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Stereoselective Synthesis of Spiro Bis-*C*,*C*-α-arylglycosides by Tandem Heck Type *C*-Glycosylation and Friedel−Crafts Cyclization

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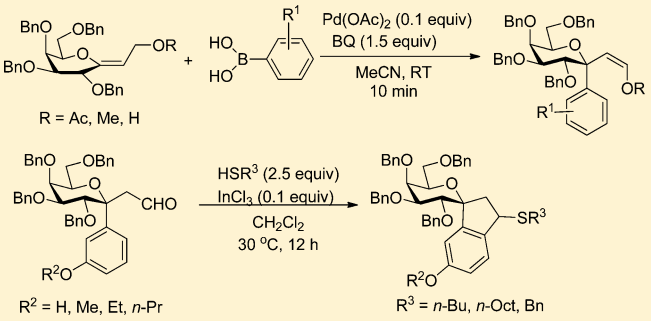
Supporting Information

ABSTRACT: Spiro bis-*C*,*C*-α-arylglycosides were synthesized in three steps in 78−85% overall yields starting from *exo*-glycals. The initial Heck type *C*-aryl addition of *exo*-glycals with arylboronic acids afforded α-aryl-β-substituted *C*-glycosides with exclusive α-stereoselectivity. Among the products, β-ethanal α-aryl *C*-glycosides further reacted with alkylthiol in the presence of $InCl_3$, followed by *in situ* Friedel−Crafts cyclization to yield the desirable final products. We proposed a mechanism to explain how the α-aryl group serves as a main determinant of the cyclization.



Aryl-*C*-glycosides are structurally unique carbohydrates with an aromatic moiety directly linked to the anomeric carbon.[1] These compounds display diverse biological activities,[2] such as inhibition of platelet aggregation, antibacterial, and antitumor activities, explaining the reason why increasing attention has been drawn to the synthesis. Among a number of preparation methods developed,[3,4] most of them are focused on transition-metal-catalyzed cross-coupling reactions to construct the glycosidic C−C bond. Earlier approaches relied on the use of preactivated glycans, including iodinated or stannylated glycals,[5] and aryl organometallic reagents.[6] There are often common problems in association with a restricted choice of substrates and the concomitant high toxicity. In the past decade, the Heck reaction has been employed for the syntheses of aryl-*C*-glycosides by direct coupling of *endo*-glycals with aromatic compounds, such as aryl halides,[7] arylboronic acids,[8] benzoic acids,[4c] and aryl hydrazines.[4e] Because the involved reagents are moisture-stable and environmentally friendly, this method has become one of the most reliable and practical approaches to aryl-*C*-glycosylation. In general, there are two reaction routes. One proceeds via the formation of 2,3-dideoxy-*C*-glycoside that is results from β-heteroatom elimination when the glycal substrate is protected by electron-withdrawing groups (e.g., acetate). In contrast, β-hydride elimination occurs to give 2-deoxy-*C*-glycoside if the glycal is protected by electron-donating groups (e.g., silyl or benzyl ether). However, few of the directed *C*-arylglycosylation methods were provided for the conversion of fully protected *exo*-glycals to α-aryl-*C*-glycosides.[9] Herein we developed an efficient three-step synthesis to prepare spiro bis-*C*,*C*-α-arylglycosides. Heck type *C*-arylation of *exo*-glycals afforded the desired α-aryl-*C*-glycosides that were further subjected to two consecutive reactions, including a thiolate addition and Friedel−Crafts cyclization in the presence of $InCl_3$ (0.1 equiv), to yield desirable products. The skeleton of spiro-aryl-*C*-glycosides prevalently exists in many natural products and other compounds, including several sodium glucose cotransporter 2 inhibitors.[15]

exo-Glycals **1a−d** were prepared from methyl-α-D-glycopyranosides according to previous reports.[10] *exo*-Galactals **1a** and **1b** were first reacted with various arylboronic acids (1.5 equiv) in the presence of $Pd(OAc)_2$ (0.1 equiv) and *p*-benzoquinone (BQ, 1.5 equiv)[13] to afford the desired products (**3−9**) as α-aryl-*C*-glycosides in high yields (80−91%) with exclusive α-stereoselectivity (entries 1−7 in Table 1). Several arylboronic acids were examined, including phenylboronic acid (entry 1), 4-methyl-, 4-ethyl-, 4-*tert*-butyl-, 4-methoxy-, and 4-benzyloxyphenylboronic acids (entries 2−7, respectively). The reactions were carried out in acetonitrile at room temperature for 10 min. Interestingly Heck type aryl-*C*-glycosylation of **1a** and **1b** (the allyl alcohol was protected with acetate or methyl, respectively) led to the formation of β-alkoxyvinyl α-aryl-*C*-galactosides via β-hydride elimination.[11] By contrast, the reactions of **1c** and **1d** (there was no protection for the allyl alcohol) gave α-aryl-β-

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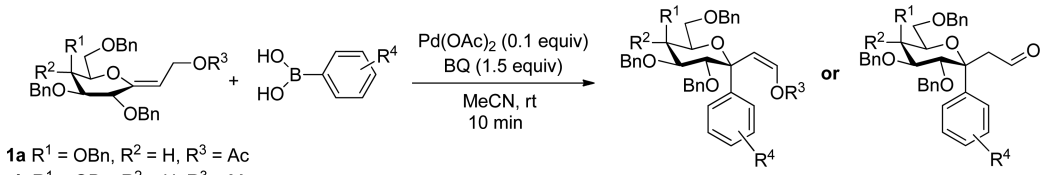
Table 1. Synthesis of α-Aryl-*C*-glycosides 3−27 by Heck Type Reaction of *exo*-Glycals 1a−d[a]



1a R^1 = OBn, R^2 = H, R^3 = Ac
b R^1 = OBn, R^2 = H, R^3 = Me
c R^1 = OBn, R^2 = H, R^3 = H
d R^1 = H, R^2 = OBn, R^3 = H

2 **3-9** **10-27**

entry	substrate	arylboronic acid	R^4	product (yield)[b]
1	**1a**	**2a**	*p*-H	**3** (83%, α only)
2	**1a**	**2b**	*p*-CH_3	**4** (86%, α only)
3	**1a**	**2c**	*p*-Et	**5** (86%, α only)
4	**1a**	**2d**	*p*-*t*-Bu	**6** (80%, α only)
5	**1a**	**2e**	*p*-OCH_3	**7** (91%, α only)
6	**1a**	**2f**	*p*-OBn	**8** (88%, α only)
7	**1b**	**2e**	*p*-OCH_3	**9** (91%, α only)
8	**1c**	**2a**	*p*-H	**10** (92%, α only)
9	**1c**	**2b**	*p*-CH_3	**11** (95%, α only)
10	**1c**	**2d**	*p*-*t*-Bu	**12** (90%, α only)
11	**1c**	**2e**	*p*-OCH_3	**13** (95%, α only)
12	**1c**	**2f**	*p*-OBn	**14** (96%, α only)
13	**1c**	**2g**	*p*-Cl	**15** (83%, α only)
14	**1c**	**2h**	*p*-CO_2CH_3	**16** (88%, α only)
15	**1c**	**2i**	*m*-Ph	**17** (89%, α only)
16	**1c**	**2j**	*m*-Me	**18** (88%, α only)
17	**1c**	**2k**	*m*-OMe	**19** (87%, α only)
18	**1c**	**2l**	*m*-OEt	**20** (88%, α only)
19	**1c**	**2m**	*m*-OPr	**21** (86%, α only)
20	**1c**	**2n**	*m*-OH	**22** (89%, α only)
21	**1c**	**2o**	*o*-OCH_3	**23** (0%, −)
22	**1d**	**2a**	*p*-H	**24** (92%, α only)
23	**1d**	**2e**	*p*-OCH_3	**25** (95%, α only)
24	**1d**	**2k**	*m*-OMe	**26** (93%, α only)
25	**1d**	**2l**	*m*-OPr	**27** (95%, α only)

[a]All reactions were carried out at room temperature with arylboronic acid in the presence of $Pd(OAc)_2$ (0.1 equiv) and BQ (1.5 equiv). [b]The new stereogenic center of products was determined by ^{1}H NMR.

ethanal-*C*-galactosides **10**−**24** under the same conditions in which *p*- (entries 8−14 and 22−23) and *m*-substituted arylboronic acids (15−20 and 24−25) were examined. The desirable products were obtained in 83−96% yields with exclusive α-stereoselectivity. No reaction was found when 2-methoxyphenylboronic acid was used likely due to the steric hindrance (entry 21).

The observed stereoselectivity was consistent with the previous studies on *endo*-glycals;[4a] i.e., σ-aryl-Pd complexes could undergo aryl palladation to give the organopalladium σ-adduct and the organopalladium appeared to attack from the less hindered side. The regioselectivity was realized by the previously proposed interaction, that of the highest occupied molecular orbital of the enol ether π-system with the antibonding (σ*) Pd(II)-aglycon orbital.[14] The resulting σ-bond formation between the electron-deficient palladium(II) center and the enol ether β-carbon was accompanied by the migration of the electron-rich carbon of the aglycon to the enol ether σ-carbon.[14]

The resulting α-aryl-*C*-glycosides were characterized in depth by using several spectrometric methods, including ^{1}H and ^{13}C NMR, DEPT, and IR. For instance, the structure of α-aryl-*C*-galactosides **13** (entry 11) was determined in accordance with several characteristic signals in the ^{1}H NMR spectrum, including the new aldehyde proton (H2′) at δ 9.42 ($J_{2',1'}$ = 3.2 Hz), H1′ at δ 2.69 ($J_{1',2'}$ = 3.2 Hz), and the aromatic OCH_3 (R^4 in Table 1) at δ 3.70. Likewise, there are diagnostic signals in the ^{13}C NMR spectrum, such as C2′-carbonyl at δ 200.9, the anomeric carbon at δ 81.7, C1′ at δ 55.8, and the aromatic OCH_3 at δ 55.1. The corresponding IR absorption spectrum exhibited a major peak at 1716 cm^{-1}, in agreement with the stretching bond of C2′-carbonyl. In the NOESY spectrum, the cross peak between H2 and H1′ in product **13** confirmed the aforementioned stereoselectivity (see Supporting Information for 2D-COSY and -NOESY spectra of compound **13**).

Furthermore, if the aforementioned products have both aldehyde- and aromatic group-containing substituents, they can be substrates for two successive reactions in CH_2Cl_2, namely thiolate addition and Friedel−Crafts cyclization.[12] For example, nucleophilic addition of *n*-octanethiol to α-aryl-β-ethanal-*C*-glycoside **19** occurred in the presence of 0.1 equiv of $ZnCl_2$ in CH_2Cl_2 (entry 1 in Table 2), which was followed by Friedel−Crafts cyclization to give spiro bis-*C*,*C*-α-arylglycosides **29** as a mixture of *R*/*S* diastereomers (ratio of 3/1). To optimize the reaction, we surveyed five other Lewis acids (entries 2−6) and five solvents (entries 7−11). The combination of $InCl_3$ and

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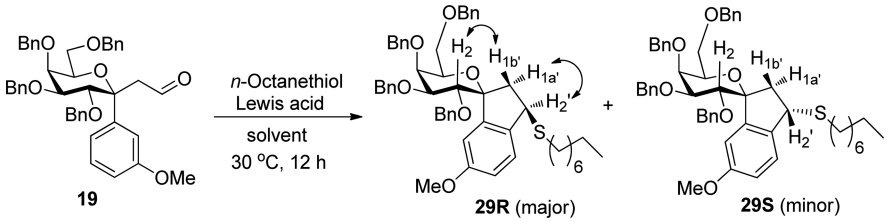
Table 2. Effect of Lewis Acid and Solvent on the Formation of Spiro Bis-*C*,*C*-α-arylglycosides 29[a]



entry	Lewis acid	solvent	yield
1	$ZnCl_2$	CH_2Cl_2	74%[b]
2	$BF_3{\cdot}OEt_2$	CH_2Cl_2	0%
3	$InCl_3$	CH_2Cl_2	94%[b]
4	$AlCl_3$	CH_2Cl_2	0%
5	$FeCl_3$	CH_2Cl_2	0%
6	$SnCl_2$	CH_2Cl_2	88%[b]
7	$InCl_3$	CH_3CN	5%[b]
8	$InCl_3$	CH_3NO_2	51%[b]
9	$InCl_3$	DMF	0%
10	$InCl_3$	THF	0%
11	$InCl_3$	toluene	0%

[a]All reactions were carried out in the presence of Lewis acids (0.1 equiv) and *n*-octanethiol (3.0 equiv). [b]The products contained *R*/*S*-isomers (ratio of 3/1, determined by ^{1}H NMR).

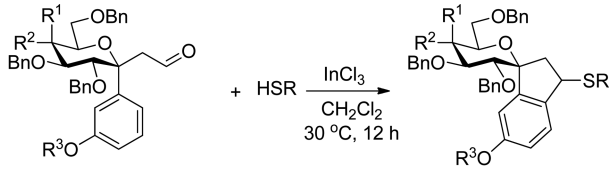
CH_2Cl_2 was found to provide the desired product (**29**) with the highest isolated yield (entry 3).

Meanwhile, we also examined the reactions of two other thiol nucleophiles (entries 1 and 3 in Table 3), three α-aryl *C*-galactosides (**20**−**22**, with different *m*-substituents in the aryl, entries 4−12), and two α-aryl *C*-glucosides (**26** and **27** that are 4-epimers of compounds **19** and **21**, entries 13−16). To our delight, these reactions successfully led to the formation of spiro bis-*C*,*C*-α-arylglycosides **28**−**43** in 90−95% yields. Their structures and the new stereochemical configuration were determined in a vigorous manner by ^{1}H and ^{13}C NMR, DEPT, and other spectroscopic methods. For instance, the structural determination of product **29** relied on the following fingerprint signals in the ^{1}H NMR spectrum, including the new H2′ at δ 4.2 (m), H1a′ at δ 2.42 (dd, $J_{1a',2'}$ = 6.5 Hz, $J_{1a',1b'}$ = 13.0 Hz), and H1b′ (m) at δ 2.27. The ^{13}C NMR spectrum contained the characteristic signals corresponding to the seven quaternary and aromatic carbons (at δ 158.1, 142.2, 138.9, 138.6, 138.4, 138.2, and 137.8), the anomeric carbon (δ 86.6), C1′ (δ 48.3), and C2′ (δ 44.8). The NOE cross peak in the NOESY spectrum, between H2 and H1b′, H2′, and H1a′ and the absence of an NOE cross peak between H2 and H1a′ in spiro-cyclization products **29** were also observed (see Supporting Information for 2D-COSY and -NOESY spectra of compound **29**).

A different outcome was obtained when there was an alteration in the aforementioned *m*-substituent. α-Aryl-*C*-galactosides **11** and **13** have *p*-methyl and *p*-methoxy groups, respectively. As opposed to the excepted spiro bis-*C*,*C*-α-arylgalactosides, the reactions produced dithioacetals **44** and **45** in excellent yields (Scheme 1), indicating that there were two thiol additions without the occurrence of cyclization. Likewise, the formation of dithioacetal **46** was observed in 90% yield if the *m*-substituent is a methyl group (i.e., α-aryl-*C*-galactoside **18** was examined).

The aforementioned results prompted us to propose a plausible mechanism interpreting the formation of spiro bis-*C*,*C*-α-arylglycosides vs dithioacetals. As shown in Scheme 2, the aldehyde of α-aryl-*C*-glycoside **47** is subjected to the nucleophilic addition of *n*-butanethiol, promoted by the chelation with $InCl_3$. Depending on the substituent and its position in the α-aryl group, the resulting thio-aldehyde

Table 3. Consecutive Thiolate Addition and Friedel−Crafts Cyclization To Produce Spiro Bis-*C*,*C*-α-arylglycosides[a]



19 R^1 = OBn, R^2 = H, R^3 = Me
20 R^1 = OBn, R^2 = H, R^3 = Et
21 R^1 = OBn, R^2 = H, R^3 = Pr
22 R^1 = OBn, R^2 = H, R^3 = H
26 R^1 = H, R^2 = OBn, R^3 = Me
27 R^1 = H, R^2 = OBn, R^3 = Pr

entry	substrate	HSR	product (yield, *R*/*S* ratio)[b]
1	**19**	1-butanethiol	**28** (92%, 3/1)
2	**19**	1-octanethiol	**29** (91%, 3/1)
3	**19**	benzylthiol	**30** (95%, 3/1)
4	**20**	1-butanethiol	**31** (91%, 3/1)
5	**20**	1-octanethiol	**32** (92%, 3/1)
6	**20**	benzylthiol	**33** (94%, 3/1)
7	**21**	1-butanethiol	**34** (90%, 3/1)
8	**21**	1-octanethiol	**35** (93%, 3/1)
9	**21**	benzylthiol	**36** (95%, 3/1)
10	**22**	1-butanethiol	**37** (91%, 3/1)
11	**22**	1-octanethiol	**38** (92%, 3/1)
12	**22**	benzylthiol	**39** (94%, 3/1)
13	**26**	1-butanethiol	**40** (92%, 3/1)
14	**26**	1-octanethiol	**41** (93%, 3/1)
15	**27**	1-butanethiol	**42** (92%, 3/1)
16	**27**	*n*-octanethiol	**43** (95%, 3/1)

[a]All reactions were carried out in the presence of Lewis acids (0.1 equiv) and *n*-octanethiol (3.0 equiv). [b]The ratio of *R*/*S*-isomers was determined by ^{1}H NMR.

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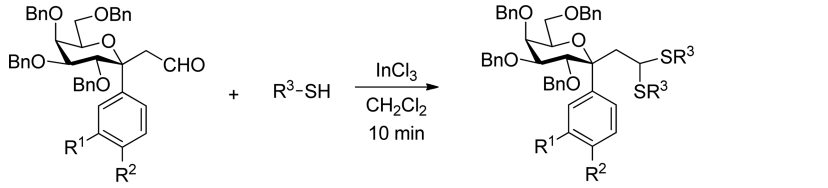
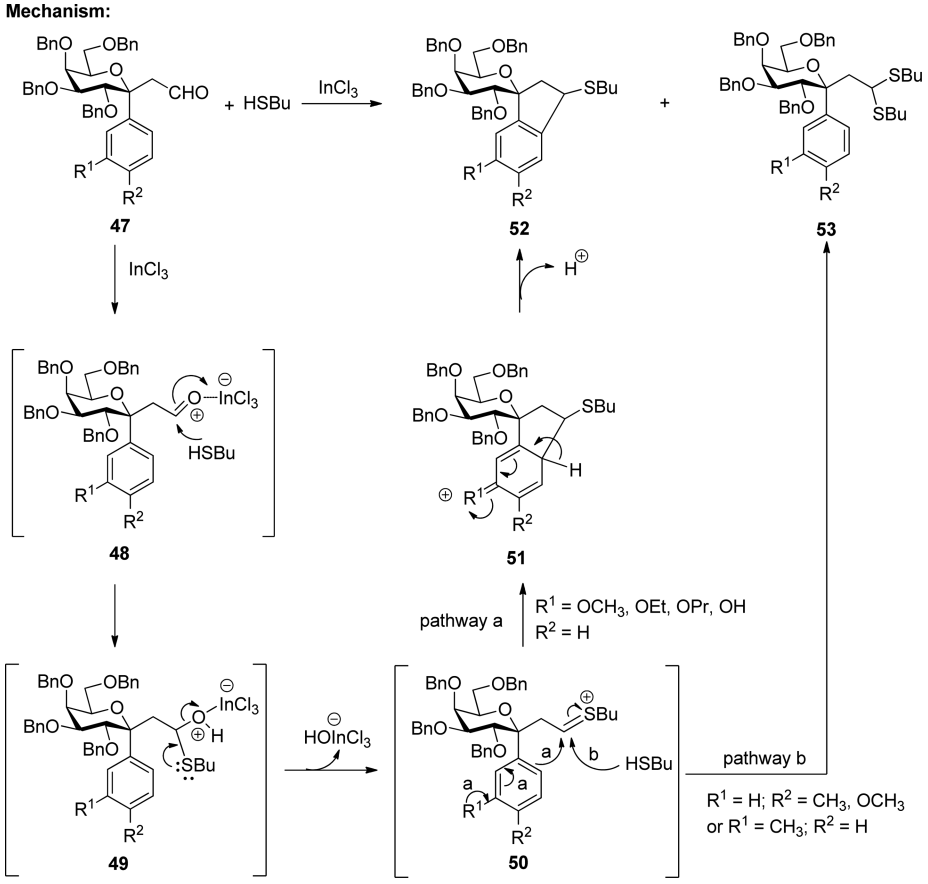
Scheme 1. Synthesis of Dithioacetal Derivatives 44−66 by $InCl_3$-Assisted Thioacetalization of α-Aryl-*C*-glycosides 11, 13, and 18



11 R^1 = H, R^2 = CH_3
13 R^1 = H, R^2 = OCH_3
18 R^1 = CH_3, R^2 = H

44 R^1 = H, R^2 = CH_3, R^3 = Bn (96%)
45 R^1 = H, R^2 = OCH_3, R^3 = Bn (95%)
46 R^1 = CH_3, R^2 = H, R^3 = *n*-Bu (93%)

Scheme 2. Possible Mechanism Proposed To Explain the Formation of Spiro-α-*C*-arylglycosides or Thioacetals Derivates



intermediate (**50**) proceeds with two different routes. When the α-aryl group of **50** contains a methoxy or hydroxyl substituent at the *m*-position (i.e., R^1 of **50**), the aryl group appears to be activated to cyclize with the thio-aldehyde, leading to formation of spiro bis-*C*,*C*-α-arylgalactosides **52**. On the other hand, the cyclization does not occur if the aforementioned methoxy group is changed to the *p*-position or if the *m*-substituent is an alkyl group. Under such circumstances, only thiol additions take place to form dithioacetal (e.g., compound **53**). Our observations and the proposed mechanism supported the idea that the resonance triggered by the *m*-hydroxyl or *m*-alkoxy group is a prerequisite for Friedel−Crafts cyclization. Without the precondition, the thio-aldehyde can only react with another thiol to form the dithioacetal adduct.

In summary, spiro bis-*C*,*C*-α-arylglycosides were successfully synthesized in three steps, including Heck type coupling of *exo*-glycals with several arylboronic acids, thiolate addition of an alkylthiol, and an intramolecular Friedel−Crafts cyclization. A plausible mechanism was proposed to explain how the spiro-*C*-arylglycosides were constructed in a concise manner. The developed procedure should be versatile to prepare a diversity of molecules since the first two reactions are applicable to different types of substrates.

EXPERIMENTAL SECTION

General Procedure. All purchased chemicals were of reagent grade. All reactions were carried out under a nitrogen atmosphere and monitored by TLC analysis (layer thickness: 250 μm). Column chromatography was carried out with silica gel 60 (70−230 mesh for gravity column, or 230−400 mesh for flash column). All commercial reagents were used without further purification. The *exo*-glycals were prepared according to the literature.[10] Proton NMR spectra were recorded at 400 or 500 MHz with $CDCl_3$ (δ_H 7.24) and Acetone-d_6 (δ_H 2.09) as the internal standard; carbon-13 NMR spectra were recorded at 100 or 125 MHz with $CDCl_3$ [δ_C 77.0 (central line of a triplet)] and acetone-d_6 [δ_C 29.9 (central line of a septet) and 206.7].

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Splitting patterns were shown by abbreviations, such as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). High resonance mass (HRMS) analysis data were recorded using the EI mode or ESI mode by Q-TOF.

Typical Procedure of Heck Type C-Glycosylation To Prepare *C*-Aryl-α-D-Glycosides 3−27. To a solution of *exo*-galactal **1a**, **1b**, **1c**, or **1d** (0.08 mmol, 1.0 equiv) and arylboronic acid (0.12 mmol, 1.5 equiv) in anhydrous CH_3CN (2.0 mL) were added $Pd(OAc)_2$ (0.008 mmol, 0.1 equiv) and BQ (0.12 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature under N_2 for 10 min. After the reaction was complete, CH_2Cl_2 (50 mL) was added to the reaction mixture, washed twice with H_2O (20 mL for each), washed twice with brine (20 mL for each), and dried over $MgSO_4$. The collected organic layer was concentrated under reduced pressure. Finally, the reaction mixture was purified by silica gel column chromatography with *n*-hexane/ethyl acetate (5/1) to give *C*-aryl-α-D-glycosides **3−27** in 80−96% yields.

2,3,4,6-Tetra-O-benzyl-1-α-C-phenyl-1-β-C-(1-O-acetylvinyl)-D-galactopyranose ***3***. Compound **1a** (0.08 mmol, 50.0 mg) was treated according to the aforementioned method to give the pale yellow oil **3** (45.4 mg, 83%): $[\alpha]^{25}_D$ +44.0 (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 2918, 1653, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.30−7.13 (m, 23H), 7.03 (d, *J* = 12.4 Hz, 1H), 5.68 (d, *J* = 12.4 Hz, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.89 (d, *J* = 11.6 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.60 (brs, 2H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 11.6 Hz, 1H), 4.16 (d, *J* = 10.4 Hz, 1H), 3.79−3.77 (m, 2H), 3.50 (d, *J* = 6.4 Hz, 2H), 3.39−3.37 (m, 1H), 1.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.7, 139.5, 138.9, 138.7, 138.5, 138.1, 137.3, 128.4, 128.30, 128.2, 128.1, 127.6, 127.5, 127.4, 127.3, 120.0, 83.0, 80.4, 80.0, 77.2, 76.5, 75.4, 74.6, 73.3, 72.6, 71.9, 69.0, 20.6 ; HRMS (EI) *m*/*z* calcd for $C_{44}H_{44}O_7$ (M^+) 684.3087, found 684.3082.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-methylphenyl)-1-β-C-(1-O-acetylvinyl)-D-galactopyranose ***4***. Compound **1a** (0.08 mmol, 50.0 mg) was treated according to the aforementioned method to give the pale yellow oil **4** (48.0 mg, 86%): $[\alpha]^{25}_D$ +53.0 (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) 2918, 1668, 1375, 1101 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.29−7.19 (m, 20H), 7.04 (d, *J* = 12.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.69 (d, *J* = 12.4 Hz, 1H), 4.94 (d, *J* = 11.6 Hz, 1H), 4.91 (d, *J* = 12.4 Hz, 1H), 4.69 (d, *J* = 11.2 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 12.0 Hz, 1H), 4.17 (d, *J* = 10.0 Hz, 1H), 3.83−3.79 (m, 2H), 3.53 (d, *J* = 6.4 Hz, 2H), 3.44−3.30 (m, 1H), 2.25 (s, 3H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 139.0, 138.8, 138.6, 138.2, 137.3, 137.0, 136.4, 129.0, 128.4, 128.3, 128.2, 128.0, 127.6, 127.5, 127.3, 120.2, 83.0, 80.4, 80.1, 76.5, 75.5, 74.7, 73.4, 72.7, 71.8, 69.1, 21.1, 20.7 ; HRMS (EI) *m*/*z* calcd for $C_{45}H_{46}O_7$ (M^+) 698.3244, found 698.3237.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-ethylphenyl)-1-β-C-(1-O-acetylvinyl)-D-galactopyranose ***5***. Compound **1a** (0.08 mmol, 50.0 mg) was treated according to the aforementioned method to give the pale yellow oil **5** (49.0 mg, 86%): $[\alpha]^{25}_D$ +26.6 (*c* 0.75, $CHCl_3$); IR ($CHCl_3$) 2918, 2856, 1681, 1456, 1101, cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.29−7.17 (m, 20H), 7.06−7.01 (m, ArH, 3H), 5.68 (d, *J* = 12.4 Hz, 1H), 4.94−4.88 (m, 2H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.63 (brs, 2H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.15 (d, *J* = 10.0 Hz, 1H), 3.82−3.79 (m, 2H), 3.52 (d, *J* = 6.4 Hz, 2H), 3.42−3.39 (m, 1H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.96 (s, 3H), 1.15 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 143.2, 139.0, 138.8, 138.6, 138.1, 137.2, 136.6, 128.3, 128.2, 128.0, 127.6, 127.5, 127.3, 120.1, 83.0, 80.4, 80.1, 76.5, 75.4, 74.7, 73.3, 72.6, 71.8, 69.0, 28.4, 20.7, 15.3; HRMS (EI) *m*/*z* calcd for $C_{46}H_{48}O_7$ (M^+) 712.3400, found 712.3410.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-tert-butylphenyl)-1-β-C-(1-O-acetylvinyl)-D-galactopyranose ***6***. Compound **1a** (0.08 mmol, 50.0 mg) was treated according to the aforementioned method to give the pale yellow oil **6** (47.4 mg, 80%): $[\alpha]^{25}_D$ +60.0 (*c* 0.65, $CHCl_3$); IR ($CHCl_3$) 2916, 2864, 1656, 1359, 1107, cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.26−7.16 (m, 22H), 7.07 (d, *J* = 12.4 Hz, 1H), 5.69 (d, *J* = 12.4 Hz, 1H), 4.94−4.88 (m, 2H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.63 (brs, 2H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 11.6 Hz, 1H), 4.14 (d, *J* = 10.0 Hz, 1H), 3.82−3.79 (m, 2H), 3.52 (d, *J* = 6.4 Hz, 2H), 3.43−3.40 (m, 1H), 1.95 (s, 3H), 1.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.9, 150.0, 139.0, 138.8, 138.6, 138.0, 136.9, 136.3, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 125.2, 120.0, 83.1, 80.3, 80.1, 76.5, 75.4, 74.7, 73.4, 72.7, 71.8, 69.0, 34.4, 31.3, 31.3, 31.0, 20.7; HRMS (EI) *m*/*z* calcd for $C_{48}H_{52}O_7$ (M^+) 740.3713, found 740.3722.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-methoxyphenyl)-1-β-C-(1-O-acetylvinyl)-D-galactopyranose ***7***. Compound **1a** (0.08 mmol, 50.0 mg) was treated according to the aforementioned method to give the pale yellow oil **7** (52.0 mg, 91%): $[\alpha]^{25}_D$ +34.7 (*c* 0.3, $CHCl_3$); IR ($CHCl_3$) 3290, 2920, 1635, 1373, cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.29−7.18 (m, 20H), 6.99 (d, *J* = 12.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 2H), 5.67 (d, *J* = 12.4 Hz, 1H), 4.93−4.88 (m, 2H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.63 (brs, 2H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.32 (d, *J* = 11.6 Hz, 1H), 4.13 (d, *J* = 11.2 Hz, 1H), 3.78−3.77 (m, 2H), 3.71 (s, 3H), 3.50 (d, *J* = 6.4 Hz, 2H), 3.40−3.37 (m, 1H), 1.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 167.8, 158.6, 138.9, 138.8, 138.5, 138.1, 137.4, 131.2, 129.7, 128.3, 128.20, 128.0, 127.6, 120.3, 113.6, 82.9, 80.3, 80.0, 76.4, 75.4, 74.6, 73.3, 72.6, 71.7, 69.1, 55.1, 20.7; HRMS (EI) *m*/*z* calcd for $C_{45}H_{46}O_8$ (M^+) 714.3193, found 714.3183.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-benzyloxyphenyl)-1-β-C-(1-O-acetylvinyl)-D-galactopyranose ***8***. Compound **1a** (0.08 mmol, 50.0 mg) was treated according to the aforementioned method to give the pale yellow oil **8** (55.6 mg, 88%): $[\alpha]^{25}_D$ +23.3 (*c* 0.3, $CHCl_3$); IR ($CHCl_3$) 2960, 1642, 1493, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.36−7.17 (m, 25H), 6.99 (d, *J* = 12.4 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 5.66 (d, J = 12.4 Hz, 1H), 5.02−4.87 (m, 4H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.62 (brs, 2H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 4.32 (d, *J* = 11.6 Hz, 1H), 4.13 (d, *J* = 10.8 Hz, 1H), 3.78−3.76 (m, 2H), 3.50 (d, *J* = 6.0 Hz, 2H), 3.40−3.36 (m, 1H), 1.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 158.0, 139.0, 138.8, 138.5, 138.2, 137.4, 137.1, 131.6, 129.8, 128.6, 128.3, 128.2, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 120.3, 114.5, 82.9, 80.3, 80.0, 76.5, 75.4, 74.7, 73.3, 72.6, 71.8, 70.0, 69.1, 20.7; HRMS (EI) *m*/*z* calcd for $C_{51}H_{50}O_8$ (M^+) 790.3506, found 790.3500.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-methoxyphenyl)-1-β-C-(1-O-methoxyvinyl)-D-galactopyranose ***9***. Compound **1b** (0.09 mmol, 52.2 mg) was treated according to the aforementioned method to give the pale yellow oil **9** (56.2 mg, 91%): $[\alpha]^{25}_D$ +23.3 (*c* 1.75, $CHCl_3$); IR ($CHCl_3$) 3035, 1656, 1361, 1103 cm^{-1}; ^1H NMR (CD_3COCD_3, 500 MHz) δ 7.59 (d, *J* = 9.0 Hz, 2H), 7.30−7.12 (m, 20H), 6.99 (d, *J* = 9.0 Hz, 2H), 5.91 (d, *J* = 13.0 Hz, 1H), 4.94 (d, *J* = 13.0 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.68−4.64 (m, 2H), 4.48 (d, *J* = 11.0 Hz, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.04 (d, *J* = 10.5 Hz, 1H), 3.89−3.88 (brs, 1H), 3.78 (dd, *J* = 3.0 Hz, *J* = 11.0 Hz, 1H), 3.64 (s, 3H), 3.53 (dd, *J* = 6.5 Hz, *J* = 9.5 Hz, 1H), 3.48 (dd, *J* = 6.5 Hz, *J* = 9.5 Hz, 1H), 3.37−3.34 (m, 1H), 3.25 (s, 3H); ^{13}C NMR (CD_3COCD_3, 125 MHz) δ 158.7, 149.8, 139.6, 139.2, 139.1, 138.8, 132.4, 130.0, 129.9, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.3, 113.1, 110.2, 84.0, 81.0, 80.3, 76.5, 76.2, 74.7, 72.8, 72.1, 71.6, 69.5, 55.1, 54.5; HRMS (EI) *m*/*z* calcd for $C_{44}H_{46}O_7$ (M^+) 686.3244, found 686.3248.

2,3,4,6-Tetra-O-benzyl-1-α-C-phenyl-1-β-C-ethanal-D-galactopyranose ***10***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **10** (53.2 mg, 92%): $[\alpha]^{25}_D$ +27.4 (*c* 1.45, $CHCl_3$); IR ($CHCl_3$) 2916, 2864, 1716, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.43 (t, *J* = 3.0 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 2H), 7.26−7.15 (m, 23H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.64−4.58 (m, 3H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.27 (d, *J* = 10.5 Hz, 1H), 3.79−3.75 (m, 2H), 3.54−3.44 (m, 3H), 2.70 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.8, 139.8, 138.8, 138.1, 138.0, 128.60, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 81.6, 80.7, 80.3, 76.1, 75.2, 74.6, 73.4, 72.3, 71.9, 69.0, 55.6; HRMS (EI) *m*/*z* calcd for $C_{42}H_{42}O_6$ (M^+) 642.2981, found 642.2988.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-methylphenyl)-1-β-C-ethanal-D-galactopyranose ***11***. Compound **1c** (0.09 mmol, 50.9 mg) was

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treated according to the aforementioned method to give the pale yellow oil **11** (56.1 mg, 95%): $[\alpha]^{25}_{D}$ +45.2 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) 2916, 1716, 1454, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.43 (1H, t, *J* = 3.2 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.27−7.14 (m, 20H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.89 (d, *J* = 11.6 Hz, 1H), 4.64−4.57 (m, 3H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 4.24 (d, *J* = 9.6 Hz, 1H), 3.78−3.75 (m, 2H), 3.53−3.44 (m, 3H), 2.69 (d, *J* = 3.2 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.9, 138.8, 138.2, 138.0, 137.4, 136.7, 129.3, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 81.7, 80.6, 80.4, 76.1, 75.3, 74.6, 73.4, 72.3, 71.8, 69.1, 55.7, 21.0; HRMS (EI) *m*/*z* calcd for $C_{43}H_{44}O_6$ (M^+) 656.3138, found 656.3130.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-tert-butylphenyl)-1-β-C-ethanal-D-galactopyranose ***12***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **12** (56.3 mg, 90%): $[\alpha]^{25}_{D}$ +27.4 (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 2916, 2872, 1761, 1454, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.44 (t, *J* = 2.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.25−7.17 (m, 22H), 4.95 (d, *J* = 10.8 Hz, 1H), 4.89 (d, *J* = 11.6 Hz, 1H), 4.62 (brs, 2H), 4.58 (d, *J* = 10.8 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.24 (d, *J* = 10.0 Hz, 1H), 3.79−3.75 (m, 2H), 3.52−3.48 (m, 3H), 2.69 (d, *J* = 3.2 Hz, 2H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.1, 150.4, 138.8, 138.2, 138.0, 136.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 125.5, 81.8, 80.6, 80.4, 76.1, 75.2, 74.6, 73.43, 72.4, 71.7, 69.0, 55.6, 34.4, 31.3, 31.2; HRMS (EI) *m*/*z* calcd for $C_{46}H_{50}O_6$ (M^+) 698.3607, found 698.3610.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-methoxyphenyl)-1-β-C-ethanal-D-galactopyranose ***13***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **13** (57.5 mg, 95%): $[\alpha]^{25}_{D}$ +53.6 (*c* 1.55, $CHCl_3$); IR ($CHCl_3$) 2916, 1716, 1361, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.42 (brs, 1H), 7.63 (d, *J* = 9.0 Hz, 2H), 7.25−7.15 (m, 20H), 6.75 (d, *J* = 9.0 Hz, 2H), 4.96 (d, *J* = 10.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.62−4.57 (m, 3H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 10.0 Hz, 1H), 3.79 (brs, 1H), 3.75 (dd, *J* = 1.5 Hz, *J* = 10.0 Hz, 1H), 3.70 (s, 3H), 3.51−3.45 (m, 3H), 2.96 (brs, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.9, 158.8, 138.8, 138.1, 138.0, 131.5, 129.1, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5, 113.9, 81.7, 80.4, 80.3, 76.0, 75.2, 74.6, 73.3, 72.3, 71.6, 69.0, 55.8, 55.1; HRMS (EI) *m*/*z* calcd for $C_{43}H_{44}O_7$ (M^+) 672.3087, found 672.3082.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-benzyloxyphenyl)-1-β-C-ethanal-D-galactopyranose ***14***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **14** (64.6 mg, 96%): $[\alpha]^{25}_{D}$ +10.5 (*c* 0.4, $CHCl_3$); IR ($CHCl_3$) 2916, 2866, 1716, 1103 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.41 (brs, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.35−7.15 (m, 25H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.96−4.94 (m, 3H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 11.2 Hz, 2H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.32 (d, *J* = 11.6 Hz, 1H), 4.22 (d, *J* = 10.4 Hz, 1H), 3.78 (brs, 1H), 3.74 (dd, *J* = 2.8 Hz, *J* = 10.4 Hz, 1H), 3.50−3.44 (m, 3H), 2.67 (d, *J* = 2.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.9, 158.1, 138.9, 138.2, 138.1, 136.9, 131.9, 129.2, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 114.8, 81.7, 80.5, 80.3, 77.3, 76.1, 75.3, 74.7, 73.4, 72.3, 71.7, 67.0, 69.1, 55.8; HRMS (EI) *m*/*z* calcd for $C_{49}H_{48}O_7$ (M^+) 748.3400, found 748.3408.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-chlorophenyl)-1-β-C-ethanal-D-galactopyranose ***15***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **15** (50.5 mg, 83%): $[\alpha]^{25}_{D}$ +36.2 (*c* 1.45, $CHCl_3$); IR ($CHCl_3$) 2916, 2860, 1716, 1091 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.42 (t, *J* = 2.5 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.25−7.17 (m, 22H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.64−4.55 (m, 3H), 4.50 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 10.5 Hz, 1H), 4.33 (d, *J* = 10.5 Hz, 1H), 4.24 (d, *J* = 10.5 Hz, 1H), 3.78 (brs, 1H), 3.66 (dd, *J* = 2.5 Hz, *J* = 10.5 Hz, 1H), 3.51−3.44 (m, 2H), 3.39−3.37 (m, 1H), 2.66 (d, *J* = 2.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.3, 138.6, 138.4, 138.0, 137.9, 133.6, 129.4, 128.8, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 81.2, 80.4, 80.1, 76.2, 75.0, 74.6, 73.4, 72.2, 72.1, 69.0, 55.3; HRMS (EI) *m*/*z* calcd for $C_{42}H_{41}O_6Cl$ (M^+) 676.2592, found 676.2588.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-methylbenzoate)-1-β-C-ethanal-D-galactopyranose ***16***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **16** (55.4 mg, 88%): $[\alpha]^{25}_{D}$ +48.0 (*c* 0.1, $CHCl_3$); IR ($CHCl_3$) 2916, 2864, 1716, 1454, 1085 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.43 (t, *J* = 4.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.26−7.17 (m, 20H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.89 (d, *J* = 11.6 Hz, 1H), 4.65−4.60 (m, 3H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 10.8 Hz, 1H), 3.83 (s, 3H), 3.78 (brs, 1H), 3.67 (dd, *J* = 2.4 Hz, *J* = 10.8 Hz, 1H), 3.54−3.45 (m, 2H), 3.40−3.37 (m, 1H), 2.69 (d, *J* = 4.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.1, 166.7, 145.3, 138.7, 137.9, 129.8, 129.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 81.2, 80.8, 80.2, 76.2, 76.3, 75.1, 74.7, 73.5, 72.4, 69.0, 55.1, 52.1; HRMS (EI) *m*/*z* calcd for $C_{44}H_{44}O_8$ (M^+) 700.3036, found 700.3028.

2,3,4,6-Tetra-O-benzyl-1-α-C-(3-phenylphenyl)-1-β-C-ethanal-D-galacopyranose ***17***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **17** (57.5 mg, 89%): $[\alpha]^{25}_{D}$ +16.9 (*c* 0.45, $CHCl_3$); IR ($CHCl_3$) 2918, 2866, 1716, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.38 (brs, 1H), 8.40 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.74−7.43 (m, 27H), 5.33 (d, *J* = 11.2 Hz, 1H), 5.22 (d, *J* = 11.6 Hz, 1H), 4.96−4.88 (m, 3H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 10.8 Hz, 1H), 4.11−4.09 (m, 2H), 3.89−3.85 (m, 2H), 3.80−3.75 (m, 1H), 3.08 (d, *J* = 2.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.7, 141.4, 140.9, 140.5, 138.8, 138.2, 138.0, 129.1, 128.8, 128.7, 128.4, 128.3, 127.9, 127.7, 127.6, 127.3, 127.1, 126.7, 126.4, 81.7, 80.8, 80.1, 76.1, 75.3, 74.6, 73.5, 72.2, 72.2, 69.4, 55.6; HRMS (EI) *m*/*z* calcd for $C_{48}H_{46}O_6$ (M^+) 718.3294, found 718.3303.

2,3,4,6-Tetra-O-benzyl-1-α-C-(3-methylphenyl)-1-β-C-ethanal-D-galactopyranose ***18***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **18** (52.0 mg, 88%): $[\alpha]^{25}_{D}$ +58.3 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) 2960, 1716, 1454, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.43 (t, *J* = 3.0 Hz, 1H), 7.56−7.52 (m, 2H), 7.28−7.17 (m, 20H), 7.10 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 5.99 (d, *J* = 11.5 Hz, 1H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.65−4.58 (m, 3H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.34 (d, *J* = 11.5 Hz, 1H), 4.26 (d, *J* = 10.0 Hz, 1H), 3.78−3.76 (m, 2H), 3.53 (dd, *J* = 3.0 Hz, *J* = 11.5 Hz, 1H), 3.49−3.45 (m, 2H), 2.69 (d, *J* = 3.0 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.9, 139.8, 138.8, 138.2, 138.1, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 125.0, 81.7, 80.7, 80.1, 76.0, 75.3, 74.6, 73.4, 72.1, 71.9, 69.2, 55.6, 21.7; HRMS (ESI^+): *m*/*z* $[M + Na]^+$ calcd for $C_{43}H_{44}O_6Na$ 679.3030; found 679.3036.

2,3,4,6-Tetra-O-benzyl-1-α-C-(3-methoxylphenyl)-1-β-C-ethanal-D-galactopyranose ***19***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **19** (52.6 mg, 87%): $[\alpha]^{25}_{D}$ +58.0 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) 2916, 1716, 1454, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.46 (t, *J* = 3.0 Hz, 1H), 7.34−7.11 (m, 23H), 6.72−6.70 (m, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.64−4.59 (m, 3H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.33 (d, *J* = 11.5 Hz, 1H), 4.26 (d, *J* = 10.0 Hz, 1H), 3.78−3.76 (m, 2H), 3.56−3.52 (m, 5H), 3.48−3.45 (m, 1H), 2.71 (d, *J* = 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.8, 159.8, 141.4, 138.8, 138.2, 138.0, 129.6, 128.4, 128.30, 127.9, 127.8, 127.7, 127.6, 127.5, 120.1, 113.8, 113.0, 81.7, 80.7, 80.3, 76.1, 75.3, 74.6, 73.5, 72.4, 72.1, 69.4, 55.5, 55.0; HRMS (ESI^+): *m*/*z* $[M + Na]^+$ calcd for $C_{43}H_{44}O_7Na$ 695.2979; found 695.2984.

2,3,4,6-Tetra-O-benzyl-1-α-C-(3-ethoxylphenyl)-1-β-C-ethanal-D-galactopyranose ***20***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **20** (54.3 mg, 88%): $[\alpha]^{25}_{D}$ +71.8 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) 2916, 1716, 1454, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.45 (t, *J* = 3.0 Hz, 1H), 7.33−7.10 (m, 23H), 6.71−6.69 (m, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.64−4.59 (m,

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3H), 4.52 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.33 (d, J = 11.5 Hz, 1H), 4.26 (d, J = 10.0 Hz, 1H), 3.79−3.73 (m, 4H), 3.56−3.53 (m, 2H), 3.46 (dd, J = 9.0 Hz, J = 12.0 Hz, 1H), 2.70 (d, J = 3.0 Hz, 2H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.8, 159.1, 141.3, 138.8, 138.2, 138.0, 129.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 120.0, 114.5, 113.3, 81.7, 80.7, 80.3, 76.1, 75.3, 74.6, 73.5, 72.3, 72.1, 69.4, 63.2, 55.5, 14.7; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{44}H_{46}O_7Na$ 709.3136; found 709.3144.

2,3,4,6-Tetra-O-benzyl-1-α-C-(3-propoxylphenyl)-1-β-C-ethanal-D-galactopyranose ***21***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **21** (54.2 mg, 86%): $[\alpha]^{25}_D$ +71.4 (c 1.5, $CHCl_3$); IR ($CHCl_3$) 2924, 1716, 1454, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.46 (t, J = 3.0 Hz, 1H), 7.35−7.17 (m, 22H), 7.12 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 6.71 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 4.98 (d, J = 11.5 Hz, 1H), 4.90 (d, J = 11.5 Hz, 1H), 4.62−4.59 (m, 3H), 4.52 (d, J = 11.5 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.34 (d, J = 12.0 Hz, 1H), 4.26 (d, J = 10.5 Hz, 1H), 3.79−3.77 (m, 2H), 3.67 (t, J = 6.5 Hz, 2H), 3.56−3.52 (m, 2H), 3.46 (dd, J = 8.5 Hz, J = 11.0 Hz, 1H), 2.71 (d, J = 3.0 Hz, 2H), 1.65−1.60 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.8, 159.4, 141.3, 138.8, 138.2, 138.0, 129.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 119.9, 114.6, 113.5, 81.8, 80.7, 80.4, 76.1, 75.3, 74.7, 73.5, 72.3, 72.0, 69.4, 69.3, 55.5, 22.5, 10.5; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{45}H_{48}O_7Na$ 723.3292; found 723.3299.

2,3,4,6-Tetra-O-benzyl-1-α-C-(3-hydroxylphenyl)-1-β-C-ethanal-D-galactopyranose ***22***. Compound **1c** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **22** (52.7 mg, 89%): $[\alpha]^{25}_D$ +38.3 (c 1.5, $CHCl_3$); IR ($CHCl_3$) 2920, 1716, 1454, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.44 (t, J = 3.0 Hz, 1H), 7.30−7.07 (m, 23H), 6.64 (dd, J = 2.5 Hz, J = 8.0 Hz, 1H), 4.96 (d, J = 11.0 Hz, 1H), 4.90 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 11.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 12.0 Hz, 1H), 4.35 (d, J = 12.0 Hz, 1H), 4.24 (d, J = 10.5 Hz, 1H), 3.77−3.74 (m, 2H), 3.55 (dd, J = 6.0 Hz, J = 9.0 Hz, 1H), 3.51 (dd, J = 5.5 Hz, J = 6.0 Hz, 1H), 3.45 (dd, J = 5.5 Hz, J = 9.0 Hz, 1H), 2.68 (d, J = 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.8, 155.9, 141.5, 138.7, 138.2, 138.1, 138.0, 129.9, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 120.0, 114.8, 114.7, 81.5, 80.6, 80.1, 76.2, 75.2, 74.6, 73.5, 72.3, 72.1, 69.5, 55.4; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{42}H_{42}O_7Na$ 681.2823; found 681.2829.

2,3,4,6-Tetra-O-benzyl-1-α-C-phenyl-1-β-C-ethanal-D-glucopyranose ***24***. Compound **1d** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **24** (53.2 mg, 92%): $[\alpha]^{25}_D$ +45.0 (c 0.6, $CHCl_3$); IR ($CHCl_3$) 2929, 1666, 1462, 1087 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.51 (t, J = 2.8 Hz, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.28−7.14 (m, 20H), 7.03−7.01 (m, 2H), 4.94 (d, J = 10.8 Hz, 1H), 4.84 (d, J = 10.8 Hz, 1H), 4.75 (d, J = 10.8 Hz, 1H), 4.70 (d, J = 10.8 Hz, 1H), 4.63 (d, J = 11.2 Hz, 1H), 4.56 (d, J = 12.4 Hz, 1H), 4.48−4.42 (m, 2H), 3.90 (dd, J = 9.2 Hz, J = 9.6 Hz, 1H), 4.27 (d, J = 10.0 Hz, 1H), 3.65−3.60 (m, 3H), 3.44−3.42 (m, 1H), 2.76 (d, J = 2.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.7, 139.7, 138.2, 137.9, 137.8, 128.9, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 85.4, 83.2, 80.4, 79.5, 76.2, 75.4, 75.2, 73.3, 73.2, 69.0, 55.7; HRMS (EI) m/z calcd for $C_{42}H_{42}O_6$ (M+) 642.2981, found 642.2973.

2,3,4,6-Tetra-O-benzyl-1-α-C-(4-methoxyphenyl)-1-β-C-ethanal-D-glucopyranose ***25***. Compound **1d** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **25** (57.5 mg, 95%): $[\alpha]^{25}_D$ +19.4 (c 1.4, $CHCl_3$); IR ($CHCl_3$) 3035, 1718, 1359, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.50 (t, J = 2.8 Hz, 1H), 7.66 (d, J = 8.8 Hz, 2H), 7.28−7.15 (m, 18H), 7.03−7.01 (m, 2H), 6.79 (d, J = 8.8 Hz, 2H), 4.93 (d, J = 11.2 Hz, 1H), 4.83 (d, J = 10.8 Hz, 1H), 4.75 (d, J = 11.2 Hz, 1H), 4.70 (d, J = 10.8 Hz, 1H), 4.62 (d, J = 10.8 Hz, 1H), 4.55 (d, J = 12.4 Hz, 1H), 4.48−4.42 (m, 2H), 3.89 (dd, J = 9.2 Hz, J = 9.6 Hz, 1H), 3.72 (s, 3H), 3.68 (d, J = 10.0 Hz, 1H), 3.63−3.59 (m, 2H), 3.44−3.42 (m, 3H), 2.74 (d, J = 2.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.9, 159.0, 138.3, 138.2, 137.9, 131.4, 129.1, 128.4, 127.9, 127.90, 127.8, 127.7, 127.6, 114.2, 85.5, 83.2, 80.1, 79.5, 76.4, 75.4, 75.1, 73.3, 73.0, 69.0, 55.9, 55.2; HRMS (EI) m/z calcd for $C_{43}H_{44}O_7$ (M$^+$) 672.3087, found 672.3083.

2,3,4,6-Tetra-O-benzyl-1-α-C-(3-methoxyphenyl)-1-β-C-ethanal-D-glucopyranose ***26***. Compound **1d** (0.09 mmol, 50.9 mg) was treated according to the aforementioned method to give the pale yellow oil **26** (56.2 mg, 93%): $[\alpha]^{25}_D$ +15.5 (c 1.4, $CHCl_3$); IR ($CHCl_3$) 2914, 1716, 1261, 1087 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.52 (t, J = 3.0 Hz, 1H), 7.37−7.36 (m, 1H), 7.29−7.15 (m, 20H), 7.03−7.01 (m, 2H), 6.74−6.72 (m, 1H), 4.95 (d, J = 11.0 Hz, 1H), 4.84 (d, J = 11.0 Hz, 1H), 4.75 (d, J = 11.0 Hz, 1H), 4.71 (d, J = 11.0 Hz, 1H), 4.63 (d, J = 10.5 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.43 (d, J = 10.5 Hz, 1H), 3.91 (dd, J = 9.0 Hz, J = 10.0 Hz, 1H), 3.70 (d, J = 10.0 Hz, 1H), 3.62−3.58 (m, 6H), 3.52−3.47 (m, 1H), 2.75 (d, J = 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.6, 160.0, 141.2, 138.3, 138.2, 138.0, 137.9, 129.8, 128.4, 127.9, 127.8, 127.7, 127.5, 120.0, 113.6, 113.3, 85.4, 83.2, 80.3, 79.5, 76.2, 75.4, 75.1, 73.4, 73.3, 69.2, 55.5, 55.1; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{43}H_{44}O_7Na$ 695.2979; found 695.2985.

2,3,4,6-Tetra-O-benzyl-1-α-C-(3-ethoxyphenyl)-1-β-C-ethanal-D-glucopyranose ***27***. Compound **1d** (0.09 mmol, 50.9 mg) was treated according to the method to give the pale yellow oil **27** (59.9 mg, 95%): $[\alpha]^{25}_D$ +10.3 (c 1.4, $CHCl_3$); IR ($CHCl_3$) 2920, 1716, 1261, 1089 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.52 (t, J = 3.0 Hz, 1H), 7.36 (brs, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.29−7.14 (m, 19H), 7.03−7.01 (m, 2H), 6.72 (dd, J = 2.5 Hz, J = 8.0 Hz, 1H), 4.95 (d, J = 11.0 Hz, 1H), 4.83 (d, J = 11.0 Hz, 1H), 4.75 (d, J = 11.0 Hz, 1H), 4.71 (d, J = 11.0 Hz, 1H), 4.63 (d, J = 11.0 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.43 (d, J = 11.0 Hz, 1H), 3.92 (dd, J = 9.0 Hz, J = 10.0 Hz, 1H), 3.74 (t, J = 6.5 Hz, 2H), 3.70 (d, J = 10.0 Hz, 1H), 3.61−3.58 (3H, m, H6, H4), 3.53−3.50 (1H, m, H5), 2.75 (2H, d, J = 3.0 Hz, H1′), 1.68−1.64 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.7, 159.5, 141.1, 138.3, 138.0, 137.9, 129.8, 128.4, 127.9, 127.8, 127.7, 127.6, 127.5, 119.8, 114.5, 113.6, 85.5, 83.2, 80.3, 79.5, 76.1, 75.4, 75.1, 73.4, 73.3, 69.5, 69.2, 55.6, 22.5, 10.5; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{45}H_{48}O_7Na$ 723.3292; found 723.3294.

Typical Procedure To Prepare Spiro[Indane-1,2′-pyran]glycosides ***28−48***. To a solution of α-aryl-C-glycoside (0.07 mmol, 1.0 equiv) and n-butanethiol (0.21 mmol, 3.0 equiv) in anhydrous CH_2Cl_2 (2.0 mL) was added $InCl_3$ (0.007 mmol, 0.1 equiv). The reaction mixture was stirred at room temperature for 24 h. Upon reaction completion, the reaction mixture was mixed with CH_2Cl_2 (50 mL), washed twice with H_2O (20 mL for each), washed twice with brine (20 mL for each), and dried over $MgSO_4$. The collected organic layer was concentrated under reduced pressure. Finally, the reaction mixture was purified by silica gel column chromatography with n-hexane/ethyl acetate (20:1) to give C-aryl-α-D-glycoside derivatives **28−48** in 90−95% yields.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***28***. Compound **19** (0.07 mmol, 47.0 mg) was treated according to the aforementioned method to give the pale yellow oil **28** (47.9 mg, 92%): IR ($CHCl_3$) 3028, 2927, 1608, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30−7.04 (m, 21H), 6.81−6.79 (m, 2H), 4.91 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.74 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.24−4.20 (m, 4H), 4.08 (d, J = 10.0 Hz, 1H), 4.04 (d, J = 2.5 Hz, 1H), 3.66 (s, 3H), 3.58 (dd, J = 5.5 Hz, J = 8.5 Hz, 1H), 3.47 (dd, J = 8.5 Hz, J = 8.5 Hz, 1H), 3.23 (dd, J = 5.5 Hz, J = 8.5 Hz, 1H), 2.41 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.29−2.18 (m, 3H), 1.43−1.35 (m, 2H), 1.24−1.18 (m, 2H), 0.75 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.0, 142.2, 138.9, 138.6, 138.3, 138.2, 137.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.50, 127.2, 126.1, 113.6, 112.2, 86.6, 81.4, 78.3, 75.6, 74.6, 73.8, 73.3, 72.0, 71.1, 68.6, 55.5, 48.3, 44.8, 32.0, 29.1, 22.1, 13.7; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{47}H_{52}O_6SNa$ 767.3377; found 767.3382.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***29***. Compound **19** (0.07 mmol, 47.0 mg) was treated according to the aforementioned method to give the pale yellow oil **29** (51.0 mg, 91%): IR ($CHCl_3$) 2924, 1610, 1454, 1099, 698 cm^{-1}; ^{1}H

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NMR ($CDCl_3$, 500 MHz) δ 7.30−7.03 (m, 21H), 6.81−6.80 (m, 2H), 4.91 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.74 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.63 (d, J = 11.5 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.24−4.22 (m, 4H), 4.08 (d, J = 10.0 Hz, 1H), 4.05 (brs, 1H), 3.66 (s, 3H), 3.60−3.57 (m, 1H), 3.47 (dd, J = 8.0 Hz, J = 9.0 Hz, 1H), 3.23 (dd, J = 5.5 Hz, J = 9.0 Hz, 1H), 2.42 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.30−2.18 (m, 3H), 1.41−1.37 (m, 2H), 1.18−1.15 (m, 10H), 0.79 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.1, 142.2, 138.9, 138.6, 138.4, 138.2, 137.8, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.2, 126.1, 113.6, 112.2, 86.6, 81.4, 78.4, 75.6, 74.6, 73.8, 73.4, 72.0, 71.1, 68.6, 55.5, 48.3, 44.8, 31.8, 29.7, 29.4, 29.2, 29.0, 22.6, 14.1; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{51}H_{60}O_6SNa$ 823.4003; found 823.4010.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***30***. Compound **19** (0.07 mmol, 47.0 mg) was treated according to the aforementioned method to give the pale yellow oil **30** (51.7 mg, 95%): IR ($CHCl_3$) 2908, 1604, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30−7.05 (m, 21H), 6.80−6.76 (m, 2H), 4.90 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.75 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.62 (d, J = 11.5 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.25−4.21 (m, 3H), 4.08 (d, J = 10.0 Hz, 1H), 4.04 (brs, 1H), 3.66 (s, 3H), 3.59−3.57 (m, 1H), 3.52−3.44 (m, 4H), 3.22 (dd, J = 5.5 Hz, J = 9.0 Hz, 1H), 2.42 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.31 (dd, J = 9.0 Hz, J = 13.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.2, 142.4, 138.9, 138.6, 138.5, 138.3, 138.0, 137.9, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.4, 126.8, 126.2, 113.7, 112.3, 86.8, 81.5, 78.4, 75.7, 74.7, 73.9, 73.4, 72.1, 71.2, 68.7, 55.5, 48.1, 45.1, 34.1; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{50}H_{50}O_6SNa$ 801.3220; found 801.3226.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***31***. Compound **20** (0.07 mmol, 48.0 mg) was treated according to the aforementioned method to give the pale yellow oil **31** (48.3 mg, 91%): IR ($CHCl_3$) 2927, 1608, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30−7.00 (m, 21H), 6.79−6.78 (m, 2H), 4.91 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.75 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.24−4.21 (m, 4H), 4.08 (d, J = 10.0 Hz, 1H), 4.04 (d, J = 2.5 Hz, 1H), 3.85 (q, J = 7.0 Hz, 2H), 3.60−3.57 (m, 1H), 3.47 (dd, J = 8.0 Hz, J = 9.0 Hz, 1H), 3.23 (dd, J = 5.5 Hz, J = 9.0 Hz, 1H), 2.41 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.29−2.19 (m, 3H), 1.40−1.36 (m, 2H), 1.32 (t, J = 7.0 Hz, 3H), 1.23−1.18 (m, 2H), 0.75 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.4, 142.1, 138.9, 138.6, 138.2, 138.2, 137.9, 128.4, 128.3, 128.2, 128,1, 128.0, 127.7, 127.6, 127.5, 127.2, 126.0, 114.1, 112.7, 86.6, 81.3, 78.4, 75.6, 74.6, 73.8, 73.3, 71.9, 71.0, 68.6, 48.3, 44.8, 32.0, 29.1, 22.1, 14.8, 13.7; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{48}H_{54}O_6SNa$ 781.3533; found 781.3537.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***32***. Compound **20** (0.07 mmol, 48.0 mg) was treated according to the aforementioned method to give the pale yellow oil **32** (52.4 mg, 92%): IR ($CHCl_3$) 2924, 1608, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38−7.03 (m, 21H), 6.79 (brs, 2H), 4.91 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.75 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.24−4.21 (m, 4H), 4.08 (d, J = 10.0 Hz, 1H), 4.05 (brs, 1H), 3.85 (q, J = 7.0 Hz, 2H), 3.60−3.57 (m, 1H), 3.47 (dd, J = 8.0 Hz, J = 8.5 Hz, 1H), 3.23 (dd, J = 5.0 Hz, J = 8.5 Hz, 1H), 2.45−2.39 (m, 1H), 2.31−2.18 (m, 3H), 1.59−1.48 (m, 2H), 1.32 (t, J = 7.0 Hz, 3H), 1.20−1.14 (m, 10H), 0.79 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.4, 142.1, 138.9, 138.6, 138.2, 137.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.2, 126.0, 114.2, 112.7, 86.6, 81.3, 78.4, 75.6, 74.6, 73.8, 73.3, 71.9, 71.0, 68.6, 63.6, 48.3, 44.8, 31.8, 29.9, 29.4, 29.2, 29.0, 22.6, 14.8, 14.1; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{52}H_{62}O_6SNa$ 837.4159; found 837.4161.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***33***. Compound **20** (0.07 mmol, 48.0 mg) was treated according to the aforementioned method to give the pale yellow oil **33** (52.1 mg, 94%): IR ($CHCl_3$) 2924, 1604, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33−7.05 (m, 26H), 6.79−6.75 (m, 2H), 4.91 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.75 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.24−4.20 (m, 4H), 4.07 (d, J = 10.0 Hz, 1H), 4.04 (d, J = 2.5 Hz, 1H), 3.84 (q, J = 7.0 Hz, 2H), 3.61−3.57 (m, 1H), 3.46−3.43 (m, 3H), 3.22 (dd, J = 5.5 Hz, J = 9.5 Hz, 1H), 2.41 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.31 (dd, J = 10.0 Hz, J = 13.0 Hz, 1H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.5, 142.2, 138.9, 138.6, 138.4, 138.2, 137.9, 137.8, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.3, 126.7, 126.1, 114.2, 112.8, 86.7, 81.3, 78.4, 75.7, 74.6, 73.8, 73.3, 72.0, 71.1, 68.6, 63.7, 48.0, 45.0, 43.0, 14.8; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{51}H_{52}O_6SNa$ 815.3377; found 815.3377.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***34***. Compound **21** (0.07 mmol, 49.0 mg) was treated according to the aforementioned method to give the pale yellow oil **34** (48.6 mg, 90%): IR ($CHCl_3$) 2927, 1608, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31−7.04 (m, 21H), 6.78 (brs, 2H), 4.91 (d, J = 11.0 Hz, 1H), 4.89 (d, J = 11.0 Hz, 1H), 4.75 (d, J = 12.0 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.24−4.21 (m, 4H), 4.08 (d, J = 10.0 Hz, 1H), 4.05 (d, J = 2.5 Hz, 1H), 3.75 (t, J = 6.5 Hz, 2H), 3.60−3.58 (m, 1H), 3.47 (dd, J = 8.0 Hz, J = 9.0 Hz, 1H), 3.23 (dd, J = 5.0 Hz, J = 9.0 Hz, 1H), 2.40 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.29−2.17 (m, 3H), 1.75−1.68 (m, 2H), 1.42−1.36 (m, 2H), 1.26−1.18 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H), 0.76 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.6, 142.1, 138.9, 138.6, 138.2, 138.1, 137.8, 128.4, 128.3, 128.2, 128,1, 128.0, 127.7, 127.6, 127.5, 127.2, 126.0, 114.2, 112.7, 86.7, 81.3, 78.3, 75.6, 74.6, 73.7, 73.4, 71.9, 71.0, 69.7, 68.6, 48.3, 44.8, 32.0, 29.1, 22.7, 22.1, 13.7, 10.6; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{49}H_{56}O_6SNa$ 795.3690; found 795.3695.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***35***. Compound **21** (0.07 mmol, 49.0 mg) was treated according to the aforementioned method to give the pale yellow oil **35** (53.9 mg, 93%): IR ($CHCl_3$) 2924, 1608, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31−7.04 (m, 21H), 6.79−6.78 (m, 2H), 4.91 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.75 (d, J = 12.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.24−4.20 (m, 4H), 4.08 (d, J = 10.0 Hz, 1H), 4.05 (d, J = 2.5 Hz, 1H), 3.75 (t, J = 6.5 Hz, 2H), 3.61−3.58 (m, 1H), 3.47 (dd, J = 5.5 Hz, J = 9.0 Hz, 1H), 3.23 (dd, J = 5.0 Hz, J = 9.0 Hz, 1H), 2.41 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.29−2.18 (m, 3H), 1.73−1.69 (m, 2H), 1.41−1.36 (m, 2H), 1.20−1.14 (m, 10H), 0.96 (t, J = 7.5 Hz, 3H), 0.79 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.6, 142.1, 138.9, 138.6, 138.2, 138.1, 137.8, 128.4, 128.3, 128.2, 128,1, 128.0, 127.7, 127.6, 127.5, 127.2, 126.0, 114.2, 112.5, 86.6, 81.3, 78.4, 75.6, 74.6, 73.8, 73.3, 71.9, 71.0, 69.7, 68.6, 48.3, 44.8, 31.8, 29.9, 29.3, 29.2, 29.1, 29.0, 22.7, 22.6, 14.1, 10.6; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{53}H_{64}O_6SNa$ 851.4316; found 851.4317.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***36***. Compound **21** (0.07 mmol, 49.0 mg) was treated according to the aforementioned method to give the pale yellow oil **36** (53.6 mg, 95%): IR ($CHCl_3$) 2924, 1604, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31−7.05 (m, 26H), 6.79−6.75 (m, 2H), 4.91 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.75 (d, J = 12.0 Hz, 1H), 4.66 (d, J = 11.5 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 11.5 Hz, 1H), 4.24−4.21 (m, 4H), 4.07 (d, J = 10.0 Hz, 1H), 4.04 (d, J = 2.5 Hz, 1H), 3.74 (t, J = 6.5 Hz, 2H), 3.60−3.58 (m, 1H), 3.46−3.43 (m, 3H), 3.22 (dd, J = 5.0 Hz, J = 9.0 Hz, 1H), 2.41 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.30 (dd, J = 9.0 Hz, J = 13.0 Hz, 1H), 1.73−1.69 (2H, m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.7, 142.2, 138.9, 138.6, 138.4, 138.2, 137.8, 137.7, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.3, 126.7, 126.0, 114.2, 112.8, 86.7, 81.3, 78.4, 75.6, 74.6, 73.8, 73.4, 71.9, 71.1, 69.7, 68.6, 48.0, 45.0, 34.0, 22.7, 10.6; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{52}H_{54}O_6SNa$ 829.3533; found 829.3534.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***37***. Compound **22** (0.08 mmol, 52.6 mg) was treated according to the aforementioned method to give the pale yellow oil **37** (53.1 mg, 91%): IR ($CHCl_3$) 3363, 2927, 1585, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36−7.00 (m, 21H), 6.71 (d, J = 2.0 Hz, 1H), 6.41 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 4.91 (d, J = 12.0 Hz, 1H), 4.88 (d, J = 12.0 Hz, 1H), 4.75 (d, J = 11.5 Hz, 1H), 4.67 (d, J =

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11.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.57 (d, J = 11.5 Hz, 1H), 4.24−4.18 (m, 4H), 4.09 (d, J = 10.0 Hz, 1H), 4.04 (d, J = 2.5 Hz, 1H), 3.62−3.59 (m, 1H), 3.45 (dd, J = 8.0 Hz, J = 9.0 Hz, 1H), 3.24 (dd, J = 5.5 Hz, J = 9.0 Hz, 1H), 2.41 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.31−2.17 (m, 3H), 1.42−1.36 (m, 2H), 1.26−1.18 (m, 2H), 0.77 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.1, 141.8, 138.8, 138.3, 138.1, 138.0, 137.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 126.2, 115.9, 113.0, 86.6, 81.7, 78.6, 76.0, 74.6, 73.9, 73.4, 72.3, 71.0, 68.7, 48.3, 44.8, 32.0, 29.2, 22.1, 13.7; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{46}H_{50}O_6SNa$ 753.3220; found 753.3220.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***38***. Compound **22** (0.08 mmol, 52.6 mg) was treated according to the aforementioned method to give the pale yellow oil **38** (57.8 mg, 92%): IR ($CHCl_3$) 3363, 2924, 1585, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36−7.01 (m, 21H), 6.72 (d, J = 2.0 Hz, 1H), 6.46 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 4.91 (d, J = 11.5 Hz, 1H), 4.88 (d, J = 11.5 Hz, 1H), 4.74 (d, J = 11.5 Hz, 1H), 4.67 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 4.56 (d, J = 11.5 Hz, 1H), 4.23−4.18 (m, 4H), 4.09 (d, J = 10.0 Hz, 1H), 4.03 (d, J = 2.5 Hz, 1H), 3.62−3.59 (m, 1H), 3.45 (dd, J = 8.0 Hz, J = 9.0 Hz, 1H), 3.24 (dd, J = 5.5 Hz, J = 9.0 Hz, 1H), 2.42 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.29−2.17 (m, 3H), 1.42−1.38 (m, 2H), 1.22−1.15 (m, 10H), 0.80 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.1, 141.8, 140.8, 138.8, 138.3, 138.2, 137.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.0, 126.2, 115.9, 113.0, 86.6, 81.7, 78.6, 76.0, 74.6, 73.9, 73.4, 72.3, 71.0, 68.7, 48.3, 44.8, 31.8, 29.9, 29.5, 29.2, 29.1, 22.6, 14.1; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{50}H_{58}O_6SNa$ 809.3846; found 809.3847.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]-galactoside ***39***. Compound **22** (0.08 mmol, 52.6 mg) was treated according to the aforementioned method to give the pale yellow oil **39** (57.5 mg, 94%): IR ($CHCl_3$) 3363, 2924, 1585, 1454, 1099, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33−7.04 (m, 25H), 6.97−6.94 (m, 1H), 6.72 (d, J = 2.5 Hz, 1H), 6.34 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 4.91 (d, J = 12.0 Hz, 1H), 4.88 (d, J = 12.0 Hz, 1H), 4.75 (d, J = 11.5 Hz, 1H), 4.68 (d, J = 11.5 Hz, 1H), 4.61 (d, J = 11.5 Hz, 1H), 4.56 (d, J = 11.5 Hz, 1H), 4.25−4.18 (m, 4H), 4.09 (d, J = 10.0 Hz, 1H), 4.03 (d, J = 2.5 Hz, 1H), 3.63−3.60 (m, 1H), 3.48−3.42 (m, 3H), 3.22 (dd, J = 5.0 Hz, J = 9.5 Hz, 1H), 2.42 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.30 (dd, J = 9.0 Hz, J = 13.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.2, 141.8, 138.8, 138.4, 138.2, 138.0, 137.7, 137.5, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 126.8, 126.2, 116.0, 113.1, 86.7, 81.7, 78.7, 76.1, 74.6, 73.9, 73.4, 72.3, 71.0, 69.0, 48.0, 44.9, 34.2; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{49}H_{48}O_6SNa$ 787.3064; found 787.3070.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]glucoside ***40***. Compound **26** (0.07 mmol, 47.0 mg) was treated according to the aforementioned method to give the pale yellow oil **40** (48.0 mg, 92%): IR ($CHCl_3$) 2927, 1454, 1093, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (d, J = 8.5 Hz, 1H), 7.25−7.12 (m, 18H), 7.05−7.04 (m, 2H), 6.97 (brs, 1H), 6.82 (d, J = 8.0 Hz, 1H), 4.87 (d, J = 11.0 Hz, 1H), 4.83 (d, J = 11.0 Hz, 1H), 4.79 (d, J = 11.0 Hz, 1H), 4.75 (d, J = 11.0 Hz, 1H), 4.60 (d, J = 11.0 Hz, 1H), 4.56 (d, J = 11.0 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.35 (d, J = 12.0 Hz, 1H), 4.28 (dd, J = 7.0 Hz, J = 8.5 Hz, 1H), 4.24 (dd, J = 8.5 Hz, J = 10.0 Hz, 1H), 3.75−3.72 (m, 5H), 3.58 (dd, J = 3.5 Hz, J = 11.0 Hz, 1H), 3.52−3.49 (m, 1H), 3.40 (d, J = 11.0 Hz, 1H), 2.39 (dd, J = 7.0 Hz, J = 13.0 Hz, 1H), 2.33−2.21 (m, 3H), 1.42−1.38 (m, 2H), 1.26−1.20 (m, 2H), 0.77 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.2, 142.2, 138.5, 138.3, 138.2, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.0, 113.4, 86.3, 85.0, 81.9, 79.0, 75.3, 75.0, 74.8, 73.3, 72.3, 68.9, 55.6, 48.0, 44.8, 31.9, 29.2, 22.1, 13.7; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{47}H_{52}O_6SNa$ 767.3377; found 767.3375.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]glucoside ***41***. Compound **26** (0.07 mmol, 47.0 mg) was treated according to the aforementioned method to give the pale yellow oil **41** (52.1 mg, 93%): IR ($CHCl_3$) 2924, 1454, 1091, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (d, J = 8.5 Hz, 1H), 7.25−7.12 (m, 19H), 7.05−7.03 (m, 2H), 6.82 (dd, J = 2.5 Hz, J = 8.5 Hz, 1H), 4.87 (d, J = 11.0 Hz, 1H), 4.83 (d, J = 11.0 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 4.77 (d, J = 11.0 Hz, 1H), 4.60 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 11.0 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.34 (d, J = 12.0 Hz, 1H), 4.28 (dd, J = 7.5 Hz, J = 8.0 Hz, 1H), 4.24 (dd, J = 9.0 Hz, J = 9.0 Hz, 1H), 3.76−3.72 (m, 5H), 3.58 (dd, J = 3.5 Hz, J = 11.0 Hz, 1H), 3.52−3.50 (m, 1H), 3.40 (dd, J = 1.5 Hz, J = 11.0 Hz, 1H), 2.39 (dd, J = 7.5 Hz, J = 13.0 Hz, 1H), 2.33−2.20 (m, 3H), 1.43−1.40 (m, 2H), 1.22−1.18 (m, 10H), 0.80 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.2, 142.2, 138.5, 138.3, 138.2, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.0, 113.4, 86.3, 85.0, 81.9, 79.0, 75.3, 75.0, 74.8, 73.3, 72.3, 68.9, 55.6, 48.0, 44.8, 31.8, 29.8, 29.5, 29.2, 29.0, 22.6, 14.1; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{51}H_{60}O_6SNa$ 823.4003; found 823.4002.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]glucoside ***42***. Compound **27** (0.07 mmol, 49.0 mg) was treated according to the aforementioned method to give the pale yellow oil **42** (49.7 mg, 92%): IR ($CHCl_3$) 2931, 1454, 1091, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31−7.09 (m, 20H), 7.07−7.04 (m, 1H), 6.95 (brs, 1H), 6.81 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 4.89 (d, J = 11.0 Hz, 1H), 4.85 (d, J = 11.0 Hz, 1H), 4.82 (d, J = 12.0 Hz, 1H), 4.77 (d, J = 10.5 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 10.5 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.35 (d, J = 12.0 Hz, 1H), 4.29−4.23 (m, 2H), 3.83−3.80 (m, 2H), 3.75−3.72 (m, 2H), 3.59 (dd, J = 3.5 Hz, J = 11.0 Hz, 1H), 3.52−3.50 (m, 1H), 3.40 (d, J = 11.0 Hz, 1H), 2.39 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.32−2.24 (m, 3H), 1.75−1.71 (m, 2H), 1.42−1.39 (m, 2H), 1.27−1.22 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H), 0.77 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.8, 142.1, 138.6, 138.3, 137.9, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 125.9, 113.9, 86.3, 85.0, 81.9, 79.1, 75.3, 75.0, 74.9, 73.3, 72.3, 69.8, 68.9, 48.0, 44.8, 38.9, 31.9, 29.2, 22.7, 13.7, 10.7; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{49}H_{56}O_6SNa$ 795.3690; found 795.3690.

2,3,4,6-Tetra-O-benzyl-1,1-C,C-spiro[Indane-1,2′-pyran]glucoside ***43***. Compound **27** (0.07 mmol, 49.0 mg) was treated according to the aforementioned method to give the pale yellow oil **43** (55.1 mg, 95%): IR ($CHCl_3$) 2926, 1454, 1093, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29−7.13 (m, 20H), 7.05−7.03 (m, 1H), 6.95 (d, J = 2.5 Hz, 1H), 6.81 (dd, J = 2.5 Hz, J = 8.5 Hz, 1H), 4.89 (d, J = 11.0 Hz, 1H), 4.85 (d, J = 11.0 Hz, 1H), 4.82 (d, J = 12.0 Hz, 1H), 4.77 (d, J = 10.5 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 10.5 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.35 (d, J = 12.0 Hz, 1H), 4.29−4.23 (m, 2H), 3.83−3.79 (m, 2H), 3.77−3.73 (m, 2H), 3.60 (dd, J = 3.5 Hz, J = 11.0 Hz, 1H), 3.50 (ddd, J = 2.0 Hz, J = 3.5 Hz, J = 10.0 Hz, 1H), 3.40 (dd, J = 2.0 Hz, J = 11.0 Hz, 1H), 2.39 (dd, J = 6.5 Hz, J = 13.0 Hz, 1H), 2.32−2.18 (m, 3H), 1.75−1.71 (m, 2H), 1.45−1.39 (m, 2H), 1.22−1.15 (m, 10H), 0.97 (t, J = 7.5 Hz, 3H), 0.80 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.8, 142.1, 138.6, 138.3, 137.9, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 125.9, 114.0, 86.3, 85.0, 82.0, 79.1, 75.3, 75.0, 74.9, 73.3, 72.3, 69.8, 68.9, 48.0, 44.9, 39.2, 31.8, 29.8, 29.4, 29.2, 29.0, 22.6, 14.1, 10.6; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{53}H_{64}O_6SNa$ 851.4316; found 851.4314.

2,3,4,6-Tetra-O-benzyl-1-C-(dibenzylthioacetal)-α-1-C-(4-methylphenyl)-D-galactopyranose ***44***. Compound **11** (0.08 mmol, 52.5 mg) was treated according to the aforementioned method to give the pale yellow oil **44** (68.0 mg, 96%): $[\alpha]^{25}_D$ +102.0 (c 1.4, $CHCl_3$); IR ($CHCl_3$) 2922, 1494, 1454, 1099 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, J = 8.0 Hz, 2H), 7.29−7.17 (m, 20H), 7.06−7.02 (m, 6H), 6.98−6.95 (m, 4H), 6.86 (d, J = 8.0 Hz, 2H), 4.95 (d, J = 11.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.65 (d, J = 11.5 Hz, 1H), 4.55 (brs, 2H), 4.51 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 12.0 Hz, 1H), 4.35 (d, J = 12.0 Hz, 1H), 4.23 (d, J = 10.5 Hz, 1H), 3.75 (brs, 1H), 3.69−3.67 (m, 1H), 3.64 (d, J = 13.0 Hz, 1H), 3.61 (dd, J = 2.5 Hz, J = 10.5 Hz, 1H), 3.57 (d, J = 13.0 Hz, 1H), 3.58−3.45 (m, 4H), 3.43 (d, J = 13.0 Hz, 1H), 2.47−2.38 (m, 2H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.2, 138.5, 138.4, 138.3, 137.0, 136.5, 129.1, 129.0, 128.9, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 127.2, 126.6, 81.8, 81.3, 81.0, 76.2, 75.7, 74.6, 73.4, 72.3, 71.9, 69.1, 48.8, 45.2, 35.5, 35.4, 21.0; HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{57}H_{58}O_5S_2Na$ 909.3618; found 909.3622.

2,3,4,6-Tetra-O-benzyl-1-C-(dibenzylthioacetal)-α-1-C-(4-methoxylphenyl)-D-galactopyranose ***45***. Compound **13** (0.07 mmol,

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47.0 mg) was treated according to the aforementioned method to give the pale yellow oil **45** (60.0 mg, 95%): $[\alpha]^{25}_{D}$ +65.5 (*c* 1.4, $CHCl_3$); IR ($CHCl_3$) 2918, 1506, 1454, 1068 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, *J* = 9.0 Hz, 2H), 7.30−7.17 (m, 20H), 7.06−7.02 (m, 6H), 6.97−6.94 (m, 4H), 6.57 (d, *J* = 9.0 Hz, 2H), 4.96 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.56 (brs, 2H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.21 (d, *J* = 10.5 Hz, 1H), 3.75 (brs, 1H), 3.70 (s, 3H), 3.66−3.63 (m, 2H), 3.58 (dd, *J* = 2.5 Hz, *J* = 10.5 Hz, 1H), 3.56 (d, *J* = 13.0 Hz, 1H), 3.54−3.47 (m, 3H), 3.44−3.41 (m, 2H), 2.45 (dd, *J* = 4.5 Hz, *J* = 15.5 Hz, 1H), 2.37 (dd, *J* = 7.5 Hz, *J* = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.4, 139.2, 139.1, 138.5, 138.4, 138.3, 131.8, 129.2, 129.1, 129.0, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 127.4, 127.3, 126.6, 113.5, 81.7, 81.5, 80.9, 76.2, 75.7, 74.6, 73.4, 72.3, 71.9, 69.1, 55.1, 48.8, 45.1, 35.5, 35.3; HRMS (ESI^+): *m*/*z* $[M + Na]^+$ calcd for $C_{57}H_{58}O_6S_2Na$ 925.3567; found 925.3570.

2,3,4,6-Tetra-O-benzyl-1-C-(di-n-butylthioacetal)-α-1-C-(3-methylphenyl)-D-galactopyranose **46**. Compound **18** (0.08 mmol, 52.5 mg) was treated according to the aforementioned method to give the pale yellow oil **46** (60.9 mg, 93%): $[\alpha]^{25}_{D}$ +46.5 (*c* 1.4, $CHCl_3$); IR ($CHCl_3$) 2924, 2360, 1608, 1454, 1103 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.30−7.15 (m, 20H), 7.07 (d, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 11.5 Hz, 1H), 5.00 (d, *J* = 11.5 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 10.5 Hz, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 3.98−3.96 (m, 1H), 3.78 (d, *J* = 2.5 Hz, 1H), 3.69 (dd, *J* = 2.5 Hz, *J* = 10.5 Hz, 1H), 3.55−3.51 (m, 3H), 2.55−2.31 (m, 6H), 1.38−1.31 (m, 4H), 1.24−1.17 (m, 4H), 0.75 (t, *J* = 7.5 Hz, 3H), 0.73 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.0, 139.5, 139.2, 138.4, 138.3, 137.4, 128.7, 128.3, 128.1, 128.0, 127.5, 127.4, 127.3, 127.2, 127.0, 125.2, 81.7, 81.0, 80.3, 75.9, 75.6, 74.5, 73.4, 72.0, 71.9, 69.3, 49.7, 44.9, 31.3, 31.2, 30.9, 30.5, 22.1, 22.1, 21.7, 13.7, 13.6; HRMS (ESI^+): *m*/*z* $[M + Na]^+$ calcd for $C_{51}H_{62}O_5S_2Na$ 841.3931; found 841.3938.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02891.

^1H and ^{13}C NMR spectra of compounds **3**−**46**, plus 2D-COSY and -NOESY spectra of **13** and **29** (PDF)

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Notes

The authors declare no competing financial interest.

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