An Efficient Synthesis of Triazolo-carbohydrate Mimetics and Their Conformation Analysis

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1. Preparation of triazolo-mannose mimic 6b

(2S,3S,4R)-2,3,4-Tri(benzyloxy)-1,1-dimethoxyhex-5-ene (2b). According to the synthetic procedure for 2a, 1,1-dimethoxyhex-5-ene derivative 2b was prepared in 100% yield (6.29 g, 13.6 mmol) by the reaction of (2S,3S,4R)-2,3,4-tribenzyloxyhex-5-enal 1b (5.7 g, 13.6 mmol), 1-pTsOH·H2O (30 mg) and HCl(OMe)3 (35 mL). Colorless oil. 

δ(CDCl3) = 3.42 (3H, s), 3.87-3.89 (1H, m), 3.94 (1H, dd, J = 7.5, 5.6 Hz), 4.15 (1H, dd, J = 11.5 Hz), 4.69 (1H, d, J = 11.5 Hz), 4.73 (1H, d, J = 11.5 Hz), 4.75 (1H, d, J = 11.5 Hz), 5.25 (1H, dd, J = 10.3, 1.5 Hz), 5.33 (1H, dd, J = 17.3, 1.5 Hz), 5.83 (1H, ddd, J = 17.3, 10.3, 7.5 Hz), 7.20-7.35 (15H, m); 13C NMR (100 MHz, CDCl3) δ 55.8, 73.1, 73.2, 127.5, 127.8, 127.8, 127.9, 127.9, 128.1, 128.2, 128.2, 136.0, 138.6, 138.7, 138.9. MS (ESI-TOF) m/z 485 [M+Na]+. HRMS calcd for C29H34NaO5 [M+Na]+, 485.2304; found, 485.2324. Anal. Caled for C29H34O5: C, 75.30; H, 7.41. Found: C, 75.37; H, 7.47.

(2S,3R,4S)-Tri(benzyloxy)-5,5-dimethoxypentanal (3b). According to the synthetic procedure for 3a, 5,5-dimethoxypentanal derivative 3b was prepared in 86% yield (4.39 g, 9.46 mmol) by the reaction of 2b (5.1 g, 11 mmol), OsO4 (0.11 M in H2O, 4.5 mL, 0.5 mmol), NMO (3.8 g, 33 mmol) and NaIO4 (5 g) in a mixture of acetone (200 mL), H2O (50 mL) and tert-butyl alcohol (6.5 mL). Colorless oil. 

δ(CDCl3) = 3.37 (3H, s), 3.44 (3H, s), 3.77-3.82 (1H, m), 4.03-4.05 (1H, m), 4.09-4.13 (1H, m), 4.53 (1H, d, J = 11.5 Hz), 4.81 (1H, d, J = 11.5 Hz), 4.95 (1H, d, J = 11.5 Hz), 4.98 (1H, d, J = 11.5 Hz), 7.25-7.36 (15H, m); 13C NMR (100 MHz, CDCl3) δ 55.2, 56.2, 70.6, 73.7, 74.7, 78.9, 81.0, 82.6, 105.4, 118.6, 127.4, 127.8, 127.8, 127.9, 128.1, 128.2, 128.2, 136.0, 138.6, 138.7, 138.9. MS (ESI-TOF) m/z 487 [M+Na]+; HRMS calcd for C28H32NaO6 [M+Na]+, 487.2097; found, 487.2082.

(2S,3S,4R)-2,3,4-Tri(benzyloxy)-1,1-dimethoxyhex-5-ene (4b). According to the synthetic procedure for 4a, 1,1-dimethoxyhex-5-ene derivative 4b was prepared in 52% yield (1.23 g, 2.72 mmol) by the reaction of 3b (2.3 g, 13.5 mmol), Ohira-Bestmann reagent (2.88 g, 15 mmol) and K2CO3 (2.3 g, 13.5 mmol) in MeOH (400 mL). Colorless oil. 

δ(CDCl3) = 3.34 (3H, s), 3.39 (3H, s), 3.87-3.91 (1H, m), 3.94 (1H, dd, J = 5.6, 4.9 Hz), 4.49-4.58 (3H, m), 4.63 (1H, d, J = 4.9 Hz), 4.76 (1H, d, J = 11.4 Hz), 4.79 (1H, d, J = 11.1 Hz), 4.87 (1H, d, J = 11.7 Hz), 4.98 (1H, d, J = 11.4 Hz), 7.25-7.42 (15H, m); 13C NMR (100 MHz, CDCl3) δ 55.1, 55.8, 73.1, 73.2, 74.3, 79.1, 79.5, 83.0, 105.0, 127.5, 127.8, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 137.3, 137.7, 138.2, 201.1; MS (ESI-TOF) m/z 487 [M+Na]+; HRMS calcd for C29H34NaO6 [M+Na]+, 487.2097; found, 487.2082.

(4R,5S,6S,7R)-4,5,6-Tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (5b-α) and (4R,5S,6S,7S)-4,5,6-tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (5b-β).

According to the synthetic procedure for 5a, these compounds were prepared in 91% yield (5b-α 88.0 mg, 0.187 mmol, 43% yield; 5a-β 98.2 mg, 0.208 mmol, 48% yield) by the reaction of 4b (200 mg, 0.43 mmol) and TMSN3 (260 μL, 2.2 mmol) in the presence of In(OTf)3 (12.5 mg, 22 μmol) in 1,2-dichloroethane (6.0 mL). 5b-α as a less polar isomer. Colorless oil. 

δ(CHCl3) = 2.55 (1H, s); 1H NMR (400 MHz, CHCl3) δ 2.55 (1H, d, J = 2.1 Hz), 3.39 (3H, t), 3.42 (3H, s), 3.87-3.89 (1H, m), 3.94 (1H, dd, J = 5.6, 4.9 Hz), 4.49-4.58 (3H, m), 4.63 (1H, d, J = 4.9 Hz), 4.76 (1H, d, J = 11.4 Hz), 4.79 (1H, d, J = 11.1 Hz), 4.87 (1H, d, J = 11.7 Hz), 4.98 (1H, d, J = 11.4 Hz), 7.25-7.42 (15H, m); 13C NMR (100 MHz, CDCl3) δ 55.1, 55.6, 69.4, 70.9, 73.6, 74.8, 77.3, 78.7, 81.1, 81.6, 105.0, 127.4, 127.6, 127.9, 127.9, 128.1, 128.2, 128.3, 128.4, 137.7, 137.8, 138.6; MS (ESI-TOF) m/z 483 [M+Na]+; HRMS calcd for C29H34NaO6 [M+Na]+, 483.2147; found, 483.2135.

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derivative (1H, dd, J = 3.4, 2.1 Hz), 4.28 (1H, dd, J = 7.5, 2.1 Hz), 4.64-4.75 (4H, m), 4.78 (1H, d, J = 12.0 Hz), 4.79 (1H, d, J = 12.0 Hz), 4.96 (1H, d, J = 7.5 Hz), 5.58 (1H, d, J = 3.4 Hz), 7.26-7.41 (15H, m), 7.57 (1H, s); 13C NMR (100 MHz, CDCl3) δ 58.4, 71.5, 72.9, 73.3, 73.4, 76.1, 81.7, 86.5, 127.8, 127.9, 127.9, 128.0, 128.1, 128.5, 128.6, 132.2, 134.3, 137.2, 137.6, 137.7; MS (ESI-TOF) m/z 472 [(M+H)+]; HRMS calcd for C28H30N3O4 [M+Na]+, 472.2236; found, 472.2264.

(4R,5S,6S,7R)-4,5,6,7-Trihydroxy-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (6b-α). According to the synthetic procedure for 6a-α, triol 6b-α was obtained in 88% yield (76.1 mg, 0.379 mmol) by the debenzylation reaction of 5b-α (200 mg, 0.43 mmol) in the presence of Pd(OH)2 on carbon (20 w/w%, 238 mg) in MeOH (5.0 mL) under H2 atmosphere (1 atm). Colorless oil.

(4R,5S,6S,7S)-4,5,6,7-Trihydroxy-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (6b-β). According to the synthetic procedure for 6a-α, triol 6b-β was obtained in 79% yield (60.5 mg, 0.305 mmol) by the debenzylation reaction of 5b-β (180 mg, 0.39 mmol) in the presence of Pd(OH)2 on carbon (20 w/w%, 218 mg) in MeOH (5.0 mL) under H2 atmosphere (1 atm). Colorless oil.

2. Preparation of triazolo-galactose mimic 6c

(2R,3S,4S)-2,3,4-Tri(benzyloxy)-1,1-dimethoxyhex-5-ene (2c). According to the synthetic procedure for 2a, 1,1-dimethoxyhex-5-ene derivative 2c was prepared in 91% yield (1.26 g, 2.72 mmol) by the reaction of (2R,3S,4S)-2,3,4-tri(benzyloxy)hex-5-enal 1c (1.3 g, 3.0 mmol), pTsOH·H2O (43 mg) and HC(O)Me3 (7 mL). Colorless oil. [α]D25 (c 1.00, CHCl3) +18.1; IR (neat) ν 3030, 2928, 1454, 1094, 734, 697 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 2.72 (3H, s), 3.43 (3H, s), 3.73 (1H, dd, J = 7.7, 2.6 Hz), 3.80 (1H, dd, J = 7.1, 2.6 Hz), 4.09 (1H, t, J = 7.7 Hz), 4.12 (1H, d, J = 11.5 Hz), 4.47-4.56 (4H, m), 4.69 (1H, d, J = 11.3 Hz), 4.78 (1H, d, J = 11.5 Hz), 5.34 (1H, brd, J = 10.2 Hz), 5.41 (1H, brd, J = 17.5 Hz), 5.90 (1H, ddd, J = 17.5, 10.2, 7.7 Hz), 7.17-7.34 (15H, m); 13C NMR (100 MHz, CDCl3) δ 35.9, 56.2, 69.9, 74.3, 74.4, 78.7, 79.8, 81.0, 105.6, 119.3, 127.3, 127.4, 127.5, 127.9, 128.0, 128.1, 128.2, 136.5, 138.5, 138.6, 138.9; MS (ESI-TOF) m/z 485 [(M+Na)+]; HRMS calcd for C39H34NaO5 [M+Na]+, 485.2304; found, 485.2286.

(2R,3S,4R)-Tri(benzyloxy)-5,5-dimethoxypentanal (3e). According to the synthetic procedure for 3a, 5,5-dimethoxypentanal derivative 3e was prepared in 89% yield (1.03 g, 2.22 mmol) by the reaction of 2c (1.2 g, 2.5 mmol), OsO4 (0.11 M in H2O, 1.2 mL,
0.13 mmol), NMO (0.5 g, 4.5 mmol) and NaO₄ (3 g) in a mixture of acetone (40 mL), H₂O (10 mL) and tert-butyl alcohol (3 mL). Colorless oil. [α]D²⁵ (c 1.00, CHCl₃) +9.10; [α]D (c 1.00, CHCl₃) +9.10; 1H NMR (400 MHz, CDCl₃) δ 3.28 (3H, s), 3.42 (3H, s), 3.66 (1H, dd, J = 6.3, 3.3 Hz), 3.98-4.02 (2H, m), 4.27 (1H, d, J = 11.7 Hz), 4.45 (1H, d, J = 6.3 Hz), 4.51 (1H, d, J = 11.4 Hz), 4.55 (1H, d, J = 11.3 Hz), 4.57 (1H, d, J = 11.7 Hz), 4.63 (1H, d, J = 11.3 Hz), 4.77 (1H, d, J = 11.4 Hz), 7.19-7.30 (15H, m), 9.64 (1H, d, J = 1.4 Hz); 13C NMR (100 MHz, CDCl₃) δ 54.7, 56.3, 72.3, 74.1, 74.3, 78.8, 79.6, 83.6, 105.5, 127.7, 127.7, 128.1, 128.2, 128.2, 128.3, 137.3, 137.8, 138.1, 201.2; MS (ESI-TOF) m/z 487 [M+Na]⁺; HRMS calcd for C₂₉H₃₂NaO₅ [M+Na]⁺, 487.2097; found: 487.2077.

(2R,3S,4S)-2,3,4-Tri(benzyloxy)-1,1-dimethoxyhex-5-yne (4c). According to the synthetic procedure for 4a, 1,1-dimethoxyhex-5-yne derivative 4c was prepared in 68% yield (0.69 g, 1.50 mmol) by the reaction of 3c (1.0 g, 2.2 mmol), Ohira-Bestmann reagent (3.6 g, 19 mmol) and K₂CO₃ (3.0 g, 22 mmol) in MeOH (230 mL). Colorless oil. [α]D²⁵ (c 1.00, CHCl₃) +52.5; 1H NMR (400 MHz, CDCl₃) δ 2.52 (1H, d, J = 2.0 Hz), 3.29 (3H, s), 3.45 (3H, s), 3.76 (1H, dd, J = 7.0, 2.5 Hz), 3.92 (1H, dd, J = 7.9, 2.5 Hz), 4.28 (1H, d, J = 11.4 Hz), 4.43 (1H, dd, J = 7.9, 2.0 Hz), 4.47 (1H, d, J = 11.5 Hz), 4.51 (1H, d, J = 7.0 Hz), 4.66 (1H, d, J = 11.2 Hz), 4.78 (1H, d, J = 11.5 Hz), 4.80 (1H, d, J = 11.4 Hz), 5.01 (1H, d, J = 11.2 Hz), 7.18-7.35 (13H, m), 7.40 (2H, d, J = 7.5 Hz). 13C NMR (100 MHz, CDCl₃) δ 53.9, 56.3, 68.6, 70.3, 74.4, 74.9, 75.2, 75.8, 80.3, 81.8, 105.3, 127.4, 127.5, 127.6, 127.9, 127.9, 128.1, 128.1, 128.3, 137.6, 138.5, 138.7; MS (ESI-TOF) m/z 483 [M+Na]⁺; HRMS calcd for C₂₉H₃₂NaO₅ [M+Na]⁺, 483.2147; found, 483.2122. Anal. Caled for C₂₉H₃₂O₅: C, 75.63; H, 7.00. Found: C, 75.49; H, 7.00.

(4S,5S,6R,7R)-4,5,6,7-tetrahydro-1,2,3-triazolo[1,5-a]pyridine (5c-α) and (4S,5S,6R,7S)-4,5,6,7-tetrahydro-1,2,3-triazolo[1,5-a]pyridine (5c-β).

According to the synthetic procedure for 5a, these compounds were prepared in 90% yield (5c-α 30.2 mg, 0.064 mmol, 32% yield; 5c-β 54.7 mg, 0.116 mmol, 58% yield) by the reaction of 4c (92 mg, 0.20 mmol) and TMSN₃ (120 μL, 1.0 mmol) in the presence of In(OOT)₃ (5.6 mg, 10 μmol) in 1,2-dichloroethane (2.8 mL). 5c-α as a less polar isomer. Colorless oil. [α]D²⁵ (c 1.01, CHCl₃) +35.4; 1H NMR (400 MHz, CDCl₃) δ 3.65 (3H, s), 4.26 (1H, dd, J = 9.6, 3.8 Hz), 4.44 (1H, dd, J = 9.6, 3.6 Hz), 4.62 (1H, d, J = 12.2 Hz), 4.70 (1H, d, J = 12.2 Hz), 4.74 (1H, d, J = 11.8 Hz), 4.84 (1H, d, J = 3.8 Hz), 4.86 (1H, d, J = 12.0 Hz), 4.89 (1H, d, J = 11.8 Hz), 4.96 (1H, d, J = 12.0 Hz), 5.61 (1H, d, J = 3.6 Hz), 7.30-7.44 (15H, m), 7.56 (1H, s); 13C NMR (100 MHz, CDCl₃) δ 59.0, 66.7, 71.7, 73.7, 74.2, 74.7, 74.9, 86.4, 127.8, 127.8, 128.0, 128.1, 128.1, 128.4, 128.5, 128.3, 123.2, 137.1, 137.7, 138.0; MS (ESI-TOF) m/z 472 [M+H]⁺; HRMS calcd for C₂₈H₂₃N₃O₄ [M+H]⁺, 472.2236; found, 472.2347. 5c-β as a more polar isomer. White amorphous solid. Mp. 56.0-62.0 °C; [α]D²⁵ (c 1.00, CHCl₃) +51.7; IR (neat) ν 3031, 2929, 1454, 1191, 1118, 740, 698 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 3.69 (1H, dd, J = 9.2, 3.1 Hz), 3.79 (3H, s), 4.51 (1H, d, J = 12.5 Hz), 4.58 (1H, dd, J = 9.2, 4.6 Hz), 4.67 (1H, d, J = 12.0 Hz), 4.71 (1H, d, J = 12.5 Hz), 4.75 (1H, d, J = 3.1 Hz), 4.78 (1H, d, J = 3.1 Hz), 4.89 (1H, d, J = 11.3 Hz), 4.96 (1H, d, J = 11.3 Hz), 5.56 (1H, d, J = 4.6 Hz), 7.30-7.43 (15H, m), 7.57 (1H, s); 13C NMR (100.6 MHz, CDCl₃) δ 59.1, 65.1, 70.8, 72.6, 74.9, 77.9, 79.4, 90.9, 127.7, 127.8, 127.8, 127.9, 127.9, 128.0, 128.3, 128.4, 131.9, 131.9, 137.0, 137.5, 137.7; MS (ESI-TOF) m/z 472 [M+H]⁺; HRMS calcd for C₂₇H₂₃N₃O₄ [M+H]⁺, 472.2236; found, 472.2232. Anal. Caled for C₂₉H₂₃N₃O₄: C, 71.32; H, 6.20; N, 8.91. Found: C, 71.01; H, 6.20; N, 8.99.

(4S,5S,6R,7R)-4,5,6-Trihydroxy-7-methoxy-4,5,6,7-tetrahydro-1,2,3-triazolo[1,5-a]pyridine (6c-α). According to the synthetic - S4 -
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128.2, 128.3, 136.4, 138.6, 138.6, 139.0; MS (ESI-TOF) 83.7, 127.7, 127.8, 127.8, 127.9, 128.0, 128.1, 128.3, 128.3, 128.4, 137.4, 137.8, 138.2, 201.6; MS (ESI-TOF)

9.1 mL, 1.0 mmol), NMO (3.0 g, 16.4 mmol) in a mixture of acetone (120 mL), H2O (30 mL) and

tert 3. Preparation of triazolo-gulose mimic ent-5b tert-Butyl(dimethyl)((2S,3S,4S)-2,3,4-tri(benzyloxy)hex-5-enyl)oxy]silane (7e). According to the synthetic procedure for 7a, TBS ether 7c was prepared in 96% yield (5.53 g, 10.4 mmol) by the reaction of (2S,3S,4S)-2,3,4-tri(benzyloxy)hex-5-en-1-ol (4.5 g, 11 mmol),3 which was prepared by NaBH4 reduction of 1b, imidazole (1.1 g, 16 mmol) and tert-butyl/chlorodimethylsilane (2.0 g, 13 mmol) in DMF (50 mL). Colorless oil. [α]D 25 (c 1.00, CHCl3) +14.8; IR (neat) ν 3358, 2927, 1456, 1254, 1115, 1056, 838 cm−1; 1H NMR (400 MHz, CDCl3) δ 3.70-3.75 (1H, m), 4.04-4.09 (1H, m), 4.19 (1H, d, J = 11.7 Hz), 4.51-4.57 (3H, m), 4.59 (1H, d, J = 11.8 Hz), 4.67 (1H, d, J = 11.3 Hz), 5.32 (1H, brd, J = 17.5 Hz), 5.36 (1H, brd, J = 10.2 Hz), 5.92 (1H, dd, J = 17.5, 10.2, 7.7 Hz), 7.19-7.30 (15H, m); 13C NMR (100 MHz, CDCl3) δ -5.4, -5.4, 18.2, 25.9, 62.9, 70.1, 73.5, 74.5, 79.6, 80.1, 80.8, 119.2, 127.4, 127.4, 127.5, 127.6, 128.0, 128.1, 128.2, 128.3, 136.4, 138.6, 138.6, 139.0; MS (ESI-TOF) m/z 555 [M+Na]+; HRMS calcd for C35H33NaO5Si [M+H]+, 559.2597; found, 555.2863.

(2R,3R,4S)-2,3,4-Tri(benzyloxy)-5-[(tert-butyl(dimethyl)silyl)oxy]pentanal (8c). According to the synthetic procedure for 8a, pentanal derivative 8c was prepared in 84% yield (4.22 g, 7.90 mmol) by the reaction of 7e (5.0 g, 9.4 mmol), OsO4 (0.11 M in H2O, 9.1 mL, 1.0 mmol), NMO (3.0 g, 16.4 mmol) in a mixture of acetonitrile (120 mL), H2O (30 mL) and tert-butyl alcohol (9 mL) and following treatment of reaction mixture by Na2S2O5 (5 g). Colorless oil. [α]D 25 (c 0.20, CHCl3, +12.0; IR (neat) ν 3031, 2928, 2856, 1733, 1455, 1254, 1092, 837, 697 cm−1; 1H NMR (400 MHz, CDCl3) δ 0.03 (3H, s), 0.04 (3H, s), 0.90 (9H, s), 3.70-3.75 (1H, m), 3.82-3.85 (2H, m), 4.01 (1H, m), 4.11 (1H, dd, J = 3.8, 1.4 Hz), 4.46 (1H, d, J = 11.8 Hz), 4.55 (1H, d, J = 11.9 Hz), 4.59-4.69 (4H, m), 7.26-7.38 (15H, m), 9.70 (1H, d, J = 1.4 Hz); 13C NMR (100 MHz, CDCl3) δ −5.4, −5.4, 18.2, 25.9, 62.9, 72.7, 73.2, 73.7, 79.8, 80.0, 83.7, 127.7, 127.8, 127.8, 127.9, 128.0, 128.1, 128.3, 128.3, 128.4, 137.4, 137.8, 138.2, 201.6; MS (ESI-TOF) m/z 557 [M+Na]+; HRMS calcd for C35H33NaO5Si [M+Na]+, 557.2699; found, 557.2689.

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**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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**1,3,5-Tri(benzyloxy)-5,5-dimethoxypentanal derivative (2a).** According to the synthetic procedure for 2a, 1,3,5-tri(benzyloxy)-5,5-dimethoxypentanal derivative 2a was prepared in 88% yield (2.48 g, 5.31 mmol) by the reaction of tert-butyl(dimethyl)[(2S,3R,4R)-2,3,4-tri(benzyloxy)-5,5-dimethoxypentyl]oxy]silane (3.5 g, 6.0 mmol) and TBAF (1.0 M in THF, 12 mL, 12 mmol) in THF (5 mL). Colorless oil. [α]D<sup>25</sup> (c 0.21, CHCl<sub>3</sub>) +16.7; IR (neat) ν 3459, 3030, 2928, 2856, 1454, 1207, 1072, 737, 698 cm<sup>-1</sup>; 1H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.45 (1H, brs), 3.33 (3H, s), 3.41 (3H, s), 3.67-3.74 (4H, m), 3.88 (1H, dd, J = 5.7, 3.3 Hz), 4.53-4.69 (6H, m), 4.76 (1H, d, J = 11.5 Hz), 7.21-7.32 (15H, m); 13C NMR (100 MHz, CDCl<sub>3</sub>) δ 55.6, 55.8, 61.4, 72.6, 73.7, 74.2, 79.7, 79.9, 105.1, 127.5, 127.5, 127.6, 127.8, 127.9, 129.7, 129.8, 132.8, 138.3, 138.4, 138.5; MS (ESI-TOF) m/z 489 [M+Na]<sup>+</sup>; HRMS calcd for C<sub>23</sub>H<sub>34</sub>NaO<sub>6</sub>)C<sub>23</sub>H<sub>34</sub>O<sub>6</sub>Si [M+Na]<sup>+</sup>, 489.2255; found, 489.2255. Anal. Calcd for C<sub>23</sub>H<sub>34</sub>O<sub>6</sub>Si: C, 72.08; H, 7.35. Found: C, 72.08; H, 7.35. Found: C, 71.97; H, 7.37.

**1,3,5-Tri(benzyloxy)-5,5-dimethoxypentanal-1-ol derivative (2c).** The physical data of 2c was obtained in 89% yield (3.87 g, 6.65 mmol) by the reaction of 8c (4.0 g, 7.5 mmol) and HC(OOMe) (15 mL) in the presence of pTsOH·H<sub>2</sub>O (50 mg). Colorless oil. [α]D<sup>25</sup> (c 1.03, CHCl<sub>3</sub>) +11.7; IR (neat) ν 3030, 2928, 2856, 1455, 1254, 836, 697 cm<sup>-1</sup>; 1H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.04 (6H, s), 0.90 (9H, s), 3.41 (3H, s), 3.47 (3H, s), 3.75-3.83 (4H, m), 3.92-3.95 (1H, m), 4.59 (1H, d, J = 11.6 Hz), 4.61 (1H, d, J = 4.9 Hz), 4.61 (1H, d, J = 11.8 Hz), 4.67 (1H, d, J = 11.8 Hz), 4.70 (1H, d, J = 11.5 Hz), 4.73 (1H, d, J = 11.5 Hz), 4.84 (1H, d, J = 11.6 Hz), 7.26-7.36 (15H, m); 13C NMR (100 MHz, CDCl<sub>3</sub>) δ 74.2, 79.7, 79.9, 105.1, 127.4, 127.6, 127.9, 128.1, 128.2, 138.9, 139.1; MS (ESI-TOF) m/z 603 [M+Na]<sup>+</sup>; HRMS calcd for C<sub>34</sub>H<sub>48</sub>NaO<sub>6</sub>Si [M+Na]<sup>+</sup>, 603.3118; found, 603.3127. Anal. Calcd for C<sub>34</sub>H<sub>48</sub>NaO<sub>6</sub>Si: C, 70.31; H, 8.33. Found: C, 70.47; H, 8.29.

**4,5,6-Tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (4a).** According to the synthetic procedure for 4a, 4,5,6-tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (ent-4a) was prepared from 4,5,6-tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (ent-3a) and TMDS (120 μL, 1.0 mmol) in the presence of In(OTf)<sub>3</sub> (5.6 mg, 10 μmol) in 1,2-dichloroethane (3.0 mL). The physical data of 4a were coincident with those of 4a, except for specific optical rotation. [α]D<sup>25</sup> (c 0.21, CHCl<sub>3</sub>) +29.8.

**4,5,6-Tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (4b).** According to the synthetic procedure for 4b, 4,5,6-tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (ent-4b) was prepared from ent-3b under the same conditions in a case of 4b. The physical data of 4b were coincident with those of 4b, except for specific optical rotation. [α]D<sup>25</sup> (c 0.99, CHCl<sub>3</sub>) +52.7.

**5,5-Dimethoxypentanal derivative (2d).** According to the synthetic procedure for 2d, these compounds were prepared in 86% yield (ent-5b-α, 45.2 mg, 95 μmol, 48% yield; ent-5b-β 36.0 mg, 76 μmol, 38% yield) by the reaction of ent-5b (92.1 mg, 0.20 mmol) and TMSN<sub>3</sub> (120 μL, 1.0 mmol) in the presence of In(OTf)<sub>3</sub> (5.6 mg, 10 μmol) in 1,2-dichloroethane (3.0 mL). The physical data of ent-5b-α were coincident with those of 5b-α, except for specific optical rotation. [α]D<sup>25</sup> (c 0.21, CHCl<sub>3</sub>) +23.5. The physical data of ent-5b-β were also coincident with those of 5b-β, except for specific optical rotation. [α]D<sup>25</sup> (c 1.00, CHCl<sub>3</sub>) +74.5.
4. Preparation of triazolo-altrose mimic ent-5c

tert-Butyl(dimethyl)[({2R,3S,4R}-2,3,4-tri(benzaldehyde)-hex-5-en-1-ol)(xy)oxy]silane (7b). According to the synthetic procedure for 7a, TBS ether 7b was prepared in 89% yield (3.98 g, 7.49 mmol) by the reaction of (2R,3S,4R)-2,3,4-tri(benzaldehyde)-hex-5-en-1-ol (3.5 g, 8.4 mmol), which was prepared by NaBH₄ reduction of 1b, imidazole (743 mg, 11 mmol) and tert-butylchloromethylsilane (1.52 g, 10 mmol) in DMF (9.0 mL). Colorless oil. [α]D²⁵ (c 1.00, CHCl₃) = 141; IR (neat) ν 2928, 2856, 1455, 1253, 1093, 836, 734, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.05 (6H, s), 0.91 (9H, s), 3.67-3.72 (1H, m), 3.72-3.79 (1H, m), 3.63 (1H, dd, J = 10.9, 5.3 Hz), 3.96 (1H, dd, J = 10.9, 2.9 Hz), 4.13 (1H, dd, J = 7.7, 4.2 Hz), 4.34 (1H, d, J = 11.9 Hz), 4.40 (1H, d, J = 11.5 Hz), 4.63 (1H, d, J = 11.9 Hz), 4.65 (1H, d, J = 11.5 Hz), 4.70-4.73 (2H, m), 5.27 (1H, brd, J = 10.4 Hz), 5.33 (1H, brd, J = 17.4 Hz), 5.91 (1H, ddd, J = 17.4, 10.4, 7.7 Hz), 7.18-7.36 (15H, m); ¹³C NMR (100 MHz, CDCl₃) δ 84.2, 127.5, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 137.3, 137.8, 138.1, 202.2; MS (ESI-TOF) m/z 533 [M+H]⁺; HRMS calcd for C₃₂H₄₃O₅Si [M+H]⁺, 535.2880; found, 535.2889.

(2S,3R,4R)-2,3,4-Tri(benzaldehyde)-5-[tert-butyl(dimethyl)silyl]oxy]pentanal (8b). According to the synthetic procedure for 8a, pentanal derivative 8b was prepared in 92% yield (3.49 g, 6.50 mmol) by the reaction of 7b (3.78 g, 7.1 mmol), OsO₄ (0.11 M in H₂O, 6.4 mL, 0.7 mmol), NMO (1.6 g, 14 mmol) in a mixture of acetone (100 mL), H₂O (35 mL) and tert-butyl alcohol (3 mL) and following treatment of reaction mixture by NaIO₄ (15 g). Colorless oil. [α]D²⁵ (c 1.02, CHCl₃) = 34.1; IR (neat) ν 3032, 2952, 2929, 1731, 1455, 1327, 1253, 1096, 1028, 736, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.01 (3H, s), 0.02 (3H, s), 0.88 (9H, s), 3.66-3.74 (1H, m), 3.78 (1H, dd, J = 11.2, 4.2 Hz), 3.95 (1H, dd, J = 11.2, 2.9 Hz), 4.03-4.07 (2H, m), 4.32 (1H, d, J = 11.5 Hz), 4.47 (1H, d, J = 11.8 Hz), 4.52 (1H, d, J = 11.3 Hz), 4.57 (1H, d, J = 11.3 Hz), 4.62 (1H, d, J = 11.8 Hz), 4.64 (1H, d, J = 11.5 Hz), 7.18-7.30 (15H, m), 9.58 (1H, d, J = 1.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 7.3, 5.3, 18.3, 25.9, 61.4, 72.0, 73.2, 74.1, 78.4, 78.9, 84.2, 127.5, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 137.3, 137.8, 138.1, 202.2; MS (ESI-TOF) m/z 535 [M+H]⁺; HRMS calcd for C₃₃H₄₅O₄Si [M+H]⁺, 537.2980; found, 537.2989.

tert-Butyl(dimethyl)[({2R,3S,4R}-2,3,4-tri(benzaldehyde)-5,5-dimethoxypentenyl]oxy)silane. This compound was obtained in 100% yield (3.48 g, 6.00 mmol) by the reaction of 8b (3.2 g, 6.0 mmol) and HC(OMe)₃ (15 mL) in the presence of pTsOH·H₂O (20 mg). Colorless oil. [α]D²⁵ (c 0.98, CHCl₃) = 720; IR (neat) ν 3031, 2929, 2856, 1454, 1096, 1028, 836, 734, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.02 (3H, s), 0.02 (3H, s), 0.89 (9H, s), 3.28 (3H, s), 3.43 (3H, s), 3.73 (1H, ddd, J = 7.2, 4.8, 2.3 Hz), 3.76-3.82 (2H, m), 3.88 (1H, dd, J = 7.2, 2.6 Hz), 4.01 (1H, dd, J = 11.2, 2.3 Hz), 4.32 (1H, d, J = 11.7 Hz), 4.50 (1H, d, J = 11.6 Hz), 4.53 (1H, d, J = 7.1 Hz), 4.63 (1H, d, J = 11.6 Hz), 4.70 (1H, d, J = 11.7 Hz), 4.72 (1H, d, J = 11.6 Hz), 4.81 (1H, d, J = 11.6 Hz), 7.18-7.35 (15H, m); ¹³C NMR (100 MHz, CDCl₃) δ 7.3, 5.3, 18.3, 25.9, 53.5, 55.9, 62.2, 71.8, 74.2, 74.3, 78.2, 78.8, 79.5, 105.4, 127.2, 127.4, 127.8, 127.9, 128.1, 128.2, 128.2, 138.9, 139.1; MS (ESI-TOF) m/z 603 [M+Na]⁺; HRMS calcd for C₃₄H₄₈NaO₆Si [M+Na]⁺, 603.3118; found, 603.3062.

(2R,3R,4S)-2,3,4-Tri(benzaldehyde)-5,5-dimethoxypent-1-en-1-ol (9b). According to the synthetic procedure for 9a, 5,5-dimethoxypent-1-en-1-ol derivative 9b was prepared in 98% yield (2.74 g, 5.88 mmol) by the reaction of tert-butyl(dimethyl)[({2R,3R,4S}-2,3,4-tri(benzaldehyde)-5,5-dimethoxypentyl]oxy]silane (3.4 g, 6.0 mmol) and TBAF (1.0 M in THF, 12 mL, 12 mmol) in THF (5 mL). Colorless oil. [α]D²⁵ (c 1.00, CHCl₃) = 870; IR (neat) ν 3481, 3031, 2933, 1454, 1092, 1029, 735, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.28 (3H, s), 3.43 (3H, s), 3.65-3.70 (2H, m), 3.74 (1H, brd, J = 12.0 Hz), 3.85 (1H, dd, - S7 -
$J = 12.0, 3.6 \text{ Hz}$, 3.90 (1H, dd, $J = 6.9, 2.9 \text{ Hz}$), 4.29 (1H, d, $J = 11.6 \text{ Hz}$), 4.48 (1H, d, $J = 12.0 \text{ Hz}$), 4.50 (1H, d, $J = 6.7 \text{ Hz}$), 4.51 (1H, d, $J = 12.0 \text{ Hz}$), 4.63 (1H, d, $J = 11.5 \text{ Hz}$), 4.72 (1H, d, $J = 11.5 \text{ Hz}$), 4.81 (1H, d, $J = 11.6 \text{ Hz}$), 7.19-7.34 (15H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 54.1, 56.2, 60.2, 71.2, 74.1, 74.6, 78.1, 7.7, 78.9, 105.6, 127.5, 127.6, 127.6, 127.7, 128.0, 128.0, 128.2, 128.3, 128.4, 138.1, 138.4, 138.6; MS (ESI-TOF) m/z 489 [M+Na]$^+$. HRMS calcd for C$_{28}$H$_{34}$NaO$_6$ [M+Na]$^+$, 489.2253; found, 489.2232.

(2S,3R,4S)-2,3,4-Tri(benzyloxy)-5,5-dimethoxypentanal (ent-3c). According to the synthetic procedure for ent-3a, 5,5-dimethoxypentanal derivative ent-3c was prepared in 88% yield (2.20 g, 4.73 mmol) by the reaction of 9b (2.5 g, 5.4 mmol) and DMP (3.3 g, 8.0 mmol) in CH$_2$Cl$_2$ (15 mL). The physical data of ent-3c were coincident with those of 3c, except for specific optical rotation. $[\alpha]_	ext{D}^{25}$ (c 1.00, CHCl$_3$) –8.20.

(2S,3R,4R)-2,3,4-Tri(benzyloxy)-1,1-dimethoxyhex-5-yne (ent-4c). This compound was prepared from ent-3c under the same conditions in a case of 4c. The physical data of ent-4c were coincident with those of 4c, except for specific optical rotation. $[\alpha]_	ext{D}^{25}$ (c 1.01, CHCl$_3$) –54.2.

(4R,5R,6S,7S)-4,5,6-Tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (ent-5c-α) and (4R,5R,6S,7R)-4,5,6-tri(benzyloxy)-7-methoxy-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridine (ent-5c-β). According to the synthetic procedure for 5c, these compounds were prepared in 89% yield (ent-5c-α 85.3 mg, 0.181 mmol, 28% yield; ent-5c-β 187.6 mg, 0.398 mmol, 61% yield) by the reaction of ent-4c (300 mg, 0.65 mmol) and TMSN$_3$ (0.40 mL, 3.3 mmol) in the presence of In(OTf)$_3$ (18.2 mg, 32.5 µmol) in 1,2-dichloroethane (9.0 mL). The physical data of ent-5c-α were coincident with those of 5c-α, excluding specific optical rotation. $[\alpha]_	ext{D}^{25}$ (c 1.01, CHCl$_3$) –36.8. The physical data of ent-5c-β were also coincident with those of 5c-β, except for specific optical rotation. $[\alpha]_	ext{D}^{25}$ (c 0.98, CHCl$_3$) –51.3.
5. $^1$H and $^{13}$C NMR spectra of 2a, 3a, 4a, 5a and 6a
6. $^1$H and $^{13}$C NMR spectra of 7a, 8a and 9a
$^1$H and $^{13}$C NMR spectra of 2b, 3b, 4b, 5b and 6b.
**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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**Current Data Parameters**
- **NAME:** 3b
- **EXPNO:** 46
- **PROCNR:** 1

**2D - Acquisition Parameters**
- **DATUM:** 20070724
- **TEM:** 200
- **JLWAVE:** 1.2424
- **Dpitch:** 0.5°
- **SPACING:** 0.1024°
- **VPO:** 0.00001
- **VSP:** 0.00000
- **WDIR:** 0.00000
- **WSP:** 0.00000

**2D - Recording parameters**
- **T1:** 300.00 MHz
- **T2:** 400.00 MHz

**2D - Jmix parameters**
- **Jf:** 45.00 Hz
- **Jj:** 90.00 Hz

**Current Data Parameters**
- **NAME:** 3b
- **EXPNO:** 46
- **PROCNR:** 1

**2D - Acquisition Parameters**
- **DATUM:** 20070724
- **TEM:** 200
- **JLWAVE:** 1.2424
- **Dpitch:** 0.5°
- **SPACING:** 0.1024°
- **VPO:** 0.00001
- **VSP:** 0.00000
- **WDIR:** 0.00000
- **WSP:** 0.00000

**2D - Recording parameters**
- **T1:** 300.00 MHz
- **T2:** 400.00 MHz

**2D - Jmix parameters**
- **Jf:** 45.00 Hz
- **Jj:** 90.00 Hz

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**Chemical Structure**

```
OHC
\Bn\Bn
\OMe\OMe
3b
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**Detailed Annotations**

- Chemical shift values and spectral data are not transcribed here.
- Further details are provided in the Supplementary Information section (ESI).
8. $^1$H and $^{13}$C NMR spectra of 2c, 3c, 4c, 5c and 6c

![NMR spectra of 2c, 3c, 4c, 5c, and 6c](image-url)
9. $^1$H and $^{13}$C NMR spectra of 7c, 8c and 9c
Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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10. $^1$H and $^{13}$C NMR spectra of 7b, 8b and 9b
References

