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"Ring Opening–Ring Closure" Strategy for the Synthesis of Aryl-*C*-glycosides

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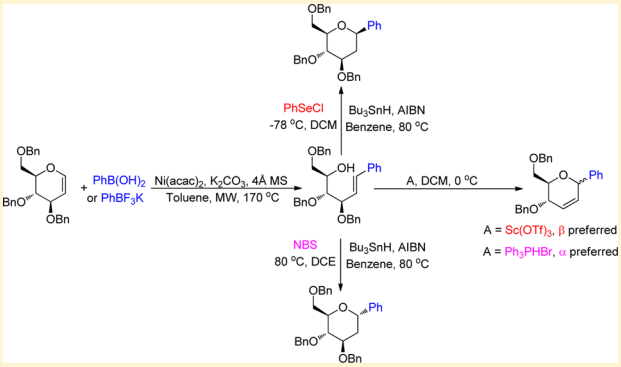
Supporting Information

ABSTRACT: A new "ring-opening–ring closure" strategy for the synthesis of aryl-*C*-glycosides was described. This strategy exploited the nickel-catalyzed regioselective β-O elimination of glycals by reactions with various aryl boronic acids or potassium aryltrifluoroborates to yield the ring-opened products, which underwent the Lewis acid, protonic acid, PhSeCl, or NBS mediated ring closure reactions to afford diverse aryl-*C*-glycosides. After Lewis acids and protonic acids were screened, it was found that, starting from the ring-opened substrates, the Ph_3PHBr or $Sc(OTf)_3$ mediated ring closure reaction provided α- or β-preferred aryl-*C*-$\Delta^{2,3}$-glycosides, respectively. Furthermore, β-D-phenyl-*C*-glycosides were successfully prepared via the PhSeCl-mediated cyclization reaction, whereas the α-D-phenyl-*C*-glycoside was obtained via the NBS-mediated cyclization reaction. After removal of the 2-substituted functionalities by Bu_3SnH/AIBN, the synthesis of 2-deoxy-aryl-*C*-glycosides was ultimately realized in a stereoselective manner.



INTRODUCTION

As naturally occurring structural units, aryl-*C*-glycosides are ubiquitous which exhibit significant biological activities and pharmacological potentials.[1] For example, pluramycin A, an antitumor and antibacterial antibiotic produced by *Streptomyces pluncolorescens*, inhibits protein and nucleic acid syntheses by intact cells of *E. coli* B at the concentration innocuous to energy generation.[2] Therefore, considerable efforts have been devoted to the development of more practical and efficient methods for the preparation of these kinds of compounds.[3] The currently available methodologies for the synthesis of aryl-*C*-glycosides mainly include the following: (1) the electrophilic substitutions of glycosyl donors toward electron-rich aryl acceptors,[4] (2) the O–C migration of *O*-glycosides to *C*-glycosides,[5] (3) the transition-metal-mediated *C*-glycosylations,[6] and (4) the de novo synthesis of a sugar ring moiety.[7] Among these approaches, the transition-metal-mediated *C*-glycosylations have attracted much attention since the reactions are usually completed under mild conditions in regio- and/or stereospecific manners.[8] For instance, a new access to these compounds by the cross-coupling reactions of glycosyl bromides with aryl zinc reagents or aryl Grignard reagents using Ni (0)[9] or Co[10] as catalysts was reported recently. Although progress has been made, more efficient approaches to prepare this type of compounds are still needed. Herein, we report a new "ring opening–ring closure" strategy for the preparation of aryl-*C*-glycosides. This new strategy was inspired by two aspects. One is the previously reported method for the synthesis of alkyl-*C*-glycosides which employed the Wittig reaction and cyclization sequence,[11] and the other is the fact that the $Pd(OAc)_2$ catalyzed cross-coupling reaction of peracetylated glycals with aryl boronic acids yielded the ring-opened byproduct.[12] We envisioned that, by screening proper reaction conditions, the ring-opened byproduct could probably become the dominant product. Then the ring-opened product would stereoselectively cyclize to afford the corresponding aryl-*C*-glycosides (Figure 1).

Based on our continuous work toward the development of new methods for aryl-*C*-glycoside synthesis,[13] the first step of the transition-metal-catalyzed reaction between protected glycals and aryl metal reagents may involve the insertion of the aryl transition metal into the C=C bond of the glycal affording the reactive intermediate. As shown in Figure 2, the intermediate would undergo β-eliminations probably by three routes.[13b] The first route carries out 3-β-H elimination to afford the enol ether type of aryl-*C*-glycosides; the second route undergoes 3-β-O elimination to yield aryl-*C*-$\Delta^{2,3}$-glycosides; the third route performs 5-β-O elimination to provide the alcohol products. In fact, the 3-β-H elimination pathway was demonstrated by Liu and co-workers.[14] On the other hand, it was reported that the 5-β-O elimination product could be avoided by screening solvents and the 3-β-O elimination product was obtained exclusively.[12] Here we want to explore the possibility of the microwave-assisted nickel-catalyzed regioselective 5-β-O elimination reaction of perbenzylated glycals with aryl boronic acids or potassium aryltrifluoroborates, which would be subsequently followed by

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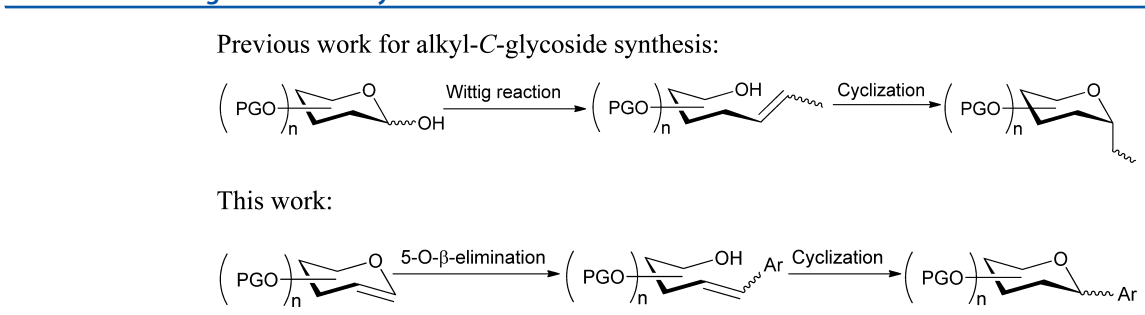


Figure 1. Proposed strategy for aryl-*C*-glycoside synthesis.

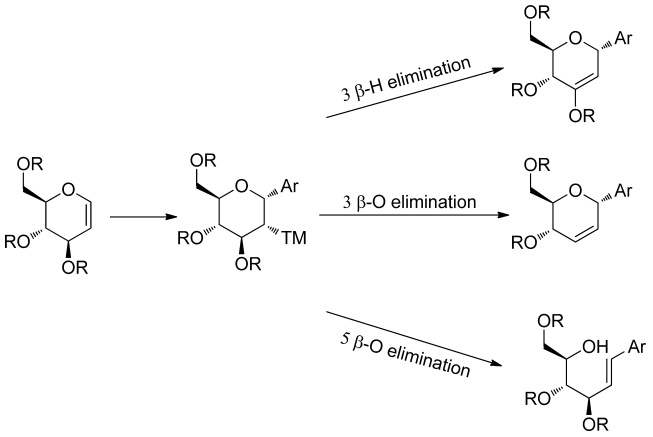


Figure 2. Three possible routes for β-eliminations.

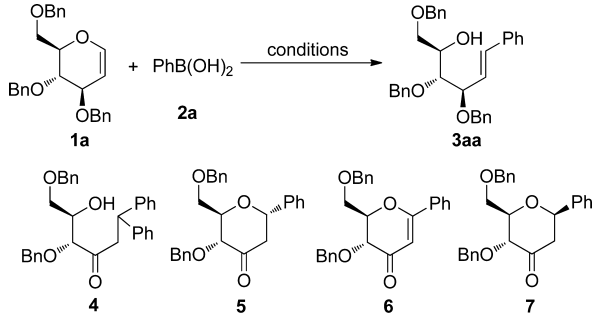
the $Sc(OTf)_3$, Ph_3PHBr, PhSeCl, or NBS mediated cyclization reaction to yield various aryl-*C*-glycosides.

RESULTS AND DISCUSSION

We began to investigate the reaction of perbenzylated glucal **1a** with phenyl boronic acid **2a**. Perbenzylated glucal **1a** was chosen for several reasons. First, compared with the acetyl or benzoyl protective group, benzyl is an electron-donating group, which would facilitate the insertion of aryl transition metal species; second, compared with other electron-donating groups such as *tert*-butyldimethylsilyl (TBS) and methyl groups, the benzyl is more common and the benzene ring might assist the reaction by chelating with the transition metal center; last but not least, the benzyl group could be compatible with other functional groups of aryl units and could be easily removed from the sugar ring under mild conditions in high yield.

Initially, the palladium catalyst was used to check the reaction. The reaction did not occur until the oxidants were employed (Table 1, entries 1−5). The results demonstrated that the effect of oxidants played an important role in the reaction. BAIB as the oxidant afforded the ring-opened alcohol **4** in 28% yield, whereas BQ, DDQ, and $Na_2S_2O_8$ as oxidants provided α-*C*-glycoside **5** in 30% yield, enone type *C*-glycoside **6** in 34% yield, and β-*C*-glycoside **7** in 31% yield, respectively. Subsequently, the nickel catalysts were investigated, and fortunately, the ring-opened product **3aa** was obtained exclusively in 43% isolated yield (entry 11) in the presence of $Ni(acac)_2$ and K_3PO_4 in toluene at 110 °C under air. When other nickel catalysts were used, almost no reactions occurred (entries 6−10). Further studies indicated that the presence of any phosphorus or nitrogen ligands would destroy the reaction. Bases were examined in order to improve the reaction efficiency. Among these bases, inorganic bases such as K_2CO_3 and Na_2CO_3 gave comparable results with K_3PO_4 (entries 12−13), whereas stronger bases such as Cs_2CO_3, NaOH, and $KOBu^t$ resulted in almost no products (entries 14−16); the organic base such as Et_3N gave a lower yield than K_3PO_4 (entry 17). When the microwave irradiation and molecular sieves were used, it was observed that the reaction yield was greatly increased (entries 18−19). The higher temperature led to the better yield (in 93% yield, entry 20). Therefore, the optimized reaction conditions are $Ni(acac)_2$ as the catalyst, K_2CO_3 as the base, and toluene as the solvent in the presence of 4 Å molecular sieves under microwave heating for 1.5 h at 170 °C.

Table 1. Screening of Optimal Conditions[a]



entry	catalyst	base/additive	solvent	temp (°C)	yield (%)
1	$Pd(OAc)_2$	–	toluene	110	0
2[b]	$Pd(OAc)_2$	BAIB	MeCN	100	28% of **4**
3[b]	$Pd(OAc)_2$	BQ	MeCN	100	30% of **5**
4[b]	$Pd(OAc)_2$	DDQ	MeCN	100	34% of **6**
5[b]	$Pd(OAc)_2$	$Na_2S_2O_8$	MeCN	100	31% of **7**
6	$NiCl_2$	K_3PO_4	toluene	110	trace
7	NiI_2	K_3PO_4	toluene	110	trace
8	$Ni(PPh_3)_2Cl_2$	K_3PO_4	toluene	110	0
9	$Ni(dppe)Cl_2$	K_3PO_4	toluene	110	0
10	$Ni(dppp)Cl_2$	K_3PO_4	toluene	110	0
11	$Ni(acac)_2$	K_3PO_4	toluene	110	43 (33)[c]
12	$Ni(acac)_2$	K_2CO_3	toluene	110	42
13	$Ni(acac)_2$	Na_2CO_3	toluene	110	40
14	$Ni(acac)_2$	Cs_2CO_3	toluene	110	trace
15	$Ni(acac)_2$	NaOH	toluene	110	trace
16	$Ni(acac)_2$	$KOBu^t$	toluene	110	0
17	$Ni(acac)_2$	Et_3N	toluene	110	30 (0)[d]
18[b]	$Ni(acac)_2$	K_2CO_3/4 Å MS	toluene	110	73
19[b]	$Ni(acac)_2$	K_2CO_3/3 Å MS	toluene	110	56
20[e]	$Ni(acac)_2$	K_2CO_3/4 Å MS	toluene	170	93

[a]Reaction conditions: **1a** (0.05 mmol), **2a** (0.1 mmol), catalyst (10% mmol), base (0.1 mmol), MS (100 mg), and solvent (1.0 mL) for 24 h. [b]Microwave heating for 1 h. [c]Catalyst (1.0 equiv) was used. [d]Et_3N (1.0 mL) was used. [e]Microwave heating for 1.5 h.

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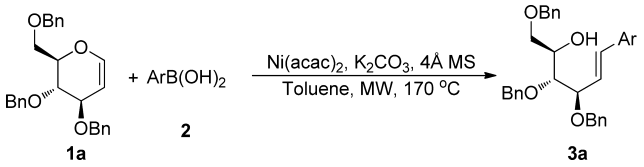
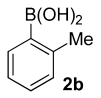
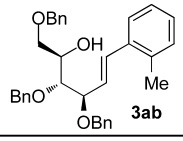
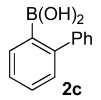
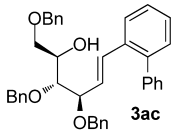
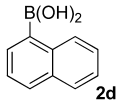
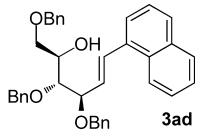
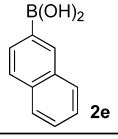
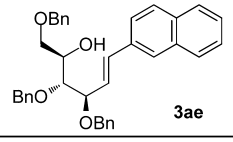
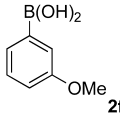
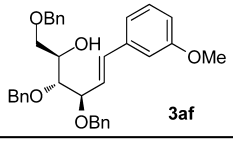
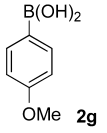
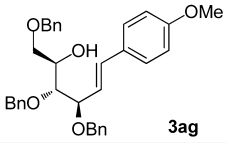
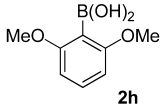
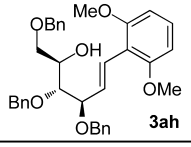
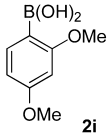
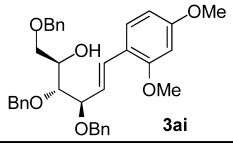
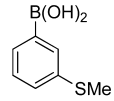
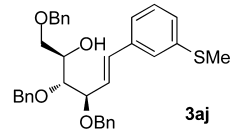
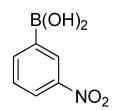
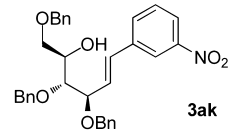
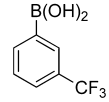
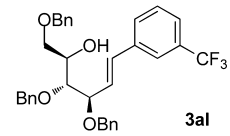
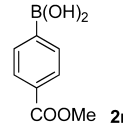
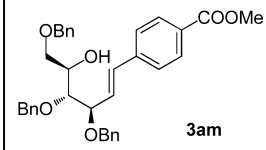
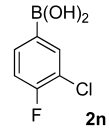
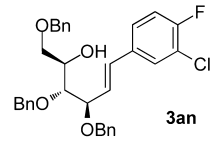
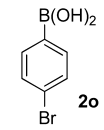
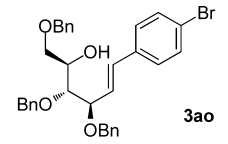
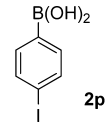
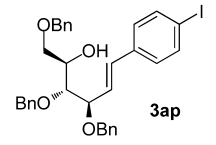
Table 2. Reactions with Various Aryl Boronic Acids[a]



Entry	Substrate	Product	Yield (%)[b]
1	 **2b**	 **3ab**	88
2	 **2c**	 **3ac**	80
3	 **2d**	 **3ad**	84
4	 **2e**	 **3ae**	77
5	 **2f**	 **3af**	68
6	 **2g**	 **3ag**	73
7	 **2h**	 **3ah**	55
8	 **2i**	 **3ai**	67
9	 **2j**	 **3aj**	73
10	 **2k**	 **3ak**	63
11	 **2l**	 **3al**	72
12	 **2m**	 **3am**	71
13	 **2n**	 **3an**	78
14	 **2o**	 **3ao**	83
15	 **2p**	 **3ap**	86

[a]Reaction conditions: **1a** (0.05 mmol), **2** (0.1 mmol), $Ni(acac)_2$ (10% mol), K_2CO_3 (0.1 mmol), 4 Å MS (100 mg), toluene (1.0 mL), under microwave heating at 170 °C for 1.5 h. [b]Isolated yield.

With the optimal conditions in hand, the scope of aryl boronic acids was investigated (Table 2). The results showed that the reaction could be applied to a wide variety of aryl boronic acids, both electron-donating substituted groups (entries 5−9) and electron-withdrawing substituted groups (entries 10−12) are tolerated. Notably, reactions of fluoro-, chloro-, bromo-, and iodo-substituted phenyl boronic acids with **1a** proceeded very well, providing the desired products **3an**, **3ao**, and **3ap** (entries 13−15), which could be used for further transformations. The more electron-rich α-naphthaleneboronic acid and β-naphthaleneboronic acid also performed smoothly in this transformation, generating products **3ad** and **3ae** in 84% and 77% yield, respectively (entries 3, 4). Furthermore, the steric hindrance of boronic acids did not influence the reaction efficiency (entries 1, 2).

This nickel catalyzed regioselective β-elimination reaction was further expanded to a range of substituted glycals (Table 3). The results indicated that reactions of perbenzylated glycals proceeded smoothly in good yields. Perbenzylated galactal **1b**, like its glucose counterpart, reacted with phenyl boronic acid (entry 1), boronic acid containing the electron-donating substituent (entry 2), and boronic acid containing the electron-withdrawing substituent (entry 3), affording the corresponding products **3ba**, **3bb**, and **3bc** in 85%, 70%, and

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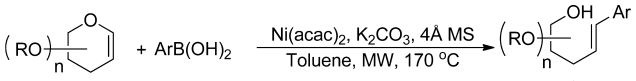
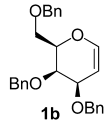
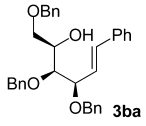
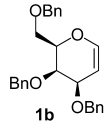
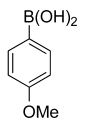
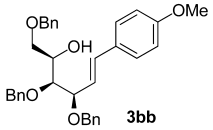
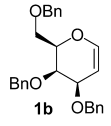
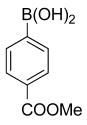
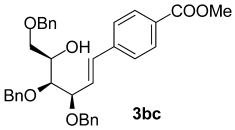
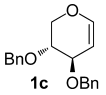
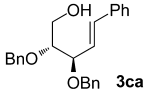
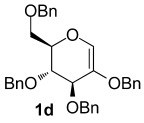
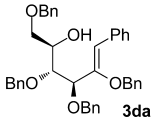
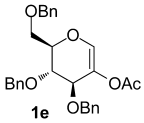
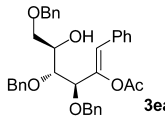
Table 3. Reactions with Different Glycals[a]



Entry	Glycal	Boronic acid	Product	Yield (%)[b]
1	 1b	PhB(OH)2	 3ba	85
2	 1b		 3bb	70
3	 1b		 3bc	76
4	 1c	PhB(OH)2	 3ca	76
5	 1d	PhB(OH)2	 3da	71
6	 1e	PhB(OH)2	 3ea	0

[a]Reaction conditions: glycal (0.05 mmol), aryl boronic acid (0.1 mmol), $Ni(acac)_2$ (10% mol), K_2CO_3 (0.1 mmol), 4 Å MS (100 mg), toluene (1.0 mL), under microwave heating at 170 °C for 1.5 h. [b]Isolated yield.

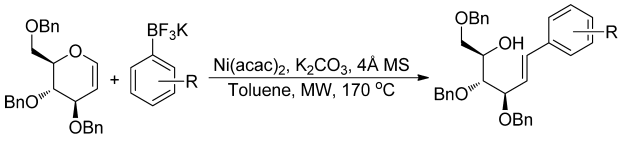
76% yield, respectively. Perbenzylated xylal **1c** also reacted with phenyl boronic acid to give the alcohol product **3ca** in 76% yield (entry 4). It is noteworthy that the reaction of 2-substituted glucals provided different results. The benzyloxy substituted glucal **1d** underwent the reaction smoothly, producing the (*Z*)-styrene derivative **3da** in 71% yield (entry 5), whereas the acetoxy substituted glucal **1e** did not undergo this reaction (entry 6).

Other aryl metallic compounds such as benzeneboronic acid pinacol ester, potassium phenyltrifluoroborate, and phenyl tri-*n*-butyltin were also examined. It was found that only potassium phenyltrifluoroborate was able to react with glucal **1a** to afford (*E*)-styrene derivative **3aa** in 61% yield under the optimized conditions (Scheme 1). Moreover, the reaction of 4-*tert*-butyl substituted potassium phenyltrifluoroborate with **1a** provided **3aq** in 48% yield under the same conditions.

The disclosed method provides a convenient protocol for the preparation of ω-alkenyl-1-alcohol derivatives from simple and readily available starting materials by nickel-catalyzed regioselective 5β-O elimination, which results in useful skeleton structures for further transformations.

Next, the ring-opened products were "closed" to afford *C*-glycosides. For this purpose, the Lewis acids were screened. The use of different Lewis acids had a dramatic impact on the

Scheme 1. Reactions of Potassium Aryltrifluoroborates with Glucal 1a



outcome of the reaction (data not shown). Significantly improved results were obtained when scandium(III) trifluoromethanesulfonate was used, affording aryl-*C*-$\Delta^{2,3}$-glycosides as a mixture of α/β anomers with the β-isomer preferred (Table 4). The α- and β-configurations of aryl-*C*-$\Delta^{2,3}$-glycosides were determined on the basis of ^1H and ^{13}C NMR analyses.[15] On the other hand, the protonic acids were also examined. The PPh_3HBr gave the optimal results. The use of other protonic acids resulted in either poor stereoselectivity or a low yield. With the optimal conditions in hand, the scope of substrates was explored. As shown in Table 4, it was found that the reaction could be applied to a wide variety of ring-opened styrene-ol structures. The electron-rich aryl substituent did not affect the reaction. The halogen was also tolerated under the reaction conditions (entries 7−8). Catalyzed by $Sc(OTf)_3$, the ring-opened alcohol was converted smoothly into the Ferrier rearrangement type product with the α/β ratio ranging from 1:1.1 to 1:5.6 (entries 1−5, 7−8). Notably, the *p*-methoxy substituted substrate gave β-aryl-*C*-$\Delta^{2,3}$-glycoside in low yield (entry 6). By contrast, the α-anomers were prepared in a highly stereoselective manner by PPh_3HBr mediated cyclization.[16] Exceptions were found when α- or β-naphthalene was used as the substituent, which afforded a mixture of α/β anomers (entries 4−5). In addition, the acid-sensitive group was not compatible with this transformation (entry 6).

The formation of aryl-*C*-$\Delta^{2,3}$-glycoside products could be attributed to the allyl cation induced by Lewis acids or protonic acids. Since 2-deoxy-aryl-*C*-glycoside is a component of some naturally occurring bioactive compounds, it is in demand to develop an efficient approach to synthesize these kinds of compounds. Therefore, following the reported protocol,[17] the PhSeCl-mediated cyclization was successfully applied to the ring-opened substrates, leading to the formation of β-D-phenyl-*C*-glycosides **9a** and **9b**. The extra phenylselenyl group was finally removed by Bu_3SnH/AIBN in high yield (Scheme 2).[18]

By contrast, in virtue of the previous reports on NBS-mediated cyclization, the preparation of α-D-aryl-*C*-glycoside **11a** was also realized, as exemplified in Scheme 3. Subsequently, the bromine atom was also removed by Bu_3SnH/AIBN in benzene to provide *C*-glycoside **12** in high yield.[19] Moreover, NIS was also applied to the cyclization reaction, affording the corresponding α-phenyl-*C*-glycoside **11b**. It is noteworthy that compounds **11a** and **11b** are conformationally flexible, which are more stable in the $^1C_4$ conformation.[20] Thus, a new and efficient protocol for the stereoselective synthesis of 2-deoxy-aryl-*C*-glycosides was developed.

CONCLUSION

In summary, we have developed an efficient and practical "ring opening−ring closure" strategy for the preparation of 2-deoxy-aryl-*C*-glycosides starting from glycals. The key step involved the microwave-assisted nickel-catalyzed regioselective 5β-O elimination of glycals, producing the ring-opened intermediate

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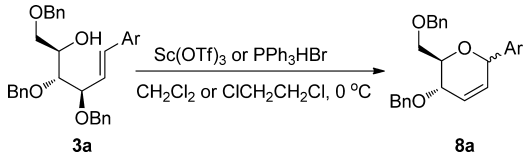
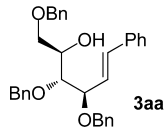
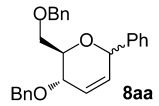
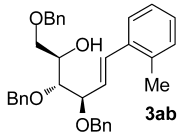
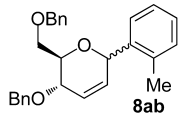
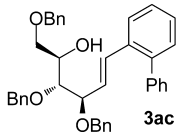
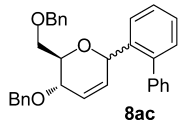
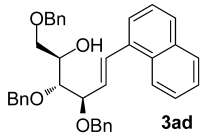
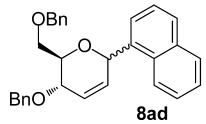
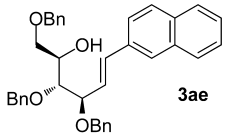
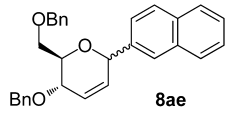
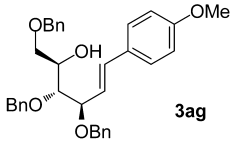
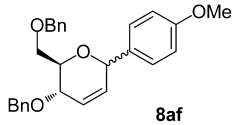
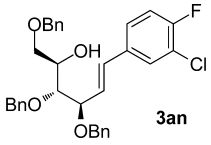
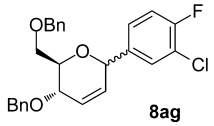
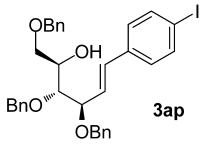
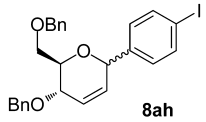
Table 4. $Sc(OTf)_3$ or PPh_3HBr Mediated Cyclization Reactions[a]



3a **8a**

Entry	Alcohol	C-Glycoside	$Sc(OTf)_3$ Yield (%)[b] α/β ratio	PPh_3HBr Yield (%)[b] α/β ratio
1	 **3aa**	 **8aa**	92, 1:3	94, α only
2	 **3ab**	 **8ab**	89, 1:2.4	78, α only
3	 **3ac**	 **8ac**	74, 1:5.6	71, α only
4	 **3ad**	 **8ad**	82, 1:2	76, 2:1
5	 **3ae**	 **8ae**	86, 1:3	76, 2.5:1
6	 **3ag**	 **8af**	40, β only	----
7	 **3an**	 **8ag**	74, 1:1.1	82, α only
8	 **3ap**	 **8ah**	86, 1:4.6	72, α only

[a]Reaction conditions: **3a** (0.1 mmol, 1.0 equiv), $Sc(OTf)_3$ (5% mmol) or PPh_3HBr (0.5−1.0 equiv), dry CH_2Cl_2 or $ClCH_2CH_2Cl$ (0.5 mL), 0 °C. [b]Isolated yield, α/β ratio was determined by ^1H NMR analysis of the crude product.

products. These ring-opened products underwent the Lewis acid or protonic acid mediated cyclization to yield aryl-*C*-$\Delta^{2,3}$-glycosides. On the other hand, the ring-opened products were treated with NBS or PhSeCl to yield the cyclized products α- or β-2-deoxy-aryl-*C*-glycosides, respectively. The disclosed approach may find wide applications in the synthesis of various aryl-*C*-glycosides with biological importance.

EXPERIMENTAL SECTION

General Methods. All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. All reaction solvents were purified before use. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride (CaH_2). Toluene was distilled over sodium. All reactions were carried out under anhydrous conditions with freshly distilled solvents, unless otherwise noted. Reactions were monitored by analytical thin-layer chromatography (TLC) on silica

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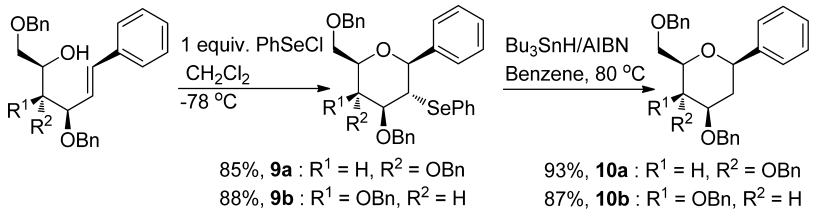
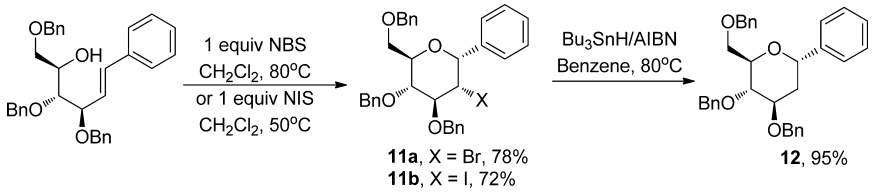
Scheme 2. Synthetic Approach to 2-Deoxy-β-D-phenyl-glycosides



Scheme 3. Synthetic Approach to 2-Deoxy-α-D-phenyl-*C*-glycoside



gel 60 F_{254} precoated on aluminum plates. Spots were detected under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate. Solvents were evaporated under reduced pressure and below 40 °C (bath temperature). Column chromatography was performed on silica gel (200−300 mesh). ^{1}H NMR spectra were recorded on a spectrometer at 25 °C. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in deuterated chloroform. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). High-resolution mass spectrometry was performed on a spectrometer. The microwave heating was performed on a dynamic model (Discover SP, CEM; external sensor type used for measuring reaction mixture temperatures).

The perbenzyl protected glucal,[21] galactal,[21] xylal,[22] 2-acetoxyperbenzyl glucal,[23] 2-benzoxyperbenzyl glucal,[24] and per *tert*-butyldimethylsilyl glucal[13a] were prepared according to the previous reports.

General Procedure for Nickel-Catalyzed Reaction of Perbenzylated Glycals with Aryl Boronic Acids or Potassium Aryltrifluoroborates. A mixture of perbenzylated glycals (0.05 mmol, 1.0 equiv), aryl boronic acid or potassium aryltrifluoroborate (0.1 mmol, 2.0 equiv), $Ni(acac)_2$ (0.1 equiv), K_2CO_3 (2.0 equiv), 4 Å molecular sieves (100 mg), and dry toluene (1.0 mL) was heated to 170 °C for 1.5 h by microwave irradiation. The solvent was evaporated. Then the mixture was diluted with CH_2Cl_2 and washed with distilled water, and the organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure; the residue was subjected to column chromatography to afford the pure product.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-phenyl-hex-5-en-2-ol (3aa). Yield 93% (23.0 mg) from phenyl boronic acid, yield 61% (15.0 mg) from potassium phenyltrifluoroborate, colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −13.4 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.82 (d, 1H, *J* = 5.6 Hz), 3.60 (dd, 1H, *J* = 5.2, 10.0 Hz), 3.63 (dd, 1H, *J* = 4.0, 10.4 Hz), 3.68 (dd, 1H, *J* = 4.0, 6.8 Hz), 4.04−4.09 (m, 1H), 4.25 (dd, 1H, *J* = 3.2, 7.6 Hz), 4.40 (d, 1H, *J* = 11.6 Hz), 4.51 (s, 2H), 4.59 (d, 1H, *J* = 11.6 Hz), 4.64 (d, 1H, *J* = 12.0 Hz), 4.68 (d, 1H, *J* = 12.0 Hz), 6.30 (dd, 1H, *J* = 8.0, 16.0 Hz), 6.58 (d, 1H, *J* = 16.0 Hz), 7.24−7.38 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.4, 70.6, 70.9, 73.3, 74.2, 79.7, 81.0, 126.6, 127.6, 127.7, 127.8, 127.9, 128.1, 128.1, 128.3, 128.3, 128.4, 128.6, 133.6, 136.4, 137.9, 138.0, 138.1; FT-HRMS (ESI) calcd for $C_{33}H_{34}O_4Na$ [M + Na]$^+$: 517.2349, found 517.2346.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(*o*-tolyl)-hex-5-en-2-ol (3ab). Yield 88% (22.4 mg), colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −30.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.82 (d, 1H, *J* = 5.2 Hz), 3.59−3.66 (m, 2H), 3.69 (dd, 1H, *J* = 3.6, 6.8 Hz), 4.05−4.10 (m, 1H), 4.27 (dd, 1H, *J* = 3.2, 8.0 Hz), 4.43 (d, 1H, *J* = 12.0 Hz), 4.51 (s, 2H), 4.59 (d, 1H, *J* = 11.6 Hz), 4.66 (d, 1H, *J* = 11.6 Hz), 4.69 (d, 1H, *J* = 12.0 Hz), 6.18 (dd, 1H, *J* = 8.0, 16.0 Hz), 6.80 (d, 1H, *J* = 16.0 Hz), 7.16−7.19 (m, 3H), 7.23−7.34 (m, 15H), 7.40 (t, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 70.4, 70.6, 71.0, 73.4, 74.2, 79.8, 81.1, 125.8, 126.1, 127.68, 127.70, 127.82, 127.86, 127.9, 128.1, 128.3, 128.38, 128.43, 130.3, 131.5, 135.47, 135.54, 137.9, 138.0, 138.1; FT-HRMS (ESI) calcd for $C_{34}H_{36}O_4Na$ [M + Na]$^+$: 531.2500, found 531.2515.

(2*R*,3*R*,4*R*,*E*)-6-((1,1′-Biphenyl)-2-yl)-1,3,4-tris(benzyloxy)-hex-5-en-2-ol (3ac). Yield 80% (22.8 mg), colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −6.4 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.83 (d, 1H, *J* = 5.2 Hz), 3.57 (d, 2H, *J* = 4.8 Hz), 3.62 (dd, 1H, *J* = 4.0, 6.8 Hz), 4.01−4.06 (m, 1H), 4.09 (dd, 1H, *J* = 3.6, 8.0 Hz), 4.30 (d, 1H, *J* = 12.0 Hz), 4.47 (s, 2H), 4.57 (d, 1H, *J* = 11.2 Hz), 4.60 (d, 1H, *J* = 12.0 Hz), 4.62 (d, 1H, *J* = 11.2 Hz), 6.25 (dd, 1H, *J* = 8.0, 16.0 Hz), 6.60 (d, 1H, *J* = 16.0 Hz), 7.19−7.39 (m, 23H), 7.53−7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.4, 70.5, 70.9, 73.3, 74.0, 79.7, 80.8, 126.2, 127.1, 127.45, 127.51, 127.64, 127.69, 127.73, 127.8, 128.07, 128.09, 128.1, 128.29, 128.33, 128.4, 129.7, 130.1, 132.9, 134.5, 137.7, 138.0, 138.1, 140.8, 141.0; FT-HRMS (ESI) calcd for $C_{39}H_{38}O_4Na$ [M + Na]$^+$: 593.2662, found 593.2662.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(naphthalen-1-yl)-hex-5-en-2-ol (3ad). Yield 84% (22.8 mg), colorless oil, R_f = 0.62 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +98.5 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (d, 1H, *J* = 5.2 Hz), 3.62−3.69 (m, 2H), 3.75 (dd, 1H, *J* = 3.6, 6.8 Hz), 4.10−4.15 (m, 1H), 4.40 (dd, 1H, *J* = 3.6, 7.6 Hz), 4.52−4.54 (m, 3H), 4.62 (d, 1H, *J* = 11.2 Hz), 4.69 (d, 1H, *J* = 11.6 Hz), 4.78 (d, 1H, *J* = 12.0 Hz), 6.33 (dd, 1H, *J* = 7.6, 15.6 Hz), 7.21−7.56 (m, 20H), 7.80 (d, 1H, *J* = 8.0 Hz), 7.85−7.88 (m, 1H), 8.02−8.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.5, 70.9, 71.0, 73.4, 74.2, 79.9, 81.0, 123.7, 123.9, 125.6, 125.8, 126.1, 127.65, 127.68, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 128.5, 129.8, 130.7, 131.1, 133.6, 134.2, 137.9, 138.0, 138.1; FT-HRMS (ESI) calcd for $C_{37}H_{40}NO_4$ [M + NH_4]$^+$: 562.2952, found 562.2960.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(naphthalen-2-yl)-hex-5-en-2-ol (3ae). Yield 77% (20.9 mg), colorless oil, R_f = 0.62 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −30.0 (*c* 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (d, 1H, *J* = 5.2 Hz), 3.63 (dd, 1H, *J* = 5.2, 9.6 Hz), 3.66 (dd, 1H, *J* = 4.0, 10.0 Hz), 3.72 (dd, 1H, *J* = 3.6, 6.8 Hz), 4.07−4.13 (m, 1H), 4.31 (dd, 1H, *J* = 4.0, 7.6 Hz), 4.44 (d, 1H, *J* = 11.6 Hz), 4.51 (s, 2H), 4.61 (d, 1H, *J* = 11.6 Hz), 4.66 (d, 1H, *J* = 11.6 Hz), 4.70 (d, 1H, *J* = 12.0 Hz), 6.41 (dd, 1H, *J* = 7.6, 16.0 Hz), 6.74 (d, 1H, *J* = 16.0 Hz), 7.21−7.34 (m, 15H), 7.42−7.48 (m, 2H), 7.56 (dd, 1H, *J* = 1.2, 4.4 Hz), 7.70 (s, 1H), 7.77−7.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.5, 70.8, 71.0, 73.4, 74.2, 79.9, 81.1, 123.6, 126.0, 126.3, 126.6, 127.0, 127.6, 127.66, 127.68, 127.8, 128.0, 128.1, 128.15, 128.22, 128.3, 128.36, 128.4, 133.1, 133.5, 133.6, 133.9, 137.9, 138.0, 138.1; FT-HRMS (ESI) calcd for $C_{37}H_{36}O_4Na$ [M + Na]$^+$: 567.2500, found 567.2519.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(3-methoxyphenyl)-hex-5-en-2-ol (3af). Yield 68% (17.8 mg), colorless oil, R_f = 0.60 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +31.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.81 (d, 1H, *J* = 5.2 Hz), 3.58−3.65 (m,

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2H), 3.68 (dd, 1H, J = 4.0, 6.8 Hz), 3.82 (s, 3H), 4.04−4.09 (m, 1H), 4.25 (dd, 1H, J = 3.6, 7.6 Hz), 4.41 (d, 1H, J = 12.0 Hz), 4.50 (s, 2H), 4.58 (d, 1H, J = 11.6 Hz), 4.64 (d, 1H, J = 12.0 Hz), 4.67 (d, 1H, J = 12.0 Hz), 6.30 (dd, 1H, J = 8.0, 16.0 Hz), 6.56 (d, 1H, J = 16.0 Hz), 6.83 (dd, 1H, J = 2.0, 8.0 Hz), 6.91 (s, 1H), 6.97 (d, 1H, J = 7.6 Hz), 7.23−7.33 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 70.4, 70.7, 71.0, 73.4, 74.2, 79.7, 81.0, 111.8, 113.6, 119.3, 126.9, 127.7, 127.8, 127.9, 128.1, 128.3, 128.39, 128.43, 129.6, 133.5, 137.8, 137.9, 138.0, 138.1, 159.8; FT-HRMS (ESI) calcd for $C_{34}H_{36}O_5Na$ [M + Na]$^+$: 547.2450, found 547.2437.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(4-methoxyphenyl)-hex-5-en-2-ol (3ag). Yield 73% (19.1 mg), colorless oil, R_f = 0.60 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −17.5 (c 5.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (d, 1H, J = 5.2 Hz), 3.62−3.69 (m, 2H), 3.71 (dd, 1H, J = 4.0, 6.8 Hz), 3.86 (s, 3H), 4.08−4.12 (m, 1H), 4.26 (dd, 1H, J = 3.6, 8.0 Hz), 4.43 (d, 1H, J = 12.0 Hz), 4.54 (s, 2H), 4.63 (d, 1H, J = 11.6 Hz), 4.69 (d, 1H, J = 11.6 Hz), 4.71 (d, 1H, J = 12.0 Hz), 6.19 (dd, 1H, J = 8.0, 16.0 Hz), 6.56 (d, 1H, J = 16.0 Hz), 6.91 (d, 2H, J = 8.8 Hz), 7.28−7.38 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 70.5 (2 × C), 71.0, 73.4, 74.2, 80.0, 81.1, 114.0, 124.1, 127.65, 127.68, 127.81, 127.83, 128.08, 128.12, 128.3, 128.36, 128.38, 129.2, 133.3, 138.0, 138.1, 138.2, 159.5; FT-HRMS (ESI) calcd for $C_{34}H_{36}O_5Na$ [M + Na]$^+$: 547.2450, found 547.2446.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(2,6-dimethoxyphenyl)-hex-5-en-2-ol (3ah). Yield 55% (15.2 mg), colorless oil, R_f = 0.58 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +14.1 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.89 (d, 1H, J = 5.2 Hz), 3.60 (dd, 1H, J = 5.6, 10.0 Hz), 3.64 (dd, 1H, J = 3.6, 10.0 Hz), 3.71 (dd, 1H, J = 4.0, 6.8 Hz), 3.82 (s, 6H), 4.07−4.12 (m, 1H), 4.20 (dd, 1H, J = 4.0, 8.4 Hz), 4.43 (d, 1H, J = 12.0 Hz), 4.49 (s, 2H), 4.60 (d, 1H, J = 11.6 Hz), 4.71 (d, 1H, J = 12.0 Hz), 4.78 (d, 1H, J = 11.6 Hz), 6.57 (d, 2H, J = 8.4 Hz), 6.72 (dd, 1H, J = 8.4, 16.0 Hz), 6.92 (d, 1H, J = 16.0 Hz), 7.17 (t, 1H, J = 8.4 Hz), 7.23−7.37 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.7, 70.1, 70.6, 71.1, 73.3, 74.3, 81.7, 82.0, 103.9, 113.9, 124.8, 127.4, 127.52, 127.54, 127.8, 128.0, 128.17, 128.23, 128.29, 128.31, 128.4, 130.3, 138.3, 138.4, 138.6, 158.6; FT-HRMS (ESI) calcd for $C_{35}H_{38}O_6Na$ [M + Na]$^+$: 577.2561, found 577.2554.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(2,4-dimethoxyphenyl)-hex-5-en-2-ol (3ai). Yield 67% (18.5 mg), colorless oil, R_f = 0.58 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +58.8 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 (d, 1H, J = 5.2 Hz), 3.59 (dd, 1H, J = 5.2, 10.0 Hz), 3.63 (dd, 1H, J = 4.0, 10.0 Hz), 3.68 (dd, 1H, J = 4.0, 6.4 Hz), 3.82 (s, 6H), 4.06−4.09 (m, 1H), 4.22 (dd, 1H, J = 3.6, 8.4 Hz), 4.40 (d, 1H, J = 12.0 Hz), 4.50 (s, 2H), 4.59 (d, 1H, J = 11.2 Hz), 4.67 (d, 1H, J = 12.0 Hz), 4.68 (d, 1H, J = 11.6 Hz), 6.22 (dd, 1H, J = 8.0, 16.0 Hz), 6.45 (d, 1H, J = 2.0 Hz), 6.48 (dd, 1H, J = 2.4, 8.4 Hz), 6.83 (d, 1H, J = 16.0 Hz), 7.24−7.33 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.40, 55.42, 70.3, 70.6, 71.1, 73.3, 74.2, 80.7, 81.4, 98.5, 104.8, 118.6, 124.6, 127.56, 127.6, 127.8, 127.9, 128.1, 128.2, 128.3, 128.7, 138.2, 138.2, 138.4, 158.0, 160.7; FT-HRMS (ESI) calcd for $C_{35}H_{38}O_6Na$ [M + Na]$^+$: 577.2560, found 577.2559.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(3-(methylthio)phenyl)-hex-5-en-2-ol (3aj). Yield 73% (19.7 mg), colorless oil, R_f = 0.60 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −11.5 (c 4.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H), 2.79 (d, 1H, J = 5.2 Hz), 3.61−3.63 (m, 2H), 3.67 (dd, 1H, J = 3.6, 6.8 Hz), 4.03−4.07 (m, 1H), 4.25 (dd, 1H, J = 3.6, 7.6 Hz), 4.40 (d, 1H, J = 12.0 Hz), 4.51 (s, 2H), 4.58 (d, 1H, J = 11.6 Hz), 4.62 (d, 1H, J = 11.6 Hz), 4.67 (d, 1H, J = 12.0 Hz), 6.28 (dd, 1H, J = 8.0, 16.0 Hz), 6.53 (d, 1H, J = 16.0 Hz), 7.12−7.17 (m, 2H), 7.24−7.32 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8, 70.4, 70.8, 71.0, 73.4, 74.2, 79.7, 81.0, 123.4, 124.7, 126.0, 127.4, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 128.43, 129.0, 133.0, 137.0, 137.9, 138.1, 138.9; FT-HRMS (ESI) calcd for $C_{34}H_{36}O_4SNa$ [M + Na]$^+$: 563.2227, found 563.2220.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(3-nitrophenyl)-hex-5-en-2-ol (3ak). Yield 63% (16.9 mg), colorless oil, R_f = 0.55 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −28.6 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (d, 1H, J = 5.2 Hz), 3.64−3.65 (m, 2H), 3.68 (dd, 1H, J = 3.6, 7.2 Hz), 4.01−4.07 (m, 1H), 4.29 (dd, 1H, J = 3.2, 6.8 Hz), 4.43 (d, 1H, J = 12.0 Hz), 4.53 (s, 2H), 4.57 (d, 1H, J = 11.6 Hz), 4.61 (d, 1H, J = 11.6 Hz), 4.67 (d, 1H, J = 12.0 Hz), 6.38 (dd, 1H, J = 7.2, 16.0 Hz), 6.61 (d, 1H, J = 16.0 Hz), 7.22−7.36 (m, 15H), 7.48 (t, 1H, J = 8.0 Hz), 7.60 (d, 1H, J = 7.6 Hz), 8.09−8.11 (m, 1H), 8.16 (t, 1H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.4, 70.9, 71.3, 73.5, 74.2, 79.2, 80.5, 121.2, 122.3, 127.79, 127.83, 127.92, 128.1, 128.3, 128.4, 128.5, 129.5, 130.4, 130.7, 132.3, 137.6, 137.9, 138.2; FT-HRMS (ESI) calcd for $C_{33}H_{33}NO_6Na$ [M + Na]$^+$: 562.2194, found 562.2187.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(3-(trifluoromethyl)-phenyl)-hex-5-en-2-ol (3al). Yield 72% (20.2 mg), colorless oil, R_f = 0.63 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −13.2 (c 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (brs, 1H), 3.61−3.64 (m, 2H), 3.68 (dd, 1H, J = 3.6, 7.2 Hz), 4.05 (brs, 1H), 4.27 (dd, 1H, J = 3.6, 7.2 Hz), 4.42 (d, 1H, J = 12.0 Hz), 4.52 (s, 2H), 4.58 (d, 1H, J = 11.6 Hz), 4.61 (d, 1H, J = 12.0 Hz), 4.66 (d, 1H, J = 12.0 Hz), 6.32 (dd, 1H, J = 8.0, 16.0 Hz), 6.58 (d, 1H, J = 16.0 Hz), 7.21−7.32 (m, 15H), 7.43 (t, 1H), 7.50 (t, 2H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.4, 70.9, 71.0, 73.4, 74.1, 79.4, 80.7, 124.04 (d, 1C, J = 270.8 Hz), 123.16, 123.19, 123.23, 123.26, 124.21, 124.25, 124.28, 124.32, 127.7, 127.74, 127.79, 127.85, 128.0, 128.2, 128.3, 128.35, 128.4, 128.9, 129.0, 129.6, 130.95 (d, 1C, J = 32.1 Hz), 131.7, 137.2, 137.7, 137.91, 137.93; FT-HRMS (ESI) calcd for $C_{34}H_{33}F_3O_4Na$ [M + Na]$^+$: 585.2201, found 585.2204.

Methyl 4-((3*R*,4*R*,5*R*,*E*)-3,4,6-Tris(benzyloxy)-5-hydroxy-hex-1-en-1-yl)benzoate (3am). Yield 71% (19.6 mg), colorless oil, R_f = 0.60 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −22.8 (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78 (d, 1H, J = 5.6 Hz), 3.63−3.65 (m, 2H), 3.68 (dd, 1H, J = 3.2, 7.2 Hz), 3.92 (s, 3H), 4.03−4.08 (m, 1H), 4.28 (dd, 1H, J = 3.2, 7.2 Hz), 4.42 (d, 1H, J = 12.0 Hz), 4.51(s, 2H), 4.59 (s, 2H), 4.67 (d, 1H, J = 12.0 Hz), 6.38 (dd, 1H, J = 7.2, 16.0 Hz), 6.61 (d, 1H, J = 16.0 Hz), 7.25−7.35 (m, 15H), 7.38 (d, 2H, J = 8.4 Hz), 7.99 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1, 70.3, 70.9, 71.0, 73.4, 74.2, 79.4, 80.8, 126.4, 127.73, 127.76, 127.82, 127.87, 128.1, 128.2, 128.32, 128.38, 128.43, 129.2, 129.7, 129.9, 132.2, 137.7, 137.9, 140.8, 166.8; FT-HRMS (ESI) calcd for $C_{35}H_{36}O_6K$ [M + K]$^+$: 591.2143, found 591.2139.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(3-chloro-4-fluoro-phenyl)-hex-5-en-2-ol (3an). Yield 78% (21.3 mg), colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −42.6 (c 3.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (d, 1H, J = 5.2 Hz), 3.60−3.64 (m, 2H), 3.65 (dd, 1H, J = 3.2, 6.8 Hz), 4.01−4.06 (m, 1H), 4.23 (dd, 1H, J = 3.6 Hz, 7.6 Hz), 4.40 (d, 1H, J = 11.6 Hz), 4.52 (s, 2H), 4.57 (d, 1H, J = 11.6 Hz), 4.60 (d, 1H, J = 11.6 Hz), 4.65 (d, 1H, J = 12.0 Hz), 6.16 (dd, 1H, J = 7.6, 16.0 Hz), 6.45 (d, 1H, J = 16.0 Hz), 7.08 (t, 1H, J = 8.4 Hz), 7.14−7.17 (m, 1H), 7.25−7.33 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.4, 70.9, 71.0, 73.4, 74.2, 79.4, 80.7, 116.5, 116.7, 121.1, 121.3, 126.2, 126.3, 127.75, 127.82, 127.84, 127.9, 128.0, 128.1, 128.2, 128.35, 128.40, 128.44, 130.9, 133.0, 133.7, 133.8, 137.7, 138.0, 156.3, 158.8; FT-HRMS (ESI) calcd for $C_{33}H_{32}ClFO_4Na$ [M + Na]$^+$: 569.1854, found 569.1848.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(4-bromophenyl)-hex-5-en-2-ol (3ao). Yield 83% (23.7 mg), colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −57.7 (c 3.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.79 (d, 1H, J = 5.2 Hz), 3.61−3.65 (m, 2H), 3.69 (dd, 1H, J = 3.6, 7.2 Hz), 4.04−4.09 (m, 1H), 4.27 (dd, 1H, J = 3.6, 7.6 Hz), 4.43 (d, 1H, J = 12.0 Hz), 4.53 (s, 2H), 4.62 (s, 2H), 4.68 (d, 1H, J = 12.0 Hz), 6.28 (dd, 1H, J = 7.6, 16.0 Hz), 6.53 (d, 1H, J = 16.0 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.27−7.37 (m, 15H),7.47 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.4, 70.89, 70.93, 73.4, 74.2, 79.5, 80.8, 127.6, 127.76, 127.82, 127.9, 128.1, 128.2, 128.3, 128.40, 128.44, 131.7, 132.2, 135.3, 137.8, 138.0; FT-HRMS (ESI) calcd for $C_{33}H_{33}BrO_4Na$ [M + Na]$^+$: 595.1449, found 595.1447.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(4-iodophenyl)-hex-5-en-2-ol (3ap). Yield 86% (26.6 mg), colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −9.6 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (d, 1H, J = 5.2 Hz), 3.61−3.62 (m, 2H), 3.66 (dd, 1H, J = 3.6, 6.8 Hz), 4.01−4.07 (m, 1H), 4.24 (dd, 1H, J = 3.2, 7.2 Hz), 4.40 (d, 1H, J = 12.0 Hz), 4.51 (s, 2H), 4.59 (s, 2H), 4.65 (d, 1H, J = 12.0 Hz), 6.27 (dd, 1H, J = 7.6, 16.0 Hz), 6.48 (d, 1H, J = 16.0 Hz), 7.06 (d, 2H, J = 8.4 Hz), 7.25−7.34 (m, 15H), 7.64 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.4, 70.9, 70.93, 73.4, 74.2, 79.5, 80.9, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 128.39, 128.43, 132.3, 135.9, 137.6, 137.8,

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137.99, 138.02; FT-HRMS (ESI) calcd for $C_{33}H_{33}IO_4Na$ $[M + Na]^+$: 643.1316, found 643.1293.

(2*R*,3*R*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(4-(*tert*-butyl)phenyl)-hex-5-en-2-ol (3aq). Yield 48% (13.2 mg) from potassium 4-*tert*-butylphenyltrifluoroborate, colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +50.0 (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H), 2.81 (d, 1H, *J* = 5.2 Hz), 3.59 (dd, 1H, *J* = 5.2, 10.0 Hz), 3.62 (dd, 1H, *J* = 4.0, 10.0 Hz), 3.67 (dd, 1H, *J* = 4.0, 6.8 Hz), 4.03−4.09 (m, 1H), 4.23 (dd, 1H, *J* = 4.0, 8.0 Hz), 4.39 (d, 1H, *J* = 12.0 Hz), 4.50 (s, 2H), 4.58 (d, 1H, *J* = 11.6 Hz), 4.66 (d, 1H, *J* = 11.6 Hz), 4.67 (d, 1H, *J* = 12.0 Hz), 6.27 (dd, 1H, *J* = 8.0, 16.0 Hz), 6.57 (d, 1H, *J* = 16.0 Hz), 7.25−7.38 (m, 19H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.3, 34.6, 70.4, 70.5, 71.0, 73.4, 74.3, 79.9, 81.2, 125.5, 125.7, 126.4, 127.67, 127.72, 127.8, 128.1, 128.3, 128.38, 128.41, 133.6, 138.0, 138.1, 138.2, 151.1; FT-HRMS (ESI) calcd for $C_{37}H_{42}O_4Na$ $[M + Na]^+$: 573.2975, found 573.2970.

(2*R*,3*S*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-phenyl-hex-5-en-2-ol (3ba). Yield 85% (21.0 mg), colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +23.3 (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 2.84 (d, 1H, *J* = 6.0 Hz), 3.54 (d, 2H, *J* = 5.6 Hz), 3.68 (dd, 1H, *J* = 3.2, 6.0 Hz), 4.10−4.12 (m, 1H), 4.24 (t, 1H, *J* = 6.8 Hz), 4.42 (d, 1H, *J* = 11.6 Hz), 4.48 (d, 1H, *J* = 12.0 Hz), 4.50 (d, 1H, *J* = 10.4 Hz), 4.53 (d, 1H, *J* = 11.6 Hz), 4.67 (d, 1H, *J* = 11.6 Hz), 4.67 (d, 1H, *J* = 11.2 Hz), 6.22 (dd, 1H, *J* = 8.0, 16.0 Hz), 6.62 (d, 1H, *J* = 16.0 Hz), 7.22−7.40 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.8, 70.7, 71.0, 73.4, 74.1, 80.2, 80.3, 126.6, 126.9, 127.7, 127.81, 127.84, 127.9, 128.0, 128.30, 128.33, 128.36, 128.41, 128.6, 134.4, 136.3, 137.9, 138.00, 138.03; FT-HRMS (ESI) calcd for $C_{33}H_{34}O_4Na$ $[M + Na]^+$: 517.2344, found 517.2340.

(2*R*,3*S*,4*R*,*E*)-1,3,4-Tris(benzyloxy)-6-(4-methoxyphenyl)-hex-5-en-2-ol (3bb). Yield 70% (18.3 mg), colorless oil, R_f = 0.62 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +2.4 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 2.86 (d, 1H, *J* = 6.0 Hz), 3.54 (d, 2H, *J* = 5.6 Hz), 3.67 (dd, 1H, *J* = 3.2, 6.0 Hz), 3.82 (s, 3H), 4.08−4.13 (m, 1H), 4.21 (t, 1H, *J* = 6.8 Hz), 4.41 (d, 1H, *J* = 11.6 Hz), 4.48 (d, 1H, *J* = 12.0 Hz), 4.50 (d, 1H, *J* = 9.6 Hz), 4.53 (d, 1H, *J* = 11.6 Hz), 4.66 (d, 1H, *J* = 12.0 Hz), 4.68 (d, 1H, *J* = 11.2 Hz), 6.07 (dd, 1H, *J* = 8.0, 16.0 Hz), 6.55 (d, 1H, *J* = 16.0 Hz), 6.87 (d, 2H, *J* = 8.8 Hz), 7.21−7.33 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 69.9, 70.5, 71.1, 73.4, 74.1, 80.37, 80.44, 114.0, 124.6, 127.6, 127.7, 127.77, 127.83, 127.9, 128.32, 128.36, 128.39, 128.4, 129.2, 133.9, 138.0, 138.10, 138.12, 159.5; FT-HRMS (ESI) calcd for $C_{34}H_{36}O_5Na$ $[M + Na]^+$: 547.2450, found 547.2442.

Methyl 4-((3*R*,4*S*,5*R*,*E*)-3,4,6-Tris(benzyloxy)-5-hydroxy-hex-1-en-1-yl)benzoate (3bc). Yield 76% (21.0 mg), colorless oil, R_f = 0.60 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +14.0 (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 2.77 (d, 1H, *J* = 6.4 Hz), 3.51−3.58 (m, 2H), 3.69 (dd, 1H, *J* = 2.8, 6.0 Hz), 3.92 (s, 3H), 4.07−4.12 (m, 1H), 4.26 (t, 1H, *J* = 6.8 Hz), 4.44 (d, 1H, *J* = 11.6 Hz), 4.49 (d, 1H, *J* = 12.0 Hz), 4.52 (d, 1H, *J* = 12.0 Hz), 4.53 (d, 1H, *J* = 12.0 Hz), 4.64 (d, 1H, *J* = 11.2 Hz), 4.66 (d, 1H, *J* = 11.6 Hz), 6.32 (dd, 1H, *J* = 7.6, 16.0 Hz), 6.65 (d, 1H, *J* = 16.0 Hz), 7.18−7.34 (m, 15H), 7.41 (d, 2H, *J* = 8.4 Hz), 8.00 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1, 69.8, 71.1 (2 × C), 73.4, 74.2, 80.0, 80.3, 126.5, 127.73, 127.75, 127.82, 127.88, 127.92, 128.28, 128.37, 128.39, 128.45, 129.3, 129.96, 130.02, 133.00, 137.8, 137.9, 138.0, 140.8, 166.8; FT-HRMS (ESI) calcd for $C_{35}H_{36}O_6Na$ $[M + Na]^+$: 575.2399, found 575.2401.

(2*R*,3*R*,*E*)-2,3-Bis(benzyloxy)-5-phenyl-pent-4-en-1-ol (3ca). Yield 76% (14.2 mg), colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ −31.2 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 2.07 (dd, 1H, *J* = 5.2, 5.6 Hz), 3.61−3.70 (m, 2H), 3.75−3.80 (m, 1H), 4.18 (t, 1H, *J* = 6.8 Hz), 4.46 (d, 1H, *J* = 12.0 Hz), 4.68 (d, 1H, *J* = 11.6 Hz), 4.70 (d, 1H, *J* = 12.0 Hz), 4.83 (d, 1H, *J* = 11.6 Hz), 6.21 (dd, 1H, *J* = 8.0, 16.0 Hz), 6.62 (d, 1H, *J* = 16.0 Hz), 7.26−7.41 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 62.2, 70.7, 73.5, 81.0, 81.3, 126.0, 126.6, 127.7, 127.80, 127.84, 127.97, 128.0, 128.4, 128.5, 128.6, 134.0, 136.3, 138.2, 138.4; FT-HRMS (ESI) calcd for $C_{25}H_{26}O_3Na$ $[M + Na]^+$: 397.1774, found 397.1772.

(2*R*,3*R*,4*S*,*Z*)-1,3,4,5-Tetrakis(benzyloxy)-6-phenyl-hex-5-en-2-ol (3da). Yield 71% (21.3 mg), colorless oil, R_f = 0.65 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +11.5 (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 2.30 (d, 1H, *J* = 6.0 Hz), 3.52 (dd, 1H, *J* = 5.6, 9.6 Hz), 3.59 (dd, 1H, *J* = 3.2, 9.6 Hz), 3.81 (dd, 1H, *J* = 3.2, 7.2 Hz), 4.01−4.04 (m, 1H), 4.27 (d, 1H, *J* = 2.8 Hz), 4.39 (d, 1H, *J* = 11.6 Hz), 4.44 (s, 2H), 4.49 (d, 1H, *J* = 11.2 Hz), 4.68 (d, 1H, *J* = 11.2 Hz), 4.70 (d, 1H, *J* = 11.6 Hz), 4.85 (s, 2H), 6.20 (s, 1H), 7.17−7.35 (m, 23H), 7.62 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.0, 71.1, 71.9, 72.0, 73.3, 74.8, 77.91, 79.7, 113.5, 126.7, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 135.3, 137.3, 137.8, 138.0, 138.1, 152.3; FT-HRMS (ESI) calcd for $C_{40}H_{44}NO_5$ $[M + NH_4]^+$: 618.3214, found 618.3211.

General Procedure for Microwave-Assisted $Pd(OAc)_2$-Catalyzed Reaction of Benzyl Protected Glucal with Phenylboronic Acid. A mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), oxidant (0.2 mmol), and MeCN (1.0 mL) was heated for 1 h at 100 °C under microwave irradiation. The solvent was evaporated. Then the mixture was subjected to column chromatography to afford the product.

(4*R*,5*R*)-4,6-Bis(benzyloxy)-5-hydroxy-1,1-diphenyl-hexan-3-one (4). Yield 28% (13.4 mg), colorless oil, R_f = 0.62 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +40.6 (*c* 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (d, 1H, *J* = 6.0 Hz), 3.28 (dd, 1H, *J* = 7.2, 17.6 Hz), 3.45 (dd, 1H, *J* = 8.0, 17.6 Hz), 3.49 (d, 2H, *J* = 4.8 Hz), 3.81 (d, 1H, *J* = 6.8 Hz), 3.99−4.04 (m, 1H), 4.15 (d, 1H, *J* = 11.6 Hz), 4.32 (d, 1H, *J* = 11.6 Hz), 4.41 (d, 1H, *J* = 11.6 Hz), 4.46 (d, 1H, *J* = 11.6 Hz), 4.65 (t, 1H, *J* = 7.2 Hz), 7.15−7.35 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.1, 45.3, 70.0, 70.8, 72.8, 73.4, 84.2, 126.4, 127.8, 127.9, 128.0, 128.4, 128.5, 137.1, 137.7, 144.0, 144.1, 208.8; FT-HRMS (ESI) calcd for $C_{32}H_{36}NO_4$ $[M+NH_4]^+$: 498.2639, found 498.2636.

(2*R*,3*R*,6*R*)-3-Benzyloxy-2-benzyloxymethyl-6-phenyl-dihydro-2*H*-pyran-4(3*H*)-one (7). Yield 31% (12.5 mg), colorless oil, R_f = 0.66 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +87.1 (*c* 0.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.76 (d, 2H, *J* = 6.8 Hz), 3.83−3.85 (m, 3H), 4.28 (d, 1H, *J* = 9.6 Hz), 4.50 (d, 1H, *J* = 11.2 Hz), 4.58 (d, 1H, *J* = 12.4 Hz), 4.67 (d, 1H, *J* = 12.4 Hz), 4.68 (t, 1H, *J* = 7.2 Hz), 4.94 (d, 1H, *J* = 11.2 Hz), 7.26−7.38 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 50.0, 69.2, 73.5, 73.6, 79.4, 79.7, 80.9, 125.7, 127.6, 127.7, 128.0, 128.2, 128.2, 128.4, 128.4, 128.6, 137.4, 138.2, 140.1, 205.7; FT-HRMS (ESI) calcd for $C_{26}H_{26}O_4Na$ $[M + Na]^+$: 425.1723, found 425.1727.

General Procedure for $Sc(OTf)_3$-Catalyzed Cyclization Reaction (Method A). At 0 °C, the ring-opened alcohol (0.1 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 or $ClCH_2CH_2Cl$ (0.5 mL). The $Sc(OTf)_3$ (0.05 equiv) was added as one portion. The mixture was stirred until the alcohol was consumed which was monitored by TLC. After the reaction was completed (usually the color of the reaction was turned gray or dark), the mixture was washed by water and extracted by CH_2Cl_2. The combined organic layers were dried, and the solvent was evaporated. The residue was subjected to column chromatography to afford the product.

General Procedure for PPh_3HBr-Mediated Cyclization Reaction (Method B). At 0 °C, the ring-opened alcohol (0.1 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 or $ClCH_2CH_2Cl$ (0.5 mL). The PPh_3HBr (0.5−1.0 equiv) was added as one portion. The mixture was stirred until the alcohol was consumed which was monitored by TLC. After the reaction was completed (usually the color of the reaction was turned yellow), the mixture was washed by water and extracted by CH_2Cl_2. The combined organic layers were dried, and the solvent was evaporated. The residue was subjected to column chromatography to yield the product.

(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)benzene (8aa). Yield 92% (35.5 mg) by Method A, α:β = 1:3; yield 94% (36.3 mg) by Method B, α only. For α-anomer: colorless oil, R_f = 0.70 (petroleum ether/acetone = 2:1); ^1H NMR (400 MHz, $CDCl_3$): δ 3.59−3.63 (m, 1H), 3.67−3.72 (m, 2H), 4.20 (d, 1H, *J* = 7.2 Hz), 4.46 (d, 1H, *J* = 12.4 Hz), 4.49 (d, 1H, *J* = 13.2 Hz), 4.59 (d, 1H, *J* = 12.8 Hz), 4.62 (d, 1H, *J* = 12.0 Hz), 5.31 (brs, 1H), 6.10 (brd, 1H, *J* = 10.4 Hz), 6.14 (brd, 1H, *J* = 10.4 Hz), 7.25−7.36 (m, 13H), 7.44 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.1, 70.1, 70.7, 71.1, 73.3, 74.1, 127.1, 127.5, 127.7, 127.8, 127.9, 128.0, 128.28, 128.33, 128.37, 129.6, 138.17, 138.20, 139.5; FT-HRMS (ESI) calcd for $C_{52}H_{52}O_6Na$ $[2M + Na]^+$: 795.3656, found 795.3668. For β-anomer: colorless oil, R_f = 0.71

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(petroleum ether/acetone = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (dd, 1H, J = 5.6, 11.2 Hz), 3.80−3.85 (m, 2H), 4.16 (d, 1H, J = 8.8 Hz), 4.51 (d, 1H, J = 11.2 Hz), 4.60 (d, 2H, J = 10.8 Hz), 4.65 (d, 1H, J = 11.6 Hz), 5.19 (brs, 1H), 5.86 (d, 1H, J = 10.4 Hz), 6.00 (d, 1H, J = 10.4 Hz), 7.23−7.34 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.9, 70.5, 71.2, 73.4, 77.4, 77.8, 126.0, 127.1, 127.5, 127.6, 127.8, 127.88, 127.91, 128.3, 128.38, 128.43, 131.7, 138.1, 138.4, 140.8; FT-HRMS (ESI) calcd for $C_{26}H_{26}O_3Na$ $[M + Na]^+$: 409.1769, found 409.1777. The spectroscopic data of **8aa** coincide with the previous reports.[15,25]

***o*-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)toluene (8ab).** Yield 89% (35.6 mg) by Method A, α:β = 1:2.4; yield 78% (31.2 mg) by Method B, α only. For α-anomer: colorless oil, R_f = 0.69 (petroleum ether/acetone = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 3.52 (dd, 1H, J = 5.2, 13.6 Hz), 3.60−3.67 (m, 2H), 4.21−4.23 (m, 1H), 4.44 (d, 1H, J = 12.4 Hz), 4.52 (d, 1H, J = 11.6 Hz), 4.54 (d, 1H, J = 12.4 Hz), 4.64 (d, 1H, J = 11.6 Hz), 5.48 (dd, 1H, J = 2.0, 4.8 Hz), 6.02 (ddd, 1H, J = 1.6, 3.2, 10.4 Hz), 6.20 (dt, 1H, J = 2.0, 10.4 Hz), 7.11−7.15 (m, 1H), 7.19−7.35 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 69.1, 70.39, 70.41, 71.2, 71.7, 73.2, 125.2, 127.5, 127.7, 127.8, 127.9, 128.3, 128.4, 128.7, 130.0, 130.7, 136.7, 138.2, 138.3; FT-HRMS (ESI) calcd for $C_{27}H_{32}NO_3$ $[M + NH_4]^+$: 418.2377, found 418.2380. The spectroscopic data coincide with the previous report.[15] For β-anomer: colorless oil, R_f = 0.70 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +91.2 (c 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 3.74 (dd, 1H, J = 5.6, 10.8 Hz), 3.81−3.88 (m, 2H), 4.17 (d, 1H, J = 8.4 Hz), 4.52 (d, 1H, J = 11.6 Hz), 4.59 (d, 1H, J = 12.0 Hz), 4.64 (d, 1H, J = 10.8 Hz), 4.70 (d, 1H, J = 11.6 Hz), 5.39 (brs, 1H), 5.88 (d, 1H, J = 10.4 Hz), 6.02 (d, 1H, J = 10.4 Hz), 7.13−7.19 (m, 3H), 7.25−7.33 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 70.0, 70.6, 71.2, 73.4, 75.0, 78.0, 126.1, 126.2, 127.3, 127.4, 127.66, 127.70, 127.75, 127.81, 127.9, 128.3, 128.4, 130.6, 131.0, 135.9, 138.1, 138.5; FT-HRMS (ESI) calcd for $C_{27}H_{28}NaO_3$ $[M + Na]^+$: 423.1936, found 423.1925.

2-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-1,1′-biphenyl (8ac). Yield 74% (34.2 mg) by Method A, α:β = 1:5.6; yield 71% (32.8 mg) by Method B, α only. For α-anomer: colorless oil, R_f = 0.69 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ −37.4 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (dd, 1H, J = 3.2, 10.4 Hz), 3.66 (dd, 1H, J = 4.8, 10.8 Hz), 3.97−4.00 (m, 1H), 4.07−4.09 (m, 1H), 4.48 (d, 1H, J = 12.4 Hz), 4.51 (d, 1H, J = 12.4 Hz), 4.59 (d, 1H, J = 11.6 Hz), 4.68 (d, 1H, J = 11.6 Hz), 5.28−5.29 (m, 1H), 5.83 (ddd, 1H, J = 2.8, 4.4, 10.4 Hz), 6.10 (dt, 1H, J = 4.4, 10.4 Hz), 7.28−7.41 (m, 16H), 7.49−7.51 (m, 2H), 7.58−7.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.3, 70.0, 70.8, 70.9, 71.1, 73.2, 126.4, 127.0, 127.1, 127.5, 127.7, 128.0, 128.1, 128.3, 128.4, 128.9, 129.7, 130.5, 130.7, 135.9, 138.3, 140.8, 143.0; FT-HRMS (ESI) calcd for $C_{32}H_{34}NO_3$ $[M + NH_4]^+$: 480.2533, found 480.2537. For β-anomer: colorless oil, R_f = 0.70 (petroleum ether/acetone = 2:1), $[\alpha]^{25}_D$ +6.8 (c 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65−3.81 (m, 3H), 4.15 (d, 1H, J = 6.4 Hz), 4.48 (d, 1H, J = 11.6 Hz), 4.54 (d, 1H, J = 12.0 Hz), 4.62 (d, 2H, J = 12.0 Hz), 5.21 (brs, 1H), 5.79 (d, 1H, J = 10.4 Hz), 5.97 (d, 1H, J = 10.4 Hz), 7.22−7.36 (m, 16H), 7.44−7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.1, 70.6, 71.0, 73.3, 74.2, 77.8, 126.1, 127.1, 127.5, 127.66, 127.69, 127.74, 128.0, 128.3, 128.4, 129.6, 130.1, 131.9, 137.7, 138.1, 138.5, 140.5, 141.8; FT-HRMS (ESI) calcd for $C_{32}H_{31}O_3$ $[M + H]^+$: 463.2268, found 463.2276.

1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-naphthalene (8ad). Yield 82% (35.7 mg) by Method A, α:β = 1:2; yield 76% (33.1 mg) by Method B, α:β = 2:1. For α-anomer: colorless oil, R_f = 0.69 (petroleum ether/acetone = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46−3.50 (m, 1H), 3.62−3.66 (m, 2H), 4.28−4.30 (m, 1H), 4.35 (d, 1H, J = 12.0 Hz), 4.49 (d, 1H, J = 12.0 Hz), 4.53 (d, 1H, J = 11.6 Hz), 4.66 (d, 1H, J = 11.6 Hz), 6.04 (d, 1H, J = 2.4 Hz), 6.17 (ddd, 1H, J = 3.2, 4.8, 10.4 Hz), 6.28 (dt, 1H, J = 3.6, 10.4 Hz), 7.14−7.16 (m, 2H), 7.21−7.41 (m, 9H), 7.49−7.58 (m, 3H), 7.80−7.88 (m, 2H), 8.39 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.0, 70.5, 70.9, 71.27, 71.32, 73.1, 124.6, 124.8, 125.7, 126.3, 126.9, 127.4, 127.75, 127.79, 128.0, 128.2, 128.4, 128.5, 129.1, 129.7, 132.2, 134.1, 134.3, 138.21, 138.24; FT-HRMS (ESI) calcd for $C_{30}H_{28}O_3Na$ $[M + Na]^+$: 459.1931, found 459.1937. The spectroscopic data coincide with the previous report.[15] For β-anomer: colorless oil, R_f = 0.70 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +46.7 (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (dd, 1H, J = 5.6, 10.8 Hz), 3.88 (dd, 1H, J = 2.0, 10.8 Hz), 4.02 (ddd, 1H, J = 2.0, 5.6, 8.8 Hz), 4.27 (dd, 1H, J = 3.2, 8.8 Hz), 4.56 (d, 1H, J = 11.6 Hz), 4.57 (d, 1H, J = 12.8 Hz), 4.63 (d, 1H, J = 12.4 Hz), 4.70 (d, 1H, J = 11.6 Hz), 5.89 (d, 1H, J = 3.2 Hz), 6.08 (s, 2H), 7.24−7.34 (m, 10H), 7.42−7.50 (m, 3H), 7.59 (d, 1H, J = 6.8 Hz), 7.79 (d, 1H, J = 8.0 Hz), 7.84−7.87 (m, 1H), 8.14−8.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.0, 70.7, 71.3, 73.4, 75.0, 78.4, 123.8, 124.9, 125.4, 125.5, 126.0, 126.4, 127.4, 127.7, 127.8, 127.9, 128.3, 128.4, 128.6, 128.7, 130.9, 131.4, 133.9, 136.1, 138.1, 138.5; FT-HRMS (ESI) calcd for $C_{30}H_{32}NO_3$ $[M + NH_4]^+$: 454.2377, found 454.2377.

2-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-naphthalene (8ae). Yield 86% (37.5 mg) by Method A, α:β = 1:3; yield 76% (33.1 mg) by Method B, α:β = 2.5:1. For α-anomer: colorless oil, R_f = 0.69 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ −45.8 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (dd, 1H, J = 2.4, 10.4 Hz), 3.70 (dd, 1H, J = 4.4, 10.0 Hz), 3.72−3.76 (m, 1H), 4.23 (dd, 1H, J = 2.0, 8.0 Hz), 4.46 (d, 1H, J = 12.0 Hz), 4.51 (d, 1H, J = 11.6 Hz), 4.59 (d, 1H, J = 12.4 Hz), 4.64 (d, 1H, J = 11.6 Hz), 5.46 (brd, 1H), 6.21 (s, 2H), 7.26−7.31 (m, 10H), 7.45−7.48 (m, 2H), 7.59 (dd, 1H, J = 1.6, 8.4 Hz), 7.79−7.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.3, 70.3, 70.8, 71.3, 73.3, 74.2, 126.1, 126.3, 126.9, 127.55, 127.58, 127.8, 127.87, 127.94, 128.2, 128.3, 128.4, 129.5, 133.0, 133.1, 137.0, 138.20, 138.24; FT-HRMS (ESI) calcd for $C_{30}H_{32}NO_3$ $[M + NH_4]^+$: 454.2377, found 454.2373. For β-anomer: colorless oil, R_f = 0.70 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +26.0 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (dd, 1H, J = 5.2, 10.8 Hz), 3.85 (dd, 1H, J = 1.6, 10.8 Hz), 3.90 (ddd, 1H, J = 1.6, 5.6, 8.4 Hz), 4.20−4.23 (m, 1H), 4.55 (d, 1H, J = 11.6 Hz), 4.58 (d, 1H, J = 12.4 Hz), 4.65 (d, 1H, J = 12.4 Hz), 4.69 (d, 1H, J = 11.6 Hz), 5.36 (brs, 1H), 5.93 (dt, 1H, J = 1.6, 10.4 Hz), 6.04 (dt, 1H, J = 3.6, 10.4 Hz), 7.26−7.36 (m, 10H), 7.45−7.47 (m, 3H), 7.81−7.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.0, 70.6, 71.3, 73.4, 77.6, 77.9, 125.1, 125.9, 126.0, 126.2, 127.5, 127.7, 127.8, 128.0, 128.3, 128.4, 131.6, 133.2, 133.3, 138.1, 138.2, 138.5; FT-HRMS (ESI) calcd for $C_{30}H_{32}NO_3$ $[M + NH_4]^+$: 454.2377, found 454.2375.

1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-4-methoxybenzene (8af). Yield 40% (16.6 mg) by Method A. β-Anomer: colorless oil, R_f = 0.68 (petroleum ether/acetone = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (dd, 1H, J = 5.6, 11.2 Hz), 3.79−3.84 (m, 2H), 3.80 (s, 3H), 4.12−4.16 (m, 1H), 4.51 (d, 1H, J = 11.2 Hz), 4.56 (d, 1H, J = 12.4 Hz), 4.61 (d, 1H, J = 12.4 Hz), 4.66 (d, 1H, J = 11.6 Hz), 5.14 (brs, 1H), 5.84 (dt, 1H, J = 3.2, 10.0 Hz), 6.00 (dt, 1H, J = 4.0, 10.4 Hz), 6.87 (d, 2H, J = 8.8 Hz), 7.28−7.34 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 70.0, 70.6, 71.3, 73.4, 77.3, 77.9, 113.8, 126.0, 127.5, 127.8, 127.8, 127.9, 128.3, 128.4, 128.6, 131.8, 159.4; FT-HRMS (ESI) calcd for $C_{27}H_{28}O_4Na$ $[M + Na]^+$: 439.1874, found 439.1872. The spectroscopic data coincide with the previous report.[15]

1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-3-chloro-4-fluorobenzene (8ag). Yield 74% (32.4 mg) by Method A, α:β = 1:1.1; yield 82% (35.9 mg) by Method B, α only. For α-anomer: colorless oil, R_f = 0.69 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ −11.2 (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.59−3.70 (m, 3H), 4.16 (dd, 1H, J = 2.0, 7.6 Hz), 4.47 (d, 1H, J = 12.0 Hz), 4.49 (d, 1H, J = 11.6 Hz), 4.59 (d, 1H, J = 12.0 Hz), 4.62 (d, 1H, J = 11.6 Hz), 5.24 (brs, 1H), 6.04 (ddd, 1H, J = 1.6, 2.8, 10.4 Hz), 6.16 (dt, 1H, J = 2.0, 10.4 Hz), 7.10 (t, 1H, J = 8.8 Hz), 7.25−7.35 (m, 11H), 7.48 (dd, 1H, J = 2.0, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.1, 70.0, 70.9, 71.3, 72.8, 73.4, 116.3, 116.5, 120.9, 121.0, 127.6, 127.7, 127.8, 128.0, 128.3, 128.4, 128.6, 130.2, 136.9, 138.0, 138.1, 156.5, 158.9; FT-HRMS (ESI) calcd for $C_{26}H_{28}ClFNO_3$ $[M + NH_4]^+$: 456.1742, found 456.1740. For β-anomer: colorless oil, R_f = 0.70 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +7.0 (c 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71 (dd, 1H, J = 5.6, 10.8 Hz), 3.78−3.82 (m, 2H), 4.11−4.14 (m, 1H), 4.50 (d, 1H, J = 11.6 Hz), 4.56 (d, 1H, J = 12.0 Hz), 4.62 (d, 1H, J = 12.0 Hz), 4.65 (d, 1H, J = 11.6 Hz), 5.13 (d, 1H, J = 1.2 Hz), 5.79 (dt, 1H, J = 1.6, 10.4 Hz), 6.02 (dt, 1H, J = 2.0, 10.0 Hz), 7.09 (t, 1H, J = 8.8 Hz), 7.18−7.22 (m, 1H), 7.27−7.34 (m, 10H), 7.40 (dd, 1H, J = 2.0, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.7, 70.2, 71.4, 73.4, 76.2, 77.8, 116.3, 116.6, 126.8, 126.9, 127.0, 127.6, 127.8, 127.9, 128.0, 128.3, 128.4, 129.5, 130.7, 137.9,

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138.3; FT-HRMS (ESI) calcd for $C_{26}H_{24}ClFO_3Na$ $[M + Na]^+$: 461.1281, found 461.1298.

1-(4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosyl)-4-iodobenzene (8ah). Yield 86% (44.0 mg) by Method A, α:β = 1:4.6; yield 72% (36.9 mg) by Method B, α only. For α-anomer: colorless oil, R_f = 0.69 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ −126.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.58−3.69 (m, 3H), 4.16 (dd, 1H, *J* = 2.0, 7.6 Hz), 4.46 (d, 1H, *J* = 12.0 Hz), 4.48 (d, 1H, *J* = 11.6 Hz), 4.58 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 11.6 Hz), 5.23 (brs, 1H), 6.04 (ddd, 1H, *J* = 1.6, 2.8, 10.4 Hz), 6.14 (dt, 1H, *J* = 2.0, 10.4 Hz), 7.18 (d, 2H, *J* = 8.4 Hz), 7.24−7.34 (m, 10H), 7.66 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.1, 70.0, 70.9, 71.2, 73.3, 73.5, 127.6, 127.79, 127.85, 127.93, 128.3, 128.4, 128.9, 129.95, 137.5, 138.06, 138.12, 139.3; FT-HRMS (ESI) calcd for $C_{26}H_{29}NIO_3$ $[M + NH_4]^+$: 530.1187, found 530.1184. For β-anomer: colorless oil, R_f = 0.70 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ −29.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (dd, 1H, *J* = 5.6, 10.8 Hz), 3.78−3.83 (m, 2H), 4.11−4.15 (m, 1H), 4.51 (d, 1H, *J* = 11.6 Hz), 4.56 (d, 1H, *J* = 12.4 Hz), 4.61 (d, 1H, *J* = 12.4 Hz), 4.65 (d, 1H, *J* = 11.6 Hz), 5.12 (d, 1H, *J* = 1.6 Hz), 5.79 (dt, 1H, *J* = 1.6, 10.4 Hz), 5.99 (dt, 1H, *J* = 2.0, 10.0 Hz), 7.09 (d, 2H, *J* = 8.4 Hz), 7.25−7.34 (m, 10H), 7.66 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.8, 70.3, 71.3, 73.4, 76.8, 77.8, 126.4, 127.5, 127.8, 127.9, 128.3, 128.4, 129.0, 131.0, 137.5, 138.0, 138.4, 140.5; FT-HRMS (ESI) calcd for $C_{52}H_{50}I_2O_6Na$ $[2M + Na]^+$: 1047.1589, found 1047.1604.

(2*R*,3*R*,4*S*,5*S*,6*S*)-3,4-Bis(benzyloxy)-2-(benzyloxymethyl)-6-phenyl-5-(phenylselanyl)tetrahydro-2*H*-pyran (9a). At −78 °C, compound **3aa** (0.31 mmol) was dissolved in dry CH_2Cl_2 (2.5 mL), PhSeCl (0.32 mmol) was added, and the mixture was stirred for 4 h. After the reaction was completed, the mixture was washed by dilute $NaHCO_3$ (aq) and extracted by CH_2Cl_2. The solvent was evaporated, and the residue was subjected to column chromatography to give **9a** (171.0 mg, 85% yield) as a colorless oil: R_f = 0.70 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +7.1 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26 (t, 1H, *J* = 11.2 Hz), 3.57 (ddd, 1H, *J* = 2.0, 4.0, 9.6 Hz), 3.72 (dd, 1H, *J* = 8.8, 10.8 Hz), 3.72 (dd, 1H, *J* = 1.6, 11.2 Hz), 3.79 (dd, 1H, *J* = 4.0, 10.8 Hz), 3.82 (t, 1H, *J* = 8.8 Hz), 4.38 (d, 1H, *J* = 11.2 Hz), 4.49 (d, 1H, *J* = 12.0 Hz), 4.59 (d, 1H, *J* = 12.0 Hz), 4.67 (d, 1H, *J* = 10.4 Hz), 4.88 (d, 1H, *J* = 10.4 Hz), 4.95 (d, 1H, *J* = 10.4 Hz), 5.09 (d, 1H, *J* = 10.4 Hz), 6.98 (t, 2H, *J* = 7.2 Hz), 7.04−7.13 (m, 3H), 7.20−7.33 (m, 18H), 7.39−7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.4, 69.1, 73.4, 75.0, 75.9, 79.5, 80.1, 83.8, 84.8, 127.3, 127.4, 127.6, 127.7, 127.89, 127.93, 128.0, 128.1, 128.26, 128.30, 128.4, 128.55, 128.64, 129.0, 134.9, 138.2, 138.3, 138.5, 139.0; FT-HRMS (ESI) calcd for $C_{39}H_{42}NO_4Se$ $[M + NH_4]^+$: 668.2274, found 668.2273.

(2*R*,3*S*,4*S*,5*S*,6*S*)-3,4-Bis(benzyloxy)-2-(benzyloxymethyl)-6-phenyl-5-(phenylselanyl)tetrahydro-2*H*-pyran (9b). Compound **9b** was prepared from compound **3ba** as described in the preparation of compound **9a**, yielding **9b** (177.0 mg, 88% yield) as a colorless oil: R_f = 0.70 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +15.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.53 (dd, 1H, *J* = 4.8, 8.0 Hz), 3.54 (dd, 1H, *J* = 2.4, 11.2 Hz), 3.62 (dd, 1H, *J* = 4.8, 7.6 Hz), 3.66 (dd, 1H, *J* = 4.8, 7.6 Hz), 3.74 (t, 1H, *J* = 11.2 Hz), 4.08 (d, 1H, *J* = 2.4 Hz), 4.38 (d, 1H, *J* = 11.2 Hz), 4.38 (d, 1H, *J* = 11.2 Hz), 4.42 (d, 1H, *J* = 11.6 Hz), 4.61 (d, 1H, *J* = 11.6 Hz), 4.63 (d, 1H, *J* = 11.2 Hz), 4.79 (d, 1H, *J* = 11.6 Hz), 4.95 (d, 1H, *J* = 11.6 Hz), 7.04 (t, 2H, *J* = 7.6 Hz), 7.13−7.19 (m, 3H), 7.22−7.36 (m, 18H), 7.43 (d, 2H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 49.9, 68.7, 72.0, 73.0, 73.4, 74.4, 77.1, 81.8, 83.7, 127.3, 127.4, 127.56, 127.65, 127.67, 127.74, 128.0, 128.1, 128.3, 128.4, 128.5, 135.4, 137.8, 138.1, 139.1, 139.5; FT-HRMS (ESI) calcd for $C_{39}H_{39}SeO_4$ $[M + H]^+$: 651.2012, found 651.2006.

(2*R*,3*R*,4*R*,6*R*)-3,4-Bisbenzyloxy-2-benzyloxymethyl-6-phenyltetrahydropyran (10a). In a sealed tube, Bu_3SnH (0.22 mmol, 2.0 equiv) and a catalytic amount of AIBN (5%−20% equiv) were added to the solution of compound **9a** (74.0 mg, 0.11 mmol, 1.0 equiv) in dry benzene (1.0 mL) at room temperature. Then the mixture was heated to 80 °C for about 12 h (monitored by TLC). After the reaction was completed, the solvent was evaporated and the mixture was washed by distilled water and extracted by CH_2Cl_2. After evaporation of the solvent, the residue was subjected to column chromatography to give **10a** (51.0 mg, 93% yield) as a colorless oil: R_f = 0.71 (petroleum ether/acetone = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (dt, 1H, *J* = 11.6, 13.2 Hz), 2.39 (ddd, 1H, *J* = 2.0, 5.2, 13.2 Hz), 3.59 (ddd, 1H, *J* = 2.4, 4.0, 6.0 Hz), 3.65 (dd, 1H, *J* = 8.4 Hz, 9.6 Hz), 3.78−3.86 (m, 3H), 4.42 (dd, 1H, *J* = 1.6, 11.6 Hz), 4.58 (d, 1H, *J* = 12.4 Hz), 4.63 (d, 1H, *J* = 10.8 Hz), 4.65 (d, 1H, *J* = 11.6 Hz), 4.67 (d, 1H, *J* = 12.4 Hz), 4.72 (d, 1H, *J* = 11.6 Hz), 4.95 (d, 1H, *J* = 10.8 Hz), 7.24−7.39 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.2, 69.6, 71.4, 73.4, 75.1, 77.5, 78.4, 79.5, 81.2, 125.9, 127.5, 127.6, 127.63, 127.7, 128.0, 128.31, 128.34, 128.4, 138.5, 138.6, 141.5; FT-HRMS (ESI) calcd for $C_{33}H_{34}O_4Na$ $[M + Na]^+$: 517.2349, found 517.2350. The spectroscopic data coincide with the previous report.[26]

(2*R*,3*S*,4*R*,6*R*)-3,4-Bisbenzyloxy-2-benzyloxymethyl-6-phenyltetrahydropyran (10b). Compound **10b** was prepared from compound **9b** as described in the preparation of compound **10a**, yielding **10b** (47.3 mg, 87% yield) as a colorless oil: R_f = 0.71 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +5.8 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05−2.08 (m, 1H), 2.20−2.29 (m, 1H), 3.64−3.75 (m, 4H), 3.96 (brs, 1H), 4.40 (dd, 1H, *J* = 2.0, 11.2 Hz), 4.44 (d, 1H, *J* = 12.0 Hz), 4.49 (d, 1H, *J* = 11.6 Hz), 4.62 (s, 2H), 4.67 (d, 1H, *J* = 11.6 Hz), 4.98 (d, 1H, *J* = 12.0 Hz), 7.22−7.38 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.3, 69.4, 70.0, 72.5, 73.5, 74.2, 77.8, 78.2, 78.9, 126.2, 127.2, 127.3, 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 128.3, 128.4, 138.1, 138.5, 139.2, 141.6; FT-HRMS (ESI) calcd for $C_{33}H_{34}O_4Na$ $[M + Na]^+$: 517.2355, found 517.2358.

(2*R*,3*R*,4*S*,5*S*,6*R*)-3,4-Bis(benzyloxy)-2-(benzyloxymethyl)-5-bromo-6-phenyltetrahydro-2*H*-pyran (11a). In a sealed tube, NBS (0.32 mmol) was added to the solution of compound **3aa** (0.31 mmol) in dry CH_2Cl_2 (2.5 mL) at room temperature. Then the mixture was heated to 80 °C for about 12 h (monitored by TLC). After the reaction was completed, the mixture was washed by distilled water and extracted by CH_2Cl_2. The solvent was evaporated, and the residue was subjected to column chromatography to yield **11a** (140.0 mg, 78% yield) as a colorless oil: R_f = 0.67 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +12.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (dd, 1H, *J* = 3.2, 6.4 Hz), 3.78−3.87 (m, 2H), 3.89−3.96 (m, 2H), 4.52 (d, 1H, *J* = 12.4 Hz), 4.54 (d, 1H, *J* = 11.2 Hz), 4.63 (d, 1H, *J* = 12.0 Hz), 4.67 (d, 1H, *J* = 12.0 Hz), 4.68 (d, 1H, *J* = 11.2 Hz), 4.71 (d, 1H, *J* = 12.0 Hz), 4.81 (dd, 1H, *J* = 3.2, 5.6 Hz), 5.11 (d, 1H, *J* = 5.6 Hz), 7.20−7.35 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 53.6, 68.5, 72.9, 73.3, 73.6, 74.4, 75.0, 76.3, 77.4, 126.8, 127.5, 127.6, 127.7, 127.8, 127.9, 128.07, 128.08, 128.3, 128.4, 128.51, 128.54, 137.6, 137.90, 137.94, 138.3; FT-HRMS (ESI) calcd for $C_{33}H_{37}BrNO_4$ $[M + NH_4]^+$: 590.1901, found 590.1900.

(2*R*,3*R*,4*S*,5*S*,6*R*)-3,4-Bis(benzyloxy)-2-(benzyloxymethyl)-5-iodo-6-phenyltetrahydro-2*H*-pyran (11b). Compound **11b** was prepared from compound **3aa** and NIS at 50 °C as described in the preparation of compound **11a**, yielding **11b** (138.4 mg, 72% yield) as a colorless oil: R_f = 0.67 (petroleum ether/acetone = 2:1); $[\alpha]^{25}_D$ +23.6 (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.34 (dd, 1H, *J* = 3.2, 6.0 Hz), 3.77−3.88 (m, 3H), 3.97 (dd, 1H, *J* = 1.6, 10.4 Hz), 4.52 (d, 1H, *J* = 12.0 Hz), 4.55 (d, 1H, *J* = 12.0 Hz), 4.64 (d, 2H, *J* = 12.0 Hz), 4.68 (d, 1H, *J* = 11.2 Hz), 4.69 (d, 1H, *J* = 11.6 Hz), 4.97 (dd, 1H, *J* = 3.6, 6.0 Hz), 5.13 (d, 1H, *J* = 6.0 Hz), 7.20−7.40 (m, 20H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.0, 68.5, 72.6, 73.3, 73.5, 74.5, 75.3, 77.3, 77.7, 126.8, 127.5, 127.6, 127.7, 127.8, 127.9, 127.96, 128.03, 128.1, 128.25, 128.32, 128.39, 128.43, 128.49, 128.52, 137.4, 137.9, 138.3, 138.6; FT-HRMS (ESI) calcd for $C_{33}H_{37}NIO_4$ $[M + NH_4]^+$: 638.1762, found 638.1771.

(2*R*,3*R*,4*R*,6*S*)-3,4-Bisbenzyloxy-2-benzyloxymethyl-6-phenyltetrahydropyran (12). In a sealed tube, Bu_3SnH (0.14 mmol, 2.0 equiv) and a catalytic amount of AIBN (5%−20% equiv) were added to the solution of compound **11a** (40.0 mg, 0.07 mmol, 1.0 equiv) in dry benzene (0.5 mL) at room temperature. Then the mixture was heated to 80 °C for about 12 h (monitored by TLC). After the reaction was completed, the mixture was washed by distilled water and extracted by CH_2Cl_2. The solvent was evaporated, and the residue was subjected to column chromatography to give **12** (33.0 mg, 95% yield) as white semisolids: R_f = 0.72 (petroleum ether/acetone = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (ddd, 1H, *J* = 4.8, 9.6, 14.4 Hz), 2.57 (dt, 1H, *J* = 4.0, 13.6 Hz), 3.61 (dd, 1H, *J* = 4.0, 8.0 Hz), 3.65 (t, 1H, *J* = 8.0 Hz), 3.71 (ddd, 1H, *J* = 2.8, 4.0, 9.2 Hz), 3.72 (dd, 1H, *J* = 2.8, 10.4 Hz), 3.78 (dd,

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1H, J = 4.4, 10.4 Hz), 4.52 (d, 1H, J = 11.2 Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.65 (d, 1H, J = 12.0 Hz), 4.68 (d, 2H, J = 12.0 Hz), 4.79 (d, 1H, J = 11.2 Hz), 5.12 (t, 1H, J = 4.0 Hz), 7.16−7.36 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.4, 69.1, 71.9, 72.0, 73.1, 73.4, 74.2, 77.2, 77.7, 126.4, 127.2, 127.6, 127.6, 127.7, 127.8, 127.9, 127.9, 128.3, 128.4, 128.5, 138.3, 138.4, 138.5, 139.9; FT-HRMS (ESI) calcd for $C_{33}H_{38}NO_4$ [M + NH_4]$^+$: 512.2795, found 512.2798. The spectroscopic data coincide with the previous report.[27]

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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