

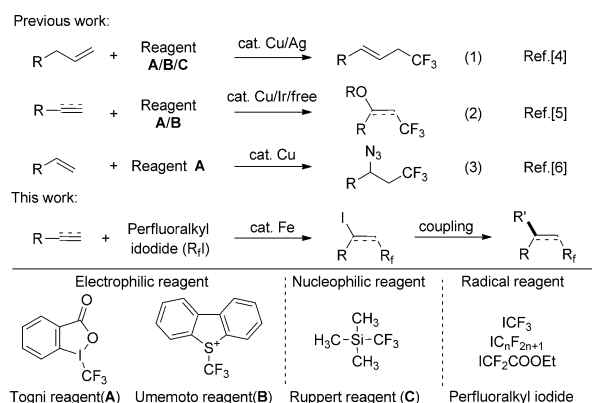
# Iron-Catalyzed 1,2-Addition of Perfluoroalkyl Iodides to Alkynes and Alkenes\*\*

Tao Xu, Chi Wai Cheung, and Xile Hu\*

**Abstract:** Iron catalysis has been developed for the intermolecular 1,2-addition of perfluoroalkyl iodides to alkynes and alkenes. The catalysis has a wide substrate scope and high functional-group tolerance. A variety of perfluoroalkyl iodides including  $\text{CF}_3\text{I}$  can be employed. The resulting perfluoroalkylated alkyl and alkenyl iodides can be further functionalized by cross-coupling reactions. This methodology provides a straightforward and streamlined access to perfluoroalkylated organic molecules.

The introduction of fluorine atoms into organic molecules often leads to dramatic changes in their properties such as solubility, metabolic stability, and bioavailability.<sup>[1]</sup> Additionally, fluoroalkyl groups, especially the trifluoromethyl group, are strongly electron-withdrawing and highly hydrophobic. Because of these desirable properties, fluoroalkylated compounds are widely used in materials science, argochemistry, and medicinal chemistry.<sup>[2]</sup> Efficient and general methodologies for the synthesis of fluoroalkylated organic molecules, therefore, are in high demand.<sup>[3]</sup>

As alkenes and alkynes are ubiquitous feedstock materials, trifluoroalkylation of unsaturated C–C bonds is an attractive method to introduce the trifluoroalkyl groups into organic molecules.<sup>[4]</sup> Significant progress has been made recently in copper- and silver-catalyzed allylic trifluoromethylation [Eq. (1), Scheme 1],<sup>[4c–f]</sup> transition-metal-catalyzed/metal-free electrophilic oxytrifluoromethylation of alkynes and olefins [Eq. (2)],<sup>[5]</sup> and copper-catalyzed trifluoromethylazidation of alkenes [Eq. (3)].<sup>[6]</sup> The trifluoromethylating reagents employed in these studies are often electrophilic  $\text{CF}_3$  sources such as the Togni reagent (**A**) and the Umemoto reagent (**B**), and sometimes the nucleophilic  $\text{CF}_3$  source  $\text{TMSCF}_3$  (Ruppert's reagent; **C**) is used. The reagents **A** and **B** are expensive, and **C** requires an activating agent such as a fluoride and thus poses a constrain in the functional-group compatibility.<sup>[7]</sup> Herein, we describe an iron-catalyzed 1,2-addition of perfluoroalkyl iodides to alkynes and alkenes. Compared with **A–C**, perfluoroalkyl iodides and related



**Scheme 1.** Comparison of various methods for the perfluoroalkylation of alkenes and alkynes.

compounds are less costly and more suitable for large-scale synthesis.<sup>[8]</sup> Moreover, our method allows the incorporation of both  $\text{CF}_3$  and I functional groups into an alkyne or alkene without generating a byproduct from the perfluoroalkylating reagent. Therefore, it is comparatively more atom economical. Furthermore, the method can be applied to perfluoroalkylation which is less developed.<sup>[9]</sup>

Addition of perfluoroalkyl iodides to alkynes had previously been achieved using a radical initiator such as AIBN,<sup>[10a]</sup>  $\text{Et}_3\text{B}$ ,<sup>[10b,c]</sup>  $\text{Na}_2\text{S}_2\text{O}_3$ ,<sup>[10d]</sup> or light.<sup>[10e]</sup> However, these reactions had a very limited substrate scope. Only less than ten examples of simple alkynes and several perfluoroalkylating reagents could be applied. Additionally, trifluoromethylation was hard to achieve using these methods. The light-induced addition of perfluoroalkyl iodides to alkenes and alkynes has been improved in recent years. Stephenson and co-workers reported visible-light-induced radical addition of perfluoroalkyl halides to alkynes and alkenes.<sup>[11a]</sup> Cho and co-workers also reported visible-light photoredox catalysis for the trifluoromethylation of alkynes with  $\text{CF}_3\text{I}$  to give alkynyl and alkenyl  $\text{CF}_3$  products.<sup>[11b]</sup> Nevertheless, these reactions require precious iridium and ruthenium photocatalysts. On the contrary, the iron-catalyzed perfluoroalkylation method described herein requires only the inexpensive, environmentally friendly, and ligandless  $\text{FeBr}_2$  as the catalyst.<sup>[12]</sup> The reaction protocol is operationally simple, the substrate scope is large, and the functional-group tolerance is excellent.

The addition of perfluorobutyl iodide to 1-octyne (**1a**) was chosen as the test reaction (Table 1). In the presence of  $\text{Cs}_2\text{CO}_3$ ,  $\text{FeBr}_2$  could catalyze this reaction in high yields with a catalyst loading of only 5 mol % (entries 1–3). Cobalt, nickel, and copper also catalyzed the same reaction, but often in lower yields (see Table S1 in the Supporting Information).

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**Table 1:** Optimization of reaction conditions.<sup>[a]</sup>

$\text{C}_6\text{H}_{13}\text{—C}\equiv\text{C—H} + \text{C}_4\text{F}_9\text{I} \xrightarrow[1,4\text{-dioxane, } 60^\circ\text{C}]{\text{cat. FeBr}_2} \text{C}_6\text{H}_{13}\text{—C}(\text{C}_4\text{F}_9)=\text{CH—H}$					
	<b>1a</b>	<b>2a</b>			<b>3a</b>
Entry	Cat. (mol %)	R <sub>I</sub> (equiv)	Base (equiv)	Conv. [%]	Yield [%]
1	FeBr <sub>2</sub> (10)	1.2	Cs <sub>2</sub> CO <sub>3</sub> (1.5)	96	68
2	FeBr <sub>2</sub> (10)	1.5	Cs <sub>2</sub> CO <sub>3</sub> (1.5)	95	92
3	FeBr <sub>2</sub> (5)	1.5	Cs <sub>2</sub> CO <sub>3</sub> (1.5)	95	90
4	FeCl <sub>2</sub> (10)	1.5	Cs <sub>2</sub> CO <sub>3</sub> (1.5)	97	87
5	[Fe(acac) <sub>3</sub> ] (10)	1.5	Cs <sub>2</sub> CO <sub>3</sub> (1.5)	95	67
6	FeBr <sub>2</sub> (5)	1.5	Et <sub>3</sub> N (1.5)	59	44
7	FeBr <sub>2</sub> (5)	1.5	<i>t</i> BuOLi (1.5)	99	0
8	FeBr <sub>2</sub> (5)	1.5	<i>t</i> BuOK (1.5)	97	0
9	FeBr <sub>2</sub> (5)	1.5	pyridine	11	0
10 <sup>[b]</sup>	FeBr <sub>2</sub> (5)	1.5	Cs <sub>2</sub> CO <sub>3</sub> (0.8)	99	95 (87)
11 <sup>[c]</sup>	FeBr <sub>2</sub> (5)	1.5	Cs <sub>2</sub> CO <sub>3</sub> (0.8)	8	0
12	FeBr <sub>2</sub> (5)	1.5	—	0	0
13	—	1.5	—	0	0
14 <sup>[b]</sup>	—	1.5	Cs <sub>2</sub> CO <sub>3</sub> (0.25)	96	95 (87)

[a] The reactions were conducted on a 0.5 mmol scale under N<sub>2</sub>. Unless otherwise specified, yields were determined by GC for the screening reactions using *n*-decane as the internal standard. [b] The yield of the isolated product is given within the parentheses. [c] The reaction was conducted in the air. acac = acetylacetonate.

However, only iron catalysis was further pursued. Other iron salts also catalyzed the reaction in similar or lower yields (entries 4 and 5). Et<sub>3</sub>N could be used as a base, but the yield was modest (entry 6). Other bases such as *t*BuOLi, *t*BuOK, and pyridine could not be used (entries 7–9). The optimized reaction conditions were 5 mol % FeBr<sub>2</sub> as the catalyst, 1.5 equivalents of perfluoroalkyl iodide as the substrate, and 0.8 equivalents of Cs<sub>2</sub>CO<sub>3</sub> as the base. Under these reaction conditions, the yield was 95 % (entry 10). The reaction needed to be run under a nitrogen atmosphere, because when run open to the air no product was obtained (entry 11). Without a base, the reaction did not occur (entries 12 and 13). Intriguingly, this particular addition reaction also occurred with only Cs<sub>2</sub>CO<sub>3</sub> as the base and without FeBr<sub>2</sub> as the catalyst. For example, the yield was 63 % using 2 equivalents of Cs<sub>2</sub>CO<sub>3</sub>. Optimization was carried out for the Cs<sub>2</sub>CO<sub>3</sub>-mediated or Cs<sub>2</sub>CO<sub>3</sub>-catalyzed reaction (see Table S2). The optimized reaction conditions required a high concentration of reagents and 0.25 equivalents of Cs<sub>2</sub>CO<sub>3</sub>, thus giving a yield of 95 % (entry 14).<sup>[13]</sup> It turned out that this iron-free, Cs<sub>2</sub>CO<sub>3</sub>-catalyzed method only worked for a very small number of simple alkenes and alkynes, such as 1-octyne. On the contrary, the FeBr<sub>2</sub>-catalyzed perfluoroalkylation method could be applied to a great number of substrates. Therefore, the scope of the Cs<sub>2</sub>CO<sub>3</sub>-catalyzed method is presented later on, along with the discussion on the mechanism of the iron-catalyzed method.

With the optimized reaction conditions known, the iron-catalyzed method was first applied to the perfluoroalkylation of various alkynes (Table 2).<sup>[14]</sup> Not only perfluoroalkyl iodides such as C<sub>4</sub>F<sub>9</sub>I, C<sub>6</sub>F<sub>13</sub>I, but also C<sub>6</sub>F<sub>12</sub>ClI and EtOOCF<sub>2</sub>I can be efficiently transformed into the corresponding products. The addition is *E* selective, with an *E/Z*

**Table 2:** Scope of the iron-catalyzed addition reaction of R<sub>I</sub> to alkynes.<sup>[a]</sup>

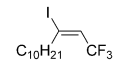
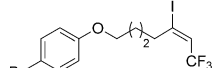
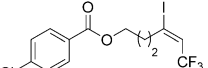
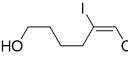
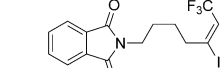
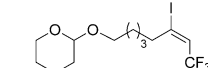
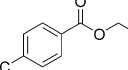
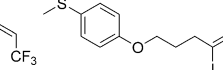
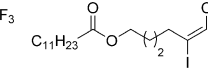
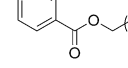
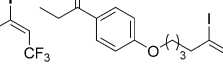
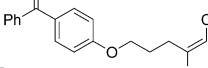
$\text{C}_6\text{H}_{13}\text{—C}\equiv\text{C—H} + \text{C}_6\text{F}_{13}\text{I} \xrightarrow[\text{cat. FeBr}_2]{\text{Cs}_2\text{CO}_3, 1,4\text{-dioxane, } 60^\circ\text{C}} \text{C}_6\text{H}_{13}\text{—C}(\text{C}_6\text{F}_{13})=\text{CH—H}$	$\text{C}_6\text{H}_{13}\text{—C}\equiv\text{C—H} + \text{C}_6\text{F}_{13}\text{I} \xrightarrow[\text{cat. FeBr}_2]{\text{Cs}_2\text{CO}_3, 1,4\text{-dioxane, } 60^\circ\text{C}} \text{C}_6\text{H}_{13}\text{—C}(\text{C}_6\text{F}_{13})=\text{CH—H}$	$\text{C}_6\text{H}_{13}\text{—C}\equiv\text{C—H} + \text{C}_6\text{F}_{13}\text{I} \xrightarrow[\text{cat. FeBr}_2]{\text{Cs}_2\text{CO}_3, 1,4\text{-dioxane, } 60^\circ\text{C}} \text{C}_6\text{H}_{13}\text{—C}(\text{C}_6\text{F}_{13})=\text{CH—H}$	$\text{C}_6\text{H}_{13}\text{—C}\equiv\text{C—H} + \text{C}_6\text{F}_{13}\text{I} \xrightarrow[\text{cat. FeBr}_2]{\text{Cs}_2\text{CO}_3, 1,4\text{-dioxane, } 60^\circ\text{C}} \text{C}_6\text{H}_{13}\text{—C}(\text{C}_6\text{F}_{13})=\text{CH—H}$
<b>3b</b> 88% ( <i>E</i> ) <sup>[b]</sup>	<b>3c</b> 83% ( <i>E/Z</i> =7.7:1) <sup>[b]</sup>	<b>3d</b> 67% ( <i>E</i> only)	<b>3e</b> 76% ( <i>E/Z</i> =6.6:1) <sup>[c]</sup>
<b>3f</b> 75% ( <i>E</i> only)	<b>3g</b> 63% ( <i>E/Z</i> =6.4:1) <sup>[b]</sup>	<b>3h</b> 60% ( <i>E/Z</i> =6.5:1) <sup>[c]</sup>	<b>3i</b> 62% ( <i>E</i> only) <sup>[b]</sup>
<b>3j</b> 72% ( <i>E/Z</i> =5.8:1)	<b>3k</b> 86% ( <i>E/Z</i> =6.2:1) <sup>[c]</sup>	<b>3l</b> 87% ( <i>E/Z</i> =7.4:1)	<b>3m</b> 77% ( <i>E/Z</i> =5.3:1)
<b>3n</b> 75% ( <i>E/Z</i> =7.3:1)	<b>3o</b> 84% ( <i>E/Z</i> =6.6:1) <sup>[c]</sup>	<b>3p</b> 63% ( <i>E/Z</i> =4.7:1)	<b>3q</b> 66% ( <i>E/Z</i> =6.3:1) <sup>[c]</sup>
<b>3r</b> 79% ( <i>E/Z</i> =6.0:1)	<b>3s</b> 80% ( <i>E/Z</i> =5.7:1)	<b>3t</b> 75% ( <i>E/Z</i> =5.6:1) <sup>[c]</sup>	<b>3u</b> 82% ( <i>E/Z</i> =6.7:1)
<b>3v</b> 75% ( <i>E/Z</i> =7.0:1)	<b>3w</b> 71% ( <i>E/Z</i> =11:1) <sup>[d]</sup>		

[a] Reaction conditions: alkyne (0.5 mmol), R<sub>I</sub> (1.5 equiv), FeBr<sub>2</sub> (10 mol %), Cs<sub>2</sub>CO<sub>3</sub> (80 mol %), 1,4-dioxane (2 mL), 60 °C, 18–24 h. Yields are those of the isolated products. [b] FeBr<sub>2</sub> (5 mol %). [c] The yield of the *Z* product was determined by GC and reported as relative to the yield of the isolated *E* product. [d] R<sub>I</sub> (2.5 mmol).

ratio generally larger than 5:1. The addition to aryl alkynes is completely stereoselective, thus yielding only *E* isomers (**3d**, **3f**). The functional-group tolerance is high. A free hydroxy group is tolerated (**3i**) and in this case, the stereoselectivity is unusually high for an alkyl alkyne substrate (*E* only), possibly because of the chelating ability of the hydroxy group. Amide (**3j**, **3t**), ester (**3l**, **3o**, **3u**, **3v**), ketone (**3e**, **3n**, **3r**), nitrile (**3q**), acetal (**3g**), arylhalide (**3h**, **3m**, **3o**, **3s**, **3v**), thioether (**3k**, **3p**), and ether (**3h**, **3m**, **3r**, **3s**) groups were all compatible. An internal alkyne could be used as a substrate as well (**3w**). Considering the important function of the CF<sub>3</sub> group, substantial efforts were made to investigate the scope of the iron-catalyzed addition of CF<sub>3</sub>I to alkynes. Gratifyingly, the method has again a broad scope and high functional-group tolerance (Table 3). The addition was efficient in the presence of keto, ester, amide, alcohol, ether, thioether, acetal, and aryl-halide groups and the reactions are *E* selective.

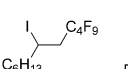
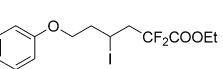
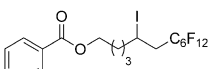
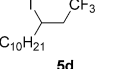
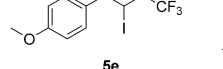
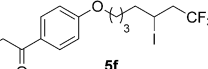
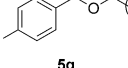
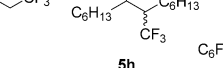
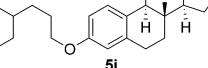
The iron-based method was then expanded for perfluoroalkylation of alkenes. To our delight, the optimized protocol in Table 1 also worked for alkenes (Table 4).<sup>[10f,15]</sup> Both terminal and internal olefins could be used. When an internal

**Table 3:** Scope of the iron-catalyzed addition reaction of CF<sub>3</sub>I to alkynes.<sup>[a]</sup>

		
73% (E/Z=7.6:1)	53% (E only) <sup>[b,c]</sup>	59% (E/Z=5.9:1, brsm 70%)
		
68% (E only) <sup>[b]</sup>	80% (E/Z=5.8:1) <sup>[b,c]</sup>	50% (E/Z=5.2:1) <sup>[b]</sup>
		
54% (E/Z=7.4:1) <sup>[b,c,d]</sup>	52% (E only) <sup>[b,e]</sup>	76% (E/Z=6.5:1) <sup>[b]</sup>
		
67% (E/Z=7.1:1) <sup>[b]</sup>	68% (E/Z=8.7:1) <sup>[b,c,d]</sup>	41% (E only) <sup>[b,c]</sup>

[a] Reaction conditions: alkyne (0.5 mmol), CF<sub>3</sub>I (3.0 equiv), FeBr<sub>2</sub> (10 mol %), Cs<sub>2</sub>CO<sub>3</sub> (80 mol %), 1,4-dioxane (2 mL), 60°C, 18–24 h. Yields are those of isolated products. [b] FeBr<sub>2</sub> (20 mol %), Cs<sub>2</sub>CO<sub>3</sub> (150 mol %). [c] CF<sub>3</sub>I (5.0 equiv). [d] The yield of the Z product was determined by GC and reported as relative to the yield of the isolated E product. [e] The alkyne was treated with CF<sub>3</sub>I (3.0 equiv) twice.

**Table 4:** Scope of the iron-catalyzed addition reaction of R<sub>f</sub>I to alkenes.<sup>[a]</sup>

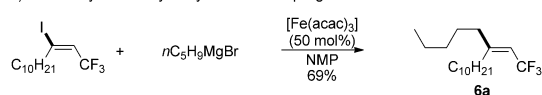
		
89% <sup>[b]</sup>	90%	87%
		
95% <sup>[b]</sup>	64% <sup>[c,d]</sup>	71%
		
94% (70% <sup>[b]</sup> )	74% (1:1) <sup>[c]</sup>	93%

[a] Reaction conditions: alkene (0.5 mmol), R<sub>f</sub>I (generally 1.5 equiv; for CF<sub>3</sub>I, 3.0 equiv), FeBr<sub>2</sub> (10 mol %), Cs<sub>2</sub>CO<sub>3</sub> (80 mol %), 1,4-dioxane (2 mL), 60°C, 18–24 h. Yields are those of isolated products. [b] FeBr<sub>2</sub> (5 mol %). [c] CF<sub>3</sub>I (5.0 equiv), FeBr<sub>2</sub> (20 mol %), Cs<sub>2</sub>CO<sub>3</sub> (150 mol %). [d] 80°C.

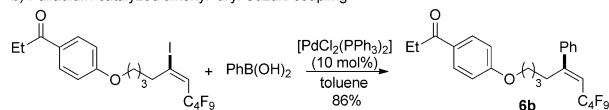
olefin was used, the diastereoisomers were obtained in a 1:1 ratio (**5h**). Again ester, keto, aryl-halide, and ether groups were tolerated. An estrone derivative could be smoothly perfluoroalkylated (**5i**), thus demonstrating the utility of the method for the functionalization of natural products.

The iron-catalyzed addition of perfluoroalkyl iodides to alkenes and alkynes produces perfluoroalkylated molecules with a neighboring alkyl or vinyl iodide functional group. The I group is a versatile leaving group for further functionalization, for example, by cross-coupling reactions. This versatility was demonstrated in a series of examples in Scheme 2.<sup>[16]</sup> An

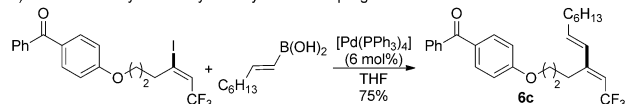
a) Iron-catalyzed alkenyl-alkyl Kumada coupling



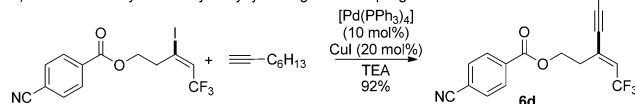
b) Palladium-catalyzed alkenyl-aryl Suzuki coupling



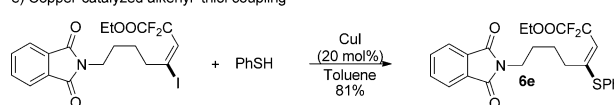
c) Palladium-catalyzed alkenyl-alkenyl Suzuki coupling



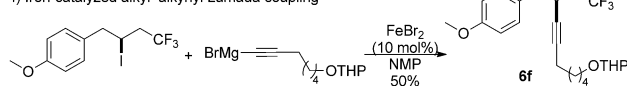
d) Palladium-catalyzed alkenyl-alkynyl Sonogashira coupling



e) Copper-catalyzed alkenyl-thiol coupling



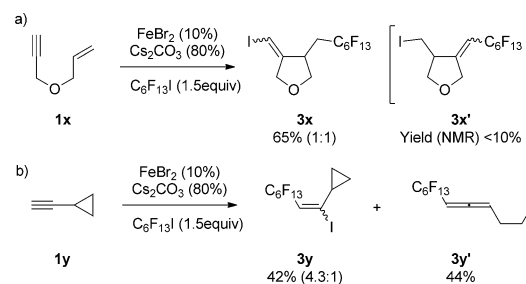
f) Iron-catalyzed alkyl-alkynyl Kumada coupling



**Scheme 2.** Further functionalization of addition products by cross-coupling reactions. NMP = *N*-methylpyrrolidone, TEA = triethylamine, THF = tetrahydrofuran, THP = tetrahydropyran.

iron-catalyzed alkenyl-alkyl Kumada coupling gave **6a** in a 69% yield (Scheme 2a) and palladium-catalyzed Suzuki coupling and Sonogashira coupling gave **6b**, **6c**, and **6d** in high yields (Scheme 2b–d). Copper-catalyzed C–S bond formation and iron-catalyzed alkyl-alkynyl Kumada coupling furnished **6e** and **6f** in good yields (Scheme 2e,f). The neighboring perfluoroalkyl groups do not impede the coupling reactions.

Several experiments were conducted to probe the involvement of radicals in the iron-catalyzed reactions (Scheme 3). When an ether-tethered enyne (**1x**) was used as the substrate, ring-closed products were formed (Scheme 3a). The major product **3x** results from the addition of C<sub>6</sub>F<sub>13</sub> to the alkene

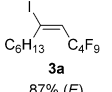
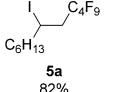
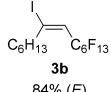
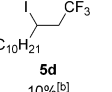
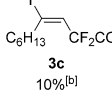
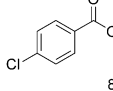
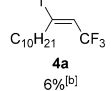
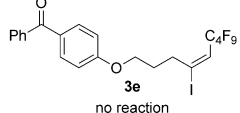
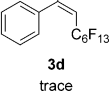
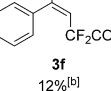


**Scheme 3.** Reactions to probe the involvement of radicals in the catalysis.

and I to the alkyne, while the minor product **3x'** results from the addition of  $C_6F_{13}$  to the alkyne and I to the alkene.<sup>[17]</sup> When the cyclopropyl-containing alkyne **1y** was used as the substrate, both the cyclopropyl-containing product **3y** and allene-containing product **3y'** were produced in about 40% yield each (Scheme 3b). The outcomes of the reactions are consistent with the formation of a perfluoroalkyl radical and its addition to alkene or alkyne to form an alkyl or alkenyl radical, which is prone to ring-closing cyclization or ring-opening rearrangement. The involvement of a radical was further corroborated by the quenching of the perfluoroalkylation reaction in the presence of TEMPO (1.0 equiv).

As mentioned above, for certain simple alkynes and alkenes,  $CS_2CO_3$  can catalyze the addition of perfluoroalkyl iodides without the iron catalyst. Table 5 shows the scope of

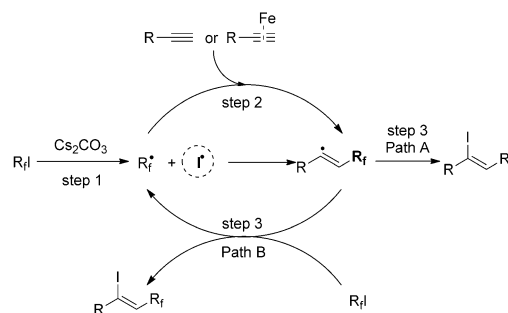
**Table 5:** The substrate scope of the  $CS_2CO_3$ -catalyzed addition reaction.<sup>[a]</sup>

Alkynes:	Alkenes:
 <b>3a</b> 87% (E)	 <b>5a</b> 82%
 <b>3b</b> 84% (E)	 <b>5d</b> 10% [b]
 <b>3c</b> 10% [b]	 <b>5g</b> 8% [b]
 <b>4a</b> 6% [b]	 <b>3e</b> no reaction
 <b>3d</b> trace	
 <b>3f</b> 12% [b]	

[a] Reaction conditions: alkyne or alkene (1.0 mmol),  $R_fI$  (1.5 equiv),  $CS_2CO_3$  (25 mol%), dioxane (2 mL), 60°C, 18–24 h. Unless otherwise specified, yields are those of isolated products. [b] Yield determined by GC.

the  $CS_2CO_3$ -catalyzed reactions. Only the addition of  $C_4F_9I$  and  $C_6F_{13}I$  to unfunctionalized alkyl alkynes and alkenes such as 1-octyne and 1-octene was efficient (**3a**, **3b**, **5a**). If the alkyne or alkene is functionalized, then the yield was very low (**3e**, **5g**). Even with simple alkyl alkenes and alkynes, the addition of  $CF_3I$  and  $EtOOC CF_2I$  was inefficient (**3c**, **4a**, **5d**). Aryl alkynes were not suitable substrates (**3d**, **3f**).

Although the  $CS_2CO_3$ -catalyzed reactions are not synthetically useful, they shed some insight into the mechanism of the iron-catalyzed reactions which require  $CS_2CO_3$  as a base. It seems that  $CS_2CO_3$  alone is sufficient to activate certain perfluoroalkyl iodides at 60°C, presumably leading to the formation of perfluoroalkyl radicals which add to simple alkynes. The addition reaction is likely difficult so that it is limited to simple alkynes and alkenes. The role of the iron catalyst is then to activate the alkenes and alkynes, thereby facilitating the addition reactions to a large number of substrates and achieving functional-group tolerance. A tentative catalytic cycle is shown in Figure 1. After the perfluoroalkyl radical is produced by the help of  $CS_2CO_3$  (step 1), it adds to the unsaturated C–C bond, activated by the iron catalyst, to give a carbon radical (step 2). The latter reacts



**Figure 1.** A tentative catalytic cycle for the catalysis.

with an iodide radical generated from Step 1 (step 3, Path A). Alternatively, the carbon radical can react with another molecule of perfluoroalkyl iodide to give the addition product and regenerate the perfluoroalkyl radical (step 3, Path B). While the role of iron in activating alkenes and alkynes is confirmed by the drastically different scopes of the iron-catalyzed and iron-free reactions, the iron catalyst might additionally act in concert with  $CS_2CO_3$  to activate the perfluoroalkyl iodides.

In summary, a simple, broadscope, and tolerant iron-catalyzed perfluoroalkylation method is reported. This methodology provides a streamlined access to perfluoroalkylated organic compounds starting from readily available alkenes and alkynes. The synthetic utility of the addition products is demonstrated in a series of transition-metal-catalyzed cross-coupling reactions.

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