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Fluorination of tertiary alcohols derived from di-*O*-isopropylidenehexofuranose and *O*-isopropylidenepentofuranose

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In dedication to Professor Alain Tressaud on the occasion of his 70th birthday.

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ABSTRACT

The stereo- and regioselectivity of the dehydroxyfluorination of various tertiary alcohols derived from di-*O*-isopropylidenehexofuranose and 1,2-*O*-isopropylidenepentofuranose has been studied. Reactions have been accomplished using DAST and PFPDEA (1,1,3,3,3-pentafluoropropene-diethylamine adduct) as fluorinating reagents. Dehydroxyfluorination of allylic alcohol **2a** has occurred with an inversion of configuration and allylic rearrangement leading to two ciral regioisomers **6a** and **7a**. Analogous reaction of **2b** has given allylic chiral fluoride **7b** as the only product. In case of phenylacetylene, styryl and benzylic alcohols **3a**/**3b-5a**/**5b** the single diastereoisomers **8a**/**8b-10a**/**10b** have been obtained. Additionally, the participation of 1,2-*O*-substituent effect in carbocation stabilization during fluorination have been discussed.

1. Introduction

Placing a fluorine atom into molecules, due to its steric and polar characteristic can have a remarkable effect upon the physical, chemical and biological properties [1]. This effect is especially apparent in a group of fluorinated carbohydrates and their derivatives. Their numerous applications in medicinal chemistry varies from radio labeled sugars used as sensors in medicinal imaging (e.g. [^{18}F]-2-fluoro-2-deoxy-D-glucose – FDG [2]) to building blocks for the synthesis of nucleosides with antiviral and antitumor properties (e.g. 2′,2′-difluoro-2′-deoxycytidine-*gemcitabine* [3]; 2′-fluoromethylene-2′-deoxycytidine-*tezacitabine* [4] – inhibitors of RNR) [Fig. 1].

Dehydroxyfluorination, effective with primary, secondary and tertiary alcohols, is one of the methods of introducing a fluorine into organic compounds. Regarding the direct conversion of hydroxyl groups to fluorides, numerous reagents are available [5]. Among the most useful, diethylaminosulfur trifluoride (DAST) has been employed [6]. In alternative method α-fluoroamine and α-fluoroenamine derivatives have been applied [5,7–9]. Among them Yarovenko's (diethylamine adduct of chlorotrifluoroethene) [7] and Ishikawa's (diethylamine adduct of hexafluoropropene) [8] as fluorinating reagents have been used. Application of 1,1,3,3,3-pentafluoropropene diethylamine adduct (PFPDEA) as a dehydroxyfluorination reagent has also been studied [9]. Among organic fluorine compounds, allylic and propargylic fluorides constitute an important class of chiral building blocks essential for organic synthesis [10]. A direct dehydroxyfluorination of allylic alcohols using DAST (Scheme 1) can occurred with a retention or an inversion of configuration. Additionally, transposition of the double bond has been observed [6a,10–12]. Allylic substitution has not been limited to DAST but also has occurred with other fluorinating reagents [12a]. In general, fluorination of the substituted with alkyl groups allylic alcohols leads to low regioselectivity, while phenyl or conjugated double bonds substituents increase regioselectivity [11a,13a].

While regio- and stereoselectivity during fluorination of allylic alcohols remain uncertain, several methodologies have been proposed to solve this problem [14]. Grée et al. have achieved the regio- and stereocontrol of fluorination by temporary complexation of the π-system with a transition metals [15]. Moreover, Prakesch et al. demonstrated a complete regiocontrol and good stereocontrol of dehydroxyfluorination of propargylic alcohols followed by hydrometallation or hydrogenation [15c,16]. However, still preservation of the absolute configuration at the fluorine-containing stereocenter was not complete. Furthermore, Gouverneur et al. reported for the first time enantioselective synthesis of propargylic fluorides using an electrophilic fluorine

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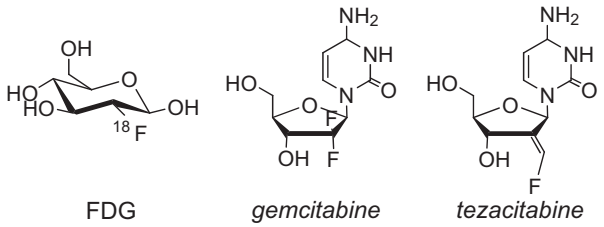


Fig. 1. Examples of fluorinated sugar derivatives.

source [17]. Starting from highly enantioenriched allenylsilanes, complete chirality transfer was achieved. Nevertheless, a disadvantage of this approach – extended and time-costly synthesis of starting materials – limits its application on larger scales (Scheme 2).

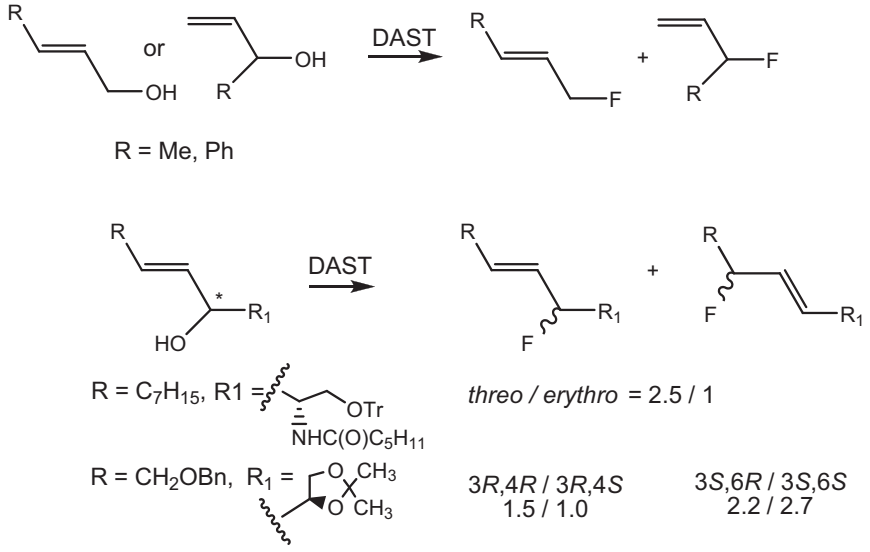
Recently, Jiang et al. reported successful synthesis of chiral propargylic or secondary allylic fluorides with enantioselectivity up to 99% ee [18]. This method involved organocatalytic α-fluorination of aldehyde and next homologation of the intermediate to obtain chiral fluorides (Scheme 2). Also, Grée et al. reported an alternative method for fluorination dienic alcohols that are complexed with iron tricarbonyl leading to nonracemic products [15a]. However, fluorination of chiral secondary dienyl alcohol complexes occurs with retention of configuration for one enantiomer and with partial racemisation for the opposite one. Although the influence of the structural features of the starting allylic alcohols on the stereo- and regioselectivity of fluorination has been extensively studied, there is a need for alternative, efficient methodology for obtaining optically active alcohols. This possibility could be achieved by applying carbohydrates as chiral tools or blocks in an organic synthesis. In a search for novel inhibitors of ribonucleoside reductases [19], we attempted the synthesis of 2′-fluoro-2′-vinyl-2′-deoxycytidine as a Tezacitabine [4] analogues. In our approach, first we studied fluorination, using PFPDEA and DAST, with carbohydrate precursors. In this paper we report the results of our studies concerning the dehydroxyfluorination of tertiary alcohols derived from *O*-isopropylidenehexo- and -pentofuranose compounds, additionally modified at C-3 with the vinyl, phenyl, styryl or phenylacetylene substituents. Resulting stereocontrol strongly affected by neighboring 1,2-*O*-isopropylidene groups in rigid pentofuranose rings would be also discussed.

2. Results and discussion

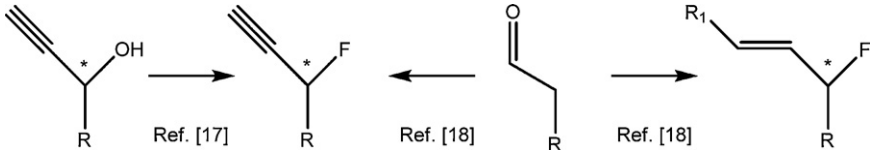
Our synthesis were started from easily to handle diacetone glucose and 5-*O*-benzyl-1,2-*O*-isopropylidenexylofuranose derivatives. Treatment of 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose-3-ulose **1a** [20] and 5-*O*-benzyl-3-oxo-1,2-*O*-isopropylidene-α-D-*erythro*-pentofuranose **1b** [21] with different Grignard reagents or addition of lithium acetylide yield two series of tertiary alcohols (Scheme 3). Treatment of ketones **1a** and **1b** with vinyl magnesium bromide gave **2a** [22] and **2b** with 59% and 52% yields, respectively.

Next, the prepared tertiary allylic alcohol **2a** was examined towards dehydroxyfluorination. Reaction of pentafluoropropene diethyl amine adduct [PFPDEA, RT (48 h)] prepared in our laboratory [9] with **2a** gave, after isolation, only two products **6a** and **7a** with 31% and 34% yields, respectively (Scheme 4). Corresponding reaction of **2a** with DAST [−78 °C (1 h), RT (1 h)] gave only **6a**/**7a** with 1.6/1 ratio and lower yield (26%/16%).

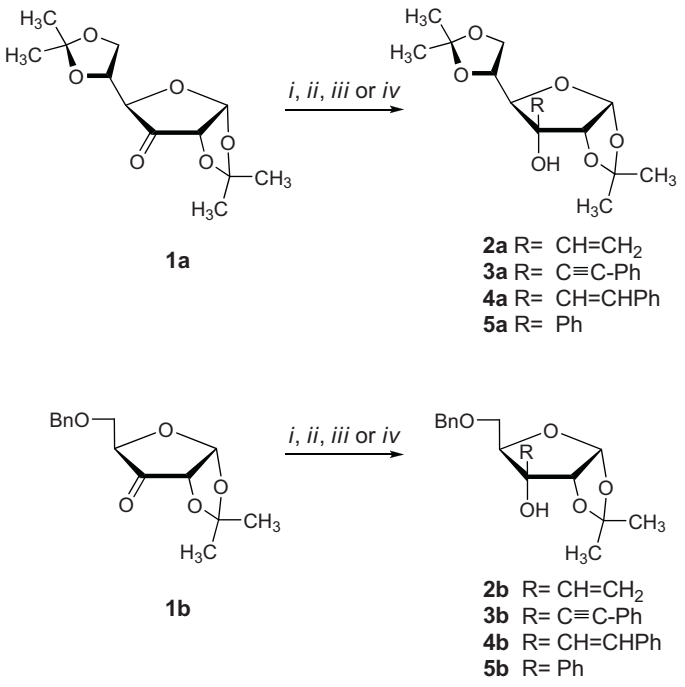
The signals in ^{19}F NMR spectra for **6a** appeared at δ −181.3 (ddd, ^{3}J = 31.5, 21.6, 11.5 Hz) whereas for product **7a** they were located at δ −214.6 (tddd, ^{2}J = 46.7 Hz, ^{3}J = 13.2 Hz, ^{5}J = 5.4, 2.5 Hz). The larger values of coupling constants in **6a** observed for fluorine and vicinal hydrogen atom H-4 (*trans*, ^{3}J = 31.5 Hz) as well as smaller coupling constants between fluorine and H-2 (*cis*, ^{3}J = 11.5 Hz) supported the stereochemical assignment at C-3 as being 3*R* [23].



Scheme 1.



Scheme 2.



Scheme 3. Reagents and conditions (i) vinylmagnesium bromide, THF, RT, overnight (ii) phenyl acetylene, *n*-BuLi, THF, −78 °C, then **1a** or **1b**, 4 h (iii) **3a** or **3b**, Et_2O, 0 °C, then $LiAlH_4$, 3.5 h (*iv*) phenylmagnesium bromide, THF, RT, overnight.

The fluorination leading to isomer **6a** appears to have occurred with an inversion of configuration and preferentially to the less hindered top-face. This is in accordance with the stereoselective β-face $NaBH_4$ reduction of ulose **1a** [24] as well as the addition of magnesium vinyl bromide to 3-keto nucleoside analogue [22b]. Product **7a** possesses characteristic up-field shielding of fluorine atom signal (δ −214.6, tddd) typical for terminal CH_2F group. It is worth mentioning that the geminal CH_2F protons are magnetically nonequivalent. These protons have different chemical shifts and coupling constants to each particular nucleus, *i.e.* δ 5.03 (dddd, ^2J = 46.5 Hz, ^2J = 1.9 Hz, ^3J = 5.4 Hz, ^5J = 0.5 Hz, H-b) and δ 5.19 (ddd, ^2J = 47.2 Hz, ^2J = 1.4 Hz, ^3J = 7.5 Hz, H-b′), respectively [25]. Determining D-*gluco* configuration in **6a** with an inversion of configuration could support proposed for fluorination by PFPDEA mechanism as S_Ni [9]. On the other hand, Todoroki et al. during a fluorination of chiral tertiary allylic system with conjugated double bonds with DAST observed mainly retention of configuration [26]. They also proposed S_Ni mechanism since the steric effect in abscisic acid (ABA) derivatives would not allow to invert the configuration at carbon C-1′ during fluorination. In our case however, the stereoselective fluorination occurring from the α – side as well as the presence of product **7a** indicates a considerable S_N1 component in this reaction. Fluorination seems to be strongly affected by stabilization of planar allylic carbocation (derived from transformation of hydroxyl group into good leaving group with PFPDEA or DAST) by oxygen of 1,2-*O*-isopropylidene group situated on bottom-side of ring as illustrated in Scheme 5.

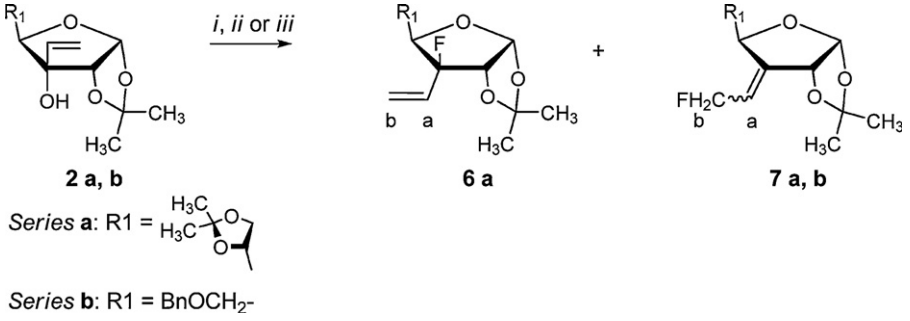
Analogous stabilization was reported for chiral allylic and propargylic alcohols by Bresciani et al. but modest regio- and stereoselectivity during fluorination with similar yields (with a range of reagents) comparing to our reactions would indicated additional influence of a rigid pentofuranose ring [11c,27]. It is well known that stereoselective bond formation especially in carbohydrates, could be achieved by various neighboring protecting groups [28].

Reaction of **2a** with DAST [1.5 eq, −78 °C (1 h), RT (1 h)] gave only **6a**/**7a** with ratio 1.6:1 and lower yields (26%/16%). In order to obtain higher regioselectivity, we applied modified procedure of fluorination. Thus, the problem with regiocontrol of DAST-induced fluorination giving a mixture of primary and tertiary allylic fluorides, in case of chiral 19-norwitamin D analogues, was solved by a large excess of fluorinating reagents and/or changing of solvent [29]. As a result, the reported reaction conditions afforded considerably better results of terminal fluoride (61% and 81%) in comparison to standard condition (1.5 eq of DAST) and no tertiary fluoride as a rearrangement product. So, reaction of **2a** with DAST [10 eq, −78 °C (1 h), RT (1 h)] gave **6a**/**7a** with 2:1 ratio and 45% yield (both products).

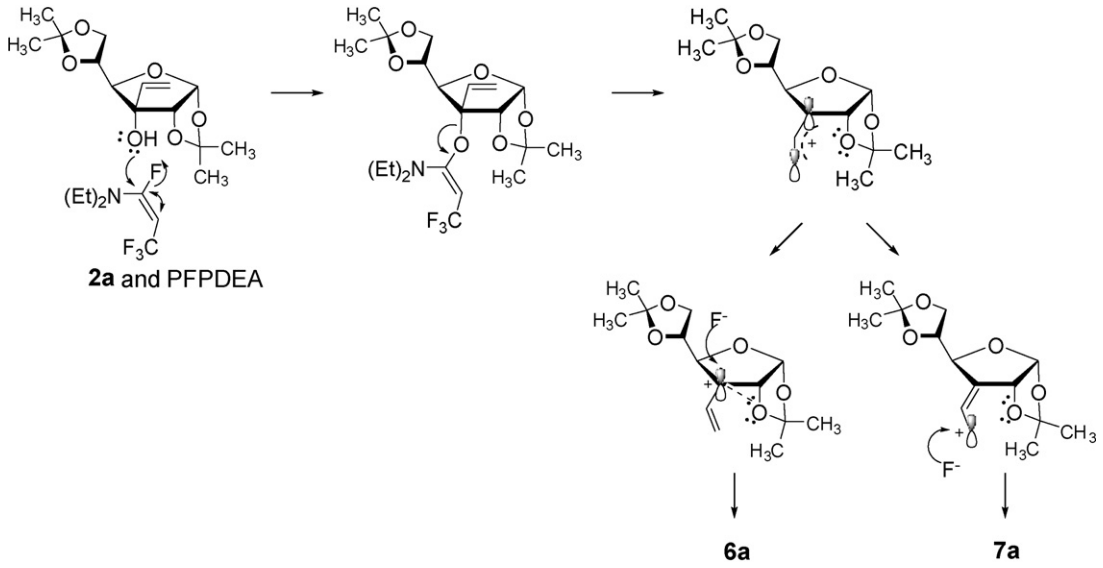
Surprisingly, reaction of **2b** with DAST gave **7b** with 51% yield as the single product (Scheme 4). The position of the introduced fluorine atom in **7b** was deduced from ^{19}F NMR and ^1H NMR spectra. ^1H NMR spectra showed signals at δ 5.10 (dddd, H-b) and δ 5.12 (ddd, H-b′) of the methylene protons coupled with a fluorine atom with large vicinal coupling constant $^2J \approx 47$ Hz. The fluorine signals of **7b** as for **7a** appeared at δ: −214.3 as a tddd with a coupling constants $^2J \approx 47$ Hz. Analogous reaction of **2b** with PFPDEA gave mixture containing only 10% of **7b** (^{19}F NMR of crude reaction mixture) while reaction with DAST [10 eq, −78 °C (1 h), RT (1 h)] yields **7b** (53%). The presence of one diastereoisomer **7b** as the only product would suggest influence of combination of steric and electronic effects on planar allylic carbocation.

Taking into account that conjugated system participates in regioselectivity control in fluorination as well as substituent effect determines its stereoselectivity [11a,13a], compounds **3a** and **3b** were synthesized. Reaction of ketones **1a** and **1b** with lithium phenyl acetylide gave **3a** [30] and **3b** with a 46% and 60% yields, respectively [31]. Deoxyfluorination of compounds **3a**/**3b** were carried out with DAST yielding the single products **8a** (84%) and **8b** (79%) without transposition of multiple bond during reaction time (Scheme 6).

Analogous reaction of **3a**/**3b** with PFPDEA gave chiral fluorides **8a** and **8b** with lower yields (29% and 20%, respectively). Determination of configuration at C-3 was based on the analysis of coupling constants of fluorine and vicinal H-4 and H-2 atoms.



Scheme 4. (i) PFPDEA (**6a**/**7a**: 31%/34%; **7b**: 10%), (ii) DAST (1.5eq, **6a**/**7a**: 26%/16%, **7b**: 51%), (iii) DAST (10 eq, **6a**/**7a**: 2/1, 45%, **7b**: 53%).



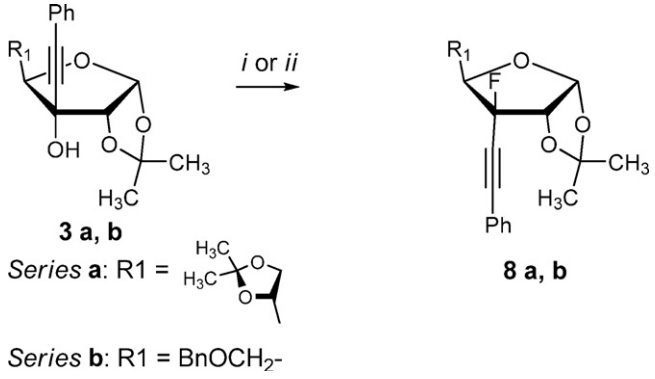
Scheme 5. Stabilization of allylic carbocation intermediate by adjacent bottom-face ether oxygen causing regio- and stereocontrol of fluorination leading to **6a** or **7a**.

Thus, tertiary propargylic fluoride **8a** had coupling constants ^3J = 25.3 Hz (F – H-4, *trans*), slightly different from this in **6a**, but ^3J = 11.1 Hz (F – H-2, *cis*) analogous to **6a**, while its fluoride signal was located at δ: −163.9 (dd). Similarly compound **8b** had coupling constants ^3J = 24.6 Hz (F – H-4, *trans*), and ^3J = 11.0 Hz (F-H-2, *cis*) while in ^{19}F NMR the signal of fluorine appeared at δ: −165.0. Parallel results were presented by Grée and co-workers [16a,32]. They fluorinated non terminal enentioenriched propargylic alcohols at low temperature (−75 °C, −95 °C) with DAST. While reaction of one enantiomer gave fluoride with high ee (96%) and yield (85%), the other enantiomer underwent temperature-dependent reaction to give fluoride with 55% yield but lower ee (75%). Another method to diastereoselectively synthesize enantioenriched propargylic fluorides was developed via S_N1 type reaction of DAST with diastereomeric propargylic alcohol cobalt–carbonyl complexes [33]. This approach resulted fluorides with good yields and moderate to high diastereoselectivities.

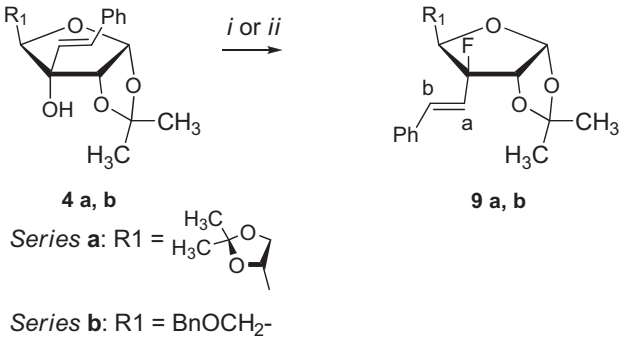
Next, study on regioselectivity of deoxyfluorination was provided on compounds **4a** and **4b**, obtained by treatment of **3a**/**3b** with $LiAlH_4$ (96% and 80%) [34] (Scheme 3). Analysis of ^{1}H NMR spectra of **4a** and **4b** confirmed *E*-alkene configuration at double bond. Consequently, the fluorination of **4a**/**4b** using PFPDEA and DAST was carried out (Scheme 7).

As a result, the single chiral fluorides **9a**/**9b** were isolated with ^{19}F NMR δ: −178.8 (ddd, ^3J = 31.0, 21.4, 11.5 Hz) for **9a**, while for **9b** the signals in ^{19}F NMR were located at δ: −181.6 (ddd, ^3J = 27.2, 21.4, 11.1 Hz). So, the introduction of fluorine atom afforded with the inversion of configuration at C-3 (D-*gluco*, D-*xylo*). The products **9a**/**9b** were obtained with yields 74% and 64%, respectively. The chemical shift of fluorine and protons were shielded comparing to **8a**. The stereochemical assignment for **9a** and **9b** (3*R*) was confirmed by coupling constants between fluorine and protons H-4 (*trans*, ^3J = 21.4 Hz) and H-2 (*cis*, ^3J = 11.5 Hz) for **9a**, while for **9b** coupling constants were $^3J_{4\text{-F}}$ = 27.2 Hz and $^3J_{2\text{-F}}$ = 11.1 Hz. Moreover, examination of ^{13}C NMR spectra of **9a** allowed to distinguish besides ^1J = 184.1 Hz for C-3 and fluorine (δ 101.6, d), the smaller ^2J = 37.8 Hz at δ 85.5 (d, C-2) and δ 81.6 (d, ^2J = 19.6 Hz, C-4), as well as for vinylic carbon at δ 121.3 (d, ^2J = 17.9 Hz, C-a) [23]. Analogously, in ^{13}C NMR spectra of **9b** signals for C-3 appeared at δ: 101.6 as dublet with ^1J = 185.0 Hz, while for C-2 were located at δ 85.3 (d, J = 37.3 Hz,), for C-4 at δ 81.3 (d, J = 19.4 Hz,) as well as for vinylic carbon C-a at δ 121.1 (d, J = 17.6 Hz). Fluorination of **4a**/**4b** using PFPDEA gave **9a**/**9b** with yields 47%/30%. The regioselectivity of reaction **4a**/**4b** with DAST or PFPDEA is in accordance with literature data. Thus, fluorination of phenyl substituted or conjugated double bonds substituents alcohols increase regioselectivity towards more conjugated products [11a,13a].

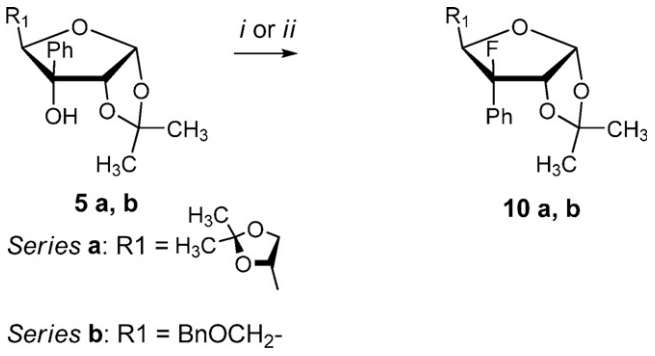
To compare the fluorination stereoselectivity, benzylic type alcohols **5a** and **5b** were obtained (Scheme 3). In both cases the only one diastereoisomeric alcohol **5a** and **5b** were isolated after Grignard reaction of ketone **1a**/**1b** with phenyl magnesium bromide (besides a few percent of second diastereoisomer reported by Fisher and Horton for **1a**) [35]. Fluorination of compounds **5a**/**5b** carried out with DAST gave the single products **10a**/**10b** with yields 58%/28% (Scheme 8).



Scheme 6. (i) DAST (**8a**: 84%; **8b**: 79%;), (ii) PFPDEA (**8a**: 29%; **8b**: 20%).



Scheme 7. (i) DAST (**9a**: 74%; **9b**: 64%), (ii) PFPDEA (**9a**: 47%; **9b**: 30%).



Scheme 8. (i) DAST (**10a**: 58%, **10b**: 28%), (ii) PFPDEA (**10a**: 22%; **10b**: 15%).

The ^{1}H NMR as well as ^{19}F NMR spectra confirmed that **10a**/**10b** had C-3 *gluco*/*xylo* configurations. The signals of fluorine atom in **10a** appeared at δ −175.4 (dd) – the value typical for tertiary benzylic fluorides while for **10b** were located at δ −176.5 (dd). Their chemical shifts could be compared to this of **8a** (δ: −178.8). In ^{1}H NMR spectra of compound **10a**/**10b**, the coupling constants for the fluorine atoms and protons H-4 were larger, (^{3}J = 30.2 Hz, ^{3}J = 28.1 Hz), while between fluorines and protons H-2 were smaller (^{3}J = 11.5 Hz, ^{3}J = 11.6 Hz).

This observation is in accordance with data concerning more stable orthogonal conformation of benzylic fluoride which benefits from a π–σ* C–F interaction, which narrows the C–C–F angle and lengthens the C–F bond relative to the planar conformer [1e,36]. Fluorination occurring preferentially from one side is in contrast to the results obtained by reaction of racemic phenyl substituted α-hydroxy ester with DAST [37]. Starting from racemic mixture Takeuchi et al. received racemic tertiary fluoroacetate derivatives but with excellent yield. Fluorination of **5a**/**5b** using PFPDEA gave **10a**/**10b** with 22%/15% yields.

In summary, the study towards a dehydroxyfluorination of tertiary alcohols derived from 1,2;5,6-di-*O*-isopropylideneglucofuranose and 5-*O*-benzyl-1,2-*O*-isopropylidenexylofuranose derivatives were presented. Fluorination of allylic alcohol **2a** occurs with an inversion of configuration from the less hindered top- face and allylic rearrangement to give two chiral regioisomers **6a** and **7a**. Analogous reactions of **2b** with DAST or PFPDEA yield only **7b**. The stereoselectivity of **2a**, **2b**–**5a**, **5b** fluorinations was strongly affected by stabilization of intermediate carbocation by neighboring 1,2-*O*-isopropylidene groups in rigid hexofuranose or pentofuranose rings and was also demonstrated for chiral fluorides **6a**, **6b**–**10a**, **10b**. The synthesis of tertiary fluorides derived from sugars has been accomplished using DAST and PFPDEA as dehydroxyfluorination reagents. In comparison to DAST, fluorination of **2a** with PFPDEA, gave compounds **6a**/**7a** with better yield. Fluorination of **3a,b**–**5a,b** provided with DAST gave better results comparing to this with PFPDEA. The stereo- and regioselectivity of fluorine introduction was determined by ^{19}F NMR and ^{1}H NMR spectroscopy.

3. Experimental

3.1. General procedures

^{1}H (Me_4Si) NMR spectra were determined with solutions in $CDCl_3$ at 400 MHz, ^{13}C (Me_4Si) at 100.6 MHz and ^{19}F NMR (CCl_3F) at 376.4 MHz. Elementar analysis were performed using EuroScience Elementar Analyser Euro EA apparatus. Low-resolution and high-resolution mass spectra were recorded by electron impact (MS-EI) techniques using AMD-402 spectrometer unless otherwise noted. IR spectra were performed using spectrometer FT-IR IFS 66/s from Bruker. Optical rotations were measured using a 243 B Perkin-Elmer polarimeter [α] *D* values are determined at 589 nm and 25 °C. Reagent grade chemicals were used and solvents were dried by refluxing with sodium metal-benzophenone (THF), with $CaCl_2$ (CH_2Cl_2) and distilled under an argon atmosphere. All moisture sensitive reactions were carried out under an argon atmosphere using oven-dried glassware. Reaction temperatures below 0 °C were performed using a cooling bath (liquid N_2/hexane or CO_2/*iso*-propanol). TLC was performed on Merck Kieselgel 60-F_{254} with EtOAc/hexane as developing systems, and products were detected by inspection under UV light (254 nm) and with a solution phosphomolybdenic acid. Merck Kieselgel 60 (230–400 mesh) was used for column chromatography. DAST was obtained from Aldrich. PFPDEA was prepared as reported [9], distilled under reduced pressure and the purity of PFPDEA was conveniently evaluated by ^{19}F NMR in $CDCl_3$. Carbohydrate substrates have to be well dried prior to use. Compounds **1a** [20], **1b** [21], **2a** [22], **3a** [30], **5a** [35] were prepared as described.

3.2. Preparation of 5-O-benzyl-1,2-O-isopropylidene-C-3-vinyl-α-D-ribofuranose 2b

To the magnetically stirred suspension of magnesium turnings (41 mg, 1.72 mmol) and a few crystals of I_2 in dry THF (2 mL) in Carius tube at −20 °C vinyl bromide (207 mg, 1.94 mmol) was added. The reaction mixture was refluxed for 2 h. Next, the solution of ketone **1b** (120 mg, 0.43 mmol) in anhydrous THF (1 mL) at 0 °C was added and the reaction was stirred at room temperature overnight. Then, the resulting mixture was partitioned (1 N HCl/H_2O//Et_2O). The combined extracts were washed with water, brine, dried ($MgSO_4$), evaporated and was carefully column chromatographed (10% EtOAc/hexane) to give **2b** (68 mg, 52%) as slightly yellow oil. Compound **2b** had: [α] *D* 25 +10° (c 0.3, $CHCl_3$); IR (KBr) ν 3463, 3028, 2989, 2930, 2878, 1640, 1592, 1423, 1386, 1373, 1284, 1192, 1167, 1111, 1008, 928, 877, 725 cm^{-1}; ^{1}H NMR: δ 1.36 (3H, s, *i*-Pr), 1.60 (3H, s, *i*-Pr), 2.78 (1H, d, J = 1.1 Hz, OH), 3.49 (1H, dd, $J_{5\text{-}5'}$ = 10.7 Hz, $J_{5\text{-}4}$ = 7.5 Hz, H-5), 3.57 (1H, dd, $J_{5'\text{-}5}$ = 10.7 Hz, $J_{5'\text{-}4}$ = 3.3 Hz, H-5′), 4.10 (1H, dd, $J_{4\text{-}5}$ = 7.4 Hz, $J_{4\text{-}5'}$ = 3.3 Hz, H-4), 4.21 (1H, d, $J_{2\text{-}1}$ = 3.8 Hz, H-2), 4.50 (1H, d, J = 12.1 Hz, Bn), 4.60 (1H, d, J = 12.1 Hz, Bn), 5.26 (1H, dd, $J_{b\text{-}a}$ = 10.8 Hz, $J_{b\text{-}b'}$ = 1.7 Hz, H-b), 5.51 (1H, dd, $J_{b'\text{-}a}$ = 17.3 Hz, $J_{b'\text{-}b}$ = 1.7 Hz, H-b′), 5.73 (1H, ddd, $J_{a\text{-}b'}$ = 17.3 Hz, $J_{a\text{-}b}$ = 10.8 Hz, $J_{a\text{-}OH}$ = 0.9 Hz, H-a), 5.86 (1H, d, $J_{1\text{-}2}$ = 3.8 Hz, H-1), 7.27–7.38 (5H, m, Ph); ^{13}C NMR: δ 26.5, 26.6, 68.9, 73.4, 79.6, 81.4, 83.1, 103.9, 112.8, 116.1, 127.6, 128.3, 133.7, 137.9; MS *m*/*z* (rel. int.) 91 $[C_7H_7]^+$ (100), 291 $[M-Me]^+$ (7), 306 $[M]^+$ (5); HRMS (EI) Calcd for $C_{17}H_{22}O_5$ $[M]^+$: 306.14673; Found: 306.14728.

3.3. Preparation of 5-O-benzyl-1,2-O-isopropylidene-C-3-phenylethynyl-α-D-ribofuranose 3b

To a stirred solution of phenyl acethylene (0.44 mL, 408 mg, 4.0 mmol) in dry THF (3 mL) at −78 °C, *n*-BuLi (2 mL, 4.0 mmol, 2 M in *n*-hexane) was added. After stirring at −78 °C for 2 h, a solution of ketone **1b** (556 mg, 2.0 mmol) in THF (2 mL) was added dropwise and the reaction was stirred for additional 4 h at −78 °C. Then, the reaction mixture was poured into saturated aqueous NH_4Cl (10 mL). Next, water (40 mL) was added and then reaction was extracted with Et_2O. The combined organic layers were washed with H_2O, brine, dried ($MgSO_4$), evaporated and carefully column chromatographed ($CHCl_3$ → 1% MeOH/$CHCl_3$) to give acethylenic product (461 mg, 60%) as white solid. Compound **3b** had: [α] *D* 25 −20° (c 0.5, $CHCl_3$); IR (KBr) ν 3469, 2989, 2930, 2865, 2228, 1487, 1455, 1444, 1382, 1375, 1165, 1133, 1097, 1052, 1038, 884, 754, 698, 691 cm^{-1}; ^{1}H NMR: δ 1.39 (3H, s, *i*-Pr), 1.61 (3H, s, *i*-Pr), 3.08 (1H, s, OH), 3.86 (1H, dd, $J_{5\text{-}5'}$ = 10.2 Hz, $J_{5\text{-}4}$ = 7.0 Hz, H-5),

3.95 (1H, dd, $J_{5'-5}$ = 10.2 Hz, $J_{5'-4}$ = 4.5 Hz, H-5′), 4.20 (1H, dd, J_{4-5} = 6.9 Hz, $J_{4-5'}$ = 4.5 Hz, H-4), 4.57 (1H, d, J = 12.0 Hz, Bn), 4.64 (1H, d, J_{2-1} = 3.8 Hz, H-2), 4.68 (1H, d, J = 12.0 Hz, Bn), 5.94 (1H, d, J_{1-2} = 3.7 Hz, H-1), 7.26–7.42 (10H, m, Ph); ^{13}C NMR: δ 26.6, 26.7, 69.5, 73.7, 75.6, 80.7, 83.7, 84.9, 88.0, 104.3, 113.4, 121.6, 127.7, 127.8, 128.3, 128.9, 131.8, 137.7; MS m/z (rel. int.) 91 $[C_7H_7]^+$ (100), 365 [M-Me]$^+$ (5), 380 [M]$^+$ (3); Anal. Calcd for $C_{23}H_{24}O_5 \times 0.25\ H_2O$: C, 71.76; H, 6.42. Found: C, 71.79; H, 6.41.

3.4. Preparation of 1,2;5,6-di-O-isopropylidene-C-3-(E)-styryl-α-D-allofuranose 4a

To the solution of **3a** (114 mg, 0.32 mmol) in Et_2O (7 mL), a suspension of $LiAlH_4$ (16 mg, 0.41 mmol) in Et_2O (8 mL) at 0 °C was added. The reaction mixture was stirred at room temperature for 3.5 h and then was quenched by addition of water (24 μL), 10% aqueous solution of KOH (48 μL) and water (72 μL). The mixture was filtered and the precipitate was washed with Et_2O. The combined organic layers were dried ($MgSO_4$) and the product was column chromatographed (20% EtOAc/hexane) to give alcohol **4a** (110 mg, 96%) as an oil. Compound **4a** had [α] D 25 −16° (c 0.3, $CHCl_3$); IR (KBr) ν 3461, 3085, 3060, 3028, 2997, 2986, 2972, 2945, 2936, 2895, 2887, 1382, 1372, 1212, 1166, 1156, 973, 878, 855, 750, 691 cm^{-1}; ^{1}H NMR: δ 1.29 (3H, s, *i*-Pr), 1.37 (3H, s, *i*-Pr), 1.44 (3H, s, *i*-Pr), 1.65 (3H, s, *i*-Pr), 2.95 (1H, s, OH), 3.91–4.06 (3H, m, H-6′, H-6, H-5), 4.17 (1H, q, $J_{4-5/6/6'}$ = 6.1 Hz, H-4), 4.36 (1H, d, J_{2-1} = 3.6 Hz, H-2), 5.87 (1H, d, J_{1-2} = 3.6 Hz, H-1), 6.14 (1H, d, J_{a-b}=16.1 Hz, H-a), 6.92 (1H, d, J_{b-a}=16.1 Hz, H-b), 7.22–7.49 (5H, m, Ph); ^{13}C NMR: δ 25.3, 26.4, 26.6, 26.7, 66.8, 73.9, 80.4, 81.6, 83.8, 103.8, 109.4, 113.2, 125.7, 126.6, 127.9, 128.7, 131.3, 136.2; MS m/z (rel. int.) 91 $[C_7H_7]^+$(25), 347 [M-Me]$^+$ (8), 362 [M]$^+$ (1); HRMS (EI) Calcd for $C_{19}H_{23}O_6$ [M−Me]$^+$: 347.14948; Found: 347.14768.J4-5/6/6′ = 6.1 Hz,

3.5. Preparation of 5-O-benzyl-1,2-O-isopropylidene-C-3-(E)-styryl-α-D-ribofuranose 4b

Analogous treatment of **3b** (122 mg, 0.32 mmol) in Et_2O (7 mL), with a suspension of $LiAlH_4$ (16 mg, 0.41 mmol) in Et_2O (8 mL, 3.5 h) gave after isolation compound **4b** (98 mg, 80%) as a white solid. Compound **4b** had [α] D 25 −17° (c 0.5, $CHCl_3$); IR (KBr) ν 3441, 3028, 2993, 2934, 2904, 2868, 1600, 1577, 1495, 1386, 1166, 1146, 1099, 999, 880, 753, 696 cm^{-1}; ^{1}H NMR: δ 1.37 (3H, s, *i*-Pr), 1.63 (3H, s, *i*-Pr), 2.93 (1H, s, OH), 3.55 (1H, dd, $J_{5-5'}$ = 10.7 Hz, J_{5-4} = 7.2 Hz, H-5), 3.64 (1H, dd, $J_{5'-5}$ = 10.7 Hz, $J_{5'-4}$ = 3.5 Hz, H-5′), 4.17 (1H, dd, J_{4-5} = 7.2 Hz, $J_{4-5'}$ = 3.5 Hz, H-4), 4.30 (1H, d, J_{2-1} = 3.8 Hz, H-2), 4.46 (1H, d, J = 12.1 Hz, Bn), 4.59 (1H, d, J = 12.1 Hz, Bn), 5.94 (1H, d, J_{1-2} = 3.8 Hz, H-1), 6.09 (1H, d, J_{a-b} = 16.0 Hz, H-a), 6.87 (1H, d, J_{b-a} = 16.0 Hz, H-b), 7.24–7.41 (10H, m, Ph); ^{13}C NMR: δ 26.5, 26.6, 69.8, 73.5, 79.8, 81.8, 83.4, 103.9, 112.9, 124.9, 126.5, 127.6, 127.7, 127.9, 128.3, 128.6, 130.6, 136.3, 137.8; MS m/z (rel. int.) 91 $[C_7H_7]^+$ (100), 367 [M−Me]$^+$(2); Anal. Calcd for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85. Found: C, 72.10; H, 7.05.

3.6. Preparation of 5-O-benzyl-1,2-O-isopropylidene-C-3-phenyl-α-D-ribofuranose 5b

To the magnetically stirred suspension of magnesium turnings (24 mg, 1.0 mmol) and a few crystals of I_2 in dry THF (1.5 mL) in Carius tube at −20 °C bromobenzene (69 μL, 104 mg, 0.66 mmol) was added. The reaction mixture was refluxed for 2 h. Next, the solution of ketone **1b** (93 mg, 0.33 mmol) in anhydrous THF (1 mL) at 0 °C was added and the reaction was stirred at room temperature overnight. Then, the resulting mixture was partitioned (1 N HCl/H_2O//Et_2O). The combined extracts were washed with water, brine, dried ($MgSO_4$), evaporated and carefully column chromatographed (10% EtOAc/hexane) to give **5b** (62 mg, 52%) as slightly yellow oil. Compound **5b** had: [α] D 25 +4° (c 0.2, $CHCl_3$); IR (KBr) ν 3368, 3063, 3031, 2989, 2933, 2869, 1605, 1498, 1450, 1383, 1375, 1257, 1216, 1102, 1078, 1023, 873, 763, 697 cm^{-1}; ^{1}H NMR: δ 1.40 (3H, s, *i*-Pr), 1.65 (3H, s, *i*-Pr), 3.09 (1H, dd, $J_{5-5'}$ = 10.8 Hz, J_{5-4} = 7.9 Hz, H-5), 3.28 (1H, s, OH), 3.34 (1H, dd, $J_{5'-5}$ = 10.8 Hz, $J_{5'-4}$ = 3.1 Hz, H-5′), 4.29 (1H, dd, J_{4-5} = 7.8 Hz, $J_{4-5'}$ = 3.1 Hz, H-4), 4.32 (1H, d, J = 11.9 Hz, Bn), 4.40 (1H, d, J_{2-1} = 4.0 Hz, H-2), 4.46 (1H, d, J = 11.9 Hz, Bn), 6.12 (1H, d, J_{1-2} = 4.0 Hz, H-1), 7.27–7.42 (10H, m, Ph); ^{13}C NMR: δ 26.5, 26.6, 69.2, 73.3, 80.0, 83.3, 84.4, 92.9, 105.1, 112.8, 124.3, 125.0, 126.6, 127.5, 127.6, 127.7, 128.2, 137.9, 138.7; MS m/z (rel. int.) 91 $[C_7H_7]^+$ (100), 341 [M−Me]$^+$ (6), 356 [M]$^+$ (5); HRMS (EI) Calcd for $C_{21}H_{24}O_5$ [M]$^+$: 356.16238; Found: 356.16451.

3.7. Preparation of 3-deoxy-3-fluoro-1,2;5,6-di-O-isopropylidene-C-3(R)-vinyl-α-D-glucofuranose 6a and 3-deoxy-C-3-(2-fluoroethylidene)-1,2;5,6-di-O-isopropylidene-α-D-ribohexofuranose 7a

PFPDEA (156 mg, 0.84 mmol) in anhydrous CH_2Cl_2 (2 mL) was added dropwise to the solution of **2a** (120 mg, 0.42 mmol) in CH_2Cl_2 (4 mL), and the mixture was stirred for 18 h at room temperature. Then solvent was evaporated to give crude mixture of **6a**/**7a** (∼60%, 1:1; ^{1}H NMR and ^{19}F NMR). The reaction mixture was partitioned (H_2O//CH_2Cl_2) and the separated inorganic layer was extracted (CH_2Cl_2), dried ($MgSO_4$), evaporated and carefully column chromatographed (0 → 30% EtOAc/hexane) to give **6a** (38 mg, 31%) and **7a** (41 mg, 34%) as slightly yellow oils. Compound **6a** [less polar than **7a** and **2a** on TLC (EtOAc/hexane, 2:8)] had [α] D 25 +77° (c 0.3, $CHCl_3$); IR (KBr/neat) ν 2989, 2937, 2899, 1456, 1417, 1384, 1375, 1252, 1218, 1165, 1080, 1012, 875 cm^{-1}; ^{1}H NMR: δ 1.33 (3H, s, *i*-Pr), 1.34 (3H, s, *i*-Pr), 1.42 (3H, s, *i*-Pr), 1.54 (3H, s, *i*-Pr), 3.99 (1H, ddd, $J_{6'-6}$ = 8.7 Hz, $J_{6'-5}$ = 6.4 Hz, $J_{6'-b}$ = 1.9 Hz, H-6′), 4.06 (1H, dd, $J_{6-6'}$ = 8.9 Hz, J_{6-5} = 5.7 Hz, H-6′), 4.24 (1H, q, $J_{5-4/6/6'}$ = 5.5 Hz, H-5), 4.25 (1H, dd, J_{4-F} = 31.5 Hz, J_{4-5} = 5.1 Hz, H-4), 4.43 (1H, dd, J_{2-F} = 11.4 Hz, J_{2-1} = 3.7 Hz, H-2), 5.41 (1H, ddd, J_{b-a} = 11.3 Hz, $J_{b-6'}$ = 2.1 Hz, $J_{b-b'}$ = 1.2 Hz, H-b), 5.53 (1H, dd, $J_{b'-a}$ = 17.5 Hz, $J_{b'-b}$ = 1.2 Hz, H-b′), 5.94 (1H, d, J_{1-2} = 3.7 Hz, H-1), 5.99 (1H, ddd, J_{a-F} = 21.6 Hz, $J_{a-b'}$ = 17.5 Hz, J_{a-b} = 11.3 Hz, H-a); ^{13}C NMR: δ 25.4 (*i*-Pr), 26.5 (*i*-Pr), 26.9 (*i*-Pr), 29.7 (*i*-Pr), 65.8 (d, J = 5.1 Hz, C-5), 72.4 (d, J = 4.7 Hz, C-6), 81.4 (d, J = 19.5 Hz, C-4), 85.5 (d, J = 37.7 Hz, C-2), 101.2 (d, J = 184.1 Hz, C-3), 104.8 (C-1), 109.0 (*i*-Pr), 113.0 (*i*-Pr), 117.9 (d, J = 12.0 Hz, C-b), 130.5 (d, J = 19.5 Hz, C-a); ^{19}F NMR: δ −181.3 (ddd, J_{F-4} = 31.5 Hz, J_{F-a} = 21.6 Hz, J_{F-2} = 11.5 Hz, 1F); MS (APCI) m/z 289.2 [M+ H]$^+$; HRMS (EI) Calcd for $C_{13}H_{18}O_5F$ [M−Me]$^+$: 273.11383; Found: 273.11422.

Compound **7a** [more polar than **6a** and less polar than **2a** on TLC (EtOAc/hexane, 2:8)] had [α] D 25 +52° (c 0.2, $CHCl_3$); IR (KBr/neat) ν 3093, 2990, 2940, 2901, 1457, 1417, 927, 875, 845, 802 cm^{-1}; ^{1}H NMR: δ 1.36 (3H, s, *i*-Pr), 1.38 (3H, s, *i*-Pr), 1.44 (3H, s, *i*-Pr), 1.48 (3H, s, *i*-Pr), 3.95 (1H, dd, $J_{6'-6}$ = 7.3 Hz, $J_{6'-5}$ = 4.7 Hz, H-6′), 4.00–4.06 (1H, m, H-6), 4.06–4.10 (1H, m, H-5), 4.64 (1H, tdd, J_{4-F} = 5.0 Hz, J_{4-5} = 3.4 Hz, $J_{4-6/a}$ = 1.9 Hz, H-4), 5.03 (1H, dddd, J_{b-F} = 46.5 Hz, J_{b-a} = 5.4 Hz, $J_{b-b'}$ = 1.9 Hz, J_{b-2} = 0.5 Hz, H-b), 5.14 (1H, tdd, J_{2-1} = 4.0 Hz, J_{2-F} = 2.5 Hz, J_{2-b} = 0.5 Hz, H-2), 5.19 (1H, ddd, $J_{b'-F}$ = 47.2 Hz, $J_{b'-b}$ = 1.4 Hz, $J_{b'-a}$ = 7.5 Hz, H-b′), 5.85 (1H, d, J_{1-2} = 4.3 Hz, H-1), 6.14 (1H, dddt, J_{a-F} = 12.9 Hz, J_{a-b} = 5.5 Hz, $J_{a-b'}$ = 7.2 Hz, $J_{a-4/5}$ = 1.9 Hz, H-a); ^{13}C NMR: δ 25.4 (*i*-Pr), 26.6 (*i*-Pr), 27.2 (*i*-Pr), 27.3 (*i*-Pr), 60.4 (C-6), 66.9 (C-5), 78.4 (C-4), 79.9 (d, J = 161.0 Hz, C-b), 79.9 (C-2), 104.9 (C-1), 109.9 (*i*-Pr), 112.7 (*i*-Pr), 123.2 (d, J = 19.7 Hz, C-a), 142.7 (d, J = 10.7 Hz, C-3); ^{19}F NMR: δ −214.6 (tddd, $J_{F-b/b'}$ = 46.7 Hz, J_{F-a} = 13.2 Hz, J_{F-4} = 5.4 Hz, J_{F-2} = 2.5 Hz, 1F); MS (APCI) m/z 289.2 [M+ H]$^+$; HRMS (EI) Calcd for $C_{13}H_{18}O_5F$ [M−Me]$^+$: 273.11383; Found: 273.11403.

Note 1: Analogous treatment of **2a** in CH_2Cl_2 with DAST (1.5 eq, 1 h, −78 °C; 1 h, RT) gave **6a**/**7a** (1.6:1) with 26%/16% yields.

Note 2: Analogous treatment of **2a** in CH_2Cl_2 with DAST (10 eq, 1 h, −78 °C; 1 h, RT) gave **6a**/**7a** (2:1) with 45% yield.

3.8. Preparation of 5-O-benzyl-3-deoxy- C-3-(2-fluoroethylidene)-1,2-O-isopropylidene-α-D-erythropentofuranose 7b

To a mixture of DAST (58 mg, 60 μL, 0.45 mmol) in dry CH_2Cl_2 (2 mL) at −78 °C, a solution of alcohol **2b** (93 mg, 0.3 mmol) in CH_2Cl_2 (2 mL) was added dropwise. The mixture was stirred at −78 °C for 2 h, and then additional 1 h at room temperature. Then, the reaction mixture was poured into saturated $NaHCO_3$ containing ice chips and extracted with CH_2Cl_2. The combined organic layer were washed with H_2O, dried (Na_2SO_4), filtered and evaporated under reduced pressure. The product was purified on a silica gel (5% EtOAc/hexane) to give a fluoride **7b** (48 mg, 51%) as an oil. Compound **7b** had [α] *D* 25 +74° (c 1.8, $CHCl_3$); IR (KBr/neat) ν 3065, 3030, 2989, 2938, 2868, 1725, 1654, 1636, 1603, 1586, 1497, 1455, 1384, 1245, 1216, 1162, 1079, 877, 755 cm^{-1}; ^1H NMR: δ 1.39 (3H, s, *i*-Pr), 1.46 (3H, s, *i*-Pr), 3.56 (1H, dd, $J_{5-5'}$ = 10.3 Hz, J_{5-4} = 4.4 Hz, H-5), 3.67 (1H, dd, $J_{5'-5}$ = 10.3 Hz, $J_{5'-4}$ = 3.7 Hz, H-5′), 4.55 (1H, d, *J* = 12.2 Hz, Bn), 4.60 (1H, d, *J* = 12.1 Hz, Bn), 4.87-4.82 (1H, m, H-4), 5.10 (1H, ddd, J_{b-F} = 46.3 Hz, J_{b-a} = 5.9 Hz, $J_{b-b'}$ = 1.3 Hz, H-b), 5.11–5.16 (1H, m, H-2), 5.12 (1H, ddd, $J_{b'-F}$ = 47.1 Hz, $J_{b'-a}$ = 7.5 Hz, $J_{b'-b}$ = 1.3 Hz, H-b′), 5.80 (1H, dddt, J_{a-F} = 12.6 Hz, $J_{a-b'}$ = 7.4 Hz, J_{a-b} = 5.5 Hz, $J_{a-4/2}$ = 1.9 Hz, H-a), 5.93 (1H, d, J_{1-2} = 3.5 Hz, H-1), 7.20–7.49 (5H, m, Ph); ^{13}C NMR: δ 27.3 (*i*-Pr), 27.4 (*i*-Pr), 71.9 (d, *J* = 2.5 Hz, C-4), 73.4 (Bn), 78.4 (d, *J* = 1.4 Hz, C-5), 79.3 (d, *J* = 1.4 Hz, C-2), 79.8 (d, *J* = 161.4 Hz, C-b), 105.2 (C-1), 112.5 (*i*-Pr), 121.5 (d, *J* = 19.8 Hz, C-a), 127.6 (Ph), 127.7 (Ph), 128.4 (Ph), 137.8 (Ph), 143.2 (d, *J* = 10.9 Hz, C-3); ^{19}F NMR: δ -214.30 (tddd, $J_{F-b/b'}$ = 46.6 Hz, J_{F-a} = 12.2 Hz, $J_{F-2/4}$ = 5.5, 2.6 Hz, 1F); MS *m*/*z* (rel. int.) 91 $[C_7H_7]^+$ (100), 293 $[M-Me]^+$ (14), 308 $[M]^+$ (10); HRMS (EI) Calcd for $C_{17}H_{21}O_4F$ $[M]^+$: 308.14240; Found: 308.14359.

Note 1: Analogous treatment of **2b** in CH_2Cl_2 with PFPDEA (48 h, RT) gave **7b** with 10% yield.

Note 2: Analogous treatment of **2b** in CH_2Cl_2 with DAST (10eq, 1 h, −78 °C; 1 h, RT) gave **7b** with 53% yield.

3.9. Preparation of 3-deoxy-3-fluoro-1,2;5,6-di-O-isopropylidene- C-3(R)- phenylethynyl-α- D-glucofuranose 8a

To a mixture of DAST (77 mg, 0.48 mmol) in dry CH_2Cl_2 (2 mL) at −78 °C, a solution of alcohol **3a** (114 mg, 0.32 mmol) in CH_2Cl_2 (2 mL) was added dropwise. The mixture was stirred at −78 °C for 2 h, and then additional 1 h at room temperature. Then, the reaction mixture was poured into saturated $NaHCO_3$ containing ice chips and extracted with CH_2Cl_2. The combined organic layer were washed with H_2O, dried (Na_2SO_4), filtered and evaporated under reduced pressure. The product was purified on a silica gel (5% EtOAc/hexane) to give a fluoride **8a** (96 mg, 84%) as an oil. Compound **8a** had [α] *D* 25 +85° (c 0.2, $CHCl_3$); IR (KBr/neat) ν 3057, 2989, 2936, 2903, 2239, 1599, 1574, 1491, 1455, 1444, 1382, 1373, 1075, 1047, 1028, 1004, 874, 844, 691 cm^{-1}; ^1H NMR: δ 1.43 (3H, s, *i*-Pr), 1.45 (3H, s, *i*-Pr), 1.55 (3H, s, *i*-Pr), 1.63 (3H, s, *i*-Pr), 4.14–4.20 (2H, m, H-6/6′), 4.46 (1H, dd, J_{4-F} = 25.3 Hz, J_{4-5} = 5.8 Hz, H-4), 4.53 (1H, q, $J_{5-4/6/6'}$ = 5.3 Hz, H-5), 4.72 (1H, dd, J_{2-F} = 11.1 Hz, J_{2-1} = 3.7 Hz, H-2), 6.06 (1H, d, J_{1-2} = 3.6 Hz, H-1), 7.34–7.64 (5H, m, Ph); ^{13}C NMR: δ 25.2 (*i*-Pr), 26.7 (*i*-Pr), 26.7 (*i*-Pr), 26.9 (*i*-Pr), 65.9 (d, *J* = 3.8 Hz, C-5), 72.7 (d, *J* = 3.5 Hz, C-6), 80.2 (d, *J* = 27.4 Hz, C-a), 83.0 (d, *J* = 22.3 Hz, C-4), 84.6 (d, *J* = 38,7 Hz, C-2), 91.7 (d, *J* = 9.6 Hz, C-b), 95.1 (d, *J* = 178.8 Hz, C-3), 104.9 (C-1), 109.3 (*i*-Pr), 113.2 (*i*-Pr), 121.3 (Ph), 128.2 (Ph), 129.3 (Ph), 131.9 (Ph); ^{19}F NMR: δ −163.9 (dd, J_{F-4} = 25.3 Hz, J_{F-2} = 11.1 Hz, 1F); MS *m*/*z* (rel. int.) 347 $[M-Me]^+$ (99); HRMS (EI) Calcd for $C_{19}H_{20}O_5F$ $[M-Me]^+$: 347.12949; Found: 347.12930.

Note: Analogous treatment of **3a** in CH_2Cl_2 with PFPDEA (48 h, RT) gave **8a** with 29% yield.

3.10. Preparation of 5-O-benzyl-3-deoxy-3-fluoro-1,2-O-isopropylidene-C-3(R)- phenylethynyl-α-D-xylofuranose 8b

Analogous treatment of **3b** (103 mg, 0.27 mmol) with DAST (65 mg, 53 μL, 0.4 mmol) in dry CH_2Cl_2 (2 mL) at −78 °C (1 h), and next at room temperature (1 h) gave a fluoride **8b** (82 mg, 79%) as an oil. Compound **8b** had [α] *D* 25 +84° (c 0.8, $CHCl_3$); IR (KBr/neat) ν, 3063, 3032, 2990, 2935, 2869, 2237, 1598, 1491, 1453, 1384, 1375, 1216, 1065, 1104, 1028, 1004, 876, 758, 692 cm^{-1}; ^1H NMR: δ 1.38 (3H, s, *i*-Pr) 1.57 (3H, s, *i*-Pr), 3.79 (1H, ddd, $J_{5-5'}$ = 10.9 Hz, J_{5-4} = 7.0 Hz, J_{5-F} = 0.9 Hz, H-5), 3.99 (1H, dd, $J_{5'-5}$ = 10.9 Hz, $J_{5'-4}$ = 3.8 Hz, H-5′), 4.53 (1H, ddd, J_{4-F} = 24.6 Hz, J_{4-5} = 6.9 Hz, $J_{4-5'}$ = 3.8 Hz, H-4), 4.60 (1H, d, *J* = 11.9 Hz, Bn), 4.65 (1H, dd, J_{2-F} = 11.0 Hz, J_{2-1} = 3.8 Hz, H-2), 4.68 (1H, d, *J* = 11.9 Hz, Bn), 6.03 (1H, d, J_{1-2} = 3.7 Hz, H-1), 7.28–7.40 (10H, m, Ph); ^{13}C NMR: δ 26.7 (*i*-Pr), 26.8 (*i*-Pr), 67.3 (d, *J* = 6.3 Hz, C-5), 73.5 (CH_2), 79.9 (d, *J* = 27.1 Hz, C-b), 82.6 (d, *J* = 21.7 Hz, C-4), 84.2 (d, *J* = 38.4 Hz, C-2), 91.5 (d, *J* = 9.5 Hz, C-a), 95.2 (d, *J* = 178.9 Hz, C-3), 105.0 (C-1), 113.2 (*i*-Pr), 124.4 (d, *J* = 4.1 Hz, Ph), 127.7 (Ph), 128.2 (Ph), 128.3 (Ph), 129.3 (Ph), 132.1 (d, *J* = 2.8 Hz, Ph), 137.8 (Ph); ^{19}F NMR: δ −165.0 (dd, J_{F-4} = 24.6 Hz, J_{F-2} = 10.9 Hz, 1F); MS *m*/*z* (rel. int.) 91 $[C_7H_7]^+$ (100), 382 $[M]^+$ (16); HRMS (EI) Calcd for $C_{23}H_{23}O_4F$ $[M]^+$: 382.15805; Found: 382.15707.

Note: Analogous treatment of **3b** in CH_2Cl_2 with PFPDEA (48 h, RT) gave **8b** with 20% yield.

3.11. Preparation of 3-deoxy-3-fluoro-1,2;5,6-di-O-isopropylidene-C-3(R)-(E)-styryl-α-D-glucofuranose 9a

To a mixture of DAST (65 mg, 0.4 mmol) in dry CH_2Cl_2 (2 mL) at -78 °C, a solution of alcohol **4a** (97 mg, 0.27 mmol) in CH_2Cl_2 (2 mL) was added dropwise. The mixture was stirred at −78 °C for 2 h, and then additional 1 h at room temperature. Then, the reaction mixture was poured into saturated $NaHCO_3$ containing ice chips and extracted with CH_2Cl_2 The combined organic layer were washed with H_2O, dried (Na_2SO_4), filtered and evaporated under reduce pressure. The product was purified on a silica gel (5% EtOAc/hexane) to give a fluoride **9a** (72 mg, 74%) as an oil. Compound **9a** had [α] *D* 25 +142° (c 0.3, $CHCl_3$); IR (KBr) ν 3062, 3051, 3031, 2995, 2985, 2933, 2901, 1656, 1600, 1492, 1448, 1379, 1369, 1247, 1219, 1065, 1053, 1036, 1008, 972, 945, 902, 874, 751, 735, 694 cm^{-1}; ^1H NMR: δ 1.32 (3H, s, *i*-Pr), 1.34 (3H, s, *i*-Pr), 1.41 (3H, s, *i*-Pr), 1.58 (3H, s, *i*-Pr), 4.05 (1H, dd, $J_{6'-6}$ = 8.6 Hz, $J_{6'-5}$ = 6.6 Hz, H-6′), 4.11 (1H, dd, $J_{6-6'}$ = 8.7 Hz, J_{6-5} = 5.5 Hz, H-6), 4.31 (1H, ddd, J_{5-4} = 4.3 Hz, J_{5-6} = 5.4 Hz, $J_{5-6'}$ = 6.7 Hz, H-5), 4.38 (1H, dd, J_{4-F} = 31.0 Hz, J_{4-5} = 4.6 Hz, H-4), 4.50 (1H, dd, J_{2-F} = 11.5 Hz, J_{2-1} = 3.6 Hz, H-2), 5.99 (1H, d, J_{1-2} = 3.6 Hz, H-1), 6.31 (1H, dd, J_{a-F} = 21.4 Hz, J_{a-b} = 16.3 Hz, H-a), 6.82 (1H, d, J_{b-a} = 16.3 Hz, H-b), 7.19–7.55 (5H, m, Ph); ^{13}C NMR: δ 25.3 (*i*-Pr), 26.4 (*i*-Pr), 26.6 (*i*-Pr), 27.1 (*i*-Pr), 65.9 (d, *J* = 4.8 Hz, C-5), 72.6 (d, *J* = 4.5 Hz, C-6), 81.6 (d, *J* = 19.6 Hz, C-4), 85.5 (d, *J* = 37.8 Hz, C-2), 101.6 (d, *J* = 184.1 Hz, C-3), 104.9 (C-1), 108.9 (*i*-Pr), 113.0 (*i*-Pr), 121.3 (d, *J* = 17.9 Hz, C-a), 126.8 (Ph), 128.2 (Ph), 128.6 (Ph), 132.1 (d, *J* = 11.5 Hz, C-b), 135.91 (Ph); ^{19}F NMR: δ -178.8 (ddd, J_{F-4} = 31.0 Hz, J_{F-a} = 21.4 Hz, J_{F-2} = 11.5 Hz, 1F); MS *m*/*z* (rel. int.) 364 $[M]^+$ (10), 349 $[M-Me]^+$ (20); HRMS (EI) Calcd for $C_{20}H_{25}O_5F$ $[M]^+$: 364.16861; Found: 364.16728.

Note: Analogous treatment of **4a** in CH_2Cl_2 with PFPDEA (48 h, RT) gave **9a** with 47% yield.

3.12. Preparation of 5-O-benzyl-3-deoxy-3-fluoro-1,2-O-isopropylidene-C-3(R)- (E)-styryl-α-D-ribofuranose 9b

Analogous treatment of **4b** (70 mg, 0.18 mmol) with DAST (45 mg, 36 μL, 0.27 mmol) in dry CH_2Cl_2 (2 mL) at -78 °C (1 h), and

next at room temperature (1 h) gave a fluoride **9b** (45 mg, 64%) as an oil. Compound **9b** had [α] *D* 25 +102° (c 0.7, $CHCl_3$); IR (KBr) ν 3061, 3029, 2989, 2934, 2869, 1655, 1601, 1496, 1453, 1379, 1383, 1375, 1248, 1215, 1165, 1102, 1069, 1008, 971, 876, 749, 696 cm^{-1}; ^1H NMR: δ 1.35 (3H, s, *i*-Pr), 1.58 (3H, s, *i*-Pr), 3.72 (1H, ddd, $J_{5\text{-}5'}$ = 10.8 Hz, $J_{5\text{-}4}$ = 6.8 Hz, $J_{5\text{-}F}$ = 0.9 Hz, H-5), 3.78 (1H, dd, $J_{5'\text{-}5}$ = 10.8 Hz, $J_{5'\text{-}4}$ = 4.1 Hz, H-5′), 4.44 (1H, ddd, $J_{4\text{-}F}$ = 27.2 Hz, $J_{4\text{-}5}$ = 6.7 Hz, $J_{4\text{-}5'}$ = 4.0 Hz, H-4), 4.50 (1H, dd, $J_{2\text{-}F}$ = 11.4 Hz, $J_{2\text{-}1}$ = 3.4 Hz, H-2), 4.53 (1H, d, *J* = 11.9 Hz, Bn), 4.59 (1H, d, *J* = 11.9 Hz, Bn), 6.04 (1H, d, $J_{1\text{-}2}$ = 3.6 Hz, H-1), 6.32 (1H, dd, $J_{a\text{-}F}$ = 21.5 Hz, $J_{a\text{-}b}$ = 16.3 Hz, H-a), 6.80 (1H, d, $J_{b\text{-}a}$ = 16.4 Hz, H-b), 7.23–7.45 (10H, m, Ph); ^{13}C NMR: δ 26.4 (*i*-Pr), 26.9 (*i*-Pr), 67.1 (d, *J* = 7.9 Hz, C-5), 73.4 (CH_2), 81.3 (d, *J* = 19.4 Hz, C-4), 85.3 (d, *J* = 37.3 Hz, C-2), 101.6 (d, *J* = 185.0 Hz, C-3), 104.9 (C-1), 112.9 (*i*-Pr), 121.1 (d, *J* = 17.6 Hz, C-a), 126.8 (Ph), 127.5 (Ph), 127.6 (Ph), 128.2 (Ph), 128.3 (Ph), 128.6 (Ph), 132.0 (d, *J* = 11.7 Hz, C-b),135.8 (Ph), 137.8 (Ph); ^{19}F NMR: δ -181.59 (ddd, $J_{F\text{-}4}$ = 27.2 Hz, $J_{F\text{-}a}$ = 21.5 Hz, $J_{F\text{-}2}$ = 11.1 Hz, 1F); MS *m*/*z* (rel. int.) 91 $[C_7H_7]^+$ (84), 369 $[M\text{-}Me]^+$ (15), 384 $[M]^+$ (11); HRMS (EI) Calcd for $C_{23}H_{25}O_4F$ $[M]^+$: 384.17368; Found: 384.17172.

Note: Analogous treatment of **4b** in CH_2Cl_2 with PFPDEA (48 h, RT) gave **9b** with 30% yield.

3.13. Preparation of 3-deoxy-3-fluoro-1,2;5,6-di-O-isopropylidene-C-3(R)-phenyl-α-D-glucofuranose 10a

To the solution of DAST (81 mg, 0.5 mmol) in dry CH_2Cl_2 (3 mL) at -78 °C the solution of alcohol **5a** (113 mg, 0.34 mmol) in CH_2Cl_2 (3 mL) was added dropwise. The mixture was stirred at −78 °C for 2 h, and then additional 1 h at room temperature. Then, the reaction mixture was poured into saturated $NaHCO_3$ containing ice chips and extracted with CH_2Cl_2 The combined organic extracts were washed with water, dried (Na_2SO_4), filtered and evaporated under reduced pressure. The product was purified on silica gel (5% EtOAc/hexane) to give **10a** (66 mg, 58% yield). Compound **10a** had [α] *D* 25 +87° (c 0.3, $CHCl_3$); IR (KBr/neat) ν 3062, 2988, 2935, 1499, 1450, 1382, 1373, 1257, 1215, 1165, 1076, 1048, 1039, 1023, 872, 847, 763, 697, 674 cm^{-1}; ^1H NMR: δ 1.24 (3H, s, *i*-Pr), 1.28 (3H, s, *i*-Pr), 1.31 (3H, s, *i*-Pr), 1.62 (3H, s, *i*-Pr), 3.97-4.06 (1H, m, H-6′), 4.15 (1H, dd, $J_{6\text{-}6'}$ = 8.4 Hz, $J_{6\text{-}5}$ = 5.7 Hz, H-6), 4.20 (1H, ddd, $J_{5\text{-}4}$ = 4.4 Hz, $J_{5\text{-}6}$ = 6.1 Hz, $J_{5\text{-}6'}$ = 8.8 Hz, H-5), 4.53 (1H, dd, $J_{2\text{-}F}$ = 11.6 Hz, $J_{2\text{-}1}$ = 3.7 Hz, H-2), 4.76 (1H, dd, $J_{4\text{-}F}$ = 30.2 Hz, $J_{4\text{-}5}$ = 4.4 Hz, H-4), 6.07 (1H, d, $J_{1\text{-}2}$ = 3.5 Hz, H-1), 7.31–7.59 (5H, m, Ph); ^{13}C NMR: δ 25.0 (*i*-Pr), 25.1 (*i*-Pr), 26.2 (*i*-Pr), 26.9 (*i*-Pr), 65.5 (d, *J* = 5.8 Hz, C-5), 72.8 (d, *J* = 4.6 Hz, C-6), 82.1 (d, *J* = 19.1 Hz, C-4), 85.0 (d, *J* = 40.9 Hz, C-2), 100.9 (d, *J* = 180.0 Hz, C-3), 105.1 (C-1), 108.7 (*i*-Pr), 113.1 (*i*-Pr), 125.8 (d, *J* = 10.3 Hz, Ph), 127.9 (d, *J* = 1.5 Hz, Ph), 128.5 (Ph), 133.5 (d, *J* = 21.0 Hz, Ph); ^{19}F NMR: δ −175.4 (dd, $J_{F\text{-}4}$ = 30.2 Hz, $J_{F\text{-}2}$ = 11.5 Hz, 1F); MS *m*/*z* (rel. int.) 323 $[M\text{-}Me]^+$ (100); HRMS (EI) Calcd for $C_{17}H_{20}O_5F$ $[M-Me]^+$: 323.12949; Found: 323.12764.

Note: Analogous treatment of **5a** in CH_2Cl_2 with PFPDEA (18 h, RT) gave **10a** with 22% yield.

3.14. Preparation of 5-O-benzyl-3-deoxy-3-fluoro-1,2-O-isopropylidene-C-3(R)- phenyl-α-D-xylofuranose 10b

Analogous treatment of **5b** (35 mg, 0.1 mmol) with DAST (32 mg, 26 μL, 0.2 mmol) in dry CH_2Cl_2 (2 mL) at −78 °C (1 h), and next at room temperature (1 h) gave a fluoride **10b** (10 mg, 28%) as an oil. Compound **10b** had [α] *D* 25 +60° (c 0.2, $CHCl_3$); IR (KBr/neat) ν 3063, 3031, 2988, 2933, 2869, 1604, 1586, 1497, 1450, 1384, 1373, 1257, 1216, 1165, 1102, 1078, 1050, 1021, 872, 763, 697 cm^{-1}; ^1H NMR: δ 1.32 (3H, s, *i*-Pr), 1.61 (3H, s, *i*-Pr), 3.64 (1H, dd, $J_{5\text{-}5'}$ = 11.0 Hz, $J_{5\text{-}4}$ = 3.5 Hz, H-5), 3.76 (1H, ddd, $J_{5'\text{-}5}$ = 10.9 Hz, $J_{5'\text{-}4}$ = 6.9 Hz, $J_{5\text{-}F}$ = 0.9 Hz, H-5′), 4.43 (1H, d, *J* = 12.0 Hz, Bn), 4.55 (1H, d, *J* = 11.6 Hz, Bn), 4.55 (1H, dd, $J_{2\text{-}F}$ = 11.6 Hz, $J_{2\text{-}1}$ = 3.9 Hz, H-2), 4.84 (1H, ddd, $J_{4\text{-}F}$ = 28.1 Hz, $J_{4\text{-}5'}$ = 6.9 Hz, $J_{4\text{-}5}$ = 3.5 Hz, H-4), 6.11 (1H, d, $J_{1\text{-}2}$ = 3.4 Hz, H-1), 7.15–7.51 (10H, m, Ph); ^{13}C NMR: δ 26.4 (*i*-Pr), 26.9 (*i*-Pr), 67.6 (d, *J* = 7.8 Hz, C-5), 73.4 (Bn), 81.8 (d, *J* = 18.7 Hz, C-4), 85.0 (d, *J* = 40.7 Hz, C-2), 102.0 (d, *J* = 180.2 Hz, C-3), 105.3 (C-1), 113.1 (*i*-Pr), 126.0 (d, *J* = 10.1 Hz, Ph), 127.5 (d, *J* = 1.5 Hz, Ph), 128.2 (Ph), 128.3 (Ph), 128.6 (Ph), 133.6 (d, *J* = 21.0 Hz, Ph), 137.9 (Ph); ^{19}F NMR: δ −176.50 (dd, $J_{F\text{-}4}$ = 28.3 Hz, $J_{F\text{-}2}$ = 11.4 Hz, 1F); MS *m*/*z* (rel. int.) 91 $[C_7H_7]^+$ (100), 358 $[M]^+$ (16); HRMS (EI) Calcd for $C_{21}H_{23}O_4F$ $[M]^+$: 358.15805; Found: 358.15816.

Note: Analogous treatment of **5b** in CH_2Cl_2 with PFPDEA (48 h, RT) gave **10b** with 15% yield.

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