

A Copper-Catalyzed Reductive Defluorination of  $\beta$ -Trifluoromethylated Enones via Oxidative Homocoupling of Grignard Reagents

Xiaoting Wu,<sup>†</sup> Fang Xie,<sup>\*,†</sup> Ilya D. Gridnev,<sup>‡</sup> and Wanbin Zhang<sup>\*,†</sup>

<sup>†</sup>Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

<sup>‡</sup>Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Supporting Information

**ABSTRACT:** An efficient copper-catalyzed reductive defluorination of  $\beta$ -trifluoromethylated enones via an oxidative homocoupling of Grignard reagents is reported. The reaction proceeded smoothly with a wide range of substrates, including the ones bearing aromatic heterocycles, such as furyl and thienyl ring systems in high yields (80–92%, except one example) under mild conditions. This provides a practical method for synthesis of *gem*-difluoroolefin ketones. It is also worth noting



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that this homocoupling process of Grignard reagents using  $\beta$ -trifluoromethylated enones as "oxidizing reagents" is effective for both the Csp<sup>2</sup>-Csp<sup>2</sup> and Csp<sup>3</sup>-Csp<sup>3</sup> bond formations, including for substrates whose  $\beta$ -hydride elimination of the corresponding transition metal alkyl complex is particularly facile, affording coupling products with high yields (83-95%), simultaneously.

gem-Difluoroalkenes are versatile building blocks in organic synthesis, in which the gem-difluorovinyl group can be transformed into various functionalities.<sup>1</sup> Therefore, gemdifluoroalkene compounds have attracted significant interest and have become very important synthetic targets in academia and industry.<sup>1c,2</sup> 2-Trifluoromethyl-1-alkenes are reactive compounds, and their selective defluorination is a promising method for the preparation of difluoro compounds due to the availability of trifluoromethylated compounds.<sup>1c,2k-m</sup> Furthermore, in recent decades, the addition of nucleophiles to  $\alpha$ trifluoromethyl alkenes and subsequent  $\beta$ -fluoride elimination via an S<sub>N</sub>2' reaction has been extensively explored, allowing for rapid access to gem-difluoroalkenes.<sup>2k,3</sup>

For  $S_N 2'$  reactions of organic fluorides, metaphorically, an electron can be regarded as the smallest nucleophile. In general, it is not easy to cleave a C-F bond due to its strong bond energy. However, a C-F bond of the trifluoromethyl group that is attached to a  $\pi$  system can be readily cleaved under electroreductive conditions, since electron acceptance into the  $\pi$ -system and subsequent extrusion of a fluoride ion contribute greatly to the driving force of the reaction. However, to date, only a few reductive-type defluorinations for the preparation of gem-difluorovinyl groups have been reported, and they mostly consist of electrochemical reductions,<sup>4</sup> the use of reductive metal magnesium,<sup>5</sup> and photocatalytic conditions<sup>2m,6</sup> (Scheme 1, previous work). As is well-known, oxidative homocoupling reactions of organometallic reagents occur with an oxidant; the oxidant can be regarded as an electron acceptor. Inspired by the mechanism of oxidative coupling reactions of organometallic reagents," we envisioned that an oxidative coupling reaction

Scheme 1. Cleavage of C–F Bond in the Trifluoromethyl Group Attached to a  $\pi$  Electron System under Electroreductive Conditions



may provide a convenient electron source and that compounds bearing a CF<sub>3</sub> group attached to a  $\pi$ -system may accept electrons and thus act as an "oxidizing reagent". This strategy provides a convenient electron source, which results in a reductive-type reaction of the trifluoromethyl group bonded to a  $\pi$ -electron system. gem-Difluoroalkenes are thus obtained

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accompanied by an oxidative homocoupling reaction of organometallic reagents (Scheme 1, our strategy).

gem-Difluoroolefin ketones are versatile synthons for many fluorinated compounds and possess unique reactivity toward intramolecular S<sub>N</sub>V reactions.<sup>8</sup> However, only two methodologies have been developed for their preparation: one required precious metal iridium as the catalyst via a photocatalytic decarboxylative/defluorinative reaction,<sup>6a</sup> and another required harsh reaction conditions and utilized hazardous and expensive reagents.9 On the other hand, homocoupling reactions of Grignard reagents allow for easy and efficient access to symmetrical compounds, and homocoupling reactions of aryl and alkenyl Grignard reagents have been extensively explored;<sup>10</sup> however, the oxidative homocoupling of alkyl Grignard reagents, <sup>11,12</sup> especially those bearing  $\beta$ -hydrogens, <sup>12</sup> remains a challenge due to the difficulty of alkyl-alkyl couplings using transition metal catalysts. As part of our project on the Cu-catalyzed functionalization of enones,<sup>13</sup> herein, we report a highly efficient synthesis of gemdifluoroolefin ketones via a copper-catalyzed reductive defluorination. Simultaneously, symmetrical biaryls, alkenes, and alkanes can be obtained effectively via oxidative homocoupling of Grignard reagents. In particular, this coupling process is also effective for Csp<sup>3</sup>-Csp<sup>3</sup> bond formations (Scheme 1, this work).

We began our study using  $\beta$ -trifluoromethylated enone 1a as a model substrate (Table 1), which can be readily obtained in

	Table 1. Optimization of the Reaction Conditions"								
	$Ph$ $CF_3$ + $PhMgBr$ $CIX$ $DCM, 3 h$								
		1a	Ph Ph +	Ph-Ph +	Ph Ol Ph	H Ph			
2a			2a	3a	4				
					yield	(%) <sup>c</sup>			
	entry	ligand	CuX (mol %)	2a:4 <sup>b</sup>	2a	3a			
	1	-	_	4:96 <sup>b</sup>	trace <sup>b</sup>	trace <sup>b</sup>			
	2	_	Cu(I)TC (2.5)	69:31	66	65			
	3	$PPh_3$	Cu(I)TC (2.5)	90:10	88	89			
	4	$PPh_3$	Cu(I)I (2.5)	83:17	81	81			
	5	$PPh_3$	$Cu(II)(OAc)_2$ (2.5)	75:25	73	77			
	6	$PPh_3$	Cu(II)Br <sub>2</sub> (2.5)	77:23	74	76			
	7	$PPh_3$	Cu(I)TC (1.0)	91:9	91	93			
	8	$PPh_3$	Cu(I)TC (0.1)	81:19	80	82			

<sup>*a*</sup>The reaction of 1a (0.20 mmol) with PhMgBr (2.5 equiv) was performed in DCM (2.0 mL) at room temperature for 3 h in the presence of the complex *in situ* from CuX (*n* mol %) and PPh<sub>3</sub> (2*n* mol %). <sup>*b*</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>*c*</sup>Yield of products isolated after chromatography.

high yield by the reaction of commercially available trifluoroacetophenone and a Wittig reagent.<sup>14</sup> A blank experiment using **1a** with PhMgBr in the absence of a copper salt provided 1,2addition product **4** as the major product (entry 1). Under our assumption above (Scheme 1), the reaction was carried out by employing PhMgBr and Cu(I)TC (copper(I)-thiophene-2carboxylate) in the presence of **1a** in DCM and at room temperature over 3 h. To our delight, the *gem*-difluoroolefins ketone **2a** and biphenyl **3a** products were obtained in yields of 66% and 65%, respectively, accompanied by a minor 1,2addition product **4** (**2a**:**4** = 69:31) (entry 2). Next, PPh<sub>3</sub> was used as a ligand of Cu(I)TC, and the yields of 2a and 3a (88% and 89%, respectively) increased (entry 3). Following screening of the copper salts and the amount of catalyst (entries 4–8), 1.0 mol % of Cu(I)TC was found to give the best result. The yields of 2a and 3a were further improved to 91% and 93%, respectively, and only a small quantity of 1,2-addition product (2a:4 = 91:9) was observed (entry 7).

With the optimized reaction conditions (Table 1, entry 7) in hand, the scope of substrates 1 was then examined (Table 2).

## Table 2. Substrates Scope of $\beta$ -Trifluoromethylated Enones<sup>*a*</sup>

0 ∎ R1	CF <sub>3</sub> <sup>+</sup> Ph	MgBr	Cu(I)TC PPh <sub>3</sub> ( DCM,	(1.0 r 2.0 m rt, 3 h	$\xrightarrow{\text{nol }\%)} \mathbb{R}^1 \xrightarrow{\mathbb{CF}_2} \mathbb{R}^2$	+ Ph-	Ph
	1a-x				2a-x	3a	
entrv	2	yiel	d/% <sup>*</sup>	entrv	2	yield	/% "
0.11.7		2	3a	, sind y		2	3a
1	O CF <sub>2</sub> Ph 2a	91	93	13	Ph 2m	83	83
2	Et 2b	66	69	14 Me	O CF <sub>2</sub> Ph 2n	88	89
3	Cy 2c Ph	81	83	15 Me	O CF <sub>2</sub> Ph 20	82	85
4	Me O CF <sub>2</sub> Ph 2d	87	89	16	O CF <sub>2</sub> Ph 2p	92	91
5 Me	O CF <sub>2</sub> Ph	90	93	17	0 CF <sub>2</sub> Ph 2q	89	91
6 Me	O CF <sub>2</sub> Ph	90	91	18	O CF <sub>2</sub> Ph	91	92
7 MeO	O CF <sub>2</sub> Ph	92	92	19	O CF <sub>2</sub> Ph	92	92
8	F O CF <sub>2</sub> Ph 2h	86	87	20	Ph 2t Ph	91	91
9 F.	O CF <sub>2</sub> Ph	88	90	21	Ph 2u Me	90	91
10 F	O CF <sub>2</sub> Ph	88	92	22		90	92
11	O CF <sub>2</sub> Ph	89	88	23	Ph 2w	85	86
12 F <sub>3</sub> C	O CF <sub>2</sub> Ph	80	84	24	O CF <sub>2</sub> Ph (4E)-2x	89	91

<sup>*a*</sup>The reaction of 1a-x (0.50 mmol) with PhMgBr (2.5 equiv) was performed in DCM (5.0 mL) at room temperature for 3 h in the presence of the complex formed *in situ* from Cu(I)TC (0.005 mmol, 1.0 mol %) and PPh<sub>3</sub> (0.01 mmol, 2.0 mol %). <sup>*b*</sup>Yield of products (2*a*-*x*) and product 3*a* isolated after chromatography.

The reaction proceeded smoothly with a wide range of substrates. The influence of the R<sup>1</sup> group in substrates **1** was first investigated. When R<sup>1</sup> was an alkyl group, such as Et or Cy, the desired products (2b-c) were afforded in moderate to good yields (66% and 81%, respectively). When R<sup>1</sup> was either a phenyl or substituted phenyl group, good to high yields (80–92%) of the corresponding *gem*-difluoroolefins ketones (2a,

**2d–q**) were obtained, irrespective of the electronic properties or substitution pattern on the aromatic ring. In addition, the reaction scope was expanded to include substrates bearing aromatic heterocycles, such as furyl and thienyl ring systems. The desired products (**2r–s**) were obtained with excellent yields (91% and 92%, respectively). With R<sup>2</sup> being a substituted phenyl group bearing electron-rich or electron-poor substituents, the reactions proceeded well to afford the corresponding *gem*-difluoroolefins ketones (**2t–w**) in high yields (85–91%). Finally,  $\beta$ -CF<sub>3</sub>- $\alpha$ , $\beta$ , $\gamma$ , $\delta$ -dienone (**1x**) was also employed as a substrate in this reaction, giving the corresponding product (4*E*)-**2x** in 89% yield.

Additionally, it is also worth noting that the oxidative homocoupling product **3a** of PhMgBr provided similarly high yields using this Cu-catalyzed reductive-type reaction of trifluoromethyl groups bonded to a  $\pi$ -electron system. This suggests that the Cu-catalyzed system could also be of use for the oxidative homocoupling of Grignard reagents using **1** as an "oxidizing reagent", a reaction which has not been previously reported. Subsequently, the scope of Grignard reagents in the reaction with **1a** was investigated (Table 3). First, various





<sup>*a*</sup>The reaction of 1a (0.50 mmol) with RMgBr (2.5 equiv) was performed in DCM (5.0 mL) at room temperature for 3 h in the presence of the complex *in situ* from Cu(I)TC (0.005 mmol, 1.0 mol %) and PPh<sub>3</sub> (0.01 mmol, 2.0 mol %). <sup>*b*</sup>Yield of products (3a–o) and product 2a isolated after chromatography.

substituted aryl magnesium reagents were coupled in high yields (90–95%). Functional groups, such as alkyl (3b), alkoxy (3c, 3f-h), fluorine (3d), and trifluoromethyl (3e), were all well tolerated, irrespective of the substitution pattern on the aromatic ring. 1- or 2-Naphthylmagnesium reagents were also amenable to this reaction and afforded their corresponding binaphthyls 3i and 3j with high yields (94% and 95%, respectively). A phenyl substituted alkenyl Grignard reagent also afforded its corresponding conjugated diene (3k)

smoothly, with the coupling also being highly stereoselective. Of particular note is that the Csp<sup>3</sup>–Csp<sup>3</sup> homocoupling products (**31**–**30**) were obtained in good yields (83–92%) including those from reactions with PhCH(CH<sub>3</sub>)MgBr, Ph(CH<sub>2</sub>)<sub>2</sub>MgBr, and Ph(CH<sub>2</sub>)<sub>3</sub>MgBr (**3m**, 83%; **3n**, 92%; **3o**, 91%). These three substrates are especially challenging since  $\beta$ -hydride elimination of the corresponding transition metal alkyl complex is particularly facile. Notably, the homocoupling product of PhCH(CH<sub>3</sub>)MgBr is only *meso-2*,3-diphenylbutane (**3m**) with none of the D,L-2,3-diphenylbutane being observed.

We next turned our attention to the reaction mechanism. According to a blank experiment (Table 1, entry 1), the major product was 1,2-addition product 4, with only trace amounts of 2a and 3a being observed in the absence of the copper salt under the optimized reaction conditions (Table 1, entry 7), which indicated that this reaction required a copper catalyst. Furthermore, when 2.0 equiv of TEMPO were used as a radical scavenger in this reaction system (see Supporting Information), 2a and 3a were isolated in yields of 90% and 92%, respectively, yields that are identical to those obtained in the absence of TEMPO. This result suggests that the reaction does not proceed through a radical process. On the basis of the experimental results and previous reports, <sup>4,7</sup> a possible catalytic pathway for the reaction of 1a with PhMgBr has been proposed (Scheme 2). The reaction process may begin with an





organocopper reagent PhCu(I), which formed via transmetalation of PhMgBr and Cu(I)TC. Treatment with another equivalent of PhMgBr results in the formation of a copper monoanionic salt A.<sup>7a,b</sup> Subsequent oxidative homocoupling with 1a acting as an oxidant, electron acceptance into the  $\pi$ system of 1a, and extrusion of a fluoride ion afford biphenyl 3a and the copper species **B**. The copper species **B** is readily transmetalated with another equivalent of PhMgBr to provide the magnesium species **C**, which is hydrolyzed to form the target product 2a. The organocopper reagent PhCu(I) is regenerated to complete the catalytic cycle.

To further demonstrate the utility of our methodology for the synthesis of *gem*-difluoroolefin ketones, a gram-scale reaction was conducted, and *gem*-difluoroolefin ketone 2a and biphenyl 3a were obtained in 88% and 89% yields, respectively (Scheme 3a). In addition, MeMgBr and EtMgBr were used in place of PhMgBr, and 2a was obtained easily in high yields (92% and 90%, respectively), accompanied by the formation of

# Scheme 3. Gram-Scale Reactions of 1a

1a	PhMgBr (2.5 equiv) optimized reaction conditions (Table 1, entry 7)	2a + Ph─Ph 88% yield 89% yield (8.20 g) (4.90 g)	(a)
	RMgBr (2.5 equiv)	2a + R−R R = Me 92% yield (1.19 g) R = Et 90% yield (1.16 g)	(b)

ethane or butane, which are readily expelled as gas from the reaction mixture (Scheme 3b).

To test the versatility of *gem*-difluoroolefin ketones obtained via the aforementioned sequence, we performed several transformations on  $\gamma$ , $\gamma$ -difluoroallylic ketone **2a** (Scheme 4).



The product **2a** can be readily converted to the corresponding  $\gamma,\gamma$ -difluoro allylic alcohol **5** in a yield of 99% by addition of PhMgBr. Fortunately, **5** can be readily converted to 2-fluorinated dihydrofuran **6** in a yield of 95% via an intramolecular S<sub>N</sub>V reaction, thus averting tedious syntheses of fluorine-containing five-membered heterocycles, which usually require harsh reaction conditions.<sup>2d,8,15</sup> In addition, the corresponding *gem*-difluorodiene 7 was obtained in 99% yield via a dehydration reaction of **5**. Interestingly, hydrogenation of compound **2a** with H<sub>2</sub> in the presence of a Pd/C catalyst and in different solvents allowed for the selective formation of the hydrogenated products in high yields (**8**, 99%; **9**, 99%). In addition, **2a** can also be converted to tetrasubstituted 2*H*-pyrrole **10** in a yield of 92% by reaction with benzyl amine in the presence of a ZnCl<sub>2</sub> catalyst.

In conclusion, we have developed an efficient synthesis of *gem*-difluoroolefin ketones via a copper-catalyzed reductive defluorination, accompanying an oxidative homocoupling of Grignard reagents for the synthesis of symmetrical alkanes or biaryls. This reaction can be performed under mild conditions providing high yields for the two desired products, simultaneously. In particular, this coupling process is effective for  $Csp^3-Csp^3$  bond formation, including for substrates whose  $\beta$ -hydride elimination of the corresponding transition metal alkyl complex is particularly facile.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b00379.

Experimental procedures and characterization data for all reactions and products, including <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra (PDF)

# AUTHOR INFORMATION

#### **Corresponding Authors**

\*xiefang@sjtu.edu.cn. \*wanbin@sjtu.edu.cn.

### ORCID ®

Wanbin Zhang: 0000-0002-4788-4195

#### Notes

The authors declare no competing financial interest.

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