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The 4-(*tert*-Butyldiphenylsiloxy)-3-fluorobenzyl Group: A New Alcohol Protecting Group, Fully Orthogonal with the *p*-Methoxybenzyl Group and Removable under Desilylation Conditions

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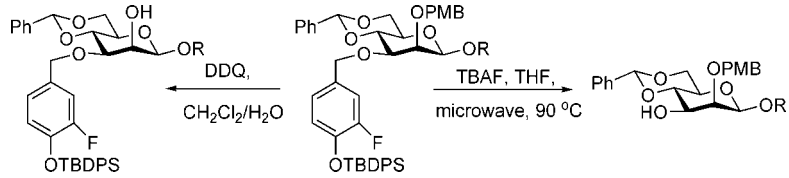

A new benzyl ether-type protecting group for alcohols, the 4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl group, is introduced. The protecting group is introduced by means of the readily prepared benzyl bromide and is cleaved with tetrabutylammonium fluoride in dimethylformamide under microwave irradiation. The fluoride substituent provides stability to oxidizing conditions, such that the new protecting group is fully compatible with the removal of *p*-methoxybenzyl ethers with DDQ. Applications of the new protecting group in the direct stereocontrolled synthesis of β-mannopyranosides are presented.

Introduction

Benzyl and silyl ethers are some of the most widely used alcohol protecting groups.[1] The high degree of mutual orthogonality which they display makes combinations of them attractive protecting systems for complex polyols, whether in the context of total synthesis, combinatorial library synthesis, or oligosaccharide synthesis. In addition to their differing reactivity patterns, the two types of protecting group differ significantly in their steric properties. The appreciably greater bulk of the silyl ethers leads to the much reduced chelating ability of α-siloxycarbonyl systems[2] and contributes to the inverted conformations adopted by some polylsilylated six-membered ring systems.[3] In the course of a study[4] targeted at the synthesis of the common core pentasaccharide of the *N*-linked glycoproteins, we uncovered an unanticipated consequence of the steric bulk of silyl ether protecting groups. Thus, while 4,6-*O*-benylidene-protected thiomannopyranosides, and their sulfoxides, carrying benzyl ethers at positions 2 and 3 are known to be superb donors in the direct stereocontrolled formation of β-mannopyranoside linkages,[5] an analogous system **1** carrying a 3-*O*-*tert*-butyldimethylsilyl group

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(4) Dudkin, V. Y.; Crich, D. *Tetrahedron Lett.* **2003**, *44*, 1787–1789.

(5) (a) Crich, D.; Sun, S. *J. Org. Chem.* **1997**, *62*, 1198–1199. (b) Crich, D.; Sun, S. *Tetrahedron* **1998**, *54*, 8321–8348. (c) Crich, D.; Smith, M. *J. Am. Chem. Soc.* **2001**, *123*, 9015–9020. (d) Crich, D.; Lim, L. B. L. *Org. React.* **2004**, *64*, 115–251. (e) Crich, D. In *Glycochemistry: Principles, Synthesis, and Applications*; Wang, P. G., Bertozzi, C. R., Eds.; Dekker: New York, 2001; pp 53−75. (f) Crich, D.; Banerjee, A.; Li, W.; Yao, Q. *J. Carbohydr. Chem.* **2005**, *24*, 415–424. (g) Crich, D.; Banerjee, A.; Yao, Q. *J. Am. Chem. Soc.* **2004**, *126*, 14930–14934. (h) Crich, D.; Banerjee, A. *Org. Lett.* **2005**, *7*, 1935–1938. (i) Crich, D.; Yao, Q. *J. Am. Chem. Soc.* **2004**, *126*, 8232–8236. (j) Dudkin, V. Y.; Miller, J. S.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 736–738.

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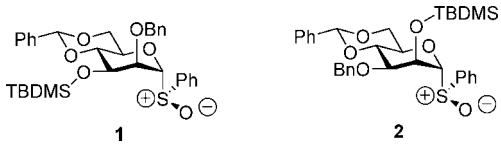
in place of a benzyl ether was found to favor the formation of α-mannosides. This result was even more surprising in view of the fact that the regioisomeric 3-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl system **2** showed adequate β-selectivity. Thus, the more remote 3-*O*-silyl group in **1** had a greater influence on the stereochemical outcome of the glycosylation than the 2-*O*-silyl ether adjacent to the reactive site in **2**. We rationalized this effect in terms of a buttressing interaction between the 3-*O*-silyl and 2-*O*-benzyl ethers in **1**, which forces the benzyl closer to the anomeric center leading ultimately to the reduced stereoselectivity.[6,7]

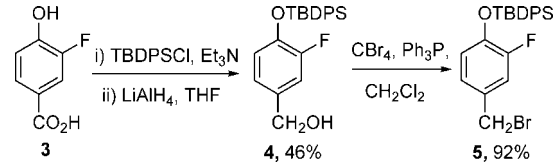


This interesting reactivity pattern alerted us to the need for a protecting group having the steric characteristics of a benzyl ether but which is removable under typical desilylation conditions. We report here on the design and successful implementation of such a system.[8]

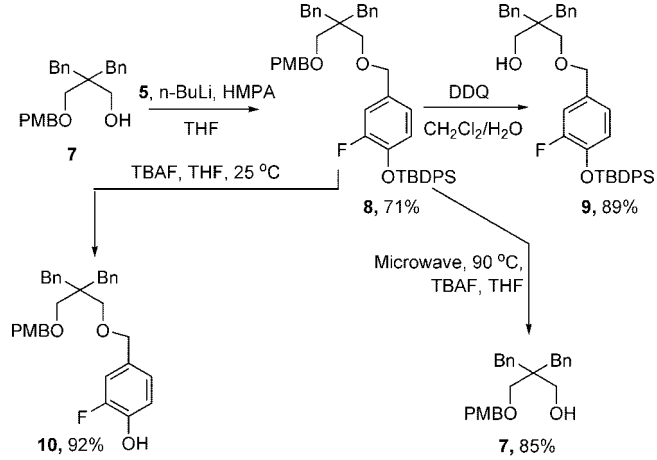
Results and Discussion

A significant range of substituted benzyl ether protecting groups is reported in the literature,[1,9] many of which have been applied in carbohydrate chemistry.[10] However, until the description of the *p*-siletanylbenzyl ether,[11] none could be considered to be cleavable under typical desilylation conditions.[12] In designing such a protecting group, we first considered the obvious simple *p*-siloxybenzyl type systems but dismissed them on the grounds that they would be too acid sensitive and subject to cleavage under the same oxidative conditions commonly used for the removal of *p*-methoxybenzyl[1,13] and naphthylmethyl ethers.[14] Rather, we focused on *p*-siloxybenzyl systems bearing an electron-withdrawing substituent intended to provide enhanced stability under acidic and oxidative conditions, in much the same way that a 3-chloro substituent enhances the stability of the 4-azidobenzyl ethers.[15] In view of our requirement for a system with the steric properties of a simple benzyl ether we targeted therefore the 3-fluoro-4-siloxybenzyl groups.

SCHEME 1. Assembly of 4-(*tert*-Butyldiphenylsiloxy)-3-fluorobenzyl Bromide



SCHEME 2. Orthogonality with *p*-Methoxybenzyl Ethers



Starting from commercially available 3-fluoro-4-hydroxybenzoic acid (**3**), 4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl bromide (**5**) was assembled in three convenient steps (Scheme 1).

Before proceeding to applications in oligosaccharide synthesis, the orthogonality of the new protecting group with *p*-methoxybenzyl ethers was tested. Thus, monoalkylation of 2,2-dibenzyl-1,3-propanediol **6** with *p*-methoxybenzyl chloride gave **7**, which was converted to the fully protected **8** on treatment with sodium hydride in THF in the presence of HMPA, followed by the addition of **5** (Scheme 2). Exposure of **8** to DDQ in wet dichloromethane at room temperature resulted in cleavage of the *p*-PMB ether in 89% yield. On the other hand, exposure of **8** to tetrabutylammonium fluoride in a variety of solvents, including DMF, at room temperature resulted only in the removal of the silyl ether, giving phenol **10** in high yield. This result was not totally unexpected in view of similar observations reported in the literature on saponification of *p*-acetoxybenzyl ethers.[9b] Fortunately, when desilylation was conducted under microwave irradiation at 90 °C, a satisfactory 85% yield of the desired alcohol **7** was obtained (Scheme 2). The complete orthogonality of the new protecting group with *p*-methoxybenzyl ethers, for which the system had been designed, was thus established.

Turning to applications in glycosidic bond formation, treatment of phenyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside **11** with

(6) (a) Crich, D.; Dudkin, V. *Tetrahedron Lett.* **2000**, *41*, 5643–5646. Also see: (b) Codée, J. D. C.; Hossain, L. H.; Seeberger, P. H. *Org. Lett.* **2005**, *7*, 3251–3254.

(7) We have provided one solution to this problem in the form of the minimally sterically bulky propargyl ethers. (a) Crich, D.; Jayalath, P. *Org. Lett.* **2005**, *7*, 2277–2280. (b) Crich, D.; Jayalath, P.; Hutton, T. K. *J. Org. Chem.* **2006**, *71*, 3064–3070. (c) Crich, D.; Wu, B. *Org. Lett.* **2006**, *8*, 4879–4882. (d) Crich, D.; Karatholuvhu, M. S. *J. Org. Chem.* **2008**, *73*, 5173–5176.

(8) During the course of this investigation, Seeberger and co-workers reported their solution to this problem in the form of the triisopropylsilyloxymethyl ether: (a) Codée, J. D. C.; Kröck, L.; Castagner, B.; Seeberger, P. H. *Chem.—Eur. J.* **2008**, *14*, 3987–3994.

(9) (a) Plante, O. J.; Buchwald, S. L.; Seeberger, P. H. *J. Am. Chem. Soc.* **2000**, *122*, 7148–7149. (b) Jobron, L.; Hindsgaul, O. *J. Am. Chem. Soc.* **1998**, *121*, 5835–5836. (c) Kang, J.; Lim, G. J.; Yoon, S. K.; Kim, M. Y. *J. Org. Chem.* **1995**, *60*, 564–577. (d) Xia, J.; Alderfer, J. L.; Piskorz, C. F.; Matta, K. L. *Chem.—Eur. J.* **2000**, *6*, 3442–3451. (e) Gaunt, M. J.; Yu, J.; Spencer, J. B. *J. Org. Chem.* **1998**, *63*, 4172–4173. (f) Lipták, A.; Borbás, A.; Jánossy, L.; Szilágyi, L. *Tetrahedron Lett.* **2000**, *41*, 4949–4953. (g) Reddy, C. R.; Chittiboyina, A. G.; Kache, R.; Jung, J.-C.; Watkins, E. B.; Avery, M. A. *Tetrahedron* **2005**, *61*, 1289–1295.

(10) Crich, D., Ed. *Handbook of Reagents for Organic Synthesis: Reagents for Glycoside, Nucleotide, and Peptide Synthesis*; Wiley: Chichester, 2005.

(11) Lam, H.; House, S. E.; Dudley, G. B. *Tetrahedron Lett.* **2005**, *46*, 3283–3285.

(12) A *p*-siloxybenzylidene acetal protecting group for diols has been described: (a) Kaburagi, Y.; Osajima, H.; Shimada, K.; Tokuyama, H.; Fukuyama, T. *Tetrahedron Lett.* **2004**, *45*, 3817–3821. For a siletanylbenzylidene acetal, see: House, S. E.; Poon, K. W. C.; Lam, H.; Dudley, G. B. *J.Org. Chem.* **2006**, *71*, 420–422.

(13) Wuts, P. G. M. In *Handbook of Reagents for Organic Synthesis: Reagents for Glycoside, Nucleotide, and Peptide Synthesis*; Crich, D., Ed.; Wiley: Chichester, 2005; pp 425−428.

(14) Csávás, M.; Szabó, Z. B.; Borbás, A.; Lipták, A. In *Handbook of Reagents for Organic Synthesis: Reagents for Glycoside, Nucleotide, and Peptide Synthesis*; Crich, D., Ed.; Wiley: Chichester, 2005; pp 459−460.

(15) Egusa, K.; Fukase, K.; Kusumoto, S. *Synlett* **1997**, 675–676.

(16) (a) Garegg, P. J.; Iversen, T.; Oscarson, S. *Carbohydr. Res.* **1976**, *50*, C12–C14. (b) Pozsgay, V. *Carbohydr. Res.* **1979**, *69*, 284–286. (c) Lergenmüller, M.; Nukada, T.; Kuramochi, K.; Dan, A.; Ogawa, T.; Ito, Y. *Eur. J. Org. Chem.* **1999**, 1367–1376. (d) Crich, D.; Li, W.; Li, H. *J. Am. Chem. Soc.* **2004**, *126*, 15081–15086.

SCHEME 3. Preparation of Glycosyl Donor 13

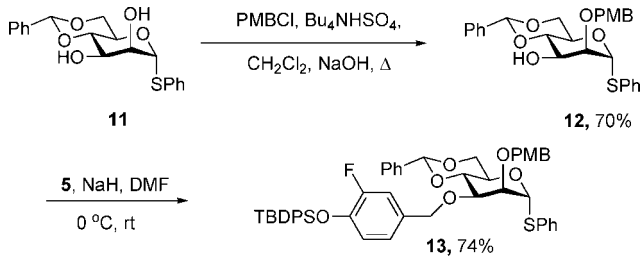
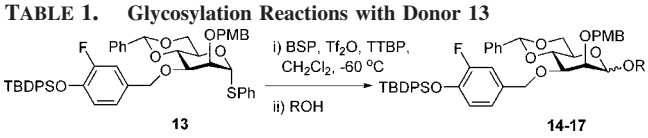
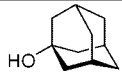
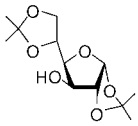
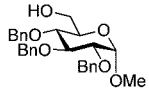
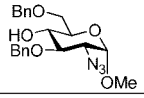


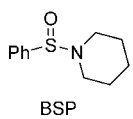
TABLE 1. Glycosylation Reactions with Donor 13

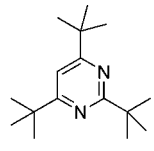


ROH	Product	Yield	β:α ratio
	**14**	85%	11.7:1
	**15**	82%	β only
	**16**	79%	8.2:1
	**17**	62%	β only

p-methoxybenzyl chloride under phase-transfer conditions[16] afforded the 2-*O*-PMB ether **12**. Benzylation with **5** and sodium hydride in DMF then provided the orthogonally protected glycosyl donor **13** (Scheme 3).

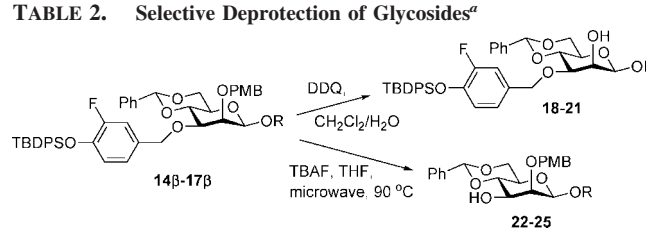
With acceptor **13** in hand, the glycosylation of a series of four acceptor alcohols was undertaken. These reactions were carried out in dichloromethane at −60 °C, with prior activation of the thioglycoside with a combination of 1-benzenesulfinyl piperidine (BSP),[5c,d,f] and trifluoromethanesulfonic anhydride in the presence of the convenient non-nucleophilic base 2,4,6-tri-*tert*-butylpyrimidine (TTBP),[17] before addition of the alcohol. Like the action of trifluoromethanesulfonic anhydride on glycosyl sulfoxides,[18] this activation protocol converts the thioglycoside to a covalent α-glycosyl trifluoromethanesulfonate,[5c] which then undergoes S_N2-like reaction with the alcohol with the intermediacy of a transient contact ion pair.[19] As is clear from Table 1, all couplings proceeded in high yield and with excellent β-selectivity.[20]

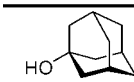
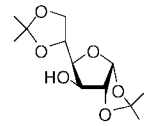
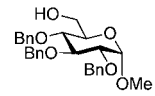
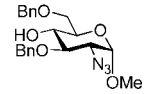

BSP


TTBP

Glycosides **14**−**17** were then subjected to partial deprotection by exposure to DDQ at room temperature and by treatment with TBAF in THF at 90 °C under microwave heating conditions

TABLE 2. Selective Deprotection of Glycosides[a]



ROH	DDQ Product (% yield)	TBAF Product (% yield)
	**18** (80)	**22** (74)[b] **22** (77)[c]
	**19** (80)	**23** (76)[b]
	**20** (84)	**24** (78)[b]
	**21** (82)	**25** (78)[b]

[a] The deprotections were conducted with the anomerically pure β-anomer. [b] Heating in a microwave reactor. [c] Conventional heating in DMF solution.

with the results set out in Table 2. As in the model experiments (Scheme 2), all attempts at debenzylation with TBAF at lower temperatures resulted only in the cleavage of the silyl group.

In a final demonstration of the ability of the new protecting group to support β-mannosylation reactions, donor **13** was coupled to alcohols **18** and **22** to generate the disaccharides **25** and **26**, both with excellent β-selectivity (Scheme 4), thereby establishing the viability of this new protecting group for use in the synthesis of mannans containing both the β-(1→2)[5g] and β-(1→3)[16d] linkages.

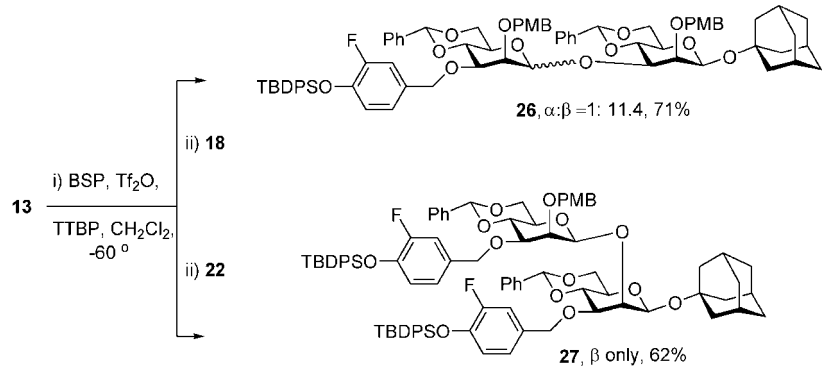
While the focus of this project has been on the application of the new benzyl protecting group in glycosylation reactions, we anticipate that it will also find use in the broader context of organic synthesis. In particular, we anticipate that the new protecting group will find application in situations requiring chelation control and the subsequent cleavage of the protecting group under desilylation conditions. Finally, we note that while we have concentrated here on benzyl ethers derived from bromide **5** based on the *tert*-butyldiphenylsilyl moiety, we expect that analogous chemistry will be possible with the corresponding 4-(*tert*-butyldimethylsiloxy)-3-fluorobenzyl and 4-(triisopropylsiloxy)-3-fluorobenzyl systems.

Experimental Section

General Experimental Details. Experiments conducted using microwave irradiation were carried out with a Biotage Initiator Exp

(17) Crich, D.; Smith, M.; Yao, Q.; Picione, J. *Synthesis* **2001**, 323–326.
(18) Crich, D.; Sun, S. *J. Am. Chem. Soc.* **1997**, *119*, 11217–11223.
(19) Crich, D.; Chandrasekera, N. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5386–5389.

SCHEME 4. Disaccharide Synthesis



US operating at a high absorbance level and with temperature determination by means of an infrared sensor.

4-(*tert*-Butyldiphenylsiloxy)-3-fluorobenzyl Alcohol (4). To a stirred solution of 3-fluoro-4-hydroxybenzoic acid (2.0 g, 12.8 mmol) and Et_3N (10.7 mL, 76.8 mmol) in CH_2Cl_2 (30 mL) was added TBDPSCl (8.4 mL, 32.0 mmol) dropwise at room temperature. The reaction mixture was stirred at rt overnight and then diluted with CH_2Cl_2 and washed with brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. The residue was then dissolved in dry THF (30 mL) at 0 °C, and $LiAlH_4$ (947 mg, 25.6 mmol) was added portionwise. After 10 min, the cooling bath was removed, and the reaction mixture was heated to reflux with stirring for 4 h. The reaction mixture was cooled to room temperature, and then water was added dropwise until a white solid precipitated. To this mixture was added Na_2SO_4, and the mixture was filtered through Celite. The filter cake was washed with CH_2Cl_2, and the filtrate was concentrated and the residue purified by flash chromatography over silica gel (15% ethyl acetate in hexane) to afford **4** (2.25 g, 46%): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79−7.77 (m, 4H), 7.46−7.40 (m, 6H), 7.06−7.04 (dd, J = 2.0, 11.0 Hz, 1H), 6.72 (d, J = 9.0 Hz, 1H), 6.65 (t, J = 8.5 Hz, 1H), 4.46 (s, 2H), 2.30 (s, 1H), 1.19 (s, 9H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 153.7 (d, J = 246.7 Hz), 142.8 (d, J = 12.9 Hz), 135.5, 134.6 (d, J = 5.0 Hz), 132.6, 130.1, 127.9, 122.5 (d, J = 2.5 Hz), 121.3, 115.2 (d, J = 18.9 Hz), 64.3, 26.6, 19.8; HRESIMS calcd for $C_{23}H_{25}O_2FSiNa$ $[M + Na]^+$ 403.1506, found 403.1496.

4-(*tert*-Butyldiphenylsiloxy)-3-fluorobenzyl Bromide (5). To a stirred solution of **4** (2.20 g, 5.8 mmol) and PPh_3 (2.27 g, 8.7 mmol) in CH_2Cl_2 (10 mL) was added CBr_4 (2.92 g, 8.8 mmol) portionwise. The resulting solution was stirred for 1 h at rt before it was concentrated, and the residue was purified by chromatography over silica gel (1% ethyl acetate in hexane) to afford **5** (2.32 g, 92%): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76−7.74 (m, 4H), 7.48−7.44 (m, 2H), 7.42−7.38 (m, 4H), 7.12−7.09 (dd, J = 2.0, 11.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.59 (t, J = 8.5 Hz, 1H), 4.37 (s, 2H), 1.16 (s, 9H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 153.5 (d, J = 246.7 Hz), 143.7 (d, J = 12.9 Hz), 135.5, 132.3, 131.2 (d, J = 6.3 Hz), 130.2, 127.9, 124.7 (d, J = 2.5 Hz), 121.4, 117.2 (d, J = 18.9 Hz), 33.0, 26.5, 19.7; HRESIMS calcd for $C_{23}H_{24}OBrFSiNa$ $[M + Na]^+$ 465.0662, found 465.0654.

General Procedure for the Removal of 4-(*tert*-Butyldiphenylsilyloxy)-3-fluorobenzyl Group Using a Microwave Reactor (Method A). To a stirred solution of the substrate and 4 Å molecular sieves in THF (0.05 M) was added TBAF (2 equiv, 1.0 M in THF). The reaction mixture was heated to 90 °C in a microwave reactor for 2 h and then cooled to rt and filtered through Celite. Purification by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures, afforded the corresponding alcohols.

(20) The anomeric stereochemistry of the coupled products was assigned on the basis of the characteristic chemical shift of the mannose H-5 resonance in the ^{1}H NMR spectrum[5b] and was confirmed by the measurement of anomeric $^1J_{CH}$ coupling constants. Bock, K.; Pedersen, C. *J. Chem. Soc., Perkin Trans. 2* **1974**, 293–297.

General Procedure for the Removal of 4-(*tert*-Butyldiphenylsilyloxy)-3-fluorobenzyl Group with Conventional Heating (Method B). To a stirred solution of the substrate and 4 Å molecular sieves in DMF (0.05 M) was added TBAF (2 equiv, 1.0 M in THF). The reaction mixture was heated to 90 °C for 3 h and then cooled to rt, filtered through Celite, and washed with EtOAc. The filtrate was diluted with EtOAc and washed with H_2O. The aqueous phase was extracted with EtOAc three times, and the combined organic phase was dried and concentrated. Purification by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures, afforded the corresponding alcohols.

General Procedure for the Removal of *p*-Methoxybenzyl Group. To a stirred solution of the substrate in CH_2Cl_2/H_2O (9/1, 0.05 M) was added DDQ (2 equiv) in one portion. The reaction mixture was stirred at rt for 2 h and then diluted with CH_2Cl_2 and washed with brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. Chromatographic purification on silica gel, eluting with hexane/ethyl acetate mixtures, afforded the corresponding alcohols.

2,2-Dibenzyl-3-(4-methoxybenzyloxy)propan-1-ol (7). From 2,2-Dibenzylpropane-1,3-diol 6. To a stirred solution of 2,2-dibenzylpropane-1,3-diol (309 mg, 1.21 mmol) in THF (5 mL) at 0 °C was added sodium hydride (60%, 63 mg, 1.57 mmol). After 10 min, PMBCl (213 μL, 1.57 mmol) was added and the reaction mixture stirred under reflux for 6 h. The reaction mixture was concentrated, dissolved in CH_2Cl_2, and washed with saturated NH_4Cl and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. Chromatographic purification (7.5% ethyl acetate in hexane) on silica gel gave **7** (369 mg, 81%). From **8**: Prepared by the general procedure for the removal of 4-(*tert*-butyldiphenylsilyloxy)-3-fluorobenzyl group using a microwave reactor (method A) with a yield of 25.4 mg (85%): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32−7.20 (m, 12H), 6.94−6.92 (m, 2H), 4.43 (s, 2H), 3.83 (s, 3H), 3.47 (d, J = 5.5 Hz, 2H), 3.25 (s, 2H), 2.82 (d, J = 13.5 Hz, 1H), 2.78 (d, J = 13.5 Hz, 1H), 2.37 (t, J = 5.5 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 159.3, 137.9, 130.7, 130.1, 129.5, 128.1, 126.2, 113.9, 73.7, 73.1, 66.5, 55.4, 43.4, 39.4; HRESIMS calcd for $C_{25}H_{28}O_3Na$ $[M + Na]^+$ 399.1931, found 399.1930.

2,2-Dibenzyl-1-[4-(*tert*-butyldiphenylsilyloxy)-3-fluorobenzyloxy]-3-(4-methoxybenzyloxy)propane (8). To a stirred solution of **7** (157 mg, 0.417 mmol) in HMPA (404 μL, 0.417 mmol) and anhydrous THF (4 mL) at 0 °C was added *n*-BuLi (184 μL, 0.459 mmol). The reaction mixture was stirred at 0 °C for 5 min, and then bromide **5** (222 mg, 0.500 mmol) in THF (1 mL) was added. The ice bath was removed and the stirring continued for 10 h at rt. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel (2.5% ethyl acetate in hexane) to give **8** (219 mg, 71%): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78−7.76 (m, 4H), 7.48−7.35 (m, 8H), 7.26−7.16 (m, 10H), 7.12−7.10 (dd, J = 2.0, 11.0 Hz, 1H), 6.96−6.94 (m, 2H), 6.78 (d, J = 8.5 Hz, 1H), 6.65 (t, J = 8.5 Hz, 1H), 4.42 (s, 2H), 4.32

(s, 2H), 3.85 (s, 3H), 2.93 (s, 2H), 2.89 (s, 2H), 2.853 (s, 2H), 2.849 (s, 2H), 1.18 (s, 9H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 159.2, 153.6 (d, J = 245.5 Hz), 142.7 (d, J = 11.3 Hz), 138.4, 135.5, 132.6, 132.2 (d, J = 5.0 Hz), 130.7, 130.6, 130.1, 129.5, 127.8, 126.0, 123.2 (d, J = 2.6 Hz), 121.0, 115.9 (d, J = 17.6 Hz), 113.8, 72.7, 72.2, 70.0, 69.7, 55.4, 43.9, 39.0, 26.6, 19.7; HRESIMS calcd for $C_{48}H_{51}O_4FSiNa$ [M + Na]$^+$ 761.3438, found 761.3400.

2,2-Dibenzyl-3-[4-(*tert*-butyldiphenylsilyloxy)-3-fluorobenzyloxy]-propan-1-ol (9). Prepared by the general procedure for the removal of *p*-methoxybenzyl group from **8** with a yield of 29.6 mg (89%): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74−7.72 (m, 4H), 7.46−7.35 (m, 6H), 7.26−7.16 (m, 10H), 7.05−7.02 (dd, J = 2.0, 11.5 Hz, 1H), 6.72 (d, J = 8.5 Hz, 1H), 6.60 (t, J = 8.5 Hz, 1H), 4.30 (s, 2H), 3.43 (d, J = 5.5 Hz, 2H), 3.16 (s, 2H), 2.77 (d, J = 13.5 Hz, 1H), 2.73 (d, J = 13.5 Hz, 1H), 2.12 (t, J = 5.5 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 153.4 (d, J = 246.7 Hz), 142.9 (d, J = 11.3 Hz), 137.8, 135.5, 132.6, 131.5 (d, J = 5.0 Hz), 130.6, 130.1, 128.0, 127.8, 126.2, 123.2, 121.1 (d, J = 2.6 Hz), 115.9 (d, J = 18.8 Hz), 73.7, 72.7, 66.2, 43.4, 39.4, 26.5, 19.7; HRESIMS calcd for $C_{40}H_{43}O_3FSiNa$ [M + Na]$^+$, 641.2858, found 641.2854.

2,2-Dibenzyl-1-(4-hydroxy-3-fluorobenzyloxy)-3-(4-methoxybenzyloxy)propane (10). To a stirred solution of **8** (16.2 mg, 21.9 μmol) in THF (1 mL) was added TBAF (33.0 μL, 1.0 M in THF). The reaction mixture was stirred at rt for 2 h. The reaction mixture was concentrated, and chromatographic purification (10% ethyl acetate in hexane) on silica gel afforded **10** (12.5 mg, 92%): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34−7.32 (m, 2H), 7.23−7.13 (m, 10H), 7.05−6.97 (m, 2H), 6.94−6.91 (m, 2H), 5.18 (s, 1H), 4.40 (s, 2H), 4.36 (s, 2H), 3.84 (s, 3H), 2.93 (s, 2H), 2.92 (s, 2H), 2.84 (s, 4H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 159.2, 150.9 (d, J = 236.6 Hz), 142.9 (d, J = 13.8 Hz), 138.4, 131.6 (d, J = 5.0 Hz), 130.7, 130.6, 129.5, 127.8, 125.9, 124.3 (d, J = 2.6 Hz), 117.0, 115.1 (d, J = 17.6 Hz), 113.8, 72.7, 72.1, 69.6, 55.3, 43.9, 39.0; HRESIMS calcd for $C_{32}H_{33}O_4FNa$ [M + Na]$^+$ 523.2255, found 523.2252.

Phenyl 4,6-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-1-thio-α-D-mannopyranoside (12). To a mixture of **11** (1.25 g, 3.5 mmol), tetrabutylammonium hydrogensulfate (235 mg, 0.69 mmol), and PMBCl (0.57 mL, 4.2 mmol) in CH_2Cl_2 (50 mL) was added 1 M aq NaOH (17 mL). The reaction mixture was stirred under reflux for 24 h and then allowed to cool to room temperature and diluted with CH_2Cl_2. The organic layer was separated. The aqueous phase was extracted twice with CH_2Cl_2. The combined organic layer was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. Chromatographic purification (50% hexane in CH_2Cl_2) afforded **12** (1.16 g, 70%) as a white crystalline solid: mp 113 °C; $[\alpha]^{22}_D$ +124.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.25 m, 10H), 6.91−6.88 (m, 2H), 5.57 (s, 1H), 5.53 (s, 1H), 4.68 (d, J = 11.2 Hz, 1H), 4.58 (d, J = 11.2 Hz, 1H), 4.32−4.26 (dt, J = 4.8, 9.6 Hz, 1H), 4.24−4.20 (dd, J = 4.8, 10.4 Hz, 1H), 4.12−4.07 (m, 2H), 3.97 (t, J = 9.6 Hz, 1H), 3.83 (t, J = 10.4 Hz, 1H), 3.80 (s, 3H), 2.47 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 159.9, 137.5, 133.9, 132.0, 130.0, 129.5, 129.4, 128.5, 128.0, 126.6, 114.3, 102.4, 86.6, 79.9, 79.8, 73.1, 69.2, 68.7, 64.9, 55.5; HRESIMS calcd for $C_{27}H_{28}O_6SNa$ [M + Na]$^+$ 503.1504, found 503.1500.

Phenyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-1-thio-α-D-mannopyranoside (13). To a stirred solution of **12** (700 mg, 1.6 mmol) in DMF (8 mL) at 0 °C was added NaH (60% in mineral oil, 70.8 mg, 1.8 mmol). After 15 min, **5** (857 mg, 1.9 mmol) in DMF (2 mL) was added and the reaction mixture stirred at rt for 10 h. The reaction mixture was diluted with EtOAc and washed with H_2O. The aqueous phase was extracted with EtOAc three times, and the combined organic phase was dried and concentrated. Chromatographic purification (7.5% ethyl acetate in hexane) on silica gel gave **13** (947 mg, 74%): colorless oil; $[\alpha]^{23}_D$ +51.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75−7.73 (m, 4H), 7.50−7.24 (m, 18H), 7.06−7.03 (dd, J = 2.0, 11.5 Hz, 1H), 6.85 (s, 1H), 6.83 (s, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.60 (t, J = 8.5 Hz, 1H), 5.62 (s, 1H), 5.47 (s, 1H), 4.66−4.58 (m, 3H), 4.46 (d, J = 12.0 Hz, 1H), 4.27−4.20 (m, 3H), 3.97−3.96 (dd, J = 1.0, 3.0 Hz, 1H), 3.90−3.85 (m, 2H), 3.78 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.7, 153.9 (d, J = 245.6 Hz), 143.0 (d, J = 12.0 Hz), 137.7, 135.7, 134.1, 132.8, 132.2 (d, J = 6.5 Hz), 131.9, 130.3, 130.1, 129.8, 129.4, 129.1, 128.4, 128.0, 127.9, 126.3, 123.3 (d, J = 3.8 Hz), 121.2 (d, J = 1.9 Hz), 116.0 (d, J = 18.6 Hz), 114.1, 101.7, 87.3, 79.2, 77.5, 76.1, 72.7, 72.4, 68.7, 65.7, 55.5, 26.7, 19.9; HRESIMS calcd for $C_{50}H_{51}O_7FSSiNa$ [M + Na]$^+$ 865.3007, found 865.2997.

General Glycosylation Procedure Using the BSP/TTBP/Tf_2O System. To a stirred solution of donor (1 equiv), BSP (1.2 equiv), TTBP (1.5 equiv), and 4 Å molecular sieves in CH_2Cl_2 (0.05 M in donor) at −60 °C was added Tf_2O (1.2 equiv). After 30 min of stirring at −60 °C, a 0.15 M solution of the glycosyl acceptor (1.5 equiv) in CH_2Cl_2 was slowly added. The reaction mixture was stirred for a further 2 h at −60 °C before saturated $NaHCO_3$ was added to quench the reaction. The reaction mixture was allowed to reach room temperature and then filtered through a pad of Celite and washed with CH_2Cl_2, after which the filtrate was washed with saturated $NaHCO_3$ and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. Purification by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures, afforded the corresponding coupled products.

1-Adamantanyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-β-D-mannopyranoside (14β) and 1-Adamantanyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (14α). Prepared by the general glycosylation procedure with a yield of 419 mg (85%, β/α = 11.7:1). **14β**: white crystalline solid; mp 139 °C; $[\alpha]^{23}_D$ −19.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75−7.73 (m, 4H), 7.48−7.27 (m, 13H), 7.00 (d, J = 12.0 Hz, 1H), 6.85 (s, 1H), 6.83 (s, 1H), 6.63 (d, J = 8.5 Hz, 1H), 6.56 (t, J = 8.5 Hz, 1H), 5.59 (s, 1H), 4.92 (d, J = 12.5 Hz, 1H), 4.87 (d, J = 12.5 Hz, 1H), 4.76 (s, 1H), 4.48 (d, J = 12.5 Hz, 1H), 4.36 (d, J = 12.0 Hz, 1H), 4.28−4.25 (dd, J = 5.0, 10.5 Hz, 1H), 4.16 (t, J = 9.5 Hz, 1H), 3.93 (t, J = 10.0 Hz, 1H), 3.77 (s, 3H), 3.72 (d, J = 3.0 Hz, 1H), 3.52−3.49 (dd, J = 3.0, 10.0 Hz, 1H), 3.33−3.28 (dt, J = 4.5, 9.5 Hz, 1H), 2.19 (s, 3H), 1.88 (d, J = 11.0 Hz, 3H), 1.78 (d, J = 11.5 Hz, 3H), 1.68 (d, J = 12.5 Hz, 3H), 1.63 (d, J = 12.5 Hz, 3H), 1.15 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.4, 153.8 (d, J = 245.6 Hz), 142.9 (d, J = 12.1 Hz), 137.9, 135.7, 132.8, 132.4 (d, J = 6.5 Hz), 130.8, 130.7, 130.3, 129.0, 128.4, 128.0, 126.3, 123.1 (d, J = 2.8 Hz), 121.1 (d, J = 1.9 Hz), 115.9 (d, J = 19.5 Hz), 113.7, 101.6, 95.2 ($^1J_{CH}$ = 153.6 Hz), 78.7, 78.5, 76.1, 75.5, 74.2, 71.7, 69.1, 67.5, 55.5, 42.7, 36.5, 30.9, 26.8; HRESIMS calcd for $C_{54}H_{61}O_8FSiNa$ [M + Na]$^+$ 907.4017, found 907.4018. **14α**: colorless oil; $[\alpha]^{22}_D$ +37.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74−7.72 (m, 4H), 7.49−7.27 (m, 13H), 7.08−7.05 (dd, J = 2.0, 11.5 Hz, 1H), 6.87 (s, 1H), 6.85 (s, 1H), 6.70 (d, J = 8.5 Hz, 1H), 6.58 (t, J = 8.5 Hz, 1H), 5.62 (s, 1H), 5.09 (d, J = 2.0 Hz, 1H), 4.71 (d, J = 12.0 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.21−4.18 (dd, J = 5.0, 10.0 Hz, 1H), 4.15 (t, J = 9.5 Hz, 1H), 3.99−3.93 (dt, J = 5.0, 10.5 Hz, 1H), 3.94−3.91 (dd, J = 3.0, 9.5 Hz, 1H), 3.82 (t, J = 10.0 Hz, 1H), 3.79 (s, 3H), 3.60−3.59 (dd, J = 2.0, 3.0 Hz, 1H), 2.11 (s, 3H), 1.70−1.55 (m, 12H), 1.14 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.6, 153.8 (d, J = 244.7 Hz), 142.8 (d, J = 12.3 Hz), 134.0, 135.7, 132.9, 132.7 (d, J = 6.5 Hz), 130.5, 130.2, 130.1, 129.0, 128.4, 128.0, 126.2, 123.1 (d, J = 2.6 Hz), 121.1, 115.8 (d, J = 19.6 Hz), 114.0, 101.5, 92.7 ($^1J_{CH}$ = 167.9 Hz), 79.8, 77.3, 76.6, 74.9, 73.1, 72.5, 69.2, 64.0, 55.5, 42.5, 36.4, 30.8, 26.7, 19.9; HRESIMS calcd for $C_{54}H_{61}O_8FSiNa$ [M + Na]$^+$ 907.4017, found 907.4019.

4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranosyl-(1→3)-1,2:5,6-di-isopropylidene-α-D-glucofuranose (15). Prepared by the general glycosylation procedure with a yield of 120.6 mg (82%): colorless oil; $[\alpha]^{23}_D$ −31.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.74−7.72 (m, 4H), 7.48−7.27 (m, 13H), 7.02−6.99 (dd, *J* = 2.0, 11.5 Hz, 1H), 6.85 (s, 1H), 6.83 (s, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 8.5 Hz, 1H), 5.92 (d, *J* = 3.5 Hz, 1H), 5.59 (s, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.54 (s, 1H), 4.45−4.41 (m, 3H), 4.33−4.27 (m, 3H), 4.18−4.13 (m, 2H), 4.09−4.06 (dd, *J* = 6.0, 8.5 Hz, 1H), 3.91 (t, *J* = 10.0 Hz, 1H), 3.81 (d, *J* = 3.0 Hz, 1H), 3.78 (s, 3H), 3.53−3.50 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.32−3.27 (dt, *J* = 4.5, 10.0 Hz, 1H), 1.52 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) *δ* 159.6, 153.9 (d, *J* = 245.5 Hz), 143.0 (d, *J* = 12.2 Hz), 137.6, 135.7, 132.8, 132.1 (d, *J* = 5.5 Hz), 130.4, 130.3, 129.1, 128.5, 128.0, 126.2, 123.3 (d, *J* = 3.8 Hz), 121.2, 115.9 (d, *J* = 18.6 Hz), 113.9, 112.2, 108.9, 105.2 (d, *J* = 183.8 Hz), 101.6, 100.6 ($^1J_{CH}$ = 155.7 Hz), 83.1, 81.2, 80.7, 78.7, 78.1, 75.7, 74.6, 73.3, 72.0, 68.7, 68.0, 66.4, 55.5, 27.0, 26.9, 26.7, 26.5, 25.7, 19.9; HRESIMS calcd for $C_{56}H_{65}O_{13}FSiNa$ $[M + Na]^+$ 1015.4076, found 1015.4038.

Methyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (16*β*) and Methyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (16α). Prepared by the general glycosylation procedure with a yield of 133.8 mg (79%, *β*/α = 8.2:1). **16*β***: colorless oil; $[\alpha]^{23}_D$ −1.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.74−7.71 (m, 4H), 7.48−7.17 (m, 28H), 7.02−7.00 (dd, *J* = 2.0, 11.5 Hz, 1H), 6.84 (s, 1H), 6.82 (s, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.57 (t, *J* = 8.5 Hz, 1H), 5.57 (s, 1H), 5.04 (d, *J* = 11.0 Hz, 1H), 4.87−4.80 (m, 4H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 4.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.5 Hz, 1H), 4.40 (d, *J* = 12.5 Hz, 1H), 4.28−4.24 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.16−4.03 (m, 4H), 3.90 (t, *J* = 10.0 Hz, 1H), 3.80−3.77 (dd, *J* = 5.0, 12.0 Hz, 1H), 3.69 (s, 3H), 3.65 (d, *J* = 3.0 Hz, 1H), 3.55−3.52 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.50−3.45 (m, 2H), 3.41−3.39 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.36 (s, 3H), 3.23−3.18 (dt, *J* = 5.0, 10.0 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) *δ* 159.5, 153.9 (d, *J* = 245.5 Hz), 143.0 (d, *J* = 12.1 Hz), 139.0, 138.6, 138.2, 137.7, 135.7, 132.8, 132.2 (d, *J* = 5.5 Hz), 130.5, 130.4, 130.3, 129.1, 128.74, 128.67, 128.6, 128.47, 128.45, 128.4, 128.2, 128.0, 127.9, 126.2, 123.2 (d, *J* = 1.8 Hz), 121.2, 115.9 (d, *J* = 18.6 Hz), 113.8, 102.2 ($^1J_{CH}$ = 156.7 Hz), 101.6, 98.0 ($^1J_{CH}$ = 169.3 Hz),.82.5, 80.1, 78.8, 78.1, 76.1, 75.0, 74.6, 74.1, 73.6, 71.8, 69.9, 68.8, 68.4, 67.7, 55.40, 55.36, 26.7, 19.9; HRESIMS calcd for $C_{72}H_{77}O_{13}FSiNa$ $[M + Na]^+$ 1219.5015, found 1219.4989. **16α**: colorless oil; $[\alpha]^{23}_D$ +25.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.73−7.71 (m, 4H), 7.46−7.23 (m, 28H), 7.06−7.03 (dd, *J* = 2.0, 12.0 Hz, 1H), 6.83 (s, 1H), 6.81 (s, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.55 (t, *J* = 8.5 Hz, 1H), 5.59 (s, 1H), 5.00 (d, *J* = 10.5 Hz, 1H), 4.92 (d, *J* = 11.0 Hz, 1H), 4.83−4.77 (m, 3H), 4.69−4.56 (m, 6H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.19−4.15 (m, 2H), 4.00 (t, *J* = 10.0 Hz, 1H), 3.84−3.62 (m, 10H), 3.50−3.47 (dd, *J* = 3.5, 10.0 Hz, 1H), 3.40 (t, *J* = 9.5 Hz, 1H), 3.31 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) *δ* 159.5, 153.7 (d, *J* = 245.6 Hz), 142.9 (d, *J* = 12.2 Hz), 138.8, 138.30, 138.25, 137.9, 135.7, 132.8, 132.6 (d, *J* = 5.7 Hz), 130.2, 129.9, 129.0, 128.73, 128.71, 128.69, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 126.3, 123.1 (d, *J* = 1.8 Hz), 121.1, 115.8 (d, *J* = 19.4 Hz), 114.0, 101.7, 99.7 ($^1J_{CH}$ = 171.7 Hz), 98.0 ($^1J_{CH}$ = 169.5 Hz), 82.3, 80.3, 79.3, 78.0, 76.6, 76.1, 75.8, 75.2, 73.5, 73.2, 69.9, 66.4, 64.4, 55.5, 55.3, 26.7, 19.9; HRESIMS calcd for $C_{72}H_{77}O_{13}FSiNa$ $[M + Na]^+$ 1219.5015, found 1219.5043.

Methyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (17). Prepared by the general glycosylation procedure with a yield of 126.4 mg (62%): colorless oil; $[\alpha]^{24}_D$ −7.2 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.76−7.74 (m, 4H), 7.47−7.18 (m, 23H), 7.07−7.05 (dd, *J* = 2.0, 11.0 Hz, 1H), 6.84−6.82 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.62 (t, *J* = 8.5 Hz, 1H), 5.49 (s, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 4.82−4.67 (m, 5H), 4.40 (d, *J* = 12.5 Hz, 1H), 4.42−4.37 (m, 3H), 4.07−4.01 (m, 3H), 3.89−3.85 (dd, *J* = 8.5, 10.0 Hz, 1H), 3.78 (s, 3H), 3.70−3.56 (m, 4H), 3.52−3.48 (m, 1H), 3.49 (s, 3H), 3.41 (t, *J* = 10.0 Hz, 1H), 3.29−3.26 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.07−3.02 (dt, *J* = 5.0, 10.0 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) *δ* 159.5, 153.9 (d, *J* = 245.5 Hz), 143.0 (d, *J* = 11.7 Hz), 138.9, 137.8, 137.7, 135.7, 132.8, 132.5 (d, *J* = 5.7 Hz), 130.7, 130.4, 130.3, 129.1, 128.9, 128.5, 128.4, 128.32, 128.30, 128.1, 127.7, 126.3, 122.9 (d, *J* = 2.8 Hz), 121.2, 115.6 (d, *J* = 19.6 Hz), 113.8, 101.6, 101.5 (d, *J* = 161.9 Hz), 98.9 (d, *J* = 173.1 Hz), 78.9, 78.8, 78.5, 76.4, 75.3, 75.0, 73.9, 71.9, 70.5, 68.6, 68.4, 67.5, 63.2, 55.7, 55.5, 26.8, 19.9; HRESIMS calcd for $C_{65}H_{70}N_3O_{12}FSiNa$ $[M + Na]^+$ 1154.4611, found 1154.4583.

1-Adamantanyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-*β*-D-mannopyranoside (18). Prepared by the general procedure for the removal of the *p*-methoxybenzyl group from **14** with a yield of 97.3 mg (80%): colorless oil; $[\alpha]^{22}_D$ −5.3 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.73−7.71 (m, 4H), 7.48−7.34 (m, 11H), 7.10−7.07 (dd, *J* = 2.0, 11.0 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.57 (t, *J* = 8.5 Hz, 1H), 5.58 (s, 1H), 4.82 (s, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.5 Hz, 1H), 4.30−4.27 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.11 (t, *J* = 9.5 Hz, 1H), 3.92 (d, *J* = 3.0 Hz, 1H), 3.87 (t, *J* = 10.5 Hz, 1H), 3.60−3.57 (dd, *J* = 4.0, 9.5 Hz, 1H), 3.34−3.29 (dt, *J* = 5.0, 10.0 Hz, 1H), 2.59 (s, 1H), 2.18 (s, 3H), 1.86 (d, *J* = 11.0 Hz, 3H), 1.78 (d, *J* = 11.5 Hz, 3H), 1.66 (d, *J* = 12.5 Hz, 3H), 1.61 (d, *J* = 12.5 Hz, 3H), 1.12 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) *δ* 153.9 (d, *J* = 245.6 Hz), 143.1 (d, *J* = 12.2 Hz), 137.7, 135.7, 132.8, 132.0 (d, *J* = 5.6 Hz), 130.3, 129.2, 128.5, 128.0, 126.3, 123.6 (d, *J* = 2.8 Hz), 121.3, 116.2 (d, *J* = 19.6 Hz), 101.7, 93.5, 78.4, 77.2, 76.1, 71.78, 71.75, 69.0, 66.9, 42.6, 36.4, 30.9, 26.8, 19.9; HRESIMS calcd for $C_{46}H_{53}O_7FSiNa$ $[M + Na]^+$ 787.3442, found 787.3457.

4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-*β*-D-mannopyranosyl-(1→3)-1,2:5,6-diisopropylidene-α-D-glucofuranose (19). Prepared by the general procedure for the removal of the *p*-methoxybenzyl group from **15** with a yield of 17.7 mg (80%): colorless oil; $[\alpha]^{23}_D$ −15.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.75−7.73 (m, 4H), 7.50−7.24 (m, 18H), 7.06−7.03 (dd, *J* = 2.0, 11.5 Hz, 1H), 6.85 (s, 1H), 6.83 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.60 (t, *J* = 8.5 Hz, 1H), 5.62 (s, 1H), 5.47 (s, 1H), 4.66−4.58 (m, 3H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.27−4.20 (m, 3H), 3.97−3.96 (dd, *J* = 1.0, 3.0 Hz, 1H), 3.90−3.85 (m, 2H), 3.78 (s, 3H), 2.19−1.78 (br s, 1H), 1.15 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) *δ* 153.9 (d, *J* = 245.6 Hz), 143.2 (d, *J* = 11.2 Hz), 137.5, 135.7, 132.8, 131.7 (d, *J* = 5.5 Hz), 130.3, 129.2, 128.5, 128.0, 126.2, 123.6 (d, *J* = 3.8 Hz), 121.3, 116.2 (d, *J* = 18.6 Hz), 112.3, 109.2, 105.4, 101.7, 98.3, 83.1, 80.8, 79.0, 78.6, 76.4, 73.4, 72.1, 70.0, 68.9, 67.3, 67.0, 27.0, 26.9, 26.7, 26.6, 25.7, 19.9; HRESIMS calcd for $C_{48}H_{57}O_{12}FSiNa$ $[M + Na]^+$ 895.3501, found 895.3481.

Methyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-*β*-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (20). Prepared by the general procedure for the removal of the *p*-methoxybenzyl group from **16** with a yield of 45.9 mg (84%): colorless oil; $[\alpha]^{24}_D$ +15.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.73−7.70 (m, 4H), 7.47−7.20 (m, 26H), 7.10−7.08 (dd, *J* = 2.0, 11.0 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.58 (t, *J* = 8.5 Hz, 1H), 5.55 (s, 1H), 5.02 (d, *J* = 11.0 Hz, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.68−4.57 (m, 5H), 4.29−4.26 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.18 (s, 1H), 4.09−3.99 (m, 3H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.84 (t, *J* = 9.5 Hz, 1H), 3.81−3.77 (ddd, *J* = 2.0, 5.0, 10.0 Hz, 1H), 3.61−3.58 (dd, *J* = 5.5, 10.0 Hz, 1H), 3.54−3.51 (dd, *J*

= 3.5, 10.0 Hz, 1H), 3.49−3.46 (dd, J = 3.0, 9.5 Hz, 1H), 3.44 (t, J = 10.0 Hz, 1H), 3.36 (s, 3H), 3.24−3.19 (dt, J = 5.0, 10.0 Hz, 1H), 2.41 (s, 1H), 1.13 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 153.9 (d, J = 246.6 Hz), 143.2 (d, J = 12.1 Hz), 138.9, 138.6, 138.3, 137.6, 135.7, 132.8, 131.8 (d, J = 5.7 Hz), 130.3, 129.2, 128.74, 128.67, 128.5, 128.4, 128.22, 128.17, 128.0, 127.9, 126.2, 123.6 (d, J = 2.8 Hz), 121.2, 116.2 (d, J = 18.6 Hz), 101.8, 100.7, 98.1,.82.4, 80.1, 78.5, 77.7, 76.6, 76.0, 75.0, 73.6, 71.8, 70.0, 69.9, 68.8, 68.6, 67.1, 55.4, 26.7, 19.9; HRESIMS calcd for $C_{64}H_{69}O_{12}FSiNa$ [M + Na]$^+$ 1099.4440, found 1099.4418.

Methyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-*β*-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (21). Prepared by the general procedure for the removal of the *p*-methoxybenzyl group from **17** with a yield of 24.8 mg (82%): colorless oil; $[\alpha]^{23}_D$ +24.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73−7.71 (m, 4H), 7.47−7.18 (m, 19H), 7.07−7.05 (dd, J = 2.0, 11.0 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.58 (t, J = 8.5 Hz, 1H), 5.47 (s, 1H), 5.04 (d, J = 11.0 Hz, 1H), 4.81−4.72 (m, 3H), 4.59 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.46 (s, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.06−3.64 (m, 8H), 3.48−3.43 (m, 2H), 3.43 (s, 3H), 3.41 (t, J = 10.0 Hz, 1H), 3.29−3.26 (dd, J = 3.0, 10.0 Hz, 1H), 3.07−3.02 (dt, J = 5.0, 10.0 Hz, 1H), 2.46 (s, 1H), 1.14 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 153.9 (d, J = 245.6 Hz), 143.2 (d, J = 11.2 Hz), 138.5, 137.7, 137.6, 135.7, 132.7, 131.8 (d, J = 5.5 Hz), 130.3, 129.2, 128.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 126.2, 123.3 (d, J = 2.8 Hz), 121.3, 116.0 (d, J = 19.5 Hz), 101.7, 100.5, 98.9, 78.9, 78.3, 78.5, 75.3, 75.0, 73.9, 71.8, 70.3, 69.8, 68.6, 68.3, 67.0, 63.4, 55.6, 26.7, 19.9; HRESIMS calcd for $C_{57}H_{62}N_3O_{11}FSiNa$ [M + Na]$^+$ 1034.4035, found 1034.4011.

1-Adamantanyl 4,6-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranoside (22). Compound **22** was prepared by the general procedure for the removal of the 4-(*tert*-butyldiphenylsilyloxy)-3-fluorobenzyl group using microwave reactor (method A) from **14** with a yield of 49.5 mg (74%). Compound **22** was also prepared by the general procedure for the removal of the 4-(*tert*-butyldiphenylsilyloxy)-3-fluorobenzyl group with conventional heating (method B) from **14** with a yield of 45.3 mg (77%): colorless oil; $[\alpha]^{24}_D$ −65.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.31 (m, 7H), 6.91 (s, 1H), 6.89 (s, 1H), 5.53 (s, 1H), 5.08 (d, J = 11.5 Hz, 1H), 4.89 (s, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.29−4.26 (dd, J = 5.0, 10.5 Hz, 1H), 3.87 (t, J = 10.5 Hz, 1H), 3.82 (s, 3H), 3.82−3.73 (m, 3H), 3.36−3.31 (dt, J = 5.0, 9.5 Hz, 1H), 2.39 (d, J = 8.5 Hz, 1H), 2.20 (s, 3H), 1.90 (d, J = 11.0 Hz, 3H), 1.83 (d, J = 11.5 Hz, 3H), 1.69 (d, J = 12.5 Hz, 3H), 1.64 (d, J = 12.0 Hz, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.7, 153.9 (d, J = 245.6 Hz), 143.0 (d, J = 12.0 Hz), 137.7, 135.7, 134.1, 132.8, 132.2 (d, J = 6.5 Hz), 131.9, 130.3, 130.1, 129.8, 129.4, 129.1, 128.4, 128.0, 127.9, 126.3, 123.3 (d, J = 3.8 Hz), 121.2 (d, J = 1.9 Hz), 116.0 (d, J = 18.6 Hz), 114.1, 101.7, 87.3, 79.2, 77.5, 76.1, 72.7, 72.4, 68.7, 65.7, 55.5, 26.7, 19.9; HRESIMS calcd for $C_{31}H_{38}O_7Na$ [M + Na]$^+$ 545.2515, found 545.2515.

4,6-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranosyl-(1→3)-1,2:5,6-diisopropylidene-α-D-glucofuranose (23). Prepared by the general procedure for the removal of 4-(*tert*-butyldiphenylsilyloxy)-3-fluorobenzyl group using a microwave reactor (method A) from **15** with a yield of 19.7 mg (76%): colorless oil; $[\alpha]^{23}_D$ −53.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.47 (m, 2H), 7.37−7.27 (m, 5H), 6.92 (s, 1H), 6.90 (s, 1H), 5.94 (d, J = 3.5 Hz, 1H), 5.55 (s, 1H), 4.90 (d, J = 11.5 Hz, 1H), 4.71 (s, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 3.5 Hz, 1H), 4.44 (d, J = 11.0 Hz, 1H), 4.42 (d, J = 11.0 Hz, 1H), 4.36 (d, J = 3.5 Hz, 1H), 4.33−4.28 (m, 2H), 4.18−4.15 (dd, J = 6.5, 8.5 Hz, 1H), 4.10−4.10 (dd, J = 5.5, 8.5 Hz, 1H), 3.89−3.79 (m, 3H), 3.82 (s, 3H), 3.38−3.33 (dt, J = 5.0, 10.0 Hz, 1H), 2.52 (s, 1H), 1.53 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.6, 137.4, 130.2, 130.1, 129.4, 128.5, 126.5, 114.3, 112.3, 109.1, 105.2, 102.2, 100.3, 83.0, 81.0, 80.7, 79.5, 77.9, 75.3, 73.2, 70.9, 68.7, 67.4, 66.7, 55.5, 26.98, 26.94, 26.5, 25.8; HRESIMS calcd for $C_{33}H_{42}O_{12}Na$ [M + Na]$^+$ 653.2574, found 653.2556.

Methyl 4,6-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (24). Prepared by the general procedure for the removal of 4-(*tert*-butyldiphenylsilyloxy)-3-fluorobenzyl group using a microwave reactor (method A) from **16** with a yield of 13.3 mg (78%): colorless oil; $[\alpha]^{23}_D$ −15.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.27 (m, 22H), 6.89 (s, 1H), 6.88 (s, 1H), 5.51 (s, 1H), 5.02 (d, J = 11.0 Hz, 1H), 4.96 (d, J = 11.0 Hz, 1H), 4.91 (d, J = 11.0 Hz, 1H), 4.84 (d, J = 11.0 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 12.0 Hz, 1H), 4.59 (s, 1H), 4.52 (d, J = 11.5 Hz, 1H), 4.34 (s, 1H), 4.29−4.26 (dd, J = 5.0, 10.0 Hz, 1H), 4.17−4.15 (dd, J = 2.0, 10.0 Hz, 1H), 4.04 (t, J = 9.5 Hz, 1H), 3.88−3.75 (m, 7H), 3.71−3.66 (dt, J = 3.5, 9.5 Hz, 1H), 3.58−3.54 (dd, J = 5.5, 10.5 Hz, 1H), 3.51−3.49 (dd, J = 3.5, 10.0 Hz, 1H), 3.45 (t, J = 10.0 Hz, 1H), 3.37 (s, 3H), 3.28−3.23 (dt, J = 5.0, 10.0 Hz, 1H), 2.35 (d, J = 9.0 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.7, 138.8, 138.5, 138.3, 137.5, 130.4, 130.2, 129.3, 128.72, 128.70, 128.5, 128.43, 128.38, 128.3, 128.2, 128.1, 128.0, 126.4, 114.2, 102.5, 102.2, 98.1, 82.4, 80.2, 79.5, 78.1, 77.9, 76.2, 75.5, 75.1, 73.7, 70.9, 70.0, 68.8, 68.7, 67.3, 55.5, 55.4; HRESIMS calcd for $C_{49}H_{54}O_{12}Na$ [M + Na]$^+$ 857.3513, found 857.3504.

Methyl 4,6-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (25). Prepared by the general procedure for the removal of the 4-(*tert*-butyldiphenylsilyloxy)-3-fluorobenzyl group using a microwave reactor (method A) from **17** with a yield of 21.2 mg (78%): colorless oil; $[\alpha]^{24}_D$ −9.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) 7.49−7.27 (m, 17H), 6.88−6.86 (m, 2H), 5.43 (s, 1H), 5.19 (d, J = 11.0 Hz, 1H), 4.91 (d, J = 11.5 Hz, 1H), 4.81 (d, J = 3.5 Hz, 1H), 4.76 (d, J = 12.0 Hz, 1H), 4.70 (d, J = 11.0 Hz, 1H), 4.57 (d, J = 11.0 Hz, 1H), 4.48 (s, 1H), 4.44 (d, J = 11.5 Hz, 1H), 4.08−4.03 (m, 2H), 3.86 (t, J = 9.5 Hz, 1H), 3.80 (s, 3H), 3.73−3.62 (m, 5H),3.50−3.47 (m, 2H), 3.47 (s, 3H), 3.38 (t, J = 10.0 Hz, 1H), 3.07−3.02 (dt, J = 5.0, 10.0 Hz, 1H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.7, 138.7, 137.54, 137.48, 130.4, 130.1, 129.4, 129.0, 128.6, 128.5, 128.43, 128.40, 128.3, 128.2, 127.8, 126.5, 126.3, 114.1, 102.2, 101.8, 98.9, 79.3, 78.9, 78.8, 77.9, 75.9, 75.3, 74.0, 71.0, 70.5, 68.6, 68.3, 67.1, 63.2, 55.7, 55.5; HRESIMS calcd for $C_{42}H_{47}N_3O_{11}Na$ [M + Na]$^+$ 792.3108, found 792.3138.

1-Adamantanyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-α-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranoside (26α) and 1-Adamantanyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranosyl-(1→3)-4,6-*O*-benzylidene-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranoside (26*β*). Prepared by the general glycosylation procedure. Radical chromatographic purification (5% ethyl acetate in toluene) on silica gel provided **26** with a yield of 48.2 mg (71%, β/α = 11.4:1). **26α**: colorless oil; $[\alpha]^{24}_D$ −12.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69−7.27 (m, 22H), 7.06−7.03 (dd, J = 2.0, 11.0 Hz, 1H), 6.91 (s, 1H), 6.89 (s, 1H), 6.74 (s, 1H), 6.72 (s, 1H), 6.63−6.62 (m, 3H), 6.51 (t, J = 8.5 Hz, 1H), 5.61 (s, 1H), 5.56 (s, 1H), 5.34 (s, 1H), 4.84 (d, J = 11.5 Hz, 1H), 4.82 (s, 1H), 4.77 (d, J = 12.5 Hz, 1H), 4.49 (d, J = 12.5 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 4.33 (d, J = 12.0 Hz, 1H), 4.28−4.12 (m, 5H), 3.96−3.78 (m, 5H), 3.72 (s, 3H), 3.72−3.66 (m, 2H), 3.48 (s, 3H), 3.40−3.35 (dt, J = 5.0, 10.0 Hz, 1H), 2.18 (s, 3H), 1.86 (d, J = 12.0 Hz, 3H), 1.77 (d, J = 11.5 Hz, 3H), 1.68−1.59 (m, 6H), 1.10 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.39, 159.38, 153.9 (d, J = 245.7 Hz), 142.9 (d, J = 12.2 Hz), 137.9, 137.8, 135.6, 132.8, 132.4 (d, J = 5.0 Hz), 130.3, 130.2, 129.9, 129.7, 129.6, 129.0, 128.6, 128.5, 128.4, 128.0, 126.4, 126.3, 123.0 (d, J = 2.8 Hz), 121.0, 115.8 (d, J = 19.6 Hz), 113.84, 113.80, 102.0, 101.6, 99.8 ($^1J_{CH}$ = 169.5 Hz), 95.0 ($^1J_{CH}$ = 155.4 Hz), 79.2, 79.1, 78.2, 75.8, 75.7, 75.0, 74.6, 72.3, 72.0, 69.1, 69.0, 67.2, 64.9, 55.4,

55.1, 42.6, 36.4, 30.8, 26.7, 19.9; HRESIMS calcd for $C_{75}H_{83}O_{14}FSiNa$ $[M + Na]^+$ 1277.5434, found 1277.5403. **26*β***: colorless oil; $[\alpha]^{24}_D$ −54.2 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.73−7.72 (m, 4H), 7.49−7.17 (m, 21H), 6.70−6.65 (m, 5H), 6.57 (t, J = 8.5 Hz, 1H), 5.61 (s, 1H), 5.49 (s, 1H), 4.93 (d, J = 12.5 Hz, 1H), 4.871 (s, 1H), 4.87 (d, J = 12.0 Hz, 1H), 4.82 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.44 (d, J = 12.5 Hz, 1H), 4.36 (d, J = 12.0 Hz, 1H), 4.32−4.29 (dd, J = 5.0, 10.5 Hz, 1H), 4.18−4.15 (dd, J = 5.0, 10.5 Hz, 1H), 4.10 (t, J = 9.5 Hz, 1H), 4.06−4.03 (dd, J = 3.0, 10.5 Hz, 1H), 4.00 (t, J = 10.0 Hz, 1H), 3.96 (t, J = 10.0 Hz, 1H), 3.88 (s, 1H), 3.83 (t, J = 10.5 Hz, 1H), 3.80 (d, J = 3.0 Hz, 1H), 3.73 (s, 3H), 3.60 (s, 3H), 3.60−3.59 (m, 1H), 3.42−3.38 (dt, J = 5.0, 9.5 Hz, 1H), 3.16−3.13 (dd, J = 3.0, 9.5 Hz, 1H), 2.85−2.80 (dt, J = 4.5, 9.5 Hz, 1H), 2.22 (s, 3H), 1.94 (d, J = 11.0 Hz, 3H), 1.86 (d, J = 11.0 Hz, 3H), 1.70 (d, J = 12.0 Hz, 3H), 1.66 (d, J = 12.5 Hz, 3H), 1.13 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.6, 159.2, 153.9 (d, J = 245.7 Hz), 142.9 (d, J = 11.2 Hz), 137.8, 135.7, 132.8, 132.5 (d, J = 5.5 Hz), 131.0, 130.8, 130.4, 130.24, 130.21, 129.1, 129.0, 128.41, 128.37, 128.0, 126.5, 126.2, 122.8 (d, J = 3.7 Hz), 121.1, 115.7 (d, J = 19.6 Hz), 113.9, 113.7, 102.0, 101.5, 97.4 ($^1J_{CH}$ = 156.5 Hz), 95.8 ($^1J_{CH}$ = 154.0 Hz), 78.4, 77.8, 77.2, 75.9, 75.0, 74.3, 73.76, 73.74, 73.6, 71.2, 69.1, 68.7, 67.9, 67.7, 55.45, 55.42, 42.8, 36.4, 30.9, 26.8, 19.0; HRESIMS calcd for $C_{75}H_{83}O_{14}FSiNa$ $[M + Na]^+$ 1277.5434, found 1277.5483.

1-Adamantanyl 4,6-*O*-Benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-2-*O*-(4-methoxybenzyl)-*β*-D-mannopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-[4-(*tert*-butyldiphenylsiloxy)-3-fluorobenzyl]-*β*-D-mannopyranoside (27). Prepared by the general glycosylation procedure with a yield of 98.4 mg (62%). **27**: colorless oil; $[\alpha]^{23}_D$ −29.7 (*c* 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75−7.71 (m, 8H), 7.48−7.34 (m, 22H), 7.26−7.22 (dd, J = 2.0, 12.0 Hz, 1H), 6.91−6.89 (dd, J = 1.5, 12.0 Hz, 1H), 6.84 (s, 1H), 6.82 (s, 1H), 6.63 (d, J = 8.5 Hz, 1H), 6.76 (t, J = 8.0 Hz, 1H), 6.58−6.51 (m, 3H), 5.59 (s, 1H), 5.47 (s, 1H), 4.97 (d, J = 12.0 Hz, 1H), 4.93 (d, J = 12.0 Hz, 1H), 4.87 (s, 1H), 4.80 (s, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.31−4.22 (m, 5H), 4.15 (t, J = 9.5 Hz, 1H), 4.04 (t, J = 9.5 Hz, 1H), 4.01 (d, J = 3.5 Hz, 1H), 3.90 (t, J = 10.0 Hz, 1H), 3.76 (t, J = 9.5 Hz, 1H), 3.74 (s, 3H), 3.60−3.58 (dd, J = 3.0, 10.0 Hz, 1H), 3.43−3.41 (dd, J = 3.0, 10.0 Hz, 1H), 3.37−3.32 (dt, J = 5.0, 9.5 Hz, 1H), 3.29−3.25 (dt, J = 5.0,10.0 Hz, 1H), 2.18 (s, 3H), 1.76 (d, J = 10.0 Hz, 3H), 1.70 (d, J = 11.0 Hz, 3H), 1.67 (d, J = 11.5 Hz, 3H), 1.60 (d, J = 12.0 Hz, 3H), 1.14 (s, 9H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ 159.3, 153.88 (d, J = 245.0 Hz), 153.85 (d, J = 246.1 Hz), 142.83 (d, J = 12.1 Hz), 142.79 (d, J = 12.1 Hz), 137.9, 137.7, 135.7, 132.91, 132.88, 132.87, 132.7 (d, J = 5.7 Hz), 132.3 (d, J = 6.0 Hz), 131.2, 131.0, 130.2, 129.1, 129.0, 128.5, 128.4, 128.0, 126.30, 126.26, 123.1 (d, J = 2.8 Hz), 121.0, 120.9, 116.0 (d, J = 18.5 Hz), 115.7 (d, J = 19.6 Hz), 113.7, 104.4 ($^1J_{CH}$ = 154.0 Hz), 101.8, 101.5, 94.6 ($^1J_{CH}$ = 154.0 Hz), 79.1, 78.5, 78.3, 76.6, 75.7, 74.0, 73.9, 70.7, 70.6, 69.2, 68.9, 68.0, 67.5, 55.4, 42.8, 36.4, 30.8, 26.8; HRESIMS calcd for $C_{90}H_{98}O_{14}F_2Si_2Na$ $[M + Na]^+$ 1519.6361, found 1519.6327.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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