Supporting Information

Desymmetrization of 4,6-diprotected-*myo*-inositol

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1. General Information

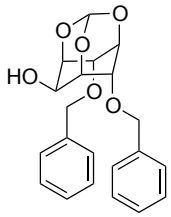
^{1}H NMR spectra were recorded on a 250 MHz and 400 MHz spectrometer. Chemical shifts are reported in ppm with $CHCl_3$ or DMSO as an internal reference ($CHCl_3$: 7.26 ppm; DMSO: 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad, m = multiplet), integration and coupling constants (Hz). ^{13}C NMR spectra were recorded on a 75 MHz and 100 MHz NMR spectrometer. Chemical shifts are reported in ppm with $CHCl_3$ or DMSO as an internal standard ($CHCl_3$: 77.0 ppm; DMSO: 39.43 ppm). MS: The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation $[M]^+$ refers to the molecule-ion. IR spectra were collected as KBr pellets or as solids (ATR and DRIFT). The deposit of the absorption band was given in wave numbers $\tilde{\nu}$ in cm^{-1}. High performance liquid chromatography (HPLC) was performed on *Varian* HPLC-System (Modell Varian 920 LC) using the specified HPLC colums with chiral stationary phase. Unless otherwise specified, all starting materials, reagents and solvents are commercially available and were used without further purification. Flash column chromatography was carried out on silica gel. Routine monitoring of reactions were performed using silica gel coated aluminum plates (silica gel 60, F254). All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried glassware.

2. Experimental and Characterization Data

General Procedure for the 4,6-protection of *myo*-inositol-orthoformate.

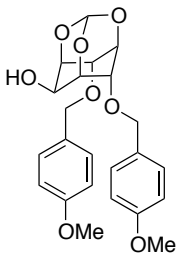
Myo-inositol-1,3,5-monoorthoformate (20.0 mmol, 1.00 equiv.) was dissolved in 40 mL of dry dimethylformamide. At ambient temperature lithium hydride (80.0 mmol, 4.00 equiv.) was added and the resulting solution was stirred for 30 minutes. Afterwards the respective Bromide (46.0 mmol, 2.30 equiv.) was added and the solution stirred for further 48 hours. Water (300 ml) was added and the product was extracted with ethyl acetate (3 x 100 ml). The combined organic layers were dried over Na_2SO_4 and filtered. The volatiles were removed and the residue was subjected to column chromatography to yield the respective 4,6-protected-myo-inositol-orthoformate.

4,6-Di-*O*-benzyl-*myo*-inositol-1,3,5-orthoformate (8a)



Yield = 75%. – $\mathbf{R}_f$ = 0.14 (Cyclohexane/Ethyl acetate 5.5/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): d = 3.10 (d, *J* = 11.6 Hz, 1 H, OH), 4.20-4.25 (m, 3 H, CH), 4.38 (t, *J* = 3.7 Hz, 2 H, CH), 4.46-4.48 (m, 1 H, CH), 4.58 (d, *J* = 11.5 Hz, 2 H, CH_2), 4.66 (d, *J* = 11.5 Hz, 2 H, CH_2), 5.48 (d, *J* = 1.1 Hz, 1 H, CH), 7.27-7.31 (m, 10 H, H_{ar}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): d = 61.4 C(t), 67.8 C(t), 71.7 C(s), 72.9 C(t), 73.7 C(t), 103.3 C(t), 127.6 C(t), 127.9 C(t), 128.4 C(t), 137.4 C(q) ppm. – **IR** (*Diamond*-ATR): $\tilde{\nu}$ = 3501 (w), 3019 (vw), 2977 (vw), 2889 (vw), 1498 (w), 1451 (w), 1405 (w), 1378 (w), 1350 (w), 1301 (w), 1163 (m), 1123 (w), 1101 (m), 1068 (m), 1020 (m), 1003 (m), 956 (m), 941 (m), 886 (m), 827 (m), 802 (m), 767 (m), 695 (m), 515 (m), 462 (m), 413 (w) cm^{-1}. – **MS** (EI, Matrix: 3-NBA) *m/z* (%): 370 (5) $[M]^+$, 279 (40) $[C_{14}H_{15}O_6]^+$, 205 (5) $[C_{12}H_{13}O_3]^+$, 173 (15) $[C_{11}H_9O_2]^+$, 91 (100) $[C_7H_7]^+$, 77 (10) $[C_6H_5]^+$. – **HRMS** (EI, Matrix: 3-NBA) ($C_{21}H_{22}O_6$): calc. 370.1417; found 370.1416.

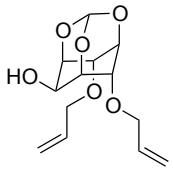
4,6-Di-*O*-(para-methoxy-benzyl)-*myo*-inositol-1,3,5-orthoformate (8b)



Yield = 40%. – $\mathbf{R}_f$ = 0.23 (Cyclohexane/Ethyl acetate 6/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): d = 3.00 (d, *J* = 11.5 Hz, 1 H, OH), 3.80 (s, 6 H, 2 x OCH_3),4.15-4.19 (m, 3 H, CH), 4.33-4.35 (m, 2 H, CH), 4.40-4.42 (m, 1 H, CH), 4.50 (d, *J* = 11.1 Hz, 2 H, CH_2), 4.59 (d, *J* = 11.1 Hz, 2

H, CH_2), 5.45 (d, *J* = 0.8 Hz, 1 H, CH), 6.81-6.83 (m, 4 H, H_{ar}), 7.17-7.19 (m, 4 H, H_{ar}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): d = 55.3 C(p), 61.5 C(t), 67.8 C(t), 71.3 C(s), 73.0 C(t), 73.4 C(t), 103.3 C(t), 113.8 C(t), 129.4 C(t), 129.6 C(q), 159.3 C(q) ppm. – **IR** (Diamond-ATR): $\tilde{\nu}$ = 3463 (vw), 2952 (vw), 2837 (vw), 1612 (w), 1584 (vw), 1512 (w) 1462 (vw), 1441 (vw), 1406 (vw), 1302 (w), 1163 (m), 1095 (m), 1032 (w), 999 (m), 980 (m), 954 (m), 935 (w), 887 (w), 807 (w), 776 (w), 730 (w), 707 (vw), 637 (vw) 512 (m) cm^{-1}. – **MS** (EI, Matrix: 3-NBA) *m/z* (%): 430 (5) $[M]^+$, 309 (55) $[C_{15}H_{17}O_7]^+$, 173 (45) $[C_7H_9O_5]^+$, 121 (100) $[C_8H_9O]^+$, 91 (5) $[C_7H_7]^+$, 77 (5) $[C_6H_5]^+$, 43 (5) $[C_2H_3O]^+$. – **HRMS** (EI, Matrix: 3-NBA) ($C_{23}H_{26}O_8$): calc. 430.1630; found 430.1627.

4,6-Di-*O*-allyl-*myo*-inositol-1,3,5-orthoformate (8c)

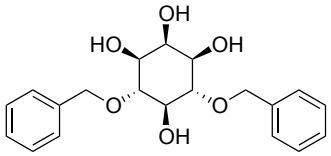


Yield = 78%. – **R_f** = 0.15 (Cyclohexane/Ethyl acetate 6/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): d = 3.19 (d, *J* = 11.8 Hz, 1 H, OH), 4.02-4.13 (m, 5 H, 2 x CH_2, CH), 4.19-4.21 (m, 2 H, CH), 4.26-4.28 (m, 2 H, CH), 4.39-4.42 (m, 1 H, CH), 5.17-5.31 (m, 4 H, 2 x CH_2), 5.47 (d, *J* = 1.2 Hz, 1 H, CH), 5.82-5.92 (m, 2 H, CH) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): d = 61.4 C(t), 67.8 C(t), 70.6 C(s), 73.0 C(t), 73.5 C(t), 103.3 C(t), 117.4 C(s), 134.0 C(t) ppm. – **IR** (Film on KBr): $\tilde{\nu}$ = 3473 (w), 3080 (vw), 2962 (w), 2878 (w), 1646 (vw), 1459 (vw), 1459 (w), 1409 (w), 1350 (w), 1305 (w), 1248 (w), 1164 (s), 1102 (m), 993 (s), 956 (m), 888 (w), 806 (w), 774 (vw), 519 (m) cm^{-1}. – **MS** (EI, Matrix: 3-NBA) *m/z* (%): 270 (5) $[M]^+$, 212 (5) $[C_{10}H_{12}O_5]^+$, 170 (5) $[C_9H_{14}O_3]^+$, 153 (10) $[C_9H_{13}O_2]^+$, 113 (100) $[C_6H_9O_2]^+$, 83 (10) $[C_5H_7O]^+$, 41 (95) $[C_3H_5]^+$. – **HRMS** (EI, Matrix: 3-NBA) ($C_{13}H_{18}O_6$): calc. 270.1179; found 270.1181.

General Procedure for the deprotection of *myo*-inositol-1,3,5-orthoformate.

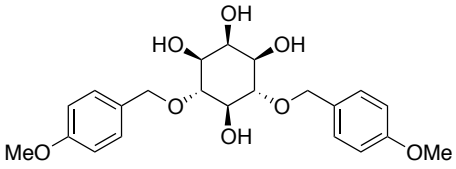
The respective 4,6-protected *myo*-inositol-1,3,5-orthoformate (10.0 mmol, 1.00 equiv.) was dissolved in 10 ml methanol and para-toluene-sulfonic acid (10.0 mmol, 1.00 equiv.) was added. The solution was stirred for 24 hours. The volatiles were removed and the residue was subjected to column chromatography (ethyl acetate) to yield the respective 4,6-protected-myo-inositol.

4,6-Di-*O*-benzyl-*myo*-inositol (4a)



Yield = 99%. – $\mathbf{R}_f$ = 0.40 (Ethyl acetate). – **^{1}H NMR** (400 MHz, $CDCl_3$): d = 2.67 (bs, 4 H, 4 x OH), 3.53-3.56 (m, 3 H, CH), 3.64-3.69 (m, 2 H, CH), 4.11 (bs, 1 H, CH), 4.82 (d, *J* = 4.8 Hz, 2 H, CH), 4.88 (d, *J* = 4.8 Hz, 2 H, CH_2), 7.29-7.37 (m, 10 H, H_{ar}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): d = 71.5 C(t), 71.8 C(t), 74.6 C(t), 75.1 C(s), 81.5 C(t), 128.0 C(t), 128.1 C(t), 128.7 C(t), 138.4 C(q) ppm. – **IR** (Diamond-ATR): $\tilde{\nu}$ = 3526 (w), 3347 (w), 3026 (vw), 2876 (vw), 1494 (vw), 1453 (vw), 1417 (vw), 1390 (vw), 1355 (w), 1331 (vw), 1292 (w), 1217 (w), 1181 (vw), 1131 (w), 1114 (w), 1085 (w), 1052 (m), 1001 (m), 989 (m), 932 (w), 910 (w), 892 (w), 837 (vw), 754 (w), 720 (m), 692 (m), 563 (w), 498 (w), 449 (vw) cm^{-1}. – **MS** (EI, Matrix: 3-NBA) *m/z* (%): 360 (5) $[M]^+$, 269 (80) $[C_{13}H_{17}O_6]^+$, 176 (5) $[C_6H_8O_6]^+$, 107 (65) $[C_7H_7O]^+$, 91 (100) $[C_7H_7]^+$, 77 (10) $[C_6H_5]^+$, 43 (5) $[C_2H_3O]^+$. – **HRMS** (EI, Matrix: 3-NBA) ($C_{20}H_{24}O_6$): calc. 360.1574; found 360.1572

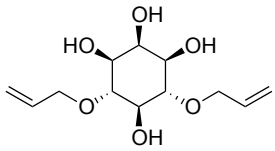
4,6-Di-*O*-(para-methoxy-benzyl)-*myo*-inositol (4b)



Yield = 92%. – $\mathbf{R_f}$ = 0.32 (ethyl acetate). – **^{1}H NMR** (400 MHz, $CDCl_3$): d = 2.45 (bs, 1 H, OH), 2.46(bs, 1 H, OH), 2.49 (bs, 1 H, OH), 2.61 (bs, 1 H, OH), 3.51-3.54 (bm, 3 H, CH), 3.62-3.67 (m, 2 H, CH), 3.81 (bs, 6 H, 2 x CH_3), 4.13 (bs, 1 H, CH), 4.77 (d, *J* = 11.1 Hz, 2 H, CH_2), 4.83 (d, *J* = 11.1 Hz, 2 H, CH_2), 6.89-6.91 (m, 4 H, H_{ar}), 7.30-7.32 (m, 4 H, H_{ar}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): d = 55.3 C(p), 71.5 C(t), 71.8 C(t), 74.7 C(t), 74.8 C(s), 81.2 C(t), 114.1 C(t), 129.7 C(t), 130.6 C(q), 159.5 C(q) ppm. – **IR** (Diamond-ATR): $\tilde{\nu}$ = 3532 (w), 3332 (w), 2921 (vw), 2836 (vw), 1611 (w), 1584 (w), 1513 (m), 1466 (w), 1439 (w), 1404 (w), 1356 (w), 1333 (w), 1304 (w), 1248 (m), 1184 (w), 1173 (w), 1114 (m), 1094 (w), 1062 (m), 1029 (m), 1002 (m), 990 (m), 930 (w), 890 (w), 847 (w), 829 (w), 811 (m), 766 (w), 757 (w)

cm^{-1}. – **MS** (EI, Matrix: 3-NBA) *m/z* (%): 420 (5) $[M]^+$, 299 (50) $[C_{14}H_{19}O_4]^+$, 201 (5) $[C_6H_{10}O_5]^+$, 137 (80) $[C_8H_9O_2]^+$, 121 (100) $[C_8H_9O]^+$, 91 (100) $[C_7H_7]^+$, 77 (5) $[C_6H_5]^+$, 43 (5) $[C_2H_3O]^+$. – **HRMS** (EI, Matrix: 3-NBA) ($C_{22}H_{28}O_8$): calc. 420.1785; found 420.1784.

4,6-Di-*O*-allyl-*myo*-inositol-1,3,5-orthoformat (4c)

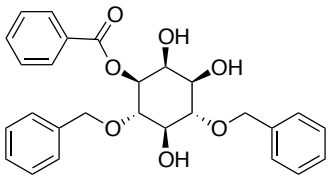


Yield = 90%. – $\mathbf{R_f}$ = 0.80 (Ethyl acetate): – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.83 (d, *J* = 2.3 Hz, 1 H, OH), 3.07 (d, *J* = 4.5 Hz, 2 H, 2 x OH), 3.42-3.56 (m, 6 H, 6 x CH), 4.13 (d, *J* = 1.9 Hz, 1 H, OH), 4.29-4.39 (m, 4 H, 2 x CH_2), 5.18-5.32 (m, 4 H, 2 x CH_2), 5.92-6.02 (m, 2 H, 2 x CH) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 71.6 C(t), 71.7 C(t), 73.9 C(s), 74.5 C(t), 81.3 C(t), 117.4 C(s), 135.0 C(t) ppm. – **IR** (Diamond-ATR): $\tilde{\nu}$ = 3300 (m), 3074 (vw), 2916 (w), 2876 (w), 1687 (w), 1424 (w), 1532 (m), 1263 (w), 1193 (m), 1138 (m), 1097 (s), 1063 (s), 995 (s), 922 (s), 711 (m), 605 (m), 566 (m), 493 (m), 457 (m) cm^{-1}. – **MS** (EI, Matrix: 3-NBA) *m/z* (%): 260 (5) $[M]^+$, 219 (5) $[C_9H_{15}O_6]^+$, 203 (100) $[C_9H_{15}O_5]^+$, 163 (25) $[C_6H_{17}O_5]^+$, 99 (20) $[C_5H_7O_2]^+$, 73 (10) $[C_3H_5O_2]^+$, 41 (10) $[C_3H_5]^+$. – **HRMS** (EI, Matrix: 3-NBA) ($C_{12}H_{20}O_6$): calc. 260.1262; found 260.1259.

General Procedure for the asymmetric desymmetrization

Under argon atmosphere the respective 4,6-protected-*myo*-inositol (0.10 mmol, 1.00 equiv.) and the phosphonit catalyst (0.03 mmol, 0.30 equiv.) were dissolved in 0.5 mL (0.2 M) propionitril and cooled to −78 °C. Hünig's base (0.10 mmol, 1.00 equiv.) and benzoyl chloride (0.15 mmol, 1.50 equiv.) were added successively. The reaction was stirred for the given reaction time before 5 mL water were added to quench the reaction. The product was extracted with dichloromethane (2 x 10 mL). The volatiles were removed and the residue was subjected to column chromatography (cyclohexane/ethyl acetate 2/1) to yield the product.

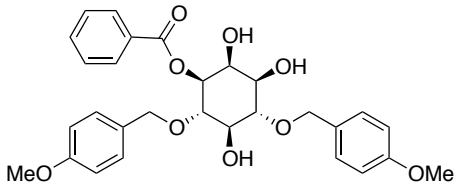
1-*O*-Benzoyl -4,6-di-*O*-benzyl-*myo*-inositol (3a)



R$_f$ = 0.18 (Cyclohexane/Ethyl acetate 2/1). – **^{1}H NMR** (400 MHz, $CDCl_3$): d = 2.47 (bs, 1 H, OH), 2.52 (d, *J* = 3.5 Hz, 1 H, OH), 2.57 (d, *J* = 2.0 Hz, 1 H, OH), 3.66-3.81 (m, 3 H, CH), 4.07-4.11 (m, 1 H, CH), 4.35 (bs, 1 H, CH), 4.70-5.02 (m, 4 H, 2 x CH_2), 5.11-5.14 (m, 1 H, CH), 7.20-7.24 (m, 4 H, H_{ar}), 7.32-7.61 (m, 9 H, H_{ar}), 8.08-8.10 (m, 2 H, H_{ar}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): d = 70.1 C(t), 71.3 C(t), 74.0 C(t), 75.0 C(t), 75.1 C(s), 75.5 C(s), 79.5 C(t), 80.7 C(t), 127.9 C(t), 128.0 C(t), 128.1 C(t), 128.5 C(t), 128.6 C(t), 128.7 C(t), 128.7 C(t), 129.6 C(t), 129.8 C(t), 138.0 C(q), 138.3 C(q), 138.5 C(q), 165.7 C(q) ppm. – **IR** (Diamond-ATR): $\tilde{\nu}$ = 3405 (w), 3062 (vw), 3032 (vw), 2907 (vw), 1698 (w), 1601 (vw), 1495 (vw), 1452 (w), 1356 (w), 1315 (w), 1272 (w), 1211 (w), 1178 (vw), 1091 (m), 1067 (m), 1023 (w), 978 (w), 940 (w), 899 (w), 851 (vw), 729 (w), 694 (m), 578 (w), 545 (w) cm^{-1}. – **MS** (EI, Matrix: 3-NBA) *m/z* (%): 464 (5) $[M]^+$, 373 (30) $[C_{20}H_{21}O_7]^+$, 267 (20) $[C_{13}H_{15}O_6]^+$, 107 (10) $[C_7H_7O]^+$, 105 (95) $[C_7H_5O]^+$, 91 (100) $[C_7H_7]^+$, 77 (20) $[C_6H_5]^+$, 43 (20) $[CO_2]^+$. – **HRMS** (EI, Matrix: 3-NBA) ($C_{27}H_{28}O_7$): calc. 464.1833; found 464.1835.

Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak OD column (heptanes/isopropanol 85/15, 10 °C, 1.0 mL/min). Enantiomer 1: t_R = 19.8 min, minor enantiomer: t_R = 30.6 min.

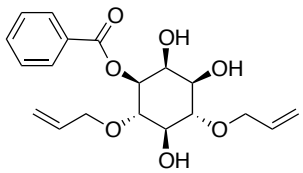
1-*O*-Benzoyl -4,6-di-*O*-(para-methoxy-benzyl)-*myo*-inositol (3b)



R_f = 0.13 (Cyclohexane/Essigsäureethylester 2/1). − **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.57 (bs, 2 H, OH), 2.60 (d, *J* = 2.2 Hz, 1 H, OH), 3.60−3.71 (m, 3 H, CH), 3.74 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.03−4.08 (m, 1 H, CH), 4.30−4.32 (m, 1 H, CH), 4.59−4.93 (m, 4 H, 2 x CH_2), 5.07−5.10 (m, 1 H, CH), 6.74−6.76 (m, 2 H, H_{ar}), 6.88−6.90 (m, 2 H, H_{ar}), 7.13−7.15 (m, 2 H, H_{ar}), 7.30−7.32 (m, 2 H, H_{ar}), 7.44−7.48 (m, 2 H, H_{ar}), 7.57−7.61 (m, 1 H, H_{ar}), 8.07−8.10 (m, 2 H, H_{ar}) ppm. − **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 55.2 C(p), 55.3 C(p), 70.1 C(t), 71.3 C(t), 74.0 C(t), 74.7 C(s), 74.9 C(t), 75.1 C(s), 79.2 C(t), 80.3 C(t), 113.9 C(t), 114.1 C(t), 128.5 C(t), 129.6 C(t), 129.7 C(t), 129.8 C(t), 130.2 C(t), 130.6 C(t), 133.3 C(t), 159.3 C(q), 159.4 C(q), 165.7 C(q) ppm. − **IR** (Diamond-ATR): $\tilde{\nu}$ = 3417 (w), 3070 (vw), 3002 (vw), 2910 (w), 2834 (w), 1697 (m), 1611 (w), 1586 (w), 1511 (w), 1451 (w), 1420 (vw), 1356 (w), 1315 (w), 1280 (m), 1241 (m), 1171 (w), 1102 (m), 1069 (m), 1015 (m), 945 (w), 846 (w), 814 (w), 703 (m), 669 (vw), 563 (w), 508 (w), 451 (w) cm^{-1}. − **MS** (EI, Matrix: 3-NBA) *m/z* (%): 524 (5) $[M]^+$, 403 (20) $[C_{21}H_{23}O_8]^+$, 298 (10) $[C_{14}H_{18}O_7]^+$, 137 (35) $[C_8H_9O_2]^+$, 121 (100) $[C_8H_9O]^+$. − **HRMS** (EI, Matrix: 3-NBA) ($C_{29}H_{32}O_9$): calc. 524.2046; found 524.2048.

Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak OD column (heptanes/isopropanol 85/15, 10 °C, 1.0 mL/min). Enantiomer 1: t_R = 40.8 min, minor enantiomer: t_R = 74.9 min.

1-*O*-Benzoyl -4,6-di-*O*-allyl-*myo*-inositol (3c)

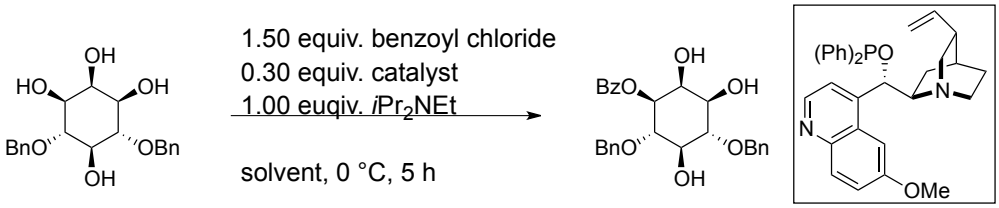


R$_f$ = 0.19 (Cyclohexane/Ethyl acetate 2/1): 0.19. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.64 (bs, 3 H, OH), 3.56−3.66 (m, 3 H, CH), 3.91−3.96 (m, 1 H, CH), 4.20−4.26 (m, 2 H, C*H*$_2$CH=CH$_2$), 4.27−4.32 (m, 1 H, C*H*$_2$CH=CH$_2$), 4.33−4.35 (m, 1 H, CH), 4.46−4.50 (m, 1 H, C*H*$_2$CH=CH$_2$), 5.02−5.06 (m, 1 H, CH$_2$CH=C*H*$_2$), 5.07−5.10 (m, 1 H, CH$_2$CH=C*H*$_2$), 5.16−5.23 (m, 2 H, 1 x CH$_2$CH=C*H*$_2$, 1 x CH), 5.30−5.35 (m, 1 H, CH$_2$CH=C*H*$_2$), 5.78−5.87 (m, 1 H, CH$_2$C*H*=CH$_2$), 5.94−6.04 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.45−7.49 (m, 2 H, H$_{ar}$), 7.58−7.61 (m, 1 H, H$_{ar}$), 8.08−8.10 (m, 2 H, H$_{ar}$) ppm. − **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 70.1 C(t), 71.3 C(t), 73.9 C(t), 73.9 C(s), 74.2 C(s), 74.7 C(t), 79.0 C(t), 80.4 C(t), 117.4 C(s), 117.4 C(s), 128.5 C(t), 129.7 C(q), 129.8 C(t), 133.4 C(t), 134.6 C(t), 135.0 C(t), 165.7 C(q) ppm. − **IR** (Diamond-ATR): ṽ = 3409 (w), 3078 (vw), 2922 (w), 1719 (w), 1691 (w), 1601 (vw), 1584 (vw), 1451 (w), 1425 (vw), 1346 (w), 1315)w), 1271 (m), 1177 (w), 1093 (m), 1067 (m), 1021 (m), 915 (w), 850 (vw), 804 (vw), 705 (m), 686 (w), 608 (w), 541 (w) cm^{-1}. – **MS** (EI, Matrix: 3-NBA) *m/z* (%): 364 (10) $[M]^+$, 307 (80) $[C_{16}H_{19}O_6]^+$, 259 (5) $[C_{12}H_{19}O_6]^+$, 105 (100) $[C_7H_5O]^+$, 77 (15) $[C_6H_5]^+$, 41 (25) $[C_3H_5]^+$. – **HRMS** (EI, Matrix: 3-NBA) ($C_{19}H_{24}O_7$): calc. 364.1522; found 364.1524.

Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak OD column (heptanes/isopropanol 85/15, 10 °C, 1.0 mL/min). Enantiomer 1: t_R = 8.3 min, minor enantiomer: t_R = 20.4 min.

3. Optimization tables

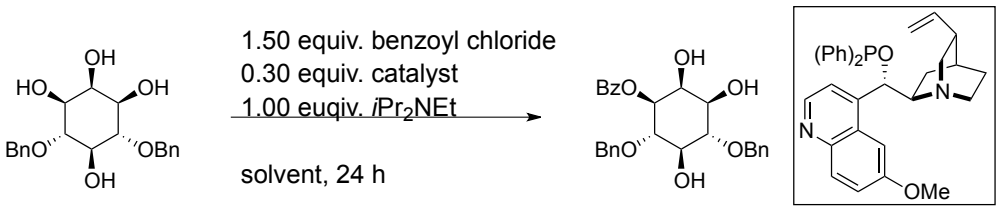
Table 1 Solventscreen



Entry	Solvent	Yield[a]	*ee*[b]
1	CH_2Cl_2	70%	60%
2	$CHCl_3$	75%	80%
3	CCl_4	-	-
4	1,2-Dichlorethane	58%	71%
5	Et_2O	26%	61%
6	THF	31%	75%
7	Toluene	40%	87%
8	DMF	-	-
9	Acetonitirile	88%	81%
10	Propionitrile	72%	87%

0.2 mmol scale. [a] isolated yield after column chromatography. [b] determined by HPLC

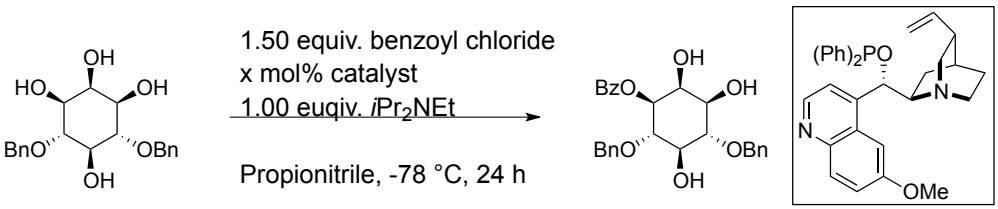
Table 2 Chloroform and propionitrile at low temperatures



Entry	Solvent	Temperature	Yield[a]	*ee*[b]
1	$CHCl_3$[c]	−55 °C	81%	93%
2	Propionitril	−78 °C	94%	99%

0.2 mmol scale. [a] isolated yield after column chromatography. [b] determined by HPLC. [c] m.p.: −63.5 °C

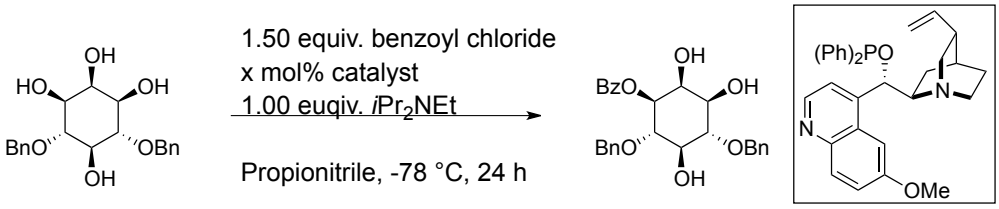
Table 3 Catalyst loading screen



Entry	Catalyst loading	Yield[a]	*ee*[b]
1	1 mol%	32%	40%
2	2 mol%	26%	96%
3	5 mol%	28%	97%
4	7 mol%	47%	97%
5	10 mol%	74%	97%
6	15 mol%	88%	98%
7	20 mol%	99%	99%

0.2 mmol scale. [a] isolated yield after column chromatography. [b] determined by HPLC

Table 4 Catalyst loading screen on a 1.38 mmol scale

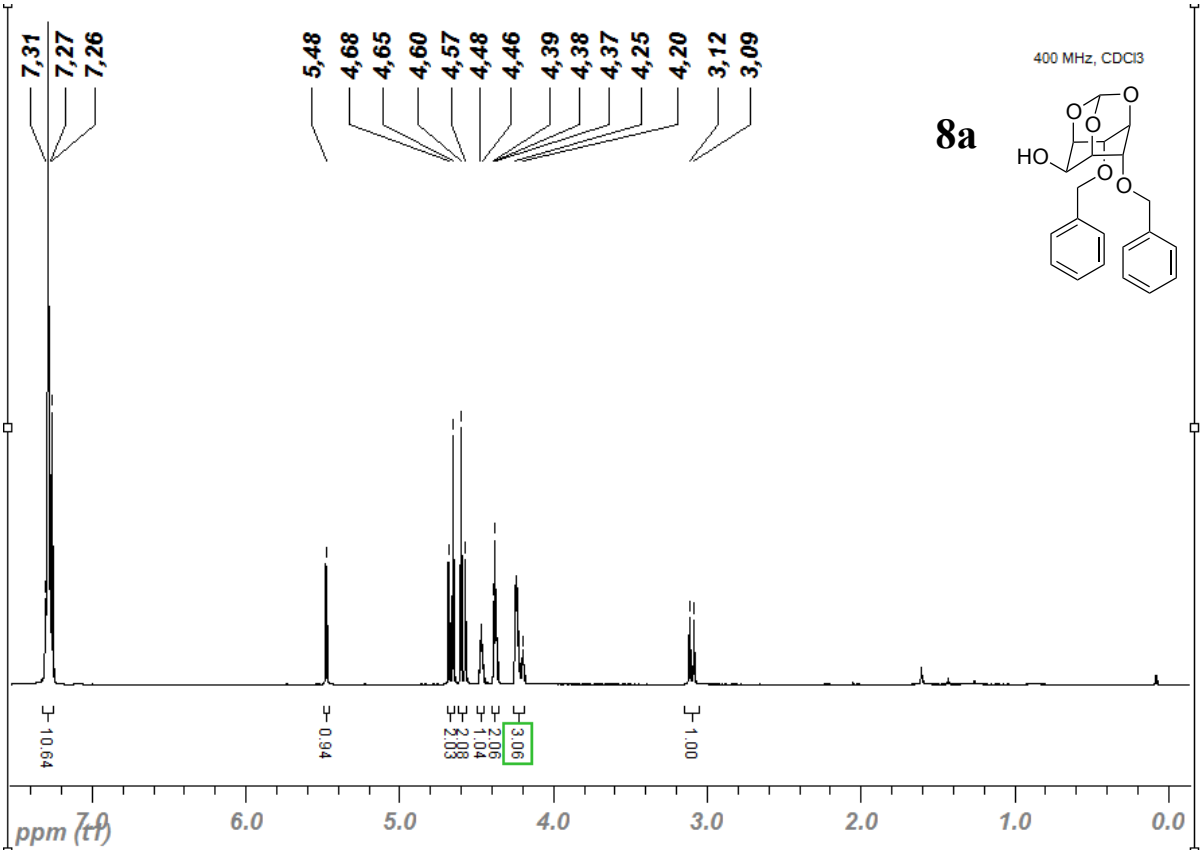


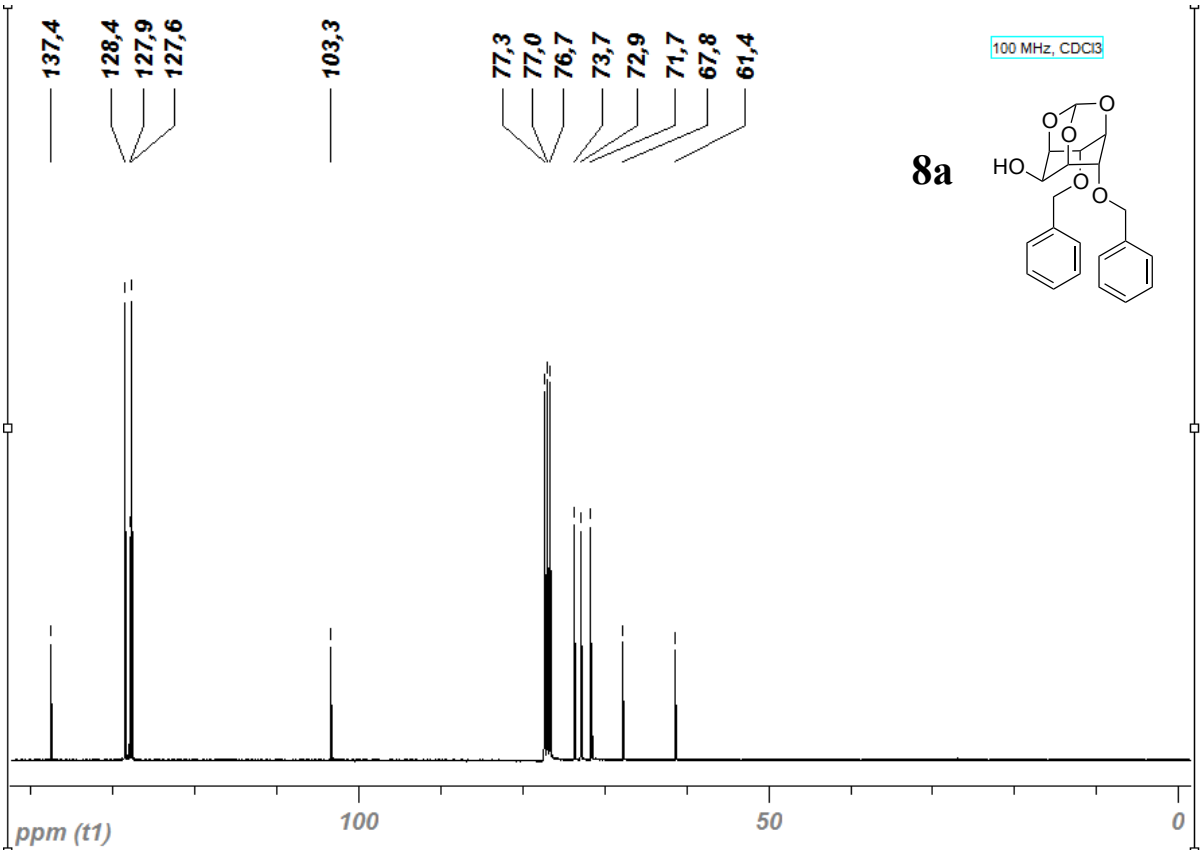
Entry	Catalyst loading	Starting Material	yield[a]	*ee*[b]
1	10 mol%	500 mg	65%	97%
2	20 mol%	500 mg	72%	98%
3	30 mol%	500 mg	77%	99%

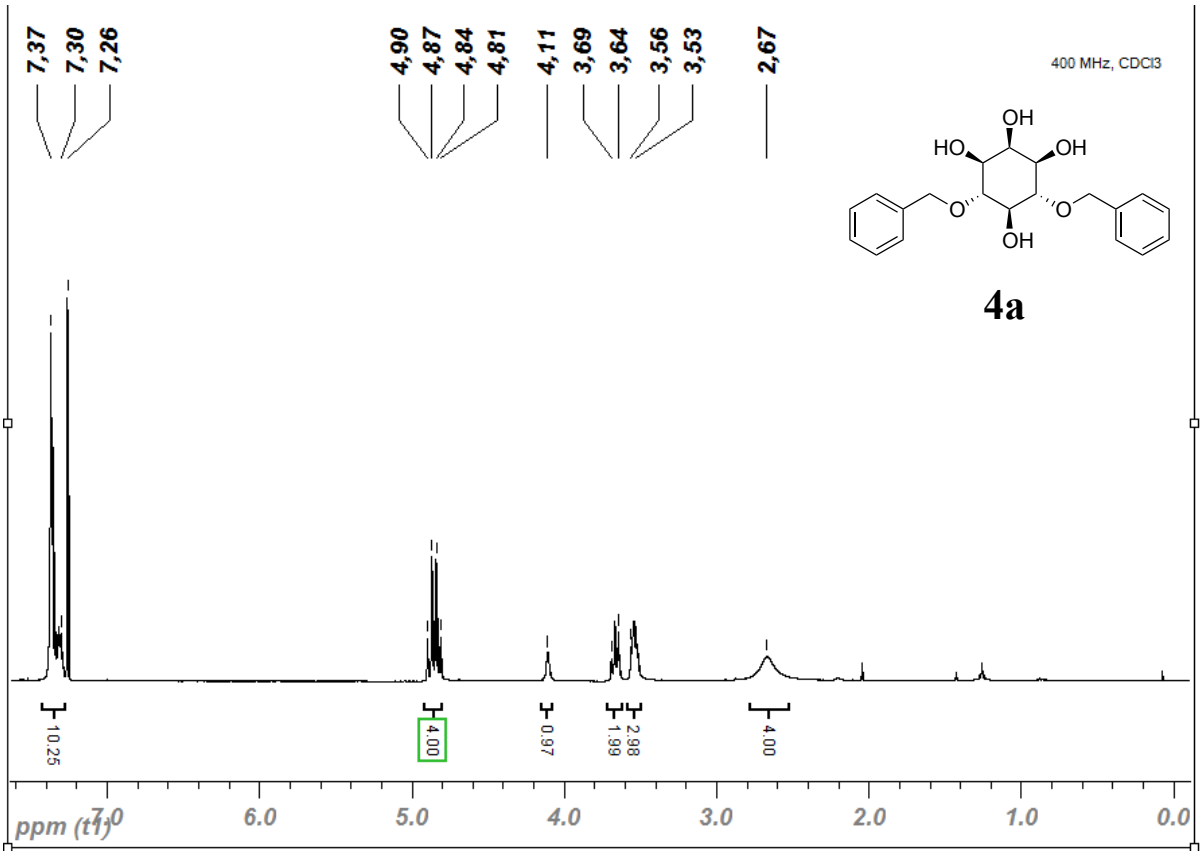
1.38 mmol scale. [a] isolated yield after column chromatography. [b] determined by HPLC

4. Spectra

4.1 NMR-Spectra



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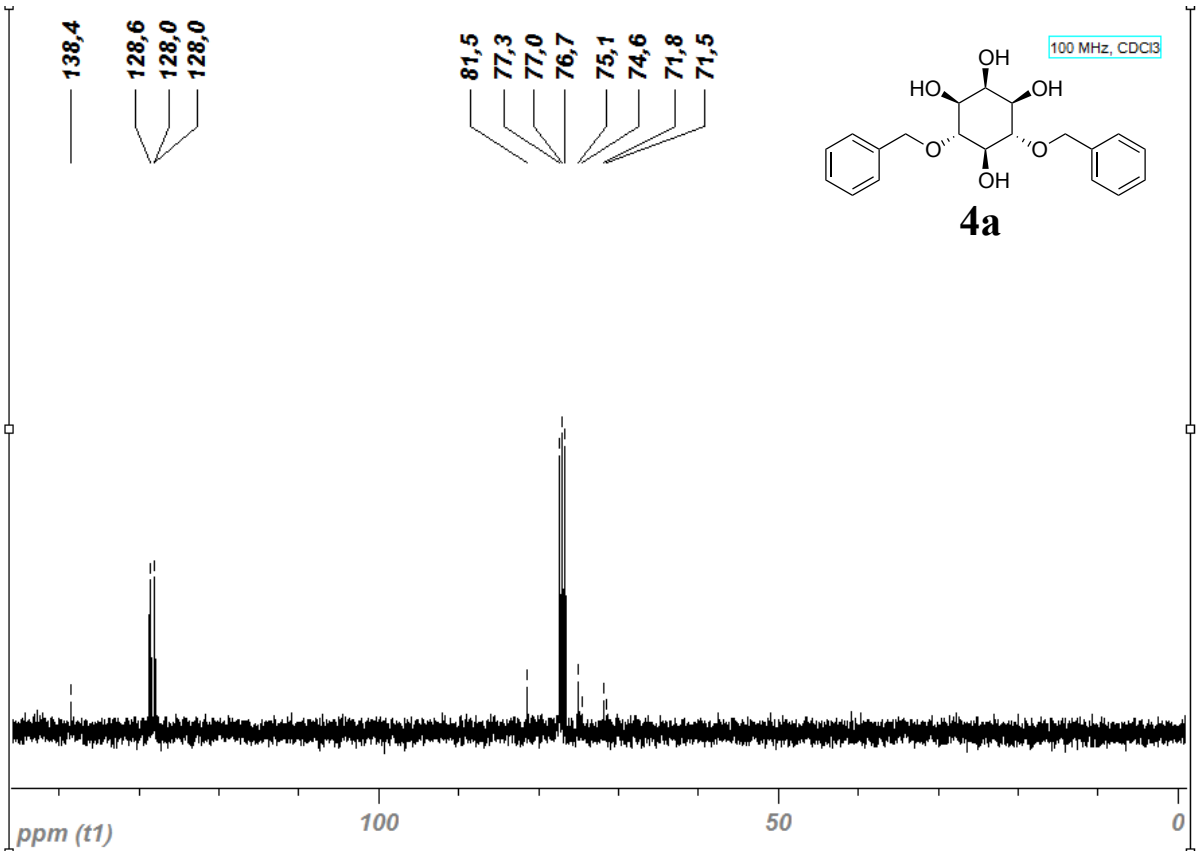
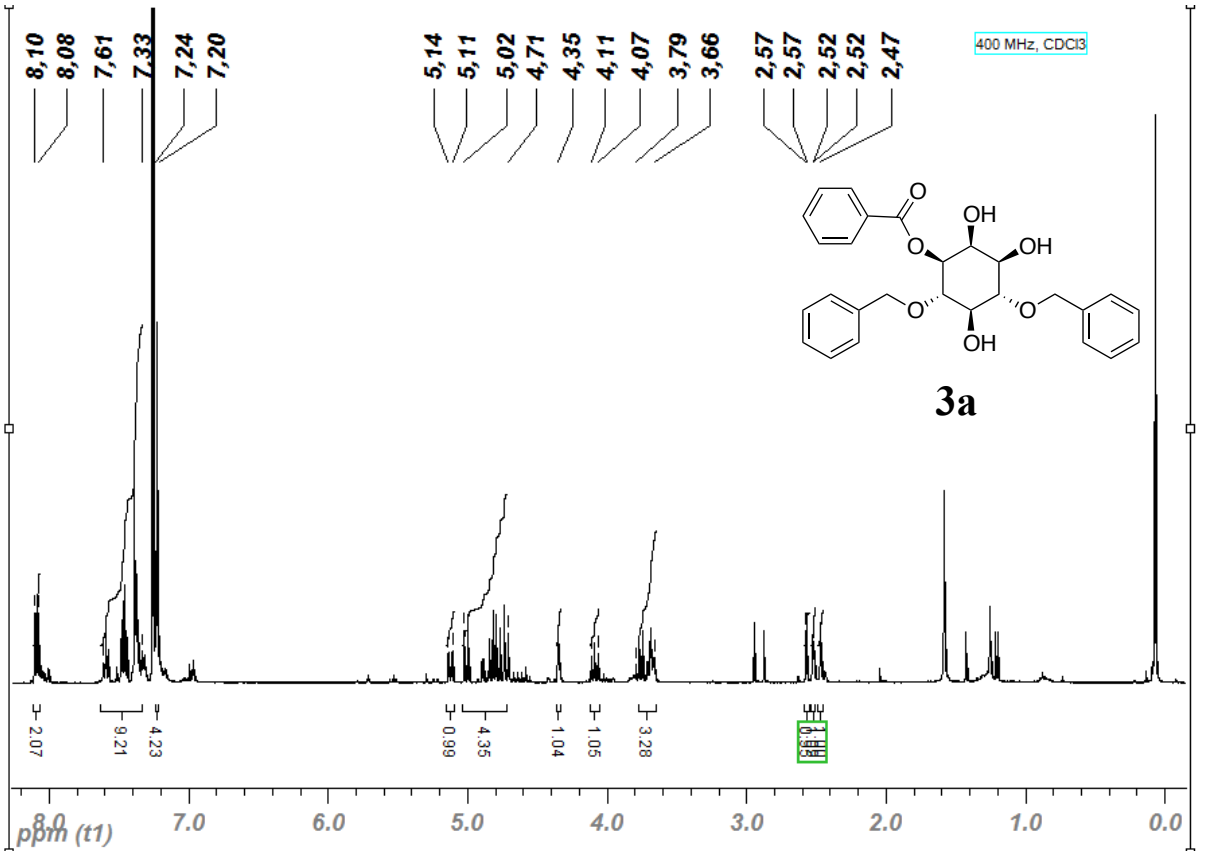
7,30
7,26
4,90
4,87
4,84
4,81
4,11
3,69
3,64
3,56
3,53
2,67
400 MHz, CDCl3
OH
HO
OH
O
O
OH
4a
10,25
4,00
0,97
2,98
1,99
4,00
ppm (t1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


138,4
128,6
128,0
128,0
81,5
77,3
77,0
76,7
75,1
74,6
71,8
71,5
100 MHz, CDCl3
OH
HO
OH
O
O
OH
4a
ppm (t1)
100
50
0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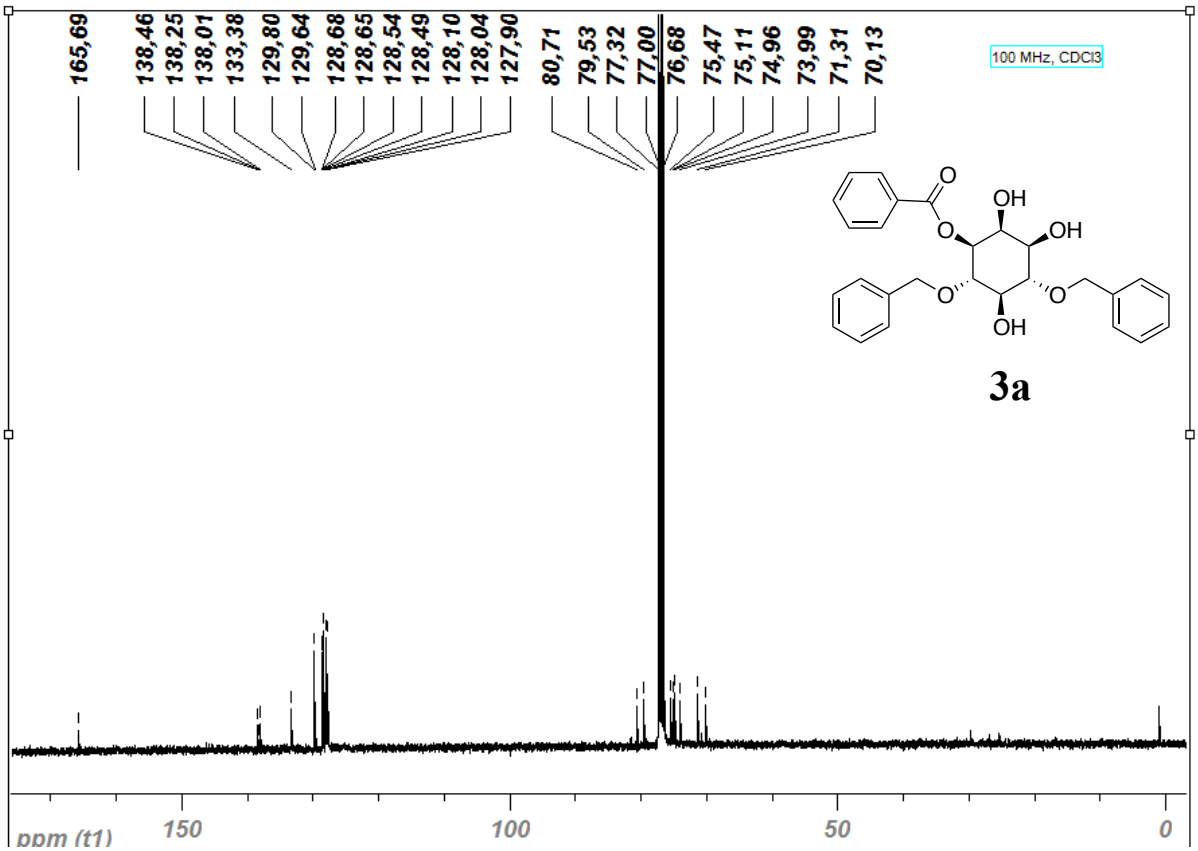
8,08
7,61
7,33
7,24
7,20
5,14
5,11
5,02
4,71
4,35
4,11
4,07
3,79
3,66
2,57
2,57
2,52
2,52
2,47
400 MHz, CDCl3
O
OH
OH
O
O
O
OH
3a
2.07
9.21
4.23
0.99
4.35
1.04
1.05
3.28
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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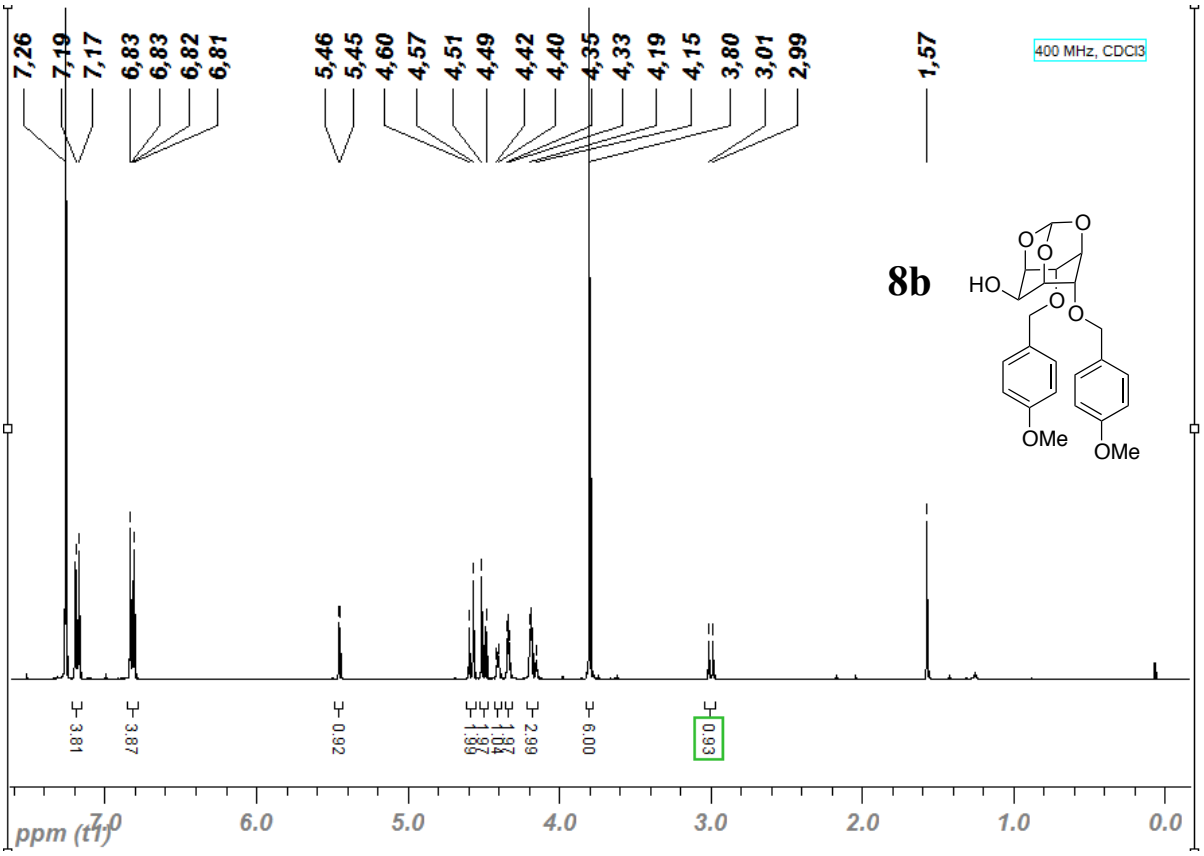
138,46
138,25
138,01
133,38
129,80
129,64
128,68
128,65
128,54
128,49
128,10
128,04
127,90
80,71
79,53
77,32
77,00
76,68
75,47
75,11
74,96
73,99
71,31
70,13
100 MHz, CDCl3
O
OH
OH
O
O
O
OH
3a
150
100
50
0
ppm (t1)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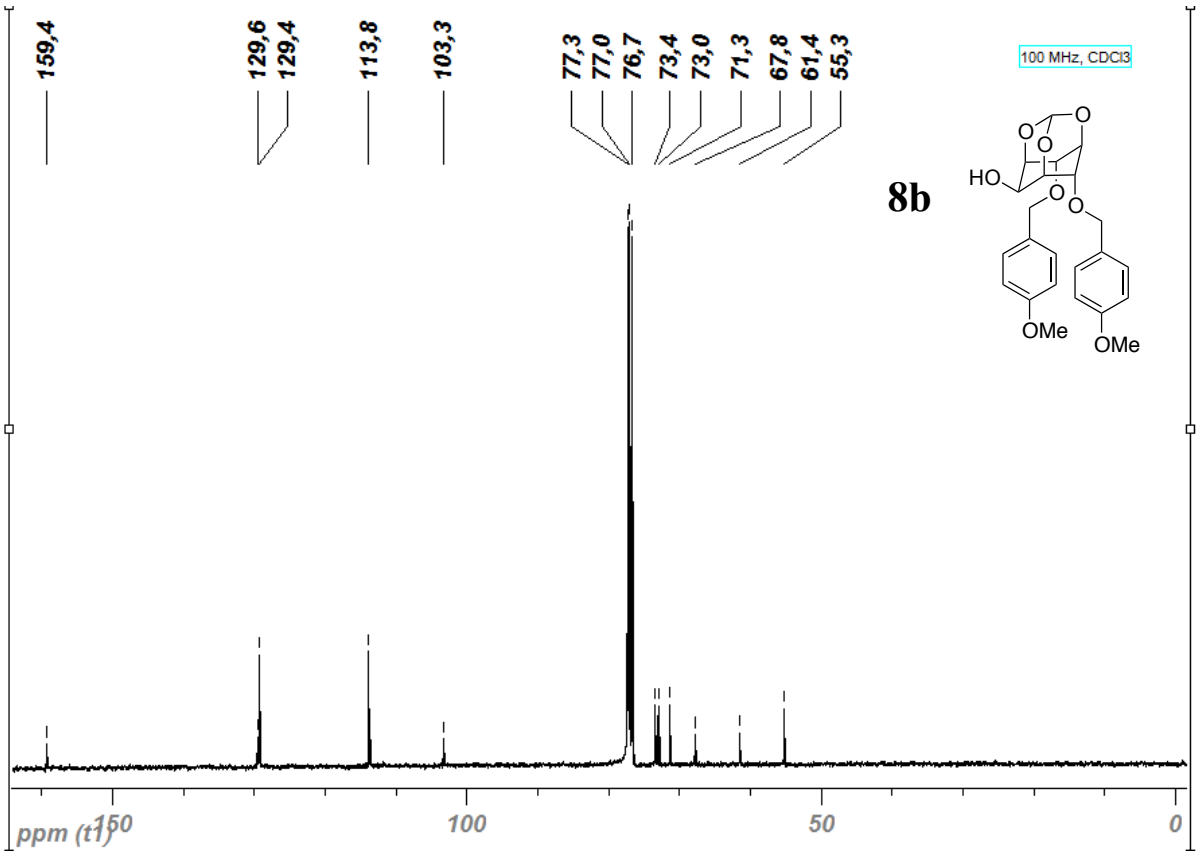
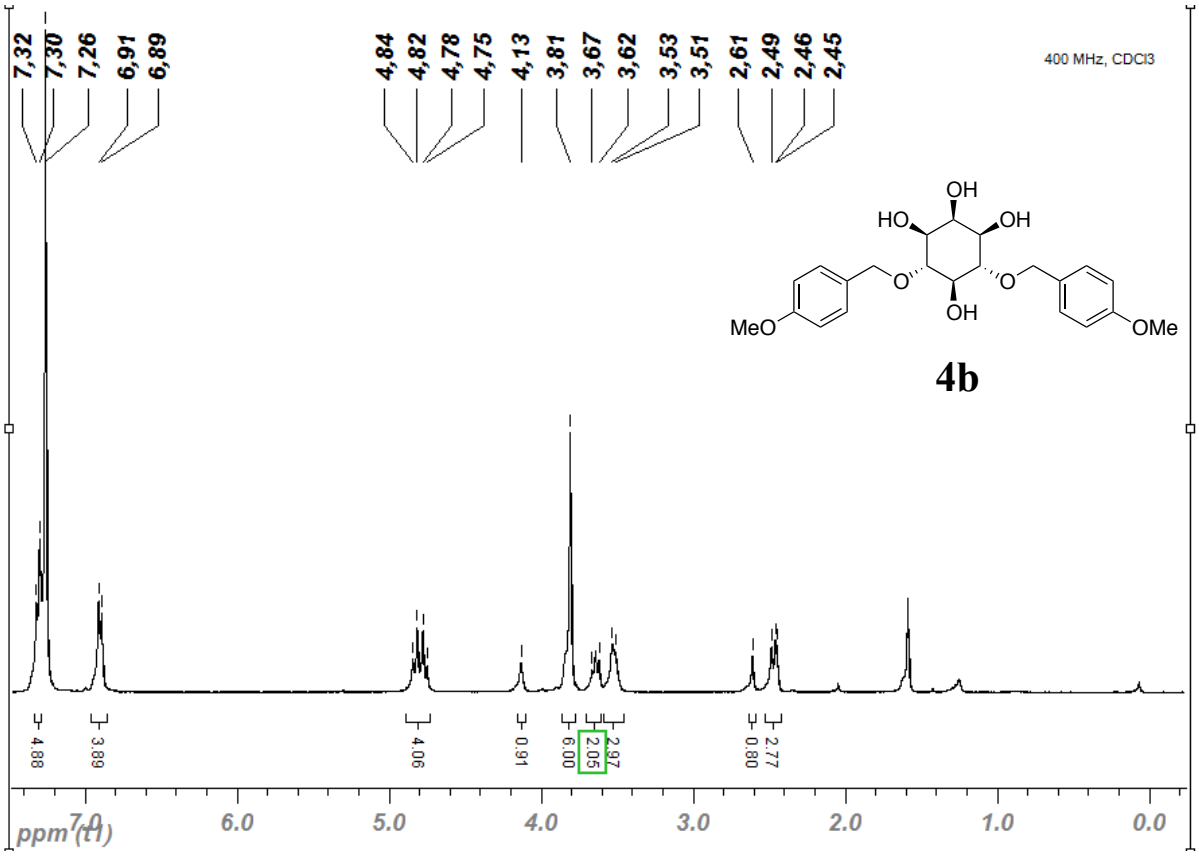
7,19
7,17
6,83
6,83
6,82
6,81
5,46
5,45
4,60
4,57
4,51
4,49
4,42
4,40
4,35
4,33
4,19
4,15
3,80
3,01
2,99
1,57
400 MHz, CDCl3
8b
HO
OMe
OMe
3,81
3,87
0,92
1,89
1,87
1,87
2,69
9,00
0,83
ppm (t1)
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0


159,4
129,6
129,4
113,8
103,3
77,3
77,0
76,7
73,4
73,0
71,3
67,8
61,4
55,3
100 MHz, CDCl3
8b
HO
OMe
OMe
ppm (t1)
150
100
50
0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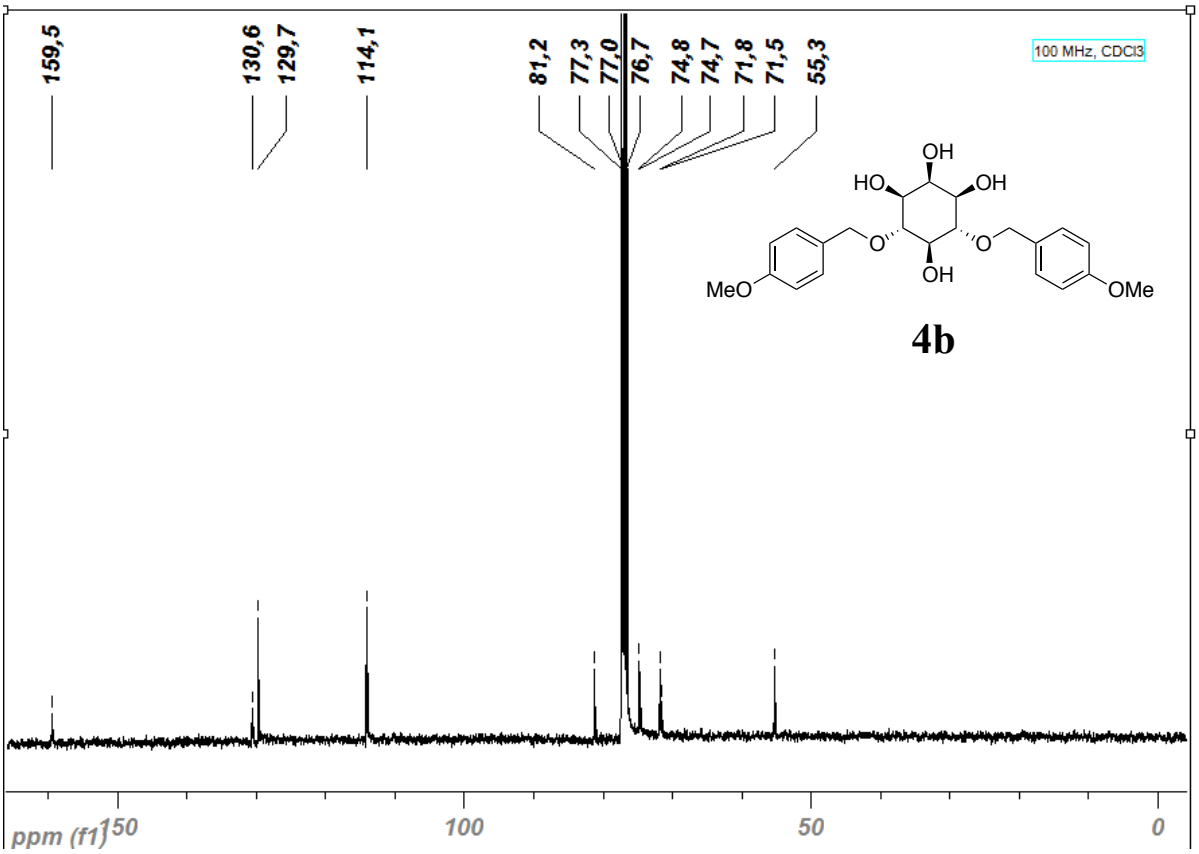
7,26
6,91
6,89
4,84
4,82
4,78
4,75
4,13
3,81
3,67
3,62
3,53
3,51
2,61
2,49
2,46
2,45
400 MHz, CDCl3
OH
HO
OH
O
O
OH
MeO
OMe
4b
4.88
3.89
4.06
1.91
6.00
2.05
2.87
0.80
2.77
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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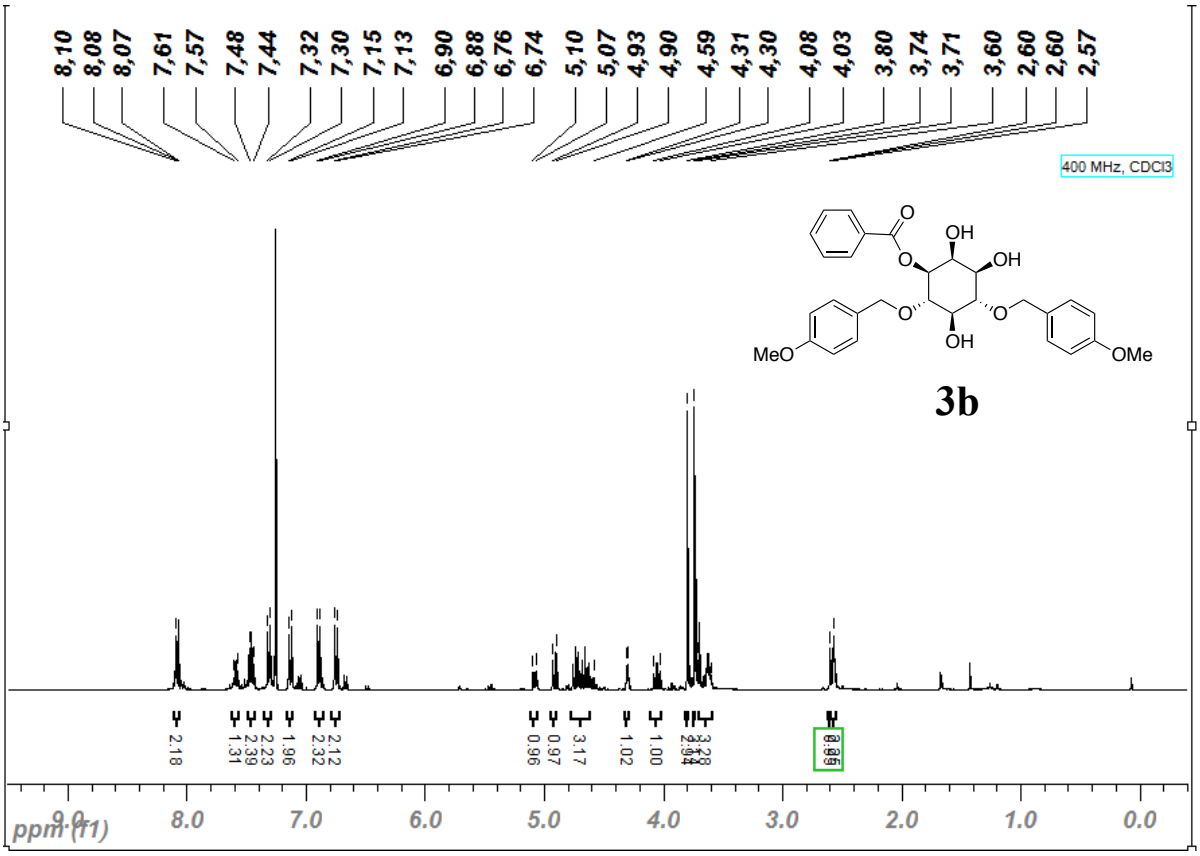
129,7
114,1
81,2
77,3
77,0
76,7
74,8
74,7
71,8
71,5
55,3
100 MHz, CDCl3
OH
HO
OH
O
O
OH
MeO
OMe
4b
150
100
50
0
ppm (f1)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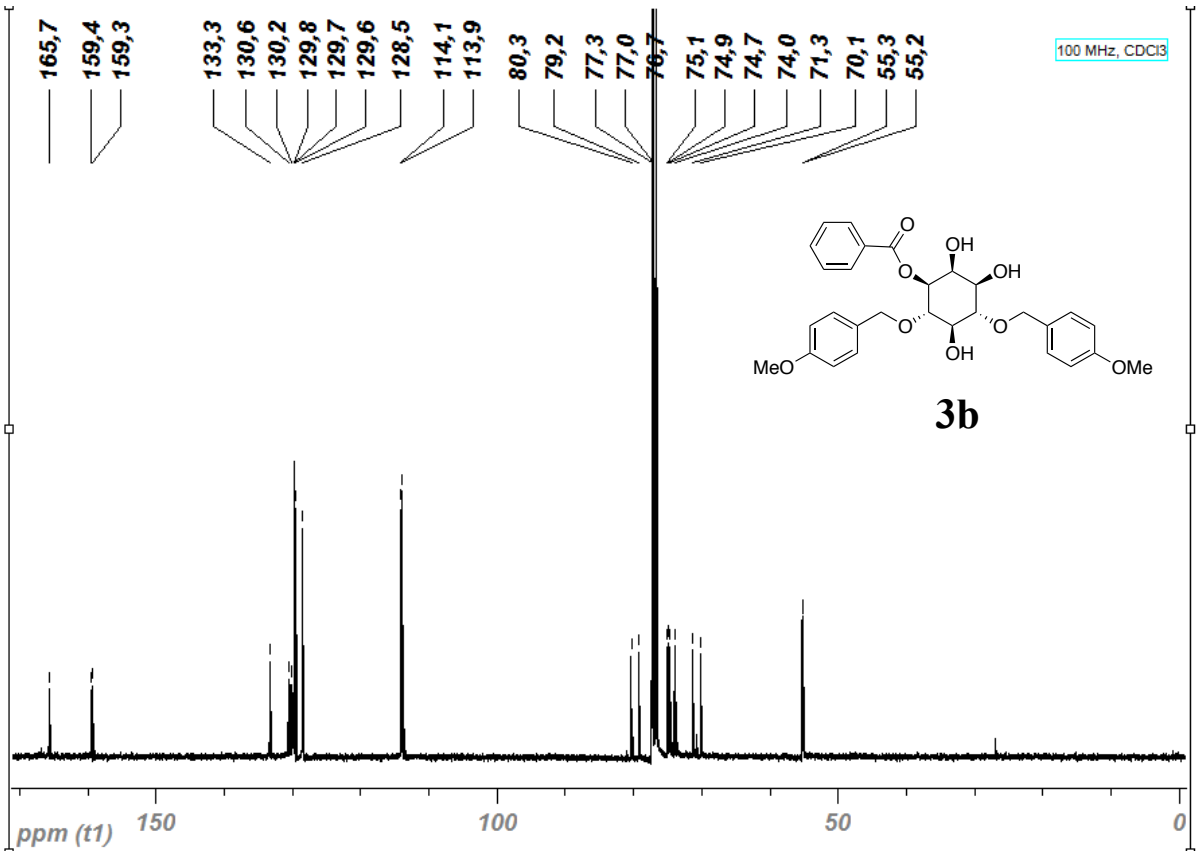
8,07
7,61
7,57
7,48
7,44
7,32
7,30
7,15
7,13
6,90
6,88
6,76
6,74
5,10
5,07
4,93
4,90
4,59
4,31
4,30
4,08
4,03
3,80
3,74
3,71
3,60
2,60
2,60
2,57
400 MHz, CDCl3
OH
OH
OH
MeO
OMe
3b
ppm (t1)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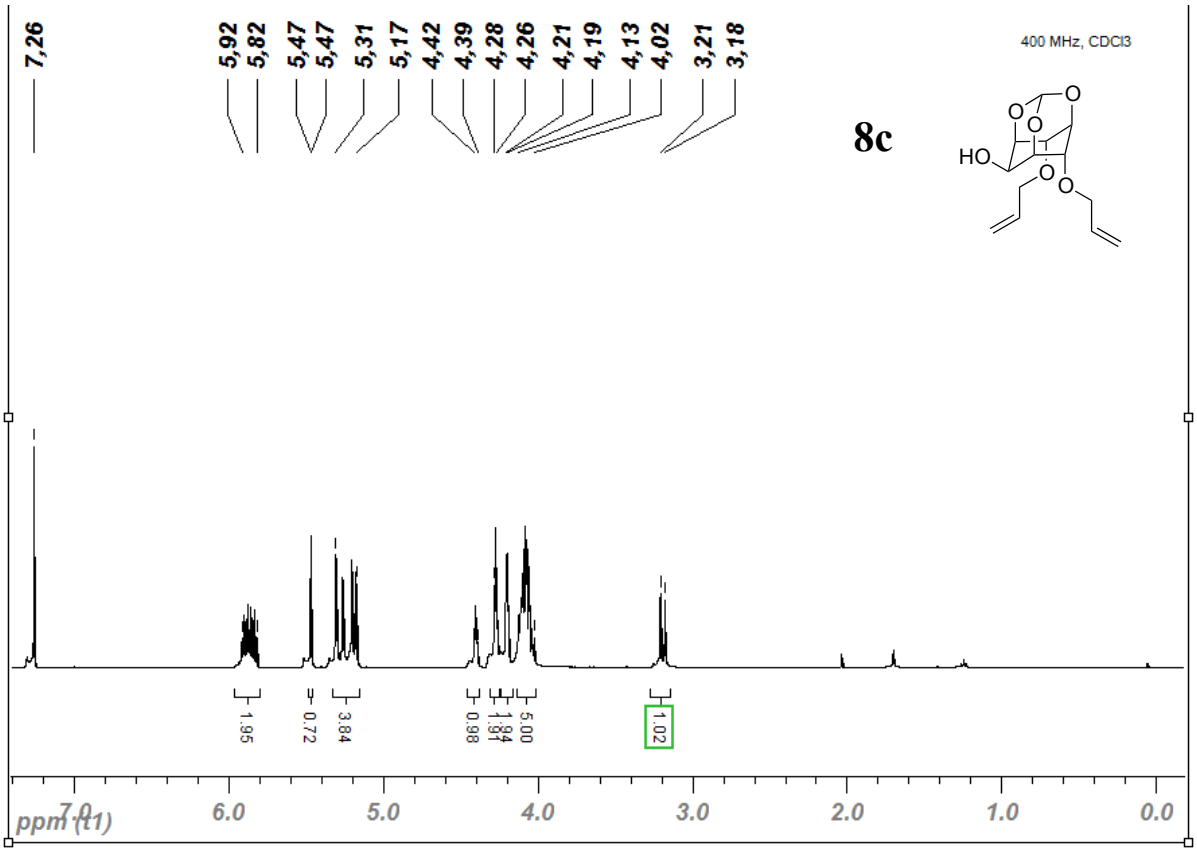
159,3
133,3
130,6
130,2
129,8
129,7
129,6
128,5
114,1
113,9
80,3
79,2
77,3
77,0
76,7
75,1
74,9
74,7
74,0
71,3
70,1
55,3
55,2
100 MHz, CDCl3
OH
OH
OH
MeO
OMe
3b
ppm (t1)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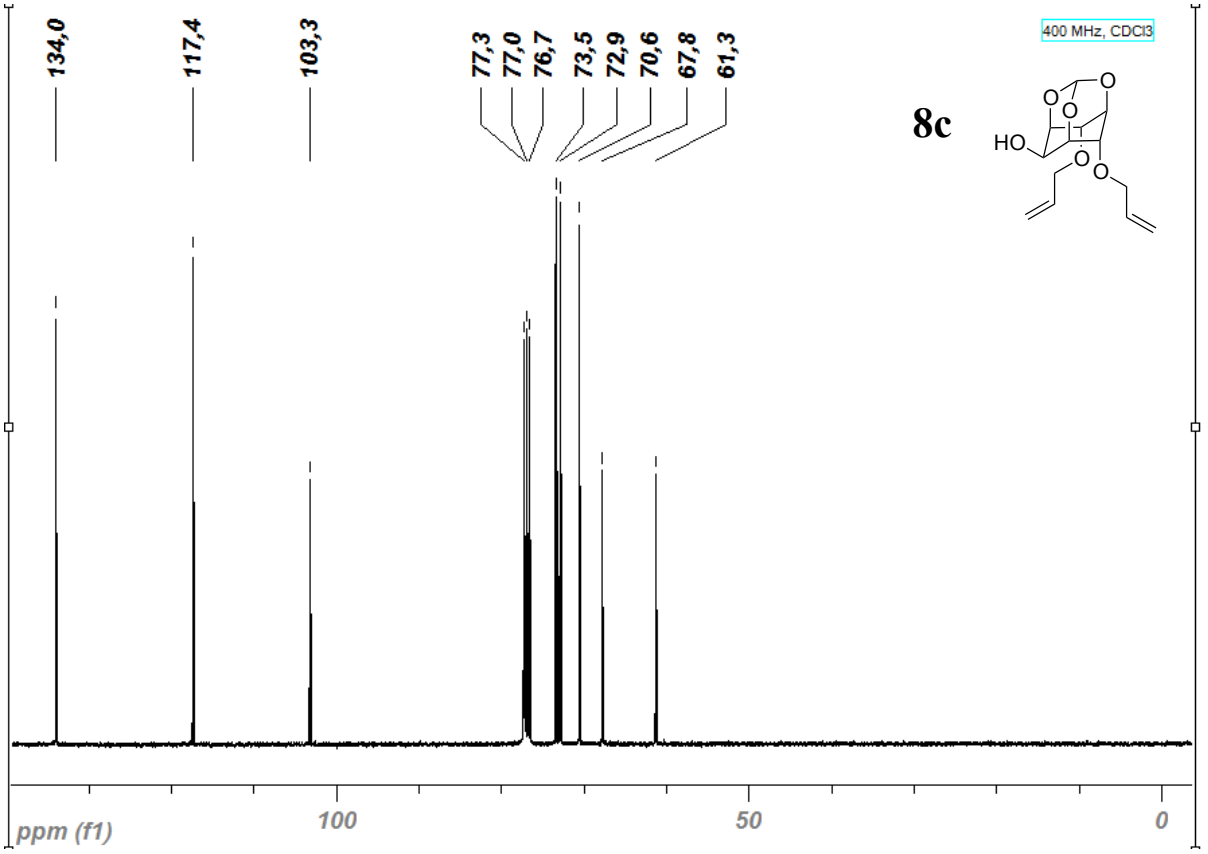
5,82
5,47
5,47
5,31
5,17
4,42
4,39
4,28
4,26
4,21
4,19
4,13
4,02
3,21
3,18
8c
400 MHz, CDCl3
HO
O
1.95
0.72
3.84
0.98
1.94
1.84
5.00
1.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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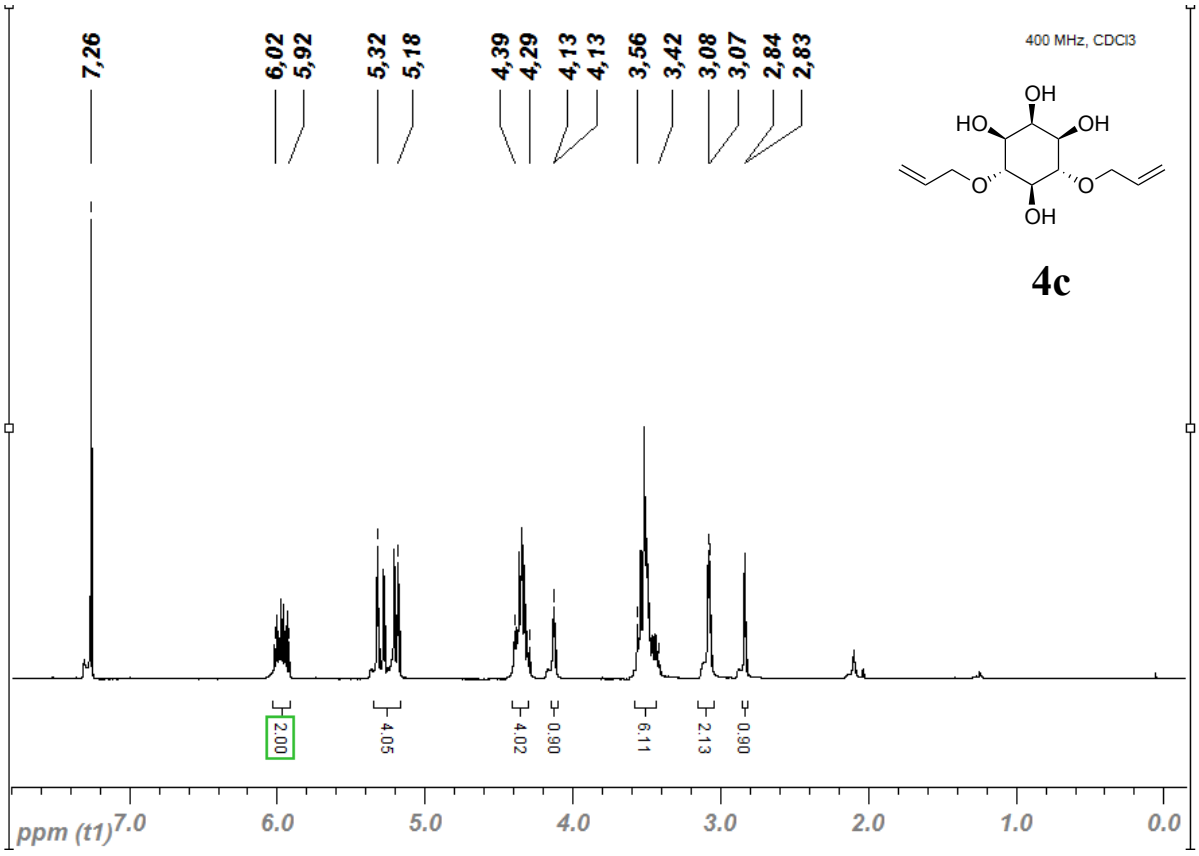
117,4
103,3
77,3
77,0
76,7
73,5
72,9
70,6
67,8
61,3
8c
400 MHz, CDCl3
HO
O
100
50
0
ppm (f1)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6,02
5,92
5,32
5,18
4,39
4,29
4,13
4,13
3,56
3,42
3,08
3,07
2,84
2,83
400 MHz, CDCl3
OH
HO
OH
O
O
OH
4c
2.00
4.05
4.02
0.90
6.11
2.13
0.90
ppm (t1)
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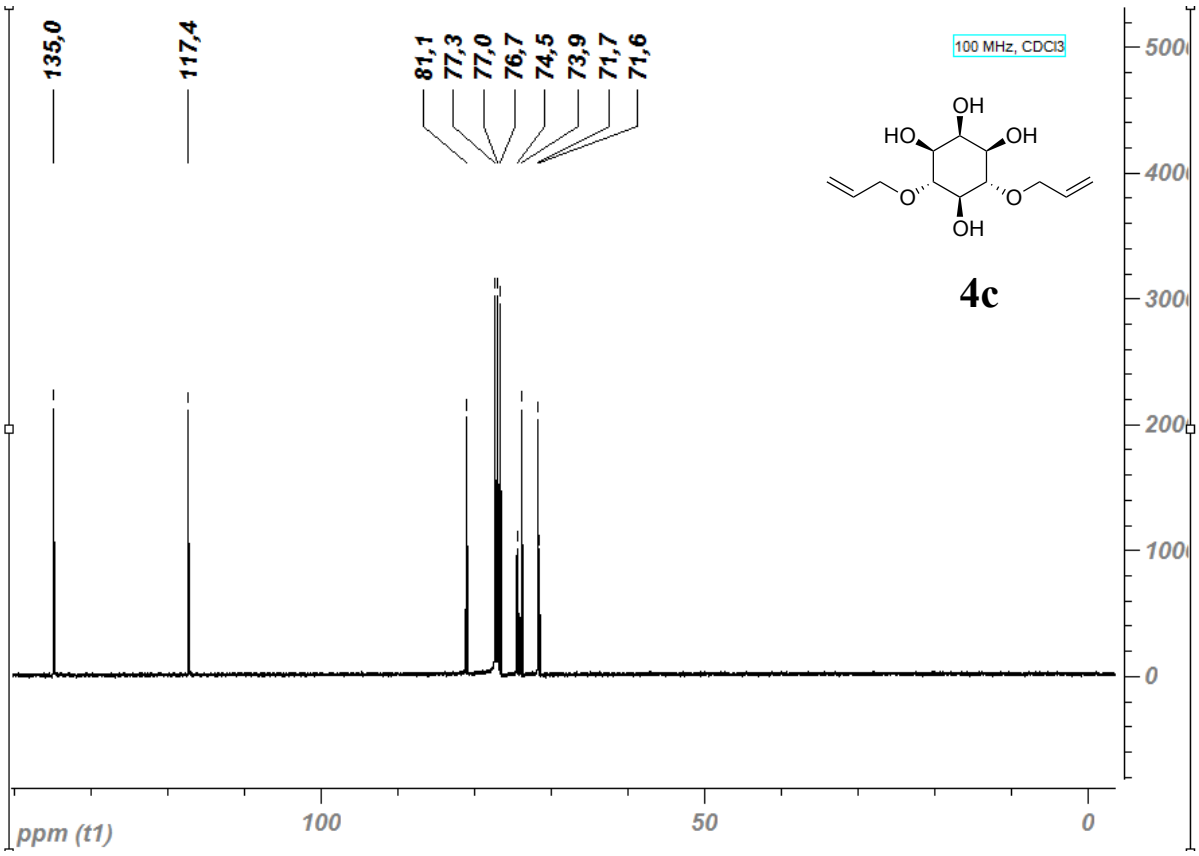
6.0
5.0
4.0
3.0
2.0
1.0
0.0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117,4
81,1
77,3
77,0
76,7
74,5
73,9
71,7
71,6
100 MHz, CDCl3
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O
O
OH
4c
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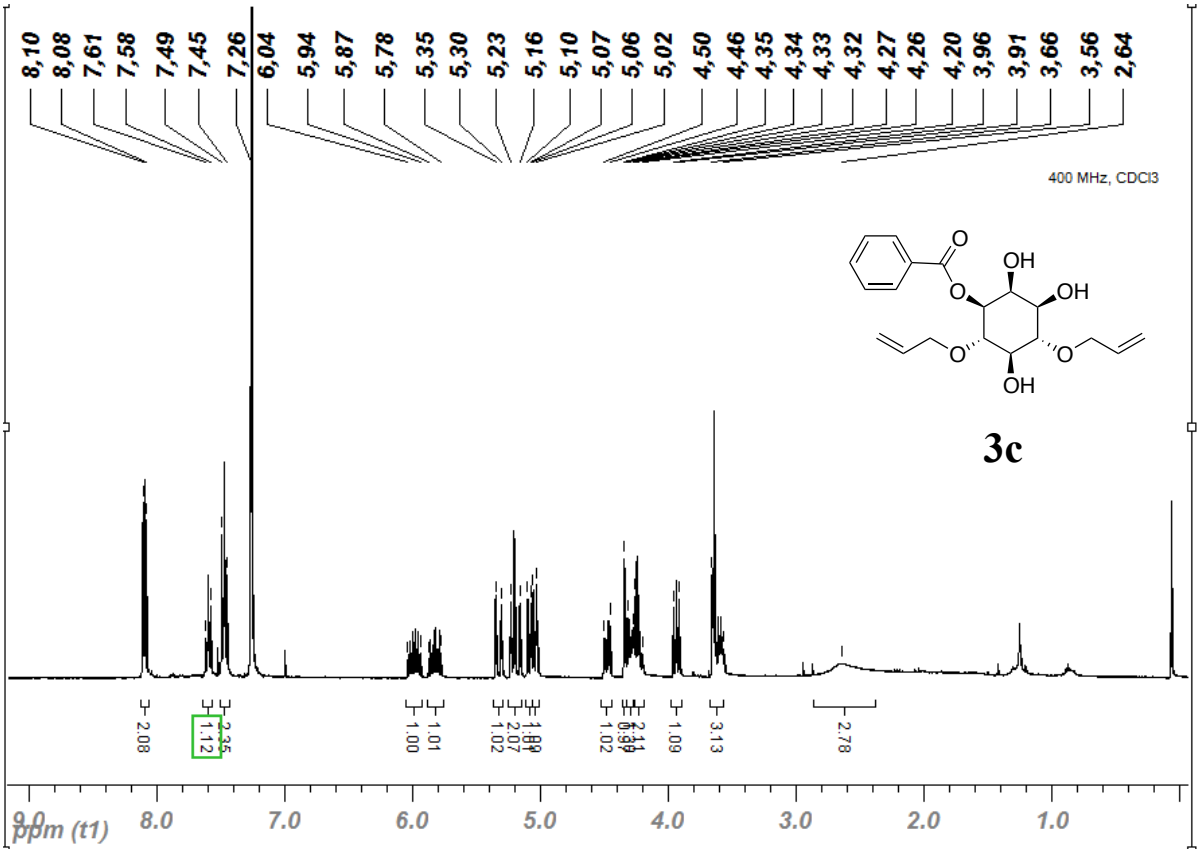
300
200
100
0
ppm (t1)
100
50
0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6,04
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5,30
5,23
5,16
5,10
5,07
5,06
5,02
4,50
4,46
4,35
4,34
4,33
4,32
4,27
4,26
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3,91
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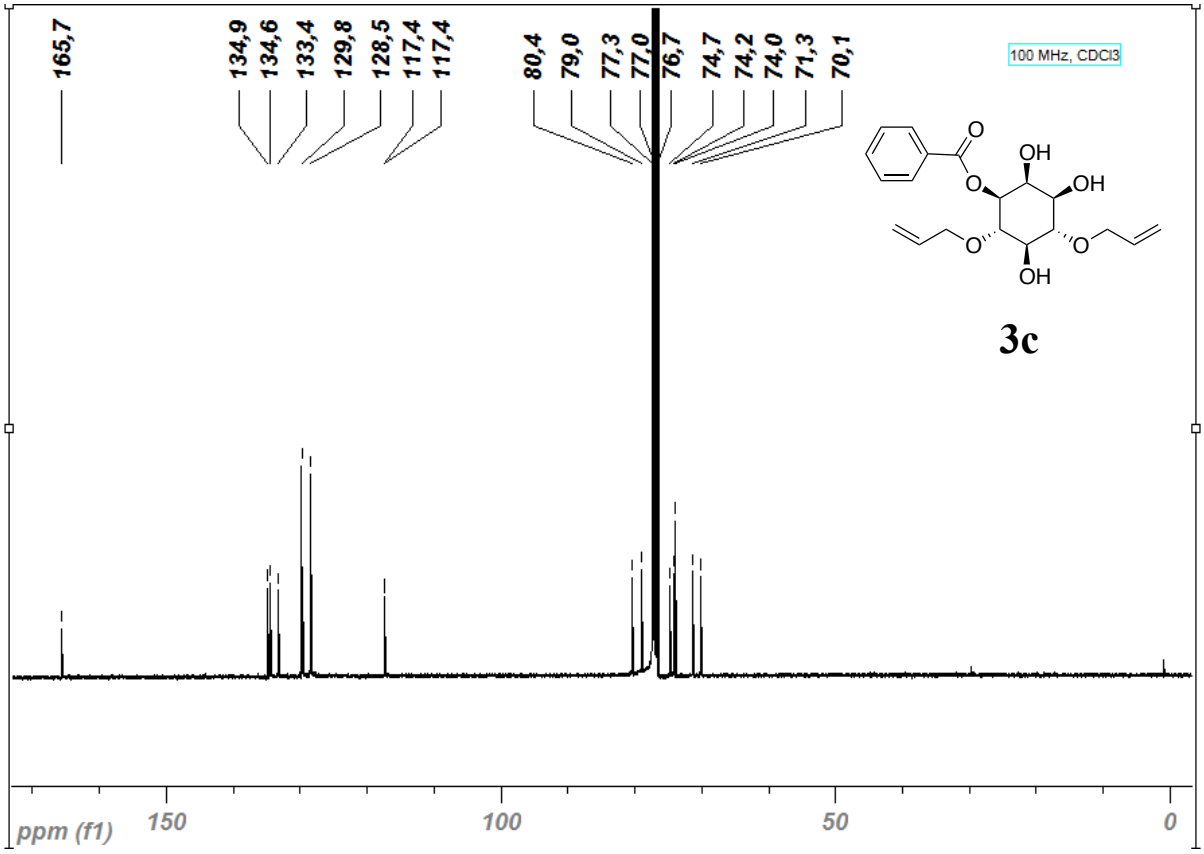
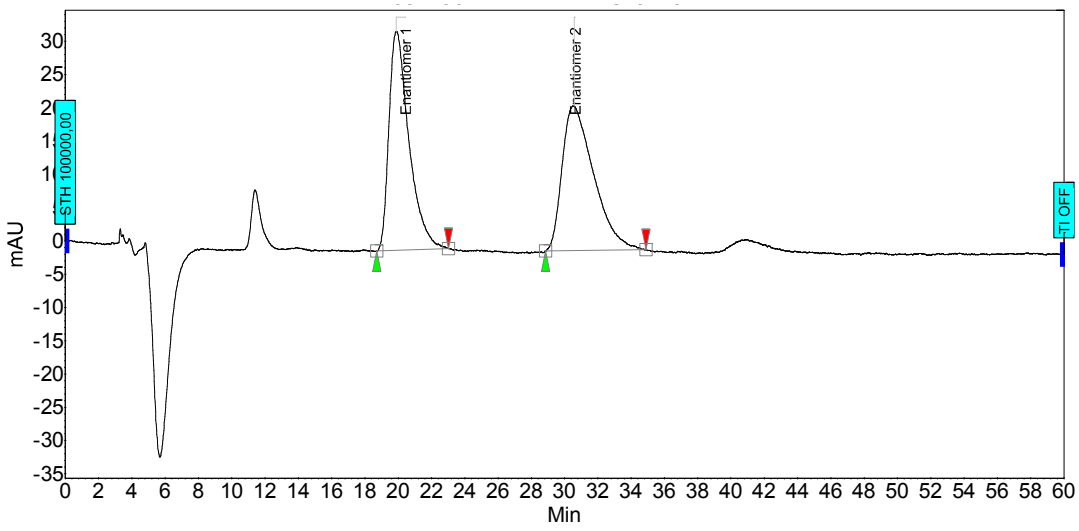
400 MHz, CDCl3
3c
2.08
1.12
2.25
1.00
1.01
2.07
1.02
1.09
3.13
2.78
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


165,7
134,9
134,6
133,4
129,8
128,5
117,4
117,4
80,4
79,0
77,3
77,0
76,7
74,7
74,2
74,0
71,3
70,1
100 MHz, CDCl3
3c
ppm (f1)
150
100
50
0

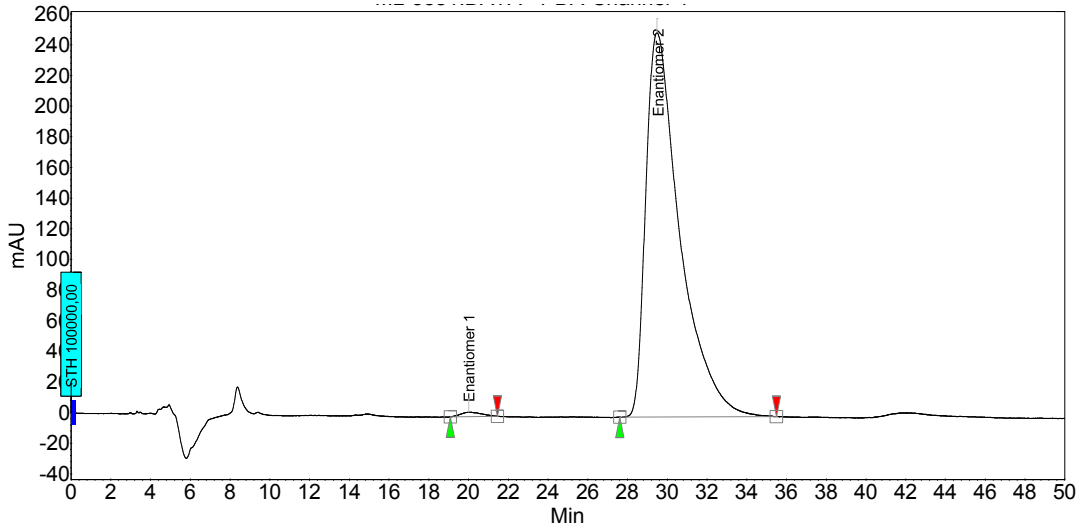
4.2 HPLC-spectra

3-*O*-Benzoyl -4,6-di-*O*-benzyl-*myo*-inositol (3a)



Peak results :

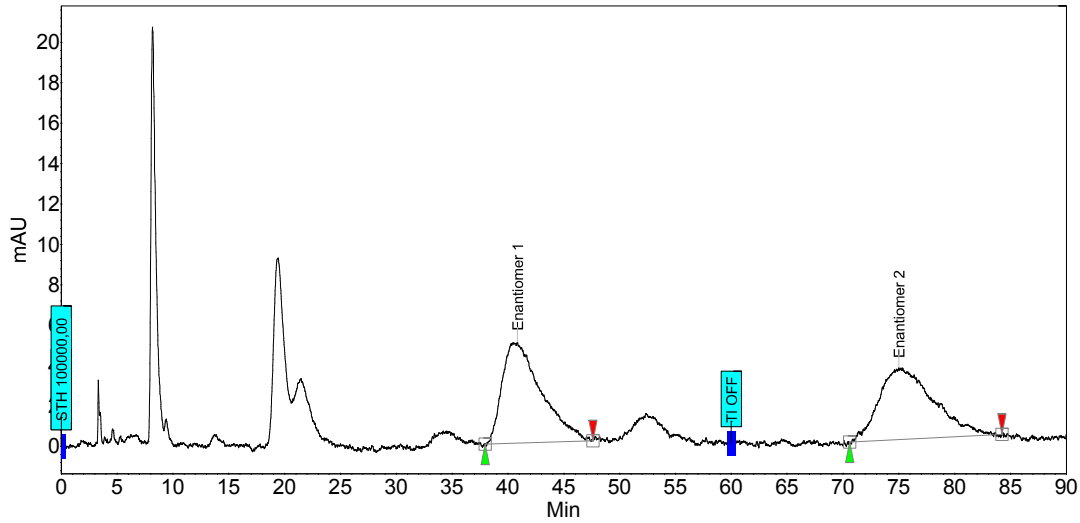
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	Enantiomer 1	19,88	49,00	32,9	45,8	49,001
2	Enantiomer 2	30,57	51,00	21,7	47,6	50,999
Total			100,00	54,6	93,4	100,000



Peak results :

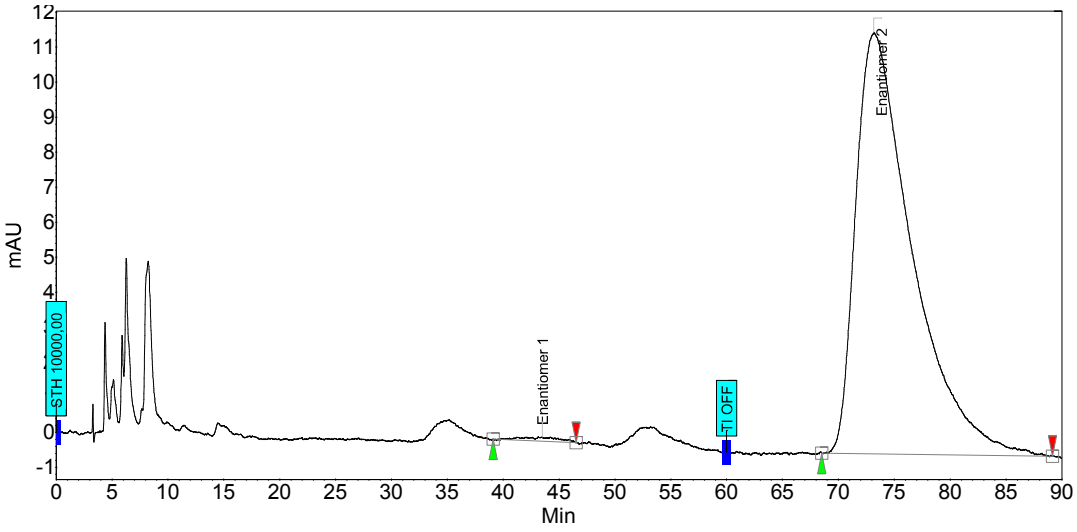
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	Enantiomer 1	20,01	0,68	2,8	3,4	0,680
2	Enantiomer 2	29,48	99,32	250,7	497,5	99,320
Total			100,00	253,5	500,9	100,000

3-*O*-Benzoyl -4,6-di-*O*-(para-methoxy-benzyl)-*myo*-inositol (3b)



Peak results :

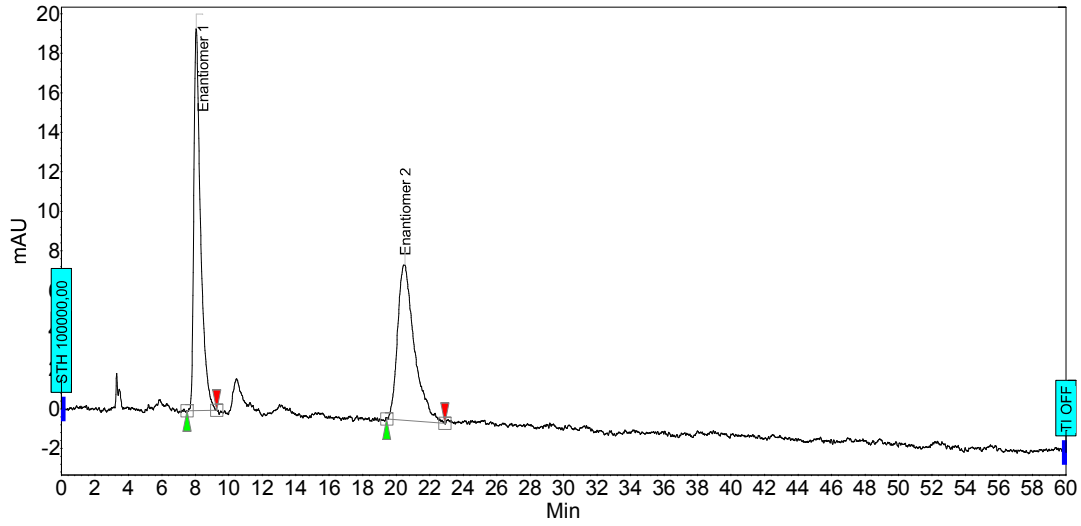
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	Enantiomer 1	40,84	50,45	5,0	20,2	50,454
2	Enantiomer 2	74,99	49,55	3,6	19,8	49,546
Total			100,00	8,6	40,0	100,000



Peak results :

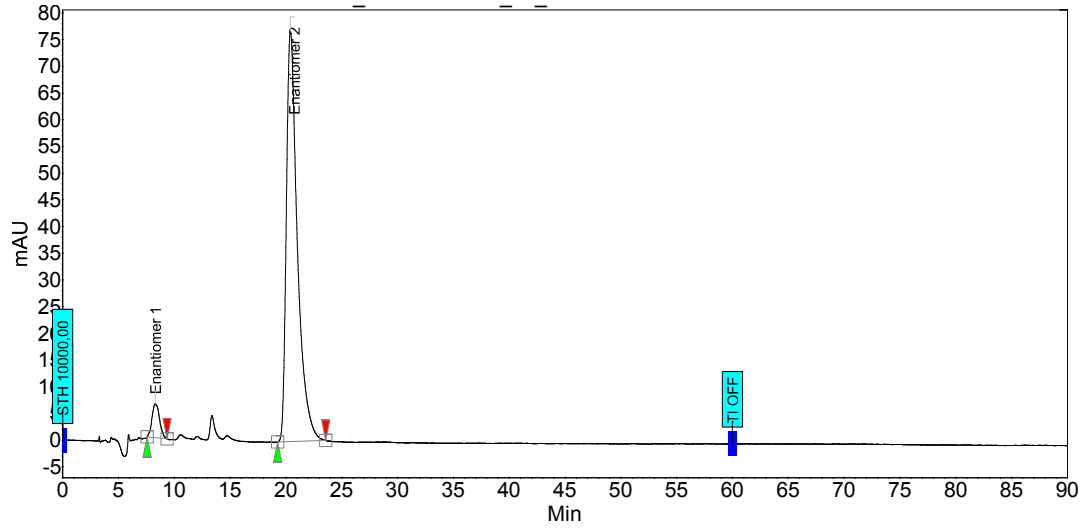
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	Enantiomer 1	43,49	0,66	0,1	0,5	0,656
2	Enantiomer 2	73,17	99,34	12,0	70,1	99,344
Total			100,00	12,2	70,6	100,000

3-*O*-Benzoyl -4,6-di-*O*-allyl-*myo*-inositol (3c)



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	Enantiomer 1	8,05	49,79	19,3	9,0	49,787
2	Enantiomer 2	20,52	50,21	7,9	9,1	50,213
Total			100,00	27,2	18,1	100,000



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	Enantiomer 1	8,29	5,32	6,3	4,9	5,323
2	Enantiomer 2	20,40	94,68	76,8	87,9	94,677
Total			100,00	83,2	92,8	100,000

5. Crystallographic Data

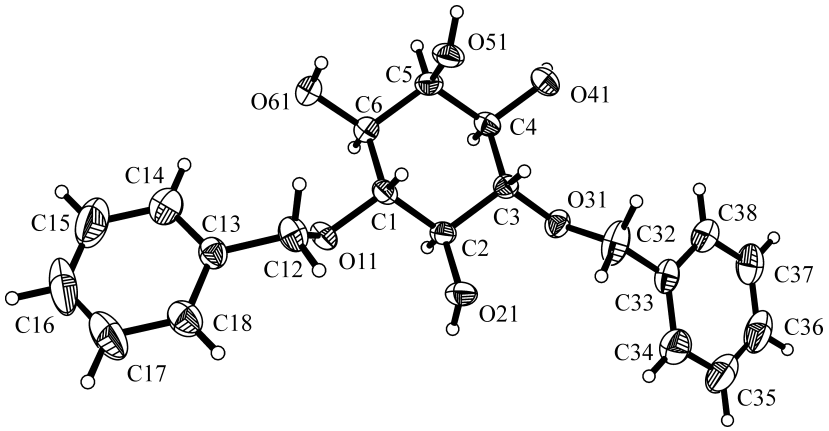
X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% (**4c (CCDC-938830), 9 (CCDC-938831)**) or 50% (**4a (CCDC-938829)**) probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For the compound **4a (CCDC-938829)** the CH2-Ph group was found disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. A disordered over two positions H_2O molecule was found in the asymmetrical unit of compound **9 (CCDC-938831).** Several restraints (SADI, DFIX, DANG) were used in order to improve refinement stability.

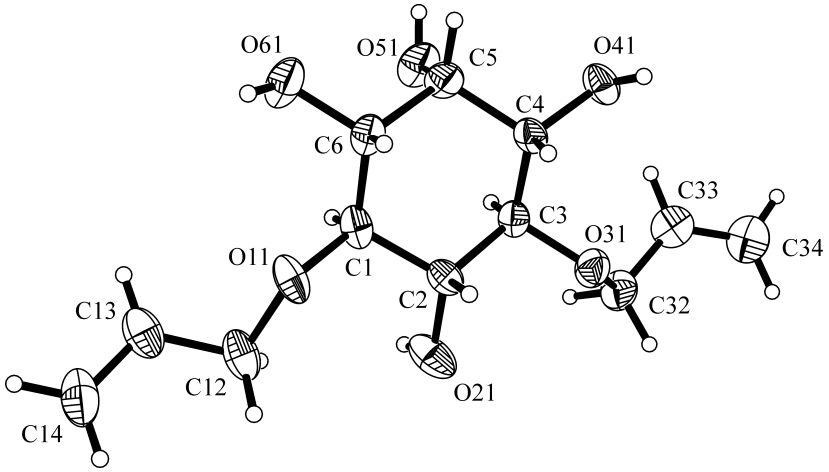
X-ray crystal structure analysis of 4a (CCDC-938829): formula $C_{20}H_{24}O_6$, M = 360.39, colourless crystal, 0.23 x 0.15 x 0.12 mm, a = 16.5605(3), b = 6.6101(1), c = 16.8166(3) Å, β = 93.303(1)°, V = 1837.8(5) Å^3, ρ_{calc} = 1.303 gcm^{-3}, μ = 0.096 mm^{-1}, empirical absorption correction ($0.978 \leq T \leq 0.988$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 12943 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 4501 independent (R_{int} = 0.037) and 3543 observed reflections [$I>2\sigma(I)$], 279 refined parameters, R = 0.056, wR^2 = 0.131, max. (min.) residual electron density 0.27(-0.20) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 4c (CCDC-938830): formula $C_{12}H_{20}O_6$, M = 260.28, colourless crystal, 0.20 x 0.20 x 0.07 mm, a = 21.6206(4), b = 11.0216(2), c = 23.9782(5) Å, β = 108.049(1)°, V = 5432.68(18) Å^3, ρ_{calc} = 1.273 gcm^{-3}, μ = 0.102 mm^{-1}, empirical absorption correction ($0.979 \leq T \leq 0.992$), Z = 4, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 15088 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 6704 independent (R_{int} = 0.037) and 4318 observed reflections [$I>2\sigma(I)$], 363 refined parameters, R = 0.084, wR^2 = 0.227, max. (min.) residual electron density 0.51(-0.42) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

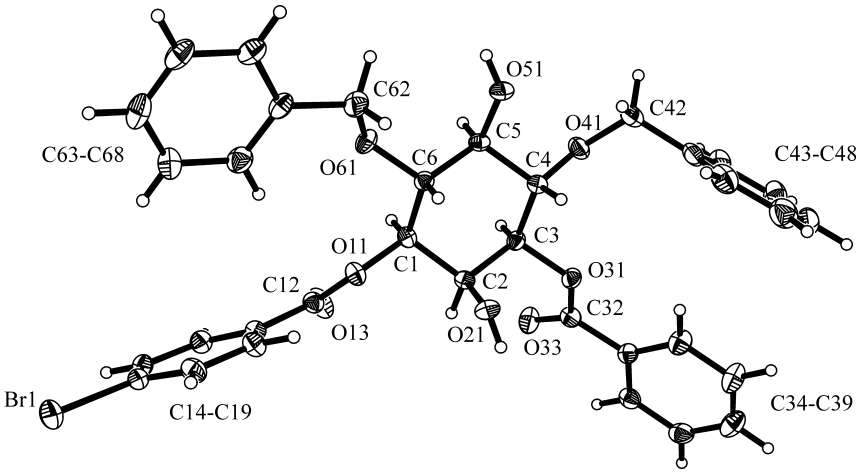
X-ray crystal structure analysis of 9 (CCDC-938831): formula $C_{34}H_{31}BrO_8$ x 2 H_2O, M = 683.53, colourless crystal, 0.28 x 0.23 x 0.23 mm, a = 11.9744(2), b = 8.0367(2), c = 17.1372(3) Å, β = 108.858(1)°, V = 1560.67(2) Å^3, ρ_{calc} = 1.455 gcm^{-3}, μ = 1.376 mm^{-1}, empirical absorption correction ($0.699 \leq T \leq 0.742$), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 8893 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 4744 independent (R_{int} = 0.021) and 4550 observed reflections [$I>2\sigma(I)$], 439 refined parameters, R = 0.031, wR^2 = 0.070, max. (min.) residual electron density 0.17(-0.21) e.Å^{-3}, hydrogen atom at O51 was refined freely; the hydrogen atoms from the water molecule (O71, O72 and O72A) were refined freely, but with O-H distance restraints (SADI) and with fixed U-value. Flack parameter was refined to -0.014(8).


O51
C5
O61
C6
O41
C4
C14
C1
C3
O31
C38
C15
C13
C12
O11
C2
C32
C37
C33
O21
C16
C18
C36
C34
C17
C35

50%


O61
O51
C5
O41
C4
C6
C33
C3
O31
C34
O11
C1
C2
C32
C13
C12
O21
C14

30%


O51
C62
C42
C5
O41
C63-C68
C6
C4
C43-C48
O61
C3
O11
C1
O31
C12
C2
C32
O13
O21
O33
Br1
C14-C19
C34-C39

30%