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Development of (Trifluoromethyl)zinc Reagent as Trifluoromethyl Anion and Difluorocarbene Sources

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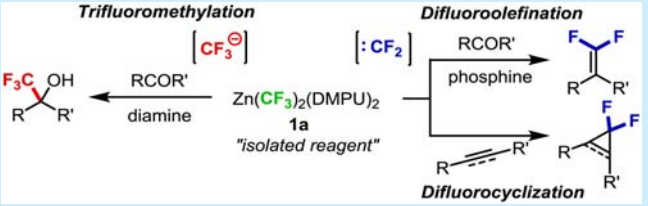
Supporting Information

ABSTRACT: The trifluoromethylation of carbonyl compounds is accomplished by the stable (trifluoromethyl)zinc reagent generated and then isolated from CF_3I and $ZnEt_2$, which can be utilized as a trifluoromethyl anion source (CF_3^-). The reaction proceeds smoothly with diamine as a ligand and ammonium salt as an initiator, providing the corresponding trifluoromethylated alcohol products. Moreover, the (trifluoromethyl)zinc reagent can also be employed as a difluorocarbene source ($:CF_2$) not only for *gem*-difluoroolefination of carbonyl compounds with phosphine but also for *gem*-difluorocyclization of alkenes or alkynes via the thermal decomposition, respectively.



The introduction of fluorine atoms into small organic molecules is a powerful strategy to increase the binding affinity to molecular receptors in the development of novel pharmaceuticals and agrochemicals.[1] Indeed, the modern pharmaceutical and agrochemical industry critically depends on the recent progress of organic fluorine chemistry. In the past decades, considerable effort has been devoted to the development of efficient nucleophilic, electrophilic, and radical approaches to introduce the trifluoromethyl (CF_3) group.[2] Particularly, the (trifluoromethyl)metal species (MCF_3) have played an important role in the development of these methods.[3] However, the main obstacle is that the (trifluoromethyl)metal species with lithium and magnesium are labile even at very low temperatures and consequently decompose via α-fluorine elimination to produce metal fluoride and singlet difluorocarbene. Therefore, the Ruppert−Prakash reagent (Me_3SiCF_3), which can be stabilized through an Si−CF_3 bond, is commonly utilized as the most convenient trifluoromethylating reagent.[4] It has also been recognized that the (trifluoromethyl)zinc reagent can be applied to the trifluoromethylations. The (trifluoromethyl)zinc reagent ($Zn(CF_3)I$) generated in situ from trifluoromethyl iodide (CF_3I) and zinc dust is reported to serve for a variety of trifluoromethylations.[5] However, the reproducibility of this method in which ultrasonic irradiation is required during the course of the preparation and reaction remains problematic. Recently, it has been demonstrated that the (trifluoromethyl)zinc reagent prepared in situ from TMP_2Zn and fluoroform (CHF_3) is efficient in the trifluoromethylation of aryl iodide catalyzed by copper chloride.[6] It has also been reported that the combination of trifluoromethyl bromide (CF_3Br) and zinc dust in DMF can lead to the (trifluoromethyl)zinc reagent ($Zn(CF_3)Br{\cdot}2DMF$) as the stable solid, which is applicable to the copper-mediated trifluoromethylation of aryl iodide.[7] However, these methods suffer from intrinsic disadvantages such as the use of laborious preparation of TMP_2Zn and ozone-depleting CF_3Br, respectively. Accordingly, the development of a reaction with the zinc-based reagent remains far behind compared to the silicon-based counterpart. We have recently succeeded in the aromatic trifluoromethylation catalyzed by copper iodide with the stable bis(trifluoromethyl)zinc reagent **1a** generated and then isolated from CF_3I, $ZnEt_2$, and DMPU.[8−10] Encouraged by this reagent, we continued to explore the potential of the zinc reagent **1** through application to a variety of reactions. Herein, we describe the trifluoromethylation of carbonyl compounds[4,11] with the (trifluoromethyl)zinc reagent bearing diamine ligand, which can be utilized as a trifluoromethyl anion source (CF_3^-). Furthermore, the zinc reagent as a difluorocarbene source ($:CF_2$) is applicable not only to *gem*-difluoroolefination of carbonyl compounds[12,13] with phosphine but also to *gem*-difluorocyclization of alkenes and alkynes[12b,14,15] via thermal decomposition, respectively.

We commenced our studies by examining the trifluoromethylation reaction of 1-naphthaldehyde **2a** with the zinc reagent **1** in DMF at 40 °C (Scheme 1). No product could be observed when $Zn(CF_3)_2(DMPU)_2$ **1a** was employed. The reagent $Zn(CF_3)IL_2$ (L = DMF, DMPU),[8b] which can be generated and isolated by the reaction of zinc dust with CF_3I, was also totally inactive to **2a**. To our delight, after treatment of $Zn(CF_3)_2(TMEDA)$[8a] bearing diamine ligand, the structure was unambiguously confirmed by X-ray analysis and the desired product **3a** was obtained in 72% yield after 24 h. A variety of *N,N* ligands such as 1,10-phenanthoroline, 2,2′-bipyridine and other ethylenediamine derivatives were investigated, but TMEDA was found to lead to the highest yield of **3a**. Significantly, monitoring the change of conversion in reaction time by ^{19}F NMR analysis clarified that an induction period of at least 3 h exists on this reaction system.

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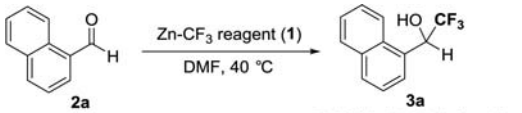
Scheme 1. Nucleophilic CF_3 Addition to Aldehyde[a]

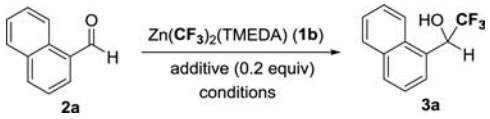


reaction time[b]	1.5 h	3 h	6 h	12 h	24 h
yield[c]	trace	trace	17%	64%	72%

[a]Conditions: **2a** (0.1 mmol) and **1** (0.2 mmol) in DMF (1.0 mL) at 40 °C for 24 h. [b]Reaction using **1b**. [c]Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard.

On the basis of the result observed above, we investigated the effect of additive as an initiator (Table 1). Thus, 0.2 equiv of KO-*t*-Bu or KF was found to facilitate the reaction without an induction period to give the alcohol **3a** in 85% and 47% yields, respectively, even after 6 h (entries 1 and 2). Various ammonium salts can also be applied to the reaction as initiators, and especially *n*-Bu_4NOAc gave higher yields after 3 h (entries 5 vs 1−4). DMF is often selected as an effective solvent for the trifluoromethylation reaction using trifluoromethylating reagents[3c,4] because the trifluoromethyl anion can be trapped by DMF to provide the reservoir of trifluoromethylating hemiaminolate species.[16] Accordingly, whether noncoordinating solvents can be exploited or not for the reaction was examined. Consequently, it was found that the reaction proceeded smoothly even in dichloromethane to give the product in 96% yield, while the reactivity was slightly decreased compared to DMF (entries 5 vs. 6). The reaction took place even at room temperature, in spite of moderate yield (entry 7).

Table 1. Effect of Activator in CF_3 Addition to Aldehyde[a]



entry	additive	conditions	yield[b] (%)
1	KO-*t*-Bu	DMF, 40 °C, 6 h	85
2	KF	DMF, 40 °C, 6 h	47
3	*n*-Bu_4NBr	DMF, 40 °C, 6 h	37
4	Me_4NF	DMF, 40 °C, 6 h	55
5	*n*-Bu_4NOAc	DMF, 40 °C, 3 h	92
6	*n*-Bu_4NOAc	CH_2Cl_2, 40 °C, 3 h	51 (96)[c]
7	*n*-Bu_4NOAc	DMF, rt, 24 h	50

[a]Conditions: **2a** (0.1 mmol) and **1b** (0.2 mmol) in solvent (1.0 mL). [b]Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard. [c]Reaction time was 6 h.

With the optimized reaction conditions in hand, various aldehydes and ketones **2** were employed for the reaction, giving the corresponding alcohols **3** in good to excellent yields (Figure 1). Aromatic aldehydes bearing the electron-donating and -withdrawing *para*-substituents resulted in high yields of the products **3b−f**. Interestingly, the reaction of aldehyde with the electron-donating *para*-substituent showed a faster reaction rate than with the electron-withdrawing one (**3d** vs **3e**). The reaction of aromatic aldehydes with *ortho*-substituents led to slightly lower yields (**3h−j**) compared with *para*- and *meta*-substituents. Although cinnamaldehyde also served as an acceptable substrate for the reaction, nonanal with an α-proton provided only a trace

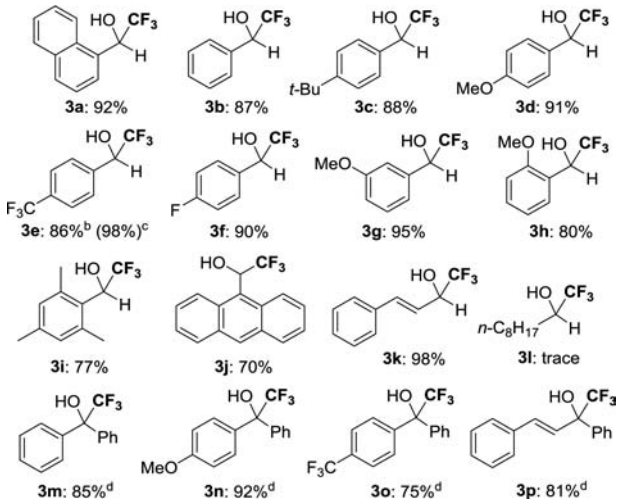
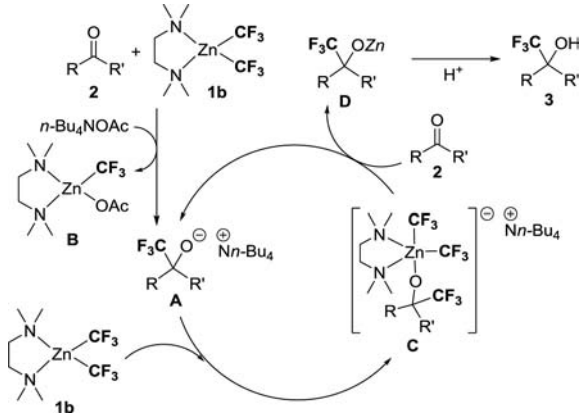


Figure 1. Scope and limitation of carbonyl compounds. (a) Conditions: **2** (0.1 mmol), *n*-Bu_4NOAc (0.02 mmol), and **1b** (0.2 mmol) in DMF (1.0 mL) at 40 °C for 3 h. Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard. (b) Reaction time was 6 h. (c) CH_2Cl_2 instead of DMF was used and reaction time was 12 h. (d) Conditions: **2m−p** (0.1 mmol), *n*-Bu_4NOAc (0.04 mmol), and **1b** (0.4 mmol) in DMF (1.0 mL) at 50 °C for 12 h.

amount of the product. Benzophenone derivatives and chalcone were trifluoromethylated smoothly to give the desired products **3m−o** in good yields, while a larger amount of *n*-Bu_4NOAc and **1b** was needed.

On the basis of our results and previous reports[4] involved in trifluoromethylations of carbonyl compounds using the Ruppert−Prakash reagent, the reaction is likely to proceed through an autocatalytic process (Scheme 2). The reaction process would start from the generation of alkoxide **A** bearing tetrabutylammonium cation and zinc species **B** with acetate, involving activation of *n*-Bu_4NOAc as an initiator to zinc reagent **1b**. Subsequently, the trifluoromethyl anion can be transferred into carbonyl compound **2** via a putative zincate **C** generated by the reaction of zinc reagent **1b** with alkoxide **A**. As a result, alkoxide **A** is regenerated to autocatalyze the following reaction. Finally, zinc alkoxide **D** obtained simultaneously is converted to the desired alcohol product **3** via protonation by water.

Scheme 2. Plausible Reaction Mechanism



With the aim of enhancing the utility of the isolated zinc reagent, we next explored *gem*-difluoroolefination of carbonyl compounds employing the zinc reagent as a difluorocarbene

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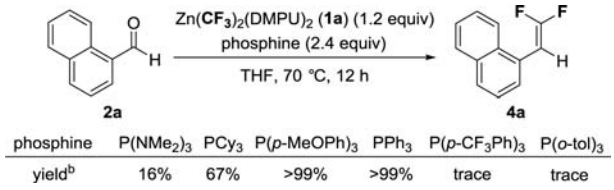
source. The reaction in THF by treatment of the zinc reagent **1a** and aldehyde **2a** in the presence of phosphine, which is necessary to generate in situ the (difluoromethylene)phosphonium ylide (CF_2 = PR_3) as an active species, proceeded smoothly to provide the difluoroolefinated product **4a** (Scheme 3). However, the

Scheme 3. Difluoroolefination to Aromatic Aldehyde[a]

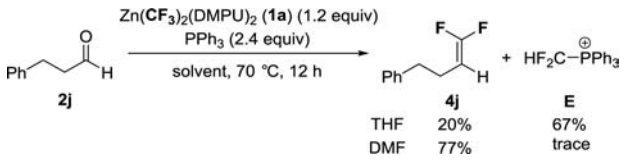


[a]Conditions: **2a** (0.1 mmol), **1a** (0.12 mmol), and phosphine (0.24 mmol) in THF (1.0 mL) at 70 °C for 12 h. [b]Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard.

reaction employing **1b** instead of **1a** did not occur because the ligand exchange between monodentate phosphine and TMEDA is inefficient for generating the phosphonium ylide, in sharp contrast to the case of DMPU. Regarding the effect of phosphine, PPh_3 and P(*p*-MeOPh)$_3$, as a type of triarylphosphine, were more suitable for the present reaction than more electron-rich analogues such as $P(NMe_2)_3$ and PCy_3, affording the product **4a** quantitatively. It was also found that the reactions with electron-poor or bulky triarylphosphines such as P(*p*-CF_3Ph)$_3$ and P(*o*-tol)$_3$ resulted in almost complete recovery of substrate.

Under the optimized conditions employing cheaper PPh_3, aliphatic aldehyde **2j** also underwent the reaction, but the yield of the desired product **4j** was low (20%). In contrast to the reaction of **2a**, the phosphonium salt **E**[13c] formed by protonation of the phosphonium ylide was confirmed in 67% yield by ^{19}F NMR analysis (Scheme 4). The replacement of a solvent from THF to DMF is thus found to improve the yield of product **4a** to 77%, along with only a trace amount of **E**.

Scheme 4. Difluoroolefination to Aliphatic Aldehyde[a]



[a]Yields were determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard.

According to this protocol, a variety of aldehydes were difluoroolefinated affording the corresponding products **4** in good to excellent yields (Figure 2). Benzaldehyde derivatives with electron-donating and -withdrawing *para*-substituents showed relatively high reactivity in excellent yields (**4a**–**d**). The reactions with aromatic aldehydes bearing *ortho*-substituents also took place (**4f**–**h**), while the reactivity was decreased owing to steric hindrance. It was demonstrated that fluoroalkylated ketones were applicable to the reaction in 86% yield (**4k**). The reactions with ketones resulted in the formation of the corresponding products (**4l**–**o**) due to improvement of the reaction conditions, while yields were decreased.

Finally, it was further clarified that the zinc reagent **1a** was successfully applied to *gem*-difluorocyclization of alkenes and

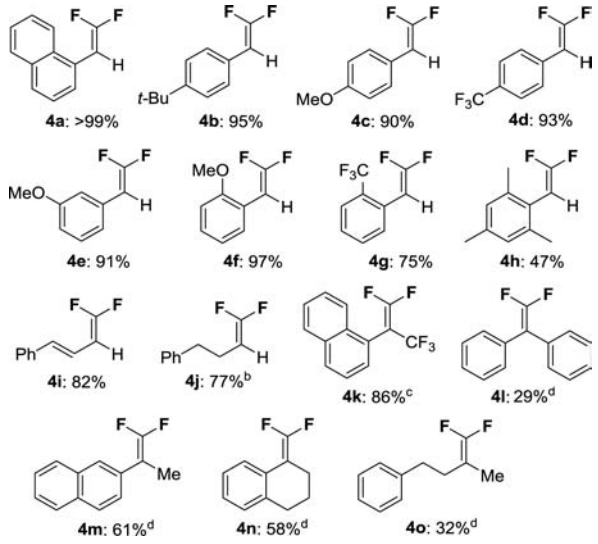
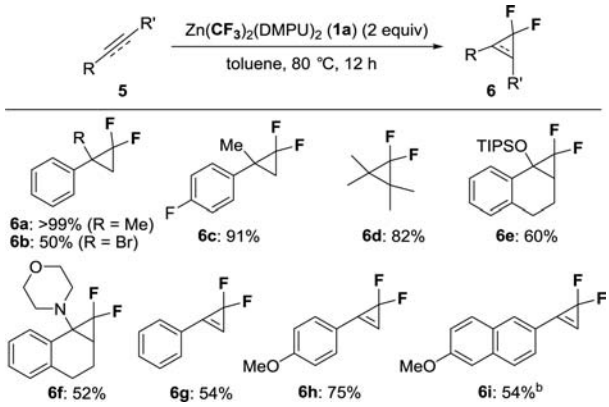


Figure 2. Scope and limitation of carbonyl compounds. (a) Conditions: **2** (0.1 mmol), **1a** (0.12 mmol), and triphenylphosphine (0.24 mmol) in THF (1.0 mL) at 70 °C for 12 h. Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard. (b) DMF instead of THF was used as solvent. (c) At 80 °C for 3 h. (d) Conditions: **2** (0.1 mmol), **1a** (0.3 mmol), and P-*n*-Bu_3 (0.3 mmol) in DMF (1.0 mL) at 110 °C for 3 h. Zinc reagent **1a** was added dropwise over 1 h.

alkynes **5** (Scheme 5). After surveying a wide range of solvents and additives as activators of **1a**, we found that the reactions

Scheme 5. Difluorocyclopropanation and -cyclopropenation[a]



[a]Conditions: **5** (0.1 mmol) and **1a** (0.2 mmol) in toluene (1.0 mL) at 80 °C for 12 h. Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard. [b]Use of PPh_3 (0.2 mmol).

occurred efficiently without any additives in toluene at 80 °C, providing the difluorocyclopropanated and -cyclopropenated products **6**. In the case of cyclopropanation, styrene derivatives and electron-rich tri- and tetrasubstituted alkynes could be exploited for the reaction (**6a**–**f**). Furthermore, cyclopropenation with terminal alkynes proceeded to give the corresponding products in moderate to good yields (**6g**–**i**). Addition of PPh_3 was found to improve the yield in **6i** because the ylide CF_2=PR_3 generated in situ can be utilized as the reservoir of difluorocarbene.[13b]

In summary, we have succeeded in the trifluoromethylation reaction of carbonyl compounds by using the stable bis-(trifluoromethyl)zinc reagent, which can be utilized as a

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trifluoromethyl anion source (CF_3^-). The reaction proceeds smoothly with TMEDA as a ligand and ammonium salt as an initiator to provide the corresponding secondary and tertiary alcohol products bearing a trifluoromethyl substituent. Additionally, the zinc reagent can be applied as a difluorocarbene source ($:CF_2$) not only for *gem*-difluoroolefination of carbonyl compounds with (difluoromethylene)phosphonium ylide generated by addition of phosphine but also to *gem*-difluorocyclization of alkenes and alkynes via the thermal decomposition of the zinc reagent, respectively. Development of catalytic asymmetric reactions with the (trifluoromethyl)zinc reagent is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02439.

Experimental procedures and compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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