Metal Trifluoromethanesulfonate-Catalyzed Regioselective Reductive Ring Opening of Benzylidene Acetals

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A systematic study of various metal trifluoromethanesulfonates as efficient catalysts in the regioselective reductive ring opening of benzylidene acetals is described, including the effects of solvents, reducing agents, and temperature. These catalysts are found to be effective in cleaving the 4,6-*O*-acetal rings of hexopyranosides at either O4 or O6, respectively. When used in conjunction with a 1 M solution of BH_3·THF in THF without extra addition of any solvent, it affects the ring fission at the O6 position to generate the corresponding primary alcohols, whereas O4-opening takes place in acetonitrile in the presence of dimethylethylsilane as the reductant leading to the secondary hydroxyl derivatives in high selectivity and yields. These methodologies can be applied to a wide range of substrates containing various functional groups.

Keywords: Metal trifluoromethanesulfonates; Catalysis; Cleavage reactions; Benzylidene acetals; Reduction; Regioselectivity.

INTRODUCTION

Carbohydrates and glycoconjugates play significant roles in a diverse set of biological processes, including viral and bacterial infections, cell growth and proliferation, and cell-cell communication, as well as immuno-responses.[1] Characterization of the molecular properties within the carbohydrates and their binding biomolecules, responsible for specific recognition, is an urgent issue. Due to the difficulties in obtaining homogeneous materials in workable quantities from natural sources, synthetic methods to construct these biologically potent domains have acquired immense importance.[2]

The distinction of all hydroxyl groups present on a monosaccharide is one of the major challenges toward the preparation of oligosaccharides and glycoconjugates. The development of a successful protecting group scheme that allows for the manipulation of individual hydroxyls has received much attention.[3] Substituted and unsubstituted benzylidene acetals are valuable protecting groups[4] that block the 4,6-dihydroxyl groups of hexopyranosides. The arylidene acetals **1**, as illustrated in Fig. 1, can be selectively cleaved under appropriate reaction conditions to furnish the primary alcohols **2** (path a) and the secondary alcohols **3** (path b), respectively. The corresponding substituted[5] and unsubstituted benzyl groups are known to be differentiated easily and offer an excellent opportunity to establish

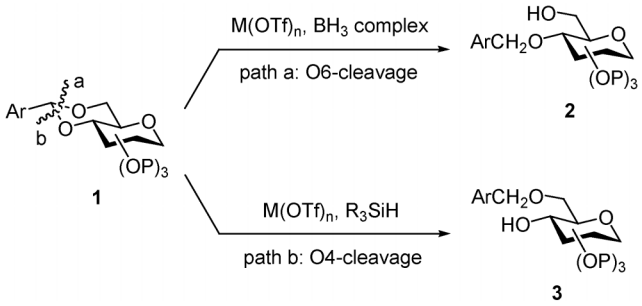

Fig. 1. Metal trifluoromethanesulfonate-catalyzed regioselective reductive ring opening of benzylidene acetals **1** to the primary alcohols **2** (path a) and the secondary alcohols **3** (path b), respectively.

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orthogonal protecting group patterns. A number of effective reagents for regioselective ring opening of 4,6-*O*-benzylidene acetals have been documented in the literature. AlH_3[6] and DIBAL-H[7] are often used for O6-cleavage, except with the substrates containing base-sensitive functionalities. The acid-activated reductive cleavage is an alternative solution in opening the acetal ring at either O6 or O4. A variety of combinations, for example, BH_3·THF/Ph_2BBr[8] or Bu_2BOTf,[9] BH_3·Me_3N/$AlCl_3$ in toluene,[10] BH_3·Me_2NH/BF_3·OEt_2 in dichloromethane,[11] Et_3SiH/$PhBCl_2$,[12] and polymethylhydrosiloxane/$AlCl_3$[13] give the desired 6-alcohols as the major isomers. For the synthesis of the corresponding 4-alcohols, BH_3·Me_3N/$AlCl_3$ in tetrahydrofuran,[10] BH_3·Me_2NH/BF_3·OEt_2 in acetonitrile,[11] $NaCNBH_3$/HCl[14] or TfOH,[15] Et_3SiH/CF_3CO_2H,[16] TfOH[12] or BF_3·OEt_2,[11b,17] and Bu_3SnH/$MgBr_2$·OEt_2[18] have been reported. However, most of these traditional acids are moisture-unstable and have to be used in stoichiometric or excess amounts, yielding the hydrolyzed 4,6-diol as a major side product. There is a need to search for new Lewis acids as efficient catalysts for selective cleavage. We report herein a systematic screening of various metal trifluoromethanesulfonates [$M(OTf)_n$] to open the benzylidine acetals at either O4 or O6 via altering the reactivity of reducing agents (Fig. 1). The amounts of catalysts and the effects of reducing agents and solvents, as well as temperature, are also described.

RESULTS AND DISCUSSION

Regioselective Ring Opening of Benzylidene Acetals to the Primary Alcohols

$M(OTf)_n$ are water-stable and reusable Lewis acid catalysts and have been widely applied in numerous organic reactions.[19] However, the reports on use of these $M(OTf)_n$ in conjunction with a reducing agent are rare.[20] In our preliminary investigation, borane-reductive O6-ring opening of the benzylidene acetal **4** catalyzed by $V(O)(OTf)_2$[21] or $Cu(OTf)_2$[22] could provide the corresponding primary alcohol **5** in excellent selectivity. An extensive study of various $M(OTf)_n$ and reducing agents at room temperature is outlined in Table 1. All $M(OTf)_n$ using 15 mol% were found to effectively catalyze the bond cleavage (entries 1-13). Amongst these, $Cu(OTf)_2$ and $Zn(OTf)_2$ are cheaper and the former has an edge over the latter on the basis of reactivity; the reaction was completed in 45 min (entry 13, 94%). Since commercially available BH_3·THF reagent was prepared as a 1 M solution in tetrahydrofuran, it was realized that the use of additional solvent, dichloromethane, was not necessary, and its exclusion gave similar results (entry 14, 92%).

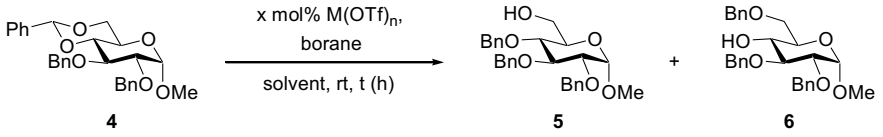
A set of experiments was performed to determine the minimum catalytic amount of $Cu(OTf)_2$ required for optimum activity. When the concentration of catalyst was lowered to 10 mol% (entry 15) and 5 mol% (entry 16), similar selectivity and yields were obtained. Decreasing it to 1 mol% caused an extension of reaction time and a drop in yield (entry 17).

A combination of 5 mol% $Cu(OTf)_2$ with various borane reagents was further studied. Treatment of **4** with BH_3·Me_2S complex (entry 18) led to the 6-alcohol **5**[23] and 4-alcohol **6**[14a] in 78% and 3% yields, respectively. A ten-fold increase of the catalyst amount effected this transformation in a much shorter time and gave **5** in a similar yield (entry 19). In entry 20, when BH_3·NMe_3 complex was used as the reductant, compound **6** (40%) was isolated as the sole product along with recovery of the starting material (55%). A change in the catalyst concentration did show a deviation in the product ratio (entries 21 and 22). Reaction of **4** using a combination of 5 mol% $Cu(OTf)_2$ and a bulkier reagent 9-BBN was sluggish (entry 23), and it took overnight stirring to furnish **5** in a modest yield (40%) together with the hydrolyzed 4,6-diol (40%) and unreacted starting material (15%). While employment of a stoichiometric amount of $Cu(OTf)_2$ resulted in a considerable decrease in reaction time (7.5 h, entry 24), the other isomer **6** was also isolated in 15% yield along with the major 6-alcohol **5** (65%). These results have revealed that different borane reagents may affect the regioselective outcome of the reactions.

We further proceeded to investigate the scope and possible limitations of this methodology in a wide range of substrates. To test the compatibility of different protecting groups, under this set of optimized conditions [1 M BH_3·THF in THF, 5 mol% $Cu(OTf)_2$, without additional solvent], a variety of hexopyranoside, furanoside and non-carbohydrate compounds were selected for the reductive ring cleavage of benzylidene acetals. As depicted in Table 2, facile conversions to the corresponding primary alcohols were observed in most of the cases, while lowering the reaction temperature to 0 °C or use of an additional amount of catalyst, in a few instances, was beneficial.

In the D-glucose series, compound **7** could be converted into the expected 4-OBn derivative **8** (entry 1, 4.5 h, 87%), while the 2,3-di-OBz **9** gave the corresponding 6-al-

Table 1. $M(OTf)_n$-catalyzed regioselective borane-reductive O6-ring opening of 4,6-*O*-benzylidene acetal **4** to the corresponding 6-alcohol **5**



4 **5** **6**

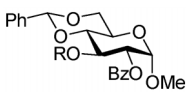
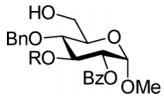
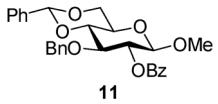
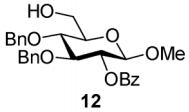
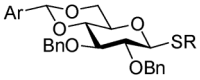
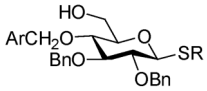
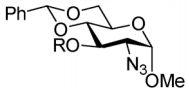
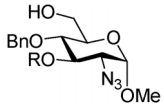
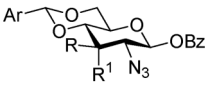
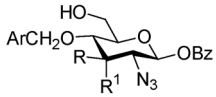
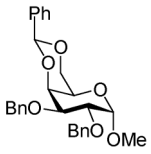
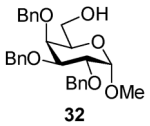
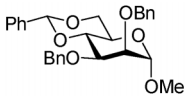
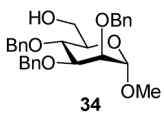
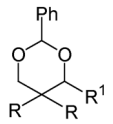
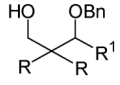
Entry	$M(OTf)_n$	x mol%	Borane	Solvent	t (h)	Yield (%)	
						5	**6**
1	$La(OTf)_3$	15	BH_3•THF[a]	CH_2Cl_2	21	86	0
2	$Pr(OTf)_3$	15	BH_3•THF	CH_2Cl_2	5	91	0
3	$Nd(OTf)_3$	15	BH_3•THF	CH_2Cl_2	4	94	0
4	$Sm(OTf)_3$	15	BH_3•THF	CH_2Cl_2	3.5	92	0
5	$Eu(OTf)_3$	15	BH_3•THF	CH_2Cl_2	3	87	0
6	$Gd(OTf)_3$	15	BH_3•THF	CH_2Cl_2	3	88	0
7	$Yb(OTf)_3$	15	BH_3•THF	CH_2Cl_2	2	94	0
8	$Sc(OTf)_3$	15	BH_3•THF	CH_2Cl_2	5	94	0
9	$In(OTf)_3$	15	BH_3•THF	CH_2Cl_2	2.5	82	0
10	$V(O)(OTf)_2$	15	BH_3•THF	CH_2Cl_2	3	94	0
11	$Zn(OTf)_2$	15	BH_3•THF	CH_2Cl_2	4	94	0
12	AgOTf	15	BH_3•THF	CH_2Cl_2	4	88	0
13	$Cu(OTf)_2$	15	BH_3•THF	CH_2Cl_2	0.75	94	0
14	$Cu(OTf)_2$	15	BH_3•THF	-	0.75	92	0
15	$Cu(OTf)_2$	10	BH_3•THF	-	1.5	93	0
16	$Cu(OTf)_2$	5	BH_3•THF	-	2.5	95	0
17	$Cu(OTf)_2$	1	BH_3•THF	-	27	70	0
18	$Cu(OTf)_2$	5	BH_3•Me_2S[b]	-	10	78	3
19	$Cu(OTf)_2$	50	BH_3•Me_2S	-	5	75	5
20	$Cu(OTf)_2$	5	BH_3•Me_3N	CH_2Cl_2	25	0	40
21	$Cu(OTf)_2$	50	BH_3•Me_3N	CH_2Cl_2	26	15	55
22	$Cu(OTf)_2$	100	BH_3•Me_3N	CH_2Cl_2	25	20	55
23	$Cu(OTf)_2$	5	9-BBN[c]	-	27	40	0
24	$Cu(OTf)_2$	100	9-BBN	-	7.5	65	15

[a] 1 M solution in THF.
[b] 2 M solution in THF.
[c] 0.5 M solution in THF.

cohol **10**[10] in modest yield (entry 2, 23 h, 53%). By increasing the catalyst concentration to 15 mol%, the latter transformation was carried out in a short period (5 h) and the product **10** was generated in very high yield (91%, entry 3). As compared to their 2,3-di-OBn analog **4** (0.75 h), these reactions took a longer time for completion. It is evident that the electron-donating groups in the substrate speed up the reaction, while the electron-withdrawing groups slow it down. Obviously, the reaction rate is closely associated with the nucleophilicity of the oxygen atom at C6 for the Lewis acid catalyst. Similarly, the β-form glucopyranoside **11** (entry 4) and thioglycoside **13** (entry 5) underwent a high-yielding ring fission to generate the 6-OH derivatives **12**[5b] (92%) and **14** (93%), respectively. The reaction conditions were also found to be suitable for substituted benzylidene acetals, as exemplified by cleavage of the PMP-acetal **15** (PMP = *p*-methoxyphenyl, entry 6, 0.75 h) that rapidly produced the primary alcohol **16** in excellent yield (97%). The structural assignment of all the products was unambiguously done through a series of NMR experiments. First, ^1H-^{13}C COSY was performed to mark the anomeric carbon and the doublet anomeric proton. ^1H-^1H COSY then established the correlation between all of the ring protons starting from H1. The regioselectivity was confirmed by observing the correlation between OH and H6/H4 protons. This general protocol was followed throughout the study.

In the D-glucosamine series, the α-form 3-OBn **17** (entry 7) and 3-OBz **19** (entry 10) gave the O6-ring opened

Table 2. BH_3•THF-reductive ring opening of various benzylidene acetals at O6 using $Cu(OTf)_2$ as the catalyst

Entry	Acetal	x mol%	T (°C)	t (h)	Product	Yield (%)
						
1	**7** : R = H	5	rt	4.5	**8** : R = H	87
2	**9** : R = Bz	5	rt	23	**10** : R = Bz	53
3	**9** : R = Bz	15	rt	5	**10** : R = Bz	91
4	 **11**	5	rt	4	 **12**	92
						
5	**13** : R = Tol, Ar = Ph	5	rt	3.5	**14** : R = Tol, Ar = Ph	93
6	**15** : R = Et, Ar = PMP	5	rt	0.75	**16** : R = Et, Ar = PMP	97
						
7	**17** : R = Bn	5	rt	6.5	**18** : R = Bn	55
8	**17** : R = Bn	15	rt	3.5	**18** : R = Bn	67
9	**17** : R = Bn	15	0	14	**18** : R = Bn	86
10	**19** : R = Bz	5	rt	5	**20** : R = Bz	56
11	**19** : R = Bz	15	0	9	**20** : R = Bz	57
						
12	**21** : R = OBn, R^1 = H, Ar = Ph	5	rt	3	**22** : R = OBn, R^1 = H, Ar = Ph	82
13	**23** : R = OBz, R^1 = H, Ar = Ph	5	rt	21	**24** : R = OBz, R^1 = H, Ar = Ph	63
14	**23** : R = OBz, R^1 = H, Ar = Ph	15	rt	4.5	**24** : R = OBz, R^1 = H, Ar = Ph	90
15	**25** : R = OBn, R^1 = H, Ar = 2-Naph	5	rt	8	**26** : R = OBn, R^1 = H, Ar = 2-Naph	86
16	**27** : R = OBz, R^1 = H, Ar = 2-Naph	5	rt	16	**28** : R = OBz, R^1 = H, Ar = 2-Naph	89
17	**29** : R = H, R^1 = OBn, Ar = Ph	5	rt	4.5	**30** : R = H, R^1 = OBn, Ar = Ph	62
18	**29** : R = H, R^1 = OBn, Ar = Ph	15	0	20	**30** : R = H, R^1 = OBn, Ar = Ph	90
19	 **31**	5	14	2.5	 **32**	89
20		5	rt	3.5	 **34**	84
						
21	**35** : R = R^1 = H	5	rt	0.75	**36** : R = R^1 = H	89
22	**37** : R = Me, R^1 = H	5	rt	0.75	**38** : R = Me, R^1 = H	92
23	**39** : R = H, R^1 = Me	5	rt	1.5	**40** : R = H, R^1 = Me	90

products **18** and **20** in 55% and 56% yields, respectively. Increasing the catalyst concentrations to 15 mol% and conducting the reaction at 0 °C improved the yield remarkably in the case of the former (entry 9, 86%), whereas a substantial amount of the hydrolyzed 4,6-diol (30%) still prevailed in the latter (entry 11, 57%). The β-form benzoates **21**, **25**, and **27**, individually, delivered the desired products **22** (entry 12, 82%), **26**[24] (entry 15, 82%), and **28**[25] (entry 16, 82%) at ambient temperature. The absolute configuration of compound **22** was determined through X-ray single-crystal analysis (see Supporting Information). The 3-OBz analog **23**, although sluggish to react under the optimized conditions (entry 13, 63%), successfully furnished the expected **24** rapidly and in excellent yield (90%), when 15 mol% $Cu(OTf)_2$ was used (entry 14). A similar phenomenon was observed in the case of the allosamine derivative **29** (entries 17 and 18), and the corresponding 6-alcohol **30**[26] was obtained in 90% yield. In entries 19 and 20, the D-*galacto*- and D-*manno*-configured 4,6-*O*-benzylidene acetals **31** and **33** also yielded the desired 4-OBn derivatives **32**[10] (89%) and **34**[27] (84%), respectively.

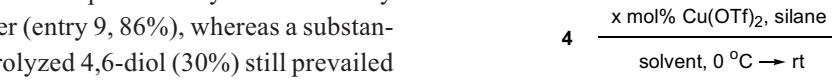
Finally, we examined ring opening of some common non-sugar substrates. The symmetrical 1,3-*O*-benzylidene acetals **35** (entry 21) and **37** (entry 22) underwent a smooth cleavage in a rapid manner to afford the primary alcohols **36**[28] (89%) and **38**[29] (92%), respectively. Likewise, in the case of the unsymmetrical acetal **39**, excellent regioselectivity was observed, and the expected compound **40**[30] was obtained in 90% yield (entry 23).

Regioselective Ring Opening of Benzylidene Acetals to the Secondary Alcohols

The catalytic properties of $M(OTf)_n$ for the regioselective reductive cleavage of benzylidene acetal at O4 were further investigated. A preliminary screening was carried out using three representative members, $V(O)(OTf)_2$, $Sc(OTf)_3$ and $Cu(OTf)_2$. Initial trial experiments with the model compound **4** were conducted in dichloromethane at ambient temperature in the presence of 30 mol% catalyst and 5 equiv of triethylsilane. Of these, $V(O)(OTf)_2$ and $Sc(OTf)_3$ virtually remained inert under the conditions, and only $Cu(OTf)_2$ provided the 4-alcohol **6** in 68% yield. These results guided us to discover the inherent potential of $Cu(OTf)_2$ first.

Table 3 summarizes a systematic study of $Cu(OTf)_2$-catalyzed silane-reductive O4-opening of the acetal **4**, including the effects of solvents, silane agents, and catalyst concentrations. The addition of catalyst was carried out at 0 °C, and the reaction was gradually warmed up to room temperature. When 1 mol% $Cu(OTf)_2$ was used together with triethylsilane in dichloromethane (entry 1), the reaction took 15 h to provide the secondary alcohol **6**[14b] (62%) as the only regioisomer. A smaller reducing agent Me_2EtSiH offered a marginally improved yield of **6** (65%) in a much shorter reaction time (entry 2, 9 h). Use of a more polar solvent like nitromethane speeded up the reactions of **4** with Et_3SiH (entry 3, 1 h) and Me_2EtSiH (entry 4, 1 h), affording **6** as the sole product in 60% and 68% yields, respectively. Although no other regioisomer was detected, hydrolysis of compound **4** to the corresponding 4,6-diol seemed to become a dominant factor in limiting the yield. Tetrahydrofuran and toluene gave disappointing results (entries 5-8). Nevertheless, reduction of **4** in acetonitrile using Et_3SiH (entry 9, 1 h) readily furnished the expected compound **6** (76%) along with the minor isomer **5** (7%), while Me_2EtSiH led to **6** in 84% yield (entry 10, 0.5 h), exclusively. The hy-

Table 3. $Cu(OTf)_2$-catalyzed silane-reductive ring opening of compound **4** to the corresponding 4-alcohol **6** in various solvents



Entry	mol% of $Cu(OTf)_2$	Silane[a]	Solvent	t (h)	Yield (%)	
					5	**6**
1	1	Et_3SiH	CH_2Cl_2	15	0	62
2	1	Me_2EtSiH	CH_2Cl_2	9	0	65
3	1	Et_3SiH	CH_3NO_2	1	0	60
4	1	Me_2EtSiH	CH_3NO_2	1	0	68
5	1	Et_3SiH	THF	21	0	0
6	1	Me_2EtSiH	THF	21	0	14
7	1	Et_3SiH	Toluene	16	0	0
8	1	Me_2EtSiH	Toluene	16	0	0
9	1	Et_3SiH	CH_3CN	1	7	76
10	1	Me_2EtSiH	CH_3CN	0.5	0	84
11	1	Me_2EtSiH	CH_3CN[b]	15	0	0
12	1	Me_2EtSiH	CH_3CN[c]	16	1	5
13	1	Et_3SiH	EtCN	8	2	75
14	1	Me_2EtSiH	EtCN	6	3	83
15	1	$(i\text{-Pr})_3SiH$	CH_3CN	4	9	29
16	1	$NaCNBH_3$	CH_3CN	21	0	0
17	0.5	Me_2EtSiH	CH_3CN	4	3	75
18	5	Me_2EtSiH	CH_3CN	0.5	3	80
19	10	Me_2EtSiH	CH_3CN	0.5	2	82

[a] Two equivalents of silane were used.
[b] Anhydrous 4 Å MS were added extra.
[c] Anhydrous $CuSO_4$ was added extra.

drolyzed product was encountered to the extent of 10% in these cases. Extra addition of anhydrous 4 Å MS (entry 11) or $CuSO_4$ (entry 12), for avoiding this side reaction, proved to be futile exercises. Surprisingly, the former gave back unchanged starting material, whereas the latter generated **6** in a negligibly small amount (5%). Propionitrile was found to be a good solvent for this type of reaction with either Et_3SiH (entry 13, 75%, 8 h) or Me_2EtSiH (entry 14, 83%, 6 h). Similar results were obtained as those with acetonitrile, except that a longer time was needed to complete the reaction, and compound **5** also appeared in trace amounts.

We further examined (*i*-Pr)$_3$SiH (entry 15) and $NaCNBH_3$ (entry 16) as reducing agents in acetonitrile. However, both cases displayed poor yields and selectivity. In order to fine-tune the reaction conditions, different catalytic amounts of $Cu(OTf)_2$ were investigated. In entry 17, when the catalyst concentration was halved, the transformation took place gradually (4 h) to afford compound **6** in 75% yield, whereas increasing the concentration of catalyst to either 5 mol% (entry 18) or 10 mol% (entry 19) did not improve the yields of **6** (80-82%). From the above studies, 1 mol% of $Cu(OTf)_2$ turned out to be the minimum requirement for optimum activity.

Finally, a variety of $M(OTf)_n$ was screened to estimate their catalytic activities in the regioselective O4-opening of acetal **4** with Me_2EtSiH in acetonitrile (Table 4). None of the lanthanide series metal trifluoromethanesulfonates (entries 1-7) or $Zn(OTf)_2$ (entry 11) produced the expected alcohol **6**. Interestingly, $Sc(OTf)_3$, which was inert in dichloromethane in our preliminary studies, was found to be effective in CH_3CN, and compound **6** was isolated in 75% yield (entry 8). $In(OTf)_3$ (entry 9, 73%) and AgOTf (entry 12, 75%) also worked well, while $V(O)(OTf)_2$ gave poor results (entry 10, 30%). In comparison with the above catalysts, $Cu(OTf)_2$ exhibited the best yields in all our attempts (Table 3, entry 10, 84%).

With this optimized set of reaction conditions [1 mol% $Cu(OTf)_2$, Me_2EtSiH, CH_3CN, 0 °C → rt], a number of α- and β-hexopyranosides bearing different protecting groups were examined to check the generality of this protocol. As described in Table 5, a rapid conversion (1-2 h) of the 4,6-*O*-benzylidene acetals to the corresponding 4-OH-6-OBn derivatives was observed. In entries 1 and 2, reactions of the benzoates **7** and **9** led to the O4-opened products **41** and **42**[14a] in 71% and 85% yields, respectively. Similar high selectivity was realized in cases of the β-form glucopyranoside **11** and thioglycoside **13**, providing the secondary alcohols **43** (entry 3, 74%) and **44** (entry 4, 79%), individually, in good yields. In the D-glucosamine series, the α-methyl 3-OBn and 3-OBz acetals **17** (entry 5) and **19** (entry 6) furnished the desired adducts **45** (80%) and **46** (83%), respectively. Similarly, the 1,3-di-OBz analog **23** afforded compound **47** in 87% yield (entry 7). These experiments revealed that the electron-withdrawing group at the O3 position does not affect the reactivity of substrates, in contrast to that observed in the borane-reductive O6-opening reactions. In entry 8, the D-mannopyranosyl sugar **33** successfully underwent a facile regioselective cleavage to give the 6-OBn derivative **48**[31] (70%), while the non-carbohydrate compound **39** (entry 9) yielded the regioisomers 1-OH-3-OBn **40** (22%) and 1-OBn-3-OH **49**[32] (24%), along with the 1,3-di-OBn ether **50** (36%) as the major product.Interestingly, extra additions of 1 equiv benzaldehyde and 1 equiv Me_2EtSiH to the reaction mixture could increase the yield of **50** to 52%.

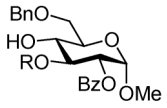
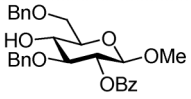
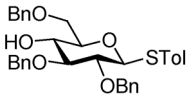
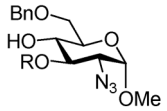
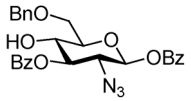
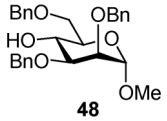
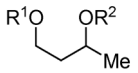
Table 4. Me_2EtSiH-reductive ring opening of compound **4** to the corresponding 4-alcohol **6** in acetonitrile using 1 mol% $M(OTf)_n$ as the catalyst

Entry	$M(OTf)_n$	t (h)	Yield (%)	
			5	**6**
1	$La(OTf)_3$	20	0	0
2	$Pr(OTf)_3$	18	0	0
3	$Nd(OTf)_3$	18	0	0
4	$Sm(OTf)_3$	18	0	0
5	$Eu(OTf)_3$	18	0	0
6	$Gd(OTf)_3$	18	0	0
7	$Yb(OTf)_3$	20	0	0
8	$Sc(OTf)_3$	1	8	75
9	$In(OTf)_3$	1.5	5	73
10	$V(O)(OTf)_2$	20	0	30
11	$Zn(OTf)_2$	18	0	0
12	AgOTf	0.5	5	75

CONCLUSIONS

Metal trifluoromethanesulfonates have been developed as versatile catalysts for regioselective borane- and dimethylethylsilane-reductive ring cleavages of various benzylidene acetals to the corresponding primary and secondary alcohols, respectively. The selectivity is very high and the reaction conditions are mild enough to apply to a wide range of substrates containing various protecting groups.

Table 5. 1 Mol% $Cu(OTf)_2$-catalyzed Me_2EtSiH-reductive O4-ring opening of various benzylidene acetals in acetonitrile

Entry	Acetal	t (h)	Product	Yield (%)
				
1	**7**	1	**41** : R = H	71
2	**9**	1	**42** : R = Bz	85
3	**11**	0.5	 **43**	74
4	**13**	1.5	 **44**	79
				
5	**17**	1	**45** : R = Bn	80
6	**19**	0.5	**46** : R = Bz	83
7	**23**	0.5	 **47**	87
8	**33**	1	 **48**	70
				
9	**39**	2	**40** : R^1 = H, R^2 = Bn	22
			49 : R^1 = Bn, R^2 = H	24
			50 : $R^1 = R^2$ = Bn	36

EXPERIMENTAL SECTION

General

All reactions were conducted in flame-dried glassware, under dry nitrogen atmosphere. $Cu(OTf)_2$ was desiccated with anhydrous P_2O_5 under a high vacuum system overnight. Dichloromethane was purified and dried from a safe purification system containing activated Al_2O_3. Acetonitrile was freshly distilled from calcium hydride under nitrogen. Anhydrous *N*,*N*-dimethylformamide, pyridine, and methanol were purchased from Sigma-Aldrich and used as such. All reagents obtained from commercial sources were used without purification, unless otherwise mentioned. Flash column chromatography was carried out on Silica Gel 60 (230-400 mesh, E. Merck). TLC was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25 mm, E. Merck); detection was executed by spraying with a solution of $Ce(NH_4)_2(NO_3)_6$ (0.5 g), $(NH_4)_6Mo_7O_{24}$ (24 g) and H_2SO_4 (28 mL) in water (500 mL) and subsequent heating on a hot plate. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Optical rotations were measured with Jasco DIP-370 and Horiba Sepa-300 polarimeters at 589 nm (Na) at ~25 °C. ^1H, ^{13}C NMR, DEPT, ^1H-^1H COSY, ^1H-^{13}C COSY, and NOESY spectra were recorded with Bruker AMX400, AV400, AV500, and AV600 MHz instruments. Chemical shifts are in ppm from Me_4Si, generated from the $CDCl_3$ lock signal at δ 7.24. IR spectra were taken with a Perkin-Elmer Paragon 1000 FT-IR spectrometer using NaCl plates. Elemental analyses were measured with a Perkin-Elmer 2400CHN instrument. Mass spectra were obtained with a FAB JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan).

General Procedure for Regioselective Ring Opening of Benzylidene Acetals to the Primary Alcohols

A 1 M solution of borane/tetrahydrofuran complex in tetrahydrofuran (5 mL, 5 mmol) was added to a benzylidene acetal (1 mmol) at room temperature under nitrogen. The mixture was stirred for 10 min, and freshly dried copper(II) trifluoromethanesulfonate (18 mg, 0.05 mmol) was added to the solution. After stirring for a period of time (Tables 1 and 2), the mixture was cooled down to 0 °C, and the reaction was quenched by sequential additions of triethylamine (0.14 mL, 1 mmol) and methanol (1.8 mL, *caution*: hydrogen gas was evolved). The resultant mixture was concentrated at reduced pressure followed by coevaporation with methanol. The residue was purified by flash column chromatography on silica gel to give the expected primary alcohol (Tables 1 and 2).

Methyl 2,3,4-Tri-*O*-benzyl-α-D-glucopyranoside (5)

$[\alpha]_D^{29}$ +26.3 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) ν 3475, 3027, 2905, 1452, 1363, 1055, 1026, 735, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 15H, ArH), 4.98 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.86 (d, *J* = 11.1 Hz, 1H, CH_2Ph), 4.82 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.78 (d, *J* = 12.1 Hz, 1H, CH_2Ph), 4.64 (d, *J* = 12.1 Hz, 1H, CH_2Ph), 4.62 (d, *J* = 11.1 Hz, 1H, CH_2Ph), 4.56 (d, *J* = 3.6 Hz, 1H, H-1), 3.99 (t, *J* = 9.4 Hz, 1H, H-3), 3.75 (ddd, *J* = 11.6, 5.4, 2.7 Hz, 1H, H-6a), 3.70-3.61 (m, 2H, H-6b, H-5), 3.50 (dd, *J* = 9.6, 9.4 Hz, 1H, H-4), 3.48 (dd, *J* = 9.4, 3.6 Hz, 1H, H-2), 3.35 (s,

3H, OCH_3), 1.60 (dd, J = 7.4, 5.4 Hz, 1H, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7 (C), 138.1 (2 × C), 128.5 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.93 (CH), 127.85 (CH), 127.6 (CH), 98.1 (CH), 81.9 (CH), 79.9 (CH), 77.4 (CH), 75.7 (CH_2), 75.0 (CH_2), 73.4 (CH_2), 70.6 (CH), 61.8 (CH_2), 55.2 (CH_3); HRMS [FAB, $(M-H)^+$] calcd for $C_{28}H_{31}O_6$ 463.2121, found 463.2111.

Methyl 2-*O*-Benzoyl-4-*O*-benzyl-α-D-glucopyranoside (8)

$[\alpha]_D^{30}$ +151.3 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$) ν 3448, 2926, 1721, 1454, 1277, 1103, 1029 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.2 Hz, 2H, BzH), 7.57 (t, J = 7.2 Hz, 1H, BzH), 7.44 (t, J = 7.2 Hz, 2H, BzH), 7.36-7.33 (m, 4H, ArH), 7.31-7.28 (m, 1H, ArH), 5.00 (d, J = 3.6 Hz, 1H, H-1), 4.89 (dd, J = 10.0, 3.6 Hz, 1H, H-2), 4.86 (d, J = 11.4 Hz, 1H, CH_2Ph), 4.76 (d, J = 11.4 Hz, 1H, CH_2Ph), 4.27 (td, J = 10.0, 3.3 Hz, 1H, H-3), 3.86 (ddd, J = 11.5, 7.7, 3.3 Hz, 1H, H-6a), 3.79 (ddd, J = 11.5, 7.7, 3.3 Hz, 1H, H-6b), 3.72 (dt, J = 10.0, 3.3 Hz, 1H, H-5), 3.59 (t, J = 10.0 Hz, 1H, H-4), 3.34 (s, 3H, OCH_3), 2.26 (d, J = 3.3 Hz, 1H, 3-OH), 1.80 (t, J = 7.7 Hz, 1H, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (C), 138.1 (C), 133.4 (CH), 129.9 (CH), 129.5 (C), 128.6 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 97.1 (CH), 77.8 (CH), 74.7 (CH_2), 74.1 (CH), 72.0 (CH), 70.5 (CH), 61.8 (CH_2), 55.3 (CH_3); HRMS (FAB, MH^+) calcd for $C_{24}H_{25}O_7$ 389.1600, found 389.1597.

Methyl 2,3-Di-*O*-benzoyl-4-*O*-benzyl-α-D-glucopyranoside (10)

$[\alpha]_D^{29}$ +140.9 (*c* 0.8, $CHCl_3$); IR ($CHCl_3$) ν 3445, 2848, 1725, 1447, 1280, 1106, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (dt, J = 7.2, 1.4 Hz, 4H, BzH), 7.48 (tq, J = 7.2, 1.4 Hz, 2H, BzH), 7.35 (dt, J = 7.2, 2.8 Hz, 4H, BzH), 7.18-7.15 (m, 5H, ArH), 6.04 (t, J = 9.2 Hz, 1H, H-3), 5.12 (d, J = 3.4 Hz, 1H, H-1), 5.10 (dd, J = 9.2, 3.4 Hz, 1H, H-2), 4.62 (d, J = 11.1 Hz, 1H, CH_2Ph), 4.60 (d, J = 11.1 Hz, 1H, CH_2Ph), 3.93 (t, J = 9.2 Hz, 1H, H-4), 3.90-3.86 (m, 3H, H-5, H-6a, H-6b), 3.38 (s, 3H, OCH_3), 1.92 (bs, 1H, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (C), 165.6 (C), 137.4 (C), 133.3 (CH), 133.0 (CH), 129.9 (C), 129.8 (CH), 129.2 (C), 128.5 (CH), 128.3 (CH), 128.0 (CH), 97.0 (CH), 75.8 (CH), 74.7 (CH_2), 72.5 (CH), 72.4 (CH), 70.7 (CH), 61.5 (CH_2), 55.3 (CH_3); HRMS (FAB, MH^+) calcd for $C_{28}H_{29}O_8$ 493.1862, found 493.1850.

Methyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-β-D-glucopyranoside (12)

$[\alpha]_D^{29}$ +53.6 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) ν 3487, 3059, 2928, 1726, 1269, 1212, 1209, 1147, 1094 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J = 7.2, 1.2 Hz, 2H, BzH), 7.56 (dt, J = 7.2, 1.2 Hz, 1H, BzH), 7.43 (t, J = 7.2 Hz, 2H, BzH), 7.35-7.28 (m, 5H, ArH), 7.12 (s, 5H, ArH), 5.23 (dd, J = 9.2, 8.0 Hz, 1H, H-2), 4.86 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.75 (d, J = 11.2 Hz, 1H, CH_2Ph), 4.67 (d, J = 11.0, 1H, CH_2Ph), 4.67 (d, J = 11.2 Hz, 1H, CH_2Ph), 4.48 (d, J = 8.0 Hz, 1H, H-1), 3.91 (dd, J = 12.0, 2.5 Hz, 1H, H-6a), 3.85 (t, J = 9.2 Hz, 1H, H-3), 3.76 (dd, J = 12.0, 4.4 Hz, 1H, H-6b), 3.74 (t, J = 9.2 Hz, 1H, H-4), 3.48-3.44 (m, 1H, H-5), 3.45 (s, 3H, OCH_3), 2.01 (bs, 1H, 6-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2 (C), 137.8 (C), 137.7 (C), 133.1 (CH), 129.9 (C), 129.8 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 102.1 (CH), 82.6 (CH), 77.6 (CH), 75.4 (CH), 75.1 (CH_2), 75.1 (CH_2), 73.7 (CH), 61.8 (CH_2), 57.0 (CH_3); HRMS (FAB, MH^+) calcd for $C_{28}H_{31}O_7$ 479.2070, found 479.2079.

***p*-Methylphenyl 2,3,4-Tri-*O*-benzyl-1-thio-β-D-glucopyranoside (14)**

$[\alpha]_D^{22}$ –10.9 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$) ν 3502, 2919, 2858, 1454, 1399, 1274, 1209, 1155, 1071 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.45-7.36 (m, 4H, ArH), 7.35-7.25 (m, 13H, ArH), 7.14 (d, J = 7.9 Hz, 2H, ArH), 4.91 (d, J = 10.1 Hz, 1H, CH_2Ph), 4.89 (d, J = 8.9 Hz, 1H, CH_2Ph), 4.85 (d, J = 8.9 Hz, 1H, CH_2Ph), 4.84 (d, J = 9.0 Hz, 1H, CH_2Ph), 4.75 (d, J = 10.1 Hz, 1H, CH_2Ph), 4.65 (d, J = 9.0 Hz, 1H, CH_2Ph), 4.65 (d, J = 9.3 Hz, 1H, H-1), 3.85 (d, J = 11.9 Hz, 1H, H-6a), 3.70 (t, J = 9.3 Hz, 1H, H-3), 3.68 (m, 1H, H-6b), 3.54 (t, J = 9.3 Hz, 1H, H-4), 3.45 (t, J = 9.3 Hz, 1H, H-2), 3.35 (ddd, J = 9.3, 4.7, 2.6 Hz, 1H, H-5), 2.33 (s, 3H, CH_3), 1.94 (bs, 1H, 6-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3 (C), 138.0 (C), 137.9 (C), 137.8 (C), 132.6 (CH), 129.8 (CH), 129.4 (C), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 87.8 (CH), 86.5 (CH), 81.1 (CH), 79.2 (CH), 77.6 (CH), 75.8 (CH_2), 75.5 (CH_2), 75.1 (CH_2), 62.1 (CH_2), 21.1 (CH_3); HRMS (FAB, MNa^+) calcd for $C_{34}H_{36}O_5SNa$ 579.2181, found 579.2185.

Ethyl 2,3-Di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-1-thio-β-D-glucopyranoside (16)

$[\alpha]_D^{22}$ –7.2 (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) ν 3320, 2896, 1514, 1452, 1391, 1353, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.26 (m, 10H, ArH), 7.18 (d, J = 8.6 Hz, 2H, 4-OMePhH), 6.83 (d, J = 8.6 Hz, 2H, 4-OMePhH), 4.91 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.89 (d, J = 10.4 Hz, 1H, CH_2Ph), 4.86 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.76 (d, J = 10.6 Hz, 1H, CH_2Ph), 4.72 (d, J = 10.4 Hz, 1H, CH_2Ph), 4.56 (d, J = 10.6

Hz, 1H, CH_2Ph), 4.47 (d, *J* = 9.6 Hz, 1H, H-1), 3.83 (ddd, *J* = 12.0, 6.0, 2.7 Hz, 1 H, H-6a), 3.77 (s, 3H, $ArOCH_3$), 3.67 (t, *J* = 9.6 Hz, 1H, H-3), 3.68-3.62 (m, 1H, H-6b), 3.53 (t, *J* = 9.6 Hz, 1H, H-4), 3.38 (t, *J* = 9.6 Hz, 1H, H-2), 3.33 (ddd, *J* = 9.6, 4.7, 2.7 Hz, 1H, H-5), 2.73 (ddt, *J* = 14.9, 7.4, 5.2 Hz, 2H, SCH_2CH_3), 1.88 (t, *J* = 6.0 Hz, 1H, 6-OH), 1.30 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (C), 138.5 (C), 137.9 (C), 130.1 (C), 129.8 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 113.9 (CH), 86.5 (CH), 85.3 (CH), 81.8 (CH), 79.3 (CH), 77.4 (CH), 75.7 (CH_2), 75.6 (CH_2), 74.8 (CH_2), 62.2 (CH_2), 55.3 (CH_3), 25.2 (CH_2), 15.2 (CH_3); HRMS (FAB, MH^+) calcd for $C_{30}H_{37}O_6S$ 525.2311, found 525.2315.

Methyl 2-Azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (18)

$[\alpha]_D^{22}$ +87.3 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν 3467, 2916, 2105, 1496, 1454, 1361, 1258, 1148, 1119, 1051, 1029 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.44-7.20 (m, 10H, ArH), 4.90 (d, *J* = 10.8 Hz, 1H, CH_2Ph), 4.88 (d, *J* = 10.8 Hz, 1H, CH_2Ph), 4.88 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.79 (d, *J* = 3.5 Hz, 1H, H-1), 4.68 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.00 (dd, *J* = 10.1, 9.5 Hz, 1H, H-3), 3.81 (d, *J* = 11.5 Hz, 1H, H-6a), 3.74 (d, *J* = 11.5 Hz, 1H, H-6b), 3.70 (dt, *J* = 9.5, 3.0 Hz, 1H, H-5), 3.62 (t, *J* = 9.5 Hz, 1H, H-4), 3.42 (s, 3H, OCH_3), 3.40 (dd, *J* = 10.1, 3.5 Hz, 1H, H-2), 1.71 (bs, 1H, 6-OH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8 (C), 137.1 (C), 128.5 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 98.7 (CH), 80.3 (CH), 77.9 (CH), 75.5 (CH_2), 75.0 (CH_2), 71.2 (CH), 63.7 (CH), 61.6 (CH_2), 55.2 (CH_3); HRMS [FAB, $(M-H)^+$] calcd for $C_{21}H_{24}O_5N_3$ 398.1716, found 398.1729.

Methyl 2-Azido-3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-D-glucopyranoside (20)

$[\alpha]_D^{29}$ +137.8 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) ν 3487, 2925, 2108, 1728, 1269, 1094, 1070, 1053 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, 2H, *J* = 7.5 Hz, 2H, BzH), 7.56 (t, *J* = 7.5 Hz, 1H, BzH), 7.43 (t, *J* = 7.5 Hz, 2H, BzH), 7.20-7.11 (m, 5H, ArH), 5.85-5.77 (m, 1H, H-3), 4.88 (d, *J* = 3.4 Hz, 1H, H-1), 4.60 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.56 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 3.81 (m, 4H, H-4, H-5, H-6a, H-6b), 3.45 (s, 3H, OCH_3), 3.27 (dd, *J* = 10.6, 3.4 Hz, 1H, H-2), 1.74 (bs, 1H, 6-OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5 (C), 137.3 (C), 133.3 (CH), 129.9 (CH), 129.6 (C), 128.5 (CH), 128.4 (CH), 128.9 (CH), 128.0 (CH), 99.3 (CH), 75.7 (CH), 74.8 (CH_2), 72.9 (CH), 71.0 (CH), 61.7 (CH), 61.4 (CH_2), 55.4 (CH_3); HRMS (FAB, MH^+) calcd for $C_{21}H_{24}O_6N_3$ 414.1665, found 414.1660.

2-Azido-3,4-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl Benzoate (22)

$[\alpha]_D^{22}$ –79.4 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν 3510, 3029, 2880, 2114, 1726, 1453, 1260, 1075, 1036 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.0, 1.2 Hz, 2H, BzH), 7.60 (dt, *J* = 8.0, 1.2 Hz, 1H, BzH), 7.46 (t, *J* = 8.0 Hz, 2H, BzH), 7.38-7.27 (m, 10H, ArH), 5.71 (d, *J* = 8.5 Hz, 1H, H-1), 4.91 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.89 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.87 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.69 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 3.87 (dd, *J* = 12.0, 2.5 Hz, 1H, H-6a), 3.72-3.67 (m, 3H, H-2, H-4, H-6b), 3.61 (t, *J* = 9.6 Hz, 1H, H-3), 3.54 (ddd, *J* = 9.6, 3.7, 2.5 Hz, 1H, H-5), 1.69 (bs, 1H, 6-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6 (C), 137.6 (2 × C), 133.9 (CH), 130.1 (CH), 128.8 (C), 128.7 (CH), 128.6 (CH), 128.53 (CH), 128.49 (CH), 128.1 (CH), 128.0 (CH), 93.5 (CH), 82.9 (CH), 76.7 (CH), 76.3 (CH), 75.7 (CH_2), 75.1 (CH_2), 65.5 (CH), 61.2 (CH_2); HRMS (FAB, MH^+) calcd for $C_{27}H_{28}O_6N_3$ 490.1978, found 490.1974.

2-Azido-3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-β-D-glucopyranosyl Benzoate (24)

$[\alpha]_D^{30}$ +46.3 (*c* 1.0, $CHCl_3$); mp 137-138 °C; IR ($CHCl_3$) ν 3372, 2950, 2097, 1720, 1646, 1538, 1259, 1082 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09-8.04 (m, 4H, Bz-H), 7.62-7.58 (m, 2H, Bz-H), 7.48-7.44 (m, 4H, Bz-H), 7.17-7.12 (m, 5H, Ar-H), 5.87 (d, *J* = 8.4 Hz, 1H, H-1), 5.49 (dd, *J* = 10.2, 9.2 Hz, 1H, H-3), 4.59, 4.58 (ABq, *J* = 11.1 Hz, 2H, CH_2Ph), 3.95-3.91 (m, 2H, H-4, H-6a), 3.82-3.77 (m, 2H, H-2, H-6b), 3.68 (dt, *J* = 9.7, 2.8 Hz, 1H, H-5), 1.77 (bs, 1H, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3 (C), 164.4 (C), 137.0 (C), 134.0 (C), 133.5 (CH), 130.1 (CH), 129.8 (CH), 129.4 (C), 129.3 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 93.6 (CH), 76.2 (CH), 74.7 (CH_2), 74.6 (2 × CH), 63.7 (CH), 60.9 (CH_2); HRMS (FAB, MH^+) calcd for $C_{27}H_{26}O_7N_3$ 504.1771, found 504.1785.

2-Azido-3-*O*-benzyl-2-deoxy-4-*O*-(2-naphthylmethyl)-β-D-glucopyranosyl Benzoate (26)

$[\alpha]_D^{28}$ –101.2 (*c* 0.60, $CHCl_3$); mp 137-139 °C; IR ($CHCl_3$) ν 3500, 2896, 2108, 1736, 1261, 1074, 1049, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2H, BzH), 7.84-7.78 (m, 3H, ArH), 7.73 (s, 1H, ArH), 7.61 (dt, *J* = 7.4, 1.2 Hz, 1H, ArH), 7.50-7.45 (m, 4H, ArH), 7.42-7.31 (m, 6H, ArH), 5.75 (d, *J* = 8.2 Hz, 1H, H-1), 5.02 (d, *J* = 11.2 Hz, 1H, CH_2Ar), 4.96-4.85 (m, 3H, CH_2Ar), 3.92 (dd, *J* = 12.3, 2.4 Hz, 1H, H-6a), 3.79-3.63 (m, 4H, H-2, H-3, H-4, H-6b), 3.59 (ddd, *J* = 9.7, 3.8, 2.4 Hz, 1H, H-5),

1.77 (s, 1H, OH-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (C), 137.6 (C), 135.1 (C), 133.9 (CH), 133.2 (C), 133.0 (C), 130.1 (CH), 128.7 (C), 128.6 (CH), 128.5 (C), 128.3 (CH), 128.03 (CH), 127.95 (CH), 127.9 (CH), 127.7 (CH), 126.7 (CH), 126.2 (CH), 126.1 (CH), 125.7 (CH), 93.5 (CH), 82.9 (CH), 76.9 (CH), 76.3 (CH), 75.7 (CH_2), 75.1 (CH_2), 65.5 (CH), 61.2 (CH_2); HRMS (FAB, MH^+) calcd for $C_{31}H_{30}N_3O_6$ 540.2134, found 540.2148.

2-Azido-3-*O*-benzoyl-2-deoxy-4-*O*-(2-naphthylmethyl)-β-D-glucopyranosyl Benzoate (28)

$[\alpha]_D^{24}$ -84.9 (*c* 1.06, $CHCl_3$); IR ($CHCl_3$) ν 3442, 2111, 1732, 1265, 1086 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.3, 1.1 Hz, 2H, BzH), 7.95 (dd, *J* = 8.3, 1.1 Hz, 2H, BzH), 7.67-7.64 (m, 2H, BzH), 7.61-7.51 (m, 4H, BzH), 7.47-7.44 (m, 2H, ArH), 7.41-7.35 (m, 4H, ArH), 7.25-7.22 (m, 1H, ArH), 5.89 (d, *J* = 8.4 Hz, 1H, H-1), 5.50 (dd, *J* = 10.0, 9.4 Hz, 1H, H-3), 4.78, 4.72 (ABq, *J* = 11.3 Hz, 2H, CH_2Naph), 3.99 (t, *J* = 9.4 Hz, 1H, H-4), 3.98 (ddd, *J* = 12.5, 4.9, 2.8 Hz, 1H, H-6a), 3.85 (dd, *J* = 10.0, 8.4 Hz, 1H, H-2), 3.84 (ddd, *J* = 12.5, 8.4, 2.8 Hz, 1H, H-6b), 3.72 (dt, *J* = 9.4, 2.8 Hz, 1H, H-5), 1.83 (dd, *J* = 8.4, 4.9 Hz, 1H, OH-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3 (C), 164.4 (C), 134.5 (C), 134.0 (CH), 133.5 (CH), 133.04 (C), 132.98 (C), 130.1 (CH), 129.8 (CH), 129.2 (C), 128.6 (CH), 128.5 (C), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 127.2 (CH), 126.1 (CH), 126.00 (CH), 125.97 (CH), 93.6 (CH), 76.3 (CH), 74.9 (CH_2), 74.7 (CH), 74.5 (CH), 63.8 (CH), 61.0 (CH_2); HRMS (FAB, M^+) calcd for $C_{31}H_{27}N_3O_7$ 553.1849, found 553.1842. Anal. Calcd for $C_{31}H_{27}N_3O_7$: C, 67.26; H, 4.92; N, 7.59. Found: C, 67.06; H, 4.92; N, 7.59.

2-Azido-3,4-di-*O*-benzyl-2-deoxy-β-D-allopyranosyl Benzoate (30)

$[\alpha]_D^{29}$ –130.3 (*c* 1.0, $CHCl_3$); mp 155-156 °C; IR ($CHCl_3$) ν 3510, 2913, 2098, 1736, 1596, 1347, 1261, 1066, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H, ArH), 7.59-7.55 (m, 1H, ArH), 7.45-7.25 (m, 12H, ArH), 6.28 (d, *J* = 8.4 Hz, 1H, H-1), 4.88 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.80 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.62 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.22 (t, *J* = 2.4 Hz, 1H, H-3), 4.18 (ddd, *J* = 9.6, 6.0, 3.0 Hz, 1H, H-5), 3.90 (ddd, *J* = 12.2, 5.1, 3.0 Hz, 1H, H-6a), 3.75 (ddd, *J* = 12.2, 8.0, 6.0 Hz, 1H, H-6b), 3.62 (dd, *J* = 9.6, 2.4 Hz, 1H, H-4), 3.49 (dd, *J* = 8.4, 2.4 Hz, 1H, H-2), 1.71 (dd, *J* = 8.0, 5.1 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 (C), 137.9 (C), 137.4 (C), 133.7 (CH), 130.0 (CH), 128.9 (C), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 92.3 (CH), 74.94 (CH_2), 74.86 (CH), 74.7 (CH), 73.9 (CH_2), 72.1 (CH), 62.4 (CH), 61.5 (CH_2); HRMS (FAB, M-H^+) calcd for $C_{27}H_{26}N_3O_6$ 488.1822, found 488.1826. Anal. Calcd for $C_{27}H_{27}N_3O_6$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.19; H, 5.28; N, 8.44.

Methyl 2,3,4-Tri-*O*-benzyl-α-D-galactopyranoside (32)

$[\alpha]_D^{29}$ +5.2 (*c* 1.8, $CHCl_3$); IR ($CHCl_3$) ν 3483, 3064, 2919, 1496, 1454, 1399, 1351, 1196, 1096, 1055 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 15H, ArH), 4.96 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.88 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.83 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.74 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.70 (d, *J* = 3.6 Hz, 1H, H-1), 4.68 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.62 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.04 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2), 3.92 (dd, *J* = 10.0, 2.8 Hz, 1H, H-3), 3.86 (d, *J* = 2.8 Hz, 1H, H-4), 3.73-3.69 (m, 2H, H-5, H-6a), 3.49-3.47 (m, 1H, H-6b), 3.35 (s, 3H, OCH_3), 1.69 (d, *J* = 7.0 Hz, 1H, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7 (C), 138.4 (C), 138.2 (C), 128.6 (CH), 128.5 (CH), 128.43 (CH), 128.36 (CH), 128.1 (CH), 128.0 (CH), 127.7 (CH), 127.61 (CH), 127.56 (CH), 98.8 (CH), 79.1 (CH), 76.5 (CH), 75.1 (CH), 74.4 (CH_2), 73.62 (CH_2), 73.58 (CH_2), 70.2 (CH), 62.4 (CH_2), 55.4 (CH_3); HRMS [FAB, $(M-H)^+$] calcd for $C_{28}H_{31}O_6$ 463.2121, found 463.2112.

Methyl 2,3,4-Tri-*O*-benzyl-α-D-mannopyranoside (34)

$[\alpha]_D^{21}$ +27.6 (*c* 2.6, $CHCl_3$); IR ($CHCl_3$) ν 3409, 2923, 1454, 1274, 1113, 1068, 1026 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 15H, ArH), 4.92 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.76 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.68 (d, *J* = 2.0 Hz, 1H, H-1), 4.67 (d, *J* = 12.0, 1H, CH_2Ph), 4.63 (d, *J* = 11.0, 1H, CH_2Ph), 4.62 (s, 2H, CH_2Ph), 3.95 (m, 1H, H-6a), 3.88 (dd, *J* = 9.5, 3.0 Hz, 1H, H-6b), 3.83 (dd, *J* = 11.8, 3.0 Hz, 1H, H-3), 3.78 (dd, *J* = 3.0, 2.0 Hz, 1H, H-2), 3.76 (dd, *J* = 11.8, 9.5 Hz, 1H, H-4), 3.60 (ddd, *J* = 9.5, 4.5, 3.0 Hz, 1H, H-5), 3.29 (s, 3H, OCH_3), 1.99 (bs, 1H, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.60 (C), 138.56 (C), 138.4 (C), 128.5 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 99.3 (CH), 80.1 (CH), 75.1 (CH_2), 74.9 (CH), 74.8 (CH), 73.0 (CH_2), 72.2 (CH_2), 72.0 (CH), 69.3 (CH_2), 54.7 (CH_3); HRMS [FAB, $(M-H)^+$] calcd for $C_{28}H_{31}O_6$ 463.2121, found 463.2115.

3-Benzyloxy-1-propanol (36)

IR ($CHCl_3$) ν 3397, 2930, 2868, 1454, 1101, 1075 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.16 (m, 5H, ArH), 4.43 (s, 2H, CH_2Ph), 3.69 (t, *J* = 5.7 Hz, 2H, CH_2O), 3.57 (t, *J* = 5.7 Hz, 2H, CH_2O), 1.90 (t, *J* = 9.0 Hz, 1H, OH), 1.77 (quin, *J* = 5.7 Hz, 2H, CH_2); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 138.1 (C), 128.4 (CH), 127.7 (CH), 127.6 (CH), 73.3 (CH_2), 69.4 (CH_2), 61.9 (CH_2), 32.1 (CH_2); HRMS (FAB, MH^+) calcd for $C_{10}H_{15}O_2$ 167.1702, found 167.1701.

3-Benzyloxy-2,2-dimethyl-1-propanol (38)

IR ($CHCl_3$) ν 3427, 2957, 2871, 1099 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 5H, ArH), 4.50 (s, 2H, CH_2Ph), 3.44 (s, 2H, CH_2O), 3.31 (s, 2H, CH_2O), 2.56 (bs, 1H, OH), 0.91 (s, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (C), 128.4 (CH), 127.7 (CH), 127.5 (CH), 79.5 (CH_2), 73.5 (CH_2), 71.8 (CH_2), 36.2 (C), 21.9 (2 × CH_3); HRMS (FAB, MH^+) calcd for $C_{12}H_{19}O_2$ 195.1385, found 195.1384.

3-Benzyloxy-1-butanol (40)

IR ($CHCl_3$) ν 3422, 2932, 1206, 1087, 1055 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.24 (m, 5H, ArH), 4.61 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 4.42 (d, *J* = 11.6 Hz, 1H, CH_2Ph), 3.80-3.70 (m, 3H, OCH_2, OCH), 2.57 (bs, 1H, OH), 1.81-1.70 (m, 2H, CH_2), 1.24 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4 (C), 128.4 (CH), 127.7 (CH), 127.6 (CH), 74.5 (CH), 70.4 (CH_2), 60.8 (CH_2), 38.8 (CH_2), 19.3 (CH_3); HRMS (FAB, MH^+) calcd for $C_{11}H_{17}O_2$ 181.1229, found 181.1232.

General Procedure for Regioselective Ring Opening of Benzylidene Acetals to the Secondary Alcohols

To a solution of a benzylidene acetal (1 mmol) in acetonitrile (2.3 mL per mmol of acetal) was added dimethylethylsilane (0.26 mL, 2 mmol) at room temperature under nitrogen. The reaction flask was immersed in an ice-bath, a solution of freshly dried copper(II) trifluoromethanesulfonate (3.6 mg, 0.01 mmol) in acetonitrile (2.3 mL per mmol of acetal) was added to the mixture, and the resultant solution was gradually warmed up to room temperature. After stirring for a period of time (Tables 3 and 4), the mixture was diluted with EtOAc (5 mL per mmol of acetal), and the reaction solution was opened to the air and continuously stirred for 2 h (pH = 5~6). The resultant mixture was washed by sat'd $NaHCO_{3(aq)}$, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Purification of the residue via flash column chromatography on silica gel provided the expected secondary alcohol (Tables 3 and 4).

Methyl 2,3,6-Tri-*O*-benzyl-α-D-glucopyranoside (6)

^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 15H, ArH), 4.98, 4.72 (ABq, *J* = 11.4 Hz, 2H, CH_2Ph), 4.75, 4.64 (ABq, *J* = 12.3 Hz, 2H, CH_2Ph), 4.62 (d, *J* = 3.5 Hz, 1H, H-1), 4.57, 4.52 (ABq, *J* = 12.1 Hz, 2H, CH_2Ph), 3.77 (t, *J* = 9.2 Hz, 1H, H-3), 3.70-3.60 (m, 3H, H-5, H-6a, H-6b), 3.58 (td, *J* = 9.2, 2.2 Hz, 1H, H-4), 3.51 (dd, *J* = 9.2, 3.5 Hz, 1H, H-2), 3.37 (s, 3H, OCH_3), 2.30 (d, *J* = 2.2 Hz, 1H, 4-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8 (C), 138.1 (C), 138.0 (C), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 98.2 (CH), 81.5 (CH), 79.6 (CH), 75.4 (CH_2), 73.6 (CH_2), 73.2 (CH_2), 70.8 (CH), 69.9 (CH), 69.5 (CH_2), 55.2 (CH_3).

Methyl 2-*O*-Benzoyl-6-*O*-benzyl-α-D-glucopyranoside (41)

$[\alpha]_D^{25}$ +88.7 (*c* 1.9, $CHCl_3$); IR ($CHCl_3$) ν 3430, 3062, 2920, 1718, 1601, 1450, 1276, 1046, 909, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H, BzH), 7.54 (t, *J* = 7.4 Hz, 1H, BzH), 7.41 (t, *J* = 7.4 Hz, 2H, BzH), 7.25-7.34 (m, 5H, ArH), 5.00 (d, *J* = 3.7 Hz, 1H, H-1), 4.92 (dd, *J* = 9.3, 3.7 Hz, 1H, H-2), 4.62, 4.57 (ABq, *J* = 12.1 Hz, 2H, CH_2Ph), 4.10 (t, *J* = 9.3 Hz, 1H, H-3), 3.83-3.63 (m, 4H, H-4, H-5, H-6a, H-6b), 3.36 (s, 3H, OCH_3), 3.09 (d, *J* = 2.1 Hz, 1H, 4-OH), 2.83 (bs, 1H, 3-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4 (C), 137.8 (C), 133.3 (CH), 129.9 (CH), 129.5 (C), 128.43 (CH), 128.38 (CH), 127.8 (CH), 127.7 (CH), 97.2 (CH), 73.8 (CH), 73.7 (CH_2), 71.9 (CH), 71.8 (CH), 69.7 (CH_2), 69.6 (CH), 55.3 (CH_3); HRMS (FAB, MH^+) calcd for $C_{21}H_{25}O_7$ 389.1600, found 389.1597.

Methyl 2,3-Di-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (42)

^1H NMR (400 MHz, $CDCl_3$) δ 8.00-7.23 (m, 15H, ArH), 5.73 (dd, *J* = 10.1, 8.8 Hz, 1H, H-3), 5.24 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 5.12 (d, *J* = 3.6 Hz, 1H, H-1), 4.65, 4.60 (ABq, *J* = 12.0 Hz, 2H, CH_2Ph), 4.00-3.92 (m, 2H, H-4, H-5), 3.84 (dd, *J* = 10.4, 3.9 Hz, 1H, H-6a), 3.79 (dd, *J* = 10.4, 3.2 Hz, 1H, H-6b), 3.41 (s, 3H, OCH_3), 3.05 (bs, 1H, 4-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2 (C), 165.9 (C), 137.8 (C), 133.3 (CH), 129.8 (CH), 129.3 (C), 129.2 (C), 128.4 (CH), 128.3 (CH), 127.8 (CH), 127.7 (CH), 97.1 (CH), 74.1 (CH), 73.7 (CH_2), 71.4 (CH), 70.5 (CH), 70.2 (CH), 69.5 (CH_2), 55.4 (CH_3).

Methyl 2-*O*-Benzoyl-3,6-di-*O*-benzyl-β-D-glucopyranoside (43)

$[\alpha]_D^{32}$ −170.7 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) ν 3493, 2870, 1726, 1601, 1451, 1270, 1069, 1027, 985, 739, 711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H, BzH), 7.56 (t, *J* = 7.4 Hz, 1H, BzH), 7.43 (t, *J* = 7.4 Hz, 2H, BzH), 7.40-7.10 (m, 10H, ArH), 5.22 (dd, *J* = 9.4, 7.9 Hz, 1H, H-2), 4.71, 4.66 (ABq, *J* = 11.5 Hz, 2H, CH_2Ph), 4.63, 4.57 (ABq, *J* = 12.0 Hz, 2H, CH_2Ph), 4.44 (d, *J* = 7.9 Hz, 1H, H-1), 3.79 (td, *J* = 9.4, 2.2 Hz, 1H, H-4), 3.79 (m, 2H, H-6a, H-6b), 3.66 (t, *J* = 9.4 Hz, 1H, H-3), 3.53 (dt, *J* = 9.4, 4.8 Hz, 1H, H-5), 3.44 (s, 3H, OCH_3), 2.71 (d, *J* = 2.2 Hz,

1H, 4-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2 (C), 137.9 (C), 137.7 (C), 133.1 (CH), 129.9 (C), 129.8 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 102.0 (CH), 82.2 (CH), 74.4 (CH_2), 74.1 (CH), 73.8 (CH_2), 73.3 (CH), 72.3 (CH), 70.3 (CH_2), 56.8 (CH_3); HRMS [FAB, $(M-H)^+$] calcd for $C_{28}H_{29}O_7$ 477.1913, found 477.1922.

_p_-Methylphenyl 2,3,6-Tri-*O*-benzyl-1-thio-β-D-gluco-pyranoside (44)

$[\alpha]_D^{26}$ +2.6 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) ν 3437, 2913, 2867, 1452, 1210, 1061, 806, 734, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.24 (m, 17H, ArH), 7.03 (d, *J* = 7.9 Hz, 2H, ArH), 4.90, 4.72 (ABq, *J* = 10.3 Hz, 2H, CH_2Ph), 4.88, 4.76 (ABq, *J* = 11.3 Hz, 2H, CH_2Ph), 4.60 (d, *J* = 9.5 Hz, 1H, H-1), 4.57, 4.53 (ABq, *J* = 11.9 Hz, 2H, CH_2Ph), 3.77 (dd, *J* = 10.4, 4.2 Hz, 1H, H-6a), 3.73 (dd, *J* = 10.4, 5.1 Hz, 1H, H-6b), 3.62 (td, *J* = 8.7, 2.0 Hz, 1H, H-4), 3.51 (t, *J* = 8.7 Hz, 1H, H-3), 3.43 (dd, *J* = 9.5, 8.7 Hz, 1H, H-2), 3.43 (m, 1H, H-5), 2.53 (d, *J* = 2.0 Hz, 1H, 4-OH), 2.29 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5 (C), 138.0 (C), 137.9 (C), 137.8 (C), 132.6 (CH), 129.8 (C), 129.7 (CH), 128.6 (CH), 128.42 (CH), 128.41 (CH), 128.3 (CH), 127.94 (CH), 127.91 (CH), 127.9 (CH), 127.7 (CH), 88.0 (CH), 86.2 (CH), 80.5 (CH), 78.0 (CH), 75.5 (CH_2), 75.3 (CH_2), 73.7 (CH_2), 71.8 (CH), 70.4 (CH_2), 21.1 (CH_3); HRMS (FAB, MH^+) calcd for $C_{34}H_{37}O_5S$ 557.2362, found 557.2367.

Methyl 2-Azido-3,6-di-*O*-benzyl-2-deoxy-α-D-gluco-pyranoside (45)

$[\alpha]_D^{26}$ –19.9 (*c* 2.2, $CHCl_3$); IR ($CHCl_3$) ν 3474, 2913, 2105, 1601, 1452, 1260, 1053, 736, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.25 (m, 10H, ArH), 4.91, 4.78 (ABq, *J* = 11.2 Hz, 2H, CH_2Ph), 4.77 (d, *J* = 3.5 Hz, 1H, H-1), 4.60, 4.54 (ABq, *J* = 12.4 Hz, 2H, CH_2Ph), 3.79 (dd, *J* = 10.0, 8.2 Hz, 1H, H-3), 3.76-3.63 (m, 4H, H-4, H-5, H-6a, H-6b), 3.41 (s, 3H, OCH_3), 3.35 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2), 2.49 (d, *J* = 1.9 Hz, 1H, 4-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1 (C), 137.7 (C), 128.6 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 98.8 (CH), 80.0 (CH), 75.1 (CH_2), 73.7 (CH_2), 72.1 (CH), 69.9 (CH), 69.7 (CH_2), 63.0 (CH), 55.3 (CH_3); HRMS (FAB, MH^+) calcd for $C_{21}H_{26}N_3O_5$ 400.1872, found 400.1882.

Methyl 2-Azido-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-α-D-glucopyranoside (46)

$[\alpha]_D^{32}$ +2.5 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) ν 3477, 2910, 2107, 1724, 1602, 1450, 1272, 1051, 740, 710 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 2H, BzH), 7.57 (t, *J* = 7.8 Hz, 1H, BzH), 7.44 (t, *J* = 7.8 Hz, 2H, BzH), 7.33-7.24 (m, 5H, ArH), 5.52 (m, 1H, H-3), 4.90 (d, *J* = 3.5 Hz, 1H, H-1), 4.62, 4.57 (ABq, *J* = 12.0 Hz, 2H, CH_2Ph), 3.90-3.72 (m, 4H, H-4, H-5, H-6a, H-6b), 3.46 (s, 3H, OCH_3), 3.42 (d, *J* = 10.5, 3.5 Hz, 1H, H-2), 3.10-3.00 (bs, 1H, 4-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1 (C), 137.7 (C), 133.5 (CH), 130.0 (CH), 129.2 (CH), 128.43 (CH), 128.38 (CH), 127.7 (CH), 127.6 (CH), 98.9 (CH), 74.3 (CH), 73.7 (CH_2), 70.6 (CH), 70.3 (CH), 69.1 (CH_2), 61.2 (CH), 55.3 (CH_3); HRMS (FAB, MH^+) calcd for $C_{21}H_{24}N_3O_6$ 414.1665, found 414.1675. Anal. Calcd for $C_{21}H_{23}N_3O_6$: C, 61.01; H, 5.61; N, 10.16. Found: C, 61.02; H, 5.71; N, 9.99.

2-Azido-3-*O*-benzoyl-6-*O*-benzyl-2-deoxy-β-D-gluco-pyranosyl Benzoate (47)

$[\alpha]_D^{26}$ –115.6 (*c* 2.0, $CHCl_3$); IR ($CHCl_3$) ν 3485, 2918, 2871, 2110, 1736, 1600, 1451, 1266, 1069, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 4H, BzH), 7.62 (m, 2H, BzH), 7.47 (m, 4H, BzH), 7.32 (m, 5H, ArH), 5.85 (d, *J* = 8.7 Hz, 1H, H-1), 5.25 (dd, *J* = 10.1, 9.2 Hz, 1H, H-3), 4.60, 4.53 (ABq, *J* = 12.0 Hz, 2H, CH_2Ph), 4.00 (t, *J* = 9.2 Hz, 1H, H-4), 3.93 (dd, *J* = 10.1, 8.7 Hz, 1H, H-2), 3.86-3.81 (m, 1H, H-6a), 3.79-3.73 (m, 2H, H-6b, H-5), 3.10-3.20 (bs, 1H, 4-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7 (C), 164.4 (C), 137.5 (C), 133.9 (CH), 133.7 (CH), 130.1 (CH), 130.0 (CH), 129.0 (C), 128.62 (C), 128.56 (CH), 128.55 (CH), 128.45 (CH), 127.9 (CH), 127.8 (CH), 93.6 (CH), 76.3 (CH), 75.4 (CH), 73.8 (CH_2), 70.1 (CH), 69.0 (CH_2), 63.3 (CH); HRMS (FAB, MH^+) calcd for $C_{27}H_{26}N_3O_7$ 504.1775, found 504.1771.

Methyl 2,3,6-Tri-*O*-benzyl-α-D-mannopyranoside (48)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.35 (m, 15H, ArH), 4.77 (d, *J* = 1.6 Hz, 1H, H-1), 4.66, 4.65 (ABq, *J* = 12.3 Hz, 2H, CH_2Ph), 4.60, 4.59 (ABq, *J* = 12.1 Hz, 2H, CH_2Ph), 4.57, 4.51 (ABq, *J* = 11.8 Hz, 2H, CH_2Ph), 4.03 (td, *J* = 9.4, 1.8 Hz, 1H, H-4), 3.80-3.67 (m, 5H, H-2, H-3, H-5, H-6a, H-6b), 3.34 (s, 3H, OCH_3), 2.48 (d, *J* = 1.8 Hz, 1H, 4-OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3 (C), 138.2 (C), 128.5 (CH), 128.3 (CH), 127.84 (CH), 127.76 (CH), 127.72 (CH), 127.65 (CH), 127.6 (CH), 127.5 (CH), 99.1 (CH), 79.7 (CH), 73.8 (CH), 73.5 (CH_2), 72.6 (CH_2), 71.8 (CH_2), 71.4 (CH), 70.4 (CH_2), 67.8 (CH), 54.9 (CH_3).

1-Benzyloxy-3-butanol (49)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.22 (m, 5H, ArH), 4.51 (s, 2H, CH_2Ph), 4.95-4.05 (m, 1H, H-3), 3.72-3.59 (m, 2H, H-1), 2.80-2.79 (bs, 1H, 3-OH), 1.81-1.65 (m, 2H, H-2), 1.18 (d, *J* = 6.2 Hz, 3H, H-4); ^{13}C NMR (125

MHz, $CDCl_3$) δ 137.9 (C), 128.5 (CH), 127.7 (CH), 127.6 (CH), 73.3 (CH_2), 69.2 (CH_2), 67.7 (CH), 38.1 (CH_2), 23.3 (CH_3).

1,3-Dibenzyloxybutane (50)

IR ($CHCl_3$) ν 2970, 2926, 1603, 1454, 1110, 1027, 735, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 10H, ArH), 4.57, 4.41 (ABq, J = 11.6 Hz, 2H, CH_2Ph), 4.47, 4.46 (ABq, J = 11.9 Hz, 2H, CH_2Ph), 3.77-3.68 (m, 1H, H-3), 3.65-3.51 (m, 2H, H-1), 1.92-1.72 (m, 2H, H-2), 1.21 (d, J = 6.4 Hz, 3H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0 (C), 138.6 (C), 129.5 (CH), 128.33 (CH), 128.29 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 73.0 (CH_2), 72.2 (CH), 70.5 (CH_2), 67.0 (CH_2), 37.0 (CH_2), 19.8 (CH_3); HRMS (FAB, MH^+) calcd for $C_{18}H_{23}O_2$ 271.1698, found 271.1700.

ACKNOWLEDGEMENTS

This work was supported by the National Science Council of Taiwan (NSC 95-2113-M-007-028-MY3, NSC 96-2627-M-007-002, NSC 96-2321-B-007-003, NSC 96-2752-B-007-002-PAE, NSC 96-3011-P-007-005) and Academia Sinica (94C007 and AS-95-TP-AB1).

Received December 31, 2008.

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