Supporting Information

An Expeditious Synthesis of Sialic Acid Derivatives by Copper(I)-Catalyzed Stereodivergent Propargylation of Unprotected Aldoses

Xiao-Feng Wei,¹ Yohei Shimizu,¹,* and Motomu Kanai¹,²,*

¹Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
²ERATO, Japan Science Technology Agency, Kanai Life Science Catalysis Project, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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1. General Information

NMR spectra were recorded on JEOL JNM-LA500 (500 MHz for \(^1\)H NMR and 125 MHz for \(^{13}\)C NMR), JEOL ECX500 (500 MHz for \(^1\)H NMR and 125 MHz for \(^{13}\)C NMR), and JEOL ECX400 (400 MHz for \(^1\)H NMR and 100 MHz for \(^{13}\)C NMR). Chemical shifts were reported in ppm on the δ scale relative to residual CHCl₃ (δ = 7.26 for \(^1\)H NMR and δ = 77.0 for \(^{13}\)C NMR), CHD₂OD (δ = 3.31 for \(^1\)H NMR and δ = 49.0 for \(^{13}\)C NMR), or HDO (δ = 4.79 for \(^1\)H NMR) as an internal reference. Infrared spectra (IR) were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. ESI-mass spectra were measured on a Waters ZQ4000 spectrometer (for LRMS) and a JEOL JMS-T100LC AccuTOF spectrometer (for HRMS). Preparative HPLC were conducted by using a JASCO HPLC system equipped with a UV-2075 spectrometer, PU-2086 pumps, a DG-2080-53 degasser, and an MX-2080-32 mixer. Reactions were carried out in dry solvents under argon atmosphere, unless otherwise stated. Reagents were purchased from Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI), or Wako Pure Chemical Industries, Ltd., and used after purification by distillation or used without purification for solid substrates. Water for the HPLC analysis was purified using a Millipore MilliQ water purification system.

2. Copper-Catalyzed Stereodivergent Propargylation of Aldoses

2-1. General procedure for the stereodivergent propargylation of aldoses (Condition A)

A flame-dried 20-mL test tube was charged with mesitylcopper (0.5 mg, 0.0027 mmol), (S,S,S)-Ph-SKP (1.7 mg, 0.0026 mmol), and d-mannose 1a (18 mg, 0.10 mmol) under argon atmosphere. B(OMe)₃ (22 µL, 0.20 mmol) and dry DMF (125 µL) were then added to this mixture. The mixture was stirred for 10 min at room temperature. Allenylboronate 2 (29 µL, 0.16 mmol) was added. After stirring for 16 h at room temperature, the reaction was quenched by the addition of MeOH and concentrated in vacuo. The process of MeOH addition followed by evaporation was repeated two-times to give a crude product. The diastereoselectivity was determined by \(^1\)H NMR analysis.
Products were purified by preparative reverse phase HPLC using a gradient of acetonitrile versus 0.1% TFA in water, affording 3a as a white solid (19.8 mg, 90% yield). Preparative HPLC was carried out as follows: YMC-Triart C18 (20 mm I.D. × 250 mm) column using a linear gradient of 0-50% acetonitrile in 0.1% aqueous TFA over 30 min at room temperature with a flow rate of 7.0 mL min⁻¹.

The configurations of 3a and 3j were determined after converting to KDN (6a) and Neu5Ac (6j), respectively. The NMR data of synthesized KDN (6a) and Neu5Ac (6j) were identical to the reported ones (KDN: Nakamura, M.; Furuhat a, K.; Yamasaki, T.; Ogura, H. Chem. Pharm. Bull. 1991, 39 3140., Neu5Ac: Lorpitthaya, R.; Suryawanshi, S. B.; Wang, S.; Pasunooti, K. K.; Cai, S.; Ma, J.; Liu, X.-W. Angew. Chem. Int. Ed. 2011, 50, 12054). The configurations of other products were tentatively assigned accordingly.

2-2. Optimization for the stereodivergent propargylation of 2-deoxy aldoses

The propargylation reaction between 2-deoxy-D-ribose (1g) and allenylboronate 2 was studied as a model reaction for 2-deoxy sugar substrates. Combinations of cationic copper salts and weak bases were examined to suppress protonolysis of allenylcopper species. A variety of mild bases, such as KOAc, PhCOONa, cesium pivalate, CF₃SO₃Na, and KOAc were examined, but the desired product was obtained only in trace amounts (Table S1, entries 2-6). Ultimately, CF₃COOK was identified as the optimum base, providing the product in 65% yield with an 18:1 diastereoselectivity (entry 7).

2-3. General procedure for the stereodivergent propargylation of 2-deoxy aldoses (Condition B)
A flame-dried 20-mL test tube was charged with CuClO4(MeCN)4 (0.8 mg, 0.0025 mmol), (S,S,S)-Ph-SKP (1.7 mg, 0.0026 mmol), CF3COOK (0.8 mg, 0.0053 mmol), MS 3A 40 mg and 2-deoxy-D-ribose (1g: 13.4 mg, 0.10 mmol) under argon atmosphere. B(OMe)3 (22 µL, 0.20 mmol) and dry DMF (125 µL) were then added to this mixture. The mixture was stirred at room temperature for 10 min. Allenylboronate 2 (58 µL, 0.32 mmol) was added. After stirring for 16 h at room temperature, the reaction was quenched by the addition of MeOH and concentrated in vacuo. The process of MeOH addition followed by evaporation was repeated two-times to give a crude product. The diastereoselectivity was determined by 1H NMR analysis. Products were purified by preparative reverse phase HPLC using a gradient of acetonitrile versus 0.1% TFA in water, affording 3g as a white solid (11.3 mg, 65% yield). Preparative HPLC was carried out as follows: YMC-Triart C18 (20 mm I.D × 250 mm) column using a linear gradient of 0-50% acetonitrile in 0.1% aqueous TFA over 30 min at room temperature with a flow rate of 7.0 mL min⁻¹.

2-4. Gram-scale synthetic procedure for the stereodivergent propargylation of D-mannose
A flame-dried 20-mL bottle was charged with mesitylcopper (3.7 mg, 0.02 mmol), (S,S,S)-Ph-SKP (13.2 mg, 0.02 mmol), and D-Mannose 1a (1.8 g, 10 mmol) under argon atmosphere. B(OMe)₃ (2.2 mL, 20 mmol) and dry DMF (6.3 mL) were then added to this mixture. The mixture was stirred for 10 min at room temperature. Allenylboronate 2 (2.7 mL, 15 mmol) was added. After stirring for 16 h at room temperature, the reaction was quenched by the addition of MeOH and concentrated in vacuo. Addition of MeOH-concentration process was repeated two-times to give a crude product. The crude solid was washed successively with EtOAc and MeOH to provide 3a as a white solid (1.91 g, 87% yield).

2-5. Effect of B(OMe)₃
The ¹H NMR spectra in DMSO-d₆ of a sample containing D-mannose and 2 equiv of B(OMe)₃ (Figure S1) indicates the existence of complicated complexation between mannose and B(OMe)₃. The most notable difference between Figure S1 (mannose + 2 equiv of B(OMe)₃) and Figure S2 (mannose only) is the appearance of an aldehyde C-H proton (9.66 ppm) in Figure S1. The ratio of the aldehyde form to other species was determined to be 0.15% by ¹H NMR analysis using MeCN as internal standard. Thus, the addition of B(OMe)₃ significantly increased the aldehyde form. Although the concentration of the aldehyde form was still low, this observation indicates that the
addition of B(OMe)₃ facilitates the propargylation reaction by stabilizing the aldehyde form of aldoses (see Fig. 2 in the text).

**Figure S1.** Mannose + 2 equiv of B(OMe)₃ + 1 equiv of MeCN

**Figure S2.** Mannose
2-6. Characterization of propargylation products

(2R,3R,4R,5R,6S)-non-8-yne-1,2,3,4,5,6-hexaol (3a)
A white solid, Yield: 90%. ¹H NMR (500 MHz, D₂O) δ 3.99 (t, J = 6.9 Hz, 1H), 3.79 (d, J = 9.6 Hz, 1H), 3.77-3.74 (m, 1H), 3.70 (d, J = 8.7 Hz, 1H), 3.67-3.63 (m, 1H), 3.60 (d, J = 9.6 Hz, 1H), 3.58-3.53 (m, 1H), 2.47-2.36 (m, 2H), 2.28 (t, J = 2.3 Hz, 1H); ¹³C NMR (125 MHz, D₂O) δ 82.8, 71.8, 71.6, 70.1, 69.7, 68.5, 63.9, 23.6; IR (KBr): 3365, 3231, 1445, 1306, 1094, 849, 729 cm⁻¹; HRMS (ESI): m/z calcld for C₉H₁₆O₆ [M+Na]⁺ 243.0840 Found 243.0842; [α]D²₃.² = +0.2 (c = 0.53, H₂O).

(2R,3R,4R,5R,6R)-non-8-yne-1,2,3,4,5,6-hexaol (4a)
A white solid, Yield: 81%. ¹H NMR (500 MHz, D₂O) δ 3.88 (dt, J = 8.6, 4.6 Hz, 1H), 3.74-3.57 (m, 5H), 3.50 (dd, J = 11.7, 6.0 Hz, 1H), 2.42 (dt, J = 17.2, 3.5 Hz, 1H), 2.34 (ddd, J = 17.2, 8.0, 2.6 Hz, 1H), 2.22 (t, J = 2.6 Hz, 1H); ¹³C NMR (125 MHz, D₂O) δ 82.7, 72.8, 71.5, 71.4, 71.2, 70.5, 70.2, 63.9, 21.7; IR (KBr): 3375, 2962, 2896, 1423, 1392, 1088, 1035, 752, 634 cm⁻¹; HRMS (ESI): m/z calcld for C₉H₁₆O₆ [M+Na]⁺ 243.0840 Found 243.0835; [α]D²₂.² = +6.4 (c = 0.50, H₂O).

(2R,3S,4R,5S,6S)-non-8-yne-1,2,3,4,5,6-hexaol (3b)
A white solid, Yield: 73%. ¹H NMR (500 MHz, D₂O) δ 3.83 (t, J = 6.5 Hz, 1H), 3.77 (d, J = 9.5 Hz, 1H), 3.75-3.69 (m, 2H), 3.53 (d, J = 6.3 Hz, 2H), 3.51 (d, J = 10.3 Hz, 1H), 2.52 (dt, J = 17.4, 2.5 Hz, 1H), 2.37 (ddd, J = 17.4, 5.4, 2.5 Hz, 1H), 2.22 (t, J = 2.5 Hz, 1H); ¹³C NMR (125 MHz, CD₃OD) δ 75.1, 72.0, 71.3, 69.7, 68.0, 64.9, 40.9, 28.7; IR
(KBr): 3297, 1422, 1112, 1086, 1033 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_9\)H\(_{16}\)O\(_6\) [M+Na]\(^+\) 243.0840 Found 243.0842; \([\alpha]_D^{22.4} = +4.4\) (\(c = 0.50\), H\(_2\)O).

\(\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH}\)

\((2\text{R},3\text{S},4\text{R},5\text{S},6\text{R})\)-non-8-yn-1,2,3,4,5,6-hexaol (4b)

A white solid, Yield: 66%. \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 3.80-3.73\) (m, 3H), 3.60 (d, \(J = 9.2\) Hz, 1H), 3.54-3.49 (m, 3H), 2.44-2.40 (m, 1H), 2.34-2.28 (m, 1H), 2.22 (brs, 1H); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD) \(\delta 81.9, 73.6, 73.2, 71.7, 71.4, 71.2, 64.9, 24.3\); IR (KBr): 3398, 2925, 1427, 1096, 1028, 667 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_9\)H\(_{16}\)O\(_6\) [M+Na]\(^+\) 243.0840 Found 243.0842; \([\alpha]_D^{22.4} = +4.4\) (\(c = 0.50\), H\(_2\)O).

\(\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH}\)

\((2\text{R},3\text{R},4\text{R},5\text{S},6\text{S})\)-non-8-yn-1,2,3,4,5,6-hexaol (3c)

A white solid, Yield: 76%. \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 3.86\) (t, \(J = 2.9\) Hz, 1H), 3.74-3.70 (m, 1H), 3.66-3.57 (m, 4H), 3.49 (dd, \(J = 11.4, 5.9\) Hz, 1H), 2.45 (dt, \(J = 17.3, 3.4\) Hz, 1H), 2.36 (ddd, \(J = 17.3, 6.3, 2.3\) Hz, 1H), 2.21 (t, \(J = 2.3\) Hz, 1H); \(^{13}\)C NMR (125 MHz, D\(_2\)O) \(\delta 81.9, 74.6, 73.6, 71.8, 71.7, 69.2, 68.8, 63.1, 23.0\); IR (KBr): 3280, 2918, 1427, 1096, 1028, 667 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_9\)H\(_{16}\)O\(_6\) [M+Na]\(^+\) 243.0840 Found 243.0835; \([\alpha]_D^{22.1} = +6.1\) (\(c = 0.35\), H\(_2\)O).

\(\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH}\)

\((2\text{R},3\text{R},4\text{R},5\text{S},6\text{R})\)-non-8-yn-1,2,3,4,5,6-hexaol (4c)

A white solid, Yield: 72%. (inseparable mixture of 3c and 4c) For 4c: \(^1\)H NMR (500 MHz, D\(_2\)O) \(\delta 3.95\) (dd, \(J = 5.7, 1.7\) Hz, 1H), 3.89 (td, \(J = 6.9, 2.9\) Hz, 1H), 3.80-3.60 (m, 5H), 2.52 (dd, \(J = 6.9, 2.9\) Hz, 1H), 2.27 (t, \(J = 2.9\) Hz, 1H); \(^{13}\)C NMR (125 MHz, D\(_2\)O) \(\delta 82.0, 74.7, 73.9, 71.8, 71.7, 70.6, 70.0, 63.5, 23.7\); IR (KBr): 3387, 2925, 1675, 1204, 1076 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_9\)H\(_{16}\)O\(_6\) [M+Na]\(^+\) 243.0840 Found 243.0832.
(2R,3S,4R,5S)-oct-7-yne-1,2,3,4,5-pentaol (3d)
A white solid. Yield: 84%. $^1$H NMR (500 MHz, D$_2$O) $\delta$ 4.00 (t, $J = 7.1$ Hz, 1H), 4.89 (t, $J = 6.4$ Hz, 1H), 3.65-3.56 (m, 4H), 2.47 (ddd, $J = 16.9$, 7.5, 2.6 Hz, 1H), 2.40 (ddd, $J = 16.9$, 6.7, 2.6 Hz, 1H), 2.32 (t, $J = 2.6$ Hz, 1H); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$ 82.6, 71.6, 71.2, 71.0, 70.2, 69.1, 63.9, 23.7; IR (KBr): 3388, 3217, 1452, 1389, 1294, 1231, 1105, 1052, 735, 657 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_8$H$_{14}$O$_5$ [M+Na]+$^+$ 213.0734 Found 213.0737; $[\alpha]_D^{22.8} = +4.3$ ($c = 0.15$, MeOH).

(2R,3S,4R,5R)-oct-7-yne-1,2,3,4,5-pentaol (4d)
A white solid. Yield: 81%. $^1$H NMR (500 MHz, D$_2$O) $\delta$ 3.87 (dt, $J = 8.6$, 4.5 Hz, 1H), 3.80-3.77 (m, 1H), 3.66 (dd, $J = 8.1$, 5.1 Hz, 1H), 3.53-3.48 (m, 3H), 2.41 (dt, $J = 17.2$, 2.9 Hz, 1H), 2.33 (ddd, $J = 17.2$, 7.9, 2.9 Hz, 1H), 2.21 (t, $J = 2.9$ Hz, 1H); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$ 82.6, 72.9, 71.6, 71.5, 71.2, 71.0, 63.7, 21.8; IR (KBr): 3326, 2952, 2900, 1458, 1411, 1222, 1095, 1048, 1030, 860, 695, 654 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_8$H$_{14}$O$_5$ [M+Na]+$^+$ 213.0734 Found 213.0731; $[\alpha]_D^{20.8} = +9.4$ ($c = 0.86$, H$_2$O).

(2R,3S,4R,5S)-oct-7-yne-1,2,3,4,5-pentaol (3e)
A white solid. Yield: 95%. $^1$H NMR (500 MHz, D$_2$O) $\delta$ 3.76 (dd, $J = 11.2$, 6.2 Hz, 1H), 3.71 (dd, $J = 6.2$, 2.0 Hz, 1H), 3.67 (dd, $J = 11.8$, 2.9 Hz, 1H), 3.63-3.60 (m, 1H), 3.51-3.47 (m, 2H), 2.40 (ddd, $J = 17.4$, 4.8, 2.3 Hz, 1H), 2.30 (ddd, $J = 17.4$, 6.4, 2.3 Hz, 1H), 2.22 (t, $J = 2.3$ Hz, 1H); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$ 81.7, 72.0, 71.9, 71.8, 71.7, 71.2, 63.5, 23.4; IR (KBr): 3430, 3285, 1434, 1089, 1042 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_8$H$_{14}$O$_5$ [M+Na]+$^+$ 213.0734 Found 213.0737; $[\alpha]_D^{21.5} = -0.4$ ($c = 0.52$, H$_2$O).
(2R,3S,4R,5R)-oct-7-yne-1,2,3,4,5-pentaol (4e)
A white solid, Yield: 93%. ¹H NMR (500 MHz, D₂O) δ 3.72-3.64 (m, 4H), 3.60 (ddd, J = 8.8, 6.3, 2.8 Hz, 1H), 3.51 (dd, J = 11.9, 6.3 Hz, 1H), 2.51 (dt, J = 17.3, 2.6 Hz, 1H), 2.37 (ddd, J = 17.3, 5.6, 2.6 Hz, 1H), 2.22 (t, J = 2.6 Hz, 1H); ¹³C NMR (125 MHz, D₂O) δ 82.2, 71.9, 71.9, 71.5, 69.8, 68.9, 63.9, 23.9; IR (KBr): 3305, 2949, 1286, 1082, 1041, 644 cm⁻¹; HRMS (ESI): m/z calcd for C₈H₁₄O₅ [M+Na]⁺ 213.0734 Found 213.0737; [α]D²².₇ = -4.8 (c = 0.48, H₂O).

(2R,3S,4S,5S)-oct-7-yne-1,2,3,4,5-pentaol (3f)
A white solid, Yield: 65%. ¹H NMR (400 MHz, D₂O) δ 3.75-3.64 (m, 3H), 3.60-3.57 (m, 1H), 3.52-3.43 (m, 2H), 2.49 (dt, J = 17.3, 2.3 Hz, 1H), 2.36 (ddd, J = 17.3, 6.0, 2.3 Hz, 1H), 2.22 (t, J = 2.3 Hz, 1H); ¹³C NMR (100 MHz, D₂O) δ 82.0, 73.7, 73.0, 72.0, 70.2, 69.0, 63.0, 23.4; IR (KBr): 3389, 2934, 1421, 1067, 657 cm⁻¹; HRMS (ESI): m/z calcd for C₈H₁₄O₅ [M+Na]⁺ 213.0734 Found 213.0741; [α]D²².₆ = +6.4 (c = 0.91, H₂O).

(2R,3S,4S,5R)-oct-7-yne-1,2,3,4,5-pentaol (4f)
A white solid, Yield: 60%. ¹H NMR (500 MHz, D₂O) δ 3.81-3.79 (m, 1H), 3.70-3.67 (m, 1H), 3.61-3.55 (m, 3H), 3.51-3.47 (dd, J = 11.5, 6.9 Hz, 1H), 2.41-2.32 (m, 2H), 2.24 (m, 1H); ¹³C NMR (125 MHz, D₂O) δ 81.9, 73.2, 72.5, 71.9, 71.8, 70.4, 63.4, 23.5; IR (KBr): 3388, 1420, 1067, 669 cm⁻¹; HRMS (ESI): m/z calcd for C₈H₁₄O₅ [M+Na]⁺ 213.0727 Found 213.0734; [α]D²².₈ = +2.9 (c = 0.68, H₂O).
(2R,3S,5S)-oct-7-yne-1,2,3,5-tetraol (3g)
A white solid, Yield: 65%. ¹H NMR (500 MHz, CD₂OD) δ 3.97 (dq, J = 8.1, 5.7 Hz, 1H), 3.74-3.67 (m, 2H), 3.56 (dd, J = 11.3, 6.5 Hz, 1H), 3.46 (dt, J = 6.3, 2.9 Hz, 1H), 2.41-2.30 (m, 2H), 2.28 (t, J = 2.9 Hz, 1H), 1.99 (ddd, J = 14.3, 4.6, 2.9 Hz, 1H), 1.66-1.60 (dt, J = 14.3, 9.2 Hz, 1H); ¹³C NMR (125 MHz, CD₂OD) δ 81.7, 76.3, 72.4, 71.4, 70.0, 64.4, 39.5, 27.8; IR (KBr): 3376, 2923, 1677, 1424, 1204, 1071, 651 cm⁻¹; HRMS (ESI): m/z calcd for C₈H₁₄O₄ [M+Na]⁺ 197.0785 Found 197.0781; [α]D²².⁹ = -1.6 (c = 0.57, MeOH).

(2R,3S,5R)-oct-7-yne-1,2,3,5-tetraol (4g)
A white solid, Yield: 53%. ¹H NMR (500 MHz, CD₂OD) δ 3.98 (dddd, J = 9.2, 6.3, 2.9 Hz, 1H), 3.786 (ddd, J = 9.8, 6.3, 2.4 Hz, 1H), 3.71 (dd, J = 11.2, 3.9 Hz, 1H), 3.56 (dd, J = 11.2, 6.6 Hz, 1H), 3.48 (dt, J = 6.6, 3.9 Hz, 1H), 2.40 – 2.31 (m, 2H), 2.27 (t, J = 2.8 Hz, 1H), 1.77 (ddd, J = 14.4, 9.8, 2.7 Hz, 1H), 1.69 (ddd, J = 14.4, 9.8, 2.7 Hz, 1H); ¹³C NMR (125 MHz, CD₂OD) δ 81.9, 76.6, 71.3, 70.2, 67.8, 64.7, 40.2, 28.7; IR (KBr): 3375, 2921, 1420, 1064, 652 cm⁻¹; HRMS (ESI): m/z calcd for C₈H₁₄O₄ [M+Na]⁺ 197.0785 Found 197.0781; [α]D²⁰.⁶ = -28.2 (c = 0.64, H₂O).

(2R,3R,4R,6S)-non-8-yne-1,2,3,4,6-pentaol (3h)
A white solid, Yield: 74%. ¹H NMR (500 MHz, CD₂OD) δ 4.03-3.97 (m, 1H), 3.87 (ddd, J = 7.6, 6.7, 2.2 Hz, 2H), 3.64-3.58 (m, 2H), 3.36 (dd, J = 7.6, 2.2 Hz, 1H), 2.41-2.31 (m, 2H), 2.27 (t, J = 2.7 Hz, 1H), 1.88 (ddd, J = 14.3, 9.8, 2.4 Hz, 1H), 1.69 (ddd, J = 14.3, 9.8, 2.4 Hz, 1H); ¹³C NMR (100 MHz, D₂O) δ 82.5, 74.4, 71.9, 71.2, 68.3, 66.8, 63.7, 39.2, 27.6; IR (KBr): 3280, 3192, 2952, 1466, 1422, 1065, 1030, 707
cm⁻¹; HRMS (ESI): m/z calcd for C₉H₁₆O₅ [M+Na]⁺ 227.0890 Found 227.0887; [α]₀²².₈ = +23.8 (c = 0.49, H₂O).

(2R,3R,4R,6R)-non-8-yne-1,2,3,4,6-pentaol (4h)
A white solid, Yield: 67%. ¹H NMR (500 MHz, CD₃OD) δ 4.00 (dq, J = 8.0, 5.6 Hz, 1H), 3.87-3.81 (m, 2H), 3.61 (d, J = 6.6 Hz, 2H), 3.37 (dd, J = 7.5, 2.1 Hz, 1H), 2.42-2.31 (m, 2H), 2.28 (t, J = 2.6 Hz, 1H), 2.02 (ddd, J = 14.2, 4.7, 3.0 Hz, 1H), 1.55 (ddd, J = 14.2, 9.1, 8.1 Hz, 1H); ¹³C NMR (125 MHz, CD₃OD) δ 81.7, 84.6, 9, 71.8, 71.7, 70.1, 64.8, 40.2, 27.9; IR (neat): 3375, 1422, 1069 cm⁻¹; HRMS (ESI): m/z calcd for C₉H₁₆O₅ [M+Na]⁺ 227.0890 Found 227.0882; [α]₀²¹.₅ = +9.4 (c = 0.53, H₂O).

(2R,3S,4R,6S)-non-8-yne-1,2,3,4,6-pentaol (3i)
A white solid, Yield: 59%. ¹H NMR (400 MHz, CD₃OD) δ 4.13-4.09 (m, 1H), 4.00-3.91 (m, 1H), 3.78 (dd, J = 10.9, 3.5 Hz, 1H), 3.67 (ddd, J = 8.0, 5.9, 3.5 Hz, 1H), 3.60 (dd, J = 10.9, 5.9 Hz, 1H), 3.33 (s, 1H), 2.36 (dd, J = 6.2, 2.7 Hz, 2H), 2.26 (t, J = 2.7 Hz, 1H), 1.94 (ddd, J = 14.3, 10.4, 2.6 Hz, 1H), 1.53 (ddd, J = 14.3, 9.8, 2.6 Hz, 1H); ¹³C NMR (125 MHz, CD₃OD) δ 82.0, 75.5, 73.2, 71.3, 68.3, 68.0, 65.1, 41.2, 28.6; IR (neat): 3290, 1420, 1092, 1074, 1025 cm⁻¹; HRMS (ESI): m/z calcd for C₉H₁₆O₅ [M+Na]⁺ 227.0890 Found 227.0900; [α]₀²³.₈ = +31.9 (c = 0.28, MeOH).

(2R,3S,4R,6R)-non-8-yne-1,2,3,4,6-pentaol (4i)
A white solid, Yield: 52%. ¹H NMR (500 MHz, CD₃OD) δ 4.06 (dt, J = 7.4, 1.8 Hz, 1H), 3.94 (dq, J = 11.0, 5.8 Hz, 1H), 3.78 (dd, J = 11.0, 3.5 Hz, 1H), 3.67 (ddd, J = 8.1, 6.0, 3.5 Hz, 1H), 3.60 (dd, J = 8.1, 5.7 Hz, 1H), 3.36 (dd, J = 10.4, 5.2 Hz, 1H),
2.42-2.33 (m, 2H), 2.28 (t, J = 2.6 Hz, 1H), 1.85-1.82 (m, 2H); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD) δ 81.7, 74.5, 73.0, 71.4, 69.9, 69.5, 65.1, 40.3, 27.9; IR (KBr): 3280, 2918, 1432, 1089, 1033, 638 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_9\)H\(_{16}\)O\(_5\) [M+Na]\(^+\) 227.0890 Found 227.0900; \([\alpha]\)\(_D\)\(^{22.4}\) = +6.5 (c = 0.26, H\(_2\)O).

\[
\text{N-}((4S,5R,6R,7S,8R)-4,6,7,8,9-pentahydroxynon-1-yn-5-yl)acetamide (3j)}
\]
A white solid, Yield: 70%. \(^1\)H NMR (500 MHz, D\(_2\)O) δ 4.13 (t, J = 6.9 Hz, 1H), 3.94 (d, J = 10.4 Hz, 1H), 3.78 (d, J = 10.4 Hz, 1H), 3.68 (dd, J = 12.0, 2.9 Hz, 1H), 3.61-3.57 (m, 1H), 3.47 (dd, J = 12.0, 6.3 Hz, 1H), 3.31 (d, J = 9.2 Hz, 1H), 2.62-2.22 (m, 3H), 1.89 (s, 3H); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD) δ 174.8, 81.8, 72.4, 71.4, 71.2, 69.7, 68.7, 65.2, 54.7, 25.3, 22.6; IR (KBr): 3499, 3362, 1623, 1541, 1074 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_{11}\)H\(_{19}\)NO\(_6\) [M+Na]\(^+\) 284.1105 Found 284.1106; \([\alpha]\)\(_D\)\(^{22.8}\) = -28.9 (c = 0.67, H\(_2\)O).

\[
\text{N-}((4R,5R,6R,7S,8R)-4,6,7,8,9-pentahydroxynon-1-yn-5-yl)acetamide (4j)}
\]
A white solid, Yield: 51%. \(^1\)H NMR (500 MHz, D\(_2\)O) δ 4.10 (dd, J = 8.9, 5.7 Hz, 1H), 3.98 (ddd, J = 7.7, 5.7, 4.3 Hz, 1H), 3.84-3.82 (m, 1H), 3.67 (dd, J = 11.9, 2.8 Hz, 1H), 3.57 (ddd, J = 9.1, 6.3, 2.8 Hz, 1H), 3.46 (dd, J = 11.9, 6.3 Hz, 1H), 3.38 (dd, J = 9.1, 0.8 Hz, 1H), 2.41 (ddd, J = 17.0, 4.1, 2.6 Hz, 1H), 2.30 (ddd, J = 17.0, 7.7, 2.6 Hz, 1H), 2.24 (t, J = 2.6 Hz, 1H), 1.87 (s, 3H); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD) δ 174.9, 82.1, 71.7, 71.1, 70.2, 69.4, 63.7, 54.3, 22.7, 22.6; IR (neat): 3293, 1639, 1547, 1424, 1378, 1203, 1078, 1031 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_{11}\)H\(_{19}\)NO\(_6\) [M+Na]\(^+\) 284.1105 Found 284.1118; \([\alpha]\)\(_D\)\(^{23.3}\) = -4.4 (c = 0.84, MeOH).
(2R,3R,4R,5S,6S)-5-acetamidonon-8-yne-1,2,3,4,6-pentayl pentabenoate (3k-Bz)

A white solid, Yield: 55%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.10-8.09 (m, 2H), 7.95-7.93 (m, 2H), 7.86-7.84 (m, 4H), 7.70-7.69 (m, 2H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.50-7.43 (m, 5H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.33-7.26 (m, 7H), 7.10 (t, $J = 7.5$ Hz, 2H), 6.12 (d, $J = 6.9$ Hz, 1H), 6.05 (d, $J = 9.8$ Hz, 1H), 5.86 (dd, $J = 7.3$, 2.0 Hz, 2H), 5.20 (dd, $J = 13.0$, 6.3 Hz, 1H), 5.11 (dd, $J = 8.2$, 6.3 Hz, 1H), 4.67 (dd, $J = 11.9$, 4.4 Hz, 1H), 4.48 (dd, $J = 11.9$, 6.9 Hz, 1H), 2.75 (dd, $J = 17.0$, 7.1, 2.6 Hz, 1H), 2.68 (dd, $J = 17.0$, 6.0, 2.6 Hz, 1H), 2.01 (s, 3H), 1.93 (t, $J = 2.6$ Hz, 1H); $^{13}$C NMR (125 MHz, acetone-d$_6$) $\delta$ 170.4, 166.3, 166.1, 165.9, 165.8, 134.3, 134.2, 134.0, 133.9, 133.7, 131.0, 130.9, 130.9, 130.8, 130.7, 130.6, 130.5, 130.3, 130.2, 129.4, 129.3, 129.2, 129.1, 129.0, 79.8, 72.5, 72.0, 71.9, 71.0, 70.4, 69.5, 64.3, 50.5, 50.4, 22.9, 21.9; IR (neat): 3390, 1721, 1683, 1259, 1092, 1067, 708 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{46}$H$_{39}$NO$_{11}$ [M+Na]$^+$ 804.2416 Found 804.2399; [$\alpha$]$_D^{22.9}$ = -13.9 (c = 0.65, MeOH).

(2R,3R,4R,5S,6R)-5-acetamidonon-8-yne-1,2,3,4,6-pentayl pentabenoate (4k-Bz)

A white solid, Yield: 40%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 7.4$ Hz, 2H), 7.95 (d, $J = 7.4$ Hz, 2H), 7.86-7.80 (m, 6H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.49 (dd, $J = 13.1$, 7.4 Hz, 2H), 7.42 (dd, $J = 10.8$, 4.4 Hz, 4H), 7.32-7.24 (m, 8H), 5.93-5.89 (m, 4H), 5.26 (dd, $J = 11.3$, 5.6 Hz, 1H), 5.16 (dd, $J = 9.8$, 6.3 Hz, 1H), 4.73 (dd, $J = 11.9$, 4.3 Hz, 1H), 4.48 (dd, $J = 11.9$, 7.4 Hz, 1H), 2.75 (dd, $J = 17.3$, 5.0, 2.6 Hz, 1H), 2.64 (dd, $J = 17.3$, 5.7, 2.6 Hz, 1H), 1.92 (t, $J = 2.6$ Hz, 1H), 1.90 (s, 3H); $^{13}$C NMR (125 MHz, acetone-d$_6$) $\delta$ 170.9, 166.3, 166.1, 166.0, 165.9, 134.2, 134.1, 134.0, 133.9, 133.8, 133.8, 130.9, 130.8, 130.6, 130.5, 130.3, 130.2, 129.3, 129.2, 129.1, 129.0, 79.6, 73.2, 72.8, 71.4, 70.9, 70.2, 64.5, 50.4, 22.8, 22.3; IR (neat): 3376, 1719, 1683, 1246, 1092, 1067, 708 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{46}$H$_{39}$NO$_{11}$ [M+Na]$^+$ 804.2416 Found 804.2399; [$\alpha$]$_D^{22.8}$ = -17.4 (c = 0.45, MeOH).
(2R,3S,4R,5S,6R)-5-acetamidonon-8-yne-1,2,3,4,6-pentayl pentabenzoate (3l-Bz)
A white solid, Yield: 45%. \( ^1 \)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.05-7.99 (m, 4H), 7.84-7.82 (m, 2H), 7.74-7.71 (m, 5H), 5.99-5.92 (m, 2H), 5.85 (dt, \( J = 5.9, 3.0 \) Hz, 1H), 5.23 (dd, \( J = 13.2, 6.3 \) Hz, 1H), 5.16 (dd, \( J = 7.3, 1.8 \) Hz, 1H), 4.87 (dd, \( J = 12.3, 3.0 \) Hz, 1H), 4.59 (dd, \( J = 12.3, 5.9 \) Hz, 1H), 2.72 (ddd, \( J = 17.2, 6.4, 2.7 \) Hz, 1H), 2.65 (ddd, \( J = 17.2, 5.9, 2.7 \) Hz, 1H), 1.51 (s, 3H), 1.86 (t, \( J = 2.7 \) Hz, 1H); \( ^{13} \)C NMR (125 MHz, acetone-d\(_6\)) \( \delta \) 171.1, 166.5, 166.1, 165.8, 165.7, 134.2, 134.1, 134.1, 134.1, 134.0, 133.9, 130.8, 130.7, 130.6, 130.6, 130.5, 130.4, 130.4, 130.2, 129.4, 129.4, 129.3, 129.2, 129.2, 129.0, 79.8, 72.4, 72.0, 71.3, 71.2, 70.4, 63.2, 51.9, 51.8, 23.0, 22.2; IR (neat): 3418, 1717, 1653, 1261, 1093, 709 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_{46}\)H\(_{39}\)NO\(_{11}\) [M+Na]+ 804.2416 Found 804.2399; [\( \alpha \)]\(_D\)\(^{22.8}\) = +12.6 (c = 0.44, MeOH).

(2R,3S,4R,5S,6R)-5-acetamidonon-8-yne-1,2,3,4,6-pentayl pentabenzoate (4l-Bz)
A white solid, Yield: 51%. \( ^1 \)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.11-8.07 (m, 2H), 8.07-8.03 (m, 2H), 8.03-7.99 (m, 2H), 7.92-7.88 (m, 2H), 7.84 (d, \( J = 8.2 \) Hz, 2H), 7.58 (dd, \( J = 15.3, 7.5 \) Hz, 2H), 7.53 (dd, \( J = 13.0, 6.9 \) Hz, 2H), 7.44-7.33 (m, 10H), 7.19 (t, \( J = 7.7 \) Hz, 2H), 6.33 (dd, \( J = 8.2, 3.1 \) Hz, 1H), 5.81-5.72 (m, 4H), 5.01-4.95 (m, 1H), 4.79 (dd, \( J = 12.4, 2.7 \) Hz, 1H), 4.49 (dd, \( J = 12.4, 5.0 \) Hz, 1H), 2.67-2.56 (m, 2H), 1.78 (s, 3H), 1.70 (t, \( J = 2.1 \) Hz, 1H); \( ^{13} \)C NMR (125 MHz, acetone-d\(_6\)) \( \delta \) 170.9, 166.5, 166.5, 166.4, 166.3, 134.5, 134.2, 134.2, 134.0, 133.9, 130.8, 130.8, 130.7, 130.6, 130.6, 130.5, 130.5, 130.3, 130.3, 130.2, 129.5, 129.3, 129.2, 129.2, 100.8, 79.7, 72.3, 72.1, 71.8, 70.6, 63.1, 51.5, 22.7, 22.5; IR (neat): 3384, 1711, 1674, 1241, 1090, 1066, 1024, 706 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_{46}\)H\(_{39}\)NO\(_{11}\) [M+Na]+ 804.2416 Found 804.2399; [\( \alpha \)]\(_D\)\(^{23.1}\) = +19.8 (c = 1.17, MeOH).
(2R,3R,4R,5S,6S)-3-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydropyran-2-yl)oxy)non-8-yne-1,2,4,5,6-pentaol (3m)
A white solid, Yield: 56%. $^1$H NMR (500 MHz, D$_2$O) $\delta$ 4.39 (d, $J = 8.0$ Hz, 1H), 3.93 (s, 1H), 3.78-3.38 (m, 12H), 2.45 (dt, $J = 17.3$, 2.5 Hz, 1H), 2.35 (ddd, $J = 17.3$, 6.1, 2.5 Hz, 1H), 2.23 (t, $J = 2.5$ Hz, 1H); $^{13}$C NMR (125 MHz, D$_2$O) $\delta$ 104.1, 82.2, 82.1, 75.9, 73.7, 73.2, 72.1, 71.9, 71.8, 69.3, 69.1, 68.9, 62.7, 61.7, 23.1; IR (neat): 3398, 1642, 1424, 1074 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{15}$H$_{26}$O$_{11}$ [M+Na]$^+$ 405.1368 Found 405.1367; $\left[\alpha\right]_D^{23.0} = +7.4$ (c = 0.87, H$_2$O).

(2R,3R,4R,5S,6R)-3-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydropyran-2-yl)oxy)non-8-yne-1,2,4,5,6-pentaol (4m)
A white solid, Yield: 45%. $^1$H NMR (500 MHz, D$_2$O) $\delta$ 4.34 (d, $J = 7.5$ Hz 1H), 3.90-3.87 (m, 1H), 3.81-3.47 (m, 11H), 3.38-3.35 (m, 1H), 2.38 (ddd, $J = 9.4$, 7.4, 2.5 Hz, 1H), 2.33-2.26 (m, 1H), 2.23 (t, $J = 2.0$ Hz, 1H). $^{13}$C NMR (125 MHz, D$_2$O) $\delta$ 103.7, 82.5, 79.8, 75.6, 73.5, 73.2, 71.9, 71.8, 71.7, 70.6, 70.0, 69.2, 62.7, 61.5, 23.8; IR (neat): 3409, 1643, 1423, 1075 cm$^{-1}$; HRMS (ESI): m/z calcd for C$_{15}$H$_{26}$O$_{11}$ [M+Na]$^+$ 405.1368 Found 405.1367; $\left[\alpha\right]_D^{23.1} = +6.7$ (c = 1.09, H$_2$O).
3. Rapid Synthesis of Sialic Acid Derivatives

3-1. General procedure for sialic acid synthesis

3-Deoxy-D-glycero-β-D-galacto-2-nonulosonic acid (6a)

To a 100 mL round bottom flask containing compound 3a (1.1 g, 5 mmol) in 22.5 mL H2O was added Br2 (2.0 g, 25 mmol). The resulting reaction mixture was stirred for 10 min at room temperature to afford 5a. Excess amounts of bromine were removed via extraction with hexane (30 mL, 3 times). The aqueous solution containing the product was used directly into the next step without purification.

To a solution of 5a in H2O (22.5 mL) was added K2CO3 (3.46 g, 25 mmol). The mixture was stirred for 1 h at room temperature until TLC analysis indicated completion of the reaction. Subsequently, CH3COOH was added to the reaction mixture until pH = 4. To the mixture were added tBuOH (22.5 mL) and 2-methyl-2-buten (5.3 mL, 50 mmol). NaClO2 (497 mg, 5.5 mmol) dissolved in 5 mL water was added dropwise, and the mixture was stirred for 10 min at room temperature. The solvent was evaporated, and the resulting crude residue was passed through a Dowex 1X8 resin (formate form) using aqueous formic acid solution (0-1 M) as an eluent. The solvent was removed via lyophilization to afford 6a as white powder (1.02 g, 76% yield).

3-2. Characterization of sialic acids

(4S,5R,6R)-2-(dibromomethyl)-6-((1R,2R)-1,2,3-trihydroxypropyl)tetrahydro-2H-pyran-2,4,5-triol (5a)

1H NMR (500 MHz, D2O) δ 5.81 (s, 1H), 3.90-3.85 (m, 2H), 3.81 (d, J = 9.8 Hz, 2H), 3.70-3.68 (m, 1H), 3.63 (dd, J = 10.9, 5.7 Hz, 1H), 3.44 (t, J = 9.75 Hz, 1H), 2.42 (dd, J = 12.6, 5.2 Hz, 1H) 1.59 (t, J = 12.6 Hz, 1H); 13C NMR (125 MHz, CD3OD) δ 97.9, 73.7, 72.3, 71.8, 71.0, 69.9, 65.0, 53.9, 39.5; IR (KBr): 3376, 1655, 1420, 1066, 1034;
HRMS (ESI): m/z calcd for C9H16Br2O7 [M+Na]+ 418.9135 Found 418.9146; [α]D23.5 = -12.7 (c = 0.49, MeOH).

KDN (6a)

1H NMR (500 MHz, D2O) δ 3.93-3.88 (m, 2H), 3.79-3.75 (m, 2H), 3.67-3.64 (m, 1H), 3.57 (dd, J = 12.0, 6.3 Hz, 1H), 3.49 (t, J = 9.8 Hz, 1H), 2.18 (dd, J = 13.2, 4.6 Hz, 1H), 1.74 (t, J = 13.2 Hz, 1H); 13C NMR (125 MHz, D2O) δ 173.9, 95.9, 72.4, 71.1, 70.7, 69.3, 68.5, 63.9, 39.2; IR (KBr): 3399, 1743, 1440, 1281, 1210, 691 cm⁻¹ HRMS (ESI): m/z calcd for C9H16O9 [M-H]- 267.0721 Found 267.0721. [α]D25 = -42 (c = 1, H2O).

Neu5Ac (6j)
The reaction was conducted by following the general procedure, using 3j (26.1 mg, 0.1 mmol), Br2 (40 mg, 0.5 mmol) in H2O (0.5 mL). The reaction mixture was stirred at room temperature for 5 min. Excess amounts of bromine were removed via extraction with hexane. The aqueous solution containing the product was used directly into the next step. K2CO3 (69.1 mg, 0.5 mmol) was added to the aqueous solution (0.5 mL) containing the crude product. The reaction was stirred for 30 min. Then CH3COOH was added dropwise until pH = 4, and Pinnick oxidation using NaClO2 (9.9 mg, 0.11 mmol), tBuOH (0.5 mL), and 2-methyl-2-butene (0.11 mL, 1 mmol) was carried out in one pot. The solution was evaporated, and the resulting crude residue was passed through a Dowex 1X8 resin (formate form) using aqueous formic acid solution (0-1 M) as an eluent. The solvent was removed via lyophilization to afford 6j as white powder (22.9 mg, 74% yield).

1H NMR (500 MHz, D2O) δ 3.94-3.86 (m, 2H), 3.77 (t, J = 10.2 Hz, 1H), 3.69 (dd, J = 11.9, 2.6 Hz, 1H), 3.60 (dd, J = 9.1, 6.4, 2.6 Hz, 1H), 3.46 (dd, J = 11.9, 6.4 Hz, 1H), 3.38 (dd, J = 9.1, 0.7 Hz, 1H), 2.11 (dd, J = 13.0, 4.9 Hz, 1H), 1.89 (s, 3H), 1.70 (dd, J = 13.0, 11.6 Hz, 1H); 13C NMR (125 MHz, D2O) δ 175.6, 174.0, 96.0, 71.1, 70.9, 68.9, 67.4, 63.9, 52.8, 39.5, 22.8; IR (KBr): 3433, 3398, 1719, 1637, 1559, 1457, 1128, 1069,
1036 cm⁻¹ HRMS (ESI): m/z calcd for C₁₁H₁₉NO₉ [M-H]⁻ 308.0987 Found 308.0994, [α]D²¹⁴ = -13.2 (c = 0.27, H₂O).

4-epi-Neu5Ac (6j')

Using 4j (26.1 mg, 0.1 mmol), the reaction was conducted by following the procedure for preparing 6j. The corresponding product was obtained as a pale pink solid (20.1 mg, 65% from 4j). Mixture of anomers. For the major isomer: ¹H NMR (500 MHz, D₂O) δ 4.20 (d, J = 10.8 Hz, 1H), 4.05-3.94 (m, 2H), 3.64 (dd, J = 11.8, 2.4 Hz, 1H), 3.61 (ddd, J = 9.0, 5.6, 2.4 Hz, 1H), 3.50-3.40 (m, 2H), 2.02 (dd, J = 14.9, 3.3 Hz, 1H), 1.97 (dd, J = 14.9, 3.3 Hz, 1H), 1.87 (s, 3H); ¹³C NMR (125 MHz, D₂O) δ 174.9, 174.0, 95.8, 70.7, 69.1, 66.7, 66.4, 63.9, 48.3, 36.8, 22.6; IR (KBr): 3397, 1750, 1735, 1654, 1637, 1628, 1125, 1089, 1031 cm⁻¹ HRMS (ESI): m/z calcd for C₁₁H₁₉NO₉ [M-H]⁻ 308.0987 Found 308.0994,

(4S,5R,6S)-6-((R)-1,2-dihydroxyethyl)-2,4,5-trihydroxytetrahydro-2H-pyran-2-carboxylic acid (6d)

Using 4d (19 mg, 0.1 mmol), the reaction was conducted by following the procedure for preparing 6j. The corresponding product was obtained as a white solid. (19.5 mg, 82% from 4d).

¹H NMR (500 MHz, D₂O) δ 3.91-3.88 (m, 1H), 3.81 (ddd, J = 11.6, 9.2, 5.1 Hz, 1H), 3.62-3.58 (m, 1H), 3.53 (dd, J = 11.6, 7.6 Hz, 1H), 3.49-3.41 (m, 2H), 2.07 (dd, J = 13.0, 5.1 Hz, 1H), 1.65 (t, J = 13.0, 1H); ¹³C NMR (125 MHz, D₂O) δ 174.5, 96.1, 73.3, 70.8, 69.3, 69.3, 63.5, 39.3; IR (KBr): 3406, 1685, 1438, 1403, 1207, 1142, 624 cm⁻¹; HRMS (ESI): m/z calcd for C₈H₁₄O₈ [M-H]⁻ 237.0615 Found 237.0626; [α]D²²⁶ = -4.5 (c = 6.78, H₂O)
The reaction was conducted by following the general procedure, using 3m (100 mg, 0.26 mmol), KBr (74.8 mg, 0.63 mmol), and Oxone (193 mg, 0.63 mmol) in H2O (2.4 mL). The reaction mixture was stirred at room temperature for 5 min. Inorganic salts were roughly removed using C18 reverse phase column, and the crude product was used directly for the next step without further purification. K2CO3 (144 mg, 1.0 mmol) was added to the crude product dissolved in H2O (2.4 mL). The reaction was stirred for 30 min. Then CH3COOH was added dropwise until pH = 4, and Pinnick oxidation using NaClO2 (25.9 mg, 0.29 mmol), tBuOH (2.4 mL), and 2-methyl-2-butene (275 μL, 0.90 mmol) was carried out in one pot. The crude product was passed through a Dowex 1X8 resin (acetate form) using aqueous CH3COOH solution (0-2 M) as an eluent. Products were purified by preparative reverse phase HPLC using a gradient of acetonitrile versus 0.1% TFA in water, affording 6m as a white solid (59.3 mg, 53% from 3m). Preparative HPLC was carried out as follows: YMC-Triart C18 (20 mm I.D × 250 mm) column using a linear gradient of 0-50% acetonitrile in 0.1% aqueous TFA over 30 min at room temperature with a flow rate of 7.0 mL min⁻¹.

1H NMR (400 MHz, D2O) δ 4.33 (dd, J = 7.7, 2.1 Hz, 1H), 4.17 (dd, J = 9.3, 2.1 Hz, 1H), 3.83-3.76 (m, 5H), 3.63-3.48 (m, 6H), 3.40-3.35 (m, 1H), 2.92 (ddd, J = 18.1, 5.1, 2.2 Hz, 1H), 2.41 (dd, J = 18.1, 2.2 Hz, 1H); 13C NMR (125 MHz, D2O) δ 180.4, 103.5, 87.1, 76.8, 75.6, 73.2, 71.7, 71.4, 69.3, 68.5, 67.9, 62.8, 61.9, 40.3; IR (neat): 3389, 1758, 1638, 1077, 1043; HRMS (ESI): m/z calcd for C15H26O14 [M-H]⁻ 429.1249 Found 429.1266; [α]D²¹ = +21.5 (c = 2.28, H2O).
4e
4f
3g 3-s-kp 2-d-ribose alkyne ca.
4g r-skp 2-d-ribose carb-1-1
Neu5Ac (6j)
Neu5Ac (6j)
4-epi-Neu5Ac (6')

**Diagram:**

- Chemical structure of 4-epi-Neu5Ac (6')

**Textual Information:**

- Chemical formula: HOH\(\rightarrow\)HOH\(\rightarrow\)HOH\(\rightarrow\)HOH\(\rightarrow\)HOH\(\rightarrow\)HOH\(\rightarrow\)HOH\(\rightarrow\)HOH

- 4-epi-Neu5Ac (6')

**Additional Details:**

- **DFILE:** wei epi Neu5Ac- most new.pdf
- **COMMENT:**
- **DATIM:** 2015-09-02 23:09:35
- **OBMan 1H**
- **EDMOD proton.jsp**
- **OFQFQ:** 500.16 MHz
- **OBSET:** 2.41 KHz
- **OFDTH:** 6.01 Hz
- **POINT:** 16384
- **FRQSO:** 9384.30 Hz
- **SCANS:** 14
- **ACQTM:** 1.7459 sec
- **FD:** 5.0000 sec
- **FWL:** 5.55 usec
- **INRUC:** 1H
- **CTEMP:** 21.2 c
- **SILNT:** D2O
- **EXREF:** 4.65 ppm
- **BF:** 0.12 HZ
- **GAIN:** 34
