

Supporting Information for

AuBr₃-catalyzed azidation of per-*O*-acetylated and per-*O*-benzoylated sugars

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Plausible catalytic cycle, experimental data and copies of ¹H and ¹³C NMR spectra of glycosyl azides 1–15 were provided

Contents	Page
Plausible catalytic cycle	S2
Experimental data of compounds 1–15	S3
References	S8
¹ H, ¹³ C, NMR spectra of compounds 1–9	S9
¹ H, ¹³ C, NMR spectra of compounds 10–15	S27

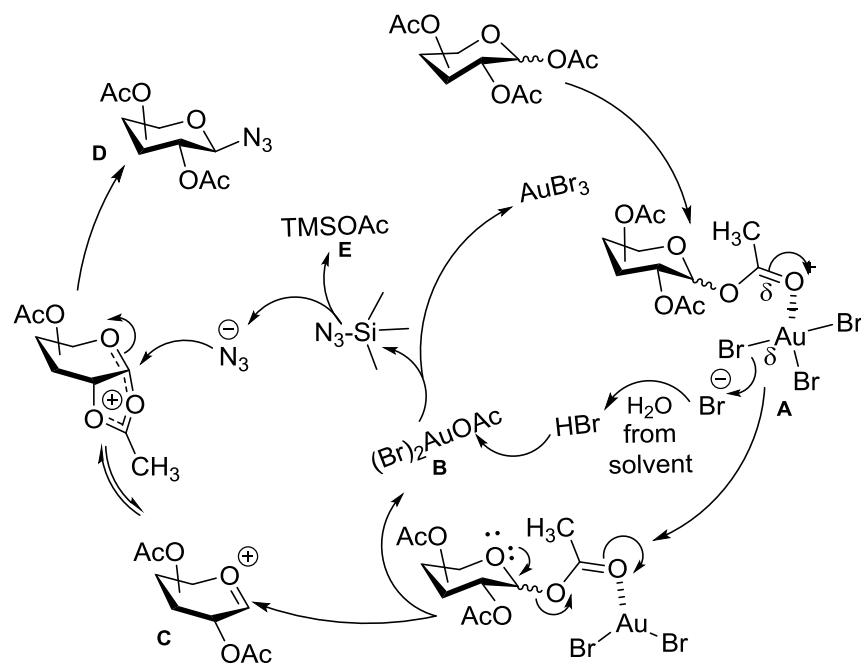


Figure S1: Plausible mechanism for AuBr_3 -catalyzed azido glycosidation

Experimental data of compounds 1–15

2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosyl azide (1).¹ White solid: R_f =0.5(EtOAc:hexane 45:55); m.p. 124-125 °C (lit. m.p. 127 °C); $[\alpha]_D^{25}$ -33.0 (c 0.53, CHCl₃); IR (CHCl₃) ν 2113, 1747, 1214, 1036 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.22 (t, J = 9.5 Hz, 1H), 5.10 (t, J = 9.7 Hz, 1H), 4.95 (t, J = 9.2 Hz, 1H), 4.64 (d, J = 8.9 Hz, 1H), 4.27 (dd, J = 12.5, 4.8 Hz, 1H), 4.17 (dd, J = 12.5, 2.3 Hz, 1H), 3.79 (ddd, J = 10.0, 4.8, 2.3 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 170.1, 169.3, 169.2, 87.9, 74.1, 72.6, 70.7, 67.9, 61.7, 20.7, 20.5 (3 X COCH₃); HRMS (TOF): $[M + Na]^+$ calcd for C₁₄H₁₉O₉N₃Na 396.1019, found 396.1022.

2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl azide (2).¹ White solid: R_f =0.4(EtOAc:hexane 35:65); m.p. 93-95 °C (lit. m.p. 95-97 °C); $[\alpha]_D^{25}$ -16.2 (c 0.34, CHCl₃); IR (CHCl₃) ν 2114, 1742, 1208, 1049 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.41 (dd, J = 3.2, 0.7 Hz, 1H), 5.15 (dd, J = 10.4, 8.7 Hz, 1H), 5.02 (dd, J = 10.3, 3.4 Hz, 1H), 4.59 (d, J = 8.7 Hz, 1H), 4.20 – 4.11 (m, 2H), 4.03-3.98 (m, 1H), 2.16 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 170.2, 170.1, 169.5, 88.4, 73.0, 70.8, 68.1, 66.9, 61.3, 20.8, 20.7, 20.7, 20.6; HRMS (TOF): $[M + Na]^+$ calcd for C₁₄H₁₉O₉N₃Na 396.1019, found 396.1032.

2,3,4,6-Tetra-O-acetyl- α -D-mannopyranosyl azide (3).¹ Thick liquid: R_f =0.5(EtOAc:hexane 35:65); $[\alpha]_D^{25}$ +124.3 (c 0.41, CHCl₃); IR (CHCl₃) ν 2116, 1742, 1207, 1045 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.38 (d, J = 1.8 Hz, 1H), 5.30 – 5.21 (m, 2H), 5.14 (dd, J = 2.8, 2.0 Hz, 1H), 4.29 (dd, J = 12.4, 5.5 Hz, 1H), 4.18-4.11 (m, 2H), 2.15 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 169.9, 169.8, 169.7, 87.6, 70.7, 69.2, 68.3, 65.7, 62.2, 20.9, 20.8, 20.7, 20.7; HRMS (TOF): $[M + Na]^+$ calcd for C₁₄H₁₉O₉N₃Na 396.1019, found 396.1019.

2,3,5-Tri-O-acetyl- β -D-xylopyranosyl azide (4).¹ Thick liquid: $R_f=0.4$ (EtOAc:hexane 25:75); IR (CHCl₃) ν 2114, 1743, 1204, 1066 cm⁻¹; $[\alpha]_D^{25} +92.0$ (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 5.17 (t, J = 8.9 Hz, 1H), 4.96 (td, J = 9.2, 5.3 Hz, 1H), 4.85 (t, J = 8.5 Hz, 1H), 4.62 (d, J = 8.1 Hz, 1H), 4.19 (dd, J = 11.7, 5.3 Hz, 1H), 3.42 (dd, J = 11.7, 9.6 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 170.1, 169.8, 169.4, 88.4, 71.6, 70.4, 68.5, 64.3, 20.7, 20.7, 20.6; HRMS (TOF): $[M + Na]^+$ calcd for C₁₁H₁₅O₇N₃Na 324.0808, found 324.0813.

2,3,4-Tri-O-acetyl- β -L-fucopyranosyl azide (5). White solid: $R_f=0.5$ (EtOAc:hexane 30:70); m.p. 101-103 °C; $[\alpha]_D^{25} +35.3$ (c 0.77, CHCl₃); IR (CHCl₃) ν 2111, 1742, 1210, 1055 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (major isomer) 5.26 (d, J = 3.0 Hz, 1H), 5.13 (dd, J = 10.3, 8.7 Hz, 1H), 5.02 (dd, J = 10.3, 3.4 Hz, 1H), 4.57 (d, J = 8.7 Hz, 1H), 3.93 – 3.86 (m, 1H), 2.18 (s, 3H), 2.07 (s, 3H), 1.98 (s, 3H), 1.25 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 170.2, 169.6, 88.3, 71.6, 71.3, 70.1, 68.3, 20.8, 20.7, 20.7, 16.1; HRMS (TOF): $[M + Na]^+$ calcd for C₁₂H₁₇O₇N₃Na 338.0964, found 338.0968.

2,3,6-Tri-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl)- β -D-glucopyranosyl azide (6). White solid: $R_f=0.6$ (EtOAc:hexane 25:75); mp- 170-172 °C; $[\alpha]_D^{25} -26.6$ (c 0.42, CHCl₃); IR (CHCl₃) ν 2113, 1746, 1215, 1038 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.20 – 5.08 (m, 2H), 5.04 (t, J = 9.6 Hz, 1H), 4.93 – 4.81 (m, 2H), 4.60 (d, J = 8.8 Hz, 1H), 4.54-4.47 (m, 2H), 4.36 (dd, J = 12.5, 4.4 Hz, 1H), 4.10 (dd, J = 12.2, 5.0 Hz, 1H), 4.02 (dd, J = 12.5, 2.1 Hz, 1H), 3.82 – 3.74 (m, 1H), 3.72 – 3.61 (m, 2H), 2.12 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 170.3, 170.3, 169.7, 169.5, 169.4, 169.1, 100.9, 87.8, 76.1, 74.9, 72.9, 72.3, 72.1, 71.6, 70.9, 67.8, 61.7, 61.6, 20.9, 20.7, 20.6, 20.6, 20.5; HRMS (TOF): $[M + Na]^+$ calcd for C₂₆H₃₅O₁₇N₃Na 684.1864, found 684.1804.

2,3,4,6-Tetra-O-acetyl- α -D-glucopyranosyl-(1-4)-2,3,6-tri-O-acetyl- α -D-glucopyranosyl-(1-4)-2,3,6-tri-O-acetyl- β -D-glucopyranosyl azide (7).¹ White solid: R_f =0.3(EtOAc:hexane 25:75); mp- 96-98 °C (lit. m.p. 95-96 °C); $[\alpha]_D^{25}$ +65.8 (c 0.3, CHCl₃); IR (CHCl₃) ν 2116, 1742, 1214, 1028 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.41 – 5.33 (m, 3H), 5.32-5.23 (m, 2H), 5.06 (t, J = 9.9 Hz, 1H), 4.84 (dd, J = 10.5, 4.0 Hz, 1H), 4.80 – 4.68 (m, 3H), 4.48 (ddd, J = 14.8, 12.4, 2.4 Hz, 2H), 4.31 (dd, J = 12.3, 4.3 Hz, 1H), 4.24 (dd, J = 12.5, 3.5 Hz, 1H), 4.17 (dd, J = 12.3, 3.2 Hz, 1H), 4.04 (dd, J = 12.5, 2.2 Hz, 1H), 4.01 – 3.89 (m, 4H), 3.84 – 3.78 (m, 1H), 2.18 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 9H, 3 $\times$ COCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 170.7, 170.6, 170.5, 170.1, 170.0, 169.8, 169.6, 169.5, 96.0, 95.8, 87.5, 75.0, 74.3, 73.6, 72.5, 71.8, 71.6, 70.5, 70.2, 69.5, 69.2, 68.6, 67.9, 62.8, 62.4, 61.5, 21.0, 20.9, 20.8, 20.7, 20.6; HRMS (TOF): $[M + Na]^+$ calcd for C₃₈H₅₁N₃NaO₂₅ 972.2709, found 972.2708.

2,3,5-Tri-O-acetyl- β -D-ribofuranosyl azide (8).¹ Thick liquid: R_f =0.6(EtOAc:hexane 25:75); IR (CHCl₃) ν 2110, 1743, 1208, 1051 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.35 (d, J = 2.0 Hz, 1H), 5.32 (dd, J = 6.8, 4.9 Hz, 1H), 5.13 (dd, J = 4.8, 2.0 Hz, 1H), 4.41 (dd, J = 12.2, 3.2 Hz, 1H), 4.36 – 4.32 (m, 1H), 4.14 (dd, J = 12.2, 4.3 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 169.6, 169.5, 92.8, 79.5, 74.6, 70.6, 63.1, 20.7, 20.6, 20.5; HRMS (TOF): $[M + H]^+$ calcd for C₁₁H₁₆O₇N₃ 302.0988, found 302.3091.

3,4,6-Tri-O-acetyl-2-N-acetyl-2-deoxy- β -D-glucopyranosyl azide (9).¹ White solid: R_f =0.2(EtOAc:hexane 70:30); mp- 153-155 °C (lit. m.p. 158-161 °C); $[\alpha]_D^{25}$ -28.8 (c 0.34, CHCl₃); IR (CHCl₃) ν 2114, 1723, 1245, 1091 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.83 (br s, 1H), 5.25 (t, J = 9.6 Hz, 1H), 5.09 (t, J = 9.7 Hz, 1H), 4.76 (d, J = 9.3 Hz, 1H), 4.26 (dd, J = 12.4, 4.8 Hz, 1H), 4.16 (dd, J = 12.4, 2.1 Hz, 1H), 3.92 (dt, J = 10.4, 9.1 Hz, 1H), 3.79 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 170.8, 170.6, 169.4, 88.5, 74.1, 72.3, 68.2, 62.0, 54.2, 23.3, 20.8, 20.7, 20.7; HRMS (TOF): $[M+H]^+$ calcd for C₁₄H₂₁O₈N₄ 373.1359, found 372.9190.

2,3,4,6-Tetra-O-benzoyl- α -D-mannopyranosyl azide (10). White solid: $R_f=0.6$ (EtOAc:hexane 25:75); mp- 143-145 °C; $[\alpha]_D^{25}$ -77.3 (c 0.68, CHCl₃); IR (CHCl₃) ν 2105, 1725, 1251, 1045, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, J = 8.0, 0.8 Hz, 2H), 8.02 (dd, J = 8.4, 1.2 Hz, 2H), 7.94 (dd, J = 8.0, 0.8 Hz, 2H), 7.82 (dd, J = 8.1, 1.1 Hz, 2H), 7.62-7.54 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.34 (m, 7H), 7.26 (dd, J = 10.7, 5.0 Hz, 2H), 6.13 (t, J = 10.1 Hz, 1H), 5.81 (dd, J = 10.2, 3.2 Hz, 1H), 5.68 (d, J = 1.8 Hz, 1H), 5.61 (dd, J = 3.2, 2.0 Hz, 1H), 4.75 (dd, J = 12.3, 2.4 Hz, 1H), 4.60 (ddd, J = 10.0, 4.2, 2.4 Hz, 1H), 4.50 (dd, J = 12.3, 4.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 165.5, 165.5, 165.4, 133.8, 133.7, 133.4, 133.3, 130.0, 129.9, 129.9, 129.8, 129.0, 128.9, 128.8, 128.8, 128.6, 128.6, 128.5, 87.7, 71.0, 70.2, 69.3, 66.4, 62.6; HRMS (TOF): $[M + Na]^+$ calcd for C₃₄H₂₇O₉N₃Na 644.1645, found 644.1647.

2,3,4,6-Tetra-O-benzoyl- β -D-glucopyranosyl azide (11). White solid: $R_f=0.4$ (EtOAc:hexane 15:85); mp- 68-70 °C; $[\alpha]_D^{25}$ -0.98 (c 0.52, CHCl₃); IR (CHCl₃) ν 2113, 1727, 1259, 1094, 708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.06-8.03 (m, 2H), 7.98-7.95 (m, 2H), 7.92-7.88 (m, 2H), 7.84-7.80 (m, 2H), 7.58 – 7.47 (m, 3H), 7.44 – 7.24 (m, 9H), 5.93 (td, J = 9.6, 0.8 Hz, 1H), 5.72 (t, J = 9.9 Hz, 1H), 5.54 – 5.47 (m, 1H), 4.98 (d, J = 8.6 Hz, 1H), 4.68 (dd, J = 12.3, 3.0 Hz, 1H), 4.52 (dd, J = 12.3, 5.1 Hz, 1H), 4.25 (ddd, J = 9.6, 5.0, 3.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 165.8, 165.2, 165.1, 133.8, 133.7, 133.5, 133.4, 130.1, 129.9, 129.9, 129.8, 129.5, 128.8, 128.7, 128.6, 128.5, 128.4, 88.4, 74.6, 72.8, 71.3, 69.2, 62.9; HRMS (TOF): $[M + Na]^+$ calcd for C₃₄H₂₇O₉N₃Na 644.1645, found 644.1647.

2,3,4-Tri-O-benzoyl- α -L-rhamnopyranosyl azide (12). White solid: $R_f=0.4$ (EtOAc:hexane 15:85); mp- 142-144 °C; $[\alpha]_D^{25}$ +68.0 (c 0.42, CHCl₃); IR (CHCl₃) ν 2113, 1724, 1243, 1094, 705 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.05-8.02 (m, 2H), 7.92 – 7.87 (m, 2H), 7.77 – 7.72 (m, 2H), 7.57-7.51 (m, 1H), 7.47 – 7.39 (m, 3H), 7.37-7.28 (m, 3H), 7.17 (t, J = 8.0 Hz, 2H), 5.69-5.58 (m, 2H), 5.53 (d, J = 1.8 Hz, 1H), 5.49 (dd, J = 2.9, 2.0 Hz, 1H), 4.33-4.24 (m, 1H), 1.34 (d, J = 6.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 165.6,

165.5, 133.8, 133.6, 133.4, 130.1, 129.8, 129.8, 129.2, 129.1, 129.0, 128.8, 128.6, 128.43, 87.7, 71.3, 70.6, 69.3, 69.0, 17.8; HRMS (TOF): $[M + Na]^+$ calcd for $C_{27}H_{23}O_7N_3Na$ 524.1434, found 524.1429.

2,3-Di-O-benzoyl-5-O-tert-butyldiphenylsilyl α -D-arabinofuranosyl azide (13). Thick liquid: $R_f=0.6$ (EtOAc:hexane 10:90); $[\alpha]_D^{25} +86.0$ (c 0.14, $CHCl_3$); IR ($CHCl_3$) ν 2110, 1709, 1360, 1224, 703 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, $J = 7.3, 1.0$ Hz, 2H), 7.97 (dd, $J = 7.3, 0.9$ Hz, 2H), 7.73 (dd, $J = 7.8, 1.3$ Hz, 4H), 7.65 – 7.55 (m, 2H), 7.49 (t, $J = 7.8$ Hz, 2H), 7.43 – 7.32 (m, 8H), 5.71 (d, $J = 4.5$ Hz, 1H), 5.64 (s, 1H), 5.38 – 5.36 (m, 1H), 4.55 (q, $J = 4.6$ Hz, 1H), 4.04 (d, $J = 4.6$ Hz, 2H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.5, 135.8, 135.7, 133.8, 133.7, 133.2, 133.1, 130.1, 129.9, 129.2, 128.8, 128.6, 128.6, 127.9, 94.6, 85.1, 82.2, 77.2, 63.4, 26.9, 19.4; MALDI (TOF): $[M + Na]^+$ calcd for $C_{35}H_{35}N_3NaO_6Si$ 644.2193, found 644.5349.

2,3,6-Tri-O-benzoyl-4-O-(2,3,4,6-tetra-O-benzoyl- α -D-glucopyranosyl)- β -D-glucopyranosyl azide (14). White solid: $R_f=0.7$ (EtOAc:hexane 30:70); mp- 107-109 $^{\circ}C$; $[\alpha]_D^{25} +53.0$ (c 0.86, $CHCl_3$); IR ($CHCl_3$) ν 2112, 1725, 1254, 1090, 733 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.94 – 7.89 (m, 2H), 7.82 – 7.74 (m, 4H), 7.70 – 7.62 (m, 4H), 7.60 – 7.44 (m, 4H), 7.44 – 7.31 (m, 8H), 7.30 – 7.10 (m, 11H), 6.01 (t, $J = 10.0$ Hz, 1H), 5.72 (d, $J = 9.2$ Hz, 1H), 5.68 (d, $J = 4.2$ Hz, 1H), 5.58 (t, $J = 9.7$ Hz, 1H), 5.24 – 5.14 (m, 2H), 4.91 – 4.82 (m, 2H), 4.70 (dd, $J = 12.3, 4.1$ Hz, 1H), 4.48 – 4.30 (m, 3H), 4.20 (dd, $J = 12.3, 3.7$ Hz, 1H), 4.11 (ddd, $J = 9.5, 3.7, 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 165.7, 165.5, 165.2, 165.2, 165.1, 133.7, 133.6, 133.5, 133.4, 133.2, 130.1, 130.0, 130.0, 129.9, 129.8, 129.7, 129.5, 129.3, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 96.6, 88.0, 75.1, 74.7, 72.7, 71.7, 71.0, 69.9, 69.4, 69.2, 63.2, 62.6; HRMS (TOF): $[M + Na]^+$ calcd for $C_{61}H_{49}O_{17}N_3Na$ 1118.2960, found 1118.2979.

2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl- β -D-galactopyranosyl)- β -D-glucopyranosyl azide (15). White solid: $R_f=0.5$ (EtOAc:hexane 20:80); mp- 132-134 °C; $[\alpha]_D^{25} +35.7$ (c 0.8, CHCl₃); IR (CHCl₃) ν 2112, 1726, 1261, 1092, 706 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.08 – 7.96 (m, 10H), 7.92 (dd, J = 8.2, 1.0 Hz, 2H), 7.75 (dd, J = 8.3, 1.1 Hz, 2H), 7.67 – 7.55 (m, 3H), 7.54 – 7.29 (m, 14H), 7.19 (dt, J = 15.7, 7.8 Hz, 4H), 5.86 (t, J = 9.5 Hz, 1H), 5.80 – 5.74 (m, 2H), 5.49 – 5.40 (m, 2H), 4.93 (d, J = 7.9 Hz, 1H), 4.86 (d, J = 8.8 Hz, 1H), 4.65 (dd, J = 12.2, 1.6 Hz, 1H), 4.57 (dd, J = 12.4, 4.1 Hz, 1H), 4.32 (t, J = 9.5 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.77 (d, J = 6.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 165.6, 165.4, 165.3, 165.3, 165.2, 164.8, 133.6, 133.6, 133.5, 133.4, 133.3, 130.0, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 101.0, 88.2, 75.5, 75.2, 72.6, 71.8, 71.5, 71.1, 69.9, 67.5, 62.1, 61.1; MALDI (TOF): $[M + Na]^+$ calcd for C₆₁H₄₉O₁₇N₃Na 1118.2960, found 1117.2369.

References

¹Salunke, S. B.; Babu, N. S.; Chen, C.-T. *Chem. Commun.* **2011**, 47, 10440–10442. doi:10.1039/C1CC13370E

