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One-pot synthesis of dialkyldifluoromethane and alkyldifluoromethyl iodides from the reaction of difluorodiiodomethane with alkenes in sulphinatodehalogenation systems

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Abstract

The reaction of difluorodiiodomethane (CF_2I_2) with alkenes ($RCH{=}CH_2$), initiated by $Na_2S_2O_4/NaHCO_3$, is described. When the reaction is carried out at low temperature (5–8 °C), the monoadducts $RCHICH_2CF_2I$ are produced, whereas at 20 °C bis-adducts $(RCH_2CH_2)CF_2$ are the only products. The results are rationalized in terms of a single electron transfer mechanism. © 1997 Elsevier Science S.A.

Keywords: Addition; Alkenes; Alkyldifluoromethyl iodides; Dialkyldifluoromethane; Difluorodiiodomethane; Electron transfer; Temperature

1. Introduction

Profound changes in the biological effects of organic compounds are observed when the hydrogen atoms are replaced by fluorines [1]. Very recently, it has been documented that the introduction of the difluoromethylene functionality into organic compounds may enhance the biological stability and may prove to be particularly significant as a replacement for oxygen at biochemically labile positions [2].

Previous reports on the introduction of the difluoromethylene group have focused on the Reformatsky reaction using halodifluoromethylated compounds as starting materials [3]. The fluorination of the carbonyl group with Diethylaminosulphurtrifluoride (DAST) has also been documented [4]. All the methods suffer from either harsh conditions or toxic reagents. It would be of interest to find a more suitable method for the preparation of difluoromethylene-functionalized compounds.

A previous report on the synthesis of bromodifluoromethylated compounds has shown that the bromodifluoromethyl group is not sufficiently active to proceed to further addition [5]

$$CF_2Br_2 + CH_2{=}CHR \xrightarrow[CH_3CN/H_2O]{Na_2S_2O_4/NaHCO_3} BrCF_2CH_2CHBrR \nrightarrow (RCHBrCH_2)_2CF_2$$

The corresponding iododifluoromethylated compound may proceed to further addition under suitable conditions, because it is well known that the perfluoroalkyl iodides are more reactive than the corresponding bromides.

Ten years ago, the benzoyl peroxide-induced addition reaction of CF_2I_2 to alkenes was developed [6], but only the iododifluoromethylated compounds were obtained even in the presence of excess alkenes

$$CF_2I_2 + RCH{=}CH_2 \xrightarrow{(C_6H_5COO)_2} ICF_2CH_2CHIR$$

Since a good, convenient preparation method of difluorodiiodomethane (1) has been found in our laboratory [7], we decided to investigate its reaction with alkenes in the hope of finding a simple and efficient approach to difluoromethylene-functionalized alkanes. Very recently, we have found that metals, such as iron or zinc, can initiate the addition reaction very easily [8]. However, these methods only result in the formation of monoadducts, which will not react further with another equivalent of alkenes to give difluoromethylene-functionalized alkanes. Therefore we aimed to find an efficient initiator for 1 to afford bis-adducts, dialkyldifluoromethane, in one pot.

Sulphinatodehalogenation is a well-known method of initiating the addition of perfluoroalkyl iodides to alkenes or alkynes [9]. This method is also applicable to the reaction of iododifluoromethane with alkenes and alkynes [10]

$$HCF_2I + RCH{=}CH_2 \xrightarrow{Na_2S_2O_4/NaHCO_3} HCF_2CH_2CHIR$$

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This success encouraged us to investigate the behaviour of difluorodiiodomethane in such a system.

2. Results and discussion

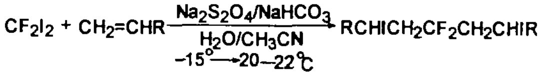
Difluorodiiodomethane (5 mmol) was added dropwise to a mixture of alkenes (15 mmol), $Na_2S_2O_4$ (5 mmol) and $NaHCO_3$ (5 mmol) in acetonitrile (5 ml) and water (2 ml) at − 15 °C. After the addition, the solution was warmed to 20–25 °C and kept at this temperature for 3 h. Dialkyldifluoromethanes **3** were obtained after simple work-up (Scheme 1).

As the reaction was carried out in a two-phase solution (acetonitrile and aqueous layers), the yield of the water-soluble substrate $CH_2{=}CHCH_2OH$ (**2f**) was very low (entry 7). The addition of potassium chloride to the reaction mixture reduced the solubility of $CH_2{=}CHCH_2OH$ in water and, as a result, the yield of the adduct was increased strongly (entry 8). Functional groups, such as alkyl, ester and ether, can all be tolerated in the reaction, resulting in the corresponding difluoromethane derivatives $(RCHICH_2)_2CF_2$. In the reaction of **1** with diallyl ether, the sole product was ditetrahydrofuran derivative.

The ratio of acetonitrile to water played an important role. If the ratio was less than unity, the adducts decreased and $CF_2{=}CF_2$ was mainly formed. The presence of a catalytic amount of water in acetonitrile slowed down the reaction significantly. The optimum ratio of CH_3CN to H_2O was 2.5 : 1.

The temperature shows an interesting and significant influence on the reaction. When difluorodiiodomethane was added dropwise at 20 °C, tetrafluoroethylene ($CF_2{=}CF_2$) was obtained instead of adducts (entry 2). On controlling the addition temperature at − 15 °C and then letting the reaction proceed at 20 °C for 3–4 h, bis-adducts **3** were the only product (Table 1). However, to our surprise, on addition at − 15 °C, followed by reaction at 5–8 °C for 1–1.5 h, solely monoadducts, alkyldifluoromethyl iodide **4**, resulted (Scheme 2); no bis-adducts **3** appeared even with a longer reaction time (24 h) at the same temperature (Table 2, entries 3 and 4).

Comparing Table 1 and Table 2, we can see that the formation of the products is very sensitive to the reaction temperature.



$$CF_2I_2 + CH_2{=}CHR \xrightarrow[H_2O/CH_3CN,\ -15^\circ \to 20\text{–}22^\circ C]{Na_2S_2O_4/NaHCO_3} RCHICH_2CF_2CH_2CHIR$$

1 2 3

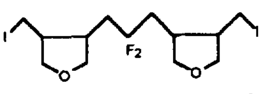
2 R=$CH_2OCH_2CH{=}CH_2$ (a)
$(CH_2)_4CH_3$ (b)
$(CH_2)_3CH_3$ (c)
CH_2OCOCH_3 (d)
$CH_2OC_2H_5$ (e)
CH_2OH (f)
$SiMe_3$ (g)

Scheme 1.

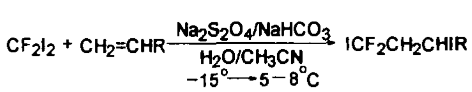
Table 1
The reaction of **1** with **2** in CH_3CN–H_2O (2.5 : 1, v/v) in the presence of $Na_2S_2O_4/NaHCO_3$[a]

Entry	2	t (h)	Product (%)[b]
1	**2a**	3	**3a**[c] (81)
2	**2a**[d]	5 min	$CF_2{=}CF_2$ (97)
3	**2b**	3	**3b** (74)
4	**2c**	3	**3c** (78)
5	**2d**	4	**3d** (76)
6	**2e**	4	**3e** (75)
7	**2f**	4	**3f** (20)
8	**2f**[e]	4	**3f** (52)
9	**2g**	4	**3g** (68)

[a] **1** : **2** : $Na_2S_2O_4$: $NaHCO_3$ = 1 : 3 : 1 : 1; the addition temperature was − 15 °C; the reaction was continued at 20–22 °C unless otherwise noted.
[b] Isolated yields based on **1**.
[c] **3a**:



[d] The reaction was continued at 20 °C.
[e] Brine was used instead of water.



$$CF_2I_2 + CH_2{=}CHR \xrightarrow[H_2O/CH_3CN,\ -15^\circ \to 5\text{–}8^\circ C]{Na_2S_2O_4/NaHCO_3} ICF_2CH_2CHIR$$

1 2 4

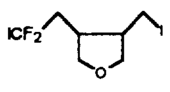
2 R=$CH_2OCH_2CH{=}CH_2$ (a)
$(CH_2)_4CH_3$ (b)
$(CH_2)_3CH_3$ (c)
CH_2OCOCH_3 (d)
$CH_2OC_2H_5$ (e)
CH_2OH (f)
$SiMe_3$ (g)

Scheme 2.

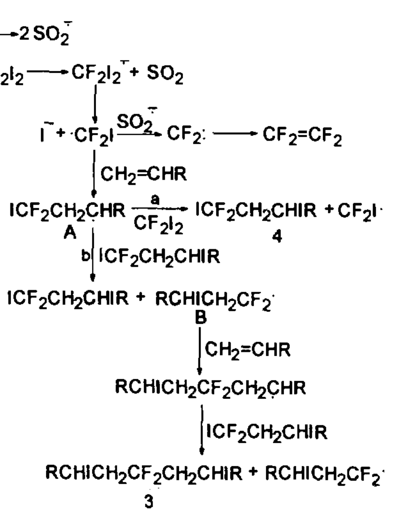
Table 2
Reaction of CF_2I_2 with alkenes initiated by $Na_2S_2O_4/NaHCO_3$ in CH_3CN–H_2O (2.5 : 1, v/v) at 5–8 °C[a]

Entry	2	t (h)	4 (%)[c]
1	**2a**	1	71[b]
2	**2b**	1	68
3	**2c**	1	66
4	**2c**	24	66
5	**2d**	1.5	60
6	**2e**	1.5	64
7	**2f**	1	20
8	**2f**[d]	1	48
9	**2g**	1	52

[a] **1** : **2** : $Na_2S_2O_4$: $NaHCO_3$ = 1 : 3 : 1 : 1.
[b] **4a**:



[c] Isolated yields based on **1**.
[d] Brine was used instead of water.



Scheme 3.

Similar to the reaction of perfluoroalkyl iodides with unsaturated alkenes or alkynes in sulphinatodehalogenation systems [11], a single electron transfer reaction mechanism was proposed (Scheme 3).

Difluorodiiodomethane accepts an electron from SO_2 to form the difluorodiiodomethane radical anion, which decomposes to the difluoroiodomethyl radical and iodide anion. At higher addition temperature (20 °C), the radical further reduces and undergoes α-elimination to give difluorocarbene and then tetrafluoroethene [8]. When the reaction proceeds at 5–8 °C, path a is probably the main procedure, resulting in monoadducts **4** through interaction of the intermediate **A** and **1**. However, when the reaction temperature is 20–22 °C, difluorodiiodomethane is rapidly consumed and the concentration of ICF_2CH_2CHIR is increased; high temperature may promote the iodine abstraction of intermediate **A** from monoadducts **4**, and therefore path b prevails. The resulting electrophilic intermediate **B** undergoes further addition to electron-rich alkenes and then removes an iodine from ICF_2CH_2CHIR to afford the bis-adducts **3** and **B**, constructing a radical chain reaction.

There is an apparent question about whether the monoadducts **4** can accept an electron from $SO_2^{\cdot-}$ to give intermediate **B**

$$ICF_2CH_2CHIR + SO_2^{\cdot-} \rightarrow SO_2 + {}^{\cdot}CF_2CH_2CHIR + I^-$$

However, this pathway is less likely for the following reasons: it was observed that the conversion of **4** to **3** required as long as 20 h at 20–22 °C using sodium dithionite as the initiator, while at the same temperature, 3 h was sufficient to complete the reaction of CF_2I_2 with alkenes to give **3** (Table 1). This indicates that the electron transfer reaction between $RCHICH_2CF_2I$ and $SO_2^{\cdot-}$ is not important in the production of intermediate **B**.

In conclusion, we have described a very convenient method for the preparation of alkyldifluoromethyl iodides or dialkyldifluoromethane-functionalized compounds depending on the reaction conditions: at lower reaction temperatures, monoadducts are produced, whereas at higher temperatures, bis-adducts are obtained.

3. Experimental section

Boiling (melting) points were uncorrected. IR spectra were recorded on a Shimadzu IR-440 spectrometer. ^{19}F nuclear magnetic resonance (NMR) spectra were obtained on a Varian EM-360 spectrometer (60 MHz) using trifluoroacetic acid as external standard, downfield shifts being designated as negative. ^1H NMR spectra were carried out on an FX-90Q (90 MHz) instrument with Me_4Si as internal standard. Mass spectra (MS) were measured on a Finnigan GC-MS-4021 mass spectrometer. All reactions were routinely monitored using thin layer chromatography (TLC) or ^{19}F NMR spectroscopy.

CF_2I_2 was prepared by a literature procedure [7]. $CH_2{=}CHCH_2OH$ was freshly distilled prior to use.

3.1. General procedure for the preparation of 3 exemplified by the reaction of 1 with diallyl ether

Difluorodiiodomethane (**1**) (1.5 g, 5 mmol) was added dropwise to a mixture of diallyl ether (2.94 g, 15 mmol), $Na_2S_2O_4$ (0.87 g, 5 mmol) and $NaHCO_3$ (0.41 g, 5 mmol) in CH_3CN (5 ml) and H_2O (2 ml) at −15 °C. After the addition was complete, the solution was warmed to 20 °C and stirred for 3 h. The reaction mixture was poured into water (10 ml), extracted with ether (3×20 ml) and washed with water (20 ml). The residue was purified by column chromatography on silica gel, eluting with petroleum ether, to afford 2.03 g (81%) of the product **3a** as an oil. Analysis: calculated for $C_{13}H_{20}F_2I_2O_2$: C, 31.20%; H, 4.00%; found: C, 31.09%; H, 4.01%. MS m/z (relative intensity): 501 ($M^+ + 1$, 1.98), 499 ($M^+ - 1$, 2.90), 481 ($M^+ - F$, 50.07), 461 ($M^+ - F - HF$, 37.39), 353 ($M^+ - I - HF$, 70.63), 333 ($M^+ - I - 2HF$, 56.92), 83 (100). IR (film) (cm^{-1}): 2900, 2850, 1420, 1380, 1025. ^1H NMR ($CDCl_3$) δ (ppm): 1.7–4.1 (20H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): 20.0 (2F, m).

3.1.1. 6,10-Diiodo-8,8-difluoropentadecane (3b)

The reaction of **1** with 1-heptene (1.47 g, 15 mmol) for 3 h yielded 1.85 g (74%) of **3b** as an oil after chromatography using petroleum ether as the eluent. Analysis: calculated for $C_{15}H_{28}F_2I_2$: C, 36.00%; H, 5.60%; found: C, 35.55%; H, 5.15%. MS m/z (relative intensity): 373 ($M^+ - I$, 7.5), 333 ($M^+ - I - 2HF$, 43.0), 225 ($M^+ - I - HI - HF$, 22.0), 205 ($M^+ - I - HI - HF$, 22.0), 55 (100.0). IR (film) (cm^{-1}): 1545, 1120, 900. ^1H NMR ($CDCl_3$) δ (ppm): 1.0 (6H, t, J=7 Hz), 1.40–1.80 (16H, m), 2.40–3.10 (4H, m), 4.40 (2H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): 17.0–19.0 (2F, m).

3.1.2. 5,9-Diiodo-7,7-difluorotridecane (3c)

The reaction of **1** with 1-hexene (1.26 g, 15 mmol) for 3 h yielded 1.84 g (78%) of **3c** as an oil after chromatography using petroleum ether as the eluent. HRMS: calculated for

$C_{13}H_{24}F_2$ [M − I] 345.0891; found: 345.0906. MS m/z (relative intensity): 345 (M^+ − I, 18.50), 305 (M^+ − I − 2HF, 62.0), 197 (M^+ − I − HI − HF, 42.0), 177 (M^+ − I − HI − 2HF, 100.0), 69 (85.30). IR (film) (cm^{-1}): 1545, 1460, 1120, 1050. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.00 (6H, t, J = 7 Hz), 1.40–1.80 (12H, m), 2.40–3.10 (4H, m), 4.40 (2H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): 17.0–19.0 (2F, m).

3.1.3. 2,6-Diiodo-4,4-difluoro-7-acetoxyheptyl acetate (3d)

The reaction of **1** with allyl acetate (1.5 g, 15 mmol) for 4 h yielded 1.92 g (76%) of **3d** as an oil after chromatography using a 1 : 5 mixture of ethyl acetate and petroleum ether as the eluent. HRMS: calculated for $C_{11}H_{16}F_2IO_4$ [M − I] 377.0061; found: 377.0078. MS m/z (relative intensity): 377 (M^+ − I, 36.30), 317 (M^+ − I − CH_3COO, 13.86), 43 (CH_3CO^+, 100.0). IR (film) (cm^{-1}): 1740, 1420, 1360, 1230, 1020. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.13 (6H, s), 2.43–2.86 (4H, m), 4.33 (6H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): 18.30 (2F, m).

3.1.4. 2,6-Diiodo-4,4-difluoro-7-ethoxyheptyl ethyl ether (3e)

The reaction of **1** with allyl ethyl ether (1.29 g, 15 mmol) for 4 h yielded 1.78 g (75%) of **3e** as an oil after chromatography using petroleum ether as the eluent. Analysis: calculated for $C_{11}H_{20}F_2I_2O_4$: C, 27.73%; H, 4.20%; found: C, 27.57%; H, 4.13%. MS m/z (relative intensity): 349 (M^+ − I, 4.75), 329 (M^+ − I − HF, 11.03), 303 (M^+ − HI − C_2H_5O, 44.63), 255 (100.0), 199 (36.20), 59 ($C_2H_5OCH_2^+$, 95.37). IR (film) (cm^{-1}): 2950, 2750, 1380, 1350, 1350, 1240, 1100. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.30 (6H, t, J = 6 Hz), 2.40–3.00 (4H, m), 3.46–3.730 (8H, m), 5.20 (m, 2H). ^{19}F NMR ($CDCl_3$) δ (ppm): 19.0 (2F, m).

3.1.5. 2,6-Diiodo-4,4-difluoro-1,7-heptandiol (3f)

The reaction of **1** with allyl alcohol (0.87 g, 15 mmol) for 4 h in CH_3CN (5 ml) and brine (2 ml) (saturated with KCl) yielded 1.09 g (52%) of **3f** as an oil after chromatography using a 1 : 2 mixture of ethyl acetate and petroleum ether as the eluent. HRMS: calculated for $C_7H_{12}F_2I_2O_2$: 419.8895; found: 419.8891. MS m/z (relative intensity): 420 (M^+, 1.57), 293 (M^+ − I, 6.15), 255 (84.17), 127 (45.95), 85 (100.00). IR (film) (cm^{-1}): 3300, 2900, 1420, 1360, 1020. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.50–3.20 (4H, m), 3.56 (2H, s), 3.95 (4H, d, J = 8 Hz), 4.30–4.63 (2H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): 18.20 (2F, m).

3.1.6. 1,5-Diiodo-1,5-ditrimethylsilyl-3,3-difluoropentane (3g)

The reaction of **1** with **2g** (1.5 g, 15 mmol) for 4 h yielded 1.71 g (68%) of **3g** as an oil after chromatography using a 1 : 20 mixture of ethyl acetate and petroleum ether as the eluent. Analysis: calculated for $C_{11}H_{24}F_2I_2Si_2$: C, 26.19%; H, 4.76%; found: C, 26.08%; H, 4.89%. MS m/z (relative intensity): 504 (M^+, 1.98), 377 (M^+ − I, 2.88), 77 (53.11), 73 (100.0). IR (film) (cm^{-1}): 1250, 1180, 1075. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.20 (18H, s), 2.16–2.70 (4H, m), 3.50 (2H, t, J = 7 Hz). ^{19}F NMR ($CDCl_3$) δ (ppm): 16.30 (2F, m).

3.2. General procedure for the preparation of 4 exemplified by the reaction of 1 with diallyl ether

Difluorodiiodomethane (**1**) (1.5 g, 5 mmol) was added dropwise to a mixture of diallyl ether (2.94 g, 15 mmol), $Na_2S_2O_4$ (0.87 g, 5 mmol) and $NaHCO_3$ (0.41 g, 5 mmol) in CH_3CN (5 ml) and H_2O (2 ml) at −15 °C. After the addition was complete, the solution was warmed to 5–8 °C and stirred for 1 h. The reaction mixture was poured into water (10 ml), extracted with ether (3 × 20 ml) and washed with water (20 ml). The residue was purified by column chromatography on silica gel, eluting with petroleum ether, to afford 1.43 g (71%) of the product 3-iodomethyl-4-(2′-iodo-2′,2′-difluoroethyl)tetrahydrofuran (**4a**) as colourless crystals: m.p., 68–69 °C. Analysis: calculated for $C_7H_{10}F_2I_2O$: C, 20.90%; H, 2.49%; found: C, 20.80%; H, 2.38%. MS m/z (relative intensity): 402 (M^+, 0.04), 275 (M^+ − I, 43.10), 127 (69.00), 99 (100.0). IR (KCl) (cm^{-1}): 2850, 2700, 1425, 1240, 1210, 1175, 1045, 1015. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.10–4.40 (10H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): −4.00 (2F, m).

3.2.1. 1,3-Diiodo-1,1-difluorooctane (4b)

The reaction of **1** (1.5 g, 5 mmol) and 1-heptene (1.47 g, 15 mmol) for 1 h yielded 1.37 g (68%) of **4b** as an oil after chromatography using petroleum ether as the eluent. HRMS: calculated for $C_8H_{14}F_2I_2$: 401.9153; found: 401.9149. MS m/z (relative intensity): 402 (M^+, 5.0), 127 (I^+, 100.0). IR (film) (cm^{-1}): 2910, 1160, 1060, 895. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.86 (3H, t, J = 6 Hz), 1.10–2.30 (8H, m), 2.70–3.40 (2H, m), 4.20 (1H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): −42.2 (2F, m).

3.2.2. 1,3-Diiodo-1,1-difluoroheptane (4c) [6]

The reaction of **1** (1.5 g, 5 mmol) and 1-hexene (1.26 g, 15 mmol) for 1 h yielded 1.28 g (66%) of **4c** as an oil after chromatography using petroleum ether as the eluent. MS m/z (relative intensity): 388 (M^+, 6.0), 133 (M^+ − HI − I, 100.0). IR (film) (cm^{-1}): 2900, 1160, 1060, 900. ^{1}H NMR (CCl_4) δ (ppm): 1.00 (3H, t, J = 6 Hz), 1.20–2.20 (6H, m), 2.80–3.50 (2H, m), 4.30 (1H, m). ^{19}F NMR (CCl_4) δ (ppm): −41.30 (2F, m).

3.2.3. 2,4-Diiodo-4,4-difluorobutyl acetate (4d)

The reaction of **1** (1.5 g, 5 mmol) and allyl acetate (1.5 g, 15 mmol) for 1.5 h yielded 1.2 g (60%) of **4d** as an oil after chromatography using a 1 : 10 mixture of ethyl acetate and petroleum ether as the eluent. Analysis: calculated for $C_6H_8F_2I_2O_2$: C, 17.82%; H, 1.98%; found: C, 18.06%; H, 1.93%. MS m/z (relative intensity): 405 (M^+ + 1, 2.0), 217 (100.0), 43 (81.0). IR (film) (cm^{-1}): 1740, 1380, 1360, 1220, 1040. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.0 (3H, s), 3.0–

3.50 (2H, m), 4.20 (3H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): −41.0 (2F, m).

*3.2.4. 2,4-Diiodo-4,4-difluorobutyl ethyl ether (**4e**)*

The reaction of **1** (1.5 g, 5 mmol) and allyl ethyl ether (1.29 g, 15 mmol) for 1.5 h yielded 1.25 g (64%) of **4e** as an oil after chromatography using petroleum ether as the eluent. Analysis: calculated for $C_6H_{10}F_2I_2O_2$: C, 18.46%; H, 2.56%; found: C, 18.72%; H, 2.60%. MS m/z (relative intensity): 391 ($M^+ + 1$, 0.24), 390 (M^+, 2.10), 345 ($M^+ - C_2H_5O$, 11.20), 217 ($M^+ - HI - C_2H_5O$, 100.00), 215 (75.29). IR (film) (cm^{-1}): 3000, 2900, 1100, 980. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.20 (3H, t, J = 6 Hz), 2.80–3.23 (2H, m), 3.40–3.66 (4H, m), 4.23 (1H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): −42.60 (2F, m).

*3.2.5. 2,4-Diiodo-4,4-difluorobutanol (**4f**)*

The reaction of **1** (1.5 g, 5 mmol) and allyl alcohol (0.87 g, 15 mmol) in CH_3CN (5 ml) and brine (2 ml) (saturated with KCl) for 1 h yielded 0.87 g (48%) of **4f** as an oil after chromatography using a 1 : 5 mixture of ethyl acetate and petroleum ether as the eluent. HRMS: calculated for $C_4H_6F_2I_2O$: 361.8476; found: 361.8455. MS m/z (relative intensity): 362 (M^+, 1.24), 187 (100.0), 127 (I^+, 21.91). IR (film) (cm^{-1}): 3300, 1420, 1040, 980. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.13–3.80 (3H, m), 4.05 (2H, d, J = 8 Hz), 4.40–4.70 (1H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): −40.30 (2F, m).

*3.2.6. 1,3-Diiodo-1,1-difluoro-3-trimethylsilylpropane (**4g**)*

The reaction of **1** (1.5 g, 5 mmol) and **2g** (1.5 g, 15 mmol) for 1 h yielded 1.05 g (52%) of **4g** as an oil after chromatography using petroleum ether as the eluent. Analysis: calculated for $C_6H_{12}F_2I_2Si$: C, 17.82%; H, 2.97%; found: C, 18.11%; H, 3.04%. MS m/z (relative intensity): 404 (M^+, 5.63), 277 ($M^+ - I$, 4.78), 185 (100.00). IR (film) (cm^{-1}): 2950, 1410, 1340, 1260, 1180, 1080. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.23 (9H, s), 2.60–3.23 (3H, m). ^{19}F NMR ($CDCl_3$) δ (ppm): −42.20 (2F, m).

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