Supporting Information for:

Stereoselective Gold-Catalyzed Cycloaddition of Functionalized Ketoenynes: Synthesis of (+)-Orientalol F

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Contents

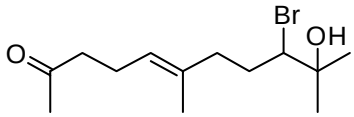
General methods

All reactions were carried out under Ar unless otherwise specified. Solvents were dried using a Solvent Purification System (SPS) or using standard procedures. NBS was recrystallized from water and dried in a freeze dryer before use. All catalysts were synthesized according to literature procedures.[1] The rest of the reagents were used directly as provided from the commercial sources. Analytical thin layer chromatography was carried out using TLC aluminium sheets with 0.2 mm of silica gel (Merk GF_{234}). Flash chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm). NMR spectra were recorded at 23ºC on the following spectrometers: Bruker Avance 400 Ultrashield (400 MHz for ^{1}H, and 100 MHz for ^{13}C), Bruker Avance 500 Ultrashield (500 MHz for ^{1}H, and 125 MHz for ^{13}C), and Bruker Digital Avance 800 (800 MHz for ^{1}H). For some compounds PENDANT NMR spectra (Polarization Enhancement Nurtured During Attached Nucleus Testing) are provided

instead of standard ^{13}C NMR spectra. ESI mass spectra were recorded on a Waters LCT Premier spectrometer. Elemental analyses were performed on a LECO CHNS 932 micro-analyzer at the Universidad Complutense de Madrid. Melting points were determined using a Büchi melting point apparatus.

Experimental procedures

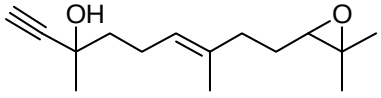
(*E*)-9-bromo-10-hydroxy-6,10-dimethylundec-5-en-2-one (31)[2]



Geranylacetone (10.0 mL, 44.7 mmol) was disolved in a mixture of THF (80 mL) and water (48 mL). The solution was cooled to 0 ºC with an ice bath and then a freshly prepared solutions of NBS (7.96 g, 44.7 mmol) were added dropwise using an addition funnel (10 portions of 796 mg, each dissolved in 12.8 mL of a 5:3 THF/H_2O mixture). When the addition was completed the mixture was diluted with CH_2Cl_2 (100 mL), the phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. After removal of the solvents the residue was purified by flash chromatography (5:1 hexane/EtOAc) to give the bromohydrine **31** as a colorless oil (7.35 g, 56%).

^1H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, J = 7.0 Hz, 1H), 3.93 (d, J = 11.1 Hz, 1H), 2.47 (t, J = 7.3 Hz, 2H), 2.37-2.23 (m, 3H), 2.18-2.03 (m, 2H), 2.14 (s, 3H), 2.02-1.93 (m, 1H), 1.84-1.71 (m, 1H), 1.61 (s, 3H), 1.33 (s, 6H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 208.7 (C), 134.5 (C), 124.3 (CH), 72.5 (C), 70.5 (CH), 43.6 (CH_2), 38.0 (CH_2), 31.9 (CH_2), 30.0 (CH_3), 26.5 (CH_3), 26.0 (CH_3), 22.4 (CH_2), 15.8 (CH_3). HRMS-ESI calcd for $C_{13}H_{23}O_2BrNa$ $(M+Na)^+$: 313.0774; found: 313.0763.

(*E*)-9-(3,3-dimethyloxiran-2-yl)-3,7-dimethylnon-6-en-1-yn-3-ol (*rac*-23)

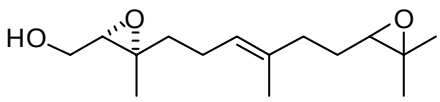


An ethynylmagnesium bromide solution (0.5 M in THF, 34.5 mL, 17.3 mmol) was added to a cooled solution of bromohydrine **31** (1.67 g, 5.74 mmol) in THF (40 mL) at 0 ºC. Once the addition was completed the cooling bath was removed and the mixture was let to warm up to room temperature. Then it was heated to 50 ºC and stirred at that temperature for 3 h. The reaction was monitored by TLC. After 3 hours, the heating was stopped and the mixture

was cooled down to room temperature. After quenching the reaction by addition of sat. aq. NH_4Cl solution the aqueous phase was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvents were removed by evaporation. Chromatographic purification (4:1 to 3:1 hexane/EtOAc) yielded the desired epoxide ***rac*-23** as a light yellow oil (1.25 g, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (t, J = 7.0 Hz, 1H), 2.70 (t, J = 6.1 Hz, 1H), 2.46 (s, 1H), 2.36-2.04 (m, 5H), 1.74-1.68 (m, 2H), 1.68-1.59 (m, 2H), 1.66 (s, 3H), 1.50 (s, 3H), 1.30 (s, 3H), 1.25 (s, 3H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 135.2 (C), 124.2 (CH), 87.5 (C), 71.5 (CH), 68.2 (C), 64.2 (CH), 58.4 (C), 43.1 (CH_2), 36.3 (CH_2), 29.84 (CH_3, one isomer), 29.82 (CH_3, other isomer), 27.4 (CH_2), 24.9 (CH_3), 23.5 (CH_2), 18.8 (CH_3), 16.03 (CH_3, one isomer), 16.01 (CH_3, other isomer). HRMS-ESI calcd for $C_{15}H_{24}O_2Na$ $(M+Na)^+$: 259.1669; found: 259.1665.

((2S,3S)-3-((E)-6-(3,3-dimethyloxiran-2-yl)-4-methylhex-3-enyl)-3-methyloxiran-2-yl)methanol (32)[3]

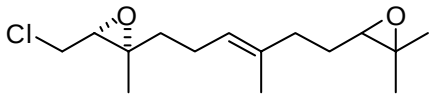


$Ti(OiPr)_4$ (255 mg, 0.897 mmol) was added at 0 ºC to a solution of L-(+)-DET (278 mg, 1.35 mmol) in CH_2Cl_2 (14 mL) containing molecular sieves (4 Å, 0.5 g). The mixture was cooled to -20 ºC and a solution of TBHP in CH_2Cl_2 (4.5 M, 6.0 mL, 27 mmol) was added. After stirring the solution for 30 min at this temperature (±)-epoxyfarnesol **21**[4] (4.28 g, 18.0 mmol) was added slowly. After stirring for another 2 h the reaction was quenched with water (5.1 mL) and the mixture was let to warm to room temperature during 40 min. Then aq. NaOH (30%, containing 4% NaCl, 1.0 mL) was added which led to a phase separation upon 20 min of vigorous stirring. The aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent were removed under reduced pressure. Chromatographic purification (3:1 hexane/Et_2O) yielded the desired diepoxide **32** as a colorless oil (4.53 g, 99%).

IR (neat): 3431*s*, 2960*m*, 2925*s*, 1453*s*, 1379*s*, 1323*w*, 1249*m*, 1118*m*, 1033*s*, 958*w*, 899*w*, 865*s*, 795*w*, 680*m*, 529*w*, 506*w* cm^{-1}. ^{1}H NMR (400 MHz, CDCl3) δ 5.16-5.12 (m, 1H), 3.79-3.72 (m, 1H), 3.69-3.63 (m, 1H), 2.96-2.91 (m, 1H), 2.68 (t, J = 6.2 Hz, 1H), 2.46-2.37 (m, 1H), 2.17-2.03 (m, 4H), 1.72-1.57 (m, 3H), 1.60 (s, 3H), 1.50-1.40 (m, 1H), 1.28 (s, 6H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 134.9 (C, one

isomer), 134.8 (C, other isomer), 124.1 (CH, one isomer), 124.0 (CH, other isomer), 64.3 (CH, one isomer), 64.2 (CH, other isomer), 63.1 (CH, one isomer), 63.0 (CH, other isomer), 61.4 (CH_2), 61.10 (C, one isomer), 61.06 (C, other isomer), 58.6 (C, one isomer), 58.5 (C, other isomer), 38.5 (CH_2, one isomer), 38.4 (CH_2, other isomer), 36.40 (CH_2, one isomer), 36.39 (CH_2, other isomer), 27.4 (CH_2, one isomer), 27.2 (CH_2, other isomer), 24.9 (CH_3), 23.7 (CH_2, one isomer), 23.6 (CH_2, other isomer), 18.8 (CH_3), 16.9 (CH_3, one isomer), 16.8 (CH_3, other isomer), 16.0 (CH_3). HRMS-ESI calcd for $C_{15}H_{26}O_3Na$ $(M+Na)^+$: 277.1774; found: 277.1787.

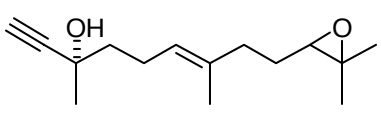
(2S,3R)-3-(chloromethyl)-2-((E)-6-(3,3-dimethyloxiran-2-yl)-4-methylhex-3-enyl)-2-methyloxirane (22)[5]



A mixture of diepoxide **32** (4.28 g, 16.8 mmol), triphenylphosphine (5.29 g, 20.2 mmol) and $NaHCO_3$ (428 mg, 5.09 mmol) in CCl_4 (34 mL) was refluxed for 6.5 h. After removal of the solvent chromatographic purification (3:1 hexane/Et_2O) of the crude material yielded epoxychloride **22** as a colorless oil (4.26 g, 93%).

IR (neat): 2960*m*, 2924*s*, 2859*w*, 1452*s*, 1378*s*, 1323*w*, 1250*m*, 1181*w*, 1119*m*, 1072*w*, 908*m*, 861*s*, 794*w*, 732*s*, 680*m* cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 5.14 (t, J = 7.0 Hz, 1H), 3.66 (dd, J = 11.4, 5.9 Hz, 1H), 3.42 (dd, J = 11.4, 7.2 Hz, 1H), 3.01 (t, J = 6.5 Hz, 1H), 2.67 (t, J = 6.2 Hz, 1H), 2.17-2.02 (m, 4H), 1.75-1.57 (m, 3H), 1.61 (s, 3H), 1.49-1.38 (m, 1H), 1.29 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 135.1 (C), 123.7 (CH), 64.0 (CH), 62.0 (C), 61.4 (CH, one isomer), 61.4 (CH, other isomer), 58.2 (C, one isomer), 58.2 (C, other isomer), 42.1 (CH_2), 38.1 (CH_2, one isomer), 38.1 (CH_2, other isomer), 36.2 (CH_2), 27.3 (CH_2), 24.8 (CH_3), 23.5 (CH_2), 18.7 (CH_3), 16.2 (CH_3), 15.9 (CH_3). HRMS-ESI calcd for $C_{15}H_{26}ClO_2$ $(M+H)^+$ 273.1616; found: 273.1615.

(3*S*,*E*)-9-(3,3-dimethyloxiran-2-yl)-3,7-dimethylnon-6-en-1-yn-3-ol (23)[5]

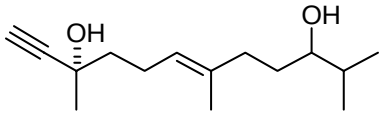


Epoxychloride **22** (4.26 g, 15.6 mmol) was added slowly at -35 ºC to a solution of *n*-BuLi (2.5 M in hexane, 31.2 mL, 78.0 mmol) in THF (45 mL). After stirring for 2 h the reaction was quenched by the addition of sat. aq. NH_4Cl solution. The aqueous phase was extracted with CH_2Cl_2,

the combined organic layers were dried over anhydrous Na_2SO_4 and the solvents were evaporated. Chromatographic purification (2:1 hexane/Et_2O) of the crude material yielded the desired epoxide **23** as a pale yellow oil (3.52 g, 95%).

The analytical data (NMR spectrascopy and mass spectrometry) is identical to the data of ***rac*-23**.

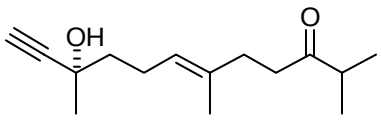
(3*S*,*E*)-3,7,11-trimethyldodec-6-en-1-yne-3,10-diol (33)



Following a procedure by *Taber and Houze*[6] for the opening of epoxides sodium cyanoborohydride (33 mg, 0.52 mmol) was added at room temperature to a solution of epoxide **23** (49 mg, 0.21 mmol) in THF (2 mL) containing a small amount of bromocresol green. The solution became dark blue. Then $BF_3{\cdot}OEt_2$ (53 µL, 0.42 mmol) was added dropwise until the solution turned yellow (one drop). The mixture was stirred at room temperature and several additions were made every time the solution turned green. The reaction was monitored by TLC. After 3.5 h more sodium cyanoborohydride was added (15 mg, 0.24 mmol) and the addition of $BF_3{\cdot}OEt_2$ continued. After 5 hours the reaction was stopped by addition of aq. HCl (10%, 0.5 mL) and the mixture was stirred for 15 min. at room temperature. Then aq. NaOH (10%) was added until the yellow mixture turned blue. The aqueous phase was extracted with EtOAc several times and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After evaporation of the solvents the crude oil was purified by flash chromatography (3:1 hexane/EtOAc) to afford **33** as colorless oil (37 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25-5.21 (m, 1H), 3.38-3.30 (ddd, J = 8.6, 5.0, 3.2 Hz, 1H), 2.46 (s, 1H), 2.37-2.23 (m, 1H), 2.23-2.11 (m, 3H), 2.09-2.00 (m, 1H), 1.74-1.53 (m, 5H), 1.66 (s, 3H), 1.50 (s, 3H), 1.49-1.40 (m, 1H), 0.92 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 136.3 (C), 123.9 (CH), 87.5 (C), 76.6 (CH), 71.5 (CH), 68.2 (C), 43.1 (CH_2), 36.3 (CH_2), 33.5 (CH), 32.1 (CH_2), 29.9 (CH_3), 23.5 (CH_2), 18.8 (CH_3), 17.2 (CH_3), 16.0 (CH_3). HRMS-ESI calcd for $C_{15}H_{26}O_2Na$ $(M+Na)^+$: 261.1825; found: 261.1826. Elem. Anal. calcd for $C_{15}H_{26}O_2$: C 75.58; H 10.99; found: C 75.25; H 10.88.

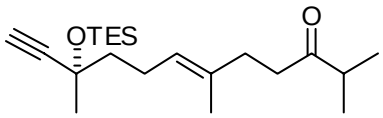
(*S*,*E*)-10-hydroxy-2,6,10-trimethyldodec-6-en-11-yn-3-one (34)



Dess-Martin periodinane (6.58 g, 15.5 mmol) was added in one portion to a stirred solution of diol **33** (2.86 g, 12.0 mmol) in CH_2Cl_2 (120 mL) at 0 ºC. The cooling bath was removed and water (216 μL, 12.0 mmol) was added dropwise. The mixture was stirred at room temperature for 2 h. Then the reaction mixture was filtered through celite (washing with EtOAc). Removal of the solvents from the filtrate and chromatogrphic purification (4:1 hexane/EtOAc) of the crude material yielded ketone **34** as colorless oil (2.43 g, 86%, 95:5 *er*). 78 mg (3%) of the starting material was recovered as well.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.15 (m, 1H), 2.60 (sept, J = 7.0 Hz, 1H), 2.56-2.51 (m, 2H), 2.45 (s, 1H), 2.35-2.13 (m, 4H), 1.72-1.66 (m, 2H), 1.65 (s, 3H), 1.50 (s, 3H), 1.09 (d, J = 7.0 Hz, 6H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 214.4 (C), 135.0 (C), 124.0 (CH), 87.5 (C), 71.5 (CH), 68.2 (C), 43.0 (CH_2), 40.9 (CH), 38.9 (CH_2), 33.5 (CH_2), 29.8 (CH_3), 23.4 (CH_2), 18.2 (2xCH_3), 16.13 (CH_3). HRMS-ESI calcd for $C_{15}H_{24}O_2Na$ (M+Na)$^+$: 259.1669; found: 259.1670. Elem. Anal. calcd for $C_{15}H_{24}O_2$: C 76.23; H 10.24; found: C 75.88; H 10.20.

(*S*,*E*)-2,6,10-trimethyl-10-(triethylsilyloxy)dodec-6-en-11-yn-3-one ((*S*)-1)



Triethylamine (1.59 mL, 11.4 mmol) was added to a solution of propargylic alcohol **34** (1.50 g, 6.35 mmol) in CH_2Cl_2 (50 mL). The mixture was cooled to 0 ºC and triethylsilyl trifluoromethanesulfonate (1.72 mL, 7.62 mmol) was added dropwise. The cooling bath was removed after the addition and the mixture was stirred for 30 min. Then an aq. NH_4Cl solution (pH = 8) was added and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent the crude material was purified by flash chromatography (10:1 hexane/EtOAc) to give the desired silyl ether **(*S*)-1** as colorless oil (2.14 g, 95 % yield).

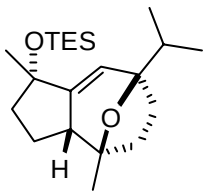
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (tq, J = 7.2, 1.2 Hz, 1H), 2.60 (sept, J = 6.9 Hz, 1H), 2.56-2.51 (m, 2H), 2.40 (s, 1H), 2.26-2.07 (m, 4H), 1.70-1.54 (m, 2H), 1.62 (s, 3H), 1.45 (s, 3H), 1.09 (d, J = 6.9 Hz, 6H), 0.96 (t, J = 7.9 Hz, 9H), 0.72-0.63 (m, 6H).

^{13}C PENDANT (100 MHz, $CDCl_3$) δ 214.6 (C), 134.1 (C), 124.4 (CH), 88.2 (C), 71.8 (CH), 68.8 (C), 45.1 (CH_2), 40.9 (CH), 39.1 (CH_2), 33.5 (CH_2), 30.9 (CH_3), 23.3 (CH_2), 18.2 (CH_3), 16.0 (2xCH_3), 7.0 (CH_3), 6.1 (CH_2). HRMS-ESI calcd for $C_{21}H_{38}O_2SiNa$ $(M+Na)^+$: 373.2533; found: 373.2531.

General procedure for the cyclization of enyne 1 with metal catalysts

To a solution of enyne **1** in CH_2Cl_2 (0.1-0.05 M) containing activated molecular sieves (4 Å), was added the metal catalyst (3 mol%) in one portion. In the case of gold chlorides a preformed catalyst solution was added to enyne solution (the gold chloride and the silver salt were stirred in CH_2Cl_2 for 2 min and after settling of the solids the supernatant was used). The reaction mixtures were stirred for the time given in **Table 1** after which the catalyst was quenched by addition of a few drops of Et_3N. The mixture was then filtered through SiO_2 (eluting with CH_2Cl_2 and Et_2O). After evaporation the crude material was purified by flash chromatography (60:1 to 40:1 pentane/Et_2O) providing the oxatricycle **2** as a colorless oil and the methyl ketone **11** as a pale yellow oil. For yields and product distribution see **Table 1**.

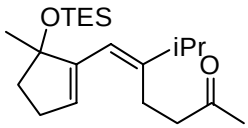
Oxatricycle (2)



^{1}H NMR (400 MHz, C_6D_6) δ 5.85 (d, J = 2.7 Hz, 1H), 2.80-2.72 (m, 1H), 2.02 (sept, J = 6.9 Hz, 1H), 1.88 (dd, J = 12.0, 8.1 Hz, 1H), 1.80 (ddd, J = 10.8, 8.9, 1.7 Hz, 1H), 1.76-1.67 (m, 2H), 1.56 (ddd, J = 12.6, 7.9, 5.9 Hz, 1H), 1.50-1.40 (m, 1H), 1.38-1.28 (m, 1H), 1.34 (s, 3H), 1.32 (s, 3H), 1.28-1.18 (m, 1H), 1.16 (d, J = 6.8 Hz, 3H), 1.08-1.02 (m, 12 H), 0.67-0.60 (m, 6H). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (d, J = 2.6 Hz, 1H), 2.74-2.66 (m, 1H), 1.94-1.82 (m, 2H), 1.79-1.62 (m, 5H), 1.47-133 (m, 2H), 1.31 (s, 3H), 1.30 (s, 3H), 0.99-0.93 (m, 15 H), 0.63-0.54 (m, 6H). ^{13}C PENDANT (100 MHz, C_6D_6) δ 149.5 (C), 118.6 (CH), 86.1 (C), 82.6 (C), 80.0 (C), 48.8 (CH), 41.5 (CH_2), 39.1 (CH_2), 34.7 (CH), 31.3 (CH_2), 29.0 (CH_3), 26.4 (CH_3), 23.1 (CH_2), 18.3 (CH_3), 18.2 (CH_3), 7.5 (CH_2+CH_3). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 148.9 (C), 117.6 (CH), 86.0 (C), 82.6 (C), 79.5 (C), 48.3 (CH), 41.1 (CH_2), 38.3 (CH_2), 34.0 (CH), 30.8 (CH_2), 28.7 (CH_3), 26.1 (CH_3), 22.8 (CH_2), 18.1 (CH_3), 17.8 (CH_3), 7.1 (CH_3), 6.7 (CH_2). The structure assignment of this compound was confirmed by 2D COSY, HSQC, HMBC and

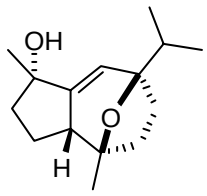
NOESY spectra. HRMS-ESI calcd for $C_{21}H_{38}O_2SiNa$ (M+Na)$^+$: 373.2533; found: 373.2497.

(*E*)-6-methyl-5-((5-methyl-5-(triethylsilyloxy)cyclopent-1-enyl)methylene)heptan-2-one (11)



^{1}H NMR (400 MHz, C_6D_6) δ 6.01 (s, 1H), 5.58 (bs, 1H), 2.66-2.52 (m, 2H), 2.36-2.17 (m, 4H), 2.16-2.05 (m, 1H), 2.04-1.93 (m, 1H), 1.89-1.81 (ddd, J = 12.5, 8.0, 3.0 Hz, 1H), 1.67 (s, 3H), 1.33 (s, 3H), 1.09-1.02 (m, 15 H), 0.70-0.61 (m, 6H). ^{13}C-NMR (100 MHz, C_6D_6) δ 205.9, 150.1, 146.6, 125.2, 116.7, 86.5, 42.7, 40.8, 35.7, 30.00, 29.3, 28.1, 25.6, 22.4, 22.3, 7.5, 7.0. HRMS-ESI calcd for $C_{21}H_{38}O_2SiNa$ (M+Na)$^+$: 373.2533; found: 373.2491.

Oxatricyclic alcohol (4)

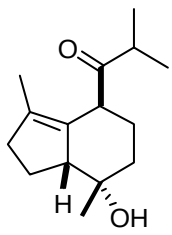


A TBAF solution (1.0 M in THF, 650 μL, 0.650 mmol) was added at 0 ºC to a cooled solution of protected oxatricyle **2** (190 mg, 0.542 mmol) in THF (5 mL). The mixture was stirred and warmed up to room temparature during 2 h. Then an aq. NH_4Cl solution (pH = 8) was added and the aqueous phase was extracted with Et_2O and EtOAc. The combined organic layers were dried over Na_2SO_4 and the solvents were removed under reduced pressure. Chromatographic purification (5:1 hexane/Et_2O) of the crude material yielded alcohol **4** as colorless oil (122 mg, 88%).

^{1}H NMR (800 MHz, C_6D_6) δ 5.64 (d, J = 2.7 Hz, 1H), 2.71-2.67 (m, 1H), 1.98 (sept, J = 6.9 Hz, 1H), 1.79 (dt, J = 12.7, 8.5 Hz, 1H), 1.67-1.60 (m, 3H), 1.47 (ddd, J = 13.0, 9.1, 7.4 Hz, 1H), 1.39 (m_c 1H), 1.33-1.26 (m, 1H), 1.31 (s, 3H), 1.28 (s, 3H), 1.22-1.15 (m, 1H), 1.12 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 7.0 Hz, 3H, overlapping with bs, 1H). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (d, J = 2.6 Hz, 1H), 2.77-2.69 (m, 1H), 1.95-1.85 (m, 2H), 1.81-1.60 (m, 5H), 1.49-1.33 (m, 2H), 1.36 (s, 3H), 1.34 (s, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H). ^{13}C PENDANT (100 MHz, C_6D_6) δ 150.7 (C), 119.4 (CH), 85.8 (C), 82.4 (C), 77.2 (C), 51.4 (CH), 41.7 (CH_2), 39.1 (CH_2), 34.6 (CH), 31.0 (CH_2), 28.2 (CH_3), 26.3 (CH_3), 23.9 (CH_2), 18.3 (CH_3), 18.2 (CH_3). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 150.1 (C), 119.1 (CH), 85.8 (C), 82.3 (C), 77.5 (C), 51.1 (CH), 41.3 (CH_2), 38.6 (CH_2), 34.00 (CH), 30.6 (CH_2), 28.0 (CH_3), 26.0 (CH_3), 23.8 (CH_2),

18.1 (CH_3), 17.8 (CH_3). The structure assignment of this compound was confirmed by 2D COSY, HSQC, HMBC and NOESY spectra. HRMS-ESI calcd for $C_{15}H_{24}O_2Na$ $(M+Na)^+$: 259.1669; found: 259.1676.

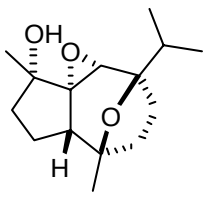
1-((4*R*,7*R*,7a*S*)-7-hydroxy-3,7-dimethyl-2,4,5,6,7,7a-hexahydro-1H-inden-4-yl)-2-methylpropan-1-one (15)



To a solution of the oxatricyclic alcohol **4** (10 mg, 0.042 mmol) in CH_2Cl_2 (1 mL) was added one drop of TFA at -20ºC. The solution turned orange after one minute and completion was observed by TLC after 2 min. Then an aq. $NaHCO_3$ solution (5%) was added and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated. Chromatographic purification (4:1 hexane/EtOAc) of the crude material yielded the product **15** as a yellow oil (8 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (d, J = 5.6 Hz, 1H), 2.76 (sept, J = 6.8 Hz, 1H), 2.55-2.48 (m, 1H), 2.41-2.22 (m, 2H), 2.14 (bd, J = 13.8 Hz, 1H), 1.89-1.82 (m, 2H), 1.82-1.72 (m, 1H) 1.75 (s, 3H), 1.60 (ddd, J = 12.8, 4.0, 3.0 Hz, 1H), 1.42-1.28 (m, 2H), 1.05 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H), 0.96 (s, 3H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 214.5 (C), 134.3 (C), 132.4 (C), 74.6 (C), 57.1 (CH), 45.5 (CH), 38.7 (CH_2), 37.7 (CH), 37.6 (CH_2), 24.2 (CH_2), 21.5 (CH_2), 19.6 (CH_3), 19.2 (CH_3), 18.5 (CH_3), 14.3 (CH_3). The structure assignment of this compound was confirmed by 2D COSY, HSQC, HMBC and NOESY spectra. HRMS-ESI calcd for $C_{15}H_{24}O_2Na$ $(M+Na)^+$: 259.1669; found: 259.1672.

***cis*-epoxyalcohol ((±)-17)[7]**

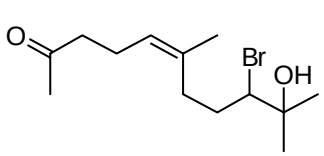


To a cooled solution of oxatricyclic alcohol **4** (16 mg, 0.069 mmol) in CH_2Cl_2 (1 mL) at 0 ºC were sequentially added molecular sieves (4 Å), $VO(acac)_2$ (2.8 mg, 0.011 mmol) and a *tert*-butylhydroperoxide solution (5 M in decane, 0.054 mL, 0.27 mmol). After the addition the mixture was warmed up to room temperature during 30 min. and stirred at room temparature for 2.5 h. When no remaning starting material was observed by TLC two drops of a sat. aq. Na_2SO_3 solution were added to the mixture and stirring was continued

for 10 min. Then Na_2SO_4 was added and the mixture was filtered through a short pad of SiO_2 (eluting with CH_2Cl_2 and EtOAc). After evaporation of the solvents epoxyalcohol **(±)-17** was obtained as colorless oil (18 mg, 100 % yield). After storing the compounds several days in the fridge colorless crystals were formed.

m.p.: 44-46 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 3.41 (s, 1H), 2.68 (bs, 1H), 2.16-2.03 (m, 3H), 1.99-1.82 (m, 2H), 1.78 (dt, J = 13.9, 8.6 Hz, 1H), 1.50-1.18 (m, 4H), 1.37 (s, 3H), 1.16 (s, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 86.2, 80.9, 73.9, 72.7, 61.4, 48.5, 41.2, 34.4, 34.3 , 32.1, 26.9, 26.4, 21.8, 17.6, 17.3. HRMS-ESI calcd for $C_{15}H_{24}O_3Na$ (M+Na)$^+$: 275.1618; found: 275.1630. Structure confirmed by X-ray diffraction.

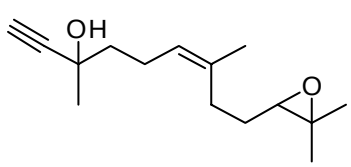
(*Z*)-9-bromo-10-hydroxy-6,10-dimethylundec-5-en-2-one (35)



Same procedure as for geranylacetone and as described by *Watanabe et al.*[8] using nerylacetone as substrate. Chromatographic purification (5:1 hexane/EtOAc) yielded compound **35** as colorless oil (33%) as well as 21% of recovered nerylacetone.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, J = 7.1 Hz, 1H), 3.96 (dd, J = 11.3, 1.3 Hz, 1H), 2.47 (t, J = 7.2 Hz, 2H), 2.36-2.25 (m, 4H), 2.14 (s, 3H), 2.05-1.95 (m, 1H), 1.84-1.72 (m, 1H), 1.66 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 208.6 (C), 134.6 (C), 125.2 (CH), 72.5 (C), 70.7 (CH), 43.9 (CH_2), 32.1 (CH_2), 30.5 (CH_2), 30.00 (CH_3), 26.5 (CH_3), 25.9 (CH_3), 23.1 (CH_3), 22.3 (CH_2). HRMS-ESI calcd for $C_{13}H_{23}BrO_2Na$ (M+Na)$^+$: 313.0774; found: 313.0784.

(*Z*)-9-(3,3-dimethyloxiran-2-yl)-3,7-dimethylnon-6-en-1-yn-3-ol (36)

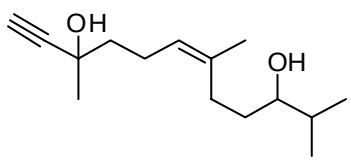


An ethynylmagnesium bromide solution (0.5 M in THF, 12.7 mL, 6.37 mmol) was added to a cooled solution of the bromohydrine **35** (843 mg, 2.89 mmol) in THF (20 mL) at 0 ºC. After the addition the cooling bath was removed and the mixture was heated to 50ºC for 5 h. Then it was cooled to room temperature and stirred overnight. After 20 h the reaction was quenched by the addition of a sat. aq. NH_4Cl solution followed by extraction with EtOAc. The combined organic layers were

dried over Na_2SO_4 and solvents were evaporated. Chromatographic purification (5:1 hexane/EtOAc) of the crude material yielded epoxid **36** as pale yellow oil (463 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (t, J = 7.2 Hz, 1H), 2.76-2.69 (m, 1H), 2.44 (s, 1H), 2.37-2.13 (m, 5H), 1.77-1.55 (m, 4H), 1.70 (s, 3H), 1.49 (s, 3H), 1.31 (s, 3H), 1.27 (s, 3H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 135.03 (C, one isomer), 134.95 (C, other isomer), 125.2 (CH, one isomer), 125.1 (CH, other isomer), 87.7 (C, one isomer), 87.5 (C, other isomer), 71.41 (CH, one isomer), 71.36 (CH, other isomer), 68.0 (C, one isomer), 67.9 (C, other isomer), 64.02 (CH, one isomer), 64.00 (CH, other isomer), 58.62 (C, one isomer), 58.60 (C, other isomer), 43.39 (CH_2, one isomer), 43.35 (CH_2, other isomer), 30.0 (CH_3, one isomer), 29.7 (CH_3, other isomer), 28.5 (CH_2), 27.2 (CH_2, one isomer), 27.1 (CH_2, other isomer), 24.9 (CH_3), 23.30 (CH_3, one isomer), 23.27 (CH_3, other isomer), 23.25 (CH_2, one isomer), 23.18 (CH_2, other isomer), 18.72 (CH_3). HRMS-ESI calcd for $C_{15}H_{24}O_2Na$ $(M+Na)^+$: 259.1669; found: 259.1669.

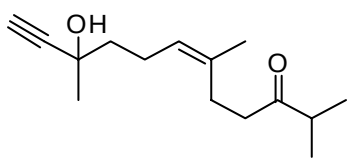
(*Z*)-3,7,11-trimethyldodec-6-en-1-yne-3,10-diol (37)



Same procedure as for compound **33** using epoxyalcohol **36** as substrate.[6] Chromatographic purification (2:1 hexane/EtOAc) yielded diol **37** as colorless oil (75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (t, J = 7.2 Hz, 1H), 3.38-3.29 (m, 1H), 2.50-2.11 (m, 4H), 2.45 (s, 1H), 1.77-1.52 (m, 6H), 1.69 (s, 3H), 1.51-1.39 (m, 1H), 1.49 (s, 3H), 0.94-0.88 (m, 6H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 136.12 (C, one isomer), 136.06 (C, other isomer), 124.82 (CH, one isomer), 124.76 (CH, other isomer), 87.7 (C, one isomer), 87.6 (C, other isomer), 76.4 (CH, one isomer), 76.3 (CH, other isomer), 71.42 (CH, one isomer), 71.35 (CH, other isomer), 68.1 (C, one isomer), 68.0 (C, other isomer), 43.5 (CH_2, one isomer), 43.4 (CH_2, other isomer), 33.6 (CH), 32.1 (CH_2, one isomer), 32.0 (CH_2, other isomer), 30.0 (CH_3, one isomer), 29.8 (CH_3, other isomer), 28.21 (CH_2, one isomer), 28.16 (CH_2, other isomer), 23.3 (CH_3), 23.2 (CH_2, one isomer), 23.1 (CH_2, other isomer), 18.83 (CH_3, one isomer), 18.82 (CH_3, other isomer), 17.3 (CH_3, one isomer), 17.2 (CH_3, other isomer). HRMS-ESI calcd for $C_{15}H_{26}O_2Na$ $(M+Na)^+$: 261.1825; found: 261.1814.

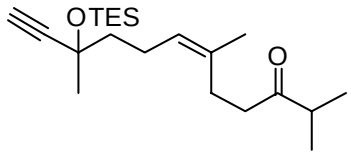
(*Z*)-10-hydroxy-2,6,10-trimethyldodec-6-en-11-yn-3-one (38)



Same procedure as for compound **34** using diol **37** as substrate. Chromatographic purification (6:1 hexane/EtOAc) yielded ketone **38** as colorless oil (73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (t, J = 7.2 Hz, 1H), 2.60 (sept, J = 6.9 Hz, 1H), 2.55-2.48 (m, 2H), 2.44 (s, 1H), 2.35-2.13 (m, 5H), 1.72-1.64 (m, 2H), 1.69 (s, 3H), 1.49 (s, 3H), 1.09 (d, J = 6.9 Hz, 6H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 214.4 (C), 134.9 (C), 125.3 (CH), 87.5 (C), 71.5 (CH), 68.1 (C), 43.3 (CH_2), 40.9 (CH), 38.6 (CH_2), 29.8 (CH_3), 26.0 (CH_2), 23.3 (CH_2), 23.2 (CH_3), 18.2 (2xCH_3). HRMS-ESI calcd for $C_{15}H_{24}O_2Na$ (M+Na)$^+$: 259.1669; found: 259.1662.

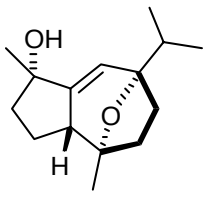
(*Z*)-2,6,10-trimethyl-10-(triethylsilyloxy)dodec-6-en-11-yn-3-one ((±)-18)



Same procedure as for compound **1** using ketone **38** as substrate. Chromatographic purification (40:1 hexane/ Et_2O) yielded silyl ether **(±)-18** as colorless oil (94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, J = 7.2 Hz, 1H), 2.61 (sept, J = 6.9 Hz, 1H), 2.53-2.47 (m, 2H), 2.40 (s, 1H), 2.32-2.25 (m, 2H), 2.25-2.07 (m, 2H), 1.70-1.57 (m, 2H), 1.67 (d, J = 1.2 Hz, 3H), 1.45 (s, 3H), 1.10 (d, J = 6.9 Hz, 6H), 0.95 (t, J = 7.8 Hz, 9H), 0.71-0.63 (m, 6H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 214.4 (C), 134.2 (C), 125.6 (CH), 88.1 (C), 71.8 (CH), 68.8 (C), 45.4 (CH_2), 40.8 (CH), 38.9 (CH_2), 30.9 (CH_3), 26.0 (CH_2), 23.3 (CH_3), 23.2 (CH_2), 18.3 (2xCH_3), 7.0 (CH_3), 6.1 (CH_2). HRMS-ESI calcd for $C_{21}H_{38}OSiNa$ (M+Na)$^+$: 373.2533; found: 373.2524.

Pubinernoid B ((±)-19)



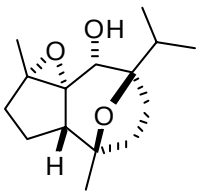
Gold catalyst **12** (3.3 mg, 0.0043 mmol) was added at room temperature to a solution of enyne **(±)-18** (30 mg, 0.086 mmol) in CH_2Cl_2 (1 mL) containing activated molecular sieves (4 Å). The mixture was stirred for 1 h and was then quenched by addition of one drop of Et_3N. After filtration through SiO_2 the solvent was removed under reduced pressure. Chromatographic purification (40:1 hexane/Et_2O) of the crude material

yielded a mixture of isomers as colorless oil (9.6 mg, 32%). This mixture was used in the following deprotection without further purification.

A TBAF solution (1.0 M in THF, 86 μL, 0.086 mmol) was added slowly to a cooled solution of the previous mixture in THF (1 mL) at 0 ºC. After 10 min the cooling bath was removed and the solution was let to warm to room temperature. After 3 h the reaction was stopped by addition of a sat. aq. NH_4Cl solution. The mixture was extracted with Et_2O, the combined organic layers were dried over Na_2SO_4 and the solvents were removed under reduced pressure. Chromatographic purification (8:1 hexane/EtOAc) of the crude material yielded Pubinernoid B (**(±)-19**) as pale yellow oil (3.2 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (d, J = 2.04 Hz, 1H), 2.02 (ddd, J = 12.3, 6.6, 2.4 Hz, 1H), 1.92 (sept, J =6.9 Hz, 1H), 1.87-1.69 (m, 6H), 1.63 (dtd, J = 11.6, 7.0, 1.9 Hz, 1H), 1.50-1.36 (m, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 0.98 (d, J = 7.0 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (C), 122.5 (CH), 84.4 (C), 78.9 (C), 76.4 (C), 51.6 (CH), 40.0 (CH_2), 40.0 (CH_2), 36.8 (CH_2), 34.6 (CH), 29.1 (CH_3), 24.8 (CH_2), 23.4 (CH_3), 17.9 (CH_3), 17.1 (CH_3). HRMS-ESI calcd for $C_{15}H_{24}O_2Na$ (M+Na)$^+$: 259.1669; found: 259.1680.

Epoxyalcohol (24)

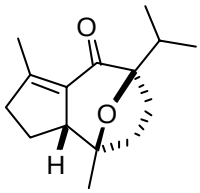


CrO_3 (76 mg, 0.76 mmol) was added at 0 ºC to a solution of pyridine (123 μL, 1.52 mmol) in CH_2Cl_2 (2 mL). The mixture was warmed to room temperature during 15 min until most of the CrO_3 was dissolved. Then alcohol **4** (30 mg, 0.13 mmol) was added at once and the suspension was stirred for another 30 min. The reaction mixture was then directly transfered to a chromatographic column (15:1 hexane/Et_2O) yielding epoxyalcohol **24** as colorless oil (25 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (dd, J = 10.3, 1.2 Hz, 1H), 2.25 (d, J = 10.3 Hz, 1H), 2.16-2.07 (m, 1H), 2.06-1.85 (m, 4H), 1.69 (tdd, J = 12.8, 3.9, 1.2 Hz, 1H), 1.55-1.47 (m, 1H), 1.52 (s, 3H), 1.44-1.32 (m, 2H), 1.23 (s, 3H), 1.09-0.97 (m, 1H) 1.06 (d, J = 6.9 Hz, 3H), 1.05 (d, J = 6.9 Hz, 3H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 87.6 (C), 82.9 (C), 71.3 (C), 67.2 (CH), 65.0 (C), 50.3 (CH), 33.3 (CH), 32.9 (CH_2), 31.4 (CH_2), 28.2 (CH_2), 24.3 (CH_3), 20.1 (CH_2), 18.2 (CH_3), 17.3 (CH_3), 15.2 (CH_3). The structure

assignment of this compound was confirmed by 2D COSY, HSQC, HMBC and NOESY spectra. HRMS-ESI calcd for $C_{15}H_{24}O_3Na$ $(M+Na)^+$: 275.1618; found: 275.1622.

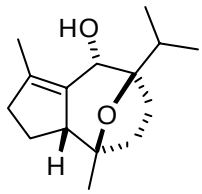
Enone (25)



PDC (53 mg, 0.14 mmol) was added to a solution of alcohol **4** (8.3 mg, 0.035 mmol) in CH_2Cl_2 (0.5 mL). The mixture was stirred at 40 ºC for 24 h. Then Et_2O (0.5 mL) was added, the mixture was filtered through a short pad of SiO_2 (eluting with Et_2O and EtOAc) and solvents were evaporated. Chromatographic purification (10:1 pentane/Et_2O) of the crude material yielded enone **25** as colorless oil (12 mg, 37%) together with epoxyalcohol **24** (13 mg, 37%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26-3.16 (bs, 1H), 2.57-2.43 (m, 1H), 2.35-2.25 (m 1H), 2.19 (sept, J = 6.9 Hz, 1H), 2.10-1.95 (m, 5H), 1.94-1.86 (m, 1H), 1.67-1.58 (m, 1H), 1.53-1.35 (m, 2H), 1.33 (s, 3H), 1.04 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9 (C), 154.4 (C), 131.9 (C), 91.1 (C), 84.4 (C), 57.9 (CH), 38.8 (CH_2), 33.3 (CH_2), 30.6 (CH), 30.0 (CH_2), 26.0 (CH_2), 24.6 (CH_3), 18.4 (CH_3), 17.3 (CH_3), 15.9 (CH_3). The structure assignment of this compound was confirmed by 2D COSY, HSQC, HMBC and NOESY spectra. HRMS-ESI calcd for $C_{15}H_{22}O_2Na$ $(M+Na)^+$: 257.1512; found: 257.1514.

Orientalol F ((+)-3)



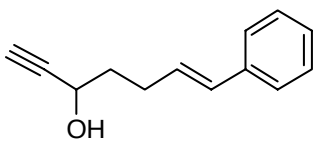
Method A[9] (from Epoxyalcohol **24**): A schlenck flask was charged with WCl_6 (69 mg, 0.17 mmol) in the glovebox. THF (1.7 mL) was added, the suspension was cooled to -78 ºC and *n*-BuLi (2.2 M in hexanes, 158 μL, 0.349 mmol) was added. After the addition the cooling bath was replaced by an ice bath. In a different flask a solution of the epoxyalcohol **24** (11 mg, 0.044 mmol) in THF (0.5 mL) was cooled to 0 ºC and 0.6 mL of the preformed [W^{4+}] solution was added. The reaction mixture was warmed up to room temperature during 30 min followed by stirring at 45ºC for another 30 min. The initial brown solution turned to green. As TLC showed completion the reaction was quenched by addition of an aq. solution of sodium/potassium tartrate (1.5 M) and NaOH

(2M). The mixture was extracted with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4 and solvents were evaporated. Chromatographic purification (14:1 hexane/EtOAc) of the crude material yielded Orientalol F (**(+)-3**) as a colorless oil (7.5 mg, 73%, 94:6 *er*). **(±)-3** was obtained as pale yellow solid in an analog fashion.

Method B (from Enone **25**): $NaBH_4$ (4 mg, 0.1 mmol) was added at room temperature to a solution of Enone **25** (26 mg, 0.11 mmol) and $CeCl_3{\cdot}(H_2O)_7$ (41 mg, 0.11 mmol) in MeOH (3 mL). After stirring the mixture for 36 h the reaction was quenched by the addition of brine. The mixture was extracted with EtOAc, the combined organic phases were dried over Na_2SO_4 and solvents were evaporated. Chromatographic purification (10:1 hexane/Et_2O) of the crude material yielded Orientalol F (**(+)-3**) as a colorless oil (26 mg, 100%, 94:6 *er*).

$[\alpha]_D^{25}$ = +12.2 (CH_2Cl_2, *c* 0.5); $[\alpha]_D^{25}$ = +11.0 (1:1 MeOH/CH_2Cl_2, *c* 0.5).[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48-4.40 (m, 1H), 2.74-2.64 (m, 1H), 2.40-2.27 (m 1H), 2.27-2.14 (m, 1H), 1.95 (sept, *J* = 6.9 Hz, 1H), 1.89 (s, 3H), 1.86-1.75 (m, 2H), 1.75-1.58 (m, 2H), 1.43 (d, *J* = 7.3 Hz, 1H), 1.36-1.16 (m, 2H), 1.19 (s, 3H), 1.05 (d, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5 (C), 133.0 (C), 86.6 (C), 84.4 (C), 73.9 (CH), 57.6 (CH), 39.0 (CH_2), 31.5 (CH), 31.6 (CH_2), 28.6 (CH_2), 24.0 (CH_2), 23.9 (CH_3), 18.1 (CH_3), 17.2 (CH_3), 14.6 (CH_3). HRMS-ESI calcd for $C_{15}H_{25}O_2$ $(M+H)^+$: 237.1849; found: 237.1851.

(*E*)-7-phenylhept-6-en-1-yn-3-ol (39)

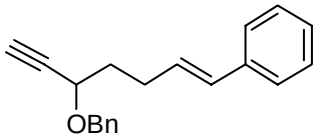


Ethynylmagnesium bromide (0.5 M in THF, 34 mL) was added over 30 min to a solution of (*E*)-5-phenylpent-4-enal (2.15 g, 13.4 mmol) in THF (20 mL) at 0 ºC. The mixture was stirred at room temperature for 3 h before the reaction was quenched by addition of sat. aq. NH_4Cl solution. The aqueous phase was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and solvents were evaporated. Chromatographic purification (5:1 pentane/Et_2O) of the crude material yielded alcohol **39** as a yellow oil (1.35 g, 54%).

IR (neat): 3288*s*, 3024*w*, 2924*m*, 2114*w*, 1650*w*, 1597*w*, 1494*m*, 1446*m*, 1284*m*, 1157*w*, 1095*w*, 1067*s*, 1014*s*, 963*s*, 910*w*, 740*s*, 691*s* cm^{-1}. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.36-7.28 (m, 4H), 7.21 (t, J = 7.1 Hz, 1H), 6.45 (d, J = 15.8 Hz, 1H), 6.23 (dt, J = 15.8, 6.9 Hz, 1H), 4.45 (dq, J = 6.5, 1.9 Hz, 1H), 2.51 (d, J = 2.1 Hz, 1H), 2.42 (dt, J = 7.9, 7.0 Hz, 2H), 1.94-1.81 (m, 2H), 1.85 (d, J = 5.6 Hz, 1H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 137.5 (C), 130.8 (CH), 129.2 (CH), 128.5 (CH), 127.0 (CH), 126.0 (CH), 84.6 (C), 73.3 (CH), 61.7 (CH), 37.0 (CH_2), 28.5 (CH_2). HRMS-ESI calcd for $C_{13}H_{15}O$ (M+H)$^+$: 187.1117; found: 187.1110.

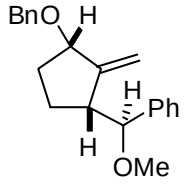
(*E*)-(5-(benzyloxy)hept-1-en-6-ynyl)benzene (26)



NaH (60% in mineral oil, 129 mg, 3.22 mmol) was added to a solution of (*E*)-7-phenylhept-6-en-1-yn-3-ol (**39**, 400 mg, 2.15 mmol) in THF (7 mL) at 0 ºC. After 45 min NBu_4I (40 mg, 0.11 mmol) and benzyl bromide (551 mg, 3.22 mmol) were added and the reaction mixture was stirred for 4 h at room temperature. After quenching the reaction by addition of water the aqueous phase was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and solvents were evaporated. Chromatographic purification (100:1 pentane/Et_2O) of the crude material yielded benzyl ether **26** as a yellow oil (560 mg, 94%).

IR (neat): 3287*m*, 3026*w*, 2924*m*, 2858*m*, 2110*w*, 1650*w*, 1597*w*, 1495*m*, 1453*m*, 1390*w*, 1332*m*, 1206*w*, 1178*w*, 1089*m*, 1070*s*, 1027*m*, 963*s*, 911*w*, 735*s*, 692*s* cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (m, 9H), 7.18-7.13 (m, 1H), 6.35 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.8, 6.9 Hz, 1H), 4.80 (d, J = 11.7 Hz, 1H), 4.48 (d, J = 11.7 Hz, 1H), 4.12 (dt, J = 6.5, 2.0 Hz, 1H), 2.46 (d, J = 2.0 Hz, 1H), 2.38 (q, J = 7.5 Hz, 2H), 1.95 (dq, J = 13.9, 7.2 Hz, 1H), 1.90 (dq, J = 13.7, 7.0 Hz, 1H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 137.7 (C), 137.5 (C), 130.6 (CH), 129.4 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 126.9 (CH), 125.9 (CH), 82.6 (C), 74.1 (CH), 70.5 (CH_2), 67.6 (CH), 35.2 (CH_2), 28.6 (CH_2). HRMS-ESI calcd for $C_{20}H_{20}ONa$ (M+Na)$^+$: 299.1406; found: 299.1410.

((*R)-((1*S**,3*R**)-3-(benzyloxy)-2-methylenecyclopentyl)(methoxy)methyl)benzene (27)**



A solution of (*E*)-(5-(benzyloxy)hept-1-en-6-ynyl)benzene (**26**, 50 mg, 0.18 mmol) and gold catalyst **12** (2.8 mg, 0.0036 mmol) in a mixture of CH_2Cl_2 (0.9 mL) and methanol (0.9 mL) was heated in a microwave to 100 °C for 20 min. The reaction mixture was then filtered through SiO_2 and the solvents were evaporated. Chromatographic purification (30:1 pentane/Et_2O) of the crude material yielded the product **27** as colorless oil (53 mg, 95%).

IR (neat): 3063*w*, 3028*w*, 2924*m*, 2819*w*, 1494*m*, 1453*s*, 1329*w*, 1306*w*, 1236*w*, 1201*w*, 1155*w*, 1105*m*, 1087*s*, 1066*s*, 1027*m*, 967*w*, 942*w*, 911*s*, 761*w*, 733*s*, 698*s* cm^{-1}. ^1H NMR (500 MHz, C_6D_6) δ 7.39 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 7.1 Hz, 2H), 7.23-7.09 (m, 6H), 4.94 (s, 1H), 4.53 (d, J = 12.2 Hz, 1H), 4.38 (s, 1H), 4.28 (d, J = 12.1 Hz, 1H), 4.11 (d, J = 8.7 Hz, 1H), 3.91 (dd, J = 5.2, 2.1 Hz, 1H), 3.04 (s, 3H), 2.85 (ddd, J = 12.4, 9.6, 5.0 Hz, 1H), 2.40-2.33 (m, 1H), 2.01-1.94 (m, 2H), 1.58 (dddd, J = 20.0, 9.7, 5.4, 0.6 Hz, 1H). ^{13}C PENDANT (100 MHz, $CDCl_3$) δ 149.9 (C), 141.1 (C), 139.0 (C), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 127.5 (CH), 127.3 (CH), 113.7 (CH_2), 87.7 (CH), 82.6 (CH), 69.3 (CH_2), 56.8 (CH_3), 49.2 (CH), 31.7 (CH_2), 27.2 (CH_2). HRMS-ESI calcd for $C_{21}H_{24}O_2Na$ (M+Na)$^+$: 331.1669; found: 331.1682.

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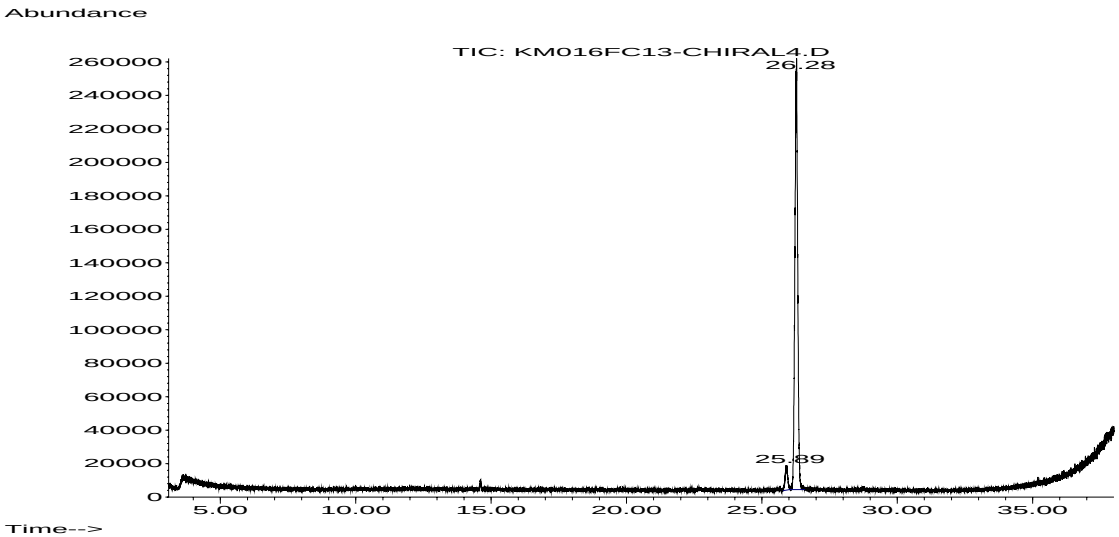
GC / MS

Sample	**(*S*,*E*)-10-hydroxy-2,6,10-trimethyldodec-6-en-11-yn-3-one (34)**
Method	**Column**: HP-CHIRAL-20B 30 m x 0.25 mm, 0.25µm **Inj vol**: 1 µL **split** 1:100 **Tinj/aux**: 220/250 ºC **He flow**: 1.5 mL/min **oven**: 50 ºC up to 170ºC at 10ºC/min, 20 min at 170ºC and 170-230ºC at 10ºC/min

Chromatogram



Signal : TIC

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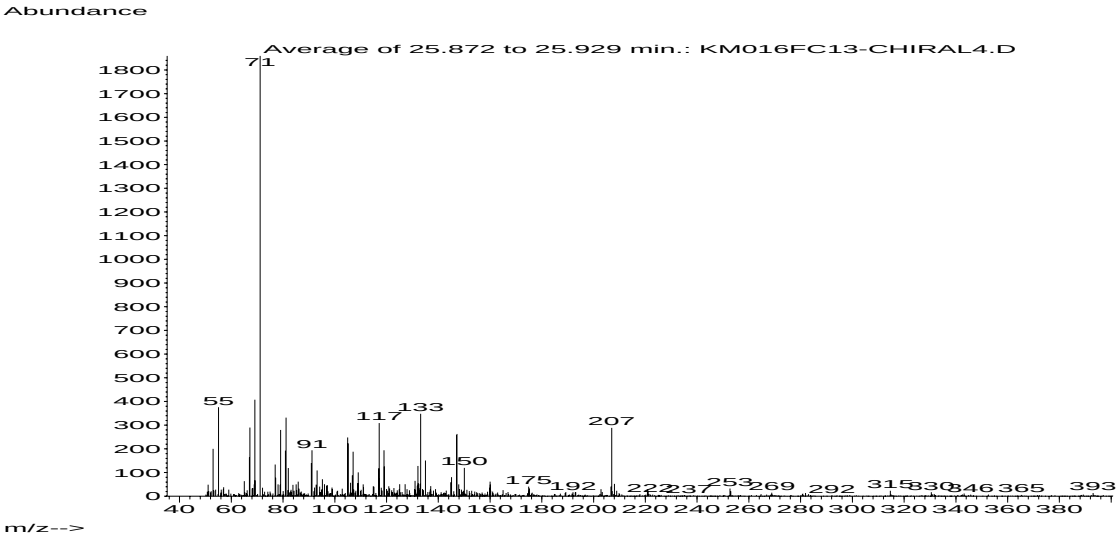
2	26.280	14862	14987	15184	BB	248317	18345162	100.00%	95.063%	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365
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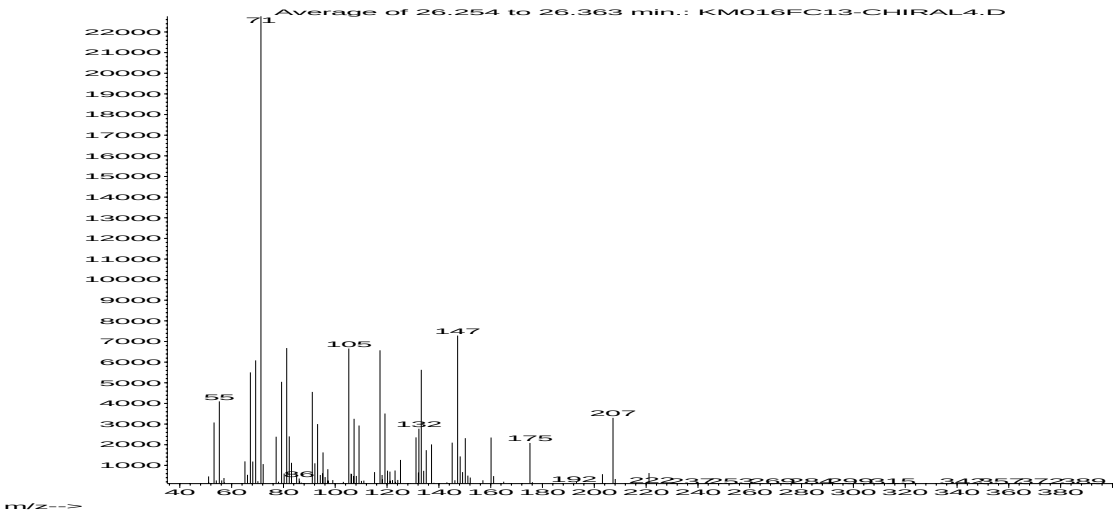
m/z-->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105
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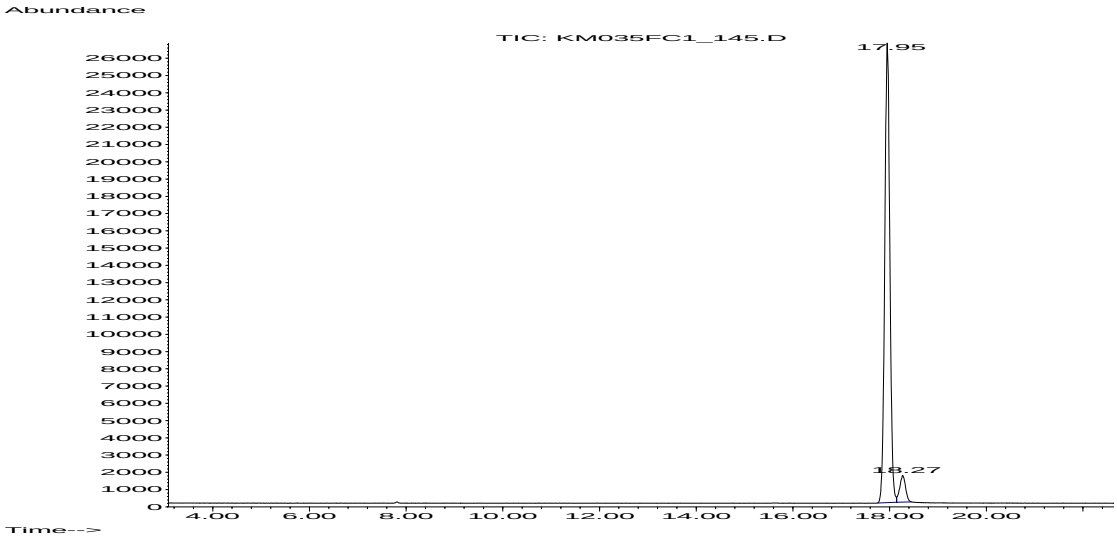
132
207
175
192
m/z-->

GC / MS

Sample	**Orientalol F ((+)-3)**
Method	**Column**: GTA 30mx0.25mm, 0.12µm **Inj vol**: 1 µL **split** 1:100 **Tinj/aux**: 170/170 ºC **He flow**: 1.5 mL/min **split** 100:1 (1µL**)** **145ºC**
Chromatogram	



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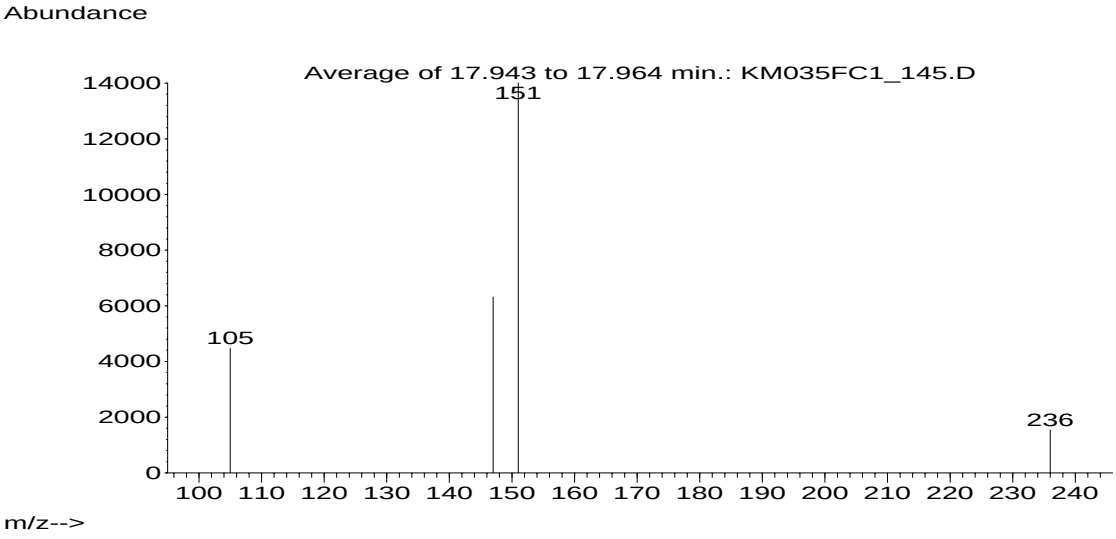
2	18.268	2134	2151	2176	M2	1563	129791	6.60%	6.195%

Sum of corrected areas: 2095007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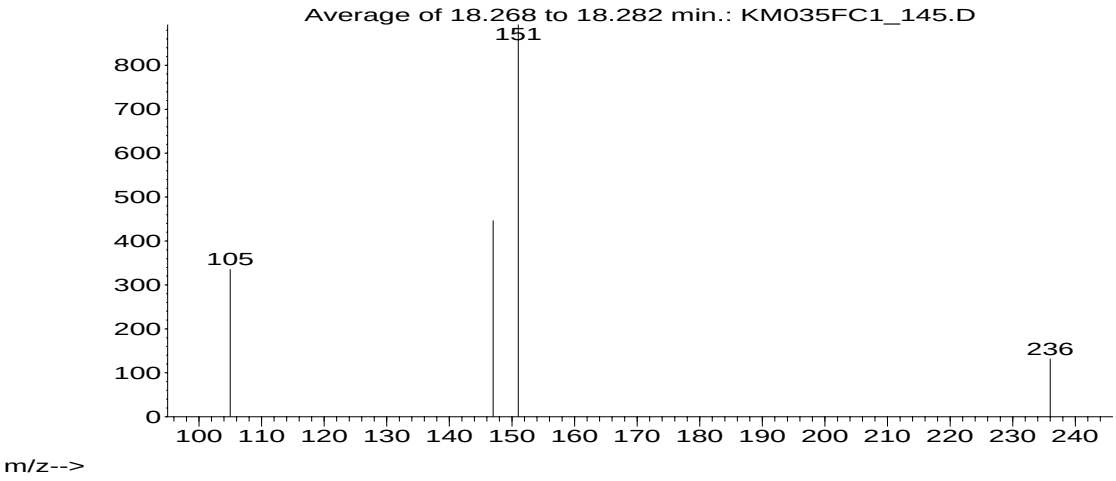
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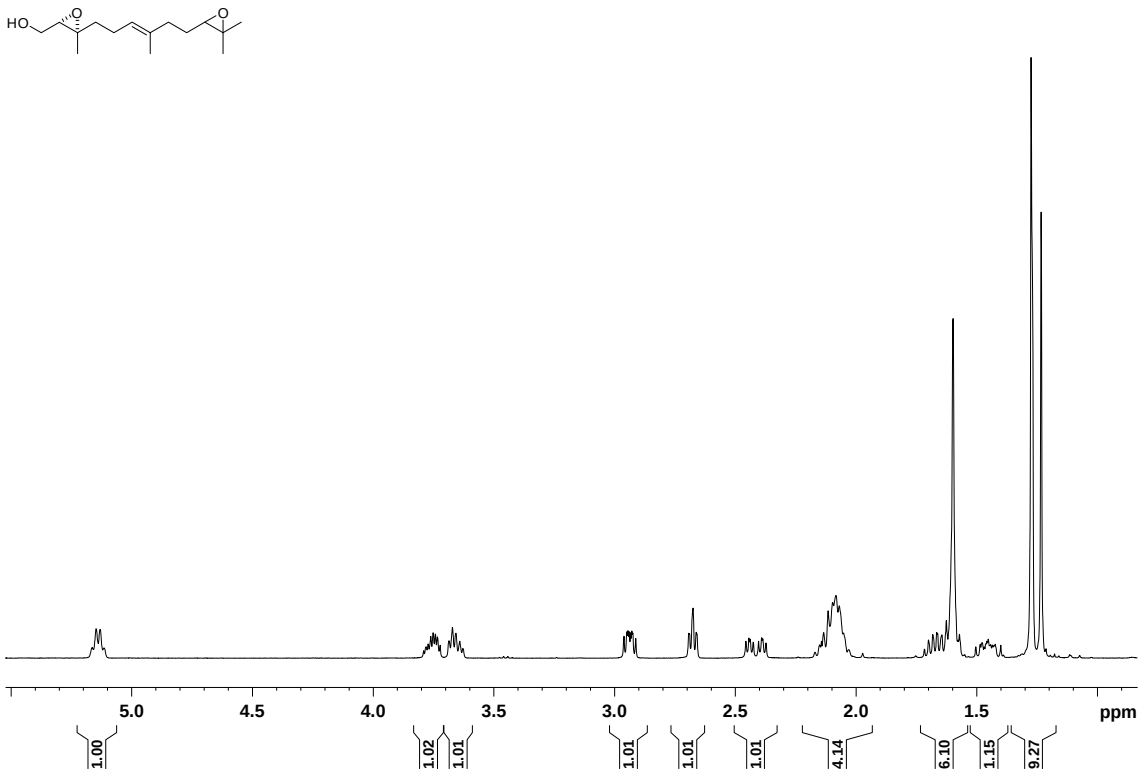
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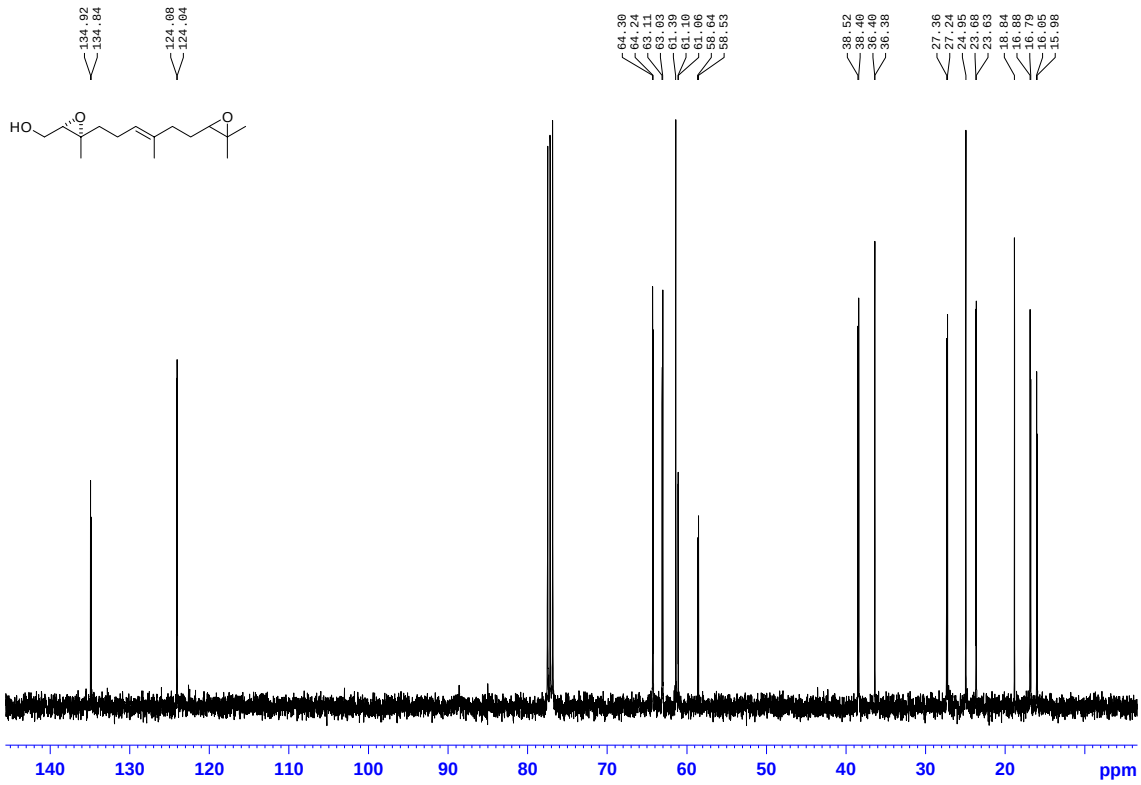
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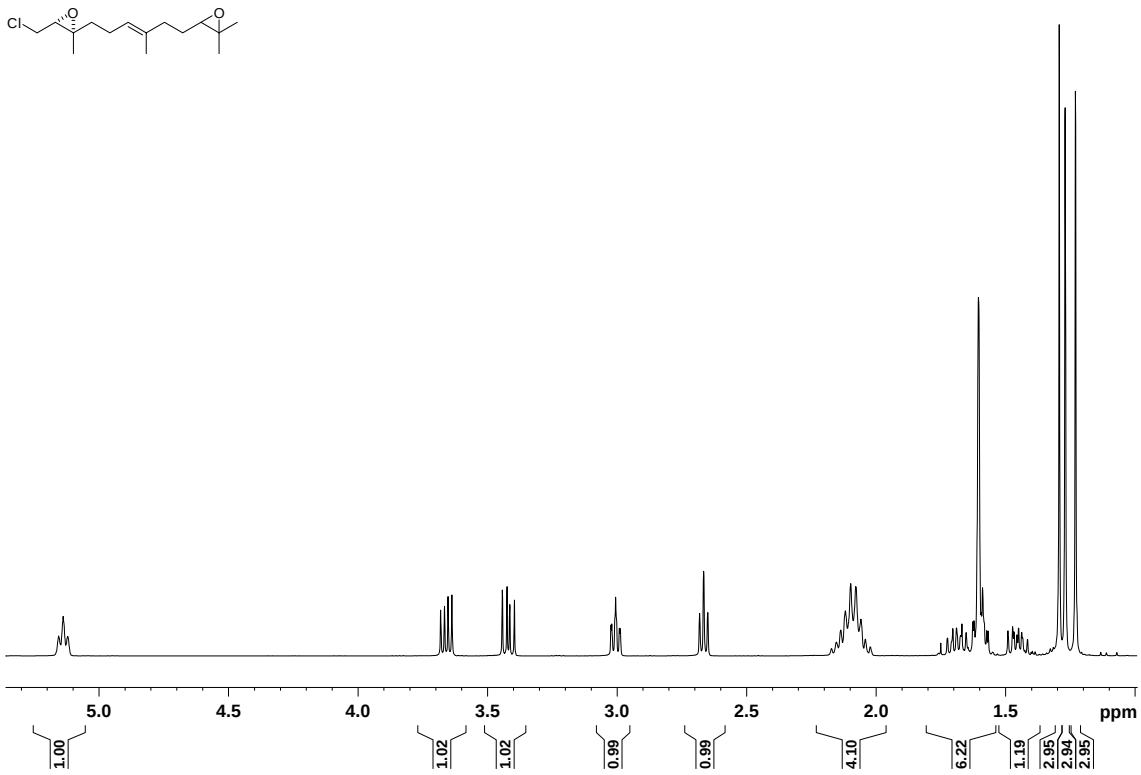
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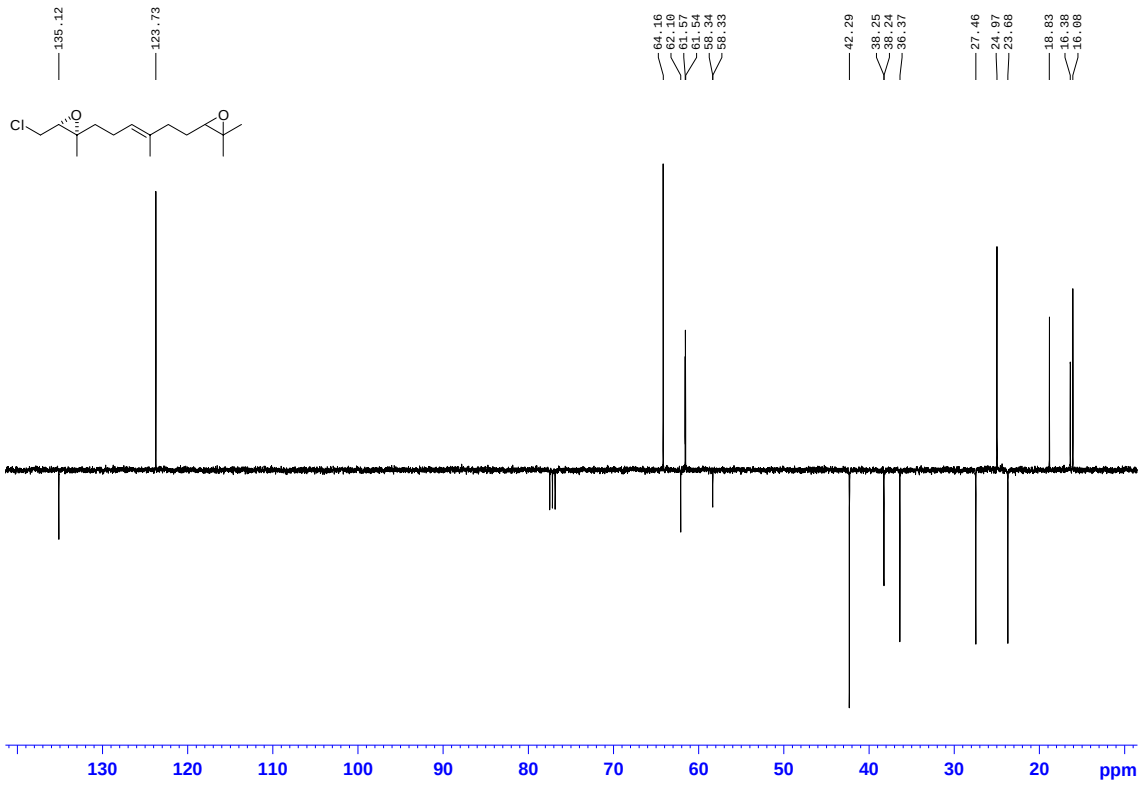
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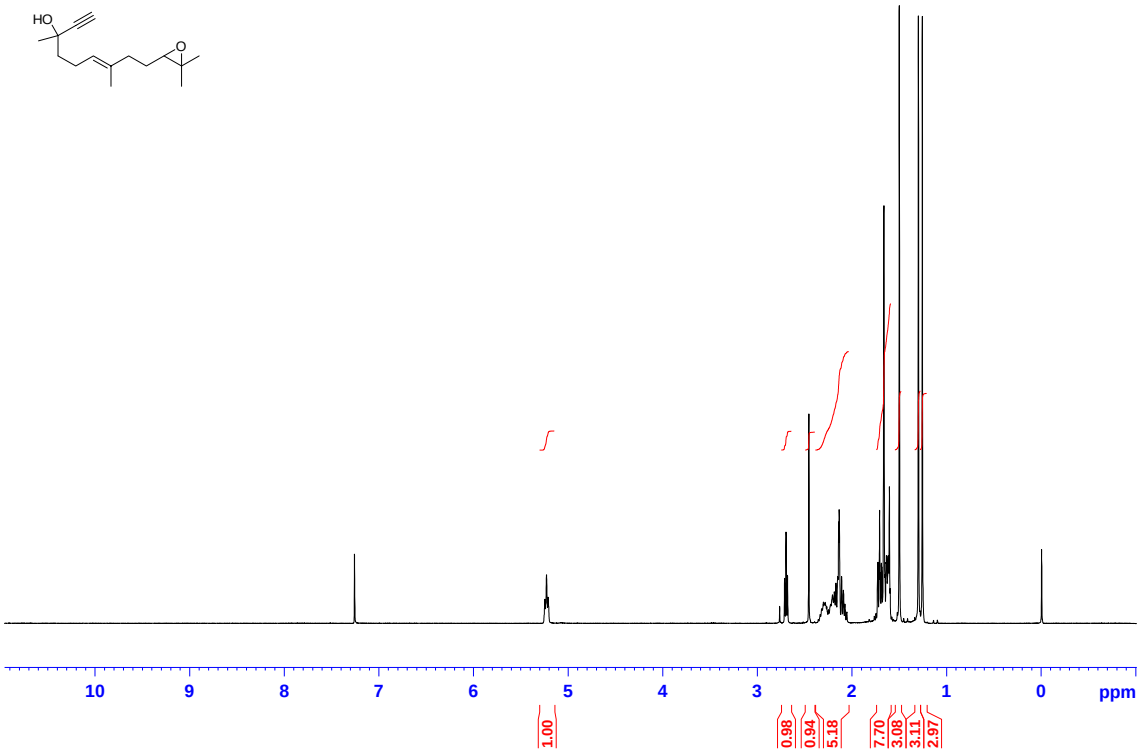
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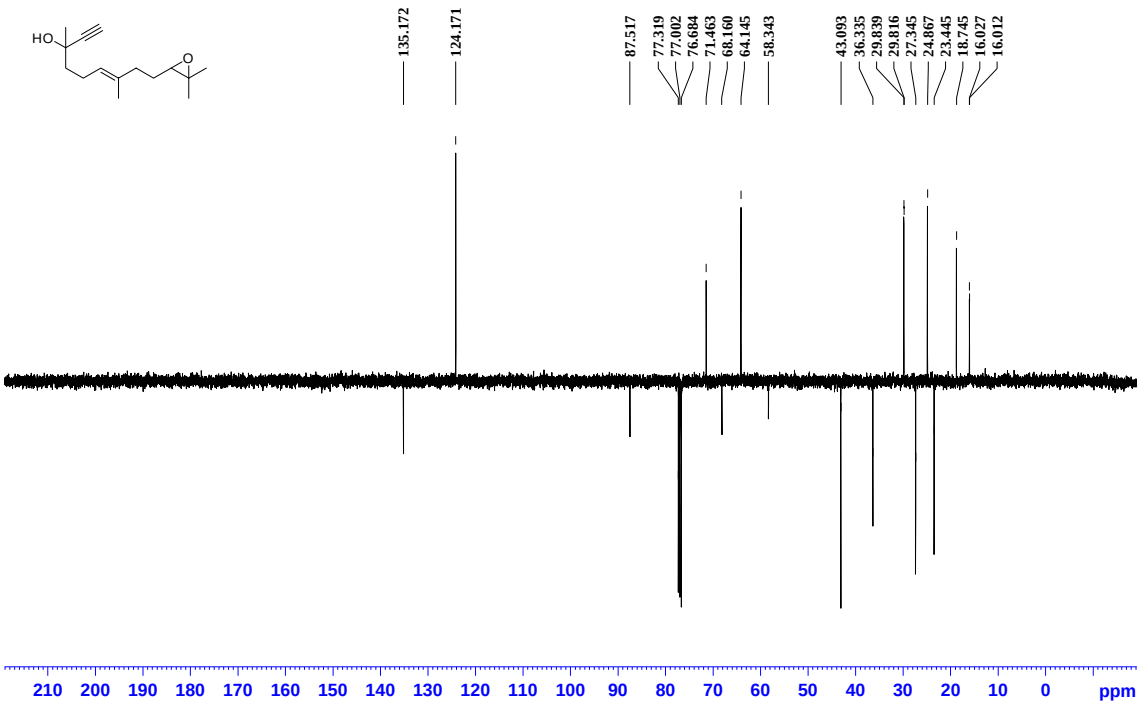
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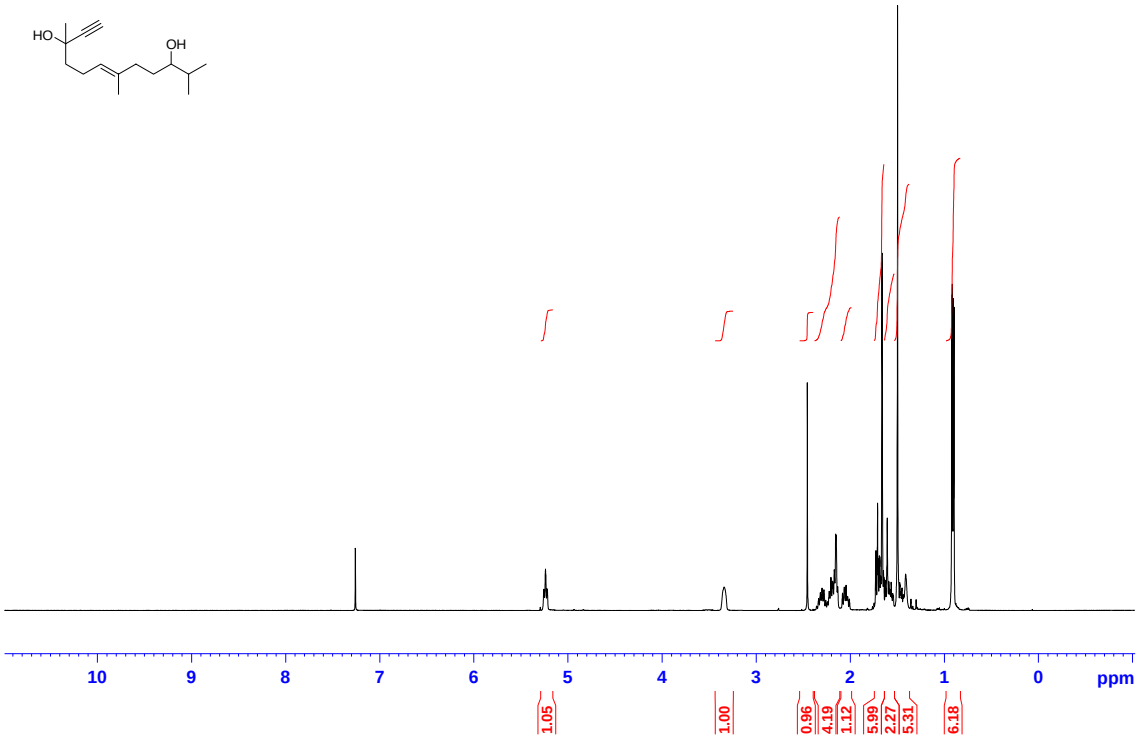
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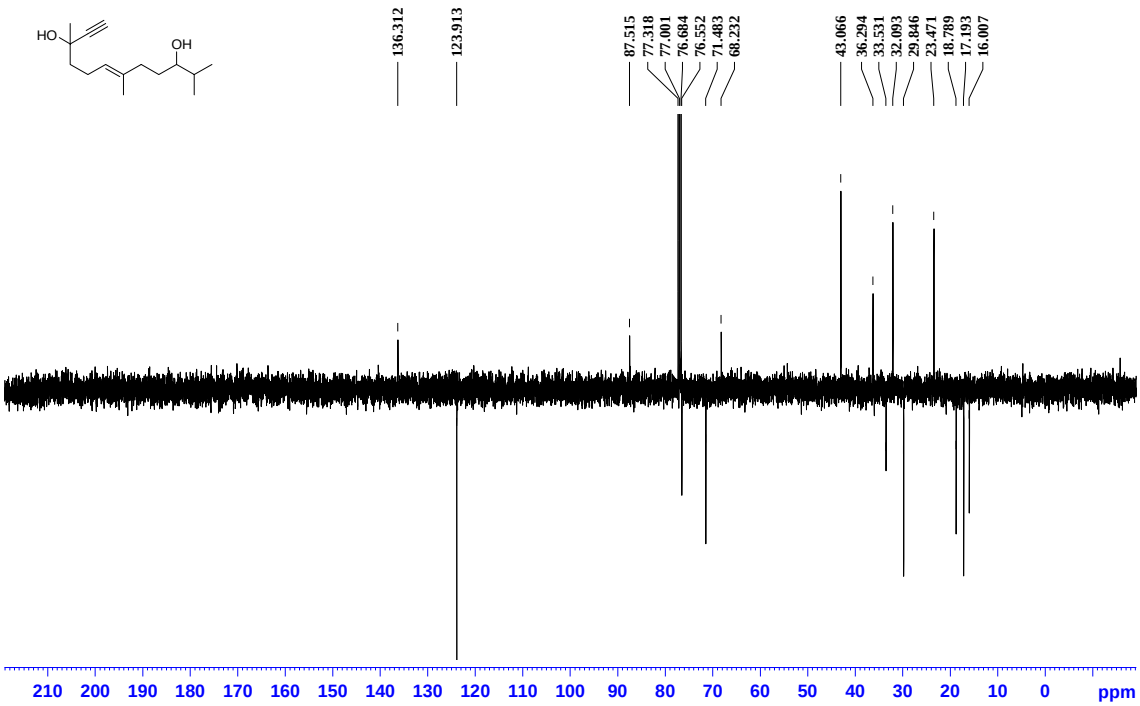
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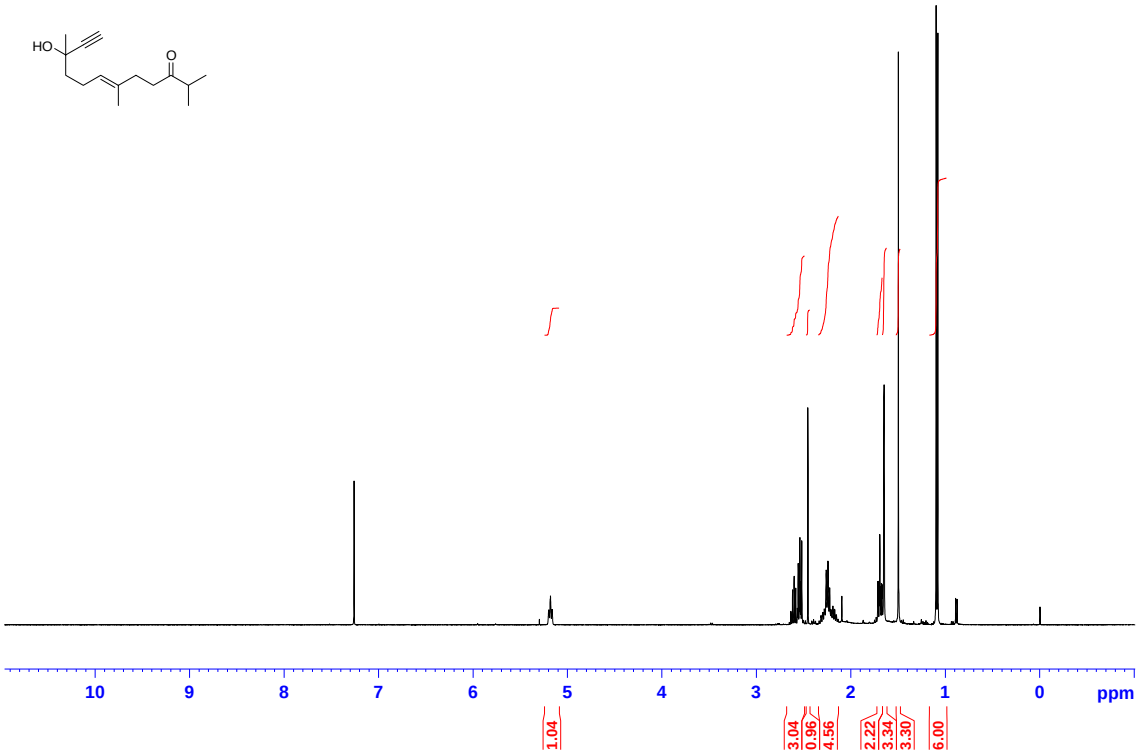
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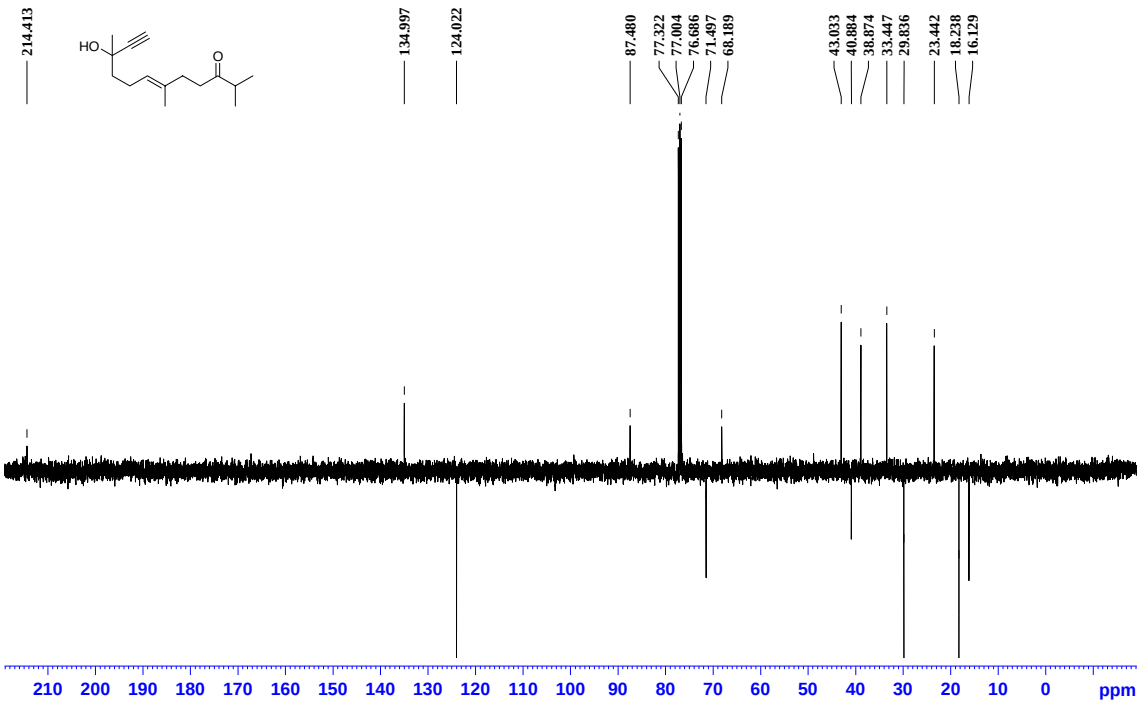
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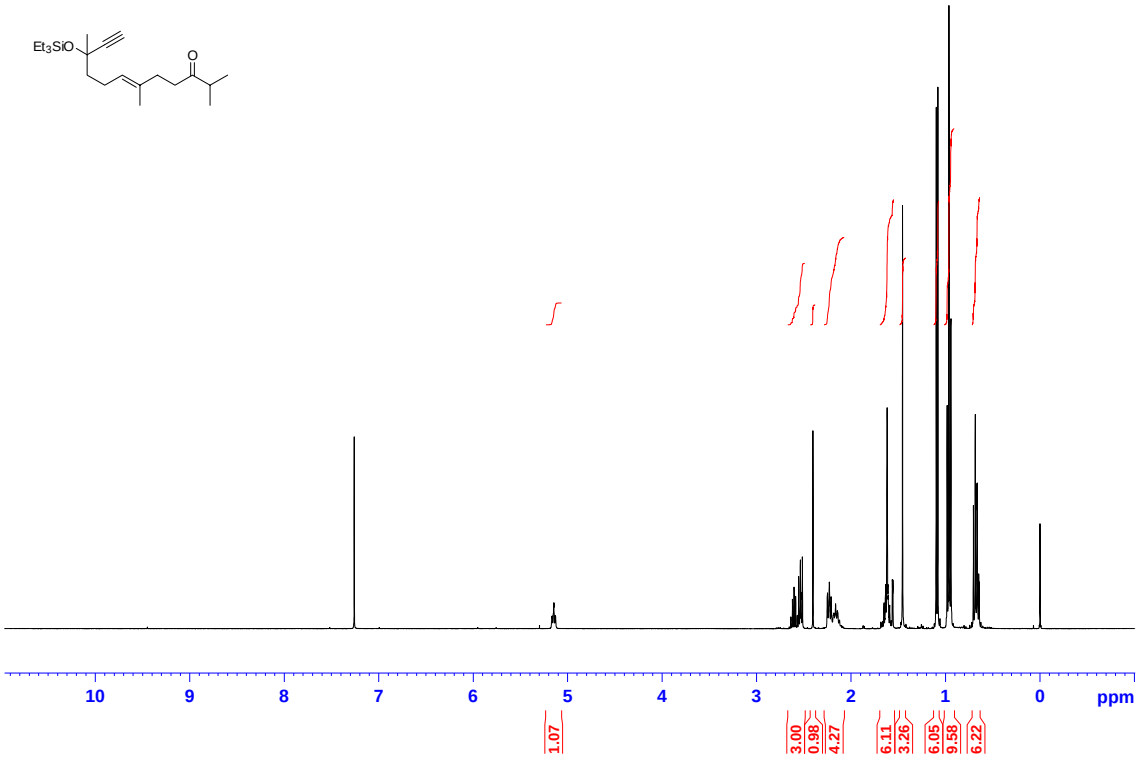
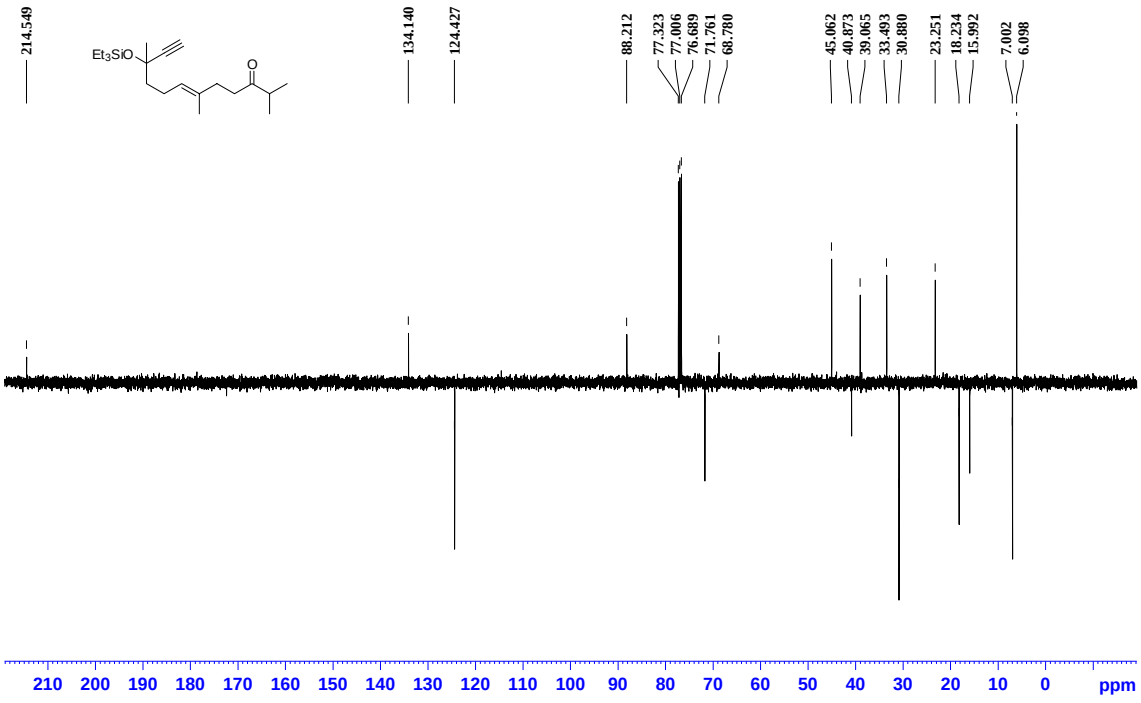
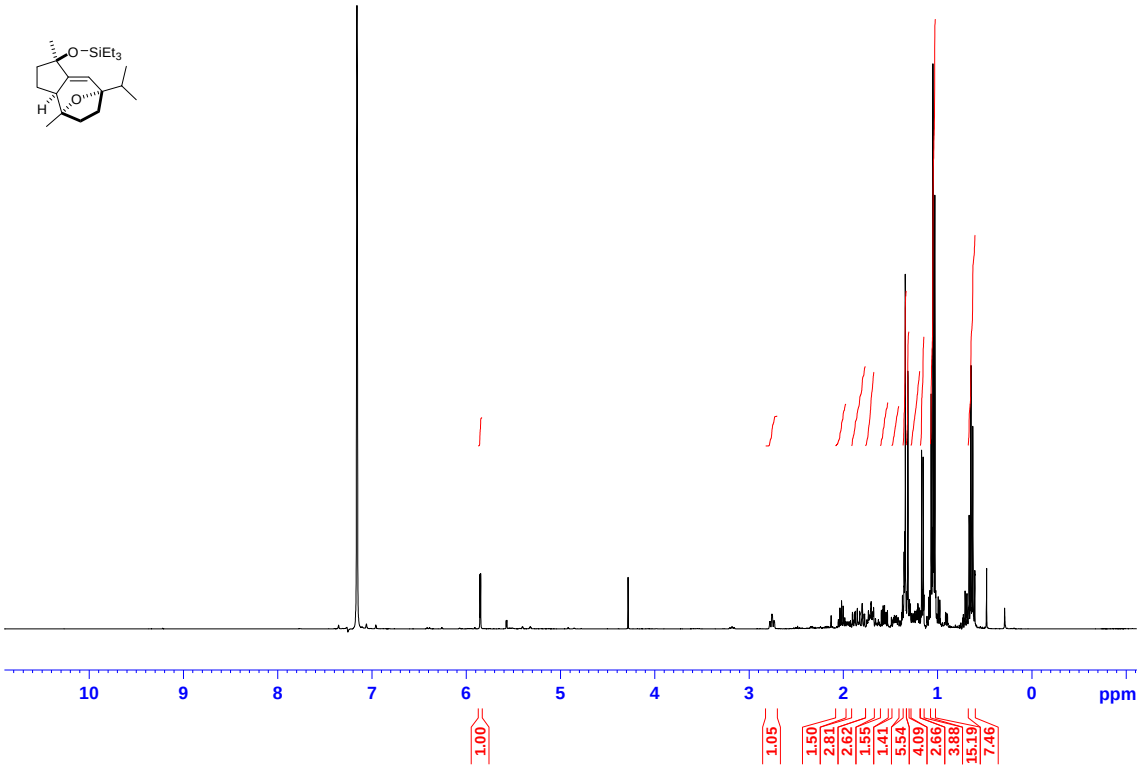
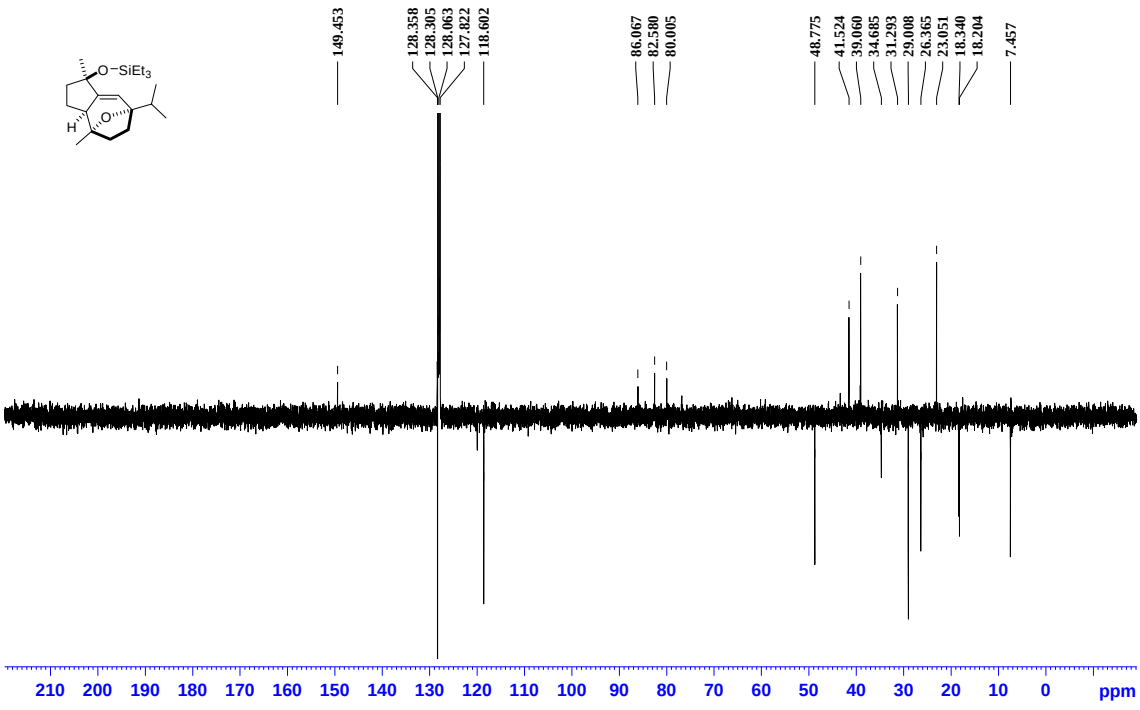
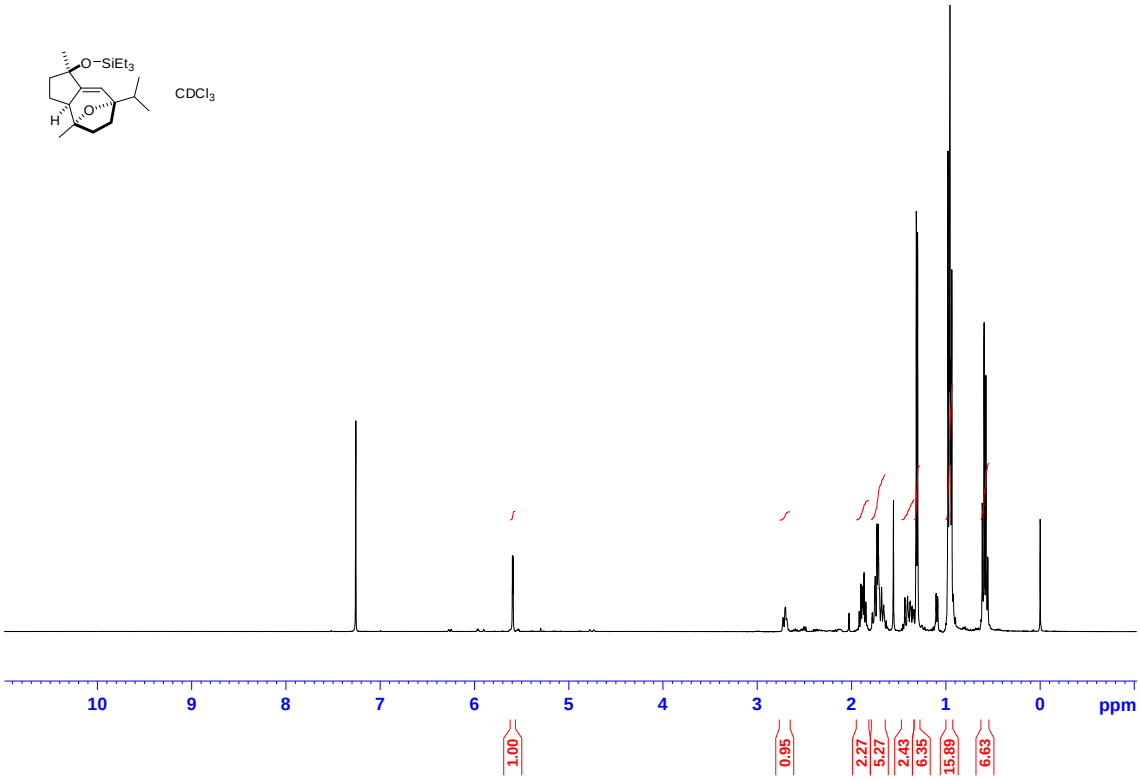
ppm

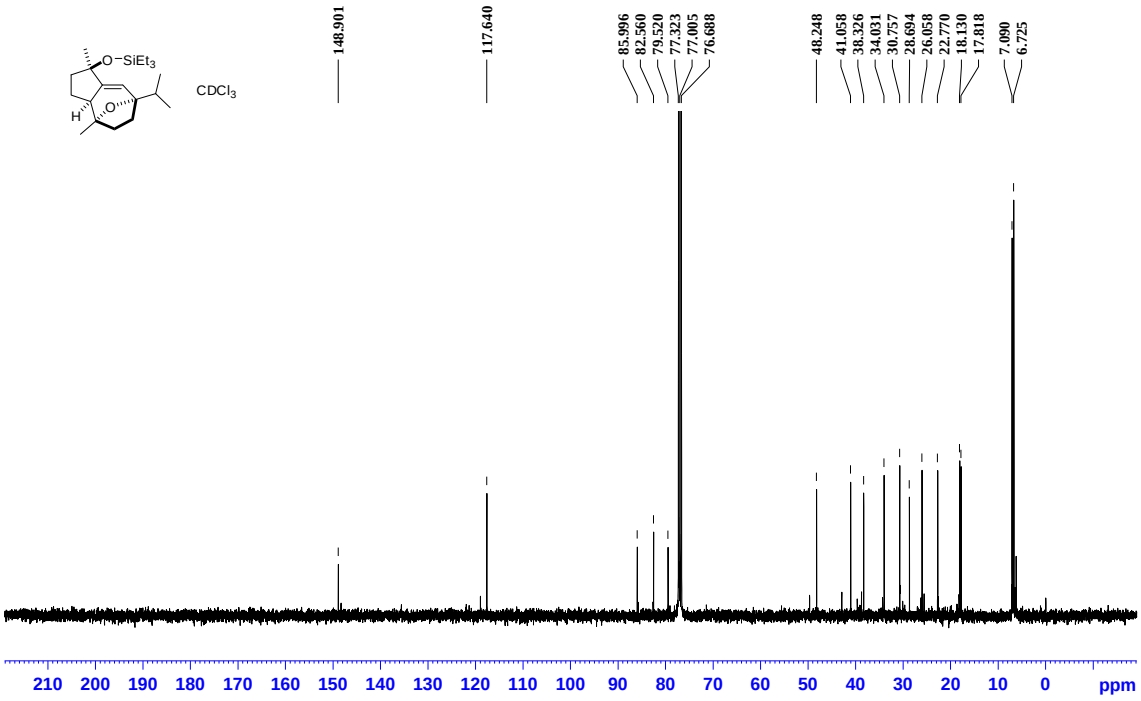

Et3SiO
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.07
3.00
0.98
4.27
6.11
3.26
6.05
9.58
6.22

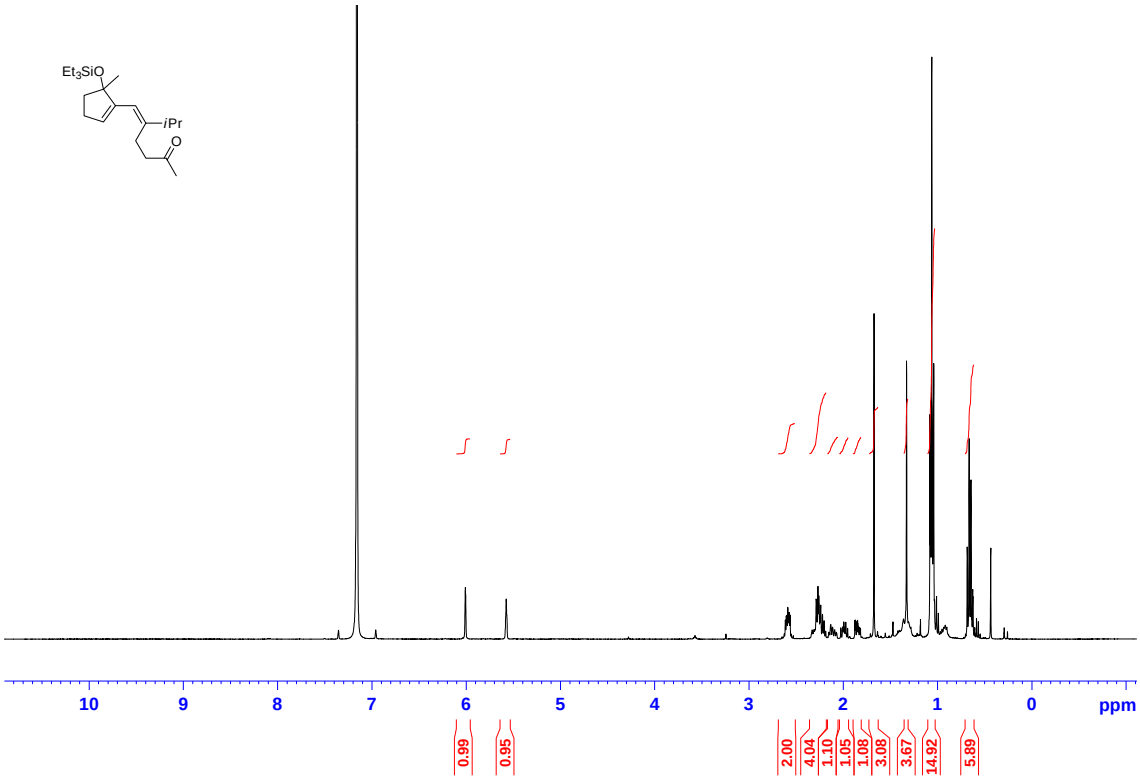

214.549
Et3SiO
O
134.140
124.427
88.212
77.323
77.006
76.689
71.761
68.780
45.062
40.873
39.065
33.493
30.880
23.251
18.234
15.992
7.002
6.098
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

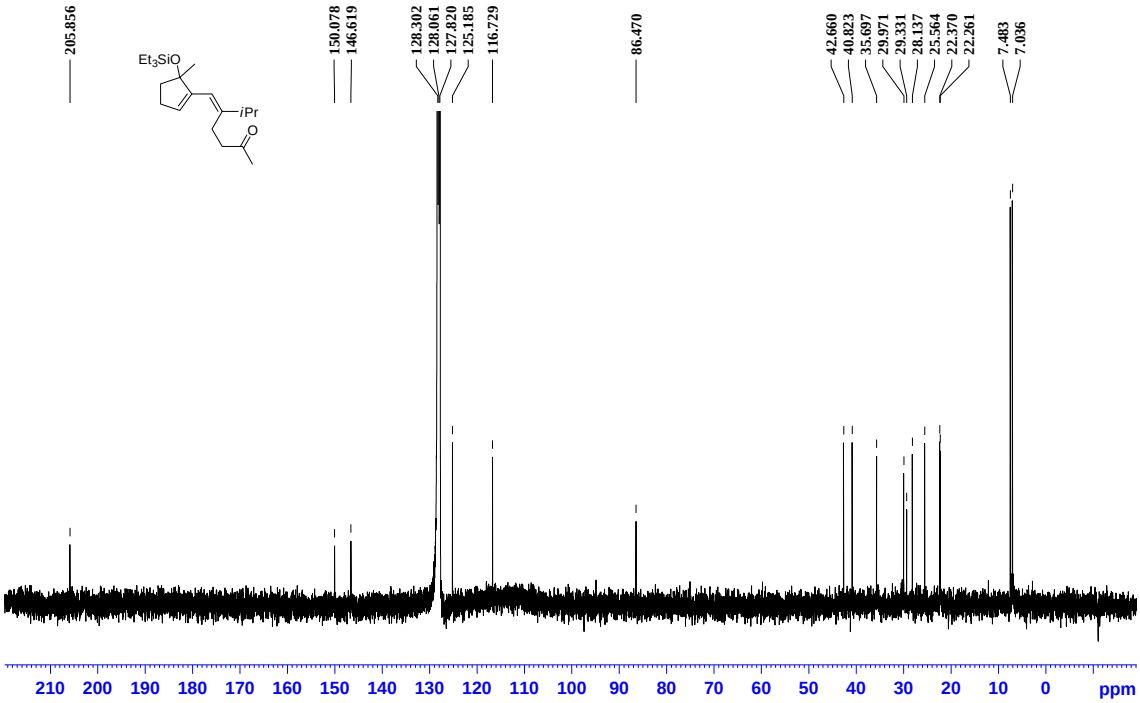

O–SiEt3
H
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
1.50
2.81
2.62
1.55
1.41
5.54
4.09
2.66
3.88
15.19
7.46

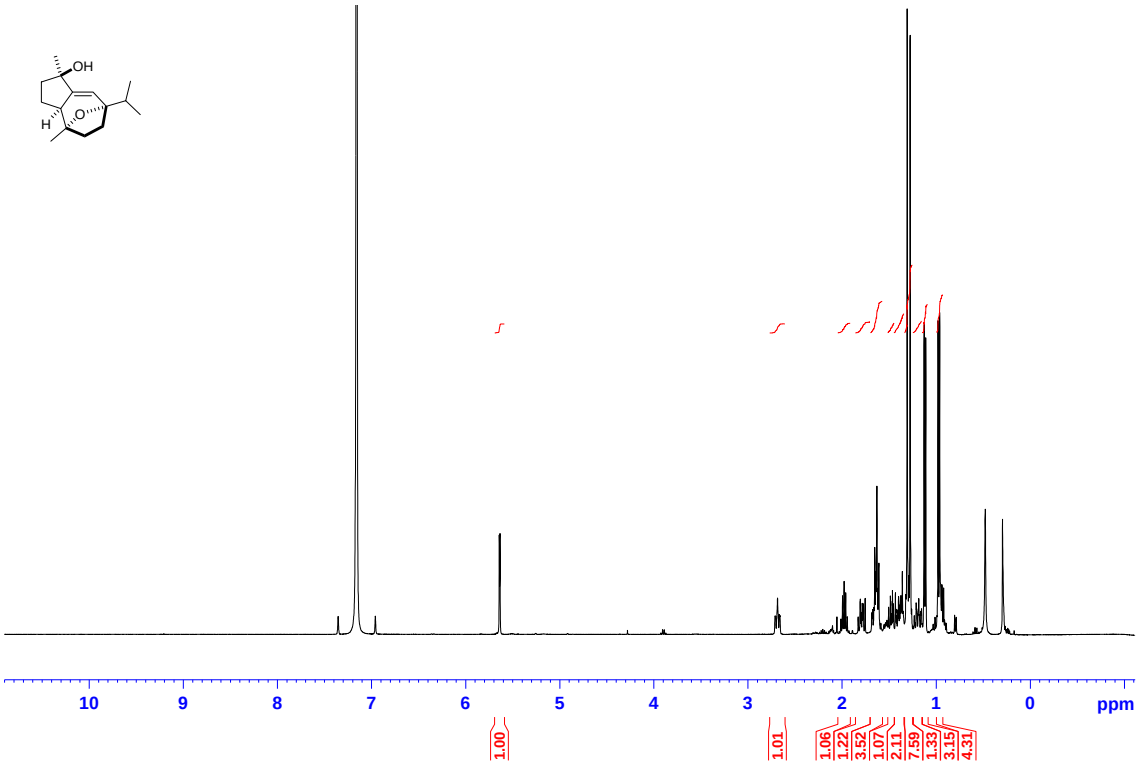

O–SiEt3
H
O
149.453
128.358
128.305
128.063
127.822
118.602
86.067
82.580
80.005
48.775
41.524
39.060
34.685
31.293
29.008
26.365
23.051
18.340
18.204
7.457
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

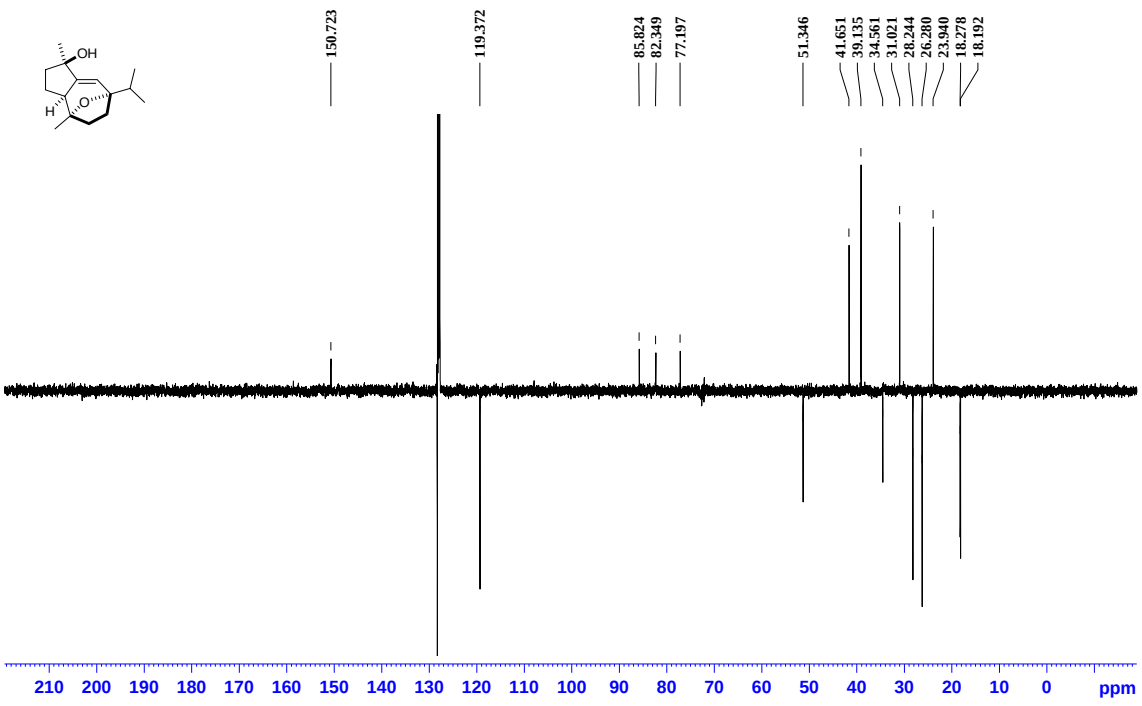

O–SiEt3
H
O
CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.95
2.27
5.27
2.43
6.35
15.89
6.63

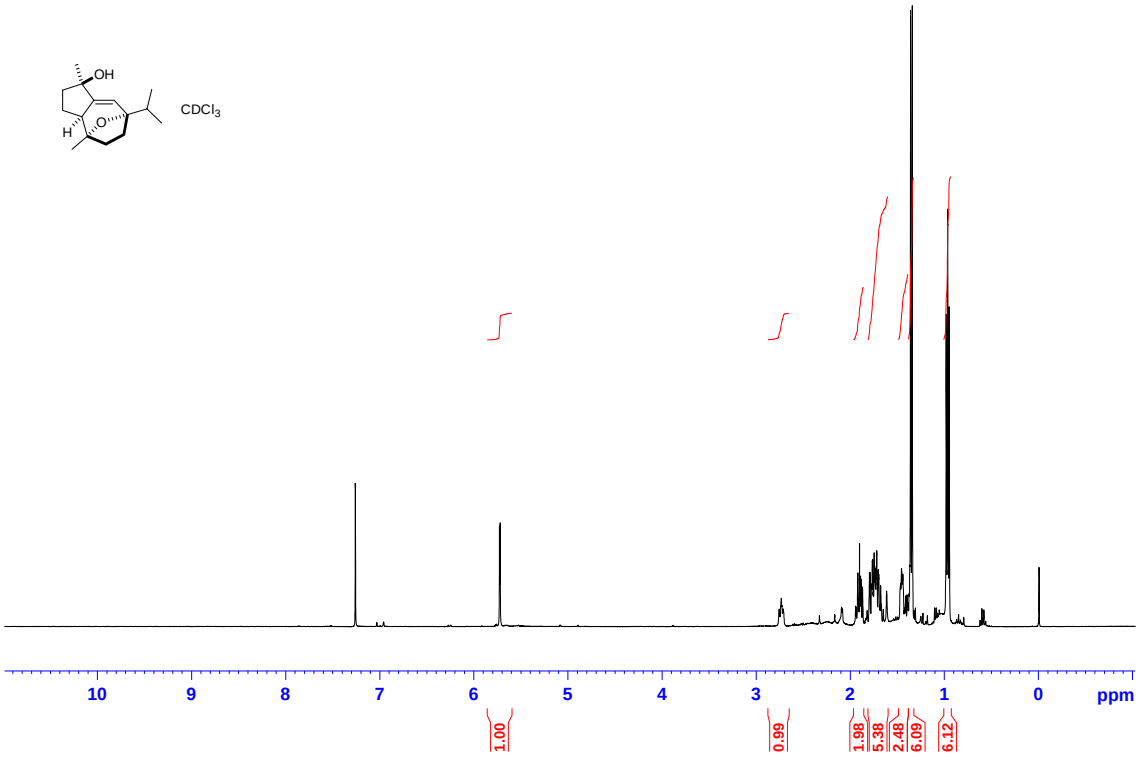

O–SiEt3
H
O
CDCl3
148.901
117.640
85.996
82.560
79.520
77.323
77.005
76.688
48.248
41.058
38.326
34.031
30.757
28.694
26.058
22.770
18.130
17.818
7.090
6.725
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

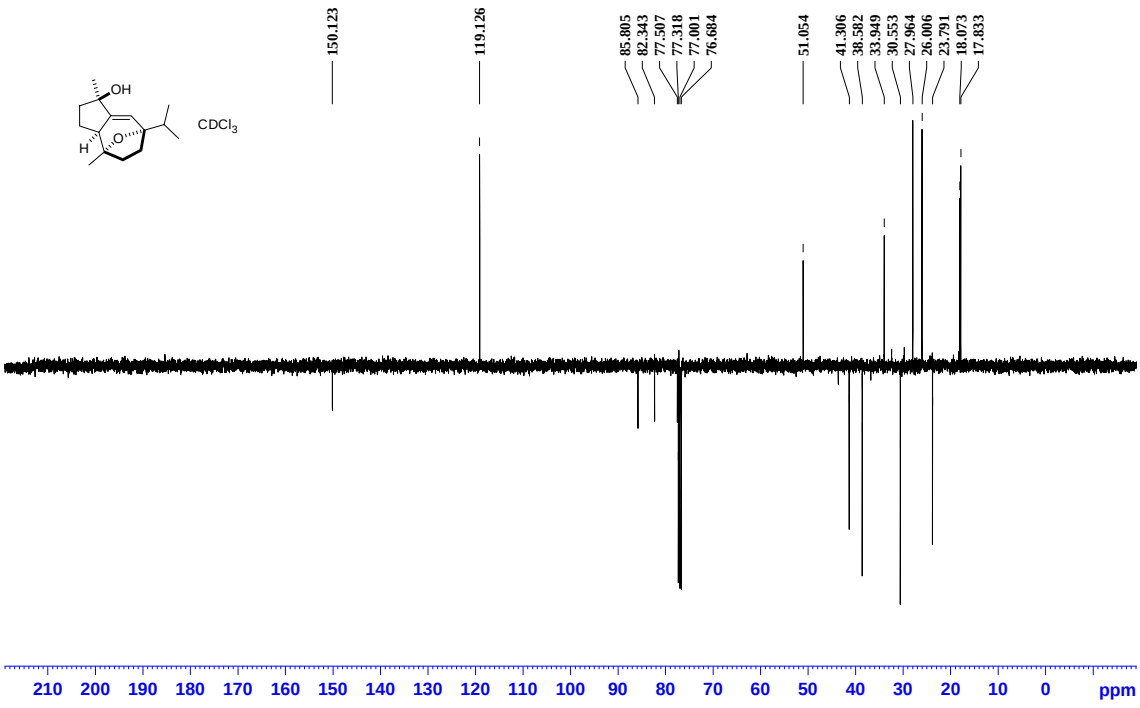


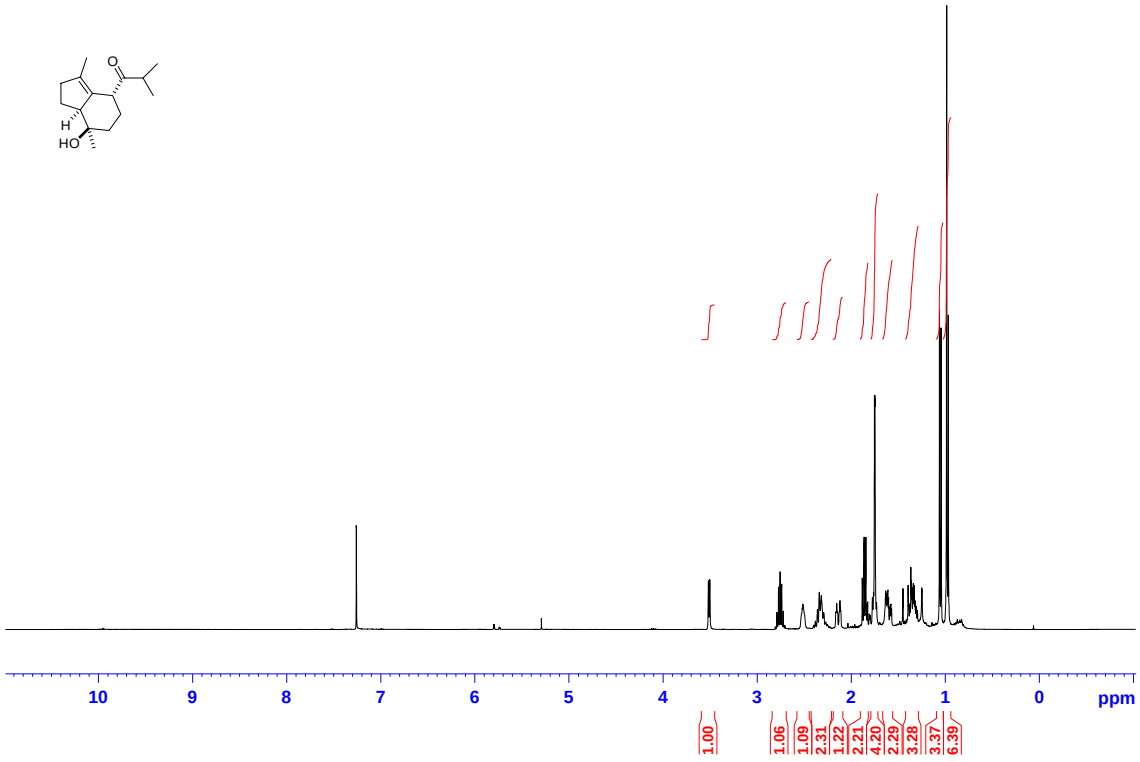


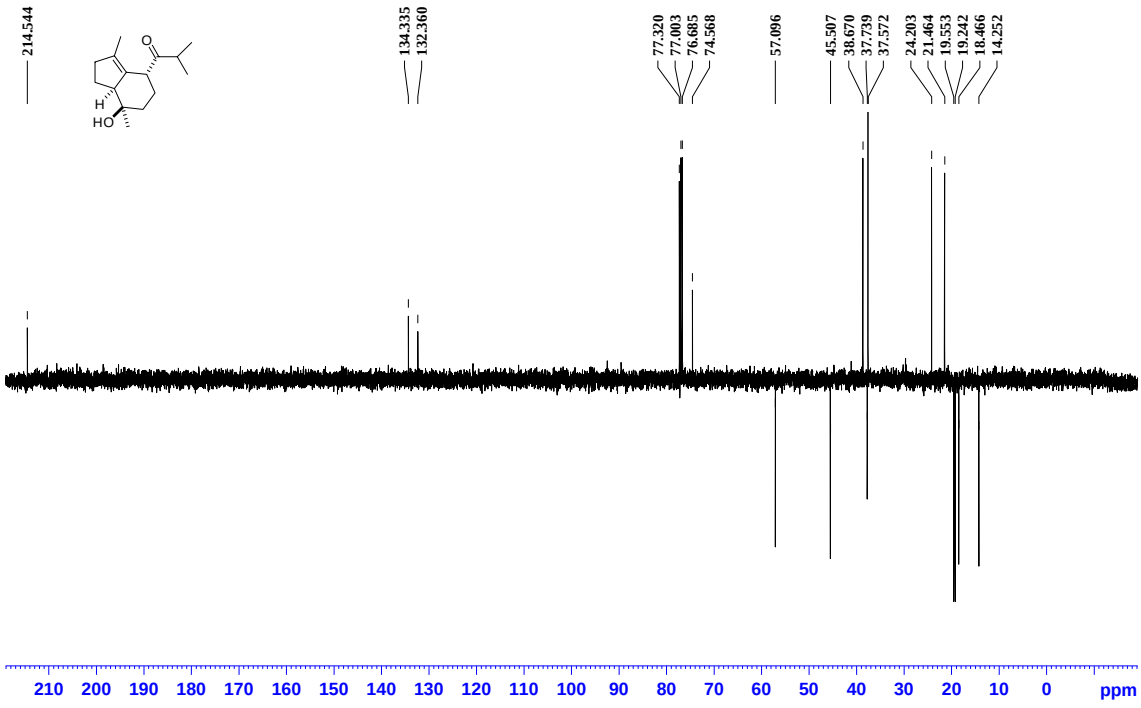

OH
H
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.06
1.22
3.52
1.07
2.11
7.59
1.33
3.15
4.31

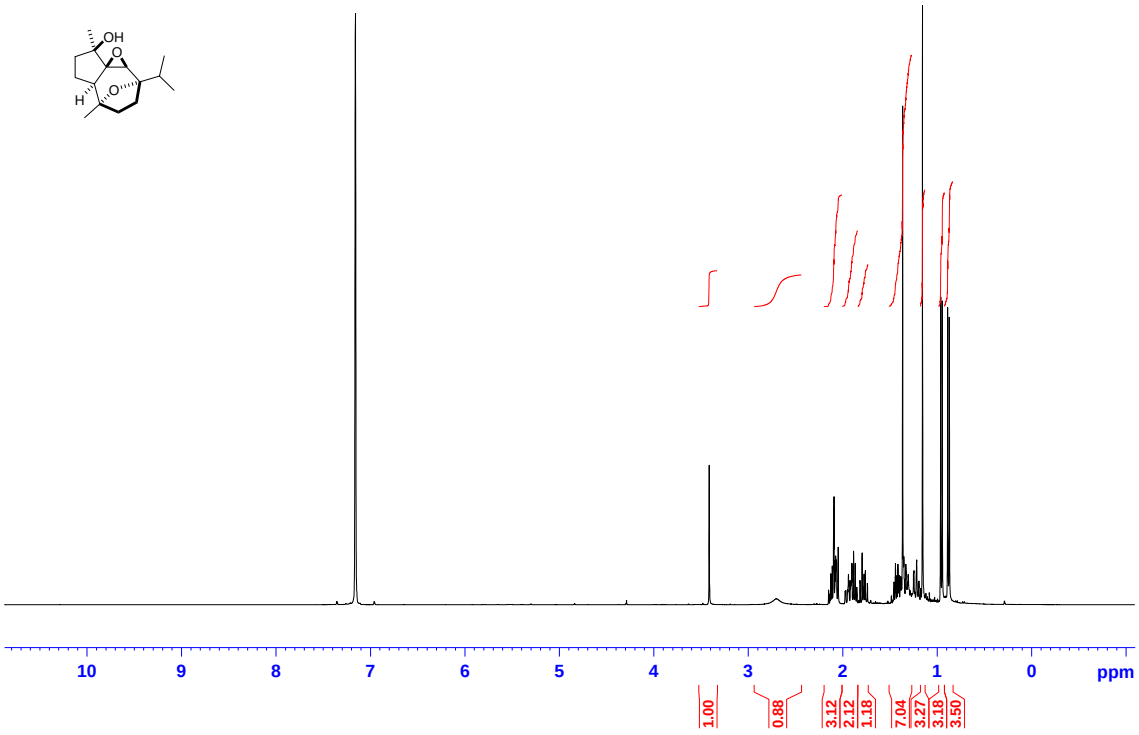

OH
H
O
150.723
119.372
85.824
82.349
77.197
51.346
41.651
39.135
34.561
31.021
28.244
26.280
23.940
18.278
18.192
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

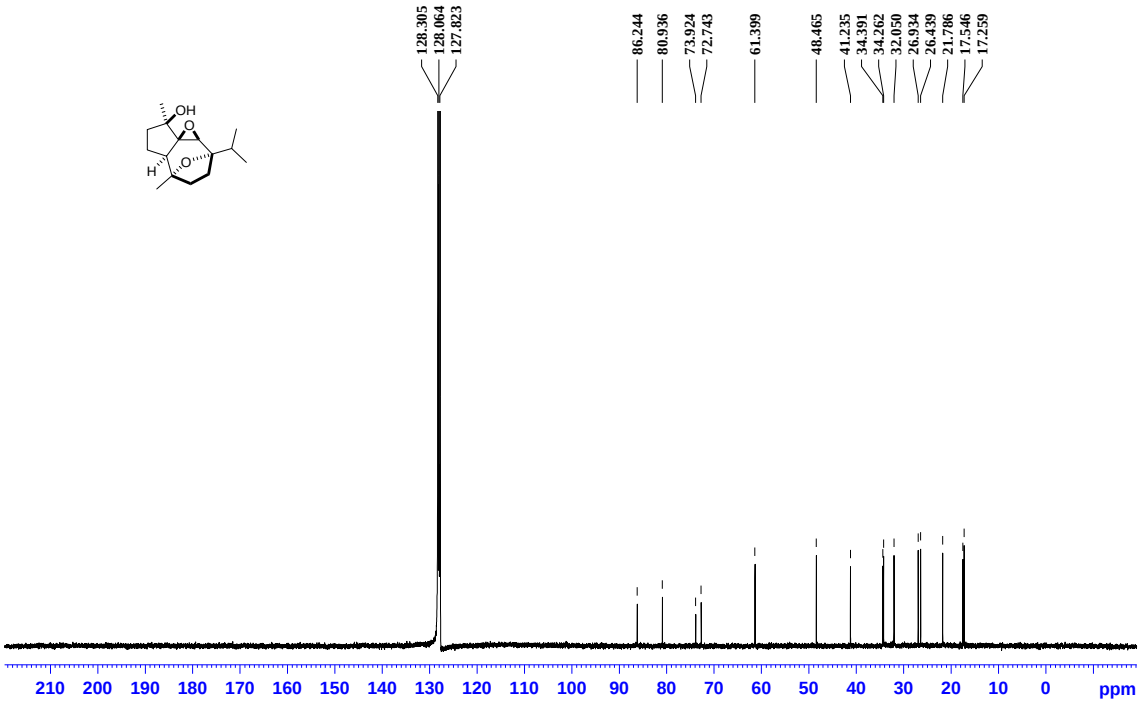

OH
H
O
CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.98
5.38
2.48
6.09
6.12

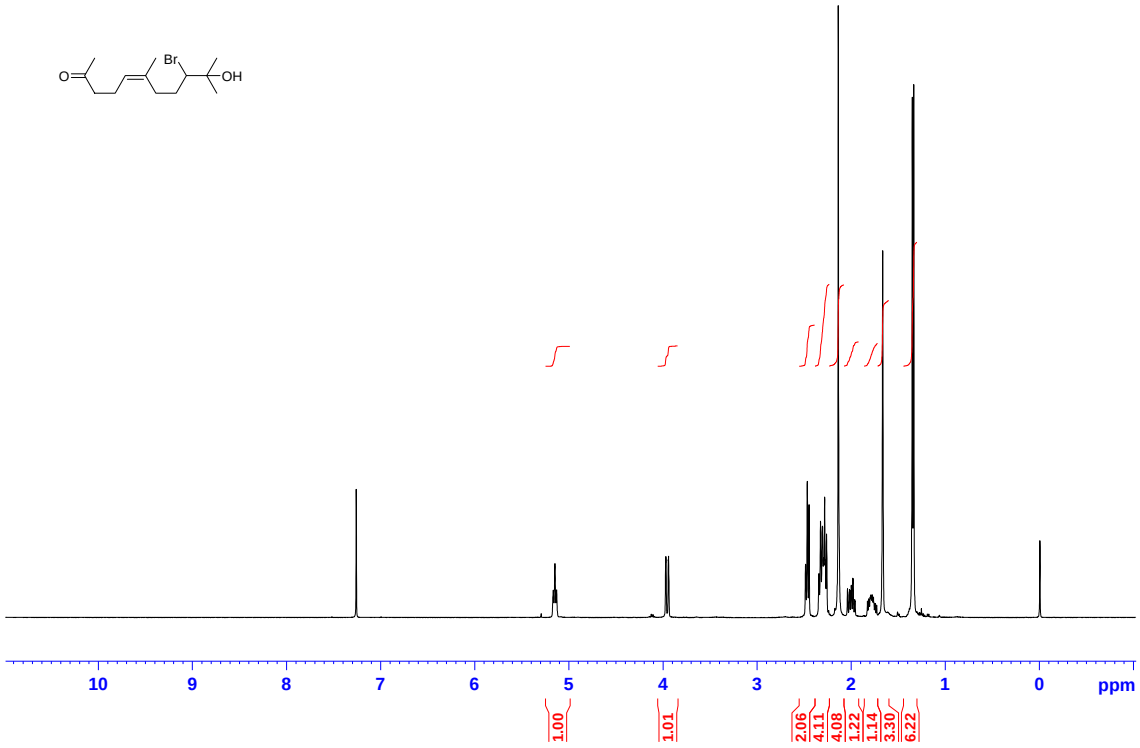

150.123
119.126
85.805
82.343
77.507
77.318
77.001
76.684
51.054
41.306
38.582
33.949
30.553
27.964
26.006
23.791
18.073
17.833
OH
H
O
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

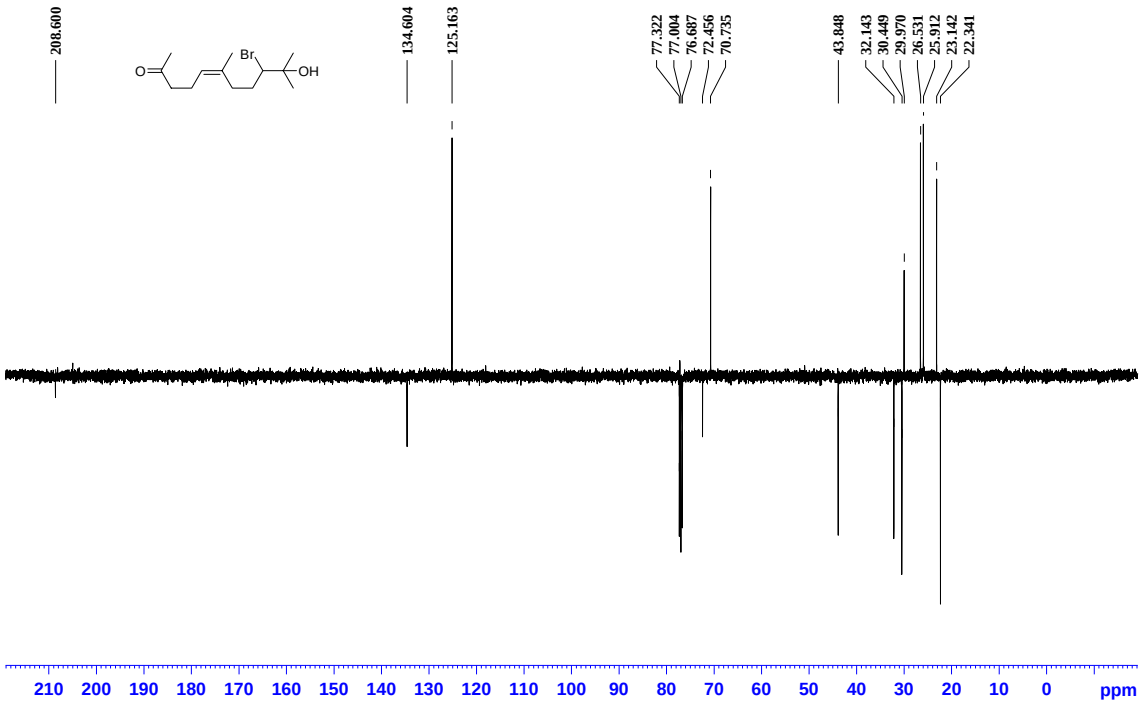

O
H
HO
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
1.09
2.31
1.22
2.21
4.20
2.29
3.28
3.37
6.39

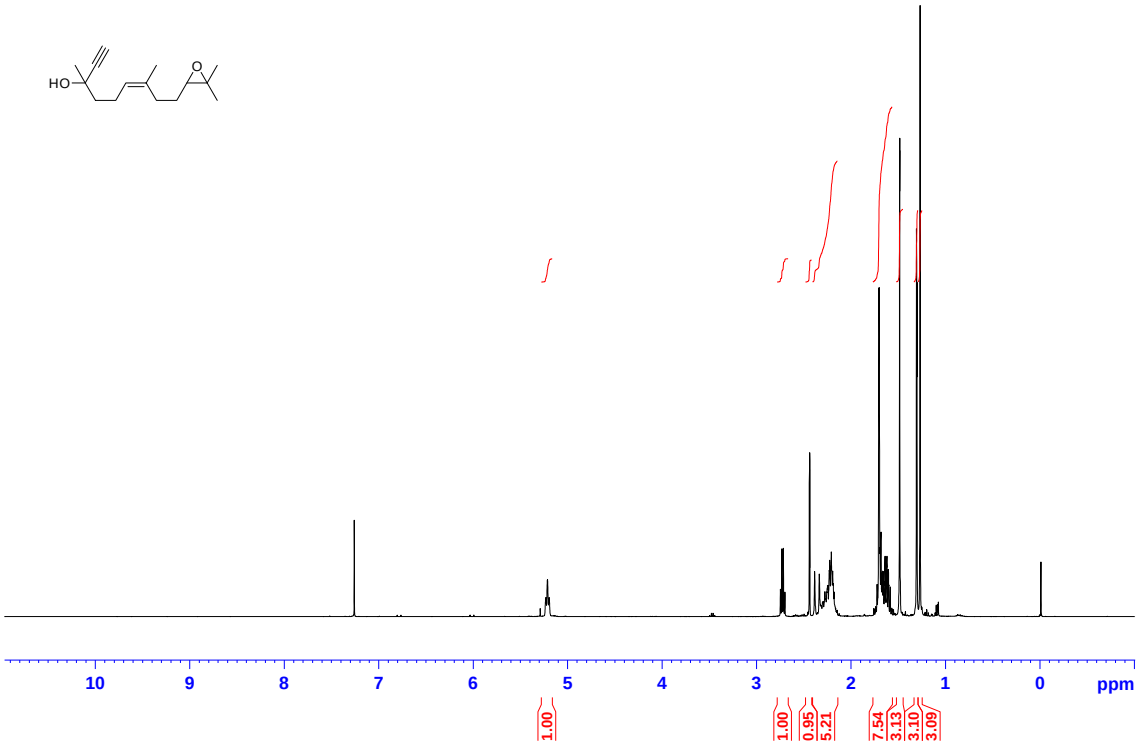

214.544
134.335
132.360
77.320
77.003
76.685
74.568
57.096
45.507
38.670
37.739
37.572
24.203
21.464
19.553
19.242
18.466
14.252
O
H
HO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

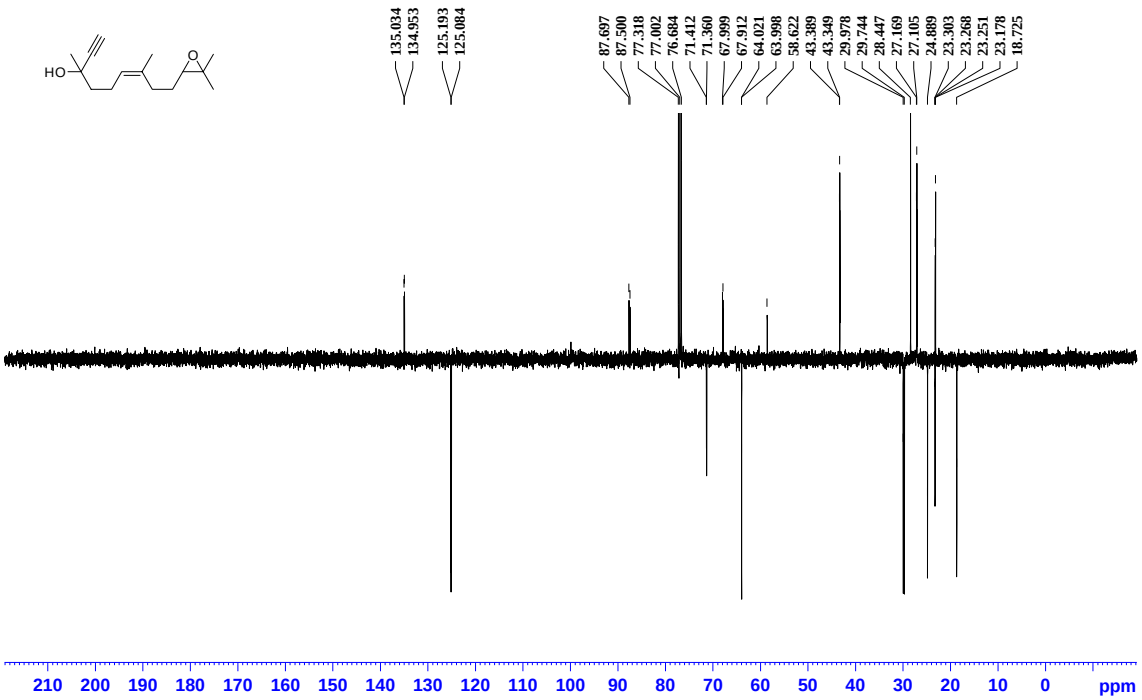

OH
O
H
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.88
3.12
2.12
1.18
7.04
3.27
3.18
3.50

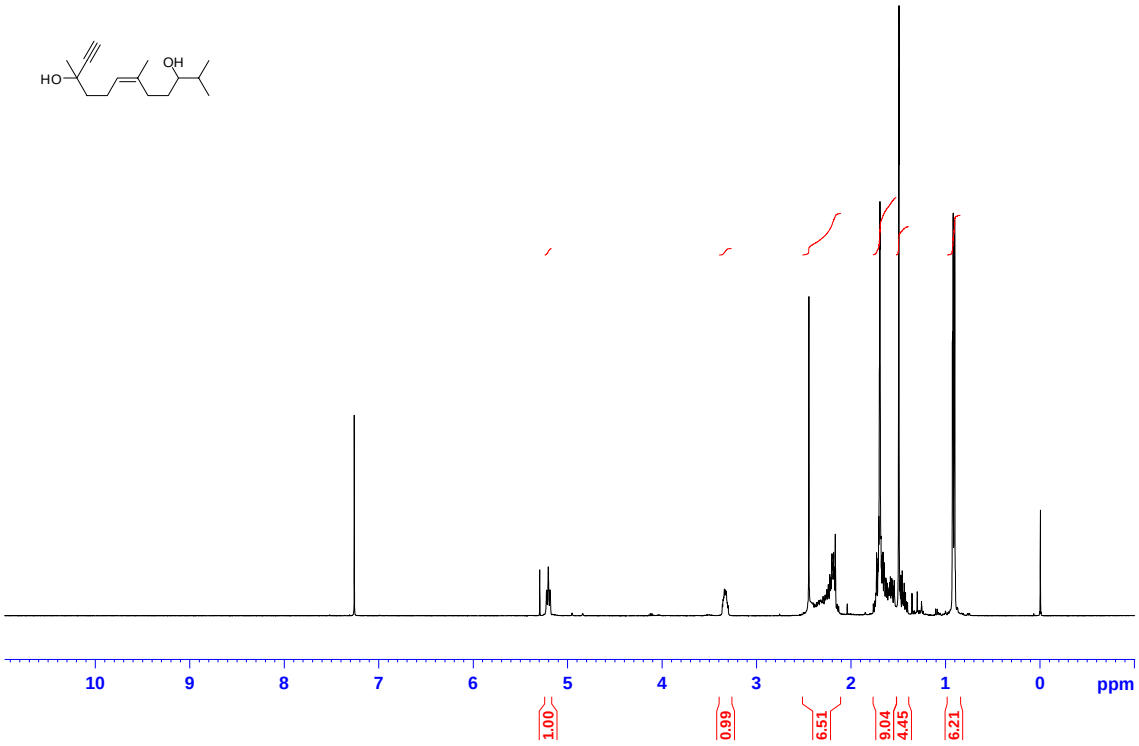

128.305
128.064
127.823
86.244
80.936
73.924
72.743
61.399
48.465
41.235
34.391
34.262
32.050
26.934
26.439
21.786
17.546
17.259
OH
O
H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

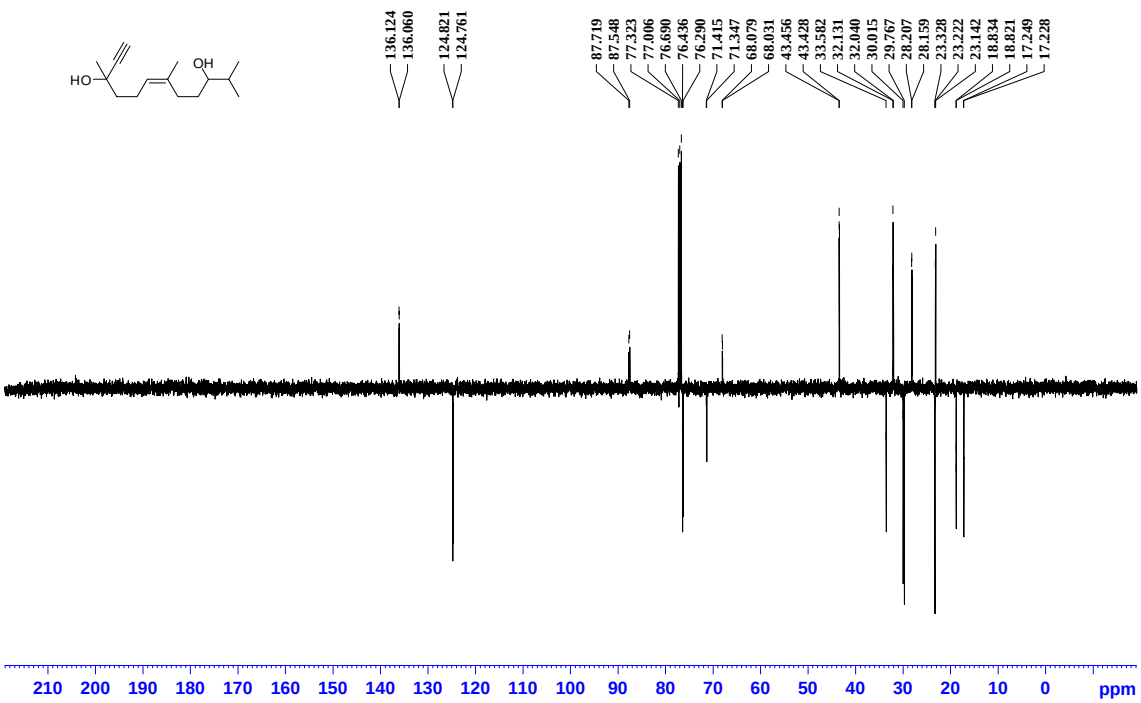

Br
O
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.06
4.11
4.08
1.22
1.14
3.30
6.22

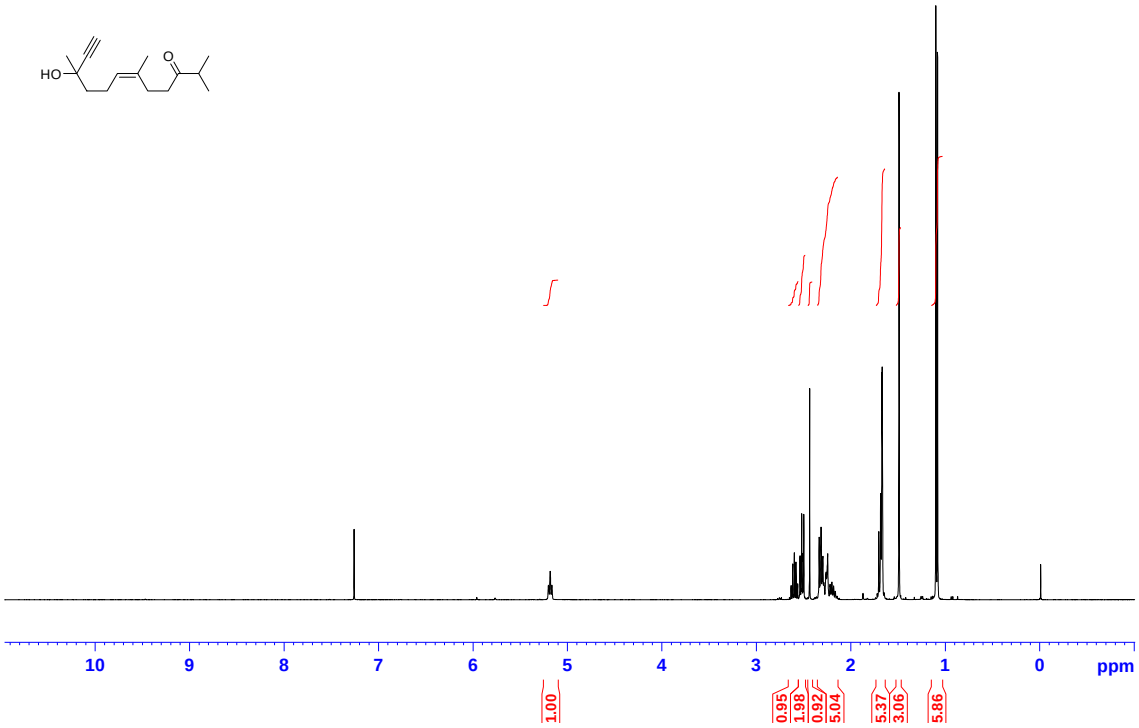

208.600
Br
O
OH
134.604
125.163
77.322
77.004
76.687
72.456
70.735
43.848
32.143
30.449
29.970
26.531
25.912
23.142
22.341
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

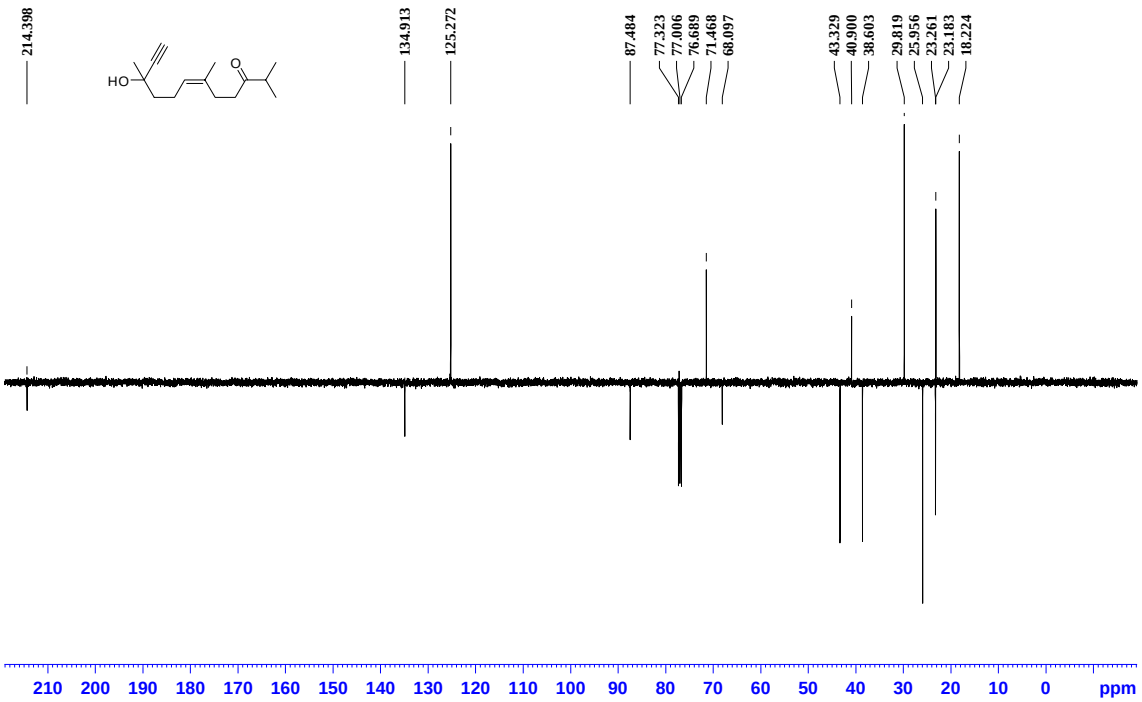

HO
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
0.95
5.21
7.54
3.13
3.10
3.09

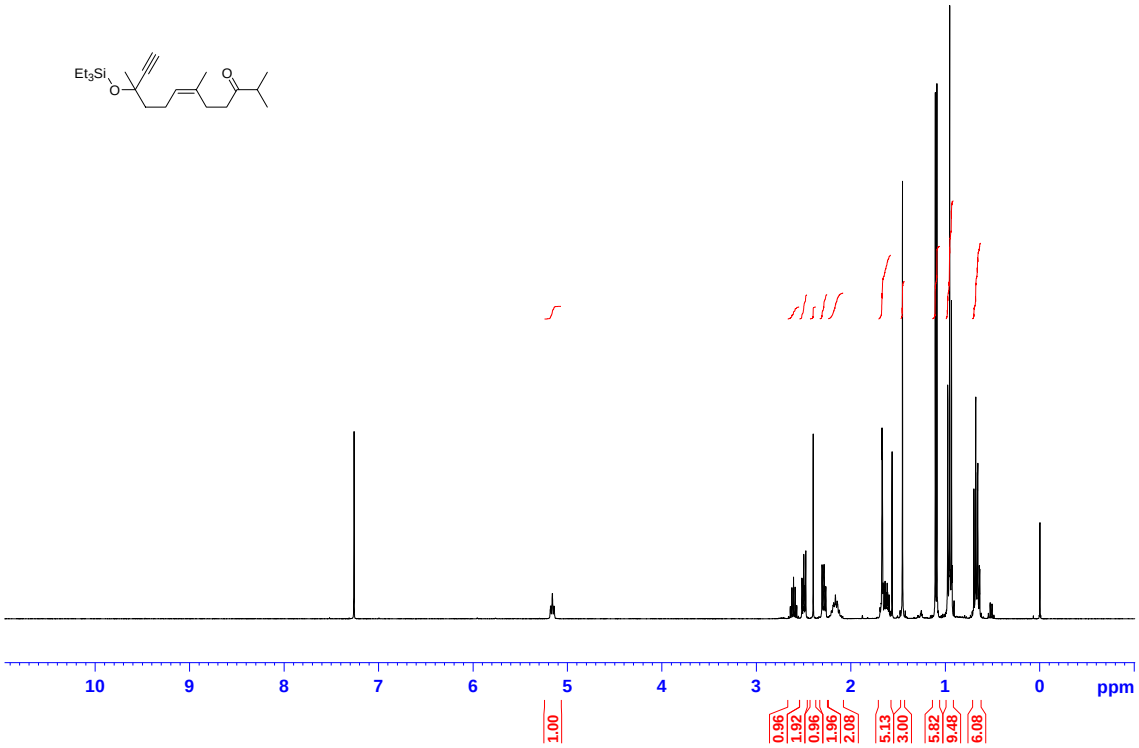

HO
O
135.034
134.953
125.193
125.084
87.697
87.500
77.318
77.002
76.684
71.412
71.360
67.999
67.912
64.021
63.998
58.622
43.389
43.349
29.978
29.744
28.447
27.169
27.105
24.889
23.303
23.268
23.251
23.178
18.725
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

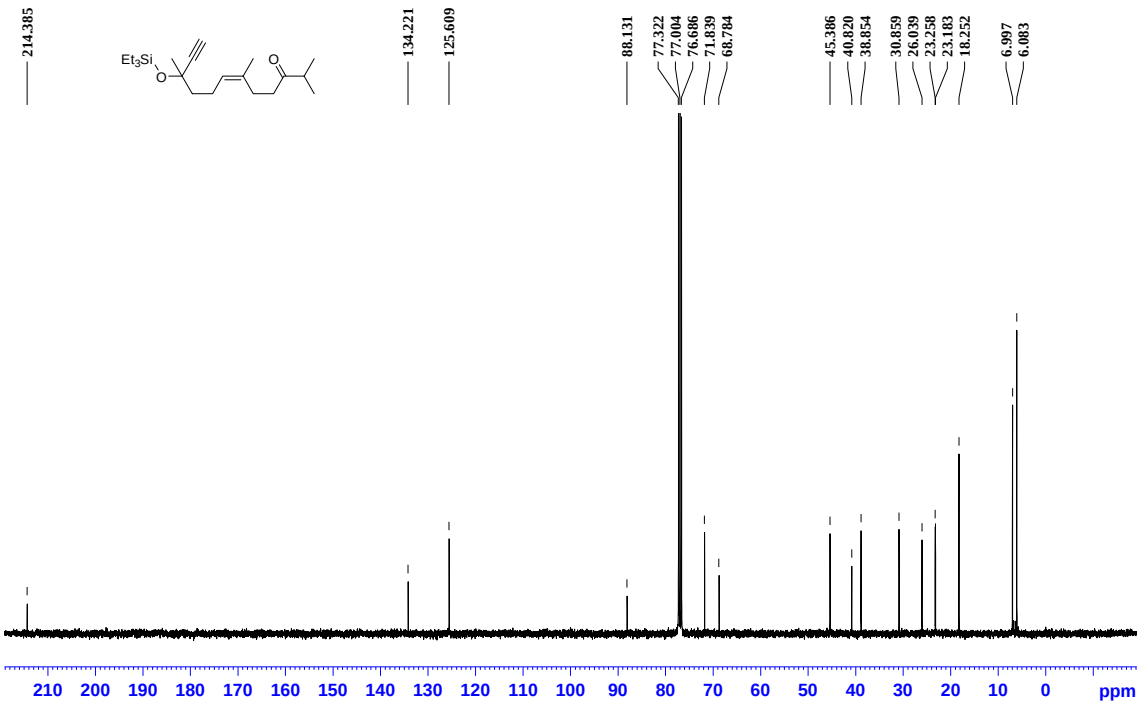

HO
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
6.51
9.04
4.45
6.21

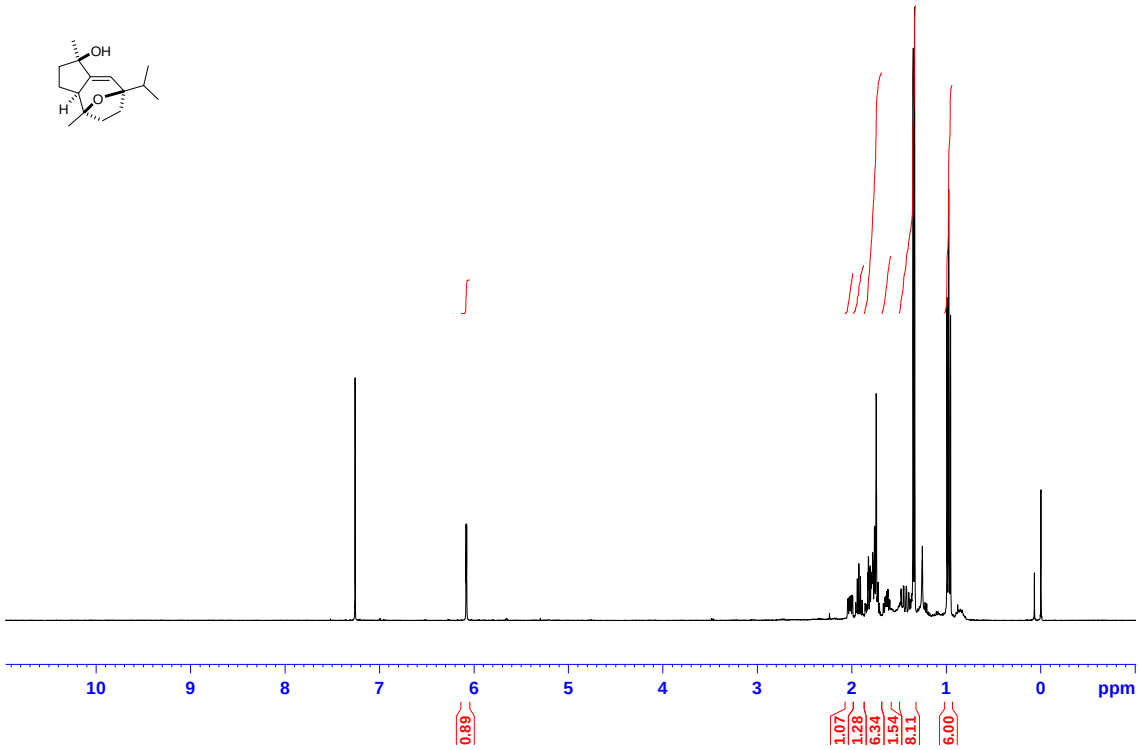

HO
OH
136.124
136.060
124.821
124.761
87.719
87.548
77.323
77.006
76.690
76.436
76.290
71.415
71.347
68.079
68.031
43.456
43.428
33.582
32.131
32.040
30.015
29.767
28.207
28.159
23.328
23.222
23.142
18.834
18.821
17.249
17.228
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

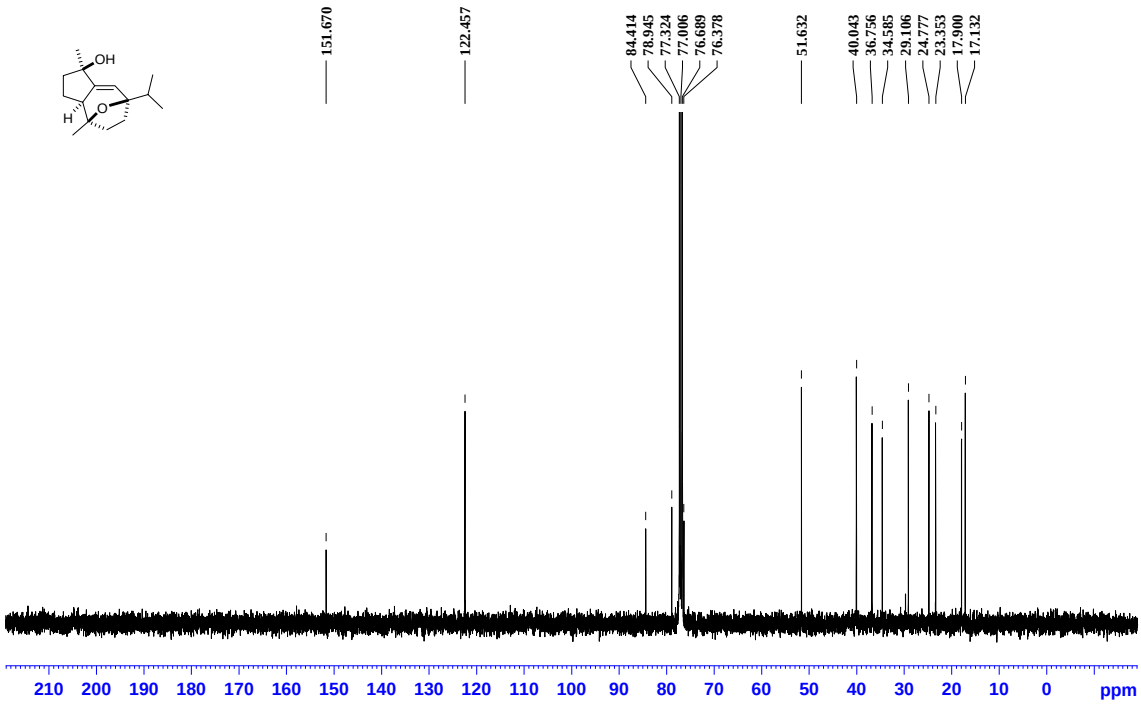

HO
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.95
1.98
0.92
5.04
5.37
3.06
5.86

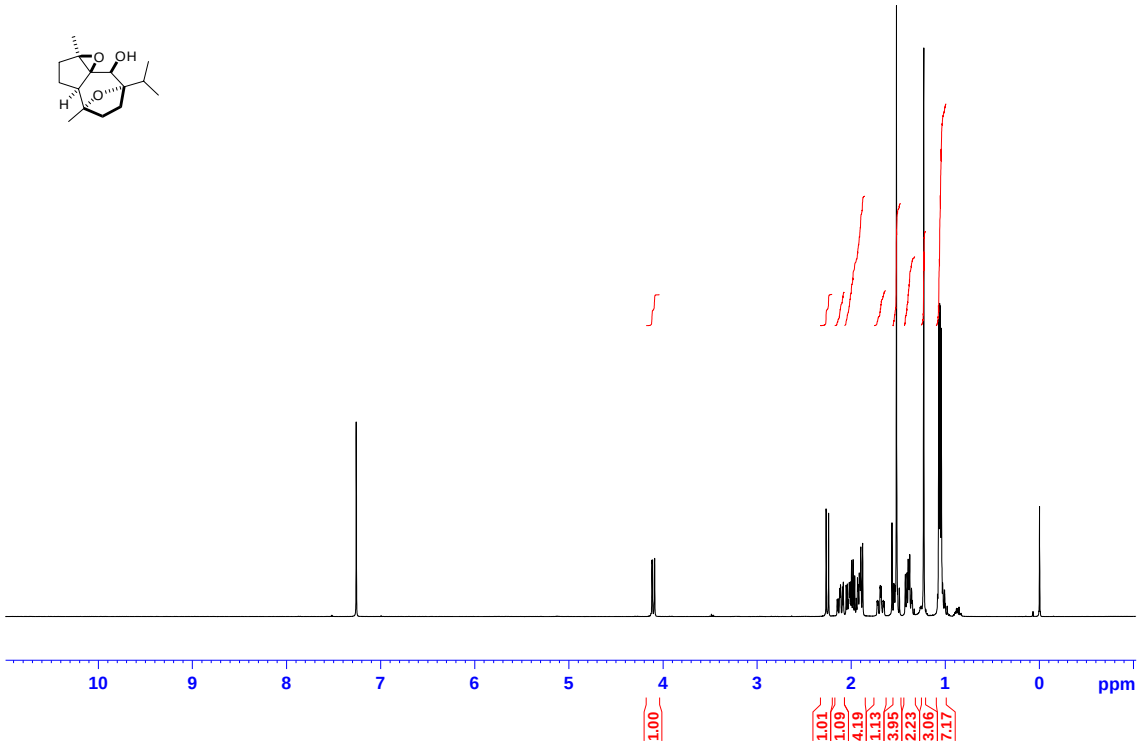

214.398
HO
O
134.913
125.272
87.484
77.323
77.006
76.689
71.468
68.097
43.329
40.900
38.603
29.819
25.956
23.261
23.183
18.224
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

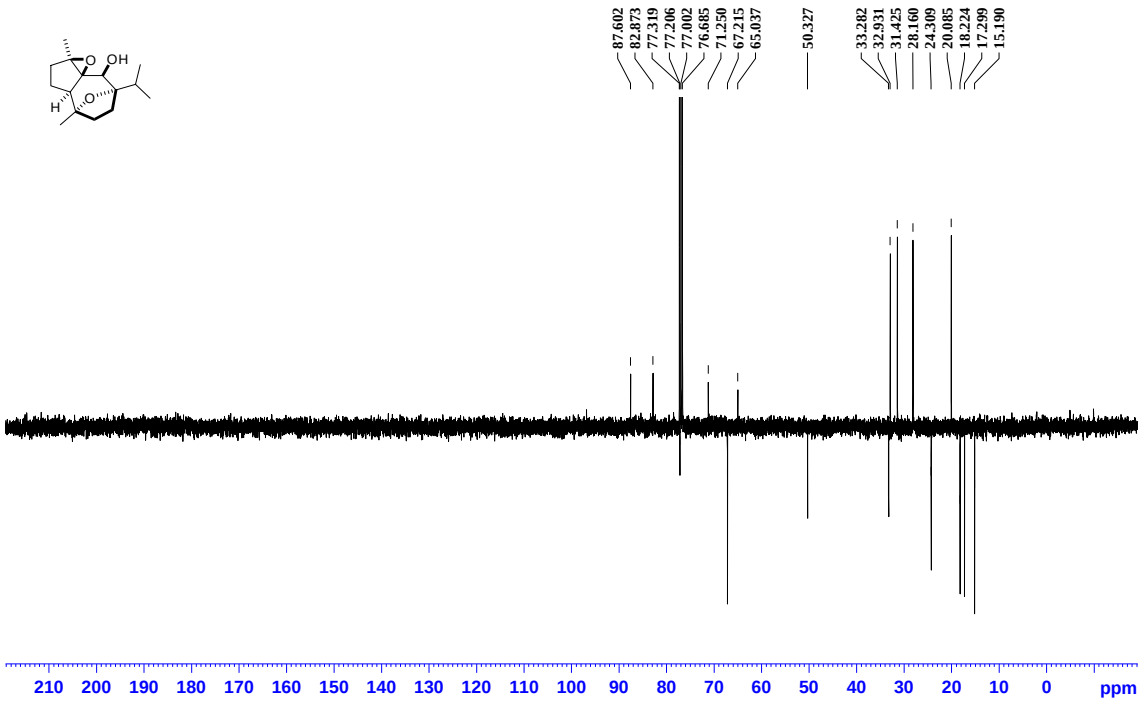

Et3Si
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.96
1.92
0.96
1.96
2.08
5.13
3.00
5.82
9.48
6.08

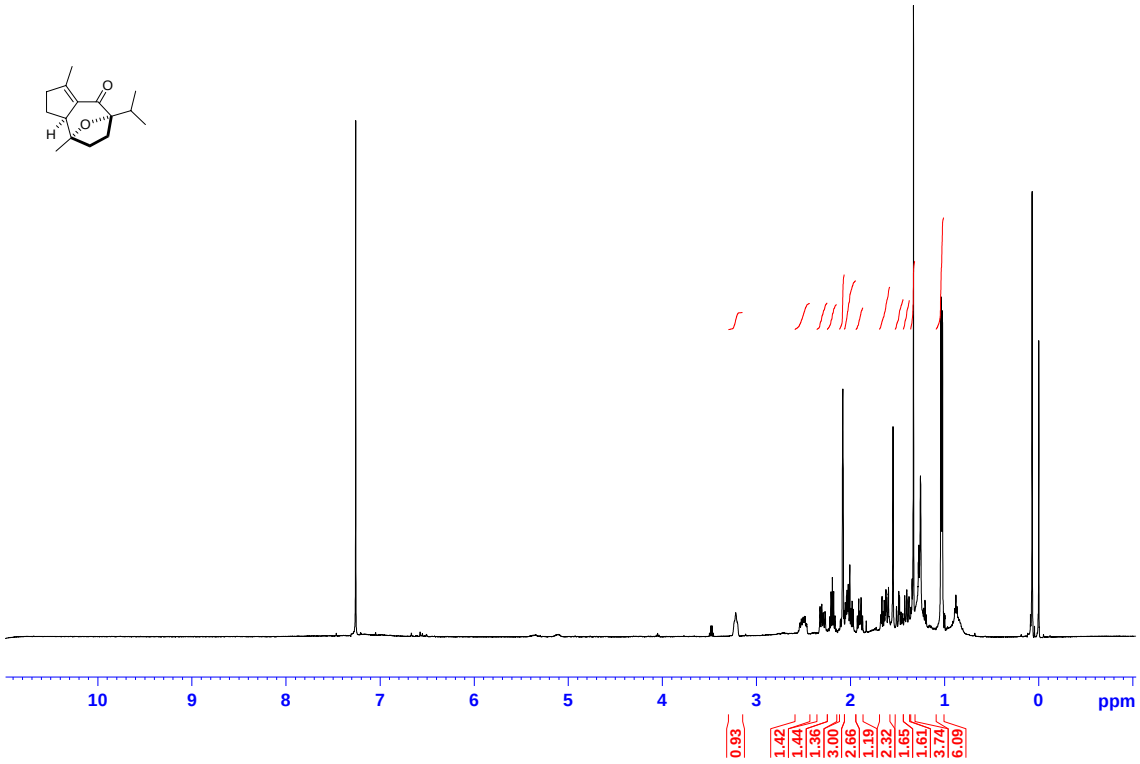

214.385
Et3Si
O
O
134.221
125.609
88.131
77.322
77.004
76.686
71.839
68.784
45.386
40.820
38.854
30.859
26.039
23.258
23.183
18.252
6.997
6.083
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

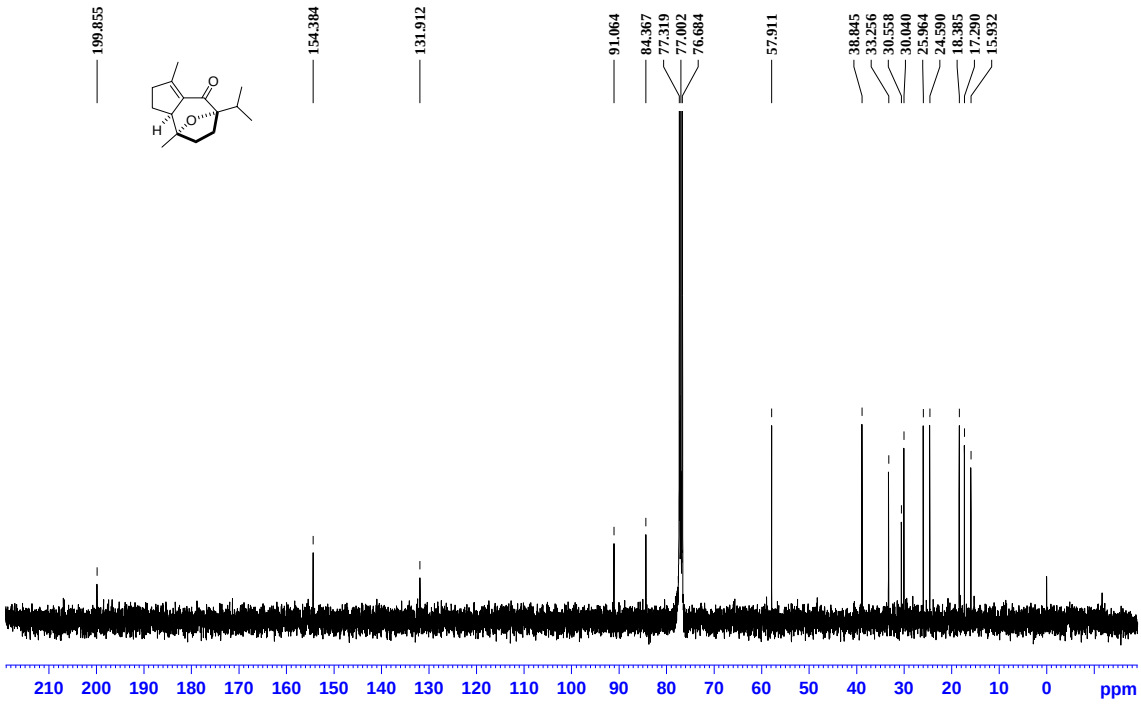


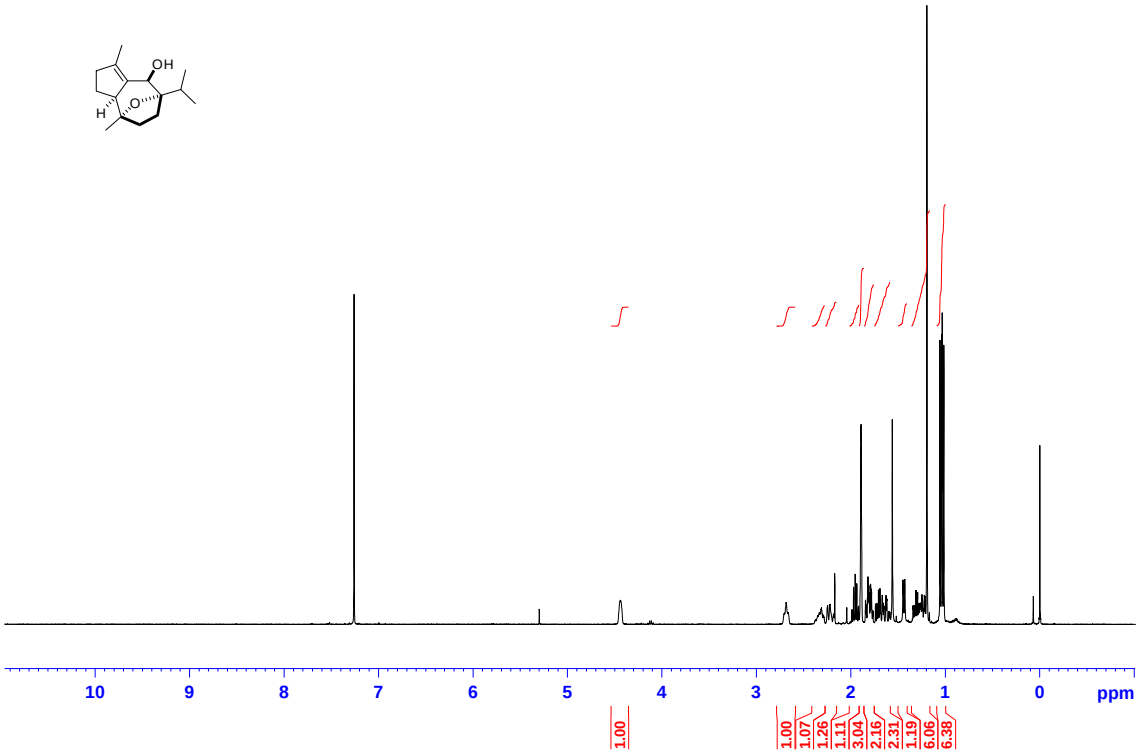



O
OH
H
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.09
4.19
1.13
3.95
2.23
3.06
7.17


O
OH
H
O
87.602
82.873
77.319
77.206
77.002
76.685
71.250
67.215
65.037
50.327
33.282
32.931
31.425
28.160
24.309
20.085
18.224
17.299
15.190
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
1.42
1.44
1.36
3.00
2.66
1.19
2.32
1.65
1.61
3.74
6.09


199.855
154.384
131.912
91.064
84.367
77.319
77.002
76.684
57.911
38.845
33.256
30.558
30.040
25.964
24.590
18.385
17.290
15.932
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OH
H
O
10
9
8
7
6
5
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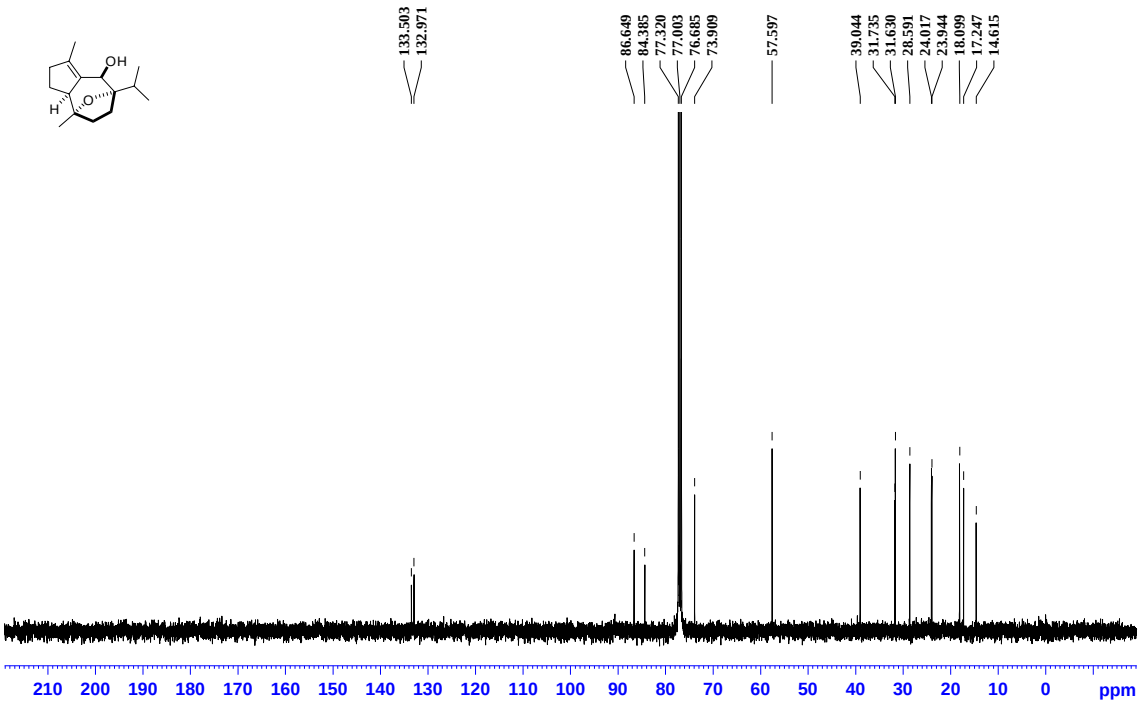
6.38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28.591
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23.944
18.099
17.247
14.615
210
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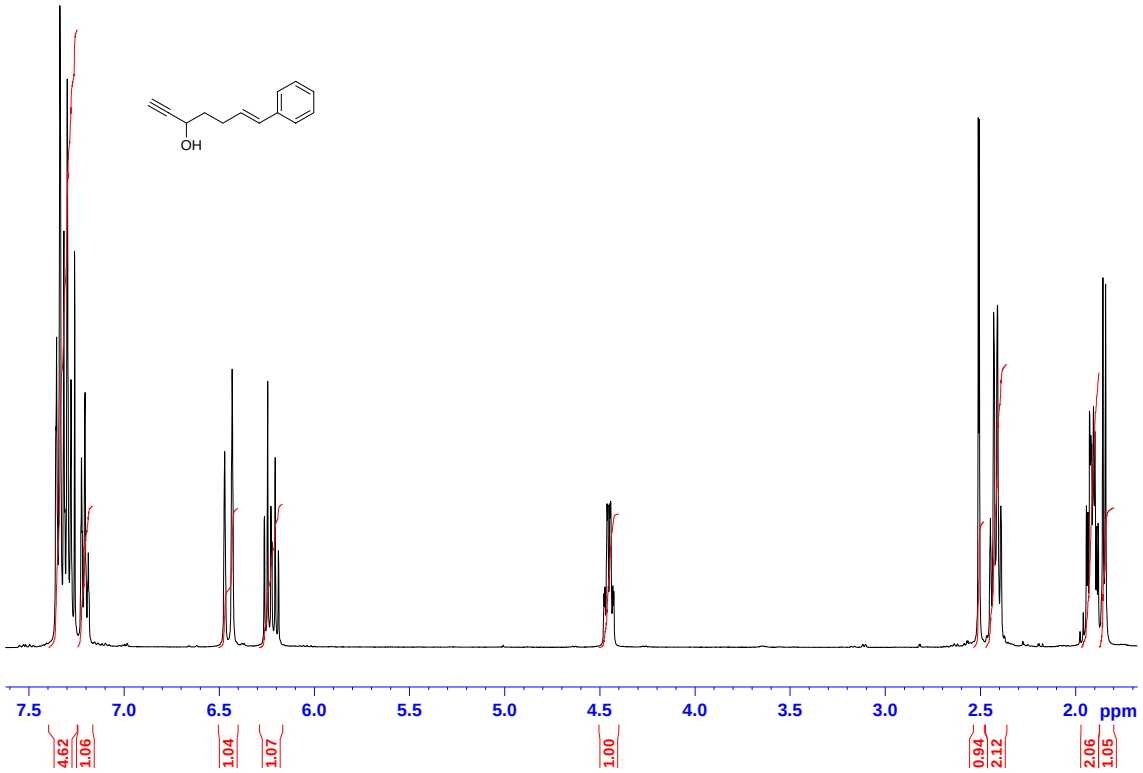
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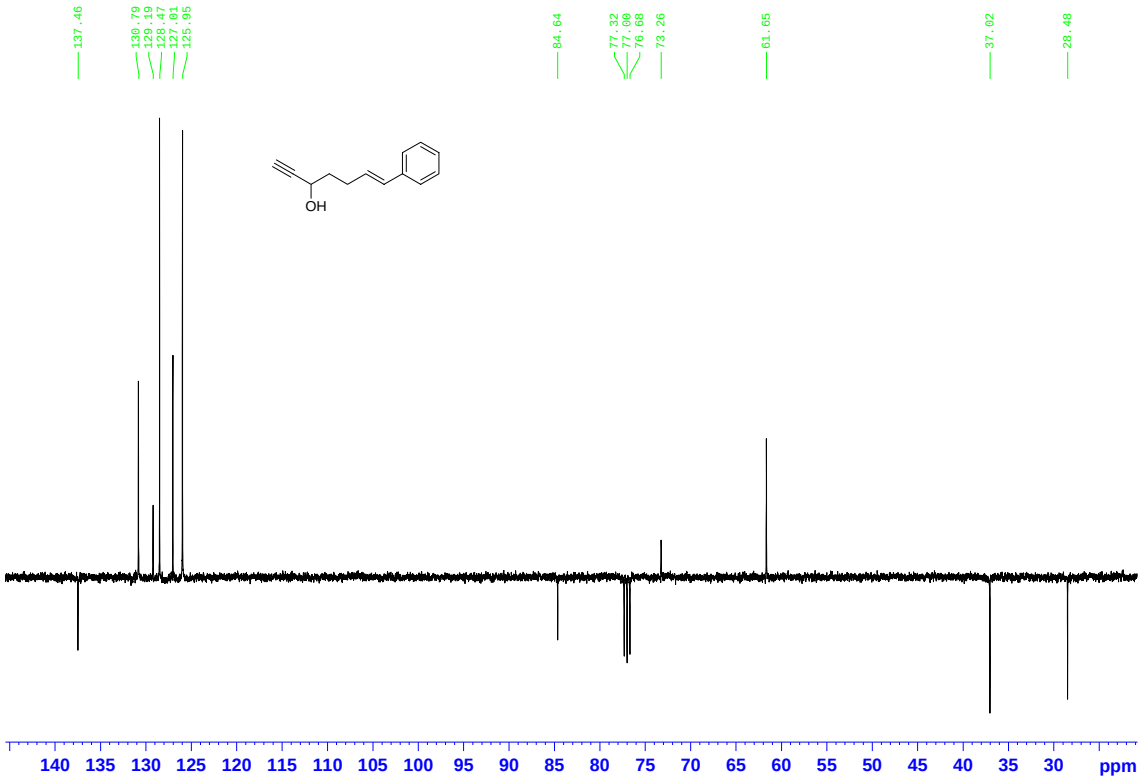
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77.32
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76.68
73.26
61.65
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28.48
OH
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135
130
125
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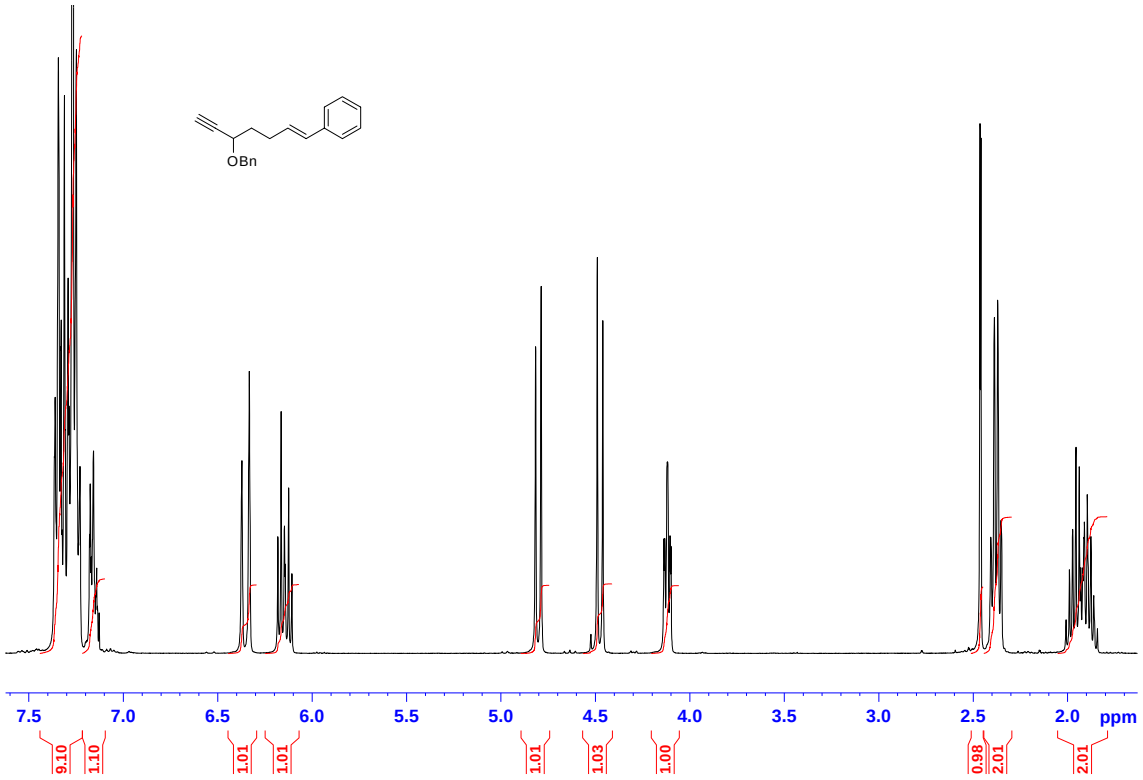
ppm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1.01
1.01
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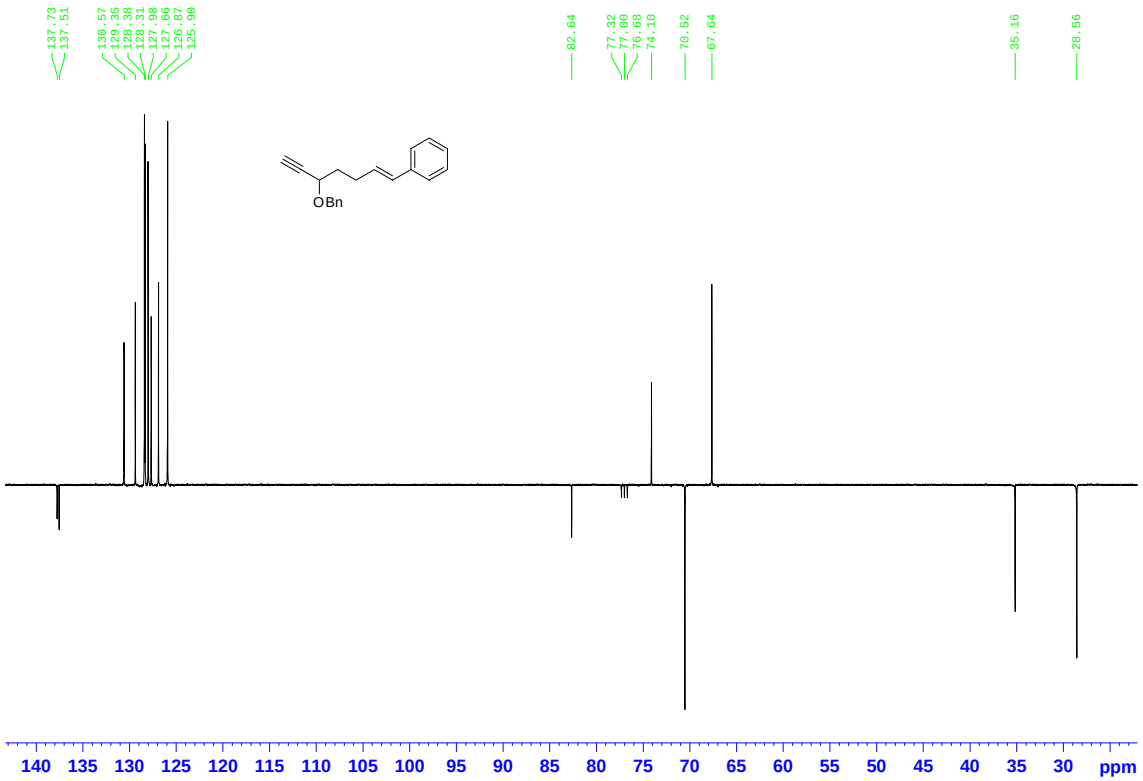
2.01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130
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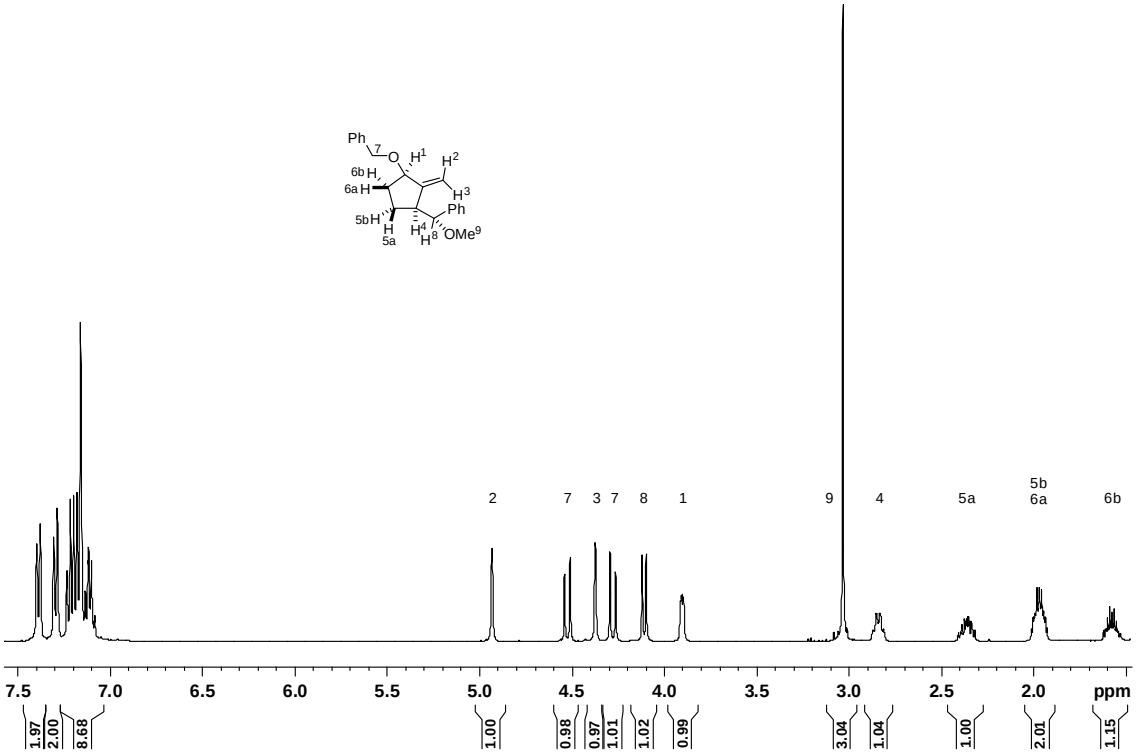
30
ppm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H2
6b H
6a H
H3
Ph
5b H
H
5a
H4
H8
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7
3
7
8
1
9
4
5a
5b
6a
6b
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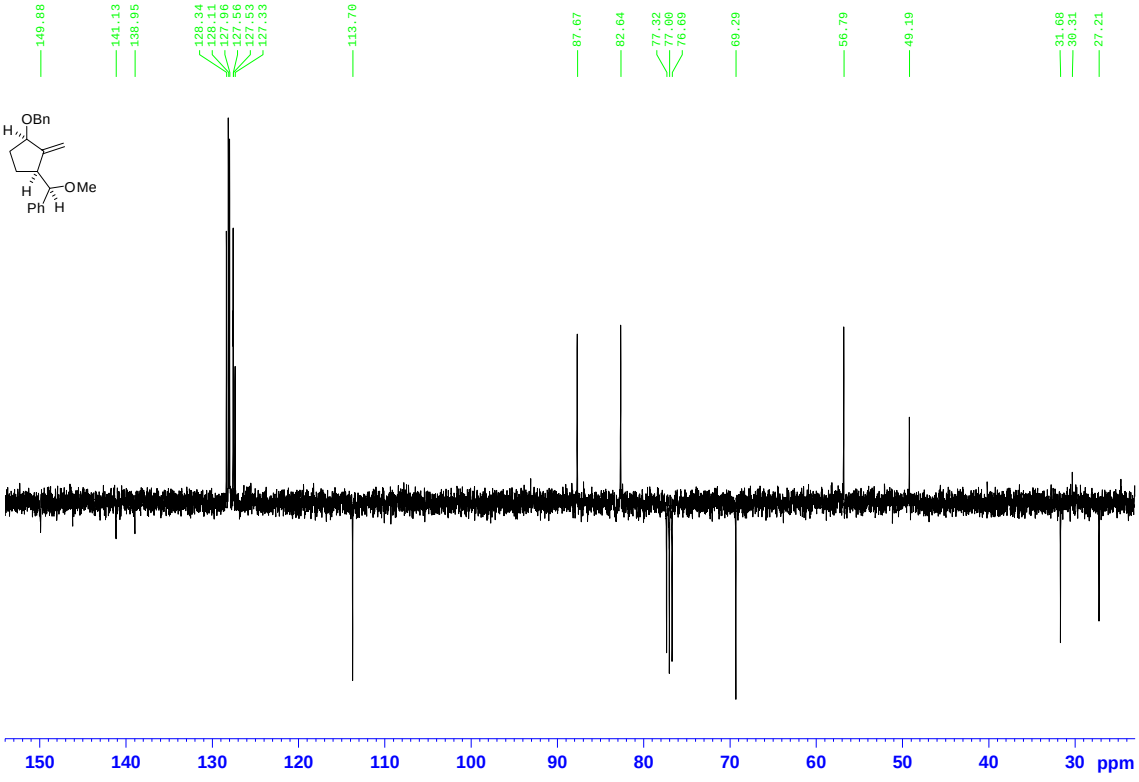
1.15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127.53
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113.70
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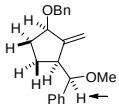
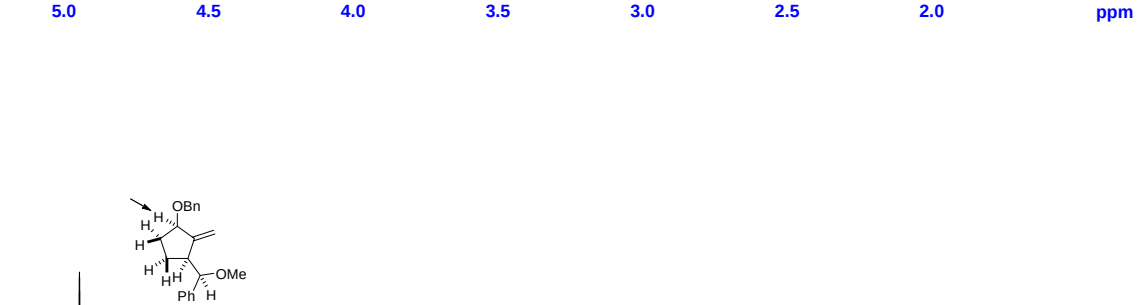
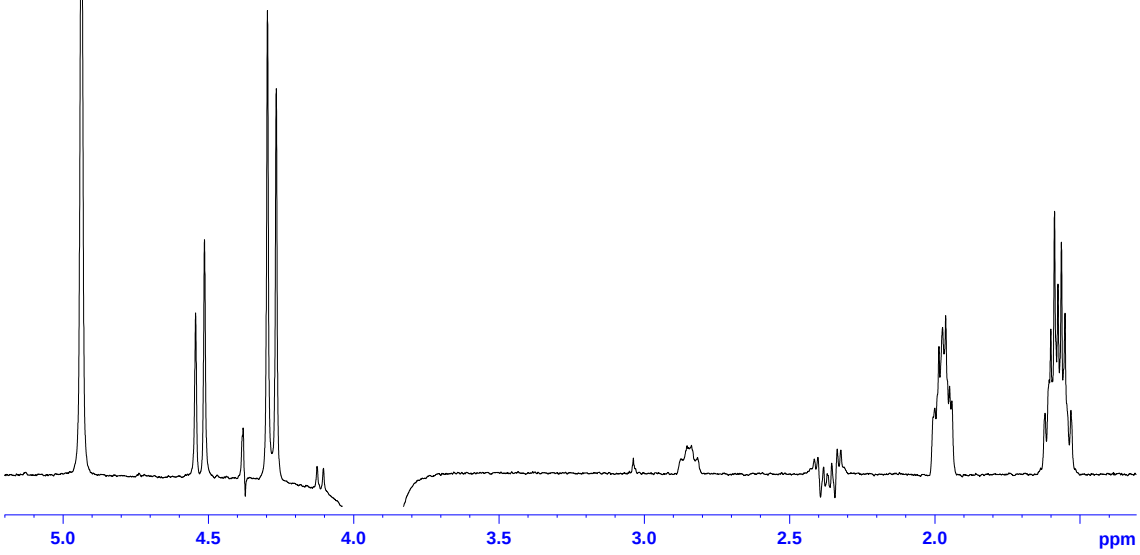
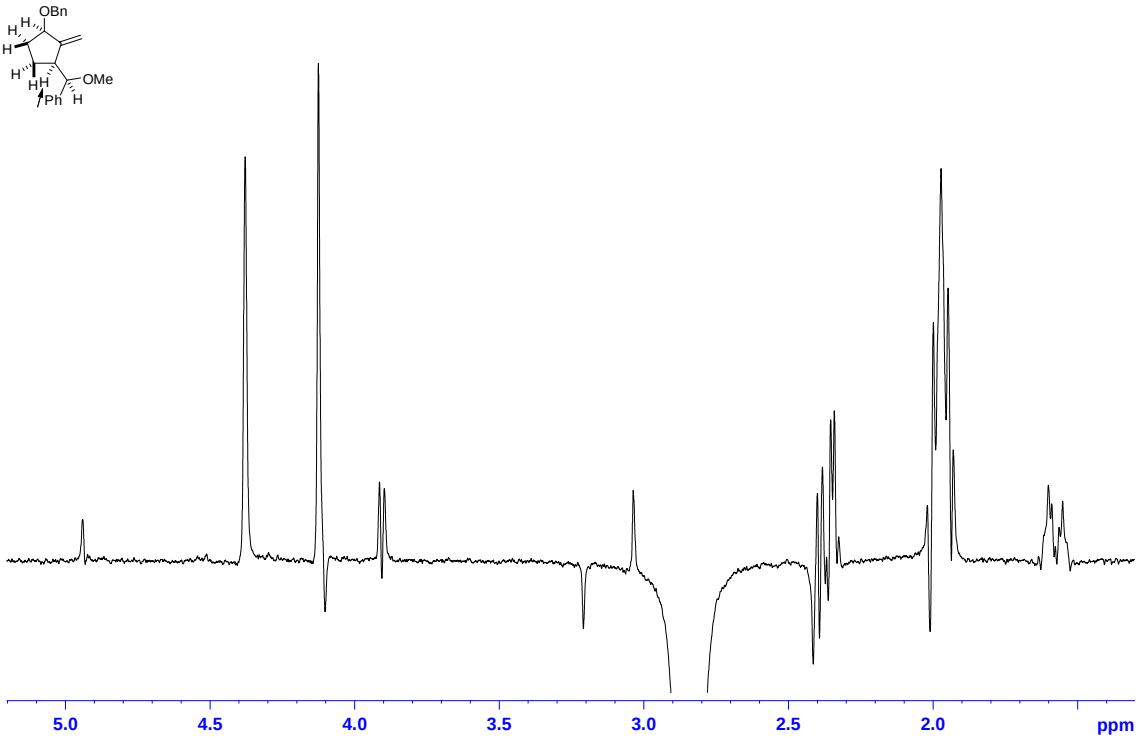
49.19
31.68
30.31
27.21
OBn
H
H
OMe
Ph
H
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

NOESY1D-experiments on ((*R)-((1*S**,3*R**)-3-(benzyloxy)-2-methylenecyclopentyl) (methoxy)methyl)benzene (27)**





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4.0
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3.0
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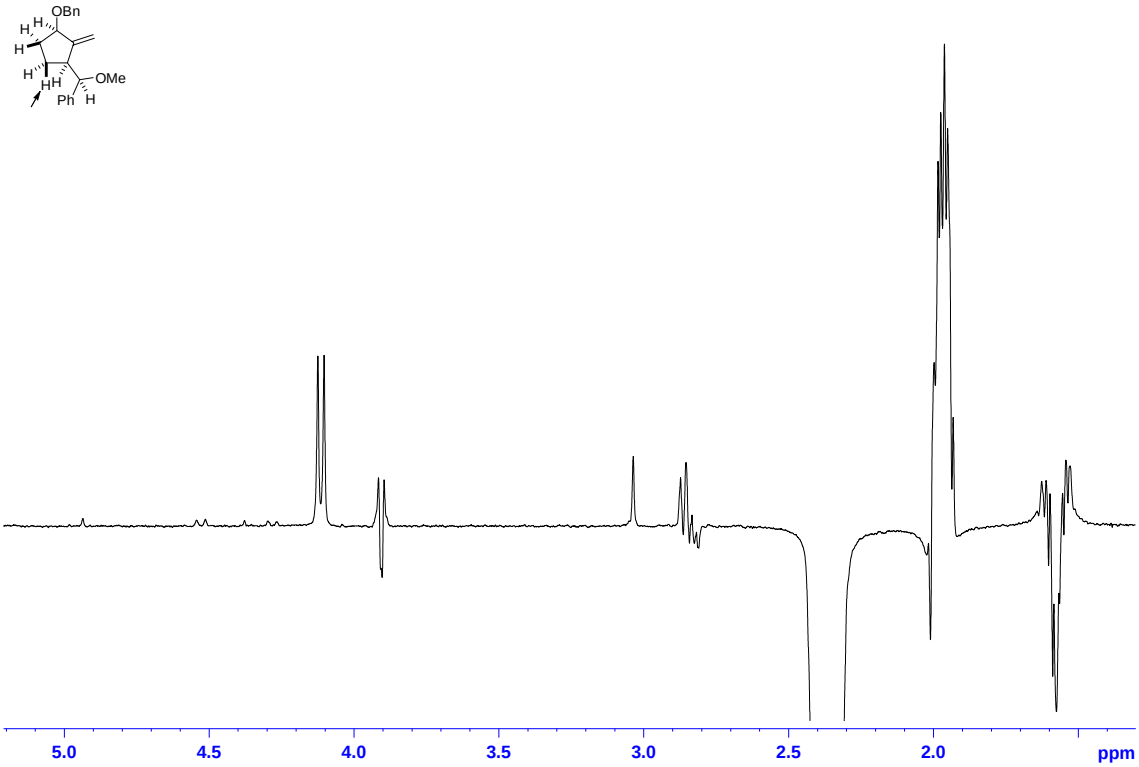
2.0
ppm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OMe
Ph
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4.0
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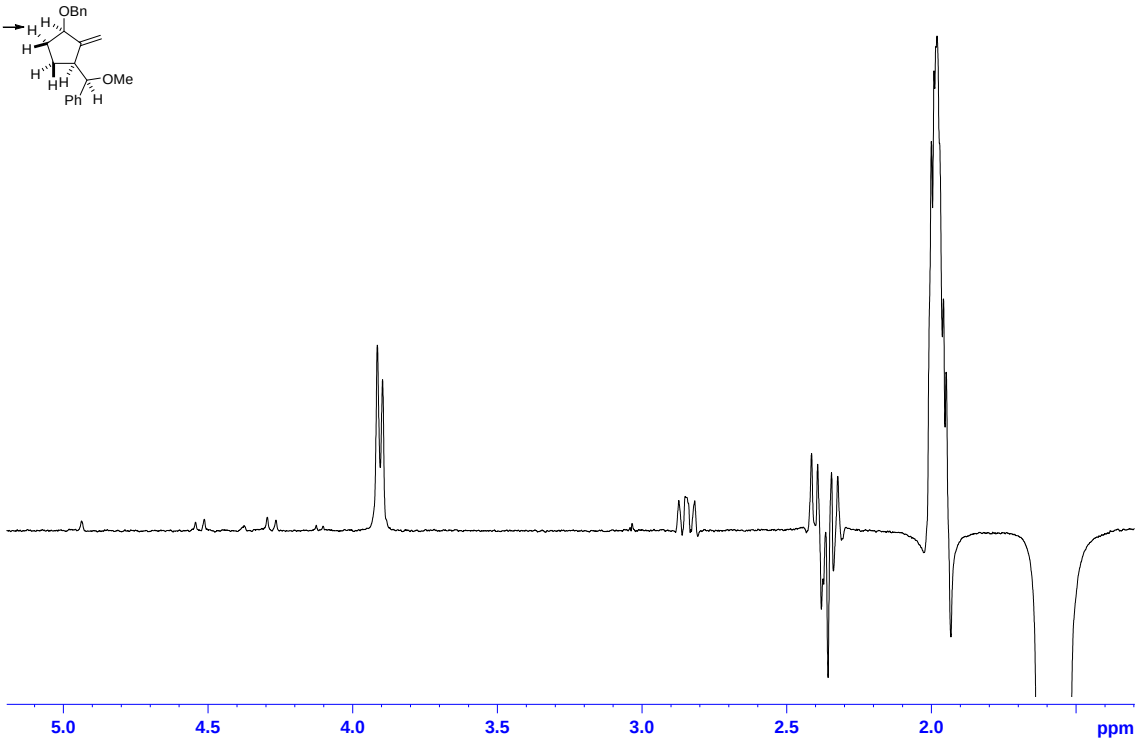
2.5
2.0
ppm



Crystallographic data for compound (±)-3

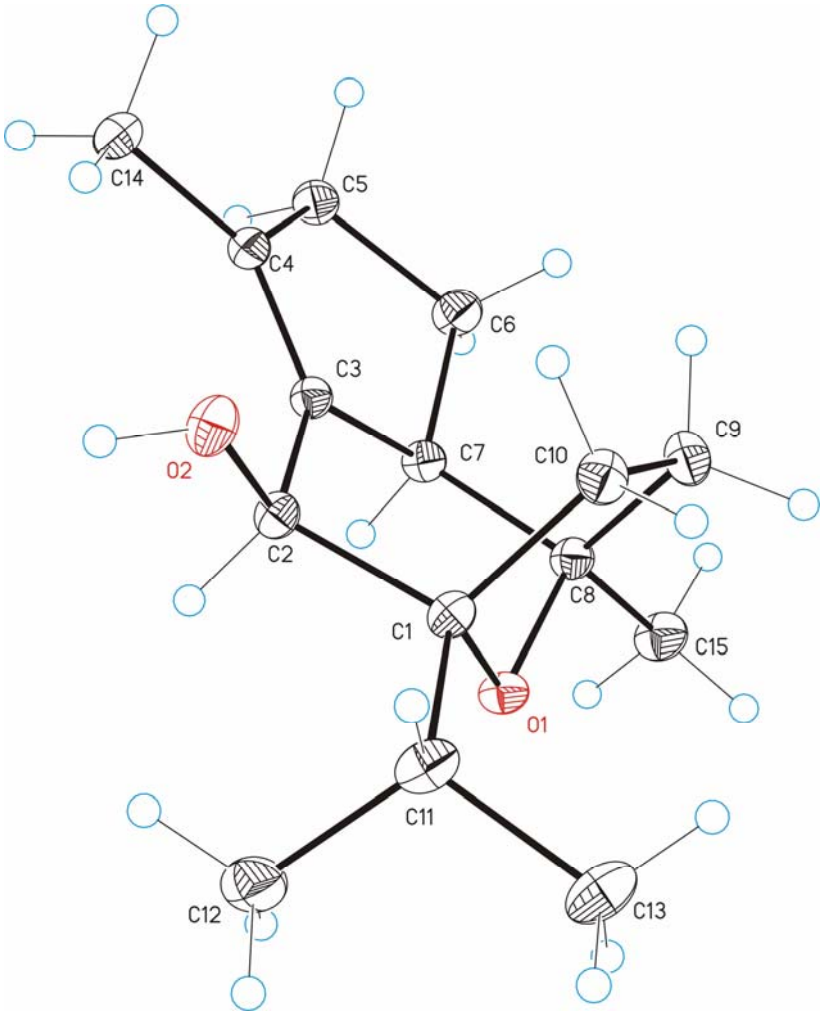


Table 1. Crystal data and structure refinement for e20849P21c.

Identification code	e20849p21c	
Empirical formula	C15 H24 O2	
Formula weight	236.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.8542(4) Å	α = 90°.
	b = 7.8544(2) Å	β = 108.2520(10)°.
	c = 11.0204(3) Å	γ = 90°.
Volume	1303.27(6) Å3	
Z	4	
Density (calculated)	1.205 Mg/m3	
Absorption coefficient	0.077 mm-1	

F(000)	520
Crystal size	0.60 x 0.60 x 0.20 mm3
Theta range for data collection	3.74 to 39.32°.
Index ranges	-28<=h<=27, -13<=k<=13, -14<=l<=19
Reflections collected	30679
Independent reflections	7505 [R(int) = 0.0191]
Completeness to theta = 39.32°	97.1 %
Absorption correction	SADABS (Broker-Nonius)
Max. and min. transmission	0.9847 and 0.9550
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	7505 / 0 / 159
Goodness-of-fit on F2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.1092
R indices (all data)	R1 = 0.0430, wR2 = 0.1137
Largest diff. peak and hole	0.556 and -0.227 e.Å-3

Table 2. Bond lengths [Å] and angles [°] for e20849P21c.

O(1)-C(1)	1.4478(5)
O(1)-C(8)	1.4522(6)
C(1)-C(11)	1.5367(7)
C(1)-C(10)	1.5452(7)
C(1)-C(2)	1.5496(6)
O(2)-C(2)	1.4194(6)
C(2)-C(3)	1.5066(6)
C(3)-C(4)	1.3424(6)
C(3)-C(7)	1.5163(6)
C(4)-C(14)	1.4936(7)
C(4)-C(5)	1.5151(7)
C(5)-C(6)	1.5353(7)
C(6)-C(7)	1.5387(7)
C(7)-C(8)	1.5360(6)
C(8)-C(15)	1.5164(7)
C(8)-C(9)	1.5374(7)
C(9)-C(10)	1.5380(7)
C(11)-C(12)	1.5319(9)
C(11)-C(13)	1.5326(7)

C(1)-O(1)-C(8)	106.03(3)
O(1)-C(1)-C(11)	109.54(4)
O(1)-C(1)-C(10)	104.33(4)
C(11)-C(1)-C(10)	114.24(4)
O(1)-C(1)-C(2)	106.91(3)
C(11)-C(1)-C(2)	112.16(4)
C(10)-C(1)-C(2)	109.14(4)
O(2)-C(2)-C(3)	113.99(4)
O(2)-C(2)-C(1)	107.47(4)
C(3)-C(2)-C(1)	109.39(4)
C(4)-C(3)-C(2)	131.39(4)
C(4)-C(3)-C(7)	111.42(4)
C(2)-C(3)-C(7)	117.12(4)
C(3)-C(4)-C(14)	130.03(4)
C(3)-C(4)-C(5)	110.55(4)
C(14)-C(4)-C(5)	119.29(4)
C(4)-C(5)-C(6)	103.77(4)
C(5)-C(6)-C(7)	104.35(4)
C(3)-C(7)-C(8)	111.32(4)
C(3)-C(7)-C(6)	103.14(4)
C(8)-C(7)-C(6)	118.26(4)
O(1)-C(8)-C(15)	107.62(4)
O(1)-C(8)-C(7)	105.58(4)
C(15)-C(8)-C(7)	112.28(4)
O(1)-C(8)-C(9)	102.65(4)
C(15)-C(8)-C(9)	114.38(4)
C(7)-C(8)-C(9)	113.28(4)
C(8)-C(9)-C(10)	104.46(4)
C(9)-C(10)-C(1)	104.48(4)
C(12)-C(11)-C(13)	109.78(5)
C(12)-C(11)-C(1)	113.68(4)
C(13)-C(11)-C(1)	111.79(4)

Symmetry transformations used to generate equivalent atoms:

Table 3. Torsion angles [°] for e20849P21c.

C(8)-O(1)-C(1)-C(11)	-161.49(4)
C(8)-O(1)-C(1)-C(10)	-38.79(4)
C(8)-O(1)-C(1)-C(2)	76.77(4)
O(1)-C(1)-C(2)-O(2)	-179.56(4)
C(11)-C(1)-C(2)-O(2)	60.37(5)
C(10)-C(1)-C(2)-O(2)	-67.26(5)
O(1)-C(1)-C(2)-C(3)	-55.31(5)
C(11)-C(1)-C(2)-C(3)	-175.39(4)
C(10)-C(1)-C(2)-C(3)	56.98(5)
O(2)-C(2)-C(3)-C(4)	-24.74(7)
C(1)-C(2)-C(3)-C(4)	-145.08(5)
O(2)-C(2)-C(3)-C(7)	158.74(4)
C(1)-C(2)-C(3)-C(7)	38.40(5)
C(2)-C(3)-C(4)-C(14)	-1.17(9)
C(7)-C(3)-C(4)-C(14)	175.51(5)
C(2)-C(3)-C(4)-C(5)	-176.91(5)
C(7)-C(3)-C(4)-C(5)	-0.24(6)
C(3)-C(4)-C(5)-C(6)	-15.77(6)
C(14)-C(4)-C(5)-C(6)	167.97(4)
C(4)-C(5)-C(6)-C(7)	24.69(5)
C(4)-C(3)-C(7)-C(8)	143.87(4)
C(2)-C(3)-C(7)-C(8)	-38.93(5)
C(4)-C(3)-C(7)-C(6)	16.06(5)
C(2)-C(3)-C(7)-C(6)	-166.74(4)
C(5)-C(6)-C(7)-C(3)	-24.66(5)
C(5)-C(6)-C(7)-C(8)	-147.98(4)
C(1)-O(1)-C(8)-C(15)	164.39(4)
C(1)-O(1)-C(8)-C(7)	-75.51(4)
C(1)-O(1)-C(8)-C(9)	43.38(4)
C(3)-C(7)-C(8)-O(1)	54.66(5)
C(6)-C(7)-C(8)-O(1)	173.79(4)
C(3)-C(7)-C(8)-C(15)	171.66(4)
C(6)-C(7)-C(8)-C(15)	-69.21(6)
C(3)-C(7)-C(8)-C(9)	-56.90(5)
C(6)-C(7)-C(8)-C(9)	62.24(5)
O(1)-C(8)-C(9)-C(10)	-30.15(5)

C(15)-C(8)-C(9)-C(10)	-146.40(4)
C(7)-C(8)-C(9)-C(10)	83.20(5)
C(8)-C(9)-C(10)-C(1)	7.38(5)
O(1)-C(1)-C(10)-C(9)	18.09(5)
C(11)-C(1)-C(10)-C(9)	137.66(4)
C(2)-C(1)-C(10)-C(9)	-95.89(4)
O(1)-C(1)-C(11)-C(12)	-72.94(5)
C(10)-C(1)-C(11)-C(12)	170.46(4)
C(2)-C(1)-C(11)-C(12)	45.60(5)
O(1)-C(1)-C(11)-C(13)	52.03(6)
C(10)-C(1)-C(11)-C(13)	-64.57(6)
C(2)-C(1)-C(11)-C(13)	170.57(4)

Symmetry transformations used to generate equivalent atoms:

Crystallographic data for compound (±)-17

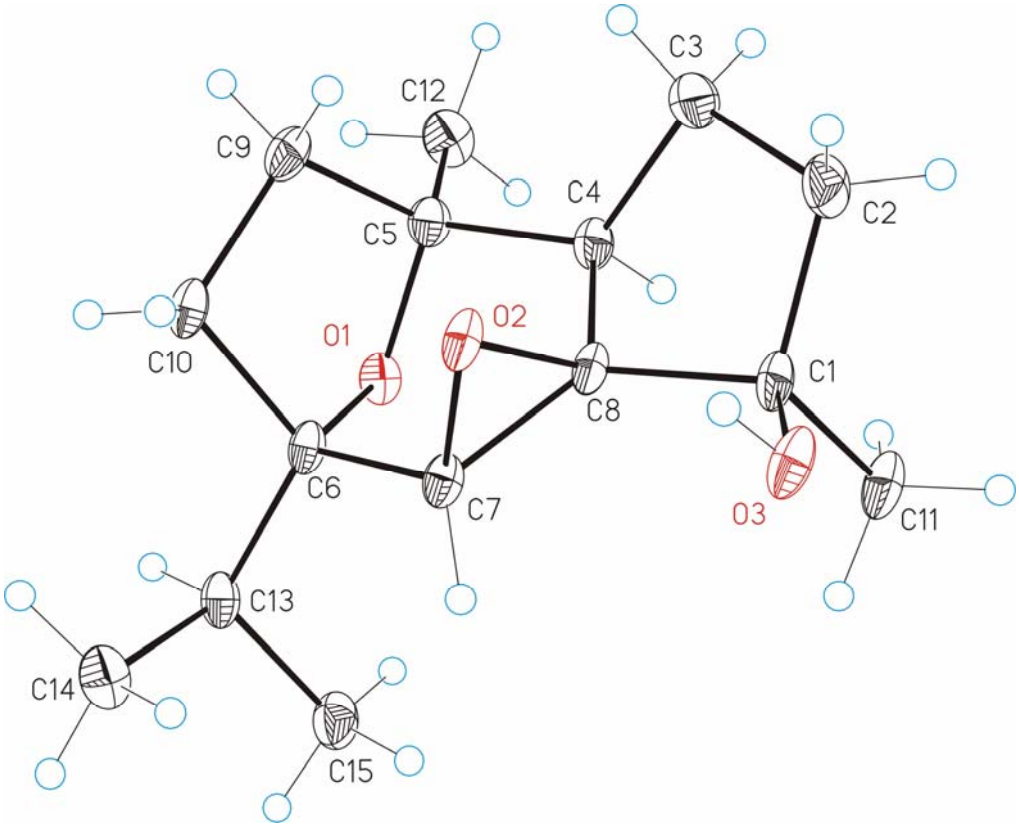


Table 1. Crystal data and structure refinement for E20847_0m.

Identification code	e20847_0m	
Empirical formula	C15 H24 O3	
Formula weight	252.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7861(5) Å	α = 106.620(3)°.
	b = 8.9090(5) Å	β = 93.492(4)°.
	c = 9.9947(6) Å	γ = 109.880(3)°.
Volume	694.03(7) $Å^3$	
Z	2	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	276	
Crystal size	0.20 x 0.10 x 0.02 mm^3	
Theta range for data collection	2.77 to 32.29°.	
Index ranges	-12<=h<=13, -13<=k<=13, -14<=l<=13	

Reflections collected	11917
Independent reflections	4520 [R(int) = 0.0462]
Completeness to theta = 32.29°	91.4 %
Absorption correction	SADABS (Bruker-Nonius)
Max. and min. transmission	0.9984 and 0.9838
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4520 / 0 / 168
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0616, wR2 = 0.1632
R indices (all data)	R1 = 0.0928, wR2 = 0.1838
Largest diff. peak and hole	0.606 and -0.324 e.$Å^{-3}$

Table 2. Bond lengths [Å] and angles [°] for E20847_0m.

O(1)-C(6)	1.4432(17)
O(1)-C(5)	1.4538(19)
C(1)-O(3)	1.4134(19)
C(1)-C(11)	1.518(2)
C(1)-C(8)	1.5273(19)
C(1)-C(2)	1.562(2)
O(2)-C(8)	1.4517(17)
O(2)-C(7)	1.4535(19)
C(2)-C(3)	1.553(2)
C(3)-C(4)	1.537(2)
C(4)-C(8)	1.500(2)
C(4)-C(5)	1.542(2)
C(5)-C(12)	1.511(2)
C(5)-C(9)	1.547(2)
C(6)-C(13)	1.528(2)
C(6)-C(10)	1.535(2)
C(6)-C(7)	1.540(2)
C(7)-C(8)	1.460(2)
C(9)-C(10)	1.542(2)
C(13)-C(15)	1.525(2)
C(13)-C(14)	1.534(2)
C(6)-O(1)-C(5)	104.88(11)
O(3)-C(1)-C(11)	106.25(12)
O(3)-C(1)-C(8)	112.19(11)

C(11)-C(1)-C(8)	112.88(13)
O(3)-C(1)-C(2)	113.51(14)
C(11)-C(1)-C(2)	112.43(12)
C(8)-C(1)-C(2)	99.75(11)
C(8)-O(2)-C(7)	60.36(9)
C(3)-C(2)-C(1)	107.87(13)
C(4)-C(3)-C(2)	104.52(13)
C(8)-C(4)-C(3)	101.19(13)
C(8)-C(4)-C(5)	112.28(11)
C(3)-C(4)-C(5)	123.51(13)
O(1)-C(5)-C(12)	107.64(14)
O(1)-C(5)-C(4)	104.19(11)
C(12)-C(5)-C(4)	111.23(12)
O(1)-C(5)-C(9)	103.81(11)
C(12)-C(5)-C(9)	113.34(12)
C(4)-C(5)-C(9)	115.59(13)
O(1)-C(6)-C(13)	107.75(12)
O(1)-C(6)-C(10)	102.11(11)
C(13)-C(6)-C(10)	113.91(11)
O(1)-C(6)-C(7)	109.33(10)
C(13)-C(6)-C(7)	112.92(12)
C(10)-C(6)-C(7)	110.17(13)
O(2)-C(7)-C(8)	59.76(9)
O(2)-C(7)-C(6)	112.97(11)
C(8)-C(7)-C(6)	116.47(12)
O(2)-C(8)-C(7)	59.88(9)
O(2)-C(8)-C(4)	115.95(11)
C(7)-C(8)-C(4)	119.84(13)
O(2)-C(8)-C(1)	111.62(12)
C(7)-C(8)-C(1)	131.79(13)
C(4)-C(8)-C(1)	106.57(11)
C(10)-C(9)-C(5)	104.38(12)
C(6)-C(10)-C(9)	103.26(11)
C(15)-C(13)-C(6)	112.56(11)
C(15)-C(13)-C(14)	111.84(13)
C(6)-C(13)-C(14)	110.75(13)

Symmetry transformations used to generate equivalent atoms:

Table 3. Torsion angles [°] for E20847_0m.

O(3)-C(1)-C(2)-C(3)	-138.02(13)
C(11)-C(1)-C(2)-C(3)	101.34(15)
C(8)-C(1)-C(2)-C(3)	-18.50(16)
C(1)-C(2)-C(3)-C(4)	-7.96(17)
C(2)-C(3)-C(4)-C(8)	31.71(15)
C(2)-C(3)-C(4)-C(5)	158.19(14)
C(6)-O(1)-C(5)-C(12)	-160.77(11)
C(6)-O(1)-C(5)-C(4)	81.04(12)
C(6)-O(1)-C(5)-C(9)	-40.35(13)
C(8)-C(4)-C(5)-O(1)	-51.42(16)
C(3)-C(4)-C(5)-O(1)	-172.94(13)
C(8)-C(4)-C(5)-C(12)	-167.11(14)
C(3)-C(4)-C(5)-C(12)	71.36(19)
C(8)-C(4)-C(5)-C(9)	61.79(17)
C(3)-C(4)-C(5)-C(9)	-59.73(19)
C(5)-O(1)-C(6)-C(13)	167.86(10)
C(5)-O(1)-C(6)-C(10)	47.60(13)
C(5)-O(1)-C(6)-C(7)	-69.07(13)
C(8)-O(2)-C(7)-C(6)	-108.26(13)
O(1)-C(6)-C(7)-O(2)	95.05(13)
C(13)-C(6)-C(7)-O(2)	-145.02(12)
C(10)-C(6)-C(7)-O(2)	-16.40(15)
O(1)-C(6)-C(7)-C(8)	28.62(17)
C(13)-C(6)-C(7)-C(8)	148.56(13)
C(10)-C(6)-C(7)-C(8)	-82.83(15)
C(7)-O(2)-C(8)-C(4)	110.94(15)
C(7)-O(2)-C(8)-C(1)	-126.78(14)
C(6)-C(7)-C(8)-O(2)	102.38(13)
O(2)-C(7)-C(8)-C(4)	-104.50(14)
C(6)-C(7)-C(8)-C(4)	-2.1(2)
O(2)-C(7)-C(8)-C(1)	93.03(17)
C(6)-C(7)-C(8)-C(1)	-164.59(15)
C(3)-C(4)-C(8)-O(2)	78.89(14)
C(5)-C(4)-C(8)-O(2)	-54.68(18)
C(3)-C(4)-C(8)-C(7)	147.53(13)
C(5)-C(4)-C(8)-C(7)	14.0(2)

C(3)-C(4)-C(8)-C(1)	-46.02(15)
C(5)-C(4)-C(8)-C(1)	-179.59(12)
O(3)-C(1)-C(8)-O(2)	32.97(17)
C(11)-C(1)-C(8)-O(2)	152.97(12)
C(2)-C(1)-C(8)-O(2)	-87.51(14)
O(3)-C(1)-C(8)-C(7)	-35.3(2)
C(11)-C(1)-C(8)-C(7)	84.7(2)
C(2)-C(1)-C(8)-C(7)	-155.81(16)
O(3)-C(1)-C(8)-C(4)	160.48(13)
C(11)-C(1)-C(8)-C(4)	-79.51(16)
C(2)-C(1)-C(8)-C(4)	40.01(16)
O(1)-C(5)-C(9)-C(10)	16.65(14)
C(12)-C(5)-C(9)-C(10)	133.14(14)
C(4)-C(5)-C(9)-C(10)	-96.78(14)
O(1)-C(6)-C(10)-C(9)	-35.08(14)
C(13)-C(6)-C(10)-C(9)	-150.94(13)
C(7)-C(6)-C(10)-C(9)	80.99(14)
C(5)-C(9)-C(10)-C(6)	10.99(15)
O(1)-C(6)-C(13)-C(15)	63.33(15)
C(10)-C(6)-C(13)-C(15)	175.84(13)
C(7)-C(6)-C(13)-C(15)	-57.51(17)
O(1)-C(6)-C(13)-C(14)	-170.65(11)
C(10)-C(6)-C(13)-C(14)	-58.14(16)
C(7)-C(6)-C(13)-C(14)	68.51(15)

Symmetry transformations used to generate equivalent atoms: