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## Difluoromethylcarbene for iron-catalyzed cyclopropanation†

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**Difluoroethylsulfonium salt,  $\text{Ph}_2\text{S}^+\text{CH}_2\text{CF}_2\text{H OTf}^-$ , was developed into a convenient difluoromethylcarbene reagent for the iron-catalyzed cyclopropanation of terminal olefins, giving various difluoromethylcyclopropanes with excellent diastereoselectivities and in high yields.**

The past decades have witnessed considerable advances in carbene chemistry. Carbenes are usually highly reactive and relatively short-lived, but can be “tamed” by attaching heteroatoms<sup>1</sup> or a transition metal<sup>1b–d,2</sup> to the carbene carbon. Consequently, carbenes have found widespread applications in a variety of research areas, such as cycloaddition,<sup>3</sup> insertion<sup>3a,4</sup> and olefin metathesis reactions,<sup>5</sup> and transition-metal catalysis.<sup>5b,6</sup> Because fluorine plays an increasingly important role in the pharmaceutical and agrochemical industries,<sup>7</sup> fluorinated carbenes<sup>8</sup> have received a great deal of attention from the chemical community. There have been extensive studies on many fluorinated carbenes, including difluorocarbene<sup>8a,9</sup> and trifluoromethylcarbene,<sup>10</sup> and their synthetic utility has been clearly demonstrated. Although the difluoromethyl functionality ( $\text{CF}_2\text{H}$ ) has proved to be a valuable pharmacophore<sup>7b,11</sup> and determined efforts have been devoted to the incorporation of this group into organic molecules,<sup>12</sup> the chemistry of difluoromethylcarbene ( $\text{HCF}_2\text{CH:}$ ) is a research area that remains largely unexplored.<sup>13</sup>

Diazo compounds have served as one of the most commonly used classes of carbene precursors, and it can thus be conceived that difluoromethylcarbene could be produced from difluoromethyl diazomethane ( $\text{HCF}_2\text{CHN}_2$ ). Although significant efforts have been directed towards the preparation of this diazo compound,<sup>14</sup> no attempt has been successful until recently, when Mykhailiuk developed a convenient approach for the formation of  $\text{HCF}_2\text{CHN}_2$  and applied it to [3+2] cycloadditions with alkyne.<sup>15</sup>

On the basis of Mykhailiuk's strategy, Koenigs reported a continuous-flow method for the preparation of  $\text{HCF}_2\text{CHN}_2$ ,<sup>13,16</sup> and found that  $\text{HCF}_2\text{CHN}_2$  can act as a difluoromethylcarbene precursor.<sup>13</sup> However, low efficiency for its use as a carbene precursor was observed.<sup>13</sup> Furthermore,  $\text{HCF}_2\text{CHN}_2$  is a potentially explosive and toxic gas, which limits its synthetic applicability. Therefore, the development of mild and efficient difluoromethylcarbene agents is highly desirable.

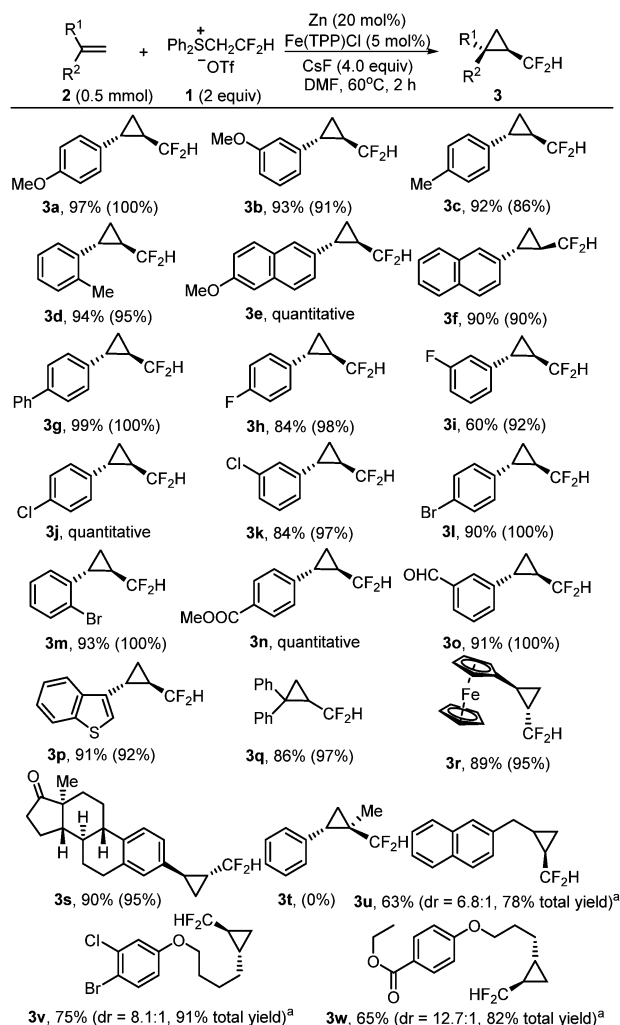
Based on our previous observation that fluorinated carbenes can be converted from ylides such as phosphonium ylide<sup>17</sup> and sulfonium ylide<sup>18</sup> through the cleavage of the  $\text{X}^+-\text{C}^-$  bond ( $\text{X} = \text{P}$  or  $\text{S}$ ), we speculated that difluoromethyl sulfonium ylide  $\text{R}_2\text{S}^+-\text{CHCF}_2\text{H}$  may be used as a difluoromethylcarbene precursor. Indeed, ylide  $\text{Ph}_2\text{S}^+-\text{CHCF}_2\text{H}$ , formed from sulfonium salt  $\text{Ph}_2\text{S}^+\text{CH}_2\text{CF}_2\text{H OTf}^-$  (**1**), was converted into difluoromethylcarbene catalyzed by an Fe complex, a process which allows for the convenient cyclopropanation of olefins to give difluoromethylcyclopropanes. The preliminary results of this study are described herein.

Using the same reaction conditions as those used for the cyclopropanation of aryl olefins with trifluoromethylcarbene catalyzed by  $\text{Fe}(\text{TPP})\text{Cl}$  ( $\text{TPP} = 5,10,15,20\text{-tetraphenyl-21H,23H-porphine}$ ) described by us recently,<sup>18</sup> we did not obtain the desired product in the attempts to perform the cyclopropanation of olefin **2a** ( $4\text{-MeOC}_6\text{H}_4\text{CHCH}_2$ ) with difluoromethylcarbene generated from sulfonium salt **1**. Fortunately, it was found that the presence of a catalytic amount of zinc powder gave the desired product in a high yield [see the ESI,† Table S1]. We then explored the substrate scope of the cyclopropanation with difluoromethylcarbene (Scheme 1). A series of electron-rich, -neutral and -deficient aryl olefins were converted smoothly into the desired products in good to excellent yields (**3a–3s**). To our delight, high diastereoselectivity was observed in all of the reactions ( $\text{trans/cis} > 20/1$ , as determined by  $^{19}\text{F}$  NMR spectroscopy) (**3a–3s**). There were no obvious steric effects on the cyclopropanation of terminal aryl olefins, as evidenced by the high yields of sterically hindered products **3d**, **3m** and **3q**. In addition, ferrocene derivatives have found widespread applications in catalytic<sup>19</sup> and pharmaceutical

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization of data for all compounds. See DOI: 10.1039/c7cc01636k



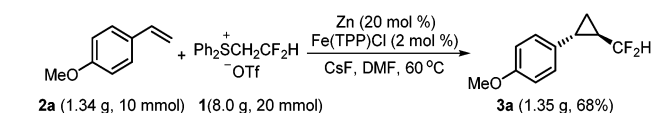
**Scheme 1** Substrate scope for cyclopropanation with difluoromethylcarbene. Isolated yields. The yields and dr values in parentheses were determined by  $^{19}\text{F}$  NMR spectroscopy. <sup>a</sup>For the conversion of aliphatic olefins, the reaction conditions were slightly different: 10 mol% of  $\text{Fe(PPP)Cl}$ , 0.4 equiv. of  $\text{Zn}$ ,  $50^\circ\text{C}$  for 8 h.

chemistry,<sup>20</sup> and the incorporation of the  $\text{CF}_2\text{H}$ -cyclopropyl motif into the ferrocene scaffold (**3r**) may result in improved activity. A convenient route to  $\text{CF}_2\text{H}$ -cyclopropyl estrone derivative **3s** was also developed, further demonstrating the synthetic utility of this transformation.

Internal olefin was inert under these reaction conditions (**3t**), and this can be explained by the proposed reaction mechanism shown below. The conversion is not only applicable to aryl olefins, but also to aliphatic olefins. However, aliphatic olefins exhibited lower reactivity and the products were obtained with lower diastereoselectivities (**3u–3w**).

To obtain a good yield on a small scale (0.5 mmol), 5 mol% of the catalyst was required. Interestingly, increasing the reaction scale with a reduced catalyst loading (2 mol%) could still give the desired product in a good yield (Scheme 2), which further demonstrates the practicality of this transformation.

Difluoromethyl-cyclopropanes are valuable structural motifs in pharmaceutical and agricultural chemistry.<sup>21</sup> A striking example is

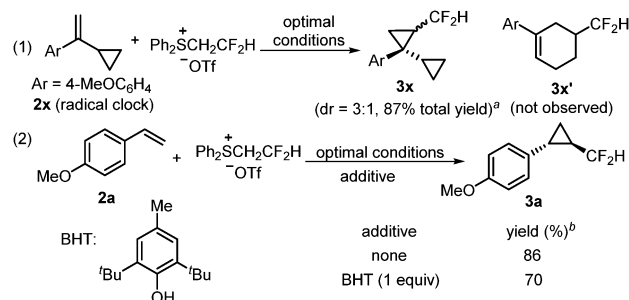


**Scheme 2** Large-scale reaction.

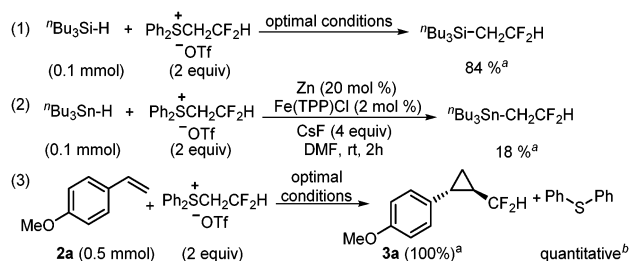
voxilaprevir, which demonstrates potent activity against the hepatitis C virus (HCV) and is in phase II clinical trials for treatment of HCV infections.<sup>22</sup> It is thus desirable to develop efficient protocols for the construction of the difluoromethyl-cyclopropane functionality.<sup>23</sup> Traditional methods, including cyclization of difluoromethylated substrates<sup>24</sup> and deoxyfluorination of cyclopropyl aldehyde,<sup>25</sup> suffer from tedious synthetic procedures and/or the need for hazardous fluorinating reagents. Hanamoto and coworkers found that difluoromethyl vinyl sulfonium salt could undergo cyclization with active methylene compounds to give  $\text{HCF}_2$ -containing cyclopropanes.<sup>26</sup> However, a multi-step synthesis is required to access the vinyl sulfonium salt, and the methylene compounds need to be highly activated. The cyclopropanation of olefins with difluoromethyl diazomethane described by Koenigs is a catalytic one-step protocol for the synthesis of  $\text{HCF}_2$ -containing cyclopropanes.<sup>13</sup> However, difluoromethyl diazomethane is a potentially explosive and toxic gas. Furthermore, low yields of the cyclopropanes were obtained, almost no diastereoselectivity was observed, and the conversion of olefins was limited to aryl olefins. Compared with these reported methods, this direct catalytic and diastereoselective strategy is apparently more convenient and promising.

The radical process should not be involved in this cyclopropanation reaction. Under the optimal reaction conditions, radical clock **2x** underwent cyclopropanation of the double bond to afford product **3x**, and cyclopropyl-ring-opening product **3x'** was not observed, meaning that the radical mechanism could be excluded [Scheme 3, eqn (1)]. The presence of the radical scavenger dibutylhydroxytoluene (BHT) did not lead to an obvious decrease in the yield of the desired product, further supporting this hypothesis [eqn (2)].

$\text{Fe}$ -difluoromethylcarbene ( $\text{Fe}=\text{CHCF}_2\text{H}$ ) is speculated to be a key intermediate in this cyclopropanation. Further evidence was thus collected to probe the generation of this carbene complex. As this complex is highly reactive, no attempt on its isolation or characterization was successful. A large number of reports have shown that transition metal can catalyze the



**Scheme 3** Exclusion of the radical mechanism. <sup>a</sup>Isolated yield. <sup>b</sup>Determined by  $^{19}\text{F}$  NMR spectroscopy.

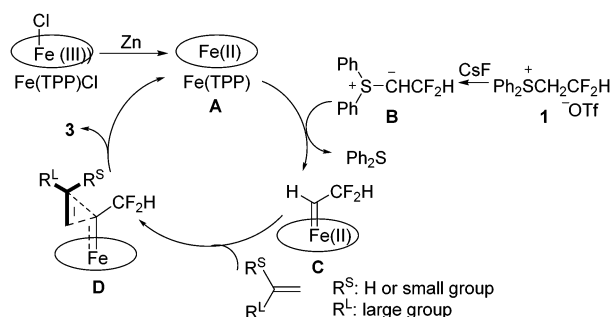


**Scheme 4** Evidence for the mechanism involving an  $\text{Fe}=\text{CHCF}_2\text{H}$  species. <sup>a</sup>Determined by  $^{19}\text{F}$  NMR spectroscopy. <sup>b</sup>Isolated yield.

insertion of carbene into a Si–H or a Sn–H bond.<sup>27</sup> Under the above  $\text{Fe}(\text{TPP})\text{Cl}$  catalyzed cyclopropanation conditions, it was found that the insertion of a  $\text{HCF}_2\text{CH}$  moiety into a Si–H or a Sn–H bond occurred successfully [Scheme 4, (eqn (1) and (2))], indicating the formation of Fe-difluoromethylcarbene. The quantitative isolation of  $\text{Ph}_2\text{S}$  further suggested the conversion from sulfur ylide  $\text{Ph}_2\text{S}^+-\text{CHCF}_2\text{H}$  to difluoromethylcarbene  $\text{HCF}_2\text{CH}$ : [eqn (3)].

In our previous study on iron-catalyzed cyclopropanation with trifluoromethylcarbene,<sup>18</sup> a reductant was not necessary. This might be because the reductivity of  $\text{Ph}_2\text{S}^+-\text{CHCF}_3$  is strong enough to reduce  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$ . However, for cyclopropanation with difluoromethylcarbene, the desired conversion was completely suppressed in the absence of the reductant (zinc powder) (see the ESI,<sup>†</sup> Table S1, entry 17), which suggests that difluoromethyl ylide  $\text{Ph}_2\text{S}^+-\text{CHCF}_2\text{H}$  is a weak reductant and that the addition of a stronger reducing agent is crucial.

On the basis of the above results and related reports,<sup>18,19a,20</sup> on the iron-catalyzed cyclopropanation of double bonds with carbenes, a reaction mechanism is proposed in Scheme 5.  $\text{Fe}(\text{TPP})\text{Cl}$  is first reduced by Zn to  $\text{Fe}^{\text{II}}$ , which is then trapped by difluoromethyl ylide **B** (produced by deprotonation of **1**) to afford the Fe-difluoromethylcarbene complex **C** ( $\text{Fe}=\text{CHCF}_2\text{H}$ ). The olefin substrate approaches carbene intermediate **C** to form transition state **D**, in which the substituents ( $\text{R}^{\text{S}}$  and  $\text{R}^{\text{L}}$ ) in the olefin substrate project up and out of the porphyrin plane. Compared with the orientation in which the substituents point towards the porphyrin ring, the orientation in transition state **D** suffers weaker steric effects and is thus preferred. The unavoidable strong steric repulsion between the substituents and the porphyrin ring explains the inertness of internal olefins.



**Scheme 5** Plausible reaction mechanism.

The strong steric interaction between substituent  $\text{R}^{\text{L}}$  and the difluoromethyl group results in high *trans* selectivity. The cyclopropanation of **D** affords the final product and simultaneously releases the  $\text{Fe}^{\text{II}}$  complex **A**.

In conclusion, difluoroethyl sulfonium triflate  $\text{Ph}_2\text{S}^+\text{CH}_2\text{CF}_2\text{H OTf}^-$  was found to be a convenient difluoromethylcarbene reagent for iron-catalyzed cyclopropanation. This work represents the first example for the safe and efficient generation of difluoromethylcarbene, and is the first protocol for the one-step synthesis of  $\text{HCF}_2$ -containing cyclopropanes with a wide substrate scope, excellent diastereoselectivities and in high yields. The strategy for the formation of carbene from the sulfur ylide may also find synthetic utility in other research areas.

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