SUPPORTING INFORMATION FOR

Synthesis of a chiral building block for highly functionalized polycyclic ethers.

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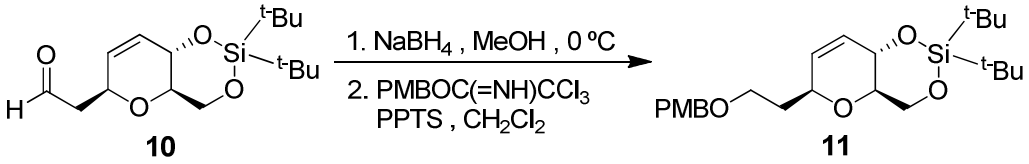
Experimental procedure

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.

(1*S*,6*R*,8*S*)-3,3-di*tert*-butyl-8-(2'-*p*-methoxybencyloxyethyl)-2,4,7-trioxy-3-silinebicyclic[4,4,0]dec-9-ene (11)

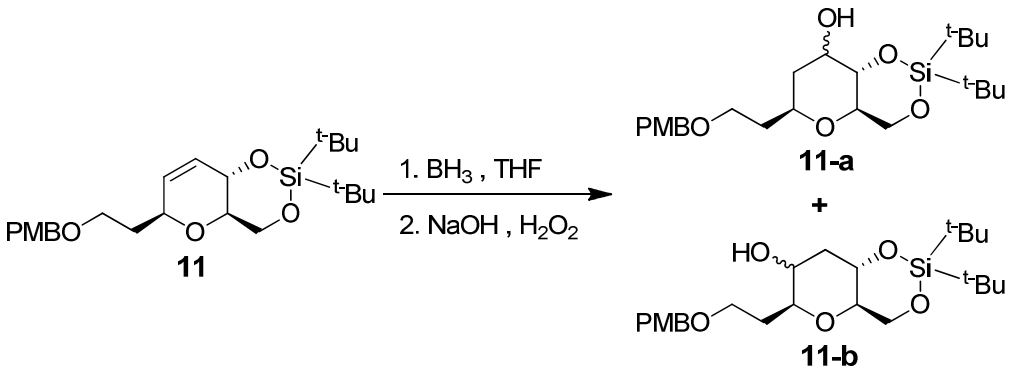


To a solution of aldehyde **10** (6.28 g, 20.12 mmol) in MeOH (30 mL), cooled at 0ºC was slowly added $NaBH_4$ (913 mg, 24.15 mmol) and the mixture stirred for 30 min in the same conditions. Then, water (30 mL) was added and the product extracted with EtOAc (3 x 50 mL). The organics were washed with water (3x150 mL) and brine (150 mL), dried over Na_2SO_4 and the solvent evaporated under reduced pressure affording a white solid.

To a solution of PMBOH (3.76 mL, 30.18 mmol) in THF (50 mL) cooled at 0ºC was added NaH (60%) (72 mg, 3 mmol) and the mixture stirred for 1 h in the same conditions. Then, CCl_3CN (3 mL, 3.18 mmol) was added and stirred for 30 mn and a saturated aqueous solution of $NaHCO_3$ (30 mL) was added. The resulting mixture was extracted with EtOAc (2x40 mL) and the combined

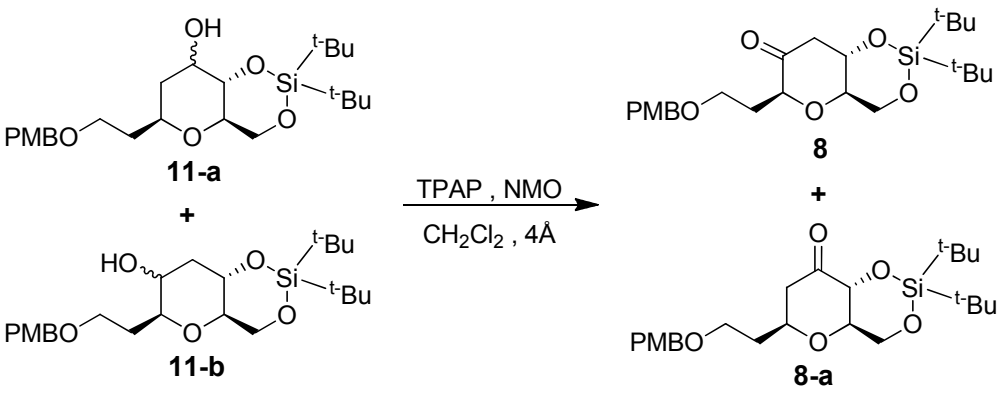
organic phases were washed with brine (70 mL), dried over Na_2SO_4 and the solvent removed under reduced pressure affording a residue which was dissolved in CH_2Cl_2 (40 mL). The alcohol which was obtained in the first step and a catalytic amount of PPTS were added and the mixture stirred for 48 h. Then, a saturated aqueous solution of $NaHCO_3$ (40 mL) was added and the resulting organic phase was washed with water (3x40 mL) and brine (40 mL), filtered and evaporated to give a residue which was chromatographed on silica gel using 1% EtOAc/Hexane as eluent, affording compound **11** (7.52 g, 89%) as a white solid; m.p.= 60 ºC; Rf: 0.55 (20% EtOAc/Hexane);**IR (NaCl,cm^{-1}):** 2960.30, 2933.69, 2880.69, 2859.36, 1647.83, 1132.58; **[α]$^{22}_{D}$**= -14.51 (c 1.43, $CHCl_3$); **^{1}H-NMR ($CDCl_3$, δ):** 7.26 (2H, d, J=8.7 Hz, H_o-PMB), 6.88 (2H, d, J=8.7 Hz, H_m-PMB), 5.83 (1H, d, J=10.3 Hz, H-9 ó H-10), 5.64 (1H, d, J=10.3 Hz, H-9 ó H-10), 4.43 (2H, s, C**H**$_2$-PMP), 4.37 (2H, m, H-1, H-8), 4.16 (1H, dd, J=10.0, 5.1Hz, H-5), 3.85 (1H, t, J=10.0 Hz, H-5), 3.80 (3H, s, OC**H**$_3$-PMB), 3.54 (3H, m, 2H-2', H-6), 1.85 (1H, m, H-1'), 1.74 (1H, m, H-1'), 1.06 (9H, s, CH_3-^{t}Bu), 1.00 (9H, s, CH_3-^{t}Bu);**^{13}C-NMR ($CDCl_3$, δ):**159.1 (C_p-PMB), 130.5 (C-PMB), 129.7 (CH-9 ó CH-10), 129.6 (CH-9 ó CH-10), 129.2 (CH_o-PMB), 113.7 (CH_m-PMB), 74.6 (CH-6), 72.8 (CH-1), 72.6 (CH_2-PMB), 70.3 (CH-8), 67.2 (CH_2-5), 65.9 (CH_2-2'), 55.2 (O**C**H_3-PMB), 35.4 (CH_2-1'), 27.5 (CH_3-^{t}Bu), 27.1 (CH_3-^{t}Bu), 22.6 (C-^{t}Bu), 20.0 (C-^{t}Bu); **MS (ESI) [m/z, (%)]:**457 (M^++Na, 100), 315 (17);**HRMS (ESI):**457.2380 calculated for$C_{24}H_{38}NaO_5Si$, found 457.2390.

(1*S*,6*R*,8*S*)-3,3-di*tert*-butyl-8-(2'-*p*-methoxybencyloxyethyl)-2,4,7-trioxy-3-silinebicyclic[4,4,0]decan-10-ol (11-a) and (1*S*,6*R*,8*S*)-3,3-di*tert*-butyl-8-(2'-*p*-methoxybencyloxyethyl)-2,4,7-trioxy-3-silinebicyclic[4,4,0]decan-9-ol (11-b)



To a solution of**258** (4 g, 9.21 mmol) in THF (40 mL) cooled at 0 ºC, was added BH_3·THF (18.42 mL of a 1 M solution in THF, 18.42 mmol) and stirring was continued for 30 min. Then, were added 3 M aqueous solution of NaOH (7.5 mL) and 30% aqueous solution of H_2O_2 (2.04 mL)the temperature was allowed to reach to room temperature and stirred for 12 h. The reaction was quenched with water (30 mL) and the product extracted with EtOAc (3x40 mL). The combined organic phases were dried, filtered and evaporated. Finally, the residue was filtered through silica gel (30% EtOAC/Hexane) to give a mixture of alcohols **11-a** and **11-b**.

(1*S*,6*R*,8*S*)-3,3-di*tert*-butyl-8-(2'-*p*-methoxybencyloxyethyl)-2,4,7-trioxy-3-silinebicyclic[4,4,0]dec-9-one (8) and(1*S*,6*R*,8*S*)-3,3-di*tert*-butyl-8-(2'-*p*-methoxybencyloxyethyl)-2,4,7-trioxy-3-silinebicyclic[4,4,0]dec-10-one (8-a)



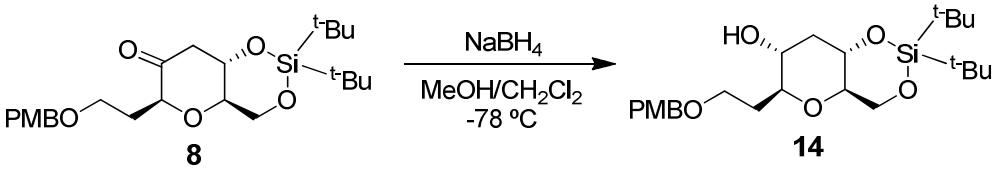
To a solution of a mixture of alcohols **11-a** and **11-b** (4 g, 8.83 mmol) in CH_2Cl_2 (40 mL) were added 4Å molecular sieves (2 g), NMO (3.10 g, 25 mmol) and a catalytic amount of TPAP. The resulting greenish solution was stirred at room temperature for 12 h. The solvent was rotatory evaporated to afford a residue which was chromatographed on silica gel using 5% EtOAc/Hexane as eluent, affording ketone **8** (2.4 g, 60%) along with its isomeric ketone **8-a** (1.23 g, 31%).

Compound **8**. White solid, m.p.= 81ºC, Rf: 0.62 (30% AcOEt/Hexano); **IR (NaCl,cm^{-1}):**2962.13, 2934.16, 2880.17, 2859.92, 1727.91, 1513.85, 1132.05;**[α]$^{26}_{D}$**= -16.54 (c 1.86, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):** 7.23 (2H, d, J=8.6

Hz, H_o-PMB), 6.87 (2H, d, J=8.6 Hz, H_m-PMB), 4.42 (1H, d, J=11.6 Hz, C**H**$_2$-PMP), 4.38 (1H, d, J=11.6 Hz, C**H**$_2$-PMP), 4.19 (1H, dd, J=10.3, 5.0Hz, H-5), 4.09 (1H, ddd, J=10.9, 9.4, 5.7 Hz, H-1), 3.98 (1H, dd, J=7.7, 4.2 Hz, H-8), 3.85 (1H, t, J=10.2 Hz, H-5), 3.80 (3H, s, OC**H**$_3$-PMB), 3.57 (3H, m, 2H-2', H-6), 2.97 (1H, dd, J=15.7, 5.7 Hz, H-10), 2.42 (1H, dd, J=15.7, 11.0 Hz, H-10), 2.19 (1H, m, H-1'), 1.77 (1H, m, H-1'), 1.04 (9H, s, CH_3-^{t}Bu), 1.01 (9H, s, CH_3-^{t}Bu);**^{13}C-NMR ($CDCl_3$, δ):**205.1 (C=O), 159.2 (C_p-PMB), 130.4 (C-PMB), 129.2 (CH_o-PMB), 113.7 (CH_m-PMB), 79.6 (CH-8), 76.1 (CH-6), 73.1 (CH-1), 72.4 (CH_2-PMB), 66.5 (CH_2-5), 65.2 (CH_2-2'), 55.2 (O**C**H$_3$-PMB), 48.1 (CH_2-10), 29.4 (CH_2-1'), 27.3 (CH_3-^{t}Bu), 27.0 (CH_3-^{t}Bu), 22.6 (C-^{t}Bu), 19.9 (C-^{t}Bu);**MS (ESI) [m/z, (%)]:**473 (M^++Na, 100), 313 (30);**HRMS (ESI):**473.2329 calculated for$C_{24}H_{38}NaO_6Si$, found 473.2319.

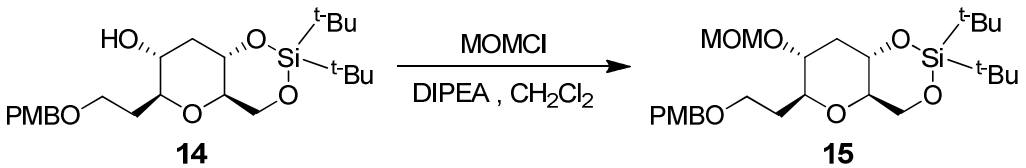
Compound **8-a**. White solid, m.p.= 76 ºC, Rf: 0.5 (30% AcOEt/Hexano);**IR (NaCl,cm^{-1}):**2961.98, 2933.69, 2880.17, 2858.24, 1736.58, 1512.79, 1247.57, 1133.94;**[α]$^{24}_D$**= -19.34 (c 1.60, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):**7.22 (2H, d, J=8.3 Hz, H_o-PMB), 6.87 (2H, d, J=8.3 Hz, H_m-PMB), 4.41 (3H, m, C**H**$_2$-PMP, H-1), 4.16 (1H, dd, J=10.0, 4.6 Hz, H-5), 3.95 (1H, t, J=10.2 Hz, H-5), 3.88 (1H, m, H-6), 3.79 (3H, s, OC**H**$_3$-PMB), 3.52 (3H, 2H-2', H-8), 2.51 (1H, dd, J=13.7, 2.4 Hz, H-9), 2.43 (1H, m, H-9), 1.83 (2H, m, 2H-1'), 1.04 (9H, s, CH_3-^{t}Bu), 1.00 (9H, s, CH_3-^{t}Bu);**^{13}C-NMR ($CDCl_3$, δ):**202.4 (C=O), 159.2 (C_p-PMB), 130.2 (C-PMB), 129.2 (CH_o-PMB), 113.7 (CH_m-PMB), 80.1 (CH-1), 77.0 (CH-8), 75.7 (CH-6), 72.6 (CH_2-PMP), 66.7 (CH_2-5), 65.3 (CH_2-2'), 55.2 (O**C**H$_3$-PMB), 47.3 (CH_2-9), 36.0 (CH_2-1'), 27.3 (CH_3-^{t}Bu), 26.9 (CH_3-^{t}Bu), 22.6 (C-^{t}Bu), 20.1 (C-^{t}Bu);**MS (ESI) [m/z, (%)]:**473 (M^++Na, 100), 338 (21), 313 (12); **HRMS (ESI):**473.2329 calculated for$C_{24}H_{38}NaO_6Si$, found 473.2328.

(1*S*,6*R*,8*S*,9*R*)-3,3-di*tert*-butyl-8-(2'-*p*-methoxybencyloxyethyl)-2,4,7-trioxy-3-silinebicyclic[4,4,0]dec-9-ol (14)



To a solution of ketona **8** (2.33 g, 5.15 mmol) in MeOH (20 mL) and CH_2Cl_2 (20 mL) cooled at -78 ºC was slowly added $NaBH_4$ (292 mg, 7.72 mmol) and the mixture stirred for 1 h in the same conditions. Then, water (40 mL) was added and the product extracted with EtOAc (3 x 40 mL) and the organics washed with water (3x100 mL) and brine (100 mL), dried over Na_2SO_4 and the solvent evaporated under reduced pressure affording alcohol **14** (2.34 g, 99%) as a white solid; m.p.= 115 ºC, Rf: 0.25 (20% EtOAc/Hexane);**IR (NaCl,cm^{-1}):**3420.14, 2960.23, 2933.87, 2859.92, 1513.85, 1092.48; **$[\alpha]^{25}_D$**= -25.13 (c 1.48, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):** 7.24 (2H, d, J=8.5 Hz, H_o-PMB), 6.88 (2H, d, J=8.5 Hz, H_m-PMB), 4.46 (1H, d, J=11.4 Hz, C**H**$_2$-PMP), 4.43 (1H, d, J=11.4 Hz, C**H**$_2$-PMP), 4.08 (1H, dd, J=10.0, 4.8 Hz, H-5), 3.79 (3H, s, OC**H**$_3$-PMB), 3.73 (2H, m, H-1, H-5), 3.58 (2H, m, 2H-2'), 3.39 (1H, m, H-9), 3.22 (2H, m, H-6, H-8), 2.44 (1H, m, H-10), 1.99 (1H, m, H-1'), 1.84 (1H, m, H-1'), 1.47 (1H, dd, J=22.3, 11.1 Hz, H-10), 1.03 (9H, s, CH_3-^{t}Bu), 0.98 (9H, s, CH_3-^{t}Bu);**^{13}C-NMR ($CDCl_3$, δ):**159.3 (C_p-PMB), 129.4 (CH_o-PMB), 128.5 (C-PMB), 113.8 (CH_m-PMB), 81.0 (CH-8), 77.1 (CH-6), 72.8 (CH_2-PMB), 72.5 (CH-1), 69.2 (CH-9), 66.8 (CH_2-5), 66.5 (CH_2-2'), 55.2 (O**C**H_3-PMB), 41.1 (CH_2-10), 33.5 (CH_2-1'), 27.4 (CH_3-^{t}Bu), 27.1 (CH_3-^{t}Bu), 22.5 (C-^{t}Bu), 19.8 (C-^{t}Bu); **MS (ESI) [m/z, (%)]:**475 (M^++Na, 100);**HRMS (ESI):**475.2486 calculated for $C_{24}H_{40}NaO_6Si$, found 475.2486.

(1*S*,6*R*,8*S*,9*R*)-3,3-di*tert*-butyl-8-(2'-*p*-methoxybencyloxyethyl)-9-(methoxymethoxy)-2,4,7-trioxy-3-silinebicyclic[4,4,0]decane (15)

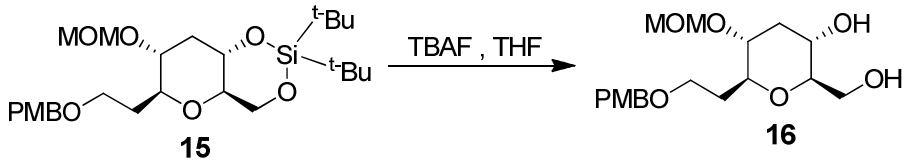


14 **15**

To a solution of alcohol **14** (1 g, 2.21 mmol) in CH_2Cl_2 (10 mL) was added DIPEA (1.93 mL, 11.06 mmol) and the mixture stirred for 10 min, cooled to 0ºC and MOMCl (839 µL, 11.06 mmol) added. Stirring was continued for 12 h

allowing the mixture to reach gradually room temperature. The reaction was quenched with water (10 mL) and was extracted with CH_2Cl_2 (2x10 mL). The combined organic layers were washed with H_2O (30 mL) and brine (30 mL) and were dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The residue was chromatographed on silica gel using 3% EtOAc/Hexane as eluent, affording compound **15** (1.01 g, 93%)as a colourless liquid; Rf: 0.51 (20% EtOAc/Hexane);**IR (NaCl,cm^{-1}):** 2960.65, 2932.78, 2859.15, 1512.89, 1092.47, 854.35;**[α]$^{26}_{D}$**= -43.56 (c 2.80, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):** 7.25 (2H, d, J=8.6 Hz, H_o-PMB), 6.87 (2H, d, J=8.6 Hz, H_m-PMB), 4.72 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.60 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.47 (1H, d, J=11.6 Hz, C**H**$_2$-PMP), 4.40 (1H, d, J=11.6 Hz, C**H**$_2$-PMP), 4.05 (1H, dd, J=10.1, 4.9 Hz, H-5), 3.80 (3H, s, OC**H**$_3$-PMB), 3.74 (1H, t, J=10.1 Hz, H-5), 3.73 (1H, m, H-9), 3.55 (2H, dd, J=7.9, 6.1 Hz, 2H-2'), 3.37 (3H, s, OC**H**$_3$-MOM), 3.33 (2H, m, H-1, H-8), 3.24 (1H, dt, J=10.1, 4.9 Hz, H-6), 2.58 (1H, m, H-10), 2.16 (1H, m, H-1'), 1.55 (1H, m, H-10), 1.47 (1H, m, H-1'), 1.03 (9H, s, CH_3-^{t}Bu), 0.99 (9H, s, CH_3-^{t}Bu);**^{13}C-NMR ($CDCl_3$, δ):**159.1 (C_p-PMB), 130.6 (C-PMB), 129.2 (CH_o-PMB), 113.7 (CH_m-PMB), 95.2 (CH_2-MOM), 77.5 (CH-8), 76.8 (CH-6), 74.5 (CH-1), 72.4 (CH_2-PMB), 72.3 (CH-9), 66.8 (CH_2-5), 66.1 (CH_2-2'), 55.6 (O**C**H_3-OMOM), 55.2 (O**C**H_3-PMB), 39.3 (CH_2-10), 31.9 (CH_2-1'), 27.4 (CH_3-^{t}Bu), 27.0 (CH_3-^{t}Bu), 22.6 (C-^{t}Bu), 19.9 (C-^{t}Bu);**MS (ESI) [m/z, (%)]:**520 (M^++1+Na, 27), 519 (M^++Na, 100);**HRMS (ESI):**519.2748 calculated for$C_{26}H_{44}NaO_7Si$, found 519.2747.

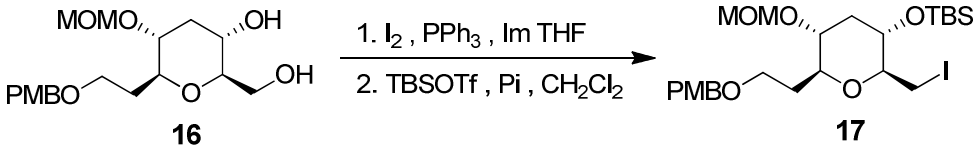
(1*S*,2*R*,4*S*,5*R*)-2-hidroxymethyl-4-(2'-*p*-methoxybencyloxyethyl)-5-(methoxymethoxy)-3-tetrahydro-2H-pyran-1-ol (16)



To a solution of **16** (1 g, 2.04 mmol) in THF (10 mL) was added TBAF (6.6 mL of a 1 M solution in THF, 6.6 mmol) and the mixture was stirred at room temperature for 12 h, quenched with an aqueous saturated solution of NH_4Cl

(15 mL) and the product extracted with EtOAc (3 x 20 mL). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 70% EtOAc/Hexane as eluent, affording diol **16** (690 mg, 96%) as a colourless liquid;Rf: 0.30 (EtOAc);**IR (NaCl,cm^{-1}):**3428.36, 2920.98, 2884.25, 1512.89, 1248.96, 1098.36;**[α]$^{30}_{D}$**= +37.35 (c 1.69, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):** 7.25 (2H, d, J=8.6 Hz, H_o-PMB), 6.87 (2H, d, J=8.6 Hz, H_m-PMB), 4.69 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.59 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.46 (1H, d, J=11.6 Hz, C**H**$_2$-PMP), 4.40 (1H, d, J=11.6 Hz, C**H**$_2$-PMP), 3.79 (3H, s, OC**H**$_3$-PMB), 3.72 (2H, m, C**H**$_2$-OH), 3.58 (3H, m, 2H-2', H-5), 3.35 (3H, s, OC**H**$_3$-MOM), 3.29 (2H, m, H-1, H-4), 3.12 (1H, m, H-2), 2.95 (1H, s, OH), 2.50 (1H, m, H-6), 2.17 (1H, m, H-1'), 1.60 (1H, m, H-1'), 1.45 (1H, dd, J=22.2, 11.3 Hz, H-6);**^{13}C-NMR ($CDCl_3$, δ):**159.1 (C_p-PMB), 130.4 (C-PMB), 129.3 (CH_o-PMB), 113.7 (CH_m-PMB), 95.3 (CH_2-MOM), 80.7 (CH-2), 77.3 (CH-4), 74.5 (CH-1), 72.5 (CH_2-PMB), 66.3 (CH-5), 66.2 (CH_2-2'), 62.9 (**C**H_2-OH), 55.6 (O**C**H_3-OMOM), 55.2 (O**C**H_3-PMB), 39.1 (CH_2-6), 31.9 (CH_2-1');**MS (ESI) [m/z, (%)]:**379 (M^++Na, 100);**HRMS (ESI):**379.1727 calculated for $C_{18}H_{28}NaO_7$, found 379.1726.

(2*S*,3*R*,5*S*,6*S*)-5-(*tert*-butyldimethylsililoxy)-2-(2'-*p*-methoxybencyloxyethyl)-3-(methoxymethoxy)-6-iodomethyl-1-tetrahydro-2H-pyrane (17)

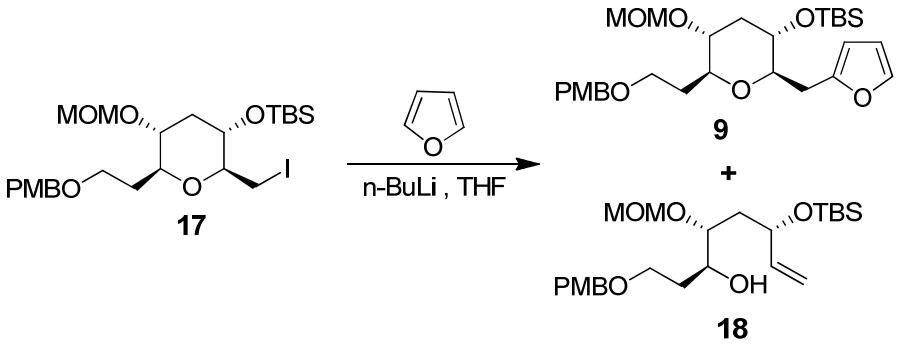


16 **17**

To a solution of diol **16** (570 mg, 1.6 mmol) in THF (15 mL) were added PPh_3 (630 mg, 2.4 mmol), Imidazole (326 mg, 4.80 mmol). When the mixture was completely dissolved, I_2 (487 mg, 1.92 mmol) was added at 0ºC. The solution was stirred till room temperature for 2 h and then a saturated aqueous solution of $NaHCO_3$ (30 mL) was added. The resulting mixture was extracted with EtOAc (2x30 mL) and the organics were washed with a 10% aqueous solution of $Na_2S_2O_4$ (60 mL) and brine (60 mL), dried over Na_2SO_4 and the solvent removed under reduced pressure. The obtained residue was dissolved

in CH_2Cl_2 (10 mL) and pyridine (2 mL), cooled to 0ºC and TBSOTf (441 µL, 1.92 mmol) added and the mixture stirred to room temperature for 2 h. Water (15 mL) was added and the organic phase was washed with a 10% aqueous solution of HCl (2 x 10 mL) and brine (10 mL), dried over Na_2SO_4 and the solvent was filtered and evaporated to give a residue which was chromatographed on silica gel using 5% EtOAc/Hexane as eluent, affording iodide **17** (750 mg, 80%) as a colourless liquid;Rf: 0.52 (30% EtOAc/Hexane);**IR (NaCl,cm^{-1}):**2920.98, 2884.17, 1512.66, 1247.58, 1095.78, 789.37;**[α]$^{26}_{D}$**= -1.10 (c 1.20, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):** 7.28 (2H, d, J=8.6 Hz, H_o-PMB), 6.87 (2H, d, J=8.6 Hz, H_m-PMB), 4.69 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.59 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.47 (2H, s, C**H**$_2$-PMP), 3.80 (3H, s, OC**H**$_3$-PMB), 3.66 (2H, m, 2H-2'), 3.47 (1H, m, H-3), 3.35 (3H, s, OC**H**$_3$-MOM),3.34 (3H, m, H-2, H-5, H-6), 3.16 (1H, dd, 1H, J=10.3, 7.4Hz, C**H**$_2$-I), 2.94 (1H, m, C**H**$_2$-I), 2.39 (1H, m, H-4), 2.16 (1H, m, H-1'), 1.62 (1H, m, H-1'), 1.49 (1H, dd, J=22.4, 11.0 Hz, H-4), 0.88 (9H, s, CH_3-^{t}Bu), 0.10 (3H, s, CH_3-Si), 0.09 (3H, s, CH_3-Si);**^{13}C-NMR ($CDCl_3$, δ):**159.0 (C_p-PMB), 130.7 (C-PMB), 129.3 (CH_o-PMB), 113.6 (CH_m-PMB), 95.3 (CH_2-MOM), 80.3 (CH-6), 77.3 (CH-2), 74.5 (CH-5), 72.6 (CH_2-PMP), 70.2 (CH-3), 66.2 (CH_2-2'), 55.5 (O**C**H_3-OMOM), 55.2 (O**C**H_3-PMB), 39.7 (CH_2-4), 31.9 (CH_2-1'), 25.7 (CH_3-^{t}Bu), 17.8 (C-^{t}Bu), 7.9 (**C**H_2-I), -4.0 (CH_3-Si), -4.6 (CH_3-Si);**MS (ESI) [m/z, (%)]:**603 (M^++Na, 100), 580 (M^++1, 26), 519 (48), 283 (60);**HRMS (ESI):**603.1609 calculated for$C_{24}H_{41}INaO_6Si$, found 603.1617.

(2*R*,3*S*,5*R*,6*S*)-3-(*tert*-butyldimethylsililoxy)-2-(furanylmethyl)-6-(2'-*p*-methoxybencyloxyethyl)-5-(methoxymethoxy)-1-tetrahydro-2H-pyrane(9) and(3*S*,4*R*,6*S*)-6-(*tert*-butyldimethylsililoxy)-1-(2'-*p*-methoxybencyloxyethyl)-4-(methoxymethoxy)-oct-7-en-3-ol (18)



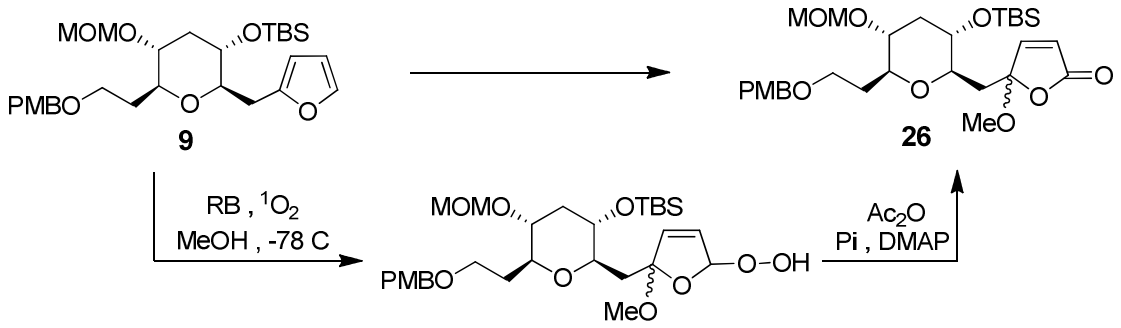
To a solution of furan (320 µL, 4.40 mmol) in THF (5 mL) at 0 ºC was added *n*-BuLi (1.76 mL of a 2.5 M solution in hexanes, 4.40 mmol) and the mixture stirred for 30 mn affording a yellow solution. Iodide **17** (640 mg, 1.10 mmol) in THF (4 mL) was added via cannula and the mixture stirred at 0 ºC for 3 h. After quenching with water (15 mL), the product was extracted with EtOAc (3x20 mL). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 2% EtOAc/Hexane as eluent, affording compound **9** (420 mg, 74%) and alcohol **18** (85 mg, 13%).

Compound **9**.Yellow liquid, Rf: 0.35 (20% EtOAc/Hexane);**IR (NaCl,cm^{-1}):**2920.25, 2884.15, 1614.78, 1244.08, 1095.15;**[α]$^{26}_{D}$**= -5.95 (c 1.41, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):**7.27 (1H, d, J=1.8, H-5 furan), 7.22 (2H, d, J=8.6 Hz, H_o-PMB), 6.87 (2H, d, J=8.6 Hz, H_m-PMB), 6.27 (1H, dd, J=2.9, 1.9 Hz, H-4 furan), 6.05 (1H, d, J=2.9 Hz, H-3), 4.70 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.58 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.33 (2H, s, C**H**$_2$-PMP), 3.80 (3H, s, OC**H**$_3$-PMB), 3.54-3.25 (6H, m, H-2, 2H-2', H-3, H-5, H-6), 3.36 (3H, s, OC**H**$_3$-MOM), 3.13 (1H, dd, J=15.4, 1.5 Hz, C**H**$_2$-furan), 2.59 (1H, dd, J=15.4, 9.3 Hz, C**H**$_2$-furan), 2.41 (1H, dt, J=10.8, 4.2Hz, H-4), 2.15 (1H, m, H-1'), 1.56 (1H, m, H-1'), 1.49 (1H, dd, J=22.2, 10.9 Hz, H-4), 0.90 (9H, s, CH_3-^{t}Bu), 0.09 (6H, s, CH_3-Si);**^{13}C-NMR ($CDCl_3$, δ):**159.1 (C_p-PMB), 153.3 (C-2 furan), 140.6 (CH-5 furan), 130.7 (C-PMB), 129.2 (CH_o-PMB), 113.6 (CH_m-PMB), 110.2 (CH-4 furan), 106.1 (CH-3 furan), 95.2 (CH_2-MOM), 80.4 (CH-6), 77.1 (CH-2), 74.7 (CH-5), 72.6 (CH_2-PMP), 70.0 (CH-3), 66.3 (CH_2-2'), 55.5 (O**C**H$_3$-OMOM), 55.2 (O**C**H$_3$-PMB), 40.2 (CH_2-4), 32.1 (CH_2-1'), 30.6 (**C**H$_2$-furan), 25.7 (CH_3-^{t}Bu), 17.9 (C-^{t}Bu), -4.1 (CH_3-Si), -4.8 (CH_3-Si);**MS (ESI) [m/z, (%)]:**543 (M^++Na, 100), 521 (M^++1, 18);**HRMS (ESI):**543.2748 calculated for $C_{28}H_{44}NaO_7Si$, found 543.2745.

Compound **18**. Yellow liquid, Rf: 0.16 (20% EtOAc/Hexane);**IR (NaCl,cm^{-1}):**3469.31, 2953.45, 2930.31, 2882.78, 2856.06, 1513.85, 1034.62;**[α]$^{30}_{D}$**= -6.13 (c 1.75, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):** 7.25 (2H, d, J=8.6 Hz, H_o-PMB), 6.87 (2H, d, J=8.6 Hz, H_m-PMB), 5.79 (1H, ddd, J=17.1, 10.3, 6.6 Hz, H-7), 5.15 (1H, d, 17.1 Hz, H-8), 5.06 (1H, d, 10.3 Hz, H-8), 4.67 (1H, d, J=6.8 Hz, C**H**$_2$-MOM), 4.61 (1H, d, J=6.8 Hz, C**H**$_2$-MOM), 4.45 (2H, s, C**H**$_2$-PMB), 4.29 (1H, dd,

J=12.2, 6.6 Hz, H-6), 3.79 (3H, s, OC**H**$_3$-PMB), 3.75 (1H, ddd, J=12.3, 5.8, 3.1 Hz, H-4), 3.62 (3H, m, H-3, 2H-1), 3.40 (3H, s, OC**H**$_3$-MOM), 1.86 (1H, m, H-5), 1.74 (2H, m, 2H-2), 1.62 (1H, ddd, J=14.3, 7.5, 3.8 Hz, H-5), 0.89 (9H, s, CH_3-^{t}Bu), 0.06 (3H, s, CH_3-Si), 0.04 (3H, s, CH_3-Si);**^{13}C-NMR ($CDCl_3$, δ):**159.1 (C_p-PMB), 141.0 (CH-7), 130.3 (C-PMB), 129.2 (CH_o-PMB), 114.5 (CH_2-8), 113.7 (CH_m-PMB), 97.2 (CH_2-MOM), 80.5 (CH-3), 72.7 (CH_2-PMP), 71.4 (CH-4 ó CH-6), 71.3 (CH-4 ó CH-6), 67.9 (CH_2-1), 55.7 (O**C**H_3-OMOM), 55.2 (O**C**H_3-PMB), 39.3 (CH_2-5), 31.8 (CH_2-2), 25.8 (CH_3-^{t}Bu), 18.1 (C-^{t}Bu), -4.4 (CH_3-Si), -4.9 (CH_3-Si); **MS (ESI) [m/z, (%)]:**477 (M^++Na, 100), 455 (M^++1, 76); **HRMS (ESI):**477.2642 calculatedfor $C_{24}H_{42}NaO_6Si$, found 477.2638.

(2'*R*,3'*S*,5'*R*,6'*S*)-5-[3'-(*tert*-butyldimethylsililoxy)-6'-(2''-*p*-methoxybencyloxyethyl)-5'-(methoxymethoxy)-1'-(tetrahydro-2H-pyran-2-yl)methyl]-5-methoxy-5H-furan-2-one (26)

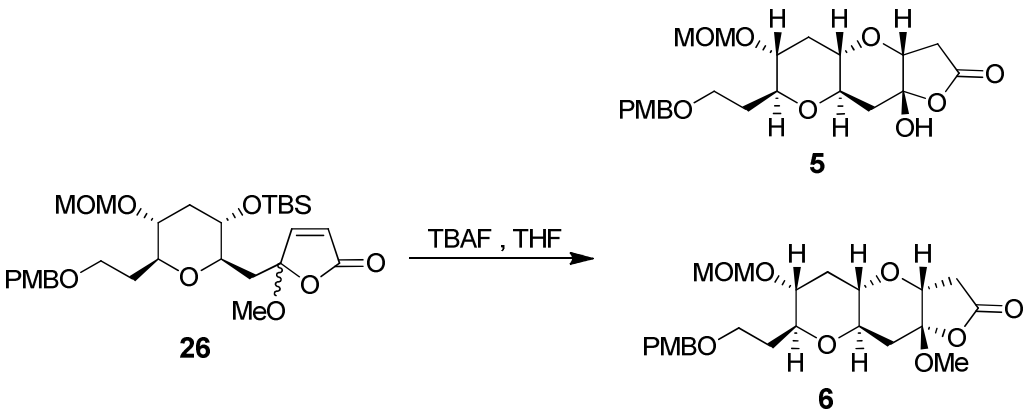


A solution of compound **9** (370mg, 0.71mmol) and a catalytic amount of 4,5,6,7-tetrachloro-2´,4´,5´,7´-tetraiodofluorescein disodium salt (Rose Bengal) in MeOH (5 mL), previously purged with O_2, was cooled at -78 ºC, and irradiated with a 200 W lamp for 1 h, stirring under oxygen atmosphere. The solvent was evaporated, and the residue was rapidly filtered through a column on silica gel (50%EtOAc/Hexane) in order to get rid of the catalyst. After solvent evaporation the residue was dissolved in pyridine (4 mL) and Ac_2O (452 µL) and DMAP (catalytic) were added at 0 ºC. The reaction mixture was stirred for 12 h at room temperature, then water (20 mL) was added and the product was extracted with EtOAc (3x20 mL). The combined organic phases were washed

with a 10% aqueous solution of HCl (2 x 50 mL) and brine (50 mL), dried over Na_2SO_4 and the solvent was filtered and evaporated to give a residue which was chromatographed on silica gel using 5% EtOAc/Hexane as eluent, affording compound **26** (305 mg, 76%) as a colourless liquid;Rf: 0.27 (20% EtOAc/Hexane);**IR (NaCl,cm^{-1}):**2953.45, 2932.23, 2886.92, 2857.99, 1776.12, 1249.65, 1100.19; **^{1}H-NMR ($CDCl_3$, δ):** (major diastereomer); 7.25 (2H, m, H_o-PMB), 7.00 (1H, d, J=5.6 Hz, H-4), 6.87 (2H, m, H_m-PMB), 5.93 (1H, d, J=5.6 Hz, H-3), 4.69 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.58 (1H, d, J=6.9 Hz, C**H**$_2$-MOM), 4.44 (2H, s, C**H**$_2$-PMP), 3.78 (3H, s, OC**H**$_3$-PMB), 3.54 (1H, dd, J=7.3 5.8 Hz), 3.45 (2H, m), 3.34 (3H, s, OC**H**$_3$-MOM), 3.26 (2H, m), 3.18 (1H, s, OC**H**$_3$), 2.90 (1H, m), 2.71 (1H, m, H-1), 2.38 (1H, m, H-1), 2.16 (2H, m, H-1'', H-4'), 1.49 (2H, m, H-1'', H-4'), 0.87 (9H, s, CH_3-^{t}Bu), 0.05 (6H, s, CH_3-Si);**^{13}C-NMR ($CDCl_3$, δ):**(major diastereomer); 170.1 (C=O), 159.1 (C_p-PMB), 155.3 (CH-4), 130.3 (C-PMB), 129.2 (CH_o-PMB), 122.4 (CH-3), 113.7 (CH_m-PMB), 110.0 (C-5), 95.2 (CH_2-MOM), 77.5 (CH-6'), 77.2 (CH-2'), 74.4 (CH_2-PMP), 72.5 (CH-5'), 69.6 (CH-3'), 66.5 (CH_2-2''), 55.5 (O**C**H$_3$-OMOM), 55.2 (O**C**H$_3$-PMB), 51.1 (O**C**H$_3$), 39.9 (CH_2-4'), 39.3 (CH_2-1), 31.9 (CH_2-1''), 25.6 (CH_3-^{t}Bu), 17.8 (C-^{t}Bu), -4.1 (CH_3-Si), -4.8 (CH_3-Si); **MS (ESI) [m/z, (%)]:**589 (M^++Na, 100);**HRMS (ESI):**589.2803 calculated for$C_{29}H_{46}NaO_9Si$, found 589.2801.

(1*S*,3*R*,7*R*,9*R*,11*S*,12*R*)-7-methoxy-11-(2'-*p*-methoxybencyloxyethyl)-12-(methoxymethoxy)-2,6,10-trioxytricyclic[7,4,0,0^{3,7}]tridecan-5-one (6) and

(1*S*,3*R*,7*R*,9*R*,11*S*,12*R*)-7-hidroxy-11-(2'-*p*-methoxybencyloxyethyl)-12-(methoxymethoxy)-2,6,10-trioxytricyclic[7,4,0,0^{3,7}]tridecan-5-one (5)



26 **5** **6**

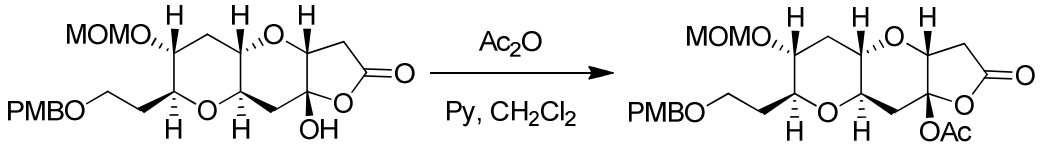
To a solution of **26** (275 mg, 0.49 mmol) in THF (2 mL) was added TBAF (1.47 mL of a 1 M solution in THF, 1.47 mmol) and the mixture was stirred at room temperature for 24 h. Then quenched with an aqueous saturated solution of NH_4Cl (10 mL) and the product extracted with EtOAc (3 x 10 mL). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 5% EtOAc/Hexane as eluent, affording compound **6** (129 mg, 60%) and compound **5** (40 mg, 20%).

Compound **6**: white solid; m.p.= 115 ºC, Rf: 0.21 (20% EtOAc/Hexane);**IR (NaCl,cm^{-1}):**2933.20, 2887.88, 1796.37, 1425.89, 1090.55, 1036.55; **[α]$^{21}_{D}$**= -39.88 (c 1.45, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):** 7.24 (2H, d, J=8.6 Hz, H_o-PMB), 6.87 (2H, d, J=8.6 Hz, H_m-PMB), 4.68 (1H, d, J=6.9 Hz, C**H**$_2$-OMOM), 4.59 (1H, d, J=6.9 Hz, C**H**$_2$-OMOM), 4.47 (1H, d, J=11.7 Hz, C**H**$_2$-PMB), 4.38 (1H, d, J=11.7 Hz, C**H**$_2$-PMB), 3.96 (1H, d, J=4.4 Hz, H-9), 3.80 (3H, s, OC**H**$_3$-PMB), 3.55 (2H, m, 2H-2'), 3.36 (3H, s, OCH_3), 3.34 (3H, s, OC**H**$_3$-OMOM), 3.32 (2H, m, H-1, H-11), 3.07 (2H, m, H-3, H-12), 2.88 (1H, dd, J=17.3, 4.5 Hz, H-8), 2.72 (1H, dd, J=13.1, 4.5 Hz, H-4), 2.45 (1H, m, H-13), 2.39 (1H, d, J=17.3 Hz, H-8), 2.16 (1H, m, H-1'), 1.57 (2H, m, H-1', H-4), 1.43 (1H, m, H-13);**^{13}C-NMR ($CDCl_3$, δ):**175.1 (C=O), 159.1 (C_p-PMB), 130.5 (C-PMB), 129.2 (CH_o-PMB), 113.6 (CH_m-PMB), 106.5 (C-7), 95.4 (CH_2-MOM), 77.4 (CH-1), 76.7 (CH-9), 74.6 (CH-11), 73.8 (CH-12), 73.0 (CH-3), 72.4 (CH_2-PMB), 65.8 (CH_2-2'), 55.6 (O**C**H_3-OMOM), 55.2 (O**C**H_3-PMB), 49.8 (OCH_3), 36.3 (CH_2-8), 35.6 (CH_2-13), 33.6 (CH_2-4), 31.9 (CH_2-1');**MS (ESI) [m/z, (%)]:**476 (M^++1+Na, 31), 475 (M^++Na, 100), 338 (44);**HRMS (ESI):**475.1911 calculated for $C_{23}H_{32}NaO_9$, found 475.1917.

Compound **5**: White solid; m.p.= 140-143 ºC, Rf: 0.13 (20% EtOAc/Hexane);**IR (NaCl, cm^{-1}):** 3359.39, 2928.38, 1785.76, 1729.83, 1611.23, 1512.88, 1105.98, 1037.52, 909.27, 822.49;**[α]$^{21}_{D}$**= -25.6(c 1.0, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):** 7.25 (2H, d, J=7.2 Hz, H_o-PMB), 6.91 (2H, d, J=8.8 Hz, H_m-PMB), 4.65 (2H, m, CH_2-OMOM), 4.44 (2H, m, CH_2-PMP), 4.03 (1H, d, J=4.3 Hz, H-3), 3.82 (3H, s, CH_3-PMB), 3.56 (2H, m, H-2'), 3.35 (3H, s, CH_3-OMOM), 3.09 (2H, m), 2.95 (1H, m), 2.51 (4H, m), 2.16 (2H, m), 1.75 (1H, m), 1.57 (2H, m), 0.86 (1H, m); **^{13}C-NMR ($CDCl_3$, δ):** 175.36 (C-5), 159.23 (C-PMB), 130.65 (C-PMB), 129.54 (CH_o-PMB), 113.90 (CH_m-PMB), 104.24 (C-7), 95.61 (CH_2-OMOM), 77.41 (CH),

76.58 (CH), 74.71 (CH), 74.06 (CH), 73.04 (CH), 72.47 (CH_2-PMP), 65.89 (CH_2-2'), 55.71 (CH_3-OMOM), 55.36 (CH_3-PMB), 38.04 (CH_2), 36.33 (CH_2), 35.68 (CH_2), 31.89 (CH_2); **MS (ESI) [m/z, (%)]:** 503.18 (26), 461.17 (M^++1+Na, 100), 445.18 (10);**HRMS (ESI):** 475.17962 calculated for $C_{22}H_{30}NaO_9$, found 461.17820.

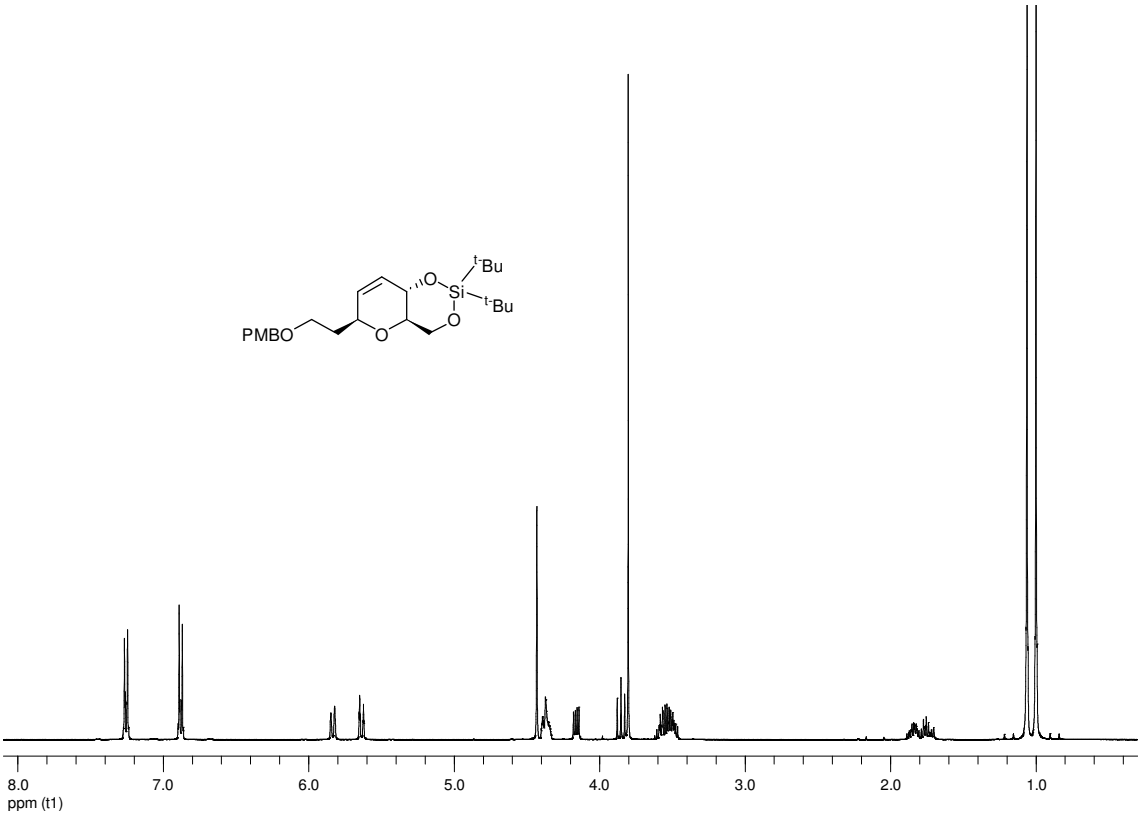
(1*S*,3*R*,7*R*,9*R*,11*S*,12*R*)-7-acetoxy-11-(2'-*p*-methoxybencyloxyethyl)-12-(methoxymethoxy)-2,6,10-trioxytricyclic[7,4,0,$0^{3,7}$]tridecan-5-one (27)



(**5**) (**27**)

To a solution of alcohol (**5**) (25 mg, 0.06 mmol) in DCM (1.0 mL) was added Py (77 µL, 0.30 mmol) and Ac_2O (13µL, 0.12mmol) at r.t. The reaction mixture was stirred at r.t. for 16h. Then quenched with water (5 mL) and the product extracted with EtOAc (3x10 mL). The combined organic phases were dried, filtered and evaporated to give a residue which was chromatographed on silica gel using 10% EtOAc/Hexane as eluent, affording compound **27** (23 mg, 80%) as a colourless oil;Rf: 0.13 (20% EtOAc/Hexane);**IR (NaCl, cm^{-1}):**2932.58, 1789.23, 1732.56, 1611.87, 1513.45, 1039.26, 825.36;**$[\alpha]^{21}_D$**= -45.5(c 1.0, $CHCl_3$);**^{1}H-NMR ($CDCl_3$, δ):**7.24 (2H, d, J=8.7 Hz, H_o-PMB), 6.85 (2H, d, J=8.7 Hz, H_m-PMB), 4.41(4H, m, CH_2-OMOM, CH_2-PMP), 3.95 (1H, d, J=3.9 Hz, H-3), 3.71-3.56 (2H, m; CH-2'), 3.38 (3H, s, CH_3-PMB), 3.30 (1H, m, H-11), 3.24-3.12 (3H, m, H-12, H-8), 3.10 (3H, s, CH_3-OMOM), 2.97 (1H, m, H-9), 2.81 (1H, m, H-1), 2.31 (2H, m, 1H-13, 1H-1'), 2.22 (1H, m, H-4), 2.09 (1H, m, H-4), 1.68 (1H, m, 1H-1'), 1.38 (3H, s, CH_3-OAc), 1.30 (1H, m, 1H-13;);**^{13}C-NMR ($CDCl_3$, δ):**173.24 (C-OAc), 167.74 (C=O), 159.82 (C-PMB), 131.34 (C-PMB), 129.46 (C_o-PMB), 114.13 (C_m-PMB), 106.70 (C-7), 95.57 (CH_2-OMOM), 77.55 (CH-11), 75.16 (CH-12, CH-3), 74.20 (CH-1), 73.07 (CH-9), 72.83 (CH_2-PMP), 66.28

(CH_2-2'), 55.32 (CH_3-OMOM), 54.87 (CH_3-PMB), 35.95 (CH_2-13), 35.11 (CH_2-8), 35.00 (CH_2-4), 32.71 (CH-1'), 21.01 (CH_3-OAc);**MS (ESI) [m/z, (%)]:** 503.23 (M^++1+Na, 100), 427.25 (13), 415.89 (28);**HRMS (ESI):** 503.14856 calculated for $C_{24}H_{32}NaO_{10}$, found 503.14867.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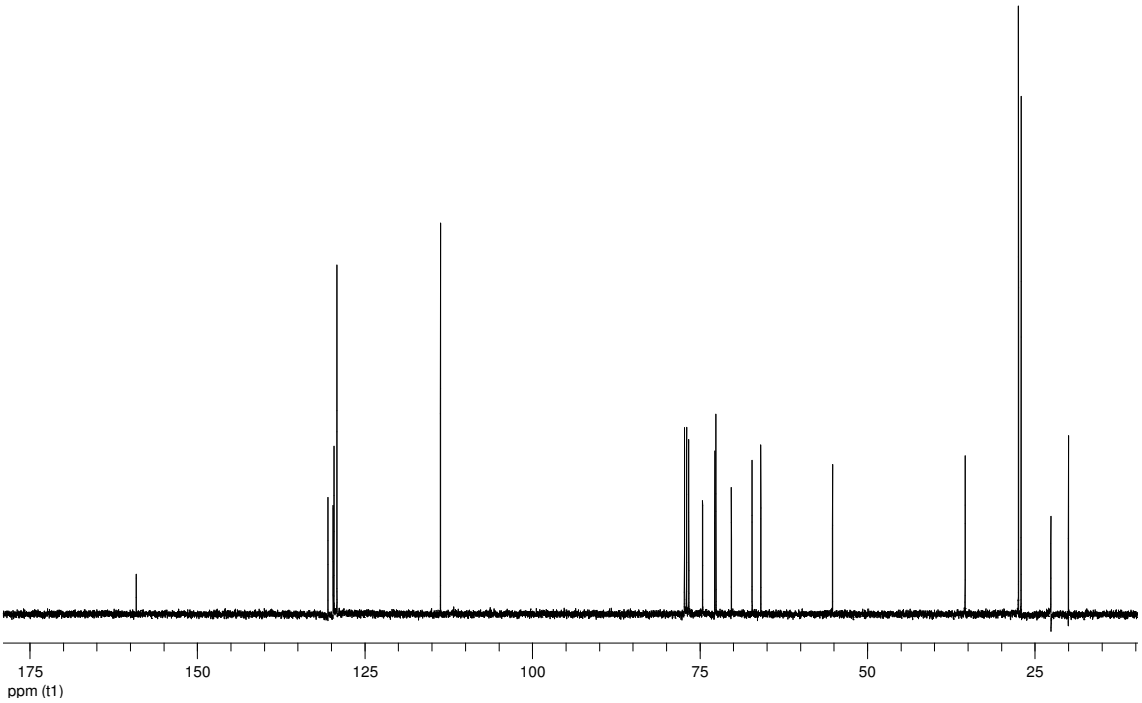
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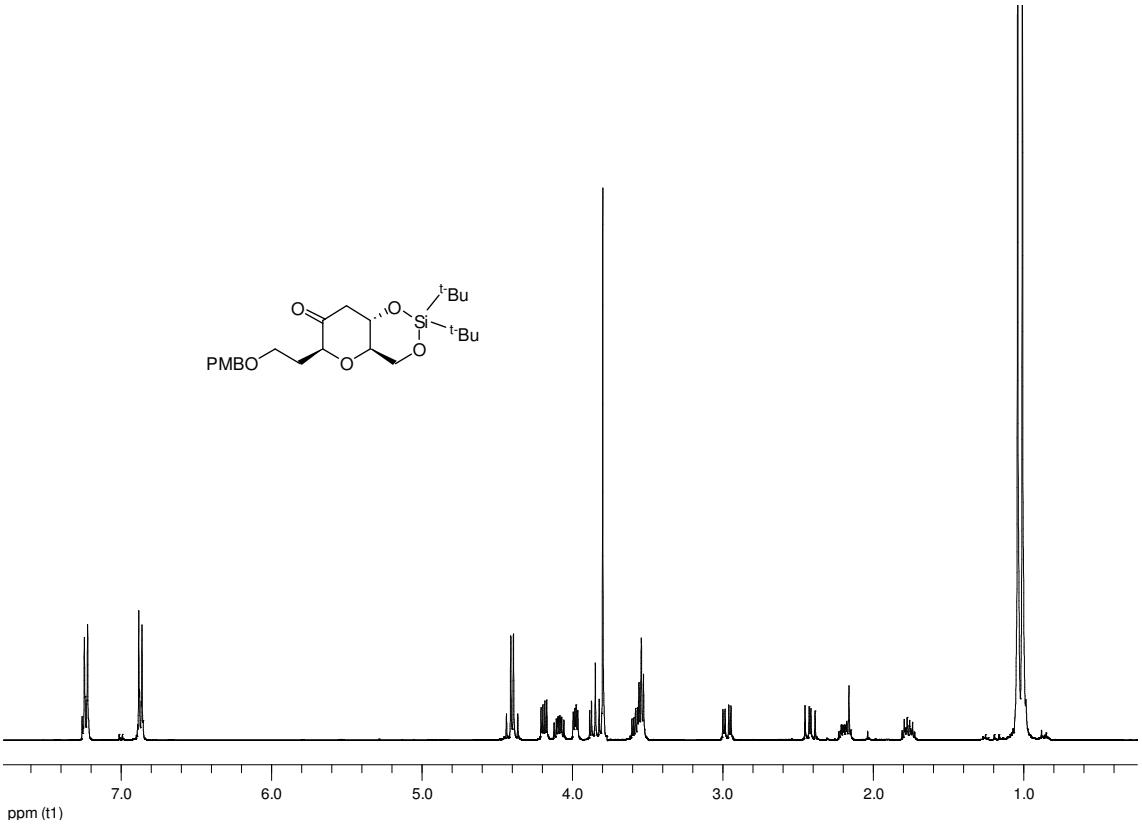
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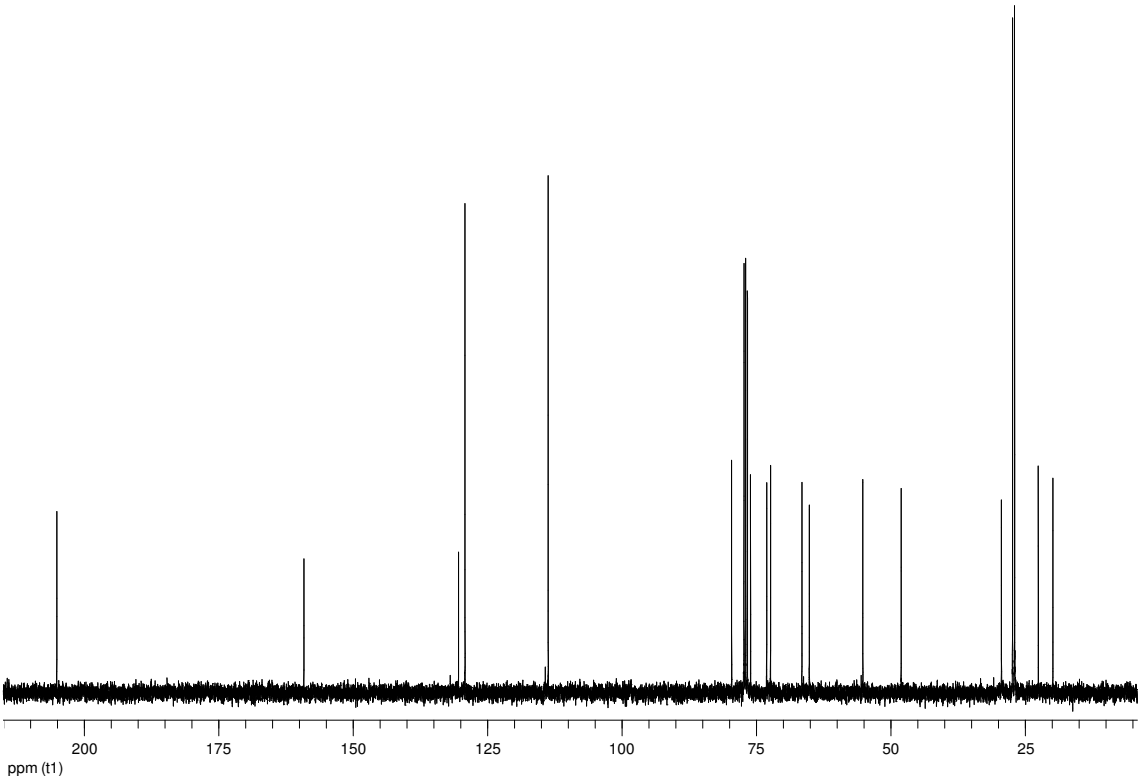
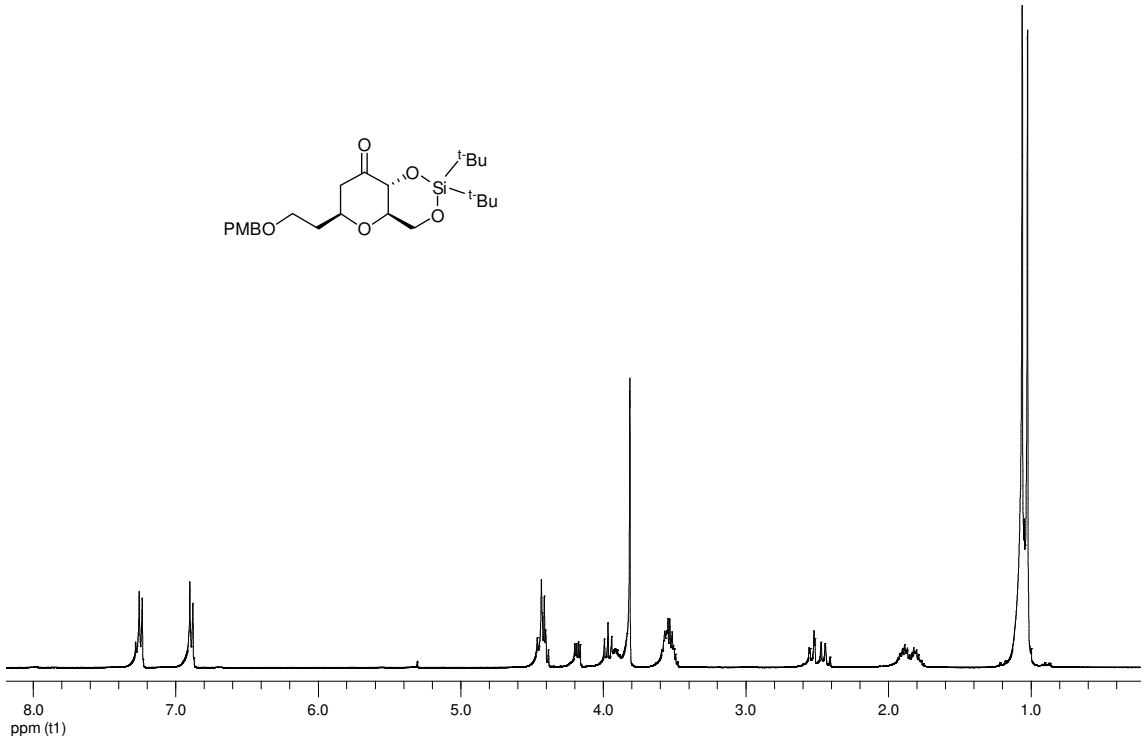
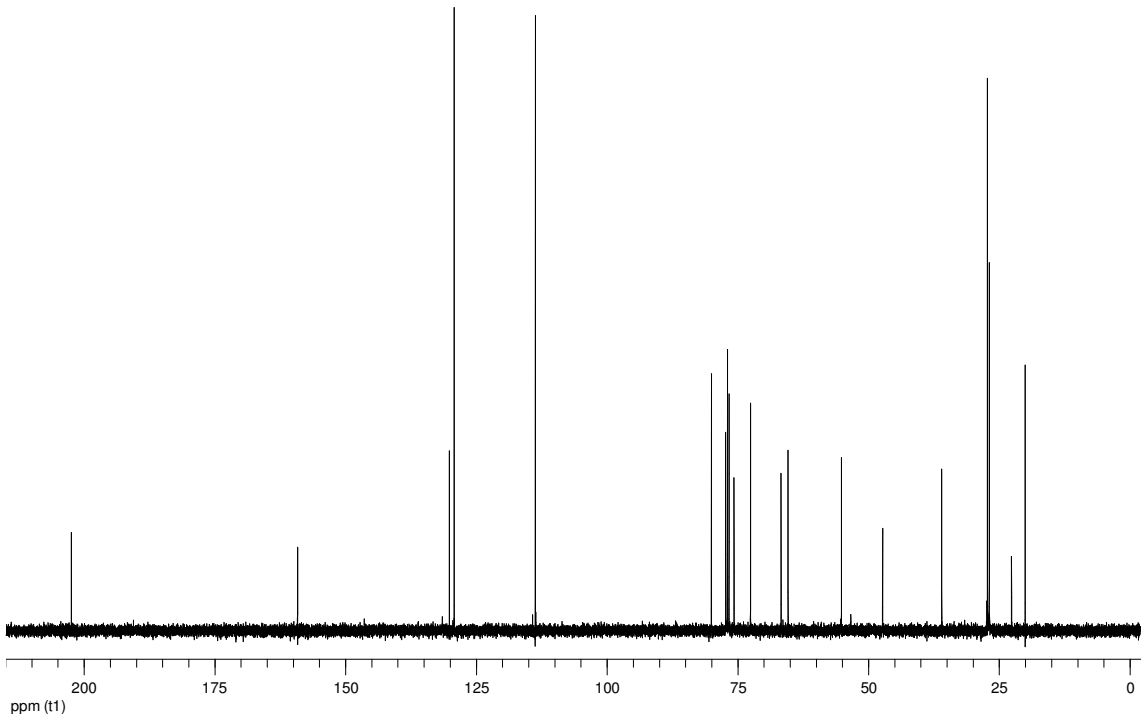
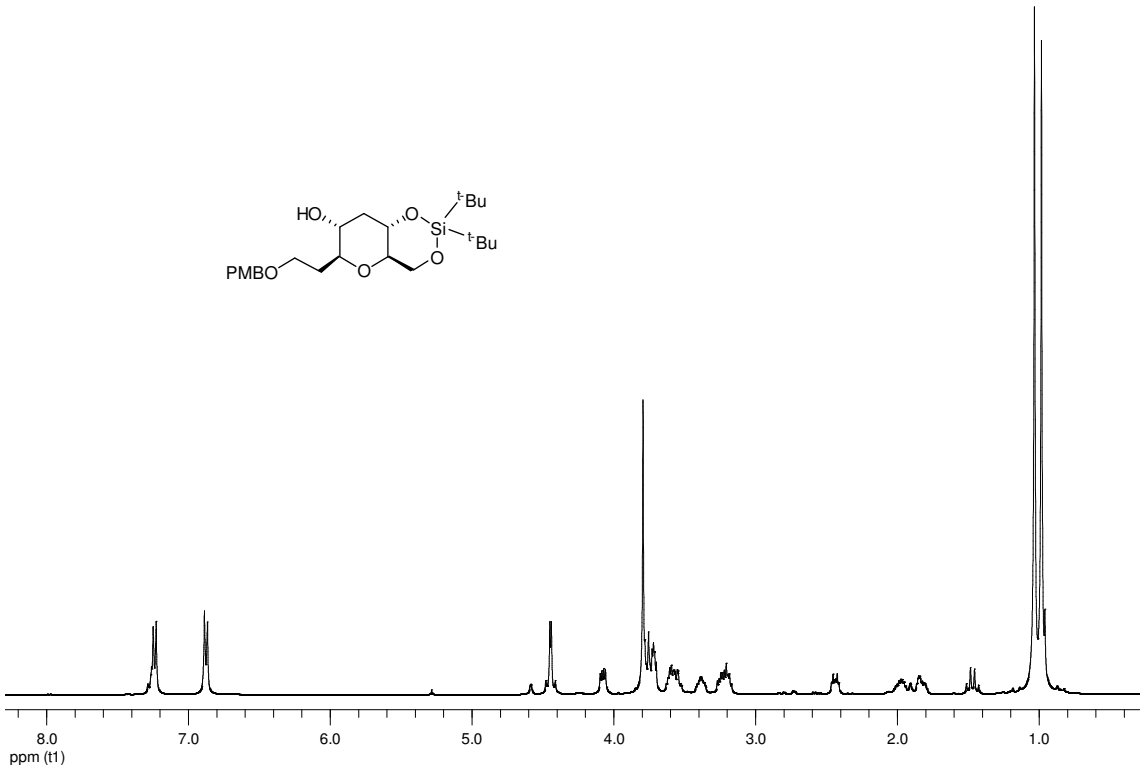
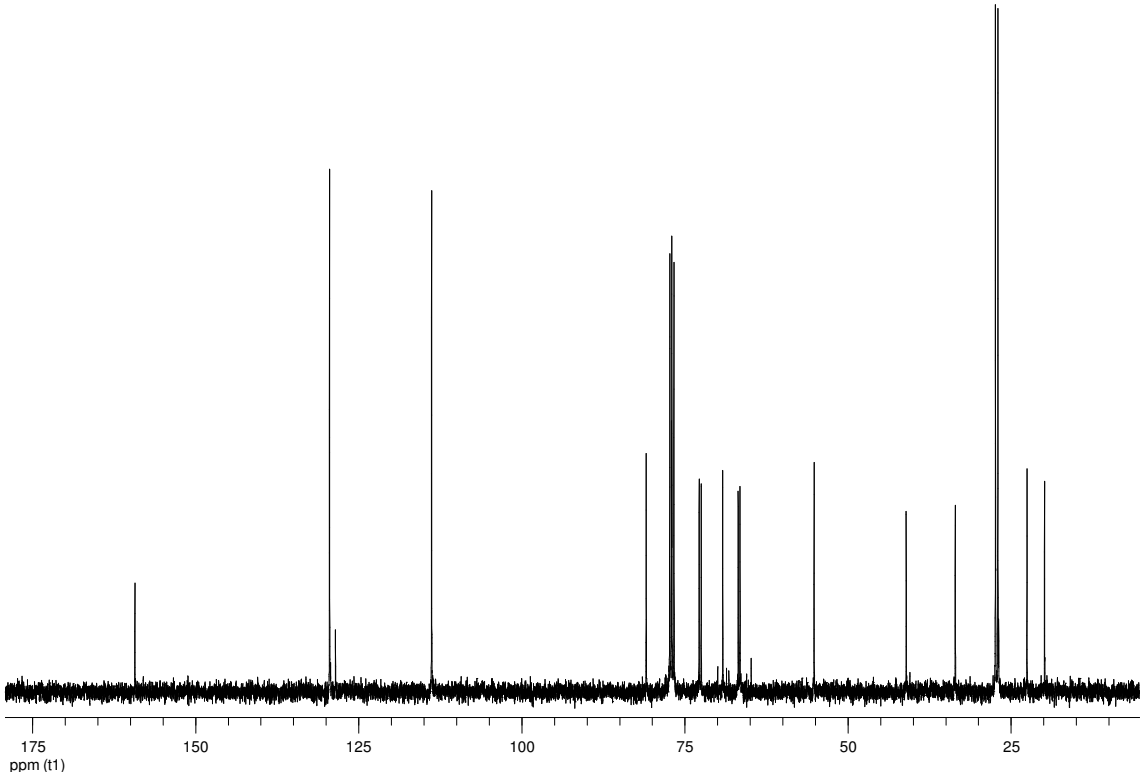
1.0
ppm (t1)

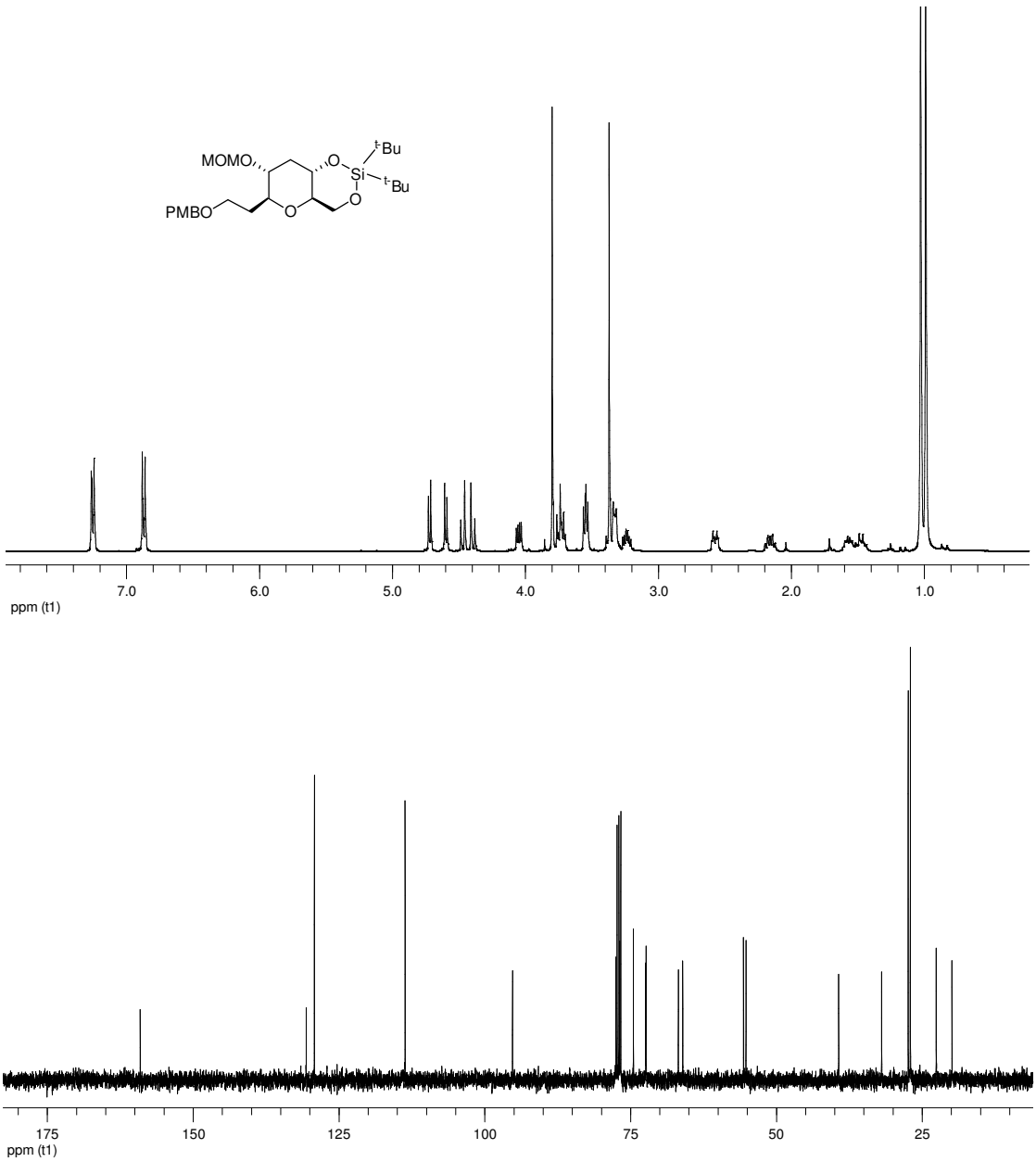

200
175
150
125
100
75
50
25
ppm (t1)

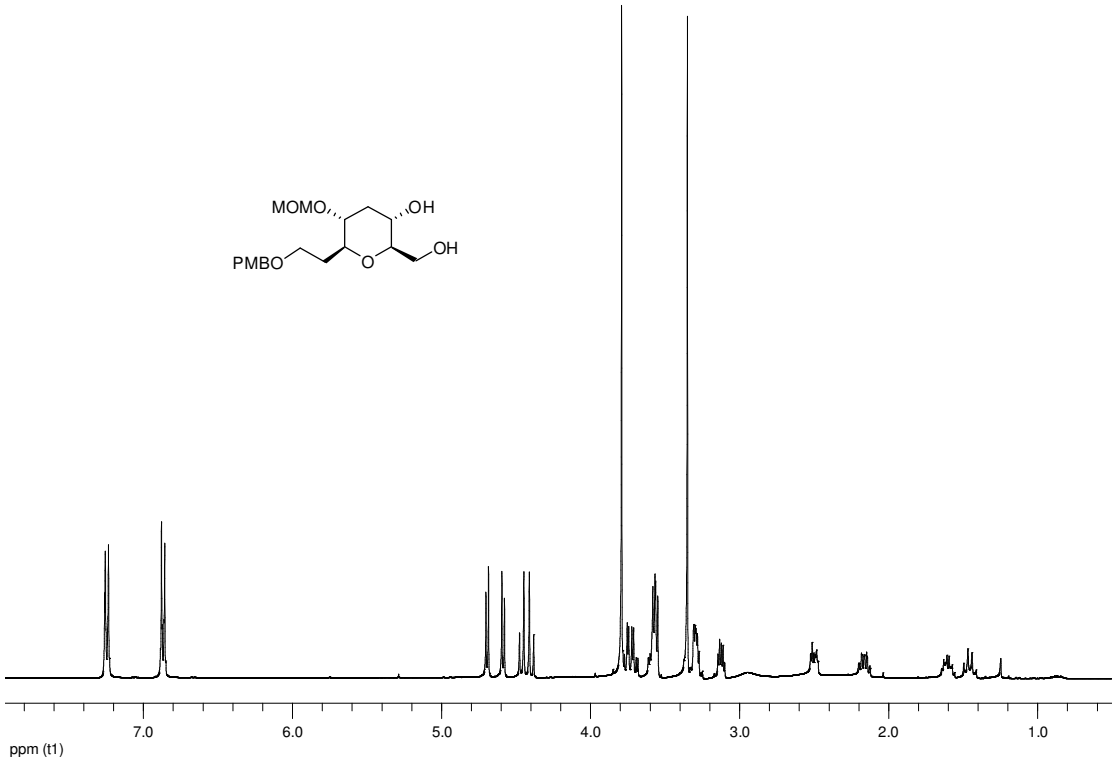

O
t-Bu
O
Si
t-Bu
PMBO
O
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

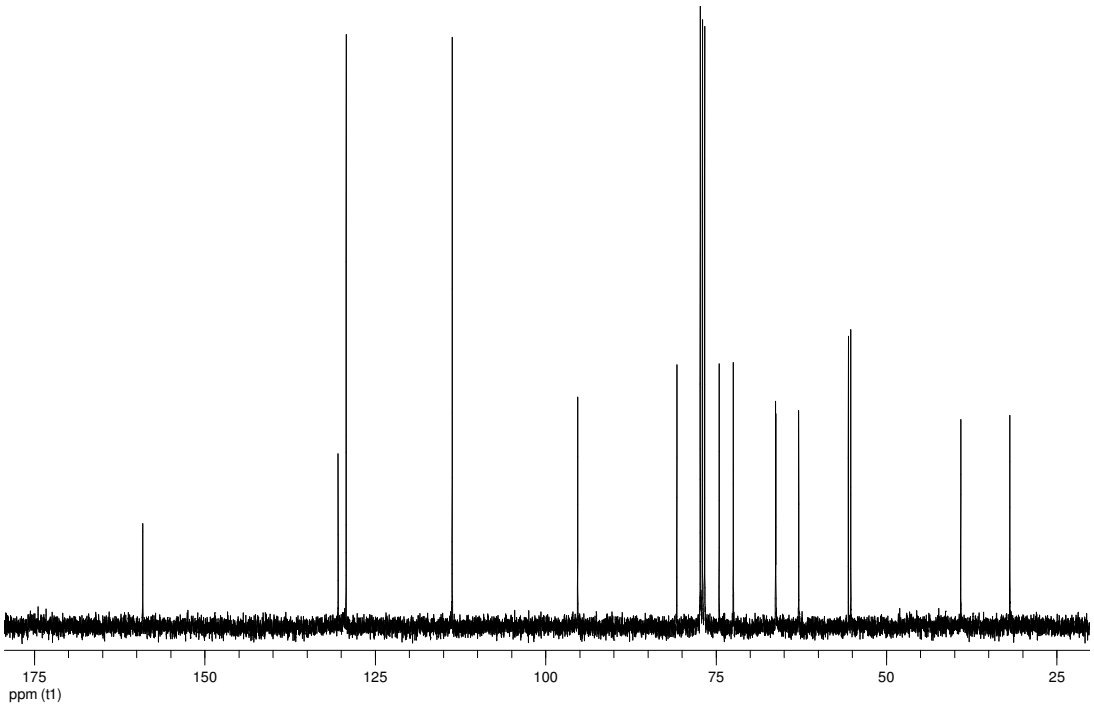

200
175
150
125
100
75
50
25
0
ppm (t1)

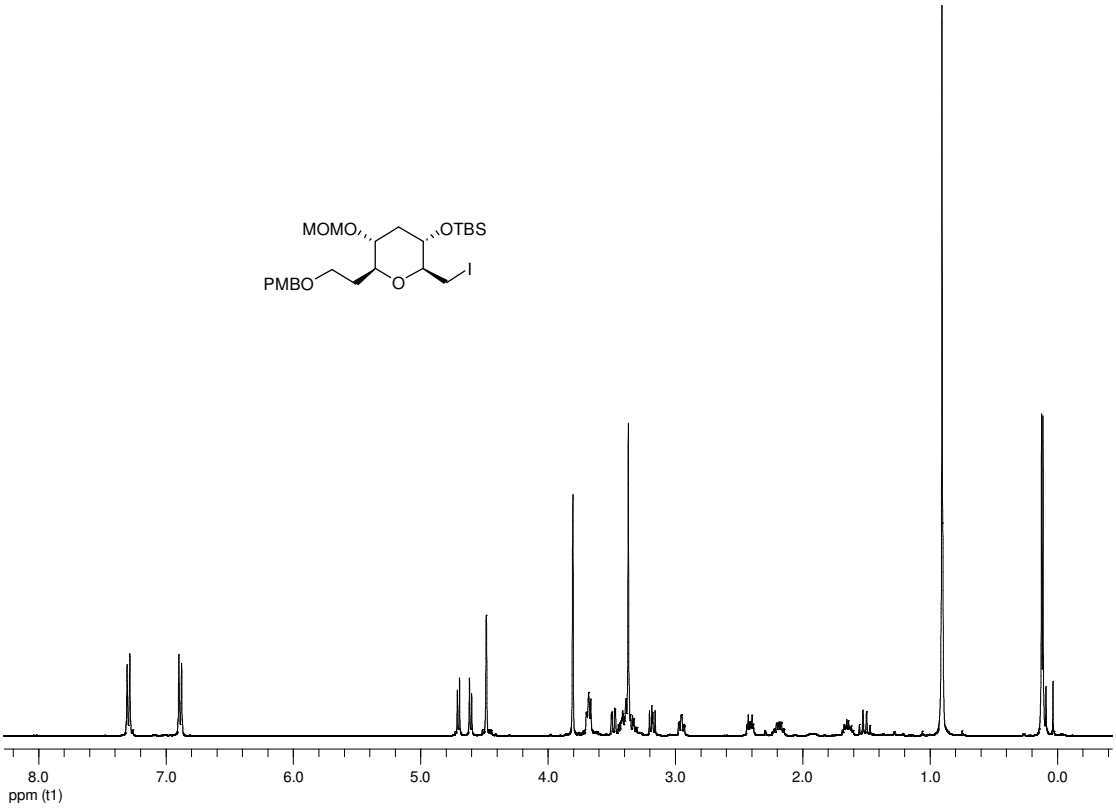

HO
O
Si
O
O
PMBO
tBu
tBu
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

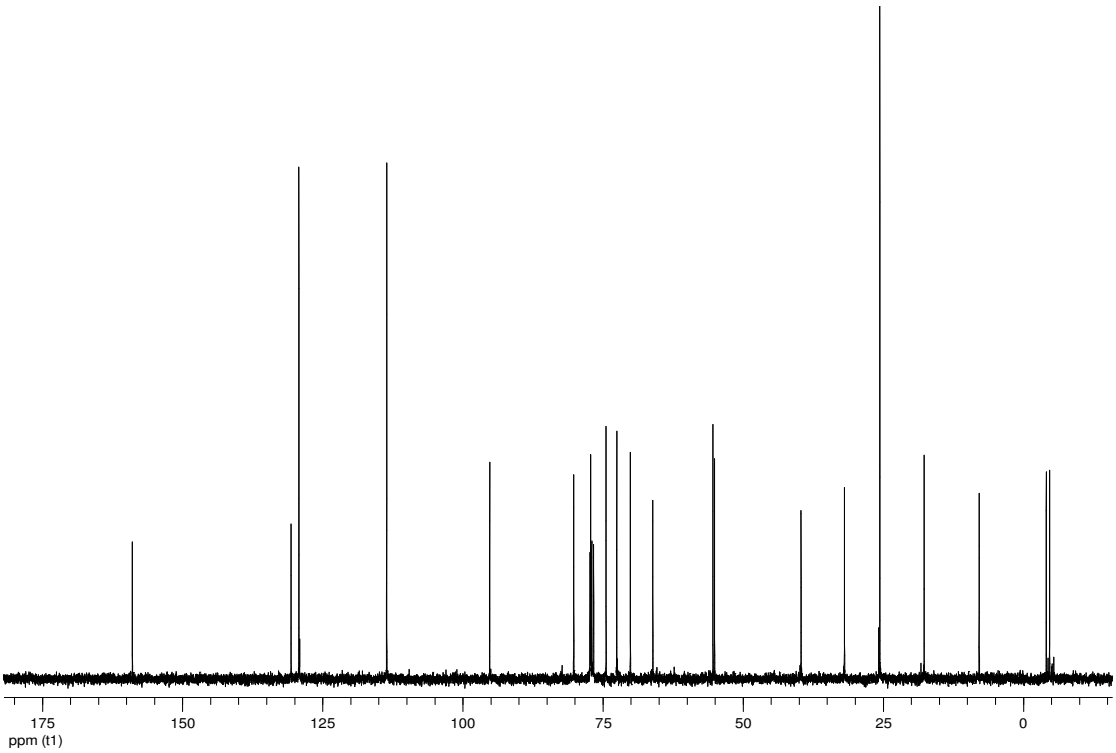

175
150
125
100
75
50
25
ppm (t1)

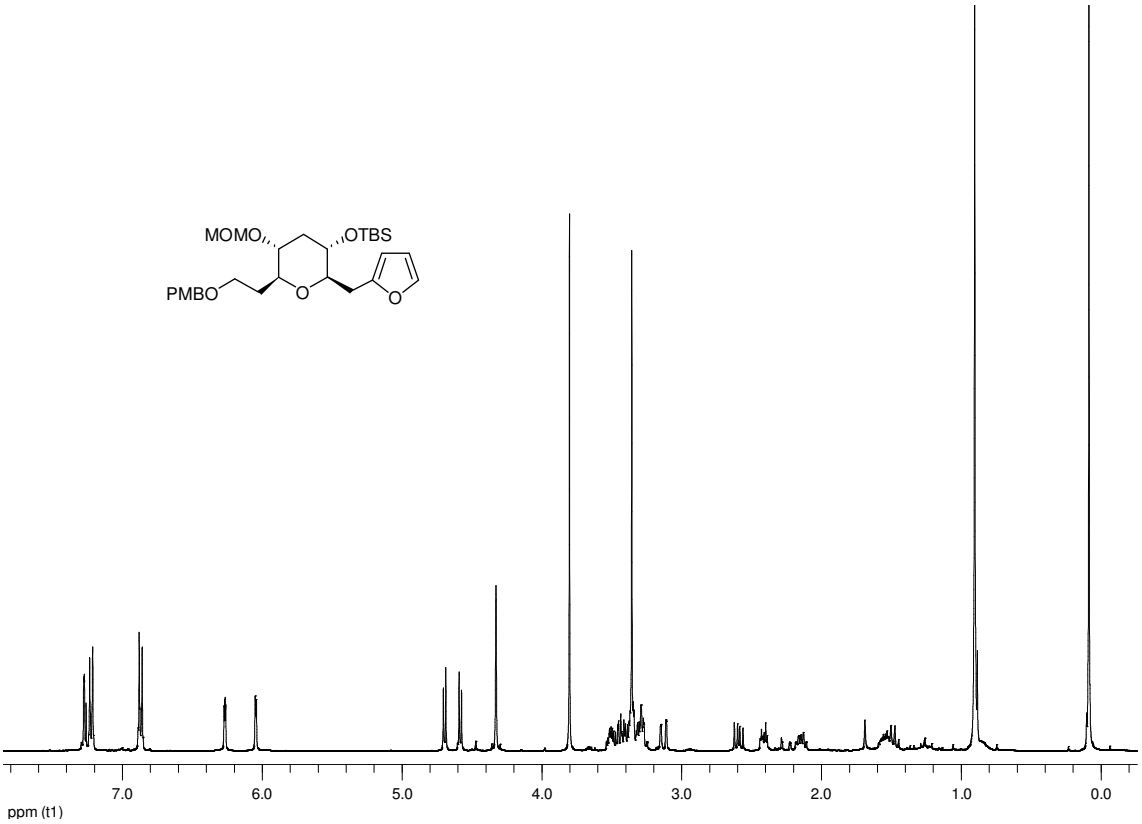

MOMO
PMBO
O
Si
O
O
O
tBu
tBu
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
175
150
125
100
75
50
25
ppm (t1)

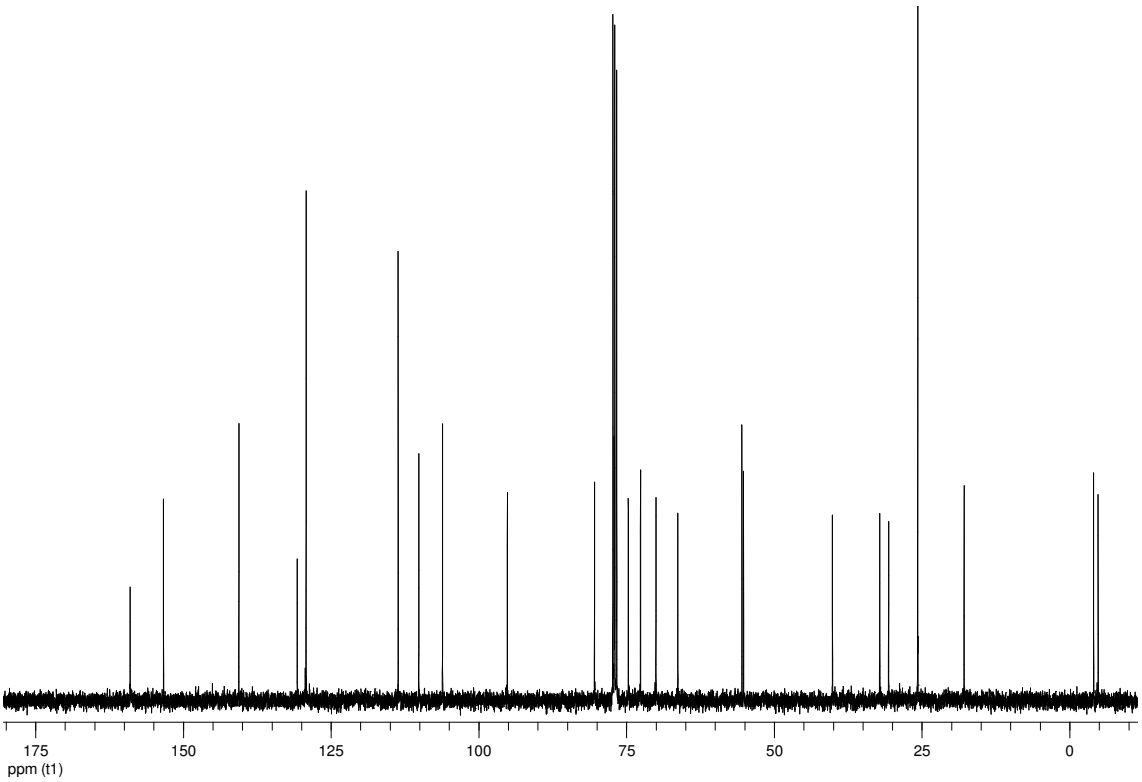

MOMO
OH
OH
PMBO
O
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

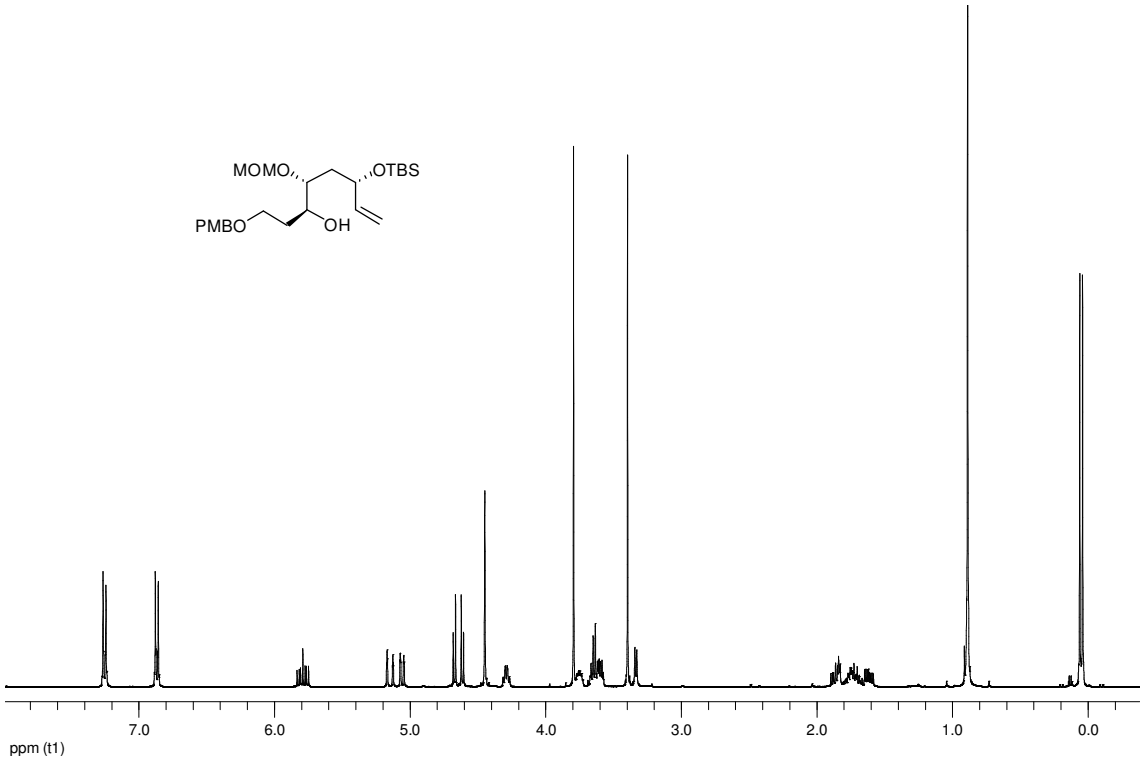

175
150
125
100
75
50
25
ppm (t1)

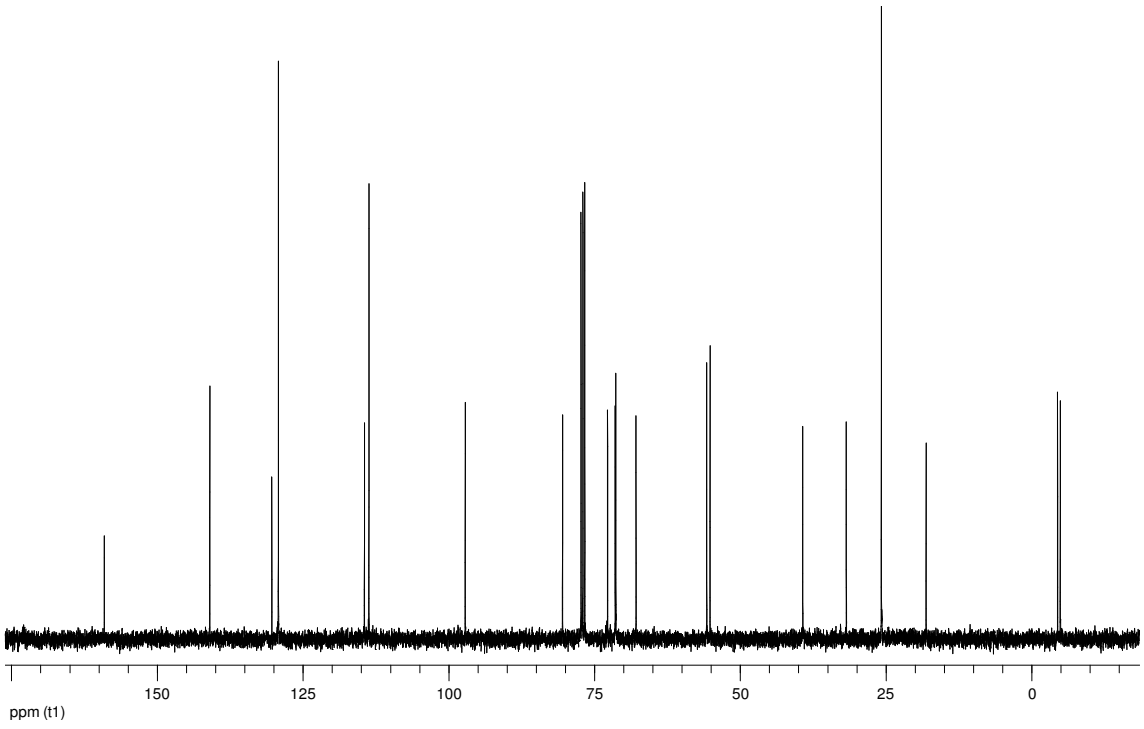

MOMO
OTBS
PMBO
O
I
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

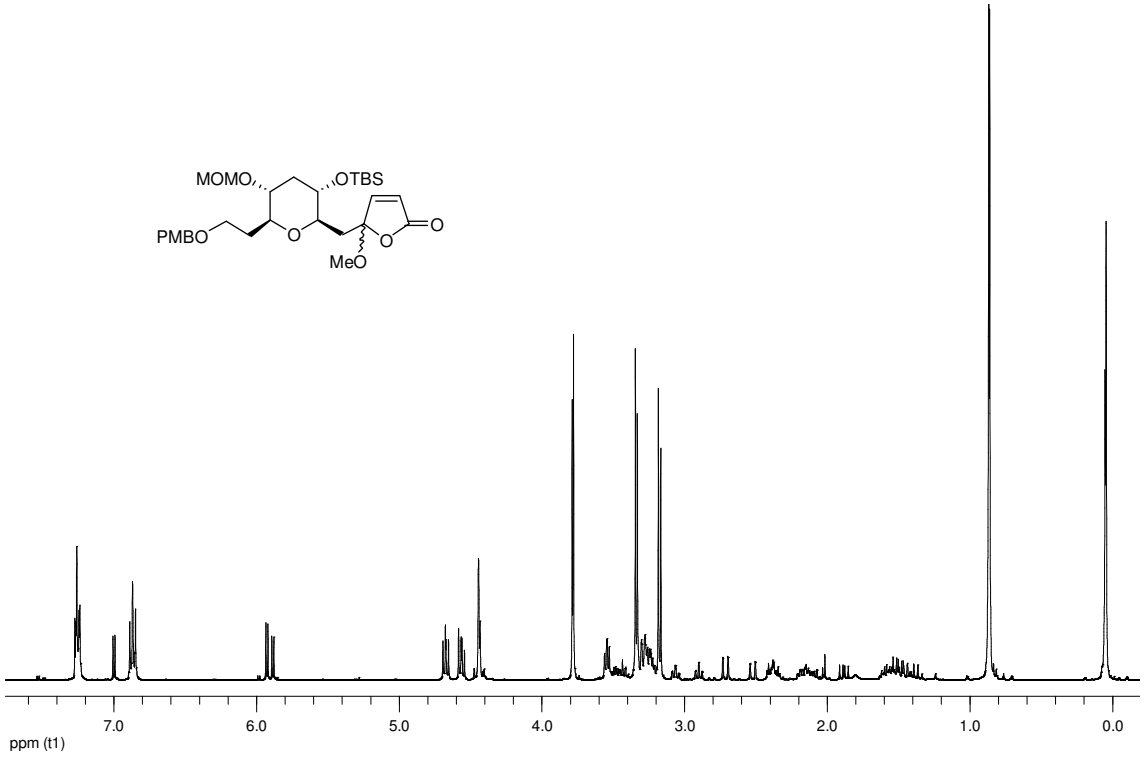

175
150
125
100
75
50
25
0
ppm (t1)

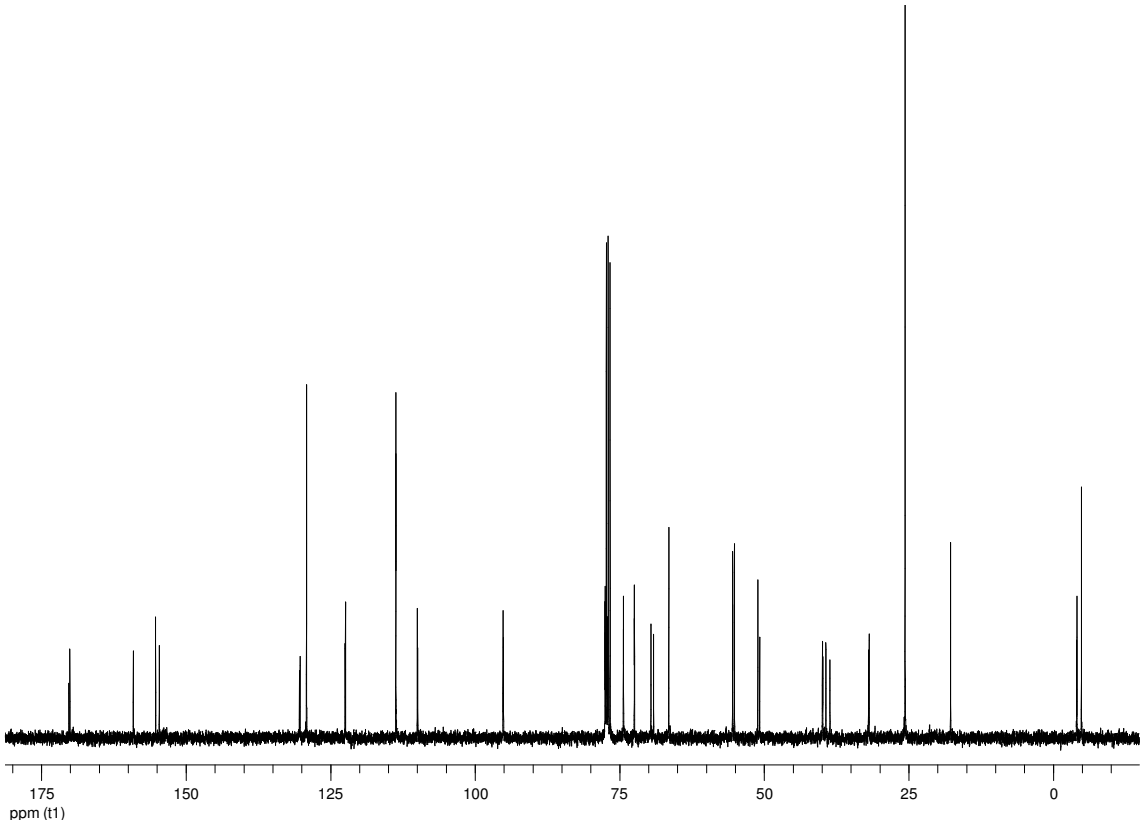

MOMO
OTBS
PMBO
O
O
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

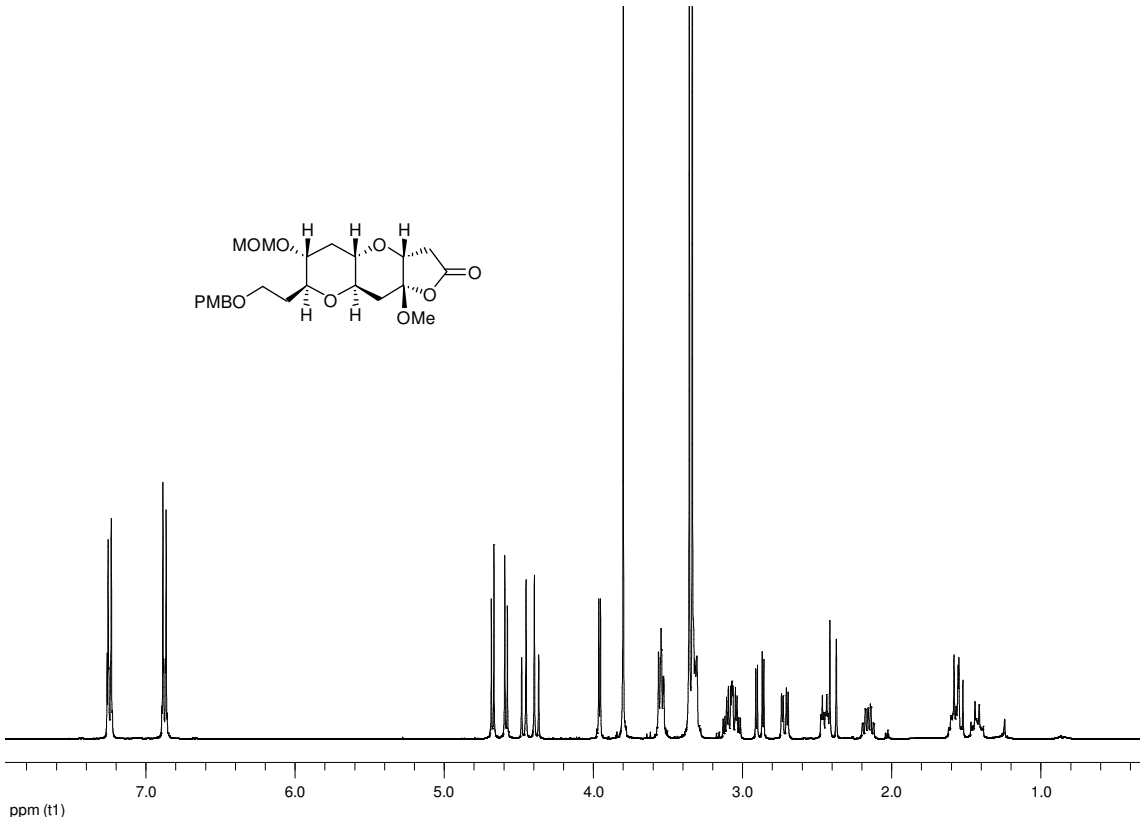

175
150
125
100
75
50
25
0
ppm (t1)

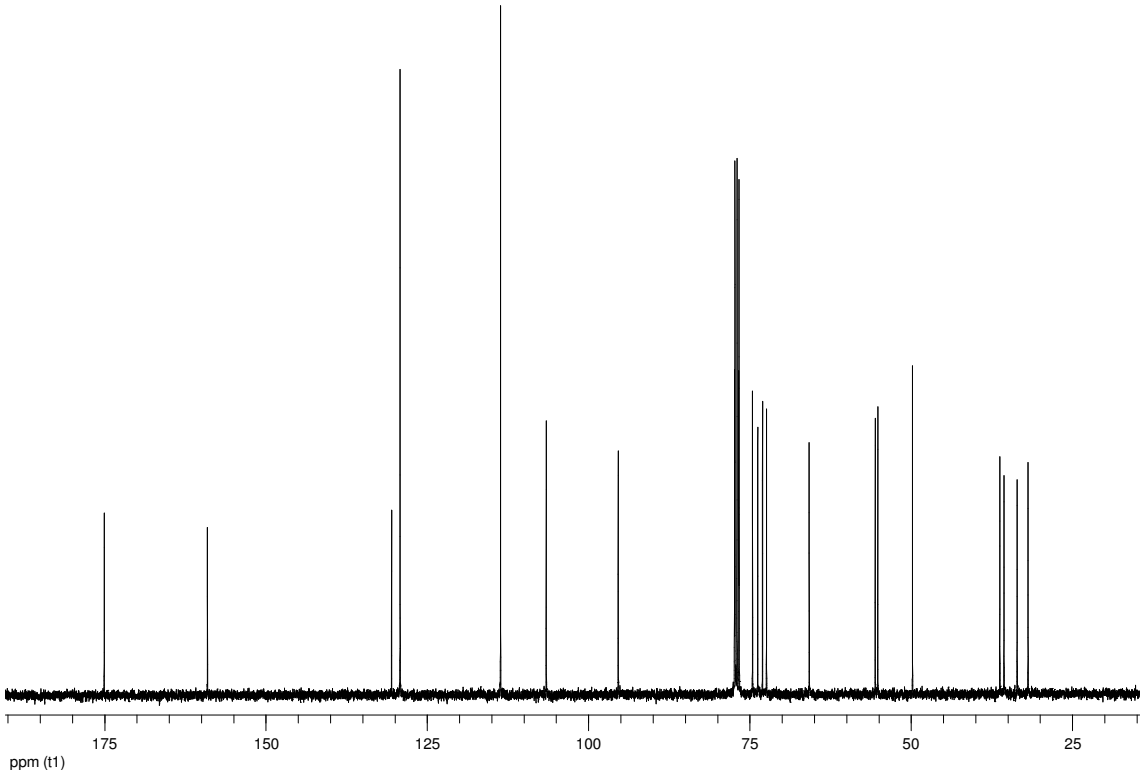

MOMO
OTBS
PMBO
OH
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

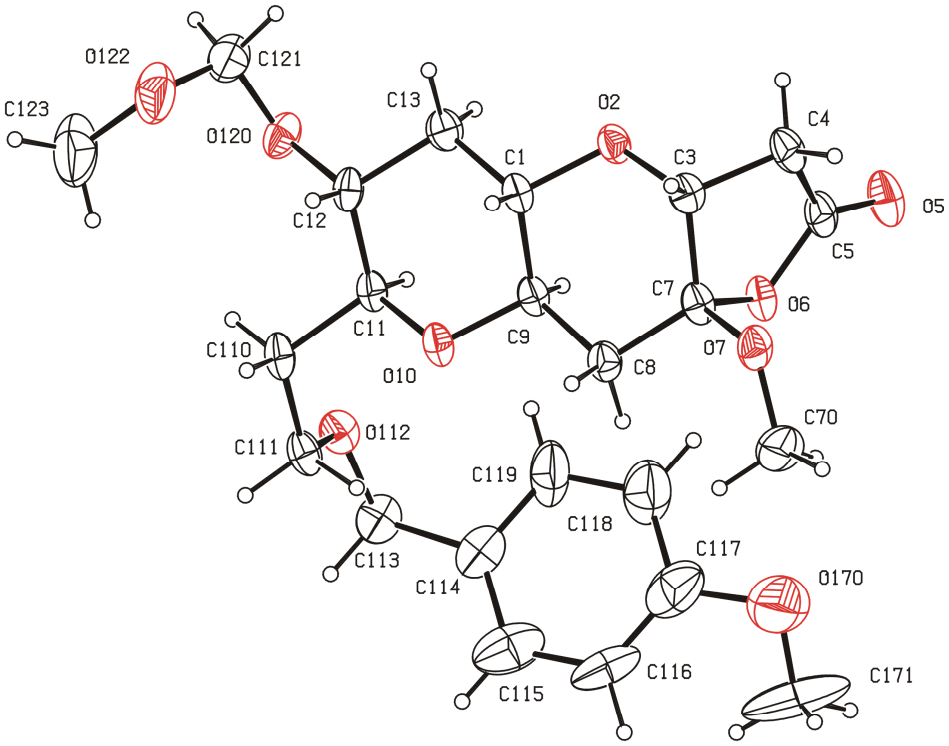

150
125
100
75
50
25
0
ppm (t1)

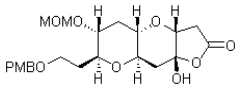

MOMO
OTBS
PMBO
O
O
O
MeO
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

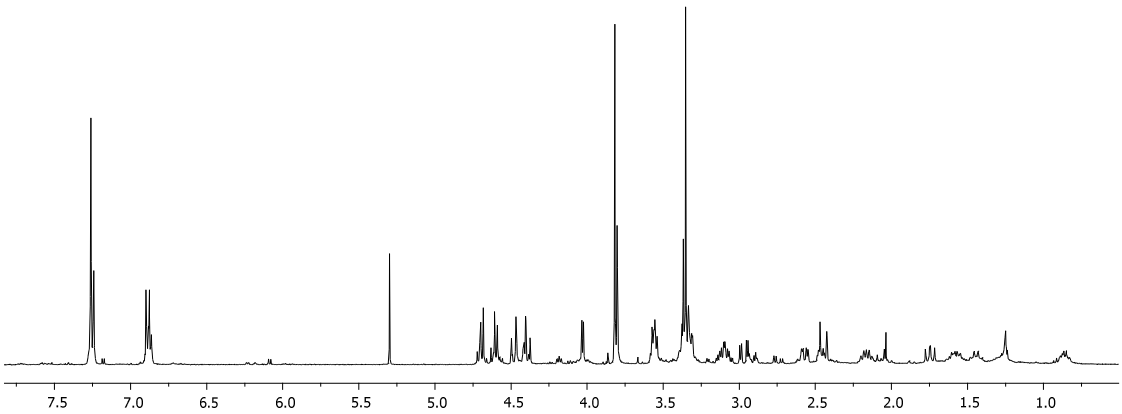

175
150
125
100
75
50
25
0
ppm (t1)

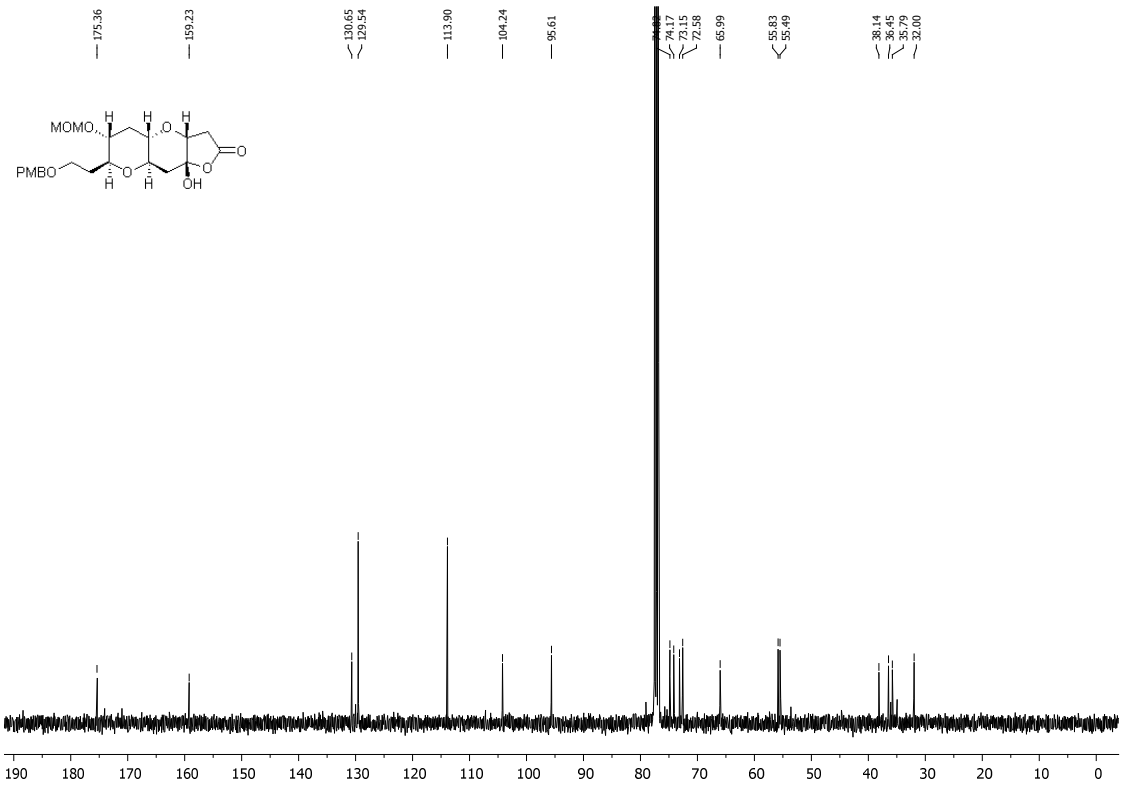

MOMO
PMBO
H
H
H
H
O
O
O
O
OMe
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

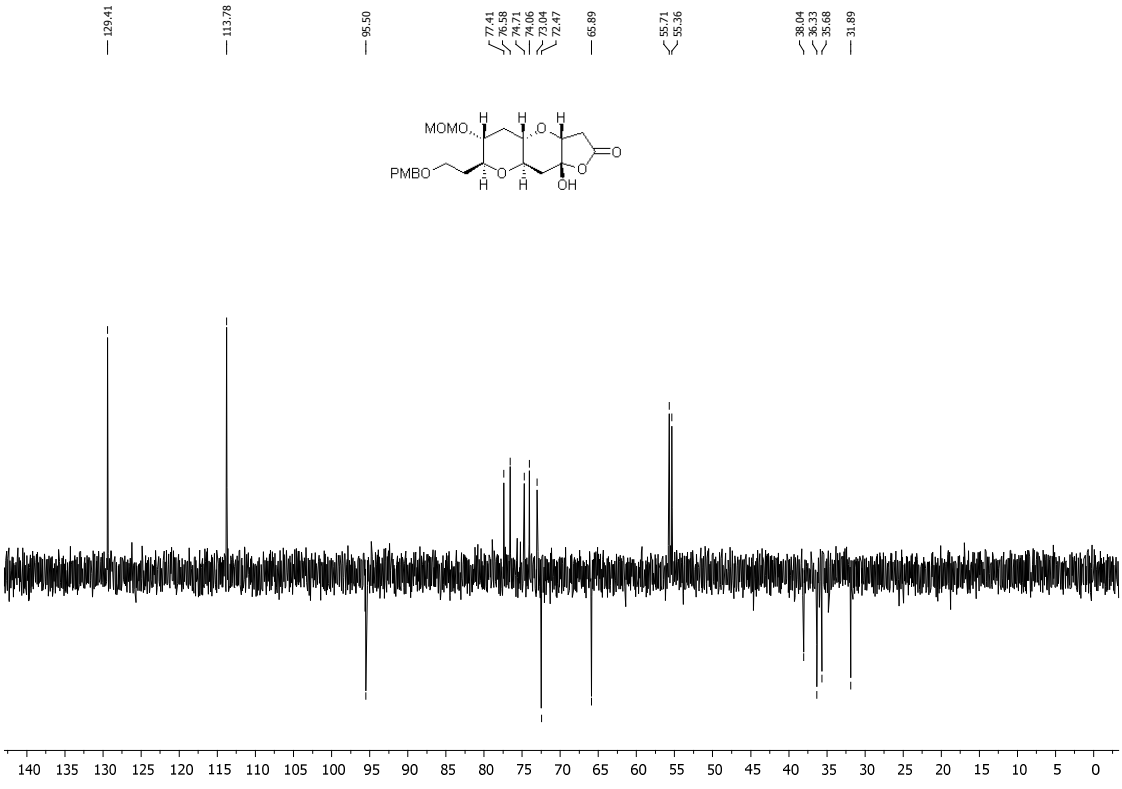

175
150
125
100
75
50
25
ppm (t1)

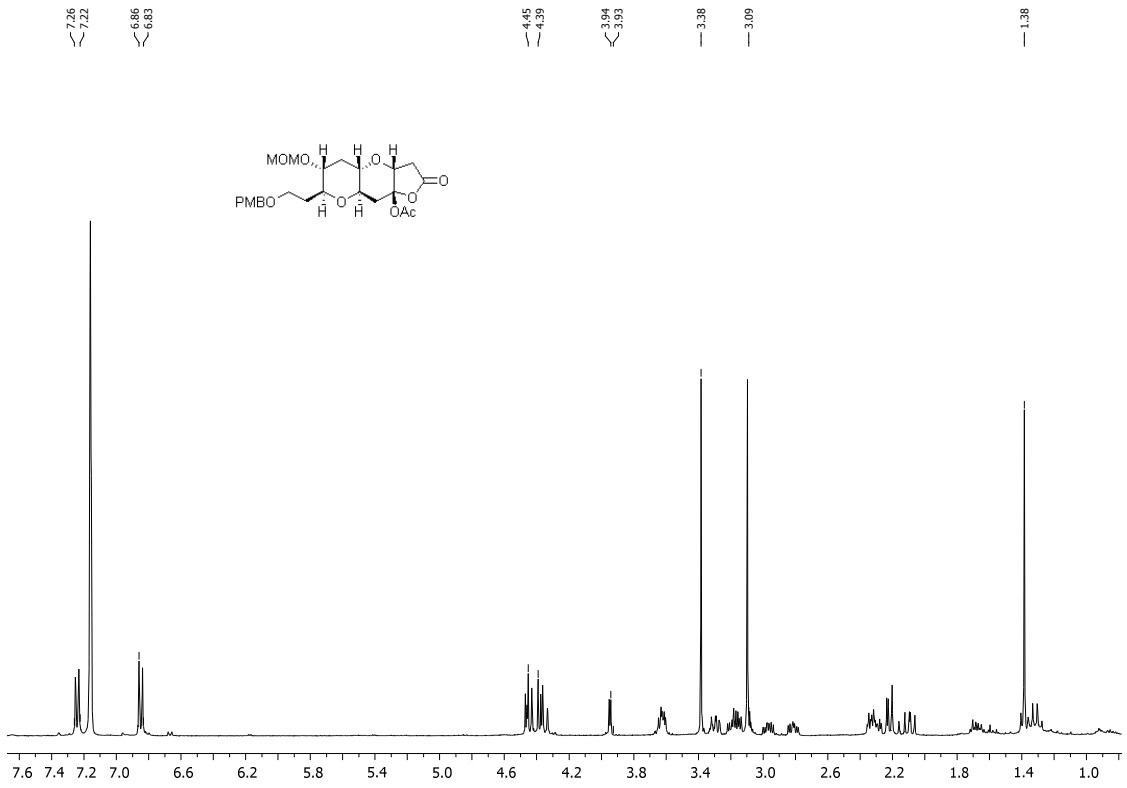

O122
C121
C123
O120
C13
O2
C4
C1
C3
O5
C12
C5
C7
O6
C11
C9
C110
O10
C8
O7
C70
O112
C111
C119
C118
C113
C117
C114
O170
C116
C171
C115

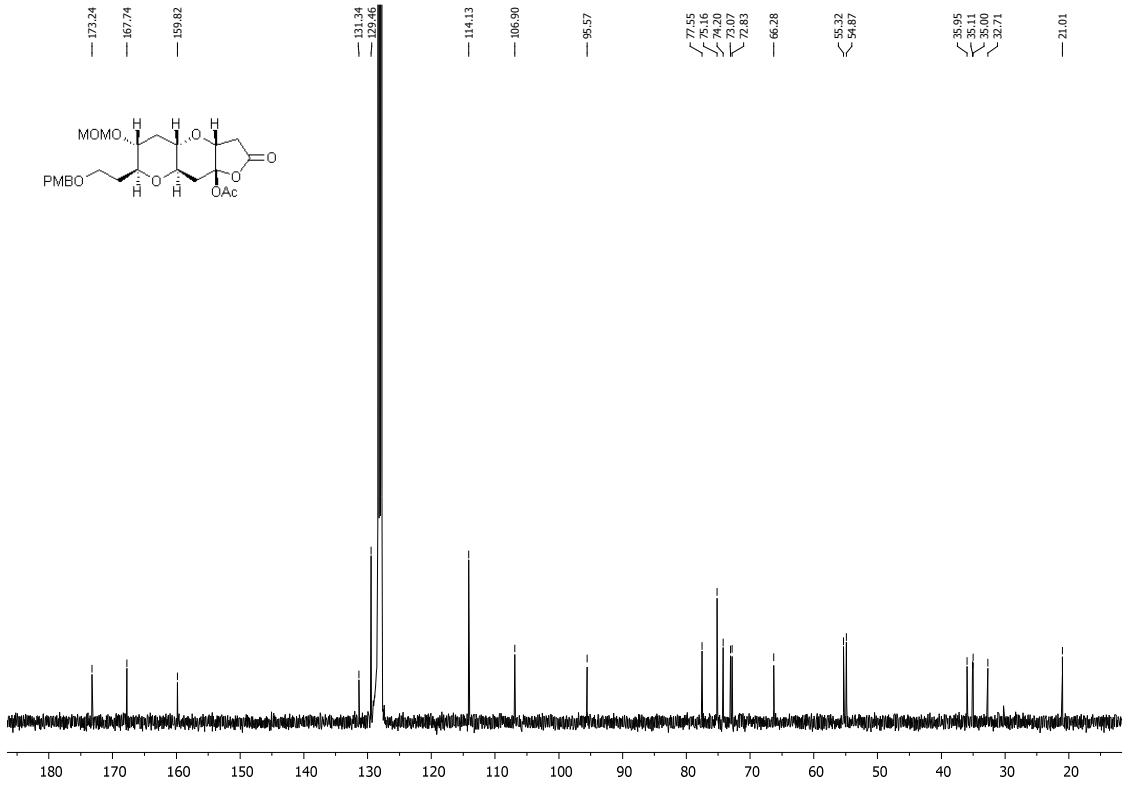

MOMO
PMBO
O
OH

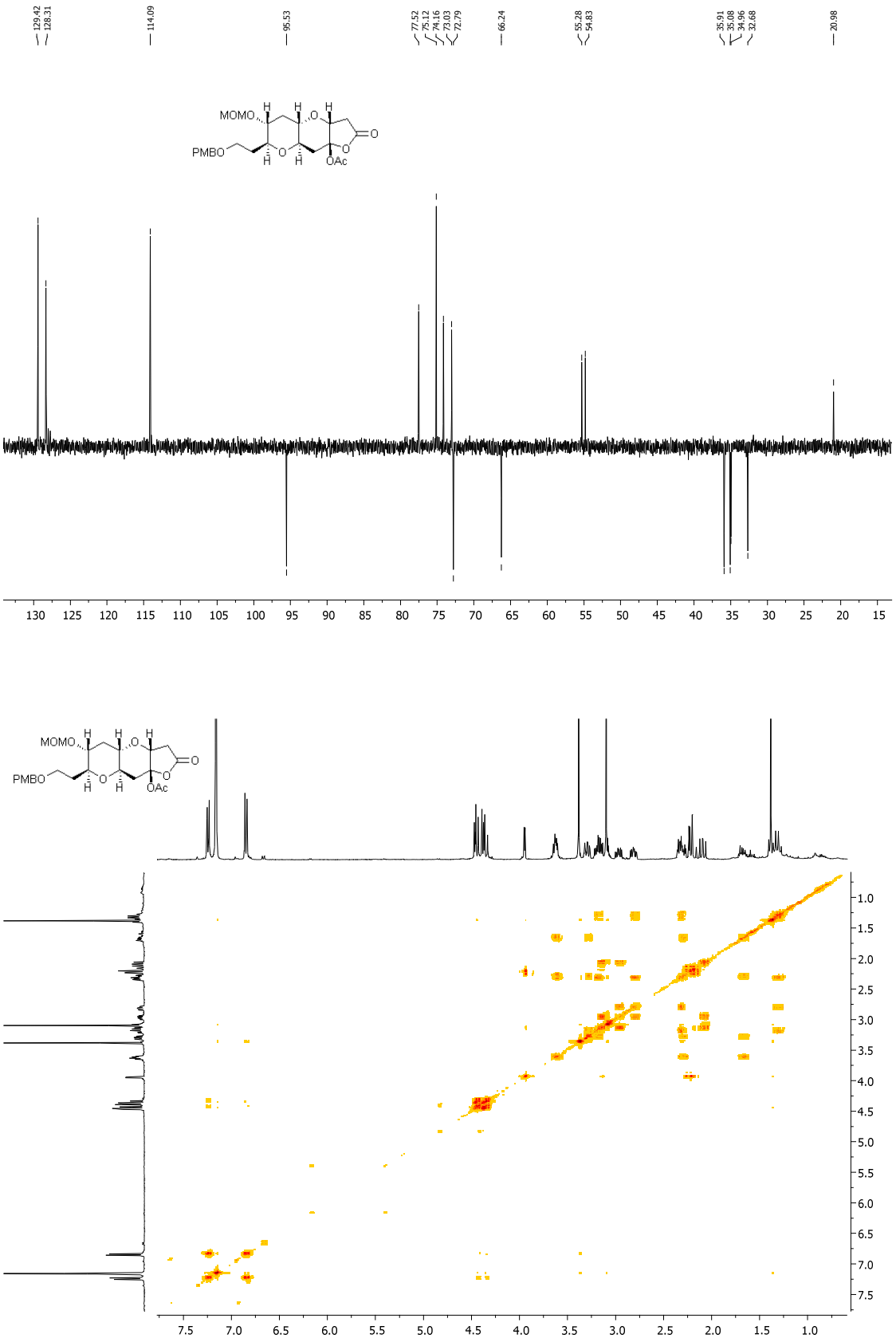

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


175.36
159.23
130.65
129.54
113.90
104.24
95.61
74.17
73.15
72.58
65.99
55.83
55.49
38.14
36.45
35.79
32.00
MOMO
PMBO
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

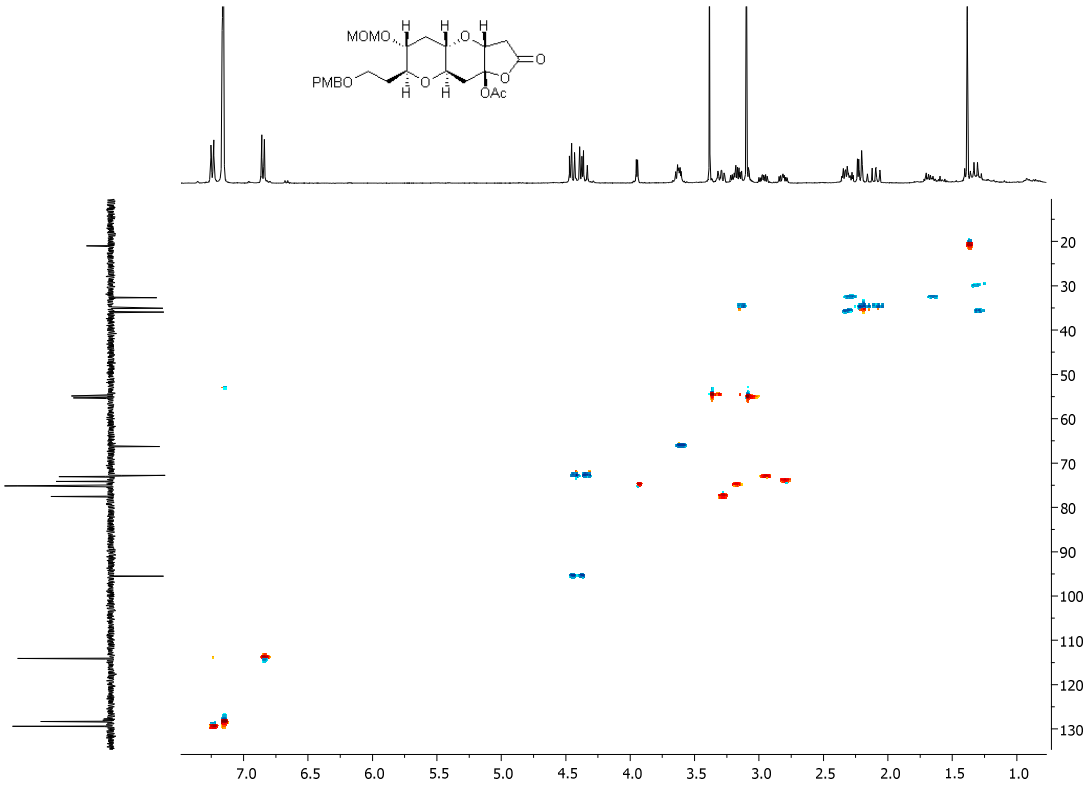

129.41
113.78
95.50
77.41
76.58
74.71
74.06
73.04
72.47
65.89
55.71
55.36
38.04
36.33
35.68
31.89
MOMO
PMBO
OH
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0


7.26
7.22
6.86
6.83
4.45
4.39
3.94
3.93
3.38
3.09
1.38
MOMO
PMBO
OAc
7.6 7.4 7.2 7.0 6.6 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

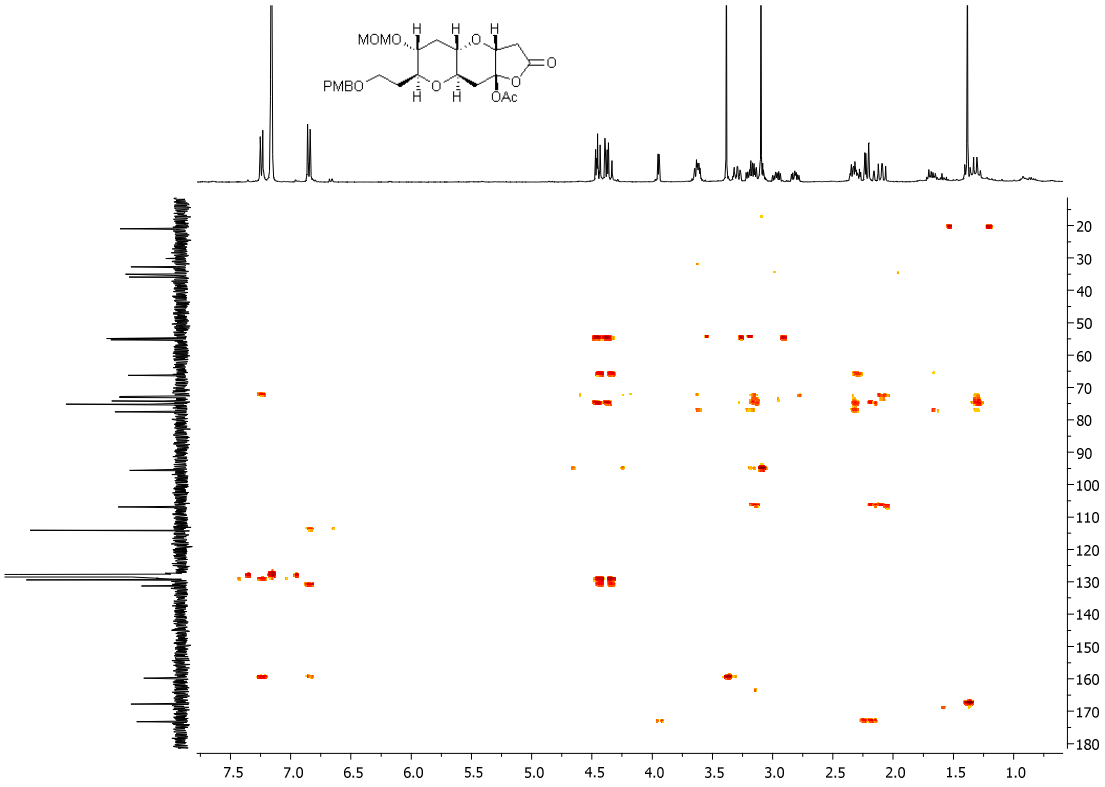

173.24
167.74
159.82
131.34
129.46
114.13
106.90
95.57
77.55
75.16
74.20
73.07
72.83
66.28
55.32
54.87
35.95
35.11
35.00
32.71
21.01
MOMO
PMBO
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20



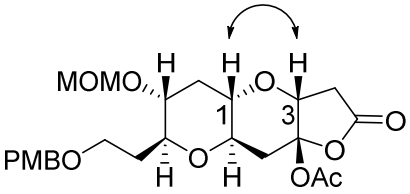
COSY spectrum of **27**

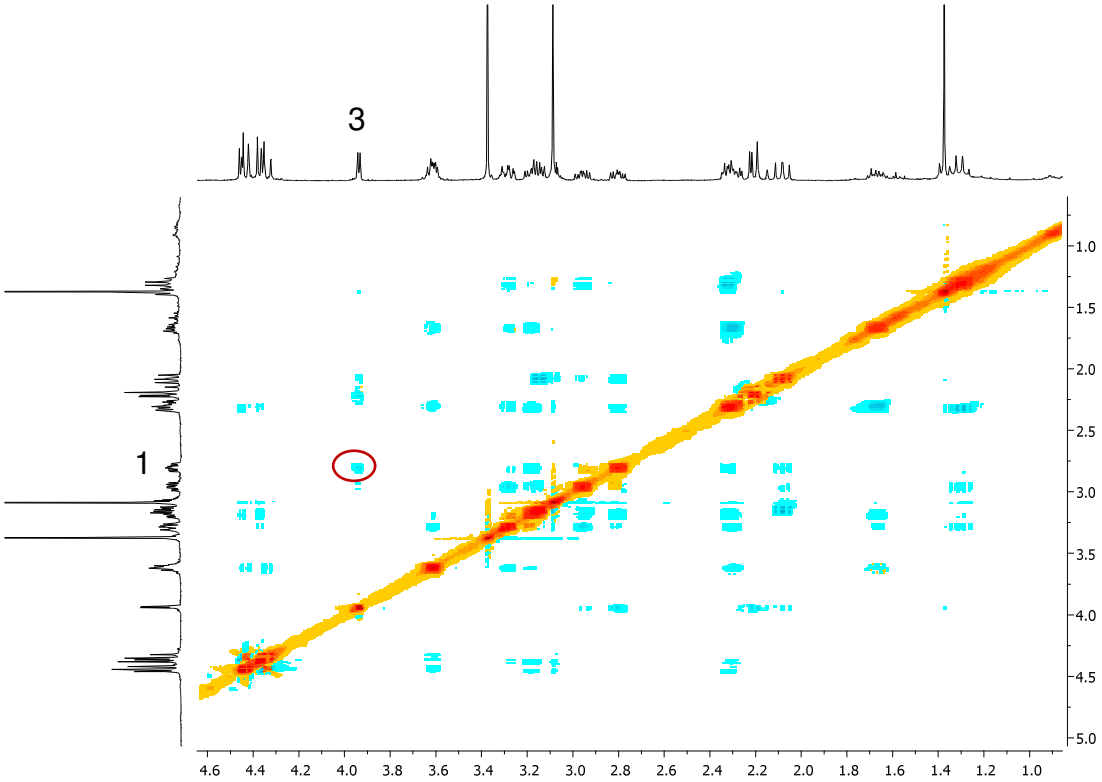


HSQC spectrum of **27**



HMBC spectrum of **27**





NOESY spectrum of **27**