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Note

Aryl C-glycosylation of phenols with glycosyl trifluoroacetimidates

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Abstract—Aryl C-glycosylation of a variety of phenols with glycosyl trifluoroacetimidates in the presence of TMSOTf was examined, leading to the corresponding *ortho*-hydroxyaryl C-glycosides in variable yields.

Keywords: C-Glycosylation; Aryl C-glycosides; Glycosyl trifluoroacetimidates; Phenols

The Friedel–Crafts reaction between glycosyl donors and electron-rich aromatic compounds is the earliest and the most straightforward approach,[1] which is also employed by Nature,[2] for the synthesis of aryl C-glycosides.[3] When a phenol is used in the reaction, the corresponding O-glycoside might be produced first, which then undergoes an O → C rearrangement to give the *ortho*-hydroxyaryl C-glycoside in a regioselective manner.[3,4] In this thermodynamically controlled C-glycosylation reaction, matching of the reactivities of the glycosyl donor and the aromatic acceptor, which determines the reaction conditions, has proven to be critical for producing the desired C-glycoside. Otherwise, competing side reactions of the two components and the resulting coupling products will lead to complex mixtures. Among the various glycosyl donors that have been applied in the aryl C-glycosylation, glycosyl trichloroacetimidates are one of the most successful types and require mild activation conditions using TMSOTf or $BF_3{\cdot}OEt_2$ as promoters.[5] Recently, glycosyl trifluoroacetimidates have been developed as valuable alternatives to the glycosyl trichloroacetimidates.[6] The glycosyl trifluoroacetimidates are relatively more self stable, but can behave as efficiently as the corresponding glycosyl trichloroacetimidates during glycosylation. Here, we report the C-glycosylation of a variety of phenols with perbenzylated gluco-, galacto-, and mannopyranosyl trifluoroacetimidates.

We first tried the coupling of 2,3,4,6-tetra-*O*-benzyl-glucopyranosyl trifluoroacetimidate (**1a**)[6] with *p*-methylphenol (**2a**) and 7-hydroxycoumarin (**2b**). Even under forcing conditions (1.2 equiv of TMSOTf at rt), only the corresponding α-O-glycosides (**3aa** and **3ab**) were isolated as the major products (Table 1, entries 1 and 2); the desired C-glycosides were not detected. The more electron-rich mono- and dimethoxyphenols **2c–f** were then employed as acceptors for the C-glycosylation with trifluoroacetimidate **1a**. Under a variety of conditions with TMSOTf or $BF_3{\cdot}EtO_2$ as a promoter, the reactions led to complex mixtures. Thus, only the major products (1.2 equiv of TMSOTf, 0 °C → rt) were isolated, which were characterized and shown to be the expected *ortho*-hydroxyaryl-β-C-glycosides (**3ac–af**). The yields were quite low (21–37%) except for **3af** (71%). When naphthen-2-ol (**2g**), which bears an exceedingly nucleophilic 1-carbon, was used as an acceptor, the C-glycoside **3ag** was obtained in a good 69% yield. These results are in accordance with those of the corresponding coupling reactions using 2,3,4,6-tetra-*O*-benzyl-glucopyranosyl trichloroacetimidate (0.05–0.1 equiv of TMSOTf, −30 °C → rt)[5c] and 2,3,4,6-tetra-*O*-benzyl-glucopyranosyl diphenylphosphate (1.2 equiv of TMSOTf, 0 °C → rt)[7] as donors. However, when a catalytic amount of TMSOTf (0.1 equiv) was used to promote the coupling of **1a** and **2g**, only the

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Table 1. Coupling of the glycosyl *N*-phenyltrifluoroacetimidates (**1a**–**c**) with phenol acceptors (**2a**–**h**)[a]

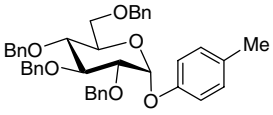
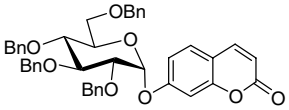
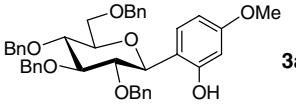
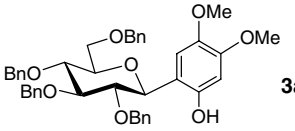
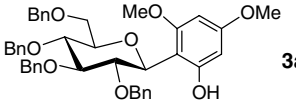
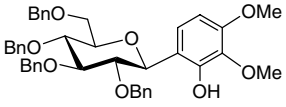
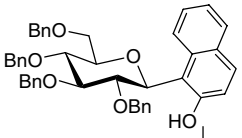
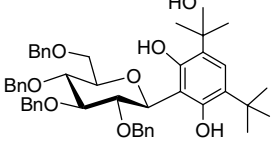
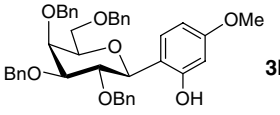
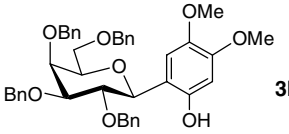
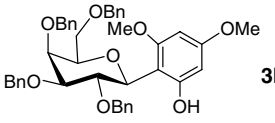
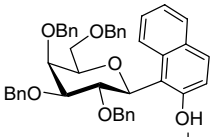
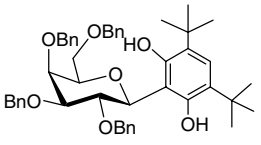
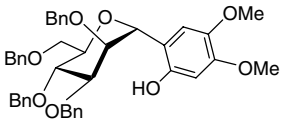
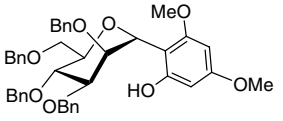
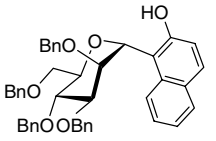
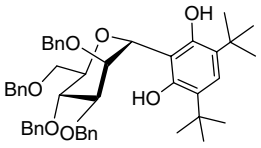
Entry	Donor	Acceptor	Product	Yield (%)[b]
1	**1a**	**2a**	 **3aa**	47[c]
2		**2b**	 **3ab**[5c]	41
3		**2c**	 **3ac**[5c]	27
4		**2d**	 **3ad**[5c]	21
5		**2e**	 **3ae**[5c]	37
6		**2f**	 **3af**[5c]	71
7		**2g**	 **3ag**[7]	69
8		**2h**	 **3ah**	56
9	**1b**	**2c**	 **3bc**	59[c]
10		**2d**	 **3bd**	45[c]
11		**2e**	 **3be**	67[c]
12		**2f**	—	—[d]
13		**2g**	 **3bg**	76[c]
14		**2h**	 **3bh**	69[c]

Table 1 (*continued*)

Entry	Donor	Acceptor	Product	Yield (%)[b]
15	**1c**	**2c**	—	—[d]
16		**2d**	 **3cd**	48[e]
17		**2e**	 **3ce**	76[e]
18		**2f**	—	—[d]
19		**2g**	 **3cg**[7]	96
20		**2h**	 **3ch**	74[e]

[a] Reaction conditions: **1** (1.2 equiv), **2** (1.0 equiv), TMSOTf (1.2 equiv), CH_2Cl_2, 4 Å MS, 0 °C → rt.
[b] Isolated yields (based on phenol **2**).
[c] The anomeric configuration was confirmed by ^1H NMR analysis of the corresponding debenzylation product.
[d] It was not possible to purify the desired C-glycoside.
[e] The anomeric configuration of the mannopyranosides **3cd**, **3ce**, and **3ch** was assumed to be α, as that of the known compound **3cg**.

corresponding α-O-glycoside[7] was obtained (~60%). The last phenol employed as an acceptor is 4,6-di-*tert*-butyl-1,3-dihydroxybenzene (**2h**) in an attempt to obtain the corresponding 2-(β-D-glucopyranosyl)-1,3-dihydroxybenzene derivative **3ah**. Compound **3ah**, if its 4,6-di-*tert*-butyl group could be taken off, would be a key intermediate for the synthesis of puerarin and related isoflavone-C-glycosides.[8] Gratifyingly, coupling of the resorcinol derivative **2h** with trifluoroacetimidate **1a** afforded the desired 2-C-β-D-glucopyranoside **3ah** in a good 56% yield (Fig. 1).

However, deprotection of the 4,6-di-*tert*-butyl groups in **3ah** under a variety of acidic conditions (in the presence of CF_3COOH, H_3PO_4, $AlCl_3$, K-10, or $Zn(OAc)_2$)[9] led to complex mixtures; the desired compound **4** was obtained in not more than 20% yield (CF_3COOH, rt)

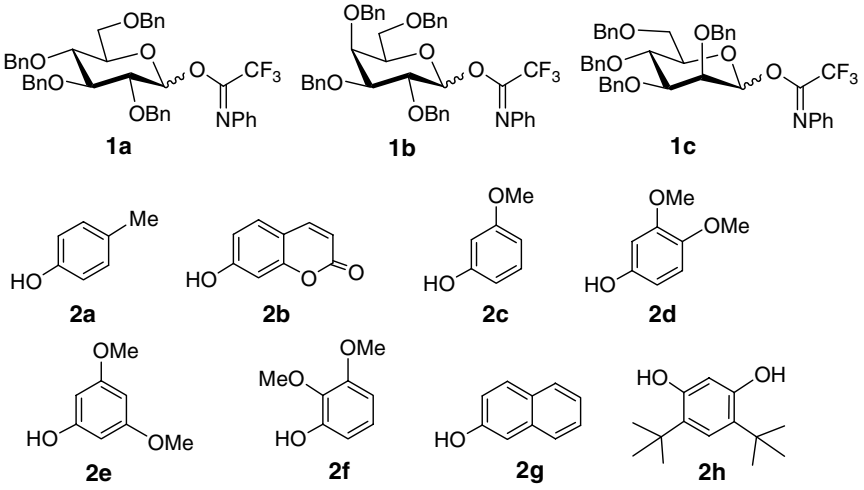
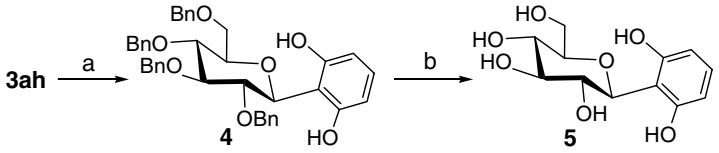


Figure 1. Glycosyl trifluoroacetimidate donors (**1a**–**c**) and phenol acceptors (**2a**–**h**).



Scheme 1. Reagents and conditions: (a) CF_3COOH, rt, 19%; (b) H_2, Pd/C, CH_3OH/EtOAc, rt, 64%.

(Scheme 1). The removal of the benzyl groups in **4** by hydrogenolysis gave 2-(β-D-glucopyranosyl)-1,3-dihydroxybenzene **5**. The analytical data of **5** are in full agreement with those for the natural product isolated from *Pterocarpes marsupium*,[10] which further confirmed the assigned structure for the C-glycosylation product **3ah**.

The C-glycosylation of the electron-rich phenols **2c–h** with 2,3,4,6-tetra-*O*-benzyl-galacto- and mannopyranosyl trifluoroacetimidates (**1b** and **1c**)[6] was also examined with the promotion of TMSOTf (1.2 equiv, 0 °C → rt). All the reactions led to a number of spots on the TLC; only the major products were purified and characterized (Table 1). In general, the C-mannopyranosides were obtained in the highest yields, while the corresponding C-glucopyranosides gave the lowest yields (cf., **3ad/3bd/3cd**; **3ae/3be/3ce**; **3ag/3bg/3cg**; and **3ah/3bh/3ch**).

In summary, the treatment of the electron-rich phenols with glycosyl trifluoroacetimidates in the presence of TMSOTf led to the corresponding *ortho*-hydroxyaryl C-glycosides as the major products. The regioselectivity of the C-glycosylation was fully determined by the phenolic acceptor and the stereoselectivity was controlled by the glycosyl donors to give the relatively more stable C-β-gluco- and galactopyranosides and the C-α-mannopyranosides. It was found that C-glycosylation with mannopyranosyl donors gave the highest yields, while the glucopyranosyl donors gave the lowest yields.

1. Experimental

1.1. General methods

See Ref. 11.

1.2. Typical procedure for the coupling of glycosyl *N*-phenyltrifluoroacetimidates with phenols

A mixture of the glycosyl trifluoroacetimidate **1c** (426 mg, 0.6 mmol), naphthen-2-ol **2g** (72 mg, 0.5 mmol), and 4 Å MS (~200 mg) in anhydrous CH_2Cl_2 (5 mL) was stirred at 0 °C for 30 min under a N_2 atmosphere. Then, TMSOTf (0.12 mL, 0.6 mmol) was added. After stirring at 0 °C for 1 h, the mixture was warmed to rt within ~3 h. The reaction was quenched by the addition of Et_3N (0.5 mL) and stirring continued for 30 min. The resulting mixture was filtered through Celite. The filtrates were concentrated to give a brown syrup, which was subjected to silica gel column chromatography (15:1, petroleum ether–EtOAc) to afford **3cg** (319 mg, 96%) as a yellow oil.

1.2.1. *p*-Methylphenyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (3aa). $[\alpha]_D^{24}$ +72.8 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.36–6.94 (m, 23H), 5.51 (br s, 1H), 5.04 (d, $J = 11.1$ Hz, 1H), 4.88 (d, $J = 10.8$ Hz, 2H), 4.77–4.42 (m, 5H), 4.20 (t, $J = 9.6$ Hz, 1H), 3.92 (d, $J = 9.3$ Hz, 1H), 3.82 (d, $J = 9.9$ Hz, 1H), 3.75 (br s, 2H), 3.62 (d, $J = 10.5$ Hz, 1H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.8, 138.3, 138.2, 137.9, 130.7, 128.3, 128.0, 127.9, 127.7, 127.6, 126.8, 122.0, 114.6, 96.1, 81.9, 80.1, 75.7, 75.1, 73.4, 72.9, 70.9, 68.4, 29.7. HR-MALDI MS (*m*/*z*): calcd for $C_{41}H_{42}O_6Na$ $[M+Na]^+$: 653.2873. Found: 653.2897.

1.2.2. 4,6-Di-*tert*-butyl-2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-1,3-dihydroxybenzene (3ah). $[\alpha]_D^{24}$ +18.1 (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.37–6.97 (m, 21H), 4.98 (d, $J = 11.1$ Hz, 2H), 4.91 (d, $J = 11.7$ Hz, 1H), 4.85 (d, $J = 11.8$ Hz, 1H), 4.64 (dd, $J = 11.8$, 6.9 Hz, 2H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 12.0$ Hz, 1H), 4.29 (d, $J = 10.8$ Hz, 1H), 3.99–3.88 (m, 1H), 3.82 (d, $J = 9.0$ Hz, 1H), 3.78–3.66 (m, 3H), 3.57 (d, $J = 9.6$ Hz, 1H), 1.26 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.4, 137.9, 137.8, 128.4, 128.3, 128.0, 127.8, 127.6, 127.4, 124.7, 112.6, 86.5, 81.5, 78.7, 75.7, 75.4, 75.2, 73.4, 67.5, 34.6; HR-MALDI MS (*m*/*z*): calcd for $C_{48}H_{56}O_7Na$ $[M+Na]^+$: 767.3918. Found: 767.3929.

1.2.3. 2-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-5-methoxyphenol (3bc). $[\alpha]_D^{24}$ −8.94 (*c* 1.0 $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.35–7.24 (m, 17H), 7.06 (d, $J = 6.9$ Hz, 3H), 6.49 (s, 1H), 6.44 (d, $J = 6.9$ Hz, 2H), 5.07 (d, $J = 8.7$ Hz, 1H), 4.76 (s, 2H), 4.67 (d, $J = 11.4$ Hz, 1H), 4.49–4.41 (m, 3H), 4.30 (d, $J = 9.3$ Hz, 1H), 4.17 (t, $J = 9.3$ Hz, 1H), 4.07 (s, 1H), 3.79 (s, 3H), 3.66 (d, $J = 6.6$ Hz, 2H), 3.57 (d, $J = 6.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.1, 156.9, 138.4, 137.7, 130.2, 128.5, 128.4, 128.3, 128.2, 127.9, 127.7, 127.4, 116.2, 105.6, 102.6, 83.6, 81.9, 75.5, 74.4, 73.7, 72.6, 68.5, 55.3; HR-MALDI MS (*m*/*z*): calcd $C_{41}H_{42}O_7Na$ $[M+Na]^+$: 669.2823. Found: 669.2831.

1.2.4. 6-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-3,4-dimethoxyphenol (3bd). $[\alpha]_D^{27}$ +3.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.39–7.24 (m, 18H), 7.06 (br s, 2H), 6.65 (s, 1H), 6.54 (s, 1H), 5.09 (d, *J* = 11.7 Hz, 1H), 4.79 (br s, 2H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 9.9 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 12.3 Hz, 1H), 4.23–4.18 (m, 2H), 4.07 (br s, 1H), 3.92 (d, *J* = 10.5 Hz, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 3.68 (d, *J* = 6.6 Hz, 2H), 3.59 (d, *J* = 5.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 138.5, 138.4, 137.7, 128.5, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 114.3, 112.8, 101.8, 83.6, 81.9, 78.8, 75.6, 74.5, 73.7, 73.6, 72.6, 68.5, 56.3, 55.9; HR-MALDI MS (*m*/*z*): calcd $C_{42}H_{44}O_8Na$ $[M+Na]^+$: 699.2928. Found: 699.2940.

1.2.5. 2-(Tetra-*O*-benzyl-β-D-galactopyranosyl)-3,5-dimethoxyphenol (3be). $[\alpha]_D^{27}$ +24.5 (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.28–7.13 (m, 18H), 6.97 (br s, 2H), 6.04 (s, 1H), 5.97 (s, 1H), 5.05 (d, *J* = 11.7 Hz, 1H), 4.99 (d, *J* = 11.7 Hz, 1H), 4.90 (d, *J* = 6.3 Hz, 1H), 4.69 (t, *J* = 11.4 Hz, 2H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.44 (d, *J* = 10.2 Hz, 1H), 4.36 (d, *J* = 12.3 Hz, 1H), 4.19 (t, *J* = 9.3 Hz, 1H), 3.99 (s, 1H), 3.95 (d, *J* = 11.2 Hz, 1H), 3.69 (s, 3H), 3.61 (s, 3H), 3.61–3.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4, 158.4, 158.2, 138.6, 138.2, 137.7, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 105.5, 94.5, 90.0, 83.9, 78.9, 75.5, 74.4, 74.1, 73.8, 73.5, 72.8, 68.4, 55.5, 55.3; HR-MALDIMS (*m*/*z*): calcd $C_{42}H_{44}O_8Na$ $[M+ Na]^+$: 699.2928. Found: 699.2949.

1.2.6. 1-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-naphthen-2-ol (3bg). $[\alpha]_D^{24}$ 50.1 (*c* 1.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 2H), 7.35–7.08 (m, 18H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 2H), 6.32 (d, *J* = 7.8 Hz, 2H), 5.28 (d, *J* = 9.6 Hz, 1H), 5.05 (d, *J* = 11.7 Hz, 1H), 4.72 (s, 2H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.39–4.29 (m, 3H), 4.11 (d, *J* = 9.6 Hz, 1H), 4.06 (s, 1H), 3.73 (t, *J* = 6.6 Hz, 2H), 3.52 (d, *J* = 6.3 Hz, 2H), 3.45 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.8, 138.5, 137.7, 137.2, 132.7, 130.3, 128.6, 127.9, 127.8, 127.6, 127.5, 127.4, 126.5, 122.9, 122.8, 119.5, 115.5, 100.3, 83.9, 79.1, 75.6, 74.5, 73.8, 73.6, 73.3, 73.1, 72.9, 72.8, 72.2, 68.5; HR-MALDI MS (*m*/*z*): calcd for $C_{42}H_{44}O_8Na$ $[M+Na]^+$: 689.2874. Found: 689.2889.

1.2.7. 4,6-Di-*tert*-butyl-2-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-1,3-dihydroxybenzene (3bh). $[\alpha]_D^{27}$ +4.6 (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.36–7.01 (m, 21H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.88–4.64 (m, 5H), 4.49 (br s, 1H), 4.33 (d, *J* = 10.5 Hz, 2H), 4.12 (br s, 1H), 3.72 (t, *J* = 8.1 Hz, 2H), 3.60 (d, *J* = 5.7 Hz, 2H), 1.36 (s, 18H);^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.6, 137.9, 137.7, 136.8, 128.5, 128.2, 127.9, 127.5, 127.4, 124.6, 112.9, 84.4, 78.9, 77.6, 75.9, 75.8, 74.2, 73.5, 72.8, 72.1, 68.1, 34.5; HR-MALDI MS (*m*/*z*): calcd for $C_{48}H_{56}O_8Na$ $[M+Na]^+$: 767.3918. Found: 767.3923.

1.2.8. 6-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-3,4-dimethoxyphenol (3cd). $[\alpha]_D^{27}$ +10.6 (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.35–7.13 (m, 20H), 6.49 (s, 1H), 6.33 (s, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.69 (s, 2H), 4.67–4.46 (m, 6H), 4.17 (t, *J* = 9.6 Hz, 1H), 3.96 (s, 1H), 3.86 (s, 3H), 3.76–3.72 (m, 6H), 3.54 (d, *J* = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.4, 112.6, 111.5, 101.9, 84.2, 82.3, 79.6, 77.8, 75.3, 74.6, 74.4, 73.5, 72.3, 68.8, 56.8, 55.9; HR-MALDI MS (*m*/*z*): calcd for $C_{42}H_{44}O_8Na$ $[M+Na]^+$: 699.2928. Found: 699.2913.

1.2.9. 2-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-3,5-dimethoxyphenol (3ce). $[\alpha]_D^{27}$ +20.2 (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 8.66 (s, 1H), 7.32–7.14 (m, 20H), 6.11 (s, 1H), 5.93 (s, 1H), 4.91 (s, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.67–4.42 (m, 7H), 4.15 (t, *J* = 9.6 Hz, 1H), 3.93 (br s, 1H), 3.77 (s, 3H), 3.74 (t, *J* = 9.0 Hz, 3H), 3.66 (s, 3H), 3.53 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.9, 158.9, 157.1, 138.5, 138.3, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 127.2, 103.2, 94.5, 90.3, 84.1, 79.6, 76.8, 76.2, 75.2, 74.5, 74.4, 73.4, 72.1, 68.8, 55.4, 55.3; HR-MALDI MS (*m*/*z*): calcd for $C_{42}H_{44}O_8Na$ $[M+Na]^+$: 699.2928. Found: 699.2919.

1.2.10. 4,6-Di-*tert*-butyl-2-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-1,3-dihydroxybenzene (3ch). $[\alpha]_D^{27}$ −1.1 (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.25–6.90 (m, 21H), 5.37 (d, *J* = 11.8 Hz, 1H), 4.52–4.36 (m, 5H), 4.29 (d, *J* = 9.3 Hz, 2H), 4.14–4.02 (m, 3H), 3.89–3.71 (m, 4H), 1.31 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.0, 137.7, 136.6, 128.7, 128.4, 128.1, 127.9, 127.6, 124.3, 112.9, 75.9, 75.6, 73.3, 73.2, 72.5, 71.5, 67.2, 34.6; HR-MALDI MS (*m*/*z*): calcd for $C_{48}H_{56}O_8Na$ $[M+Na]^+$: 767.3907. Found: 767.3907.

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