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# Oxidant-induced addition reaction of perfluoroalkyl halides to alkenes and alkynes

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## Abstract

Ceric sulfate, cerium(IV) ammonium nitrate, sodium persulfate, ammonium persulfate and potassium permanganate can smoothly induce the addition reaction of perfluoroalkyl halides (**1**) to electron-rich olefins (**2**) and alkynes (**4**) to give monoadducts (**3** or **5**). The perfluoroalkyl radical generated *via* possible pathways from **1** is discussed.

*Keywords:* Alkene; Alkyne; Perfluoroalkyl halide

## 1. Introduction

The addition reaction of perfluoroalkyl halides ($R_FX$) to olefins or alkynes is one of the most important methods for introducing perfluoroalkyl group to organic compounds. Such a process is traditionally accomplished with photochemical [1–4], thermal [5], electrolytic [6] and free radical initiations [7]. Recently, however, some reductive systems were found to be more effective. For example: metals, transition metals, inorganic reductants, as well as redox systems, such as Cu [8,9], Zn [10], Mg [11], Ni [12], Fe [13], Pd [14,15], Pt [16], $Fe(CO)_4$ [17], $Na_2S_2O_4$ [18], thiourea dioxide [19], $(NH_4)_2S_2O_8/HCO_2Na$ [20], $CrCl_3/Fe$ [21], Co(II)/Zn [22] were successfully applied to this reaction. To the best of our knowledge, oxidants have not been used to such process except one example, i.e., lead tetraacetate (LTA) and lead dioxide, which was discovered in our laboratory in 1988 [23]. Very recently, it was found that LTA not only can induce smoothly the addition of difluodiiodomethane($CF_2I_2$) to normal alkenes but also to polyfluoalkylethenes, vinylidene fluoride, tetrafluoroethylene and hexafluoropropene [24]. The results prompted us to seek other oxidants, because, they, different from the reductive systems, may become a unique initiation system for the addition of perfluoroalkyl halides to alkenes and alkynes.

Herein, we present the results of the addition reaction in the presence of ceric sulfate, cerium(IV) ammonium nitrate, sodium persulfate, ammonium persulfate and potassium permanganate.

## 2. Results and discussion

### 2.1. Reaction initiated by ceric sulfate [$Ce(SO_4)_2 \cdot 4H_2O$] and cerium(IV) ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$]

In the presence of $Ce(SO_4)_2 \cdot 4H_2O$ (50 mol%) or $(NH_4)_2Ce(NO_3)_6$ (10 mol%) perfluoroalkyl halides reacted smoothly with olefins to give the corresponding perfluoroalkylated adducts. For example, treatment of $\omega$-chlorooctafluoroalkyl iodide (**1a**) with hexene-1 in the presence of $Ce(SO_4)_2 \cdot 4H_2O$ (10 mol%) in *N,N*-dimethylformamide (DMF) at 80°C for 8.0 h, gave the adduct in good yield (81%) (Scheme 1).

It was found that DMF can be used as a solvent in this reaction although in which the catalyst is not very soluble (e.g., 1.25 mmol of $Ce(SO_4)_2 \cdot 4H_2O$ in 10 ml DMF). When methanol, which has a better solubility for ceric salts than

$$\underset{1}{R_FX} + \underset{2}{RCH{=}CH_2} \xrightarrow[DMF]{Ce(IV)} \underset{3}{RCHXCH_2R_F}$$

1: $R_F = Cl(CF_2)_4$ (a); $R_F = Cl(CF_2)_6$ (b); $R_F = CF_3(CF_2)_5$ (c); $X = I$
$R_F = CF_2Br$(d); $X = Br$

2: $R = n\text{-}C_4H_9$(a'); $R = HOCH_2$(b'); $R = n\text{-}C_6H_{13}$(c'); $R = n\text{-}C_8H_{17}$(d'); $R = n\text{-}C_9H_{19}$(e')
$R = n\text{-}C_{10}H_{21}$(f'); $R = Me_3Si$(g'); $R = CH_2OCH_2CH{=}CH_2$(h'); $R = n\text{-}C_{14}H_{21}$(i');

Scheme 1

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Table 1
Solvent effect on the reaction of **1a** with **2a′** and **2c′** in the presence of $Ce(SO_4)_2 \cdot 4H_2O$ [a]

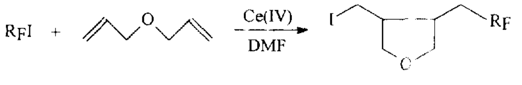
| Entry | Solvent | **1a** (Conv. %) [b] | **3** (Yield %) [c] | **1b** (Conv. %) [b] | **3** (Yield %) [c] |
|---|---|---|---|---|---|
| 1 | DMF | 100 | 81 | 100 | 82 |
| 2 | MeOH [d] | 95 | 78 | 100 | 80 |
| 3 | DMF–MeOH [d,e] | 50 | 31 | 60 | 38 |
| 4 | DMSO | 45 | 34 | 40 | 30 |
| 5 | HOAc | 0 | 0 | 0 | 0 |
| 6 | DG | 0 | 0 | 0 | 0 |

[a] **1**:**2**:Ce(IV) = 1:3:0.5 at 80°C for 8.0 h.
[b] Conv. % was determined by $^{19}F$ NMR.
[c] Isolated yield.
[d] ~5% $R_FH$ was also obtained.
[e] V/V = 2:1.

Table 2
Temperature effect on the reaction of **1a** with **2a′** in the presence of Ce(IV) in DMF [a]

| Entry | $T$ (°C) | $t$ (h) | **1a** (Conv. %) | **3** (Yield %) |
|---|---|---|---|---|
| 1 | 25 | 10 | 0 | 0 |
| 2 | 60 | 10 | 80 | 63 |
| 3 | 80 | 8 | 100 | 81 |
| 4 | 100 | 8 | 100 | 58 |

[a] **1**:**2**:Ce(IV) = 1:3:0.5.



**2h′**

Scheme 2.

DMF, was utilized, the yield of the adduct was comparable, but ~5% of $R_FH$ was also obtained as a byproduct. Quite unexpectedly, both the conversion and yield were decreased if a mixture of DMF/MeOH (V/V = 2:1) was utilized in the reaction. The similar results were also obtained if methylsulfoxide (DMSO) was employed in spite that the catalyst is very soluble. In diglyme (DG) and acetic acid (HOAc) the reaction did not take place at all (Table 1). All these may relate to different association abilities of ligands with Ce(IV) ion.

The temperature variation also affected the reaction. For example, when the reaction of **1a** with **2a′** took place at 60°C for 10 h, only 80% conversion and 63% yield were given. The yield was also decreased if the temperature was higher than 80°C (Table 2).

When diallyl ether (DAE) was used as a substrate, the formation of tetrahydrofuran derivatives indicated the involvement of free radical intermediate (Scheme 2). The results are listed in Table 3.

Another direct proof of free radical intermediate comes from the spin-trapping by ESR. ω-Chlorooctanfluorobutyl radical was apparently existent in its spin adduct with $t$-butyl nitroxide ($a_F = 2.10$ mT; $a_N = 1.18$ mT, $g = 2.0053$) (Fig. 1).

The addition reaction of perfluoroalkyl iodide with alkynes was carried out at higher temperature (120°C) and for longer time (18 ~ 20 h) as compared that with alkenes, because alkynes, as expected, are less reactive than alkenes (Scheme 3). The adducts were obtained as a mixture of *cis/trans* isomers. The data are collected in Table 4.

Table 3
Reaction of **1** with **2** in the presence of $Ce(SO_4)_2 \cdot 4H_2O$ in DMF [a,b]

| Entry | **2** (R = ) | **3** (Yield %) [c] | | | |
|---|---|---|---|---|---|
| | | **1a** | **1b** | **1c** | **1d** |
| 1 | $C_4H_9$(a′) | 81(83) [d] | 73(77) [d] | 84(83) [d] | 83(80) [d] |
| 2 | $HOCH_2$(b′) | 73(79) | 74(83) | 56(50) | – |
| 3 | $C_6H_{13}$(c′) | 82(80) | 85(84) | 82(81) | 86(81) |
| 4 | $C_8H_{17}$(d′) | 84(82) | 78(79) | 84(80) | – |
| 5 | $C_9H_{19}$(e′) | 84(81) | 81(82) | 85(81) | 86(83) |
| 6 | $C_{10}H_{21}$(f′) | 80(81) | 83(82) | – | 79(80) |
| 7 | $Me_3Si$(g′) | 68(74) | – | – | – |
| 8 | $CH_2OCH{=}CH_2$(h′) | 65(78) | 81(81) | – | 83(78) |
| 9 | $C_{14}H_{29}$(i′) | 78(–) | –(80) | – | – |

[a] **1**:**2**:$Ce(SO_4)_2 \cdot 4H_2O$ = 1:3:0.5; $T$ = 80°C, $t$ = 8 h.
[b] Conversion was 100%.
[c] Isolated yield.
[d] Isolated yields in parentheses were in the reaction initiated by $(NH_4)_2Ce(NO_3)_6$; **1**:**2**:$(NH_4)_2Ce(NO_3)_6$ = 1:3:0.1.

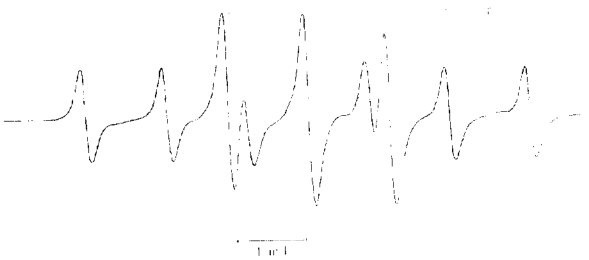
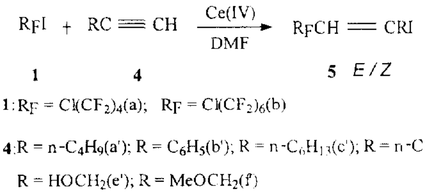


Fig. 1. ESR spectrum of $Cl(CF_2)_4NOBu$-*t*, generated from a solution of *t*-butyl nitroxide with $Cl(CF_2)_4I$ and hexene-1.



Scheme 3.

### 2.2. Reaction initiated by sodium and ammonium persulfate [$Na_2S_2O_8$ and $(NH_4)_2S_2O_8$]

Similarly perfluoroalkyl iodide reacted successfully with olefins in $MeCN–H_2O$ (2:1 V/V) at 60°C for 6–8 h in the presence of $Na_2S_2O_8$ or $(NH_4)_2S_2O_8$ (10 mol%) (Scheme 4, Table 5).

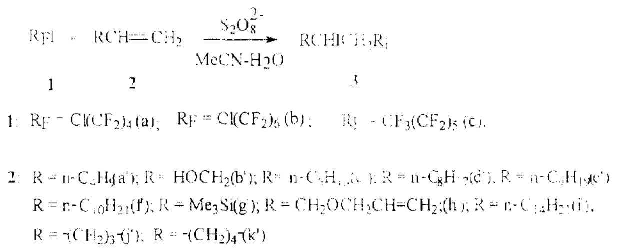
Cyclohexene and cyclopentene can also react with $R_FI$ to give the 1:1 adducts in good yields (Scheme 5).

The reaction of $R_FI$ with diallyl ether also gave tetrahydrofuran derivatives and ESR spectrum showed the existence of $R_F$ radical as well.

It is known that thermal decomposition of persulfate solution may generate the hydroxyl radical [25] (Scheme 6) which can be trapped by *t*-butyl alcohol [26]. The addition of *t*-butyl alcohol to the reaction mixture was found little influence as compared with that in its absence. The possibility initiated by hydroxyl radical seems to be excluded.

### 2.3. Reaction initiated by potassium permanganate ($KMnO_4$)

Potassium permanganate can also induce the reaction of perfluoroalkyl iodide with alkenes in $MeCN–H_2O$ (2:1 V/V) at 80°C (Scheme 7). The adducts were obtained with low conversions and yields as shown in Table 6.



Scheme 4

When diallyl ether was used as a substrate, tetrahydrofuran derivative was obtained. $R_F$ radical was also detected by ESR spectrum.

### 2.4. Other inorganic and organic oxidants

Some other inorganic and organic oxidants listed below (Table 7) have been tested in the addition reaction of perfluoroalkyl halides to olefins under the given conditions. Unfortunately, they could not induce the reaction and the starting materials were recovered completely.

In order to have an insight into this addition reaction, we examined the reduction potentials of some of the oxidants used [27,28] (see Table 8). It was found when the reduction potential of the oxidant is equal to or higher than 1.60 V vs. SCE, the oxidant could initiate the addition reaction to alkenes used successfully, otherwise it could not, that is, the oxidant with

$$E^0_{\mathrm{Red}} \geq 1.60$$

is an effective initiator.

### 2.5. Mechanism consideration

It is obviously that the reaction occurred through a perfluoroalkyl radical, $R_F\cdot$, based on the facts that tetrahydrofuran

Table 4
Reaction of **1** with **4** in the presence of Ce(IV) in DMF [a,b]

| Entry | **4** (R=) | $Ce(SO_4)_2 \cdot 4H_2O$ **5**, Yield % (*E/Z*) | | $(NH_4)_2Ce(NO_3)_6$ [b] **5**, Yield % (*E/Z*) | |
|---|---|---|---|---|---|
| | | **1a** | **1b** | **1a** | **1b** |
| 1 | $C_4H_9$(a') | 73(3/1) | 71(1/1) | – | – |
| 2 | $C_6H_5$(b') | 55(3/1) | 74(11/1) | 53(6/1) | 78(5/1) |
| 3 | $C_6H_{13}$(c') | 68(3/1) | – | 52(4/1) | – |
| 4 | $C_7H_{15}$(d') | 59(4/1) | 76(3/1) | 61(6/1) | 71(5/1) |
| 5 | $HOCH_2$(e') | 48(10/1) | 65(65/0) | – | 67(9/1) |
| 6 | $MeOCH_2$(f') | 48(2/5) | – | – | – |

[a] For $Ce(SO_4)_2 \cdot 4H_2O$, **1**:**4**:Ce(IV) = 1:1.5:0.5; for $(NH_4)_2Ce(NO_3)_6$, **1**:**4**:Ce(IV) = 1:1.5:0.1, *T* = 120°C, *t* = 18 ~ 20 h.
[b] Conversion was complete.

Table 5
Reaction of **1** with **2** in the presence of $Na_2S_2O$ in $MeCN–H_2O$ [a,b]

| Entry | **2** (R = ) | **3** (Yield %) [c] | | |
|---|---|---|---|---|
| | | **1a** | **1b** | **1c** |
| 1 | $C_4H_9$(a′) | 81(83) [d] | 84(73) [d] | 81(87) [d] |
| 2 | $HOCH_2$(b′) | 73(79) | 83(81) | 61(63) |
| 3 | $C_6H_{13}$(c′) | 85(88) | 83(82) | 83(84) |
| 4 | $C_8H_{17}$(d′) | 83(86) | 85(86) | 85(85) |
| 5 | $C_9H_{19}$(e′) | 85(83) | 87(85) | 88(85) |
| 6 | $C_{10}H_{21}$(f′) | 83(85) | 84(85) | – |
| 7 | $Me_3Si$(g′) | 68(74) | – | – |
| 8 | DAE(h′) | 65(78) | 77(76) | – |
| 9 | $C_{14}H_{29}$(i′) | 78(80) | – | – |
| 10 [e] | $-(CH_2)_3-$ (j′) | 88(84) | 86(83) | – |
| 11 [e] | $-(CH_2)_4-$ (k′) | 70(76) | 77(78) | – |

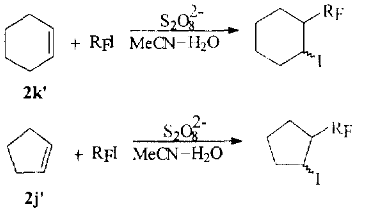
[a] **1**:**2**:$Na_2S_2O_8$ = 1:3:0.1, $T$ = 60°C, $t$ = 6 ~ 8 h.

[b] Conversion was complete.

[c] Isolated yield.

[d] Isolated yields in parentheses in the reaction initiated by $(NH_4)_2S_2O_8$; **1**:**2**:$(NH_4)_2S_2O_8$ = 1:3:0.1, $T$ = 60°C, $t$ = 6 ~ 8 h.

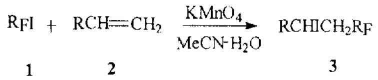
[e] For **2j′**, $E$:$Z$ = 1:1; for **2k′**, only $Z$ product was obtained.



Scheme 5.

$$S_2O_8^{2-} \longrightarrow 2\,SO_4^{-\cdot}$$
$$SO_4^{-\cdot} + H_2O \longrightarrow HSO_4^{-} + OH^{\cdot}$$

Scheme 6.



$$\underset{1}{R_FI} + \underset{2}{RCH{=}CH_2} \xrightarrow[MeCN\text{-}H_2O]{KMnO_4} \underset{3}{RCHICH_2R_F}$$

**1**: $R_F = Cl(CF_2)_4$ (a); $R_F = Cl(CF_2)_6$ (b);

**2**: R = n-$C_4H_9$(a′); R = $HOCH_2$(b′); R = n-$C_6H_{13}$(c′); R = n-$C_{10}H_{21}$(f′)
R = $Me_3Si$(g′); R = $CH_2OCH_2CH{=}CH_2$(h′); R = n-$C_{14}H_{29}$(i′)

Scheme 7.

Table 6
Reaction of **1a** with **2** in the presence of $KMnO_4$ in $MeCN–H_2O$ [a,b]

| Entry | **2** (R = ) | **1a** (Conv. %) | **3** (Yield %) |
|---|---|---|---|
| 1 | $C_4H_9$(a′) | 33 | 21 |
| 2 | $HOCH_2$(b′) | 95 | 76 |
| 3 | $C_6H_{13}$(c′) | 60 | 42 |
| 4 | $C_{10}H_{21}$(f′) | 70 | 51 |
| 5 | $Me_3Si$(g′) | 45 | 35 |
| 6 | $CH_2{=}CHCH_2OCH_2$(h′) | 50 | 36 |
| 7 | $C_{14}H_{29}$(i′) | 40 | 33 |

[a] **1**:**2**:$KMnO_4$ = 1:3:0.1, $T$ = 60°C, $t$ = 8.0 h.

[b] V/V = 2:1.

derivatives were obtained when DAE was employed as a substrate and spin-trapping of perfluoroalkyl adducts with $t$-butyl nitroxide. However, how is the $R_F$ generated? Importantly, as it was shown, among the oxidants only those having the reductive potential equal to or higher than 1.6 V can smoothly catalyze the addition reaction. It, seemingly, implies that the radical cation of alkene formed by the strong oxidant might be involved in the initiation step, like the mechanism proposed by Norman et al. [29] in the addition reaction of styrene with acetic acid in the presence of LTA as follows: Scheme 8.

The alkene transfers an electron to the oxidant to give a radical cation of olefin which abstracts halogen from $R_FX$ to produce an alkyl cation and $R_F$. The addition of $R_F$ to alkene affords a new radical which abstracts halogen from $R_FX$ to yield the product and simultaneously regenerates $R_F$. However, the oxidation potentials of the olefins used seem too high to be oxidized to form the olefin radical cation (e.g., octane-1 $E^0_{ox}$ = 2.70 V vs. $Ag^+/AgNO_3$) [30], although the polar solvent can certainly compensate for this unfavourableness to some extent.

On the other hand, there is an alternative intermediate, i.e., radical cation of perfluoroalkyl iodide, $(R_FI)^{+\cdot}$ generated from $R_FI$ with the strong oxidant. Indeed, the same radical cation was proposed to be the intermediate in the preparation of perfluoroalkanesulfonic esters from perfluroalkyl iodide in the presence of perfluoroalkanesulfonic acids under the electrochemical oxidation [31].

From the favorable free energy change required for efficiently catalyzing this addition reaction to alkenes, the only use of strong oxidants with $E^0_{red} \geq 1.6$ V vs. SCE for matching the very poor electron donors, $R_FI$, with $E^0_{ox}$ = 1.68 V vs. SCE [32] may point to the initial formation of $(R_FI)^{+\cdot}$ rather than alkene radical cation as described as follows: Scheme 9.

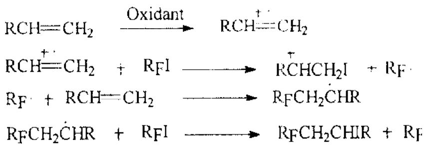
Table 7
Different oxidants tested in the addition reaction of **1a** to **2a'** [a]

| Oxidant | Conditions | | |
|---|---|---|---|
| | Solvent | $T$ (°C) | $t$ (h) |
| $Mn_2OAc_3$ | HOAc | 75 | 10 |
| $CoCl_2$ | DMF | 80 | 10 |
| $CeCl_3 \cdot 7H_2O$ | DMF | 80 | 9 |
| $CrCl_3 \cdot 7H_2O$ | DMF | 80 | 10 |
| $YCl_3$ | DMF | 80 | 10 |
| $FeCl_3$ | DMF | 80 | 10 |
| $BiCl_3$ | DMF | 80 | 10 |
| $In(NO_3)_2 \cdot 41/2H_2O$ | DMF | 80 | 10 |
| $Cr_2O_3$ | DMF | 80 | 10 |
| $CrO_3$ | DMF | 80 | 10 |
| $MnO_2$ | DMF–HOAc (1:1) | 90 | 10 |
| $Zr(NO_3)_4 \cdot 5H_2O$ | DMF | 80 | 10 |
| $K_2Cr_2O_7$ | MeCN–$H_2O$ (2:1) | 80 | 11 |
| PDC [b] | DMF | 80 | 10 |
| PCC [c] | DMF | 80 | 10 |
| Chloranil [d] | DMF | 80 | 10 |
| $[N(C_6H_3Br_2 2,4)_3]^+SbCl_6$ | $CH_2Cl_2$ | 25 | 24 |
| $[N(C_6H_4Br\text{-}3)_3]^-SbCl_6^-$ | $CH_2Cl_2$ | 25 | 24 |

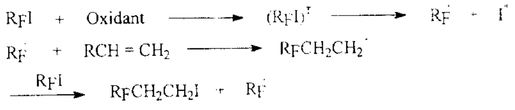
[a] **1a**:**2a'** = 1:3.
[b] PDC = pyridinium dichromate.
[c] PCC = pyridinium chlorochromate.
[d] Chloranil = 2,3,5,6-tetrachloro-1,4-benzoquinone.

Table 8
The reduction potential of some different oxidants

| Entry | Oxidant | M ($n$) | $E^0_{Red}$ (V) | Reference |
|---|---|---|---|---|
| 1 | $Na_2S_2O_8, (NH_4)_2S_2O_8$ | $S_2O_8^{2-}$ | 2.01 | [23] |
| 2 | $KMnO_4$ | $MnO_4^-$ | 1.695 | [23] |
| 3 | $Pb(OAc)_4$, $PbO_2$ | $Pb^{4+}$ | 1.69 | [23] |
| 4 | $Ce(SO_4)_2$, $(NH_4)_2Ce(NO_3)_6$ | $Ce^{4+}$ | 1.61 | [23] |
| 5 | $Mn_2(OAc)_3$ | $Mn^{3+}$ | 1.51 | [23] |
| 6 | $K_2Cr_2O_7$ | $Cr_2O_7^{2-}$ | 1.33 | [23] |
| 7 | $FeCl_3$ | $Fe^{3+}$ | 0.771 | [23] |
| 8 | chloranil | | 0.02 | [24] |
| 9 | $[N(C_6H_3Br_2\text{-}2,4)_3]^+SbCl_6^-$ | | 1.14 | [24] |
| 10 | $[N(C_6H_4Br\text{-}3)_3]^+SbCl_6$ | | 0.70 | [24] |



Scheme 8.



Scheme 9.

The perfluoroalkyl iodide is oxidized to form $(R_FI)^+$ which decomposed quickly to give $R_F$ and iodonium ion. The $R_F$ generated is trapped by alkene to produce a new radical which then abstracts an iodine from $R_FI$ to afford the product and another $R_F$ as a chain carrier.

## 3. Conclusion

The addition reactions of perfluoroalkyl halides to alkenes or alkynes in the presence of different kind of oxidants provides a mild and convenient method to fluoroalkylate alkenes or alkynes. Compared with other systems, using the oxidants as the initiators offers the mono-adduct without $R_FH$ and bis-adduct. The possible intermediate, e.g., radical cations of alkenes and perfluoroalkyl iodides may be involved, the later, being thought most likely.

## 4. Experimental

$^1H$ NMR spectra were recorded on Varian EM-360A (60 MHz), FX-90Q (90 MHz) and Bruker AM-300 (300 MHz)

NMR spectrometers. $^{19}$F NMR spectra were recorded on a Varian EM-360L (56.4 MHz) NMR spectrometer. Chemical shifts were reported in parts per million relative to TMS as an internal/external standard for $^{1}$H and to $CF_3COOH$ as an external standard for $^{19}$F. $^{1}$H NMR of most compounds were measured by 90 MHz unless otherwise noted.

ESR spectra were recorded on a Varian E-112 X-band spectrometer.

All the reagents were A.R. or C.P. without further purification.

### *4.1. General procedure for the addition reaction of **1** with **2***

#### *4.1.1. Ce(IV)*

Under a nitrogen atmosphere, a mixture of **1** (2.5 mmol), olefin (7.5 mmol), 50 mol% of $Ce(SO_4)_2 \cdot 4H_2O$ or 10 mol% of $(NH_4)_2Ce(NO_3)_6$ in DMF (10.0 ml) was stirred with a magnetic stirrer at 80°C for 8.0 h. After that $H_2O$ (25 ml) was added and the mixture was extracted with ether three times (20 ml ether each). The combined organic layer was washed with brine for three times and dried over $Na_2SO_4$. After removal of the solvent, the crude material was purified by flash chromatography using petroleum ether as eluent.

#### *4.1.2. $S_2O_8^{2-}$*

Under a nitrogen atmosphere, a mixture of **1** (2.5 mmol), olefin (7.5 mmol), 10 mol% of $(NH_4)_2S_2O_8$ or $Na_2S_2O_8$ in MeCN (6.0 ml) and $H_2O$ (3.0 ml) was stirred with a magnetic stirrer at 60°C for 6–8 h. After that $H_2O$ (25 ml) was added and the mixture was extracted with ether three times (20 ml ether each). The combined organic layer was washed with brine for three times and dried over $Na_2SO_4$. After removal of the solvent, the crude material was purified by flash chromatography using petroleum ether as eluent.

#### *4.1.3. $KMnO_4$*

Under a nitrogen atmosphere, a mixture of **1** (2.5 mmol), olefin (7.5 mmol), 10 mol% of $KMnO_4$ in MeCN (6.0 ml) and $H_2O$ (3.0 ml) was stirred with a magnetic stirrer at 60°C for 6–8 h. After that, $H_2O$ (25 ml) was added and the mixture was extracted with ether three times (20 ml ether each). The combined organic layer was washed with brine for three times and dried over $Na_2SO_4$. After removal of the solvent, the crude material was purified by flash chromatography using petroleum ether as eluent.

### *4.2. General procedure for the addition reaction of **1** with alkynes (**4**)*

Under a nitrogen atmosphere, a mixture of **1** (2.5 mmol), alkyne (7.5 mmol), 50 mol% of $Ce(SO_4)_2.4H_2O$ or 10 mol% of $(NH_4)_2Ce(NO_3)_6$ in DMF (10.0 ml) was stirred with a magnetic stirrer at 120°C for 8–20 h. After that $H_2O$ (25 ml) was added and the mixture was extracted with ether three times (20 ml ether each). The combined organic layer was washed with brine for three times and dried over $Na_2SO_4$. After removal of the solvent, the crude material was purified by flash chromatography using petroleum ether as eluent.

All the addition compounds either with alkenes or alkynes were know. Listed are their $^{1}$H NMR and $^{19}$F NMR with references.

**3aa′** [33] $^{1}$H NMR: 0.81–1.10(t, 3H), 1.15–1.67(stack, 4H), 1.67–1.93(stack, 2H), 2.50–3.17(stack, 2H), 4.13–4.50(m, 1H). $^{19}$F NMR: −9.3(s, 2F), 34.7(m, 2F), 42.3(s, 2F), 45.7(s, 2F).

**3ab′** [34] $^{1}$H NMR: 2.10–3.20(stack, 2H), 3.40–3.67(stack, 2H), 3.93–4.23(m, 1H). $^{19}$F NMR: −9.7(s, 2F), 35.7(m, 2F), 42.3(s, 2F), 45.3(s, 2F).

**3ac′** [35] $^{1}$H NMR (60 MHz): 0.97–2.07(stack, 13H), 3.20–3.27(stack, 2H), 4.07–4.57(m, 1H). $^{19}$F NMR: −9.7(t, 2F), 35.5(m, 2F), 42.3(t, 2F), 45.5(t, 2F).

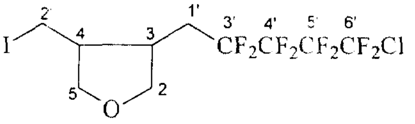
**3ad′** [36] $^{1}$H NMR: 0.97(t, 3H), 1.22–1.72(stack, 12H), 1.72–2.15(stack, 2H), 3.35–3.55(stack, 2H), 4.25–4.45(m, 1H). $^{19}$F NMR: −10.0(t, 2F), 34.7–37.0(m, 2F), 42.3–43.7(stack, 4F).

**3ae′** [36] $^{1}$H NMR: 1.00(t, 3H), 1.23–1.63(stack, 14H), 1.63–2.03(stack, 2H), 2.63–3.23(stack, 2H), 4.23–4.53(m, 1H). $^{19}$F NMR: −9.7(t, 2F), 35.0–36.7(m, 2F), 42.3(t, 2F), 45.7(t, 2F).

**3af′** $^{1}$H NMR: 1.00(t, 3H), 1.15–1.72(stack, 16H), 1.92–2.20(stack, 2H), 3.22(broad, 2H), 4.05–4.45(m, 1H). $^{19}$F NMR: −9.7(t, 2F), 34.3–37.3(m, 2F), 42.3(t, 2F), 45.7(t, 2F).

**3ag′** [35] $^{1}$H NMR: 0.30(s, 9H, 3Me), 2.33–3.47(stack, 3H). $^{19}$F NMR: −9.7(s, 2F), 37.3(m, 2F), 42.3(s, 2F), 45.7(s, 2F).

**3ah′** [35] Since $^{1}$H NMR of this compound and its analogues were previously recorded by 60 MHz, the signals were not identified clearly. Herein when using 300 MHz, the results were shown much better.



$^{1}$H NMR (300 MHz): 2.00(m, 1H, H-3), 2.23–2.26 (m, 1H, H-4), 2.66–2.79(stack, 2H, H-1′), 3.01–3.18(stack, 2H, H-2′), 3.58–3.74(stack, 2H, H-2), 3.74–4.02(stack, 2H, H-5). $^{19}$F NMR (282 MHz): −8.3(t, 2F, F-6′), 33.1 ~ 36.0(qq, 2F, F-3′), 40.4(t, 2F, F-5′), 43.2(s, 2F, F-4′).

**3ai′** $^{1}$H NMR (60 MHz): 1.00–1.50(stack, 29H), 2.07–2.62(stack, 2H), 4.10–4.50(m, 1H). $^{19}$F NMR: −10.3(s, 2F), 33.7–36.3(m, 2F), 41.7(s, 2F), 45.0(s, 2F).

**3aj′** [23] $^{1}$H NMR (60 MHz): 1.63–2.33(stack, 6H), 3.13–3.53(m, 1H), 4.28–4.63(m, 1H). $^{19}$F NMR: −10.0(s, 2F), 39.0(m, 1F), 41.0(m, 1F), 42.3–43.3(stack, 4F).

**3ak′** [23] $^{1}$H NMR: 1.67–2.30(stack, 8H), 3.20–3.40(m, 1H), 4.57(broad, 1H). $^{19}$F NMR: −10.0(m, 2F), 39.3(m, 2F), 41.0–42.7(stack, 4F).

**3ba′** [33] $^1$H NMR: 1.20–1.37(t, 3H), 1.77–2.07(stack, 2H), 2.37–3.17(stack, 6H), 4.40–4.53(m, 1H). $^{19}$F NMR: −9.7(t, 2F), 35.7–37.0(m, 2F), 42.7–43.3(m, 2F), 43.7–45.0(stack, 4F), 45.7–46.7(m, 2F).

**3bb′** $^1$H NMR: 3.30–3.70(stack, 2H), 3.70–3.85(stack, 2H), 3.95–4.15(m, 1H). $^{19}$F NMR: −9.7(t, 2F), 36.0(m, 2F), 42.8(m, 2F), 44.0(stack, 4F), 46.0(m, 2F).

**3bc′** [35] $^1$H NMR: 1.0(m, 3H), 1.25–1.55(stack, 8H), 1.75–1.98(stack, 2H), 2.65–3.25(stack, 2H),4.28–4.48(m, 1H). $^{19}$F NMR: −9.3(t, 2F), 35.3–36.7(m, 2F), 42.3–43.0(m, 2F), 43.3–44.7(stack, 4F), 45.3–46.3(m, 2F).

**3bd′** [36] $^1$H NMR: 0.87–1.07(stack, 3H), 1.17–1.57(stack, 12H), 1.62–2.17(stack, 2H), 2.70–3.50(stack, 2H), 4.27–4.57(m, 1H). $^{19}$F NMR: −9.7(t, 2F). 35.0–37.3(m, 2F), 43.0(m, 2F), 44.0(stack, 6F).

**3be′** [36] $^1$H NMR (60 MHz): 0.97(s, 3H), 1.13–1.63(stack, 14H), 1.93–2.33(stack, 2H), 2.50–3.40(stack, 2H), 4.57–4.83(m, 1H). $^{19}$F NMR: −10.0(t, 2F), 33.6–35.6(m, 2F), 41.6–42.8(m, 2F). 42.8–43.6(stack, 4F), 45.3(m, 2F).

**3bf′** $^1$H NMR: 0.9(stack, 3H), 1.23(stack, 16H), 1.53–2.13(stack, 2H), 3.13(broad, 2H), 4.05–4.45(m, 1H). $^{19}$F NMR: −10.0(t, 2F), 34.3–36.0(m, 2F), 41.8–42.6(s, 2F), 43.3(s, 4F), 45.0–46.0(t, 2F).

**3bh′** [35] $^1$H NMR: 2.08–2.50(stack, 2H), 2.70–2.97(stack, 2H), 3.15–3.35(stack, 2H), 3.45–3.85(stack, 2H), 3.95–4.15(stack, 2H). $^{19}$F NMR: −9.5(s, 2F), 35.0–38.0(m, 2F), 43.0(s, 2F), 44.3(s, 4F), 46.3(s, 2F).

**3ca′** $^1$H NMR (60 MHz): 1.00(brs, 3H, Me), 1.20–2.15(stack, 6H), 2.40–3.40(stack, 2H), 4.00–4.60(m, 1H). $^{19}$F NMR: 4.3(brs, 3F), 35.3–37.7(m, 2F), 44.8(s, 2F),46.7(s, 4F), 49.3(s, 2F).

**3cb′** [37] $^1$H NMR: 3.25–3.60(stack, 2H), 3.60–3.80(stack,2H),3.90–4.10(m, 1H). $^{19}$F NMR: 3.0(brs, 3F), 35.0–36.0(m, 2F), 45.0(s, 2F),46.7(s, 4F), 48.3(s, 2F).

**3cc′** [8,9] $^1$H NMR (60 MHz): 0.70(brs, 3H, Me), 0.90–1.40(stack, 10H), 1.40–1.90(stack, 2H), 3.90–4.20(m,1H). $^{19}$F NMR: 4.0(t, 3F), 35.0–37.7(m, 2F), 44.0–47.5(stack, 6F), 49.0(m, 2F).

**3cd′** $^1$H NMR (60 MHz): 1.00(brs, 3H, Me), 1.10–2.10(stack, 14H), 2.35–3.25(stack, 2H), 4.00–4.60(m, 1H). $^{19}$F NMR: 4.0(s, 3F), 36.0–37.0(m, 2F), 43.0–47.0(stack, 6F), 49.0(s, 2F).

**3ce′** $^1$H NMR: 0.93(t, 3H, Me), 1.13–1.63(stack, 14H), 1.63–2.00(stack, 2H), 2.53–3.17(stack, 2H), 4.23–4.37(m, 1H). $^{19}$F NMR: 3.0(brs, 3F), 33.7–35.7.(m, 2F), 44.3(s, 2F),46.0(s, 4F), 48.7(s, 2F).

**3da′** [38] $^1$H NMR (60 MHz): 1.00–1.20(t, 3H), 1.35–1.80(stack, 4H), 1.85–2.15(stack, 2H), 2.90–3.57(stack, 2H), 4.17–4.47(m, 1H). $^{19}$F NMR: −35.0(t, 2F)

**3dc′** [39] $^1$H NMR (60 MHz): 1.00–1.10(t, 3H), 1.25–1.80(stack, 10H), 1.90–2.10(stack, 2H), 2.95–3.56(stack, 2H), 4.20–4.50(m, 1H). $^{19}$F NMR: −35.0(t, 2F)

**3de′** $^1$H NMR (60 MHz): 1.10–1.20(t, 3H), 1.30–1.80(stack, 12H), 1.95–2.15(stack, 2H), 2.90–3.45(stack, 2H), 4.10–4.45(m, 1H). $^{19}$F NMR: −35.0(t, 2F)

**3df′** $^1$H NMR (60 MHz): 1.05–1.15(m, 3H), 1.25–1.80(stack,14H), 1.85–2.35(stack, 2H), 2.75–3.52(stack, 2H), 4.05–4.50(m, 1H). $^{19}$F NMR: −35.0(t, 2F).

**3dh′** [38] $^1$H NMR (60 MHz): 2.10–3.05(stack, 4H), 3.05–4.35(stack, 6H). $^{19}$F NMR: −34.0∼−35.0(t, 2F).

**5aa′** [14] $^1$H NMR (60 MHz): 0.90–1.70(stack, 7H), 2.10–2.90(stack, 2H), 6.00–6.60(t, 1H). $^{19}$F NMR: −9.3(t, 2F), 26.7–27.0(dd, 2F, E), 34.0–34.3(dd, 2F, Z), 42.7(s, 2F), 45.7(s, 2F).

**5ab′** [14] $^1$H NMR: 7.23(s, 1H), 7.90(s, 5H). $^{19}$F NMR: −9.6(s, 2F), 26.3–28.0(m, 2F, E), 33.0–34.0(m, 2F, Z), 42.3(s, 2F), 45.0(s, 2F).

**5ac′** $^1$H NMR (60 MHz): 0.97–1.90(stack, 11H), 2.03–2.97(stack, 2H), 6.00–6.63(t, 1H). $^{19}$F NMR: −9.5(t, 2F), 27.5–28.7(dd, 2F, E), 33.7–34.7(m, 2F, Z), 42.3(s, 2F), 45.3(s, 2F).

**5ad′** $^1$H NMR (60 MHz): 1.00(t, 3H), 1.20–2.00(stack, 10H), 2.00–2.90(stack, 2H), 6.10–6.60(t, 1H). $^{19}$F NMR: −9.7(s, 2F), 28.3(s, 2F, E), 34.3(s, 2F, Z), 42.5(s, 2F), 45.7(s, 2F).

**5af′** $^1$H NMR (60 MHz): 3.38(s, 3H, OMe), 3.85–4.35(stack, 2H), 5.88–6.85(m, 1H). $^{19}$F NMR: −9.5(s, 2F), 27.0–27.3(d, 2F, E), 34.3–34.6(m, 2F, Z), 42.0(s, 2F), 45.1(t, 2F).

**5ba′** [14] $^1$H NMR: 0.87–1.17(t, 3H), 1.27–1.77(stack, 4H), 2.07–2.57(m, 1H), 2.57–2.97(m, 1H), 6.17–6.57(m, 1H). $^{19}$F NMR: −9.5(s, 2F), 28.5(m, 2F, E), 34.3(m, 2F, Z), 43.3(s, 2F), 44.3(s, 4F), 46.3(s, 2F).

**5bb′** [14] $^1$H NMR (60 MHz): 6.47(m, 1H), 6.77–7.67(stack, 5H). $^{19}$F NMR: −9.7(s, 2F), 27.3–28.3(m, 2F, E), 34.3(m, 2F, Z), 43.0(s, 2F). 43.5(stack, 4F), 45.3–46.3(m, 2F).

**5bd′** $^1$H NMR (60 MHz): 1.0(m, 3H), 1.15–1.95(stack, 10H), 2.10–2.85(stack, 2H), 6.05–6.55(m, 1H). $^{19}$F NMR: −9.3(s, 2F), 28.0(m, 2F, E), 34.0(m, 2F, Z), 43.0(s, 2F), 44.0(stack, 4F), 45.7–46.7(s, 2F).

**5be′** [40] $^1$H NMR: 2.10–2.44(m, 1H), 4.07–4.57(stack, 2H), 5.97–6.77(m, 1H). $^{19}$F NMR: −9.7(t, 2F), 25.7–27.7(m, 2F, E), 32.3–33.3(m, 2F, Z). 44.0–45.0(stack, 4F), 45.3–46.3(m, 2F).

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