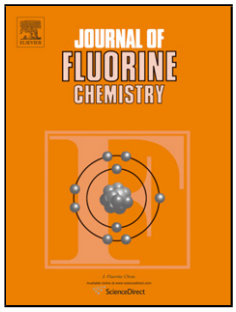

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Synthetic utilization of tetrafluoroethylene-containing silyl reagent (CH_2=$CHCF_2CF_2SiEt_3$) in Cu(I)-mediated cross-coupling reaction with various iodoarenes

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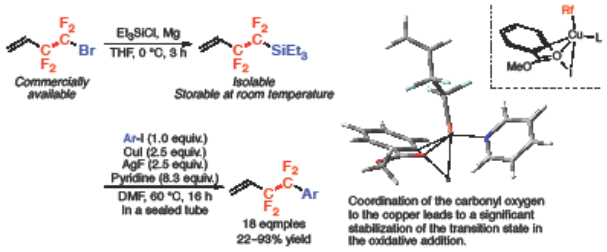
Graphical Abstract



Graphical abstract

Highlight

- Triethyl (1,1,2,2-tetrafluorobut-3-en-1-yl)silane could smoothly couple with various iodoarenes in the presence of Cu(I).
- A directing group (CHO, CO_2Et, etc.) at the *ortho* position in iodoarenes dramatically facilitated the reaction.
- It was theoretically proved that the acceleration effect was due to the coordination of the carbonyl oxygen to the Cu atom.

Abstract: In this article, we revealed synthetic utilization of thermally stable as well as easy-handling triethyl (1,1,2,2-tetrafluorobut-3-en-1-yl)silane as the tetrafluoroethylenating agent through Cu(I)-mediated cross-coupling reaction with various iodoarenes, in which would offer promising building block for versatile CF_2CF_2-containing organic molecules through easy carbon chain elongation at both ends. Specifically, the above tetrafluoroethylene-containing silyl reagent, readily prepared from commercially available 4-bromo-3,3,4,4-tetrafluorobut-1-ene, smoothly reacted with various iodoarenes in the presence of Cu(I), Ag(I), and pyridine in DMF at 60 °C for 16 h, the corresponding CF_2CF_2-containing aromatic compounds being afforded in moderate to good yields. Additionally, it was revealed that the coupling reaction dramatically facilitated when iodoarenes with an *ortho*-directing group, e.g., COOMe, were used as an electrophile, in which the acceleration effect was theoretically proved to stabilize the whole reaction system by coordination of the carbonyl oxygen to the copper atom.

Keyword: Tetrafluoroethylene fragment, Cu(I)-catalyzed cross-coupling reaction, silyl reagent

1. Introduction

In 1998, DiMagno *et al.* reported that replacement of three contiguous hydroxymethylene fragments (-$(CHOH)_3$-) in D-glucose with a hexafluoropropylene moiety (-$(CF_2)_3$-) caused expression of unique biological activities originated from the "Polar hydrophobicity" [1]. Since then, enormous attention has been paid to the synthesis and the evaluation of physical properties for perfluoroalkylenated materials [2]. Among such perfluoroalkylenated substances, particularly in recent years, substances having a *tetrafluoroethylene* group (-CF_2CF_2-) have been watched with keen interest [3]. This is because interesting biological activities were found in tetrafluoroethylenated glucose, galactose, etc [4]. Besides, it gradually becomes apparent that molecules containing a tetrafluoroethylenated carbocycle as a part of mesogen have a large negative dielectric anisotropy ($\Delta\varepsilon$) and become recognized as promising liquid-crystalline molecules (Fig. 1) [5].

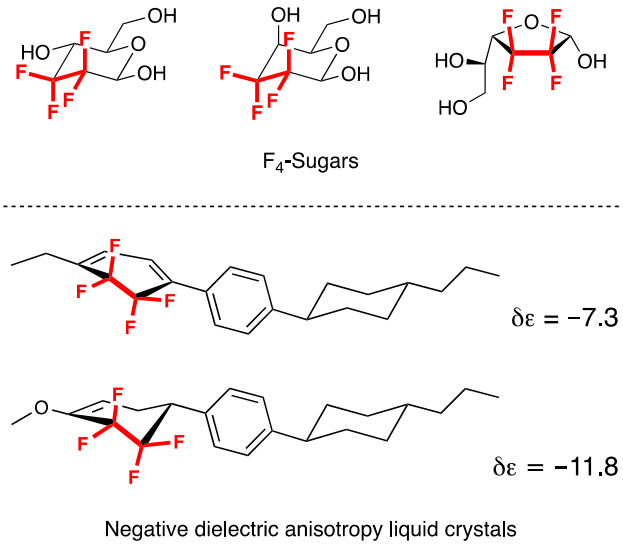


Fig. 1 Various tetrafluoroethylenated materials.

From viewpoint of synthetic application, tetrafluoroethylenating agents, in which *carbon chain elongation can be easily carried out at both ends of a tetrafluoroethylene group*, are extremely valuable for the facile and effective synthesis of various tetrafluoroethylenated molecules, but only two such reagents had been known until we started the present research program: one is 1,2-dibromo-1,1,2,2-tetrafluoroethane (**1**: Halon 2402) [6], and the other is tetrafluoroethylene (**2**: TFE) (Fig. 2) [7]. However, the former is prohibited to use because of the high ozone layer depletion and global warming potentials, and the latter requires careful attention to the handling due to the immediate formation of explosive peroxide when it comes in contact with air.

In order to offer facile, effective, and useful synthetic protocol for the promising tetrafluoroethylenated molecules, we have taken a considerable attention to the synthetic applicability in the commercially available 4-bromo-3,3,4,4-tetrafluorobut-1-ene (**3**), which can easily make carbon-chain elongation through functional groups incorporated at the both ends.

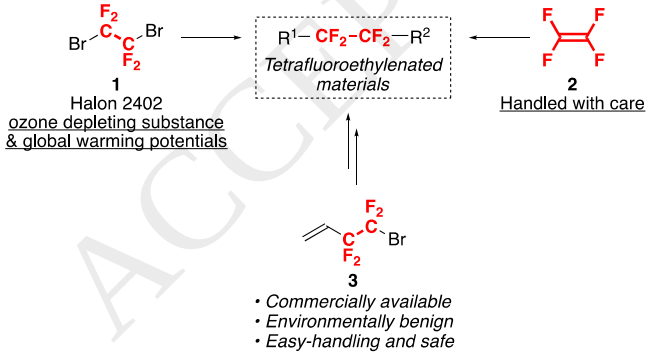
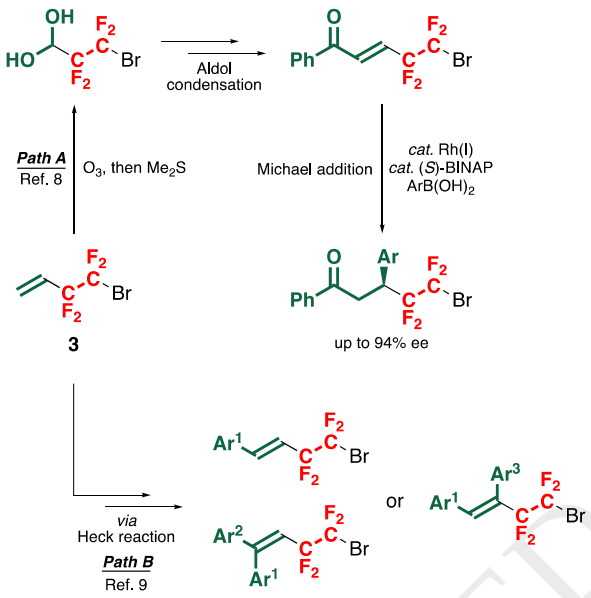


Fig. 2 Synthetic strategies for the preparation of CF_2CF_2-containing materials.

After extensive surveys using promising fluorinate substance **3**, it was demonstrated that successful carbon-chain elongations of **3** at the left ends could be realized by independent C–C bond formation

involving suitable functional group transformations (Scheme 1). For example, the alkene part at the left-hand side of **3** can be converted into the corresponding hydrate through ozonolysis, which reacted with enamine derived from acetophenone, followed by acidic hydrolysis, affording the α,β-unsaturated carbonyl compound containing CF_2CF_2Br unit at the β position (Path A) [8]. Under the influence of rhodium catalyst with (*S*)-BINAP ligand, the CF_2CF_2-containing α,β-unsaturated carbonyl compound undergoes smooth Michael addition reaction with various arylboronic acids, leading to the corresponding adducts in high yields and with excellent enantioselectivity. Besides, direct install of aromatic functionality into the alkene moiety in **3** can be realized by the Pd(0)-catalyzed Heck reaction with various aryldiazonium salts, providing the multi-substituted alkenes in good yield in a highly stereoselective fashion (Path B) [9].

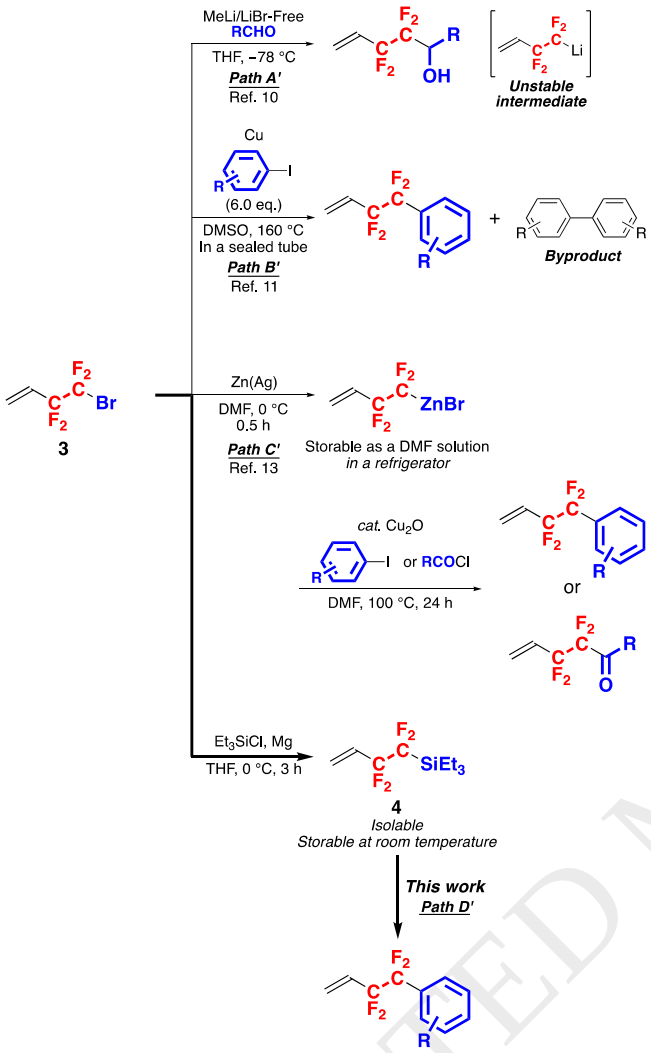


Scheme 1. Synthetic transformations at the alkene part of **3**.

In contrast, functional group transformation at the right-hand side of **3**, *i.e.*, the CF_2CF_2Br moiety, has somewhat lag behind in the development of effective transformation protocol, though there have been reported several chemical transformations at the reactive site so far (Scheme 2). First, coupling reaction of in-situ generated lithium species with various carbonyl compounds affords the corresponding tetrafluoroethylenated bishomoallyl alcohol derivatives (Path A') [10]. Second, Cu-mediated Ullmann-type cross-coupling reaction of **3** with iodoarenes gives rise to the corresponding CF_2CF_2-attached aromatic compounds (Path B') [11]. However, many obstacles still remain unresolved issues on carrying out these reactions: (1) use of thermally unstable and easily decomposed lithium species [10, 12], (2) formation of homo-coupling adducts of iodoarenes, like biaryls, as a major byproduct, and the accompanied need for a large amount of iodoarene (6.0 equiv).

As a promising protocol to overcome such drawbacks, very recently, we successfully developed organozinc reagent, *i.e.*, $CH_2{=}CHCF_2CF_2ZnBr$, with thermal and air stability, which applied to the

effective carbon-chain extension through Cu(I)-catalyzed cross-coupling with haloarenes and acid chlorides, providing the corresponding tetrafluoroethylenated aromatics and ketones, respectively (Path C') [13]. However, a problem still remains: the organozinc reagent should be available only in DMF solution and stored in a refrigerator, which should be settled for more easy handling.



Scheme 2. Synthetic transformations at the CF_2CF_2Br moiety of **3**.

Therefore, we focused on the tetrafluoroethylene-containing silyl reagent, that is, triethyl (1,1,2,2-tetrafluorobut-3-ene-1-yl)silane (**4**) [10], which can be easily prepared from **3** in a single pot, isolated in pure form, and stored at room temperature for a long period of time. In this article, we disclose a clear applicability for the tetrafluoroethylene-containing silyl reagent **4** to the Cu(I)-mediated cross-coupling reaction with various iodoarenes (Path D') [14]. Additionally, we successfully revealed the C–C bond formation dramatically accelerated in case of iodoarene with a directing group at the ortho-position using both experimental and theoretical approaches.

2. Results and discussion

Initial studies began with the investigation of the reaction conditions for the cross-coupling of **4** which was easily prepared from **3** and chlorotriethylsilane in the presence of magnesium turnings [10], with

iodobenzene (**5a**). The results are summarized in Table 1. Thus, treatment of 1.0 equiv. of **5a** with 1.2 equiv. of **4** under the influence of 1.5 equiv. each of CuI and KF in DMSO in a sealed tube at 60 °C for 16 h did not afford the desired product **6a** at all, and the byproduct **7**, in which a triethylsilyl group of **4** was replaced with hydrogen, was given in 43% yield (Entry 1). At this time, the starting material **4** was not recovered at all. As shown in Entries 2–4, other fluoride ion sources, like cesium fluoride (CsF), tetrabutylammonium fluoride (TBAF), or silver fluoride (AgF), were employed for this coupling reaction. As a result, the desired coupling product **6a** was obtained in only 9% yield, along with **7** in 33% yield, when AgF was employed as a fluoride ion (Entry 4).

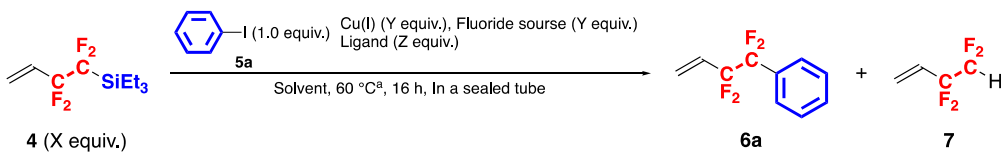
In order to examine the solvent effect, next, the reactions were conducted in various solvents. In the case of CH_3CN, THF, pyridine, and 1,3-dimethyl-2-imidazolidinone (DMI), as shown in Entries 5–7 and 10, no significant change was observed in yield of the desired **6a**. Meanwhile, a large amount of undesired **7** was formed or the starting material **4** was recovered. On the other hand, a slight improvement of yield of **6a** was detected when the reaction was carried out using *N*,*N*'-dimethylpropyleneurea (DMPU), *N*-methylpyrrolidone (NMP), and *N*,*N*-dimethylformamide (DMF) as a solvent (Entries 8, 9, and 11).

With DMF as a solvent, subsequently, the ligand effect on the copper was investigated. As seen in Entries 12–14, 2,2'-bipyridyl, 1,10-phenanthroline, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) did not bring about any satisfactory results. Surprisingly, when 5.0 equiv. of pyridine was used as a ligand, the yield of **6a** was improved from 13% to 26% (Entry 15), though increasing pyridine up to 10 equiv. did not cause any change in the yield (Entry 16).

Furthermore, various other copper salts, such as CuBr, CuCl, and Cu_2O, were examined (Entries 17-19), however, none of them worked well for the reaction, indicating that CuI was found to be the copper salt of choice. It should be noted that decreasing the amount of CuI to 0.6 equiv. resulted in a sluggish formation of the desired **6a** (Entry 20).

Finally, the influence of the molar ratio of **4** and **5a** on this reaction was investigated. Very interestingly, increasing the amount of **4** from 1.2 equiv. to 2.0 equiv. caused a significant improvement of the yield of the desired compound, the **6a** being obtained in 42% yield (Entry 21). However, the use of the excess amount of **4** (up to 3.0 equiv.) did not lead to further satisfactory result (Entry 22). When 3.0 or 6.0 equiv. of **5a** was used relative to **4**, no significant change was observed in the yield of the desired **6a** (Entries 23 and 24). When the reaction temperature was lowered to room temperature or raised to 80 °C, significant decrease of the yield of **6a** was observed (Entries 25 and 26).

Table 1.
Investigation of the reaction conditions for the cross-coupling of **4** with **5a**.



4 (X equiv.) **6a** **7**

Entry	Cu(I)	Fluoride source	Ligand	Molar ratio **5a** : X : Y : Z	Solvent	Yield[b]/% of **6a**	Yield[b]/% of **7**	Recovery[b]/% of **4**
1	CuI	KF	None	1.0 : 1.2 : 1.5 : 0	DMSO	0	43	0
2	CuI	CsF	None	1.0 : 1.2 : 1.5 : 0	DMSO	0	47	0
3	CuI	TBAF	None	1.0 : 1.2 : 1.5 : 0	DMSO	0	23	0
4	CuI	AgF	None	1.0 : 1.2 : 1.5 : 0	DMSO	9	33	0
5	CuI	AgF	None	1.0 : 1.2 : 1.5 : 0	CH_3CN	8	77	0
6	CuI	AgF	None	1.0 : 1.2 : 1.5 : 0	THF	0	0	quant.
7	CuI	AgF	None	1.0 : 1.2 : 1.5 : 0	Pyridine	4	48	0
8	CuI	AgF	None	1.0 : 1.2 : 1.5 : 0	DMPU	11	45	0
9	CuI	AgF	None	1.0 : 1.2 : 1.5 : 0	NMP	12	32	0
10	CuI	AgF	None	1.0 : 1.2 : 1.5 : 0	DMI	5	22	34
11	CuI	AgF	None	1.0 : 1.2 : 1.5 : 0	DMF	13	11	0
12	CuI	AgF	2,2'-Bipyridyl	1.0 : 1.2 : 1.5 : 2.5	DMF	0	17	0
13	CuI	AgF	1,10-Phenanthroline	1.0 : 1.2 : 1.5 : 2.5	DMF	0	37	0
14	CuI	AgF	TMEDA	1.0 : 1.2 : 1.5 : 2.5	DMF	0	47	0
15	CuI	AgF	Pyridine	1.0 : 1.2 : 1.5 : 5.0	DMF	26	22	0
16	CuI	AgF	Pyridine	1.0 : 1.2 : 1.5 : 10.0	DMF	26	26	0
17	CuBr	AgF	Pyridine	1.0 : 1.2 : 1.5 : 5.0	DMF	13	16	0
18	CuCl	AgF	Pyridine	1.0 : 1.2 : 1.5 : 5.0	DMF	3	17	0
19	Cu_2O	AgF	Pyridine	1.0 : 1.2 : 1.5 : 5.0	DMF	0	19	0
20	CuI	AgF	Pyridine	1.0 : 1.2 : –[c] : 5.0	DMF	13	42	0
21	CuI	AgF	Pyridine	1.0 : 2.0 : 2.5 : 8.3	DMF	42	18	0
22	CuI	AgF	Pyridine	1.0 : 3.0 : 3.75 : 12.5	DMF	49	21	0
23	CuI	AgF	Pyridine	3.0 : 1.0 : 1.25 : 4.17	DMF	44	19	0
24	CuI	AgF	Pyridine	6.0 : 1.0 : 1.25 : 4.17	DMF	46	19	0
25[d]	CuI	AgF	Pyridine	1.0 : 1.2 : 1.5 : 5.0	DMF	18	57	0
26[e]	CuI	AgF	Pyridine	1.0 : 1.2 : 1.5 : 5.0	DMF	21	60	0

[a] Bath temp.
[b] Determined by ^{19}F NMR.
[c] With 0.6 equiv. of CuI and 1.5 equiv. of AgF.
[d] Conducted at room temperature.
[e] Conducted at 80 °C.

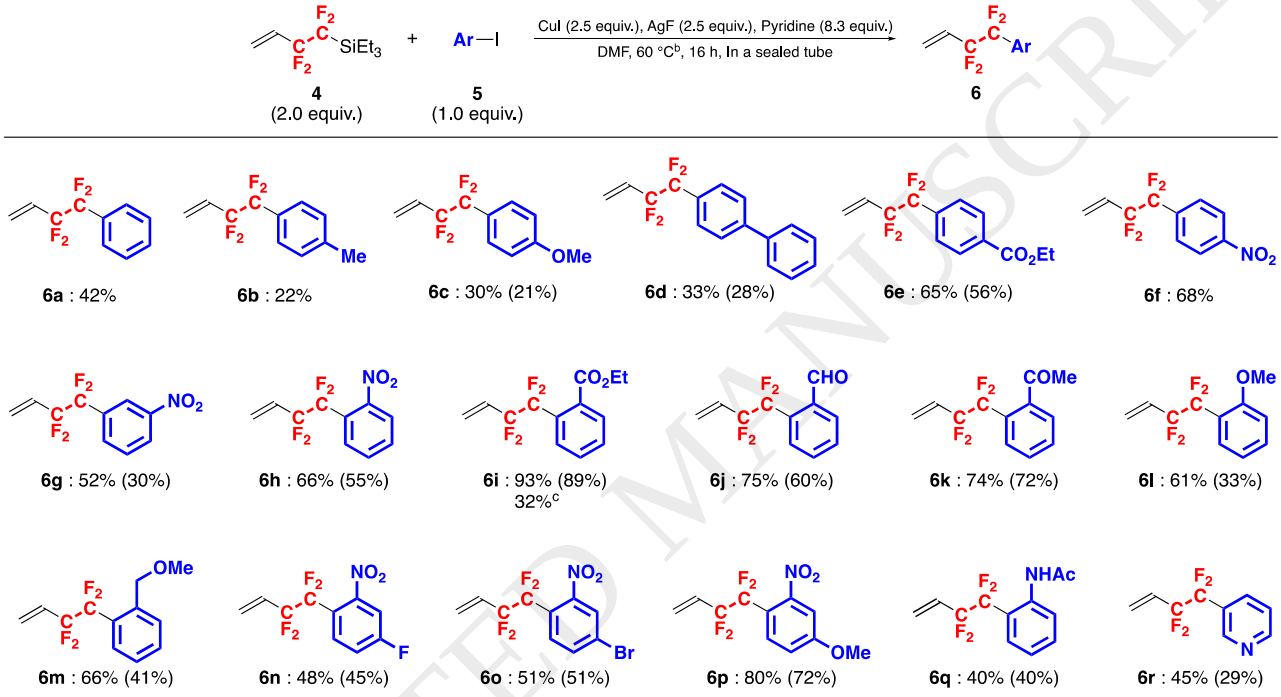
On the basis of the above reaction screening, the reaction conditions shown in Entry 21 (Table 1) were determined to be optimal. Then, our attention was next directed toward the investigation of the substrate scope, and the results are collected in Table 2.

First, when *para*-iodotoluene (**5b**) or *para*-iodoanisole (**5c**) having an electron-donating group, such as a methyl or a methoxy group, on benzene ring was used instead of **5a**, the yields of **6b** or **6c** substantially decreased. A similar phenomenon was observed in the case of *para*-phenyliodobenzene (**5d**). On the other hand, the cross-coupling reaction of ethyl *para*-iodobenzoate (**5e**) or *para*-iodonitrobenzene (**5f**) possessing an electron-withdrawing group on benzene ring proceeded relatively smoothly to give the corresponding coupling products **6e** and **6f** in 65% and 68% yield, respectively. *meta*-Iodonitrobenzene was also found to be a good coupling partner to afford the corresponding adduct **6g** in an acceptable yield.

It should be noted that a coordinating substituent at the *ortho* position of the aromatic ring caused a significant increase of the yield; a carbonyl functionality at the *ortho* position of the benzene ring facilitated the reaction well, coupling products being afforded in 74-93% yield (**6i-k**). A methoxy or a methoxymethyl substituent at the *ortho* position of the benzene ring were expected to retard the present coupling reaction due to their electron-donating characteristics, but in fact, the Cu(I)-mediated cross-coupling reaction with iodoarenes **5l** and **5m** proceeded effectively to afford the

desired products, **6l** and **6m**, in 61% and 66% yield, respectively. *ortho*-Iodonitrobenzene derivatives, *e.g.*, **5h**, **5n**, **5o**, and **5p**, could participate in the coupling reaction well to give the corresponding products **6h**, **6n-p** in moderate to high yields. Unfortunately, the reaction using *ortho*-iodoacetanilide (**5q**) or 3-iodopyridine (**5r**) proceeded sluggishly to give rise to the corresponding products **6q** and **6r** in only 40% and 45% yield, respectively. When methyl *ortho*-bromobenzoate was used instead of methyl *ortho*-iodobenzoate (**5i**), the desired adduct **6i** was obtained in only 32% yield.

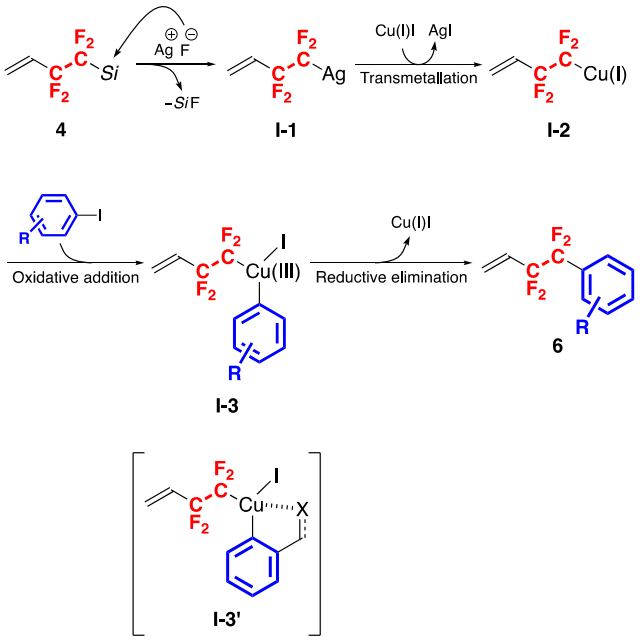
Table 2.
Cross-coupling reaction of **4** with various iodoarenes **5**[a]



[a] Yields are determined by ^{19}F NMR. Values in parentheses are of isolated yield.
[b] Bath temp.
[c] Ethyl 2-bromobenzoate was used instead of ethyl 2-iodobenzoate.

The reaction mechanism of the present cross-coupling reaction can be proposed as shown in Scheme 3.

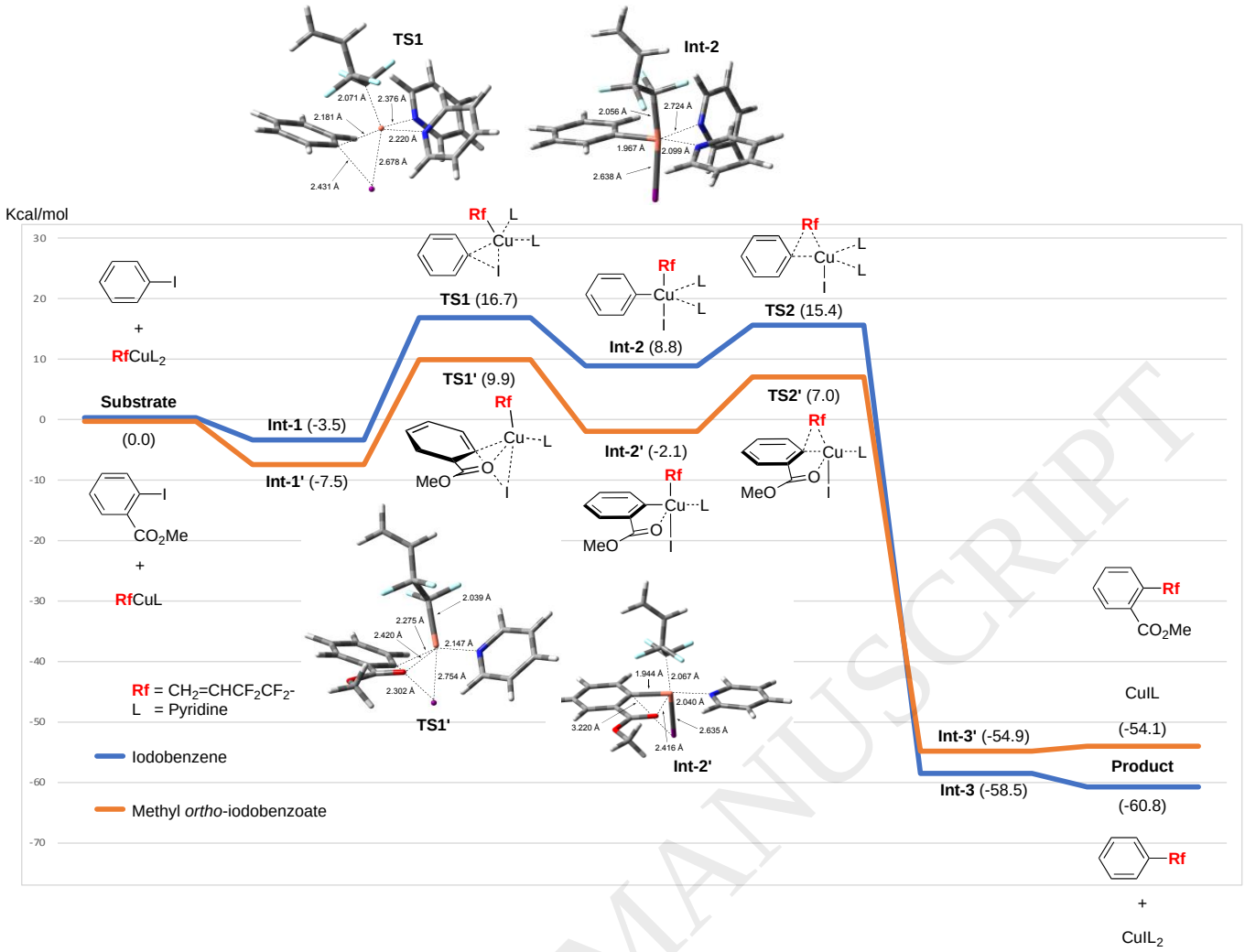
That is to say, nucleophilic attack of fluoride ion derived from AgF against a silicon center in **4**, followed by immediate elimination of triethylfluorosilane, causes a formation of a tetrafluoroethylene-containing silver intermediate **I-1**, which smoothly undergoes transmetallation by Cu(I)I to produce the corresponding copper species **I-2**. The carbon–iodine bond of iodoarene substrates oxidatively adds to the copper intermediate **I-2**, giving rise to the copper(III) intermediate **I-3**. Finally, subsequent reductive elimination of the **I-3** successfully produces the desired cross-coupling product **6**. High reaction efficiency in the case of introducing substituents, like a nitro, an ethoxycarbonyl, a formyl, an acetyl group, and so on, into the *ortho* position of iodoarenes may stem from stabilization of **I-3'** through coordination of the substituent to the copper center [15].



Scheme 3. A proposed reaction mechanism.

To gain further understanding on the reaction mechanism for the present smooth coupling reaction of the *ortho*-substituted iodoarenes, the free energy of fully optimized molecular geometries of all the stationary points and transition states were calculated with density functional theory (DFT) methods using B3LYP functional with 6-31+G(d,p) basis sets [16]. In order to more accurately evaluate the *ortho*-substitution effect, the calculation was also done for the reaction of iodoarene without a substituent at the *ortho* position. Fig. 3. shows energy profiles for the coupling reactions with iodobenzene and methyl *ortho*-iodobenzoate *via* initial intermediates (**Int-1**/**Int-1'**), the transition states for the oxidative addition (**TS1**/**TS1'**), the second intermediates (**Int-2**/**Int-2'**), the transition states for the reductive eliminations (**TS2**/**TS2'**), and the third intermediates (**Int-3**/**Int-3'**) [17].

For the coupling reaction using iodobenzene (blue line in Fig. 3.), the energy level of the transition state **TS1** in the oxidative addition is very high, that is, 16.7 kcal/mol, when the initial state is used as a reference. In addition, the activation energy at that time is also extremely high as 20.2 kcal/mol. When it comes to the reductive elimination, the activation energy is not as high as in the case of the oxidative addition, only 6.6 kcal/mol, though the energy level of the transition state **TS2** in this process is still high, that is, 15.4 kcal/mol. This stems from the fact that one of the distances between the pyridine nitrogen and the copper atom in **Int-2** is 2.724 Å, which is extremely long, so that **Int-2** is not sufficiently stabilized and has a high energy level. However, the energy level of the transition state in the reductive elimination is 1.3 kcal/mol lower than that in the oxidative addition, hence indicating that the rate-determining step in the copper(I)-mediated coupling reaction using iodobenzene is likely to be the oxidative addition step.



		Oxidative addition			Reductive elimination			Kcal/mol
Substrate	Substrate (Initial state)	**Int-1** or **Int-1'**	Transition state	Activation energy	**Int-2** or **Int-2'**	Transition state	Activation energy	**Int-3** or **Int-3'**	Product (Final state)
Iodobenzene	0	- 3.5	16.7	20.2	8.8	15.4	6.6	- 58.5	- 60.8
Methyl *o*-iodobenzoate	0	- 7.5	9.9	17.4	- 2.1	7.0	9.1	- 54.9	- 54.1

Fig. 3. Energy diagrams of the coupling reaction of iodobenzene or methyl *o*-iodobenzoate with the CF_2CF_2-containing copper reagent (CH_2=CH-CF_2CF_2Cu(Pyridine)$_n$)

For the coupling reaction using methyl *ortho*-iodobenzoate (orange line in Fig. 3.), on the other hand, the intermediate **Int-1'** is somewhat more stable than **Int-1**, that is, -7.5 kcal/mol for **Int-1'** *vs* -3.5 kcal/mol for **Int-1**, against the initial state. It is highly possible that the interaction occurring between the carbonyl oxygen of methyl *ortho*-iodobenzoate and the hydrogen at 2 position of pyridine ligand on copper resulted in the formation of a more stable complex (the calculated structure of **Int-1'** is not shown in Fig. 3. See the supplementary materials). In transition state **TS1'**, the distance between the carbonyl oxygen of methyl *ortho*-iodobenzoate and the copper atom is 2.420 Å, indicative of the relatively strong interaction. Since **TS1'** is stabilized by this coordination effect, the energy level of **TS1'** is only 9.9 kcal/mol. Therefore, the activation energy (17.4 kcal/mol) of the oxidative addition is also 2.8 kcal/mol lower than that in case of

using iodobenzene (20.2 kcal/mol). This coordination also brings a remarkable effect in the subsequent intermediate **Int-2'**. That is, the distance between the carbonyl oxygen of the methoxycarbonyl group in **Int-2'** and the copper atom is 2.416 Å, which is almost the same in **TS1'**. Accordingly, a large stabilization occurs and the energy level of **Int-2'** is reduced to -2.1 kcal/mol. Even in the transition state of the reductive elimination, the energy level is considerably low (7.0 kcal/mol) due to the stabilization effect by this coordination. Due to the large stabilization of intermediate **Int-2'**, the activation energy is 9.1 kcal/mol, which is higher by 2.5 kcal/mol than that in the case of iodobenzene. However, as in the case of iodobenzene, the energy level of the transition state in the reductive elimination is lower by 2.9 kcal/mol than that in the oxidative addition, indicating that this cross-coupling may also be a reaction in which the oxidative addition is the rate-determining step.

From the above results, it could be theoretically proved that introduction of a carbonyl substituent to the *ortho* position generates a large stabilizing effect in the whole reaction system due to the coordination of the carbonyl oxygen to the copper atom, resulting in the increase of the reaction efficiency.

3. Conclusions

In summary, we examined the Cu(I)-mediated cross-coupling reaction of easily handled tetrafluoroethylene-containing silyl reagent ($BrCF_2CF_2SiEt_3$, **4**), which is readily accessible from commercially available 4-bromo-3,3,4,4-tetrafluorobut-1-ene (**3**), with a variety of iodoarenes. As a result of intensive investigation, it was found that the desired coupling products could be obtained through the reaction under the influence of copper(I) iodide, silver fluoride, and pyridine in DMF at 60 ° C for 16 h, and various kinds of iodoarenes could be applied for this reaction as well. In particular, iodoarenes having a coordinating substituent at the *ortho* position furnished the products in good to high yields. It could be theoretically proved that this high reaction efficiency stems from a large stabilization in the whole reaction system through coordination of the coordinating substituent to the copper atom. It was demonstrated that the present synthetic protocol was facile and efficient pathway for the transformation of the right-hand side of **3**, which would become promising entry to offer various CF_2CF_2-containing materials, given the possible synthetic transformation at the opposite side using our previous protocol.

4. Experimental

4.1. General methods

Infrared spectra (IR) were determined in a liquid film on a NaCl plate with a JASCO FT/IR-4100 typeA spectrometer. ^1H and ^{13}C NMR spectra were measured with a Bruker AVANCE Ⅲ 400 NMR spectrometer in a chloroform-*d* ($CDCl_3$) solution and residual $CHCl_3$ as an internal standard. A Bruker AVANCE Ⅲ

400 NMR spectrometer was used for determining the yield of the product with benzotrifluoride ($CF_3C_6H_5$). ^{19}F NMR (376.05 MHz) spectra were measured with a Bruker AVANCE Ⅲ 400 NMR spectrometer in a chloroform-*d* ($CDCl_3$) solution with trichlorofluoromethane ($CFCl_3$) as an internal standard. High-resolution mass spectra (HRMS) were taken on a JEOL JMS-700MS spectrometer by electron impact (EI), chemical ionization (CI), and fast atom bombardment (FAB) methods.

All reactions were routinely monitored by ^{19}F NMR spectroscopy or TLC, and carried out under an atmosphere of argon.

All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use. Thin-layer chromatography (TLC) was done with Merck silica gel 60 F_{254} plates, and column chromatography was carried out using Wakogel C-200 (75–150 μm) and Wakogel 60N (38–100 μm), as adsorbent.

4.2. Preparation of a silyl reagent 4[10]

To a suspension of Mg (0.44 g, 18.0 mmol) in THF (30.0 mL) was added a chlorotriethylsilane (2.3 g, 15.0 mmol) at 0 °C. After about 5 min, to this mixture was dropwise added 4-bromo-3,3,4,4-tetrafluorobut-1-ene (**3** : 3.7 g, 18.0 mmol) over 30 min. and the whole was stirred at the same temperature for 3 h. To the mixture was added excess amount of hexane (100 mL) and then the whole was filtered. After the mixture was concentrated in *vacuo*, the residue was purified by silica gel column chromatography: hexane only; to give triethyl(1,1,2,2-tetrafluorobut-3-en-1-yl)silane (**4**).

Triethyl-(1,1,2,2-tetrafluorobut-3-en-1-yl)silane (4). Yield: 79% (Determined by ^{19}F NMR); Known compound; ^{1}H NMR ($CDCl_3$) δ 0.84 (q, *J* = 7.2 Hz, 6H, C*H*$_2$CH$_3$), 1.04 (t, *J* = 7.2 Hz, 9H, CH$_2$C*H*$_3$), 5.65 (d, *J* = 11.6 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.81 (d, *J* = 17.3, Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 5.99 (dtd, *J* = 17.3, 12.0, 11.6 Hz, 1H, CF$_2$C*H*-) ppm; ^{13}C NMR ($CDCl_3$) δ 1.41 (CH$_2$*C*H$_3$), 6.64 (d, *J* = 11.7 Hz, *C*H$_2$CH$_3$), 117.5 (tt, *J* = 242.7, 31.3 Hz, *C*F$_2$), 123.1 (t, *J* = 9.0 Hz, *C*H$_2$=), 123.9 (tt, *J* = 270.4, 51.2 Hz, *C*F$_2$), 126.9 (t, *J* = 25.6 Hz, CF$_2$*C*H=); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ –110.99 (d, *J* = 12.0 Hz, 2F, C*F*$_2$CH=), –126.9 (s, 2F, C*F*$_2$SiE$_3$); IR (neat) ν 3108, 2960, 2884, 2742, 1912, 1653, 1461, 1419, 1383, 1243, 1091, 1029, 981, 955, 919, 889, 802, 741, 604, 579, 491, 408 cm^{-1}; HRMS (EI^+) calcd. for $[M]^+$ $C_{17}H_{18}F_4Si$: 242.1114, Found 242.1100.

4.3. General procedure for the cross-coupling reaction of the silyl reagent with various iodoarenes

A sealed tube was charged with CuI (0.19 g, 1.0 mmol, 2.5 equiv.), AgF (0.13 g, 1.0 mmol, 2.5 equiv.), pyridine (0.27 mL, 8.3 equiv.), various iodoarenes (0.4 mmol, 1.0 equiv.), triethyl(1,1,2,2-tetrafluorobut-3-en-1-yl)silane (**4** : 0.19 g, 0.8 mmol, 2.0 equiv.) and DMF (3.2 mL, 0.25 M) in glove box. The sealed tube was brought under an atmosphere of argon and capped. The resulting mixture was stirred at 60 °C for 16 h, and then cooled room temperature. The resulting mixture was passed through short column. The eluent was concentrated in *vacuo* to give the crude materials, which were purified by silica gel column chromatography, leading to the desired coupling products.

*4.3.1. 3,3,4,4-Tetrafluoro-4-phenylbut-1-ene (**6a**)*

Yield: 42% (Determined by ^{19}F NMR); Known compound; ^{1}H NMR ($CDCl_3$) δ 5.69 (d, *J* = 11.6 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.83 (dt, *J* = 17.2, 1.6 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.02 (ddt, *J* = 17.2, 11.6, 11.5 Hz, 1H, CF$_2$C*H*=), 7.44 to 7.58 (m, 5H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 115.1 (tt, *J* = 248.8, 37.2 Hz, *C*F$_2$), 116.4 (tt, *J* = 252.1, 35.5 Hz, *C*F$_2$), 124.1 (t, *J* = 9.9 Hz, *C*H$_2$=), 126.7 (t, *J* = 24.8 Hz, CF$_2$*C*H=), 126.9 (td, *J* = 6.6, 1.7 Hz, Ar), 127.0–127.7 (m, Ar), 128.2 (Ar), 131.0 (t, *J* = 1.7 Hz, Ar); ^{19}F NMR ($CDCl_3$): *δ* –112.56 (s, 2F, C*F*$_2$Ar), –114.95 (d, *J* = 11.46 Hz, 2F, C*F*$_2$CH=); IR (neat): *ν* 3071, 1653, 1424, 1286, 1243, 1130, 1070, 949 cm^{-1}; HRMS (FAB) calcd for [M]$^+$ $C_{10}H_8F_4$: 204.0562, found 204.0558.

*4.3.2. 3,3,4,4-Tetrafluoro-4-(4-methylphenyl)but-1-ene (**6b**)*

Yield: 22% (Determined by ^{19}F NMR); Known compound; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H, C*H*$_3$), 5.68 (d, *J* = 11.2 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.82 (dt, *J* = 17.5, 2. 0 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.01 (ddt, *J* = 17.5, 11.2, 11.4 Hz, 1H, CF$_2$C*H*=), 7.26 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.44 (d, *J* = 8.4 Hz, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 21.3 (*C*H$_3$), 115.1 (tt, *J* = 248.4, 37.6 Hz, *C*F$_2$), 116.6 (tt, *J* = 251.3, 35.1 Hz, *C*F$_2$), 124.0 (t, *J* = 9.5 Hz, *C*H$_2$=), 126.8 (t, *J* = 24.8 Hz, CF$_2$C*H*=), 126.6–127.1 (m, Ar), 127.9 (t, *J* = 24.8 Hz, Ar), 128.9 (Ar), 141.2 (t, *J* = 1.7 Hz, Ar); ^{19}F NMR ($CDCl_3$): *δ* –112.24 (s, 2F, C*F*$_2$Ar), –115.04 (d, *J* = 11.4 Hz, 2F, C*F*$_2$CH=); IR (neat): *ν* 3043, 2927, 1617, 1420, 1288, 1243, 1121, 1074, 982, 818 cm^{-1}; HRMS (FAB) calcd for [M]$^+$ $C_{11}H_{10}F_4$: 218.0719, found 218.0726.

*4.3.3. 3,3,4,4-Tetrafluoro-4-(4-methoxyphenyl)but-1-ene (**6c**)*

Yield: 21% (20 mg, 0.085 mmmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3H, C*H*$_3$), 5.67 (d, *J* = 11.3 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.81 (dt, *J* = 17.2, 2.0 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.00 (ddt, *J* = 17.2, 11.4, 11.3 Hz, 1H, CF$_2$C*H*=), 6.95 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.48 (d, *J* = 8.8 Hz, 2H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 55.7 (*C*H$_3$), 114.0 (Ar), 115.5 (tt, *J* = 249.0, 38.2 Hz, *C*F$_2$), 116.9 (tt, *J* = 251.6, 35.1 Hz, *C*F$_2$), 123.2 (t, *J* = 25.4 Hz, Ar), 124.3 (t, *J* = 9.2 Hz, *C*H$_2$=), 127.3 (t, *J* = 24.9 Hz, CF$_2$*C*H=), 128.7 (t, *J* = 6.3 Hz, Ar), 161.9 (Ar); ^{19}F NMR ($CDCl_3$): *δ* –111.52 (s, 2F, C*F*$_2$Ar), –115.01 (d, *J* = 11.4 Hz, 2F, C*F*$_2$CH=); IR (neat): *ν* 2938, 1519, 1420, 1260, 1181, 1095, 1074, 982, 832 cm^{-1}; HRMS (FAB) calcd for [M]$^+$ $C_{11}H_{10}F_4O$: 234.0668, found 234.0672.

*4.3.4. 4-(1,1,2,2-Tetrafluoro-3-buten-1-yl)biphenyl (**6d**)*

Yield: 28% (32 mg, 0.11 mmol); White solid (hexane, R_f = 0.42); m.p. = 73–75 °C; ^{1}H NMR ($CDCl_3$) δ 5.72 (d, *J* = 11.2 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.87 (dt, *J* = 17.4, 1.9 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.06 (dtd, *J* = 17.4, 11.3, 11.2 Hz, 1H, CF$_2$C*H*=), 7.40 (tt, *J* = 7.3, 1.6 Hz, 1H, Ar*H*), 7.48 (tm, *J* = 7.4 Hz, 2H, Ar*H*), 7.61 to 7.69 (m, 6H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$) δ 115.3 (tt, *J* = 249.2, 37.6 Hz, *C*F$_2$), 116.6 (tt, *J* = 251.8, 35.3 Hz, *C*F$_2$), 124.3 (t, *J* = 9.2 Hz, *C*H$_2$=), 126.9 (t, *J* = 24.0 Hz, CF$_2$*C*H=), 127.1 (*Ar*), 127.4 (*Ar*), 127.5 (t, *J* = 6.6 Hz, *Ar*), 128.1 (*Ar*), 129.1 (*Ar*), 129.7 (t, *J* = 25.0 Hz, *Ar*), 140.2 (*Ar*), 144.0 (*Ar*) ppm; ^{19}F

NMR ($CDCl_3$) δ –112.28 (s, 2F, CF_2Ar), –114.82 (d, *J* = 11.4 Hz, 2F, CF_2CH=) ppm; IR (KBr) ν 3083, 3065, 3037, 2957, 2925, 2852, 1955, 1928, 1883, 1727, 1672, 1651, 1613, 1584, 1570, 1490, 1452, 1421, 1406, 1365, 1344, 1309 cm^{-1}; HRMS (FAB) calcd. for $[M]^+$ $C_{16}H_{12}F_4$: 280.0875, Found 280.0864.

*4.3.5. Ethyl 4-(1,1,2,2-tetrafluorobut-3-en-1-yl)benzoate (**6e**)*

Yield: 56% (68 mg, 0.25 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 1.41 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 4.41 (q, *J* = 7.2 Hz, 2H, CH_2CH_3), 5.71 (d, *J* = 11.2 Hz, 1H, *trans*-CH_2=$CHCF_2$), 5.83 (dt, *J* = 17.2, 2.0 Hz, 1H, *cis*-CH_2=$CHCF_2$), 6.01 (ddt, *J* = 17.2, 11.5, 11.2 Hz, 1H, CF_2CH=), 7.63 (d, *J* = 8.0 Hz, 2H, Ar*H*), 8.13 (d, *J* = 8.0 Hz, 2H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 14.6 (CH_2CH_3), 61.7 (CH_2CH_3), 115.3 (tt, *J* = 249.4, 36.9 Hz, CF_2), 116.4 (tt, *J* = 252.3, 35.7 Hz, CF_2), 124.8 (t, *J* = 9.3 Hz, CH_2=), 126.7 (t, *J* = 24.7 Hz, CF_2CH=), 127.3 (t, *J* = 6.4 Hz, Ar), 129.7 (Ar), 133.4 (Ar), 135.2 (t, *J* = 24.8 Hz, Ar), 166.0 (C=O); ^{19}F NMR ($CDCl_3$): *δ* –112.88 (s, 2F, CF_2Ar), –114.70 (d, *J* = 11.5 Hz, 2F, CF_2CH=); IR (neat): *ν* 2985, 1725, 1412, 1279, 1218, 1136, 1076, 981, 855 cm^{-1}; HRMS (FAB) calcd for $[M+H]^+$ $C_{13}H_{13}F_4O_2$: 277.0852, found 277.0853.

*4.3.6. 3,3,4,4-Tetrafluoro-4-(4-nitrophenyl)but-1-ene (**6f**)*

Yield: 68% (Determined by ^{19}F NMR); Known compound; ^{1}H NMR ($CDCl_3$): δ 5.77 (d, *J* = 11.2 Hz, 1H, *trans*-CH_2=$CHCF_2$), 5.88 (dt, *J* = 17.3, 2.0 Hz, 1H, *cis*-CH_2=$CHCF_2$), 6.04 (ddt, *J* = 17.3, 11.4, 11.2 Hz, 1H, CF_2CH=), 7.77 (d, *J* = 8.7 Hz, 2H, Ar*H*), 8.32 (d, *J* = 8.7 Hz, 2H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 115.0 (tt, *J* = 249.5, 37.1 Hz, CF_2), 115.8 (tt, *J* = 252.9, 36.5 Hz, CF_2), 123.6 (Ar), 125.2 (t, *J* = 9.4 Hz, CH_2=), 126.0 (t, *J* = 24.5 Hz, CF_2CH=), 128.5 (t, *J* = 6.4 Hz, Ar), 137.0 (t, *J* = 25.0 Hz, Ar), 149.8 (Ar); ^{19}F NMR ($CDCl_3$): *δ* –112.72 (s, 2F, CF_2Ar), –114.25 (d, *J* = 11.4 Hz, 2F, CF_2CH=); IR (neat): *ν* 3121, 1613, 1533, 1421, 1284, 1242, 1139, 1077, 945, 849 cm^{-1}; HRMS (FAB) calcd for $[M]^+$ $C_{10}H_7F_4NO_2$: 249.0413, found 249.0422.

*4.3.7. 3,3,4,4-Tetrafluoro-4-(3-nitrophenyl)but-1-ene (**6g**)*

Yield: 30% (32 mg, 0.13 mmol); Yellow oil (Hexane/Et_2O = 40/1, R_f =0.29); ^{1}H NMR ($CDCl_3$) δ 5.78 (d, *J* = 11.2 Hz, 1H, *trans*-CH_2=$CHCF_2$), 5.89 (dt, *J* = 17.2, 2.0 Hz, 1H, *cis*-CH_2=$CHCF_2$), 6.07 (dtdm, *J* = 17.2, 11.3, 11.2 Hz, 1H, CF_2CH=), 7.69 (t, *J* = 7.9 Hz, 1H, Ar*H*), 7.91 (d, *J* = 7.9 Hz, 1H, Ar*H*), 8.40 (dm, *J* = 7.9 Hz, 1H, Ar*H*), 8.45 (s, 1H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$) δ 115.0 (tt, *J* = 249.0, 37.2 Hz, CF_2), 115.6 (tt, *J* = 253.7, 37.3 Hz, CF_2), 122.5 (t, *J* = 6.8 Hz, *Ar*), 125.2 (t, *J* = 9.2 Hz, CH_2=), 126.0 (t, *J* = 24.6 Hz, CF_2CH=), 126.1 (*Ar*), 129.8 (*Ar*), 132.9 (t, *J* = 26.0 Hz, *Ar*), 133.0 (t, *J* = 6.1 Hz, *Ar*), 148.3 (*Ar*) ppm; ^{19}F NMR ($CDCl_3$) δ –112.26 (s, 2F, CF_2Ar), –114.18 (d, *J* = 11.3 Hz, 2F, CF_2CH=) ppm; IR (neat) ν 3096, 2959, 2928, 2878, 1982, 1927, 1724, 1651, 1591, 1539, 1484, 1442, 1420, 1352, 1301, 1275, 1244, 1220 cm^{-1}; HRMS (FAB) calcd. for $[M+H]^+$ $C_{10}H_8F_4NO_2$: 250.0486, Found 250.0491.

*4.3.8. 3,3,4,4-Tetrafluoro-4-(2-nitrophenyl)but-1-ene (**6h**)*

Yield: 55% (56 mg, 0.22 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 5.76 (d, *J* = 11.4 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.91 (dt, *J* = 17.0, 2.0 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.07 (ddtm, *J* = 17.0, 11.4, 11.3 Hz, 1H, CF$_2$C*H*=), 7.55 to 7.59 (m, 1H, Ar*H*), 7.63 to 7.72 (m, 3H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 115.1 (tt, *J* = 250.5, 36.9 Hz, *C*F$_2$), 115.5 (tt, *J* = 254.4, 37.3 Hz, *C*F$_2$), 122.6 (t, *J* = 25.7 Hz, CF$_2$*C*H=), 123.9 (Ar), 125.1 (t, *J* = 9.3 Hz, *C*H$_2$=), 125.9 (t, *J* = 24.4 Hz, Ar), 130.1 (tt, *J* = 6.9, 2.6 Hz, Ar), 131.0 (Ar), 132.6 (Ar), 149.8 (Ar); ^{19}F NMR ($CDCl_3$): *δ* −107.35 (s, 2F, C*F*$_2$Ar), −113.02 (d, *J* = 11.4 Hz, 2F, C*F*$_2$CH=); IR (neat): *ν* 3086, 2904, 1609, 1540, 1420, 1372, 1220, 1163, 1119, 980, 851 cm^{-1}; HRMS (FAB) calcd for [M+Na]$^+$ $C_{10}H_7F_4NNaO_2$: 272.0311, found 272.0313.

*4.3.9. Ethyl 2-(1,1,2,2-tetrafluorobut-3-en-1-yl)benzoate (**6i**)*

Yield: 89% (102 mg, 0.37 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 4.36 (q, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_3$), 5.70 (d, *J* = 11.0 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.86 (dt, *J* = 17.3, 2.2 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.07 (ddt, *J* = 17.3, 11.4, 11.0 Hz, 1H, CF$_2$C*H*=), 7.47 to 7.62 (m, 4H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 14.1 (CH$_2$*C*H$_3$), 61.9 (*C*H$_2$CH$_3$), 115.2 (tt, *J* = 250.2, 37.2 Hz, *C*F$_2$), 116.6 (tt, *J* = 253.4, 36.1 Hz, *C*F$_2$), 124.2 (t, *J* = 9.3 Hz, *C*H$_2$=), 126.8 (t, *J* = 24.4 Hz, CF$_2$*C*H=), 127.7 (t, *J* = 24.5 Hz, Ar), 128.5 (Ar), 128.7–128.9 (m, Ar), 129.7 (Ar), 131.1 (Ar), 133.8 (t, *J* = 3.3 Hz, Ar), 168.6 (*C*=O); ^{19}F NMR ($CDCl_3$): *δ* −106.44 (s, 2F, C*F*$_2$Ar), −113.42 (d, *J* = 11.4 Hz, 2F, C*F*$_2$CH=); IR (neat): *ν* 3076, 2988, 2903, 1739, 1578, 1415, 1370, 1269, 1152 cm^{-1}; HRMS (FAB) calcd for [M+H]$^+$ $C_{13}H_{13}F_4O_2$: 277.0852, found 277.0847.

*4.3.10. 2-(1,1,2,2-Tetrafluorobut-3-en-1-yl)benzaldehyde (**6j**)*

Yield: 60% (54 mg, 0.23 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 5.78 (d, *J* = 11.5 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.91 (dt, *J* = 17.3, 2.0 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.09 (ddtm, *J* = 17.3, 11.5, 11.4 Hz, 1H, CF$_2$C*H*=), 7.63 to 7.71 (m, 3H, Ar*H*), 8.11 to 8.13 (m, 1H, Ar*H*), 10.36 (t, *J* = 1.7 Hz, 1H, C*H*O) ppm; ^{13}C NMR ($CDCl_3$): *δ* 115.1 (tt, *J* = 249.1 Hz, 37.5 Hz, *C*F$_2$), 117.5 (tt, *J* = 253.3, 37.7 Hz, *C*F$_2$), 125.3 (t, *J* = 9.2 Hz, Ar), 126.0 (t, *J* = 24.7 Hz, CF$_2$*C*H=), 128.7 (t, *J* = 9.5 Hz, *C*H$_2$=), 128.8 (Ar), 131.3 (t, *J* = 24.8 Hz, Ar), 131.7 (Ar), 133.1 (Ar), 135.7 (t, *J* = 1.4 Hz, Ar), 191.0 (tt, *J* = 7.3, 3.9 Hz, *C*=O); ^{19}F NMR ($CDCl_3$): *δ* −103.57 (s, 2F, C*F*$_2$Ar), −114.28 (d, *J* = 11.4 Hz, 2F, C*F*$_2$CH=); IR (neat): *ν* 3075, 2925, 1699, 1597 1417, 1213, 1128, 922 cm^{-1}; HRMS (FAB) calcd for [M+H]$^+$ $C_{11}H_9F_4O$: 233.0590, found 233.0593.

*4.3.11. 2-(1,1,2,2-Tetrafluorobut-3-en-1-yl)acetophenone (**6k**)*

Yield: 72% (70 mg, 0.28 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, C*H*$_3$), 5.71 (d, *J* = 11.4 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.86 (dtm, *J* = 17.3, 2.3 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.04 (ddtm, *J* = 17.3, 11.42, 11.36 Hz, 1H, CF$_2$C*H*=), 7.23 to 7.25 (m, 1H, Ar*H*), 7.47 to 7.60 (m, 3H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 31.8 (*C*H$_3$), 115.2 (tt, *J* = 249.8, 37.5 Hz, *C*F$_2$), 116.9 (tt, *J* = 253.0, 36.3 Hz, *C*F$_2$), 124.6 (t, *J* = 9.3 Hz, *C*H$_2$=), 125.8 (Ar), 126.1 (t, *J* = 24.7 Hz, Ar), 126.4 (t, *J* = 24.4 Hz, CF$_2$*C*H=), 128.8 (tt, *J* = 7.1, 2.6 Hz, Ar), 129.0 (Ar), 131.3 (Ar), 142.6 (t, *J* = 2.9 Hz, Ar), 203.8 (*C*=O); ^{19}F NMR ($CDCl_3$, $CFCl_3$): *δ*

–105.50 (s, 2F, CF_2Ar), –113.53 (d, J = 11.4 Hz, 2F, CF_2CH=); IR (neat): ν 3415, 3072, 2989, 2942, 1709, 1569, 1412, 1250, 1208, 1143, 1108, 1086, 1054, 941, 922 cm^{-1}; HRMS (FAB) Calcd for $[M+H]^+$ $C_{12}H_{11}F_4O$: 247.0746, Found 247.0749.

*4.3.12. 3,3,4,4-Tetrafluoro-4-(2-methoxyphenyl)but-1-ene (**6l**)*

Yield: 33% (31 mg, 0.13 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3H, CH_3), 5.64 (d, J = 11.7 Hz, 1H, *trans*-CH_2=CHCF_2), 5.80 (dt, J = 17.1, 2.1 Hz, 1H, *cis*-CH_2=CHCF_2), 6.07 (ddt, J = 17.1, 11.7, 11.5 Hz, 1H, CF_2CH=), 6.98 to 7.49 (m, 4H, ArH) ppm; ^{13}C NMR ($CDCl_3$) δ 56.2 (OCH_3), 112.9 (Ar), 115.8, (tt, J = 249.9, 36.9 Hz, CF$_2$), 117.2 (tt, J = 253.6, 35.9 Hz, CF$_2$), 119.1 (t, J = 23.3 Hz, Ar), 120.5 (Ar), 123.4 (t, J = 9.3 Hz, CH$_2$=), 127.7 (t, J = 24.5 Hz, CF$_2$$C$H=), 129.8 (t, J = 8.49 Hz, Ar), 133.0 (Ar), 158.6 (t, J = 2.5 Hz, Ar); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ –109.59 (s, 2F), –114.87 (d, J = 11.5 Hz, 2F); IR (neat) 3008, 2945, 2843, 1605, 1588, 1497, 1468, 1439, 1420, 1300, 1266, 1210, 1183, 1168, 1106, 1059, 1027, 982, 953, 933, 916, 798, 757, 676, 473 cm^{-1}; HRMS (FAB) Calcd for $[M]^+$ $C_{11}H_{10}F_4O$: 234.0668, Found 234.0672.

*4.3.13. 3,3,4,4-Tetrafluoro-4-(2-methoxymethylphenyl)but-1-ene (**6m**)*

Yield: 41% (87 mg, 0.35 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 3.43 (s, 3H, CH_3), 4.65 (s, 2H, ArCH_2), 5.72 (d, J = 11.2 Hz, 1H, *trans*-CH_2=CHCF_2), 5.86 (dt, J = 17.3, 2.2 Hz, 1H, *cis*-CH_2=CHCF_2), 6.05 (dtd, J = 17.3, 11.4, 11.2 Hz, 1H, CF_2CH=), 7.36 (t, J = 7.4 Hz, 1H, ArH), 7.49 (d, J = 7.4 Hz, 1H, ArH), 7.52 (t, J = 7.4 Hz, 1H, ArH), 7.70 (d, J = 7.4 Hz, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 58.5 (CH$_3$), 71.3 (tt, J = 6.56, 3.28 Hz, ArCH$_2$), 115.6 (tt, J = 249.3, 38.1 Hz, CF$_2$), 117.9 (tt, J = 252.98, 36.54 Hz, CF$_2$), 124.4 (t, J = 9.28 Hz, CH$_2$=), 126.8 (t, J = 24.97 Hz, CF$_2$$C$H=), 127.0 (Ar), 127.7 (t, J = 23.77 Hz, Ar), 128.5 (t, J = 8.09 Hz, Ar), 128.6 (Ar), 131.3 (Ar), 138.6 (Ar); ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ –106.44 (s, 2F, CF$_2$Ar), –114.28 (d, J = 11.37 Hz, 2F, CF_2CH=); IR (neat): ν 2987, 2931, 2897, 2827, 1452, 1420, 1213, 1196, 1116, 1097, 1061, 960, 938, 918, 765, 687 cm^{-1}; HRMS (FAB) calcd for $[M+Na]^+$ $C_{12}H_{12}F_4NaO$: 271.0722, found 271.0715.

*4.3.14. 3,3,4,4-Tetrafluoro-4-(4-fluoro-2-nitrophenyl)but-1-ene (**6n**)*

Yield: 45% (52 mg, 0.19 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 5.74 (d, J = 11.2 Hz, 1H, *trans*-CH_2=CHCF_2), 5.87 (dt, J = 17.3, 1.8 Hz, 1H, *cis*-CH_2=CHCF_2), 6.03 (dtd, J = 17.3, 11.3, 11.2 Hz, 1H, CF_2CH=), 7.29 (dd, J = 7.6, 2.52 Hz, 1H, ArH), 7.33 to 7.37 (m, 1H, ArH), 7.70 (dd, J = 8.9, 5.2 Hz, 1H, ArH) ppm; ^{13}C NMR ($CDCl_3$): δ 112.0 (d, J = 27.1 Hz, Ar), 115.1 (tt, J = 250.4, 37.0, CF$_2$), 115.4 (tt, J =254.4, 37.5 Hz, CF$_2$), 118.5 (d, J = 21.4 Hz, Ar), 118.7 (Ar), 125.3 (t, J = 9.8 Hz, CH$_2$=), 125.6 (t, J = 24.4 Hz, CF$_2$$C$H=), 132.3 to 132.5 (m, Ar), 150.7 (Ar), 163.9 (d, J = 257.7 Hz, Ar); ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ –104.18 to –104.23 (m, 1F, ArF), –106.94 (s, 2F, CF_2Ar), –112.82 (d, J = 11.32 Hz, 2F, CF_2CH=); IR (neat): ν 3087, 2908, 2351, 1929, 1717, 1621, 1550, 1508, 1421, 1369, 1230, 1117, 953, 729 cm^{-1}; HRMS (FAB) Calcd for $[M]^+$ $C_{10}H_6F_5NO_2$: 267.0139, found 267.0134.

*4.3.15. 3,3,4,4-Tetrafluoro-4-(4-bromo-2-nitrophenyl)but-1-ene (**6o**)*

Yield: 51% (67 mg, 0.20 mmol); Yellow oil (hexane/AcOEt = 5/1, R_f = 0.43); ^{1}H NMR ($CDCl_3$) δ 5.74 (d, *J* = 11.2 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.87 (d, *J* = 17.3 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.02 (dtd, *J* = 17.3, 11.3, 11.2 Hz, 1H, CF$_2$C*H*=), 7.54 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.70 (d, *J* = 1.8 Hz, 1H, Ar*H*), 7.75 (d, *J* = 8.6 Hz, 1H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$) δ 114.9 (tt, *J* = 250.8, 37.1 Hz, *C*F$_2$), 115.4 (tt, *J* = 254.7, 37.6 Hz, *C*F$_2$), 121.4 (t, *J* = 26.1 Hz, CF$_2$*C*H=), 125.3 (t, *J* = 9.6 Hz, *C*H$_2$=), 125.4 (t, *J* = 24.2 Hz, *Ar*), 126.4 (*Ar*), 126.9 (*Ar*), 131.3 to 131.4 (m, *Ar*), 134.3 (*Ar*), 149.9 (*Ar*) ppm; ^{19}F NMR ($CDCl_3$) δ –107.48 (s, 2F, C*F*$_2$Ar), –112.72 (d, *J* = 11.3 Hz, 2F, C*F*$_2$CH=) ppm; IR (neat) ν 3422, 3094, 2902, 1932, 1601, 1550, 1483, 1420, 1365, 1288, 1218, 1129, 1058, 920, 830 cm^{-1}; MS (FAB) m/z 307 ($C_6H_3NO_2BrCF_2CFCHC^+H_2$, 51), 176 (79), 154 (100), 138 (98), 137 (100), 136 (100), 89 (56), 77 ($CF_2CHC^+H_2$, 85).

*4.3.16. 3,3,4,4-Tetrafluoro-4-(4-methoxy-2-nitrophenyl)but-1-ene (**6p**)*

Yield: 72% (83 mg, 0.30 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3H, C*H*$_3$), 5.70 (d, *J* = 11.2 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.83 (dt, *J* = 17.3, 1.8 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.00 (dtd, *J* = 17.3, 11.7, 11.2 Hz, 1H, CF$_2$C*H*=), 7.00 (d, *J* = 2.5 Hz, 1H, Ar*H*), 7.08 (dm, *J* = 8.9 Hz, 1H, Ar*H*), 7.54 (d, *J* = 8.9 Hz, 1H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): *δ* 56.0 (*C*H$_3$), 109.5 (Ar), 113.8 (t, *J* = 26.2 Hz, Ar), 115.1 (tt, *J* = 250.1, 37.4 Hz, *C*F$_2$), 115.7 (tt, *J* = 253.5, 36.9 Hz, *C*F$_2$), 116.3 (Ar), 124.8 (t, *J* = 9.3 Hz, *C*H$_2$=), 126.0 (t, *J* = 24.4 Hz, CF$_2$*C*H=), 131.3 (t, *J* = 7.1 Hz, Ar), 150.7 (Ar), 162.3 (Ar); ^{19}F NMR ($CDCl_3$, $CFCl_3$): *δ* –106.74 (s, 2F, C*F*$_2$Ar), –113.17 (d, *J* = 11.67 Hz, 2F, C*F*$_2$CH=); IR (neat): *ν* 3095, 2935, 2850, 2370, 2313, 1621, 1546, 1421, 1371, 1098, 1055, 795 cm^{-1}; HRMS (FAB) Calcd for [M+Na]$^+$ $C_{11}H_9F_4NNaO_3$: 302.0417, found 302.0418.

*4.3.17. 2-(1,1,2,2-Tetrafluorobut-3-en-1-yl)acetanilide (**6q**)*

Yield: 40% (40 mg, 0.15 mmol); Pale yellow oil (hexane/AcOEt = 2/1, R_f = 0.29); ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3H, C*H*$_3$), 5.72 (d, *J* = 10.8 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.85 (d, *J* = 17.4 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 5.90 to 6.03 (m, 1H, CF$_2$C*H*=), 7.21 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.45 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.51 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.66 (s, 1H, ArN*H*), 8.14 (d, *J* = 7.8 Hz, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$) δ 24.8 (*C*H$_3$), 115.9 (tt, *J* = 250.0, 36.6 Hz, *C*F$_2$), 117.6 (tt, *J* = 251.7, 35.3 Hz, *C*F$_2$), 120.1 (t, *J* = 22.2 Hz, *Ar*), 124.4 (*Ar*), 124.9 (t, *J* = 9.4 Hz, *C*H$_2$=), 125.0 (*Ar*), 126.2 (t, *J* = 24.6 Hz, CF$_2$*C*H=), 128.6 (t, *J* = 8.4 Hz, *Ar*), 132.2 (*Ar*), 136.2 (*Ar*), 168.4 (*C*=O) ppm; ^{19}F NMR ($CDCl_3$) δ –109.01 (s, 2F, C*F*$_2$Ar), –114.83 (d, *J* = 10.5 Hz, 2F, C*F*$_2$CH=) ppm; IR (neat) ν 3478, 3304, 3049, 1676, 1526, 1446, 1297, 1238, 1210, 1100, 1042, 1006, 934 cm^{-1}; HRMS (FAB) calcd. for [M+H]$^+$ $C_{12}H_{12}F_4NO$: 262.0855, Found 262.0857.

*4.3.18. 3-(1,1,2,2-Tetrafluorobut-3-en-1-yl)pyridine (**6r**)*

Yield: 29% (24 mg, 0.12 mmol); Known compound; ^{1}H NMR ($CDCl_3$) δ 5.74 (d, *J* = 11.2 Hz, 1H, *trans*-C*H*$_2$=CHCF$_2$), 5.86 (dt, *J* = 17.2, 2.1 Hz, 1H, *cis*-C*H*$_2$=CHCF$_2$), 6.04 (ddt, *J* = 17.2, 11.5, 11.2 Hz, 1H,

CF_2CH=), 7.41 (dd, *J* = 8.0, 4.51 Hz, 1H, Ar*H*), 7.87 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.76 (d, *J* = 4.5 Hz, 1H, Ar*H*), 8.80 (s, 1H, Ar*H*) ppm; ^{13}C NMR ($CDCl_3$): δ 115.0 (tt, *J* = 249.2, 37.4 Hz, CF_2), 115.8 (tt, *J* = 252.4, 36.6 Hz, CF_2), 123.2 (Ar), 125.1 (t, *J* = 9.4 Hz, CH_2=), 126.1 (t, *J* = 24.6 Hz, CF_2CH=), 127.0 (t, *J* = 24.9 Hz, Ar), 134.8 (t, *J* = 6.2 Hz, Ar), 148.2 (t, *J* = 6.8 Hz, Ar), 152.0 (Ar); ^{19}F NMR ($CDCl_3$): δ −113.14 (s, 2F, CF_2Ar), −114.62 (d, *J* = 11.5 Hz, 2F, CF_2CH=); IR (neat) ν 2928, 2858, 1728, 1424, 1292, 1114, 1094, 965 cm^{-1}; HRMS (FAB) Calcd for $[M+H]^+$ $C_9H_8F_4N$: 206.0593, found 206.0586.

Supporting Information

Supporting information for this article is available online at http://. Include are ^{1}H, ^{13}C NMR, and ^{19}F NMR spectra.

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[17] In the coupling reaction of a fluoroalkyl copper with a halide, it is also possible that the reaction may proceed in a radical manner. However, since a simple oxidative addition-reductive elimination mechanism between a fluoroalkyl copper and a halide has been reasonably proposed in many publications so far, we similarly proposed the latter mechanism in this study.