Supporting Information for:

2,3-Anhydrosugars in Glycoside Bond Synthesis. Application to α -D-Galactofuranosides

Yu Bai and Todd L. Lowary^{*,#}

Alberta Ingenuity Centre for Carbohydrate Science and Department of Chemistry, The

University of Alberta, Gunning-Lemieux Chemistry Centre,

Edmonton, AB T6G 2G2, Canada.

Email: tlowary@ualberta.ca

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Synthesis of 34–37 and measurement of $^1J_{C1,H1}$ values.

The routes used for the synthesis of **34–37** are shown in Scheme S1 and S2. Starting from **22** (see main text of paper) and the known intermediates **41**¹ and **S1**,² all four compounds could be obtained without difficulty as illustrated below. Once synthesized, the $^1J_{C1,H1}$ values were extracted from 1H -coupled HMQC spectra.

Scheme S1. (a) $(CH_3O)_2C(CH_3)_2$, acetone, *p*-TsOH, rt; (b) DIAD, Ph_3P , THF, 0 °C → rt, 2 steps, 49%; (c) NIS, AgOTf, CH_2Cl_2 , 0 °C, 89%; (d) NaOCH₃, CH₃OH, rt, 87%; $(CH_3O)_2C(CH_3)_2$, acetone, *p*-TsOH, rt; (b) DIAD, Ph_3P , THF, 0 °C → rt, 2 steps, 74%

Scheme S2. (a) BnBr, NaH, DMF, 0 °C $\rightarrow$ rt, 98%; (b) *n*-octanol, NIS, AgOTf, CH₂Cl₂, 0 °C, 62% + 17% β -anomer; (c) H₂, Pd(OH)₂/C, CH₃OH, rt, 85%; (d) (CH₃O)₂C(CH₃)₂, acetone, *p*-TsOH, rt; (e) DIAD, Ph₃P, THF, 0 °C $\rightarrow$ rt, 2 steps, 65%; (f) NIS, AgOTf, CH₂Cl₂, 0 °C, 70%, 8:1 α : β ; (g) H₂, Pd(OH)₂/C, CH₃OH, rt, 82%; (h) (CH₃O)₂C(CH₃)₂, acetone, *p*-TsOH, rt; (i) DIAD, Ph₃P, THF, 0 °C $\rightarrow$ rt, 2 steps, 39%

General Methods. All reagents used were purchased from commercial sources and were used without further purification unless noted. Solvents used in reactions were purified by successive passage through columns of alumina and copper under nitrogen. Unless stated otherwise, all reactions were carried out under a positive pressure of argon and were monitored by TLC on silica gel G-25 UV₂₅₄ (0.25 mm). Spots were detected under UV light and/or by charring with 10% H₂SO₄ in ethanol, or in acidified ethanolic anisaldehyde. Solvents were evaporated under reduced pressure and below 50 °C (water bath). Column chromatography was performed on Silica Gel 60 (40–60 mM). The ratio between silica gel and crude product ranged from 100:1 to 20:1 (w/w). Iatrobeds refers to a beaded silica gel 6RS–8060, which is manufactured by Iatron Laboratories (Tokyo). Melting points were recorded on an electrothermal melting point apparatus. ¹H NMR spectra were recorded on at 400, 500 or 600 MHz, and chemical shifts are referenced to either TMS (0.0, CDCl₃) or CD₃OD (4.78, CD₃OD). ¹³C NMR APT spectra³ were recorded at 100 or 125 MHz, and ¹³C chemical shifts are referenced to CDCl₃ (77.23, CDCl₃) or CD₃OD (48.9, CD₃OD). ¹H NMR data are reported as though they are first order, and the peak assignments were made on the basis of 2D-NMR (¹H–¹H COSY and HMQC) experiments. ESI-MS spectra were recorded on samples suspended in THF or CH₃OH and added NaCl. Optical rotations were measured at 22 ± 2 °C at the sodium D line (589 nm) and are in units of deg·mL(dm·g)⁻¹.

***n*-Octyl 2,3,5,6-tetra-*O*-acetyl-**β**-D-galactofuranosyl-(1→5)-2,3-anhydro-**α**-D-lyxofuranoside (S2).** To a mixture of **22** (250 mg, 0.55 mmol), **41**¹ (134 mg, 0.55 mmol) and 4 Å molecular sieves (250 mg) in CH₂Cl₂ (15 mL) was added *N*-iodosuccinimide (156 mg, 0.66

mmol) and silver triflate (42 mg, 0.16 mmol) in that order at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture turned dark red and was neutralized by the addition of triethylamine. The solution was then diluted with CH₂Cl₂ (35 mL) and filtered through Celite. The filtrate was washed with a sat. aq. Na₂S₂O₃ soln. (3 × 30 mL), dried (Na₂SO₄), and concentrated to give a crude residue that was purified by chromatography (3:1, hexanes: EtOAc) to provide **S2** (281 mg, 89%) as a colorless oil. *R*_f 0.29 (2:1, hexanes:EtOAc); [α]_D -21.4 (*c* 0.6, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 5.37 (ddd, 1 H, *J* = 7.0, 4.4, 3.8 Hz, H-5'), 5.10–5.08 (m, 2 H, H-1', H-2'), 5.02 (s, 1 H, H-1), 5.02–5.00 (m, 1 H, H-3'), 4.34 (dd, 1 H, *J* = 11.8, 4.4 Hz, H-6'), 4.27 (dd, 1 H, *J* = 5.9, 3.8 Hz, H-4'), 4.21 (dd, 1 H, *J* = 11.8, 7.0 Hz, H-6'), 4.19–4.16 (m, 1 H, H-4), 3.78 (dd, 1 H, *J* = 9.9, 7.3 Hz, H-5), 3.75 (dd, 1 H, *J* = 2.9, 0.7 Hz, H-3), 3.71 (ddd, 1 H, *J* = 9.5, 6.7, 6.7 Hz, octyl OCH₂), 3.65 (dd, 1 H, *J* = 9.9, 5.9 Hz, H-5), 3.65 (d, 1 H, *J* = 2.9 Hz, H-2), 3.44 (ddd, 1 H, *J* = 9.5, 6.7, 6.7 Hz, octyl OCH₂), 2.12 (s, 3 H, acyl CH₃), 2.10 (s, 3 H, acyl CH₃), 2.07 (s, 3 H, acyl CH₃), 2.05 (s, 3 H, acyl CH₃), 1.60–1.53 (m, 2 H, octyl CH₂), 1.35–1.22 (m, 10 H, octyl CH₂), 0.87 (dd, 3 H, *J* = 7.0, 7.0 Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 170.5 (C=O), 170.0 (C=O), 169.9 (C=O), 169.6 (C=O), 105.5 (C-1'), 101.2 (C-1), 81.3 (C-2'), 80.0 (C-4'), 76.5 (C-3'), 74.5 (C-4), 69.2 (C-5'), 68.6 (octyl OCH₂), 65.4 (C-5), 62.6 (C-6'), 56.4 (C-2), 54.4 (C-3), 31.8 (octyl CH₂), 29.6 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 26.0 (octyl CH₂), 22.6 (octyl CH₂), 20.8 (acyl CH₃), 20.7 (acyl CH₃), 20.66 (acyl CH₃), 20.6 (acyl CH₃), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₂₇H₄₂O₁₃Na: 597.2518, found: 597.2518.

***n*-Octyl β-D-galactofuranosyl-(1→5)-2,3-anhydro-α-D-lyxofuranoside (S3).** To a solution of **S2** (221 mg, 0.39 mmol) in CH₃OH (4 mL) and CH₂Cl₂ (4 mL) was added solid

NaOCH₃ until the pH was ~10. The solution was stirred at rt for 5 h, followed by neutralization with acetic acid. The resulting mixture was concentrated and purified by chromatography (11:1, CH₂Cl₂:CH₃OH), to provide **S3** (136 mg, 87%) as a colorless oil. *R_f* 0.38 (10:1, CH₂Cl₂:CH₃OH); [α]_D -28.9 (*c* 0.2, CH₃OH); ¹H NMR (500 MHz, CD₃OD, δ_H) 5.00 (s, 1 H, H-1), 4.91 (d, 1 H, *J* = 1.7 Hz, H-1'), 4.13 (dd, 1 H, *J* = 6.1, 6.0 Hz, H-4), 4.00 (dd, 1 H, *J* = 6.3, 3.7 Hz, H-3'), 3.97 (dd, 1 H, *J* = 3.7, 1.7 Hz, H-2'), 3.96 (dd, 1 H, *J* = 6.3, 3.1 Hz, H-4'), 3.86–3.82 (m, 2 H, H-3, H-5), 3.73–3.68 (m, 2 H, H-5', octyl OCH₂), 3.64 (d, 1 H, *J* = 2.9 Hz, H-2), 3.63–3.56 (m, 3 H, H-6' × 2, H-5), 3.46 (ddd, 1 H, *J* = 9.6, 6.6, 6.6 Hz, octyl OCH₂), 1.60–1.52 (m, 2 H, octyl CH₂), 1.34–1.22 (m, 10 H, octyl CH₂), 0.87 (dd, 3 H, *J* = 6.9, 6.9 Hz, octyl CH₃); ¹³C NMR (125 MHz, CD₃OD, δ_C) 109.7 (C-1'), 102.7 (C-1), 84.7 (C-4'), 83.2 (C-2'), 78.8 (C-3'), 76.4 (C-4), 72.7 (C-5'), 69.4 (octyl OCH₂), 67.1 (C-5), 64.5 (C-6'), 57.1 (C-2), 55.3 (C-3), 33.0 (octyl CH₂), 32.6 (octyl CH₂), 30.8 (octyl CH₂), 30.5 (octyl CH₂), 30.4 (octyl CH₂), 27.2 (octyl CH₂), 14.4 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₁₉H₃₄O₉Na: 429.2095, found: 429.2093.

***p*-Tolyl 2,3,5,6-tetra-*O*-benzyl-1-thio-α/β-D-galactofuranoside (S4).** To a solution of an anomeric mixture of **23** and **24** (643 mg, 2.22 mmol) in DMF (15 mL) at 0 °C was added NaH (0.585 g, 14.6 mmol, 60% dispersion in oil) and the solution was stirred for 10 min. Benzyl bromide (1.3 mL, 11.1 mmol) was added dropwise and the solution was stirred for 5 h at rt. The reaction mixture was quenched by adding a few drops of CH₃OH, diluted with CH₂Cl₂ (50 mL), and washed with a sat. aq. NaHCO₃ soln. (3 × 40 mL) and water (3 × 40 mL). The organic layer was dried (Na₂SO₄), filtered, concentrated, and the resulting residue was purified

by chromatography (7:1, hexanes:EtOAc) to provide **S4** (1.402 g, 98%) as a colorless oil. R_f 0.50 (6:1, hexanes: EtOAc); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 7.51–7.47 (m, 1 H, Ar), 7.43–7.23 (m, 21 H, Ar), 7.13–7.09 (m, 2 H, Ar), 5.67 (d, 0.4 H, $J = 4.7$ Hz, H-1 α), 5.59 (d, 0.6 H, $J = 2.8$ Hz, H-1 β), 4.81 (d, 0.4 H, $J = 11.8$ Hz, $\text{PhCH}_2\alpha$), 4.77–4.66 (m, 1.8 H, PhCH_2), 4.59–4.46 (m, 5.2 H, PhCH_2), 4.39 (dd, 0.6 H, $J = 7.1, 3.4$ Hz, H-4 β), 4.36 (d, 0.6 H, $J = 11.7$ Hz, $\text{PhCH}_2\beta$), 4.30–4.26 (m, 0.8 H, H-2 α , H-3 α), 4.17–4.10 (m, 1.6 H, H-4 α , H-3 β , H-2 β), 4.40 (ddd, 0.4 H, $J = 6.5, 6.5, 4.6$ Hz, H-5 α), 3.86 (ddd, 0.6 H, $J = 5.9, 5.9, 3.4$ Hz, H-5 β), 3.78–3.69 (m, 1.6 H, H-6 $\beta \times 2$, H-6 α), 3.61 (dd, 0.4 H, $J = 10.5, 6.5$ Hz, H-6 α), 2.35 (s, 1.8 H, tolyl $\text{CH}_3\beta$), 2.34 (s, 1.2 H, tolyl $\text{CH}_3\alpha$); ^{13}C NMR (125 MHz, CDCl_3 , δ_{C}) 138.9 (Ar α), 138.4 (Ar β), 138.33 (Ar α), 138.3 (Ar β), 137.84 (Ar α), 137.8 (Ar β), 137.5 (Ar α), 137.4 (Ar β), 137.3 (Ar α), 136.8 (Ar β), 132.1 (Ar β), 131.8 (Ar α), 131.3 (Ar α), 130.9 (Ar β), 129.7 (Ar α), 129.6 (Ar β), 128.5–127.4 (Ar), 90.3 (C-1 β), 90.0 (C-1 α), 88.6 (C-2 β), 84.4 (C-2 α), 84.1 (C-4 α), 82.9 (C-3 β), 82.0 (C-3 α), 80.6 (C-4 β), 78.6 (C-5 α), 76.3 (C-5 β), 73.5 ($\text{PhCH}_2\beta$), 73.4 ($\text{PhCH}_2\alpha$), 73.36 ($\text{PhCH}_2\alpha$), 73.3 ($\text{PhCH}_2\beta$), 72.4 ($\text{PhCH}_2\alpha$), 72.2 ($\text{PhCH}_2\beta$), 72.0 ($\text{PhCH}_2\beta$), 71.9 ($\text{PhCH}_2\alpha$), 70.8 (C-6 $\alpha\beta$), 21.14 (tolyl $\text{CH}_3\beta$), 21.1 (tolyl $\text{CH}_3\alpha$). HRMS (ESI) calcd. for (M + Na) $\text{C}_{41}\text{H}_{42}\text{O}_5\text{SNa}$: 669.2645, found: 669.2642.

***n*-Octyl 2,3,5,6-tetra-*O*-benzyl- α -D-galactofuranoside (S5).** To a mixture of **S4** (490 mg, 0.76 mmol), *n*-octanol (0.14 mL, 0.91 mmol) and 4 Å molecular sieves (0.5 g) in CH_2Cl_2 (20 mL) was added *N*-iodosuccinimide (216 mg, 0.91 mmol) at 0 °C. After stirring for 10 min at 0 °C, the reaction mixture was neutralized with triethylamine. The resulting solution was then diluted with CH_2Cl_2 (30 mL) and filtered through Celite. The filtrate was washed with a sat. aq.

Na₂S₂O₃ soln. (3 × 30 mL), dried (Na₂SO₄), and concentrated to give a crude residue that was purified by chromatography (10:1, hexanes:EtOAc) to give **S5** (307 mg, 62%) and the corresponding β-glycoside anomer (82 mg, 17%); *R_f* 0.47 (6:1, hexanes:EtOAc)) as colorless oils. Data for major isomer: **S5**: *R_f* 0.37 (6:1, hexanes:EtOAc); [α]_D +27.7 (*c* 0.8, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.41–7.20 (m, 20 H, Ar), 4.90 (d, 1 H, *J* = 4.3 Hz, H-1), 4.76 (d, 2 H, *J* = 12.1 Hz, PhCH₂), 4.66 (d, 2 H, *J* = 11.6 Hz, PhCH₂), 4.58 (d, 1 H, *J* = 11.6 Hz, PhCH₂), 4.52 (d, 2 H, *J* = 11.8 Hz, PhCH₂), 4.48 (d, 1 H, *J* = 12.1 Hz, PhCH₂), 4.31 (dd, 1 H, *J* = 7.5, 7.0 Hz, H-3), 4.07 (dd, 1 H, *J* = 7.5, 4.3 Hz, H-2), 3.99 (dd, 1 H, *J* = 7.0, 6.6 Hz, H-4), 3.75–3.65 (m, 3 H, H-5, H-6, octyl OCH₂), 3.60 (dd, 1 H, *J* = 10.4, 6.3 Hz, H-6), 3.33 (ddd, 1 H, *J* = 9.6, 7.0, 7.0 Hz, octyl OCH₂), 1.64–1.52 (m, 2 H, octyl CH₂), 1.36–1.24 (m, 10 H, octyl CH₂), 0.91 (dd, 3 H, *J* = 7.0, 7.0 Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 138.9 (Ar), 138.3 (Ar × 2), 137.8 (Ar), 128.4 (Ar × 2), 128.32 (Ar × 2), 128.3 (Ar × 2), 128.2 (Ar × 2), 128.1 (Ar × 2), 127.9 (Ar), 127.85 (Ar × 2), 127.8 (Ar × 2), 127.6 (Ar), 127.55 (Ar × 2), 127.5 (Ar), 127.4 (Ar), 100.0 (C-1), 84.2 (C-2), 81.3 (C-3), 80.4 (C-4), 79.9 (C-5), 73.4 (PhCH₂), 73.1 (PhCH₂), 72.35 (PhCH₂), 72.3 (PhCH₂), 70.5 (C-6), 68.0 (octyl OCH₂), 31.9 (octyl CH₂), 29.54 (octyl CH₂), 29.5 (octyl CH₂), 29.3 (octyl CH₂), 26.3 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₄₂H₅₂O₆Na: 675.3656, found: 675.3657.

***n*-Octyl α-D-galactofuranoside (S6).** To a solution of **S5** (201 mg, 0.31 mmol) in methanol (2.0 mL) was added 20% palladium hydroxide on carbon and the reaction was stirred under positive pressure of hydrogen for 12 h. The resulting mixture was filtered through Celite and concentrated to give a crude residue that was purified by chromatography (11:1,

CH₂Cl₂:CH₃OH) to yield **S6** (76 mg, 85%) as a white foam. *R_f* 0.36 (10:1, CH₂Cl₂:CH₃OH); [α]_D +83.5 (*c* 0.2, CH₃OH); ¹H NMR (500 MHz, CD₃OD, δ_H) 4.83 (d, 1 H, *J* = 4.6 Hz, H-1), 4.07 (dd, 1 H, *J* = 7.8, 7.0 Hz, H-3), 3.93 (dd, 1 H, *J* = 7.8, 4.6 Hz, H-2), 3.78 (ddd, 1 H, *J* = 9.6, 6.7, 6.7 Hz, octyl OCH₂), 3.71 (dd, 1 H, *J* = 7.0, 5.2 Hz, H-4), 3.64–3.59 (m, 2 H, H-5, H-6), 3.57–3.51 (m, 1 H, H-6), 3.45 (ddd, 1 H, *J* = 9.6, 6.7, 6.7 Hz, octyl OCH₂), 1.64–1.57 (m, 2 H, octyl CH₂), 1.40–1.24 (m, 10 H, octyl CH₂), 0.91–0.86 (m, 3 H, octyl CH₃); ¹³C NMR (125 MHz, CD₃OD, δ_C) 102.9 (C-1), 83.6 (C-4), 78.9 (C-2), 76.4 (C-3), 74.5 (C-5), 69.8 (octyl OCH₂), 64.2 (C-6), 33.0 (octyl CH₂), 30.8 (octyl CH₂), 30.6 (octyl CH₂), 30.4 (octyl CH₂), 27.2 (octyl CH₂), 23.7 (octyl CH₂), 14.4 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₁₄H₂₈O₆Na: 315.1778, found: 315.1778.

***n*-Octyl 2,3,5,6-tetra-*O*-benzyl-α/β-D-galactofuranosyl-(1→5)-2,3-anhydro-α-D-lyxofuranoside (S7).** To a mixture of **S4** (490 mg, 0.76 mmol), **41**¹ (186 μL, 0.76 mmol) and 4 Å molecular sieves (0.5 g) in CH₂Cl₂ (20 mL) was added *N*-iodosuccinimide (216 mg, 0.91 mmol) and silver triflate (59 mg, 0.23 mmol) in that order at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was neutralized with triethylamine, diluted with CH₂Cl₂ (30 mL) and then filtered through Celite. The filtrate was washed with a sat. aq. Na₂S₂O₃ soln. (3 × 30 mL), dried (Na₂SO₄), and concentrated to give a crude residue that was purified by chromatography (6:1, hexanes:EtOAc) to give an α/β mixture of **S7** (405 mg, 70%) as a colorless oil in an 8:1 α:β ratio. NMR data only for α-anomer: *R_f* 0.27 (6:1, hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.42–7.25 (m, 20 H, Ar), 5.03 (s, 1 H, H-1), 4.94 (d, 1 H, *J* = 4.4 Hz, H-1'), 4.82–4.49 (m, 8 H, PhCH₂), 4.39 (dd, 1 H, *J* = 7.7, 7.3 Hz, H-3'), 4.17 (dd, 1 H, *J* = 8.4, 5.0 Hz, H-4), 4.11 (dd, 1

H, $J = 7.7, 4.4$ Hz, H-2'), 4.03 (dd, 1 H, $J = 7.3, 4.9$ Hz, H-4'), 3.88 (dd, 1 H, $J = 9.8, 5.0$ Hz, H-5), 3.77–3.66 (m, 4 H, H-5', H-6' $\times$ 2, octyl OCH₂), 3.75 (d, 1 H, $J = 2.8$ Hz, H-3), 3.63 (d, 1 H, $J = 2.8$ Hz, H-2), 3.55 (dd, 1 H, $J = 9.8, 8.4$ Hz, H-5), 3.45 (ddd, 1 H, $J = 9.4, 6.7, 6.7$ Hz, octyl OCH₂), 1.64–1.58 (m, 2 H, octyl CH₂), 1.39–1.27 (m, 10 H, octyl CH₂), 0.95–0.91 (dd, 3 H, $J = 7.0, 7.0$ Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 138.7 (Ar), 138.31 (Ar), 138.3 (Ar), 137.8 (Ar), 128.7 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 101.1 (C-1), 100.4 (C-1'), 84.3 (C-2'), 80.33 (C-3'), 80.3 (C-4'), 78.6 (C-5'), 74.5 (C-4), 73.5 (PhCH₂), 73.2 (PhCH₂), 72.5 (PhCH₂), 72.4 (PhCH₂), 70.5 (C-6'). 68.5 (octyl OCH₂), 66.0 (C-5), 56.7 (C-2), 54.7 (C-3), 31.9 (octyl CH₂), 29.7 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.1 (octyl CH₂), 22.7 (octyl CH₂), 14.2 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₄₇H₅₈O₉Na: 789.3973, found: 789.3973.

***n*-Octyl α -D-galactofuranosyl-(1 $\rightarrow$ 5)-2,3-anhydro- α -D-lyxofuranoside (S8).** To a solution of **S7** (140 mg, 0.18 mmol) in CH₃OH (2.0 mL) was added 20% palladium hydroxide on carbon and the reaction was stirred under positive pressure of hydrogen for 12 h. The resulting mixture was filtered through Celite and concentrated to give a crude residue that was purified by chromatography (11:1, CH₂Cl₂:CH₃OH) to yield **S8** (61 mg, 82%) as a colorless oil. R_f 0.38 (10:1, CH₂Cl₂:CH₃OH); $[\alpha]_D^{+98.7}$ (c 0.2, CH₃OH); ¹H NMR (500 MHz, CD₃OD, δ_H) 5.02 (s, 1 H, H-1), 4.87 (d, 1 H, $J = 4.7$ Hz, H-1'), 4.19 (dd, 1 H, $J = 6.5, 5.9$ Hz, H-4), 4.16 (dd, 1 H, $J = 8.1, 7.3$ Hz, H-3'), 3.95 (dd, 1 H, $J = 8.1, 4.7$ Hz, H-2'), 3.88 (d, 1 H, $J = 2.9$ Hz, H-3), 3.86 (dd, 1 H, $J = 10.1, 6.5$ Hz, H-5), 3.75 (dd, 1 H, $J = 7.3, 4.0$ Hz, H-4'), 3.74–3.68 (m, 2 H, H-5, octyl OCH₂), 3.65 (d, 1 H, $J = 2.9$ Hz, H-2), 3.64–3.54 (m, 3 H, H-6' $\times$ 2, H-5'), 3.46 (ddd, 1 H, $J =$

9.5, 6.6, 6.6 Hz, octyl OCH₂), 1.61–1.52 (m, 2 H, octyl CH₂), 1.34–1.23 (m, 10 H, octyl CH₂), 0.91–0.83 (m, 3 H, $J = 7.0, 7.0$ Hz, octyl CH₃); ¹³C NMR (125 MHz, CD₃OD, δ_C) 103.2 (C-1'), 102.7 (C-1), 83.4 (C-4'), 78.9 (C-2'), 76.3 (C-4), 75.7 (C-3'), 73.6 (C-5'), 69.5 (octyl OCH₂), 68.3 (C-5), 64.3 (C-6'), 57.3 (C-2), 55.2 (C-3), 33.0 (octyl CH₂), 30.8 (octyl CH₂), 30.5 (octyl CH₂), 30.4 (octyl CH₂), 27.2 (octyl CH₂), 23.7 (octyl CH₂), 14.4 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₁₉H₃₄O₉Na: 429.2095, found: 429.2094.

2-deoxy-2-thiotolyl-D-idose (26). A solution of **13** (62 mg, 0.2 mmol) in 50% aqueous acetic acid (20 mL) was stirred for 12 h. Concentration of the solution and chromatography (10:1, CH₂Cl₂: CH₃OH) gave **26** (38 mg, 72%) as a colorless oil. R_f 0.19 (10:1, CH₂Cl₂:CH₃OH); ¹H NMR (500 MHz, CD₃OD, δ_H) 7.42–7.35 (m, 2 H, Ar), 7.17–7.09 (m, 2 H, Ar), 5.51 (d, 0.23 H, $J = 4.8$ Hz, H-1 β -furanose), 5.25 (d, 0.13 H, $J = 2.6$ Hz, H-1 α -pyranose), 5.17 (d, 0.48 H, $J = 2.1$ Hz, H-1 α -furanose), 5.08 (d, 0.16 H, $J = 4.1$ Hz, H-1 β -pyranose), 4.37 (dd, 0.23 H, $J = 6.2, 6.2$ Hz, H-3 β -furanose), 4.24 (dd, 0.23 H, $J = 6.2, 3.5$ Hz, H-4 β -furanose), 4.21–4.18 (m, 0.16 H), 4.18–4.13 (m, 1.13 H), 3.98–3.93 (m, 0.64 H), 3.89 (m, 0.23 H, H-5 β -furanose), 3.81–3.55 (m, 2.61 H), 3.52 (dd, 0.48 H, $J = 2.8, 2.1$ Hz, H-2 α -furanose), 3.24 (dd, 0.13 H, $J = 3.3, 2.6$ Hz, H-2 α -pyranose), 3.00 (dd, 0.16 H, $J = 6.1, 4.1$ Hz, H-2 β -pyranose), 2.32–2.27 (m, 3 H, tolyl CH₃); ¹³C NMR (125 MHz, CD₃OD, δ_C) 138.6–129.8 (Ar), 103.5 (C-1 α -furanose), 97.8 (C-1 β -furanose), 95.3 (C-1 β -pyranose), 94.1 (C-1 α -pyranose), 82.6, 79.2, 77.8, 77.3, 77.0, 76.9, 72.5, 72.2, 72.19, 72.15, 72.1, 71.9, 71.1, 70.9, 64.4, 64.3, 64.2, 63.0, 61.8, 61.0, 60.6, 56.7, 54.2, 21.1, 21.0. HRMS (ESI) calcd. for (M + Na) C₁₃H₁₈O₅SNa: 309.0769, found: 309.0767.

***n*-Octyl 2,3-anhydro-5,6-*O*-isopropylidene- α -D-gulofuranoside (34).** To a solution of **S6** (61 mg, 0.21 mmol) and 2,2-dimethoxypropane (0.21 mL, 1.7 mmol) in acetone (1.5 mL) was added *p*-toluenesulfonic acid (0.4 mg, cat.) at rt. The solution was stirred for 4 h, and neutralized with triethylamine. The mixture was concentrated and the resulting oil was dissolved in THF (2.0 mL), followed by the addition of PPh₃ (67 mg, 0.25 mmol). DIAD (51 μ L, 0.25 mmol) was then added dropwise at 0 °C and the reaction mixture was warmed to rt and stirred for 30 min. The resulting solution was concentrated and the residue was purified by chromatography (4:1, hexanes:EtOAc) to yield **34** (43 mg, 65% over two steps) as a white foam. *R*_f 0.26 (4:1, hexanes:EtOAc); [α]_D +44.9 (*c* 1.0, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ _H) 5.08 (s, 1 H, H-1), 4.15 (ddd, 1 H, *J* = 6.7, 6.6, 6.6 Hz, H-5), 4.11 (dd, 1 H, *J* = 8.5, 6.6 Hz, H-6), 3.98 (dd, 1 H, *J* = 8.5, 6.7 Hz, H-6), 3.88 (dd, 1 H, *J* = 6.6, 0.7 Hz, H-4), 3.82 (ddd, 1 H, *J* = 9.6, 6.8, 6.8 Hz, octyl OCH₂), 3.66 (d, 1 H, *J* = 3.0 Hz, H-2), 3.58 (dd, 1 H, *J* = 3.0, 0.7 Hz, H-3), 3.55 (ddd, 1 H, *J* = 9.6, 6.8, 6.8 Hz, octyl OCH₂), 1.64–1.58 (m, 2 H, octyl CH₂), 1.46 (s, 3 H, isopropylidene CH₃), 1.37 (s, 3 H, isopropylidene CH₃), 1.35–1.22 (m, 10 H, octyl CH₂), 0.89–0.84 (dd, 3 H, *J* = 7.0, 7.0 Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ _C) 109.7 (isopropylidene C), 101.6 (C-1), 77.3 (C-4), 75.4 (C-5), 69.9 (octyl OCH₂), 65.4 (C-6), 54.9 (C-2), 53.9 (C-3), 31.8 (octyl CH₂), 29.7 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 26.6 (isopropylidene CH₃), 25.9 (octyl CH₂), 25.2 (isopropylidene CH₃), 22.6 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₁₇H₃₀O₅Na: 337.1986, found: 337.1984.

***n*-Octyl 2,3-anhydro-5,6-*O*-isopropylidene- β -D-gulofuranoside (35).** To a solution of **S1**¹ (29 mg, 0.10 mmol) and 2,2-dimethoxypropane (0.10 mL, 0.80 mmol) in acetone (1.0 mL)

was added *p*-toluenesulfonic acid (0.2 mg) at rt. The solution was stirred for 3 h and neutralized with Et₃N. TLC showed a spot at *R_f* 0.55 (15:1, CH₂Cl₂: CH₃OH). The mixture was concentrated and the resulting oil was dissolved in THF (1.0 mL), followed by the addition of PPh₃ (31 mg, 0.12 mmol). DIAD (23 μ L, 0.12 mmol) was then added dropwise at 0 °C. The reaction mixture was warmed to rt over 30 min and then concentrated. The residue was purified by chromatography (8:1, hexanes:EtOAc) to yield **35** (15 mg, 49% over two steps) as a white foam. *R_f* 0.58 (4:1, hexanes:EtOAc); [α]_D -29.1 (*c* 0.4, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ _H) 5.08 (s, 1 H, H-1), 4.30 (ddd, 1 H, *J* = 7.1, 6.6, 6.5 Hz, H-5), 4.12 (dd, 1 H, *J* = 8.3, 6.5 Hz, H-6), 4.04 (d, 1 H, *J* = 7.1 Hz, H-4), 3.94 (dd, 1 H, *J* = 8.3, 6.6 Hz, H-6), 3.79 (ddd, 1 H, *J* = 9.5, 6.7, 6.7 Hz, octyl OCH₂), 3.64 (d, 1 H, *J* = 2.9 Hz, H-2), 3.61 (d, 1 H, *J* = 2.9 Hz, H-3), 3.46 (ddd, 1 H, *J* = 9.5, 6.7, 6.7 Hz, octyl OCH₂), 1.61–1.54 (m, 2 H, octyl CH₂), 1.47 (s, 3 H, isopropylidene CH₃), 1.38 (s, 3 H, isopropylidene CH₃), 1.36–1.24 (m, 10 H, octyl CH₂), 0.99–0.86 (dd, 3 H, *J* = 7.0, 7.0 Hz octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ _C) 109.8 (isopropylidene C), 101.3 (C-1), 77.1 (C-4), 75.2 (C-5), 68.7 (octyl OCH₂), 65.7 (C-6), 55.7 (C-2), 53.5 (C-3), 31.8 (octyl CH₂), 29.6 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 26.7 (isopropylidene CH₃), 26.0 (octyl CH₂), 25.2 (isopropylidene CH₃), 22.6 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₁₇H₃₀O₅Na: 337.1986, found: 337.1984.

***n*-Octyl 2,3-anhydro-5,6-*O*-isopropylidene- α -D-gulofuranosyl-(1→5)-2,3-anhydro- α -D-lyxofuranoside (**36**).** To a solution of **S8** (44 mg, 0.11 mmol) and 2,2-dimethoxypropane (0.11 mL, 0.87 mmol) in acetone (1.0 mL) was added *p*-toluenesulfonic acid (0.2 mg, cat.) at rt. The solution was stirred for 4 h, and neutralized with triethylamine. The mixture was

concentrated and the resulting oil was dissolved in THF (1.0 mL), followed by the addition of PPh₃ (34 mg, 0.13 mmol). DIAD (25 μ L, 0.13 mmol) was then added dropwise at 0 °C. The reaction mixture was warmed to rt and kept stirring for 40 min. The resulting mixture was concentrated and the residue was purified by chromatography (4:1, hexanes:EtOAc) to yield **36** (18 mg, 39% over two steps) as a white foam. *R*_f 0.22 (2:1, hexanes:EtOAc); [α]_D +38.3 (*c* 2.3, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ _H) 5.18 (s, 1 H, H-1'), 5.02 (s, 1 H, H-1), 4.35 (ddd, 1 H, *J* = 7.3, 6.7, 6.6 Hz, H-5'), 4.21 (dd, 1 H, *J* = 7.0, 5.7 Hz, H-4), 4.12 (dd, 1 H, *J* = 8.3, 7.3 Hz, H-6'), 4.00–3.94 (m, 2 H, H-6', H-5), 3.91 (d, 1 H, *J* = 6.7 Hz, H-4'), 3.84–3.78 (m, 1 H, H-5), 3.79 (d, 1 H, *J* = 2.8 Hz, H-2), 3.74–3.68 (m, 1 H, octyl OCH₂), 3.71 (d, 1 H, *J* = 2.9 Hz, H-2'), 3.64 (d, 1 H, *J* = 2.8 Hz, H-3), 3.60 (d, 1 H, *J* = 2.9 Hz, H-3'), 3.43 (ddd, 1H, *J* = 9.3, 6.9, 6.9 Hz, octyl OCH₂), 1.59–1.52 (m, 2 H, octyl CH₂), 1.46 (s, 3 H, isopropylidene CH₃), 1.38 (s, 3 H, isopropylidene CH₃), 1.34–1.21 (m, 10 H, octyl CH₂), 0.89–0.85 (m, 3 H, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ _C) 109.82 (isopropylidene C), 101.6 (C-1'), 101.1 (C-1), 77.4 (C-4'), 75.3 (C-5'), 74.7 (C-4), 68.5 (octyl OCH₂), 66.9 (C-5), 65.4 (C-6'), 56.4 (C-3), 54.7 (C-2'), 54.4 (C-2), 53.9 (C-3'), 31.8 (octyl CH₂), 29.6 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 26.6 (isopropylidene CH₃), 26.0 (octyl CH₂), 25.2 (isopropylidene CH₃), 22.6 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₂₂H₃₆O₈Na: 451.2302, found: 451.2308.

***n*-Octyl 2,3-anhydro-5,6-*O*-isopropylidene- β -D-gulofuranosyl-(1 $\rightarrow$ 5)- α -D-lyxofuranoside (**37**).** To a solution of **S3** (106 mg, 0.26 mmol) and 2,2-dimethoxypropane (0.26 mL, 2.1 mmol) in acetone (2.0 mL) was added *p*-toluenesulfonic acid (0.5 mg, cat.) at rt. The solution was stirred for 3 h, and neutralized with triethylamine at which point TLC showed a

spot at R_f 0.58 (10:1, CH_2Cl_2 : CH_3OH). The mixture was concentrated and the resulting oil was dissolved in THF (2.0 mL), followed by the addition of PPh_3 (82 mg, 0.31 mmol). DIAD (61 μL , 0.31 mmol) was then added dropwise at 0 °C and then the reaction mixture was warmed to rt over 30 min, and stirred for another 40 min. The resulting mixture was concentrated and the residue was purified by chromatography (4:1, hexanes:EtOAc) to yield **37** (83 mg, 74% over two steps) as a white foam. R_f 0.27 (4:1, hexanes:EtOAc); $[\alpha]_D$ -4.0 (c 1.0, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 5.16 (s, 1 H, H-1'), 5.05 (s, 1 H, H-1), 4.29 (ddd, 1 H, J = 6.8, 6.6, 6.5 Hz, H-5'), 4.19–4.15 (m, 1 H, H-4), 4.10 (dd, 1 H, J = 8.5, 6.5 Hz, H-6'), 4.07 (d, 1 H, J = 6.8 Hz, H-4'), 3.97 (dd, 1 H, J = 10.5, 5.3 Hz, H-5), 3.94 (dd, 1 H, J = 8.5, 6.6 Hz, H-6'), 3.73 (ddd, 1 H, J = 9.6, 6.7, 6.7 Hz, octyl OCH_2), 3.72–3.68 (m, 3 H, H-2, H-3', H-5), 3.64–3.62 (m, 2 H, H-2', H-3), 3.45 (ddd, 1H, J = 9.6, 6.7, 6.7 Hz, octyl OCH_2), 1.60–1.53 (m, 2 H, octyl CH_2), 1.47 (s, 3 H, isopropylidene CH_3), 1.38 (s, 3 H, isopropylidene CH_3), 1.36–1.23 (m, 10 H, octyl CH_2), 0.90–0.88 (m, 3 H, octyl CH_3); ^{13}C NMR (125 MHz, CDCl_3 , δ_{C}) 109.8 (isopropylidene C), 101.8 (C-1'), 101.3 (C-1), 77.3 (C-4'), 75.2 (C-5'), 75.1 (C-4), 68.6 (C-5), 67.3 (octyl OCH_2), 65.7 (C-6'), 56.0 (C-2'), 55.6 (C-2), 54.2 (C-3'), 53.4 (C-3), 31.8 (octyl CH_2), 29.6 (octyl CH_2), 29.3 (octyl CH_2), 29.2 (octyl CH_2), 26.7 (isopropylidene CH_3), 26.0 (octyl CH_2), 25.2 (isopropylidene CH_3), 22.6 (octyl CH_2), 14.1 (octyl CH_3). HRMS (ESI) calcd. for (M + Na) $\text{C}_{22}\text{H}_{36}\text{O}_8\text{Na}$: 451.2302, found: 451.2307.

Cyclohexyl 2,3-anhydro-5,6-*O*-isopropylidene- α -D-gulofuranoside (46). The glycosylation was carried out following the general protocol, and **46** was isolated by chromatography (4:1, hexanes:EtOAc) as a white foam. R_f 0.25 (4:1, hexanes: EtOAc); $[\alpha]_D$

+61.8 (*c* 1.0, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 5.19 (d, 1 H, *J* = 0.6 Hz, H-1), 4.36 (ddd, 1 H, *J* = 6.6, 6.6, 6.5 Hz, H-5), 4.11 (dd, 1 H, *J* = 8.5, 6.6 Hz, H-6), 4.00 (dd, 1 H, *J* = 8.5, 6.6 Hz, H-6), 3.87 (dd, 1 H, *J* = 6.5, 0.8 Hz, H-4), 3.67–3.61 (m, 1 H, cyclohexyl OCH), 3.64 (dd, 1 H, *J* = 3.0, 0.6 Hz, H-2), 3.58 (dd, 1 H, *J* = 3.0, 0.8 Hz, H-3), 2.01–1.89 (m, 2 H, cyclohexyl CH₂), 1.77–1.71 (m, 2 H, cyclohexyl CH₂), 1.56–1.50 (m, 1 H, cyclohexyl CH₂), 1.46 (s, 3 H, isopropylidene CH₃), 1.37 (s, 3 H, isopropylidene CH₃), 1.46–1.13 (m, 5 H, cyclohexyl CH₂); ¹³C NMR (125 MHz, CDCl₃, δ_C) 109.7 (isopropylidene C), 100.0 (C-1), 77.7 (cyclohexyl OCH), 77.3 (C-4), 75.6 (C-5), 65.5 (C-6), 55.4 (C-2), 53.8 (C-3), 33.4 (cyclohexyl CH₂), 32.3 (cyclohexyl CH₂), 26.6 (isopropylidene CH₃), 25.5 (cyclohexyl CH₂ × 2), 25.2 (isopropylidene CH₃), 24.2 (cyclohexyl CH₂). HRMS (ESI) calcd. for (M + Na) C₁₅H₂₄O₅Na: 307.1516, found: 307.1516.

***tert*-Butyl 2,3-anhydro-5,6-*O*-isopropylidene- α -D-gulofuranoside (47).** The glycosylation was carried out following the general protocol, and **47** was isolated by chromatography (4:1, hexanes:EtOAc) as a white foam. *R*_f 0.21 (4:1, hexanes: EtOAc); [α]_D +67.0 (*c* 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃, δ_H) 5.24 (s, 1 H, H-1), 4.37 (ddd, 1 H, *J* = 6.8, 6.5, 6.0 Hz, H-5), 4.10 (dd, 1 H, *J* = 8.5, 6.5 Hz, H-6), 4.05 (dd, 1 H, *J* = 8.5, 6.8 Hz, H-6), 3.87 (d, 1 H, *J* = 6.0 Hz, H-4), 3.59–3.58 (m, 2 H, H-2, H-3), 1.47 (s, 3 H, isopropylidene CH₃), 1.37 (s, 3 H, isopropylidene CH₃), 1.29 (s, 9 H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃, δ_C) 109.5 (isopropylidene C), 96.5 (C-1), 77.0 (C-4), 75.6 (C(CH₃)₃), 75.5 (C-5), 65.5 (C-6), 56.0 (C-2), 53.5 (C-3), 28.6 (C(CH₃)₃ × 3), 26.6 (isopropylidene CH₃), 25.2 (isopropylidene CH₃). HRMS (ESI) calcd. for (M + Na) C₁₃H₂₂O₅Na: 281.1359, found: 281.1357.

Methyl 2,3-anhydro-5,6-*O*-isopropylidene- α -D-gulofuranosyl-(1 $\rightarrow$ 2)-3,5-di-*O*-benzyl- α -D-arabinofuranoside (48). The glycosylation was carried out following the general protocol, and **48** was isolated by chromatography (1:1, hexanes: EtOAc) as a colorless syrup. R_f 0.44 (1:1, hexanes:EtOAc); $[\alpha]_D +77.5$ (c 2.0, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.35–7.27 (m, 10 H, Ar), 5.02 (s, 1 H, H-1), 4.98 (d, 1 H, J = 0.5 Hz, H-1'), 4.64–4.54 (m, 4 H, PhCH₂), 4.34 (ddd, 1 H, J = 6.5, 6.5, 6.5 Hz, H-5'), 4.25 (d, 1 H, J = 2.9 Hz, H-2), 4.20–4.17 (m, 1 H, H-4), 4.08 (dd, 1 H, J = 8.5, 6.5 Hz, H-6'), 4.01 (dd, 1 H, J = 8.5, 6.5 Hz, H-6'), 3.93–3.90 (m, 2 H, H-4', H-3), 3.67–3.60 (m, 3 H, H-5 $\times$ 2, H-3'), 3.54 (dd, 1 H, J = 3.0, 0.5 Hz, H-2'), 3.40 (s, 3 H, OCH₃), 1.47 (s, 3 H, isopropylidene CH₃), 1.34 (s, 3 H, isopropylidene CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 138.2 (Ar), 138.1 (Ar), 128.34 (Ar $\times$ 2), 128.3 (Ar $\times$ 2), 127.9 (Ar $\times$ 2), 127.8 (Ar $\times$ 2), 127.7 (Ar), 127.6 (Ar), 109.7 (isopropylidene C), 108.0 (C-1), 101.1 (C-1'), 87.4 (C-2), 84.0 (C-3), 80.4 (C-4), 77.4 (C-4'), 75.1 (C-5'), 73.4 (PhCH₂), 72.4 (PhCH₂), 69.7 (C-5), 65.4 (C-6'), 55.2 (OCH₃), 54.9 (C-2'), 54.2 (C-3'), 26.6 (isopropylidene CH₃), 25.2 (isopropylidene CH₃). HRMS (ESI) calcd. for (M + Na) C₂₉H₃₆O₉Na: 551.2252, found: 551.2254.

***n*-Octyl 2,3-anhydro-5,6-di-*O*-benzyl- α -D-gulofuranoside (49).** The glycosylation was carried out following the general protocol, and **49** was isolated by chromatography (4:1, hexanes:EtOAc) as a colorless oil. R_f 0.42 (4:1, hexanes: EtOAc); $[\alpha]_D +28.9$ (c 0.4, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.40–7.27 (m, 10 H, Ar), 5.08 (d, 1 H, J = 0.5 Hz, H-1), 4.79 (d, 1 H, J = 12.0 Hz, PhCH₂), 4.74 (d, 1 H, J = 12.0 Hz, PhCH₂), 4.60 (d, 1 H, J = 12.0 Hz, PhCH₂), 4.55 (d, 1 H, J = 12.0 Hz, PhCH₂), 4.10 (dd, 1 H, J = 7.1, 0.8 Hz, H-4), 3.91 (ddd, 1 H, J = 7.1,

4.9, 3.6 Hz, H-5), 3.82–3.74 (m, 3 H, H-6 $\times$ 2, octyl OCH₂), 3.67 (dd, 1 H, J = 3.0, 0.8 Hz, H-3), 3.65 (dd, 1 H, J = 3.0, 0.5 Hz, H-2), 3.58 (ddd, 1 H, J = 9.6, 7.0, 7.0 Hz, octyl OCH₂), 1.68–1.60 (m, 2 H, octyl CH₂), 1.40–1.24 (m, 10 H, octyl CH₂), 0.90–0.87 (dd, 3 H, J = 7.0, 7.0 Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 138.7 (Ar), 138.2 (Ar), 128.4 (Ar $\times$ 2), 128.3 (Ar $\times$ 2), 127.9 (Ar $\times$ 2), 127.7 (Ar $\times$ 2), 127.6 (Ar), 127.5 (Ar), 101.5 (C-1), 78.5 (C-5), 78.0 (C-4), 73.5 (PhCH₂), 73.2 (PhCH₂), 70.5 (C-6), 69.5 (octyl OCH₂), 55.5 (C-2), 54.8 (C-3), 31.8 (octyl CH₂), 29.8 (octyl CH₂), 29.4 (octyl CH₂), 29.3 (octyl CH₂), 26.0 (octyl CH₂), 22.7 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₂₈H₃₈O₅Na: 477.2612, found: 477.2613

Cyclohexyl 2,3-anhydro-5,6-di-*O*-benzyl- α -D-gulofuranoside (50). The glycosylation was carried out following the general protocol, and **50** was purified by chromatography (4:1, hexanes:EtOAc) as a colorless oil. R_f 0.34 (4:1, hexanes: EtOAc); $[\alpha]_D$ -24.8 (c 0.5, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.40–7.26 (m, 10 H, Ar), 5.19 (s, 1 H, H-1), 4.78 (d, 1 H, J = 12.0 Hz, PhCH₂), 4.74 (d, 1 H, J = 12.0 Hz, PhCH₂), 4.60 (d, 1 H, J = 12.0 Hz, PhCH₂), 4.55 (d, 1 H, J = 12.0 Hz, PhCH₂), 4.08 (dd, 1 H, J = 7.1, 0.8 Hz, H-4), 3.91 (ddd, 1 H, J = 7.1, 4.9, 3.4 Hz, H-5), 3.80 (dd, 1 H, J = 10.8, 3.4 Hz, H-6), 3.77 (dd, 1 H, J = 10.8, 4.9 Hz, H-6), 3.65 (dd, 1 H, J = 2.9, 0.8 Hz, H-3), 3.64–3.60 (m, 1 H, cyclohexyl OCH), 3.63 (d, 1 H, J = 2.9 Hz, H-2), 2.02–1.92 (m, 2 H, cyclohexyl CH₂), 1.80–1.74 (m, 2 H, cyclohexyl CH₂), 1.60–1.54 (m, 1 H, cyclohexyl CH₂), 1.48–1.32 (m, 2 H, cyclohexyl CH₂), 1.30–1.15 (m, 3 H, cyclohexyl CH₂); ¹³C NMR (125 MHz, CDCl₃, δ_C) 138.8 (Ar), 138.3 (Ar), 128.4 (Ar $\times$ 2), 128.3 (Ar $\times$ 2), 127.9 (Ar $\times$ 2), 127.7 (Ar $\times$ 2), 127.6 (Ar), 127.5 (Ar), 100.4 (C-1), 78.6 (C-5), 78.1 (C-4), 78.0 (cyclohexyl OCH), 73.4 (PhCH₂), 73.2 (PhCH₂), 70.6 (C-6),

56.0 (C-2), 54.6 (C-3), 33.6 (cyclohexyl CH₂), 32.5 (cyclohexyl CH₂), 25.6 (cyclohexyl CH₂), 24.3 (cyclohexyl CH₂ × 2). HRMS (ESI) calcd. for (M + Na) C₂₆H₃₂O₅Na: 447.2141, found: 447.2142.

***tert*-Butyl 2,3-anhydro-5,6-di-*O*-benzyl- α -D-gulofuranoside (51).** The glycosylation was carried out following the general protocol, and **51** was isolated by chromatography (4:1, hexanes:EtOAc) as a colorless oil. *R_f* 0.22 (4:1, hexanes: EtOAc); [α]_D -21.0 (*c* 0.5, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ _H) 7.40–7.25 (m, 10 H, Ar), 5.25 (s, 1 H, H-1), 4.79 (d, 1 H, *J* = 11.9 Hz, PhCH₂), 4.73 (d, 1 H, *J* = 11.9 Hz, PhCH₂), 4.60 (d, 1 H, *J* = 12.0 Hz, PhCH₂), 4.56 (d, 1 H, *J* = 12.0 Hz, PhCH₂), 4.06 (dd, 1 H, *J* = 7.2, 0.8 Hz, H-4), 3.92 (ddd, 1 H, *J* = 7.2, 5.0, 3.5 Hz, H-5), 3.81 (dd, 1 H, *J* = 10.9, 3.5 Hz, H-6), 3.77 (dd, 1 H, *J* = 10.9, 5.0 Hz, H-6), 3.63 (dd, 1 H, *J* = 3.0, 0.8 Hz, H-3), 3.57 (d, 1 H, *J* = 3.0 Hz, H-2), 1.32 (s, 9 H, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃, δ _C) 138.9 (Ar), 138.3 (Ar), 128.3 (Ar × 2), 128.2 (Ar × 2), 127.8 (Ar × 2), 127.6 (Ar × 2), 127.55 (Ar), 127.4 (Ar), 96.3 (C-1), 78.8 (C-5), 78.2 (C-4), 75.6 (C(CH₃)₃), 73.4 (PhCH₂), 73.2 (PhCH₂), 70.8 (C-6), 56.7 (C-2), 54.2 (C-3), 28.7 (C(CH₃)₃ × 3). HRMS (ESI) calcd. for (M + Na) C₂₄H₃₀O₅Na: 421.1986, found: 421.1989.

***n*-Octyl 2,3-anhydro-5,6-di-*O*-benzyl- α -D-gulofuranosyl-(1→5)-2,3-anhydro- α -D-lyxofuranoside (52).** The glycosylation was carried out following the general protocol, and **52** was isolated by chromatography (3:1, hexanes:EtOAc) as a colorless oil. *R_f* 0.27 (3:1, hexanes:EtOAc); [α]_D +27.6 (*c* 0.9, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ _H) 7.40–7.25 (m, 10 H, Ar), 5.17 (s, 1 H, H-1'), 5.04 (s, 1 H, H-1), 4.77 (d, 1 H, *J* = 12.0 Hz, PhCH₂), 4.73 (d, 1 H, *J* = 12.0 Hz, PhCH₂), 4.60 (d, 1 H, *J* = 12.0 Hz, PhCH₂), 4.55 (d, 1 H, *J* = 12.0 Hz, PhCH₂), 4.23

(dd, 1 H, $J = 7.8, 5.4$ Hz, H-4), 4.12 (d, 1 H, $J = 7.0$ Hz, H-4'), 3.94 (dd, 1 H, $J = 9.9, 5.4$ Hz, H-5), 3.89 (ddd, 1 H, $J = 7.0, 4.8, 3.7$ Hz, H-5'), 3.82-3.72 (m, 5 H, H-5, H-3', H-6' $\times 2$, octyl OCH₂), 3.68 (s, 2 H, H-2, H-3), 3.66 (d, 1 H, $J = 2.8$ Hz, H-2'), 3.45 (ddd, 1 H, $J = 9.5, 6.6, 6.6$ Hz, octyl OCH₂), 1.62–1.54 (m, 2 H, octyl CH₂), 1.35–1.24 (m, 10 H, octyl CH₂), 0.90–0.86 (dd, 3 H, $J = 6.9, 6.9$ Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 138.6 (Ar), 138.1 (Ar), 128.4 (Ar $\times 2$), 128.3 (Ar $\times 2$), 127.9 (Ar $\times 2$), 127.7 (Ar $\times 2$), 127.6 (Ar), 127.5 (Ar), 101.5 (C-1'), 101.2 (C-1), 78.3 (C-5'), 78.1 (C-4), 74.6 (C-4'), 73.5 (PhCH₂), 73.1 (PhCH₂), 70.4 (C-6'), 68.6 (octyl OCH₂), 66.8 (C-5), 56.6 (C-2'), 55.3 (C-2), 54.8 (C-3), 54.4 (C-3'), 31.8 (octyl CH₂), 29.6 (octyl CH₂), 29.4 (octyl CH₂), 29.2 (octyl CH₂), 26.0 (octyl CH₂), 22.6 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₃₃H₄₄O₈Na: 591.2928, found: 591.2926.

Methyl 2,3-anhydro-5,6-*O*-benzyl- α -D-gulofuranosyl-(1 $\rightarrow$ 2)-3,5-di-*O*-benzyl- α -D-arabinofuranoside (53). The glycosylation was carried out following the general protocol, and **53** was purified by chromatography (3:1, hexanes:EtOAc) as a colorless oil. R_f 0.21 (3:1, hexanes:EtOAc); $[\alpha]_D +53.7$ (c 0.4, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.36–7.25 (m, 20 H, Ar), 5.06 (s, 1 H, H-1), 4.98 (s, 1 H, H-1'), 4.75 (d, 1 H, $J = 11.7$ Hz, PhCH₂), 4.69 (d, 1 H, $J = 11.7$ Hz, PhCH₂), 4.64–4.53 (m, 6 H, PhCH₂), 4.24 (d, 1 H, $J = 2.8$ Hz, H-2), 4.20 (ddd, 1 H, $J = 6.8, 5.4, 4.0$ Hz, H-4), 4.01 (dd, 1 H, $J = 7.0, 0.6$ Hz, H-4'), 3.94 (dd, 1 H, $J = 6.8, 2.8$ Hz, H-3), 3.89 (ddd, 1 H, $J = 7.0, 4.7, 3.7$ Hz, H-5'), 3.80–3.74 (m, 2 H, H-6' $\times 2$), 3.68–3.61 (m, 3 H, H-5 $\times 2$, H-3'), 3.52 (d, 1 H, $J = 3.0$ Hz, H-2'), 3.36 (s, 3 H, OCH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 138.6 (Ar), 138.2 (Ar), 138.1 (Ar), 138.0 (Ar), 128.5 (Ar $\times 2$), 128.4 (Ar $\times 2$), 128.33 (Ar $\times 2$), 128.3 (Ar $\times 2$), 127.9 (Ar $\times 2$), 127.8 (Ar $\times 2$), 127.7 (Ar $\times 3$), 127.69 (Ar $\times 2$), 127.65 (Ar),

127.6 (Ar), 127.55 (Ar), 107.8 (C-1), 101.4 (C-1'), 88.1 (C-2), 83.9 (C-3), 80.4 (C-4), 78.7 (C-5'), 78.3 (C-4'), 73.5 (PhCH₂), 73.4 (PhCH₂), 73.3 (PhCH₂), 72.4 (PhCH₂), 70.5 (C-6'), 69.8 (C-5), 55.3 (C-2'), 55.1 (OCH₃), 54.7 (C-3'). HRMS (ESI) calcd. for (M + Na) C₄₀H₄₄O₉Na: 691.2878, found: 691.2878.

***n*-Octyl 2,3-anhydro-5,6-di-*O*-benzoyl- α -D-gulofuranoside (54).** The glycosylation was carried out following the general protocol, and **54** was isolated by chromatography (4:1, hexanes:EtOAc) as a white foam. *R_f* 0.26 (4:1, hexanes: EtOAc); [α]_D +44.1 (*c* 0.3, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ _H) 8.10–8.07 (m, 2 H, Ar), 8.03 (m, 2 H, Ar), 7.59–7.50 (m, 2 H, Ar), 7.46–7.39 (m, 4 H, Ar), 5.77 (dd, 1 H, *J* = 10.1, 5.5 Hz, H-5), 5.13 (d, 1 H, *J* = 0.5 Hz, H-1), 4.82–4.78 (m, 2 H, H-6 $\times$ 2), 4.24 (dd, 1 H, *J* = 5.5, 0.8 Hz, H-4), 3.82 (dd, 1 H, *J* = 3.0, 0.8 Hz, H-3), 3.77 (ddd, 1H, *J* = 9.6, 6.6, 6.6 Hz, octyl OCH₂), 3.71 (dd, 1 H, *J* = 3.0, 0.5 Hz, H-2), 3.62 (ddd, 1 H, *J* = 9.6, 6.9, 6.9 Hz, octyl OCH₂), 1.65–1.59 (m, 2 H, octyl CH₂), 1.38–1.22 (m, 10 H, octyl CH₂), 0.87 (dd, 3 H, *J* = 7.0, 7.0 Hz, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ _C) 166.1 (C=O), 165.8 (C=O), 133.2 (Ar), 133.1 (Ar), 129.9 (Ar $\times$ 2), 129.84 (Ar), 129.8 (Ar), 129.7 (Ar $\times$ 2), 128.4 (Ar $\times$ 4), 101.2 (C-1), 74.8 (C-4), 71.6 (C-5), 69.3 (octyl OCH₂), 63.4 (C-6), 55.4 (C-2), 54.1 (C-3), 31.8 (octyl CH₂), 29.8 (octyl CH₂), 29.4 (octyl CH₂), 29.2 (octyl CH₂), 26.0 (octyl CH₂), 22.6 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₂₈H₃₄O₇Na: 505.2197, found: 505.2197.

Cyclohexyl 2,3-anhydro-5,6-di-*O*-benzoyl- α -D-gulofuranoside (55). The glycosylation was carried out following the general protocol, and **55** was isolated by chromatography (4:1, hexanes:EtOAc) as a white foam. *R_f* 0.19 (4:1, hexanes: EtOAc); [α]_D

+67.9 (*c* 0.7, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 8.10–8.07 (m, 2 H, Ar), 8.03–8.00 (m, 2 H, Ar), 7.58–7.51 (m, 2 H, Ar), 7.46–7.39 (m, 4 H, Ar), 5.78 (ddd, 1 H, *J* = 5.4, 5.0, 5.0 Hz, H-5), 5.22 (d, 1 H, *J* = 0.5 Hz, H-1), 4.80 (d, 2 H, *J* = 5.0 Hz, H-6 × 2), 4.22 (dd, 1 H, *J* = 5.4, 0.9 Hz, H-4), 3.80 (dd, 1 H, *J* = 2.9, 0.9 Hz, H-3), 3.70 (dd, 1 H, *J* = 2.9, 0.5 Hz, H-2), 3.69–3.60 (m, 1 H, cyclohexyl OCH), 1.99–1.87 (m, 2 H, cyclohexyl CH₂), 1.78–1.70 (m, 2 H, cyclohexyl CH₂), 1.57–1.48 (m, 1 H, cyclohexyl CH₂), 1.45–1.15 (m, 5 H, cyclohexyl CH₂); ¹³C NMR (125 MHz, CDCl₃, δ_C) 166.1 (C=O), 165.8 (C=O), 133.2 (Ar), 133.1 (Ar), 129.9 (Ar × 2), 129.8 (Ar × 2), 129.7 (Ar × 2), 129.4 (Ar × 2), 128.4 (Ar × 2), 100.2 (C-1), 77.6 (cyclohexyl OCH), 74.8 (C-4), 71.7 (C-5), 63.5 (C-6), 56.0 (C-2), 54.2 (C-3), 33.5 (cyclohexyl CH₂), 32.6 (cyclohexyl CH₂), 25.5 (cyclohexyl CH₂), 24.2 (cyclohexyl CH₂), 24.1 (cyclohexyl CH₂). HRMS (ESI) calcd. for (M + Na) C₂₆H₂₈O₇Na: 475.1727, found: 475.1730.

***tert*-Butyl 2,3-anhydro-5,6-di-*O*-benzoyl- α -D-gulofuranoside (56).** The glycosylation was carried out following the general protocol, and **56** was isolated by chromatography (4:1, hexanes:EtOAc) as a white foam. *R_f* 0.17 (4:1, hexanes: EtOAc); [α]_D +82.5 (*c* 0.4, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 8.10–8.07 (m, 2 H, Ar), 8.03–8.00 (m, 2 H, Ar), 7.58–7.51 (m, 2 H, Ar), 7.46–7.38 (m, 4 H, Ar), 5.77 (ddd, 1 H, *J* = 5.9, 5.6, 4.5 Hz, H-5), 5.29 (d, 1 H, *J* = 0.6 Hz, H-1), 4.84–4.80 (m, 2 H, H-6 × 2), 4.21 (dd, 1 H, *J* = 5.6, 0.9 Hz, H-4), 3.79 (dd, 1 H, *J* = 2.9, 0.9 Hz, H-3), 3.65 (dd, 1 H, *J* = 2.9, 0.6 Hz, H-2), 1.27 (s, 9 H, C(CH₃)₃ × 3); ¹³C NMR (125 MHz, CDCl₃, δ_C) 166.1 (C=O), 165.8 (C=O), 133.1 (Ar), 133.0 (Ar), 129.93 (Ar), 129.9 (Ar), 129.8 (Ar × 2), 129.7 (Ar × 2), 128.4 (Ar × 2), 128.35 (Ar × 2), 96.4 (C-1), 75.8 (C(CH₃)₃), 75.0

(C-4), 71.9 (C-5), 63.5 (C-6), 56.9 (C-2), 53.7 (C-3), 28.6 (C(CH₃)₃ × 3). HRMS (ESI) calcd. for (M + Na) C₂₄H₂₆O₇Na: 449.1571, found: 449.1573.

***n*-Octyl 2,3-anhydro-5,6-di-*O*-benzoyl- α -D-gulofuranosyl-(1→5)-2,3-anhydro- α -D-lyxofuranoside (57).** The glycosylation was carried out following the general protocol, and **57** was isolated by chromatography (2:1, hexanes:EtOAc) as a white foam. *R_f* 0.18 (2:1, hexanes:EtOAc); [α]_D +42.6 (*c* 0.6, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ _H) 8.10–8.07 (m, 2 H, Ar), 8.03–8.00 (m, 2 H, Ar), 7.58–7.52 (m, 2 H, Ar), 7.46–7.39 (m, 4 H, Ar), 5.78 (ddd, 1 H, *J* = 5.5, 5.1, 5.1 Hz, H-5'), 5.23 (d, 1 H, *J* = 0.5 Hz, H-1'), 5.03 (s, 1 H, H-1), 4.78 (d, 2 H, *J* = 5.1 Hz, H-6' × 2), 4.27 (dd, 1 H, *J* = 5.5, 0.9 Hz, H-4'), 4.22 (dd, 1 H, *J* = 6.9, 6.0 Hz, H-4), 3.94–3.87 (m, 2 H, H-5 × 2), 3.84 (dd, 1 H, *J* = 2.9, 0.9 Hz, H-3'), 3.82 (dd, 1 H, *J* = 2.9, 0.5 Hz, H-2'), 3.75 (d, 1 H, *J* = 2.8 Hz, H-3), 3.72 (ddd, 1 H, *J* = 9.5, 6.7, 6.7 Hz, octyl OCH₂), 3.64 (d, 1 H, *J* = 2.8 Hz, H-2), 3.43 (ddd, 1 H, *J* = 9.5, 6.8, 6.8, octyl OCH₂), 1.58–1.52 (m, 2 H, octyl CH₂), 1.35–1.23 (m, 10 H, octyl CH₂), 0.88–0.86 (m, 3 H, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ _C) 166.1 (C=O), 165.8 (C=O), 133.2 (Ar), 133.1 (Ar), 129.9 (Ar × 2), 129.8 (Ar × 2), 129.7 (Ar × 2), 128.4 (Ar × 4), 101.3 (C-1'), 101.2 (C-1), 75.0 (C-4'), 74.8 (C-4), 71.5 (C-5'), 68.5 (octyl OCH₂), 66.7 (C-5), 63.3 (C-6'), 56.5 (C-2), 55.3 (C-3), 54.4 (C-2'), 54.2 (C-3'), 31.8 (octyl CH₂), 29.6 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 26.0 (octyl CH₂), 22.6 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₃₃H₄₀O₁₀Na: 619.2514, found: 619.2518.

Methyl 2,3-anhydro-5,6-*O*-benzoyl- α -D-gulofuranosyl-(1→2)-3,5-di-*O*-benzyl- α -D-arabinofuranoside (58). The glycosylation was carried out following the general protocol, and

58 was isolated by chromatography (2:1, hexanes:EtOAc) as a colorless syrup. R_f 0.26 (2:1, hexanes:EtOAc); $[\alpha]_D +59.3$ (c 0.6, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 8.09–8.06 (m, 2 H, Ar), 8.04–8.00 (m, 2 H, Ar), 7.58–7.53 (m, 2 H, Ar), 7.45–7.40 (m, 4 H, Ar), 7.35–7.24 (m, 10 H, Ar), 5.78 (ddd, 1 H, $J = 5.7, 5.0, 5.0$ Hz, H-5'), 5.03 (s, 1 H, H-1), 5.00 (s, 1 H, H-1'), 4.76 (d, 2 H, $J = 5.0$ Hz, H-6' $\times$ 2), 4.64–4.56 (m, 4 H, PhCH_2), 4.27 (d, 1 H, $J = 5.7$ Hz, H-4'), 4.22 (d, 1 H, $J = 3.0$ Hz, H-2), 4.20–4.16 (m, 1 H, H-4), 3.93 (dd, 1 H, $J = 6.9, 3.0$ Hz, H-3), 3.82 (d, 1 H, $J = 2.9$ Hz, H-3'), 3.67 (dd, 1 H, $J = 10.8, 3.7$ Hz, H-5), 3.64 (dd, 1 H, $J = 10.8, 5.4$ Hz, H-5), 3.61 (d, 1 H, $J = 2.9$ Hz, H-2'), 3.28 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, CDCl_3 , δ_{C}) 166.0 (C=O), 165.7 (C=O), 138.2 (Ar), 138.1 (Ar), 133.22 (Ar), 133.2 (Ar), 129.9 (Ar $\times$ 2), 129.8 (Ar $\times$ 2), 129.7 (Ar), 129.66 (Ar), 128.44 (Ar $\times$ 2), 128.4 (Ar $\times$ 2), 128.34 (Ar $\times$ 2), 128.3 (Ar $\times$ 2), 127.9 (Ar $\times$ 2), 127.8 (Ar $\times$ 2), 127.7 (Ar), 127.6 (Ar), 107.8 (C-1), 101.4 (C-1'), 88.2 (C-2), 84.2 (C-3), 80.1 (C-4), 75.4 (C-4'), 73.4 (PhCH_2), 72.5 (PhCH_2), 71.5 (C-5'), 69.8 (C-5), 63.3 (C-6'), 55.5 (C-2'), 55.0 (OCH_3), 54.3 (C-3'). HRMS (ESI) calcd. for (M + Na) $\text{C}_{40}\text{H}_{40}\text{O}_{11}\text{Na}$: 719.2463, found: 719.2461.

***n*-Octyl 3-*O*-benzyl-5,6-*O*-isopropylidene- α -D-galactofuranoside (64)** and ***n*-Octyl 2-*O*-benzyl-5,6-*O*-isopropylidene- α -D-idofuranoside (65)**. Compound **34** was subjected to the general epoxide opening procedure, yielding separable **64** and **65** as colorless oils. **64**: R_f 0.46 (4:1, hexanes:EtOAc); $[\alpha]_D +36.5$ (c 0.2, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 7.40–7.27 (m, 5 H, Ar), 4.98 (d, 1 H, $J = 4.8$ Hz, H-1), 4.87 (d, 1 H, $J = 11.7$ Hz, PhCH_2), 4.62 (d, 1 H, $J = 11.7$ Hz, PhCH_2), 4.27 (ddd, 1 H, $J = 9.8, 6.2, 4.8$ Hz, H-2), 4.11 (dd, 1 H, $J = 7.3, 7.3$ Hz, H-4), 3.91–3.84 (m, 3 H, H-5, H-6, octyl OCH_2), 3.80–3.74 (m, 2 H, H-3, H-6), 3.48

(ddd, 1 H, $J = 9.6, 6.7, 6.7$ Hz, octyl OCH₂), 2.67 (d, 1 H, $J = 9.8$ Hz, OH), 1.64–1.54 (m, 2 H, octyl CH₂), 1.43 (s, 3 H, isopropylidene CH₃), 1.37 (s, 3 H, isopropylidene CH₃), 1.38–1.24 (m, 10 H, octyl CH₂), 0.92–0.87 (m, 3 H, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 137.6 (Ar), 128.4 (Ar × 2), 128.0 (Ar), 127.9 (Ar × 2), 109.7 (isopropylidene C), 101.6 (C-1), 83.8 (C-3), 81.9 (C-5), 78.2 (C-4), 78.0 (C-2), 71.7 (PhCH₂), 68.8 (octyl OCH₂), 65.2 (C-6), 31.8 (octyl CH₂), 29.5 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 26.6 (isopropylidene CH₃), 26.1 (octyl CH₂), 25.5 (isopropylidene CH₃), 22.6 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₂₄H₃₈O₆Na: 445.2561, found: 445.2559. **65**: R_f 0.38 (4:1, hexanes:EtOAc); [α]_D +35.6 (*c* 0.26, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.40–7.29 (m, 5 H, Ar), 5.09 (s, 1 H, H-1), 4.61 (s, 2 H, PhCH₂), 4.32 (ddd, 1 H, $J = 7.3, 7.2, 7.2$ Hz, H-5), 4.24–4.19 (m, 2 H, H-4, H-6), 4.08 (br s, 1 H, H-3), 3.94 (s, 1 H, H-2), 3.85 (ddd, 1 H, $J = 9.6, 6.8, 6.8$ Hz, octyl OCH₂), 3.73 (dd, 1 H, $J = 8.3, 7.2$ Hz, H-6), 3.42 (ddd, 1 H, $J = 9.6, 6.6, 6.6$ Hz, octyl OCH₂), 2.99 (d, 1 H, $J = 11.3$ Hz, OH), 1.60–1.52 (m, 2 H, octyl CH₂), 1.52 (s, 3 H, isopropylidene CH₃), 1.45 (s, 3 H, isopropylidene CH₃), 1.35–1.24 (m, 10 H, octyl CH₂), 0.92–0.85 (m, 3 H, octyl CH₃); ¹³C NMR (125 MHz, CDCl₃, δ_C) 137.3 (Ar), 128.5 (Ar × 2), 128.0 (Ar), 127.7 (Ar × 2), 109.7 (isopropylidene C), 105.6 (C-1), 86.2 (C-2), 84.9 (C-4), 77.0 (C-5), 74.4 (C-3), 72.0 (PhCH₂), 68.2 (octyl OCH₂), 66.1 (C-6), 31.8 (octyl CH₂), 29.5 (octyl CH₂), 29.3 (octyl CH₂), 29.2 (octyl CH₂), 26.7 (isopropylidene CH₃), 26.1 (octyl CH₂), 25.6 (isopropylidene CH₃), 22.6 (octyl CH₂), 14.1 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₂₄H₃₈O₆Na: 445.2561, found: 445.2562.

***n*-Octyl 3,5,6-tri-*O*-benzyl- α -D-galactofuranoside (66) and *n*-Octyl 2,5,6-tri-*O*-benzyl- α -D-idofuranoside (67).** Compound **49** was subjected to the general

epoxide opening procedure, yielding an inseparable mixture of **66** and **67** as colorless oils: R_f 0.41 (4:1, hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 7.43–7.25 (m, 15 H, Ar), 5.08 (s, 0.74 H, Ido H-1), 4.96 (d, 0.26 H, $J = 4.7$ Hz, Gal H-1), 4.82–4.74 (m, 2 H, PhCH_2), 4.63–4.52 (m, 4 H, PhCH_2), 4.40 (dd, 0.74 H, $J = 7.4, 3.8$ Hz, Ido H-4), 4.24 (br s, 0.26 H, Gal H-2), 4.12 (br s, 0.74 H, Ido H-3), 4.05–3.99 (m, 0.52 H, Gal H-3, Gal H-4), 3.74 (s, 0.74 H, Ido H-2), 3.71 (ddd, 0.74 H, $J = 7.4, 4.6, 4.6$ Hz, Ido H-5), 3.80–3.64 (m, 3.26 H, Gal H-5, Gal H-6 $\times$ 2, Ido H-6 $\times$ 2, octyl OCH_2), 3.45–3.40 (m, 0.26 H, Gal octyl OCH_2), 3.39 (ddd, 0.74 H, $J = 9.5, 6.6, 6.6$ Hz, Ido octyl OCH_2), 3.27 (d, 0.74 H, $J = 9.2$ Hz, Ido OH), 2.71 (d, 0.26 H, $J = 7.0$ Hz, Gal OH), 1.58–1.47 (m, 2 H, octyl CH_2), 1.34–1.25 (m, 10 H, octyl CH_2), 0.92–0.89 (m, 3 H, octyl CH_3); ^{13}C NMR (125 MHz, CDCl_3 , δ_{C}) 138.7 (Ar), 138.3 (Ar), 138.1 (Ar), 138.0 (Ar), 137.5 (Ar), 128.5 (Ar), 128.4 (Ar), 128.35 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.86 (Ar), 127.8 (Ar), 127.7 (Ar), 127.68 (Ar), 127.6 (Ar), 127.57 (Ar), 127.5 (Ar), 127.46 (Ar), 105.6 (Ido C-1), 101.2 (Gal C-1), 86.7 (Ido C-2), 83.9 (Ido C-4), 83.3 (Gal C-3), 81.3 (Gal C-4), 79.0 (Gal C-5), 78.5 (Ido C-5), 77.8 (Gal C-2), 74.1 (Ido C-3), 73.6 (Ido PhCH_2), 73.4 (Gal PhCH_2), 73.2 (Gal PhCH_2), 72.9 (Ido PhCH_2), 71.8 (Ido PhCH_2), 71.75 (Gal PhCH_2), 70.6 (Gal C-6), 70.3 (Ido C-6), 68.5 (Gal octyl OCH_2), 68.1 (Ido octyl OCH_2), 31.3 (octyl CH_2), 29.5 (Gal octyl CH_2), 29.5 (Ido octyl CH_2), 29.4 (Gal octyl CH_2), 29.3 (Ido octyl CH_2), 29.2 (octyl CH_2), 26.1 (octyl CH_2), 22.7 (octyl CH_2), 14.1 (octyl CH_3). HRMS (ESI) calcd. for $(\text{M} + \text{Na}) \text{C}_{35}\text{H}_{46}\text{O}_6\text{Na}$: 585.3187, found: 585.3184.

***n*-Octyl 3-*O*-benzyl- α -D-galactofuranoside (68) and *n*-Octyl 2-*O*-benzyl- α -D-idofuranoside (69).** Compound **54** was subjected to the general epoxide

opening procedure, yielding **68** and **69** as colorless oils. **68**: R_f 0.30 (1:1, hexanes:EtOAc); $[\alpha]_D^{+30.8}$ (c 1.0, CH_2Cl_2); ^1H NMR (500 MHz, CD_3OD , δ_{H}) 7.38–7.25 (m, 5 H, Ar), 4.87 (d, 1 H, J = 4.6 Hz, H-1), 4.82 (d, 1 H, J = 11.6 Hz, PhCH_2), 4.62 (d, 1 H, J = 11.6 Hz, PhCH_2), 4.17 (dd, 1 H, J = 6.8, 4.6 Hz, H-2), 4.09 (dd, 1 H, J = 6.8, 6.2 Hz, H-3), 3.89 (dd, 1 H, J = 6.2, 5.0 Hz, H-4), 3.80 (ddd, 1 H, J = 9.6, 6.9, 6.9 Hz, octyl OCH_2), 3.62–3.54 (m, 2 H, H-5, H-6), 3.51–3.45 (m, 2 H, H-6, octyl OCH_2), 1.65–1.58 (m, 2 H, octyl CH_2), 1.40–1.25 (m, 10 H, octyl CH_2), 0.95–0.85 (m, 3 H, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD , δ_{C}) 139.6 (Ar), 129.3 (Ar $\times$ 2), 129.0 (Ar $\times$ 2), 128.7 (Ar), 103.5 (C-1), 84.1 (C-3), 82.6 (C-4), 79.0 (C-2), 74.5 (C-5), 73.1 (PhCH_2), 70.0 (octyl OCH_2), 64.1 (C-6), 33.0 (octyl CH_2), 30.7 (octyl CH_2), 30.6 (octyl CH_2), 30.4 (octyl CH_2), 27.2 (octyl CH_2), 23.7 (octyl CH_2), 14.4 (octyl CH_3). HRMS (ESI) calcd. for ($\text{M} + \text{Na}$) $\text{C}_{21}\text{H}_{34}\text{O}_6\text{Na}$: 405.2248, found: 405.2246. **69**: R_f 0.13 (1:1, hexanes:EtOAc); $[\alpha]_D^{+19.6}$ (c 1.4, CH_2Cl_2); ^1H NMR (500 MHz, CD_3OD , δ_{H}) 7.35–7.27 (m, 5 H, Ar), 4.97 (d, 1 H, J = 1.5 Hz, H-1), 4.64 (d, 1 H, J = 11.9 Hz, PhCH_2), 4.60 (d, 1 H, J = 11.9 Hz, PhCH_2), 4.24 (dd, 1 H, J = 5.3, 2.4 Hz, H-3), 4.15 (dd, 1 H, J = 5.3, 5.2 Hz, H-4), 3.92–3.90 (m, 1 H, H-2), 3.88 (ddd, 1 H, J = 5.9, 5.4, 5.2 Hz, H-5), 3.77 (ddd, 1 H, J = 9.6, 6.7, 6.7 Hz, octyl OCH_2), 3.65 (dd, 1 H, J = 11.2, 5.4 Hz, H-6), 3.60 (dd, 1 H, J = 11.2, 5.9 Hz, H-6), 3.42 (ddd, 1 H, J = 9.6, 6.6, 6.6 Hz, octyl OCH_2), 1.60–1.52 (m, 2 H, octyl CH_2), 1.38–1.27 (m, 10 H, octyl CH_2), 0.91–0.87 (m, 3 H, octyl CH_3); ^{13}C NMR (125 MHz, CD_3OD , δ_{C}) 139.3 (Ar), 129.4 (Ar $\times$ 2), 129.0 (Ar $\times$ 2), 128.8 (Ar), 108.0 (C-1), 89.8 (C-2), 83.1 (C-4), 75.8 (C-3), 73.0 (PhCH_2), 72.3 (C-5), 69.6 (octyl OCH_2), 64.4 (C-6), 33.0 (octyl CH_2), 30.6 (octyl CH_2), 30.5 (octyl CH_2), 30.4 (octyl CH_2), 27.3 (octyl

CH₂), 23.7 (octyl CH₂), 14.4 (octyl CH₃). HRMS (ESI) calcd. for (M + Na) C₂₁H₃₄O₆Na: 405.2248, found: 405.2248.

References for Supporting Information

1. Callam, C. S.; Gadikota, R. R.; Lowary, T. L. *J. Org. Chem.* **2001**, *66*, 4549–4558.
2. Ferrières, V.; Bertho, J.-N.; Plusquellec, D. *Carbohydr. Res.* **1998**, *311*, 25–35.
3. (a) Patt, S.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535–539; (b) Torres, A. M.; Nakashima, T. T.; McClung, R. E. D. *J. Magn. Reson. Ser. A* **1993**, *101*, 285–289.

compound-13
 100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-14
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

compound-14
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-15
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-15
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-16a
400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

compound-16a
 100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-16b
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

Compound-16b
 100 MHz APY in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Compound-17a
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: s2pul

compound-17a
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-17b
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

compound-17b
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-18a
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: szpul

compound-18a
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-18b
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: s2pul

compound-18b
 125 MHz AP7 in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apc

compound-21
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: szpul

compound-21
 100 MHz AP7 in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apc

compound-22
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

compound-22
 125 MHz APT in CDCl₃ (ref. to CHCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-23
 100 MHz APT 1m CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

Compound-26
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: zgpg30

compound-26
 125 MHzAPT in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

compound-33
600 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: zgpg30

33

compound-33
 125 MHz Apt in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

compound-34
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

compound-34
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-35
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

Compound-35
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

compound-36
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

compound-36
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-37
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

Compound-37
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

compound-46
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: szpul

compound-46
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-47
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

compound-47
 100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

Compound-48
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-48
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-49
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

compound-49
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-50
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-50
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-51
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

Compound-51

125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-52
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-52
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-53
500 MHz 1D 1H CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-53
 125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apf

compound-54
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-54
 125 MHz NPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: spt

compound-55
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-55

125 MHz APF in CDCl₃ (ref. to CHCl₃ @ 77.0 ppm)
C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apc

compound-56
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-56

125 MHz APt in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apc

Pulse Sequence: apt

compound-58
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

Compound-58
 125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apc

compound-59
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-59
 125 MHz AP7 in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

compound-60
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: szpul

compound-60
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-61
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-61
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-64
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-64
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

Compound-65
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-65
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-66, 67
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-66,67
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-68
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: zgpg30

compound-68
 125 MHzAPT in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

compound-69
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: szpul

compound-69
 125 MHz APF in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

compound-72
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: zgpg30

compound-72
 125 MHzAPT in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

compound-73
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: zgpg30

compound-73
 125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

compound-74
600 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: zgpg30

compound-74
 125 MHz APY in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

compound-76
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-76
 125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apf

Compound-77
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-77
 125 MHzAPT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

compound-78
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-78
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse sequence: apt

Pulse Sequence: s2pul

compound-79
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-80
600 MHz 1D in CD₂Cl₂ (ref. to CD₂Cl₂ @ 5.32 ppm)

Pulse Sequence: zgpg30

Pulse Sequence: apt

compound-81
600 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: szpul

compound-81
 125 MHzAPT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apt

compound-82
 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apc

compound-83
600 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: zgpg30

compound-83
 125 MHzAPT in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

83

compound-S2
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

Compound-S2
 125 MHzAPT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

compound-S3
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: szpul

compound-S3
 125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

compound-S4
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

compound-S5
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-S5
 125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apf

Compound-S6
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: szpul

Compound-S6
 125 MHzAPT in CD3OD (ref. to CD3OD @ 49.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Compound-S7
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm)

Pulse Sequence: zgpg30

compound-S7
 125 MHzAPT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
 C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

Compound-S8
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)

Pulse Sequence: zgpg30

compound-S8
 125 MHzAPT in CD₃OD (ref. to CD₃OD @ 49.0 ppm)
 C & CH₂ same, CH & CH₃ opposite side of solvent signal