Supporting information

for

Perfluorophenylboronic Acid-Catalyzed Direct α-Stereoselective Synthesis of 2-Deoxygalactosides from Deactivated Peracetylated D-Galactal

Madhu Babu Tatina, a Ziad Moussa, b Xia Mengxin, a Zaher M. A. Judeh a, *

1 School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, N1.2–B1-14, Singapore 637459

* Indicates the main/corresponding author

Tel.: +65-6790-6738; fax: +65-6794-7553; e-mail: zaher@ntu.edu.sg

2 Department of Chemistry, College of Science, United Arab Emirates University, Al Ain, United Arab Emirates, P.O.Box 15551

Experimental data and copies of 1H and 13C NMR spectra of glycosides 4a-o, 6a–11a, and 12 are provided

[a] Madhu Babu Tatina, Ziad Moussa, Xia Mengxin, Zaher M. A. Judeh*
School of Chemical and Biomedical Engineering
Nanyang Technological University
Singapore, 62 Nanyang Drive, N1.2–B1-14, Singapore 637459
E-mail: zaher@ntu.edu.sg

[b] Ziad Moussa,
Department of Chemistry, College of Science,
United Arab Emirates University,
Al Ain, United Arab Emirates, P.O.Box 15551
Supporting information for this article is given via a link at the end of the document.
Table of contents

1. Materials and methods

2. General procedure for the synthesis of compounds 4a-o and 6a–11a

3. $^1$H NMR and $^{13}$C NMR spectra of glycosides 4a-o, 6a–11a, and 12
1. Materials and methods

Chemical reagents were purchased from Sigma-Aldrich or Alfa Aesar and were used as received without further purification. $^1$H NMR spectra were recorded at 300 MHz on a Bruker Avance DPX 300. $^{13}$C NMR spectra were recorded at 75.47 MHz on a Bruker Avance DPX 300. Unless stated otherwise, data refer to solutions in CDCl$_3$ with TMS as an internal reference. HRMS were recorded on a Qstar XL MS/MS system. Analytical TLC was performed using Merck 60 F254 precoated silica gel plates (0.2 mm thickness) and visualized using UV radiation (254 nm) or stained using ceric ammonium nitrate in 30% H$_2$SO$_4$ solution. Flash chromatography was performed using Merck silica gel 60 (60–120 mesh).

2 General procedure for the synthesis of 2-deoxy galactosides 4a-o and 6a-11a, and 12

2.1 Benzyl 3,4,6-tri-$O$-acetyl-2-deoxy-D-galactopyranoside (4a)$^1$

Prepared by the general procedure using 3,4,6-tri-$O$-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and benzyl alcohol 3 (0.4 mmol, 42 µl). Column chromatography purification using EtOAc:Hexane (2:8) gave 4a as colorless liquid (123 mg, 88%). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.46 – 7.30 (m, 5H), 5.37-5.36 (m, 2H), 5.12 (d, $J = 3.1$ Hz, 1H), 4.71 (d, $J = 11.8$ Hz, 1H), 4.52 (d, $J = 11.8$ Hz, 1H), 4.22 (d, $J = 11.8$ Hz, 1H), 4.12 (d, $J = 6.5$ Hz, 1H), 4.12 (d, $J = 6.5$ Hz, 1H), 2.16 (s, 3H), 2.13 – 2.11 (m, 1H), 2.08 (s, 3H), 2.00 (s, 3H), 1.97 – 1.90 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.5, 170.3, 170.0, 137.1, 128.5,128.0,127.9, 96.5, 69.2, 66.8, 66.7, 66.2, 62.4, 30.1, 20.8, 20.76, 20.74. HRMS (ESI$^+$): m/z [M + H]$^+$ calcld for C$_{19}$H$_{25}$O$_8$:381.1549; found: 381.1558.

2.2 2-phenyl ethyl 3,4,6-tri-$O$-acetyl-2-deoxy-D-galactopyranoside (4b)

Prepared by the general procedure using 3,4,6-tri-$O$-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 2-phenylethanol (0.4 mmol, 49 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4b as white solid (104 mg, 72%). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.37 – 7.14 (m, 5H), 5.25 (t, $J = 5.0$ Hz, 2H), 5.00 (d, $J = 2.7$ Hz, 1H), 4.00 (d, $J = 6.5$ Hz, 2H), 3.90 – 3.74 (m, 2H), 3.68 (dd, $J = 11.3$, 4.8 Hz, 1H), 2.91 (t, $J = 6.8$ Hz, 2H), 2.13 (s, 3H), 2.09 (dd, $J = 7.9$, 6.1 Hz, 1H), 2.05 (s, 3H), 2.01 (d, $J = 3.6$ Hz, 3H), 1.91 – 1.82 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.5, 170.3, 170.0, 137.1, 128.5,128.0,127.9, 96.5, 69.2, 66.8, 66.7, 66.2, 62.4, 30.1, 20.8, 20.76, 20.74. HRMS (ESI$^+$): m/z [M + H]$^+$ calcld for C$_{20}$H$_{27}$O$_8$:395.1549; found: 395.1536.
2.3 Cyclohexyl 3,4,6-tri-O-acyl-2-deoxy-D-galactopyranoside (4c)

Prepared by the general procedure using 3,4,6-tri-O-acyetyl-D-galactal (0.34 mmol, 100 mg) and cyclohexanol (0.4 mmol, 42 µl). Column chromatography purification using EtOAc:Hexane (2:8) gave 4c as colorless liquid (102 mg, 75%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 5.32 (dd, \(J = 11.0, 4.2\) Hz, 2H), 5.17 (d, \(J = 3.0\) Hz, 1H), 4.23 (d, \(J = 6.5\) Hz, 1H), 4.09 (dd, \(J = 6.5, 2.5\) Hz, 1H), 2.14 (s, 3H), 2.08 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.91 – 1.81 (m, 2H), 1.73 (bs, 3H), 1.53 (bs, 1H), 1.41 – 1.19 (m, 5H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 170.5, 170.4, 170.1, 95.5, 75.4, 66.8, 66.6, 66.4, 62.6, 31.5, 30.74, 25.5, 24.2, 23.9, 20.8, 20.7, 20.6. HRMS (ESI\(^+\)): m/z [M + H]\(^+\) calcd for C\(_{18}\)H\(_{29}\)O\(_8\): 373.1862; found: 373.1880.

2.4 O-[3,4,6-Tri-O-acyetyl-2-deoxy-D-galactopyranosyl]-N-carbobenzyloxy-L-serine methyl ester (4d)

Prepared by the general procedure using 3,4,6-tri-O-acyetyl-D-galactal (0.34 mmol, 100 mg) and \(N\)-(tert-butoxycarbonyl)-L-serine methyl ester (0.4 mmol, 42 µl). Column chromatography purification using EtOAc:Hexane (4:6) gave 4d as colorless liquid (162 mg, 84%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.37 (m, 5H), 5.76 (d, \(J = 8.3\) Hz, 1H), 5.33 (d, \(J = 2.7\) Hz, 1H), 5.26 – 5.10 (m, 4H), 4.99 (d, \(J = 3.0\) Hz, 1H), 4.64 – 4.48 (m, 1H), 4.12-4.05 (m, 3H), 3.94 (bs, 2H), 3.79 (s, 3H), 2.14 (s, 3H), 2.09 – 2.06 (m, 1H), 2.04 (s, 3H), 1.99 (s, 3H), 1.84 (dd, \(J = 12.8, 5.1\) Hz, 1H) \(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 170.5, 170.4, 170.2, 170.1, 95.5, 75.4, 66.8, 66.6, 66.4, 62.6, 31.5, 30.74, 25.5, 24.2, 23.9, 20.8, 20.7, 20.6. HRMS (ESI\(^+\)): m/z [M + H]\(^+\) calcd for C\(_{18}\)H\(_{29}\)O\(_8\): 373.1862; found: 373.1880.

2.5 tert-butyl 3,4,6-tri-O-acyetyl-2-deoxy-D-galactopyranoside (4e)

Prepared by the general procedure using 3,4,6-tri-O-acyetyl-D-galactal (0.34 mmol, 100 mg) and \(t\)-butanol (0.4 mmol, 38 µl). Column chromatography purification using EtOAc:Hexane (2:8) gave 4e as colorless liquid (95 mg, 75%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 5.35-5.32 (m, 3H), 4.33 (t, \(J = 6.4\) Hz, 1H), 4.07 (dd, \(J = 6.6, 2.8\) Hz, 2H), 2.14 (s, 3H), 2.08 (ddd, \(J = 12.6, 6.4, 2.7\) Hz, 1H), 2.04 (s, 3H), 1.99 (s, 3H), 1.76 – 1.65 (m, 1H), 1.25 (s, 9H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 170.5, 170.4, 170.2, 170.0, 136.1, 128.5, 128.2, 128.1, 98.2, 68.4, 67.2, 67.1, 66.4, 65.8, 62.4, 54.3, 52.7, 29.9, 20.8, 20.6.

2.6 phenoxy 3,4,6-tri-O-acyetyl-2-deoxy-D-galactopyranoside (4f)

Prepared by the general procedure using 3,4,6-tri-O-acyetyl-D-galactal (0.34 mmol, 100 mg) and phenol (0.4 mmol, 38 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4f as cream solid (105mg, 78%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.39 – 7.23 (m, 2H), 7.05 (m, 3H), 5.77 (d, \(J = 2.7\) Hz, 1H), 5.53 (ddd, \(J = 12.3, \)
5.1, 3.1 Hz, 1H), 5.42 (d, J = 2.6 Hz, 1H), 4.28 (t, J = 6.6 Hz, 1H), 4.09 (dd, J = 6.6, 2.5 Hz, 2H), 2.28 (td, J = 12.6, 3.5 Hz, 1H), 2.18 (s, 3H), 2.16 – 2.11 (m, 1H), 2.04 (s, 3H), 1.94 (s, 3H). 13C NMR (75 MHz, CDCl3) δ 170.4, 170.3, 170.1, 156.3, 129.5, 122.3, 116.4, 95.8, 67.5, 66.4, 66.0, 62.0, 30.2, 20.9, 20.7, 20.6. HRMS (ESI⁺): m/z [M + H]⁺ calcd for C18H23O8:367.1393; found: 367.1407.

2.7 3-methylphenoxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4g)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 136 mg) and m-cresol (0.4 mmol, 44 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4g as colorless liquid (98 mg, 70%). 1H NMR (300 MHz, CDCl3) δ 7.25 – 7.04 (m, 1H), 6.91 – 6.81 (m, 3H), 5.75 (d, J = 2.8 Hz, 1H), 5.52 (ddd, J = 12.3, 5.1, 3.1 Hz, 1H), 5.42 (d, J = 2.8 Hz, 1H), 4.29 (t, J = 6.4 Hz, 1H), 4.15 – 4.06 (m, 2H), 2.35 (s, 3H), 2.25 (dd, J = 12.5, 3.5 Hz, 1H), 2.18 (s, 3H), 2.05 (s, 3H), 1.95 (s, 3H). 13C NMR (75 MHz, CDCl3) δ 170.4, 170.3, 170.1, 156.3, 139.5, 123.1, 117.2, 113.3, 95.8, 67.5, 66.5, 66.0, 62.1, 30.2, 21.5, 20.9, 20.7, 20.6. HRMS (ESI⁺): m/z [M + H]⁺ calcd for C19H25O8: 381.1549; found: 381.1558.

2.8 4-methylphenoxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4h)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and p-cresol (0.4 mmol, 44 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4h as colorless liquid (112 mg, 80%). 1H NMR (300 MHz, CDCl3) δ 7.10 (d, J = 8.5 Hz, 2H), 6.98 (t, J = 5.6 Hz, 2H), 5.71 (d, J = 2.7 Hz, 1H), 5.52 (ddd, J = 12.3, 5.1, 3.1 Hz, 1H), 5.41 (d, J = 2.5 Hz, 1H), 4.38 – 4.21 (m, 1H), 4.19 – 3.99 (m, 2H), 2.31 (s, 3H), 2.24 (dd, J = 12.5, 3.5 Hz, 1H), 2.18 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H). 13C NMR (75 MHz, CDCl3) δ 170.4, 170.3, 170.1, 154.2, 131.7, 129.9, 116.4, 96.0, 67.4, 66.5, 66.0, 62.0, 30.3, 20.9, 20.7, 20.6. HRMS (ESI⁺): m/z [M+H]⁺ calcd for C19H25O8:381.1549; found: 381.1556.

2.9 4-tert-butylphenoxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4i)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 4-tert-butylphenol (0.4 mmol, 60 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4i as white solid (133 mg, 86%). 1H NMR (300 MHz, CDCl3) δ 7.35 – 7.22 (m, 2H), 7.01 (d, J = 8.8 Hz, 2H), 5.74 (d, J = 2.8 Hz, 1H), 5.53 (ddd, J = 12.3, 5.1, 3.1 Hz, 1H), 5.42 (d, J = 2.5 Hz, 1H), 4.40 – 4.22 (m, 1H), 4.17 – 4.01 (m, 2H), 2.26 (tt, J = 9.4, 4.7 Hz, 1H), 2.18 (s, 3H), 2.11 (dd, J = 12.7, 5.1 Hz, 1H), 2.05 (s, 3H), 1.94 (s, 3H), 1.32 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 170.4, 170.3, 170.1, 154.2, 131.7, 129.9, 116.4, 96.0, 67.4, 66.5, 66.0, 62.0, 30.3, 20.9, 20.7, 20.6.
2.10 4-methoxyphenoxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4j)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 4-methoxyphenol (0.4 mmol, 50 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4j as cream solid (102 mg, 70%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.01 (d, $J = 9.1$ Hz, 2H), 6.84 (d, $J = 9.1$ Hz, 2H), 5.64 (d, $J = 2.7$ Hz, 1H), 5.50 (dd, $J = 12.6, 3.5$ Hz, 1H), 2.17 (s, 3H), 2.15 – 2.07 (m, 1H), 2.04 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.4, 170.3, 170.0, 155.0, 150.3, 117.8, 114.5, 96.6, 67.4, 66.5, 66.0, 62.1, 55.6, 30.3, 20.8, 20.7, 20.6. HRMS (ESI$^+$): m/z [M+H]$^+$ calcd for C$_{19}$H$_{24}$O$_9$: 397.1449; found: 397.1490.

2.11 3,5-methoxyphenoxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4k)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 3,5-dimethoxyphenol (0.4 mmol, 62 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4k as cream solid (117 mg, 75%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.28 (d, $J = 2.2$ Hz, 2H), 6.17 (d, $J = 2.2$ Hz, 1H), 5.72 (d, $J = 2.6$ Hz, 1H), 5.61 – 5.44 (m, 1H), 5.40 (d, $J = 2.8$ Hz, 1H), 4.26 (t, $J = 6.4$ Hz, 1H), 4.16 – 4.07 (m, 2H), 3.77 (s, 6H), 2.26 (td, $J = 12.7, 3.5$ Hz, 1H), 2.17 (s, 3H), 2.14 – 2.10 (m, 1H), 2.04 (s, 3H), 1.96 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5, 170.3, 170.0, 155.0, 150.3, 117.8, 114.5, 96.6, 67.4, 66.5, 66.0, 62.1, 55.3, 30.2, 20.8, 20.7, 20.5. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for C$_{20}$H$_{27}$O$_{10}$: 427.1604; found: 427.1632.

2.12 3-methoxyphenoxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4l)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 3-methoxyphenol (0.4 mmol, 62 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4l as cream solid (107 mg, 74%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.20 (t, $J = 8.1$ Hz, 1H), 6.76 – 6.53 (m, 3H), 5.75 (d, $J = 2.7$ Hz, 1H), 5.52 (dd, $J = 12.3, 5.1, 3.0$ Hz, 1H), 5.42 (s, 1H), 4.28 (t, $J = 6.5$ Hz, 1H), 4.10 (d, $J = 6.5$ Hz, 2H), 3.81 (s, 3H), 2.27 (td, $J = 12.6, 3.5$ Hz, 1H), 2.18 (s, 3H), 2.14 – 2.08 (m, 1H), 2.10 – 2.00 (m, 3H), 1.96 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5, 170.3, 170.1, 157.5, 152.9, 108.6, 108.0, 102.8, 95.8, 95.2, 94.6, 67.5, 66.4, 66.0, 62.0, 55.3, 30.2, 20.9, 20.7, 20.5. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for C$_{19}$H$_{25}$O$_9$: 397.1499; found:397.1499.

2.13 Naphthalen-2-yloxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4m)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 2-naphthol (0.4 mmol, 50 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4m as green solid (117 mg, 75%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.60 – 7.10 (m, 7H), 7.06 (d, $J = 7.8$ Hz, 1H), 7.04 (d, $J = 7.8$ Hz, 1H), 6.75 (d, $J = 7.8$ Hz, 2H), 6.70 (d, $J = 7.8$ Hz, 2H), 5.38 (s, 3H), 4.28 (t, $J = 6.5$ Hz, 1H), 4.10 (d, $J = 6.5$ Hz, 2H), 3.81 (s, 3H), 2.27 (td, $J = 12.6, 3.5$ Hz, 1H), 2.18 (s, 3H), 2.14 – 2.08 (m, 1H), 2.10 – 2.00 (m, 3H), 1.96 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5, 170.3, 170.1, 157.5, 152.9, 108.6, 108.0, 102.8, 95.8, 95.2, 94.6, 67.5, 66.4, 66.0, 62.0, 55.3, 30.2, 20.9, 20.7, 20.5. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for C$_{19}$H$_{25}$O$_9$: 397.1499; found:397.1499.
mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4m as cream solid (128 mg, 84%). 1H NMR (300 MHz, CDCl₃) δ 8.23 (dd, J = 6.0, 3.8 Hz, 1H), 7.92 – 7.76 (m, 1H), 7.59 – 7.49 (m, 3H), 7.39 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 5.96 (d, J = 2.3 Hz, 1H), 5.70 (ddd, J = 12.0, 5.5, 3.0 Hz, 1H), 5.48 (d, J = 2.7 Hz, 1H), 4.33 (t, J = 6.7 Hz, 1H), 4.12 (d, J = 6.6 Hz, 2H), 2.45–2.28 (m, 2H), 2.21 (s, 3H), 2.09 (s, 3H), 1.93 (s, 3H).

13C NMR (75 MHz, CDCl₃) δ 170.4, 170.3, 170.2, 151.9, 134.5, 127.6, 126.5, 125.74, 125.71, 122.0, 121.7, 108.3, 96.1, 67.8, 66.5, 66.2, 62.0, 30.5, 20.9, 20.7, 20.6.

2.14 4-fluorophenoxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4n)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal (0.34 mmol, 100 mg) and 4-fluorophenol (0.4 mmol, 45 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave 4n as cream solid (101 mg, 72%). 1H NMR (300 MHz, CDCl₃) δ 7.06 – 6.94 (m, 4H), 5.67 (d, J = 2.8 Hz, 1H), 5.50 (ddd, J = 12.3, 3.5 Hz, 1H), 2.27 (td, J = 12.6, 3.2 Hz, 1H), 2.18 (s, 3H), 2.12 (dd, J = 12.6, 5.7 Hz, 1H), 2.04 (s, 3H), 1.96 (s, 3H).

13C NMR (75 MHz, CDCl₃) δ 170.4, 170.3, 170.1, 159.8, 156.6, 152.4, 150.39, 117.8, 117.7, 116.0, 115.7, 96.4, 67.6, 66.4, 65.9, 62.1, 30.2, 20.8, 20.7, 20.6. HRMS (ESI⁺): m/z [M + H]⁺ caledd for C₁₈H₂₂O₈F:385.1299; found: 385.1282.

2.15 4-formylphenoxy 3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (4o)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal (0.34 mmol, 100 mg) and 4-hydroxybenzaldehyde (0.4 mmol, 49 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave 4o as colorless gummy liquid (81 mg, 56%). 1H NMR (300 MHz, CDCl₃) δ 9.92 (s, 1H), 7.86 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 5.87 (s, 1H), 5.50 (dd, J = 12.1, 3.8 Hz, 1H), 5.42 (s, 1H), 4.21 (t, J = 6.5 Hz, 1H), 4.08 (m, 2H), 2.31 (td, J = 12.7, 3.2 Hz, 1H), 2.18 (s, 3H), 2.12 (bs, 1H), 2.05 (s, 3H), 1.92 (s, 3H).

13C NMR (75 MHz, CDCl₃) δ 190.8, 170.2, 170.1, 159.7, 156.6, 152.4, 150.39, 117.8, 117.7, 116.0, 115.7, 96.4, 67.6, 66.4, 65.9, 62.1, 30.2, 20.8, 20.7, 20.5.

2.16 Methyl 2,3,4-tri-O-acetyl-6-O-(3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl)-α-D-glucopyranoside (6a)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal (0.34 mmol, 100 mg) and 2,3,4-tri-O-acetyl-methyl-α-D–glucopyranoside (0.4 mmol, 128 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave 6a as colorless liquid (126 mg, 58%). 1H NMR (300 MHz, CDCl₃) δ 5.49 (t, J = 9.7 Hz, 1H), 5.41 – 5.22 (m, 2H), 5.05 (dd, J = 11.1, 8.4 Hz, 2H), 4.99 – 4.84 (m, 2H), 4.21 – 4.03 (m, 3H), 3.96 (ddd, J = 10.2, 5.3, 2.3 Hz, 1H), 3.72 (ddd, J = 11.1, 5.4 Hz, 1H), 3.53 (ddd, J = 11.1, 2.4 Hz, 1H), 3.43 (s, 3H), 2.17 (d, J = 9.9 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.92 (dd, J = 12.8, 5.1 Hz, 1H).

13C NMR (75 MHz, CDCl₃) δ 170.5, 170.3, 170.1, 169.9, 169.7, 169.6, 97.3, 96.5, 70.8, 70.2, 69.1, 67.9, 66.8, 66.6, 66.0, 65.6, 62.5, 55.3,
29.9, 20.8, 20.7, 20.6. HRMS (ESI\(^+\)): m/z [M + H]\(^+\) calcd for C\(_{25}\)H\(_{37}\)O\(_{16}\): 593.2082; found: 593.2078.

2.17 Methyl 2,3,4-tri-O-benzoyl-6-O-(3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl)-a-D-glucopyranoside (7a)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 2,3,4-tri-O-benzoyl-methyl-\(\alpha\)-D-glucopyranoside (0.4 mmol, 202 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave 7a as colorless liquid (157 mg, 55%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.98 (dd, \(J = 10.6, 4.2\) Hz, 4H), 7.92 – 7.80 (m, 2H), 7.53 (t, \(J = 7.0\) Hz, 2H), 7.40 (m, 5H), 7.34 – 7.18 (m, 2H), 6.17 (t, \(J = 9.5\) Hz, 1H), 5.64 (t, \(J = 9.9\) Hz, 1H), 5.44 – 5.18 (m, 3H), 5.06 (d, \(J = 2.9\) Hz, 1H), 4.34 – 4.07 (m, 3H), 3.98 (dd, \(J = 6.4, 2.8\) Hz, 2H), 3.88 (dd, \(J = 11.0, 4.9\) Hz, 1H), 3.64 (dd, \(J = 10.9, 2.8\) Hz, 1H) 3.50 (s, 3H), 2.13 (s, 3H), 2.08 (d, \(J = 1.6\) Hz, 1H), 2.00 (s, 3H), 1.92 (s, 3H), 1.89 – 1.81 (m, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 170.4, 170.2, 169.9, 165.7, 165.2, 133.4, 133.3, 133.1, 129.9, 129.8, 129.7, 129.2, 129.06, 129.0, 128.48, 128.42, 128.2, 97.4, 97.0, 71.9, 70.4, 69.5, 68.2, 66.7, 66.6, 66.1, 66.0, 62.6, 55.6, 29.8, 20.9, 20.7, 20.6. HRMS (ESI\(^+\)): m/z [M + H]\(^+\) calcd for C\(_{40}\)H\(_{43}\)O\(_{16}\): 779.2551; found: 779.2577.

2.18 Phenyl 2,3,4-tri-O-acetyl-6-(3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl)-1-thio-\(\beta\)-D-glucopyranoside (8a)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 2,3,4-tri-O-acetyl-thio-\(\alpha\)-D-mannoside (0.4 mmol, 159 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave 8a as colorless liquid (152 mg, 62%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.37 (d, \(J = 8.1\) Hz, 2H), 7.17 (d, \(J = 8.0\) Hz, 2H), 5.32 – 5.16 (m, 3H), 5.02-4.92 (m, 2H), 4.71 (d, \(J = 10.0\) Hz, 1H), 4.24 (d, \(J = 5.7\) Hz, 1H), 4.15 – 4.03 (m, 3H), 3.80 – 3.63 (m, 2H), 3.63 – 3.53 (m, 1H), 2.36 (s,3H), 2.15 (s, 3H), 2.13 (bs, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.88 (dd, \(J = 12.6, 5.1\) Hz, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 170.5, 170.2, 169.9, 165.7, 165.2, 133.4, 133.3, 133.1, 129.9, 129.8, 129.7, 129.2, 129.06, 129.0, 128.48, 128.42, 128.2, 97.4, 97.0, 71.9, 70.4, 69.5, 68.2, 66.7, 66.6, 66.1, 66.0, 62.6, 55.6, 29.8, 20.9, 20.7, 20.6. HRMS (ESI\(^+\)): m/z [M + H]\(^+\) calcd for C\(_{40}\)H\(_{43}\)O\(_{15}\)S: 685.2166; found: 685.2178.

2.19 Phenyl 2,3,4-tri-O-acetyl-6-(3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl)-1-thio-\(\beta\)-D-mannopyranoside (9a)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 2,3,4-tri-O-acetyl-thio-\(\alpha\)-D-mannoside (0.4 mmol, 159 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave 9a as colorless liquid (157 mg, 64%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.38 (d, \(J = 8.0\) Hz,
2.20 Methyl 2,3-di-O-acetyl-5-O-(3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl)-α-D-ribofuranoside (10a)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 2,3-di-O-acetyl-methyl-α-D-ribofuranoside (0.4 mmol, 99 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave 10a as colorless liquid (114 mg, 60%). ¹H NMR (300 MHz, CDCl₃) δ 5.38-5.35 (m, 2H), 5.22 (d, J = 4.9 Hz, 1H), 4.92 (s, 1H), 4.28 – 4.18 (m, 2H), 3.79 (dd, J = 11.1, 4.6 Hz, 1H), 3.62 (dd, J = 10.7, 4.7 Hz, 1H), 3.40 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 2.09 (m, 1H), 2.00 (s, 3H), 1.92 (dd, J = 12.7, 5.2 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 170.5, 170.3, 169.9, 106.6, 97.9, 74.7, 71.8, 68.3, 66.8, 66.6, 66.0, 62.3, 55.3, 29.9, 20.8, 20.7, 20.6, 20.5. HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₂₂H₃₃O₁₄: 521.1870; found: 521.1876.

2.21 Methyl 2,3-di-O-acetyl-5-O-(3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranosyl)-α-D-arabinofuranoside (11a)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and 2,3-di-O-acetyl-methyl-α-D-arabinofuranoside (0.4 mmol, 99 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave 11a as colorless liquid (124 mg, 65%). ¹H NMR (300 MHz, CDCl₃) δ 5.36 (m, 2H), 5.10 (m, 3H), 4.93 (s, 1H), 4.27 (t, J = 6.5 Hz, 1H), 4.21 – 4.05 (m, 3H), 3.94 (dd, J = 11.1, 4.6 Hz, 1H), 3.75 (dd, J = 11.0, 3.3 Hz, 1H), 3.42 (s, 3H), 2.15 (s, 3H), 2.13 (br s, 1H), 2.12 (s, 3H), 2.08 (s, 6H), 2.00 (s, 3H), 1.92 (dd, J = 12.5, 5.1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 170.5, 170.3, 169.9, 169.9, 169.7, 106.6, 97.7, 81.6, 81.3, 68.3, 66.8, 66.6, 66.0, 62.3, 55.3, 29.9, 20.8, 20.7, 20.6, 20.7. HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₂₂H₃₃O₁₄: 521.1870; found: 521.1871.

2.22 Trideuteromethyl-3,4,6-tri-O-acetyl-2-deoxy-D-galactopyranoside (12)

Prepared by the general procedure using 3,4,6-tri-O-acetyl-D-galactal 2 (0.34 mmol, 100 mg) and CD₃OD (0.4 mmol, 17 µl). Column chromatography purification using EtOAc:Hexane (2:8) gave 12 as
white solid (96 mg, 85%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.35 – 5.21 (m, 2H), 4.90 (d, $J$ = 3.2 Hz, 1H), 4.11 (m, 3H), 2.14 (s, 3H), 2.05 (s, 3H), 2.0 (dd, $J$ = 12.0, 3.0 Hz, 1H), 1.98 (s, 3H), 1.88-184 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5, 170.3, 170.0, 98.4, 66.6, 66.5, 66.1, 62.5, 30.0, 20.8, 20.7.

References


3. Spectral images of compounds 4a-n, 6a-11a, and 12

$^1$H NMR of compound 4a

$^{13}$C NMR of compound 4a
$^1$H NMR of compound 4b

$^{13}$C NMR of compound 4b
$^1$H NMR of compound 4c

$^{13}$C NMR of compound 4c
$^1$H NMR of compound 4d

$^{13}$C NMR of compound 4d
$^1$H NMR of compound 4e

$^{13}$C NMR of compound 4e
$^1$H NMR of compound 4f

$^{13}$C NMR of compound 4f
$^1$H NMR of compound 4g

$^{13}$C NMR of compound 4g
$^1$H NMR of compound 4h

$^{13}$C NMR of compound 4h
$^1$H NMR of compound 4i

$^{13}$C NMR of compound 4i
\(^1\text{H}\) NMR of compound 4j

\(^{13}\text{C}\) NMR of compound 4j
$^1$H NMR of compound 4k

$^{13}$C NMR of compound 4k
^1H NMR of compound 4l

\[ \text{Proton NMR spectrum of compound 4l} \]

^13C NMR of compound 4l

\[ \text{Carbon NMR spectrum of compound 4l} \]
$^1$H NMR of compound 4m

$^{13}$C NMR of compound 4m
$^1$H NMR of compound 4n

$^{13}$C NMR of compound 4n
$^{1}H$ NMR of compound 4o

$^{13}C$ NMR of compound 4o
$^1$H NMR of compound 6a

$^{13}$C NMR of compound 6a
$^1$H NMR of compound 7a

$^{13}$C NMR of compound 7a
$^1$H NMR of compound 8a

$^{13}$C NMR of compound 8a
$^1$H NMR of compound 9a

$^{13}$C NMR of compound 9a
$^1$H NMR of compound 10a

$^{13}$C NMR of compound 10a
$^1$H NMR of compound 11a

$^{13}$C NMR of compound 11a
$^1$H NMR of compound 12

$^{13}$C NMR of compound 12
DEPT of compound 12

$^1$H NMR of compound 2-deoxy methyl galactoside