Supporting Information for

Skeletal Rearrangements Resulting from Reactions of 1,6:2,3- and 1,6:3,4-Dianhydro-β-D-hexopyranoses with Diethylaminosulfur Trifluoride

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Experimental Procedures for the Synthesis of Compounds 8, 11, 12, 31, 36 and 37

1,6:2,3-Dianhydro-β-D-talopyranose (8)

To a solution of 1,6:2,3-dianhydro-β-D-mannopyranose (**3**, 837 mg, 5.813 mmol) in anhydrous dichloromethane (10 mL) and anhydrous pyridine (2 mL) triflic anhydride (1.3 mmol, 7.73 mmol) was added under cooling (–35 °C) and stirring. The temperature was allowed to rise to 0 °C within 2 h and the reaction mixture was poured onto ice and extracted into dichloromethane. The dichloromethane solution was dried and concentrated to afford 1.545 g (96 %) of the crude crystalline triflate **7** which was without further purification dissolved in dry dimethylformamide (10 mL) and tetrabutylammonium nitrite (3.5 g, 12.1 mmol) was immediately added. The solution was stirred at 70 °C for 12 h, then concentrated to about one half its volume and chromatographed in S1 to afford **8** (2.0 g) containing DMF and **7**. Second chromatography in S1 gave first unreacted **7** (39 mg, 2 %), further elution afforded pure **8** (594 mg, 71 %), mp 123–124 °C, $[\alpha]^{25}_{D}$ –82 (*c* 0.25 in H_2O); ref. [1] gives mp 132 °C, $[\alpha]^{25}_{D}$ –88 (in H_2O); NMR spectra were in accord with the published data,[2] found: C, 49.7; H, 5.6. Calc. for $C_6H_8O_4$: C, 50.0; H, 5.6%.

1,6:3,4-Dianhydro-β-D-allopyranose (11)

To a solution of 1,6:3,4-dianhydro-β-D-altropyranose (**9**, 600 mg, 4.14 mmol) in anhydrous dichloromethane (8 mL) and anhydrous pyridine (1.7 mL) triflic anhydride (0,95 mL, 5.65 mmol) was added under cooling (–35

°C) and stirring. The temperature was allowed to rise to 0 °C within 2 h and the reaction mixture was poured onto ice and extracted into dichloromethane. The dichloromethane solution was dried and concentrated to afford crude crystalline triflate **10 (**959 mg, 83 %). Crude **10** (800 mg, 2.90 mmol) was without further purification dissolved in dry dimethylformamide (7 mL) and tetrabutylammonium nitrite (1.8 g, 6.2 mmol) was immediately added. The solution was stirred at rt for 3 days, then concentrated to about one half its volume and chromatographed in S1 to afford **11** (0.74 g) contaminated with DMF. Second chromatography in S1 afforded **11** (313 mg, 52 %), mp 102–104 °C; $[\alpha]^{25}_{D}$ –120 (*c* 0.17 in $CHCl_3$) ref.[1] gives mp 102–103 °C, $[\alpha]^{25}_{D}$ –134 (in H_2O); NMR spectra were in accord with the published data,[2] found: C, 49.7; H, 5.5. Calc. for $C_6H_8O_4$: C, 50.0; H, 5.6%.

1,6:2,3-Dianhydro-β-D-allopyranose (12)

To a solution of 1,6:2,3-dianhydro-β-D-gulopyranose (**4**, 478 mg, 3.32 mmol) in anhydrous dichloromethane (6 mL) and anhydrous pyridine (1.5 mL) triflic anhydride (0,75 mL, 4.46 mmol) was added under cooling (-35 °C) and stirring. The temperature was allowed to rise to 0 °C within 2 h and the reaction mixture was poured onto ice and extracted into dichloromethane. The dichloromethane solution was dried and concentrated to afford crude crystalline triflate **5** (911 mg, 99 %) which was without further purification dissolved in dry dimethylformamide (3 mL) and tetrabutylammonium nitrite (1.4 g, 4.8 mmol) was immediately added. The solution was stirred at rt for 3 days, then concentrated to about one half its volume and chromatographed in S1 to afford **12** (275 mg, 58 %), mp 93.5–99 °C; $[\alpha]^{25}_{D}$ +58 (*c* 0.34 in H_2O) ref.[1] gives mp 94–96 °C, $[\alpha]^{25}_{D}$ +55 (in H_2O); NMR spectra were in accord with the published data,[2] found: C, 50.2; H, 5.7. Calc. for $C_6H_8O_4$: C, 50.0; H, 5.6%.

1,6-Anhydro-3-azido-4-*O*-benzyl-3-deoxy-β-D-galactopyranose (31)

Dianhydro derivative **30**[3] (330 mg, 1.41 mmol), lithium azide (380 mg, 7.76 mmol) and dimethylformamide (3 mL) were stirred at 110 °C under argon for 30 h. TLC in S2 showed that most of the starting **30** had been consumed. The dark brown reaction mixture was diluted with water and extracted with dichloromethane. The dichloromethane solution was washed with brine, dried and concentrated. Chromatography of the residue afforded first dianhydro derivative **30** (52 mg, 16 %). Further elution afforded **31** (280 mg, 74 %) as colorless sirup, $[\alpha]^{25}_{D}$ –17 (*c* 0.6 in $CHCl_3$), ref. [3] gives $[\alpha]^{25}_{D}$ –22 (*c* 0.5 in $CHCl_3$), NMR spectra were in accord with the published data,[3] found: C, 56.1; H, 5.4.; Calc. for $C_{13}H_{15}O_4N_3$: C, 56.3; H, 5.4 %.

1,6-Anhydro-3-azido-2-*O*-benzyl-3-deoxy-4-*O*-tosyl-β-D-mannopyranose (36)

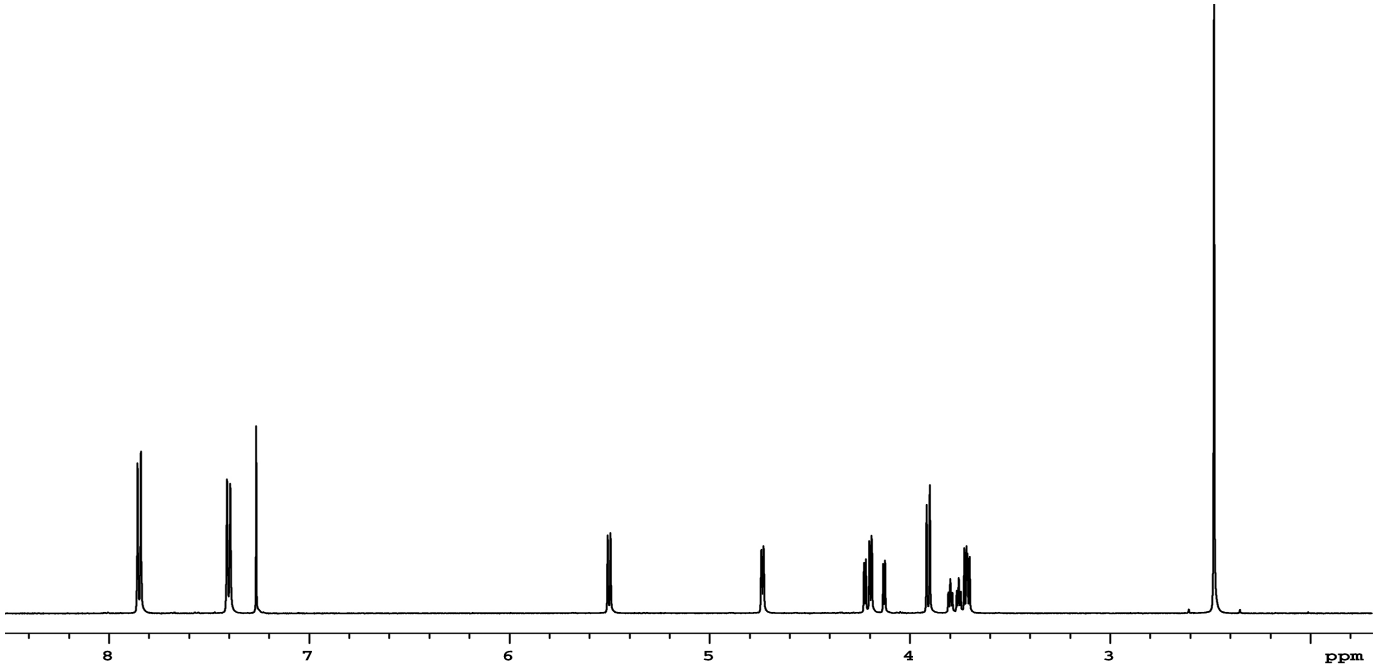
Dianhydro derivative **34**[3] (650 mg, 2.77 mmol), lithium azide (780 mg, 15.92 mmol) and dimethylformamide (8

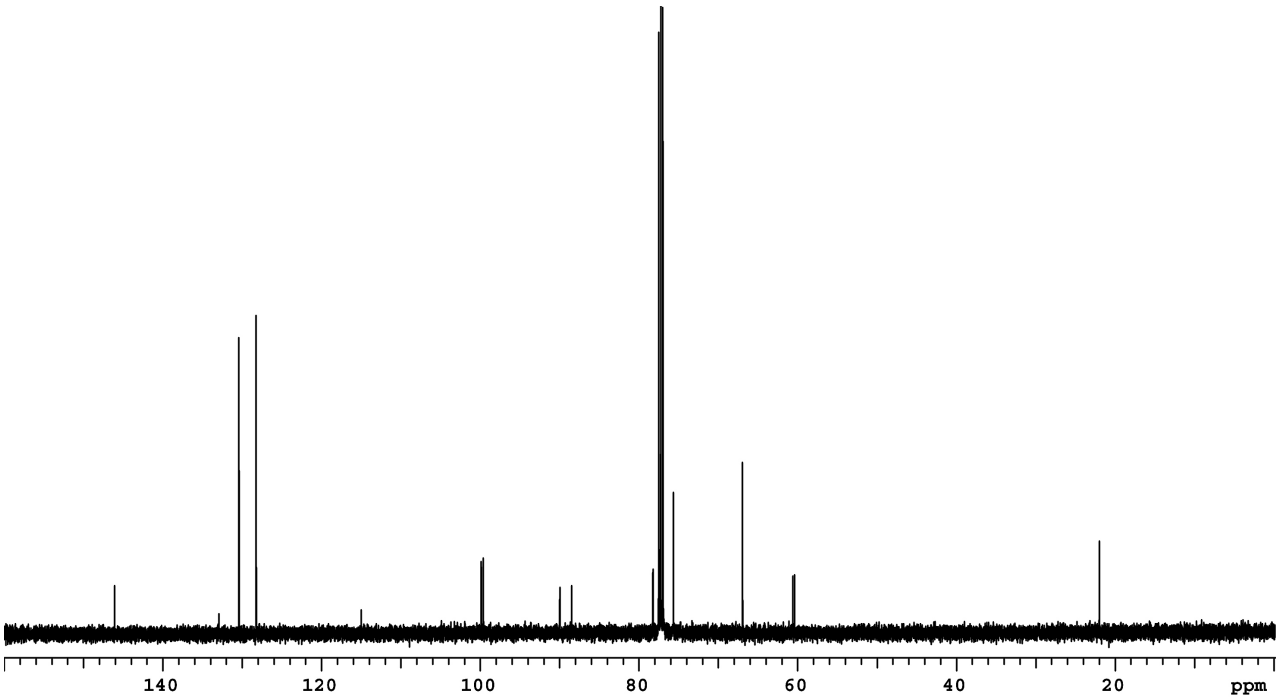
mL) were stirred at 110 °C under argon for 30 h. TLC in S2 showed that most of the starting **34** had been consumed. The dark brown reaction mixture was diluted with water and extracted with dichloromethane. The dichloromethane solution was washed with brine, dried and concentrated. Chromatography of the residue afforded first dianhydro derivative **34** (35 mg, 5 %). Further elution afforded **35** (701 mg, 91 %) as colorless sirup which was without further purification dissolved in anhydrous pyridine and tosyl chloride (2.0 g, 10.5 mmol) was added. After standing at rt for 48 h was the reaction mixture poured onto ice, extracted into dichloromethane, dried, concentrated and the residue was codistilled three times with toleuene to afford **36** (1.048 g, 88 %), mp 78–80 °C, ref.[3] gives mp 79–81 °C, NMR spectra were in accord with the published data,[3] found: C, 55.8; H, 5.0.; N, 9.4. Calc. for $C_{20}H_{21}O_6N_3S$: C, 55.7; H, 5.0; N, 9.7 %

1,6-Anhydro-3-azido-3-deoxy-4-*O*-tosyl-β-D-mannopyranose (37)

A solution of $KBrO_3$ (460 mg, 2.75 mmol) in ethyl acetate (10.5 mL) was added to a solution of **36** (424 mg, 0.98 mmol) in ethyl acetate (10.5 mL). Then a solution of $Na_2S_2O_4$ (407 mg, 2.34 mmol) in water (7.5 mmol) was added under vigorous stirring. The stirring continued for 5 h until the starting compound **36** was consumed (TLC in S2, **37** gives only weakly coloured spot). The reaction mixture was extracted in dichloromethane, dried and concentrated. The crystalline residue was chromatographed in S3 to afford **37** with traces of benzoic acid. The product was dissolved in ethyl acetate and washed with aqueous K_2CO_3 and brine, dried and concentrated to afford pure **37** (220 mg, 66 %), mp 160–162 °C, $[\alpha]^{25}_D$ –85 (*c* 0.29 in $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 7.85 (2 H, d, *J* 8.3, Ar-H), 7.41 (2 H, d, *J* 8.1, Ar-H), 5.33 (1 H, s, H1), 4.56 (1 H, s, H4), 4.50 (1 H, d, $J_{5,6ex}$ 6.2, H5), 4.05 (1 H, d, $J_{6en,6ex}$ 8.1, H6en), 3.83 (2 H, s, H2 and H3), 3.73 (1 H, dd, $J_{6en,6ex}$ 8.0, $J_{5,6ex}$ 5.9, H6ex), 2.48 (4 H, s, OH and CH_3); δ_C 145.87 (Ar-C), 132.88 (Ar-C), 130.30 (Ar-CH), 127.84 (Ar-CH), 100.98 (C1), 77.60 (C4), 74.05 (C5), 66.17 (C2), 64.9 (C6), 61.66 (C3), 21.71 (CH_3), found: C, 45.9; H, 4.5. Calc. for $C_{13}H_{15}O_6N_3S$: C, 45.7; H, 4.4 %.

Copies of ^{1}H and ^{13}C NMR for compound 38 (for which elemental analysis is not available)





Computational details

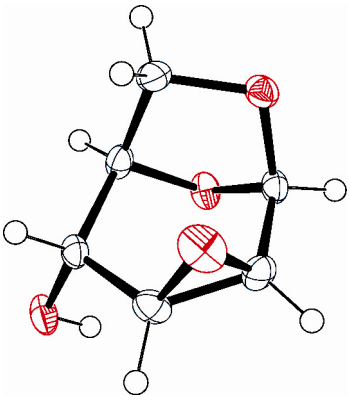
All calculations reported in this work were performed with the *Gaussian 03* program package.[4] The equilibrium geometries were optimized with the hybrid density functional B3LYP[5,6] in combination with 6-311+G(d,p) basis set. In order to include effects exerted by the solvent chloroform, the same level of theory was used in combination with the polarizable continuum model (PCM).[7] The NMR shielding tensors were calculated at a same level of theory using the same stationary points with the GIAO[8] (gauge-independent atomic orbital) method.

Crystallographic data

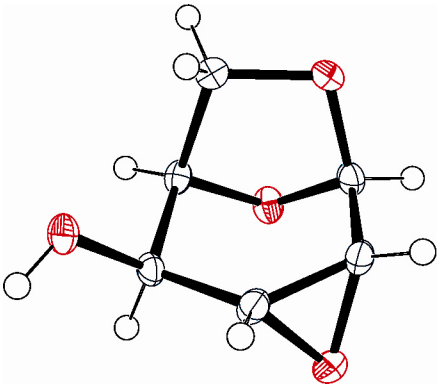
Diffraction data were collected at 150 K on a Nonius KappaCCD diffractometer (Enraf-Nonius) with the graphite monochromated Mo-Kα radiation. Cryostream Cooler (Oxford Cryosystem) was used for the low temperature measurements. The structures were solved by direct methods (SIR92[9], SHELXL97[10]) and refined by full-matrix least-squares on F^2 values (CRYSTALS[11]). All heavy atoms were refined anisotropically. Hydrogen atoms were localized from the expected geometry and difference electron density maps and were refined isotropically. ORTEP-3[12] and Accelrys DS Visualizer[13] was used for structure presentation.

The crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

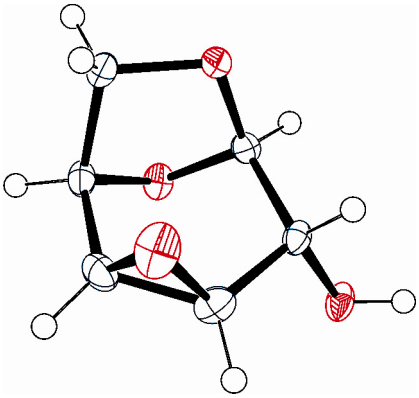
X-ray of **3**: $C_6H_8O_4$, M= 144.13 g/mol, orthorhombic system, space group $P2_12_12_1$, a=6.2773(3), b=9.4898(6), c=10.1036(6) Å, Z=4, V=601.87(6) $Å^3$, Dc=1.59 $g.cm^{-3}$, μ(Mo Kα)=0.14 mm^{-1}, T=150 K, crystal dimensions of 0.3 x 0.4 x 0.6 mm. The structure converged to the final R=0.0264 and R_w=0.0301 using 743 independent reflections (θ_{max}=27.53°). CCDC registration number 832048.



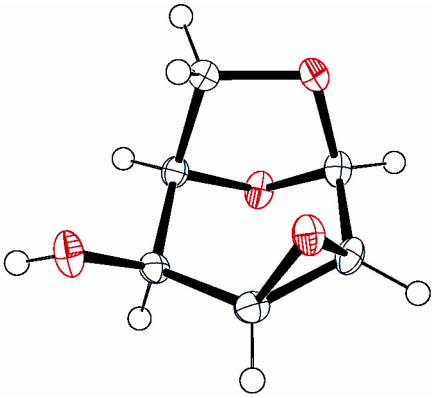
X-ray of **4**: $C_6H_8O_4$, M= 144.13 g/mol, orthorhombic system, space group $P2_12_12_1$, a=6.7114(3), b=10.2593(4), c=17.4506(7) Å, Z=4, V=1201.55(9) $Å^3$, Dc=1.59 $g.cm^{-3}$, μ(Mo Kα)=0.14 mm^{-1}, T=150 K, crystal dimensions of 0.3 x 0.4 x 0.6 mm. The assymetric part is created by two sugar molecules. The structure converged to the final R=0.0253 and R_w=0.0305 using 1383 independent reflections (θ_{max}=27.49°). CCDC registration number 832049.



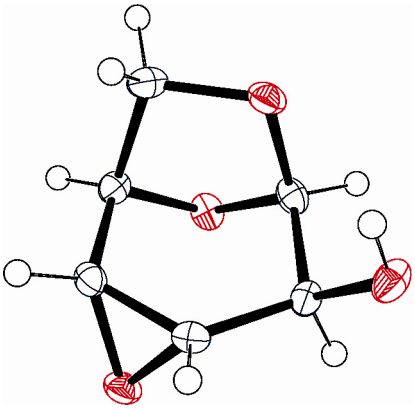
X-ray of **6**: $C_6H_8O_4$, M= 144.13 g/mol, monoclinic system, space group $P2_1$, a=5.07899(2), b=11.0036(5), c=10.9164(5) Å, β=90.128(2)°, Z=2, V=610.07(5) $Å^3$, Dc=1.57 $g.cm^{-3}$, μ(Mo Kα)=0.13 mm^{-1}, T=150 K, crystal dimensions of 0.3 x 0.4 x 0.4 mm. The assymetric part is created by two sugar molecules. The structure converged to the final R=0.0214 and R_w=0.0252 using 1346 independent reflections (θ_{max}=27.56°). CCDC registration number 832050.



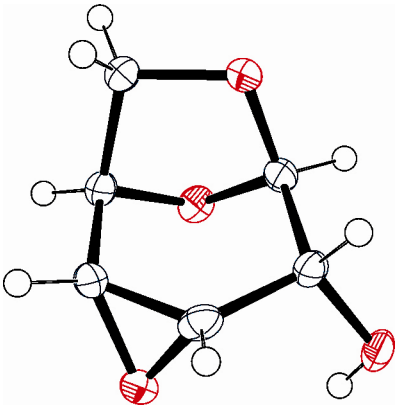
X-ray of **8**: $C_6H_8O_4$, M= 144.13 g/mol, orthorhombic system, space group $P2_12_12_1$, a=5.6736(2), b=9.5781(4), c=10.7139(4) Å, Z=4, V=582.76(4) $Å^3$, Dc=1.64 $g.cm^{-3}$, μ(Mo Kα)=0.40 mm^{-1}, T=150 K, crystal dimensions of 0.4 x 0.4 x 0.5 mm. The structure converged to the final R=0.0245 and R_w=0.0291 using 719 independent reflections (θ_{max}=27.51°). CCDC registration number 832051.



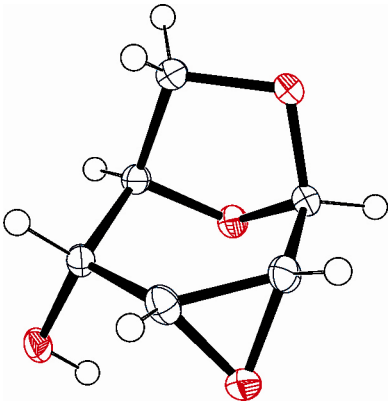
X-ray of **9**: $C_6H_8O_4$, M= 144.13 g/mol, orthorhombic system, space group $P2_12_12_1$, a=6.4573(3), b=9.4912(5), c=10.0281(7) Å, Z=4, V=614.60(5) $Å^3$, Dc=1.56 $g.cm^{-3}$, μ(Mo Kα)=0.13 mm^{-1}, T=150 K, crystal dimensions of 0.25 x 0.5 x 0.5 mm. The structure converged to the final R=0.0242 and R_w=0.0283 using 746 independent reflections (θ_{max}=27.55°). CCDC registration number 832052.



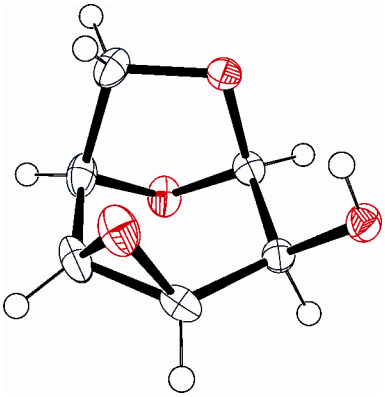
X-ray of **11**: $C_6H_8O_4$, M= 144.13 g/mol, orthorhombic system, space group $P2_12_12_1$, a=6.1219(3), b=8.5353(6), c=11.8539(8) Å, Z=4, V=619.39(7) $Å^3$, Dc=1.55 $g.cm^{-3}$, μ(Mo Kα)=0.13 mm^{-1}, T=150 K, crystal dimensions of 0.2 x 0.3 x 0.6 mm. The structure converged to the final R=0.0255 and R_w=0.0295 using 696 independent reflections (θ_{max}=27.51°). CCDC registration number 832053.



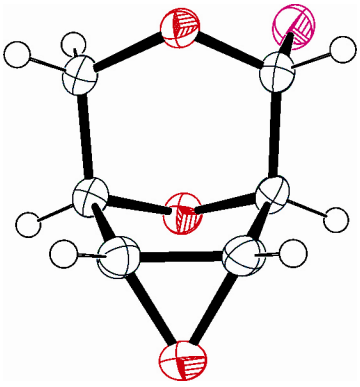
X-ray of **12**: $C_6H_8O_4$, M= 144.13 g/mol, monoclinic system, space group $P2_1$, a=6.6936 (5), b=7.0452(5), c=6.7070(5) Å, β=99.357(2)°, Z=2, V=312.08(4) $Å^3$, Dc=1.53 $g.cm^{-3}$, μ(Mo Kα)=0.13 mm^{-1}, T=150 K, crystal dimensions of 0.3 x 0.3 x 0.7 mm. The assymetric part is created by two sugar molecules. The structure converged to the final R=0.0235 and R_w=0.0268 using 692 independent reflections (θ_{max}=27.49°). CCDC registration number 832054.



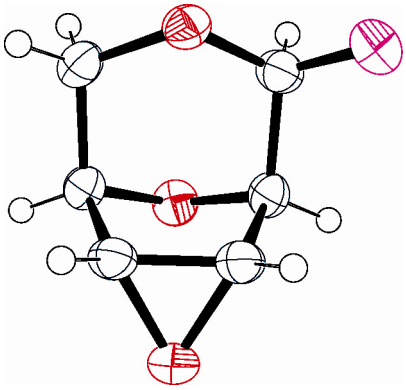
X-ray of **14**: $C_6H_8O_4$, M= 144.13 g/mol, monoclinic system, space group *P2₁*, a=6.1357(4), b=5.1847(3), c=9.4064(6) Å, β=93.064(2)°, Z=2, V=298.81(3) Å^3, Dc=1.60 g.cm^{-3}, μ(Mo Kα)=0.14 mm^{-1}, T=150 K, crystal dimensions of 0.2 x 0.2 x 0.4 mm. The structure converged to the final R=0.0242 and R_w=0.0275 using 739 independent reflections (θ_{max}=28.07°). CCDC registration number 832055.



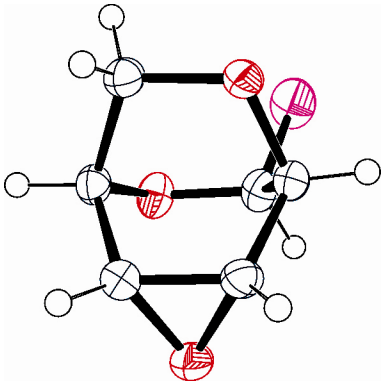
X-ray of **15**: $C_6H_7F_1O_3$, M= 146.12 g/mol, monoclinic system, space group *P2₁*, a=7.6980(2), b=8.7730(2), c=8.8850(3) Å, β=94.976(2)°, Z=2, V=597.78(3) Å^3, Dc=1.62 g.cm^{-3}, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.25 x 0.25 x 0.4 mm. The assymetric part is created by two sugar molecules. The structure converged to the final R=0.0273 and R_w=0.0308 using 1284 independent reflections (θ_{max}=27.47°). CCDC registration number 832056.



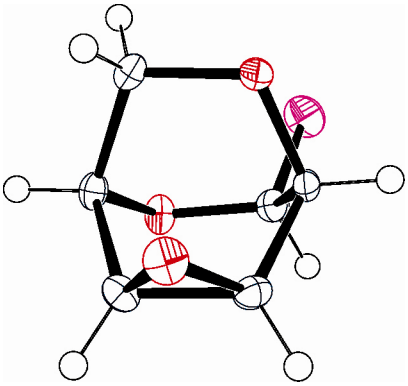
X-ray of **16**: $C_6H_7F_1O_3$, M= 146.12 g/mol, monoclinic system, space group $P2_1$, a=8.1930(3), b=7.1640(3), c=10.9410(5) Å, β=109.287(2)°, Z=2, V=606.14(4) $Å^3$, Dc=1.60 $g.cm^{-3}$, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.2 x 0.2 x 0.5 mm. The assymetric part is created by two sugar molecules. The structure converged to the final R=0.0304 and R_w=0.0345 using 1098 independent reflections (θ_{max}=27.40°). CCDC registration number 832057.



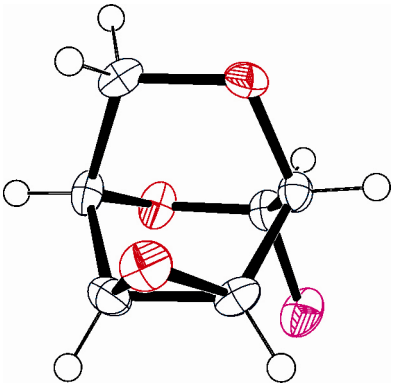
X-ray of **17**: $C_6H_7F_1O_3$, M= 146.12 g/mol, orthorhombic system, space group $P2_12_12_1$, a=6.3628(2), b=9.2072(3), c=10.1628(3) Å, Z=4, V=595.37(3) $Å^3$, Dc=1.63 $g.cm^{-3}$, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.25 x 0.3 x 0.5 mm. The structure converged to the final R=0.0295 and R_w=0.0341 using 722 independent reflections (θ_{max}=27.51°). CCDC registration number 832058.



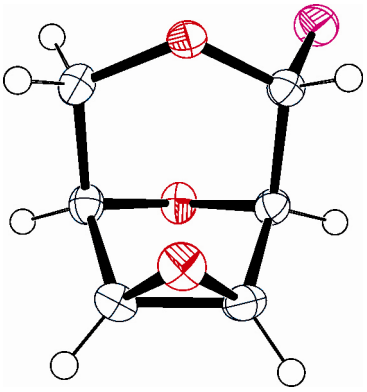
X-ray of **19**: $C_6H_7F_1O_3$, M= 146.12 g/mol, orthorhombic system, space group $P2_12_12_1$, a=5.7591(3), b=6.2197(3), c=16.2984(8) Å, Z=4, V=583.81(5) $Å^3$, Dc=1.66 $g.cm^{-3}$, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.15 x 0.18 x 0.25 mm. The structure converged to the final R=0.0271 and R_w=0.0308 using 771 independent reflections (θ_{max}=30.30°). CCDC registration number 832059.



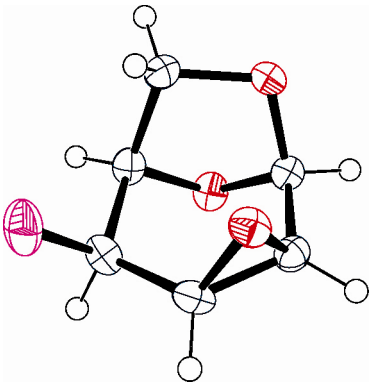
X-ray of **20**: $C_6H_7F_1O_3$, M= 146.12 g/mol, monoclinic system, space group $P2_1$, a=6.1181(3), b=7.1297(3), c=6.9272(4) Å, β=94.628(2)°, Z=2, V=301.18(3) $Å^3$, Dc=1.61 $g.cm^{-3}$, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.36 x 0.38 x 0.66 mm. The structure converged to the final R=0.0235 and R_w=0.0277 using 749 independent reflections (θ_{max}=29.73°). CCDC registration number 832060.



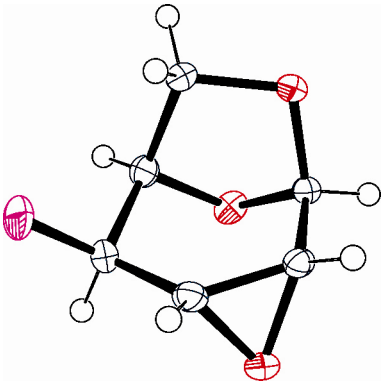
X-ray of **21**: $C_6H_7F_1O_3$, M= 146.12 g/mol, orthorhombic system, space group $P2_12_12_1$, a=6.2710(2), b=7.6812(2), c=12.1999(3) Å, Z=4, V=587.65(3) $Å^3$, Dc=1.65 $g.cm^{-3}$, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.3 x 0.3 x 0.4 mm. The structure converged to the final R=0.0267 and R_w=0.0298 using 759 independent reflections (θ_{max}=27.47°). CCDC registration number 832061.



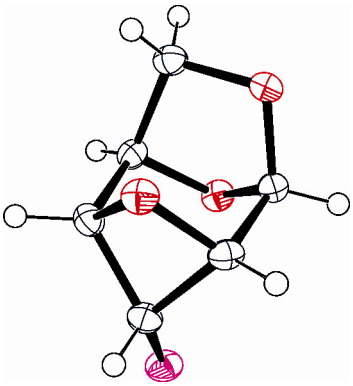
X-ray of **22**: $C_6H_7F_1O_3$, M= 146.12 g/mol, orthorhombic system, space group $P2_12_12_1$, a=6.3457(2), b=7.8536(4), c=12.1288(5) Å, Z=4, V=604.46(4) $Å^3$, Dc=1.61 $g.cm^{-3}$, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.25 x 0.25 x 0.27 mm. The structure converged to the final R=0.0281 and R_w=0.0295 using 745 independent reflections (θ_{max}=27.46°). CCDC registration number 832062.



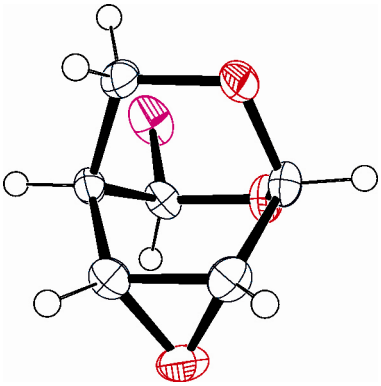
X-ray of **23**: $C_6H_7F_1O_3$, M= 146.12 g/mol, orthorhombic system, space group $P2_12_12_1$, a=7.2178(10), b=8.7675(13), c=9.500(2) Å, Z=4, V=601.2(2) $Å^3$, Dc=1.61 $g.cm^{-3}$, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.13 x 0.21 x 0.61 mm. The structure converged to the final R=0.0295 and R_w=0.0334 using 767 independent reflections (θ_{max}=30.08°). CCDC registration number 832063.



X-ray of **26**: $C_6H_7F_1O_3$, M= 146.12 g/mol, triclinic system, space group *P1*, a=5.1716(2), b=5.2806(2), c=6.0820(3) Å, α=68.403(2), β=67.501(2), γ=80.743(3)°, Z=1, V=142.64(1) $Å^3$, Dc=1.70 $g.cm^{-3}$, μ(Mo Kα)=0.08 mm^{-1}, T=150 K, crystal dimensions of 0.25 x 0.3 x 0.65 mm. The structure converged to the final R=0.0261 and R_w=0.0274 using 629 independent reflections (θ_{max}=27.45°). CCDC registration number 832064.



X-ray of **27**: $C_6H_7F_1O_3$, M= 146.12 g/mol, orthorhombic system, space group $P2_12_12_1$, a=6.7058(5), b=8.1556(5), c=10.7504(7) Å, Z=4, V=587.94(7) $Å^3$, Dc=1.65 $g.cm^{-3}$, μ(Mo Kα)=0.15 mm^{-1}, T=150 K, crystal dimensions of 0.1 x 0.3 x 0.6 mm. The structure converged to the final R=0.0261 and R_w=0.0308 using 691 independent reflections (θ_{max}=27.91°). CCDC registration number 832065.



X-ray of **29**: $C_{13}H_{13}F_1O_4$, M= 252.24 g/mol, monoclinic system, space group $P2_1$, a=6.2240(4), b=10.6879(6), c=8.8554(4) Å, β=106.700(4)°, Z=2, V=564.23(6) $Å^3$, Dc=1.48 $g.cm^{-3}$, μ(Mo Kα)=0.12 mm^{-1}, T=150 K, crystal dimensions of 0.3 x 0.3 x 0.4 mm. The structure converged to the final R=0.0310 and R_w=0.0309 using 1057 independent reflections (θ_{max}=27.08°). CCDC registration number 832066.

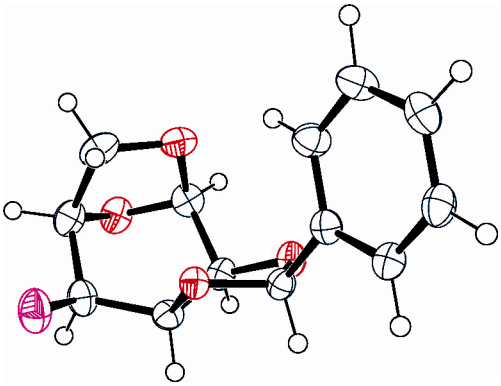
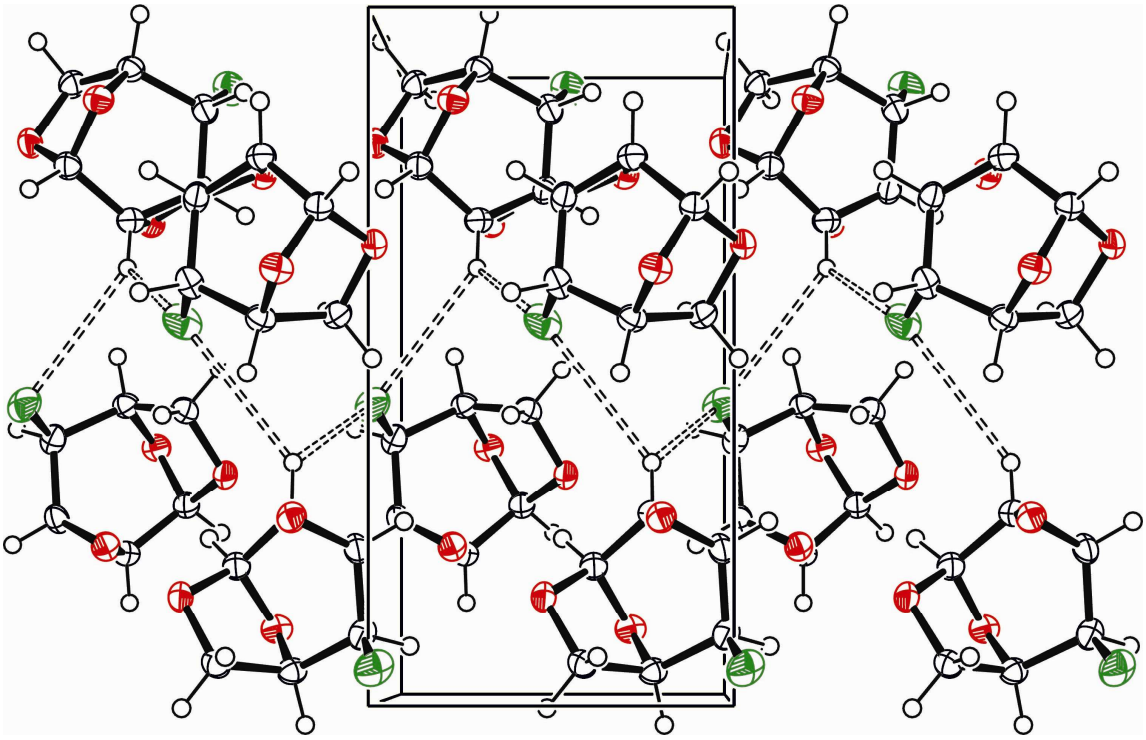


Fig. 1. Molecular packing of compound **22** showing the CH···F intermolecular interaction in the direction [100]. The distance H(2)-F is close to 2.50 Å.



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