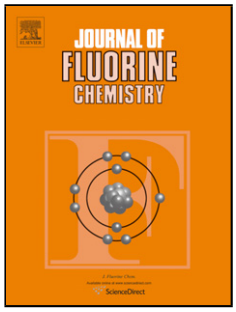

Title: Synthesis of fluoromethyl ethers and fluoromethyl esters by the reaction of the corresponding methylthiomethyl ethers and methylthiomethyl esters with IF_5-pyridine-HF

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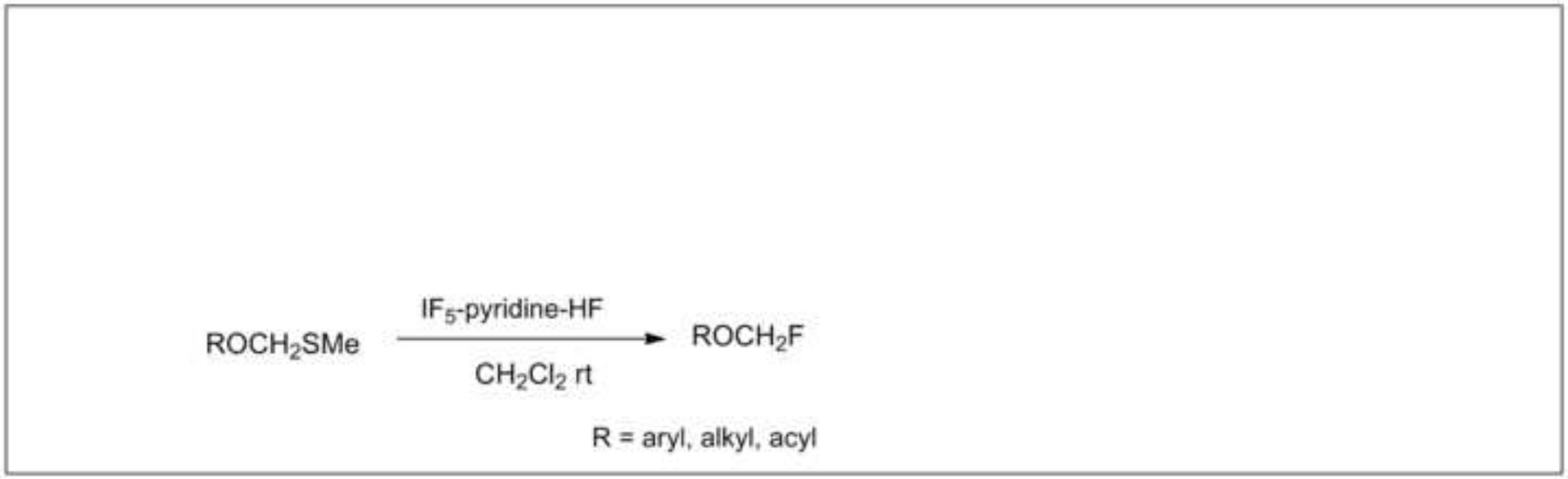
***Graphical Abstract - Pictogram**



*Graphical Abstract - Synopsis

Synthesis of fluoromethyl ethers and fluoromethyl esters by the reaction of the corresponding methylthiomethyl ethers and methylthiomethyl esters with IF_5-pyridine-HF

Masataka Kunigami, Shoji Hara*
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Fluoromethyl ethers were synthesized from the corresponding methylthiomethyl ethers.> A stable fluorination reagent, IF_5-pyridine-HF, was used for the reaction.> Fluoromethyl ester was also synthesized in a similar way.>*O*-Fluoromethyl ether of a *D*-tyrosine derivative was synthesized by this method.

Synthesis of fluoromethyl ethers and fluoromethyl esters by the reaction of the corresponding methylthiomethyl ethers and methylthiomethyl esters with IF_5-pyridine-HF

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Keywords: *stable fluorinating reagent, IF_5-pyridine-HF, fluoromethyl ether, fluoromethyl ester*

Abstract

Fluoromethyl ethers of various functionalized phenols were synthesized from the corresponding methylthiomethyl ethers by the reaction with IF_5-pyridine-HF. A fluoromethyl ether of an aliphatic alcohol and a fluoromethyl ester of a carboxylic acid were also synthesized.

1. Introduction

Organofluorine compounds are widely used, as medicines, pesticides, functional materials, and so on [1]. Recently, effective synthetic method of fluoromethyl ether is attracting attention for the introduction of ^{18}F atom to the PET tracer [2]. Fluoromethyl ethers have been synthesized using various methods, including halogen exchange reaction [3], fluoromethylation of alkoxides [4], fluorodecarboxylation of alkoxyacetic

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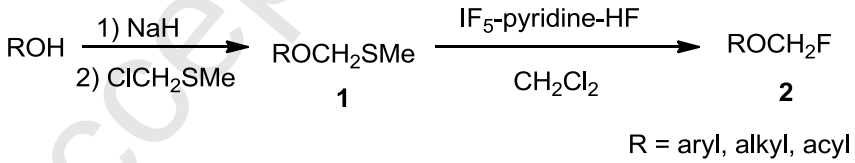
acids [5], oxidative fluorination of benzylic alcohols [6], and desulfurizing fluorination of methylthiomethyl ethers [7]. Among them, the conversion of the methylthiomethyl ethers has an advantage over other methods because the starting methylthiomethyl ether can be easily prepared from the corresponding hydroxyl compounds [8], and therefore, the method can be used to introduce the fluoromethyl group to various substrates. DAST [7a-c] and XeF_2 [7d] were used in the desulfurizing fluorination reaction of methylthiomethyl ether. However, they decompose in air by the contact with moisture under generating HF, and therefore, application of a stable reagent to the desulfurizing fluorination reaction of methylthiomethyl ether was desired [9]. Recently, we reported that the air- and moisture stable fluorinating reagent, IF_5-pyridine-HF, can be used for the fluorination reactions of various sulfur compounds [10]. During our continuing studies on the fluorination reaction using IF_5-pyridine-HF, we found that the desulfurizing fluorination reaction of methylthiomethyl ethers and the ester of various hydroxyl compounds can be achieved using IF_5-pyridine-HF (Scheme 1).



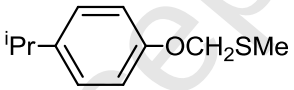
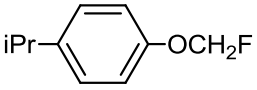
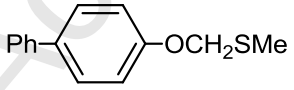
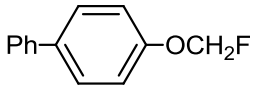
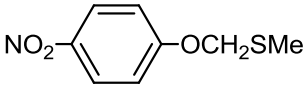
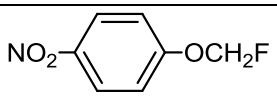
Scheme 1

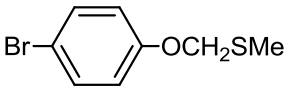
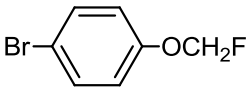
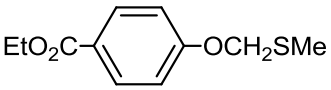
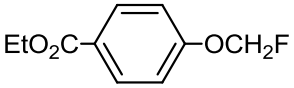
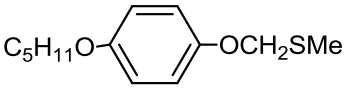
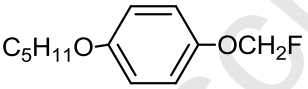
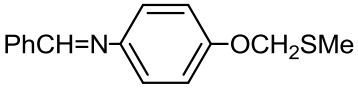
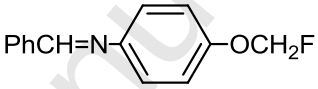
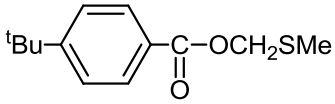
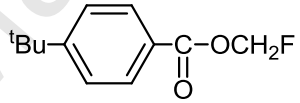
2. Results and discussion

The reaction of methylthiomethyl ethers prepared from phenols **1** with IF_5-pyridine-HF is generally completed in a few hours at room temperature, and the corresponding fluoromethyl ethers **2** were obtained in good to moderate yields, as

shown in Table 1. The reaction is applicable to substrates having both an electron-donating group (**1a**, **1f** and **1g**), and an electron-withdrawing group (**1b**, **1c**, **1d**, and **1e**) on the benzene ring. When a strong electron-withdrawing group, such as a nitro group, was attached (**1c**), the reaction was sluggish and a long reaction time was required (Entry 3). On the other hand, when an aniline derivative (**1g**) was used, due to the strong electron-donating effect of the nitrogen substituent, the product (**2g**) was unstable. Therefore, it was necessary to carry out the reaction at a lower temperature (-10 ˚C) for a longer time (Entry 7). The reaction is also applicable to the synthesis of fluoromethyl estes of carboxylic acids (Entry 8) and fluoromethyl ethers of aliphatic alcohols (Entry 9).

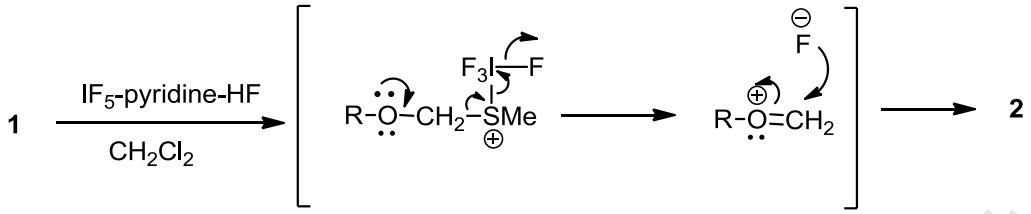
Table 1 Reaction of methylthiomethyl ether and ester **1** with IF_5-pyridine-HF[a]

Entry	**1**	React. time (h)	Product **2**	Yield (%)[b]
1	 **1a**	3	 **2a**	67 (92)
2	 **1b**	3.5	 **2b**	78 (83)
3	 **1c**	32	 **2c**	50 (67)[c]

4	 **1d**	3	 **2d**	66 (87)
5	 **1e**	4	 **2e**	65 (76)
6	 **1f**	4	 **2f**	63 (79)
7	 **1g**	96	 **2g**	(65)[d]
8	 **1h**	48	 **2h**	59 (74)[c,e]
9	$C_{10}H_{21}$-OCH_2SMe **1i**	3	$C_{10}H_{21}$-O-CH_2F **2i**	(95)

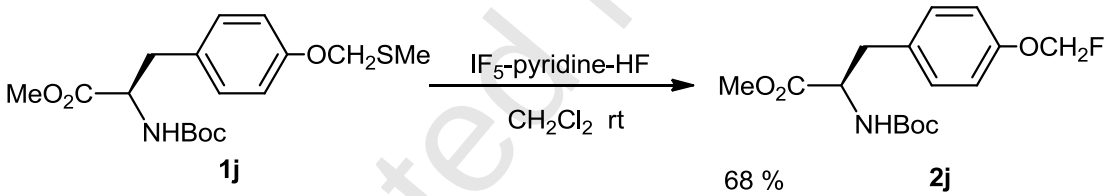
[a] If otherwise not mentioned, the reaction was performed in CH_2Cl_2 at room temperature using 1.1 eq of IF_5-pyridine-HF to **1**. [b] Isolated yield based on 1 used, in parentheses, ^{19}F NMR yield using fluorobenzene as an internal standard. [c]1.5 eq of IF_5-pyridine-HF to **1** was used. [d]The reaction was carried out at -10 °C. [e] The reaction was carried out at 40 °C.

The reaction must be proceeding through an oxonium ion intermediate, and a strong electron-withdrawing substituent on the benzene ring disturbed the formation of the oxonium ion intermediate and slowed down the reaction rate (Entry 3) (Scheme 2).



Scheme 2

The O-fluoromethyl ether of tyrosine is a potential candidate for a PET tracer [2], and the present reaction can be used for the synthesis of the *O*-fluoromethyl ether of tyrosine. When the *O*-methylthiomethyl ether of a *D*-tyrosine derivative (**1j**) was subjected to the reaction with IF_5-pyridine-HF, the *O*-fluoromethyl ether of the tyrosine derivative (**2j**) was obtained in 68% yield (Scheme 3).



Scheme 3

3. Conclusion

We have shown that an air- and moisture stable fluorinating reagent, IF_5-pyridine-HF, can be used for the synthesis of fluoromethyl ethers of functionalized phenols and aliphatic alcohols, and fluoromethyl esters of carboxylic acids. The present method was applied to the synthesis of the *O*-fluoromethyl ether of a *D*-tyrosine derivative, which is a potential PET tracer candidate. As the starting methylthiomethyl ether can be easily prepared from the corresponding hydroxyl compound, the present method is useful for

the introduction of the fluoromethyl group to various hydroxy compounds.

4. Experimental

4.1. General

The melting points were measured with a Yanagimoto micro melting-point apparatus. The IR spectra were recorded using a JASCO FT/IR-410. The ^{1}H NMR (400 MHz) spectra, ^{19}F NMR (376 MHz) spectra, and ^{13}C NMR (100 MHz) were recorded in $CDCl_3$ on a JEOL JNM-A400II FT NMR and the chemical shift, δ, is referred to TMS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F), respectively. The EI-high-resolution mass spectra were measured on a JEOL JMS-700TZ. Methylthiomethyl ethers and esters were prepared from the corresponding hydroxyl compounds and methylthiomethyl chloride according to the literature [7]. IF_5 was donated from Daikin Industries, Ltd. [11].

Preparation of IF_5-pyridine-HF [10].

To a 500-mL round flask made of Teflon™ FEP, IF_5 (94g, 0.37 mol) was introduced from a stainless cylinder, and then CCl_4 (200 mL) was introduced at 0 °C. When pyridine-HF (37.5g, 0.37 mol) in CCl_4 (50 mL) was added, a white precipitate appeared immediately. The resulting heterogeneous mixture was stirred at 0 °C for 30 min and at room temperature for 1 h. A white solid was separated by filtration in air and washed with CCl_4 (50 mL x 3). The solid was transferred into a Teflon™ FEP round flask and solvent was removed under reduced pressure. The resulting white solid, IF_5-pyridine-HF, can be handled in air without special cares, and stored in Teflon™ bottle in a refrigerator for a few months. The reaction using IF_5-pyridine-HF was performed in a bottle made of Teflon™ FEP with a screw-cap. Glassware is gradually corroded by IF_5-pyridine-HF,

therefore, use of Teflon™ or polyethylene ware is recommended.

*4.2. General procedure for the reaction of methylthiomethyl ether **1** with IF_5-pyridine-HF.*

To a Teflon™ FEP bottle, IF_5-pyridine-HF (177 mg, 0.55 mmol) and CH_2Cl_2 (2 mL) were introduced at room temperature. To the resulting white suspension, a methylthiomethyl ether (**1**) (0.5 mmol) in CH_2Cl_2 (1 mL) was added at room temperature. The mixture changed to dark red immediately, and was stirred at room temperature. The reaction can be monitored by tlc or GLPC, and was continued until the consumption of **1** was confirmed. Then, the mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL X 3). The combined organic layer was washed with aq $NaHCO_3$ and aq $Na_2S_2O_3$, and dried over $MgSO_4$. After concentration under reduced pressure, **2** was isolated by column chromatography.

*4.2.1. 1-(Fluoromethoxy)-4-isopropylbenzene (**2a**)*

IR (neat) 2962, 1512, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.69 (d, J = 54.9 Hz, 2H, FC$\underline{H_2}$OAr), 2.94-2.83 (m, 1H), 1.23 (d, J = 6.8 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –148.49 (t, J = 55.5 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 154.9 (d, $^3J_{C\text{-}F}$ = 2.9 Hz), 144.0, 127.5 (d, $^5J_{C\text{-}F}$ = 1.9 Hz, 2C), 116.5 (d, $^4J_{C\text{-}F}$ = 1.4 Hz, 2C), 101.0 (d, $^1J_{C\text{-}F}$ = 218.4 Hz), 33.4, 24.1(2C); HRMS (EI) calcd for $C_{10}H_{13}FO$ 168.09504, found 168.09516.

*1-(Fluoromethoxy)-1,1'-biphenyl (**2b**)*

White solid. Mp 72-74 ˚C; IR (KBr) 1487, 1242, 950, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.7 Hz, 4H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 5.76 (d, *J* = 54.5 Hz, 2H, FC$\underline{H_2}$OAr); ^{19}F NMR (376 MHz, $CDCl_3$) δ –149.06 (t, *J* = 54.6 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 156.2 (d, $^{3}J_{C-F}$ = 2.9 Hz), 140.3, 136.5, 128.75 (2C), 128.3 (2C), 127.1, 126.8 (2C), 116.8 (d, $^{4}J_{C-F}$ = 1.7 Hz, 2C), 100.7 (d, $^{1}J_{C-F}$ = 218.6 Hz); HRMS (EI) calcd for $C_{13}H_{11}FO$ 202.07939, found 202.07963.

*1-(Fluoromethoxy)-4-nitrobenzene (**2c**)*

White solid. Mp 69-70 ˚C; IR (KBr) 3087, 1597, 1348, 1075, 975, 850 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.2 Hz, 2H), 7.18 (d, *J* = 9.1 Hz, 2H), 5.80 (d, *J* = 53.4 Hz, 2H, FC$\underline{H_2}$OAr); ^{19}F NMR (376 MHz, $CDCl_3$) δ –152.05 (t, *J* = 53.8 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 161.1 (d, $^{3}J_{C-F}$ = 2.9 Hz), 143.4, 125.9 (2C), 116.4 (d, $^{4}J_{C-F}$ = 1.7 Hz, 2C), 99.6 (d, $^{1}J_{C-F}$ = 222.2 Hz); HRMS (EI) calcd for $C_7H_6FNO_3$ 171.0332, found 171.0346.

*1-(Fluoromethoxy)-4-bromobenzene (**2d**)*

IR (neat) 2925, 1490, 1230, 981 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.68 (d, *J* = 54.4 Hz, 2H, FC$\underline{H_2}$OAr); ^{19}F NMR (376 MHz, $CDCl_3$) δ –149.74 (t, *J* = 53.7 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 155.8, 132.6 (2C), 118.5 (d, $^{4}J_{C-F}$ = 1.9 Hz, 2C), 116.1, 100.6 (d, $^{1}J_{C-F}$ = 220.0 Hz); HRMS (EI) calcd for C_7H_6BrFO 203.95917, found 203.95861.

*Ethyl 4-(fluoromethoxy)benzoate (**2e**)*

IR (neat) 2984, 1715, 1608, 1510, 1277, 1233, 1172, 985 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 5.77 (d, *J* = 54.0 Hz, 2H, FC*H*$_2$OAr), 4.37 (q, *J* = 7.2 Hz, 2H, $CH_3C\underline{H_2}OCO$), 1.39 (t, *J* = 7.2 Hz, 3H, *C*$H_3$$CH_2OCO$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –150.76 (t, *J* = 54.7 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 166.0, 160.0 (d, $^{3}J_{C-F}$ = 3.6 Hz), 131.6 (2C), 125.6 (2C), 115.8, 99.9 (d, $^{1}J_{C-F}$ = 220.3 Hz), 60.9, 14.3; HRMS (EI) calcd for $C_{10}H_{11}FO_3$ 198.06922, found 198.06898.

*1-(Fluoromethoxy)-4-pentyloxybenzene (**2f**)*

IR (neat) 2956, 1509, 1214, 1098, 973, 829 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 9.1 Hz, 2H), 6.84 (d, *J* = 9.1 Hz, 2H), 5.64 (d, *J* = 55.2 Hz, 2H, F*C*$\underline{H_2}$OAr), 3.92 (t, *J* = 6.5 Hz, 2H, $CH_2C\underline{H_2}OAr$), 1.81-1.74 (m, 1H), 1.47-1.35 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –147.79 (t, *J* = 54.6 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 155.4, 150.7 (d, $^{3}J_{C-F}$ = 3.9 Hz), 118.0, 115.3, 101.7 (d, $^{1}J_{C-F}$ = 214.7 Hz), 68.4, 29.0, 28.1, 22.4, 14.0; HRMS (EI) calcd for $C_{12}H_{17}FO$ 212.12126, found 212.12071.

*N-Benzylidene-4-(fluoromethoxy)aniline (**2g**)*

White solid. Mp 56-58 ˚C; IR (KBr) 2940, 2876, 1623, 1508, 1225, 1093, 955, 835, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H, Ph-C$\underline{H}$=N-), 7.91-7.88 (m, 2H), 7.49-7.45 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 5.72 (d, *J* = 54.8 Hz, 2H, FC$\underline{H_2}$OAr); ^{19}F NMR (376 MHz, $CDCl_3$) δ –148.46 (t, *J* = 52.9 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 159.7, 155.2 (d, $^{3}J_{C-F}$ = 2.9 Hz), 147.6, 136.2, 131.3, 128.8 (2C), 128.7 (2C), 122.2 (2C), 117.3 (2C), 101.0 (d, $^{1}J_{C-F}$ = 218.4 Hz); HRMS (EI) calcd

for $C_{14}H_{12}FNO$ 229.09029, found 229.08960.

*Fluoromethyl 4-(tert-butyl)benzoate (**2h**)*

IR (neat) 2966, 1726, 1264, 1083, 968 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 5.95 (d, *J* = 50.8 Hz, 2H, FC*H*$_2$OCOAr), 1.35 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –158.06 (t, *J* = 51.9 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 164.7, 157.8, 130.1 (2C), 125.7, 125.6 (2C), 93.7 (d, $^{1}J_{C\text{-}F}$ = 219.9 Hz), 35.2, 31.0 (3C); HRMS (EI) calcd for $C_{12}H_{15}FO_2$ 210.10561, found 210.10506.

*1-(Fluoromethoxy)decane (**2i**)*

IR (neat) 2928, 1467, 1174, 958 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (d, *J* = 56.7 Hz, 2H, FC*H*$_2$OR), 3.71 (dt, *J* = 6.7, 1.9 Hz, 2H, FCH_2OC*H*$_2$R), 1.66-1.59 (m, 2H), 1.35-1.26 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –150.54 (t, *J* = 56.4 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 103.8 (d, $^{1}J_{C\text{-}F}$ = 211.9 Hz), 70.8, 31.9, 29.6-29.3 (5C), 25.9, 22.7, 14.0; HRMS (APCI) calcd for (M^{+}-F) $C_{11}H_{23}O$ 171.17434, found 171.17451.

*Methyl 2-tert-butoxycarbonylamino-3-(4-fluoromethoxyphenyl)propionate (**2j**)*

White solid. Mp 50-53 ˚C; IR (KBr) 3349, 2979, 1738, 1690, 1529, 1290, 1227, 1167, 984 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 5.69 (d, *J* = 54.7 Hz, 2H, FC*H*$_2$OAr), 4.97 (d, *J* = 7.8 Hz, 1H, N*H*), 4.59-4.54 (m, 1H), 3.72 (s, 3H, C*H*$_3$OCO), 3.11-2.99 (m, 2H), 1.42 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –149.05 (t, *J* = 55.5 Hz, 1F); ^{13}C NMR (100MHz, $CDCl_3$) δ 172.2, 155.8 (d, $^{3}J_{C\text{-}F}$ = 2.9 Hz), 155.0, 131.1, 130.5 (2C), 116.7 (2C), 100.7 (d, $^{1}J_{C\text{-}F}$ = 218.4 Hz), 79.9,

54.4, 52.2, 37.5, 28.2 (3C); HRMS (EI) calcd for $C_{16}H_{22}FNO_5$ 327.1476, found 327.1459.

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