## **Copper-Catalyzed Diastereoselective Synthesis of Trifluoromethylated Tetrahydrofurans**

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**Abstract:** The copper-catalyzed intramolecular diastereoselective trifluoromethylcycloetherification of homoallylic alcohols with Togni's reagent as trifluoromethylating reagent was realized under mild conditions. Various trifluoromethylated tetrahydrofurans were synthesized in moderate to good yields.

a- Moreover, a wide range of common functional of groups was tolerated.

**Keywords:** copper; homoallylic alcohols; Togni's reagent; trifluoromethylated tetrahydrofurans; trifluoromethylcycloetherification

ly studied. For example, the Buchwald<sup>[7]</sup> and Sodeoka<sup>[8]</sup> groups have successfully developed the intramo-

## Introduction

Introducing a trifluoromethyl group into organic compounds can significantly improve their hydrophobicity, metabolic activity, electronegativity and bioavailability. Thus, many molecules bearing trifluoromethyl groups, especially heterocycles, have been applied in the field of agrochemicals and pharmaceuticals.<sup>[1]</sup> On the other hand, substituted tetrahydrofurans are key structural blocks in a large group of bioactive natural products.<sup>[2]</sup> Recently, several effective methods for the syntheses of tetrahydrofurans have been reported, including the transition metal- or Lewis acid-promoted ones.<sup>[3]</sup> To date, only few reactions for trifluoromethylcycloetherification have been reported,<sup>[4]</sup> although the halocycloetherification reactions have made significant progress.<sup>[5]</sup>

Nowadays, an immense number of efficient methods for the bifunctionalization of alkenes to synthesize some valuable trifluoromethylated building blocks have been developed.<sup>[6]</sup> The intramolecular trifluoromethylcyclizations of alkenes using an oxygen or nitrogen atom as nucleophile have been extensive-



**Scheme 1.** Trifluoromethylcycloetherification of homoallylic alcohols.

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lecular oxytrifluoromethylation of alkenes and aminotrifluoromethylation of alkenes, respectively. Liang<sup>[9]</sup> has also reported a method for the trifluoromethylation of alkenes involving oximes. However, the intramolecular trifluorooxylation of styrenes has been rarely studied. As part of an ongoing program for the synthesis of trifluoromethylated blocks,<sup>[10]</sup> we herein report the copper-catalyzed diastereoselective trifluoromethylcycloetherification of homoallylic alcohols (Scheme 1).

### **Results and Discussion**

In our preliminary experiments, 4-phenylbut-3-en-1-ol (**1a**, E:Z=3:1) was chosen as the substrate. The model reaction was carried out with 1.0 equivalent of Togni's reagent I (**2**), 1.5 equivalents of **1a** and 20 mol% of CuTc in dichloromethane (DCM) at 80°C in a sealed tube. Gratifyingly, the corresponding tetrahydrofuran **3a** was obtained in 75% yield with excellent diastereoselectivity (Table 1, entry 1). The structure of the major product was established to have the *syn*-configuration by NOE experiments. Inspired by the result, we screened different conditions to find a suitable protocol for the selective formation of tetrahydrofurans. Firstly, we focused on the catalyst effects. Copper is essential for the reaction as no reaction was detected in the absence of copper salt

<b>Table 1.</b> Optimization of the reaction conditions. <sup>[a]</sup>					
Ph	.5 equiv.)		F <sub>3</sub> [Cu] (2) additive ( D solve 80 °	E [Cu] (20 mol%) additive (10 mol%) solvent, N <sub>2</sub> , 80 °C, 8 h 3a	
Entry	Catalyst	Solvent	Additive	Yield [%, syn:anti] <sup>[b]</sup>	
1 2	CuTc -	DCM DCM		75, >95:5 NR <sup>[c]</sup>	
3 4	CuCl CuCN	DCM DCM	-	51, > 95:5 71 > 95:5	
5	$CuCl_2$	DCM	-	48, >95:5	
0 7	$Cu(OAC)_2$ $Cu(OTf)_2$	DCM DCM	_	66, >95:5 37, >95:5	
9 <sup>[e]</sup>	CuTe CuTe	DCM DCM	_	77, >95:5 50, >95:5	
10 <sup>[d]</sup> 11 <sup>[d]</sup>	CuTc CuTc	MeOH DMA		49, >95:5 34, >95:5	
$12^{[d]}$ 13 <sup>[d]</sup>	CuTc	DMSO DCE	_	54, > 95:5 61 > 95:5	
14 <sup>[d]</sup> 15 <sup>[d]</sup>	CuTe	acetone	_	61, > 95.5 61, > 95.5 71 > 95.5	
$15^{[d,f]}$ $17^{[d,g]}$	CuTc	DCM	_	62, >95:5 77 > 05:5	
17 <sup>[d,h]</sup>	CuTe	DCM DCM	-	77, >95:5 56, >95:5	
19 <sup>[d]</sup> 20 <sup>[d]</sup>	CuTc CuTc	DCM DCM	Phen PPh <sub>3</sub>	51, >95:5 67, >95:5	
21 <sup>[d,i]</sup> 22 <sup>[j]</sup>	CuTc CuTc	DCM DCM	Cs <sub>2</sub> CO <sub>3</sub>	$NR^{[c]}$ 75, >95:5	

- <sup>[a]</sup> Reaction conditions: **1a** (0.15 mmol), **2** (0.10 mmol), copper catalyst (0.02 mmol), solvent (1.0 mL), 80 °C, 8 h, under  $N_2$ .
- <sup>[b]</sup> Determined by <sup>19</sup>F NMR spectroscopy using hexafluorobenzene as internal standard.
- [c] NR = no reaction.
- <sup>[d]</sup> 10 mol% of CuTc was used.
- <sup>[e]</sup> 5 mol % of CuTc was used.
- <sup>[f]</sup> The temperature was 60 °C.
- <sup>[g]</sup> 2.0 equiv. of **1a** were used.
- <sup>[h]</sup> 1.0 equiv. of 1a was used.
- [i] 1.0 equiv. of  $Cs_2CO_3$  was used.
- <sup>[j]</sup> The reaction time was 3 h.

(entry 2). However, other copper catalysts, such as CuCl, CuCN, CuCl<sub>2</sub>, Cu(OAc)<sub>2</sub> and Cu(OTf)<sub>2</sub>, afforded low yields of **3a**, albeit with high selectivity for the syn-isomer (entries 3-7). Further investigation showed that the catalyst loading could be lowered down to 10 mol% without any erosion in yield and selectivity (entry 8), whereas a lower yield was obtained with 5 mol% of CuTc (entry 9). Then the solvent effect was studied using 10 mol% of CuTc as the catalyst. Various solvents were screened to examine the feasibility of the reaction. It was found that lower yields were obtained with methanol (MeOH), dimethylacetamide (DMA) or dimethyl sulfoxide (DMSO) (entries 10–12). Dichloroethane (DCE), acetone and acetonitrile (CH<sub>3</sub>CN) could not improve the yield of **3a** (entries 13–15). DCM was the best solvent for this reaction among the solvents tested. Carrying out the reaction in DCM at 60 °C gave *syn*-isomer **3a** in 62% yield (entry 16). When 2.0 equiv. of **1a** were used, **3a** was still obtained in 77% yield. Using 1.0 equiv. of **1a** only gave a 56% yield of **3a** (entries 17 and 18). Attempts to use phenanthroline or triphenylphosphine (PPh<sub>3</sub>) as additive did not further improve the yield (entries 19 and 20). The reaction did not occur in the presence of 1.0 equiv. of Cs<sub>2</sub>CO<sub>3</sub> (entry 21). Under the optimal conditions, the reaction time could be shortened to 3 h (entry 22).

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With the optimized reaction conditions in hand, we studied the scope of homoallylic alcohols for this copper-catalyzed trifluoromethylcycloetherification. As shown in Table 2, a range of homoallylic alcohols **1** including aromatic alcohols and aliphatic alcohols could react with Togni's reagent 2 to give products 3 with excellent diastereoselectivities. Both electronrich and electron-deficient alcohols are compatible with the reaction conditions. The substrates bearing methoxy, methyl or aryl substituents gave the expected products 3b-3f in moderate to good yields. Substrates bearing functional groups, such as amine and hydroxy, were also tolerated in this cyclization reaction to give the corresponding products 3g-3i in excellent yields. Halide-substituted substrates also reacted well to give the cyclic products 3j-3l in moderate yields. However, the reaction of 3,4,5-trifluorophenylsubstituted homoallylic alcohol afforded only 47% yield of **3m**, probablely due to the electron-withdrawing effect of the fluorine atoms. The substrates containing an electron-deficient substituent such as trifluoromethyl, nitro or cyano afforded the corresponding cyclic products **3n-3p** in moderate yields. Homoallylic alcohols containing other substituents, such as naphthyl and heteroaromatic rings, could also react with 2 to give the corresponding products 3q and 3r, albeit the lower yield. When an alkyl substituent was used, the reactions could also occur to give the corresponding cyclic products 3s-3u, but the yields were somewhat lower and the diastereoselectivity was poor. It is worth mentioning that the reaction of 1v containing two phenyl groups took place successfully to give the expected product 3v in good yield (75%). To further explore the scope of this reaction, we also tested the reaction of other related compounds. Unfortunately, the reaction of (E:Z)-5-phenylpent-4-en-1-ol (1w) afforded the desired product 3w in less than 5% yield with the recovery of an amount of starting material 1w. In the case of (E:Z)-6-phenylhex-5-en-1ol (1x), the reaction did not occur at all. The reasons are not clear at present. However, the expected product 3y could be obtained in 50% yield from the reaction of amine substrate 1y with excellent diastereoselectivity.

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[a] Reaction conditions: 1 (0.15 mmol), 2a (0.1 mmol), CuTc (0.01 mmol), DCM (1.0 mL), 80 °C, 3 h, under N<sub>2</sub>, isolated yield for syn-isomer (total yields for products 3 determined by <sup>19</sup>F NMR spectroscopy using hexafluorobenzene as internal standard in the parentheses).

syn:anti > 95:5

- <sup>[b]</sup> Reaction time was 6 h.
- <sup>[c]</sup> Catalyst loading was 20 mol% and reaction time was 20 h.

<sup>[d]</sup> Reaction time was 12 h.

Furthermore, the cyclization of E-3-phenylprop-2en-1-ol (1z) was investigated under the standard conditions. To our surprise, no expected cyclic product was obtained. Only 14% of E-4 was observed and most of the 1z was recovered. However, the cyclization of terminal alkene 1aa worked well to give product 3aa in 69% isolated yield (Scheme 2).

In order to gain insight into the reaction mechanism, we performed the reaction of **1a** and **2** in the presence of 1.5 equiv. of LiCl using acetone as solvent, <sup>19</sup>F NMR analysis showed that the trifluoromethylcycloetherification reaction was inhibited, and the chloride trapping product **5** was obtained in 31% yield (Scheme 3).

Next, the reaction of Z-1a and CuTc in the absence of 2 in DCM was conducted, and E-1a was not detected in the reaction system, indicating that the transformation of Z-1a to E-1a was not involved in this reac-



Scheme 2. Reactions of *E*-1z and 1aa under the standard conditions.



**5**, 31% by <sup>19</sup>F NMR

Scheme 3. Reaction of 1a and 2 in the presence of LiCl.

tion. When the reaction of Z-1a and 2 in the presence of CuTc was quenched after 20 min, only Z-1a and 3a were observed by <sup>1</sup>H NMR analysis.

Based on the above experiments, a plausible mechanism is proposed as outlined in Scheme 4. Initially, the interaction of the Togni I reagent and Cu catalyst gives the iodine(III) species  $\mathbf{A}$ , which reacts with



**Scheme 4.** Proposed mechanism for the trifluoromethylcycloetherification.

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carbon-carbon double bond in homoallylic alcohols 1 to produce the corresponding intermediates B-1 and **B-2**, and regeneration of the copper(I) species at the same time. The transformation between B-2 and B-1 is feasible *via* the rotation of a C-C single bond. Then intramolecular cyclization of intermediates B-1 and B-2 takes place via transition states C-1 and C-2 to give syn-3 and anti-3, respectively. According to the experimental results, the cyclization of intermediate **B-1** with the syn-configuration is more favored and syn-products were formed predominantly, probably because the di-pseudo-equatorial transition state C-1 is more stable than C-2.<sup>[11]</sup> When R is an aryl group, the cations **B** are more stable and easy to form due to the stabilization effect of the aromatic ring. Therefore, aromatic alcohols gave better results in terms of yield and diastereoselectivity.

#### Conclusions

In summary, we have developed a facile method for the diastereoselective trifluoromethylcycloetherification of homoallylic alcohols. The reaction tolerates a wide range of functional groups and provides an efficient protocol for the synthesis of various trifluoromethylated tetrahydrofuran derivatives that may be used as important intermediates in organic synthesis. The plausible mechanisms are also proposed on the basis of experimental results. Further research on the application of this reaction is currently underway in our laboratory.

#### **Experimental Section**

# Typical Procedure for the Synthesis of Homoallylic Alcohols

Under an argon atmosphere, a solution of triphenylphosphine (9.5 g, 36.2 mmol) and 3-bromopropan-1-ol (5.0 g, 36.0 mmol) in *p*-xylene (30 mL) was stirred under reflux for 6 h. Then the reaction mixture was cooled to room temperature and ether (50 mL) was added. The solids were collected by filtration and dried under vacuum to afford 3-(triphenylphosphonium)propan-1-ol bromide as a white solid which was used in the next step without further purification.

Then 5.25 mmol (876.8 mg) of lithium bis(trimethylsilyl)amide were added dropwise to a suspension of 2.25 mmol (900.0 mg) of (3-propan-1-ol)triphenylphosphonium bromide in 5 mL of tetrahydrofuran at -20 °C. The solution was stirred at -20 °C for 1 hour and 1.88 mmol of aldehyde were added dropwise. After 2 h, the mixture was warmed to room temperature and stirred for another 12 h, and then saturated aqueous NH<sub>4</sub>Cl solution was added. The organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/Petroleum ether = 1/5).

#### General Procedure for the Trifluoromethylcycloetherification Reaction

To a reactor charged with Togni I (0.1 mmol, 33 mg), CuTc (0.01 mmol, 1.9 mg), and dichloromethane (1.0 mL) was added the homoallylic alcohol (0.15 mmol) under an  $N_2$  atmosphere. The mixture was stirred at 80 °C. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give product **3** (dichloromethane/petroleum ether).

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