Simple One-pot Regioselective 6-O-Phosphorylation of Carbohydrates and Trehalose Desymmetrization

A. Abragam Joseph,^{*a, b*} Chun-Wei Chang,^{*a*} Cheng-Chung Wang^{*a*}*

^aInstitute of Chemistry, Academia Sinica, Nankang, Taipei 115, Taiwan. ^bDepartment of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan.

E-mail: wangcc@chem.sinica.edu.tw

SUPPORTING INFORMATION

General Information

All reactions were conducted in flame-dried glassware, under nitrogen atmosphere. Dichloromethane, diethyl ether, *N*,*N*-dimethyformamide, methanol were purified and dried from a safe purification system containing activated Al₂O₃. All reagents obtained from commercial sources were used without purification. unless otherwise mentioned. Flash column chromatography was carried out on Silica Gel Geduran[®] Si 60 (0.040-0.063, E. Merck) and DAVISIL® (LC60A 40-63 micron), TLC was performed on precoated glass plates of Silica Gel 60 F254 (0.25mm, E. Merck); detection was executed by spraying with a solution of cerium(IV) sulfate, ammonium molybdate and H₂SO₄ in water and subsequent heating on a hot plate. Optical rotations were measured on Jasco DIP-370 using a 100 mm cell at 589 nm. ¹H, ¹³C NMR, DEPT, ¹H-¹H COSY, ¹H-¹³C COSY, and NOESY spectrum were recorded with Bruker AV400, AVIII 400 and DRX 500, AV 500 MHz instruments. Chemical shifts are in ppm from Me₄Si, generated from the

CDCl₃ lock signal at δ 7.24, CD₂Cl₂ lock signal at 5.32 and D₂O lock signal at 4.80. All ¹³C NMR spectra contain the ¹³C at the bottom trace, and the middle and the upper traces are DEPT 90, 135 respectively. Multiplicities are reports by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; *J* = coupling constant values in Hertz. Mass spectra was analyzed on a Waters Premier XE instrument with ESI source.

Procedures for One-Pot Regioselective Phosphorylation of 1, 4, 7, 10, 13, 16, 19, 22, 25 and 28. TMSOTf (0.1 equiv) was added at room temperature under an N₂ atmosphere to a suspension of compound 1, 4, 7, 10, 13, 16, 19, 22, 25, 28 (100 mg, 1 equiv) and HMDS (0.6 equiv per hydroxyl group) in CH₂Cl₂ (1.0 mL). After stirring for 30-40 min, pyridine (1.1 mL), diphenyl chlorophosphate (3.0 equiv) were added with stirring. The mixture was allowed to stir at room temperature for 36 h. The mixture was concentrated and purified by flash column chromatography (Hex/EtOAc 20:1) to yield 2 (82%), 5 (83%), 8 (85%), 11 (84%), 14 (82%), 17 (78%), 20 (63%), 23 (44%), 26 (49%) and 29 (48%).

General Procedure for the Hydrogenation and Salinization of 2, 5, 8, 11, 14, 17, 20, 23, 26 and 29. To a solution of compound 2, 5, 8, 11, 14, 17, 20, 23, 26 and 29 (50 mg, 1 equiv) in 75% EtOH (5 mL) was added PtO_2 (2.05 equiv). After stirring for 12 h at room temperature under an H₂ atmosphere, the mixture was filtered through a celite pad. The solvent was evaporated *in vacuo* and washed with Ethyl acetate and water. The water layer was lyophilized to give a white powder, which was mixed with potassium hydroxide (2.05 equiv) in H₂O (1 mL). The solution was stirred for 4 h and lyophilized to give the product 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 without further purification.



Methyl 6-*O*-diphenylphosphoryl-2,3,4-tri-*O*-trimethylsilyl-α-D-glucopyranoside (2). Procedures were as shown in the general procedures to afford **2** as a colourless syrup (272 mg, 82%) and the fully trimethylsilylated α-methoxy glucose (27 mg, 11%) (recovered yield of **2**: 92%). $[α]^{32}_{D}$ 61.9 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.14 (m, 10H, Ph), 4.50 (d, *J* = 3.4 Hz, 1H, H-1), 4.49 (ddd, *J* = 10.4, 7.8, 5.2 Hz, 1H, H-6a), 4.26 (ddd, *J* = 11.0, 7.8, 5.2 Hz, 1H, H-6b), 3.72 (t, *J* = 9.2 Hz, 1H, H-3), 3.68 (ddd, *J* = 11.4, 9.2, 1.9 Hz, 1H, H-5), 3.40 (t, *J* = 9.2 Hz, 1H, H-4), 3.36 (dd, *J* = 3.8, 9.4 Hz, 1H, H-2), 0.13 (s, 9H, TMS), 0.12 (bs, 18H, TMS); ¹³C NMR (100 MHz, CDCl₃) δ 150.92 (C), 150.85 (C), 130.77 (C), 129.88 (CH), 129.86 (CH), 125.4 (CH), 120.3 (CH), 120.2 (CH), 99.9 (CH), 75.1 (CH), 73.8 (CH), 72.1 (CH), 70.3 (CH, *J*cp = 6.3 Hz), 68.4 (CH₂, *J*cp = 5.8 Hz), 55.1 (CH₃), 1.5 (CH₃), 1.1 (CH₃), 0.7 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -11.35; HRMS (ESI) calcd for C₂₈H₄₈O₉Si₃P [M+H]⁺ 643.2344, found 643.2342.



Methyl α-D-glucose 6-phosphate dipotassium salt (3). Procedure were as shown in the general procedures to afford **3** as a white powder (26 mg, 97%). $[\alpha]^{30}_{D}$ 62.9 (*c* 0.5, H₂O); ¹H NMR (400 MHz, D₂O) δ 4.83 (s, 1H, H-1), 4.01 (ddd, *J* = 2.8, 7.0, 11.1 Hz, 1H, H-6a), 3.96 (dd, *J* = 4.1, 11.6 Hz, 1H, H-6b), 3.71-3.63 (m, 4H, H-2, H-3, H-4, H-5), 3.46 (s, 1H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 99.5 (CH), 72.7 (CH), 71.4 (CH), 71.3 (CH), 71.3 (CH), 68.9 (CH),

62.4 (CH₂), 55.1 (CH₃); ³¹P NMR (162 MHz, D₂O) δ 5.09; HRMS (ESI) calcd for C₇H₁₄O₉P [M-2K+H]⁻ 273.0375, found 273.0378.



6-O-Diphenylphosphoryl-1,2,3,4-tetra-O-trimethylsilyl-D-glucopyranose (5). Procedures were as shown in the general procedures to afford 5 as a colourless syrup (315 mg, 83%) and the fully trimethylsilylated glucose (35 mg, 12%) (recovered yield of 5: 94%). $[\alpha]^{32}_{D}$ 38.1 (c 0.5, CHCl₃); ¹H NMR (400 MHz, $CDCl_3$) δ 7.32-7.13 (m, 20H, Ph), 4.88 (d, J = 3.0 Hz, 1H, H-1 α), 4.54 (ddd, J =10.7, 5.9, 1.5 Hz, 1H, H-6a β), 4.47 (d, J = 6.5 Hz, 1H, H-1 β), 4.46 (ddd, J =10.9, 7.3, 2.1 Hz, 1H, H-6a α), 4.26 (ddd, J = 11.3, 7.3, 2.1 Hz, 1H, H-6b α), 4.16 (ddd, J = 10.4, 5.9, 1.5 Hz, 1H, H-6b β), 4.10 (t, J = 5.9 Hz, 1H, H-4 β), $3.86 (ddd, J = 11.3, 9.1, 2.1 Hz, 1H, H-5\alpha), 3.85 (ddd, J = 10.7, 5.9, 1.5 Hz, 1H)$ H-5 β), 3.75 (t, J = 9.1 Hz, 1H, H-3 α), 3.39 (t, J = 9.1 Hz, 1H, H-4 α), 3.36 (t, J = 5.9 Hz, 1H, H-3 β), 3.22 (t, J = 9.1. 3.0 Hz, 1H, H-2 α), 3.21 (dd, J = 6.5, 5.9 Hz, 1H, H-2β), 0.13 (s, 18H, TMS), 0.12 (s, 18H, TMS), 0.10 (s, 18H, TMS), 0.09 (s, 18H, TMS); ¹³C NMR (100 MHz, CDCl₃) δ 151.0 (C), 150.92 (C), 150.89 (C), 150.8 (C), 129.9 (CH), 125.5 (CH), 125.4 (CH), 120.4 (CH), 120.3 (CH), 120.26 (CH), 98.3 (CH), 94.0 (CH), 78.1 (CH), 77.6 (CH), 77.43 (CH), 77.35 (CH), 77.2 (CH), 76.9 (CH), 75.1 (CH), 75.0 (CH), 74.0 (CH), 73.9 (CH), 71.9 (CH), 70.9 (CH), 70.8 (CH), 68.4 (CH₂, $J_{cp} = 5.9$ Hz), 1.43 (CH₃), 1.08 (CH₃), 0.60 (CH₃), 0.32 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -11.72; HRMS (ESI) calcd for $C_{30}H_{53}O_9NaSi_4P[M+Na]^+$ 723.2402, found 723.2406.



Glucose 6-phosphate dipotassium salt (6). Procedure were as shown in the general procedures to afford **6** as a white powder (23 mg, quant). (α:β= 0.5/1), $[\alpha]^{29}{}_{\rm D}$ 119.7 (*c* 0.5, H₂O); ¹H NMR (400 MHz, D₂O) δ 5.26 (d, *J* = 3.8 Hz, 1H, H-1α), 4.67 (d, *J* = 7.9 Hz, 1H, H-1β), 4.06 (ddd, *J* = 11.2, 6.6, 3.2 Hz, 1H, H-6aα), 4.02-3.97 (m, 2H, H-6aβ, H–6bβ), 3.92 (ddd, *J* = 10.7, 6.6, 3.2 Hz, 1H, H-6bα), 3.88 (ddd, *J* = 11.2, 6.6, 3.2 Hz, 1H, H-6bα), 3.88 (ddd, *J* = 11.2, 6.6, 3.2 Hz, 1H, H-6bβ), 3.74 (t, *J* = 9.5 Hz, 1H, H-3α), 3.64-3.56 (m, 3H, H-2α, H-4α, H-4β), 3.53-3.49 (m, 2H, H-3β, H-5β), 3.28 (t, *J* = 7.9 Hz, 1H, H-2β); ¹³C NMR (100 MHz, D₂O) δ 96.7 (CH), 92.7 (CH), 75.4 (CH, *J*cp = 6.6 Hz), 75.3 (CH), 74.7 (CH), 72.4 (CH), 71.9 (CH), 71.0 (CH, *J*cp = 6.6 Hz), 69.2 (CH), 62.8 (CH₂, *J*cp = 4.2 Hz), 62.7 (CH₂, *J*cp = 4.2 Hz); ³¹P NMR (162 MHz, D₂O) δ 5.12; HRMS (ESI) calcd for C₆H₁₂O₉PK₂ [M]⁺ 336.9493, found 336.9498.



6-*O*-Diphenylphosphoryl-1,2,3,4-tetra-*O*-trimethylsilyl-D-galactopyranose (8). Procedures were as shown in the general procedures to afford 8 as a colourless syrup (325 mg, 85%) and the fully trimethylsilylated galactose (42 mg, 14%) (recovered yield of 8: 99%). (α :β= 6.2/1). [α]³²_D 58.1 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.14 (m, 20H, Ph), 5.04 (d, *J* = 2.1 Hz, 1H, H-1 α), 4.40 (d, *J* = 7.2 Hz, 1H, H-1 β), 4.29-4.20 (m, 5H, H-5 β , H-6a α , H-6b α , H-6a β , H-6b β), 4.12 (dt, *J* = 6.5, 1.3 Hz, 1H, H-5 α), 3.84-3.76 (m, 3H, H-2α, H-3α, H-4α), 3.63-3.55 (m, 2H, H-2β, H-4β), 3.33 (dd, J = 9.2, 2.6 Hz, 1H, H-3β), 0.14 (s, 9H, TMS), 0.13 (s, 9H, TMS), 0.12 (s, 9H, TMS), 0.11 (s, 9H, TMS) , 0.10 (s, 9H, TMS) , 0.094 (s, 9H, TMS) , 0.092 (s, 9H, TMS) , 0.08 (s, 9H, TMS); ¹³C NMR (100 MHz, CDCl) δ 150.8 (C), 150.7 (C), 130.0 (CH), 125.6 (CH), 125.5 (CH), 120.3 (CH), 120.2 (CH), 98.7 (CH), 94.7 (CH), 75.1 (CH), 73.1 (CH, Jcp = 7.4 Hz), 72.5 (CH), 71.7 (CH), 70.3 (CH), 69.9 (CH), 69.6 (CH), 69.3 (CH, Jcp = 8.4 Hz), 67.3 (CH₂, Jcp = 5.6 Hz), 1.0 (CH₃), 0.9 (CH₃), 0.82 (CH₃), 0.76 (CH₃), 0.6 (CH₃), 0.5 (CH₃), 0.3 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -12.04; HRMS (ESI) calcd for C₃₀H₅₃O₉NaSi₄P [M+Na]⁺ 723.2402, found 723.2399.



Galactose 6-phosphate dipotassium salt (9). Procedure were as shown in the general procedures to afford **9** as a white powder (23 mg, 97%). (α:β= 0.36/1). $[α]^{28}{}_{D}$ 115.6 (*c* 0.5, H₂O); ¹H NMR (400 MHz, D₂O) δ 5.30 (d, *J* = 3.3 Hz, 1H, H-1), 4.64 (d, *J* = 7.8 Hz, 1H, H-1β), 4.19-4.00 (m, 4H, H-6aα, H-6bα, H-6aβ, H-6bβ), 3.91-3.89 (m, 4H, H-4α, H-4β, H-5α, H-5β), 3.85-3.81 (m, 2H, H-2α, H-4β), 3.93-3.67 (m, 2H, H-3α, H-3β), 3.48 (t, *J* = 7.8 Hz, 1H, H-2β); ¹³C NMR (100 MHz,D₂O) δ 97.3 (CH), 93.0 (CH), 73.9 (CH, *J*cp = 6.3 Hz), 73.0 (CH), 72.7 (CH), 72.5 (CH), 70.4 (CH), 69.7 (CH), 69.5 (CH), 69.5 (CH), 69.4 (CH), 69.3 (CH), 69.1 (CH), 69.0 (CH), 68.9 (CH), 68.5 (CH), 66.2 (CH), 65.3 (CH₂), 63.4 (CH₂), 62.6 (CH₂), 62.4 (CH₂); ³¹P NMR (162 MHz, D₂O) δ 0.82; HRMS (ESI) calcd for C₆H₁₄O₉P [M+H]⁺ 261.0375, found 261.0369.



6-*O***-Diphenylphosphoryl-1,2,3,4-tetra-***O***-trimethylsilyl-α-D-mannopyranose (11). Procedures were as shown in the general procedures to afford 11 as a colourless syrup (320 mg, 84%) and the fully trimethylsilylated mannose (45 mg, 15%) (recovered yield of 11: 99%). [\alpha]^{32}_{D} 5.8 (***c* **0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.13 (m, 10H, Ph), 4.88 (s, 1H, H-1), 4.45 (ddd,** *J* **= 10.4, 6.4, 1.7 Hz, 1H, H-6a), 4.28 (ddd,** *J* **= 10.7, 6.4, 1.7 Hz, 1H, H-6b), 3.87-3.78 (m, 3H, H-3, H-4,H-5), 3.63 (t,** *J* **= 1.8 Hz, 1H, H-2), 0.14 (s, 9H, TMS), 0.10 (s, 9H, TMS) , 0.09 (s, 9H, TMS); ¹³C NMR (100 MHz, CDCl₃) δ 151.0 (C), 150.9 (C), 139.9 (CH), 129.8 (CH), 125.34 (CH), 125.31 (CH), 120.6 (CH), 120.5 (CH), 120.4 (CH), 120.3 (CH), 95.6 (CH), 75.3 (CH), 72.8 (CH₃), 0.6 (CH₃), 0.5 (CH₃), 0.0 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -11.31; HRMS (ESI) calcd for C_{30}H_{53}O_9NaSi_4P [M+Na]^+ 723.2402, found 723.2411.**



Mannose 6-phosphate dipotassium salt (12). Procedure were as shown in the general procedures to afford 12 as a white powder (23 mg, 98%). $[\alpha]^{29}{}_{\rm D}$ 107.4 (*c* 0.5, H₂O); ¹H NMR (400 MHz, CDCl₃) δ 5.21 (d, *J* = 1.3 Hz, 1H, H-1α), 4.93 (s, 1H, H-1β), 4.08-3.83 (m, 4H, H-2a, H-2β, H-6aα, H-6bα), 3.80-3.64 (m, 6H, H-3α, H-3β, H-5α, H-5β, H-6aβ, H-6bβ), 3.46 (t, *J* = 3.3 Hz, 1H, H-4α), 3.43 (t, *J* = 3.3 Hz, 1H, H4β); ¹³C NMR (100 MHz, CDCl₃) δ 94.6 (CH), 94.1 (CH), 75.7 (CH), 72.8 (CH), 71.9 (CH), 71.8 (CH₂), 71.5 (CH), 71.0 (CH),

70.1 (CH), 69.6 (CH₂), 69.5 (CH₂), 66.5 (CH), 66.2 (CH), 63.0 (CH₂), 60.5 (CH₂); ³¹P NMR (162 MHz, D₂O) δ 4.97; HRMS (ESI) calcd for C₆H₁₄O₉P [M+H]⁺ 261.0375, found 261.0377.



Methyl 6-*O*-diphenylphosphoryl-2,3,4-tri-*O*-trimethylsilyl-α-D-mannopyranoside (14). Procedures were as shown in the general procedures to afford 14 as a colourless syrup (272 mg, 82%) and the fully trimethylsilylated mannose (27 mg, 11%) (recovered yield of 14: 92%). $[\alpha]^{24}{}_{\rm D}$ 5.6 (*c* 0.15, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.13 (m, 10H, Ph), 4.88 (s, 1H, H-1), 4.45 (ddd, *J* = 10.4, 6.4, 1.7 Hz, 1H, H-6a), 4.28 (ddd, *J* = 10.7, 6.4, 1.7 Hz, 1H, H-6b), 3.87-3.78 (m, 3H, H-3, H-4,H-5), 3.63 (t, *J* = 1.9, 1.8 Hz, 1H, H-2), 0.14 (s, 9H, TMS), 0.10 (s, 9H, TMS) , 0.09 (s, 9H, TMS); ¹³C NMR (100 MHz, CDCl₃) δ 151.0 (C), 150.9 (C), 139.9 (CH), 129.8 (CH), 125.34 (CH), 125.31 (CH), 120.6 (CH), 120.5 (CH), 120.4 (CH), 120.3 (CH), 95.6 (CH), 75.3 (CH), 72.8 (CH, *J*cp = 7.5 Hz), 72.3 (CH), 68.5 (CH₂, *J*cp = 5.7 Hz), 68.3 (CH), 0.9 (CH₃), 0.8 (CH₃), 0.5 (CH₃), 0.0 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -11.68; HRMS (ESI) calcd for C₂₈H₄₇O₉NaSi₃P [M+Na]⁺ 665.2163, found 665.2161.



Methyl α -D-mannopyranoside 6-phosphate dipotassium salt (15). Procedure were as shown in the general procedures to afford 15 as a white powder (26 mg,

quant). $[\alpha]^{25}{}_{D}$ 33.8 (*c* 0.23, H₂O); ¹H NMR (500 MHz, CDCl₃) δ 4.79 (s, 1H, H-1), 4.09 (ddd, *J* = 12.0, 5.0, 3.7 Hz, 1H, H-6a), 3.98 (d, *J* = 12.0, 5.0, 2.0 Hz, 1H, H-6b), 3.95 (dd, *J* = 3.4, 1.6 Hz, 1H, H-2), 3.89 (t, *J* = 10.0 Hz, 1H, H-4), 3.80 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3), 3.6-3.67 (m, 1H, H-5), 3.44 (s, 3H, OCH₃); ¹³C NMR (125 MHz, D₂O) δ 101.2 (CH), 72.1 (d, *J*_{CP} = 7.3 Hz, CH), 70.3 (CH), 70.1 (CH), 66.1 (CH), 62.6 (d, *J*_{CP} = 4.0 Hz, CH₂), 57.8 (CH₃); ³¹P NMR (202 MHz, D₂O) δ 4.69; HRMS (ESI) calcd for C₇H₁₄O₉P [M–2K+H]⁻ 273.0375, found 273.0367.



6-O-Diphenylphosphoryl-2-deoxy-1,3,4-tri-O-trimethylsilyl-α-D-gluco-

pyranoside (17). Procedures were as shown in the general procedures to afford **17** as a colourless syrup (290 mg, 78%) and the fully trimethylsilylated 2-deoxy-D-glucopyranose (44 mg, 16%) (recovered yield of **17**: 93%). [α]³⁰_D 49.5 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.14 (m, 10H, Ph), 5.13 (s, 1H, H-1), 4.42 (td, J = 10.7, 7.0 Hz, 1H, H-6a), 4.34 (td, J = 10.7, 7.0 Hz, 1H, H-6b), 3.96 (td, J = 12.0, 9.0 Hz, 1H, H-3), 3.82 (ddd, J = 10.7, 9.0, 7.0 Hz, 1H, H-5), 3.44 (t, J = 9.0 Hz, 1H, H-4), 1.88 (dd, J = 12.0, 4.3, 1H, H-2ax), 1.54 (t, J = 12.0 Hz, 1H, H-2eq), 0.13 (s, 9H, TMS), 0.11 (s, 9H, TMS), 0.09 (s, 9H, TMS); ¹³C NMR (100 MHz, CDCl₃) δ 151.0 (C), 151.01 (C), 150.96 (C), 150.89 (C), 129.9 (CH), 129.8 (CH), 125.4 (CH), 125.3 (CH), 120.42 (CH), 120.38 (CH), 120.34 (CH), 92.3 (CH), 72.9 (CH), 71.4 (CH, *J*cp = 7.0 Hz), 70.1 (CH), 68.5 (CH₂, *J*cp = 5.8 Hz), 41.2 (CH₂), 0.9 (CH₃), 0.8 (CH₃), 0.07 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -11.35; HRMS (ESI) calcd for C₂₇H₄₅O₈NaSi₃P [M+Na]⁺ 635.2058, found 635.2064.



2-Deoxy-D-glucose 6-phosphate dipotassium. (18). Procedure were as shown in the general procedures to afford **18** as a white powder (26 mg, quant). $[\alpha]^{30}_{D}$ -1175.3 (*c* 0.5, H₂O); ¹H NMR (400 MHz, D₂O) δ 4.08-3.91 (m, 6H, H-3 α , H-3 β , H-5 α , H-5 β , H-6 α , H-6 $\beta\alpha$), 3.84-3.75 (m, 4H, H-1 α , H-1 β , H-6 $\alpha\beta$, H-6 $\beta\beta$), 3.61-3.55 m, 2H, H-4 α , H-4 β), 1.97-1.78 (m, 2H, H-2 α a, H-2 α b), 1.65-1.58 (m, 2H, H-2 β a, H-2 β b); ¹³C NMR (100 MHz, D₂O) δ 72.5 (CH), 71.9 (CH), 71.7 (CH), 70.8 (CH, *J*cp = 53.2 Hz), 67.1 (CH), 65.4 (CH₂, *J*cp = 4.3 Hz), 58.8 (CH), 35.4 (CH), 25.8 (CH); ³¹P NMR (162 MHz, D₂O) δ 1.34; HRMS (ESI) calcd for C₆H₁₂O₈P [M-2K+H]⁻ 243.0270, found 243.0276.



6-*O*-Diphenylphosphoryl-2,3,4,2',3',4',6'-hepta-*O*-trimethylsilyl-α,α'trehalose (20). Procedures were as shown in the general procedures to afford 20 as a colourless syrup (198 mg, 63%) and the fully trimethylsilylated trehalose (84 mg, 31%) (recovered yield of 20: 92%). $[\alpha]^{32}_{D}$ 81.2 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.28 (m, 4H, Ph), 7.24-7.21 (m, 2H, Ph), 7.17-7.13 (m, 4H, Ph), 4.85 (d, *J* = 3.1 Hz, 1H, H-1'), 4.81 (d, *J* = 3.0 Hz, 1H, H-1), 4.41 (ddd, *J* = 9.6, 7.3, 3.6 Hz, 1H, H-6'a), 4.30 (ddd, *J* = 9.3, 7.3, 3.6 Hz, 1H, H-6'b), 3.95 (ddd, *J* = 9.3, 7.3, 3.6 Hz, 1H, H-5), 3.86 (t, *J* = 9.3 Hz, 1H, H-3), 3.84 (t, J = 9.3 Hz, 1H, H-3'), 3.74 (td, J = 9.3, 2.5 Hz, 1H, H-5'), 3.69-3.63 (m, 2H, H-6'a, H-6'b), 3.45 (t, J = 9.3 Hz, 1H, H-4), 3.43 (t, J = 9.3 Hz, 1H, H-4'), 3.34 (dd, J = 9.3, 3.1 Hz, 1H, H-2'), 3.25 (dd, J = 9.3, 3.0 Hz, 1H, H-2), 0.12 (s, 9H, TMS), 0.11 (s, 9H, TMS), 0.10 (s, 9H, TMS), 0.09 (s, 9H, TMS), 0.08 (s, 9H, TMS); ¹³C NMR (125 MHz, CDCl₃) δ 150.8 (C), δ 150.74 (C), δ 150.68 (C), δ 150.63 (C), 129.7 (CH), 125.2 (CH), 120.11 (CH), 120.07 (CH), 120.0 (CH), 94.7 (CH), 94.4 (CH), 73.50 (CH), 73.48 (CH), 73.38 (CH), 72.8 (CH), 72.5 (CH), 71.6 (CH), 71.5 (d, $J_{CP} = 6.6$ Hz, CH), 67.9 (d, $J_{CP} = 5.9$ Hz, CH₂), 61.9 (CH), 1.07 (CH₃), 1.05 (CH₃), 1.00 (CH₃), 0.90 (CH₃), 0.86 (CH₃), 0.18 (CH₃), 0.11 (CH₃); ³¹P NMR (202 MHz, CDCl₃) δ -11.50; HRMS (ESI) calcd for C₄₅H₈₇O₁₄NaSi₇P [M+Na]⁺ 1101.4116, found 1101.4114.



Trehalose 6-phosphate dipotassium salt (21). Procedure were as shown in the general procedures to afford **21** as a white powder (23 mg, quant). $[α]^{30}_{D}$ 110.5 (*c* 0.5, H₂O); ¹H NMR (400 MHz, D₂O) δ 5.23 (d, *J* =4.1 Hz, 1H, H-1), 5.20 (d, *J*=3.4 Hz, 1H, H-1'), 4.05 (ddd, *J*= 11.7, 6.8, 3.6 Hz, 1H, H-6a), 3.96 (ddd, *J*= 11.5, 5.0, 2.5 Hz, 1H, H-6b), 3.91-3.82 (m, 5H, H-3, H-3', H-5, H-5', H-6a'), 3.76 (t, *J* = 8.3 Hz, 1H, H-4), 3.70 (dd, *J* = 9.8, 4.1 Hz, 1H, H-6b'), 3.64 (dd, *J* = 9.4, 3.4 Hz, 1H, H-2'), 3.46 (t, *J* = 9.3 Hz, 1H, H-4'); ¹³C NMR (100 MHz, CDCl₃) δ 93.5 (CH), 93.3 (CH), 72.5(CH), 72.2 (CH), 72.2 (CH), 71.8 (CH), 71.3 (CH), 71. 0 (CH), 69.7 (CH), 69.7 (CH), 69.2 (CH), 62.5 (CH₂), 60.6 (CH₂); ³¹P NMR (162 MHz, D₂O) δ 4.89; HRMS (ESI) calcd for C₁₂H₂₂O₁₄P [M-2K+H]⁻ 421.0747, found 421.0742.



6'-O-Diphenylphosphoryl-1,2,3,6,2',3',4'-hepta-O-trimethylsilyl-lactose

(23). Procedures were as shown in the general procedures to afford 23 as a colourless syrup (140 mg, 44%) and the fully trimethylsilylated lactose (130 mg, 49%) (recovered yield of 23: 86%). $[\alpha]^{30}$ 188.8 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.29 (m, 4H, Ph), 7.20-7.14 (m, 6H, Ph), 5.01 (s, 1H, H-1), 4.36 (dd, J = 9.6, 5.7, 1.6 Hz, 1H, H-6'a), 4.264 (d, J = 7.7 Hz, 1H, H-1'), 4.259 (ddd, J = 9.4, 5.7, 1.6 Hz, 1H, H-6'b), 3.98 (d, J = 11.0 Hz, 1H, H-6a), 3.79 (bs, 1)1H, H-4'), 3.72 (ddd, J = 11.0, 8.6, 4.7 Hz, 1H, H-5), 3.70 (t, J = 8.7 Hz, 1H, H-3'), 3.65-3.59 (m, 3H, H-2', H-4, H-6b'), 3.52 (ddd, J = 9.6, 5.7, 1.6 Hz, 1H, H-5'), 3.40 (dd, J = 7.7, 1.6 Hz, 1H, H-2), 3.30 (dd, J = 9.2, 2.4 Hz, 1H, H-3'), 0.12 (bs, 18H, TMS), 0.10 (s, 9H, TMS), 0.08 (bs, 27H, TMS), 0.05 (s, 9H, TMS); ¹³C NMR (100 MHz, CDCl₃) δ 150.77 (C), 150.72 (C), 130.0 (CH), 125.6 (CH), 120.29 (CH), 120.25 (CH), 102.4 (CH), 94.2 (CH), 75.8 (CH), 75.2 (CH), 74.1 (CH), 72.7 (CH), 71.9 (CH), 71.1 (CH, Jcp = 6.5 Hz), 66.5 (CH₂, Jcp = 5.3 Hz), 60.8 (CH₂), 1.1 (CH₃), 1.0 (CH₃), 0.7 (CH₃), 0.6 (CH₃), 0.5 (CH₃), 0.3 (CH₃), 0.0 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -11.72; HRMS (ESI) calcd for $C_{45}H_{87}O_{14}NaSi_7P[M+Na]^+$ 1101.4116, found 1101.4108.



Lactose 6'-phosphate dipotassium salt (24). Procedure were as shown in the general procedures to afford 24 as a white powder (23 mg, quant). $[\alpha]_{D}^{30}$ -

1088.4 (*c* 0.5, H₂O); ¹H NMR (400 MHz, D₂O) δ 5.28 (d, J = 3.1 Hz, 1H, H-1α), 4.71 (d, J = 7.7 Hz, 1H, H-1[']), 4.51 (d, J = 7.8 Hz, 1H, H-1β), 4.09-3.56 (m, 17H, H-2α, H-3α, H-3β, H-4α, H-4β, H-5α, H-5β, H-6aα, H-6bα, H-6aβ, H-6bβ, H-2['], H-3['], H-4['], H-5['], H-6[']a, H-6[']b), 3.31 (t, J = Hz, 1H, H-2β); ¹³C NMR (100 MHz, CDCl₃) δ 103.1 (CH), 96.7 (CH), 92.5 (CH), 73.4 (CH), 74.7 (CH), 74.5 (CH), 74.3 (CH), 74.2 (CH), 72.4 (CH), 71.6 (CH), 71.5 (CH), 71.1 (CH), 69.9 (CH), 68.2 (CH), 62.3 (CH₂), 60.4 (CH₂), 60.2 (CH₂); ³¹P NMR (162 MHz, D₂O) δ 4.86; HRMS (ESI) calcd for C₁₂H₂₂O₁₄P [M-H]⁻ 421.0747, found 421.0749.



6'-O-Diphenylphosphoryl-1,2,3,6,2',3',4'-hepta-O-trimethylsilyl-cellobiose

(26). Procedures were as shown in the general procedures to afford 26 as a colourless syrup (155 mg, 49%) and the fully trimethylsilylated cellobiose (131 mg, 49%) (recovered yield of 26: 96%). $[\alpha]^{30}_{D}$ 189.6 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.30 (m, 4H, Ph), 7.24-7.20 (m, 4H, Ph), 7.16-7.13 (m, 2H, Ph), 4.50 (ddd, *J* = 10.5, 6.3, 2.2 Hz, 1H, H-6'a), 4.47 (d, *J* = 7.4 Hz, 1H, H-1), 4.42 (d, *J* = 7.6 Hz, 1H, H-1'), 4.10 (ddd, *J* = 10.0, 7.8, 5.2 Hz, 1H, H-6'b), 3.88 (ddd, *J* = 11.1, 3.7 Hz, 1H, H-6a), 3.78-3.72 (m, 2H, H-3, H-6b), 3.45 (t, *J* = 8.8 Hz, 1H, H-4'), 3.39 (ddd, *J* = 10.5, 8.8, 6.3 Hz, 1H, H-5'), 3.31 (t, *J* = 8.8 Hz, 1H, H-3'), 3.25-3.20 (m, 4H, H-2, H-2'. H-4, H-5), 0.16 (s, 9H, TMS), 0.14 (s, 9H, TMS), 0.13 (s, 9H, TMS), 0.12 (s, 9H, TMS), 0.10 (s, 9H, TMS), 0.08 (s, 9H, TMS); ¹³C NMR (100 MHz, CDCl₃) δ 150.91 (C), 150.87 (C), 150.84 (C), 130.1 (CH), 130.0 (CH), 125.5 (CH), 125.4 (CH), 120.52 (CH), 120.49 (CH), 102.0 (CH), 98.6 (CH), 78.2 (CH), 77.0 (CH), 76.6 (CH), 75.9 (CH), 75.7 (CH), 75.6 (CH), 75.0 (CH), 72.3 (CH), 68.7 (CH₂, Jcp = 5.1 Hz),

1.5 (CH₃), 1.4 (CH₃), 1.3 (CH₃), 1.2 (CH₃), 0.7 (CH₃), 0.3 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -11.48; HRMS (ESI) calcd for C₄₅H₈₇O₁₄NaSi₇P [M+Na]⁺ 1101.4116, found 1101.4109.



Cellobiose 6'-phosphate dipotassium salt (27). Procedures were as shown in the general procedures to afford **27** as a white powder (23 mg, 99%). $[\alpha]^{29}_{D}$ - 118.3 (*c* 0.5, H₂O); ¹H NMR (400 MHz, D₂O) δ 5.27 (d, *J* = 3.8 Hz, 1H), 4.71 (d, *J* = 8.1 Hz, 1H), 4.55 (d, *J* = 8.1 Hz, 1H), 4.69-3.96 (m, 4H), 3.93-3.86 (m, 4H), 3.69-3.54 (m, 8H), 3.39 (dd, J = 8.1, 4.4 Hz, 1H), 3.33 (dd, J = 8.1, 3.6 Hz, 1H); ¹³C NMR (100 MHz, D₂O) δ 102.19 (CH), 95.8 (CH), 91.8 (CH), 79.4 (CH), 79.3 (CH), 75.5 (CH, *J*cp = 7.0 Hz), 75.0 (CH), 74.8 (CH), 74.0 (CH), 73.9 (CH), 73.4 (CH), 71.4 (CH), 71.2 (CH), 70.1 (CH), 69.1 (CH), 69.0 (CH₂), 62.7 (CH₂, *J*cp = 3.7 Hz), 60.2 (CH₂), 60.1 (CH₂); ³¹P NMR (162 MHz, D₂O) δ 5.05; HRMS (ESI) calcd for C₁₂H₂₂O₁₄PK₂ [M+H]⁺ 499.0021, found 499.0016.



6'-*O*-Diphenylphosphoryl-2,3,4,6,1',2',3'-hexa-*O*-trimethylsilyl-α,α'sucrose (29). Procedures were as shown in the general procedures to afford 29 as a colourless syrup (151 mg, 48%) and the fully trimethylsilylated sucrose (128 mg, 48%) (recovered yield of 29: 92%). $[\alpha]_{D}^{30}$ 36.1 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.28 (m, 4H, Ph) 7.23-7.20 (m, 2H, Ph), 7.18-

7.14 (m, Ph, 4H), 5.18 (d, J = 3.3 Hz, 1H, H-1), 4.59 (ddd, J = 12.0, 6.4, 2.5 Hz, 1H, H-6'a), 4.33 (ddd, J = 10.7, 6.4, 2.5 Hz, 1H, H-6'b), 4.32 (d, J = 8.0 Hz, 1H, H-4), 3.99-3.98 (m, 2H, H-3', H-5'), 3.82-3.65 (m, 4H, H-1', H-3, H-4, H-5), 3.55 (d, J = 11.7 Hz, 1H, H-6a), 3.44 (t, J = 9.3 Hz, 1H, H-2'), 3.41 (d, J = 11.5 Hz, 1H, H-6b), 3.29 (dd, J = 9.5, 3.3 Hz, 1H, H-2), 0.17 (s, 9H, TMS), 0.156 (s, 18H, TMS), 0.155 (s, 9H, TMS), 0.12 (s, 9H, TMS), 0.10 (s, 9H, TMS), 0.09 (s, 9H, TMS), 0.07 (s, 9H, TMS); ¹³C NMR (100 MHz, CDCl₃) δ 150.9 (C), 129.9 (CH), 125.4 (CH), 120.4 (CH), 104.2 (C), 92.2 (CH), 80.2 (CH₂, Jcp = 6.9 Hz), 76.5 (CH), 73.8 (CH), 73.5 (CH), 73.0 (CH), 72.1 (CH), 70.5 (CH₂, Jcp = 6.4 Hz), 63.0 (CH₂), 62.3 (CH₂), 1.4 (CH₃), 1.2 (CH₃), 0.9(CH₃), 0.8 (CH₃), 0.5 (CH₃), 0.0 (CH₃); ³¹P NMR (162 MHz, CDCl₃) δ -11.86; HRMS (ESI) calcd for C₄₅H₈₇O₁₄NaSi₇P [M+Na]⁺ 1101.4116, found 1101.4124.



Sucrose 6'-phosphate dipotassium salt (30). Procedures were as shown in the general procedures to afford **30** as a white powder (22 mg, 97%). $[α]^{30}_{D}$ -152.9 (*c* 0.5, H₂O); ¹H NMR (400 MHz, D₂O) δ 5.44(d, *J* = 3.9 Hz, 1H, H-1), 4.28-4.22 (m, 2H, H-3', H-4'), 4.09 (ddd, *J* = 10.3, 4.7, 2.3 Hz, 1H, H-6'a), 4.02-3.88 (m, 5H, H-1'ax, H-1'eq, H-5, H-5', H-6'b), 3.86-3.74 (m, 4H, H-2', H-3, H-6a, H-6b), 3.57 (dd, *J* = 10.0, 3.9 Hz, 1H, H-2), 3.39 (t, *J* = 9.8 Hz, 1H, H-4); ¹³C NMR (100 MHz, D₂O) δ 102.8 (C), 92.4 (CH), 80.4 (CH, *J*cp = 8.2 Hz), 76.2 (CH), 73.8 (CH), 72.5 (CH, *J*cp = 7.9 Hz), 71.3 (CH), 69.9 (CH), 69.6 (CH₂), 64.0 (CH₂), 61.1 (CH₂), 60.4 (CH₂); ³¹P NMR (162 MHz, D₂O) δ 4.35; HRMS (ESI) calcd for C₁₂H₂₂O₁₄PK₂ [M+H]⁺ 499.0021, found 499.0045.



4',6'-*O*-Benzylidene-6-*O*-diphenylphosphoryl–α,α'-trehalose (31).

Compound 20 (121.5 mg, 0.118 mmol) was mixed with benzaldehyde (15 µL, 0.142 mmol) in CH₂Cl₂ (1.2 mL) under N₂, and TMSOTf (2 µL, 0.012 mmol) was added at 0 °C. After stirring for 30 min, the reaction mixture was evaporated to give a yellow oil, which was dissolved in MeOH (2 mL). The mixture was added acidic Amberlite resin IR-120 (50 mg) and stirred at room temperature for 1 h. The resin was filtered off and the filtrate was concentrated in vacuo. The mixture was purified by flash column chromatography (MeOH/Chloroform 1:9) on silica gel to furnish the desired product **31** (71 mg, 90%). $[\alpha]^{25}_{D}$ 143.8 (c 0.1, MeOH); ¹H NMR (500 MHz, (MeOD) δ 7.46-7.43 (m, 2H, Ph), δ 7.37-7.33 (m, 4H, Ph), δ 30-7.27 (m, 3H, Ph), 7.21-7.17 (m, 6H, Ph), 5.52 (s, 1H, PhCH), 5.02 (d, J = 3.9 Hz, 1H, H-1'), 4.98 (d, J = 3.8 Hz, 1H, H-1), 4.51-4.38 (m, 2H, H-6a, H-6b), 4.17 (dd, J = 10.1, 5.1 Hz, 1H, H-6'eq), 4.07-4.00 (m, 2H, H-5, H-5'), 3.94 (t, J = 9.6 Hz, 1H, H-3'), 3.76 (t, J = 9.6 Hz, 1H, H-3), 3.67 (t, *J* = 10.1 Hz, 1H, H-6'ax), 3.53 (dd, *J* = 9.6, 3.9 Hz, 1H, H-2'), 3.45-3.28 (m, 3H, H-2, H-4, H-4'); ¹³C NMR (125 MHz, MeOD) δ 152.04 (C), 151.96 (CH), 139.3 (C), 131.2 (CH), 130.0 (CH), 129.2 (CH), 127.7 (CH), 126.9 (CH), 121.34 (CH), 121.29 (CH), 103.2 (CH), 96.3 (CH), 95.8 (CH), 83.2 (CH), 74.5 (CH), 73.9 (CH), 73.1 (CH), 72.2 (CH, Jcp = 6.2 Hz), 71.8 (CH), 71.3 (CH), 70.1 (CH₂), 69.9 (CH₂, Jcp = 6.0 Hz), 64.3 (CH); ³¹P NMR (162 MHz, MeOD) δ -11.45; HRMS (ESI) calcd for C₃₁H₃₅O₁₄NaP [M+Na]⁺ 685.1662, found 685.1666.



4,6-*O***-Benzylidene–α,α'-trehalose (32).** A solution of compound **31** (40 mg, 0.06 mmol), NaNO₂ (22 mg, 0.30 mmol) and DMF (1 mL) was subjected to microwave irradiation (200 W, 150 °C) for 30 mins. The mixture was concentrated and purified by column chromatograph (MeOH/Chloroform 1:5) on silica gel to yield the compound **32** (25 mg, 96%). $[\alpha]^{24}_{D}$ 15.5 (*c* 0.1, MeOH); ¹H NMR (500 MHz, (CD₃)₂CO) δ 7.53-7.49 (m, 2H, Ph), 7.36-7.34 (m, 3H, Ph), 5.58 (s, 1H, PhCH), 5.15 (d, *J* = 3.8 Hz, 1H, H-1), 5.09 (d, *J* = 3.7 Hz, 1H, H-1'), 4.17 (dd, *J* = 9.9, 4.9 Hz, 1H, H-6eq), 4.10 (td, *J* = 9.9, 5.0 Hz, 1H, H-5), 4.03 (t, *J* = 9.2 Hz, 1H, H-3), 3.93 (ddd, *J* = 9.5, 4.7, 2.7 Hz, 1H, H-5'), 3.87 (t, *J* = 9.5 Hz, 1H, H-3'), 3.77-3.58 (m, 3H, H-2, H-6'a, H-6'b), 3.48-3.45 (m, 2H, H-2', H-4), 3.40 (t, *J* = 9.5 Hz, 1H, H-4'), 2.78 (bs, 6H, OH); ¹³C NMR (125 MHz, (CD₃)₂CO) δ 139.3 (C), 129.5 (CH), 128.7 (CH), 127.3 (CH), 102.2 (CH), 95.5 (CH), 95.2 (CH), 82.9 (CH), 74.5 (CH), 73.9 (CH), 73.5 (CH), 73.2 (CH), 72.1 (CH), 71.4 (CH), 69.6 (CH₂), 63.7 (CH), 62.8 (CH₂).



4,6-*O***-Benzylidene-2,3,2',3'4',6'-hexa-***O***-benzyl** $-\alpha$, α '**-trehalose (33).** To a solution of **32** (20.0mg, 0.046 mmol) and benzyl bromide (39 µL, 0.334 mmol)

in DMF (0.5 mL) was added sodium hydride (22 mg, 0.557 mmol) at 0 °C. The mixture was stirred at room temperature overnight and was guenched by the slow addition of water (7 mL) at 0 °C. The mixture was extracted with EtOAc twice. The organic layer was dried over anhydrous MgSO₄, filtered, and evaporated under reduced pressure. The residue was purified by silica gel chromatography with hexane/EtOAc 5:1 as the eluent to afford compound 33 as a colorless oil (40.7 mg, 91%). $[\alpha]^{24}$ 36.2 (c 0.21, CDCl₃); ¹H NMR (500 MHz, CDCl₃) & 7.51-7.49 (m, 2H, Ph), 7.40-7.20 (m, 31H, Ph), 7.14-7.12 (m, 2H, Ph), 5.55 (s, 1H, PhCH), 5.18-5.17 (m, 2H, H-1, H-1'), 4.97 (d, J = 14.7 Hz, 1H, PhCH₂), 4.95 (d, J = 14.5 Hz, 1H, PhCH₂), 4.86-4.66 (m, 7H, PhCH₂), 4.53 (d, J = 11.8 Hz, 1H, PhCH₂), 4.46 (d, J = 11.5 Hz, 1H, PhCH₂), 4.38 (d, J = 12.4Hz, 1H, PhCH₂), 4.27 (td, J = 9.7, 4.7 Hz, 1H, H-5), 4.17-4.10 (m, 3H, H-4', H-5', H-6eq), 4.03 (t, J = 7.4 Hz, 1H, H-3), 3.69-3.57 (m, 5H, H-2, H-2', H-3', H-4, H-6ax), 3.50 (dd, J = 10.7, 2.9 Hz, 1H, H-6'a), 3.37 (d, J = 10.7 Hz, 1H, H-6'b); ¹³C NMR (125 MHz, CDCl₃) δ 138.9 (C), 138.8 (C), 138.4 (C), 138.2 (C), 138.1 (C), 137.9 (C), 137.6 (C), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.89 (CH), 127.88 (CH), 127.7 (CH), 127.6 (CH), 127.54 (CH), 127.52 (CH), 126.1 (CH), 101.2 (CH), 95.0 (CH), 94.5 (CH), 82.4 (CH), 81.8 (CH), 79.4 (CH), 78.9 (CH), 78.7 (CH), 77.7 (CH), 75.6 (CH₂), 75.3 (CH₂), 75.0 (CH₂), 73.5 (CH₂), 73.2 (CH₂), 70.7 (CH), 69.1 (CH₂), 68.2 (CH₂), 62.9 (CH); HRMS (ESI) calcd for $C_{61}H_{62}O_{11}Na [M+Na]^+ 993.4190$, found 993.4205.



6-O-Diphenylphosphoryl-2,3,4,2',3',4',6'-hepta-O-benzyl-α,α'-trehalose

(34). Compound 20 (118 mg, 0.115 mmol) was mixed with acidic Amberlite resin IR-120 (50 mg), and the mixture was stirred at room temperature for 1 h. The resin was filtered, and the filtrate was concentrated in vacuo to give a colorless oil. The oil was mixed with 2,4,6-tris(benzyloxy)-1,3,5-triazinee (321 mg, 0.803 mmol) in 1,4-dioxane (4 mL) under N₂. TfOH (14 µL, 0.092 mmol) was added at room temperature. After the system was stirred for 4 h, the reaction mixture was evaporated to give a yellow oil. The mixture was purified by flash column chromatography (Hex/EtOAc 3:1) on silica gel to furnish the desired product **34** (98 mg, 71%) $[\alpha]_{D}^{30}$ 203.4 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.10 (m, 45H, Ar-H), 5.15 (d, J = 3.7 Hz, 1H, H-1), 5.10 (d, J = 3.4 Hz, 1H, H-1'), 4.98 (d, J = 2.6 Hz, 1H, CH₂Ph), 4.95 (d, J = 2.4 hz, 1H, CH₂Ph), 4.86 (m, 4H, CH₂Ph), 4.70-4.6 (m, 3H, CH₂Ph), 4.60-4.52 (m, 4H, CH₂Ph), 4.47-4.37 (m, 3H, CH₂Ph), 4.15-4.11 (m, 4H, H-5, H-5' H-6a, H-6b), 3.99 (t, J = 9.3 Hz, 2H, H-3, H-3'), 3.65 (t, J = 9.6 Hz, 1H, H-4'), 3.56 (dd, J =9.2, 3.7 Hz, 1H, H-2), 3.52 (dd, J = 6.6, 3.2 Hz, 1H, H-4), 3.48 (d, J = 11.1 Hz, 1H, H-6'a), 3.41 (dd, J = 9.6, 3.4 Hz, 1H, H-2'), 3.38 (dd, J = 11.2, 2.3 Hz, 1H, H-6'b); ¹³C NMR (100 MHz, CDCl₃) δ 150.9 (C), 150.8 (C), 150.7 (C), 139.0, 138.9, 138.5, 138.3, 138.2, 138.1, (Ch₂), 129.9 (CH), 129.8 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 125.5 (CH), 125.4 (CH), 120. (CH), 120.2 (CH), 94.6 (CH), 94.3 (CH), 82.0 (CH), 81.6 (CH), 79.6 (CH), 79.5 (CH), 78.0 (CH), 77.7 (CH), 77.0 (CH), 75.8 (CH₂), 75.7 (CH₂), 75.2 (CH₂), 73.7 (CH₂), 73.2 (CH₂), 72.9 (CH₂), 71.0 (CH), 69.9 (CH), 69.8 (CH), 67.5 (CH₂), 67.5 (CH₂); ³¹P NMR (162 MHz, CDCl₃) δ -11.45; HRMS (ESI) calcd for $C_{73}H_{73}O_{14}PNa [M+Na]^+$ 1227.4636, found 1227.4618.



2,3,4,2',3',4',6'-hepta-O-benzyl-a,a'-trehalose (35). A mixture of compound **34** (27mg, 0.022 mmol), NaNO₂ (8mg, 0.116 mmol) and DMF (1.5 mL) was subjected to microwave irradiation (200 W, 150 °C) for 30 mins. The mixture was concentrated and purified by column chromatograph (Hex/EtOAc 3:1) on silica gel to yield the compound **35** (16 mg, 75%). $[\alpha]^{30}_{D}$ 181.0 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.18 (m, 33H, Ar-H), 7.11-7.08 (m, 2H, Ar-H), 5.15 (d, J = 3.8 Hz, 1H, H-1), 5.14 (d, J = 3.8 Hz, 1H, H-1'), 4.97 (d, J = 1.7 Hz, 1H, CH₂Ph), 4.95 (d, J = 1.7 Hz, 1H, CH₂Ph), 4.85-4.77 (m, 4H, CH₂Ph), 4.69-4.60 (m, 5H, CH₂Ph), 4.49-4.34 (m, 3H, CH₂Ph), 4.11 (dt, J =11.1, 4.8, 2.7 Hz, 1H, H-5'), 4.05-3.98 (m, 3H, H-3, H-3', H-5), 3.64 (t, J= 9.6 Hz, 1H, H-4), 3.58-3.54 (m, 4H, H-2, H-4', H-6a, H-6b), 3.50 (dd, J = 8.3, 3.8 Hz, 1H, H-2'), 3.74 (dd, J = 3,7, 5,9 Hz, 1H, H-6'a), 3.35 (dd, J= 10.5, 2.0 Hz, 1H, H-6'b), 1.43 (t, J = 6.4 Hz, 1H, OH); ¹³C NMR (100 MHz, CDCl₃) δ 139.0 (C), 138.6 (C), 138.5 (C), 138.3 (C), 138.1 (C), 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6 (7× OCH₂Ph), 94.4 (CH), 94.2 (CH), 82.0 (CH), 81.8 (CH), 79.8 (CH), 79.6 (CH), 78.0 (CH), 77.7 (CH), 77.4 (CH), 75.8 (CH₂), 75.2 (CH₂), 73.7 (CH₂), 73.2 (CH₂), 73.1(CH₂), 71.4 (CH), 70.0 (CH), 68.5 (CH₂), 61.8 (CH₂), 29.9 (CH₂); HRMS (ESI) calcd for $C_{61}H_{64}O_{11}Na [M+Na]^+$ 995.4346, found 995.4352.





0.1278 0.1211

Current Data Parameters NAME aaj-389-all data EXPNO 1 PROCNO 1



CHANNEL f1 NUC1 IH P1 10.30 usec PL1 -2.00 dB PL1W 23.88643074 W SF01 400.1320424 MHz F2 - Processing parameters S1 10384 S1 10384

 F2 - Processing parameters

 SI
 16384

 SF
 400.1300155 MHz

 WDW
 no

 SSB
 0

 LB
 0 Hz

 GB
 0

 PC
 1.00





Current Data Parameters NAME aaj-301 EXPNO 2 PROCNO 1

F2 - Acquisition Parameters Date_____20120619 Time_____18.22 = CHANNEL f1 == _____ NUCI P1 PL1 PL1W SF01

CHANNEL f2

waltz16 1H

1H 90.00 usec -2.00 dB 13.70 dB 16.70 dB 16.12334061 W 0.43396533 W

0.21749784 W 400.1320007 MHz

 F2 - Processing parameters
 SI
 32768

 SF
 161.9755127 MHz
 WDW

 WDW
 EM
 SSB
 0

 LB
 1.00 Hz
 GB
 0

 PC
 1.00
 1.00

CPDPRG2 NUC2 PCPD2 PL12 PL13 PL2W PL13 PL2W PL13W SF02 4

O ∕ ─OPh OPh TMSO TMSO TMSO ′ÒMe 2

150

200

250

300

100

50

-50

0

-100

-150

-11.3784

-250

ppm

-200





 \cap

н`о ОМе

3

°OK юĸ

Current Data Parameters NAME aai-391 EXPNO PROCNO 2 -1 F2 - Acquisition Parameters Date 20130902 F2 - Acquisition t an answer Date_ 20130902 Time 22.34 INSTRUM spect PROBHD 5 mm PABBO BB-DYL DBCC song 30 ne 22... vSTRUM spect PROBHD 5 mm PABBO PULPROG zgpg30 TD 65336 SOLVENT D2C NS 23 DS 0 SWH 104166 FIDRES 1.57 AQ 0.314' RG 2' DW DE TE D1 D11 D00 HO 0 104166.664 Hz 1.589457 Hz 0.3146228 sec HO == CHANNEL f1 === 31P 13.50 usec 2.00 dB 16.00742149 W 161.9755930 MHz -NUC1 P1 PL1 PL1W SF01 -----CPDPRG2 NUC2 PCPD2 PL2 PL12 PL13 PL2W PL12W PL12W PL12W PL13W SF02
 F2 - Processing parameters

 SI
 32768

 SF
 161.9755127 MHz

 WDW
 EM

 SSB
 0

 LB
 1.00 Hz

 GB
 0

 PC
 1.00

> 150 100 50 -50 -100 -150 -200 -250 300 250 200 0 ppm

5.0940





Current Data Parameters NAME aajglu6p-31p EXPNO 2 PROCNO 1
 PROCNO
 1

 F2 - Acquisition Parameters
 Date_
 20120831

 Time
 9.25
 INSTRUM
 spect

 PROBHD 5
 5mm PABO BB PULPROG
 zgpg30

 TD
 65536
 SOLVENT
 CDC13

 NS
 7
 DS
 0

 SWH
 104166.664 Hz
 FIDRES
 1.589457 Hz

 AQ
 0.3146228 sec
 RG
 2050

 DW
 4.800 usec
 DE
 6.50 usec

 TE
 300.0 K
 D1
 0.3000000 sec

 D1
 0.3000000 sec
 TD0
 1
 == CHANNEL f1 ==== 31P 13.50 usec 2.00 dB 16.00742149 W 161.9755930 MHz ____ NUCI P1 PL1 PL1W SF01 CHANNEL f2 === G2 waltz16 1H 90.00 usec -2.00 dB 13.70 dB 16.70 dB 16.12334061 W 0.43396533 W 0.21749784 W 400.1320007 MHz CPDPRG2 NUC2 PCPD2 PL12 PL13 PL13 PL2W 1 PL12W PL13W SF02 4
 F2 - Processing parameters
 SI
 32768

 SF
 161.9755127 MHz
 WDW
 EM

 WDW
 EM
 LB
 1.00 Hz
 GB
 0

 PC
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00



| an an da an an bha a dha an la Ra fa da Range guna bha an la Ra fa da | hand leave to the section of the sec | na hafa sha yashan (Myan İda Jafasa). Mariya yasha yashan (Myan İda Jafasa) | na na sana ka na r>Na ka na k | an an an an an an an an an an an an an a | u de la cola de la companya de la colación de la colación de la companya de la colación de la colación de la co Companya de la colación de la colación de la colación de la colación de la colación de la colación de la colación | ik olisatéhas aktivese Presidentifikas | na da anta frantsia da ma maadada. Ma da ma da frantsia da ma maadada da m | a affanan manlandi faliti ma a dan sa | n fa di tanàna amin'ny kaodim-paositra dia kaodim- n-paositra dia kaodim-paositra dia kaodim-paositra dia kaodim-paositra dia kaodim-paositra dia kaodim-paositra | | er de stat het het en er lit die en internet die stat di Stat gester die stat die stat die stat die stat die stat die stat die stat die stat die stat die stat die stat d | |
|--|--|--|---|--|--|---|---|---------------------------------------|--|------|--|-----|
| 300 | 250 | 200 | 150 | 100 | 50 | 0 | -50 | -100 | -150 | -200 | -250 | ppm |

-11.7199



| | 0 0- ^Р \-ОК ОК | 96.69 75.45 75.31 75.31 77.33 71.93 60.21 62.49 62.49 | | | | | | | |
|--|--|---|---|--|--|---|--|--|--|
| HO HO 6 | OH OH | | | | | · · · · · · · · · · · · · · · · · · · | | | |
| Current Data Parameters NAME aaj-448-A-all EXPNO 2 PROCNO 1 | d veregionen die voor die op oorde de netari fenti ya Kati Sanga Tanga Tanga Tanga Tanga | land and faith the last of the faith of the stand of the | ft petertigifgelier/Inendelennikinsherft | Alexing from the second second second second second second second second second second second second second se | ning and and a firm and a firm and a firm and a firm and a firm and a firm and a firm and a firm and a firm and | | | |
| F2 - Acquisition Parameters Date_ 20130918 Time 0.36 INSTRUM spect PROBHD 5 mm Dual 13C/ PULPROG zg0dc TD 32768 SOLVENT D20 NS 4300 DS 2 SWH 23980.814 Hz FIDRES 0.731836 Hz AQ 0.6832628 sec RG 18390.4 DW 20.850 usec DE 6.50 usec DE 6.50 usec TE 299.8 K D1 3.0000000 sec D11 0.03000000 sec TD0 1 | | | | | | | | | |
| CHANNEL J1 twist NIGC marks and the first state of the firs | ngen van fan de de de de de de de de de de de de de | nga dina di kana kana kana kana kana kana kana kan | ************************************** | м (ріталий (с.)) і с | Minutes () () () () () () () () () (| <u>, en anti-a a a de la la de la de la de la de la de la de la de la de la de la de la de la de la de la de la d</u> | | | |
| F2 - Processing parameters SI 32768 SF 100.6127690 MHz WDW EM SSB 0 LB 3.00 Hz GB 0 PC 1.40 | | | | had window and a second second | ₩1411111111111111111111111111111111111 | As we have a second state of a state of a | | | |

0 ppm

Current Data Parameters NAME aaj-448-A EXPNO 2 PROCNO 1

 PROCNO
 1

 F2 - Acquisition Parameters
 Date_
 20130917

 Time
 22.09
 INSTRUM
 spect

 PROBHD 5
 spect
 BBD
 BDD

 PROBHD 5
 spect
 BDD
 65536

 SOLVENT
 D20
 NS
 37

 DS
 0
 SWH
 104166.664 Hz

 FIDRES
 1.389457 Hz
 AQ
 0.3146228 sec

 RG
 2050
 DW
 4.800 usec

 DE
 6.50 usec
 TE
 300.0 K

 D1
 0.03000000 sec
 D11
 0.03000000 sec

 TD0
 1
 1
 CUMPUE C
 == CHANNEL fl === 31P 13.50 usec 2.00 dB 16.00742149 W 161.9755930 MHz -----CPDPRG2 waltz16



NUC1 P1 PL1 PL1W SF01

| NUC2 | 1H |
|-----------|--------------------|
| PCPD2 | 90.00 usec |
| PL2 | -2.00 dB |
| PL12 | 13.70 dB |
| PL13 | 16.70 dB |
| PL2W | 16.12334061 W |
| PL12W | 0.43396533 W |
| PL13W | 0.21749784 W |
| SFO2 | 400.1320007 MHz |
| | |
| F2 - Proc | cessing parameters |
| CT. | 22760 |

| D1 | | J4/00 | | | | | |
|-----------|-----------------|---------|--|--|--|--|--|
| SF | 161.9755127 MHz | | | | | | |
| WDW | | EM | | | | | |
| SSB | 0 | | | | | | |
| LB | | 1.00 Hz | | | | | |
| GB | 0 | | | | | | |
| PC | | 1.00 | | | | | |

| **** | **** | | | | | | **** | | | | **** | ***** |
|------|------|-----|-----|-----|----|---|------|------|------|------|------|-------|
| 300 | 250 | 200 | 150 | 100 | 50 | 0 | -50 | -100 | -150 | -200 | -250 | ppm |

5.1154





Current Data Parameters NAME aaj-gal-31p EXPNO 2 PROCNO 1

 $\begin{array}{cccc} PROCNO & 1 \\ F2 - Acquisition Parameters \\ Date 20130912 \\ Time 22.13 \\ INSTRUM spect \\ PROBHD 5 rmm QNP 11H/13 \\ PULPROG zgpg30 \\ TD 32768 \\ SOLVENT CDC13 \\ NS 38 \\ DS 0 & Z23724 \\ SOLVENT CDC13 \\ NS 38 \\ DS 0 & Z23724 \\ SOLVENT & CDC13 \\ NS 38 \\ DS 0 & Z23724 \\ SOLVENT & CDC13 \\ NS & 38 \\ DS 0 & Z23724 \\ SOLVENT & CDC13 \\ NS & 38 \\ DS 0 & Z23724 \\ SOLVENT & CDC13 \\ SOLVENT & CDC13 \\ NS & 38 \\ DS 0 & Z23724 \\ SOLVENT & CDC13 \\ SOLVENT & CDC13 \\ NS & 38 \\ SOLVENT & CDC13 \\ NS & SOLVENT \\ SOLVENT & CDC13 \\ NS & SOLVENT \\ SOLVENT & CDC13 \\ NS & SOLVENT \\ SOLVENT & CDC13 \\ NS & SOLVENT \\ SOLVENT & SO$ == CHANNEL f1 === 31P 10.10 usec ____ NUCI PI PLI PLIW SFO1 9.00 dB 8.75950909 W 121.4948509 MHz
 CHANNEL f2

 CPDPRG2
 waltz16

 NUC2
 1H

 PCPD2
 90.00 usec

 PL12
 -4.00 dB

 PL13
 17.50 dB

 PL2W
 26.37401772 W

 PL1W
 0.37254289 W

 PL13W
 0.18671374 W

 SFO2
 300.1319510 MHz

 F2 - Processing parameters

 SI
 32768

 SF
 121.4948510 MHz

 WDW
 EM

 SSB
 0

 LB
 1.00 Hz

 GB
 0

 PC
 1.00





-12.0365




HO

250

300

200

150

100

50

-50

0

-100

-150

-200

-250

ppm

Current Data Parameters NAME aaj-255-A EXPNO 8 PROCNO 1
 FROCINO
 1

 F2 - Acquisition Parameters Date
 20120514

 Time
 8.46

 INSTRUM
 spect

 PROBHD 5 mm PABBO BB-PULPROG
 zgpg30

 TD
 65356

 SOLVENT
 D20

 NS
 100

 DS
 0

 SWH
 104166.664 Hz,

 FIDRES
 1.589457 Hz,

 AQ
 0.3140228 sec

 RG
 2050

 DW
 4.800 usec

 TE
 300.0 K

 D1
 2.00000000 sec

 D11
 0.0300000 sec

 TD0
 1
 == CHANNEL f1 === 31P 13.50 usec 2.00 dB 16.00742149 W 161.9755930 MHz -NUCI P1 PL1 PL1W SF01 == CHANNEL f2 = CPDPRG2 NUC2 PCPD2 PL12 PL13 PL2W 11 PL12W 11 PL12W 11 PL12W SF02 4 ____ waltz16 1H 90.00 usec -2.00 dB 13.70 dB 13.70 dB 16.70 dB 16.12334061 W 0.43396533 W 0.21749784 W 400.1320007 MHz
 F2 - Processing parameters
 SI
 32768

 SF
 161.9755127 MHz
 WDW

 WDW
 EM
 SSB
 0

 LB
 1.00 Hz
 GB
 0

 PC
 1.00
 1.00



9

0.8225





> Current Data Parameters NAME aaj-324-31p EXPNO 2 PROCNO 1 F2 - Acquisition Parameters Date_____20120910 Time_____9.19 INSTRUM_____spect PROBHD_5 num PABBO BB-PULPROG_____ggg30 TD_____ENT____65536_____ CDC13 39 TD SOLVENT NS DS â DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0 0 104166.664 Hz 1.589457 Hz 0.3146228 sec 2050 • 4.800 usec 6.50 usec 6.50 Usec 300.0 K 2.00000000 sec 0.03000000 sec 1 CHANNEL f1 === 31P 13.50 usec 2.00 dB 16.00742149 W 161.9755930 MHz NUCI PI PLI PLIW SFOI == CHANNEL f2 == G2 waltz16 1H 90.00 usec -2.00 dB 13.70 dB ___ CPDPRG2 NUC2 PCPD2 PL2 PL12 PL13 PL2W 1 13.70 dB 16.70 dB 16.12334061 W 0.43396533 W 0.21749784 W 400.1320007 MHz PL2W PL12W PL13W SFO2
> F2 - Processing parameters
>
>
> SI
> 32768
>
>
> SF
> 161.9755127 MHz
>
>
> WDW
> EM
>
>
> SSB
> 0
>
>
> LB
> 1.00 Hz
>
>
> GB
> 0
>
>
> PC
> 1.00



300 250 200 150 100 50 0 -50 -100 -150 -200 -250 ppm

-11.3092





Current Data Parameters NAME aaj-Man6p-salt EXPNO 2 PROCNO 1

 F2 - Acquisition Parameters Date
 20130909

 Time
 22.02

 INSTRUM
 spect

 PROBHD S num PABBO BB-PULPROG
 25930

 TD
 65536

 SOLVENT
 D20

 NS
 17

 DS
 0

 SWH
 104166.664 Hz

 FIDRES
 1.589457 Hz

 AQ
 0.3146228 sec

 RG
 2050

 DW
 4.800 usec

 DE
 6.50 usec

 TE
 300.0 K

 DI
 2.00000000 sec

 DI
 2.00000000 sec

 DI
 2.00020000 sec

 DI
 2.0000000 sec

 DI
 2.0000000 sec

 DI
 13.50 usec

 PL1
 2.50 udB

 PL1
 2.00 dB

 PLIW
 16.0274149 W

 SFO1
 16.12354061 W

 PL12
 13.70 dB

 PL13
 16.70 dB

 PL14
 0.21749784 W

 SFO2
 400.1320007 MHz

 F2- Processing parameters

 F2 - Processing parameters
 SI
 32768

 SF
 161.9755127 MHz
 WDW
 EM

 WDW
 EM
 SSB
 0
 LB
 1.00 Hz
 GB
 0

 PC
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00
 1.00





4.9670







.

NAME EXPNO

PROCNO

INSTRUM PROBHD PULPROG

TD SOLVENT

NS DS

SWH FIDRES AQ RG DW DE

TE D1

TDO

NUC1 P1 PL1

SF01 F2

F2 SI SF WDW SSB LB GB GB PC

0 0 Hz õ



180 170 160 150 140 130 120 110 100

ppm



Ö Ĥ.

| 2 - Processing parameters I 32768 F 202.4563100 MHz DW no SB 0 B 0 Hz B 0 C 1.00 | | | | | | | | | |
|--|--------|--|---------|---|--|--|----|-----|--|
| THE CHANNEL f2 F2 PDPRG2 waltz16 UC2 1H CPD2 90.00 use L2 -5.00 dB L12 14.60 dB L13 19.00 dB FO2 500.1320005 MHz | = C | | | · | | | | | |
| CHANNEL fl ====== UC1 31P 1 7.90 use L1 6.00 dB FO1 202.4461871 MHz | = C | | | | | | | | |
| 5 0 Dz NH 75187.969 Hz LDRES 1.147277 Hz Q 0.4358644 sec J 10321.3 N 6.650 W 6.650 use E 2.0000000 sec 1 2.0000000 sec LITA 1.8999998 sec DO 1 1 | 2 | | | | | | | | |
| 2 - Acquisition Parameters ate 20130508 ime 21.46 SSTRUM spect XOBHD_5_mm_PABBO_BB/ JLPROG JLPROG zgpg30 0 65536 DLVENT D20 5 4 | ÷., | | | | | | | | |
| nrrent Data Parameters ME CWC-306-2 CPNO 7 OCCNO 1 | | | -4.6892 | | | | 15 | ÓМе | |

0



8.59 8.70 8.42







| Current Data Parameters NAME aai-362-salt-all data | | | Q | | | | 72.5371.92 | - 71.74 - 70.85 - 67.09 - 65.44 | - 58.81 | | - 35.42 | - 25.85 | - 9.70 | |
|--|--|--------------------------|---|---|--|-----------------------------|---------------------------------------|--|---|------|--------------------|---------|--|-----------------|
| EXPNO 2 PROCNO 1 F2 - Acquisition Parameters Data 20121228 | | | 0~ ^P ~0 | К | | | \mathcal{A} | / // | | | | | | |
| Time 22.38 INSTRUM spect PROBHD 5 mm PABBO BB- PULPROG zgpg30 TD 22768 | | но | | | | / | | | | | | | | · · · |
| SOLVENT D20 NS 3500 DS 0 SWH 23148.148 Hz A FUDRESturned 706435.Hz | da ba an da starra na dia da | 1 | 0 8 | H | | | | | s. Kash., Kashar Kasad | | .M. I. Later I. a. | | | ken und Altaleu |
| RG 2050 DW 21.600 usec DE 8.50 usec DE 3.00.0 K DI 2.00000000 sec DI 0.03000000 sec DI0 1 | na angan sa banggang ng ardin and a state of the | n an a finn an | lander in the first | h fan fan skip fan fan skip | MANYA MAN A KANY | | n a na mana a mana | | | | | i Aliyataya |
| CHANNEL fl NUC1 13C PI 9.80 usec PL1 -2.00 dB PL1W 55.33689499 W SFO1 100.6238359 MHz | | | | | | | - | | | | | | | |
| CHANNEL f2 == CPDPRG2 waltz16 NUC2 1H PCPD2 90.00 usec PL12 13.70 dB PL13 16.70 dB PL2W 16.12334061 W PL12W 0.43396533 W PL13W 0.21749784 W SFQ2 400.1326011 MHz | | | | | | | | | | | | | | |
| Instruction Instruction SF 100.6127690 MHz SSB 0 LB 3.00 Hz GB 0 PC 1.00 | politik ili site terapolitik i | | an an an an an an an an an an an an an a | ininin in the second second second second second second second second second second second second second second | | in the state | | V Your Up the | alan u dir. adar 11. ind Ala part yang tang tang | | | | 1949) (1999) 1949) (1999) (1999) | ili ini ini i |
| | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | 1 | |
| | ant and a | | int to a | | | | | | | | | | | 1. 100.1 |
| n an | | | | | ing the spectrum of the sector | | | | | | Mullingelik | | | |
| 190 180 | 170 160 | 150 140 |) 130 | 120 | 110 100 | 90 | 80 | 70 | 60 50 |) 40 | 30 | 20 | 10 | 0 рри |

Current Data Parameters NAME aaj-deoxy-6-p EXPNO 2 ۳, PROCNO

F2 - Acquisition Parameters Date 20121226

F2 - Acquisition Parameters Date_20121226 Time 9.29 INSTRUM spect PROBID 5 mm PABBO BB-PULPROG zgpg30 TD 65526
 PROBUT
 5 mm PLBBO

 PULPROG
 zgpg30

 TD
 65536

 SOLVENT
 D20

 NS
 33

 DS
 0

 SWH
 104166.664 Hz

 FIDRES
 1.589457 H

 AQ
 0.3146228 sec

 RG
 2050

 DW
 4.800 usec

 DE
 6.50 usec

 TE
 300.0 K

 D1
 2.00000000 sec

 D11
 0.0300000 sec

 TD0
 1
 104166.664 Hz 1.589457 Hz = CHANNEL f1 = 31P 13.50 usec NUCI PI PL1 PL1W SF01 2.00 dB 16.00742149 W 161.9755930 MHz CHANNEL f2 ------RG2 waltz16 IH 90.00 usec CPDPRG2 NUC2 PCPD2 PL12 PL13 PL13 PL2W PL13W PL12W SF02 40 -90.00 usec -2.00 dB 13.70 dB 16.70 dB 16.12334061 W 0.43396533 W 0.21749784 W 400.1320007 MHz

 F2 - Processing parameters

 SI
 32768

 SF
 161.9755127 MHz

 WDW
 EM

 SSB
 0

 LB
 1.00 Hz

 GB
 0

 PC
 1.00



200

50

1.3360

| | en al konstantin kan beranda kan baran da Angelaran genalaran giri ken beratan dapat | gan an ada adama da bisa waxaya o yaya wa | stanta ta parte da la sub da la starra di a dal matta Managementa ingentaria a producto a presenta a mag | al filmla natu, 1004-10 malast Masanggi Patri papatan anga | and a standard and a standard and a standard and a standard and a standard and a standard and a standard and a A standard a | ا برای باد میکند این میکند آن با مکار این مکار آند. این این این این این میکند میکند این میکند این میکند. | l firsenliteten til en sternijkentiste Manne på filse og stjätteten for | al di Lang Bandan wata da kan Maning Power Pilang Pilang Pilang | ndelet och den stallet den stallet den stallet och den stallet som stallet som stallet som stallet som stallet Revense som som stallet som stallet som stallet som stallet som stallet som stallet som stallet som stallet som | illementen deringen etneldeten. Anventen der som et alle som et alle | an shorte the of little cost of a region of the former game proj |
|--|---|---|---------------------------------------|---|---|---|---|--|--|---|---|---|
| ···· · · · · · · · · · · · · · · · · · | | · · · · · · · · · · · · · · · · · · · | | | | · · · · · · | · · · · · · | | · · · · · · · · · · · · · · · · · · · | · · · · · | | |
| 300 | 250 | 200 | 150 | 100 | 50 | 0 | -50 | -100 | -150 | -200 | -250 | DD M |

0

-50

-100

-150

-200

-250

ppm





OPh **OPh**

 \cap

OTMS

отмѕ

`OTMS

 \sim

Ò





-11.5044



| Electronic Supplementary | Material (ES | SI) for Chemical | Communications |
|---------------------------------|---------------|------------------|----------------|
| This journal is © The Roya | al Society of | Chemistry 2013 | 3 |



> Current Data Parameters NAME aaj-tmp-2k salt EXPNO 2 PROCNO 1

 F2 - Acquisition Parameters Date_20121229

 Date_20121229

 Time
 11.28

 INSTRUM spect

 PROBHD 5 mm PABBO BB-PULPROG zgp30

 TD
 65536

 SOLVENT
 D20

 NS
 19

 DS
 0

 SWH
 104166.664 Hz

 FIDRES
 1.589457 Hz

 AQ
 0.3146228 sec

 RG
 2050

 DW
 4.800 usec

 DE
 6.50 usec

 TE
 300.0 K sc

 D11
 0.0300000 sec

 D11
 0.3300000 sec

 D11
 3.19

 PUCI
 3.19

 SFOI
 160.755330 MHz

> == CHANNEL f2 = 52 waltz16 1H

13.70 dB 16.70 dB 16.12334061 W 0.43396533 W 0.21749784 W 400.1320007 MHz

 F2 - Processing parameters
 SI
 32768

 SF
 161.9755127 MHz
 WDW

 WDW
 EM
 SSB
 0

 LB
 1.00 Hz
 GB
 0

 PC
 1.00
 1.00
 1.00

90.00 usec -2.00 dB

CPDPRG2 NUC2 PCPD2 PL2

PL2 PL12 PL13 PL2W PL12W PL13W SFO2

- 4.8857

| | · · · · · · · · · | | · · · · · | | · · · · · · · · · · · · · · · · · · · | ··· · · · · | | · · · · · · · · · · · · · · · · · · · | · · · · · · · · · | · · · · · · · · · · · · · · · · · · · | · | |
|-----|-------------------|-----|-----------|-----|---------------------------------------|-------------|-----|---------------------------------------|-------------------|---------------------------------------|------|-----|
| 300 | 250 | 200 | 150 | 100 | 50 | 0 | -50 | -100 | -150 | -200 | -250 | ppm |



.







Current Data Parameters NAME aaj-Imp-pure EXPNO 2 PROCNO 1 F2 - Acquisition Parameters Date 20120831 Time 9.25 INSTRUM spect PROBHD 5 mm PABBO BB-PULPROG zgp30 TD 65536 SOLVENT CDC13 NS 7 DS 0 SWH 104166.664 Hz FIDRES 1.589457 Hz AQ 0.3146228 sec RG 2050 DW 4.800 usec TE 300.0 K DI 2.00000000 sec D11 0.0300000 sec TD0 1



CHANNEL f2 ==== CPDPRG2 waltz16 NUC2 IH PCPD2 90,00 usec PL2 -2.00 dB PL12 13.70 dB PL13 16.70 dB PL2W 16.12334061 W PL12W 0.43396533 W PL13W 0.21749784 W SFO2 400.1320007 MHz

F2 - Processing parameters SI 32768 SF 161.9755127 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.00

| فتربا هائية وفيائل والطور بالمراد المراجع | فعرومه ألبأة يساحرهما ويستؤوين | بالعناقير الأحياقا ومتعريداتها والتعار | بالطريطة وألاحط وأشيم فاستر | وأراويس الرأو المعناور مرائب ورقمان | أميلاسيرين أأفر والصاحيما الأهيطا | ومعاد أنظرى ومطالعات السرطا | وأفريسا فليلادهم وخراف فالشباط فكسبان وفا | الحديث وسراولها الشأاسة ليساي | فرفاط بالارسان واسترياسه واستحد فساغ وار | خفانية أتر أقلقا يساحا فكالطا تستبسرا | ويتباعدهم ومعاورة ومناعدة والمعادية والمعادية | ومحمدة بالمسائلة يعتديك يحادث |
|---|--------------------------------|---|-----------------------------|--|--------------------------------------|-----------------------------|---|-------------------------------|--|---|---|--|
| and the state of the second second second second second second second second second second second second second | البيار المسرين بريدين ويستبك | and the state of a state of the state of the state of the state of the state of the state of the state of the s | անություններություններ | ويعاولان والمعروبا المكرينية والمعارفة | الووالى والاندير وسنمين والقاطر ويعي | بالاسرية فالالتراماته ويرور | فعلوها أقصار فروسا ببغر كالخار سمياسيا | المحاولة أليرين وحاصصا بالريا | إدغالك والمتحاط فيتحر فاطرعتك يعر | աղումիկյուներությ | بوأو المعرقات والأمارك بالإسريانا فر | and the second s |
| | | | | | | · | | | | 1 () () () () () () () () () (| | |
| | | | | | | | | | | | | |
| 300 | 250 | 200 | 150 | 100 | 50 | 0 | -50 | -100 | -150 | -200 | -250 | nnm |

--11.7199





Current Data Parameters NAME aaj-LMP 2K SALT EXPNO 2 PROCNO 1

 F2 - Processing parameters

 SI
 32768

 SF
 161.9755127 MHz

 WDW
 EM

 SSB
 0

 LB
 1.00 Hz

 GB
 0

 PC
 1.00

| والقرارية الروادة وطراطية والأفتيسيون | والمراجعة والمراجع والمراجع والمراجع | i An suite bhang sallan an dda at ann da dao bh | Internet along which which along the last of the last of the last of the second s | ومعطيته فرشا تفسيم بالتحم | alan antional lines of the state of the | til smålastan att skalades att ta sa mittels | والمراجع والمراجع والمراجع والمراجع | ورور وحالية والمعالية والمعالية والمعالية المعالية المالية المالية | ldaa dadwaa , duchala , edi dhuu yilaan dal | in de Referen webe den wiere earlie de Jeron | ويستحدر ومطاوره والمروا والمقاور وا | ala dana ito fallo, a jatiki aku sa |
|--|--|--|--|---|---|--|--|--|---|--|---|-------------------------------------|
| and the second sec | and and and the first fi | a den gin de ser a norsking in liger hersel na ser | | dfffarfiller and fare and end of the fare | an fina on 11 octores and o | ana ana bula ka ƙalara ara | والمرمان معاويتهم والمتابع ماليت المتعار | an an an an an an an an an an an an an a | anna feang thing of Divergent Admillion of Ja | لى دۇرۇر مەر ۋە بايى يەر يەر يېڭ يۇل يەر . ئى دۇرۇر يېڭ يەر يەر يەر يېڭ يەر يەر يەر يەر يەر يەر يەر يەر يەر يەر | la far far far far far far far far far fa | alala al cara na antistata da s |
| | | | | | | | | • • • • • | | | | |
| 300 | 250 | 200 | 150 | 100 | 50 | 0 | -50 | -100 | -150 | -200 | -250 | ppm |

4.8597





Current Data Parameters NAME aaj-342-crude EXPNO 2 PROCNO 1

 F2 - Acquisition Parameters

 Date
 20121030

 Time
 16.25

 INSTRUM
 spect

 PROBHD 5 mm PABBO BB PULPROG

 PULPROG
 zgpg30

 TD
 65536

 SOLVENT
 CDC13

 NS
 20

 DS
 0

 SWH
 104166.664 Hz

 FIDRES
 1.589457 Hz

 AQ
 0.3146228 sec

 RG
 2050

 DW
 4.800 usec

 DE
 6.50 usec

 TE
 300.0 K

 D11
 0.03000000 sec

 D11
 0.3000000 sec

 D11
 31P

 PLI
 2.00 dB

 PLI
 2.00 dB

 PLI
 161.9755930 MHz

 CHANNEL f2

 CPDPRG2
 waltz16

 NUC2
 1H

 PCPD2
 90.00 usec

 PL12
 -2.00 dB

 PL12
 13.70 dB

 PL13
 16.70 dB

 PL12W
 16.12334061 W

 PL12W
 0.43396533 W

 PL13W
 0.21749784 W

 SFO2
 400.1320007 MHz

 F2 - Processing parameters
 SI
 32768

 SF
 161.9755127 MHz
 WDW

 WDW
 EM
 SSB
 0

 LB
 1.00 Hz
 GB
 0

 PC
 1.00
 1.00
 1.00





-11.4831




.

> Current Data Parameters NAME aaj-343-salt EXPNO 2 PROCNO 1

F2 - Acquisition Parameters Date_ 20121102 Time INSTRUM 16.49 LINSTRUM spect PROBHD 5 mm PABBO BB-PULPROG zona²⁰ TD zgpg30 65536 TD ID SOLVENT NS DS D20 28 0 DS SWH FIDRES AQ RG DW DE TE DI DI DI DI DI1 TD0 104166.664 Hz 1.589457 Hz 1.589457 Hz 0.3146228 sec 2050 4.800 usec 6.50 usec 300.0 K 2.00000000 sec 0.03000000 sec 1 CHANNEL f1 = NUCI P1 PL1 31P 13.50 usec 2.00 dB **PLIW** 16.00742149 W SF01 161.9755930 MHz = CHANNEL f2 = -----CPDPRG2 NUC2 PCPD2 PL2 PL12 waltz16 1H 90.00 usec -2.00 dB 13.70 dB PL12 PL13 PL2W PL12W 15.70 dB 16.70 dB 16.12334061 W 0.43396533 W PL13W 0.21749784 W SF02 400.1320007 MHz F1 - Acquisition parameters TD 256 ID SFO1 FIDRES SW 400.1318 MHz 15.258808 Hz 9.762 ppm QF FnMODE
 F2 - Processing parameters

 SI
 32768

 SF
 161.9755127 MHz

 WDW
 EM

 SSB
 0

 LB
 1.00 Hz

 GB
 0

 PC
 1.00
 F1 - Processing parameters SI 1024 MC2 QF SF 400.1300000 MHz WDW SSB 0 LB 0.30 Hz GB 0.1

250

300

200

150

100

50

0

-50

-100

-150

-200

-250

ppm



- 5.0534





Current Data Parameters NAME AAJ-SUC6'P EXPNO 2 PROCNO 1

F2 - Acquisition Parameters Date_____20120915 Time_____11.27 INSTRUM spect PROBHD 5 mm PABBO BB-PULPROG zgpg30 TD 65536 SOLVENC TD TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE DI 2 D11 (TD0 CDCI3 18 20 104166.664 Hz 1.589457 Hz 0.3146228 sec 2050 4.800 usec 4.800 usec 6.50 usec 300.0 K 2.00000000 sec 0.03000000 sec 1 CHANNEL fl NUCI PI PL1 PL1W SF01 31P 13.50 usec 2.00 dB 16.00742149 W 161.9755930 MHz CHANNEL f2 CPDPRG2 waltz16 1H 90.00 usec

OTMS TMSO TMSO TMSO OTMS

 CPDPRG2
 walts 16

 NUC2
 IH

 PCPD2
 90.00 usec

 PL12
 -2.00 dB

 PL13
 16.70 dB

 PL2W
 16.12334061 W

 PL13W
 0.31749784 W

 SF02
 400.1320007 MHz

 F2 - Processing parameters
 SI

 SSI
 161.9755127 MHz

 WDW
 EM

 SSB
 0

 LB
 1.00 Hz

 GB
 0



-11.8570





Current Data Parameters NAME aaj-sucmp-2K EXPNO 2 PROCNO 1

 $F_2 - Acquisition Parameters Date 20120917 Time 9.28 INSTRUM spect PROBHD 5 mm PABBO BB-PULPROG zgg30 TD 65536 SOLVENT D20 NS 16 DS 0 SWH 104166.664 Hz FIDRES 1.589457 Hz AQ 0.3146228 sec RG 2050 DW 4.800 usec DE 650 usec TE 300.0 K D1 2.0000000 sec D11 0.03000000 sec TD0 1 I 0.31P P1 2.000 AB P1 P1 13.50 usec PL1 2.00 AB PL1W 16.00742149 W SF01 161.9755930 MHz$

CHANNEL f2 === CPDPRG2 waltz16 NUC2 1H PCPD2 90.00 usec PL2 -2.00 dB PL13 16.70 dB PL13 16.70 dB PL2W 16.12334061 W PL12W 0.43396533 W PL13W 0.21749784 W SF02 400.1320007 MHz F2 - Processing parameters SI 32768 SF 161.9755127 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.00

| | | • • • • • • • • | | | | | | | | | | |
|-----|-----|-----------------|-----|-----|----|---|-----|------|------|------|------|-------|
| 300 | 250 | 200 | 150 | 100 | 50 | 0 | -50 | -100 | -150 | -200 | -250 | . ррт |

4.3530







0 _II _P_OPh

OPh

<u></u>.





- - -









> Current Data Parameters NAME aaj-446-p EXPNO 2 PROCNO 1

 PROCNO
 1

 F2- Acquisition Parameters
 Date_
 20130824

 Time
 10.56
 INSTRUM
 spect

 PROBHD 5 num PABBO BB PULPROG
 zgpg30
 TD

 65536
 SOLVENT
 CDCl3
 NS
 11

 DS
 0
 SWH
 104166.664 Hz
 FIDRES
 1.589457 Hz

 AQ
 0.3146228 sec
 RG
 2050
 DW
 4.800 usec
 DE
 6.50 usec
 TE
 300.0 K
 D11
 2.00000000 sec
 D11
 0.03000000 sec
 D11
 0.03000000 sec
 D11
 0.03000000 sec
 TD4
 TO4106 11
 TE
 TUCI
 31P
 PI
 13.50 usec
 PL
 2.00 dB
 PLIW
 16.072149 W
 SFO1
 161.9755930 MHz
 TUCE
 CHDPRG2
 water16
 TUCE
 TUCE
 TH
 TUCE
 TUE
 TUE
 CDDPRG2
 water16
 TUE
 | CPDPRG2 | waltz16 | |
|------------|------------------|--|
| NUC2 | 111 | |
| PCPD2 | 90.00 usec | |
| PL2 | -2.00 dB | |
| PL12 | 13.70 dB | |
| PL13 | 16.70 dB | |
| PL2W | 16.12334061 W | |
| PL12W | 0.43396533 W | |
| PL13W | 0.21749784 W | |
| SF02 | 400.1320007 MHz | |
| F2 - Proce | ssing parameters | |
| SI | 32768 | |
| | | |

SF 161.9755127 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.00



-11.4507





.