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Stereoselective Phenylselenoglycosylation of Glycals Bearing a Fused Carbonate Moiety toward the Synthesis of 2-Deoxy-β-galactosides and β-Mannosides

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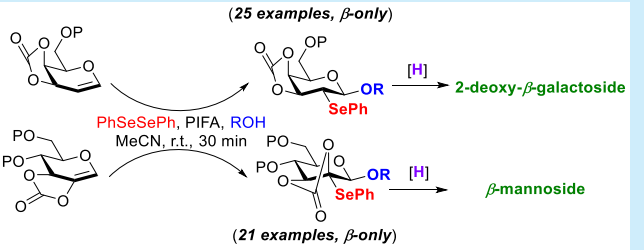
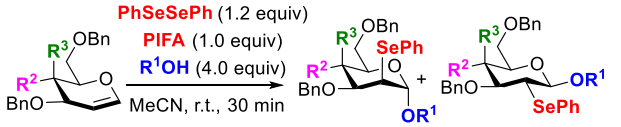
ABSTRACT: A phenylselenoglycosylation reaction of glycal derivatives mediated by diphenyl diselenide and phenyliodine(III) bis(trifluoroacetate) under mild conditions is described. Stereoselective glycosylation has been achieved by installing fused carbonate on those glycals. 3,4-*O*-Carbonate galactals and 2,3-*O*-carbonate 2-hydroxyglucals are converted into corresponding glycosides in good yields with excellent β-selectivity, resulting in 2-phenylseleno-2-deoxy-β-galactosides and 2-phenylseleno-β-mannosides which are good precursors of 2-deoxy-β-galactosides and β-mannosides, respectively.



Oligosaccharides and glycoconjugates play essential roles in multitudinous biological processes.[1] Intense efforts have been dedicated to the chemical preparation of oligosaccharides for biological studies.[2] Due to their specific structural features, stereoselective construction of several kinds of glycosidic linkages, such as 2-deoxy-β-glycosides[3] and β-mannosides,[4] are particularly challenging. Lacking *C*2 substituents that can direct the anomeric selectivity makes the stereoselective synthesis of 2-deoxy-glycosides rather difficult. Thermodynamically, the formation of 2-deoxy-α-glycosides is superior to β-anomers because of anomeric effect. In addition, without electron-withdrawing groups at *C*2, the 2-deoxyglycosidic bonds are more acid sensitive. Although direct synthesis[5] and de novo synthesis[6] are known, indirect synthesis is the most commonly used strategy for the preparation of 2-deoxy-β-glycosides. Typically a temporary substituent such as halogen,[7] ester,[8] thioether,[9] or selenoether[10] is installed at *C*2 for directing the formation of glycosidic bonds, which is removed later by reductive cleavage. As a type of 1,2-*cis* glycoside, β-mannosides

Table 1. PIFA-PhSeSePh-Promoted Glycosylation of Glucal 1 and Galactal 2

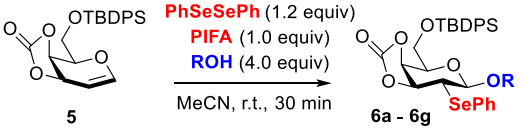


1 R2 = OBn, R3 = H 3aα - 3fα 3aβ - 3fβ
2 R2 = H, R3 = OBn 4α 4β

entry	glycal	R1OH	result[a]
1	**1**	MeOH	96%, **3aα**:**3bβ** = 1:1.5
2	**1**	EtOH	98%, **3bα**:**3bβ** = 1:1.5
3	**1**	*i*-PrOH	95%, **3cα**:**3cβ**= 1:1.3
4	**1**	*n*-BuOH	92%, **3dα**:**3dβ** = 1:1.8
5	**1**	BnOH	90%, **3eα**:**3eβ** = 1:1.3
6	**1**	*t*-BuOH	88%, **3fα**:**3fβ** = 1:1.1
7	**2**	MeOH	98%, **4α**:**4β** = 1:1.4

[a]Yield of both isomers. Ratio was determined by ^{1}H NMR.

Table 2. PIFA-PhSeSePh-Promoted Glycosylation of Galactal 5



5 6a - 6g

entry	ROH	result[a]
1	MeOH	**6a**, 95%, β only
2	EtOH	**6b**, 92%, β only
3	*i*-PrOH	**6c**, 90%, β only
4	*n*-BuOH	**6d**, 90%, β only
5	BnOH	**6e**, 92%, β only
6	CyOH	**6f**, 84%, β only
7	PMBOH	**6g**, 84%, β only

[a]Yield of both isomers. Ratio was determined by ^{1}H NMR.

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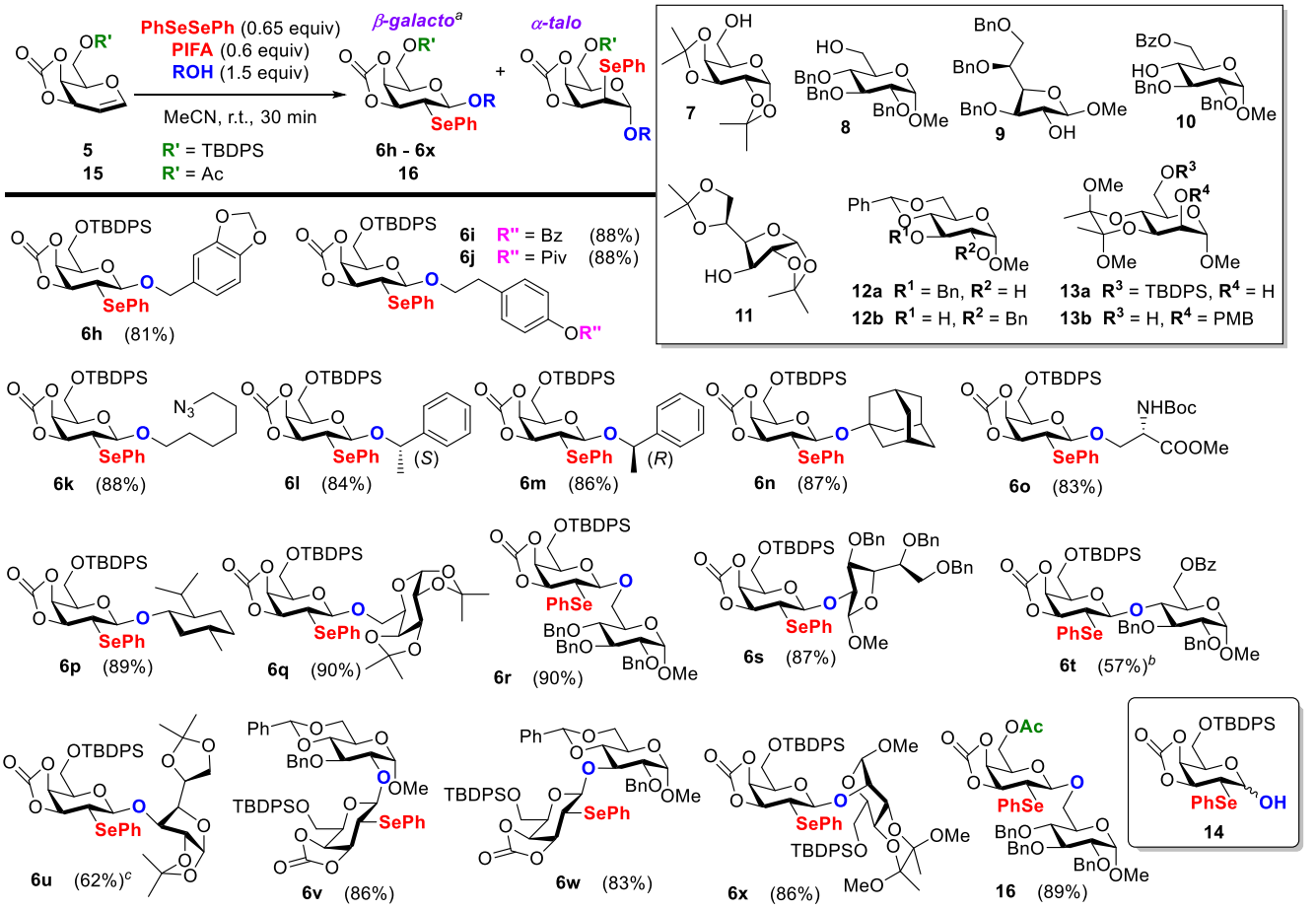
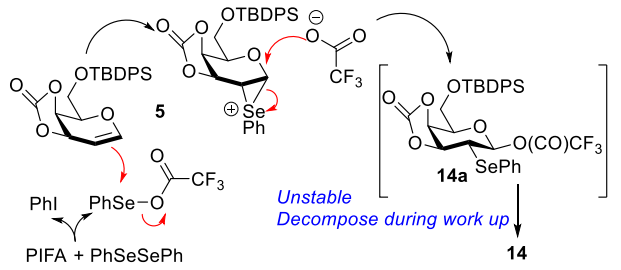
Scheme 1. Stereoselective Synthesis of 2-Phenylseleno-2-deoxy-β-galactosides via PIFA-PhSeSePh-Mediated Activation of 3,4-*O*-Carbonate Galactals

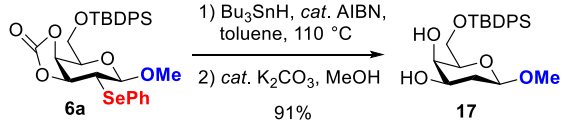


[a]Yield for isolated product. All reactions were finished in 30 min. [b]**14** was obtained in 36% yield. [c]**14** was obtained in 30% yield.

Scheme 2. Proposed Mechanism for the Generation of 14



Scheme 3. Removal of *C*2 Phenylseleno to Obtain 2-Deoxygalactoside



are difficult to synthesize due to the steric effect of axial *C*2-substituent and anomeric effect. Several direct synthetic strategies have been developed, including insoluble silver salt mediated activation of mannosyl halides,[11] the use of 4,6-*O*-tethered mannosyl donors,[12] intramolecular aglycone delivery,[13] hydrogen-bond-mediated aglycone delivery,[14] boronic acid or borinic acid mediated activation of 1,2-anhydro-mannose,[15] the use of 2,6- or 3,6-lactones,[16] and β-selective anomeric *O*-alkylation of mannose lactols.[17] Indirect syntheses by converting β-glucosides or β-2-ulosyl-glycosides into β-mannosides have been developed as well.[18] Despite this progress, syntheses of 2-deoxy-β-glycosides and β-mannosides are still challenging. Herein, we report our efforts toward the stereoselective construction of 2-deoxy-β-glycosides and β-mannosides.

2-Phenylseleno-2-deoxy-glycosides are good precursors of 2-deoxy-glycosides as the *C*2 selenoether can be cleanly removed by reductive cleavage. However, 2-deoxy-glycosyl donors bearing *C*2 equatorial selenoether may epimerize and afford α-linkages.[10b] Recently, one-step α-selective glycosylation activated by the addition of electrophilic selenium species to glycals has been reported.[10a] Therefore, we are motivated to develop a method for the stereoselective synthesis of 2-deoxy-β-glycosides based on the activation of glycals by selenium electrophile. With the experience of the dihydroxylation of olefin mediated by hypervalent iodine species,[19] we attempted to use this type of oxidant for the introduction of *C*2 selenoether. We found that perbenzylated glucal **1** and galactal **2** reacted with simple alcohols in the presence of phenyliodine(III) bis-(trifluoroacetate) (PIFA) and PhSeSePh in acetonitrile at room temperature to afford the corresponding glycosides in excellent yields (Table 1). Moreover, the reactions showed the potential toward the formation of β-glycosides. It has been reported that glycosyl donors bearing carbonate[7c,d,20] or

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Scheme 4. Proposed Reaction Mechanism for the Construction of β-Mannosides from 2,3-*O*-Carbonate-2-hydroxyglucal

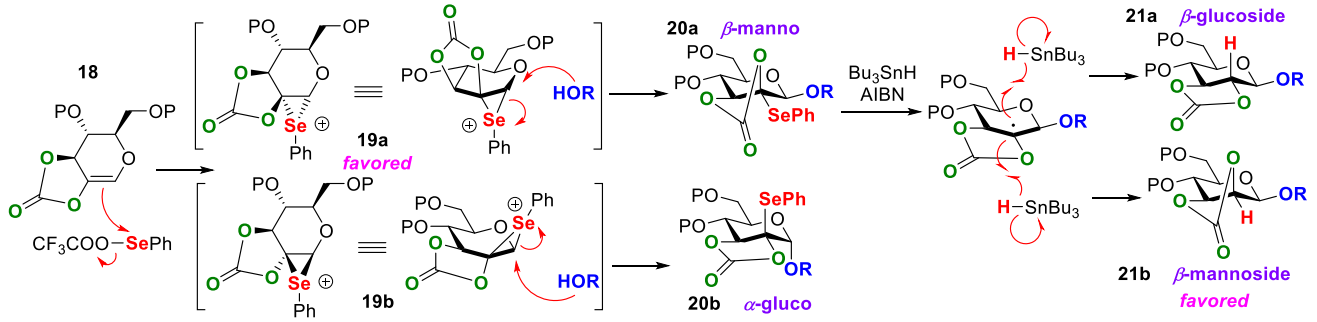
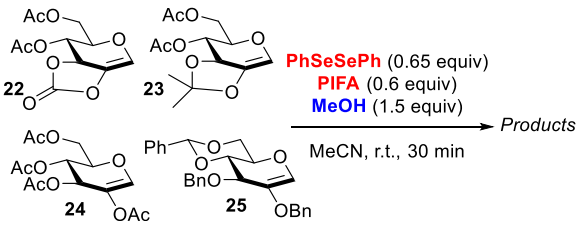
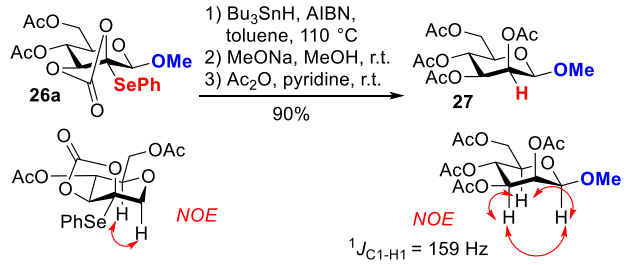


Table 3. Glycosylation of 2-Hydroxyglucals 22−25



entry	donor	result
1	**22**	93%, **26a**
2	**23**	decomposed
3	**24**	no reaction
4	**25**	decomposed

Scheme 5. Cleavage of *C*2 Phenoseleno to Obtain β-Mannoside



carbamate[21] moiety sometimes provide excellent stereo-outcomes in glycosylation reactions. With this in mind, we synthesized conformationally restricted galactal **5** bearing 3,4-*O*-carbonate and 6-*O*-TBDPS. The reactions of **5** with simple alcohols under the aforementioned condition were conducted and we were pleased to find that the corresponding glycosides were obtained in high yields with excellent β-selectivity (Table 2). After optimization, we confirmed the optimal conditions as 0.65 equiv of PhSeSePh and 0.6 equiv of PIFA in acetonitrile at room temperature.[22]

With the optimal condition in hands, we carried out the glycosylation of various acceptors, including noncarbohydrate and sugar-derived alcohols. Noncarbohydrate substrates included simple alcohols, piperonyl alcohol, 4-benzoxyphenethanol, 4-pivaloxyphenethanol, 6-azidohexanol, (*S*)-α-phenethyl alcohol, (*R*)-α-phenethyl alcohol, 1-adamantanol, *N*-Boc-L-serine methyl ester, and menthol. The reactions of galactal **5** with these noncarbohydrate acceptors all afforded the corresponding 2-phenylseleno-2-deoxy-β-galactosides in high yields (83−95%, Scheme 1). Notably, the glycosylation with a tertiary alcohol, 1-adamantanol, afforded the corresponding glycoside **6n** in 87% yield. We also surveyed the glycosylation of **5** with some sugar-derived acceptors (**7**−**13**). All of the primary alcohols and many secondary alcohols reacted with **5** smoothly, resulting in the corresponding β-linked disaccharides in 83−90% yields. The coupling with sugar **10** and **11** gave disaccharide **6t** and **6u** in 57% and 62% with lactol **14** isolated in 36% and 30% yield, respectively. Although we conducted the reactions with **10** and **11** again under absolutely anhydrous condition, the results did not change much. We reasoned that the lactol **14** formed from the reactions of **5** with **10** and **11** was possibly generated by the hydrolysis of intermediate **14a**, which was formed via the attack of 1,2-episelenonium ion by trifluoroacetate anion (Scheme 2). Such a side reaction was not noticeable when the less sterically hindered acceptors (**7**, **8**, **9**, **12a**/**b**, **13a**) reacted with **5**. Taken together, the glycosylation of conformationally restricted galactal **5** with different kinds of acceptors in the presence of PIFA and PhSeSePh in acetonitrile provided the expected 2-phenylseleno-2-deoxy-β-galactosides, with undetectable formation of the corresponding α-talosides. Many commonly used protecting groups were tolerable and in general, the glycosylation reactions afforded the products in a short period of time with satisfactory yields. Considering that 6-*O*-TBDPS may also contribute to the β-selectivity because it provided prominent steric hindrance on β-face and favored the attack of electrophiles from α-face, we prepared another conformationally restricted galactal **15** bearing 6-*O*-Ac. The glycosylation of **15** with acceptor **8** under the optimal condition provided β-linked disaccharide **16** in 89% yield. This result indicated that the excellent β-selectivity highly depended on the restricted conformation caused by 3,4-*O*-carbonate moiety. To demonstrate the subsequent removal of *C*2 selenoether and 3,4-*O*-carbonate, compound **6a** was treated with Bu_3SnH and AIBN in toluene at 110 °C followed by the deacylation in methanol to afford 2-deoxy-β-galactoside **17** in a total yield of 91% (Scheme 3).

The success in stereoselective phenylselenoglycosylation of galactals prompted us to use glucals bearing carbonate moiety for the stereoselective construction of 2-deoxy-β-glucosides. Unfortunately, our attempts to synthesizing 3,4-*O*-carbonate glucals failed due to the *trans*- relationship of *C*3 and *C*4 hydroxyl. Meanwhile, we proposed an approach toward the construction of β-mannosides via the phenylselenoglycosylation of 2-hydroxy (protected by ether or ester) glucals. Although the 3,4-*O*-carbonate moiety could not be installed on 2-hydroxyglucal either due to the similar geometry with nomal glucals, the formation of 2,3-*O*-carbonate-2-hydroxyglucal **18** is feasible and its phenylselenoglycosylation could be stereoselective due to the chiral *C*3 hydroxyl group (Scheme 4). Activation of **18** by phenylselenium cation could generate two intermediates **19a**

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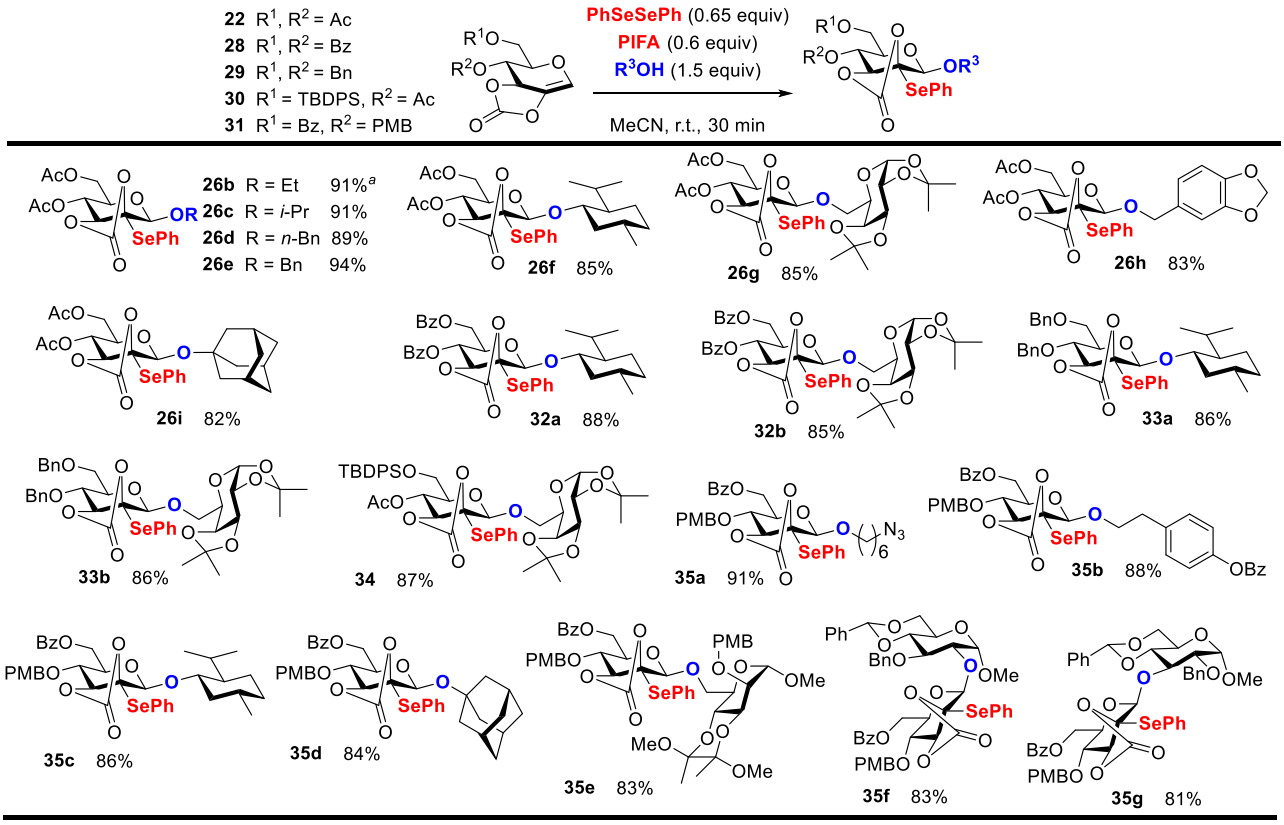
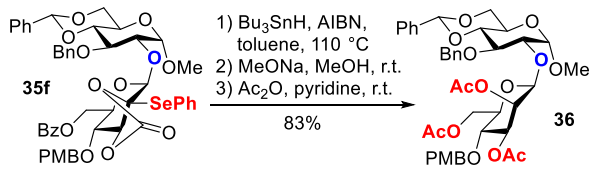
Scheme 6. Phenylselenoglycosylation of 2,3-*O*-Carbonate-2-hydroxyglucals



[a]Isolated yields for all the products.

Scheme 7. Diastereoselective Reduction of 35f



and **19b**. The subsequent attack of acceptors at the anomeric position from the opposite side to the episelenonium ion would produce β-linked glycoside **20a** and α-linked **20b**, respectively. Due to the ring strain of 2,3-fused carbonate, the formation of 2,3-*cis* fused intermediate **19a** and product **20a** would be favored. Subsequent reductive removal of *C*2 selenoether of **20a** could also be achieved in a stereoselective manner because of the ring strain as well,[23] resulting in the corresponding β-mannoside **21b**.

Based on this hypothesis, we synthesized 2,3-*O*-carbonate protected **22**. 2,3-*O*-Isopropylidene-protected **23**, structurally flexible peracetylated donor **24**, and 4,6-*O*-benzylidene protected donor **25** were also prepared for comparison. These four donors were subjected to the glycosylation with methanol under the optimal condition (Table 3). Most of donor **24** was recovered after 24 h probably due to the poor reactivity caused by the electron-withdrawing effect of 2-*O*-Ac. On the other hand, the electron-rich olefins of **23** and **25** may be too sensitive to electrophilic species and they probably reacted with PIFA directly, resulting in complex byproducts. Interestingly, only the reaction using **22** as the donor afforded encouraging result. The product **26a** (Scheme 5) was identified as β-glycoside.[24] Although we failed to get **26a** crystallized for X-ray crystallographic analysis, the C−Se bond should be equatorial based on the 1,2-*trans* relationship with glycosidic bond (see Scheme 4, **20a**), because it was generated by the attack of nucleophiles to episelenonium ion (see Scheme 4, **19a**). Treatment of **26a** under the condition of Bu_3SnH and AIBN followed by the removal of 2,3-*O*-carbonate and global acetylation gave compound **27** in 90% yield (Scheme 5), which was identified as methyl 2,3,4,6-tetra-*O*-acetyl-β-mannoside.[25] In addition, the NMR of **27** also agreed with its reported data.[26] We did not observe the formation of corresponding glucosides or α-mannoside. Thus, our proposed scheme for the stereoselective construction of β-mannosides from 2,3-*O*-carbonate-2-hydroxyglucal was shown to be effective.

To explore the generality of this strategy, various 2,3-*O*-carbonate-2-hydroxyglucal donors were subjected to the phenylselenoglycosylation reaction. Those 2-hydroxyglucals included 4,6-di-*O*-acetyl derivative **22**, 4,6-di-*O*-benzoyl derivative **28**, 4,6-di-*O*-benzyl derivative **29**, 4-*O*-acetyl-6-*O*-(*tert*-butyl)diphenylsilyl derivative **30**, and 4-*O*-(*p*-methoxybenzyl)-6-*O*-benzoyl derivative **31**. We were pleased to find that all these donors reacted with the tested acceptors smoothly to afford the corresponding 2-phenylseleno-2,3-*O*-carbonate-β-mannosides in good to excellent yields (81−94%, Scheme 6). No isomeric glucosides were detected with ^{1}H NMR. In particular, the glycosylation of donor **31** with sugar-derived secondary alcohol **13a** and **13b** gave the corresponding β-linked disaccharides **35f** and **35g** in 83% and 81% yield, respectively. Interestingly, the inductive effect of protecting groups at *C*4 and *C*6 did not seem to exert much influence on the reactivity of those donors. For example, the glycosylation of **26**, **28**, **29**, and **30** with 1,2:3,4-di-*O*-isopropylidene-α-galactose **7** produced the corresponding

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disaccharide **26g**, **32b**, **33b**, and **34** in 85%, 85%, 86%, and 87% yield, respectively. A similar phenomenon was observed when we compared the glycosylation of **26**, **28**, **29**, and **31** with menthol or the reaction of **26** and **31** with 1-adamantanol. The lack of reactivity of 2-hydroxyglucal **24** bearing 2,3-di-*O*-Ac and the high reactivity of **22** bearing 2,3-*O*-carbonate clearly indicated the essential role of 2,3-*O*-carbonate in the activation of 2-hydroxy-glucal. Presumably, the ring strain of the bicyclic structure containing a carbon−carbon double bond at the bridgehead carbon was the main driving force for this type of glycosylation. Therefore, it was not surprising that *C*4 and *C*6 substituents showed less influence on yields. In addition, the diastereoselective reduction of disaccharide **35f** was conducted following the same procedure how we got **27** from **26a** and disaccharide **36** was obtained in an overall yield of 83% (Scheme 7). The structure of **36** was confirmed to be β-mannosyl-(1 → 2)-glucoside by comprehensive NMR experiments.[27]

In conclusion, PhSeSePh in the presence of PIFA promoted the highly stereoselective phenylselenoglycosylation of glycal derivatives bearing carbonate for the construction of 2-deoxy-β-galactosides and β-mannosides. The typical carbohydrate protecting groups were stable under this condition and the reaction yields were generally high. Under the optimal condition, conformationally restricted 3,4-*O*-carbonate-galactals were converted into 2-phenylseleno-2-deoxy-galactosides with excellent β-selectivity. An indirect synthetic strategy for the stereoselective construction of β-mannosides has been developed via the phenylselenoglycosylation of 2-hydroxyglucals bearing 2,3-*O*-carbonate. 2,3-*O*-carbonate protecting group was critical to the reactivity of such 2-hydroxyglucal donors as well as the stereocontrol of the glycosylation step and the subsequent removal of *C*2 phenylseleno group. Further studies on the application of this method in the synthesis of complex carbohydrate molecules are now underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00732.

Experimental procedures, characterization data, and ^{1}H, ^{13}C NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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