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**Deoxyfluorination of alcohols using
N,N-diethyl- α,α -difluoro-(*m*-methylbenzyl)amine**

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Abstract: Deoxyfluorination of alcohols was carried out using *N,N*-diethyl- α,α -difluoro-(*m*-methylbenzyl)amine (DFMBA). Primary alcohols were effectively converted to fluorides under microwave irradiation or conventional heating. Deoxyfluorination of an anomeric hydroxy group in sugars by DFMBA proceeded at below room temperature and glycosyl fluorides could be obtained in good yields. The deoxyfluorination reaction chemoselectively proceeded and various protecting groups on the sugar can survive under the reaction conditions.

1. Introduction

Deoxyfluorination reaction of alcohols is useful for the synthesis of organo fluorine compounds, and diethylaminosulfur trifluoride (DAST) has been the most frequently used.¹ Recently, α -fluoroamines, such as 2,2-difluoro-1,3-dimethylimidazolidine (DFI),² have been reevaluated as thermally stable deoxyfluorination reagents. *N,N*-Dimethyl- α,α -difluorobenzylamine was also used for the deoxyfluorination reaction of simple alcohols.³ However, due to the mild reactivity of the reagent, relatively high reaction temperature was required to convert butanol to butyl fluoride. In order to apply the reagent for the deoxyfluorination of more complex alcohols, higher reaction temperature would be required and its thermal stability was problematic.⁴ Quite recently, a similar fluoroamine, *N,N*-diethyl- α,α -difluoro(*m*-methylbenzyl)amine (DFMBA, **1**), was reported to have high thermal stability (ARC 180 °C)⁶ and we successfully used DFMBA for the deoxyfluorination reaction of sugars.⁷ We wish to report here details of the deoxyfluorination reaction of various alcohols using DFMBA.

Keywords: Deoxyfluorination; DFMBA; Fluoro sugars; Microwave.

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2. Result and discussion

2. 1. Fluorination of alcohols using DFMB

DFMB is a colorless liquid and can be conveniently prepared from the corresponding amide in two steps through a chloroiminium salt.⁶ It slowly reacted with 1-dodecanol (**2a**) at room temperature to give 1-dodecyl fluoride (**3a**) in 12% yield after 17 h and most of **2a** remained as an ester (**4a**) (Eq 1). Under reflux in heptane, the fluorination reaction was completed in 1 h to give **3a** in good yield. Recently, microwave irradiation is reported to be effective to complete the thermal reaction in short time, and we applied the microwave irradiation to the reaction.⁸ The reaction was carried out using a modified household microwave oven. In an acetonitrile or without a solvent, the reaction mixture was refluxed vigorously under the irradiation of microwave and the reaction was completed in 10 min to give **3a** in good yields. However, a dark tarry material was also formed. Both DFMB and acetonitrile can absorb microwave energy very well and the reaction mixture could reach a high temperature. As it is difficult to control the reaction temperature in the household oven, we used a hydrocarbon solvent which does not absorb microwave energy well.⁸ Though the reaction mixture was refluxed vigorously even in heptane under microwave irradiation, the formation of the tarry material was not observed and **3a** was obtained in good yield in 10 min (Table 1).

Table 1. Reaction of 1-Dodecanol **2a** with DFMB **1**^a

React. temp.	React. Time	Solvent	Yield of 3a (%) ^b	Yield of 4a (%) ^c
25 °C	17 h	Heptane	12	76
98 °C	10 min	Heptane	67	7
98 °C	1 h	Heptane	86	trace
MW	10 min	CH ₃ CN	83	trace
MW	10 min	—	85	trace
MW	10 min	Heptane	88	trace

a) The reaction was carried out using 1.2 equiv. of **1** to **2a**.

b) Isolated yield based on **2a**. c) GC yield.

The deoxyfluorination reaction of various alcohols was carried out using **1** as shown in Table 2. Under the microwave irradiation, primary alcohols **2b**, **c**, **d**, **h**, **i** could be converted to the corresponding fluorides **3b**, **c**, **d**, **h**, **i** in good yields without the formation of olefinic by-products or the esters **4**, and the functional groups, such as the double bond **2b**, ether **2c** and ester group **2i**, remained unchanged. On the other hand, secondary alcohols **2e**, **f**, **g** were converted to the corresponding fluorides in moderate yields and olefinic by-products were also formed (8 - 40%). A benzylic alcohol **2j** is more reactive than the others, and it could be converted to the fluoride **3j** in high yield without the microwave irradiation.

Table 2 Deoxyfluorination of alcohols using DFMBAs^a

Substrate	Condition	Solvent	Product	Yield, % ^b
$\text{CH}_2=\text{CH}(\text{CH}_2)_9-\text{OH}$ 2b	MW 10min	Heptane	$\text{CH}_2=\text{CH}(\text{CH}_2)_9-\text{F}$ 3b	86
2c	MW 10min	Heptane	3c	72
$\text{C}_{10}\text{H}_{21}-\text{CHFCH}_2-\text{OH}$ 2d	MW 30min	Dodecane	$\text{C}_{10}\text{H}_{21}-\text{CHFCH}_2-\text{F}$ 3d	87 ^c
$\text{C}_{10}\text{H}_{21}-\underset{\text{OH}}{\text{CH}_2\text{CH}_2}\text{F}$ 2e	MW 30min	Dodecane	$\text{C}_{10}\text{H}_{21}-\underset{\text{F}}{\text{CH}_2\text{CH}_2}\text{F}$ 3d	63 ^{c,d}
$\text{C}_{10}\text{H}_{21}-\underset{\text{OH}}{\text{CH}}\text{CH}_3$ 2f	MW 30min	Dodecane	$\text{C}_{10}\text{H}_{21}-\underset{\text{F}}{\text{CH}}\text{CH}_3$ 3f	72 ^{c,e}
$\text{Hex}-\underset{\text{OH}}{\text{CH}}-\text{Hex}$ 2g	MW 30min	Dodecane	$\text{Hex}-\underset{\text{F}}{\text{CH}}-\text{Hex}$ 3g	50 ^{c,f}
$\text{HO}-(\text{CH}_2)_{12}-\text{OH}$ 2h	MW 10min	Heptane	$\text{F}-(\text{CH}_2)_{12}-\text{F}$ 3h	91
$\text{HO}-(\text{CH}_2)_4-\text{COOBu}$ 2i	MW 10min	Heptane	$\text{F}-(\text{CH}_2)_4-\text{COOBu}$ 3i	80
2j	50 °C 2h	Heptane	3j	95 ^c

a) If otherwise not mentioned, the reaction was carried out using 1.2 equiv. of **1** to **2**.

b) Isolated yield based on **2** used. c) 1.5 equiv. of **1** to **2** was used. d) Olefinic by-products were also formed (8%). e) Olefinic by-products were also formed (20%).

f) Olefinic by-products were also formed (40%).

The proposed reaction mechanism is as follows. The alcohol **2** reacts with DFMBAs **1** to give an adduct. This step is fast even at room temperature and hydrolysis at this stage gives ester **4**. A fluoride attacks the alkyl group of the alcohol to give alkyl fluoride **3** and an amide. This step is slow, and heating or the microwave irradiation is required to complete the reaction (Scheme 1).

Scheme 1

2.2. Deoxyfluorination of sugars using DFMBBA

Fluorinated carbohydrates have recently received much attention because of their important role in the study of enzyme-carbohydrate interactions as well as their interesting biological activities,⁹ and we applied **1** to the fluorinated carbohydrate synthesis. The reaction of methyl 2,3-*O*-isopropylidene-β-D-ribofuranose (**5b**) with DAST was previously reported to cause migration of a methoxy group from 1- to 5-position, and an unexpected 5-*O*-methyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl fluoride (**7**) was obtained instead of the desired 5-deoxy-5-fluoro derivative (**6b**).¹⁰ In the reaction of **5b** with **1** under the microwave irradiation, the desired **6b** could be obtained in 51% yield but **7** was also formed in 20 % yield. Under the microwave irradiation conditions, it was difficult to control the reaction temperature and selectivity, and we examined the reaction under conventional thermal heating conditions. The fluorination reaction was slow under the thermal conditions, and **6a** was obtained only in 28 % yield at 98 °C in 3 h. Moreover, migration of the methoxy group also took place under the thermal conditions. In order to accelerate the fluorination at the 5-position of **5b**, we added spray dry KF as a fluoride source and used a polar solvent, dioxane, to dissolve the KF. By carrying out the reaction at 100 °C for 16 h, migration of the methoxy group could be prevented and **6b** could be selectively obtained in 67% yield (Eq. 2).

Reagent	Solvent	Condition	Yield of 6b , %	Yield of 7 , %
DAST	CH ₂ Cl ₂	-15 °C - rt	—	55 ¹⁰
DFMBA	Heptane	MW 10 min	51	20
DFMBA	Heptane	98 °C 3 h	28	11
DFMBA, KF	Dioxane	100 °C 16 h	67	—

Similarly, an α -isomer (**6c**) could be stereospecifically obtained in 63% yield from an α -ribofuranose derivative (**5c**) (Table 3). Under the same conditions, 1,2,3,4-tetra-*O*-acetyl- α -D-glucopyranose (**5d**) could be converted to 1,2,3,4-tetra-*O*-acetyl-6-deoxy-6-fluoro- α -D-glucopyranose (**6d**) in 68 % yield. The conversion of 1,2,3,4-di-*O*-isopropylidene- α -D-galactopyranose (**5a**) to the corresponding fluoride (**6a**) could be achieved in 20 min under the microwave irradiation without affecting an acetonide protecting group. DFMBA **1** can be also used for the deoxyfluorination of nucleosides, and 2',3'-*O*-isopropylideneuridine (**5e**) could be converted to a 5'-deoxy-5'-fluorouridine derivative (**6e**) in 55% yield without migration of an uracil ring under the microwave irradiation.¹¹

Table 3. Deoxyfluorination of hydroxy groups in sugars and a nucleoside using DFMB **1**^a

Substrate	Condition	Product	Yield, % ^b
5a	MW 20 min heptane	6a	70
5b	100 °C 16 h dioxane	6b	67 ^c
5c	100 °C 24 h dioxane	6c	63 ^c
5d	100 °C 6 h dioxane	6d	68 ^c
5e	MW 10 min heptane	6e	55

a) If otherwise not mentioned, 2 equiv. of **1** to substrate was used. b) Isolated yield based on substrate used. c) 4 eq of KF and 2.5 equiv. of **1** to substrate were used.

2. 3. Glycosyl fluorides synthesis using DFMB

Glycosyl fluorides have been used as a key compound for polysaccharides synthesis and many reagents have been developed for their synthesis from the corresponding sugars.¹²

The hydroxy group of the sugars at the 1-position is highly reactive and even HF can be used for the conversion of the sugars to glucosyl fluorides.¹³ However, some protecting groups of sugars are sensitive to acidic reagents, and mild reagents for the synthesis of glycosyl fluorides have been desired. Various sugars having protecting groups such as acetonide (**8a**, **d**, **e**), benzyl ether (**8b**), acetate (**8c**) and, silyl ether (**8d**) reacted with **1** at below room temperature quickly without affecting the protecting groups to give the corresponding glycosyl fluorides in good yields as shown in Table 4. Moreover, the hydroxy groups at other than the 1-position were not converted to the fluoride by **1** at below room temperature, and, therefore, the glycosyl fluoride synthesis can be carried out without protection of the hydroxy groups. For instance, 2,3-*O*-isopropylidene-D-ribofuranose (**8e**) reacted with 2.4 eq of **1** at 0 °C to give 2,3-*O*-isopropylidene-5-*O*-*m*-methylbenzoyl-D-ribofuranosyl fluoride (**9e**) in 70% yield. Under the reaction conditions, only the hydroxy group at the 1-position was selectively deoxyfluorinated and the hydroxy group at the 5-position was only acylated. Furthermore, D-xylopyranose (**8f**), having four free hydroxy groups, can be directly converted to 2,3,4-tri-*O*-*m*-methylbenzoyl-D-xylopyranosyl fluoride (**9f**) in 60% yield by the reaction with 8 eq of **1**. In most of the cases, selectivity for α - or β -isomers was not observed and a mixture of both isomers was obtained regardless of the stereochemistry of the starting materials. Therefore, the reaction proceeds not via an S_N2 mechanism but through an oxonium intermediate.¹⁴ In the cases of a glucose (**8c**) and a xylose derivative (**8f**), the β -isomers (**9c** and **9f**) were selectively formed by the neighboring-group participation of the acyloxy groups at the 2-position.¹⁴

Table 4. Deoxyfluorination of hydroxy groups at 1-position in sugars using DFMBA **1**^a

Substrate	Product	Yield, % ^b
8a α only	9a $\alpha : \beta = 43 : 57$	90 ^c
8b α only	9b $\alpha : \beta = 40 : 60$	85
8c $\alpha : \beta = 60 : 40$	9c β only	80
8d $\alpha : \beta = 10 : 90$	9d $\alpha : \beta = 75 : 25$	80 ^d
8e $\alpha : \beta = 10 : 90$	9e $\alpha : \beta = 70 : 30$ Ar = <i>m</i> -tolyl	70 ^{d,e}
8f	9f β only Ar = <i>m</i> -tolyl	60 ^{c,f}

a) If otherwise not mentioned, the reaction was carried out in CH₂Cl₂ at room temperature for 1 h with 1.2 equiv. of **1**. b) Isolated yield based on sugar used. c) The reaction was carried out without solvent. d) The reaction was carried out at 0 °C. e) 2.4 equiv. of **1** to sugar was used. f) The reaction was carried out for 12 h using 8 equiv. of **1**.

3. Experimental

3. 1. General

The IR spectra were recorded using a JASCO FT/IR-410. The ^1H NMR (400MHz), ^{19}F NMR (376MHz), and ^{13}C NMR (100 MHz) spectra were recorded in CDCl_3 on a JEOL JNM-A400II FT NMR and the chemical shift, δ , are referred to TMS (^1H , ^{13}C) and CFCl_3 (^{19}F), respectively. The EI-low and high-resolution mass spectra were measured on a JEOL JMS-700TZ, JMS-FABmate or JMS-HX110. A commercially available GoldStar microwave oven (500W, MW-JIK96H5) was modified to accept a port for connecting a reactor to a reflux condenser located outside the oven.¹⁵ A hole of 10 mm diameter was drilled in the oven top and an 80 mm length of TeflonTM PFA tube was snugly fitted into the hole. A reflux condenser located outside was connected to the port tightly and another side of the port in the oven was used to connect to a reactor which is a TeflonTM PFA tube with a diameter of 10 mm and a length of 80 mm sealed at one end. DF MBA **1** was obtained from Mitubishi Gas Chemical Company Inc. and used without further purification. Though handling **1** with glassware is possible, it is recommended to use equipment made of TeflonTM. As **1** is slightly moisture-sensitive, it should be handled as quickly as possible in air and kept in a TeflonTM bottle with a tight screw cap. Alcohols **2d**, **2e** were prepared from 1,2-dodecene oxide by the reaction with Et_3N -3HF.¹⁶ Sugar derivatives **5a**, **5d**, **8a** were purchased from Sigma-Aldrich Co. and **8b**, **8f** were obtained from Junsei Chemical Co. Ltd. Other derivatives **5b**,¹⁷ **5c**,¹⁷ **5e**,¹⁸ **8c**,¹⁹ **8d**,²⁰ **8e**²¹ were prepared from the corresponding sugars or nucleoside according to the literature. The spray dry KF was obtained from Morita Chemical Industries Co. Ltd. and dried before use under the condition of 100 °C / 0.01 mHg for 1 h.

3.2. Fluorination of alcohols using DF MBA

3.2.1. Preparation of 1-fluorododecane (3a).²² Into a reactor consisting of a TeflonTM PFA tube with a diameter of 10 mm sealed at one end, were introduced heptane (1 ml), **1** (256 mg, 1.2 mmol), and **2a** (186 mg, 1.0 mmol). The open end of the reactor was connected to a port in a microwave oven and the port was connected to a reflux condenser located outside the oven. Then, the reaction mixture was submitted to microwave irradiation for 10 min. During the irradiation, the reaction mixture was refluxed vigorously. After the reaction, the reaction mixture was poured into aq

NaHCO₃ and extracted with ether three times. The combined ethereal layers were dried over MgSO₄, concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane) gave 1-fluorododecane **3a** (165 mg, 0.88 mmol) in 88 % yield.

IR (neat): 2925, 2855, 1466, 1389, 1050, 1010 cm⁻¹. ¹H NMR δ = 4.44 (2H, dt, J = 47.3, 6.3 Hz), 1.74 - 1.64 (2H, m), 1.39 - 1.26 (18H, m), 0.88 (3H, t, J = 6.7 Hz). ¹³C NMR δ = 14.07 (1C, s), 22.71 (1C, s), 25.19 (1C, d, J = 5.0 Hz), 29.29 (1C, s), 29.39 (1C, s), 29.56 (1C, s), 29.60 (1C, s), 29.67 (1C, s), 29.69 (1C, s), 30.46 (1C, d, J = 19.0 Hz), 31.96 (1C, s), 84.11 (1C, d, J = 163.8 Hz). ¹⁹F NMR δ = -218.36 - -218.75 (1F, m). HRMS (EI) Calcd for C₁₂H₂₅F (M⁺) 188.1940. Found 188.1942.

3.2.2. 1-Fluoro-10-undecene (3b).²³ IR(neat): 2927, 2855, 1641, 1465 cm⁻¹. ¹H NMR δ = 5.86 - 5.76 (1H, m), 5.02 - 4.91 (2H, m), 4.44 (2H, dt, J = 47.3, 6.1 Hz), 2.07 - 2.01 (2H, m), 1.75 - 1.63 (2H, m), 1.39 - 1.29 (12H, m). ¹³C NMR δ = 25.13 (1C, d, J = 4.9 Hz), 28.90 (1C, s), 29.08 (1C, s), 29.21 (1C, s), 29.37 (1C, s), 29.45 (1C, s), 30.40 (1C, d, J = 19.0 Hz), 33.78 (1C, s), 84.15 (1C, d, J = 164.6 Hz), 114.09 (1C, s), 139.13 (1C, s). ¹⁹F NMR δ = -218.37 - -218.75 (1F, m). HRMS (EI) Calcd for C₁₁H₂₁F (M⁺) 172.1627. Found 172.1631.

3.2.3. 2-Benzyloxyethyl fluoride (3c).²³ IR(neat): 3031, 2952, 2862, 1496, 1454, 1358 cm⁻¹. ¹H NMR δ = 7.36 - 7.28 (5H, m), 4.60 (2H, s), 4.59 (2H, dt, J = 47.6, 4.2 Hz), 3.72 (2H, dt, J = 29.3, 4.2 Hz). ¹³C NMR δ = 69.12 (1C, d, J = 19.8 Hz), 73.31 (1C, s), 83.09 (1C, d, J = 168.7 Hz), 127.71 (2C, s), 127.73 (1C, s), 128.41 (2C, s), 137.77 (1C, s). ¹⁹F NMR δ = -223.43 - -223.84 (1F, m). HRMS (EI) Calcd for C₉H₁₁OF (M⁺) 154.0794. Found 154.0786.

3.2.4. 1,2-Difluorododecane (3d).²⁴ IR (neat) 2926, 2855, 1467, 1042 cm⁻¹. ¹H NMR δ = 4.79 - 4.34 (3H, m), 1.74 - 1.26 (18H, m), 0.88 (3H, t, J = 6.8 Hz). ¹³C NMR δ = 14.09 (1C, s), 15.26 (1C, s), 22.67 (1C, s), 24.74 (1C, d, J = 5.0 Hz), 29.31 (1C, s), 29.39 (1C, s), 29.53 (1C, d, J = 5.8 Hz), 30.02 (1C, dd, J = 20.7, 6.6 Hz), 31.88 (1C, s), 65.84 (1C, s), 84.16 (1C, dd, J = 173.7, 23.2 Hz), 91.85 (1C, dd, J = 172.0, 19.0 Hz). ¹⁹F NMR δ = -189.18 - -189.60 (1F, m), -230.19 - -230.54 (1F, m).

3.2.5. 2-Fluorododecane (3f).²⁵ IR (neat) 2926, 2855, 1466, 1384, 1130 cm⁻¹. ¹H NMR δ = 4.65 (dm, 1H, J = 50.5 Hz), 1.71 - 1.26 (20H, m), 0.88 (3H, t, J = 6.8 Hz). ¹³C NMR δ = 14.10 (1C, s), 20.99 (1C, d, J = 23.2 Hz), 22.69 (1C, s), 25.09 (1C, d, J = 5.0 Hz), 29.57 (1C, s), 29.33(1C, s), 29.47(1C, s), 29.55 (1C, s), 29.60 (1C, s), 31.91 (1C, s), 36.95 (1C, d, J = 20.7 Hz), 91.06 (1C, d, J = 164.6 Hz). ¹⁹F NMR δ = -172.45 - -172.89 (1F, m).

3.2.6. 7-Fluorotridecane (3g). IR (neat) 2932, 2859, 1467 cm⁻¹. ¹H NMR δ = 4.46 (1H, dm, J = 49.3 Hz), 1.29 - 1.67 (20H, m), 0.89 (6H, t, J = 6.7 Hz). ¹³C NMR δ = 14.05 (2C, s), 22.60 (2C, s), 25.13 (2C, d, J = 5.0 Hz), 29.22 (2C, s), 31.78 (2C, s), 35.22 (2C, d, J = 20.7 Hz), 94.53 (1C, d, J = 167.1 Hz). ¹⁹F NMR δ = -180.76 - -180.38 (m, 1F). HRMS (EI) Calcd for C₁₃H₂₆ (M⁺-HF) 182.2035. Found 182.2027.

3.2.7. 1, 12-Difluorododecane (3h).²³ IR (neat) 2928, 2855, 1467, 1390 cm⁻¹. ¹H NMR δ = 4.49 (4H, dt, J = 47.3, 6.3 Hz), 1.75 - 1.62 (4H, m), 1.55 - 1.28 (16 H, m). ¹³C NMR δ = 25.13 (2C, d, J = 5.0 Hz), 29.22 (2C, s), 29.48 (4C, s), 30.39 (2C, d, J = 19.9 Hz), 84.17 (2C, d, J = 163.8 Hz). ¹⁹F NMR δ = -218.38 - -218.77 (m, 2 F). HRMS (EI) Calcd for C₁₂H₂₄F₂ (M⁺) 206.1846. Found 206.1843.

3.2.8. Butyl 5-fluoropentanoate (3i). IR (neat) 2962, 1736, 1172 cm⁻¹. ¹H NMR δ = 4.46 (2H, dt, J = 47.6, 5.6 Hz), 4.08 (2H, t, J = 6.6 Hz), 2.36 (2H, t, J = 6.3 Hz), 1.80 - 1.71 (4H, m), 1.65 - 1.56 (2H, m), 1.43 - 1.33 (2H, m), 0.94 (3H, t, J = 7.4 Hz). ¹³C NMR δ = 13.58 (1C, s), 19.04 (1C, s), 20.77 (1C, d, J = 5.0 Hz), 29.69 (1C, d, J = 19.9 Hz), 30.58 (1C, s), 33.64 (1C, s) 64.14 (1C, s) 83.47 (1C, d, J = 165.4 Hz), 173.25 (1C, s). ¹⁹F NMR δ = -219.25 - -219.66 (m, 1F). HRMS (EI) Calcd for C₉H₁₇O₂F (M⁺) 176.1213. Found 176.1216.

3.2.9. Preparation of *p*-bromobenzyl fluoride (3j).²⁶ DFMB (256 mg, 1.5 mmol), *p*-bromobenzyl alcohol (187 mg, 1.0 mmol), and CHCl₃ (2 ml) were introduced into a reaction vessel made of Teflon™ PFA with a tight screw cap and kept at 50 °C for 2 h in an oil bath. The mixture was poured into aq NaHCO₃ and extracted with ether three times. The combined ethereal layers were dried over MgSO₄, concentrated under

reduced pressure. Purification by column chromatography (silica gel/hexane-Et₂O) gave **3j** in 95 % yield; IR (neat) 2961, 1593, 1487, 1407, 1374, 1213, 1071, 1011 cm⁻¹. ¹H NMR δ = 7.52 (2H, d, J = 7.3 Hz), 7.24 (2H, d, J = 7.3 Hz), 5.33 (2H, d, J = 47.6 Hz). ¹³C NMR δ = 83.71 (1C, d, J = 167.1 Hz), 122.75 (2C, d, J = 3.3 Hz), 129.0 (2C, d, J = 5.8 Hz), 131.73 (1C, s), 135.13 (1C, d, J = 18.2 Hz). ¹⁹F NMR δ = -208.64 (1F, t, J = 47.6 Hz).

3.3. Deoxyfluorination of sugars using DFMBBA

3.3.1. 6-Fluoro-1,2;3,4-di-*O*-isopropylidene-6-deoxy- α -D-galactopyranose (6a).^{27, 28} IR (neat) 2990, 1384, 1256, 1213, 1072 cm⁻¹. ¹H NMR δ = 5.56 (1H, d, J = 4.9 Hz), 4.65-4.48 (3H, m), 4.35 (1H, dd, J = 5.1, 2.4 Hz), 4.27 (1H, dd, J = 8.1, 2.0 Hz), 4.10 - 4.07 (1H, m), 1.55 (3H, s), 1.45 (3H, s), 1.34 (6H, s). ¹³C NMR δ = 24.39 (1C, s), 24.88 (1C, s), 25.90 (1C, s), 26.00 (1C, s), 66.60 (1C, d, J = 22.3 Hz), 70.39 (1C, s), 70.47 (1C, s), 70.55 (1C, s), 82.04 (1C, d, J = 167.9 Hz), 96.15 (1C, s), 108.78 (1C, s), 109.63 (1C, s). ¹⁹F NMR δ = -231.73 (1F, dt, J = 47.6, 14.0 Hz). HRMS (EI) Calcd for C₁₂H₁₉O₅F (M⁺) 262.1216. Found 262.1215.

3.3.2. Preparation of methyl 5-fluoro-2,3-*O*-isopropylidene-5-deoxy- β -D-ribofuranoside (6b).²⁸ DFMBBA (533 mg, 2.5 mmol), KF (232 mg, 4.0 mmol), **5b** (204 mg, 1.0 mmol), and 1,4-dioxane (1 ml) were introduced into a reaction vessel made of Teflon™ PFA with a tight screw cap and kept at 100 °C for 16 h in an oil bath. After the reaction, the mixture was poured into aq NaHCO₃ and extracted with ether three times. The combined ethereal layers were dried over MgSO₄, concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane-Et₂O) gave **6b** in 67 % yield; IR (neat) 2941, 2837, 1458, 1383, 1212, 1090, 871 cm⁻¹. ¹H NMR δ = 4.99 (1H, d, J = 2.4 Hz), 4.71 (1H, d, J = 6.1 Hz), 4.60 (1H, d, J = 5.9 Hz), 4.39 (3H, dm, J = 37.8 Hz), 3.33 (3H, s), 1.50 (3H, s), 1.33 (3H, s). ¹³C NMR δ = 24.87 (1C, s), 26.37 (1C, s), 54.85 (1C, s), 81.00 (1C, d, J = 4.1 Hz), 82.91 (1C, d, J = 172.9 Hz), 84.36 (1C, s), 84.59 (1C, s), 85.05 (1C, s), 109.21 (1C, s). ¹⁹F NMR δ = -225.39 - -225.68 (1F, m). HRMS (EI) Calcd for C₉H₁₄O₄F (M⁺-H) 205.0876. Found 205.0869.

3.3.3. Methyl 5-fluoro-2,3-*O*-isopropylidene-5-deoxy- α -D-ribofuranoside (6c).²⁸ IR (neat) 2939, 1371, 1215, 1098 cm⁻¹. ¹H NMR δ = 4.96 (1H, s), 4.67 - 4.62 (2H, m), 4.58 (2H, dm, J = 47.8 Hz), 4.25 (1H, dm, J = 30.7 Hz), 3.51 (3H, s), 1.58 (3H, s), 1.37 (3H, s). ¹³C NMR δ = 25.56 (1C, s), 25.89 (1C, s), 56.14 (1C, s), 79.71 (1C, d, J = 26.5 Hz), 79.66 (1C, s), 80.46 (1C, s), 83.18 (1C, d, J = 172.0 Hz), 103.17 (1C, s), 115.26 (1C, s). ¹⁹F NMR δ = -232.72 (1F, dt, J = 47.8, 30.7 Hz).

3.3.4. 1,2,3,4-Tetra-*O*-acetyl-6-deoxy-6-fluoro- α -D-glucopyranose (6d).²⁹ Mp 122-125 °C (lit²⁶ 128-129 °C). IR (KBr) 2959, 1757, 1370, 1217, 1079, 1038 cm⁻¹. ¹H NMR δ = 5.74 (1H, d, J = 8.1 Hz), 5.32 - 5.11 (3H, m), 4.60 - 4.37 (2H, m), 3.89 - 3.79 (1H, m), 2.12 (3H, s), 2.06 (3H, s), 2.04 (3H, s), 2.03 (3H, s). ¹³C NMR δ = 25.55 (1C, s), 20.76 (1C, s), 67.46 (1C, d, J = 6.6 Hz), 70.11 (1C, s), 72.70 (1C, s), 73.20 (1C, s), 80.61 (1C, s), 91.55 (1C, s), 168.95 (1C, s), 169.15 (1C, s), 169.28 (1C, s), 170.12 (1C, s). ¹⁹F NMR δ = -232.73 (1F, dt, J = 47.0, 22.6 Hz).

3.3.5. 5'-Fluoro-2',3'-*O*-isopropylidene-5'-deoxyuridine (6e).³⁰ IR (neat) 2990, 1687, 1437, 1382, 1274, 1082 cm⁻¹. ¹H NMR δ = 9.18 (1H, brs), 7.33 (1H, d, J = 8.1 Hz), 5.84 (1H, s), 5.76 (1H, d, J = 8.1 Hz), 4.94 - 4.88 (2H, m), 4.74 - 4.71 (1H, m), 4.62 - 4.59 (1H, m), 4.43 - 4.35 (1H, m), 1.60 (3H, s), 1.36 (3H, s). ¹³C NMR δ = 25.15 (1C, s), 27.02 (1C, s), 79.90 (1C, d, J = 7.4 Hz), 82.84 (1C, d, J = 172.4 Hz), 84.50 (1C, s), 85.62 (1C, d, J = 18.2 Hz), 93.73 (1C, s), 102.66 (1C, s), 114.57 (1C, s), 141.49 (1C, s), 150.19 (1C, s), 163.61 (1C, s). ¹⁹F NMR δ = -229.973 - -230.292 (1F, m). HRMS Calcd for C₁₂H₁₅N₂O₅F (M⁺) 286.0965. Found 286.0967.

3.4. Glycosyl fluorides synthesis using DFMB

3.4.1. Preparation of 2,3;5,6-di-*O*-isopropylidene-D-mannofuranosyl fluoride (9a).³¹ DFMB (205 mg, 1.2 mmol), **8a** (187 mg, 1.0 mmol), and CH₂Cl₂ (2 ml) were introduced into a reaction vessel made of Teflon™ PFA with a tight screw cap and the mixture was stirred at room temperature for 1 h. After the reaction, the mixture was poured into aq NaHCO₃ and extracted with ether three times. The combined ethereal layers were dried over MgSO₄, concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane-Et₂O) gave **9a** in 90 % yield as a mixture of

α and β isomers in a ratio of 43:57.

(9a- α), IR (neat) 2989, 1374, 1212, 1130, 1070, 972, 849 cm^{-1} . ^1H NMR δ = 5.69 (1H, d, J = 59.5 Hz), 4.77 - 4.43 (2H, m), 4.43 - 4.38 (1H, m), 4.18 - 4.05 (3H, m), 1.46 (6H, s), 1.39 (3H, s), 1.35 (3H, s). ^{13}C NMR δ = 24.49 (1C, s), 25.14 (1C, s), 25.80 (1C, s), 26.86 (1C, s), 66.64 (1C, s), 72.68 (1C, s), 78.56 (1C, s), 82.60 (1C, s), 84.72 (1C, d, J = 42.2 Hz), 109.39 (1C, s), 113.20 (1C, s), 113.64 (1C, d, J = 221.6 Hz). ^{19}F NMR δ = -129.25 (1F, dd, J = 59.5, 6.7 Hz). HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{19}\text{O}_5\text{F}$ ($\text{M}^+ + \text{H}$) 263.1295. Found 263.1317.

(9a- β), Mp 113-114 $^{\circ}\text{C}$ (lit³¹ 114 - 115 $^{\circ}\text{C}$). IR (neat) 2985, 1377, 1263, 1216, 1125, 1089, 1062, 1001, 846, 527 cm^{-1} . ^1H NMR δ = 5.51 (1H, dd, J = 3.7, 66.5 Hz), 4.87 - 4.84 (1H, m), 4.75 - 4.69 (1H, m), 4.50 - 4.46 (1H, m), 4.22 - 4.17 (1H, m), 4.11 (2H, d, J = 3.7 Hz), 1.57 (3H, s), 1.46 (3H, s), 1.41 (3H, s), 1.39 (3H, s). ^{13}C NMR δ = 25.24 (2C, s), 25.67 (1C, s), 26.94 (1C, s), 66.45 (1C, s), 73.52 (1C, s), 77.55 (1C, s), 81.00 (1C, d, J = 1.7 Hz), 81.23 (1C, d, J = 19.8 Hz), 107.42 (1C, d, J = 234.9 Hz), 109.39 (1C, s), 115.74 (1C, s). ^{19}F NMR δ = -125.13 (1F, ddd, J = 66.5, 15.3, 5.5 Hz). HRMS (EI) $\text{C}_{12}\text{H}_{20}\text{O}_5\text{F}$ ($\text{M}^+ + \text{H}$) 263.1295. Found 263.1288

3.4.2. 2,3,5-Tri-*O*-benzyl- α -D-arabinofuranosyl fluoride (9b- α).¹³ IR (neat) 2895, 1725, 1496, 1453, 1376, 1110, 872, 752, 699 cm^{-1} . ^1H NMR δ = 7.30 - 7.17 (15H, m), 5.55 (1H, d, J = 67.1 Hz), 4.63 - 4.47 (6H, m), 4.18 - 4.01 (3H, m), 3.56 - 3.47 (2H, m). ^{13}C NMR δ = 69.32 (1C, s), 72.04 (1C, s), 72.09 (1C, s), 73.36 (1C, s), 82.45 (1C, s), 84.07 (1C, s), 86.82 (1C, d, J = 33.9 Hz), 113.50 (1C, d, J = 225.0 Hz), 127.66 - 128.50 (15C, s), 136.89 (1C, s), 137.41 (1C, s), 137.83 (1C, s). ^{19}F NMR δ = -127.30 (1F, ddd, J = 65.3, 20.8, 5.5 Hz). HRMS (EI) Calcd for $\text{C}_{26}\text{H}_{27}\text{O}_4\text{F}$ (M^+) 422.1893. Found 422.1896.

(9b- β), Mp 78-79 $^{\circ}\text{C}$ (lit¹³ 77 - 78 $^{\circ}\text{C}$). IR (neat) 3062, 3030, 2865, 1454, 1115, 1028, 738, 698 cm^{-1} . ^1H NMR δ = 7.30 - 7.17 (15H, m), 5.79 (5H, d, J = 61.5 Hz), 4.73 - 4.45 (7H, m), 4.17 (1H, dd, J = 9.3, 2.2 Hz), 3.96 (1H, dd, J = 5.1, 2.0 Hz), 3.64 - 3.57 (2H, m). ^{13}C NMR δ = 71.52 (1C, s), 72.48 (1C, s), 72.63 (1C, s), 73.45 (1C, s), 81.53 (1C, s), 82.35 (1C, s), 84.52 (1C, d, J = 21.5 Hz), 108.32 (1C, d, J = 229.9 Hz), 127.66 -

128.51 (15C, s), 137.18 (1C, s), 137.73 (1C, s), 137.87 (1C, s). ^{19}F NMR δ = -121.23 (1F, dd, J = 61.6, 9.2 Hz). HRMS (EI) Calcd for $\text{C}_{26}\text{H}_{27}\text{O}_4\text{F}$ (M^+) 422.1893. Found 422.1882.

3.4.3. 2,3,4,5-Tetra-*O*-acetyl- α -D-glucopyranosyl fluoride (9c).³² Mp 77-78 °C. IR (neat) 2942, 1761, 1439, 1378, 1227, 1109, 1042 cm^{-1} . ^1H NMR δ = 5.37 (1H, dd, J = 52.0, 6.1 Hz), 5.22 - 5.20 (2H, m), 5.18 - 5.08 (1H, s), 4.29 - 4.20 (2H, m), 3.93 - 3.88 (1H, s), 2.11 (6H, s), 2.05 (6H, s). ^{13}C NMR δ = 20.49 - 20.61 (4C, s), 61.68 (1C, s), 67.36 (1C, s), 71.10 (1C, d, J = 28.9 Hz), 71.70 (1C, d, J = 8.3 Hz), 71.96 (1C, d, J = 4.1 Hz), 106.14 (1C, d, J = 219.2 Hz), 169.05 (1C, s), 169.23 (1C, s), 169.95 (1C, s), 170.49 (1C, s). ^{19}F NMR δ -137.83 (1F, dd, J = 51.9, 10.4 Hz). HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_9\text{F}$ ($\text{M}^+ + \text{H}$) 351.1091. Found 351.1115.

3.4.4. 2,3-*O*-Isopropylidene-5-*O*-dimethyl^tbutylsilyl- α -D-ribofuranosyl fluoride (9d- α). IR (neat) 2932, 1858, 1472, 1381, 1258, 1215, 1108, 838 cm^{-1} . ^1H NMR δ = 5.63 (1 H, dd, J = 66.5, 3.7 Hz), 4.70 - 4.61 (2H, m), 4.47 (1H, brs), 3.75 (2H, d, J = 2.6 Hz), 1.57 (3H, s), 1.38 (3H, s), 0.89 (9H, s), 0.07 (3H, s), 0.05 (3H, s). ^{13}C NMR δ = -5.55 (1C, s), -5.36 (1C, s), 18.25 (1C, s), 25.69 (1C, s), 25.71 (1C, s), 25.82 (3C, s), 63.23 (1C, s), 79.52 (1C, s), 81.10 (1C, d, J = 19.9 Hz), 84.26 (1C, d, J = 2.5 Hz), 114.84 (1C, s), 108.54 (1C, d, J = 234.0 Hz). ^{19}F NMR δ = -127.19 (1F, dd, J = 66.5, 14.6 Hz). HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{27}\text{O}_4\text{FSiNa}$ ($\text{M}^+ + \text{Na}$) 329.1561. Found 329.1567.

(9d- β). IR (neat) 2932, 1858, 1472, 1381, 1258, 1215, 1108, 838 cm^{-1} . ^1H NMR δ = 5.74 (1H, d, J = 62.9 Hz), 4.80 - 4.73 (2H, m), 4.39 - 4.35 (1H, m), 3.75 - 3.71 (1H, m), 3.56 - 3.51 (1H, m), 1.47 (3H, s), 1.34 (3H, s), 0.90 (9H, s), 0.07 (3H, s), 0.06 (3H, s). ^{13}C NMR δ = -5.32 (1C, s), -5.30 (1C, s), 18.44 (1C, s), 25.08 (1C, s), 26.01 (3C, s), 26.51 (1C, s), 63.77 (1C, s), 81.19 (1C, s), 85.17 (1C, d, J = 40.5 Hz), 89.22 (1C, d, J = 2.5 Hz), 112.81 (1C, s), 115.61 (1C, d, J = 222.5 Hz). ^{19}F NMR δ = -114.94 (1F, dm, J = 62.9 Hz).

3.4.5. 2,3-*O*-Isopropylidene-5-*O*-(*m*-methylbenzoyl)- α -D-ribofuranosyl fluoride (9e- α). IR (neat) 2986, 1723, 1383, 1278, 1200, 1105, 745 cm^{-1} . ^1H NMR δ = 7.80 -

7.78 (2H, m), 7.38 - 7.23 (2H, m), 5.67 (1H, dd, $J = 64.9, 3.4$ Hz), 4.76 - 4.67 (3H, m), 4.53 - 4.34 (3H, m), 2.38 (3H, s), 1.56 (3H, s), 1.36 (3H, s). ^{13}C NMR $\delta = 21.23$ (1C, s), 25.67 (1C, s), 25.71 (1C, s), 63.94 (1C, s), 79.41 (1C, s), 81.03 (1C, d, $J = 20.7$ Hz), 81.79 (1C, d, $J = 1.7$ Hz), 108.01 (1C, d, $J = 235.3$ Hz), 116.00 (1C, s), 126.64 (1C, s), 128.37 (1C, s), 129.30 (1C, s), 130.13 (1C, s), 134.11 (1C, s), 138.33 (1C, s), 166.12 (1C, s). ^{19}F NMR $\delta = -130.22$ (1F, dd, $J = 14.6, 65.3$ Hz). HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{19}\text{O}_5\text{F}$ (M^+) 310.1217. Found 310.1216.

(**9e- β**), IR (neat) 2990, 1724, 1383, 1278, 1200, 745 cm^{-1} . ^1H NMR $\delta = 7.85 - 7.83$ (2H, m), 7.37 - 7.29 (2H, m), 5.80 (1H, d, $J = 61.7$ Hz), 4.85 - 4.81 (2H, m), 4.70 - 4.65 (1H, m), 4.39 - 4.36 (2H, m), 2.38 (3H, s), 1.47 (3H, s), 1.32 (3H, s). ^{13}C NMR $\delta = 21.23$ (1C, s), 24.87 (1C, s), 26.29 (1C, s), 64.50 (1C, s), 80.94 (1C, s), 84.99 (1C, d, $J = 40.5$ Hz), 86.37 (1C, d, $J = 2.5$ Hz), 113.66 (1C, d, $J = 107.5$ Hz), 116.41 (1C, s), 126.87 (1C, s), 128.30 (1C, s), 129.42 (1C, s), 130.25 (1C, s), 134.02 (1C, s), 138.23 (1C, s), 166.20 (1C, s). ^{19}F NMR $\delta = -116.39$ (1F, dt, $J = 61.7, 3.7$ Hz).

3.4.6. 2,3,4-Tri-*O*-(*m*-methylbenzoyl)- α -D-xylopyranosyl fluoride (9f). IR (neat) 2957, 1733, 1590, 1185, 739, 681 cm^{-1} . ^1H NMR $\delta = 7.89 - 7.80$ (6H, m), 7.41 - 7.33 (4H, m), 7.25 - 7.16 (2H, m), 5.80 (1H, d, $J = 48.8$ Hz), 5.67 (1H, s), 5.32 (1H, s), 5.23 (1H, s), 4.60 (1H, d, $J = 15.9$ Hz), 4.11 (1H, d, $J = 18.5$ Hz), 2.41 (3H, s), 2.26 (3H, s), 2.23 (3H, s). ^{13}C NMR $\delta = 21.02$ (1C, s), 21.11 (1C, s), 21.25 (1C, s), 60.70 (1C, s), 68.99 (1C, s), 69.13 (1C, s), 71.23 (1C, d, $J = 24.8$ Hz), 104.26 (1C, d, $J = 229.9$ Hz), 126.86 - 138.28 (18C, s), 165.70 (1C, s), 165.77 (1C, s), 165.84 (1C, s). ^{19}F NMR $\delta = -137.56$ (1F, dd, $J = 48.8, 4.9$ Hz). HRMS (EI) Calcd for $\text{C}_{29}\text{H}_{27}\text{O}_7\text{F}$ (M^+) 506.1741. Found 506.1744.

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