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SUPPORTING INFORMATION FOR

Improved methodology for the synthesis of 1α,25-dihydroxy-20-*epi*-vitamin D_3 (MC 1288) and Gemini analog Ro-438-3582

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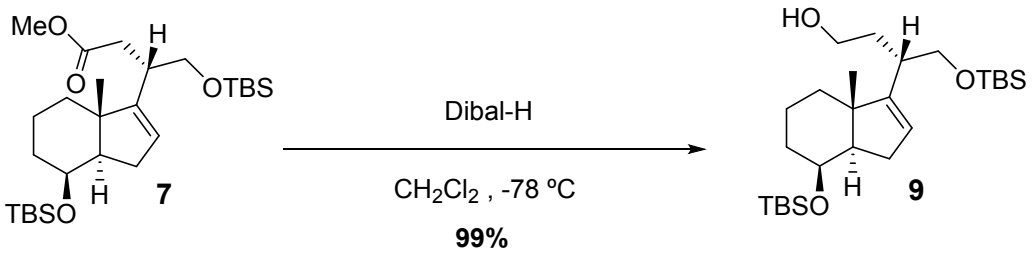
Experimental procedure

General: Solvents were purified and dried by standard procedures before use. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker ARX-400 spectrometer (400 MHz for ^{1}H NMR, 100.61 MHz for ^{13}C NMR) using TMS as internal standard (Chemical shifts in δ values, J in Hz). Flash chromatography (FC) was performed on silica gel (Merck 60, 230-400 mesh); analytical TLC was performed on plates precoated with silica gel (Merck 60 F254, 0.25mm); mass spectra (FAB, EI) were recorded using FISONS VG and electron spray ionization (ESI-MS) spectroscopy was recorded using Bruker FTMS APEXIII. Melting points were obtained in open capillary tubes and are not corrected. Optical rotations were obtained using a Jasco P-2000 polarimeter. IR spectra were recorded with a JASCO FT/I(*R*)-6100 spectrophotometer.

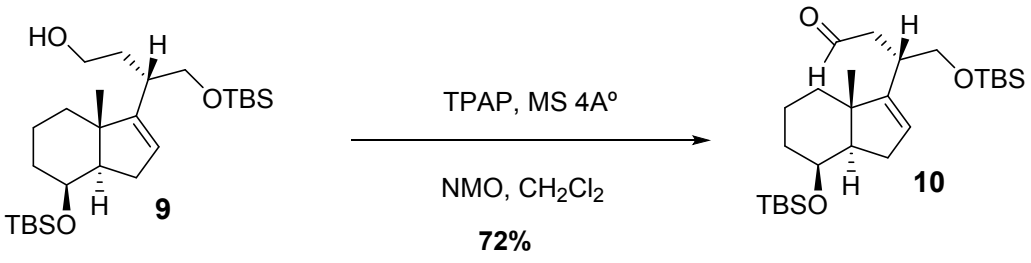
(*S*)-4-((tert-butyldimethylsilyl)oxy)-3-((3a*S*,7*S*,7a*R*)-7-((tert-butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl)butan-1-ol (9)



To a solution ester **7** (1.4 g, 2.7 mmol) en CH_2Cl_2 (15 mL) at -78 ºC was added Dibal-H (8.3 mL, 8.3 mmol, 1M sln in hexane) and the mixture was stirred for 3 h. ^{t}BuOMe (26 mL) and H_2O (3.2 mL) were added and the mixture allowed to reach room temperatura. Stirring was contnued till the formation of a White gel before adding H_2O (3.2 mL) and a 4 M aqueous solution of NaOH (3.2 mL). Stirring was continued till the formation of a white solid. Na_2SO_4 and silica gel were added and the mixture stirred for 20 mn. The solid was separated by filtration and the filtrate was concentrated to afford a residue which was chromatographed on silica gel using 3% EtOAc/Hexane as eluent, affording compound **9** (1.22 g, 99%) as a colourless liquid; Rf: 0.47 (20% EtOAc/Hexane); **IR (NaCl, cm^{-1}):** 3349, 2927, 2856, 1471, 1252, 1025, 833, 771, 667; **$[\alpha]^{23}_{D}$=**

+24.56 (c 1.32, $CHCl_3$); ^{1}**H-NMR ($CDCl_3$, δ):** 5.35 (1H, d, *J*=1.7 Hz, H-16), 4.08 (1H, s, H-8), 3.61 (4H, m, H-21), 3.09 (1H, s, OH), 2.21 (2H, m), 1.83 (5H, m), 1.53 (3H, m), 1.26 (2H, m), 1.01 (3H, s, CH_3-18), 0.91 (9H, s, CH_3-^{t}Bu), 0.89 (9H, s, CH_3-^{t}Bu), 0.08 (6H, s, 2 CH_3-Si), 0.03 (6H, s, 2 CH_3-Si); ^{13}**C- NMR ($CDCl_3$, δ):** 156.36 (C-17), 122.3 (CH-16), 68.87 (CH-8), 67.86 (CH_2-21), 61.72 (CH_2), 54.45 (CH-14), 47.01 (C-13), 37.85 (CH-20), 37.74 (CH_2), 35.22 (CH_2), 34.63 (CH_2), 31.05 (CH_2), 25.91 (CH_3-^{t}Bu), 25.77 (CH_3-^{t}Bu), 19.20 (CH_3-18), 18.27 (C-^{t}Bu), 17.97 (CH_2), -4.86 (CH_3-Si), -5.19 (CH_3-Si), -5.35 (CH_3-Si), -5.45 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 491(M^++Na,44), 451 (16), 337 (M^+-OTBS,100); **HRMS (ESI):** 491.3317 calculated for $C_{26}H_{52}NaO_3Si_2$,found 491.3324.

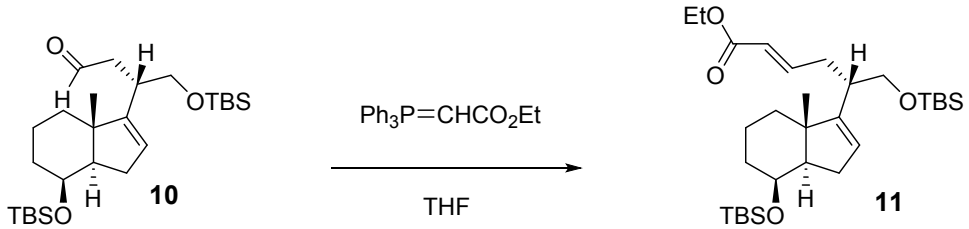
(*S*)-4-((tert-butyldimethylsilyl)oxy)-3-((3a*S*,7*S*,7a*R*)-7-((tert-butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl)butanal (10)



To a solution of alcohol **9** (497 mg, 1.057 mmol) in CH_2Cl_2 (11 mL) were added 4Å molecular sieves (235 mg), NMO (372 mg, 3.17 mmol) and a catalytic amount of TPAP.The resulting greenish suspension was stirred at room temperatura for 3 h. The solvent was rotatory evaporated to afford a residue which was chromatographed on silica gel using 1% EtOAc/Hexane as eluent, affording aldehyde **10** (352 mg, 72%) as a colourless liquid; Rf: 0.94 (10% EtOAc/Hexane); **IR (NaCl, cm^{-1}):** 3419, 3405, 2928, 2856, 1716, 1471, 1252,1061, 835; **[α]$^{23}_D$=** +25.84 (c 1.42, $CHCl_3$); ^{1}**H- NMR ($CDCl_3$, δ):** 9.69 (1H, s, CHO), 5.43 (1H, s, H-16), 4.11 (1H, s, H-8), 3.72 (1H, dd, *J*=9.7/3.9 Hz, H-21), 3.48 (1H, t, *J*=9.8 Hz, H-21), 2.78 (1H, m), 2.60 (1H, ddd, *J*=15.9/7.2/2.9 Hz, H-22), 2.42 (1H, ddd, *J*=15.9/6.5/2.2 Hz, H-22), 2.23 (1H, dd, *J*=13.7/12.6 Hz), 1.90 (2H, m), 1.59 (5H, m), 1.30 (1H, m), 1.08 (3H, s, CH_3-18), 0.89 (18H, s, CH_3-^{t}Bu), 0.00 (12H, s, 2 CH_3-Si); ^{13}**C- NMR ($CDCl_3$, δ):** 202.9 (C=O), 154.2 (C-17), 124.3 (CH-16), 68.8 (CH-8), 66.9 (CH_2-21), 54.4 (CH-14), 47.4 (CH_2), 46.8 (C-13),

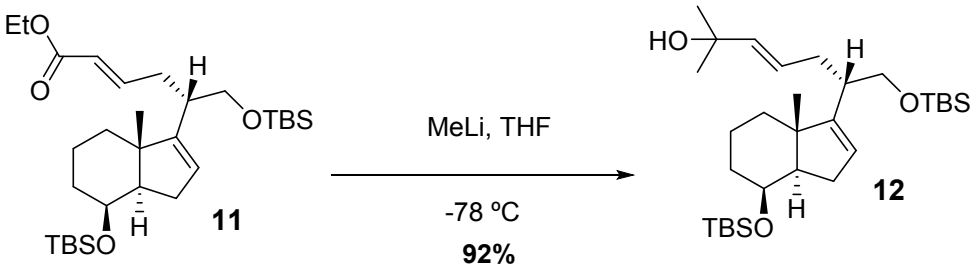
35.3 (CH_2), 35.2 (CH-20), 34.4 (CH_2), 31.1 (CH_2), 25.8 (CH_3-^{t}Bu), 25.7 (CH_3-^{t}Bu), 19.3 (CH_3-18), 18.2 (C-^{t}Bu), 17.9 (C-^{t}Bu), 17.8 (CH_2), -4.8 (CH_3-Si), -5.2 (CH_3-Si), -5.4 (CH_3-Si), -5.42 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 595 (100), 481 (9), 357 (M^+-OTBS+Na,10); **HRMS (ESI):** 466.3317 calculated for $C_{26}H_{50}O_3Si_2$, found 466.3324.

Ethyl(*S*,*E*)-6-((tert-butyldimethylsilyl)oxy)-5-((3a*S*,7S,7a*R*)-7-((tert-butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl)hex-2-enoate (11)



To a solution of aldehyde **10** (352 mg, 0.75 mmol) in THF (6 mL) was added $Ph_3P{=}CHCO_2Et$ (530 mg, 1.5 mmol) and the mixture was stirred at room temperatura for 2 h. The solvent was rotatory evaporated to afford a residue which was chromatographed on silica gel using 1% EtOAc/Hexane as eluent, affording compound **10** (390 mg, 96%) as a colourless liquid, Rf: 0.90 (10% EtOAc/Hexane); **IR (NaCl, cm^{-1}):** 2927, 2855, 1721, 1471, 1253, 1200, 1080, 834, 773, 677; **$[\alpha]^{24}_D$=** +10.62 (c 1.37, $CHCl_3$); ^{1}**H- NMR ($CDCl_3$, δ):** 6.92 (1H, m, H-23), 5.77 (1H, d, *J*=16 Hz, H-24), 5.37 (1H, s, H-16), 4.19 (2H, c, *J*=7 Hz, CH_2-OEt), 4.10 (1H, s, H-8), 3.59 (1H, dd, *J*=10/4 Hz, H-21), 3.48 (1H, t, *J*=10 Hz, H-21), 2.53 (1H, dd, *J*=16.2/7.8 Hz), 2.25 (3H, m), 1.90 (2H, m), 1.67 (3H, m), 1.47 (1H, m), 1.29 (3H, t, *J*=7 Hz, CH_3-OEt), 1.25 (1H, m), 1.01 (3H, s, CH_3-18), 0.9 (9H, s, CH_3-^{t}Bu), 0.89 (9H, s, CH_3-^{t}Bu), 0.03 (12H, s, 4 CH_3-Si); ^{13}**C- NMR ($CDCl_3$, δ):** 166.6 (C=O), 154.5 (C-17), 148.4 (CH-23), 123.5 (CH-24), 122.3 (CH-16) 68.9 (CH-8), 66.3 (CH_2-21), 60.0 (**C**H_2-OEt), 54.3 (CH-14), 46.9 (C-13), 38.9 (CH-20), 35.2 (CH_2), 35.1 (CH_2), 34.6 (CH_2), 31.1 (CH_2), 25.9 (CH_3-^{t}Bu), 25.7 (CH_3-^{t}Bu), 19.3 (C-^{t}Bu), 18.3 (2 C-^{t}Bu), 18.0 (CH_2), 14.3 (CH_3-OEt), -4.8 (CH_3Si), -5.2 (CH_3-Si), -5.3(CH_3-Si), -5.4 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 559 (M^++Na,100), 403 (43); **HRMS (ESI):** 537.3789 calculated for $C_{30}H_{57}O_4Si_2$, found 537.3793.

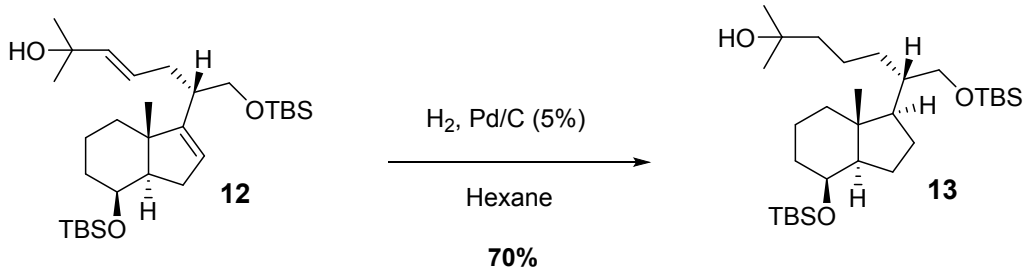
(*S*,*E*)-7-((tert-butyldimethylsilyl)oxy)-6-((3a*S*,7*S*,7a*R*)-7-((tert-butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl)-2-methylhept-3-en-2-ol (12)



To a solution of ester **11**(65 mg, 0.121 mmol) in THF (2 mL) at -78 ºC was added MeLi·LiBr (0.41 ml, 0.61 mmol, 1.5 M solution in ethyl ether) and the mixture was stirred for 30 mn. H_2O (20 mL) was added and the product extracted with CH_2Cl_2 (3 x15 mL). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 20% EtOAc/Hexane as eluent, affording compound **12** (58 mg, 92%) as a colourless liquid, Rf: 0.43 (10% AcOEt/Hexano); **IR (ATR, cm^{-1}):** 3361, 2952, 2927, 2855, 1471, 1462, 1360, 834, 771; **$[\alpha]^{22}_D$** = +26.49(c 1.00, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 5.57 (2H, m, H-23, H-24), 5.32 (1H, s, H-16), 4.11 (1H, s, H-8), 3.55 (1H, m, H-22), 3.48 (1H, t, *J* = 9.3, Hz H-22), 2.35 (1H, m), 2.23 (2H, m), 2.10 (1H, m), 1.90 (2H, m), 1.65 (3H, m), 1.47 (3H, m), 1.30 (6H, 2 CH_3), 1.01 (3H, s, CH_3-18), 0.95 (18H, s, 6 CH_3-^{t}Bu), 0.05 (6H, s, 2 CH_3-Si), 0.03 (6H, s, 2 CH_3-Si); **^{13}C-NMR ($CDCl_3$, δ):**155.2 (C-17), 139.4 (CH-24), 125.5 (CH), 122.6 (CH), 70.7 (C-25), 68.9 (CH-8), 66.3 (CH_2-22), 54.4 (CH-14), 46.8 (C-13), 39.5 (CH-20), 35.3 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 31.1 (CH_2), 29.9 (CH_3), 29.9 (CH_3), 25.9 (CH_3-^{t}Bu), 25.8 (CH_3-^{t}Bu), 19.2 (CH_3-18), 18.3 (C-^{t}Bu), 18.0 (CH_2), -4.3 (CH_3-Si), -4.8 (CH_3-Si), -5.2 (CH_3-Si), -5.3 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 505 (M^+-OH,100), 506 (27), 545

(M$^+$+Na,12), 546 (3); **HRMS (ESI):** 545.3817 calculated for $C_{30}H_{58}NaO_3Si_2$, found 545.3831.

(*S*)-7-((tert-butyldimethylsilyl)oxy)-6-((1*R*,3a*R*,4*S*,7a*R*)-4-((tert-butyldimethylsilyl)oxy)-7a-methyloctahydro-1H-inden-1-yl)-2-methylheptan-2-ol (13)

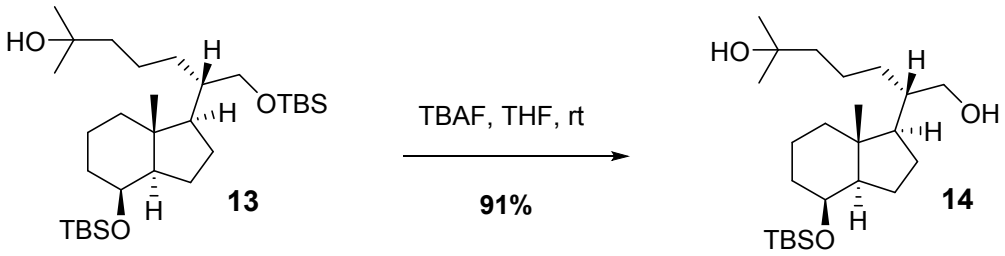


To a mixture of alcohol **12** (19 mg, 0.036 mmol) in hexane (2 mL) was added a catalytic amount of Pd/C (5%) and the suspensión was stirred for 4 h at room temperature under H_2. The use of hexane as a solvent was preferred because it gave better yields. Use of EtOAc for example gave low yields due to hydrogenolysis.

The mixture was then filtered through celite and the filtrate was rotatory evaporated to afford a residue which was chromatographed on silica gel using 5% EtOAc/Hexane as eluent, affording compound **13** (13 mg, 70%) as a colourless liquid, Rf: 0.26 (10% EtOAc/Hexane); **IR (NaCl, cm^{-1}):** 3392, 2953, 2929, 2884, 2857, 1252, 853; **[α]$^{24}_D$=** +13.80 (c 2.56, $CHCl_3$); **^{1}H- NMR ($CDCl_3$, δ):** 3.98 (1H, s , CH-8), 3.61 (1H, dd, *J*=9.9/2.8 Hz, H-21), 3.42 (1H, dd, *J*=9.9/5.1 Hz, H-21), 1.89 (1H, m), 1.73 (3H, m), 1.58-1.15 (15H, m), 1.19 (6H, s, CH_3-26/CH_3-27), 0.90 (3H, s, CH_3-18), 0.88 (9H, s, CH_3-^{t}Bu), 0.87 (9H, s, CH_3-^{t}Bu), 0.01 (6H, s, CH_3-Si), -0.00 (3H, s, CH_3-Si), -0.02 (3H, s, CH_3-Si); **^{13}C- NMR ($CDCl_3$, δ):** 71.1 (C-25), 69.4 (CH-8), 63.2 (CH_2-21), 52.9 (CH-14), 50.7 (CH-17), 44.6 (CH_2), 42.1 (C-13), 41.9 (CH-20), 40.5 (CH_2), 34.4 (CH_2), 29.7 (CH_2), 29.2 (CH_3-26 o CH_3-27), 29.1 (CH_3-26 o CH_3-27), 26.4 (CH_2), 25.9 (CH_3-^{t}Bu), 25.8 (CH_3-^{t}Bu), 22.9 (CH_2), 20.5 (CH_2), 18.2 (C-^{t}Bu), 17.9 (CH_2), 17.7 (C-^{t}Bu), 14.0 (CH_3-18), -4.8 (CH_3-Si), -5.2 (CH_3-Si), -5.4 (CH_3-Si), -5.5 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 215 (79), 471 (50), 509 (M$^+$-OH,36),

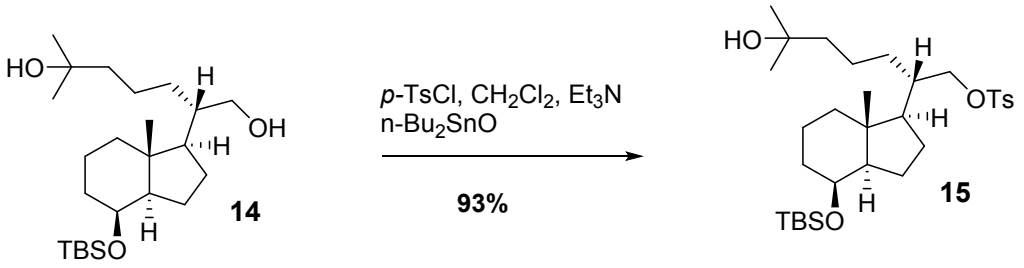
527 (M^++1,100); **HRMS (ESI):** 527.4310 calculated for $C_{30}H_{63}O_3Si_2$, found 527.4320.

(*S*)-2-((1*R*,3a*R*,4*S*,7a*R*)-4-((tert-butyldimethylsilyl)oxy)-7a-methyloctahydro-1H-inden-1-yl)-6-methylheptane-1,6-diol (14)



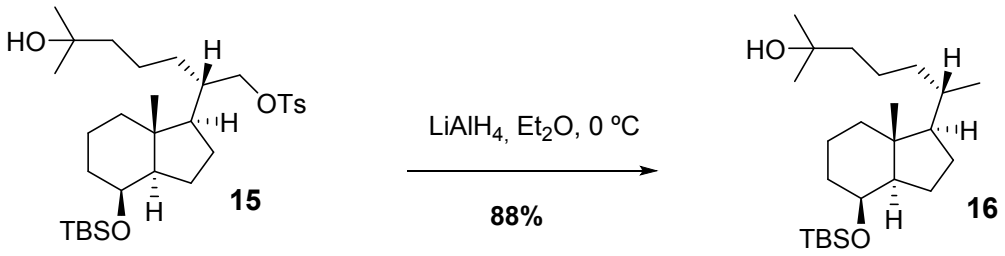
To a solution of **13** (140 mg, 0.266 mmol) in THF (2 mL) was added TBAF (532 µL of a 1 M solution in THF, 0.532 mmol) and the mixture was stirred at room temperature for 16 h, quenched with an aqueous saturated solution of NH_4Cl (3 mL) and the product extracted with EtOAc (3 x 15 mL). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 50% EtOAc/Hexane as eluent, affording diol **14** (109 mg, 91%) as a white solid (mp: 113ºC), Rf: 0.22 (50% EtOAc/Hexane); **IR (NaCl, cm^{-1}):** 3366, 2953, 2929, 2884,2858, 1252; **$[\alpha]^{30}_D$**= + 5.74 (c 0.61, $CHCl_3$); ^{1}**H- NMR ($CDCl_3$, δ):** 3.97 (1H, s, CH-8), 3.67 (1H, dd, *J*=11.0/2.8, H-21), 3.47 (1H, dd, *J*=11.0/5.2 Hz, H-21), 2.23 (2H, s, 2 OH), 1.88 (1H, m), 1.77 (2H, m), 1.64 (1H, m), 1.56-1.14 (15H, m), 1.17 (6H, s, CH_3-26/CH_3-27), 0.90 (3H, s, CH_3-18), 0.86 (9H, s, CH_3-*t*Bu), -0.02 (3H, s, CH_3-Si), -0.03 (3H, s, CH_3-Si); ^{13}**C-NMR ($CDCl_3$, δ):** 71.1 (C-25), 69.4 (CH-8), 63.5 (CH_2-21), 52.9 (CH-14), 50.8 (CH-17), 44.2 (CH_2), 42.2 (C-13), 41.9 (CH-20), 40.5 (CH_2), 34.4 (CH_2), 29.6 (CH_2), 29.4 (CH_3), 29.3 (CH_3), 26.5 (CH_2), 25.8 (CH_3-^{t}Bu), 22.9 (CH_2), 20.7 (CH_2), 17.8 (CH_2), 17.7 (C-^{t}Bu), 13.9 (CH_3-18), -4.8 (CH_3-Si), -5.2 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 395 (M^+-OH,21), 435 (M^++Na,100); **HRMS (ESI):** 435.3264 calculated for $C_{24}H_{48}NaO_3Si_2$, found 435.3262.

(*S*)-2-((1*R*,3a*R*,4*S*,7a*R*)-4-((tert-butyldimethylsilyl)oxy)-7a-methyloctahydro-1H-inden-1-yl)-6-hydroxy-6-methylheptyl 4-methylbenzenesulfonate (15)



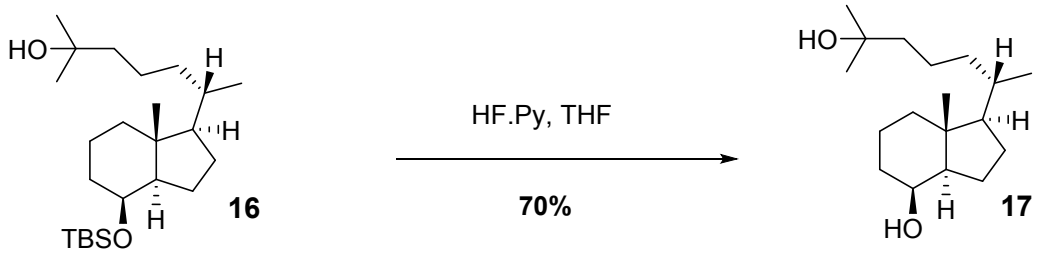
To a solution of diol **14** (70 mg, 0.169 mmol) in CH_2Cl_2 (3 mL) were added p-TsCl (100 mg, 0.51 mmol), n-$BuSnO_2$ (22 mg, 0.085 mmol) and Et_3N (0.15 mL, 1.02 mmol). The mixture was stirred for 4 days at room temperatura, adding *p*-TsCl (0.17 mmol) and Et_3N (0.51 mmol) every 24 h. H_2O (10 ml) was added and the aqueous phase extracted with CH_2Cl_2 (3 x 15 mL). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 20% EtOAc/Hexane as eluent, affording tosylate **15** (89 mg, 93%) as a colourless liquid, Rf: 0.83 (50% EtOAc/Hexane); **IR (ATR, cm^{-1}):** 2957, 2923, 2852, 1463, 1377; **$[\alpha]^{23}_D$=** +15.762 (c 1.00, $CHCl_3$); **^{1}H- NMR ($CDCl_3$, δ):** 7.81 (2H, d, *J*= 7.5 Hz, CH-Ts), 7.36 (2H, d, *J*=7.5 Hz, CH-Ts), 4.07 (1H, d, *J*=8.4 Hz, H-21), 4.00 (1H, s, H-8), 3.94 (1H, m, H-21), 2.46 (3H, s, CH_3-Ts), 1.92-1.02 (20H, m), 1.16 (6H, s, CH_3-26/CH_3-27), 0.90 (3H, s, CH_3-18), 0.89 (9H, s, CH_3-*t*Bu), 0.02 (6H, s, CH_3-Si); **^{13}C- NMR ($CDCl_3$, δ):** 144.6 (C-Ts), 133.0 (C-Ts), 129.8 (CH-Ts), 127.9 (CH-Ts), 71.7 (CH_2-21), 70.8 (C-25), 69.2 (CH-8), 52.7 (CH-14), 50.3 (CH-17), 43.9 (CH_2), 42.1 (C-13), 40.3 (CH_2), 39.7 (CH-20), 34.3 (CH_2), 29.5 (CH_2), 29.3 (CH_3), 29.1(CH_3), 26.3 (CH_2), 25.8 (CH_3-^{t}Bu), 22.7 (CH_2), 21.6 (CH_3-Ts), 20.4 (CH_2), 18.0 (C-^{t}Bu), 17.6 (CH_2), 13.8 (CH_3-18), -4.8 (CH_3-Si), -5.2 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 377.32 (M^+-Ts-OH_2, 100), 549.34 (M^+-OH, 17), 589.33 (M^++Na, 38); **HRMS (ESI):** 589.3353 calculated for $C_{31}H_{54}O_5SSi$, found 589.3348.

(*S*)-6-((1*R*,3a*R*,4*S*,7a*R*)-4-((tert-butyldimethylsilyl)oxy)-7a-methyloctahydro-1H-inden-1-yl)-2-methylheptan-2-ol (16)



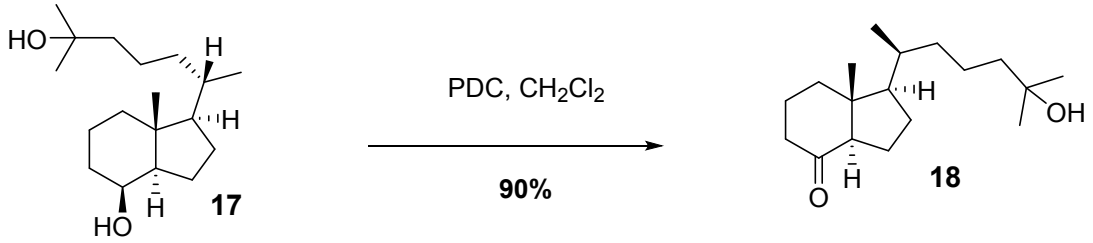
To a suspension of $LiAlH_4$ (80 mg, 2.06 mmol) in Et_2O (2.75 ml) at 0ºC was added dropwise a solution of tosylate **15** (78 mg, 0.137 mmol) in Et_2O (1.5 mL). The cooling bath was then removed and the mixture stirred at room temperature for 16 h. H_2O (10 mL) was added and the product extracted with Et_2O (4 x 15 ml). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 30% EtOAc/Hexane as eluent, affording alcohol **16** (47 mg, 88%) as a colourless liquid, Rf: 0.59 (50% EtOAc/Hexane); **IR (ATR, cm^{-1}):** 3348, 2956, 2920, 2851, 1463, 1377; **$[\alpha]^{23}_D$=** -30.8320 (c 0.25, $CHCl_3$); **^{1}H- NMR ($CDCl_3$, δ):** 4.01 (1H, s, H-8), 1.95-1.05 (20H, m), 1.23 (6H, s, CH_3-26/CH_3-27), 0.93 (3H, s, CH_3-18), 0.91 (9H, s, CH_3-^{t}Bu), 0.83 (3H, d, *J*=6.4 Hz, CH_3-21), 0.03 (3H, s, CH_3-Si), 0.01 (3H, s, CH_3-Si); **^{13}C-NMR ($CDCl_3$, δ):** 71.1 (C-25), 69.5 (CH-8), 56.4 (CH), 53.1 (CH), 44.3 (CH_2), 42.2 (C-13), 40.7 (CH_2), 35.7 (CH_2), 34.7 (CH-20), 34.5 (CH_2), 30.3 (CH_3), 29.3 (CH_3), 27.2 (CH_2), 25.8 (CH_3-^{t}Bu), 23.0 (CH_2), 20.8 (CH_2), 18.5 (CH_3-21), 18.0 (C-^{t}Bu), 17.7 (CH_2), 14.0 (CH_3-18), -4.8 (CH_3-Si), -5.2 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 379.3394 (M^+-OH, 100); **HRMS (ESI):** 379.3390 calculated for $C_{24}H_{47}OSi$, found 379.3394.

(1R,3aR,4S,7aR)-1-((S)-6-hydroxy-6-methylheptan-2-yl)-7a-methyloctahydro-1H-inden-4-ol (17)



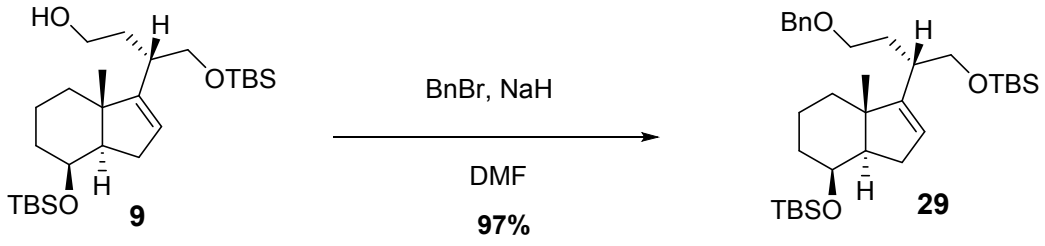
To a solution of alcohol 16 (87 mg, 0.219 mmol) in THF (10 mL) at 0ºC was added dropwise HF·py 70% (2 mL). The cooling bath was then removed and the mixture stirred at room temperature for 3 days, HF·py 70% (2 mL) beeing added every 24 h. The mixture was recooled at 0ºC and $NaHCO_3$ added dropwise till pH 6. The product was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 50% EtOAc/Hexane as eluent, affording diol **17** (43 mg, 70%) as a colourless liquid, Rf: 0.22 (30% EtOAc/Hexane); **IR (ATR, cm^{-1}):** 3385, 2955, 2924, 2853, 1464, 1367; **$[\alpha]^{21}_D$=** +18.0644 (c 1.00, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 4.09 (1H, s, H-8), 2.01-1.26 (15H, m), 1.25 (6H, s, CH_3-26/CH_3-27), 1.23-1.07 (4H, m), 0.95 (3H, s, CH_3-18), 0.84 (3H, d, *J*=6.4 Hz, CH_3-21); **C-NMR ($CDCl_3$, δ):** 71.1 (C-25), 69.4 (CH-8), 56.3 (CH), 52.7 (CH), 44.3 (CH_2), 41.9 (C-13), 40.3 (CH_2), 35.7 (CH_2), 34.7 (CH-20), 33.6 (CH_2), 29.3 (CH_3), 29.3 (CH_3), 27.1 (CH_2), 22.4 (CH_2), 20.9 (CH_2), 18.5 (CH_3-21), 17.5 (CH_2), 13.8 (CH_3-18); **MS (ESI) [m/z, (%)]:** 195.09 (40), 248.11 (M^+-2OH, 100), 283.26 (M^++1, 1), 311.21 (10); **HRMS (ESI):** 283.2631 calculated for $C_{18}H_{35}O_2$, found 283.2636.

(1*R*,3a*R*,7a*R*)-1-((*S*)-6-hydroxy-6-methylheptan-2-yl)-7a-methyloctahydro-4H-inden-4-one (18)



To a solution of diol **17** (38 mg, 0.135 mmol) in CH_2Cl_2 (2.5 mL) was added pyridinium dichromate (PDC) (152 mg, 0.40 mmol) and the mixture stirred for 16 h, filtered over celite and the filtrate concentrated to afford a residue which was chromatographed on silica gel using 60% EtOAc/Hexane as eluent, affording ketone **18** (33 mg, 90%) as a colourless liquid, Rf: 0.20 (30% EtOAc/Hexane); **IR (ATR, cm^{-1}):** 3436, 2956, 2922, 2852, 1733, 1463, 1376, 1364, 1176; **$[\alpha]^{22}_D$=** -38.744 (c 1.00, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 2.42 (1H, m, CH-14), 2.24 (2H, m, CH_2-9), 2.13-1.25 (15H, m), 1.25 (6H, s, CH_3-26/CH_3-27), 0.88 (3H, d, *J* = 6.4 Hz, CH_3-21), 0.65 (3H, s, CH_3-18); **^{13}C-NMR ($CDCl_3$, δ):** 212.0 (C-8), 71.0 (C-25), 62.0 (CH-14), 56.2 (CH), 49.9 (C-13), 44.2 (CH_2), 40.9 (CH_2), 38.8 (CH_2), 35.9 (CH_2), 34.8 (CH-20), 29.3 (CH_3), 29.2 (CH_3), 27.1 (CH_2), 24.0 (CH_2), 20.8 (CH_2), 18.9 (CH_2), 18.5 (CH_3-21), 12.7 (CH_3-18); **MS (ESI) [m/z, (%)]:** 248.11 (M^+-OH_2,100), 282.21 (M^++2, 2.4), 303.23 (M^++Na, 2); **HRMS (ESI):** 303.2294 calculated for $C_{18}H_{32}NaO_2$, found 303.2300.

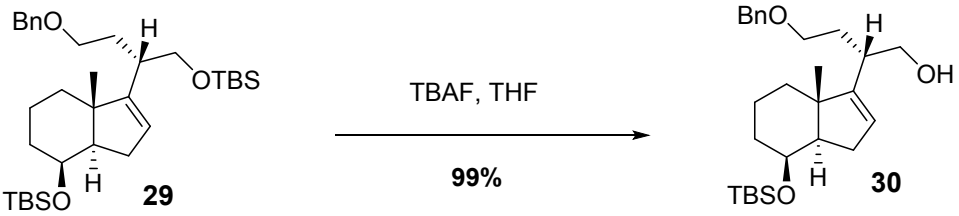
(((3aS,7S,7aR)-3-((S)-4-(benzyloxy)-1-((tert-butyldimethylsilyl)oxy)butan-2-yl)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-7-yl)oxy)(tert-butyl)dimethylsilane (29)



To a solution of alcohol **9** (1.12 g, 2.5 mmol) in DMF (30 mL) at 0 ºC was added portionwise NaH (205 mg, 5.1 mmol, 60% dispersión in mineral oil) and the mixture stirred for 30 mn. Benzyl bromide (BnBr) (0.4 mL, 3.6 mmol) was added and the cooling bath removed. Stirring was continued for 24 h before quenching with H_2O (20 mL). The product was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated

to give a residue which was chromatographed on silica gel using 0.5% EtOAc/Hexane as eluent, benzyl ether **29** (1.3 g, 97%) as a colourless liquid, Rf: 0.75 (10% AcOEt/Hexano); **IR (NaCl, cm^{-1}):** 2949.68, 2931.33, 2878.25, 2857.45, 1025.64; **[α]$^{21}_{D}$=** +34.35 (c 2.14, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 7.27 (5H, m, 5H-Bn), 5.34 (1H, s, H-16), 4.53 (2H, s, C**H**$_2$-Bn), 4.05 (1H, s ancho, H-8), 3.55 (1H, dd, J=9.7, 4.6 Hz, H-21), 3.43 (3H, m, H-21, 2H-23), 2.20 (2H, m), 2.0 (1H, m), 1.86 (2H, m), 1.71-1.33 (6H, m), 1.21 (1H, m), 0.99 (3H, s, CH_3-18), 0.86 (18H, s, CH_3-*t*Bu), -0.001 (12H, s, CH_3-Si); **^{13}C-NMR ($CDCl_3$, δ):** 155.8 (C-17), 138.7 (C-Bn), 128.3 (CH_m-Bn), 127.6 (CH_o-Bn), 127.3 (CH_p-Bn), 122.6 (CH-16), 72.6 (CH_2-OBn), 69.7 (CH-8), 69.0 (CH_2-21), 67.3 (CH_2-23), 54.4 (CH-14), 46.8 (C-13), 36.4 (CH-20), 35.3 (CH_2), 34.6 (CH_2), 32.5 (CH_2), 31.0 (CH_2), 25.9 (CH_3-*t*Bu), 25.7 (CH_3-*t*Bu), 19.3 (CH_3-18), 18.2 (C-*t*Bu), 17.9 (CH_2), -4.8 (CH_3-Si), -5.1 (CH_3-Si), -5.3 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 559 (M^++1, 100), 557 (M^+-1, 5), 451 (M^+-OBn, 26), 427 (16); **HRMS (ESI):** 559.3997 calculated for $C_{33}H_{59}O_3Si_2$, found 559.3992.

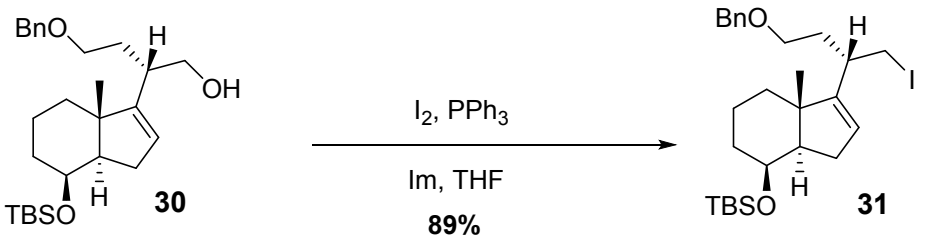
(S)-4-(benzyloxy)-2-((3aS,7S,7aR)-7-((tert-butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl)butan-1-ol (30)



To a solution of benzyl ether **29** (1.4 g, 2.7 mmol) in THF (20 mL) was added TBAF (5.4 mL of a 1 M solution in THF, 5.4 mmol) and the mixture was stirred at room temperature for 2 h, quenched with an aqueous saturated solution of NH_4Cl (15 mL) and the product extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated to give a residue which was chromatographed on silica gel using 1% EtOAc/Hexane as eluent, affording

alcohol **30** (1.1 g, 99%) as a colourless liquid, Rf: 0.25 (10% EtOAc/Hexano); **IR (NaCl, cm^{-1}):** 3369.33, 2949.68, 2931.58, 2878.36, 2856.89, 1102.32; **$[\alpha]^{22}_D$=** +19.78 (c 0.92, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 7.27 (5H, m, 5H-Bn), 5.42 (1H, s, H-16), 4.52 (2H, s, C**H_2**-Bn), 4.11 (1H, s ancho, H-8), 3.61 (2H, m, 2H-23), 3.55 (1H, m, H-21), 3.48 (1H, m, H-21), 2.41 (1H, m, H-15), 2.27 (1H, m, H-20), 1.95-1.66 (6H, m), 1.62 (1H, ddd, J=11.5, 6.1, 1.8 Hz), 1.48 (2H, m), 1.27 (1H, m), 1.06 (3H, s, CH_3-18), 0.91 (9H, s, CH_3-*t*Bu), 0.05 (3H, s, CH_3-Si), 0.05 (3H, s, CH_3-Si); **^{13}C-NMR ($CDCl_3$, δ):** 155.7 (C-17), 137.9 (C-Bn), 128.3 (CH_m-Bn), 127.7 (CH_o-Bn), 127.6 (CH_p-Bn), 123.0 (CH-16), 73.1 (CH_2-OBn), 68.8 (CH-8), 68.6 (CH_2-21), 65.7 (CH_2-23), 54.6 (CH-14), 46.8 (C-13), 37.6 (CH-20), 35.2 (CH_2), 34.5 (CH_2), 32.8 (CH_2), 30.9 (CH_2), 25.7 (CH_3-*t*Bu), 19.1 (CH_3-18), 18.1 (C-*t*Bu), 17.9 (CH_2), -4.9 (CH_3-Si), -5.2 (CH_3-Si); **MS (FAB^+) [m/z, (%)]:** 445 (M^++1, 100), 444 (M^+, 12), 353 (14), 337 (M^+-OBn, 12), 313 (15); **HRMS (FAB^+):** 445.3132 calculated for $C_{27}H_{45}O_3Si$, found 445.3130.

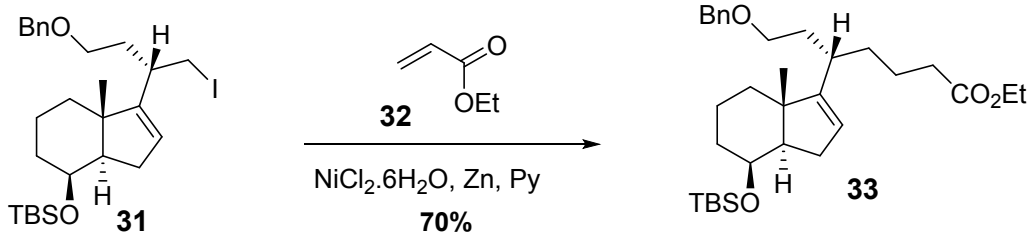
(((3aS,7S,7aR)-3-((S)-4-(benzyloxy)-1-iodobutan-2-yl)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-7-yl)oxy)(tert-butyl)dimethylsilane (31)



To a solution of alcohol **30** (521 mg, 1.26 mmol) in THF (20 mL) at room temperature were added siquentially PPh_3 (397 mg, 1.5 mmol) and imidazole (258 mg, 3.78 mmol). After cooling the mixture to 0 ºC, I_2 (352 mg, 1.4 mmol) was added and stirring continued for 30 min. The reaction was quenched with an aqueous saturated solution of $NaHCO_3$ (40 mL) and the product extracted with EtOAc (30 mL). The organic phase was washed with a 10% aqueous solution of $Na_2S_2O_3$ (30 mL) and brine (30 mL), dried over Na_2SO_4, filtered and concentrated to give a residue which was chromatographed on silica gel using 1%

EtOAc/Hexane as eluent, affording iodide **31** (618 mg, 89%) as a colourless liquid, Rf: 0.7 (10% AcOEt/Hexano); **IR (NaCl, cm^{-1}):** 2948.68, 2931.58, 2878.16, 2856.19, 1641.53, 1145.69; **[α]$^{22}_{D}$=** +11.14 (c 0.85, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 7.28 (5H, m, 5H-Bn), 5.39 (1H, s, H-16), 4.48 (2H, s, C**H**$_2$-Bn), 4.08 (1H, s ancho, H-8), 3.41 (2H, m, 2H-23), 3.29 (2H, m, 2H-21), 2.35 (1H, m, H-15), 2.23 (1H, m, H-20), 1.97-1.70 (4H, m), 1.69 (2H, m), 1.58 (1H, m), 1.43 (2H, m), 1.24 (1H, m), 0.99 (3H, s, CH_3-18), 0.88 (9H, s, CH_3-*t*Bu), 0.01 (6H, s, CH_3-Si); **^{13}C-NMR ($CDCl_3$, δ):** 155.9 (C-17), 138.8 (C-Bn), 128.7 (CH_m-Bn), 128.0 (CH_o-Bn), 127.9 (CH_p-Bn), 124.4 (CH-16), 73.2 (CH_2-OBn), 69.3 (CH-8), 68.4 (CH_2-23), 54.9 (CH-14), 47.1 (C-13), 37.1 (CH-20), 35.7 (CH_2), 35.1 (CH_2), 34.9 (CH_2), 31.3 (CH_2), 26.2 (CH_3-*t*Bu), 20.0 (CH_3-18), 18.4 (C-*t*Bu), 18.3 (CH_2), 14.5 (CH_2), -4.4 (CH_3-Si), -4.7 (CH_3-Si); **MS (FAB$^+$) [m/z, (%)]:** 555 (M^++1, 81), 554 (M^+, 43), 553 (M^+-1, 100), 427 (91), 315 (70), 265 (71), 187 (70), 171 (73); **HRMS (FAB$^+$):** 554.2072 calculated for $C_{27}H_{43}O_2SiI$, found 554.2077.

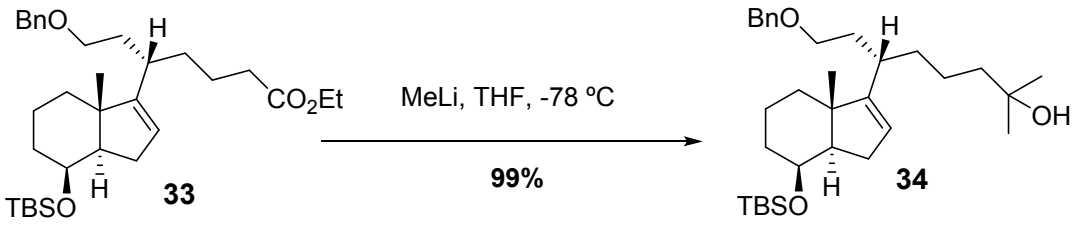
Ethyl (S)-7-(benzyloxy)-5-((3aS,7S,7aR)-7-((tert-butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl)heptanoate (33)



To a suspension of Zn (189 mg, 2.9 mmol) in pyridine (4 mL) were added $NiCl_2 \cdot 6H_2O$ (137 mg, 0.58 mmol) and ethyl acrilate (0.26 mL, 2.9 mmol) and the resulting mixture was heated at 65 ºC for 30 mn. The colour of the mixture turned reddish Brown. The mixture was allowed to reach room temperature then a solution of iodide **31**(106 mg, 0.18 mmol) in pyridine (3 mL) was added and

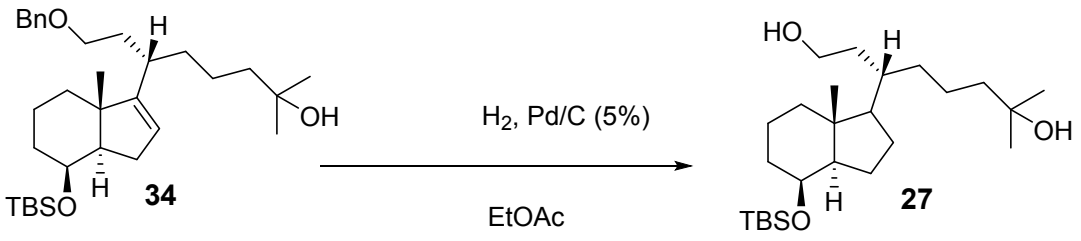
stirring continued for 2 h. The suspensión was then filtered through celite and ethyl acetate (10 mL) was added. The organic phase was washed with a 10% aqueous solution of HCl (2 x 20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and concentrated, affording a residue which was chromatographed on silica gel using 1% EtOAc/Hexane as eluent, giving ester **33** (76 mg, 70%) as a colourless liquid, Rf: 0.16 (10% AcOEt/Hexano); **IR (NaCl, cm^{-1}):** 2928.38, 2853.06, 2855.10, 1736.18, 1652.32; **$[\alpha]^{23}_D$=** +17.18 (c 1.59, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 7.29 (5H, m, 5H-Bn), 5.29 (1H, s, H-16), 4.47 (2H, s, C**H**$_2$-Bn), 4.11 (2H, q, J=7.1 Hz, OC**H**$_2$CH$_3$), 4.07 (1H, s ancho, H-8), 3.44 (2H, m, 2H-1'), 2.24 (2H, m, 2H-24), 2.12 (1H, m), 1.87 (2H, ddd, J=14.2, 5.6, 2.9 Hz, 2H-15), 1.79-1.55 (7H, m), 1.55-1.38 (5H, m), 1.30 (1H, m), 1.24 (3H, t, J= 7.1Hz, OCH$_2$C**H**$_3$), 1.01 (3H, s, CH$_3$-18), 0.89 (9H, s, CH$_3$-*t*Bu), 0.02 (6H, s, CH$_3$-Si); **^{13}C-NMR ($CDCl_3$, δ):** 173.7 (C=O), 157.4 (C-17), 138.6 (C-Bn), 128.3 (CH$_m$-Bn), 127.6 (CH$_o$-Bn), 127.4 (CH$_p$-Bn), 121.7 (CH-16), 72.8 (CH$_2$-OBn), 69.0 (CH-8), 68.6 (CH$_2$-1'), 60.1 (O**C**H$_2$CH$_3$), 54.8 (CH-14), 46.7 (C-13), 35.5 (CH$_2$), 35.2 (CH$_2$), 34.6 (CH$_2$), 34.5 (CH$_2$), 34.0 (CH$_2$), 33.9 (CH-20), 33.8 (CH$_2$), 30.8 (CH$_2$), 25.7 (CH$_3$-*t*Bu), 22.9 (CH$_2$), 19.2 (CH$_3$-18), 18.0 (C-*t*Bu), 17.9 (CH$_2$), 14.2 (OCH$_2$**C**H$_3$), -4.9 (CH$_3$-Si), -5.2 (CH$_3$-Si); **EM (ESI) [m/z, (%)]:** 529 (M^++1, 100), 528 (M^+, 26), 527 (M^+-1, 32), 421 (M^+-OBn, 22), 289 (40); **EMAR (ESI):** 529.3707 calculated for $C_{32}H_{53}O_4Si$, found 529.3705.

(S)-8-(benzyloxy)-6-((3aS,7S,7aR)-7-((tert-butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl)-2-methyloctan-2-ol (34)



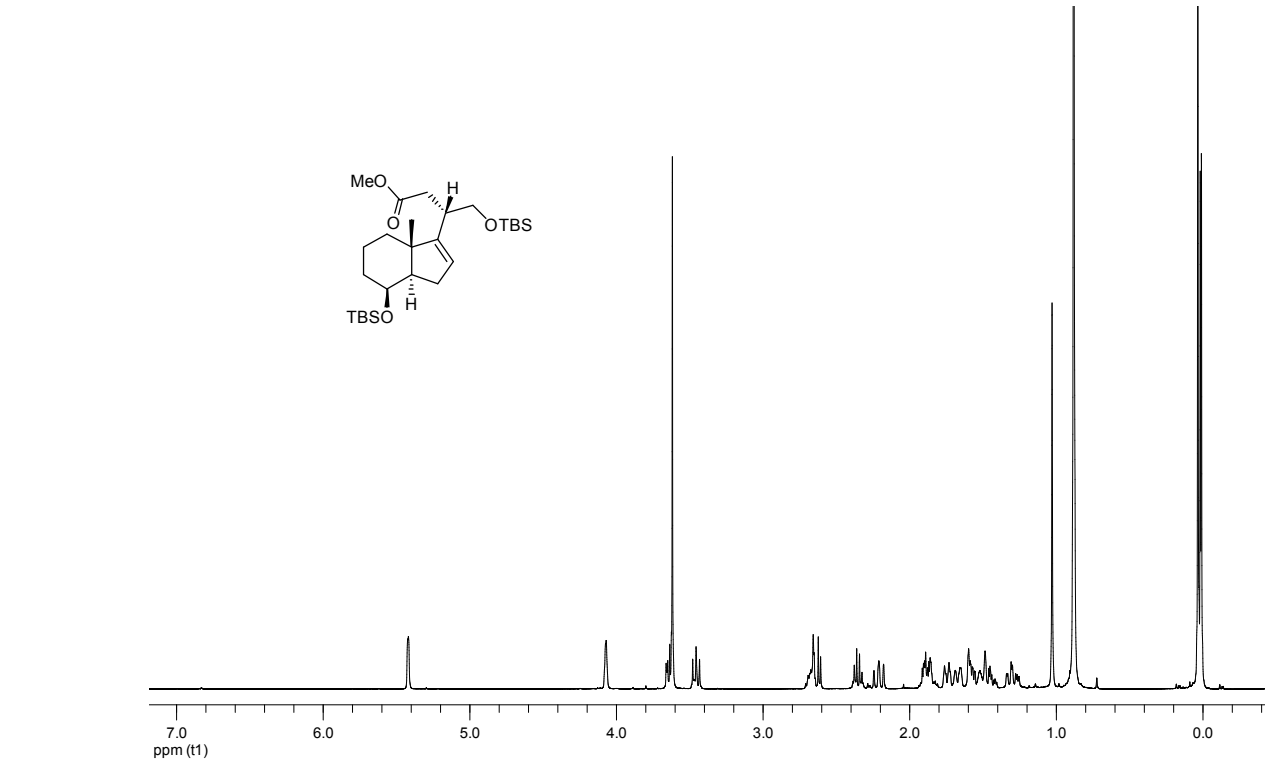
To a solution of ester **33** (180 mg, 0.31 mmol) in THF (3 mL) at -78 ºC was added MeLi·LiBr (1.1 ml, 1.6 mmol, 1.5 M solution in ethyl ether) and the mixture was stirred for 30 mn. H_2O (10 mL) was added and the product extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated to give a residue which was chromatographed on silica gel using 10% EtOAc/Hexane as eluent, affording alcohol **34** (180 mg, 99%) as a colourless liquid, Rf: 0.1 (10% EtOAc/Hexano); **IR (NaCl, cm^{-1}):** 3394.15, 2930.31, 2856.06, 1365.35, 1026.91; **[α]$^{22}_D$=** +19.69 (c 1.76, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 7.32 (5H, m, 5H-Bn), 5.28 (1H, s, H-16), 4.49 (1H, d, J=11.8 Hz, C**H**$_2$-Bn), 4.46 (1H, d, J=11.8 Hz, C**H**$_2$-Bn), 4.08 (1H, s ancho, H-8), 3.44 (2H, m, 2H-1'), 2.23 (1H, m, H-15), 2.13 (1H, m, H-15), 1.87 (2H, m), 1.77-1.54 (6H, m), 1.52-1.22 (8H, m), 1.18 (6H, s, CH_3-26, CH_3-27), 1.02 (3H, s, CH_3-18), 0.89 (9H, s, CH_3-*t*Bu), 0.03 (6H, s, CH_3-Si); **^{13}C-NMR ($CDCl_3$, δ):** 157.9 (C-17), 138.6 (C-Bn), 128.2 (CH_m-Bn), 127.6 (CH_o-Bn), 127.4 (CH_p-Bn), 121.5 (CH-16), 72.7 (CH_2-OBn), 71.0 (C-25), 69.1 (CH-8), 68.7 (CH_2-1'), 54.9 (CH-14), 46.7 (C-13), 44.1 (CH_2), 35.5 (CH_2), 35.2 (CH_2), 35.0 (CH_2), 34.6 (CH_2), 33.9 (CH-20), 30.8 (CH_2), 29.2 (CH_3-26 o CH_3-27), 29.1 (CH_3-26 o CH_3-27), 25.7 (CH_3-*t*Bu), 22.2 (CH_2), 19.3 (CH_3-18), 18.0 (C-*t*Bu), 17.9 (CH_2), -4.9 (CH_3-Si), -5.2 (CH_3-Si); **MS (ESI) [m/z, (%)]:** 514 (M^+, 15), 513 (M^+-1, 52), 421(82), 257 (32); **HRMS (ESI):** 513.3758 calculated for $C_{32}H_{53}O_3Si$, found 513.3757.

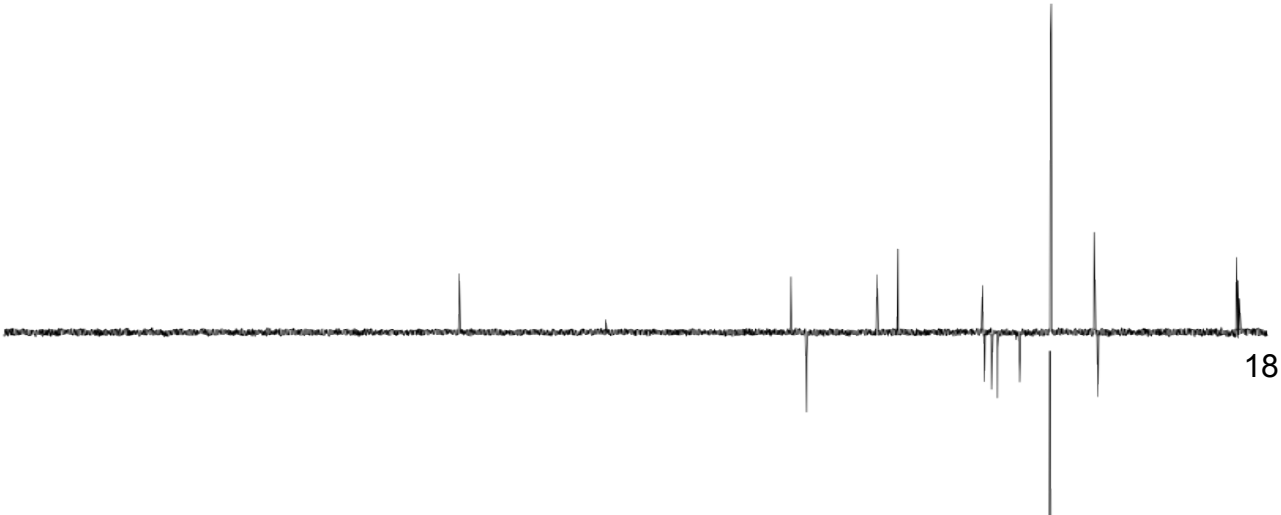
(3S)-3-((3aR,4S,7aR)-4-((tert-butyldimethylsilyl)oxy)-7a-methyloctahydro-1H-inden-1-yl)-7-methyloctane-1,7-diol (27)

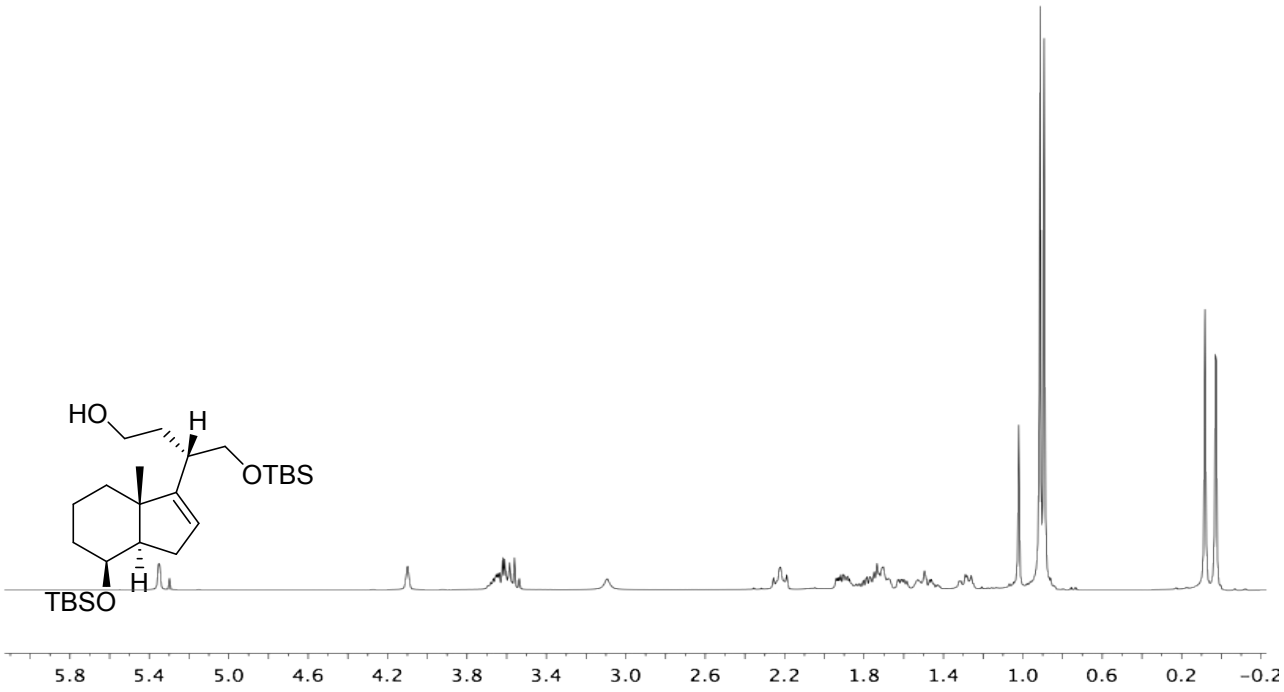


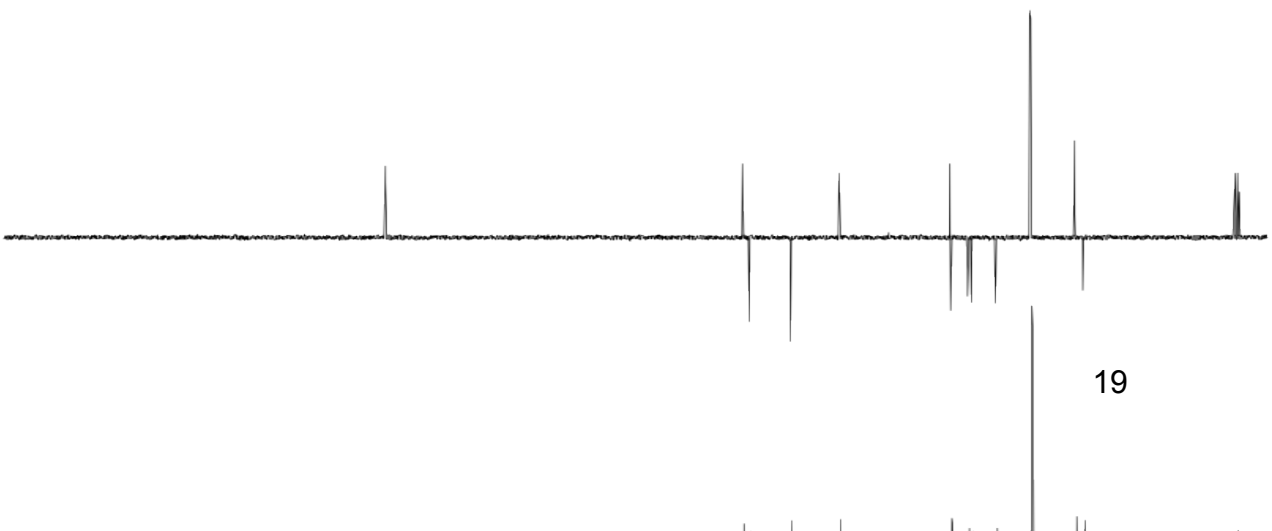
To a solution of alcohol **34** (191 mg, 0.37 mmol) in EtOAc (5 mL) at room temperature was added Pd/C (20 mg) and the mixture was stirred for 45 h under H_2 atmosphere. The mixture was then filtered through celite and the filtrate was rotatory evaporated to afford a residue which was chromatographed on silica gel using 10% EtOAc/Hexane as eluent, affording compound **27** (125 mg, 98%) as a colourless liquid.

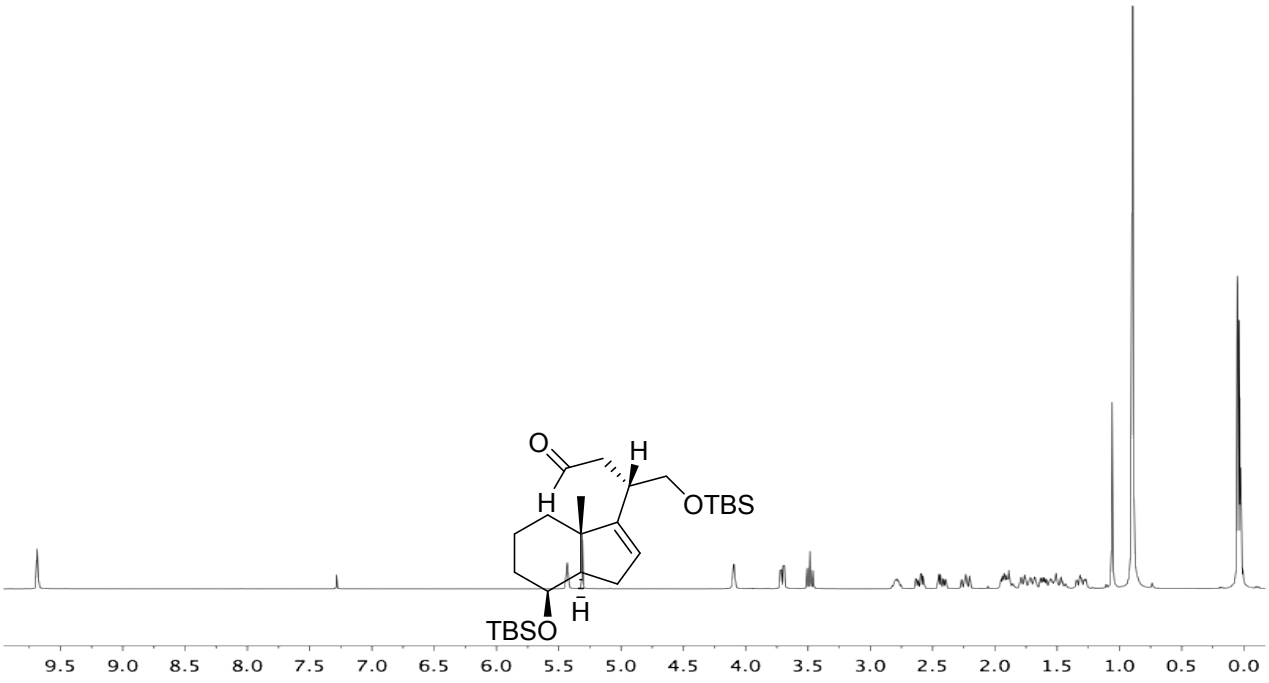
^{1}H-RMN ($CDCl_3$, δ): 3.98 (1H, s, H-8), 3.63 (2H, m, CH_2-1'), 1.94-1.17 (20H, m), 1.19 (6H, s, CH_3-26/27), 0.90 (3H, s, CH_3-18), 0.87 (9H, s, CH_3-*t*Bu), -0.01 (3H, s, CH_3-Si), -0.02 (CH_3-Si); **^{13}C-RMN ($CDCl_3$, δ):** 71.42 (C-25), 69.80 (CH-8), 61.01 (CH_2-1'), 53.92 (CH-14), 53.44 (CH-17), 44.81 (CH_2), 42.61 (C-13), 40.91 (CH_2), 36.41 (CH-20), 34.85 (CH_2), 34.63 (CH_2), 32.11(CH_2), 29.73 (CH_3-26/27), 29.66 (CH_3-26/27), 27.00 (CH_2), 26.20 (CH_3-*t*Bu), 23.27 (CH_2), 20.27 (CH_2), 18.41 (CH_2), 18.07 (C-*t*Bu), 14.32 (CH_3-18), -4.39 (CH_3-Si), -4.76 (CH_3-Si).

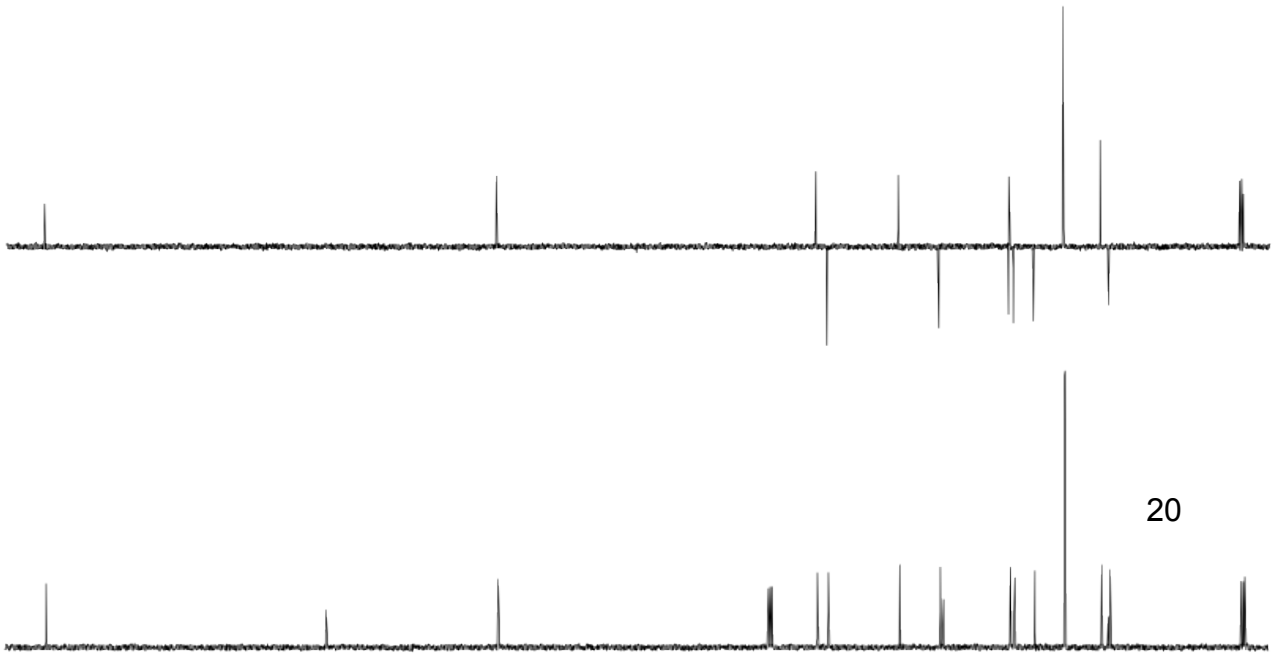

MeO
O
H
OTBS
TBSO
H
7.0
ppm (t1)
6.0
5.0
4.0
3.0
2.0
1.0
0.0

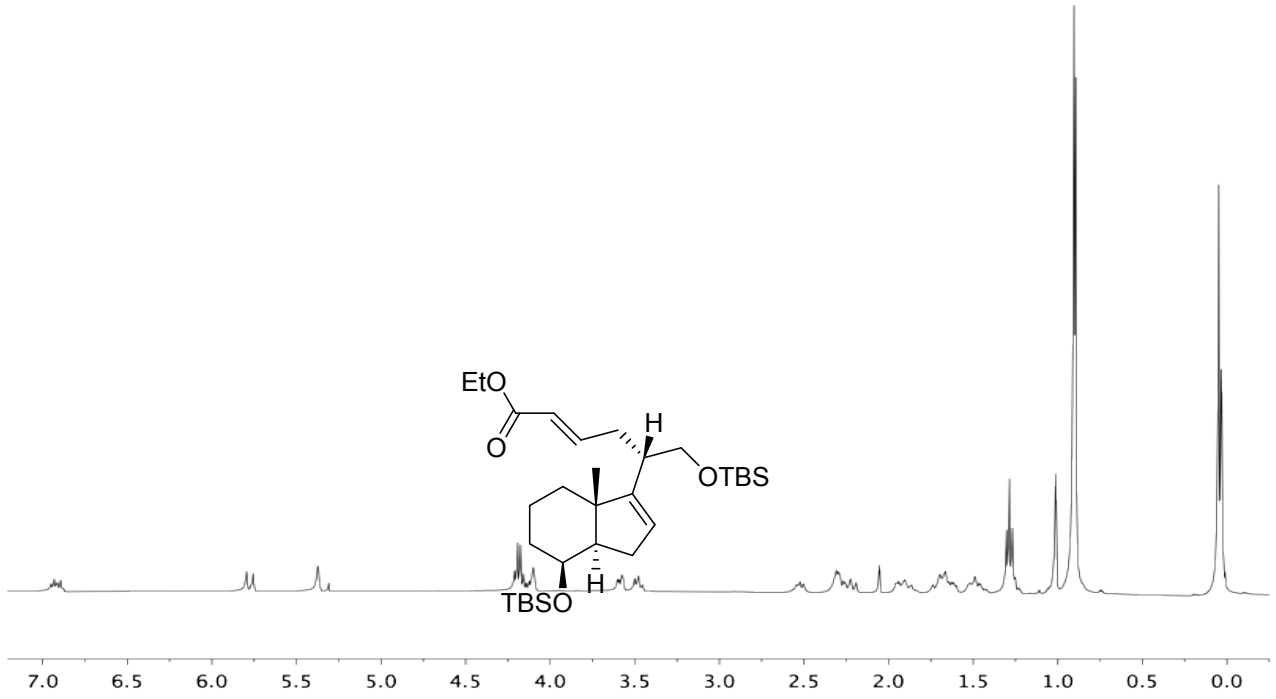



HO
H
OTBS
H
TBSO
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2




O
H
H
OTBS
TBSO
H
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

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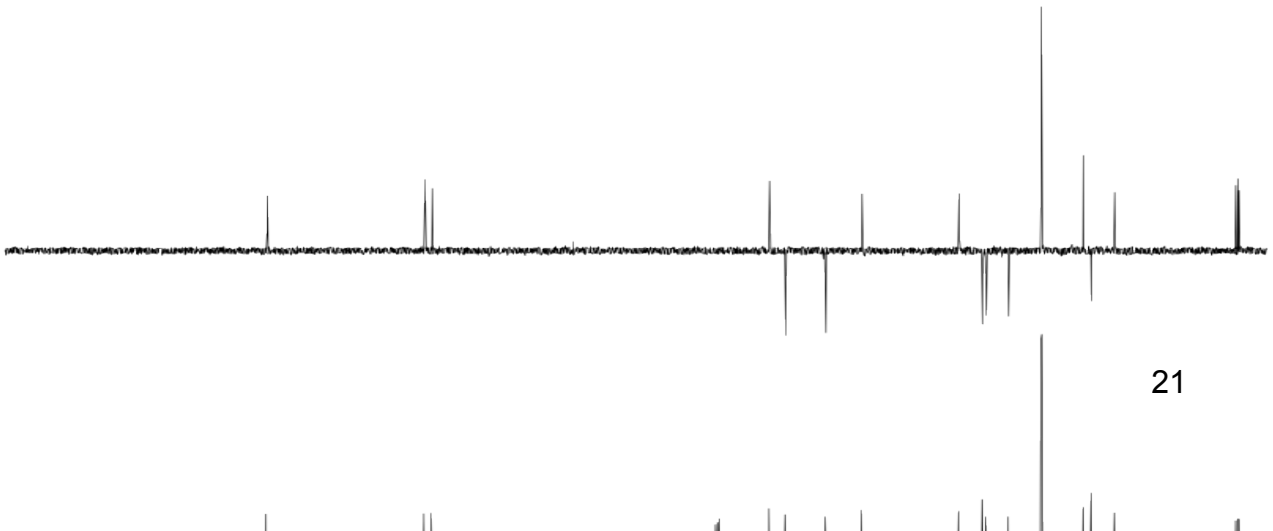
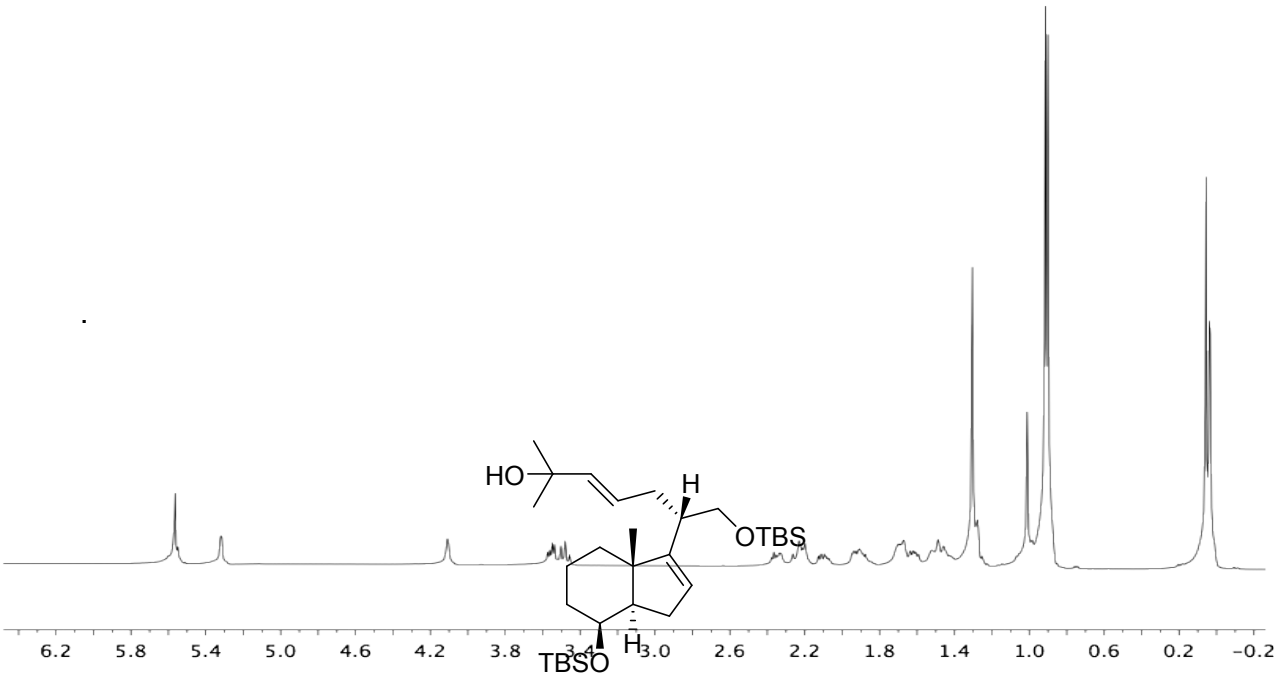
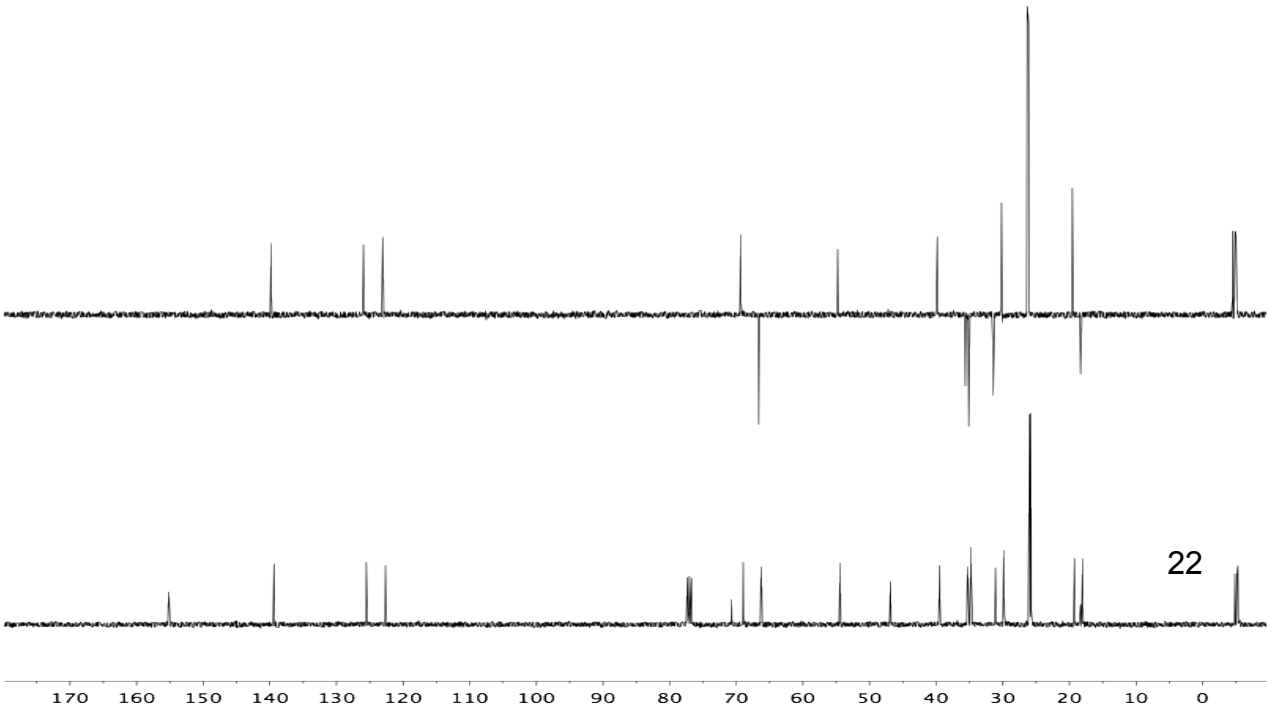
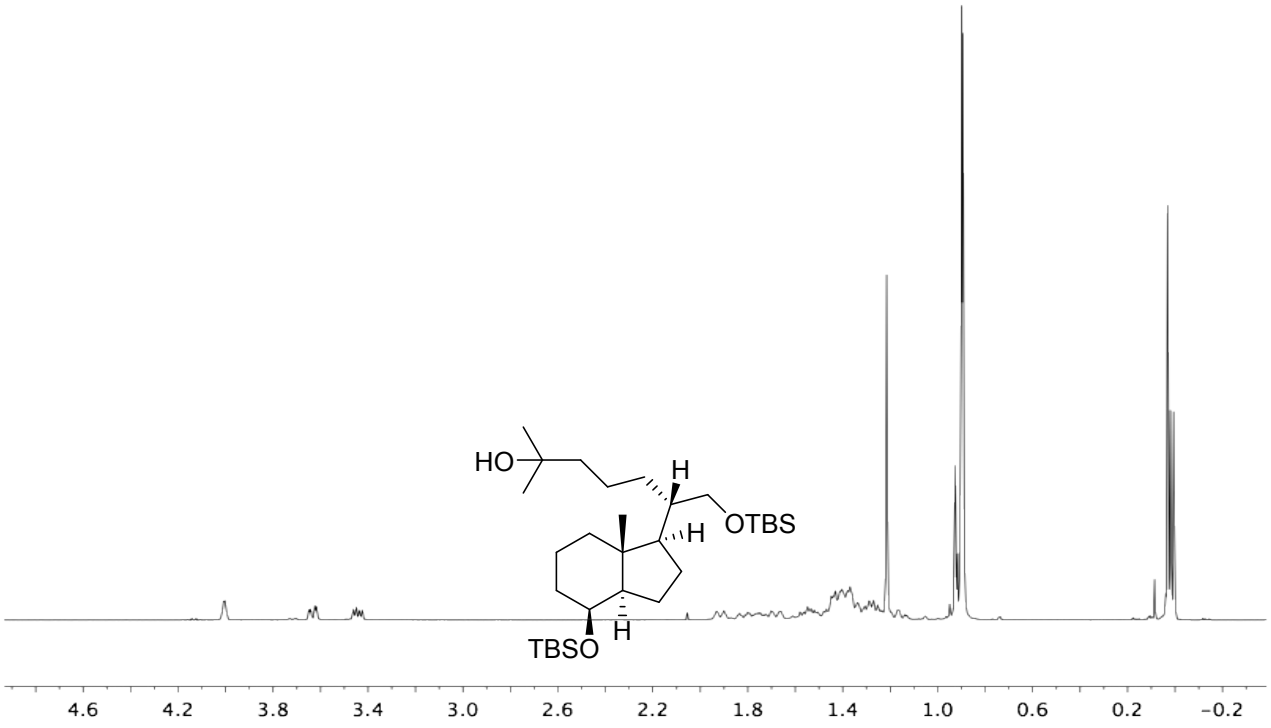
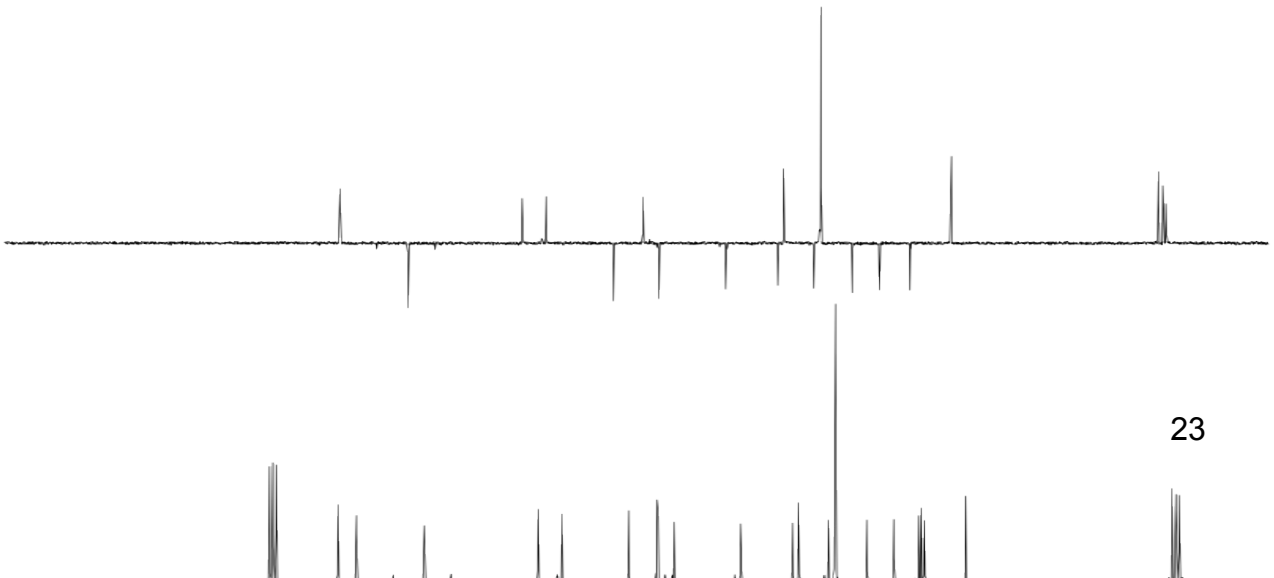
O
H
OTBS
TBSO
H
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

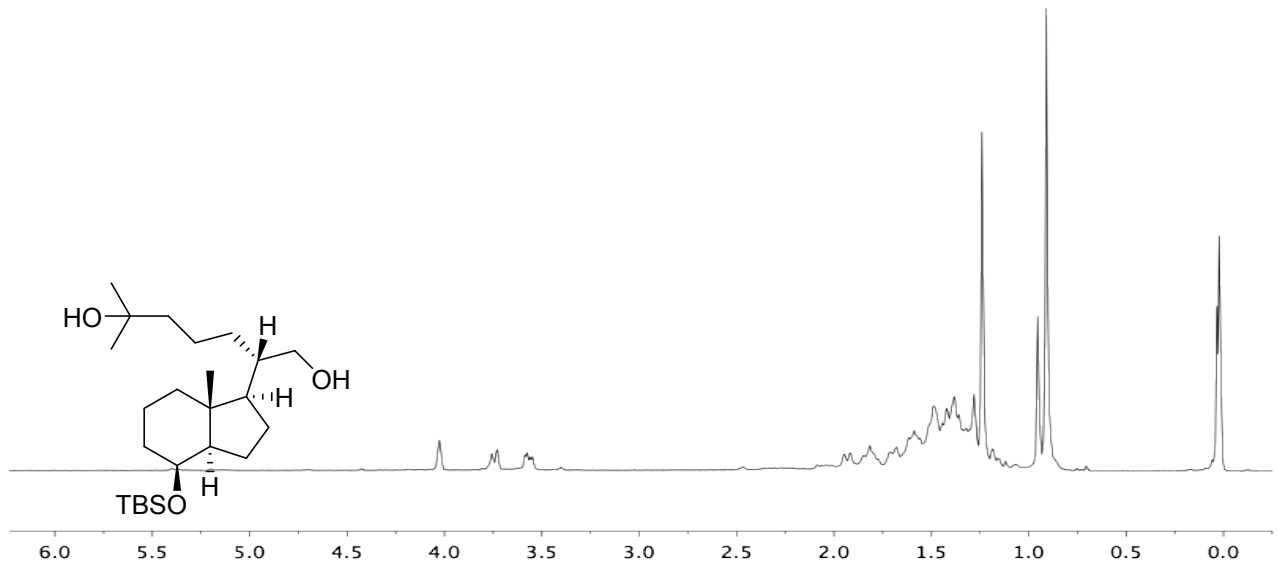


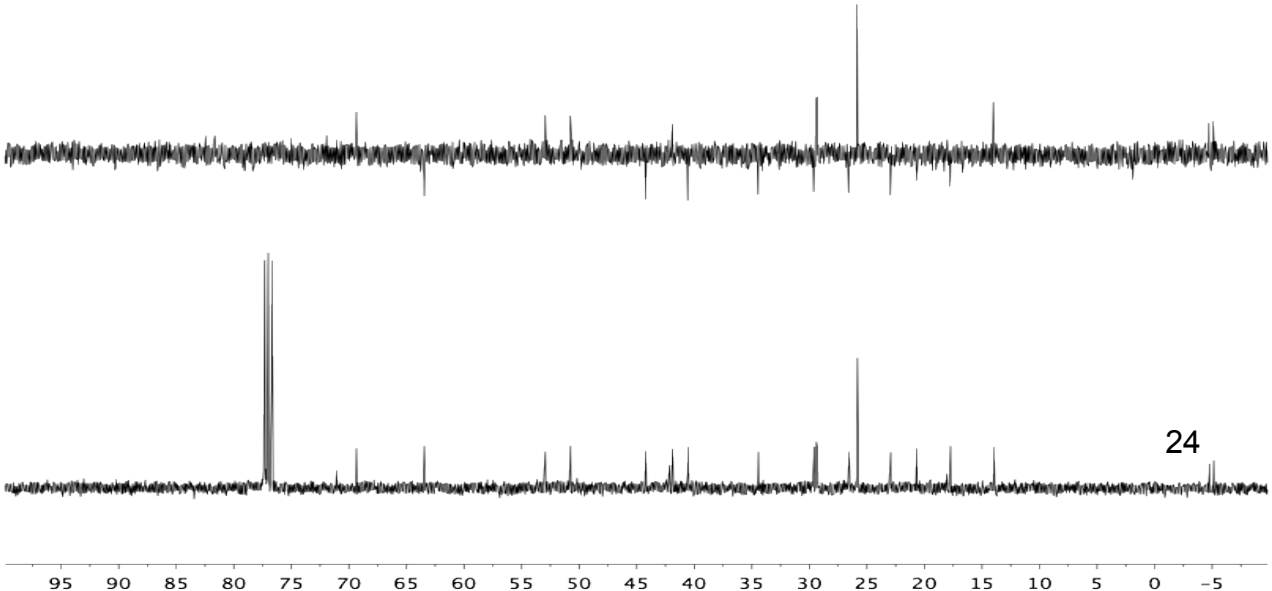

HO
H
OTBS
TBSO
H
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


HO
H
OTBS
H
H
TBSO
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2




HO
H
OH
H
H
TBSO
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


24
95
90
85
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75
70
65
60
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50
45
40
35
30
25
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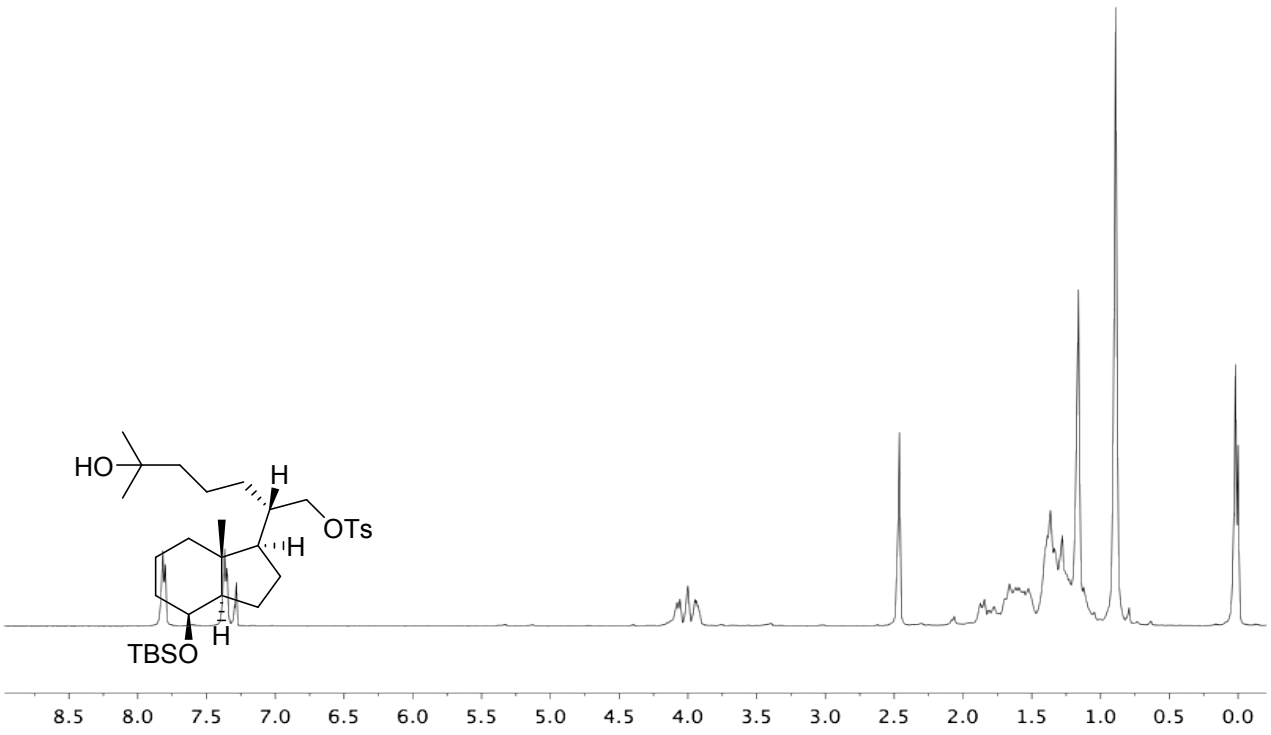
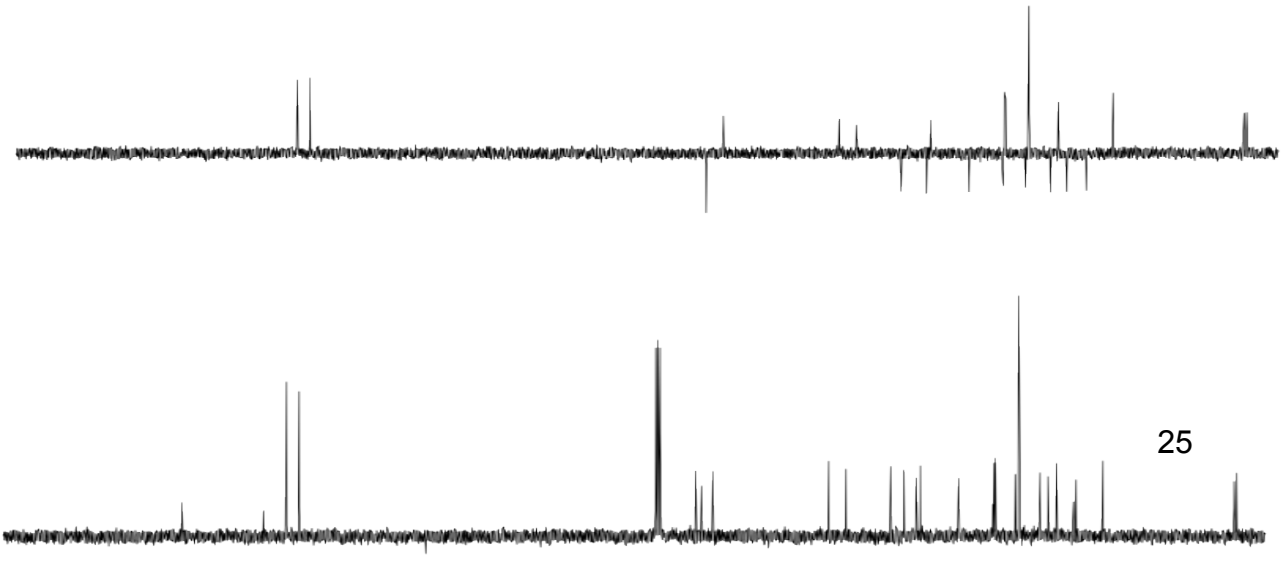
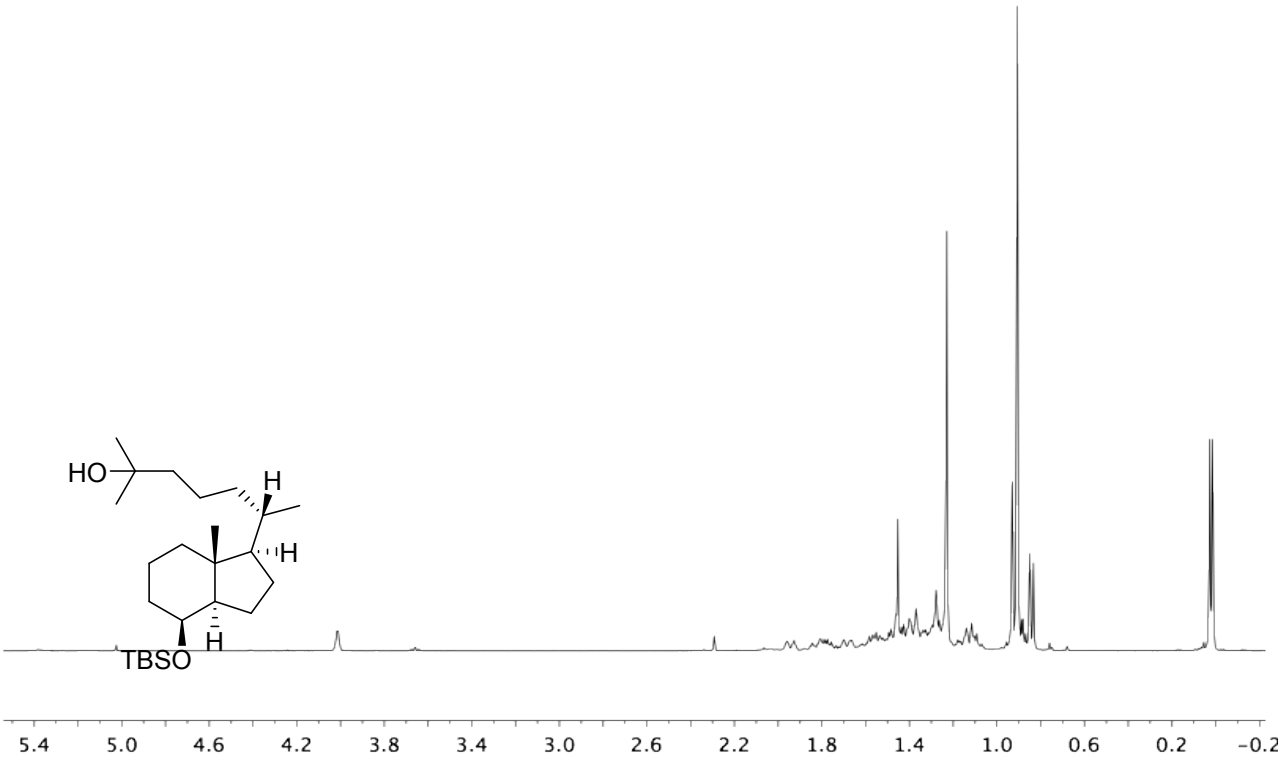
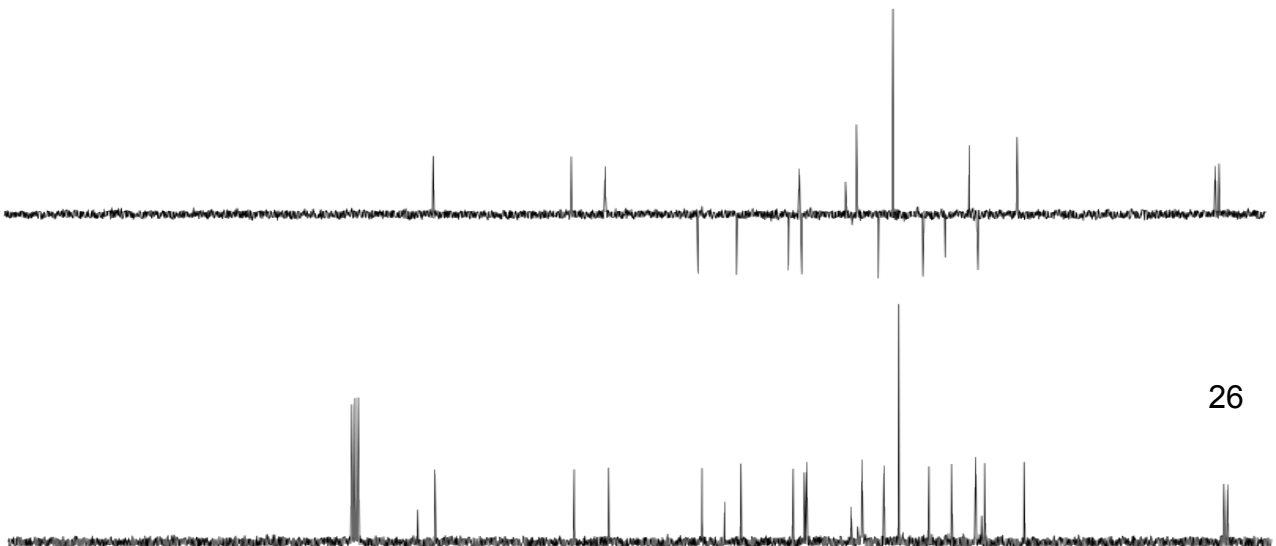
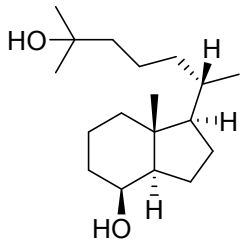
15
10
5
0
−5


HO
H
OTs
H
H
TBSO
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

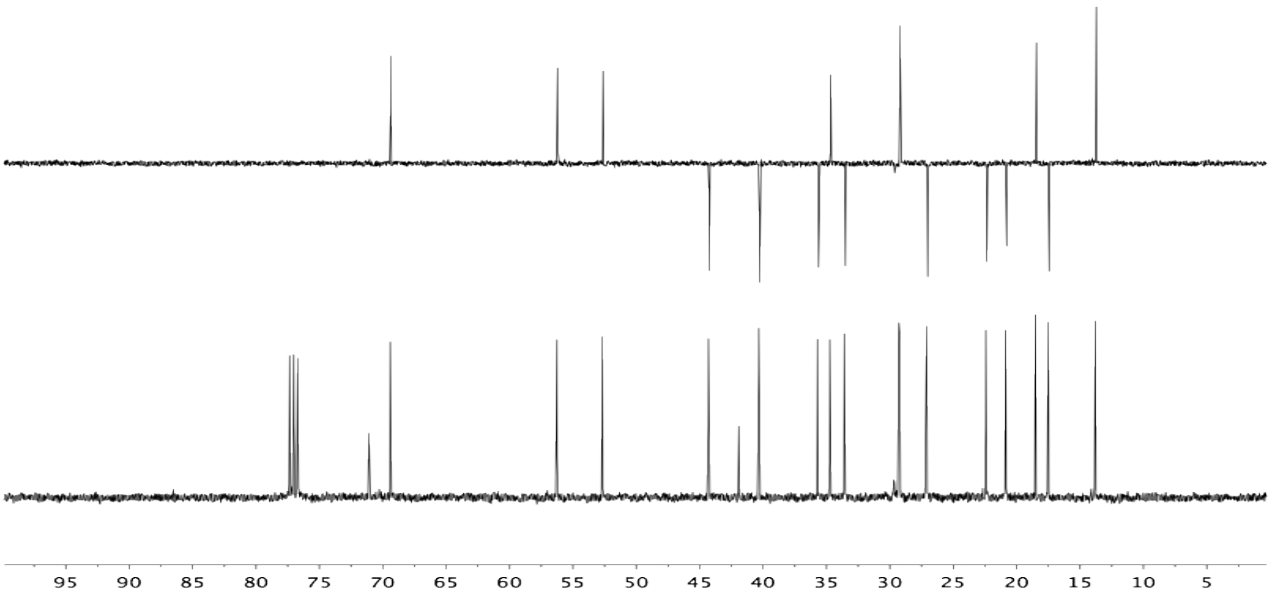



HO
H
H
H
TBSO
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2




HO
H
H
H
HO

6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


95
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45
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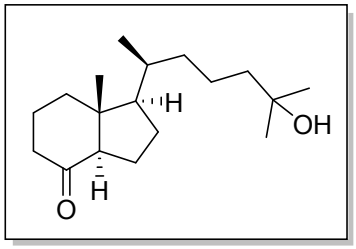
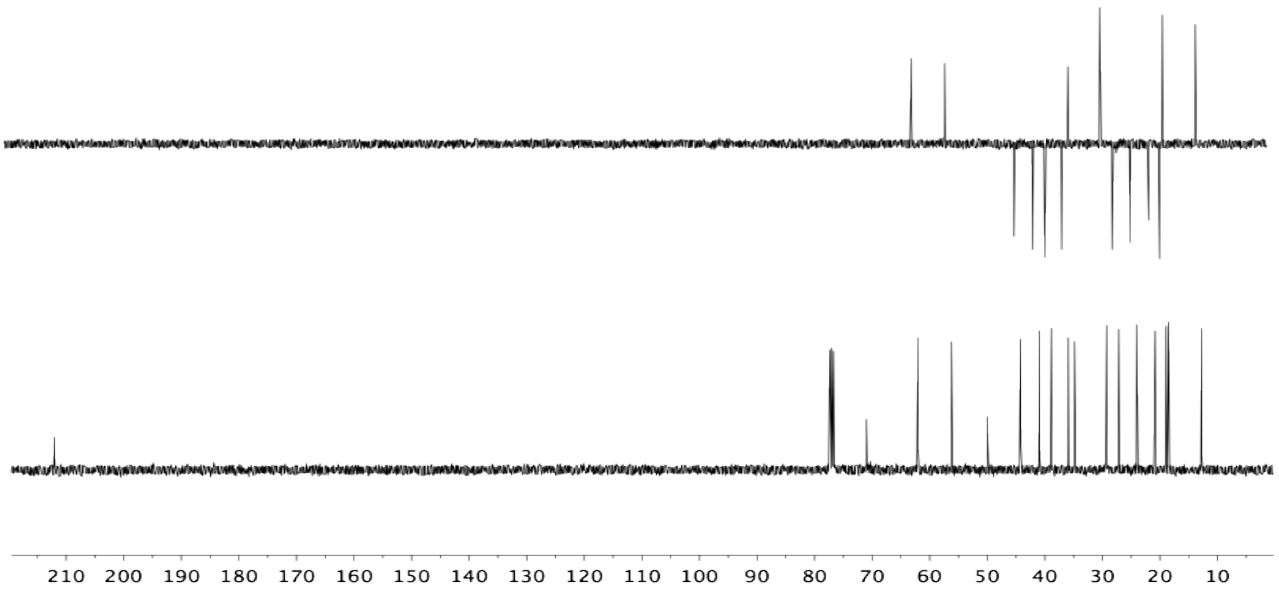
35
30
25
20
15
10
5


H
OH
H
O

5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2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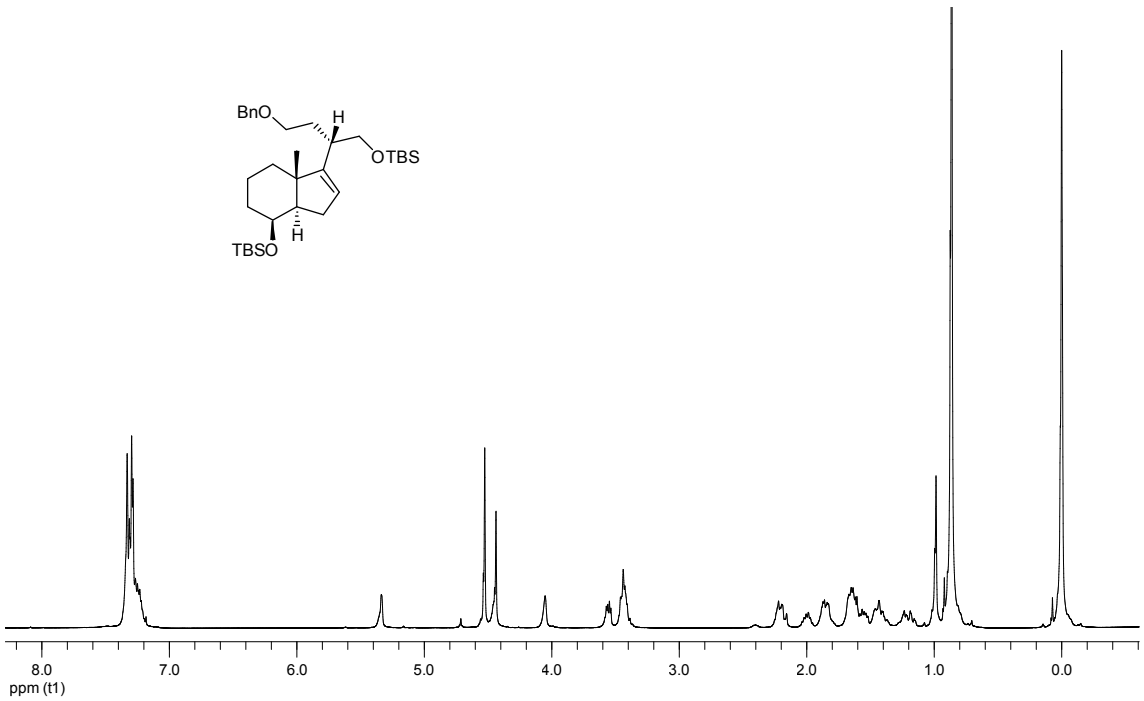
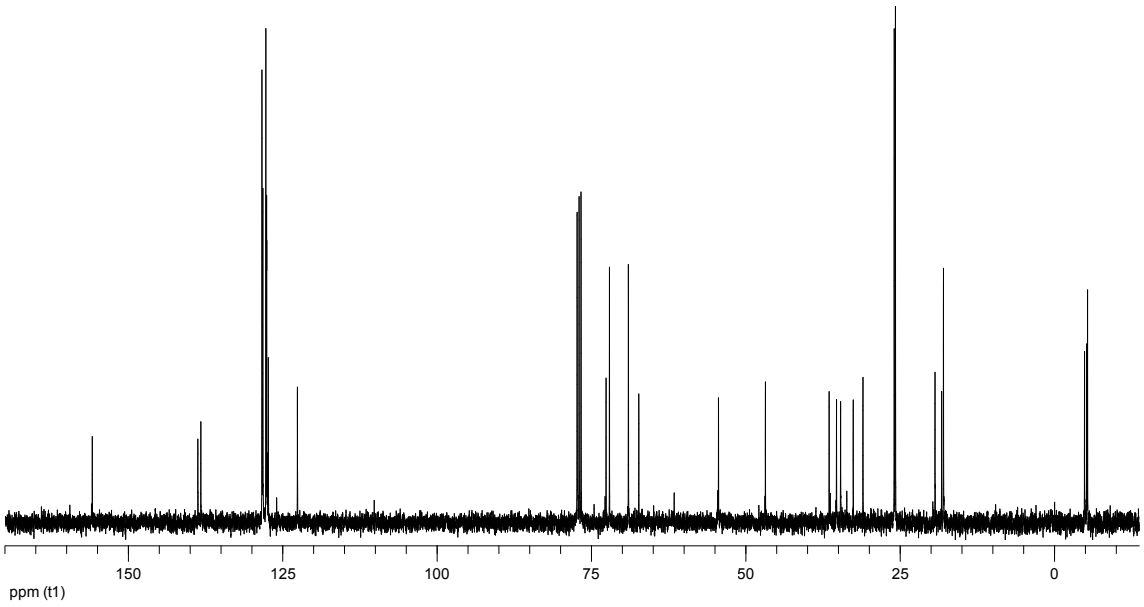
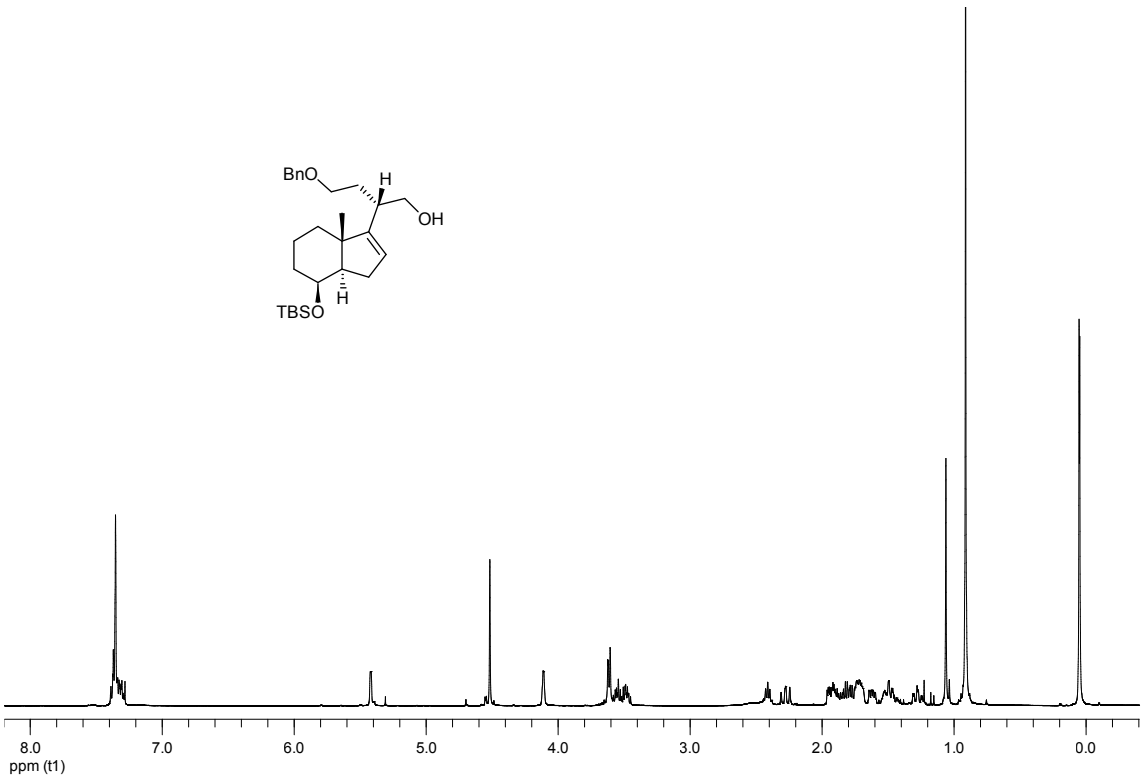

BnO
H
OTBS
TBSO
H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


150
125
100
75
50
25
0
ppm (t1)


BnO
H
OH
TBSO
H
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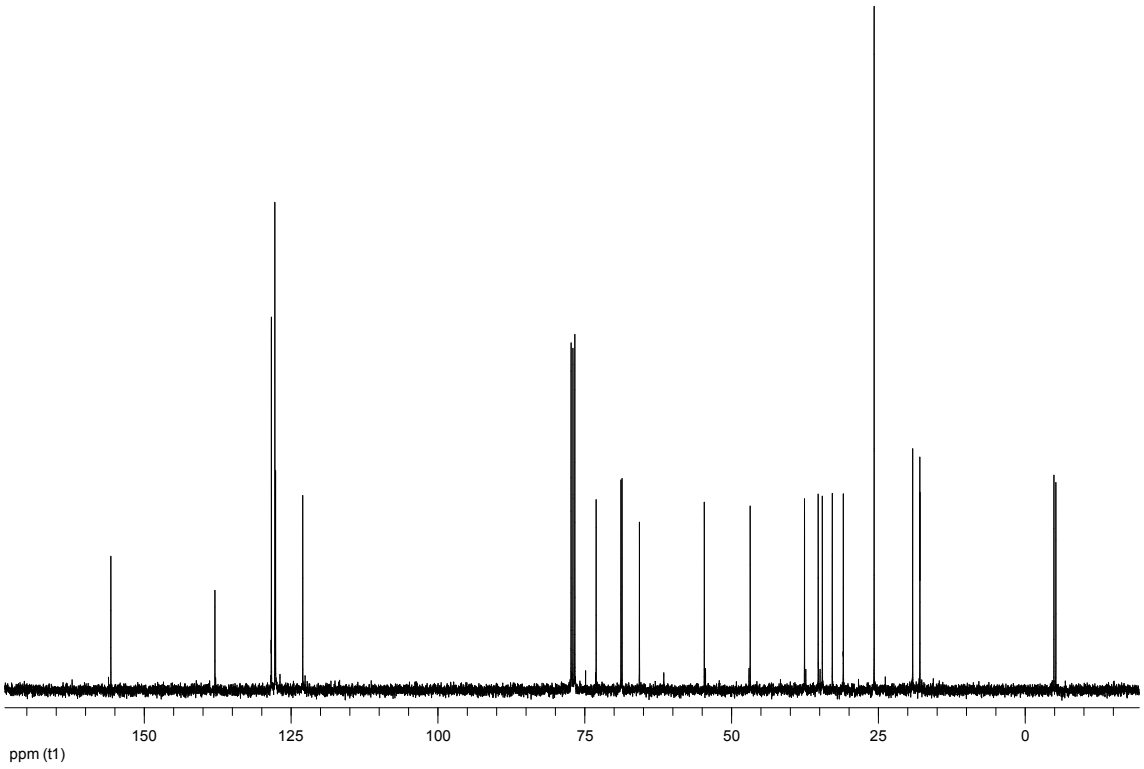
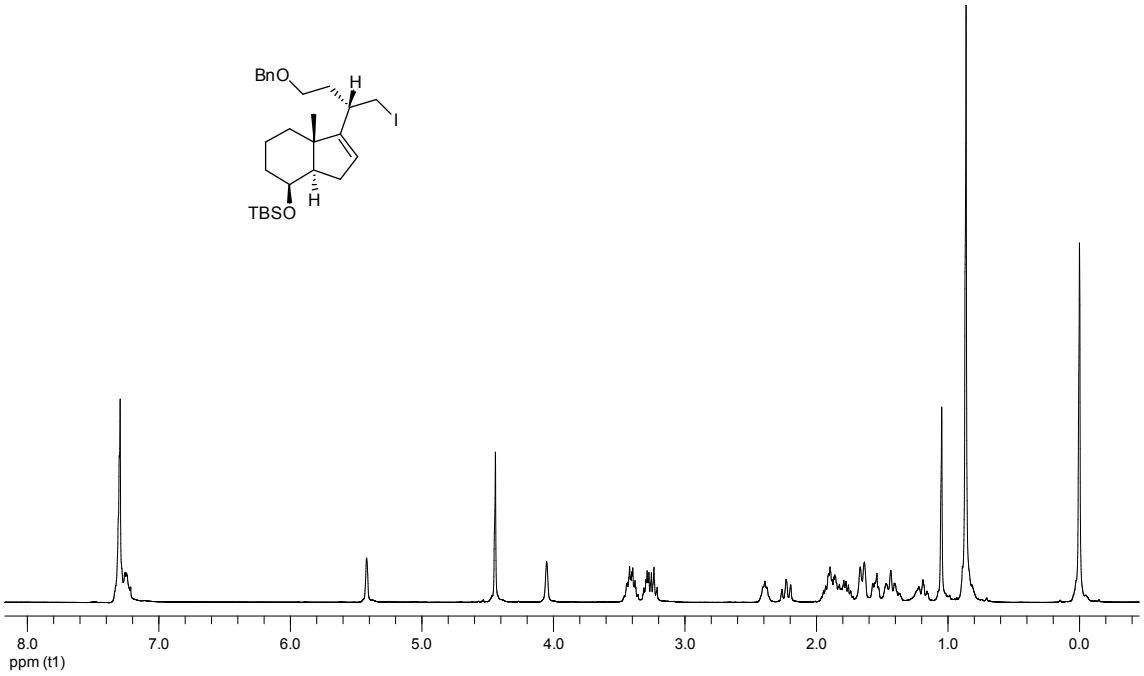
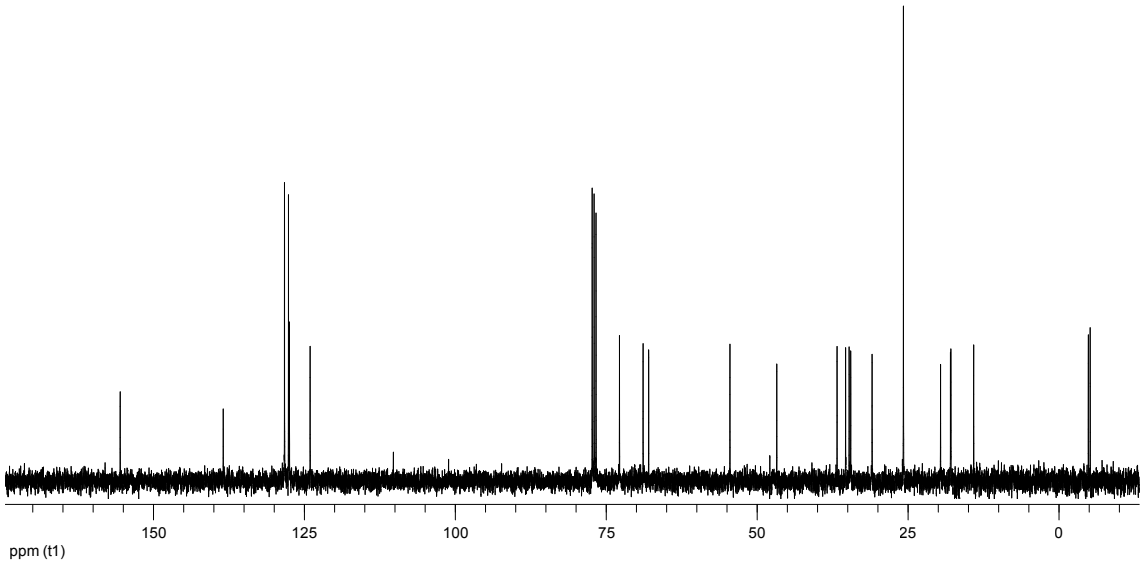
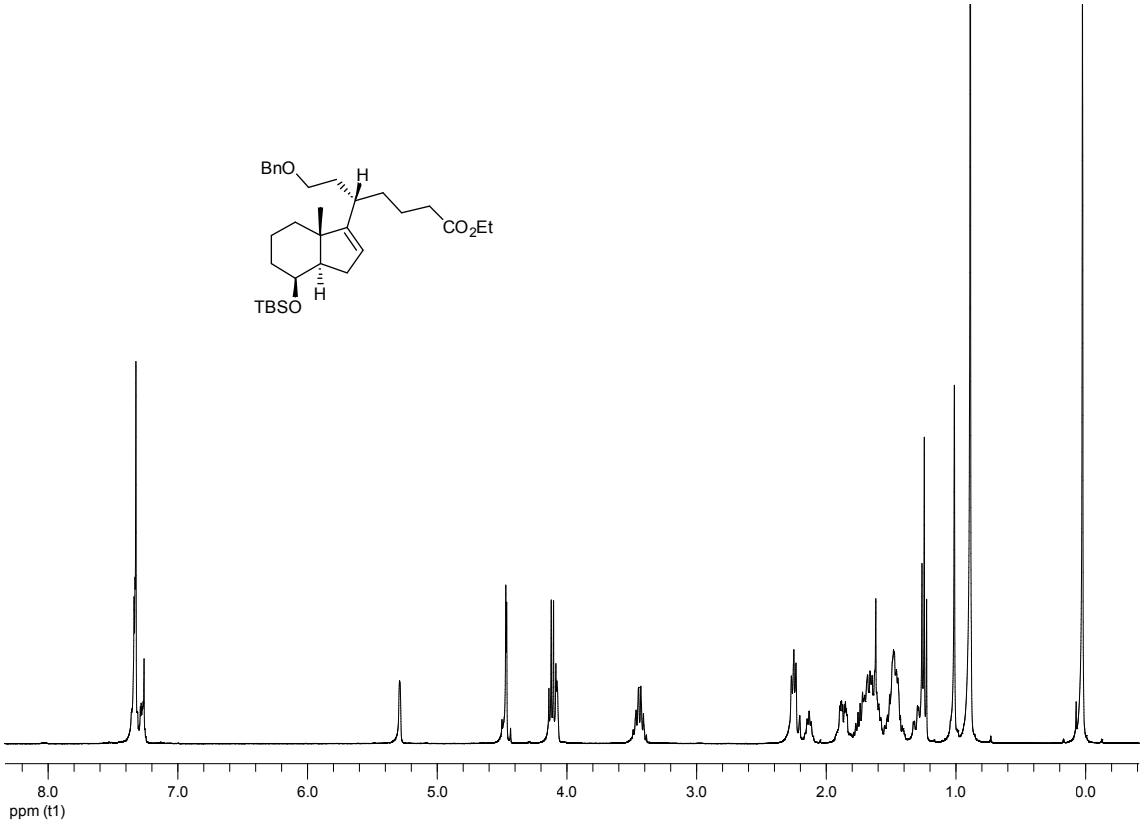
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


150
125
100
75
50
25
0
ppm (t1)


BnO
H
I
H
TBSO
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


150
125
100
75
50
25
0
ppm (t1)


BnO
H
CO2Et
TBSO
H
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5.0
4.0
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2.0
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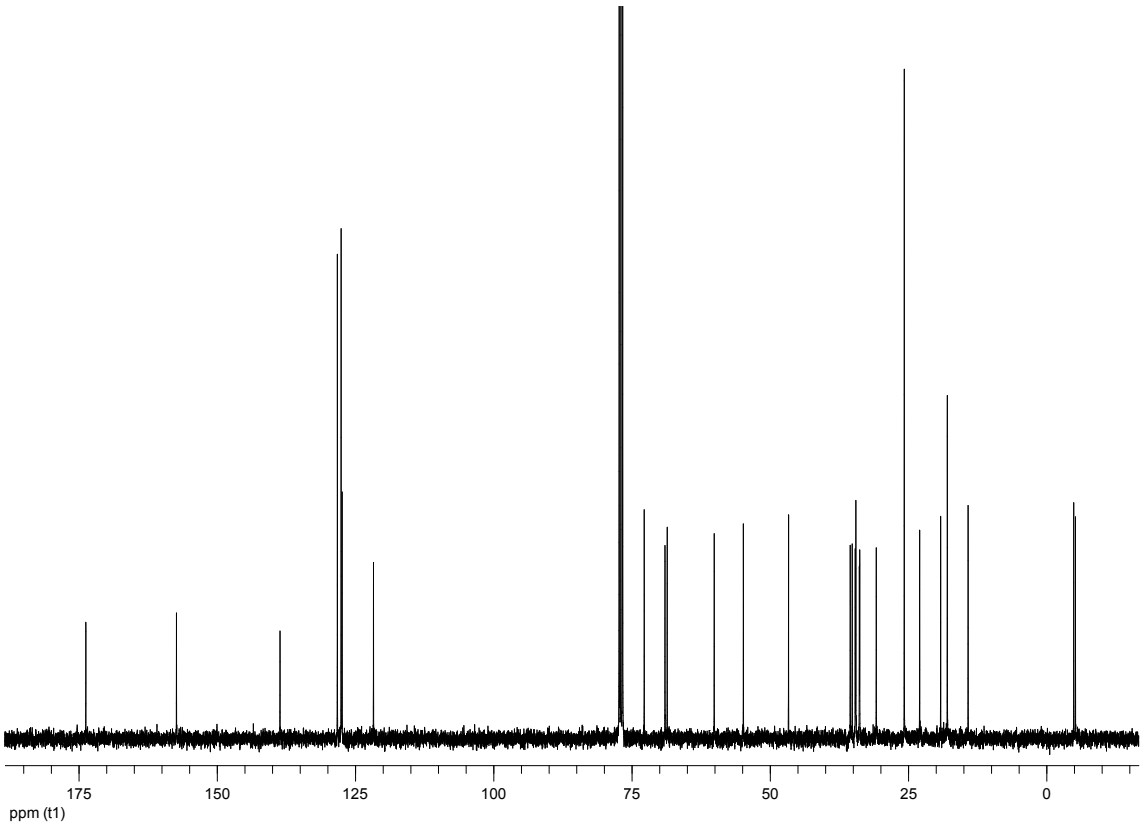
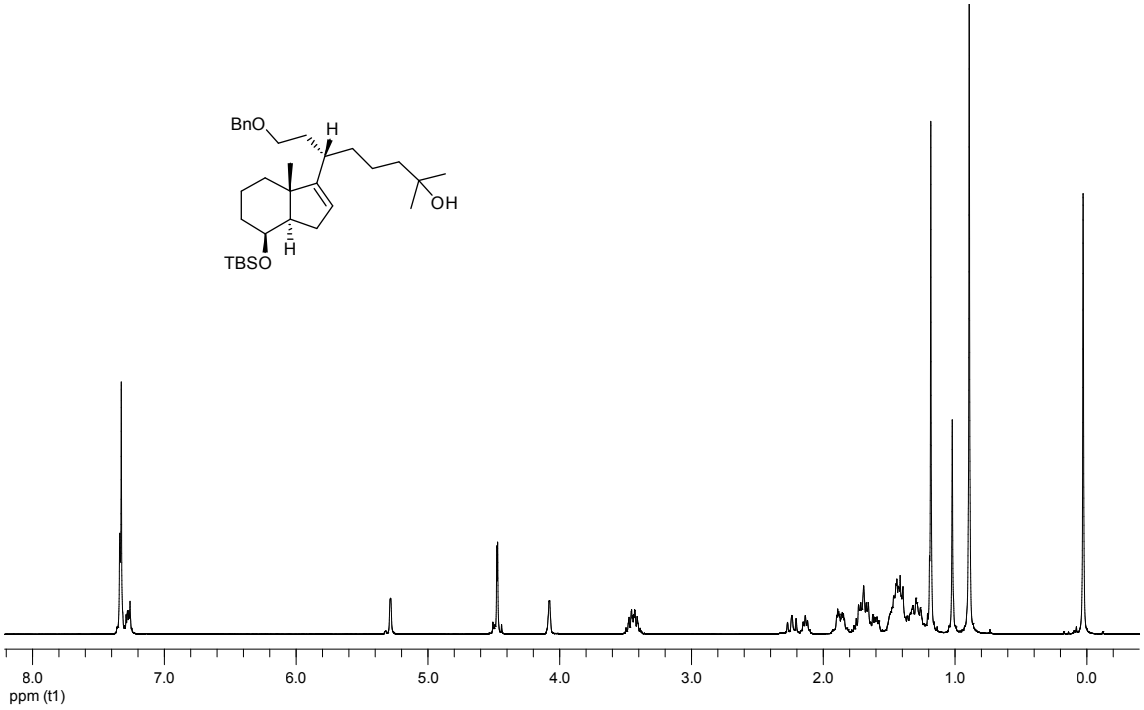
ppm (t1)


175
150
125
100
75
50
25
0
ppm (t1)


BnO
H
OH
H
TBSO
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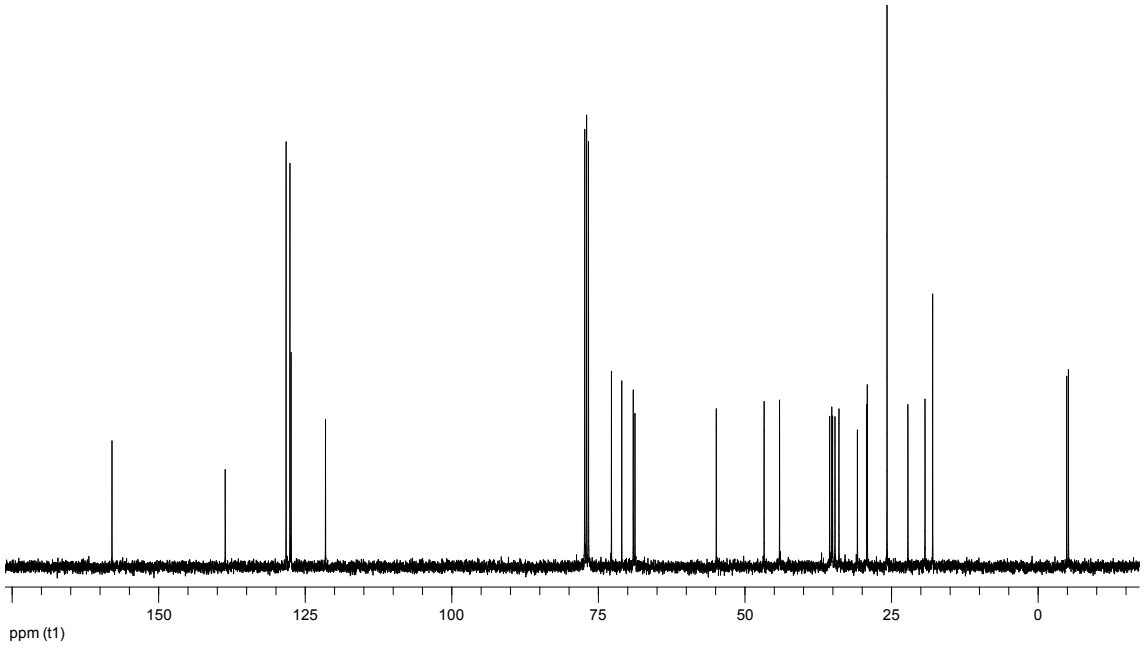
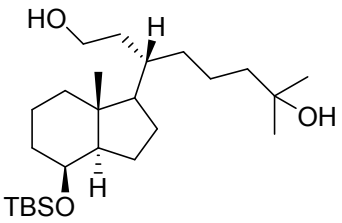
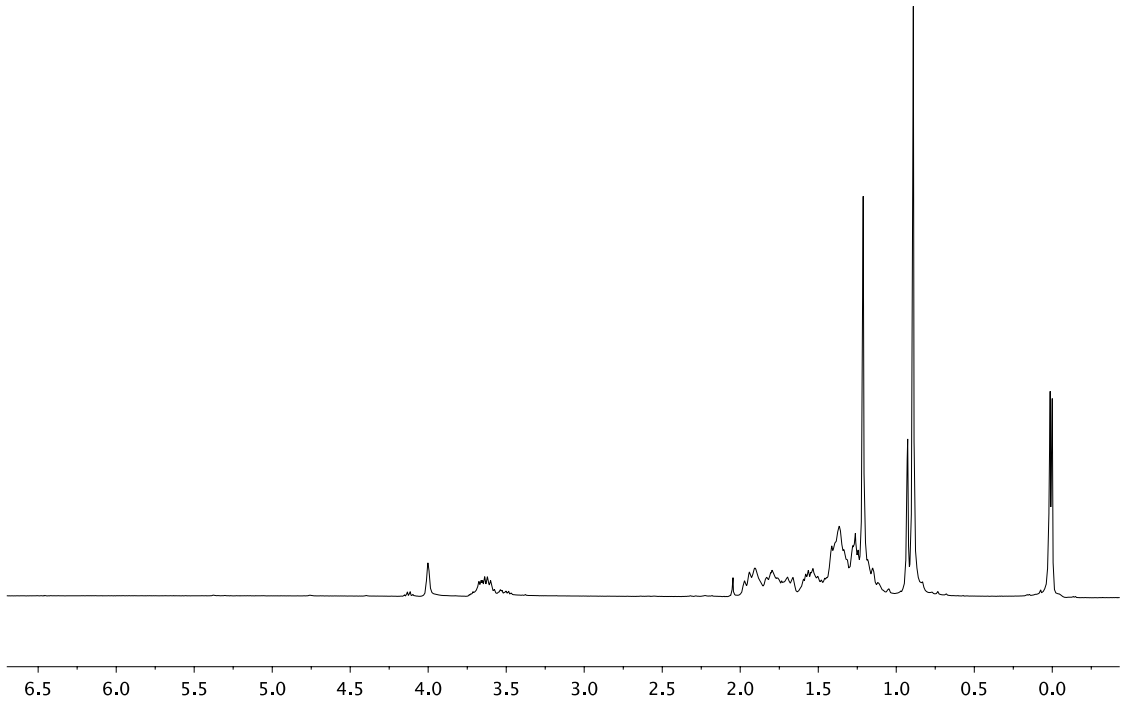
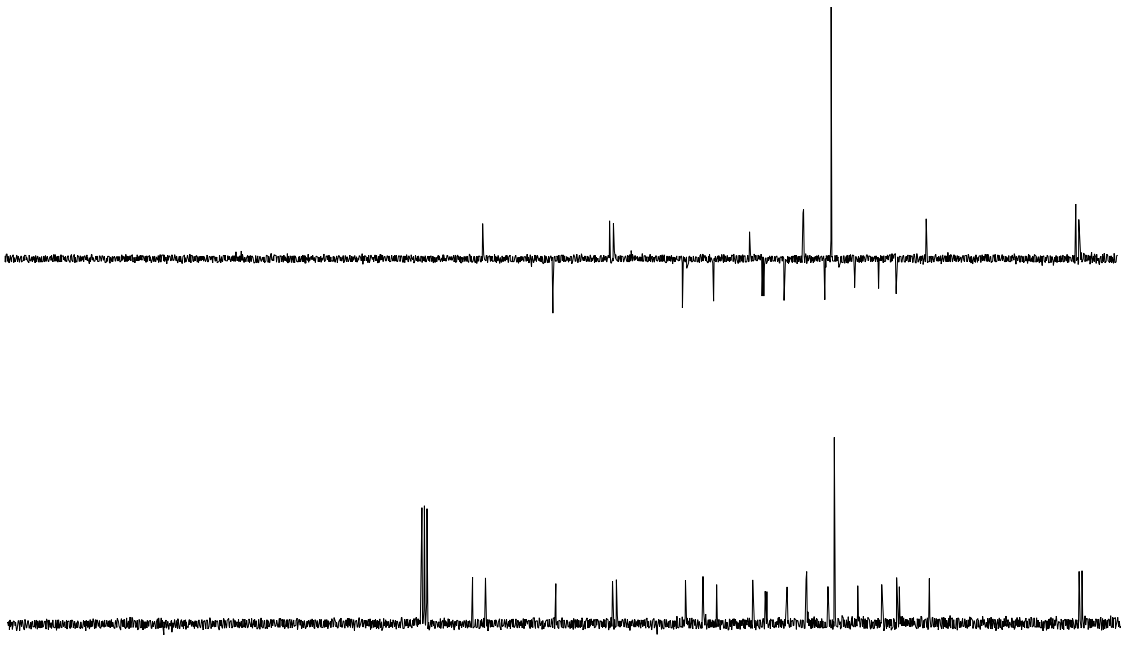
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


150
125
100
75
50
25
0
ppm (t1)


HO
H
OH
H
TBSO


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


125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5