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C-Glycosylation of Substituted β-Naphthols with Trichloroacetimidate Glycosyl Donors

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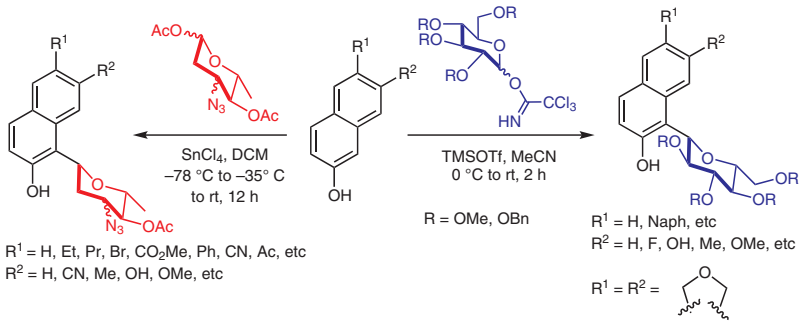

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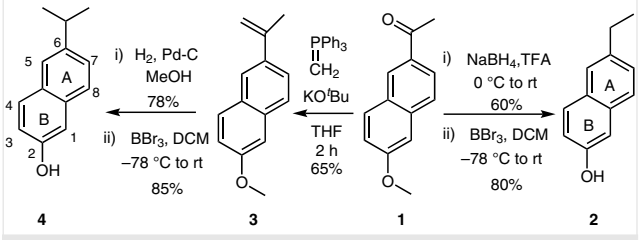
Abstract Several glycosyl donors have been systematically investigated for C-glycosylation of substituted β-naphthols to delineate the effect of the substituents. Whereas glycosylations of the parent 2-naphthol are smoothly achievable, those of differently substituted 2-naphthols are cumbersome. Efficiency of the glycosylation depends on the nature of both the glycosyl donors and the substituents of the arene ring. Among various glycosyl donors, trichloroacetimidate glycosyl donors are found to be superior for glycosylation with substituted 2-naphthols.

Key words C-glycosylation, 2-naphthols, Lewis acids, trichloroacetimidate, glycosyl donors, substituent effects

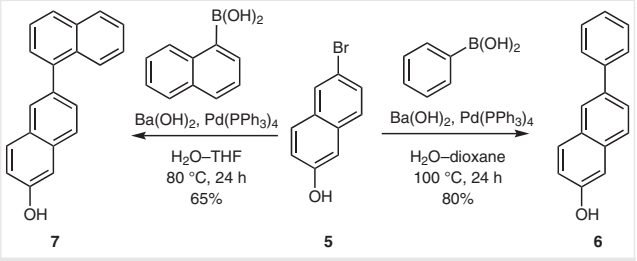
C-Aryl glycosides are a class of compounds in which a carbohydrate moiety is attached to an aromatic ring through a C–C bond at the anomeric position.[1] Many methodologies have been developed over the last few decades for the synthesis of *C*-aryl glycosides.[2] Complex natural products have been synthesized by application of the methodologies. Depending upon the core structures of the aglycon moieties in naturally occurring *C*-aryl glycosides, glycosylation of different arenes, phenols or naphthols are carried out to achieve a total synthesis. Phenols and α-naphthols have been studied extensively for glycosylation.[3] However, studies on glycosylation of β-naphthols are scanty. Only the parent β-naphthol has been studied for its glycosylation[4] with different glycosyl donors, which include (i) anomeric OH/OMe as glycosyl donors;[5] (ii) anomeric acetate;[6] (iii) anomeric fluoride;[7] (iv) anomeric phosphates[8] and (v) anomeric trichloroacetimidate[9] as glycosyl donors. In connection with our studies on the synthesis of *C*-glycosylated natural product,[10] we recently reported on the deleterious effect of a C7 methyl group on the *C*-glycosylation of β-naphthol with an acetate glycosyl donor.[11] In a continuation of this study, we examined glycosylation reactions of differently substituted β-naphthols with different glycosyl donors. Herein, we report on the suitability of trichloroacetimidate glycosyl donors for various β-naphthols.

Since our long-term objective was to achieve a total synthesis of a *C*-glycosylated natural product, namely, mayamycin,[12] by the application of glycosylation of a suitable 2-naphthol derivative at an early stage of the synthetic route, we considered varying the substituents of ring A of the naphthols. For that purpose, we prepared various 2-naphthols with different substituents at the C6 or C7 position from commercially available naphthols. First, we investigated the effect of alkyl, aryl, ester, and bromo substituents at the C6 position of 2-naphthols on glycosylation with different glycosyl donors. To this end, 6-ethyl-2-naphthol (**2**)[13] and 6-isopropyl-2-naphthol (**4**)[14] were synthesized from commercially available ketone **1** (Scheme 1) by following reported methods.



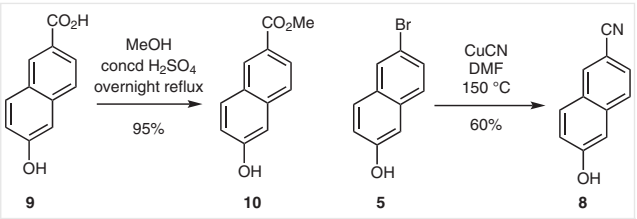
Scheme 1 Synthesis of 6-ethyl-2-naphthol (**2**) and 6-isopropyl-2-naphthol (**4**)

6-Phenyl-2-naphthol (**6**)[15] and 6-naphthyl-2-naphthol (**7**)[16] were synthesized in a single step from commercially available 6-bromo-2-naphthol (**5**) by using reported methods (Scheme 2).



Scheme 2 Synthesis of 6-phenyl-2-naphthol (**6**) and 6-naphthyl-2-naphthol (**7**)

For 2-naphthols containing electron-withdrawing groups at the C6 position, we chose methyl-6-hydroxy-2-naphthoate (**10**)[17] and 6-cyano-2-naphthol (**8**),[18] which were obtained as indicated in Scheme 3.



Scheme 3 Synthesis of methyl-6-hydroxy-2-naphthoate (**10**) and 6-cyano-2-naphthol (**8**)

We also prepared 7-methyl-2-naphthol (**11**),[11] 7-methoxy-2-naphthol (**12**),[19] 7-fluoro-2-naphthol (**13**), and 7-hydroxy-2-naphthol (**14**), which have a substituent at the C7 position (Figure 1).

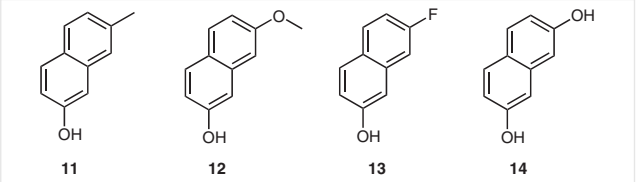
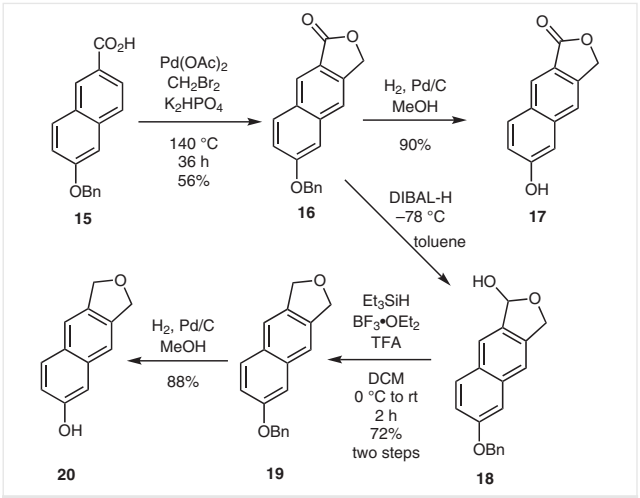


Figure 1 2-Naphthols having C7 substituents

Two 6,7-fused β-naphthols, namely **17** and **20**, were synthesized, as shown in Scheme 4. Naphthofuranone **17** was obtained by Yu lactonization[20] of **15** followed by debenzylation of **16** (H_2, Pd/C) (Scheme 4). Naphthofuran **20** was prepared by a sequence of (i) reduction of lactone **16** with diisobutylaluminum hydride (DIBAL-H) to furnish alcohol **18**, (ii) reduction of lactol **18** with Et_3SiH and borontrifluoride diethyl etherate to **19**, and (iii) debenzylation of naphthofuran **19**.

Keeping in mind the structures of aryl *C*-glycoside natural products, we chose to experiment with glycosyl donor **21** for *C*-glycosylation of the 2-naphthols (Figure 2).

Azido acetate **21**[21] was selected because of its higher reactivity[22] and because of our earlier success with *C*-glycosylation of the parent 2-naphthol.[10] With azido sugar **21**, the glycosylation reactions of naphthols **2**, **4**, **5**, **6**, and **10** were carried out at –78 °C with $SnCl_4$. The results are summarized in Table 1. However, the reactions of donor **21** with naphthols **11**, **12**, and **14** were not successful under the same reaction conditions (Scheme 5).



Scheme 4 Synthesis of 6,7-fused β-naphthols **17** and **20** having a fused ring between C6 and C7

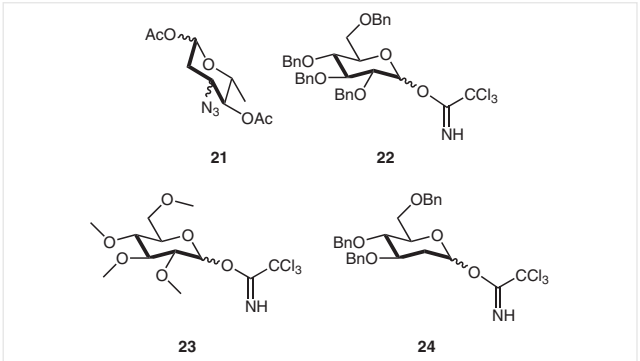
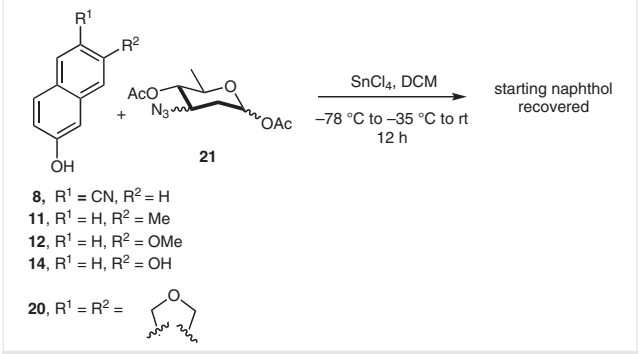
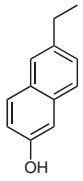
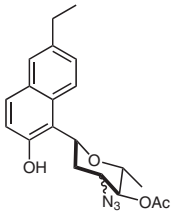
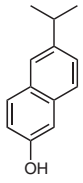
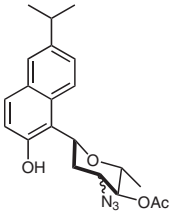
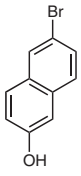
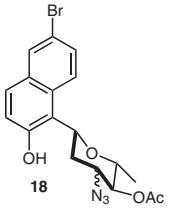
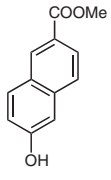
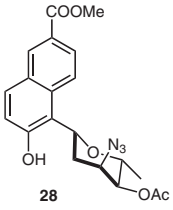
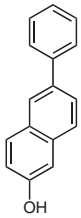
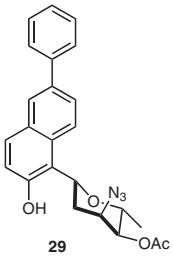


Figure 2 Glycosyl donors used in this study



Scheme 5 Attempted glycosylation of **21** with naphthols **8**, **11**, **12**, **14**, and **20**

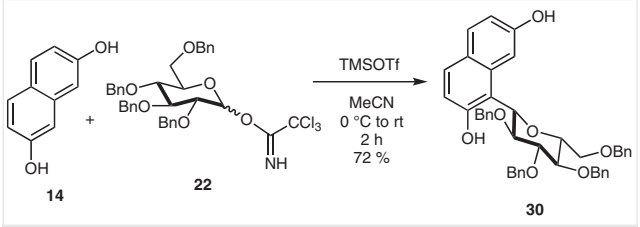
Table 1 Summary of C-Glycosylations of 2-Naphthols with Glycosyl Donor **21**

Entry	Glycosyl acceptor	Product	Yield (%)[a,b]
1	 **2**	 **25a** (N_3 in equatorial), **25b** (N_3 in axial)	**25a** 52 **25b** 29
2	 **4**	 **26a** (N_3 in equatorial), **26b** (N_3 in axial)	**26a** 44 **26b** 30
3	 **5**	 **27a** (N_3 in equatorial), **27b** (N_3 in axial)	**27a** 42 **27b** 35
4	 **10**	 **28**	59
5	 **6**	 **29**	63

[a] Reaction conditions: $SnCl_4$, DCM, –78 to –35 °C to r.t., 12 h.
[b] The ratio of the products was determined after column chromatographic purification. In all cases anomeric configuration was β. Two isomers in entries 1, 2 and 3 are due to different configuration at C3 of the sugar. For entries 4 and 5 only one isomer was obtained.

From the glycosylation studies (Table 1), it is evident that alkyl or aryl substituents at the C6 position do not pose any problem in glycoside formation. Glycosylation of 6-ethyl-2-naphthol (**2**), and 6-isopropyl-2-naphthol (**4**), occurred smoothly with glycosyl donor **21** (entries 1 and 2) producing the desired *C*-glycosides **25** (**a** and **b**) and **26** (**a** and **b**) in good yields. Similarly, bromonaphthol **5** gave **27a** and **27b** in 42% and 35% yield, respectively (entry 3). However, in case of naphthol **10**, in which an ester group is present at the C6 position (entry 4), *C*-glycoside **28** was obtained only in 59% yield. For naphthol **6**, with a phenyl substituent at the C6 position, *C*-glycoside **29** was furnished in 63% isolated yield (entry 5). The reactions of donor **21** with naphthols **8**, **11**, **12**, **14**, and **20** were not fruitful and did not give any pure products. These results clearly show that C7 substituents of 2-naphthols have a deleterious effect on the glycosylation with donor **21**.

As a test case, we changed the glycosyl donor and used glycosyl donor **22**[23] for the substituted 2-naphthol **14** having a hydroxyl group at C7. Interestingly, the glycosylation reaction proceeded smoothly in the presence of TMSOTf to furnish glycoside **30** in 72% isolated yield (Scheme 6). Similar trichloroacetimidates have been used in the glycosylation of 7-hydroxy-2-naphthol (**14**)[9c] and 7-methoxy-2-naphthol (**12**)[9d] in the presence of TMSOTf in DCM.



Scheme 6 Glycosylation of donor **22** with naphthol **14**

The success of the glycosylation reaction (Scheme 6) encouraged us to further explore the reactivity of trichloroacetimidate glycosyl donors towards glycosylation with different 2-naphthols; the results are summarized in Table 2.

For 6-naphthyl-2-naphthol (**7**) we used **23**[23] as glycosyl donor and TMSOTf as Lewis acid, and obtained glycoside **31** in 86% isolated yield (Table 2, entry 1). The high yield of the glycosylation reaction using **23** as glycosyl donor prompted us to carry out glycosylations with other naphthols. 7-Fluoro-2-naphthol (**13**) and 7-methoxy-2-naphthol (**12**) in reaction with glycosyl donor **23** resulted in glycosides **32** and **33** in 92% and 81% isolated yields, respectively (entries 2 and 3). Most interestingly, 7-methyl-2-naphthol (**11**), which was inert to glycosylation with donor **21**, also reacted with donor **23**, giving *C*-glycoside **34** in 93% isolated yield (entry 4). Naphthol **20** also reacted with donor **23** under the standard conditions and glycoside **35** was obtained in 67% isolated yield (entry 5). 2-Deoxytrichloroacetimidate donor **24**[23] also furnished glycoside **36** in good yield on

treatment with naphthol **11** under the standard conditions (entry 6). Similar reactions of acetate donor **21** were carried out with naphthols **8**, **11**, **12**, **14**, and **20**. However, the corresponding glycosylated products were not obtained, and only starting naphthols were recovered.

Attempts at glycosylation of **8** and **17** (Figure 3) with donors **21**, **22**, and **23** failed to give any pure products. This is probably due to deactivation of the naphthalene ring with the electron-withdrawing substituents. Likewise, naphthols **37** and **38** did not undergo glycosylation with glycosyl donors **21**, **22**, or **23** under different conditions.

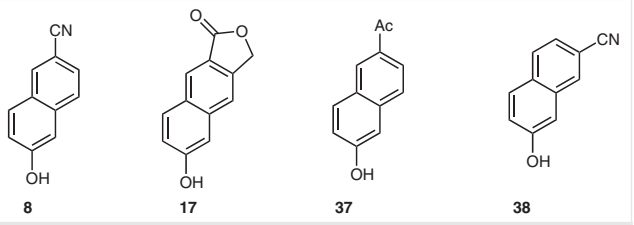
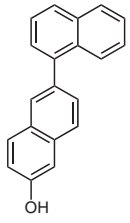
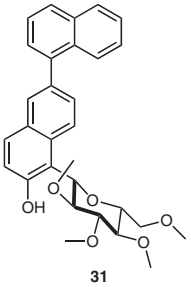
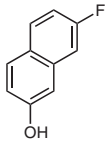
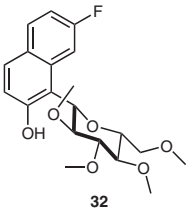
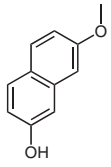
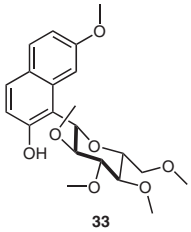
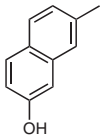
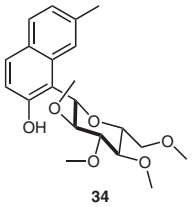
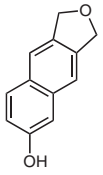
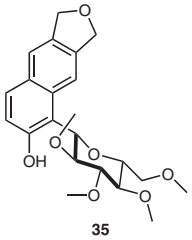
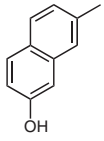
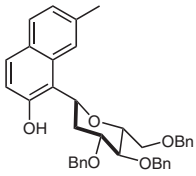


Figure 3 Naphthols that did not undergo glycosylation with any glycosyl donors

Table 2 Summary of C-Glycosylations of 2-Naphthols with Glycosyl Donors **23** and **24**

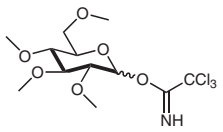
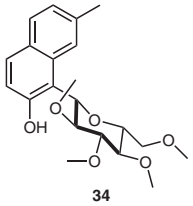
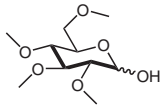
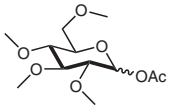
Entry	Glycosyl acceptor	Product	Yield (%)
1	 **7**	 **31**	86[a]
2	 **13**	 **32**	92[a]
3	 **12**	 **33**	81[a]
4	 **11**	 **34**	93[a]
5	 **20**	 **35**	67[a]
6	 **11**	 **36**	68[b]

[a] Reaction conditions: **23**, TMSOTf, MeCN, 0 °C to r.t., 2 h.
[b] Reaction conditions: **24**, TMSOTf, MeCN, 0 °C to r.t., 2 h.

Finally, a comparative study of glycosylation of the naphthols **11** was done with three different glycosyl donors, namely, **23**, **39**, and **40**. These donors differ only in the nucleofuge at the anomeric carbon (Table 3). We have used the same naphthol **11** in all the three cases. When trichloroacetimidate group (entry 1) was present at the anomeric position, the reaction was very smooth, giving the *C*-glycoside **34** in 93% isolated yield. For the other two donors, in which the anomeric carbon has OH or OAc, the yields of glycosylations were low, and significant amounts of starting naphthol were recovered. For glycosyl donor **39**, the yield of glycoside **34** was only 15%. When acetate was present at the anomeric position, only a trace amount of the product was detected in the ^{1}H NMR spectrum and the product could not be purified. This may be due to facile formation of oxacarbenium ion at low temperature from **40**, at which the nucleophilicity of **11** was insufficient for the Friedel–Crafts reaction. Thus, donor **40** was completely consumed but did not take part in a productive pathway. Nevertheless, glycosyl donor **23** proved to be useful.

In conclusion, various substituted 2-naphthols were synthesized and their C-glycosylation with different glycosyl donors was studied under Lewis acidic conditions. From these studies it is evident that neither electron-donating nor weak electron-withdrawing groups at the C6 position pose any problem to glycosylation with different glycosyl donors. However, strong electron-withdrawing groups at

Table 3 Comparison of C-Glycosylations of Naphthol **11** with **23** and Two Glycosyl Donors

Entry	Glycosyl donor	Product	Conditions	Yield (%)
1	 **23**	 **34**	TMSOTf, MeCN, 0 °C to r.t., 2 h	93
2	 **39**	**34**	TMSOTf, MeCN, 0 °C to r.t., 2 h	15
3	 **40**	**34**	TMSOTf, MeCN, 0 °C to r.t., 2 h	≤1[a]

[a] Only detected by ^{1}H NMR spectroscopic analysis.

both the C6 and C7 position retard the reaction. Although alkyl substituents at the C7 position can cause problems in glycosylation with donors **21**, **39**, and **40**, C7 substituted naphthols undergo smooth glycosylation with donors **22**, **23**, and **24**. It is concluded that trichloroacetimidate glycosyl donors are superior for glycosylation of substituted β-naphthols. An extension of this study to the total synthesis of mayamycin is underway.

All commercially available reagents were used without further purification. Melting points were determined in open-end capillary tubes and are uncorrected. Solvents were dried prior to use by following standard procedures. TLC were carried out on precoated plates (Merck silica gel 60, GF254), and the spots were visualized with UV, fluorescent light, or by staining with 10% H_2SO_4 in methanol. Flash column chromatography was performed on silica gel (230–400 mesh). ^{1}H and ^{13}C NMR spectra for all the compounds were recorded at 200/400/600 and 50/100/150 MHz (Bruker Avance 200, Bruker Avance II 400, Bruker Ascend 600), respectively; the chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CHCl_3$; δ_H = 7.26 and δ_C = 77.23). Multiplets are reported with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. Mass spectra were recorded with a MS-TOF mass spectrometer. The phrase 'usual work-up' or 'worked up in the usual manner' indicates washing of the organic phase with water (2 × 1/4 the volume of organic phase) and brine (1 × 1/4 the volume of organic phase), and drying (anhydrous Na_2SO_4), filtration, and concentration under reduced pressure. In most of the cases, yields refer to isolated yields after purification.

Glycosylation of Donor 21 with 2-Naphthols (2, 4, 5, 6, and 10); General Procedure

To a stirred solution of 2-naphthol derivative (0.5 mmol) and glycosyl donor **21** (0.75 mmol) and 4 Å molecular sieves in DCM (15 mL) was added tin(IV) chloride (2.48 mL, 1 M in DCM, 2.48 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min and then the temperature was gradually increased to –35 °C and kept overnight. The reaction was quenched with saturated sodium bicarbonate solution and the mixture was extracted with DCM. The organic phase was dried and concentrated to give the crude product, which was purified by flash column chromatography (EtOAc/hexane) to obtain the desired *C*-glycosides.

Glycosylation of Trichloroacetimidate Glycosyl Donors (22, 23, and 24) with 2-Naphthols (7, 11, 12, 13, 14, and 20); General Procedure

To a stirred solution of trichloroacetimidate glycosyl donor (0.6 mmol), and 2-naphthol derivative (0.5 mmol) in anhydrous MeCN (5 mL) was added trimethylsilyl trifluoromethanesulfonate (0.05 mL) dropwise at 0 °C under argon atmosphere. The mixture was stirred at r.t. for 2 h, then cooled 0 °C and the reaction was quenched with triethylamine and the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (EtOAc/hexane) to afford the desired glycosides.

6-(Benzyloxy)naphtho[2,3-*c*]furan-1(3*H*)-one (16)

A 30 mL reaction tube equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) followed by K_2HPO_4 (261 mg, 1.5 mmol) and 6-(benzyloxy)-2-naphthoic acid **15** (139 mg, 0.5 mmol), and dibromomethane (10 mL). The reaction tube was sealed with a Teflon cap and the reaction mixture was stirred at 140 °C for 36 h, after which it was filtered through a Celite pad, and the filtrate was concentrated in vacuum. The residue was purified by flash column chromatography (20% EtOAc/hexane) to give lactone **16** (81.2 mg, 56%) as off-white solid; mp 167–169 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 7.95 (d, *J* = 9.1 Hz, 1 H), 7.75 (s, 1 H), 7.51–7.27 (m, 7 H), 5.45 (s, 2 H), 5.23 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 159.4, 141.3, 138.3, 136.4, 131.7, 129 (2C), 128.5, 127.8, 127, 121.6, 120.8, 119.5, 107.3, 70.5, 69.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}O_3$: 291.1021; found: 291.1006.

6-Hydroxynaphtho[2,3-*c*]furan-1(3*H*)-one (17)

To a stirred solution of **16** (1.0 g, 3.58 mmol) in MeOH (30 mL), 10% Pd/C (100 mg) was added and the reaction mixture was hydrogenated using hydrogen gas contained in a balloon for 6 h. The reaction mixture was filtered through Celite, solvent was evaporated under reduced pressure and purified by column chromatography on silica gel (25% EtOAc/hexane) to obtain **17** (551 mg, 90%) as a white solid; mp 145–147 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.31 (s, 1 H), 8.42 (s, 1 H), 8.05 (d, *J* = 8.9 Hz, 1 H), 7.87 (s, 1 H), 7.25 (d, *J* = 2.5 Hz, 1 H), 7.20 (dd, *J* = 8.9, 2.4 Hz, 1 H), 5.49 (s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.2, 158.5, 141.7, 138.5, 138.1, 132.1, 127.8, 126.6, 120.4, 119.3, 109.2, 70.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_8O_3{}^{23}Na$: 223.0371; found: 223.0352.

6-Hydroxynaphtho[2,3-*c*]furan-1(3*H*)-one (19)

Under nitrogen atmosphere, to a stirred solution of **16** (66.7 mg, 0.23 mmol) in anhydrous toluene (5 mL) at –78 °C was added DIBAL-H (0.26 mL, 1 M in cyclohexane, 0.26 mmol) over 5 min. MeOH (1 mL) was added and the mixture was allowed to warm to r.t. The solvent was removed under reduced pressure. This crude alcohol **18** was directly used in the next step. To a stirred solution of crude **18** in DCM (5 mL) was added $BF_3{\cdot}OEt_2$ (5 drops) and Et_3SiH (0.1 mL) at 0 °C. The reaction mixture was then allowed to warm r.t. and stirring was continued for 2 h. The reaction was quenched with saturated sodium bicarbonate solution and the mixture was extracted with DCM. The organic phase was dried and concentrated and purified by flash column chromatography (10% EtOAc/hexane) to obtain **19** (45.7 mg, 72% over two steps) as a yellow solid; mp 151–153 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 9.7 Hz, 1 H), 7.60 (s, 1 H), 7.56 (s, 1 H), 7.51–7.35 (m, 5 H), 7.23–7.21 (m, 2 H), 5.20 (s, 4 H), 5.18 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157, 139, 137.1, 136.3, 134.5, 129.5, 128.9, 128.8, 128.3, 127.8, 119.3, 119.1, 118.3, 107.6, 73.1, 73.0, 70.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}O_2$: 277.1229; found: 277.1225.

1,3-Dihydronaphtho[2,3-*c*]furan-6-ol (20)

To a stirred solution of **19** (247 mg, 0.9 mmol) in MeOH (15 mL), 10% Pd/C (25 mg) was added and the reaction mixture was hydrogenated using hydrogen gas in balloon for 6 h. The reaction mixture was filtered through Celite, solvent was evaporated under reduced pressure and purified by column chromatography on silica gel (20% EtOAc/hexane) to obtain **20** (147 mg, 88%) as a white solid; mp 132–134 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.66 (s, 1 H), 7.71 (d, *J* = 8.8 Hz, 1 H), 7.64 (s, 1 H), 7.56 (s, 1 H), 7.10 (s, 1 H), 7.03 (d, *J* = 8.7 Hz, 1 H), 5.05 (s, 4 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 155.4, 138.9, 135.3, 134.7, 129.7, 128.7, 119.5, 118.7, 117.7, 109.3, 72.2, 72.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{11}O_2$: 187.0759; found: 187.0763.

(2*R*,3*S*,4*R*,6*R*)-4-Azido-6-(6-ethyl-2-hydroxynaphthalen-1-yl)-2-methyltetrahydro-2*H*-pyran-3-yl Acetate (25a)

The general procedure for glycosylation of donor **21** with naphthol **2** was followed using azido acetate **21** (193 mg, 0.75 mmol) and naphthol **2** (86 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexane) to afford **25a** (96 mg, 52%) as a colorless semisolid; $[\alpha]^{35}_D$ +64.5 (*c* 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 7.65 (d, *J* = 8.9 Hz, 1 H), 7.59–7.53 (m, 2 H), 7.35 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.09 (d, *J* = 8.8 Hz, 1 H), 5.50 (dd, *J* = 11.8, 2.2 Hz, 1 H), 4.90 (t, *J* = 9.6 Hz, 1 H), 3.85–3.73 (m, 2 H), 2.77 (q, *J* = 7.6 Hz, 2 H), 2.46–2.38 (m, 1 H), 2.19 (s, 3 H), 2.11–2.00 (m, 1 H), 1.37 (d, *J* = 6.2 Hz, 3 H), 1.31 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 153.2, 139.1, 129.9, 129.3, 129.1, 128.3, 127.1, 120.5, 120.1, 113.9, 76.7, 76.3, 75.2, 61.2, 36.2, 28.7, 21.1, 18.2, 15.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{23}N_3O_4{}^{23}Na$: 392.1586; found: 392.1599.

(2*R*,3*S*,4*S*,6*R*)-4-Azido-6-(6-ethyl-2-hydroxynaphthalen-1-yl)-2-methyltetrahydro-2*H*-pyran-3-yl Acetate (25b)

Compound **25b** was obtained along with compound **25a** (53 mg, 29%) as a colorless semisolid; $[\alpha]^{35}_D$ +44.5 (*c* 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1 H), 7.62 (dd, *J* = 11.3, 8.9 Hz, 2 H), 7.58–7.53 (m, 1 H), 7.36 (dd, *J* = 8.6, 2.0 Hz, 1 H), 7.07 (d, *J* = 8.8 Hz, 1 H), 5.74 (dd, *J* = 8.6, 5.0 Hz, 1 H), 4.90 (dd, *J* = 10.0, 3.3 Hz, 1 H), 4.32–4.22 (m, 2 H), 2.77 (q, *J* = 7.6 Hz, 2 H), 2.18–2.21 (m, 5 H), 1.36 (d, *J* = 6.2 Hz, 3 H), 1.30 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 153.3, 139.1, 129.7, 129.2, 129.1, 128.3, 126.8, 120.8, 119.9, 114.2, 74.8, 73.2, 72.0, 58.6, 35.8, 28.7, 20.8, 18.3, 15.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{23}N_3O_4{}^{23}Na$: 392.1586; found: 392.1599.

(2*R*,3*S*,4*R*,6*R*)-4-Azido-6-(2-hydroxy-6-isopropylnaphthalen-1-yl)-2-methyltetrahydro-2*H*-pyran-3-yl Acetate (26a)

The general procedure for glycosylation of donor **21** with naphthol **4** was followed using azido acetate **21** (193 mg, 0.75 mmol) and naphthol **4** (93 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexane) to afford **26a** (84 mg, 44%) as a colorless semisolid; $[\alpha]^{35}_D$ +84.6 (*c* 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 7.66 (d, *J* = 8.9 Hz, 1 H), 7.58–7.56 (m, 2 H), 7.42–7.36 (m, 1 H), 7.09 (d, *J* = 8.9 Hz, 1 H), 5.50 (dd, *J* = 11.6, 2.2 Hz, 1 H), 4.90 (td, *J* = 9.6, 1.7 Hz, 1 H), 3.87–3.74 (m, 2 H), 3.04 (p, *J* = 7.0 Hz, 1 H), 2.42 (ddd, *J* = 13.9, 4.9, 2.3 Hz, 1 H), 2.19 (s, 3 H), 2.08–2.05 (m, 1 H), 1.37 (d, *J* = 6.1 Hz, 3 H), 1.32 (d, *J* = 6.9 Hz, 6 H)

^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 153.2, 143.7, 130.1, 129.2, 129.2, 126.9, 125.6, 120.6, 120.0, 113.9, 76.7, 76.3, 75.2, 61.2, 36.2, 33.9, 24.2, 24.1, 21.1, 18.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{25}N_3O_4{}^{23}Na$: 406.1743; found: 406.1730.

(2*R*,3*S*,4*S*,6*R*)-4-Azido-6-(2-hydroxy-6-isopropylnaphthalen-1-yl)-2-methyltetrahydro-2*H*-pyran-3-yl acetate (26b)

Compound **26b** was obtained along with compound **26a** (57 mg, 30%) as a colorless semisolid; $[\alpha]^{35}_{D}$ +78.5 (*c* 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1 H), 7.63 (t, *J* = 9.6 Hz, 2 H), 7.56 (d, *J* = 1.9 Hz, 1 H), 7.40 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.07 (d, *J* = 8.8 Hz, 1 H), 5.73 (t, *J* = 6.9 Hz, 1 H), 4.90 (dd, *J* = 9.9, 3.3 Hz, 1 H), 4.33–4.22 (m, 2 H), 3.03 (p, *J* = 6.9 Hz, 1 H), 2.22–2.17 (m, 5 H), 1.36 (d, *J* = 6.2 Hz, 3 H), 1.32 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 153.3, 143.6, 129.8, 129.3, 129.1, 126.9, 125.4, 120.9, 119.9, 114.2, 74.8, 73.3, 72.0, 58.6, 35.8, 33.9, 24.2, 24.1, 20.8, 18.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{25}N_3O_4{}^{23}Na$: 406.1743; found: 406.1745.

(2*R*,3*S*,4*R*,6*R*)-4-Azido-6-(6-bromo-2-hydroxynaphthalen-1-yl)-2-methyltetrahydro-2*H*-pyran-3-yl Acetate (27a)

The general procedure for glycosylation of donor **21** with naphthol **5** was followed using azido acetate **21** (193 mg, 0.75 mmol) and naphthol **5** (111 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (7% EtOAc/hexane) to afford **27a** (88 mg, 42%) as a white semisolid; $[\alpha]^{35}_{D}$ +66.6 (*c* 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 7.92 (d, *J* = 2.0 Hz, 1 H), 7.62 (d, *J* = 8.9 Hz, 1 H), 7.56–7.48 (m, 2 H), 7.13 (d, *J* = 9.0 Hz, 1 H), 5.46 (dd, *J* = 11.8, 2.2 Hz, 1 H), 4.90 (t, *J* = 9.7 Hz, 1 H), 3.84–3.72 (m, 2 H), 2.36 (ddd, *J* = 14.1, 4.9, 2.2 Hz, 1 H), 2.19 (s, 3 H), 2.09–2.02 (m, 1 H), 1.37 (d, *J* = 6.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 154.2, 131.2, 130.3, 130.2, 129.5, 129.3, 122.3, 121.4, 116.9, 114.3, 76.4, 75.5, 75.1, 57.6, 36.2, 21.1, 18.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}BrN_3O_4{}^{23}Na$: 442.0378; found: 442.0383.

(2*R*,3*S*,4*S*,6*R*)-4-Azido-6-(6-bromo-2-hydroxynaphthalen-1-yl)-2-methyltetrahydro-2*H*-pyran-3-yl Acetate (27b)

Compound **27b** was obtained along with compound **27a** as a colorless semisolid (73 mg, 35%); $[\alpha]^{35}_{D}$ +62.3 (*c* 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1 H), 7.90 (d, *J* = 1.3 Hz, 1 H), 7.59 (d, *J* = 8.9 Hz, 1 H), 7.53 (s, 2 H), 7.11 (d, *J* = 8.9 Hz, 1 H), 5.68 (dd, *J* = 10.8, 2.8 Hz, 1 H), 4.90 (dd, *J* = 9.9, 3.3 Hz, 1 H), 4.33–4.23 (m, 2 H), 2.23–2.09 (m, 5 H), 1.37 (d, *J* = 6.2 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 154.2, 131.0, 130.3, 130.1, 129.4, 129.3, 122.6, 121.2, 116.9, 114.5, 74.7, 73.0, 72.1, 58.4, 35.8, 20.8, 18.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}BrN_3O_4{}^{23}Na$: 442.0378; found: 442.0383.

Methyl 5-((2*R*,4*S*,5*S*,6*R*)-5-Acetoxy-4-azido-6-methyltetrahydro-2*H*-pyran-2-yl)-6-hydroxy-2-naphthoate (28)

The general procedure for glycosylation of donor **21** with naphthol **10** was followed using azido acetate **21** (193 mg, 0.75 mmol) and naphthol **10** (101 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (20% EtOAc/hexane) to afford **28** (117 mg, 59%) as a yellow semisolid; $[\alpha]^{35}_{D}$ +44.6 (*c* 0.4, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.94 (s, 1 H), 8.50 (d, *J* = 1.8 Hz, 1 H), 8.06 (dd, *J* = 8.9, 1.9 Hz, 1 H), 7.79 (d, *J* = 8.9 Hz, 1 H), 7.68 (d, *J* = 8.9 Hz, 1 H), 7.15 (d, *J* = 8.9 Hz, 1 H), 5.75 (dd, *J* = 10.3, 3.5 Hz, 1 H), 4.91 (dd, *J* = 10.0, 3.3 Hz, 1 H), 4.33–4.26 (m, 2 H), 3.96 (s, 3 H), 2.20–2.18 (m, 5 H), 1.37 (d, *J* = 6.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 167.4, 156.2, 133.4, 132.1, 131.7, 128.0, 126.7, 124.9, 121, 120.9, 114.6, 74.7, 73.2, 72.2, 58.4, 52.4, 35.8, 20.9, 18.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{22}N_3O_6$: 400.1509; found: 400.1518.

(2*R*,3*S*,4*S*,6*R*)-4-Azido-6-(2-hydroxy-6-phenylnaphthalen-1-yl)-2-methyltetrahydro-2*H*-pyran-3-yl Acetate (29)

The general procedure for glycosylation of donor **21** with naphthol **6** was followed using azido acetate **21** (193 mg, 0.75 mmol) and naphthol **6** (110 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (25% EtOAc/hexane) to afford **29** (131 mg, 63%) as a yellow gum; $[\alpha]^{35}_{D}$ +58.3 (*c* 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (s, 1 H), 7.97 (d, *J* = 1.8 Hz, 1 H), 7.76–7.75 (m, 4 H), 7.49–7.36 (m, 4 H), 7.13 (d, *J* = 8.9 Hz, 1 H), 5.78 (t, *J* = 6.9 Hz, 1 H), 4.93–4.90 (m, 1 H), 4.34–4.27 (m, 2 H), 2.24–2.19 (m, 5 H), 1.38 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 154.1, 141.0, 136, 130.5, 130.1, 129.2, 129.1, 128.8, 128.5, 127.4, 127.3, 126.9, 126.7, 121.5, 120.5, 114.3, 74.8, 73.3, 72.1, 58.6, 35.9, 20.8, 18.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{23}N_3O_4{}^{23}Na$: 440.1586; found: 440.1583.

1-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2*H*-pyran-2-yl)naphthalene-2,7-diol (30)

The general procedure for glycosylation of donor **22** with naphthol **14** was followed using donor **22** (409 mg, 0.6 mmol) and naphthol **14** (80 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (30% EtOAc/hexane) to afford **30** (245 mg, 72%) as a yellowish solid; mp 183–185 °C; $[\alpha]^{35}_{D}$ +112.6 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1 H), 7.68 (d, *J* = 8.7 Hz, 2 H), 7.37–7.32 (m, 10 H), 7.31–7.28 (m, 6 H), 7.21–7.16 (m, 2 H), 7.09 (d, *J* = 7.3 Hz, 1 H), 7.04–7.00 (m, 2 H), 6.95 (dd, *J* = 8.8, 2.3 Hz, 1 H), 6.40 (d, *J* = 7.5 Hz, 2 H), 5.22 (d, *J* = 9.6 Hz, 1 H), 4.98 (d, *J* = 11.0 Hz, 1 H), 4.91–4.86 (m, 2 H), 4.65–4.55 (m, 2 H), 4.47 (d, *J* = 12.0 Hz, 1 H), 4.22 (d, *J* = 9.6 Hz, 1 H), 4.03–3.95 (m, 2 H), 3.86–3.78 (m, 2 H), 3.74–3.64 (m, 2 H), 3.52–3.48 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.7, 154.6, 138.9, 138.3, 138.0, 137.2, 134.3, 130.6, 130.5, 128.8, 128.7, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 124.3, 117.6, 115.0, 113.6, 105.9, 86.4, 82.1, 79.0, 77.4 (2C), 75.9, 75.6, 75.5, 73.7, 68.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{44}H_{42}O_7{}^{23}Na$: 705.2828; found: 705.2826.

5′-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)-1,2′-binaphthyl-6′-ol (31)

The general procedure for glycosylation of donor **23** with naphthol **7** was followed using donor **23** (228 mg, 0.6 mmol) and naphthol **7** (135 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (20% EtOAc/hexane) to afford **31** (210 mg, 86%) as a light-brown gum; $[\alpha]^{35}_{D}$ +69.3 (*c* 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1 H), 8.08 (d, *J* = 8.9 Hz, 1 H), 7.98–7.82 (m, 4 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.61 (dt, *J* = 9.7, 3.0 Hz, 1 H), 7.57–7.46 (m, 3 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 8.8 Hz, 1 H), 5.31 (d, *J* = 9.7 Hz, 1 H), 3.72–3.60 (m, 8 H), 3.58–3.41 (m, 7 H), 2.84 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 140.3, 135.5, 134.1, 132.0, 130.6, 129.3, 129.1, 128.5, 127.8, 127.4, 126.3, 126.2, 126, 125.7, 122.6, 120.3, 115.0, 88.1, 84.4, 79.1, 79.0, 77.0, 70.8, 61.3, 60.9, 60.6, 59.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{32}O_6{}^{23}Na$: 511.2097; found: 511.2099.

7-Fluoro-1-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-2-ol (32)

The general procedure for glycosylation of donor **23** with naphthol **13** was followed using donor **23** (228 mg, 0.6 mmol) and naphthol **13** (81 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (25% EtOAc/hexane) to afford **32** (175 mg, 92%) as a brown semisolid; $[\alpha]^{35}_D$ +103.5 (*c* 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1 H), 7.70 (dt, *J* = 8.8, 3.0 Hz, 2 H), 7.60 (d, *J* = 12.2 Hz, 1 H), 7.12–7.02 (m, 2 H), 5.06 (d, *J* = 9.6 Hz, 1 H), 3.68 (s, 3 H), 3.66 (d, *J* = 2.7 Hz, 1 H), 3.65–3.59 (m, 4 H), 3.54–3.37 (m, 7 H), 2.75 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6 (d, J_{C-F} = 242.7 Hz), 155.6, 134 (d, J_{C-F} = 9.4 Hz), 130.7 (d, J_{C-F} = 9.5 Hz), 130.4, 125.9, 119.2 (d, J_{C-F} = 2.7 Hz), 114.7 (d, J_{C-F} = 5.4 Hz), 113.3 (d, J_{C-F} = 24.9 Hz), 107.0 (d, J_{C-F} = 23 Hz), 88.0, 84.3, 79.0, 78.9, 77.1, 70.8, 61.2, 60.9, 60.4, 59.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{26}FO_6$: 381.1713; found: 381.1720.

7-Methoxy-1-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-2-ol (33)

The general procedure for glycosylation of donor **23** with naphthol **12** was followed using donor **23** (228 mg, 0.6 mmol) and naphthol **12** (87 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (15% EtOAc/hexane) to afford **33** (158 mg, 81%) as a yellowish semisolid; $[\alpha]^{35}_D$ +92.5 (*c* 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 8.8, 3.5 Hz, 2 H), 7.27 (s, 1 H), 6.98 (dd, *J* = 8.8, 3.0 Hz, 2 H), 5.13 (d, *J* = 9.7 Hz, 1 H), 3.92 (s, 3 H), 3.68–3.61 (m, 8 H), 3.54–3.40 (m, 4 H), 3.41 (s, 3 H), 2.75 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.3, 155.3, 134.1, 130.1, 129.9, 124.4, 117.4, 114.9, 114.1, 102.8, 87.9, 84.3, 78.9, 77.1, 70.7, 61.0, 60.7, 60.2, 59.4, 55.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{29}O_7$: 393.1913; found: 393.1910.

7-Methyl-1-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)naphthalen-2-ol (34)

The general procedure for glycosylation of donor **23** with naphthol **11** was followed using donor **23** (228 mg, 0.6 mmol) and naphthol **11** (79 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (20% EtOAc/hexane) to afford **34** (174 mg, 93%) as a white semisolid; $[\alpha]^{35}_D$ +56.2 (*c* 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H), 7.73 (s, 1 H), 7.68–7.65 (m, 1 H), 7.63–7.61 (m, 1 H), 7.14 (d, *J* = 8.2 Hz, 1 H), 7.09–7.05 (m, 1 H), 5.22 (d, *J* = 9.8 Hz, 1 H), 3.69–3.41 (m, 15 H), 2.72 (s, 3 H), 2.50 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.7, 154.8, 136.2, 133, 130.2, 128.3, 125.5, 121.9, 118.8, 114.5, 88.0, 84.2, 79.0 (2C), 76.8, 70.8, 61.1, 60.8, 60.3, 59.5, 22.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{29}O_6$: 377.1964; found: 377.1962.

5-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)-1,3-dihydronaphtho[2,3-*c*]furan-6-ol (35)

The general procedure for glycosylation of donor **23** with naphthol **20** was followed using donor **23** (228 mg, 0.6 mmol) and naphthol **20** (93 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (25% EtOAc/hexane) to afford **35** (135 mg, 67%) as a yellow semisolid; $[\alpha]^{35}_D$ +43.2 (*c* 0.3, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (s, 1 H), 7.83 (s, 1 H), 7.69 (d, *J* = 8.9 Hz, 1 H), 7.56 (s, 1 H), 7.12 (d, *J* = 8.8 Hz, 1 H), 5.24–5.16 (m, 5 H), 3.68 (s, 3 H), 3.66 (d, *J* = 2.9 Hz, 1 H), 3.62 (s, 3 H), 3.56–3.48 (m, 5 H), 3.41 (s, 3 H), 2.74 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 139.0, 135.3, 132.6, 130.3, 119.9, 119.7, 115.1, 114.2, 113.0, 88.0, 84.2, 78.9, 76.9, 73.3, 72.9, 61.2, 60.9, 60.4, 59.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{29}O_7$: 405.1913; found: 405.1908.

1-((2*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2*H*-pyran-2-yl)-7-methylnaphthalen-2-ol (36)

The general procedure for glycosylation of donor **24** with naphthol **11** was followed using donor **24** (346 mg, 0.6 mmol) and naphthol **11** (79 mg, 0.5 mmol). The crude product was purified by flash column chromatography on silica gel (30% EtOAc/hexane) to afford **36** (195 mg, 68%) as an off-white semisolid; $[\alpha]^{35}_D$ +76.8 (*c* 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (s, 1 H), 7.67 (d, *J* = 7.7 Hz, 2 H), 7.40–7.24 (m, 16 H), 7.16 (d, *J* = 8.3 Hz, 1 H), 7.08 (d, *J* = 8.9 Hz, 1 H), 5.45 (dd, *J* = 11.8, 2.2 Hz, 1 H), 4.98 (d, *J* = 10.9 Hz, 1 H), 4.74–4.44 (m, 5 H), 3.87 (ddd, *J* = 26.6, 9.2, 3.0 Hz, 3 H), 3.77–3.64 (m, 2 H), 2.52 (s, 3 H), 2.49 (s, 1 H), 2.01 (ddd, *J* = 16.7, 12.5, 9.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 138.6, 138.5, 138.1, 136.6, 131.1, 129.0, 128.7, 128.6, 128.3, 128.1, 127.9, 125.2, 119.9, 119.4, 114.7, 80.3, 79.1, 77.5, 75.7, 75.4, 73.6, 71.5, 68.2, 36.2, 22.5.

HRMS (ESI): *m*/*z* [M+NH_4]$^+$ calcd for $C_{38}H_{42}NO_5$: 592.3063; found: 592.3043.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591746.

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