Supporting Information for:

β -Directing Effect of Electron-Withdrawing Groups at *O*-3, *O*-4, and *O*-6 Positions and α -Directing Effect by the Remote Participation of 3-*O*-Acyl and 6-*O*-Acetyl Groups of Donors in Mannopyranosylations

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Section A: General Methods	S10
Section B: Synthesis and characterization data	
Synthesis and characterization data for S1	S11
Synthesis and characterization data for S2	S12
Synthesis and characterization data for S3	S13
Synthesis and characterization data for S4	S14
Synthesis and characterization data for S5	S14
Synthesis and characterization data for 6	S15
Synthesis and characterization data for 7	S15
Synthesis and characterization data for 8	S16
Synthesis and characterization data for 1	S17

Synthesis and characterization data for 2	S17
Synthesis and characterization data for 3	S18
Synthesis and characterization data for 4	S19
Synthesis and characterization data for 5	S19
Synthesis and characterization data for S6	S20
Synthesis and characterization data for S7	S21
Synthesis and characterization data for S8	S22
Synthesis and characterization data for S9	S22
Synthesis and characterization data for S10	S23
Synthesis and characterization data for S11	S23
Synthesis and characterization data for 9	S24
Synthesis and characterization data for 10	S25
Synthesis and characterization data for 11	S25
Synthesis and characterization data for 12	S26
Synthesis and characterization data for S12	S27
Synthesis and characterization data for S13	S27
Synthesis and characterization data for S14	S28
Synthesis and characterization data for S15	S29
Synthesis and characterization data for S16	S30
Synthesis and characterization data for S17	S31
Synthesis and characterization data for 13	S31
Synthesis and characterization data for 14	S32
Synthesis and characterization data for 15	S33
Synthesis and characterization data for 16	S33

Synthesis and characterization data for S18	S34
Synthesis and characterization data for S19	S35
Synthesis and characterization data for 67	S36
Physical and spectral characterization data for 23	S36
Physical and spectral characterization data for 24α	S37
Physical and spectral characterization data for 24β	S38
Physical and spectral characterization data for 25	S38
Physical and spectral characterization data for 26	S39
Physical and spectral characterization data for 27	S40
Physical and spectral characterization data for 28	S41
Physical and spectral characterization data for 29	S42
Physical and spectral characterization data for 30α	S43
Physical and spectral characterization data for 30β	S44
Physical and spectral characterization data for 31	S44
Physical and spectral characterization data for 32	S45
Physical and spectral characterization data for 33	S46
Physical and spectral characterization data for 34	S47
Physical and spectral characterization data for 35α	S48
Physical and spectral characterization data for 35β	S49
Physical and spectral characterization data for 36α	S49
Physical and spectral characterization data for 36β	S50
Physical and spectral characterization data for 37α	S51
Physical and spectral characterization data for 37β	S52
Physical and spectral characterization data for 38α	S52

Physical and spectral characterization data for 38β	S53
Physical and spectral characterization data for 39	S54
Physical and spectral characterization data for 40	S54
Physical and spectral characterization data for 41	S55
Physical and spectral characterization data for 42	S56
Physical and spectral characterization data for 43α	S57
Physical and spectral characterization data for 43β	S58
Physical and spectral characterization data for 44α	S59
Physical and spectral characterization data for 44β	S59
Physical and spectral characterization data for 45α	S60
Physical and spectral characterization data for 45β	S61
Physical and spectral characterization data for 46α	S61
Physical and spectral characterization data for 47	S62
Physical and spectral characterization data for 48α	S63
Physical and spectral characterization data for 48β	S64
Physical and spectral characterization data for 49α	S64
Physical and spectral characterization data for 49β	S65
Physical and spectral characterization data for 50	S66
Physical and spectral characterization data for 51α	S67
Physical and spectral characterization data for 51β	S67
Physical and spectral characterization data for 52α	S68
Physical and spectral characterization data for 52β	S69
Physical and spectral characterization data for 53α	S70
Physical and spectral characterization data for 53β	S70

Physical and spectral characterization data for 54α	S71
Physical and spectral characterization data for 55	S72
Physical and spectral characterization data for 56α	S72
Physical and spectral characterization data for 56β	S73
Physical and spectral characterization data for 57α	S74
Physical and spectral characterization data for 58α	S75
Physical and spectral characterization data for 59α	S76
Physical and spectral characterization data for 59β	S77
Physical and spectral characterization data for 60α	S77
Physical and spectral characterization data for 60β	S78
Physical and spectral characterization data for 61α	S79
Physical and spectral characterization data for 62α	S80
Physical and spectral characterization data for 63	S80
Physical and spectral characterization data for 64α	S81
Physical and spectral characterization data for 64β	S82
Physical and spectral characterization data for 65α	S83
Physical and spectral characterization data for 66α	S84
Physical and spectral characterization data for 78α	S84
Physical and spectral characterization data for 79α	S85
Physical and spectral characterization data for 79β	S86
Physical and spectral characterization data for 80	S86
Physical and spectral characterization data for 81	S87
References	S88
Section C: ^1H NMR and ^{13}C NMR spectra	

^1H NMR and ^{13}C NMR spectra for S1	S90
^1H NMR and ^{13}C NMR spectra for S2	S91
^1H NMR and ^{13}C NMR spectra for S3	S92
^1H NMR and ^{13}C NMR spectra for S4	S93
^1H NMR and ^{13}C NMR spectra for S5	S94
^1H NMR and ^{13}C NMR spectra for 6	S95
^1H NMR and ^{13}C NMR spectra for 7	S96
^1H NMR and ^{13}C NMR spectra for 8	S97
^1H NMR and ^{13}C NMR spectra for 1	S98
^1H NMR and ^{13}C NMR spectra for 2	S99
^1H NMR and ^{13}C NMR spectra for 3	S100
^1H NMR and ^{13}C NMR spectra for 4	S101
^1H NMR and ^{13}C NMR spectra for 5	S102
^1H NMR and ^{13}C NMR spectra for S6	S103
^1H NMR and ^{13}C NMR spectra for S7	S104
^1H NMR and ^{13}C NMR spectra for S8	S105
^1H NMR and ^{13}C NMR spectra for S9	S106
^1H NMR and ^{13}C NMR spectra for S10	S107
^1H NMR and ^{13}C NMR spectra for S11	S108
^1H NMR and ^{13}C NMR spectra for 9	S109
^1H NMR and ^{13}C NMR spectra for 10	S110
^1H NMR and ^{13}C NMR spectra for 11	S111
^1H NMR and ^{13}C NMR spectra for 12	S112
^1H NMR and ^{13}C NMR spectra for S12	S113

¹ H NMR and ¹³ C NMR spectra for S13	S114
¹ H NMR and ¹³ C NMR spectra for S14	S115
¹ H NMR and ¹³ C NMR spectra for S15	S116
¹ H NMR and ¹³ C NMR spectra for S16	S117
¹ H NMR and ¹³ C NMR spectra for S17	S118
¹ H NMR and ¹³ C NMR spectra for 13	S119
¹ H NMR and ¹³ C NMR spectra for 14	S120
¹ H NMR and ¹³ C NMR spectra for 15	S121
¹ H NMR and ¹³ C NMR spectra for 16	S122
¹ H NMR and ¹³ C NMR spectra for S18	S123
¹ H NMR and ¹³ C NMR spectra for S19	S124
¹ H NMR and ¹³ C NMR spectra for 67	S125
¹ H NMR and ¹³ C NMR spectra for 68	S126
Mass spectra for the mixture containing a bicyclic product with a seven-membered trichlorooxazepine ring	S127
¹ H NMR and ¹³ C NMR spectra for 23	S128
¹ H NMR and ¹³ C NMR spectra for 24α	S129
¹ H NMR and ¹³ C NMR spectra for 24β	S130
¹ H NMR and ¹³ C NMR spectra for 25	S131
¹ H NMR and ¹³ C NMR spectra for 26	S132
¹ H NMR and ¹³ C NMR spectra for 27	S133
¹ H NMR and ¹³ C NMR spectra for 28	S134
¹ H NMR and ¹³ C NMR spectra for 29	S135
¹ H NMR and ¹³ C NMR spectra for 30α	S136
¹ H NMR and ¹³ C NMR spectra for 30β	S137

¹ H NMR and ¹³ C NMR spectra for 31	S138
¹ H NMR and ¹³ C NMR spectra for 32	S139
¹ H NMR and ¹³ C NMR spectra for 33	S140
¹ H NMR and ¹³ C NMR spectra for 34	S141
¹ H NMR and ¹³ C NMR spectra for 35α	S142
¹ H NMR and ¹³ C NMR spectra for 35β	S143
¹ H NMR and ¹³ C NMR spectra for 36α	S144
¹ H NMR and ¹³ C NMR spectra for 36β	S145
¹ H NMR and ¹³ C NMR spectra for 37α	S146
¹ H NMR and ¹³ C NMR spectra for 37β	S147
¹ H NMR and ¹³ C NMR spectra for 38α	S148
¹ H NMR and ¹³ C NMR spectra for 38β	S149
¹ H NMR and ¹³ C NMR spectra for 39	S150
¹ H NMR and ¹³ C NMR spectra for 40	S151
¹ H NMR and ¹³ C NMR spectra for 41	S152
¹ H NMR and ¹³ C NMR spectra for 42	S153
¹ H NMR and ¹³ C NMR spectra for 43α	S154
¹ H NMR and ¹³ C NMR spectra for 43β	S155
¹ H NMR and ¹³ C NMR spectra for 44α	S156
¹ H NMR and ¹³ C NMR spectra for 44β	S157
¹ H NMR and ¹³ C NMR spectra for 45α	S158
¹ H NMR and ¹³ C NMR spectra for 45β	S159
¹ H NMR and ¹³ C NMR spectra for 46α	S160
¹ H NMR and ¹³ C NMR spectra for 47	S161

¹ H NMR and ¹³ C NMR spectra for 48α	S162
¹ H NMR and ¹³ C NMR spectra for 48β	S163
¹ H NMR and ¹³ C NMR spectra for 49α	S164
¹ H NMR and ¹³ C NMR spectra for 49β	S165
¹ H NMR and ¹³ C NMR spectra for 50	S166
¹ H NMR and ¹³ C NMR spectra for 51α	S167
¹ H NMR and ¹³ C NMR spectra for 51β	S168
¹ H NMR and ¹³ C NMR spectra for 52α	S169
¹ H NMR and ¹³ C NMR spectra for 52β	S170
¹ H NMR and ¹³ C NMR spectra for 53α	S171
¹ H NMR and ¹³ C NMR spectra for 53β	S172
¹ H NMR and ¹³ C NMR spectra for 54α	S173
¹ H NMR and ¹³ C NMR spectra for 55	S174
¹ H NMR and ¹³ C NMR spectra for 56α	S175
¹ H NMR and ¹³ C NMR spectra for 56β	S176
¹ H NMR and ¹³ C NMR spectra for 57α	S177
¹ H NMR and ¹³ C NMR spectra for 58α	S178
¹ H NMR and ¹³ C NMR spectra for 59α	S179
¹ H NMR and ¹³ C NMR spectra for 59β	S180
¹ H NMR and ¹³ C NMR spectra for 60α	S181
¹ H NMR and ¹³ C NMR spectra for 60β	S182
¹ H NMR and ¹³ C NMR spectra for 61α	S183
¹ H NMR and ¹³ C NMR spectra for 62α	S184
¹ H NMR and ¹³ C NMR spectra for 63	S185

¹ H NMR and ¹³ C NMR spectra for 64α	S186
¹ H NMR and ¹³ C NMR spectra for 64β	S187
¹ H NMR and ¹³ C NMR spectra for 65α	S188
¹ H NMR and ¹³ C NMR spectra for 66α	S189
¹ H NMR and ¹³ C NMR spectra for 78α	S190
¹ H NMR and ¹³ C NMR spectra for 79α	S191
¹ H NMR and ¹³ C NMR spectra for 79β	S192
¹ H NMR and ¹³ C NMR spectra for 80	S193
¹ H NMR and ¹³ C NMR spectra for 81	S194
¹ H NMR and ¹³ C NMR spectra for 82α	S195
¹ H NMR and ¹³ C NMR spectra for 82β	S196
¹ H NMR and 2D NMR spectra for 69	S197
¹ H NMR and 2D NMR spectra for 70	S198
¹ H NMR and 2D NMR spectra for 71	S199
¹ H NMR and 2D NMR spectra for 72	S200
¹ H NMR and 2D NMR spectra for 73	S201
¹ H NMR and 2D NMR spectra for 74	S202

Section A: General Methods

All reactions were conducted under a positive pressure of dry argon with dry, freshly distilled solvents unless otherwise noted. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Dichloromethane was distilled from calcium hydride. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography was

performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization on TLC was achieved by UV light (254 nm) and a typical TLC indication solution (cerium sulfate / molybdic acid solution). NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane (TMS). The residue was purified by Recycling Preparative High-Performance Gel Permeation Chromatography using CHCl_3 as the eluting solvent.

Experimental section

Allyl 2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)-D-mannopyranoside (S1**).** To a solution of allyl 2,3,6-tri-*O*-benzyl-D-mannopyranoside¹ (763 mg, 1.55 mmol) in CH_2Cl_2 (10 mL) were added *o*- $\text{CF}_3\text{PhSO}_2\text{Cl}$ (0.48 mL, 3.11 mmol), pyridine (0.50 mL, 6.22 mmol), and DMAP (38 mg, 0.311 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl , and then extracted with CH_2Cl_2 . The combined organic layer was washed with 1N HCl and brine, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **S1** (928 mg, 85%): colorless oil, R_f = 0.42

(hexane/EtOAc, 4:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.68-3.71 (m, 1H), 3.74 (dd, J = 11.2, 5.6 Hz, 1H), 3.82 (dd, J = 14.0, 2.0 Hz, 1H), 3.85 (dd, J = 9.6, 2.8 Hz, 1H), 3.90-3.99 (m, 2H), 4.03 (d, J = 11.6 Hz, 1H), 4.16 (dd, J = 13.0, 4.8 Hz, 1H), 4.29 (d, J = 11.6 Hz, 1H), 4.53 (d, J = 10.8 Hz, 1H), 4.56 (d, J = 11.0 Hz, 1H), 4.57 (s, 2H), 4.88 (d, J = 1.6 Hz, 1H), 5.12-5.23 (m, 3H), 5.75-5.90 (m, 1H), 6.97-7.03 (m, 2H), 7.18-7.41 (m, 15H), 7.56-7.63 (m, 1H), 8.07-8.13 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 68.2, 69.0, 70.4, 71.1, 72.8, 73.5, 74.5, 77.1, 78.5, 96.8, 117.7, 121.2, 123.9, 127.3, 127.44, 127.45, 127.5, 127.65, 127.68, 127.70, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 131.7, 131.9, 133.1, 133.5, 136.0, 137.7, 138.0, 138.4. HRMS Calcd for $\text{C}_{37}\text{H}_{37}\text{F}_3\text{O}_8\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 721.2059; found, 217.2054.

Allyl 2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl-D-mannopyranoside (S2). To a solution of allyl 2,3,6-tri-*O*-benzyl-D-mannopyranoside¹ (2.69 g, 5.48 mmol) in CH_2Cl_2 (20 mL) were added BnSO_2Cl (2.09 g, 10.97 mmol), pyridine (1.77 mL, 21.9 mmol), and DMAP (134 mg, 1.097 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl , and then extracted with CH_2Cl_2 . The combined organic layer was washed with 1N HCl and brine, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/ CH_2Cl_2 , 5:1:1) to afford compound **S2** (3.39 g, 96%): colorless oil, R_f = 0.42 (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.73 (dd, J = 11.2, 6.0 Hz, 1H), 3.81 (dd, J = 10.8, 2.0 Hz, 1H), 3.85-4.01 (m, 3H), 4.03 (dd, J = 9.6, 3.2 Hz, 1H), 4.16 (d, J = 13.6 Hz, 1H), 4.17-4.22 (m, 1H), 4.34 (d, J = 13.6 Hz, 1H), 4.50 (d, J = 11.2 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.56-4.62 (m, 2H), 4.68 (s, 2H), 4.97 (d, J = 1.6 Hz, 1H), 5.11 (t, J = 9.6 Hz, 1H), 5.19 (dd, J = 10.4, 1.6 Hz, 1H), 5.25 (dd, J = 17.2, 1.6 Hz, 1H), 5.82-5.91

(m, 1H), 7.20-7.36 (m, 20H); ^{13}C NMR (100 MHz, CDCl_3) δ 57.3, 68.2, 69.1, 70.5, 71.5, 72.6, 73.6, 74.0, 77.2, 77.3, 96.5, 117.7, 127.4, 127.76, 127.81, 127.83, 127.89, 127.94, 128.0, 128.2, 128.3, 128.4, 128.6, 128.7, 128.8, 130.6, 133.5, 137.4, 137.8, 138.3. Anal. Calcd for $\text{C}_{37}\text{H}_{40}\text{O}_8\text{S}$: C, 68.92; H, 6.25; S, 4.97. Found: C, 68.92; H, 6.28; S, 4.79.

Allyl 2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-D-mannopyranoside (S3). To a solution of allyl 2,3,6-tri-*O*-benzyl-D-mannopyranoside¹ (880 mg, 1.79 mmol) in CH_2Cl_2 (10 mL) were added *p*- NO_2BzCl (666 mg, 3.59 mmol), pyridine (0.58 mL, 7.18 mmol), and DMAP (43.8 mg, 0.359 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl , and then extracted with CH_2Cl_2 . The combined organic layer was washed with 1N HCl and brine, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 6:1) to afford compound **S3** (1.10 g, 96%): colorless oil, R_f = 0.24 (hexane/EtOAc, 6:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.58-3.69 (m, 2H), 3.88 (t, J = 2.0 Hz, 1H), 3.94-4.04 (m, 2H), 4.23 (dd, J = 13.2, 5.2 Hz, 1H), 4.38 (d, J = 12.4 Hz, 1H), 4.46 (s, 2H), 4.57 (d, J = 12.4 Hz, 1H), 4.73 (d, J = 12.4 Hz, 1H), 4.81 (d, J = 12.4 Hz, 1H), 4.95 (d, J = 1.2 Hz, 1H), 5.21 (d, J = 10.4 Hz, 1H), 5.27 (dd, J = 17.2, 1.6 Hz, 1H), 5.69 (t, J = 10.0 Hz, 1H), 5.85-5.95 (m, 1H), 7.10-7.41 (m, 15H), 7.97-8.03 (m, 2H), 8.16-8.23 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 68.3, 70.2, 70.9, 71.7, 73.1, 73.6, 77.0, 97.5, 117.6, 123.4, 127.5, 127.69, 127.72, 127.8, 128.0, 128.2, 128.3, 128.5, 130.8, 133.7, 135.5, 137.88, 137.89, 138.1, 150.5, 163.8. Anal. Calcd for $\text{C}_{37}\text{H}_{37}\text{NO}_9$: C, 69.47; H, 5.83; N, 2.19. Found: C, 69.54; H, 5.74; N, 2.16.

Allyl 2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl-D-mannopyranoside (S4). To a solution of allyl 2,3,6-tri-*O*-benzyl-D-mannopyranoside¹ (830 mg, 1.69 mmol) in CH₂Cl₂ (10 mL) were added BzCl (0.393 mL, 3.38 mmol), pyridine (0.547 mL, 6.77 mmol), and DMAP (41.3 mg, 0.338 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH₄Cl, and then extracted with CH₂Cl₂. The combined organic layer was washed with 1N HCl and brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **S4** (892 mg, 95%): colorless oil, *R_f* = 0.37 (hexane/EtOAc, 4:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.62 (d, *J* = 10.8, 2.8 Hz, 1H), 3.67 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.86 (t, *J* = 2.0 Hz, 1H), 3.94-4.03 (m, 3H), 4.21 (dd, *J* = 12.8, 4.8 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.51 (s, 2H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 12.4 Hz, 1H), 4.81 (d, *J* = 12.4 Hz, 1H), 4.95 (d, *J* = 1.2 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 5.26 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.65 (t, *J* = 10.0 Hz, 1H), 5.81-5.96 (m, 1H), 7.11-7.60 (m, 18H), 7.95-8.01 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 68.2, 69.6, 70.1, 70.9, 72.0, 73.0, 73.6, 74.3, 77.3, 97.6, 117.6, 127.5, 127.6, 127.7, 127.8, 128.1, 128.29, 128.33, 128.4, 128.5, 129.9, 130.1, 133.1, 133.8, 138.1, 138.2, 138.3, 165.7. Anal. Calcd for C₃₇H₃₈O₇: C, 74.73; H, 6.44. Found: C, 74.71; H, 6.55.

2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)-D-mannopyranose (S5).

A mixture of compound **S1** (1.33 g, 1.90 mmol) and PdCl₂ (67.5 mg, 0.381 mmol) in MeOH (15 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/CH₂Cl₂, 4:1:1) to afford compound **S5** (1.04 g, 83%): colorless oil, *R_f* = 0.11 (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); ¹H NMR (400

MHz, CDCl₃) δ 3.58-3.62 (m, 1H), 3.69 (dd, J = 10.4, 7.6 Hz, 1H), 3.76-3.83 (m, 2H), 3.98 (d, J = 11.6 Hz, 1H), 4.12-4.20 (m, 2H), 4.23 (d, J = 11.6 Hz, 1H), 4.44-4.58 (m, 4H), 4.99 (t, J = 9.6 Hz, 1H), 5.12 (d, J = 1.6 Hz, 1H), 6.92-7.00 (m, 2H), 7.14-7.40 (m, 15H), 7.53-7.60 (m, 1H), 8.03-8.10 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 69.56, 69.64, 71.1, 72.8, 73.6, 74.9, 76.3, 78.7, 92.3, 121.1, 123.9, 127.3, 127.6, 127.6, 127.7, 127.8, 127.9, 127.96, 127.99, 128.02, 128.1, 128.2, 128.4, 128.5, 131.6, 131.8, 133.2, 133.3, 135.8, 137.6, 137.7, 138.0. Anal. Calcd for C₃₄H₃₃F₃O₈S: C, 62.00; H, 5.05; S, 4.87. Found: C, 62.09; H, 5.07; S, 4.66.

2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl-D-mannopyranose (6). A mixture of compound **S2** (910 mg, 1.41 mmol) and PdCl₂ (50.0 mg, 0.282 mmol) in MeOH (15 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/CH₂Cl₂, 4:1:1) to afford compound **6** (755 mg, 88%): colorless oil, R_f = 0.20 (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.67 (dd, J = 10.4, 8.0 Hz, 1H), 3.74-3.79 (m, 2H), 3.98 (dd, J = 10.0, 3.2 Hz, 1H), 4.10-4.18 (m, 2H), 4.31 (d, J = 14.4 Hz, 1H), 4.32 (d, J = 12.4 Hz, 1H), 4.45 (d, J = 11.2 Hz, 1H), 4.48 (s, 2H), 4.52 (d, J = 12.4 Hz, 1H), 4.63 (s, 2H), 4.92 (t, J = 10.0 Hz, 1H), 5.20 (brs, 1H), 7.15-7.37 (m, 25H); ¹³C NMR (100 MHz, CDCl₃) δ 57.3, 69.6, 71.5, 72.6, 73.6, 74.4, 76.7, 77.3, 92.0, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.46, 128.54, 128.6, 128.69, 128.73, 128.8, 130.6, 137.3, 137.5, 137.9. Anal. Calcd for C₃₄H₃₆O₈S: C, 67.53; H, 6.00; S, 5.30. Found: C, 67.49; H, 6.16; S, 5.33.

2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-D-mannopyranose (7). A mixture of compound **S3** (990 mg, 1.55 mmol) and PdCl₂ (54.9 mg, 0.310 mmol) in MeOH (10

mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to afford compound **7** (745 mg, 80%): colorless oil, $R_f = 0.17$ (hexane/EtOAc, 3:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.43 (dd, $J = 10.6, 2.8$ Hz, 1H), 3.59 (d, $J = 3.6$ Hz, 1H), 3.66 (dd, $J = 10.4, 6.8$ Hz, 1H), 3.85 (t, $J = 2.0$ Hz, 1H), 4.01 (dd, $J = 9.6, 3.2$ Hz, 1H), 4.19-4.24 (m, 1H), 4.35 (d, $J = 12.0$ Hz, 1H), 4.45 (s, 2H), 4.55 (d, $J = 12.4$ Hz, 1H), 4.73 (d, $J = 12.0$ Hz, 1H), 4.81 (d, $J = 12.4$ Hz, 1H), 5.30 (brs, 1H), 5.58 (t, $J = 10.0$ Hz, 1H), 7.11-7.40 (m, 15H), 7.97-8.04 (m, 2H), 8.15-8.24 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 70.0, 70.2, 70.7, 71.6, 73.1, 73.6, 74.1, 76.4, 93.1, 123.5, 127.72, 127.75, 127.77, 127.80, 127.9, 128.00, 128.03, 128.1, 128.2, 128.3, 128.35, 128.39, 128.4, 128.49, 128.53, 130.9, 135.3, 137.5, 137.8, 138.1, 150.6, 163.9. Anal. Calcd for $\text{C}_{34}\text{H}_{33}\text{NO}_9$: C, 68.10; H, 5.55; N, 2.34. Found: C, 68.12; H, 5.69; N, 2.14.

2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl-D-mannopyranose (8). A mixture of compound **S4** (890 mg, 1.50 mmol) and PdCl_2 (53.1 mg, 0.299 mmol) in MeOH (10 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/ CH_2Cl_2 , 3:1:1) to afford compound **8** (688 mg, 83%): colorless oil, $R_f = 0.23$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.55 (d, $J = 10.8, 2.4$ Hz, 1H), 3.69 (dd, $J = 10.4, 8.0$ Hz, 1H), 3.75 (d, $J = 3.6$ Hz, 1H), 3.82 (t, $J = 1.6$ Hz, 1H), 4.00 (dd, $J = 9.6, 2.8$ Hz, 1H), 4.18-4.26 (m, 1H), 4.42 (d, $J = 12.4$ Hz, 1H), 4.46 (s, 2H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.72 (d, $J = 12.4$ Hz, 1H), 4.80 (d, $J = 12.4$ Hz, 1H), 5.28 (dd, $J = 3.2, 2.0$ Hz, 1H), 5.55 (t, $J = 10.0$ Hz, 1H), 7.11-7.61 (m, 18H), 7.92-8.01 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 69.6, 70.2, 70.4, 71.9, 73.0, 73.5, 74.4,

76.7, 93.1, 127.6, 127.66, 127.73, 127.9, 128.0, 128.1, 128.3, 128.41, 128.44, 128.7, 129.9, 130.0, 133.2, 137.7, 138.0, 138.3, 165.7. Anal. Calcd for C₃₄H₃₄O₇: C, 73.63; H, 6.18. Found: C, 73.62; H, 6.13.

2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)-D-mannopyranosyl

Trichloroacetimidate (1). To a solution of **S5** (850 mg, 1.29 mmol) in CH₂Cl₂ (10 mL) were added Cl₃CCN (1.29 mL, 12.9 mmol) and DBU (19.5 µL, 0.129 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to afford compound **1** (875 mg, 84%): colorless oil, R_f = 0.36 (hexane/EtOAc, 3:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.68 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.72-3.75 (m, 1H), 3.77 (dd, *J* = 7.2, 2.0 Hz, 1H), 3.87 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.08 (d, *J* = 12.0 Hz, 1H), 4.09-4.12 (m, 1H), 4.21 (d, *J* = 12.0 Hz, 1H), 4.53 (s, 2H), 4.59 (d, *J* = 12.4 Hz, 1H), 4.63 (d, *J* = 12.4 Hz, 1H), 5.33 (t, *J* = 9.6 Hz, 1H), 6.28 (d, *J* = 2.0 Hz, 1H), 6.99-7.37 (m, 15H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 8.14 (t, *J* = 7.6 Hz, 1H), 8.56 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 68.4, 71.6, 72.8, 73.1, 73.3, 73.5, 75.9, 77.3, 90.8, 95.3, 127.2, 127.3, 127.4, 127.65, 127.73, 127.78, 127.82, 127.9, 127.96, 128.02, 128.08, 128.14, 128.27, 128.33, 128.4, 128.51, 128.54, 128.7, 128.8, 131.6, 131.8, 131.9, 132.0, 132.1, 133.3, 133.5, 135.9, 137.0, 137.6, 137.8, 138.3, 160.1. HRMS Calcd for C₃₆H₃₃Cl₃F₃NO₈SNa [M + Na]⁺, 824.0842; found, 824.0845.

2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl-D-mannopyranosyl Trichloroacetimidate (2).

To a solution of **6** (502 mg, 0.830 mmol) in CH₂Cl₂ (5 mL) were added Cl₃CCN (0.83 mL, 8.30 mmol) and DBU (12.5 µL, 0.0830 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by

flash column chromatography (hexane/EtOAc, 3:1) to afford compound **2** (535 mg, 86%): colorless oil, $R_f = 0.28$ (hexane/EtOAc, 3:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.72 (dd, $J = 11.2, 4.8$ Hz, 1H), 3.78 (dd, $J = 11.4, 2.0$ Hz, 1H), 3.94 (brs, 1H), 4.01 (dd, $J = 9.6, 2.8$ Hz, 1H), 4.08-4.11 (m, 1H), 4.22 (d, $J = 13.6$ Hz, 1H), 4.40 (d, $J = 13.6$ Hz, 1H), 4.49 (d, $J = 11.6$ Hz, 1H), 4.51 (d, $J = 11.6$ Hz, 1H), 4.55 (d, $J = 11.8$ Hz, 1H), 4.58 (d, $J = 11.8$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.74 (d, $J = 12.0$ Hz, 1H), 5.24 (t, $J = 9.6$ Hz, 1H), 6.37 (d, $J = 1.6$ Hz, 1H), 7.22-7.37 (m, 20H), 8.63 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 57.4, 68.4, 71.8, 72.5, 72.65, 72.71, 73.1, 73.4, 73.5, 76.1, 90.8, 95.2, 127.5, 127.7, 127.8, 127.9, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 128.9, 129.0, 130.7, 136.9, 137.4, 138.1, 160.1. HRMS Calcd for $\text{C}_{36}\text{H}_{36}\text{Cl}_3\text{NO}_8\text{SNa}$ $[\text{M} + \text{Na}]^+$, 770.1125; found, 770.1122.

2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-*D*-mannopyranosyl Trichloroacetimidate

(3). To a solution of **7** (320 mg, 0.534 mmol) in CH_2Cl_2 (5 mL) were added Cl_3CCN (0.535 mL, 5.34 mmol) and DBU (8.1 μL , 0.0534 mmol) at 0 $^\circ\text{C}$. The resulting solution was stirred at 0 $^\circ\text{C}$ for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **3** (319 mg, 80%): colorless oil, $R_f = 0.50$ (hexane/EtOAc, 3:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.64 (d, $J = 12.0$ Hz, 1H), 3.65 (d, $J = 12.0$ Hz, 1H), 3.95-4.03 (m, 2H), 4.12-4.17 (m, 1H), 4.35 (d, $J = 12.0$ Hz, 1H), 4.44 (d, $J = 11.6$ Hz, 1H), 4.45 (d, $J = 11.6$ Hz, 1H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.80 (s, 2H), 5.81 (t, $J = 9.6$ Hz, 1H), 6.39 (d, $J = 1.2$ Hz, 1H), 7.09-7.43 (m, 15H), 7.95-8.05 (m, 2H), 8.17-8.21 (m, 2H), 8.63 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 69.8, 70.0, 71.6, 72.6, 72.9, 73.0, 73.6, 75.5, 90.9, 96.0, 123.4, 127.5, 127.8, 127.9, 128.0, 128.05, 128.11, 128.2, 128.4, 128.5, 128.6, 130.9, 135.3,

137.3, 137.6, 150.5, 160.2, 163.7. HRMS Calcd for $C_{36}H_{33}Cl_3N_2O_9Na$ $[M + Na]^+$, 765.1149; found, 765.1147.

2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl-D-mannopyranosyl Trichloroacetimidate (4). To a solution of **8** (455 mg, 0.820 mmol) in CH_2Cl_2 (6 mL) were added Cl_3CCN (0.823 mL, 8.20 mmol) and DBU (12.4 μ L, 0.0820 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 6:1) to afford compound **4** (477 mg, 83%): colorless oil, R_f = 0.35 (hexane/EtOAc, 6:1, v/v); 1H NMR (400 MHz, $CDCl_3$) δ 3.62-3.69(m, 2H), 3.95 (dd, J = 16.0, 3.2 Hz, 1H), 3.98 (dd, J = 7.6, 4.8 Hz, 1H), 4.14-4.21 (m, 1H), 4.43 (d, J = 12.4 Hz, 1H), 4.49 (s, 2H), 4.53 (d, J = 12.4 Hz, 1H), 4.78 (d, J = 12.4 Hz, 1H), 4.82 (d, J = 12.4 Hz, 1H), 5.77 (t, J = 10.0 Hz, 1H), 6.38 (d, J = 2.0 Hz, 1H), 7.15-7.34 (m, 13H), 7.44-7.60 (m, 5H), 7.96-8.01 (m, 2H), 8.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.7, 69.6, 71.9, 72.9, 73.0, 73.5, 73.6, 75.8, 96.2, 127.4, 127.7, 128.82, 127.83 128.05, 128.12, 128.2, 128.36, 128.41, 128.43, 128.6, 129.88, 129.92, 133.2, 137.6, 137.8, 138.0, 160.3, 165.5. HRMS Calcd for $C_{36}H_{34}Cl_3NO_7Na$ $[M + Na]^+$, 720.1299; found, 720.1295.

2,3,6-Tri-*O*-benzyl-4-*O*-acetyl-D-mannopyranosyl Trichloroacetimidate (5). To a solution of 2,3,6-tri-*O*-benzyl-4-*O*-acetyl-D-mannopyranose² (515 mg, 1.05 mmol) in CH_2Cl_2 (6 mL) were added Cl_3CCN (1.05 mL, 10.5 mmol) and DBU (16.0 μ L, 0.105 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 4:1) to afford compound **5** (556 mg, 83%): colorless oil, R_f = 0.38 (hexane/EtOAc, 3:1, v/v); 1H NMR (400 MHz, $CDCl_3$) δ 3.54-3.64 (m, 2H), 3.86 (dd, J

= 9.6, 2.8 Hz, 1H), 3.88-4.01 (m, 1H), 3.99-4.05 (m, 1H), 4.48 (q, J = 12.4 Hz, 1H), 4.52 (s, 2H), 4.75 (s, 2H), 5.49 (t, J = 9.6 Hz, 1H), 6.33 (d, J = 3.2 Hz, 1H), 7.21-7.42 (m, 15H), 8.58 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 68.4, 69.7, 72.1, 73.0, 73.1, 73.4, 73.6, 76.1, 96.1, 127.7, 127.9, 127.96, 128.0, 128.1, 128.4, 128.49, 128.54, 137.87, 137.91, 138.1, 160.3, 169.9. HRMS Calcd for $\text{C}_{31}\text{H}_{32}\text{Cl}_3\text{NO}_7\text{Na}$ $[\text{M} + \text{Na}]^+$, 658.1142; found, 658.1140.

Allyl 2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl-D-mannopyranoside (S6). To a solution of allyl 2,3,4-tri-*O*-benzyl-D-mannopyranoside³ (2.0 g, 4.08 mmol) in CH_2Cl_2 (20 mL) were added BnSO_2Cl (1.55 g, 8.15 mmol), pyridine (1.32 mL, 16.3 mmol), and DMAP (100 mg, 0.815 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl , and then extracted with CH_2Cl_2 . The combined organic layer was washed with 1N HCl and brine, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 6:1) to afford compound **S6** (2.34 g, 89%): colorless oil, R_f = 0.45 (hexane/EtOAc, 3:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.74-3.85 (m, 2H), 3.87-3.97 (m, 3H), 4.11 (dd, J = 13.2, 4.0 Hz, 1H), 4.33 (d, J = 14.0 Hz, 1H), 4.35-4.43 (m, 3H), 4.44 (d, J = 14.0 Hz, 1H), 4.64 (s, 2H), 4.66 (d, J = 12.0 Hz, 1H), 4.75 (d, J = 12.0 Hz, 1H), 4.84 (d, J = 10.8 Hz, 1H),

4.88 (brs, 1H), 5.16 (d, $J = 10.4$ Hz, 1H), 5.22 (dd, $J = 17.2, 1.2$ Hz, 1H), 5.76-5.84 (m, 1H), 7.24-7.38 (m, 20H); ^{13}C NMR (100 MHz, CDCl_3) δ 57.0, 68.2, 69.2, 70.6, 72.3, 73.2, 74.1, 74.9, 75.3, 80.1, 97.4, 117.6, 127.7, 127.8, 127.88, 127.93, 128.0, 128.1, 128.2, 128.49, 128.51, 128.54, 128.9, 129.0, 131.0, 133.5, 138.1, 138.2, 138.4. HRMS Calcd for $\text{C}_{37}\text{H}_{40}\text{O}_8\text{SNa}$ $[\text{M} + \text{Na}]^+$, 667.2342; found, 667.2344.

Allyl 2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)-D-mannopyranoside (S7). To a solution of allyl 2,3,4-tri-*O*-benzyl-D-mannopyranoside³ (630 mg, 1.28 mmol) in CH_2Cl_2 (10 mL) were added *p*-NO₂BzCl (477 mg, 2.57 mmol), pyridine (0.42 mL, 5.14 mmol), and DMAP (31.4 mg, 0.257 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl , and then extracted with CH_2Cl_2 . The combined organic layer was washed with 1N HCl and brine, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 6:1) to afford compound **S7** (720 mg, 88%): colorless oil, $R_f = 0.53$ (hexane/EtOAc, 4:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.88 (t, $J = 2.4$ Hz, 1H), 3.91 (d, $J = 6.4$ Hz, 1H), 3.97 (dd, $J = 12.8, 6.0$ Hz, 1H), 4.05 (dd, $J = 9.2, 2.8$ Hz, 1H), 4.08 (q, $J = 9.6$ Hz, 1H), 4.16 (dd, $J = 11.6, 3.6$ Hz, 1H), 4.54 (d, $J = 9.6$ Hz, 1H), 4.57 (d, $J = 9.6$ Hz, 1H), 4.63 (d, $J = 10.8$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.69 (d, $J = 12.4$ Hz, 1H), 4.73 (d, $J = 12.4$ Hz, 1H), 4.79 (d, $J = 12.0$ Hz, 1H), 4.95 (d, $J = 4.8$ Hz, 1H), 4.96 (d, $J = 4.8$ Hz, 1H), 5.18 (dd, $J = 10.4, 1.6$ Hz, 1H), 5.23 (dd, $J = 17.2, 1.2$ Hz, 1H), 7.12-7.47 (m, 15H), 8.03-8.12 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 64.5, 68.3, 70.2, 72.3, 73.1, 73.8, 75.0, 75.3, 80.4, 97.2, 117.7, 123.6, 127.86, 127.88, 127.90, 128.0, 128.4, 128.55, 128.59, 130.9, 133.6, 135.5, 138.0, 138.34, 138.36, 150.6, 164.5. HRMS Calcd for $\text{C}_{37}\text{H}_{37}\text{NO}_9\text{Na}$ $[\text{M} + \text{Na}]^+$, 662.2366; found, 662.2369.

Allyl 2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl-D-mannopyranoside (S8). To a solution of allyl 2,3,4-tri-*O*-benzyl-D-mannopyranoside³ (749 mg, 1.53 mmol) in CH₂Cl₂ (10 mL) were added BzCl (0.354 mL, 3.05 mmol), pyridine (0.494 mL, 6.11 mmol), and DMAP (37.3 mg, 0.305 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH₄Cl, and then extracted with CH₂Cl₂. The combined organic layer was washed with 1N HCl and brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 6:1) to afford compound **S8** (852 mg, 94%): colorless oil, *R*_f = 0.60 (hexane/EtOAc, 4:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.47 (d, *J* = 2.0 Hz, 1H), 3.86 (d, *J* = 2.0 Hz, 1H), 3.91-3.95 (m, 1H), 3.97 (d, *J* = 7.6 Hz, 1H), 4.02 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.10 (d, *J* = 9.6 Hz, 1H), 4.16 (dd, *J* = 12.8, 4.8 Hz, 1H), 4.54-4.58 (m, 2H), 4.61 (d, *J* = 10.8, Hz, 1H), 4.68 (s, 2H), 4.70 (d, *J* = 12.4 Hz, 1H), 4.79 (d, *J* = 12.4 Hz, 1H), 4.93 (d, *J* = 0.8 Hz, 1H), 4.95 (d, *J* = 7.6 Hz, 1H), 5.16 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.22 (dd, *J* = 17.2, 1.2 Hz, 1H), 7.15-7.57 (m, 18H), 8.01-8.09 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 64.0, 68.2, 70.5, 72.4, 72.9, 74.6, 75.1, 75.5, 80.4, 97.2, 117.6, 127.7, 127.8, 127.87, 127.93, 128.33, 128.45, 128.48, 128.6, 129.0, 129.9, 130.3, 130.7, 133.0, 133.8, 138.2, 138.46, 138.50, 166.5. HRMS Calcd for C₃₇H₃₈O₇Na [M + Na]⁺, 617.2515; found, 617.2511.

2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl-D-mannopyranose (S9). A mixture of compound **S6** (1.00 g, 1.55 mmol) and PdCl₂ (55.0 mg, 0.310 mmol) in MeOH (7 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to afford compound **S9** (875 mg, 93%): colorless oil, *R*_f = 0.15 (hexane/EtOAc, 3:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 2.01

(brs, 1H), 3.73-3.78 (m, 2H), 3.86 (d, $J = 9.6$ Hz, 1H), 3.94 (dd, $J = 9.6, 2.4$ Hz, 1H), 3.96-4.01 (m, 1H), 4.27 (d, $J = 14.4$ Hz, 1H), 4.27-4.39 (m, 2H), 4.43 (d, $J = 10.8$ Hz, 1H), 4.58 (s, 2H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.69 (d, $J = 12.0$ Hz, 1H), 4.82 (d, $J = 10.8$ Hz, 1H), 5.14 (d, $J = 1.2$ Hz, 1H), 7.16-7.31 (m, 20H); ^{13}C NMR (100 MHz, CDCl_3) δ 56.8, 69.6, 70.3, 72.1, 73.0, 74.2, 75.0, 75.1, 79.5, 92.6, 127.6, 127.7, 127.8, 127.86, 127.9, 127.98, 128.0, 128.2, 128.41, 128.44, 128.60, 128.62, 128.8, 128.9, 130.9, 138.0, 138.1, 138.3. HRMS Calcd for $\text{C}_{34}\text{H}_{36}\text{O}_8\text{SNa}$ $[\text{M} + \text{Na}]^+$, 627.2029; found, 627.2025.

2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)-D-mannopyranose (S10). A mixture of compound **S7** (611 mg, 0.955 mmol) and PdCl_2 (33.9 mg, 0.191 mmol) in MeOH (10 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to afford compound **S10** (503 mg, 88%): colorless oil, $R_f = 0.28$ (hexane/EtOAc, 3:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.88 (t, $J = 2.0$ Hz, 1H), 4.08 (dd, $J = 10.4, 2.4$ Hz, 1H), 4.09-4.14 (m, 2H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.65 (d, $J = 3.2$ Hz, 1H), 4.67 (d, $J = 4.4$ Hz, 1H), 4.75 (s, 2H), 4.80 (d, $J = 11.6$ Hz, 1H), 4.96 (d, $J = 4.4$ Hz, 1H), 5.27-5.32 (m, 1H), 7.15-7.43 (m, 15H), 8.03-8.12 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 64.5, 70.5, 72.4, 73.2, 73.9, 75.2, 75.3, 79.8, 93.0, 123.6, 127.89, 127.93, 127.97, 127.99, 128.2, 128.4, 128.56, 128.63, 128.82, 131.0, 135.6, 138.1, 138.4, 150.6, 164.6. HRMS Calcd for $\text{C}_{34}\text{H}_{33}\text{NO}_9\text{Na}$ $[\text{M} + \text{Na}]^+$, 622.2053; found, 622.2055.

2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl-D-mannopyranose (S11). A mixture of compound **S8** (489 mg, 0.822 mmol) and PdCl_2 (29.2 mg, 0.164 mmol) in MeOH (10 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite®

and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/CH₂Cl₂, 7:1:1) to afford compound **S11** (405 mg, 89%): colorless oil, R_f = 0.33 (hexane/EtOAc/CH₂Cl₂, 7:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 2.98 (brs, 1H), 3.83 (brs, 1H), 4.00-4.07 (m, 1H), 4.14 (s, 1H), 4.16 (dd, J = 12.8, 4.8 Hz, 1H), 4.53 (d, J = 11.6 Hz, 1H), 4.59 (d, J = 11.6 Hz, 1H), 4.63 (d, J = 10.8 Hz, 1H), 4.68 (s, 2H), 4.77 (d, J = 12.0 Hz, 1H), 4.95 (d, J = 10.8 Hz, 1H), 5.27 (d, J = 0.8 Hz, 1H), 7.15-7.41 (m, 18H), 7.98-8.05 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 64.0, 70.6, 72.4, 73.0, 74.6, 75.3, 75.4, 79.8, 92.8, 127.69, 127.73, 127.8, 127.9, 128.0, 128.06, 128.12, 128.3, 128.4, 128.46, 128.53, 128.6, 128.71, 128.74, 129.8, 129.9, 130.2, 133.1, 138.2, 138.5, 166.7. HRMS Calcd for C₃₄H₃₄O₇Na [M + Na]⁺, 577.2202; found, 577.2204.

2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl-D-mannopyranosyl Trichloroacetimidate (9).

To a solution of **S9** (1.68 g, 2.78 mmol) in CH₂Cl₂ (5 mL) were added Cl₃CCN (2.79 mL, 27.8 mmol) and DBU (41.9 μL, 0.278 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc/CH₂Cl₂, 5:1:1) to afford compound **9** (1.25 g, 60%): colorless oil, R_f = 0.45 (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.85-3.88 (m, 1H), 3.93 (dd, J = 8.8, 2.4 Hz, 1H), 3.95-3.97 (m, 1H), 3.99 (q, J = 9.2 Hz, 1H), 4.35 (d, J = 14.0 Hz, 1H), 4.38 (d, J = 14.0 Hz, 1H), 4.41-4.44 (m, 2H), 4.47 (d, J = 10.8 Hz, 1H), 4.61 (d, J = 11.6 Hz, 1H), 4.66 (d, J = 11.6 Hz, 1H), 4.73 (d, J = 12.0 Hz, 1H), 4.79 (d, J = 12.0 Hz, 1H), 4.85 (d, J = 10.4 Hz, 1H), 6.33 (d, J = 1.2 Hz, 1H), 7.20-7.40 (m, 20H), 8.58 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 57.0, 68.4, 72.4, 73.08, 73.12, 73.3, 73.6, 75.5, 78.8, 90.8, 95.7, 127.6, 127.8, 127.90, 127.93, 128.0, 128.1, 128.2, 128.4, 128.49, 128.52, 128.6, 128.7, 128.86, 128.92, 129.1,

130.9, 137.7, 137.8, 137.9, 160.3. HRMS Calcd for $C_{36}H_{36}Cl_3NO_8SNa$ $[M + Na]^+$, 770.1125; found, 770.1123.

2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)-D-mannopyranosyl Trichloroacetimidate (10). To a solution of **S10** (502 mg, 0.837 mmol) in CH_2Cl_2 (5 mL) were added Cl_3CCN (0.839 mL, 8.37 mmol) and DBU (12.6 μ L, 0.0837 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **10** (518 mg, 83%): colorless oil, R_f = 0.33 (hexane/EtOAc, 5:1, v/v); 1H NMR (400 MHz, $CDCl_3$) δ 3.92 (t, J = 2.4 Hz, 1H), 4.05 (dd, J = 9.2, 2.8 Hz, 1H), 4.06-4.10 (m, 1H), 4.19 (t, J = 9.6 Hz, 1H), 4.50 (dd, J = 12.0, 3.6 Hz, 1H), 4.57 (dd, J = 12.0, 2.0 Hz, 1H), 4.65 (d, J = 10.8 Hz, 1H), 4.68-4.77 (m, 3H), 4.79 (d, J = 11.6 Hz, 1H), 4.95 (d, J = 10.8 Hz, 1H), 7.12-7.52 (m, 15H), 7.98-8.07 (m, 4H), 8.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.0, 72.6, 72.9, 73.0, 73.3, 74.1, 75.4, 76.8, 76.9, 79.2, 95.7, 123.55, 123.58, 127.98, 128.00, 128.1, 128.17, 128.24, 128.61, 128.64, 128.7, 130.90, 130.93, 135.5, 137.8, 138.0, 150.6, 160.6, 164.4. HRMS Calcd for $C_{36}H_{33}Cl_3N_2O_9Na$ $[M + Na]^+$, 765.1149; found, 765.1147.

2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl-D-mannopyranosyl Trichloroacetimidate (11). To a solution of **S11** (475 mg, 0.856 mmol) in CH_2Cl_2 (5 mL) were added Cl_3CCN (0.859 mL, 8.56 mmol) and DBU (12.9 μ L, 0.0856 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 6:1) to afford compound **11** (508 mg, 85%): colorless oil, R_f = 0.45 (hexane/EtOAc, 4:1, v/v); 1H NMR (400 MHz, $CDCl_3$) δ 3.91 (t, J = 2.4 Hz, 1H), 4.02 (dd, J = 9.2, 2.8 Hz, 1H), 4.10 (d, J = 9.6 Hz, 1H), 4.23 (t,

$J = 10.0$ Hz, 1H), 4.57 (dd, $J = 12.0, 2.0$ Hz, 1H), 4.63 (d, $J = 10.8$ Hz, 1H), 4.66 (d, $J = 11.6$ Hz, 1H), 4.71 (d, $J = 11.6$ Hz, 1H), 4.75 (d, $J = 12.0$ Hz, 1H), 4.79 (d, $J = 12.0$ Hz, 1H), 4.95 (d, $J = 10.8$ Hz, 1H), 6.37 (d, $J = 1.6$ Hz, 1H), 7.12-7.62 (m, 18H), 7.98-8.07 (m, 2H), 8.57 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 63.1, 72.5, 72.9, 73.1, 73.2, 73.7, 74.0, 75.4, 79.1, 95.8, 127.80, 127.83, 128.0, 128.1, 128.2, 128.4, 128.48, 128.49, 128.6, 128.7, 129.9, 130.1, 133.0, 133.2, 137.7, 137.9, 138.0, 158.8, 166.3. HRMS Calcd for $\text{C}_{36}\text{H}_{34}\text{Cl}_3\text{NO}_7\text{Na}$ $[\text{M} + \text{Na}]^+$, 720.1299; found, 720.1297.

2,3,4-Tri-*O*-benzyl-6-*O*-acetyl-D-mannopyranosyl Trichloroacetimidate (12). To a solution of 2,3,4-tri-*O*-benzyl-6-*O*-acetyl-D-mannopyranose^{2,4} (371 mg, 0.753 mmol) in CH_2Cl_2 (4 mL) were added Cl_3CCN (0.755 mL, 7.53 mmol) and DBU (11.4 μL , 0.0753 mmol) at 0 $^\circ\text{C}$. The resulting solution was stirred at 0 $^\circ\text{C}$ for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to afford compound **12** (407 mg, 85%): colorless oil, $R_f = 0.30$ (hexane/EtOAc, 3:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 2.03 (s, 3H), 3.86-3.89 (m, 1H), 3.95 (dd, $J = 8.8, 3.2$ Hz, 1H), 3.98-4.02 (m, 1H), 4.03 (q, $J = 9.6$ Hz, 1H), 4.29 (dd, $J = 12.0, 4.4$ Hz, 1H), 4.38 (dd, $J = 12.0, 2.0$ Hz, 1H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.61 (d, $J = 10.4$ Hz, 1H), 4.64 (d, $J = 11.8$ Hz, 1H), 4.77 (s, 2H), 4.95 (d, $J = 10.8$ Hz, 1H), 6.33 (d, $J = 2.0$ Hz, 1H), 7.24-7.45 (m, 15H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 63.2, 72.4, 72.8, 73.0, 73.5, 73.9, 75.5, 79.0, 95.9, 128.0, 128.1, 128.2, 128.48, 128.52, 128.6, 128.7, 138.0, 160.5, 171.0. HRMS Calcd for $\text{C}_{31}\text{H}_{32}\text{Cl}_3\text{NO}_7\text{Na}$ $[\text{M} + \text{Na}]^+$, 658.1142; found, 658.1144.

Allyl 2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl-D-mannopyranoside (S12). To a solution of allyl 2,4,6-tri-*O*-benzyl-D-mannopyranoside⁵ (870 mg, 1.77 mmol) in CH₂Cl₂ (10 mL) were added BnSO₂Cl (676 mg, 3.55 mmol), pyridine (0.57 mL, 7.09 mmol), and DMAP (43.3 mg, 0.355 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH₄Cl, and then extracted with CH₂Cl₂. The combined organic layer was washed with 1N HCl and brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 4:1) to afford compound **S12** (1.03 g, 90%): colorless oil, *R*_f = 0.38 (hexane/EtOAc, 3:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.66-3.71 (m, 1H), 3.75-3.82 (m, 2H), 3.89 (dd, *J* = 3.2, 2.0 Hz, 1H), 3.90-3.96 (m, 1H), 4.05-4.15 (m, 3H), 4.24 (d, *J* = 14.0 Hz, 1H), 4.42 (d, *J* = 10.8 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.59-4.65 (m, 3H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.85 (d, *J* = 2.0 Hz, 1H), 5.00 (dd, *J* = 9.6, 3.2 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.17-5.24 (m, 1H), 5.75-5.87 (m, 1H), 7.16-7.21 (m, 2H), 7.25-7.40 (m, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 57.1, 68.2, 68.8, 71.9, 73.3, 73.5, 73.6, 75.0, 77.0, 81.2, 97.0, 117.8, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.48, 128.53, 128.9, 129.1, 130.8, 133.5, 137.8, 138.0, 138.2. HRMS Calcd for C₃₇H₄₀O₈SNa [M + Na]⁺, 667.2342; found, 667.2346.

Allyl 2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)-D-mannopyranoside (S13). To a

solution of allyl 2,4,6-tri-*O*-benzyl-D-mannopyranoside⁵ (1.17 g, 2.38 mmol) in CH₂Cl₂ (10 mL) were added *p*-NO₂BzCl (885 mg, 4.77 mmol), pyridine (0.77 mL, 9.54 mmol), and DMAP (58.3 mg, 0.477 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH₄Cl, and then extracted with CH₂Cl₂. The combined organic layer was washed with 1N HCl and brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 6:1) to afford compound **S13** (1.39 g, 91%): colorless oil, *R*_f = 0.40 (hexane/EtOAc, 5:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.75 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.86 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.89-3.93 (m, 1H), 4.00 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.01-4.06 (m, 1H), 4.19-4.25 (m, 1H), 4.25 (t, *J* = 9.6 Hz, 1H), 4.50 (d, *J* = 12.4 Hz, 1H), 4.53 (d, *J* = 11.2 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 11.2 Hz, 1H), 4.69 (d, *J* = 12.4 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 5.00 (d, *J* = 1.2 Hz, 1H), 5.17-5.21 (m, 1H), 5.26-5.32 (m, 1H), 5.52 (dd, *J* = 9.2, 3.2 Hz, 1H), 5.84-5.95 (m, 1H), 7.00-7.40 (m, 15H), 8.04-8.10 (m, 2H), 8.20-8.26 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 68.2, 68.9, 71.8, 73.0, 73.69, 73.72, 74.9, 75.4, 76.1, 96.9, 117.7, 123.6, 127.8, 127.87, 127.91, 128.0, 128.1, 128.4, 128.46, 128.49, 128.55, 128.60, 130.9, 133.7, 135.5, 137.8, 138.0, 138.3, 150.7, 163.9. HRMS Calcd for C₃₇H₃₇NO₉Na [M + Na]⁺, 667.2366; found, 667.2362.

Allyl 2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl-D-mannopyranoside (S14). To a solution of allyl 2,4,6-tri-*O*-benzyl-D-mannopyranoside⁵ (640 mg, 1.30 mmol) in CH₂Cl₂ (10 mL) were added BzCl (0.303 mL, 2.61 mmol), pyridine (0.422 mL, 5.22 mmol), and DMAP (31.9 mg, 0.261 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NH₄Cl, and then extracted with CH₂Cl₂. The combined organic layer was

washed with 1N HCl and brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 9:1) to afford compound **S14** (675 mg, 93%): colorless oil, $R_f = 0.30$ (hexane/EtOAc, 9:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.73 (dd, $J = 10.4, 2.0$ Hz, 1H), 3.83 (dd, $J = 11.2, 4.8$ Hz, 1H), 3.89-3.94 (m, 1H), 3.97-4.04 (m, 1H), 4.01 (dd, $J = 3.6, 2.0$ Hz, 1H), 4.18-4.24 (m, 1H), 4.22 (t, $J = 10.0$ Hz, 1H), 4.50 (d, $J = 10.8$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 4.59 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 4.67 (d, $J = 10.8$ Hz, 1H), 4.72 (d, $J = 12.0$ Hz, 1H), 4.97 (d, $J = 1.6$ Hz, 1H), 5.14-5.19 (m, 1H), 5.24-5.30 (m, 1H), 5.55 (dd, $J = 9.6, 3.2$ Hz, 1H), 5.82-5.94 (m, 1H), 7.02-7.07 (m, 2H), 7.13-7.19 (m, 5H), 7.24-7.48 (m, 10H), 7.54-7.61 (m, 1H), 8.01-8.09 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 68.2, 69.1, 71.8, 73.1, 73.6, 73.7, 74.7, 75.0, 76.3, 97.2, 117.5, 127.7, 127.76, 127.83, 128.0, 128.39, 128.41, 128.5, 128.6, 129.9, 130.3, 133.2, 133.8, 138.04, 138.05, 138.4, 165.8. HRMS Calcd for C₃₇H₃₈O₇Na [M + Na]⁺, 617.2515; found, 617.2519.

2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl-D-mannopyranose (S15). A mixture of compound **S12** (1.05 g, 1.63 mmol) and PdCl₂ (57.7 mg, 0.326 mmol) in MeOH (15 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to afford compound **S15** (835 mg, 85%, $\alpha/\beta = 1:1$): colorless oil, $R_f = 0.25$ (hexane/EtOAc, 2:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.04 (d, $J = 3.2$ Hz, 1H), 3.24 (d, $J = 3.2$ Hz, 1H), 3.60-3.70 (m, 2H), 3.78 (t, $J = 2.4$ Hz, 1H), 3.87 (t, $J = 9.2$ Hz, 1H), 3.89 (t, $J = 2.4$ Hz, 1H), 3.94 (d, $J = 9.2$ Hz, 1H), 3.95-4.00 (m, 1H), 3.96 (t, $J = 9.2$ Hz, 1H), 4.01-4.06 (m, 1H), 4.11 (d, $J = 13.6$ Hz, 1H), 4.24 (d, $J = 13.6$ Hz, 1H), 4.30 (d, $J = 14.0$ Hz, 1H), 4.33-4.38 (m, 1H), 4.41 (d, $J = 11.2$ Hz, 1H), 4.42 (d, $J = 14.0$ Hz, 1H), 4.46 (d, $J = 11.2$ Hz, 1H), 4.49 (d, $J = 12.0$ Hz, 1H),

4.59 (d, $J = 12.0$ Hz, 1H), 4.61-4.65 (m, 5H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.84 (d, $J = 10.8$ Hz, 1H), 5.04 (dd, $J = 8.8, 3.2$ Hz, 1H), 5.16 (dd, $J = 3.2, 2.0$ Hz, 1H), 5.20 (dd, $J = 4.0, 2.0$ Hz, 1H), 7.16-7.38 (m, 40H); ^{13}C NMR (100 MHz, CDCl_3) δ 57.0, 57.1, 69.2, 69.6, 70.5, 71.7, 72.3, 73.2, 73.3, 73.6, 73.8, 74.2, 75.0, 75.17, 75.22, 77.3, 79.6, 80.8, 92.7, 92.9, 127.8, 127.87, 127.88, 127.94, 127.98, 128.00, 128.05, 128.13, 128.2, 128.25, 128.28, 128.4, 128.5, 128.6, 128.7, 128.8, 128.91, 128.93, 129.0, 129.1, 129.2, 130.8, 131.0, 137.7, 137.9, 138.0, 138.1, 138.2, 138.4. HRMS Calcd for $\text{C}_{34}\text{H}_{36}\text{O}_8\text{SNa}$ $[\text{M} + \text{Na}]^+$, 627.2029; found, 627.2025.

2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)-*D*-mannopyranose (S16). A mixture of compound **S13** (870 mg, 1.36 mmol) and PdCl_2 (48.2 mg, 0.272 mmol) in MeOH (10 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to afford compound **S16** (695 mg, 85%, $\alpha/\beta = 1:0.5$): colorless oil, $R_f = 0.33$ (hexane/EtOAc, 2:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.15 (d, $J = 3.6$ Hz, 0.5H), 3.40 (d, $J = 3.2$ Hz, 1H), 3.71-3.79 (m, 2H), 3.84 (t, $J = 2.0$ Hz, 0.5H), 3.98 (dd, $J = 3.2, 2.0$ Hz, 1H), 4.05-4.16 (m, 3H), 4.45-4.72 (m, 8H), 4.78 (d, $J = 12.0$ Hz, 0.5H), 4.96 (d, $J = 10.8$ Hz, 0.5H), 5.29 (dd, $J = 3.6, 2.0$ Hz, 0.5H), 5.33 (dd, $J = 3.2, 2.0$ Hz, 1H), 5.55 (dd, $J = 9.2, 3.2$ Hz, 1H), 7.03-7.41 (m, 22.5H), 8.01-8.10 (m, 4H), 8.21-8.28 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 64.6, 69.3, 70.4, 71.6, 72.3, 73.1, 73.2, 73.7, 73.9, 74.0, 74.86, 74.92, 75.2, 75.4, 76.3, 79.8, 92.6, 92.8, 123.57, 123.62, 127.8, 127.92, 127.94, 128.0, 128.2, 128.3, 128.4, 128.45, 128.47, 128.6, 128.7, 128.8, 130.89, 130.93, 135.4, 135.5, 137.79, 137.82, 138.0, 138.1, 138.37, 138.40, 150.6, 150.7, 163.9, 164.7. HRMS Calcd for $\text{C}_{34}\text{H}_{33}\text{NO}_9\text{Na}$ $[\text{M} + \text{Na}]^+$, 622.2053; found, 622.2051.

2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl-D-mannopyranose (S17). A mixture of compound **S14** (740 mg, 1.24 mmol) and PdCl₂ (44.1 mg, 0.249 mmol) in MeOH (10 mL) was stirred at room temperature for 10 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to afford compound **S17** (612 mg, 89%, $\alpha/\beta = 1:0.35$): colorless oil, $R_f = 0.20$ (hexane/EtOAc, 2:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.36 (d, $J = 3.2$ Hz, 1H), 3.69 (d, $J = 2.4$ Hz, 0.35H), 3.72 (d, $J = 2.0$ Hz, 1H), 3.73 (d, $J = 5.2$ Hz, 1H), 3.77 (d, $J = 2.4$ Hz, 0.35H), 3.78 (d, $J = 5.6$ Hz, 0.35H), 4.00 (dd, $J = 3.2, 2.4$ Hz, 1H), 4.05 (dd, $J = 2.0, 1.2$ Hz, 0.35H), 4.11 (t, $J = 10.0$ Hz, 1H), 4.18 (t, $J = 9.6$ Hz, 0.35H), 4.49 (d, $J = 11.2$ Hz, 1H), 4.52-4.65 (m, 3.35H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.64 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 11.2$ Hz, 1H), 4.70 (d, $J = 12.4$ Hz, 0.35H), 4.85 (d, $J = 11.6$ Hz, 0.35H), 5.27 (dd, $J = 10.0, 3.2$ Hz, 0.35H), 5.31 (t, $J = 2.0$ Hz, 1H), 5.60 (d, $J = 3.2, 8.8$ Hz, 1H), 7.01-7.38 (m, 20.25H), 7.40-7.48 (m, 2.7H), 7.54-7.61 (m, 1.35H), 8.00-8.08 (m, 2.7H), 8.00-8.05 (m, 2H), 8.61 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 68.9, 69.4, 71.4, 73.0, 73.1, 73.6, 73.8, 74.0, 74.3, 74.9, 75.1, 75.3, 75.5, 76.5, 77.0, 77.3, 92.8, 93.9, 127.76, 127.78, 127.81, 128.0, 128.17, 128.21, 128.39, 128.44, 128.5, 128.6, 128.65, 128.71, 130.0, 130.2, 133.2, 133.5, 137.7, 137.8, 137.9, 138.0, 138.05, 138.14, 165.75, 165.81. Anal. Calcd for C₃₄H₃₄O₇: C, 73.63; H, 6.18. Found: C, 73.66; H, 6.23.

2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl-D-mannopyranosyl Trichloroacetimidate (13). To a solution of **S15** (911 mg, 1.78 mmol) in CH₂Cl₂ (10 mL) were added Cl₃CCN (1.78 mL, 17.8 mmol) and DBU (26.8 μ L, 0.178 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **13** (893 mg, 79%): colorless oil, $R_f = 0.23$ (hexane/EtOAc, 5:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ

3.70 (dd, $J = 11.2, 2.0$ Hz, 1H), 3.82 (dd, $J = 11.2, 4.0$ Hz, 1H), 3.96-4.01 (m, 1H), 4.05 (dd, $J = 3.2, 2.4$ Hz, 1H), 4.14 (d, $J = 14.0$ Hz, 1H), 4.22 (t, $J = 9.6$ Hz, 1H), 4.24 (d, $J = 14.0$ Hz, 1H), 4.48 (d, $J = 10.4$ Hz, 1H), 4.51 (d, $J = 11.6$ Hz, 1H), 4.66 (d, $J = 10.8$ Hz, 1H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.73 (d, $J = 12.0$ Hz, 1H), 4.98 (dd, $J = 9.2, 3.2$ Hz, 1H), 6.32 (d, $J = 2.0$ Hz, 1H), 7.19-7.42 (m, 20H), 8.59 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 57.3, 68.5, 72.9, 73.4, 73.7, 74.9, 75.2, 75.4, 80.0, 95.9, 127.6, 127.8, 128.0, 128.06, 128.09, 128.13, 128.4, 128.5, 128.58, 128.60, 129.0, 129.1, 130.8, 137.60, 137.62, 138.2, 160.4. HRMS Calcd for $\text{C}_{36}\text{H}_{36}\text{Cl}_3\text{NO}_8\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 770.1125; found, 770.1127.

2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)-*D*-mannopyranosyl Trichloroacetimidate (14). To a solution of **S16** (633 mg, 1.06 mmol) in CH_2Cl_2 (6 mL) were added Cl_3CCN (1.06 mL, 10.6 mmol) and DBU (16.1 μL , 0.106 mmol) at 0 $^\circ\text{C}$. The resulting solution was stirred at 0 $^\circ\text{C}$ for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **14** (631 mg, 80%): colorless oil, $R_f = 0.35$ (hexane/EtOAc, 5:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.78 (dd, $J = 11.2, 1.2$ Hz, 1H), 3.90 (dd, $J = 11.2, 3.6$ Hz, 1H), 3.93 (d, $J = 2.4$ Hz, 1H), 4.05 (dd, $J = 9.2, 2.8$ Hz, 1H), 4.09 (dd, $J = 3.2, 2.4$ Hz, 1H), 4.09-4.14 (m, 1H), 4.20 (t, $J = 9.6$ Hz, 1H), 4.23 (dd, $J = 3.2, 2.4$ Hz, 1H), 4.40 (t, $J = 9.6$ Hz, 1H), 4.50 (dd, $J = 12.0, 3.6$ Hz, 1H), 4.52-4.58 (m, 3H), 4.59 (d, $J = 11.2$ Hz, 1H), 4.64 (d, $J = 11.2$ Hz, 1H), 4.65 (d, $J = 10.8$ Hz, 1H), 4.68-4.82 (m, 6H), 4.95 (d, $J = 10.8$ Hz, 1H), 5.51 (dd, $J = 9.6, 3.2$ Hz, 1H), 6.36 (d, $J = 1.6$ Hz, 1H), 6.46 (d, $J = 2.0$ Hz, 1H), 7.05-7.43 (m, 30H), 8.00-8.08 (m, 6H), 8.21-8.27 (m, 2H), 8.60 (s, 1H), 8.65 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 63.9, 68.5, 72.6, 72.8, 73.3, 73.8, 73.97, 74.03, 74.66, 74.69, 75.0, 75.4, 79.2, 95.7, 95.9, 123.55, 123.62, 127.8, 127.98, 128.04, 128.10, 128.13, 128.2, 128.5,

128.6, 128.7, 130.9, 135.2, 135.4, 137.4, 137.7, 137.8, 137.9, 138.2, 150.6, 150.7, 160.5, 160.7, 163.9, 164.4. HRMS Calcd for $C_{36}H_{33}Cl_3N_2O_9Na$ $[M + Na]^+$, 765.1149; found, 765.1146.

2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl-D-mannopyranosyl Trichloroacetimidate (15). To a solution of **S17** (580 mg, 1.05 mmol) in CH_2Cl_2 (6 mL) were added Cl_3CCN (1.05 mL, 10.5 mmol) and DBU (15.8 μ L, 0.105 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **15** (607 mg, 83%): colorless oil, R_f = 0.60 (hexane/EtOAc, 3:1, v/v); 1H NMR (400 MHz, $CDCl_3$) δ 3.76 (dd, J = 11.2, 1.6 Hz, 1H), 3.88 (dd, J = 11.6, 4.0 Hz, 1H), 4.09-4.15 (m, 1H), 4.24 (dd, J = 3.2, 2.0 Hz, 1H), 4.38 (t, J = 9.6 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 10.8 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.728 (d, J = 12.0 Hz, 1H), 4.730 (d, J = 10.8 Hz, 1H), 4.76 (d, J = 12.0 Hz, 1H), 5.55 (dd, J = 9.4, 3.6 Hz, 1H), 6.44 (d, J = 2.0 Hz, 1H), 7.06-7.18 (m, 7H), 7.26-7.39 (m, 8H), 7.42-7.47 (m, 2H), 7.55-7.62 (m, 1H), 8.00-8.05 (m, 2H), 8.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.7, 72.9, 73.1, 73.7, 74.0, 74.2, 74.6, 75.1, 96.1, 127.7, 127.90, 127.93, 128.1, 128.2, 128.4, 128.5, 128.6, 129.90, 129.94, 133.4, 137.6, 137.8, 138.3, 160.7, 165.8. HRMS Calcd for $C_{36}H_{34}Cl_3NO_7Na$ $[M + Na]^+$, 720.1299; found, 720.1296.

2,4,6-Tri-*O*-benzyl-3-*O*-acetyl-D-mannopyranosyl Trichloroacetimidate (16). To a solution of 2,4,6-tri-*O*-benzyl-3-*O*-acetyl-D-mannopyranose⁶ (451 mg, 0.916 mmol) in CH_2Cl_2 (5 mL) were added Cl_3CCN (0.918 mL, 9.16 mmol) and DBU (14.0 μ L, 0.0916 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then concentrated in vacuo. The residue was purified by flash column chromatography

(hexane/EtOAc, 5:1) to afford compound **16** (485 mg, 83%): colorless oil, $R_f = 0.50$ (hexane/EtOAc, 3:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 1.94 (s, 3H), 3.72 (dd, $J = 11.2, 2.0$ Hz, 1H), 3.83 (dd, $J = 11.2, 4.0$ Hz, 1H), 4.01-4.06 (m, 1H), 4.10 (dd, $J = 4.8, 2.8$ Hz, 1H), 4.19 (t, $J = 9.6$ Hz, 1H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.55 (d, $J = 10.0$ Hz, 1H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.67 (d, $J = 10.0$ Hz, 1H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.76 (d, $J = 12.0$ Hz, 1H), 5.26 (dd, $J = 9.2, 3.2$ Hz, 1H), 6.38 (d, $J = 2.0$ Hz, 1H), 7.15-7.20 (m, 2H), 7.25-7.38 (m, 13H), 8.59 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 68.6, 72.9, 73.0, 73.3, 73.6, 74.2, 74.6, 74.9, 96.0, 128.0, 128.2, 128.26, 128.33, 128.4, 128.5, 128.7, 137.7, 138.1, 138.3, 160.7, 170.3. HRMS Calcd for $\text{C}_{31}\text{H}_{32}\text{Cl}_3\text{NO}_7\text{Na}$ [$\text{M} + \text{Na}$] $^+$, 658.1142; found, 658.1145.

Phenyl 2,4,6-Tri-*O*-benzyl-3-*O*-acetyl-1-thio-D-mannopyranoside (S18). To a solution of 1,3-di-*O*-acetyl-2,4,6-tri-*O*-benzyl-D-mannopyranose⁶ (350 mg, 0.655 mmol) in CH_2Cl_2 (6 mL) were added PhSH (80.3 μL , 0.786 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.10 mL, 0.786 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 10 min and at room temperature for further 2 h. The reaction mixture was quenched with saturated aqueous NaHCO_3 , and then extracted with CH_2Cl_2 . The combined organic layer was washed with 1% NaOH and brine, dried over MgSO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to afford compound **S18** (332 mg, 87%): colorless oil, $R_f = 0.60$ (hexane/EtOAc, 4:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 1.96 (s, 3H), 3.71 (dd, $J = 11.2, 2.0$ Hz, 1H), 3.84 (dd, $J =$

11.2, 4.8 Hz, 1H), 4.11 (dd, $J = 3.2, 2.4$ Hz, 1H), 4.12 (t, $J = 9.6$ Hz, 1H), 4.30-4.36 (m, 1H), 4.47 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 12.0$ Hz, 1H), 4.53 (d, $J = 11.2$ Hz, 1H), 4.66 (d, $J = 11.2$ Hz, 1H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.69 (d, $J = 12.0$ Hz, 1H), 5.20 (dd, $J = 9.6, 3.2$ Hz, 1H), 5.60 (d, $J = 1.6$ Hz, 1H), 7.16-7.35 (m, 18H), 7.45-7.50 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 69.0, 72.4, 72.6, 73.5, 73.7, 73.9, 74.8, 77.2, 85.5, 127.5, 127.7, 127.76, 127.81, 127.96, 127.98, 128.4, 128.49, 128.53, 129.1, 131.8, 134.3, 137.7, 138.29, 138.32, 170.2. Anal. Calcd for $\text{C}_{35}\text{H}_{36}\text{O}_6\text{S}$: C, 71.89; H, 6.21; S, 5.48. Found: C, 71.79; H, 6.21, S, 5.69.

Phenyl 2,4,6-Tri-*O*-benzyl-1-thio-D-mannopyranoside (S19). A mixture of compound **S18** (332 mg, 0.568 mmol) and NaOMe (6.13 mg, 0.114 mmol) in MeOH (5 mL) was stirred at room temperature for 1 h. The reaction mixture was neutralized with DOWEX CCR-3 (H^+ mode) resin, filtered through Celite®, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 5:1) to afford compound **S19** (295 mg, 96%): colorless oil, $R_f = 0.50$ (hexane/EtOAc, 3:1, v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.74 (dd, $J = 10.8, 1.6$ Hz, 1H), 3.80 (t, $J = 9.2$ Hz, 1H), 3.84 (dd, $J = 11.2, 5.2$ Hz, 1H), 3.95-4.03 (m, 1H), 4.01 (dd, $J = 3.6, 1.6$ Hz, 1H), 4.26-4.32 (m, 1H), 4.49 (d, $J = 12.0$ Hz, 1H), 4.52 (d, $J = 11.6$ Hz, 1H), 4.55 (d, $J = 11.2$ Hz, 1H), 4.65 (d, $J = 12.0$ Hz, 1H), 4.77 (d, $J = 11.6$ Hz, 1H), 4.87 (d, $J = 11.2$ Hz, 1H), 5.68 (d, $J = 1.2$ Hz, 1H), 7.23-7.36 (m, 18H), 7.45-7.50 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 69.3, 72.2, 72.3, 72.5, 73.5, 75.1, 77.0, 79.9, 85.1, 127.62, 127.64, 127.85, 127.90, 128.07, 128.13, 128.2, 128.4, 128.5, 128.7, 129.2, 131.9, 134.3, 137.5, 138.4, 138.5. Anal. Calcd for $\text{C}_{33}\text{H}_{34}\text{O}_5\text{S}$: C, 73.04; H, 6.31; S, 5.91. Found: C, 73.05; H, 6.38, S, 6.00.

Phenyl 2,4,6-Tri-*O*-benzyl-3-*O*-trichloroacetimidoyl-1-thio-D-mannopyranoside

(**67**). To a solution of **S19** (156 mg, 0.287 mmol) in CH₂Cl₂ (5 mL) were added Cl₃CCN (57.6 μL, 0.575 mmol) and DBU (52.7 μL, 0.345 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 1 h, and then concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 7:1) to afford compound **67** (180 mg, 91%): colorless oil, *R*_f = 0.50 (hexane/EtOAc, 5:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.74 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.87 (dd, *J* = 11.0, 4.8 Hz, 1H), 4.28 (t, *J* = 9.6 Hz, 1H), 4.40 (dd, *J* = 9.2, 3.6 Hz, 1H), 4.45-4.56 (m, 3H), 4.60-4.70 (m, 3H), 4.92 (d, *J* = 10.8 Hz, 1H), 5.36 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 1H), 7.17-7.50 (m, 20H), 8.49 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 69.1, 72.7, 72.8, 73.4, 73.5, 75.0, 76.2, 79.8, 85.7, 127.8, 127.9, 128.0, 128.4, 128.47, 128.50, 129.2, 131.9, 134.3, 137.8, 138.2, 138.4, 162.0. HRMS Calcd for C₃₅H₃₄Cl₃NO₅SNa [M + Na]⁺, 708.1121; found, 708.1124.

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)-α/β-D-mannopyranosyl]-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (23**)**

Colorless oil, α:β = 1:15.5, *R*_f = 0.25 (hexane/CH₂Cl₂/EtOAc, 4:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.29 (s, 3H), 3.35 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.41 (d, *J* = 9.2 Hz, 1H), 3.43-3.49 (m, 2H), 3.56 (t, *J* = 6.4 Hz, 1H), 3.52 (d, *J* = 2.4 Hz, 1H), 3.70 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.73-3.79 (m, 1H), 3.85 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.96 (d, *J* = 12.4 Hz, 1H), 3.08 (q, *J* = 9.2 Hz, 1H), 4.08-4.14 (m, 2H), 4.18 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.52-4.55 (m, 3H), 4.55 (d, *J* = 7.2 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H),

4.73-4.85 (m, 4H), 4.97-5.05 (m, 2H), 6.90-6.94 (m, 2H), 7.11-7.41 (m, 30H), 7.56-7.61 (m, 1H), 8.04-8.10 (m, 1H); ^{13}C NMR(100MHz, CDCl_3) δ 55.1, 68.5, 69.6, 69.8, 70.8, 72.6, 73.4, 73.69, 73.73, 74.0, 74.4, 74.8, 75.8, 77.7, 78.67, 78.71, 80.0, 82.2, 97.9, 101.3, 121.2, 123.9, 127.3, 127.55, 127.62, 127.75, 127.79, 127.9, 128.0, 128.07, 128.14, 128.23, 128.26, 128.27, 128.4, 128.48, 128.52, 128.6, 131.8, 131.9, 133.2, 135.9, 137.3, 138.2, 138.4, 138.5, 138.9. Anal. Calcd for $\text{C}_{62}\text{H}_{63}\text{F}_3\text{O}_{13}\text{S}$: C, 67.38; H, 5.75; S, 2.90. Found: C, 67.29; H, 5.81; S, 2.90.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (24 α)

Colorless oil, R_f = 0.23 (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_D^{20}$ = 42.2 (c 0.5, CHCl_3); ^1H NMR (400 M Hz, CDCl_3) δ 3.33 (s, 3H), 3.38 (t, J = 9.4 Hz, 1H), 3.47 (dd, J = 9.6, 3.6 Hz, 1H), 3.58-3.67 (m, 3H), 3.71 (dd, J = 10.0, 3.2 Hz, 1H), 3.81-3.86 (m, 3H), 3.91 (dd, J = 9.6, 3.2 Hz, 1H), 3.99 (t, J = 9.2 Hz, 1 H), 4.16 (d, J = 14.0 Hz, 1H), 4.33 (d, J = 14.0 Hz, 1H), 4.44-4.58 (m, 4H), 4.57(s, 1H), 4.59 (d, J = 10.0 Hz, 1H), 4.64 (s, 2H), 4.69 (d, J = 12.4 Hz, 1H), 4.79 (d, J = 12.0 Hz, 1H), 4.82 (d, J = 10.4 Hz, 1H), 4.91 (d, J = 11.2 Hz, 1H), 4.97 (d, J = 1.2 Hz, 1H), 5.01 (d, J = 10.4 Hz, 1H), 5.11 (t, J = 9.6 Hz, 1H), 7.12-7.41 (m, 35 H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.3, 57.4, 66.3, 68.84, 68.85, 70.4, 71.4, 72.6, 73.4, 73.5, 76.0, 76.8, 77.1, 77.7, 80.1, 82.2, 97.8, 98.0, 127.5, 127.7, 127.83, 127.85, 127.90, 127.93, 128.0, 128.08, 128.14, 128.19, 128.2, 128.3, 128.5, 128.6, 128.66, 128.72, 128.8, 128.9, 130.8, 137.3, 138.0, 138.16, 138.19,

138.4, 138.7. Anal. Calcd for C₆₂H₆₆O₁₃S: C, 70.84; H, 6.33; S, 3.05. Found: C, 70.96; H, 6.26; S, 2.85.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (24 β)

Colorless oil, $R_f = 0.15$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 18.4$ (c 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.33 (s, 3 H), 3.43 (t, $J = 9.6$ Hz, 1H), 3.47-3.58 (m, 4H), 3.70 (dd, $J = 10.8, 6.4$ Hz, 1H), 3.77-3.82 (m, 2H), 3.85 (dd, $J = 11.2, 2.4$ Hz, 1H), 4.02 (t, $J = 9.2$ Hz, 1H), 4.13 (d, $J = 13.6$ Hz, 1H), 4.15 (dd, $J = 8.8, 2.8$ Hz, 1H), 4.18 (s, 1H), 4.33 (d, $J = 10.4$ Hz, 1H), 4.35 (d, $J = 7.6$ Hz, 1H), 4.48 (d, $J = 11.6$ Hz, 1H), 4.51-4.60 (m, 4H), 4.65 (d, $J = 12.4$ Hz, 1H), 4.71 (d, $J = 12.4$ Hz, 1H), 4.78 (d, $J = 12.4$ Hz, 1H), 4.80-4.85 (m, 2H), 4.93 (d, $J = 12.4$ Hz, 1H), 4.94 (q, $J = 6.8$ Hz, 1H), 5.01 (d, $J = 10.8$ Hz, 1H), 7.18-7.38 (m, 35H); ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 57.6, 68.6, 69.8, 71.3, 73.2, 73.5, 73.8, 74.0, 74.6, 74.8, 75.9, 77.5, 77.7, 79.3, 80.0, 82.2, 98.0, 101.4, 127.6, 127.77, 127.81, 127.89, 127.92, 128.0, 128.1, 128.2, 128.3, 128.36, 128.40, 128.52, 128.54, 128.6, 128.7, 128.8, 128.9, 130.7, 137.1, 138.2, 138.31, 138.34, 138.5, 138.9. HRMS Calcd for C₆₂H₆₆O₁₃SNa $[M + Na]^+$, 1073.4116; found, 1073.4113.

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α/β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (25)

Colorless oil, $\alpha:\beta = 1:7.2$, $R_f = 0.24$ (hexane/ CH_2Cl_2 /EtOAc, 4:1:1, v/v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.34 (s, 0.4H), 3.35 (s, 2.8H), 3.45-3.56 (m, 5.1H), 3.59 (dd, $J = 9.6$, 4.4 Hz, 1H), 3.68 (d, $J = 10.8$, 4.8 Hz, 1H), 3.72 (dd, $J = 10.4$, 4.8 Hz, 1H), 3.78-3.85 (m, 2.2H), 4.04 (t, $J = 9.2$ Hz, 1H), 4.17 (dd, $J = 9.2$, 1.2 Hz, 1H), 4.22 (d, $J = 12.0$ Hz, 1H), 4.23 (d, $J = 8.4$ Hz, 1H), 4.37 (d, $J = 11.6$ Hz, 1H), 4.44 (d, $J = 12.4$ Hz, 1H), 4.47 (d, $J = 11.6$ Hz, 1H), 4.53 (d, $J = 11.6$ Hz, 1H), 4.61 (d, $J = 3.6$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.73 (d, $J = 10.4$ Hz, 0.2H), 4.78-4.87 (m, 4.9H), 4.93 (d, $J = 12.4$ Hz, 1H), 5.01 (d, $J = 8.0$ Hz, 0.2H), 5.03 (d, $J = 10.2$ Hz, 1H), 5.58 (t, $J = 9.6$ Hz, 1H, β -H4), 5.68 (t, $J = 10.4$ Hz, 0.2H, α -H4), 7.03-7.45 (m, 34H), 7.82-7.86 (m, 0.3H), 7.92-8.02 (m, 2.2H), 8.10-8.13 (m, 0.3H), 8.13-8.20 (m, 2.1H); ^{13}C NMR(100MHz, CDCl_3) δ 55.2, 55.3, 66.2, 68.4, 69.7, 70.0, 70.3, 70.5, 70.9, 71.1, 71.2, 71.3, 72.8, 72.9, 73.3, 73.4, 73.5, 73.7, 73.86, 73.89, 74.8, 75.0, 75.78, 75.84, 76.0, 77.5, 77.6, 78.6, 79.9, 80.1, 82.20, 82.21, 97.9, 98.0, 98.7 (C1, α -anomer), 101.4 (C1, β -anomer), 123.3, 123.4, 127.4, 127.5, 127.6, 127.66, 127.69, 127.82, 127.86, 128.00, 128.04, 128.1, 128.17, 128.2, 128.25, 128.32, 128.38, 128.42, 128.45, 128.48, 128.55, 128.59, 130.8, 135.4, 137.55, 137.56, 137.8, 137.9, 138.11, 138.13, 138.14, 138.2, 138.4, 138.5, 138.7, 138.9, 150.47, 150.5, 163.7, 163.9. Anal. Calcd for $\text{C}_{62}\text{H}_{63}\text{NO}_{14}$: C, 71.18; H, 6.07; N, 1.34. Found: C, 71.17; H, 6.04; N, 1.24.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (26)

Colorless oil, $\alpha:\beta=1:7.1$, $R_f=0.23$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.32 (s, 0.4H), 3.35 (s, 3H), 3.45-3.56 (m, 4.6H), 3.57-3.77 (m, 5.7H), 3.78-3.87 (m, 1.1H), 3.99 (t, $J = 9.2$ Hz, 0.1H), 4.04 (t, $J = 9.2$ Hz, 1H), 4.17 (dd, $J = 10.4, 1.6$ Hz, 1H), 4.20 (s, 1H), 4.29 (d, $J = 12.8$ Hz, 1H), 4.40-4.73 (m, 6.1H), 4.76-4.87 (m, 4.7H), 4.93 (d, $J = 12.4$ Hz, 1H), 5.03 (d, $J = 11.2$ Hz, 1H), 5.32 (d, $J = 2.0$ Hz, 0.1H), 5.54 (t, $J = 9.6$ Hz, 1H), 7.10-7.43 (m, 36.5H), 7.52-7.60 (m, 1.1H), 7.82-7.87 (m, 0.3H), 7.94-7.99 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.1, 66.0, 68.2, 69.2, 69.3, 69.7, 69.8, 70.5, 71.2, 71.3, 71.6, 71.9, 72.6, 72.8, 73.0, 73.25, 73.34, 73.6, 73.7, 74.2, 74.65, 74.69, 75.0, 75.7, 75.9, 76.1, 76.4, 77.5, 78.8, 79.8, 80.0, 82.1, 82.2, 97.8 (β -OMe), 97.9 (α -OMe), 98.6 (C1, α -anomer), 101.2 (C1, β -anomer), 127.3, 127.4, 127.5, 127.58, 127.64, 127.7, 127.8, 127.9, 127.95, 127.97, 128.01, 128.06, 128.11, 128.19, 128.23, 128.28, 128.31, 128.36, 128.40, 128.5, 129.8, 129.9, 133.1, 133.2, 137.6, 137.9, 138.0, 138.1, 138.2, 138.3, 138.37, 138.43, 138.7, 138.9, 165.6. Anal. Calcd for C₆₂H₆₄O₁₂: C, 74.38; H, 6.44. Found: C, 74.31; H, 6.74.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (27)

Colorless oil, $\alpha:\beta=1:4.0$, $R_f=0.35$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 1.92 (s, 3.7H), 3.31 (s, 0.7H), 3.34 (s, 2.8H), 3.34-3.37 (m, 0.7H), 3.41-3.50 (m, 3.3H), 3.53 (dd, $J=9.6, 3.6$ Hz, 1.3H), 3.58 (dd, $J=10.8, 3.6$ Hz, 1.1H), 3.62-3.70 (m, 2.4H), 3.76-3.81 (m, 1.4H), 4.02 (t, $J=8.8$ Hz, 1H), 4.11 (s, 1H), 4.12 (dd, $J=11.6, 1.6$ Hz, 1H), 4.34 (d, $J=12.0$ Hz, 1H), 4.45-4.53 (m, 4H), 4.55 (d, $J=6.8$ Hz, 1H), 4.58-4.61 (m, 1H), 4.64 (d, $J=3.2$ Hz, 1H), 4.65 (d, $J=12.0$ Hz, 1H), 4.74-4.81 (m, 3H), 4.84 (d, $J=8.8$ Hz, 1H), 4.89 (d, $J=8.8$ Hz, 1H), 4.97 (d, $J=11.4$ Hz, 0.2H), 5.03 (d, $J=11.2$ Hz, 1H), 5.25 (t, $J=10.0$ Hz, 1H), 5.37 (t, $J=9.6$ Hz, 0.3H), 7.10-7.53 (m, 38H); ¹³C NMR (100 MHz, CDCl₃) δ 21.0, 21.1, 55.2, 68.2, 68.9, 69.4, 69.7, 69.8, 70.5, 70.6, 71.5, 71.6, 71.9, 72.6, 72.8, 73.1, 73.37, 73.43, 73.7, 73.8, 74.4, 74.8, 75.0, 75.8, 75.9, 76.4, 76.5, 76.9, 77.5, 77.7, 79.2, 79.9, 80.1, 82.2, 97.86 (β -OMe), 97.93 (α -OMe), 98.5 (C1, α -anomer), 101.2 (C1, β -anomer), 127.46, 127.54, 127.6, 127.7, 127.81, 127.84, 127.89, 127.93, 128.0, 128.05, 128.08, 128.14, 128.17, 128.28, 128.30, 128.40, 128.42, 128.45, 128.47, 128.5, 128.56, 128.59, 137.9, 138.1, 138.2, 138.3, 138.4, 138.7, 138.9, 169.7, 170.0. HRMS Calcd for C₅₇H₆₂O₁₂Na [M + Na]⁺, 961.4139; found, 961.4136.

Methyl (2,3,4,6-Tetra-*O*-benzyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (28)⁷

Colorless oil, $\alpha:\beta=1:2.7$, $R_f=0.32$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.30 (s, 1.1H), 3.33 (s, 3H), 3.35-3.49 (m, 5.9H), 3.51 (dd, $J=9.6, 3.2$

Hz, 1H), 3.57-3.88 (m, 8.2H), 3.94-4.06 (m, 1.4H), 4.12 (s, 1H), 4.16 (dd, $J = 10.4$, 2.0 Hz, 1H), 4.41-4.72 (m, 10.6H), 4.66 (d, $J = 12.0$ Hz, 1H), 4.74-5.00 (m, 7.2H), 5.01 (d, $J = 11.2$ Hz, 1H), 7.12-7.44 (m, 48H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.05, 55.08, 65.8, 68.3, 69.1, 69.7, 69.8, 71.6, 71.9, 72.0, 72.5, 73.26, 73.32, 73.5, 73.6, 73.7, 74.66, 74.73, 74.86, 74.92, 74.97, 75.01, 75.2, 75.7, 75.8, 76.0, 77.6, 79.6, 79.9, 80.0, 82.2, 82.3, 97.80 (β -OMe), 97.82 (α -OMe), 98.3 (C1, α -anomer), 101.5 (C1, β -anomer), 127.4, 127.46, 127.52, 127.56, 127.61, 127.63, 127.67, 127.73, 127.77, 127.82, 127.85, 127.94, 128.00, 128.02, 128.06, 128.09, 128.17, 128.24, 128.28, 128.34, 128.35, 128.37, 128.40, 128.5, 138.07, 138.14, 138.17, 138.20, 138.31, 138.36, 138.41, 138.5, 138.65, 138.68, 138.73, 138.8.

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)- α/β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (29)

Colorless oil, $\alpha:\beta = 1:7.2$, $R_f = 0.23$ (hexane/ CH_2Cl_2 /EtOAc, 4:1:1, v/v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.38 (s, 2.7H), 3.39-3.47 (m, 1.5H), 3.55-3.70 (m, 3.8H), 3.75-3.85 (m, 1.2H), 3.86-4.01 (m, 2.3H), 4.13-4.34 (m, 3.5H), 4.43 (d, $J = 8.4$ Hz, 1.4H), 4.48 (s, 2.2H), 4.53-4.56 (m, 0.4H), 4.69 (d, $J = 12.0$ Hz, 1H), 4.87 (brs, 0.2H), 4.97 (d, $J = 12.0$ Hz, 1H), 5.06 (t, $J = 9.6$ Hz, 1H), 5.14-5.31 (m, 2.6H), 5.49 (t, $J = 10.0$ Hz, 1H, β -H4), 5.57 (t, $J = 9.6$ Hz, 0.14H, α -H4), 6.10-6.18 (m, 1.1H), 6.89-6.95 (m, 1.9H), 7.06-7.08 (m, 0.3H), 7.15-7.62 (m, 34.2H), 7.83-8.14 (m, 8.6H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 55.7, 68.3, 68.75, 68.83, 68.9, 69.3, 69.5, 70.6, 70.7, 71.1, 72.1, 72.2, 72.8, 73.3,

73.6, 73.9, 74.3, 74.4, 74.7, 76.5, 78.3, 78.5, 78.6, 78.7, 96.9 (β -OMe), 97.2 (α -OMe), 101.9 (C1, α -anomer), 102.1 (C1, β -anomer), 121.2, 124.0, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.4, 128.5, 128.6, 128.9, 129.2, 129.3, 129.7, 129.9, 130.0, 131.8, 131.9, 133.2, 133.5, 133.6, 135.9, 136.1, 137.2, 138.2, 138.3, 138.6, 165.5, 165.8, 165.9. Anal. Calcd for $C_{62}H_{57}F_3O_{16}S$: C, 64.91; H, 5.01; S, 2.80. Found: C, 64.98; H, 4.95; S, 2.95.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (30 α)

Colorless oil, $R_f = 0.23$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_D^{20} = 42.2$ (c 0.5, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 3.43 (s, 3H), 3.50-3.54 (m, 2H), 3.62 (dd, $J = 11.2, 2.8$ Hz, 1H), 3.67-3.73 (m, 1H), 3.86 (dd, $J = 2.8, 2.0$ Hz, 1H), 3.92 (dd, $J = 11.2, 4.0$ Hz, 1H), 4.07 (dd, $J = 9.6, 2.8$ Hz, 1H), 4.17-4.23 (m, 1H), 4.19 (d, $J = 13.6$ Hz, 1H), 4.31 (d, $J = 11.6$ Hz, 1H), 4.33 (d, $J = 13.6$ Hz, 1H), 4.37 (d, $J = 11.6$ Hz, 1H), 4.49 (d, $J = 11.2$ Hz, 1H), 4.57 (d, $J = 11.2$ Hz, 1H), 4.67 (s, 2H), 4.97 (d, $J = 1.2$ Hz, 1H), 5.05 (t, $J = 10.0$ Hz, 1H), 5.19 (d, $J = 3.2$ Hz, 1H), 5.28 (dd, $J = 10.4, 4.0$ Hz, 1H), 5.67 (t, $J = 10.0$ Hz, 1H), 6.14 (t, $J = 10.0$ Hz, 1H), 7.21-7.55 (m, 29H), 7.87-7.93 (m, 4H), 7.98-8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 57.3, 65.9, 68.1, 68.8, 69.1, 70.3, 70.7, 71.6, 72.1, 72.7, 73.4, 74.2, 76.98, 77.04, 97.3, 97.8, 127.4, 127.7, 127.77, 127.84, 128.10, 128.13, 128.2, 128.4, 128.5, 128.6, 128.7, 128.8, 129.0, 129.1, 129.4, 129.8, 130.06, 130.08, 130.8, 133.3, 133.6, 137.5, 138.0, 138.3, 165.3, 165.9, 166.0. Anal.

Calcd for C₆₂H₆₀O₁₆S: C, 68.12; H, 5.53; S, 2.93. Found: C, 68.17; H, 5.63; S, 2.85.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (30β)

Colorless oil, $R_f = 0.15$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 18.4$ (c 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.43 (s, 3H), 3.53-3.62 (m, 2H), 3.67 (dd, $J = 6.4, 4.4$ Hz, 1H), 3.69 (dd, $J = 6.8, 4.0$ Hz, 1H), 3.81 (dd, $J = 11.2, 2.0$ Hz, 1H), 4.10-4.17 (m, 2H), 4.20 (dd, $J = 11.2, 1.6$ Hz, 1H), 4.29-4.37 (m, 3H), 4.45-4.54 (m, 4H), 4.87 (d, $J = 12.0$ Hz, 1H), 4.98 (t, $J = 9.6$ Hz, 1H), 5.06 (d, $J = 12.0$ Hz, 1H), 5.23-5.30 (m, 2H), 5.55 (t, $J = 9.6$ Hz, 1H), 6.19 (d, $J = 9.6$ Hz, 1H), 7.19-7.52 (m, 29H), 7.84-8.02 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 55.6, 57.5, 68.79, 68.81, 69.4, 69.5, 70.6, 71.0, 72.2, 73.3, 73.6, 74.3, 74.6, 77.2, 79.1, 97.0, 102.2, 127.5, 127.7, 127.9, 128.0, 128.1, 128.28, 128.33, 128.4, 128.5, 128.56, 128.60, 128.75, 128.83, 128.9, 129.1, 129.3, 129.7, 129.9, 130.0, 130.7, 133.2, 133.5, 133.6, 137.1, 138.2, 138.4, 165.6, 165.8, 165.9. Anal. Calcd for C₆₂H₆₀O₁₆S: C, 68.12; H, 5.53; S, 2.93. Found: C, 68.18; H, 5.71; S, 2.75.

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-α/β-D-mannopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (31)

Colorless oil, $\alpha:\beta = 1:5.0$, $R_f = 0.30$ (hexane/ CH_2Cl_2 /EtOAc, 4:1:1, v/v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.43 (s, 0.7H), 3.47 (s, 3H), 3.57 (dd, $J = 16.4, 2.4$ Hz, 1H), 3.61-3.67 (m, 3H), 3.71 (dd, $J = 11.2, 6.8$ Hz, 1H), 3.82-3.89 (m, 0.5H), 3.98 (dd, $J = 11.2, 3.6$ Hz, 1H), 4.14 (dd, $J = 9.6, 2.4$ Hz, 1H), 4.15 (d, $J = 2.4$ Hz, 1H), 4.21 (d, $J = 6.4$ Hz, 1H), 4.23 (dd, $J = 9.2, 1.2$ Hz, 1H), 4.28-4.39 (m, 3.7H), 4.47 (d, $J = 12.4$ Hz, 1H), 4.51 (s, 1H), 4.54 (d, $J = 2.4$ Hz, 0.2H), 4.73 (d, $J = 12.4$ Hz, 0.2H), 4.81 (d, $J = 12.4$ Hz, 0.2H), 4.93 (d, $J = 12.4$ Hz, 1H), 5.05 (d, $J = 12.4$ Hz, 1H), 5.22 (d, $J = 3.2$ Hz, 0.2H), 5.28 (s, 1H), 5.31 (dd, $J = 12.4, 3.6$ Hz, 1H), 5.52-5.63 (m, 2H), 5.63-5.70 (m, 0.5H), 6.14 (t, $J = 10.0$ Hz, 0.2H, $\alpha\text{-H}_4$), 6.21 (t, $J = 9.2$ Hz, 1.0H, $\beta\text{-H}_4$), 7.02-7.57 (m, 22H), 7.84-8.21 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.6, 55.7, 65.6, 68.2, 68.8, 68.90, 68.91, 69.3, 69.6, 69.7, 70.2, 70.5, 70.56, 70.58, 70.8, 71.0, 71.7, 72.0, 72.2, 73.0, 73.2, 73.4, 73.7, 74.0, 74.1, 74.3, 76.6, 76.8, 77.4, 78.3, 97.0, 97.2, 98.5 (C1, α -anomer), 102.3 (C1, β -anomer), 123.4, 127.4, 127.50, 127.54, 127.68, 127.71, 127.74, 127.8, 127.9, 128.0, 128.11, 128.2, 128.3, 128.35, 128.4, 128.52, 128.54, 128.9, 129.1, 129.2, 129.3, 129.4, 129.72, 129.75, 129.9, 130.0, 130.8, 130.9, 133.1, 133.2, 133.3, 133.4, 133.5, 133.6, 135.4, 135.6, 137.5, 137.8, 137.9, 138.3, 138.5, 150.5, 163.8, 163.9, 165.3, 165.6, 165.8, 165.9. Anal. Calcd for $\text{C}_{62}\text{H}_{57}\text{NO}_{17}$: C, 68.44; H, 5.28; N, 1.29. Found: C, 68.49; H, 5.34; N, 1.28.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (32)

Colorless oil, $\alpha:\beta=1:4.6$, $R_f=0.25$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.40 (s, 0.7H), 3.46 (m, 3H), 3.56 (dd, $J = 9.6, 2.8$ Hz, 1H), 3.60-3.72 (m, 4.9H), 3.97 (dd, $J = 11.2, 4.0$ Hz, 0.2H), 4.03 (dd, $J = 9.6, 2.8$ Hz, 0.2H), 4.11 (d, $J = 2.4$ Hz, 1H), 4.21-4.54 (m, 8.4H), 4.71 (d, $J = 12.4$ Hz, 0.2H), 5.80 (d, $J = 12.4$ Hz, 0.2H), 4.93 (d, $J = 12.4$ Hz, 1H), 5.04 (d, $J = 12.4$ Hz, 1H), 5.19-5.32 (m, 2.4H), 5.54 (t, $J = 10.0$ Hz, 1H), 5.56 (t, $J = 8.8$ Hz, 1H), 5.64 (t, $J = 10.0$ Hz, 0.4H), 6.14 (t, $J = 10.0$ Hz, 0.2H), 6.20 (t, $J = 9.2$ Hz, 1H), 7.08-7.57 (m, 32.9H), 7.84-8.05 (m, 9.7H); ¹³C NMR (100 MHz, CDCl₃) δ 55.6, 55.7, 68.3, 68.7, 68.9, 69.3, 69.4, 69.55, 69.58, 69.7, 70.3, 70.6, 70.8, 71.0, 72.1, 72.3, 73.3, 73.4, 73.7, 74.3, 74.4, 74.9, 77.4, 78.6, 96.9 (β -OMe), 97.1 (C1, α -anomer), 102.1 (C1, β -anomer), 127.5, 127.6, 127.67, 127.73, 127.74, 127.9, 128.2, 128.26, 128.29, 128.32, 128.37, 128.40, 128.43, 128.5, 128.9, 129.2, 129.4, 129.75, 129.79, 129.90, 129.93, 130.00, 130.03, 133.0, 133.1, 133.2, 133.4, 133.5, 133.6, 137.7, 138.1, 138.6, 165.6, 165.7, 165.8, 166.0. Anal. Calcd for C₆₂H₅₈O₁₅: C, 71.39; H, 5.60. Found: C, 71.41; H, 5.60.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (33)

Colorless oil, $\alpha:\beta=1:4.1$, $R_f=0.35$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 1.91 (s, 3.8H), 3.38 (s, 0.7H), 3.41-3.50 (m, 5.1H), 3.52-3.60 (m, 2.1H), 3.61-3.72 (m, 1.9H), 3.75 (t, $J = 1.6$ Hz, 0.3H), 3.84 (dd, $J = 10.0, 3.2$ Hz, 0.5H), 3.92 (dd, $J = 9.5, 4.0$ Hz, 0.3H), 4.05 (d, $J = 2.4$ Hz, 1H), 4.18-4.24 (m, 1.3H), 4.31 (d, $J =$

12.0 Hz, 1H), 4.32-4.36 (m, 0.9H), 4.37-4.54 (m, 5H), 4.62-4.78 (m, 0.8H), 4.89 (d, $J = 12.4$ Hz, 1H), 5.01 (d, $J = 12.4$ Hz, 0.9H), 5.18-5.26 (m, 0.7H), 5.25-5.32 (m, 2.3H), 5.37 (t, $J = 9.6$ Hz, 0.4H), 5.53 (t, $J = 9.6$ Hz, 1H), 5.62 (t, $J = 9.6$ Hz, 0.2H), 6.14 (t, $J = 10.0$ Hz, 0.3H), 6.20 (t, $J = 9.6$ Hz, 1H), 7.16-7.53 (m, 30H), 7.81-8.05 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 55.5, 55.6, 68.1, 68.7, 68.8, 69.0, 69.5, 70.3, 70.45, 70.51, 70.6, 71.1, 71.9, 72.1, 72.2, 72.8, 73.3, 73.4, 73.6, 74.2, 74.3, 74.5, 77.1, 77.4, 78.9, 96.8 (β -OMe), 97.0 (α -OMe), 98.4 (C1, α -anomer), 102.0 (C1, β -anomer), 127.5, 127.6, 127.65, 127.69, 127.8, 127.85, 127.9, 128.2, 128.25, 128.34, 128.4, 128.46, 128.50, 128.8, 129.1, 129.3, 129.7, 129.9, 130.0, 133.2, 133.46, 133.54, 138.1, 138.2, 138.3, 138.4, 138.5, 165.1, 165.5, 165.8, 165.9, 169.88, 169.94. HRMS Calcd for $\text{C}_{57}\text{H}_{56}\text{O}_{15}\text{Na}$ $[\text{M}+\text{Na}]^+$, 1003.3517; found, 1003.3514.

Methyl (2,3,4,6-Tetra-*O*-benzyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (34)^{8,9}

Colorless oil, $\alpha:\beta=1:2.5$, $R_f = 0.42$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.37 (s, 1.8H, α -OMe), 3.38-3.42 (m, 1H), 3.43 (s, 3H, β -OMe), 3.47-3.58 (m, 5H), 3.84-4.00 (m, 3H), 4.05 (d, $J = 2.9$ Hz, 1H), 4.15-4.20 (m, 2H), 4.28-4.35 (m, 1H), 4.37-4.60 (m, 8H), 4.69 (d, $J = 6.8$ Hz, 0.8H), 4.82-4.92 (m, 3H), 5.04 (d, $J = 12.4$ Hz, 1H), 5.17 (d, $J = 3.2$ Hz, 0.6H), 5.20-5.32 (m, 2H), 5.47-5.62 (m, 1.5H), 6.10-6.23 (m, 1.5H), 7.12-8.10 (m, 56H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 55.6, 66.3, 68.2, 68.7, 69.0, 69.1, 69.5, 69.6, 69.9, 71.0, 71.5, 71.9, 72.0, 72.17, 72.21, 72.3,

72.7, 73.3, 73.5, 74.0, 74.2, 74.8, 74.86, 74.90, 75.1, 75.2, 76.1, 80.0, 96.9, 97.0, 98.3 (C1, α -anomer), 102.4 (C1, β -anomer), 127.46, 127.48, 127.52, 127.54, 127.6, 127.7, 127.8, 127.87, 127.93, 128.0, 128.1, 128.27, 128.32, 128.36, 128.40, 128.43, 128.5, 129.0, 129.2, 129.4, 129.8, 129.9, 130.0, 133.2, 133.4, 133.46, 133.53, 138.3, 138.4, 138.5, 138.6, 138.7, 138.8, 140.0, 165.2, 165.87, 165.92.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (35 α)

Colorless oil, $R_f = 0.46$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 8.4$ (c 0.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.18 (s, 3H), 3.72 (dd, $J = 7.2, 6.8$ Hz, 1H), 3.76-3.80 (m, 1H), 3.83 (t, $J = 10.8$ Hz, 1H), 3.84 (d, $J = 12.4$ Hz, 1H), 3.94-4.01 (m, 3H), 4.04-4.08 (m, 3H), 4.17 (d, $J = 14.0$ Hz, 1H), 4.27 (dd, $J = 9.6, 4.0$ Hz, 1H), 4.38 (d, $J = 13.6$ Hz, 1H), 4.42 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 11.2$ Hz, 1H), 4.51-4.58 (m, 3H), 4.59 (d, $J = 11.6$ Hz, 1H), 4.62 (d, $J = 11.6$ Hz, 1H), 4.77 (d, $J = 1.2$ Hz, 1H), 4.80 (d, $J = 11.6$ Hz, 1H), 5.02 (t, $J = 9.6$ Hz, 1H), 5.24 (d, $J = 1.6$ Hz, 1H), 5.65 (s, 1H), 7.23-7.45 (m, 28H), 7.51-7.56 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.0, 57.5, 63.7, 69.1, 69.5, 70.9, 71.3, 72.4, 73.6, 73.7, 74.2, 76.0, 76.5, 77.1, 77.4, 79.5, 99.7, 101.0, 101.7, 126.2, 127.6, 127.8, 127.85, 127.91, 128.0, 128.1, 128.2, 128.35, 128.40, 128.44, 128.6, 128.7, 128.85, 128.93, 129.1, 130.8, 137.4, 137.7, 138.0, 138.4, 138.5. Anal. Calcd for C₅₅H₅₈O₁₃S: C, 68.88; H, 6.10; S, 3.34; Found: C, 68.72; H, 6.47; S, 3.26.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (35 β)

Colorless oil, $R_f = 0.12$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 8.4$ (c 0.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.35 (s, 3H), 3.64 (dd, $J = 9.6, 3.2$ Hz, 1H), 3.66 (d, $J = 7.2$ Hz, 1H), 3.70 (q, $J = 6.8$ Hz, 1H), 3.78 (d, $J = 5.6$ Hz, 1H), 3.79 (dd, $J = 5.6, 3.6$ Hz, 1H), 3.87 (d, $J = 8.0$ Hz, 1H), 3.96 (dd, $J = 10.0, 3.2$ Hz, 1H), 4.02-4.05 (m, 1H), 4.09 (d, $J = 2.8$ Hz, 1H), 4.14 (d, $J = 14.0$ Hz, 1H), 4.27 (dd, $J = 8.4, 2.8$ Hz, 1H), 4.32 (d, $J = 9.6$ Hz, 1H), 4.35 (d, $J = 12.4$ Hz, 1H), 4.39 (d, $J = 1.2$ Hz, 1H), 4.40 (d, $J = 11.6$ Hz, 1H), 4.44 (d, $J = 11.6$ Hz, 1H), 4.52 (d, $J = 11.2$ Hz, 1H), 4.58 (d, $J = 12.0$ Hz, 1H), 4.65 (s, 1H), 4.76 (d, $J = 0.8$ Hz, 1H), 4.85 (d, $J = 12.0$ Hz, 1H), 4.90 (d, $J = 12.0$ Hz, 1H), 4.98 (t, $J = 9.2$ Hz, 1H), 5.07 (d, $J = 12.0$ Hz, 1H), 5.50 (s, 1H), 7.18-7.43 (m, 26H), 7.43-7.53 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 57.6, 64.1, 69.1, 69.9, 70.0, 70.7, 70.8, 73.0, 73.3, 73.7, 73.8, 74.0, 74.7, 77.4, 78.6, 79.0, 99.1, 99.4, 101.8, 126.3, 127.4, 127.7, 127.8, 127.91, 127.92, 127.94, 128.2, 128.26, 128.27, 128.38, 128.4, 128.7, 128.7, 128.8, 128.9, 129.0, 130.7, 137.1, 137.7, 138.2, 138.4, 138.7. Anal. Calcd for C₅₅H₅₈O₁₃S: C, 68.88; H, 6.10; S, 3.34; Found: C, 68.75; H, 6.16; S, 3.17.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-*p*-nitrobenzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (36 α)

Colorless oil, $R_f = 0.40$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = -68.5$ (c 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.23 (s, 3H), 3.60 (dd, $J = 10.0, 2.8$ Hz, 1H), 3.67 (dd, $J = 10.4, 6.4$ Hz, 1H), 3.75-3.81 (m, 1H), 3.82 (q, $J = 10.0$ Hz, 1H), 3.94-4.02 (m, 4H), 4.04-4.12 (m, 2H), 4.28-4.32 (m, 1H), 4.38 (d, $J = 12.4$ Hz, 1H), 4.45 (d, $J = 11.6$ Hz, 1H), 4.48 (d, $J = 11.6$ Hz, 1H), 4.52-4.58 (m, 3H), 4.65 (d, $J = 11.6$ Hz, 1H), 5.27 (s, 1H), 5.62 (t, $J = 9.2$ Hz, 1H), 5.66 (s, 1H), 7.10-7.69 (m, 25H), 8.01-8.10 (m, 2H), 8.20-8.27 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 54.9, 63.8, 69.1, 70.3, 70.6, 71.0, 71.5, 72.7, 73.6, 73.7, 74.4, 75.9, 76.3, 77.0, 79.5, 100.6, 101.1, 101.7, 123.5, 126.2, 127.6, 127.7, 127.76, 127.79, 127.86, 127.88, 128.0, 128.3, 128.36, 128.38, 128.40, 128.6, 129.1, 131.0, 135.4, 137.7, 137.9, 138.2, 138.5, 150.6, 163.9. Anal. Calcd for C₅₅H₅₅NO₁₄: C, 69.24; H, 5.81; N, 1.47; Found: C, 69.23; H, 5.96; N, 1.49.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-*p*-nitrobenzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (36 β)

Colorless oil, $R_f = 0.38$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = -33.1$ (c 0.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.34 (s, 3H), 3.61 (dd, $J = 10.0, 2.8$ Hz, 1H), 3.63-3.72 (m, 3H), 3.79-3.87 (m, 2H), 3.98 (dd, $J = 10.0, 3.2$ Hz, 1H), 4.07 (d, $J = 2.4$ Hz, 1H), 4.09-4.15 (m, 1H), 4.19 (d, $J = 12.4$ Hz, 1H), 4.28-4.37 (m, 3H), 4.49 (d, $J = 12.8$ Hz, 1H), 4.67 (s, 1H), 4.69 (d, $J = 12.0$ Hz, 1H), 4.77 (brs, 1H), 4.86 (s, 1H), 4.99 (d, $J = 12.4$ Hz, 1H), 5.08 (d, $J = 12.4$ Hz, 1H), 5.57 (s, 1H), 5.61 (d, $J = 9.2$ Hz, 1H), 7.04-7.55 (m, 25H), 7.97-8.04 (m, 2H), 8.18-8.24 (m, 2H); ¹³C NMR (100 MHz,

CDCl₃) δ 55.1, 64.1, 69.0, 70.65, 70.81, 70.83, 72.9, 73.2, 73.7, 73.8, 74.10, 74.12, 75.0, 78.3, 78.6, 99.2, 99.7, 101.8, 123.5, 126.3, 127.5, 127.7, 127.75, 127.80, 127.9, 128.28, 128.30, 128.38, 128.42, 128.8, 129.0, 130.9, 135.4, 137.5, 137.59, 137.62, 138.3, 138.6, 150.6, 163.9. Anal. Calcd for C₅₅H₅₅NO₁₄: C, 69.24; H, 5.81; N, 1.47; Found: C, 69.22; H, 5.96; N, 1.50.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (37 α)

Colorless oil, R_f = 0.36 (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20}$ = -56.3 (c 1.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.18 (s, 3H), 3.61 (dd, J = 10.4, 2.0 Hz, 1H), 3.69 (dd, J = 10.8, 7.6 Hz, 1H), 3.74-3.80 (m, 1H), 3.81 (q, J = 9.6 Hz, 1H), 3.92-4.02 (m, 4H), 4.04-4.12 (m, 2H), 4.28 (dd, J = 9.2, 3.6 Hz, 1H), 4.46 (d, J = 12.4 Hz, 1H), 4.45-4.53 (m, 2H), 4.53-4.59 (m, 3H), 4.64 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 11.6 Hz, 1H), 4.83 (brs, 1H), 5.24 (brs, 1H), 5.61 (t, J = 9.2 Hz, 1H), 5.65 (s, 1H), 7.10-7.74 (m, 28H), 8.01-8.09 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 54.9, 63.8, 69.1, 69.5, 70.3, 71.5, 71.8, 72.7, 73.4, 73.7, 74.8, 75.9, 76.7, 77.0, 79.5, 100.7, 101.1, 101.7, 126.2, 127.57, 127.62, 127.77, 127.79, 127.8, 127.86, 127.90, 127.91, 128.30, 128.33, 128.4, 128.5, 128.6, 129.1, 130.0, 130.1, 133.22, 137.7, 138.16, 138.21, 138.4, 138.6, 165.8. HRMS Calcd for C₅₅H₅₆O₁₂Na [M + Na]⁺, 931.3669; found, 931.3666.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (37 β)

Colorless oil, $R_f = 0.33$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20} = -88.2$ (c 0.9, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.34 (s, 3H), 3.63-3.72 (m, 3H), 3.78-3.72 (m, 2H), 3.97 (dd, $J = 9.6, 3.2$ Hz, 1H), 4.03 (d, $J = 2.8$ Hz, 1H), 4.08-4.14 (m, 1H), 4.27 (d, $J = 6.0$ Hz, 1H), 4.28 (d, $J = 12.4$ Hz, 1H), 4.36 (s, 2H), 4.41 (d, $J = 2.0$ Hz, 1H), 4.50 (d, $J = 12.0$ Hz, 1H), 4.64 (d, $J = 12.4$ Hz, 1H), 4.66 (s, 1H), 4.77 (brs, 1H), 4.87 (d, $J = 12.4$ Hz, 1H), 4.98 (d, $J = 12.4$ Hz, 1H), 5.06 (d, $J = 12.4$ Hz, 1H), 5.55 (s, 1H), 5.53-5.62 (m, 1H), 7.05-7.65 (m, 28H), 7.91-8.09 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 64.1, 69.1, 69.7, 70.75, 70.81, 70.83, 73.2, 73.4, 73.7, 73.8, 73.9, 75.0, 78.5, 78.6, 99.2, 99.5, 101.8, 126.3, 127.4, 127.55, 127.60, 127.66, 127.71, 127.9, 128.25, 128.30, 128.35, 128.39, 128.5, 128.7, 129.0, 130.0, 130.1, 133.2, 137.7, 137.8, 138.1, 138.7, 138.9, 165.7. HRMS Calcd for C₅₅H₅₆O₁₂Na [M + Na]⁺, 931.3669; found, 931.3667.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (38 α)

Colorless oil, $R_f = 0.38$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 36.6$ (c 0.8, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 1.94 (s, 3H), 3.33 (s, 3H), 3.45 (dd, $J = 10.0, 2.8$ Hz, 1H), 3.50-3.65 (m, 3H), 3.77-3.81 (m, 2H), 3.95 (dd, $J = 9.8, 3.6$ Hz, 1H), 3.97 (d, J

= 2.8 Hz, 1H), 4.09 (t, J = 8.8 Hz, 1H), 4.25 (d, J = 2.6 Hz, 1H), 4.32 (d, J = 12.4 Hz, 1H), 4.35-4.43 (m, 3H), 4.49 (d, J = 12.4 Hz, 1H), 5.02 (d, J = 12.4 Hz, 1H), 5.31 (t, J = 9.6 Hz, 1H), 5.52 (s, 1H), 7.20-7.54 (m, 25H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 55.1, 64.1, 69.0, 69.2, 70.70, 70.74, 71.0, 73.3, 73.5, 73.7, 73.77, 73.81, 74.6, 76.9, 78.5, 78.8, 99.2, 99.4, 101.8, 126.2, 127.5, 127.6, 127.68, 127.72, 127.74, 127.9, 128.19, 128.23, 128.40, 128.44, 128.6, 128.9, 137.7, 138.0, 138.1, 138.7, 138.8, 170.0. HRMS Calcd for $\text{C}_{50}\text{H}_{54}\text{O}_{12}\text{Na}$ $[\text{M} + \text{Na}]^+$, 869.3513; found, 869.3516.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (38 β)

Colorless oil, R_f = 0.36 (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_D^{20}$ = -2.8 (c 3.1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 1.94 (s, 3H), 3.32 (s, 3H), 3.55 (dd, J = 10.8, 2.4 Hz, 1H), 3.59-3.65 (m, 1H), 3.72-3.81 (m, 2H), 3.85 (dd, J = 11.2, 3.2 Hz, 1H), 3.88-3.97 (m, 4H), 4.06 (brs, 1H), 4.26 (dd, J = 8.4, 2.8 Hz, 1H), 4.47-4.55 (m, 5H), 4.58 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.79 (d, J = 12.4 Hz, 1H), 4.80 (s, 1H), 5.18 (d, J = 1.2 Hz, 1H), 5.33 (t, J = 9.6 Hz, 1H), 5.63 (s, 1H), 7.15-7.56 (m, 25H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 55.0, 64.1, 69.0, 69.1, 70.3, 71.2, 71.8, 72.6, 73.4, 73.6, 73.8, 74.7, 75.8, 76.7, 76.9, 79.4, 100.6, 101.0, 101.7, 126.2, 127.6, 127.7, 127.80, 127.81, 127.87, 127.94, 128.3, 128.35, 128.38, 128.43, 128.5, 129.1, 137.7, 138.2, 138.3, 138.4, 138.5, 170.1. HRMS Calcd for $\text{C}_{50}\text{H}_{54}\text{O}_{12}\text{Na}$ $[\text{M} + \text{Na}]^+$, 869.3513; found, 869.3517.

Methyl (2,3,4,6-Tetra-*O*-benzyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (39)⁹

Colorless oil, $\alpha:\beta = 2.7 : 1$, $R_f = 0.33$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.21 (s, 1H), 3.34 (s, 3H), 3.45-3.51 (m, 1H), 3.53 (dd, $J = 9.2, 2.8$ Hz, 1H), 3.70 (dd, $J = 10.8, 6.4$ Hz, 1H), 3.72-3.83 (m, 4H), 3.86-3.94 (m, 4H), 3.95 (dd, $J = 10.0, 3.6$ Hz, 1H), 4.00 (d, $J = 3.2$ Hz, 1H), 4.04-4.11 (m, 1.3H), 4.20-4.30 (m, 1.3H), 4.39-4.65 (m, 10.7H), 4.75 (d, $J = 2.0$ Hz, 1H), 4.77 (d, $J = 14.0$ Hz, 0.3H), 4.89 (d, $J = 12.0$ Hz, 1H), 4.92 (d, $J = 10.8$ Hz, 1H), 4.99 (d, $J = 12.4$ Hz, 1H), 5.06 (d, $J = 12.4$ Hz, 1H), 5.21 (d, $J = 1.2$ Hz, 0.3H), 5.52 (s, 1H), 5.61 (s, 0.3H), 7.19-7.54 (m, 40H); ¹³C NMR (100 MHz, CDCl₃) δ 54.9, 55.1, 63.7, 64.0, 69.0, 69.1, 69.6, 70.1, 70.5, 71.2, 72.1, 73.1, 73.3, 73.4, 73.5, 73.6, 73.7, 73.8, 75.0, 75.2, 75.3, 76.0, 76.3, 76.6, 78.5, 79.3, 79.6, 82.1, 99.2, 99.7, 100.3, 101.0, 101.6, 101.8, 126.3, 127.3, 127.5, 127.6, 127.66, 127.72, 127.80, 127.82, 127.88, 127.91, 128.21, 128.24, 128.28, 128.29, 128.31, 128.34, 128.4, 128.46, 128.49, 128.8, 128.97, 129.02, 129.9, 137.1, 137.8, 138.2, 138.4, 138.5, 138.6, 138.7, 139.87, 138.93.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-mannopyranoside (40)

Colorless oil, $\alpha:\beta = 1:5.1$, $R_f = 0.31$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); ¹H NMR

(400 MHz, CDCl₃) δ 3.47 (s, 0.5H), 3.47 (s, 2.7H), 3.55 (dd, J = 9.2, 2.0 Hz, 1.2H), 3.57 (dd, J = 9.2, 2.4 Hz, 1.2H), 3.66 (dd, J = 11.2, 6.4 Hz, 1.1H), 3.77 (dd, J = 11.6, 6.8 Hz, 1H), 3.81 (dd, J = 10.8, 2.4 Hz, 1.1H), 3.98-4.05 (m, 0.5H), 4.12 (d, J = 14.0 Hz, 1.1H), 4.13-4.16 (m, 1H), 4.24 (dd, J = 11.2, 1.6 Hz, 1.1H), 4.28 (d, J = 11.2 Hz, 1.2H), 4.30-4.37 (m, 1.9H), 4.38-4.51 (m, 4H), 4.59 (d, J = 4.4 Hz, 0.4H), 4.79 (d, J = 12.0 Hz, 1H), 4.90 (t, J = 9.6 Hz, 1H), 4.98-5.01 (m, 1.3H), 5.03 (d, J = 11.2 Hz, 1H), 5.08 (d, J = 10.0 Hz, 0.2H), 5.64-5.70 (m, 1.2H), 5.87-5.93 (m, 2.2H), 6.03 (t, J = 10.0 Hz, 0.2H), 7.17-7.45 (m, 35H), 7.80-7.88 (m, 2.5H), 7.92-7.97 (m, 2.5H), 8.02-8.12 (m, 2.5H); ¹³C NMR (100 MHz, CDCl₃) δ 55.4, 55.6, 57.3, 57.4, 66.6, 67.2, 67.4, 68.7, 69.2, 69.4, 69.8, 70.1, 70.4, 70.7, 70.8, 71.1, 72.6, 73.3, 73.5, 73.6, 74.1, 74.4, 74.5, 76.9, 77.2, 77.3, 78.9, 97.7 (C1, α -anomer), 98.5, 98.7, 102.3 (C1, β -anomer), 127.57, 127.59, 127.63, 127.7, 127.80, 127.82, 127.9, 127.96, 128.01, 128.2, 128.26, 128.28, 128.30, 128.4, 128.5, 128.55, 128.63, 128.7, 128.8, 128.9, 129.1, 129.2, 129.3, 129.7, 129.75, 129.80, 129.9, 130.6, 130.7, 133.2, 133.5, 133.6, 137.0, 137.4, 138.1, 138.2, 138.3, 165.4, 165.5, 165.6, 165.7. Anal. Calcd for C₆₂H₆₀O₁₆S: C, 68.12; H, 5.53; S, 2.93; Found: C, 68.13; H, 5.73; S, 2.77.

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α/β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-mannopyranoside (41)

Colorless oil, α : β = 1:2.8, R_f = 0.32 (hexane/CH₂Cl₂/EtOAc, 4:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.42 (dd, J = 10.8, 3.6 Hz, 0.4H), 3.48 (s, 1.1H), 3.51 (s, 3.2H), 3.52-

3.55 (m, 0.8H), 3.58-3.65 (m, 2.6H), 3.75 (dd, $J = 10.8, 3.2$ Hz, 0.4H), 3.78 (dd, $J = 11.2, 7.2$ Hz, 1.1H), 3.87-3.94 (m, 0.4H), 3.98-4.72 (m, 0.4H), 4.11 (d, $J = 5.2$ Hz, 1H), 4.13 (d, $J = 10.0$ Hz, 1H), 4.20-4.41 (m, 7H), 4.43 (d, $J = 12.4$ Hz, 0.4H), 4.53 (s, 1H), 4.64 (d, $J = 12.4$ Hz, 0.3H), 4.72 (d, $J = 12.4$ Hz, 0.3H), 4.87 (d, $J = 12.0$ Hz, 1H), 4.98 (d, $J = 1.6$ Hz, 0.3H), 5.01 (d, $J = 12.4$ Hz, 1H), 5.02-5.07 (m, 1.1H), 5.55 (t, $J = 9.6$ Hz, 1H), 5.65 (d, $J = 10.0$ Hz, 0.3H), 5.66-5.76 (m, 1H), 5.84-5.94 (m, 2.6H), 6.01 (t, $J = 10.4$ Hz, 0.3H), 7.02-7.57 (m, 35H), 7.78-8.32 (m, 11H); ^{13}C NMR(100MHz, CDCl_3) δ 55.5, 55.6, 66.5, 67.4, 67.5, 69.3, 69.4, 69.8, 70.0, 70.1, 70.2, 70.55, 70.62, 70.78, 70.83, 71.0, 71.5, 73.0, 73.3, 73.4, 73.7, 74.1, 74.3, 77.4, 74.5, 78.1, 98.5, 98.6(C1, α -anomer), 98.8, 102.4 (C1, β -anomer), 123.4, 127.4, 127.5, 127.6, 127.69, 127.73, 127.75, 127.84, 128.0, 128.16, 128.22, 128.3, 128.37, 128.41, 128.43, 128.67, 128.72, 128.8, 129.0, 129.3, 129.37, 129.43, 129.6, 129.8, 129.85, 129.92, 130.86, 130.91, 133.3, 133.4, 133.56, 133.61, 133.7, 135.5, 135.6, 137.6, 137.8, 137.88, 137.92, 138.3, 138.4, 150.5, 163.8, 163.9, 165.53, 165.54, 165.61, 165.63, 165.7, 165.9. HRMS Calcd for $\text{C}_{62}\text{H}_{57}\text{NO}_{17}\text{Na}$ $[\text{M} + \text{Na}]^+$, 1110.3519; found, 1110.3518.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-mannopyranoside (42)

Colorless oil, $\alpha:\beta = 1:3$, $R_f = 0.35$ (hexane/ CH_2Cl_2 /EtOAc, 4:1:1, v/v/v); ^1H NMR (400 MHz, CDCl_3) δ 3.35-3.39 (m, 0.4H), 3.40 (s, 1H), 3.46 (s, 3H), 3.56 (dd, $J = 6.8, 2.8$ Hz, 1.2H), 3.60-3.72 (m, 4.7H), 3.81-3.89 (m, 0.3H), 3.94-4.05 (m, 0.3H), 4.10 (d, $J = 2.8$

Hz, 1H), 4.19-4.29 (m, 2.7H), 4.30-4.41 (m, 3.9H), 4.42-4.53 (m, 3.5H), 4.71 (d, J = 12.4 Hz, 0.3H), 4.80 (d, J = 12.4 Hz, 0.3H), 4.93 (d, J = 12.4 Hz, 1H), 4.97 (d, J = 12.0 Hz, 0.3H), 5.04 (d, J = 12.4 Hz, 1H), 5.18-5.27 (m, 0.3H), 5.27 (s, 1H), 5.29 (dd, J = 10.0, 6.4 Hz, 1H), 5.50-5.61 (m, 2H), 5.63 (t, J = 9.1 Hz, 1H), 6.13 (t, J = 10.0 Hz, 1H), 6.19 (d, J = 9.2 Hz, 1H), 7.05-7.65 (m, 35H), 7.82-8.08 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.6, 55.7, 65.7, 68.3, 68.7, 68.9, 69.3, 69.4, 69.55, 69.60, 69.7, 70.4, 70.6, 70.8, 71.1, 72.0, 72.2, 72.3, 73.0, 73.3, 73.4, 73.7, 74.3, 74.4, 74.9, 77.0, 78.6, 97.0, 97.2, 98.6 (C1, α -anomer), 102.2 (C1, β -anomer), 127.3, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.28, 128.31, 128.34, 128.39, 128.42, 128.45, 128.50, 128.6, 128.9, 129.2, 129.3, 129.37, 129.44, 129.77, 129.82, 129.90, 129.93, 130.0, 130.1, 130.2, 133.1, 133.17, 133.21, 133.4, 133.5, 133.6, 137.7, 138.06, 138.13, 138.21, 138.4, 138.6, 165.3, 165.6, 165.7, 165.9, 166.0. Anal. Calcd for $\text{C}_{62}\text{H}_{58}\text{O}_{15}$: C, 71.39; H, 5.60. Found: C, 71.26; H, 5.77.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (43 α)

Colorless oil, R_f = 0.31 (hexane/ CH_2Cl_2 /EtOAc, 4:1:1, v/v/v); $[\alpha]_{\text{D}}^{20}$ = 40.6 (c 0.2, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 3.30 (s, 3H), 3.36 (t, J = 9.2 Hz, 1H), 3.46 (dd, J = 9.2, 3.2 Hz, 1H), 3.58 (dd, J = 11.2, 1.6 Hz, 1H), 3.63-3.72 (m, 2H), 3.73-3.91 (m, 4H), 3.97 (t, J = 9.2 Hz, 1H), 4.20-4.28 (m, 3H), 4.36-4.50 (m, 4H), 4.51-4.60 (m, 2H), 4.61-4.68 (m, 3H), 4.71 (d, J = 9.6 Hz, 1H), 4.74-4.91 (m, 4H), 4.98 (d, J = 10.8 Hz,

1H), 7.18-7.37 (m, 35H); ¹³C NMR (100 MHz, CDCl₃) 55.2, 57.0, 66.2, 69.0, 69.8, 70.5, 72.1, 73.0, 73.4, 74.0, 74.8, 75.0, 75.2, 75.9, 77.7, 79.4, 80.1, 82.2, 97.9, 98.5, 127.5, 127.6, 127.7, 127.81, 127.83, 127.9, 128.06, 128.10, 128.15, 128.20, 128.23, 128.3, 128.45, 128.53, 138.2, 138.3, 138.7. Anal. Calcd for C₆₂H₆₆O₁₃S: C, 70.84; H, 6.33; S, 3.05. Found: C, 70.88; H, 6.35; S, 3.19.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (43β)

Colorless oil, $R_f = 0.25$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 17.2$ (c 2.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.31 (s, 3H), 3.33-3.37 (m, 1H), 3.42 (dd, $J = 9.6, 2.8$ Hz, 1H), 3.44-3.48 (m, 2H), 3.49 (d, $J = 4.4$ Hz, 1H), 3.71 (d, $J = 2.4$ Hz, 1H), 3.75-3.81 (m, 1H), 3.87 (t, $J = 9.6$ Hz, 1H), 4.01 (t, $J = 9.2$ Hz, 1H), 4.11 (s, 1H), 4.13 (dd, $J = 9.2, 1.6$ Hz, 1H), 4.24 (d, $J = 14.0$ Hz, 1H), 4.34 (dd, $J = 11.6, 4.0$ Hz, 1H), 4.46-4.58 (m, 7H), 4.63 (d, $J = 12.4$ Hz, 1H), 4.72 (d, $J = 12.0$ Hz, 1H), 4.75 (d, $J = 12.4$ Hz, 1H), 4.79-4.90 (m, 4H), 5.10 (d, $J = 10.8$ Hz, 1H), 7.15-7.45 (m, 35H); ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 57.1, 68.3, 69.2, 69.8, 71.7, 73.4, 73.7, 73.9, 74.2, 74.4, 74.8, 75.3, 75.8, 77.4, 80.0, 81.8, 82.2, 97.9, 101.4, 127.60, 127.64, 127.7, 127.8, 127.9, 128.0, 128.1, 128.17, 128.20, 128.25, 128.28, 128.48, 128.54, 128.8, 131.0, 137.9, 138.0, 138.1, 138.4, 138.8. Anal. Calcd for C₆₂H₆₆O₁₃S: C, 70.84; H, 6.33; S, 3.05. Found: C, 70.85; H, 6.34; S, 3.19.

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (44 α)

Colorless oil, $R_f = 0.38$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20} = 7.2$ (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.33 (s, 3H), 3.34-3.38 (m, 1H), 3.40 (d, $J = 9.6$ Hz, 1H), 3.47 (dd, $J = 9.4, 3.2$ Hz, 1H), 3.58 (d, $J = 11.2$ Hz, 1H), 3.68-3.75 (m, 1H), 3.77-3.88 (m, 2H), 3.94 (dd, $J = 9.4, 2.8$ Hz, 1H), 3.98 (d, $J = 9.6$ Hz, 1H), 4.03 (d, $J = 9.6$ Hz, 1H), 4.36 (dd, $J = 3.2, 1.8$ Hz, 1H), 4.38-4.44 (m, 1H), 4.49 (d, $J = 11.6$ Hz, 1H), 4.56-4.74 (m, 6H), 4.75-4.83 (m, 3H), 4.91 (d, $J = 10.8$ Hz, 1H), 4.93-4.97 (m, 2H), 5.00 (d, $J = 11.6$ Hz, 1H), 7.14-7.52 (m, 30H), 7.93-8.12 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 55.3, 64.4, 66.2, 69.9, 70.3, 72.1, 73.0, 73.4, 73.8, 74.9, 75.1, 75.2, 76.0, 77.8, 79.7, 80.1, 82.3, 98.1, 98.3, 123.5, 127.5, 127.80, 127.83, 127.87, 127.94, 127.98, 128.0, 128.16, 128.20, 128.3, 128.49, 128.53, 128.6, 128.65, 128.67, 130.8, 130.9, 135.5, 138.2, 138.4, 138.7, 150.6, 164.5. HRMS Calcd for C₆₂H₆₃NO₁₄Na [M + Na]⁺, 1068.4146; found, 1068.4148.

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (44 β)

Colorless oil, $R_f = 0.35$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20} = 7.5$ (c 2.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.29 (s, 3H), 3.37 (t, $J = 9.2$ Hz, 1H), 3.43-3.49 (m, 3H), 3.51 (dd, $J = 9.2, 2.4$ Hz, 1H), 3.77-3.85 (m, 1H), 3.81 (d, $J = 2.0$ Hz, 1H), 3.97 (dd, $J = 9.0, 1.6$ Hz, 1H), 3.99 (dd, $J = 9.4, 2.0$ Hz, 1H), 4.11 (d, $J = 10.0$ Hz, 1H), 4.23 (brs, 1H), 4.45-4.57 (m, 4H), 4.56-4.63 (m, 2H), 4.64 (d, $J = 9.2$ Hz, 1H), 4.75 (d, $J = 6.0$ Hz, 1H), 4.76 (d, $J = 12.0$ Hz, 1H), 4.78 (d, $J = 6.4$ Hz, 1H), 4.81 (d, $J = 11.2$ Hz, 1H), 4.92 (d, $J = 10.0$ Hz, 1H), 4.95 (d, $J = 10.8$ Hz, 1H), 4.98 (d, $J = 10.8$ Hz, 1H), 7.15-7.51 (m, 30H), 7.94-8.15 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 64.7, 68.9, 69.9, 71.6, 73.49, 73.51, 74.05, 74.13, 74.9, 75.3, 75.9, 78.0, 80.0, 82.16, 82.20, 97.9, 101.9, 123.5, 127.7, 127.8, 127.9, 127.97, 128.03, 128.1, 128.3, 128.4, 128.5, 128.57, 128.62, 130.9, 135.5, 138.0, 138.2, 138.3, 138.8, 150.5, 164.5. HRMS Calcd for C₆₂H₆₃NO₁₄Na [M + Na]⁺, 1068.4146; found, 1068.4144.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (45 α)

Colorless oil, $R_f = 0.38$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20} = 11.2$ (c 0.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.31 (s, 3H), 3.34-3.38 (m, 1H), 3.44 (dd, $J = 9.4, 3.6$ Hz, 1H), 3.60 (d, $J = 11.2$ Hz, 1H), 3.67-3.73 (m, 1H), 3.78-3.87 (m, 3H), 3.91 (dd, $J = 9.4, 3.6$ Hz, 1H), 3.97 (t, $J = 9.2$ Hz, 1H), 4.08 (t, $J = 9.5$ Hz, 1H), 4.40-4.51 (m, 3H), 4.55-4.63 (m, 4H), 4.73-4.78 (m, 3H), 4.80 (d, $J = 7.6$ Hz, 1H), 4.88 (d, $J = 11.2$ Hz, 1H), 4.91-5.01 (m, 3H), 7.10-8.14 (m, 33H), 7.92-8.13 (m, 2H); ¹³C NMR (100

MHz, CDCl₃) δ 55.2, 63.8, 66.0, 70.0, 70.5, 72.1, 72.7, 73.4, 74.5, 75.0, 75.1, 75.3, 76.0, 77.9, 79.7, 80.1, 82.3, 97.9, 98.2, 127.62, 127.66, 127.78, 127.80, 127.83, 127.89, 127.92, 128.0, 128.10, 128.14, 128.2, 128.26, 128.31, 128.38, 128.42, 128.45, 128.47, 128.55, 128.58, 128.64, 129.8, 129.9, 130.3, 133.0, 138.1, 138.2, 138.3, 138.37, 138.42, 138.5, 138.8, 166.4. HRMS Calcd for C₆₂H₆₄O₁₂Na [M + Na]⁺, 1023.4295; found, 1023.4294.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (45 β)

Colorless oil, R_f = 0.36 (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20}$ = 2.4 (c 1.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.28 (s, 3H), 3.37 (t, J = 9.6 Hz, 1H), 3.43-3.52 (m, 3H), 3.53-3.57 (m, 1H), 3.74-3.83 (m, 2H), 3.94-4.03 (m, 2H), 4.12 (d, J = 10.0 Hz, 1H), 4.19 (s, 1H), 4.44-4.62 (m, 7H), 4.64 (d, J = 12.4 Hz, 1H), 4.76 (d, J = 8.0 Hz, 1H), 4.77-4.84 (m, 3H), 4.91-4.95 (m, 2H), 4.99 (d, J = 10.8 Hz, 1H), 7.20-7.60 (m, 33H), 7.92-8.08 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.1, 64.2, 66.6, 69.9, 71.7, 73.5, 73.8, 73.86, 73.88, 74.7, 74.9, 75.4, 75.9, 77.9, 80.0, 82.2, 97.9, 101.9, 127.5, 127.8, 127.86, 127.87, 128.0, 128.09, 128.14, 128.29, 128.34, 128.4, 128.50, 128.54, 128.56, 128.59, 129.9, 130.2, 133.07, 138.11, 138.2, 138.3, 138.8, 138.9. HRMS Calcd for C₆₂H₆₄O₁₂Na [M + Na]⁺, 1023.4295; found, 1023.4290.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (46 α)

Colorless oil, $R_f = 0.36$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20} = 3.6$ (c 1.9, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 1.99 (s, 3H), 3.32 (s, 3H), 3.34-3.45 (m, 4H), 3.49 (dd, $J = 9.8, 3.2$ Hz, 1H), 3.73 (d, $J = 2.4$ Hz, 1H), 3.78-3.84 (m, 1H), 3.86 (d, $J = 9.2$ Hz, 1H), 4.01 (t, $J = 9.2$ Hz, 1H), 4.12 (s, 1H), 4.13-4.17 (m, 1H), 4.26 (dd, $J = 8.8, 5.6$ Hz, 1H), 4.35 (d, $J = 10.0$ Hz, 1H), 4.46 (d, $J = 12.0$ Hz, 1H), 4.50 (d, $J = 6.4$ Hz, 1H), 4.53-4.59 (m, 3H), 4.66 (d, $J = 12.0$ Hz, 1H), 4.78-4.87 (m, 4H), 4.91 (d, $J = 2.8$ Hz, 1H), 4.93 (d, $J = 10.4$, 1H), 5.02 (d, $J = 10.8$ Hz, 1H), 7.13-7.51 (m, 30H); ¹³C NMR (100 MHz, CDCl₃) δ 21.0, 55.2, 63.9, 68.6, 69.8, 71.6, 73.4, 73.5, 73.7, 73.8, 74.7, 74.9, 75.4, 75.9, 77.8, 79.9, 82.2, 97.9, 101.8, 127.6, 127.7, 127.76, 127.83, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.49, 128.53, 128.57, 128.60, 138.07, 138.12, 138.33, 138.7, 138.9, 171.1. HRMS Calcd for C₅₇H₆₂O₁₂Na [M+Na]⁺, 961.4139; found, 961.4137.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (47)

Colorless oil, $\alpha:\beta=1:9.1$, $R_f = 0.20$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.34-3.39 (m, 1H), 3.42 (s, 3H), 3.51 (dd, $J = 9.2, 2.4$ Hz, 1H), 3.65 (dd, $J = 11.2, 6.0$ Hz, 1H), 3.90 (d, $J = 9.6$ Hz, 1H), 4.09 (d, $J = 2.4$ Hz, 1H), 4.19-4.35 (m,

4H), 4.40-4.53 (m, 5H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.86 (d, $J = 10.4$ Hz, 1H), 4.89 (d, $J = 12.0$ Hz, 1H), 4.97 (d, $J = 12.0$ Hz, 1H), 5.20-5.28 (m, 2H), 5.58 (t, $J = 10.0$ Hz, 1H), 6.18 (t, $J = 10.0$ Hz, 1H), 7.23-7.51 (m, 29H), 7.82-8.02 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.6, 57.0, 68.4, 68.8, 68.9, 69.3, 70.5, 71.4, 72.2, 73.5, 74.0, 74.2, 74.6, 75.2, 81.7, 97.0 (β -OMe), 102.2 (C1, β -anomer), 127.6, 127.8, 127.9, 128.08, 128.12, 128.2, 128.26, 128.28, 128.31, 128.4, 128.5, 128.6, 128.8, 128.9, 129.1, 129.3, 129.7, 129.9, 130.0, 130.9, 131.0, 133.1, 133.4, 133.6, 137.9, 138.0, 138.5, 165.5, 165.8, 165.9. HRMS Calcd for $\text{C}_{62}\text{H}_{60}\text{O}_{16}\text{SNa}$ $[\text{M} + \text{Na}]^+$, 1115.3494; found, 1115.3492.

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (48 α)

Colorless oil, $R_f = 0.35$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_{\text{D}}^{20} = 61.4$ (c 0.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 3.40 (s, 3H), 3.61 (dd, $J = 8.4, 1.6$ Hz, 1H), 3.77 (brs, 1H), 3.81-3.86 (m, 1H), 3.88 (dd, $J = 11.0, 4.4$ Hz, 1H), 3.97-4.02 (m, 1H), 4.03 (d, $J = 9.2$ Hz, 1H), 4.15-4.21 (m, 1H), 4.35 (dd, $J = 11.6, 4.0$ Hz, 1H), 4.43 (d, $J = 10.8$ Hz, 1H), 4.57-4.63 (m, 2H), 4.64 (d, $J = 12.4$ Hz, 1H), 4.76 (d, $J = 12.0$ Hz, 1H), 4.93 (d, $J = 8.4$ Hz, 1H), 4.95 (d, $J = 11.2$ Hz, 1H), 5.15-5.23 (m, 2H), 5.53 (t, $J = 10.0$ Hz, 1H), 6.13 (t, $J = 9.6$ Hz, 1H), 5.46 (t, $J = 9.6$ Hz, 1H), 6.13 (d, $J = 9.6$ Hz, 1H), 7.13-7.53 (m, 24H), 7.92-8.17 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.7, 64.5, 66.3, 68.3, 69.8, 70.3, 70.5, 72.15, 72.22, 73.1, 73.7, 75.1, 79.9, 97.1, 98.3, 123.6, 127.8, 127.86, 127.88, 127.93, 128.0, 128.3, 128.46, 128.49, 128.55, 128.58, 129.06, 129.14, 129.3, 129.8,

130.0, 130.1, 130.9, 133.3, 133.6, 135.5, 138.3, 138.4, 150.6, 164.4, 165.3, 165.95, 166.01. HRMS Calcd for $C_{62}H_{57}NO_{17}Na$ $[M + Na]^+$, 1110.3524; found, 1110.3521.

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (48 β)

Colorless oil, $R_f = 0.32$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_D^{20} = 10.3$ (c 1.2, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 3H), 3.51-3.61 (m, 2H), 3.67 (dd, $J = 10.4, 7.2$ Hz, 1H), 3.99 (t, $J = 9.2$ Hz, 1H), 4.07-4.17 (m, 2H), 4.25-4.33 (m, 1H), 4.44 (dd, $J = 11.6, 4.4$ Hz, 1H), 4.47-4.68 (m, 5H), 4.87 (d, $J = 12.0$ Hz, 1H), 4.95 (d, $J = 10.8$ Hz, 1H), 5.02 (d, $J = 11.6$ Hz, 1H), 5.21 (brs, 1H), 5.22-5.27 (m, 1H), 5.46 (t, $J = 9.6$ Hz, 1H), 6.13 (d, $J = 9.6$ Hz, 1H), 7.13-7.53 (m, 24H), 7.92-8.17 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 64.7, 66.2, 69.0, 69.1, 69.7, 70.5, 71.5, 72.3, 73.7, 73.9, 74.3, 74.5, 75.2, 82.2, 97.0, 102.6, 123.6, 127.8, 127.86, 127.93, 128.00, 128.2, 128.38, 128.40, 128.6, 128.9, 129.2, 129.3, 129.8, 129.9, 130.1, 130.9, 133.3, 133.5, 133.7, 135.5, 138.0, 138.9, 150.6, 164.5, 165.7, 164.9. HRMS Calcd for $C_{62}H_{57}NO_{17}Na$ $[M + Na]^+$, 1110.3524; found, 1110.3525.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (49 α)

Colorless oil, $R_f = 0.36$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 67.3$ (c 1.9, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.39 (s, 3H), 3.60 (dd, $J = 11.0, 3.2$ Hz, 1H), 3.72-3.75 (m, 1H), 3.77-3.84 (m, 1H), 3.90 (dd, $J = 11.0, 4.4$ Hz, 1H), 3.95 (dd, $J = 9.4, 3.2$ Hz, 1H), 4.03 (t, $J = 9.6$ Hz, 1H), 4.12-4.19 (m, 1H), 4.34 (dd, $J = 11.8, 4.4$ Hz, 1H), 4.42 (dd, $J = 12.0, 2.0$ Hz, 1H), 4.52-4.59 (m, 3H), 4.65 (d, $J = 12.4$ Hz, 1H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.90 (d, $J = 1.2$ Hz, 1H), 4.94 (d, $J = 10.8$ Hz, 1H), 5.17 (q, $J = 3.6$, 1H), 5.19 (dd, $J = 9.6, 3.6$ Hz, 1H), 5.55 (t, $J = 10.0$ Hz, 1H), 6.12 (t, $J = 10.0$ Hz, 1H), 7.22-7.65 (m, 27H), 7.82-8.14 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 55.7, 63.7, 66.3, 67.8, 68.3, 69.8, 70.5, 70.6, 72.2, 72.3, 74.4, 75.1, 75.3, 80.0, 97.1, 98.2, 125.8, 127.6, 127.8, 128.0, 128.2, 128.4, 128.46, 128.51, 128.4, 128.6, 129.1, 129.2, 129.4, 129.79, 129.82, 130.0, 130.1, 130.2, 133.0, 133.2, 133.5, 136.1, 138.4, 138.5, 165.2, 166.0, 166.4. HRMS Calcd for C₆₂H₅₈O₁₅Na [M + Na]⁺, 1065.3673; found, 1065.3678.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (49 β)

Colorless oil, $R_f = 0.34$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 5.3$ (c 2.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.39 (s, 3H), 3.52-3.57 (m, 1H), 3.57 (dd, $J = 9.6, 2.4$ Hz, 1H), 3.66 (dd, $J = 10.0, 6.8$ Hz, 1H), 4.04 (t, $J = 9.6$ Hz, 1H), 4.10 (d, $J = 2.4$ Hz, 1H), 4.17 (d, $J = 10.4$ Hz, 1H), 4.24-4.33 (m, 1H), 4.43-4.63 (m, 6H), 4.91 (d, $J = 12.8$ Hz, 1H), 4.94 (d, $J = 11.6$ Hz, 1H), 5.05 (d, $J = 12.0$ Hz, 1H), 5.21 (dd, $J = 12.0, 3.2$ Hz, 1H), 5.25 (s, 1H), 5.49 (t, $J = 10.0$ Hz, 1H), 6.16 (t, $J = 10.0$ Hz, 1H), 7.22-7.62

(m, 27H), 7.82-8.05 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 64.0, 68.87, 68.91, 69.6, 70.6, 71.5, 72.3, 74.0, 74.1, 74.2, 74.4, 75.4, 82.1, 96.9, 102.6, 127.5, 127.8, 127.9, 128.2, 128.3, 128.38, 128.41, 128.5, 128.9, 129.2, 129.3, 129.8, 129.86, 129.88, 130.0, 130.1, 133.0, 133.2, 133.5, 133.6, 138.0, 138.1, 138.9, 165.6, 165.8, 166.0, 166.4. HRMS Calcd for $\text{C}_{62}\text{H}_{58}\text{O}_{15}\text{Na}$ $[\text{M} + \text{Na}]^+$, 1065.3673; found, 1065.3676.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-acetyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (50)

Colorless oil, $\alpha:\beta=2.2:1$, $R_f=0.36$ (hexane/EtOAc/ CH_2Cl_2 , 5:1:1, v/v/v); ^1H NMR (400 MHz, CDCl_3) δ 1.87 (s, 3H), 1.95 (s, 1.4H), 3.40 (s, 1.3H), 3.44 (s, 3H), 3.52 (dd, $J=9.2, 2.8$ Hz, 1H), 3.57-3.74 (m, 2.9H), 3.82-3.93 (m, 2.7H), 4.07 (d, $J=2.4$ Hz, 1H), 4.13-4.18 (m, 2.6H), 4.20-4.27 (m, 1.4H), 4.29 (d, $J=1.8$ Hz, 0.8H), 4.30-4.37 (m, 1.4H), 4.42 (s, 1H), 4.44 (d, $J=12.0$ Hz, 1H), 4.52 (d, $J=12.0$ Hz, 1H), 4.55 (d, $J=12.0$ Hz, 1H), 4.56 (d, $J=10.8$ Hz, 1H), 4.70 (q, $J=12.4$ Hz, 1.2H), 4.88-4.97 (m, 3.2H), 5.02 (d, $J=12.4$ Hz, 1H), 5.18 (d, $J=3.6$ Hz, 0.6H), 5.23-5.28 (m, 2.8H), 5.48 (t, $J=10.0$ Hz, 1H), 5.58 (d, $J=10.0$ Hz, 0.5H), 6.13 (t, $J=10.0$ Hz, 0.5H), 6.17 (t, $J=9.2$ Hz, 1H), 7.23-7.54 (m, 35H), 7.84-8.02 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.8, 21.0, 55.6, 55.7, 63.5, 63.8, 66.2, 68.2, 68.8, 69.0, 69.6, 69.7, 70.3, 70.5, 70.6, 71.4, 72.1, 72.17, 72.24, 72.7, 73.6, 73.7, 74.2, 74.4, 74.5, 74.7, 75.2, 75.3, 79.9, 82.1, 96.9 (β -OMe), 97.1 (α -OMe), 98.3 (C1, α -anomer), 102.4 (C1, β -anomer), 127.66, 127.74, 127.8, 127.9, 128.0, 128.1, 128.2, 128.26, 128.32, 128.4, 128.45, 128.47,

128.49, 128.54, 128.59, 128.8, 129.07, 129.11, 129.3, 129.7, 129.9, 129.97, 130.03, 133.2, 133.5, 133.7, 138.0, 138.1, 138.4, 138.5, 138.7, 165.2, 165.6, 165.8, 166.0, 170.93, 171.02. HRMS Calcd for C₅₇H₅₆O₁₅Na [M+Na]⁺, 1003.3517; found, 1003.3519.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannoside (51 α)

Colorless oil, R_f = 0.36 (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20}$ = 4.4 (c 0.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.30 (s, 3H), 3.74-3.80 (m, 2H), 3.82-3.86 (m, 2H), 3.88-3.97 (m, 4H), 4.02 (brs, 1H), 4.23 (d, J = 5.6 Hz, 1H), 4.32 (d, J = 14.0 Hz, 1H), 4.35-4.45 (m, 4H), 4.47 (d, J = 12.4 Hz, 1H), 4.52 (d, J = 12.4 Hz, 1H), 4.62 (d, J = 10.0 Hz, 1H), 4.63 (d, J = 11.2 Hz, 1H), 4.65 (s, 2H), 4.81 (d, J = 8.4 Hz, 1H), 4.84 (d, J = 7.6 Hz, 1H), 5.19 (d, J = 1.6 Hz, 1H), 5.61 (s, 1H), 7.22-7.42 (m, 28H), 7.50-7.52 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.0, 57.0, 63.7, 69.0, 69.5, 71.1, 72.1, 72.8, 73.6, 74.2, 75.1, 75.4, 76.1, 76.8, 79.3, 79.4, 100.3, 100.9, 101.6, 125.9, 126.2, 127.75, 127.80, 127.84, 127.9, 128.0, 128.1, 128.4, 128.54, 128.55, 128.7, 129.0, 129.06, 129.08, 131.0, 136.2, 137.7, 138.0, 138.1, 138.2, 138.3, 138.4. HRMS Calcd for C₅₅H₅₈O₁₃SNa [M + Na]⁺, 981.3496; found, 981.3494.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (51 β)

Colorless oil, $R_f = 0.33$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20} = -22.3$ (c 2.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.36 (s, 3H), 3.44 (dd, $J = 9.6, 2.4$ Hz, 1H), 3.53 (dd, $J = 9.2, 2.8$ Hz, 1H), 3.76 (q, $J = 10.4$ Hz, 1H), 3.78-3.84 (m, 1H), 3.92 (t, $J = 9.2$ Hz, 1H), 3.98 (dd, $J = 12.8, 3.2$ Hz, 1H), 4.00 (s, 1H), 4.08 (t, $J = 9.6$ Hz, 1H), 4.22 (d, $J = 14.0$ Hz, 1H), 4.25 (dd, $J = 8.8, 3.2$ Hz, 1H), 4.28-4.34 (m, 2H), 4.39 (d, $J = 14.0$ Hz, 1H), 4.47 (dd, $J = 10.8, 3.6$ Hz, 1H), 4.48 (s, 1H), 4.50 (dd, $J = 8.8, 1.6$ Hz, 1H), 4.57 (d, $J = 12.0$ Hz, 1H), 4.60 (s, 1H), 4.68 (d, $J = 12.4$ Hz, 1H), 4.74 (d, $J = 0.8$ Hz, 1H), 4.86 (d, $J = 11.6$ Hz, 1H), 4.88 (d, $J = 11.6$ Hz, 1H), 4.93 (d, $J = 12.0$ Hz, 1H), 4.99 (d, $J = 12.0$ Hz, 1H), 5.50 (s, 1H), 7.14-7.58 (m, 30H); ¹³C NMR (100 MHz, CDCl₃) δ 55.1, 56.9, 64.1, 69.0, 69.2, 71.1, 71.3, 73.7, 73.9, 74.2, 74.3, 74.7, 75.3, 77.5, 78.7, 81.6, 99.4, 100.1, 101.7, 126.3, 127.4, 127.6, 127.7, 127.77, 127.84, 128.0, 128.1, 128.30, 128.33, 128.56, 128.60, 128.7, 128.8, 129.0, 131.0, 137.4, 137.8, 137.6, 137.99, 138.02. HRMS Calcd for C₅₅H₅₈O₁₃SNa [M + Na]⁺, 981.3496; found, 981.3492.

Methyl [2,3,4-tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannoside (52 α)

Colorless oil, $R_f = 0.38$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = -39.0$ (c 1.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.35 (s, 3H), 3.56-3.61 (m, 1H), 3.62 (dd, $J =$

9.2, 2.8 Hz, 1H), 3.71-3.81 (m, 2H), 3.93 (dd, $J = 9.8, 3.6$ Hz, 1H), 4.01-4.11 (m, 3H), 4.25 (d, $J = 5.6$ Hz, 1H), 4.34 (d, $J = 2.0$ Hz, 1H), 4.51 (d, $J = 10.0$ Hz, 1H), 4.52 (q, $J = 6.0$ Hz, 1H), 4.54 (d, $J = 11.6$ Hz, 1H), 4.61 (d, $J = 11.2$ Hz, 1H), 4.63-4.69 (m, 3H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.76 (brs, 1H), 4.91 (d, $J = 11.6$ Hz, 1H), 4.96 (d, $J = 10.8$ Hz, 1H), 5.07 (d, $J = 11.6$ Hz, 1H), 5.46 (s, 1H), 7.03-7.58 (m, 25H), 7.92-8.04 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.1, 64.1, 64.3, 69.0, 70.7, 71.4, 73.4, 73.7, 73.8, 74.1, 74.15, 74.21, 75.2, 78.4, 82.1, 99.1, 99.6, 101.8, 123.5, 126.2, 127.2, 127.3, 127.7, 127.9, 128.0, 128.1, 128.3, 128.36, 128.37, 128.5, 128.56, 128.61, 129.0, 130.8, 135.3, 137.6, 138.0, 138.7, 138.9, 150.5, 164.5. Anal. Calcd for $\text{C}_{55}\text{H}_{55}\text{NO}_{14}$: C, 69.24; H, 5.81; N, 1.47. Found: C, 69.28; H, 5.87; N, 1.39.

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannoside (52 β)

Colorless oil, $R_f = 0.35$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_{\text{D}}^{20} = 17.4$ (c 0.9, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 3.29 (s, 3H), 3.70-3.74 (m, 1H), 3.79 (q, $J = 10.4$ Hz, 1H), 3.92-4.01 (m, 4H), 4.03-4.11 (m, 3H), 4.25 (dd, $J = 9.2, 4.0$ Hz, 1H), 4.44 (d, $J = 12.0$ Hz, 1H), 4.52 (dd, $J = 11.6, 4.4$ Hz, 1H), 4.53 (d, $J = 11.6$ Hz, 1H), 4.59 (dd, $J = 11.6, 2.0$ Hz, 1H), 4.61-4.71 (m, 5H), 4.82 (d, $J = 11.6$ Hz, 1H), 4.96 (d, $J = 10.8$ Hz, 1H), 5.27 (d, $J = 1.6$ Hz, 1H), 5.63 (s, 1H), 7.13-7.63 (m, 25H), 8.02-8.14 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 54.9, 63.9, 64.7, 69.0, 70.8, 72.1, 72.7, 73.7, 74.0, 75.2, 75.4, 76.1, 76.3, 79.5, 99.9, 101.1, 101.7, 123.5, 126.2, 127.75, 127.78, 127.9, 128.0, 128.1,

128.39, 128.41, 128.51, 128.52, 128.59, 128.61, 129.1, 130.9, 135.5, 137.7, 138.0, 138.4, 138.5, 150.8, 164.6. HRMS Calcd for $C_{55}H_{55}NO_{14}Na$ $[M + Na]^+$, 976.3520; found, 976.3521.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (53 α)

Colorless oil, $R_f = 0.33$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_D^{20} = -2.3$ (c 2.4, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 3.24 (s, 3H), 3.70-3.75 (m, 1H), 3.76 (q, $J = 9.2$ Hz, 1H), 3.90-3.97 (m, 3H), 3.98-4.11 (m, 4H), 4.23 (dd, $J = 9.2, 3.6$ Hz, 1H), 4.46-4.55 (m, 3H), 4.57-4.65 (m, 2H), 4.66-4.72 (m, 3H), 4.79 (d, $J = 11.6$ Hz, 1H), 4.96 (d, $J = 10.4$ Hz, 1H), 5.25 (s, 1H), 7.20-7.58 (m, 33H), 7.97-8.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.7, 63.8, 64.2, 69.0, 71.0, 72.2, 72.5, 73.5, 74.7, 75.2, 75.6, 76.1, 76.2, 79.4, 79.5, 99.9, 101.1, 101.6, 126.2, 127.5, 127.6, 127.8, 127.88, 127.94, 128.0, 128.2, 128.3, 128.37, 128.43, 128.47, 128.51, 128.54, 128.6, 129.1, 129.9, 130.2, 133.1, 137.8, 138.1, 138.5, 166.5. HRMS Calcd for $C_{55}H_{56}O_{12}Na$ $[M+Na]^+$, 931.3669; found, 931.3665.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (53 β)

Colorless oil, $R_f = 0.15$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_D^{20} = -52.5$ (c 4.7,

CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.32 (s, 3H), 3.60 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.62-3.65 (m, 1H), 3.73-3.83 (m, 2H), 3.93 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.03 (d, *J* = 9.6 Hz, 1H), 4.05 (d, *J* = 2.8 Hz, 1H), 4.09 (d, *J* = 9.6 Hz, 1H), 4.24 (q, *J* = 5.2 Hz, 1H), 4.36 (d, *J* = 2.0 Hz, 1H), 4.47-4.55 (m, 3H), 4.61-4.65 (m, 2H), 4.59 (d, *J* = 6.0 Hz, 1H), 4.67 (dd, *J* = 11.8, 1.2 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.76 (brs, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.99 (brs, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 5.48 (s, 1H), 6.98-7.13 (m, 3H), 7.20-7.37 (m, 20H), 7.47-7.56 (m, 5H), 7.97-8.01 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.0, 63.9, 64.0, 69.0, 70.4, 71.3, 73.1, 73.6, 73.7, 73.8, 74.2, 74.4, 75.4, 78.3, 82.0, 99.0, 99.6, 101.7, 126.2, 127.2, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.25, 128.28, 128.4, 128.5, 128.6, 128.9, 129.8, 130.0, 133.0, 137.6, 138.0, 138.1, 138.6, 138.8, 166.4. Anal. Calcd for C₅₅H₅₆O₁₂: C, 72.67; H, 6.21. Found: C, 72.58; H, 6.37.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (54 α)

Colorless oil, *R_f* = 0.38 (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); [α]_D²⁰ = −68.9 (c 3.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 2.06 (s, 3H), 3.33 (s, 3H), 3.70-3.76 (m, 1H), 3.78 (t, *J* = 10.0 Hz, 1H), 3.88-3.98 (m, 6H), 4.04 (brs, 1H), 4.23 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.28-4.33 (m, 1H), 4.37 (d, *J* = 11.2 Hz, 1H), 4.49 (d, *J* = 12.4 Hz, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 4.57 (d, *J* = 10.4 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 1.2 Hz, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.94 (d, *J* = 10.4 Hz, 1H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.62

(s, 1H), 7.22-7.43 (m, 23H), 7.47-7.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 55.0, 63.7, 63.8, 69.0, 70.7, 72.0, 72.3, 73.5, 74.7, 74.8, 75.4, 76.0, 76.5, 76.8, 79.4, 79.5, 100.1, 101.0, 101.6, 126.2, 127.6, 127.7, 127.8, 127.85, 127.89, 128.0, 128.3, 128.35, 128.38, 128.49, 128.50, 128.6, 129.0, 137.7, 138.1, 138.4, 138.47, 138.49, 171.0. HRMS Calcd for $\text{C}_{50}\text{H}_{54}\text{O}_{12}\text{Na}$ $[\text{M} + \text{Na}]^+$, 869.3513; found, 869.3510.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (55)

Colorless oil, $\alpha:\beta=1:15.9$, $R_f = 0.35$ (hexane/EtOAc/ CH_2Cl_2 , 5:1:2, v/v/v); $[\alpha]_{\text{D}}^{20} = 11.7$ (c 1.8, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 3.27-3.37 (m, 4H), 3.39-3.51 (m, 4H), 3.70 (d, $J = 2.4$ Hz, 1H), 3.75-3.81 (m, 1H), 3.87 (t, $J = 9.2$ Hz, 1H), 4.01 (t, $J = 9.2$ Hz, 1H), 4.08-4.16 (m, 2H), 4.23 (d, $J = 14.0$ Hz, 1H), 4.33 (dd, $J = 11.2, 4.0$ Hz, 1H), 4.46-4.58 (m, 7H), 4.62 (d, $J = 12.0$ Hz, 1H), 4.71 (d, $J = 12.0$ Hz, 1H), 4.75 (d, $J = 12.0$ Hz, 1H), 4.79-4.89 (m, 4H), 5.00 (d, $J = 10.8$ Hz, 1H), 7.16-7.38 (m, 35H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.2, 57.1, 68.3, 69.3, 69.9, 71.7, 73.5, 73.8, 74.0, 74.3, 74.4, 74.9, 75.4, 75.9, 77.5, 80.1, 81.8, 82.3, 98.0, 101.5, 127.66, 127.69, 127.8, 127.86, 127.91, 128.07, 128.12, 128.2, 128.26, 128.31, 128.33, 128.55, 128.60, 128.8, 131.1, 138.0, 138.1, 138.2, 138.5, 138.9. Anal. Calcd for $\text{C}_{62}\text{H}_{66}\text{O}_{13}\text{S}$: C, 70.84; H, 6.33; S, 3.05. Found: C, 70.78; H, 6.46; S, 3.07.

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (56 α)

Colorless oil, $R_f = 0.43$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 22.7$ (c 0.9, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.38 (s, 3H), 3.46-3.54 (m, 2H), 3.61 (dd, $J = 11.2, 1.6$ Hz, 1H), 3.68 (dd, $J = 10.8, 1.6$ Hz, 1H), 3.71 (dd, $J = 11.2, 4.0$ Hz, 1H), 3.74-3.80 (m, 1H), 3.80-3.85 (m, 1H), 3.88 (dd, $J = 11.2, 4.8$ Hz, 1H), 3.96-4.03 (m, 2H), 4.23 (t, $J = 9.6$ Hz, 1H), 4.44 (d, $J = 1.6$ Hz, 1H), 4.47 (d, $J = 1.6$ Hz, 1H), 4.49 (d, $J = 11.2$ Hz, 1H), 4.55 (d, $J = 11.2$ Hz, 1H), 4.57 (d, $J = 3.6$ Hz, 1H), 4.61 (d, $J = 11.2$ Hz, 1H), 4.65 (d, $J = 12.4$ Hz, 1H), 4.66 (d, $J = 12.4$ Hz, 1H), 4.69 (d, $J = 12.4$ Hz, 1H), 4.78 (d, $J = 12.0$ Hz, 1H), 4.81 (d, $J = 10.4$ Hz, 1H), 4.96 (d, $J = 11.2$ Hz, 1H), 4.99 (d, $J = 10.4$ Hz, 1H), 5.03 (d, $J = 1.6$ Hz, 1H), 5.47 (dd, $J = 9.2, 3.2$ Hz, 1H), 6.98-7.38 (m, 30H), 8.05 (d, $J = 9.2$ Hz, 1H), 8.23 (d, $J = 9.2$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.3, 66.3, 68.8, 70.0, 71.8, 73.0, 73.53, 73.54, 73.7, 74.8, 75.1, 75.3, 75.9, 76.1, 77.9, 80.3, 82.4, 98.1, 98.2, 123.6, 127.7, 127.8, 127.9, 128.07, 128.11, 128.2, 128.38, 128.44, 128.46, 128.53, 128.6, 130.9, 135.5, 137.9, 138.1, 138.3, 138.4, 138.8, 150.7, 163.9. HRMS Calcd for C₆₂H₆₃NO₁₄Na [M + Na]⁺, 1068.4146; found, 1068.4142.

Methyl [2,4,6-tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (56 β)

Colorless oil, $R_f = 0.33$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 8.9$ (c 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.29 (s, 3H), 3.37 (t, $J = 9.2$ Hz, 1H), 3.43-3.55 (m, 4H), 3.77-3.85 (m, 2H), 3.94-4.02 (m, 2H), 4.12 (dd, $J = 10.4, 1.6$ Hz, 1H), 4.23 (s, 1H), 4.45-4.67 (m, 8H), 4.73-4.84 (m, 4H), 4.92 (d, $J = 12.0$ Hz, 1H), 4.95 (d, $J = 10.8$ Hz, 1H), 4.98 (d, $J = 10.4$ Hz, 1H), 7.16-7.45 (m, 30H), 8.01-8.09 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 64.7, 68.9, 69.9, 71.6, 73.49, 73.51, 74.05, 74.12, 74.9, 75.3, 75.9, 78.0, 80.0, 82.16, 82.20, 97.9, 101.9, 123.5, 127.7, 127.8, 127.9, 127.97, 128.04, 128.1, 128.3, 128.4, 128.5, 128.6, 130.9, 135.5, 137.97, 138.01, 138.1, 138.3, 138.8, 150.5, 164.5. HRMS Calcd for C₆₂H₆₃NO₁₄Na [M + Na]⁺, 1068.4146; found, 1068.4142.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (57 α)

Colorless oil, $R_f = 0.40$ (hexane/EtOAc/CH₂Cl₂, 5:1:1, v/v/v); $[\alpha]_D^{20} = 28.6$ (c 0.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.37 (s, 3H), 3.50 (t, $J = 9.2$ Hz, 1H), 3.52 (dd, $J = 9.6, 2.0$ Hz, 1H), 3.59 (dd, $J = 10.8, 2.0$ Hz, 1H), 3.66 (dd, $J = 11.2, 1.6$ Hz, 1H), 3.70 (dd, $J = 11.2, 4.4$ Hz, 1H), 3.73-3.79 (m, 1H), 3.81-3.86 (m, 1H), 3.88 (dd, $J = 11.2, 4.4$ Hz, 1H), 3.98 (t, $J = 9.2$ Hz, 1H), 4.00-4.03 (m, 1H), 4.21 (t, $J = 9.6$ Hz, 1H), 4.44 (d, $J = 12.0$ Hz, 1H), 4.46 (d, $J = 10.8$ Hz, 1H), 4.54 (d, $J = 3.2$ Hz, 1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.60 (d, $J = 10.0$ Hz, 1H), 4.63 (d, $J = 11.2$ Hz, 1H), 4.65 (d, $J = 10.8$ Hz, 1H), 4.66 (d, $J = 11.6$ Hz, 1H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.78 (d, $J = 12.0$ Hz, 1H), 4.81 (d,

$J = 10.8$ Hz, 1H), 4.95 (d, $J = 11.2$ Hz, 1H), 4.98 (d, $J = 10.8$ Hz, 1H), 5.01 (d, $J = 2.0$ Hz, 1H), 5.50 (dd, $J = 9.6, 3.2$ Hz, 1H), 6.98-7.05 (m, 2H), 7.11-7.18 (m, 5H), 7.21-7.39 (m, 23H), 7.40-7.48 (m, 2H), 7.54-7.61 (m, 1H), 8.00-8.07 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.3, 66.2, 68.9, 70.0, 71.6, 73.0, 73.5, 73.6, 74.6, 74.9, 75.2, 75.8, 76.1, 77.9, 80.2, 82.4, 98.0, 98.5, 127.67, 127.72, 127.8, 127.99, 128.04, 128.2, 128.3, 128.37, 128.43, 128.5, 128.6, 129.9, 130.2, 133.2, 138.1, 138.3, 138.37, 138.41, 138.9, 165.7. Anal. Calcd for $\text{C}_{62}\text{H}_{64}\text{O}_{12}$: C, 74.38; H, 6.44. Found: C, 74.41; H, 6.55.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (58 α)

Colorless oil, $R_f = 0.38$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_{\text{D}}^{20} = 28.4$ (c 2.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 1.95 (s, 3H), 3.35 (s, 3H), 3.46 (dd, $J = 10.0, 8.8$ Hz, 1H), 3.49 (dd, $J = 9.6, 3.6$ Hz, 1H), 3.57 (dd, $J = 10.8, 1.6$ Hz, 1H), 3.61-3.69 (m, 2H), 3.71-3.80 (m, 2H), 3.83 (dd, $J = 11.2, 4.8$ Hz, 1H), 3.88 (dd, $J = 2.8, 2.0$ Hz, 1H), 3.97 (t, $J = 9.2$ Hz, 1H), 4.04 (t, $J = 9.6$ Hz, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 4.46 (d, $J = 12.0$ Hz, 1H), 4.53 (d, $J = 10.8$ Hz, 1H), 4.55 (d, $J = 2.0$ Hz, 1H), 4.58 (d, $J = 11.2$ Hz, 1H), 4.61 (d, $J = 11.2$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 1H), 4.64 (d, $J = 12.0$ Hz, 1H), 4.65 (d, $J = 12.0$ Hz, 1H), 4.77 (d, $J = 11.6$ Hz, 1H), 4.80 (d, $J = 10.4$ Hz, 1H), 4.92 (d, $J = 11.2$ Hz, 1H), 4.95 (d, $J = 1.6$ Hz, 1H), 4.97 (d, $J = 10.4$ Hz, 1H), 5.23 (dd, $J = 9.6, 3.2$ Hz, 1H), 7.12-7.16 (m, 2H), 7.23-7.35 (m, 28H); ^{13}C NMR (100 MHz, CDCl_3) δ

21.2, 55.2, 66.2, 68.9, 70.0, 71.7, 72.9, 73.51, 73.54, 73.9, 74.7, 75.1, 75.8, 76.1, 77.9, 80.2, 82.4, 98.0, 98.3, 127.6, 127.70, 127.74, 127.75, 127.80, 127.83, 127.96, 128.02, 128.1, 128.2, 128.41, 128.42, 128.5, 128.6, 138.2, 138.3, 138.4, 138.5, 138.9, 170.3.

HRMS Calcd for $C_{57}H_{62}O_{12}Na$ $[M + Na]^+$, 961.4139; found, 961.4141.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (59 α)

Colorless oil, R_f = 0.55 (hexane/EtOAc/ CH_2Cl_2 , 5:1:2, v/v/v); $[\alpha]_D^{20}$ = 70.4 (c 1.5, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 3.42-3.49 (m, 4H), 3.54-3.64 (m, 3H), 3.87 (dd, J = 11.6, 4.8 Hz, 1H), 4.02-4.13 (m, 3H), 4.19-4.25 (m, 1H), 4.36 (d, J = 12.0 Hz, 1H), 4.42 (d, J = 10.8 Hz, 1H), 4.53 (d, J = 13.6 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.62-4.72 (m, 3H), 4.89 (d, J = 1.6 Hz, 1H), 5.06 (dd, J = 9.6, 2.8 Hz, 1H), 5.22 (d, J = 3.6 Hz, 1H), 5.28 (dd, J = 10.4, 3.6 Hz, 1H), 5.64 (t, J = 10.0 Hz, 1H), 6.12 (t, J = 10.0 Hz, 1H), 7.17-7.54 (m, 29H), 7.83-7.92 (m, 4H), 7.96-8.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 56.4, 65.9, 68.3, 68.6, 69.2, 70.8, 72.2, 72.3, 73.4, 73.47, 73.50, 75.2, 77.0, 81.2, 97.1, 98.2, 127.7, 127.89, 127.94, 128.0, 128.2, 128.39, 128.43, 128.9, 129.0, 129.2, 129.4, 129.8, 130.1, 131.0, 133.2, 133.5, 137.9, 138.0, 138.2, 165.4, 165.89, 165.93. HRMS Calcd for $C_{62}H_{60}O_{16}SNa$ $[M + Na]^+$, 1115.3500; found, 1115.3497.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (59 β)

Colorless oil, $R_f = 0.43$ (hexane/EtOAc/CH₂Cl₂, 5:1:2, v/v/v); $[\alpha]_D^{20} = 17.2$ (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.36-3.43 (m, 4H), 3.63-3.73 (m, 3H), 3.99 (t, $J = 9.6$ Hz, 1H), 4.04 (d, $J = 14.0$ Hz, 1H), 4.11-4.14 (m, 2H), 4.12 (d, $J = 14.0$ Hz, 1H), 4.25-4.32 (m, 1H), 4.39 (d, $J = 10.8$ Hz, 1H), 4.44 (d, $J = 12.0$ Hz, 1H), 4.47 (s, 1H), 4.57 (d, $J = 10.8$ Hz, 1H), 4.58 (d, $J = 12.0$ Hz, 1H), 4.61 (dd, $J = 9.6, 3.2$ Hz, 1H), 4.72 (d, $J = 12.0$ Hz, 1H), 5.01 (d, $J = 12.0$ Hz, 1H), 5.22 (s, 1H), 5.23 (dd, $J = 13.6, 3.6$ Hz, 1H), 5.46 (t, $J = 10.0$ Hz, 1H), 6.15 (t, $J = 9.6$ Hz, 1H), 7.14-7.18 (m, 2H), 7.25-7.53 (m, 27H), 7.82-8.01 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 55.6, 57.3, 68.8, 69.1, 69.7, 70.6, 72.3, 73.1, 73.7, 75.0, 75.7, 77.1, 81.9, 96.9, 101.7, 127.6, 127.7, 128.0, 128.1, 128.2, 128.3, 128.46, 128.49, 128.56, 128.60, 129.0, 129.1, 129.2, 129.4, 129.8, 130.0, 130.1, 130.8, 133.2, 133.5, 133.6, 137.7, 138.3, 138.7, 165.6, 165.9, 166.0. Anal. Calcd for C₆₂H₆₀O₁₆S: C, 68.12; H, 5.53; S, 2.93. Found: C, 68.08; H, 5.62; S, 2.81.

Methyl [2,4,6-tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (60 α)

Colorless oil, $R_f = 0.45$ (hexane/EtOAc/CH₂Cl₂, 5:1:2, v/v/v); $[\alpha]_D^{20} = 27.3$ (c 2.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.48 (s, 3H), 3.58 (dd, $J = 10.8, 1.6$ Hz, 1H), 3.65 (dd, $J = 10.8, 2.4$ Hz, 1H), 3.72 (dd, $J = 10.8, 3.6$ Hz, 1H), 3.83-3.89 (m, 1H), 3.92-4.02 (m, 2H), 4.23 (t, $J = 9.6$ Hz, 1H), 4.25-4.30 (m, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 4.44 (d, $J = 12.0$ Hz, 1H), 4.51 (d, $J = 11.6$ Hz, 1H), 4.57 (d, $J = 11.6$ Hz, 1H), 4.65 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 4.98 (d, $J = 1.6$ Hz, 1H), 5.21-5.29 (m, 2H), 5.51 (dd, $J = 9.6, 3.2$ Hz, 1H), 5.59 (t, $J = 10.0$ Hz, 1H), 6.16 (t, $J = 10.0$ Hz, 1H), 7.03-7.07 (m, 2H), 7.11-7.17 (m, 5H), 7.21-7.51 (m, 17H), 7.84-7.89 (m, 2H), 7.92-8.01 (m, 4H), 8.02-8.07 (m, 2H), 8.20-8.25 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 55.7, 66.4, 68.4, 68.7, 69.8, 70.6, 71.8, 72.3, 73.0, 73.4, 73.6, 74.7, 75.1, 76.1, 97.0, 98.0, 123.6, 127.7, 127.76, 127.79, 127.9, 128.0, 128.35, 128.39, 128.43, 128.5, 129.1, 129.2, 129.4, 129.8, 130.1, 130.9, 133.2, 133.4, 133.5, 135.6, 137.9, 138.1, 138.3, 150.6, 163.8, 165.3, 166.0. HRMS Calcd for C₆₂H₅₇NO₁₇Na [M + Na]⁺, 1110.3524; found, 1110.3528.

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (60 β)

Colorless oil, $R_f = 0.38$ (hexane/EtOAc/CH₂Cl₂, 5:1:2, v/v/v); $[\alpha]_D^{20} = 10.0$ (c 1.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.39 (s, 3H), 3.52-3.57 (m, 1H), 3.59 (dd, $J = 9.2, 2.4$ Hz, 1H), 3.67 (dd, $J = 10.8, 7.6$ Hz, 1H), 3.99 (t, $J = 9.2$ Hz, 1H), 4.11 (d, $J = 2.4$ Hz, 1H), 4.13 (d, $J = 11.6$ Hz, 1H), 4.25-4.33 (m, 1H), 4.43 (dd, $J = 12.0, 4.8$ Hz, 1H), 4.48 (s, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 4.57 (d, $J = 12.0$ Hz, 1H), 4.60 (d, $J = 10.8$

Hz, 1H), 4.64 (d, $J = 12.0$ Hz, 1H), 4.87 (d, $J = 12.0$ Hz, 1H), 4.95 (d, $J = 10.8$ Hz, 1H), 5.02 (d, $J = 12.0$ Hz, 1H), 5.17-5.26 (m, 2H), 5.46 (t, $J = 9.6$ Hz, 1H), 6.14 (t, $J = 9.6$ Hz, 1H), 7.17-7.54 (m, 24H), 7.80-7.90 (m, 4H), 7.92-8.13 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.6, 64.7, 69.0, 69.1, 69.7, 70.5, 71.5, 72.3, 73.7, 73.9, 74.3, 74.5, 75.2, 82.2, 97.0, 102.6, 123.6, 127.8, 127.85, 127.92, 128.0, 128.2, 128.9, 129.2, 129.3, 129.8, 129.9, 130.1, 130.9, 133.3, 133.5, 133.7, 135.4, 137.98, 138.02, 138.9, 150.6, 164.5, 165.7, 165.9, 166.0. HRMS Calcd for $\text{C}_{62}\text{H}_{57}\text{NO}_{17}\text{Na}$ $[\text{M} + \text{Na}]^+$, 1110.3524; found, 1110.3518.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (61 α)

Colorless oil, $R_f = 0.60$ (hexane/EtOAc/ CH_2Cl_2 , 5:1:2, v/v/v); $[\alpha]_{\text{D}}^{20} = 40.4$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 3.47 (s, 3H), 3.58 (dd, $J = 11.2, 2.0$ Hz, 1H), 3.62 (dd, $J = 10.4, 2.4$ Hz, 1H), 3.72 (dd, $J = 11.2, 4.0$ Hz, 1H), 3.83-3.98 (m, 3H), 4.21 (t, $J = 9.6$ Hz, 1H), 4.23-4.30 (m, 1H), 4.42 (d, $J = 12.4$ Hz, 1H), 4.48 (d, $J = 10.8$ Hz, 1H), 4.51 (d, $J = 12.4$ Hz, 1H), 4.61 (d, $J = 12.4$ Hz, 1H), 4.64 (d, $J = 12.4$ Hz, 1H), 4.66 (d, $J = 10.8$ Hz, 1H), 4.94 (d, $J = 2.0$ Hz, 1H), 5.21 (d, $J = 3.2$ Hz, 1H), 5.24 (dd, $J = 10.0, 3.2$ Hz, 1H), 5.52 (dd, $J = 9.6, 3.2$ Hz, 1H), 5.55 (t, $J = 10.0$ Hz, 1H), 6.14 (t, $J = 9.6$ Hz, 1H), 7.03-7.60 (m, 27H), 7.82-8.07 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.7, 66.4, 68.4, 68.8, 69.9, 70.6, 71.7, 72.3, 73.1, 73.4, 73.5, 74.4, 74.8, 76.1, 96.9, 98.1, 127.6, 127.67, 127.72, 128.0, 128.3, 128.38, 128.43, 128.5, 129.1, 129.2, 129.4,

129.8, 129.9, 130.1, 130.2, 133.2, 133.5, 138.0, 138.2, 138.4, 165.4, 165.7, 165.9. Anal.
Calcd for C₆₂H₅₈O₁₅: C, 71.39; H, 5.60. Found: C, 71.32; H, 5.67.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (62 α)

Colorless oil, $R_f = 0.48$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 41.6$ (c 2.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 1.94 (s, 3H), 3.45 (s, 3H), 3.53-3.62 (m, 2H), 3.69 (dd, $J = 10.8, 4.0$ Hz, 1H), 3.77-3.85 (m, 2H), 3.91 (dd, $J = 11.2, 6.0$ Hz, 1H), 4.04 (t, $J = 9.6$ Hz, 1H), 4.20-4.27 (m, 1H), 4.41 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 11.2$ Hz, 1H), 4.50 (d, $J = 11.6$ Hz, 1H), 4.58-4.66 (m, 3H), 4.88 (d, $J = 1.6$ Hz, 1H), 5.16-5.27 (m, 3H), 5.51 (t, $J = 10.0$ Hz, 1H), 6.13 (t, $J = 9.6$ Hz, 1H), 7.13-7.54 (m, 24H), 7.83-8.00 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 55.7, 66.3, 68.5, 68.8, 70.0, 70.7, 71.7, 72.3, 73.0, 73.4, 73.5, 73.7, 74.6, 76.1, 96.9, 98.0, 127.6, 127.7, 127.78, 127.83, 127.9, 128.0, 128.38, 128.42, 128.48, 128.53, 129.1, 129.2, 129.4, 129.8, 130.1, 133.2, 133.41, 133.44, 138.1, 138.4, 138.5, 165.4, 165.9, 170.2. HRMS Calcd for C₅₇H₅₆O₁₅Na [M+Na]⁺, 1003.3517; found, 1003.3514.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (63)

Colorless oil, $\alpha:\beta = 1:11.8$, $R_f = 0.35$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = -33.8$ (c 2.9, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.36 (s, 3H), 3.41-3.47 (m, 1H), 3.53 (dd, $J = 9.2, 2.8$ Hz, 1H), 3.71-3.83 (m, 2H), 3.92 (t, $J = 9.6$ Hz, 1H), 3.96-4.01 (m, 2H), 4.08 (dd, $J = 9.6, 8.8$ Hz, 1H), 4.21 (d, $J = 14.0$ Hz, 1H), 4.25 (dd, $J = 8.8, 3.2$ Hz, 1H), 4.27-4.33 (m, 2H), 4.39 (d, $J = 14.0$ Hz, 1H), 4.44-4.51 (m, 3H), 4.57 (d, $J = 11.6$ Hz, 1H), 4.60 (s, 1H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.74 (d, $J = 1.2$ Hz, 1H), 4.87 (d, $J = 12.0$ Hz, 2H), 4.92 (d, $J = 12.0$ Hz, 1H), 5.00 (d, $J = 12.0$ Hz, 1H), 5.47 (s, 1H), 7.20-7.39 (m, 25H), 7.42-7.50 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 55.1, 56.9, 64.2, 69.0, 69.2, 71.1, 71.4, 73.7, 73.96, 74.04, 74.2, 74.3, 74.8, 75.3, 78.7, 81.6, 99.4, 100.1, 101.7, 126.3, 127.4, 127.6, 127.7, 127.76, 127.83, 128.0, 128.1, 128.28, 128.32, 128.55, 128.57, 128.61, 128.8, 129.0, 131.0, 137.7, 138.0, 138.5, 138.9. HRMS Calcd for C₅₅H₅₈O₁₃SNa [M + Na]⁺, 981.3496; found, 981.3497.

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (64 α)

Colorless oil, $R_f = 0.53$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = -35.8$ (c 2.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.28 (s, 3H), 3.76 (dd, $J = 10.8, 2.0$ Hz, 1H), 3.75-3.80 (m, 1H), 3.83 (dd, $J = 10.8, 4.8$ Hz, 1H), 3.90 (t, $J = 10.4$ Hz, 1H), 3.96-4.03

(m, 2H), 4.09 (dd, $J = 3.6, 2.0$ Hz, 1H), 4.12-4.20 (m, 4H), 4.26 (dd, $J = 10.4, 4.8$ Hz, 1H), 4.45 (d, $J = 12.4$ Hz, 1H), 4.52 (d, $J = 10.8$ Hz, 1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.58 (d, $J = 10.8$ Hz, 1H), 4.64 (d, $J = 11.2$ Hz, 1H), 4.71 (d, $J = 12.0$ Hz, 1H), 4.74 (d, $J = 1.2$ Hz, 1H), 4.87 (d, $J = 11.2$ Hz, 1H), 5.32 (d, $J = 1.6$ Hz, 1H), 5.54 (dd, $J = 9.2, 3.2$ Hz, 1H), 5.70 (s, 1H), 7.04-7.40 (m, 23H), 7.50-7.55 (m, 2H), 8.02-8.07 (m, 2H), 8.19-8.25 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 54.9, 63.9, 69.0, 69.1, 72.1, 72.5, 73.7, 73.8, 73.9, 75.9, 76.3, 76.8, 79.5, 99.9, 101.1, 101.6, 123.6, 126.2, 127.7, 127.77, 127.83, 127.87, 127.91, 128.0, 128.1, 128.3, 128.4, 128.6, 129.0, 130.9, 135.5, 137.7, 137.8, 138.0, 138.2, 138.6, 150.6, 163.9. HRMS Calcd for $\text{C}_{55}\text{H}_{55}\text{NO}_{14}\text{Na}$ $[\text{M} + \text{Na}]^+$, 976.3520; found, 976.3525.

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (64 β)

Colorless oil, $R_f = 0.25$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_D^{20} = -35.1$ (c 0.9, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 3.35 (s, 3H), 3.57-3.61 (m, 1H), 3.62 (dd, $J = 8.4, 2.8$ Hz, 1H), 3.75 (d, $J = 12.0$ Hz, 1H), 3.79 (d, $J = 12.0$ Hz, 1H), 3.93 (dd, $J = 10.0, 3.2$ Hz, 1H), 4.03 (t, $J = 8.4$ Hz, 1H), 4.04-4.09 (m, 2H), 4.24 (d, $J = 5.2$ Hz, 1H), 4.34 (d, $J = 3.2$ Hz, 1H), 4.49-4.56 (m, 3H), 4.61 (d, $J = 10.8$ Hz, 1H), 4.63-4.68 (m, 3H), 4.70 (d, $J = 12.4$ Hz, 1H), 4.76 (t, $J = 1.2$ Hz, 1H), 4.91 (d, $J = 12.0$ Hz, 1H), 4.96 (d, $J = 10.8$ Hz, 1H), 5.07 (d, $J = 12.0$ Hz, 1H), 5.46 (s, 1H), 7.04-7.09 (m, 3H), 7.21-7.37 (m, 18H), 7.43-7.53 (m, 4H), 7.92-8.00 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.1, 64.1,

64.3, 69.0, 70.7, 71.4, 73.5, 73.7, 73.8, 74.1, 74.16, 74.23, 75.3, 78.5, 82.1, 99.1, 99.6, 101.8, 123.5, 126.3, 127.2, 127.3, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.58, 128.63, 129.0, 130.9, 135.3, 137.6, 138.0, 138.7, 138.9, 150.5, 164.5. HRMS Calcd for $C_{55}H_{55}NO_{14}Na$ $[M + Na]^+$, 976.3520; found, 976.3523.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (65 α)

Colorless oil, $R_f = 0.63$ (hexane/EtOAc/ CH_2Cl_2 , 4:1:1, v/v/v); $[\alpha]_D^{20} = -28.8$ (c 4.4, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 3.26 (s, 3H), 3.72-3.78 (m, 2H), 3.81 (dd, $J = 10.8, 5.2$ Hz, 1H), 3.90 (t, $J = 10.4$ Hz, 1H), 3.96 (dd, $J = 10.0, 3.2$ Hz, 1H), 3.98-4.04 (m, 1H), 4.11 (dd, $J = 3.2, 2.0$ Hz, 1H), 4.12-4.20 (m, 3H), 4.22-4.28 (m, 2H), 4.44 (d, $J = 12.4$ Hz, 1H), 4.48 (d, $J = 10.4$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 4.62 (d, $J = 11.6$ Hz, 1H), 4.67 (d, $J = 10.4$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.74 (d, $J = 1.2$ Hz, 1H), 4.84 (d, $J = 11.6$ Hz, 1H), 5.30 (d, $J = 1.6$ Hz, 1H), 5.56 (dd, $J = 9.6, 3.6$ Hz, 1H), 5.71 (s, 1H), 7.04-7.46 (m, 25H), 7.51-7.61 (m, 3H), 8.01-8.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.8, 63.9, 68.9, 69.2, 72.0, 72.6, 73.58, 73.64, 73.8, 74.3, 75.0, 76.1, 76.2, 76.6, 76.8, 77.2, 77.5, 79.4, 100.1, 101.1, 101.5, 127.65, 127.70, 127.74, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.9, 129.8, 130.2, 133.2, 137.8, 137.9, 138.1, 138.3, 138.7, 165.8. HRMS Calcd for $C_{55}H_{56}O_{12}Na$ $[M + Na]^+$, 931.3669; found, 931.3667.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (66 α)

Colorless oil, $R_f = 0.48$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = -17.6$ (c 1.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 1.94 (s, 3H), 3.25 (s, 3H), 3.69-3.79 (m, 3H), 3.86 (t, $J = 10.4$ Hz, 1H), 3.91-4.01 (m, 4H), 4.11 (dd, $J = 3.2, 1.6$ Hz, 1H), 4.12 (t, $J = 9.6$ Hz, 1H), 4.22 (d, $J = 12.4$ Hz, 1H), 4.23 (dd, $J = 10.4, 4.8$ Hz, 1H), 4.44 (d, $J = 12.4$ Hz, 1H), 4.47 (d, $J = 11.2$ Hz, 1H), 4.51 (d, $J = 12.0$ Hz, 1H), 4.62 (d, $J = 11.6$ Hz, 1H), 4.63 (d, $J = 11.2$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 4.71 (d, $J = 1.2$ Hz, 1H), 4.83 (d, $J = 11.6$ Hz, 1H), 5.24 (d, $J = 2.0$ Hz, 1H), 5.28 (dd, $J = 8.4, 3.6$ Hz, 1H), 5.67 (s, 1H), 7.15-7.20 (m, 4H), 7.24-7.40 (m, 19H), 7.50-7.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 54.8, 63.9, 68.9, 69.2, 72.0, 72.5, 73.56, 73.59, 73.7, 73.8, 74.9, 76.0, 76.3, 76.6, 79.4, 100.0, 101.1, 101.5, 126.2, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 128.9, 137.9, 138.2, 138.25, 138.28, 138.7, 170.3. HRMS Calcd for C₅₀H₅₄O₁₂Na [M + Na]⁺, 869.3513; found, 869.3516.

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (78 α)

Colorless oil, $R_f = 0.40$ (hexane/EtOAc/CH₂Cl₂, 4:1:1, v/v/v); $[\alpha]_D^{20} = 18.7$ (c 4.7,

CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.42(s, 3H), 3.55 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.60 (d, *J* = 5.6 Hz, 1H), 3.65 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.69-3.76 (m, 5H), 3.86 (d, *J* = 8.8 Hz, 1H), 3.87-3.92 (m, 1H), 3.93 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.12-4.16 (m, 2H), 4.17 (d, *J* = 5.6 Hz, 1H), 4.31 (d, *J* = 14.0 Hz, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.45-4.49 (m, 3H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.59 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.65 (d, *J* = 10.8 Hz, 1H), 4.68 (d, *J* = 12.4 Hz, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 5.15 (d, *J* = 12.0 Hz, 1H), 5.33 (d, *J* = 1.6 Hz, 1H), 7.04-7.40 (m, 35H); ¹³C NMR (100 MHz, CDCl₃) δ 55.4, 57.3, 69.2, 69.4, 69.8, 71.45, 71.48, 72.3, 73.2, 73.4, 73.6, 75.0, 75.5, 77.0, 77.2, 78.0, 80.1, 81.6, 97.8, 99.9, 126.7, 127.2, 127.4, 127.6, 127.7, 127.8, 127.9, 127.96, 128.04, 128.07, 128.11, 128.2, 128.25, 128.28, 128.4, 128.5, 128.58, 128.61, 128.77, 128.81, 130.7, 137.5, 137.9, 138.2, 138.3, 138.8. HRMS Calcd for C₆₂H₆₆O₁₃SNa [M+Na]⁺, 1073.4122; found, 1073.4125.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl-α-D-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (79α)

Colorless oil, *R*_f = 0.42 (hexane/EtOAc/CH₂Cl₂, 7:1:1, v/v/v); [α]_D²⁰ = −10.9 (c 2.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 3.40 (s, 3H), 3.56 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.62-3.65 (m, 2H), 3.67-3.77 (m, 3H), 3.76 (d, *J* = 9.6 Hz, 1H), 3.82-3.89 (m, 3H), 4.11 (d, *J* = 3.2 Hz, 1H), 4.15 (d, *J* = 5.6 Hz, 1H), 4.17-4.23 (m, 2H), 4.31 (d, *J* = 11.2 Hz, 1H), 4.34 (d, *J* = 11.2 Hz, 1H), 4.42 (d, *J* = 10.8 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.55-4.64 (m, 5H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 10.4 Hz, 1H), 5.13 (d, *J* = 11.6 Hz, 1H), 5.31 (d, *J* = 1.6 Hz, 1H), 7.22-7.43 (m, 35H);

^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 56.9, 69.2, 69.3, 69.8, 71.5, 72.2, 73.3, 73.5, 73.9, 75.1, 75.2, 76.1, 77.1, 79.8, 80.1, 81.7, 97.9, 100.4, 126.8, 127.46, 127.53, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.27, 128.30, 128.5, 128.57, 128.63, 128.8, 131.1, 137.9, 138.25, 138.28, 138.4, 138.5. HRMS Calcd for $\text{C}_{62}\text{H}_{66}\text{O}_{13}\text{SNa}$ $[\text{M}+\text{Na}]^+$, 1073.4122; found, 1073.4120.

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (79 β)

Colorless oil, R_f = 0.38 (hexane/EtOAc/ CH_2Cl_2 , 3:1:1, v/v); $[\alpha]_D^{20}$ = 25.1 (c 1.3, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 3.36 (s, 3H), 3.38-3.44 (m, 2H), 3.51 (dd, J = 11.2, 3.6 Hz, 1H), 3.55 (dd, J = 11.2, 3.6 Hz, 1H), 3.65-3.71 (m, 2H), 3.78-3.91 (m, 2H), 3.93 (d, J = 9.2 Hz, 1H), 4.01 (d, J = 14.0 Hz, 1H), 4.13 (d, J = 14.4 Hz, 1H), 4.22 (d, J = 14.4 Hz, 1H), 4.24 (d, J = 10.4 Hz, 1H), 4.33-4.39 (m, 2H), 4.46-4.58 (m, 6H), 4.65 (d, J = 12.0 Hz, 1H), 4.86 (d, J = 11.6 Hz, 1H), 5.01 (d, J = 11.6 Hz, 1H), 5.02-5.08 (m, 2H), 5.41 (d, J = 1.2 Hz, 1H), 7.12-7.41 (m, 35H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.4, 57.6, 57.7, 68.4, 69.0, 69.5, 72.4, 72.8, 73.3, 73.4, 73.7, 74.9, 76.7, 77.12, 77.13, 80.4, 81.1, 97.9, 98.9, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.3, 128.4, 128.52, 128.53, 128.6, 128.90, 128.92, 129.1, 129.3, 130.7, 131.0, 131.1, 137.6, 138.0, 138.3, 139.0. HRMS Calcd for $\text{C}_{62}\text{H}_{66}\text{O}_{13}\text{SNa}$ $[\text{M}+\text{Na}]^+$, 1073.4122; found, 1073.4126.

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (80)

Colorless oil, $\alpha:\beta = 3.7:1$, $R_f = 0.50$ (hexane/EtOAc/CH₂Cl₂, 5:1:2, v/v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.41 (s, 3H), 3.44 (d, $J = 11.2$ Hz, 1H), 3.54 (dd, $J = 9.6, 3.6$ Hz, 1H), 3.59 (dd, $J = 11.2, 3.6$ Hz, 1H), 3.62-3.77 (m, 4H), 3.85 (t, $J = 2.8$ Hz, 1H), 3.90 (t, $J = 8.8$ Hz, 1H), 4.02-4.12 (m, 3H), 4.19 (d, $J = 14.0$ Hz, 1H), 4.35 (d, $J = 12.0$ Hz, 1H), 4.38 (d, $J = 12.0$ Hz, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.56-4.64 (m, 3H), 4.68 (d, $J = 11.6$ Hz, 1H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.96 (dd, $J = 9.2, 2.8$ Hz, 1H), 5.14 (d, $J = 11.6$ Hz, 1H), 5.28 (d, $J = 2.4$ Hz, 1H), 7.06-7.37 (m, 35H); ¹³C NMR (100 MHz, CDCl₃) δ 55.4, 57.2, 68.7, 69.4, 69.6, 72.6, 73.0, 73.2, 73.4, 73.6, 74.8, 75.1, 78.0, 80.1, 81.5, 97.8, 100.1, 127.1, 127.3, 127.4, 127.5, 127.6, 127.65, 127.74, 127.89, 127.93, 128.1, 128.16, 128.22, 128.3, 128.4, 128.5, 128.6, 128.9, 129.0, 130.8, 137.9, 138.0, 138.2, 138.4, 139.0. HRMS Calcd for C₆₂H₆₆O₁₃SNa [M+Na]⁺, 1073.4122; found, 1073.4121.

2,3-Di-O-benzyl-4,6-di-O-benzylsulfonyl-D-mannopyranosyl Trichloroacetimidate (81)

Colorless oil, $R_f = 0.25$ (hexane/EtOAc, 3:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 3.88-3.92 (m, 1 H), 3.99 (dd, $J = 9.6, 2.8$ Hz, 1 H), 4.07-4.13 (m, 1H), 4.26 (d, $J = 14.0$ Hz, 1H), 4.28 (dd, $J = 11.6, 5.2$ Hz, 1H), 4.33 (d, $J = 14.0$ Hz, 1H), 4.37 (d, $J = 14.0$ Hz, 1H), 4.39 (dd, $J = 11.6, 2.0$ Hz, 1H), 4.47 (d, $J = 14.0$ Hz, 1H), 4.51 (d, $J = 12.0$ Hz, 1H),

4.54 (d, $J = 12.0$ Hz, 1H), 4.70 (s, 2H), 5.09 (t, $J = 10.0$ Hz, 1H), 6.33 (d, $J = 1.6$ Hz, 1H), 7.21-7.43 (m, 20H), 8.66 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 57.0, 57.6, 68.2, 71.7, 72.1, 72.8, 73.0, 75.1, 75.8, 90.7, 94.8, 127.5, 127.7, 128.1, 128.2, 128.39, 128.42, 128.55, 128.63, 128.8, 128.9, 128.96, 129.0, 129.2, 129.3, 130.8, 130.9, 136.8, 137.2, 160.0. HRMS Calcd for $\text{C}_{36}\text{H}_{36}\text{Cl}_3\text{NO}_8\text{Na}$ $[\text{M} + \text{Na}]^+$, 720.1119; found, 720.1138.

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Allyl 2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)- α -D-mannopyranoside (S1)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranoside (S2)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranoside (S3)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α -D-mannopyranoside (S4)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)- α -D-mannopyranose (S5)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranose (6)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranose (7)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α -D-mannopyranose (8)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)- α -D-mannopyranosyl

Trichloroacetimidate (1)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl Trichloroacetimidate (2)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl Trichloroacetimidate (3)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α -D-mannopyranosyl Trichloroacetimidate (4)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- α -D-mannopyranosyl Trichloroacetimidate (5)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α -D-mannopyranoside (S6)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranoside (S7)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranoside (S8)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α -D-mannopyranose (S9)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranose (S10)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranose (S11)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α -D-mannopyranosyl Trichloroacetimidate (9)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)-D-mannopyranosyl Trichloroacetimidate (10)

(¹H NMR 400MHz, CDCl₃)

(¹³C NMR 100MHz, CDCl₃)

2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranosyl Trichloroacetimidate (11)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3,4-Tri-*O*-benzyl-6-*O*-acetyl- α -D-mannopyranosyl Trichloroacetimidate (12)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α -D-mannopyranoside (S12)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranoside (S13)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Allyl 2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl- α -D-mannopyranoside (S14)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl-D-mannopyranose (S15)

(¹H NMR 400MHz, CDCl₃)

(¹³C NMR 100MHz, CDCl₃)

(¹H NMR 400MHz, CDCl₃)

(¹³C NMR 100MHz, CDCl₃)

2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl-D-mannopyranose (S17)

(¹H NMR 400MHz, CDCl₃)

(¹³C NMR 100MHz, CDCl₃)

2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α -D-mannopyranosyl Trichloroacetimidate (13)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)-D-mannopyranosyl Trichloroacetimidate (14)

(¹H NMR 400MHz, CDCl₃)

(¹³C NMR 100MHz, CDCl₃)

2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl- α -D-mannopyranosyl Trichloroacetimidate (15)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,4,6-Tri-*O*-benzyl-3-*O*-acetyl- α -D-mannopyranosyl Trichloroacetimidate (16)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Phenyl 2,4,6-Tri-*O*-benzyl-3-*O*-acetyl-1-thio- α -D-mannopyranoside (S18)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Phenyl 2,4,6-Tri-*O*-benzyl-1-thio- α -D-mannopyranoside (S19)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Phenyl 2,4,6-Tri-*O*-benzyl-3-*O*-trichloroacetimidoyl-1-thio- α -D-mannopyranoside (67)

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Bicyclic Trichlorooxazine 68

(^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Mass spectra for the mixture containing a bicyclic product with a seven-membered trichorooxazepine ring

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)- α/β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (23) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (24 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (24 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α/β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (25) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (26) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (27) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

¹H NMR spectrum of compound 10 in CDCl₃. The spectrum shows a complex multiplet in the aromatic region (6.5-7.5 ppm) and a complex multiplet in the aliphatic region (3.5-5.5 ppm). Integration values are provided below the peaks.

Chemical structure of compound 10 is shown above the spectrum:

O=C1C(=O)N(C1)C2=CC=CC=C2C3=CC=CC=C3

Integration values (from left to right):

- 7.424, 7.407, 7.385, 7.366, 7.356, 7.338, 7.318, 7.295, 7.281, 7.265, 7.262, 7.250, 7.230, 7.216, 7.203, 7.196, 5.028, 5.000, 4.968, 4.955, 4.924, 4.896, 4.869, 4.842, 4.830, 4.814, 4.802, 4.791, 4.771, 4.760, 4.671, 4.641, 4.618, 4.612, 4.588, 4.579, 4.571, 4.561, 4.546, 4.538, 4.530, 4.516, 4.512, 4.501, 4.489, 4.150, 4.122, 4.023, 3.999, 3.838, 3.815, 3.793, 3.789, 3.765, 3.737, 3.721, 3.691, 3.671, 3.449, 3.430, 3.425, 3.407, 3.393, 3.325, 3.303

Integration values (from left to right):

- 1.000, 0.811, 1.172, 1.172, 1.488, 1.062, 2.731, 0.721, 1.309, 0.769, 3.092, 4.203, 0.879, 0.916, 0.882, 1.424, 1.723, 1.906, 2.285, 0.644, 0.689, 0.996, 1.815, 1.536, 0.898, 2.631, 0.947

138.84
138.73
138.68
138.65
138.46
138.41
138.36
138.31
138.20
138.17
138.14
138.07
128.47
128.40
128.37
128.35
128.34
128.28
128.24
128.17
128.09
128.06
128.02
128.00
127.94
127.85
127.82
127.77
127.73
127.67
127.63
127.61
127.56
127.52
127.46
127.41
102.36
101.49
98.26
97.82
97.80
82.27
82.15
79.99
79.88
79.55
77.64
76.00
75.80
75.70
75.16
75.01
74.97
74.92
74.86
74.73
74.66
73.69
73.61
73.26
72.46
71.99
69.80
69.73
69.11
68.28
55.61
55.08
55.05

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*o*-trifluoromethylbenzenesulfonyl)- α/β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (29) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (30 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (30 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α/β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (31) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (32) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- α / β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (33) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4,6-Tetra-*O*-benzyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (34)^{8,9} (¹H NMR 400MHz, CDCl₃)

(¹³C NMR 100MHz, CDCl₃)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (35 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (35 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (36 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (36 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (37 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (37 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (38 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-acetyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (38 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4,6-tetra-*O*-benzyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (39)⁹ (¹H NMR 400MHz, CDCl₃)

(¹³C NMR 100MHz, CDCl₃)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-mannopyranoside (40) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)- α/β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-mannopyranoside (41) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzoyl- α / β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-mannopyranoside (42) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (43 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (43 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (44 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (44 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (45 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (45 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (46 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (47) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (48 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (48 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (49 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (49 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-acetyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (50) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3) (^1H NMR 400MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannoside (51 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (51 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannoside (52 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,3,4-Tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannoside (52 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (53 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzoyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (53 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-benzylidene- α -D-mannopyranoside (54 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- β -D-glucopyranoside(55 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (56 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (56 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside(57 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (58 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (59 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (59 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (60 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (60 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (61 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (62 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α/β -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (63) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- α -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (64 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl [2,4,6-Tri-*O*-benzyl-3-*O*-(*p*-nitrobenzoyl)- β -D-mannopyranosyl]-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (64 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzoyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (65 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-acetyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 2)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (66a) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,6-Tri-*O*-benzyl-4-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (78a) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (79 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3,4-Tri-*O*-benzyl-6-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (79 β) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,4,6-Tri-*O*-benzyl-3-*O*-benzylsulfonyl- α / β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-glucopyranoside (80) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

2,3-Di-*O*-benzyl-4,6-di-*O*-benzylsulfonyl-D-mannopyranosyl Trichloroacetimidate (81)

(¹H NMR 400MHz, CDCl₃)

(¹³C NMR 100MHz, CDCl₃)

Methyl (2,3-Di-*O*-benzyl-di-*O*-4,6-*O*-benzylsulfonyl- α -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (82 α) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

Methyl (2,3-Di-*O*-benzyl-di-*O*-4,6-*O*-benzylsulfonyl- β -D-mannopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-mannopyranoside (**82 β**) (^1H NMR 400MHz, CDCl_3)

(^{13}C NMR 100MHz, CDCl_3)

α -Manopyranosyl Triflates 69 (^1H NMR 400MHz, CDCl_3)

(2D ^1H , ^{13}C -HSQC, CDCl_3)

α -Manopyranosyl Triflates 70 (^1H NMR 400MHz, CDCl_3)

(2D ^1H , ^{13}C -HSQC, CDCl_3)

α -Manopyranosyl Triflates 71 (^1H NMR 400MHz, CDCl_3)

(2D ^1H , ^{13}C -HSQC, CDCl_3)

α -Manopyranosyl Triflates 72 (^1H NMR 400MHz, CDCl_3)

(2D ^1H , ^{13}C -HSQC, CDCl_3)

α -Manopyranosyl Triflates 73 (^1H NMR 400MHz, CDCl_3)

(2D ^1H , ^{13}C -HSQC, CDCl_3)

α -Manopyranosyl Triflates 74 (^1H NMR 400MHz, CDCl_3)

(2D ^1H , ^{13}C -HSQC, CDCl_3)