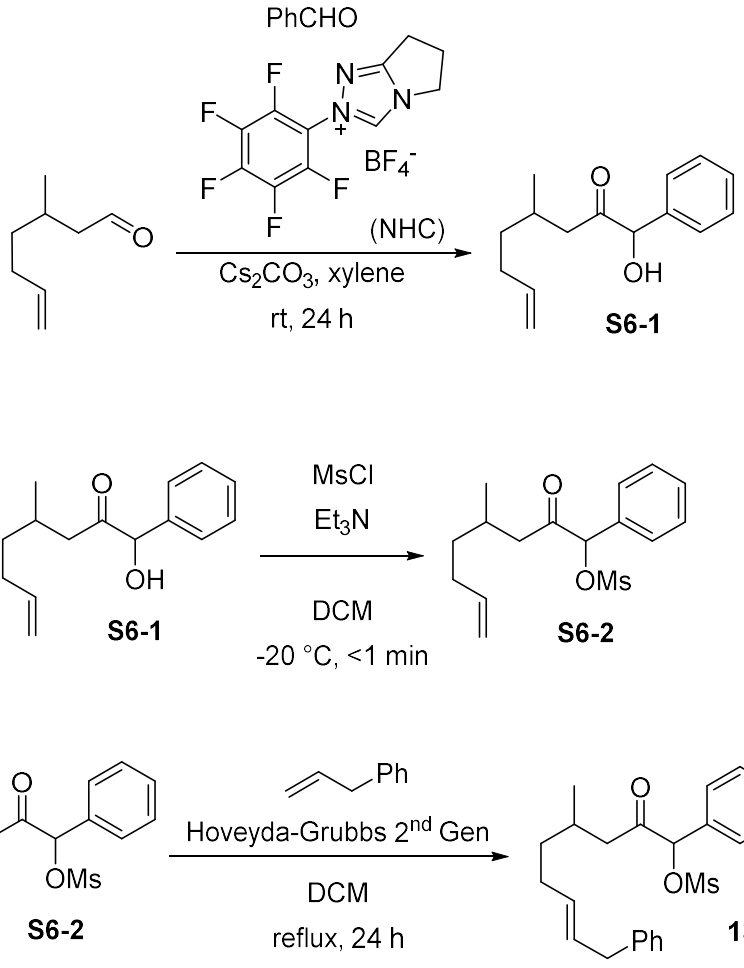


Prepared by **G.P.1**, using **S5-3** (31.6 mg, 0.128 mmol, 1 eq), mesyl chloride (20 µL, 0.256 mmol, 2 eq), triethylamine (53 µL, 0.384 mmol, 3 eq), DMAP (1.64 mg, 0.0128 mmol, 0.1 eq) and CH_2Cl_2 (1 mL). Dry flash chromatography (petroleum-ether/ethyl acetate = 85/15) afforded 36.7 mg (88%) of mesylate **10*E*** as a colorless oil (mixture of isomers, in a relative ratio 1.1:1, as determined by ^{1}H NMR).

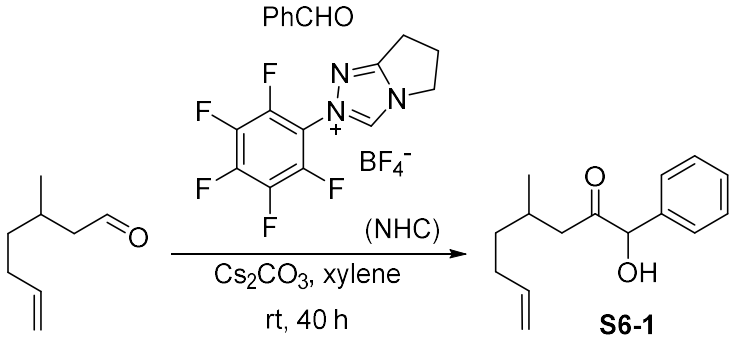
Spectral data for a mixture of isomers where H and H' correspond to the isomers in a ratio of H: H'= 1.1:1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 5H+5H'), 5.90 (s, 1H'), 5.87 (s, 1H), 5.42 – 5.26 (m, 2H+2H'), 3.04 (s, 3H+3H'), 2.45 (dd, J = 16.9, 5.2 Hz, 1H'), 2.38 (dd, J = 17.0, 5.9 Hz, 1H), 2.30 (dd, J = 17.0, 7.7 Hz, 1H), 2.22 (dd, J = 16.9, 8.3 Hz, 1H'), 2.06 – 1.80 (m, 3H+3H'), 1.64 – 1.59 (m, 3H'+3H), 1.31 – 1.05 (m, 2H'+2H), 0.86 – 0.81 (m, 3H), 0.75 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 202.1, 131.8, 131.7, 130.4, 129.7 (2×C), 128.9, 127.8, 124.7, 124.6, 85.3, 85.0, 45.4, 39.1 (2×C), 36.0, 35.8, 29.4, 29.3, 27.9, 27.8, 19.1, 18.9, 17.5.
IR (ATR) ν_{max}: 3025, 2931, 2853, 1732, 1600, 1495, 1455, 1361.
HRMS (ESI) calcd. for $C_{17}H_{24}O_4SK^+$ $[M+K]^+$: 363.1027, found: 363.1021.

Scheme S6: Preparation of precursor 13



1-Hydroxy-4-methyl-1-phenyloct-7-en-2-one (S6-1)

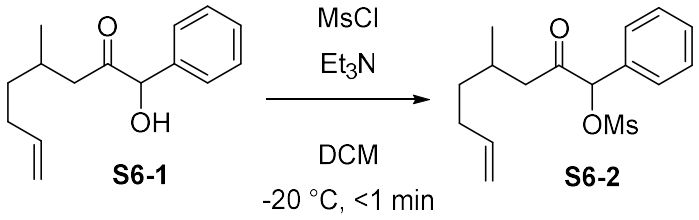


Prepared by **G.P.2**, using 3-methylhept-6-enal[12] (640 mg, 5 mmol, 5 eq), benzaldehyde (103.5 µL, 1 mmol, 1 eq), NHC (37 mg, 0.1 mmol, 0.1 eq), cesium carbonate (33 mg, 0.1 mmol, 0.1 eq) and xylene (2 mL), during 40 h. Purification by dry-flash chromatography (petroleum-ether/ethyl acetate = 99/1) followed by column chromatography (petroleum-ether/ethyl acetate = 9/1) afforded 93.3 mg (40%) of **S6-1** (a mixture of isomers in ratio H:H'= 1.5:1, as determined by ^{1}H NMR), as a colorless oil.

Spectral data for mixture of isomers in a ratio of H:H'= 1.5:1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H+5H'), 5.79 – 5.62 (m, 1H+1H'), 5.06 (s, 1H'), 5.03 (s, 1H), 5.00 – 4.86 (m, 2H+2H'), 4.39 (s, 1H+1H'), 2.37 (dd, J^1 = 16.4, J^2 = 5.5 Hz, 1H'), 2.28 (dd, J^1 = 16.5, J^2 = 6.2 Hz, 1H), 2.21 (dd, J^1 = 16.5, J^2 = 7.5 Hz, 1H), 2.14 (dd, J^1 = 16.4, J^2 = 8.2 Hz, 1H'), 2.06 – 1.81 (m, 3H+3H'), 1.36 – 1.26 (m, 1H'), 1.25 – 1.16 (m, 1H+1H'), 1.12 – 1.03 (m, 1H), 0.86 (d, J = 6.7 Hz, 3H), 0.70 (d, J = 6.7 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.1, 209.0, 138.3, 137.9, 128.9, 128.6, 127.4, 114.6, 114.5, 80.2, 79.8, 45.0, 44.9, 35.8, 35.5, 31.0, 30.8, 28.7, 28.6, 19.5, 19.3.
IR (ATR) ν_{max}: 3457, 3068, 3031, 2961, 2925, 1712, 1640, 1601, 1493, 1454 1371.
HRMS (ESI) calcd. for $C_{15}H_{24}O_2N$ $[M+NH_4]^+$: 250.1802, found: 250.1799.

4-Methyl-2-oxo-1-phenyloct-7-enyl methanesulfonate (S6-2)



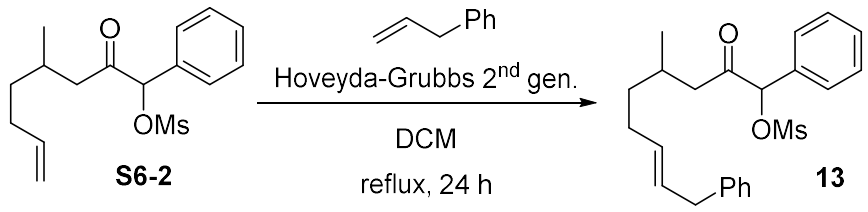
Prepared by **G.P.1**, using **S6-1** (60.4 mg, 0.26 mmol, 1 eq), mesyl chloride (40 µL, 0.52 mmol, 2 eq), triethylamine (109 µL, 0.78 mmol, 3 eq), DMAP (3 mg, 0.026 mmol, 0.1 eq) and CH_2Cl_2 (1.7 mL). Purification by dry-flash chromatography (petroleum-ether/ethyl acetate = 9/1) afforded 69.7 mg (86%) of mesylate **S6-2**, as a colorless oil (mixture of isomers in a relative ratio 1:1, as determined by ^{1}H NMR).

Spectral data for the mixture of isomers in a ratio of H:H'= 1:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 5H+5H'), 5.89 (s, 1H), 5.87 (s, 1H'), 5.78 – 5.64 (m, 1H+1H'), 4.98 – 4.86 (m, 2H+2H'), 3.03 (s, 3H+3H'), 2.46 (dd, J = 17.0, 5.3 Hz, 1H'), 2.39

[12] Hagiwara, H., Katsumi, T., Vijayendra, P. K., Hoshi, T., Suzuki, T., Ando, M., *J. Org. Chem.* **2000**, *65*, 7231-7234.

(dd, J = 17.1, 6.0 Hz, 1H), 2.31 (dd, J = 17.1, 7.5 Hz, 1H), 2.24 (dd, J = 17.0, 8.2 Hz, 1H'), 2.08 – 1.86 (m, 3H+3H'), 1.35 – 1.07 (m, 2H+2H'), 0.84 (d, J = 6.7 Hz, 3H), 0.76 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 204.2, 204.0, 139.9, 133.7 (2×C), 131.6, 130.9, 129.7 (2×C), 116.2, 116.1, 87.2, 87.0, 47.3, 41.0, 37.3, 37.1, 32.6, 32.5, 29.8, 29.7, 21.0, 20.9.
IR (ATR) ν_{max}: 3070, 3033, 2961, 2931, 2852, 1733, 1640, 1495, 1456, 1362.
HRMS (ESI) calcd. for $C_{16}H_{22}O_4SNa^+$ $[M+Na]^+$: 349.0870, found: 349.0873.

(*E*)-4-Methyl-2-oxo-1,9-diphenylnon-7-enyl methanesulfonate (13)

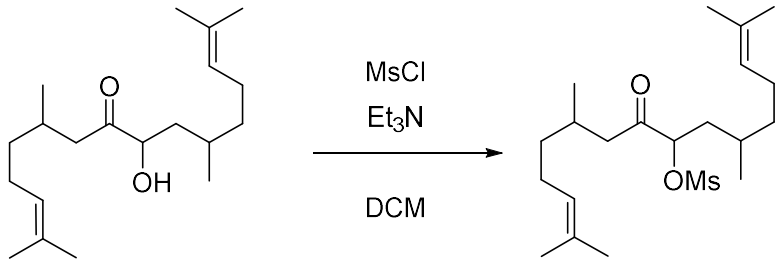


Allyl benzene (236 µL, 1.78 mmol, 20 eq) was added to the solution of **S6-2** (27.6 mg, 0.089 mmol, 1 eq) in CH_2Cl_2 (0.7 mL), followed by the addition of Hoveyda-Grubbs 2nd generation catalyst (16.8 mg, 0.027 mmol, 0.3 eq). The reaction mixture was stirred at room temperature for 16 h then at 40 °C for 24 h. The reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography (petroleum-ether/ethyl acetate = 85/15) followed by a second column chromatography with silica gel impregnated with $AgNO_3$[13] (benzene/ethyl acetate = 98/2) to afford 22.3 mg (63%) of mesylate **13**, as a colorless oil (mixture of isomers in a relative ratio 1:1, as determined by ^{1}H NMR).

Spectral data for the mixture of isomers in a ratio of H:H'= 1:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 5H+5H'), 7.31 – 7.26 (m, 2H+2H'), 7.21 – 7.14 (m, 3H+3H'), 5.89 (s, 1H), 5.87 (s, 1H'), 5.57 – 5.36 (m, 2H+2H'), 3.30 (t, J = 7.2 Hz, 2H+2H'), 3.04 (s, 3H), 3.03 (s, 3H'), 2.46 (dd, J = 17.0, 5.3 Hz, 1H'), 2.38 (dd, J = 17.0, 6.0 Hz, 1H), 2.30 (dd, J = 17.0, 7.5 Hz, 1H), 2.23 (dd, J = 16.9, 8.3 Hz, 1H'), 2.14 – 1.82 (m, 3H+3H'), 1.38 – 1.07 (m, 2H+2H'), 0.85 (d, J = 6.7 Hz, 3H), 0.76 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 202.5, 140.9, 132.1, 131.2, 130.1, 129.3, 129.2, 129.1, 128.4, 128.3, 128.2, 128.1, 125.9, 85.7, 85.4, 45.8, 39.4, 39.0, 36.3, 36.1, 29.8, 29.6, 28.3, 28.2, 19.5, 19.3.
IR (ATR) ν_{max}: 3062, 3028, 2959, 2929, 2849, 1733, 1601, 1494, 1455, 1362.
HRMS (ESI) calcd. for $C_{23}H_{28}O_4SK$ $[M+K]^+$: 439.1334, found: 439.1336.

[13] For a review on chromatography on silver nitrate impregnated silica, see: Williams, C. M.; Mander, L. N. *Tetrahedron* **2001**, *55*, 425–447, and references therein.

2,6,11,15-Tetramethyl-9-oxohexadeca-2,14-dien-8-yl methanesulfonate (16)



S4-2 **16**

Prepared by **G.P.1**, using hydroxy ketone **S4-2** (10 mg, 0.03 mmol, 1 eq), mesyl chloride (5 µL, 0.06 mmol, 2 eq), triethylamine (13.5 µL, 0.097 mmol, 3 eq), a few crystals of DMAP and CH_2Cl_2 (0.2 mL). Purification by column chromatography (petroleum-ether/ethyl acetate = 9/1) afforded 12 mg (96%) of mesylate **16,** as a colorless oil (mixture of four isomers, ratio not determined).

Spectral data for a mixture of isomers

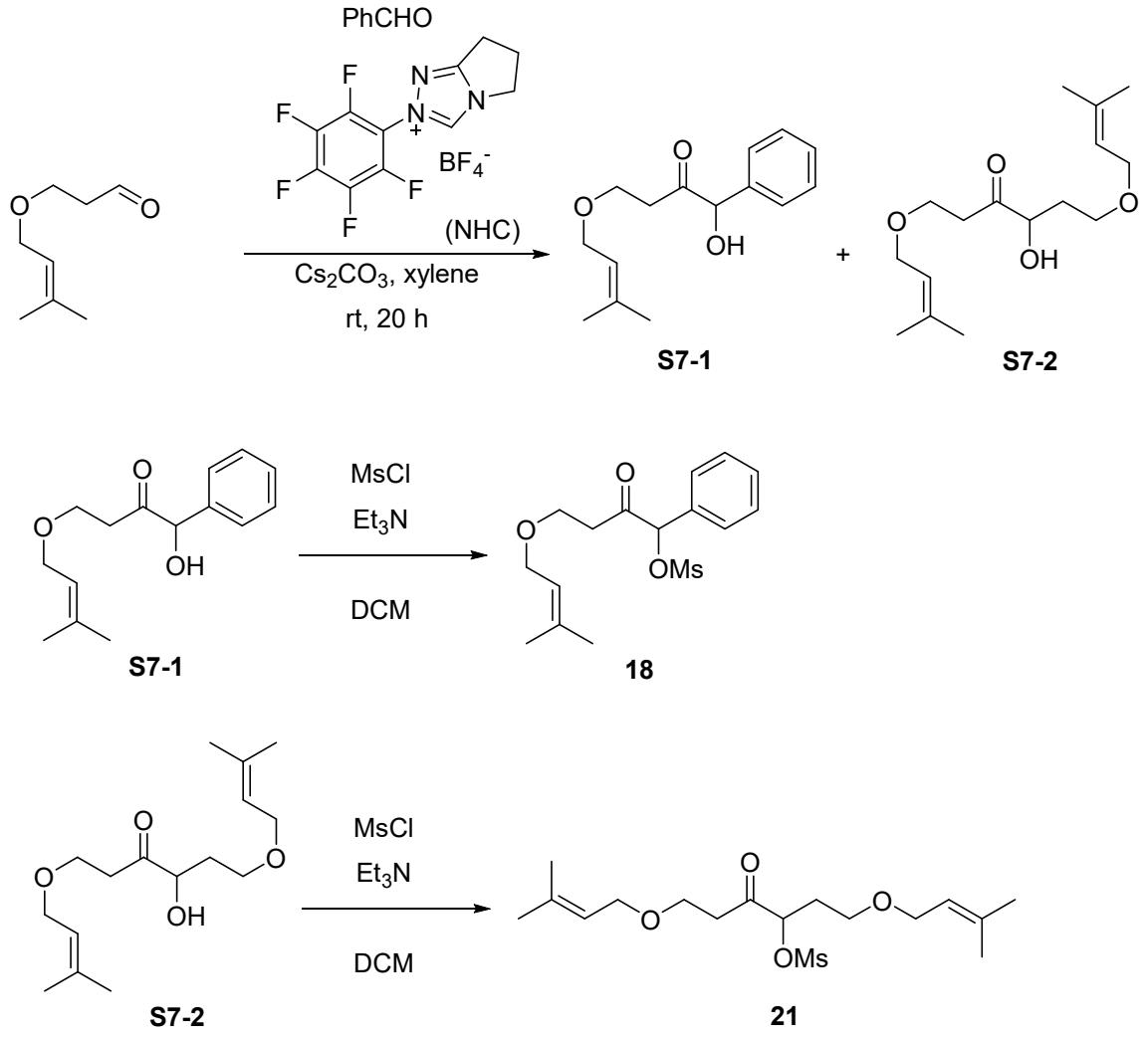
^{1}H NMR (500 MHz, $CDCl_3$) 5.12 – 5.05 (m, 2H), 5.04 – 4.95 (m, 1H), 3.14 – 3.08 (m, 3H), 2.55 – 2.44 (m, 1H), 2.39 – 2.30 (m, 1H), 2.12 – 1.90 (m, 5H), 1.82 – 1.58 (m, 14H), 1.54 – 1.45 (m, 1H), 1.38 – 1.14 (m, 4H), 1.02 – 0.96 (m, 3H), 0.94 – 0.89 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 206.0 (2×C), 205.9, 131.8, 131.7, 131.6, 124.0, 82.8, 82.6, 82.5, 82.4, 45.7, 45.6 (2×C), 45.6, 39.0, 38.9, 38.9, 38.1, 37.9, 37.4, 36.7 (2×C), 35.5 (2×C), 28.8 (2×C), 28.6, 28.2, 28.1, 25.6, 25.4, 25.3, 25.0, 19.8, 19.6, 19.6, 18.4, 17.6.

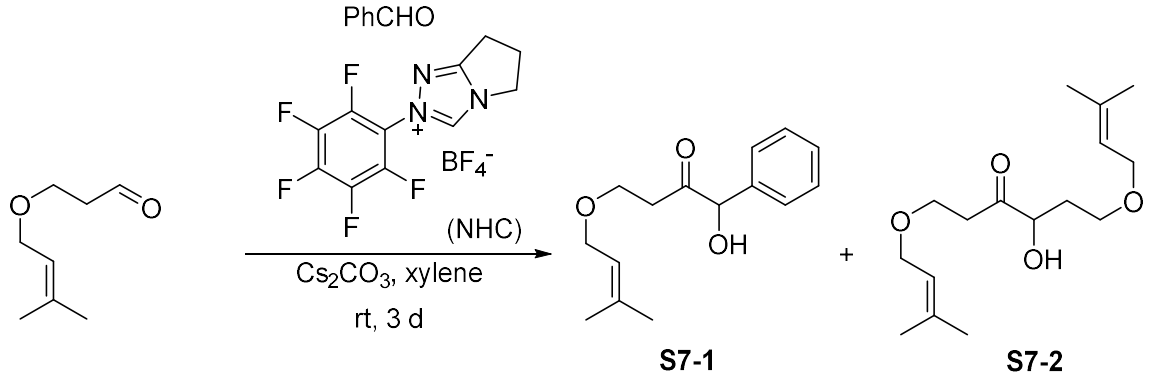
IR (ATR) ν_{max}: 2963, 2920, 2855, 1727, 1455, 1358.

HRMS (ESI) calcd. for $C_{21}H_{42}O_4SN$ $[M+NH_4]^+$: 404.2829, found: 404.2824.

Scheme S7: Preparation of precursors 18 and 21



1-Hydroxy-4-(3-methylbut-2-enyloxy)-1-phenylbutan-2-one (S7-1) and 4-hydroxy-1,6-bis(3-methylbut-2-enyloxy)hexan-3-one (S7-2)



Prepared by **G.P.2**, using 3-(3-methylbut-2-enyloxy)propanal[14] (250 mg, 1.76 mmol, 5 eq), benzaldehyde (36 µL, 0.35 mmol, 1 eq), NHC (12.8 mg, 0.035 mmol, 0.1 eq), cesium carbonate (11.5 mg, 0.035 mmol, 0.1 eq) and xylene (0.75 mL), at room temperature, during 20 h. Purification by dry-flash chromatography (petroleum-ether/ethyl acetate = 9/1), followed by column chromatography (petroleum-ether/ethyl acetate = 9/1) afforded 63.2 mg (72%) of hydroxy ketone **S7-1** and 112.1 mg (45%) of hydroxy ketone **S7-2**, both as colorless oils.

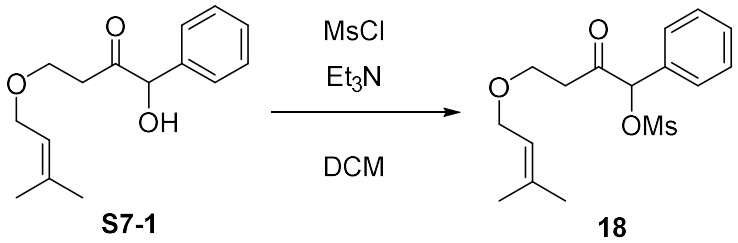
S7-1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 5.29 – 5.23 (m, 1H), 5.12 (s, 1H), 4.34 (s, 1H), 3.89 (d, J = 6.9 Hz, 2H), 3.69 – 3.62 (m, 1H), 3.59 – 3.52 (m, 1H), 2.74 – 2.66 (m, 1H), 2.51 (dt, J^1 = 16.5, J^2 = 6.0 Hz, 1H), 1.73 (s, 3H), 1.64 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 208.0, 137.7, 137.4, 128.9, 128.6, 127.4, 120.5, 80.1, 67.5, 64.6, 38.4, 25.7, 17.9.
IR (ATR) ν_{max}: 3457, 2971, 2914, 2867, 1717, 1681, 1599, 1492, 1450, 1378.
HRMS (ESI) calcd. for $C_{15}H_{20}O_3Na^+$ $[M+Na]^+$: 271.1305, found: 271.1307.

S7-2

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 – 5.24 (m, 2H), 4.26 (dt, J^1 = 6.8, J^2 = 4.1 Hz, 1H), 3.95 (d, J = 6.9 Hz, 2H), 3.91 – 3.87 (m, 2H), 3.79 (d, J = 4.2 Hz, 1H), 3.75-3.67 (m, 2H), 3.58 – 3.51 (m, 2H), 2.86 (dt, J^1 = 16.4, J^2 = 6.1 Hz, 1H), 2.75 (dt, J^1 = 16.4, J^2 = 6.6 Hz, 1H), 2.13 – 2.03 (m, 1H), 1.97 – 1.89 (m, 1H), 1.74 (s, 6H), 1.66 (s, 3H), 1.65 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.5, 136.8, 136.5, 120.4 (2×C), 74.5, 67.1 (2×C), 65.1, 64.5, 38.1, 33.0, 25.3, 25.3, 17.6, 17.5.
IR (ATR) ν_{max}: 3464, 2971, 2915, 2866, 1716, 1676, 1450, 1378, 1327.
HRMS (ESI) calcd. for $C_{16}H_{28}O_4K^+$ $[M+K]^+$: 323.1619, found: 323.1624.

4-(3-Methylbut-2-enyloxy)-2-oxo-1-phenylbutyl methanesulfonate (18)



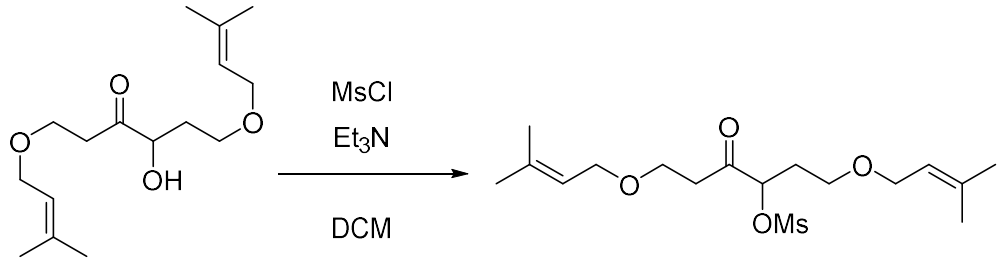
S7-1 **18**

Prepared by **G.P.**1, using **S7-1** (44.8 mg, 0.18 mmol, 1 eq), mesyl chloride (28 µL, 0.36 mmol, 2 eq), triethylamine (75 µL, 0.54 mmol, 3 eq), DMAP (2 mg, 0.018 mmol, 0.1 eq) and CH_2Cl_2 (1 mL). Purification by dry-flash chromatography (petroleum-ether/ethyl acetate = 85/15) afforded 43 mg (73%) of mesylate **18**, as a colorless oil.

[14] Comito, R. J., Finelli, F. G., MacMillan, D. W. C., *J. Am. Chem. Soc.*, **2013**, *135* (25), 9358–9361.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 5H), 5.98 (s, 1H), 5.28 – 5.23 (m, 1H), 3.89 (d, J = 6.9 Hz, 2H), 3.67 – 3.58 (m, 2H), 3.00 (s, 3H), 2.75 (dt, J^1 = 16.8, J^2 = 6.6 Hz, 1H), 2.63 (dt, J^1 = 16.8, J^2 = 6.1 Hz, 1H), 1.72 (d, J = 0.7 Hz, 3H), 1.63 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 201.6, 137.4, 132.3, 130.2, 129.5, 128.5, 120.8, 85.7, 67.7, 64.5, 39.5, 39.4, 25.9, 18.1.
IR (ATR) ν_{max}: 3031, 2970, 2919, 2864, 1734, 1674, 1495, 1453, 1360.
HRMS (ESI) calcd. for $C_{16}H_{22}O_5SNa^+$ $[M+Na]^+$: 349.1080, found: 349.1083.

1,6-Bis(3-methylbut-2-enyloxy)-4-oxohexan-3-yl methanesulfonate (21)

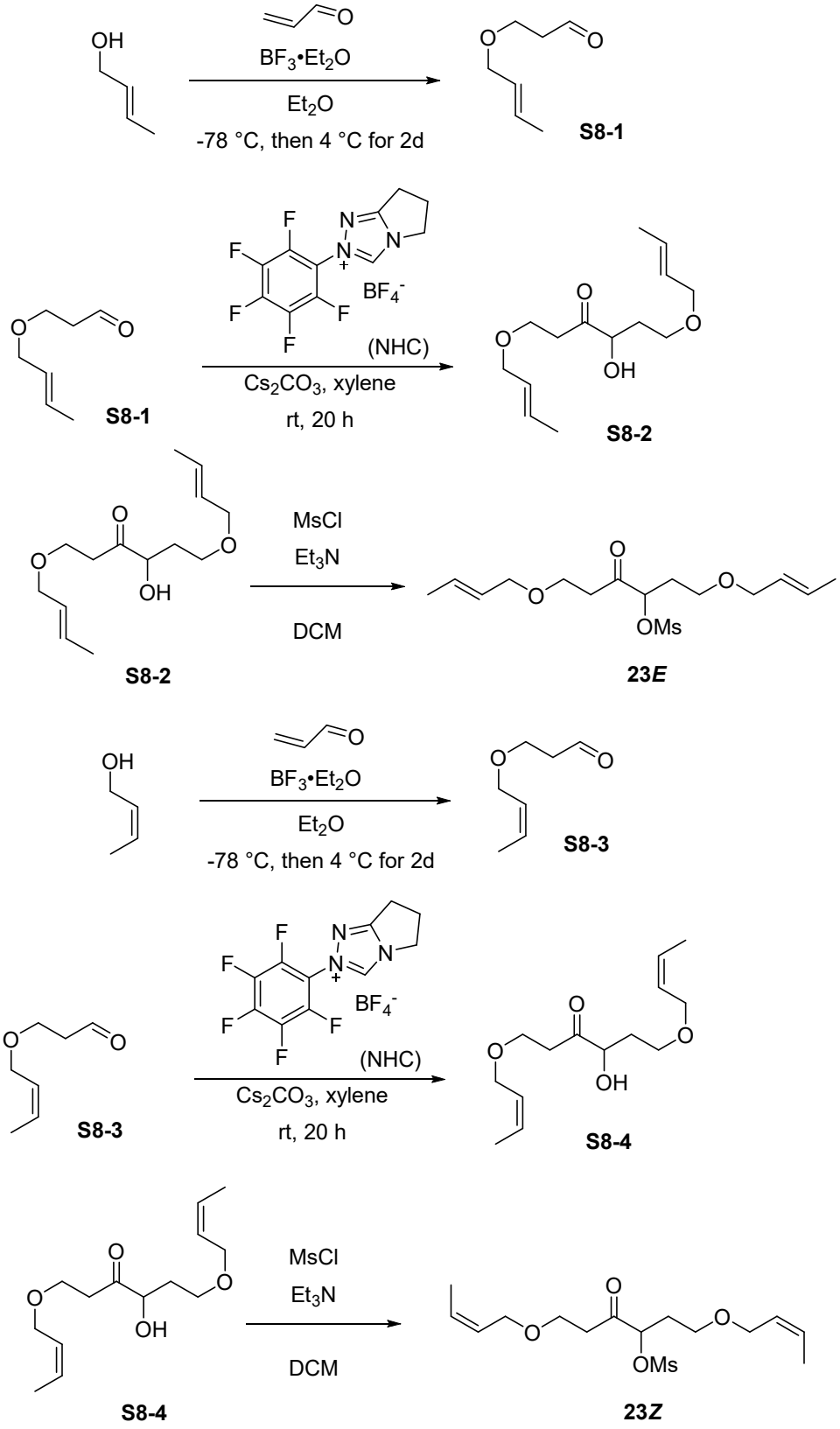


S7-2 **21**

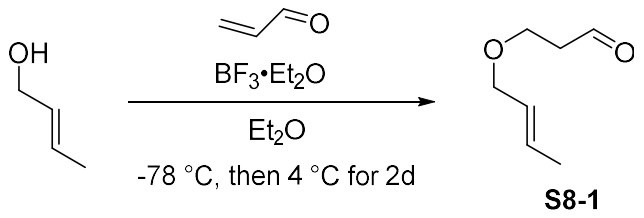
Prepared by **G.P.1**, using **S7-2** (40.6 mg, 0.14 mmol, 1 eq), mesyl chloride (22 µL, 0.285 mmol, 2 eq), triethylamine (60 µL, 0.43 mmol, 3 eq), DMAP (1.7 mg, 0.014 mmol, 0.1 eq) and CH_2Cl_2 (0.75 mL). Purification by dry-flash chromatography (petroleum-ether/ethyl acetate = 85/15) afforded 32.4 mg (63%) of mesylate **21**, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.29 – 5.22 (m, 2H), 5.10 (dd, J^1 = 7.9, J^2 = 4.1 Hz, 1H), 3.91 (t, J = 7.1 Hz, 4H), 3.68 – 3.61 (m, 2H), 3.53 – 3.45 (m, 2H), 3.06 (s, 3H), 2.84 – 2.72 (m, 2H), 2.18 – 2.10 (m, 1H), 2.05 – 1.97 (m, 1H), 1.70 (2×3H), 1.62 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 137.3, 120.9, 120.8, 81.7, 67.7, 67.6, 64.6, 64.3, 39.2, 38.7, 31.8, 25.9, 18.1.
IR (ATR) ν_{max}: 3018, 2970, 2916, 2865, 1729, 1675, 1448, 1417, 1360.
HRMS (ESI) calcd. for $C_{17}H_{30}O_6SK^+$ $[M+K]^+$: 401.1395, found: 401.1394.

Scheme S8: Preparation of precursor 23*E* and 23*Z*



(*E*)-3-(but-2-en-1-yloxy)propanal (S8-1)

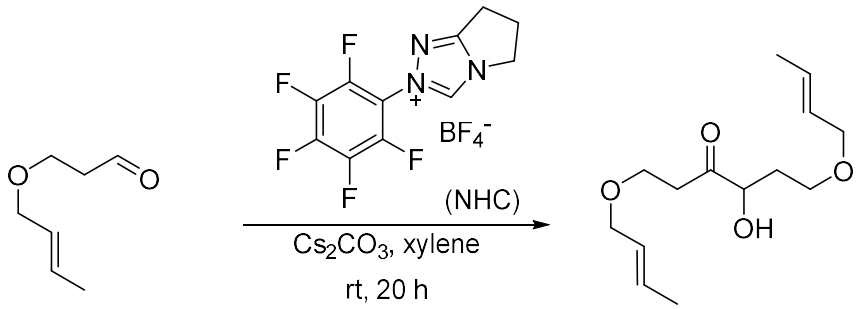


S8-1

(*E*)-crotyl alcohol (2.5 g, 35 mmol, 1 eq) was dissolved in diethyl ether (15.1 mL) and $BF_3 \cdot Et_2O$ (0.53 mL, 4.2 mmol, 0.12 eq) was added to the reaction mixture at -78 °C followed by the addition of acrolein (8.8 mL, 140 mmol, 4 eq), over the period of 30 min. After stirring for 3 days at 4 °C, the reaction was quenched with pyridine (0.8 mL), filtered through Celite and washed with diethyl ether. After concentration in *vacuo,* the residue was purified by dry flash chromatography (petroleum ether/ethyl acetate 9/1) to afford 0.99 g (22%) of aldehyde **S8-1**, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (t, J = 1.8 Hz, 1H), 5.76 – 5.64 (m, 1H), 5.61 – 5.49 (m, 1H), 3.91 (dd, J^1 = 6.3, J^2 = 0.9 Hz, 2H), 3.764 (dt, J^1 = 6.1, J^2 = 1.9 Hz, 2H), 2.69 – 2.63 (m, 2H), 1.72 – 1.68 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 201.3, 130.0, 127.3, 72.0, 63.6, 44.0, 17.8.

1,6-bis(((*E*)-but-2-en-1-yl)oxy)-4-hydroxyhexan-3-one (S8-2)



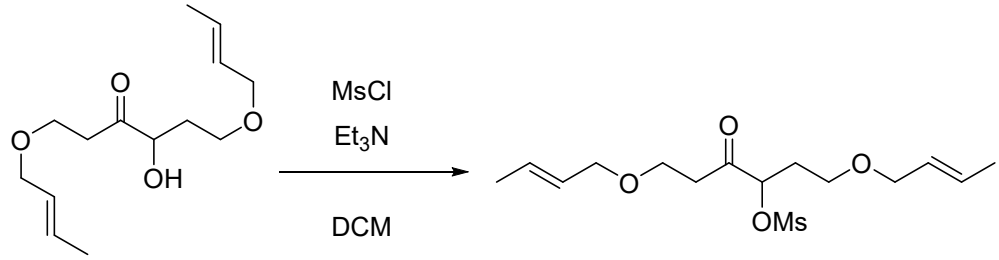
S8-1 **S8-2**

Prepared by **G.P.2.** Using aldehyde **S8-1** (50 mg, 0.39 mmol, 1 eq), NHC (8 mg, 0.036 mmol, 0.06 eq), cesium carbonate (12 mg, 0.036 mmol, 0.06 eq) and xylene (0.8 mL), during 27 h. Dry flash chromatography (petroleum ether/ethyl acetate=8/2) afforded 20.3 mg (40.6%) of hydroxy ketone **S8-2,** as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68 (ddt, J^1 = 19.3, J^2 = 12.8, J^3 = 6.4 Hz, 2H), 5.59 – 5.46 (m, 2H), 4.26 (dd, J^1 = 6.3, J^2 = 4.2 Hz, 1H), 3.88 (d, J = 6.2 Hz, 2H), 3.82 (d, J = 5.7 Hz, 2H), 3.75 – 3.63 (m, 2H), 3.56 – 3.49 (m, 2H), 2.85 (dt, J^1 = 16.3, J^2 = 6.1 Hz, 1H), 2.74 (dt, J^1 = 16.4, J^2 = 6.6 Hz, 1H), 2.13– 2.04 (m, 1H), 1.98 – 1.88 (m, 1H), 1.70 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 210.8, 129.7, 129.5, 127.4, 127.3, 74.9, 71.8, 65.4, 64.9, 38.4, 33.4, 17.7.
IR (ATR) ν_{max}: 3470, 3014, 2921, 2862, 1715, 1447, 1363, 1250, 1189, 1104.
HRMS (ESI) calcd. for $C_{14}H_{25}O_4^+$ $[M+H]^+$: 257.1747, found: 257.1742.

1,6-bis(((*E*)-but-2-en-1-yl)oxy)-4- oxohexan-3-yl methanesulfonate (23*E*)

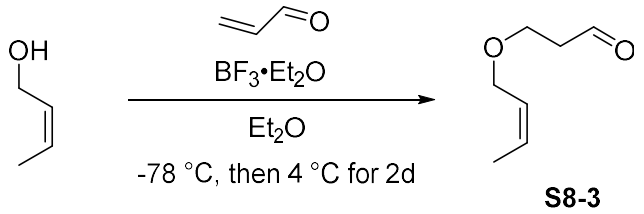


S8-2 **23*E***

Prepared by **G.P.1.** Using **S8-2** (67.1 mg, 0.26 mmol, 1 eq), mesyl chloride (41 µL, 0.52 mmol, 2 eq), triethylamine (109 µL, 0.78 mmol, 2 eq), DMAP (3 mg, 0.029 mmol, 0.1 eq) and CH_2Cl_2 (1.2 mL). Dry flash chromatography (petroleum ether/ethyl acetate 2/1) afforded 67.9 mg (78%) of mesylate **23*E***, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (dq, J^1 = 12.9, J^2 = 6.4 Hz, 2H), 5.61 – 5.52 (m, 2H), 5.18 (dd, J^1 = 7.8, J^2 = 4.1 Hz, 1H), 3.91 (t, J = 7.3 Hz, 4H), 3.71 (td, J^1 = 12.9, J^2 = 6.4 Hz, 2H), 3.60 – 3.51 (m, 2H), 3.13 (s, 3H), 2.92 – 2.79 (m, 2H), 2.26 – 2.17 (m, 1H), 2.14 – 2.04 (m, 1H), 1.77 – 1.76 – 1.71 (m, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 129.9, 129.8, 127.4, 127.3, 81.6, 72.0, 71.8, 64.5, 64.2, 39.1, 38.7, 31.7, 17.8.
IR (ATR) ν_{max}: 3479, 3016, 2937, 2862, 1729, 1673, 1448, 1354, 1242, 1176, 1103.
HRMS (ESI) calcd. for $C_{15}H_{27}O_6S^+$ $[M+H]^+$: 335.1523, found: 335.1517.

(*Z*)-3-(but-2-en-1-yloxy)propanal (S8-3)

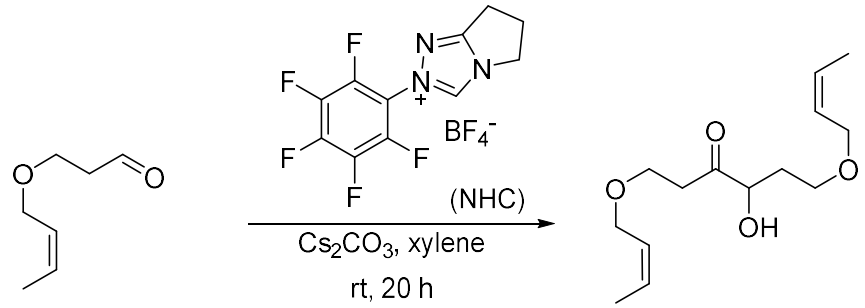


S8-3

(*Z*)-but-2-en-1-ol[15] (1.37 g, 19 mmol, 1 eq) was dissolved in diethyl ether (15 mL) and $BF_3 \cdot Et_2O$ (0.29 mL, 2.3 mmol, 0.12 eq) was added to the reaction mixture at -78 °C followed by the addition of acrolein (4.8 mL, 76.4 mmol, 4 eq), over the period of 30 min. After stirring for 2 days at 4 °C, the reaction was quenched with pyridine (0.6 mL), filtered through Celite and washed with diethyl ether. After concentration in *vacuo,* the residue was purified by dry flash chromatography (petroleum ether/ethyl acetate 9/1) to afford 0.927 g (38%) of aldehyde **S8-3**, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (t, J = 1.6 Hz, 1H), 5.74 – 5.60 (m, 1H), 5.59 – 5.49 (m, 1H), 4.05 (d, J = 6.6 Hz, 2H), 3.76 (t, J = 6.1 Hz, 2H), 2.67 (td, J^1 = 6.1, J^2 = 1.7 Hz, 2H), 1.66 (dd, J^1 = 6.9, J^2 = 0.6 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 201.4, 128.5, 126.5, 66.5, 63.8, 44.1, 13.3.
IR (ATR) ν_{max}: 3440, 3023, 2928, 2865, 2731, 2159, 1725, 1655, 1454, 1376, 1338, 1238, 1103.
HRMS (ESI) calcd. for $C_7H_{13}O_2^+$ $[M+H]^+$: 129.0910, found 129.0907.

1,6-bis(((*Z*)-but-2-en-1-yl)oxy)-4-hydroxyhexan-3-one (S8-4)



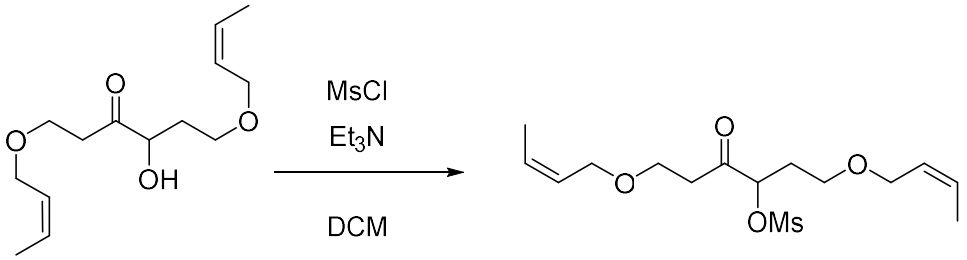
S8-3 **S8-4**

Prepared by **G.P.2.** Using aldehyde **S8-3** (300 mg, 2.34 mmol, 1 eq), NHC (25 mg, 0.07 mmol, 0.03 eq), cesium carbonate (23 mg, 0.07 mmol, 0.03 eq) and xylene (5 mL), during 27 h. Dry flesh chromatography (petroleum ether/ethyl acetate=7/3) afforded 160.9 mg (40%) of hydroxy ketone **S8-4** as a colorless oil.

[15] (*Z*)-but-2-en-1-ol was prepared according to procedure from Balduzzi, S., Brook, M. A., McGlinchey, M. J. *Organometallics*, **2005**, *24*, 2617-2627.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 – 5.58 (m, 2H), 5.56 – 5.43 (m, 2H), 4.29 – 4.23 (m, 1H), 4.02 (d, J = 6.6 Hz, 2H), 3.98 – 3.93 (m, 2H), 3.82-3.65 (m, 3H), 3.55 (t, J = 5.7 Hz, 2H), 2.85 (dt, J^1 = 16.4, J^2 = 6.0 Hz, 1H), 2.75 (dt, J^1 = 16.4, J^2 = 6.6 Hz, 1H), 2.09 (dt, J^1 = 9.3, J^2 = 4.9 Hz, 1H), 1.94 (dt, J^1 = 12.7, J^2 = 6.3 Hz, 1H), 1.64 (d, J = 5.3 Hz, 3H), 1.63 (d, J = 5.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.9, 128.2, 128.0, 126.7 (2×C), 75.0, 66.5 (2×C), 65.7, 65.2, 38.6, 33.6, 13.3 (2×C).
IR (ATR) ν_{max}: 3469, 3023, 2922, 2866, 1714, 1660, 1377, 1339, 1276, 1104.
HRMS (ESI) calcd. for $C_{14}H_{25}O_4^+$ $[M+H]^+$: 257.1747, found: 257.1742.

1,6-bis(((*Z*)-but-2-en-1-yl)oxy)-4- oxohexan-3-yl methanesulfonate (23*Z*)

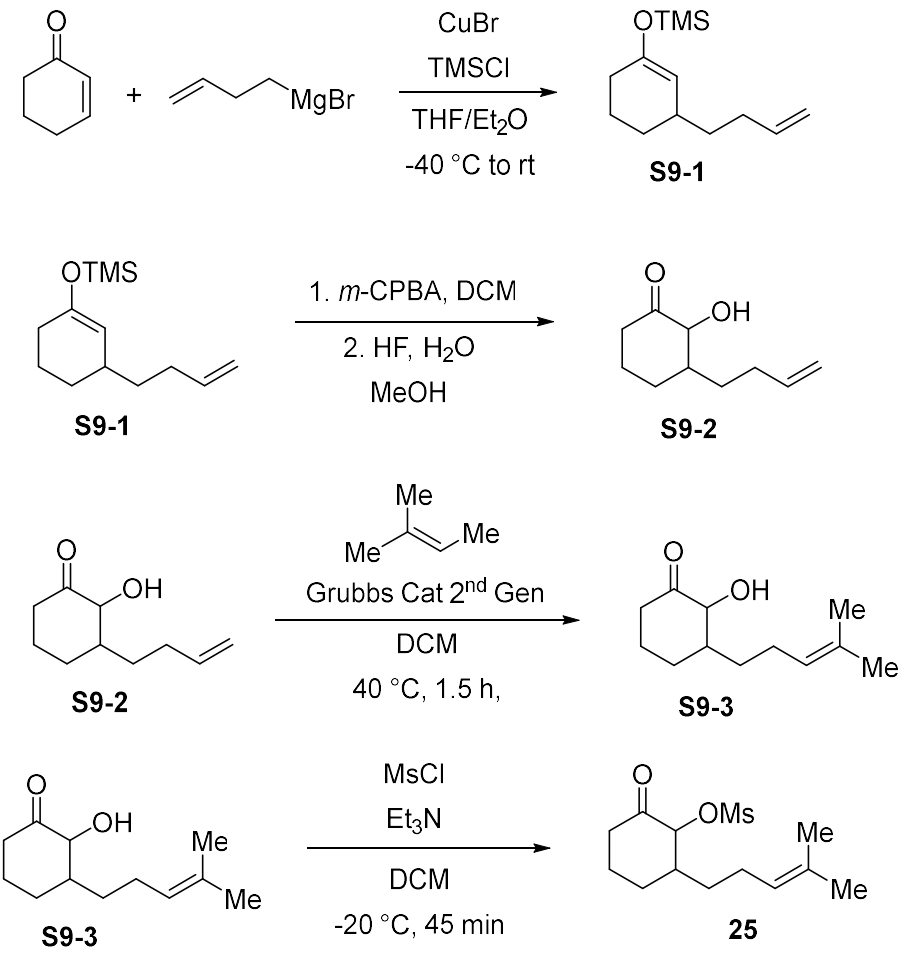


S8-4 **23*Z***

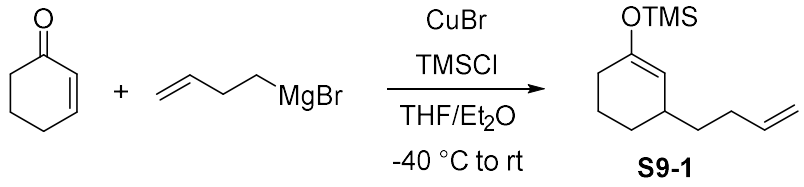
Prepared by **G.P.1.** Using **S8-4** (74.3 mg, 0.29 mmol, 1 eq), mesyl chloride (45 µL, 0.58 mmol, 2 eq), triethylamine (81 µL, 0.58 mmol, 2 eq), DMAP (3.5 mg, 0.029 mmol, 0.1 eq) and CH_2Cl_2 (1.3 mL). Dry flash chromatography (petroleum ether/ethyl acetate 7/3) afforded 72.1 mg (74%) of mesylate **23*Z***, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 – 5.61 (m, 2H), 5.55 – 5.46 (m, 2H), 5.16 (dd, J^1 = 7.8, J^2 = 4.1 Hz, 1H), 4.02 (t, J = 7.1 Hz, 4H), 3.71 (dt, J^1 = 6.3, J^2 = 1.2 Hz, 2H), 3.60 – 3.50 (m, 2H), 3.10 (s, 3H), 2.88 – 2.76 (m, 2H), 2.23 – 2.15 (m, 1H), 2.11 – 2.02 (m, 1H), 1.66 (s, 3H), 1.64 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 204.6, 128.3, 128.2, 126.7, 126.5, 81.7, 66.6, 66.4, 64.8, 64.5, 39.2, 38.7, 31.8, 13.3 (2×C).
IR (ATR) ν_{max}: 3023, 2933, 2868, 1729, 1359, 1359, 1177, 1103.
HRMS (ESI) calcd. for $C_{15}H_{27}O_6S^+$ $[M+H]^+$: 335.1523, found: 335.1516.

Scheme S9: Preparation of precursor 25



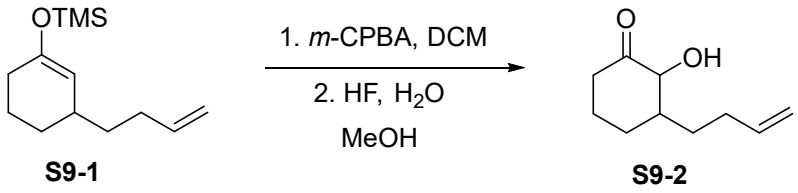
((3-(But-3-en-1-yl)cyclohex-1-en-1-yl)oxy)trimethylsilane (S9-1)



A solution of Grignard reagent [freshly prepared from Mg (0.36 g, 14.8 mmol) and 4-bromobut-1-ene (1.3 mL, 12.8 mmol) in dry Et_2O (10.4 mL)] was added dropwise to a cold (–40 °C) suspension of dry CuBr (0.75 g, 5.23 mmol) in dry THF (10.4 mL) under an argon atmosphere, with stirring. At this temperature, a solution of 2-cyclohexen-1-one (1 mL, 10.3 mmol) and TMSCl (2.65 mL, 20.9 mmol) in Et_2O (5.2 mL) was added dropwise over 45 min. The reaction mixture was kept at –40 °C for additional 15 min, then allowed to warm up to 0 °C spontaneously, when Et_3N (3.12 mL, 22.4 mmol) was added. The reaction mixture was poured into cold (0 °C) solution

of NH_4Cl (3.12 g) in water (20 mL), the layers were separated and the aqueous layer was extracted with Et_2O (2×20 mL). The combined organic extract was washed with saturated NH_4Cl (10 mL) solution (pH of water layer after washing was around 7), dried over anh. $MgSO_4$ and concentrated at rotavap. The residue was purified by short path distillation under reduced pressure to afford 1.1 g (47%) of ((3-(but-3-en-1-yl)cyclohex-1-en-1-yl)oxy)trimethylsilane (**S9-1**) (100-110 °C/1 mm Hg), as colorless liquid that was used immediately in the next step.

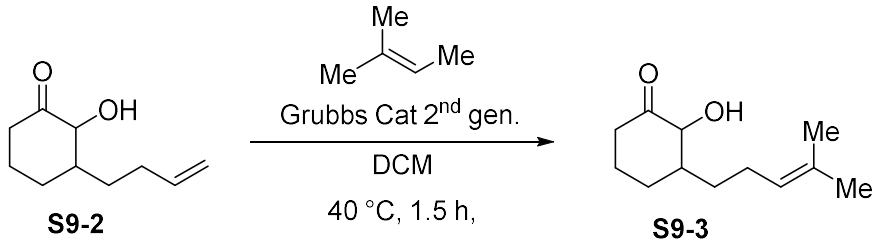
3-(But-3-en-1-yl)-2-hydroxycyclohexan-1-one (S9-2)



A solution of *m*-CPBA (560 mg, 70-75% (contains water), 2.35 mmol) in dichloromethane (3.8 mL) was added dropwise to a cold (0 °C) suspension of silylenol ether **S9-1** (434.3 mg, 1.94 mmol; from the previous step) and $NaHCO_3$ (200 mg, 2.38 mmol) in dichloromethane (9.5 mL). After stirring for 2 h at room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was dissolved in methanol (5 mL) and 50% HF (0.5 mL, 14.36 mmol) was added. After 15 min of stirring, reaction mixture was poured into a saturated $NaHCO_3$ solution in water (25 mL) and extracted with ethyl acetate (3×40 mL). The ccombined organic extract was dried over anh. $MgSO_4$ and concentrated at rotavap. Purification of the residue by column chromatography (petroleum-ether/ethyl acetate = 7/1, then toluene/ethyl acetate = 94/6) afforded 75.6 mg (23%) of hydroxy ketone (**S9-2**), as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddt, J^1 = 16.9, J^2 = 10.2, J^3 = 6.5 Hz, 1H), 5.01 (ddd, J^1 = 17.1, J^2 = 3.4, J^3 = 1.6 Hz, 1H), 4.94 (ddt, J^1 = 10.2, J^2 = 2.1, J^3 = 1.2 Hz, 1H), 3.79 (dd, J = 11.0, 1.3 Hz, 1H), 2.57 – 2.50 (m, 1H), 2.39 – 2.30 (m, 1H), 2.25 – 2.16 (m, 1H), 2.11 – 1.90 (m, 4H), 1.60 – 1.50 (m, 2H), 1.45 – 1.36 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 138.6, 114.8, 79.3, 47.5, 39.3, 32.3, 30.8, 28.8, 26.1.
IR (ATR) ν_{max}: 3441, 3074, 2930, 2860, 1717, 1430, 1287, 1259, 1107.
HRMS (ESI) calcd. for $C_{10}H_{15}O^+$ $[M+H-H_2O]^+$: 151.1174; found: 151.1122.

2-Hydroxy-3-(4-methylpent-3-en-1-yl)cyclohexan-1-one (S9-3)[16]

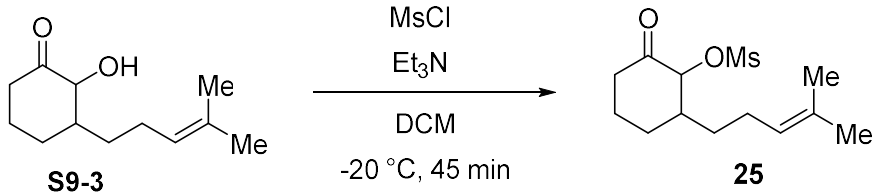


S9-2 S9-3

Grubbs 2nd generation catalyst (13.0 mg, 0.015 mmol) was added to a solution of compound **S9-2** (49.4 mg, 0.294 mmol) and 2-methyl-2-butene (8 mL) in dry CH_2Cl_2 (8 mL), and the reaction mixture was stirred for 1.5 h at 40 °C, under an argon atmosphere. SiO_2 (260 mg) was added to the reaction mixture and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 7/1) to afford 31.7 mg (55%) of 2-hydroxy-3-(4-methylpent-3-en-1-yl)cyclohexan-1-one (**S9-3**) as a very viscous, light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.11 (t, J = 7.0 Hz, 1H), 3.79 (d, J = 10.7 Hz, 1H), 3.63 (s, 1H), 2.55 (ddt, J^1 = 13.7, J^2 = 4.3, J^3 = 2.1 Hz, 1H), 2.35 (tdd, J^1 = 13.9, J^2 = 6.5, J^3 = 1.2 Hz, 1H), 2.15 – 2.05 (m, 2H), 2.03 – 1.87 (m, 3H), 1.67 (s, 3H), 1.64 – 1.50 (m, 2H), 1.60 (s, 3H), 1.45 – 1.32 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.4, 131.8, 124.3, 79.4, 47.8, 39.4, 33.29, 29.0, 26.2, 25.8, 25.2, 17.8.
IR (ATR) ν_{max}: 3479, 2928, 2861, 1715, 1449, 1381, 1260, 1098.
HRMS (ESI) calcd. for $C_{12}H_{24}NO_2^+$ $[M+NH_4]^+$: 214.1802; found: 214.1803.

2-(4-Methylpent-3-en-1-yl)-6-oxocyclohexyl methanesulfonate (25)



S9-3 25

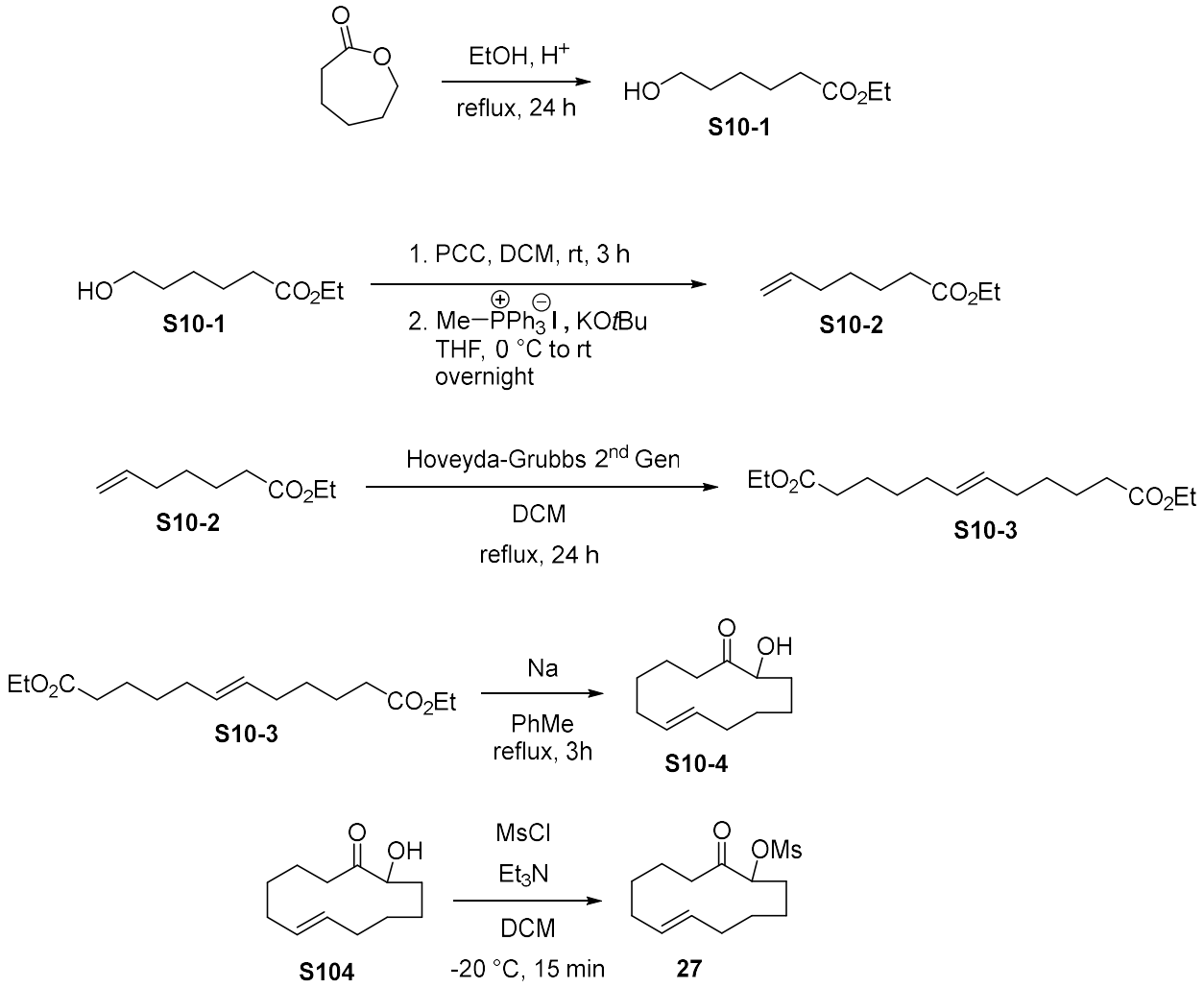
According to **G.P.1.** MsCl (20 µL, 0.258 mmol) was added to a cold (–20 °C) solution of hydroxy ketone **S9-3** (27.3 mg, 0.139 mmol), DMAP (1.7 mg, 0.014 mmol) and Et_3N (60 µL, 0.430 mmol). After 45 min TLC indicated complete conversion, when SiO_2 (150 mg) was added to the reaction mixture and the volatiles were removed under reduced pressure. The residue was purified by

[16] Following modified published protocol: Chatterjee A. K.; Sanders, D. P.; Grubbs, R. H. *Org Lett*. **2002**, *4*, 1939-1942.

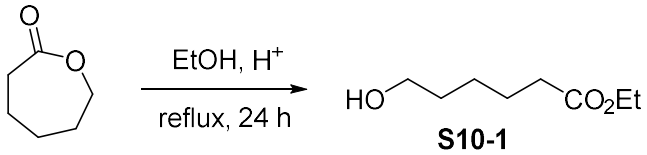
column chromatography (petroleum-ether/ethyl acetate = 2/1) to afford 34.4 mg (90 %) of 2-(4-methylpent-3-en-1-yl)-6-oxocyclohexyl methanesulfonate (**25**), as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.10 – 5.02 (m, 1H), 4.79 (d, J = 11.2 Hz, 1H), 3.21 (s, 3H), 2.59 – 2.48 (m, 1H), 2.36 (tdd, J^1 = 13.9, J^2 = 6.1, J^3 = 0.8 Hz, 1H), 2.09 (dddd, J^1 = 22.5, J^2 = 13.2, J^3 = 6.0, J^4 = 3.1 Hz, 3H), 1.97 (dt, J^1 = 22.3, J^2 = 7.8 Hz, 1H), 1.92 – 1.84 (m, 1H), 1.84 – 1.76 (m, 1H), 1.67 (d, J = 0.9 Hz, 3H), 1.63 – 1.56 (m, 1H), 1.59 (s, 3H), 1.52 – 1.42 (m, 1H), 1.42 – 1.33 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.1, 132.4, 123.6, 87.0, 44.3, 40.7, 39.6, 32.5, 29.4, 25.8, 25.3, 24.7, 17.8.
IR (ATR) ν_{max}: 2938, 2865, 1743, 1450, 1352, 1175, 1018, 971, 921.
HRMS (ESI) calcd. for $C_{13}H_{26}NO_4S^+$ $[M+NH_4]^+$: 292.1577; found: 292.1580.

Scheme S10: Preparation of precursor 27



Ethyl 6-hydroxyhexanoate (S10-1)[17]



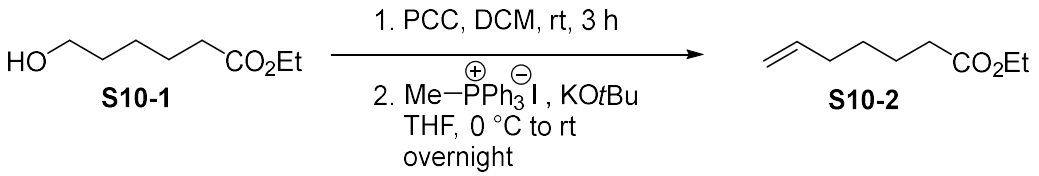
A solution of ε-caprolactone (11 mL, 11.4 g, 100 mmol) and conc. H_2SO_4 (0.5 mL) in absolute ethanol (200 mL) was refluxed for 24 h in the apparatus equipped with drying tube. After cooling to the room temperature, $NaHCO_3$ (3.5 g) was added with stirring, and the mixture was filtered

[17] Following previously reported procedure for δ-valerolactone opening: Cook, C., Liron, F., Guinchard, X., Roulland, E. *J. Org. Chem.* **2012**, *77*, 6728.

under reduced pressure. Ethanol was removed *in vacuo*, water (70 mL) was added and the product extracted with ethyl acetate (3×50 mL). The combined organic extract was dried over anh. $MgSO_4$, fitered and concentrated at rotavap. The crude product was distilled under reduced pressure to afford 13.0 g (81%) of ethyl-6-hydroxyhexanoate (**S10-1**), as clear colorless liquid (bp. 101-102 °C/1 mm Hg). NMR spectra consistent with literature.[18]

^{1}H NMR (200 MHz, $CDCl_3$) δ 4.10 (q, *J* = 7.1 Hz, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.88 (s, 1H), 1.74 – 1.47 (m, 4H), 1.47 – 1.31 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ 174.0, 62.6, 60.4, 34.3, 32.4, 25.3, 24.7, 14.3.

Ethyl hept-6-enoate (S10-2)

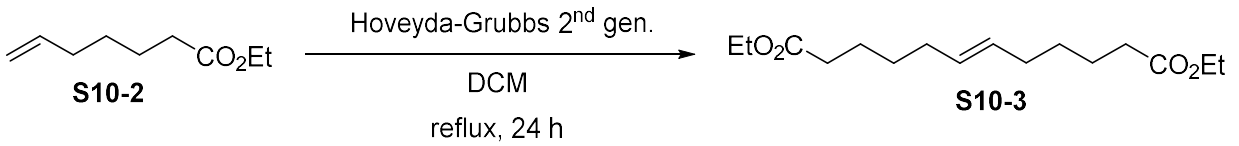


A solution of ethyl-6-hydroxyhexanoate **S10-1** (1.60 g, 10 mmol) in dry dichloromethane (2 mL) was added dropwise (over 5 min) to a suspension of PCC (3.25 g, 15 mmol) in dry dichloromethane (20 mL), with stirring, under an argon atmosphere. After 3 h, the reaction mixture was diluted with dry Et_2O (20 mL) and filtered through a pad of silica (5 g) under reduced pressure. Black residue in the flask was washed thoroughly with Et_2O (3×10 mL) and filtered each time. The combined filtrate was carefully concentrated at rotavap, to give a crude aldehyde as yellow liquid (1.57 g, 99%). The crude product was used immediately in the next step, without further purification.[19]
KO*t*-Bu (1.4 g, 12.2 mmol) was added in portions to a cold (0 °C) suspension of PPh_3MeI (5.1 g, 12.5 mmol) in THF (50 mL), with stirring, under an argon atmosphere. The suspension turned yellow, and after 45 minutes of stirring at 0 °C, a solution of aldehyde (1.57 g, 10 mmol) in dry THF (5 mL) was added dropwise, via syringe, over 5 minutes. Stirring was continued overnight, allowing reaction mixture to spontaneously warm to the room temperature. The reaction was quenched by the addition of $NH_4Cl_{(sat.)}$ (70 mL), and the product was extracted with Et_2O (3×25 mL). The combined organic extract was washed with brine (50 mL), dried over anh. $MgSO_4$, filtered and concentrated at rotavap. The residue was purified by dry-flash chromatography (petroleum-ether/ethyl acetate = 10/1) to afford 1.00 g (64% over two steps) of ethyl hept-6-enoate **S10-2**, as colorless oil. NMR spectra consistent with literature.[20]

[18] Terent'ev, A. O., Platonov, M. M.,Kutkin, A. V. *Central European Journal of Chemistry*, **2006**, *4*, 207–215.
[19] The crude product could be distilled under reduced pressure (108 °C/8 mm Hg) to give 1.0 g (64%) of aldehyde. However, this distillation only reduces the amount of aldehyde (due to its volatility), and does not improve the yield in the subsequent Wittig reaction, or the overall yield of alkene formation.
[20] Phapale, V. B., Bunuel, E., Garcia-Iglesias, M., Cardenas, D. J. *Angew. Chem. Int. Ed.* **2007**, *46*, 8790–8795.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (ddt, J^1 = 16.9, J^2 = 10.2, J^3 = 6.7 Hz, 1H), 5.06 – 4.89 (m, 2H), 4.11 (q, J = 7.1 Hz, 2H), 2.29 (t, J^1 = 7.5 Hz, 2H), 2.06 (q, J = 7.1 Hz, 2H), 1.63 (dt, J^1 = 15.4, J^2 = 7.6 Hz, 2H), 1.48 – 1.34 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 138.6, 114.8, 60.3, 34.3, 33.5, 28.5, 24.6, 14.4.

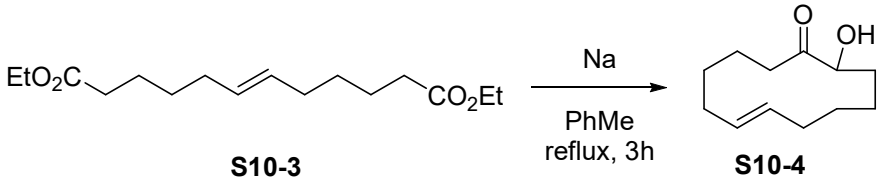
(*E*)-Diethyl dodec-6-enedioate (S10-3)



A solution of ethyl hept-6-enoate **S10-2** (1.00 g, 6.4 mmol) and Hoveyda-Grubbs 2nd generation catalyst (21.0 mg, 0.033 mmol) in dry dichloromethane (52 mL) was refluxed under an argon atmosphere, for 24 h, when TLC showed complete consumption of starting material. Reaction mixture was cooled to room temperature, silica (3 g) was added and the solvent is removed at rotavap. The residue was purified by dry-flash chromatography (petroleum-ether/ethyl acetate = 6/1) to afford (*E*)-diethyl dodec-6-enedioate (**S10-3**), as a clear liquid (530 mg, 58%). Mixture of *E*/*Z* isomers in a relative ratio 10/1, as determined by ^{1}H NMR.

Spectral data for the major isomer:
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 – 5.30 (m, 2H), 4.10 (q, J = 7.1 Hz, 4H), 2.26 (t, J = 7.5 Hz, 4H), 2.06 – 1.92 (m, 4H), 1.63 (ddt, J^1 = 30.7, J^2 = 15.4, J^3 = 7.6 Hz, 4H), 1.40 – 1.31 (m, 4H), 1.23 (t, J = 7.1 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 130.3, 60.2, 34.3, 32.2, 29.1, 24.6, 14.3.
IR (ATR) ν_{max}: 2981, 2934, 2858, 1736, 1458, 1372, 1346, 1180, 1100, 1032, 970.
HRMS (ESI) calcd. for $C_{16}H_{28}NaO_4^+$ $[M+Na]^+$: 307.1880; found: 307.1878.

(*E*)-12-Hydroxycyclododec-6-enone (S10-4)

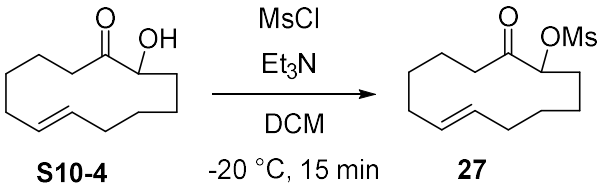


A solution of (*E*)-diethyl dodec-6-enedioate **S10-3** (155 mg, 0.545 mmol) in dry toluene (0.4 mL) was slowly added dropwise (over 2.5 h period) to a suspension of sodium (77 mg, 3.35 mmol) in dry toluene (3.6 mL), heated to reflux (130 °C oil bath), with vigorous stirring, under an argon atmosphere. After additional 30 min of stirring and heating, reaction mixture was cooled to 0 °C, quenched by addition of AcOH (0.5 mL), and water (5 mL) was added to dissolve generated salts.

The reaction mixture was extracted with toluene (2×5 mL), the combined organic extract was washed with brine (4 mL), dried over anh. $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 5/1) to afford 21 mg (20%) of (*E*)-12-hydroxycyclododec-6-enone (**S10-4**), as colorless oil.

Spectral data for the major isomer:
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 – 5.38 (m, 1H), 5.22 – 5.15 (m, 1H), 4.36 – 4.25 (m, 1H), 3.60 (d, J = 4.4 Hz, 1H), 2.90 (ddd, J^1 = 17.6, J^2 = 9.9, J^3 = 4.4 Hz, 1H), 2.22 – 2.06 (m, 4H), 2.05 – 1.81 (m, 3H), 1.76 – 1.60 (m, 2H), 1.59 – 1.41 (m, 3H), 1.38 – 1.25 (m, 2H), 0.82 – 0.70 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 213.3, 132.0, 130.8, 76.4, 36.8, 33.8, 30.2, 30.0, 26.0, 24.7, 22.1, 20.0.
IR (ATR) ν_{max}: 3478, 2928, 2855, 1710, 1453, 1402, 1366, 1100,982.
HRMS (ESI) calcd. for $C_{12}H_{20}NaO_2^+$ $[M+Na]^+$: 219.1356; found: 219.1359.

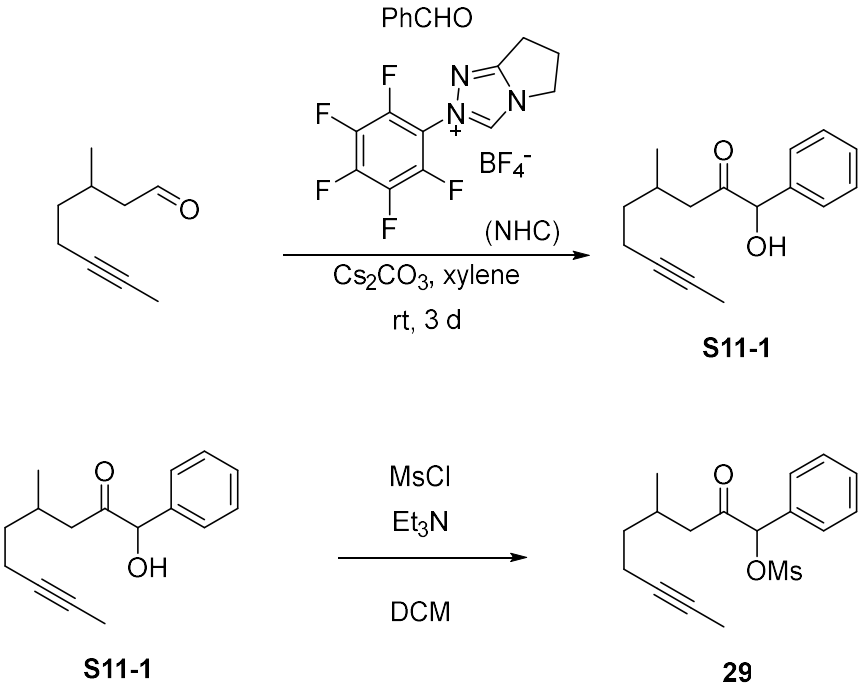
(*E*)-12-Oxocyclododec-6-en-1-yl methanesulfonate (27)



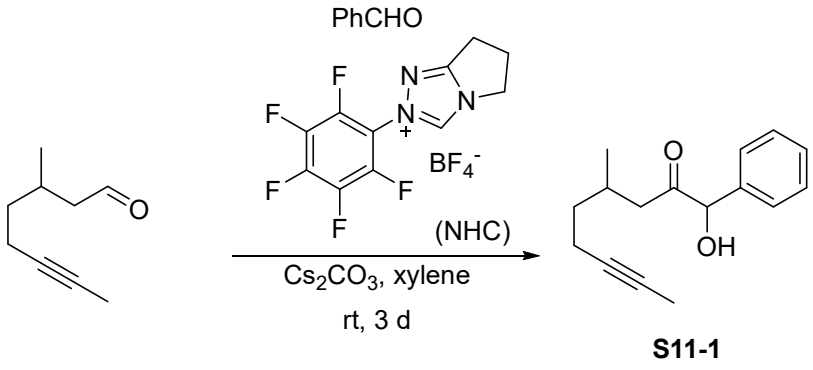
According to **G.P.1.** MsCl (33 µL, 0.426 mmol) was added to a cold (–20 °C) solution of (*E*)-12-hydroxycyclododec-6-enone **S10-4** (41 mg, 0.209 mmol), DMAP (1 mg, 0.008 mmol) and Et_3N (0.10 mL, 0.715 mmol). After 10 min TLC indicated complete conversion. SiO_2 (300 mg) was added to the reaction mixture and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 5/1) to afford 40 mg (70%) of (*E*)-12-oxocyclododec-6-en-1-yl methanesulfonate (**27**), as colorless oil.

Spectral data for the major isomer:
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 – 5.41 (m, 1H), 5.29 – 5.20 (m, 1H), 5.12 (dd, J^1 = 5.6, J^2 =4.3 Hz, 1H), 3.12 (s, 3H), 2.77 – 2.66 (m, 1H), 2.41 – 2.31 (m, 1H), 2.18 – 2.00 (m, 5H), 1.95 – 1.84 (m, 1H), 1.81 – 1.72 (m, 1H), 1.65 – 1.36 (m, 6H), 1.19 – 1.08 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 205.8, 132.6, 130.6, 84.2, 39.3, 37.52, 33.3, 30.0, 28.8, 26.3, 24.5, 22.1, 20.6.
IR (ATR) ν_{max}: 3026, 2934, 2857, 1730, 1453, 1357, 1175, 978, 954.
HRMS (ESI) calcd. for $C_{13}H_{22}NaO_4S^+$ $[M+Na]^+$: 297.1136; found: 297.1143.

Scheme S11: Preparation of precursor 29



1-Hydroxy-4-methyl-1-phenylnon-7-yn-2-one (S11-1)



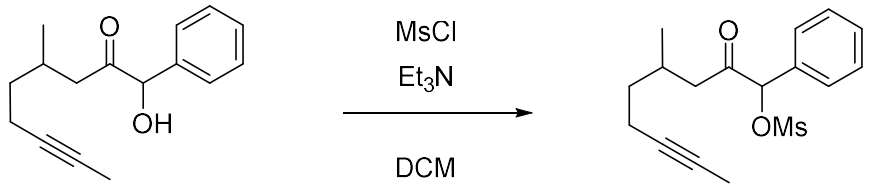
Prepared by **G.P.2**, using 3-methyloct-6-ynal[21] (540 mg, 3.9 mmol, 5 eq), benzaldehyde (80 µL, 0.78 mmol, 1 eq), NHC (28 mg, 0.078 mmol, 0.1 eq), cesium carbonate (25.4 mg, 0.078 mmol, 0.1 eq) and xylene (1.6 mL), during 3 days. Compared to work up in **G.P.2**, additional washing of the reaction mixture with sat. $NaHCO_3$ was applied. Purification by dry-flash chromatography (petroleum-ether/ethyl acetate = 925/75) followed by column chromatography (petroleum-

[21] Gao, P., Xu, P. F.,Zhai, H., *J. Org. Chem.* **2009**, *74*, 2592–2593.

ether/ethyl acetate = 85/15) afforded 56.2 mg (30%) of hydroxy ketone **S11-1,** as a colorless oil (mixture of isomers in a relative ratio of H/H'= 1.1:1, as determined by ^{1}H NMR).

Spectral data for mixture of isomers in a ratio H:H' = 1.1:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H+5H'), 5.08 (s, 1H'), 5.04 (s, 1H), 4.35 (bs, 1H), 2.45 – 2.37 (m, 1H'), 2.30 – 2.19 (m, 2H), 2.30 – 2.19 (m, 2H), 2.17 – 1.95 (m, 3H+4H'), 1.77 (t, J = 2.5 Hz, 3H'), 1.73 (t, J = 2.5 Hz, 3H), 1.45 – 1.28 (m, 1H+2H'), 1.27 – 1.15 (m, 1H), 0.86 (d, J = 6.7 Hz, 3H), 0.71 (d, J = 6.3 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.0, 208.9, 137.9, 129.0, 128.9, 128.7, 127.4, 80.2, 79.7, 78.4, 75.9, 75.8, 44.8, 44.5, 35.7, 35.5, 28.5, 28.3, 19.3, 19.0, 16.3, 16.2, 3.4 (2×C).
IR (ATR) ν_{max}: 3463, 3062, 3031, 2958, 2922, 2872, 1713, 1493, 1454, 1372.
HRMS (ESI) calcd. for $C_{16}H_{20}O_2Na^+$ $[M+Na]^+$: 267.1355, found: 267.1349.

4-Methyl-2-oxo-1-phenylnon-7-ynyl methanesulfonate (29)

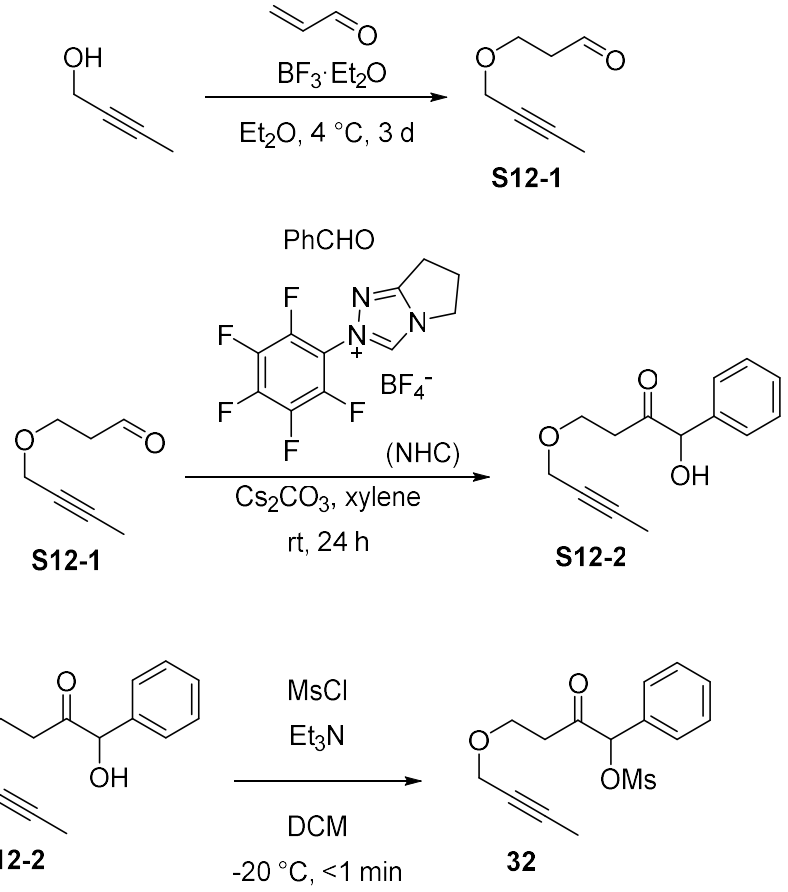


S11-1 **29**

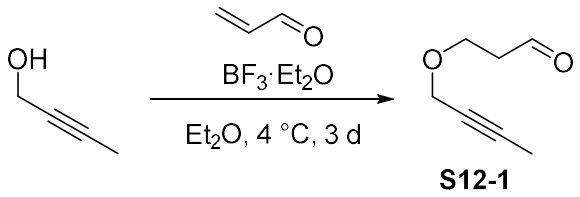
Prepared by **G.P.1** using **S11-1** (89.6 mg, 0.367 mmol, 1 eq), mesyl chloride (57 µL, 0.73 mmol, 2 eq), triethylamine (153 µL, 1.1 mmol, 3 eq), DMAP (4.4 mg, 0.037 mmol, 0.1 eq) and CH_2Cl_2 (4 mL). Dry-flash chromatography (petroleum-ether/ethyl acetate = 85/15) afforded 99.3 mg (84%) of compound **29,** as a colorless oil (mixture of isomers in a relative ratio 1.5:1, as determined by ^{1}H NMR).

Spectral data for mixture of isomers in a ratio H:H'= 1.2:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 5H+5H'), 5.91 (s, 1H'), 5.88 (s, 1H), 3.04 (s, 3H+3H'), 2.49 (dd, J = 16.7, 4.7 Hz, 1H'), 2.41 (dd, J = 17.1, 5.6 Hz, 1H), 2.32 (dd, J = 17.1, 7.8 Hz, 1H), 2.23 (dd, J = 16.7, 8.5 Hz, 1H'), 2.19 – 1.98 (m, 3H+3H'), 1.76 (t, J = 2.6 Hz, 3H'), 1.74 (t, J = 2.5 Hz, 3H), 1.45 – 1.36 (m, 1H+1H'), 1.36 – 1.20 (m, 1H+1H'), 0.84 (d, J = 6.7 Hz, 3H), 0.77 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 202.3, 132.2, 132.1, 130.1, 129.3, 128.2, 128.1, 85.7, 85.3, 78.4, 75.9, 75.8, 45.5, 45.4, 39.5, 39.4, 35.6, 35.5, 28.0, 27.9, 19.1, 19.0, 16.3, 16.2, 3.4 (2×C).
IR (ATR) ν_{max}: 3032, 2925, 2852, 1733, 1495, 1455, 1361.
HRMS (ESI) calcd. for $C_{17}H_{26}O_4SN$ $[M+NH_4]^+$: 340.1577, found: 340.1567

Scheme S12: Preparation of precursor 32



3-(But-2-ynyloxy)propanal (S12-1)[22]

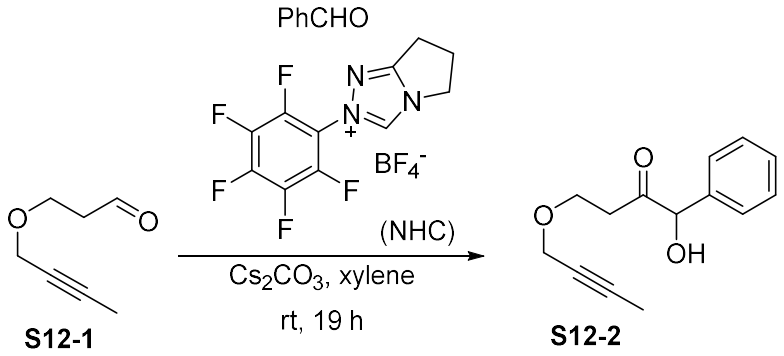


$BF_3{\cdot}Et_2O$ (0.6 mL, 4.7 mmol, 0.12 eq) was added to a cold (–78 °C) solution of 2-butin-1-ol (2.6 mL, 34.8 mmol, 1 eq) in diethyl ether (15 mL), followed by the addition of acrolein (10.2 mL, 162.5 mmol, 4 eq), over the period of 30 min. After stirring for 3 days at 4 °C, the reaction mixture was quenched with pyridine (0.8 mL), filtered through Celite and washed with diethyl ether. After concentration *in vacuo,* the residue was purified by dry-flash chromatography (petroleum-ether/ethyl acetate = 925/75) and column chromatography (petroleum-ether/ethyl acetate = 75/25) to afford 1.15 g (26%) of aldehyde **S12-1**, as a colorless oil.

[22] Prepared according to the procedure: Carless, H. A. J., Swan, D. I., Haywood, D. J., *Tetrahedron*, **1993**. *49*, 1665.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (t, J = 1.8 Hz, 1H), 4.06 (dd, J^1 = 4.6, J^2 = 2.3 Hz, 2H), 3.78 (t, J = 6.1 Hz, 2H) 2.63 (td, J^1 = 6.1, J^2 = 1.8 Hz, 2H), 1.80 (t, J = 2.3 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 200.8, 82.6, 74.6, 63.2, 58.7, 43.5, 3.4.
IR (ATR) ν_{max}: 2859, 2735, 1724, 1445, 1394, 1358, 1273.
HRMS (ESI) calcd. for $C_7H_{10}O_2Na^+$ [M+Na] $^+$: 149.0573, found 149.0570.

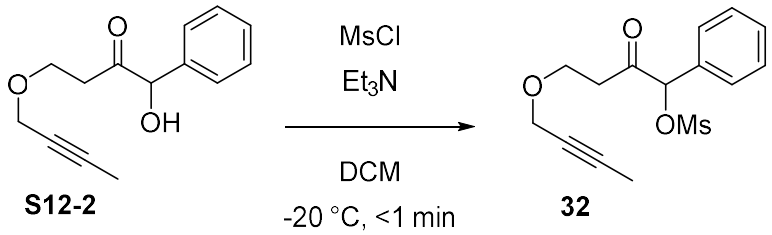
4-(But-2-ynyloxy)-1-hydroxy-1-phenylbutan-2-one (S12-2)



Prepared by **G.P.2**, using aldehyde **S12-1** (312 mg, 2.47 mmol, 5 eq), benzaldehyde (50 µL, 0.49 mmol, 1 eq), NHC (17.8 mg, 0.049 mmol, 0.1 eq), cesium carbonate (16 mg, 0.049 mmol, 0.1 eq) and xylene (1 mL), during 19 h. Two consecutive column chromatographies (petroleum-ether/ethyl acetate = 75/25 and petroleum-ether/acetone = 8/2) afforded 74 mg (65%) of hydroxy ketone **S12-2,** as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 5.13 (d, J = 4.1 Hz, 1H), 4.28 (d, J = 4.1 Hz, 1H), 4.06 (ddd, J^1 = 15.3, J^2 = 4.7, J^3 = 2.3 Hz, 1H), 4.01 (ddd, J^1 = 15.3, J^2 = 4.7, J^3 = 2.3 Hz, 1H), 3.76 – 3.70 (m, 1H), 3.68 – 3.63 (m, 1H), 2.73 (ddd, J^1 = 16.7, J^2 = 7.2, J^3 = 6.3 Hz, 1H), 2.52 (dt, J^1 = 16.7, J^2 = 5.9 Hz, 1H), 1.84 (t, J = 2.3 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 137.6, 129.0, 128.7, 127.5, 82.8, 80.1, 74.6, 64.4, 58.8, 38.2, 3.5.
IR (ATR) ν_{max}: 3455, 3062, 3031, 2917, 2872, 1718, 1601, 1493, 1452, 1360.
HRMS (ESI) calcd. for $C_{14}H_{17}O_3^+$ [M+H] $^+$: 233.1172, found: 233.1171.

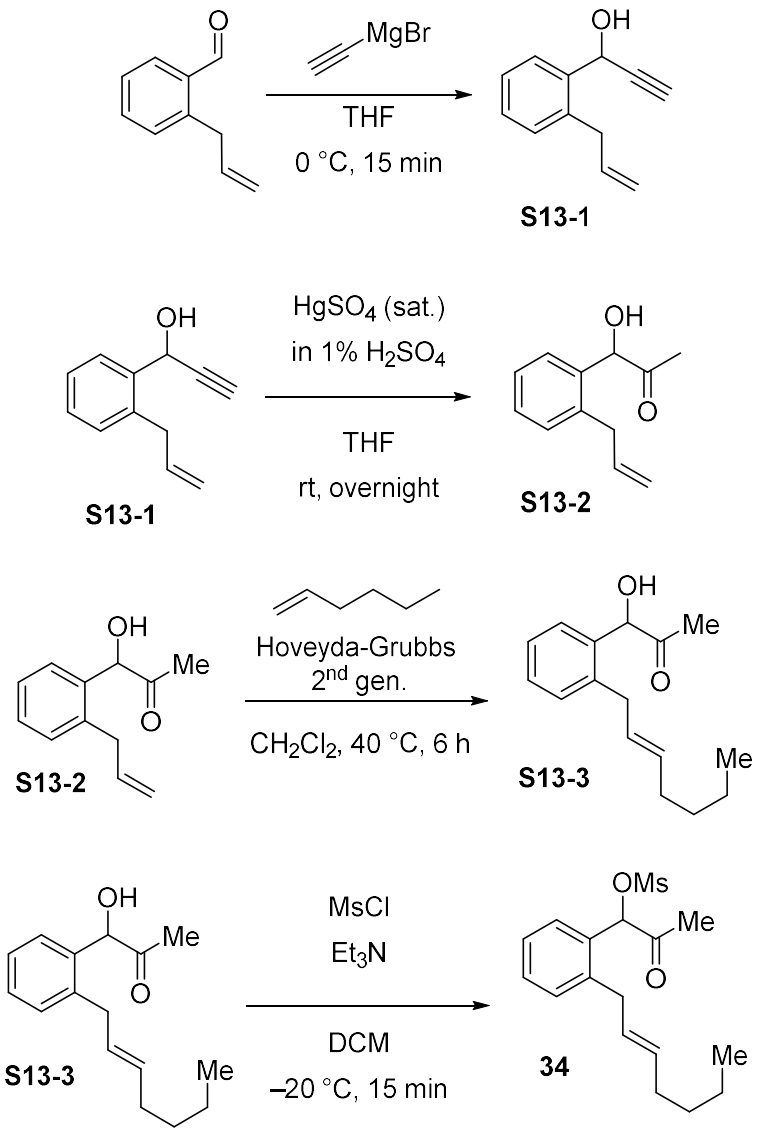
4-(But-2-ynyloxy)-2-oxo-1-phenylbutyl methanesulfonate (32)



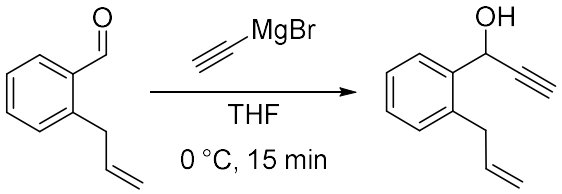
Prepared by **G.P.1**, using **S12-2** (15 mg, 0.065 mmol, 1 eq), mesyl chloride (10 µL, 0.123 mmol, 2 eq), triethylamine (27 µL, 0.194 mmol, 3 eq), DMAP (0.8 mg, 0.006 mmol, 0.1 eq) and CH_2Cl_2 (0.5 mL). Column chromatography (petroleum-ether/acetone = 8/2) afforded 16.8 mg (88%) of mesylate **32**, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 5H), 5.98 (s, 1H), 4.09 – 3.99 (m, 2H), 3.76 – 3.68 (m, 2H), 3.02 (s, 3H), 2.82 – 2.74 (m, 1H), 2.71 – 2.64 (m, 1H), 1.84 (t, J = 2.3 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 132.1, 130.1, 129.4, 128.3, 85.5, 82.9, 74.6, 64.1, 58.9, 39.3, 39.0, 3.6.
IR (ATR) ν_{max}: 3442, 3031, 2939, 2875, 1735, 1496, 1454, 1361.
HRMS (ESI) calcd. for $C_{15}H_{18}O_5SK^+$ $[M+K]^+$:349.0506, found: 349.0495.

Scheme S13: Preparation of precursor 34



1-(2-Allylphenyl)prop-2-yn-1-ol (S13-1)

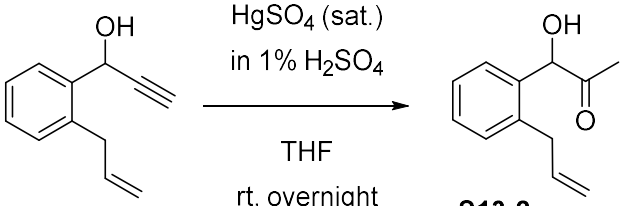


S13-1

Ethynylmagnesium bromide (15 mL, 0.5 M solution in THF, 7.5 mmol) was added dropwise to a cold (0 °C) solution of *o*-allylbenzaldehyde[23] (450 mg, 3.1 mmol) in dry THF (25 mL), under an argon atmosphere. After 15 min TLC indicated complete conversion; the reaction was quenched by the addition of NH_4Cl (sat.) (110 mL) and extracted with EtOAc (3×40 mL). The combined organic extract was dried over anh. $MgSO_4$, filtered and concentrated at rotavap. The residue was purified by dry-flash chromatography (petroleum-ether/ethyl acetate = 8/1) to afford 343.6 mg (65%) of 1-(2-allylphenyl)prop-2-yn-1-ol (**S13-1**), as a colorless oil. NMR spectra in agreement with the previously reported.[24]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 1H), 7.31 – 7.24 (m, 2H), 7.22 – 7.18 (m, 1H), 6.00 (ddt, J^1 = 17.0, J^2 = 10.1, J^3 = 6.2 Hz, 1H), 5.64 (dd, J^1 = 5.7, J^2 = 2.2 Hz, 1H), 5.09 (ddd, J^1 = 10.1, J^2 = 3.2, J^3 = 1.6 Hz, 1H), 5.02 (dq, J^1 = 17.1, J^2 = 1.7 Hz, 1H), 3.63 – 3.47 (m, 2H), 2.63 (d, J = 2.3 Hz, 1H), 2.38 (d, J = 5.8 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 137.6, 137.3, 130.4, 128.9, 127.1, 127.0, 116.3, 83.6, 74.9, 61.9, 36.7.

1-(2-Allylphenyl)-1-hydroxypropan-2-one (S13-2)



S13-1 **S13-2**

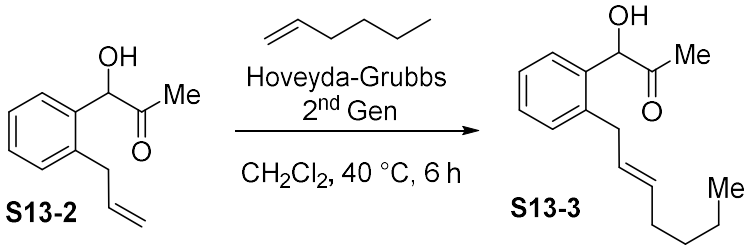
Water (5.5 mL) was added to a solution of 11-(2-allylphenyl)prop-2-yn-1-ol **S13-1** (86.4 mg, 0.502 mmol) in THF (13 mL), followed by dropwise addition of saturated $HgSO_4$ solution in 1% H_2SO_4 (1.30 mL). After 16 h of stirring at room temperature, the reaction mixture was poured into brine (60 mL) and extracted with Et_2O (3×20 mL). The combined organic extract was dried over anh.

[23] *o*-allylbenzaldehyde was synthesized as previously reported in *Org. Lett.* **2014**, *16*, 5032.
[24] *J. Org. Chem.* **2003**, *68*, 6238.

$MgSO_4$ and concentrated at rotavap. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 4/1) to afford 76.5 mg (80%) of 1-(2-allylphenyl)-1-hydroxypropan-2-one (**S13-2**), as a colorless oil.

IR$_{ATR}$: 3459, 3074, 3007, 2978, 2917, 2856, 1716, 1637, 1489, 1358, 1191, 1064, 916, 758.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.22 (m, 3H), 7.15 – 7.06 (m, 1H), 6.07 – 5.94 (m, 1H), 5.29 (d, J = 3.8 Hz, 1H), 5.12 (dq, J^1 = 10.1, J^2 = 1.6 Hz, 1H), 5.04 (dq, J^1 = 17.1, J^2 = 1.7 Hz, 1H), 4.15 (d, J = 3.9 Hz, 1H), 3.54 (qdt, J^1 = 16.1, J^2 = 5.9, J^3 = 1.5 Hz, 2H), 2.04 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 207.9, 138.5, 137.1, 136.1, 130.9, 129.0, 128.35, 127.4, 116.5, 77.2, 37.0, 25.8.

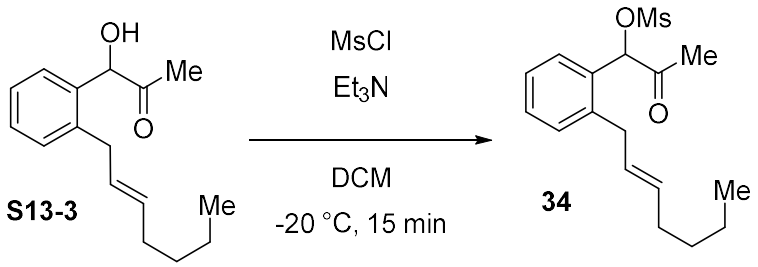
(*E*)-1-(2-(Hept-2-en-1-yl)phenyl)-1-hydroxypropan-2-one (S13-3)



A solution of 1-(2-allylphenyl)-1-hydroxypropan-2-one **S13-2** (19.1 mg, 0.1 mmol), 1-hexene (38 µL, 0.3 mmol) and Hoveyda-Grubbs 2nd generation catalyst (1.5 mg, 0.002 mmol) in dry CH_2Cl_2 (1 mL) was stirred overnight at room temperature under argon atmosphere. TLC showed slow reaction, and more Hoveyda-Grubbs 2nd generation catalyst (1.0 mg, 0.0015 mmol) and 1-hexene (26 µL, 0.2 mmol) were added and reaction mixture was heated to reflux. After 4 h of reflux one more portion of Hoveyda-Grubbs 2nd generation catalyst (1.0 mg, 0.0015 mmol) and 1-hexene (38 µL, 0.3 mmol) was added and reflux was continued overnight. SiO_2 (80 mg) was added to the reaction mixture and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 9/1) to afford 9.0 mg (38 %) of (*E*)-1-(2-(hept-2-en-1-yl)phenyl)-1-hydroxypropan-2-one (**S13-3**), as a yellow oil. Mixture of *E* and *Z* isomers in a ratio 4:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 3H), 7.08 (d, J = 7.4 Hz, 1H), 5.65 – 5.42 (m, 2H), 5.37 – 5.27 (m, 1H), 4.27 – 4.09 (m, 1H), 3.48 (qd, J^1 = 15.7, J^2 = 5.8 Hz, 2H), 2.10 – 1.94 (m, 5H), 1.41 – 1.24 (m, 4H), 0.96 – 0.86 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 208.0, 139.6, 136.1, 132.8, 130.8, 129.0, 128.42, 128.2, 127.2, 77.1, 36.0, 32.4, 31.7, 25.8, 22.4, 14.1.
IR (ATR) ν_{max}: 3462, 3064, 3022, 2958, 2927, 2857, 1717, 1601, 1452, 1358, 1066, 971, 757.
HRMS (ESI) calcd. for $C_{16}H_{22}NaO_2^+$ $[M+Na]^+$: 269.1517; found: 269.1516.

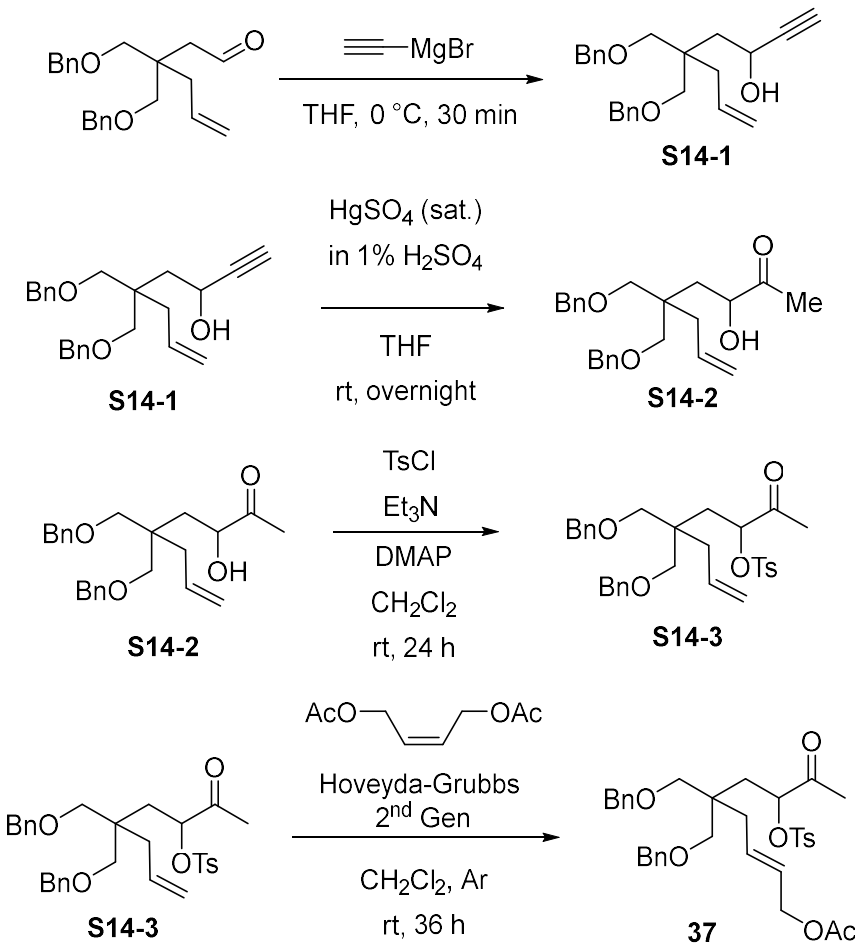
(*E*)-1-(2-(Hept-2-en-1-yl)phenyl)-2-oxopropyl methanesulfonate (34)



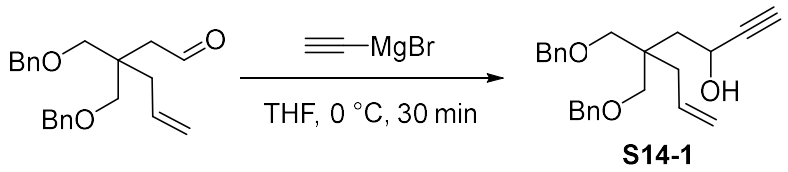
According to **G.P.1**. MsCl (10 µL, 0.129 mmol) was added to a cold (-20 °C) solution of hydroxy ketone **S13-3** (16 mg, 0.065 mmol), DMAP (1 mg, 0.008 mmol) and Et_3N (30 µL, 0.215 mmol). After 10 min TLC indicated complete conversion and SiO_2 (100 mg) was added to the reaction mixture and volatiles were removed under reduced pressure. Residue was purified by column chromatography (petroleum-ether/ethyl acetate=4/1) to afford 17.3 mg (82 %) of (*E*)-1-(2-(hept-2-en-1-yl)phenyl)-2-oxopropyl methanesulfonate (**34**), as a clear oil. Mixture of *E* and *Z* isomers in a ratio 6.7:1.

Spectral data for a mixture of *Z/E* isomers:
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 4H, minor+major), 6.24 (s, 1H, major), 6.18 (s, 1H, minor), 5.63 – 5.48 (m, 2H, minor+major), 3.57 – 3.44 (m, 2H, minor+major), 3.04 (s, 3H, major), 3.03 (s, 3H, minor), 2.16 (s, 3H, minor), 2.13 (s, 3H, major), 2.06 – 1.99 (m, 2H, minor+major), 1.41 – 1.25 (m, 4H, minor+major), 0.92 (t, J = 7.1 Hz, 3H, minor), 0.88 (t, J = 7.1 Hz, 3H, major).
^{13}C NMR (126 MHz, $CDCl_3$) δ 201.4, 140.4, 133.4, 131.1, 130.7, 130.5, 128.9, 127.7, 127.3, 82.8, 39.6, 36.1, 32.3, 31.6, 26.7, 22.4, 14.0.
IR (ATR) ν_{max}: 3025, 2958, 2929, 2859, 1737, 1601, 1453, 1359, 1176, 950, 842, 761, 529.
HRMS (ESI) calcd. for $C_{17}H_{24}KO_4S^+$ $[M+K]^+$: 363.1032; found: 363.1034.

Scheme S14: Preparation of precursor 37



5,5-Bis((benzyloxy)methyl)oct-7-en-1-yn-3-ol (S14-1)



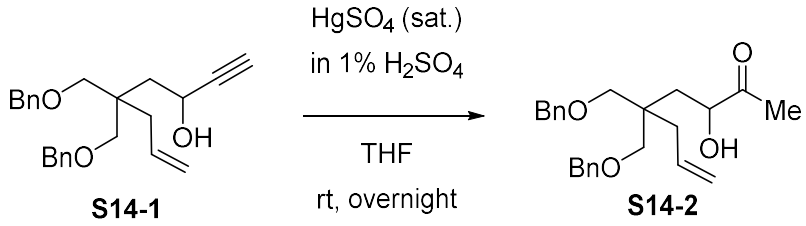
To an ice-cold solution of 3,3-bis((benzyloxy)methyl)hex-5-enal[25] (31 mg, 0.092 mmol) in THF (0.6 mL), ethynylmagnesium bromide solution (0.4 mL, 0.5 M in THF, 0.2 mmol) was added dropwise, via syringe, under an argon atmosphere. After 10 min of stirring TLC indicated complete consumption of starting material. The reaction was quenched by the addition of NH_4Cl (3 mL) and extracted with EtOAc (3×3 mL). The combined organic extract was washed with brine (3 mL),

[25] Makabe, M.; Sato, Y.; Mori, M. *J. Org. Chem*, **2004**, *69,* 6238-6243.

dried over anh. $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 9/1) to afford 23.8 mg (72%) of propargylic alcohol **S14-1,** as a pale yellow oil.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.42 – 7.20 (m, 10H), 5.86 – 5.59 (m, 1H), 5.16 – 4.97 (m, 2H), 4.61 – 4.51 (m, 1H), 4.48 (d, *J* = 3.3 Hz, 4H), 4.35 (d, *J* = 3.4 Hz, 1H), 3.44 (s, 2H), 3.41 – 3.27 (m, 2H), 2.38 (d, *J* = 2.2 Hz, 1H), 2.22 (d, *J* = 7.4 Hz, 2H), 1.91 (d, *J* = 0.9 Hz, 1H), 1.88 (d, *J* = 5.7 Hz, 1H).
^{13}C NMR (50 MHz, $CDCl_3$) δ 137.8, 133.6, 128.6, 127.9, 127.9, 118.7, 85.8, 74.0, 73.7, 72.8, 71.6, 58.8, 43.5, 41.6, 37.9.
IR (ATR) ν_{max}: 3386, 3293, 3066, 3030, 2910, 2862, 1638, 1451, 1365, 1095, 1026, 918, 739, 699, 653.
HRMS (ESI) calcd. for $C_{24}H_{28}NaO_3^+$ $[M+Na]^+$: 387.1936; found: 387.1943.

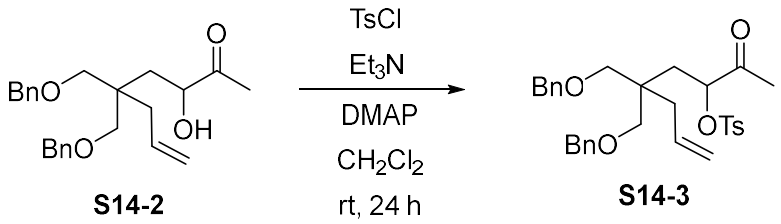
5,5-Bis((benzyloxy)methyl)-3-hydroxyoct-7-en-2-one (S14-2)



Water (1.84 mL) was added to a solution of propargylic alcohol **S14-1** (73.0 mg, 0.20 mmol) in THF (4.3 mL), followed by dropwise addition of saturated solution of $HgSO_4$ in 1% H_2SO_4 (0.45 mL). After 16 h of stirring at room temperature, the reaction mixture was poured into brine (18 mL) and extracted with Et_2O (3×6 mL). The combined organic extract was dried over anh. $MgSO_4$ and concentrated at rotavap. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 7/1) to afford 60 mg (78%) of hydroxy ketone **S14-2,** as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 10H), 5.86 – 5.67 (m, 1H), 5.14 – 4.97 (m, 2H), 4.49 (d, *J* = 8.2 Hz, 2H), 4.22 (ddd, J^1 = 10.1, J^2 = 3.9, J^3 = 1.7 Hz, 1H), 4.18 (d, *J* = 4.0 Hz, 1H), 3.50 – 3.35 (m, 4H), 2.33 – 2.20 (m, 2H), 2.15 (s, 3H), 1.88 (dd, J^1 = 14.7, J^2 = 1.8 Hz, 1H), 1.46 (dd, J^1 = 14.7, J^2 = 10.2 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 138.2, 133.9, 128.5, 127.8, 127.7, 127.7, 118.5, 74.5, 73.6, 73.56, 73.5, 73.0, 41.8, 37.8, 37.6, 25.6.
IR (ATR) ν_{max}: 3462, 3066, 3030, 2911, 2861, 1714, 1639, 1452, 1360, 1098, 739, 700.
HRMS (ESI) calcd. for $C_{24}H_{30}NaO_4^+$ $[M+Na]^+$: 405.2042; found: 405.2044.

5,5-Bis((benzyloxy)methyl)-2-oxooct-7-en-3-yl 4-methylbenzenesulfonate (S14-3)

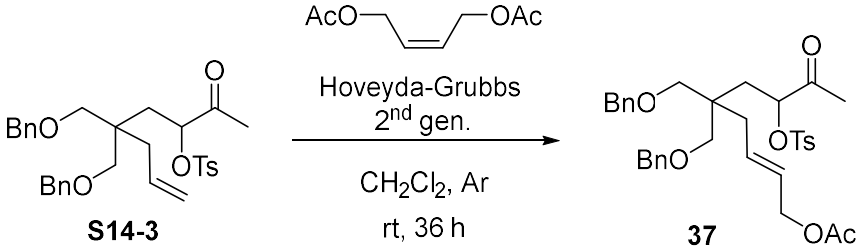


S14-2 **S14-3**

Tosyl chloride (107.0 mg, 0.767 mmol, 3.76 equiv.) was added to a solution of hydroxy ketone **S14-2** (57 mg, 0.149 mmol), DMAP (1.0 mg, 0.008 mmol) and Et_3N (0.107 mL, 0.767 mmol, 5.15 equiv.) in dry CH_2Cl_2 (1.4 mL), under an argon atmosphere, at room temperature. After 24 h of stirring, the orange reaction mixture was diluted with CH_2Cl_2 (1 mL), silica (500 mg) was added and the volatiles were removed by rotavap. Purification of the residue by column chromatography (petroleum-ether/ethyl acetate = 8/1) afforded 66.0 mg (82%) of tosyloxy ketone **S14-3,** as a very viscous colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.19 (m, 12H), 5.77 – 5.51 (m, 1H), 5.07 – 4.89 (m, 3H), 4.43 – 4.31 (m, 4H), 3.30 – 3.14 (m, 4H), 2.41 (s, 3H), 2.11 – 2.01 (m, 2H), 2.07 (s, 3H), 1.77 (d, *J* = 6.1 Hz, 1H).
^{13}C NMR (50 MHz, $CDCl_3$) δ 204.1, 145.4, 138.6, 138.5, 133.5, 130.0, 128.5, 128.3, 127.7, 118.7, 81.7, 73.2, 72.5, 71.9, 41.6, 37.2, 33.6, 25.4, 21.8.
IR (ATR) ν_{max}: 3065, 3031, 3006, 2976, 2917, 2862, 2799, 1724, 1639, 1598, 1452, 1368, 1177, 1098, 952, 916, 888768, 742, 700.
HRMS (ESI) calcd. for $C_{31}H_{36}NaO_6S^+$ $[M+Na]^+$: 559.2130; found: 559.2153.

(*E*)-5,5-Bis((benzyloxy)methyl)-8-oxo-7-(tosyloxy)non-2-en-1-yl acetate (37)



S14-3 **37**

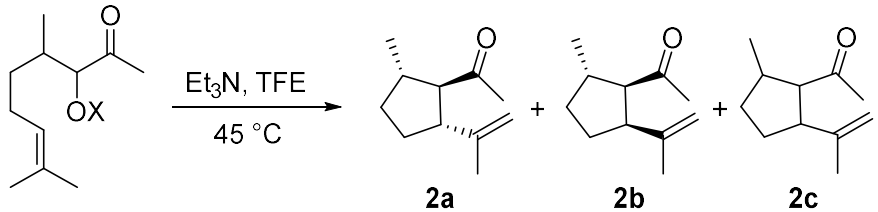
A solution of compound **S14-3** (60.0 mg, 0.112 mmol), *cis*-1,4-diacetoxy-2-butene (40 µL, 0.250 mmol) and Hoveyda-Grubbs 2nd generation catalyst (4.5 mg, 0.007 mmol) in dry CH_2Cl_2 (1 mL) was stirred overnight at room temperature, under an argon atmosphere. TLC showed slow reaction, and more Hoveyda-Grubbs 2nd generation catalyst (4.5 mg, 0.007 mmol) and *cis*-1,4-diacetoxy-2-butene (40 µL, 0.250 mmol) were added. After 6 h of stirring at room temperature one more portion

of Hoveyda-Grubbs 2nd generation catalyst (2.0 mg, 0.003 mmol) was added and stirring was continued overnight. SiO_2 (400 mg) was added to the reaction mixture and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (petroleum-ether/ethyl acetate = 4/1) to afford 44.8 mg (66 %) of allylic acetate **37,** as a pale yellow, viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.36 – 7.24 (m, 12H), 5.61 – 5.54 (m, 1H), 5.49 (dt, J^1 = 15.3, J^2 = 6.1 Hz, 1H), 5.00 (t, J = 6.1 Hz, 1H), 4.43 (d, J = 6.0 Hz, 2H), 4.40 – 4.32 (m, 4H), 3.20 (ddd, J^1 = 12.8, J^2 = 12.2, J^3 = 6.5 Hz, 4H), 2.42 (s, 3H), 2.08 – 2.02 (m, 2H), 2.06 (s, 3H), 2.04 (s, 3H), 1.76 (d, J = 6.1 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 170.9, 145.4, 138.4, 133.3, 130.6, 130.0, 128.5, 128.3, 128.0, 127.7, 81.6, 73.3, 72.3, 71.8, 65.0, 41.8, 35.6, 33.6, 25.4, 21.8, 21.1.
IR (ATR) ν_{max}: 3087, 3062, 3030, 2862, 1738, 1598, 1451, 1367, 1234, 1177, 1096, 1024, 953, 743, 699.
HRMS (ESI) calcd. for $C_{34}H_{40}NaO_8S^+$ $[M+Na]^+$: 631.2342; found: 631.2340.

2. Cyclizations of oxyallyl cations

1-(2-Ethyl-5-methylcyclopentyl)ethan-1-one (2) (General procedure for the cyclization - Method A)



		2a		2b		2c
1 ***syn*** (X=Ts)	63%	7	:	4.5	:	1
1 ***anti*** (X=Ts)	74%	9.7	:	6	:	1
1 ***syn*** **+** ***anti*** (X=Ms)	70%	6.9	:	4.5	:	1

Triethylamine (61 μL, 0.438 mmol, 1.6 eq) was added to the solution of **1** ***syn*** (93.7 mg, 0.277 mmol, 1 eq) in 2,2,2-trifluoroethanol (0.85 mL) and the reaction mixture was stirred at 45 °C for 41 h, under an argon atmosphere.[26] The reaction mixture was carefully concentrated *in vacuo* and the residue was purified by column chromatography (pentane/diethyl ether = 95/5) to afford 28.9

[26] Previously reported procedure was modified: Vander Wal, M. N., Dilger, A. K., MacMillan, D. W. C., *Chem. Sci.,* **2013**, 4, 3075.

mg (63%) of volatile compound **2**, as a colorless oil (mixture of isomers in a relative ratio 7:4.5:1, as determined by ^{1}H NMR and GC/MS).

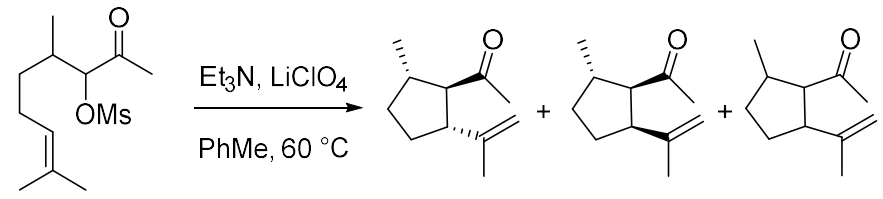
According to the General procedure – Method A. Starting from **1** ***anti*** (47.2 mg, 0.139 mmol), triethylamine (30 µL, 0.219 mmol) and 2,2,2-trifluoroethanol (0.4 mL), **2** (17.0 mg, 74%) was obtained, as mixture of isomers in a relative ratio 9.7:6:1, as determined by ^{1}H NMR and GC/MS.

According to the General procedure – Method A. Starting from **1** ***anti*** **+** ***syn*** (13.0 mg, 0.050 mmol), triethylamine (11 µL, 0.078 mmol) and 2,2,2-trifluoroethanol (0.15 mL), **2** (5.8 mg, 70%) was obtained, as mixture of isomers in a relative ratio 6.9:4.5:1, as determined by ^{1}H NMR.

Spectral data for mixture, spectra given where H: H': H'' correspond to the isomers in a ratio 5.5: 3.5: 1.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 – 4.66 (m, 2H+2H'+2H''), 3.05 – 2.94 (m, 1H'+2H''), 2.79 (dd, J = 18.2, 9.0 Hz, 1H), 2.67 (dd, J = 8.0, 8.0 Hz, 1H'), 2.56 – 2.46 (m, 1H''), 2.46– 2.36 (m, 1H'), 2.41 (t, J = 9.6 Hz, 1H), 2.27 – 2.16 (m, 1H), 2.15 (s, 3H''), 2.12 (s, 3H), 2.09 (s, 3H'), 2.05 – 1.97 (m, 1H'), 1.96 – 1.82 (m, 2H+1H'+2H''), 1.79 – 1.74 (m, 1H'), 1.72 (s, 3H), 1.69 (s, 3H''), 1.69 (s, 3H'), 1.66 – 1.56 (m, 1H), 1.52 – 1.28 (m, 1H+2H''), 1.27 – 1.15 (m, 1H'), 1.04 (d, J = 6.7 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H'), 0.86 (d, J = 7.1 Hz, 3H'').
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.4, 210.3, 210.1, 147.3, 146.6, 145.9, 111.9, 110.5, 109.2, 64.6, 64.2, 59.7, 51.8, 50.0, 46.5, 38.6, 36.9, 35.7, 34.1, 33.6, 33.4, 31.4, 31.0, 30.2, 30.1, 30.0, 29.8, 21.8, 20.9, 19.8, 19.8, 16.8.
IR (ATR) ν_{max}: 3078, 2955, 2869, 1708, 1644, 1456, 1374, 1356.
HRMS (ESI) calcd. for $C_{11}H_{19}O^+$ $[M+H]^+$: 167.1430, found: 167.1423.

Inferior yield was observed when the reaction was performed on a larger scale, due to side reactions with trifluoroethanol. Therefore, the cyclization was performed in toluene on a gram scale (4.5 mmol), under modified conditions (see Method C).

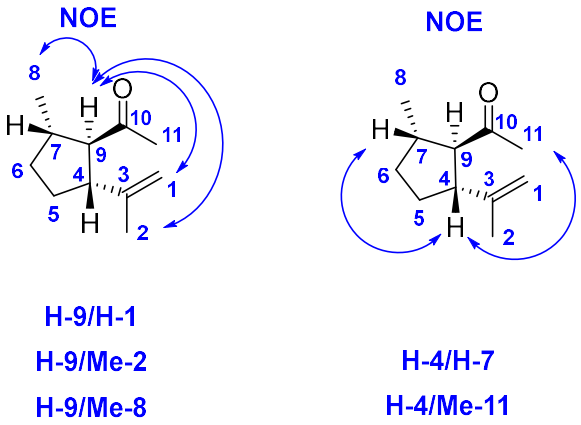
1-(2-Ethyl-5-methylcyclopentyl)ethan-1-one (2) (General procedure for the cyclization - Method C)



1 ***syn*** **+** ***anti*** **2a** **2b** **2c**
55% 6.9 : 4.5 : 1

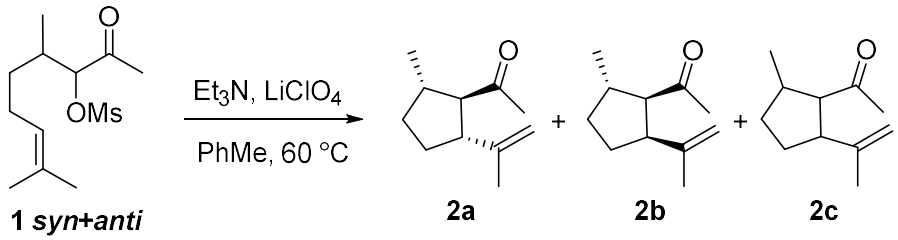
A suspension of **1** ***syn*** **+** ***anti*** (1.18 g, 4.5 mmol), trimethylamine (1.25 mL, 9 mmol) and lithium perchlorate (957.5 mg, 9 mmol) in toluene (16 mL) was stirred at 60 °C for 7 h (the reaction was performed under air, reaction vessel was capped). SiO_2 (3 g) was added, the solvent was removed at rotavap and the resulting slurry was put as a cake at the top of a SiO_2 column (8 g) and purified by column chromatography (pentane/diethyl ether = 95/5) to afford volatile product **2** (411 mg, 55%), as a colorless oil (mixture of isomers in a relative ratio 6.9:4.5:1).

Correlations (NOESY) for major diastereomer **2a**:



In order to determine whether the product distribution (**2a**:**2b**:**2c**) is constant over time, cyclization reaction of **1** reaction progress was monitored by GC/MS. This was repeated several times.

Distribution of products 2a:2b:2c over time (conditions: Method C)

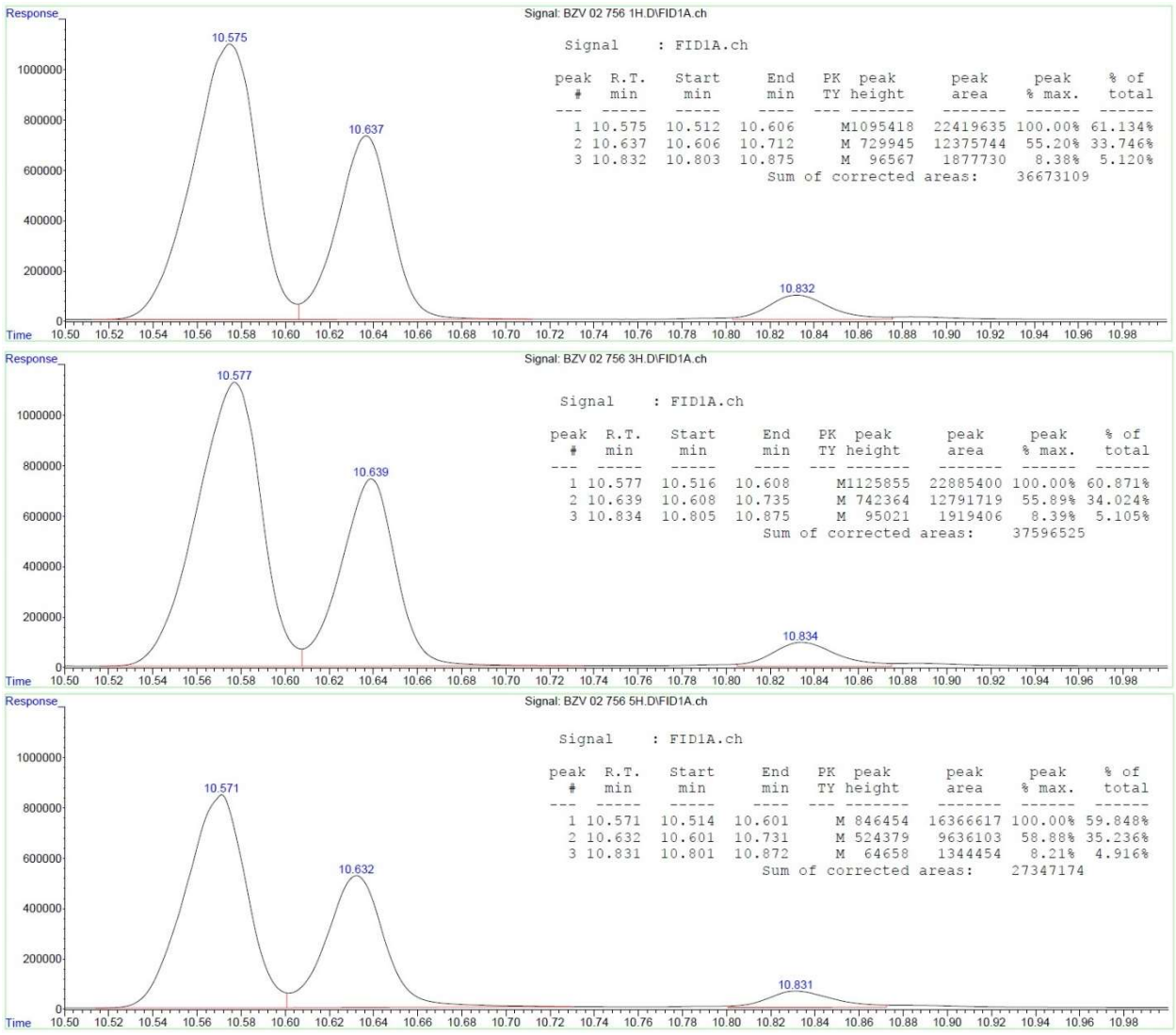


A suspension of **1** *syn* + *anti* (30.0 mg, 0.114 mmol), triethylamine (32 µL, 0.229 mmol) and lithium perchlorate (24.3 mg, 0.229 mmol) in toluene (0.40 mL) was stirred at 60 °C. At certain points of time, reaction mixture aliquots (40 µL) were taken, diluted using dichloromethane (1.00 mL) and analyzed directly by GC-MS.

Table S1: Product **2** distribution over time

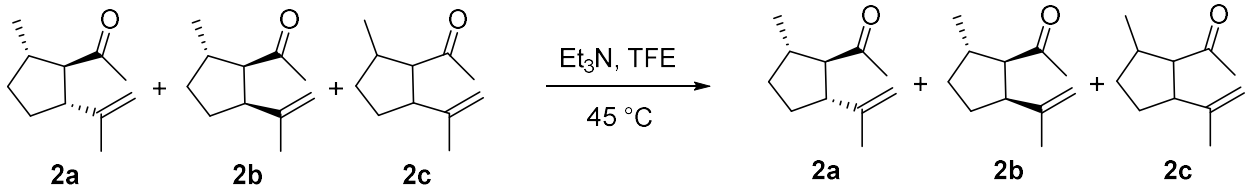
time (h)	relative ratio **2a**:**2b**:**2c**
1	61.1 : 33.7 : 5.1
3	60.9 : 34.0 : 5.1
5	59.8 : 35.2 : 4.9

GC/MS traces of reaction mixture at different reaction times:



Resubmission experiment

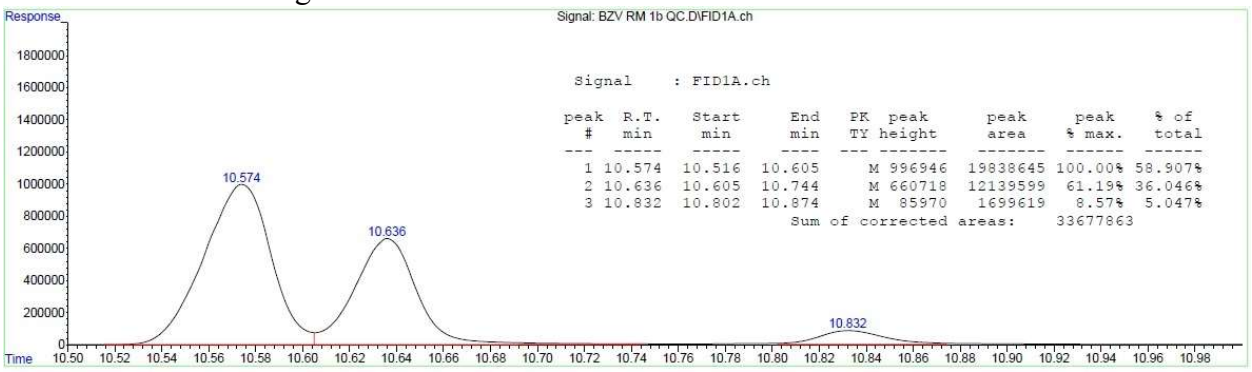
Isolated product **2** (mixture of three diastereoisomers **2a**:**2b**:**2c** in a relative ratio 61:34:5) was resubmitted to the same cyclization reaction conditions:



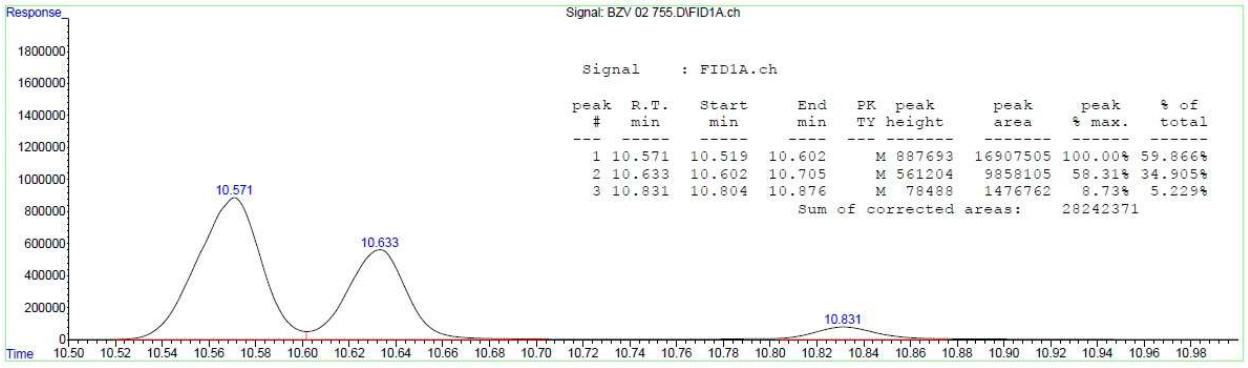
Triethylamine (9 µL, 0.065 mmol) was added to the solution of **2a+2b+2c** (13.7 mg, 0.082 mmol) in 2,2,2-trifluoroethanol (0.125 mL) under argon atmosphere and the reaction mixture was stirred at 45 °C for 7 h, then overnight at room temperature. Reaction mixture aliquot (10 µL) was taken, diluted using dichloromethane (1.00 mL) and analyzed directly by GC-MS. Another reaction mixture aliquot (10 µL) was taken, diluted with $CDCl_3$ (0.5 mL) and ^1H NMR was taken. Results showed that relative ratio **2a**:**2b**:**2c** before and after the treatment with triethylamine in 2,2,2-trifluoroethanol at 45 °C remained identical. Results are depicted in Table S2.

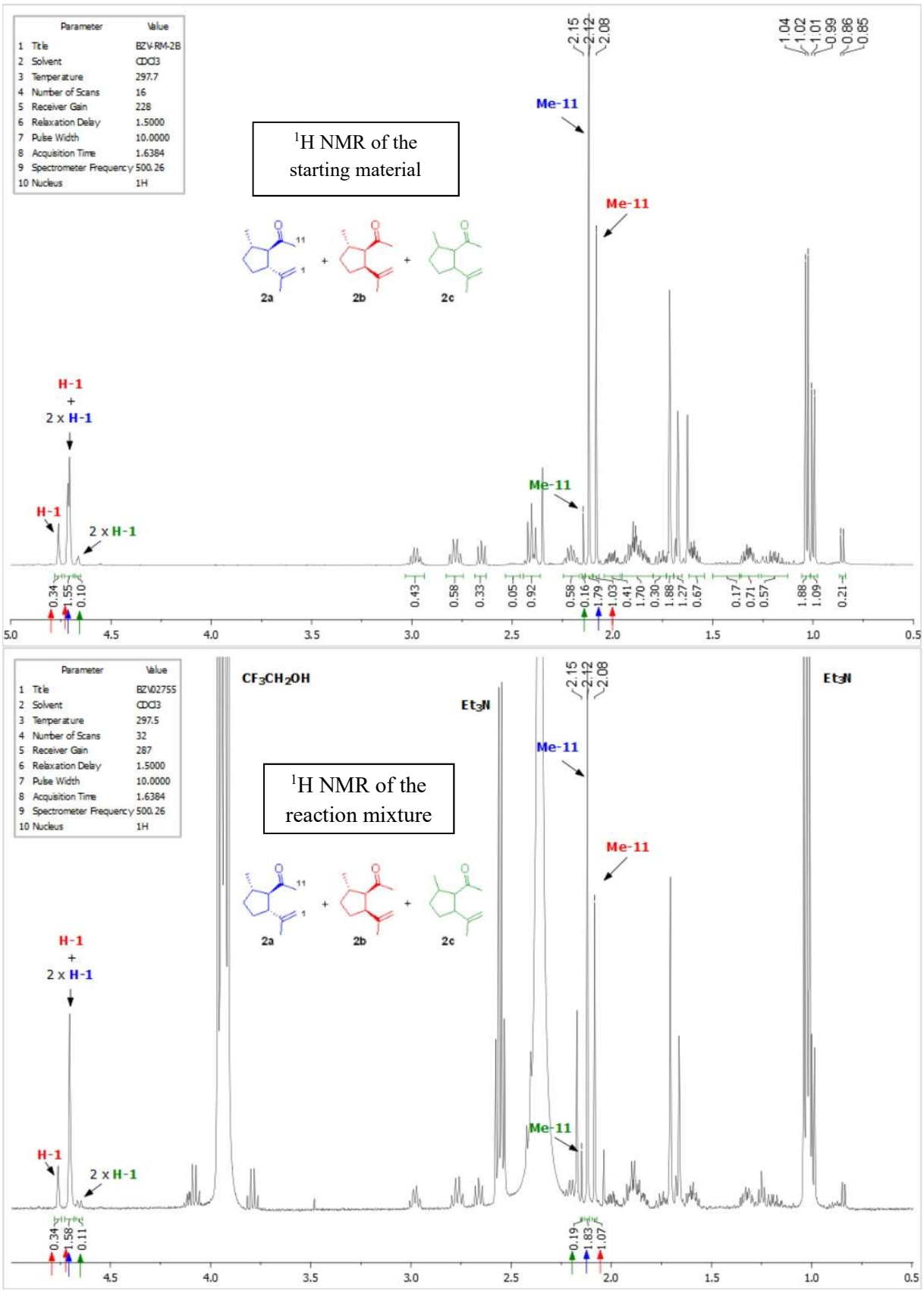
Table S2: relative ratio **2a**:**2b**:**2c**		
	before	after
by ^1H NMR	61 : 34 : 5	61 : 34 : 5
by GC/MS	58.9 : 36.0 : 5.0	59.9 : 34.9 : 5.2

GC/MS trace of starting material:

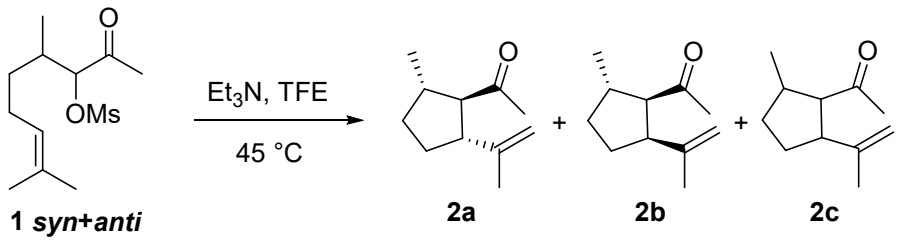


GC/MS trace of reaction mixture:




Parameter Value
1 Title BZV-RM-2B
2 Solvent CDCl3
3 Temperature 297.7
4 Number of Scans 16
5 Receiver Gain 228
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1H NMR of the starting material
2a
2b
2c
H-1
+
2 x H-1
Me-11
Me-11
Me-11
H-1
2 x H-1
2.15
2.12
2.08
1.04
1.02
1.01
0.99
0.86
0.85
0.34
1.55
0.10
0.43
0.58
0.33
0.05
0.92
0.58
0.16
1.79
1.03
0.41
1.70
0.30
1.88
1.27
0.67
0.17
0.71
0.57
1.88
1.09
0.21
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Parameter Value
1 Title BZV02755
2 Solvent CDCl3
3 Temperature 297.5
4 Number of Scans 32
5 Receiver Gain 287
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
CF3CH2OH
Et3N
Et3N
1H NMR of the reaction mixture
2a
2b
2c
H-1
+
2 x H-1
Me-11
Me-11
Me-11
H-1
2 x H-1
2.15
2.12
2.08
0.34
1.58
0.11
0.19
1.83
1.07
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

Distribution of products 2a:2b:2c over time (conditions: Method A)

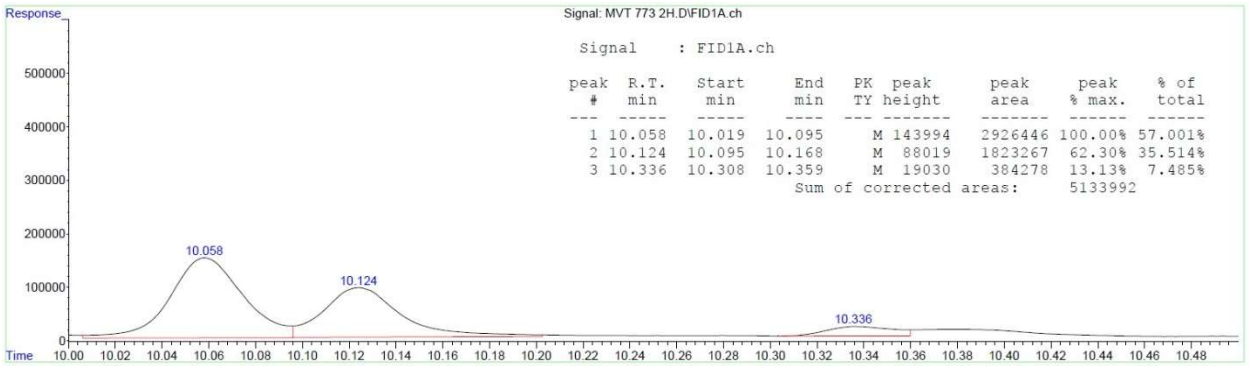


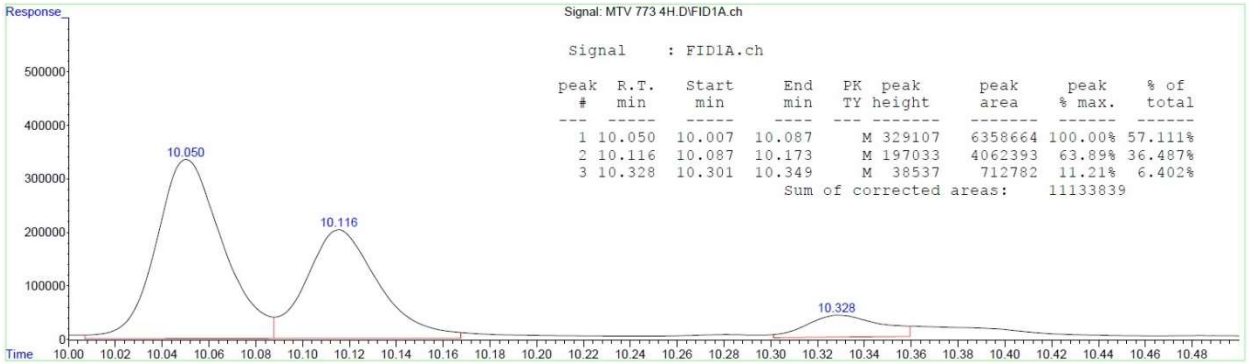
Triethylamine (71.4 µL, 0.51 mmol, 1.6 eq) was added to the solution of **1** ***syn*+*anti*** (84.0 mg, 0.320 mmol, 1 eq) in 2,2,2-trifluoroethanol (0.1 mL) under argon atmosphere and the reaction mixture was stirred at 45 °C. At certain points of time, reaction mixture aliquots (30 µL) were taken, diluted using dichloromethane (1.00 mL) and analyzed directly by GC-MS. Results are depicted in Table S3.

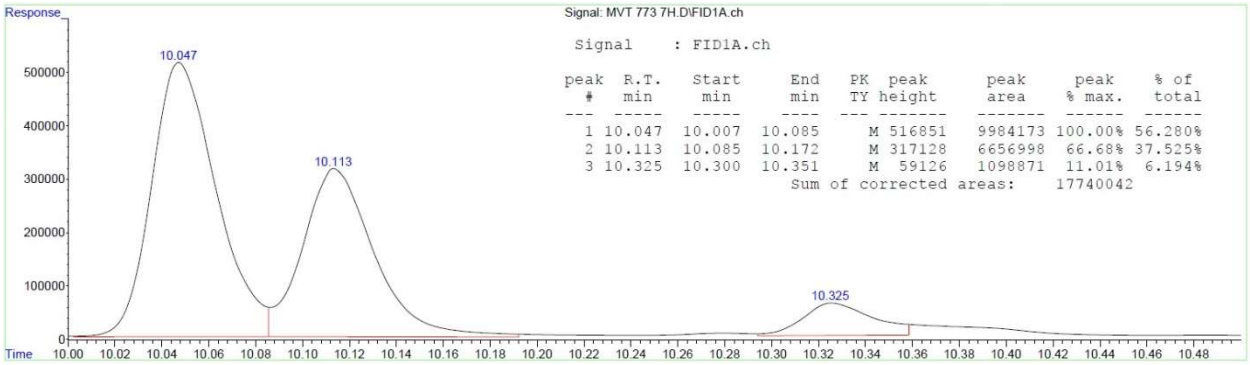
Table S3: Product **2** distribution over time

time (h)	relative ratio **2a**:**2b**:**2c**
2	57.0 : 35.5 : 7.5
4	57.1 : 36.5 : 6.4
7	56.3 : 37.5 : 6.2

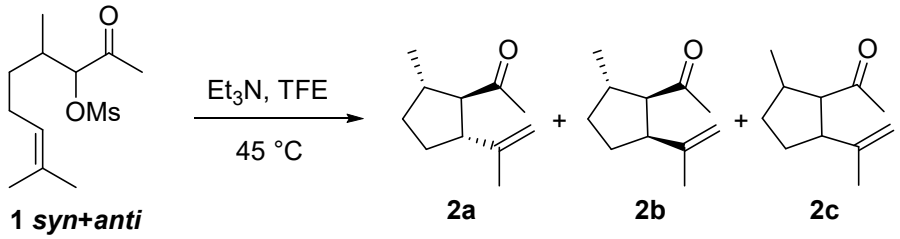
GC/MS traces of reaction mixture at different reaction times:







Distribution of products 2a:2b:2c over time (conditions: Method A)

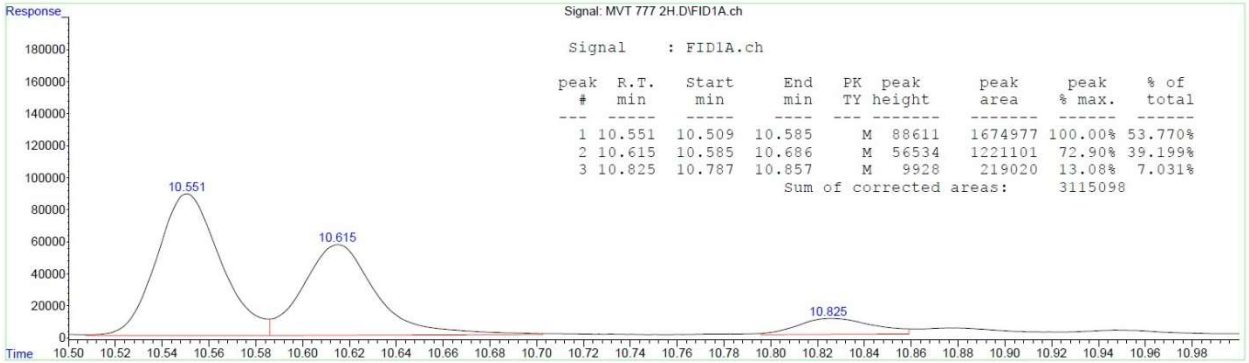


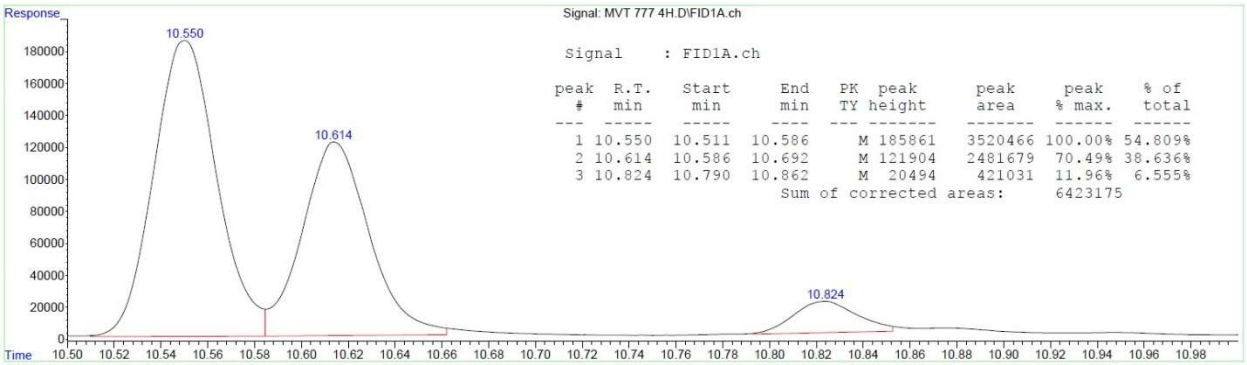
Triethylamine (18.7 µL, 0.134 mmol, 1.6 eq) was added to the solution of **1** ***syn***+***anti*** (22.0 mg, 0.084 mmol, 1 eq) in 2,2,2-trifluoroethanol (0.26 mL) under argon atmosphere and the reaction mixture was stirred at 45 °C. At certain points of time, reaction mixture aliquots (30 µL) were taken, diluted using dichloromethane (1.00 mL) and analyzed directly by GC-MS. Results are depicted in Table S4.

Table S4: Product **2** distribution over time

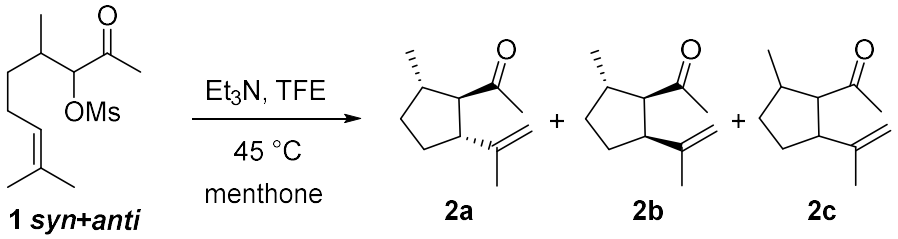
time (h)	relative ratio **2a**:**2b**:**2c**
2	53.8 : 39.2 : 7.0
4	54.8 : 38.6 : 6.6

GC/MS traces of reaction mixture at different reaction times:





Distribution of products 2a:2b:2c over time in the presence of menthone as an "*in situ*" internal standard (conditions: Method A)

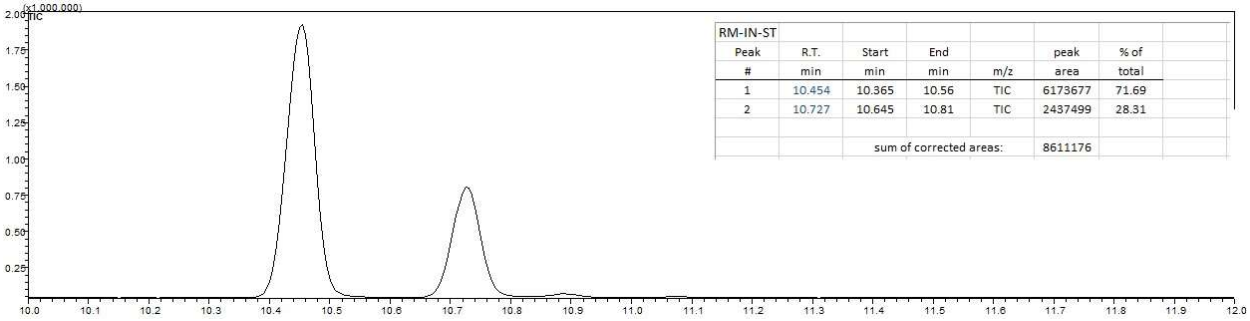


Triethylamine (71.4 µL, 0.512 mmol, 1.6 eq) was added to the solution of **1** ***syn***+***anti*** (84.0 mg, 0.320 mmol, 1 eq) and (-)-menthone (27.5 mg, 0.160 mmol) as internal standard in 2,2,2-trifluoroethanol (0.98 mL) under argon atmosphere and the reaction mixture was stirred at 45 °C. At certain points of time, reaction mixture aliquots (30 µL) were taken, diluted using dichloromethane (1.00 mL) and analyzed directly by GC-MS.

Table S2: Product **2** distribution over time

time (h)	relative ratio **2a**:**2b**:**2c**
3	66.2 : 33.7 : ----
7	58.3 : 32.9 : 8.7
23	58.9 : 33.2 : 7.8
27	58.6 : 32.6 : 8.8
31	57.1 : 33.9 : 9.0
48	57.4 : 33.3 : 9.3

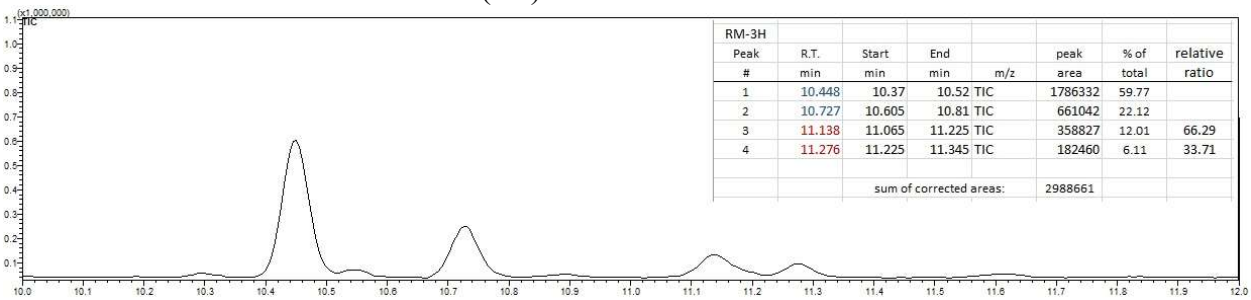
GC/MS trace of internal standard (menthone, mixture of isomers):



RM-IN-ST

Peak #	R.T. min	Start min	End min	m/z	peak area	% of total
1	10.454	10.365	10.56	TIC	6173677	71.69
2	10.727	10.645	10.81	TIC	2437499	28.31
			sum of corrected areas:		8611176	

GC/MS trace of the reaction mixture (3 h):*

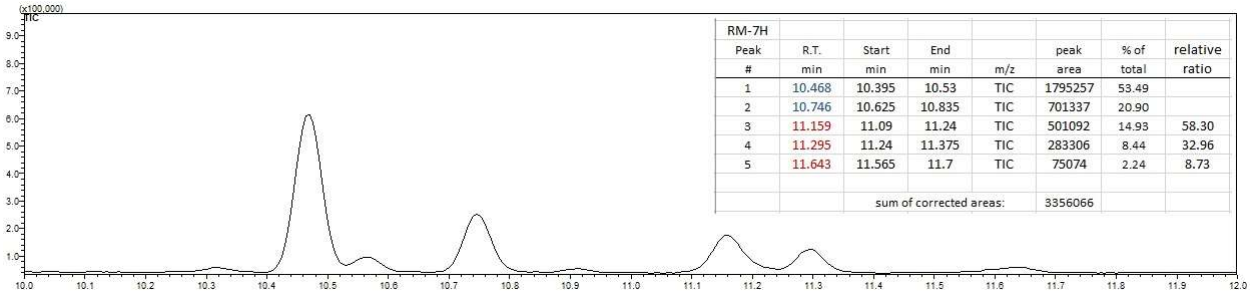


RM-3H

Peak #	R.T. min	Start min	End min	m/z	peak area	% of total	relative ratio
1	10.448	10.37	10.52	TIC	1786332	59.77	
2	10.727	10.605	10.81	TIC	661042	22.12	
3	11.138	11.065	11.225	TIC	358827	12.01	66.29
4	11.276	11.225	11.345	TIC	182460	6.11	33.71
			sum of corrected areas:		2988661		

*concentration of **2c** was too low to integrate

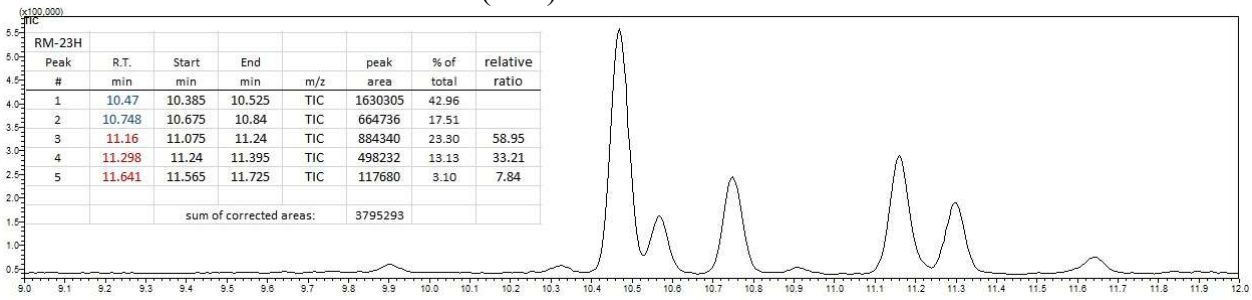
GC/MS trace of the reaction mixture (7 h):



RM-7H

Peak #	R.T. min	Start min	End min	m/z	peak area	% of total	relative ratio
1	10.468	10.395	10.53	TIC	1795257	53.49	
2	10.746	10.625	10.835	TIC	701337	20.90	
3	11.159	11.09	11.24	TIC	501092	14.93	58.30
4	11.295	11.24	11.375	TIC	283306	8.44	32.96
5	11.643	11.565	11.7	TIC	75074	2.24	8.73
			sum of corrected areas:		3356066		

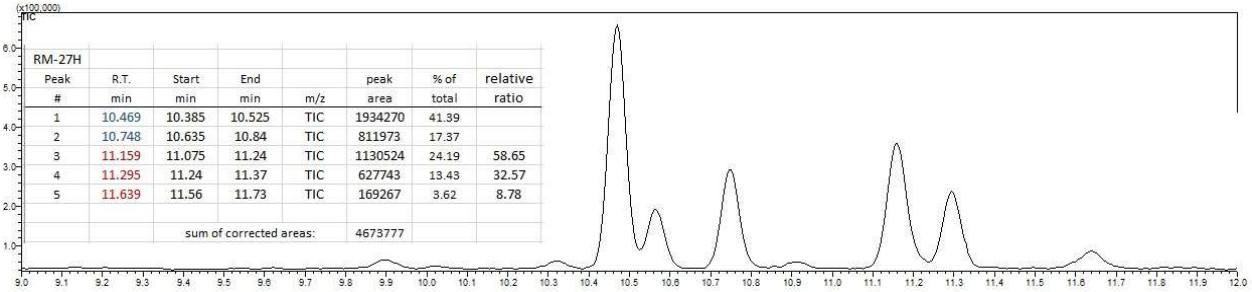
GC/MS trace of the reaction mixture (23 h):



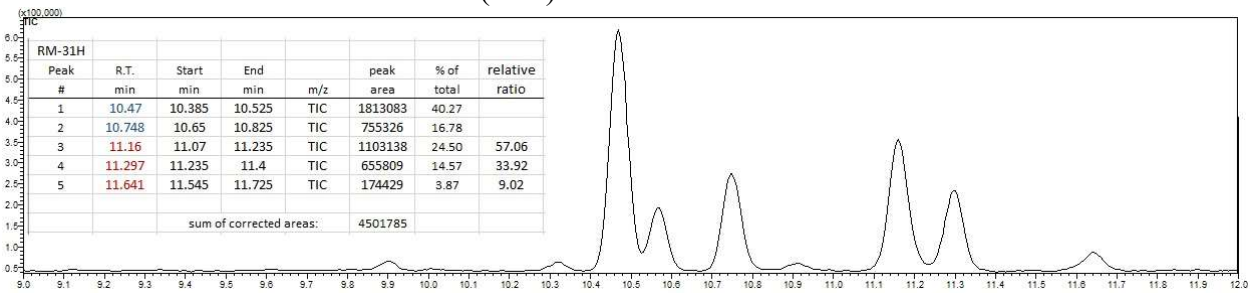
RM-23H

Peak #	R.T. min	Start min	End min	m/z	peak area	% of total	relative ratio
1	10.47	10.385	10.525	TIC	1630305	42.96	
2	10.748	10.675	10.84	TIC	664736	17.51	
3	11.16	11.075	11.24	TIC	884340	23.30	58.95
4	11.298	11.24	11.395	TIC	498232	13.13	33.21
5	11.641	11.565	11.725	TIC	117680	3.10	7.84
			sum of corrected areas:		3795293		

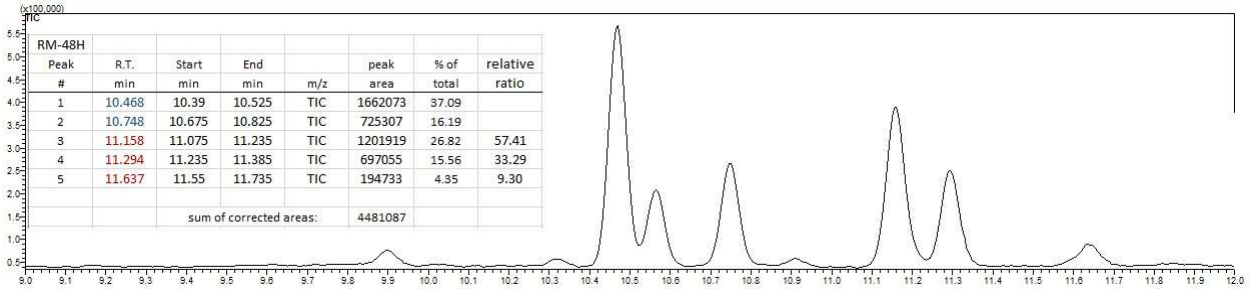
GC/MS trace of the reaction mixture (27 h):



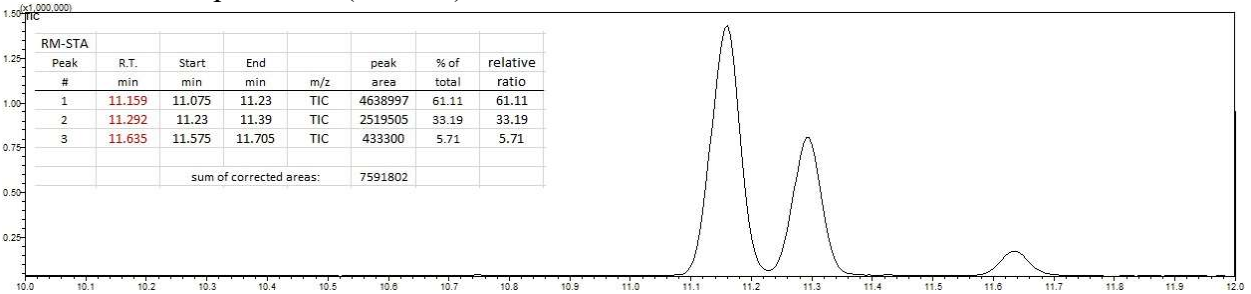
GC/MS trace of the reaction mixture (31 h):



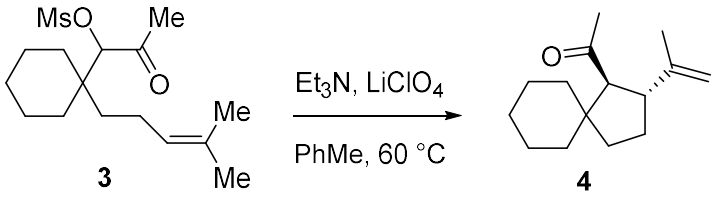
GC/MS trace of the reaction mixture (48 h):



GC/MS trace of product **2** (isolated):



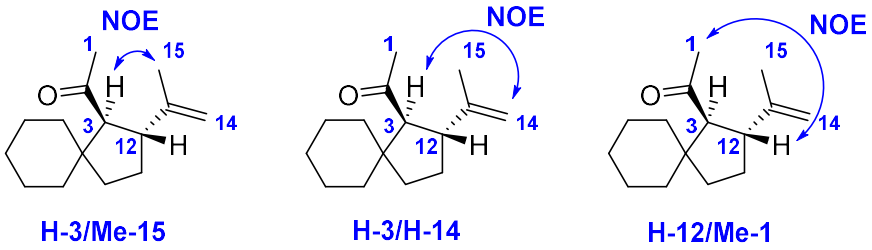
1-(2-(Prop-1-en-2-yl)spiro[4.5]decan-1-yl)ethan-1-one (4)



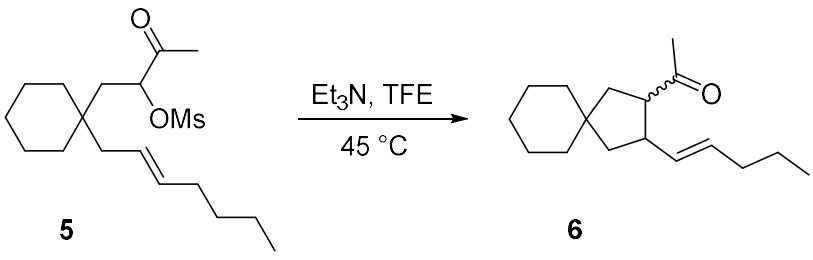
According to the General procedure – Method C. A suspension of crude mesylate **3** (0.43 mmol) from previous step, triethylamine (119 µL, 0.854 mmol) and lithium perchlorate (90.8 mg, 0.854 mmol) in toluene (3 mL) was stirred at 60 °C for 12 h. The reaction mixture was purified by column chromatography (petroleum-ether/ ethyl acetate = 9/1) to afford 63 mg (67 %) of 1-(2-(prop-1-en-2-yl)spiro[4.5]decan-1-yl)ethan-1-one **4**, as a colorless oil (single diastereoisomer).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.68 – 4.66 (m, 1H), 4.66 – 4.64 (m, 1H), 2.97 (td, J^1 = 10.9, J^2 = 7.6 Hz, 1H), 2.55 (d, J = 11.0 Hz, 1H), 2.15 (s, 3H), 1.87 (dtd, J^1 = 12.3, J^2 = 7.4, J^3 = 3.7 Hz, 1H), 1.71 – 1.66 (m, 1H), 1.68 (s, 3H), 1.62 – 1.54 (m, 6H), 1.48 – 1.37 (m, 4H), 1.33 – 1.28 (m, 1H), 1.12 (tt, J^1 = 12.7, J^2 = 3.7 Hz, 1H), 1.03 (td, J^1 = 12.6, J^2 = 3.6 Hz, 1H)..
^{13}C NMR (125 MHz, $CDCl_3$) δ 211.1, 147.1, 109.7, 67.6, 49.1, 46.8, 39.3, 35.8, 34.7, 32.9, 29.7, 26.2, 24.1, 22.8, 21.0.
IR (ATR) ν_{max}: 2928, 2857, 1707, 1644, 1449, 1355, 1162, 889.
HRMS (ESI) calcd. for $C_{15}H_{25}O^+$ $[M+H]^+$: 221.1900, found: 221.1902.

Correlations (NOESY) for compound **4**:



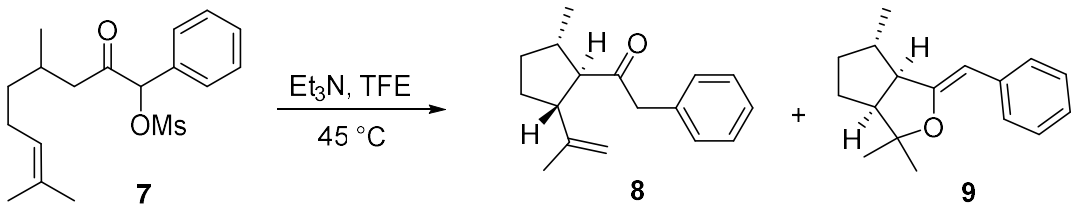
(*E*)-1-(3-(Pent-1-en-1-yl)spiro[4.5]decan-2-yl)ethan-1-one (6)



According to the General procedure – Method A. Triethylamine (20 µL, 0.143 mmol) was added to a solution of mesylate **5** (31.0 mg, 0.090 mmol) in 2,2,2-trifluoroethanol (0.42 mL), and the reaction mixture was stirred at 45 °C for 24 h, under an argon atmosphere. The reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography (petroleum-ether/ethyl acetate = 9/1, then petroleum-ether/ethyl acetate = 975/25, and finally benzene/ethyl acetate = 49/1) to afford 9.3 mg (43%) of compound **6,** as colorless oil. Obtained as a mixture of *trans* and *cis* isomers in a relative ratio 2.56:1, according to ^{1}H NMR spectrum integration of [-COC**H**$_3$] signals at 2.10 (s, 3H, minor) and 2.05 (s, 3H, major).

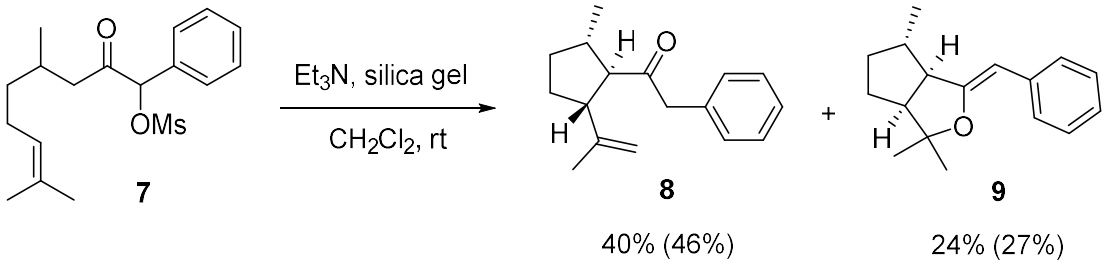
Spectral data for the mixture of diastereoisomers:
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 – 5.16 (m, 2H, minor+major), 3.39 – 3.26 (m, 1H, minor), 3.20 – 3.07 (m, 1H, minor+major), 3.03 – 2.89 (m, 1H, major), 2.74-2.64 (m, 1H, major), 2.10 (s, 3H, minor), 2.05 (s, 3H, major), 1.97 – 1.88 (m, 2H, minor+major), 1.83 – 1.69 (m, 2H, minor+major), 1.63 (m, 1H, minor+major), 1.47-1.22 (m, 13H, minor+major), 0.94 – 0.83 (m, 3H, minor+major).
^{13}C NMR (101 MHz, $CDCl_3$) δ 211.0 (minor), 210.6 (major), 133.2 (minor), 131.3 (major), 131.2 (major), 130.0 (minor), 58.3, 55.6, 55.29, 46.00, 45.6, 44.8, 42.1, 41.9, 40.0, 39.0, 38.9, 38.8, 38.0, 34.6, 31.4, 31.1, 30.0, 29.6, 26.4, 26.3, 24.3, 23.8, 23.6, 23.4, 23.0, 22.8, 14.0 (minor), 13.8 (major).
IR (ATR) ν 2928, 2857, 1707, 1644, 1449, 1355, 1162, 889.
HRMS (ESI) calcd. for $C_{17}H_{29}O^+$ $[M+H]^+$: 249.2213; found: 249.2209.

1-(2-Methyl-5-(prop-1-en-2-yl)cyclopentyl)-2-phenylethan-1-one (8) and **(*Z*)-3-benzylidene-1,1,4-trimethylhexahydro-1*H*-cyclopenta[*c*]furan (9)**



According to the General procedure – Method A. Using **7** (8 mg, 0.024 mmol, 1 eq), triethylamine (5.3 µL, 0.038 mmol, 1.6 eq) and trifluoroethanol (0.1 mL), during 1.5 h. Purification by column chromatography (benzene/ethyl acetate = 99/1) afforded 3.9 mg (68%) of compound **8,** as a colorless oil. Only traces of **9** were formed under these conditions.

1-(2-Methyl-5-(prop-1-en-2-yl)cyclopentyl)-2-phenylethan-1-one (8) and **(*Z*)-3-benzylidene-1,1,4-trimethylhexahydro-1*H*-cyclopenta[*c*]furan (9)** (General procedure for the cyclization - Method B)



Silica gel (20 mg) was added to the solution of compound **7** (7.6 mg, 0.0225 mmol, 1 eq) and triethylamine (5µL, 0.036 mmol, 1.6 eq) in CH_2Cl_2 (0.1 mL) and the reaction mixture was stirred at room temperature for 2 days. Purification of the crude reaction mixture by column chromatography (benzene/ethyl acetate = 99/1) afforded 2.2 mg (40%, 46% based on the recovered starting material)) of compound **8** and 1.3 mg (24%, 27% based on the recovered starting material) of compound **9**, as colorless oils.

Spectral data for **8**:

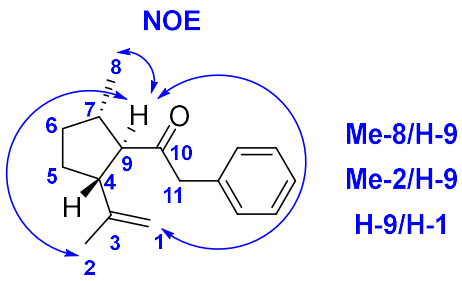
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.17 – 7.13 (m, 2H), 4.73 – 4.69 (m, 2H), 3.71 (d, J = 15.4 Hz, 1H), 3.65 (d, J = 15.4 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.55 – 2.50 (m, 1H), 2.30 – 2.20 (m, 1H), 1.93 – 1.82 (m, 2H), 1.65 (s, 3H), 1.63 – 1.56 (m, 1H), 1.34 – 1.24 (m, 1H), 0.91 (d, J = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 210.4, 146.6, 133.9, 129.7, 128.5, 126.9, 110.9, 62.6, 52.4, 50.7, 38.8, 33.6, 30.2, 19.7, 19.5.

IR (ATR) ν_{max}: 3066, 3029, 2954, 2867, 1706, 1643, 1495, 1454, 1363.

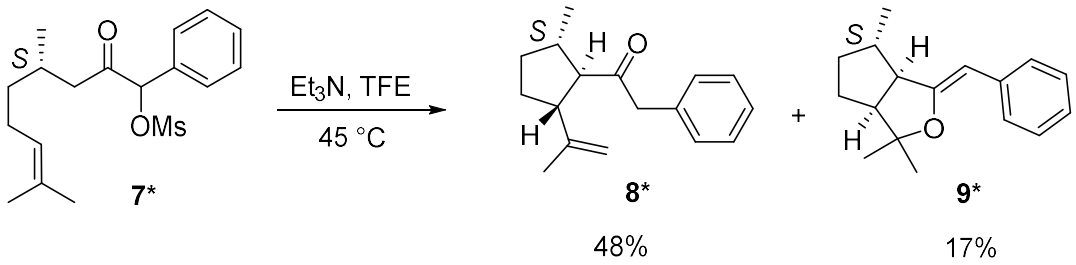
HRMS (ESI) calcd. for $C_{17}H_{23}O^+$ $[M+H]^+$: 243.1743, found: 243.1740.

Correlations (NOESY) of **8**:



Spectral data for **9**:
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.26– 7.22 (m, 2H), 7.06 – 7.01 (m, 1H), 5.14 (d, J = 1.4, 1H), 3.03 (dd, J = 8.1, 4.2, Hz, 1H), 2.41 (dd, J = 17.1, 8.8, 1H), 2.23 – 2.13 (m, 1H), 1.96 – 1.89 (m, 1H), 1.75 – 1.61 (m, 1H), 1.59 – 1.51 (m, 1H), 1.43 (s, 3H), 1.31 (s, 3H), 1.22 – 1.16 (m, 1H), 1.16 (d, J = 6.9, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 137.7, 128.1, 127.0, 124.2, 96.6, 86.6, 56.8, 51.4, 42.6, 36.0, 29.8, 27.7, 23.9, 21.4.
IR (ATR) ν_{max}: 3062, 3030, 2962, 2868, 1728, 1600, 1493, 1452, 1373.
HRMS (ESI) calcd. for $C_{17}H_{22}O^+$ $[M+H]^+$: 243.1743, found: 243. 1733.

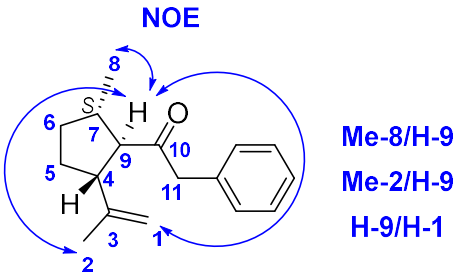
1-((1*R*,2*S*,5*R*)-2-Methyl-5-(prop-1-en-2-yl)cyclopentyl)-2-phenylethanone (8*) and (3a*R*,4*S*,6a*S*,*Z*)-3-benzylidene-1,1,4-trimethylhexahydro-1*H*-cyclopenta[*c*]furan (9*)



According to the General procedure – Method A. Using **7*** (36.7 mg, 0.108 mmol, 1 eq), triethylamine (24 µL, 0.173 mmol, 1.6 eq) and trifluoroethanol (0.36 mL), during 4 h. Purification by column chromatography (petroleum-ether/diisopropyl ether = 95/5) afforded 13.5 mg (48%) of compound **8*** and 4.8 mg (17 %) of compound **9***, both as colorless oils.

Spectral data for **8***:
$[\alpha]_D^{20}$ -44.9 (*c* 1.27, $CDCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 7.18 – 7.15 (m, 2H), 4.74 – 4.71 (m, 2H), 3.72 (d, J = 15.4 Hz, 1H), 3.66 (d, J = 15.4 Hz, 1H), 2.85 (dd, J = 18.1, 8.9 Hz, 1H), 2.57 – 2.51 (m, 1H), 2.32 – 2.21 (m, 1H), 1.94 – 1.83 (m, 2H), 1.67 – 1.66 (m, 3H), 1.65 – 1.56 (m, 1H), 1.35 – 1.25 (m, 1H), 0.92 (d, J = 6.7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.4, 146.6, 133.9, 129.7, 128.5, 126.9, 110.9, 62.6, 52.5, 50.7, 38.8, 33.6, 30.3, 19.7, 19.5.
IR (ATR) ν_{max}: 2924, 2854, 1710, 1495, 1458, 1375.
HRMS (ESI) calcd. for $C_{17}H_{23}O^+$ $[M+H^+]$: 243.1743, found: 243.1740.

Correlations (NOESY) for **8***:



Spectral data for **9***:

$[\alpha]_D^{20}$ -101.1 (c 0.26, C_6H_6).

^{1}H NMR (500 MHz, C_6D_6) δ 7.85 – 7.82 (m, 2H), 7.30– 7.24 (m, 1H), 7.04 – 6.99 (m, 2H), 5.28 (d, J = 1.4, 1H), 3.75 (ddd, J = 8.6, 4.3, 1.1, Hz, 1H), 2.08 – 1.98 (m, 1H), 1.88 (dd, J = 17.1, 8.6, 1H), 1.71 – 1.65 (m, 1H), 1.34 – 1.28 (m, 2H), 1.17 (s, 3H), 1.05 (s, 3H), 0.95 (d, J = 6.9, 3H), 0.93 – 0.88 (m, 1H).

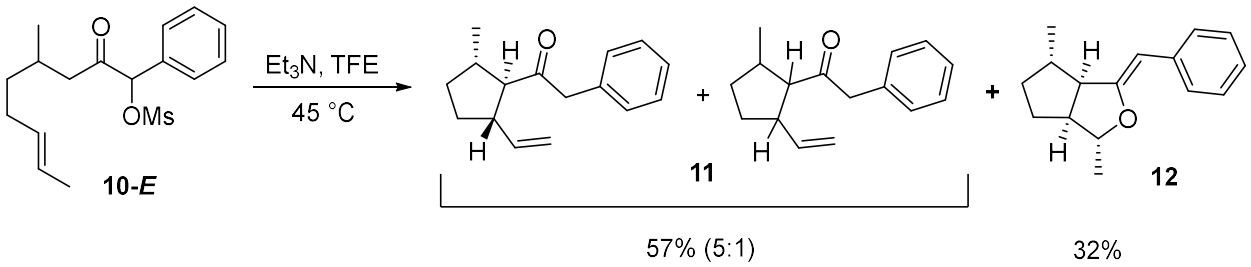
^{13}C NMR (126 MHz, C_6D_6) δ 162.2, 138.4, 128.5, 128.4, 124.8, 97.9, 86.4, 56.9, 51.4, 42.8, 36.1, 29.8, 27.8, 23.8, 21.4.

IR (ATR) ν_{max}: 3053, 3020, 2955, 2864, 1662, 1599, 1493, 1449, 1365.

HRMS (ESI) calcd. for $C_{17}H_{23}O^+$ $[M+H]^+$: 243.1743, found: 243.1736.

Note: NMR of **9** was taken in C_6D_6 because it gradually decomposes in $CDCl_3$ (probably due to acidity of chloroform). Generally, benzylidenetetrahydrofuranes were sensitive to acidic conditions, and very difficult to purify on silica and isolate in pure state.

1-(2-Methyl-5-vinylcyclopentyl)-2-phenylethan-1-one (11) and (Z)-3-benzylidene-1,4-dimethylhexahydro-1*H*-cyclopenta[*c*]furan (12)

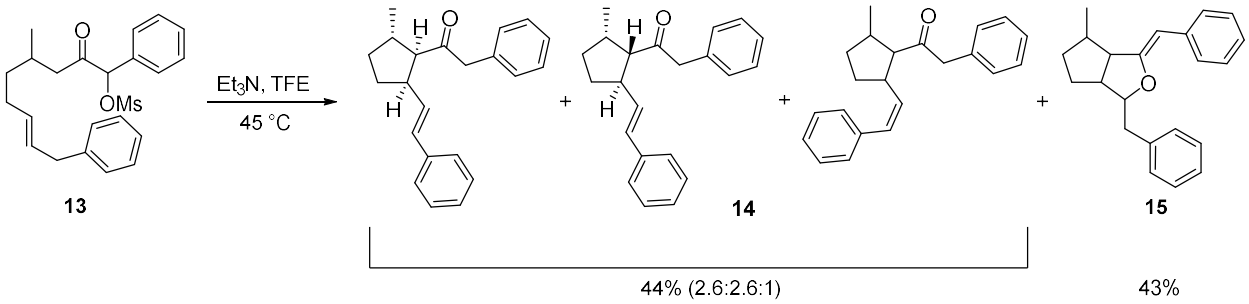


According to the General procedure – Method A. Using mesyloxy ketone **10-*E*** (9.7 mg, 0.03 mmol, 1 eq), triethylamine (6.5 µL, 0.046 mmol, 1.6 eq) and trifluoroethanol (0.1 mL), during 3 h. Purification by column chromatography (petroleum-ether/diisopropyl ether = 95/5) afforded 3.9 mg (57%) of compound **11** as a colorless oil (mixture of isomers in a relative ratio 5:1, as determined by ^{1}H NMR) and 2.2 mg (32%) of compound **12,** as a colorless oil.

Spectral data for **11**, mixture of isomers in the ratio H:H'= 5:1
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H+2H'), 7.26 – 7.22 (m, 1H+1H'), 7.17 – 7.13 (m, 2H+2H'), 5.74 – 5.62 (m, 1H+1H'), 5.04 – 5.62 (m, 2H+2H'), 3.72 (d, J = 15.4 Hz, 1H), 3.66 (d, J = 15.4 Hz, 1H), 3.68 (d, J = 15.7 Hz, 1H'), 3.59 (d, J = 15.5 Hz, 1H'), 2.98 – 2.88 (m, 1H'), 2.77 – 2.67 (m, 1H+1H'), 2.44 – 2.34 (m, 1H+1H'), 2.32 – 2.22 (m, 1H), 1.97 – 1.84 (m, 2H+2H'), 1.57 – 1.47 (m, 1H+1H'), 1.34 – 1.24 (m, 1H), 1.19 – 1.11 (m, 1H'), 0.88 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H').
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 208.9, 141.4, 139.8, 129.7, 128.5, 126.9, 126.8, 114.8, 114.3, 64.9, 62.4, 51.6, 51.1, 49.7, 47.4, 38.6, 33.5, 33.3, 32.6, 31.8, 19.7, 19.6.
IR (ATR) ν_{max}: 3066, 3030, 2954, 2869, 1708, 1640, 1495, 1455, 1369.
HRMS (ESI) calcd. for $C_{17}H_{26}ON^+$ $[M+NH_4]^+$: 246.1852, found: 246.1845.

Spectral data for **12**:
^{1}H NMR (500 MHz, C_6D_6) δ 7.89 – 7.86 (m, 2H), 7.33– 7.28 (m, 2H), 7.08 – 7.04 (m, 1H), 5.31 (d, J = 0.6 Hz, 1H), 3.95 (p, J = 6.1 Hz, 1H), 2.56 – 2.51 (m, 1H), 1.99 – 1.86 (m, 2H), 1.71 – 1.62 (m, 1H), 1.60 – 1.51 (m, 1H), 1.15– 1.00 (m, 2H), 1.06 (d, J = 6.2 Hz, 3H), 0.92 (d, J = 6.8, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 138.6, 128.9, 128.7, 128.3, 125.2, 98.1, 86.2, 56.9, 49.9, 42.0, 35.7, 29.4, 21.6, 20.1.
IR (ATR) ν_{max}: 3057, 3021, 2954, 2869, 1756, 1667, 1600, 1493, 1451, 1372, 1314.
HRMS (ESI) calcd. for $C_{16}H_{21}O^+$ $[M+H]^+$: 229.1587, found: 229.1577.

1-(2-Methyl-5-styrylcyclopentyl)-2-phenylethan-1-one (14) and 1-benzyl-3-benzylidene-4-methylhexahydro-1H-cyclopenta[c]furan (15)



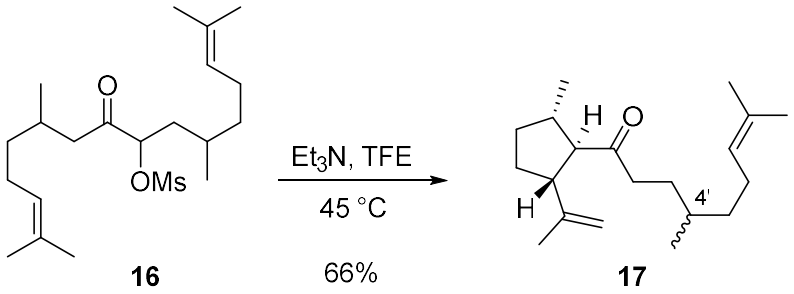
According to the General procedure – Method A. Using mesyloxy ketone **13** (8.3 mg, 0.02 mmol, 1 eq), triethylamine (4.6 µL, 0.033 mmol, 1.6 eq) and trifluoroethanol (0.1 mL), during 4 h. Purification by column chromatography (petroleum-ether/toluene = 1/2) afforded 2.8 mg (44%) of compound **14**, as a colorless oil (mixture of 4 isomers) and 2.7 mg (43%) of **15**, a colorless oil (mixture of 4 isomers, in a relative ratio: 6:1:1:1).

Spectral data for **14**, mixture of four isomers: *E*-a, *E*-b, *Z*-a, *Z*-b with the ratio *E*: *Z*= 5.25:1, where H_{Ea} and H_{Eb} are *E* isomers in the ratio of 1:1 and H_{Za} and H_{Zb} are *Z* isomers in the ratio of 1:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 6.99 (m, 10$H_{Ea+Eb+Za+Zb}$), 6.46 (d, J = 6.6 Hz, 1H_{Za}), 6.44 (d, J = 6.5 Hz, 1H_{Zb}), 6.37 (d, J = 15.7 Hz, 1H_{Ea}), 6.31 (d, J = 15.7 Hz, 1H_{Eb}), 6.08 – 5.99 (m, 1H_{Ea+Eb}), 5.60 – 5.54 (m, 1H_{Za+Zb}), 3.73 – 3.46 (m, 2$H_{Ea+Eb+Za+Zb}$), 3.35 – 3.26 (m, 1H_{Za+Zb}), 3.14 – 3.04 (m, 1H_{Ea}), 2.95 – 2.87 (m, 1H_{Eb}), 2.81 (t, J = 8.9 Hz, 1H_{Ea}), 2.68 (t, J = 8.9 Hz, 1H_{Za}), 2.56 – 2.45 (m, 2H_{Ea+Eb}), 2.41 – 2.27 (m, 2H_{Eb+Zb}), 2.06 – 1.89 (m, 2$H_{Ea+Eb+Za+Zb}$), 1.69 – 1.56 (m, 1$H_{Ea+Eb+Za+Zb}$), 1.46 – 1.13 (m, 2$H_{Ea+Eb+Za+Zb}$), 0.94 (d, J = 6.7 Hz, 3H_{Eb}), 0.90 (d, J = 6.6 Hz, 3H_{Ea}), 0.91 – 0.88 (m, 3H_{Zb}), 0.87 (d, J = 6.5 Hz, 3H_{Za}).
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.3, 209.1, 137.2, 137.1, 135.9, 133.9, 133.7, 133.6, 133.0, 131.5, 130.2, 129.7, 129.7, 129.6, 128.7, 128.6, 128.5, 128.3, 127.2, 127.2, 126.9, 126.8, 126.3, 126.1, 66.2, 66.1, 62.5, 62.6, 62.3, 51.8, 51.4, 49.1, 46.7, 38.9, 33.4, 33.3, 32.1, 19.9, 19.7.
IR (ATR) ν_{max}: 3082, 3060, 3027, 2952, 2867, 1945, 1875, 1802, 1708, 1600, 1493, 1452, 1406, 1372.
HRMS (ESI) calcd. for $C_{22}H_{28}ON^+$ $[M+NH_4]^+$: 322.2165, found: 322.2154.

Spectral data for **15,** major isomer:
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.36– 7.20 (m, 7H), 7.08 – 7.04 (m, 1H), 5.18 (s, 1H), 4.37 (dt, J = 7.1, 5.8 Hz, 1H), 3.00 (dd, J = 13.7, 7.3 Hz, 1H), 2.87 (dd, J = 13.7, 5.8 Hz, 1H), 2.79 – 2.74 (m, 1H), 2.62 – 2.54 (m, 1H), 2.11 – 2.03 (m, 1H), 1.91 – 1.82 (m, 2H), 1.38 – 1.26 (m, 2H), 1.09 (d, J = 6.8, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 137.8, 137.2, 129.5, 129.0, 128.3, 128.2, 128.1, 127.3 (2×C), 127.2, 126.4, 125.1, 124.4, 96.9, 90.5, 57.1, 52.2, 47.2, 42.1, 41.8, 35.4, 29.6, 20.4, 19.6.
IR (ATR) ν_{max}: 3084, 3061, 3027, 2955, 2931, 2867, 1753, 1699, 1600, 1494, 1453, 1410, 1375.
HRMS (ESI) calcd. for $C_{22}H_{25}O^+$ $[M+H]^+$: 305.1900, found: 305.1890.

4,8-Dimethyl-1-(2-methyl-5-(prop-1-en-2-yl)cyclopentyl)non-7-en-1-one (17)



16 **17**

According to the General procedure – Method A. Using mesyloxy ketone **16** (8.8 mg, 0.023 mmol, 1 eq), triethylamine (5 µL, 0.036 mmol, 1.6 eq) and trifluoroethanol (0.1 mL), during 4 h. Purifications by column chromatography (petroleum-ether/toluene = 3/1) afforded 4.4 mg (66%) of **17**, as a colorless oil (mixture of isomers at C-4' in a relative ratio 1:1, as determined by ^{1}H NMR).

Spectral data for the mixture of isomers **17**

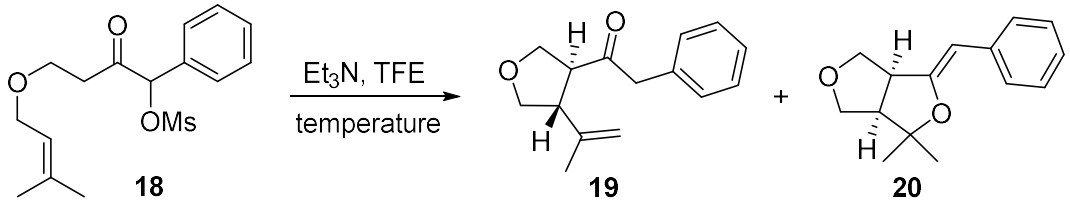
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.11 – 5.05 (m, 1H), 4.75 – 4.64 (m, 2H), 2.83 – 2.76 (m, 1H), 2.47 – 2.30 (m, 3H), 2.26 – 2.16 (m, 1H), 2.04 – 1.82 (m, 4H), 1.71 (s, 3H), 1.68 (s, 3H), 1.63 – 1.56 (m, 2H), 1.60 (s, 3H), 1.43 – 1.24 (m, 4H),), 1.18 – 1.09 (m, 1H), 1.02 (apparent dd, J = 6.7, 0.9 Hz, 3H,), 0.86 (d, J = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 213.9, 147.0, 131.4, 125.0, 110.8, 64.2, 64.1, 52.3, 52.2, 41.2, 39.0, 37.1, 37.1, 33.8, 32.3, 30.5, 30.4, 25.9, 25.7, 20.2, 20.0, 19.6, 17.9.

IR (ATR) ν_{max}: 2955, 2924, 2869, 1708, 1645, 1455, 1376.

HRMS (ESI) calcd. for $C_{20}H_{35}O$ $[M+H]^+$: 291.2682, found: 291.2676.

2-Phenyl-1-(4-(prop-1-en-2-yl)tetrahydrofuran-3-yl)ethan-1-one (19) and (*Z*)-3-benzylidene-1,1-dimethyltetrahydro-1*H*,3*H*-furo[3,4-*c*]furan (20)



According to the General procedure – Method A. Using mesyloxy ketone **18** (22.5 mg, 0.069 mmol, 1 eq), triethylamine (11 µL, 0.11 mmol, 1.6 eq) and trifluoroethanol (0.22 mL) at room temperature, during 40 min. Purification by two consecutive column chromatographies (petroleum-ether/ ethyl acetate = 85/15, followed by benzene/ ethyl acetate = 98/2) afforded 7.5 mg (47%) of compound **19** and 0.8 mg (5%) of compound **20**, both as colorless oils.

At 50 °C, reaction afforded compound **19** in 50% yield and only traces of compound **20** were formed.

Spectral data for **19**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.30– 7.25 (m, 1H), 7.19 – 7.15 (m, 2H), 4.84 – 4.80 (m, 2H), 4.00 – 4.95 (m, 1H), 3.92 – 3.84 (m, 2H), 3.75 (d, J = 15.2 Hz, 1H), 3.71 (d, J = 15.2 Hz, 1H), 3.63 (dd, J = 8.6, 7.3 Hz, 1H), 3.26 (dd, J = 15.1, 7.5 Hz, 1H), 3.13 (dd, J = 15.1, 7.5 Hz, 1H), 1.69 (s, 3H).

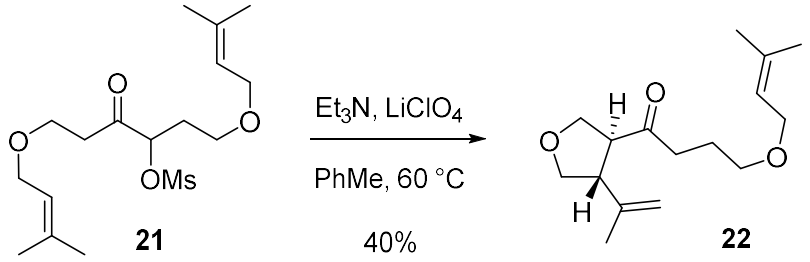
^{13}C NMR (125 MHz, $CDCl_3$) δ 206.9, 143.3, 133.4, 129.5, 128.8, 127.2, 112.7, 72.7, 70.4, 54.5, 50.6, 50.2, 19.9.

IR (ATR) ν_{max}: 3030, 2956, 2921, 2853, 1714, 1646, 1603, 1495, 1456, 1375.

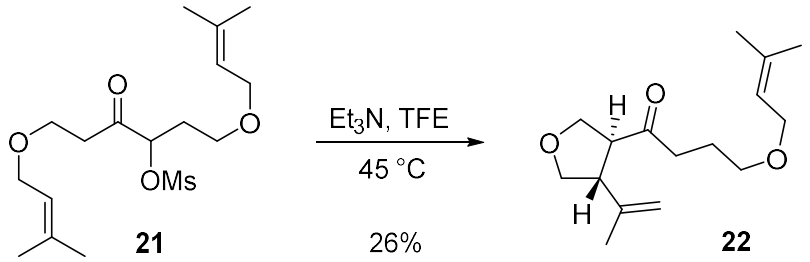
HRMS (ESI) calcd. for $C_{15}H_{22}O_2N^+$ $[M+NH_4]^+$: 248.1645, found: 248.1641.

Spectral data for **20**:
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.30– 7.23 (m, 2H), 7.10 – 7.05 (m, 1H), 5.15 (s, 1H), 4.08 – 4.03 (m, 1H), 3.99 (dd, J = 8.6, 3.0 Hz, 1H), 3.85 (dd, J = 9.3, 6.0 Hz, 1H), 3.78 (dd, J = 9.2, 7.5 Hz, 1H), 3.76 – 3.70 (m, 1H), 2.70 – 2.64 (m, 1H), 1.46 (s, 3H), 1.40 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 128.1, 127.2, 124.8, 98.6, 86.6, 75.3, 69.5, 51.6, 50.3, 30.2, 23.6.
IR (ATR) ν_{max}: 3084, 3059, 3024, 2973, 2931, 2858, 1757, 1721, 1665, 1600, 1494, 1451, 1369.
HRMS (ESI) calcd. for $C_{15}H_{22}O_2N^+$ $[M+NH_4]^+$: 248.1645, found: 248.1641.

4-((3-Methylbut-2-en-1-yl)oxy)-1-(4-(prop-1-en-2-yl)tetrahydrofuran-3-yl)butan-1-one (22)



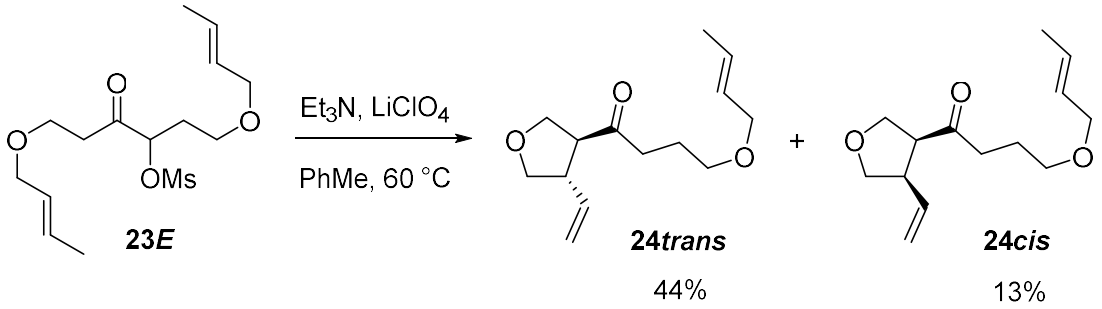
According to the General procedure – Method C. A suspension of mesyloxy ketone **21** (19.5 mg, 0.0538 mmol, 1 eq), triethylamine (15 µL, 0.107 mmol, 2 eq) and lithium perchlorate (11.4 mg, 0.107 mmol, 2 eq) in toluene (0.18 mL) was stirred at 60 °C for 20 min. The reaction mixture was directly purified by column chromatography (petroleum-ether/ethyl acetate = 85/15) to afford 5.7 mg (40%) of compound **22**, as a colorless oil.



According to the General procedure – Method A. Using **21** (28.1 mg, 0.078 mmol, 1 eq), triethylamine (17 µL, 0.124 mmol, 1.6 eq) and trifluoroethanol (0.25 mL) at 45 °C, during 10 min. Purification by column chromatography (petroleum-ether/ ethyl acetate = 85/15) afforded 5.4 mg (26%) of compound **22**, as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 – 5.28 (m, 1H), 4.85 – 4.81 (m, 2H), 4.03 (t, J = 8.4 Hz, 1H), 3.98 (t, J = 8.1 Hz, 1H), 3.95 – 3.89 (m, 3H), 3.65 (dd, J = 7.2 Hz, 1H), 3.40 (t, J = 6.4 Hz, 2H), 3.17 (dd, J = 14.9, 7.3 Hz, 1H), 3.10 (dd, J = 14.7, 7.4 Hz, 1H), 2.62 – 2.48 (m, 2H), 1.90 – 1.83 (m, 2H), 1.76 (s, 3H), 1.74 (s, 3H), 1.66 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.2, 143.5, 136.9, 121.1, 112.5, 72.5, 70.2, 68.9, 67.2, 55.7, 50.2, 39.4, 25.8, 23.7, 20.0, 18.0.
IR (ATR) ν_{max}: 2968, 2925, 2856, 1712, 1645, 1446, 1409, 1376.
HRMS (ESI) calcd. for $C_{16}H_{26}O_3Na^+$ $[M+Na]^+$: 289.1774, found: 289.1774.

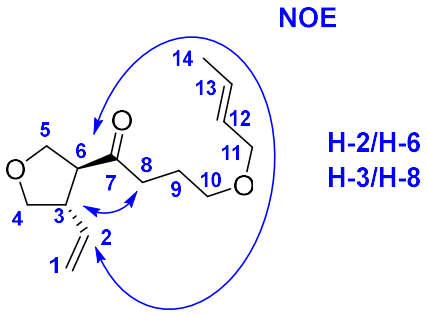
***trans*-(*E*)-4-(but-2-en-1-yloxy)-1-(4-vinyltetrahydrofuran-3-yl)butan-1-one (24*trans*) and *cis*-(*E*)-4-(but-2-en-1-yloxy)-1-(4-vinyltetrahydrofuran-3-yl)butan-1-one (24*cis*)**



According to General procedure – Method C. A suspension of **23*E*** (59.4 mg, 0.1776 mmol, 1 eq), triethylamine (50 µL, 0.36 mmol, 2 eq) and lithium perchlorate (38 mg, 0.107 mmol, 2 eq) in toluene (0.8 mL) was stirred at 60 °C for 1 hour. The reaction mixture was directly applied to a column and purified by column chromatography (petroleum ether/ ethyl acetate=7/3) to afford 18.5 mg (44%) of **24*trans*** and 5.6 mg (13%) of **24*cis***, both as colorless oils.

Spectral data for **24*trans*:**
^{1}H NMR (500 MHz, C_6D_6) δ 5.57 – 5.50 (m, 2H), 5.44 (ddd, J^1 = 17.6, J^2 = 9.9, J^3 = 8.8 Hz, 1H), 4.90 (d, J = 17.0 Hz, 1H), 4.85 (d, J = 10.1 Hz, 1H), 3.98 (dd, J^1 = 8.5, J^2 = 7.0 Hz, 1H), 3.87 (t, J = 7.9 Hz, 1H), 3.79 – 3.70 (m, 3H), 3.33 (t, J = 8.0 Hz, 1H), 3.22 (t, J = 6.0 Hz, 2H), 2.93 (p, J = 7.6 Hz, 1H), 2.56 (dd, J^1 = 15.1, J^2 = 7.5, 1H), 2.31 – 2.22 (m, 1H), 2.22 – 2.13 (m, 1H), 1.85 – 1.78 (m, 2H), 1.53 (dd, J^1 = 3.4, J^2 = 1.0, 3H).
^{13}C NMR (125 MHz, C_6D_6) δ 207.4, 138.2, 128.6 (2×C), 116.3, 73.4, 71.6, 70.0, 68.9, 57.7, 47.8, 39.6, 24.2, 17.7.
IR (ATR) ν_{max}: 3079, 3013, 2934, 2857, 1826, 1712, 1642, 1446, 1362, 1257, 1103.
HRMS (ESI) calcd. for $C_{14}H_{23}O_3^+$ $[M+H]^+$: 239.1642, found: 239.1635.

Correlations (NOESY) for **24*trans***:



Spectral data for **24*cis*:**

^{1}H NMR (500 MHz, C_6D_6) δ 5.63 (dt, J^1 = 17.1, J^2 = 9.9, 1H), 5.58 – 5.53 (m, 2H), 4.86 – 4.79 (m, 2H), 4.28 (dd, J^1 = 17.1, J^2 = 9.9, 1H), 3.79 – 3.59 (m, 5H), 3.28 – 3.20 (m, 2H), 2.77 (dd, J^1 = 15.5, J^2 = 7.8, 1H), 2.60 – 2.52 (m, 1H), 2.29 (dt, J^1 = 17.5, J^2 = 7.1, 1H), 2.14 (dt, J^1 = 17.7, J^2 = 7.0, 1H), 1.92 – 1.75 (m, 2H), 1.56 – 1.51 (m, 3H).

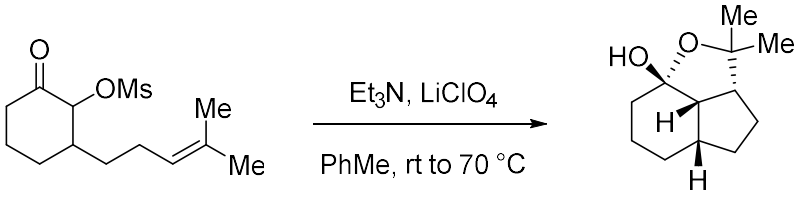
^{13}C NMR (125 MHz, C_6D_6) δ 207.4, 136.0, 128.7, 117.0, 73.3, 71.6, 69.1, 68.8, 55.2, 47.6, 40.9, 24.0, 17.7.

IR (ATR) ν_{max}: 3080, 3012, 2933, 2858, 1711, 1674, 1639, 1447, 1362, 1255, 1179, 1103.

HRMS (ESI) calcd. for $C_{14}H_{23}O_3^+$ $[M+H]^+$: 239.1642, found: 239.1632.

Note: In $CDCl_3$ **24*cis*** isomerizes to **24*trans*** (probably due to acidity of deuterochloroform). Isomerization is slow and incomplete: after ten days at room temperature solution od **24*cis*** in $CDCl_3$ gave final ratio of **24*cis***:**24*trans*** = 1.00:0.38.

1,1-Dimethyloctahydroindeno[7,1-*bc*]furan-2a(1*H*)-ol (26)

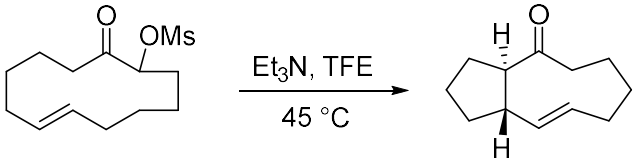


25 55% **26**

According to the General procedure – Method C. A suspension of mesylate **25** (11.5 mg, 0.042 mmol), triethylamine (12µL, 0.086 mmol) and lithium perchlorate (8.9 mg, 0.084 mmol) in dry toluene (0.14 mL) was stirred at room temperature for 2 h, then at 50 °C for 2 h, and at 70 °C for 12 h. SiO_2 (50 mg) was added to the reaction mixture, the volatiles were removed under reduced pressure and the residue was purified by column chromatography (petroleum-ether/ethyl acetate = 4/1) to afford 4.5 mg (55%) of compound **26**, as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 – 2.62 (m, 2H), 2.17 – 2.09 (m, 1H), 2.02 – 1.97 (m, 1H), 1.89 (s, 1H), 1.82 – 1.76 (m, 1H), 1.69 – 1.65 (m, 1H), 1.55 – 1.48 (m, 2H), 1.47 – 1.31 (m, 5H), 1.45 (s, 3H), 1.19 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 104.4, 84.4, 53.3, 52.2, 38.51, 38.0, 33.9, 31.6, 29.6, 26.7, 24.5, 17.9.
IR (ATR) ν_{max}: 3320, 2938, 2854, 1459, 1357, 1175, 1145, 1094, 1065, 1009, 996.
HRMS (ESI) calcd. for $C_{12}H_{19}O^+$ $[M+H-H_2O]^+$: 179.1430; found: 179.1431.

(*E*)-2,3,3a,5,6,7,8,10a-Octahydrocyclopenta[9]annulen-4(1*H*)-one (28)



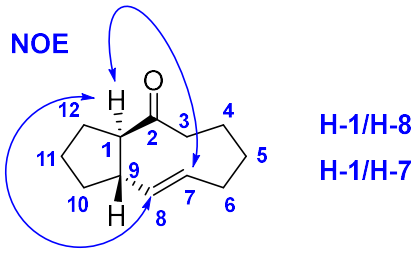
27 65% **28**

According to the General procedure – Method A. Triethylamine (36 µL, 0.258 mmol) was added to the solution of mesylate **27** (39.6 mg, 0.145 mmol) in trifluoroethanol (3.8 mL) and the reaction mixture was stirred at 45 °C for 16 h, under an argon atmosphere. The reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography (petroleum-ether/ethyl acetate = 16/1) to afford 16.9 mg (65%) of product **28,** as relatively volatile colorless liquid with characteristic odor.

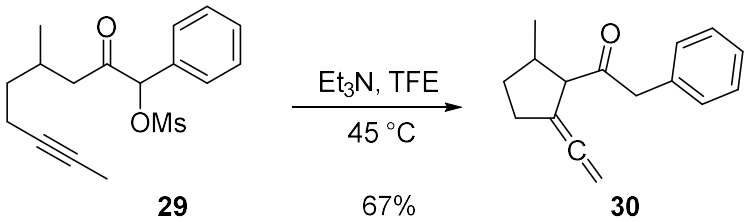
The corresponding tosylate was also used as a substrate for this cyclization, and under identical conditions (Et_3N, TFE, 45 °C, 16 h) gave compound **28** in 50% yield. Besides, tosylate is more difficult to prepare (tosylation of α-hydroxy ketone has to be performed with 4 eq. TsCl in concentrated pyridine solution over 48 h) and purify then mesylate **27**.

^{1}H NMR (500 MHz, CDCl3) δ 5.57 – 5.48 (m, 1H), 5.03 (dd, J^1 = 15.6, J^2 = 9.9 Hz, 1H), 3.19 (dt, J^1 = 11.3, J^2 = 7.7 Hz, 1H), 3.06 (dt, J^1 = 10.8, J^2 = 8.1 Hz, 1H), 2.36 – 2.19 (m, 3H), 2.07 (ddt, J^1 = 13.6, J^2 = 9.7, J^3 = 6.9 Hz, 1H), 1.92 – 1.73 (m, 5H), 1.64 – 1.27 (m, 5H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 215.1, 133.0, 132.8, 54.8, 46.6, 44.4, 34.3, 33.2, 30.7, 27.1, 27.0, 23.7.
IR (ATR) ν_{max}: 2930, 2859, 1704, 1448, 1343, 1078, 980.
HRMS (ESI) calcd. for $C_{12}H_{19}O^+$ $[M+H]^+$: 179.1430; found: 179.1432.

Correlations (NOESY) for **28**:



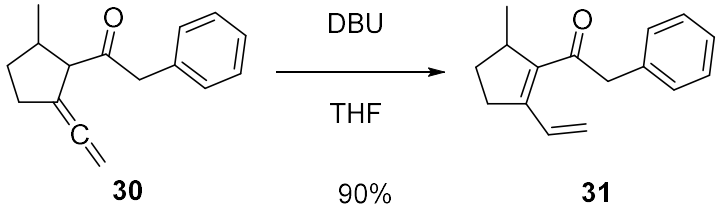
1-(2-Methyl-5-vinylidenecyclopentyl)-2-phenylethanone (30)



According to the General procedure – Method A. Using mesyloxy ketone **29** (99.3 mg, 0.308 mmol, 1 eq), triethylamine (69 µL, 0.49 mmol, 1.6 eq) and trifluoroethanol (1 mL), during 2 h. Purification by column chromatography (petroleum-ether/diisopropyl ether = 95/5) afforded 47.0 mg (67%) of allene **30**, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 4.86 – 4.77 (m, 2H), 3.86 (d, J = 15.6 Hz, 1H), 3.78 (d, J = 15.6 Hz, 1H), 3.26 – 3.20 (m, 1H), 2.54 – 2.38 (m, 3H), 1.98 – 1.90 (m, 1H), 1.35 – 1.25 (m, 1H), 0.91 (d, J = 6.7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 206.9, 202.7, 134.2, 129.7, 128.5, 126.8, 103.1, 77.5, 61.8, 48.9, 37.6, 34.1, 30.8, 18.7.
IR (ATR) ν_{max}: 3028, 2953, 2925, 2865, 1957, 1707, 1600, 1494, 1453, 1280.
HRMS (ESI) calcd. for $C_{16}H_{19}O^+$ $[M+H]^+$: 227.1430, found: 227.1422.

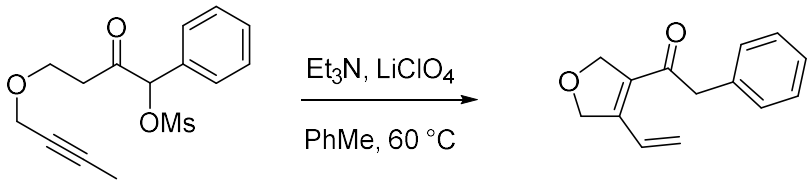
1-(5-Methyl-2-vinylcyclopent-1-enyl)-2-phenylethanone (31)



DBU (5μL, 0.034 mmol, 0.2 eq) was added to the solution of allene **30** (38.8 mg, 0.17 mmol, 1 eq) in THF (0.5 mL) and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with sat. NH_4Cl solution, extracted with diethyl ether and washed with water. The combined organic extract was dried over anh. $MgSO_4$ prior to concentrating *in vacuo*. Purification of the residue by column chromatography (petroleum-ether/ethyl acetate = 95/5) afforded 35 mg (90%) of dienone **31**, as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 7.20 – 7.16 (m, 2H), 7.11 (dd, J = 17.5, 10.8 Hz, 1H), 5.41 (d, J = 17.4 Hz, 1H), 5.35 (d, J = 10.8 Hz, 1H), 3.90 (d, J = 15.6 Hz, 1H), 3.83 (d, J = 15.6 Hz, 1H), 3.26 – 3.18 (m, 1H), 2.75 – 2.67 (m, 1H), 2.56 – 2.48 (m, 1H), 2.15 – 2.06 (m, 1H), 1.53 – 1.46 (m, 1H), 1.10 (d, J = 6.8 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 148.2, 143.7, 134.3, 131.8, 129.5, 128.4, 126.7, 120.6, 48.9, 41.7, 31.6, 30.8, 20.0.
IR (ATR) ν_{max}: 3088, 3062, 3028, 2955, 2867, 1667, 1607, 1562, 1495, 1454, 1347.
HRMS (ESI) calcd. for $C_{16}H_{18}O$ [M+Na$^+$]: 249.1250, found: 249.1242.

2-Phenyl-1-(4-vinyl-2,5-dihydrofuran-3-yl)ethanone (33)



32 25% **33**

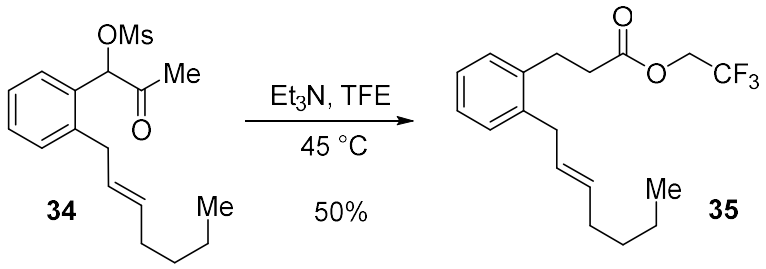
According to the General procedure – Method C. Using mesyloxy ketone **32** (37.7 mg, 0.128 mmol, 1 eq), triethylamine (36 μL, 0.256 mmol, 2 eq), lithium perchlorate (27 mg, 0.256 mmol, 2 eq), and toluene (0.5 mL), during 20 min. Purification by dry-flash chromatography (petroleum-ether/ ethyl acetate = 9/1) afforded 6.8 mg (25%) of dienone **33**, as a colorless oil.

According to the General procedure – Method A, dienone **33** was isolated in only 8% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 3H), 7.30– 7.25 (m, 1H), 7.20 – 7.15 (m, 2H), 5.54 (d, J = 11.0 Hz, 1H), 5.35 (d, J = 17.8 Hz, 1H), 3.98 – 3.90 (m, 4H), 3.78 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 146.8, 133.2, 132.2, 129.5, 128.9, 128.4, 127.3, 123.6, 76.6, 76.0, 49.8.
IR (ATR) ν_{max}: 3062, 3030, 2923, 2861, 1728, 1682, 1627, 1535, 1496, 1453, 1358.
HRMS (ESI) calcd. for $C_{16}H_{18}O$ (M+H$^+$): 227.1430, found: 227.1422.

3. Side reactions

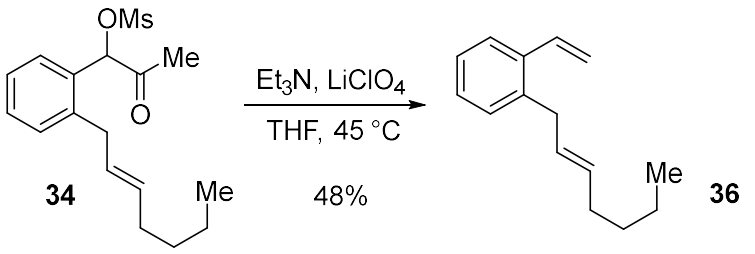
2,2,2-Trifluoroethyl (E)-3-(2-(hept-2-en-1-yl)phenyl)propanoate (35)



According to the General procedure – Method A. Triethylamine (7 µL, 0.050 mmol) was added to the solution of mesylate **34** (10.0 mg, 0.031 mmol) in trifluoroethanol (1.0 mL) and the reaction mixture was stirred at 45 °C for 3 h, under an argon atmosphere. The reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography (petroleum-ether/ethyl acetate = 94/6) to afford 5.1 mg (50%) of trifluoroethyl ester **35**, as a colorless oil with characteristic odor.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.09 (m, 4H), 5.57 – 5.48 (m, 1H), 5.48 – 5.39 (m, 1H), 4.47 (q, J = 8.5 Hz, 2H), 3.35 (dd, J^1 = 6.2, J^2 = 1.0 Hz, 2H), 2.99 (dd, J^1 = 9.8, J^2 = 6.2 Hz, 2H), 2.70 (dd, J^1 = 9.8, J^2 = 6.2 Hz, 2H), 2.01 (dd, J^1 = 13.3, J^2 = 6.6 Hz, 2H), 1.40 – 1.25 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) 171.5, 138.9, 138.0, 132.4, 130.0, 129.0, 128.4, 126.9, 126.6, 123.1 (q, J = 277.1 Hz), 60.5 (q, J = 36.5 Hz), 36.2, 34.8, 32.4, 31.7, 27.6, 22.4, 14.0.
IR (ATR) ν_{max}: 3065, 3021, 2960, 2929, 2871, 1761, 1490, 1454, 1413, 1282, 1172, 1145, 974.
HRMS (APPI) calcd. for $C_{18}H_{23}F_3O_2^+$ $[M]^+$: 328.1645; found: 328.1637.

(*E*)-1-(Hept-2-en-1-yl)-2-vinylbenzene (36)

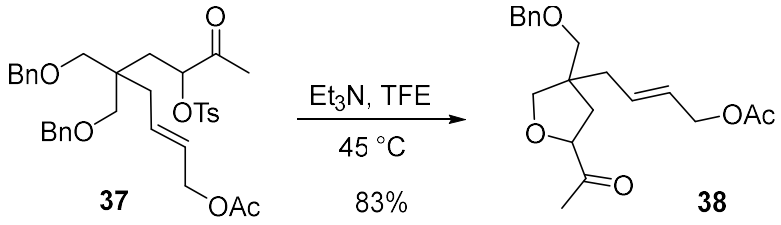


Triethylamine (17.5 µL, 0.125 mmol) and $LiClO_4$ (9.5 mg, 0.089 mmol) were added to the solution of mesyloxy ketone **34** (5.0 mg, 0.015 mmol) in tetrahydrofuran (0.30 mL), and the reaction

mixture was stirred at 45 °C for 24 h, under an argon atmosphere. The reaction mixture was carefully concentrated under reduced pressure and the residue was purified by column chromatography (petroleum-ether/ethyl acetate = 49/1) to afford 1.5 mg (48%) of styrene **36**, as very volatile colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, J^1 = 6.8, J^2 = 2.3 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.16 – 7.14 (m, 1H), 6.98 (dd, J^1 = 17.4, J^2 = 11.0 Hz, 1H), 5.63 (dd, J^1 = 17.4, J^2 = 1.4 Hz, 1H), 5.53 (dddd, J^1 = 7.5, J^2 = 6.2, J^3 = 4.4, J^4 = 3.1 Hz, 1H), 5.41 (ddd, J^1 = 15.2, J^2 = 10.1, J^3 = 6.0 Hz, 1H), 5.27 (dd, J^1 = 11.0, J^2 = 1.4 Hz, 1H), 3.38 (d, J = 5.3 Hz, 2H), 2.00 (dd, J^1 = 13.2, J^2 = 6.8 Hz, 2H), 1.35 – 1.25 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 136.8, 134.9, 132.2, 129.7, 128.2, 128.0, 126.5, 125.8, 115.4, 36.5, 32.4, 31.76, 22.4, 14.1.
IR (ATR) ν_{max}: 3086, 3062, 3021, 2957, 2926, 2856, 1626, 1482, 1452, 969, 912, 767.
HRMS (ESI) calcd. for $C_{15}H_{19}^+$ [M-H]$^+$: 199.1487; found: 199.1484.

(*E*)-4-(5-Acetyl-3-((benzyloxy)methyl)tetrahydrofuran-3-yl)but-2-en-1-yl acetate (38)



According to the General procedure – Method A. Triethylamine (9 µL, 0.065 mmol) was added to the solution of tosylate **37** (23.0 mg, 0.038 mmol) in trifluoroethanol (1.5 mL) and the reaction mixture was stirred at 45 °C for 1 h, under argon atmosphere. The reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography (petroleum-ether/ethyl acetate = 3/1) to afford 10.9 mg (83%) of compound **38,** as a colorless oil. Mixture of *cis* and *trans* isomers in a relative ratio 1.86:1, according to ^{1}H NMR spectrum integration of [C-C**H**H-C in the ring] signals at 1.78 (dd, J^1 = 13.1, J^2 = 7.8 Hz, $1H_{minor}$) and 1.72 (dd, J^1 = 13.1, J^2 = 8.2 Hz, 1H major). However, we were not able to assignate which isomer is *cis* and which one is *trans*, i. e., we do not know whether the *cis*-isomer is the major, or the minor one.

Spectral data for the mixture of diastereoisomers **38**:
^{1}H NMR (500 MHz, CDCl3) δ 7.42 – 7.27 (m, 5H minor+major), 5.73 – 5.53 (m, 2H minor+major), 4.55 – 4.43 (m, 4H minor+major), 4.39 – 4.27 (m, 1H minor+major), 3.83 (dd, J^1 = 13.7, J^2 = 8.9 Hz, 1H minor+major), 3.65 (d, J = 8.8 Hz, 1H minor+major), 3.37 – 3.21 (m, 2H

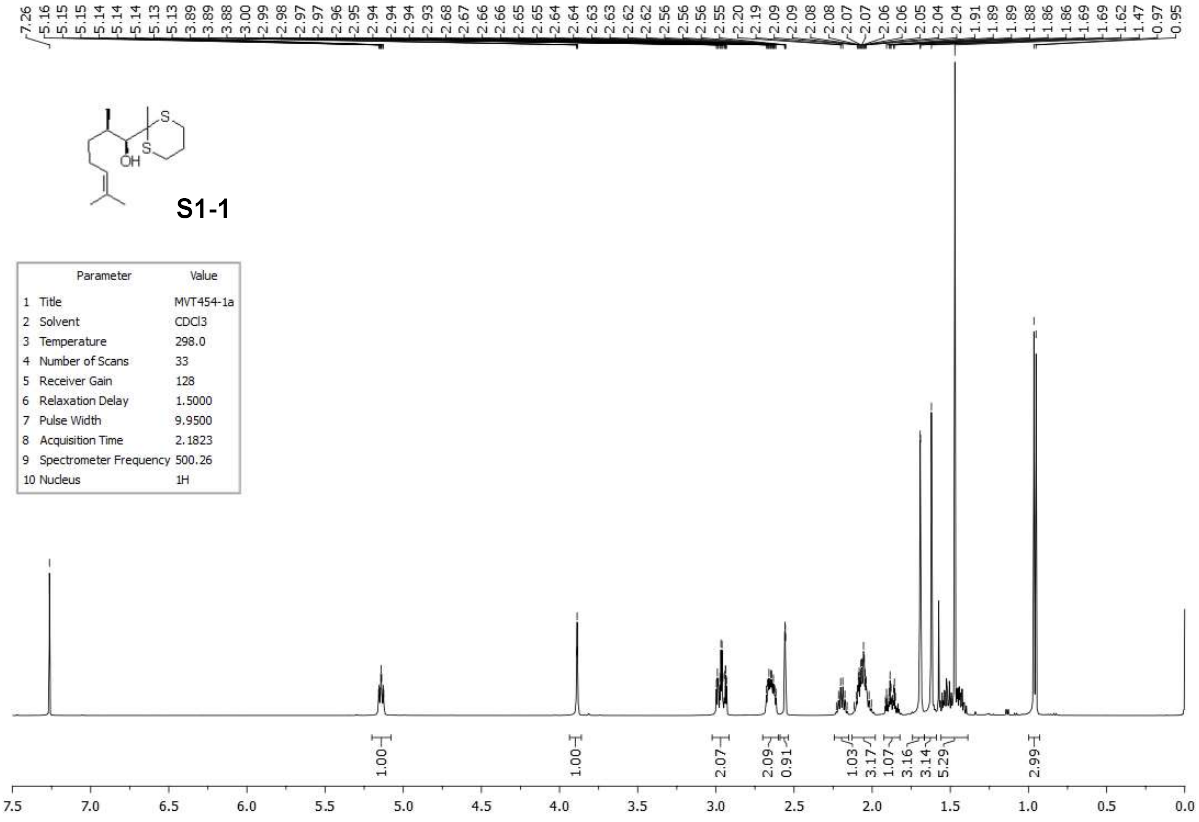
minor+major), 2.35 – 1.97 (m, 9H minor+major), 1.78 (dd, J^1 = 13.1, J^2 = 7.8 Hz, 1H minor), 1.72 (dd, J^1 = 13.1, J^2 = 8.2 Hz, 1H major).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.0, 209.9, 170.9, 138.3, 138.2, 131.23, 131.20, 128.6, 127.89, 127.85, 127.82, 127.8, 127.7, 83.7, 76.2, 75.9, 73.5, 73.4, 72.9, 64.9, 47.7, 47.6, 37.65, 37.60, 36.9, 25.88, 25.83, 21.1.

IR (ATR) ν_{max}: 3062, 3029, 2938, 2861, 1738, 1452, 1362, 1235, 1097, 1026, 974, 743.

HRMS (ESI) calcd. for $C_{20}H_{26}NaO_5^+$ $[M+Na]^+$: 369.1678; found: 369.1679

4. Copies of NMR spectra



S1-1

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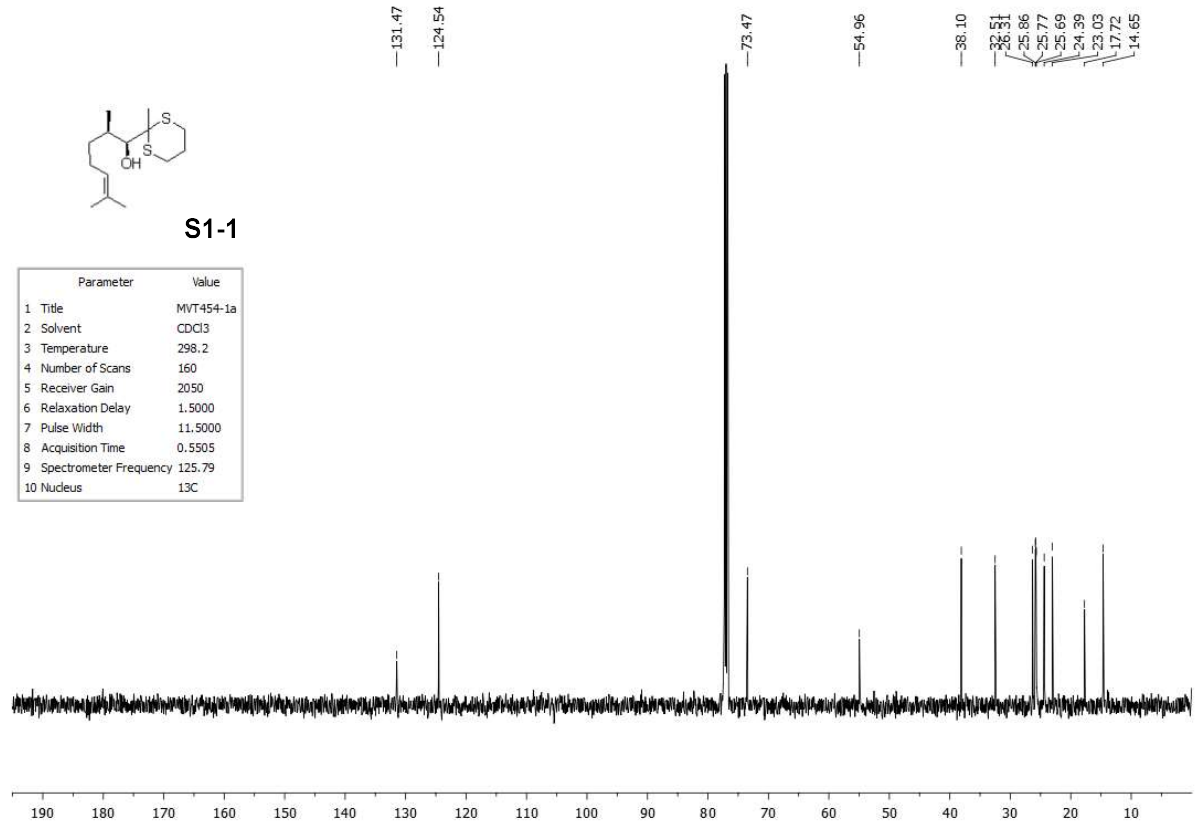
9	Spectrometer Frequency	500.26
10	Nucleus	1H



S1-1

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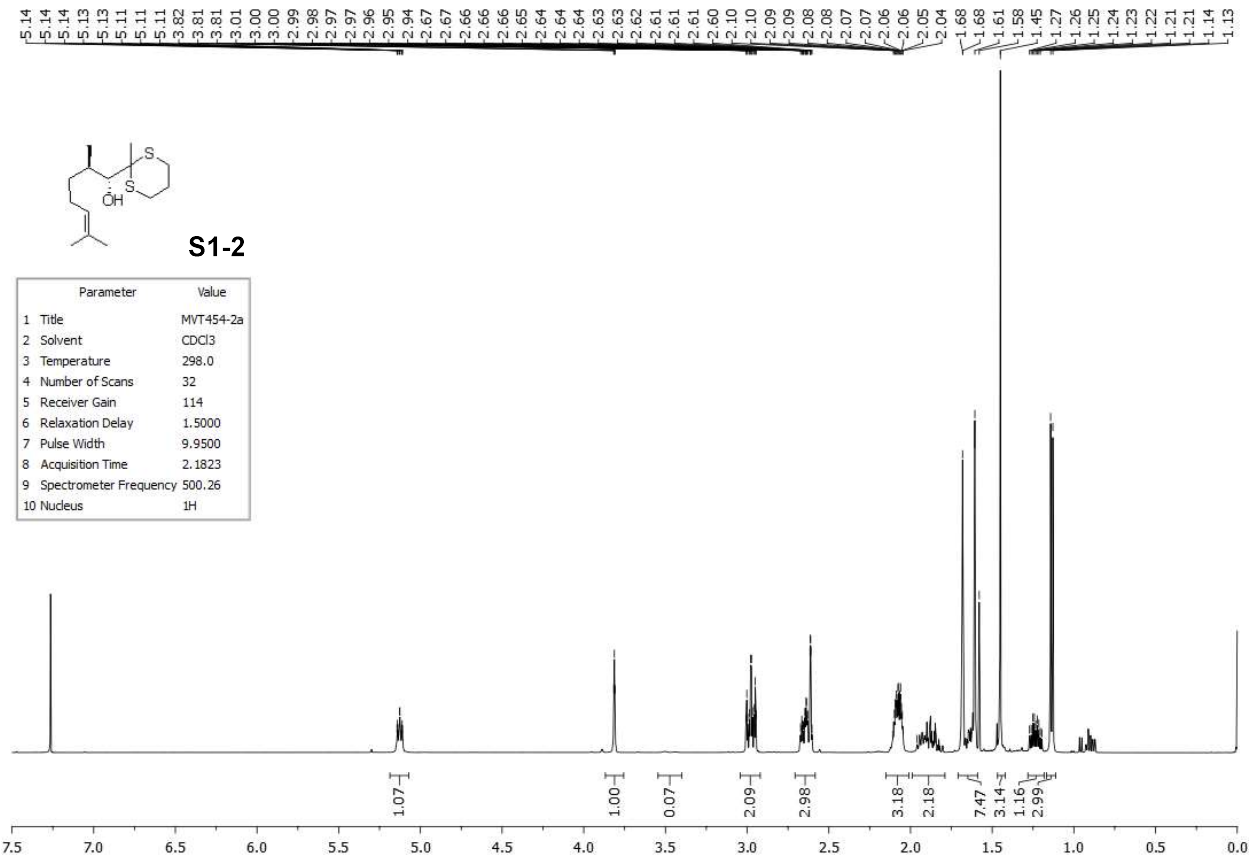
10	Nucleus	13C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S
S
OH
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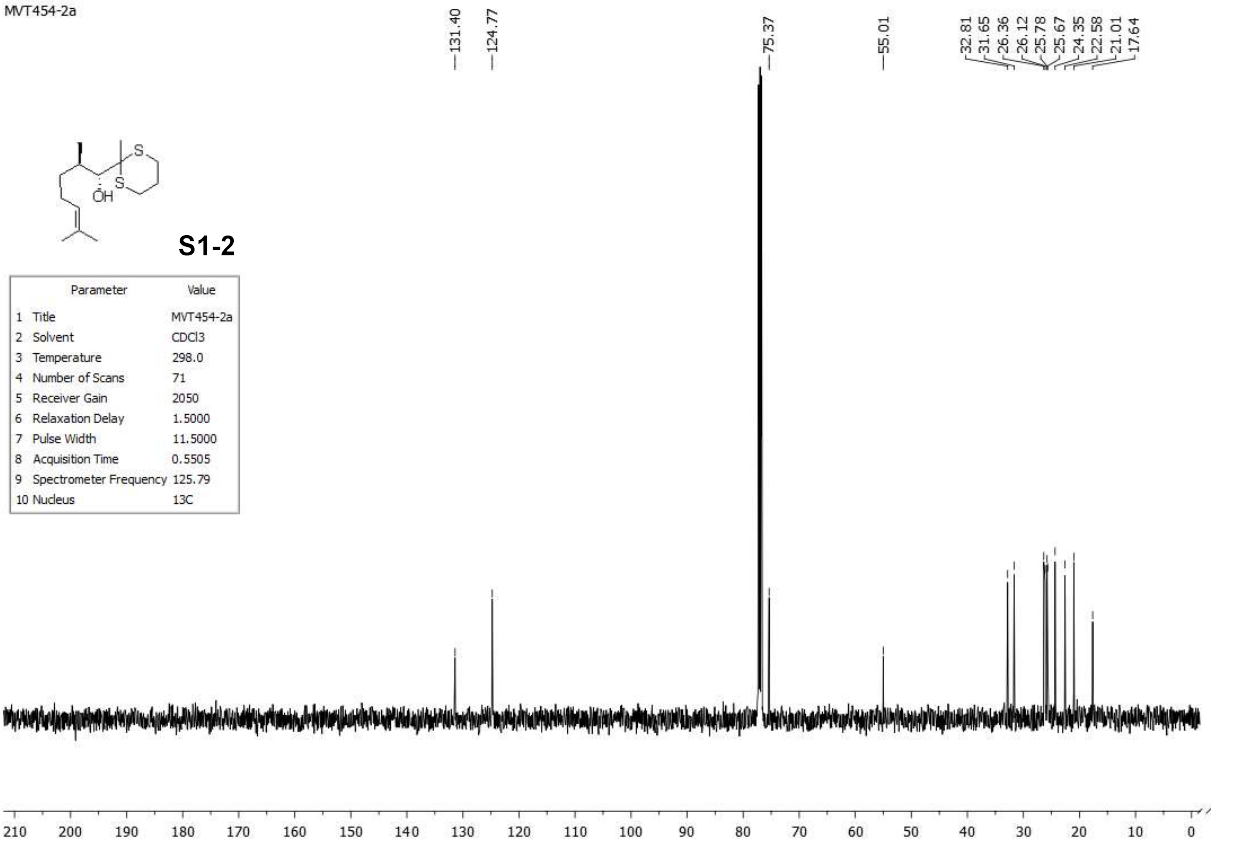
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S
OH
S1-2
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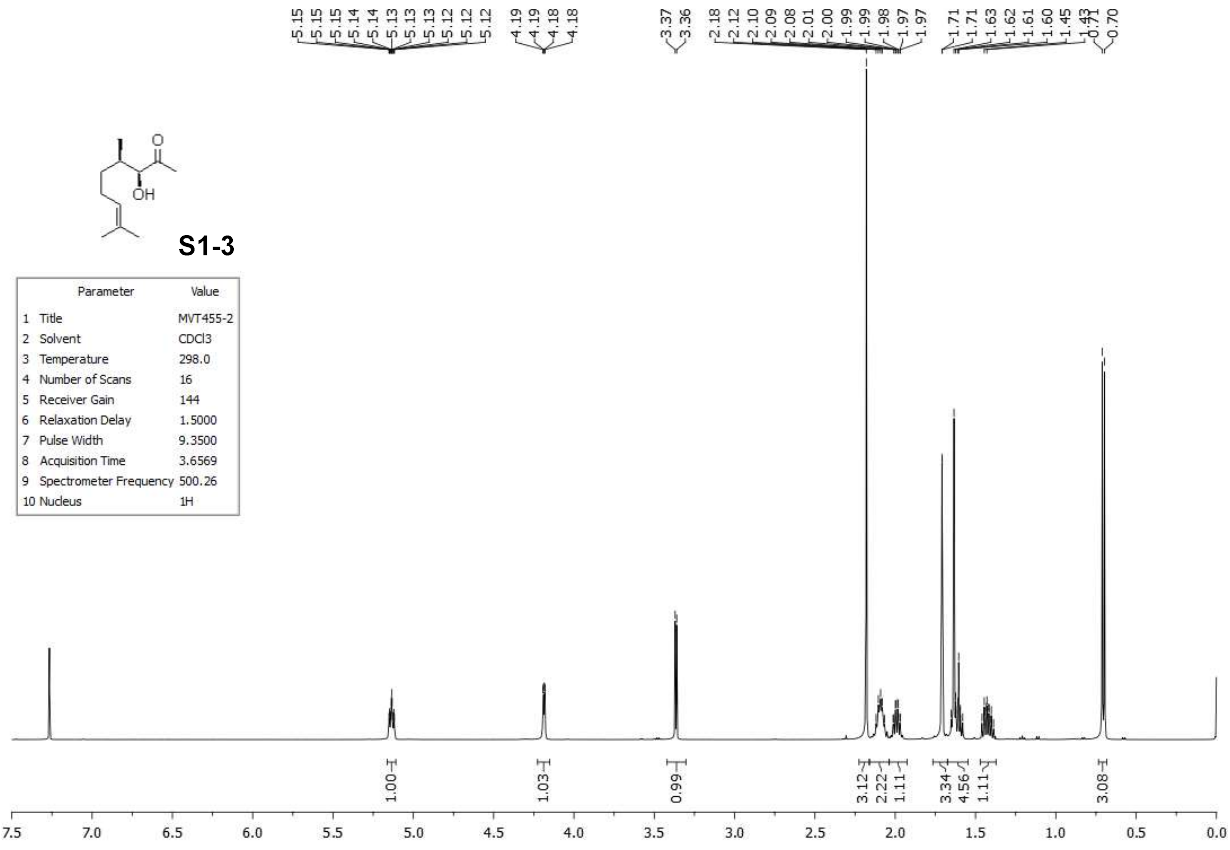
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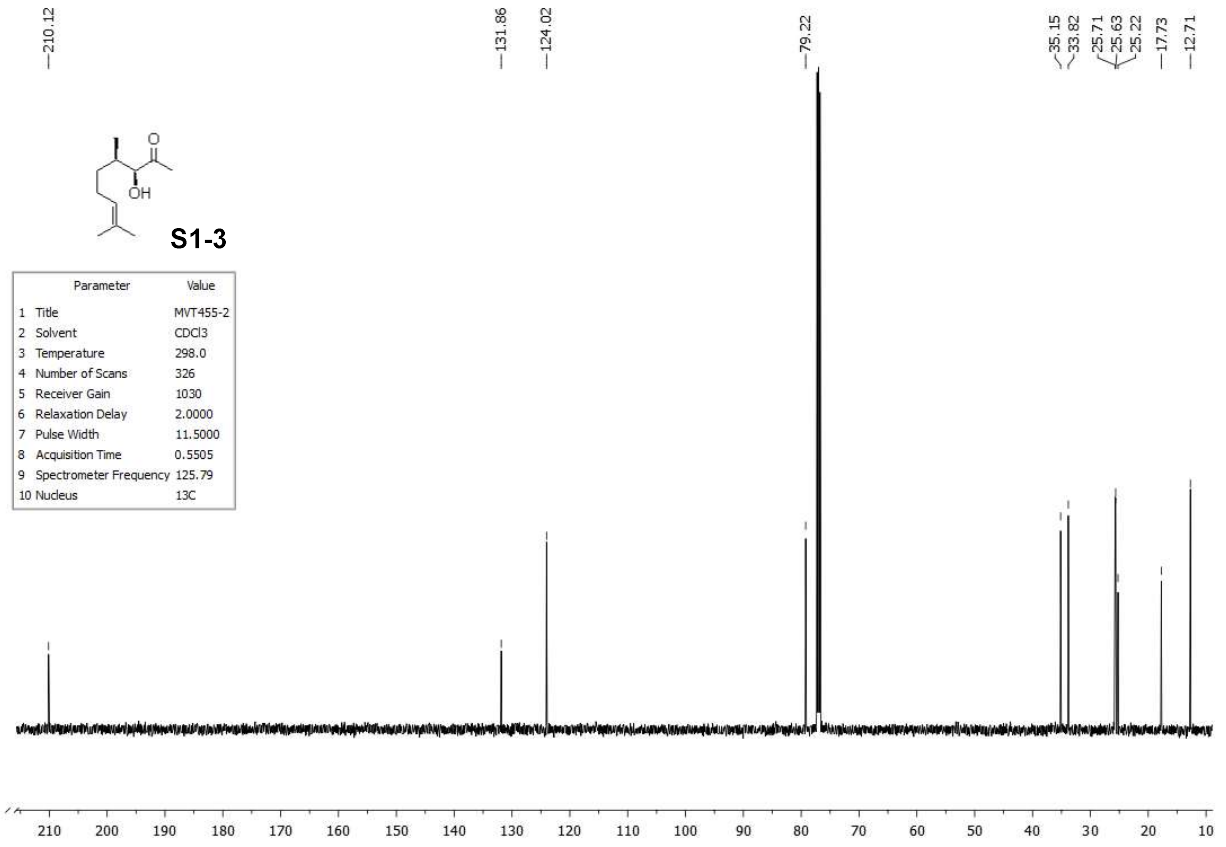
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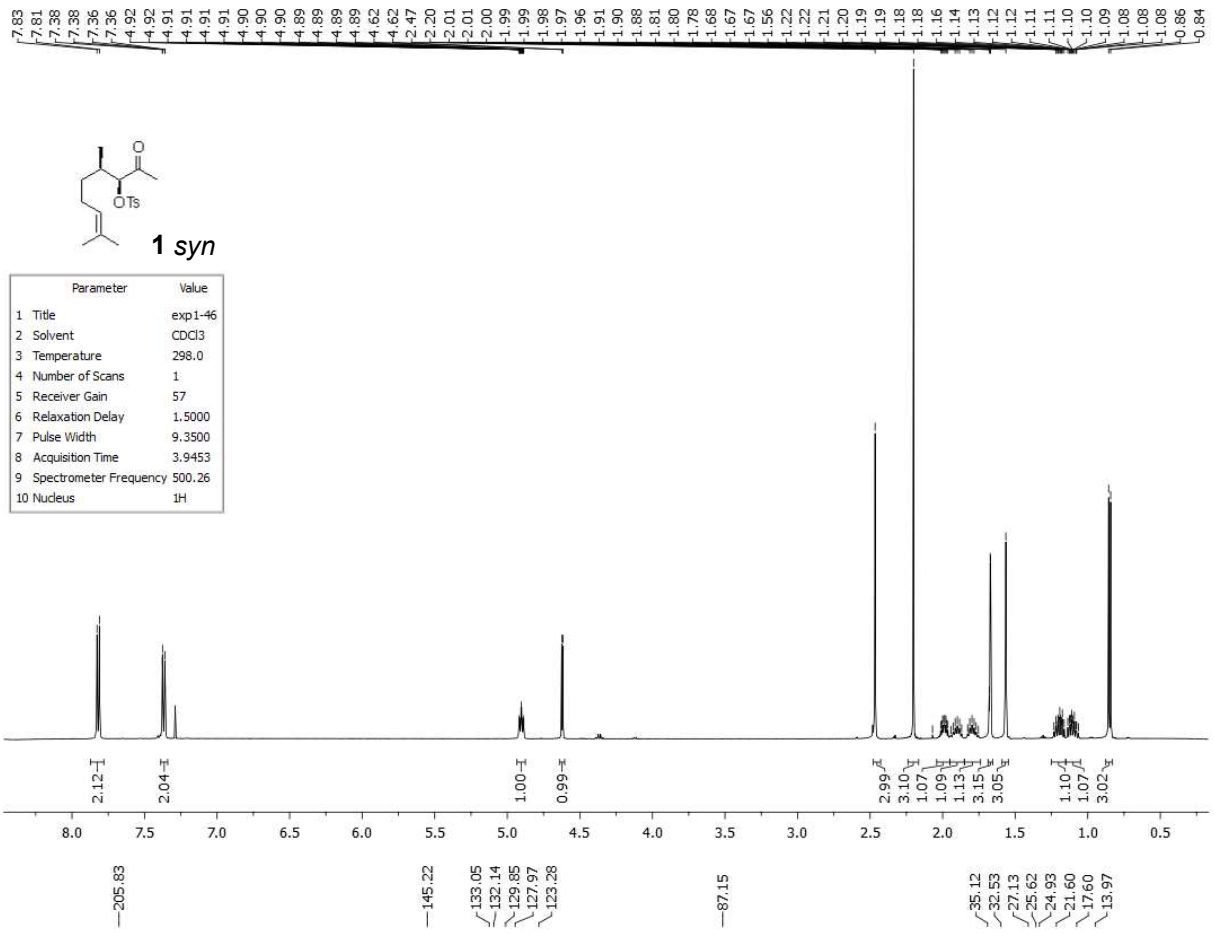
10 Nucleus 13C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10 Nucleus 1H
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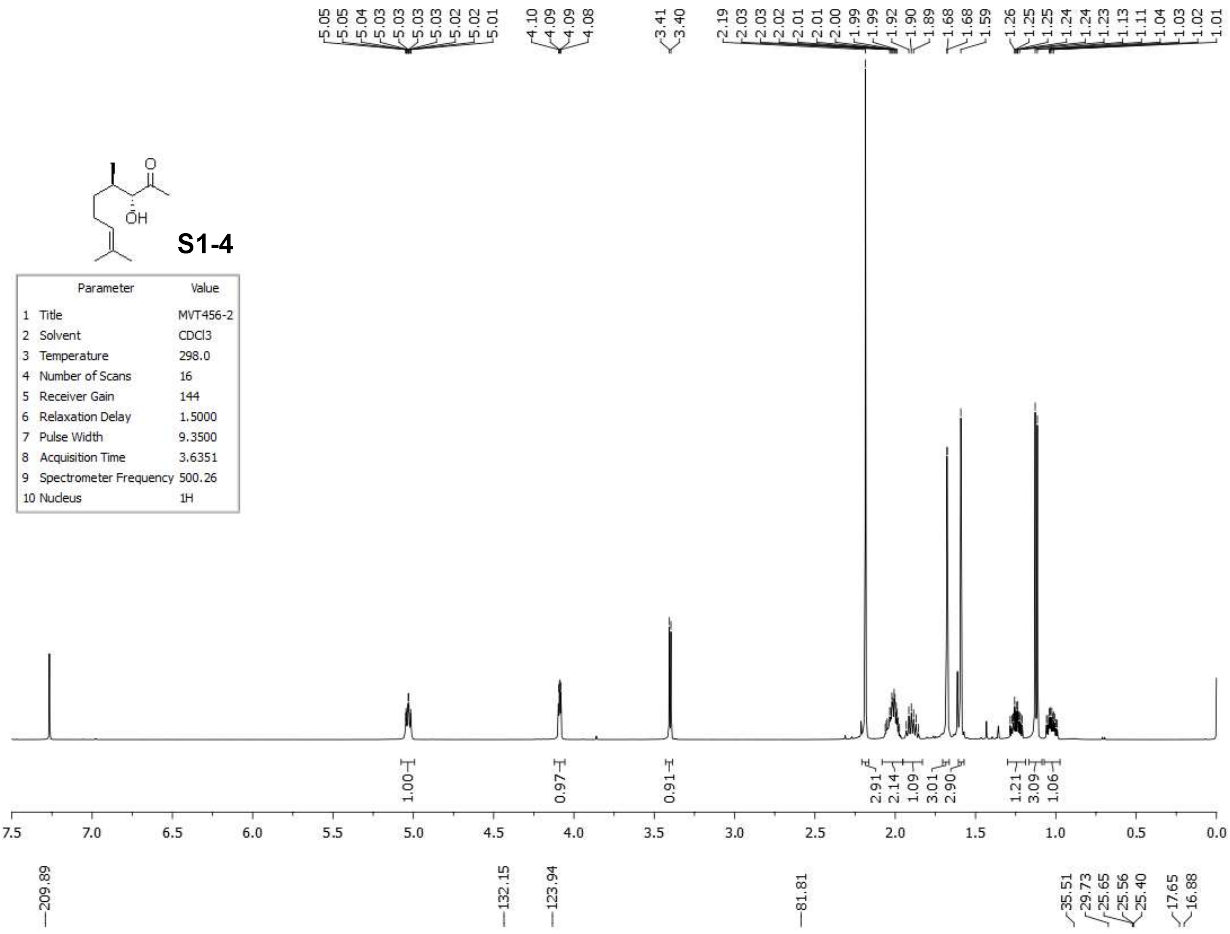
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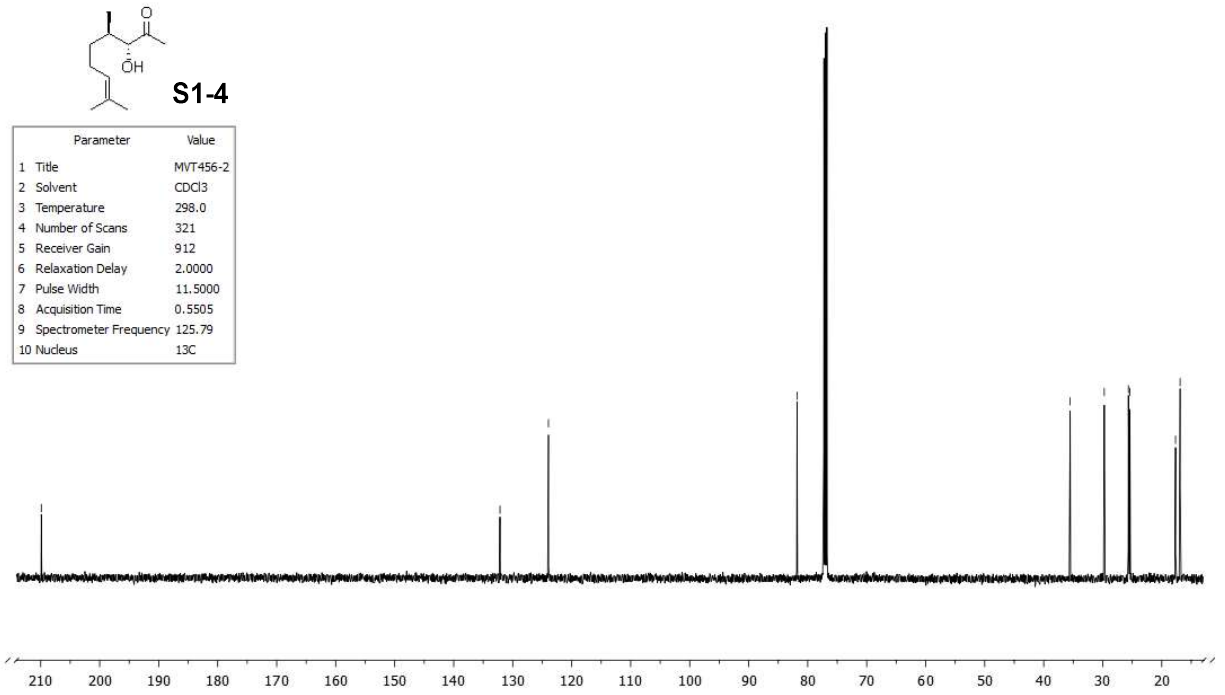
10 Nucleus 1H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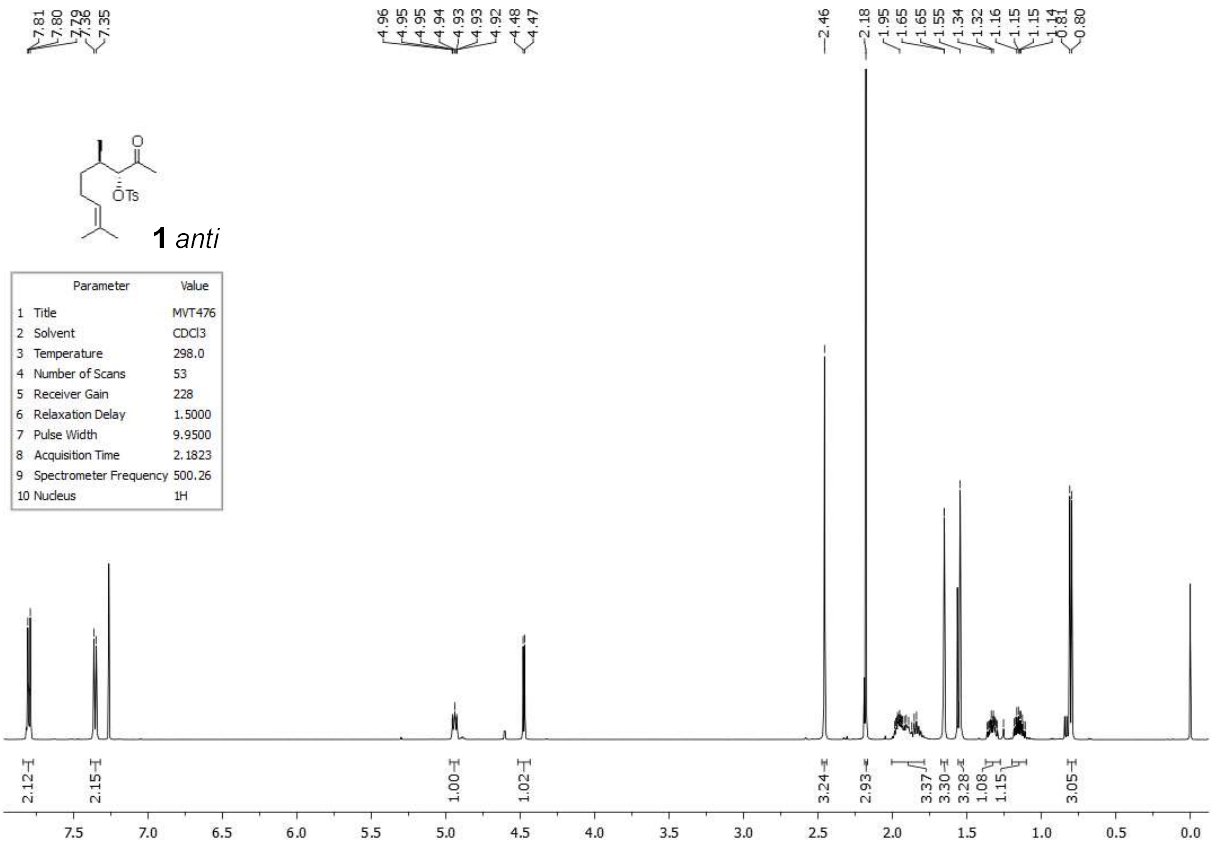
10 Nucleus 13C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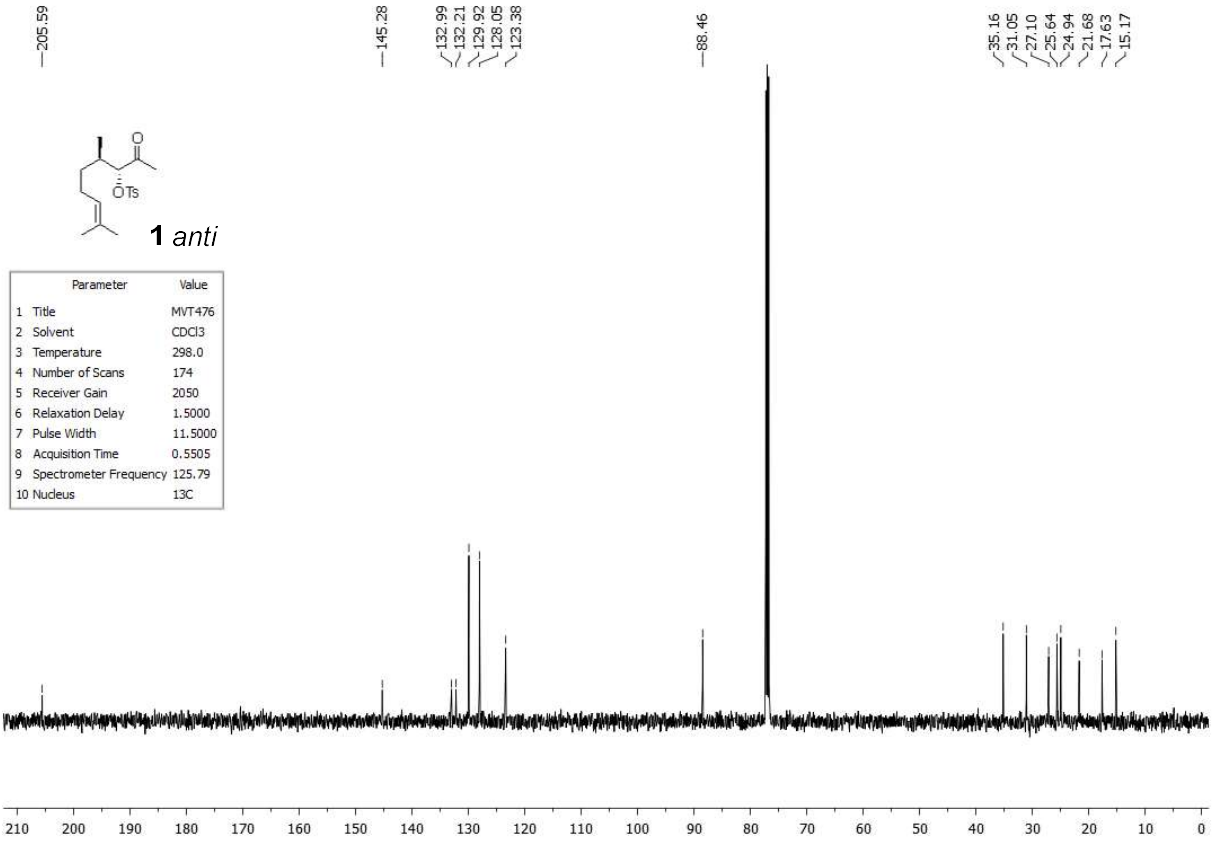
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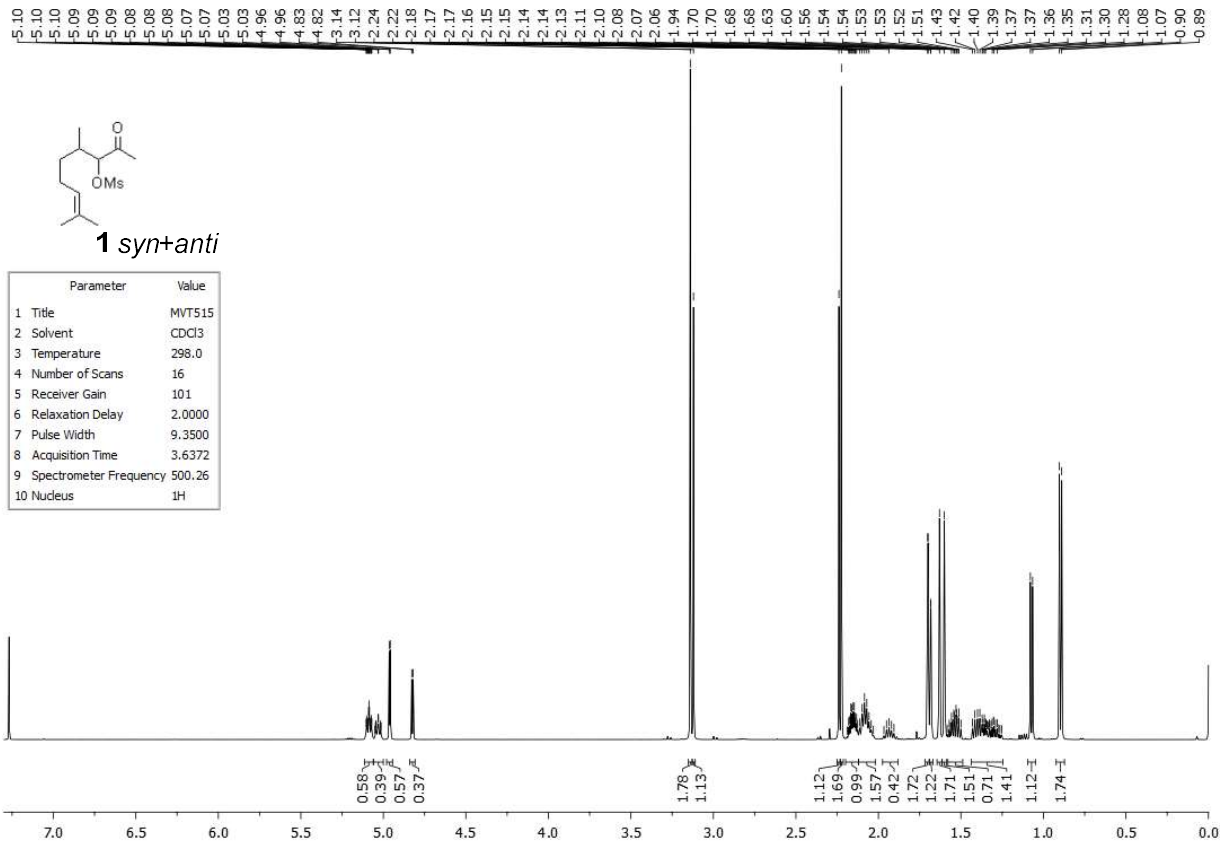
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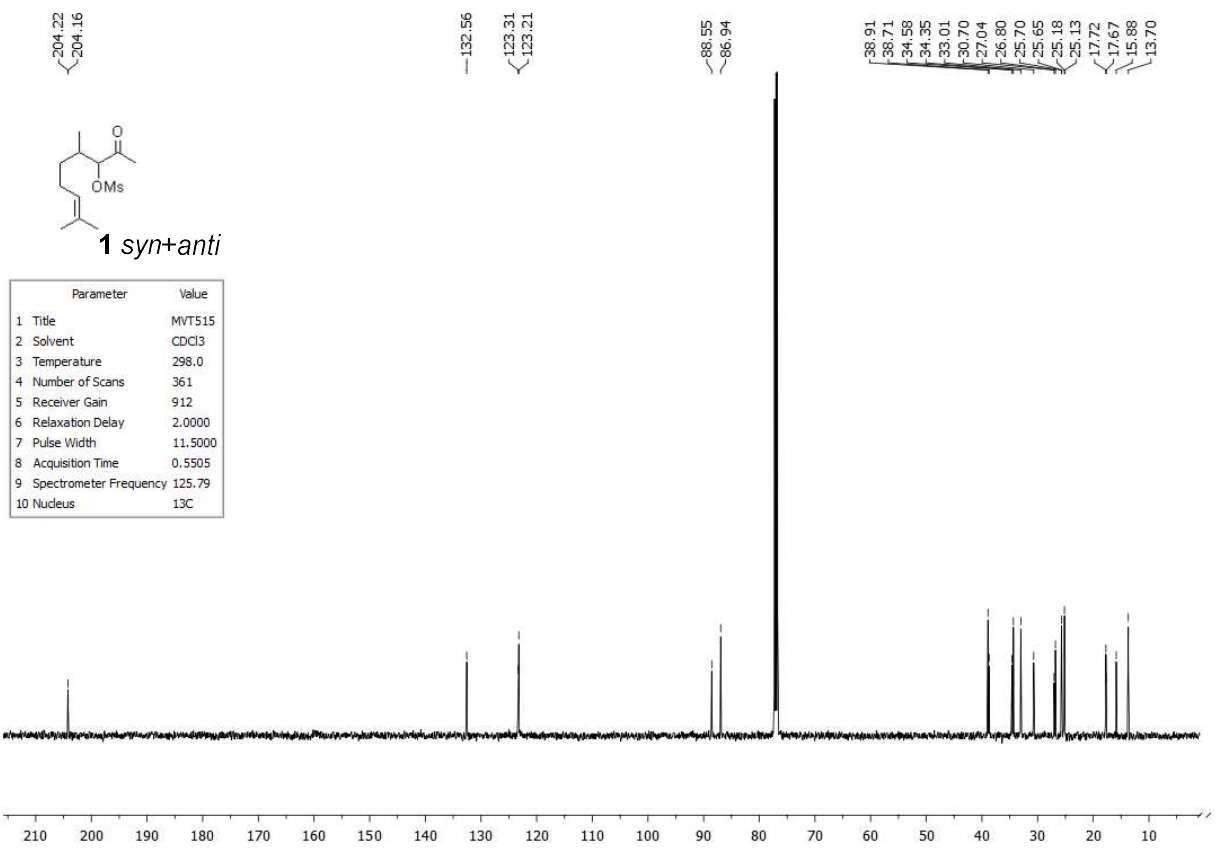
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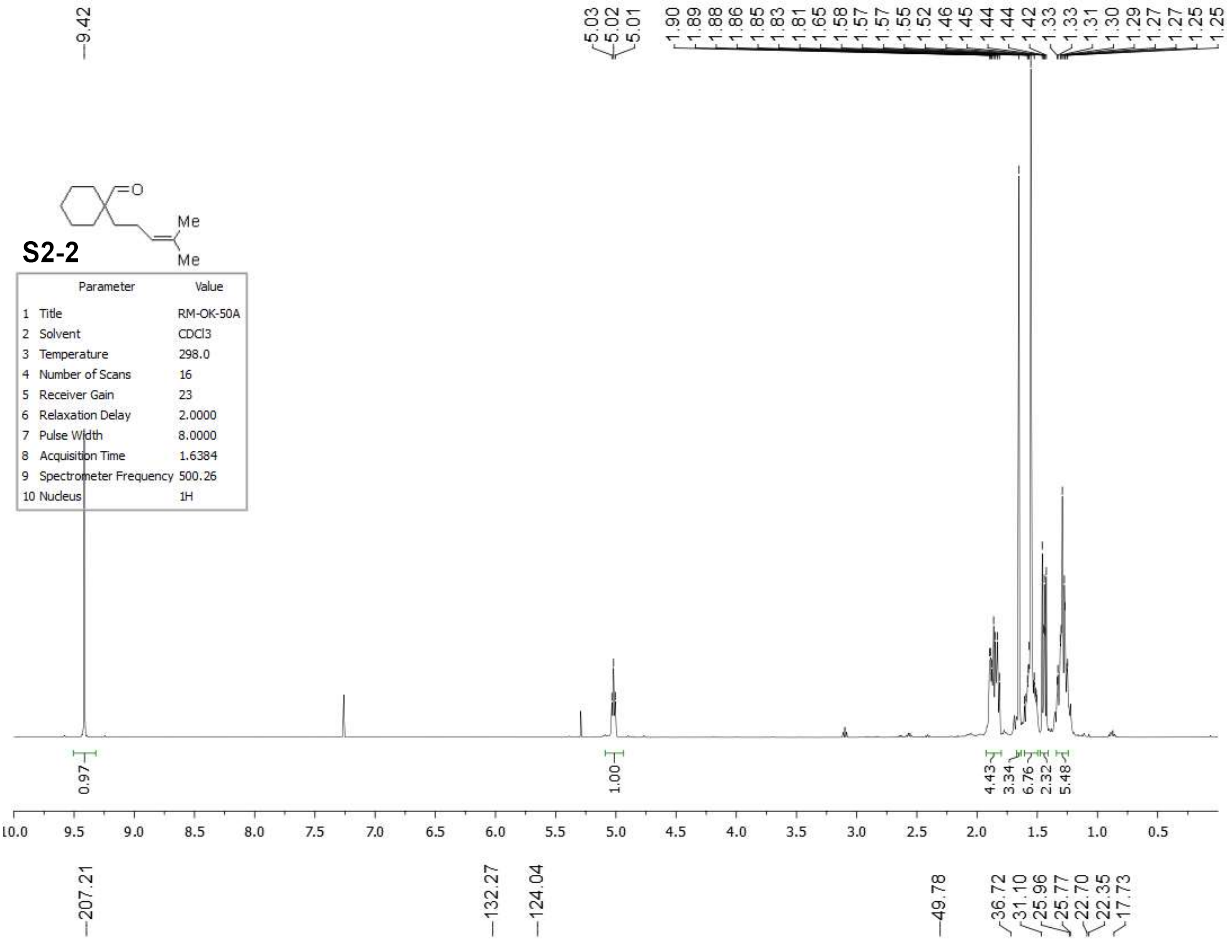
10 Nucleus 13C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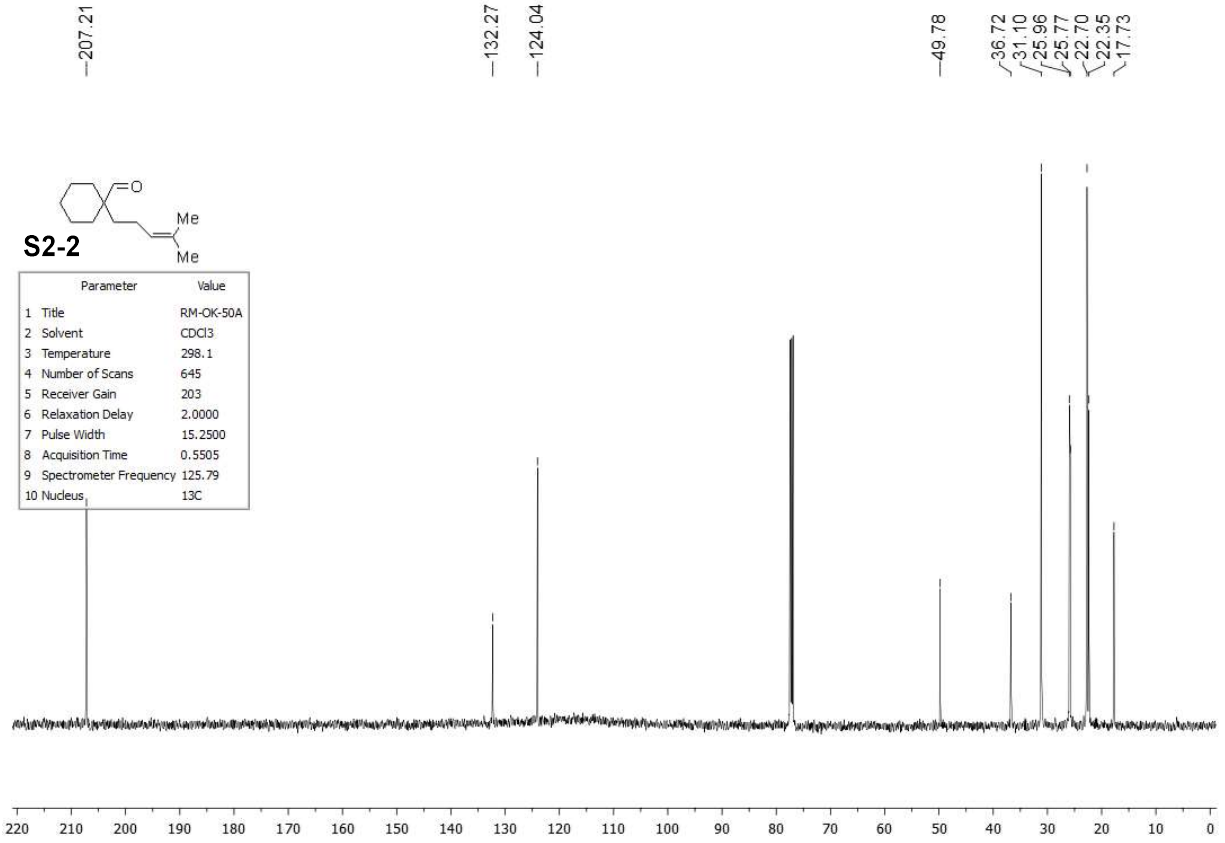
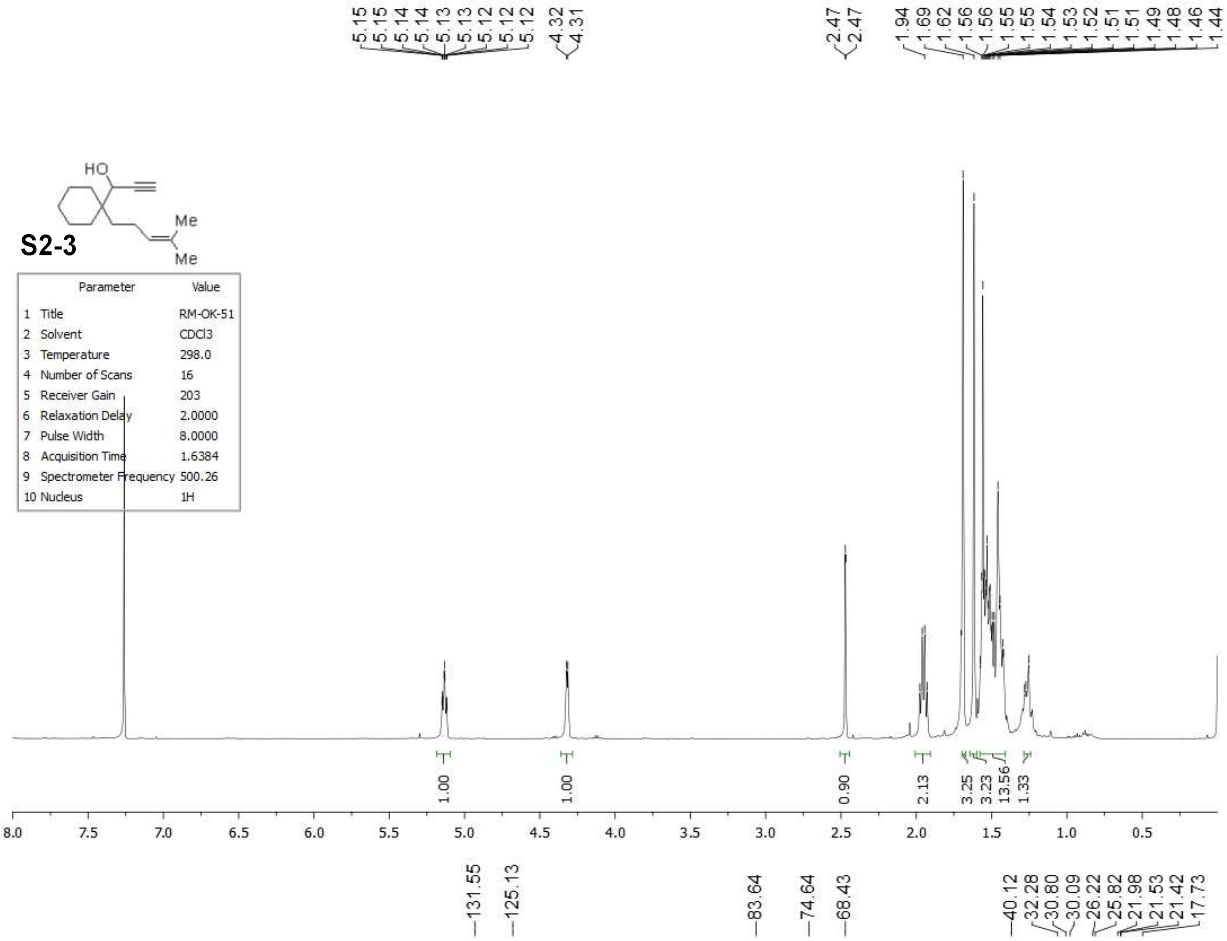
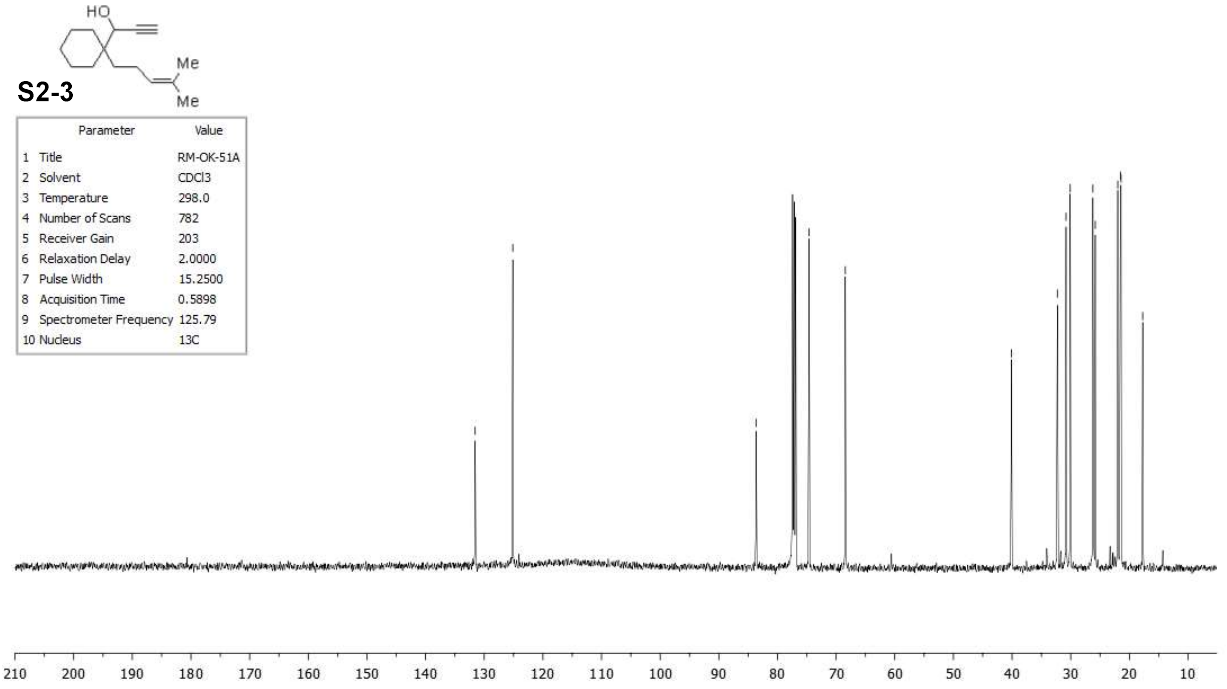
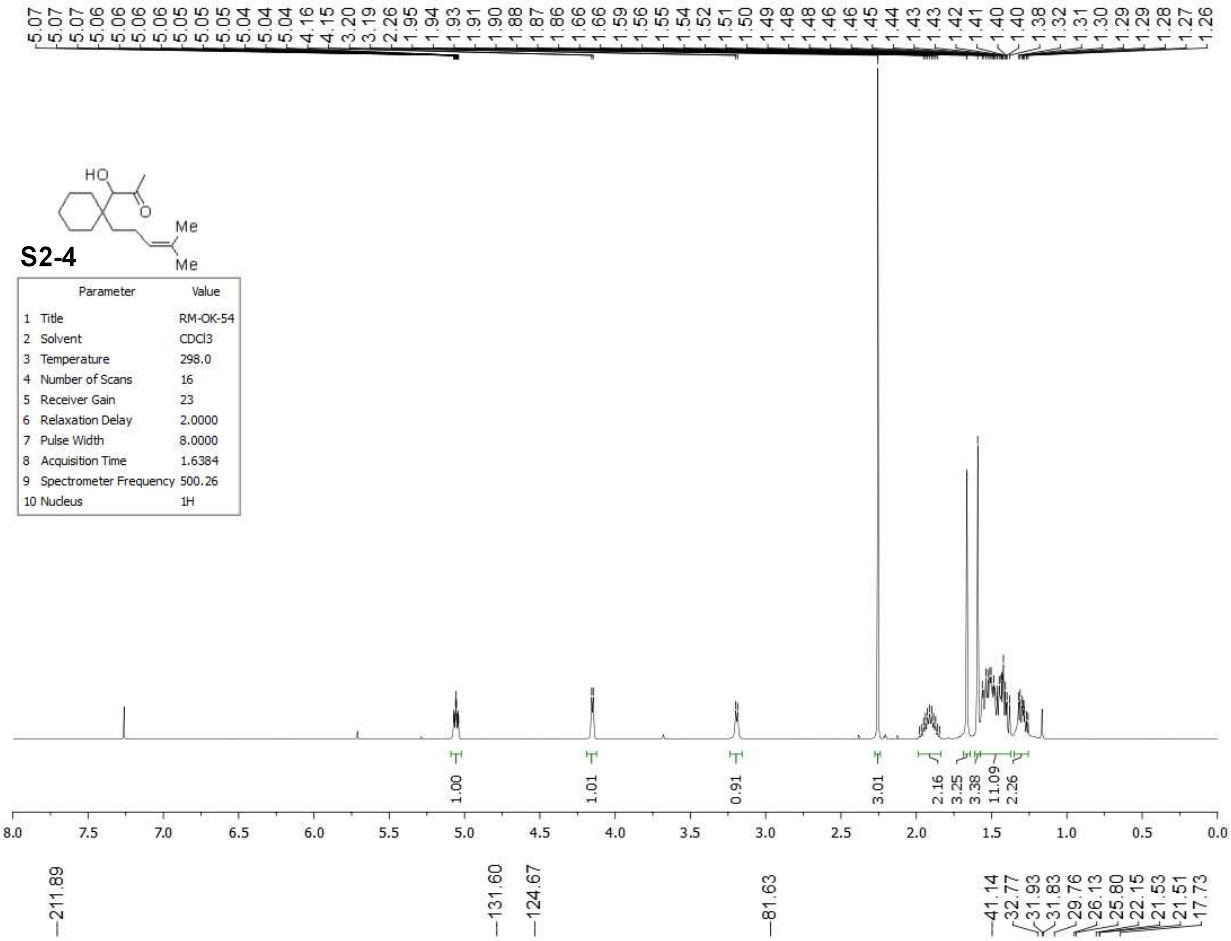
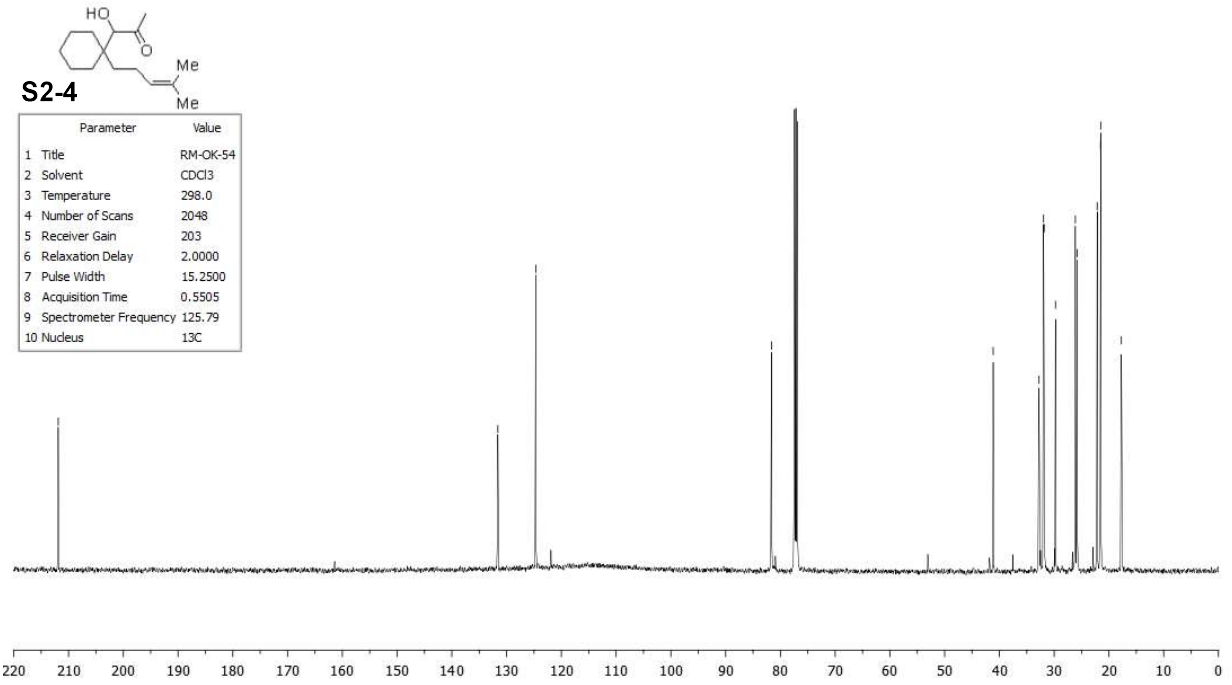
Parameter Value
1 Title RM-OK-50A
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 23
6 Relaxation Delay 2.0000
7 Pulse Width 8.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
0.97
1.00
4.43
3.34
6.76
2.32
5.48
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

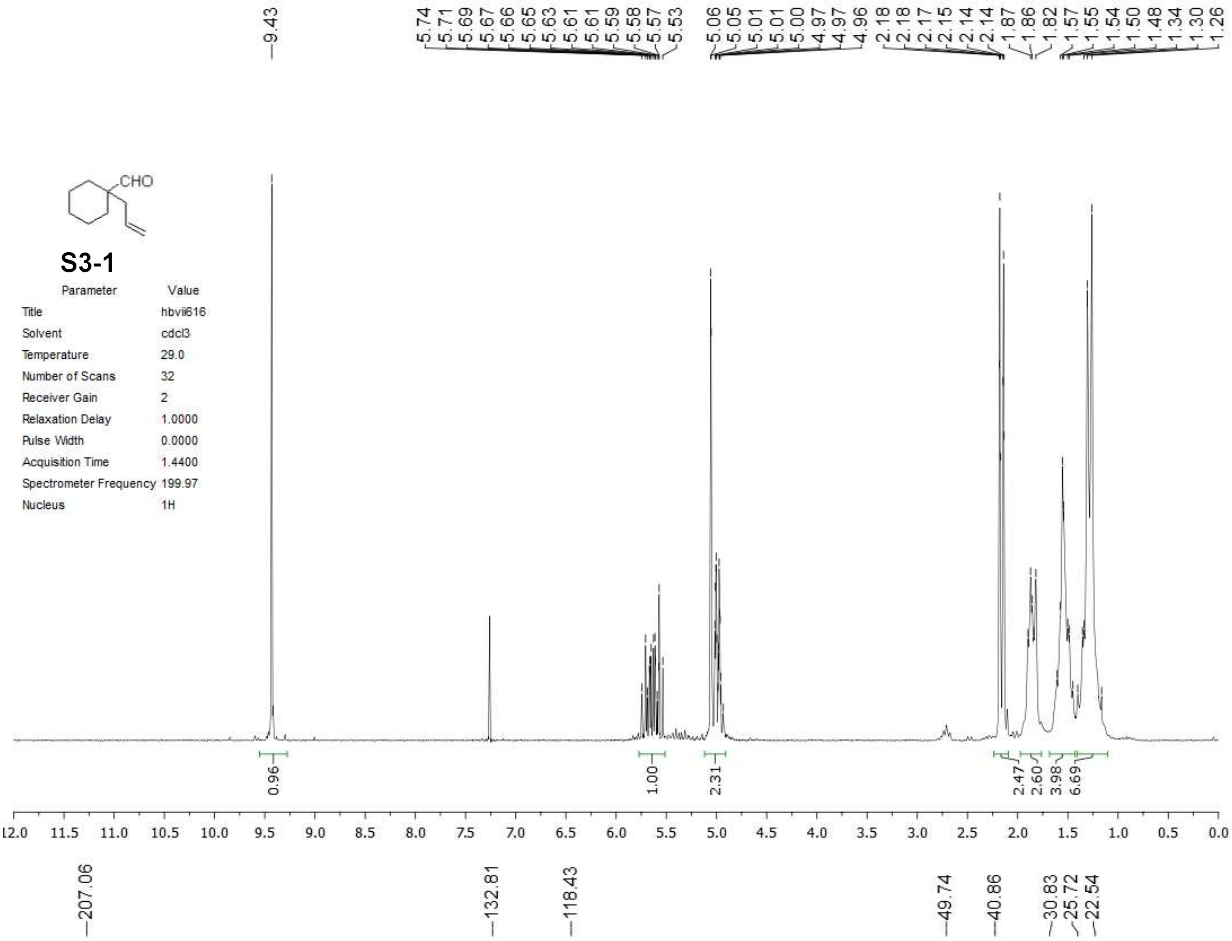

207.21
132.27
124.04
49.78
36.72
31.10
25.96
25.77
22.70
22.35
17.73
O
Me
Me
S2-2
Parameter Value
1 Title RM-OK-50A
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 645
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 15.2500
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

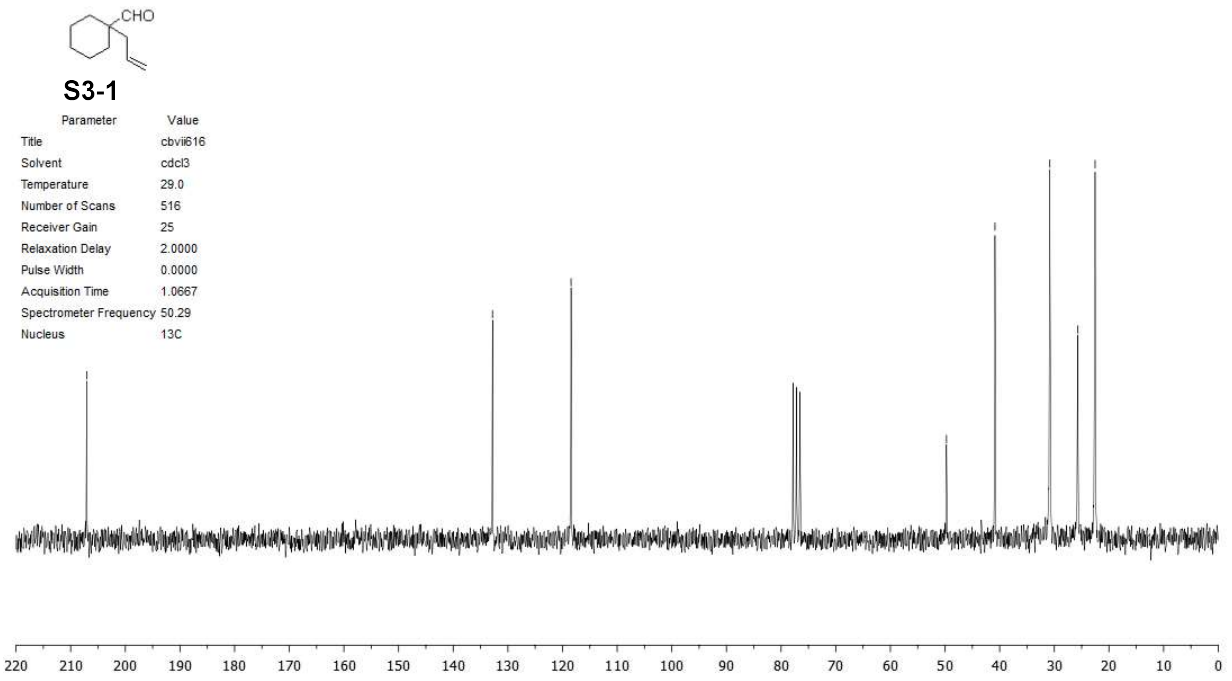

5.15
5.15
5.14
5.14
5.13
5.13
5.12
5.12
5.12
4.32
4.31
2.47
2.47
1.94
1.69
1.62
1.56
1.56
1.55
1.55
1.54
1.53
1.52
1.51
1.51
1.49
1.48
1.46
1.44
HO
Me
Me
S2-3
Parameter Value
1 Title RM-OK-51
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 8.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1.00
1.00
0.90
2.13
3.25
3.23
13.56
1.33
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
131.55
125.13
83.64
74.64
68.43
40.12
32.28
30.80
30.09
26.22
25.82
21.98
21.53
21.42
17.73

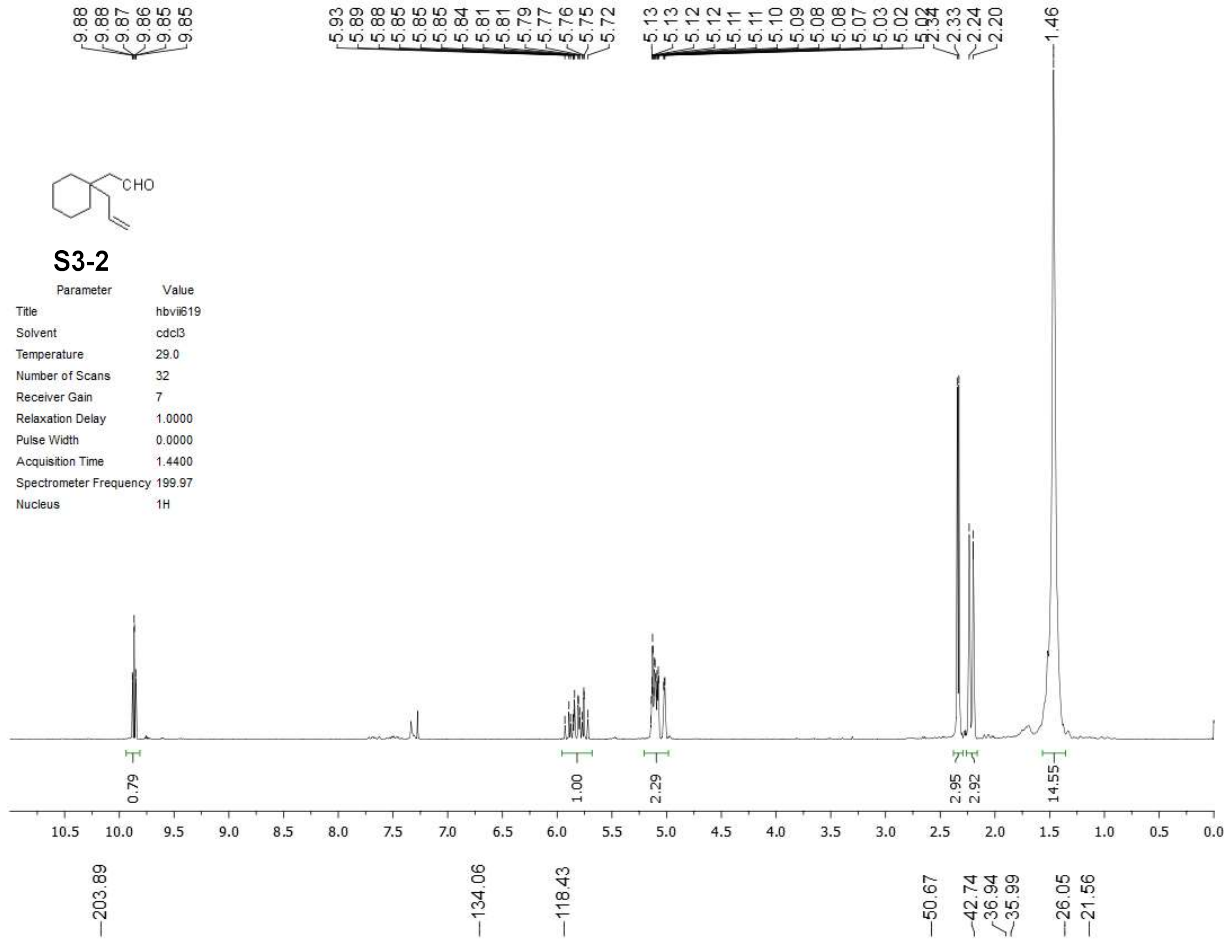

HO
Me
Me
S2-3
Parameter Value
1 Title RM-OK-51A
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 782
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 15.2500
8 Acquisition Time 0.5898
9 Spectrometer Frequency 125.79
10 Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

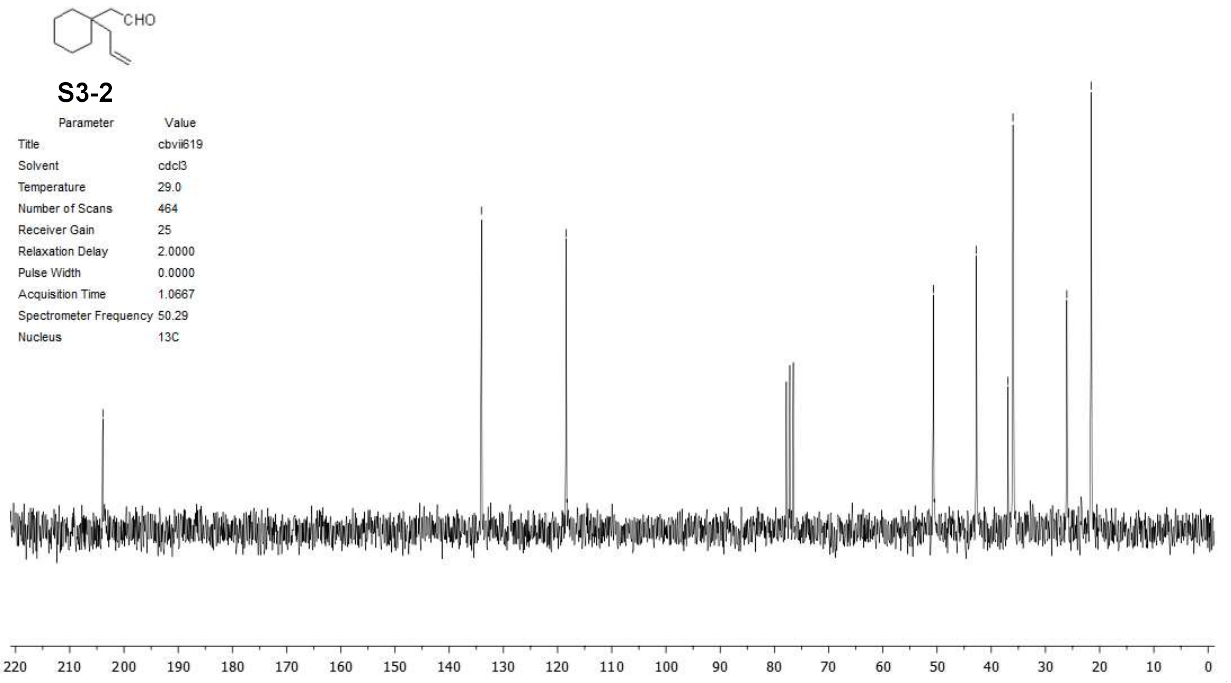

5.07 5.07 5.07 5.06 5.06 5.06 5.06 5.05 5.05 5.05 5.04 5.04 5.04 4.16 4.15 3.20 3.19 2.26 1.95 1.94 1.93 1.91 1.90 1.88 1.87 1.86 1.66 1.66 1.59 1.56 1.55 1.54 1.52 1.51 1.50 1.49 1.48 1.48 1.46 1.46 1.45 1.44 1.43 1.43 1.42 1.41 1.40 1.40 1.38 1.32 1.31 1.30 1.29 1.29 1.28 1.27 1.26
HO
O
Me
Me
S2-4
Parameter Value
1 Title RM-OK-54
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 23
6 Relaxation Delay 2.0000
7 Pulse Width 8.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1.00 1.01 0.91 3.01 2.16 3.25 3.38 11.09 2.26
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
211.89 131.60 124.67 81.63 41.14 32.77 31.93 31.83 29.76 26.13 25.80 22.15 21.53 21.51 17.73

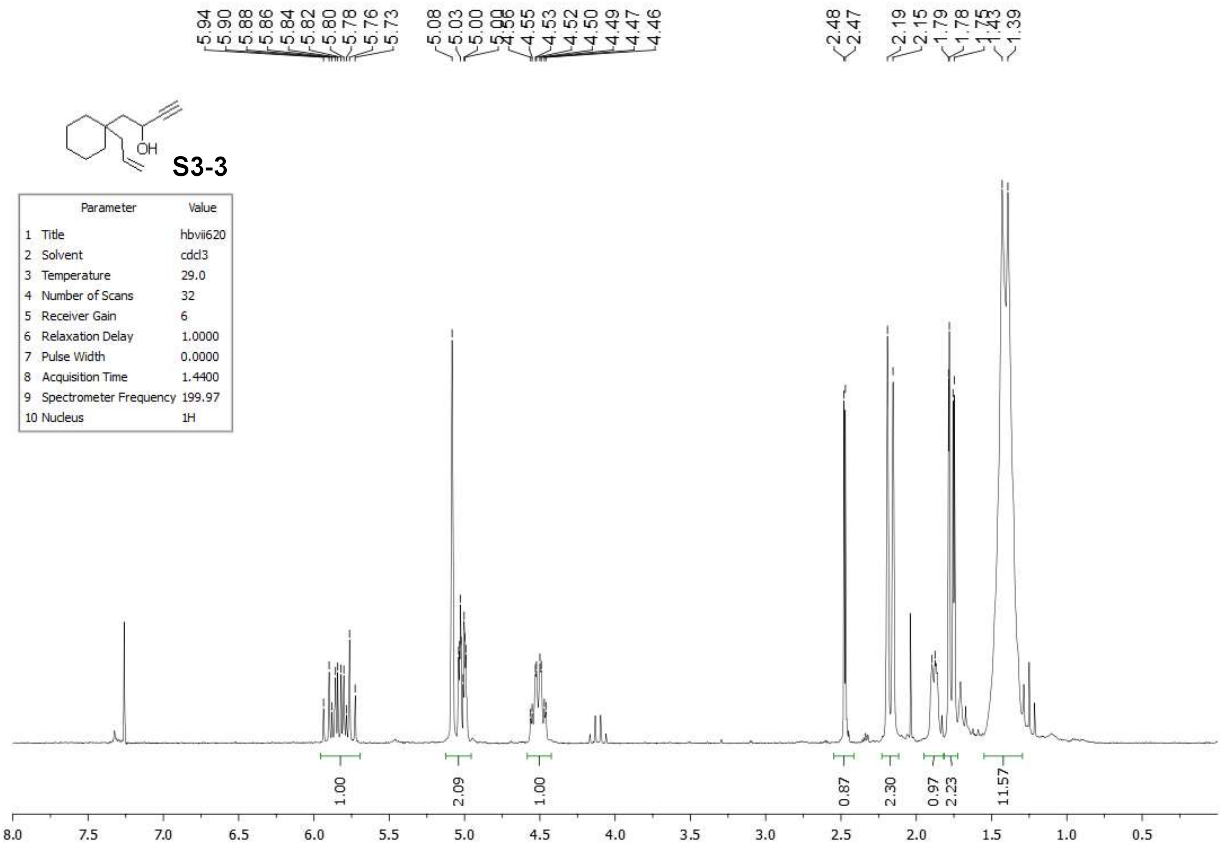

HO
O
Me
Me
S2-4
Parameter Value
1 Title RM-OK-54
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 2048
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 15.2500
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

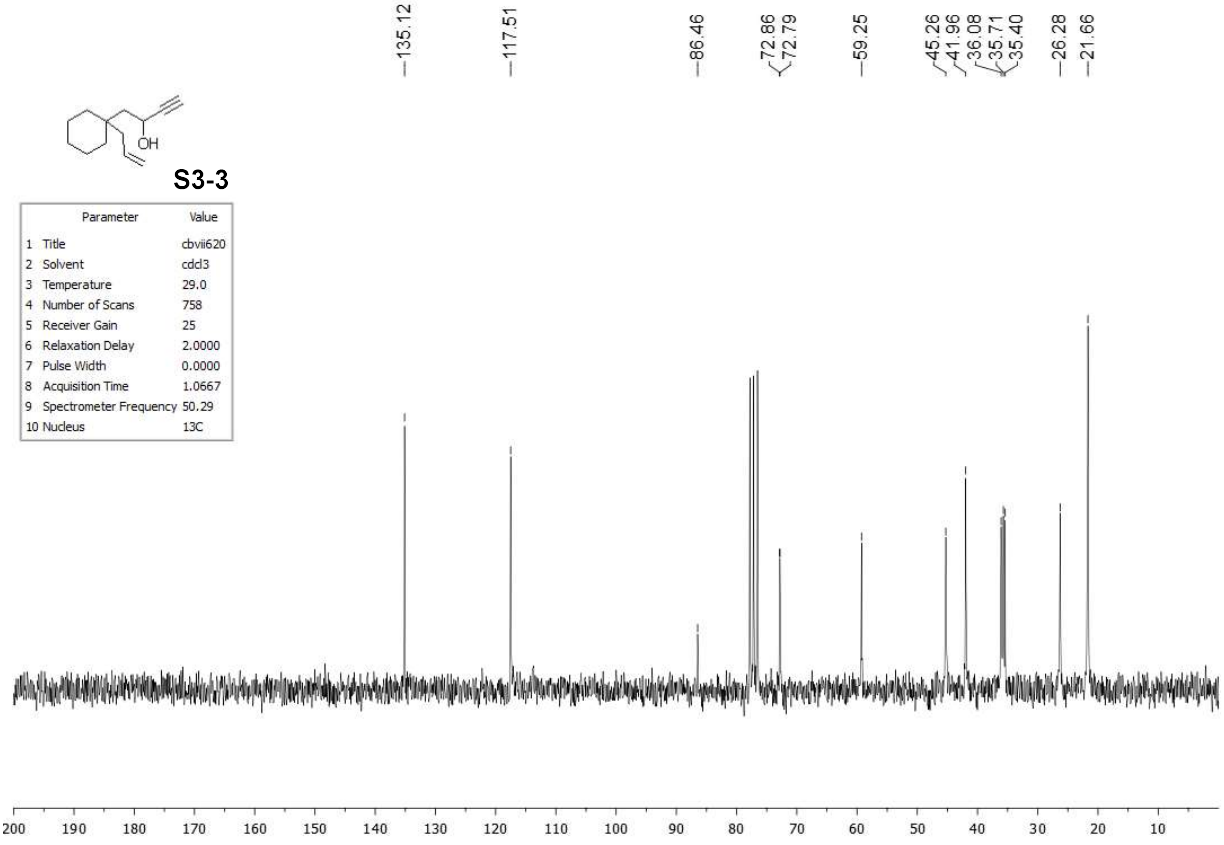

9.43
5.74
5.71
5.69
5.67
5.66
5.65
5.63
5.61
5.61
5.59
5.58
5.57
5.53
5.06
5.05
5.01
5.01
5.00
4.97
4.97
4.96
2.18
2.18
2.17
2.15
2.14
2.14
1.87
1.86
1.82
1.57
1.55
1.54
1.50
1.48
1.34
1.30
1.26
CHO
S3-1
Parameter Value
Title hbvii616
Solvent cdcl3
Temperature 29.0
Number of Scans 32
Receiver Gain 2
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.4400
Spectrometer Frequency 199.97
Nucleus 1H
0.96
1.00
2.31
2.47
2.60
3.98
6.69
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

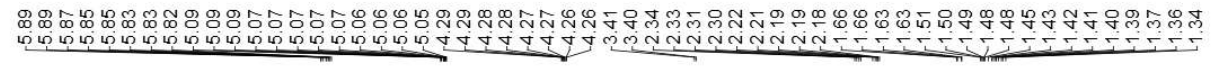

207.06
132.81
118.43
49.74
40.86
30.83
25.72
22.54
CHO
S3-1
Parameter Value
Title cbvii616
Solvent cdcl3
Temperature 29.0
Number of Scans 516
Receiver Gain 25
Relaxation Delay 2.0000
Pulse Width 0.0000
Acquisition Time 1.0667
Spectrometer Frequency 50.29
Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

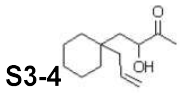

9.88
9.88
9.87
9.86
9.85
9.85
5.93
5.89
5.88
5.85
5.85
5.84
5.81
5.81
5.79
5.77
5.76
5.75
5.72
5.13
5.13
5.12
5.12
5.11
5.11
5.10
5.09
5.08
5.08
5.07
5.03
5.02
2.33
2.24
2.20
1.46
CHO
S3-2
Parameter Value
Title hbvii619
Solvent cdcl3
Temperature 29.0
Number of Scans 32
Receiver Gain 7
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.4400
Spectrometer Frequency 199.97
Nucleus 1H
0.79
1.00
2.29
2.95
2.92
14.55
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


203.89
134.06
118.43
50.67
42.74
36.94
35.99
26.05
21.56
CHO
S3-2
Parameter Value
Title cbvii619
Solvent cdcl3
Temperature 29.0
Number of Scans 464
Receiver Gain 25
Relaxation Delay 2.0000
Pulse Width 0.0000
Acquisition Time 1.0667
Spectrometer Frequency 50.29
Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


5.94
5.90
5.88
5.86
5.84
5.82
5.80
5.78
5.76
5.73
5.08
5.03
5.00
4.55
4.53
4.52
4.50
4.49
4.47
4.46
2.48
2.47
2.19
2.15
1.79
1.78
1.75
1.43
1.39
OH
S3-3
Parameter Value
1 Title hbvii620
2 Solvent cdcl3
3 Temperature 29.0
4 Number of Scans 32
5 Receiver Gain 6
6 Relaxation Delay 1.0000
7 Pulse Width 0.0000
8 Acquisition Time 1.4400
9 Spectrometer Frequency 199.97
10 Nucleus 1H
1.00
2.09
1.00
0.87
2.30
0.97
2.23
11.57
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

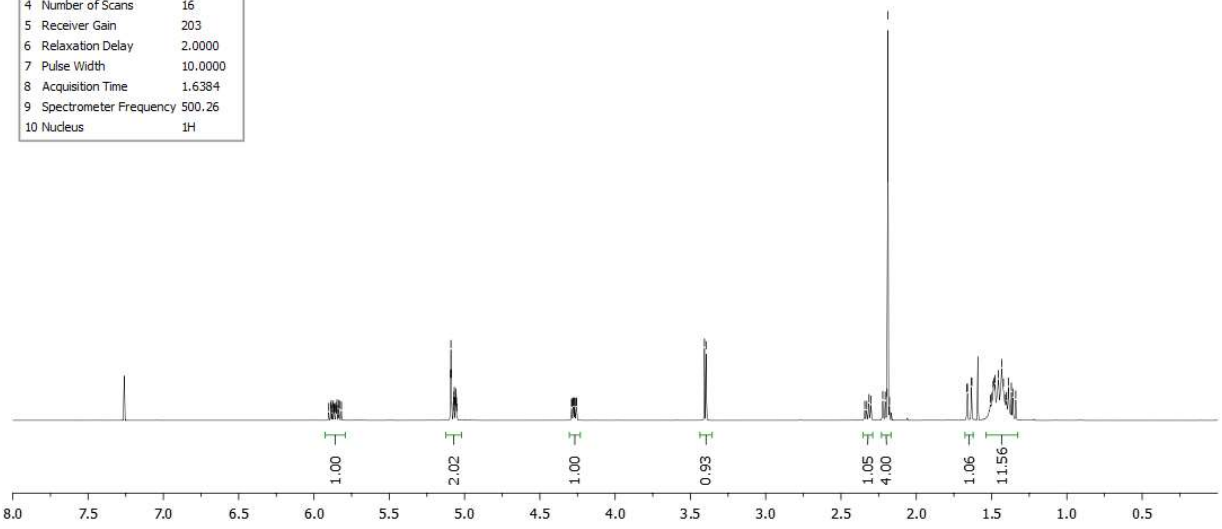

135.12
117.51
86.46
72.86
72.79
59.25
45.26
41.96
36.08
35.71
35.40
26.28
21.66
OH
S3-3
Parameter Value
1 Title cbvii620
2 Solvent cdcl3
3 Temperature 29.0
4 Number of Scans 758
5 Receiver Gain 25
6 Relaxation Delay 2.0000
7 Pulse Width 0.0000
8 Acquisition Time 1.0667
9 Spectrometer Frequency 50.29
10 Nucleus 13C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

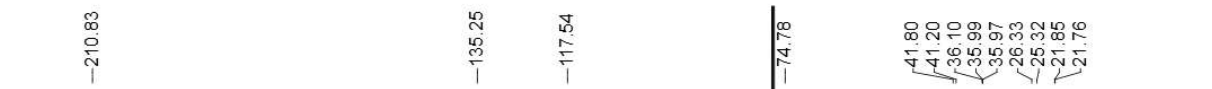


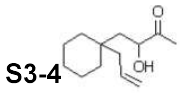


S3-4

	Parameter	Value
1	Title	BZVO2661
2	Solvent	CDCl3
3	Temperature	297.9
4	Number of Scans	16
5	Receiver Gain	203
6	Relaxation Delay	2.0000
7	Pulse Width	10.0000
8	Acquisition Time	1.6384
9	Spectrometer Frequency	500.26
10	Nucleus	1H

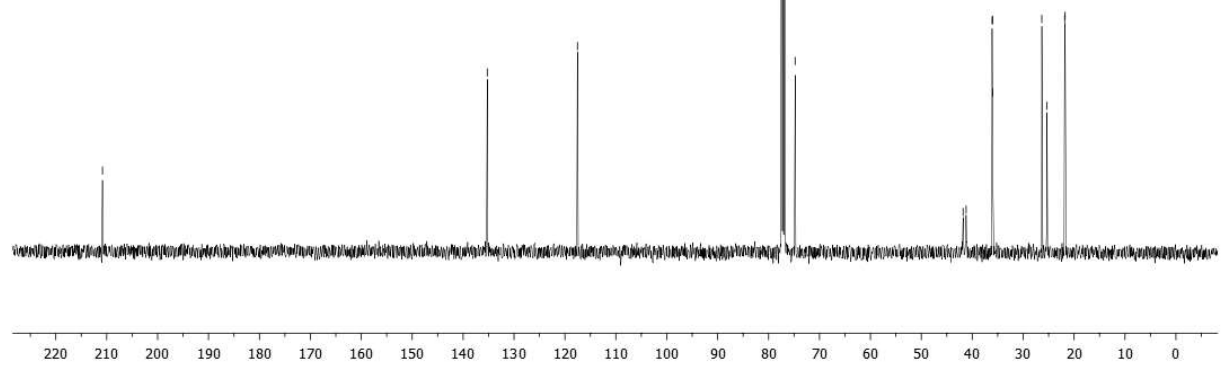


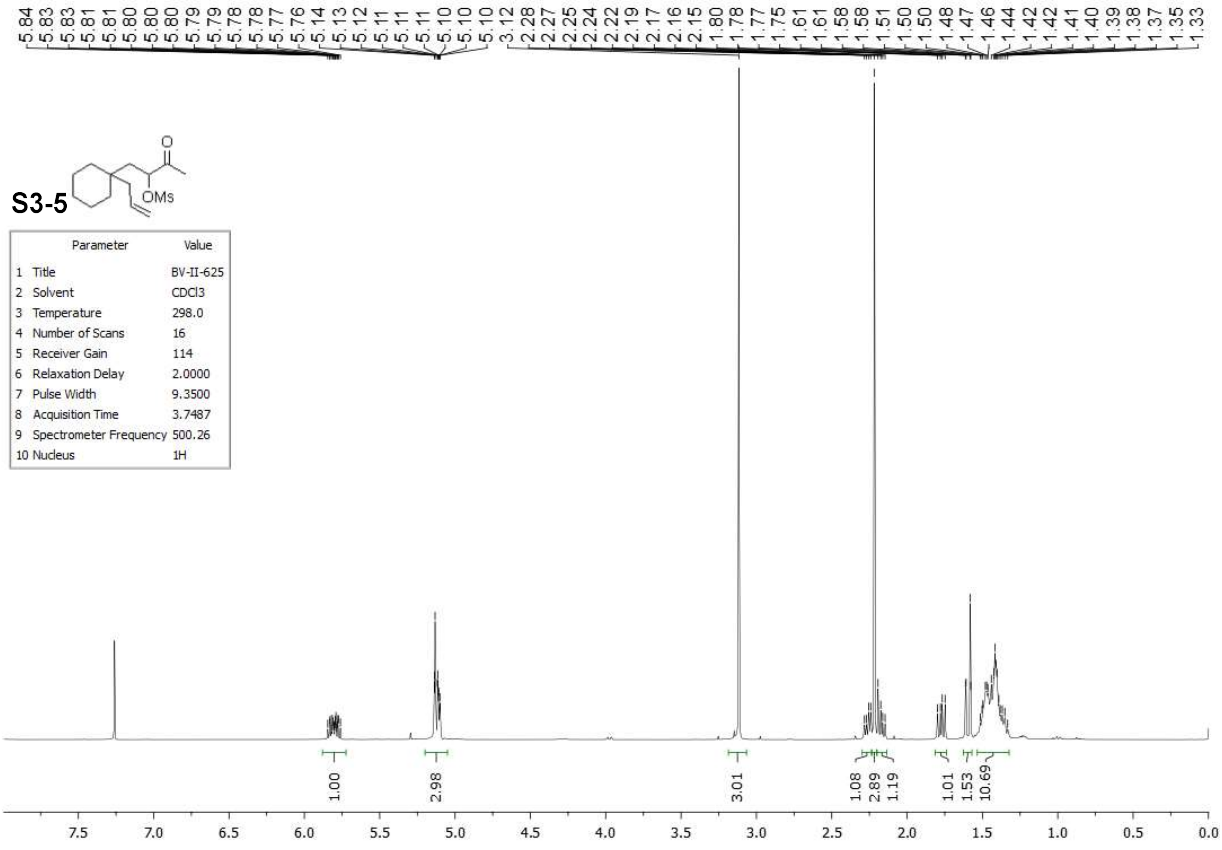


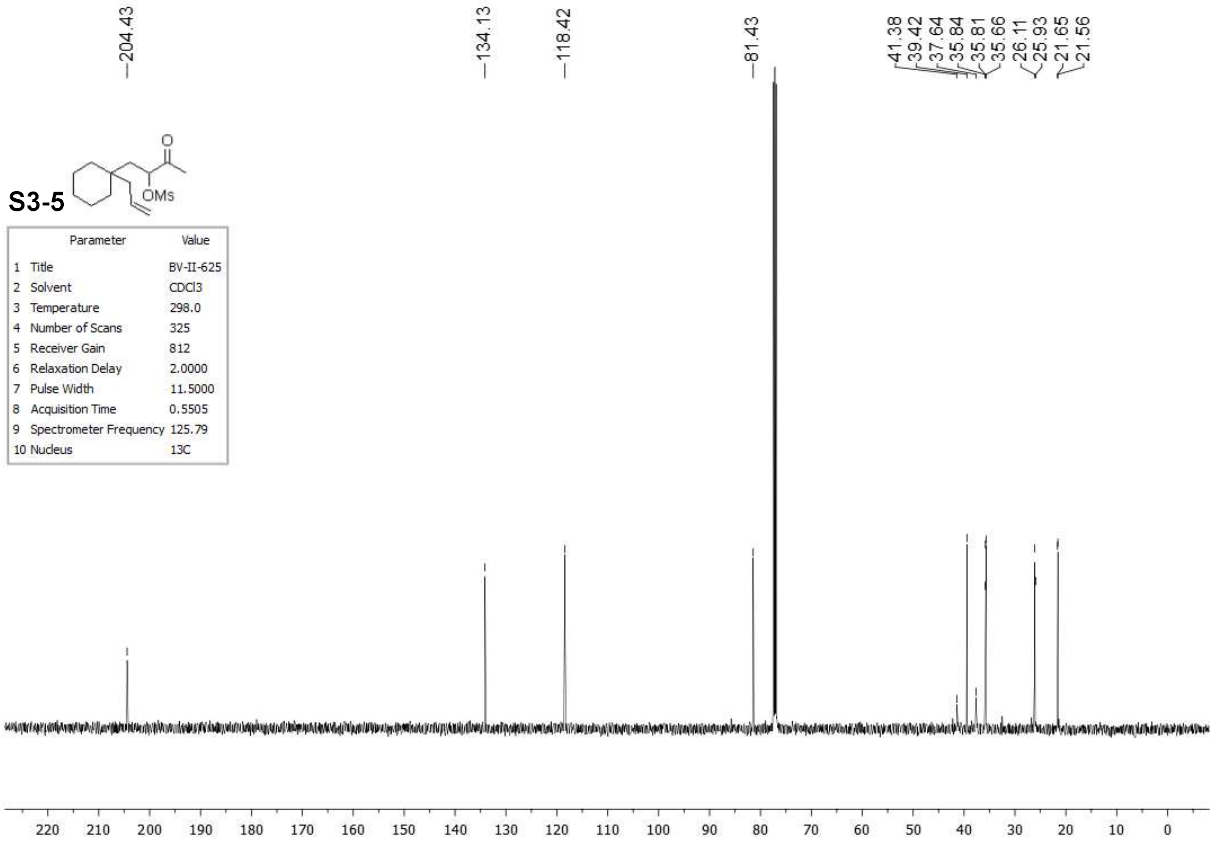


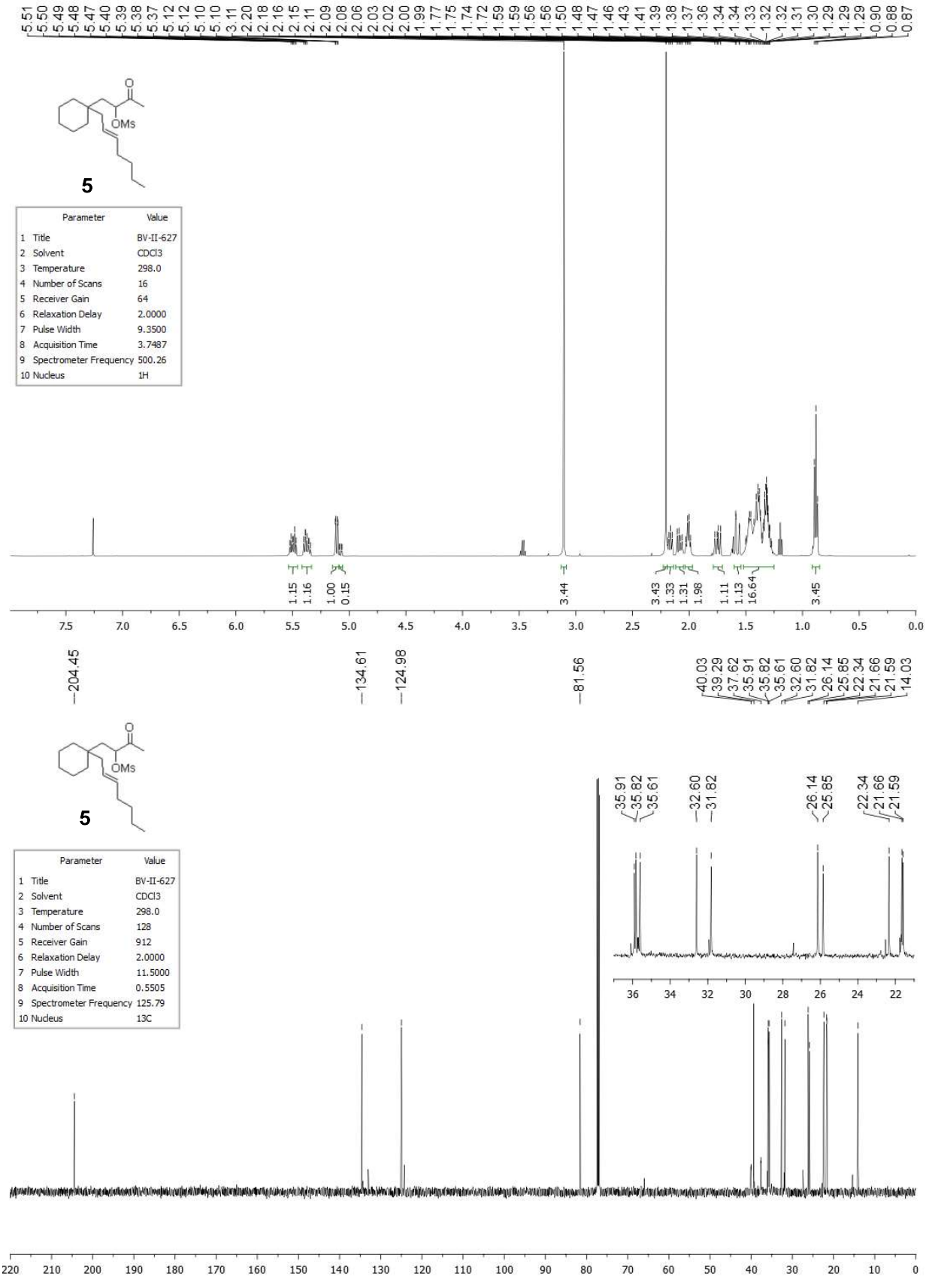
S3-4

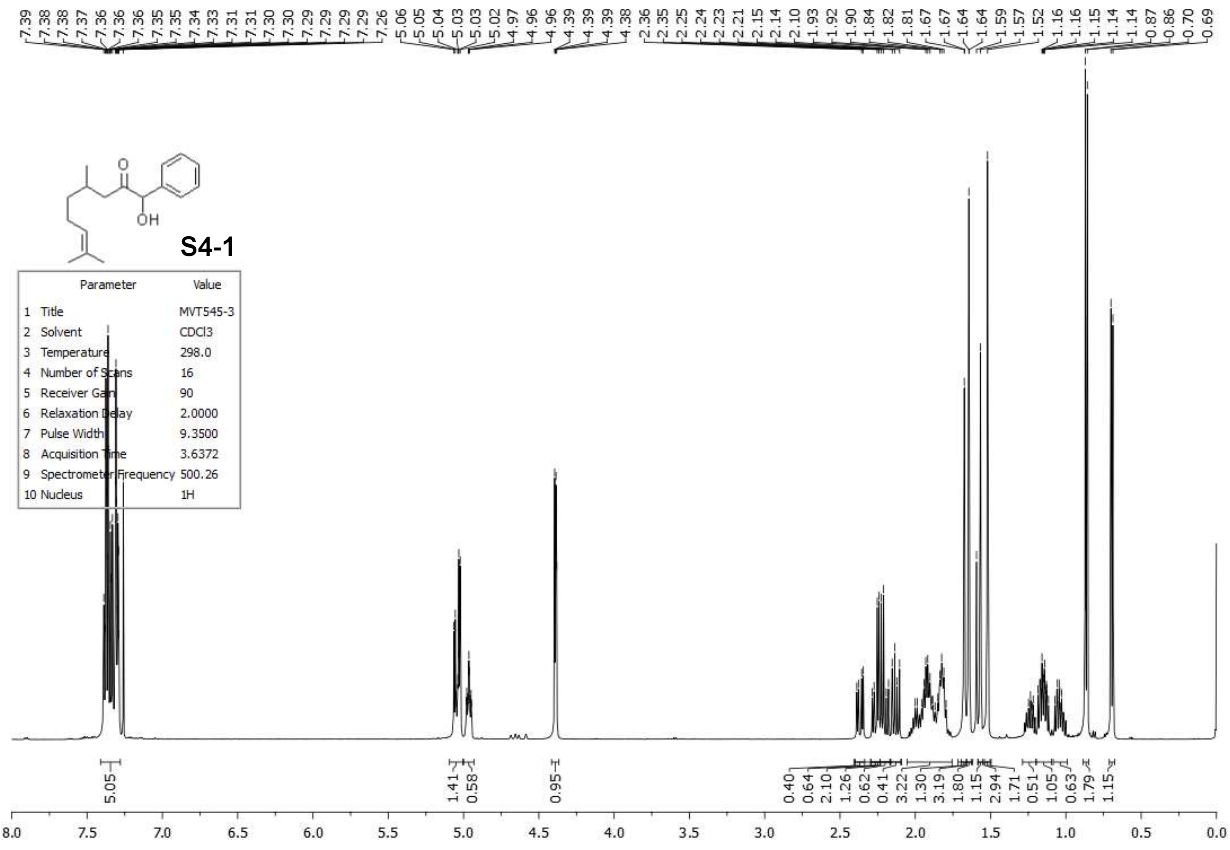
	Parameter	Value
1	Title	BZVO2661
2	Solvent	CDCl3
3	Temperature	298.1
4	Number of Scans	216
5	Receiver Gain	203
6	Relaxation Delay	2.0000
7	Pulse Width	11.5000
8	Acquisition Time	0.5505
9	Spectrometer Frequency	125.79
10	Nucleus	13C

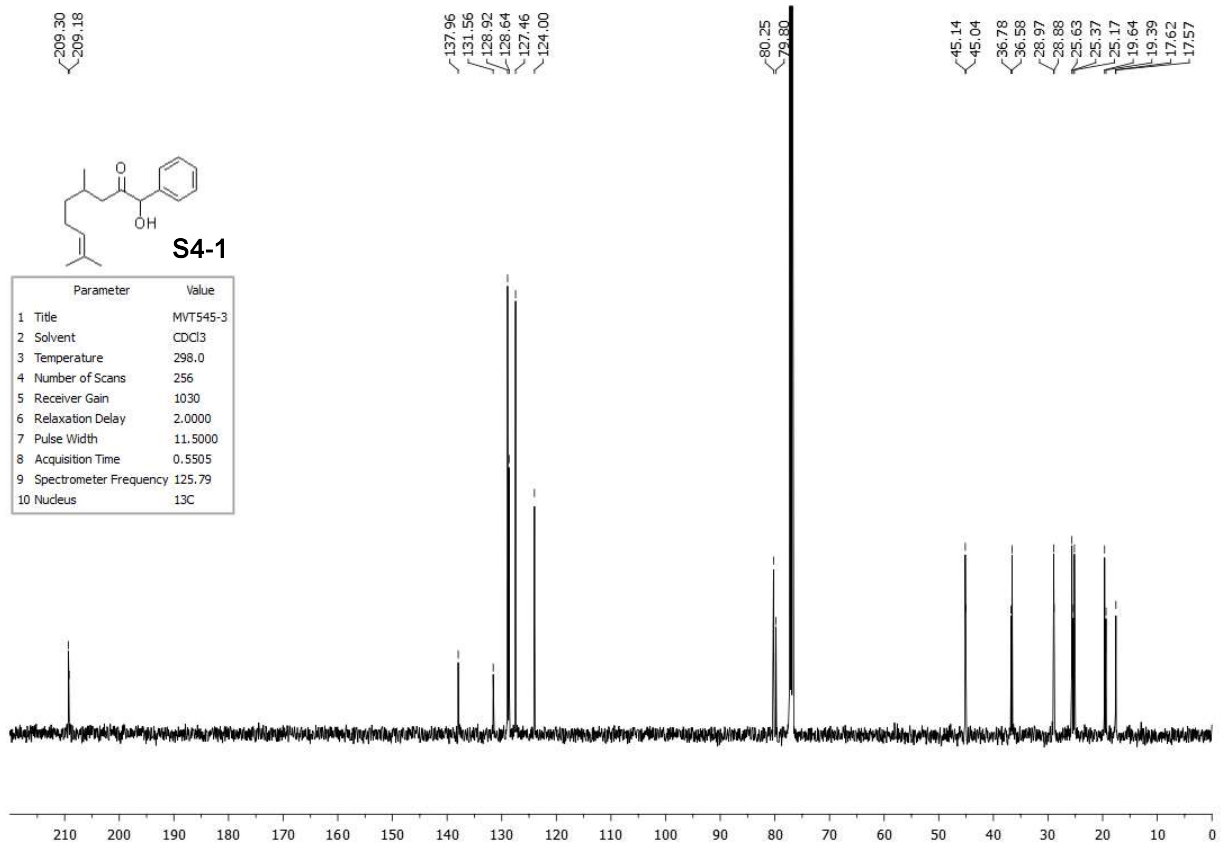


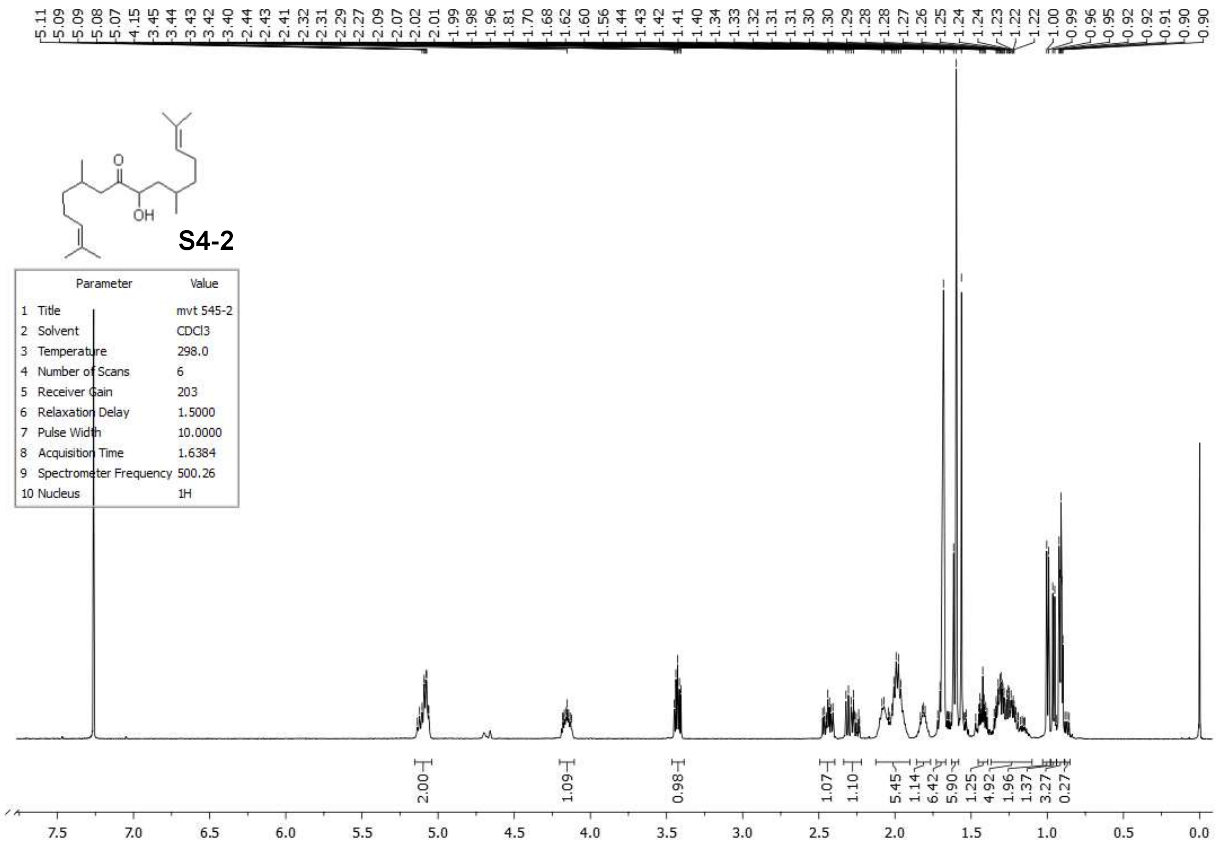

S3-5
OMs
O
Parameter Value
1 Title BV-II-625
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 114
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.7487
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1.00
2.98
3.01
1.08
2.89
1.19
1.01
1.53
10.69

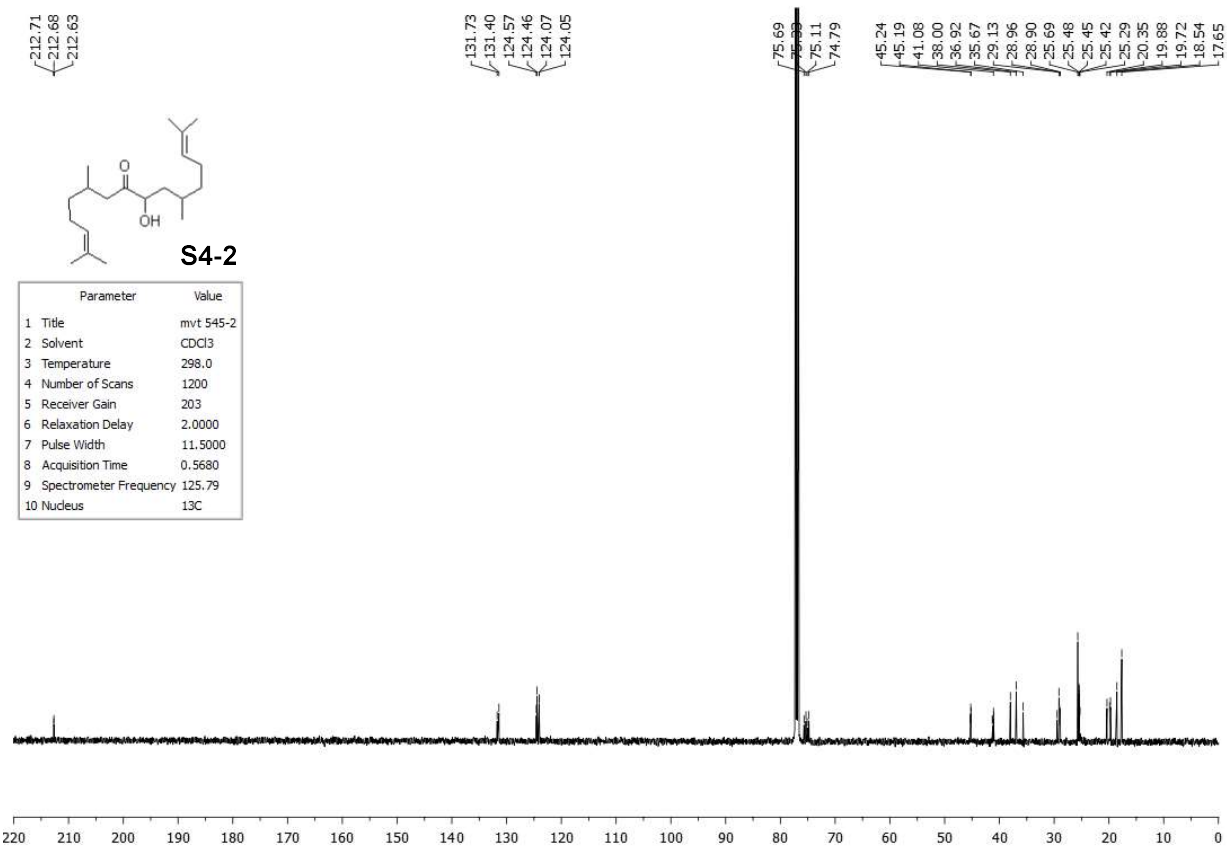

S3-5
OMs
O
Parameter Value
1 Title BV-II-625
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 325
5 Receiver Gain 812
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
204.43
134.13
118.42
81.43
41.38
39.42
37.64
35.84
35.81
35.66
26.11
25.93
21.65
21.56

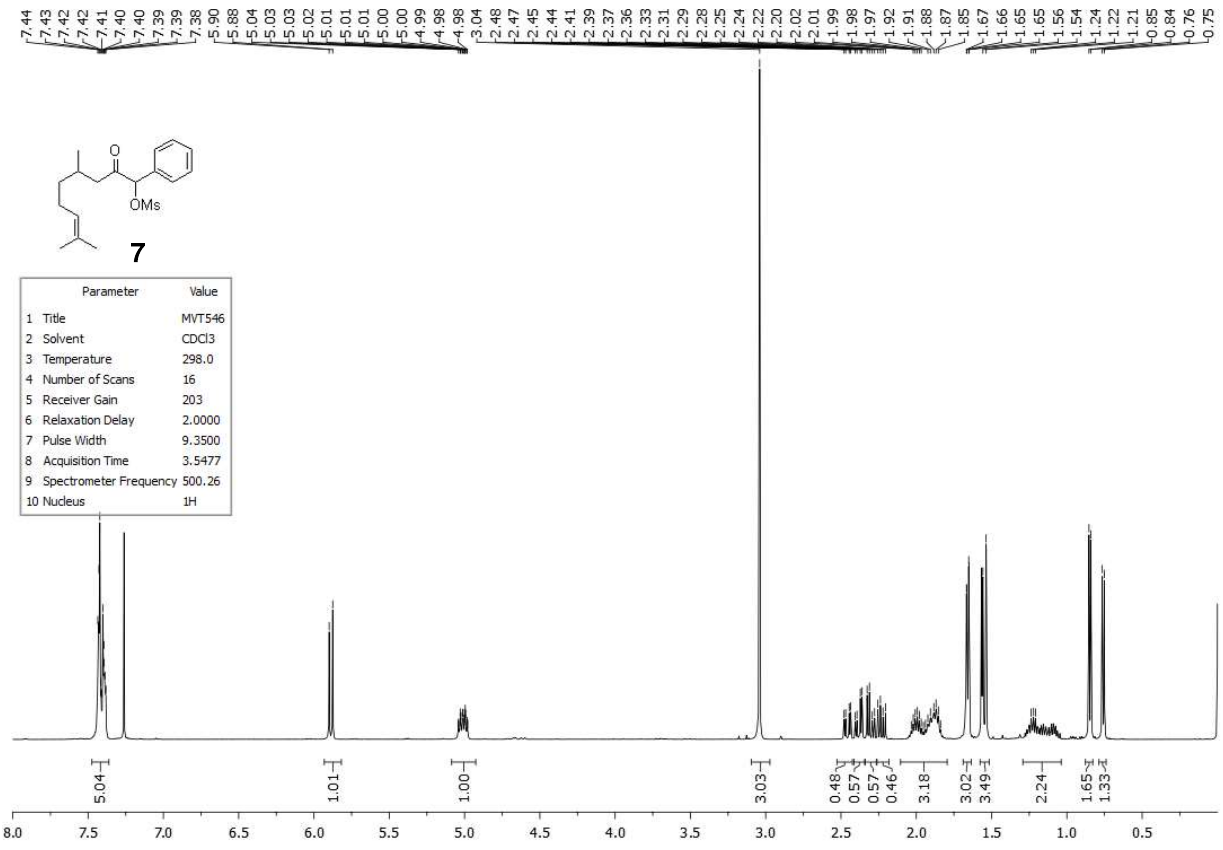

5.51 5.50 5.49 5.48 5.47 5.40 5.39 5.38 5.37 5.12 5.12 5.10 5.10 3.11 2.20 2.18 2.16 2.15 2.11 2.09 2.08 2.06 2.03 2.02 2.00 1.99 1.77 1.75 1.74 1.72 1.59 1.59 1.56 1.56 1.50 1.48 1.47 1.46 1.43 1.41 1.39 1.38 1.37 1.36 1.34 1.34 1.33 1.32 1.32 1.31 1.30 1.29 1.29 1.29 0.90 0.88 0.87
OMs
5
Parameter Value
1 Title BV-II-627
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 64
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.7487
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1.15 1.16 1.00 0.15 3.44 3.43 1.33 1.31 1.98 1.11 1.13 16.64 3.45
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
204.45 134.61 124.98 81.56
40.03 39.29 37.62 35.91 35.82 35.61 32.60 31.82 26.14 25.85 22.34 21.66 21.59 14.03
OMs
5
Parameter Value
1 Title BV-II-627
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 128
5 Receiver Gain 912
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
35.91 35.82 35.61 32.60 31.82 26.14 25.85 22.34 21.66 21.59
36 34 32 30 28 26 24 22
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

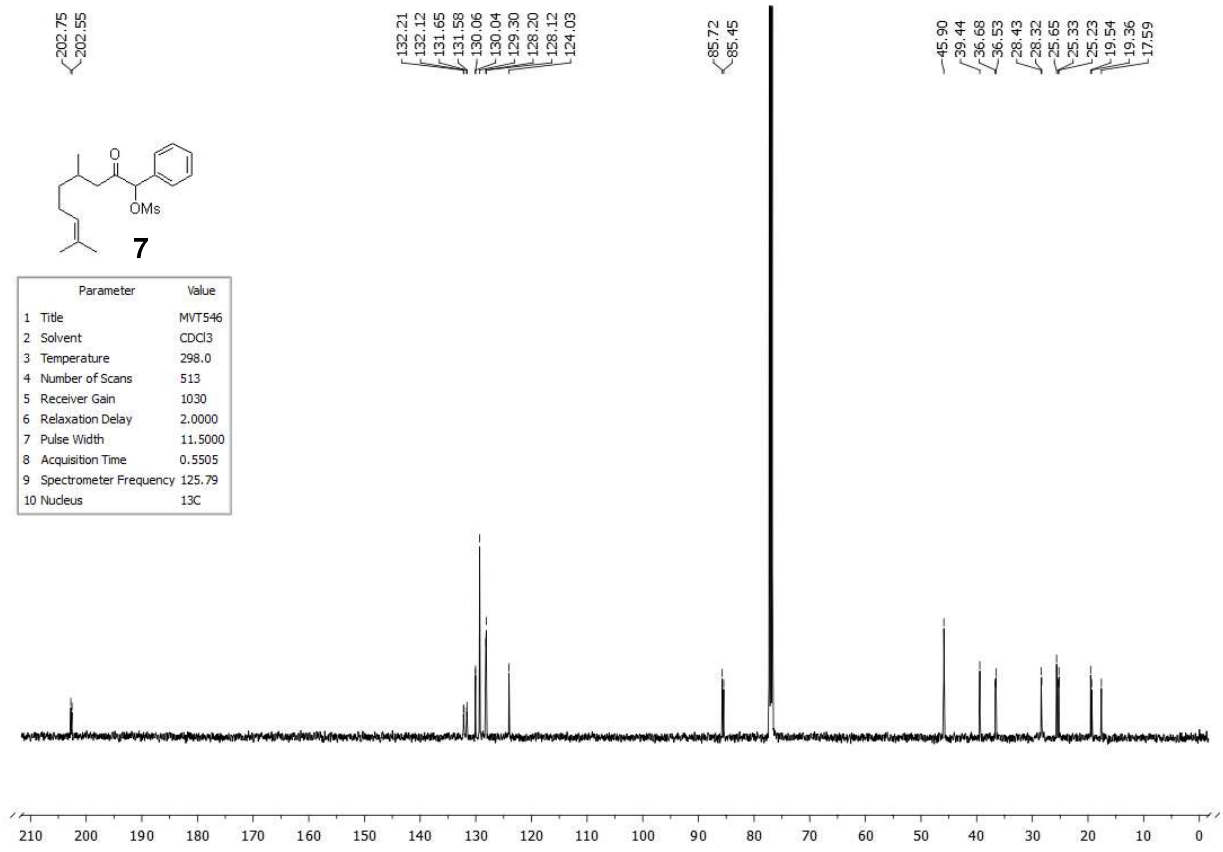

S4-1
Parameter Value
1 Title MVT545-3
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 90
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.6372
9 Spectrometer Frequency 500.26
10 Nucleus 1H

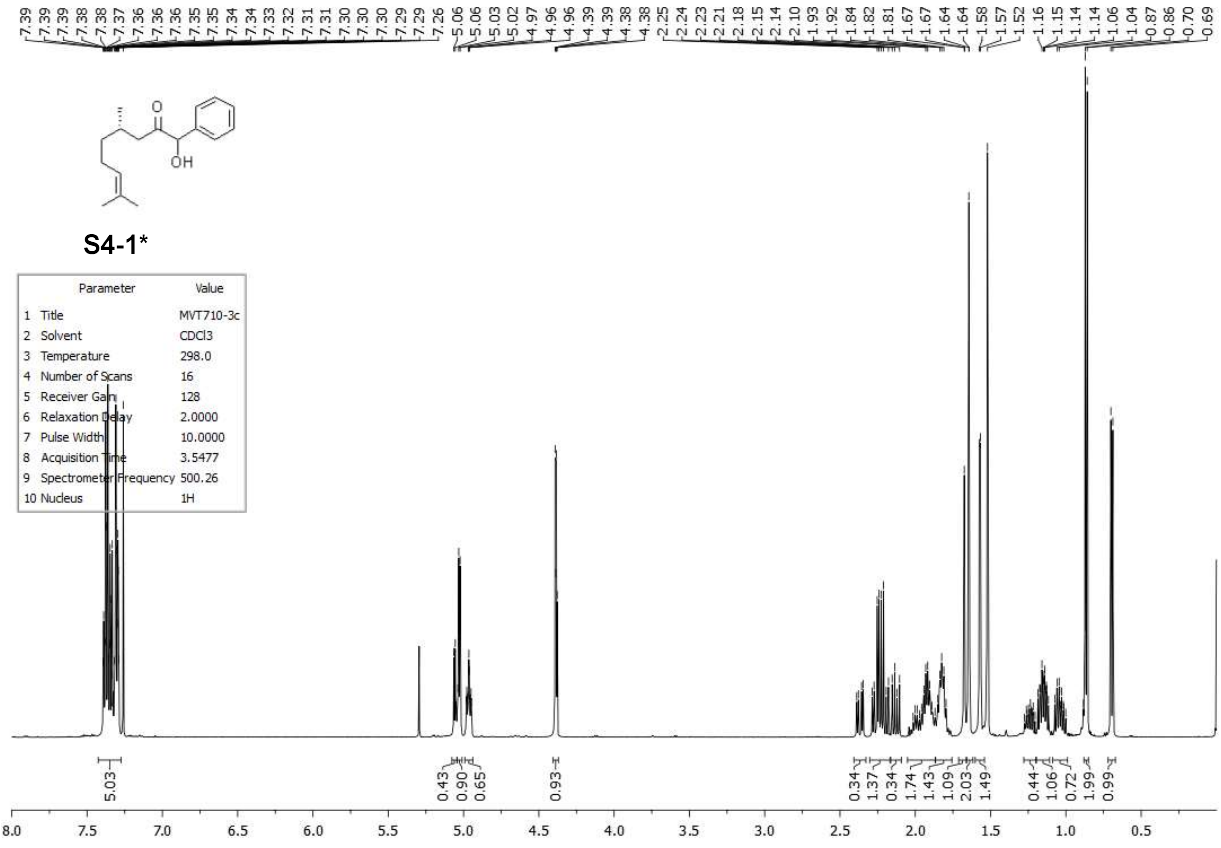

S4-1
Parameter Value
1 Title MVT545-3
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 256
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

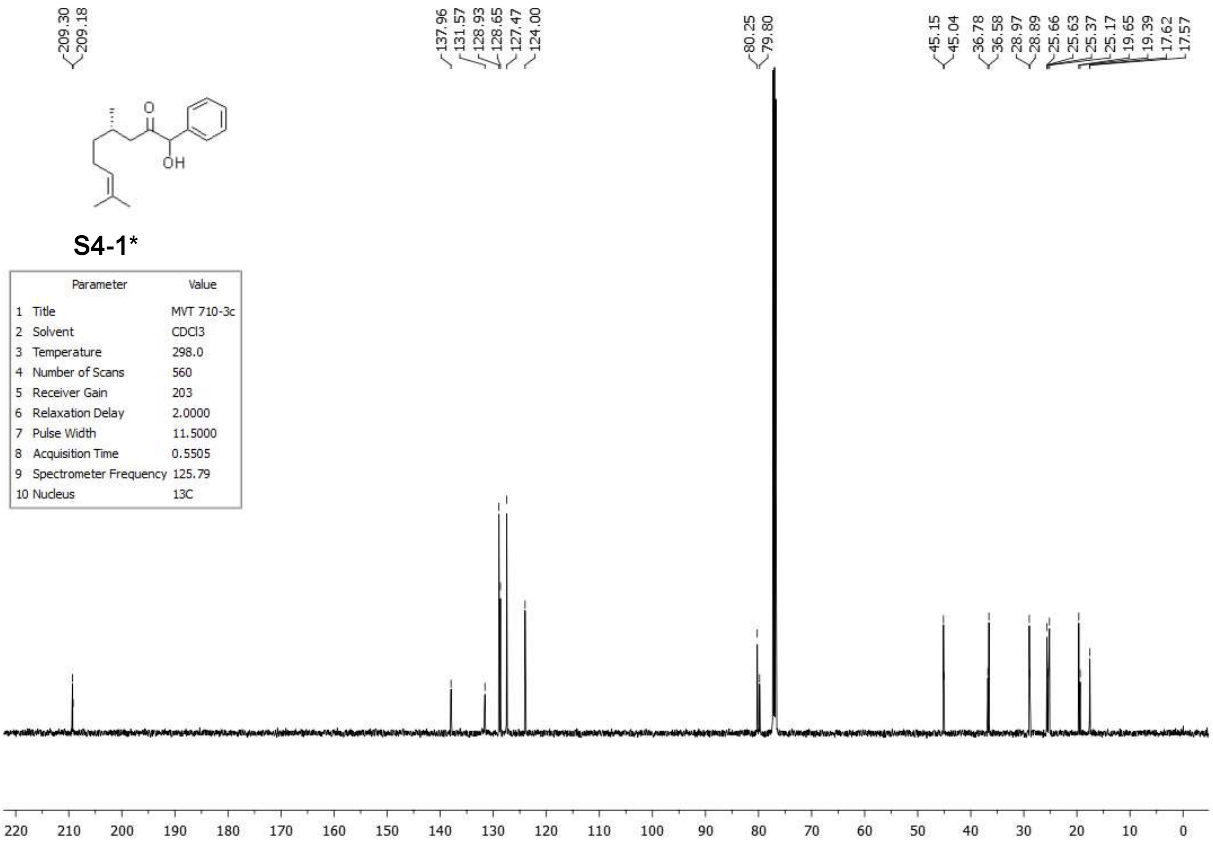

S4-2
Parameter Value
1 Title mvt 545-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 6
5 Receiver Gain 203
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H

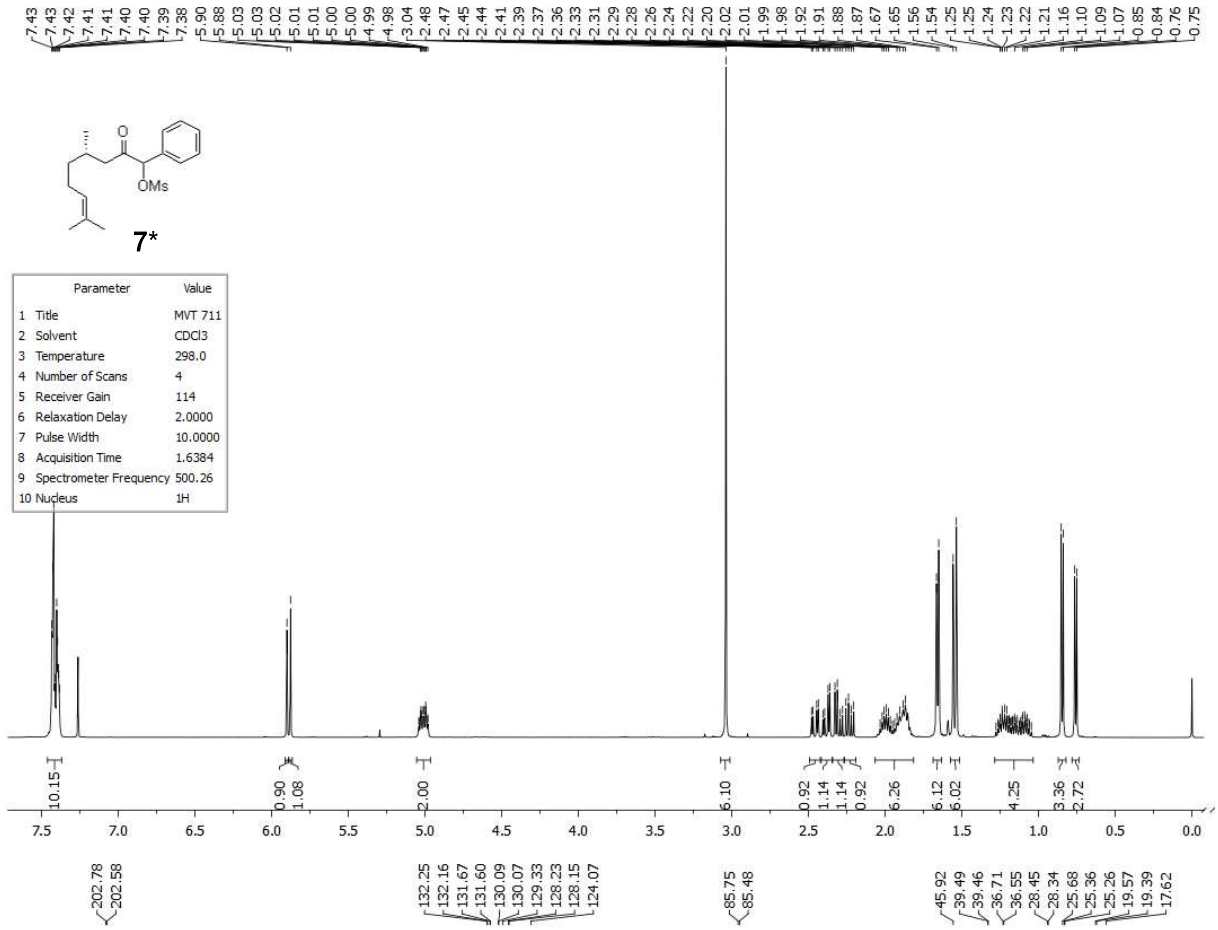

S4-2
Parameter Value
1 Title mvt 545-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 1200
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5680
9 Spectrometer Frequency 125.79
10 Nucleus 13C


7.44 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 5.90 5.88 5.04 5.03 5.03 5.02 5.01 5.01 5.01 5.00 5.00 4.99 4.98 4.98 3.04 2.48 2.47 2.45 2.44 2.41 2.39 2.37 2.36 2.33 2.31 2.29 2.28 2.25 2.24 2.22 2.20 2.02 2.01 1.99 1.98 1.97 1.92 1.91 1.88 1.87 1.85 1.67 1.66 1.65 1.65 1.56 1.54 1.24 1.22 1.21 0.85 0.84 0.76 0.75
O
OMs
7
Parameter Value
1 Title MVT546
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.5477
9 Spectrometer Frequency 500.26
10 Nucleus 1H
5.04 1.01 1.00 3.03 0.48 0.57 0.57 0.46 3.18 3.02 3.49 2.24 1.65 1.33
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


202.75 202.55 132.21 132.12 131.65 131.58 130.06 130.04 129.30 128.20 128.12 124.03 85.72 85.45 45.90 39.44 36.68 36.53 28.43 28.32 25.65 25.33 25.23 19.54 19.36 17.59
O
OMs
7
Parameter Value
1 Title MVT546
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 513
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


S4-1*
Parameter Value
1 Title MVT710-3c
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 128
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 3.5477
9 Spectrometer Frequency 500.26
10 Nucleus 1H


S4-1*
Parameter Value
1 Title MVT 710-3c
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 560
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C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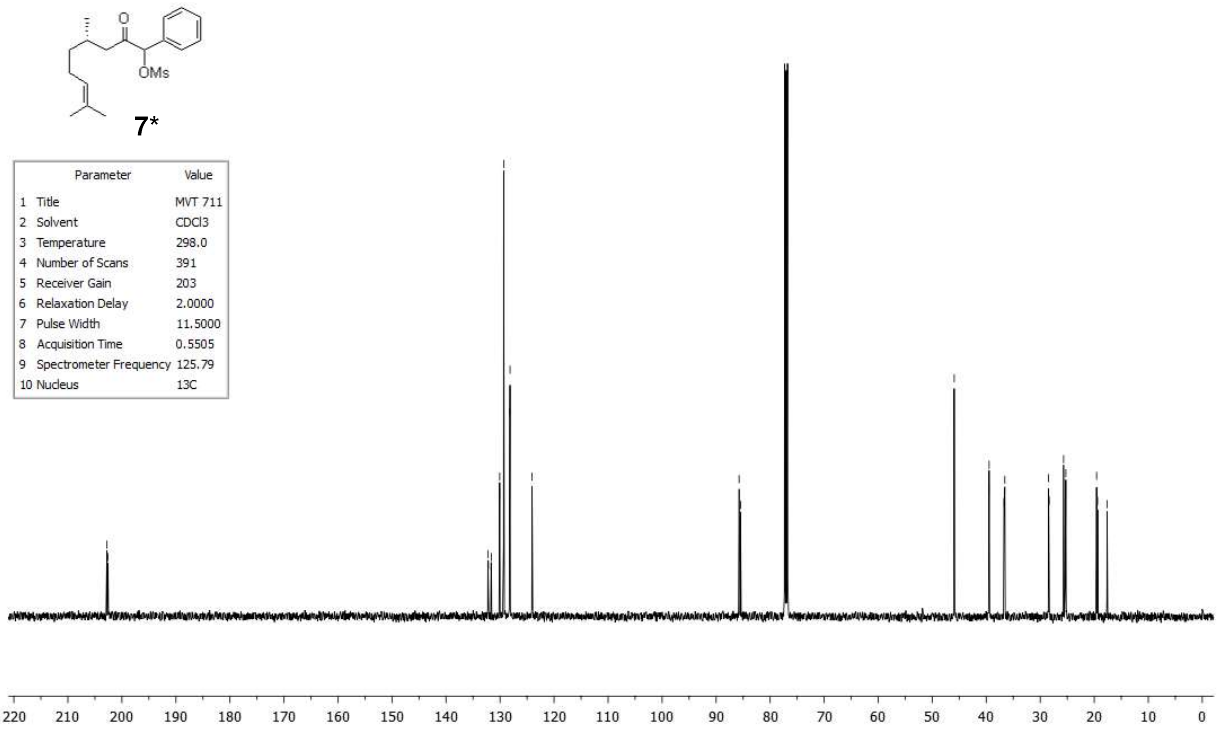
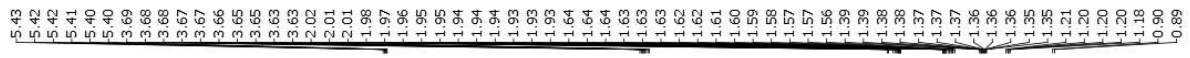
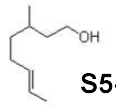
O
OMs
7*
Parameter Value
1 Title MVT 711
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 4
5 Receiver Gain 114
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
10.15 0.90 1.08 2.00 6.10 0.92 1.14 1.14 0.92 6.26 6.12 6.02 4.25 3.36 2.72
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

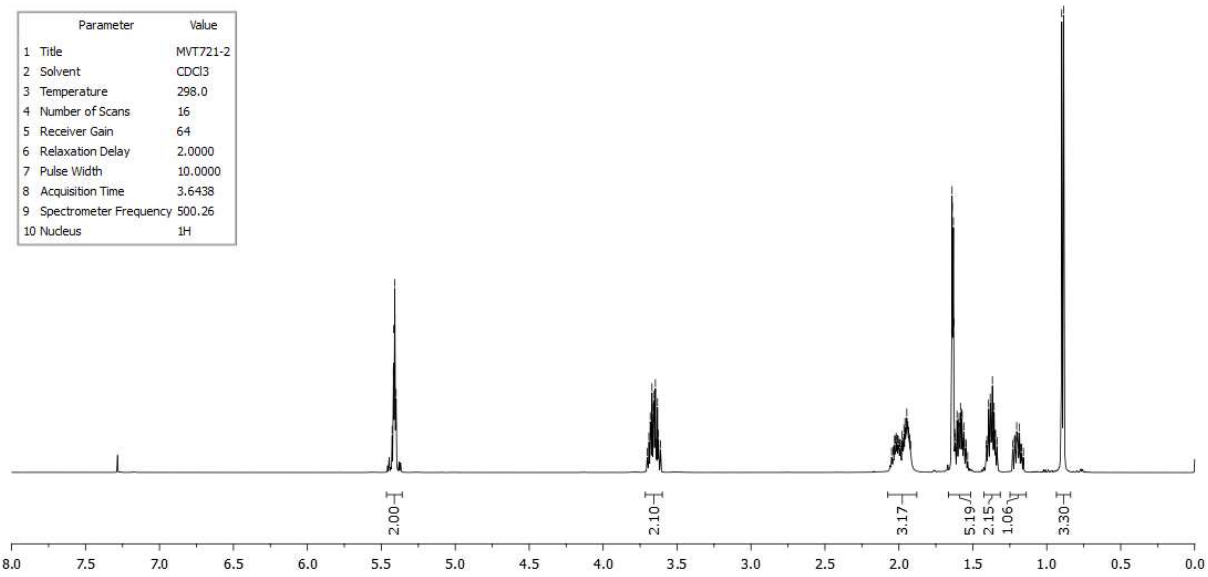

202.78 202.58 132.25 132.16 131.67 131.60 130.09 130.07 129.33 128.23 128.15 124.07 85.75 85.48 45.92 39.49 39.46 36.71 36.55 28.45 28.34 25.68 25.36 25.26 19.57 19.39 17.62
O
OMs
7*
Parameter Value
1 Title MVT 711
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 391
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

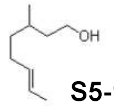




S5-1

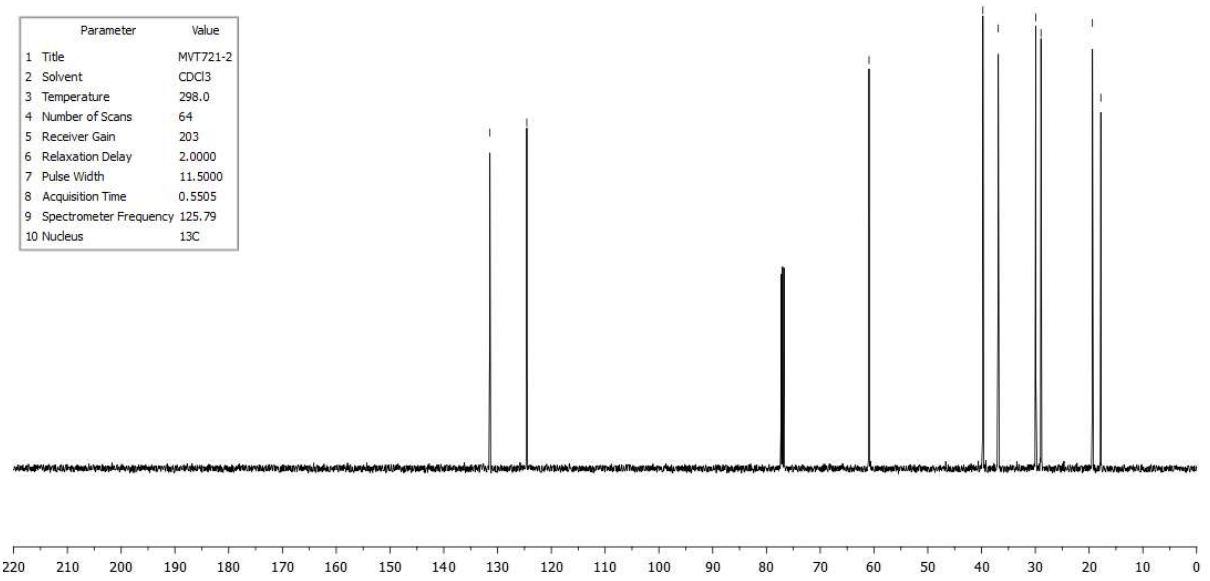
	Parameter	Value
1	Title	MVT721-2
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	16
5	Receiver Gain	64
6	Relaxation Delay	2.0000
7	Pulse Width	10.0000
8	Acquisition Time	3.6438
9	Spectrometer Frequency	500.26
10	Nucleus	1H

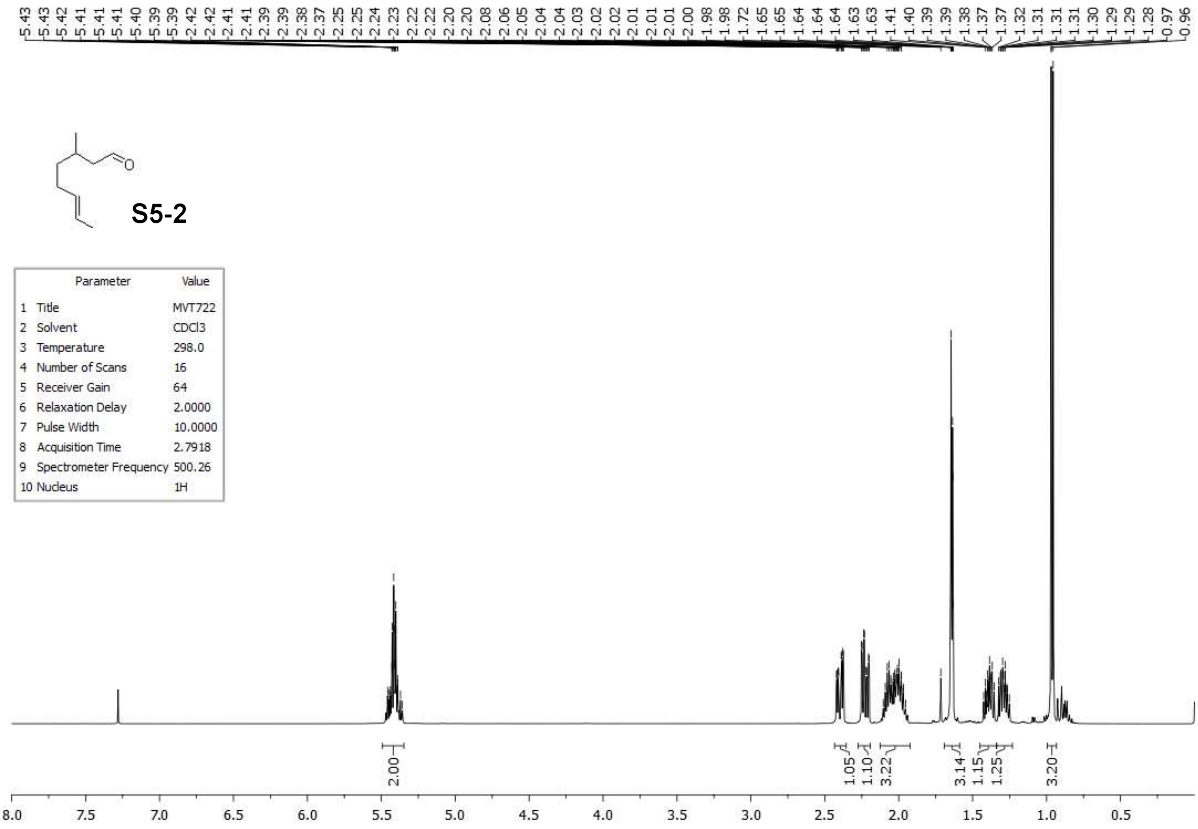


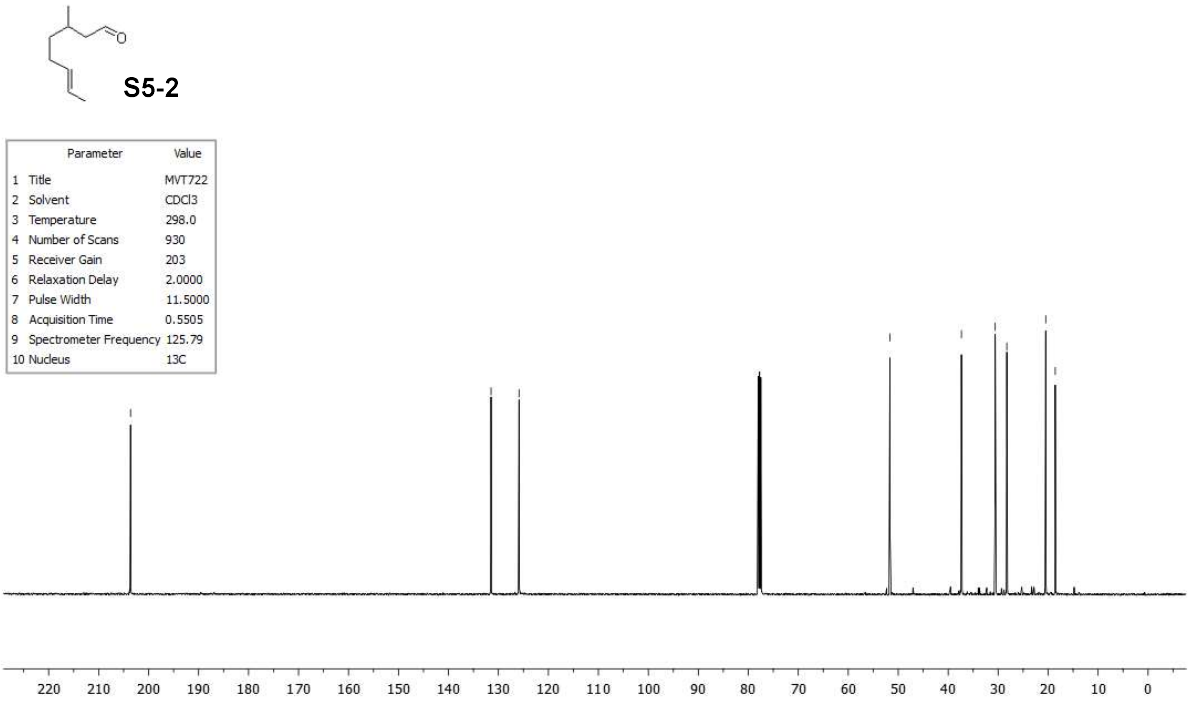


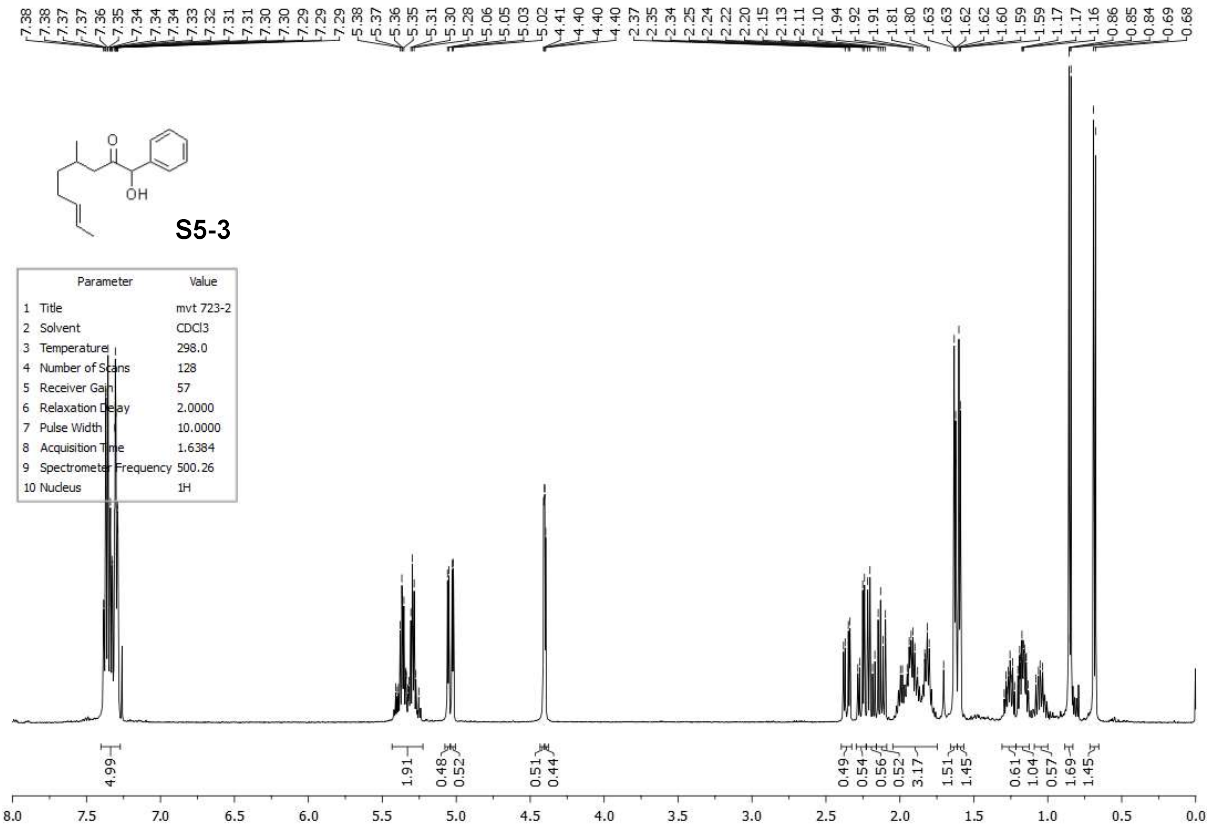
S5-1

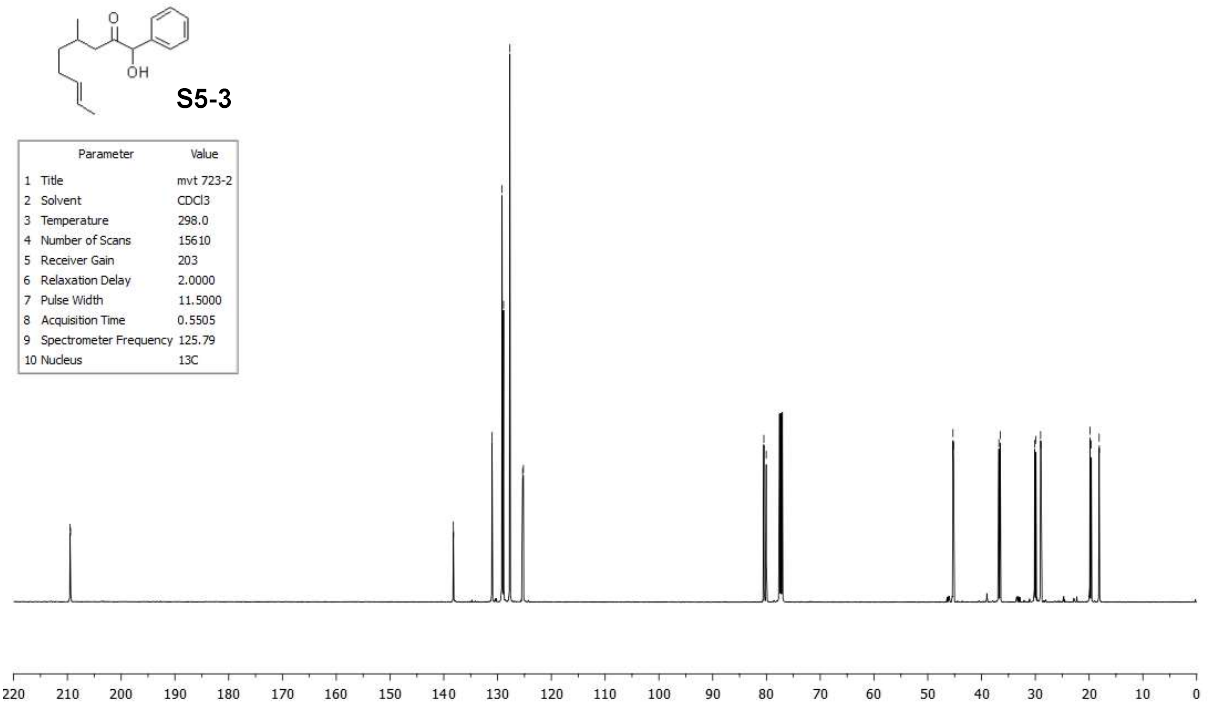
	Parameter	Value
1	Title	MVT721-2
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	64
5	Receiver Gain	203
6	Relaxation Delay	2.0000
7	Pulse Width	11.5000
8	Acquisition Time	0.5505
9	Spectrometer Frequency	125.79
10	Nucleus	13C

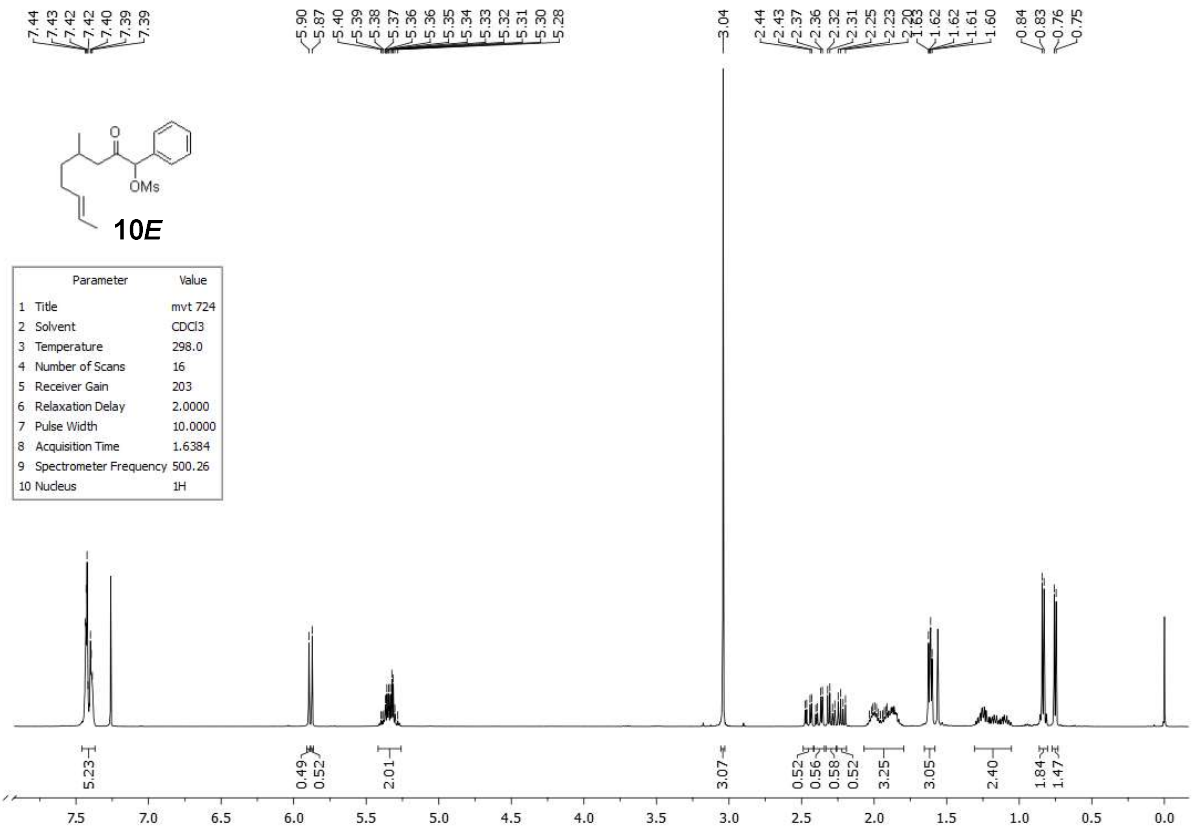



S5-2
Parameter Value
1 Title MVT722
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 64
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 2.7918
9 Spectrometer Frequency 500.26
10 Nucleus 1H


S5-2
Parameter Value
1 Title MVT722
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 930
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C


S5-3
Parameter Value
1 Title mvt 723-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 128
5 Receiver Gain 57
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H


S5-3
Parameter Value
1 Title mvt 723-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 15610
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C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7.39
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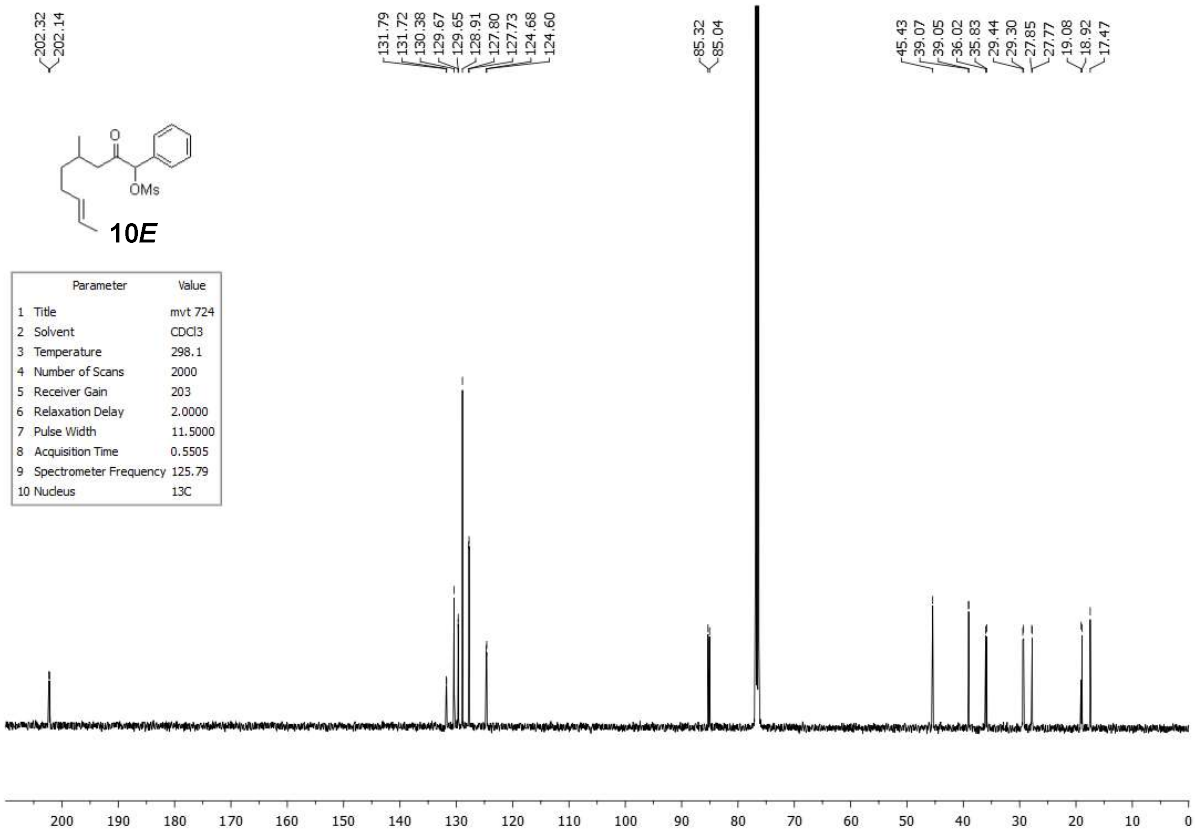
5.40
5.39
5.38
5.37
5.36
5.36
5.35
5.34
5.33
5.32
5.31
5.30
5.28
3.04
2.44
2.43
2.37
2.36
2.32
2.31
2.25
2.23
2.20
1.83
1.62
1.62
1.61
1.60
0.84
0.83
0.76
0.75
O
OMs
10E
Parameter Value
1 Title mvt 724
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
5.23
0.49
0.52
2.01
3.07
0.52
0.56
0.58
0.52
3.25
3.05
2.40
1.84
1.47
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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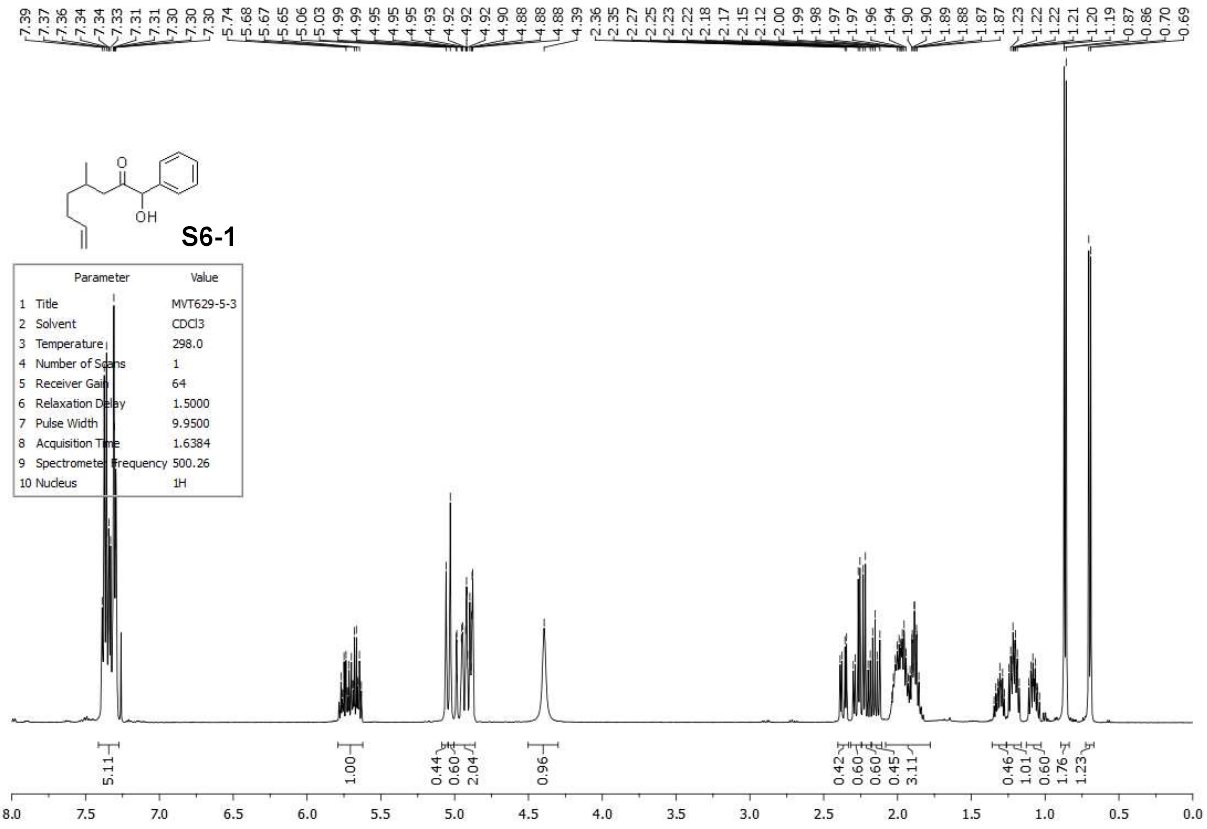
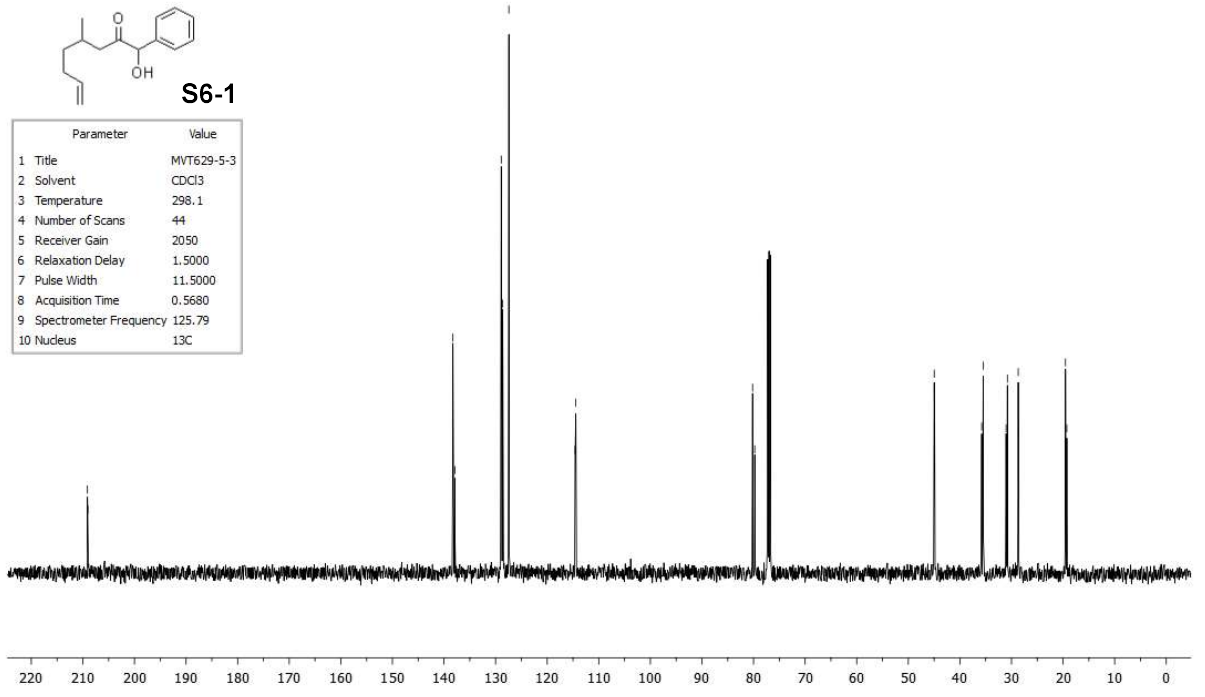
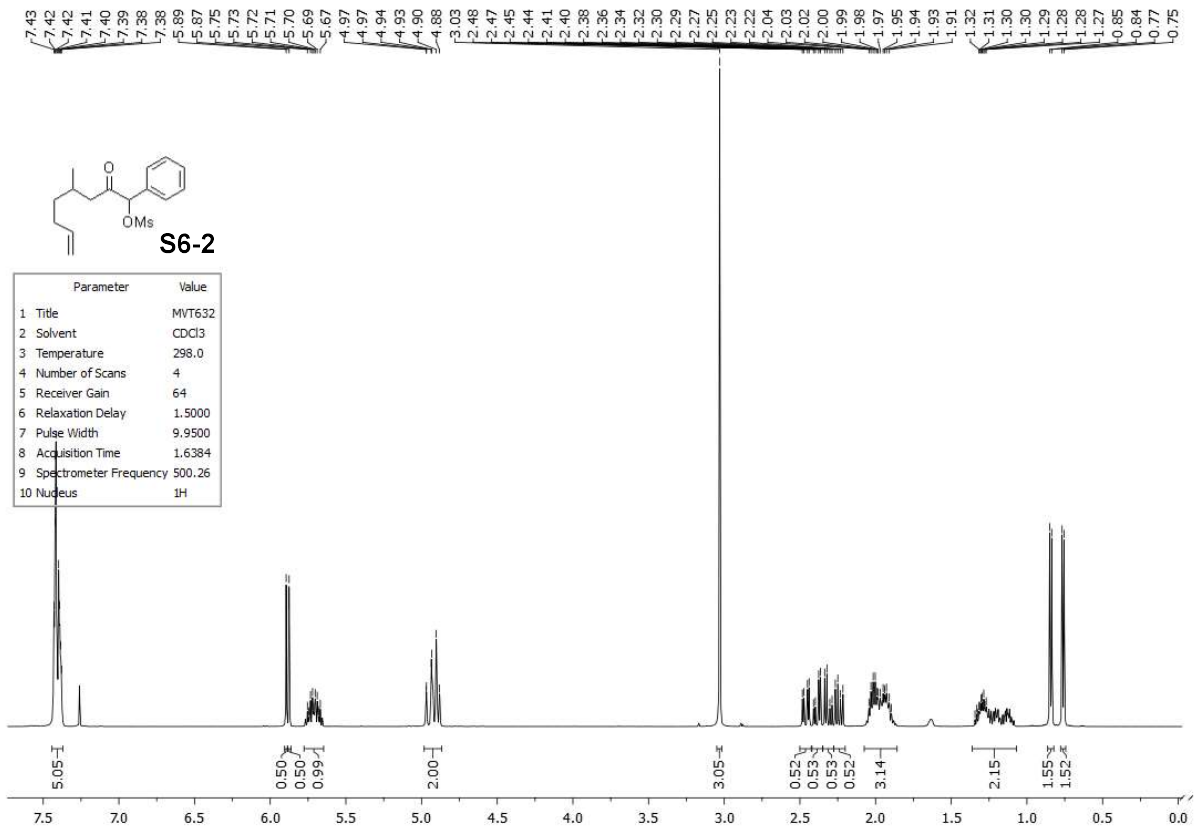
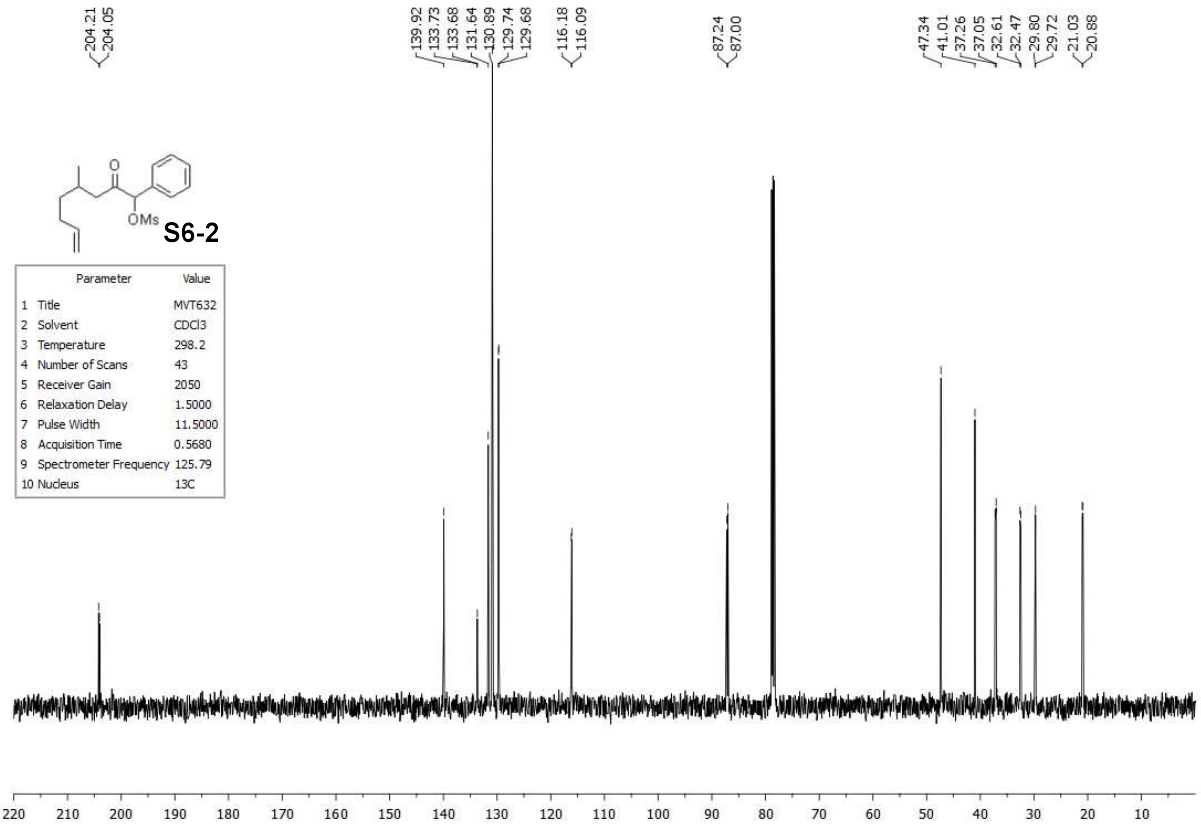
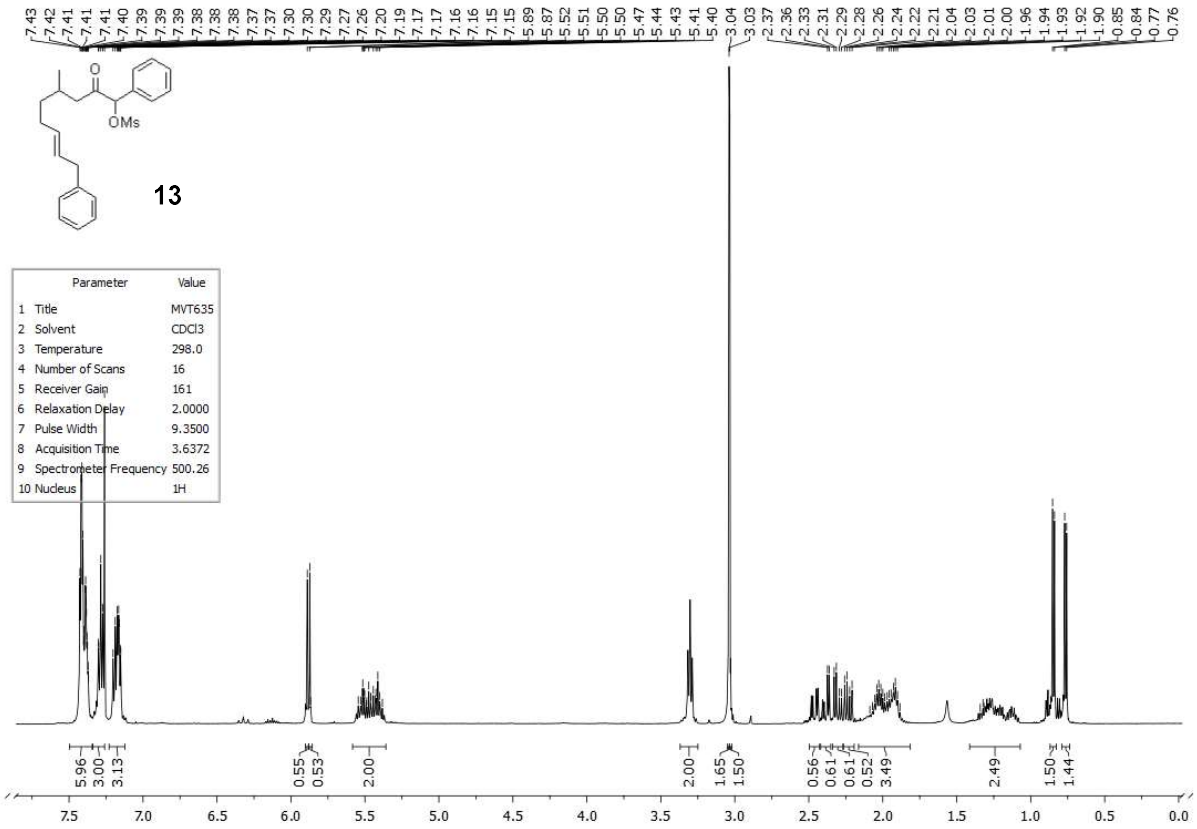
129.67
129.65
128.91
127.80
127.73
124.68
124.60
85.32
85.04
45.43
39.07
39.05
36.02
35.83
29.44
29.30
27.85
27.77
19.08
18.92
17.47
O
OMs
10E
Parameter Value
1 Title mvt 724
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 2000
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

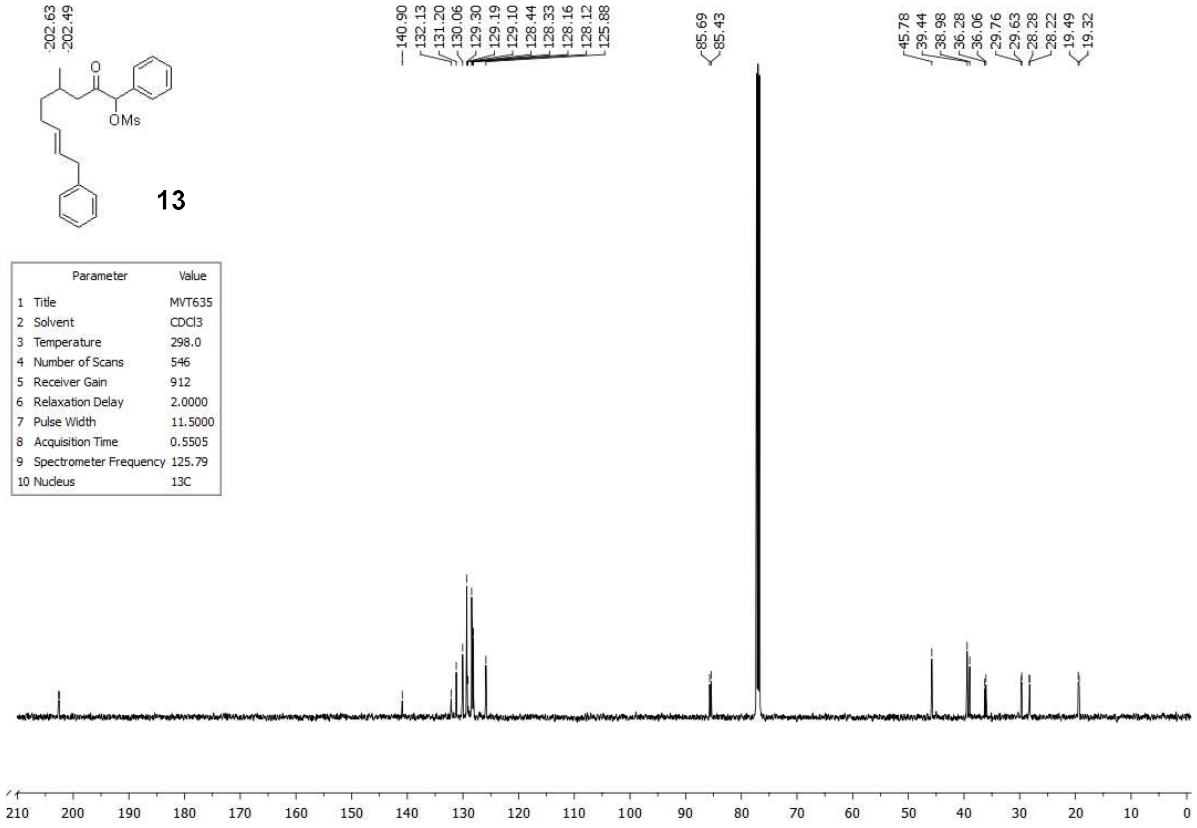

S6-1
Parameter Value
1 Title MVT629-5-3
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 1
5 Receiver Gain 64
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H

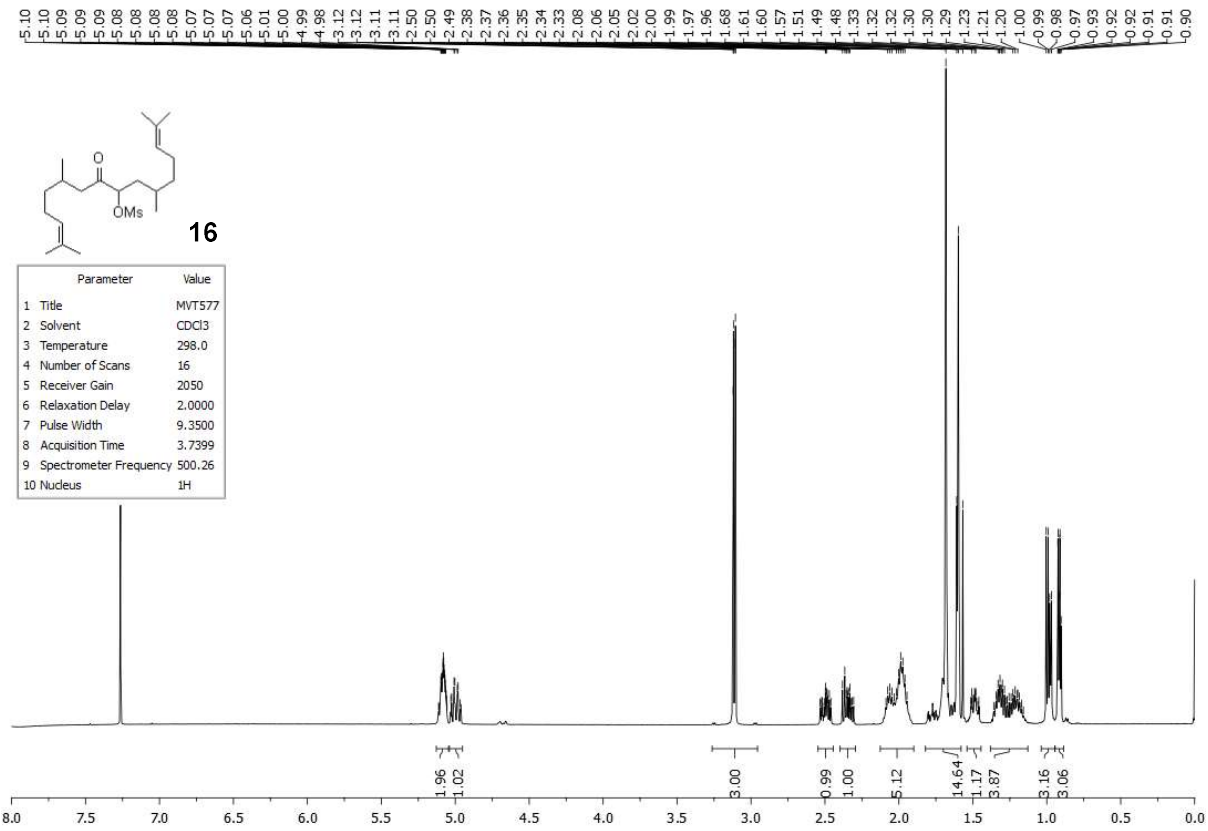

S6-1
Parameter Value
1 Title MVT629-5-3
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 44
5 Receiver Gain 2050
6 Relaxation Delay 1.5000
7 Pulse Width 11.5000
8 Acquisition Time 0.5680
9 Spectrometer Frequency 125.79
10 Nucleus 13C

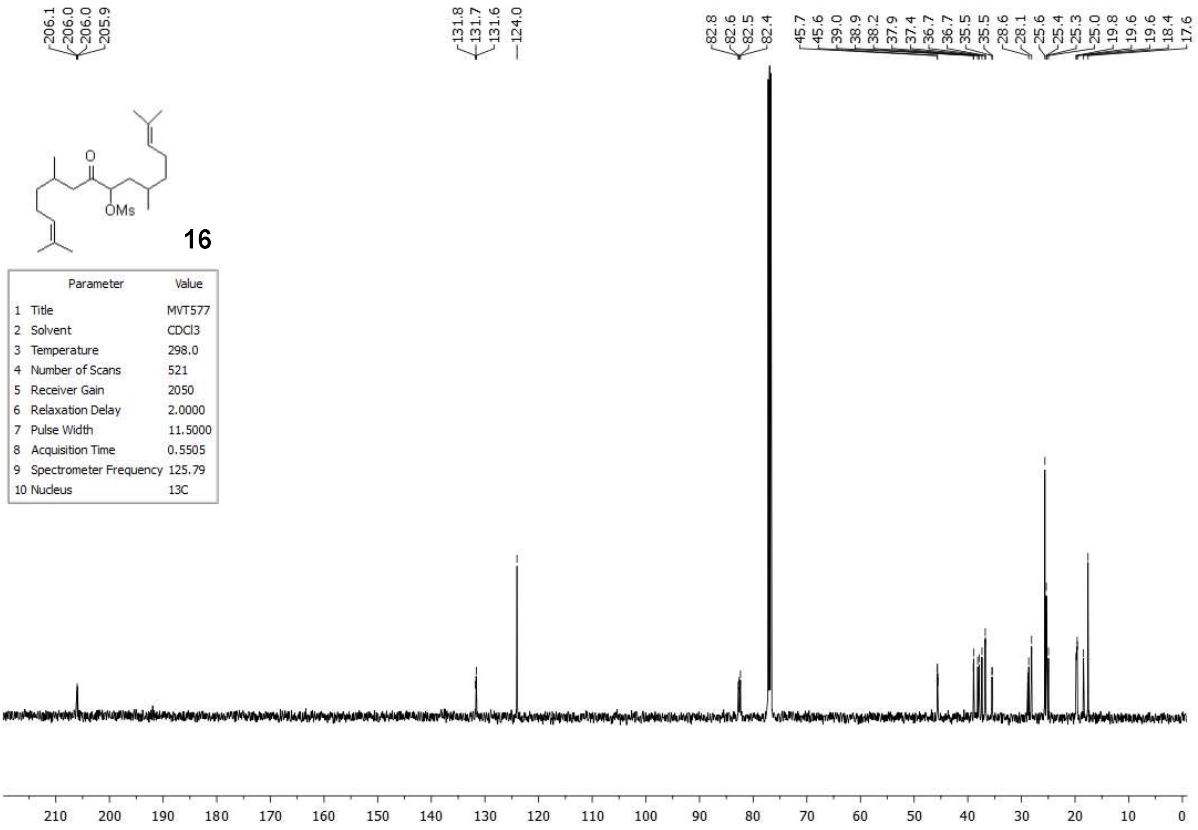

OMs
S6-2
Parameter Value
1 Title MVT632
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 4
5 Receiver Gain 64
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H

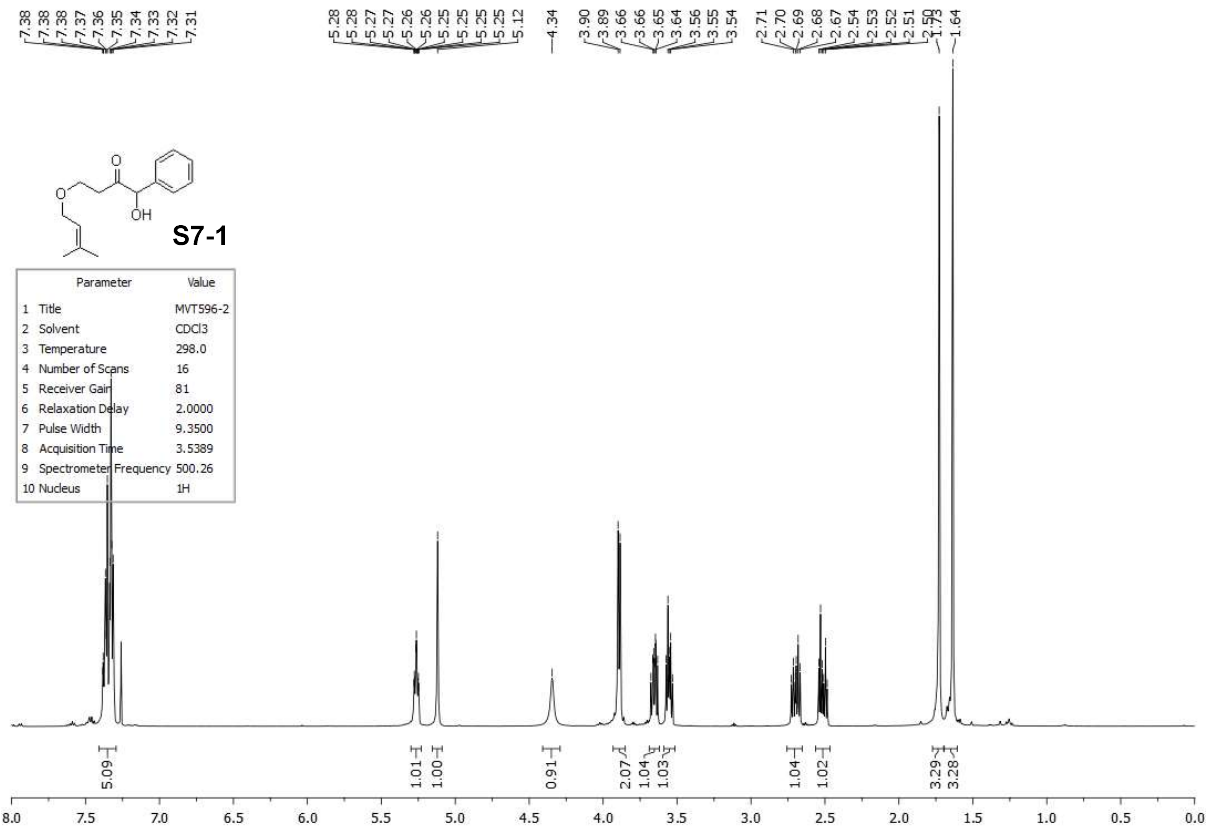

OMs
S6-2
Parameter Value
1 Title MVT632
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 43
5 Receiver Gain 2050
6 Relaxation Delay 1.5000
7 Pulse Width 11.5000
8 Acquisition Time 0.5680
9 Spectrometer Frequency 125.79
10 Nucleus 13C


OMs
13
Parameter Value
1 Title MVT635
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 161
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.6372
9 Spectrometer Frequency 500.26
10 Nucleus 1H


OMs
13
Parameter Value
1 Title MVT635
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 546
5 Receiver Gain 912
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C


16
Parameter Value
1 Title MVT577
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.7399
9 Spectrometer Frequency 500.26
10 Nucleus 1H


16
Parameter Value
1 Title MVT577
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 521
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C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5.27
5.27
5.26
5.26
5.25
5.25
5.25
5.12
4.34
3.90
3.89
3.66
3.66
3.65
3.64
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3.55
3.54
2.71
2.70
2.69
2.68
2.67
2.54
2.53
2.52
2.51
2.50
1.73
1.64
O
O
OH
S7-1
Parameter Value
1 Title MVT596-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 81
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.5389
9 Spectrometer Frequency 500.26
10 Nucleus 1H
5.09
1.01
1.00
0.91
2.07
1.04
1.03
1.04
1.02
3.29
3.28
8.0
7.5
7.0
6.5
6.0
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4.0
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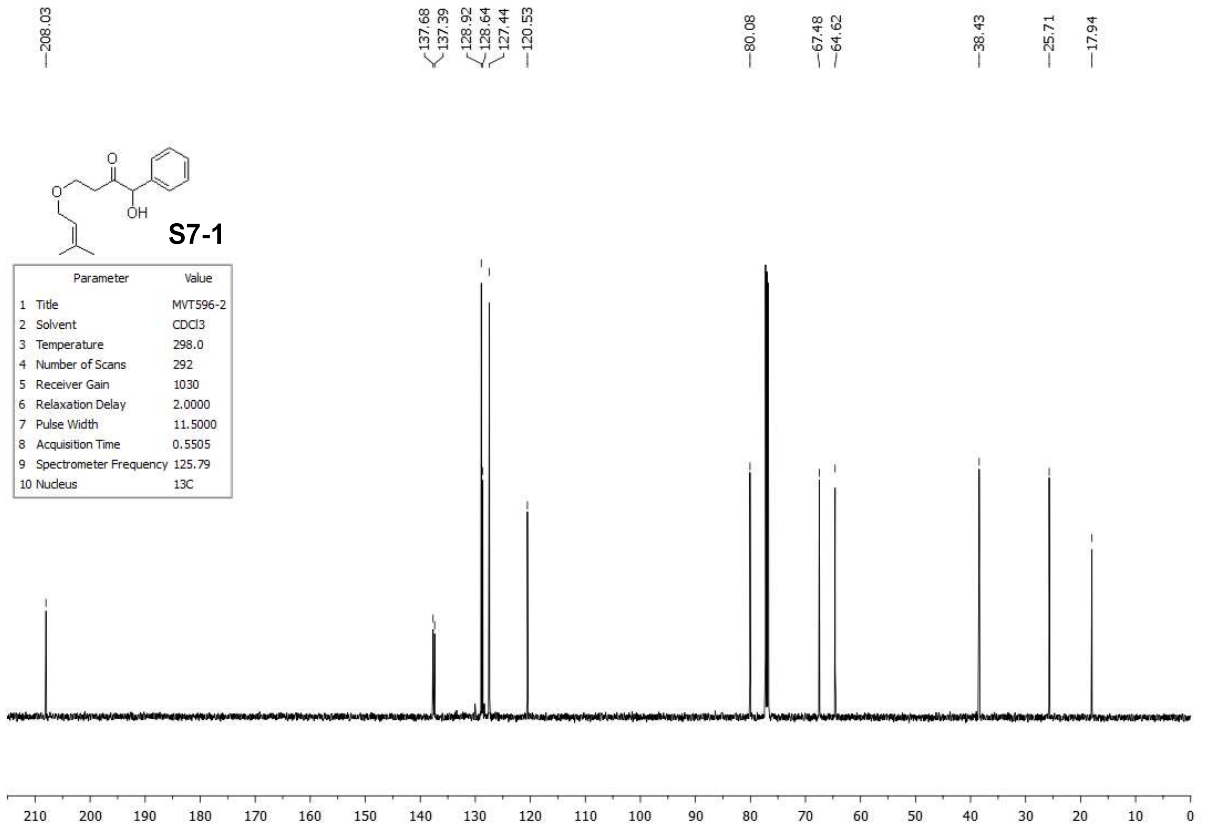
2.5
2.0
1.5
1.0
0.5
0.0


208.03
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137.39
128.92
128.64
127.44
120.53
80.08
67.48
64.62
38.43
25.71
17.94
O
O
OH
S7-1
Parameter Value
1 Title MVT596-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 292
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
210
200
190
180
170
160
150
140
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120
110
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90
80
70
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40
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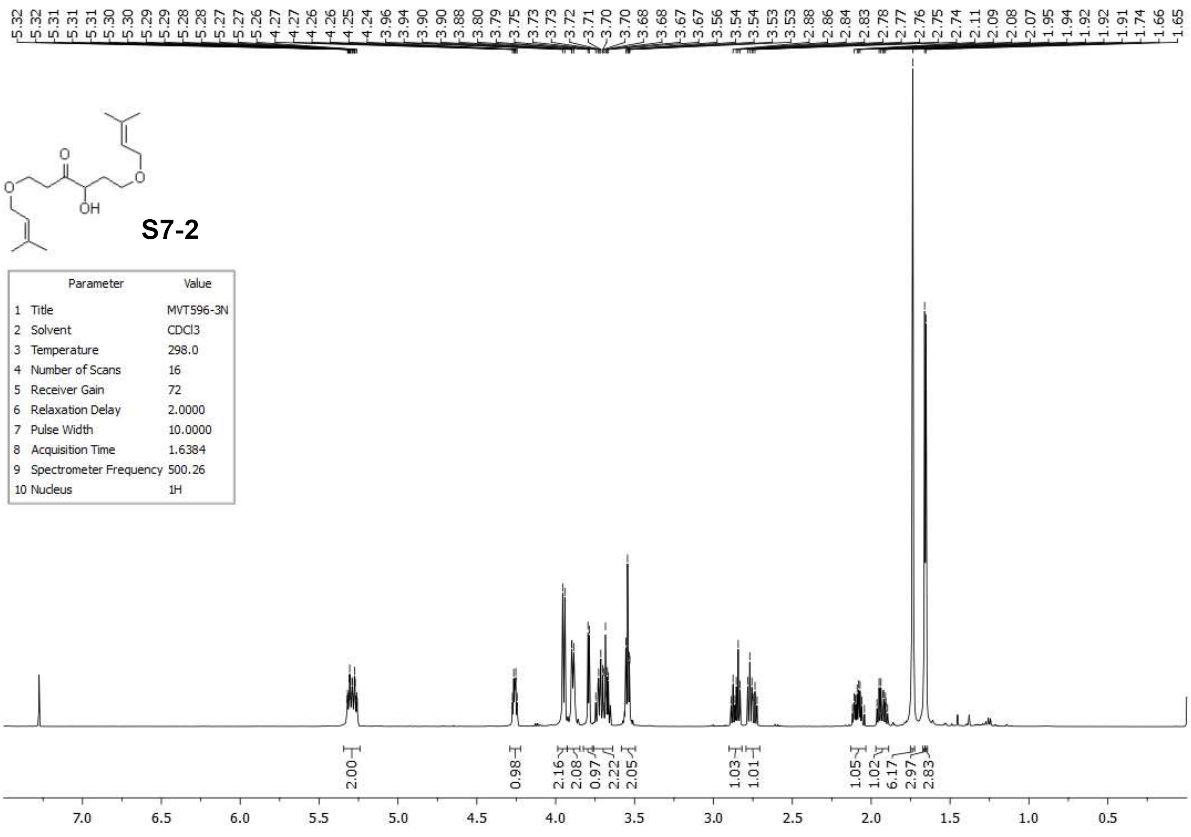
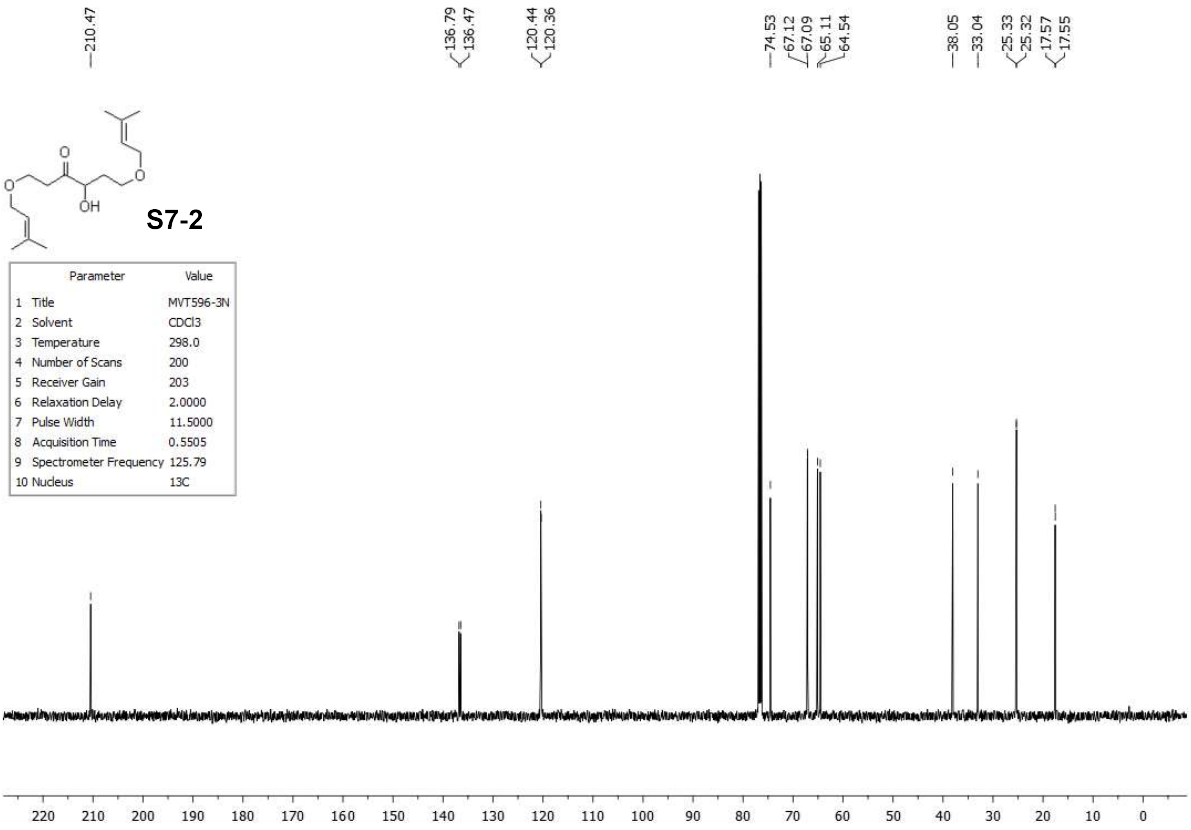
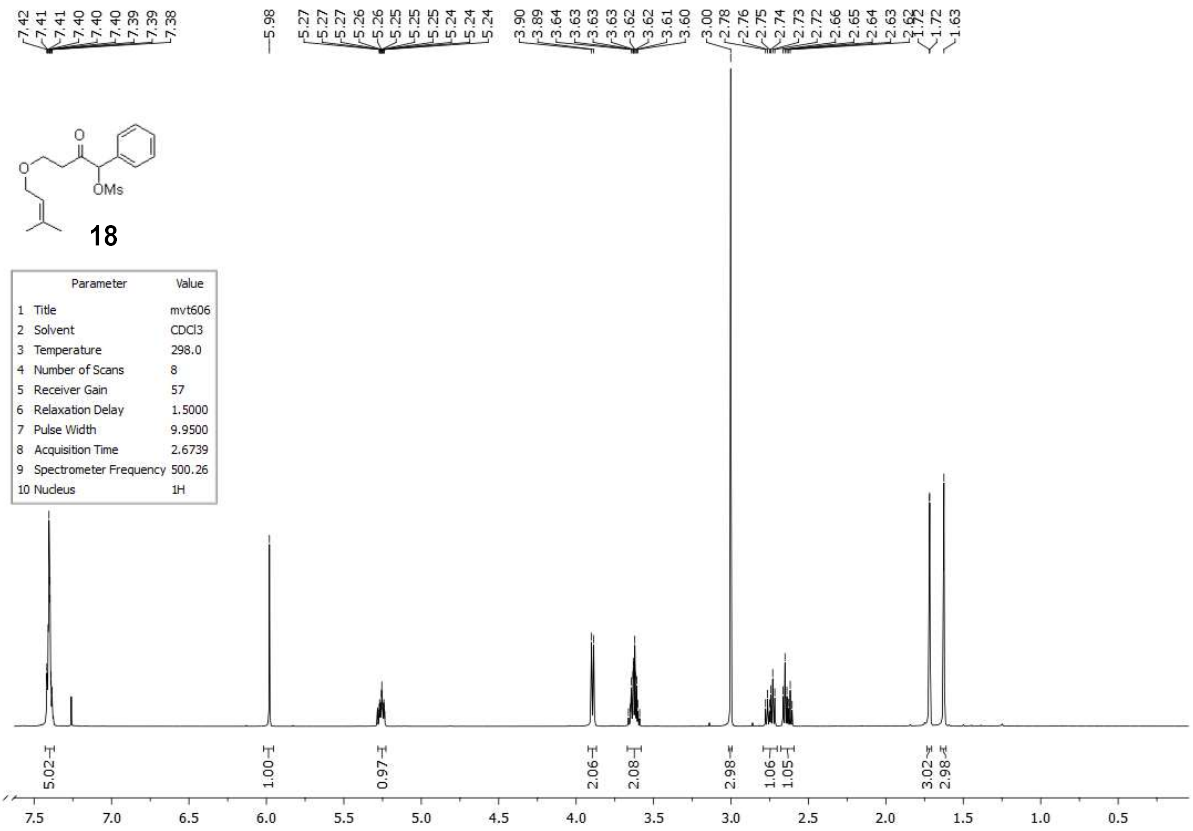
20
10
0


S7-2
Parameter Value
1 Title MVT596-3N
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 72
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H


S7-2
Parameter Value
1 Title MVT596-3N
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 200
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C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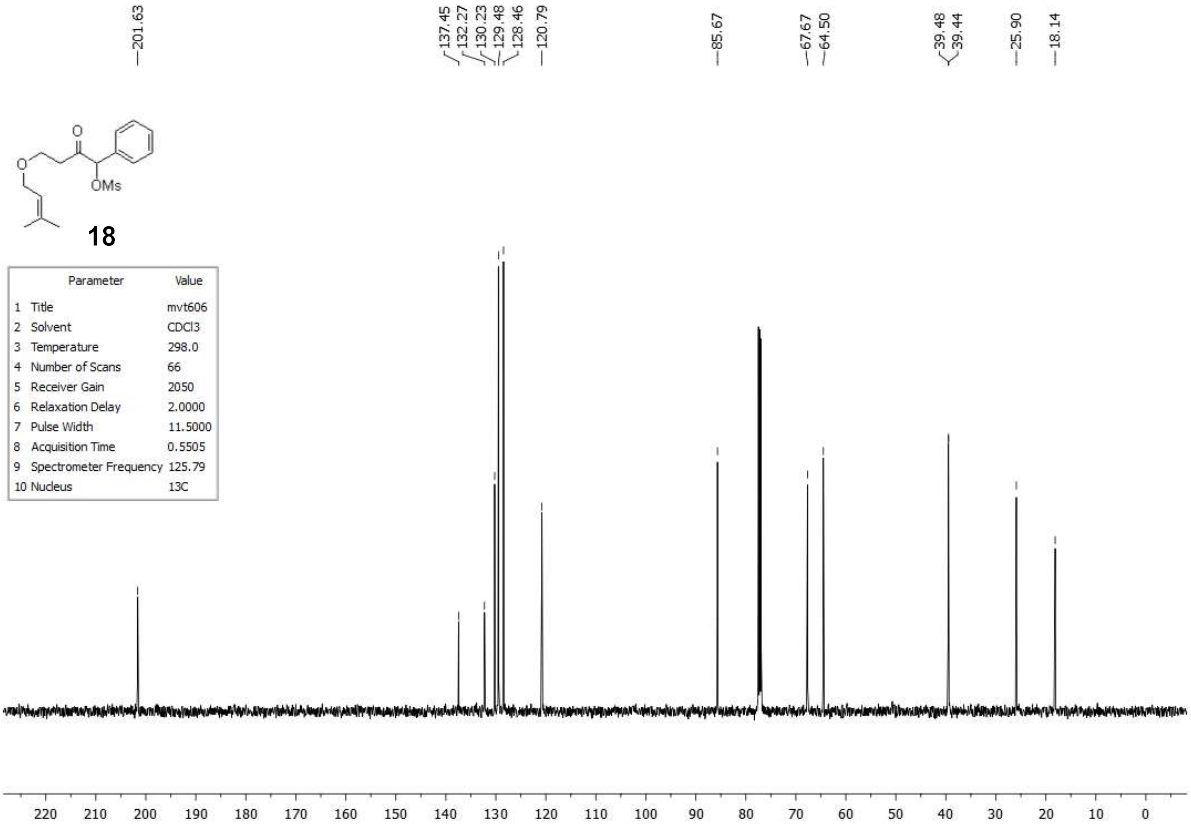
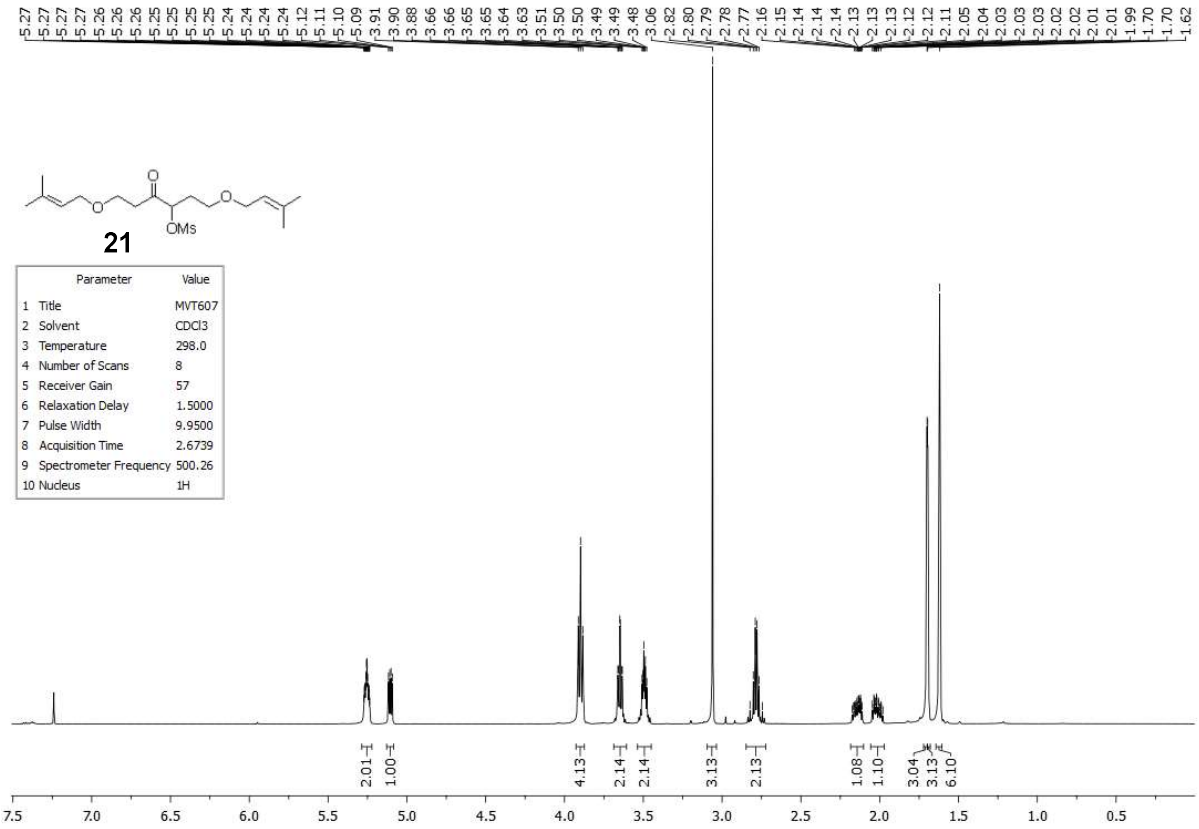
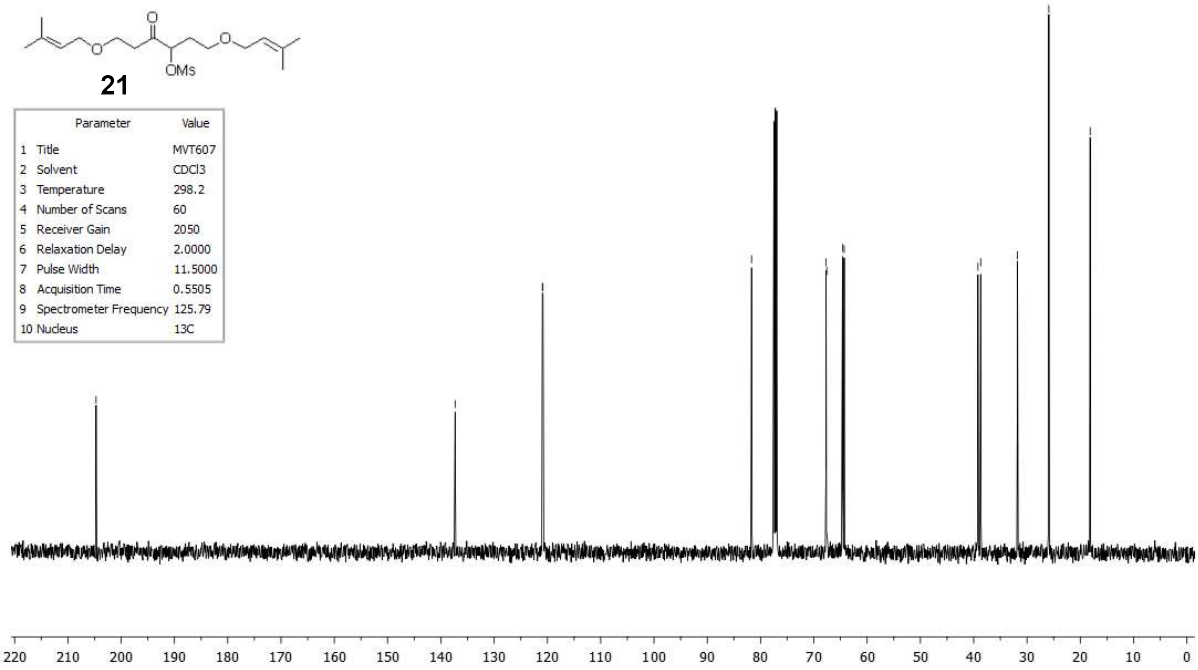
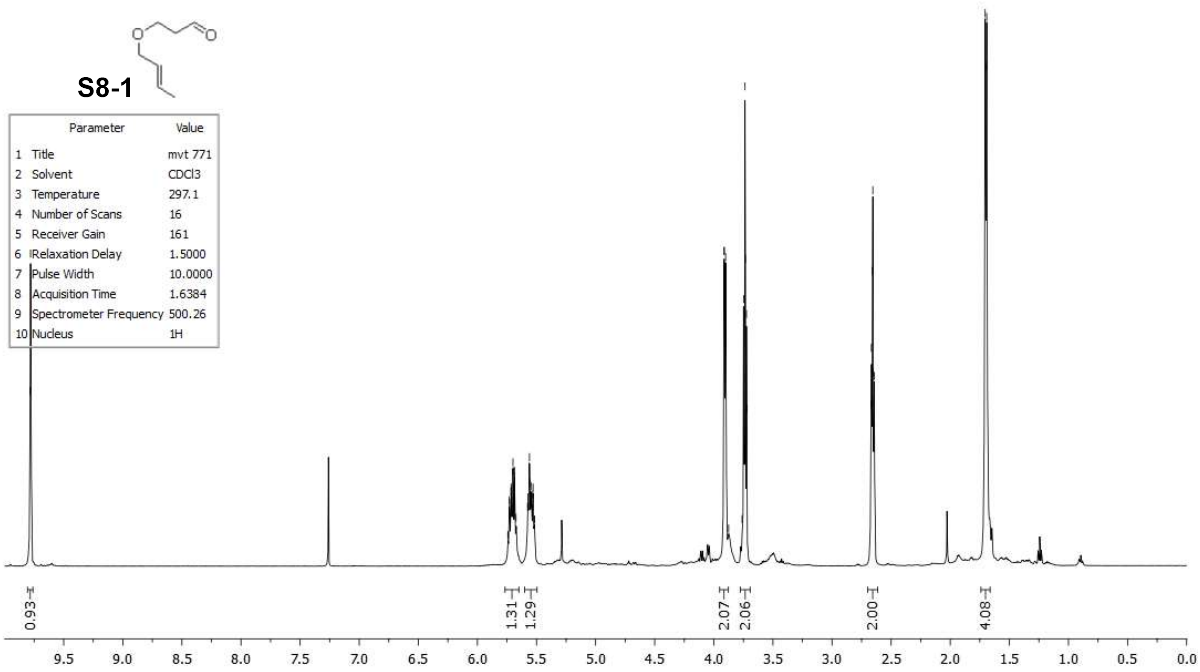
5.98
5.27 5.27 5.27 5.26 5.26 5.25 5.25 5.25 5.24 5.24 5.24
3.90 3.89 3.64 3.63 3.63 3.63 3.62 3.62 3.61 3.60
3.00 2.78 2.76 2.75 2.74 2.73 2.72 2.66 2.65 2.64 2.63 2.62 1.72 1.63
O
O
OMs
18
Parameter Value
1 Title mvt606
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 8
5 Receiver Gain 57
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 2.6739
9 Spectrometer Frequency 500.26
10 Nucleus 1H
5.02 1.00 0.97 2.06 2.08 2.98 1.06 1.05 3.02 2.98
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

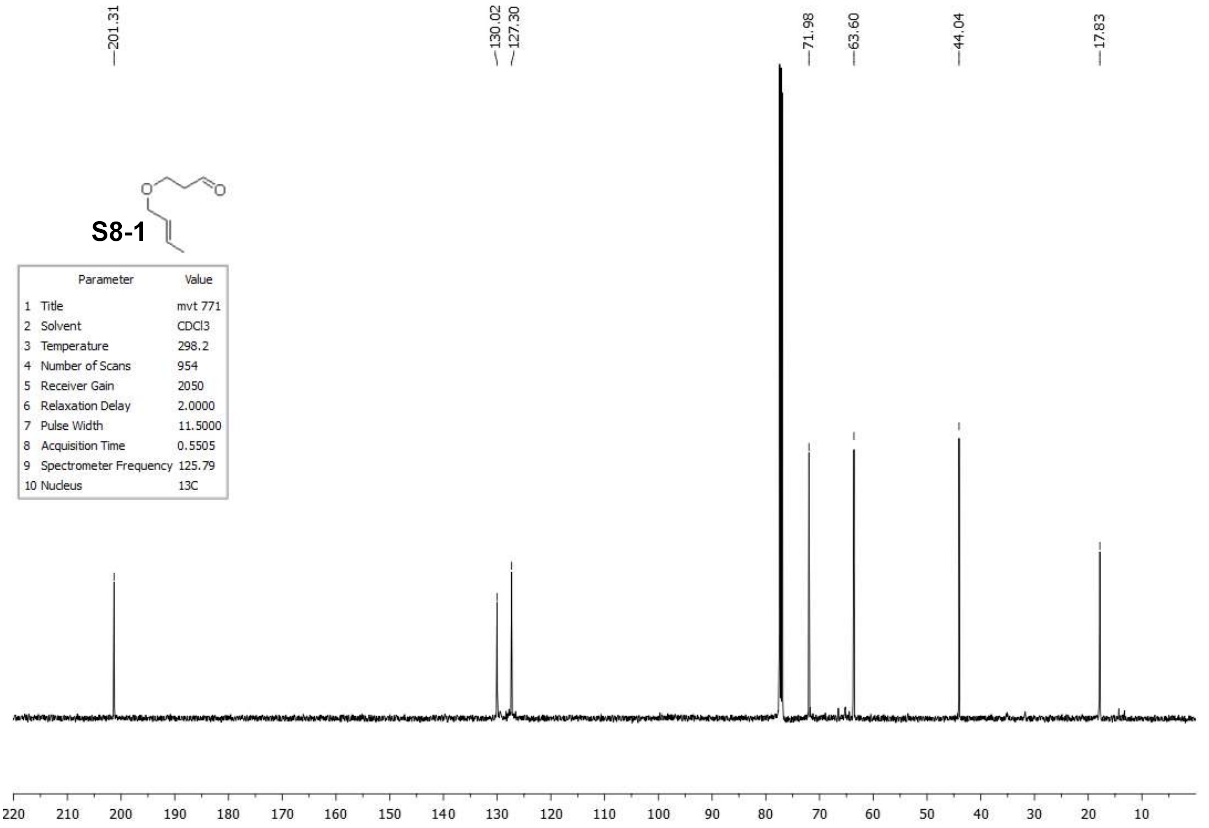

201.63
137.45 132.27 130.23 129.48 128.46 120.79
85.67
67.67 64.50
39.48 39.44
25.90
18.14
O
O
OMs
18
Parameter Value
1 Title mvt606
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 66
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

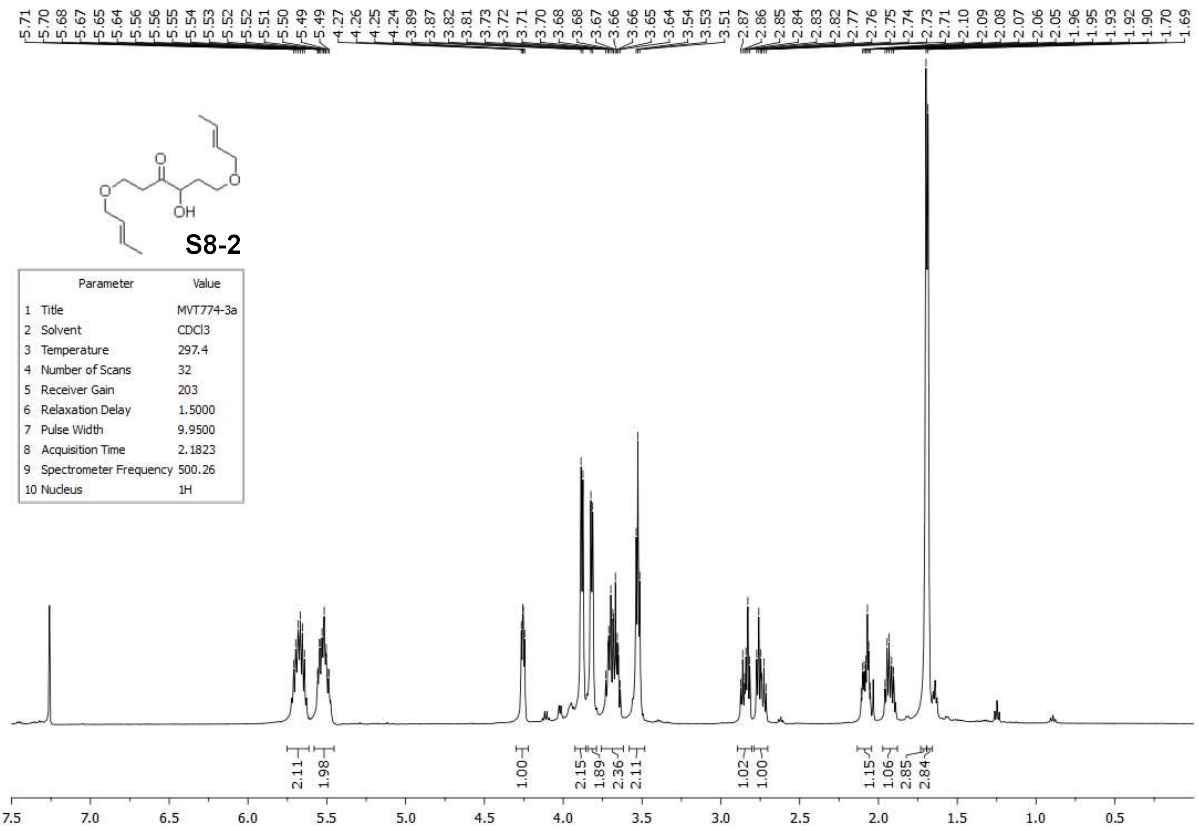

21
OMs
Parameter Value
1 Title MVT607
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 8
5 Receiver Gain 57
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 2.6739
9 Spectrometer Frequency 500.26
10 Nucleus 1H

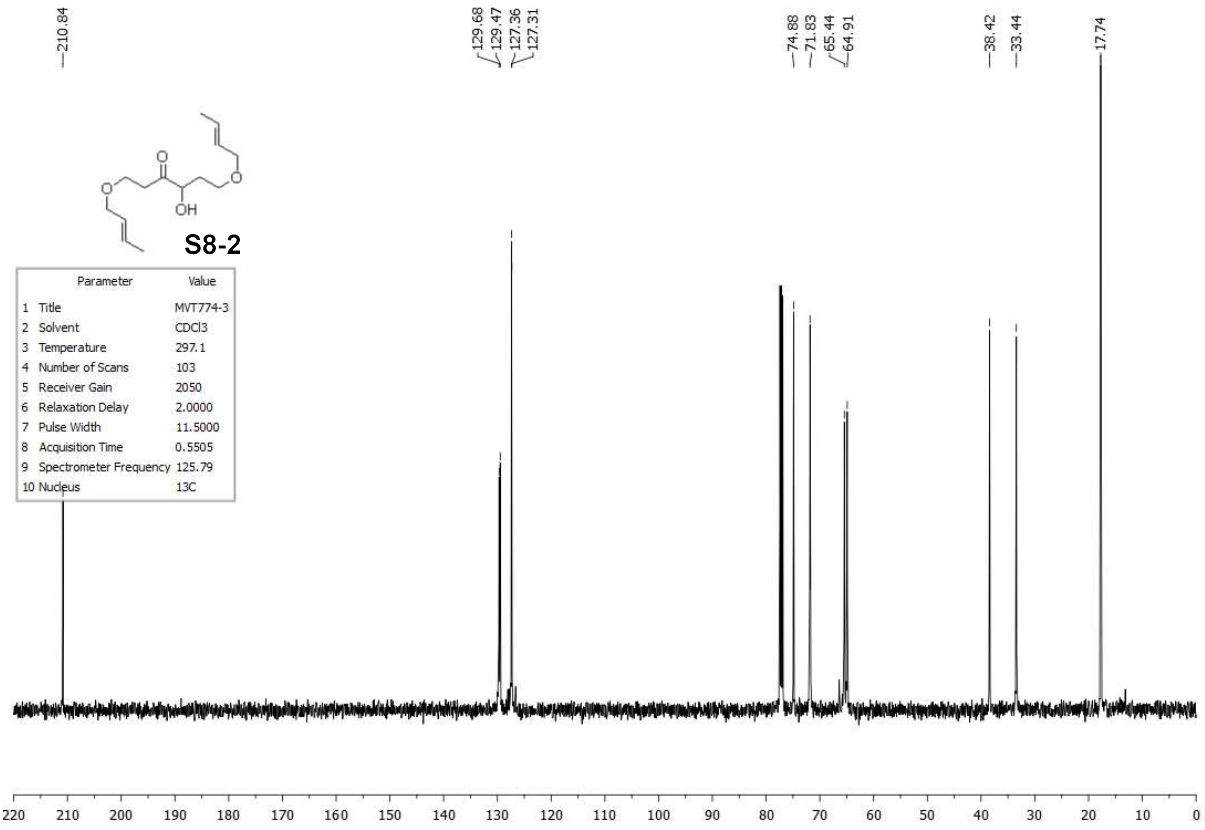

21
OMs
Parameter Value
1 Title MVT607
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 60
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

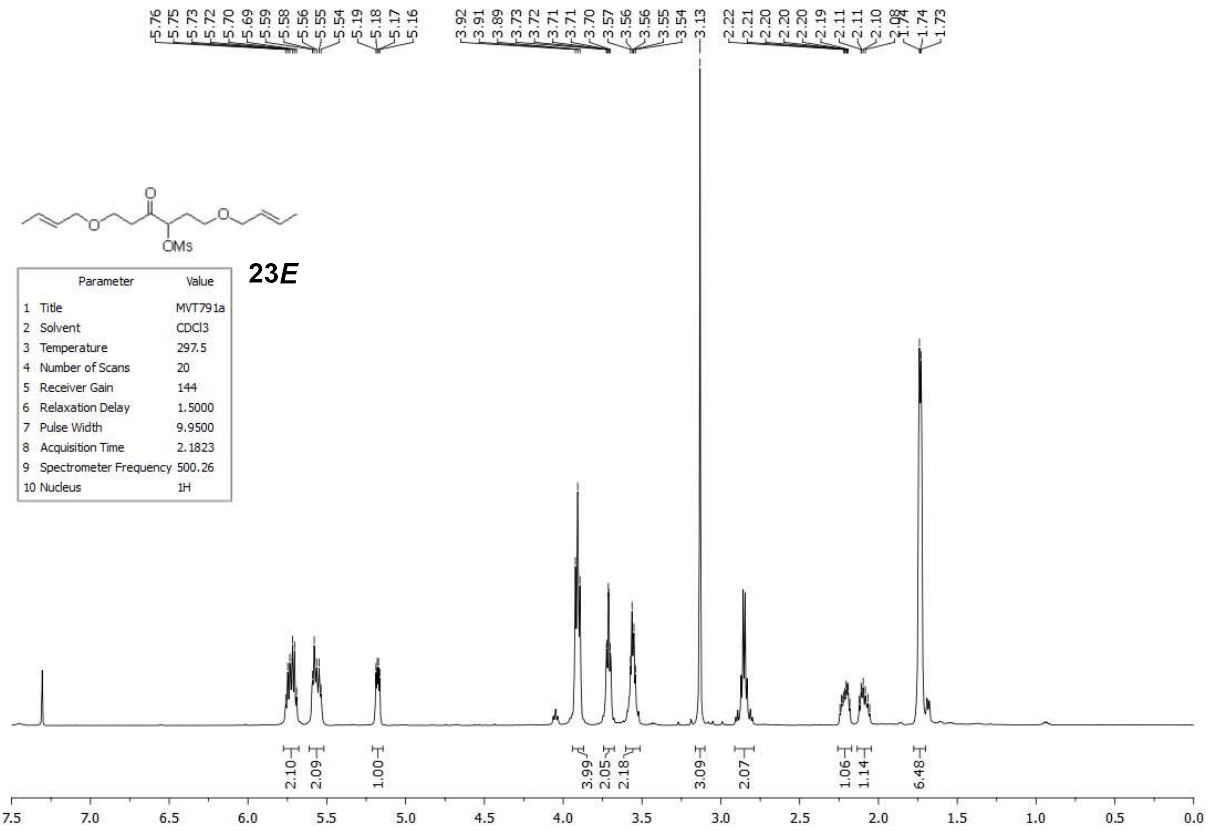

9.78
9.78
9.78
5.74
5.74
5.73
5.73
5.72
5.71
5.71
5.70
5.70
5.69
5.68
5.67
5.58
5.57
5.57
5.56
5.56
5.56
5.55
5.55
5.53
5.53
5.52
5.52
3.91
3.91
3.90
3.90
3.75
3.74
3.74
3.73
2.67
2.67
2.66
2.66
2.65
2.65
2.65
2.64
1.70
1.69
1.69

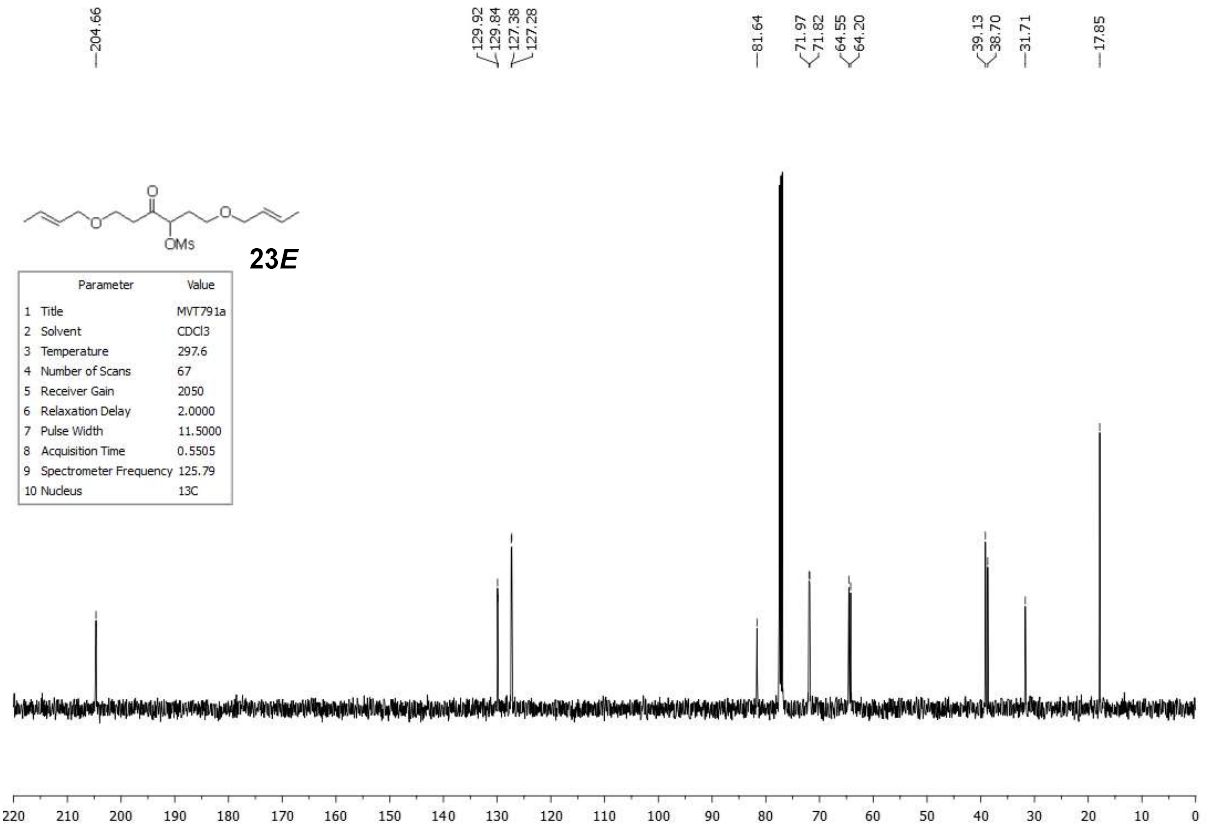

S8-1
Parameter Value
1 Title mvt 771
2 Solvent CDCl3
3 Temperature 297.1
4 Number of Scans 16
5 Receiver Gain 161
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
0.93
1.31
1.29
2.07
2.06
2.00
4.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

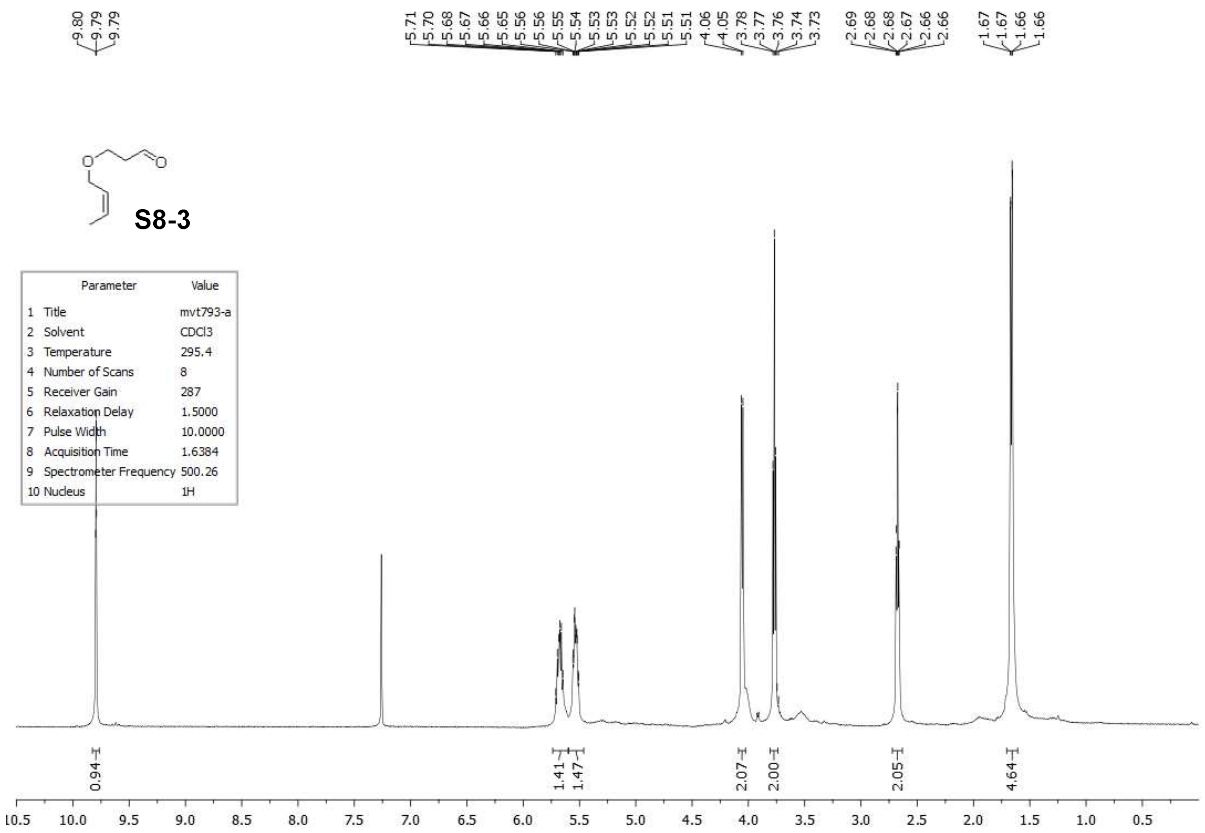

201.31
130.02
127.30
71.98
63.60
44.04
17.83
S8-1
Parameter Value
1 Title mvt 771
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 954
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

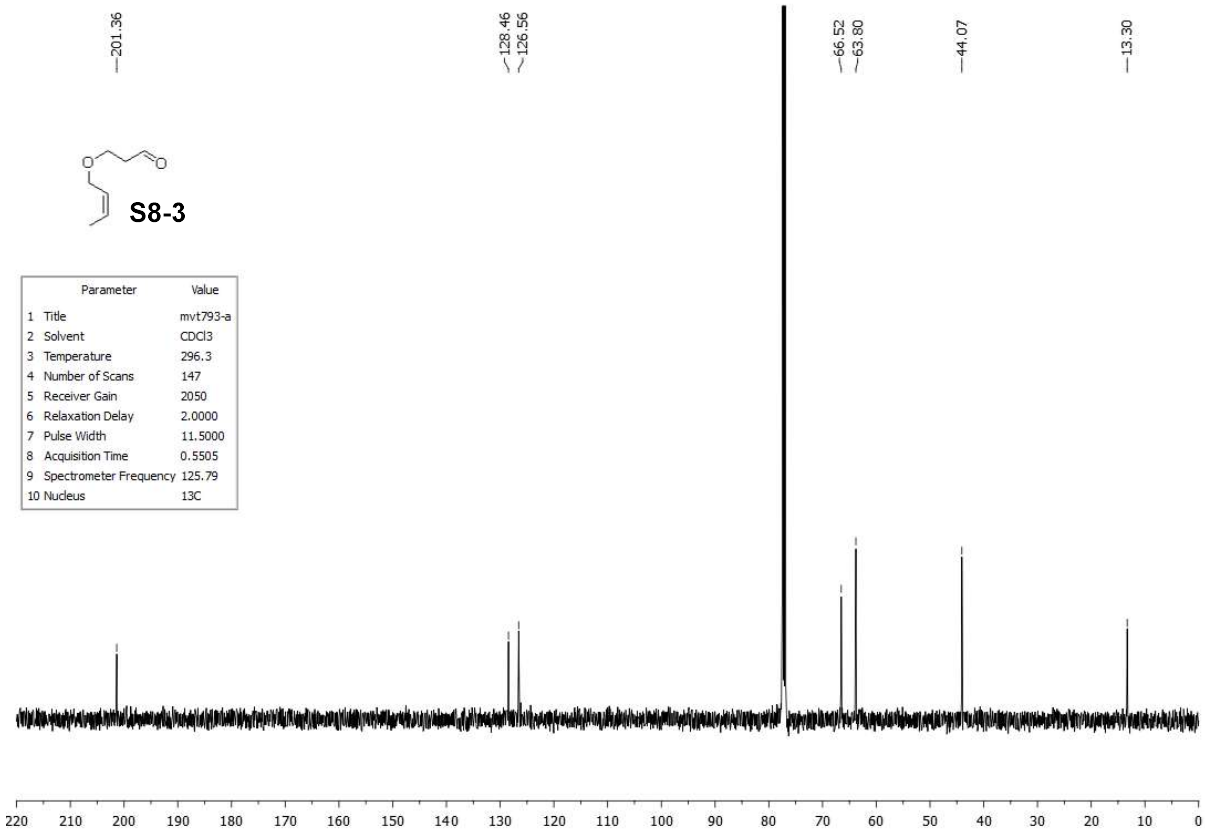

S8-2
Parameter Value
1 Title MVT774-3a
2 Solvent CDCl3
3 Temperature 297.4
4 Number of Scans 32
5 Receiver Gain 203
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 2.1823
9 Spectrometer Frequency 500.26
10 Nucleus 1H

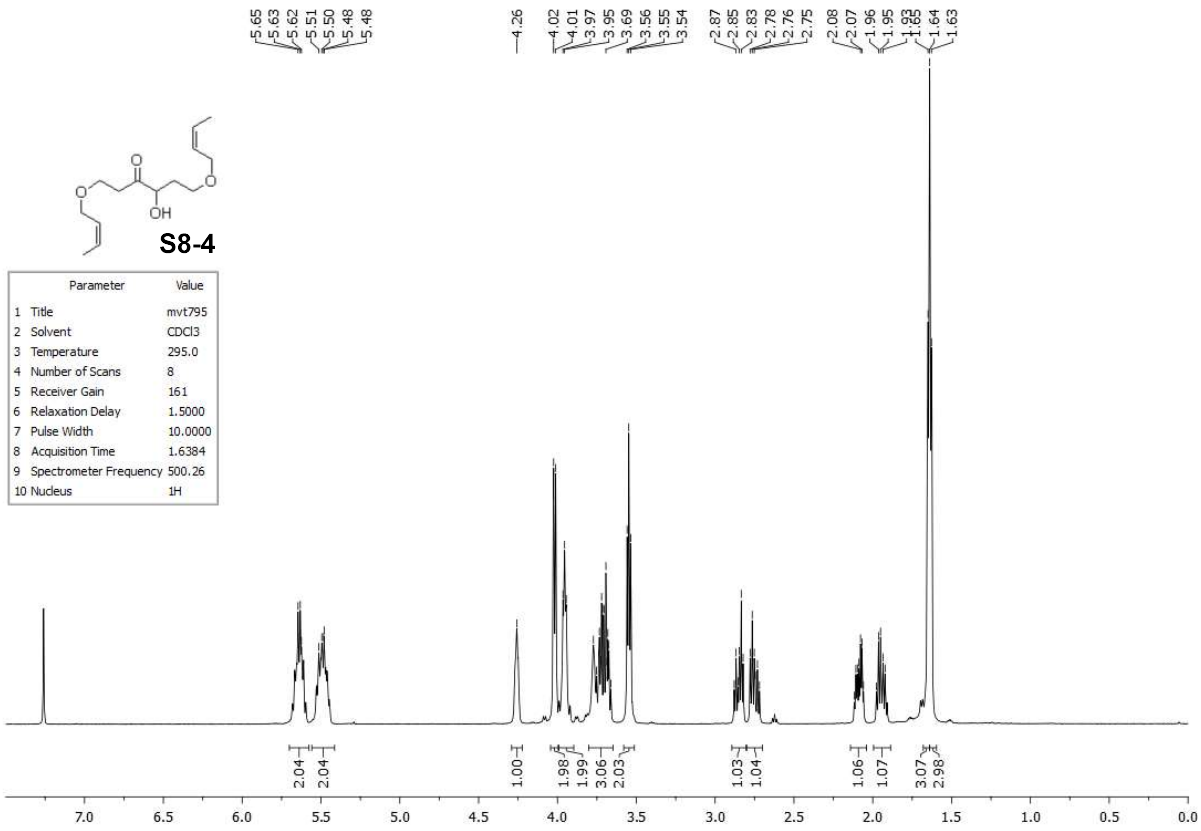

S8-2
Parameter Value
1 Title MVT774-3
2 Solvent CDCl3
3 Temperature 297.1
4 Number of Scans 103
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

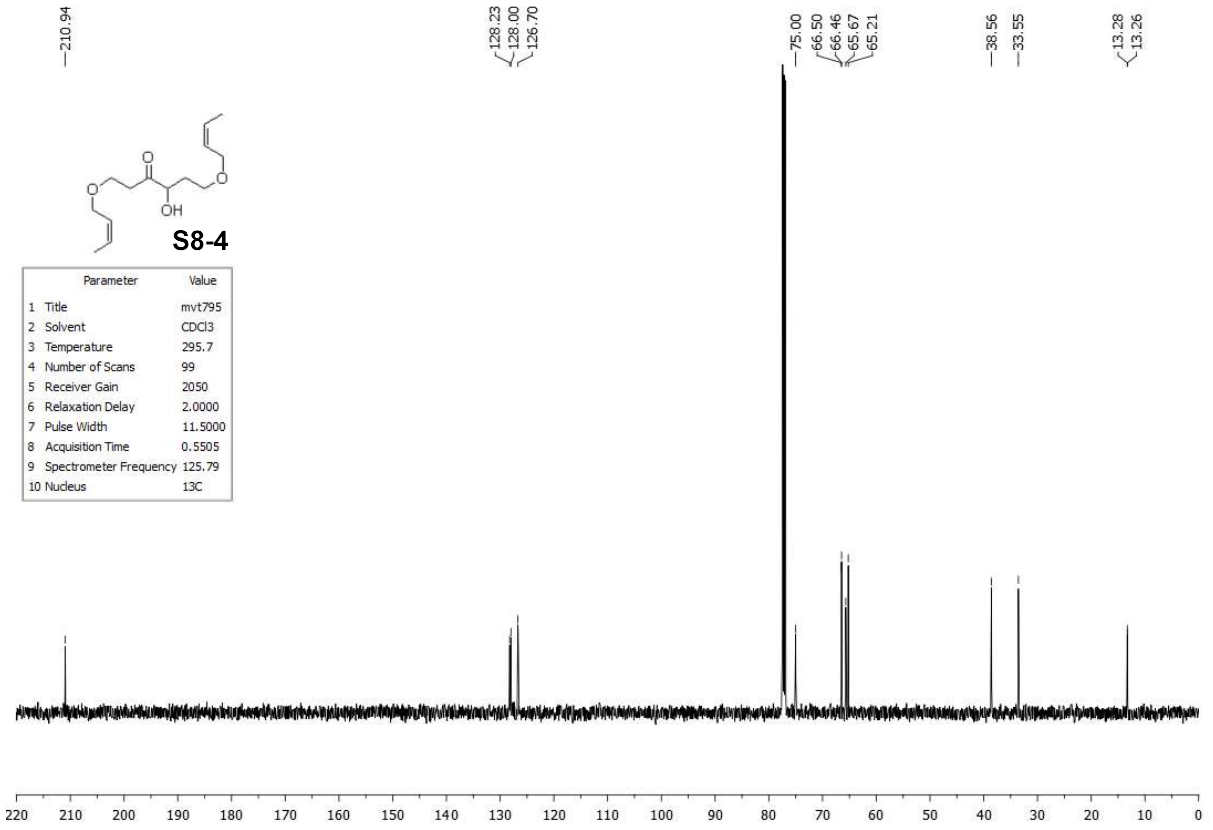

5.76
5.75
5.73
5.72
5.70
5.69
5.59
5.58
5.56
5.55
5.54
5.19
5.18
5.17
5.16
3.92
3.91
3.89
3.73
3.72
3.71
3.71
3.70
3.57
3.56
3.56
3.55
3.54
3.13
2.22
2.21
2.20
2.20
2.20
2.19
2.11
2.10
1.74
1.73
OMs
23E
Parameter Value
1 Title MVT791a
2 Solvent CDCl3
3 Temperature 297.5
4 Number of Scans 20
5 Receiver Gain 144
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 2.1823
9 Spectrometer Frequency 500.26
10 Nucleus 1H
2.10
2.09
1.00
3.99
2.05
2.18
3.09
2.07
1.06
1.14
6.48
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

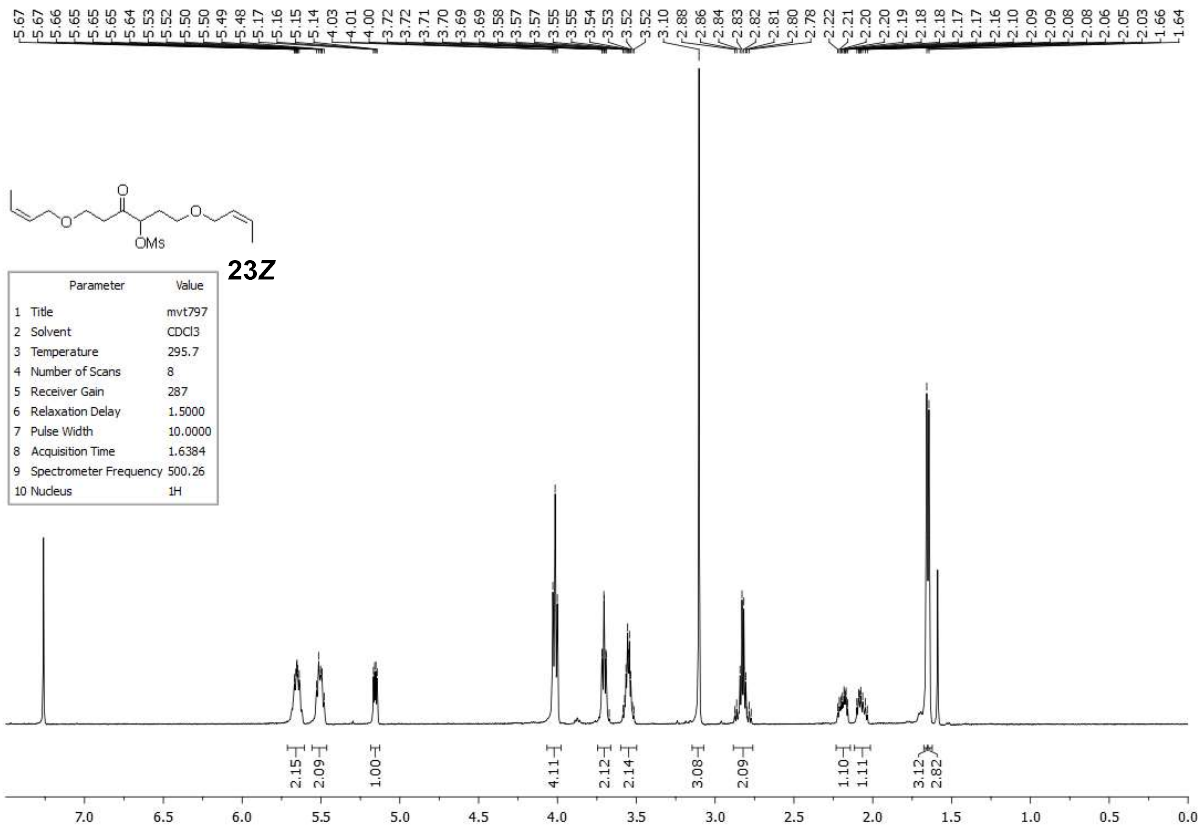

204.66
129.92
129.84
127.38
127.28
81.64
71.97
71.82
64.55
64.20
39.13
38.70
31.71
17.85
OMs
23E
Parameter Value
1 Title MVT791a
2 Solvent CDCl3
3 Temperature 297.6
4 Number of Scans 67
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

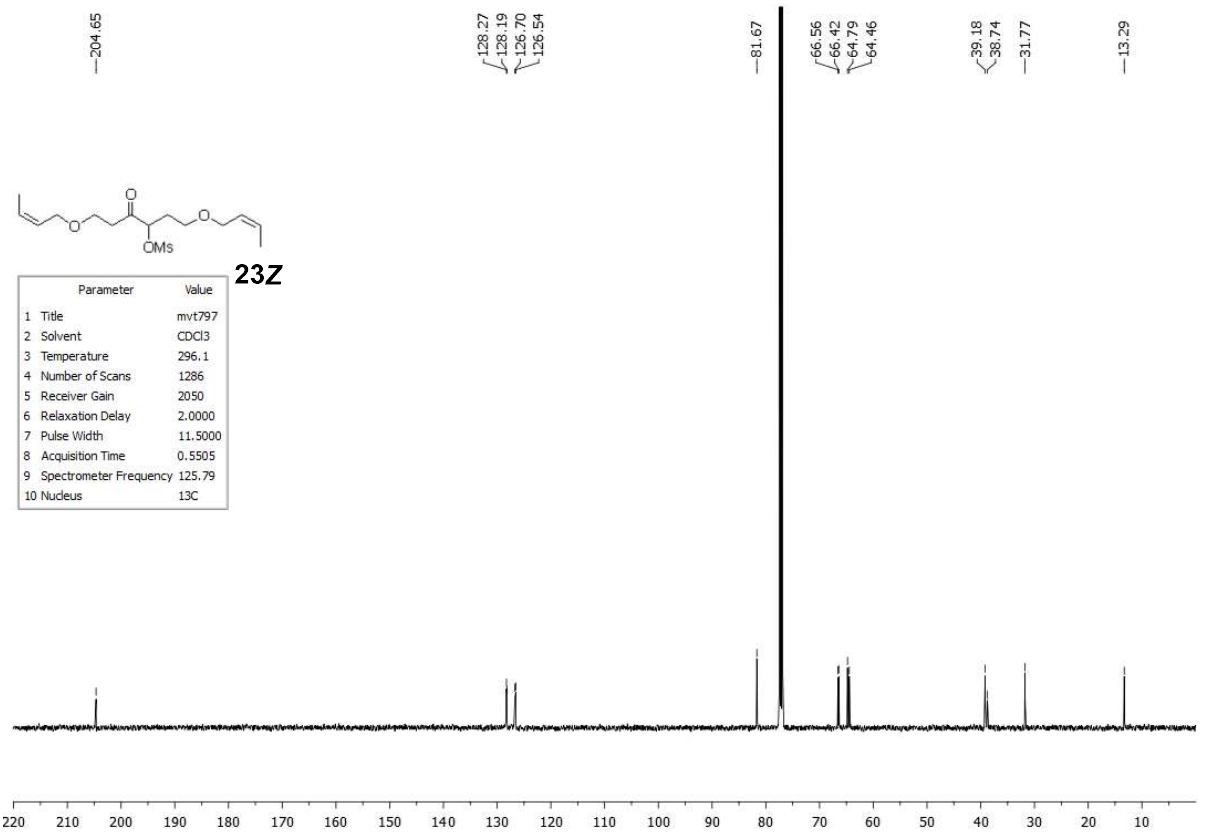

9.80
9.79
9.79
5.71
5.70
5.68
5.67
5.66
5.65
5.56
5.56
5.55
5.54
5.53
5.53
5.52
5.52
5.51
5.51
4.06
4.05
3.78
3.77
3.76
3.74
3.73
2.69
2.68
2.68
2.67
2.66
2.66
1.67
1.67
1.66
1.66
S8-3
Parameter Value
1 Title mvt793-a
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 8
5 Receiver Gain 287
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
0.94
1.41
1.47
2.07
2.00
2.05
4.64
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

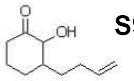

201.36
128.46
126.56
66.52
63.80
44.07
13.30
S8-3
Parameter Value
1 Title mvt793-a
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 147
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


5.65
5.63
5.62
5.51
5.50
5.48
5.48
4.26
4.02
4.01
3.97
3.95
3.69
3.56
3.55
3.54
2.87
2.85
2.83
2.78
2.76
2.75
2.08
2.07
1.96
1.95
1.93
1.85
1.64
1.63
O
O
O
OH
S8-4
Parameter Value
1 Title mvt795
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 8
5 Receiver Gain 161
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
2.04
2.04
1.00
1.98
1.99
3.06
2.03
1.03
1.04
1.06
1.07
3.07
2.98
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


210.94
128.23
128.00
126.70
75.00
66.50
66.46
65.67
65.21
38.56
33.55
13.28
13.26
O
O
O
OH
S8-4
Parameter Value
1 Title mvt795
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 99
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

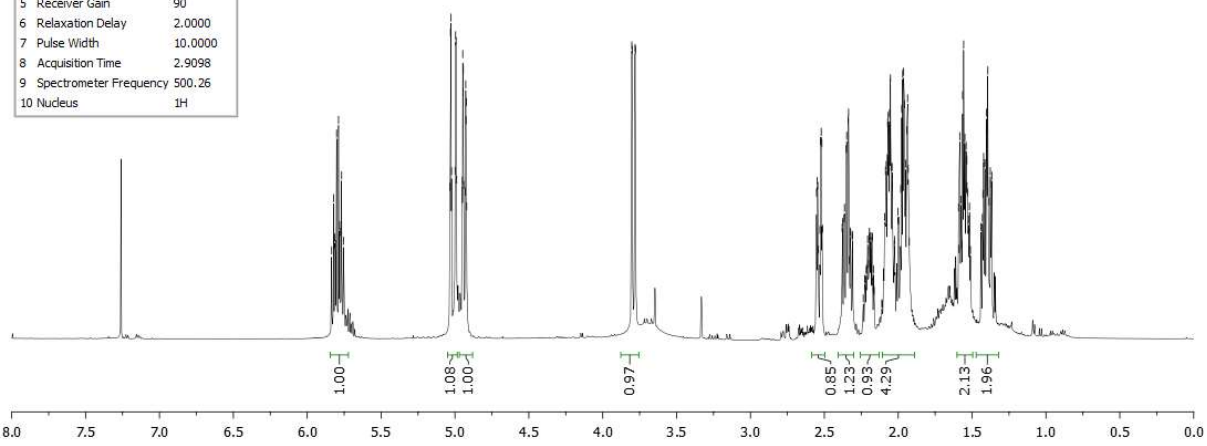

OMs
23Z
Parameter Value
1 Title mvt797
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 8
5 Receiver Gain 287
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H

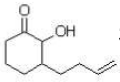

OMs
23Z
Parameter Value
1 Title mvt797
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 1286
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C



S9-2

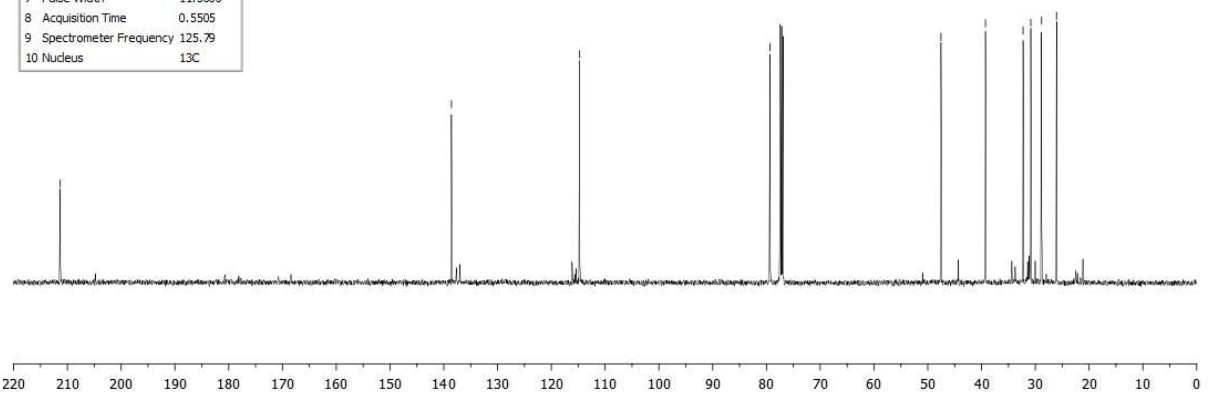
	Parameter	Value
1	Title	FO-1-68ap
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	16
5	Receiver Gain	90
6	Relaxation Delay	2.0000
7	Pulse Width	10.0000
8	Acquisition Time	2.9098
9	Spectrometer Frequency	500.26
10	Nucleus	1H

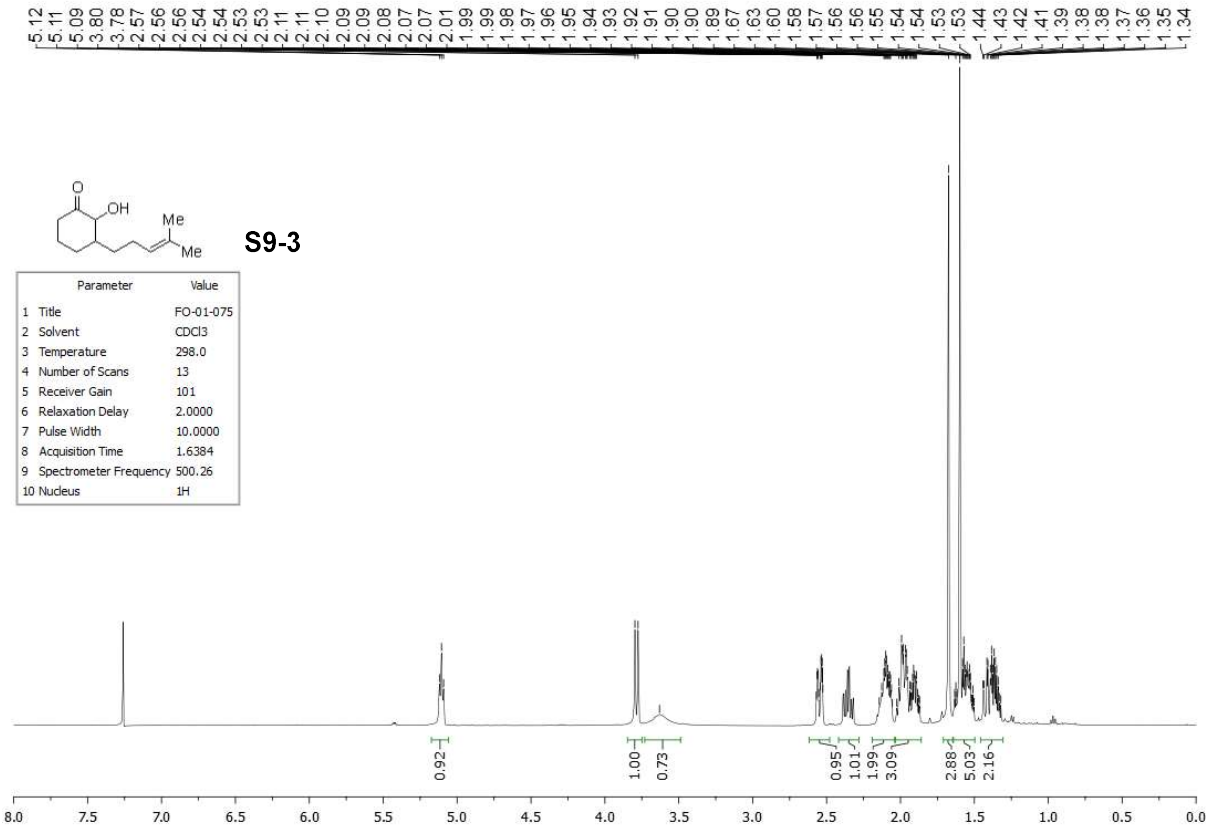


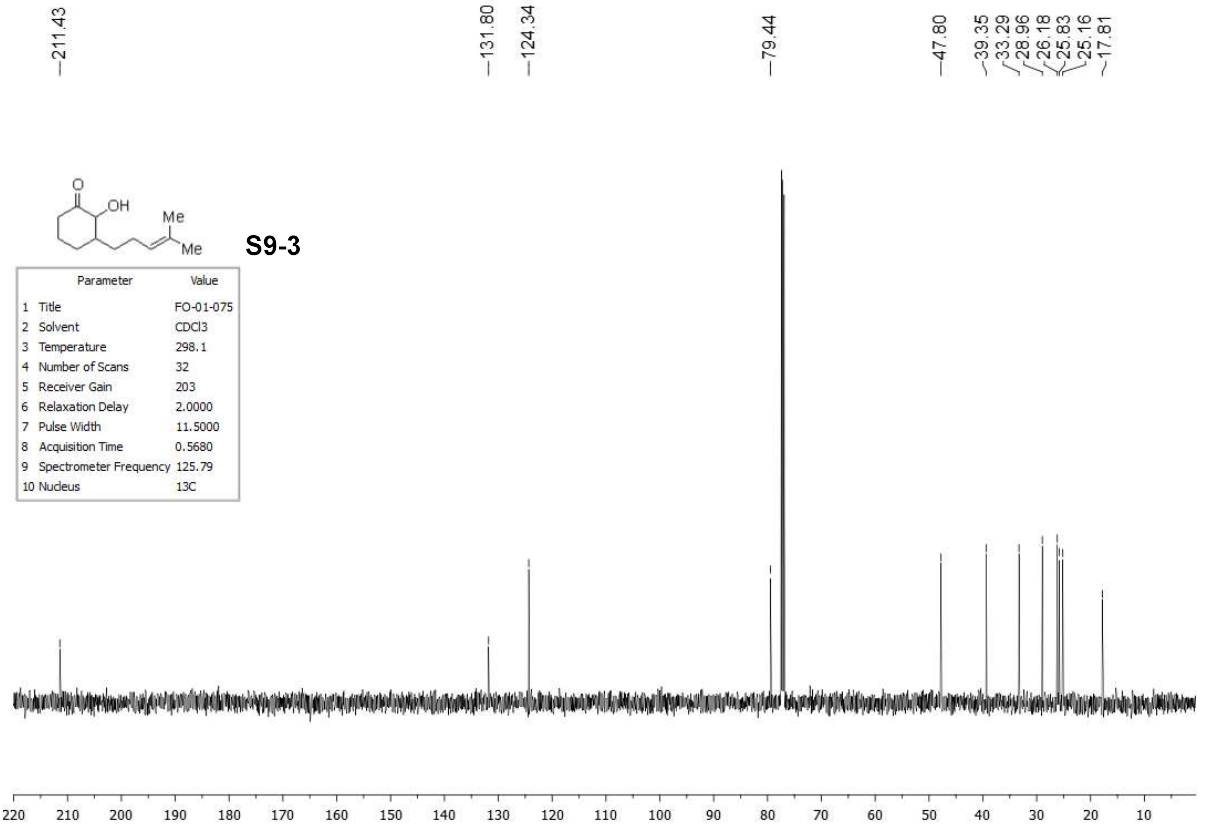


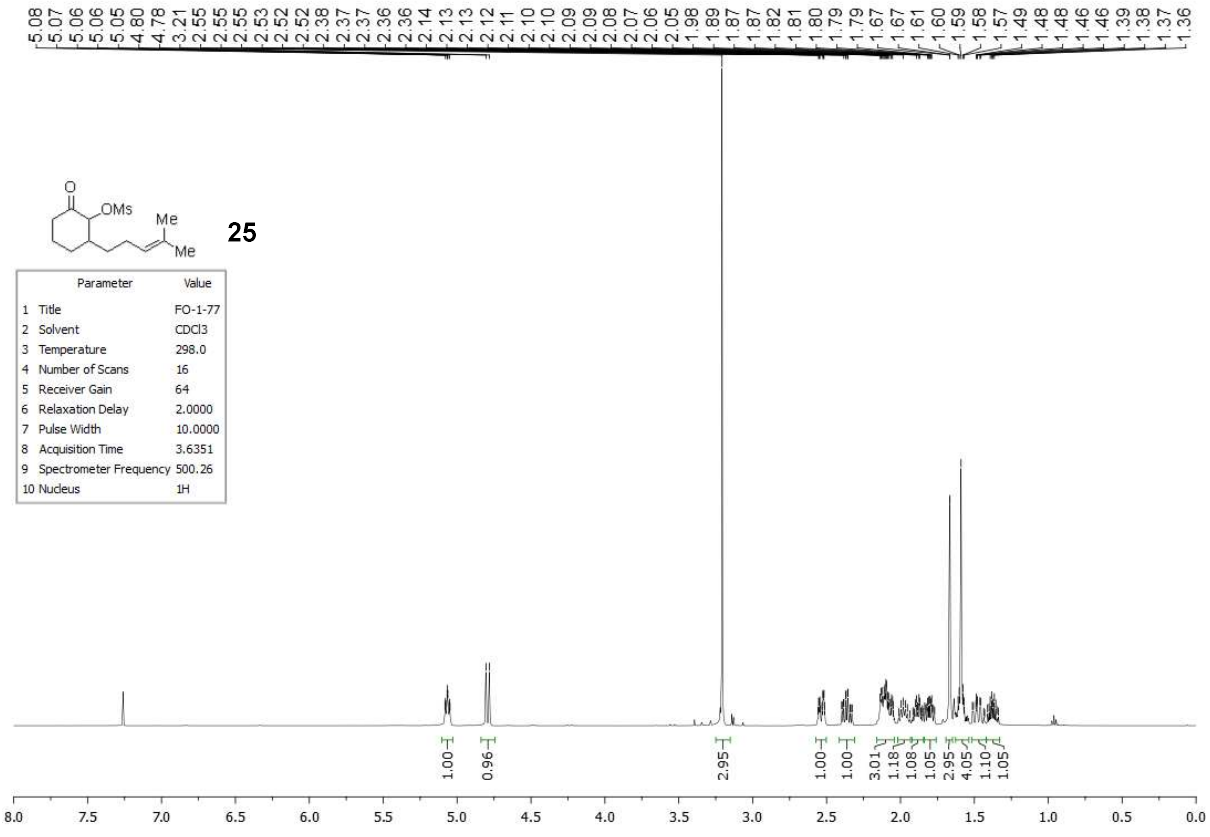
S9-2

	Parameter	Value
1	Title	FO-1-68ap
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	261
5	Receiver Gain	203
6	Relaxation Delay	2.0000
7	Pulse Width	11.5000
8	Acquisition Time	0.5505
9	Spectrometer Frequency	125.79
10	Nucleus	13C

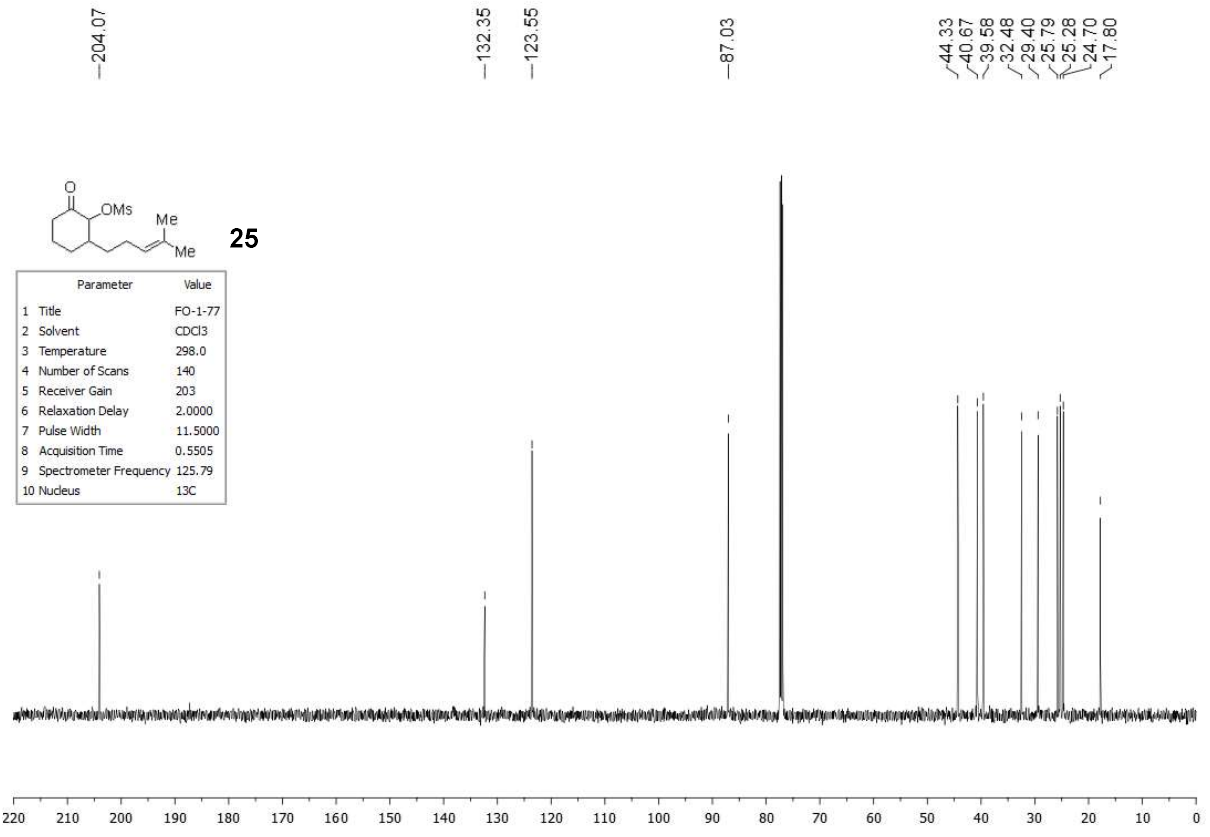



5.12 5.11 5.09 3.80 3.78 2.57 2.56 2.56 2.54 2.54 2.53 2.53 2.11 2.11 2.10 2.09 2.09 2.08 2.07 2.07 2.01 1.99 1.98 1.97 1.96 1.95 1.94 1.93 1.92 1.91 1.90 1.90 1.89 1.67 1.63 1.60 1.58 1.57 1.56 1.56 1.55 1.54 1.54 1.53 1.53 1.44 1.43 1.42 1.41 1.39 1.38 1.38 1.37 1.36 1.35 1.34
O
OH
Me
Me
S9-3
Parameter Value
1 Title FO-01-075
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 13
5 Receiver Gain 101
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
0.92 1.00 0.73 0.95 1.01 1.99 3.09 2.88 5.03 2.16
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 0.0

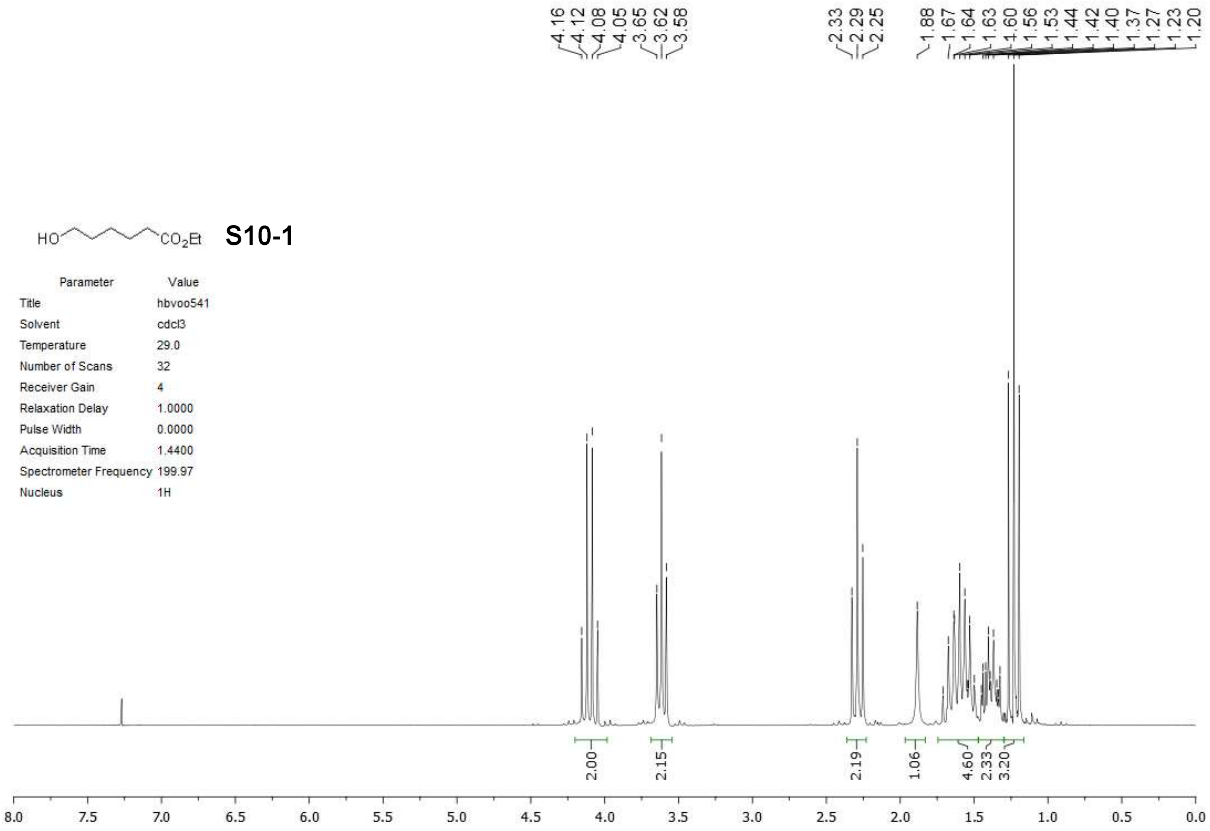

211.43 131.80 124.34 79.44 47.80 39.35 33.29 28.96 26.18 25.83 25.16 17.81
O
OH
Me
Me
S9-3
Parameter Value
1 Title FO-01-075
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 32
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5680
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

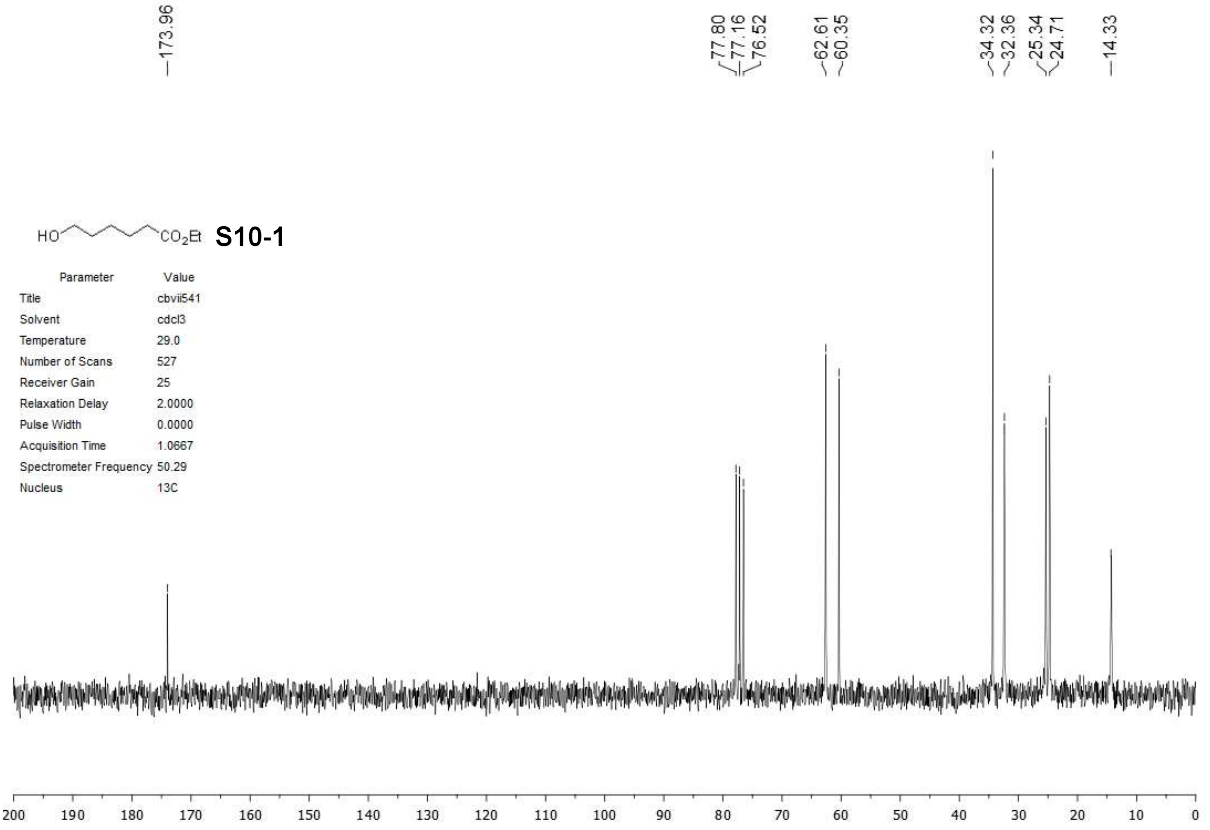


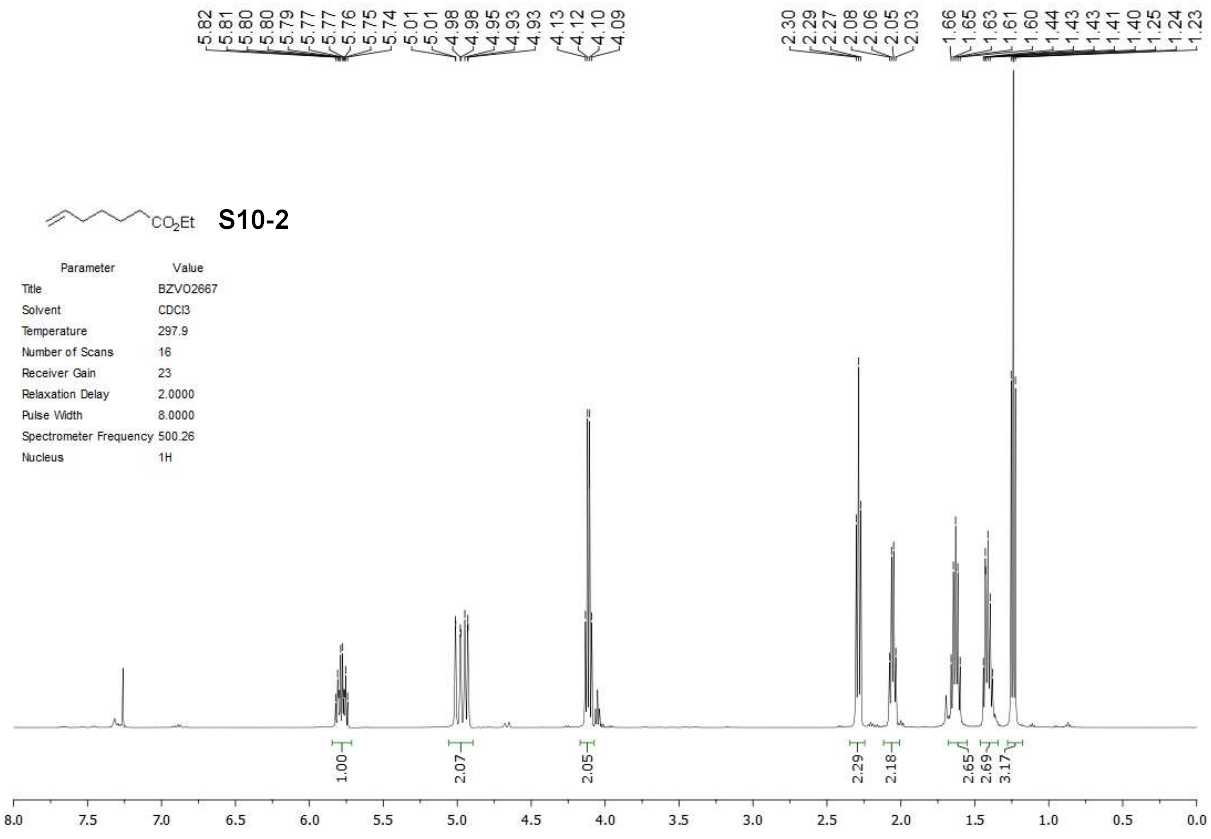
	Parameter	Value
1	Title	FO-1-77
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	16
5	Receiver Gain	64
6	Relaxation Delay	2.0000
7	Pulse Width	10.0000
8	Acquisition Time	3.6351
9	Spectrometer Frequency	500.26
10	Nucleus	1H

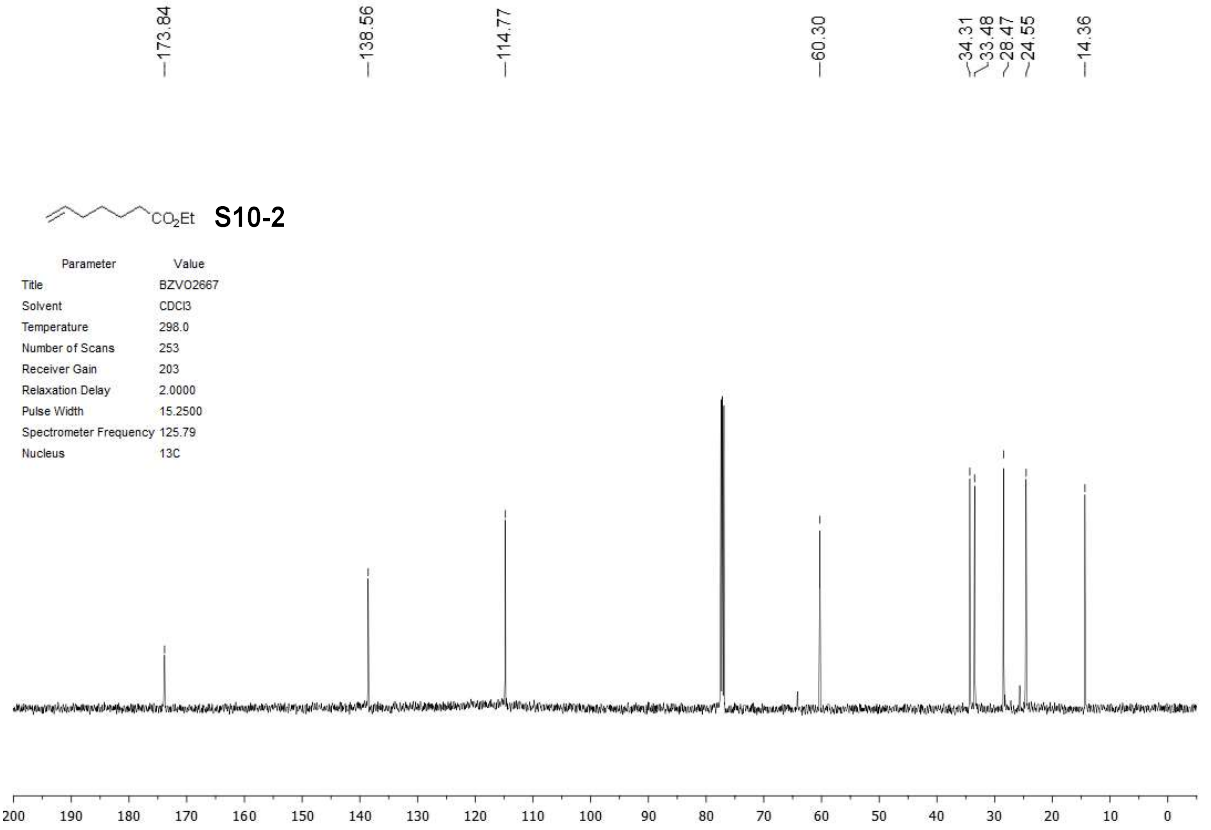


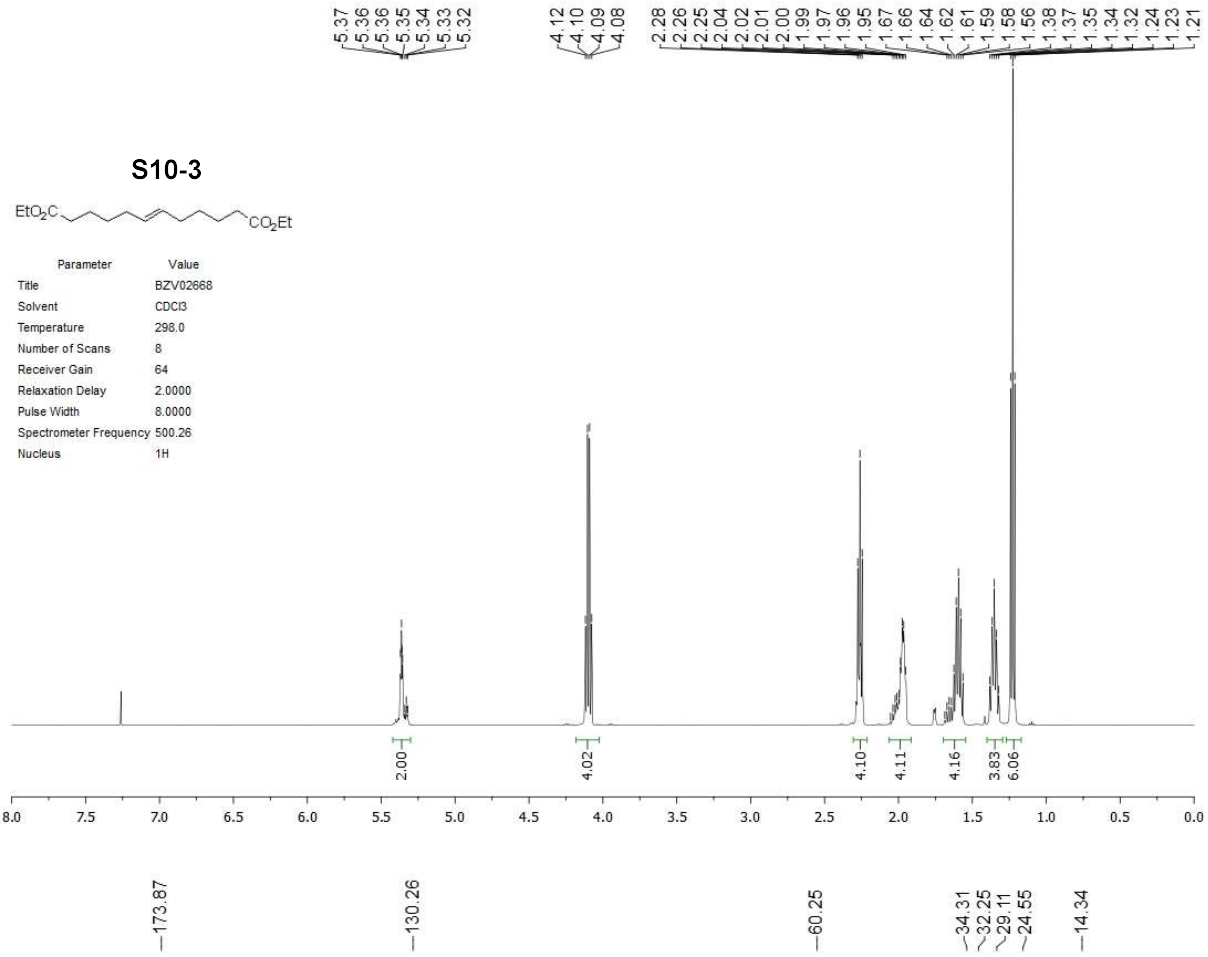
	Parameter	Value
1	Title	FO-1-77
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	140
5	Receiver Gain	203
6	Relaxation Delay	2.0000
7	Pulse Width	11.5000
8	Acquisition Time	0.5505
9	Spectrometer Frequency	125.79
10	Nucleus	13C


4.16
4.12
4.08
4.05
3.65
3.62
3.58
2.33
2.29
2.25
1.88
1.67
1.64
1.63
1.60
1.56
1.53
1.44
1.42
1.40
1.37
1.27
1.23
1.20
HO
CO2Et
S10-1
Parameter Value
Title hbvoo541
Solvent cdcl3
Temperature 29.0
Number of Scans 32
Receiver Gain 4
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.4400
Spectrometer Frequency 199.97
Nucleus 1H
2.00
2.15
2.19
1.06
4.60
2.33
3.20
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

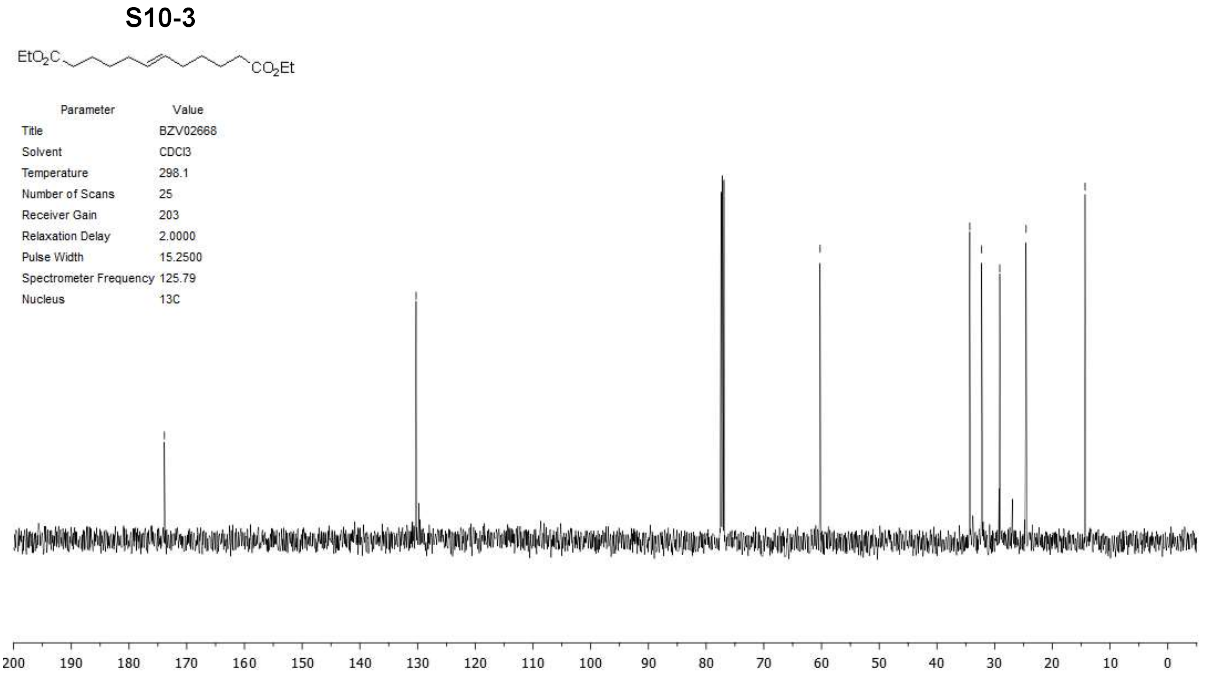

173.96
77.80
77.16
76.52
62.61
60.35
34.32
32.36
25.34
24.71
14.33
HO
CO2Et
S10-1
Parameter Value
Title cbvii541
Solvent cdcl3
Temperature 29.0
Number of Scans 527
Receiver Gain 25
Relaxation Delay 2.0000
Pulse Width 0.0000
Acquisition Time 1.0667
Spectrometer Frequency 50.29
Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

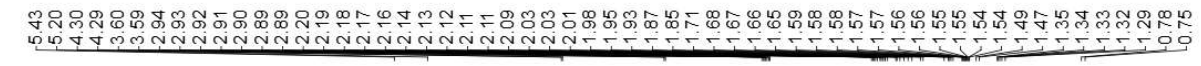

5.82
5.81
5.80
5.80
5.79
5.77
5.77
5.76
5.75
5.74
5.01
5.01
4.98
4.98
4.95
4.93
4.93
4.13
4.12
4.10
4.09
2.30
2.29
2.27
2.08
2.06
2.05
2.03
1.66
1.65
1.63
1.61
1.60
1.44
1.43
1.43
1.41
1.40
1.25
1.24
1.23
CO2Et
S10-2
Parameter Value
Title BZVO2667
Solvent CDCl3
Temperature 297.9
Number of Scans 16
Receiver Gain 23
Relaxation Delay 2.0000
Pulse Width 8.0000
Spectrometer Frequency 500.26
Nucleus 1H
1.00
2.07
2.05
2.29
2.18
2.65
2.69
3.17
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

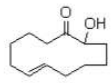

173.84
138.56
114.77
60.30
34.31
33.48
28.47
24.55
14.36
CO2Et
S10-2
Parameter Value
Title BZVO2667
Solvent CDCl3
Temperature 298.0
Number of Scans 253
Receiver Gain 203
Relaxation Delay 2.0000
Pulse Width 15.2500
Spectrometer Frequency 125.79
Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


S10-3
EtO2C
CO2Et
Parameter Value
Title BZV02668
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Receiver Gain 64
Relaxation Delay 2.0000
Pulse Width 8.0000
Spectrometer Frequency 500.26
Nucleus 1H
5.37 5.36 5.36 5.35 5.34 5.33 5.32
4.12 4.10 4.09 4.08
2.28 2.26 2.25 2.04 2.02 2.01 2.00 1.99 1.97 1.96 1.95 1.67 1.66 1.64 1.62 1.61 1.59 1.58 1.56 1.38 1.37 1.35 1.34 1.32 1.24 1.23 1.21
2.00 4.02 4.10 4.11 4.16 3.83 6.06
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

173.87
130.26
60.25
34.31
32.25
29.11
24.55
14.34

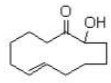

S10-3
EtO2C
CO2Et
Parameter Value
Title BZV02668
Solvent CDCl3
Temperature 298.1
Number of Scans 25
Receiver Gain 203
Relaxation Delay 2.0000
Pulse Width 15.2500
Spectrometer Frequency 125.79
Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0





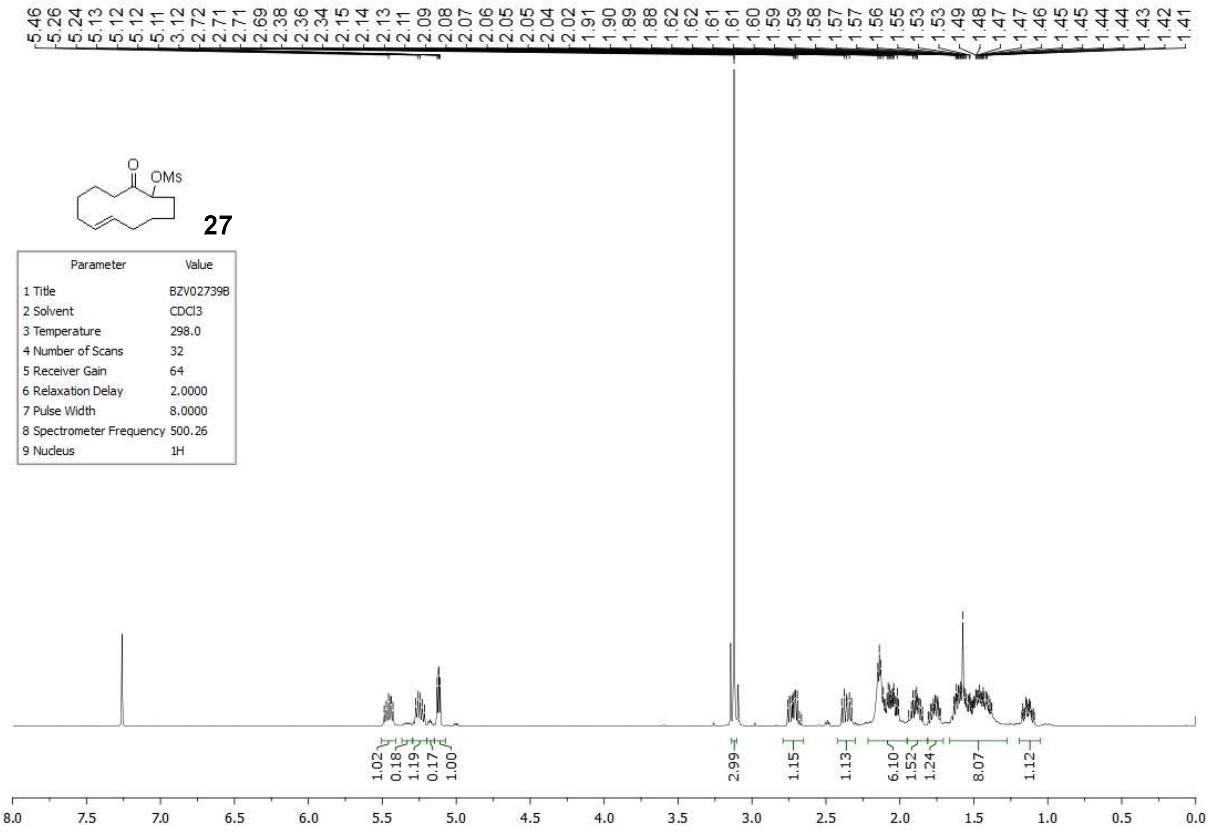
S10-4

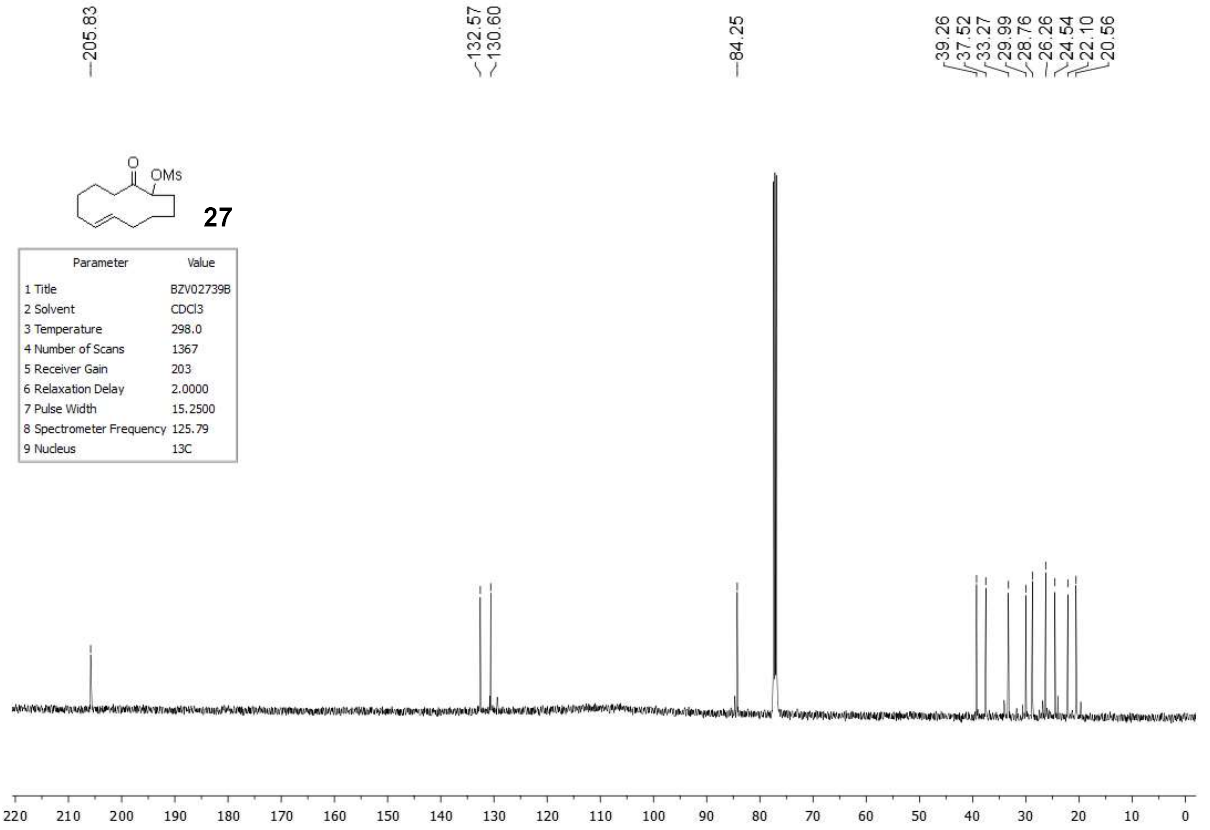
	Parameter	Value
1	Title	BZV02729A
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	16
5	Receiver Gain	64
6	Relaxation Delay	2.0000
7	Pulse Width	8.0000
8	Acquisition Time	1.6384
9	Spectrometer Frequency	500.26
10	Nucleus	1H

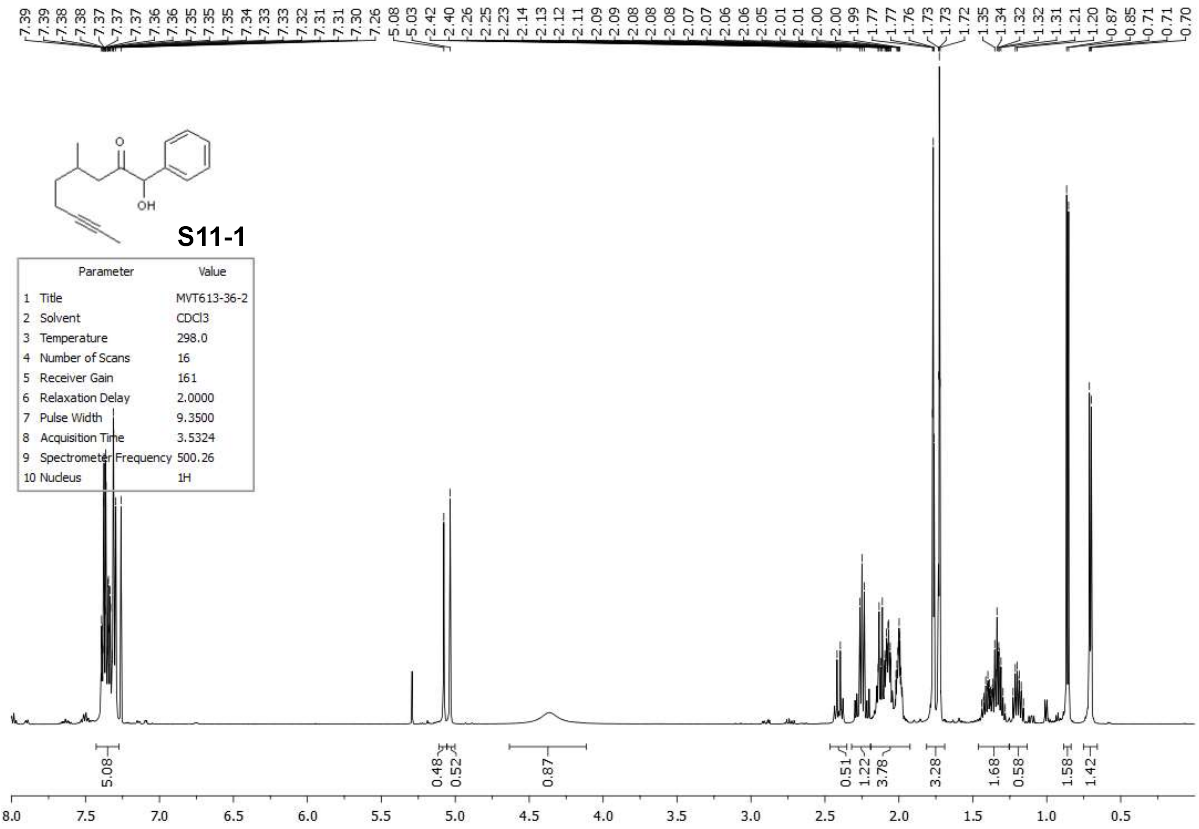


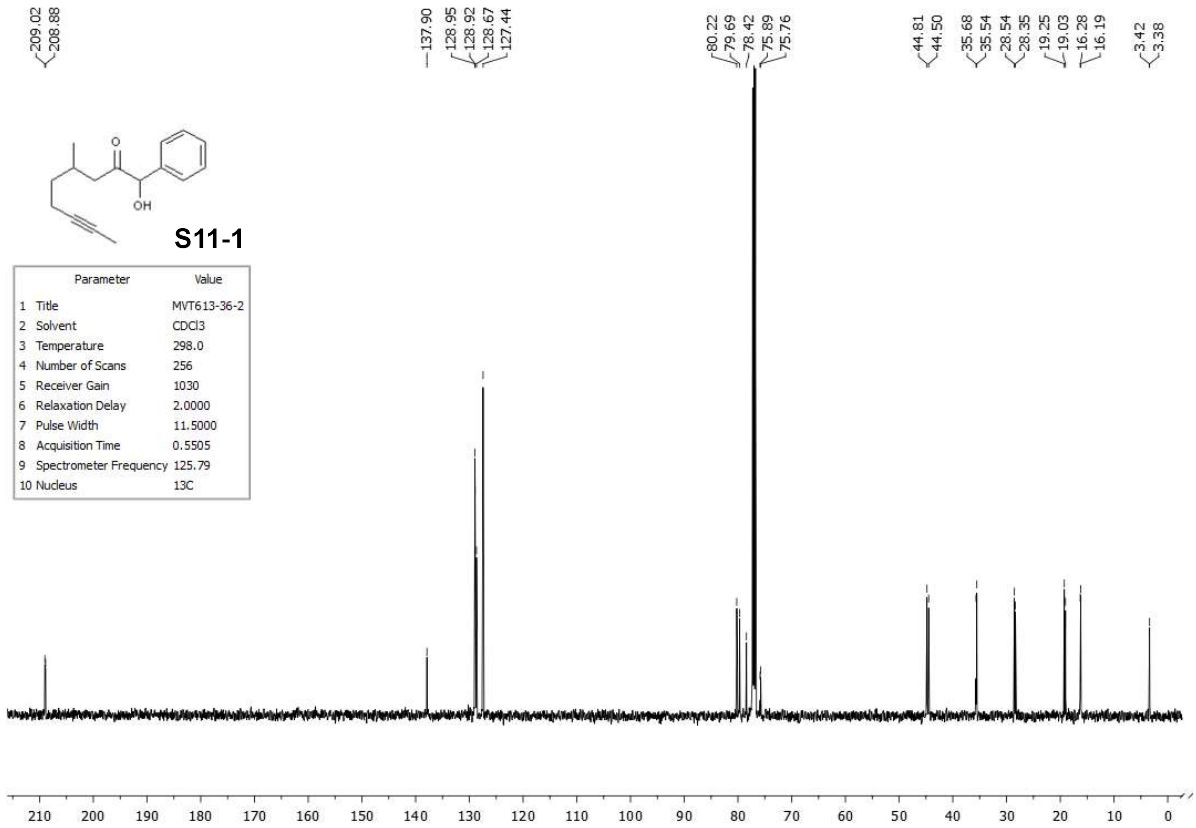
S10-4

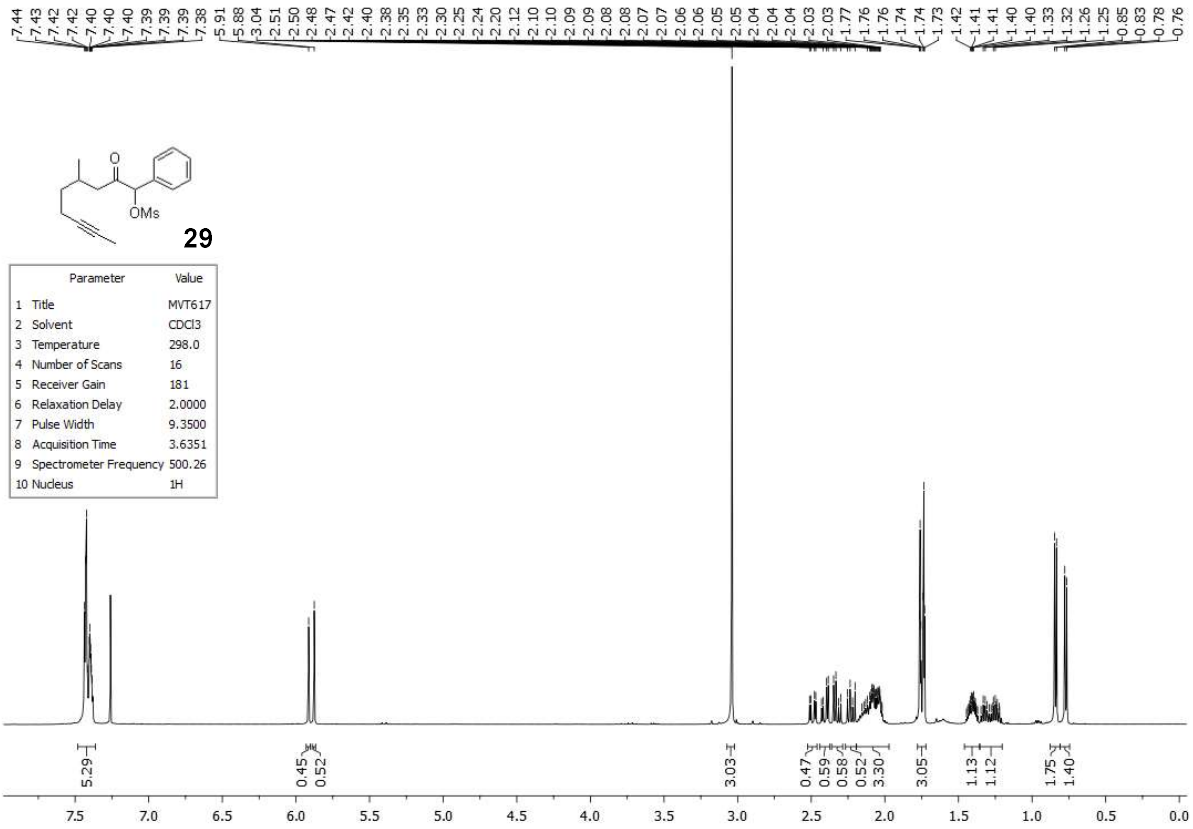
	Parameter	Value
1	Title	BZV02729A
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	325
5	Receiver Gain	203
6	Relaxation Delay	2.0000
7	Pulse Width	15.2500
8	Acquisition Time	0.5505
9	Spectrometer Frequency	125.79
10	Nucleus	13C

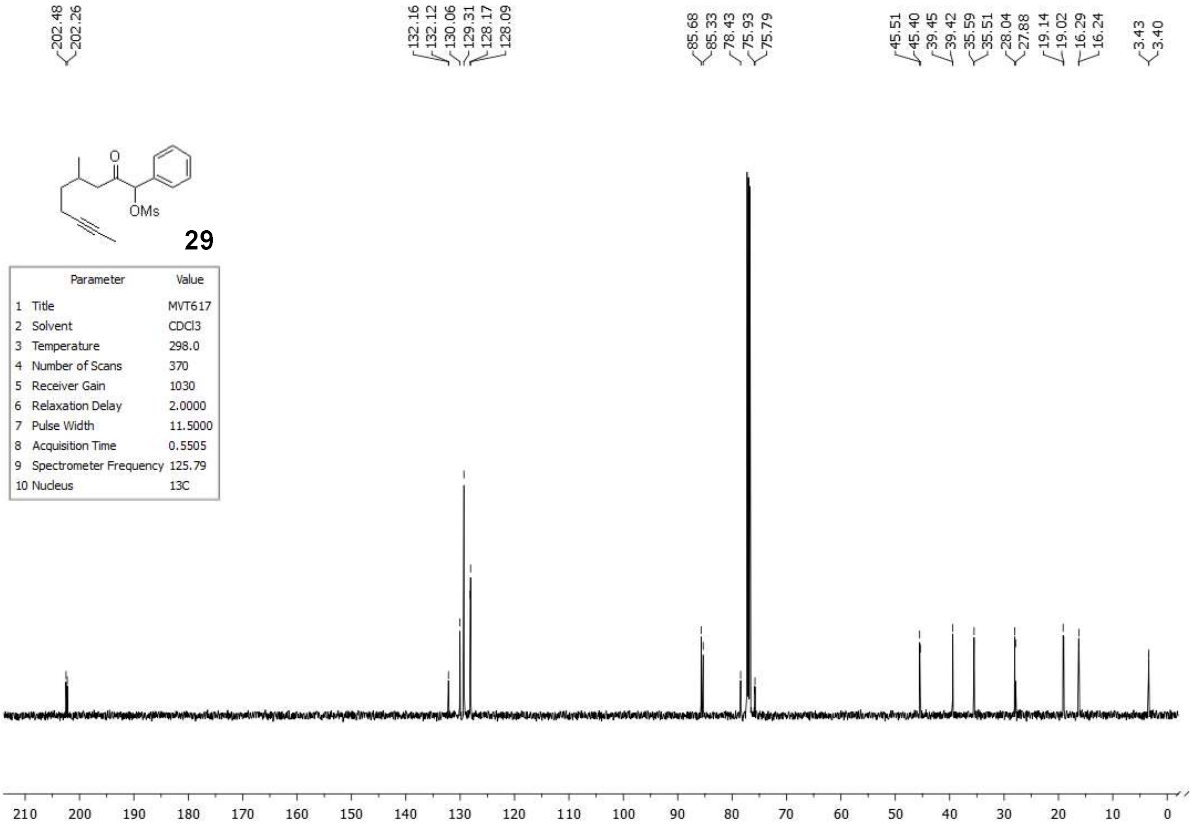

5.46 5.26 5.24 5.13 5.12 5.12 5.11 3.12 2.72 2.71 2.71 2.69 2.38 2.36 2.34 2.15 2.14 2.13 2.11 2.09 2.08 2.07 2.06 2.05 2.05 2.04 2.02 1.91 1.90 1.89 1.88 1.62 1.62 1.61 1.61 1.60 1.59 1.59 1.58 1.57 1.57 1.56 1.55 1.53 1.53 1.49 1.48 1.47 1.47 1.46 1.45 1.45 1.44 1.44 1.43 1.42 1.41
O
OMs
27
Parameter Value
1 Title BZV02739B
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 32
5 Receiver Gain 64
6 Relaxation Delay 2.0000
7 Pulse Width 8.0000
8 Spectrometer Frequency 500.26
9 Nucleus 1H
1.02 0.18 1.19 0.17 1.00 2.99 1.15 1.13 6.10 1.52 1.24 8.07 1.12
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

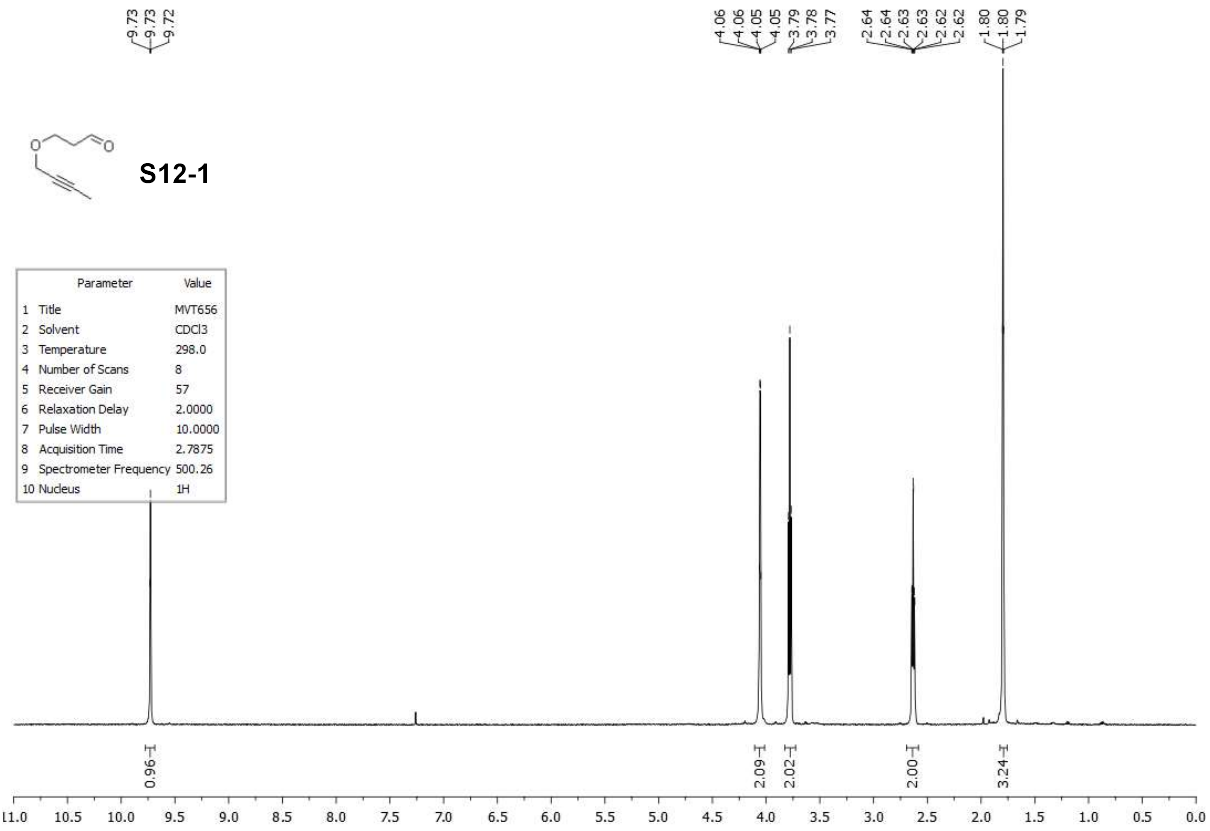

205.83
132.57
130.60
84.25
39.26
37.52
33.27
29.99
28.76
26.26
24.54
22.10
20.56
O
OMs
27
Parameter Value
1 Title BZV02739B
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 1367
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 15.2500
8 Spectrometer Frequency 125.79
9 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

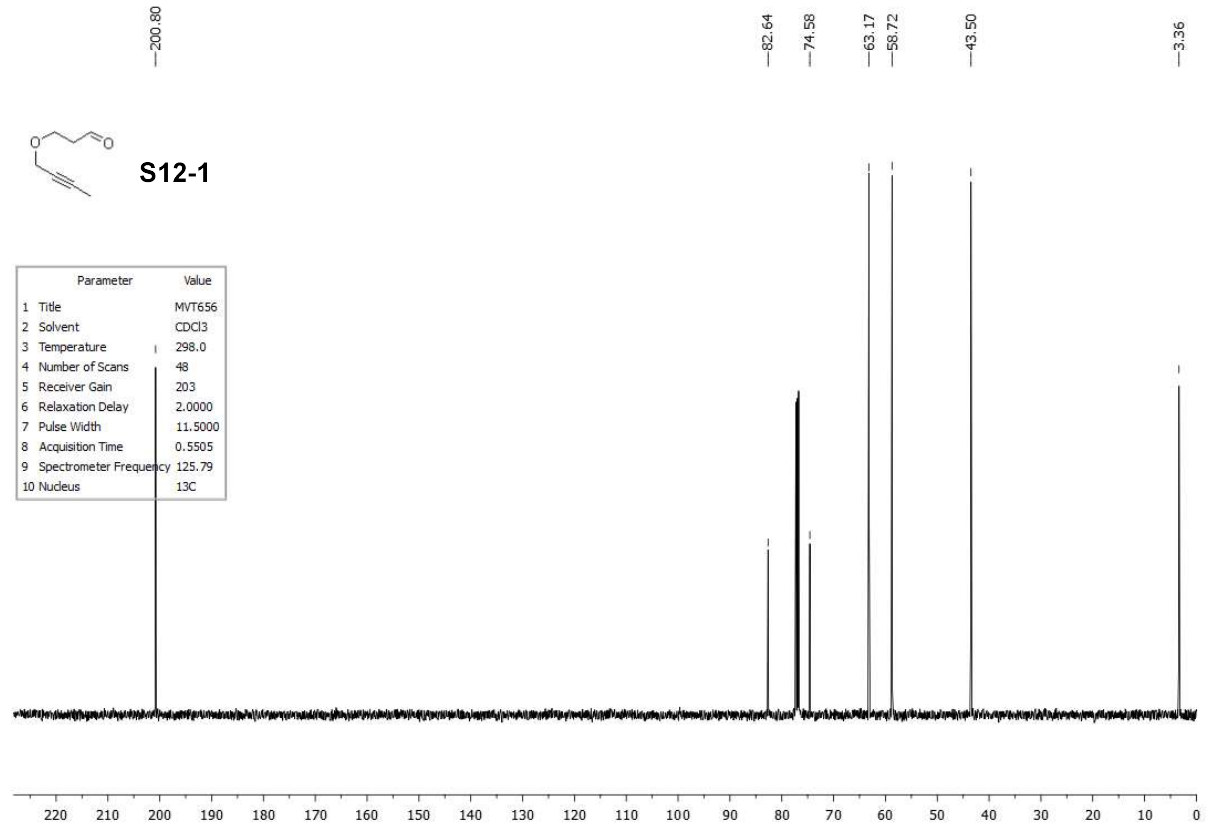

S11-1
Parameter Value
1 Title MVT613-36-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 161
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.5324
9 Spectrometer Frequency 500.26
10 Nucleus 1H

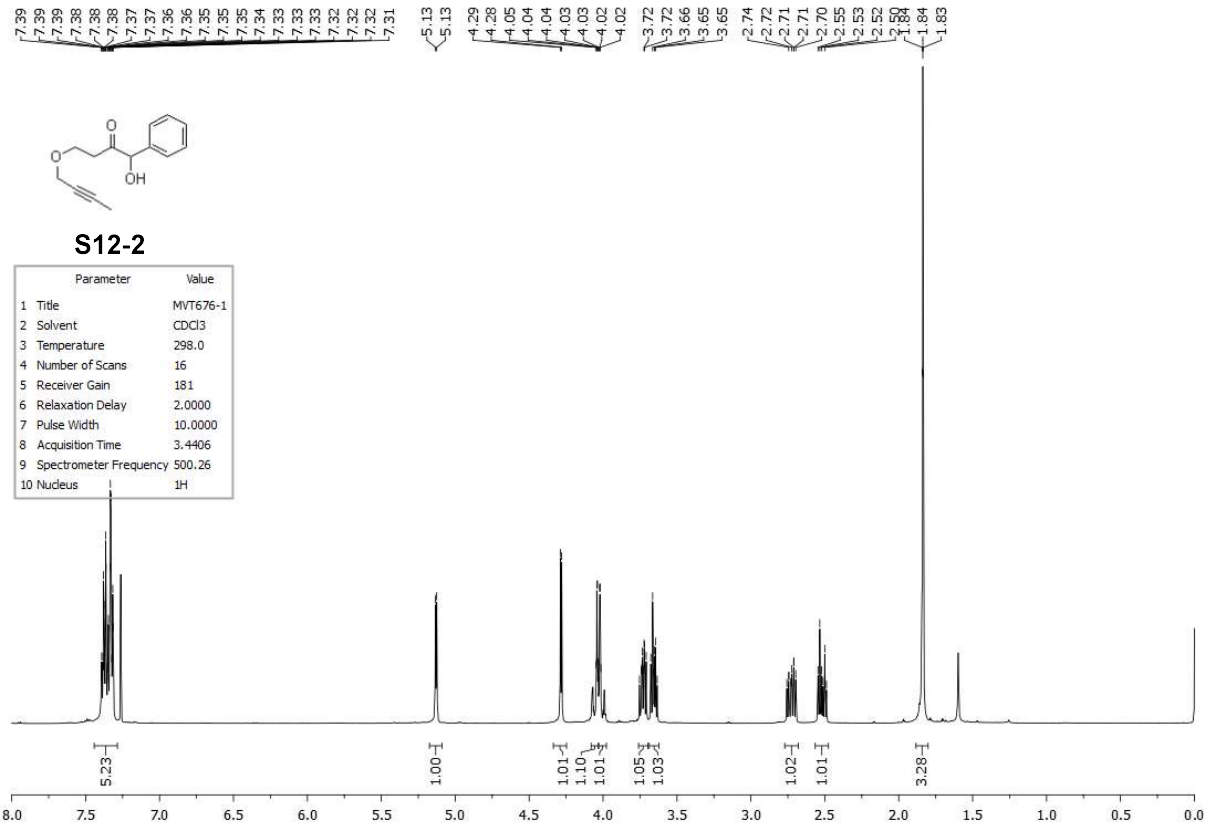

S11-1
Parameter Value
1 Title MVT613-36-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 256
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

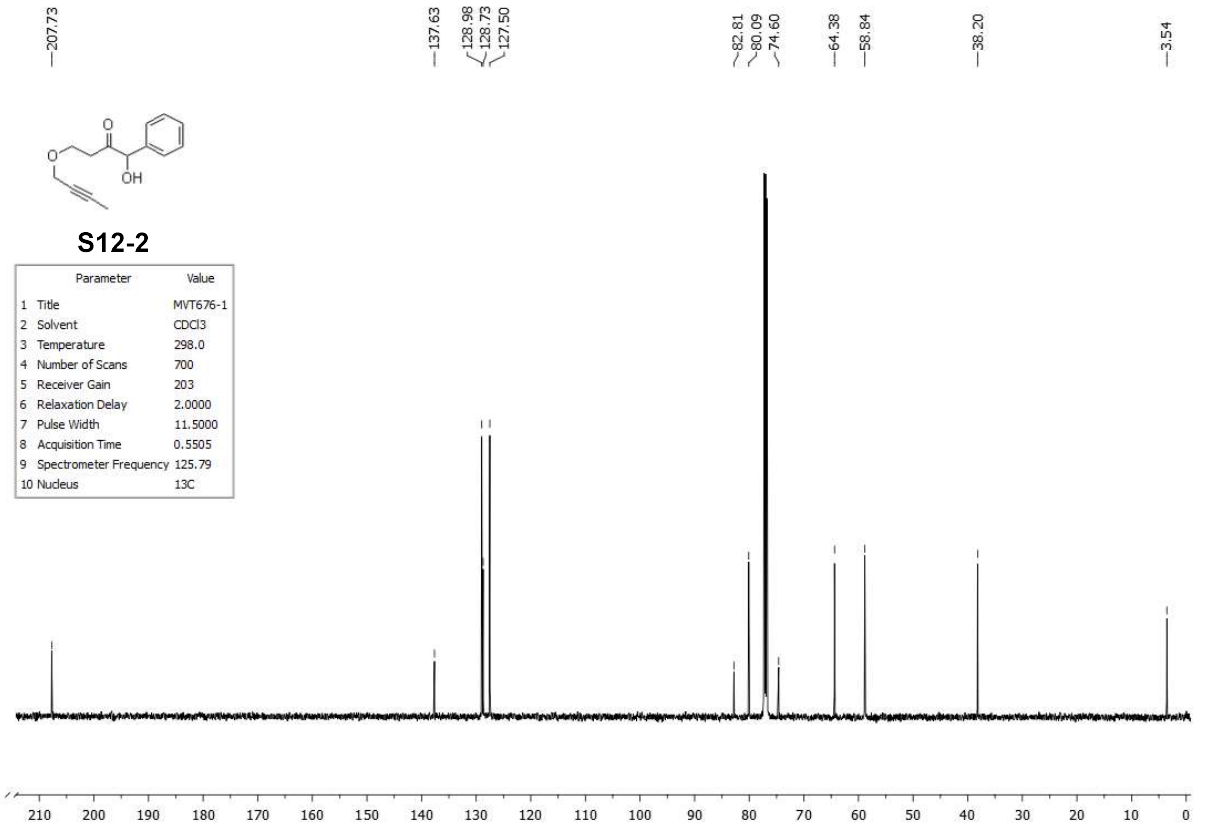

7.44 7.43 7.42 7.42 7.40 7.40 7.40 7.39 7.39 7.39 7.38 5.91 5.88 3.04 2.51 2.50 2.48 2.47 2.42 2.40 2.38 2.35 2.33 2.30 2.25 2.24 2.20 2.12 2.10 2.10 2.09 2.09 2.08 2.08 2.07 2.07 2.06 2.06 2.05 2.05 2.04 2.04 2.04 2.03 2.03 1.77 1.76 1.76 1.74 1.74 1.73 1.42 1.41 1.41 1.40 1.40 1.33 1.32 1.26 1.25 0.85 0.83 0.78 0.76
O
OMs
29
Parameter Value
1 Title MVT617
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 181
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.6351
9 Spectrometer Frequency 500.26
10 Nucleus 1H
5.29
0.45
0.52
3.03
0.47
0.59
0.58
0.52
3.30
3.05
1.13
1.12
1.75
1.40
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

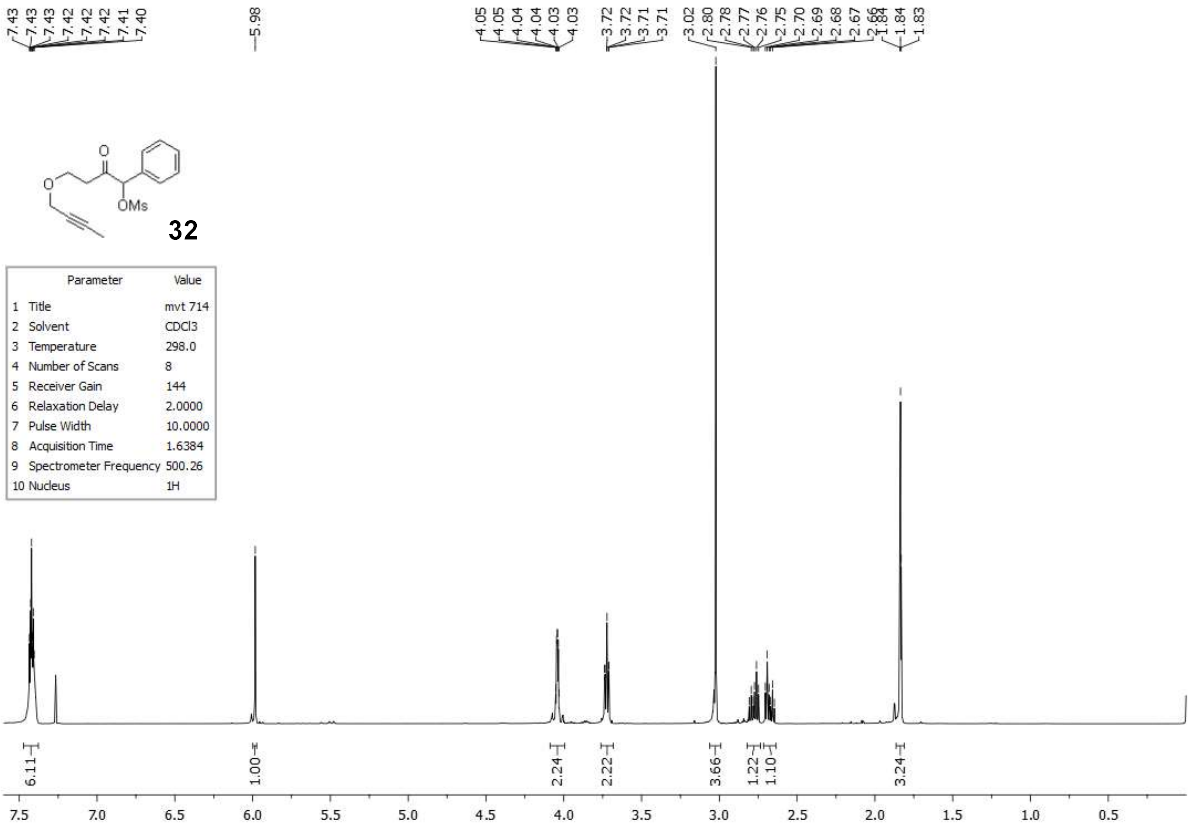

202.48 202.26 132.16 132.12 130.06 129.31 128.17 128.09 85.68 85.33 78.43 75.93 75.79 45.51 45.40 39.45 39.42 35.59 35.51 28.04 27.88 19.14 19.02 16.29 16.24 3.43 3.40
O
OMs
29
Parameter Value
1 Title MVT617
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 370
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

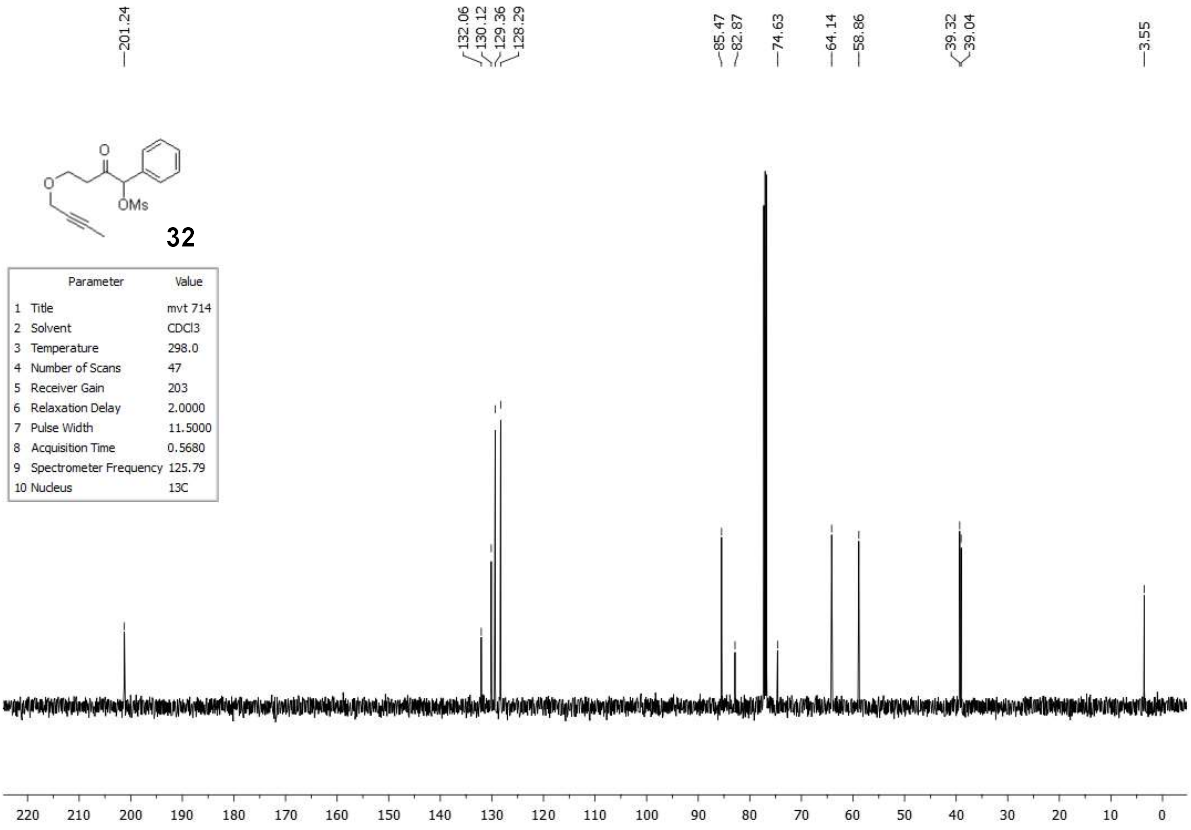

9.73
9.73
9.72
4.06
4.06
4.05
4.05
3.79
3.78
3.77
2.64
2.64
2.63
2.63
2.62
2.62
1.80
1.80
1.79
S12-1
Parameter Value
1 Title MVT656
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 8
5 Receiver Gain 57
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 2.7875
9 Spectrometer Frequency 500.26
10 Nucleus 1H
0.96
2.09
2.02
2.00
3.24
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

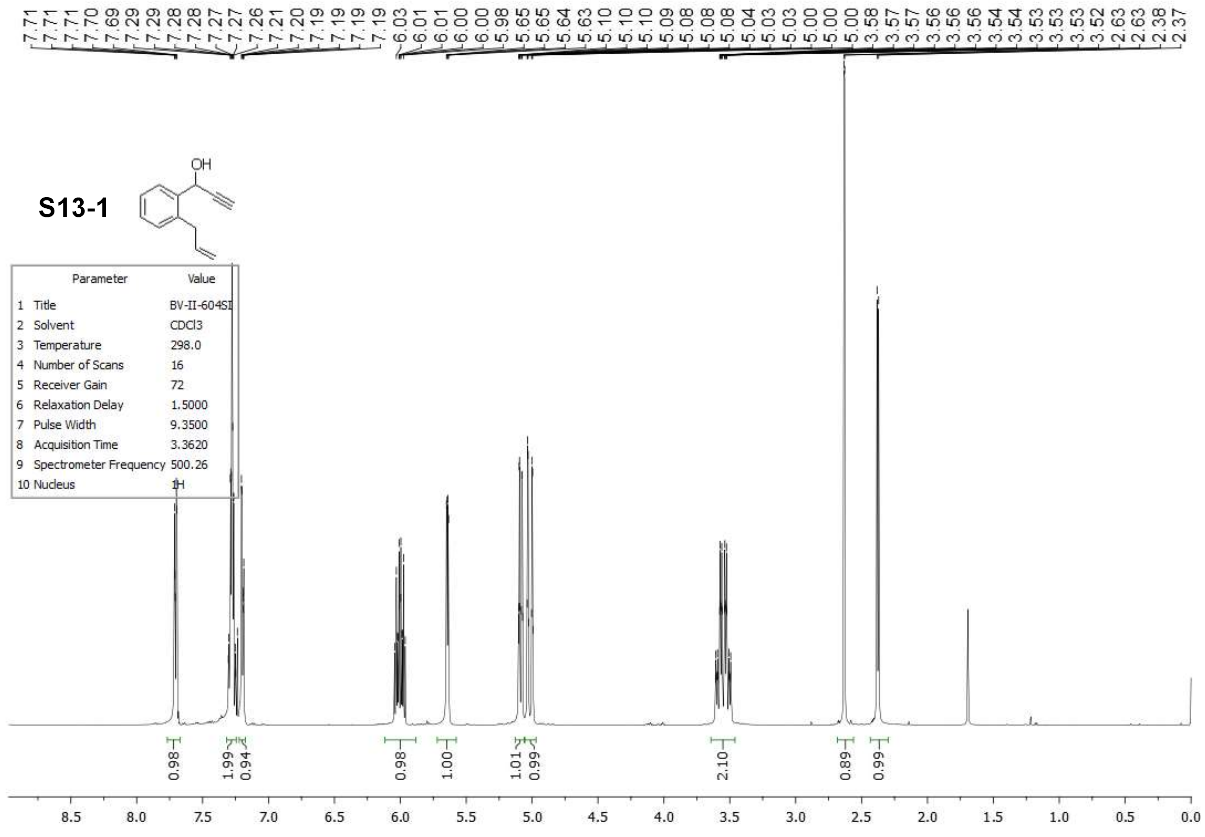

200.80
82.64
74.58
63.17
58.72
43.50
3.36
S12-1
Parameter Value
1 Title MVT656
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 48
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

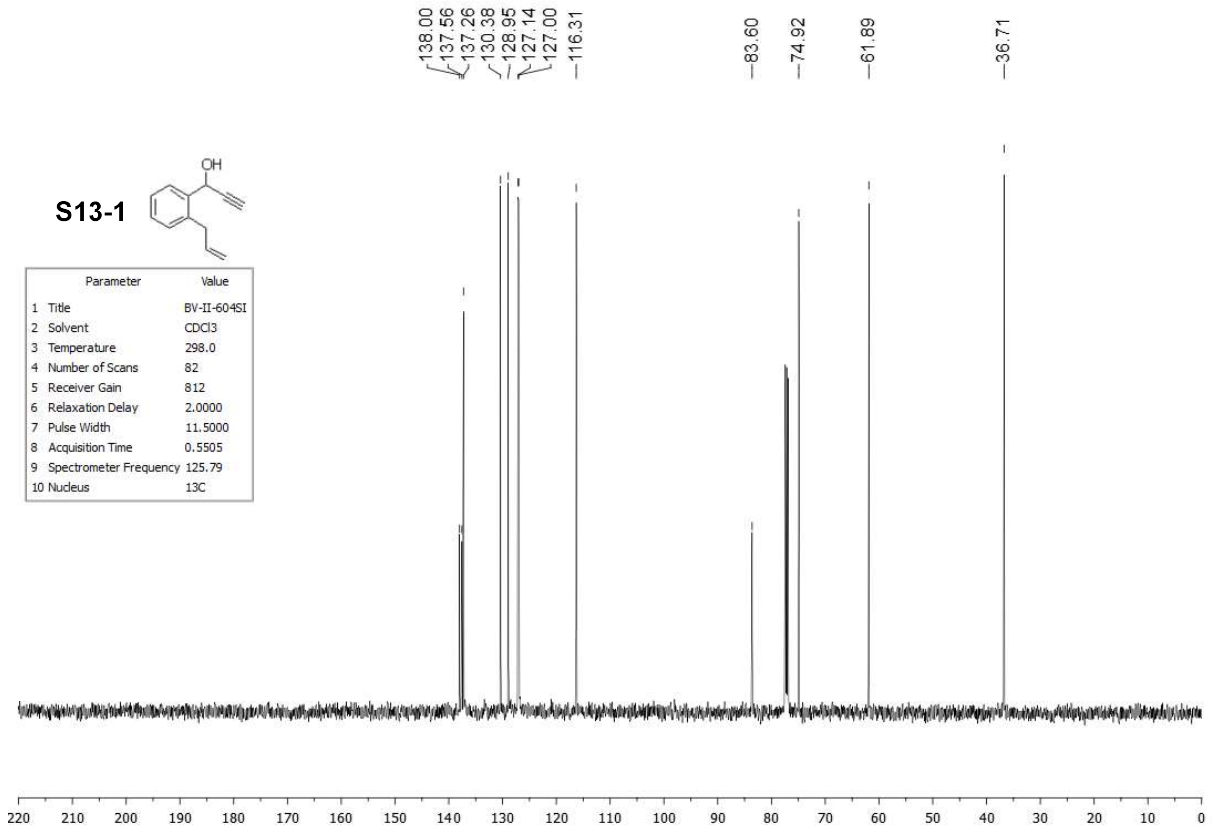

7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31
5.13 5.13
4.29 4.28 4.05 4.04 4.04 4.03 4.03 4.02 4.02
3.72 3.72 3.66 3.65 3.65
2.74 2.72 2.71 2.71 2.70 2.55 2.53 2.52 2.50 1.84 1.84 1.83
O
O
OH
S12-2
Parameter Value
1 Title MVT676-1
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 181
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 3.4406
9 Spectrometer Frequency 500.26
10 Nucleus 1H
5.23 1.00 1.01 1.10 1.01 1.05 1.03 1.02 1.01 3.28
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

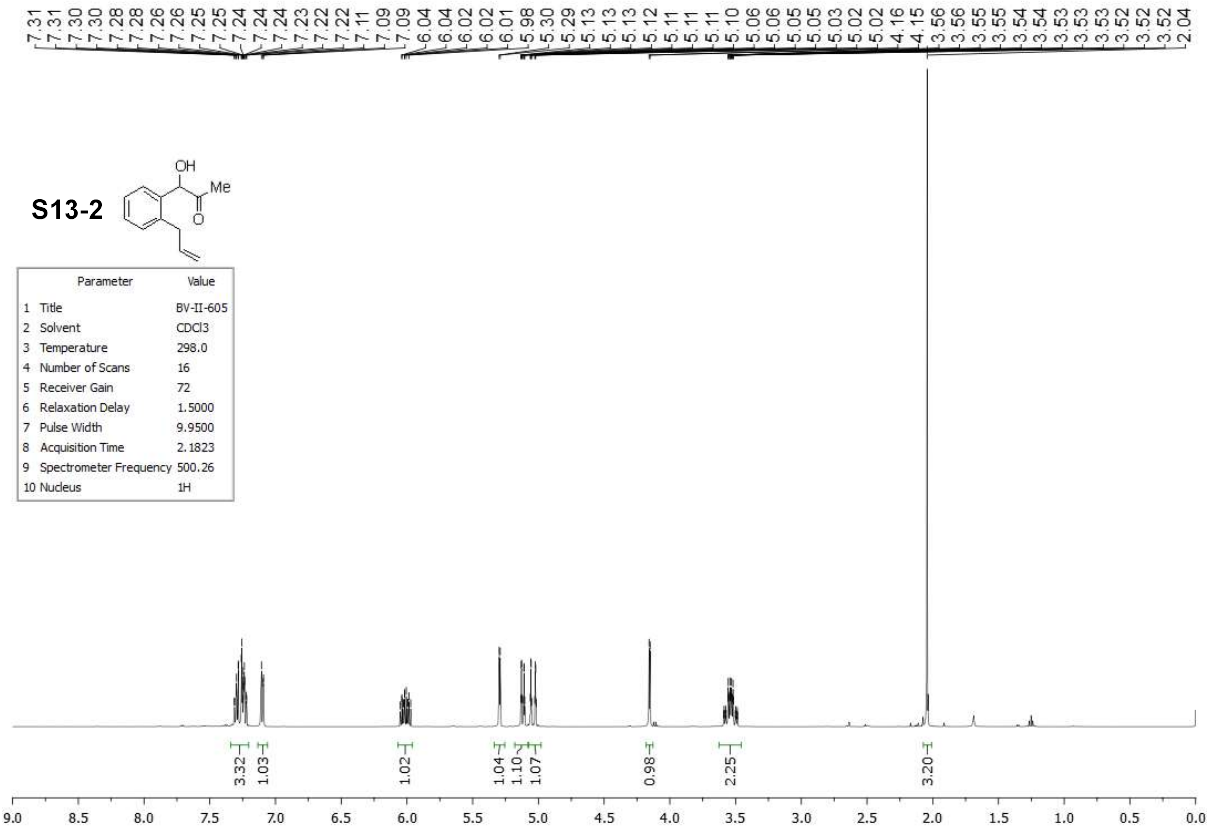

207.73
137.63
128.98 128.73 127.50
82.81 80.09 74.60
64.38 58.84
38.20
3.54
O
O
OH
S12-2
Parameter Value
1 Title MVT676-1
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 700
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

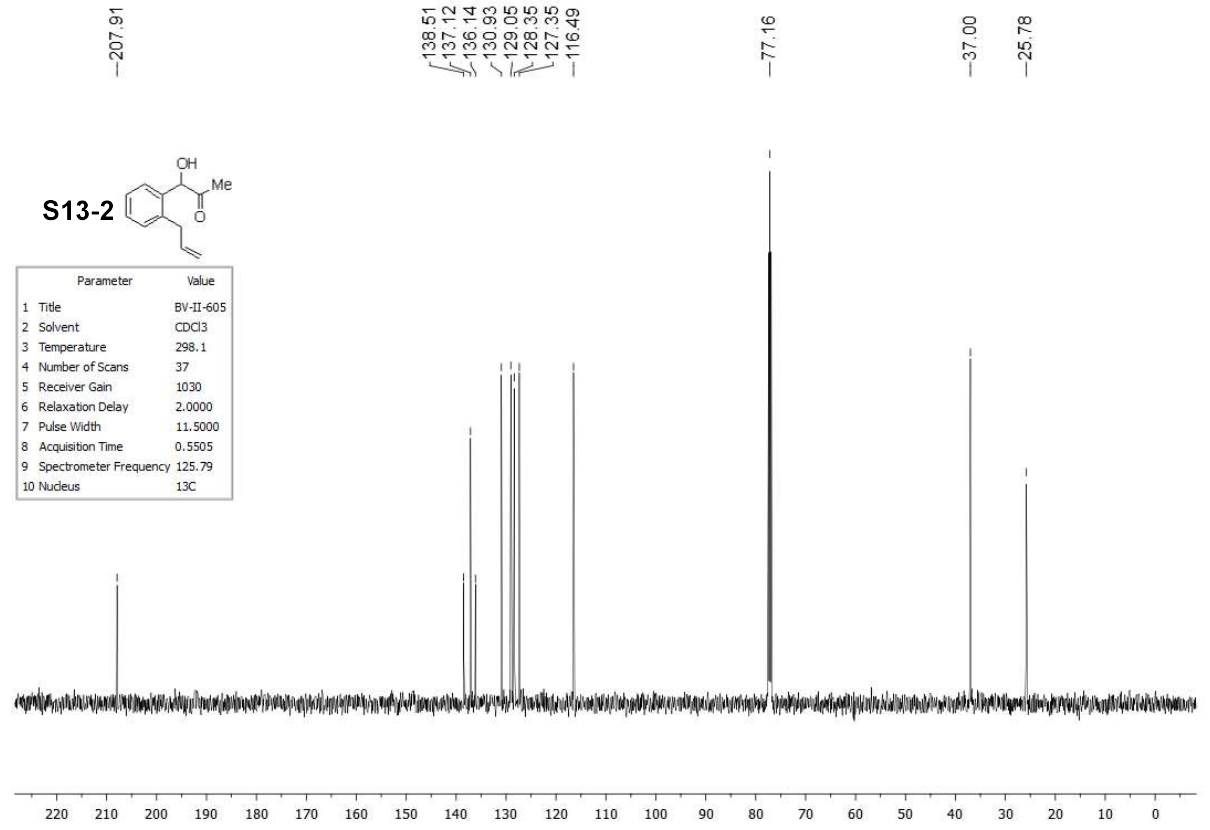

7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.40
5.98
4.05
4.05
4.04
4.04
4.03
4.03
3.72
3.72
3.71
3.71
3.02
2.80
2.78
2.77
2.76
2.75
2.70
2.69
2.68
2.67
1.84
1.84
1.83
O
O
OMs
32
Parameter Value
1 Title mvt 714
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 8
5 Receiver Gain 144
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
6.11
1.00
2.24
2.22
3.66
1.22
1.10
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

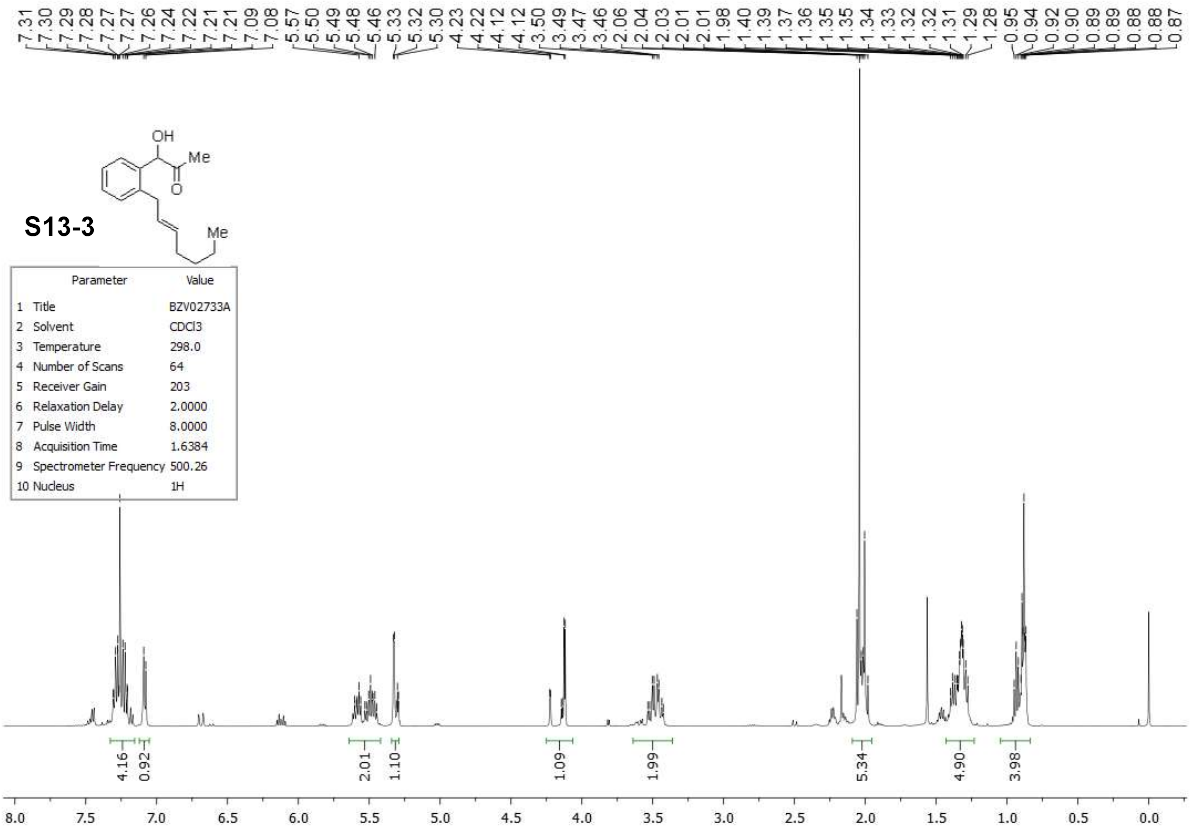

201.24
132.06
130.12
129.36
128.29
85.47
82.87
74.63
64.14
58.86
39.32
39.04
3.55
O
O
OMs
32
Parameter Value
1 Title mvt 714
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 47
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5680
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

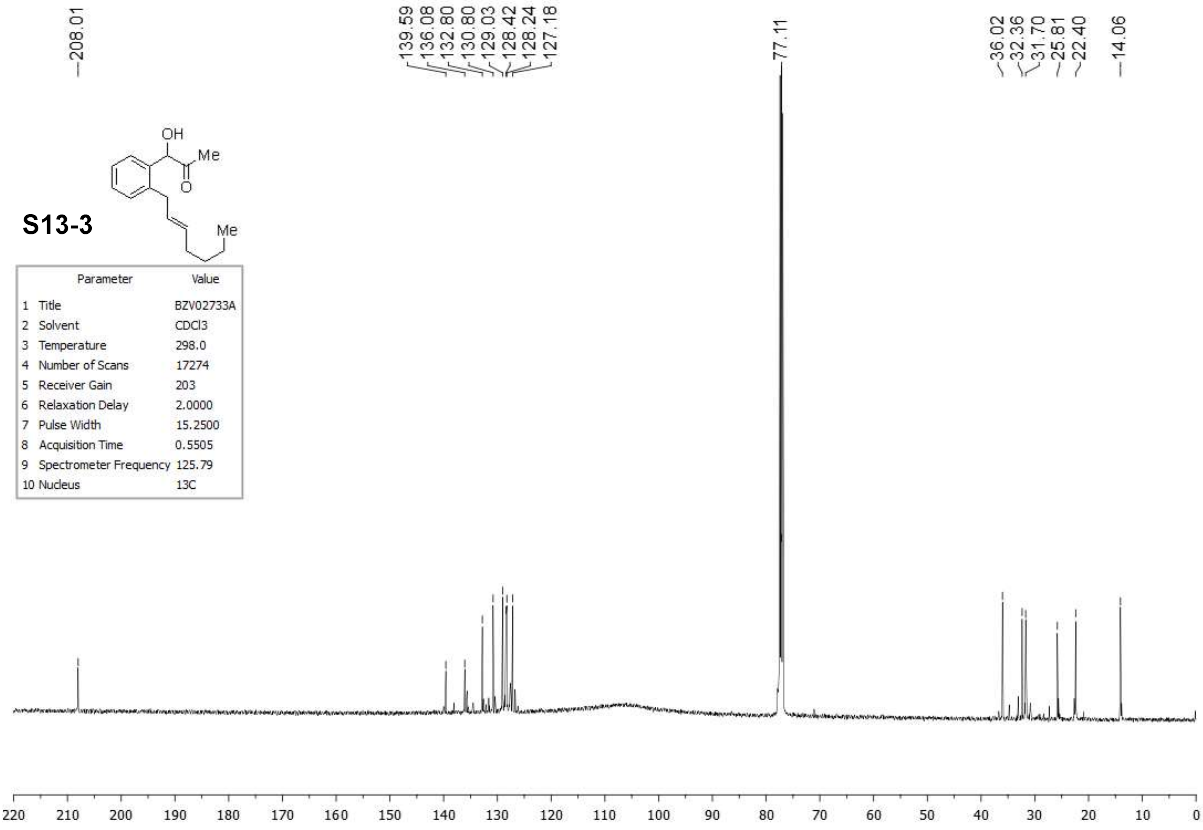

S13-1
OH
Parameter Value
1 Title BV-II-604SI
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 72
6 Relaxation Delay 1.5000
7 Pulse Width 9.3500
8 Acquisition Time 3.3620
9 Spectrometer Frequency 500.26
10 Nucleus 1H

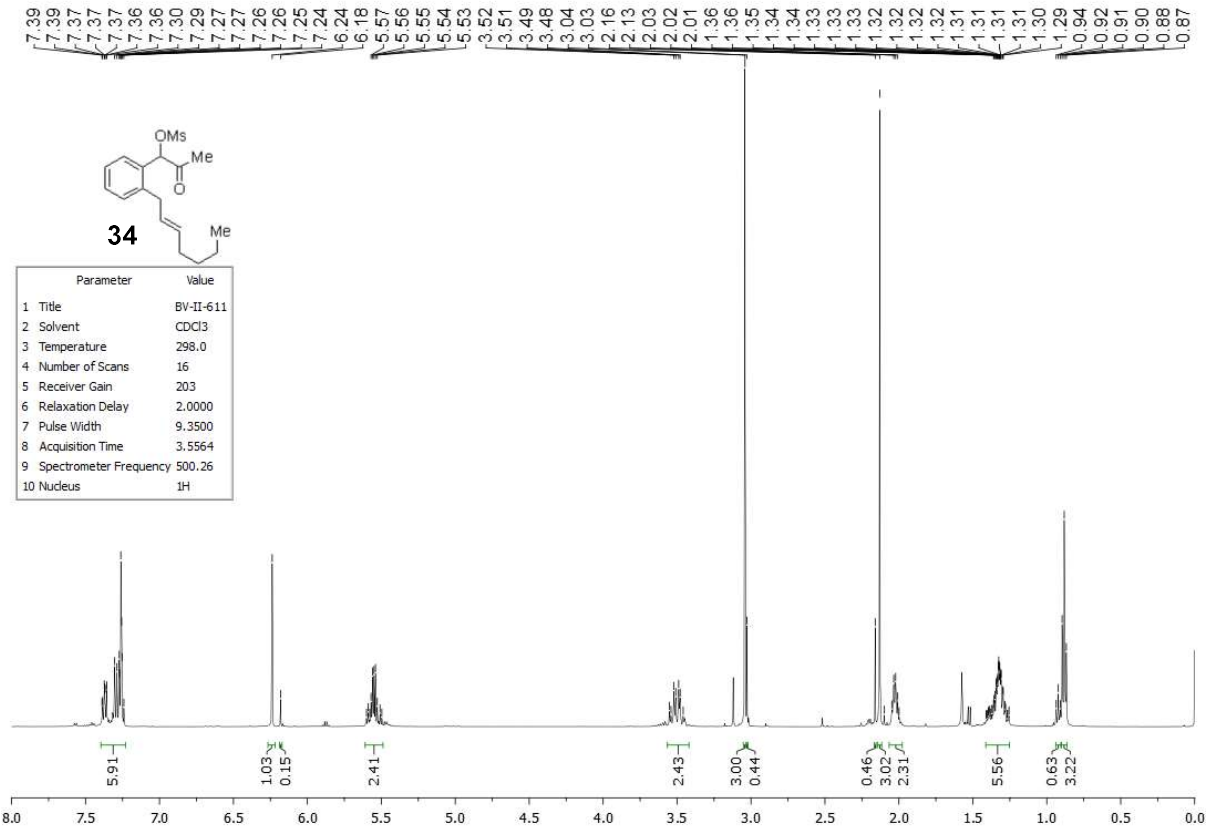

S13-1
OH
Parameter Value
1 Title BV-II-604SI
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 82
5 Receiver Gain 812
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

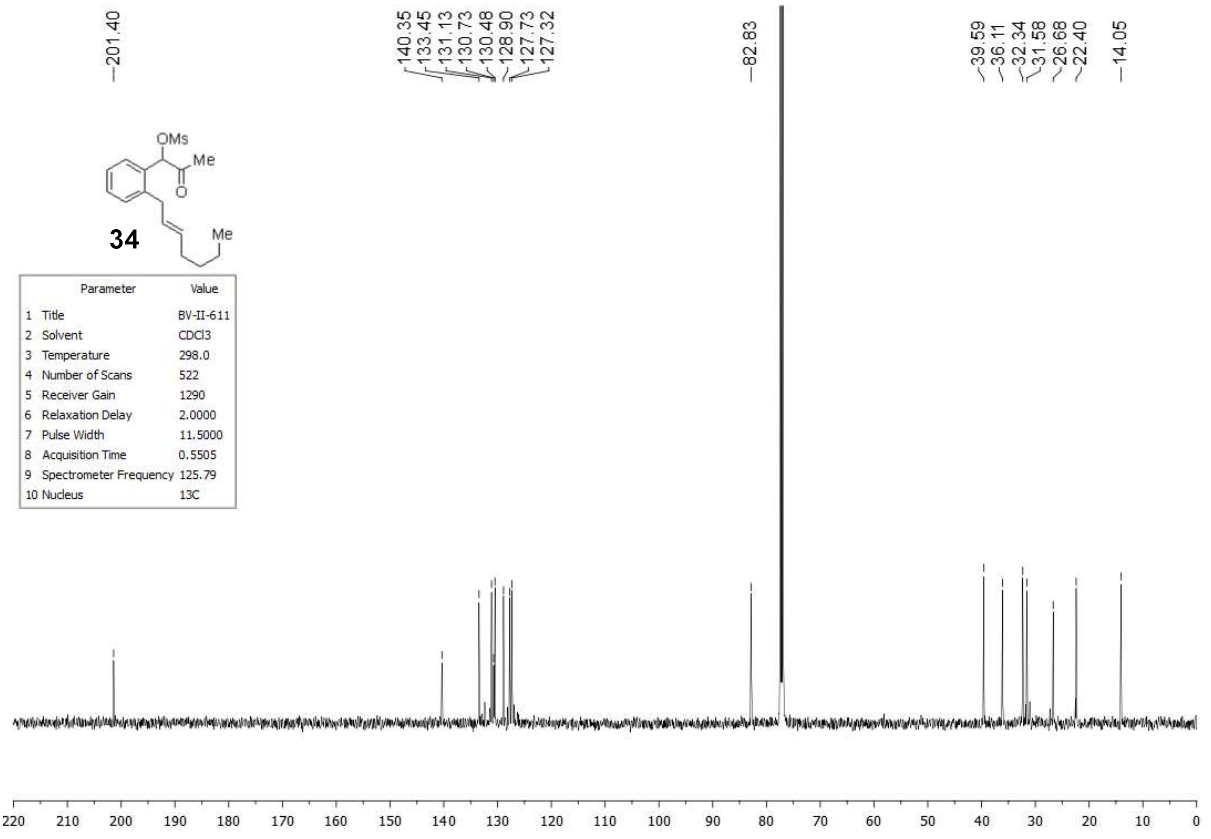

S13-2
OH
Me
O
Parameter Value
1 Title BV-II-605
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 72
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 2.1823
9 Spectrometer Frequency 500.26
10 Nucleus 1H
3.32
1.03
1.02
1.04
1.10
1.07
0.98
2.25
3.20

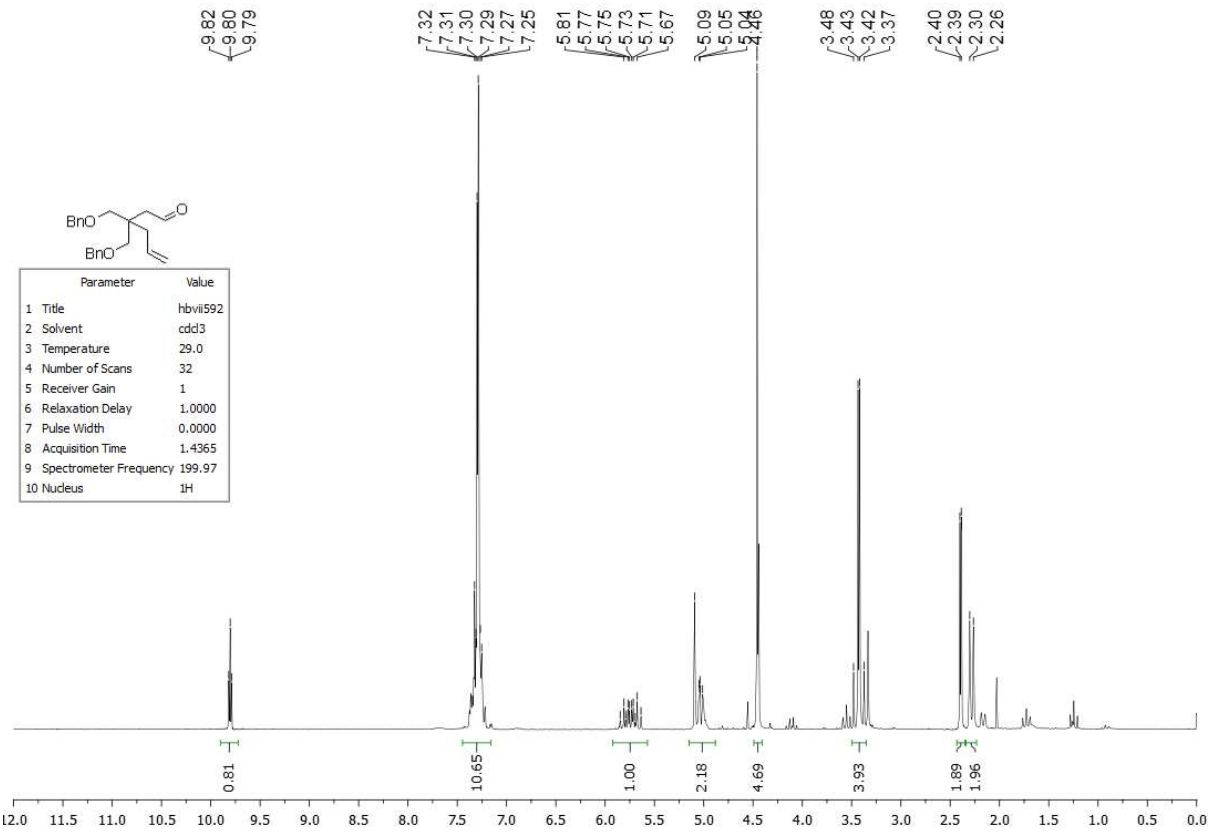

S13-2
OH
Me
O
Parameter Value
1 Title BV-II-605
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 37
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
207.91
138.51
137.12
136.14
130.93
129.05
128.35
127.35
116.49
77.16
37.00
25.78

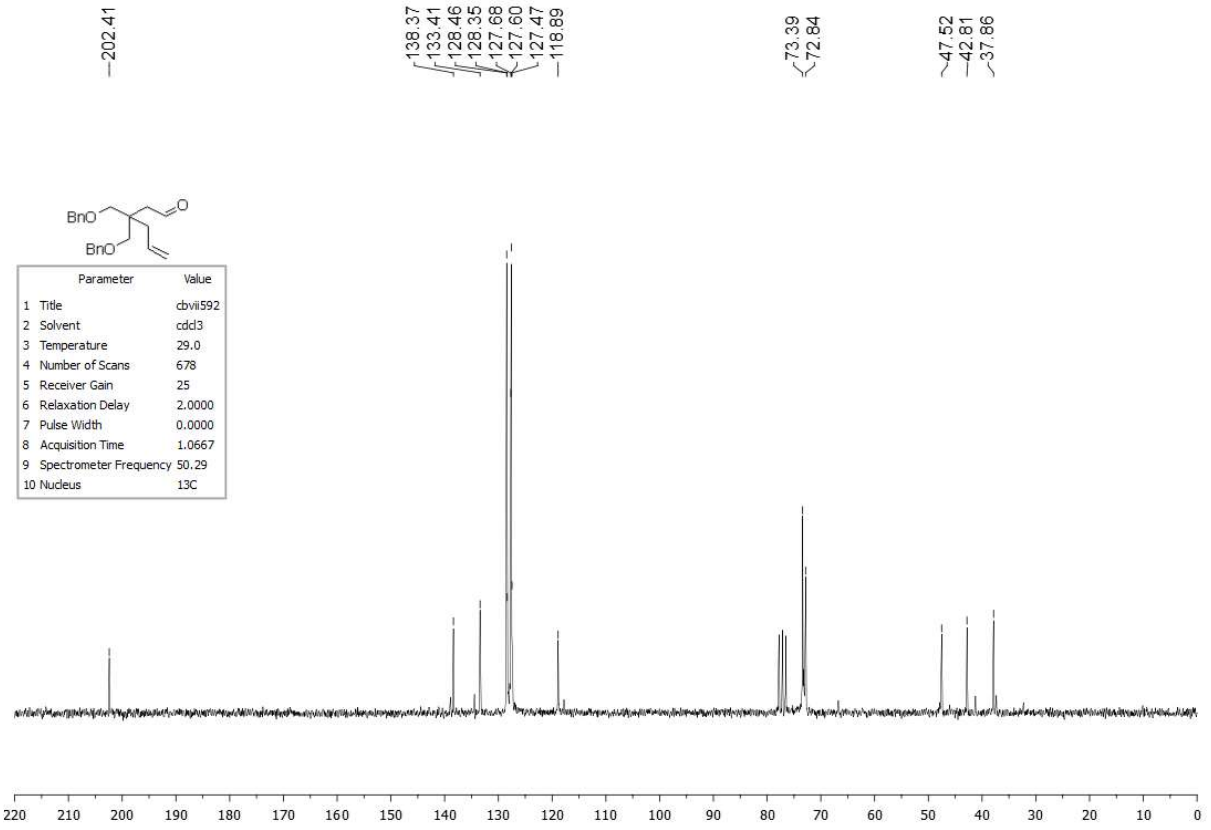

7.31 7.30 7.29 7.28 7.27 7.27 7.26 7.24 7.22 7.21 7.21 7.09 7.08 5.57 5.50 5.49 5.48 5.46 5.33 5.32 5.30 4.23 4.22 4.12 4.12 3.50 3.49 3.47 3.46 2.06 2.04 2.03 2.01 2.01 1.98 1.40 1.39 1.37 1.36 1.35 1.35 1.34 1.33 1.32 1.32 1.31 1.29 1.28 0.95 0.94 0.92 0.90 0.89 0.89 0.88 0.88 0.87
OH
Me
O
Me
S13-3
Parameter Value
1 Title BZV02733A
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 64
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 8.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
4.16 0.92 2.01 1.10 1.09 1.99 5.34 4.90 3.98
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

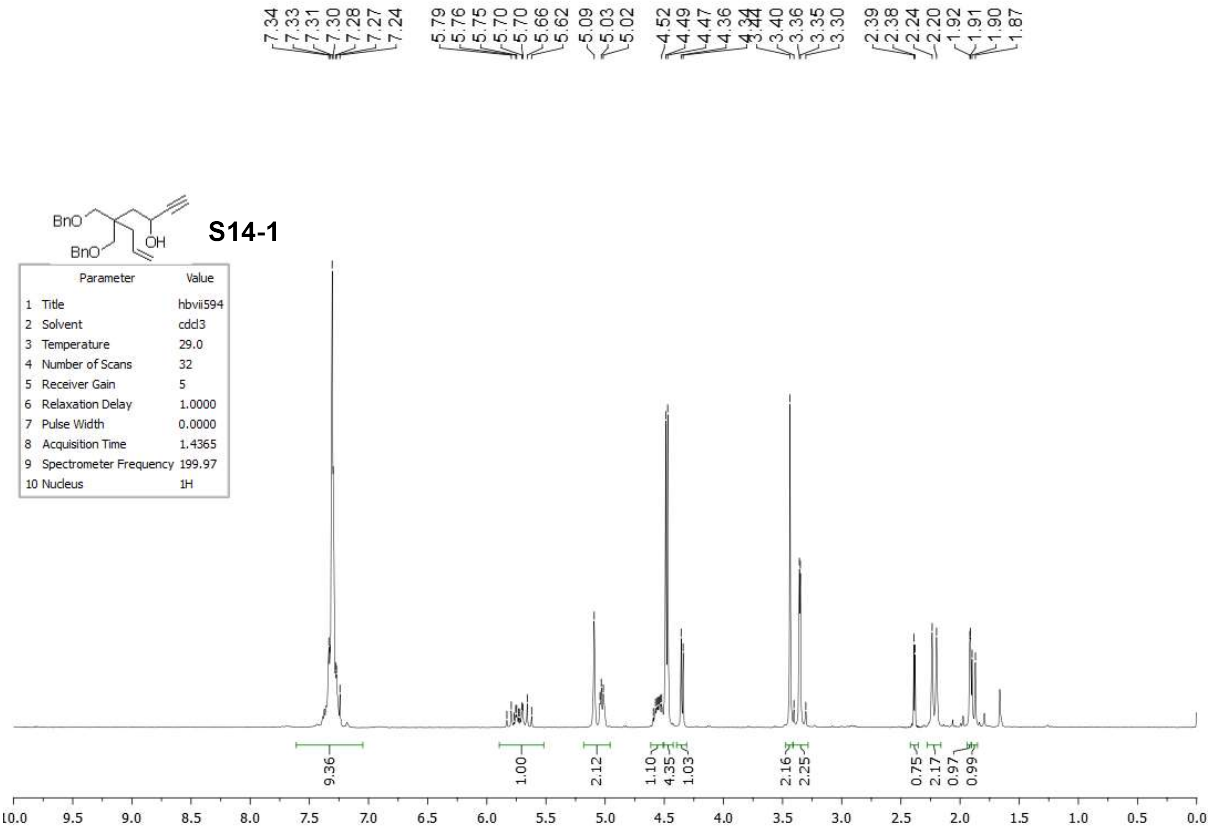

208.01
139.59 136.08 132.80 130.80 129.03 128.42 128.24 127.18
77.11
36.02 32.36 31.70 25.81 22.40 14.06
OH
Me
O
Me
S13-3
Parameter Value
1 Title BZV02733A
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 17274
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 15.2500
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

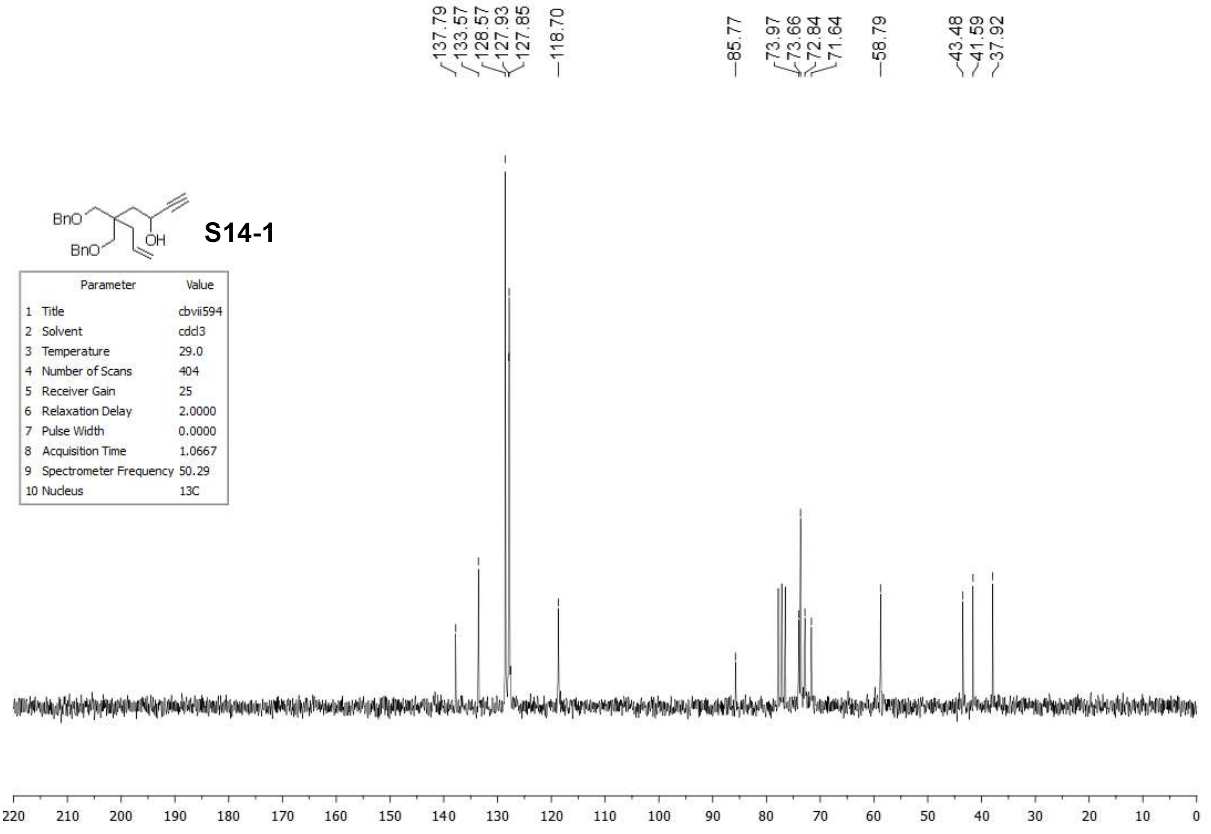

OMs
Me
O
Me
34
Parameter Value
1 Title BV-II-611
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.5564
9 Spectrometer Frequency 500.26
10 Nucleus 1H

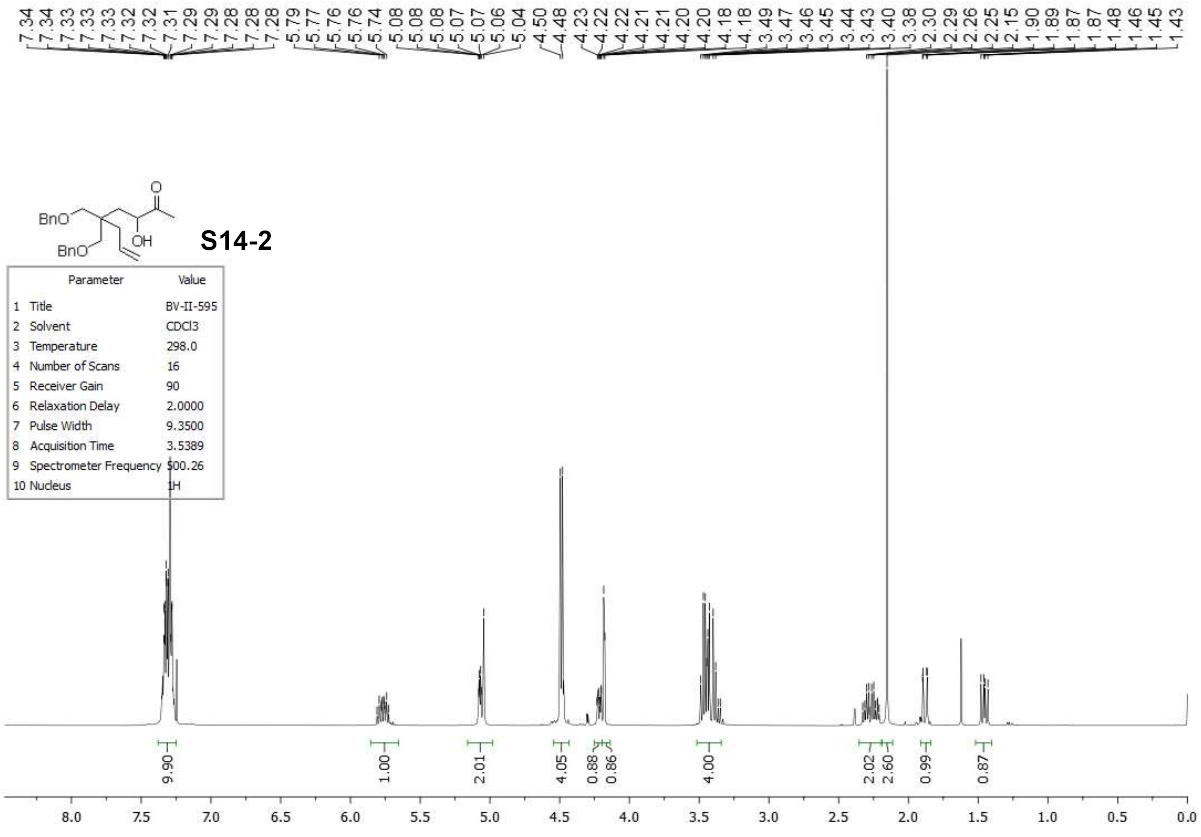

OMs
Me
O
Me
34
Parameter Value
1 Title BV-II-611
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 522
5 Receiver Gain 1290
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

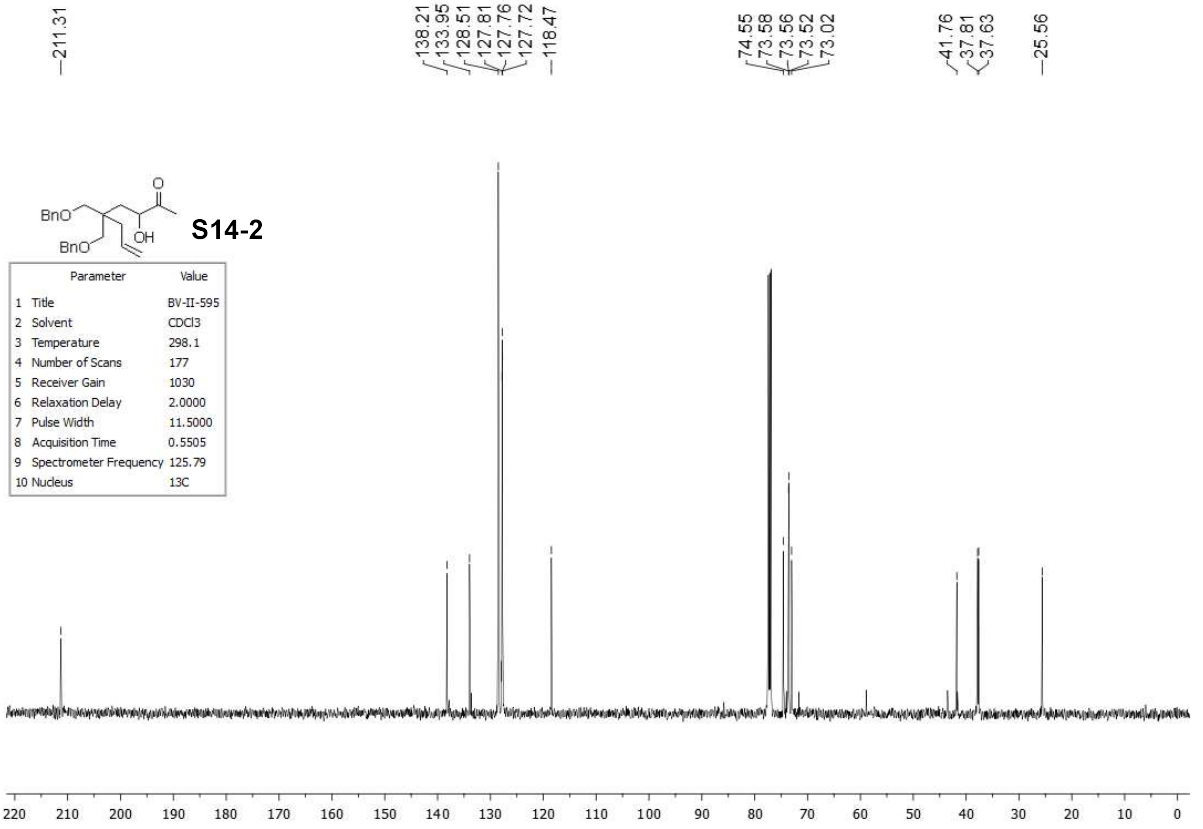

9.82
9.80
9.79
7.32
7.31
7.30
7.29
7.27
7.25
5.81
5.77
5.75
5.73
5.71
5.67
5.09
5.05
5.04
4.46
3.48
3.43
3.42
3.37
2.40
2.39
2.30
2.26
BnO
BnO
O
Parameter Value
1 Title hbvii592
2 Solvent cdcl3
3 Temperature 29.0
4 Number of Scans 32
5 Receiver Gain 1
6 Relaxation Delay 1.0000
7 Pulse Width 0.0000
8 Acquisition Time 1.4365
9 Spectrometer Frequency 199.97
10 Nucleus 1H
0.81
10.65
1.00
2.18
4.69
3.93
1.89
1.96
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

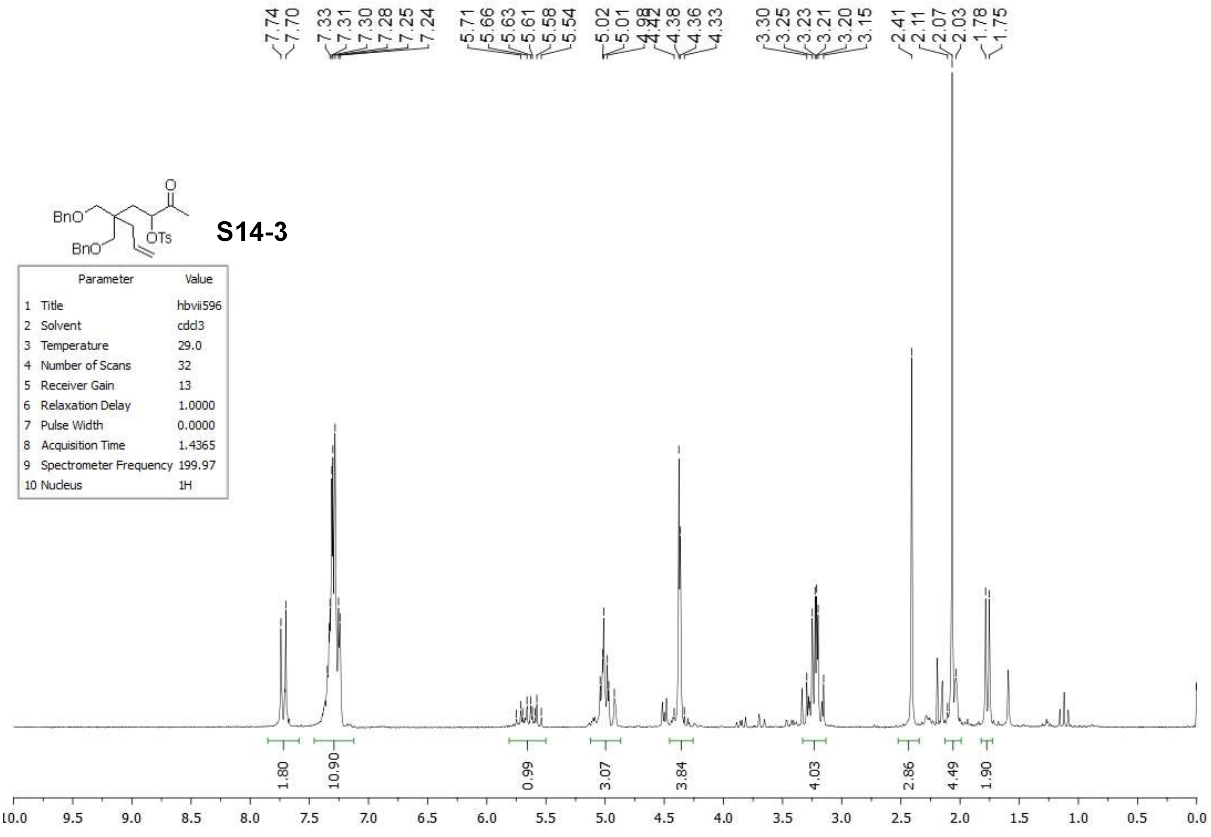

202.41
138.37
133.41
128.46
128.35
127.68
127.60
127.47
118.89
73.39
72.84
47.52
42.81
37.86
BnO
BnO
O
Parameter Value
1 Title cbvii592
2 Solvent cdcl3
3 Temperature 29.0
4 Number of Scans 678
5 Receiver Gain 25
6 Relaxation Delay 2.0000
7 Pulse Width 0.0000
8 Acquisition Time 1.0667
9 Spectrometer Frequency 50.29
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

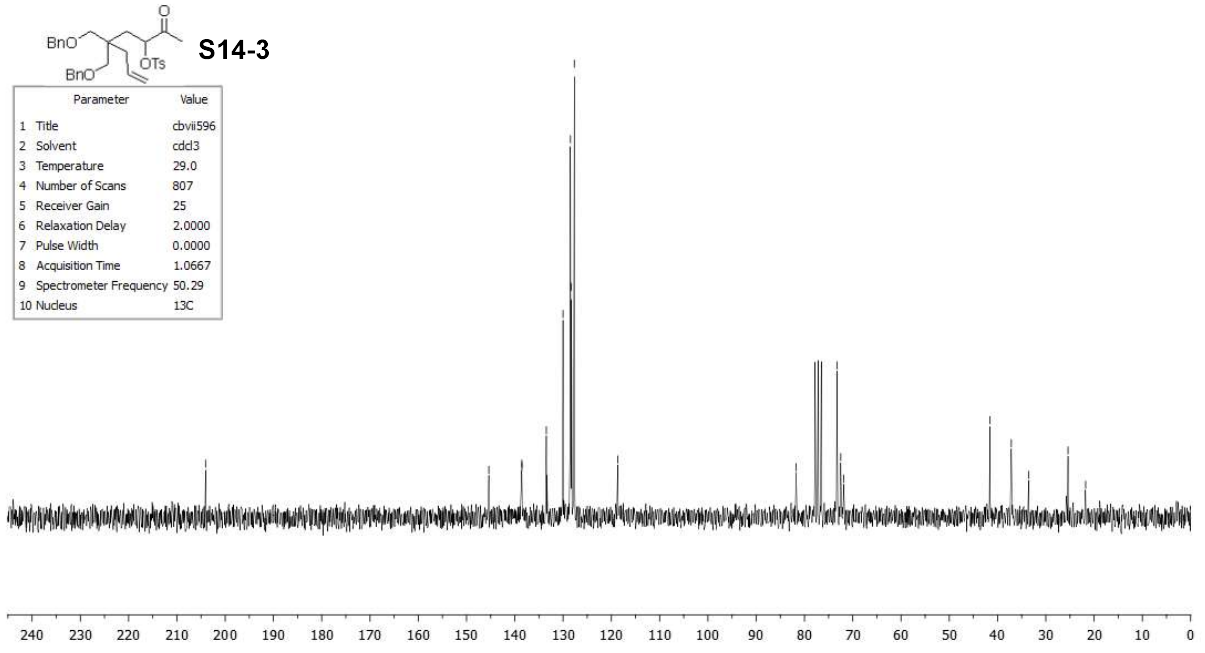

7.34
7.33
7.31
7.30
7.28
7.27
7.24
5.79
5.76
5.75
5.70
5.70
5.66
5.62
5.09
5.03
5.02
4.52
4.49
4.47
4.36
4.34
3.40
3.36
3.35
3.30
2.39
2.38
2.24
2.20
1.92
1.91
1.90
1.87
BnO
BnO
OH
S14-1
Parameter Value
1 Title hbvii594
2 Solvent cdcl3
3 Temperature 29.0
4 Number of Scans 32
5 Receiver Gain 5
6 Relaxation Delay 1.0000
7 Pulse Width 0.0000
8 Acquisition Time 1.4365
9 Spectrometer Frequency 199.97
10 Nucleus 1H
9.36
1.00
2.12
1.10
4.35
1.03
2.16
2.25
0.75
2.17
0.97
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


137.79
133.57
128.57
127.93
127.85
118.70
85.77
73.97
73.66
72.84
71.64
58.79
43.48
41.59
37.92
BnO
BnO
OH
S14-1
Parameter Value
1 Title cbvii594
2 Solvent cdcl3
3 Temperature 29.0
4 Number of Scans 404
5 Receiver Gain 25
6 Relaxation Delay 2.0000
7 Pulse Width 0.0000
8 Acquisition Time 1.0667
9 Spectrometer Frequency 50.29
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

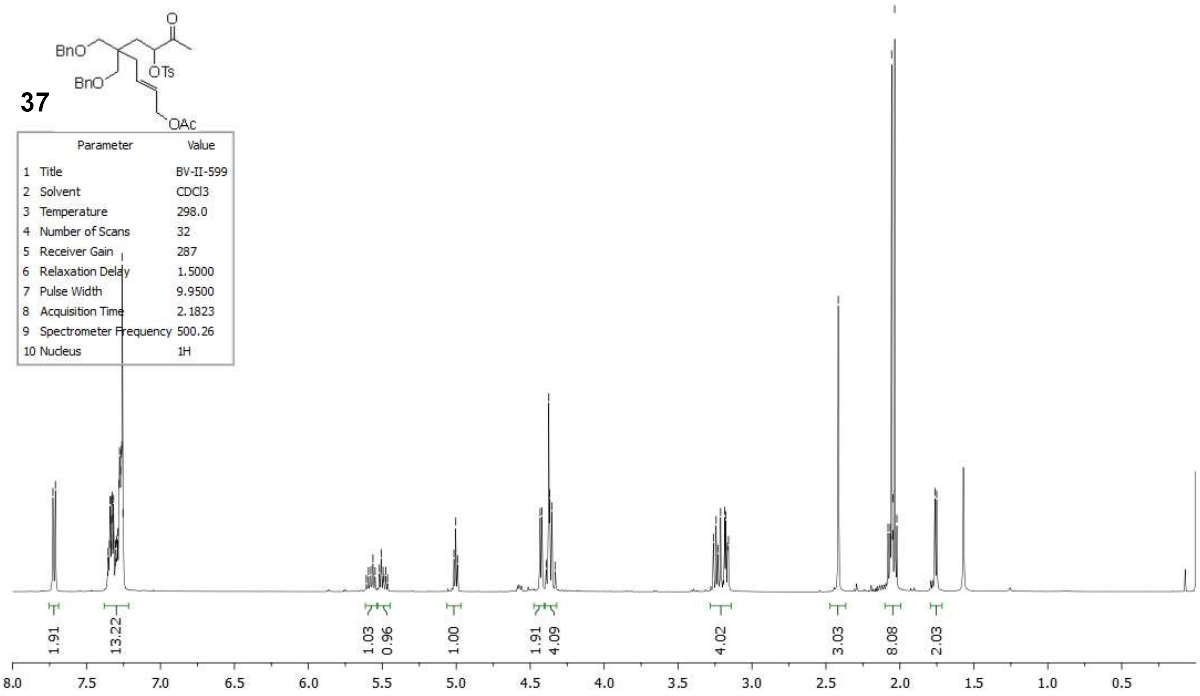

7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.29 7.29 7.28 7.28 7.28
5.79 5.77 5.76 5.76 5.74 5.08 5.08 5.08 5.07 5.07 5.06 5.04
4.50 4.48 4.23 4.22 4.22 4.21 4.21 4.20 4.20 4.18 4.18 3.49 3.47 3.46 3.45 3.44 3.43 3.40 3.38 2.30 2.29 2.26 2.25 2.15 1.90 1.89 1.87 1.87 1.48 1.46 1.45 1.43
BnO
BnO
OH
O
S14-2
Parameter Value
1 Title BV-II-595
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 90
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.5389
9 Spectrometer Frequency 500.26
10 Nucleus 1H
9.90 1.00 2.01 4.05 0.88 0.86 4.00 2.02 2.60 0.99 0.87
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

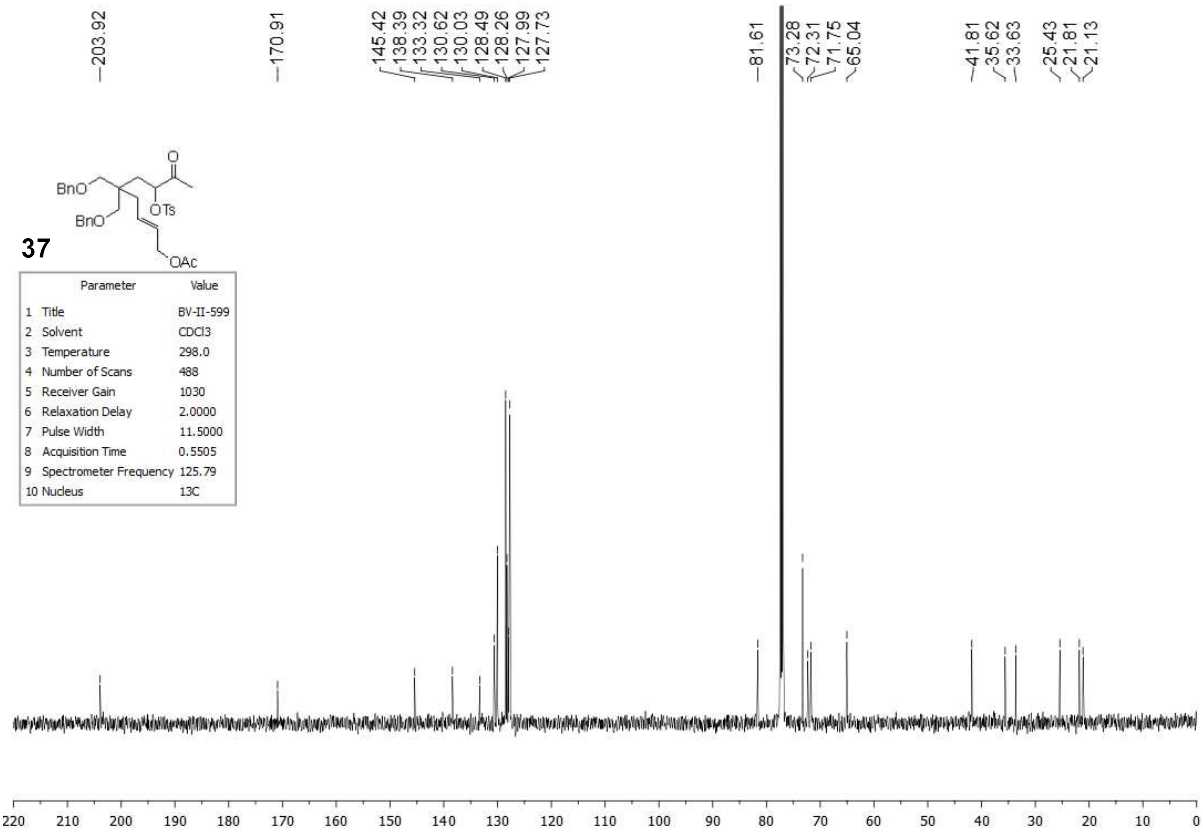

211.31
138.21 133.95 128.51 127.81 127.76 127.72 118.47
74.55 73.58 73.56 73.52 73.02
41.76 37.81 37.63
25.56
BnO
BnO
OH
O
S14-2
Parameter Value
1 Title BV-II-595
2 Solvent CDCl3
3 Temperature 298.1
4 Number of Scans 177
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

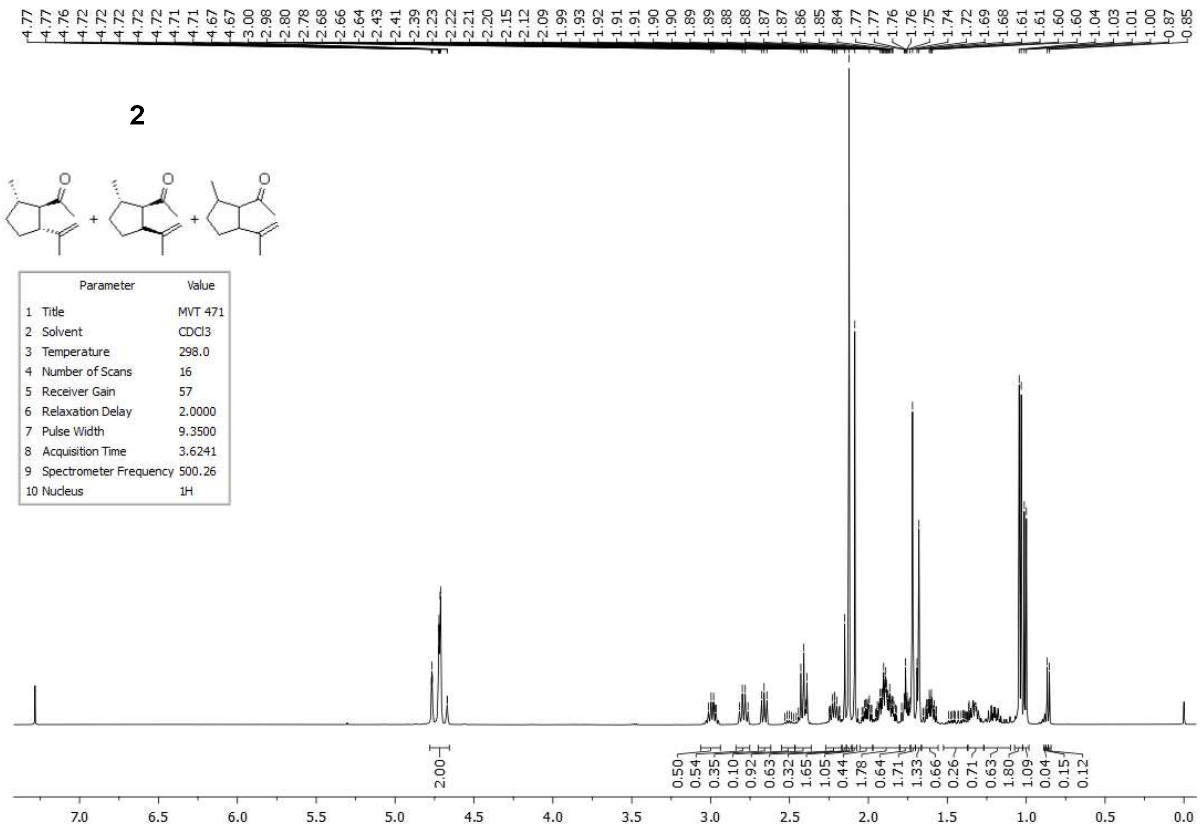

S14-3
Parameter Value
1 Title hbvii596
2 Solvent cdcl3
3 Temperature 29.0
4 Number of Scans 32
5 Receiver Gain 13
6 Relaxation Delay 1.0000
7 Pulse Width 0.0000
8 Acquisition Time 1.4365
9 Spectrometer Frequency 199.97
10 Nucleus 1H
7.74
7.70
7.33
7.31
7.30
7.28
7.25
7.24
5.71
5.66
5.63
5.61
5.58
5.54
5.02
5.01
4.98
4.42
4.38
4.36
4.33
3.30
3.25
3.23
3.21
3.20
3.15
2.41
2.11
2.07
2.03
1.78
1.75
1.80
10.90
0.99
3.07
3.84
4.03
2.86
4.49
1.90

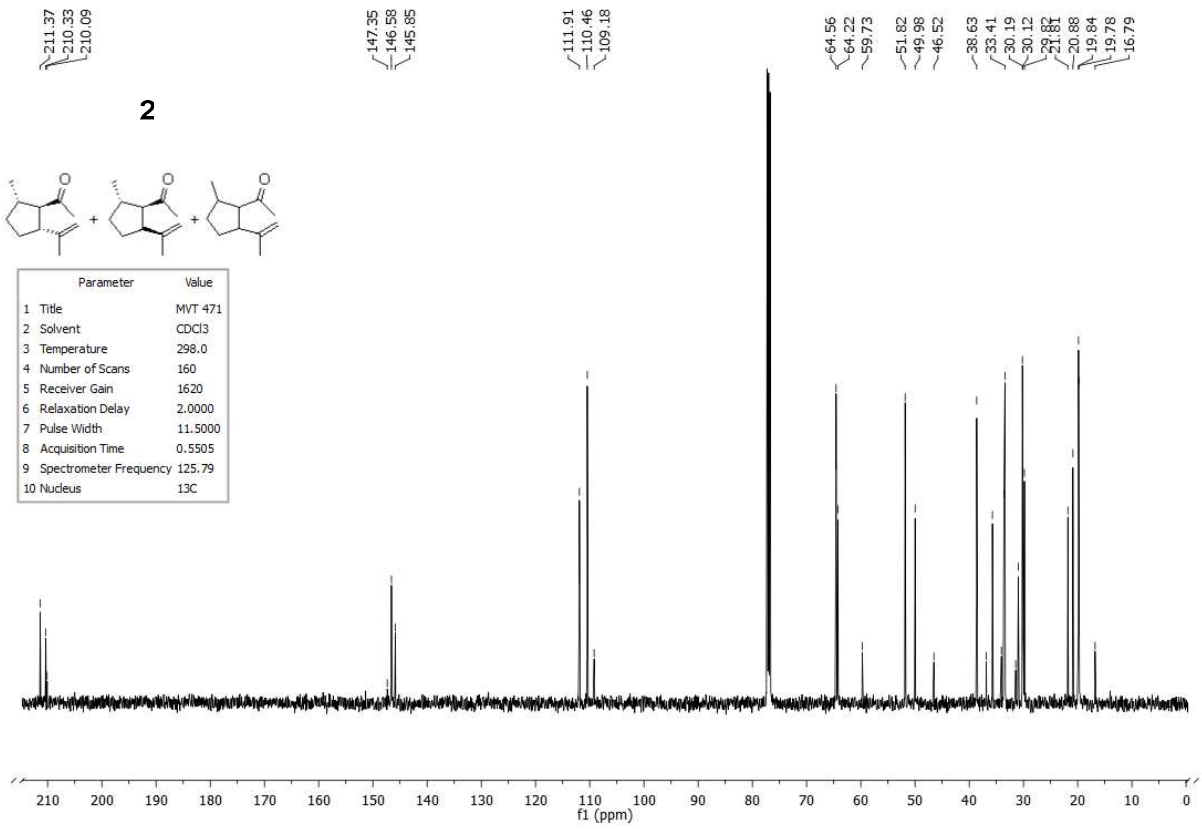

S14-3
Parameter Value
1 Title cbvii596
2 Solvent cdcl3
3 Temperature 29.0
4 Number of Scans 807
5 Receiver Gain 25
6 Relaxation Delay 2.0000
7 Pulse Width 0.0000
8 Acquisition Time 1.0667
9 Spectrometer Frequency 50.29
10 Nucleus 13C
204.06
145.38
138.55
138.52
133.47
130.02
128.47
128.28
127.68
118.69
81.74
73.25
72.48
71.87
41.59
37.15
33.59
25.40
21.75


7.73
7.71
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.26
7.25
5.56
5.51
5.02
5.00
4.99
4.43
4.42
4.39
4.37
4.37
4.35
3.26
3.24
3.23
3.21
3.18
3.18
3.17
3.16
2.42
2.08
2.07
2.06
2.05
2.04
2.02
1.76
1.75

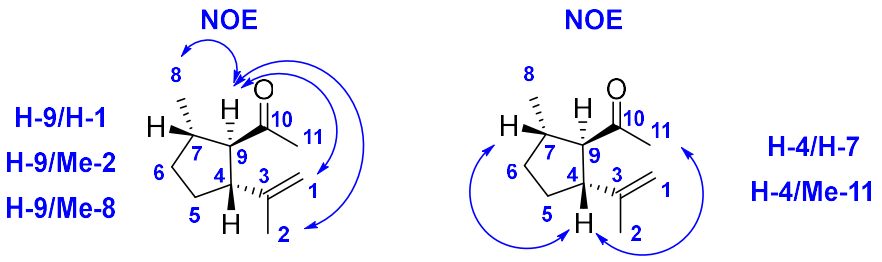

BnO
BnO
OTs
OAc
37
Parameter Value
1 Title BV-II-599
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 32
5 Receiver Gain 287
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 2.1823
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1.91
13.22
1.03
0.96
1.00
1.91
4.09
4.02
3.03
8.08
2.03
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

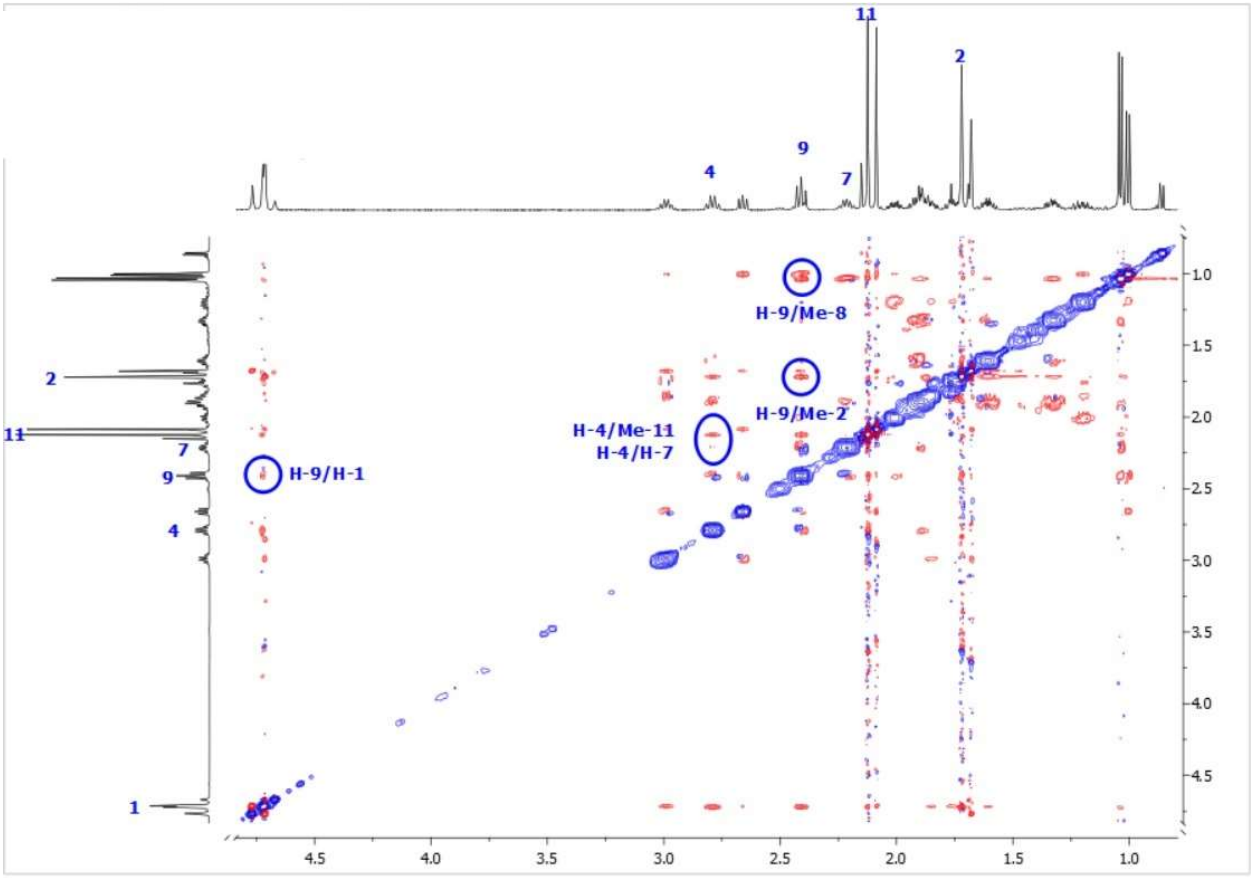

203.92
170.91
145.42
138.39
133.32
130.62
130.03
128.49
128.26
127.99
127.73
81.61
73.28
72.31
71.75
65.04
41.81
35.62
33.63
25.43
21.81
21.13
BnO
BnO
OTs
OAc
37
Parameter Value
1 Title BV-II-599
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 488
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

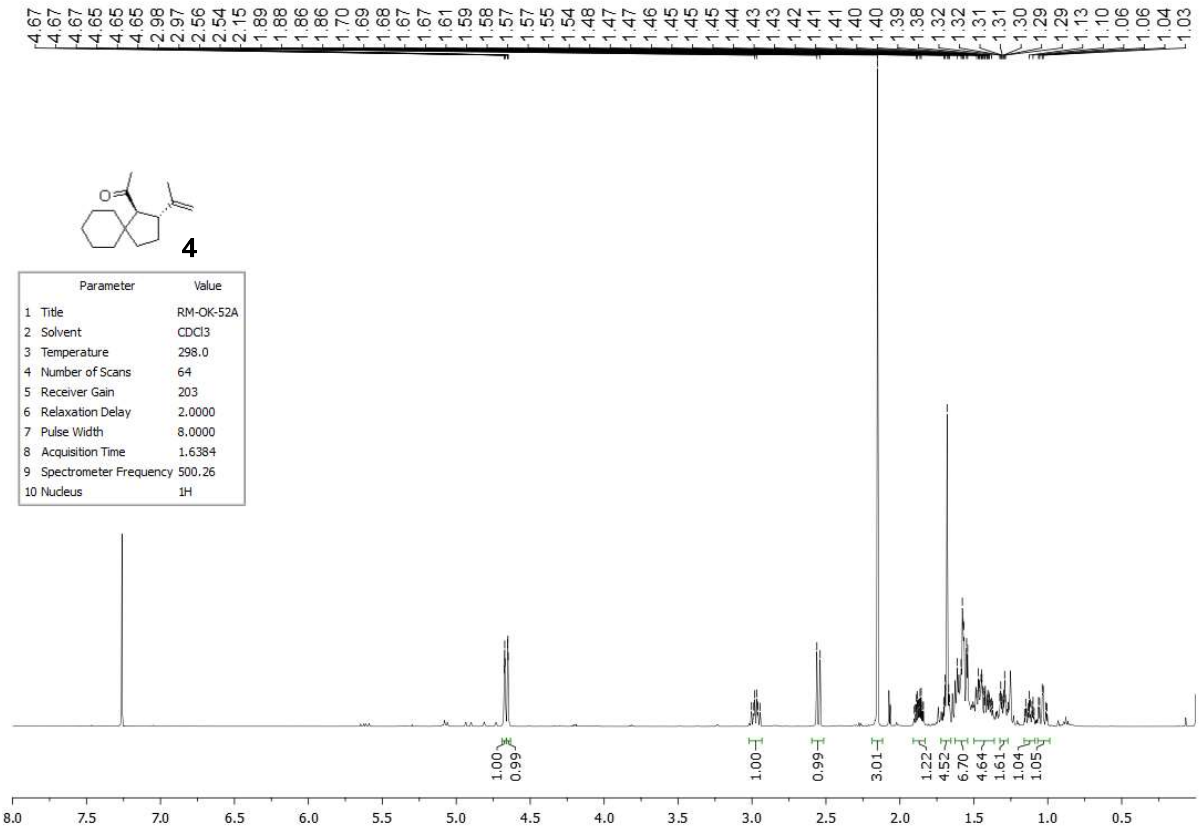

2
Parameter Value
1 Title MVT 471
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 57
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.6241
9 Spectrometer Frequency 500.26
10 Nucleus 1H

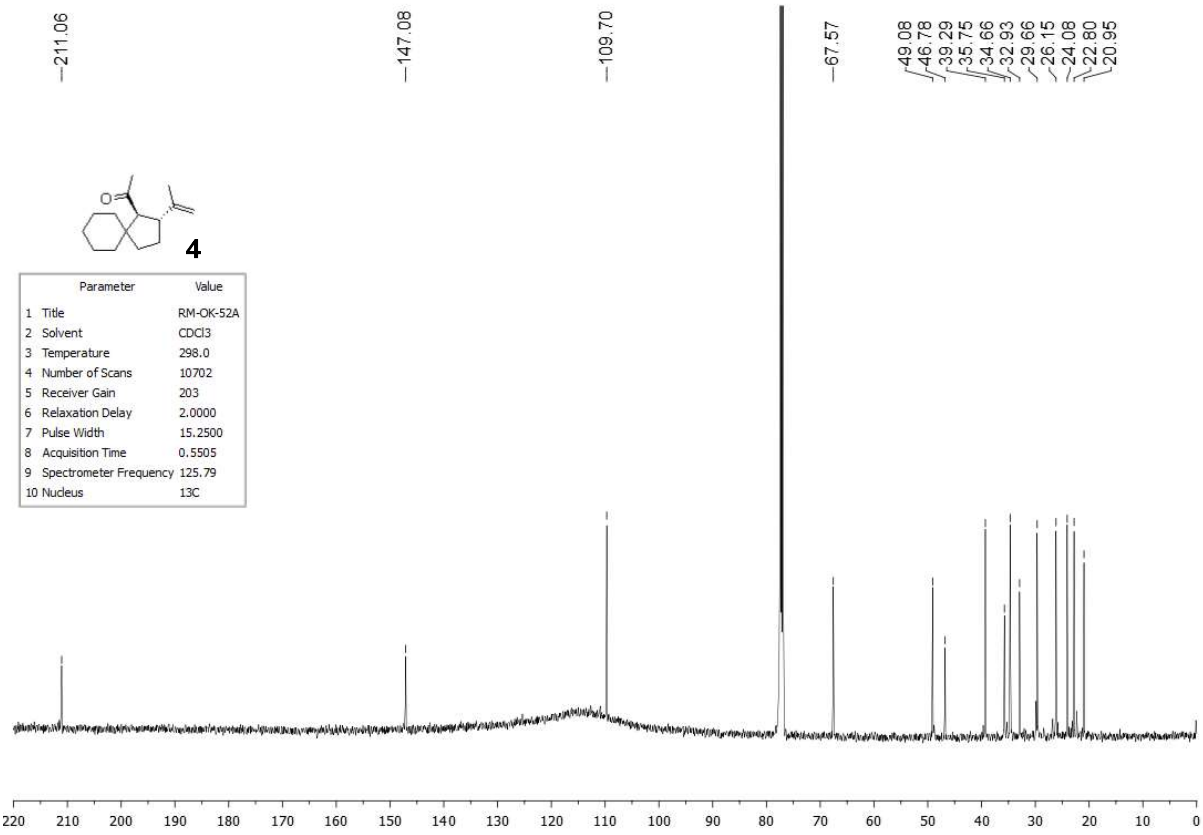

2
Parameter Value
1 Title MVT 471
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 160
5 Receiver Gain 1620
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
f1 (ppm)

Correlations (NOESY) for major diastereomer **2a**:



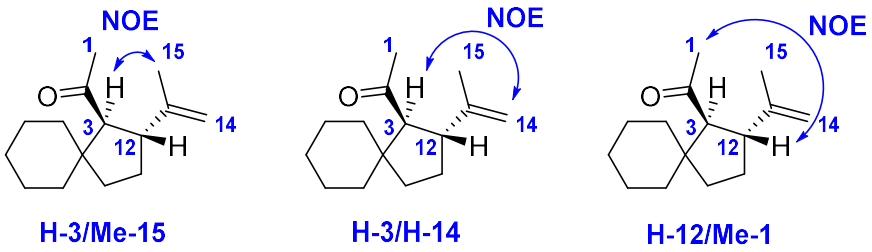



4.67 4.67 4.67 4.65 4.65 4.65 2.98 2.97 2.56 2.54 2.15 1.89 1.88 1.86 1.86 1.70 1.69 1.68 1.67 1.67 1.61 1.59 1.58 1.57 1.57 1.55 1.54 1.48 1.47 1.47 1.46 1.45 1.45 1.45 1.44 1.43 1.43 1.42 1.41 1.41 1.40 1.40 1.39 1.38 1.32 1.32 1.31 1.31 1.30 1.29 1.29 1.13 1.10 1.06 1.06 1.04 1.03
4
Parameter Value
1 Title RM-OK-52A
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 64
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 8.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1.00 0.99 1.00 0.99 3.01 1.22 4.52 6.70 4.64 1.61 1.04 1.05
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

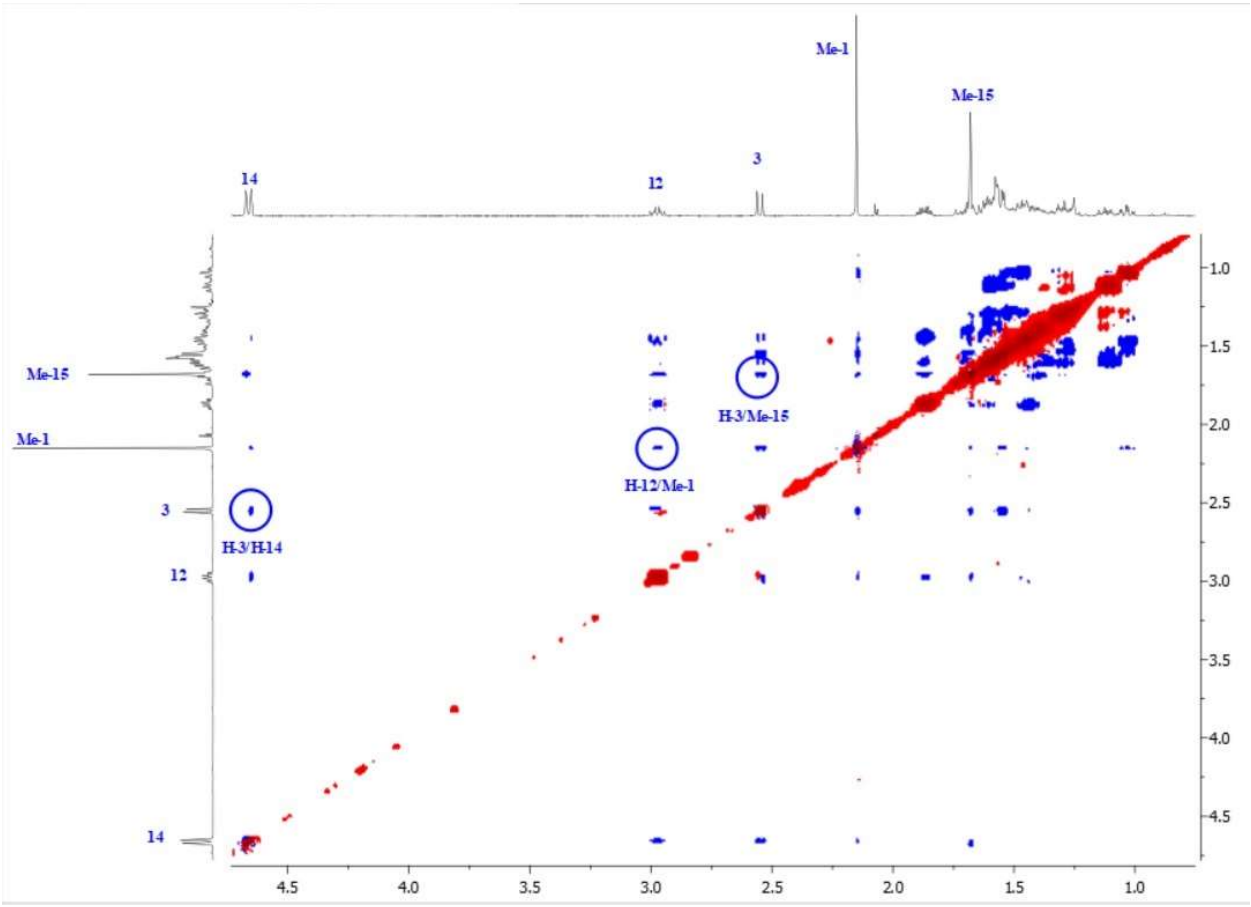

211.06 147.08 109.70 67.57 49.08 46.78 39.29 35.75 34.66 32.93 29.66 26.15 24.08 22.80 20.95
4
Parameter Value
1 Title RM-OK-52A
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 10702
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 15.2500
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

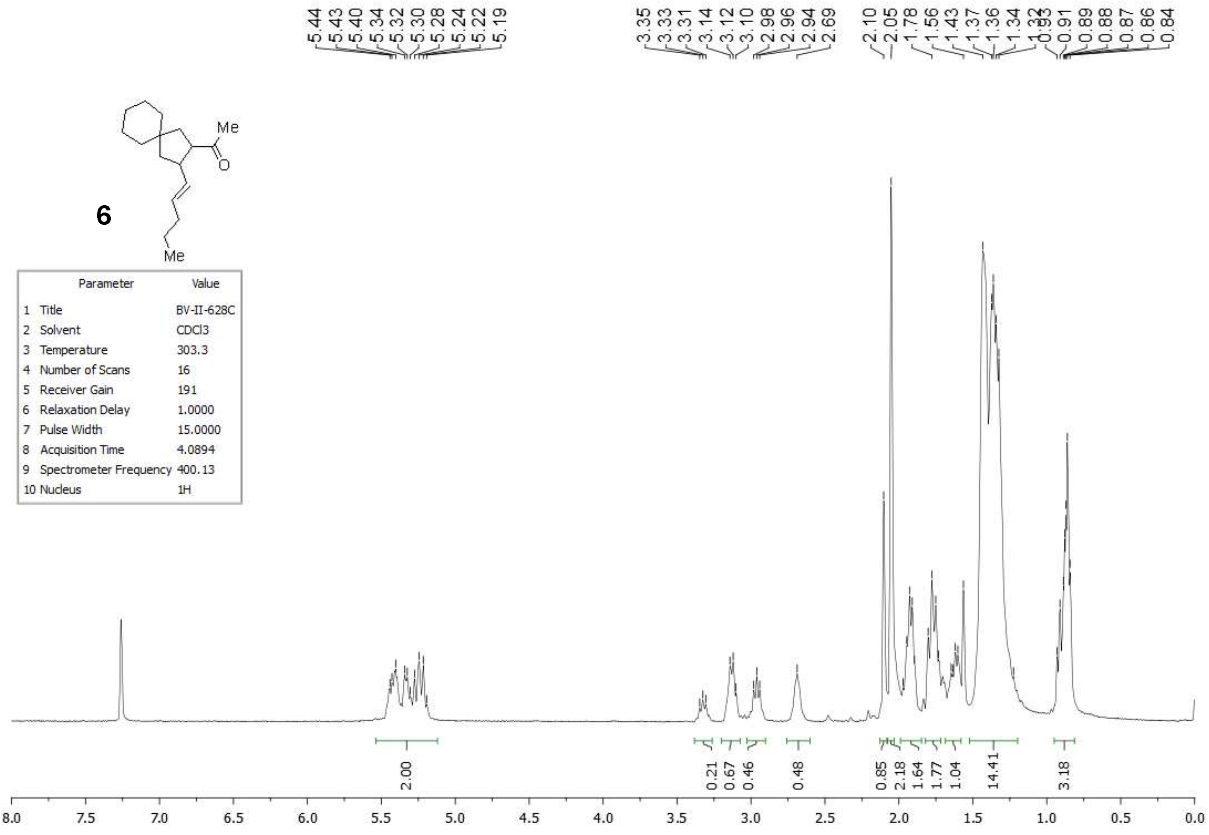
Correlations (NOESY) for compound **4**:

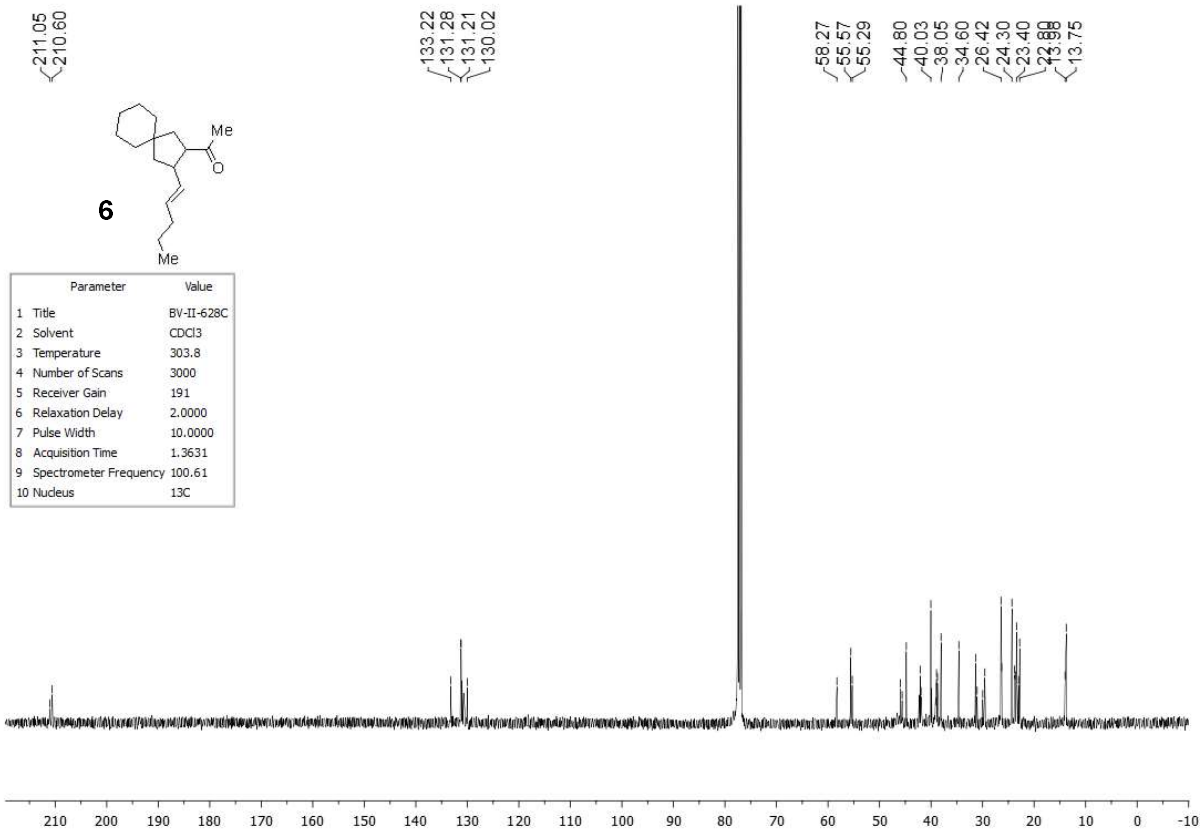
4

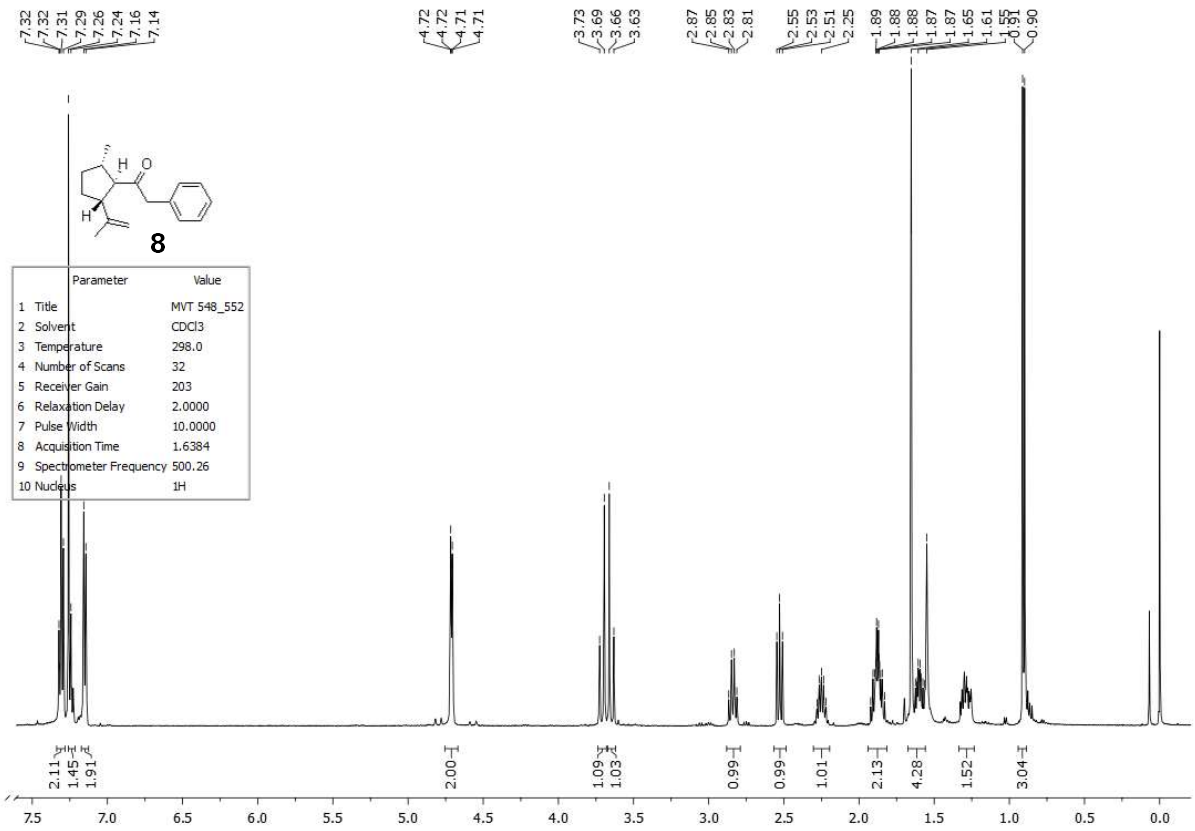


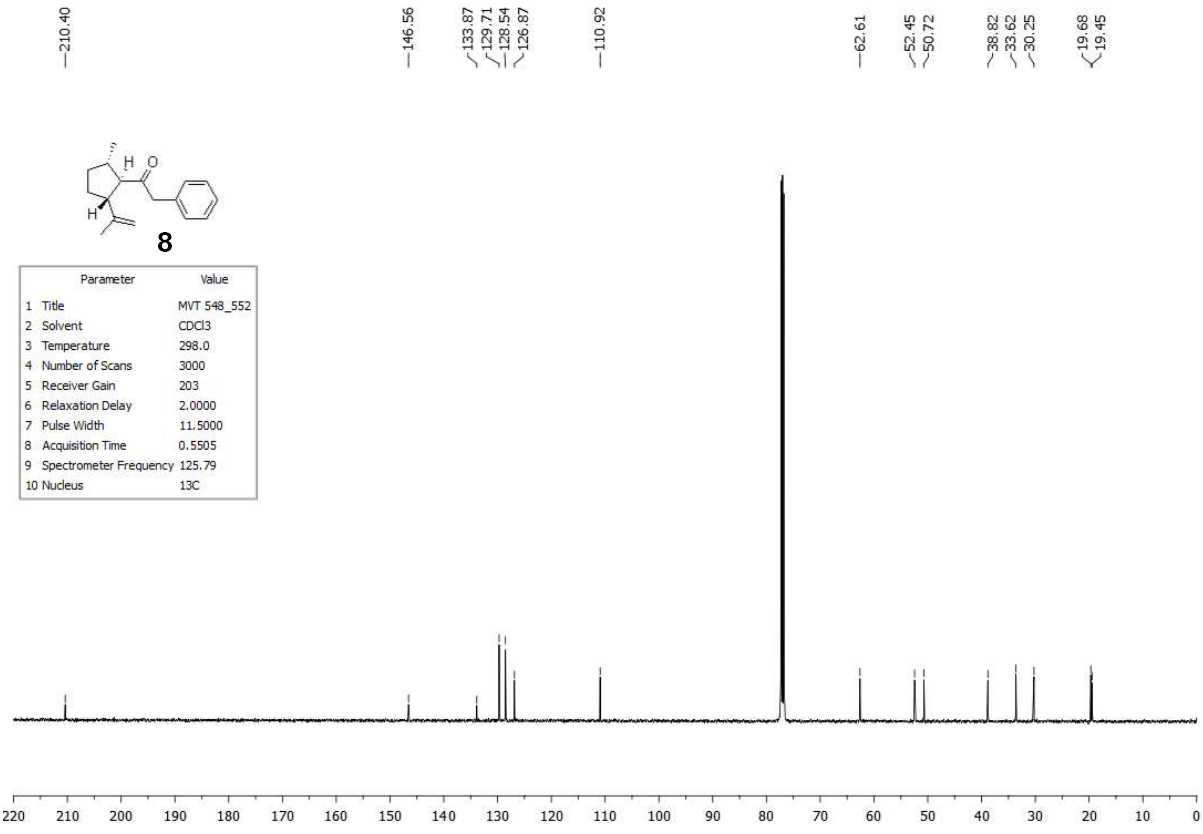
H-3/Me-15 H-3/H-14 H-12/Me-1



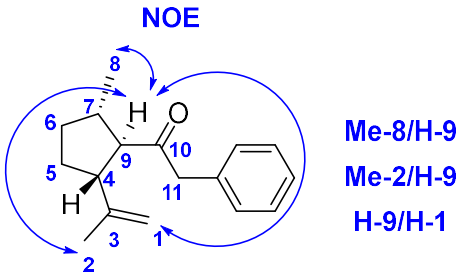

5.44
5.43
5.40
5.34
5.32
5.30
5.28
5.24
5.22
5.19
3.35
3.33
3.31
3.14
3.12
3.10
2.98
2.96
2.94
2.69
2.10
2.05
1.78
1.56
1.43
1.37
1.36
1.34
0.93
0.91
0.89
0.88
0.87
0.86
0.84
Me
O
6
Me
Parameter Value
1 Title BV-II-628C
2 Solvent CDCl3
3 Temperature 303.3
4 Number of Scans 16
5 Receiver Gain 191
6 Relaxation Delay 1.0000
7 Pulse Width 15.0000
8 Acquisition Time 4.0894
9 Spectrometer Frequency 400.13
10 Nucleus 1H
2.00
0.21
0.67
0.46
0.48
0.85
2.18
1.64
1.77
1.04
14.41
3.18
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

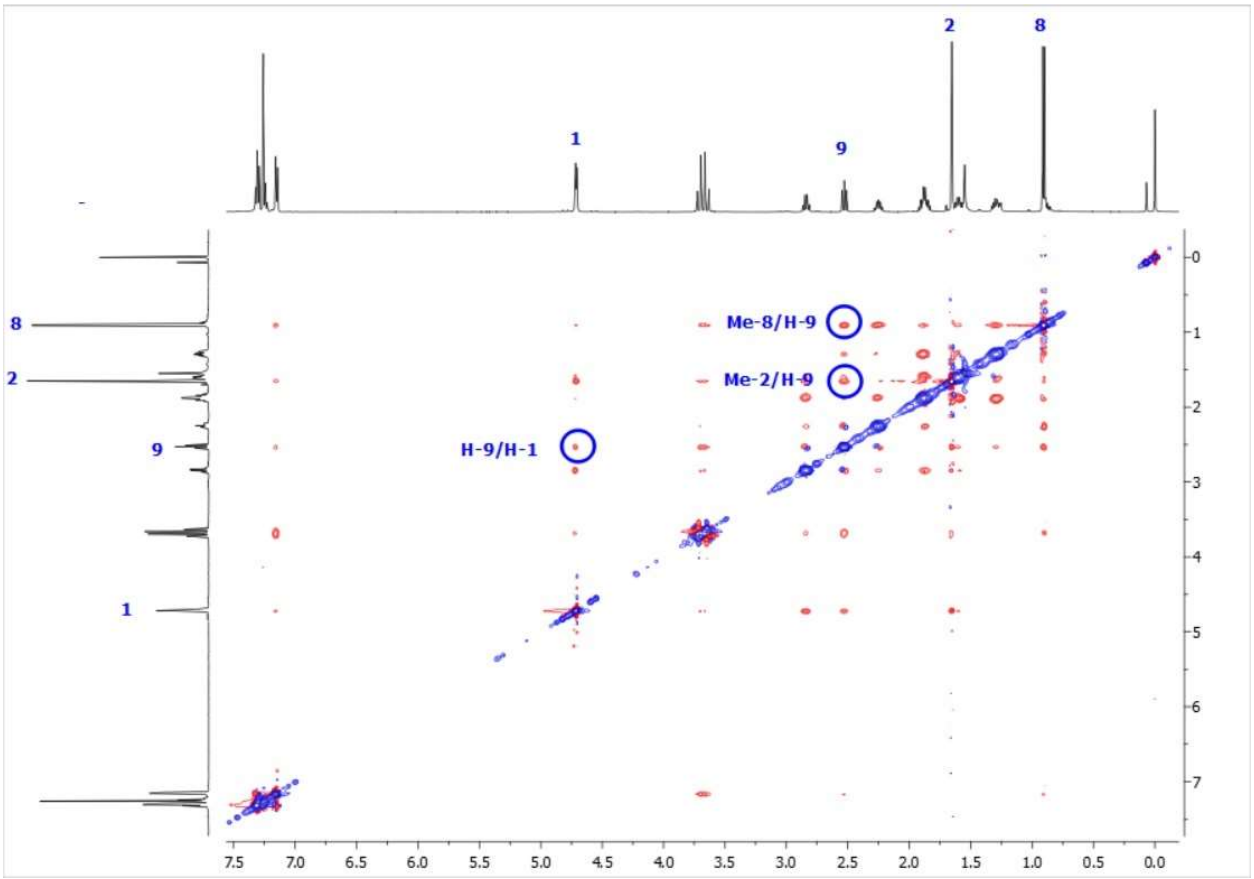

211.05
210.60
133.22
131.28
131.21
130.02
58.27
55.57
55.29
44.80
40.03
38.05
34.60
26.42
24.30
23.40
22.80
13.98
13.75
Me
O
6
Me
Parameter Value
1 Title BV-II-628C
2 Solvent CDCl3
3 Temperature 303.8
4 Number of Scans 3000
5 Receiver Gain 191
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.3631
9 Spectrometer Frequency 100.61
10 Nucleus 13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

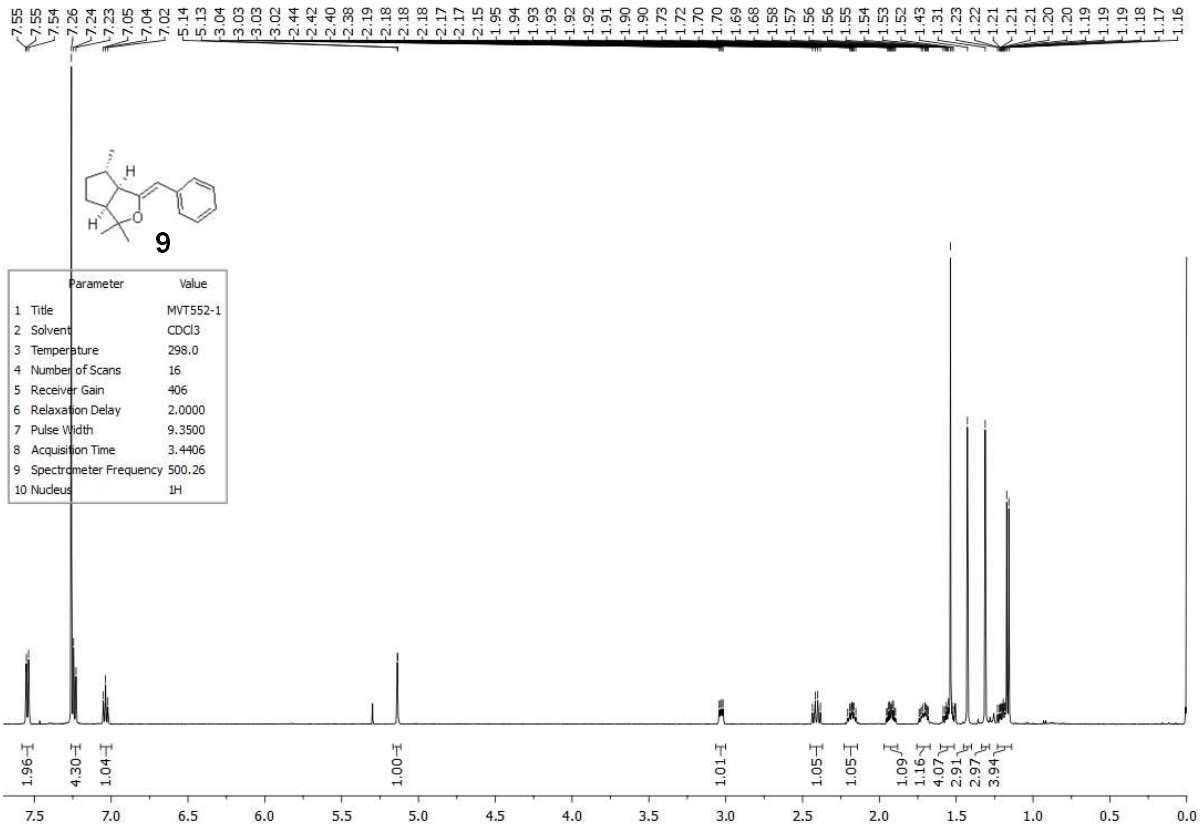

7.32
7.32
7.31
7.29
7.26
7.24
7.16
7.14
4.72
4.72
4.71
4.71
3.73
3.69
3.66
3.63
2.87
2.85
2.83
2.81
2.55
2.53
2.51
2.25
1.89
1.88
1.88
1.87
1.87
1.65
1.61
1.55
0.91
0.90
8
Parameter Value
1 Title MVT 548_552
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 32
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
2.11
1.45
1.91
2.00
1.09
1.03
0.99
0.99
1.01
2.13
4.28
1.52
3.04
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

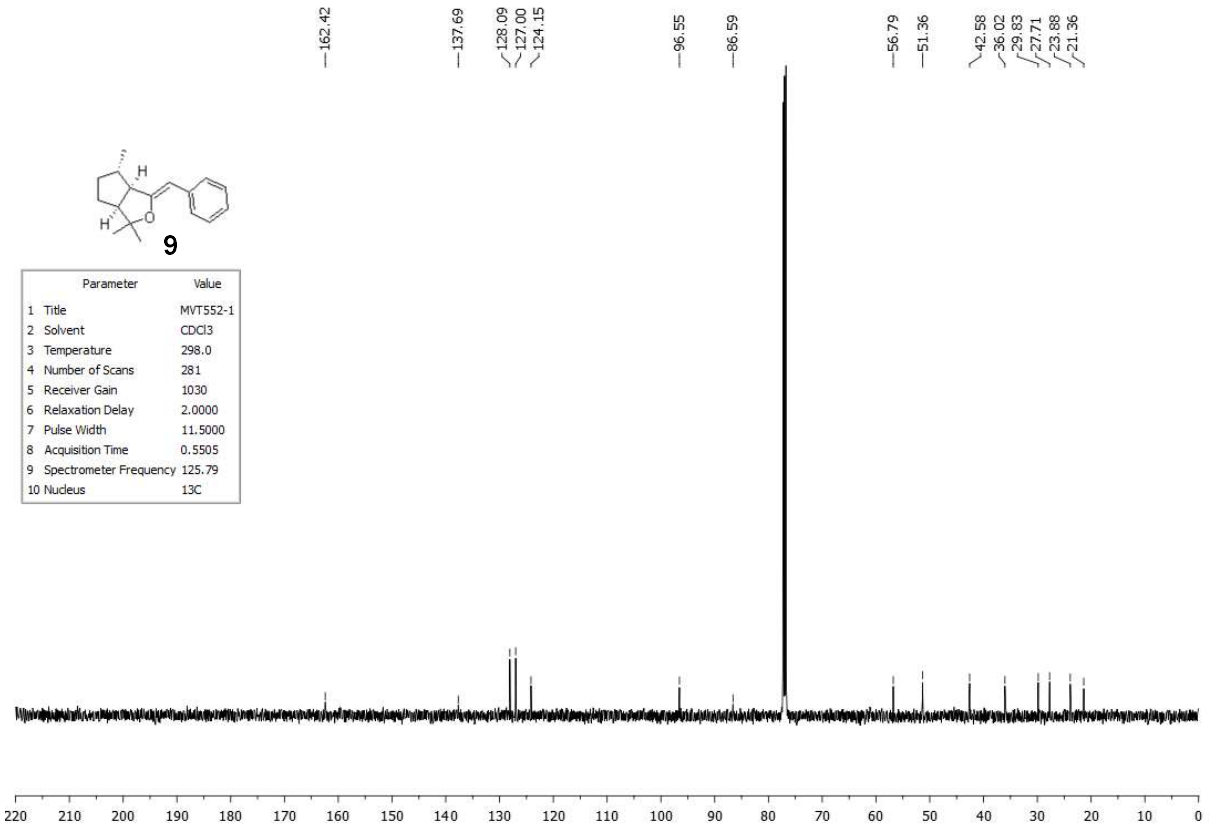

210.40
146.56
133.87
129.71
128.54
126.87
110.92
62.61
52.45
50.72
38.82
33.62
30.25
19.68
19.45
8
Parameter Value
1 Title MVT 548_552
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 3000
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

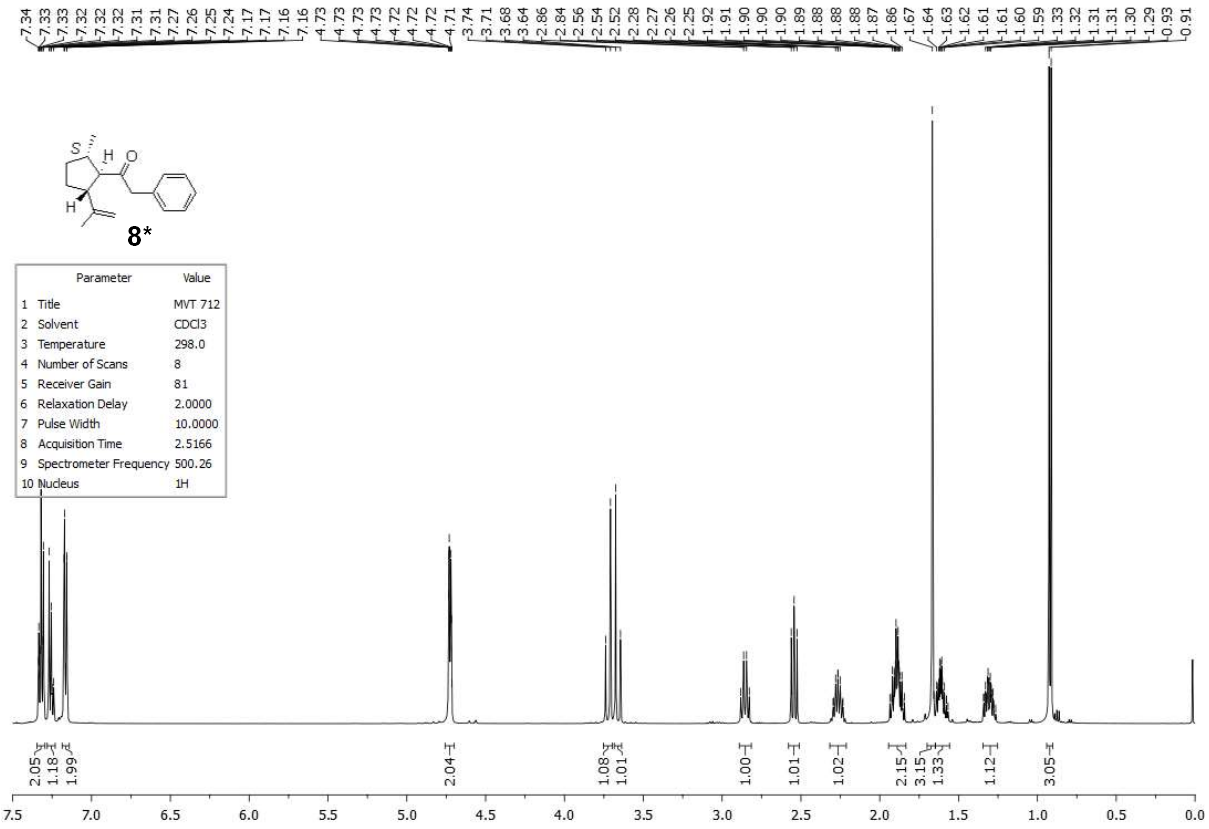
Correlations (NOESY) of **8**:

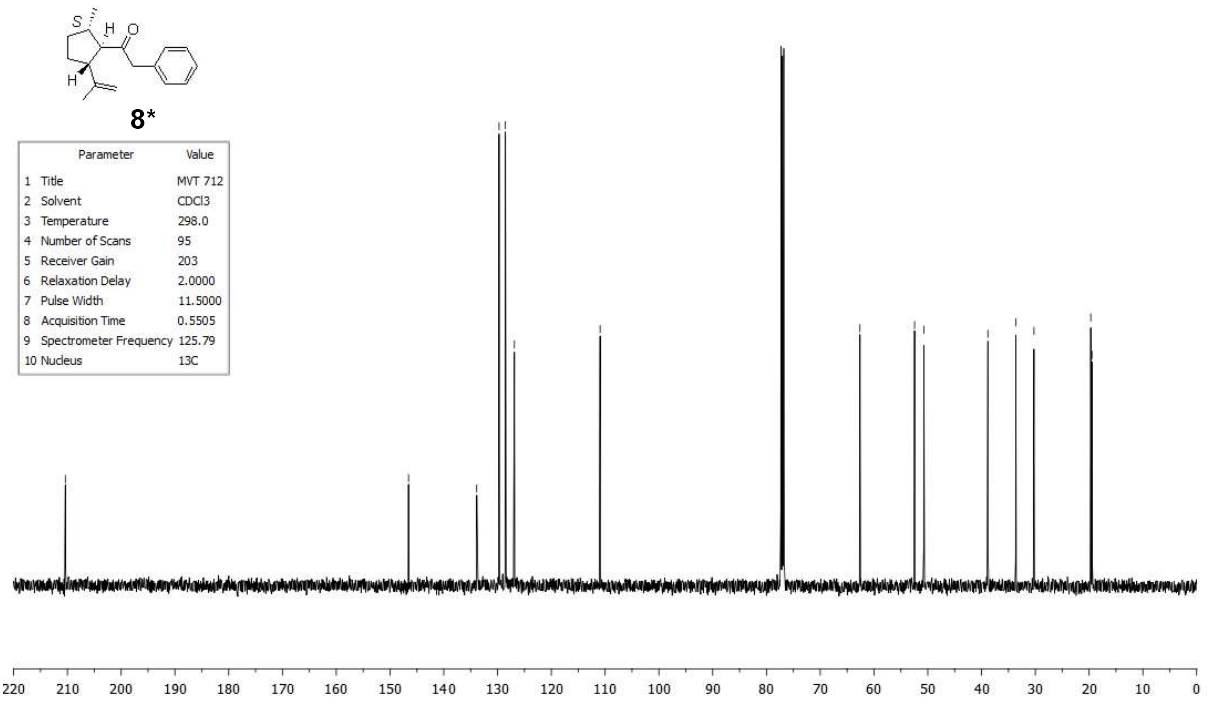




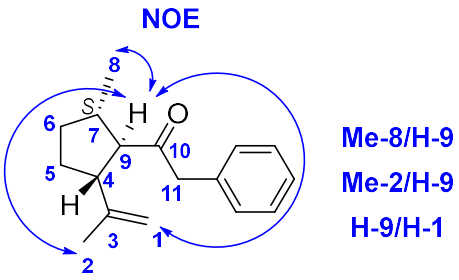

9
Parameter Value
1 Title MVT552-1
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 406
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.4406
9 Spectrometer Frequency 500.26
10 Nucleus 1H

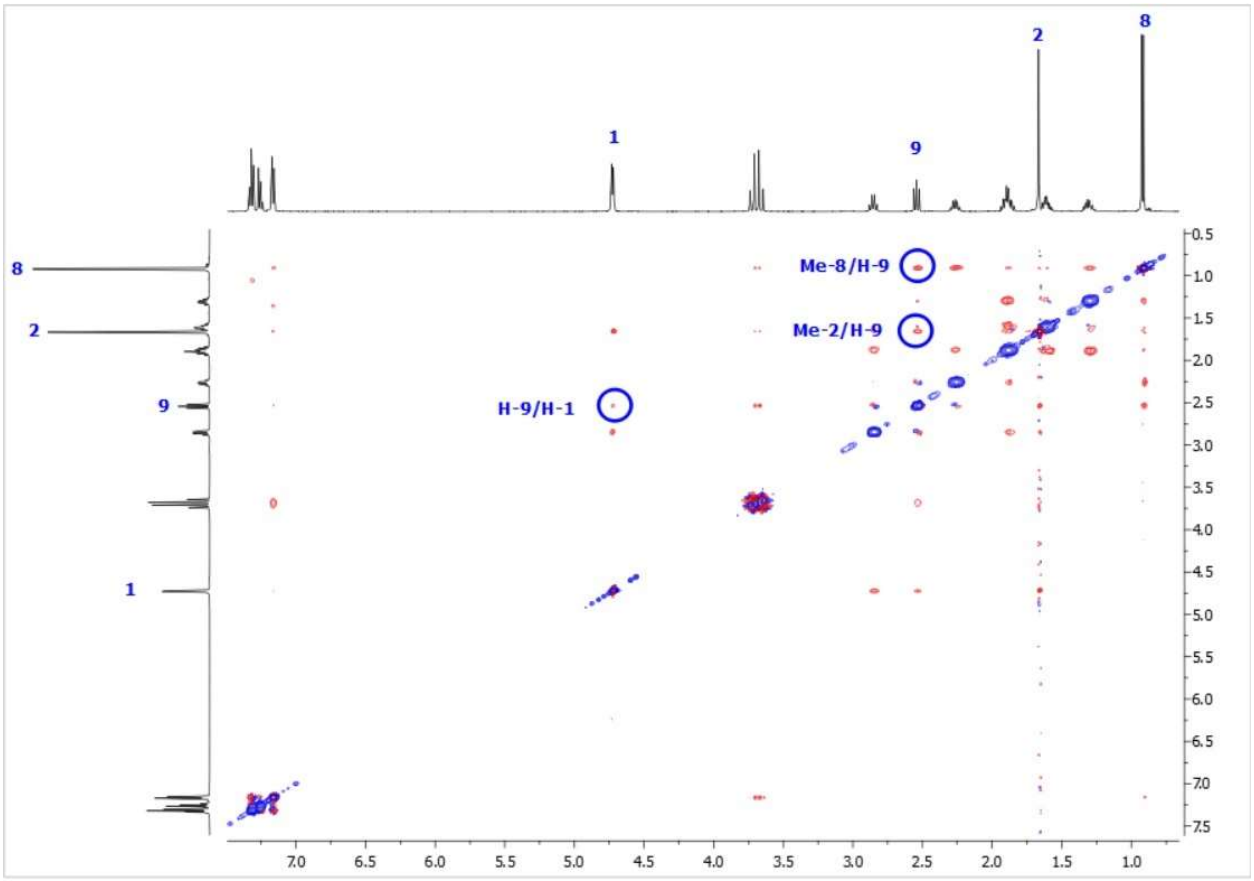

9
Parameter Value
1 Title MVT552-1
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 281
5 Receiver Gain 1030
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

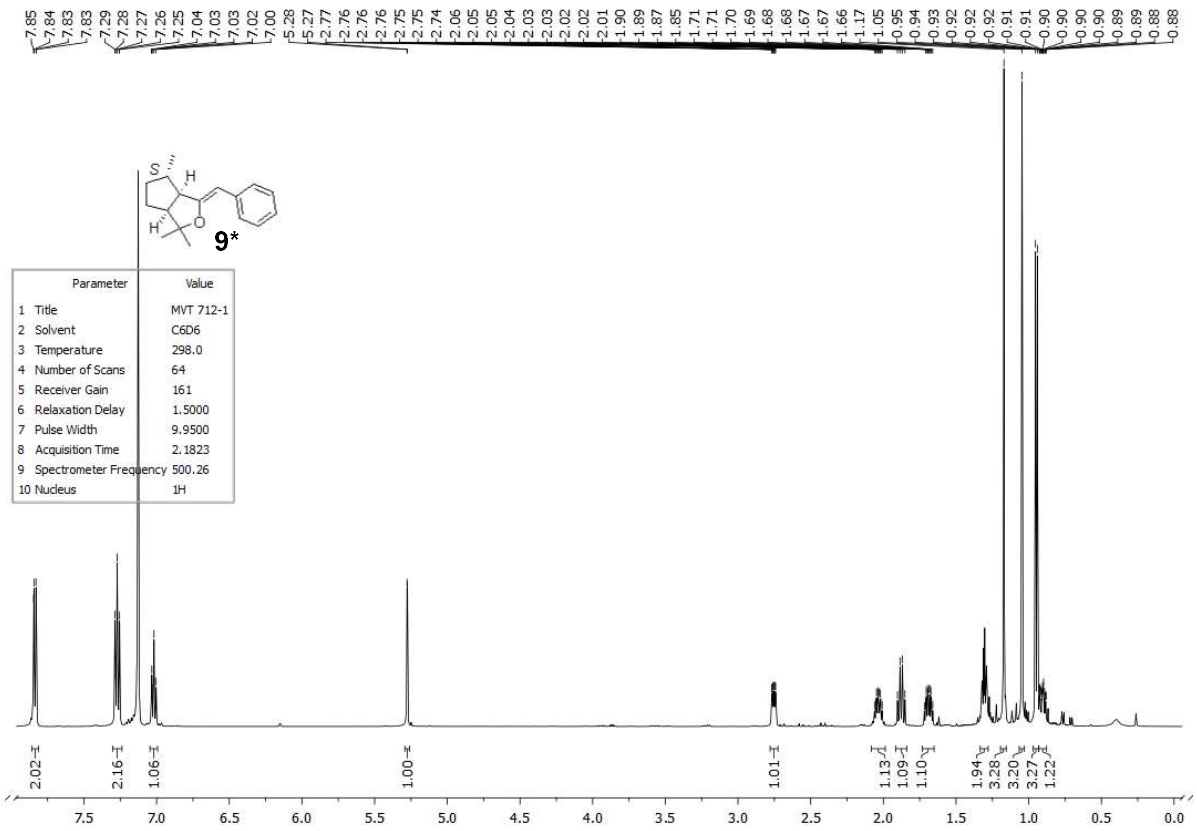

8*
Parameter Value
1 Title MVT 712
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 8
5 Receiver Gain 81
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 2.5166
9 Spectrometer Frequency 500.26
10 Nucleus 1H

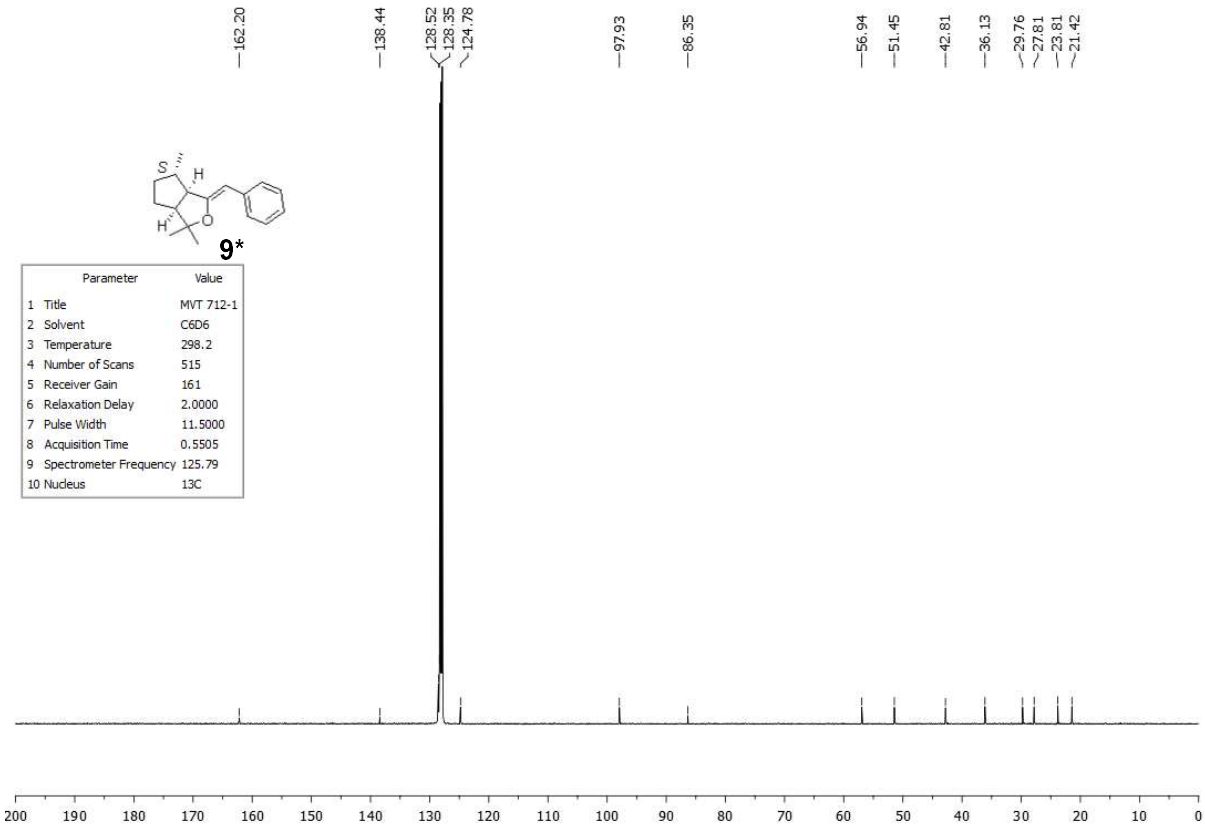

8*
Parameter Value
1 Title MVT 712
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 95
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

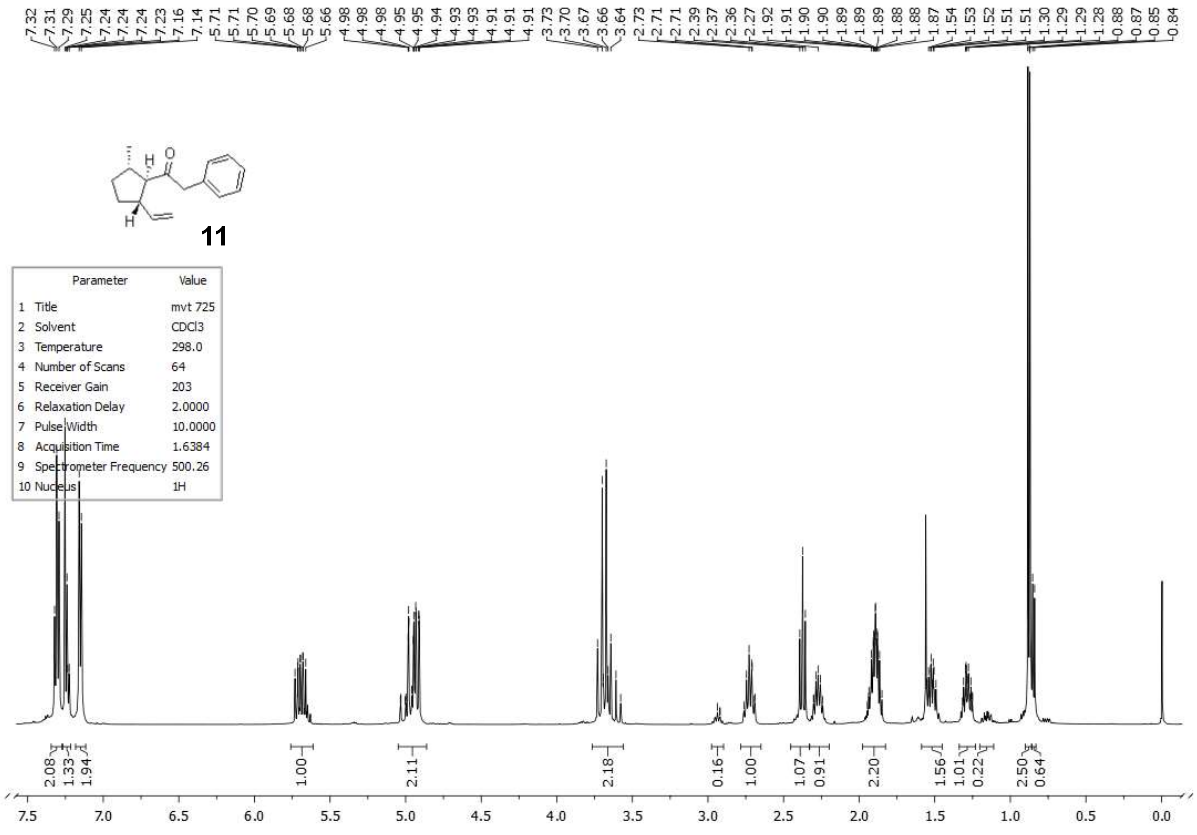
Correlations (NOESY) for **8***:

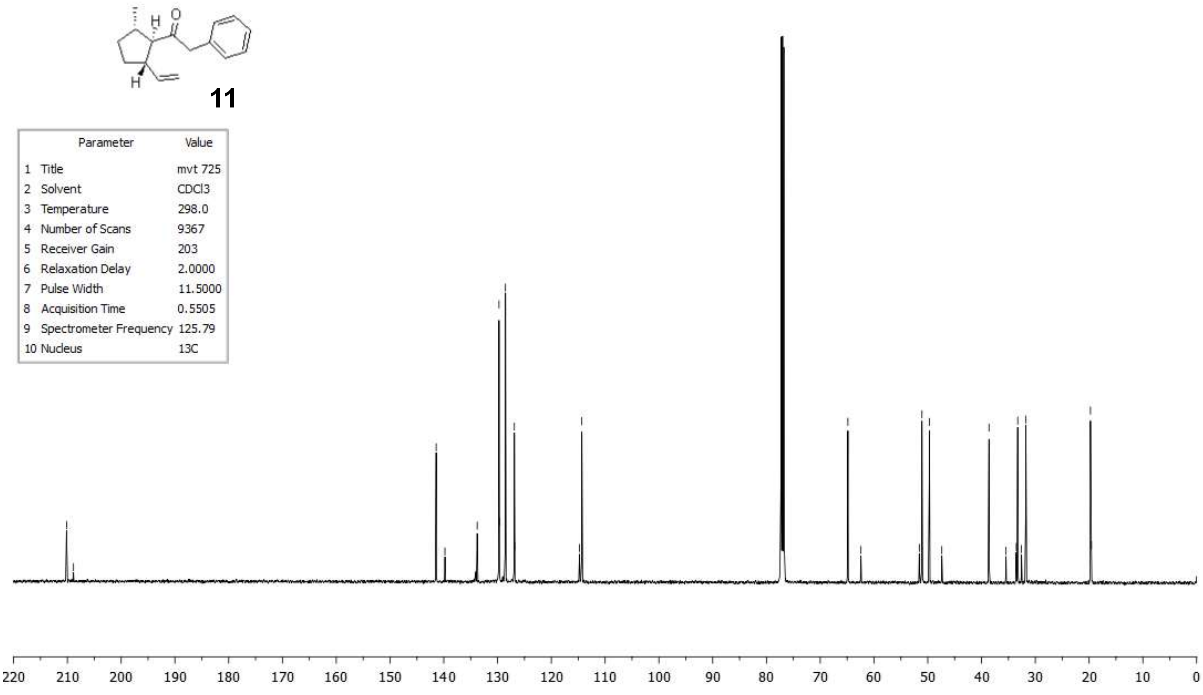


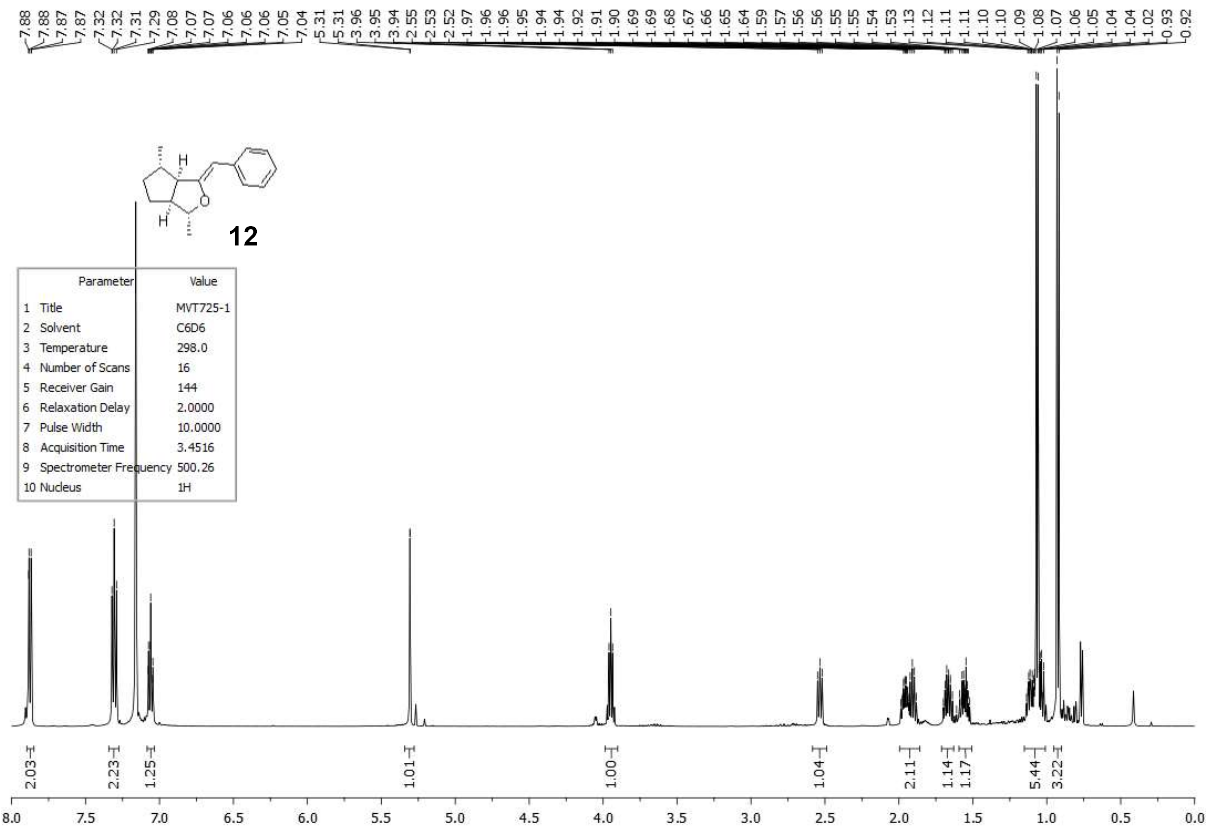


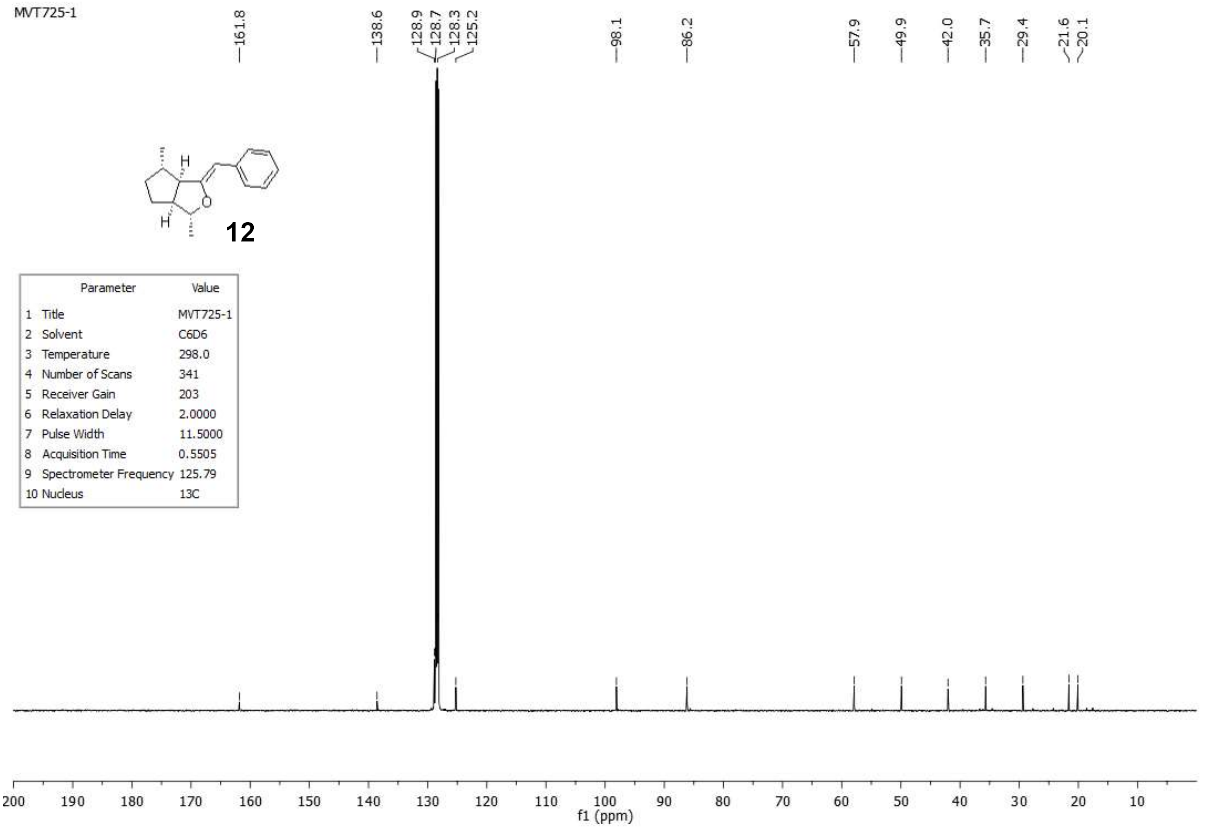

9*
Parameter Value
1 Title MVT 712-1
2 Solvent C6D6
3 Temperature 298.0
4 Number of Scans 64
5 Receiver Gain 161
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 2.1823
9 Spectrometer Frequency 500.26
10 Nucleus 1H

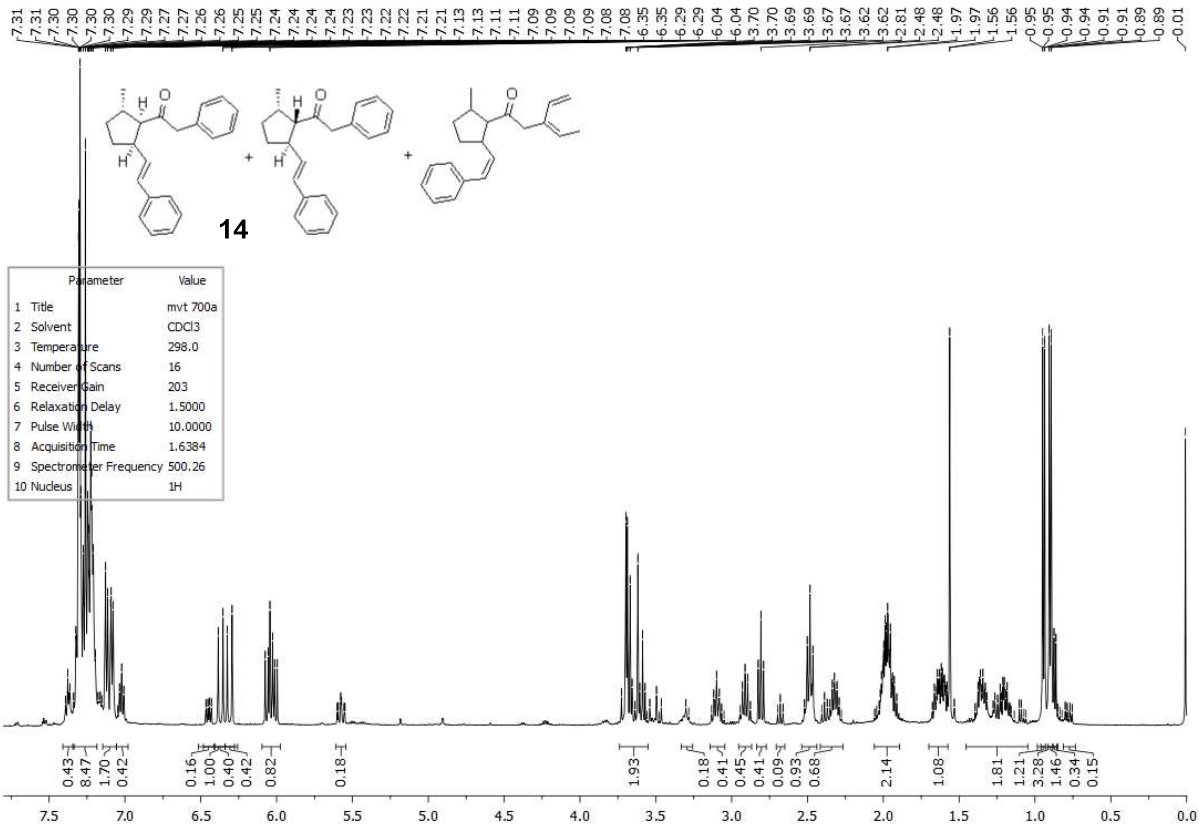

9*
Parameter Value
1 Title MVT 712-1
2 Solvent C6D6
3 Temperature 298.2
4 Number of Scans 515
5 Receiver Gain 161
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

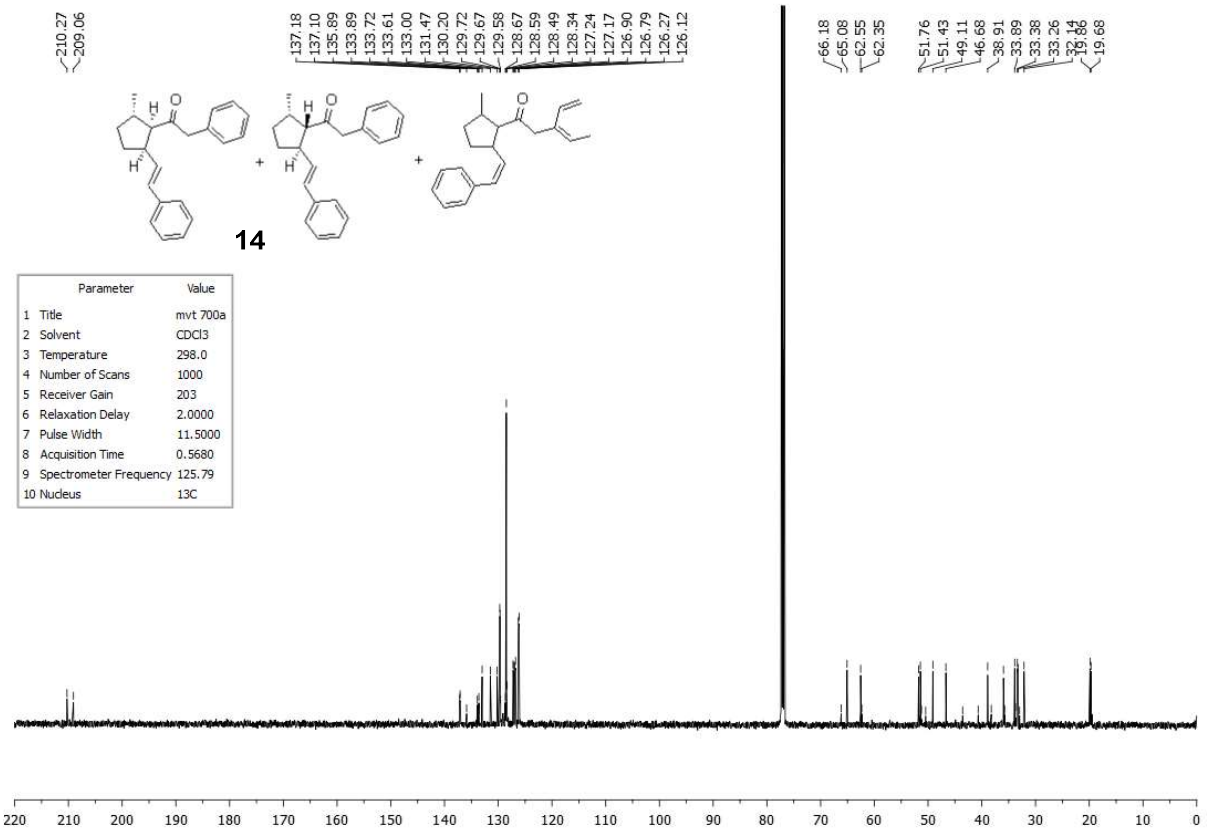

11
Parameter Value
1 Title mvt 725
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 64
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H

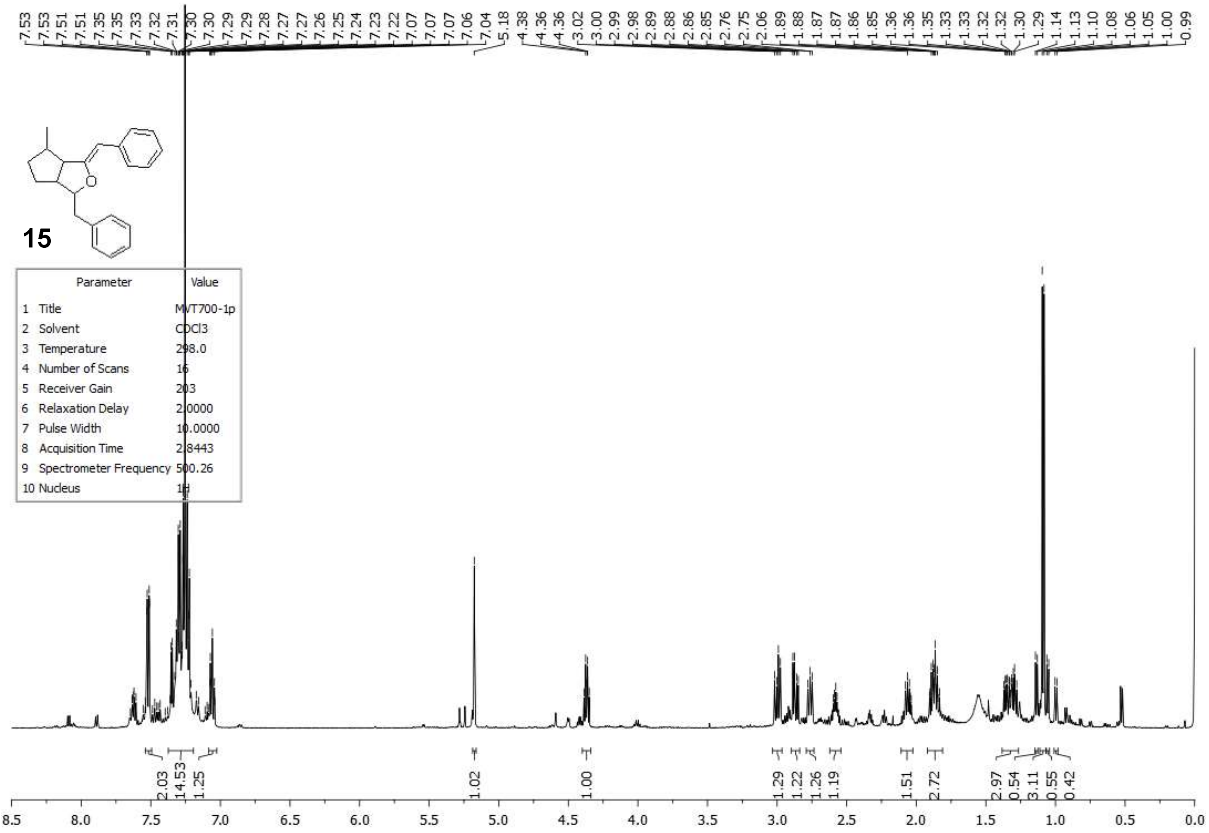

11
Parameter Value
1 Title mvt 725
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 9367
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

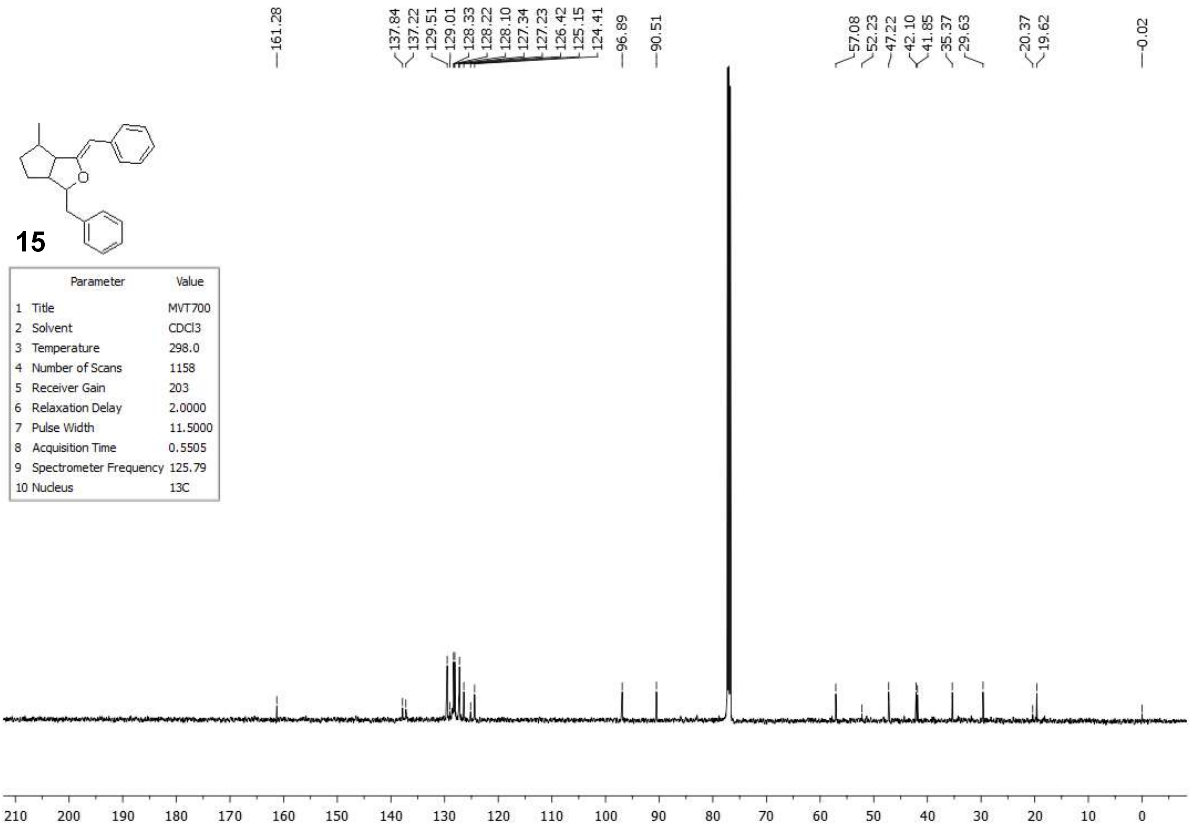

12
Parameter Value
1 Title MVT725-1
2 Solvent C6D6
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 144
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 3.4516
9 Spectrometer Frequency 500.26
10 Nucleus 1H

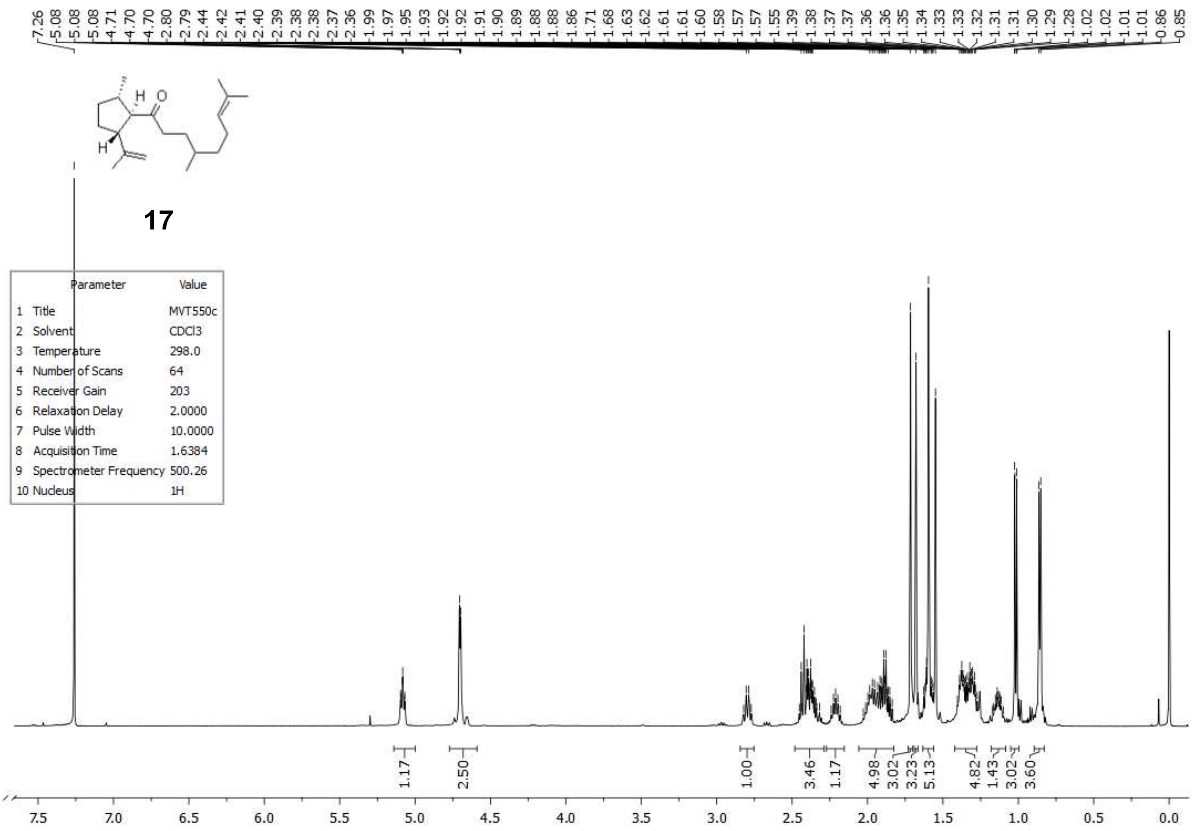

MVT725-1
12
Parameter Value
1 Title MVT725-1
2 Solvent C6D6
3 Temperature 298.0
4 Number of Scans 341
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
f1 (ppm)

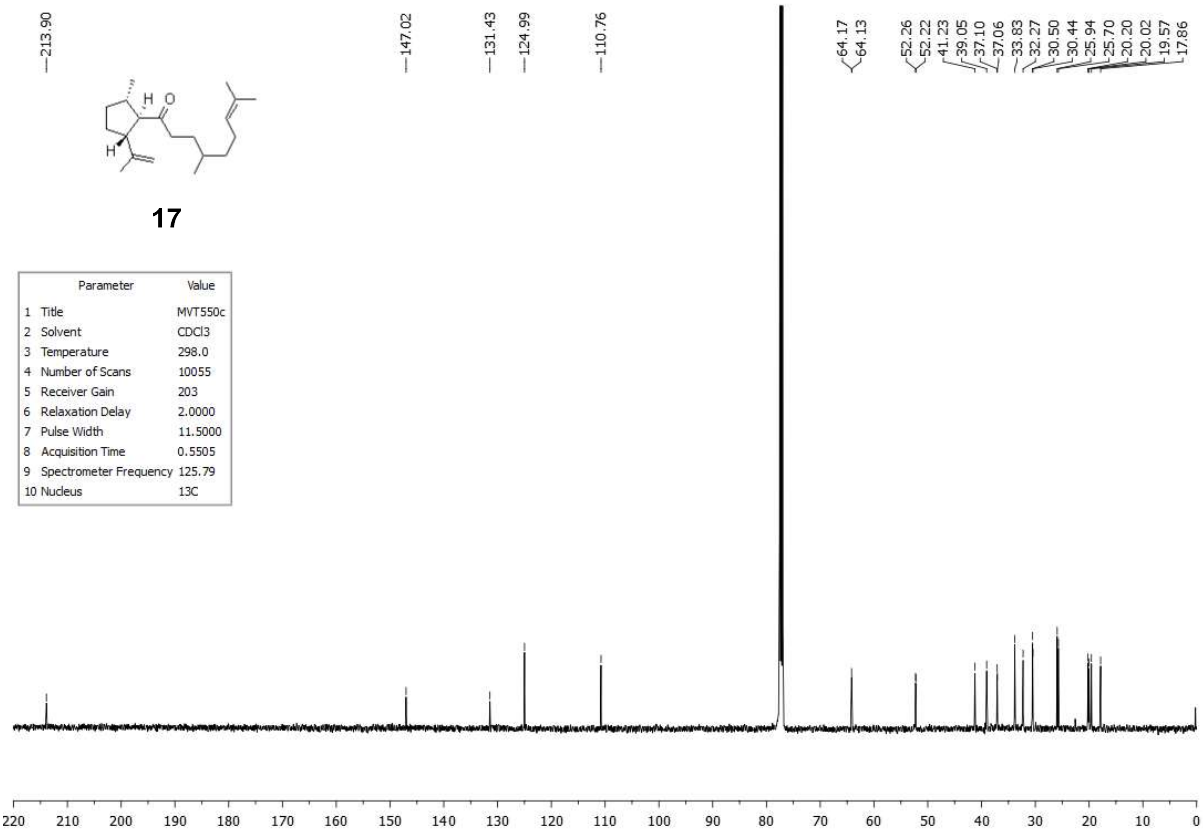

14
Parameter Value
1 Title mvt 700a
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H

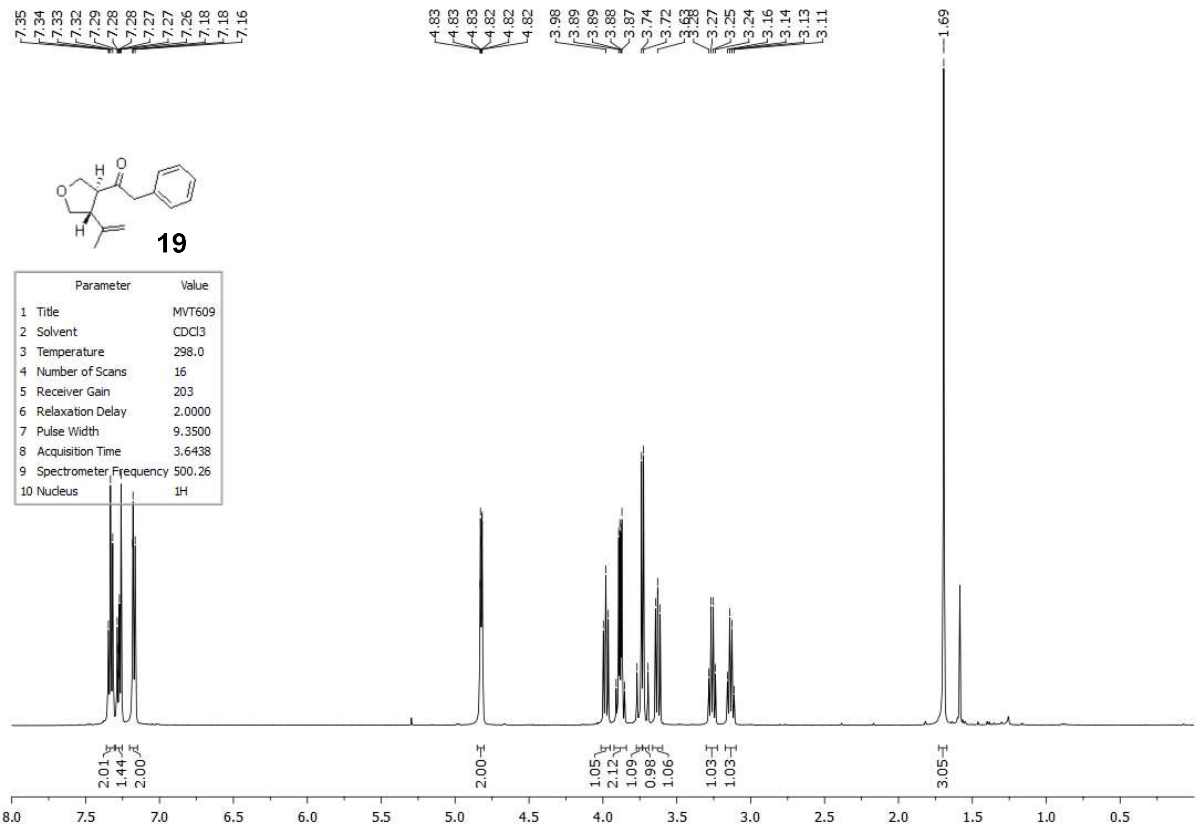

14
Parameter Value
1 Title mvt 700a
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 1000
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5680
9 Spectrometer Frequency 125.79
10 Nucleus 13C

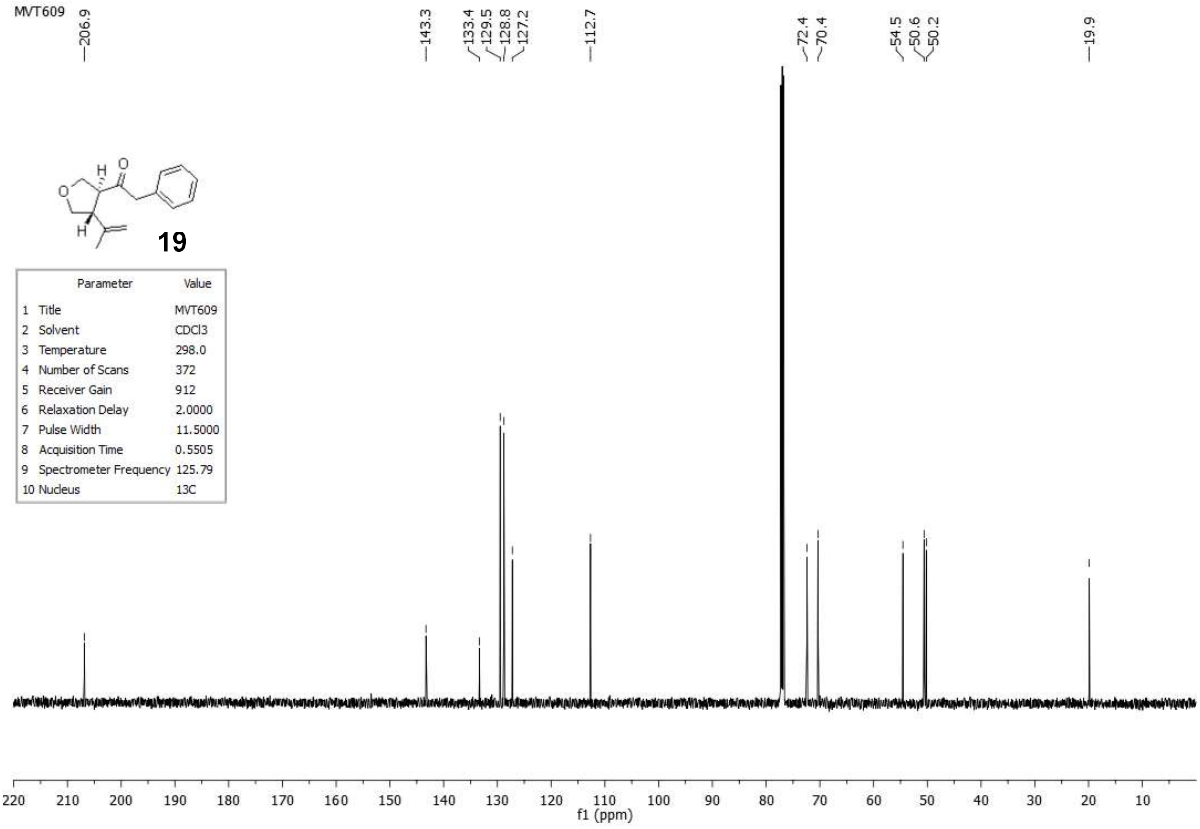

15
Parameter Value
1 Title MVT700-1p
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 2.8443
9 Spectrometer Frequency 500.26
10 Nucleus 1H

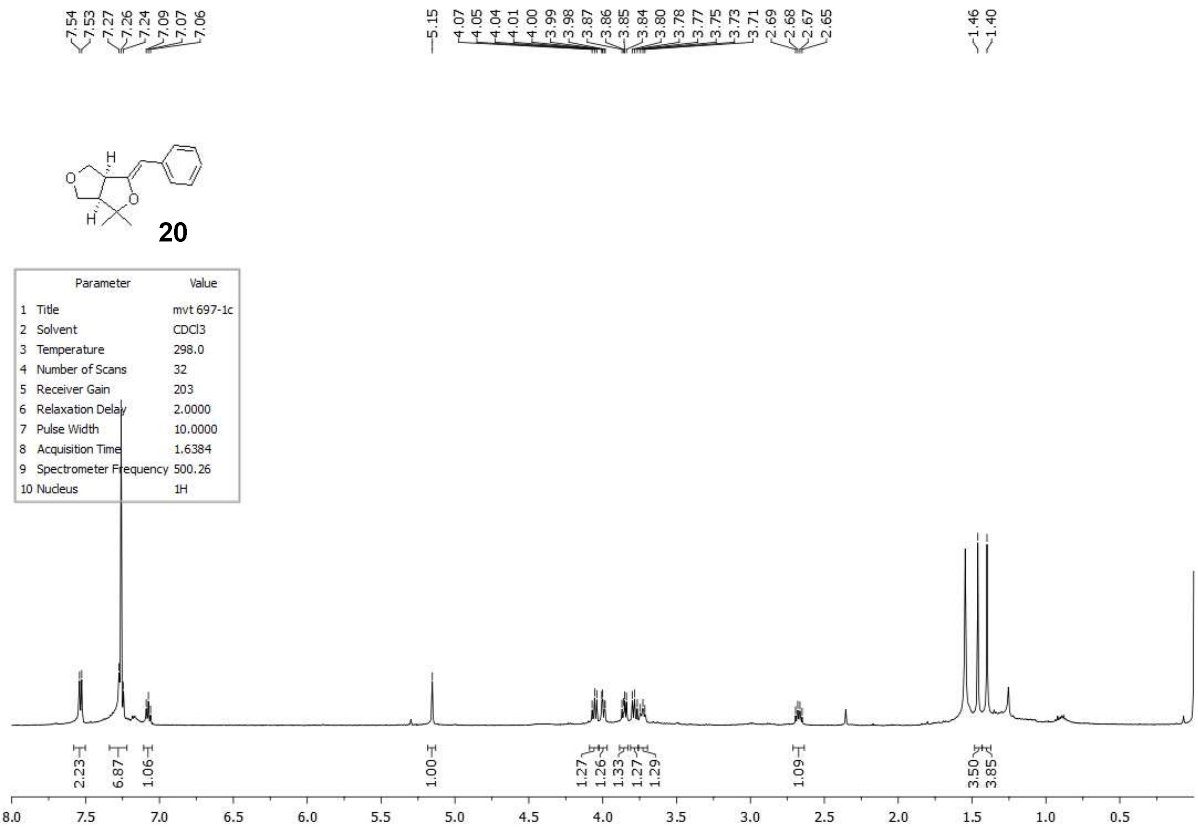

15
Parameter Value
1 Title MVT700
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 1158
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

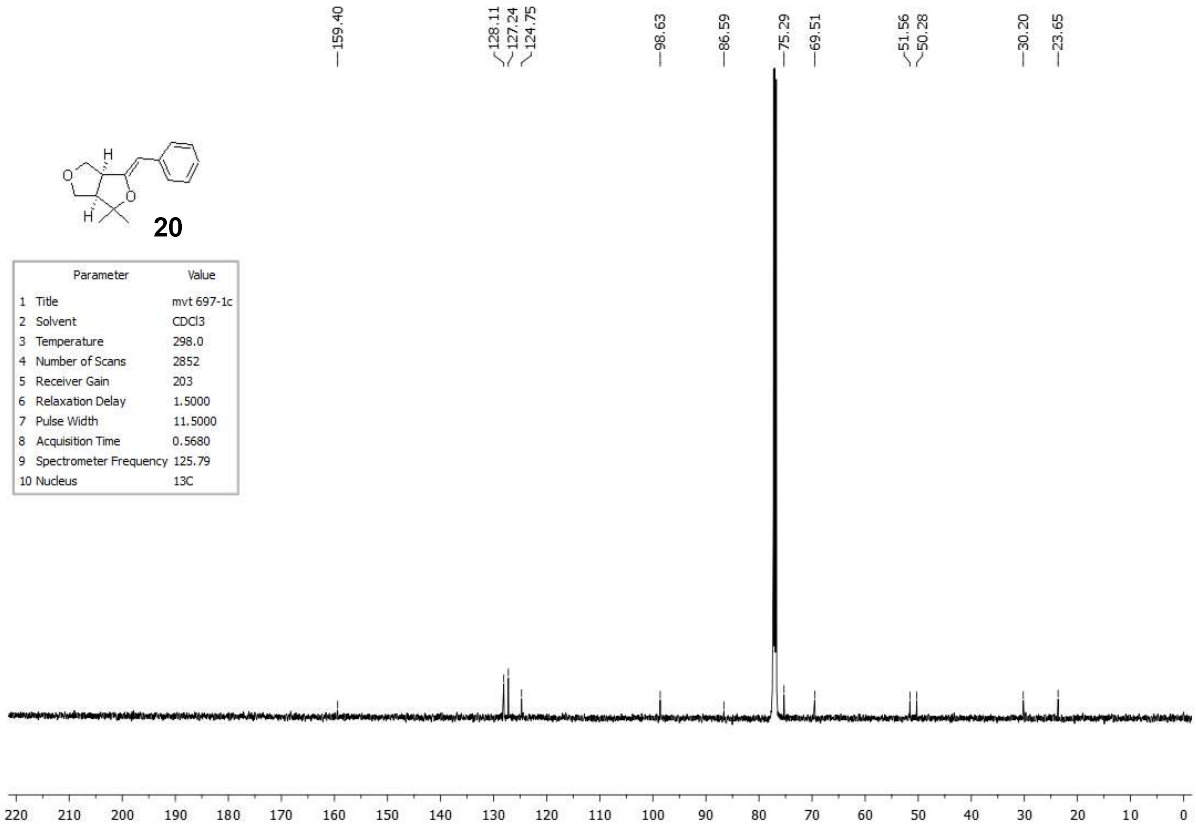

7.26 5.08 5.08 5.06 4.71 4.70 4.70 2.80 2.79 2.44 2.42 2.41 2.40 2.39 2.38 2.38 2.37 2.36 1.99 1.97 1.95 1.93 1.92 1.92 1.91 1.90 1.89 1.88 1.88 1.86 1.71 1.68 1.63 1.62 1.61 1.61 1.60 1.58 1.57 1.57 1.55 1.39 1.38 1.37 1.37 1.36 1.36 1.35 1.34 1.33 1.33 1.32 1.31 1.31 1.30 1.29 1.28 1.02 1.02 1.01 1.01 0.86 0.85
17
Parameter Value
1 Title MVT550c
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 64
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1.17 2.50 1.00 3.46 1.17 4.98 3.02 3.23 5.13 4.82 1.43 3.02 3.60
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

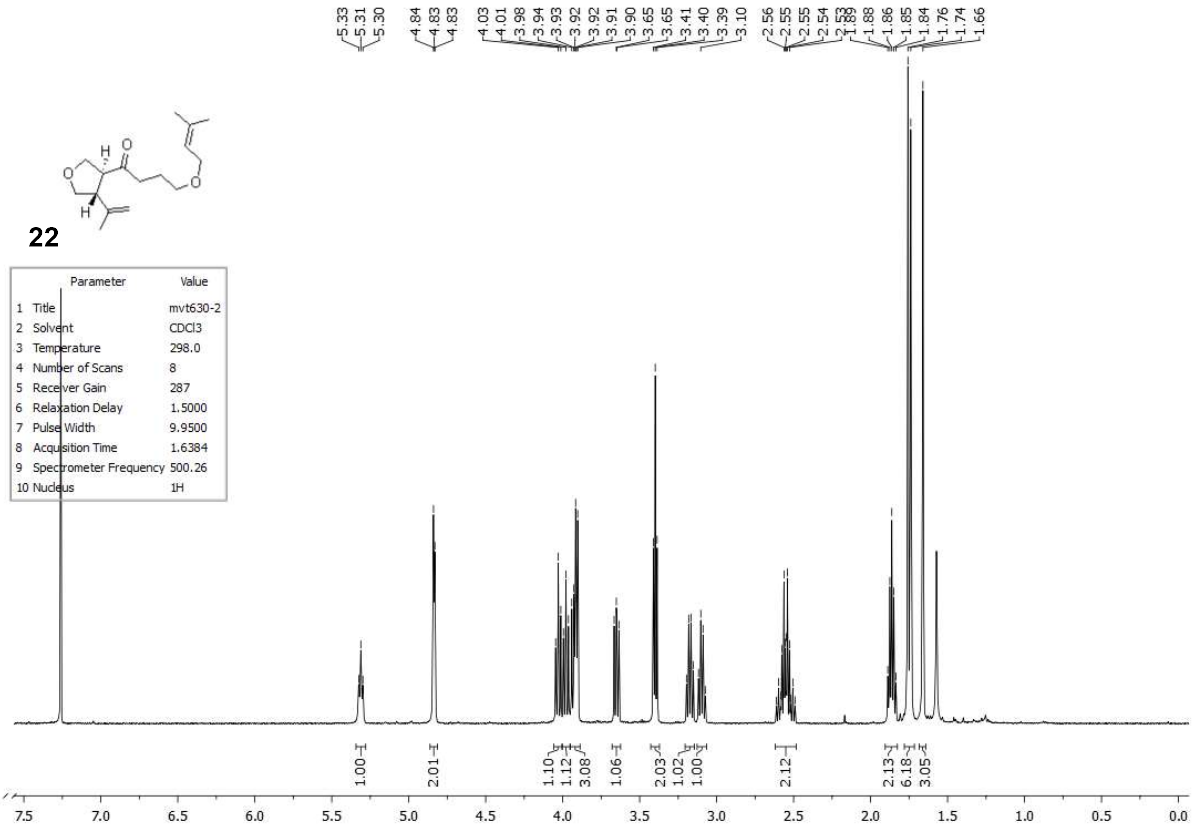

213.90 147.02 131.43 124.99 110.76 64.17 64.13 52.26 52.22 41.23 39.05 37.10 37.06 33.83 32.27 30.50 30.44 25.94 25.70 20.20 20.02 19.57 17.86
17
Parameter Value
1 Title MVT550c
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 10055
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

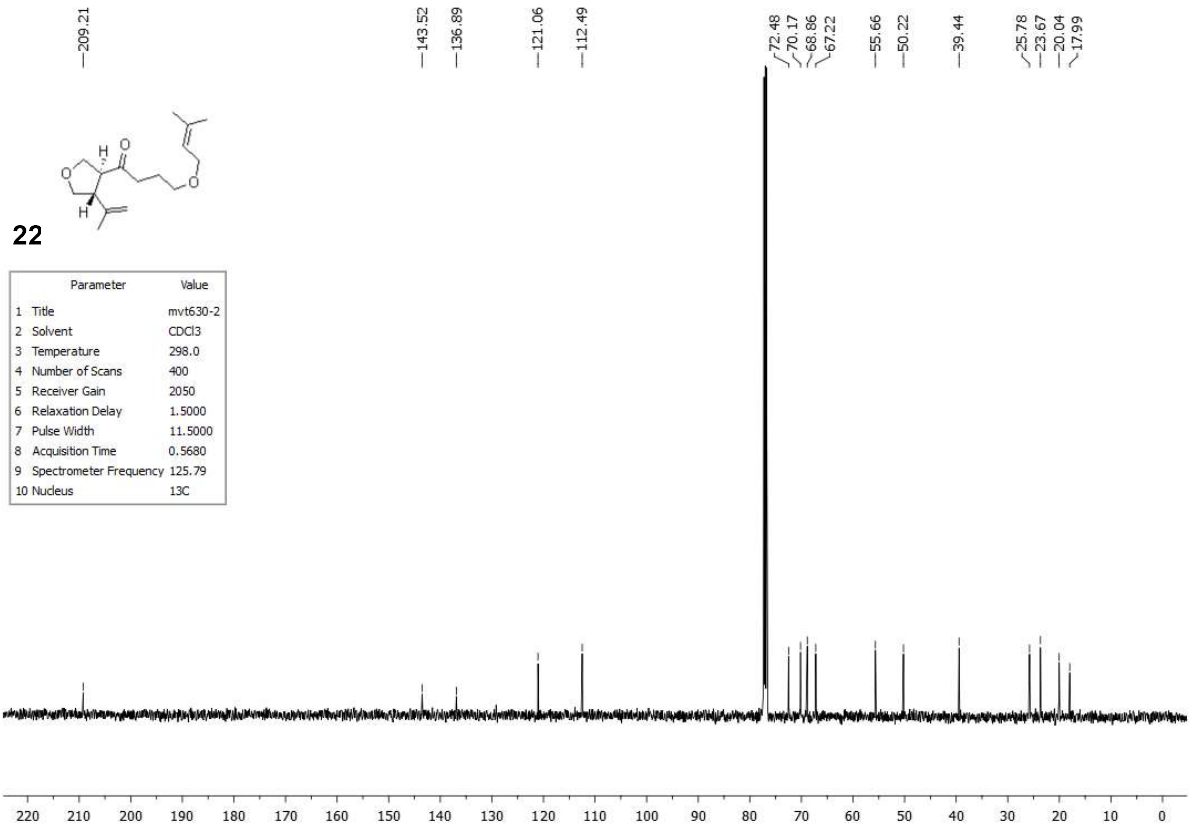

19
Parameter Value
1 Title MVT609
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.6438
9 Spectrometer Frequency 500.26
10 Nucleus 1H

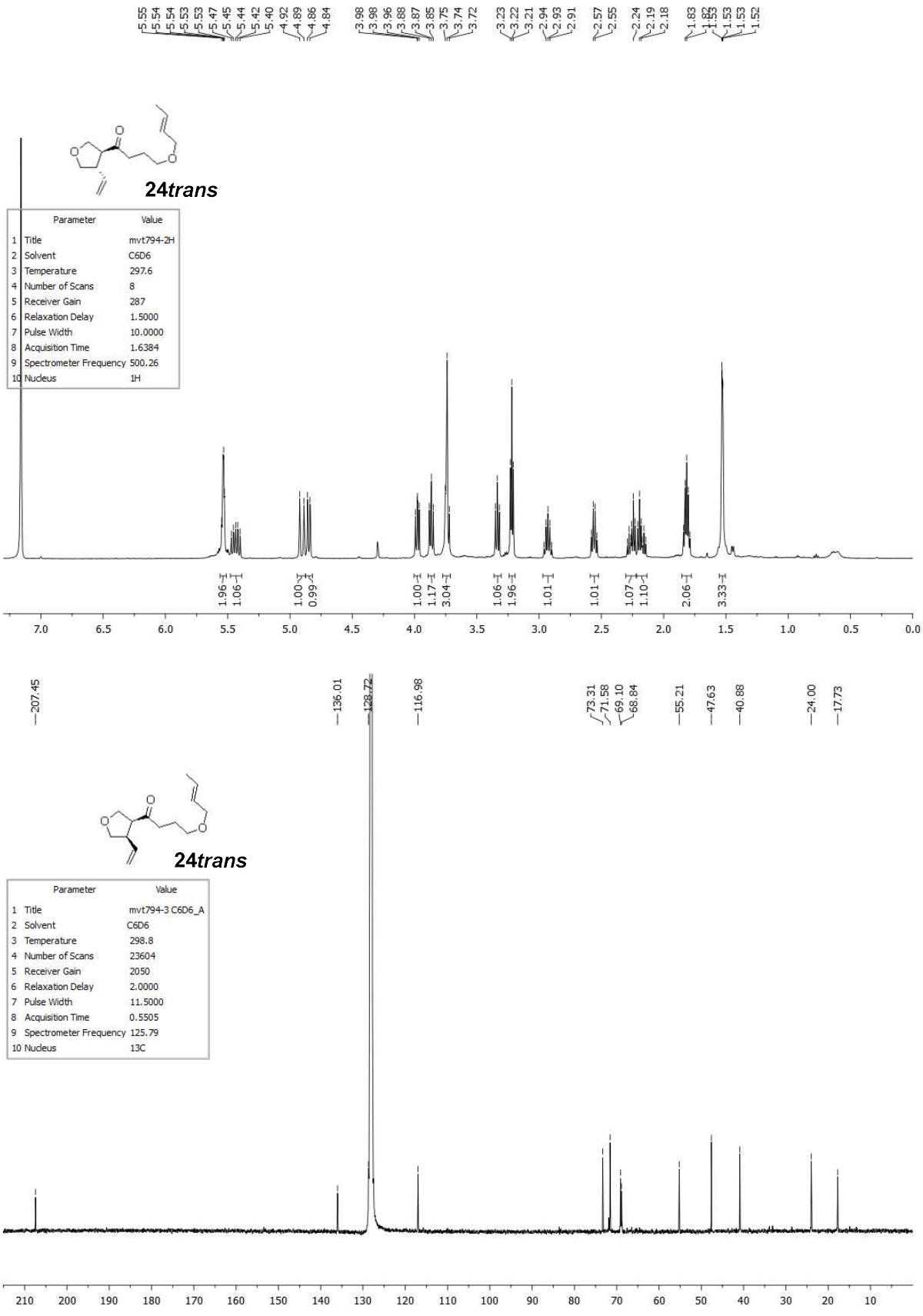

MVT609
19
Parameter Value
1 Title MVT609
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 372
5 Receiver Gain 912
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
f1 (ppm)


7.54
7.53
7.27
7.26
7.24
7.09
7.07
7.06
5.15
4.07
4.05
4.04
4.01
4.00
3.99
3.98
3.87
3.86
3.85
3.84
3.80
3.78
3.77
3.75
3.73
3.71
2.69
2.68
2.67
2.65
1.46
1.40
20
Parameter Value
1 Title mvt 697-1c
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 32
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
2.23
6.87
1.06
1.00
1.27
1.26
1.33
1.27
1.29
1.09
3.50
3.85
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

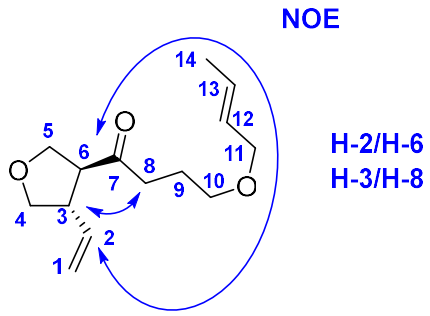

159.40
128.11
127.24
124.75
98.63
86.59
75.29
69.51
51.56
50.28
30.20
23.65
20
Parameter Value
1 Title mvt 697-1c
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 2852
5 Receiver Gain 203
6 Relaxation Delay 1.5000
7 Pulse Width 11.5000
8 Acquisition Time 0.5680
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

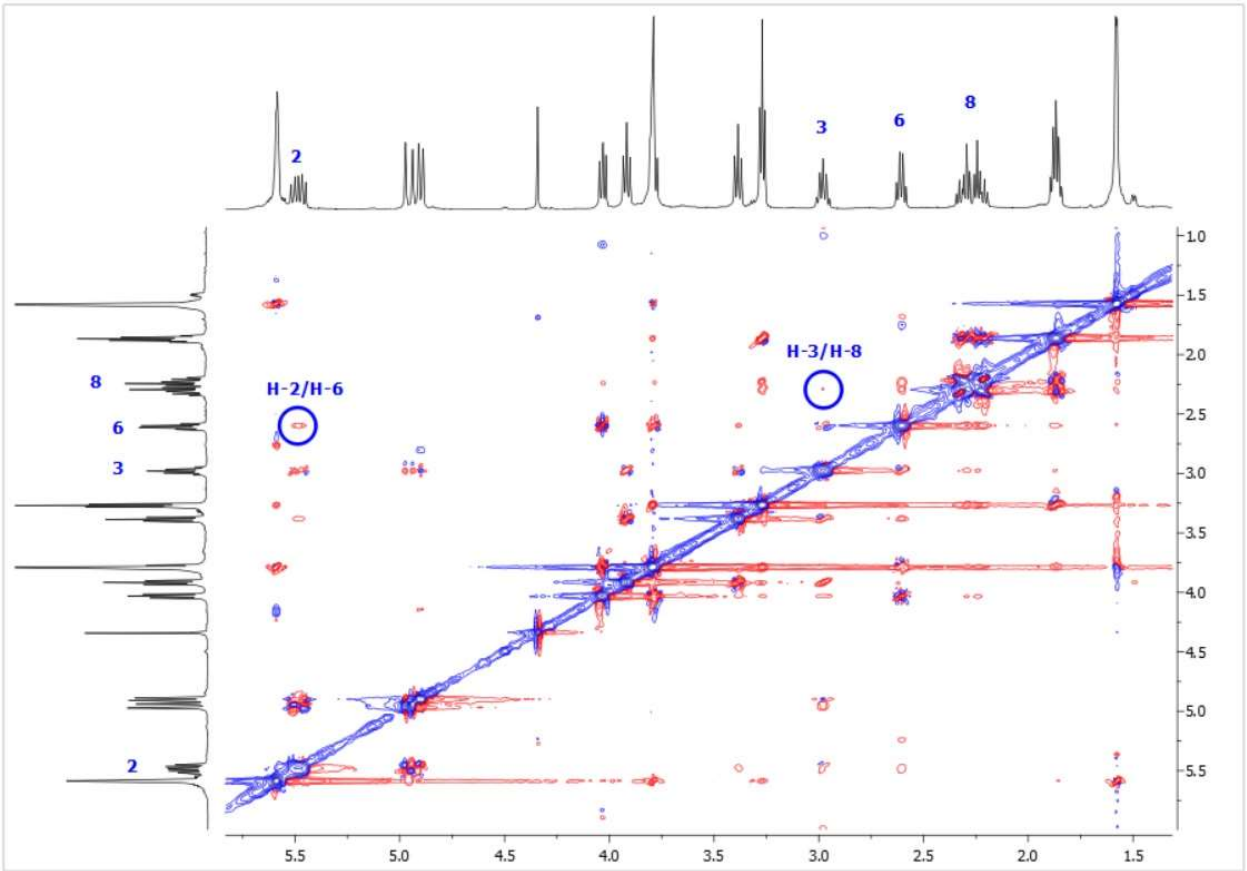

22
Parameter Value
1 Title mvt630-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 8
5 Receiver Gain 287
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H

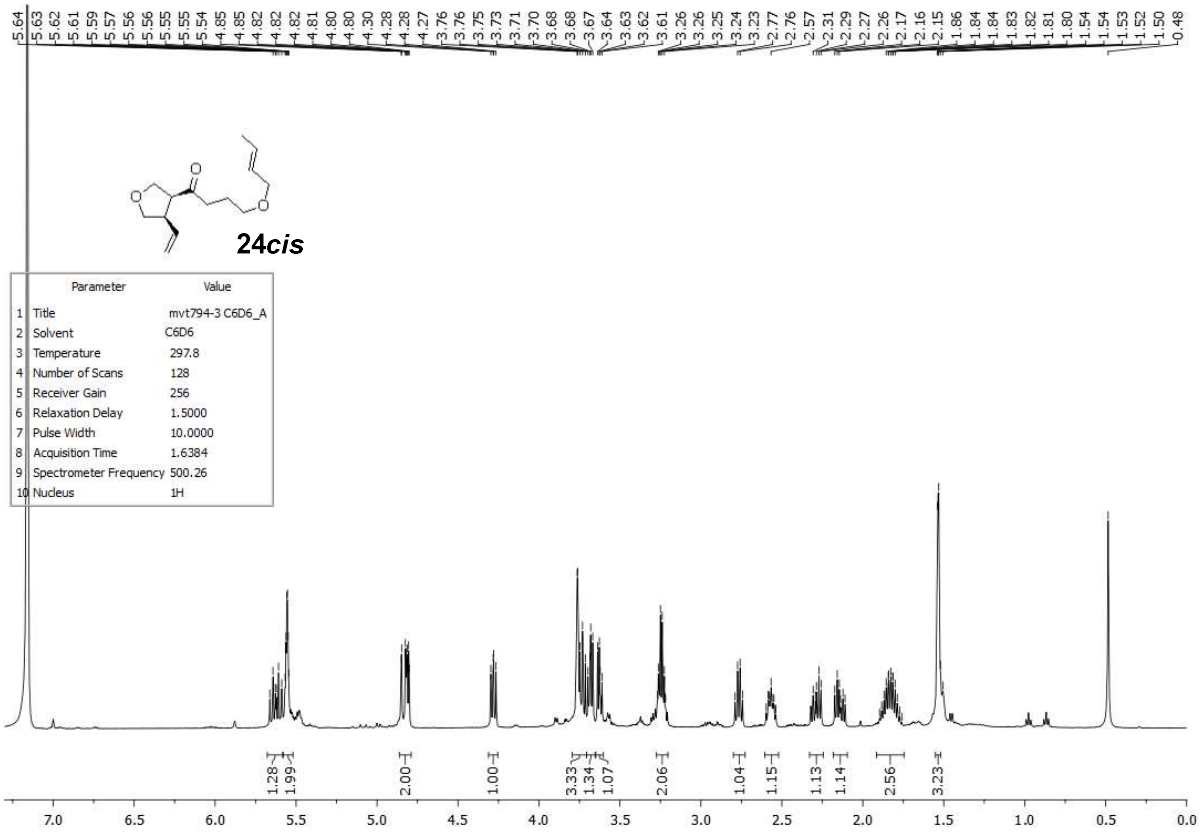

22
Parameter Value
1 Title mvt630-2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 400
5 Receiver Gain 2050
6 Relaxation Delay 1.5000
7 Pulse Width 11.5000
8 Acquisition Time 0.5680
9 Spectrometer Frequency 125.79
10 Nucleus 13C

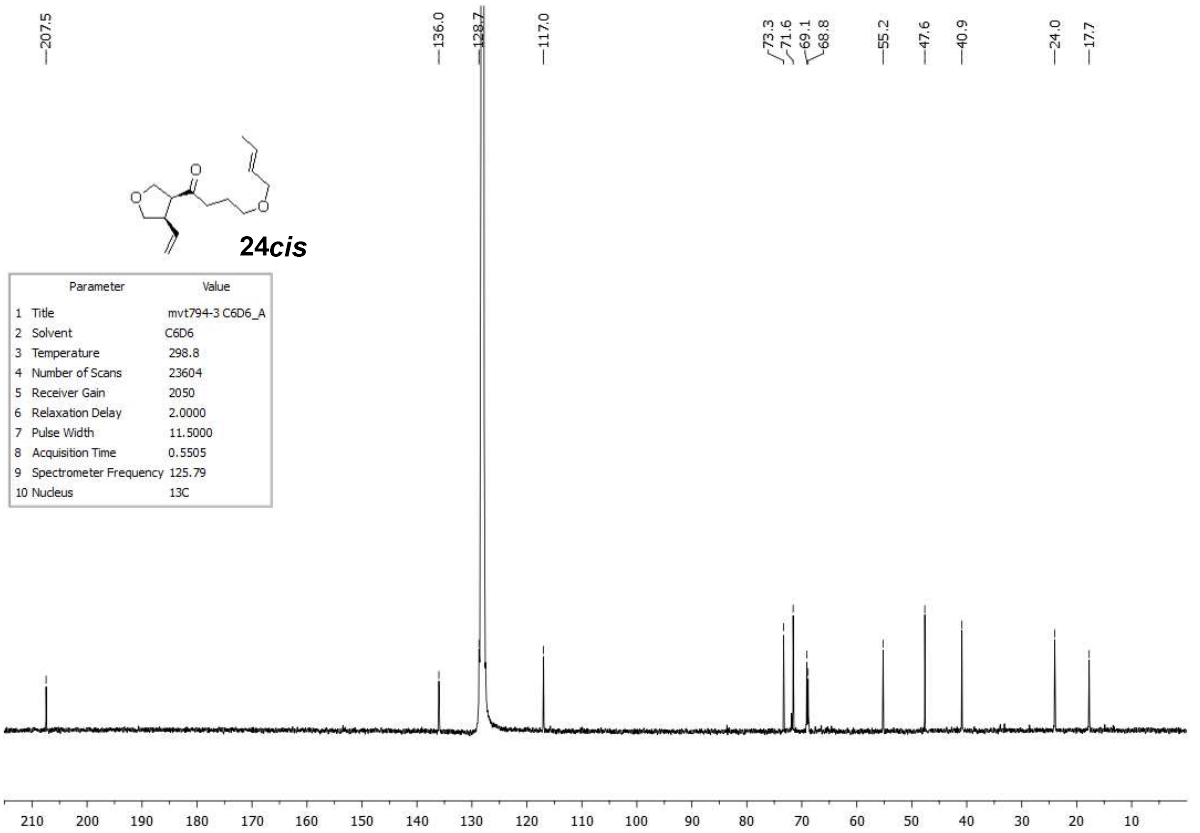

24trans
Parameter Value
1 Title mvt794-2H
2 Solvent C6D6
3 Temperature 297.6
4 Number of Scans 8
5 Receiver Gain 287
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
24trans
Parameter Value
1 Title mvt794-3 C6D6_A
2 Solvent C6D6
3 Temperature 298.8
4 Number of Scans 23604
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

Correlations (NOESY) of **24*trans***:

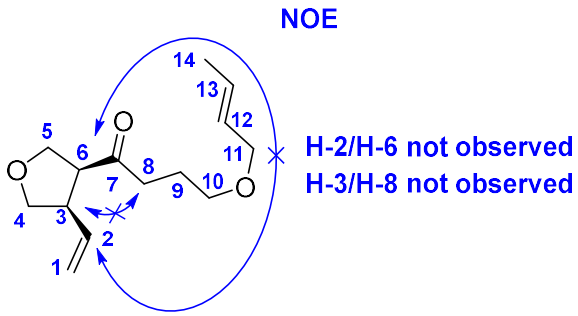


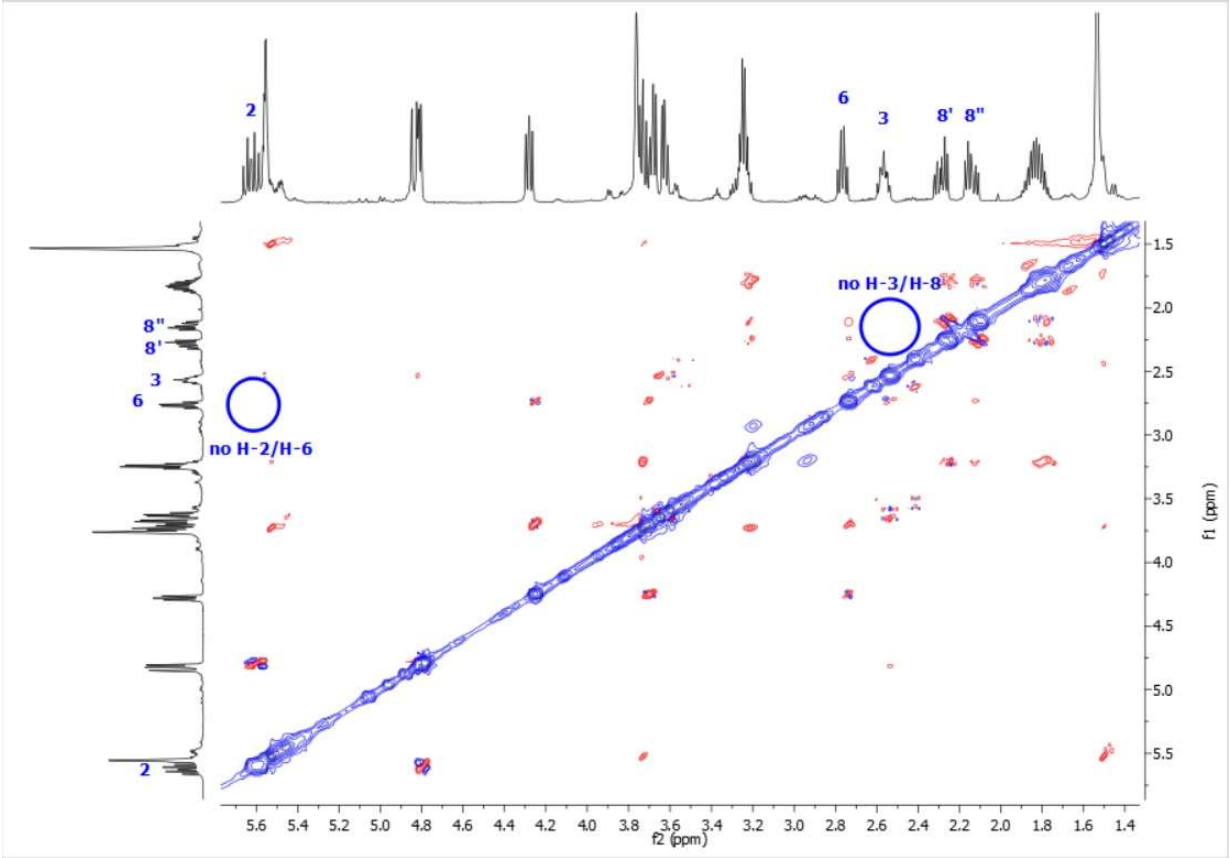


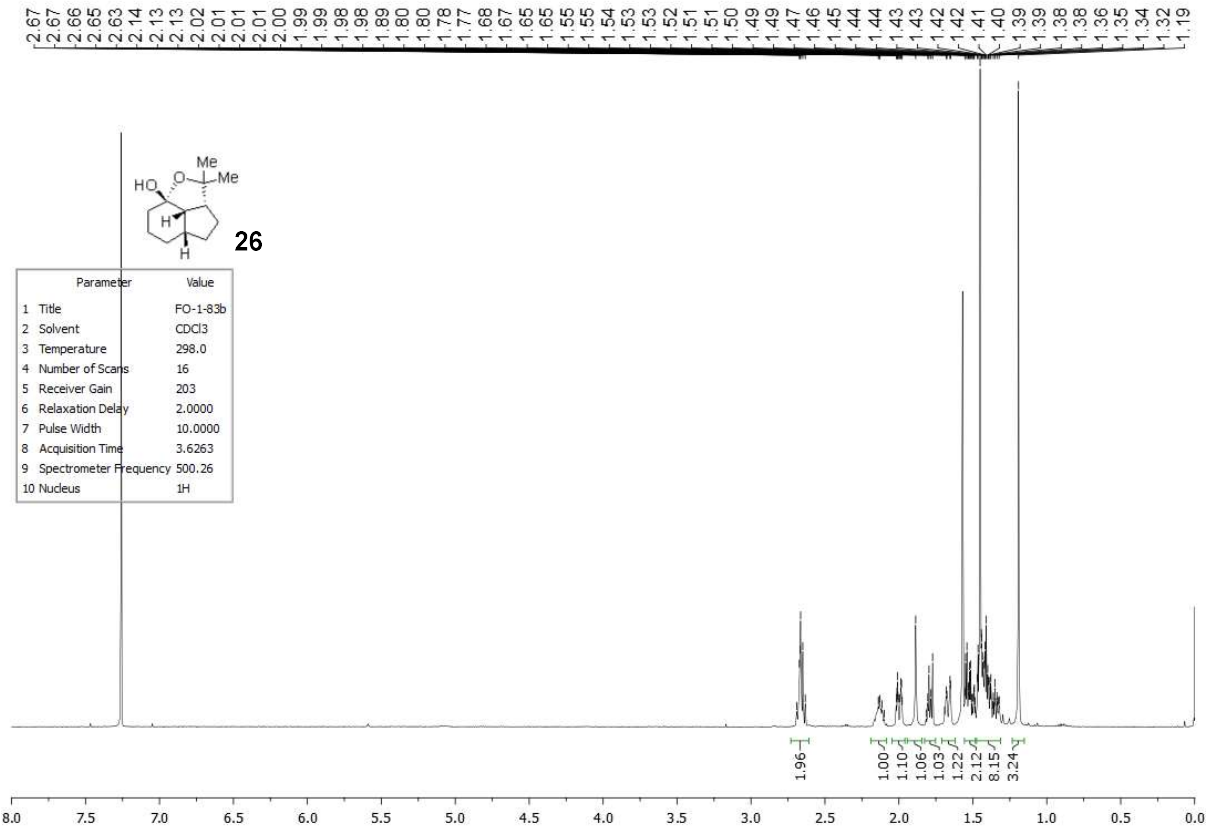

24cis
Parameter Value
1 Title mvt794-3 C6D6_A
2 Solvent C6D6
3 Temperature 297.8
4 Number of Scans 128
5 Receiver Gain 256
6 Relaxation Delay 1.5000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H

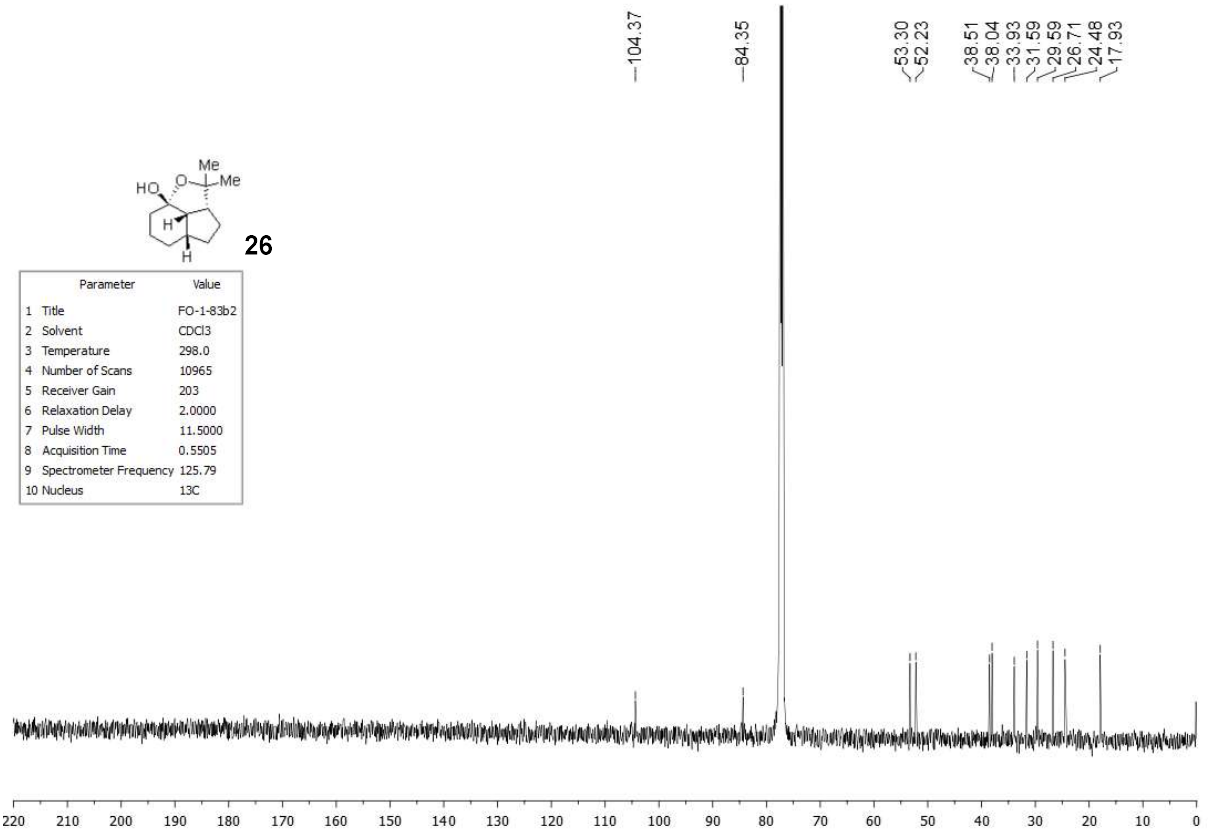

24cis
Parameter Value
1 Title mvt794-3 C6D6_A
2 Solvent C6D6
3 Temperature 298.8
4 Number of Scans 23604
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C

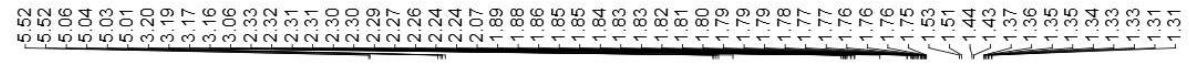
Correlations (NOESY) of **24*cis***:

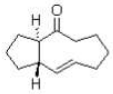





2.67 2.67 2.66 2.65 2.63 2.14 2.13 2.13 2.02 2.01 2.01 2.01 2.00 1.99 1.99 1.98 1.98 1.89 1.80 1.78 1.77 1.68 1.67 1.65 1.65 1.55 1.55 1.54 1.53 1.53 1.52 1.51 1.51 1.50 1.49 1.49 1.47 1.46 1.45 1.44 1.44 1.43 1.43 1.42 1.42 1.41 1.40 1.39 1.39 1.38 1.38 1.36 1.35 1.34 1.32 1.19
Me
HO
O
Me
H
H
26
Parameter Value
1 Title FO-1-83b
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 3.6263
9 Spectrometer Frequency 500.26
10 Nucleus 1H
1.96
1.00
1.10
1.06
1.03
1.22
2.12
8.15
3.24
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

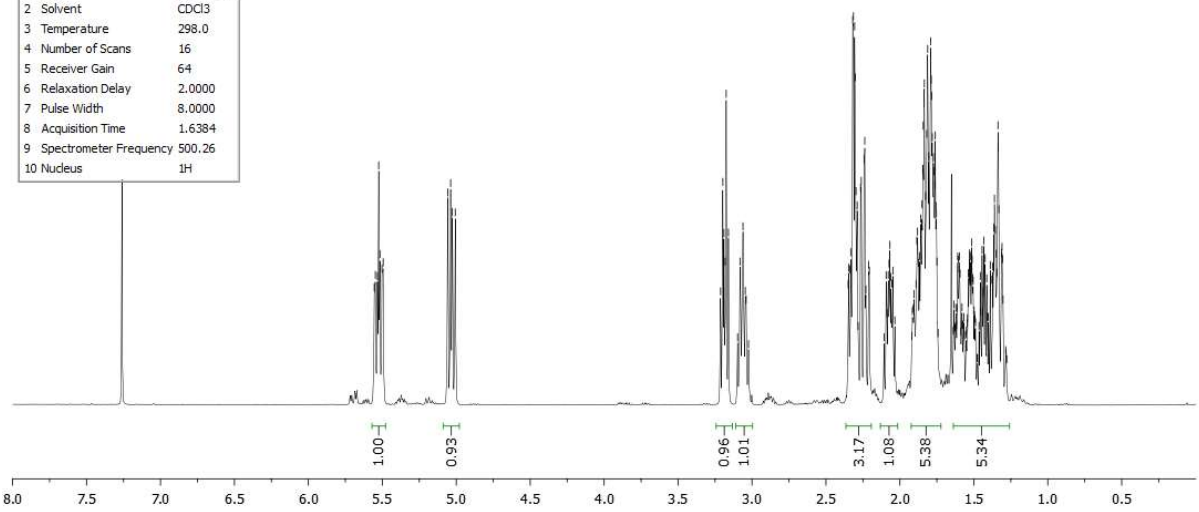

104.37
84.35
53.30
52.23
38.51
38.04
33.93
31.59
29.59
26.71
24.48
17.93
Me
HO
O
Me
H
H
26
Parameter Value
1 Title FO-1-83b2
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 10965
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

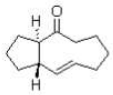




28

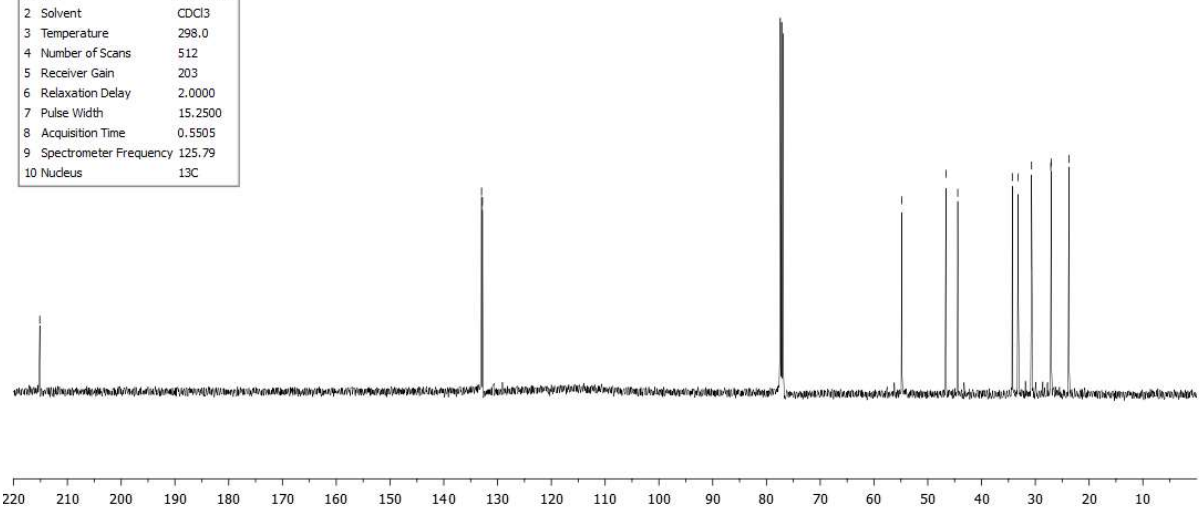
	Parameter	Value
1	Title	BZVO2742
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	16
5	Receiver Gain	64
6	Relaxation Delay	2.0000
7	Pulse Width	8.0000
8	Acquisition Time	1.6384
9	Spectrometer Frequency	500.26
10	Nucleus	1H



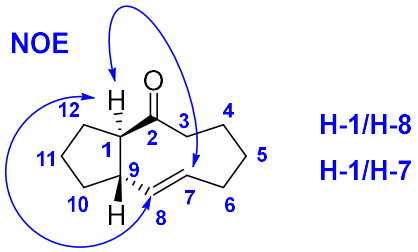


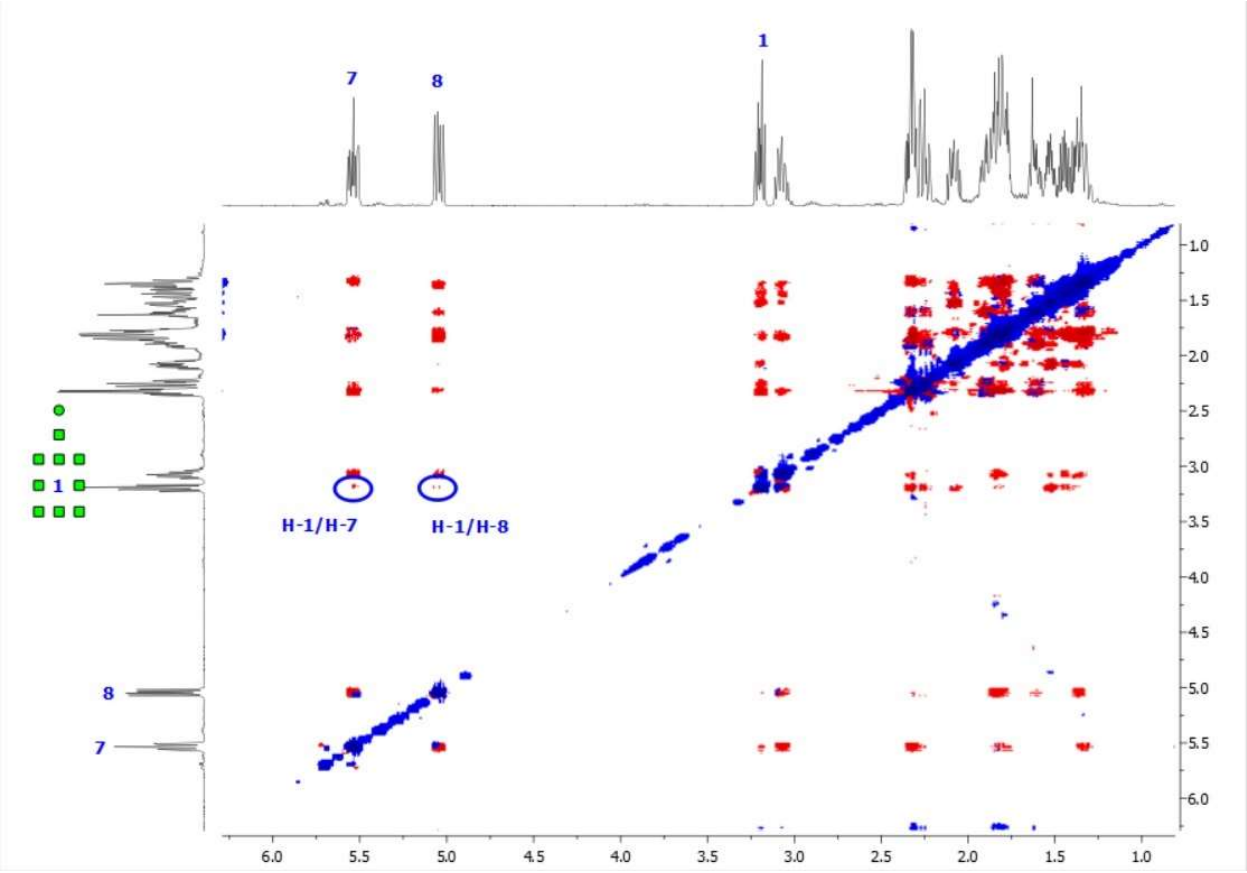
28

	Parameter	Value
1	Title	BZVO2742
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	512
5	Receiver Gain	203
6	Relaxation Delay	2.0000
7	Pulse Width	15.2500
8	Acquisition Time	0.5505
9	Spectrometer Frequency	125.79
10	Nucleus	13C

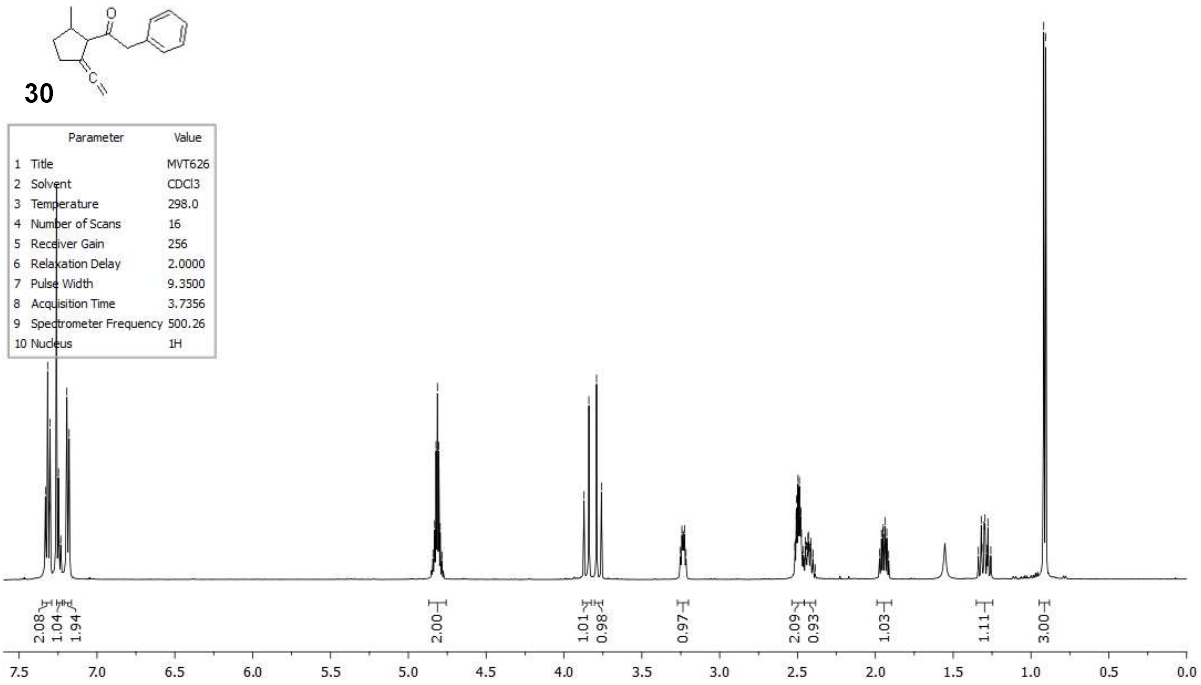


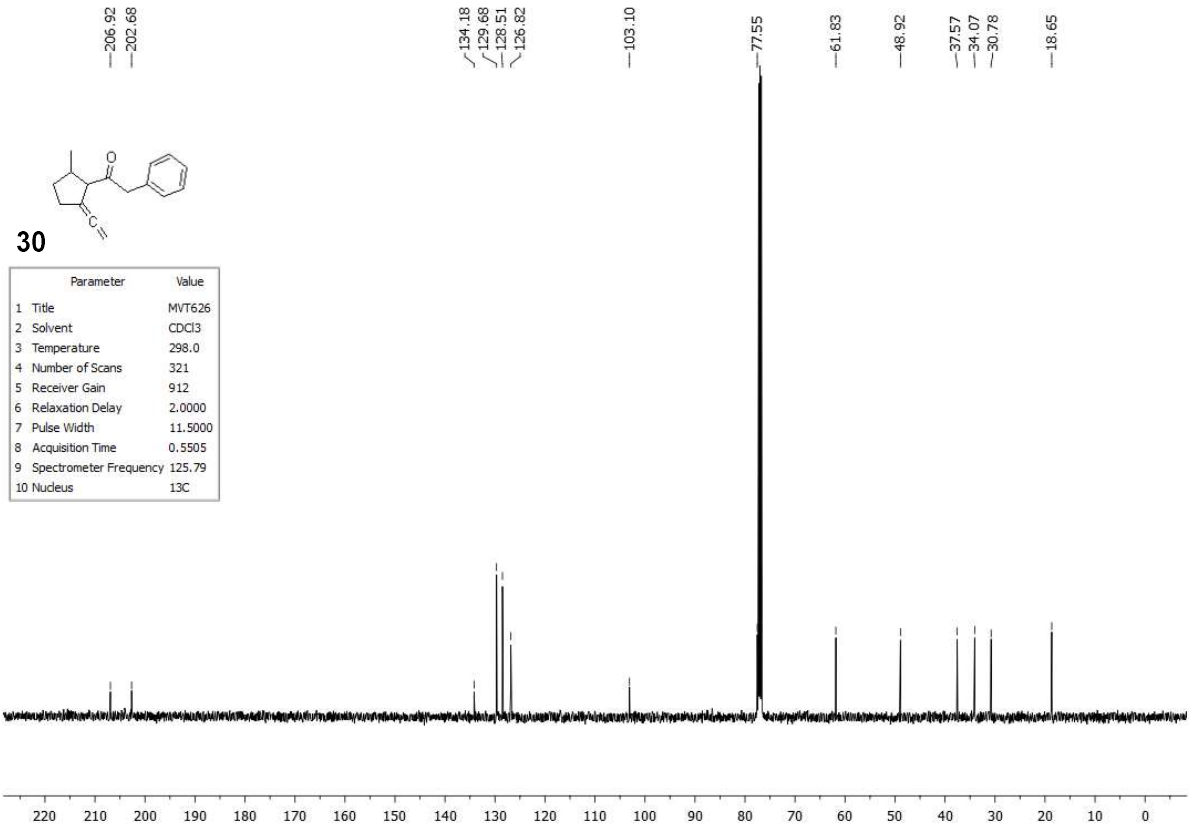
Correlations (NOESY) for **28**:

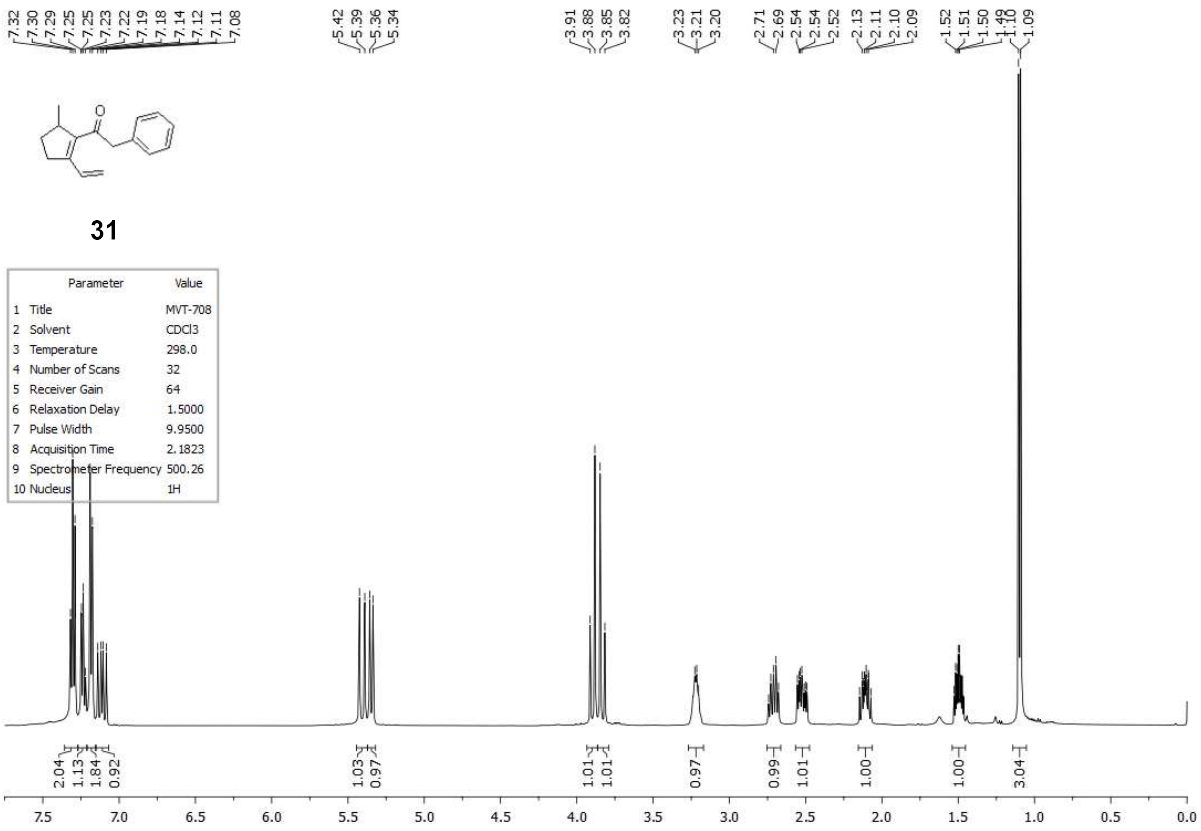


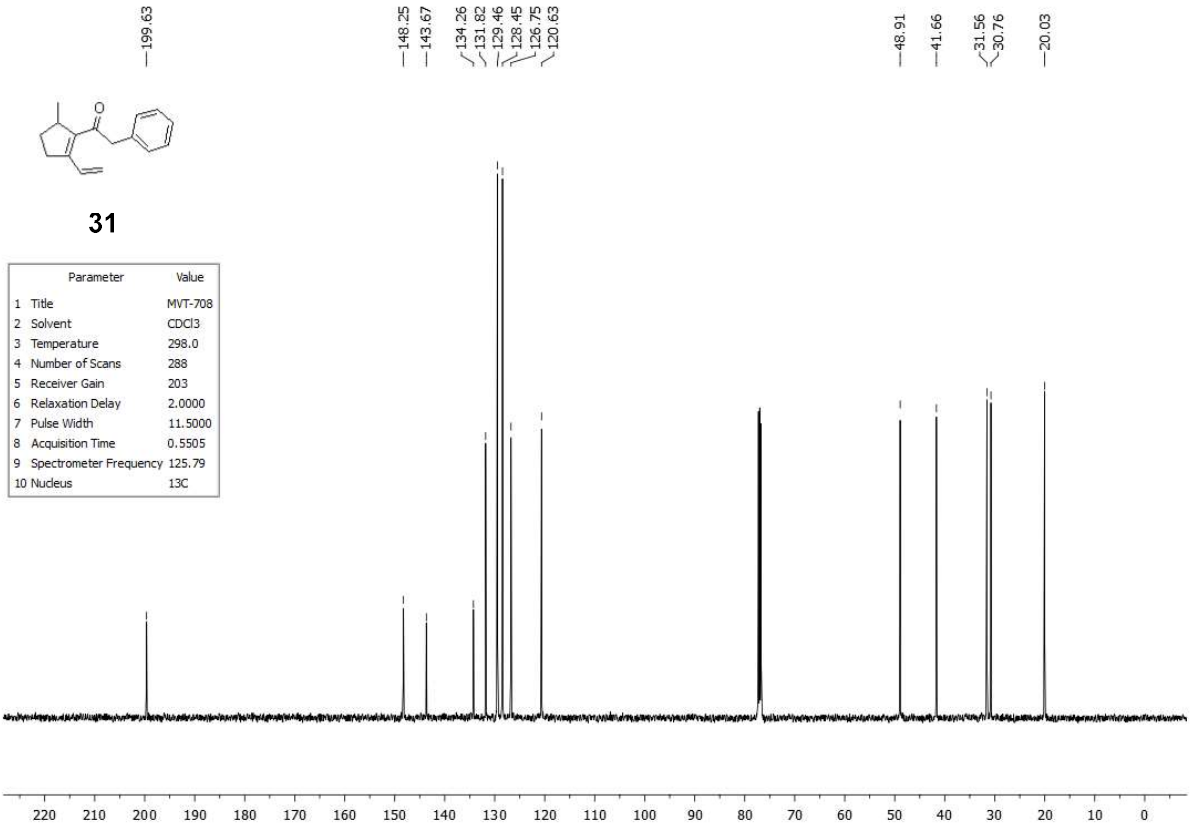



7.33 7.33 7.32 7.30 7.30 7.25 7.25 7.24 7.23 7.20 7.19 7.18
4.83 4.82 4.81 4.80 4.80 3.87 3.84 3.79 3.76 3.25 3.24 3.24 3.23 2.52 2.51 2.51 2.51 2.50 2.49 2.49 2.48 2.48 2.47 2.46 2.45 2.45 2.44 2.44 2.43 2.43 2.43 2.42 2.42 2.41 1.97 1.96 1.95 1.95 1.94 1.93 1.34 1.32 1.31 1.30 1.30 1.28 1.26 0.92 0.91

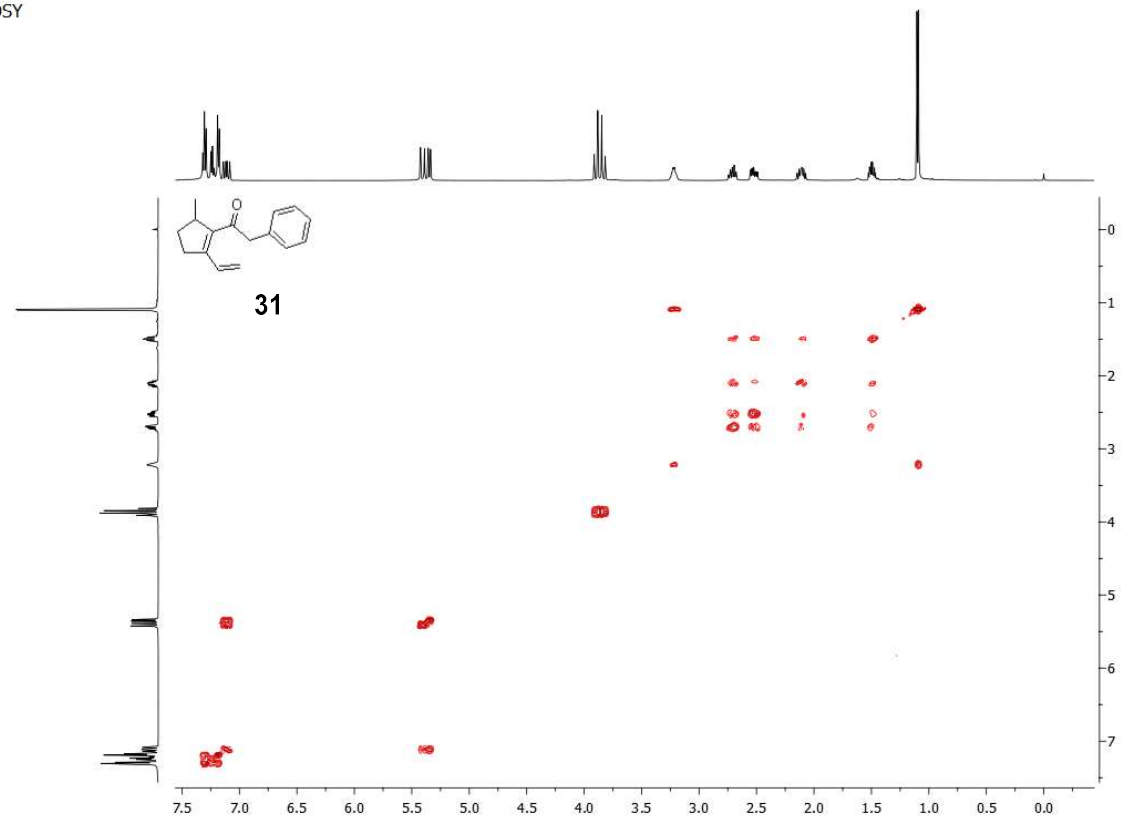

30
Parameter Value
1 Title MVT626
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 256
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.7356
9 Spectrometer Frequency 500.26
10 Nucleus 1H
2.08 1.04 1.94 2.00 1.01 0.98 0.97 2.09 0.93 1.03 1.11 3.00
7.5 7.0 6.5 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


206.92 202.68 134.18 129.68 128.51 126.82 103.10 77.55 61.83 48.92 37.57 34.07 30.78 18.65
30
Parameter Value
1 Title MVT626
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 321
5 Receiver Gain 912
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

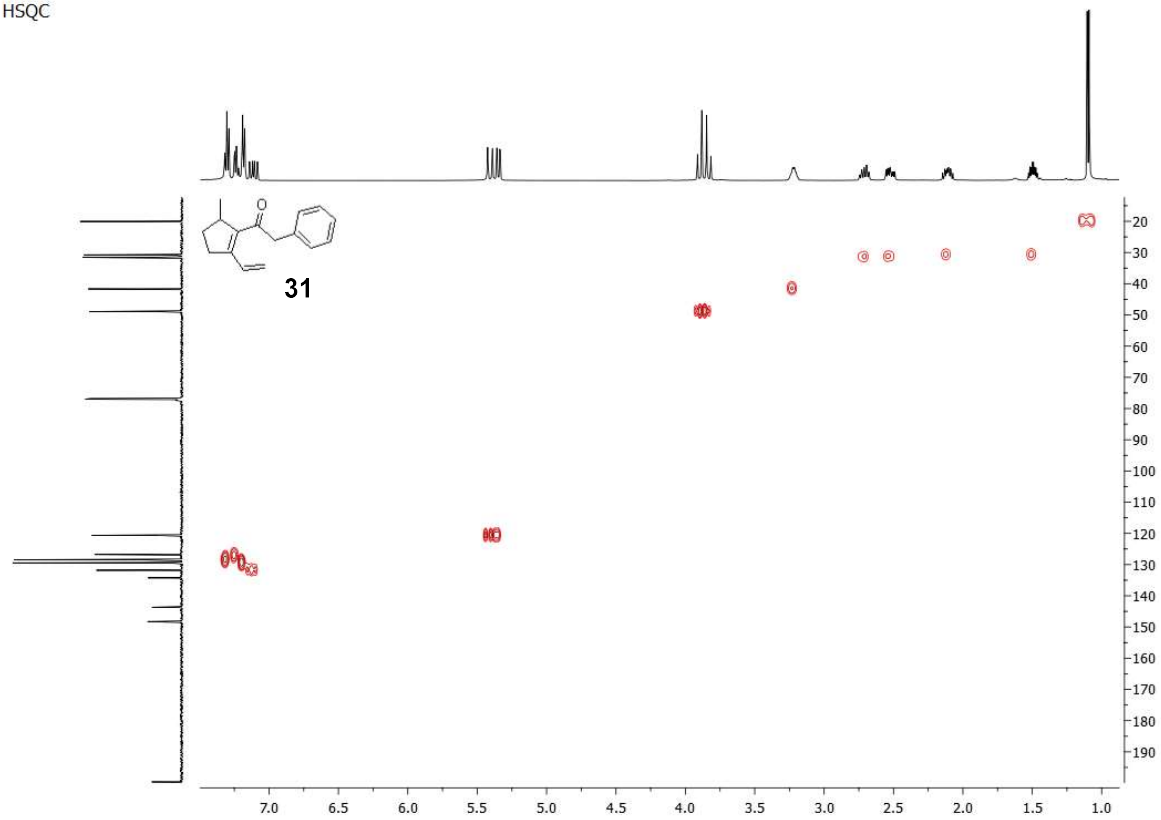

7.32
7.30
7.29
7.25
7.25
7.23
7.22
7.19
7.18
7.14
7.12
7.11
7.08
5.42
5.39
5.36
5.34
3.91
3.88
3.85
3.82
3.23
3.21
3.20
2.71
2.69
2.54
2.54
2.52
2.13
2.11
2.10
2.09
1.52
1.51
1.50
1.49
1.10
1.09
O
31
Parameter Value
1 Title MVT-708
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 32
5 Receiver Gain 64
6 Relaxation Delay 1.5000
7 Pulse Width 9.9500
8 Acquisition Time 2.1823
9 Spectrometer Frequency 500.26
10 Nucleus 1H
2.04
1.13
1.84
0.92
1.03
0.97
1.01
1.01
0.97
0.99
1.01
1.00
1.00
3.04
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

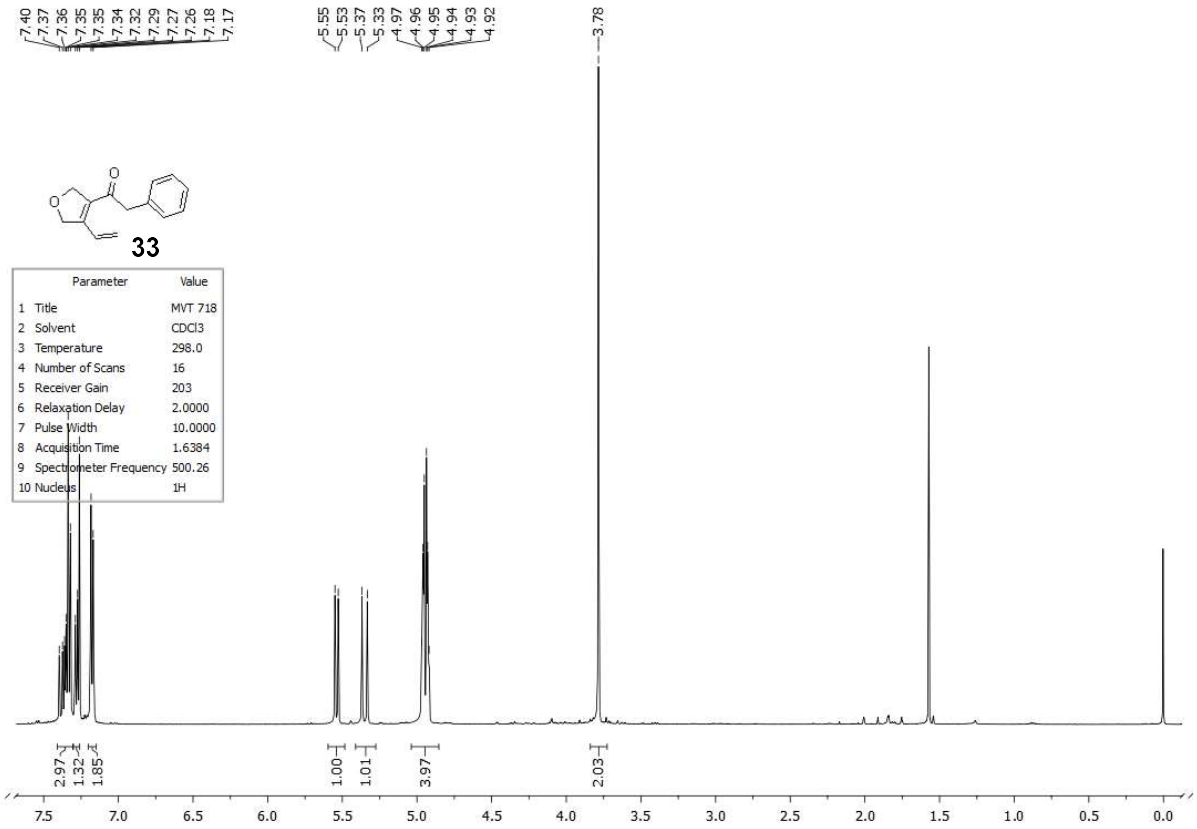

199.63
148.25
143.67
134.26
131.82
129.46
128.45
126.75
120.63
48.91
41.66
31.56
30.76
20.03
O
31
Parameter Value
1 Title MVT-708
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 288
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

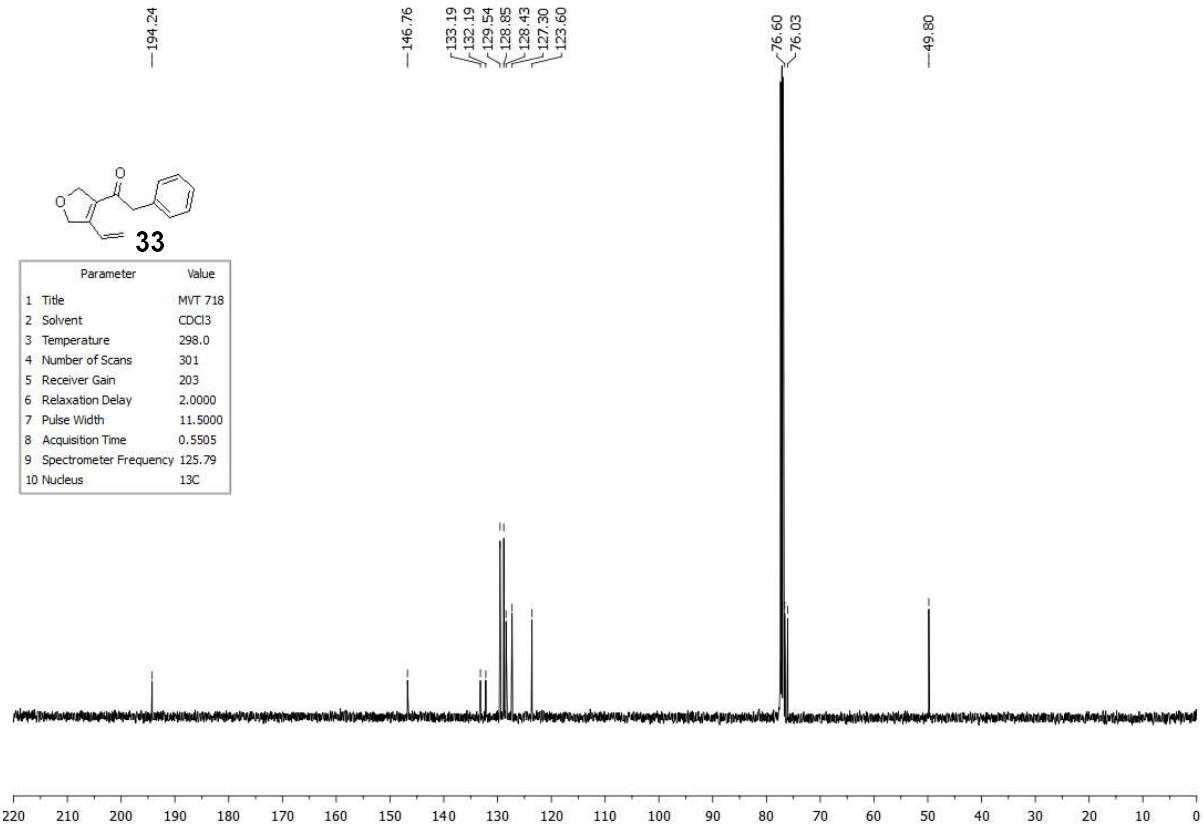
COSY

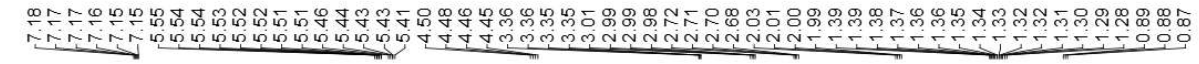

31
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

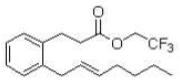
HSQC


31
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


7.40
7.37
7.36
7.35
7.35
7.34
7.32
7.29
7.27
7.26
7.18
7.17
5.55
5.53
5.37
5.33
4.97
4.96
4.95
4.94
4.93
4.92
3.78
O
O
33
Parameter Value
1 Title MVT 718
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 10.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
2.97
1.32
1.85
1.00
1.01
3.97
2.03
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

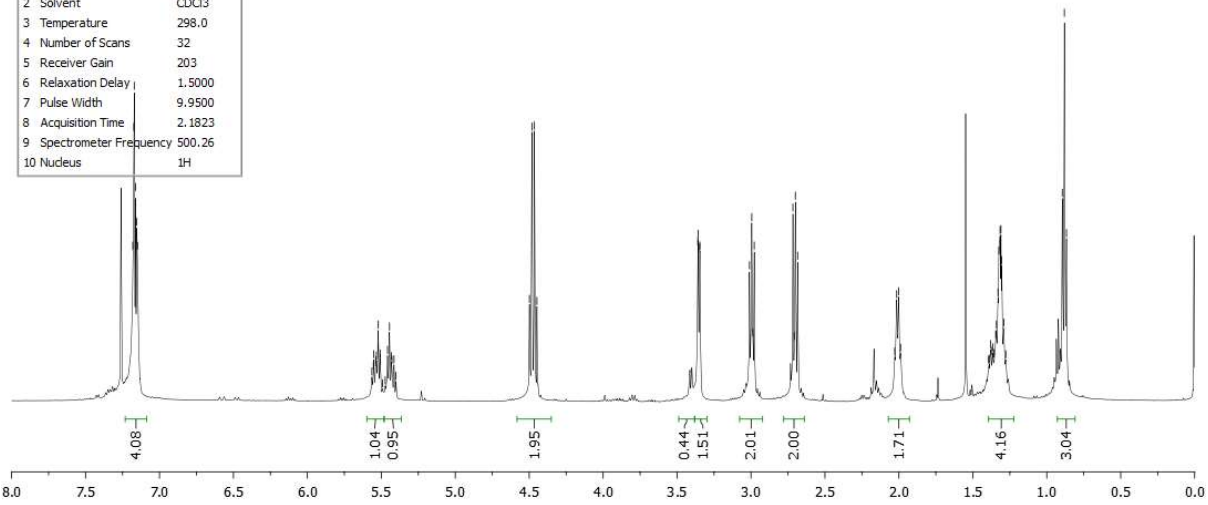

194.24
146.76
133.19
132.19
129.54
128.85
128.43
127.30
123.60
76.60
76.03
49.80
O
O
33
Parameter Value
1 Title MVT 718
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 301
5 Receiver Gain 203
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

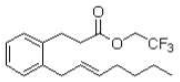




35

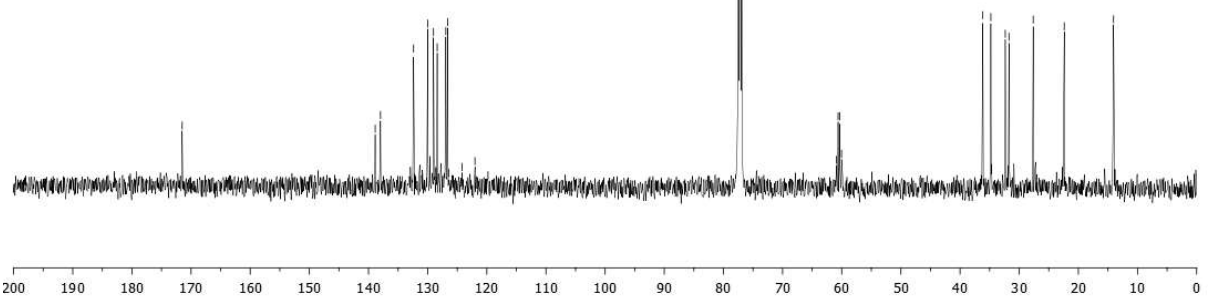
	Parameter	Value
1	Title	BV-II-608A
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	32
5	Receiver Gain	203
6	Relaxation Delay	1.5000
7	Pulse Width	9.9500
8	Acquisition Time	2.1823
9	Spectrometer Frequency	500.26
10	Nucleus	1H

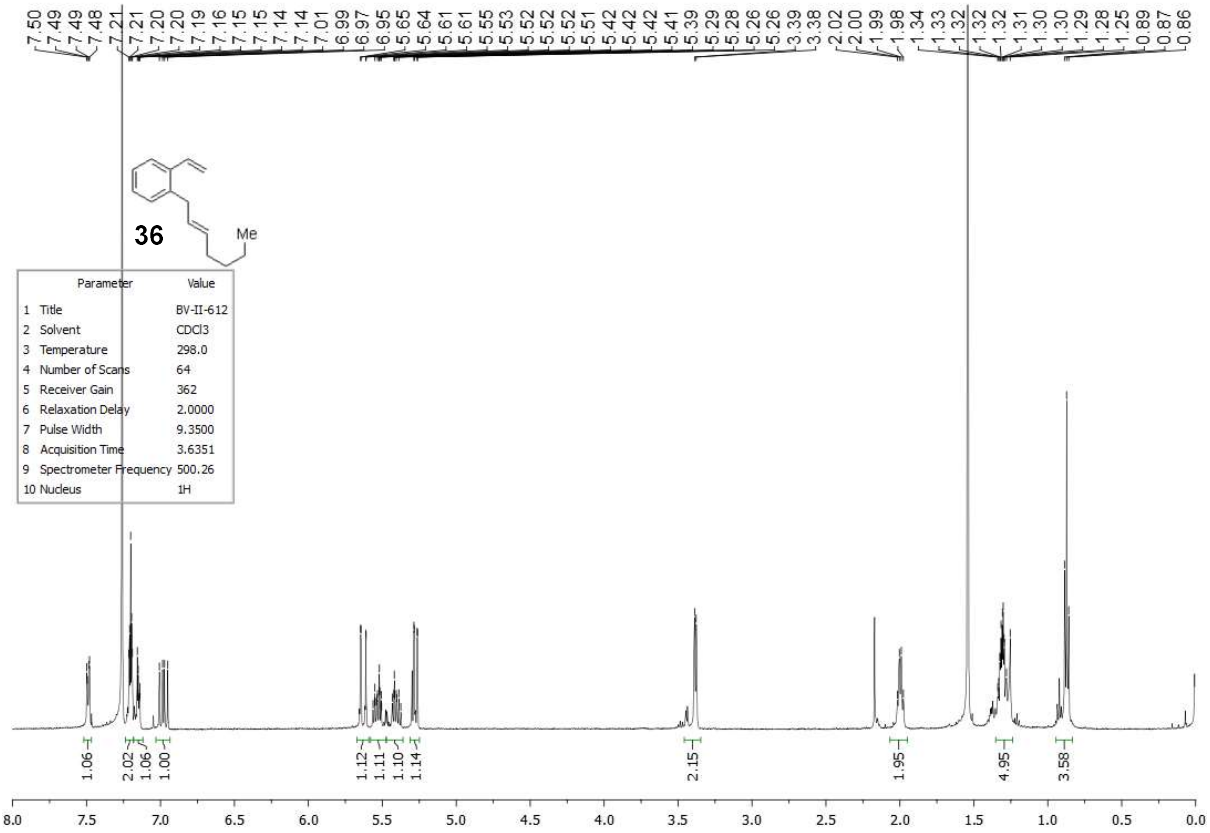


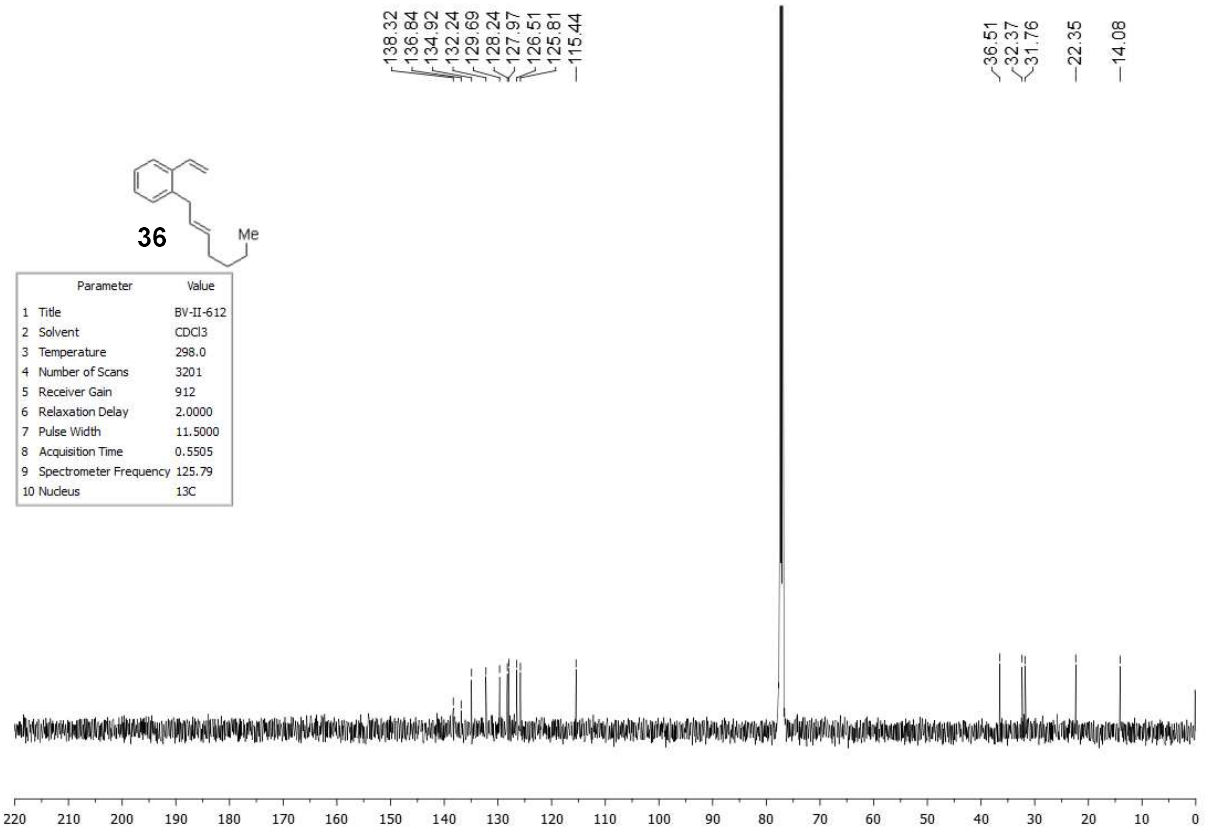


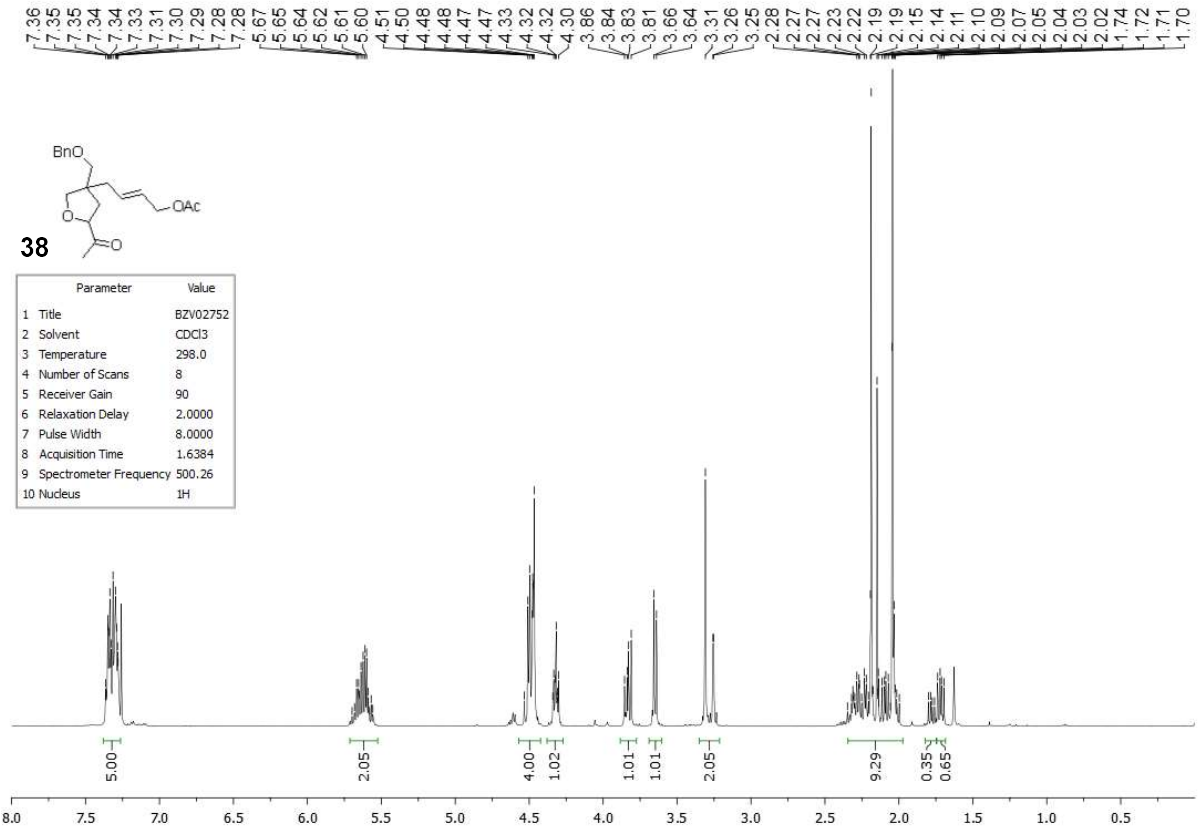
35

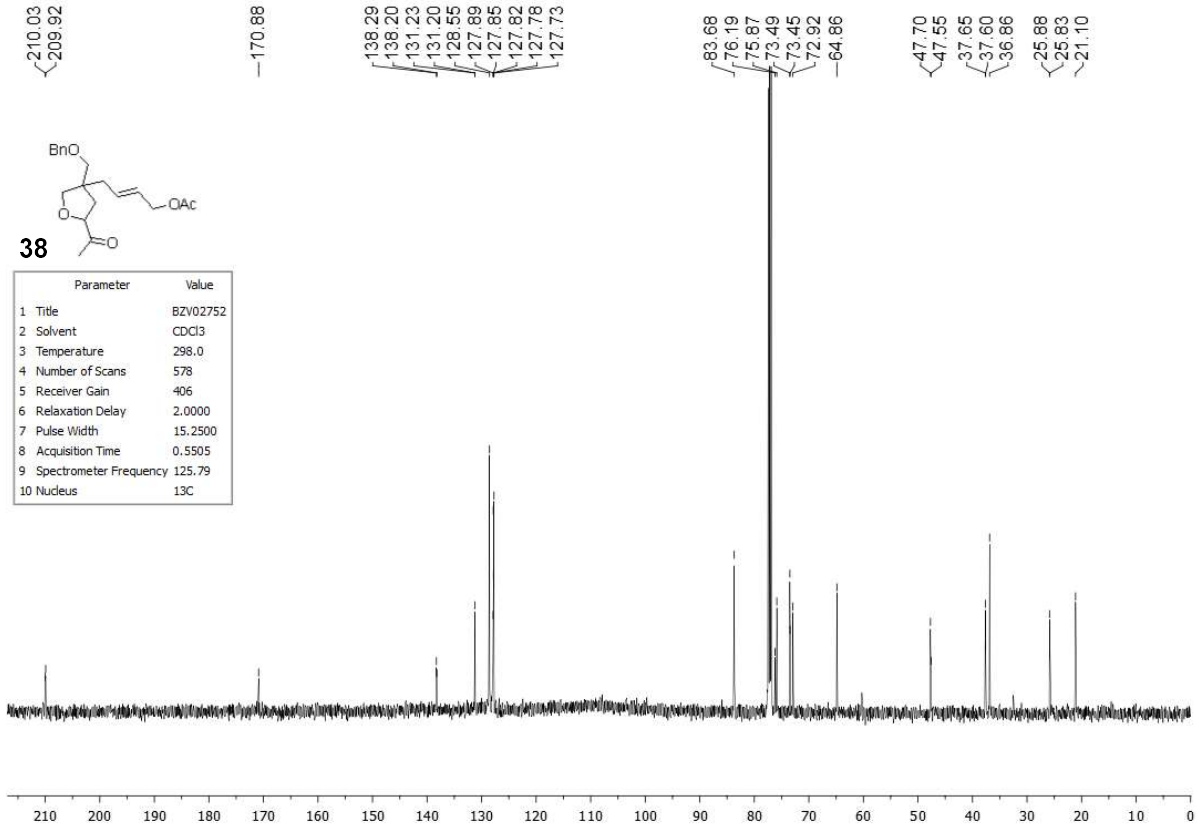
	Parameter	Value
1	Title	BV-II-608A
2	Solvent	CDCl3
3	Temperature	298.0
4	Number of Scans	512
5	Receiver Gain	1030
6	Relaxation Delay	2.0000
7	Pulse Width	11.5000
8	Acquisition Time	0.5505
9	Spectrometer Frequency	125.79
10	Nucleus	13C




36
Me
Parameter Value
1 Title BV-II-612
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 64
5 Receiver Gain 362
6 Relaxation Delay 2.0000
7 Pulse Width 9.3500
8 Acquisition Time 3.6351
9 Spectrometer Frequency 500.26
10 Nucleus 1H


36
Me
Parameter Value
1 Title BV-II-612
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 3201
5 Receiver Gain 912
6 Relaxation Delay 2.0000
7 Pulse Width 11.5000
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C


7.36
7.35
7.35
7.34
7.34
7.33
7.31
7.30
7.29
7.28
7.28
5.67
5.65
5.64
5.62
5.61
5.60
4.51
4.50
4.48
4.48
4.47
4.47
4.33
4.32
4.32
4.30
3.86
3.84
3.83
3.81
3.66
3.64
3.31
3.26
3.25
2.28
2.27
2.27
2.23
2.22
2.19
2.19
2.15
2.14
2.11
2.10
2.09
2.07
2.05
2.04
2.03
2.02
1.74
1.72
1.71
1.70
BnO
OAc
O
38
Parameter Value
1 Title BZV02752
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 8
5 Receiver Gain 90
6 Relaxation Delay 2.0000
7 Pulse Width 8.0000
8 Acquisition Time 1.6384
9 Spectrometer Frequency 500.26
10 Nucleus 1H
5.00
2.05
4.00
1.02
1.01
1.01
2.05
9.29
0.35
0.65
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


210.03
209.92
170.88
138.29
138.20
131.23
131.20
128.55
127.89
127.85
127.82
127.78
127.73
83.68
76.19
75.87
73.49
73.45
72.92
64.86
47.70
47.55
37.65
37.60
36.86
25.88
25.83
21.10
BnO
OAc
O
38
Parameter Value
1 Title BZV02752
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 578
5 Receiver Gain 406
6 Relaxation Delay 2.0000
7 Pulse Width 15.2500
8 Acquisition Time 0.5505
9 Spectrometer Frequency 125.79
10 Nucleus 13C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0