Supporting Information

Enantioselective Synthesis and Determination of the Absolute Configuration of the Male Sex Pheromone of the Parasitoid Wasp *Urolepis rufipes*

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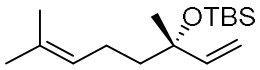
1 Experimental procedures

General procedures

Chemicals were purchased from abcr, Acros Organics, Sigma Aldrich and TCI and were used without further purification. Technical solvents were distilled before use. Reactions involving air or water sensitive reagents were carried out in flame dried glassware and under a nitrogen atmosphere. Thin layer chromatography was used to monitor reactions with Polygram SIL G/UV_{254} (Macherey & Nagel) plates and 10% molybdatophosphoric acid in ethanol for detection. Silica gel (silica gel 60, particle size 0.040–0.063 mm, mesh 230–440 ASTM, Fluka) was used for purification of the synthetic crude products by column chromatography. GC/MS analyses were performed on a GC HP6890/MSD HP5973 (Hewlett Packard) machine. The mass spectrometric analyses were performed in electron ionization mode (EI) with 70 eV. HP-5MS fused-silica capillary columns (Agilent technologies, 30 m, 0.25 mm i.d., 0.25 µm thickness) were used with helium as the carrier gas. High resolution mass spectrometry (HR-MS) data were obtained with a GC 6890 gas chromatograph (Agilent) equipped with a Phenomenex ZB5-MS column (30m, 0.25 mm i.d. 0.25 µm thickness), coupled to a time-of-flight mass spectrometer JMS-T100GC, GCAccuTOF (JEOL) in EI mode (70 eV). The software JEOL MassCenter Workstation was used. Calibration of the instrument was performed with PFK to reach resolution of 5000 (fwhm) at *m/z* = 292.9824. Enantiomeric separation was performed on a enantioselective β-DEX 225 column (Macherey & Nagel, 35 m, 0.25 mm i.d.). Gas chromatographic retention indices (RI) were obtained by using a homologues series of *n*-alkanes (C_8-C_{40}). NMR-spectra were obtained with the following instruments (Bruker): AV III-400 (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR), AV III HD-500 (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR). Tetramethylsilane was used as an internal standard (TMS, δ = 0 ppm). Multiplicities of the protons are described as singlets (s), doublets (d), triplets (t) and multiplets (m). The carbon atom connectivities are described as primary (CH_3), secondary (CH_2), tertiary (CH), or quaternary (C_q). IR-spectra were obtained on a GC/IR instrument. A HP-5MS fused-silica capillary column (Agilent technologies, 30 m, 0.25 mm i.d., 0.25 µm thickness) was used on the gas chromatograph GC 7890B (Agilent Technologies), coupled to a DiscovIR instrument (Dani Instruments), using helium as the carrier gas. Eluting samples from the GC were deposited on a ZnSe disc at -40 °C with a disc speed of 4 mm/min. The IR-spectra were processed using GRAMS/AI 9.2 software by Thermo Fisher Scientific Inc (modified by Dani Instruments). The peaks are given as wave numbers in cm^{-1} and the intensities are described as strong (s), medium (m), weak (w) and broad (br). Optical rotation values were measured on MCP 150 Modular Circular Polarimeter (Anton Paar) at 25 °C with a 15 cm cuvette and a wavelength of 589 nm.

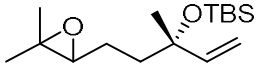
(*S*)-*tert*-Butyl((3,7-dimethylocta-1,6-dien-3-yl)oxy)dimethylsilane (12)



(*S*)-Linalool (**7**, ee 90%) was obtained by purification of coriander oil (Oleum coriandri) by column chromatography (pentane/ethyl acetate, 10:1). [S1] A solution of (*S*)-linalool (**7**, 2.43 g, 15.76 mmol, 1 eq) in DCM (24.3 mL) was cooled to 0 °C and 2,6-lutidine (2.8 mL, 23.64 mmol, 1.5 eq) and *tert*-butyldimethylsilyl triflate (TBSOTf, 4.3 mL, 18.92 mmol, 1.2 eq) were added subsequently. The mixture was stirred for 30 minutes at 0 °C and water (10 mL) was added to terminate the reaction. The organic phase was separated and washed with water (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography (pentane/diethyl ether, 100:1) to give silyl ether **12** (3.90 g, 14.54 mmol, 90%) as a colorless oil. [S2]

TLC (pentane/diethyl ether, 100:1): R_f: 0.8. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.85 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.14 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.11-5.06 (m, 1H), 4.98 (dd, *J* = 10.7, 1.7 Hz, 1H), 2.08-1.91 (m, 2H), 1.67 (d, *J* = 1.1 Hz, 3H), 1.59 (br s., 3H), 1.50-1.45 (m, 2H), 1.29 (s, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.7 (CH, 1C), 131.1 (C_q, 1C), 124.8 (CH, 1C), 111.6 (CH_2; 1C), 75.5 (C_q, 1C), 43.8 (CH_2, 1C), 27.4 (CH_3, 1C), 26.0 (CH_3, 1C), 25.7 (CH_3, 1C), 22.8 (CH_2, 1C), 18.4 (C_q, 1C), 17.6 (CH_3, 1C), -2.0 (CH_3, 2C). EI-MS (70 eV): *m/z* (%) 253 $[M\text{-}CH_3]^+$ (2), 212 (4), 211 (23), 193 (4), 186 (4), 185 (26), 136 (4), 135 (10), 129 (3), 121 (4), 115 (5), 113 (4), 93 (16), 80 (5), 77 (6), 76 (8), 75 (100), 74 (3), 73 (27), 69 (12), 67 (4), 59 (3), 57 (3), 55 (3), 47 (3), 45 (3), 41 (12). IR (GC-IR): $\tilde{\nu}$ = 3092 (m), 3063 (m), 2953 (s), 2734 (w), 1475 (s), 1253 (s), 1175 (s), 1119 (s), 1043 (s), 919 (s), 765 (s). $[\alpha]_D^{25.0}$ = +7.9 (c 1.7 in $CHCl_3$).

***tert*-Butyl(((3*S*)-5-(3,3-dimethyloxiran-2-yl)-3-methylpent-1-en-3-yl)oxy)dimethylsilane (13)**

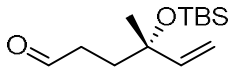


A solution of silyl ether **12** (3.80 g, 14.17 mmol, 1 eq) in DCM (114 mL) was cooled to -10 °C and *m*-CPBA (commercial grade 70-75%, 3.59 g, 15.58 mmol, 1.1 eq) was added in portionsand left stirring overnight. DCM (50 mL) was added and the organic phase was washed with aqueous Na_2SO_4-solution (3x 50 mL) and $NaHCO_3$-solution (1x 50 mL). The organic phase was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography (pentane/diethyl ether, 40:1) to give epoxide **13** (3.69 g, 12.95 mmol, 90%) as a colorless oil. Epoxide **13** was obtained as both diastereomers, which could not be separated by GC/MS, but showed a double signal set in ^{13}C-NMR. [S3]

TLC (pentane/diethyl ether, 40:1): R_f: 0.27. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.83 (dd, *J* = 17.3, 10.7 Hz, 2H), 5.15 (ddd, *J* = 17.3, 3.0, 1.6 Hz, 2H), 5.00 (d, *J* = 10.7, 1.5, 2H), 2.70-2.67 (m, 2H), 1.71-1.1.47 (m, 8H), 1.31 (dd, *J* = 7.9, 1.1 Hz, 12H), 1.25 (d, *J* = 1.7 Hz, 6H), 0.88 (s, 18H), 0.08 (d, *J* = 1.2 Hz, 6H), 0.07 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.4 (CH, 1C), 145.2 (CH, 1C), 112.1 (CH_2; 1C), 112.0 (CH, 1C), 75.2 (C_q, 1C), 75.2 (C_q, 1C), 64.6 (CH, 1C), 64.6 (CH, 1C), 58.4 (C_q, 1C), 58.3 (C_q, 1C), 40.3 (CH_2, 1C), 40.1 (CH_2, 1C), 27.5 (CH_3, 1C), 27.4 (CH_3, 1C), 25.9 (CH_3, 1C), 24.9 (CH_3, 1C), 23.7 (CH_2, 1C), 23.6 (CH_2, 1C), 18.7 (CH_3, 1C), 18.6 (CH_3, 1C), 18.3 (C_q, 1C), -2.0 (CH_3, 1C), -2.1 (CH_3, 1C), -2.1 (CH_3, 2C). EI-MS (70 eV): *m/z* (%) 269 $[M\text{-}CH_3]^+$ (2), 227 (6), 186 (9), 185 (57), 159 (7), 155 (5), 147 (7), 135 (7), 129 (17), 119 (12), 115 (10), 107 (10), 101 (6), 93 (16), 81 (20), 79 (14), 77 (9), 76 (7), 75 (100), 73 (43), 59 (12), 43 (11), 41 (12), 39 (4). IR (GC-IR): $\tilde{\nu}$ = 3095 (w), 2961 (s), 2928 (s),

2894 (m), 2859 (s), 1474 (m), 1375 (m), 1253 (s), 1180 (m), 1050 (s), 838.1 (s), 771 (s). $[\alpha]_D^{25.0}$ = +7.2 (c 1.6 in $CHCl_3$).

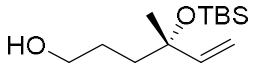
(*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-methylhex-5-enal (14)



Periodic acid (H_5IO_6, 1.76 g, 7.73 mmol, 1.2 eq) was added in portions to a solution of epoxide **13** (1.83 g, 6.45 mmol, 1 eq) in diethyl ether (22.4 mL). The mixture was stirred for three hours at room temperature and an aqueous $NaHCO_3$-solution (20 mL) was added. The aqueous phase was separated and extracted with diethyl ether (3 x 15 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography (pentane/diethyl ether, 10:1) to give aldehyde **14** (1.37 g, 5.65 mmol, 81%) as a colorless oil. [S3]

TLC (pentane/diethyl ether, 10:1): R_f: 0.5. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.77 (t, *J* = 1.6 Hz, 1), 5.79 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.18 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.04 (d, *J* = 10.7, 1.4, 1H), 2.56-2.44 (m, 2H), 1.86-1.80 (m, 2H), 1.34 (s, 3H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 202.9 (CH, 1C), 144.7 (CH, 1C), 112.7 (CH_2, 1C), 74.9 (C_q, 1C), 39.2 (CH_2, 1C), 35.6 (CH_2, 1C), 27.7 (CH_3, 1C), 25.9 (CH_3, 1C), 18.3 (C_q, 1C), -2.1 (CH_3, 1C), -2.1 (CH_3, 1C). EI-MS (70 eV): *m/z* (%) 227 $[M\text{-}CH_3]^+$ (3), 187 (4), 186 (12), 185 (79), 143 (8), 141 (6), 129 (11), 127 (4), 115 (9), 113 (8), 105 (10), 101 (4), 99 (3), 93 (28), 91 (11), 85 (4), 77 (12), 76 (7), 75 (100), 74 (5), 73 (43), 67 (3), 61 (4), 59 (8), 57 (5), 55 (5), 47 (6), 45 (7), 43 (4), 41 (9), 39 (3). IR (GC-IR): $\tilde{\nu}$ = 3097 (w), 3012 (w), 2955 (s), 2932 (s), 2900 (s), 2851 (s), 2727 (m), 1729 (s), 1474 (m), 1463 (m), 1251 (m), 1184 (m), 1129 (m), 1049 (s), 981 (m), 917 (m), 838 (s), 779 (s). $[\alpha]_D^{25.0}$ = +3.1 (c 1.5 in $CHCl_3$).

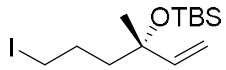
(*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-4-methylhex-5-en-1-ol (15)



A solution of aldehyde **14** (1.37, 5.65 mmol, 1 eq) in MeOH (50 mL) was cooled to 0 °C and $NaBH_4$ (0.43 g, 11.3 mmol, 2 eq) was added portions wise. The mixture was left stirring over-night. 3 N HCl (10 mL) was added and the aqueous phase was extracted with diethyl ether (3x 10 mL). The solvent was evaporated and the crude product was purified by column chroma-tography (pentane/diethyl ether, 1:1) to give alcohol **15** (1.05 g, 4.30 mmol, 71%) as a colorless oil.

TLC (pentane/diethyl ether, 1:1): R_f: 0.5. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.85 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.15 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.00 (dd, *J* = 10.7, 1.5 Hz, 1H), 3.63-3.61 (m, 2H), 1.66-1.59 (m, 2H), 1.56-1.52 (m, 2H), 1.32 (s, 3H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 145.5 (CH, 1C), 111.9 (CH_2, 1C), 75.4 (C_q, 1C), 63.4 (CH_2, 1C), 40.0 (CH_2, 1C), 27.5 (CH_2, 1C), 27.4 (CH_3, 1C), 26.0 (CH_3, 1C), 18.3 (C_q, 1C), -2.0 (CH_3, 1C), -2.1 (CH_3, 1C). EI-MS (70 eV): *m/z* (%) 230 (2), 188 (21), 187 (10), 186 (61), 147 (12), 146 (95), 128 (6), 120 (12), 116 (6), 114 (13), 98 (8), 96 (33), 86 (7), 78 (9), 77 (8), 76 (100), 75 (6), 74 (50), 68 (17), 61 (3), 60 (7), 56 (9), 48 (6), 42 (11), 40 (4). IR (GC-IR): $\tilde{\nu}$ = 3274 (m), 2957 (s), 2929 (s), 2857 (m), 1472 (w), 1253 (m), 1066 (m), 1047 (m), 918.6 (m), 836 (m), 773 (m). $[\alpha]_D^{25.0}$ = +3.8 (c 1.9 in $CHCl_3$).

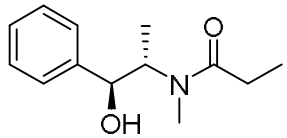
(*S*)-*tert*-Butyl((6-iodo-3-methylhex-1-en-3-yl)oxy)dimethylsilane (16)



Triphenylphosphane (0.71 g, 2.70 mmol, 1.1 eq) was dissolved in DCM (8 mL) and cooled to 0 °C. Imidazole (0.50 g, 7.36 mmol, 3 eq) and iodine (0.69 g, 2.70 mmol, 1.1 eq) were added subsequently to the solution. Alcohol **15** (0.60 g, 2.45 mmol, 1 eq), diluted in DCM (6 mL), was added to the solution and left stirring overnight. Aqueous $Na_2S_2O_3$-solution (8 mL) was added and the aqueous phase was extracted with DCM (3x 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and the solvent was removed. Column chromatography (pentane/diethyl ether, 400:1) of the crude product gave iodide **16** (0.72 g, 2.04 mmol, 82%) as a slight yellow oil.[S4]

TLC (pentane/diethyl ether, 400:1): R_f: 0.76. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.81 (dd, J = 17.3, 10.7 Hz, 1H), 5.15 (dd, J = 17.3, 1.6 Hz, 1H), 5.00 (d, J = 10.7, 1.5, 1H), 3.17 (t, J = 6.9 Hz, 2H), 1.94-1.78 (m, 2H), 1.59-1.54 (m, 2H), 1.31 (s, 3H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.2 (CH, 1C), 112.1 (CH_2, 1C), 75.1 (C_q, 1C), 44.6 (CH_2, 1C), 28.3 (CH_2, 1C), 27.7 (CH_3, 1C), 25.9 (CH_3, 1C), 18.3 (C_q, 1C), 7.9 (CH_2, 1C), -2.0 (CH_3, 1C), -2.1 (CH_3, 1C). EI-HRMS: 339.06469 (calc. mass: 339.06311) $[M\text{-}CH_3]^+$. IR (GC-IR): $\tilde{\nu}$ = 2957 (s), 2929 (s), 2895 (m), 2851 (s), 1473 (m), 1359 (m), 1252 (s), 1044 (s), 1004 (m), 921 (m), 836 (s), 774 (s). $[\alpha]_D^{25.0}$ = +6.3 (c 1.7 in $CHCl_3$).

***N*-((1*S*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl)- *N*-methylpropionamide (18)**

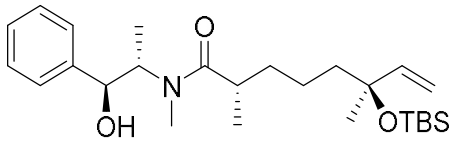


(*S*,*S*)-Pseudoephedrine (**17**, 0.602 g, 3.63 mmol, 1 eq) was dissolved in DCM (7.2mL) and cooled to 0 °C. Triethylamine (0.61 mL, 4.36 mmol, 1.2 eq) and propionylchloride (0.33 mL, 3.81mmol, 1.05 eq) were added subsequently. The solution was warmed to room temperature and left stirring for 1 hour. Water (5 mL) was added and the solution was diluted with DCM (10 mL). The organic phase was separated and washed with a saturated, aqueous $NaHCO_3$-solution (2 x 10 mL), 1 N HCl (10 mL) and brine (10 mL). The organic phase was dried over $MgSO_4$, the solvent was removed and the product *S*,*S*-**18** was obtained as a white crystalline solid (0.70g, 31.6mmol, 87%) without further purification. The enantiomer *R*,*R*-**18** was obtained with the same procedure in 93% yield using (*R*,*R*)-pseudoephedrine.[S5]

TLC (pentane/ethyl acetate, 1:1): R_f: 0.3. ^{1}H-NMR (3:1 rotamer ratio, asterisk denotes minor rotamer peaks, 400 MHz, $CDCl_3$): δ = 7.36-7.26 (m, 5H), 4.60-4.55 (m, 1H), 4.47-4.43 (m, 1H), 4.36 (br s, 1H), 4.04-3.96* (m, 0.4H), 2.92* (s, 1H), 2.81 (s, 3H), 2.56-2.37* (m, 1H), 2.35-2.25 (m, 2H), 1.18-1.16* (m, 1H), 1.12 (t, J = 7.5 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H), 0.97* (d, J = 6.8 Hz, 1H). ^{13}C-NMR (3:1 rotamer ratio, asterisks denotes minor rotamer peaks, 100 MHz, $CDCl_3$): δ = 176.2 (C_q, 1C), 175.0* (C_q, 1C), 142.4 (C_q, 1C), 141.2* (C_q, 1C), 128.7 (CH, 1C), 128.3 (CH, 1C), 127.6 (CH, 1C), 126.9 (CH, 1C), 126.4 (CH, 1C), 76.6 (CH, 1C), 75.5* (CH, 1C), 58.6* (CH, 1C), 58.2 (CH, 1C), 32.7 (CH_3, 1C), 27.6 (CH_2, 1C), 26.8* (CH_2, 1C), 26.7 (CH_2, 1C), 15.2* (CH_3, 1C), 14.4 (CH_3, 1C), 9.6* (CH_3, 1C), 9.1 (CH_3, 1C). EI-MS (70 eV): *m/z* (%) 136 $[M\text{-}C_2H_3O_2]^+$ (9), 121 (33), 107 (9), 105 (10), 94 (13), 93 (100), 92 (19), 91 (18), 81 (11), 80 (36), 79 (18), 77 (11), 71 (17), 69 (27), 68 (11), 67 (18), 55 (18), 53 (11), 43 (55), 41 (42), 39 (16), 71 (82), 69 (15), 68 (30), 67 (68), 65 (5), 57 (13), 55 (41), 53 (18), 43 (100), 42 (9), 41 (42), 39 (24). IR (GC-IR): $\tilde{\nu}$ = 3362 (s), 3085 (w), 3032 (w), 2988 (m), 2941 (m), 2872

(m), 1619 (s), 1489 (m), 1298 (m), 1049 (s). *S*,*S*-**18**: $[\alpha]_D^{25.0}$ = +99.1 (1.7 in $CHCl_3$). *R*,*R*-**18**: $[\alpha]_D^{25.0}$ = -119.0 (c 1.8 in $CHCl_3$).

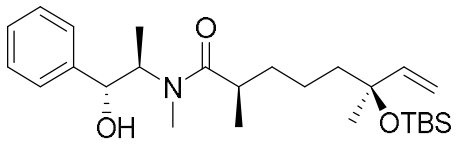
(2*S*,6*S*)-6-((tert-Butyldimethylsilyl)oxy)-*N*-((1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)-*N*,2,6-trimethyloct-7-enamide (1'*S*,2*S*,2'*S*,6*S*-19)



Diisopropylamine (0.6 mL, 3.96 mmol, 4.3 eq) was added to a solution of lithium chloride (0.50 g, 11.7 mmol, 12.7 eq) in THF (2.7 mL). The solution was cooled to – 78 °C and *n*-BuLi (1.6 M in hexanes, 2.3 mL, 4 eq) was added. After warming up the solution for five minutes at 0 °C it was cooled again to – 78 °C and a solution of amide 1 *S*,2*S*-**18** (0.41, 1.84 mmol, 2 eq) in THF (3.6 mL) cooled to 0 °C was added dropwise in a period of 10 minutes. The mixture was left stirring at – 78 °C for one hour, heated for 15 minutes to 0 °C and finally for five minutes to room temperature. The solution was cooled again to – 10 °C and iodine **16** (0.23 g, 0.92 mmol, 1 eq) in THF (0.7 mL) was added dropwise over 15 minutes. The solution was left stirring for 18 hours at 0 °C and quenched with a saturated solution of NH_4OAc (3 mL). The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic phases were washed with brine (10 mL). The solvent was removed and the crude product was purified by column chromatography (pentane/EtOAc, 2:1) to give amide 1'*S*,2*S*,2'*S*,6*S*-**19** (0.25 g, 0.55 mmol, 56%) as a slight yellow oil.[S6] The dr of 86:14 was determined by NMR.

TLC (pentane/ethyl acetate, 2:1): R_f: 0.5. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.36-7.24 (m, 5H), 5.82 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.12 (dd, *J* = 17.3, 1.6 Hz, 1H), 4.97 (dd, *J* = 10.7, 1.6 Hz, 1H), 4.61-4.57 (m, 1H), 4.47 (br. s, 1H), 2.84 (s, 3H), 2.62-2.60 (m, 1H), 1.56-1.48 (m, 2H), 1.46-1.36 (m, 3H), 1.29-1.24 (m, 4H), 1.08 (d, *J* = 6.7 Hz, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 179.3 (C_q, 1C), 145.7 (CH, 1C), 142.6 (C_q, 1C), 128.7 (CH, 1C), 128.3 (CH, 1C), 127.6 (CH, 1C), 126.9 (CH, 1C), 126.4 (CH, 1C), 111.6 (CH_2, 1C), 76.6 (CH, 1C), 75.5 (C_q, 1C), 58.0 (CH, 1C), 43.8 (CH_2, 1C), 36.7 (CH, 1C), 34.4 (CH_2, 1C), 32.6 (CH_3, 1C), 27.4 (CH_3, 1C), 25.9 (CH_3, 1C), 21.9 (CH_2, 1C), 18.3 (C_q, 1C), 17.2 (CH_3, 1C), 14.5 (CH_3, 1C), -2.1 (CH_3, 1C), -2.1 (CH_3, 1C). EI-MS (70 eV): *m/z* (%) 432 $[M\text{-}CH_3]^+$ (2), 392 (3), 391 (9), 390 (31), 341 (5), 340 (18), 298 (9), 207 (7), 186 (5), 185 (29), 148 (18), 123 (7), 115 (6), 107 (6), 81 (20), 79 (8), 77 (6), 75 (41), 73 (30), 69 (5), 67 (5), 59 (6), 58 (100), 57 (6), 55 (7), 41 (5). IR (GC-IR): $\tilde{\nu}$ = 3370 (s), 3089 (w), 3064 (w), 3031 (w), 2961 (s), 2929 (s), 2857 (s), 1619 (s), 1475 (s), 1369 (m), 1121 (m), 1045 (s), 838 (s), 773 (s). $[\alpha]_D^{25.0}$ = +37.3 (c 0.7 in $CHCl_3$).

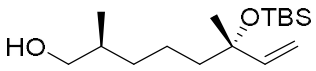
(2*R*,6*S*)-6-((*tert*-Butyldimethylsilyl)oxy)-*N*-((1*R*,2*R*)-1-hydroxy-1-phenylpropan-2-yl)-*N*,2,6-trimethyloct-7-enamide (1'*R*,2*R*,2'*R*,6*S*-19)



The diastereomer 1'*R*,2*R*,2'*R*,6*S*-**19** was prepared as just described using amide 1*R*,2*R*-**18** instead of its enantiomer. The crude product was purified by column chromatography (pentane/EtOAc, 2:1) to give amide 1'*R*,2*R*,2'*R*,6*S*-**19** (0.49 g, 1.09 mmol, 42%) as a slight yellow oil.[S6]

TLC (pentane/EtOAc, 2:1): R_f: 0.5. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.36-7.26 (m, 5H), 5.80 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.12 (dd, *J* = 17.3, 1.7 Hz, 1H), 4.95 (dd, *J* = 10.7, 1.7 Hz, 1H), 4.60-4.57 (m, 1H), 4.47 (br. s, 1H), 2.84 (s, 3H), 2.59 (sext, *J* = 6.7 Hz, 1H), 1.56-1.50 (m, 1H), 1.44-1.41 (m, 2H), 1.37-1.33 (m, 1H), 1.31-1.29 (m, 4H), 1.22-1.16 (m, 1H), 1.10-1.08 (m, 6H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 179.3 (C_q, 1C), 145.6 (CH, 1C), 142.5 (C_q, 1C), 128.7 (CH, 1C), 127.6 (CH, 1C), 126.9 (CH, 1C), 126.4 (CH, 1C), 111.6 (CH_2, 1C), 76.6 (CH, 1C), 75.5 (C_q, 1C), 58.5 (CH, 1C), 43.7 (CH_2, 1C), 36.7 (CH_3, 1C), 34.4 (CH_2, 1C), 32.6 (CH_3, 1C), 27.6 (CH_3, 1C), 25.9 (CH_3, 1C), 21.9 (CH_2, 1C), 18.3 (C_q, 1C), 17.2 (CH_3, 1C), 14.5 (CH_3, 1C), -2.1 (CH_3, 2C). EI-HRMS: 432.29316 (calc. mass: 432.29339) $[M\text{-}CH_3]^+$. IR (GC-IR): $\tilde{\nu}$ = 3370 (m), 2953 (s), 2939 (s), 2856 (m), 1621 (s), 1475 (m), 1251 (m) 1047 (s) 839 (s), 773 (1). $[\alpha]_D^{25.0}$ = -21.1 (c 2.5 in $CHCl_3$).

(2*S*,6*S*)-6-((tert-Butyldimethylsilyl)oxy)-2,6-dimethyloct-7-en-1-ol (2 *S*,6*S*-20)

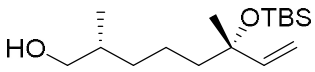


A solution of diisopropylamine (0.32 mL, 2.27 mmol, 4.2 eq) in THF (2.3 mL) was cooled to –-78 °C and *n*-BuLi (1.6 M in hexanes, 1.3 mL, 3.9 eq) was added. The solution was stirred for 10 minutes at – 78 °C and warmed to 0 °C. Borane ammonia complex (90% technical grade, 66 mg, 2.16 mmol, 4 eq) was added in one portion and the suspension was stirred for another 15 minutes at 0 °C followed by 15 minutes at room temperature. It was cooled again to 0 °C and amide 1'*S*,2*S*,2'*S*,6*S*-**19** (0.24 g, 0.54 mmol, 1 eq) in THF (1.4 mL) was added over three minutes. After stirring for two hours at room temperature, the mixture was cooled to 0 °C and excess hydride was quenched with 3 N HCl (5 mL) by stirring for 30 minutes. The aqueous phase was extracted with diethyl ether (3 x 10 mL) and the combined organic phases were washed with 3 N HCl (10 mL), 2 N NaOH-solution (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography to give alcohol 2*S*,6*S*-**20** (0.13 g, 0.44 mmol, 82%) as a colorless oil. [S6]

TLC (pentane/diethyl ether, 4:1): R_f: 0.26. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.83 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.13 (dd, *J* = 17.3, 1.6 Hz, 1H), 4.97 (dd, *J* = 10.7, 1.7 Hz, 1H), 3.50 (dd, *J* = 10.5, 5.7 Hz, 1H), 3.40 (dd, *J* = 10.5, 6.6 Hz, 1H), 1.65-1.57 (m, 1H), 1.49-1.42 (m, 3H), 1.40-1.32 (m, 3H), 1.28 (s, 3H), 1.12-1.03 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.8 (CH, 1C), 111.5 (CH_2, 1C), 75.6 (C_q, 1C), 68.4 (CH_2, 1C), 44.0 (CH_2, 1C), 35.7 (CH, 1C), 33.5 (CH_2, 1C), 27.4 (CH_3, 1C), 26.0 (CH_3, 1C), 21.2 (CH_2, 1C), 18.3 (C_q, 1C), 16.6 (CH_3, 1C), 16.5 (CH_3, 1C), -2.1 (CH_3, 2C). IR (GC-IR): $\tilde{\nu}$ = 3280 (m), 2955 (s), 2930 (s), 2660 (7), 1478 (m), 1465 (m), 1249 (m), 1049 (s), 830 (s), 769 (s). EI-MS (70 eV): *m/z* (%) 271 $[M\text{-}CH_3]^+$ (4), 187 (5), 186 (16), 185 (100), 145 (15), 137 (12), 127 (5), 115 (7), 113 (7), 95 (35), 93 (5), 82 (6), 81 (82), 79 (6), 77 (6), 76 (6), 75 (84), 74

(6), 73 (56), 69 (48), 67 (11), 59 (6), 57 (7), 55 (13), 43 (6), 41 (12). $[\alpha]_D^{25.0}$ = +12.5 (c 1.2 in $CHCl_3$).

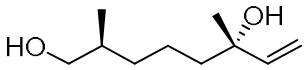
(2*R*,6*S*)-6-((tert-Butyldimethylsilyl)oxy)-2,6-dimethyloct-7-en-1-ol (2 *R*,6*S*-20)



Alcohol 2*R*,6*S*-**20** was synthesized as just described using 1'*R*,2*R*,2'*R*,6*S*-**19**. The crude product was purified by column chromatography to give alcohol 2 *R*,6*S*-**20** (0.27 g, 0.93 mmol, 82%) as a colorless oil.[S6]

TLC (pentane/diethyl ether, 4:1): R_f: 0.26. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.83 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.13 (dd, *J* = 17.3, 1.7 Hz, 1H), 4.97 (dd, *J* = 10.7, 1.7 Hz, 1H), 3.52-3.38 (m, 3H), 1.65-1.56 (m, 1H), 1.46-1.42 (m, 3H), 1.40-1.32 (m, 2H), 1.28 (s, 3H), 1.09-1.04 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.8 (CH, 1C), 111.5 (CH_2, 1C), 75.6 (C_q, 1C), 68.4 (CH_2, 1C), 44.0 (CH_2, 1C), 35.7 (CH, 1C), 33.5 (CH_2, 1C), 27.6 (CH_3, 1C), 27.5 (CH_3, 1C), 25.9 (CH_3, 1C), 21.3 (CH_2, 1C), 18.3 (C_q, 1C), 16.5 (CH_3, 1C), -2.1 (CH_3, 12C). EI-MS (70 eV): *m/z* (%) 271 $[M\text{-}CH_3]^+$ (4), 187 (5), 186 (16), 185 (100), 145 (16), 137 (11), 127 (6), 115 (7), 113 (7), 95 (34), 93 (6), 82 (6), 81 (76), 79 (8), 77 (7), 76 (7), 75 (92), 74 (6), 73 (52), 69 (41), 68 (3), 67 (12), 59 (6), 57 (8), 55 (13), 41 (14). IR (GC-IR): $\tilde{\nu}$ = 3284 (m), 2955 (s), 2928 (s), 2660 (7), 1478 (m), 1460 (m), 1249 (m), 1049 (s), 834 (s), 769 (s). $[\alpha]_D^{25.0}$ = -2.0 (c 1.7 in $CHCl_3$).

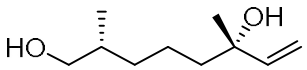
(2*S*,6*S*)-2,6-dimethyloct-7-ene-1,6-diol (2 *S*,6*S*-6)



Tetrabutylammonium fluoride (TBAF, 1 M in THF, 1.0 mL, 0.10 mmol, 2 eq) was added to a solution of alcohol 2*S*,6*S*-**20** (15 mg, 0.05 mmol, 1 eq) in THF (1.3 mL) and was heated to 60 °C for 21 hours. After cooling to room temperature, water (1 mL) was added and the aqueous phase was extracted with EtOAc (3x 4 mL). The combined organic phases were washed with brine (4 mL) and were dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography to give alcohol 2 *S*,6*S*-**6** (6.3 mg, 0.04 mmol, 70%) as a colorless oil.[S7]

TLC (pentane/ethyl acetate, 2:1): R_f: 0.30. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.91 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.20 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.05 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.52-3.41 (m, 2H), 1.65-1.61 (m, 2H), 1.55-1.48 (m, 2H), 1.42-1.39 (m, 2H), 1.28 (s, 3H), 1.15-1.09 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.2 (CH, 1C), 111.6 (CH_2, 1C), 73.3 (C_q, 1C), 68.2 (CH_2, 1C), 42.5 (CH_2, 1C), 35.7 (CH, 1C), 33.5 (CH_2, 1C), 27.7 (CH_3, 1C), 21.2 (CH_2, 1C), 16.6 (CH_3, 1C). EI-MS (70 eV): *m/z* (%) 157 $[M\text{-}CH_3]^+$ (1), 139 (2), 121 (3), 111 (3), 109 (3), 97 (4), 96 (7), 83 (6), 81 (8), 79 (3), 71 (100), 69 (11), 56 (8), 55 (19), 43 (33), 41 (15), 39 (6). IR (GC-IR): $\tilde{\nu}$ = 3291 (s), 3093 (w), 2957 (s), 2929 (s), 2855 (s), 1647 (w), 1474 (m), 1247 (m), 1045 (s), 836 (s), 775 (s). $[\alpha]_D^{25.0}$ = +9.3 (c 0.3 in $CHCl_3$).

(2*R*,6*S*)-2,6-Dimethyloct-7-ene-1,6-diol (2*R*,6*S*-6)



Deprotection of 2*R*,6*S*-**20** was performed using TBAF at room temperature while stirring for three days. Work up as just described and purification by column chromatography gave alcohol 2*R*,6*S*-**6** (35 mg, 0.20 mmol, 23%) as a colorless oil. The yield can be improved using the deprotection conditions described for 2*S*,6*S*-**6**.

TLC (pentane/ethyl acetate, 2:1): R_f: 0.30. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.91 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.20 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.05 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.51-3.41 (m, 2H), 1.65-1.61 (m, 2H), 1.54-1.50 (m, 2H), 1.42-1.37 (m, 2H), 1.28 (s, 3H), 1.14-1.10 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 145.1 (CH, 1C), 111.6 (CH_2, 1C), 73.3 (C_q, 1C), 68.2 (CH_2, 1C), 42.4 (CH_2, 1C), 35.7 (CH, 1C), 33.4 (CH_2, 1C), 27.8 (CH_3, 1C), 21.2 (CH_2, 1C), 16.6 (CH_3, 1C). EI-HRMS: 157.12045 (calc. mass: 157.12285) $[M\text{-}CH_3]^+$. IR (GC-IR): $\tilde{\nu}$ = 3351 (s), 3316 (s), 3088 (m), 3010 (m), 2935 (s), 2870 (s), 1643 (w), 1465 (m), 1370 (m), 1158 (m), 1041 (s), 996 (s), 919 (s), 737 (w). $[\alpha]_D^{25.0}$ = -2.5 (c 0.8 in $CHCl_3$).

2 Determination of the absolute configuration of 6 by chiral gas chromatography

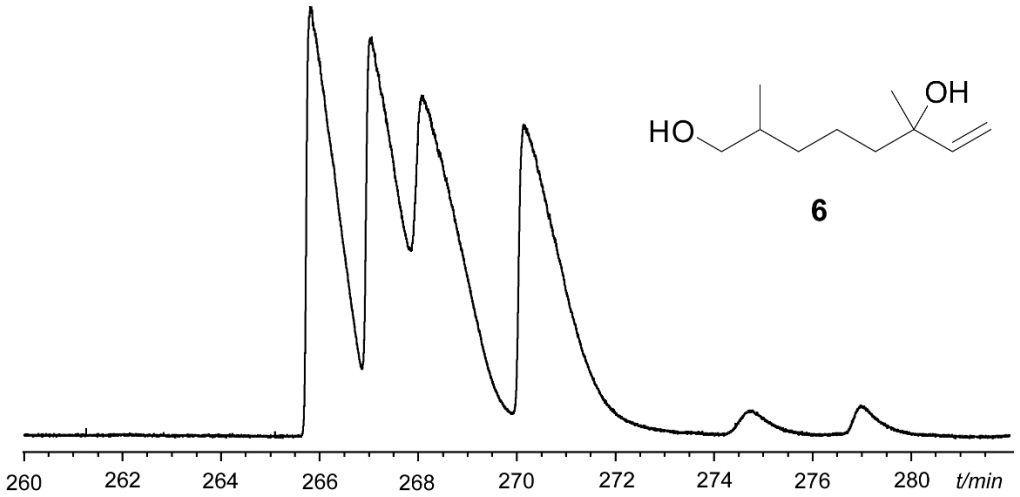


Figure S1. Gas chromatogram of a stereoisomeric mixture of 2,6-dimethyl-7-octene-1,6-diol (**6**)[S7] on a β-DEX 225 column (30 m, 0.25 mm inner diameter, 0.25 µm film thickness) with the following temperature program: isothermal 50 °C for 5 min, ramp of 0.25 °C/min until 120 °C, 20 °C/min until 220 °C, hold time for 5 min. Earlier experiments of a natural extract of *Urolepis rufipes* and the mixture of all stereoisomers showed that the first peak is the natural pheromone (see Supporting Information of Ruther et al.). [S7]

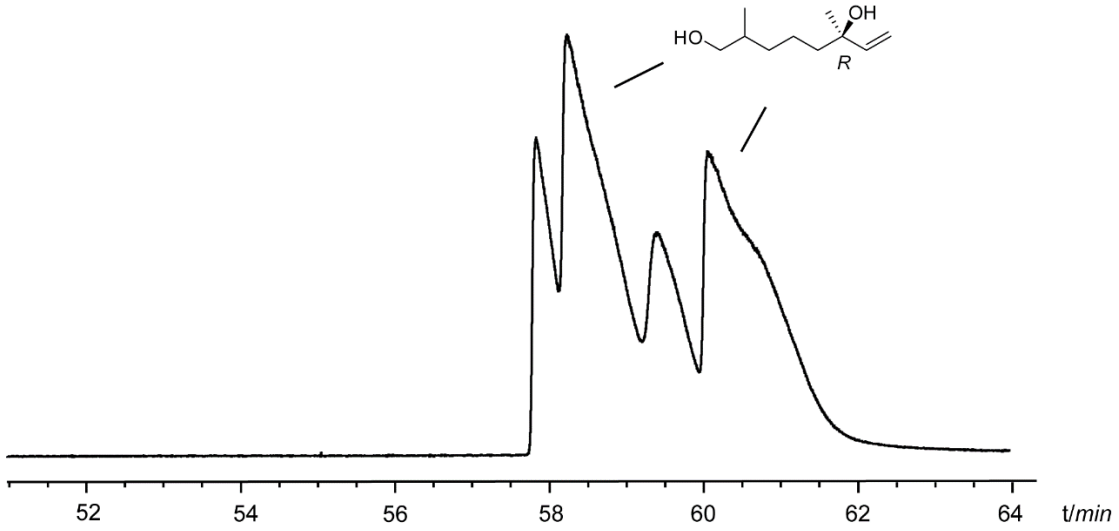


Figure S2. Gas chromatographic coinjection experiment of mixture of all stereoisomers of **6** with (2*RS*,6*R*)-2,6-dimethyl-7-octene-1,6-diol (2*RS*,6*S*-**6**) on a β-DEX 225 column with the following temperature program: isothermal 100 °C for 5 min, ramp of 0.25 °C/min until 220 °C.

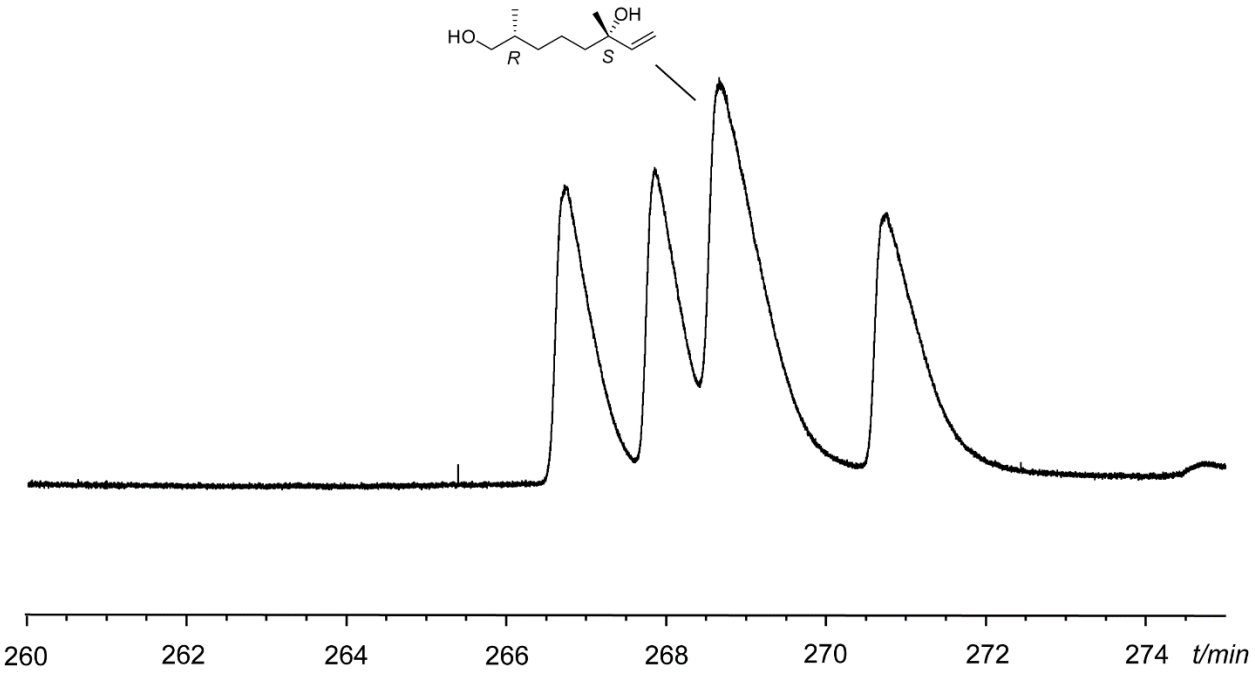


Figure S3. Gas chromatographic coinjection experiment of a racemic mixture of **6** with (2*R*,6*S*)-2,6-dimethyl-7-octene-1,6-diol (2*R*,6*S*-**6**) on a β-DEX 225 column with the same temperature program as in Figure S1. The third peak is enhanced.

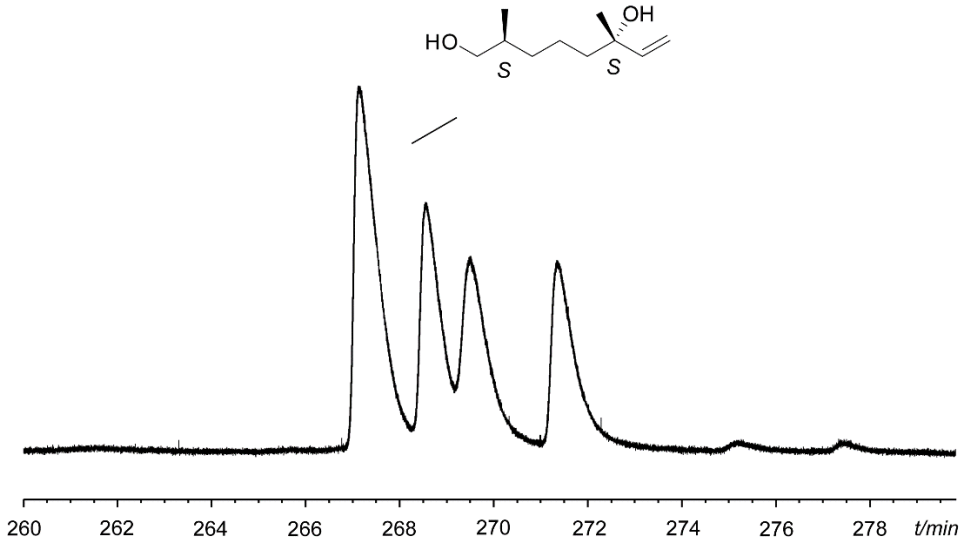


Figure S4. Gas chromatographic coinjection experiment of racemic mixture **6** with synthesized 2*S*,6*S*-**6** on a β-DEX 225 column with the same temperature program as in Figure S1. The first peak is enhanced. The natural compound is the first eluting peak. [S7]

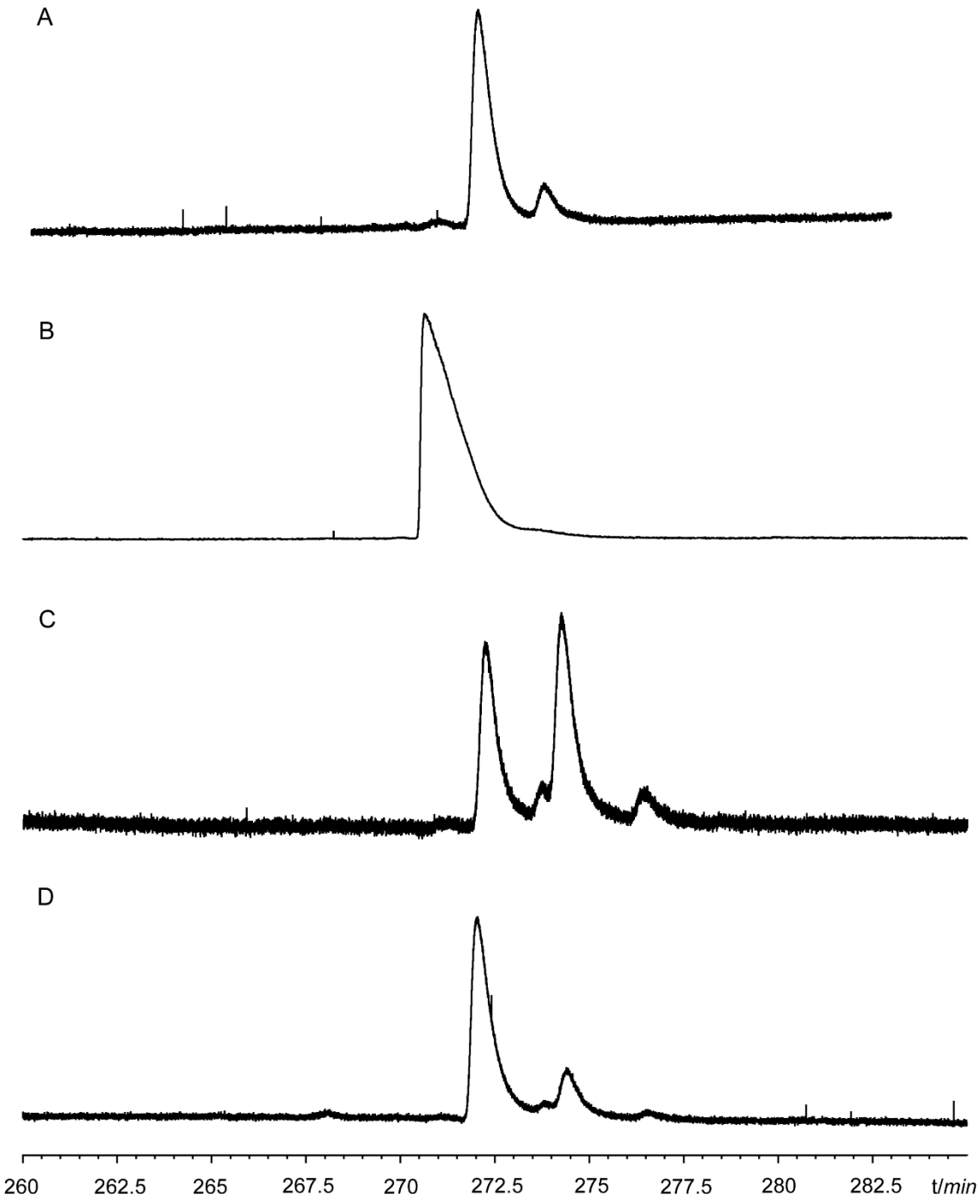


Figure S5. Gas chromatographic experiments of: A: synthesized diol 2 *S*,6*S*-**6**, showing an ee of 90 %, the same as the starting material; B: natural extract of *Urolepis rufipes*; C: Coinjection of synthetic diols 2*S*,6*S*-**6** and 2*R*,6*S*-**6**; D: Coinjection of synthetic diols 2*S*,6*S*-**6** and 2*R*,6*S*-**6** with the natural extract of *Urolepis rufipes.* A β-DEX 225 column with the same temperature program presented in Figure S1 was used, proving that the natural pheromone is the (2 *S*,6*S*)-2,6-dimethyl-7-octene-1,6-diol (2*S*,6*S*-**6**) stereoisomer.

3 Behavioral bioassay with the natural stereoisomer 2 *S*,6*S*-6 and the non-natural stereoisomer 2*R*,6*S*-6

Urolepis rufipes was reared on freeze-killed host pupae of the green bottle fly *Lucilia caesar* as described previously.[S8] Three-day-old, virgin females were isolated in 1.5-ml microcentrifuge tubes and allowed to acclimate to the laboratory conditions for at least 30 min before the experiments. Behavioral bioassays were performed in still-air two-choice olfactometer described previously.[S8] Briefly, females were exposed in a Petri dish arena to two filter paper disks, one of which was treated with 300 ng of 2 *S*,6*S*-**6** or 2*R*,6*S*-**6** dissolved in 2 µl dichloromethane (n=50 for each stereoisomer). The other disk was treated with 2 µl of the pure solvent (control). We recorded for 5 min the residence time of females within circles (2 cm diameter) drawn around each paper disk using the scientific software The Observer XT (Noldus, Wageningen, The Netherlands). Residence times spent in test and control circles was compared by a paired t-test using PAST 3.26 scientific software. [S9]

4 References

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5 NMR spectra

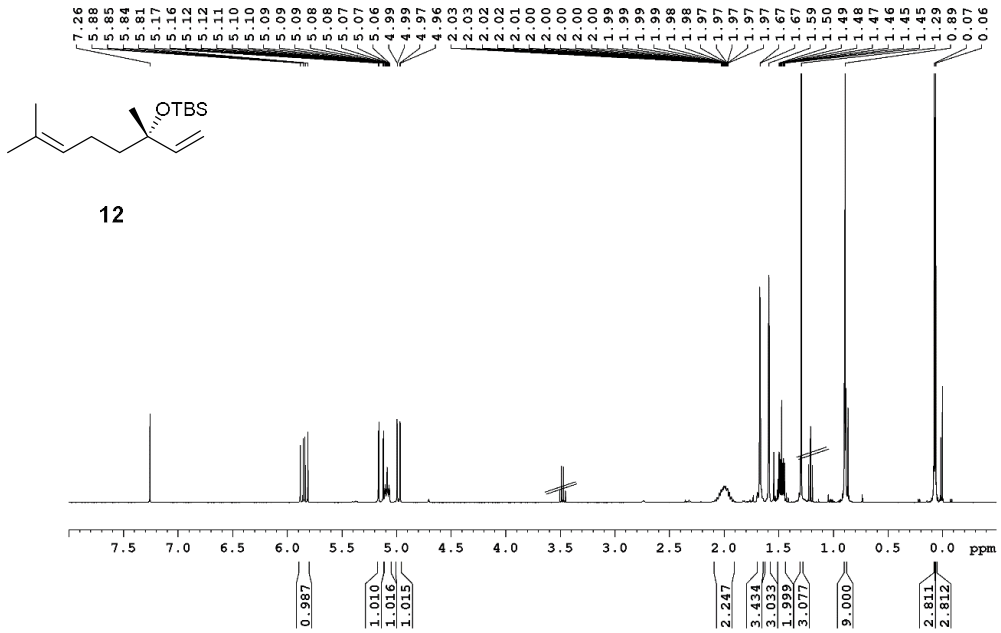

Figure S6. ^{1}H-NMR (400 MHz, $CDCl_3$) of silyl ether **12**.

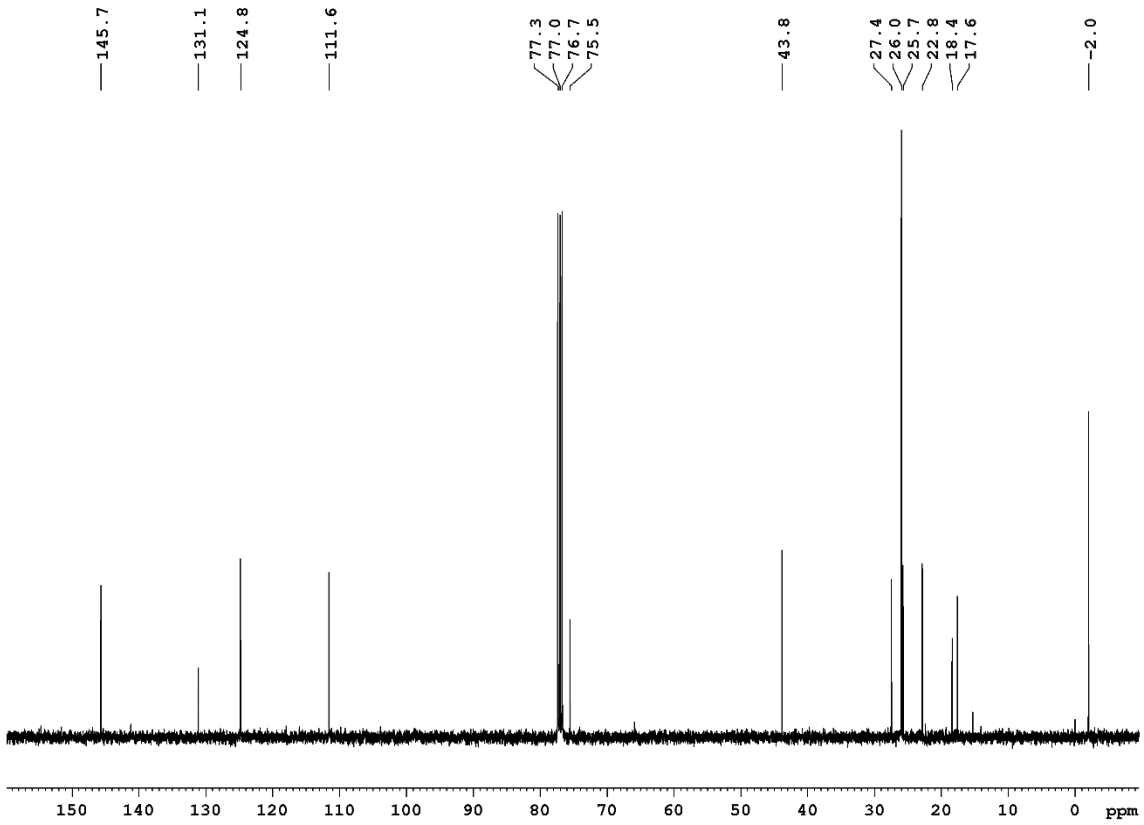

Figure S7. ^{13}C-NMR (100 MHz, $CDCl_3$) of silyl ether **12**.

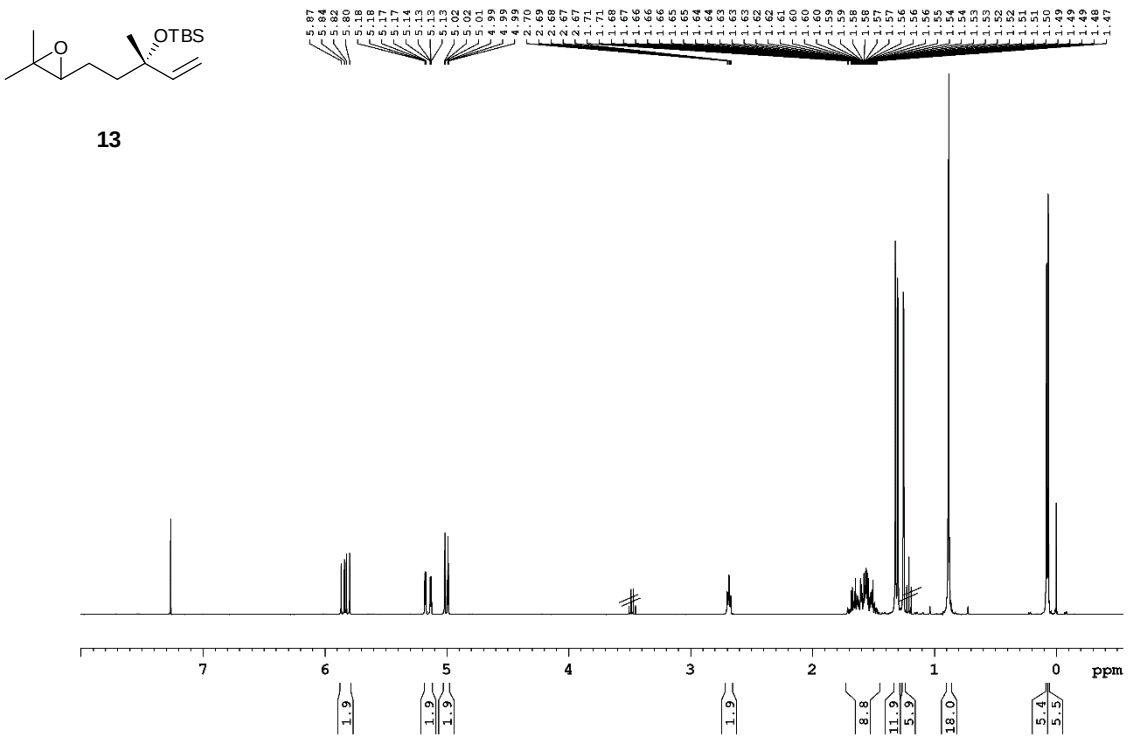

Figure S8. ^{1}H-NMR (400 MHz, $CDCl_3$) of epoxide **13**.

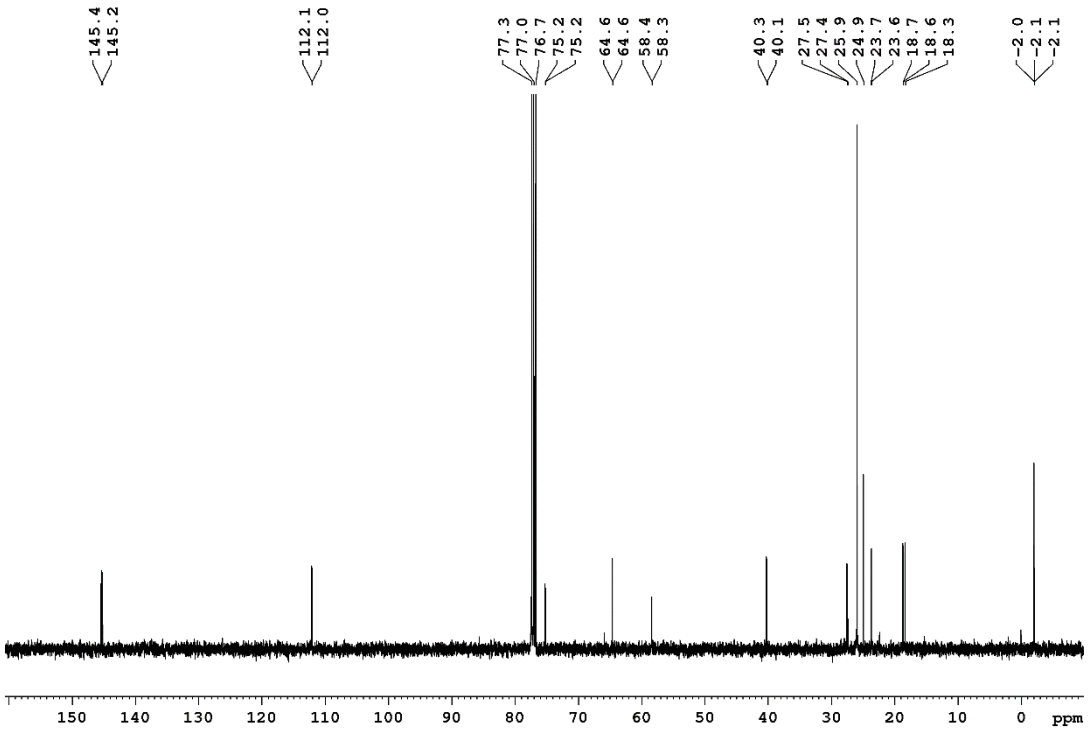

Figure S9. ^{13}C-NMR (100 MHz, $CDCl_3$) of epoxide **13**.

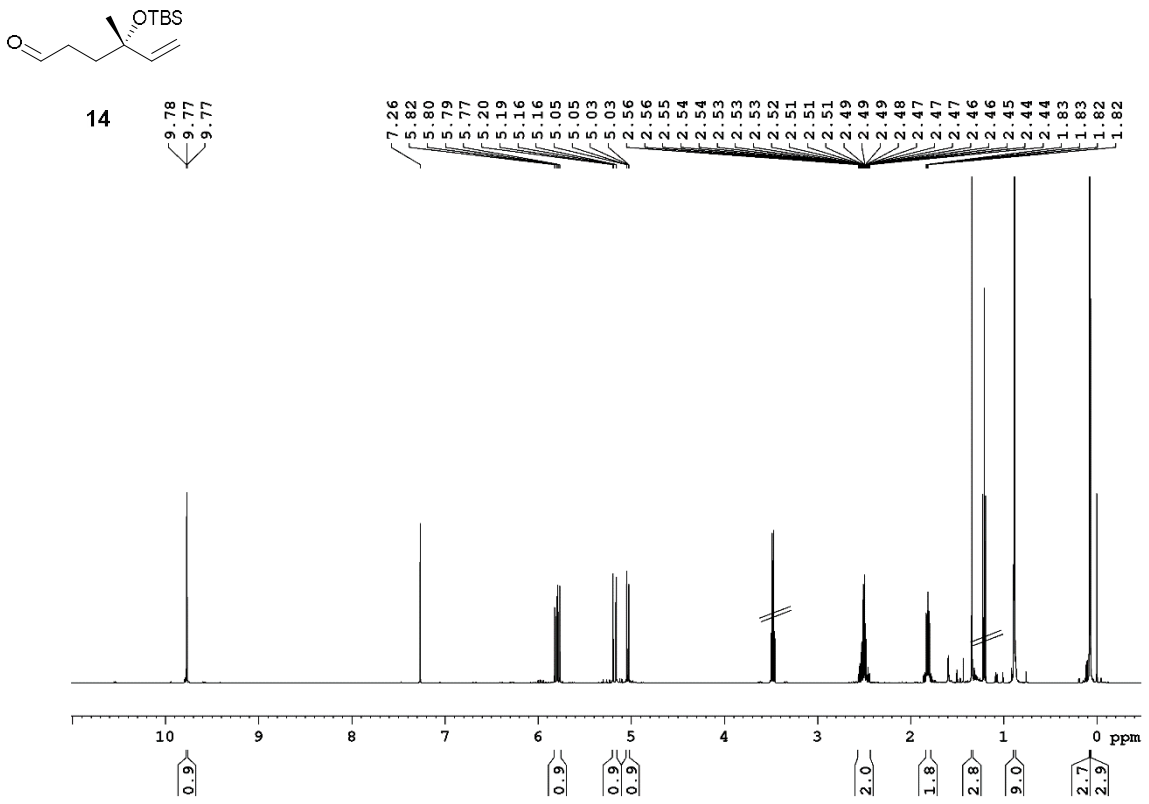

Figure S10. ^{1}H-NMR (500 MHz, $CDCl_3$) of aldehyde **14**.

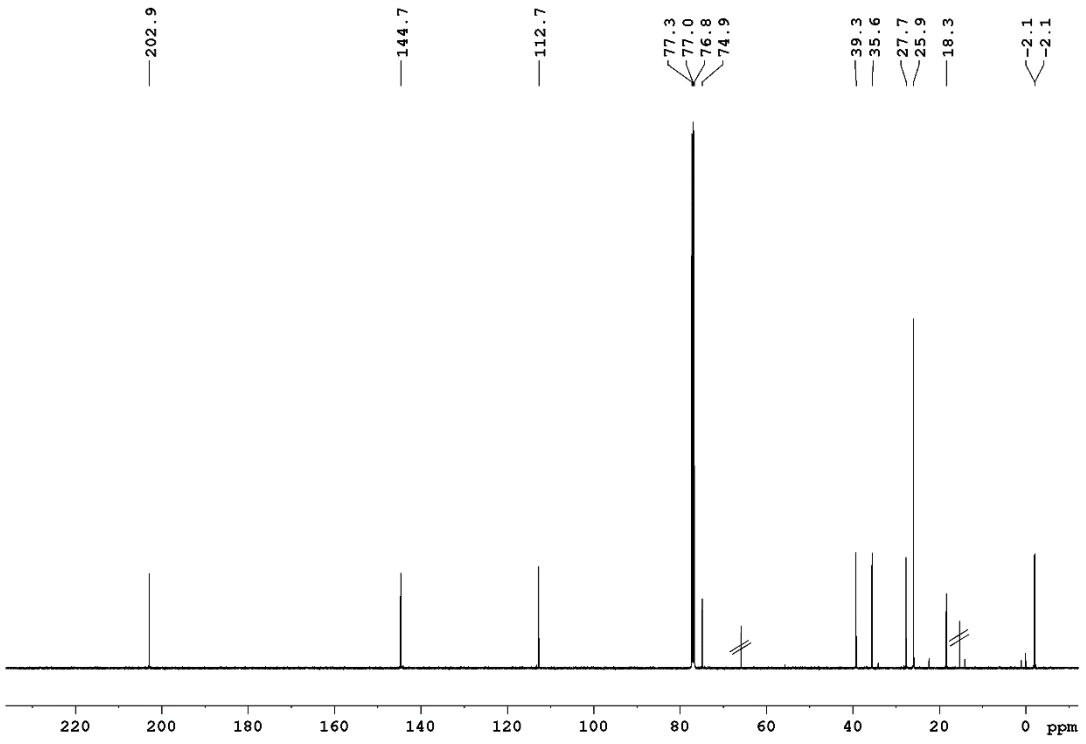

Figure S11. ^{13}C-NMR (125 MHz, $CDCl_3$) of aldehyde **14**.

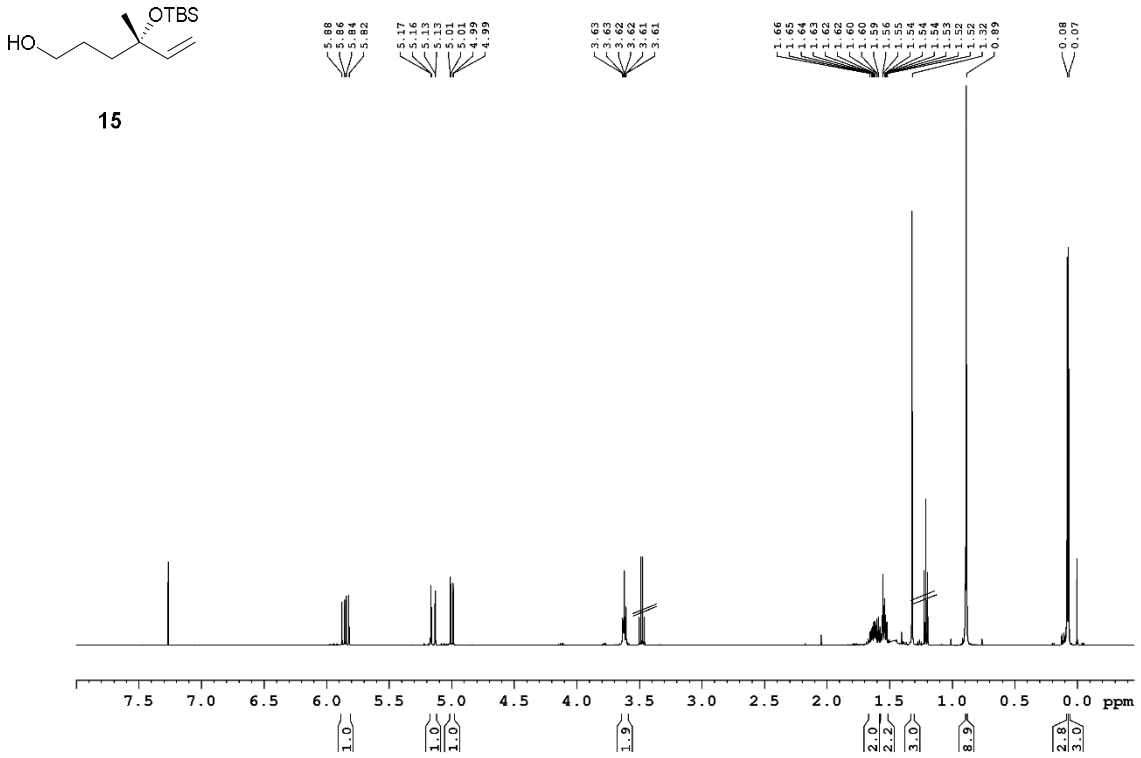

Figure S12. ^{1}H-NMR (500 MHz, $CDCl_3$) of alcohol **15**.

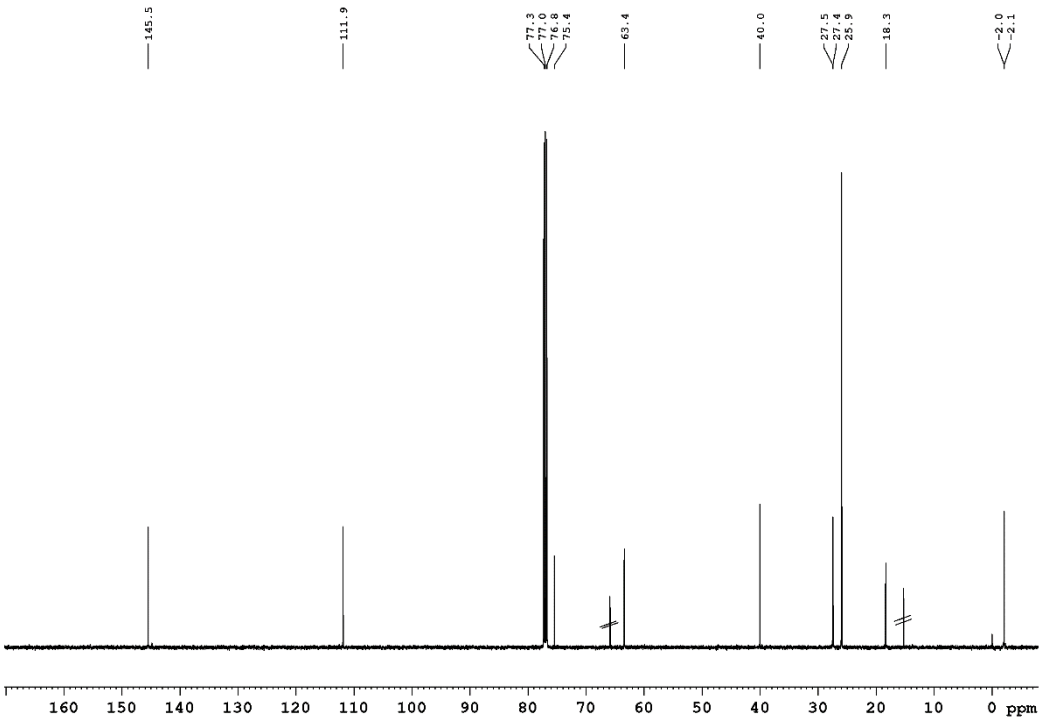

Figure S13. ^{13}C-NMR (125 MHz, $CDCl_3$) of alcohol **15**.

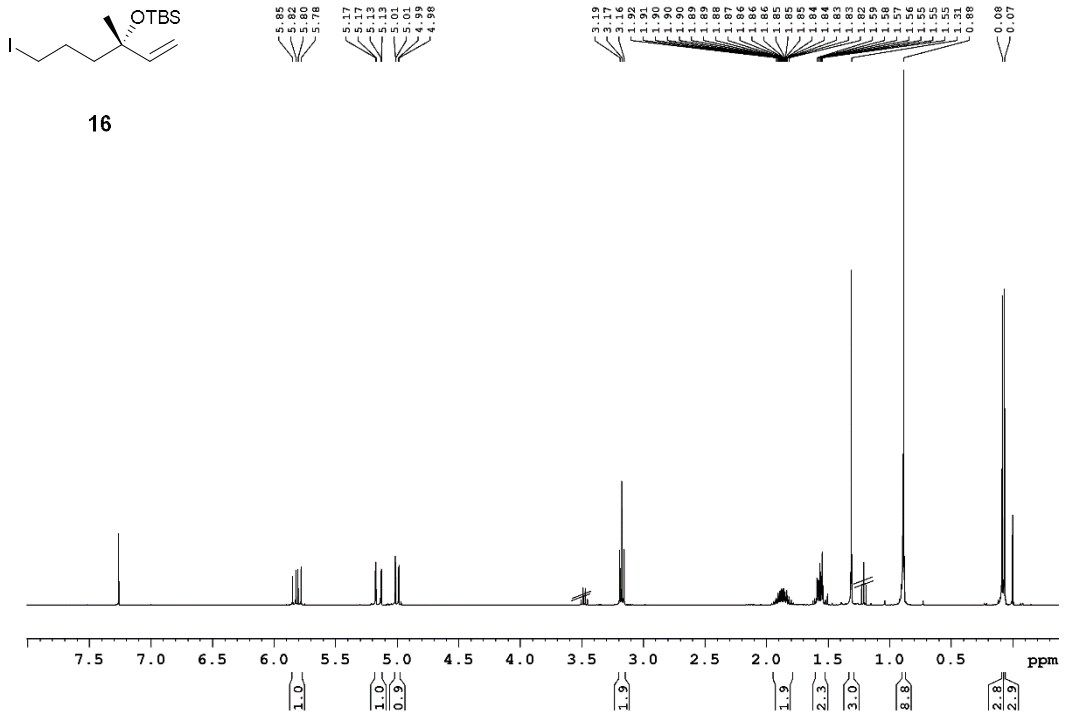

Figure S14. ^{1}H-NMR (400 MHz, $CDCl_3$) of iodide **16**.

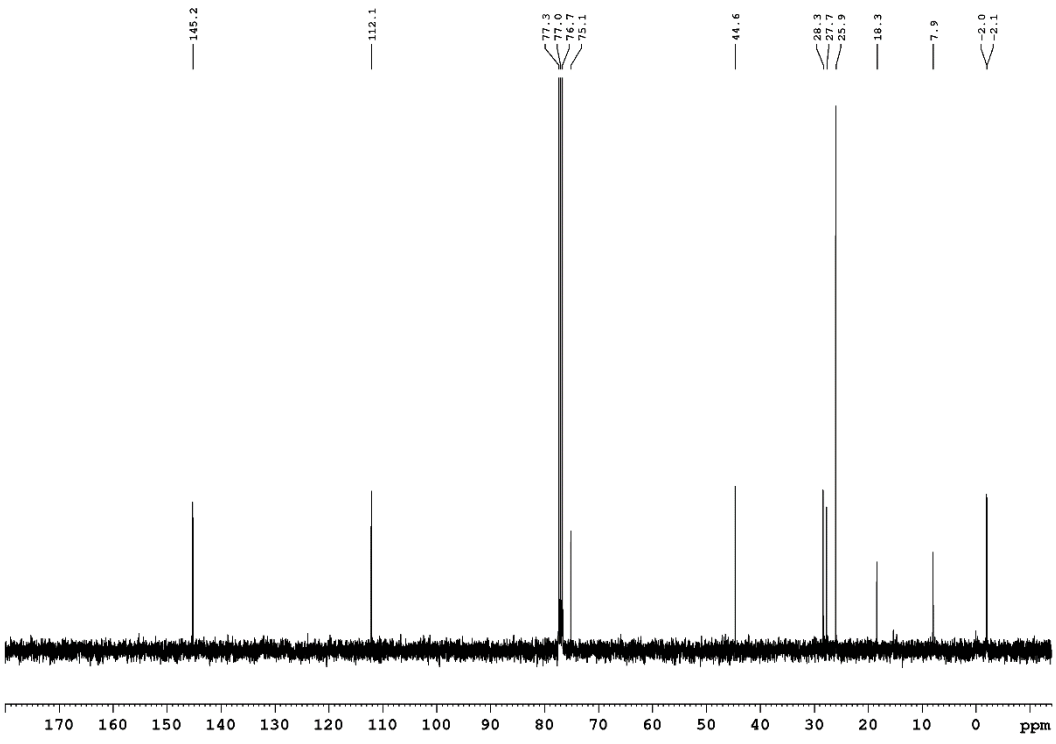

Figure S15. ^{13}C-NMR (100 MHz, $CDCl_3$) of iodide **16**.

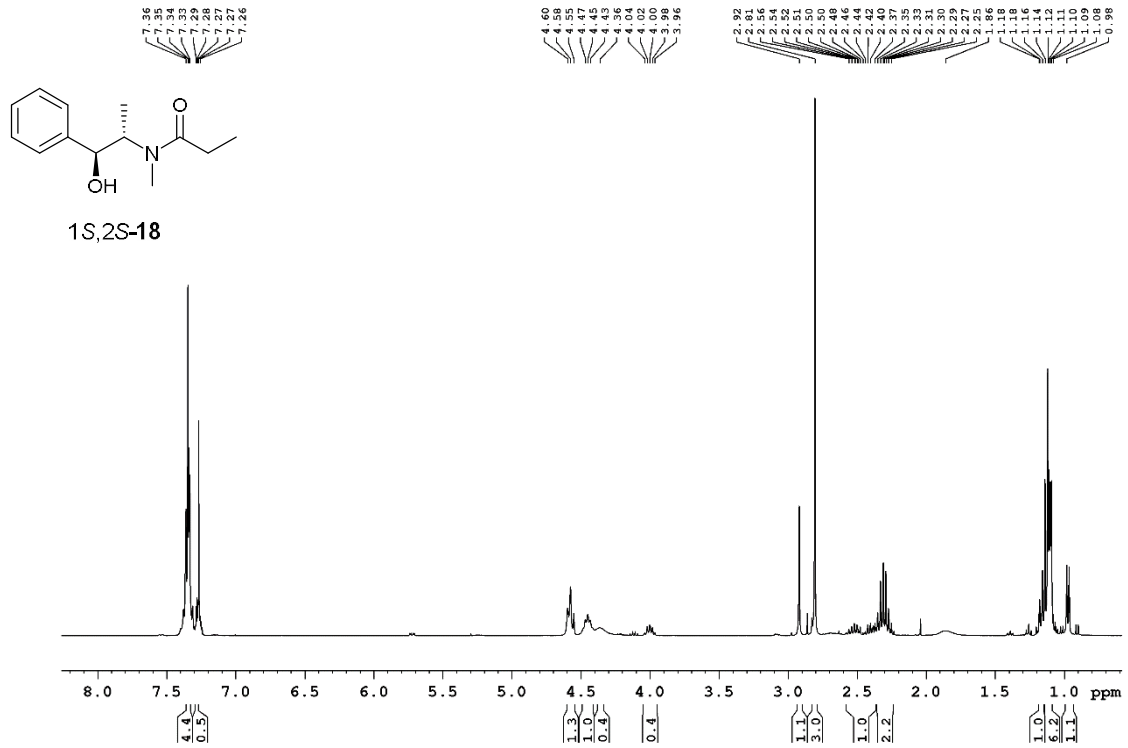

Figure S16. ^{1}H-NMR (400 MHz, $CDCl_3$) of (1*S*,2*S*)-Pseudoephedrine **18**.

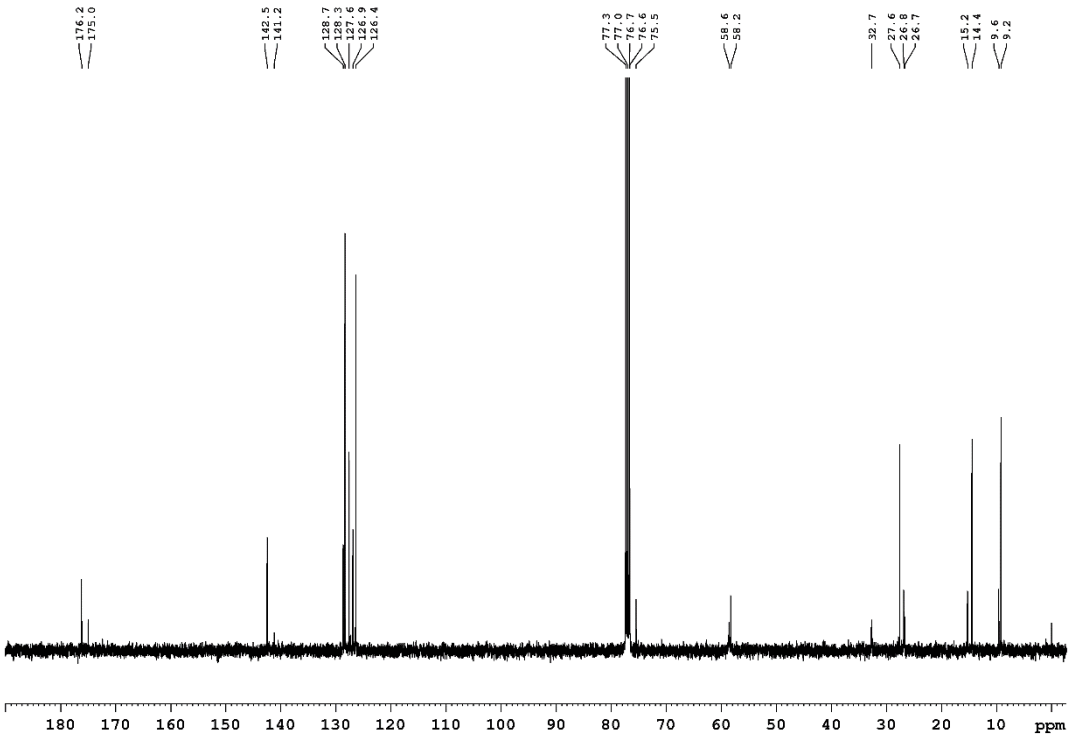

Figure S17. ^{13}C-NMR (100 MHz, $CDCl_3$) of (1*S*,2*S*)-Pseudoephedrine **18.**

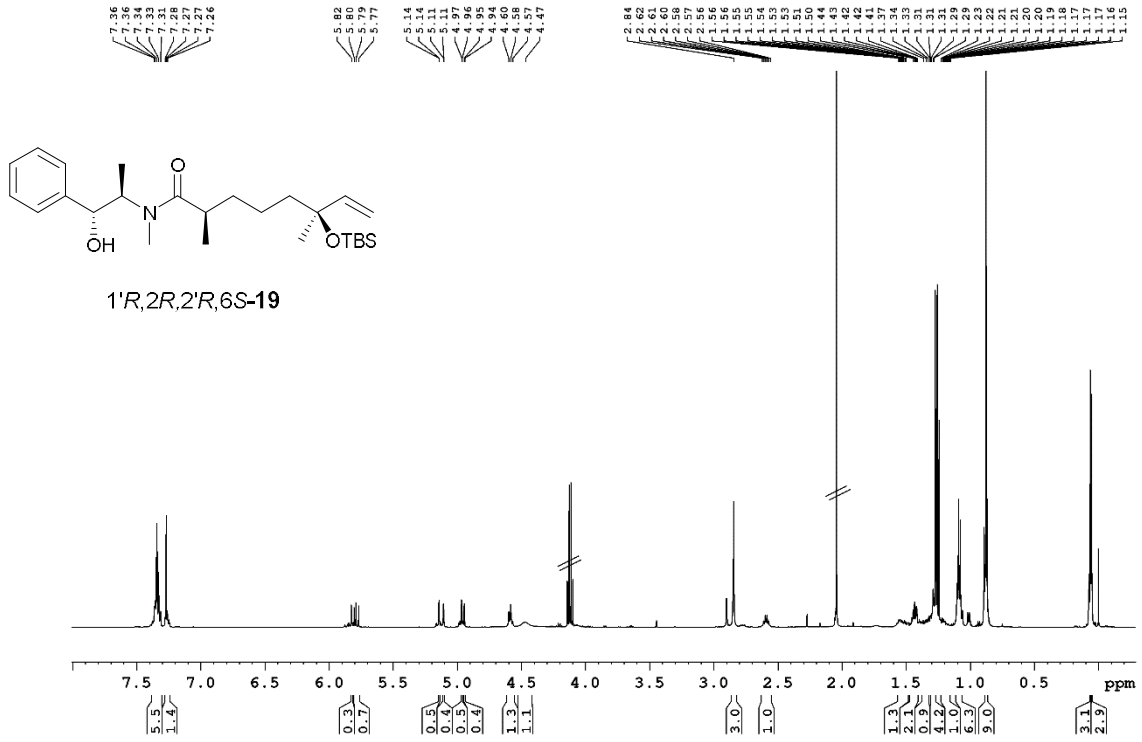

Figure S18. ^{1}H-NMR (500 MHz, $CDCl_3$) of amide 1'*R*,2*R*,2'*R*,6*S*-**19**.

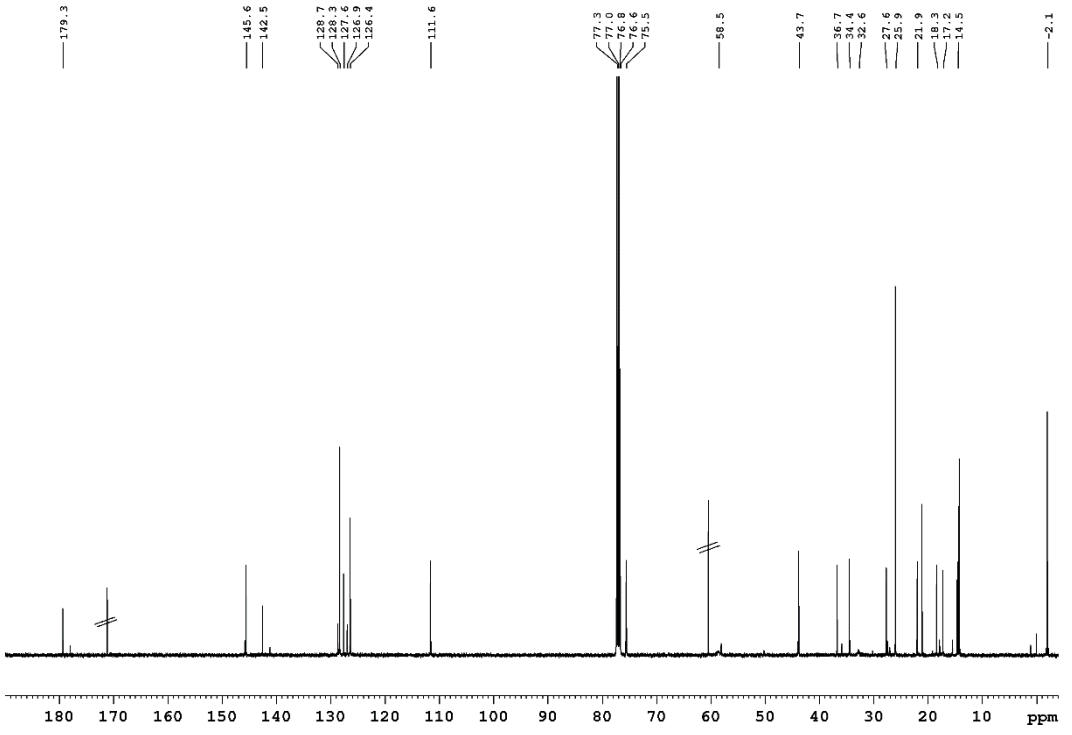

Figure S19. ^{13}C-NMR (125 MHz, $CDCl_3$) of amide 1'*R*,2*R*,2'*R*,6*S*-**19**.

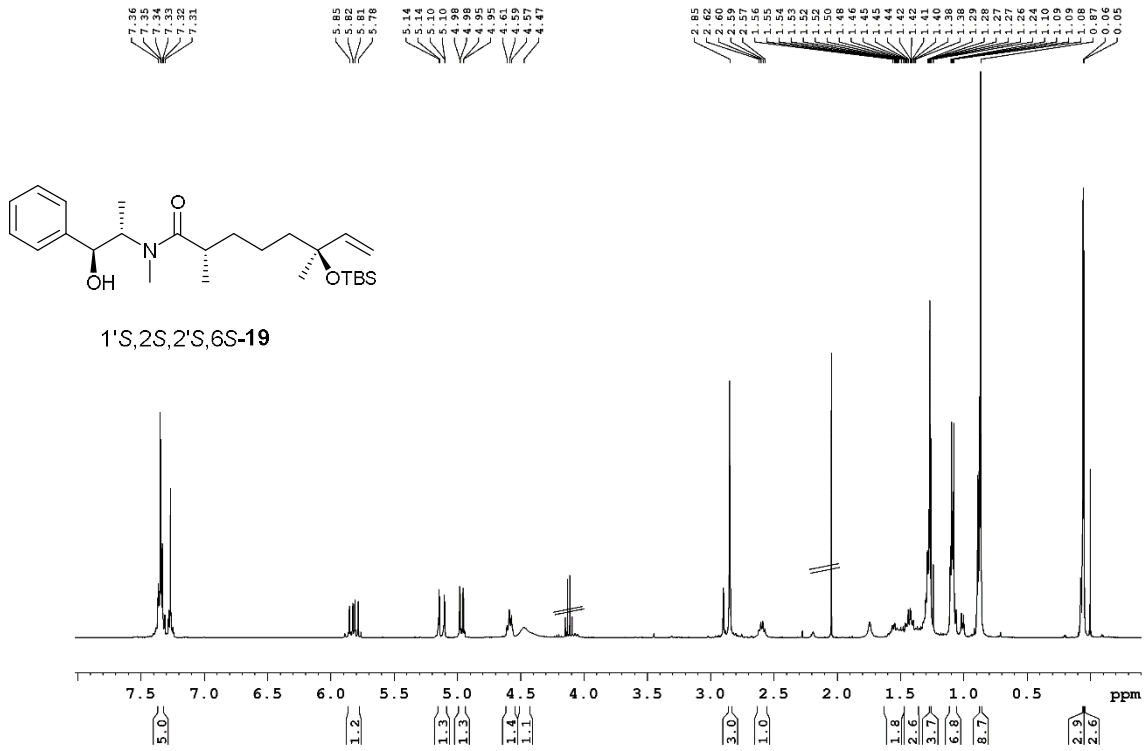

Figure S20. ^{1}H-NMR (400 MHz, $CDCl_3$) of amide 1'*S*,2*S*,2'*S*,6*S*-**19**.

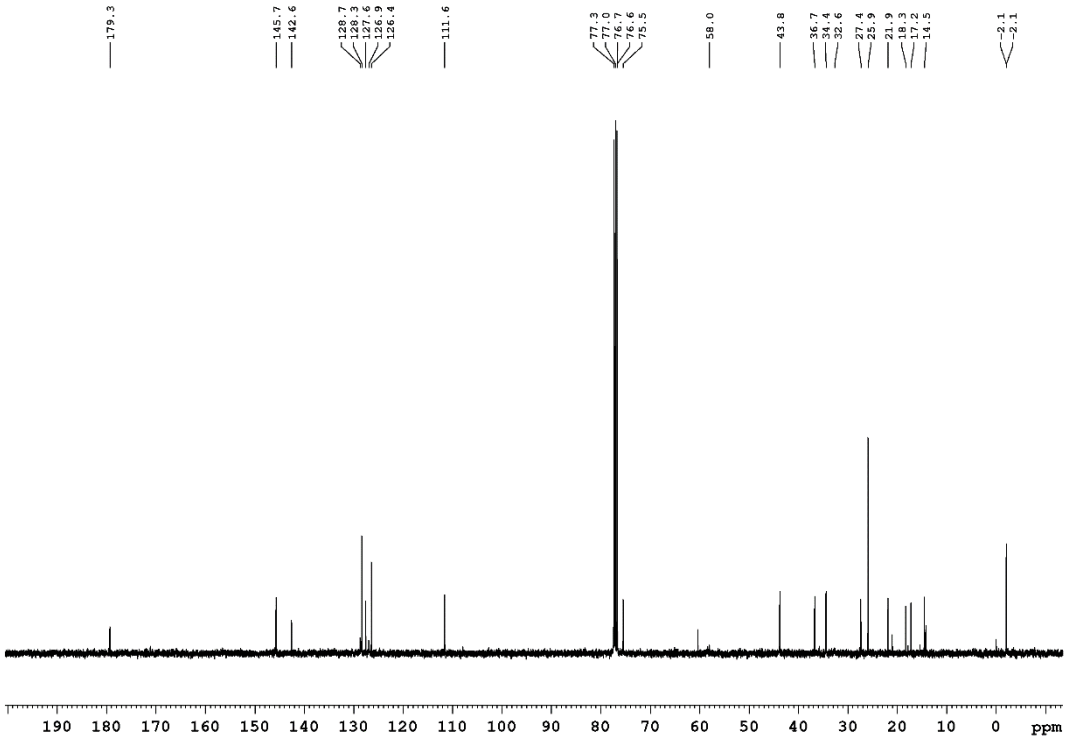

Figure S21. ^{13}C-NMR (100 MHz, $CDCl_3$) of amide 1'*S*,2*S*,2'*S*,6*S*-**19**.

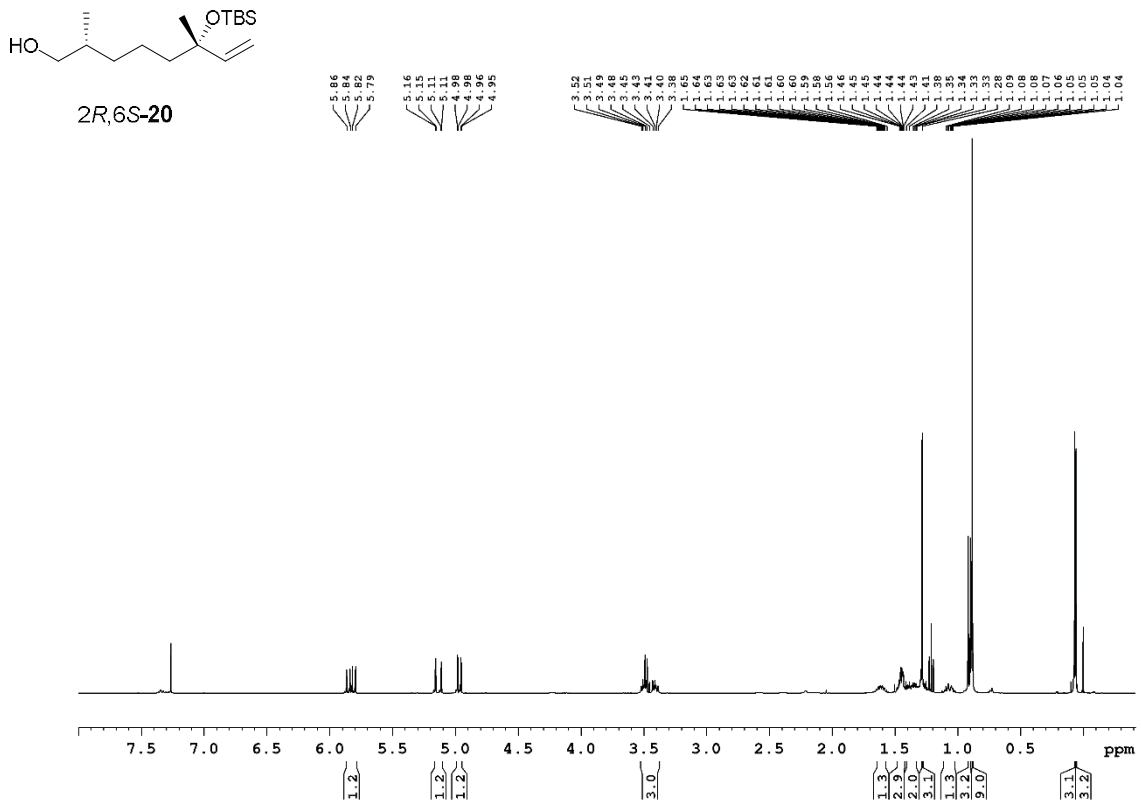

Figure S22. ^{1}H-NMR (400 MHz, $CDCl_3$) of TBS-alcohol 2*R*,6*S*-**20**.

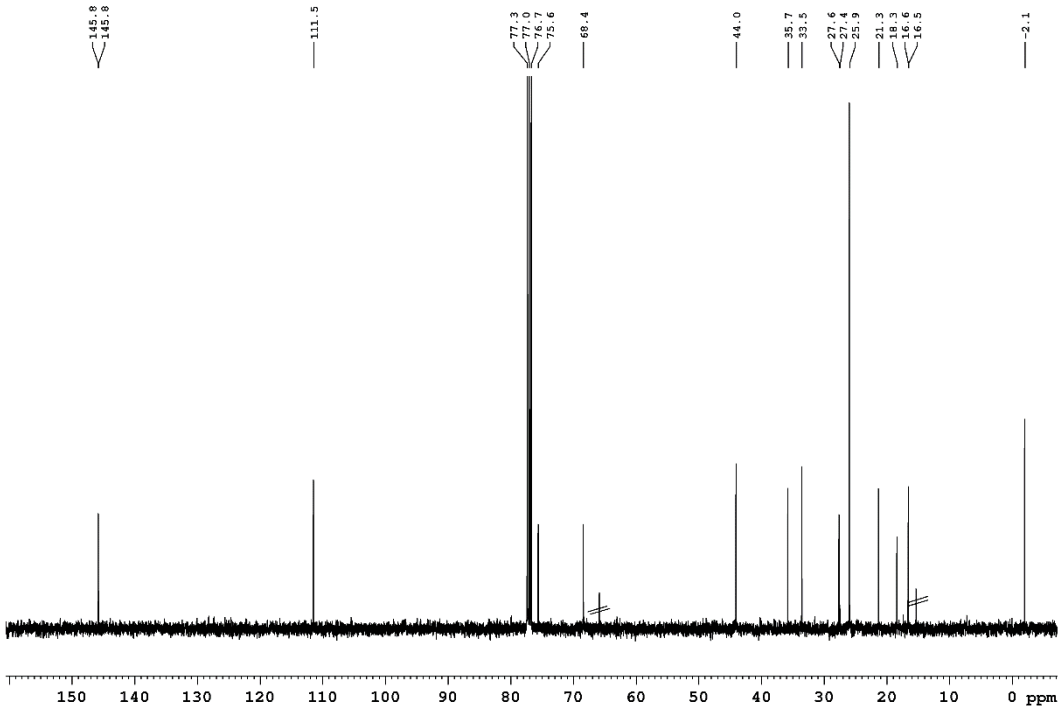

Figure S23. ^{13}C-NMR (100 MHz, $CDCl_3$) of TBS-alcohol 2*R*,6*S*-**20**.

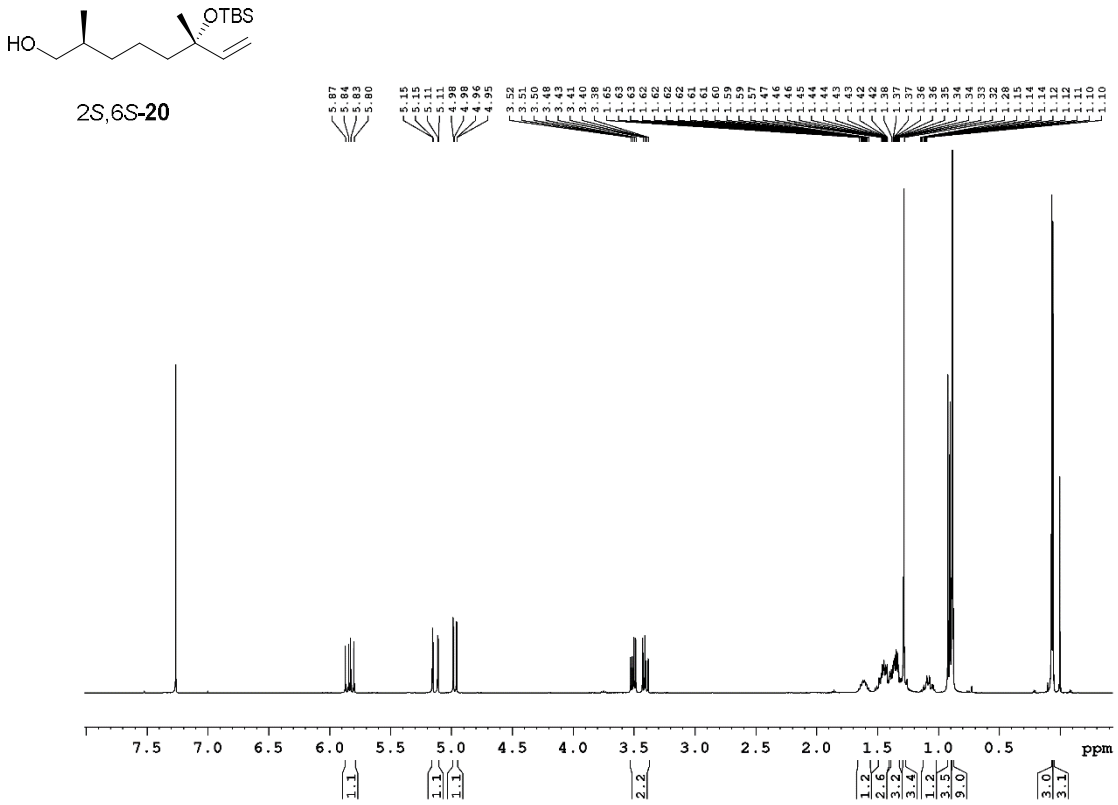

Figure S24. ^{1}H-NMR (400 MHz, $CDCl_3$) of TBS-alcohol 2*S*,6*S*-**20**.

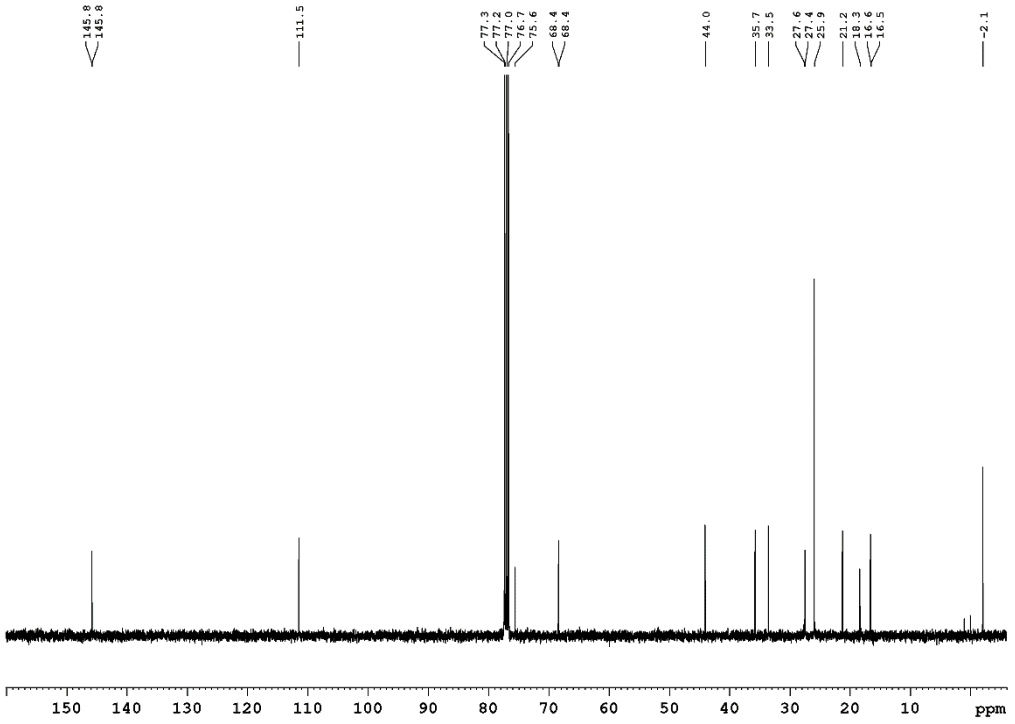

Figure S25. ^{13}C-NMR (100 MHz, $CDCl_3$) of TBS-alcohol 2*S*,6*S*-**20**.

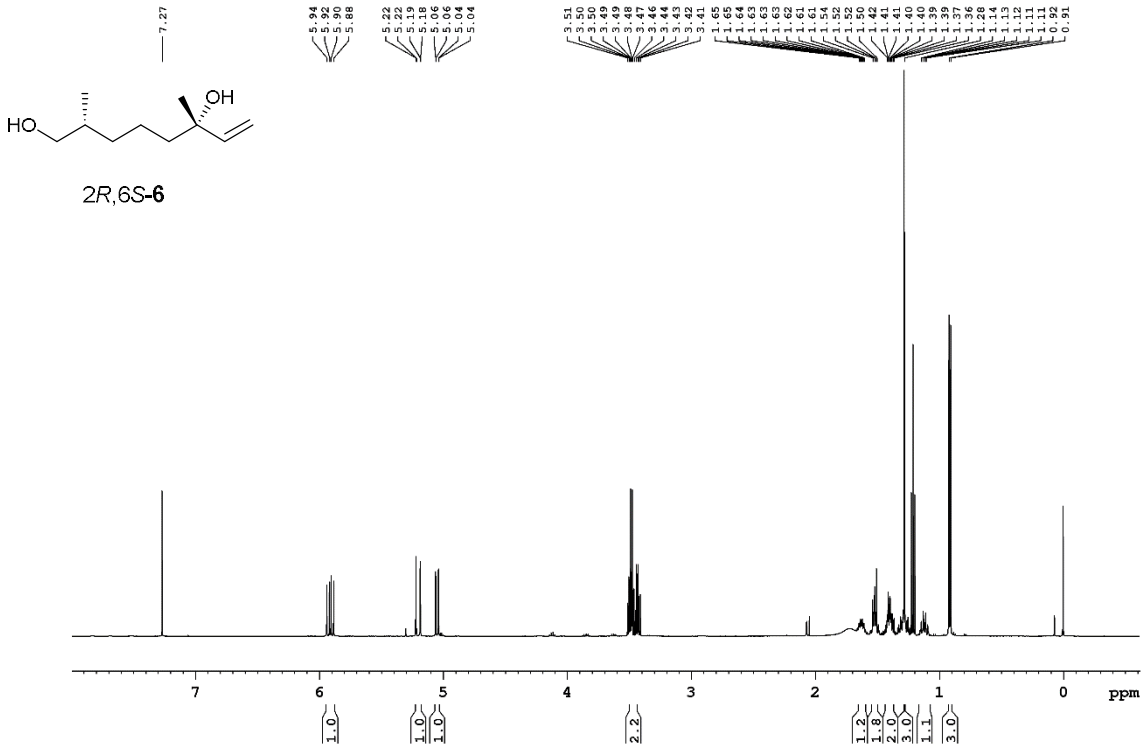

Figure S26. ^{1}H-NMR (500 MHz, $CDCl_3$) of alcohol 2*R*,6*S*-**6**.

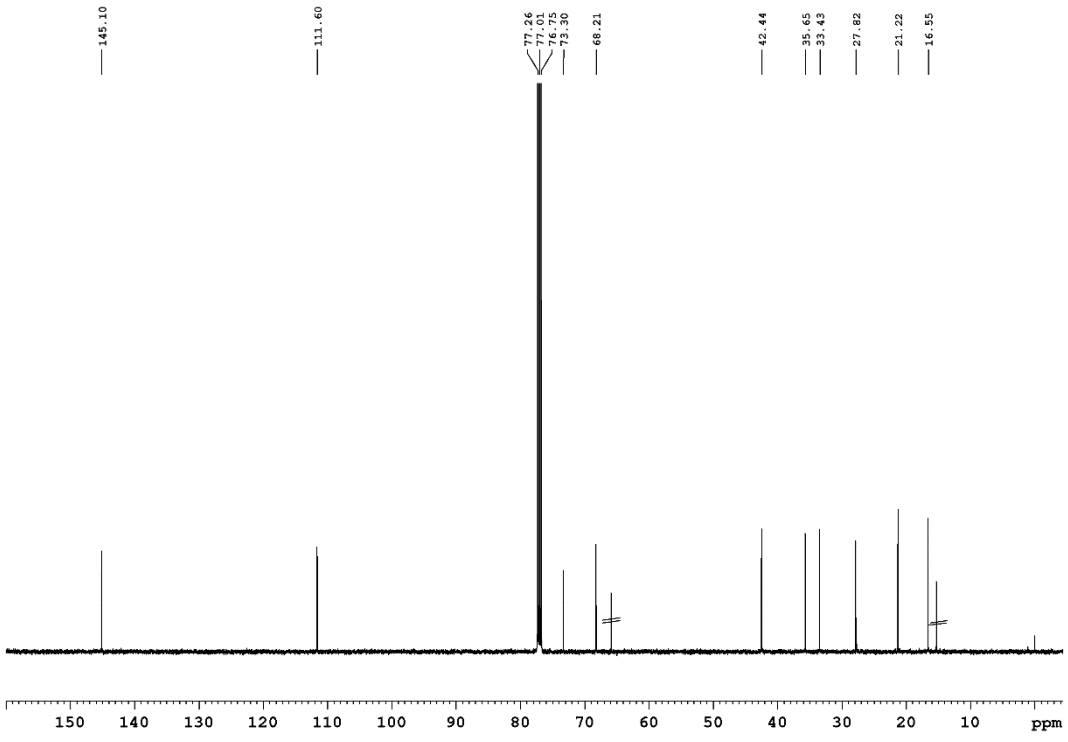

Figure S27. ^{13}C-NMR (125 MHz, $CDCl_3$) of alcohol 2*R*,6*S*-**6**.

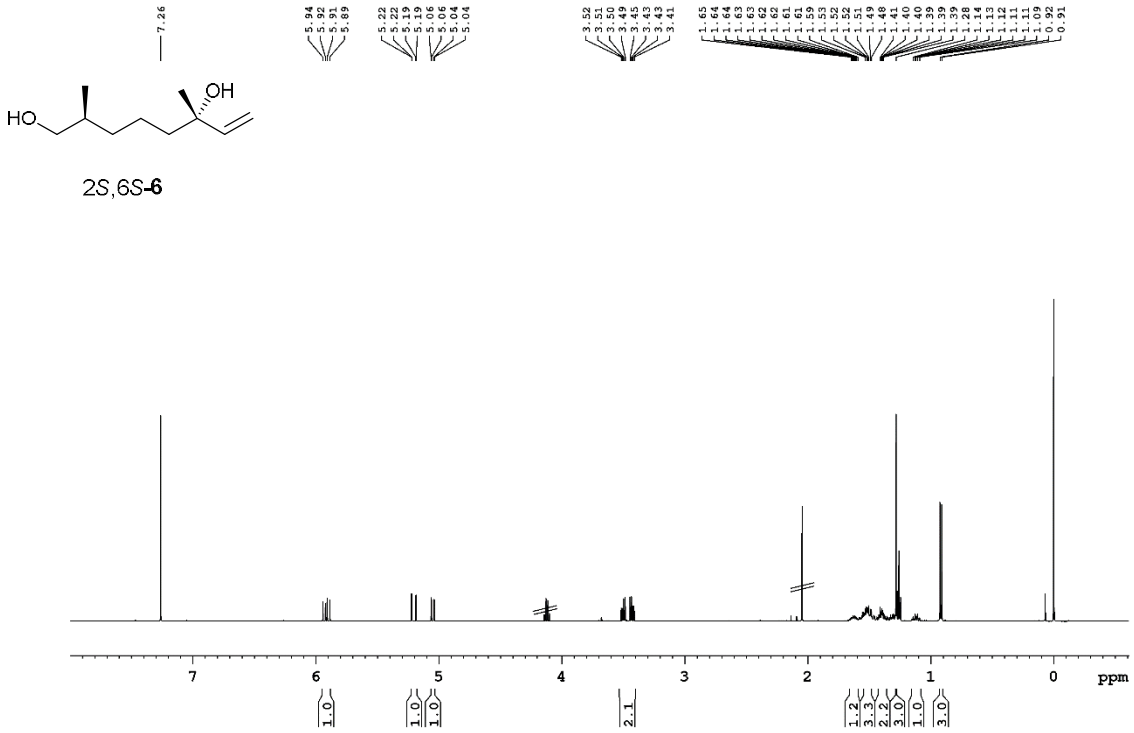

Figure S28. ^{1}H-NMR (400 MHz, $CDCl_3$) of alcohol 2*S*,6*S*-**6**.

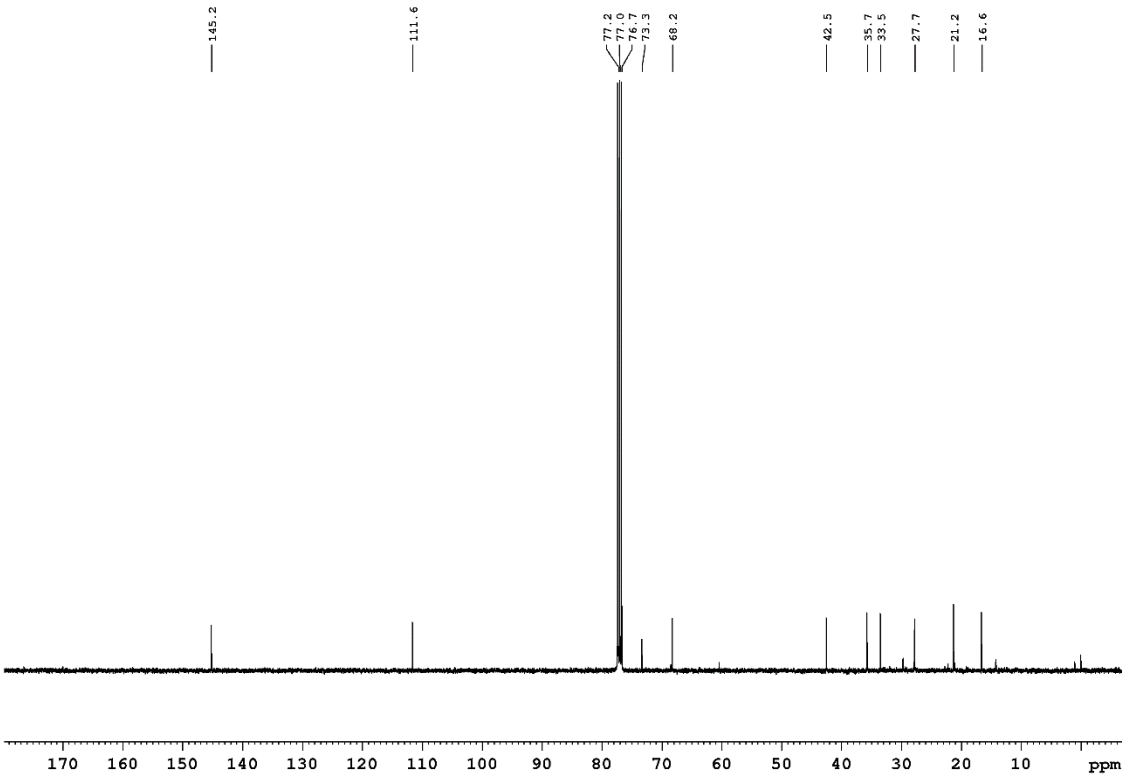

Figure S29. ^{13}C-NMR (100 MHz, $CDCl_3$) of alcohol 2*S*,6*S*-**6**.