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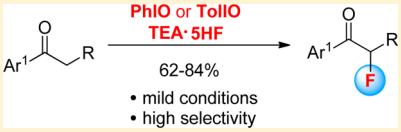
Hypervalent Iodine-Promoted α-Fluorination of Acetophenone Derivatives with a Triethylamine·HF Complex

Tsugio Kitamura,* Kensuke Muta, and Kazutaka Muta

Department of Chemistry and Applied Chemistry, Graduate School of Science and Engineering, Saga University, Honjo-machi, Saga 840-8502, Japan

Supporting Information

ABSTRACT: The direct fluorination reaction of acetophenone using iodosylarenes and TEA·5HF was conducted under mild conditions except for use of a HF reagent. The fluorination reaction was applied to acetophenone derivatives, acetonaphthones, benzyl phenyl ketone, propiophenone, butyrophenone, 1-indanone, and phenacyl chloride, giving selectively the corresponding α-fluoroketone derivatives in good yields.

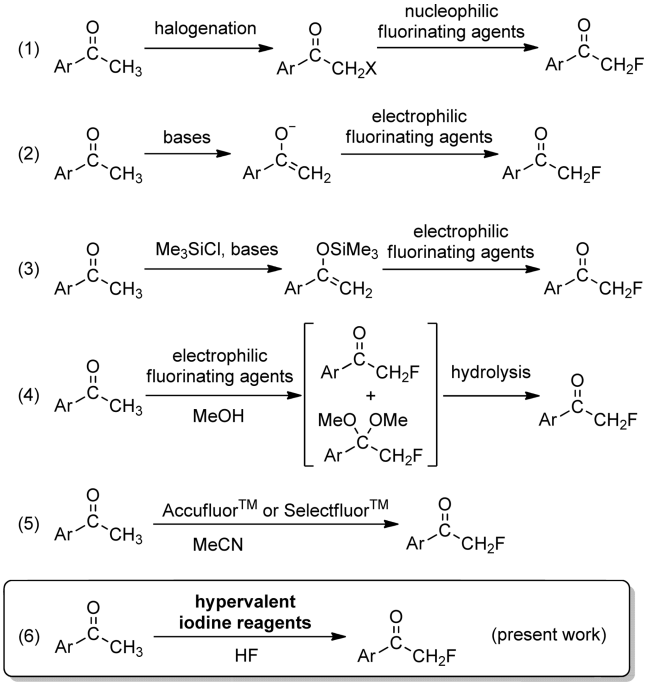


It is well-recognized that organofluorine compounds are important synthetic intermediates as agricultural chemicals or drugs.[1] Although fluorination reactions preparing such organofluorine compounds have been conducted by replacing hydrogen or a suitable group with a molecular fluorine or other electrophilic fluorinating reagents, there still remain drawbacks, such as possibility of explosion due to instability, difficulty of handling, and requirement of specific apparatus. Therefore, the development of safe and convenient fluorination reactions is still a challenging subject in this area. Use of hypervalent iodine compounds as fluorinating reagents might be one of the solutions for the drawbacks because they are safer and greener reagents.[2]

Recently, hypervalent iodine compounds have been widely used in organic synthesis.[3] They show synthetically useful characteristics, such as mild oxidizing nature, chemical behaviors similar to transition metals, and an excellent leaving ability of hypervalent iodine. For example, α-functionalization of carbonyl compounds using hypervalent iodine reagents occurs easily under mild conditions and has been demonstrated.[3b] However, the α-fluorination reaction of carbonyl compounds using hypervalent iodine reagents is limited to only a few examples. *p*-(Difluoroiodo)toluene was shown to be an efficient fluorinating reagent in the fluorination reactions of 1,3-dicarbonyl compounds and applied to the fluorination of β-ketoesters, β-ketoamides, and β-diketones.[4] However, this method was not applied to simple monocarbonyl compounds. Therefore, the fluorination of monocarbonyl compounds was conducted by a two-step process via the corresponding silyl enol ethers.[5] Recently, we reported a convenient fluorination reaction of 1,3-dicarbonyl compounds with iodosylbenzene (PhIO) and hydrofluoric acid.[6] This method involves direct use of commercially available hydrofluoric acid as the fluorine source. However, this method was limited to 1,3-dicarbonyl compounds and could not be applied to monocarbonyl compounds. The fluorination reaction of monocarbonyl compounds with hypervalent iodine reagents such as difluoroiodotoluene and iodosylbenzene has not been successful until now.

Several methods for fluorination of monocarbonyl compounds without hypervalent iodine compounds have been reported so far, as shown in Scheme 1. These methods involve (1) a two-step process consisting of halogenations and substitution,[7] (2) a two-step process including generation of enolate anions and electrophilic fluorination,[8] (3) a two-step process including transformation to silyl enol ethers and electrophilic fluorination,[5,7g,9] (4) a direct process requiring hydrolysis of acetals,[7g,10] and (5) a direct process using 1-

Scheme 1. Representative Methods for Synthesis of α-Fluoroacetophenones



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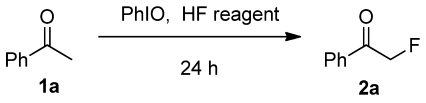
chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor) or 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Accufluor).[11] The methods 1−4 need two steps to obtain the desired monofluorinated ketones. Although the method 5 is a desired one-step reaction, an expensive fluorinating reagent is required. In the fluorination reaction of monocarbonyl compounds, therefore, there still exist drawbacks that should be solved.

Although the fluorination reaction using PhIO/hydrofluoric acid[6] was convenient, this method could not be applied to fluorination of monocarbonyl compounds. In the fluorination reaction using PhIO/hydrofluoric acid, the existence of water was considered to reduce nucleophilicity of fluoride ion and inhibit the fluorination reaction. Thus, we conducted fluorination of acetophenone derivatives using a triethylamine·HF complex as a fluorine source instead of aqueous hydrofluoric acid and found that the fluorination reaction proceeded efficiently to give α-fluoroacetophenones in good yields. Here, we wish to report for the first time direct fluorination of monocarbonyl compounds using hypervalent iodine reagents (Scheme 1, (6)).

To confirm whether the previous fluorination method using iodosylbenzene/hydrofluoric acid is effective for fluorination of acetophenone derivatives, we first examined the reaction of acetophenone (**1a**) with PhIO and hydrofluoric acid. When **1a** (1 mmol) was reacted with a mixture of PhIO (1.2 mmol) and aqueous HF (55% HF, 10 mmol) in dichloromethane (DCM) at 40 °C for 24 h, 2-fluoroacetophenone (**2a**) was formed only in 7% yield (Table 1, entry 1). Most of the starting material was recovered. This result showed that aqueous HF was not suitable for this fluorination reaction. Then, we conducted the fluorination reaction using anhydrous TEA·3HF as a HF reagent. Surprisingly, the reaction of **1a** with PhIO (1 mmol) and TEA·3HF (4.5 mmol) in DCM at 40 °C for 24 h gave **2a** in 45% yield (entry 2). Next, we conducted the fluorination reaction using TEA·5HF. The fluorination reaction with TEA·5HF (4 mmol) and PhIO (1.2 mmol) in DCM yielded **2a** in 60% yield (entry 3). Moreover, elevating the temperature to 60 °C in 1,2-dichloroethane (DCE) increased the yield of **2a** to 79% (entry 4). Decreasing the quantity of TEA·5HF to 2 mmol, the yield was not improved and **2a** was obtained in 64% yield (entry 5). The present reaction afforded monofluorinated product **2a** selectively. To confirm the selective formation of **2a**, we re-examined the fluorination reaction of **1a** using the conditions of entry 4. In the ^{1}H NMR of the crude product mixture, the presence of iodobenzene was observed in almost quantitative yield but 2,2-difluoroacetophenone was not observed around 6.3 ppm as recognizable peaks. In addition, it was difficult to observe the signals of 2,2-difluoroacetophenone around −123 ppm due to the presence of impurities. Although a small amount of 2,2-difluoroacetophenone was obtained by column chromatography on silica gel, the yield was less than 1%.

Table 1. Optimization of Fluorination of 1a with PhIO/HF Reagents[a]



entry	HF reagent (mmol)	solvent	temp (°C)	yield (%)[b]
1	55% HF (10 mmol)	DCM	40	7
2	TEA·3HF (4.5 mmol)	DCM	40	45
3	TEA·5HF (4 mmol)	DCM	40	60
4	TEA·5HF (4 mmol)	DCE	60	79
5	TEA·5HF (2 mmol)	DCE	60	64 (46)[c]

[a]Conditions: **1a** (1 mmol), PhIO (1.2 mmol), a HF reagent, solvent (2 mL), 24 h. [b]Determined by ^{1}H NMR using an internal standard. [c]Isolated yield.

With the optimized conditions of the fluorination reaction of **1a** in hand, we examined the fluorination of 2-acetylnaphthalene (**1b**). The reaction of **1b** with PhIO/TEA·5HF in DCE at 60 °C for 24 h gave the desired fluorinated product, 2-(2′-fluoroacetyl)naphthalene (**2b**), in 71% yield (Table 2, entry 1). Before further examination of the scope of the substrates, we conducted the fluorination reaction of **1b** with several iodosylarenes because we had observed very recently that *ortho*-substituted iodosylarenes efficiently promoted the fluorination reaction of 1,3-dicarbonyl compounds.[6b] However, the reaction of **1b** with *ortho*-iodosyltoluene (2-MeC_6H_4IO)/TEA·5HF resulted in a poor yield of **2b** (32%) (Table 2, entry 2). In the case of monocarbonyl compounds, the reactivity of fluorinating reagents may be further reduced by the steric hindrance because of a low concentration of an enol form compared with 1,3-dicarbonyl compounds.[12] Then, we screened the fluorination reaction about several *para*-substituted iodosylarenes. The fluorination reaction of **1b** using *p*-iodosyltoluene (4-MeC_6H_4IO), *p*-chloloiodosylbenzene (4-ClC_6H_4IO), and *p*-iodosyl(trifluoromethyl)benzene (4-$CF_3C_6H_4$IO) gave the fluorinated product **2b** in 73, 69, and 72% yields, respectively (Table 2, entries 3−5). This result suggests that the *para* substituent of iodosylarenes does not significantly affect the fluorination of **1b**. Thus, we decided to use PhIO and *p*-iodosyltoluene since they were prepared more easily than others. Using the optimized conditions, we furthermore examined the fluorination reaction of monocarbonyl compounds, such as 1-acetylnaphthalene (**1c**), acetophenone derivatives **1d**−**1f**, benzyl phenyl ketone (**1g**), propiophenone (**1h**), butyrophenone (**1i**), 1-indanone (**1j**), and 2-chloroacetophenone (**1k**).

The fluorination reaction of 1-acetylnaphthalene (**1c**) was conducted by using a fluorinating reagent of ArIO (Ar = Ph and *p*-Tol) and TEA·5HF in DCE at 60 °C for 24 h. As expected, 1-(2-fluoroacetyl)naphthalene (**2c**) was obtained in 82 and 73% yields, respectively (entries 6 and 7). Similarly, the fluorination of *p*-substituted acetophenones, such as *p*-methylacetophenone (**1d**), *p*-chloroacetophenone (**1e**), and *p*-methoxyacetophenone (**1f**), afforded the desired α-fluoroacetophenone derivatives (**2d**−**2f**) in 67−84% yields (entries 8−13). The present hypervalent iodine reagent composed of ArIO and TEA·5HF is found to be an efficient fluorinating reagent to the acetophenone derivatives.

Next, we examined the fluorination reaction of α-substituted acetophenone derivatives. When the fluorination of benzyl phenyl ketone (**1g**), propiophenone (**1h**), and butyrophenone (**1i**) was conducted under the same conditions, the desired α-fluorinated products **2g**−**2i** were obtained in 70−76% yields (entries 14−19). In addition, the fluorination of 1-indanone (**1j**) and α-chloroacetophenone (**1k**) gave 2-fluororo-1-indanone (**2j**) and 1-chloro-1-fluoroacetophenone (**2k**) in 58% yields, respectively.

This fluorination reaction is considered to proceed as follows (Scheme 2). First, ArIO reacts with HF to generate $ArIF_2$.[6]

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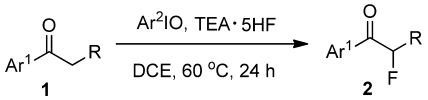
Table 2. Scope of Monocarbonyl Compounds 1 in the Fluorination Reactions[a,b,c,d]

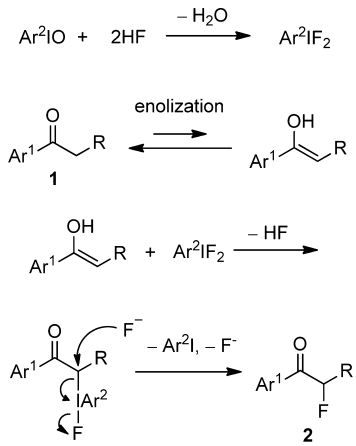


Entry	Ar^2IO	Product **2**	Yield (%)[b,c]
1	PhIO	**2b**	71
2	2-MeC_6H_4IO		32[d]
3	4-MeC_6H_4IO		73 (64)
4	4-ClC_6H_4IO		69
5	4-$CF_3C_6H_4IO$		72
6	PhIO	**2c**	82 (69)
7	4-MeC_6H_4IO		73
8	PhIO	**2d**	78 (59)
9	4-MeC_6H_4IO		74
10	PhIO	**2e**	84 (67)
11	4-MeC_6H_4IO		76
12	PhIO	**2f**	70
13	4-MeC_6H_4IO		(67)
14	PhIO	**2g**	72
15	4-MeC_6H_4IO		76 (75)
16	PhIO	**2h**	72
17	4-MeC_6H_4IO		(70)
18	PhIO	**2i**	72
19	4-MeC_6H_4IO		(70)
20	PhIO	**2j**	(66)
21	PhIO	**2k**	(62)

[a]Conditions: **1** (1 mmol), Ar^2IO (1.2 mmol), TEA·5HF (4 mmol), and DCE (2 mL) at 60 °C for 24 h. [b]Determined by ^1H NMR using an internal standard. [c]Values in parentheses represent isolated yields. [d]At 40 °C.

Acetophenones **1** undergo enolization to form the corresponding enols. The enolization is considered to be promoted by HF. The resulting enols react with the in situ-generated $ArIF_2$ to afford α-(phenyliodonio)acetophenones, which undergo substitution by fluoride ion to give α-fluoroacetophenones **2**. Compared with the reaction with aqueous HF as a fluorine source (Table 1, entry 1), the present reaction using TEA·5HF complex gives α-fluorinated products in higher yields. This result suggests that the substitution by fluoride ion become more efficient due to the absence of water in the present reaction.

Scheme 2. A Possible Mechanism for Fluorination of Acetophenones with ArIO/TEA·5HF



As mentioned above, it turned out that the iodosylarene/TEA·5HF reagent is useful to the fluorination reaction of various acetophenone derivatives. Interestingly, the present fluorination reaction does not afford double fluorination products but monofluorinated products selectively. Since there are reports that difluorinated products are formed by the fluorination reaction of enolate ions or enamines,[13] the present reaction affording monofluorinated products is synthetically significant. The selective formation of monofluorinated products can be understood by different reactivity between an enol and its fluorinated enol. The present fluorination proceeds via enols. It is considered that the inductive effect of fluorine lowers the reactivity of the enol form of the monofluorinated ketones and retards the further fluorination of monofluorinated ketones.

In conclusion, we have developed a hypervalent iodine-promoted direct fluorination reaction of acetophenone derivatives for the first time. The present fluorination reaction proceeds under mild conditions using an iodosylarene and TEA·5HF and gives α-fluoroacetophenone derivatives in good yields. The use of easily available iodosylarenes and a safer TEA·5HF complex serves as a greener and safer reaction in the fluorination reaction. The fluorination reaction can be applied to α-substituted acetophenes and indanone in addition to acetophenone derivatives. Moreover, the chlorine substituent at the α-position is tolerable under the reaction conditions and the fluorination reaction of the substrates with a chlorine functionality is possible. Because of good yields, high selectivity of monofluorination, and a convenient operation, the present fluorination reaction will attract much attention of many organic chemists.

EXPERIMENTAL SECTION

General Procedure for Preparation of α-Fluoroacetophenone Derivatives. To a 15 mL Teflon test tube were placed an iodosylarene (1.2 mmol), TEA·5HF (4 mmol), and DCE (1 mL), and the tube was capped with a rubber septum. After stirring for 15 min at room temperature, an acetophenone derivative (1 mmol) and DCE (1 mL) were added, and the mixture was stirred at 60 °C for 24 h. The reaction mixture was quenched with a saturated $NaHCO_3$ solution and extracted with DCM (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The product was separated by column chromatography on silica gel (eluent: hexane/DCM).

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2-Fluoro-1-phenylethanone (2a):[14] Isolated yield (Table 1, entry 5), 0.0635 g (64%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.54 (d, J = 47 Hz, 2H), 7.48−7.91 (m, 5H); ^{19}F NMR (283 MHz, $CDCl_3$) δ −231.84 (t, J = 47 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.5 (d, J = 181 Hz), 127.8 (d, J = 2.5 Hz), 128.9, 133.7, 134.1, 193.4 (d, J = 15.5 Hz).

2-Fluoro-1-(2-naphthyl)ethanone (2b):[15] Isolated yield (Table 2, entry 3), 0.120 g (64%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (d, J = 47 Hz, 2H), 7.56−7.67 (m, 2H), 7.88−7.98 (m, 4H), 8.41 (s, 1H); ^{19}F NMR (283 MHz, $CDCl_3$) δ −230.98 (t, J = 47 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.6 (d, J = 181 Hz), 123.1 (d, J = 1.9 Hz), 127.1, 127.84, 128.86, 129.0, 129.6, 129.8 (d, J = 3.2 Hz), 131.0, 132.3, 135.9, 193.3 (d, J = 15.5 Hz).

2-Fluoro-1-(1-naphthyl)ethanone (2c):.[10,14] Isolated yield (Table 2, entry 6), 0.130 g (69%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (d, J = 47 Hz, 2H), 7.50−8.08 (m, 6H), 8.70 (d, J = 8.4 Hz, 1H); ^{19}F NMR (283 MHz, $CDCl_3$) δ −226.20 (t, J = 47 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.9 (d, J = 184 Hz), 124.2, 125.4, 126.8, 128.08, 128.13, 128.6, 130.3, 131.18, 131.20, 134.0, 196.9 (d, J = 16.7 Hz).

2-Fluoro-1-(4-methylphenyl)ethanone (2d):[14] Isolated yield (Table 2, entry 8), 0.0898 g (59%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 5.50 (d, J = 47 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H); ^{19}F NMR (283 MHz, $CDCl_3$) δ −231.60 (t, J = 47 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 83.5 (d, J = 181 Hz), 127.9 (d, J = 2.5 Hz), 129.6, 131.2, 145.1, 193.0 (d, J = 15.5 Hz).

1-(4-Chlorophenyl)-2-fluoroethanone (2e):[14] Isolated yield (Table 2, entry 10), 0.116 g (67%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (d, J = 47 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H); ^{19}F NMR (283 MHz, $CDCl_3$) δ 230.91 (t, J = 47 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.6 (d, J = 182 Hz), 129.3, 129.4 (d, J = 3.1 Hz), 132.0 (d, J = 1.3 Hz), 140.7, 192.5 (d, J = 16.1 Hz).

2-Fluoro-1-(4-methoxyphenyl)ethanone (2f):[16] Isolated yield (Table 2, entry 13), 0.113 g (67%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93 (s, 3H), 5.51 (d, J = 47 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 7.93 (d, J = 8.7 Hz, 2H); ^{19}F NMR (283 MHz, $CDCl_3$) δ −230.98 (t, J = 47 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.5, 83.5 (d, J = 180 Hz), 114.1, 126.8 (d, J = 1.2 Hz), 130.3 (d, J = 3.1 Hz), 164.2, 191.9 (d, J = 15.5 Hz).

2-Fluoro-1,2-diphenylethanone (2g):[16] Isolated yield (Table 2, entry 15), 0.120 g (75%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (1d, J = 49 Hz, 1H), 7.38−7.68 (m, 8H), 7.93−7.96 (m, 2H); ^{19}F NMR (283 MHz, $CDCl_3$) δ −177.04 (d, J = 49 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 93.9 (d, J = 184 Hz), 127.4 (d, J = 5.6 Hz), 128.7, 129.04, 129.07 (d, J = 1.2 Hz), 129.6 (d, J = 2.5 Hz), 133.7, 134.0, 134.2 (d, J = 19.7 Hz), 194.2 (d, J = 21.7 Hz).

2-Fluoro-1-phenyl-1-propanone (2h):[17] Isolated yield (Table 2, entry 17), 0.107 g (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (dd, J = 6.8, 24 Hz, 3H), 5.69 (dq, J = 6.8, 48 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −181.52 (dq, J = 24, 48 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4 (d, J = 22.4 Hz), 90.3 (d, J = 178.8 Hz), 128.7, 129.0 (d, J = 3.9 Hz), 133.8, 134.0, 197.1 (d, J = 18.6 Hz).

2-Fluoro-1-phenyl-1-butanone (2i):[18] Isolated yield (Table 2, entry 19), 0.116 g (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, J = 7.6 Hz, 3H), 1.91−2.14 (m, 2H), 5.51 (ddd, J = 4.8, 7.6, 49 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −190.97 (ddd, J = 23, 27, 49 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.1 (d, J = 3.9 Hz), 26.1 (d, J = 21.7 Hz), 94.8 (d, J 182.7 Hz), 128.7, 128.8 (d, J = 11.4 Hz), 133.7, 134.4, 196.8 (d, J = 19.4 Hz).

2-Fluoro-1-indanone (2j):.[17,19] Isolated yield (Table 2, entry 20), 0.0991 g (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17−3.30 (m, 1H), 3.59−3.67 (m, 1H), 5.28 (ddd, J = 4.4, 7.8, 51 Hz, 1H), 7.42−7.48 (m, 2H), 7.67 (t, J = 8 Hz, 1H), 7.81 (d, J = 8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −194.06 (ddd, J = 8, 23, 51 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.4 (d, J = 21.6 Hz), 90.5 (d, J = 189.7 Hz), 124.7, 126.8, 128.4, 133.86, 136.3, 149.6, 199.9 (d, J = 14.7 Hz).

2-Chloro-2-fluoro-1-phenylethanone (2k):[20] Isolated yield (Table 2, entry 21), 0.107 g (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, J = 50, 1H), 7.53 (t, J = 8 Hz, 2H), 7.67 (t, J = 8 Hz, 1H), 8.08 (d, J = 8 Hz, 2H); ^{19}F NMR (376 Hz, $CDCl_3$) δ −146.52 (d, J = 50 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 93.87, 96.43, 128.91, 129.63, 129.66, 131.12, 134.74, 187.20, 187.42.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{19}F, and ^{13}C NMR spectra of products **2a**−**2k**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel/Fax: 0952-28-8550. E-mail: kitamura@cc.saga-u.ac.jp.

Notes

The authors declare no competing financial interest.

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