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Selective Formation of β-*O*-Aryl Glycosides in the Absence of the C(2)-Ester Neighboring Group

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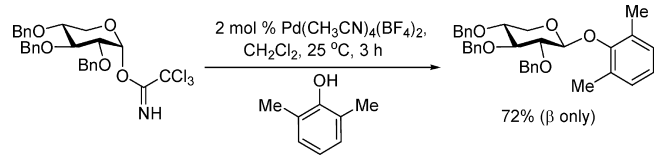

The development of a general and practical method for the stereoselective synthesis of β-*O*-aryl glycosides that exploits the nature of a cationic palladium(II) catalyst, instead of a C(2)-ester directing group, to control the β-selectivity is described. This β-glycosylation reaction is highly diastereoselective and requires 2−3 mol % of $Pd(CH_3CN)_4(BF_4)_2$ to activate glycosyl trichloroacetimidate donors at room temperature. The current method has been applied to D-glucose, D-galactose, and D-xylose donors with a nondirecting group incorporated at the C(2)-position to provide the *O*-aryl glycosides with good to excellent β-selectivity. In addition, its application is widespread to electron-donating, electron-withdrawing, and hindered phenols. The reaction is likely to proceed through a seven-membered ring intermediate, wherein the palladium catalyst coordinates to both C(1)-trichloroacetimidate nitrogen and C(2)-oxygen of the donor, blocking the α-face. As a result, the phenol nucleophile preferentially approaches to the top face of the activated donor, leading to formation of the β-*O*-aryl glycoside.

Introduction

The stereoselective synthesis of *O*-aryl glycosides has recently received considerable attention because these compounds are known to exhibit antitumor, anti-HIV, and antibiotic activities.[1] The synthesis of *O*-aryl glycosides, however, can be difficult to achieve due to the electron-withdrawing properties of aromatic rings[2] and the facile rearrangement of the resulting *O*-aryl glycosides to their corresponding *C*-aryl glycosides.[3] Additionally, steric hindrance from substituents on phenolic compounds makes them unreactive in many glycosylation methods.[4] Glycosyl acetates, halides, and trichloroacetimidates have been used as donors in the formation of β-*O*-aryl glycosides.[2] These glycosyl donors, however, only work well with specific phenol nucleophiles. For instance, glycosyl acetates and trichloroacetimidates are preferred for electron-donating phenol substrates. Glycosyl acetates usually provide the β-*O*-aryl glycosides with lower yields than trichloroacetimidates due to anomerization of both the glycosyl donor and the coupling product.[2] For instance, β-D-glucose pentaacetate undergoes anomerization to the corresponding α-D-glucose pentaacetate in the presence of 3 equiv of $BF_3 \cdot OEt_2$.[5] High temperature and long reaction time also facilitate anomerization to give the thermodynamic α-coupling product.[6] The resulting α-*O*-aryl glycosides are, however, often obtained in low yields due to the formation of the undesired *C*-aryl glycosides. On the other hand, glycosyl halides are strongly preferred for electron-withdrawing phenols.[2] In general, the β-*O*-aryl glycosides can be formed in the glycosylation reaction by employing ester functionalities as the directing group at the C(2)-position of glycosyl donors.[7] This approach, however, is not without its limitations. In some cases, formation of ortho ester side products[8] and migration of the C(2)-acyl functionality[9] are also observed in the reaction.

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(2) Jacobsson, M.; Malmberg, J.; Ellervik, U. *Carbohydr. Res.* **2006**, *341*, 1266–1281.
(3) Mahling, J.-A.; Schmidt, R. R. *Synthesis* **1993**, 325–328.
(4) (a) Ogawa, T.; Matsui, M. *Carbohydr. Res.* **1976**, *51*, C13−C18. (b) Clerici, F.; Gelmi, M. L.; Mottadelli, S. *J. Chem. Soc., Perkin Trans.1* **1994**, 985–988. (c) Mukaiyama, T.; Katsurada, M.; Iida, Y. *Chem. Lett.* **1992**, 2105–2108. (d) Kroger, L.; Thiem, J. *J. Carbohydr. Chem.* **2003**, *22*, 9–23.
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(7) (a) Nukada, T.; Berces, A.; Zgierski, M. Z.; Whitfield, D. M. *J. Am. Chem. Soc.* **1998**, *120*, 13291–13295. (b) Barresi, F.; Hindsgaul, O. *J. Carbohydr. Chem.* **1995**, *14*, 1043. (c) Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–123. (d) Schmidt, R. R.; Michel, J. *Angew. Chem., Int. Ed.* **1980**, *19*, 731–732.

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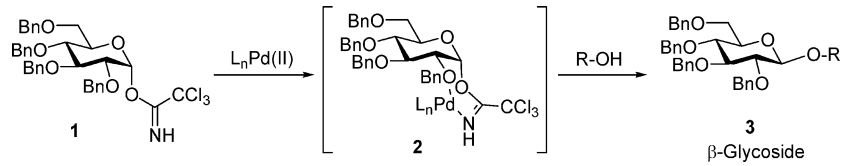


FIGURE 1. Cationic Pd(II)-catalyzed β-selective glycosylation.

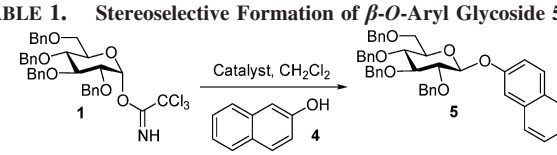
We report herein a new method for the stereoselective synthesis of β-*O*-aryl glycosides in the absence of the C(2)-ester directing group. This approach relies only on the nature of the cationic palladium catalyst, $Pd(CH_3CN)_4(BF_4)_2$, to control the β-selectivity at the newly formed glycosidic bond. The current method has been applied to a number of glycosyl trichloroacetimidate donors with a nondirecting group incorporated at the C(2)-position as well as electron-donating, electron-withdrawing, and hindered phenols to provide access to a variety of β-*O*-aryl glycosides. In general, the coupling proceeds under mild conditions with 2−3 mol % of $Pd(CH_3CN)_4(BF_4)_2$ at room temperature. In all cases, the undesired *C*-aryl glycosides are not observed in the reaction.

Results and Discussion

We have recently reported a cationic palladium(II)-directed β-selective glycosylation in the absence of the traditional C(2)-ester neighboring group effect.[10] This method relies on the ability of the palladium(II) catalyst, $Pd(PhCN)_2(OTf)_2$ or $Pd(CH_3CN)_4(BF_4)_2$, to direct β-selectivity. This reaction has been applied to a variety of primary, secondary, and tertiary aliphatic alcohols to provide the desired products with excellent β-selectivity. Mechanistic studies suggest that the cationic palladium(II) catalyst reversibly coordinates to both the C(1)-trichloroacetimidate nitrogen and the C(2)-ether oxygen of the glycosyl donor **1** to form a seven-membered ring intermediate **2** (Figure 1). Formation of this seven-membered ring species blocks the α-face. As a result, the oxygen nucleophile preferentially approaches to the top face of the activated donor, leading to the formation of β-*O*-glycoside **3**.

With the success of these glycosylation processes, we seek to further explore the scope of this reaction with phenol nucleophiles to form β-*O*-aryl glycosides. Our main concern in this investigation is the ability of the cationic palladium(II) catalyst to promote the rearrangement of the resulting *O*-aryl-glycosides to the corresponding *C*-aryl glycosides at high temperature. Thus, we initially explored the feasibility of this concept with $Pd(PhCN)_2(OTf)_2$, which is more reactive than $Pd(CH_3CN)_4(BF_4)_2$.[10b] Treatment of both D-glucose trichloroacetimidate donor **1**[11] and 2-naphthol (**4**) with 2 mol % of $Pd(PhCN)_2(OTf)_2$, generated in situ from AgOTf and $Pd(PhCN)_2Cl_2$ at −78 °C, provided the desired *O*-aryl glycoside **5** as a 2:1 mixture of α- and β-isomers (Table 1, entry 1). However, it took 6 h for the reaction to go to completion at −78 °C. Raising the temperature shortened the reaction time (entries 2 and 3). Since the *C*-aryl glycoside was not observed in the coupling reaction with $Pd(PhCN)_2(OTf)_2$ at high temperature, we decided to explore with $Pd(CH_3CN)_4(BF_4)_2$. To our delight, exposure of both **1** and **4** to 2 mol % of $Pd(CH_3CN)_4(BF_4)_2$ at 25 °C afforded the desired *O*-aryl glycoside **5** in 80% yield with excellent β-selectivity (β:α = 11:1) (entry 4). The significant increase in β-selectivity with use of $Pd(CH_3CN)_4(BF_4)_2$ suggests that these two cationic palladium catalysts operate through different mechanisms. Since $Pd(PhCN)_2(OTf)_2$ is more reactive than $Pd(CH_3CN)_4(BF_4)_2$, it promotes ionization of trichloroacetimidate donor **1** to form an oxocarbenium intermediate; therefore, a mixture of α- and β-isomers **5** was observed in the reaction. On the other hand, $Pd(CH_3CN)_4(BF_4)_2$ promotes a seven-membered ring intermediate (Scheme 1), wherein 2-naphthol (**4**) preferentially approaches the β-face of the activated donor, leading to the formation of β-*O*-aryl glycoside **5**. Compared to other activating reagents, $Pd(CH_3CN)_4(BF_4)_2$ is more β-selective. Additionally, lower catalyst loading and shorter reaction time were observed with use of this cationic palladium as the activator. For example, when 4 mol % of AgOTf was employed as the activator in the coupling process, it took 12 h for the reaction to go to completion (entry 5). The desired *O*-aryl glycoside **5** was isolated in 68% yield as a mixture of α- and β-isomers. Employing $BF_3 \cdot OEt_2$ as the activating reagent yielded **5** in 66% yield with α:β = 3:1 (entry 6). It has also been reported that glycosylation of 2-naphthol (**4**) with tetrabenzylated-D-glucopyranose in the presence of dicylohexylcarbodiimide (1 equiv.) and CuCl (2 mol %) at 80 °C provided the coupling product **5** as 2.4:1 mixture of β- and α-isomers.[12]

TABLE 1. Stereoselective Formation of β-*O*-Aryl Glycoside 5[a]



entry	Pd(II) sources	loading (mol %)	*T* (°C)	time (h)	yield (%)	β:α
1	$Pd(PhCN)_2(OTf)_2$	2	−78	6	60	2:1
2	$Pd(PhCN)_2(OTf)_2$	2	0	3	76	1:1
3	$Pd(PhCN)_2(OTf)_2$	2	25	1	75	1:1
4	$Pd(CH_3CN)_4(BF_4)_2$	2	25	2	80	11:1
5	AgOTf	4	25	12	68	1:1
6	$BF_3 \cdot OEt_2$	4	25	6	66	3:1

[a] All reactions were performed in CH_2Cl_2 (0.2 M) with 2−4 mol % of the catalyst. [b] Isolated yield. [c] ^1H NMR ratio.

With the optimal conditions at hands, we set out to define the scope of the phenol nucleophiles with this D-glucose trichloroacetimidate donor **1** (Table 2). The cationic palladium-catalyzed β-selective glycosylation reaction is effective for a variety of electron-rich and electron-withdrawing phenols, and the desired *O*-aryl glycoconjugates **12**−**15** were isolated in good yields and β-selectivity (entries 1−4).[13] Likewise, tyrosine amino acid **10** was able to couple with trichloroacetimidate donor **1** to provide the *O*-aryl glycopeptide **16** in excellent yield and good β-diastereoselectivity

(8) (a) Seeberger, P. H.; Eckhardt, M.; Gutteridge, C. E.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 10064–10072. (b) Crich, D.; Dai, Z.; Gastaldi, S. *J. Org. Chem.* **1999**, *64*, 5224–5229.

(9) Yu, H.; Ensley, H. E. *Tetrahedron Lett.* **2003**, *4*, 9363–9366.

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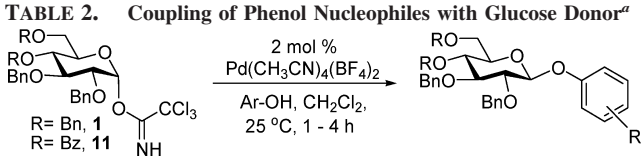
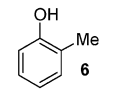
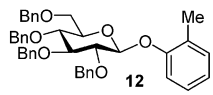
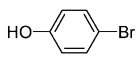
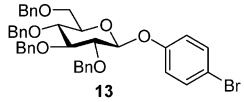
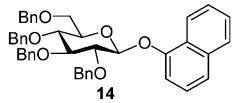
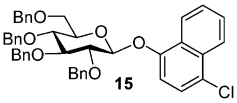
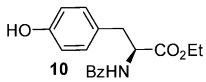
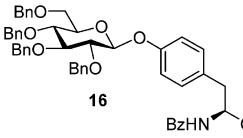
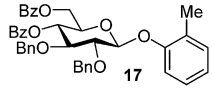
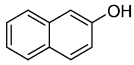
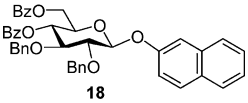
(11) (a) Zhang, J.; Yergey, A.; Kowalak, J.; Kovac, P. *Tetrahedron* **1998**, *54*, 11783–11792. (b) Nakanishi, N.; Nagafuchi, Y.; Koizumi, K. *J. Carbohydr. Chem.* **1994**, *13*, 981–990. (c) Rathore, H.; Hashimoto, T.; Igarashi, K.; Nukaya, H.; Fullerton, D. *Tetrahedron* **1985**, *41*, 5427–5438.

(12) Tsutsumi, H.; Ishido, Y. *Carbohydr. Res.* **1981**, *88*, 61–75.

TABLE 2. Coupling of Phenol Nucleophiles with Glucose Donor[a]



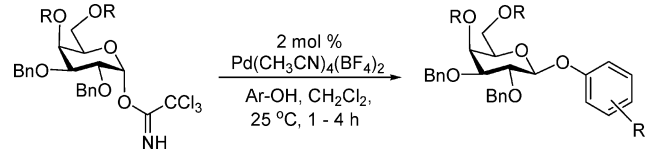
Entry	Phenols	*O*-Aryl-Glycoside	Yield[b]	β:α[c]
1	 **6**	 **12**	75%	11:1
2	 **7**	 **13**	83%	6:1
3	 **8**	 **14**	87%	7:1
4	 **9**	 **15**	88%	10:1
5	 **10**	 **16**	98%	7:1
6	 **6**	 **17**	75%	9:1
7	 **4**	 **18**	93%	8:1

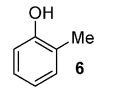
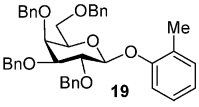
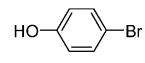
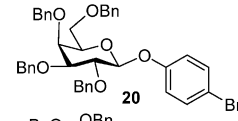
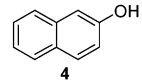
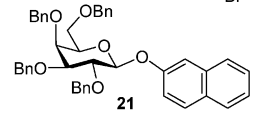
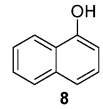
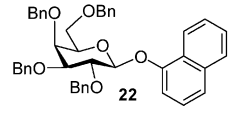
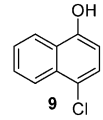
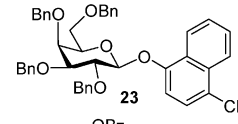
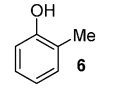
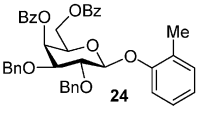
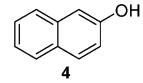
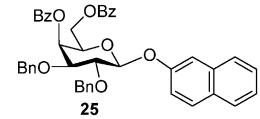
[a] All reactions were carried out in CH_2Cl_2 with 2 mol % of $Pd(CH_3CN)_4(BF_4)_2$ at 25 °C. [b] Isolated yield. [c] ^1H NMR ratio.

(entry 5). While other glycosylation methods slightly favor α-selectivity,[14] this palladium-catalyzed glycosylation reaction is *β*-selective. For example, glycosylation of 2-methylphenol (**6**) with tetrabenzylated D-glucose in the presence of *p*-nitrobenzenesulfonyl chloride (1.1 equiv) and AgOTf (1.1 equiv) at 25 °C gave *O*-aryl glycoside **12** in 65% yield with $\alpha:\beta = 3:1$.[14a] Under our conditions, coupling of **6** with tetrabenzylated D-glucose trichloroacetimidate **1** provided **12** in 75% yield with $\alpha:\beta = 1:11$ (Table 2, entry 1). It has been reported that coupling of 1-naphthol nucleophile (**8**) with dimethylphosphinothioate donor using $AgClO_4$ (1 equiv) as the activating reagent provided **14** in 65% yield as a 3:1 mixture of α- and *β*-isomers.[14b] On the other hand, our method provided **14** in 87% yield with 7:1 *β*-selectivity (entry 3).

Our next step was to determine whether the electron-withdrawing protecting groups on the D-glucose donor would affect the *β*-selectivity. Accordingly, D-glucose donor **11** with the benzoyl group incorporated at the C(4)- and C(6)-positions was examined with phenol nucleophiles **4** and **6** (Table 2, entries 6 and 7). The desired *O*-aryl glucosides **17** and **18** were obtained in good yields and diasteroselectivity. These results suggest that the nature of the protecting group on the D-glucose donors has little effect on the outcome of the stereoselectivity at the newly formed glycosidic bond.

TABLE 3. Coupling of Phenol Nucleophiles with Galactose Donor[a]



Entry	Phenols	*O*-Aryl-Glycoside	Yield[b]	β:α[c]
1	 **6**	 **19**	73%	β only
2	 **7**	 **20**	80%	6:1
3	 **4**	 **21**	86%	20:1
4	 **8**	 **22**	83%	8:1
4	 **9**	 **23**	89%	8:1
6	 **6**	 **24**	87%	7:1
7	 **4**	 **25**	78%	β only

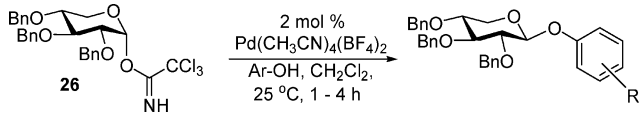
[a] All reactions were carried out in CH_2Cl_2 with 2 mol % of $Pd(CH_3CN)_4(BF_4)_2$ at 25 °C. [b] Isolated yield. [c] ^1H NMR ratio.

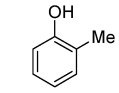
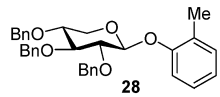
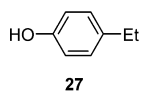
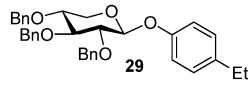
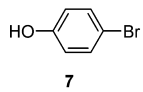
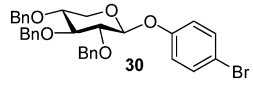
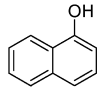
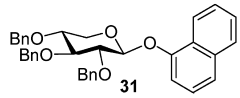
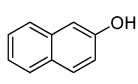
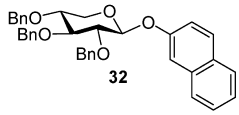
Similarly, tetrabenzyl D-galactose trichloroacetimidate substrate was found to be a viable donor (Table 3). It was able to couple to a variety of phenol nucleophiles to provide the desired *O*-aryl galactosides **19**−**23** in good yields and *β*-selectivity (entries 1−5). Notably, the efficiency of this palladium methodology is demonstrated by its ability to direct the relatively hindered 2-methylphenol (**6**) to the top face of tetrabenzyl-D-galactose trichloroacetimidate donor to exclusively form *β*-*O*-aryl galactoside **19** in 73% yield (entry 1). The current method was further explored with D-galactose donor incorporated with the benzoyl group at the C(4)- and C(6)-positions, even though participation of the axial C(4)-ester group to an activated

(13) These compounds were relatively stable on silica gel flash chromatography. Since we were not able to separate the major *β*-isomer from the minor *α*-isomer for spectral analysis, the products were subjected to preparative TLC. We found, however, that these *O*-aryl glycosides slowly decomposed on preparative TLC, particularly with compounds **5**, **14**, and **15**. As a result, it is difficult to get clean ^1H and ^{13}C NMR spectra for these molecules.

(14) (a) Koto, S.; Morishima, N.; Araki, M.; Tsuchiya, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1895–1896. (b) Yamanoi, T.; Fujioka, A.; Inazu, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1488–1491.

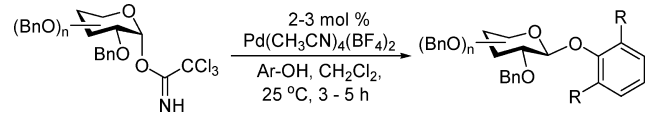
TABLE 4. Coupling of Phenol Nucleophiles with Xylose Donor[a]

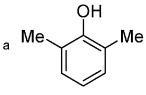
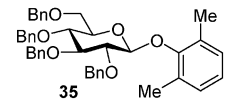
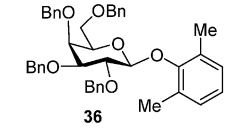
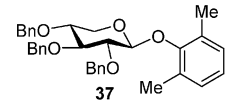
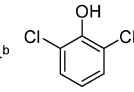
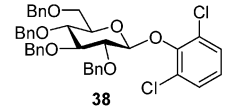
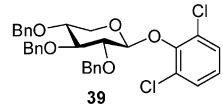


Entry	Phenols	O-Aryl-Glycoside	Yield[b]	β:α[c]
1	 6	 28	77%	β only
2	 27	 29	81%	β only
3	 7	 30	84%	β only
4	 8	 31	74%	β only
5	 4	 32	79%	30:1

[a] All reactions were carried out in CH_2Cl_2 with 2 mol % of $Pd(CH_3CN)_4(BF_4)_2$ at 25 °C. [b] Isolated yield. [c] ^{1}HNMR ratio.

TABLE 5. Selective Glycosylation of Hindered Phenol Nucleophiles[a]



Entry	Phenols	O-Aryl-Glycoside	Yield[c]	β:α[d]
1[a]	 33	 35	75%	10:1
2[a]	33	 36	75%	10:1
3[a]	33	 37	72%	β only
4[b]	 34	 38	66%	8:1
5[b]	34	 39	74%	β only

[a] The glycosylations were performed with 2 mol % of $Pd(CH_3CN)_4(BF_4)_2$. [b] The reactions were performed with 3 mol % of $Pd(CH_3CN)_4(BF_4)_2$. [c] Isolated yield. [d] ^{1}H NMR ratio.

anomeric center has previously been invoked.[15] When 2-methylphenol (**6**) was employed as the nucleophilic acceptor (entry 6), *O*-aryl galactoside **24** was isolated in 87% yield and good β-selectivity (β:α = 7:1). Use of 2-naphthol gave exclusively β-isomer **25** in 78% yield (entry 7).

Encouraged by the results obtained with both D-glucose and D-galactose donors, we decided to expand the scope of this reaction with tribenzyl D-xylose trichloroacetimidate **26** (Table 4). Since this xylose donor lacks the C(6)-methoxyl functionality, its β-face is likely to be less sterically hindered than that of D-glucose and D-galactose donors. Thus, the coupling products are expected to form with higher β-selectivity than those obtained from D-glucose and D-galactose donors. Accordingly, D-xylose donor **26** was coupled to an array of electron-rich and electron-poor phenolic compounds to provide the corresponding *O*-aryl glycosides **28**−**32** in good yields and almost exclusively as β-isomers (Table 4).

The cationic palladium-catalyzed glycosylation protocol is not limited to unhindered electron-donating and electron-withdrawing phenol nucleophiles. Table 5 sets out several examples of selective formation of β-*O*-aryl glycosides using sterically hindered phenols **33** and **34**. These phenol acceptors have been chosen for ease of comparison of this method with the existing glycosylation procedures in terms of yields and anomeric selectivity.[16] In these reactions, 2−3 mol % of $Pd(CH_3CN)_4(BF_4)_2$ is required for the reaction to go to completion. Accordingly, coupling of 2,6-dimethylphenol (**33**) with tetrabenzyl D-glucose trichloroacetimidate donor **1** provided the desired *O*-aryl glucoside **35** in 75% yield with β:α = 10:1 (Table 5, entry 1). It has been reported that coupling of 2,6-dimethylphenol (**33**) with tetrabenzyl D-glucose thioglycoside donor afforded the coupling product **35** in excellent yield (93%), albeit in low selectivity (α:β = 2.6:1).[15b] With the sulfoxide method, the *O*-aryl glucoside **35** was obtained in 70% yield as a 2:1 mixture of α- and β-isomers.[15a] Similar result was obtained with use of tetrabenzylated D-galactose trichloroacetimidate donor (entry 2). Interestingly, coupling of tribenzyl D-xylose donor **26** with 2,6-dimethylphenol (**33**) only yielded the β-isomer **37** (entry 3). Encouraged by these results, we explored the generality and applicability of this cationic palladium method with 2,6-dichlorophenol (**34**). Gratifyingly, it was found that this phenol acceptor was able to couple with D-glucose donor **1** and D-xylose donor **26** to provide the corresponding *O*-aryl glycosides **38** and **39** in moderate to good yield with good β-selectivity (entries 4 and 5).

Conclusion

In summary, we have developed an efficient method for the stereoselective synthesis of β-*O*-aryl glycosides in the absence of the traditional ester directing group at the C(2)-position of D-glucose, D-galactose, and D-xylose donors. Advantages of the cationic palladium method include its operational simplicity, using a catalytic amount of commercially available cationic palladium, $Pd(CH_3CN)_4(BF_4)_2$, as the activating reagent at ambient temperature, the applicability to a broader scope of phenol nucleophiles, and the high β-selectivity without the need of using the anchimeric assistance. In all cases, the facile

(15) Zinner, H.; Thielebeule, W. *Chem. Ber.* **1960**, *93*, 2791–2803.

(16) (a) Kahne, D.; Walker, S.; Cheng, Y.; Van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 6881–6882. (b) Crich, D.; Sun, S. *J. Am. Chem. Soc.* **1998**, *120*, 435–436.

rearrangement of the resulting *β-O*-aryl glycosides to the corresponding *C*-aryl glycosides is not observed in the coupling, a drawback of other methodologies when the reactions were performed at high temperature. The current method is likely to operate through a seven-membered ring intermediate, wherein $Pd(CH_3CN)_4(BF_4)_2$ coordinates to both the C(1)-trichloroacetimidate nitrogen and the C(2)-oxygen of glycosyl donors. Formation of this seven-membered ring intermediate blocks the bottom of the activated glycosyl donor. As a result, the phenol nucleophiles preferentially approach to the top face, leading to formation of the *β-O*-aryl glycosides.

Experimental Section

General Glycosylation Procedure with $Pd(CH_3CN)_4(BF_4)_2$: Preparation of Compound 5. A 10 mL Schlenk flask was charged with 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl trichloroacetimidate **1** (158 mg, 0.23 mmol, 1 equiv), 2-naphthol (**4**) (35 mg, 0.24 mmol, 1.04 equiv), and CH_2Cl_2 (1.1 mL). $Pd(CH_3CN)_4(BF_4)_2$ (2 mg, 0.0046 mmol, 2 mol %) was then added to the solution. The resulting mixture was stirred under argon at 25 °C for 2 h, diluted with benzene (2 mL), and purified by silica gel flash chromatography (6/1, hexane/ethyl acetate) to give the desired *O*-aryl glycoside **5** (123 mg, 80%). $R_f = 0.40$ (hexanes/ethyl acetate, 4/1). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.79−7.77 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.43−7.19 (m, 24H), 5.15 (d, J = 7.5 Hz, 1H), 5.09 (d, J = 11 Hz, 1H), 4.96 (d, J = 11 Hz, 1H), 4.87 (d, J = 11 Hz, 1H), 4.86 (d, J = 12 Hz, 1H), 4.83 (d, J = 11.5 Hz, 1H), 4.60 (d, J = 12 Hz, 1H), 4.58 (d, J = 11 Hz, 1H), 4.53 (d, J = 12 Hz, 1H), 3.84−3.76 (m, 3H), 3.72−3.70 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.2, 138.5, 138.1, 138.0, 134.4, 129.9, 129.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.78, 127.7, 127.6, 127.3, 126.4, 124.3, 119.1, 111.5, 101.8, 84.8, 82.1, 77.8, 75.8, 75.3, 75.1, 73.6, 69.0. IR (film, cm^{-1}): ν = 2919, 2862, 1465, 1453, 1359, 1310, 1252, 1214, 1070, 1027, 734, 697, 659. HRMS (ESI): calcd for $C_{44}H_{42}O_6Na$ (M + Na) 689.2879, found 689.2860.

Compound 12. $R_f = 0.44$ (hexanes/ethyl acetate, 4/1). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32−7.25 (m, 18H), 7.19−7.11 (m, 4H), 7.05 (d, J = 8 Hz, 1H), 6.95 (t, J = 7 Hz, 1H), 5.07 (d, J = 11 Hz, 2H), 5.02 (d, J = 7 Hz, 1H), 4.94 (d, J = 11 Hz, 1H), 4.86−4.82 (m, 3H), 4.58 (d, J = 12 Hz, 1H), 4.57 (d, J = 11 Hz, 1H), 4.52 (d, J = 12 Hz, 1H), 3.81−3.74 (m, 3H), 3.72−3.67 (m, 2H), 3.61 (dd, J = 9.5, 4.5 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 138.3, 130.9, 128.4, 128.3, 128.0, 127.8, 127.7, 127.0, 122.3, 114.9, 101.3, 84.9, 82.2, 77.8, 77.2, 75.8, 75.2, 73.5, 68.9, 16.7. IR (film, cm^{-1}): ν 2916, 2862, 1493, 1454, 1359, 1237, 1069, 1027, 750, 735, 696. HRMS (ESI): calcd for $C_{41}H_{42}O_6Na$ (M + Na) 653.2879, found 653.2862.

Compound 13. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.35 (d, J = 8.5 Hz, 2H), 7.33−7.25 (m, 18H), 7.16 (d, J = 5.5 Hz, 1H), 6.92 (d, J = 8.5 Hz, 1H), 4.97 (d, J = 10.8 Hz, 1H), 4.95−4.90 (m, 2H), 4.83−4.78 (m, 3H), 4.55 (t, J = 12.4 Hz, 2H), 4.49 (d, J = 12 Hz, 1H), 3.77−3.70 (m, 3H), 3.66−3.63 (m, 2H), 3.61−3.58 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.4, 128.43, 128.4, 128.36, 128.2, 128.0, 127.9, 127.8, 127.71, 127.7, 118.7, 101.6, 84.6, 81.9, 77.6, 75.8, 75.14, 75.11, 75.1, 73.5, 68.7. IR (film, cm^{-1}): ν 3030, 2913, 2867, 2454, 1453, 1233, 1064, 1002, 824, 747. HRMS (ESI): calcd for $C_{40}H_{39}Br\,O_6Na$ (M + Na) 717.1828, found 717.1840.

Compound 14. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.28 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.2 Hz, 1H), 7.46 (t, J = 8.2 Hz, 1H), 7.41 (t, J = 6.9 Hz, 1H), 7.36−7.23 (m, 19H), 7.19 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 5.21 (d, J = 7.7 Hz, 1H), 5.16 (d, J = 10.6 Hz, 1H), 4.96 (d, J = 10.8 Hz, 1H), 4.92 (d, J = 10.7 Hz, 1H), 4.85 (dd, J = 10.7, 3.6 Hz, 2H), 4.58 (d, J = 10.8 Hz, 2H), 4.56 (d, J = 12 Hz, 1H), 4.50 (d, J = 12.1 Hz, 1H), 3.94 (t, J = 8.6 Hz, 1H), 3.80 (dd, J = 17.6, 8.7 Hz, 2H), 3.74−3.66 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 153.0, 138.6, 138.1, 138.0, 134.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 126.4, 125.9, 125.6, 122.4, 122.1, 109.6, 101.5, 84.9, 82.3, 77.8, 75.9, 75.2, 75.1, 73.6, 73.1, 68.8. IR (film, cm^{-1}): ν 3062, 3030, 2905, 2865, 1596, 1578, 1462, 1454, 1395, 1361, 1263, 1239, 1085, 1071, 1027, 772, 735, 697. HRMS (ESI): calcd for $C_{44}H_{42}O_6Na$ (M + Na) 689.2879, found 689.2861.

Compound 15. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.29 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 8 Hz, 1H), 7.35−7.17 (m, 20H), 7.05 (d, J = 8.8 Hz, 1H), 5.16 (d, J = 7.7 Hz, 1H), 5.11 (d, J = 10.6 Hz, 1H), 4.96 (d, J = 10.8 Hz, 1H), 4.92 (d, J = 10.6 Hz, 1H), 4.85 (d, J = 10.9 Hz, 2H), 4.62 (t, J = 12.1 Hz, 2H), 4.49 (d, J = 11.8 Hz, 1H), 3.93 (t, J = 8.4 Hz, 1H), 3.79−3.68 (m, 3H), 3.67−3.63 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.9, 131.4, 128.4, 128.0, 127.9, 127.84, 127.8, 127.72, 127.7, 127.6, 127.5, 127.4, 126.3, 125.8, 124.3, 122.5, 109.7, 101.5, 84.8, 82.1, 77.7, 75.8, 75.4, 75.2, 75.1, 73.5, 66.2. IR (film, cm^{-1}): ν 2912, 2870, 1592, 1455, 1376, 1260, 1239, 1072, 751, 696. HRMS (ESI): calcd for $C_{44}H_{41}ClO_6Na$ (M + Na) 723.2489, found 723.2489.

Compound 16. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.72 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.32−7.14 (m, 20H), 7.03 (d, J = 8.5 Hz, 1H), 6.96 (d, J = 8.5 Hz, 1H), 6.57 (d, J = 7.5 Hz, 1H), 5.02 (d, J = 12 Hz, 1H), 4.95 (d, J = 7.2 Hz, 1H), 4.92 (d, J = 10.9 Hz, 1H), 4.85−4.77 (m, 3H), 4.56 (d, J = 17 Hz, 1H), 4.51 (d, J = 9.4 Hz, 1H), 4.47 (d, J = 10.9 Hz, 1H), 4.19−4.14 (m, 2H), 3.80−3.66 (m, 4H), 3.58−3.56 (m, 1H), 3.25−3.18 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.7, 166.8, 156.5, 138.4, 138.1, 138.0, 137.9, 133.8, 131.8, 130.5, 129.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.0, 116.9, 101.6, 84.6, 81.9, 77.6, 75.8, 75.1, 73.4, 68.7, 61.7, 53.6, 37.1, 14.2. IR (film, cm^{-1}): ν 3347, 3063, 3029, 2911, 2867, 1730, 1649, 1509, 1453, 1353, 1231, 1070, 1027, 824, 737, 697. HRMS (ESI): calcd for $C_{52}H_{53}NO_9Na$ (M + Na) 858.3618, found 858.3605.

Compound 17. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.00−7.92 (m, 4H), 7.58−7.51 (m, 2H), 7.31−7.27 (m, 12H), 7.13−7.07 (m, 6H), 5.50 (t, J = 10 Hz, 1H), 5.32 (d, J = 10 Hz, 1H), 4.84 (d, J = 10 Hz, 1H), 4.75 (d, J = 10 Hz, 1H), 4.71 (d, J = 10 Hz, 1H), 4.61 (d, J = 10 Hz, 1H), 4.57 (dd, J = 15, 5 Hz, 1H), 4.36 (dd, J = 10, 5 Hz, 1H), 4.02 (dt, J = 10, 5 Hz, 1H), 3.82 (t, J = 10 Hz, 1H), 3.76−3.71 (m, 1H), 2.19 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.2, 165.1, 137.4, 137.3, 133.4, 133.1, 129.9, 129.8, 129.7, 129.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 110.3, 108.5, 81.2, 81.1, 74.9, 74.5, 72.1, 69.8, 63.0, 16.7. IR (film, cm^{-1}): ν 3708, 3582, 2920, 1724, 1452, 1270, 1106, 1067, 1026, 911, 751, 708. HRMS (ESI): calcd for $C_{41}H_{42}NO_8$ (M + NH_4) 676.2095, found 676.2907.

Compound 18. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.98 (d, J = 10 Hz, 4H), 7.79−7.71 (m, 3H), 7.56 (t, J = 10 Hz, 11H), 7.54 (t, J = 10 Hz, 1H), 7.49−7.26 (m, 12H), 7.20−7.07 (m, 6H), 5.47 (t, J = 10 Hz, 1H), 5.27 (d, J = 10.0 Hz, 1H), 5.12 (d, J = 15 Hz, 1H), 4.91 (d, J = 10 Hz, 1H), 4.84 (d, J = 10 Hz, 1H), 4.68 (d, J = 10 Hz, 1H), 4.64 (dd, J = 15, 5 Hz, 1H), 4.41 (dd, J = 15, 10 Hz, 1H), 4.02 (dt, J = 10.0, 5.0 Hz, 1H), 3.99−3.93 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.2, 165.4, 134.1, 130.5, 130.3, 130.2, 129.1, 128.7, 127.8, 127.7, 123.8, 119.4, 118.2, 111.7, 110.4, 102.3, 81.8, 81.2, 76.4, 75.3, 71.8, 71.7, 70.3. IR (film, cm^{-1}): ν 3429, 3062, 3031, 2953, 2905, 2875, 1752, 1630, 1600, 1510, 1452, 1269, 1215, 1094, 1067, 1026, 909, 735, 711. HRMS (ESI): calcd for $C_{44}H_{38}O_8Na$ (M + Na) 717.2459, found 717.2428.

Compound 19. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39−7.27 (m, 20H), 7.14 (d, J = 7 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 7 Hz, 1H), 5.04 (d, J = 11 Hz, 1H), 5.01 (d, J = 5.5 Hz, 1H), 4.99 (d, J = 9 Hz, 1H), 4.90 (d, J = 10.5 Hz, 1H), 4.79 (d, J = 11.5 Hz, 1H), 4.76 (d, J = 11.5 Hz, 1H), 4.67 (d, J = 11.5 Hz, 1H), 4.47 (d, J = 12 Hz, 1H), 4.41 (d, J = 11.5 Hz, 1H), 4.17 (dd, J = 9.5, 8 Hz, 1H), 3.97 (d, J = 3 Hz, 1H), 3.71 (t, J = 6.5 Hz, 1H), 3.67−3.62 (m, 3H), 3.72−3.67 (m,

2H), 3.61 (dd, $J = 9.5$, 4.5 Hz, 1H), 3.59 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.5, 138.5, 138.4, 130.7, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.3, 126.7, 121.9, 114.5, 101.3, 82.3, 79.2, 75.5, 74.5, 73.8, 73.6, 73.4, 73.1, 68.9, 16.6. IR (film, cm^{-1}): ν 2920, 2856, 1494, 1454, 1238, 1102, 1069, 752, 696. HRMS (ESI): calcd for $C_{41}H_{42}O_6Na$ (M + Na) 653.2879, found 653.2853.

Compound 20. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39−7.15 (m, 22H), 6.92 (d, $J = 9$ Hz, 2H), 4.96 (t, $J = 11.5$ Hz, 2H), 4.91 (d, $J = 7.5$ Hz, 1H), 4.84 (d, $J = 10.5$ Hz, 1H), 4.77 (d, $J = 11.5$ Hz, 1H), 4.74 (d, $J = 12$ Hz, 1H), 4.64 (d, $J = 11.5$ Hz, 1H), 4.46 (d, $J = 11.5$ Hz, 1H), 4.39 (d, $J = 11.5$ Hz, 1H), 4.09 (dd, $J = 10$, 8 Hz, 1H), 3.93 (d, $J = 2.5$ Hz, 1H), 3.64 (dd, $J = 12.5$, 6 Hz, 1H), 3.62−3.55 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 156.5, 138.4, 138.3, 138.2, 137.8, 132.3, 128.5, 128.4, 128.3, 128.2, 127.9, 127.71, 127.7, 127.6, 118.7, 114.8, 101.8, 82.1, 79.1, 75.5, 74.5, 73.9, 73.6, 73.2, 73.1, 68.9. IR (film, cm^{-1}): ν 3029, 2916, 2867, 1486, 1454, 1236, 1158, 1100, 1062, 1027, 1006, 823, 734, 697. HRMS (ESI): calcd for $C_{40}H_{39}Br\ O_6Na$ (M + Na) 717.1828, found 717.1804.

Compound 21. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.74 (dd, J = 13.5, 8 Hz, 2H), 7.62 (d, $J = 8.5$ Hz, 1H), 7.40−7.23 (m, 24H), 5.11 (d, $J = 7.5$ Hz, 1H), 5.02 (d, $J = 10.5$ Hz, 1H), 4.98 (d, J = 11.5 Hz, 1H), 4.87 (d, $J = 10.5$ Hz, 1H), 4.78 (d, $J = 12$ Hz, 1H), 4.74 (d, $J = 12$ Hz, 1H), 4.65 (d, $J = 11.5$ Hz, 1H), 4.45 (d, J = 11.5 Hz, 1H), 4.39 (d, $J = 11.5$ Hz, 1H), 4.16 (dd, $J = 10$, 8 Hz, 1H), 3.95 (d, $J = 2.5$ Hz, 1H), 3.74 (t, $J = 6$ Hz, 1H), 3.68−3.61 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 129.3, 128.4, 128.3, 128.2, 127.8, 127.6, 124.2, 118.5, 101.8, 82.0, 79.2, 75.5, 74.5, 74.0, 73.7, 73.3, 73.1, 69.1. IR (film, cm^{-1}): ν 3061, 3029, 2920, 2862, 1509, 1496, 1454, 1362, 1253, 1214, 1101, 1065, 1027, 736, 696. HRMS (ESI): calcd for $C_{44}H_{42}O_6Na$ (M + Na) 689.2879, found 689.2852.

Compound 22. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.31 (d, J = 8.5 Hz, 1H), 7.79 (d, $J = 8$ Hz, 1H), 7.51−7.23 (m, 24H), 7.18 (d, $J = 8.5$ Hz, 1H), 5.19 (d, $J = 7.5$ Hz, 1H), 5.12 (d, $J = 10.5$ Hz, 1H), 5.01 (d, $J = 11.5$ Hz, 1H), 4.96 (d, $J = 10.5$ Hz, 1H), 4.80 (d, $J = 12$ Hz, 1H), 4.77 (d, $J = 11.5$ Hz, 1H), 4.68 (d, $J = 11.5$ Hz, 1H), 4.45 (d, $J = 11.5$ Hz, 1H), 4.39 (d, $J = 11.5$ Hz, 1H), 4.31 (dd, $J = 10$, 8 Hz, 1H), 3.99 (d, $J = 2.5$ Hz, 1H), 3.74 (t, J = 6.5 Hz, 1H), 3.70−3.61 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 153.0, 138.5, 138.3, 137.8, 134.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 125.9, 125.7, 125.4, 122.3, 122.1, 109.2, 101.7, 82.4, 79.3, 75.7, 74.6, 74.0, 73.6, 73.3, 73.1, 68.9. IR (film, cm^{-1}): ν 3062, 3029, 2916, 2866, 1578, 1496, 1454, 1388, 1363, 1264, 1095, 1068, 1027, 736, 697. HRMS (ESI): calcd for $C_{44}H_{42}O_6Na$ (M + Na) 689.2879, found 689.2851.

Compound 23. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.29 (d, J = 8.5 Hz, 1H), 8.18(d, $J = 8.5$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 8$ Hz, 1H), 7.37−7.20 (m, 21H), 7.01 (d, $J = 8.5$ Hz, 1H), 5.12 (d, $J = 7.5$ Hz, 2H), 5.06 (d, $J = 10.5$ Hz, 1H), 4.99 (d, $J = 11.5$ Hz, 1H), 4.94 (d, $J = 10.5$ Hz, 1H), 4.76 (t, $J = 12$ Hz, 1H), 4.66 (d, $J = 11.5$ Hz, 1H), 4.42 (d, $J = 11.5$ Hz, 1H), 4.38 (d, $J = 11.5$ Hz, 1H), 4.28 (dd, $J = 9.5$, 8 Hz, 1H), 3.96 (d, J = 2.5 Hz, 1H), 3.71 (t, $J = 6$ Hz, 1H), 3.66 (dd, $J = 10$, 3 Hz, 1H), 3.54−3.59 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 152.1, 138.4, 138.2, 138.1, 137.8, 131.1, 128.5, 128.3, 128.0, 127.8, 127.6, 126.1, 125.7, 124.2, 122.6, 109.5, 101.7, 82.4, 79.1, 75.8, 74.6, 74.1, 73.7, 73.2, 73.1, 68.9. IR (film, cm^{-1}): ν 3063, 3029, 2923, 2854, 2373, 2348, 2314, 1455, 1375, 1259, 1157, 1076, 1027, 734, 696. HRMS (ESI): calc. for $C_{44}H_{41}ClO_6Na$ (M + Na) 723.2489, found 723.2468.

Compound 24. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 81.6−7.98 (m, 4H), 7.62−7.55 (m, 2H), 7.50−7.42 (m, 4H), 7.30−7.21 (m, 10H), 7.15−6.91 (m, 4H), 5.89 (d, $J = 5$ Hz, 1H), 5.06 (d, $J = 15$ Hz, 1H), 4.99 (d, $J = 15$ Hz, 1H), 4.85 (d, $J = 20$ Hz, 2H), 4.60 (d, $J = 15$ Hz, 1H), 4.51 (d, $J = 15$ Hz, 2H), 4.15 (t, $J = 15$ Hz, 1H), 4.04 (dd, $J = 15$, 10 Hz, 1H), 3.81 (dd, $J = 15$, 5 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.2, 165.8, 155.4, 133.5, 133.3, 131.0, 130.1, 129.8, 128.3, 128.1, 127.7, 126.9, 114.8, 101.5, 79.4, 78.6, 75.7, 72.3, 71.4, 67.4, 62.9, 16.6. IR (film, cm^{-1}): ν 3063, 3031, 2953, 2915, 2871, 1724, 1601, 1493, 1452, 1314, 1271, 1108, 1069, 1026, 910, 735, 711. HRMS (ESI): calcd for $C_{41}H_{38}O_8Na$ (M + Na) 681.2459, found 681.2479.

Compound 25. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.15 (d, J = 10 Hz, 2H), 8.04 (d, $J = 10$ Hz, 2H), 7.77−7.71 (m, 2H), 7.62−7.55 (m, 2H), 7.50−7.23 (m, 19H), 5.90 (d, $J = 5$ Hz, 1H), 5.21 (d, J = 10 Hz, 1H), 5.02 (d, $J = 15$ Hz, 1H), 4.86 (d, $J = 15$ Hz, 2H), 4.62 (d, $J = 15$ Hz, 1H), 4.55−4.49 (m, 2H), 4.24 (t, $J = 15$ Hz, 1H), 4.09 (t, $J = 15$, 1H), 3.82 (dd, $J = 15$, 5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.2, 165.8, 155.4, 137.7, 134.2, 133.3, 133.2, 130.1, 129.8, 129.5, 129.4, 127.6, 127.1, 126.4, 124.4, 119.1, 111.2, 101.9, 79.2, 78.6, 75.7, 72.3, 71.7, 67.3, 63.2. IR (film, cm^{-1}): ν 3062, 3031, 2952, 2913, 2871, 1723, 1719, 1630, 1600, 1452, 1270, 1267, 1215, 1105, 1069, 1026, 910, 732, 711. HRMS (ESI): calcd for $C_{44}H_{38}O_8Na$ (M + Na) 717.2459, found 717.2492.

Compound 28. ^{1}HNMR ($CDCl_3$, 500 MHz): δ = 7.50−7.29 (m, 14H), 7.19−7.16 (m, 2H), 7.06−6.93 (m, 2H), 5.04 (d, $J = 5$ Hz, 1H), 5.02 (d, $J = 15$ Hz, 1H), 4.91 (bs, 2H), 4.84 (d, $J = 10$ Hz, 1H), 4.76 (d, $J = 10$ Hz, 1H), 4.65 (d, $J = 15$ Hz, 1H), 3.99 (dd, $J = 10$, 5 Hz, 1H), 3.73 - 3.71 (m, 3H), 3.34 (t, $J = 10$ Hz, 1H), 2.29 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.2, 138.6, 138.2, 138.1, 131.0, 127.7, 127.1, 126.3, 122.4, 114.4, 104.8, 86.8, 83.7, 77.2, 75.8, 74.2, 73.4, 63.7, 15.7. IR (film, cm^{-1}): ν = 3063, 3030, 2906, 2866, 1590, 1493, 1454, 1357, 1236, 1085, 1027, 997, 909, 751, 698. HRMS (ESI): calcd for $C_{33}H_{34}O_5Na$ (M + Na) 533.2304, found 533.2322.

Compound 29. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39−7.29 (m, 15H), 7.16 (d, $J = 10$ Hz, 1H), 7.01 (d, $J = 10$ Hz, 1H), 5.03 (d, $J = 10$ Hz, 1H), 5.01 (d, $J = 10$ Hz, 1H), 4.93 (d, $J = 15$ Hz, 1H), 4.91 (d, $J = 15$ Hz, 1H), 4.84 (d, $J = 10$ Hz, 1H), 4.78 (d, J = 10, 5 Hz, 1H), 4.67 (d, $J = 10$ Hz, 1H), 4.01 (dd, $J = 10$, 5 Hz, 1H), 3.75−3.63 (m, 3H), 3.35 (dd, $J = 10.5$, 10 Hz, 1H), 2.64 (q, $J = 10$ Hz, 2H), 1.24 (t, $J = 10$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ= 155.2, 138.7, 138.6, 138.3, 138.1, 128.7, 128.4, 128.0, 127.9, 127.7, 116.9, 102.5, 83.6, 81.6, 7.7, 75.7, 75.1, 73.4, 28.1, 15.8. IR (film, cm^{-1}): ν = 3030, 2963, 2927, 2869, 1509, 1454, 1231, 1074, 1027, 997, 829, 735, 697. HRMS (ESI): calcd for $C_{34}H_{36}O_5Na$ (M + Na) 547.2460, found 547.2477.

Compound 30. ^{1}HNMR ($CDCl_3$, 500 MHz): δ = 7.49−7.28 (m, 17H), 6.91 (d, $J = 10$ Hz, 1H), 4.95 (d, $J = 10$ Hz, 2H), 4.90 (bs, 2H), 4.82 (d, $J = 10$ Hz, 1H), 4.76 (d, $J = 10$ Hz, 1H), 4.65 (d, $J = 10$ Hz, 1H), 3.99 (dd, $J = 10$, 5 Hz, 1H), 3.68−3.58 (m, 3H), 3.34 (t, $J = 10$ Hz, 1H), 2.64 (q, $J = 10$ Hz, 2H), 1.24 (t, J = 10 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 158.5, 138.1, 138.0, 137.8, 128.5, 128.1, 127.8, 126.8, 125.8, 118.5, 102.3, 83.5, 81.4, 77.3, 75.7, 75.0, 73.4, 63.6. IR (film, cm^{-1}): ν = 3088, 3063, 2903, 2867, 1590, 1486, 1454, 1357, 1235, 1085, 1027, 1006, 909, 823, 735, 698. HRMS (ESI): calcd for $C_{32}H_{31}BrO_5Na$ (M + Na) 597.1253, found 597.1275.

Compound 31. ^{1}HNMR ($CDCl_3$, 500 MHz): δ = 8.32 (d, J = 10 Hz, 1H), 7.86 (d, $J = 10$ Hz, 1H), 7.59 (d, $J = 10$ Hz, 1H), 7.43−7.28 (m, 19H), 7.13 (d, $J = 10$ Hz, 1H), 5.29 (d, $J = 5$ Hz, 1H), 5.14 (d, $J = 10$ Hz, 1H), 4.96 (d, $J = 15$ Hz, 3H), 4.81 (d, J = 10 Hz, 1H), 4.71 (d, $J = 15$ Hz, 1H), 4.08 (dd, $J = 10$, 5 Hz, 1H), 3.93 (t, $J = 5$ Hz, 1H), 3.81−3.75 (m, 2H), 3.47−3.42 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 152.7, 138.6, 138.1, 134.6, 128.4, 127.8, 126.4, 125.7, 122.5, 122.4, 109.4, 101.8, 83.6, 81.5, 77.3, 76.8, 75.4, 73.4, 63.9. IR (film, cm^{-1}): ν = 3030, 2868, 1578, 1496, 1454, 1396, 1264, 1238, 937, 791, 771, 737, 697. HRMS (ESI): calcd for $C_{36}H_{34}O_5Na$ (M + Na) 569.2304, found 569.2304.

Compound 32. ^{1}HNMR ($CDCl_3$, 500 MHz): δ = 7.83 (dd, J = 10, 5 Hz, 2H), 7.80 (d, $J = 10$ Hz, 1H), 7.52−7.29 (m, 19H), 5.21 (d, $J = 5$ Hz, 1H), 5.09 (d, $J = 10$ Hz, 1H), 4.99 (d, $J = 10$ Hz, 1H), 4.97 (d, $J = 10$ Hz, 1H), 4.91 (d, $J = 10$ Hz, 1H), 4.82 (d, J = 10 Hz, 1H), 4.71 (d, $J = 10$ Hz, 1H), 4.10 (dd, $J = 10$, 5 Hz, 1H), 3.79−3.73 (m, 3H), 3.49−3.45 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 154.9, 138.6, 138.3, 138.1, 134.3, 128.6, 127.9,

127.8, 127.7, 126.5, 124.5, 119.0, 111.38, 102.3, 83.6, 81.6, 77.7, 76.8, 75.7, 75.2, 73.4, 64.1. IR (film, cm^{-1}): ν = 3061, 3029, 2903, 2868, 1630, 1600, 1510, 1466, 1454, 1251, 1215, 1074, 1027, 998, 908, 843, 811, 747, 697. HRMS (ESI): calcd for $C_{36}H_{34}O_5Na$ (M + Na) 569.2304, found 569.2319.

Compound 35. ^{1}H and ^{13}C NMR of *O*-aryl glycoside **27** have been reported.[13] ^{1}HNMR ($CDCl_3$, 500 MHz): δ = 7.35 (d, J = 6.7 Hz, 2H), 7.29−7.24 (m, 16H), 7.17 (d, J = 6.4 Hz, 2H), 7.01 (d, J = 7.1 Hz, 2H), 6.97−6.94 (m, 1H), 5.12 (d, J = 10.8 Hz, 1H), 4.96 (d, J = 11 Hz, 1H), 4.84−4.80 (m, 3H), 4.76 (d, J = 7.3 Hz, 1H), 4.58 (d, J = 10.7 Hz, 1H), 4.50 (d, J = 12.1 Hz, 1H), 4.44 (d, J = 12.1 Hz, 1H), 3.75−3.68 (m, 3H), 3.66−3.59 (m, 2H), 3.27 (d, J = 6.6 Hz, 1H), 2.36 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 153.2, 138.7, 138.4, 138.2, 132.0, 128.8, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 124.6, 104.2, 84.8, 82.9, 77.8, 75.8, 75.4, 75.0, 73.5, 68.9, 17.2. IR (film, cm^{-1}): ν = 3029, 2915, 2868, 1496, 1470, 1453, 1359, 1158, 1071, 1027, 734, 695.

Compound 36. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38−7.23 (m, 18H), 7.15−7.14 (m, 2H), 6.99−6.92 (m, 3H), 5.19 (d, J = 11 Hz, 1H), 5.00 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11 Hz, 1H), 4.79 (d, J = 12 Hz, 1H), 4.75 (d, J = 10.5 Hz, 1H), 4.74 (d, J = 8 Hz, 1H), 4.64 (d, J = 12 Hz, 1H), 4.35 (d, J = 12 Hz, 1H), 4.32 (d, J = 11.5 Hz, 1H), 4.10 (dd, J = 9.5, 7.5 Hz, 1H), 3.92 (d, J = 2.5 Hz, 1H), 3.63−3.58 (m, 2H), 3.49 (dd, J = 9.5, 5.5 Hz, 1H), 3.42 (t, J = 6.5 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.9, 132.1, 128.7, 128.1, 127.8, 127.7, 127.6, 127.5, 127.49, 127.43, 124.4, 82.5, 80.0, 76.7, 76.5, 76.4, 75.6, 74.5, 73.8, 73.5, 73.4, 73.1, 68.6, 17.2. IR (film, cm^{-1}): ν 3029, 2921, 2864, 1495, 1454, 1361, 1263, 1195, 1097, 1059, 1027, 733, 697, 666. HRMS (ESI): calcd for $C_{42}H_{44}O_6Na$ (M + Na) 667.3035, found 667.3015.

Compound 37. ^{1}HNMR ($CDCl_3$, 500 MHz): δ = 7.39−7.29 (m, 15H), 7.03−6.96 (m, 3H), 5.11 (d, J = 10 Hz, 1H), 4.94 (d, J = 10 Hz, 1H), 4.92 (d, J = 10 Hz, 1H), 4.86 (d, J = 10 Hz, 1H), 4.76 (d, J = 10 Hz, 1H), 4.74 (d, J = 10 Hz, 1H), 4.63 (d, J = 10 Hz, 1H), 3.90 (dd, J = 10, 5 Hz, 1H), 3.71−3.63 (m, 3H), 3.08 (t, J = 10 Hz, 1H), 2.34 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 153.0, 138.7, 138.4, 138.2, 131.8, 128.8, 128.5, 128.4 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 84.1, 82.5, 78.1, 75.7, 75.4, 73.3, 64.1, 17.1. IR (film, cm^{-1}): ν = 3064, 3029, 2912, 2862, 1496, 1454, 1400, 1378, 1357, 1192, 1076, 1028, 994, 771, 736, 697. HRMS (ESI): calcd for $C_{34}H_{36}O_5Na$ (M + Na) 547.2460, found 547.2469.

Compound 38. ^{1}HNMR ($CDCl_3$, 500 MHz): δ = 7.39 (d, J = 6.3 Hz, 2H), 7.34−7.18 (m, 20H), 7.02 (t, J = 8.1 Hz, 2H), 5.24 (d, J = 7.5 Hz, 1H), 5.17 (d, J = 10.8 Hz, 1H), 4.97 (d, J = 10.9 Hz, 1H), 4.82−4.78 (m, 3H), 4.59 (d, J = 10.8 Hz, 1H), 4.55 (d, J = 12.2 Hz, 1H), 4.43 (d, J = 12.2 Hz, 1H), 3.83 (t, J = 8.4 Hz, 1H), 3.75−3.65 (m, 3H), 3.37 (dt, J = 9.3, 3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 138.7, 138.5, 138.1, 128.4, 128.0, 127.7, 127.5, 127.4, 125.7, 103.4, 84.5, 82.6, 77.4, 75.8, 75.1, 73.5, 68.7. IR (film, cm^{-1}): ν= 3029, 2913, 2876, 1566, 1494, 1448, 1079, 775, 735, 694. HRMS (ESI): calcd for $C_{40}H_{38}Cl_2O_6Na$ (M + Na) 707.1943, found 707.1939.

Compound 39. ^{1}HNMR ($CDCl_3$, 500 MHz): δ = 7.39−7.25 (m, 17H), 7.01 (t, J = 8 Hz, 1H), 5.32 (d, J = 7 Hz, 1H), 5.08 (d, J = 11 Hz, 1H), 4.88 (d, J = 11 Hz, 1H), 4.81 (d, J = 11 Hz, 1H), 4.78 (d, J = 11 Hz, 1H), 4.67 (d, J = 12 Hz, 1H), 4.60 (d, J = 12 Hz, 1H), 4.05 (dd, J = 12, 4.5 Hz, 1H), 3.80 (dd, J = 9, 8 Hz, 1H), 3.76−3.68 (m, 2H), 3.29 (dd, J = 12, 8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 129.8, 129.1, 128.4, 128.3, 127.9, 127.8, 127.74, 127.7, 127.6, 125.6, 104.0, 82.8, 81.5, 77.9, 75.2, 74.9, 72.8, 64.1. IR (film, cm^{-1}): ν = 3030, 2905, 2871, 1566, 1496, 1451, 1439, 1241, 1089, 1073, 1050, 776, 741, 696. HRMS (ESI): calcd for $C_{32}H_{30}Cl_2O_5Na$ (M + Na) 587.1368, found 587.1398.

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

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