Supplementary Material for Organic & Biomolecular Chemistry

Supporting Information

Experimental

Synthesis and full characterisation of compounds **43**-**53**, **58**, **67**, **68**, **71**-**73**.

***tert*-Butyldimethylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-*p*-methoxybenzyl-β-D-glucopyranoside 43.** To a solution of **39**[1,2] (1.47 g, 3.61 mmol) and *p*-metoxybenzyl trichloroacetimidate[3] (6.12 g, 21.66 mmol) with 4Å molecular sieves in dry CH_2Cl_2 (18 mL) $Et_2O{\cdot}BF_3$ (155 μl, 1.223 mmol) was added at 0ºC and stirred for 18 h under an argon atmosphere. The mixture was neutralized with Et_3N, concentrated in *vacuo* and the residue was purified by flash chromatography (hexane/AcOEt 29/1) to yield 1.33 g (70%) of **43** as a colourless syrup. $[\alpha]^{20}_{;D}$ = - 85.3 (*c* = 0.8, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.49 (m, 2H, Ar*H benzylidene*), 7.39 (m, 3H, Ar*H benzylidene*), 7.31 (d, *J* = 8.5 Hz, 2H, Ar*H PMB*), 6.86 (d, *J* = 8.5 Hz, 2H, Ar*H PMB*), 5.57 (s, 1H, CH_{benzylic} *benzylidene*), 4.83 (d, *J* = 11.0 Hz, 1H, CH_{benzylic} *PMB*), 4.73 (d, *J* = 11.0 Hz, 1H, CH_{benzylic} *PMB*), 4.58 (d, $J_{1,2}$ = 8.0 Hz, 1H, H_1), 4.29 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.5 Hz, 1H, H_6), 3.80 (s, 3H, CH_3O *PMB*), 3.79 (t, $J_{6',6} = J_{6',5}$ = 10.5 Hz, 1H, $H_{6'}$), 3.70 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, H_4), 3.51 (t, $J_{3,4} = J_{3,2}$ = 9.5 Hz, 1H, H_3), 3.38 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,6'} = J_{5,4}$ = 10.0 Hz, 1H, H_5), 3.35 (dd, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_2), 0.94 (s, 9H, (CH_3)$_3$C *TBDMS*), 0.17 (s, 3H, CH_3 *TBDMS*), 0.16 (s, 3H, CH_3 *TBDMS*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 159.35 (Ar*C PMB*), 137.24 (Ar*C benzylidene*), 130.08 (Ar*C PMB*), 129.81 (2 x Ar*C*H *PMB*), 129.01 (Ar*C*H *benzylidene*), 128.24 (2 x Ar*C*H *benzylidene*), 126.02 (2 x Ar*C*H *benzylidene*), 113.76 (2 x Ar*C*H *PMB*), 101.32 (*C*H$_{\text{benzylic}}$ *benzylidene*), 97.48 (C_1), 81.65 (C_4), 78.42 (C_3), 74.46 (*C*H$_{2\ \text{benzylic}}$ *PMB*), 68.74 (C_2), 68.62 (C_6), 66.35 (C_5), 55.24 (*C*H$_3$O *PMB*), 25.55 ((*C*H$_3$)$_3$C *TBDMS*), 17.94 ((CH$_3$)$_3$*C TBDMS*), -4.36, -5.19 (*C*H$_3$ *TBDMS*). FAB-MS: *m/z* 550 $(M + Na)^+$. Anal. calcd. for $C_{27}H_{37}O_6SiN_3$ C 61.46%; H 7.07%; N 7.96%; found C 61.42%; H 7.00%; N 8.11%.

2-Azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-*p*-methoxybenzyl-α,β-D-glucopyranose 44. A solution of **43** (1.33 g, 2.52 mmol) in dry THF (12 mL) under an argon atmosphere was cooled at - 40ºC and glacial AcOH (216 μl, 3.778 mmol) first and TBAF (1.0 M solution in THF, 3.0 mL) then were added. After 2 h the mixture was diluted with Et_2O (50 mL) and washed with sat. NaCl solution (50 mL). The aqueous layer was extracted with Et_2O (2 x 25 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt 4/1) to yield and α/β anomeric mixture of **44**

(1.02 g, 98%) as a colourless syrup. *Data for a α/β = 1/1 mixture*: ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.50 (m, 4H, Ar*H benzylidene*), 7.40 (m, 6H, Ar*H benzylidene*), 7.31 (d, J = 9.0 Hz, 2H, Ar*H PMB*), 7.30 (d, J = 9.0 Hz, 2H, Ar*H PMB*), 6.863 (d, J = 9.0 Hz, 2H, Ar*H PMB*), 6.860 (d, J = 9.0 Hz, 2H, Ar*H PMB*), 5.60 (s, 1H, CH_{benzylic} *benzylidene*), 5.87 (s, 1H, CH_{benzylic} *benzylidene*), 5.29 (t, $J_{1,OH} = J_{1,2}$ = 3.5 Hz, 1H, $H_{1\alpha}$), 4.89 (d, J = 10.5 Hz, 1H, CH_{benzylic} *PMB*), 4.86 (d, J = 11.0 Hz, 1H, CH_{benzylic} *PMB*), 4.75 (d, J = 10.5 Hz, 1H, CH_{benzylic} *PMB*), 4.74 (d, J = 10.5 Hz, 1H, CH_{benzylic} *PMB*), 4.67 (dd, $J_{1,OH}$ = 5.5 Hz, $J_{1,2}$ = 8.0 Hz, 1H, $H_{1\beta}$), 4.34 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.5 Hz, 1H, $H_{6\beta}$), 4.28 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.0 Hz, 1H, $H_{6\alpha}$), 4.12 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,6'} = J_{5,4}$ = 10.0 Hz, 1H, $H_{5\alpha}$), 4.08 (t, $J_{3,2} = J_{3,4}$ = 9.5 Hz, 1H, $H_{3\alpha}$), 3.799 (s, 3H, CH_3O *PMB*), 3.797 (t, $J_{6',6} = J_{6',5}$ = 10.5 Hz, 1H, $H_{6\beta'}$), 3.795 (s, 3H, CH_3O *PMB*), 3.75 (t, $J_{6',6} = J_{6',5}$ = 10.0 Hz, 1H, $H_{6\alpha'}$), 3.72 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, $H_{4\beta}$), 3.71 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, $H_{4\alpha}$), 3.61 (t, $J_{3,2} = J_{3,4}$ = 9.5 Hz, 1H, $H_{3\beta}$), 3.48 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, 1H, $H_{2\alpha}$), 3.45 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,6'} = J_{5,4}$ 9.5 Hz, 1H, $H_{5\beta}$), 3.39 (dd, $J_{2,1}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, 1H, $H_{2\beta}$), 3.21 (d, $J_{OH,1}$ = 5.5 Hz, 1H, OH_β), 2.78 (d, $J_{OH,1}$ = 3.5 Hz, 1H, OH_α). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 159.39 (2 x Ar*C PMB*), 137.16, 137.02 (2 x Ar*C benzylidene*), 129.99, 129.94 (2 x 2 x Ar*C*H *PMB*), 129.84, 129.77 (2 x Ar*C PMB*), 129.07, 129.05 (2 x Ar*C*H *benzylidene*), 128.27 (2 x 2 x Ar*C*H *benzylidene*), 125.99, 125.94 (2 x 2 x Ar*C*H *benzylidene*), 113.85, 113.80 (2 x 2 x Ar*C*H *PMB*), 101.43, 101.30 (2 x *C*H$_{\text{benzylic}}$ *benzylidene*), 96.43 ($C_{1\beta}$), 92.63 ($C_{1\alpha}$), 82.67 ($C_{4\alpha}$), 81.48 ($C_{4\beta}$), 78.60 ($C_{3\beta}$), 75.77 ($C_{3\alpha}$), 74.70, 74.56 (*C*H$_2$ $_{\text{benzylic}}$ *PMB*), 68.87 ($C_{6\alpha}$), 68.43 ($C_{6\beta}$), 67.21 ($C_{2\beta}$), 66.37 ($C_{5\beta}$), 63.50 ($C_{2\alpha}$), 62.72 ($C_{5\alpha}$), 55.23 (2 x *C*H$_3$O *PMB*). FAB-MS: m/z 436 $(M + Na)^+$. Anal. calcd. for $C_{21}H_{23}O_6N_3$: C 61.01%; H 5.61%; N 10.16%; found C 60.78%; H 5.76%; N 10.28%.

2-Azido-4,6-benzylidene-2-deoxy-3-*O*-*p*-methoxybenzyl-α,β-D-glucopyranosyl trichloroacetimidate 45. To a solution of **44** (1.02 g, 2.47 mmol) in dry CH_2Cl_2 (12 mL), trichloroacetonitrile (3.7 mL, 36.9 mmol) and DBU (19 µl, 0.127 mmol) were added. The solution was stirred for 2 h under an argon atmosphere and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt/Et_3N 4/0.9/0.1) to yield and α/β anomeric mixture of **45** (1.31 g, 95%) as a white foam. *RMN data for α-anomer extracted from an α/β = 2/1 mixture*: ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 8.74 (s, 1H, OCN*H*CCl_3), 7.52 (m, 2H, Ar*H benzylidene*), 7.40 (m, 3H, Ar*H benzylidene*), 7.33 (d, J = 8.5 Hz, 2H, Ar*H PMB*), 6.88 (d, J = 8.5 Hz, 2H, Ar*H PMB*), 6.37 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_1), 5.62 (s, 1H, CH_{benzylic} *benzylidene*), 4.96 (d, J = 10.5 Hz, 1H, CH_{benzylic} *PMB*), 4.78 (d, J = 10.5 Hz, 1H, CH_{benzylic} *PMB*), 4.34 (dd, $J_{6,5}$= 5.0 Hz, $J_{6,6'}$ = 10.5 Hz, 1H, H_6), 4.16 (t, $J_{3,4} = J_{3,2}$ = 9.5 Hz, 1H, H_3), 4.06 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,6'}$

= $J_{5,4}$ = 10.0 Hz, 1H, H_5), 3.82 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_4), 3.80 (s, 3H, CH_3O *PMB*), 3.78 (t, $J_{6',5}$ = $J_{6',6}$ = 10.5 Hz, 1H, $H_{6'}$), 3.70 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_2). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 160.85 (OCNHCCl_3), 159.52 (Ar*C PMB*), 136.91 (Ar*C benzylidene*), 129.98 (2 x Ar*C*H *PMB*), 129.71 (Ar*C PMB*), 129.14 (Ar*C*H *benzylidene*), 128.34 (2 x Ar*C*H *benzylidene*), 125.93 (2 x Ar*C*H *benzylidene*), 113.88 (2 x Ar*C*H *PMB*), 101.45 ($CH_{benzylic}$ *benzylidene*), 94.87 (C_1), 90.72 (OCNHCCl_3), 82.23 (C_4), 75.93 (C_3), 74.89 ($CH_{2\ benzylic}$ *PMB*), 68.56 (C_6), 65.24 (C_5), 62.44 (C_2), 55.28 (CH_3O *PMB*). HRMS *m/z* calcd. for $C_{23}H_{23}O_6N_4Cl_3Na^+$: 579.0577; found 579.0581 $(M + Na)^+$, 581.0551 $(M + Na + 2)^+$, 583.0506 $(M + Na + 4)^+$.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-di-yl)-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-D-*myo*-inositol 46.[4] To a solution of **42**[5,6] (1.30 g, 2.46 mmol) and **37**[7] (1.15 g, 2.07 mmol) in dry Et_2O (38 mL) with 4Å molecular sieves under an argon atmosphere, TMSOTf (23 µl, 0.106 mmol) at - 40ºC was added. The solution was stirred for 2 h, neutralised with Et_3N and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt 24/1, 14/1, 9/1, 4/1, 2/1, 1/1) to yield 1.37 g (72%) of α-(1→6) isomer **46**, 76 mg (4%) of β-(1→6) isomer **48** and 114 mg (6%) of α-(1→5) isomer **50** as white foams. Data for **46**: TLC (hexane/AcOEt 4/1) R_f = 0.47; $[\alpha]^{20}_{;D}$ = + 37.0 (c = 1.2, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.51 (m, 2H, Ar*H*), 7.41-7.26 (m, 8H, Ar*H*), 5.58 (s, 1H, C$H_{benzylic}$ *benzylidene*), 5.41 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1b}), 4.98 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.81 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.41 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,4}$ = $J_{5,6'}$ = 10.0 Hz, 1H, H_{5b}), 4.28 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.0 Hz, 1H, H_{6b}), 4.21 (dd, $J_{2,3}$ = 4.0 Hz, $J_{2,1}$ = 5.5 Hz, 1H, H_{2a}), 4.12 (t, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H_{3b}), 4.05 (dd, $J_{1,2}$ = 5.5 Hz, $J_{1,6}$ = 6.5 Hz, 1H, H_{1a}), 3.93 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_{3a}), 3.86 (t, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, 1H, H_{4a}), 3.75 (dd, $J_{6,1}$ = 6.5 Hz, $J_{6,5}$ = 10.5 Hz, 1H, H_{6a}), 3.73 (t, $J_{6',5}$ = $J_{6',6}$ = 10.0 Hz, 1H, $H_{6b'}$), 3.71 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 3.42 (ddd, $J_{5,OH}$ = 1.0 Hz, $J_{5,4}$ = 9.0 Hz, $J_{5,6}$ = 10.0 Hz, 1H, H_{5a}), 3.40 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}), 2.56 (d, $J_{OH,5}$ = 1.0 Hz, 1H, OH), 1.96 (m, 1H, L-*camphor*), 1.88 (m, 1H, L-*camphor*), 1.71 (m, 2H, L-*camphor*), 1.50 (d, J = 13.0 Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.24 (m, 1H, L-*camphor*), 1.13-0.95 (m, 31H, L-*camphor* + *TIPDS*), 0.85 (s, 3H, CH_3 L-*camphor*), 0.84 (s, 3H, CH_3 L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 138.00, 137.40 (Ar*C*), 128.82, 128.33, 128.14, 127.74, 125,98 (Ar*C*H), 117.70 ($C_{acetalic}$ L-*camphor*), 101.22 ($CH_{benzylic}$ *benzylidene*), 96.95 (C_{1b}), 82.78 (C_{4b}), 80.04 (C_{6a}), 76.95 (C_{2a}), 76.27 (C_{3b}), 76.13 (C_{1a}), 75.73 (C_{4a}), 74.98 ($CH_{2\ benzylic}$), 72.69 (C_{3a}), 72.12 (C_{5a}), 68.93 (C_{6b}), 63.10 (C_{2b}), 62.27 (C_{5b}), 51.46, 47.95, 45.18, 45.10, 29.50, 27.00, 20.43, 20.12, 17.50, 17.36, 17.32, 17.26, 17.17, 17.07, 16.98, 12.88, 12.68, 12.17, 11.96, 9.76 (*C*, *C*H

L-*camphor* + *TIPDS*). FAB-MS: *m/z* 922 M^+, 944 $(M + Na)^+$. Anal. calcd. for $C_{48}H_{71}O_{11}N_3Si_2$: C 62.51%; H 7.76%; N 4.56%; found C 62.24%; H 7.81%; N 4.44%.

Data for **48**: TLC (hexane/AcOEt 4/1) R_f = 0.41; $[\alpha]^{20}_D$ = - 39.0 (*c* = 0.7, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.46 (m, 2H, Ar*H*), 7.41-7.35 (m, 5H, Ar*H*), 7.34-7.26 (m, 3H, Ar*H*), 5.56 (s, 1H, C$H_{benzylic}$ *benzylidene*), 4.89 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.792 (br d, $J_{1,2}$ = 6.5 Hz, 1H, H_{1b}), 4.787 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.32 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.5 Hz, 1H, H_{6b}), 4.22 (t, $J_{2,1} = J_{2,3}$ = 4.5 Hz, 1H, H_{2a}), 3.93 (dd, $J_{3,2}$ = 4.5 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_{3a}), 3.92 (dd, $J_{1,2}$ = 5.0 Hz, $J_{1,6}$ = 7.0 Hz, 1H, H_{1a}), 3.85 (t, $J_{6',5} = J_{6',6}$ = 10.0 Hz, 1H, $H_{6b'}$), 3.84 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, H_{4a}), 3.75 (br t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 3.68 (dd, $J_{6,1}$ = 7.0 Hz, $J_{6,5}$ = 10.5 Hz, 1H, H_{6a}), 3.58 (m, 2H, H_{2b} + H_{3b}), 3.52 (td, $J_{5,OH}$ = 1.0 Hz, $J_{5,4} = J_{5,6}$ = 10.0 Hz, 1H, H_{5a}), 3.43 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,4} = J_{5,6'}$ = 10.0 Hz, 1H, H_{5b}), 2.79 (d, $J_{OH,5}$ = 1.0 Hz, 1H, OH), 1.98 (m, 2H, L-*camphor*), 1.71 (m, 2H, L-*camphor*), 1.53 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.37 (m, 1H, L-*camphor*), 1.28 (m, 1H, L-*camphor*), 1.14-0.96 (m, 31H, L-*camphor* + *TIPDS*), 0.86 (s, 3H, CH_3 L-*camphor*), 0.84 (s, 3H, CH_3 L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 137.87, 137.22 (Ar*C*), 128.96, 128.32, 128.22, 127.80, 125.95 (Ar*C*H), 117.63 ($C_{acetalic}$ L-*camphor*), 102.97 (C_{1b}), 101.23 (*C*H$_{benzylic}$ *benzylidene*), 83.43 (C_{6a}), 81.42 (C_{4b}), 79.13 (C_{3b}), 76.75 (C_{2a}), 75.63 (C_{4a}), 74.90 (*C*H$_2$ $_{benzylic}$), 74.02 (C_{1a}), 73.84 (C_{5a}), 72.91 (C_{3a}), 68.69 (C_{6b}), 66.07 (C_{5b}), 65.89 (C_{2b}), 51.60, 48.05, 45.17, 29.70, 27.02, 20.46, 20.14, 17.53, 17.39, 17.35, 17.29, 17.19, 17.08, 17.00, 12.93, 12.69, 12.22, 11.99, 9.97 (*C*, *C*H L-*camphor* + *TIPDS*). FAB-MS: *m/z* 922 M^+, 944 $(M + Na)^+$. Anal. calcd. for $C_{48}H_{71}O_{11}N_3Si_2$: C 62.51%; H 7.76%; N 4.56%; found C 62.67%; H 7.47%; N 4.69%.

Data for **50**: TLC (hexane/AcOEt 4/1) R_f = 0.17; $[\alpha]^{20}_D$ = + 6.8 (*c* = 1.0, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.48 (m, 2H, Ar*H*), 7.40-7.27 (m, 8H, Ar*H*), 5.57 (s, 1H, C$H_{benzylic}$ *benzylidene*), 5.48 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1b}), 4.97 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.80 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.38 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,4} = J_{5,6'}$ = 10.0 Hz, 1H, H_{5b}), 4.29 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.0 Hz, 1H, H_{6b}), 4.20 (t, $J_{2,1} = J_{2,3}$ = 5.0 Hz, 1H, H_{2a}), 4.17 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, H_{4a}), 4.10 (t, $J_{3,2} = J_{3,4}$ = 9.5 Hz, 1H, H_{3b}), 3.90 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_{3a}), 3.82 (t, $J_{1,2} = J_{1,6}$ = 6.0 Hz, 1H, H_{1a}), 3.713 (t, $J_{6',5} = J_{6',6}$ = 10.0 Hz, 1H, $H_{6b'}$), 3.710 (t, $J_{4,3} = J_{4,5}$ = 9.0 Hz, 1H, H_{4b}), 3.65 (ddd, $J_{6,OH}$ = 3.5 Hz, $J_{6,1}$ = 7.0 Hz, $J_{6,5}$ = 10.0 Hz, 1H, H_{6a}), 3.47 (t, $J_{5,4} = J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.42 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}), 2.65 (d, $J_{OH,6}$ = 3.0 Hz, 1H, OH), 1.94 (m, 2H, L-*camphor*), 1.71 (m, 2H, L-*camphor*), 1.48 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.25 (m, 1H, L-*camphor*), 1.17-0.95 (m, 31H, L-*camphor* + *TIPDS*), 0.85 (s, 3H, CH_3 L-*camphor*), 0.82 (s, 3H, CH_3 L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 138.0, 137.40 (Ar*C*), 128.89, 128.37, 128.12, 127.79, 125.99 (Ar*C*H), 117.96 ($C_{acetalic}$

L-*camphor*), 101.14 (*C*H$_{benzylic}$ *benzylidene*), 98.60 (C$_{1b}$), 82.63 (C$_{4b}$), 78.15 (C$_{5a}$), 76.60 (C$_{1a}$), 76.47 (C$_{3b}$), 76.44 (C$_{2a}$), 76.08 (C$_{4a}$), 75.22 (C$_{6a}$), 74.98 (*C*H$_{2\ benzylic}$), 73.30 (C$_{3a}$), 68.77 (C$_{6b}$), 63.08 (C$_{2b}$), 62.47 (C$_{5b}$), 51.53, 48.01, 45.14, 45.12, 29.43, 27.03, 20.42, 19.99, 17.67, 17.58, 17.32, 17.27, 17.23, 17.22, 17.13, 13.02, 12.75, 12.37, 12.07, 9.86 (*C*, *C*H L-*camphor* + *TIPDS*). FAB-MS: *m/z* 922 M^+, 944 $(M + Na)^+$. Anal. calcd. for $C_{48}H_{71}O_{11}N_3Si_2$: C 62.51%; H 7.76%; N 4.56%; found C 62.13%; H 8.01%; N 4.36%.

2-Azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-*p*-methoxybenzyl-α-D-glucopyranosyl-(1→6)-3,4-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-di-yl)-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-D-*myo*-inositol 47. To a solution of **45** (500 mg, 0.896 mmol) and **37**[7] (416 mg, 0.747 mmol) in dry Et_2O (15 mL) with 4Å molecular sieves under an argon atmosphere, TMSOTf (7 μl, 0.039 mmol) at -40ºC was added. The solution was stirred for 2 h, neutralised with Et_3N and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt 19/1, 14/1, 9/1, 4/1, 2/1) to yield 470 mg (66%) of α-(1→6) isomer **47**, 28 mg (4%) of β-(1→6) isomer **49** and 100 mg (14%) of α-(1→5) isomer **51** as white foams. *Data for **47***: TLC (hexane/AcOEt 4/1) R_f = 0.43; $[\alpha]^{20}_{;D}$ = + 28.0 (*c* = 0.7, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.51 (m, 2H, Ar*H benzylidene*), 7.38 (m, 3H, Ar*H benzylidene*), 7.32 (d, *J* = 8.5 Hz, 2H, Ar*H PMB*), 6.85 (d, *J* = 8.5 Hz, 2H, Ar*H PMB*), 5.58 (s, 1H, C*H*$_{benzylic}$ *benzylidene*), 5.39 (d, $J_{1,2}$ = 3.5 Hz, 1H, H$_{1b}$), 4.90 (d, *J* = 11.0 Hz, 1H, C*H*$_{benzylic}$ *PMB*), 4.74 (d, *J* = 11.0 Hz, 1H, C*H*$_{benzylic}$ *PMB*), 4.40 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,4}$ = $J_{5,6'}$ = 10.0 Hz, 1H, H$_{5b}$), 4.28 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.0 Hz, 1H, H$_{6b}$), 4.20 (t, $J_{2,1}$ = $J_{2,3}$ = 5.0 Hz, 1H, H$_{2a}$), 4.10 (t, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H$_{3b}$), 4.04 (t, $J_{1,2}$ = $J_{1,6}$ = 6.0 Hz, 1H, H$_{1a}$), 3.93 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H$_{3a}$), 3.86 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H$_{4a}$), 3.79 (s, 3H, C*H*$_3$O *PMB*), 3.74 (dd, $J_{6,1}$ = 6.0 Hz, $J_{6,5}$ = 10.0 Hz, 1H, H$_{6a}$), 3.72 (t, $J_{6',5}$ = $J_{6',6}$ = 10.0 Hz, 1H, H$_{6b'}$), 3.68 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H$_{4b}$), 3.42 (t, $J_{5,4}$ = $J_{5,6}$ = 9.5 Hz, 1H, H$_{5a}$), 3.38 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H$_{2b}$), 2.56 (s, 1H, OH), 1.96 (m, 1H, L-*camphor*), 1.87 (m, 1H, L-*camphor*), 1.71 (m, 2H, L-*camphor*), 1.49 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.24 (m, 1H, L-*camphor*), 1.13-0.93 (m, 31H, L-*camphor* + *TIPDS*), 0.85 (s, 3H, C*H*$_3$ L-*camphor*), 0.83 (s, 3H, C*H*$_3$ L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 159.37 (Ar*C PMB*), 137.49 (Ar*C benzylidene*), 130.22 (Ar*C PMB*), 129.87 (2 x Ar*C*H *PMB*), 128.87 (Ar*C*H *benzylidene*), 128.19 (2 x Ar*C*H *benzylidene*), 126.04 (2 x Ar*C*H *benzylidene*), 117.76 (*C*$_{acetalic}$ L-*camphor*), 113.83 (2 x Ar*C*H *PMB*), 101.28 (*C*H$_{benzylic}$ *benzylidene*), 96.98 (C$_{1b}$), 82.83 (C$_{4b}$), 80.10 (C$_{6a}$), 77.00 (C$_{2a}$), 76.19 (C$_{1a}$), 76.01 (C$_{3b}$), 75.77 (C$_{4a}$), 74.71 (*C*H$_{2\ benzylic}$ *PMB*), 72.74 (C$_{3a}$), 72.18 (C$_{5a}$), 68.99 (C$_{6b}$), 63.14 (C$_{2b}$), 62.33 (C$_{5b}$), 55.26 (*C*H$_3$O *PMB*), 51.51, 48.00, 45.22, 45.16, 29.54, 27.04, 20.46, 20.15, 17.53, 17.39, 17.36, 17.29, 17.20, 17.10, 17.01, 12.93, 12.73, 12.23, 12.02, 9.79 (*C*, *C*H L-*camphor* +

TIPDS)**.** FAB-MS: *m/z* 951 M^+, 974 $(M + Na)^+$. Anal. calcd. for $C_{49}H_{73}O_{12}N_3Si_2$: C 61.80%; H 7.73%; N 4.41%; found C 61.77%; H 7.49%; N 4.53%.

*Data for **49***: TLC (hexane/AcOEt 4/1) R_f = 0.38; $[\alpha]^{20}_D$ = - 39.9 (*c* = 0.9, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.47 (m, 2H, Ar*H benzylidene*), 7.38 (m, 3H, Ar*H benzylidene*), 7.29 (d, *J* = 8.5 Hz, 2H, Ar*H PMB*), 6.84 (d, *J* = 8.5 Hz, 2H, Ar*H PMB*), 5.56 (s, 1H, C$H_{benzylic}$ *benzylidene*), 4.82 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$ *PMB*), 4.77 (d, $J_{1,2}$ = 8.0 Hz, 1H, H_{1b}), 4.72 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$ *PMB*), 4.31 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.5 Hz, 1H, H_{6b}), 4.22 (t, $J_{2,1}$ = $J_{2,3}$ = 4.5 Hz, 1H, H_{2a}), 3.93 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H_{3a}), 3.92 (dd, $J_{1,2}$ = 5.0 Hz, $J_{1,6}$ = 7.5 Hz, 1H, H_{1a}), 3.843 (t, $J_{6',5}$ = $J_{6',6}$ = 10.0 Hz, 1H, $H_{6b'}$), 3.837 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4a}), 3.79 (s, 3H, CH_3O *PMB*), 3.73 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 3.68 (dd, $J_{6,1}$ = 7.0 Hz, $J_{6,5}$ = 10.5 Hz, 1H, H_{6a}), 3.56 (m, 2H, H_{2b} + H_{3b}), 3.51 (td, $J_{5,OH}$ = 1.5 Hz, $J_{5,4}$ = $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.42 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,4}$ = $J_{5,6'}$ = 10.0 Hz, 1H, H_{5b}), 2.81 (d, $J_{OH,5}$ = 1.5 Hz, 1H, OH), 1.98 (m, 2H, L-*camphor*), 1.71 (m, 2H, L-*camphor*), 1.53 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.37 (m, 1H, L-*camphor*), 1.27 (m, 1H, L-*camphor*), 1.14-0.97 (m, 31H, L-*camphor* + *TIPDS*), 0.86 (s, 3H, CH_3 L-*camphor*), 0.85 (s, 3H, CH_3 L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 159.36 (Ar*C PMB*), 137.26 (Ar*C benzylidene*), 129.96 (2 x Ar*C PMB* + Ar*C*H *PMB*), 128.97 (Ar*C*H *benzylidene*), 128.23 (2 x Ar*C*H *benzylidene*), 125.96 (2 x Ar*C*H *benzylidene*), 117.63 ($C_{acetalic}$ L-*camphor*), 113.77 (2 x Ar*C*H *PMB*), 102.98 (C_{1b}), 101.23 (*C*H$_{benzylic}$ *benzylidene*), 83.49 (C_{6a}), 81.44 (C_{4b}), 78.70 (C_{3b}), 76.75 (C_{2a}), 75.62 (C_{4a}), 74.56 (*C*H$_2$ $_{benzylic}$ *PMB*), 74.01 (C_{1a}), 73.84 (C_{5a}), 72.93 (C_{3a}), 68.70 (C_{6b}), 66.11 (C_{5b}), 65.86 (C_{2b}), 55.24 (*C*H$_3$O *PMB*), 51.60, 48.05, 45.18, 29.71, 27.02, 20.46, 20.14, 17.54, 17.40, 17.36, 17.35, 17.30, 17.20, 17.08, 17.00, 12.94, 12.70, 12.23, 12.00, 9.98 (*C*, *C*H L-*camphor* + *TIPDS*). FAB-MS: *m/z* 951 M^+, 974 $(M + Na)^+$. Anal. calcd. for $C_{49}H_{73}O_{12}N_3Si_2$: C 61.80%; H 7.73%; N 4.41%; found C 61.61%; H 7.40%; N 4.43%.

*Data for **51***: TLC (hexane/AcOEt 4/1) R_f = 0.19; $[\alpha]^{20}_D$ = + 3.9 (*c* = 0.9, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.49 (m, 2H, Ar*H benzylidene*), 7.38 (m, 3H, Ar*H benzylidene*), 7.31 (d, *J* = 9.0 Hz, 2H, Ar*H PMB*), 6.85 (d, *J* = 9.0 Hz, 2H, Ar*H PMB*), 5.57 (s, 1H, C$H_{benzylic}$ *benzylidene*), 5.46 (d, $J_{1,2}$ = 4.0 Hz, 1H, H_{1b}), 4.89 (d, *J* = 10.5 Hz, 1H, C$H_{benzylic}$ *PMB*), 4.73 (d, *J* = 10.5 Hz, 1H, C$H_{benzylic}$ *PMB*), 4.36 (td, $J_{5,6}$ = 5.0 Hz, $J_{5,4}$ = $J_{5,6'}$ = 10.0 Hz, 1H, H_{5b}), 4.28 (dd, $J_{6,5}$ = 5.0 Hz, $J_{6,6'}$ = 10.0 Hz, 1H, H_{6b}), 4.20 (t, $J_{2,1}$ = $J_{2,3}$ = 5.0 Hz, 1H, H_{2a}), 4.16 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4a}), 4.08 (t, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H_{3b}), 3.90 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_{3a}), 3.81 (t, $J_{1,2}$ = $J_{1,6}$ = 6.0 Hz, 1H, H_{1a}), 3.79 (s, 3H, CH_3O *PMB*), 3.71 (t, $J_{6',5}$ = $J_{6',6}$ = 10.0 Hz, 1H, $H_{6b'}$), 3.69 (t, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, 1H, H_{4b}), 3.65 (ddd, $J_{6,OH}$ = 3.5 Hz, $J_{6,1}$ = 6.5 Hz, $J_{6,5}$ = 9.5 Hz, 1H, H_{6a}), 3.47 (t, $J_{5,4}$ = $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.41 (dd, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H_{2b}), 2.62 (d, $J_{OH,6}$ = 3.5 Hz, 1H, OH), 1.95 (m, 2H, L-*camphor*), 1.71 (m, 2H, L-*camphor*), 1.48 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.24 (m, 1H, L-*camphor*), 1.17-

0.95 (m, 31H, L-*camphor* + *TIPDS*), 0.85 (s, 3H, CH_3 L-*camphor*), 0.82 (s, 3H, CH_3 L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 159.37 (Ar*C PMB*), 137.40 (Ar*C benzylidene*), 130.18 (Ar*C PMB*), 129.82 (2 x Ar*C*H *PMB*), 128.92 (Ar*C*H *benzylidene*), 128.17 (2 x Ar*C*H *benzylidene*), 126.02 (2 x Ar*C*H *benzylidene*), 117.88 ($C_{acetalic}$ L-*camphor*), 113.82 (2 x Ar*C*H *PMB*), 101.21 ($CH_{benzylic}$ *benzylidene*), 98.66 (C_{1b}), 82.62 (C_{4b}), 78.52 (C_{5a}), 76.45 (C_{1a}), 76.41 (C_{2a}), 76.25 (C_{3b}), 76.08 (C_{4a}), 75.22 (C_{6a}), 74.70 ($CH_{2\ benzylic}$ *PMB*), 73.35 (C_{3a}), 68.77 (C_{6b}), 63.10 (C_{2b}), 62.58 (C_{5b}), 55.25 (CH_3O *PMB*), 51.49, 48.02, 45.22, 45.16, 29.43, 27.08, 20.44, 20.05, 17.67, 17.58, 17.32, 17.28, 17.24, 17.13, 13.03, 12.76, 12.37, 12.09, 9.89 (*C*, *C*H L-*camphor* + *TIPDS*). FAB-MS: *m/z* 952 M^+, 974 $(M + Na)^+$. Anal. calcd. for $C_{49}H_{73}O_{12}N_3Si_2$: C 61.80%; H 7.73%; N 4.41%; found C 61.77%; H 7.67%; N 4.19%.

2-Azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-D-*myo*-inositol 52. To a solution of **46** (1.37 g, 1.49 mmol) in dry THF (30 mL) under an argon atmosphere, TBAF (1.0 M solution in THF, 4.5 mL) was added. The solution was stirred for 1 h, diluted with AcOEt (100 mL) and washed with sat. $NaHCO_3$ solution (100 mL). The aqueous layer was extracted with AcOEt (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$, concentrated in *vacuo* and coevaporated with dry toluene (2 x 30 mL). To a solution of the above residue in dry DMF (30 mL) under an argon atmosphere, NaH (535 mg 60% in mineral oil, 13.376 mmol) first and then BnBr (1.6 mL, 13.5 mmol) were added. The solution was stirred for 10 h and NH_3 al 30% (1.5 mL) at 0ºC was added. After 10 min the mixture was diluted with AcOEt (100 mL) and washed with 10 % HCl solution (100 mL). The aqueous layer was extracted with AcOEt (2 x 50 mL) and the combined organic layers were washed with sat. NaCl solution (3 x 250 mL), dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt, 19/1, 14/1, 9/1) to yield 1.34 g (95%) of **52** as a white foam. $[\alpha]^{20}_D$ = + 50.9 (*c* = 1.0, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.43 (m, 2H, Ar*H*), 7.41-7.23 (m, 20H, Ar*H*), 7.15-7.05 (m, 3H, Ar*H*), 5.58 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 5.56 (s, 1H, C$H_{benzylic}$ *benzylidene*), 4.91 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.78 (d, *J* = 11.5 Hz, 1H, C$H_{benzylic}$), 4.76 (d, *J* = 11.5 Hz, 1H, C$H_{benzylic}$), 4.74 (d, *J* = 12.0 Hz, 1H, C$H_{benzylic}$), 4.71 (d, *J* = 11.5 Hz, 1H, C$H_{benzylic}$), 4.69 (d, *J* = 12.0 Hz, 1H, C$H_{benzylic}$), 4.68 (d, *J* = 11.5 Hz, 1H, C$H_{benzylic}$), 4.67 (d, *J* = 10.5 Hz, 1H, C$H_{benzylic}$), 4.28 (dd, $J_{2,3}$ = 3.5 Hz, $J_{2,1}$ = 6.0 Hz, 1H, H_{2a}), 4.18 (m, 2H, H_{5b} + H_{6b}), 4.01 (t, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H_{3b}), 3.99 (m, 2H, H_{1a} + H_{6a}), 3.82 (t, $J_{4,3}$ = $J_{4,5}$ = 8.0 Hz, 1H, H_{4a}), 3.78 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 8.0 Hz, 1H, H_{3a}), 3.70 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H_{4b}), 3.68 (t, $J_{6',5}$ = $J_{6',6}$ = 10.0 Hz, 1H, $H_{6b'}$), 3.43 (dd, $J_{5,4}$ = 7.0 Hz, $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.35 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}), 1.91 (m, 1H, L-*camphor*), 1.86 (m, 1H, L-*camphor*), 1.76 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.46 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-

camphor), 1.21 (m, 1H, L-*camphor*), 1.07 (s, 3H, C*H*$_3$ L-*camphor*), 0.87 (s, 3H, C*H*$_3$ L-*camphor*), 0.86 (s, 3H, C*H*$_3$ L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 138.49, 138.30, 137.86, 137.77, 137.53 (Ar*C*), 128.80, 128.37, 128.35, 128.33, 128.29, 128.26, 128.04, 127.80, 127.68, 127.68, 127.53, 126,19 (Ar*C*H), 118.04 ($C_{acetalic}$ L-*camphor*), 101.28 ($CH_{benzylic}$ *benzylidene*), 95.88 (C_{1b}), 82.97 (C_{4b}), 80.55 (C_{4a} + C_{5a}), 77.91 (C_{6a}), 76.92 (C_{3a}), 75.91 (C_{1a}), 75.40 ($CH_{2\ benzylic}$), 75.31 (C_{3b}), 74.77, 74.73 ($CH_{2\ benzylic}$), 73.93 (C_{2a}), 72.54 ($CH_{2\ benzylic}$), 68.79 (C_{6b}), 62.93 (C_{2b}), 62.52 (C_{5b}), 51.57, 47.92 (C L-*camphor*), 45.12 (*C*H L-*camphor*), 44.86, 29.81, 26.96 (CH_2 L-*camphor*), 20.58, 20.34, 9.64 (CH_3 L-*camphor*). FAB-MS: *m/z* 472 (M + Na)$^+$. Anal. calcd. for $C_{57}H_{63}O_{10}N_3$: C 72.06%; H 6.68%; N 4.42%; found C 71.81%; H 6.42%; N 4.36%.

2-Azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-D-*myo*-inositol 53.[8] To a solution of **52** (600 mg, 0.632 mmol) in dry THF (12.6 mL) with 3Å molecular sieves under an argon atmosphere, $NaCNBH_3$ (1.0 M solution in THF, 6.3 mL) first and HCl (1.0 M solution in Et_2O, 6.5 mL) dropwise then, were added. The solution was stirred for 5 min, diluted with AcOEt (50 mL) and quickly washed with sat. $NaHCO_3$ (50 mL). The aqueous layer was extracted with AcOEt (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt 9/1) to yield 541 mg (90%) of **53** as a white foam. ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.41 (m, 2H, Ar*H*), 7.38-7.21 (m, 23H, Ar*H*), 5.57 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 4.88 (d, *J* = 11.5 Hz, 1H, C$H_{benzylic}$), 4.83 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.80 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.78 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.74 (d, *J* = 12.0 Hz, 1H, C$H_{benzylic}$), 4.692 (d, *J* = 10.5 Hz, 1H, C$H_{benzylic}$), 4.690 (d, *J* = 12.0 Hz, 1H, C$H_{benzylic}$), 4.64 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.47 (d, *J* = 12.5 Hz, 1H, C$H_{benzylic}$), 4.41 (d, *J* = 12.5 Hz, 1H, C$H_{benzylic}$), 4.28 (dd, $J_{2,3}$ = 3.5 Hz, $J_{2,1}$ = 5.5 Hz, 1H, H_{2a}), 4.01 (m, 2H, H_{1a} + H_{6a}), 3.98 (dt, $J_{5,6}$ = $J_{5,6'}$ = 4.5 Hz, $J_{5,4}$ = 9.5 Hz, 1H, H_{5b}), 3.80 (m, 2H, H_{4a} + H_{3a}), 3.78 (t, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H_{3b}), 3.74 (td, $J_{4,OH}$ = 3.0 Hz, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, 1H, H_{4b}), 3.49 (dd, $J_{6,5}$ = 4.0 Hz, $J_{6,6'}$ = 10.5 Hz, 1H, H_{6b}), 3.45 (dd, $J_{6',5}$ = 4.5 Hz, $J_{6',6}$ = 10.5 Hz, 1H, $H_{6b'}$), 3.43 (br t, $J_{5,4}$ = $J_{5,6}$ = 9.0 Hz, 1H, H_{5a}), 3.30 (dd, $J_{2,1}$ = 3.0 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H_{2b}), 2.13 (d, $J_{OH,4}$ = 3.0 Hz, 1H, OH), 1.89 (m, 2H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.71 (m, 1H, L-*camphor*), 1.46 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.37 (m, 1H, L-*camphor*), 1.22 (m, 1H, L-*camphor*), 1.07 (s, 3H, C*H*$_3$ L-*camphor*), 0.87 (s, 3H, C*H*$_3$ L-*camphor*), 0.84 (s, 3H, C*H*$_3$ L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 138.36, 138.23, 138.10, 138.08, 137.85 (Ar*C*), 128.39, 128.22, 128.20, 128.05, 127.76, 127.68, 127.55, 127.50, 127.46 (Ar*C*H), 117.93 ($C_{acetalic}$ L-*camphor*), 95.44 (C_{1b}), 80.67 (C_{5a}), 80.52 (C_{4a}), 79.08 (C_{3b}), 77.71 (C_{6a}), 76.85 (C_{3a}), 75.99 (C_{1a}), 75.00, 74.66, 74.56 ($CH_{2\ benzylic}$), 73.76 (C_{2a}), 73.27, 72.40 ($CH_{2\ benzylic}$), 72.35 (C_{4b}), 69.47 (C_{5b}), 69.35 (C_{6b}), 62.62 (C_{2b}),

51.48, 47.83 (C L-*camphor*), 45.03 (*C*H L-*camphor*), 44.70, 29.74, 26.88 (*C*H_2 L-*camphor*), 20.50, 20.28, 9.58 (*C*H_3 L-*camphor*).

2-Azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-*p*-methoxybenzyl-α-D-glucopyranosyl-(1→6)-3,4,5-tri-*O*-benzyl-1,2-*O*-(L-1,7,7-trimethyl-[2,2,1]-bicyclohept-2-ylidene)-D-*myo*-inositol 58. To a solution of **47** (470 mg, 0.494 mmol) in dry THF (10 mL) under an argon atmosphere, TBAF (1.0 M solution in THF, 1.5 mL) was added. The solution was stirred for 1 h, diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ solution (50 mL). The aqueous layer was extracted with AcOEt (2 x 25 mL) and the combined organic layers dried over $MgSO_4$, concentrated in *vacuo* and coevaporated with dry toluene (2 x 10 mL). To a solution of the above residue in dry DMF (10 mL) under an argon atmosphere, NaH (178 mg 60% in mineral oil, 4.450 mmol) first and then BnBr (530 µl, 4.456 mmol) were added. The solution was stirred for 10 h and NH_3 al 30% (0.5 mL) at 0ºC was added. After 10 min the mixture was diluted with AcOEt (50 mL) and washed with HCl al 10 % (50 mL). The aqueous layer was extracted with AcOEt (2 x 25 mL) and the combined organic layers were washed with sat. NaCl solution (3 x 100 mL), dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt, 19/1, 14/1, 9/1) to yield 460 mg (95%) of **58** as a white foam. $[\alpha]^{20}_{D}$ = + 47.2 (*c* = 0.3, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.45 (m, 2H, Ar*H*), 7.41-7.24 (m, 17H, Ar*H*), 7.13 (m, 1H, Ar*H*), 7.07 (m, 2H, Ar*H*), 6.77 (d, *J* = 8.5 Hz, 2H, Ar*H PMB*), 5.58 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_{1b}), 5.56 (s, 1H, C$H_{benzylic}$ *benzylidene*), 4.83 (d, *J* = 10.5 Hz, 1H, C$H_{benzylic}$), 4.78 (d, *J* = 10.5 Hz, 1H, C$H_{benzylic}$), 4.74 (d, *J* = 12.0 Hz, 1H, C$H_{benzylic}$), 4.711 (d, *J* = 12.0 Hz, 1H, C$H_{benzylic}$), 4.705 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.70 (d, *J* = 11.5 Hz, 1H, C$H_{benzylic}$), 4.68 (d, *J* = 12.0 Hz, 1H, C$H_{benzylic}$), 4.66 (d, *J* = 11.0 Hz, 1H, C$H_{benzylic}$), 4.27 (dd, $J_{2,3}$ = 4.0 Hz, $J_{2,1}$ = 6.0 Hz, 1H, H_{2a}), 4.19 (m, 2H, H_{5b} + H_{6b}), 4.01 (t, $J_{3,2}$ = $J_{3,4}$ = 9.5 Hz, 1H, H_{3b}), 3.99 (m, 2H, H_{1a} + H_{6a}), 3.81 (t, $J_{4,3}$ = $J_{4,5}$ = 8.0 Hz, 1H, H_{4a}), 3.78 (dd, $J_{3,2}$ = 4.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, H_{3a}), 3.73 (s, 3H, CH_3O *PMB*), 3.68 (br t, $J_{6',5}$ = $J_{6',6}$ = $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 2H, $H_{6b'}$ + H_{4b}), 3.42 (dd, $J_{5,4}$ = 7.5 Hz, $J_{5,6}$ = 9.5 Hz, 1H, H_{5a}), 3.33 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_{2b}), 1.91 (m, 1H, L-*camphor*), 1.85 (m, 1H, L-*camphor*), 1.75 (m, 1H, L-*camphor*), 1.72 (m, 1H, L-*camphor*), 1.45 (d, *J* = 13.0 Hz, 1H, L-*camphor*), 1.39 (m, 1H, L-*camphor*), 1.21 (m, 1H, L-*camphor*), 1.07 (s, 3H, CH_3 L-*camphor*), 0.87 (s, 3H, CH_3 L-*camphor*), 0.86 (s, 3H, CH_3 L-*camphor*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 159.36 (Ar*C PMB*), 138.55, 138.33, 137.89, 137.59 (Ar*C*), 130.06 (Ar*C*H), 129.87 (Ar*C PMB*), 128.83, 128.40, 128.37, 128.29, 128.08, 127.83, 127.71, 127.58, 127.54, 126,23 (Ar*C*H), 118.09 ($C_{acetalic}$ L-*camphor*), 113.81 (2 x Ar*C*H *PMB*), 101.32 (*C*$H_{benzylic}$ *benzylidene*), 95.84 (C_{1b}), 83.01 (C_{4b}), 80.61 (C_{4a}), 80.57 (C_{5a}), 77.90 (C_{6a}), 77.20 (C_{3a}), 75.94 (C_{1a}), 75.53 (*C*$H_{2\ benzylic}$), 74.81 (C_{3b} + *C*$H_{2\ benzylic}$), 74.41 (*C*$H_{2\ benzylic}$), 73.98 (C_{2a}), 72.57 (*C*$H_{2\ benzylic}$), 68.83 (C_{6b}), 62.95 (C_{2b}), 62.58 (C_{5b}), 55.20 (*C*H_3O *PMB*), 51.60, 47.96

(C L-*camphor*), 45.15 (*C*H L-*camphor*), 44.92, 29.82, 26.98 (*C*H_2 L-*camphor*), 20.61, 20.36, 9.65 (*C*H_3 L-*camphor*). HRMS *m/z* calcd. for $C_{58}H_{65}O_{11}N_3Na^+$: 1002.4500 $(M + Na)^+$; found 1002.4517 $(M + Na)^+$. Anal. calcd. for $C_{58}H_{56}O_{11}N_3 \cdot H_2O$: C 69.79%; H 6.77%; N 4.21%; found C 69.93%; H 6.95%; N 4.22%.

6-*O-tert*-Butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-α,β-D-mannopyranose 67.[9] To a solution of **66**[4] (1.9 g, 2.4 mmol) in acetone (24.3 mL), H_2O (132 µl, 7.327 mmol) and NBS (650 mg, 3.652 mmol) were added at -15ºC and the mixture was stirred for 30 min with exclusion of light. Ther solution was diluted with AcOEt (100 mL) and washed with sat. NaCl solution (100 mL). The aqueous layer was extracted with AcOEt (2 x 50 mL) and the combined organic layers were washed with sat. NaCl solution (3 x 250 mL), dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt 9/1, 4/1, 2/1) to give an α/β anomeric mixture of **67 (**1.59 g, 95%) as a white foam. *Data for α–anomer extracted from an α/β = 1.0/0.4 mixture:* ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.78-7.69 (m, 4H, Ar*H*), 7.42-7.25 (m, 19H, Ar*H*), 7.22-7-17 (m, 2H, 2 x Ar*H*), 5.23 (br s, 1H, H_1), 4.94 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.81 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.68 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.66 (br s, 2H, C$H_{2\ benzylic}$), 4.62 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.14 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, H_4), 4.02 (dd, $J_{6,5}$ = 4.5 Hz, $J_{6,6'}$ = 11.5 Hz, 1H, H_6), 3.99 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_3), 3.90 (m, 2H, H_5 + H_6), 3.80 (t, $J_{2,1} = J_{2,3}$ = 2.5 Hz, 1H, H_2), 2.97 (br d, $J_{OH,1}$ = 2.5 Hz, 1H, OH), 1.07 (s, 9H, (CH_3)$_3$C *TBDPS*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 138.60, 138.57, 138.55 (Ar*C*), 135.89, 135.61 (Ar*C*H *TBDPS*), 133.91 (Ar*C TBDPS*), 133.41 (Ar*C TBDPS*), 129.49, 129.47, 128.47, 128.43, 128.30, 128.23, 127.83, 127.77, 127.73, 127.70, 127.67, 127.63, 127.59, 127.55, 127.49, 127.47, 127.44, 127.40 (Ar*C*H$_{α+β}$), 92.63 (C_1), 79.64 (C_3), 75.58 (C_2), 75.02 (C$H_{2\ benzylic}$), 74.66 (C_4), 73.13 (C_5), 72.70 (C$H_{2\ benzylic}$), 72.21 (C$H_{2\ benzylic}$), 63.43 (C_6), 26.81 ((*C*H$_3$)$_3$C *TBDPS*), 19.30 ((CH$_3$)$_3$*C TBDPS*). ^{13}C-RMN-*undecoupled* ($CDCl_3$, 125 MHz): δ 92.63 (d, $J_{C,H}$ = 168.1 Hz, C_1).

6-*O-tert*-Butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-α,β-D-mannopyranosyl trichloroacetimidate 68. To a solution of **67** (1.5 g, 2.2 mmol) in dry CH_2Cl_2 (11 mL) under an argon atmosphere, trichloroacetonitrile (3.3 mL, 32.9 mmol) and DBU (17 µl, 0.114 mmol) was added. The solution was stirred for 2 h and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt/Et_3N 4/0.9/0.1) to yield an α/β anomeric mixture of **68 (**1.75 g, 96%) as a white foam. *RMN data for α-anomer extracted from an α/β = 1.0/0.2 mixture:* ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 8.52 (s, 1H, OCN*H*CCl$_3$), 7.77-7.68 (m, 4H, Ar*H*), 7.47-7.26 (m, 19H, Ar*H*), 7.22 (m, 2H, Ar*H*), 6.40 (d, $J_{1,2}$ = 2.0 Hz, 1H, H_1), 4.98 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.84 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.78 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$),

4.71 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.68 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.65 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.32 (t, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1H, H_4), 4.02 (dd, $J_{6,5}$ = 3.5 Hz, $J_{6,6'}$ = 11.5 Hz, 1H, H_6), 3.98 (dd, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H_3), 3.94 (dd, $J_{6',5}$ = 1.5 Hz, $J_{6',6}$ = 11.5 Hz, 1H, $H_{6'}$), 3.90 (t, $J_{2,1} = J_{2,3}$ = 2.5 Hz, 1H, H_2), 3.89 (br dd, $J_{5,6}$ = 2.5 Hz, $J_{5,4}$ = 10.0 Hz, 1H, H_5), 1.07 (s, 9H, (CH_3)$_3$C *TBDPS*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 160.42 (O*C*NHCCl_3), 138.37, 138.18, 138.10 (Ar*C*), 135.92, 135.64 (Ar*C*H *TBDPS*), 133.83, 133.25 (Ar*C TBDPS*), 129.50, 128.37, 128.30, 128.06, 127.99, 127.71, 127.66, 127.61, 127.58, 127.53 (Ar*C*H), 96.24 (C_1), 91.09 (OCNH*C*Cl_3), 79.04 (C_3), 75.77 (C_5), 75.36 (*C*$H_{2\ benzylic}$), 74.03 (C_2), 73.95 (C_4), 72.69, 72.41 (*C*$H_{2\ benzylic}$), 62.71 (C_6), 26.75 ((*C*H_3)$_3$C *TBDPS*), 19.33 ((CH_3)$_3$*C TBDPS*). ^{13}C-RMN-*undecoupled* ($CDCl_3$, 125 MHz,): δ 96.24 (d, $J_{C,H}$ = 175.9 Hz, C_1).

Phenyl 6-*O*-*tert*-butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-1-thio-β-D-galactopyranoside 71. To a solution of **70**[10] (1.0 g, 2.3 mmol) in dry MeOH (23 mL) under an argon atmosphere MeONa (0.1 M solution in MeOH, 2.3 mL) was added. The solution was stirred for 10 min, neutralised with Amberlite IR-120 (H^+), filtered and concentrated in *vacuo*. To a solution of this crude product and imidazol (804 mg, 11.810 mmol) in dry THF (23 mL) under an argon atmosphere, TBDPSCl (0.71 mL, 2.73 mmol) was added. The mixture was stirred for 10 h, diluted with AcOEt (50 mL) and washed with sat. $NaHCO_3$ solution (50 mL). The aqueous layer was extracted with AcOEt (2 x 30 mL) and the combined organic layers were washed with sat. NaCl solution (3 x 100 mL), dried over $MgSO_4$, concentrated in *vacuo* and the resulting crude coevaporated with dry toluene (2 x 20 mL). To a solution of the above residue and TBAI (84 mg, 0.227 mmol) in dry THF (23 mL) under an argon atmosphere, NaH (409 mg 60% in mineral oil, 10.226 mmol) first and then BnBr (1.22 mL, 10.26 mmol) at 0ºC were added. The mixture was stirred for 24 h, diluted with AcOEt (50 mL) and washed with HCl al 10 % (50 mL). The aqueous layer was extracted with AcOEt (2 x 25 mL) and the combined organic layers dried over $MgSO_4$ and concentrated in *vacuo.* The residue was purified by flash chromatography (hexane/AcOEt 29/1, 19/1, 14/1, 9/1) to yield 1.33 g (75%) of **71** as a colourless syrup. $[\alpha]^{20}_D$ = + 19.7 (*c* = 0.8, $CHCl_3$). ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.59 (m, 4H, Ar*H*), 7.51 (m, 2H, Ar*H*), 7.43-7.24 (m, 21H, Ar*H*), 7.13 (m, 3H, Ar*H*), 4.99 (d, J = 11.0 Hz, 1H, C$H_{benzylic}$), 4.77 (d, J = 12.0 Hz, 1H, C$H_{benzylic}$), 4.73 (br d, J = 12.0 Hz, 2H, 2 x C$H_{benzylic}$), 4.70 (d, J = 10.5 Hz, 1H, C$H_{benzylic}$), 4.62 (d, J = 11.5 Hz, 1H, C$H_{benzylic}$), 4.56 (d, $J_{1,2}$ = 9.5 Hz, 1H, H_1), 3.98 (br d, $J_{4,3}$ = 2.0 Hz, 1H, H_4), 3.92 (t, $J_{2,1} = J_{2,3}$ = 9.5 Hz, 1H, H_2), 3.82 (br d, $J_{6+6',5}$ 6.5 Hz, 2H, H_6 + $H_{6'}$), 3.57 (dd, $J_{3,2}$ = 2.5 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H_3), 3.43 (t, $J_{5,6+6'}$ = 6.5 Hz, 1H, H_5), 1.04 (s, 9H, (CH_3)$_3$C *TBDPS*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 138.85, 138.39, 138.33 (Ar*C*), 135.57, 135.53 (Ar*C*H), 134.19 (Ar*C SPh*), 133.18 (2 x Ar*C TBDPS*), 131.24, 129.77, 129.71, 128.73, 128.44,

128.31, 128.11, 127.73, 127.65, 127.54, 127.27, 126.85 (Ar*C*H), 87.54 (C_1), 84.17 (C_3), 78.65 (C_5), 77.00 (C_2), 75.57, 74.38 (*C*$H_{2\ benzylic}$), 73.61 (C_4), 72.86 (*C*$H_{2\ benzylic}$), 62.32 (C_6), 26.90 ((*C*H_3)$_3$C *TBDPS*), 19.16 ((CH$_3$)$_3$*C TBDPS*).

6-*O-tert*-Butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-α,β-D-galactopyranose 72.[11] To a solution of **71** (1.30 g, 1.66 mmol) in acetone (17 mL), H_2O (90 µl, 4.996 mmol) and NBS (444 mg, 2.495 mmol) were added at -15ºC and the mixture was stirred for 30 min with exclusion of light. Ther solution was diluted with AcOEt (100 mL) and washed with sat. NaCl solution (100 mL). The aqueous layer was extracted with AcOEt (2 x 50 mL) and the combined organic layers were washed with sat. NaCl solution (3 x 250 mL), dried over $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt 9/1, 4/1, 2/1) to give an α/β anomeric mixture of **72** (1.08 g, 94%) as a white foam. *RMN data for α-anomer extracted from an α/β = 2/1mixture:* ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 7.64-7.59 (m, 4H, 4 x Ar*H*), 7.45-7.23 (m, 21H, 21 x Ar*H*), 5.21 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_1), 4.99 (d, *J* = 11.5 Hz, 1H, C*H*$_{benzylic}$), 4.85 (d, *J* = 12.0 Hz, 1H, C*H*$_{benzylic}$), 4.83 (d, *J* = 11.5 Hz, 1H, C*H*$_{benzylic}$), 4.78 (d, *J* = 12.0 Hz, 1H, C*H*$_{benzylic}$), 4.71 (d, *J* = 12.0 Hz, 1H, C*H*$_{benzylic}$), 4.61 (d, *J* = 11.0 Hz, 1H, C*H*$_{benzylic}$), 4.09 (br d, $J_{4,3}$ = 2.5 Hz, 1H, H_4), 4.04 (br dd, $J_{5,6}$ = 5.5 Hz, $J_{5,6'}$ = 9.0 Hz, 1H, H_5), 4.03 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_2), 3.92 (dd, $J_{3,4}$ = 2.5 Hz, $J_{3,2}$ = 9.5 Hz, 1H, H_3), 3.83 (dd, $J_{6',5}$ = 8.5 Hz, $J_{6',6}$ = 10.0 Hz, 1H, $H_{6'}$), 3.71 (dd, $J_{6,5}$ = 5.5 Hz, $J_{6,6'}$ = 10.0 Hz, 1H, H_6), 2.77 (br s, 1H, OH_α), 1.06 (s, 9H, (C*H*$_3$)$_3$C *TBDPS*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 138.72, 138.62 (Ar*C*), 138.09 (Ar*C*), 133.21, 133.17 (Ar*C TBDPS*), 129.74, 129.70, 129.69, 129.64, 128.33, 128.30, 128.21, 128.16, 128.14, 128.08, 127.95, 127.90, 127.81, 127.70, 127.67, 127.65, 127.59, 127.55, 127.52, 127.47, 127.34, 127.31 (Ar*C*H$_{\alpha+\beta}$), 91.80 (C_1), 78.65 (C_3), 76.55 (C_5), 74.79 (*C*$H_{2\ benzylic}$), 74.74 (C_4), 73.41 (*C*$H_{2\ benzylic}$), 72.84 (*C*$H_{2\ benzylic}$), 70.78 (C_2), 61.96 (C_6), 26.87 ((*C*H$_3$)$_3$C *TBDPS*), 19.11 ((CH$_3$)$_3$*C TBDPS*).

6-*O-tert*-Butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-α,β-D-galactopyranosyl trichloroacetimidate 73. To a solution of **72** (1.00 g, 1.45 mol) in dry CH_2Cl_2 (7.3 mL) under an argon atmosphere, trichloroacetonitrile (2.18 mL, 21.74 mmol) and DBU (11 µl, 0.074 mmol) was added. The solution was stirred for 1 h and concentrated in *vacuo*. The residue was purified by flash chromatography (hexane/AcOEt/Et_3N 4/0.9/0.1) to yield an α/β anomeric mixture of **73** (1.16 g, 96%) as a white foam. *RMN data for α-anomer extracted from an α/β = 1.0/0.2 mixture:* ^{1}H-RMN ($CDCl_3$, 500 MHz): δ 8.49 (s, 1H, OCN*H*CCl$_3$), 7.63-7.54 (m, 4H, Ar*H*), 7.44-7.22 (m, 21H, Ar*H*), 6.49 (d, $J_{1,2}$ = 3.5 Hz, 1H, H_1), 5.01 (d, *J* = 11.5 Hz, 1H, C*H*$_{benzylic}$), 4.89 (d, *J* = 12.0 Hz, 1H, C*H*$_{benzylic}$), 4.78 (d, *J* = 12.0 Hz, 1H, C*H*$_{benzylic}$), 4.74 (s, 2H, C*H*$_{2\ benzylic}$), 4.67 (d, *J* = 11.0 Hz, 1H, C*H*$_{benzylic}$), 4.23 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H_2), 4.12

(br d, $J_{4,3}$ = 2.0 Hz, 1H, H_4), 4.032 (m, 1H, H_5), 4.027 (dd, $J_{3,2}$ = 2.5 Hz, $J_{3,4}$ = 10.0 Hz, 1H, H_3), 3.81 (dd, $J_{6,5}$ = 8.0 Hz, $J_{6,6'}$ = 10.5 Hz, 1H, H_6), 3.72 (dd, $J_{6',5}$ = 6.0 Hz, $J_{6',6}$ = 10.0 Hz, 1H, $H_{6'}$), 1.03 (s, 9H, (CH_3)$_3$C *TBDPS*). ^{13}C-RMN ($CDCl_3$, 125 MHz): δ 161.17 (O*C*NHCCl_3), 138.66, 138.64, 138.43 (Ar*C*), 135.49, (Ar*C*H *TBDPS*), 133.22 (2 x Ar*C TBDPS*), 129.74, 128.33, 128.21, 128.00, 127.71, 127.68, 127.60, 127.53, 127.50, 127.43 (Ar*C*H), 95.00 (C_1), 91.48 (OCNH*C*Cl_3), 78.18 (C_3), 75.92 (C_2), 75.07 (*C*$H_{2\ benzylic}$), 74.81 (C_4), 73.55 (C_5), 73.17, 72.86 (*C*$H_{2\ benzylic}$), 62.06 (C_6), 26.86 ((*C*H_3)$_3$C *TBDPS*), 19.18 ((CH_3)$_3$*C TBDPS*).

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Docking Calculations.

Clustering histograms and RMSD tables of Docked compounds **3** and **5-32**.

Compound 3

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-10.40	6	-10.40	1	#
2	-10.30	9	-10.30	1	#
3	-9.03	7	-9.03	1	#
4	-8.84	1	-8.84	1	#
5	-8.31	3	-8.31	1	#
6	-7.98	8	-7.98	1	#
7	-7.91	10	-7.91	1	#
8	-7.81	5	-7.81	1	#
9	-7.75	2	-7.75	1	#
10	-7.48	4	-7.48	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	6	-10.40	0.00	8.92	RANKING
2	1	9	-10.30	0.00	8.21	RANKING
3	1	7	-9.03	0.00	8.91	RANKING
4	1	1	-8.84	0.00	8.02	RANKING
5	1	3	-8.31	0.00	7.62	RANKING
6	1	8	-7.98	0.00	8.47	RANKING
7	1	10	-7.91	0.00	8.37	RANKING
8	1	5	-7.81	0.00	8.46	RANKING
9	1	2	-7.75	0.00	8.86	RANKING
10	1	4	-7.48	0.00	7.46	RANKING

Compound 5

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-8.90	5	-8.82	2	##
2	-8.54	2	-8.31	3	###
3	-8.18	8	-8.18	1	#
4	-7.52	6	-7.35	2	##
5	-7.49	10	-7.49	1	#
6	-6.48	4	-6.48	1	#

Number of multi-member conformational clusters found = 3, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	5	-8.90	0.00	8.11	RANKING
1	2	7	-8.75	0.83	8.02	RANKING
2	1	2	-8.54	0.00	10.17	RANKING
2	2	9	-8.46	0.52	10.23	RANKING
2	3	3	-7.95	0.45	10.07	RANKING
3	1	8	-8.18	0.00	9.37	RANKING
4	1	6	-7.52	0.00	10.55	RANKING
4	2	1	-7.18	0.96	10.54	RANKING
5	1	10	-7.49	0.00	10.71	RANKING
6	1	4	-6.48	0.00	10.54	RANKING

Compound 6

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-9.25	7	-9.25	1	#
2	-9.06	2	-9.06	1	#
3	-8.75	4	-8.68	2	##
4	-8.49	5	-8.49	1	#
5	-8.13	6	-8.13	1	#
6	-7.94	1	-7.94	1	#
7	-7.66	9	-7.66	1	#
8	-7.08	8	-7.08	1	#
9	-6.53	10	-6.53	1	#

Number of multi-member conformational clusters found = 1, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	7	-9.25	0.00	9.60	RANKING
2	1	2	-9.06	0.00	9.73	RANKING
3	1	4	-8.75	0.00	9.79	RANKING
3	2	3	-8.61	0.94	9.50	RANKING
4	1	5	-8.49	0.00	8.72	RANKING
5	1	6	-8.13	0.00	10.11	RANKING
6	1	1	-7.94	0.00	7.95	RANKING
7	1	9	-7.66	0.00	9.56	RANKING
8	1	8	-7.08	0.00	10.62	RANKING
9	1	10	-6.53	0.00	8.67	RANKING

Compound 7

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-8.45	3	-8.17	3	###
2	-8.28	6	-8.28	1	#
3	-8.23	2	-8.23	2	##
4	-8.11	8	-8.11	1	#
5	-7.62	1	-7.62	1	#
6	-6.74	9	-6.74	1	#
7	-6.49	4	-6.49	1	#

Number of multi-member conformational clusters found = 2, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	3	-8.45	0.00	10.96	RANKING
1	2	5	-8.44	0.83	10.86	RANKING
1	3	7	-7.62	0.91	10.65	RANKING
2	1	6	-8.28	0.00	9.92	RANKING
3	1	2	-8.23	0.00	10.96	RANKING
3	2	10	-8.23	0.50	10.94	RANKING
4	1	8	-8.11	0.00	10.90	RANKING
5	1	1	-7.62	0.00	9.22	RANKING
6	1	9	-6.74	0.00	9.14	RANKING
7	1	4	-6.49	0.00	10.99	RANKING

Compound 8

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-10.24	2	-10.24	1	#
2	-9.89	8	-9.89	1	#
3	-9.63	9	-9.63	1	#
4	-9.40	6	-9.40	1	#
5	-9.20	3	-9.20	1	#
6	-8.64	5	-8.64	1	#
7	-8.38	4	-8.38	1	#
8	-7.97	7	-7.97	1	#
9	-7.73	1	-7.73	1	#
10	-7.38	10	-7.38	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	2	-10.24	0.00	7.82	RANKING
2	1	8	-9.89	0.00	8.85	RANKING
3	1	9	-9.63	0.00	9.42	RANKING
4	1	6	-9.40	0.00	7.50	RANKING
5	1	3	-9.20	0.00	9.21	RANKING
6	1	5	-8.64	0.00	9.40	RANKING
7	1	4	-8.38	0.00	8.84	RANKING
8	1	7	-7.97	0.00	7.74	RANKING
9	1	1	-7.73	0.00	7.66	RANKING
10	1	10	-7.38	0.00	9.62	RANKING

Compound 9

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-10.83	9	-10.36	3	###
2	-10.18	1	-10.18	1	#
3	-9.25	8	-8.83	2	##
4	-8.95	2	-8.95	1	#
5	-8.88	3	-8.88	1	#
6	-8.30	10	-8.30	1	#
7	-7.59	5	-7.59	1	#

Number of multi-member conformational clusters found = 2, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	9	-10.83	0.00	9.03	RANKING
1	2	6	-10.25	0.96	9.07	RANKING
1	3	4	-10.00	0.88	9.10	RANKING
2	1	1	-10.18	0.00	9.51	RANKING
3	1	8	-9.25	0.00	6.89	RANKING
3	2	7	-8.41	0.78	7.13	RANKING
4	1	2	-8.95	0.00	8.65	RANKING
5	1	3	-8.88	0.00	8.71	RANKING
6	1	10	-8.30	0.00	8.04	RANKING
7	1	5	-7.59	0.00	8.90	RANKING

Compound 10

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-8.33	2	-8.29	2	##
2	-8.03	8	-7.87	2	##
3	-7.25	4	-7.24	5	#####
4	-5.00	6	-5.00	1	#

Number of multi-member conformational clusters found = 3, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	2	-8.33	0.00	7.25	RANKING
1	2	9	-8.25	0.19	7.27	RANKING
2	1	8	-8.03	0.00	8.08	RANKING
2	2	1	-7.71	0.27	8.10	RANKING
3	1	4	-7.25	0.00	8.36	RANKING
3	2	5	-7.25	0.26	8.36	RANKING
3	3	7	-7.24	0.27	8.36	RANKING
3	4	10	-7.23	0.30	8.29	RANKING
3	5	3	-7.22	0.27	8.36	RANKING
4	1	6	-5.00	0.00	7.00	RANKING

Compound 11

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-8.34	3	-8.32	3	###
2	-7.85	8	-7.85	4	####
3	-7.13	9	-7.10	3	###

Number of multi-member conformational clusters found = 3, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	3	-8.34	0.00	11.32	RANKING
1	2	4	-8.32	0.03	11.32	RANKING
1	3	10	-8.30	0.13	11.33	RANKING
2	1	8	-7.85	0.00	10.79	RANKING
2	2	1	-7.85	0.03	10.79	RANKING
2	3	6	-7.85	0.02	10.79	RANKING
2	4	2	-7.85	0.07	10.79	RANKING
3	1	9	-7.13	0.00	9.85	RANKING
3	2	7	-7.13	0.08	9.83	RANKING
3	3	5	-7.06	0.19	9.77	RANKING

Compound 12

CLUSTERING HISTOGRAM

Cluster Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-9.89	2	-9.89	1	#
2	-9.46	7	-8.63	2	##
3	-8.28	9	-8.28	1	#
4	-7.60	4	-7.60	1	#
5	-7.17	5	-7.17	1	#
6	-6.77	10	-6.77	1	#
7	-6.10	3	-6.10	1	#
8	-6.02	6	-6.02	1	#
9	-5.37	1	-5.37	1	#

Number of multi-member conformational clusters found = 1, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	2	-9.89	0.00	10.54	RANKING
2	1	7	-9.46	0.00	9.65	RANKING
2	2	8	-7.79	0.83	9.60	RANKING
3	1	9	-8.28	0.00	9.31	RANKING
4	1	4	-7.60	0.00	9.69	RANKING
5	1	5	-7.17	0.00	9.75	RANKING
6	1	10	-6.77	0.00	9.05	RANKING
7	1	3	-6.10	0.00	8.90	RANKING
8	1	6	-6.02	0.00	9.25	RANKING
9	1	1	-5.37	0.00	8.59	RANKING

Compound 13

CLUSTERING HISTOGRAM

Cluster Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-11.04	4	-10.71	2	##
2	-7.59	6	-7.59	1	#
3	-7.36	5	-7.36	1	#
4	-7.36	10	-7.36	1	#
5	-6.76	3	-6.76	1	#
6	-6.08	9	-6.08	1	#
7	-5.73	8	-5.73	1	#
8	-5.30	2	-5.30	1	#
9	-4.79	1	-4.79	1	#

Number of multi-member conformational clusters found = 1, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	4	-11.04	0.00	10.98	RANKING
1	2	7	-10.39	0.57	10.94	RANKING
2	1	6	-7.59	0.00	9.91	RANKING
3	1	5	-7.36	0.00	8.78	RANKING
4	1	10	-7.36	0.00	10.83	RANKING
5	1	3	-6.76	0.00	9.46	RANKING
6	1	9	-6.08	0.00	9.12	RANKING
7	1	8	-5.73	0.00	10.30	RANKING
8	1	2	-5.30	0.00	9.91	RANKING
9	1	1	-4.79	0.00	10.93	RANKING

Compound 14

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-8.65	2	-8.65	1	#
2	-8.50	1	-8.50	1	#
3	-8.23	8	-8.23	1	#
4	-8.14	10	-8.04	2	##
5	-6.78	5	-6.78	1	#
6	-6.47	4	-6.47	1	#
7	-6.34	9	-6.34	1	#
8	-6.02	7	-6.02	1	#
9	-5.54	3	-5.54	1	#

Number of multi-member conformational clusters found = 1, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	2	-8.65	0.00	8.47	RANKING
2	1	1	-8.50	0.00	5.86	RANKING
3	1	8	-8.23	0.00	9.92	RANKING
4	1	10	-8.14	0.00	6.98	RANKING
4	2	6	-7.95	0.90	6.94	RANKING
5	1	5	-6.78	0.00	7.93	RANKING
6	1	4	-6.47	0.00	7.83	RANKING
7	1	9	-6.34	0.00	7.57	RANKING
8	1	7	-6.02	0.00	8.71	RANKING
9	1	3	-5.54	0.00	8.11	RANKING

Compound 15

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-6.51	10	-6.49	3	###
2	-6.24	4	-6.24	4	####
3	-5.49	9	-5.49	1	#
4	-5.45	8	-5.45	2	##

Number of multi-member conformational clusters found = 3, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	10	-6.51	0.00	7.26	RANKING
1	2	2	-6.50	0.17	7.25	RANKING
1	3	3	-6.46	0.18	7.28	RANKING
2	1	4	-6.24	0.00	7.41	RANKING
2	2	1	-6.24	0.02	7.41	RANKING
2	3	5	-6.24	0.02	7.41	RANKING
2	4	7	-6.23	0.03	7.42	RANKING
3	1	9	-5.49	0.00	8.55	RANKING
4	1	8	-5.45	0.00	7.86	RANKING
4	2	6	-5.45	0.04	7.87	RANKING

Compound 16

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-7.26	1	-7.23	2	##
2	-6.53	3	-6.53	2	##
3	-5.82	8	-5.81	2	##
4	-5.61	10	-5.61	1	#
5	-5.21	2	-5.21	1	#
6	-4.97	5	-4.97	1	#
7	-4.49	4	-4.49	1	#

Number of multi-member conformational clusters found = 3, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	1	-7.26	0.00	7.70	RANKING
1	2	9	-7.20	0.42	7.57	RANKING
2	1	3	-6.53	0.00	7.81	RANKING
2	2	7	-6.53	0.21	7.83	RANKING
3	1	8	-5.82	0.00	8.62	RANKING
3	2	6	-5.81	0.04	8.64	RANKING
4	1	10	-5.61	0.00	7.43	RANKING
5	1	2	-5.21	0.00	8.21	RANKING
6	1	5	-4.97	0.00	8.53	RANKING
7	1	4	-4.49	0.00	8.44	RANKING

Compound 17

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-8.12	3	-8.11	6	######
2	-5.89	2	-5.89	1	#
3	-5.86	5	-5.86	1	#
4	-5.80	6	-5.80	2	##

Number of multi-member conformational clusters found = 2, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	3	-8.12	0.00	7.96	RANKING
1	2	8	-8.12	0.29	7.87	RANKING
1	3	10	-8.11	0.28	7.88	RANKING
1	4	7	-8.11	0.29	7.86	RANKING
1	5	1	-8.09	0.29	7.86	RANKING
1	6	9	-8.09	0.24	7.88	RANKING
2	1	2	-5.89	0.00	8.61	RANKING
3	1	5	-5.86	0.00	7.57	RANKING
4	1	6	-5.80	0.00	8.14	RANKING
4	2	4	-5.79	0.06	8.14	RANKING

Compound 18

CLUSTERING HISTOGRAM

Cluster Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-10.92	6	-10.92	1	#
2	-9.06	2	-9.06	1	#
3	-8.65	8	-8.65	1	#
4	-8.03	5	-8.03	1	#
5	-7.98	3	-7.98	1	#
6	-7.86	9	-7.86	1	#
7	-7.70	4	-7.70	1	#
8	-7.50	7	-7.50	1	#
9	-6.99	10	-6.99	1	#
10	-6.75	1	-6.75	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	6	-10.92	0.00	7.85	RANKING
2	1	2	-9.06	0.00	9.47	RANKING
3	1	8	-8.65	0.00	9.40	RANKING
4	1	5	-8.03	0.00	7.22	RANKING
5	1	3	-7.98	0.00	7.37	RANKING
6	1	9	-7.86	0.00	9.87	RANKING
7	1	4	-7.70	0.00	7.42	RANKING
8	1	7	-7.50	0.00	10.00	RANKING
9	1	10	-6.99	0.00	5.53	RANKING
10	1	1	-6.75	0.00	8.90	RANKING

Compound 19

CLUSTERING HISTOGRAM

Cluster Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-6.77	9	-6.77	1	#
2	-6.15	6	-6.15	1	#
3	-6.13	5	-6.12	7	#######
4	-5.69	7	-5.69	1	#

Number of multi-member conformational clusters found = 1, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	9	-6.77	0.00	8.12	RANKING
2	1	6	-6.15	0.00	6.10	RANKING
3	1	5	-6.13	0.00	8.32	RANKING
3	2	2	-6.13	0.06	8.31	RANKING
3	3	4	-6.13	0.05	8.30	RANKING
3	4	1	-6.13	0.05	8.30	RANKING
3	5	8	-6.12	0.03	8.32	RANKING
3	6	3	-6.12	0.03	8.34	RANKING
3	7	10	-6.12	0.04	8.30	RANKING
4	1	7	-5.69	0.00	8.23	RANKING

Compound 20

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-9.60	7	-9.60	1	#
2	-7.78	10	-7.78	1	#
3	-7.66	3	-7.66	1	#
4	-7.51	8	-7.51	1	#
5	-7.32	5	-7.32	1	#
6	-6.23	2	-6.23	1	#
7	-5.83	1	-5.83	1	#
8	-5.42	4	-5.42	1	#
9	-5.27	6	-5.27	1	#
10	-4.23	9	-4.23	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	7	-9.60	0.00	10.56	RANKING
2	1	10	-7.78	0.00	11.28	RANKING
3	1	3	-7.66	0.00	10.76	RANKING
4	1	8	-7.51	0.00	9.84	RANKING
5	1	5	-7.32	0.00	11.06	RANKING
6	1	2	-6.23	0.00	9.66	RANKING
7	1	1	-5.83	0.00	9.18	RANKING
8	1	4	-5.42	0.00	11.19	RANKING
9	1	6	-5.27	0.00	9.98	RANKING
10	1	9	-4.23	0.00	10.39	RANKING

Compound 21

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-8.89	8	-8.71	3	###
2	-7.87	6	-7.87	5	#####
3	-6.96	2	-6.96	1	#
4	-6.33	7	-6.33	1	#

Number of multi-member conformational clusters found = 2, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	8	-8.89	0.00	11.04	RANKING
1	2	3	-8.81	0.20	11.01	RANKING
1	3	1	-8.42	0.39	10.99	RANKING
2	1	6	-7.87	0.00	10.41	RANKING
2	2	9	-7.87	0.05	10.41	RANKING
2	3	5	-7.87	0.04	10.40	RANKING
2	4	10	-7.86	0.05	10.41	RANKING
2	5	4	-7.86	0.07	10.41	RANKING
3	1	2	-6.96	0.00	10.06	RANKING
4	1	7	-6.33	0.00	10.61	RANKING

Compound 22

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-6.71	3	-6.70	5	#####
2	-6.25	10	-6.25	1	#
3	-6.03	1	-6.03	1	#
4	-4.88	6	-4.88	1	#
5	-4.64	9	-4.64	1	#
6	-4.55	5	-4.55	1	#

Number of multi-member conformational clusters found = 1, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	3	-6.71	0.00	11.16	RANKING
1	2	7	-6.70	0.03	11.16	RANKING
1	3	4	-6.70	0.05	11.16	RANKING
1	4	2	-6.69	0.05	11.16	RANKING
1	5	8	-6.69	0.05	11.15	RANKING
2	1	10	-6.25	0.00	10.78	RANKING
3	1	1	-6.03	0.00	11.23	RANKING
4	1	6	-4.88	0.00	8.67	RANKING
5	1	9	-4.64	0.00	10.26	RANKING
6	1	5	-4.55	0.00	10.47	RANKING

Compound 23

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-6.96	2	-6.96	2	##
2	-6.13	1	-6.12	5	#####
3	-6.01	10	-6.01	1	#
4	-5.81	4	-5.81	1	#
5	-5.81	6	-5.81	1	#

Number of multi-member conformational clusters found = 2, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	2	-6.96	0.00	11.62	RANKING
1	2	7	-6.96	0.05	11.63	RANKING
2	1	1	-6.13	0.00	11.29	RANKING
2	2	8	-6.13	0.03	11.30	RANKING
2	3	5	-6.13	0.01	11.30	RANKING
2	4	9	-6.11	0.11	11.35	RANKING
2	5	3	-6.11	0.07	11.28	RANKING
3	1	10	-6.01	0.00	10.34	RANKING
4	1	4	-5.81	0.00	10.23	RANKING
5	1	6	-5.81	0.00	10.06	RANKING

Compound 24

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-10.81	2	-10.81	1	#
2	-9.87	1	-8.91	2	##
3	-7.33	8	-7.33	1	#
4	-7.25	3	-7.25	1	#
5	-6.91	9	-6.91	1	#
6	-6.88	6	-6.88	1	#
7	-6.15	7	-6.15	1	#
8	-5.82	4	-5.82	1	#
9	-5.80	10	-5.80	1	#

Number of multi-member conformational clusters found = 1, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	2	-10.81	0.00	5.05	RANKING
2	1	1	-9.87	0.00	6.12	RANKING
2	2	5	-7.94	0.99	6.43	RANKING
3	1	8	-7.33	0.00	6.55	RANKING
4	1	3	-7.25	0.00	8.62	RANKING
5	1	9	-6.91	0.00	6.08	RANKING
6	1	6	-6.88	0.00	5.41	RANKING
7	1	7	-6.15	0.00	7.88	RANKING
8	1	4	-5.82	0.00	7.13	RANKING
9	1	10	-5.80	0.00	7.39	RANKING

Compound 25

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-9.05	8	-9.05	1	#
2	-7.91	4	-7.91	1	#
3	-7.46	7	-7.46	1	#
4	-7.28	1	-7.28	1	#
5	-6.48	3	-6.48	1	#
6	-6.38	2	-6.38	1	#
7	-6.12	5	-6.12	1	#
8	-5.58	9	-5.58	1	#
9	-5.57	6	-5.57	1	#
10	-3.72	10	-3.72	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	8	-9.05	0.00	8.61	RANKING
2	1	4	-7.91	0.00	7.64	RANKING
3	1	7	-7.46	0.00	8.98	RANKING
4	1	1	-7.28	0.00	9.95	RANKING
5	1	3	-6.48	0.00	8.84	RANKING
6	1	2	-6.38	0.00	7.66	RANKING
7	1	5	-6.12	0.00	8.54	RANKING
8	1	9	-5.58	0.00	8.03	RANKING
9	1	6	-5.57	0.00	7.94	RANKING
10	1	10	-3.72	0.00	7.23	RANKING

Compound 26

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-9.13	8	-9.13	1	#
2	-8.44	10	-8.44	1	#
3	-7.86	4	-7.86	1	#
4	-7.57	5	-7.57	1	#
5	-6.95	9	-6.95	1	#
6	-6.84	3	-6.84	1	#
7	-6.71	6	-6.71	1	#
8	-6.47	7	-6.47	1	#
9	-6.37	1	-6.37	1	#
10	-5.36	2	-5.36	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	8	-9.13	0.00	10.34	RANKING
2	1	10	-8.44	0.00	8.55	RANKING
3	1	4	-7.86	0.00	9.10	RANKING
4	1	5	-7.57	0.00	8.33	RANKING
5	1	9	-6.95	0.00	8.87	RANKING
6	1	3	-6.84	0.00	7.92	RANKING
7	1	6	-6.71	0.00	6.87	RANKING
8	1	7	-6.47	0.00	9.04	RANKING
9	1	1	-6.37	0.00	7.02	RANKING
10	1	2	-5.36	0.00	9.29	RANKING

Compound 27

CLUSTERING HISTOGRAM

Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-8.30	2	-8.13	6	######
2	-5.93	7	-5.93	1	#
3	-5.72	5	-5.72	1	#
4	-5.38	8	-5.37	2	##

Number of multi-member conformational clusters found = 2, out of 10 runs.

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	2	-8.30	0.00	11.28	RANKING
1	2	1	-8.30	0.05	11.27	RANKING
1	3	9	-8.30	0.05	11.28	RANKING
1	4	3	-8.30	0.06	11.26	RANKING
1	5	6	-8.20	0.13	11.31	RANKING
1	6	10	-7.39	0.56	11.06	RANKING
2	1	7	-5.93	0.00	10.67	RANKING
3	1	5	-5.72	0.00	10.17	RANKING
4	1	8	-5.38	0.00	10.19	RANKING
4	2	4	-5.36	0.03	10.20	RANKING

Compound 28

CLUSTERING HISTOGRAM

Cluster Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-9.02	8	-9.02	1	#
2	-7.91	2	-7.91	1	#
3	-7.12	7	-7.12	1	#
4	-5.83	1	-5.83	1	#
5	-4.71	4	-4.71	1	#
6	-4.70	5	-4.70	1	#
7	-3.02	6	-3.02	1	#
8	-2.77	9	-2.77	1	#
9	-2.63	3	-2.63	1	#
10	-1.18	10	-1.18	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	8	-9.02	0.00	10.05	RANKING
2	1	2	-7.91	0.00	7.83	RANKING
3	1	7	-7.12	0.00	9.78	RANKING
4	1	1	-5.83	0.00	6.90	RANKING
5	1	4	-4.71	0.00	6.33	RANKING
6	1	5	-4.70	0.00	9.71	RANKING
7	1	6	-3.02	0.00	7.48	RANKING
8	1	9	-2.77	0.00	7.68	RANKING
9	1	3	-2.63	0.00	6.14	RANKING
10	1	10	-1.18	0.00	6.29	RANKING

Compound 29

CLUSTERING HISTOGRAM

Cluster Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-7.54	6	-7.54	1	#
2	-6.28	3	-6.28	1	#
3	-5.61	1	-5.61	1	#
4	-4.67	4	-4.67	1	#
5	-4.01	8	-4.01	1	#
6	-3.64	10	-3.64	1	#
7	-3.60	2	-3.60	1	#
8	-2.33	5	-2.33	1	#
9	-0.66	7	-0.66	1	#
10	-0.62	9	-0.62	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	6	-7.54	0.00	10.17	RANKING
2	1	3	-6.28	0.00	9.91	RANKING
3	1	1	-5.61	0.00	9.93	RANKING
4	1	4	-4.67	0.00	9.42	RANKING
5	1	8	-4.01	0.00	9.51	RANKING
6	1	10	-3.64	0.00	8.72	RANKING
7	1	2	-3.60	0.00	8.24	RANKING
8	1	5	-2.33	0.00	7.34	RANKING
9	1	7	-0.66	0.00	7.59	RANKING
10	1	9	-0.62	0.00	8.54	RANKING

Compound 30

CLUSTERING HISTOGRAM

Cluster Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-5.77	1	-5.77	1	#
2	-5.72	9	-5.72	1	#
3	-5.54	2	-5.54	1	#
4	-5.39	10	-5.39	1	#
5	-5.28	6	-5.28	1	#
6	-4.50	5	-4.50	1	#
7	-3.75	8	-3.75	1	#
8	-2.83	4	-2.83	1	#
9	-2.67	3	-2.67	1	#
10	-1.83	7	-1.83	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	1	-5.77	0.00	6.44	RANKING
2	1	9	-5.72	0.00	6.82	RANKING
3	1	2	-5.54	0.00	6.15	RANKING
4	1	10	-5.39	0.00	7.77	RANKING
5	1	6	-5.28	0.00	6.78	RANKING
6	1	5	-4.50	0.00	8.84	RANKING
7	1	8	-3.75	0.00	5.87	RANKING
8	1	4	-2.83	0.00	7.15	RANKING
9	1	3	-2.67	0.00	6.17	RANKING
10	1	7	-1.83	0.00	6.13	RANKING

Compound 31

CLUSTERING HISTOGRAM

Cluster Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-9.76	2	-9.76	1	#
2	-6.39	8	-6.39	1	#
3	-4.94	5	-4.94	1	#
4	-4.08	4	-4.08	1	#
5	-3.61	10	-3.61	1	#
6	-3.57	6	-3.57	1	#
7	-3.51	7	-3.51	1	#
8	-2.99	1	-2.99	1	#
9	-2.19	9	-2.19	1	#
10	-0.02	3	-0.02	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	2	-9.76	0.00	8.49	RANKING
2	1	8	-6.39	0.00	6.49	RANKING
3	1	5	-4.94	0.00	7.70	RANKING
4	1	4	-4.08	0.00	8.78	RANKING
5	1	10	-3.61	0.00	7.20	RANKING
6	1	6	-3.57	0.00	7.56	RANKING
7	1	7	-3.51	0.00	5.96	RANKING
8	1	1	-2.99	0.00	7.64	RANKING
9	1	9	-2.19	0.00	8.54	RANKING
10	1	3	-0.02	0.00	7.76	RANKING

Compound 32

CLUSTERING HISTOGRAM

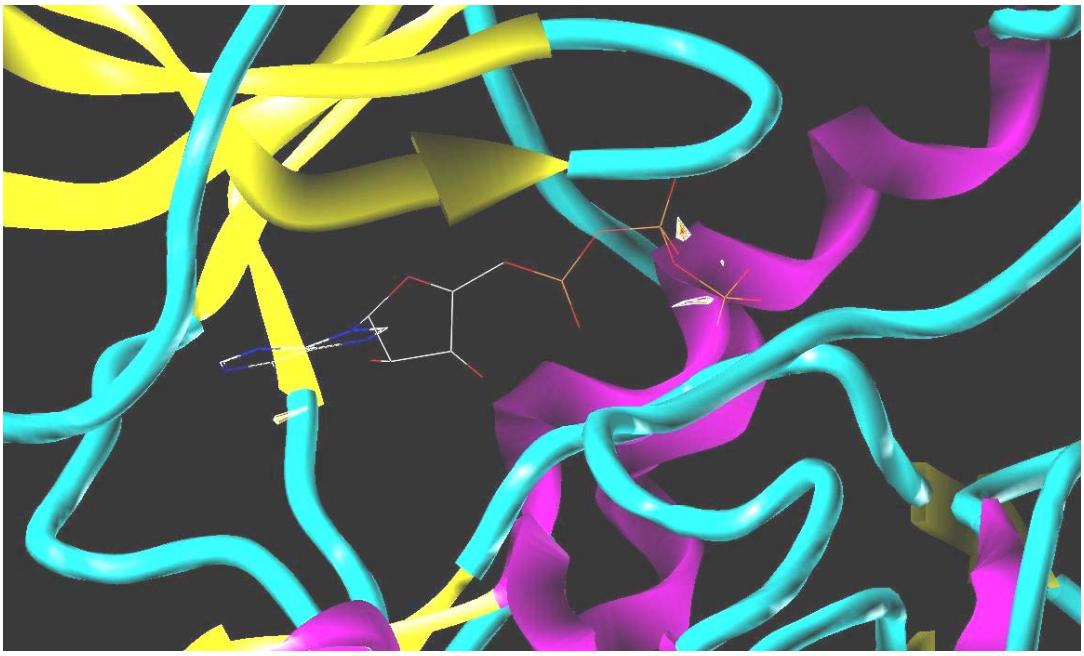
Clus-ter Rank	Lowest Docked Energy	Run	Mean Docked Energy	Num in Clus	Histogram 5 10 15 20
1	-9.30	8	-9.30	1	#
2	-5.94	10	-5.94	1	#
3	-5.24	3	-5.24	1	#
4	-4.86	4	-4.86	1	#
5	-4.37	1	-4.37	1	#
6	-4.25	7	-4.25	1	#
7	-3.62	6	-3.62	1	#
8	-2.34	9	-2.34	1	#
9	-2.31	2	-2.31	1	#
10	-1.70	5	-1.70	1	#

RMSD TABLE

Rank	Sub-Rank	Run	Docked Energy	Cluster RMSD	Reference RMSD	Grep Pattern
1	1	8	-9.30	0.00	8.71	RANKING
2	1	10	-5.94	0.00	7.08	RANKING
3	1	3	-5.24	0.00	9.57	RANKING
4	1	4	-4.86	0.00	6.93	RANKING
5	1	1	-4.37	0.00	8.45	RANKING
6	1	7	-4.25	0.00	8.55	RANKING
7	1	6	-3.62	0.00	7.30	RANKING
8	1	9	-2.34	0.00	7.63	RANKING
9	1	2	-2.31	0.00	8.17	RANKING
10	1	5	-1.70	0.00	6.54	RANKING

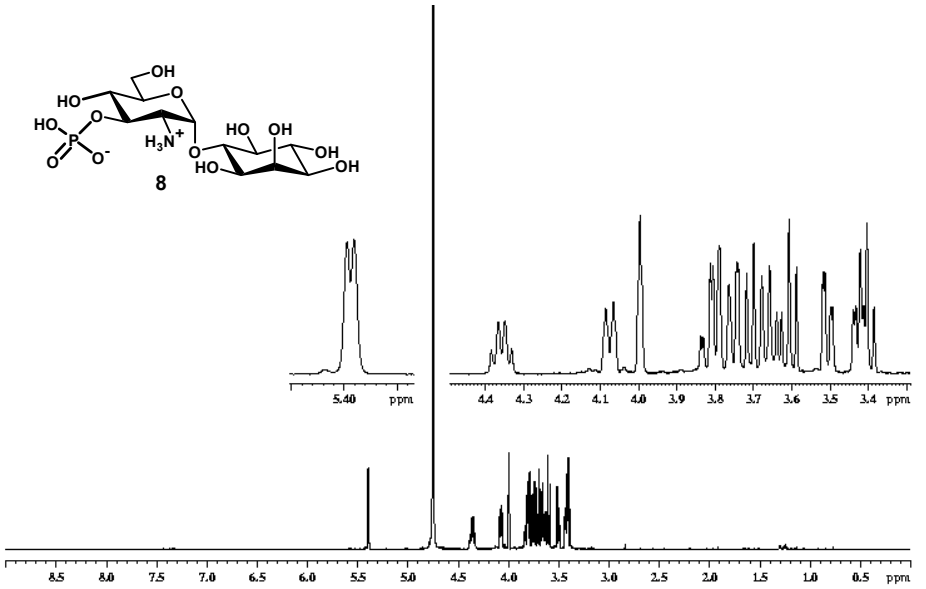
GRID Calulations

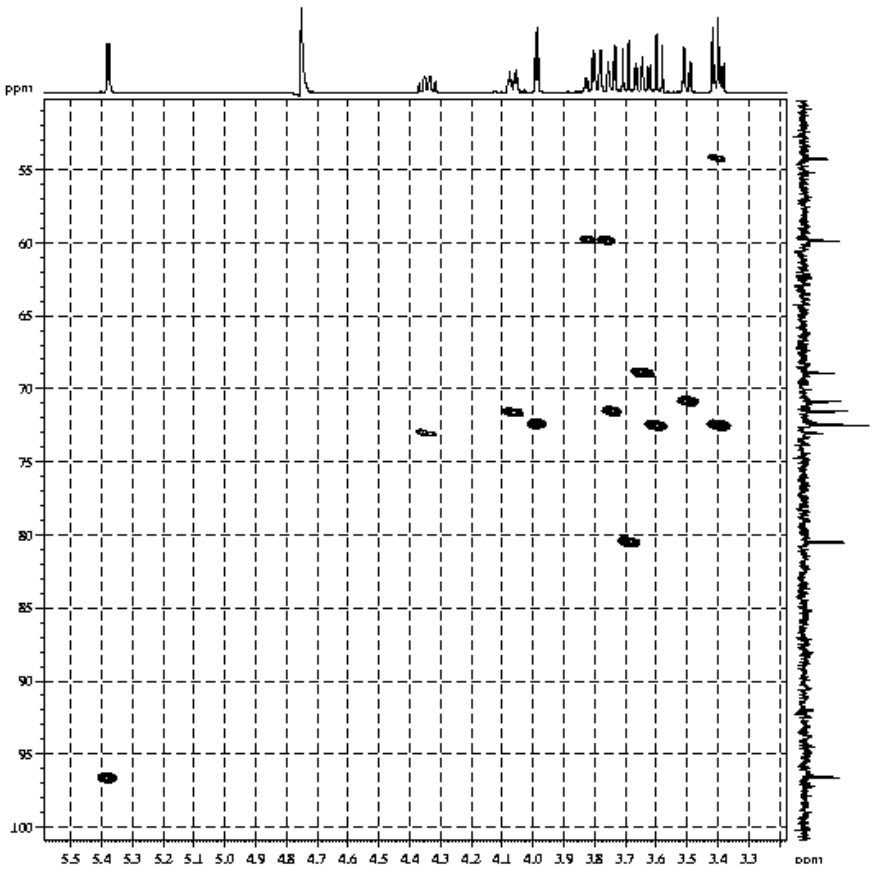
A picture of the PKA catalytic subunit active site is shown, including an ATP molecule as well as favourable energy phosphate regions, calculated using GRID program. The most favourable position has an interaction energy of -19.8305 kcal/mol.

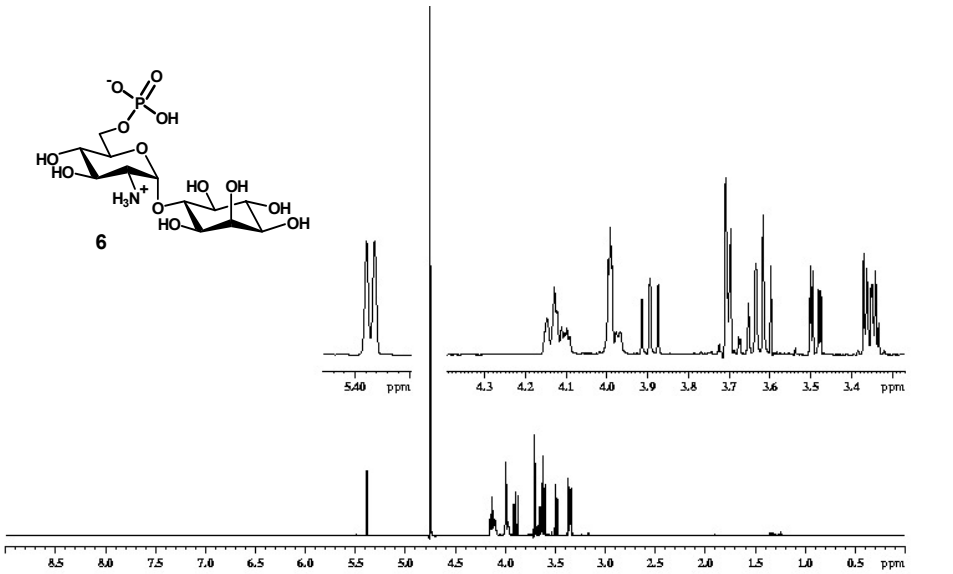


NMR spectra

^{1}H-NMR and HSQC spectra of pseudodisaccharides **8**, **9** and **34** at pH = 5.6, 6.3 and 5.5 respectively and pseudotrisaccharides **10**, **13**, **17**, **35** and **36** at pH = 6.8, 5.8, 6.5, 5.8 and 5.9 respectively, acquired on a Bruker DRX-500 spectrometer in deuterium oxide are shown:



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5.40 ppm
4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 ppm
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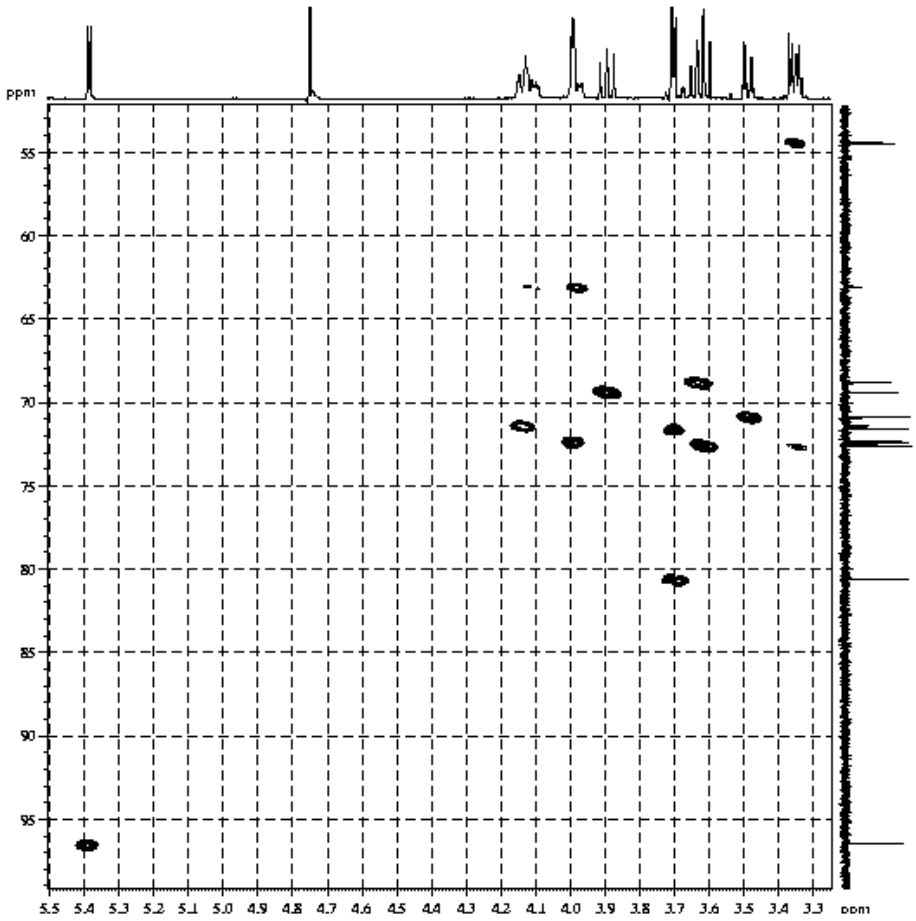
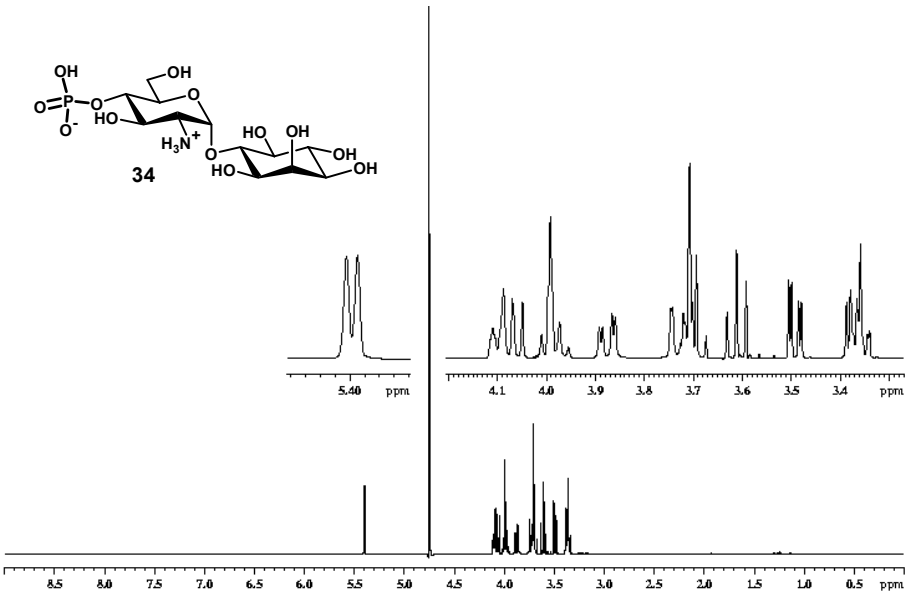
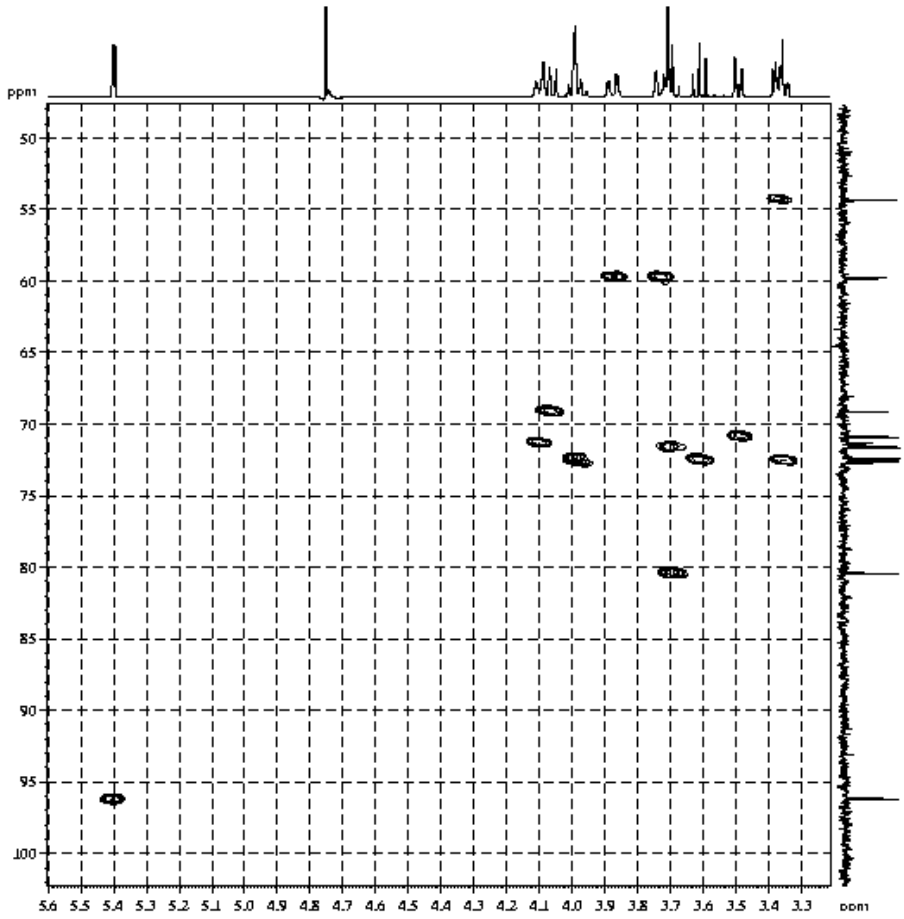

ppm
55
60
65
70
75
80
85
90
95
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 ppm


OH
OH
O
O
P
O
O
HO
O
HO
H_3N^+
O
HO
OH
OH
HO
OH
34
5.40
ppm
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


ppm
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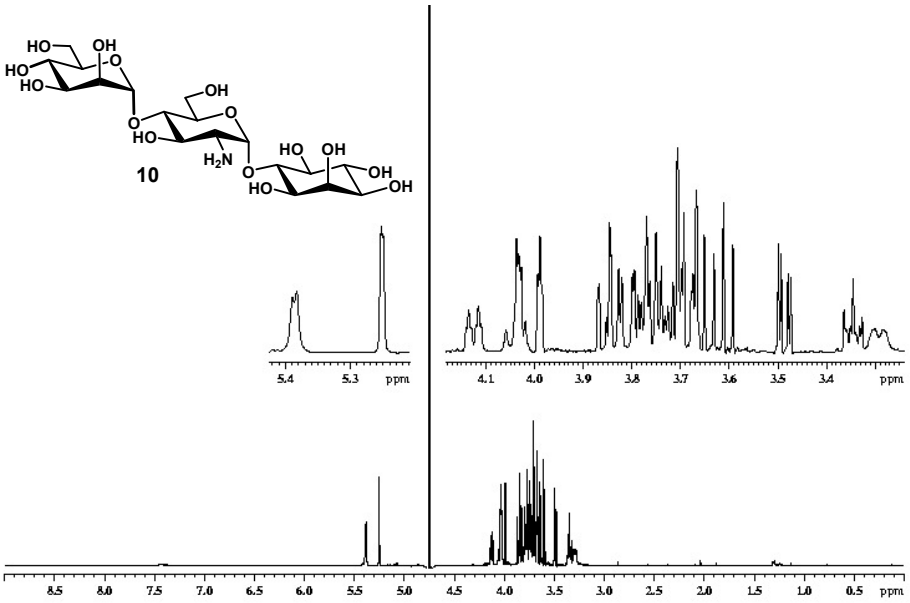
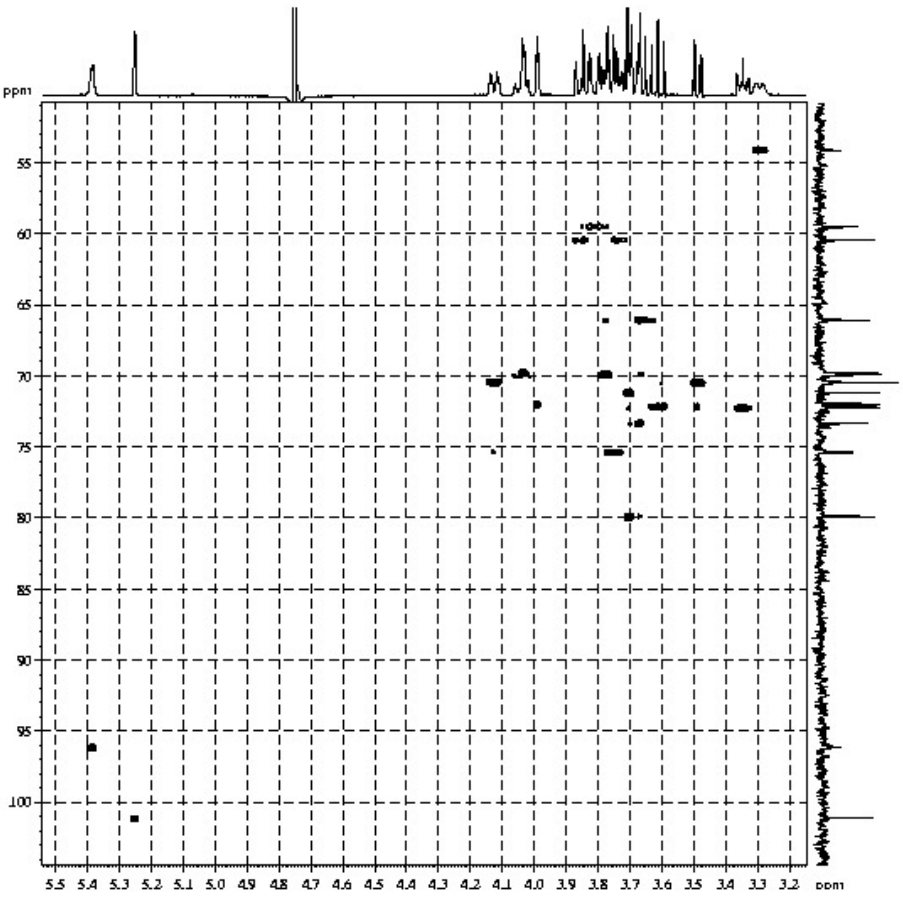
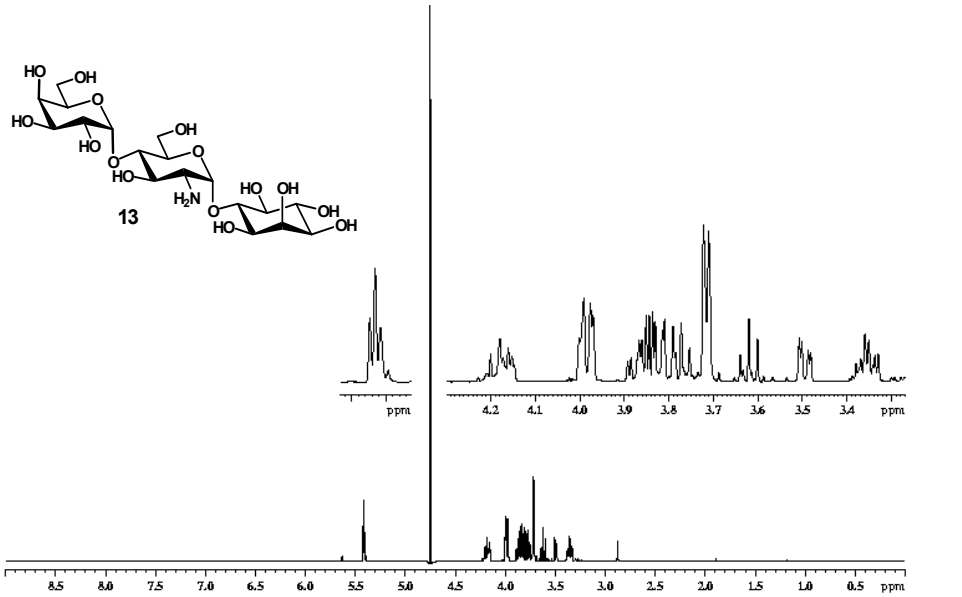
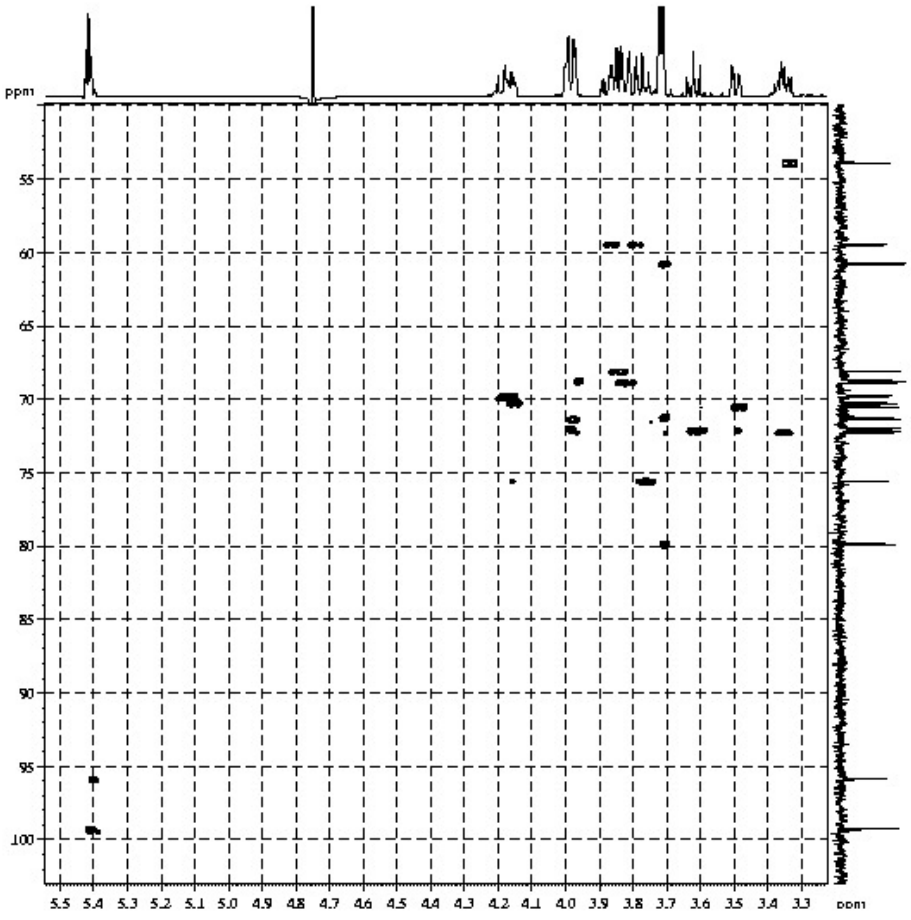
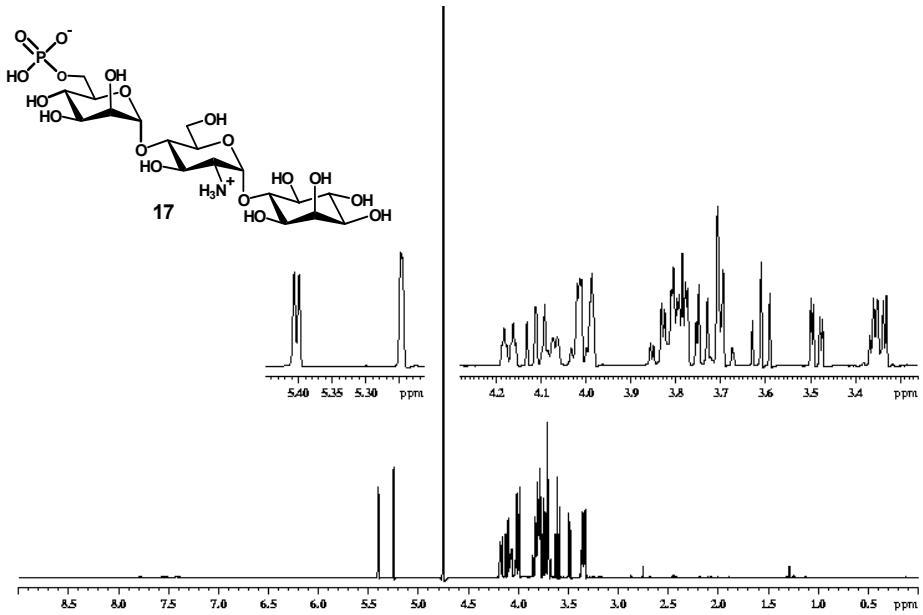
55
60
65
70
75
80
85
90
95
100
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
ppm

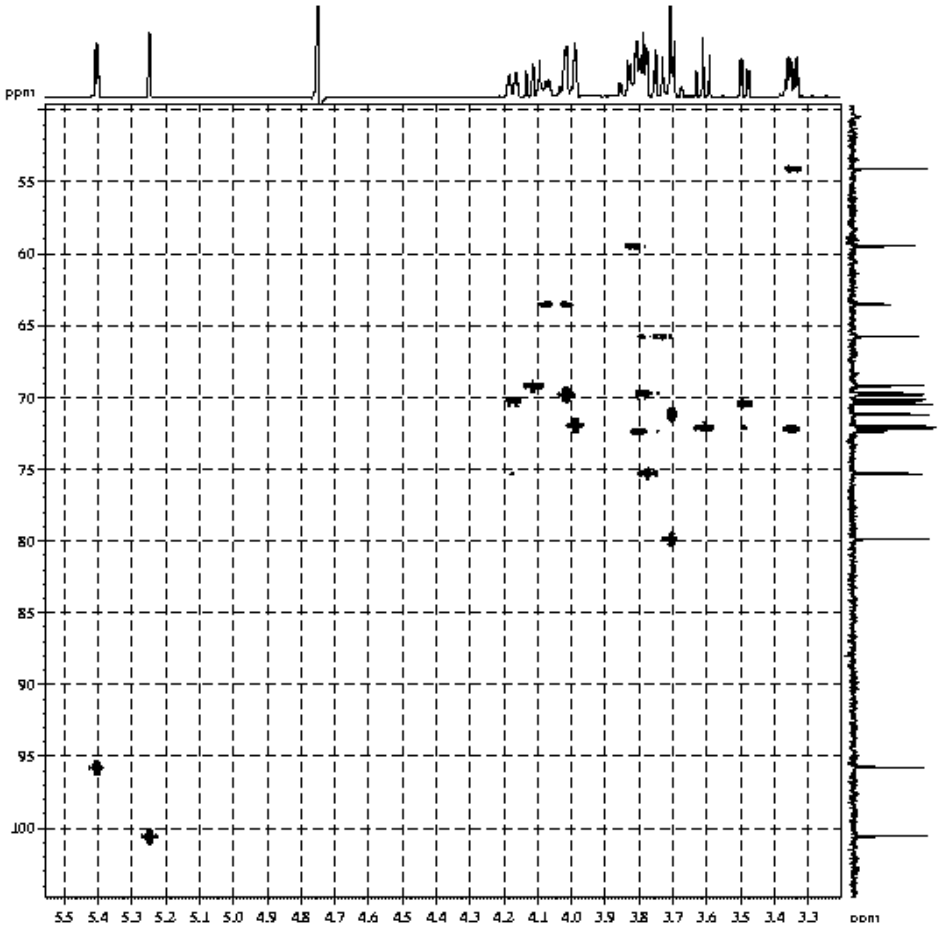

HO
OH
HO
HO
O
OH
O
HO
H_2N
O
HO
OH
OH
HO
10
5.4
5.3
ppm
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

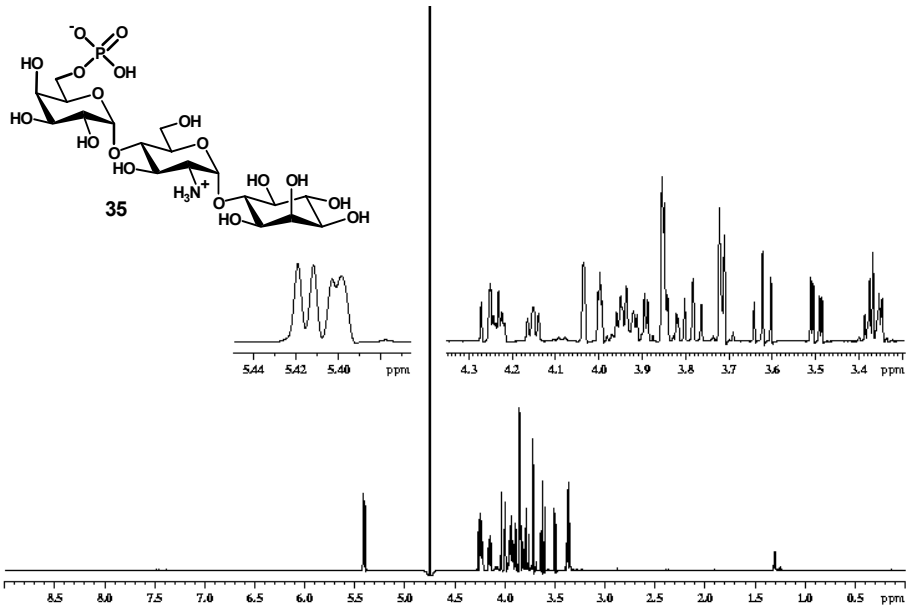

ppm
55
60
65
70
75
80
85
90
95
100
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
ppm

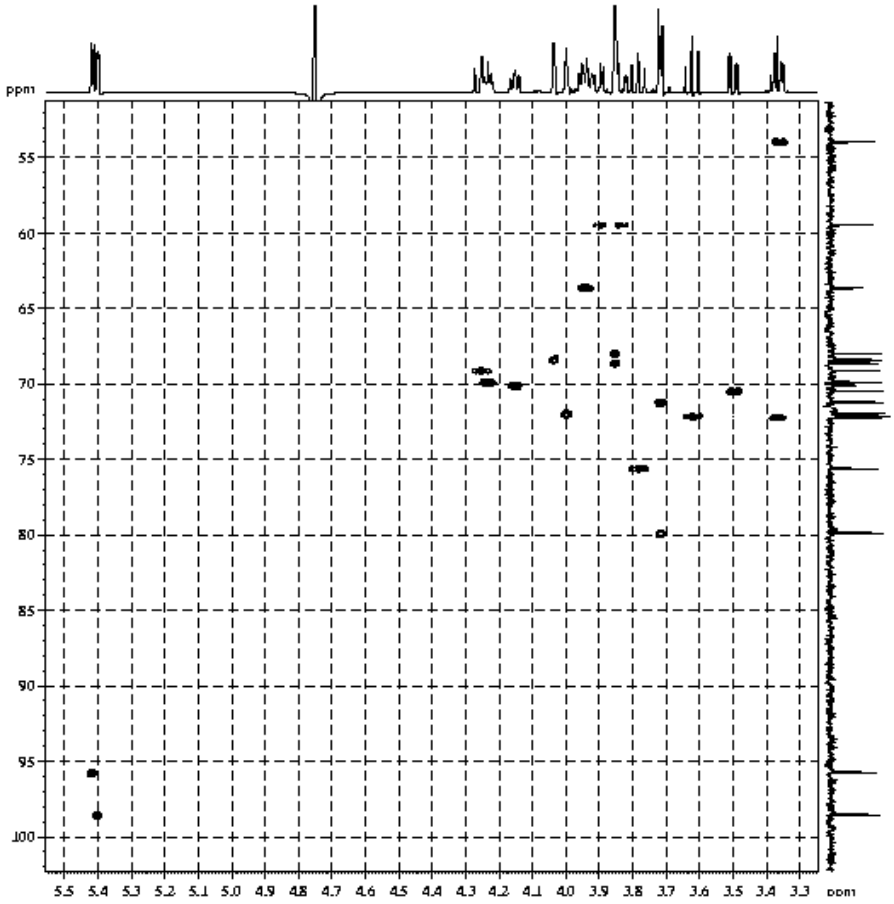

13
ppm
ppm

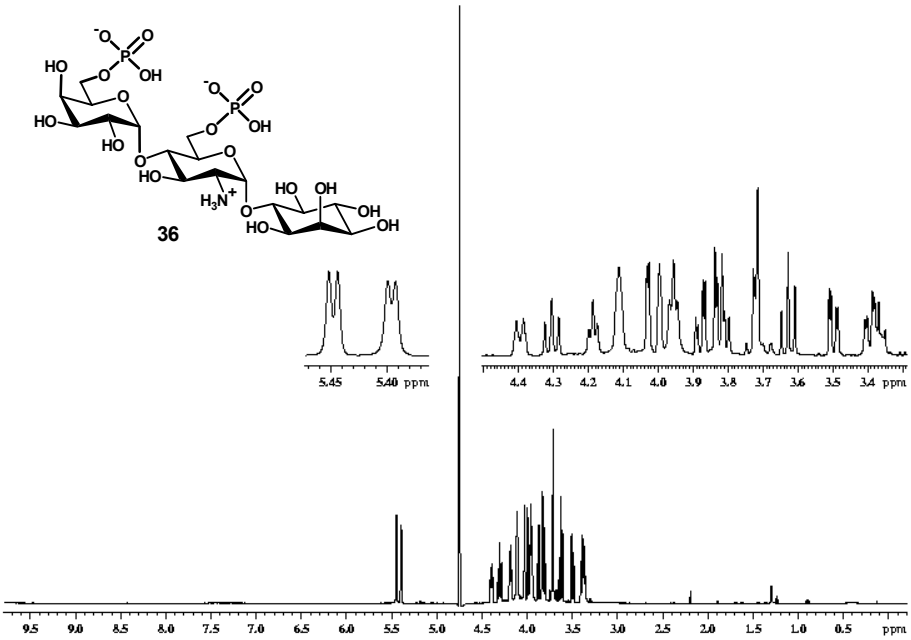

ppm
ppm

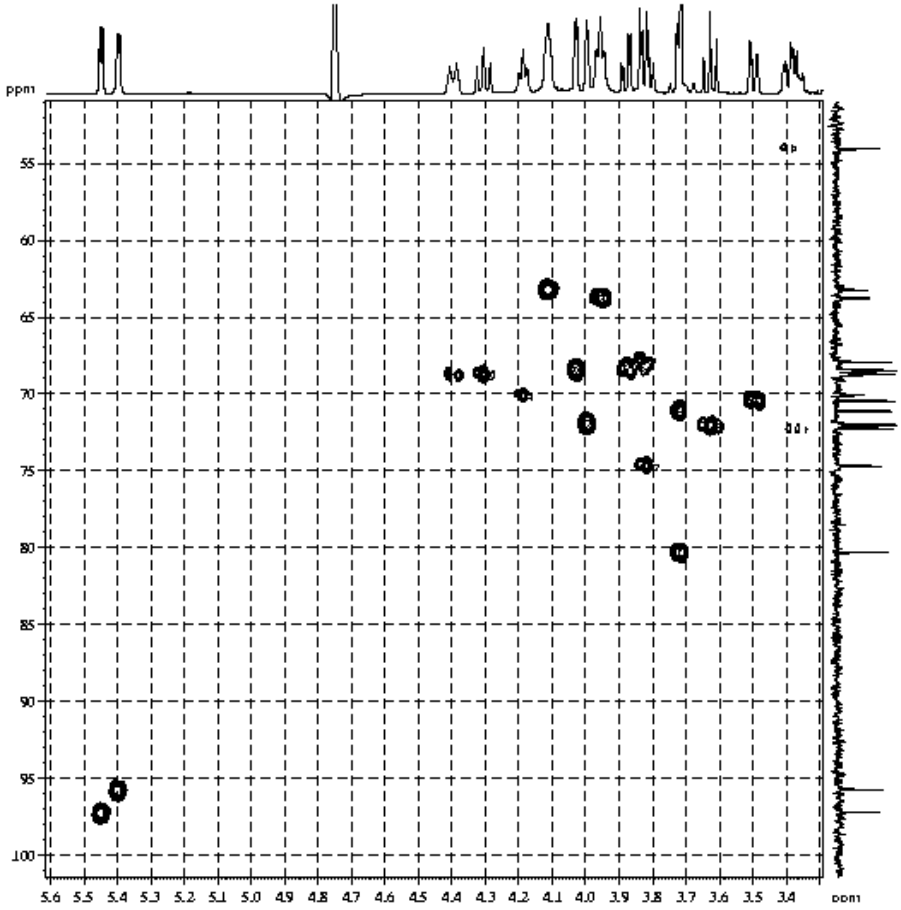

17
5.40 5.35 5.30 ppm
4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


ppm
55
60
65
70
75
80
85
90
95
100
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 ppm


35
5.44 5.42 5.40 ppm
4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


ppm
55
60
65
70
75
80
85
90
95
100
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 ppm


36
5.45
5.40 ppm
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4 ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


ppm
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60
65
70
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80
85
90
95
100
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
ppm