Efficient Synthesis of the Hexasaccharide Fragment of Landomycin A: Using Phenyl 2,3-*O*-Thionocarbonyl-1-thio-glycosides as 2-Deoxy- -glycoside Precursors

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Supporting Information

General Remarks. Solvents were distilled from the appropriate drying agents before use. Unless stated otherwise, all reactions were carried out under a positive pressure of argon and were monitored by TLC on silica gel HF₂₅₄ (0.5 mm, Qingdao, China). Spots were detected under UV light or by charging with 10% H₂SO₄ in MeOH. Flash column chromatography was carried out on silica gel H (400 mesh, Qingdao, China). Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. ¹H NMR spectra were recorded on a Bruker AM-300 spectrometer using CDCl₃ as solvent and tetramethylsilane as internal reference. Mass spectra were recorded on a HP5989A mass spectrometer.

2,3;4,5-di-*O*-Isopropylidene-D-xylose diethyl dithioacetal (4). To a suspension of D-xylose (8.0 g, 53.28 mmol) in concentrated HCl (3.2 mL), with vigorous magnetic stirring, was added EtSH (11.8 mL, 159.3 mmol) at room temperature. Stirring was continued until the two-layer mixture gave an homogeneous solution, which was then diluted with acetone (70 mL) and 2,2-dimethoxy propane (30 mL), and kept overnight. The solution was evaporated to near dryness and diluted with EtOAc. The organic layer was washed with saturated NaHCO₃ solution and brine, respectively, and dried over MgSO₄ and evaporated. The residue was applied to a silica gel column chromatography (*n*-hexane-ethyl acetate 7:1) to give **4** (12.28 g, 69%) as a yellow oil.

(Compound **4** is known, see: Kochetkov, N. K.; Dmitriev, A. *Tetrahedron* **1965**, 21, 803. For a similar preparation of the L-counterpart, see: Dondoni, A.; Marra, A.; Massi, A. *J. Org. Chem.* **1997**, 62, 6261.)

2,3-*O*-Isopropylidene-D-xylose diethyl dithioacetal (5). Compound **4** (12.28 g) in 80% HOAc (100 mL) was heated at 40 °C for 1.5 hour with stirring. The mixture was evaporated to near dryness. The residue was diluted with EtOAc, and washed with saturated NaHCO₃ and brine, respectively. The washings were re-extracted with EtOAc. The combined organic layers were dried over MgSO₄ and evaporated. The residue was purified by a silica gel column chromatography (*n*-hexane-ethyl acetate 2:1) to afford **5** (8.84 g, 82%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): 4.26 (t, 1 H, *J* = 6.3), 4.13 (dd, 1 H, *J* = 7.4, 2.2), 3.90 (m, 2 H), 3.74 (m, 2 H), 2.80-2.68 (m, 4 H), 2.58 (br s, 1 H), 2.35 (br s, 1 H), 1.45 (s, 3 H), 1.42 (s, 3 H), 1.28 (m, 6 H).

(For a similar transformation on the L-arabinose derivative, see: Kutterer, K. M. K.; Just, G. *Synth. Commun.* **1999**, 29(21), 3841)

(2R, 3R)-2,3-*O*-Isopropylidene-tartraldehyde diethyl mercaptal (6). Pb(OAc)₄ (14.33 g, 32.3 mmol) was added to a well stirred solution of **5** (8.71 g, 29.4 mmol) in dry toluene (100 mL) at 0 °C. After 20 min the reaction mixture was filtered through a pad of celite, washed with toluene (2 × 50 mL). The toluene solution was washed with saturated aqueous NaHCO₃ (2 × 100 mL). The combined aqueous phase was re-extracted with toluene. The combined organic layer was washed with aqueous NaHCO₃ again. The dried toluene extracts were evaporated to give crude **6** (7.75 g, 100%) as a pale yellow syrup, which was utilized for the next step without further purification.

3-[5-(Bisethylsulfanyl-methyl)-2,2-dimethyl-[1,3]dioxolan-4-yl]-aricylic acid ethyl ester (7): A solution of the above **6** (5.17 g, 19.5 mmol) and Ph₃P=CHCO₂Et (8.17 g, 23.5 mmol) in dry CH₂Cl₂ (25 mL) was stirred at 35 °C for 8 h. The CH₂Cl₂ was removed by vacuo. The residue was applied to a silica gel column chromatography (*n*-hexane-ethyl acetate 4:1) to afford **7** (5.12 g, 78.3%) as pale yellow oil (*Z*, *E* isomers). ¹H MNR (300 MHz, CDCl₃): 7.03 (dd, 0.5 H, *J* = 15.4, 5.2), 6.20 (m, 1 H), 5.95 (dd, 0.5 H, *J* = 11.5, 1.1), 5.68 (t, 0.5 H, *J* = 7.5), 4.70 (t, 0.5 H, *J* = 6.4), 4.22 (m, 2 H), 4.15-4.05 (m, 3.5 H), 3.92 (d, 0.5 H, *J* = 5.5), 2.82-2.62 (m, 4 H), 1.50-1.40 (m, 6 H), 1.35-1.20 (m, 9 H). ¹³C NMR (75 MHz, CDCl₃): 165.9 (165.3), 145.3 (144.6), 123.3

(122.6), 110.50 (110.42), 85.2 (83.8), 78.5 (75.0), 60.44 (60.41), 52.6 (52.4), 27.04 (26.81, 26.75), 25.38 (25.11, 25.07), 14.3 (14.1). ESI-MS: 357.1 ($M + Na^+$).

3-(2,2,5-Trimethyl-[1,3]dioxolan-4-yl)-propionic acid ethyl ester (8): To a solution of **7** (3.64 g, 10.9 mmol) in EtOH (100 mL), Raney nickel (50 g) was added. The mixture was stirred at 60 °C for 3 h, and then filtered through a pad of celite. The residue was washed with hot EtOH (150 mL). The filtrates were evaporated in vacuo. The resulting residue was purified by a silica gel column chromatography (*n*-hexane-ethyl acetate 15:1) to afford **8** (1.39 g, 59%) as a colorless liquid. 1H NMR (300 MHz, $CDCl_3$): 4.15 (q, 2 H, $J = 7.1$), 3.78-3.70 (m, 1 H), 3.68-3.59 (m, 1 H), 2.60-2.38 (m, 2 H), 2.00-1.85 (m, 1 H), 1.82-1.70 (m, 1 H), 1.38 (s, 3 H), 1.36 (s, 3 H), 1.28-1.22 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.1, 107.9, 81.3, 76.4, 60.3, 30.7, 27.2, 27.14, 27.08, 17.3, 17.2. ESI-MS (m/z): 239.1 ($M + Na^+$).

2,3,6-Tri-deoxy-4,5-*O*-isopropylidene-L-threo-hexane aldehyde (9): To a solution of **8** (1.28 g, 5.92 mmol) in CH_2Cl_2 (30 mL) was added DIBAL-H (7.10 mL, 1 M in hexane) slowly at -78 °C. After stirring for 15 min, aqueous NH_4Cl (7 mL) and Et_2O (20 mL) were added to the mixture. After stirring for another 1 h, the resulting precipitates were filtered through a pad of celite. The filtrates were washed with aqueous NH_4Cl (10 mL), H_2O (10 mL), and brine (10 mL), respectively, and then dried over $MgSO_4$ and concentrated. The residue was purified by a silica gel column chromatography (*n*-hexane-ethyl acetate 5:1) to give **9** (0.79 g, 78%) as a colorless liquid.

2,3,6-Tri-deoxy-L-threo-hexose (L-rhodinose): A similar procedure described in ref 16b was employed. (Herczegh, P.; Kovács, I.; László, A.; Dinya, Z.; Sztaricskai, J. *Liebigs Ann. Chem.* **1991**, 599.)

Acetic acid 6-acetoxy-2-methyl-tetrahydro-pyran-3-yl ester (1,4-di-*O*-acetyl-L-rhodinose, **2):** To a solution of L-rhodinose (279 mg, 2.11 mmol) in pyridine (10 mL) was added Ac_2O (5 mL). After stirring at room temperature overnight, the pyridine was

remove by vacuo followed by a silica gel column chromatography (*n*-hexane-ethyl acetate 3:1) to afford **2** (448 mg, 98%) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): 6.34 (br s, 0.2 H), 6.26 (br s, 0.2 H), 6.18 (br s, 0.1 H), 5.73 (m, 0.4 H), 5.30 (s, 0.1 H), 4.96-4.85 (m, 0.6 H), 4.78 (br s, 0.4 H), 4.30-4.23 (m, 0.2 H), 4.04-4.05 (m, 0.2 H), 3.80-3.72 (m, 0.4 H), 2.08-1.62 (m, 10 H), 1.26-1.12 (m, 3 H). MS (*m/z*, %): 157 (100), 115 (24), 97 (41), 87 (21), 69 (23), 43 (95).

Phenyl 4-*O*-benzyl-1-thio- α -D-rhamnopyranoside (11): A similar transformation (from L-**10** to L-**11**) was employed (See: Pozsgay, V. *J. Org. Chem.* **1998**, 63, 5983). ¹H NMR (300 MHz, CDCl₃): 7.45-7.22 (m, 10 H), 5.48 (s, 1 H), 4.78 (dd, 2 H, *J* = 16.2, 11.2), 4.30-4.18 (m, 2 H), 3.98-3.90 (m, 1 H), 3.46-3.40 (t, 1 H, *J* = 9.2), 2.60-2.50 (br s, 1 H, OH), 2.45-2.36 (br s, 1 H, OH), 1.38 (d, 3 H, *J* = 6.3)

Phenyl 4-*O*-benzyl-2,3-*O*-thionocarbonyl-1-thio- β -D-rhamnopyranoside (12): A solution of **11** (0.94 g, 2.73 mmol) and 1,1'-thiocarbonyldiimidazole (tech. 90%, 0.88 g, 4.91 mmol) in dry THF (15 mL) under argon was refluxed for 2 h. THF was then removed in vacuo. The residue was applied to a silica gel column chromatography (*n*-hexane-ethyl acetate 4:1) to give **12** (0.97 g, 92%) as a white amorphous solid. ¹H NMR (300 MHz, CDCl₃): 7.49-7.35 (m, 5 H), 5.82 (s, 1 H), 5.06 (t, 1 H, *J* = 6.5), 5.01 (d, 1 H, *J* = 7.2), 4.90 (d, 1 H, *J* = 11.4), 4.28-4.17 (m, 1 H), 4.66 (d, 1 H, *J* = 11.4), 3.41-3.36 (dd, 1H, *J* = 9.6, 6.6), 1.25 (d, 3 H, *J* = 6.0). ¹³C NMR (75 MHz, CDCl₃): 189.6, 132.6, 129.4, 128.5, 128.4, 128.3, 128.2, 128.1, 83.1, 81.7, 81.5, 77.6, 73.5, 65.7, 17.5. ESI-MS (*m/z*): 411.1 (M + Na⁺).

Disaccharide 13: A solution of donor **12** (916 mg, 2.36 mmol, 1.2 equiv.), acceptor **10** (582 mg, 1.96 mmol, 1.0 eq), 2,6-di-*tert*-butyl-4-methylpyridine (564 mg, 2.95 mmol, 1.5 equiv.), and 4 Å MS (1.0 g) in anhydrous CH₂Cl₂ (15 mL) was stirred at room temperature under argon for 30 min, followed by addition of a solution of MeOTf in CH₂Cl₂ (1.0 M, 2.36 mL, 1.2 equiv.). After stirring for 10 h at room temperature, the reaction mixture was diluted with CH₂Cl₂, and filtered through a pad of celite. The filtrates were concentrated. The residue was applied to a silica gel column

chromatography (*n*-hexane-ethyl acetate 4:1) to give **13** (1.21 g, 88%) as a white amorphous solid. $[\alpha]_D^{14} = 94.0$ (*c* 0.82, CHCl₃). ¹H NMR (300 MHz, CDCl₃): 7.55-7.20 (m, 15 H), 5.70 (s, 1 H), 5.24 (dd, 1 H, *J* = 11.6, 8.8), 4.72 (d, 1 H, *J* = 11.0), 4.60-4.54 (m, 2 H), 4.30 (d, 1 H, *J* = 5.5), 4.16 (t, 1 H, *J* = 6.5), 4.08-4.02 (m, 1 H), 3.60-3.53 (dd, 1 H, *J* = 10.0, 7.4), 3.48-3.38 (m, 1 H), 3.34 (d, 1 H, *J* = 8.7), 3.28-3.22 (m, 1 H), 2.38 (s, 3 H), 1.36-1.22 (m, 12 H). ¹³C NMR (75 MHz, CDCl₃): 170.8, 131.6, 131.4, 128.8, 128.85, 128.2, 127.9, 127.7, 127.6, 127.1, 108.7, 101.8, 83.3, 81.6, 81.1, 83.3, 81.6, 81.1, 77.4, 77.0, 76.6, 76.2, 76.0, 74.4, 70.6, 65.8, 27.5, 25.8, 17.3, 17.2, 13.1. ESI-MS (*m/z*): 721.2 (M + Na⁺).

Disaccharide 14: A similar transformation has been described in our previous report. (See ref. 13: Yu, B.; Yang, Z. Y. *Org. Lett.* **2001**, 3, 377).

For the corresponding 3'-OH derivative (80%): $[\alpha]_D^{12} = 172.5$ (*c* 0.95, CHCl₃). ¹H NMR (300 MHz, CDCl₃): 7.57-7.22 (m, 15 H), 5.71 (s, 1 H), 4.96 (d, 1 H, *J* = 11.4), 4.72 (d, 1 H, *J* = 10.8), 4.54 (d, 1 H, *J* = 11.7), 4.31 (d, 1 H, *J* = 5.1), 4.20 (m, 1 H), 4.05 (m, 1 H), 3.62-3.55 (m, 2 H), 3.40 (m, 1 H), 3.27 (t, 1 H, *J* = 8.7), 3.15 (dd, 1 H, *J* = 11.7, 9.0), 2.98 (br s, 1 H, OH), 1.34-1.24 (m, 12 H); ¹³C NMR (75 MHz, CDCl₃): 131.9, 131.8, 129.0, 128.9, 128.4, 128.1, 127.8, 127.5, 127.3, 109.2, 102.1, 83.8, 83.4, 81.6, 76.5, 74.9, 74.8, 71.1, 66.3, 57.9, 28.0, 26.3, 17.8, 17.7. ESI-MS (*m/z*): 647.2 (M + Na⁺).

A solution of the 3'-OH compound (391 mg, 0.626 mmol) in pyridine (4 mL) containing Ac₂O (2 mL) was stirred at room temperature overnight. The solvent was removed in vacuo. The residue was applied to a silica gel column chromatography (*n*-hexane-ethyl acetate 6:1) to give **14** (417 mg, 100%) as a white amorphous solid. ¹H NMR (300 MHz, CDCl₃): 7.45-7.19 (m, 15 H), 5.68 (s, 1 H), 5.18 (dd, 1 H, *J* = 11.4, 8.7), 4.57-4.55 (m, 3 H), 4.27 (d, 1 H, *J* = 5.4), 4.11 (t, 1 H, *J* = 6.3), 4.00-3.95 (m, 1 H), 3.55-3.43 (m, 2 H), 3.33-3.24 (m, 2 H), 1.93 (s, 3 H), 1.30-1.26 (m, 12 H)

Disaccharide 3: A similar transformation has been described in our previous report. (See ref. 13: Yu, B.; Yang, Z. Y. *Org. Lett.* **2001**, 3, 377).

For the corresponding 2,3-di-OH derivative. $[\alpha]_D^{12} = 120.0$ (c 0.78, CHCl_3), ^1H NMR (300 MHz, CDCl_3): 7.46-7.23 (m, 15 H), 5.52 (s, 1 H), 5.18 (dd, 1 H, $J = 11.4$, 9.0), 4.65-4.50 (m, 3 H), 4.49 (d, 1 H, $J = 8.7$), 4.24 (d, 1 H, $J = 3.6$), 3.78 (d, 1 H, $J = 9.3$), 3.59 (m, 1 H), 3.51 (t, 1 H, $J = 6.1$), 3.31-3.18 (m, 2 H), 1.94 (s, 3 H), 1.44 (d, 3 H, $J = 6.0$), 1.36 (d, 3 H, $J = 6.6$). ESI-MS (m/z): 649.4 ($\text{M} + \text{Na}^+$).

For disaccharide **3**: $[\alpha]_D^{16} = -58.8$ (c 1.39, CHCl_3), ^1H NMR (300 MHz, CDCl_3): 7.44-7.23 (m, 15 H), 5.76 (s, 1 H), 5.17 (dd, 1 H, $J = 11.4$, 8.7), 5.03 (t, 1 H, $J = 6.7$), 4.93 (d, 1 H, $J = 6.9$), 4.61 (s, 2 H), 4.51 (d, 1 H, $J = 9.0$), 4.15-4.04 (m, 1 H), 3.58-3.50 (m, 2 H), 3.30-3.20 (m, 2 H), 1.91 (s, 3 H), 1.37 (d, 3 H, $J = 5.7$), 1.26 (d, 3 H, $J = 6.6$). ^{13}C NMR (75 MHz, CDCl_3): 169.9, 132.6, 131.0, 129.4, 128.9, 128.6, 128.5, 127.9, 127.0, 103.0, 82.5, 81.8, 81.6, 81.0, 80.6, 74.7, 74.3, 71.6, 65.6, 54.8, 20.8, 17.9, 17.7. ESI-MS (m/z): 691.1 ($\text{M} + \text{Na}^+$).

Disaccharide 15: A solution of donor **3** (195 mg, 0.292 mmol, 1.0 equiv.), *p*-methoxyphenol (51 mg, 0.41 mmol, 1.4 equiv.), 2,6-di-*tert*-butyl-4-methylpyridine (85 mg, 0.438 mmol, 1.5 equiv.), and 4Å MS (300 mg) in anhydrous CH_2Cl_2 (7 mL) was stirred at room temperature under argon for 30 min, followed by addition of a solution of MeOTf in CH_2Cl_2 (0.442 M, 0.93 mL, 1.4 equiv.). After stirring for 10 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 , and filtered through a pad of celite. The filtrates were concentrated. The residue was applied to a silica gel column chromatography (*n*-hexane-ethyl acetate 7:1) to give **15** as a white amorphous solid.

$[\alpha]_D^{11} = -53.8$ (c 1.15, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 7.58-7.20 (m, 15 H), 6.88-6.78 (m, 4 H), 5.16 (dd, 1 H, $J = 11.4$, 9.0), 5.03 (dd, 1 H, $J = 11.4$, 9.0), 4.72 (d, 1 H, $J = 8.7$), 4.61 (t, 2 H), 4.52 (d, 1 H, $J = 8.4$), 3.78 (s, 3 H), 3.57 (t, 1 H, $J = 9.0$), 3.49 (m, 1 H), 3.32-3.18 (m, 4 H), 2.40 (s, 3 H), 1.91 (s, 3 H), 1.44 (d, 3 H, $J = 6.0$), 1.38 (d, 3 H, $J = 6.3$). ^{13}C NMR (75 MHz, CDCl_3): 170.9, 170.0, 155.3, 151.1, 137.6, 135.6, 133.8, 130.1, 128.8, 128.7, 128.4, 127.8, 126.4, 118.1, 114.4, 82.7, 80.6, 76.0, 74.7, 74.3, 71.2, 71.0, 55.6, 55.0, 54.7, 20.8, 18.3, 18.0, 13.6.

Disaccharide 16: Disaccharide **15** was added to a mixture solution of MeONa/MeOH (0.1 N, 4 mL) and CH₂Cl₂ (1.0 mL). After stirring at 40 °C for 10 h, the solvent was removed in vacuo. The residue was applied to a silica gel column chromatography (*n*-hexane-ethyl acetate 5:1) to give **16** (195 mg, 87%) as a white amorphous solid. $[\alpha]_D^{17} = 27.0$ (*c* 0.79, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 7.50-7.04 (m, 15 H), 6.88-6.78 (m, 4 H), 5.05 (dd, 1 H, *J* = 11.3, 8.8), 4.95 (d, 1 H, *J* = 8.1), 4.73 (t, 2 H, *J* = 8.8), 4.47 (d, 1 H, *J* = 8.4), 3.78 (s, 3 H), 3.62-3.53 (q, 2 H, *J* = 9.1), 3.42-3.27 (m, 3 H), 3.15 (t, 1 H, *J* = 9.0), 3.07 (dd, 1 H, *J* = 11.0, 8.8), 2.88 (br s, 1 H, OH), 2.38 (s, 3 H), 1.46 (d, 3 H, *J* = 6.0), 1.38 (d, 3 H, *J* = 6.0). ¹³C NMR (75 MHz, CDCl₃): 171.0, 155.2, 151.1, 138.2, 134.5, 133.8, 130.6, 128.9, 128.7, 128.4, 128.0, 127.8, 127.8, 118.1, 114.4, 102.1, 101.6, 83.6, 80.5, 76.0, 74.8, 74.7, 71.0, 70.9, 57.5, 55.6, 55.0, 18.3, 18.0, 13.6. ESI-MS (*m/z*): 787.3 (M + Na⁺).

Trisaccharide 17: A solution of the disaccharide acceptor **16** (126 mg, 0.165 mmol), rhodinosyl acetate **2** (107 mg, 0.495 mmol), and 4Å MS (300 mg) in anhydrous CH₂Cl₂ (6 mL) was stirred at room temperature under argon for 20 min, followed by addition of a solution of TBSOTf in CH₂Cl₂ (0.086 M, 0.1 mL). After stirring for 20 min at -78 °C, the reaction mixture was neutralized with Et₃N, diluted with CH₂Cl₂, and then filtered through a pad of celite. The filtrates were concentrated. The residue was applied to a silica gel column chromatography (*n*-hexane-ethyl acetate 7:1) to give **17** (135 mg, 89%) as a white amorphous solid. ¹H NMR (300 MHz, CDCl₃): 7.58-7.10 (m, 15 H), 6.90-6.75 (m, 4 H), 5.72 (br s), 5.60 (br s), 5.48 (d, *J* = 3.5) [altogether 1 H], 5.14-4.86 (m, 2 H), 4.82-4.60 (m, 2 H), 4.52-4.38 (m, 2 H), 3.82-3.66 (m, 4 H), 3.58-3.46 (m, 2 H), 3.38-3.08 (m, 5 H), 2.40 (s, 3 H), 2.06 (s, 3 H), 2.00-1.60 (m, 4 H), 1.40-1.20 (m, 9 H). ESI-MS (*m/z*): 943.4 (M + Na⁺).

Trisaccharide 18: A similar procedure for the preparation of **16** from **15** was employed (40 °C, 4 h). Purification by a silica gel column chromatography (*n*-hexane-ethyl acetate 5:1) gave **18** (60 mg, 77%) as a white amorphous solid. $[\alpha]_D^{15} = -25.7$ (*c* 0.74, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 7.60-7.10 (m, 15 H), 6.90-6.78 (m, 4 H), 5.60 (br s, 1 H), 5.00-4.90 (m, 1 H), 4.76-4.62 (m, 3 H), 4.48 (d, 1 H, *J* = 8.7), 4.20-4.12 (m,

1 H), 3.78 (s, 3 H, OMe), 3.74-3.68 (m, 1 H), 3.60-3.48 (m, 2 H), 3.44-3.38 (m, 1 H), 3.30-3.00 (m, 4 H), 2.40 (s, 3 H, SMe), 2.00-1.82 (m, 4 H), 1.40-1.29 (m, 6 H), 1.15 (d, 3 H, $J = 6.6$). ^{13}C NMR (75 MHz, CDCl_3): 171.0, 155.2, 151.2, 137.7, 137.3, 137.2, 133.9, 133.3, 128.9, 128.7, 128.5, 128.4, 127.9, 127.8, 125.4, 118.1, 114.4, 104.5, 103.1, 101.5, 86.1, 82.6, 80.1, 76.0, 75.1, 71.1, 71.0, 70.1, 55.6, 54.8, 54.5, 32.4, 25.6, 19.4, 18.3, 17.9, 13.6. ESI-MS (m/z): 901.4 ($\text{M} + \text{Na}^+$).

Pentasaccharide 19: A solution of the trisaccharide acceptor **18** (45 mg, 0.051 mmol, 1.0 equiv.), disaccharide donor **3** (51 mg, 0.77 mmol, 1.5 equiv.), 2,6-di-*tert*-butyl-4-methylpyridine (16 mg, 0.077 mmol, 1.5 equiv.), and 4Å MS (100 mg) in anhydrous CH_2Cl_2 (3 mL) was stirred at room temperature under argon for 30 min, followed by addition of a solution of MeOTf in CH_2Cl_2 (0.087 M, 0.243 mL, 1.4 equiv.). After stirring for 10 hour at room temperature, the reaction mixture was diluted with CH_2Cl_2 , and filtered through a pad of celite. The filtrates were concentrated. The residue was applied to a silica gel column chromatography (*n*-hexane-ethyl acetate 5:1) to give **19** (36 mg, 45%), **18** (9 mg, 20%), and **16** (6 mg, 15%) as white amorphous solids. **19**: $[\alpha]_{\text{D}}^{16} = -48.1$ (c 0.58, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 7.60-7.05 (m, 30 H), 6.86-6.78 (m, 4 H), 5.53 (br s, 1 H), 5.12 (dd, 1 H, $J = 11.4, 9.0$), 4.96-4.85 (m, 2 H), 4.72-4.63 (m, 2 H), 4.62-4.53 (m, 2 H), 4.50-4.41 (m, 3 H), 4.30 (d, 1 H, $J = 9.0$), 3.85-3.80 (m, 1 H), 3.77 (s, 3 H, OMe), 3.73-3.67 (dd, 1 H, $J = 11.4, 8.7$), 3.52-3.33 (m, 4 H), 3.27-3.02 (m, 9 H), 2.37 (s, 3 H), 2.31 (s, 3 H), 1.88 (s, 3 H), 1.82-1.60 (m, 4 H), 1.59-1.31 (m, 2 H), 1.14 (d, 3 H, $J = 6.3$). ^{13}C NMR (75 MHz, CDCl_3): 170.8, 170.0, 155.3, 151.2, 137.8, 137.7, 137.4, 135.7, 135.3, 133.9, 133.4, 132.2, 130.0, 129.3, 129.0, 128.7, 128.6, 128.5, 127.9, 126.9, 126.4, 125.6, 118.1, 114.5, 104.5, 103.0, 102.5, 102.1, 101.5, 86.2, 82.7, 80.7, 80.2, 79.4, 76.1, 75.0, 74.7, 74.4, 71.1, 71.0, 70.7, 55.8, 55.6, 55.0, 32.4, 29.7, 23.7, 20.8, 18.4, 18.3, 18.0, 17.9, 16.6, 13.6.

Pentasaccharide 20: A similar procedure for the preparation of alcohol **16** from acetate **15** was employed (40 °C, 4 h). **20** (30 mg, 97%) was obtained as a white amorphous solid. $[\alpha]_{\text{D}}^{19} = -36.4$ (c 0.84, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 7.60-7.10 (m, 30 H), 6.78-6.68 (m, 4 H), 5.74 (br s, 0.3 H), 5.53 (br s, 0.7 H), 5.00-4.88 (m,

3 H), 4.78-4.58 (m, 3 H), 4.53-4.30 (m, 4 H), 4.0-3.68 (m, 5 H, OMe), 3.56-3.00 (m, 13 H), 2.85 (br, 1H), 2.48 (s, 3 H), 2.40 (s, 3 H), 1.90-1.60 (m, 4 H), 1.42-1.28 (m, 12 H), 1.15 (d, 3 H, $J = 6.3$). ^{13}C NMR (75 MHz, CDCl_3): 170.8, 155.3, 151.2, 137.8, 137.3, 133.9, 133.4, 132.2, 130.7, 130.2, 128.9, 128.7, 128.6, 128.5, 128.1, 127.8, 126.9, 125.6, 118.1, 114.5, 104.5, 103.0, 102.6, 102.0, 101.6, 86.1, 83.7, 80.6, 80.2, 79.4, 76.2, 76.1, 75.0, 74.8, 71.0, 70.7, 57.7, 55.9, 55.6, 55.0, 32.4, 31.5, 29.7, 23.6, 22.6, 18.3, 18.0, 17.9, 16.6, 14.1, 13.6. ESI-MS (m/z): 1542.6 ($\text{M} + \text{Na}^+$).

Hexasaccharide 21: A similar procedure for the preparation of **17** from **16** and **2** was employed. Compound **21** (25 mg, 81%) was obtained as a white amorphous solid. ^1H NMR (300 MHz, CDCl_3): 7.60-7.10 (m, 30 H), 6.86-6.68 (m, 4 H), 5.74 (br s), 5.60 (br s), 5.53 (br s), 5.49 (br s) [altogether 2 H], 5.10-4.80 (m, 3 H), 4.76-4.57 (m, 4 H), 4.50-4.20 (m, 4 H), 3.90-3.65 (m, 7 H), 3.53-2.93 (m, 13 H), 2.38 (s, 3 H), 2.31 (s, 3 H), 2.06 (s, 3 H), 1.82-1.50 (m, 8 H), 1.38-1.22 (m, 15 H), 1.14 (d, 3 H, $J = 6.3$).

Hexasaccharide 22: A similar procedure in the preparation of **14** from **13** was employed. Compound **22** (16 mg, 72%) was obtained as a white amorphous solid. $[\alpha]_{\text{D}}^{15} = 1.05$ (c 0.67, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 7.60-7.10 (m, 30 H), 6.86-6.78 (m, 4 H), 5.70-5.54 (m, 2 H), 5.02 (m, 1 H), 4.74-4.62 (m, 5 H), 4.58-4.51 (m, 2 H), 4.48-4.41 (m, 2 H), 4.30 (d, 1 H, $J = 9.1$), 3.86-3.64 (m, 33 H), 3.60-3.40 (m, 4 H), 3.30-2.94 (m, 10 H), 2.10-1.60 (m, 8 H), 1.50-1.14 (m, 18 H). ESI-MS (m/z): 1508.8 ($\text{M} + \text{Na}^+$).

Hexadeoxysaccharide 1: To a solution of **22** (7 mg) in EtOH-THF (10 mL, 5:1), Raney nickel (1.0 g) was added. The mixture was stirred at 40 °C for 18 hour, and then was filtered through a pad of celite. The residue was washed with hot EtOH (40 mL). The filtrates were evaporated in vacuo. The resulting residue was purified by a silica gel column chromatography (n -hexane-ethyl acetate-acetone 1:2:2) to afford **1** (4 mg, 57%) as a white amorphous solid. $[\alpha]_{\text{D}}^{18} = -17.0$ (c 0.14, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 6.98 (d, 2 H, $J = 9.0$), 6.82 (d, 2 H, $J = 9.1$), 5.16 (br s, 1 H), 5.04 (m, 1 H), 4.87-4.75 (m, 1 H), 4.72 (br s, 1 H), 4.59-4.53 (m, 3 H), 4.14-3.84 (m, 1 H), 3.78 (s, 3

H, OMe), 3.76-3.58 (m, 5 H), 3.49-3.21 (m, 5 H), 3.20-2.97 (m, 4 H), 2.40-2.10 (m, 8 H), 2.05-1.50 (m, 8 H), 1.40-1.16 (m, 18 H). ESI-MS (m/z): 895.5 ($M + Na^+$).