Supporting Information

An Efficient Synthesis of β-*C*-Glycosides Based on the Conformational Restriction Strategy: Lewis Acid-Promoted Silane Reduction of the Anomeric Position with Complete Stereoselectivity

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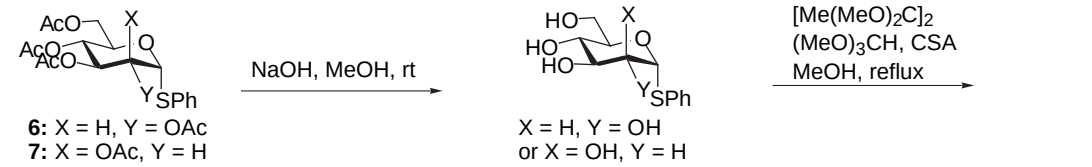
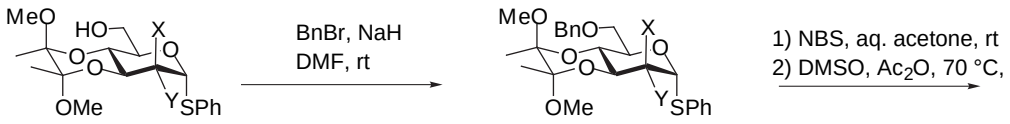
Contents: Schemes S1 and S2, Table S1, and experimental details on the synthesis of the reaction substrates and the Lewis acid-promoted silane reduction, and ^{1}H NMR charts of **3b**, **5**, and the silane reduction products from **2c** and **4a**.

Scheme S1



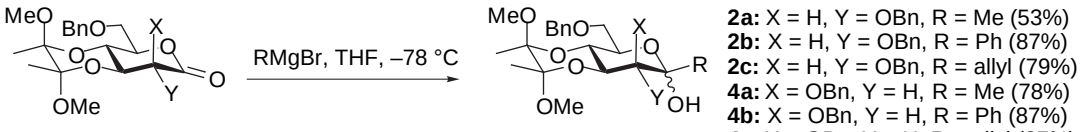
6: X = H, Y = OAc
7: X = OAc, Y = H

X = H, Y = OH
or X = OH, Y = H



X = H, Y = OH
or X = OH, Y = H

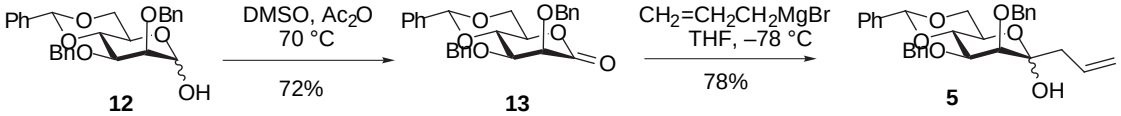
8: X = H, Y = OBn (ref. 16)
9: X = OBn, Y = H (54% from **7**)



10: X = H, Y = OBn (ref. 16)
11: X = OBn, Y = H (77%)

2a: X = H, Y = OBn, R = Me (53%)
2b: X = H, Y = OBn, R = Ph (87%)
2c: X = H, Y = OBn, R = allyl (79%)
4a: X = OBn, Y = H, R = Me (78%)
4b: X = OBn, Y = H, R = Ph (87%)
4c: X = OBn, Y = H, R = allyl (87%)

Scheme S2



12 **13** **5**

Table S1. Coupling constants between adjacent protons of the substrates in ^{1}H NMR.[a]

substrate	coupling constant (Hz)[b]		
	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
1a	9.3	9.1	
1b	9.4		
1c	9.3	9.1	
2a	9.4		
2b	9.7		9.9
2c	9.7	9.9	
3a	2.6	9.3	9.6
3b	3.4		
3c	2.4	10.0	
4a	2.6	9.7	
4b	ca. 0		
4c	2.4	9.9	11.0
5	2.7	10.3	

[a]Measured at 400 MHz in $CDCl_3$.
[b]Undecipherable coupling constants are blank.

Experimental

General Experimental Methods. Chemical shifts are reported in ppm downfield from tetramethylsilane and *J* values are given in hertz. Thin-layer chromatography was done on Merck coated plate $60F_{254}$. Silica gel chromatography was done on Merck silica gel 7734 or 9385. Reactions were carried out under an argon atmosphere.

Phenyl 2,6-Di-*O*-benzyl-3,4-*O*-[(2*S*,3*S*)-2,3-dimethoxbutan-2,3-diyl]-1-thio-β-D-mannopyranoside (9). A mixture of **7** (15 g, 34 mmol) and NaOMe (28%, 1 mL, 5 mmol) in MeOH (50 mL) was stirred at room temperature for 30 min, and then neutralized by Diaion PK 212 resins (H^+ form). After filtration off the reigns, the filtrate was evaporated, and a mixture of the resulting residue (9.2g), $[Me(MeO)_2C]_2$ (6.3 mL, 35 mmol), $(MeO)_3CH$ (15 mL, 137 mmol) and CSA (45 mg) in MeOH (120 mL) was heated under reflux for 14 h. After addition of $NaHCO_3$ (100 mg), the resulting mixture was evaporated, and the residue was partitioned between AcOEt and H_2O. The organic layer was washed with brine, dried (Na_2SO_4), and purified by column chromatography (SiO_2, 50% AcOEt in hexane) to give Phenyl 3,4-*O*-[(2*S*,3*S*)-2,3-dimethoxbutan-2,3-diyl]-1-thio-β-D-mannopyranoside as an oil (7.2 g, 55%). After stirring of a mixture of the resulting oil (3.9 g, 10 mmol) and NaH (60%, 1.0 g, 25 mmol) in DMF (20 mL) at room temperature for 1 h, BnBr (3.0 mL, 25 mmol) was added, and the resulting mixture was further stirred at room temperature for 1 h. MeOH (1 mL) was added to the mixture, and the resulting mixture was partitioned between AcOEt and H_2O. The organic layer was washed with brine and dried (Na_2SO_4), and purified by column chromatography (SiO_2, 10% AcOEt in hexane) to give **9** (5.6 g, 99%) as a colorless oil: ^{1}H NMR(400 MHz, $CDCl_3$); δ 7.46-7.20 (m, 15 H), 5.52 (s, 1 H), 4.87 (d, 1 H, *J* = 12.2), 4.69 (d, 1 H, *J* = 12.2), 4.60 (d, 1 H, *J* = 11.9), 4.50 (d, 1 H, *J* = 11.9), 4.42 (ddd, 1 H, *J* = 3.8, 4.0, 10.0), 4.27 (dd, 1 H, *J* = 10.0, 10.3), 4.05, (dd, 1 H, *J* = 3.0, 10.3), 3.97 (dd, 1 H, *J* = 3.8, 4.0), 3.80 (d, 2 H, *J* = 3.8), 3.31 (s, 3 H), 3.20 (s, 3 H), 1.34 (s, 3 H), 1.30 (s, 3 H); LRMS (FAB, positive) *m/z* 567 (MH^+).

2,6-Di-*O*-benzyl-3,4-*O*-[(2*S*,3*S*)-2,3-dimethoxbutan-2,3-diyl]-β-D-mannolactone (11). A mixture of **9** (2.8 g, 5.0 mmol) and NBS (1.3 g, 7.5 mmol) in aceton-H_2O (9:1, 10 mL) was stirred at 0 °C for 1 h, and then $NaHCO_3$ (100 mg) was added. The resulting mixture was evaporated, and the residue was partitioned between AcOEt and H_2O. The organic layer was washed with brine and dried (Na_2SO_4), and purified by column chromatography (SiO_2, 30% AcOEt in hexane) to give the hydrolyzed hemiacetalic product as a white solid (2.3 g, 95%). A mixture of the obtained white solid (1.4 g, 3.0 mmol) and Ac_2O (5 ml) in DMF (10 mL) was stirred at 80 °C for 2 h and partitioned between AcOEt and H_2O. The organic layer was washed with brine and dried (Na_2SO_4), and purified by column chromatography (SiO_2, 10% AcOEt in hexane) to give **11** as an oil (1.1 g, 77% from **9**), which was immediately used for the next Grignard reaction because of its instability.

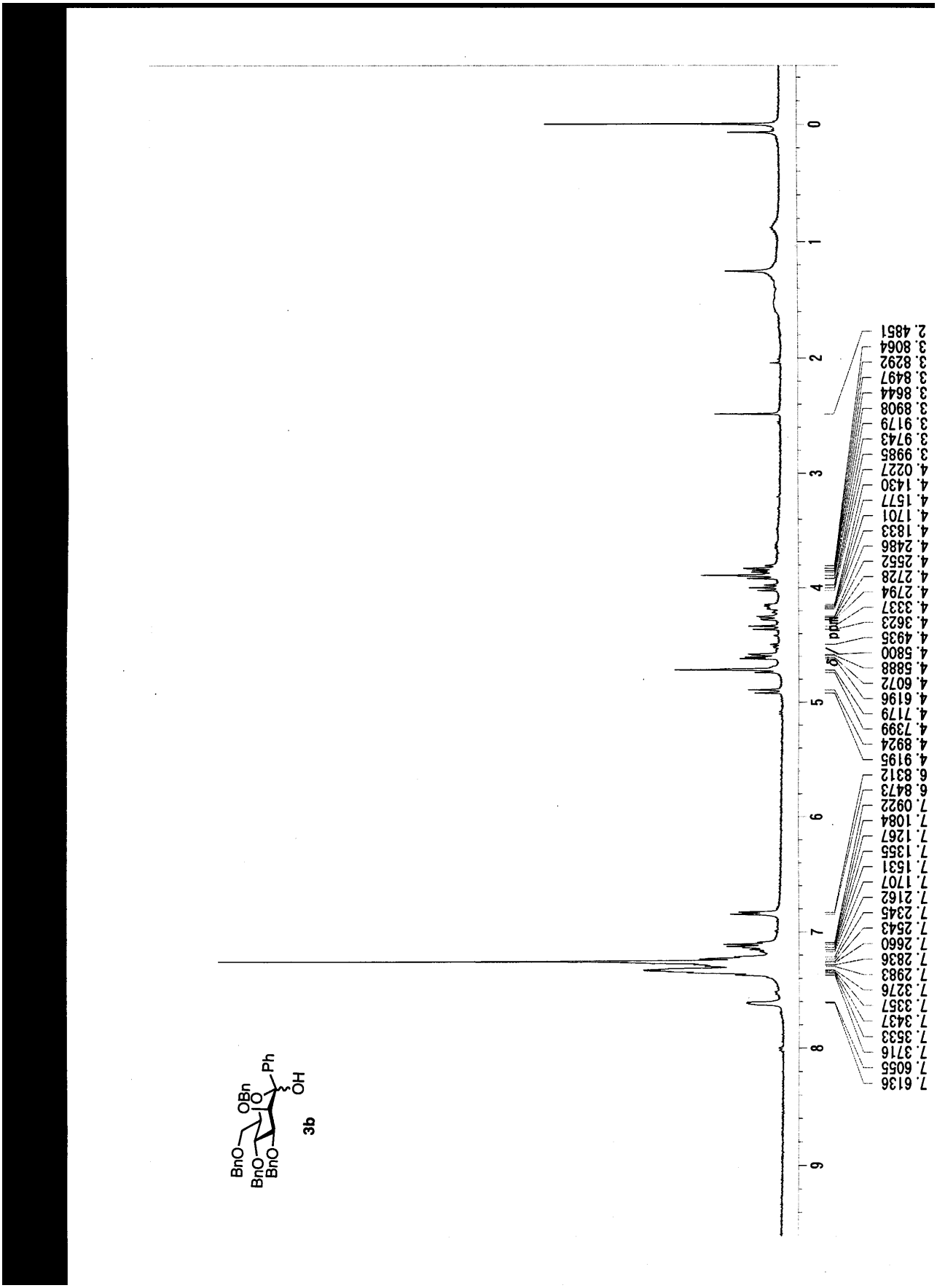
4,6-*O*-Benzyldene-3,4-*O*-[(2*S*,3*S*)-2,3-dimethoxbutan-2,3-diyl]-β-D-mannolactone (13). A mixture of **12** (420 mg, 0.9 mmol) and Ac_2O (3 ml) in DMF (6 mL) was stirred at 80 °C for 2 h and then partitioned between AcOEt and H_2O. The organic layer was washed with brine and dried (Na_2SO_4), and purified by column chromatography (SiO_2, 10% AcOEt in hexane) to give **13** as an oil (300 mg, 72%), which was immediately used for the next Grignard reaction because of its instability.

General Procedure for the Grignard Additions. A mixture of **11**, **13**, or 2,3,4,6-tetra-*O*-benzyl-β-D-mannolactone[4a] (1.0 mmol) and a Grignard reagent (1.2 mmol) in THF (10 mL) was stirred at –78 °C for 1 h, and then aqueous saturated NH_4Cl was added. The resulting mixture was partitioned between AcOEt and H_2O, and the organic layer was washed with brine and dried (Na_2SO_4), and purified by column chromatography (SiO_2, 10% AcOEt in hexane). **2a:** 78% as a colorless oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 10 H), 4.99 (d, 1 H, *J* = 11.1), 4.71 (d, 1 H, *J* = 11.1), 4.71 (d, 1 H, *J* = 12.1), 4.56 (d, 1 H, *J* = 12.1), 4.15-4.06 (m, 2 H), 3.78-3.69 (m, 3 H), 3.42 (d, 1 H, *J* = 9.4), 3.31 (s, 3 H), 3.20 (s, 3 H), 2.66 (s, 1 H), 1.42 (s, 3 H), 1.35 (s, 3 H), 1.29 (s, 3 H); LRMS (FAB, positive) *m/z* 489 (MH^+). **2b:** 94% as a colorless oil; ^{1}H NMR(400 MHz, $CDCl_3$); δ 7.60-57 (m, 2 H), 7.37-7.02 (m, 11 H), 7.01 (d, 2 H, *J* = 3.2), 4.66 (d, 1 H, *J* = 12.3), 4.56 (d, 1 H, *J* = 12.3), 4.53 (d, 1 H, *J* = 10.8), 4.27-4.22 (m, 2 H), 4.09 (dd, 1 H, *J* = 4.2, 10.0), 3.99 (dd, 1 H, *J* = 9.9, 10.0), 3.86 (dd, 1 H, *J* = 4.2, 11.2), 3.75 (d, 1 H, *J* = 0, 11.2), 3.63 (d, 1 H, *J* = 9.7), 3.33 (s, 3 H), 3.29 (s, 3 H), 3.17 (s, 1 H), 1.35 (s, 3 H), 1.33 (s, 3 H); LRMS (FAB, positive) *m/z* 551 (MH^+). **2c:** 79% as a colorless oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 10 H), 5.91-5.80 (m, 1 H), 5.15 (dd, 1 H, *J* = 2.3, 11.0), 5.08 (dd, 1 H, *J* = 2.3, 17.1), 4.99 (d, 1 H, *J* = 11.1), 4.70 (d, 1 H, *J* = 11.1), 4.63 (d, 1 H, *J* = 12.3), 4.56 (d, 1 H, *J* = 12.3), 4.18 (dd, 1 H, *J* = 9.7, 9.9), 4.06 (ddd, 1 H, *J* = 1.8, 4.1, 10.2), 3.76 (dd, 1 H, *J* = 9.9, 10.2), 3.74 (dd, 1 H, *J* = 4.1, 11.0), 3.67 (dd, 1 H, *J* = 1.8, 11.0), 3.54 (d, 1 H, 9.7), 3.31 (s, 3 H), 3.22 (s, 3 H), 2.87 (s, 1 H), 2.47-2.45 (m, 2 H), 1.35 (s, 3 H), 1.30 (s, 3 H); LRMS (FAB, positive) *m/z* 515 (MH^+); LRMS (FAB, positive) *m/z* 515 (MH^+). **3b:** 77% as a colorless oi; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.63-6.83 (m, 20 H), 4.91 (d, 1 H, *J* = 10.8), 4.74-4.71 (m, 3 H), 4.60 (d, 1 H, *J* = 12.2), 4.59(d, 1 H, *J* = 10.8), 4.35 (d, 1 H, 11.1), 4.26 (dd, 1 H, *J* = 2.7, 9.4), 4.19-4.15 (m, 1 H), 4.00 (dd, 1 H, *J* = 9.4, 9.7), 3.92-3.89 (m, 2 H), 3.87-3.81 (m, 2 H), 2.49 (s, 1 H); HRMS calcd for $C_{40}H_{40}NaO_6$ (MNa^+): 639.2723, found: 639.22728. **4a:** 69% as a colorless oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.46-7.22 (m, 10 H), 4.97 (d, 1 H, *J* = 11.1), 4.65-4.52 (m, 3 H), 4.24 (dd, 1 H, *J* = 2.6, 9.7), 4.07-4.04 (m, 2 H), 3.73 (dd, 1 H, 1.4, 10.3), 3.63 (dd, 1 H, 6.4, 10.3), 3.54 (d, 1 H, *J* = 2.6), 3.29 (s, 3 H), 3.16 (s, 3 H), 2.64 (s, 1 H), 1.42 (s, 3 H), 1.30 (s, 3 H), 1.27 (s, 3 H); LRMS (FAB, positive) *m/z* 489 (MH^+). **4b:** 87% as a colorless oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.54-6.90 (m, 15 H), 4.59 (d, 1 H, *J* = 12.4), 4.48-4.36 (m, 3 H), 4.17 (d, 1 H, *J* = 9.6), 4.03 (dd, 1 H, *J* = 9.6, 9.7), 3.76-3.68 (m, 3 H), 3.41 (s, 1 H), 3.29 (s, 3 H), 3.14 (s, 3 H), 1.95 (s, 1 H), 1.30 (s, 3 H), 1.28 (s, 3 H); LRMS (FAB, positive) *m/z* 573 (MNa^+). Anal. Calcd for $C_{32}H_{38}O_8$: C, 69.80; H, 6.96. Found: C, 69.69; H, 7.03. **4c:** 87% as a colorless oil. ^{1}H

NMR(400 MHz, $CDCl_3$) δ 7.48-7.21 (m, 10 H), 5.91-5.75 (m, 1 H), 5.25-5.13 (m, 2 H), 5.02 (d, 1 H, *J* = 11.1), 4.64-4.51 (m, 3 H), 4.26 (dd, 1 H, *J* = 2.4, 9.9), 4.14 (dd, 1 H, *J* = 9.9, 11.0), 4.05 (ddd, 1 H, 2.0, 5.8, 11.0), 3.75 (dd, 1 H, *J* = 2.0, 11.0), 3.76 (dd, 1 H, *J* = 5.8, 11.0), 3.60 (d, 1 H, *J* = 2.4), 3.29 (s, 3 H), 3.19 (s, 3 H), 2.74 (dd, 1 H, *J* = 5.4, 11.5), 2.29 (dd, 1 H, *J* = 8.3, 11.5), 1.31 (s, 3 H), 1.28 (s, 3 H); LRMS (FAB, positive) *m/z* 515 (MH^+). **5:** 78% as a colorless oil; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.52-7.26 (m, 15 H), 5.84-5.73 (m, 1 H), 5.63 (s, 1 H), 5.27 (dd, 1 H, *J* = 2.1, 8.3), 5.16 (dd, 1 H, *J* = 2.1, 17.0), 5.05 (d, 1 H, *J* = 11.1), 4.93 (d, 1 H, *J* = 12.3), 4.75 (d, 1 H, *J* = 12.3), 4.68 (d, 1 H, *J* = 11.1), 4.24 (dd, 1 H, *J* = 9.0, 9.9), 4.21-4.17 (m, 2 H), 3.94 (ddd, 1 H, *J* = 4.7, 9.9, 10.3), 3.83 (dd, 1 H, *J* = 9.9, 10.3), 3.77 (d, 1 H, *J* = 2.7), 2.78 (dd, 1 H, *J* = 5.1, 13.6), 2.61 (s, 1 H), 2.11 (dd, 1 H, *J* = 9.7, 13.6); HRMS calcd for $C_{30}H_{33}O_6$ (MNa^+): 489.2199. Found: 489.2290.

General Procedure for the Silane Reduction. A mixture of a substrate (0.20 mmol), Et_3SiH (35 μL, 0.22 mmol) and TMSOTf (40 μL, 0.22 mmol) in CH_2Cl_2 (10 mL) was stirred at –78 °C for 1 h, and then Et_3N (100 μL) was added. The resulting mixture was partitioned between AcOEt and aqueous saturated. $NaHCO_3$, and the organic layer was washed with brine and dried (Na_2SO_4), and purified by column chromatography (SiO_2, 15% AcOEt in hexane) to give the corresponding *C*-glycosidic product. ***C*-Glycoside from 1a:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.34-7.13 (m, 20 H), 4.89-4.79 (m, 4 H), 4.67-4.52 (m, 4 H), 3.72-3.77 (m, 4 H), 3.45-3.36 (m, 2 H), 3.20 (dd, 1 H, *J* = 9.0, 9.1), 1.32 (d, 3 H, *J* = 6.1). LRMS (FAB, positive) *m/z* 539 (MH^+); LRMS (FAB, positive) *m/z* 539 (MH^+). Anal. Calcd for $C_{35}H_{38}O_5$: C, 78.04; H, 7.11. Found: C, 78.11; H, 7.22. ***C*-Glycoside from 1b:** ^{1}H NMR(400 MHz, $CDCl_3$) ; δ 7.66-6.97 (m, 25 H), 4.94-4.86 (m, 3 H), 4.67-4.53 (m, 4 H), 4.39 (d, 1 H, *J* = 10.3), 4.20-4.06 (m, 2 H), 3.87-3.71 (m, 3 H), 3.55 (d, 1 H, *J* = 9.4), 3.18 (s, 1H); LRMS (FAB, positive) *m/z* 601 (MH^+). Anal. Calcd for $C_{40}H_{40}O_5$: C, 79.97; H, 6.71. Found: C, 79.82; H, 6.85. ***C*-Glycoside from 1c:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.34-7.16 (m, 20 H), 5.98-5.88 (m, 1 H), 5.13-5.04 (m, 2 H), 4.93-4.80 (m, 4 H), 4.67-4.55 (m, 4 H), 3.75-3.66 (m, 3 H), 3.60 (dd, 1 H, *J* = 9.3, 9.4), 3.41 (ddd, 1 H, *J* = 1.9, 4.2, 9.7), 3.38-3.30 (m, 2 H), 2.60 (ddd, 1 H, *J* = 1.9, 6.2, 14.7), 2.30 (ddd, 1 H, *J* = 4.2, 7.3, 14.7); LRMS (FAB, positive) *m/z* 565 (MH^+).Anal. Calcd for $C_{37}H_{40}O_5$: C, 78.69; H, 7.14. Found: C, 78.60; H, 7.11. ***C*-Glycoside from 2a:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 10 H), 4.97 (d, 1 H, *J* = 10.8), 4.66-4.58 (m, 3 H), 3.86 (dd, 1 H, *J* = 9.4, 9.4), 3.74-3.59 (m, 4 H), 3.41 (dd, 1 H, *J* = 6.1, 9.1), 3.30 (s, 3 H), 3.24 (dd, 1 H, *J* = 9.1, 9.4), 3.19 (s, 3 H), 1.35 (s, 3 H), 1.31 (d, 3 H, *J* = 6.1), 1.29 (s, 3 H); LRMS (FAB, positive) *m/z* 473 (MH^+). Anal. Calcd for $C_{27}H_{36}O_7$: C, 68.62; H, 7.68. Found: C, 68.78; H, 7.74. ***C*-Glycoside from 2b:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 2 H), 7.36-7.20 (m, 8 H), 7.18-7.16 (m, 3 H), 6.97-6.95 (m, 2 H), 4.64 (d, 1 H, *J* = 12.3), 4.55 (d, 1 H, *J* = 12.3), 4.54 (d, 1 H, *J* = 10.9), 4.26 (d, 1 H, *J* = 10.8), 4.05-3.98 (m, 2 H), 3.93 (dd, 1 H, *J* = 9.6, 9.7), 3.78-3.77 (m, 2 H), 3.72 (ddd, 1 H, *J* = 2.1, 3.9, 9.6), 3.56 (dd, 1 H, *J* = 9.0, 9.1), 3.33 (s, 3 H), 3.25 (s, 3 H), 1.37 (s, 3 H), 1.32 (s, 3 H); LRMS (FAB, positive) *m/z* 535 (MH^+). Anal. Calcd for $C_{32}H_{38}O_7$: C,

71.89; H, 7.16. Found: C, 72.03; H, 7.26. ***C*-Glycoside from 2c:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 10 H), 5.96-5.85 (m, 1 H), 5.11-5.05 (m, 2 H), 4.98 (d, 1 H, *J* = 10.9), 4.64-4.56 (m, 3 H), 3.89 (dd, 1 H, *J* = 9.1, 9.7), 3.73 (dd, 1 H, *J* =1.8, 11.1), 3.67 (dd, 1 H, *J* = 5.0, 11.1), 3.66 (dd, 1 H, *J* = 9.7, 10.2), 3.55 (ddd, 1 H, *J* = 1.8, 5.0, 10.2), 3.42 (dd, 1 H, *J* = 9.1, 9.1), 3.41-3.36 (m, 1 H), 3.30 (s, 3 H), 3.21 (s, 3 H), 2.62-2.56 (m, 1 H), 2.37-2.30 (m, 1 H), 1.36 (s, 3 H), 1.29 (s, 3H); HRMS calcd for $C_{29}H_{38}NaO_7$ (MNa^+): 521.2513, found: 521.2520. ***C*-Glycoside from 3a:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.39-7.13 (m, 20 H), 4.99 (d, 1 H, *J* = 12.0), 4.86 (d, 1 H, *J* = 10.9), 4.76-4.65 (m, 3 H), 4.58-4.51 (m, 3 H), 3.86 (dd, 1 H, *J* = 9.4, 9.6), 3.73 (dd, 1 H, *J* = 1.8, 10.8), 3.69-3.58 (m, 3 H), 3.47-3.43 (m, 2 H), 1.21 (d, 3 H, *J* = 6.2); LRMS (FAB, positive) *m/z* 539 (MH^+). Anal. Calcd for $C_{35}H_{38}O_5$: C, 78.04; H, 7.11. Found: C, 78.45; H, 7.31. ***C*-Glycoside from 3b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.11 (m, 23 H), 6.94 (d, 2 H, *J* = 7.1), 4.92 (d, 1 H, *J* = 10.8), 4.75 (d, 1 H, *J* = 12.0), 4.70-4.60 (m, 4 H), 4.48-4.44 (m, 2 H), 4.15 (d, 1 H, *J* = 11.4), 4.05 (dd, 1 H, *J* = 9.4, 9.6), 3.94 (d, 1 H, *J* = 2.6), 3.87-3.85 (m, 2 H), 3.79 (dd, 1 H, *J* = 3.0. 9.6), 3.62 (ddd, 1 H, *J* = 1.9, 4.5, 9.7); LRMS (FAB, positive) *m/z* 601 (MH^+). Anal. Calcd for $C_{40}H_{40}O_5$: C, 79.97; H, 6.71. Found: C, 79.79; H, 6.71. ***C*-Glycoside from 3c:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.37-7.16 (m, 20 H), 5.74-5.64 (m, 1 H), 5.04-4.98 (m, 2 H), 4.87 (d, 1 H, *J* = 10.9), 4.79-4.53 (m, 7 H), 3.91 (dd, 1 H, *J* = 9.3, 9.6), 3.77-3.66 (m, 3 H), 3.60 (dd, 1 H, *J* = 2.1, 9.3), 3.47-3.44 (m, 1 H), 3.33 (dd, 1 H, *J* = 6.7, 7.0), 2.51 (ddd, 1 H, *J* = 6.7, 7.1, 13.8), 2.33 (ddd, 1 H, 7.1, 7.3, 13.8); LRMS (FAB, positive) *m/z* 565 (MH^+). Anal. Calcd for $C_{37}H_{40}O_5$: C, 78.69; H, 7.14. Found: C, 78.20; H, 7.36. ***C*-Glycoside from 4a:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.45 (d, 2 H, *J* = 7.0), 7.33-7.21 (m, 8 H), 4.98 (d, 1 H, *J* = 11.6), 4.68 (d, 1 H, *J* = 11.6), 4.60 (d, 1 H, *J* = 12.3), 4.57 (d, 1 H, *J* = 12.3), 4.05 (dd, 1 H, *J* = 8.7, 9.9), 3.79 (dd, 1 H, *J* = 2.2, 8.6), 3.76 (d, 1 H, *J* = 6.2), 3.66-3.57 (m, 3 H), 3.48 (d, 1 H, *J* = 2.2), 3.27 (s, 3 H), 3.17 (s, 3 H), 1.32 (s, 3 H), 1.27 (s, 3 H), 1.21 (d, 3 H, *J* = 6.2); HRMS calcd for $C_{27}H_{36}NaO_7$ (MNa^+): 495.2359, found: 495.2349. ***C*-Glycoside from 4b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.18 (m, 10 H), 7.16-7.00 (m, 3 H), 6.99 (d, 2 H, *J* = 2.6), 4.72 (d, 1 H, *J* = 12.0), 4.61 (d, 1 H, *J* = 2.3), 4.62-4.58 (m, 2 H), 4.39 (d, 1 H, *J* = 10.8), 4.27 (dd, 1 H, *J* = 9.6, 9.9), 3.97 (dd, 1 H, *J* = 2.5, 10.1), 3.87-3.83 (m, 2 H), 3.80-3.74 (m, 2 H), 3.30 (s, 3 H), 3.19 (s, 3 H), 1.34 (s, 3 H), 1.29 (s, 3 H); LRMS (FAB, positive) *m/z* 535 (MH^+). Anal. Calcd for $C_{32}H_{38}O_7$: C, 71.89; H, 7.16. Found: C, 71.97; H, 7.16. ***C*-Glycoside from 5:** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.34-7.02 (m, 15 H), 5.65-5.54 (m, 1 H), 5.44 (s, 1 H), 4.95-4.88 (m, 3 H), 4.75 (d, 1 H, *J* = 12.0), 4.56 (d, 1 H, *J* = 12.0), 4.37 (d, 1 H, *J* = 11.1), 4.10-3.98 (m, 3 H), 3.92 (dd, 1 H, *J* = 2.7, 10.2), 3.65 (dd, 1 H, *J* = 10.2, 10.3), 3.60-3.54 (m, 2 H), 2.66-2.60 (m, 1 H), 2.28-2.23 (m, 1 H); LRMS (FAB, positive) *m/z* 473 (MH^+). Anal. Calcd for $C_{30}H_{32}O_5$: C, 76.25; H, 76.83. Found: C, 76.68; H, 6.91.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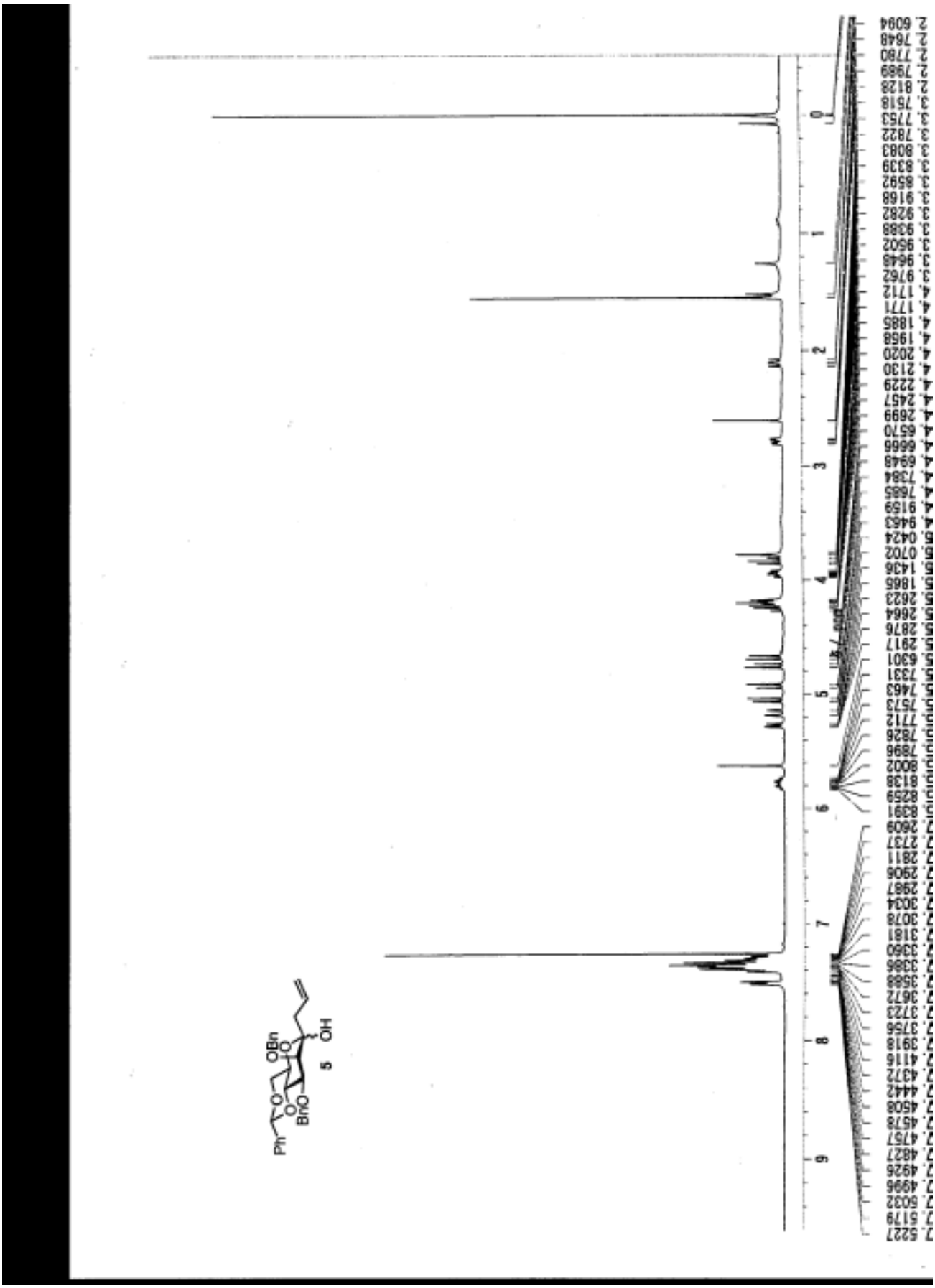

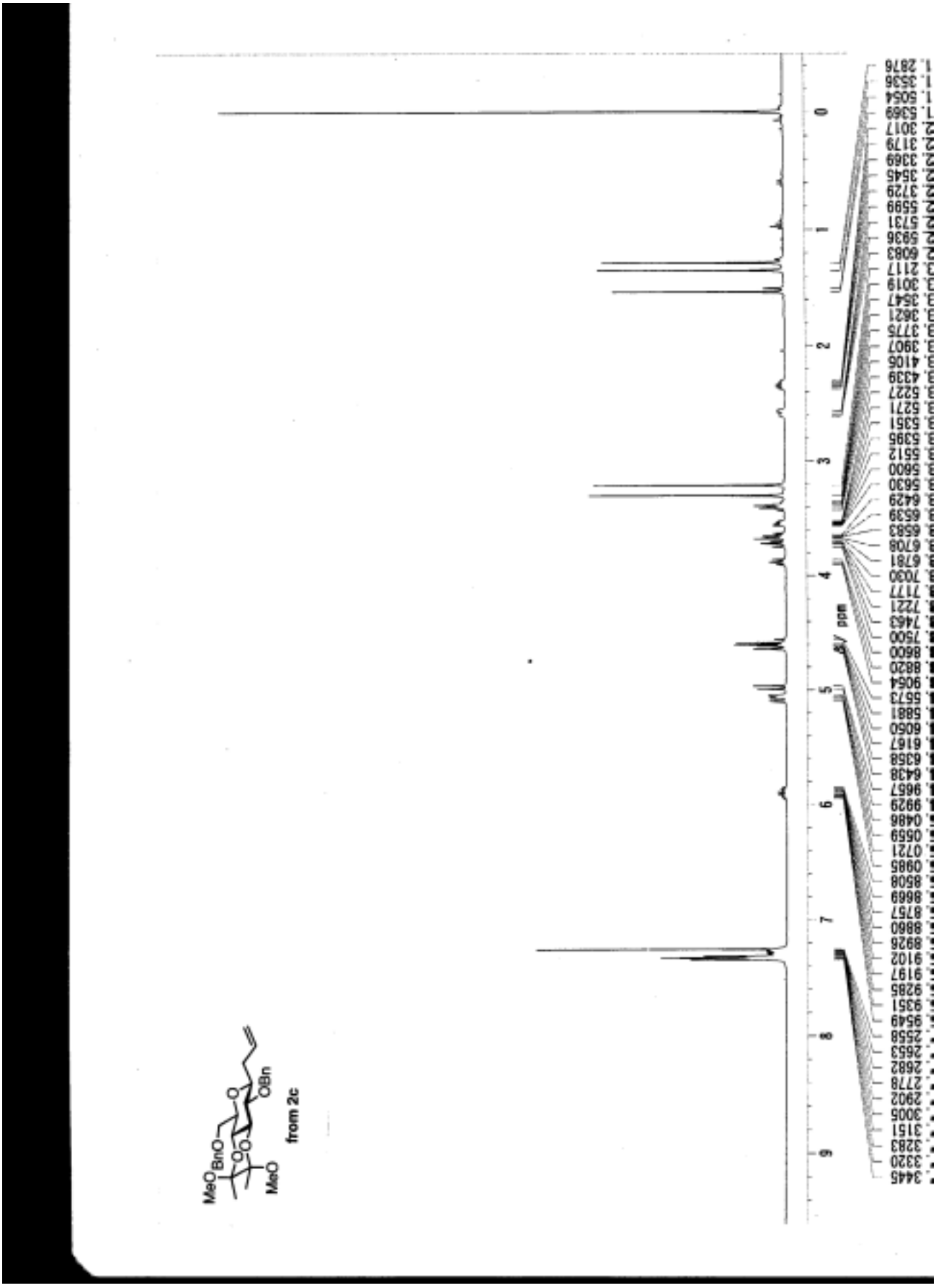
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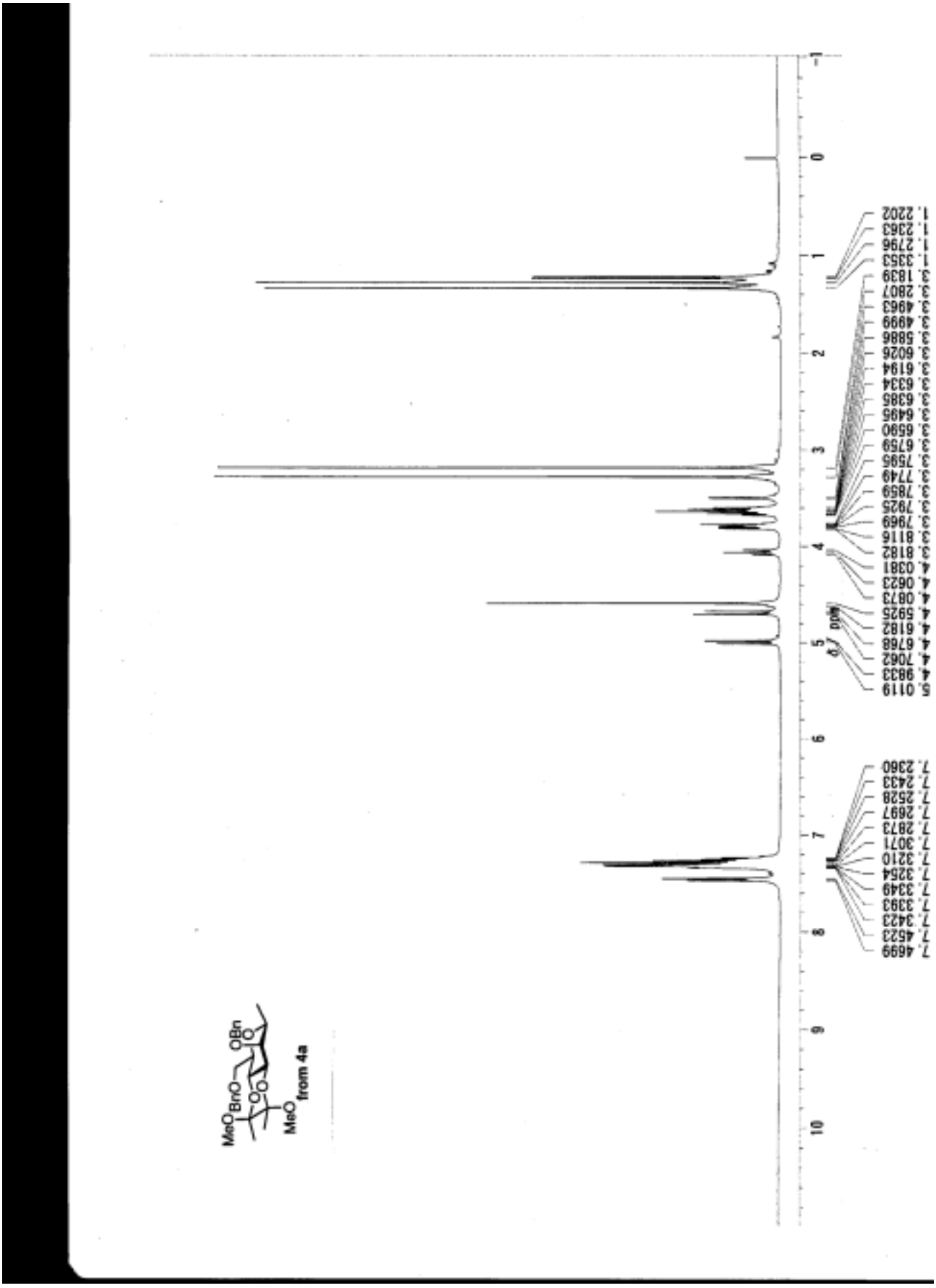
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