Synthesis of furanoid and pyranoid C-1 aryl glycals by reaction of glycosyl chlorides with organolithium reagents

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Dedicated to Prof. Benito Alcaide on the occasion of his 60th birthday

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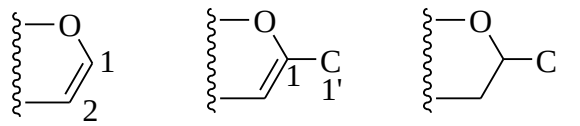
Abstract
Furanosyl and pyranosyl chlorides react with aryllithium derivatives, obtained by directed *ortho*-lithiation of activated arenes, to give C-1 aryl glycals in moderate yields.

Keywords: Glycals, *C*-glycosides, organolithium reagents, glycosyl chlorides

Introduction

The term glycal is used to define aldose derivatives having a double bond between C-1 and C-2, e.g. **1**.[1] Accordingly, C-1 glycals are $\Delta^{1,2}$ unsaturated carbohydrate derivatives with a carbon substituent at the anomeric position, e.g. **2**. These compounds are versatile synthetic intermediates, owing to the variety of transformations associated with their enol ether functionality, and have found ample use in the preparation of *C*-glycosides, e.g. **3**,[2] carbohydrate mimics,[3] and natural products[4].



1 **2** **3**

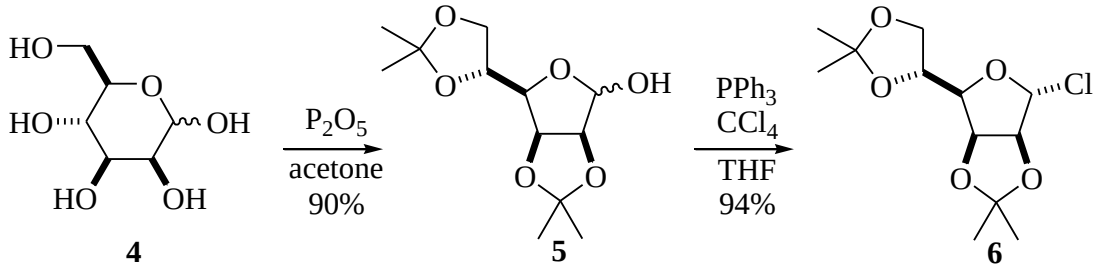
Figure 1

The preparation of C-1 glycals has been largely addressed by synthetic modifications on cyclic carbohydrate derivatives,[5] although strategies that rely on ring forming reactions from acyclic derivatives have recently emerged.[6,7] Most of the synthetic routes to C-1 glycals from cyclic carbohydrate derivatives are based on the deprotonation of glycals, which was independently reported by three research groups.[8,9,10] The ensuing lithiated species are then able to react with various carbon electrophiles, or with tributyltin chloride. The former approach leads directly to C-1 glycals, and the latter have been harnessed to palladium-mediated cross-coupling reactions for the key C1–C1' bond forming step.[11,12,13] On the other hand, lactones have also been used as starting materials in the synthesis of C-1 glycals,[14] in this case unlike the previous one the carbohydrate functions as an electrophile.

As part of our interest in the preparation of C-1 glycals,[15] we reported, some time ago, a route to both *C*-aryl and *C*-alkyl pyranoid glycals based on the of reaction of anomeric glycosyl chlorides, e.g. **6**, with commercially available organolithium reagents, where the carbohydrates exerted as the electrophilic partner.[16,17] We have since evaluated the scope of the approach[18] and, in this paper, we describe the preparation of furanoid and pyranoid C-1 aryl glycals from the reaction of furanosyl and pyranosyl chlorides with aryllithium derivatives generated by directed *ortho*-metalation of aromatic derivatives, *vide infra*. Furthermore, the furanoid C-1 glycals prepared in this study can be easily transformed into homochiral 2,5-disubstituted furans.

Results and Discussion

For our study we selected compound **6**, as the furanosyl chloride representative. Chloride **6** was easily prepared in two steps from D-mannose (**4**) by thermodynamically controlled acetonation[19] followed by anomeric chlorination[20] (Scheme 1).

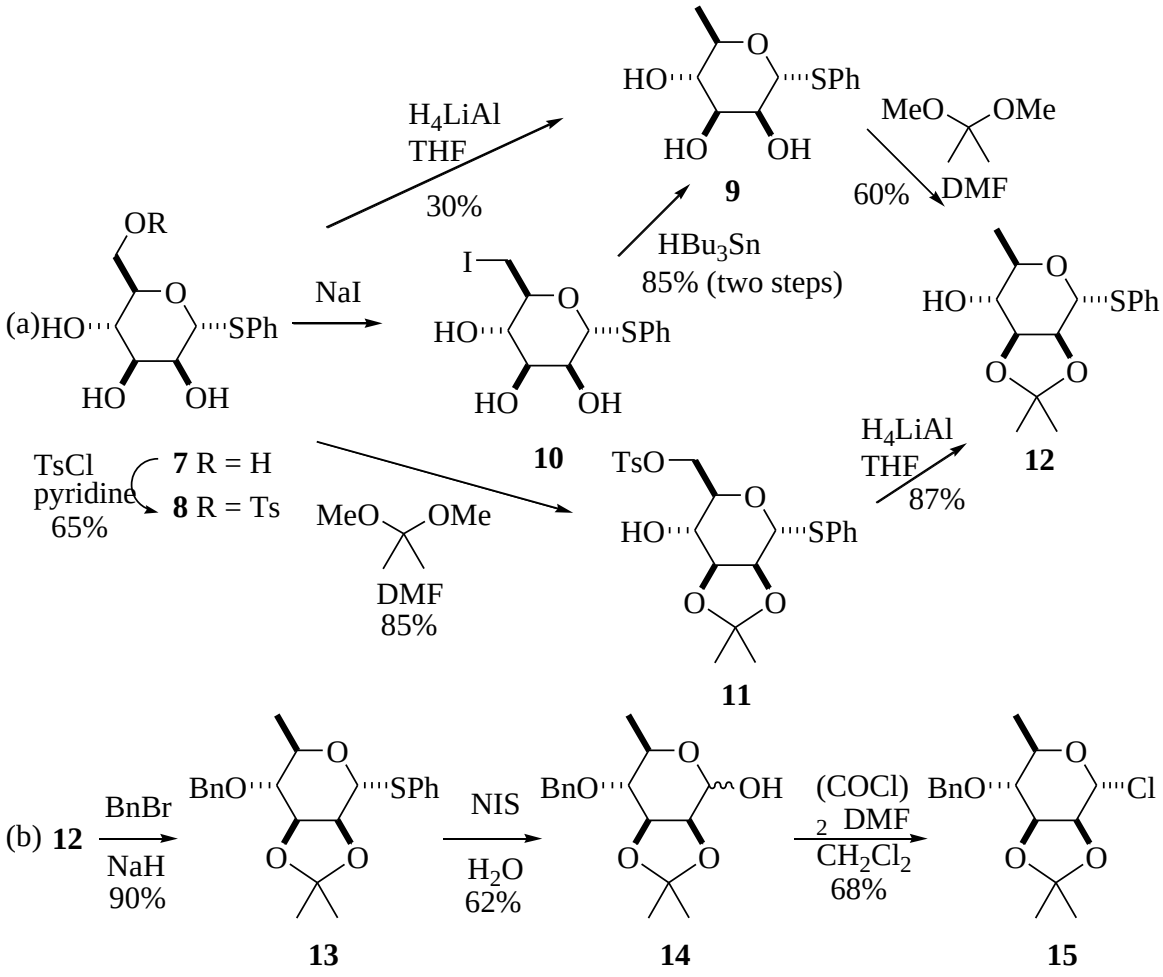


Scheme 1. Synthesis of furanosyl chloride **6**.

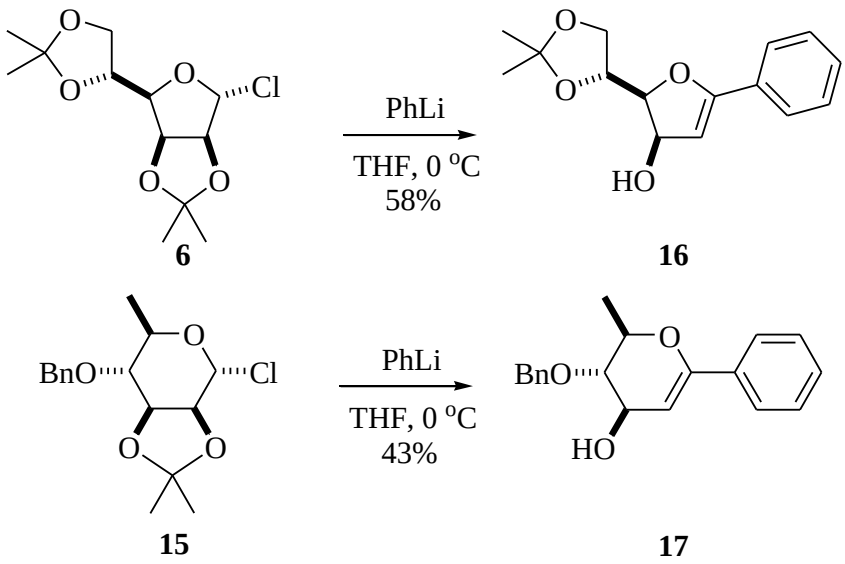
As pyranosyl chloride, we selected 6-deoxy derivative **15**, since a related compound had been used by Tius and co-workers in their synthetic approach to vineomicinone B2 methyl ester.[21] In our synthetic scheme to chloride **15**, we visualized thioglycoside **12** as the key intermediate (Scheme 2a). Our synthetic scheme started with tosyl derivative **8**, conveniently

prepared from thioglycoside **7**, by treatment with tosyl chloride (pyridine, 0 °C) in 65% yield (Scheme 2a). From compound **8**, we evaluated three different routes to **12**: *i)* the direct treatment of tosylate **8** with lithium aluminum hydride produced triol **9**, albeit in only 30% yield, from which the isopropylidene ring was installed in 60% yield; *ii)* a second route involving nucleophilic substitution of tosylate **8** with NaI followed by radical dehalogenation ($HSnBu_3$, AIBN) of the ensuing iodide, gave triol **9**, in 85% yield; *iii)* the best route proved to be acetonation of the tosylate (85% yield) followed by H_4LiAl reduction (87% yield). Once we had compound **12**, in hand, we proceeded with its benzylation, oxidative hydrolysis, and chlorination to gain access to glycosyl chloride **15**.

Before attempting the reaction of glycosyl chlorides **6** and **15** with complex aryllithium reagents, we decided to test their reaction with, commercially available, PhLi. In agreement with our previous results,[16,18] we found they both led to the expected C-1 phenyl glycals in moderate yields (Scheme 3).

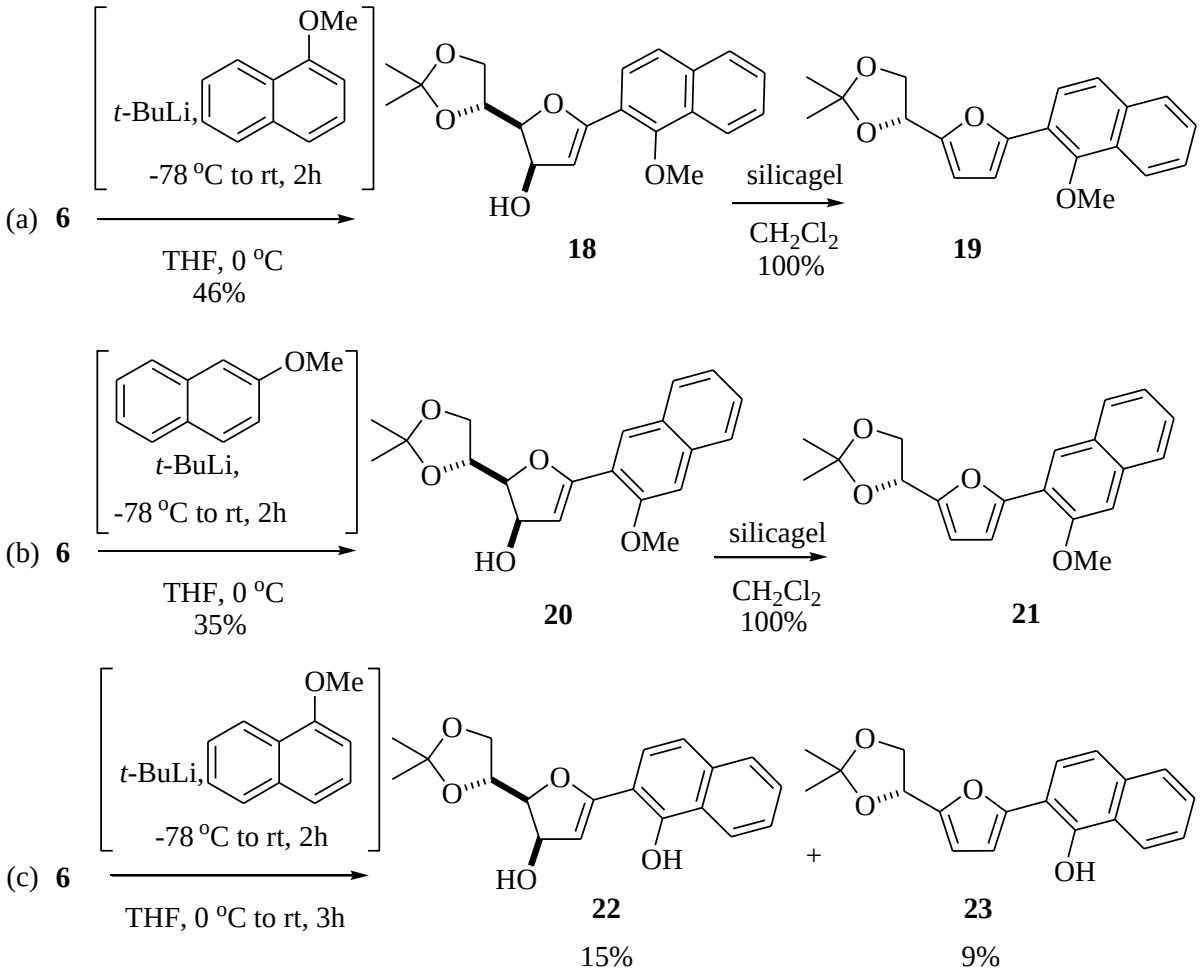


Scheme 2. Synthesis of pyranosyl chloride 15 from thiomannoside 7.



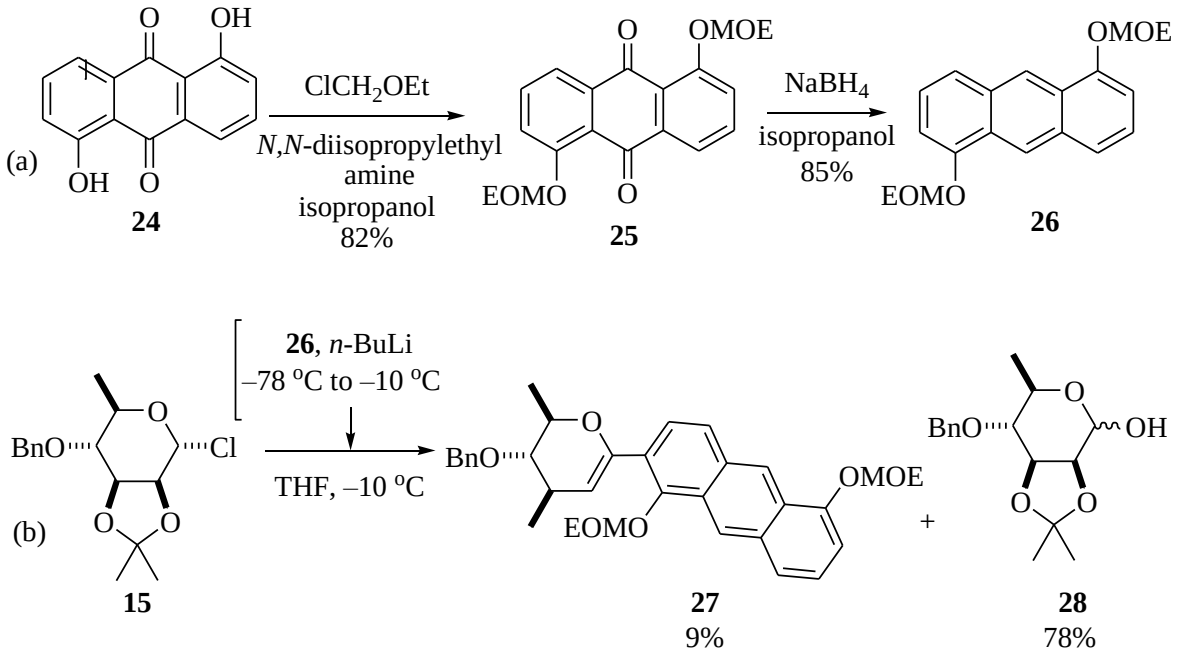
Scheme 3. Reaction of glycosyl chlorides 6 and 15 with PhLi.

We next turned our attention to the use of aryl organilithium reagents other than commercially available, PhLi. We envisaged that aryllithium derivatives generated by directed *ortho*-metalation,[22] could be used in the preparation of *C*-1 glycals. Accordingly, 2-lithio 1-methoxy naphthalene generated by reaction of 1-methoxy naphthalene with *t*-BuLi, reacted with furanosyl chloride **6**, to furnish *C*-1 glycal **18**, in 46% yield (Scheme 4a). We also carried out the directed *ortho*-metalation on 2-methoxy naphthalene, and 1-naphthol, and the results are shown in Scheme 4b,c, respectively. Varying amounts of furans **19** and **21** were observed in the crude reaction mixture of chloride **6** with the lithium salts of 1- and 2-methoxynaphthalene (Scheme 4a,b). These aryl glycals proved to be highly sensitive to acid and temperature, and so the low yield of compound **22** (Scheme 4c, obtained along with **23** as an inseparable mixture) could be rationalized because of the presence of the acidic phenolic OH group. According to that, we were able to prepare homochiral furans **19** and **21**, in quantitative yield from the corresponding C-1 glycals **18** and **19**, upon treatment with silicagel in dichloromethane. The presence of NEt_3 in the reaction work-up, and in the eluent for column chromatography, has a beneficial effect in preventing this transformation.



Scheme 4. Reaction of furanosyl chloride 6 with aryl lithiums generated by directed ortho-metalation, and furan formation.

Finally, we decided to test the reaction of lithiated of 1,5-bis(methoxyethoxy)-anthracene (**26**), with pyranosyl chloride **15**, since the expected C-1 glycal will be related to a synthetic intermediate employed by Tius and co-workers in their approach to vineomycinone B2 methyl ester.[21] We prepared compound **26** from commercially available anthrarufin (1,5-dihydroxy-9,10-anthraquinone) **24**, by methoxyethoxylation followed by sodium borohydride reduction (Scheme 5a). Subsequent, lithiation (*n*-BuLi, THF, –78 °C to –10 °C) of **26** and reaction with chloride **15**, yielded C-1 glycal **27**, in 9% yield, along with hemiacetal **28** (78%).



Scheme 5. Synthesis of C-1 glycal 27, from pyranosyl chloride 15.

Conclusions

C-1 Aryl glycosides can be prepared in moderate yields by the reaction of glycosyl chlorides with functionalized aryllithium derivates. The latter can be accesed by directed *ortho*-metalation of the corresponding activated arenes. C-1 Aryl glycals ensuing from furanosyl chloride **6**, have proven to be sensitive to acid and temperature, thus evolving to the corresponding furan derivatives.

Experimental Section

General Procedures. All reactions were performed in dry flasks fitted with glass stoppers or rubber septa under a positive pressure of Ar, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred by syringe or stainless steel cannula. Optical rotations were determined for solutions in chloroform. Flash column chromatography was performed using 230–400 mesh silica gel. Thin-layer chromatography was conducted on Kieselgel 60 F254 (Merck). Spots were observed first under UV irradiation (254 nm) then by charring with a solution of 20 % aqueous H2SO4 (200 mL) in AcOH (800 mL). Anhydrous $MgSO_4$ or Na_2SO_4 were used to dry organic solutions during workup, and evaporation of the solvents was

performed under vacuum using a rotary evaporator. Solvents were dried and purified using standard methods. Unless otherwise noted ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 MHz and 50 MHz, respectively. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.25 ppm). Elemental analyses were carried out at the *Centro Nacional de Quimica Orgánica "Manuel Lora Tamayo", Juan de la Cierva 3, 28006 Madrid,* with a Heraeus CHN-O-rapid elemental analyzer.

2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl chloride (6). 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose **5**[19] (5 g, 19.2 mmol) and PPh_3 (10.1 g, 38.6 mmol) were dissolved in dry THF (50 mL) and then CCl_4 (9.4 mL, 97.5 mmol) was added. The mixture was heated to reflux with exclusion of moisture. After the reaction was complete, Ph_3PO was filtered, the solid was washed with THF, and the filtrate was evaporated *in vacuo*. The resultant material was purified by flash chromatography (EtOAc/hexane 5%) to yield glycosyl chloride **6**[23] (5.1 g, 95%): $[\alpha]_D^{25}$ +52.0 (*c* 1.30 in $CHCl_3$); ^{1}H NMR δ□□(CDCl3, 300 MHz) 1.33 (3 H, s, Me), 1.38 (3 H, s, Me), 1.46 (3 H, s, Me), 1.47 (3 H, s, Me), 3.99 (1 H, dd, *J* = 4.4, 8.8 Hz, 6-H), 4.08 (1 H, dd, *J* = 5.9, 8.8 Hz, 6-H), 4.20 (1 H, dd, *J* 3.4, 7.8 Hz, 4-H), 4.42 (1 H, ddd, *J* = 4.4, 5.9, 7.8 Hz, 5-H), 4.88 (1 H, dd, *J* 3.4, 5.6, 3-H), 4.96 (1 H, d, *J* = 5.6, 2-H); 6.06 (1 H, s, 1-H); ^{13}C NMR δ□□(CDCl3, 50 MHz) 24.7, 25.2, 25.6, 27.0, 66.8, 72.4, 78.6, 82.4, 89.3, 97.7, 109.6, 113.4; API-ES(+) 279.1 (M^++1. $C_{12}H_{19}ClO_5$ requires 278.0921).

Phenyl 6-*O*-(*p*-toluenesulfonyl)-1-thio-α-D-mannopyranoside (8). Phenyl 1-thio-α-D-mannopyranoside **6** (6 g, 22.06 mmol) was treated with *p*-toluene-sulfonyl chloride (5.4 g, 28.7 mmol) in dry pyridine (100 mL) at 0 °C. The reaction was allowed to warm to room temperature and after 5 hours of stirring, the mixture was concentrated *in vacuo*, diluted with CH_2Cl_2, washed with aqueous $NaHCO_3$ and water. The organic layer was then dried over $MgSO_4$, filtered and concentrated. Flash chromatography (CH_2Cl_2/MeOH 92:8) of the residue afforded **8**[24] (7.04 g, 75%).: $[\alpha□]_D^{21}$ +148 (*c* 0.4 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67–7.73 (m, 2 H), 7.20–7.40 (m, 7 H), 5.46 (s, 1H, H1), 4.12–4.40 (m, 4 H), 3.75–3.90 (m, 2 H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.5, 133.5, 132.4, 131.3, 129.5, 128.6, 127.7, 127.1, 87.8, 71.9, 71.8, 70.9, 69.1, 67.1, 60.1. Anal. Calcd for $C_{19}H_{22}O_7S_2$ (426.0807): C, 53.50; H, 5.20. Found: C, 53.71; H, 5.27.

Phenyl 1-thio-α-D-rhamnopyranoside (9). Method A. A solution of compound **8** (1.87 g, 4.38 mmol) in dry THF (10 mL) was added to a cooled (0 °C) suspension of $LiAlH_4$ (5.6 g, 17.52 mmol) in dry THF (20 mL). The mixture was allowed to warm to room temperature and then stirred for an additional 24 h period. The reaction mixture was recooled to 0 ºC, diluted with Et_2O (100 mL) and then carefully treated with saturated Na_2SO_4 solution (1 mL). The mixture was stirred for 20 min, after which time was filtered though a short pad of celite and concentrated. The residue was purified by flash chromatography. (CH_2Cl_2/MeOH 95:5) to afford pure **9** (336 mg, 30 %). ^{1}H NMR □(200 MHz, $CDCl_3$) δ □□7.22–7.45 (m, 5H), 5.46 (s, 1 H,

H1), 3.50–4.20 (m, 7H), 1.30 (d, J = 6.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ□ 134.2, 131.2, 128.9, 127.2, 87.9, 73.0, 72.5, 72.1, 69.4, 29.5. m/z 256.0 (M^+).

Method B. A mixture of compound **8** (1.87 g, 4.38 mmol), and NaI (860 mg, 5.72 mmol) in 2-butanone (50 mL) was boiled under reflux for 16 h. After cooling, the reaction mixture was filtered and concentrated. The residue was immediately dissolved in *t*-BuOH (25 mL), heated to 90 ºC treated with $HSnBu_3$ (1.5 mL, 5.7 mmol) and AIBN (150 mg, 0.91 mmol) and stirred at that temperature for 20 h. After cooling to room temperature, the mixture was diluted with EtOAc (200 mL), washed with water, dried ($MgSO_4$) and concentrated. Column chromatography (CH_2Cl_2/MeOH 95:5) of the residue gave **9** (960 mg, 85%).

Phenyl 2,3-*O*-isopropylidene-6-*O*-(*p*-toluenesulfonyl)-1-thio-α-D-mannopyranoside (11). *p*-Toluenesulfonic acid monohydrate (100 mg) and 2,2-dimethoxypropane (2.6 mL, 11 mmol) were added to a solution of **8** (4.5 g, 10.5 mmol) in dry DMF (50 mL). After 7h, $NaHCO_3$ was added and the mixture was diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (Hexane/EtOAc 7:3) yielded **11** (4.2 g, 85%): $[\alpha\square]_D^{21}$ +102.2 (*c* 1.1 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.71–7.24 (m, 9 H), 5.68 (s, 1 H, H1), 4.32–4.11 (m, 5 H), 3.75–3.64 (m, 1 H, H4), 2.75 (d, J = 4.4 Hz, 1 H, OH), 2.40 (s, 3H), 1.49 (s, 3 H), 1.34 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ□ 144.6, 132.4, 132.3, 132.0, 129.5, 128.8, 127.7, 109.7, 83.8, 78.0, 76.4, 75.8, 68.7, 68.6, 27.7, 26.0, 21.4. Anal. Calcd for $C_{22}H_{26}O_7S_2$ (466.57): C, 56.63; H, 5.62. Found: C, 56.81; H, 5.49.

Phenyl 2,3-*O*-isopropylidene-1-thio-α-D-rhamnopyranoside (12). Method A. *p*-Toluenesulfonic acid monohydrate (35 mg) and 2,2-dimethoxypropane (1.0 mL, 8.5 mmol) were added to a solution of **9** (870 mg, 3.4 mmol) in dry DMF (15 mL). After 7h, $NaHCO_3$ was added and the mixture was diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (Hexane/EtOAc 85:15) yielded **12** (604 mg , 60%): m. p. 82 ºC, $[\alpha\square]_D^{21}$ +208 (*c* 1.1 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45–7.50 (m, 2 H), 7.25–7.31 (m, 3 H), 5.73 (bs, 1 H, H1), 4.34 (dd, *J* = 0.8, 5.6 Hz, 1 H, H4), 4.00–4.13 (m, 2 H, H2 and H3), 3.46 (m, 1 H, H5), 2.15 (bs, 1 H, OH), 1.52 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.29 (d, *J* = 6.2 Hz, 3 H, CH_3). Anal. Calcd for $C_{15}H_{20}O_4S$ (296.38): C, 60.79; H, 6.80, S 10.82. Found: C, 56.81; H, 5.49, S 10.73.

Method B. A solution of compound **11** (3.70 g, 7.94 mmol) in dry THF (20 mL) was added to a cooled (0 ºC) suspension of $LiAlH_4$ (3.20 g, 10 mmol) in dry THF (20 mL). The mixture was allowed to warm to room temperature and then stirred for additional 16 h. The reaction mixture was recooled to 0 ºC, diluted with Et_2O (100 mL) and then carefully treated with saturated Na_2SO_4 solution (1 mL). The mixture was stirred for 20 min after which time was filtered though a short pad of celite and concentrated. The residue was purified by flash chromatography. (Hexane/EtOAc 85:15) to afford pure **12** (2.04 g, 87 %).

Phenyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio-α-D-rhamnopyranoside (13). Compound **12** (1.22 g, 4.12 mmol) was dissolved in dry THF (75 mL), cooled to 0 °C, and treated portionwise with NaH (60%, 330 mg, 8.2 mmol, 2 equiv.). After 30 min, benzyl bromide (588 μL, 4.94 mmol, 1.2 equiv.) was added. The reaction mixture was allowed to warm to room

temperature and stirred overnight. The solution was carefully quenched with water, diluted with Et_2O, washed with H_2O, dried, and concentrated. The product was then purified by flash chromatography (Hexane/EtOAc 85:15) to afford **13** (1.44 g, 90%): m. p. 90 ºC (EtOH), $[\alpha]_D^{21}$ +224 (*c* 0.97 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.51–7.10 (m, 10 H), 5.74 (s, 1 H, H1), 4.93 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 4.65 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 4.31–4.39 (m, 2 H, H2 and H3), 4.13–4.19 (m, 1 H, H5), 3.32 (dd, *J* = 6.7, 9.9 Hz, 1 H, H4), 1.52 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.24 (d, *J* = 6.2 Hz, 3 H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.5, 133.8, 132.7, 129.3, 128.6, 128.3, 128.0, 127.8, 109.7, 84.1, 81.7, 78.7, 78.0, 73.4, 66.5, 29.0, 28.3, 26.8, 18.0. *m/z* 387.3 (M^++1), 386.2 (M^+). Anal. Calcd for $C_{22}H_{26}O_4$ S (386.50): C, 68.37; H, 6.78, S 8.30. Found: C, 68.49; H, 6.59, S 8.18.

4-*O*-Benzyl-2,3-*O*-isopropylidene-α-D-rhamnopyranose (14). Compound **13** (1.44 g, 3.72 mmol) was dissolved in CH_2Cl_2 (15 mL), cooled to 0 ºC and treated with NIS (11.2 mmol, 2.5 g) and H_2O (11.2 mmol, 201 μL). The mixture was allowed to warm to room temperature and then stirred for additional 2 h. The solution was diluted with CH_2Cl_2, successively washed with $Na_2S_2O_3$, satd aq $NaHCO_3$ and brine. The organic layer was dried and concentrated. Purification by column chromatography (Hexane/EtOAc 80:20) gave hemiketal **14** (680 mg, 62%) as a (7:3) mixture of anomers ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26–7.36 (m, 5 H), 5.35 (d, *J* = 3.7 Hz, 1 H), 4.89 (d, *J* = 11.6 Hz, 1 H), 4.82 (d, *J* = 11.6 Hz, 1 H), 4.64 (d, *J* = 11.6 Hz, 1 H), 4.61 (d, *J* = 11.6 Hz, 1 H), 4.17–4.35 (m, 2 H), 3.96 (m, 1 H), 3.29 (dd, *J* =6.0, 8.3 Hz, 1 H), 3.25 (dd, *J* = 6.9, 9.1 Hz, 1 H), 3.00 (d, *J* = 3.9 Hz, 1 H), 1.52 (s, 3 H), 1.51 (s, 3 H), 1.40 (s, 3 H), 1.38 (s, 3 H), 1.33 (d, *J* = 6.3 Hz, 3 H), 1.28 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.9, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 110.2, 109.2, 92.4, 92.1, 80.6, 80.1, 78.7, 77.9, 76.1, 74.9, 73.0, 72.6, 71.1, 65.1, 27.9, 27.6, 26.2, 18.8, 18.1

4-*O*-Benzyl-2,3-*O*-isopropylidene-α-D-rhamnopyranosyl chloride (15). Compound **14** (51 mg, 0.17 mmol) and *N*,*N*-dimethylformamide (17 μL) were dissolved in dry CH_2Cl_2 (2 mL), and then a solution of oxalyl chloride (43 μL, 0.51 mmol, 3 equiv.) in dry CH_2Cl_2 (1 mL) was added dropwise at 0 ºC. The mixture was stirred at that temperature for 30 min after which time was allowed to warm to room temperature and stirred for one additional hour. The reaction crude was then concentrated, the residue taken up in 1:1 EtOAc/hexane and the suspension filtered through silica gel, to give after evaporation of the solvents, chloride **15** (36 mg, 68%): ^{1}H NMR (300 MHz, $CDCl_3$):7.26–7.50 (m, 5 H), 6.27 (s, 1 H, 1-H), 4.92 (d, *J* = 11.5 Hz, 1 H, CH_2Ph), 4.64 (d, *J* = 11.5 Hz, 1 H, CH_2Ph, 4.31 (m, 1 H, 3-H), 4.12 (d, *J* = 4.9 Hz, 1 H, 2-H), 3.75 (dd, *J* = 6.2, 9.7 Hz, 1 H, 5-H), 3.26 (dd, J = 7.2, 9.7 Hz, 1 H, 4-H), 1.52 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.29 (d, *J* = 6.2 Hz, CH_3); *m/z* 312.1 (M^+, $C_{16}H_{21}ClO_4$ requires 312,1128), 314.2 (M^++2).

General procedure for C-1 glycal formation

A solution of the glycosyl chloride (1 mmol) in dry THF was cooled to the appropriate temperature and then treated with the corresponding organolithium reagent. After stirring for a period of time between 0.5–2 h and once TLC analyses showed total disappearance of the starting material, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl.

After partitioning between water and diethyl ether, the organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography.

1,4-Anhydro-5,6-*O*-isopropyliden-2-deoxy-1-C-phenyl-D-arabino-hex-1-enitol (16). Using the general procedure, chloride **6** (87 mg, 0.32 mmol) was treated with PhLi (0.53 mL 1.8 M solution in di-*n*-butylether, 0.96 mmol) at 0 ºC. Extractive work-up was followed by a quick flash chromatography (EtOAc/hexane 20%) to give C-1 glycal **16** (58 mg, 71%): $[\alpha]_D^{25}$ +7.8 (*c* 0.33 in $CHCl_3$); ^{1}H NMR δ (C$_6$D$_6$, 300 MHz) 1.31 (3 H, s, Me), 1.45 (3 H, s, Me), 4.10 (2 H, m, 6-H), 4.25 (1 H, t, *J* 6.7, 4-H), 4.55 (1 H, m, 5-H), 4.70 (1 H, dd, *J* 2.9, 6.7, 3-H), 5.39 (1 H, d, *J* 2.9, 2-H), 7.10 (3 H, m, Ph), 7.56 (2 H, m, Ph). ^{13}C NMR δ (C$_6$D$_6$, 50 MHz) 25.5, 27.0, 67.0, 73.6, 74.0, 85.6, 99.2, 109.2, 124.1, 125.9, 128.3, 129.4, 159.8. *m/z* 263.1 (M^++1; $C_{15}H_{18}O_4$ requires 262.1205).

1,5-Anhydro-4-benzyl-2,6-dideoxy-1-C-phenyl-D-arabino-hex-1-enitol (17). Using the general procedure, chloride **15** (37 mg, 0.12 mmol) was treated with PhLi (510 μL 1.5 M solution in diethyl-ether, 0.72 mmol) at room temperature. Extractive work-up was followed by flash chromatography (EtOAc/hexane 20%) to give C-1 glycal 1**7** (15.2 mg, 43%): ^{1}H NMR δ (CDCl$_3$, 300 MHz) 1.29 (d, *J* = 5.5 Hz, 3 H, CH_3), 3.37–3.58 (m, 2 H, 4-H and 5-H), 4.25 (br s, 1 H, 3-H), 4.61 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 4.84 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 5.35 (br. S, 1 H, 2-H), 7.27–7.36 (m, 5 H); ^{13}C NMR δ (CDCl$_3$, 50 MHz) 18.9, 71.0, 73.0, 79.6, 80.2, 96.9, 127.5, 127.7, 127.9, 128.0, 128.2, 128.3, 138.1, 148.1; *m/z* 297.1 (M^++1). Anal. Calcd for $C_{19}H_{20}O_3$ (296.1412): C, 77.00; H, 6.80. Found: C, 76.83; H, 6.88.

1,4-Anhydro-5,6-*O*-isopropyliden-2-deoxy-1-C-1-(methoxy-2-napthyl)-D-arabino-hex-1-enitol (18). A cooled (–78 ºC) solution of 1-methoxynaphtalene (293 μL, 2 mmol) in dry THF (1 mL) was treated with *t*-BuLi (1.17 mL, 1.7 M solution in pentane, 2 mmol) and the reaction mixture was allowed to warm to 0 ºC and then stirred for 2h. Chloride **6** (98 mg, 0.35 mmol) dissolved in dry THF (2 mL) was then added and the mixture was stirred at room temperature for 3h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and after partitioning between water and diethyl ether, the organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography. (EtOAc/hexane 10%) to give C-1 glycal, **18** (55 mg, 46%): $[\alpha]_D^{25}$ = +48.7 (*c* 0.79, $CHCl_3$); ^{1}H NMR δ (CDCl$_3$, 300 MHz) 1.44 (s, 3H, Me), 1.53 (s, 3H, Me), 3.94 (s, 3H, OMe), 3.90–4.41 (m, 3H), 4.65 (ddd, *J* = 5.3, 7.9, 11.2 Hz, 1 H, H5), 5.16 (dd. *J* = 2.6, 6.4, 1H, H3), 6.10 (d, *J* = 2.6 Hz, 1 H, H2), 7.40–8.19 (m, 6 H). *m/z* 342.0 (M^+. $C_{20}H_{22}O_5$ requires 342.1467), 324.0, 306.0, 253.0, 242.0, 225.0, 186.0.

(*R*)-4-[5-(1-Methoxynaphthalen-2-yl)furan-2-yl]-2,2-dimethyl-1,3-dioxolane (19). Compound **18** (50 mg, 0.15 mmol) was dissolved in dry CH_2Cl_2 and treated with silica gel. The mixture was boiled for 30 min under reflux. After cooling, the reaction mixture was concentrated. Flash chromatography ((EtOAc/hexane 5%) gave **19** (47 mg, 100%); ^{1}H NMR δ (CDCl$_3$, 300 MHz) 1.50 (s, 3H, Me), 1.59 (s, 3H, Me), 3.90 (s, 3H, OMe), 4.19–4.36 (m, 2H), 5.20 (m, 1 H), 6.55 (d, *J* = 3.4 Hz, 1 H), 7.05 (d, *J* = 3.4 Hz, 1H), 7.46–7.57 (m, 2 H), 7.65 (d, *J* = 8.8 Hz, 1 H), 7.82 (m, 1 H), 7.94 (d, *J* = 8.7 Hz, 1 H), 8.15 (m, 1 H); *m/z* 324.37 (M^+). Anal. Calcd for $C_{20}H_{20}O_4$ (324,3704): C, 74.06; H, 6.21. Found: C, 73.98; H, 6.29.

1,4-Anhydro-5,6-*O*-isopropyliden-2-deoxy-1-C(-3-methoxy-2-naphthyl)-D-arabino-hex-1-enitol (20). A cooled (–78 °C) solution of 2-methoxynaphthalene (316 mg, 2 mmol) in dry THF (1 mL) was treated with *t*-BuLi (1.17 mL 1.7 M solution in pentane, 2 mmol) and the reaction mixture was allowed to warm to 0 °C and then stirred for 2h. Chloride **6** (81 mg, 0.29 mmol) dissolved in dry THF (2 mL) was then added and the mixture was stirred at room temperature for 3h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and after partitioning between water and diethyl ether, the organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography. (EtOAc/hexane 15%) to give C-1 glycal **20** (35 mg, 35%): $[\alpha]_D^{25} = -7.2$ (*c* 0.67, $CHCl_3$); ^{1}H NMR δ (CDCl$_3$, 300 MHz) 1.45 (s, 3H, Me), 1.54 (s, 3H, Me), 1.97 (bd, *J* = 5.2 Hz, 1 H), 4.00 (s, 3H, OMe), 4.21–4.39 (m, 3H), 4.65 (ddd, *J* = 5.3, 7.9, 11.2 Hz, 1 H, H5), 5.14 (dd. *J* = 2.9, 6.4, 1H, H3), 6.17 (d, *J* = 2.9 Hz, 1 H, H2), 7.34–7.50 (m, 2 H), 7.70–7.83 (m, 2 H), 8.16 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.4, 27.0, 55.4, 67.2, 73.3, 74.8, 83.4, 104.5, 105.7, 109.4, 124.1, 126.3, 127.3, 128.2, 128.4, 128.5, 134.5, 155.4, 155.5;. *m/z* 342.0 (M^+).

(*R*)-4-[5-(3-Methoxynaphthalen-2-yl)furan-2-yl]-2,2-dimethyl-1,3-dioxolane (21). Compound **20** (25 mg, 0.077 mmol) was dissolved in dry CH_2Cl_2 and treated with silica gel. The mixture was boiled for 30 min under reflux. After cooling, the reaction mixture was concentrated. Flash chromatography ((EtOAc/hexane 5%) gave **21** (24 mg, 100%); ^{1}H NMR δ (CDCl$_3$, 300 MHz) 1.52 (s, 3H, Me), 1.61 (s, 3H, Me), 4.04 (s, 3H, OMe), 4.21–4.38 (m, 2H), 5.23 (t, *J* = 6.9 Hz, 1 H), 6.51 (d, *J* = 3.3 Hz, 1 H), 7.03 (d, *J* = 3.3 Hz, 1H), 7.20 (s, 1 H), 7.36–7.45 (m, 2 H), 7.73 (m, 1 H), 7.84 (m, 1 H), 8.23 (s, 1 H); *m/z* 324.0 (M^+);. Anal. Calcd for $C_{20}H_{20}O_4$ (324,3704): C, 74.06; H, 6.21. Found: C, 73.87; H, 6.13.

Reaction of furanosyl chloride 6 with 1-naphthol. General procedure

A cooled (–78 ºC) solution of 1-naphthol (228 mg, 2 mmol) in dry THF (1 mL) was treated with *t*-BuLi (3.0 mL 1.5 M solution in pentane, 4.5 mmol) and the reaction mixture was allowed to warm to 0 ºC and then stirred for 2h. Chloride **6** (98 mg, 0.33 mmol) dissolved in dry THF (2 mL) was then added and the mixture was stirred at room temperature for 3h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and after partitioning between water and diethyl ether, the organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography. (EtOAc/hexane 15%) to give an inseparable mixture of C-1 glycal **21** and furane **22** (35 mg, ratio **21**/**22** 5:3): ^{1}H NMR δ (CDCl$_3$, 300 MHz) 1.38 (s, 3H, Me_{major}), 1.44 (s, 3H, Me_{minor}), 1.46 (s, 3H, Me_{major}), 1.55 (s, 3H, Me_{minor}), 2.09 (bd, *J* = 3.7 Hz, 1 H_{major}), 2.88 (m, 1 H_{minor}), 3.83–5.00 (m, 4 H_{major} + 3 H_{minor}), 5.21 (m, 1 H_{major}), 6.10 (d, J = 3.3 Hz, 1 H_{major}), 6.54 (d, J = 3.4 Hz, 1 H_{minor}), 7.04 (d, J = 3.4 Hz, 1 H_{minor}), 7.40–8.30 (m, 6 H_{major} +6 H_{minor}).

1,5-Bis(ethoxymethoxy)anthracene-9,10-dione (25). A suspension of 1.00 g (4.2 mmol) of anthrarufin (1.5 g, 6.2 mmol) in chloroform (20 mL) was treated with 13.5 mL (77.6 mmol) of *N*,*N*-diisopropylethylamine (19.6 mL, 114.7 mmol) and chloromethyl ethyl ether (6.9 mL, 74.4 mmol) and was subsequently heated to reflux for 20 h. The mixture was allowed to cool to

room temperature and was washed with aqueous NaOH (1N) solution, followed by brine. The organic phase was dried over $MgSO_4$, and the solvent was evaporated. The resulting solid was washed successively with 1 N NaOH, water, and absolute ethanol to afford anthraquinone **25** (1.76 g, 82% yield) as a yellow solid: m.p 155–156 ºC; ^{1}H NMR δ (CDCl$_3$, 300 MHz): 1.22 (t, *J* = 7.0 Hz, 6 H), 3.83 (q, *J* = 7.0 Hz, 4 H); 5.43 (s, 4 H), 7.53 (dd, *J* = 1.2, 8.4 Hz, 2 H), 7.66 (dd, *J* = 7.6, 8.4 Hz, 2 H), 7.94 (dd, *J* = 1.2, 7.6 Hz, 2 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 15.0, 64.9, 93.8, 105.2, 120.8, 121.2, 134.7, 137.3, 157.3, 182.4; *m/z* 356.0 (M^+); Anal. Calcd for $C_{20}H_{20}O_6$ (356,3692): C, 67.41; H, 5.66. Found: C, 67.27; H, 5.43.

1,5-Bis(ethoxymethoxy)anthracene (26). To a suspension of anthraquinone **25** (1.54 g, 4.3 mmol) in 2-propanol (60 mL) was added $NaBH_4$ (4.9 g, 130 mmol). The mixture was heated to reflux for 8 h, poured onto ice water, and treated slowly with 6 N HCl at 0 ºC until the pH of the mixture was 4–6. The solid anthracene was filtered, and the aqueous fraction was extracted with CH_2Cl_2. The organic phase was washed with water and dried over $MgSO_4$, and the solvent was evaporated to produce additional crude anthracene as a yellow-brown solid. Flash column chromatography of the combined solids gave **6** (1.2 g, 85%) as a pale yellow solid: mp 88–89 ºC; ^{1}H NMR δ (CDCl$_3$, 300 MHz): 1.28 (t, *J* = 7.0 Hz, 6 H), 3.87 (q, *J* = 7.0 Hz, 4 H); 5.53 (s, 4 H), 7.06 (d, *J* = 7.4 Hz, 2 H), 7.36 (dd, *J* = 7.4, 8.5 Hz, 2 H), 7.69 (d, *J* = 8.5 Hz, 2 H), 8.79 (s, 2 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 15.1, 64.6, 93.4, 105.8, 120.5, 121.9, 125.1, 125.4, 132.2, 152.8; *m/z* 326.0 (M^+); Anal. Calcd for $C_{20}H_{22}O_4$ (326,3863): C, 73.60; H, 6.79. Found: C, 73.51; H, 6.63.

Reaction of furanosyl chloride 6 with 1-naphthol. General procedure

A cooled (–78 ºC) solution of 1-naphthol (228 mg, 2 mmol) in dry THF (1 mL) was treated with *t*-BuLi (3.0 mL 1.5 M solution in pentane, 4.5 mmol) and the reaction mixture was allowed to warm to 0ºC and then stirred for 2h. Chloride **6** (98 mg, 0.33 mmol) dissolved in dry THF (2 mL) was then added and the mixture was stirred at room temperature for 3h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and after partitioning between water and diethyl ether, the organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography. (EtOAc/hexane 15%) to give an inseparable mixture of C-1 glycal **21** and furane **22** (35 mg, ratio **21**/**22** 5:3): ^{1}H NMR δ (CDCl$_3$, 300 MHz) 1.38 (s, 3H, Me$_{major}$), 1.44 (s, 3H, Me$_{minor}$), 1.46 (s, 3H, Me$_{major}$), 1.55 (s, 3H, Me$_{minor}$), 2.09 (bd, *J* = 3.7 Hz, 1 H$_{major}$), 2.88 (m, 1 H$_{minor}$), 3.83–5.00 (m, 4 H$_{major}$ + 3 H$_{minor}$), 5.21 (m, 1 H$_{major}$), 6.10 (d, J = 3.3 Hz, 1 H$_{major}$), 6.54 (d, J = 3.4 Hz, 1 H$_{minor}$), 7.04 (d, J = 3.4 Hz, 1 H$_{minor}$), 7.40–8.30 (m, 6 H$_{major}$ +6 H$_{minor}$).

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