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Supplementary material

Polysulfones: solid organic catalysts for the chemoselective cleavage of methyl-substituted allyl ethers under neutral conditions. New strategy for alcohol protection/deprotection.

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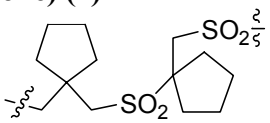
General remarks

Commercial reagents (Fluka, Aldrich) were used without purification. Solvents were distilled prior to use: THF from Na and benzophenone. Sulfur dioxide was dried by passing through a column filled with P_2O_5, Al_2O_3 for drying (Fluka 06400), Al_2O_3 basic activated Type 5016A Brockman I (Aldrich 19,944-3). Light petroleum ether used refers to the fraction boiling at 40-60°C. Solutions after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040-0.63 mm, Merck No.9385 silica gel 60, 240-400 mesh). TLC for reaction monitoring: Merck silica gel $60F_{254}$ plates; detection by UV light; Pancaldi reagent [$(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O] or $KMnO_4$. IR spectra: Perkin-Elmer-1420 spectrometer. ^{1}H NMR spectra : Bruker-ARX-400 spectrometer (400 MHz); δ (H) in ppm relative to the solvent′s residual ^{1}H signal [$CHCl_3$, δ (H) 7.27] as internal reference; all ^{1}H assignments were confirmed by 2D-COSY-45 spectra. ^{13}C NMR spectra : same instrument as above (100.6 MHz); δ (C) in ppm relative to solvent C-signal [$CDCl_3$, δ (C) 77.0] as internal reference; coupling constants *J* in Hz. MS: Nermag R-10-10C, chemical ionization (NH_3) mode *m*/*z* (amu) [% relative base peak (100%)], HRMS : Jeol AX-505. Elemental analyses : Ilse Beetz, D-96301 Kronach, Germany.

Poly(methylidenecyclopentane-sulfone) (2)[1]



2

Methylidenecyclopentane (**1**) was purified by distillation. SO_2 (1.6 ml, 0.0358 mol) was transferred to frozen methylidenecyclopentane (**1**) (1.0 g, 12.2 mmol) on the vacuum line. Mixture was allowed to warm to –20 °C. After 2 hours, at this temperature, the excess of SO_2, non-reacted methylidenecyclopentene (**1**) and 1-methylcyclopentene were evaporated under reduced pressure (0.001 Torr). Poly(methylidenecyclopentane-sulfone) (**PS**) (1.3 g, 75 %) was, powdered and neutralized with aqueous solution of NaOH (0.1 N) till pH=7 and washed 3 times by turns with water and CH_2Cl_2. Neutralized polymer was dried on the vacuum line overnight.

For characterization see:

[1]D. Marković, P. Vogel, *Angew. Chem. Int. Ed.* 2004, **43**, 2928-2930.

General procedure for deprotection of a allyl ethers

In two necked flask was added allyl ether (0.1 mmol), neutralized poly(methylidenecyclopentane-sulfone) (**2**) (10 weight%) and 2ml of cyclohexane. Reaction mixture was refluxed under inert atmosphere and followed by TLC. After reaction was finished the liberated alcohol was purified by flash chromatography.

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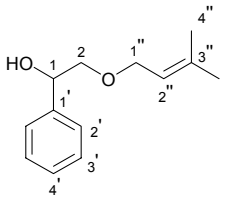
2-(3-Methylbut-2-en-1-yloxy)-1-phenylethanol (18)



NaH (55% in oil dispersion, 2 g , 45.8 mmol) was added to a stirred solution of 1-phenylethane-1,2-diol (**17**) (3.16 g, 22.9 mmol) in anhydrous DMF (40 mL) under Ar atmosphere at -40 °C. Reaction mixture was heated to -10 °C and prenyl bromide (3.41 g, 22.9 mmol) was added dropwise. Reaction was followed by TLC (CH_2Cl_2/Ethyl acetate=10/1) and, after finishing, quenched with water, extracted with CH_2Cl_2, dried over $MgSO_4$ and purified by flash chromatography (CH_2Cl_2/Ethyl acetate=10/1).

Colorless oil, 74 %

IR (film): 3425, 3061, 3028, 2970, 2911, 1950, 1878, 1813, 1668, 1451, 1377, 1328, 1255, 1197, 1097, 1027, 1005, 905.

MS (CI, NH_3): 206 ([M]; 8), 189 (43), 171 (29), 137 (25), 121 (33), 107 (100), 91 (15).

^{1}H NMR (400 MHz, $CDCl_3$): 7.43-7.26 (m, 5H, H-C(aromatic)), 5.38 (t, 1H, ^{3}J(H, H)=6.8, H-C(2″)), 4.97 (ddd, 1H, ^{3}J(H, H)= 9.3, ^{3}J(H, H)=3.1, ^{3}J(H, H)=2.5, H-C(1)), 4.07 (d, 2H, ^{3}J(H, H)=6.8, H-C(1″)), 3.60 (dd, 1H, ^{2}J(H, H)=9.9, ^{3}J(H, H)=3.1, H_a-C(2)), 3.44 (dd, 1H, ^{2}J(H, H)=9.9, ^{3}J(H, H)=9.3, H_b-C(2)), 3.00 (d, 1H, ^{3}J(H, H)= 2.5, H-O)), 1.77 and 1.69 (2×s, 2×3H, 2×H-C(4″)).

^{13}C NMR (100.6 MHz, $CDCl_3$): 140.3 (s, C(3″)), 137.6 (s, C(1′)), 128.4 (d, ^{1}J(C,H)=159, C(3′)), 127.7 (d, ^{1}J(C,H)=161, C(4′)), 126.1 (d, ^{1}J(C,H)= 156, C(2′)), 120.7 (d, ^{1}J(C,H)=157, C(2″)), 75.6 (d, ^{1}J(C,H)=141, C(1″)), 72.8 (t, ^{1}J(C,H)=145, C(2)), 67.6 (t, ^{1}J(C,H)=141, C(1)), 25.8 and 18.0 (2×q, ^{1}J(C,H)=125, 2×C(4″)).

HRMS (MALDI): calcd for $C_{13}H_{18}KO_2^+$ 245.0944 [M+K^+], found 245.0946

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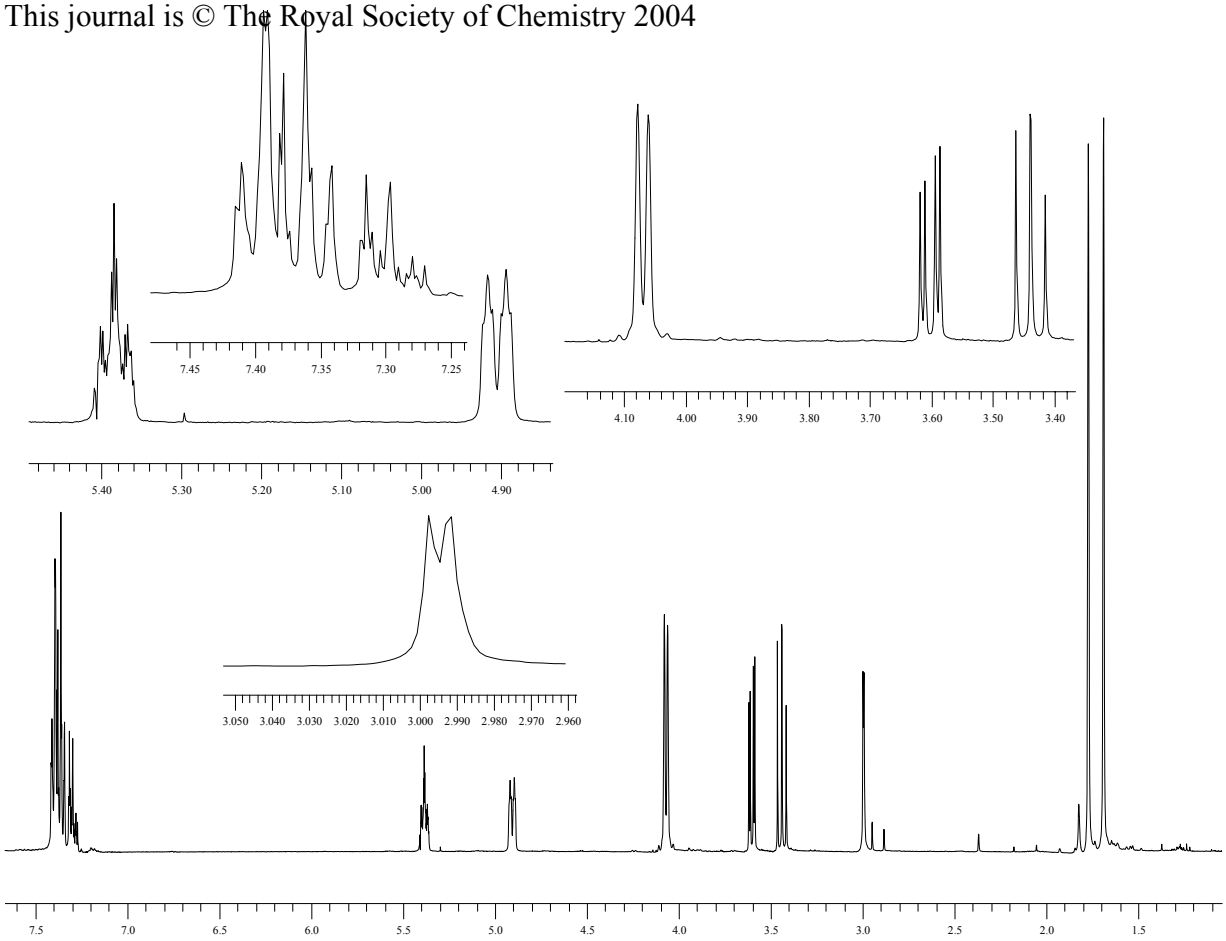
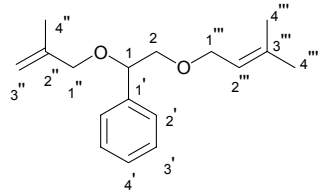


Figure S1. ^{1}H-NMR spectrum of 2-(3-methyl-but-2-en-1-yloxy)-1-phenylethanol (**18**)

[1-(2-Methylallyloxy)-2-(3-methylbut-2-en-1-yloxy)ethyl]benzene (19)



NaH (55 % in oil dispersion, 0.5 g, 11.4 mmol) was added to a stirred solution of **18** (2.36 g, 11.4 mmol) in anhydrous DMF (20 mL) under Ar atmosphere at 0 °C. Reaction mixture was stirred for 1 h and methallyl bromide (1.85 g, 13.7 mmol, 1.2 eqv.) was added. Reaction was followed by TLC (petroleum ether /ethyl acetate=10/1), quenching with water, extraction with CH_2Cl_2, dried over $MgSO_4$ and purifications by flash chromatography (petroleum ether /Ethyl acetate=10/1).

Colorless oil, 96 %

IR (film): 3063, 3029, 2971, 2915, 2858, 1952, 1810, 1771, 1716, 1651, 1454, 1197, 1059, 1027, 905.

MS (CI, NH_3): 261 ([M+1]; 3), 260 ([M]; 4), 189 (10), 161 (100), 141 (8), 123 (27), 105 (47), 91 (11).

^{1}H NMR (400 MHz, $CDCl_3$): 7.41-7.28 (m, 5H, H-C(aromatic)), 5.35 (t, 1H, ^{3}J(H, H)=7.0, H-C(2″)), 5.00 and 4.91 (2×s, 2×1H, H-C(2‴)), 4.56 (dd, 1H, ^{3}J(H, H)= 7.7, ^{3}J(H, H)=3.8, H-C(1)), 4.09 and 4.02 (2×dd, 2×1H, ^{2}J(H, H)=11.5, ^{3}J(H, H)=7.0, H-C(1‴)), 3.93 and 3.80 (2×d, 2×1H, ^{2}J(H, H)=11.5, H-C(1″)), 3.79 (dd, 1H, ^{2}J(H, H)=10.2, ^{3}J(H, H)=7.7, H_a-C(2)), 3.53 (dd, 1H, ^{3}J(H, H)=10.2, ^{3}J(H, H)=3.8, H_b-C(2)), 1.77, 1.75 and 1.66 (3×s, 3×3H, 2×H-C(4″), H-C(4″)).

^{13}C NMR (100.6 MHz, $CDCl_3$): 144.8 (s, C(2″)), 137.0 (s, C(1′)), 133.4 (s, C(3‴)), 128.7 (d, ^{1}J(C,H)=153, C(3′)), 128.2 (d, ^{1}J(C,H)=160, C(2′)), 127.5 (d, ^{1}J(C,H)= 159, C(4′)), 121.7 (d, ^{1}J(C,H)= 160, C(3″)), 112.6 (t, ^{1}J(C,H)= 150, C(3‴)), 80.8 (d, ^{1}J(C,H)=143, C(1)), 75.1 (t, ^{1}J(C,H)=142, C(1‴)), 73.1 (t, ^{1}J(C,H)=140, C(1″)), 68.3 (t, ^{1}J(C,H)=140, C(2)), 26.1 and 18.4 (2×q, ^{1}J(C,H)=126, 2×C(4‴)), 20.0 (2×q, ^{1}J(C,H)=126, 2×C(4″)).

HRMS (MALDI): calcd. for $C_{17}H_{24}KO_2^+$ 299.1413 [M+K^+], found 299.1435

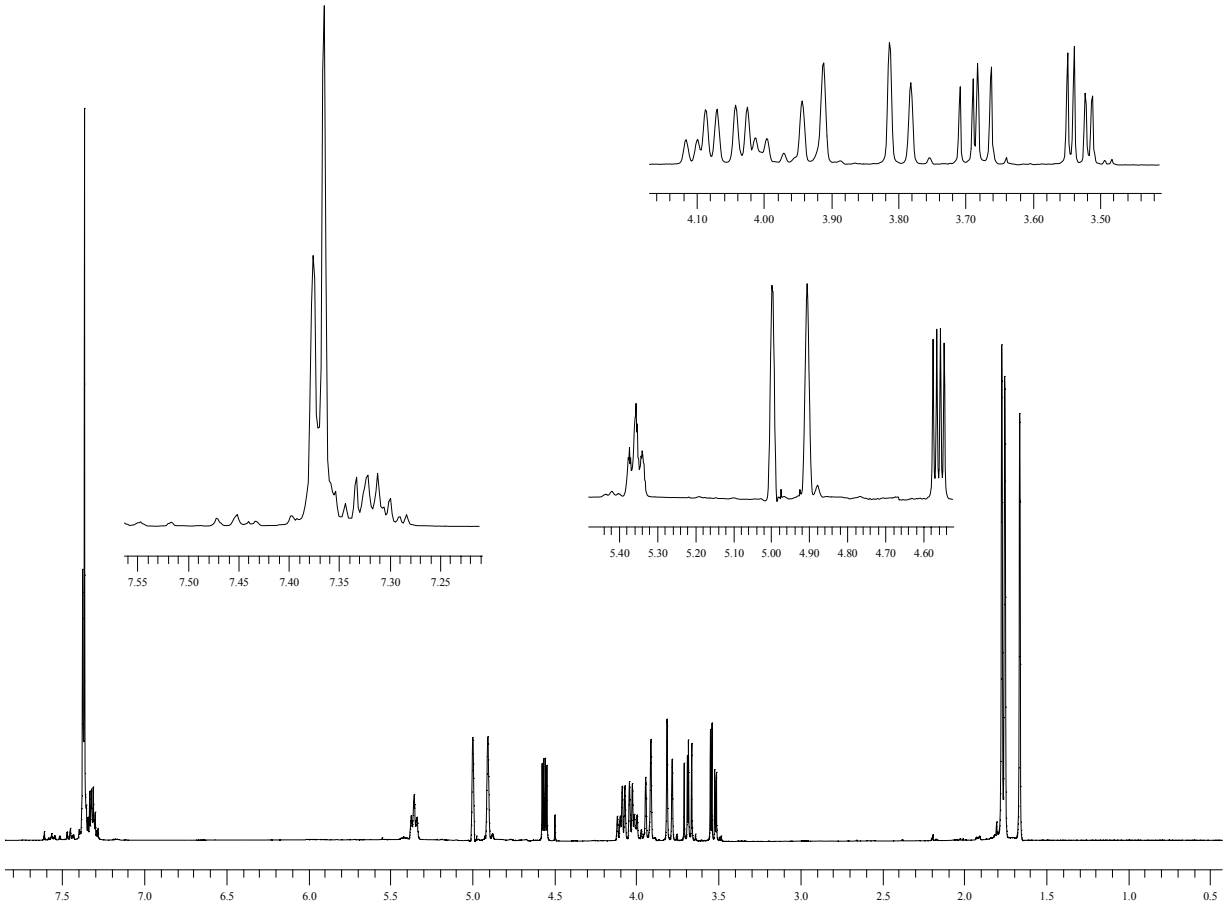
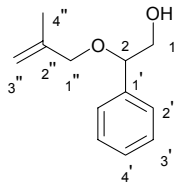


Figure S2. ^{1}H-NMR spectrum of [1-(2-methylallyloxy)-2-(3-methylbut-2-en-1-yloxy)ethyl]benzene (**19**)

2-(2-Methylallyloxy)-2-phenylethanol (8)



Yellowish oil, 94 %

IR (film): 3426, 2960, 2928, 1718, 1700, 1451, 1374, 1103, 905.

MS (CI, NH_3):192([M]; 6), 161 (10), 121 (49), 105 (100), 91 (55).

^{1}H NMR (400 MHz, $CDCl_3$/ a drop of D_2O): 7.43-7.26 (m, 5H, H-C(aromatic)), 4.97 (s, 1H, H-C(3′)), 4.92 (s, 1H, H-C(3′)), 4.49 (dd, 1H, ^{3}J(H, H)= 8.4, ^{3}J(H, H)= 3.9, H-C(2)), 3.93 (d, 1H, ^{2}J(H, H)= 12.3, H_a-C(1″)), 3.78 (d, 1H, ^{2}J(H, H)= 12.3, H_b-C(1″)), 3.72 (dd, 1H, ^{2}J(H, H)= 11.8, ^{3}J(H, H)= 8.4, H_a-C(1)), 3.63 (dd, 1H, ^{2}J(H, H)= 11.8, ^{3}J(H, H)= 3.9, H_b-C(1)), 1.77 (s, 3H, H-C(4′)).

^{13}C NMR (100.6 MHz, $CDCl_3$): 141.9 (s, C(2″)), 138.5 (s, C(1′)), 128.6 (d, ^{1}J(C,H)=159, C(3′)), 128.1 (d, ^{1}J(C,H)=161, C(4′)), 127.0 (d, ^{1}J(C,H)= 156, C(2′)), 112.5 (t, ^{1}J(C,H)=157, C(3″)), 81.8 (d, ^{1}J(C,H)=147, C(2)), 72.6 (t, ^{1}J(C,H)=137, C(1″)), 67.4 (t, ^{1}J(C,H)=145, C(1)), 19.7 (q, ^{1}J(C,H)=130, C(4″)).

HRMS (MALDI): calcd for $C_{18}H_{30}KO_6^+$ 231.0787 [M+K^+], found 231.0751.

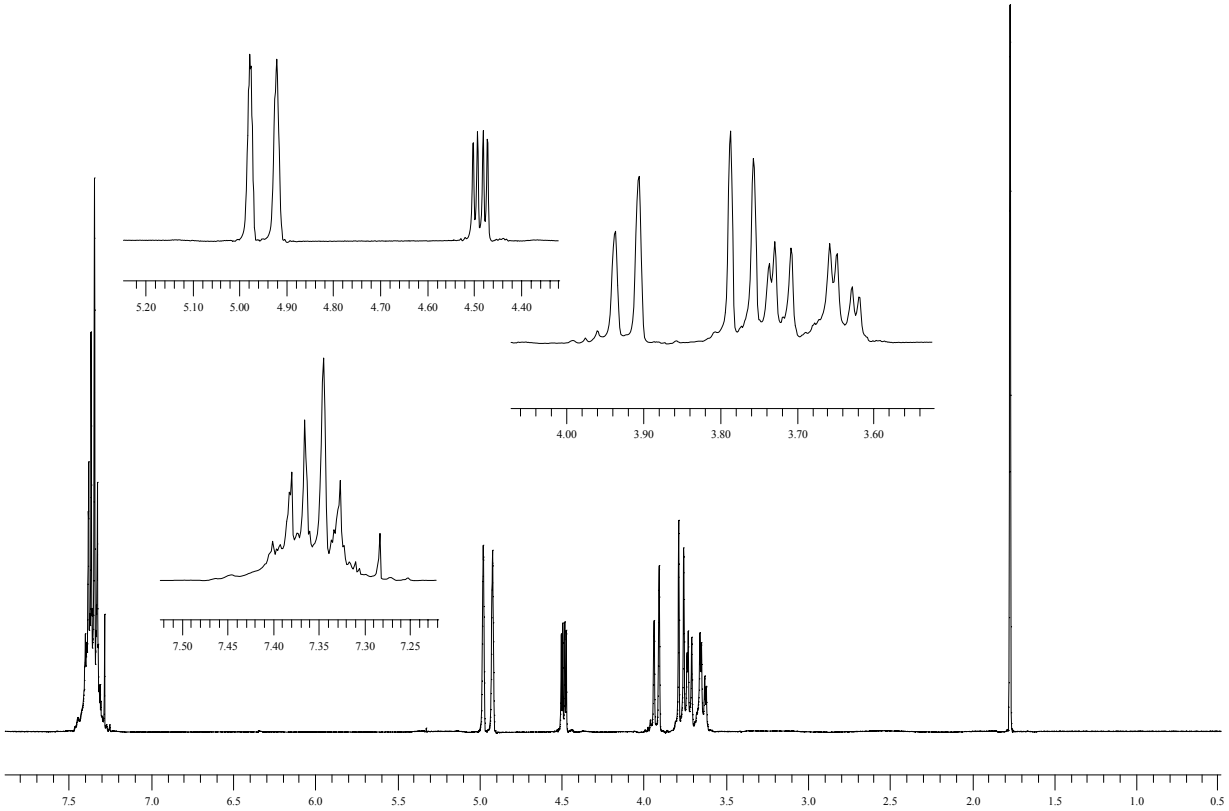


Figure S3. ^{1}H-NMR spectrum of 2-(2-methylallyloxy)-2-phenylethanol (**8**).

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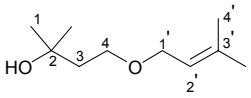
2-Methyl-4-(3-methylbut-2-en-1-yloxy)butan-2-ol (20)



NaH (55% in oil dispersion, 1g , 22.9 mmol) was added to a stirred solution of 3-methylbutane-1,3-diol (2.39 g, 22.9 mmol) in anhydrous DMF (40 mL) under Ar atmosphere at 0 °C. After stirring for 1 h, prenyl bromide (3.41 g, 22.9 mmol) was added dropwise. Consumption of starting material was confirmed after 12 h by TLC (CH_2Cl_2/Ethyl acetate=10/1). The mixture was quenched with water, extracted with CH_2Cl_2, dried over $MgSO_4$ and purified by flash chromatography (CH_2Cl_2/Ethyl acetate=10/1).

Colorless oil, 92 %

IR (film): 3382, 2931 1721, 1466, 1380, 1151, 880, 652.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.24 (m, 1H, H-C(2′)), 3.85 (d, 2H ^{2}J(H, H)= 7.0 H-C(1′)), 3.56 (t, 2H, ^{3}J(H, H)=6.0, H-C(4)), 1.67 (t, 2H, ^{3}J(H, H)=6.0, H-C(3)), 1.65 and 1.58 (2×s, 2×3H, 2×H-C(4′)), 1.14 (s, 6H, C(1)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.8 (s, C(3′)), 121.1 (d, J(C,H)=155, C(2′)), 70.9 (s, C(2)), 67.9 (t, J(C,H)=140, C(4)), 67.7(t, J(C,H)=140, C(1′)), 41.8 (t, J(C,H)=125, C(3)), 31.3 and 29.7, (2×q, J(C,H)= 125, C(1)), 26.5 and 18.0 (2×q, J(C,H)= 125, ($\underline{C}H_3)_2$C(3')).

MS (CI, NH_3): 155 (2), 139 (54), 123(4), 113 (24), 101 (13, M-C_4H_9O), 85 (100).

HRMS (MALDI): calcd. for $C_{10}H_{20}NaO_2$: 195.2543, found 195.2576.

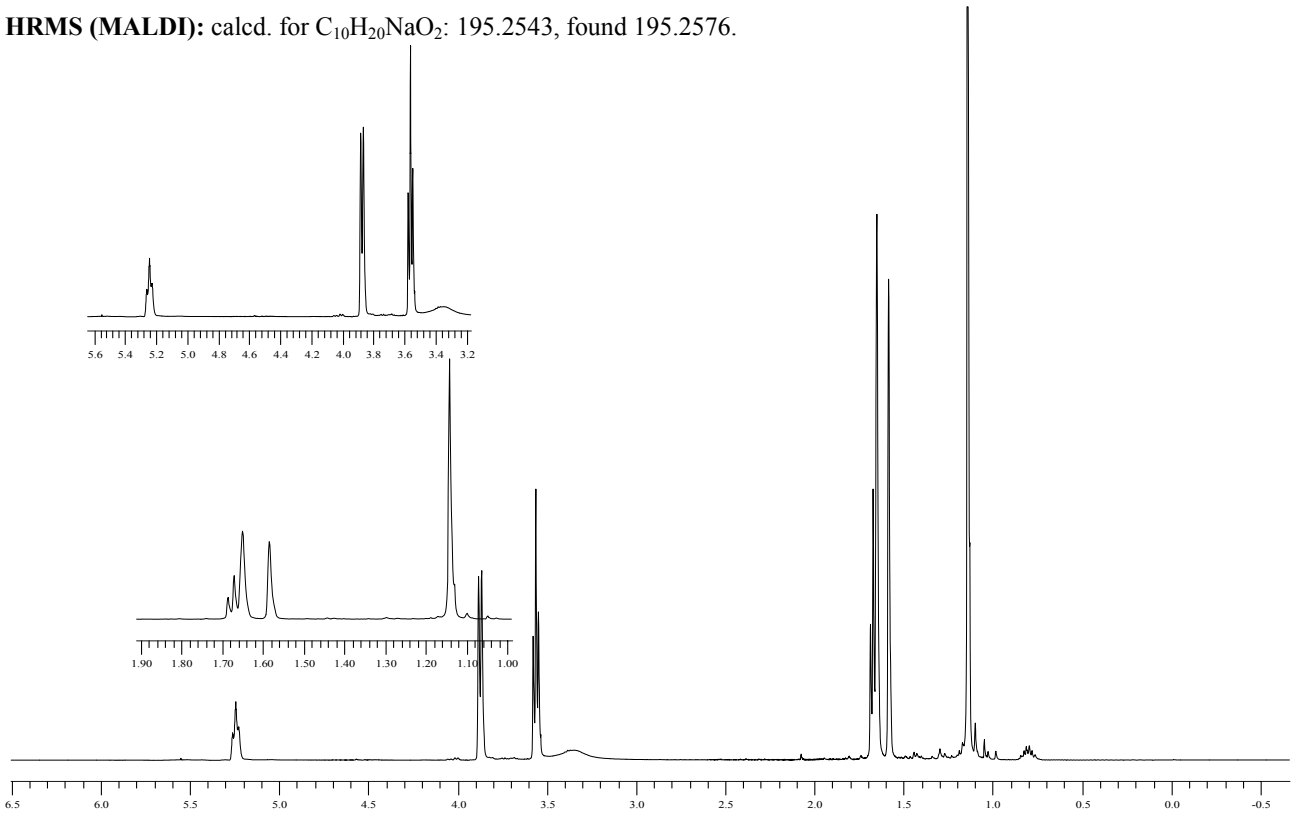
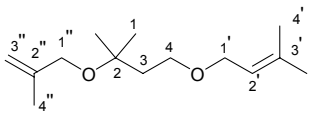


Figure S4. ^{1}H-NMR spectrum of 2-methyl-4-(3-methylbut-2-en-1-yloxy)butan-2-ol (**20**)

2-Methyl-2(2-methylallyloxy)-4-(3-methyl-but-2-en-1-yloxy)butane (9)



KH (423 mg, 10.5 mmol), washed 5 times with dry pentane and dried on vacuum line, and THF (15 mL) was added in two necked flask under nitogen atmosphere (glove box). Solution of **20** (1.82 g, 10.5 mmol) in anhydrous THF (40 mL) was slowly added for 20 min at 0 °C. After stirring for 1 h at room temperature, in the reaction mixture was added dropwise methallyl bromide (1.7 g, 12.6 mmol, 1.2 eqv.). Reaction mixture was stirred over night and quenched with water, extracted with ether, dried over $MgSO_4$ and purified by flash chromatography (petroleum ether /Ethyl acetate=10/1).

Colorless oil, 87 %

IR (film): 3074, 2971, 2930, 2858, 1652, 1448, 1378, 1364, 1166, 1098, 894.

^{1}H NMR (400 MHz, $CDCl_3$): 5.24 (tm, 1H, ^3J(H, H)= 6.8, H-C(2′)), 4.97 and 4.82 (2×s, 2×1H, H-C(2″)), 3.93 (d, 2H, ^2J(H, H))= 7.4, H-C(1′)), 3.76 (s, 2H, H-C(1″)), 3.52 (t, 2H, ^3J(H, H))= 7.4, H-C(4)), 1.83 (t, 2H, ^3J(H, H)= 7.4, H-C(3)), 1.73, 1.72 and 1.66 (3×s, 3×3H, H-C(4″), 2×H-C(4′)), 1.20 (s, 6H, H-C(1)).

^{13}C NMR (100.6 MHz, $CDCl_3$): 143.3 (s, C(3″)), 136.6 (s, C(3′)), 121.1 (d, J(C,H)=154, C(2′)), 110.7 (t, J(C,H)= 151, C(3″)), 73.9 (s, C(2)), 67.3 (t, J(C,H)=141, C(1″)), 66.3 (t, J(C,H)=141, C(4)), 65.4 (t, J(C,H)=138, C(3′)), 40.0 (t, J(C,H)=125, C(3)), 26.0, 25.9 and 25.8, (3×q, J(C,H)= 125, 2×C(1), C(4′)), 19.7 (q, J(C,H)= 125, C(4″)), 17.97 (q, J(C,H)= 125, C(4′)).

MS (CI, NH_3): 226 ([M]; 4), 199 (25), 175 (86), 139 (55), 113 (70), 85 (100).

HRMS (MALDI): calcd. for $C_{14}H_{26}KO_2$: 265.1570, found 265.1534.

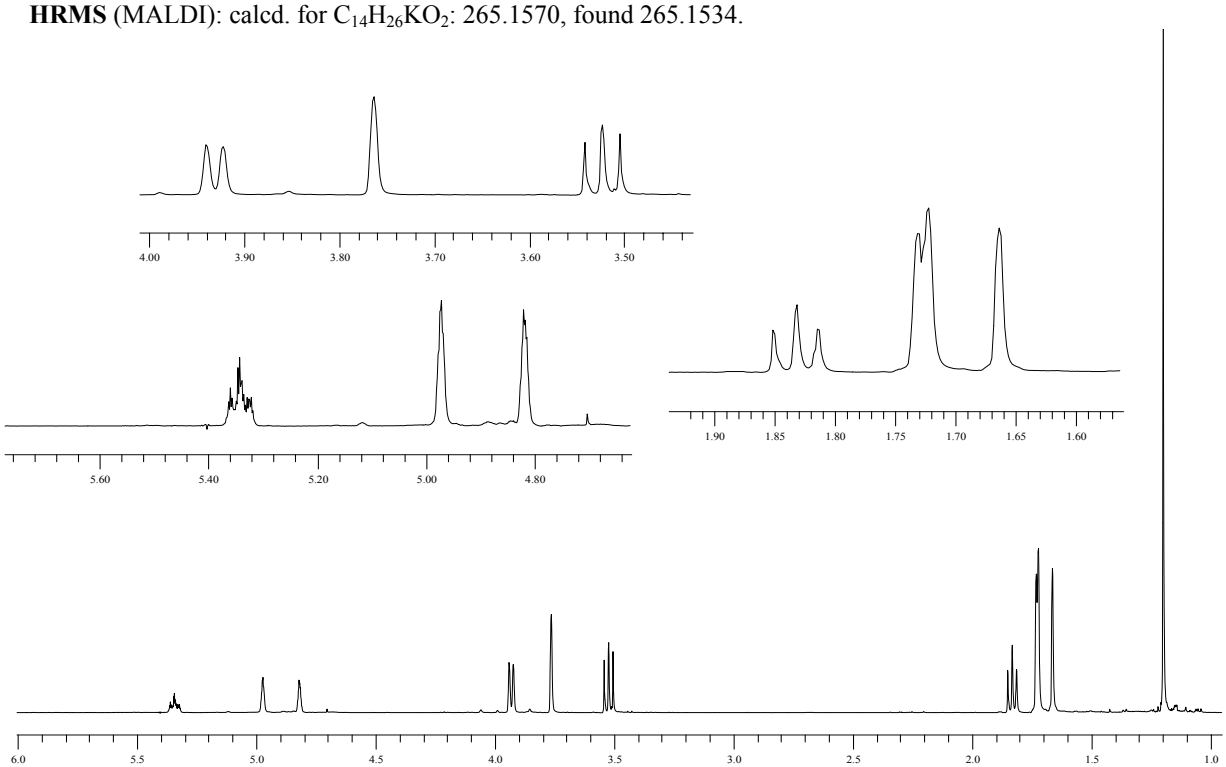


Figure S5. ^{1}H-NMR spectrum 2-Methyl-2(2-methylallyloxy)-4-(3-methyl-but-2-en-1-yloxy)butane (**9**)

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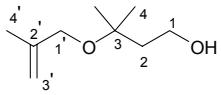
3-Methyl-3-(2-methylallyloxy)butan-1-ol (10)



Colorless oil, 86 %

IR (film): 3445, 2922, 2852, 1457, 1376, 1145, 1100, 898.

^{1}H NMR (400 MHz, $CDCl_3$): 4.96 and 4.91 (2×s, 2×1H, H-C(3′)), 3.90 (s, 2H, H-C(1′)), 3.67 (t, 2H, ^{3}J(H, H))= 5.7, H-C(1)) 3.76 (s, 2H, H-C(1″)), 3.30 (s, 1H, H-O), 1.80 (t, 2H, ^{3}J(H, H)= 5.7, H-C(2)), 1.75 (s, 3H, H-C(4′)), 1.26 (s, 6H, H-C(4)).

^{13}C NMR (100.6 MHz, $CDCl_3$): 142.0 (s, C(2′)), 121.1 (d, ^{2}J(C,H)=150, C(2′)), 110.7 (t, ^{2}J(C,H)= 151, C(3′)), 75.7 (s, C(3)), 70.9 (t, J(C,H)=153, C(1′)), 68.0 (t, J(C,H)=156, C(1)), 41.8 (t, J(C,H)=129, C(2)), 30.1, 29.8 and 19.8, (3×q, ^{2}J(C,H)= 125, 2×C(4), C(4′)).

MS (CI, NH_3): 159 ([M+1]; 15), 142 (25), 123 (45), 111 (60), 95 (100), 83 (91).

HRMS (MALDI): calcd. for $C_{14}H_{26}KO_2$: 197.0944, found 197.0987.

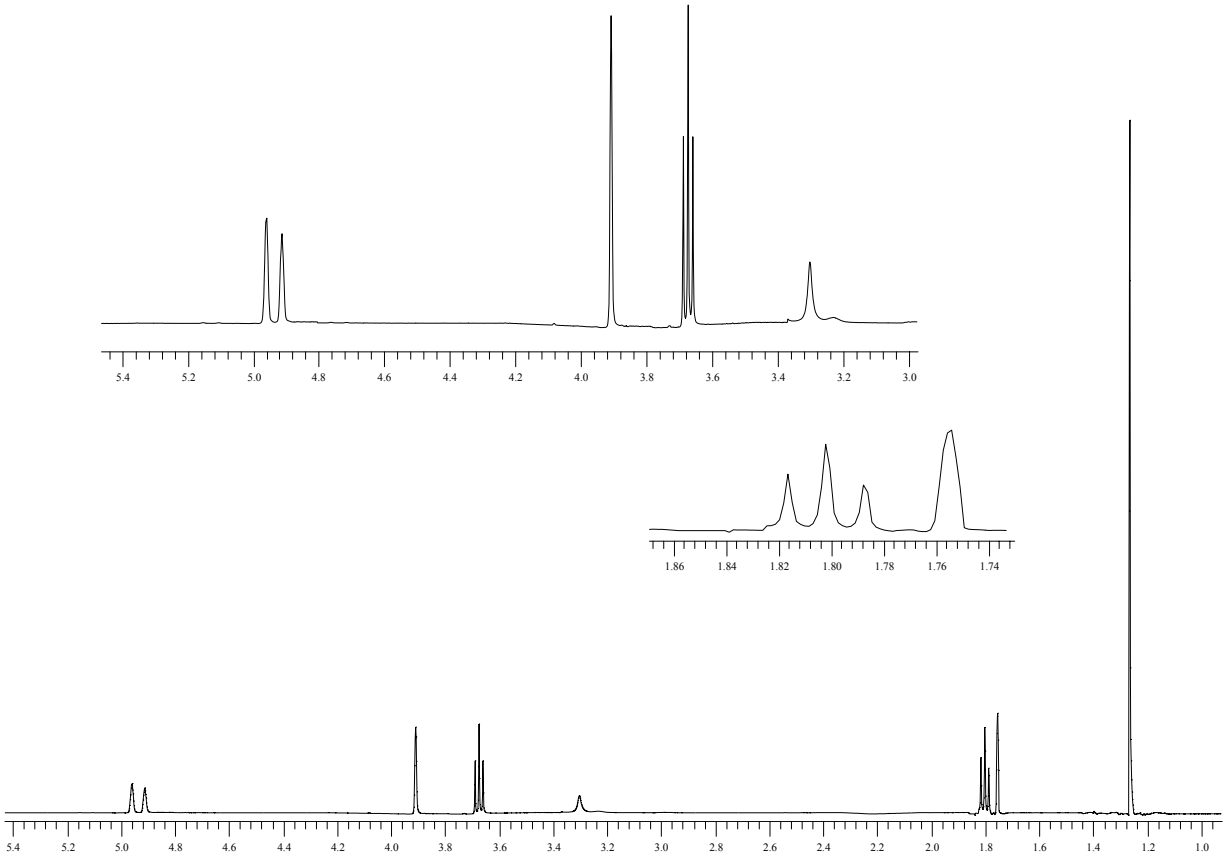


Figure S6. ^{1}H-NMR spectrum 3-methyl-3-(2-methylallyloxy)butan-1-ol (**10**)

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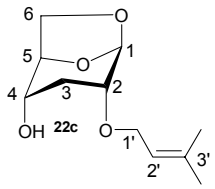
2-*O*-Prenyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (22c).

A mixture of isolevoglucosenone **21** (150 mg, 1.0 mmol), prenyl alcohol (300 mg, 2.3 mmol) and triethylamine (14 µL, 0.10 mmol) was stirred at 20°C for 2h. Excess of alcohol was then eliminated by evaporation in vacuo. The residue was chromatographed on silicagel (1:9 EtOAc/petroleum ether) affording a colorless syrup, which was dissolved in THF (5 mL), cooled to –78 °C. Successively the ketone was reduced by K-selectride (1 M, 1mL). The reaction mixture was allowed to warm to r.t. and stirred overnight. Then methanol and NH_4Cl were added, after stirring for 1h, the reaction mixture was filtrated over Celite and concentrated. The crude was purified by column chromatography (silica, PE:EtOAc 1:1) to obtain **22c** in a yield of 75% (150 mg, 0.7 mmol)



Colorless oil. 75 (%)

$[\alpha]^{25}_{589}$ -7.7, $[\alpha]^{25}_{577}$ -5.7, $[\alpha]^{25}_{546}$ -9.0 $[\alpha]^{25}_{435}$ -18.7 $[\alpha]^{25}_{405}$ -25.2 (C = 2.0, $CHCl_3$)

IR (film): 2971, 2864, 1438, 1140, 924, 638, 754

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (s, 1H, H-C(1)), 5.38 (m, 1H, H-C(2')), 4.48 (s, 1H, H-C(4)), 4.08 (m, 2H, H-C(1a'), H-C(1b')), 3.81 (m, 2H, Ha-C(6),Hb-C(6)), 3.57 (s, 1H, H-C(4)), 3.29 (s, 1H, H-C(2)), 1.91(m, 2H,Ha-C(3), Hb-C(3)), 1.70, 1.67 (2s, 6H, $(C\underline{H}_3)_2$-C(3'))

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.7 (s, C-(3')), 127.4 (s, C-(2')), 100.4 (d, ^1J(C,H)= 175, C-(1)) 77.4 (d, ^1J(C;H)= 150 C-(5)), 73.8 (d, ^1J(C,H)= 145, C-(4)), 69.9 (d, ^1J(C,H)= 140, C-(2)) 65.4 (t, ^1J(C;H)= 145, C-(6)), 65.0 (t, ^1J(C;H)= 133, C-(1')), 29.6 (1 t, ^1J(C,H) 130, C-(3)), 25.8, 25.7 16.6 (3 q, ^1J(C,H)= 125, $(\underline{C}H_3)_2C$(3'))

MS (CI, NH_3): 233 ([M+18], 99), 232 (100), 215 (36), 164 (99), 130 (99), 112 (31), 81 (71)

HRMS (MALDI): Calcd. for $C_{11}H_{18}O_4Na$: 237.1103 [$M+Na^+$], found: 237.1112

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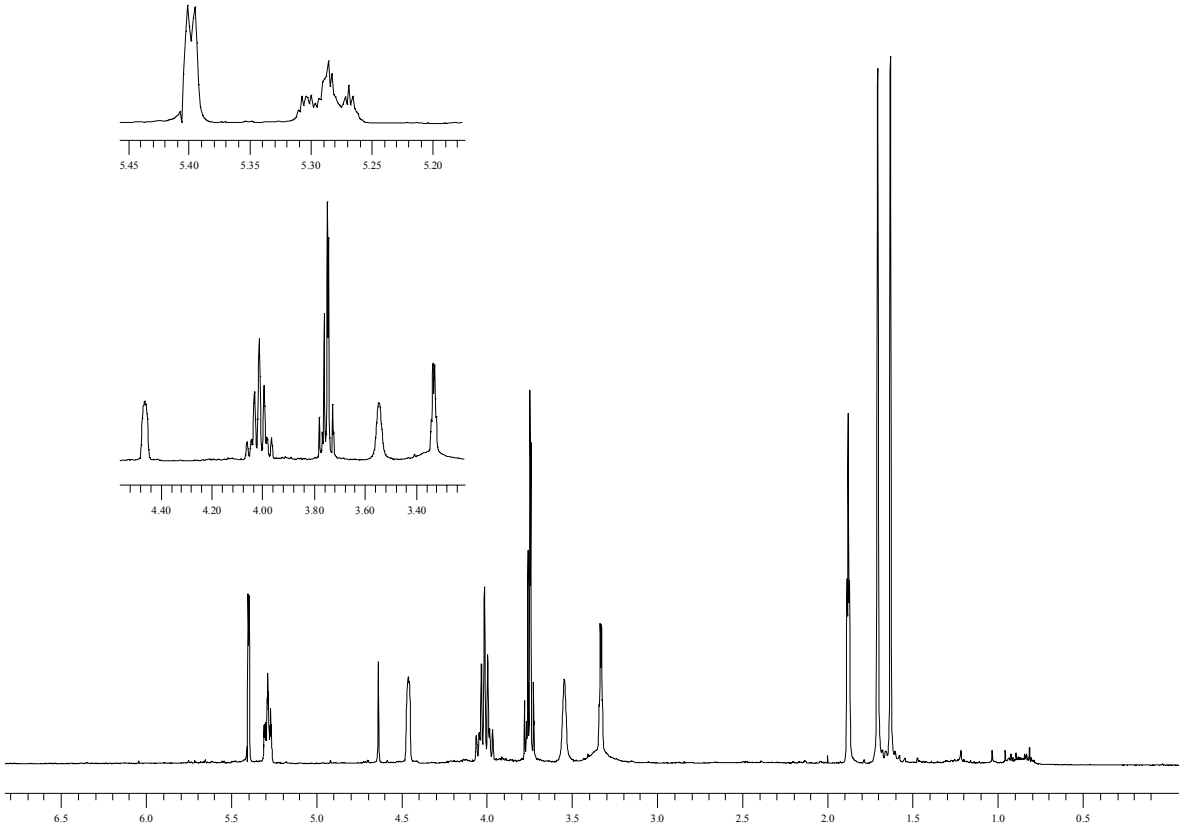
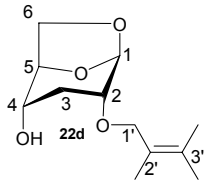


Figure S7. ^{1}H-NMR spectrum of 2-*O*-prenyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**22c**)

2-*O*-Methylprenyl-β-D-*ribo*-2,4-anhydro-3-deoxy-hexopyranose (22d).

Same procedure as for the preparation of **22c**, using 2-methylprenylalcohol instead of prenylalcohol.



Colorless oil. (80%)

$[\alpha]^{25}_{589}$ -100.5, $[\alpha]^{25}_{577}$ -106.7, $[\alpha]^{25}_{546}$ -109.0 $[\alpha]^{25}_{435}$ -107.8 $[\alpha]^{25}_{405}$ -108.2 (C = 2.0, $CHCl_3$)

IR (film): 3562, 2901, 1190, 1008, 924, 782

^{1}H NMR (400, MHz, $CDCl_3$): δ 5.40 (d 1H, ^{3}J(H-C(1),H-C(2)= 2.5, H-1), 4.50 (m, 1H, H-C(5)), 4.05 (dd, 2H, ^{2}J(Ha-C(1'),Hb-C(1')= 10.8, Ha-C(1'), Hb-C(2')), 3.77 (m, 2H,Ha-C(6), Hb-C(6)), 3.56 (m, 1H, H-4), 3.30 (m,1H, H-C(2)), 190, (m, 2H, H-C(3) and H-C(3´)), 1.70-1.63 (m, 9H, C(2')-C$\underline{H}_3$, C(2')-(C$\underline{H}_3$)$_2$)

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 130.7 (s, C3'), 125.0 (s, C(2')), 100.5 (d, ^1J(C,H)= 175, C-(1)), 77.4 (d, ^1J(C;H)= 150 C-(5)), 72.8 (1t, ^1J(C,H)= 150, C-(4)), 69.9, (t, ^1J(C,H)= 125 C-(6)), 67.0 (d, ^1J(C;H)= 150, C(2)), 65.4 (t, ^1J(C;H)= 133, C-(1')), 27.6 (1 t, ^1J(C,H) 130, C-(3)), 20.8, 20.1 16.6 (3 q, ^1J(C,H)= 125, ($\underline{C}H_3)_2C$(3'))

MS (CI, NH_3): 232 ([M+18], 5), 214 ([M], 5), 234 (7), 145 (65), 99 (63), 83 (100)

HMRS (MALDI): calcd. for $C_{12}H_{20}O_4Na$: 251.1259, [M+Na^+] found: 251.1248

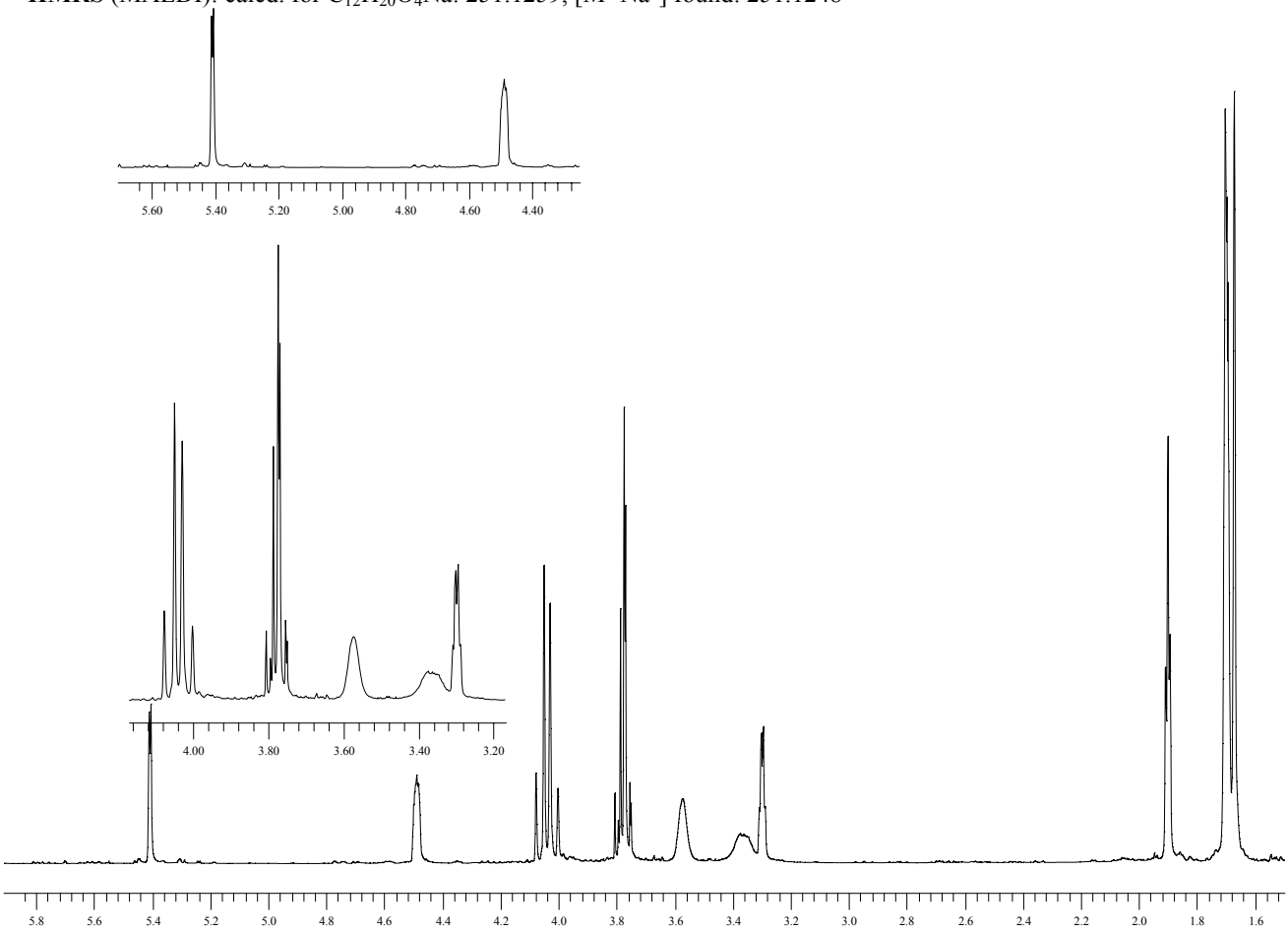


Figure S8. ^{1}H-NMR spectrum of 2-*O*-methylprenyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**22d**)

4-*O*-Methallyl-2-*O*-(2-methylprenyl)-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (26d)

To a solution of **22d** (150 mg, 0.6 mmol) in THF at 0 °C was added NaH (40 mg, 1 mmol) and stirred at this temperature for 1h. Afterwards methallyl bromide (0.2 mL, 0.8 mmol) was added and the reaction mixture was allowed to warm to r.t.. The reaction mixture was then heated under reflux until the reaction was completed, quenched by water and extracted with $CHCl_2$, dried and concentrated. The crude was purified by column chromatography (silica PE:EtOAc 1:4) to obtain **26d** in 68% (130 mg, 0.6 mmol)

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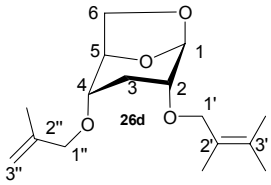

Colorless oil. (quantitative)

$[\alpha]^{25}_{589}$ -56.9, $[\alpha]^{25}_{577}$ -65.7, $[\alpha]^{25}_{546}$ -85.0 $[\alpha]^{25}_{435}$ -89.7 $[\alpha]^{25}_{405}$ -86.3 (C = 2.0, $CHCl_3$)

IR (film): 2925, 2811, 1453, 1376, 1106, 906, 705

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.46 (s, 1H,H-C(1)), 4.99, 4.91(2 d, 1H ^3J(H-C(1´)-H-C(2´))= 6.8, H-C(2´)), 4.61 (d, 1H, ^3J(H-C-(5)-Ha-C(6)) = 5.6, H-C(5)), 4.01 (m, 2H, Ha-C(2´),Hb-C(2´)), 3.75 (m, 1H, Ha-C(6)), 3.73 (dd,1H, ^2J(Ha-C(6),Hb-C(6))= 8.4, Hb-6), 3.28 (m, 2 H, H-C(2) and H-C(4)), 1.87 (s, 2H, Ha-(3) and Hb-(3)), 1.70, 1.63 (2 s, 6H, C(3')-($C\underline{H}_3$)$_2$, C(3'')-$C\underline{H}_3$))

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.2 (s, C-(2'')), 129.8 (s, C-(2')), 121.5 (s, C-(3')), 112.3 (t, ^1J(C,H)= 135, C(3'')), 101.2 (d, ^1J(C,H)= 175, C-(1)), 74.4 (d, ^1J(C;H)= 150 C(5)), 72.5 (t, ^1J(C,H)= 150, C-(6)), 71.9, 70.9,(2d, ^1J(C;H)= 150, C-(2), C-(4)), 69.4 (t, ^1J(C;H)= 133, C(-1')), 65.4 (t, ^1J(C;H)= 133, C-1''), 24.7 (t, ^1J(C,H) 130, C-(3)), 24.2, 19.7, 18.4 (3 q, ^1J(C,H)= 125, $\underline{C}H_3C(2'')$,($\underline{C}H_3$)$_2$C(3'))

MS (CI, NH_3): 300 ([M+18], 2), 282 ([M], 2), 239 (7), 134 (55), 98 (61), 83 (100)

HMRS (MALDI): calcd. for $C_{12}H_{26}KO_4$: 305.1729, [M+K$^+$] found: 305.1734

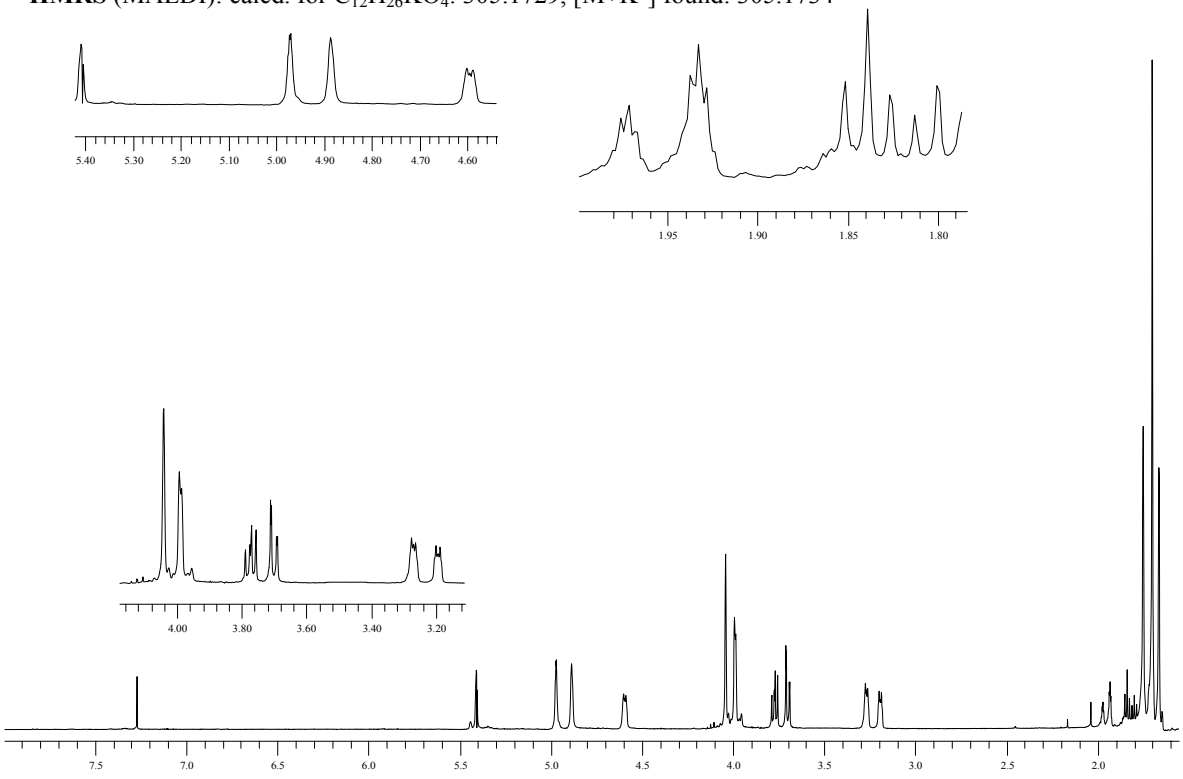

Figure S9. ^{1}H-NMR spectrum of 4-*O*-methallyl-2-*O*-(2-methylprenyl)-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**26d**)

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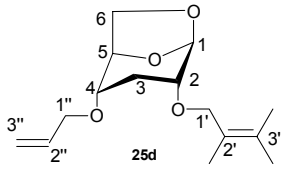
4-*O*-Allyl-2-*O*-(2-methylprenyl)-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (25d)

Same procedure as for the preparation of **26d**, using allyl bromide instead of methallyl bromide.



Colorless oil. (78%)

$[\alpha]^{25}_{589}$ -75.7, $[\alpha]^{25}_{577}$ -65.8, $[\alpha]^{25}_{546}$ -78.0 $[\alpha]^{25}_{435}$ -107.7 $[\alpha]^{25}_{405}$ -76.2 (C = 2.9, $CHCl_3$)

IR (film): 2925, 2904, 1455, 1376, 1120, 906, 786

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (m, 1H, H-C(2'')), 5.41 (s, 1H,H-C(1)), 5.39, (m, 2H, Ha-C(3''), Hb-C(3'')), 4.61 (d, 1H, ^2J(H-C(4), H-C(5)) = 2.4, H-C(5)), 4.04 (m, 2H, Ha-C(1''), Hb-C(1'')), 3.99 (m, 2H, Ha-C(1'), Hb-C(1')) 3.76 (dd, 1H, ^2J(Ha-C(6),Hb-C(6))= 4.8), Ha-C(6)) 3.70 (d, 1H, Hb-C(6), 3.34 (d, 1H,H-C(4)), 3.18 (d, 1H ^2J(H-C(1),H-C(2)= 2.4), H-C(2)), 1.93, 1.82 (2m, ^2J(Ha-C(3),Hb-C(3))= 8.8, Ha-C(3), Hb-C(3)), 172, 1.70, 1.66 (m, 9H, C$\underline{H}_3$C(3'),C$\underline{H}_3$C(2''))

^{13}C NMR (100.6 MHz$CDCl_3$): δ 135.2 (d, ^1J(C,H)= 155, C-(2'')), 129.8 (s, C-(2')), 121.9 (s, C-(3')), 121.5 (t, ^1J(C,H)= 150,C-(3'')), 101.2 (d, ^1J(C,H)= 175, C-(1)), 74.4 (d, ^1J(C;H)= 150, C(5)), 72.5, (d, ^1J(C,H)= 155, C-(4)), 71,9 (d, ^1J(C,H)= 150, C-(2)), 70.9 (t, ^1J(C,H)= 140, C-(6)), 65.6, 65.4 (2t, ^1J(C;H)= 145, C-(1'), C-(1'')), 29.7 (t, ^1J(C,H)= 130, C-(3)), 24.7, 20.8, 16.5 (3 q, ^1J(C,H)= 125, $\underline{C}H_3$C(2''), ($\underline{C}H_3)_2$C(3'))

MS: (CI, NH_3) 286, ([M+18], 8) 278 ([M], 6), 244 (8), 155 (75), 99 (83), 83 (100)

HRMS (MALDI): calcd. for: $C_{15}H_{24}NaO_4$: 291.1572 [M+Na^+], found: 291.1512

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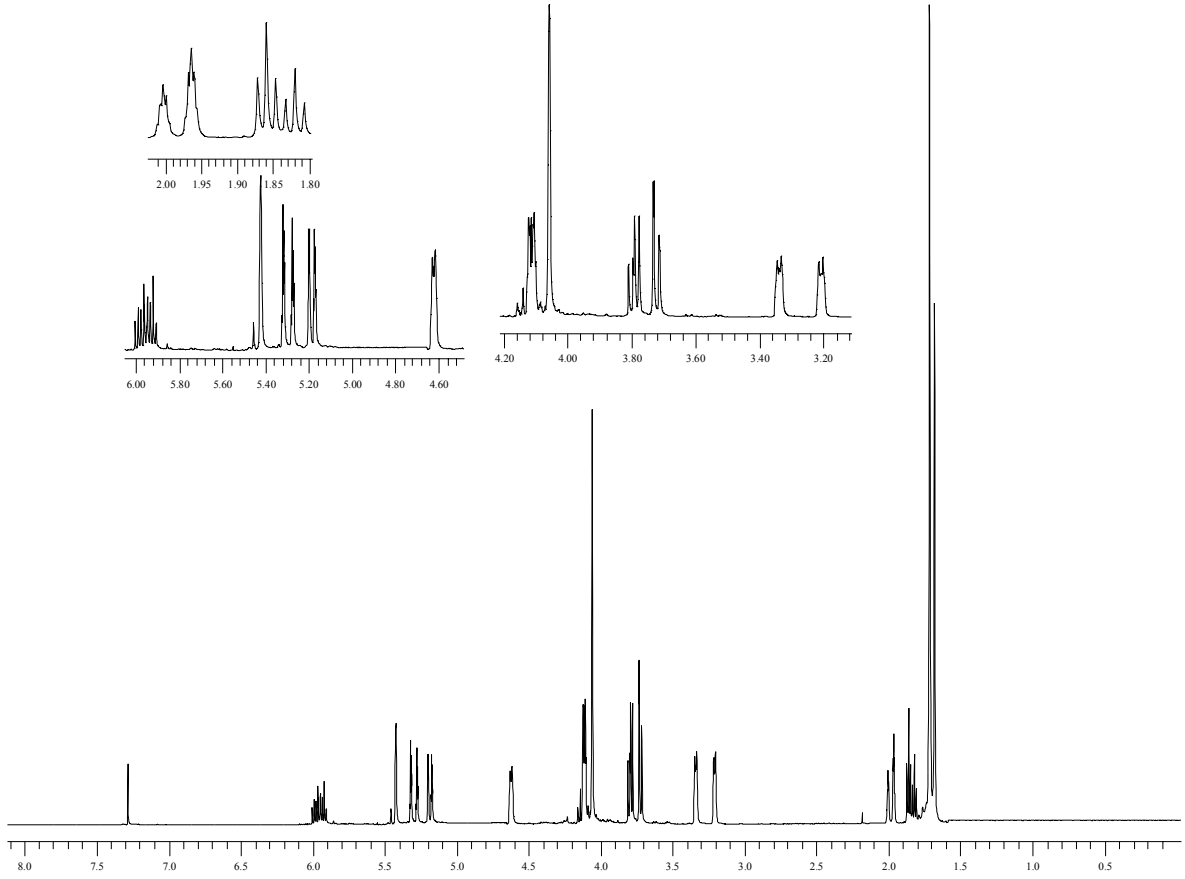
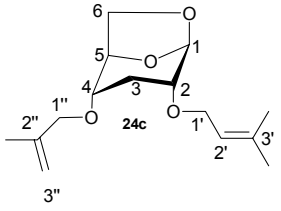


Figure S10. ^{1}H-NMR spectrum of 4-*O*-alyll-2-*O*-(2-methylprenyl)-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**25d**)

4-*O*-Methallyl-2-*O*-prenyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (24c)

Same as for the preparation of **22d**, using **22c** (150 mg, 0.6 mmol) and methallyl bromide (0.2 mL, 0.8 mmol).



Colorless oil. (68%)

$[\alpha]^{25}_{589}$ -100.9, $[\alpha]^{25}_{577}$ -106.5, $[\alpha]^{25}_{546}$ -108.0 $[\alpha]^{25}_{435}$ -150.6 $[\alpha]^{25}_{405}$ -187.2 (C = 3.5, $CHCl_3$)

IR (film): 2925, 1881, 1771, 1455, 1376, 1206, 906

^{1}H NMR (400MHz, $CDCl_3$): δ 5.58 (s, 1H,H-C(1)) 5.48 (m, 1H, H-C(2´)), 5.11, 4.99 (2 s, 2 H, Ha-C(3'') and Hb-C(3'')) 4.74 (m, 1H, H-C(5)), 4.21 (m, 2H, Ha-C(1'') and Hb-C(1'')), 4.13 (m, 2H, Ha-C(1') and Hb-C(1')), 3.90 (m, 1H, ^2J(Ha-C(6), Hb-C(6))= 8.4, Ha-C(6)), 3.86 (d,1H, Hb-(6)), 3.40 (m, 2H, H-(4) and H-(2)), 2.10, 1.99 (2m, 2H, Ha-(3) and Hb-(3)), 1.89, 1.86, 170 (3 s, 9H, C$\underline{H}_3$C(2''),(C$\underline{H}_3$)$_2$C(3'))

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.7 (s, C-(2'')), 122.9 (s, C-(3'')), 121.9 (d, ^1J(C,H) 150,C-(2'), 112.8 (t, ^1J(C,H)= 135, C-(3'')), 101.4 (d, ^1J(C,H)= 175, C-(1)), 74.9 (d, ^1J(C;H)= 150, C-(5)), 72.9, 72.3, 72.1, (2d, 1t, ^1J(C,H)= 150 C-(2), C-(4), C-(6)) 66.1 (t, ^1J(C;H)= 133, C-(1')), 65.9 (t, ^1J(C;H)= 133, C-(1'')), 26.1 (t, ^1J(C,H) 130, C-(3)), 25.2, 19.7, 18.4 (3 q ^1J(C,H)= 125, $\underline{C}$H$_3$C(2''),($\underline{C}$H$_3$)$_2$C(3'))

MS (CI, NH_3): 286 ([M+18], 10), 273 ([M],15), 235 (10), 155 (65), 100 (65), 83 (100)

HRMS (MALDI): calcd. for $C_{15}H_{24}NaO_4$: 291.1572, [M+Na$^+$] found: 291.1512

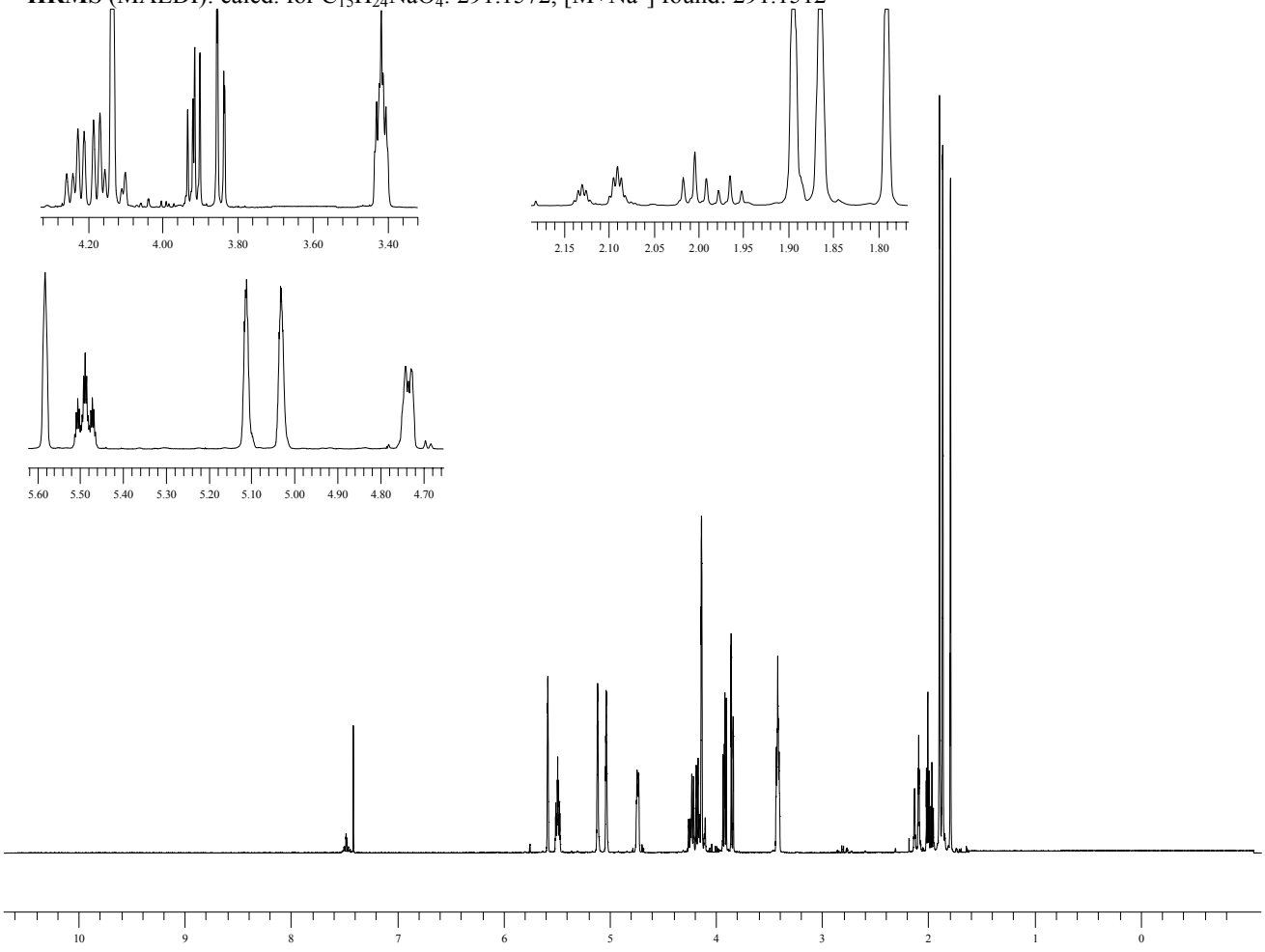
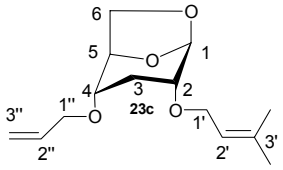


Figure S11. ^{1}H-NMR spectrum of 4-*O*-methallyl-2-*O*-prenyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**24c**)

4-*O*-Allyl-2-*O*-prenyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (23c)

Same procedure as the preparation of **26d**, using **22c** and allyl bromide.



Colorless oil. (quantitative).

$[\alpha]^{25}_{589}$ -105.8, $[\alpha]^{25}_{577}$ -110.7, $[\alpha]^{25}_{546}$ -108.0 $[\alpha]^{25}_{435}$ -170.1 $[\alpha]^{25}_{405}$ -190.2 (C = 3.0, $CHCl_3$)

IR (film): 2915, 2899, 1455, 1376, 1206, 906

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.11 (m, 1H, H-C(2'')), 5.58 (s, 1H, H-C(1)), 5.54 (m, 1H, H-C(2')), 5.50 (m, 2H, Ha-C(3'') and Hb-C(3'')) 4.75 (m, 1H, H-C(5)) 4.24 (m, 2H, Ha-C(1'') and Hb-C(1'')) 4.22 (m, 2H, Ha-C(2') and Hb-C(2')), 3.93 (dd, 1H, ^2J(Ha-C(6), Hb-C(6))= 0 8, Ha-C(6)), 3.86, (d, 1H, Hb-C(6)), 3.47(m, 1H, H-C(4)), 3.41(m, 1H, H-C(2)), 2.11, 2.00 (m, 2H, Ha-(3) and Hb-(3)), 1.86, 1.79 (s, 6H,$(C\underline{H}_3)_2$C(3')).

^{13}C NMR (100.6 MHz, $CDCl_3$): 135.7 (s, C-(3')), 125.0 (d, ^1J(C,H) 150, C-(2')), 123.9 (s, C-(2'')), 117.0 (t, ^1J(C,H)= 135, C-(3'')) 101.2 (d, ^1J(C,H)= 175, C-(1)), 74.4 (d, ^1J(C;H)= 150, C-(5)), 72.4 (1t, ^1J(C,H)= 150, C-(6)), 70.9, 70.5,(2d, 1t, ^1J(C,H)= 150 C-(2), C-(4), C-(6)), 69.4(t, ^1J(C;H)= 133, C-(1')), 65.4 (t, ^1J(C;H)= 133, C-(1'')), 24.5 (t, ^1J(C,H) 130, C-(3)), 20.7, 19.7(2 q ^1J(C,H)= 125, $(\underline{C}H_3)_2$C(3')).

MS (CI, NH_3): 286 ([M+18], 15) 273 ([M], 17), 188 (7), 149 (66), 100 (65), 83 (100).

HRMS (MALDI): calcd. for $C_{14}H_{22}KO_4$: 293.1155 [M+K$^+$], found: 293.1168 (M+K).

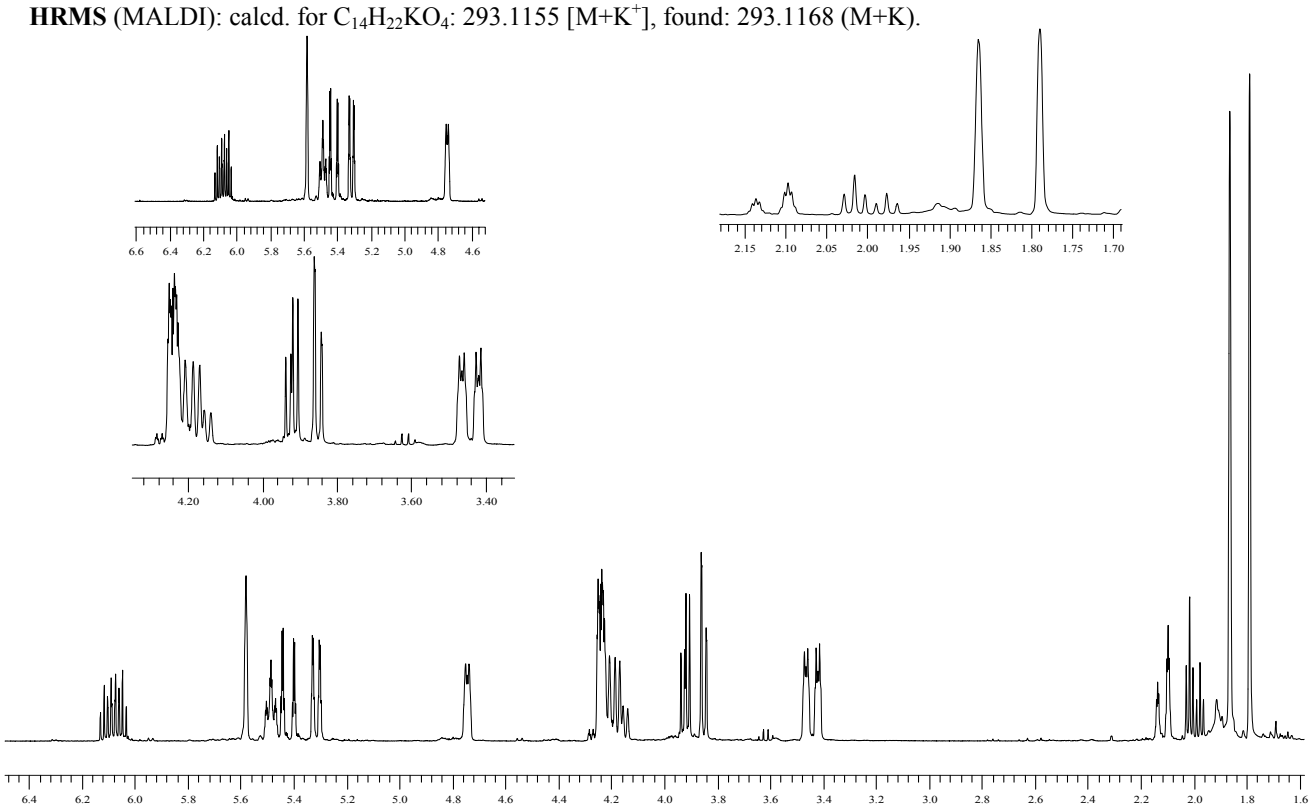


Figure S12. ^{1}H-NMR spectrum of 4-*O*-allyl-2-*O*-prenyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**23c**)

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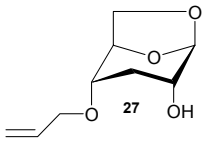
4-*O*-Allyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (27)

Same procedure as for the preparation of **18**, starting with **23c.**



Colorless oil.

Starting with **25d**: quantitative

Reference: V.A.Zubkov, R.P. Gorshkova, Y.S. Ovodov, A.S. Sviridov, , A.S. Shaskov, *Carbohydr. Res.*, **225**, 1992, 189-208.

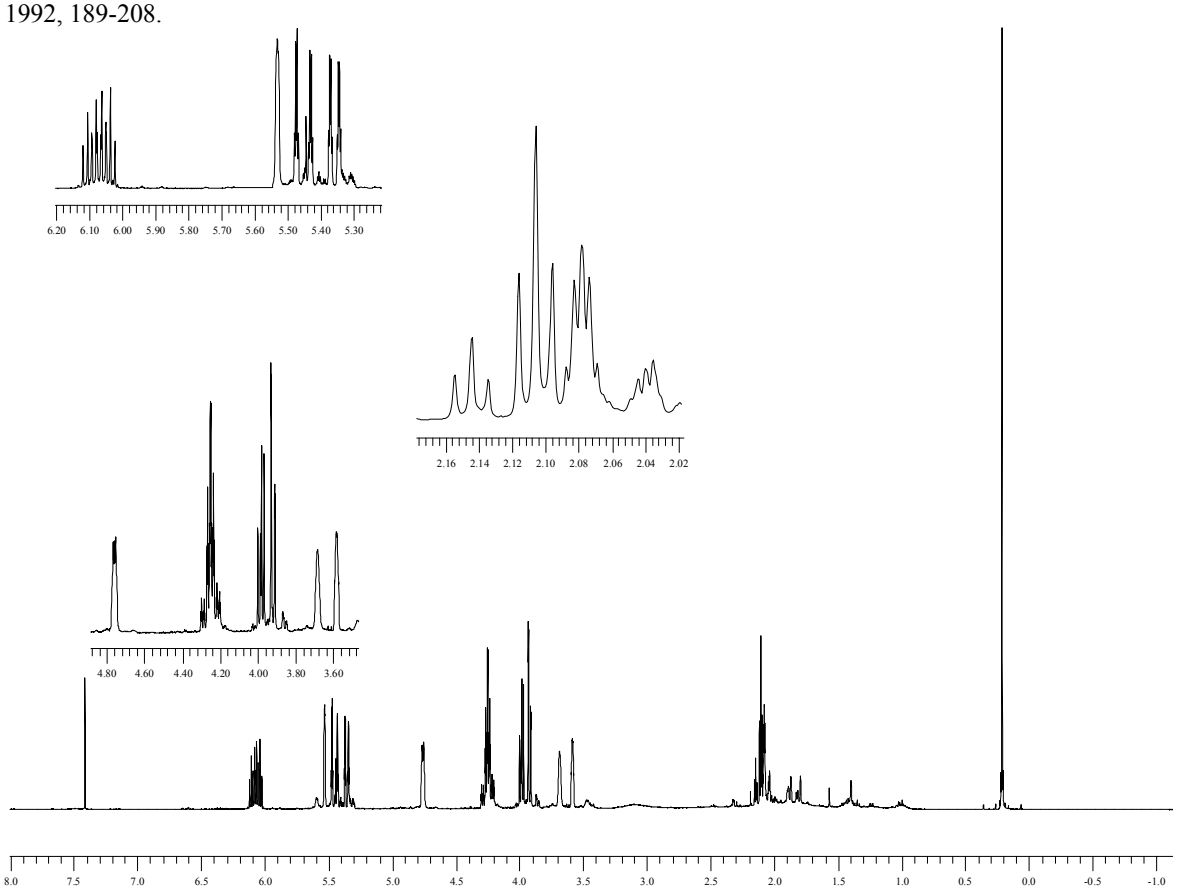


Figure S13. ^{1}H-NMR spectrum of 4-*O*-allyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**27**)

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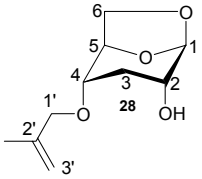
4-*O*-Methallyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (28)

Same procedure as for **18**, starting with **26d.**



Colorless oil. (quantitative)

Starting with **24c**: 78%

$[\alpha]^{25}_{589}$ -145,5, $[\alpha]^{25}_{577}$ -156.7, $[\alpha]^{25}_{546}$ -178.3 $[\alpha]^{25}_{435}$ -190.7 $[\alpha]^{25}_{405}$ -199.2 (C = 2.5, $CHCl_3$)

IR (film): 3658, 1877, 1465, 1209, 1182, 1058, 805, 765

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 (s, 1H,H-C(1)), 4.97, 4.91 (s, 2 H, Ha-C(3'') and Hb-C(3'')), 4.60 (d, 1H, ^3J(H-C(5)-H-C(6))= 5.6, H-C(5)), 4.03 (m, 2H, Ha-C(2´) and Hb-C(2')), 3.84 (m, 1H, Ha-C(6)), 3.75 (d,1H, ^2J(Ha-C(6), Hb-C(6)= 8.4, Hb-C(6)), 3.53 and 3.35 (m, 2H, H-C(4) and H-C(2)), 1.98, 1.90, (s, 2H, Ha-C(3) and Hb-C(3)), 1.75 (1 s, 3H, $C\underline{H}_3C(2'')$)

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.0 (s, C3''), 113.2 (t, ^1J(C,H)= 135, C(3'')), 102.9 (d, ^1J(C,H)= 175, C(1)), 77.1 (d, ^1J(C;H)= 150, C(5)), 74.5 (1t, ^1J(C,H)= 150, C-(6)), 73.8, 73.7(2d, 1t, ^1J(C,H)= 150, C-(2), C-(4), C-(6)), 67.9, (t, ^1J(C;H)= 133, C-(1')), 65.9 (t, ^1J(C;H)= 133, C-(1'')), 28.4 (1 t, ^1J(C,H) 130, C-(3)), 19.5, (1q, J(C,H)= 125, $\underline{C}H_3C(2'')$)

MS (CI,NH_3): 234 ([M+18]), 216, ([M], 5), 201 (8), 125 (55), 75 (63), 83 (100)

HRMS (MALDI): calcd. for $C_{10}H_{16}NaO_4$: 223.0946 [M+Na^+] found 223.0955

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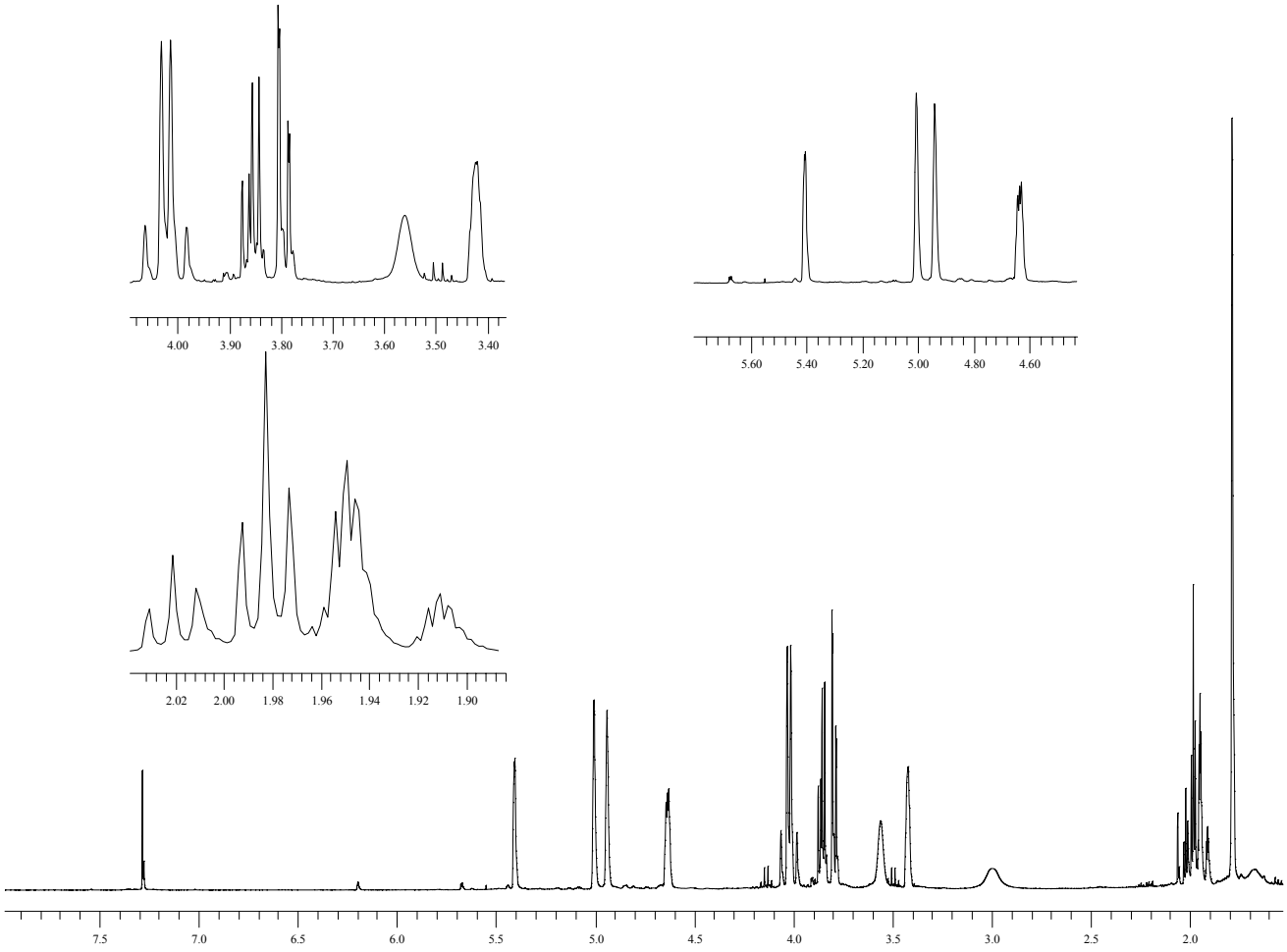
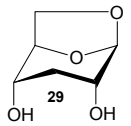


Figure S14. ^{1}H-NMR-spectrum of 4-*O*-methallyl-β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**28**)

β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (29)

Same procedure as for **18**, starting from **28.**



Colorless oil. 75%(%)

Reference: I. Cerny, M. Budesinky, T. Trnka, M, Cerny, *Carbohydr. Res*., **130**, 1984, 103-114.

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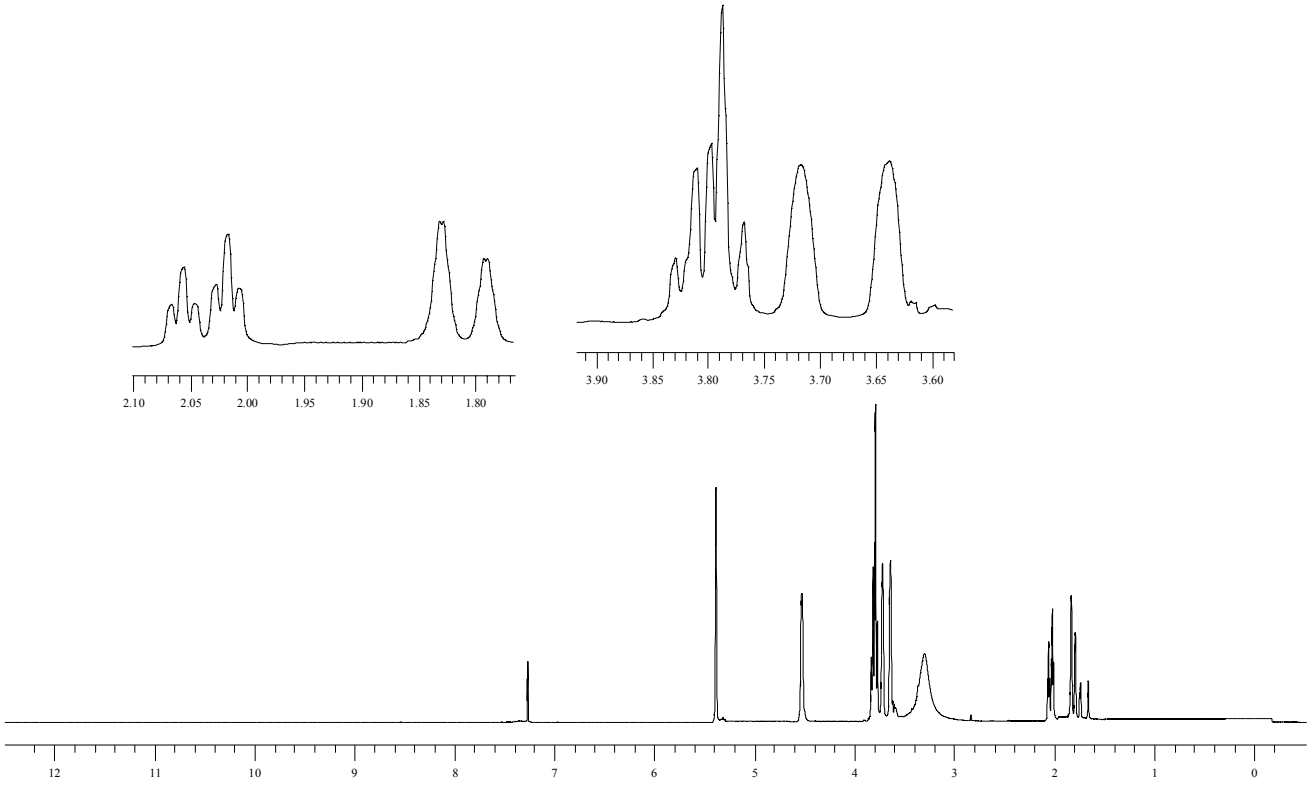
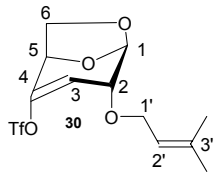


Figure S15. ^{1}H-NMR spectrum of β-D-*ribo*-2,4-anhydro-3-deoxyhexopyranose (**29**)

1,6-Anhydro-3,4-dideoxy-2-*O*-(prenyl)-4-*O*-(trifluoromethanesulfenyl)-β-D-*erythro*-hex-3-enopyranose (30/1)

n-Buli (1.6 M in hexane, 0.29 mL, 0.464 mmol) was added dropwise to a solution of $(Me_3Si)_2NH$ (0.10 mL, 0.479 mmol) in 1.5 mL of THF at 0°C. The mixture was stirred at 0°C for 15 min and cooled to –78°C. HMPA (0.080 mL) was aded followed by a solution of isolevoglucosenone **21** (78 mg, 0.236 mmol) in 1.0 mL of THF. Stirring was continued at this temperature for 2h. 2-(*N,N*-Bis(trifluoromethylsulfonyl)amino)-5-chloropyridine (157 mg, 0.40 mmol) was then added in one portion. The mixture was stirred for two hours and warmed to 20°C Water (1 mL) was added. The solution was extracted with Et_2O (5mL, 3 times). The combined organic phases were dried (anhydrous Na_2SO_4) and the solvent was removed in vacuo. The residue was purified by flash chromatography on silicagel (3:97) EtOAc/petroleum ether giving a colorless oil (58mg 85%)



Colorless oil. (85%)

$[\alpha]^{25}_{589}$ -6.8, $[\alpha]^{25}_{577}$ -6.7, $[\alpha]^{25}_{546}$ -8.0 $[\alpha]^{25}_{435}$ -17.7 $[\alpha]^{25}_{405}$ -26.2 (C = 2.9, $CHCl_3$)

IR (film): 2971, 2963, 1668, 1430, 1218, 1142, 1064, 880, 850

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (m,1H, H-C(3)), 5.60 (s, 1H, H-C(1)), 5.35 (m, 1H, H-C(3')), 4.77 (d, 1H, ^3J(H-C(5), Ha-C(6)) = 3.9, H-C(5)), 4.13 (m, 2H, Ha-C(1') and Hb-C(3')), 3.98 (d, 1H, ^2J(Ha-C(6), Hb-C(6))= 6.7, Ha-C(6)), 3.77 (m, 2H, H-C(4) and Hb-C(6)), 1.71, 1.78 (2s, 6H, $(C\underline{H}_3)_2C(3')$)

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 150.6 (s, C-(4)), 138.8 (s, C-(3')), 120.6 (d, ^1J(C,H) 150, C-(2')), 113.8 (d, ^1J(C;H)= 170, C-(3)), 100.8 (d, ^1J(C,H)= 175, C-(1)), 73.1 (d, ^1J(C,H)=150, C(5)), 71.9 (d, ^1J(C,H)=150, C-(2)), 69.3 (t, ^1J(C,H)=155, C-(6)), 66.5 (t, ^1J(C,H)=155, C-(1')), 26.1, 18.2 (2q, ^1J(C,H)= 125, $(\underline{C}H_3)_2C(3')$)

MS (CI, NH_3): 362 ([M+18],7), 344 ([M],15) 236 (9), 201 (75), 99 (62), 85 (100)

HRMS (MALDI): calcd. for $C_{12}H_{15}F_3NaO_6S$: 367.0439 [M+Na^+] found: 367.0467

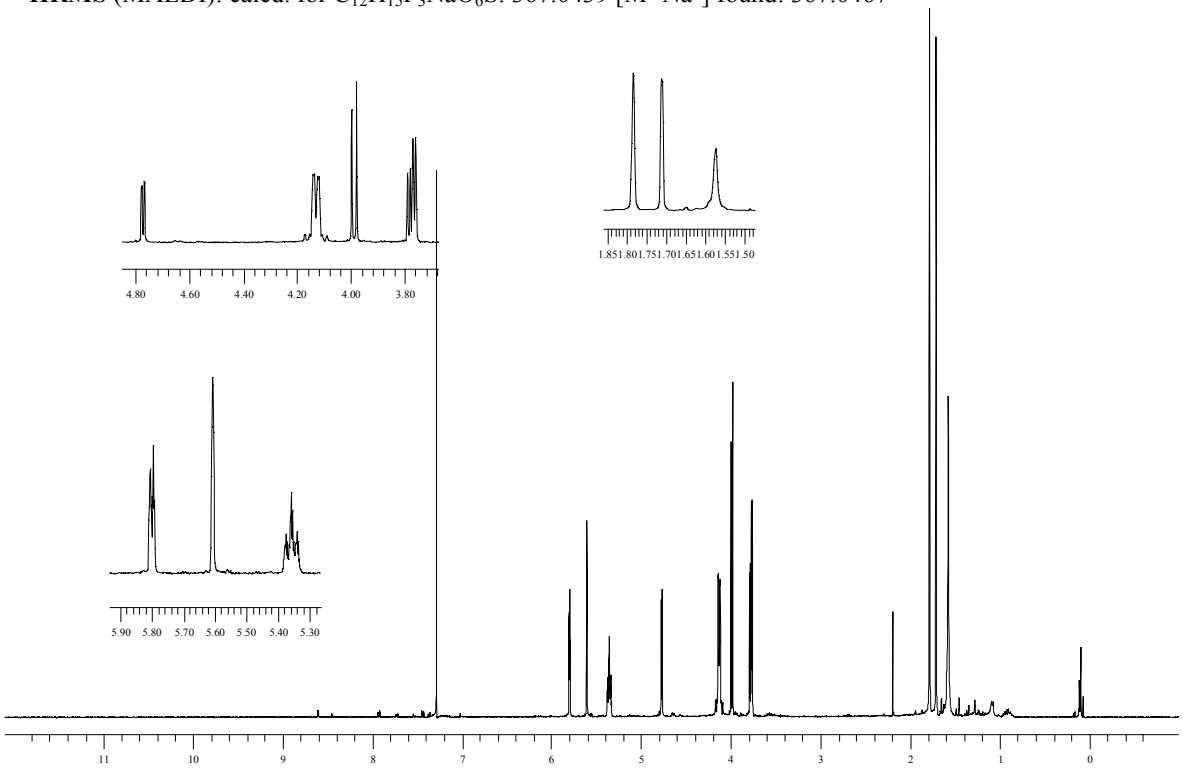


Figure S16. ^{1}H-NMR spectrum of 1,6-anhydro-3,4-dideoxy-2-*O*-(prenyl)-4-*O*-(trifluoromethanesulfenyl)-β-D-*erythro*-hex-3-enopyranose (**30**)

1,6-Anhydro-3,4-dideoxy-4-*O*-(trifluoromethanesulfenyl)-β-D-*erythro*-hex-3-enopyranose (31)

Same procedure as for the preparation of **18**, starting from (**30**/**1**)^

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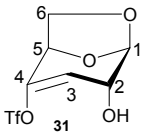

31

Colorless oil. (quantitative)

$[\alpha]^{25}_{589}$ -55.8, $[\alpha]^{25}_{577}$ -56.3, $[\alpha]^{25}_{546}$ -79.8 $[\alpha]^{25}_{435}$ -101.3 $[\alpha]^{25}_{405}$ -145.2 (C = 2.0, $CHCl_3$)

IR (film): 3664, 1765, 1355, 1119, 1082, 1043, 791, 749

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (m,1H, H-C(3)), 5.54 (s, 1H, H-C(1)), 4.75 (d, 1H, ^3J(H-C(5), Hb-C(6))= 4.3, H-C(5)), 3.99 (m, 1H, H-C(4) and Ha-C(6)), 3.78 (dd, 1H, Hb-C(6))

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 117 (d, ^1J(C;H)= 165, C-(3)), 101.9 (d, ^1J(C,H)=175), C-(1)), 71.8 (d, ^1J(C,H)=150, C-(5)), 68.9 (t, ^1J(C,H)= 150 C-(6)), 67.0 (d, ^1J(C,H)= 150, C-(2))

MS (CI, NH_3): 293 (M+18,7), 275 (M,15) 255 (10), 175 (75), 97 (77), 81 (100)

HRMS (MALDI): calcd. for $C_7H_7KO_6S$: 314.9552 [M+K^+], found 314.9541.

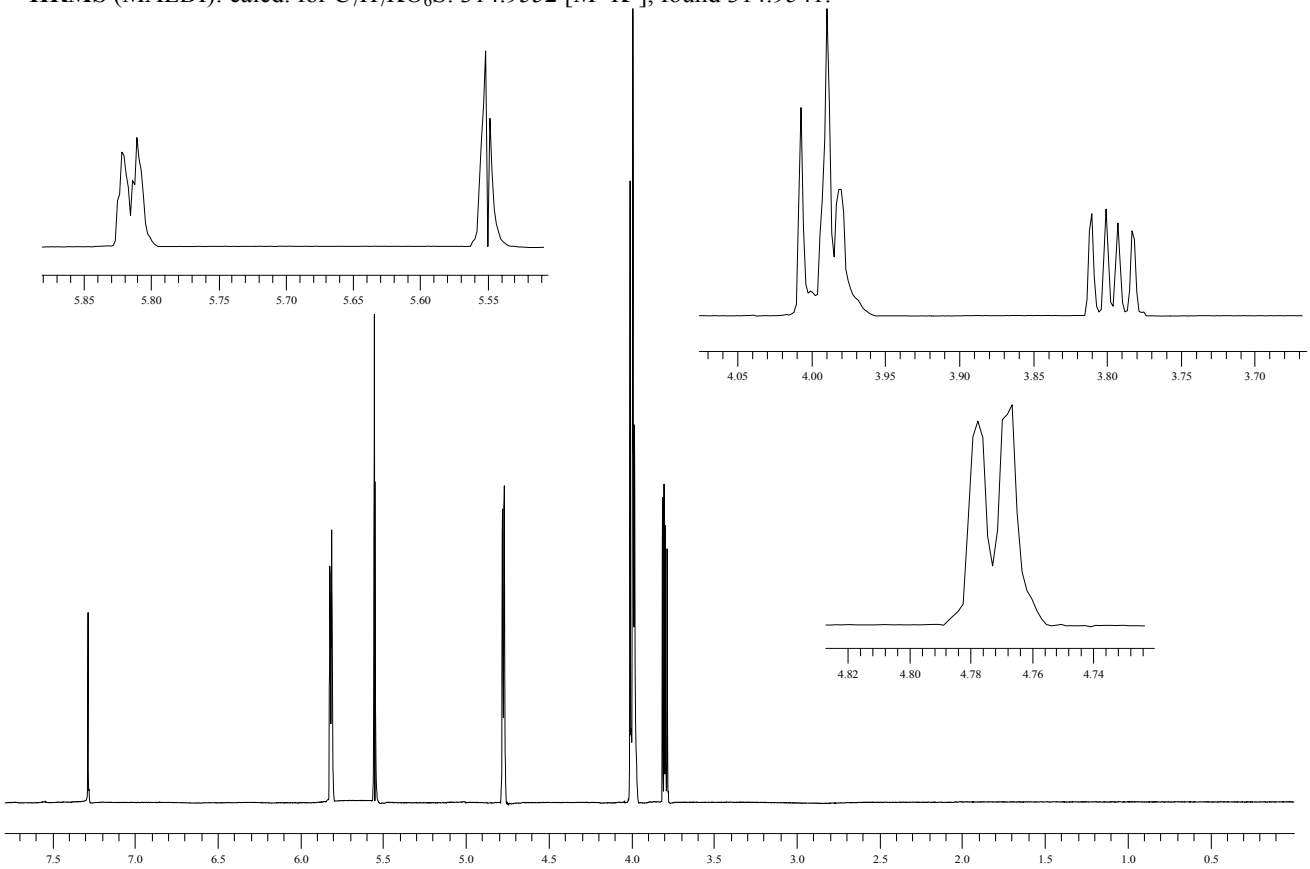

Figure S17. ^{1}H-NMR spectrum of 1,6-anhydro-3,4-dideoxy-4-*O*-(trifluoromethanesulfenyl)-β-D-*erythro*-hex-3-enopyranose (**31**)