Supporting Information

For

**Stereoselective Iterative One Pot Synthesis of N-GlycolylNeuraminic Acid-Containing Oligosaccharides**

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General Experimental. All reactions were performed using oven dried flasks under a nitrogen atmosphere. Commercial available reagents were used directly without purification. All organic solvents were dried by standard procedures. For all coupled
products the chemical shift of C1 (for the α isomer) and its $^{3}J_{C-1, H-3ax}$ coupling constant were determined based on the comparison of gated decoupled spectrum with single frequency off resonance decoupling (SFORD) experiments.

Methyl (1-Adamantanyl 7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-2-thio-β-glycero-β-D-galacto-non-2-ulopyranoside)onate (3). Compound 3 was prepared according to the literature procedure.\textsuperscript{1} $\left[\alpha\right]_{D}^{23}$ -87.2 (c, 2.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ: 5.48 (s, 1H), 5.19-5.23 (m, 2H), 4.66 (dd, $J = 2.4$, 13.2 Hz, 1H), 4.61 (dt, $J = 3.2$, 10.0 Hz, 1H), 4.33 (dd, $J = 6.4$, 12.4 Hz, 1H), 3.81(s, 3H), 3.10 (t, $J = 10.4$ Hz, 1H), 2.75 (dd, $J = 3.2$, 12.8 Hz, 1H), 2.15 (s, 3H), 2.13-2.16 (m, 1H), 2.08 (s, 3H), 2.01 (s, 3H), 1.94-1.98 (m, 4H), 1.79-1.82 (m, 4H),1.60-1.67 (m, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 171.1, 170.6, 170.5, 169.8, 159.5, 86.8, 77.5, 77.0, 72.5, 71.4, 71.3, 62.5, 59.3, 53.2, 51.3, 43.7, 39.6, 36.1, 30.0, 21.3, 20.94, 20.87. ESIHRMS Calcd for C$_{27}$H$_{37}$NO$_{11}$SNa [M+Na]$^+$: 606.1985. found 606.1992.

Methyl (1-Adamantanyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl
-3,5-dideoxy-2-thio-\(\beta\)-glycero-\(\beta\)-galacto-non-2-ulopyranoside)onate (4). To a stirred solution of 3 (0.18 g, 0.3 mmol) in dry DMF (9 mL) was added sodium hydride (37 mg, 60% in mineral oil, 0.9 mmol) portionwise at 0 °C, after which the reaction mixture was stirred for 30 min at 0 °C before acetoxyacetyl chloride (66 μL, 0.6 mmol) was added. After 2 h of stirring at 0 °C, the reaction mixture was quenched with aqueous ammonium chloride solution, then diluted with ethyl acetate (30 mL), and washed with water. The aqueous layer was extracted with ethyl acetate (30 mL), and the combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 2:1) to give desired product 4 (0.16 g, 77%). \([\alpha]_{D}^{24}\) -64.6 (c, 1.0, CHCl₃); \(^1\)H NMR (500 MHz, CDCl₃) δ: 5.66 (t, \(J = 3.0\) Hz, 1H), 5.41-5.43 (m, 1H), 5.15 (d, \(J = 17.0\) Hz, 1H), 5.01 (d, \(J = 17.0\) Hz, 1H), 4.75-4.81 (m, 2H), 4.66 (dd, \(J = 2.0, 12.0\) Hz, 1H), 4.17 (dd, \(J = 7.5, 12.5\) Hz, 1H), 3.83 (s, 3H), 3.74 (dd, \(J = 9.5, 11.0\) Hz, 1H), 2.79 (dd, \(J = 4.0, 13.0\) Hz, 1H), 2.18 (s, \(J = 13.0\) Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.98-2.01 (m, 4H), 1.87-1.89 (m, 4H), 1.64-1.69 (m, 7H); \(^1^3\)C NMR (125 MHz, CDCl₃) δ: 170.9, 170.8, 170.6, 169.8, 169.4, 153.7, 85.8, 76.6, 74.1, 73.1, 71.7, 63.8, 63.5, 60.8, 53.2, 51.6, 43.7, 38.9, 36.1, 30.1, 21.4, 20.9, 20.7. ESIHRMS calcd for C₃₁H₄₁NΟ₄SNa [M+Na]^+: 706.2145. found 706.2144.

General Procedure for Coupling Reactions with Donor 4. A solution of donor 4 (60 mg, 0.088 mmol), acceptor (0.13 mmol), and activated powdered 4Å molecular sieves (200 mg) in anhydrous CH₂Cl₂/CH₃CN (3 mL, v/v, 2:1) was cooled to -78 °C.
NIS (47 mg, 0.21 mmol) was added, followed by TfOH (8.0 μL, 0.09 mmol). The reaction mixture was stirred at -78 °C for 2 h and then poured into aq NaHCO₃ solution, diluted with CH₂Cl₂, and filtered through Celite. The organic layer was separated, washed with 20% aqueous Na₂S₂O₃ solution, brine, dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate to give corresponding coupling products.

Methyl (1-adamantanyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranoside)onate (5a). Eluant for chromatographic purification on silica gel: hexane/ethyl acetate (v/v, 2:1). [α]$_{24}^{D}$ -3.4 (c, 1.0, CHCl₃); $^1$H NMR (500 MHz, CDCl₃) δ: 5.76 (d, $J = 9.0$ Hz, 1H), 5.37-5.40 (m, 1H), 5.11 (d, $J = 17.0$ Hz, 1H), 5.04 (d, $J = 17.0$ Hz, 1H), 4.82 (d, $J = 9.5$ Hz, 1H), 4.35 (dd, $J = 2.0$, 12.5 Hz, 1H), 4.15 (dd, $J = 5.0$, 12.5 Hz, 1H), 3.96-4.02 (m, 1H), 3.76 (s, 3H), 3.63 (t, $J = 10.5$ Hz, 1H), 2.81 (dd, $J = 3.0$, 12.0 Hz, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 2.10 (s, 6H), 2.07 (t, $J = 12.0$ Hz, 1H), 2.03 (s, 3H), 1.84 (s, 6H), 1.59 (s, 6H); $^{13}$C NMR (125 MHz, CDCl₃) δ: 171.5 (C1, $^3$J$_{C-1,H-3ax} = 5.2$ Hz), 170.9, 170.6, 170.3, 170.2, 168.3, 153.8, 98.4, 79.6, 76.5, 74.8, 71.4, 69.4, 63.8, 62.9, 60.1, 52.9, 43.3, 39.6, 36.2, 31.3, 21.3, 21.1, 20.9, 20.7. ESIHRMS calcd for C$_{31}$H$_{41}$NO$_{15}$Na [M+Na]$^+$: 690.2374. found 690.2394.
Methyl 5-acetoxyacetamido-7,8,9-tri-\(O\)-acetyl-5-\(N\),4-\(O\)-carbonyl-3,5-dideoxy-\(d\)-glycerol-\(\alpha\)-\(d\)-galacto-non-2-ulopyranosylate-(2→6)-1,2;3,4-di-\(O\)-isopropylidene-\(\alpha\)-\(d\)-galactopyranoside (5b). Eluant for chromatographic purification on silica gel: hexane/ethyl acetate (v/v, 3:2). [\(\alpha\)]24\textsubscript{D} -32.8 (c, 2.0, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 5.63 (d, \(J = 7.2\) Hz, 1H), 5.49 (d, \(J = 4.8\) Hz, 1H), 5.42-5.46 (m, 1H), 5.04 (s, 2H), 4.61 (d, \(J = 9.2\) Hz, 1H), 4.57 (dd, \(J = 2.4, 8.0\) Hz, 1H), 4.28-4.31 (m, 2H), 4.07-4.21 (m, 3H), 3.84-3.89 (m, 3H), 3.79 (s, 3H), 3.71 (t, \(J = 10.4\) Hz, 1H), 3.56-3.61 (m, 1H), 2.88 (dd, \(J = 3.2, 12.0\) Hz, 1H), 2.14 (s, 3H), 2.09-2.11 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.52 (s, 3H), 1.40 (s, 3H), 1.31 (br s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 170.8, 170.7, 170.2, 170.1, 168.5 (C1, \(^3\)J\(_{C-1, H-3ax}\) = 5.2 Hz), 168.3, 153.7, 109.5, 108.8, 99.3, 96.5, 76.6, 75.1, 71.9, 71.0, 70.84, 70.78, 69.3, 66.8, 64.2, 63.8, 62.8, 59.6, 53.2, 36.5, 26.3, 26.2, 25.1, 24.9, 21.2, 21.0, 20.9, 20.6. ESIHRMS calcd for C\(_{33}\)H\(_{45}\)NO\(_{20}\)Na [M+Na\(^+\)]: 798.2433. found 798.2437.

Methyl 5-acetoxyacetamido-7,8,9-tri-\(O\)-acetyl-5-\(N\),4-\(O\)-carbonyl-3,5-dideoxy-\(d\)-glycerol-\(\alpha\)-\(d\)-galacto-non-2-ulopyranosylate-(2→6)-methyl 2,3,4-tri-\(O\)-benzyl-\(\beta\)-\(d\)-galactopyranoside (5c). Eluant for chromatographic purification on silica gel: hexane/ethyl acetate (v/v, 2:1). [\(\alpha\)]22\textsubscript{D} -1.4 (c, 2.0, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\))
δ: 7.23-7.36 (m, 15H), 5.61 (d, J = 7.6 Hz, 1H), 5.38-5.43 (m, 1H), 5.06 (s, 2H), 4.98 (d, J = 11.2 Hz, 1H), 4.89 (d, 10.4 Hz, 1H), 4.70-4.79 (m, 3H), 4.67 (d, J = 11.2 Hz, 1H), 4.61 (d, J = 9.2 Hz, 1H), 4.27-4.32 (m, 2H), 4.07-4.13 (m, 2H), 3.88-3.93 (m, 2H), 3.80 (t, J = 8.8 Hz, 1H), 3.70 (t, J = 10.4 Hz, 1H), 3.65 (s, 3H), 3.51-3.60 (m, 3H), 3.56 (s, 3H), 2.87 (dd, J = 3.2, 12.4 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.11-2.14 (m, 1H), 2.06 (s, 3H), 2.01 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 170.9, 170.7, 170.2, 170.0, 168.4, 168.3 (C1, 3JC-1, H-3ax = 5.2 Hz), 153.7, 139.05, 138.98, 138.7, 128.6, 128.5, 128.35, 128.33, 127.9, 127.8, 127.6, 127.5, 105.2, 99.4, 82.3, 79.7, 76.5, 75.3, 75.1, 74.5, 73.6, 73.2, 72.9, 71.9, 69.1, 63.8, 63.0, 59.6, 57.3, 53.4, 36.7, 21.3, 21.1, 20.9, 20.7. ESIHRMS calcd for C49H57NO20Na [M+Na]+: 1002.3372. found 1002.3376.

The minor isomer was identified in the crude reaction mixture by its H3eq signal: δ = 2.94 (dd, J = 3.2, 12.0 Hz).

Methyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-d-glycero-α-D-galacto-non-2-ulopyranosylate-(2 → 3)-methyl 2,6-di-O-benzyl-β-D-galactopyranoside (5d). Eluant for chromatographic purification on silica gel: hexane/ethyl acetate (v/v, 3:2). [α]24D -18.6 (c, 0.5, CHCl3); 1H NMR (500 MHz, CDCl3) δ: 7.27-7.38 (m, 10H), 5.63 (dd, J = 1.5, 7.5 Hz, 1H), 5.42-5.46 (m, 1H), 5.05 (s, 2H), 4.83 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 4.57 (s, 2H), 4.55 (dd, J = 1.0, 9.0 Hz, 1H), 4.34 (d, J = 7.5 Hz, 1H), 4.32 (dd, J = 3.0, 12.0 Hz, 1H), 4.07-4.13 (m,
1H), 4.04 (dd, J = 3.0, 9.5 Hz, 1H), 3.98 (dd, J = 6.5, 12.0 Hz, 1H), 3.87 (br s, 1H),
3.82 (dd, J = 6.0, 10.0 Hz, 1H), 3.79 (s, 3H), 3.71-3.76 (m, 1H), 3.61-3.67 (m, 2H),
3.57 (s, 3H), 3.54-3.57 (m, 1H), 2.79 (dd, J = 4.0, 12.5 Hz, 1H), 2.74 (d, J = 3.5 Hz,
1H), 2.21 (t, J = 13.0 Hz, 1H), 2.16 (s, 3H), 2.11 (s, 3H), 2.03 (s, 3H), 1.86 (s, 3H);
13C NMR (125 MHz, CDCl3) δ: 170.9, 170.7, 170.4, 169.8, 168.5 (C1, 3J_C-1, H-3ax = 6.2 Hz),
168.4, 153.6, 139.1, 138.3, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 77.4, 76.6, 76.4,
75.01, 74.96, 73.8, 73.0, 71.9, 69.4, 69.3, 68.6, 63.8, 63.2, 59.4, 57.2, 53.5, 35.2, 21.4,
912.2908. The minor isomer was identified in the crude reaction mixture by its H3eq
signal: δ = 3.14 (dd, J = 3.2, 12.0 Hz).

Methyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-
glycero-α/β-D-galacto-non-2-ulopyranosylate-(2 → 3)-methyl
2,4,6-tri-O-benzyl-D-galactopyranoside (5e). ESIHRMS calcd for C49H57NO20Na
[M+Na]+: 1002.3372. found 1002.3365. Inspection of the 1H NMR spectrum (in C6D6)
of the crude reaction mixture indicated that the product α/β ratio was approximately
1:1 based on integration of two isomers’ H3eq signal [ for 5ea: δ = 2.71 (dd, J = 4.0,
12.5 Hz, 1H, H3eq); for 5eb: δ = 2.48 (dd, J = 4.0, 12.5 Hz, 1H, H3eq)]. Assignment of
these two signals was unambiguously confirmed by benzylation of 5da: To a stirred
solution of pure 5da (13 mg, 0.015 mmol) in dry DMF (1 mL) was added NaH (60%
dispersion in mineral oil, 3 mg, 0.075 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 20 minutes before benzyl bromide (2 μL, 0.018 mmol) was added. After 40 minutes at 0 °C, the reaction mixture was quenched with aq NH₄Cl, diluted with ethyl acetate, and aq layer was extracted with ethyl acetate once. The combined organic solution was washed with brine, dried, and concentrated. Inspection of the crude's ¹H NMR (in C₆D₆) spectrum revealed the H₃eq resonance of 5eα at δ 2.71 ppm.

3,5-Dideoxy-α-glycero-α/β-D-galacto-non-2-ulopyranosylonic acid-(2→3)-methyl 2,4,6-tri-O-benzyl-β-D-galactopyranoside (15). To a stirred solution of 5e (95 mg, 0.1 mmol) in ethanol/H₂O (3/2, 5 mL) was added LiOH·H₂O (122 mg, 3 mmol) at room temperature. The resulting mixture was heated at 70 °C overnight, followed by careful neutralization with Amberlyst 15 ion exchange resin to pH 7-8, and filtration through Celite, eluting with methanol. The filtrate was concentrated under reduced pressure to give a residue, which was purified by RP HPLC using a gradient of 20% to 70% A over 80 mins (A: CH₃CN, B: H₂O; Varian Microsorb C18 250 x 21.4 mm, flow rate: 10 mL/min; UV detection: 215nm) to give 28 mg of pure 15α and 29 mg of pure 15β (57 mg, total, 82%). For 15α: [α]⁺²³ = -26.4 (c, 0.25, CH₃OH); ¹H NMR (500 MHz, CD₃OD) δ: 7.46 (d, J = 7.0 Hz, 2H), 7.23-7.36 (m, 13H), 5.03 (d, J = 11.5 Hz, 1H), 4.84 (d, J = 11.0 Hz, 1H), 4.74 (d, J = 11.5 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.37 (d, J = 11.5 Hz, 1H), 4.27-4.30 (m, 2H), 3.92-3.95 (m, 2H),
3.79-3.86 (m, 3H), 3.70 (dd, \( J = 4.5, 11.5 \) Hz, 1H), 3.66 (t, \( J = 6.0 \) Hz, 1H), 3.50-3.56 (m, 1H), 3.50 (s, 3H), 3.41-3.44 (m, 1H), 3.05 (t, \( J = 10.0 \) Hz, 1H), 2.89 (dd, \( J = 5.0, 12.5 \) Hz, 1H), 1.81 (t, \( J = 12.0 \) Hz, 1H); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD) \( \delta \): 173.4 (C1, \( ^{3}J_{C-1,H-3ax} = 5.1 \) Hz), 139.4, 139.0, 138.2, 128.4, 128.24, 128.20, 128.04, 127.96, 127.8, 127.6, 127.32, 127.27, 104.86 (C1’, \( ^{1}J_{C1,H1} = 158.4 \) Hz), 100.8, 78.3, 76.5, 75.6, 75.1, 75.0, 73.4, 73.2, 72.3, 72.0, 69.3, 68.2, 67.6, 62.8, 56.2, 53.2, 40.1. ESIHRMS calcd for C\(_{37}\)H\(_{46}\)NO\(_{13}\) [M-H]: 712.2969. found 712.2961. For 15β: [\( \alpha \)]\(_{23}\)D -67.2 (c, 0.5, CH\(_{3}\)OH); \(^{1}\)H NMR (500 MHz, CD\(_3\)OD) \( \delta \): 7.43 (d, \( J = 7.5 \) Hz, 2H), 7.38 (d, \( J = 7.5 \) Hz, 2H), 7.19-7.33 (m, 11H), 5.09 (d, \( J = 11.5 \) Hz, 1H), 4.94 (d, \( J = 12.0 \) Hz, 1H), 4.65 (d, \( J = 11.5 \) Hz, 1H), 4.62 (d, \( J = 11.5 \) Hz, 1H), 4.48 (d, \( J = 12.0 \) Hz, 1H), 4.40 (d, \( J = 12.0 \) Hz, 1H), 4.24-4.27 (m, 2H), 4.14 (d, \( J = 10.5 \) Hz, 1H), 4.06 (dt, \( J = 5.0, 11.0 \) Hz, 1H), 4.01 (d, \( J = 3.0 \) Hz, 1H), 3.94-3.97 (m, 1H), 3.84 (dd, \( J = 2.5, 11.5 \) Hz, 1H), 3.65-3.75 (m, 3H), 3.59 (d, \( J = 8.5 \) Hz, 1H), 3.48-3.55 (m, 2H), 3.30 (s, 3H), 3.10 (t, \( J = 10.0 \) Hz, 1H), 2.76 (dd, \( J = 5.0, 13.5 \) Hz, 1H), 1.64 (t, \( J = 13.0 \) Hz, 1H); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD) \( \delta \): 173.4 (C1, \( ^{3}J_{C-1,H-3ax} = 0 \) Hz), 140.4, 139.4, 138.2, 128.2, 128.1, 128.0, 127.93, 127.91, 127.8, 127.6, 127.3, 126.7, 105.7 (C1’, \( ^{1}J_{C1,H1} = 160.2 \) Hz), 100.2, 79.2, 77.0, 75.11, 75.08, 73.4, 73.2, 73.1, 70.7, 70.5, 69.3, 69.0, 66.3, 63.6, 56.1, 53.8, 41.2. ESIHRMS calcd for C\(_{37}\)H\(_{46}\)NO\(_{13}\) [M-H]: 712.2969. found 712.2971.

Methyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-D-
glycero-α-β-galacto-non-2-ulopyranosylonate-(2 → 3)-phenyl

2-O-benzyl-4,6-deuterium-benzylidene-1-thio-α-β-mannopyranoside (5f α).

Eluant for chromatographic purification on silica gel: hexane/ethyl acetate (v/v, 2:1).

\[ \alpha \]$_{D}^{22}$ +25.5 (c, 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.27-7.48 (m, 15H), 5.88 (d, $J = 9.6$ Hz, 1H), 5.56 (br s, 2H), 5.14 (d, $J = 17.2$ Hz, 1H), 5.00 (d, $J = 17.2$ Hz, 1H), 4.76 (s, 2H), 4.29-4.48 (m, 5H), 4.16-4.19 (m, 2H), 4.09 (t, $J = 10.0$ Hz, 1H), 3.96-4.02 (m, 1H), 3.80 (t, $J = 10.8$ Hz, 1H), 3.55 (t, $J = 10.4$ Hz, 1H), 3.12 (s, 3H), 3.12-3.15 (m, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.91 (t, $J = 12.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 171.0, 170.7, 169.9, 167.9, 166.8 (C1, $^3J_{C-1,H-3ax} = 5.2$ Hz), 153.5, 138.2, 137.7, 134.5, 131.2, 129.35, 129.30, 128.7, 128.3, 128.2, 127.8, 127.6, 126.9, 99.9, 87.2, 82.1, 77.1, 74.2, 73.9, 72.7, 71.1, 69.1, 68.6, 65.3, 63.7, 62.3, 60.1, 53.0, 37.2, 21.4, 21.0, 20.9, 20.7. ESIHRMS calcd for C$_{47}$H$_{50}$DNO$_{19}$SNa [M+Na]$^+$: 989.2736. found 989.2737.

Methyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-β-
glycero-β-α-galacto-non-2-ulopyranosylonate-(2 → 3)-phenyl

2-O-benzyl-4,6-deuterium-benzylidene-1-thio-α-β-mannopyranoside (5f β).

Eluant for chromatographic purification on silica gel: hexane/ethyl acetate (v/v, 2:1).

\[ \alpha \]$_{D}^{22}$ +78.4 (c, 0.5, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.30-7.45 (m, 15H), 5.53 (td, $J = 2.4$, 8.4 Hz, 1H), 5.43 (s, 1H), 5.29-5.35 (m, 2H), 4.97 (dd, $J = 2.4$, 9.6 Hz, 1H),
4.47-4.63 (m, 7H), 4.20-4.28 (m, 2H), 4.11 (dd, $J=8.0, 12.0$ Hz, 1H), 3.96 (br s, 1H), 3.82 (t, $J=10.4$ Hz, 1H), 3.71 (s, 3H), 3.62 (dd, $J=9.6, 11.2$ Hz, 1H), 2.73 (dd, $J=2.4, 12.0$ Hz, 1H), 2.14-2.22 (m, 1H), 2.19 (s, 3H), 2.16 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 171.0, 170.5, 170.4, 169.5, 168.4, 167.2, 153.6, 137.6, 137.2, 133.6, 132.4, 129.7, 129.4, 128.8, 128.7, 128.3, 128.2, 128.1, 126.6, 97.4, 87.3, 78.4, 76.0, 75.0, 74.1, 73.3, 71.6, 70.2, 68.9, 65.5, 63.4, 63.56, 59.2, 53.2, 36.8, 21.4, 21.1, 20.9, 20.8. ESIHRMS calcd for C$_{47}$H$_{50}$DNO$_{19}$SNa [M+Na]$^+$: 989.2736. found 989.2746.

4-Chlorophenyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (13). To a stirred solution of D-(+)-galactose (20.0 g, 0.11 mol) in acetic anhydride (105 mL, 1.1 mol) was added anhydrous pyridine (108.0 mL, 1.32 mol) dropwise at 0 °C. The reaction mixture was stirred overnight, during which the reaction temperature rose to room temperature. The reaction solvents were then removed under reduced pressure to give a residue, which was dissolved in ethyl acetate (300 mL). The organic solution was washed with 2 N aqueous HCl, water, aqueous NaHCO$_3$, and brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure to give the penta-acetate as a light yellow syrup (~ 41 g). This crude product was used directly for next step without purification after evacuation under high vacuum for 5h.

Part of the above penta-acetate (20 g, 0.051 mol) was mixed with HBr in HOAc (30
mL, 32% w/w, 0.51 mol) and stirred at room temperature for 2 h, and then diluted with dichloromethane (400 mL). The organic solution was washed with ice-cooled water twice, followed by washing with aq NaHCO₃ and brine, dried over Na₂SO₄ and concentrated under reduced pressure to give a crude bromide (~19 g), which was used directly for the next step after evacuation under high vacuum for 2 h.

A solution of crude bromide (12.6 g, 0.03 mol) in chloroform (250 mL) was mixed with a solution of tetrabutylammonium chloride (1.67 g, 6.0 mmol) in water (50 mL) before 4-chlorothiophenol (5.3 g, 0.036 mol) was added at room temperature, followed by dropwise addition of a solution of KOH (3.5 g, 0.06 mol) in water (50 mL) at 0°C. After the addition was complete, the reaction mixture was stirred at room temperature for 3 h. The organic layer was separated, washed with water, dried over Na₂SO₄ and concentrated. The residue was recrystallized from isopropanol/hexane to give the title compound 13 (10.0 g, 0.022 mol) as a white solid in 72% yield. Mp 117-118°C. [α]_D^22 -1.0 (c, 1.0, CHCl₃); ^1H NMR (500 MHz, CDCl₃) δ: 7.46 (d, J = 8.5 Hz, 2H), 9.29 (d, J = 8.5 Hz, 2H), 5.40 (d, J = 3.5 Hz, 1H), 5.19 (t, J = 10.0 Hz, 1H), 5.04 (dd, J = 3.0, 9.0 Hz, 1H), 4.65 (d, J = 9.5 Hz, 1H), 4.16-4.19 (m, 1H), 4.08-4.11 (m, 1H), 3.93 (t, J = 6.5 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H); ^13C NMR (125 MHz, CDCl₃) δ: 170.6, 170.3, 170.2, 169.6, 134.9, 134.6, 130.6, 129.2, 86.3, 74.7, 72.2, 67.4, 67.3, 61.8, 21.0, 20.9, 20.83, 20.79. ESIHRMS calcd for C₂₀H₂₅ClO₅SNa [M+Na]^+: 497.0649. found 497.0630.
4-Chlorophenyl 3,4-O-isopropylidene-1-thio-β-D-galactopyranoside (14). To a stirred solution of thioglycoside 13 (3.0 g, 6.5 mmol) in dry methanol (50 mL) was added few drops of NaOMe in methanol (25% w/w) at room temperature. The reaction mixture was stirred at the same temperature for 30 min before it was neutralized with Amberlyst-15 ion exchange resin, and filtered through Celite. The filtrate was concentrated to afford a residue (2.0 g, 6.5 mmol), which was directly used for next step without purification after evacuation under high vacuum for 1h.

A solution of the above alcohol (2.0 g, 6.5 mmol) and camphor-10-sulfonic acid (60 mg, 0.3 mmol) in dimethoxypropane (60 mL) was stirred at room temperature for 36 h, and then neutralized by triethylamine (1 mL). The volatiles were removed under reduced pressure to give a residue, which was then dissolved in methanol (50 mL), then treated with water (0.5 mL) and acetic acid (1.5 mL). The reaction mixture was stirred at room temperature for 12 h before another 0.5 mL of acetic acid was added. The stirring was continued for another 12 h and triethylamine (3.0 mL) was added followed by removal of the volatiles under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 1:1) to give the title compound 14 (1.97 g, 87%). [$\alpha$]$_{D}^{22}$ -3.0 (c, 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.41-7.44 (m, 2H), 7.21-7.24 (m, 2H), 4.42 (d, $J = 10.0$ Hz, 1H), 4.12 (dd, $J = 2.0$, 5.5 Hz, 1H), 4.06 (dd, $J = 5.5$, 6.5 Hz, 1H), 3.91 (dd, $J = 6.0$, 11.5 Hz, 1H), 3.81-3.84 (m, 1H), 3.76 (dd, $J = 4.0$, 11.5 Hz, 1H), 3.52 (dd, $J = 6.5$, 10.0 Hz, 1H), 3.31 (br s, 1H),
1.37 (s, 3H), 1.28 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 134.0, 133.4, 130.6, 129.0, 110.3, 87.2, 79.3, 77.0, 73.7, 71.3, 62.2, 27.9, 26.2. ESIHRMS calcd for C$_{15}$H$_{19}$ClO$_5$SNa [M+Na]$^+$. 369.0539. found 369.0572.

4-Chlorophenyl 2,6-di-O-benzoyl-1-thio-\(\beta\)-D-galactopyranoside (6). To a stirred solution of 14 (1.0 g, 2.9 mmol) in pyridine (10 mL) was added benzoyl chloride (1.3 mL, 11.5 mmol), followed by a catalytic amount of DMAP. The reaction mixture was stirred at room temperature for 20 min and then the solvent was removed under reduced pressure to give a residue, which was dissolved in a mixture of trifluoroacetic acid (10 mL) and water (2 mL). Stirring was continued for 30 min before the solvent was removed under reduced pressure. The residue was then diluted with ethyl acetate (50 mL) and washed with aq NaHCO$_3$, brine, and dried over Na$_2$SO$_4$. Concentration of the organic layer gave a residue, which was recrystallized from hexane/ethyl acetate to afford the title compound 6 (1.4 g, 94%) as a white solid. Mp 145-146 $^\circ$C. $\left[\alpha\right]_{D}^{23} +14.4$ (c, 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 8.03-8.07 (m, 4H), 7.59-7.63 (m, 2H), 7.45-7.49 (m, 4H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.08 (d, $J = 9.0$ Hz, 2H), 5.23 (t, $J = 10.0$ Hz, 1H), 4.79 (d, $J = 10.5$ Hz, 1H), 4.87-4.72 (m, 1H), 4.59-4.63 (m, 1H), 4.09 (d, $J = 3.0$ Hz, 1H), 3.94 (t, $J = 6.0$ Hz, 1H), 3.88 (dd, $J = 3.5, 9.0$ Hz, 1H), $^1$C NMR (125 MHz, CDCl$_3$) $\delta$: 167.2, 166.8, 134.5, 134.2, 133.9, 133.7, 131.2, 130.3, 130.0, 129.8, 129.5, 129.3, 128.78, 128.76, 86.1, 76.5, 73.9, 72.4, 69.2, 63.7. ESIHRMS calcd for
C_{26}H_{23}ClO_{7}SNa [M+Na]^+: 537.0751. found 537.0762.

Methyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-d-glycero-α/β-d-galacto-non-2-ulopyranosylonate-(2→3)-4-chlorophenyl 2,6-di-O-benzoyl-1-thio-β-d-galactopyranoside (7). A solution of donor 4 (50.0 mg, 0.07 mmol), acceptor 6 (25 mg, 0.05 mmol) and activated powdered 4Å molecular sieves (200 mg) in anhydrous CH\textsubscript{2}Cl\textsubscript{2}/CH\textsubscript{3}CN (3 mL, v/v, 2:1) and cooled to -78 °C under a nitrogen atmosphere. NIS (17.0 mg, 0.07 mmol) was added, followed by TfOH (6.5 μL, 0.07 mmol). The reaction mixture was stirred at -78 °C for 40 min and then was poured into aq NaHCO\textsubscript{3}, diluted with CH\textsubscript{2}Cl\textsubscript{2}, and filtered through Celite. The organic layer was separated, washed with 20% aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, and brine, dried and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 3:2) to give the desired product 7 (42 mg, 84%) as a mixture of isomers with α/β ratio of 6:1 as determined by inspection of the \textsuperscript{1}H NMR spectrum of the crude reaction mixture. For 7α: [α]	extsuperscript{23}_{D} +14.7 (c, 1.0, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ: 8.15 (d, J = 7.5 Hz, 2H), 8.03 (d, J = 7.5 Hz, 2H), 7.58-7.63 (m, 2H), 7.46-7.49 (m, 4H), 7.39 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 5.51-5.56 (m, 2H), 5.39 (t, J = 10.0 Hz, 1H), 4.97-5.00 (m, 2H), 4.93 (d, J = 9.5 Hz, 1H), 4.56-4.67 (m, 4H), 4.34 (dd, J = 2.0, 10.0 Hz, 1H), 4.01 (t, J = 6.0 Hz, 1H), 3.93-3.97 (m, 2H), 3.78 (d, J = 5.0 Hz, 1H),
3.74 (s, 3H), 3.52 (t, J = 10.0 Hz, 1H), 2.83 (dd, J = 3.5, 12.0 Hz, 1H), 2.67 (br s, 1H), 2.14 (s, 3H), 2.02 (t, J = 12.0 Hz, 1H), 2.06 (s, 3H), 1.99 (s, 3H), 1.52 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 171.0, 170.7, 169.9, 168.7, 168.2, 166.4, 165.5, 153.3, 134.4, 134.2, 133.66, 133.60, 131.3, 130.3, 130.14, 130.06, 129.9, 129.1, 128.8, 128.7, 97.4, 86.6, 76.3, 75.8, 75.3, 74.8, 71.5, 68.9, 68.1, 67.4, 63.9, 63.7, 63.6, 59.2, 53.6, 36.3, 21.4, 20.9, 20.6, 20.4. ESIHRMS calcd for C$_{47}$H$_{48}$ClNO$_{21}$SNa [M+Na]$^+$: 1052.2026. found 1052.2041. The minor isomer was identified in the crude reaction mixture by its H$_{3}$eq signal: δ = 2.89 (dd, J = 4.0, 12.5 Hz).

Methyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-$\alpha$-carbonyl-3,5-dideoxy-$\alpha$-glycero-$\alpha$-galacto-non-2-ulopyranosyl-(2$\rightarrow$3)-2,6-di-O-benzoyl-$\beta$-D-galactopyranosyl-(1$\rightarrow$6)- methyl 2,3,4-tri-O-benzyl-$\beta$-D-glucopyranoside (8).

Method 1 (using 4 Å molecular sieves): A solution of donor 4 (50 mg, 0.07 mmol), acceptor 6 (25 mg, 0.05 mmol), and powdered activated 4 Å molecular sieves (200 mg) in anhydrous CH$_2$Cl$_2$/CH$_3$CN (3 mL, v/v, 2:1) was cooled to -78 °C, and treated sequentially with NIS (17.0 mg, 0.07 mmol) and TfOH (6.5 μL, 0.07 mmol) under a nitrogen atmosphere. After 20 min of stirring at -78 °C, a solution of methyl 2,3,4-tri-O-benzyl-$\beta$-D-glucopyranoside (45 mg, 0.10 mmol) in CH$_2$Cl$_2$ (1 mL) and 4 Å molecular sieves (200 mg) was added, followed by NIS (17.0 mg, 0.07 mmol) and TfOH (6.5 μL, 0.07 mmol). The mixture was then warmed up to 0°C, and stirred for 2h,
and then worked up by pouring into aq NaHCO₃, dilution with CH₂Cl₂ and filtration through Celite. The organic layer was separated, washed with 20% aqueous Na₂S₂O₃, and brine, dried and concentrated. The residue was purified by column chromatography on silica gel (toluene/ethyl acetate, v/v, 2:1) to give trisaccharide 8 (32 mg, 49%).

**Method 2** (using acid washed-300 molecular sieves): A solution of donor 4 (60 mg, 0.09 mmol), acceptor 6 (52 mg, 0.1 mmol), powdered activated AW-300 molecular sieves (200 mg) in anhydrous CH₂Cl₂/CH₃CN (3 mL, v/v, 2:1) was cooled to -78 °C, and treated sequentially with NIS (20 mg, 0.09 mmol) and TfOH (4.0 μL, 0.04 mmol) under a nitrogen atmosphere. After 20 min of stirring at -78 °C, a solution of methyl 2,3,4-tri-O-benzyl-β-D-glucopyranoside (61 mg, 0.14 mmol) in CH₂Cl₂ (1 mL) and AW-300 molecular sieves (200 mg) was added, followed by NIS (40.0 mg, 0.18 mmol) and TfOH (4.0 μL, 0.04 mmol). The mixture was then warmed to 0 °C, and stirred for 2 h, and then worked up by pouring into aq NaHCO₃, dilution with CH₂Cl₂, and filtration through Celite. The organic layer was separated, washed with 20% aqueous Na₂S₂O₃, and brine, dried and concentrated. The residue was purified by column chromatography on silica gel (toluene/ethyl acetate, v/v, 2:1) to give trisaccharide 8 (65 mg, 55%). [α]$_{23}^{23}$ +10.0 (c, 1.0, CHCl₃); $^1$H NMR (500 MHz, CDCl₃) δ: 8.08 (d, $J$ = 8.0 Hz, 2H), 8.03 (d, $J$ = 8.5 Hz, 2H), 7.55 (t, $J$ = 7.0 Hz, 1H), 7.50 (t, $J$ = 7.5 Hz, 1H), 7.38 (t, $J$ = 7.5 Hz, 2H), 7.36 (t, $J$ = 7.5 Hz, 2H), 7.21-7.29 (m, 13H), 7.15-7.16 (m, 2H), 5.51-5.57 (m, 2H), 5.46 (dd, $J$ = 8.0, 9.5 Hz, 1H), 4.94-5.05 (m, 2H), 4.80-4.84 (m, 3H), 4.56-4.68 (m, 6H), 4.52 (dd, $J$ = 3.0, 9.5 Hz, 1H), 4.42 (d, $J$ = 10.5 Hz, 1H), 4.29
(dd, \( J = 2.0, 12.5 \) Hz, 1H), 4.18 (d, \( J = 10.5 \) Hz, 1H), 4.14 (d, \( J = 8.0 \) Hz, 1H), 3.93-4.00 (m, 3H), 3.71-3.77 (m, 1H), 3.74 (s, 3H), 3.63-3.66 (m, 1H), 3.47-3.54 (m, 2H), 3.41-3.44 (m, 1H), 3.27-3.31 (m, 3H), 3.18 (s, 3H), 2.84 (dd, \( J = 3.0, 12.0 \) Hz, 1H), 2.70 (d, \( J = 3.0 \) Hz, 1H), 2.14 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00-2.06 (m, 1H), 1.54 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 171.0, 170.7, 170.5, 169.9, 168.8 (C1, \( ^{3}\)J\(_{C1,H-3ax} = 5.9 \) Hz), 168.1, 166.4, 165.3, 153.3, 138.83, 138.76, 138.1, 133.5, 133.4, 130.2, 129.8, 128.68, 128.66, 128.6, 128.5, 128.3, 128.2, 128.02, 127.97, 127.8, 127.7, 104.4 (\( ^{1}\)J\(_{C1',H1'} = 157.0 \) Hz), 101.2 (\( ^{1}\)J\(_{C1'',H1''} = 158.0 \) Hz), 97.4, 84.7, 82.4, 78.2, 76.4, 75.8, 75.1, 74.8, 74.7, 74.5, 71.8, 71.4, 70.6, 68.3, 68.1, 67.0, 63.64, 63.58, 63.2, 59.3, 56.7, 53.5, 36.4, 21.3, 21.0, 20.6, 20.4. ESIHRMS calcd for C\(_{69}\)H\(_{75}\)NO\(_{27}\)Na [M+Na]\(^+\): 1372.4424. found 1372.4420.

Methyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-\( \alpha \)-glycero-\( \alpha \)-galacto-non-2-ulopyranosylonate-(2\( \rightarrow \)3)-2,6-di-O-benzoyl-\( \beta \)-\( \alpha \)-galactopyranosyl-(1\( \rightarrow \)4)-methyl 2,3,4-tri-O-benzyl-\( \beta \)-\( \alpha \)-glucopyranoside (9). A solution of donor 4 (50 mg, 0.07 mmol), acceptor 6 (44 mg, 0.08 mmol), powdered activated AW-300 molecular sieves (200 mg) in anhydrous CH\(_2\)Cl\(_2\)/CH\(_3\)CN (3 mL, v/v, 2:1) was cooled down to -78 °C, followed by sequential addition of NIS (19 mg, 0.08 mmol) and TfOH (4.0 \( \mu \)L, 0.03 mmol) under a nitrogen atmosphere. After stirring for 20 min at -78 °C, a solution of methyl 2,3,6-tri-O-benzyl-\( \beta \)-\( \alpha \)-glucopyranoside (68 mg,
0.14 mmol) in CH$_2$Cl$_2$ (1 mL) and AW-300 molecular sieves (200 mg) was added, followed by addition of NIS (35.0 mg, 0.14 mmol) and TfOH (4.0 μL, 0.03 mmol). The reaction mixture was then warmed up to 0°C, stirred for 2h at 0°C and 40 min at room temperature, then worked up by pouring into aq NaHCO$_3$ solution, dilution with CH$_2$Cl$_2$ and filtration through Celite. The organic layer was separated, washed with 20% Na$_2$S$_2$O$_3$, and brine, dried and concentrated. The residue was purified by column chromatography on silica gel (toluene/acetone, v/v, 6:1) to afford trisaccharide 9 (44 mg, 44%). [α]$^23_D$ +11.0 (c, 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.17 (d, $J = 8.0$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 2H), 7.55-7.59 (m, 2H), 7.40-7.48 (m, 7H), 7.18-7.30 (m, 12H), 5.54-5.60 (m, 2H), 5.40 (dd, $J = 8.0, 9.5$ Hz, 1H), 4.96-5.04 (m, 4H), 4.84 (dd, $J = 5.5, 11.0$ Hz, 2H), 4.66 (d, $J = 11.0$ Hz, 1H), 4.56 (t, $J = 9.0$ Hz, 1H), 4.55 (d, $J = 7.5$ Hz, 1H), 4.33-4.45 (m, 4H), 4.20 (d, $J = 8.0$ Hz, 1H), 4.16 (dd, $J = 6.0, 11.0$ Hz, 1H), 3.91-3.98 (m, 3H), 3.80 (t, $J = 6.5$ Hz, 1H), 3.70 (s, 3H), 3.60-3.70 (m, 3H), 3.50-3.53 (m, 2H), 3.49 (s, 3H), 3.36 (t, $J = 8.5$ Hz, 1H), 3.30 (dd, $J = 4.0, 9.5$ Hz, 1H), 2.81 (dd, $J = 3.5, 12.0$ Hz, 1H), 2.69 (br s, 1H), 2.16 (s, 3H), 2.07 (s, 3H), 2.02 (t, $J = 12.0$ Hz, 1H), 1.98 (s, 3H), 1.48 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 171.0, 170.8, 170.5, 169.9, 168.5 (C1, $^3$J$_{C-1,H-3ax}$ = 5.5 Hz), 168.1, 166.2, 165.2, 153.3, 139.2, 138.8, 138.7, 133.6, 133.4, 130.3, 130.12, 130.08, 129.8, 128.9, 128.6, 128.48, 128.45, 128.3, 128.2, 127.8, 127.7, 127.6, 127.4, 104.6($^1$J$_{C1',H1'} = 158.3$ Hz), 100.7 ($^1$J$_{C1''',H1'''} = 162.5$ Hz), 97.7, 83.1, 82.2, 76.4, 75.4, 74.9, 74.7, 74.6, 73.3, 71.8, 71.7, 71.6, 69.2, 68.1, 66.8, 63.8, 63.6, 62.7, 59.3, 57.2, 53.5, 36.1, 21.4, 20.9, 20.7, 20.4. ESIHRMS calcd for C$_{69}$H$_{75}$NO$_{27}$Na [M+Na]$^+$: 1372.4424. found 1372.4426.
Methyl 5-acetoxyacetamido-7,8,9-tri-\(\text{O}\)-acetyl-5-N,4-\(\text{O}\)-carbonyl-3,5-dideoxy-\(\alpha\)-\(\text{D}\)-galacto-non-2-ulopyranosyl-(2\(\rightarrow\)3)-2,6-di-\(\text{O}\)-benzoyl-\(\beta\)-\(\text{D}\)-galactopyranosyl-(1\(\rightarrow\)6)-methyl 2-azido-3,4-di-\(\text{O}\)-benzyl-2-deoxy-\(\beta\)-\(\text{D}\)-glucopyranoside (10) A solution of donor 4 (40 mg, 0.06 mmol), acceptor 6 (35 mg, 0.07 mmol), powdered activated AW-300 molecular sieves (200 mg) in anhydrous CH\(_2\)Cl\(_2\)/CH\(_3\)CN (3 mL, v/v, 2:1) was cooled to -78 °C, followed by sequential addition of NIS (14 mg, 0.06 mmol) and TfOH (3.0 \(\mu\)L, 0.03 mmol). After 20 min of stirring at -78 °C, a solution of methyl 2-azido-3,4-di-\(\text{O}\)-benzyl-2-deoxy-\(\beta\)-\(\text{D}\)-glucopyranoside (35 mg, 0.09 mmol) in CH\(_2\)Cl\(_2\) (1 mL) and AW-300 molecular sieves (200 mg) was added, followed by addition of NIS (19.0 mg, 0.12 mmol) and TfOH (3.0 \(\mu\)L, 0.03mmol). The reaction mixture was then warmed up to 0 °C, stirred for 2h at 0 °C and then worked up by pouring into aq NaHCO\(_3\) solution, dilution with CH\(_2\)Cl\(_2\), and filtration through Celite. The organic layer was separated, washed with 20% aqueous Na\(_2\)S\(_2\)O\(_3\), and brine, dried and concentrated. The residue was purified by column chromatography on silica gel (toluene/ethyl acetate, v/v, 1.5:1) to give trisaccharide 10 (38 mg, 51%). \([\alpha]\)\(_{D}\)\(^{23}\) +24.0 (c, 1.0, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.03-8.08 (m, 4H), 7.54-7.58 (m, 1H), 7.39-7.46 (m, 4H), 7.24-7.33 (m, 9H), 7.11-7.13 (m, 2H), 5.54-5.56 (m, 2H), 5.46 (dd, \(J = 8.0, 10.0\) Hz, 1H), 4.95-5.03 (m, 2H), 4.56-4.76 (m, 7H), 4.53 (dd, \(J = 3.0, 10.0\) Hz, 1H), 4.49 (d, \(J = 3.5\) Hz, 1H), 4.43 (d, \(J = 10.0\) Hz, 1H),
4.37 (d, J = 11.0 Hz, 1H), 4.31 (dd, J = 2.0, 12.5 Hz, 1H), 4.15 (d, J = 8.5 Hz, 1H),
3.92-3.99 (m, 3H), 3.82 (dd, J = 3.5, 10.0 Hz, 1H), 3.73 (s, 3H), 3.66-3.72 (m, 2H),
3.50 (dd, J = 10.0, 11.5 Hz, 1H), 3.35 (t, J = 4.0 Hz, 1H), 3.20 (dd, J = 3.5, 10.5 Hz,
1H), 3.15 (s, 3H), 2.85 (dd, J = 3.5, 12.0 Hz, 1H), 2.64 (br s, 1H), 2.14 (s, 3H),
2.00-2.03 (m, 1H), 2.02 (s, 3H), 1.99 (s, 3H), 1.49 (s, 3H); 13C NMR (125 MHz, CDCl3)
δ: 171.0, 170.7, 170.6, 169.9, 168.8 (C1, 3J_C-1, H-3ax = 5.2 Hz), 168.1, 166.4, 165.3,
153.3, 138.1, 138.0, 133.5, 133.4, 130.21, 130.17, 130.1, 129.8, 128.8, 128.7, 128.6,
128.2, 128.0, 127.9, 101.7 (1J_C1',H1' = 157.3 Hz), 98.4 (1J_C1'',H1'' = 169.1 Hz), 97.3,
80.5, 78.4, 76.3, 75.5, 75.0, 74.7, 74.4, 71.9, 71.5, 70.6, 70.1, 68.2, 68.1, 67.0, 63.7,
63.6, 63.1, 59.2, 55.1, 53.5, 36.4, 21.3, 20.9, 20.6, 20.4 ESIHRMS calcd for

Methyl 5-acetoxyacetamido-7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-d-
glycero-α-d-galacto-non-2-ulopyranosylate-(2→3)-2,6-di-O-benzoyl-β-d-
galactopyranosyl-(1→4)-methyl 2-azido-3,6-di-O-benzyl-2-deoxy-β-d-glucopyr-
anoside (11) A solution of donor 4 (40 mg, 0.06 mmol), acceptor 6 (35 mg, 0.07
mmol), powdered activated AW-300 molecular sieves (200 mg) in anhydrous
CH2Cl2/CH3CN (3 mL, v/v, 2:1) was cooled down to -78 °C, followed by sequential
addition of NIS (14 mg, 0.06 mmol) and TfOH (3.0 μL, 0.03 mmol). After 20 min of
stirring at -78 °C, a solution of methyl
2-azido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside (35 mg, 0.09 mmol) in CH₂Cl₂ (1 mL) and AW-300 molecular sieves (200 mg) was added, followed by addition of NIS (19.0 mg, 0.12 mmol) and TfOH (3.0 μL, 0.03 mmol). The reaction mixture was then warmed up to 0 °C, stirred for 2h at 0 °C and 30 min at rt, then was worked up by pouring into aq NaHCO₃ solution, dilution with CH₂Cl₂ and filtration through Celite. The organic layer was separated, washed with 20% aqueous Na₂S₂O₃, and brine, dried and concentrated. The residue was purified by column chromatography on silica gel (toluene/acetone, v/v, 7:1) to give trisaccharide 11 (35 mg, 45%). \([\alpha]^{23}_D +28.5 \ (c, \ \text{1.0, CHCl}_3)\); ¹H NMR (500 MHz, CDCl₃) δ: 8.14 (d, \(J = 7.0\) Hz, 2H), 8.00 (d, \(J = 7.0\) Hz, 2H), 7.22-7.62 (m, 16H), 5.53-5.87 (m, 2H), 5.44 (dd, \(J = 8.5, 10.0\) Hz, 1H), 5.13 (d, \(J = 10.0\) Hz, 1H), 4.97-5.05 (m, 2H), 4.86 (d, \(J = 8.0\) Hz, 1H), 4.72(d, \(J = 10.5\) Hz, 1H), 4.70 (d, \(J =3.5\) Hz, 1H), 4.50-4.58 (m, 4H), 4.38 (dd, \(J = 3.0, 10.0\) Hz, 1H), 4.31 (dd, \(J = 2.0, 12.0\) Hz, 1H), 4.23 (dd, \(J = 5.5, 11.0\) Hz, 1H), 4.09 (t, \(J = 9.0\) Hz, 1H), 3.93-3.98 (m, 2H), 3.87 (t, \(J = 10.0\) Hz, 1H), 3.82 (t, \(J = 6.0\) Hz, 1H), 3.75 (d, \(J = 3.0\) Hz, 1H), 3.70 (s, 3H), 3.66-3.68 (m, 1H), 3.55 (t, \(J = 8.0\) Hz, 2H), 3.50 (t, \(J = 11.5\) Hz, 1H), 3.33 (dd, \(J = 3.5, 10.5\) Hz, 1H), 3.30 (s, 3H), 2.77 (dd, \(J = 3.5, 12.0\) Hz, 1H), 2.76 (d, \(J = 3.5\) Hz, 1H), 2.17 (s, 3H), 2.03 (s, 3H), 2.00-2.05 (m, 1H), 1.96 (s, 3H), 1.54 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 170.7,170.5, 170.3, 169.6 (C1, \(^{1}J_{C-1,H-3ax} = 4.4\) Hz), 168.2, 167.9, 166.1, 164.8, 153.1, 138.3, 138.2, 133.4, 133.2, 129.93, 129.85, 129.8, 129.7, 129.6, 129.5, 128.9, 128.7, 128.6, 128.44, 128.41, 128.3, 128.23, 128.19, 128.1, 127.6, 127.5, 100.1 (\(^{1}J_{C1',H1'} = 164.9\)Hz), 98.5 (\(^{1}J_{C1'',H1''} = 175\) Hz), 97.6, 78.1, 76.14, 76.09, 75.3, 74.6, 74.3, 73.2, 71.6, 71.34, 71.28, 70.2, 68.1, 67.8, 66.6, 63.44, 63.39, 63.1,

**General Deprotection Protocol.** To a stirred mixture of coupled product (50-60 mg, M = 0.015 mol/L) in ethanol/water (v/v, 1.5/1) was added LiOH·H₂O (30 equiv). The resulting mixture was heated to 70 °C overnight, then cooled to room temperature, carefully neutralized with Amberlyst 15 ion exchange resin to pH ~7, diluted with methanol, and filtered. The filtrate was concentrated under vacuum, the residue (M = 0.015 mol/L) was dissolved in CH₃CN/water (v/v, 1.5/1) and solid NaHCO₃ (15 equiv) was added, followed by dropwise addition of a solution of acetoxyacetyl chloride in dry CH₃CN (M = 0.7 mol/L, 4 equiv) at 0 °C. After 1 h of stirring at 0 °C, the reaction was complete as determined by TLC (eluant: ethyl acetate/methanol/water, v/v/v, 7/2/1), and LiOH·H₂O (10 equiv) was added to the mixture. Stirring was continued at rt for 1 h before careful neutralization with Amberlyst 15 ion exchange resin to pH ~7. The reaction mixture was filtered through Celite, washing with methanol, and concentrated to give the crude product, which was purified by reverse phase HPLC using a gradient of 0% to 100% A over 90 minutes (A: CH₃CN, B: H₂O; Varian Microsorb C18 250 x 21.4 mm, flow rate: 10 mL/min; Uv detection: 215nm) to give the pure products.

![5-(2-Hydroxyacetamido)-3,5-di-deoxy-D-glycero-α-D-galacto-non-2-ulopyranosyl](attachment:image.png)
onic acid-(2→6)-1,2; 3,4-di-isopropylidene-α-D-galactopyranoside (12a). $\left[\alpha\right]^{24}_D$ -35.2 (c, 0.25, CH$_3$OH); $^1$H NMR (500 MHz, CD$_3$OD) δ: 5.44 (d, $J = 5.0$ Hz, 1H), 4.58 (dd, $J = 2.5$, 8.0 Hz, 1H), 4.30 (dd, $J = 2.5$, 5.0 Hz, 1H), 4.26 (dd, $J = 1.5$, 8.0 Hz, 1H), 4.02 (d, $J = 1.0$ Hz, 2H), 3.95-3.97 (m, 1H), 3.86-3.89 (m, 2H), 3.77-3.83 (m, 3H), 3.71 (dd, $J = 5.0$, 10.0 Hz, 1H), 3.66-3.67 (m, 1H), 3.61 (dd, $J = 5.5$, 11.5 Hz, 1H), 3.49 (dd, $J = 1.5$, 9.0 Hz, 1H), 2.84 (dd, $J = 4.5$, 12.5 Hz, 1H), 1.63 (t, $J = 12.0$ Hz, 1H), 1.51 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H); $^{13}$C NMR (500 MHz, CD$_3$OD) δ: 176.0, 172.9, 109.0, 108.6, 100.7, 96.5, 72.9, 71.8, 71.4, 70.9, 70.8, 69.2, 68.3, 67.6, 63.41, 63.38, 61.4, 52.6, 41.3, 25.3, 25.2, 24.0, 23.4. ESIHRMS calcd for C$_{23}$H$_{36}$NO$_{15}$Na [M-H]: 566.2085. found 566.2072.

![Chemical structure of 12a](image)

5-(2-Hydroxyacetamido)-3,5-di-deoxy-D-glycero-α-D-galacto-non-2-ulopyranosyl
onic acid-(2→6)-methyl 2,3,4-tri-O-benzyl-β-D-galactopyranoside (12b). $\left[\alpha\right]^{24}_D$ 13.6 (c, 0.5, CH$_3$OH); $^1$H NMR (500 MHz, CD$_3$OD) δ: 7.21-7.36 (m, 15H), 4.81 (dd, $J = 6.0$, 11.5 Hz, 2H), 4.65-4.72 (m, 4H), 4.29 (d, $J = 7.0$ Hz, 1H), 4.07 (d, $J = 2.5$ Hz, 1H), 4.04 (d, $J = 1.5$ Hz, 2H), 3.97-3.98 (m, 1H), 3.78-3.87 (m, 4H), 3.60-3.74 (m, 6H), 3.51 (s, 3H), 3.49-3.54 (m, 1H), 2.85 (dd, $J = 5.0$, 12.5 Hz, 1H), 1.69 (t, $J = 12.0$ Hz, 1H); $^{13}$C NMR (500 MHz, CD$_3$OD) δ: 176.1, 171.8, 139.1, 139.0, 138.8, 128.3, 128.1,
128.01, 127.98, 127.9, 127.7, 127.4, 127.31, 127.27, 105.0, 100.2, 82.1, 79.4, 74.8,
74.7, 73.9, 73.6, 73.3, 72.5, 71.9, 69.0, 67.8, 63.4, 62.5, 61.4, 56.2, 52.5, 41.2.
ESIHRMS calcd for C$_{39}$H$_{48}$NO$_{15}$ [M-H]: 770.3024. found 770.3037.

5-(2-Hydroxyacetamido)-3,5-di-deoxy-D-glycero-$\alpha$-D-galacto-non-2-ulopyranosyl
onic acid-(2→3)-phenyl 2-O-benzyl-4,6-deuterium-benzylidene-1-thio-$\alpha$-D-
mannopyranoside (12c). [\(\alpha\)]$_{D}^{25}$ 51.8 (c, 0.5, CH$_3$OH); $^1$H NMR (500 MHz, CD$_3$OD)
$\delta$: 7.48-7.50 (m, 3H), 7.25-7.38 (m, 12H), 4.87-4.89 (m, 1H), 4.75 (d, $J = 11.5$ Hz, 1H),
4.57 (dd, $J = 3.0$, 10.0 Hz, 1H), 4.46 (d, $J = 2.0$ Hz, 1H), 4.06-4.20 (m, 5H), 3.75-3.88
(m, 5H), 3.59-3.65 (m, 2H), 2.93 (dd, $J = 4.0$, 12.5 Hz, 1H), 1.78 (t, $J = 12.0$ Hz, 1H);
$^{13}$C NMR (500 MHz, CD$_3$OD) $\delta$: 176.2, 170.3, 138.5, 138.0, 134.2, 131.6, 128.9,
128.6, 128.4, 128.3, 127.8, 127.7, 127.4, 126.2, 100.2, 88.3, 81.3, 77.0, 74.14, 74.09,
71.9, 71.5, 68.5, 68.2, 67.2, 65.8, 63.1, 61.4, 52.4, 41.4. ESIHRMS calcd for
C$_{37}$H$_{42}$DNO$_{14}$S [M-H]: 757.2389. found 757.2375.

5-(2-Hydroxyacetamido)-3,5-di-deoxy-D-glycero-$\alpha$-D-galacto-non-2-ulopyranosyl
onic acid-(2→3)-$\beta$-D-galactopyranosyl-(1→6)-methyl 2,3,4-tri-O-benzyl-$\beta$-D-
**Glucopyranoside (12d).** \([\alpha]^{25}_D -2.8\) (c, 1.0, CH\(_3\)OH/H\(_2\)O, v/v, 1:1); \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta: 6.74-7.00\) (m, 15H), 4.48 (d, \(J = 11.0\) Hz, 1H), 4.15-4.31 (m, 6H), 3.78-4.05 (m, 6H), 3.34 (s, 3H), 3.19-3.70 (m, 16H), 3.04 (br s, 2H), 2.65 (br s, 1H), 1.69 (t, \(J = 11.5\) Hz, 1H); \(^{13}\)C NMR (500 MHz, D\(_2\)O) \(\delta: 175.9, 174.1, 138.3, 138.2, 137.5, 128.8, 128.4, 128.3, 127.8, 126.7, 104.2, 103.2, 100.0, 83.9, 81.8, 77.8, 76.0, 75.3, 75.0, 74.7, 74.2, 72.8, 71.9, 69.2, 68.4, 68.3, 67.9, 67.6, 67.3, 62.4, 61.2, 60.6, 57.7, 51.7, 50.7, 39.9.**

ESIHRMS calcd for C\(_{45}\)H\(_{58}\)NO\(_{20}\) [M-H]: 932.3552. found 932.3596.

![Glucopyranoside (12d)](image)

**5-(2-Hydroxyacetamido)-3,5-di-deoxy-\(\alpha\,\beta\)-glycero-\(\alpha\,\beta\)-galacto-non-2-ulopyranosylonic acid-(2→3)-\(\beta\,\alpha\)-galactopyranosyl-(1→6)-methyl 2-azido-3,4-di-O-benzyl-\(\alpha\,\beta\)-glucopyranoside (12e).** \([\alpha]^{25}_D +19.0\) (c, 1.0, CH\(_3\)OH/H\(_2\)O, v/v, 1:1); \(^1\)H NMR (500 MHz, CD\(_3\)OD) \(\delta: 7.26-7.34\) (m, 10H), 4.78-4.82 (m, 5H), 4.32 (d, \(J = 8.0\) Hz, 1H), 4.11 (d, \(J = 11.0\) Hz, 1H), 4.02-4.04 (m, 2H), 3.53-3.93 (m, 16H), 3.41 (s, 3H), 3.38-3.47 (m, 2H), 2.86 (dd, \(J = 4.0, 12.5\) Hz, 1H), 1.73 (t, \(J = 12.0\) Hz, 1H); \(^{13}\)C NMR (500 MHz, CD\(_3\)OD) \(\delta: 176.1, 173.9, 138.7, 138.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 104.2, 99.8, 99.0, 80.2, 78.4, 76.7, 75.4, 74.8, 73.52, 73.46, 71.7, 70.9, 69.5, 68.5, 68.3, 68.0, 67.8, 67.7, 63.5, 63.0, 61.6, 61.4, 54.6, 52.5, 51.5, 41.1.**

ESIHRMS calcd for C\(_{38}\)H\(_{51}\)N\(_4\)O\(_{19}\) [M-H]: 867.3148. found 867.3130.
Methyl 7,8,9-tri-O-acetyl-5-N,4-O-carbonyl-3,5-dideoxy-d-glycero-α/β-D-galacto-non-2-ulopyranosylonate-(2→3)-4-chlorophenyl 2,6-di-O-benzoyl-1-thio-β-D-Galactopyranoside (16). A mixed solution of donor 3 (60 mg, 0.1 mmol), acceptor 6 (63 mg, 0.12 mmol) and activated powdered AW-300 molecular sieves (200 mg) in mixed anhydrous CH₂Cl₂/CH₃CN (3 mL, v/v, 2:1) was cooled to -78 °C under a nitrogen atmosphere. NIS (27 mg, 0.12 mmol) was added, followed by TfOH (1.8 μL, 0.02 mmol). The reaction mixture was stirred at -78 °C for 40 min and quenched by pouring the mixture into aq NaHCO₃ solution, diluted with CH₂Cl₂, and filtered through Celite. The organic layer was separated, washed with 20% Na₂S₂O₃ solution, brine, dried and concentrated. Both ¹H NMR and ¹³C NMR of the crude reaction mixture indicated that product was formed in 1:1 α/β ratio. Purification by column chromatography on silica gel (hexane/ethyl acetate, v/v, 1:1) gave the desired products 16 (58 mg, 61%) as an inseparable 1:1 α/β mixture. ¹H NMR (500 MHz, CDCl₃) δ: 8.03-8.12 (m, 8H), 7.60-7.65 (m, 4H), 7.47-7.52 (m, 8H), 7.37-7.39 (m, 4H), 7.12 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 5.57 (ddd, J = 3.5, 4.0, 10.0 Hz, 1H), 5.46 (dt, J = 2.0, 6.5 Hz, 1H), 5.39 (t, J = 9.0 Hz, 1H), 5.36 (t, J = 10.0 Hz, 1H), 5.26 (d, J = 9.5 Hz, 2H), 5.10 (dd, J = 2.0, 5.5 Hz, 1H), 5.04 (dd, J = 2.0, 10.0 Hz, 1H), 4.92 (d, J = 9.5 Hz, 1H), 4.80 (d, 10.5 Hz, 1H), 4.59-4.70 (m, 5H), 4.48 (dd, 3.5, 9.5 Hz, 1H), 4.30-4.37 (m, 2H), 4.18-4.24 (m, 2H), 4.10-4.15 (m, 2H), 3.93-4.04 (m, 4H), 3.77-3.83 (m, 1H), 3.73 (s, 3H), 3.71 (d, J = 3.5 Hz, 1H), 3.58 (s, 3H), 2.98 (t, J = 10.5 Hz, 1H), 2.32-2.45 (m, 8H), 2.12-2.19 (m, 4H), 1.98-2.04 (m, 4H), 1.87-1.94 (m, 4H), 1.78-1.83 (m, 4H).
2.88 (dd, $J = 3.5, 12.5$ Hz, 1H), 2.84 (t, $J = 10.0$ Hz, 1H), 2.62 (dd, $J = 3.5, 12.5$ Hz, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.99 (t, $J = 13.0$ Hz, 1H), 1.96 (t, $J = 13.0$ Hz, 1H), 1.58 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 171.3, 171.0, 170.8, 170.6, 170.5, 170.1, 168.5, 166.6, 166.2, 165.4, 165.0, 158.9, 134.3, 134.2, 134.03, 134.96, 133.7, 133.4, 130.8, 130.7, 130.0, 129.9, 129.70, 129.6, 129.3, 128.93, 128.99, 128.7, 128.6, 128.5, 99.9, 98.3, 86.1, 77.4, 76.3, 75.9, 75.6, 75.0, 73.7, 73.2, 70.6, 69.0, 68.7, 68.4, 68.3, 67.2, 66.4, 64.1, 63.5, 62.2, 61.9, 57.8, 57.5, 53.2, 53.0, 36.9, 35.9, 21.1, 20.9, 20.69, 20.67, 20.6, 20.1. ESIHRMS calcd for C$_{43}$H$_{44}$ClNO$_{18}$Na [M+Na]$^+$: 952.1865. found 952.1907.

References:

(2) Catelani, G; Colonna, F; Marra, A. Carbohydr. Res. 1988, 182, 297-300.
3, $^1$H NMR (400 MHz, CDCl$_3$)
3, $^{13}$C NMR (100 MHz, CDCl$_3$)
4, $^1$H NMR (500 MHz, CDCl₃)
$4,^{13}\text{C} \text{ NMR} \ (125 \text{ MHz}, \text{CDCl}_3)$
5a,^1^H NMR (500 MHz, CDCl₃)
5a, $^{13}$C NMR (125 MHz, CDCl$_3$)
5b, $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$5c$, $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$5d, \ ^1H\ NMR\ (500\ MHz,\ CDCl_3)$
$^{13}$C NMR (125 MHz, CDCl$_3$)

5d, $^{13}$C NMR (125 MHz, CDCl$_3$)
$15\alpha,^1H$ NMR (500 MHz, CD$_3$OD)
$\text{H}_2\text{N}$

$\text{H}_2\text{O}$

$\text{CO}_2\text{H}$

$\text{O}$

$\text{HO}^{-}$

$\text{OBn}$

$\text{OMe}$

$15\alpha,^{13}\text{C NMR (125 MHz, CD}_3\text{OD)}$
$15\beta, {^1}\text{H NMR (500 MHz, CD}_3\text{OD)}$
$15\beta, {^{13}}C$ NMR (125 MHz, CD$_3$OD)
$\alpha$, $^1$H NMR (400 MHz, CDCl$_3$)
5f_α,\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})
$5f_\beta$, $^1$H NMR (400 MHz, CDCl$_3$)
$^1{\text{H}}$ NMR (100 MHz, CDCl$_3$)

5f, $^1{\text{C}}$ NMR (100 MHz, CDCl$_3$)
13, $^1$H NMR (500 MHz, CDCl$_3$)
$^{13,13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{14,13}$C NMR (125 MHz, CDCl$_3$)
S54

6, $^1$H NMR (500 MHz, CDCl$_3$)
$^6,^{13}C$ NMR (125 MHz, CDCl$_3$)
7, $^1$H NMR (500 MHz, CDCl$_3$)
$7$, $^{13}$C NMR (125 MHz, CDCl$_3$)
8, $^1$H NMR (500 MHz, CDCl$_3$)
8. $^{13}$C NMR (125 MHz, CDCl$_3$)
9, $^1$H NMR (500 MHz, CDCl$_3$)
9, $^{13}$C NMR (125 MHz, CDCl$_3$)
10, $^1$H NMR (500 MHz, CDCl$_3$)
10, $^{13}$C NMR (125 MHz, CDCl$_3$)
11, $^1$H NMR (500 MHz, CDCl$_3$)
11, $^{13}$C NMR (125 MHz, CDCl$_3$)
12a, \(^1\)H NMR (500 MHz, CD\(_3\)OD)
12a, $^{13}$C NMR (125 MHz, CD$_3$OD)
$^{1}$H NMR (500 MHz, CD$_3$OD)
12b, $^{13}$C NMR (125 MHz, CD$_3$OD)
12c, $^1$H NMR (500 MHz, CD$_3$OD)
12c, $^{13}$C NMR (125 MHz, CD$_3$OD)
12d, $^1$H NMR (500 MHz, D$_2$O)
$\text{12d, } ^{13}\text{C NMR (125 MHz, } \text{D}_2\text{O)}$
12e, $^1$H NMR (500 MHz, CD$_3$OD)
12e, $^{13}$C NMR (125 MHz, CD$_3$OD)
\[ \text{HN} \quad \text{O} \quad \text{CO}_2\text{Me} \quad \text{O} \quad \text{AcO} \quad \text{AcO} \quad \text{O} \quad \text{OBz} \quad \text{OBz} \quad \text{O} \quad \text{S}(p-\text{ClPh}) \]

16 \( \alpha/\beta = 1:1 \) mixture

\(^1\text{H} \text{NMR (500 MHz, CDCl}_3\))
$\text{HN} \quad \text{O} \quad \text{CO}_2\text{Me} \quad \text{O} \quad \text{AcO} \quad \text{AcO} \quad \text{OAc} \quad \text{HO} \quad \text{OBz} \quad \text{OBz} \quad \text{S}(p\text{-ClPh})$

$^{13}\text{C NMR (125 MHz, CDCl}_3)$

$16 \ \alpha/\beta = 1:1 \ \text{mixture}$