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2-Alkoxy-2-fluoro-glycosyl Fluorides as 1,2-Dielectrophilic Synthons for the Synthesis of Naphtho- and Benzo-dihydrofuran Derivatives

Mª Isabel Matheu,* Raouf Echarri, Cèlia Domènech and Sergio Castillón*

Departament de Química, Universitat Rovira i Virgili, Pça. Imperial Tarraco 1, 43005 Tarragona, Spain.

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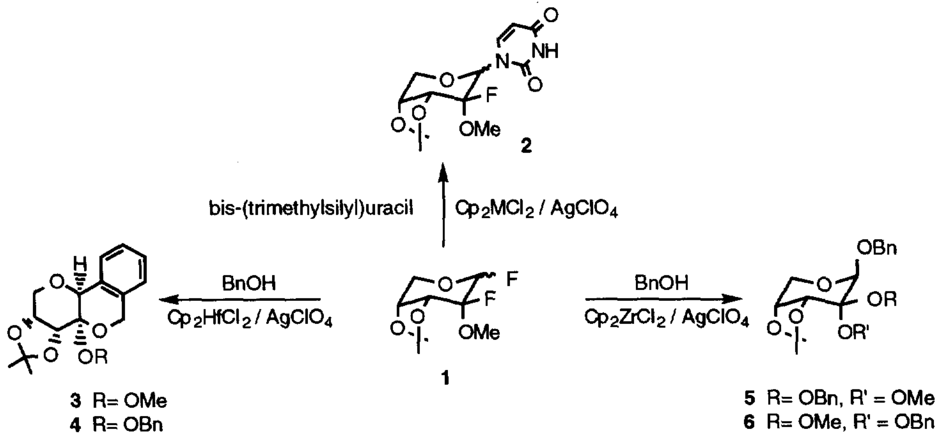
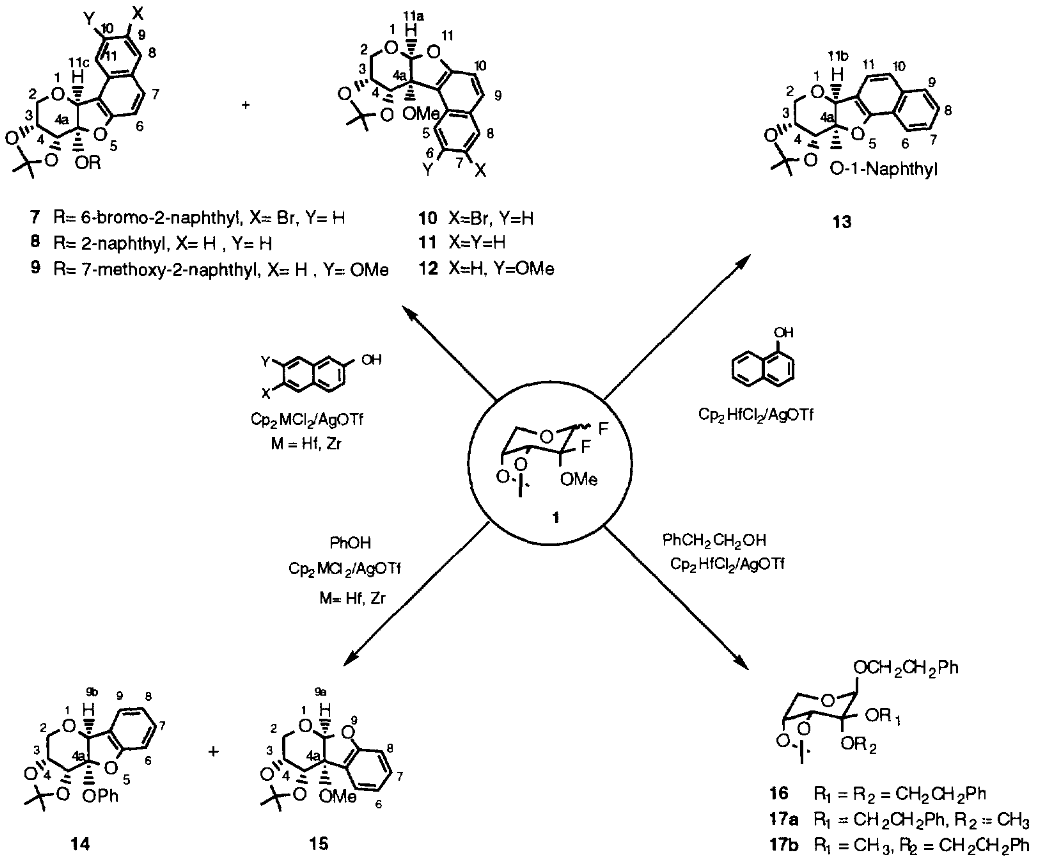
Abstract: *Benzo and naphtho-dihydrofuran derivatives were obtained by the reaction of glycosyl fluorides with phenol and naphthol derivatives in the presence of Cp_2MCl_2/ AgOTf (M= Hf, Zr). This process include a glycosylation, 1,2-migration and an intramolecular cyclization.*

In the last ten years glycosyl fluorides have been extensively used in the field of glycosylation reactions because of the availability, stability and specific activation methods[1]. We have recently shown that glycosyl fluoride **1**[2] is a stable compound which can be selectively activated with metallocene derivatives (Cp_2MCl_2/AgX; M=Hf, Zr; X=ClO_4, OTf) to give fluororibopyranosyl nucleosides **2**[3] (Scheme 1).

In a previous paper we showed that **1** behaves like a 1,2-dielectrophilic synthon when treated with nucleophiles in the presence of Cp_2MCl_2/AgX. Thus, the glycosylation of **1** with benzyl alcohol using $Cp_2HfCl_2/AgClO_4$[1f-i] in order to obtain O-glycosides gave the cyclization products **3** and **4**. Whether



Scheme 1



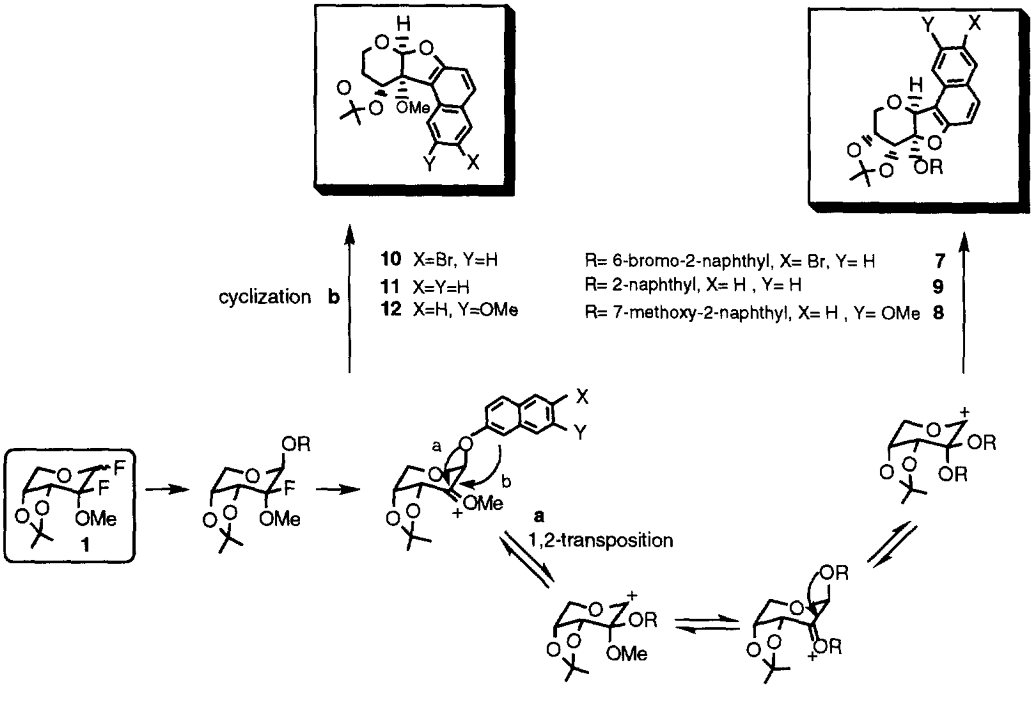
Scheme 2

isochromane derivatives are obtained or not depends on the promoter used and on the glycosyl fluoride/alcohol ratio. Thus, the use of Cp_2ZrCl_2 and/or a large excess of alcohol gave the glycosides **5** and **6**.[4]

The proposed mechanism for this transformation[5] involves the following sequence of events: a) alcohol attack at the anomeric position, b) activation of F-2, c) 1,2-migration of the anomeric substituent or the incorporation of another alcohol molecule at position 2 and d) intramolecular Friedel-Crafts cyclization. There should be an additional transacetalization reaction when obtaining **4**.

Here we study the behaviour of this reaction in order to obtain furan and oxa-cycloheptane derivatives, for which, phenols and phenethyl alcohol derivatives are needed. It is a well-known fact that 2-naphthols react easily with electrophiles, so our initial experiments were carried out using some representative naphthols.

When 2-fluoro-3,4-isopropylidene-2-O-methyl-D-*ribo*-pento-pyranosyl fluoride **1** was allowed to react with 6-bromo-2-naphthol in a sugar/alcohol ratio of 1:2 and $Cp_2HfCl_2/AgOTf$ (ratio 1: 2), a mixture of



Scheme 3

tetracyclic compounds **7** and **10** (Scheme 2) were obtained in yields of 21% and 44% respectively. Similar results were obtained using Cp$_2$ZrCl$_2$/AgOTf (32% and 44% respectively), and no O-glycosides were obtained in either case.

The most significant spectroscopic data supporting structure **7** were: (a) the lack of fluorine in the ^{1}H, ^{13}C and ^{19}F NMR spectra, (b) the presence of 11 aromatic protons at 8.30-7.00 ppm which suggests the incorporation of two units of naphthol, one of which would be cyclized. The absence of an OCH$_3$ signal at $\approx$3.5 ppm is additional information that confirms the interchange between OCH$_3$ and naphthol groups, (c) no signals appeared in the acetal region ($\approx$100ppm), (d) a HETCOR experiment enabled the signal at 43.8 ppm to be assigned to C-11c, indicating that it is not an anomeric carbon (Figure 1), (e) the absolute configuration of C-11c and C-4a was readily established on the basis of a NOESY experiment. A correlation between H-11c and one of the methyl groups of the isopropylidene group is observed, which shows that H-11c and the isopropylidene group are on the same face of the molecule. With all these data in mind, this structure is applicable to compound **7** and is the result of the glycosylation and subsequent F-2 activation, migration of anomeric group to position 2, leaving of the OCH$_3$ group and the intramolecular cyclization (Scheme 3).

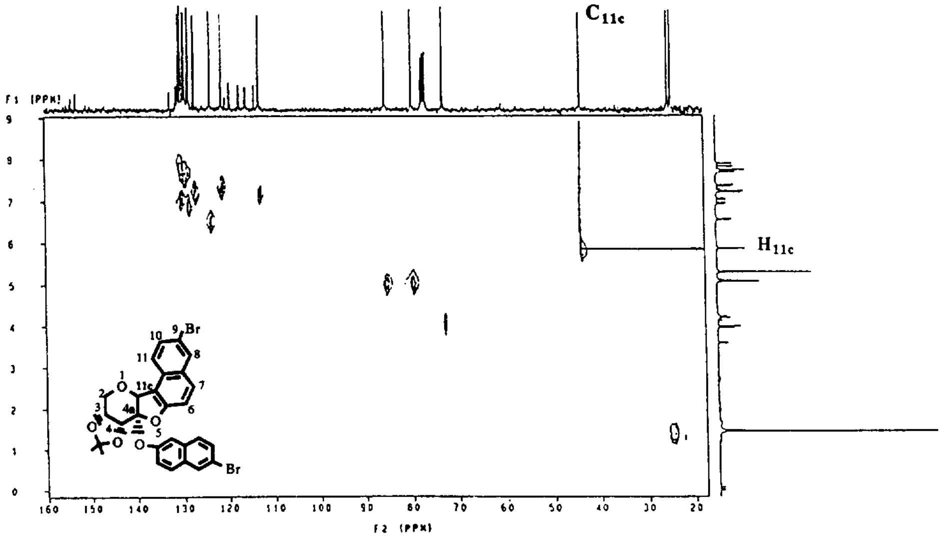


Figure 1: HETCOR experiment of compound **7**

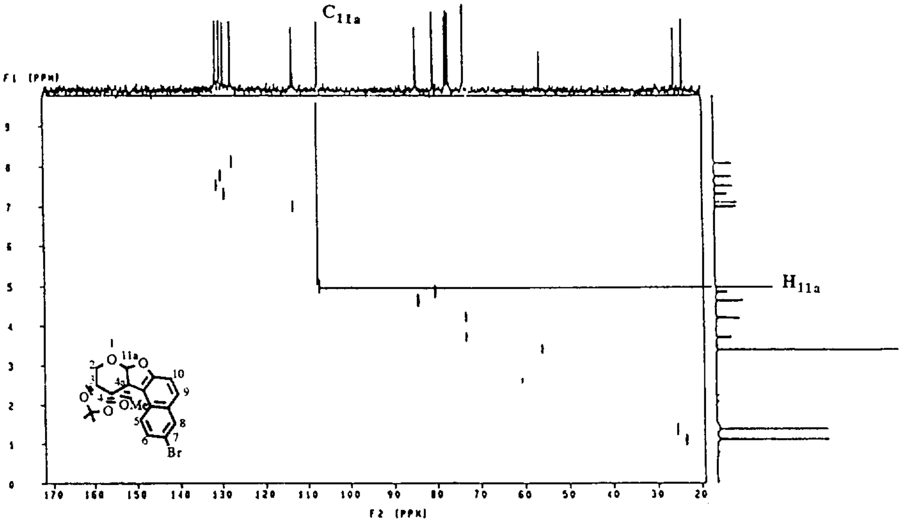


Figure 2: HETCOR experiment of compound **8**.

The ^1H and ^{13}C NMR spectra for compound **10** were similar to those of product **7**. However, the main differences were: (a) the presence of an acetalic carbon at 107.2 in the ^{13}C NMR spectrum which was assigned to C-11a (HETCOR experiment, Figure 2), (b) the signal at 3.46 ppm in the ^1H NMR spectrum and the presence of only 5 aromatic protons shows that the OCH_3 group of the starting material remains in this cyclic product.

Thus the spectroscopic data confirm that unlike the reaction with benzyl alcohol, the main product obtained (**10**) resulted from the O-glycosylation and intramolecular cyclization of the naphtalene ring over C-2. This probably has to do with the higher nucleophilic character of the α position in 2-naphthol with regard to the aromatic ring of benzylic alcohol. Consequently the cyclization (b) competes with 1,2-transposition (a). These data agree with the proposed mechanism,[5] in accordance with the consideration that glycosilation leads exclusively to the axial glycoside, and it explains that cyclization takes place only above the molecular plane (Scheme 3).

O.R. Martin[6-9] has shown that the intramolecular reaction of the 2-OBn in pyranoid derivatives is increased by the presence of activating groups, such as m-OMe. On this basis we decided to use more activated naphthols like 2-naphthol or 7-methoxy-2-naphthol. Thus, when glycosyl fluoride **1** was treated with 2-naphthol in the same reaction conditions, we obtained the cyclic products **8** and **11** in yields of 26% and 9% respectively (Scheme 2). The reaction with the more activated 7-methoxy-2-naphthol gave a mixture of the expected products **9** and **12** in yields of 36% and 13% respectively. The spectra data of all these products were in accordance with the proposed structures.

The reaction of **1** with 1-naphthol gave a mixture of products from which **13** was isolated in only a 14% yield (Scheme 2). Although the product corresponding to O-glycosylation and subsequent cyclization was expected to form, the spectrum of the mixture doesn't show either the OCH_3 signal in ^1H NMR or the anomeric carbon signal in ^{13}C NMR. On the other hand, position 2 of naphthalene undergoes electrophilic attacks with more difficulty than position 1. This fact means that 1-naphthol are less reactive towards Friedel-Crafts cyclization and it could explain the lower yield obtained, and that the main product was the result of a 1,2-transposition (Scheme 3, via a).

When the glycosyl fluoride **1** was allowed to react with phenol in the presence of Cp_2HfCl_2/AgOTf, a mixture of cyclic compounds **14** and **15** was obtained, in addition to other unidentifiable products.

The most actived 3,5-dimethoxyphenol in the same conditions led to a mixture where cyclization and O-glycoside products were detected in a yield of approximately 50%. So, using this more electron-rich phenol not only increases the activation level of the ortho position to the phenolic hydroxyl group (cyclization favoured) but also the nucleophilic character of the oxygen atom (mixture of O-glycosides favoured). Anyway, the major product was the cyclic and transcetalised compound.

In order to extend the possibilities of this process we tried to obtain seven-membered rings by reacting of **1** with phenethyl alcohol. However, no cyclization products were detected, and products **16**, **17a**, **17b** were obtained in ~51% yield as an inseparable mixture. The higher activation energy of the transition state leading to a seven-member ring explains the lack of cyclization products and the fact that the O-glycosylation reaction competes favourably.

The use of 2-methoxy-phenethyl alcohol in the reaction with **1** also gave an inseparable mixture of O-glycosides.

In conclusion benzo- and naphtho-dihydrofurans can be obtained from the 2-alkoxy-2-fluoro-glycosyl fluoride **1** by reaction with phenol and naphthol derivatives in the presence of Cp_2MCl_2/AgOTf (M= Hf, Zr). Reaction of **1** with phenethyl alcohol led only to polysubstitution and no cyclized products were formed. These reactions begin by F-1 activation, glycosylation and take place through different intermediates in equilibrium. The determining step is the competition, after the removal of F-2, among 1,2-migration, intramolecular Friedel-Craft reaction and substitution. The result depends on the activation of the aromatic ring, the size of the cycle to be formed and the alcohol concentration.

EXPERIMENTAL SECTION

General Procedures. Melting points were measured in a Büchi 510 apparatus and are uncorrected. ^1H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 300 instrument (300 MHz, 75 MHz and 288 MHz respectively), using Me_4Si, the central peak at δ 77 ppm and $CFCl_3$, respectively as internal reference. Elemental analyses were determined using a Carlo Erba apparatus. Flash column chromatography was performed on silicagel 60 A CC. Preparative thin layer chromatography was performed on silicagel 60. All the reactions were carried out under an atmosphere of dry argon in oven-dried glassware. Reaction temperatures were recorded as bath temperatures. Solvents for chromatography were distilled at atmospheric pressure prior to use. Anhydrous CH_2Cl_2 was distilled from CaH_2. Reported yields refer to chromatographically and spectroscopically homogeneous material.

General Procedure for the Reaction of 2-fluoro-3,4-isopropylidene-2-O-methyl-α and ß-D-*ribo*-pento-pyranosyl fluoride (1) with Alcohols: A mixture of Cp_2HfCl_2 (0.5 mmols), AgOTf (1 mmol) and powered molecular sieves 4 Å (previously actived) (440 mg) in dichlorometane (1.5 ml) was stirred for 10 min at room temperature. Then, the alcohol (1 mmol) in dichlorometane (0.5 ml) was added and, after 5 minutes at room temperature, the mixture was cooled to -50 °C. Afterwards, the glycosyl fluoride (**1**) (0.5 mmol) was added and the temperature was left to rise to room temperature. When the reaction finished, the reaction mixture was poured into a saturated aqueous $NaHCO_3$ solution, and filtered through a Cellite pad. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x10 ml) and the combined layers were dried ($MgSO_4$) and evaporated. The crude oil was purified by flash or thin layer chromatography.

Reaction of 2-fluoro-3,4-isopropylidene-2-O-methyl-α and ß-D-*ribo*-pento-pyranosyl fluoride (1) with 6-bromo-2-naphthol.

a) Using Cp_2HfCl_2. The general procedure was carried out with Cp_2HfCl_2 (180 mg, 0.48 mmols), AgOTf (247 mg, 0.96 mmol) and 4Å molecular sieves (422 mg), 6-bromo-2-naphthol (214 mg, 0.96 mmol) and compound **1** (107 mg, 0.48 mmol) for 3 hours. The standard work-up gave a crude oil which was purified by flash chromatography (ethyl acetate/hexane 1:6) obtaining product **7** (57 mg, 21 %) as a white solid, and product **10** (86 mg, 44%) as a syrup.

(**7**): m.p.= 204-206 °C, $[\alpha]_D$= -177.0° (c 0.3, $CHCl_3$), ^1H NMR ($CDCl_3$, 300 MHz), δ 7.79-6.40 (m, 11H, H_{Ar}), 5.77 (s, 1H, H-11c), 5.02-4.94 (m, 2H, H-3, H-4), 4.12 (dd, 1H, $J_{2ax-2eq}$= 10.5 Hz, J_{2ax-3}= 3.6 Hz, H-2ax), 3.88 (d, 1H, H-2eq), 1.37 (s, 6H, $2CH_3$); ^{13}C($CDCl_3$, 75.4 MHz), δ 154.3 (O-$\underline{C}_{Ar}$), 153.1 (O-$\underline{C}_{Ar}$), 130.5-112.7 (C_{Ar}), 113.7 (Cisopr) 85.3 (C-4), 79.6 (C-3), 72.8 (C-2), 43.8 (C-11c), 25.3 (CH_3), 24.6 (CH_3). Anal. Calcd for $C_{28}H_{23}O_5Br_2$: C, 56.21; H, 3.68. Found: C, 55.96, H, 3.72.

(**10**): $[\alpha]_D$= -113.0° (c 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$, 300 MHz), δ 8.17 (d, 1H, J_{5-6}= 9.1 Hz, H-5), 7.83 (d, 1H, J_{8-6}= 2.0 Hz, H-8), 7.60 (d, 1H, J_{10-9}= 8.8 Hz, H-10), 7.39 (dd, 1H, H-6), 7.06 (d, 1H, H-9), 5.05 (s, 1H, H-11a), 4.93 (dd, 1H, J_{3-4}= 6.0 Hz, J_{3-2ax}= 4.1 Hz, H-3), 4.72 (d, 1H, H_4), 4.28 (d, 1H, $J_{2eq-2ax}$= 11.0 Hz, H-2eq), 3.76 (dd, 1H, H-2ax), 3.46 (s, 3H, OCH_3), 1.45 (s, 3H, CH_3), 1.17 (s, 3H, CH_3); ^{13}C($CDCl_3$, 75.4 MHz), δ 156.0 (C-10a), 130.9 (C-10), 129.9 (C-8), 129.2 (C-6), 127.4 (C-5), 113.2 (C-9), 125.4, 123.5, 121.6 (C-4b, C-4c, C-8a), 112.9, 112.6 (Cisopr, C-7), 107.2 (C-11a), 93.5 (C-4a), 84.3 (C-4), 80.3 (C-3), 73.2 (C-2), 56.1 (OCH_3), 25.5 (CH_3), 23.5 (CH_3). Anal. Calcd for $C_{19}H_{19}O_5Br$: C, 56.02; H, 4.67. Found: C, 55.85, H, 4.60.

b) Using Cp_2ZrCl_2. The general procedure was followed starting from compound **1** (107 mg, 0.48 mmol), Cp_2ZrCl_2 (140 mg, 0.48 mmol), AgOTf (247 mg, 0.96 mmol), 4 Å molecular sieves (422 mg), and 6-bromo-2-naphthol (214 mg, 0.96 mmol). After 2.5 hours and the corresponding work-up, the resulting crude oil was purified by thin layer chromatography (ethyl acetate/hexane 1:6) to give compounds **7** (87 mg, 32 %) and **10** (86 mg, 44 %).

Reaction of 2-fluoro-3,4-isopropylidene-2-O-methyl-α and ß-D-*ribo*-pento-pyranosyl fluoride (1) with 2-naphthol.

Compound **1** (118 mg, 0.53 mmol) in dichloromethane (3 ml) was treated with Cp_2HfCl_2 (200 mg, 0.53 mmols), AgOTf (270 mg, 1.05 mmol) and molecular sieves 4Å (462 mg), and 2-naphthol (152 mg, 1.05 mmol) for 2 hours in accordance with the general procedure. The reaction crude oil was purified by thin layer chromatography (ethyl acetate/hexane 1:6) obtaining 60 mg (26 % yield) of compound **8** as a white solid, and 9 mg (5% yield) of compound **11** as a syrup.

(**8**): m.p.= 112-114 °C, $[\alpha]_D$= -101.0° (c 0.2, $CHCl_3$), ^1H NMR ($CDCl_3$, 300 MHz) δ 7.80-6.65 (m, 13H, H_{Ar}), 5.90 (s, 1H, H-11c), 5.05 (m, 2H, H-3, H-4), 4.21 (dd, 1H, $J_{2ax-2eq}$= 10.4 Hz, J_{2ax-3}= 3.8 Hz, H-2ax), 3.96 (d, 1H, H-2eq), 1.46 (s, 3H, CH_3), 1.44 (s, 3H, CH_3); ^{13}C ($CDCl_3$, 75.4 MHz), δ 153.1 (O-$\underline{C}_{Ar}$), 134.5 (O-$\underline{C}_{Ar}$), 130.6-112.5 (C_{Ar}), 114.0, 109.9 (C-4a, Cisopr), 85.9, 80.0 (C-4, C-3), 73.2 (C-2), 44.3 (C-11c), 25.8 (CH_3), 25.1 (CH_3). Anal. Calcd for $C_{28}H_{24}O_5$: C, 76.31; H, 5.45. Found: C, 76.40, H, 5.50.

(**11**): ^1H NMR ($CDCl_3$, 300 MHz) δ 8.28-6.96 (m, 6H, H_{Ar}), 5.45 (s, 1H, H-11a), 5.16 (d, 1H, J_{4-3}= 6.1 Hz, H-4), 4.85 (dd, 1H, J_{3-2ax}= 4.2 Hz, H-3), 4.18 (d, 1H, $J_{2eq-2ax}$= 10.2 Hz, H-2eq), 3.86 (dd, 1H, H-2ax), 3.62 (s, 3H, OCH_3), 1.49 (s, 3H, CH_3), 1.21 (s, 3H, CH_3); ^{13}C ($CDCl_3$, 75.4 MHz), δ 132.2, 128.2, 125.9, 125.9, 123.5, 115.3 (C-10, C-9, C-8, C-7, C-6, C-5), 112.4, 112.0 (C-4a, Cisopr), 111.9 (C-11a), 80.9, 80.6 (C-3, C-4), 72.3 (C-2), 58.3 (OCH_3), 25.6 (CH_3), 23.5 (CH_3).

Reaction of 2-fluoro-3,4-isopropylidene-2-O-methyl-α and ß-D-*ribo*-pento-pyranosyl fluoride (1) with 7-methoxy-2-naphthol.

Following the experimental procedure, compound **1** (64 mg, 0.29 mmol) in dichlorometane was treated with Cp_2HfCl_2 (110 mg, 0.29 mmols), AgOTf (149 mg, 0.58 mmol) molecular sieves 4Å (255 mg), and 7-methoxy-2-naphthol (100 mg, 0.58 mmol) for 1.5 hours. The reaction crude was purified by thin layer chromatography (ethyl acetate/hexane 1:6) obtaining 52 mg (36 % yield) of compound **9** as a white solid, and 13 mg (13 % yield) of compound **12** as a syrup.

(**9**): m.p.= 217-218 °C, $[\alpha]_D$= -125.0° (c 0.2, $CHCl_3$), ^1H NMR ($CDCl_3$, 300 MHz) δ 7.60-5.90 (m, $11H_{Ar}$), 5.76 (s, 1H, H-11c), 5.00 (m, 2H, H-3, H-4), 4.14 (dd, 1H, $J_{2ax\text{-}2eq}$= 10.4 Hz, $J_{2ax\text{-}3}$= 3.5 Hz, H-2ax), 3.93 (d, 1H, H-2eq), 3.10 (s, 3H, OCH_3), 2.99 (s, 3H, OCH_3), 1.40 (s, 3H, CH_3), 1.37 (s, 3H, CH_3); ^{13}C ($CDCl_3$, 75.4 MHz), δ 158.0 ($O\text{-}\underline{C}_{Ar}$), 156.7 ($O\text{-}\underline{C}_{Ar}$), 154.4 ($O\text{-}\underline{C}_{Ar}$), 153.5 ($O\text{-}\underline{C}_{Ar}$), 129.7-100.1 ($C_{Ar}$), 85.4, 79.6 (C-3, C-4), 72.8 (C-2), 54.4 (2 OCH_3), 44.0 (C-11c), 25.3 (CH_3), 24.6 (CH_3). Anal. Calcd for $C_{30}H_{28}O_7$: C, 72.06; H, 5.60. Found: C, 71.82, H, 5.59.

(**12**): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.63 (d, 1H, $J_{5\text{-}7}$= 2.5 Hz, H-5), 7.61 (d, 1H, $J_{8\text{-}7}$= 9.1 Hz, H-8), 7.56 (d, 1H, $J_{10\text{-}9}$= 8.9 Hz, H-10), 6.90 (dd, 1H, H-7), 6.80 (d, 1H, H-9), 5.40 (s, 1H, H-11-a), 5.15 (d, 1H, $J_{4\text{-}3}$= 6.0 Hz, H-4), 4.85 (dd, 1H, $J_{3\text{-}2ax}$= 4.3 Hz, H-3), 4.16 (d, 1H, $J_{2eq\text{-}2ax}$= 10.4 Hz, H-2eq), 3.90 (dd, 1H, H-2ax), 3.85 (OCH_3), 3.60 (OCH_3), 1.48 (CH_3), 1.22 (CH_3); ^{13}C ($CDCl_3$, 75.4 MHz), δ 157.9, 155.3 (C-6, C-10a), 131.9-104.7 (C_{Ar}), 115.2 (C-11a), 80.8 (C-3), 80.6 (C-4), 72.6 (C-2), 58.3, 55.4 (OCH_3), 26.1 (CH_3), 23.4 (CH_3).

Reaction of 2-fluoro-3,4-isopropylidene-2-O-methyl-α and ß-D-*ribo*-pento-pyranosyl fluoride (1) with 1-naphthol.

Following the general procedure for the reaction of the glycosyl fluoride **1** with alcohols, compound **1** (127 mg, 0.57 mmol) was treated in dichloromethane with Cp_2HfCl_2 (215 mg, 0.57 mmols), AgOTf (293 mg, 1.14 mmol) 4Å molecular sieves (502 mg), and 1-naphthol (163 mg, 1.14 mmol) for 2 hours. Successive purifications by thin layer chromatography (ethyl acetate/hexane 1:5) gave 38 mg (14 % yield) of compound of a mixture where product **13** was present in >96%.

(**13**): ^1H NMR ($CDCl_3$, 300 MHz) δ 8.55-6.40 (m, 13H, H_{Ar}), 5.76 (s, 1H, H-11b), 4.96 (d, 1H, $J_{3\text{-}4}$= 5.9 Hz, $J_{3\text{-}2ax}$= 4.4 Hz, H-3), 4.73 (d, 1H, H-4), 4.12 (dd, 1H, $J_{2ax\text{-}2eq}$= 10.4 Hz, H-2ax), 3.87 (d, 1H, H-2eq), 1.49 (s, 3H, CH_3), 1.30 (s, 3H, CH_3); ^{13}C ($CDCl_3$, 75.4 MHz), δ 128.1-108.2 (C_{Ar}), 85.0 (C-4), 79.6 (C-3), 73.8 (C-2), 44.7 (C-11b), 26.0 (CH_3), 24.6 (CH_3).

(**14**) (spectral data obtained from the mixture): ^{1}H NMR (CDCl$_3$, 300 MHz), δ 7.20-6.65 (m, 9H, H$_{Ar}$), 4.87 (dd, 1H, $J_{3\text{-}4}$= 5.8 Hz, $J_{3\text{-}2ax}$= 3.7 Hz, H-3), 4.83 (s, 1H, H-9b), 4.71 (d, 1H, H-4), 4.00 (dd, 1H, $J_{2ax\text{-}2eq}$= 10.4 Hz, H-2ax), 3.90 (d, 1H, H-2eq), 1.26 (s, 6H, 2CH$_3$). ^{13}C(CDCl$_3$, 75.4 MHz), δ 157.6 (O-$\underline{C}_{Ar}$), 154.9 (O-$\underline{C}_{Ar}$), 132.0-110.0 (C$_{Ar}$), 118.8 (C-4a), 113.3 (Cisopr), 85.0 (C-4), 79.7 (C-3), 72.6 (C-2), 53.4 (C-9b), 25.9 (CH$_3$), 24.9 (CH$_3$).

(**15**) (spectral data obtained from the mixture): ^{1}H NMR (CDCl$_3$, 300 MHz), δ 7.30-6.80 (m, 4H, H$_{Ar}$), 5.66 (s, 1H, H-9a), 5.11 (m, 1H, H-3), 4.72 (d, 1H, $J_{4\text{-}3}$= 6.2 Hz, H-4), 4.26 (dd, 1H, $J_{2ax\text{-}2eq}$= 10.8 Hz, $J_{2ax\text{-}3}$= 4.4 Hz, H-2ax), 4.17 (dd, 1H, $J_{2eq\text{-}3}$= 1.1 Hz, H-2eq), 3.68 (s, 3H, OCH$_3$), 1.51 (s, 3H, CH$_3$), 1.29 (s, 3H, CH$_3$). ^{13}C(CDCl$_3$, 75.4 MHz), δ 155.2 (C-8a), 131.6-111.1 (C$_{Ar}$), 106.8 (C-9a), 85.7 (C-4), 81.1 (C-3), 72.2 (C-2), 57.6 (OCH$_3$), 26.2 (CH$_3$), 25.0 (CH$_3$).

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