Asymmetric Catalysis

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Achiral Pyridine Ligand-Enabled Enantioselective Radical Oxytrifluoromethylation of Alkenes with Alcohols

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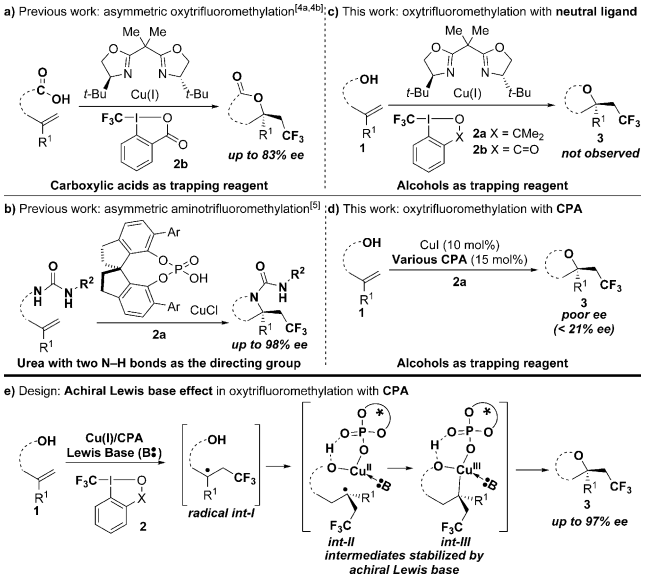
Dedicated to Professor Shizheng Zhu on the occasion of his 70th birthday

Abstract: *A conceptually novel strategy with achiral pyridine as the ancillary ligand to stabilize high-valent copper species for the first asymmetric radical oxytrifluoromethylation of alkenes with alcohols under Cu^{I}/phosphoric acid dual-catalysis has been developed. The transformation features mild reaction conditions, a remarkably broad substrate scope and excellent functional group tolerance, offering an efficient approach to a wide range of trifluoromethyl-substituted tetrahydrofurans bearing an α-tertiary stereocenter with excellent enantioselectivity. Mechanistic studies support the presumed role of the achiral pyridine as a coordinative ligand on copper metal to stabilize the key transient reaction species involved in the asymmetric induction process.*

Chiral trifluoromethyl (CF_3)-containing heterocycles have been gaining increasing interest in agrochemicals, pharmaceuticals and molecular materials because of the unique effect of the fluorine atom on physical and biological properties of many chemicals.[1] As a result, very impressive advances have been achieved in the development of radical intramolecular difunctionalization-type trifluoromethylation of alkenes to construct different types of CF_3-containing heterocycles.[2] However, the catalytic asymmetric variants remain a formidable challenge with few successful examples[3–5] largely because of the difficulty related to the stereochemical control of the involved odd-electron species.[3] In this context, we have recently discovered that a Cu^{I}/chiral phosphoric acid (CPA) dual-catalytic system realized asymmetric aminotrifluoromethylation of alkenes (Scheme 1 b).[5,6] Nevertheless, the incapability of known catalytic systems to tackle the remaining challenges has become more and more obvious and thus new strategies are highly desirable for further developing efficient asymmetric radical difunctionalization-type trifluoromethylation reactions with versatile trapping reagents.

Chiral oxygen heterocycles, such as tetrahydrofurans bearing α-tertiary stereocenters at the C2 positions, are important structural motifs in numerous biologically active compounds and pharmaceutical agents.[7] Consequently, the direct asymmetric construction of α-tertiary tetrahydrofurans has long been recognized as a preeminent goal for organic synthesis.[8] Given the apparent gaps in existing synthetic methodology, we became interested in developing asymmetric radical oxytrifluoromethylation of alkenes with alcohols to access enantioenriched functionalized α-tertiary tetrahydrofurans. However, direct stereochemical control over the reaction between a highly reactive alkyl radical intermediate and an alcohol has proved problematic. Notably, alcohol-based nucleophiles have been found to be incompatible with the copper-bis(oxazoline) catalyst system employed by Buchwald (Schemes 1 a and c, and Scheme S1 in the Supporting Information), presumably because of the low binding affinity of alcohols toward chiral metal centers.[4a,b] We had envisaged the possibility of using the hydroxy group as a hydrogen-bonding donor to anchor CPA-ligated copper catalyst for stereoinduction. However, our attempts to address this challenge by employing our developed Cu^{I}/CPA dual-catalytic system (Scheme 1 b)[5] met with poor enantioselectivity (Scheme 1 d, and Scheme S1). In our previous work, we have observed that the enantioselectivity of aminotrifluoromethylation significantly depended on the presence of an intact urea moiety bearing two acidic N–H bonds. The hydroxy group involved in the current transformation is inherently much weaker than such urea in terms of their capability as a hydrogen-bonding donor and further as an efficient



Scheme 1. Asymmetric radical difunctionalization-type trifluoromethylation of alkenes.

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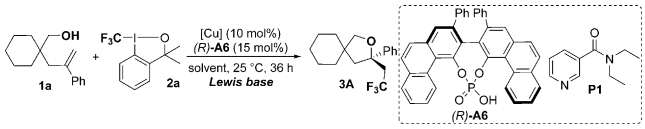
anchor for the CPA-ligated copper catalyst. This may have resulted in strong non-enantioselective background reaction with poor stereocontrol. On the basis of these observations, a conceptually different approach is highly demanded to achieve highly efficient asymmetric radical oxytrifluoromethylation of alkenes with alcohols.

It is well-known that Lewis bases can have a profound influence on the stability of high-valent organo-Cu(II/III) species, affecting their reactivity toward oxidative addition and/or carbon-carbon(heteroatom) bond-forming reductive elimination.[9,10] In light of this knowledge, we questioned whether introducing an ancillary achiral Lewis base would elicit high enantioselectivity by stabilizing high-valent copper species **int-II** and **int-III**, which have been postulated as key intermediates in previous related reactions (Scheme 1e).[4,5] Herein we report the successful realization of this new strategy using achiral pyridine as an ancillary ligand, thus enabling an unprecedented asymmetric radical oxytrifluoromethylation of alkenes with alcohols catalyzed by a dual system of Cu^I and CPA (Scheme 1e). Notably, this work represents the first successful example of achiral additive-enabled highly enantioselective radical reactions.[10]

To probe the feasibility of our assumption, we first evaluated the impact of incorporating catalytic achiral pyridine as an additive into a dual-catalytic system of CuI and (*R*)-VAPOL hydrogenphosphate **A6** (Table 1). We were encouraged to observe a significant increase in enantioselectivity from 21% *ee* to 70% *ee* obtained in the absence and presence of pyridine (entries 1 and 2), respectively. Changes of ligands and anions in copper salts led to profound variations in both the efficiency and the enantioselectivity (entries 2–6), likely suggesting that these achiral ligands/anions were critical for stabilizing the presumed transient reaction species and thus tuning their reactivity and stereochemistry. Among these copper salts examined, $CuBH_4(PPh_3)_2$ bearing PPh_3 ligand was found to be particularly effective in terms of enantioselectivity (entry 6, 77% *ee*). In order for better enantioselectivity, a variety of achiral pyridine derivatives were then screened (entries 10 and 11, and Figure S3a). Both the position and the electronic property of the substituents on the pyridine ring had a significant effect on the efficiency and the stereoselectivity of this radical reaction, and *N*,*N*-diethylnicotinamide **P1** proved to be the optimum one to give **3A** in 87% yield and 91% *ee* (entry 11). Finally, the use of a mixed solvent system of AcO*i*Pr/*c*-hexane (9/1) further improved enantioselectivity to 93% *ee* (entry 12). The use of other Cu salts such as CuI or CuCN instead of $CuBH_4(PPh_3)_2$ provided slightly inferior enantioselectivity under the otherwise optimal reaction conditions (entries 13, 14).

With the optimal reaction conditions established, we next investigated the substrate scope of alkenols (Table 2). We first explored *gem*-disubstituted alkenols bearing different tethering groups and found a series of alkenols containing three- to seven-membered rings were well tolerated to provide a set of spiro-products **3A**–**3E** in 64–88% yields with 90–97% *ee*. Changing the cyclic groups to two methyl groups in the tether had no significant influence on the reaction, giving **3F** with comparable efficiency and enantioselectivity. Next, a range of diversely functionalized alkenols **1G**–**1Q**, including those having mono-substituted phenyl rings with electron-donating or -withdrawing groups at different positions (*ortho*, *meta* or

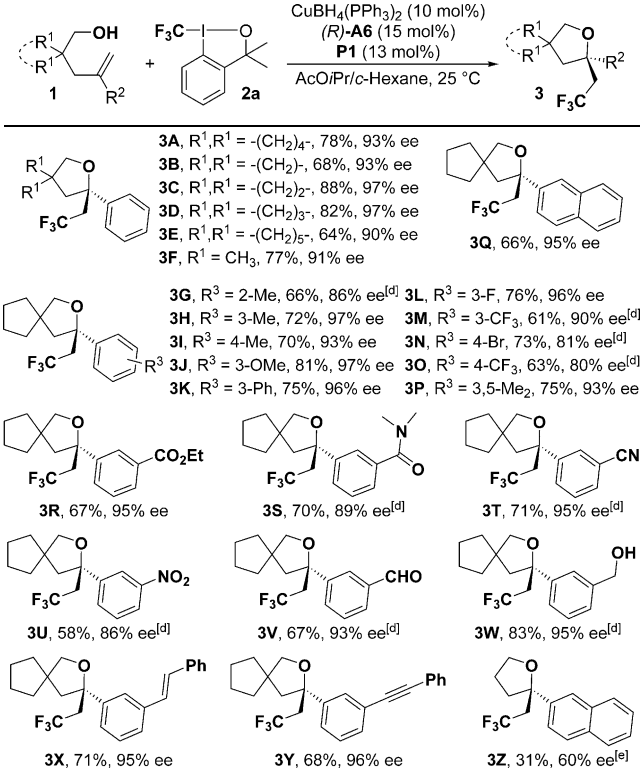
Table 1: Screening of reaction conditions.[a]



entry	[Cu]	LB	solvent	*y* [%][b]	*ee* [%][c]
1	CuI	–	EtOAc	90	21
2	**CuI**	**pyridine**	**EtOAc**	**88**	**70**
3	CuBr	pyridine	EtOAc	87	43
4	CuCl	pyridine	EtOAc	85	42
5	$CuPF_6(MeCN)_4$	pyridine	EtOAc	50	51
6	$CuBH_4(PPh_3)_2$	pyridine	EtOAc	87	77
7	$CuBH_4(PPh_3)_2$	pyridine	DCM	86	72
8	$CuBH_4(PPh_3)_2$	pyridine	MeCN	40	77
9	$CuBH_4(PPh_3)_2$	pyridine	*c*-Hexane	45	77
10	$CuBH_4(PPh_3)_2$	pyridine	AcO*i*Pr	87	80
11	$CuBH_4(PPh_3)_2$	**P1**	AcO*i*Pr	87	91
12	**$CuBH_4(PPh_3)_2$**	**P1**	–[d]	**88**	**93**
13	CuI	**P1**	–[d]	83	84
14	CuCN	**P1**	–[d]	88	89

[a] Reaction conditions: **1a** (0.05 mmol), **2a** (1.5 equiv), Cu^I (10 mol%), (*R*)-**A6** (15 mol%), Lewis base (13 mol%), solvent (0.5 mL), 25°C, 36 h under argon. [b] Yield based on ^{1}H NMR analysis of the crude product using trifluoromethoxybenzene as an internal standard. [c] *Ee* value based on HPLC analysis. [d] AcO*i*Pr/*c*-Hexane (9/1) was used as solvent.

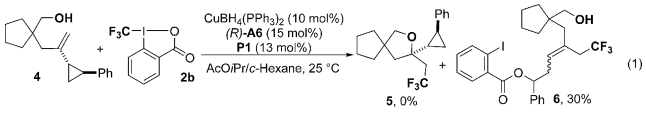
Table 2: Substrate scope.[a,b,c]



[a] All the reactions were conducted on 0.2 mmol scale. [b] Yield was isolated one based on **1**. [c] Ee was determined by HPLC analysis. [d] 1,1,1,3,3,3-Hexafluoro-2-propanol (0.4 equiv) was added. [e] Reaction temperature: 60°C; conversion: 60%.

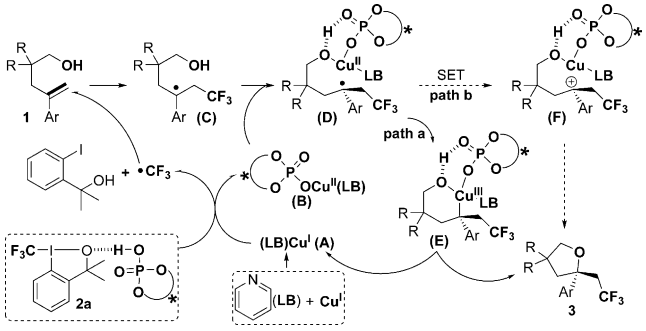
para) and a dimethyl-substituted phenyl ring as well as a polyarene naphthalene ring, were found to be suitable substrates to afford **3G**–**3Q** in 61–81 % yields with 80–97 % *ee* (Table 2). Furthermore, many common functional groups, such as ester (**3R**), amide (**3S**), nitrile (**3T**) and even nitro (**3U**) ones, were all compatible with the reaction conditions. Potentially reactive free aldehyde (**3V**) and alcohol (**3W**) were well tolerated, without the need for protecting groups in spite of the oxidative nature of this process. In addition, substrates containing the other reactive double or triple bonds afforded corresponding products **3X** and **3Y** with the additional double or triple bonds intact. More importantly, substrate **1z** without *gem*-disubstituents together with substrates featuring a heteroaryl-substituted alkene moiety or a 5-hexenol skeleton for the formation of a pyran ring (Scheme 3S) all underwent the current reaction with unsatisfactory but promising enantioselectivity, which warrant further condition optimization. These features indicate the great functional group tolerance (halides, ester, amide, nitrile, nitro, aldehyde, hydroxy, alkene and alkyne groups) of this reaction with unique chemoselectivity, highlighting the generality of this transformation and offering opportunities for further versatile modifications. The absolute configuration of **3V** has been determined by X-ray structural analysis on its hydrazone derivative.[11]

To gain some insight into the reaction mechanism, radical trapping experiments were conducted by employing 2,2,6,6-tetramethyl-1-piperidinyloxy and 1,4-benzoquinone, both of which inhibited the reaction (Scheme S2a). Next, a radical clock experiment with substrate **4** under the typical conditions did not afford the expected product **5**, while delivering **6** in 30 % yield as a mixture of *E*/*Z* isomers, presumably via a radical addition/cyclopropane ring opening/acid trapping cascade process [Eq. (1)]. These observations, together with



(1)

previous studies,[4,5,12] suggest that CF_3 radical is likely generated in situ, which upon further addition to alkene gives rise to α-CF_3 alkyl radical **C** (Scheme 2). In addition, only a trace amount of the desired product was obtained either in the presence of a copper(II) salt or in the absence of any copper catalysts (Scheme S2b). Furthermore, the reaction did not work in the absence of phosphoric acid (Scheme S2b).



Scheme 2. Mechanistic proposal.

These results indicate that copper(I) is essential as a single-electron transfer catalyst to reduce Togni's reagent in order for generating CF_3 radical and the activation of Togni's reagent could be facilitated by the phosphoric acid [Eq. (1)].[13]

Then some experiments were conducted to ascertain the role of pyridine in this reaction. In our reaction system, pyridine derivatives could act either as a Lewis basic ligand on copper metal[9] or as a Brønsted base (proton shuttle)[10c] to facilitate deprotonation of alcohol. In support for the ligand role, our initial high-resolution mass spectrometry analysis of a reaction mixture identified a Cu^I-**P1** complex formed from $CuBH_4(PPh_3)_2$ and **P1** by ligand exchange (Figure S2). To further provide support for pyridine as an ancillary ligand,[10] we have surveyed a range of electronically differentiated pyridines for this reaction (Table 1, and Figure S3a) and found that a certain level of coordinating capability toward copper but not Brønsted basicity is necessary for maintaining high enantioselectivity. In particular, poorly coordinating 2,6-di-*t*Bu-pyridine with a pK_a value (4.95 in water, Table S1) within the optimal pK_a window (3 to 5 in water) for high enantioselectivity only delivered a comparable enantioselectivity (50 % *ee*) with that obtained in the absence of any pyridine (45 % *ee*). This latter fact excludes (or strongly disfavors) a potential role of pyridine as a proton shuttle to facilitate deprotonation of alcohol.[10c] The ligand role of pyridine was further supported by its retarding effect on reaction rate (Figure S3b, conducted at 10 °C), presumably by stabilizing transient high-valent copper species.[9] Furthermore, the *ee* of products during reaction remained nearly constant, supporting a uniform enantiodetermining transition state along with the same reaction pathway for the reaction (Figure S3c). Overall, the above results support that achiral pyridine, at least primarily, acts as an ancillary ligand on copper metal to greatly enhance the level of enantiocontrol.

On the basis of above mechanistic investigations and previous studies,[4,5,12] a plausible catalytic cycle is tentatively proposed (Scheme 2). At first, achiral pyridine is favorably coordinated to Cu^I to form Cu^I-Py complex **A.** This complex next reacts with CPA-activated Togni's reagent by hydrogen bonding[13] via single electron transfer, giving the crucial chiral (LB)Cu^{II} phosphate complex **B** accompanied by the generation of CF_3 radical. Subsequently, the addition of CF_3 radical to alkene gives α-CF_3 alkyl radical **C**, which is trapped by **B** to form a Cu^{II} species **D**. Subsequently a Cu^{III} species **E** (path a) may form.[4,5,9,14] In these two steps, the achiral pyridine-coordinated copper complex and chiral phosphate counteranion work cooperatively to stabilize the reactive radical intermediate and control the stereochemistry of this reaction. Then, reductive elimination of **E** affords **3**. However, the other pathway via intramolecular single-electron oxidization of intermediate **D** to the corresponding carbocation intermediate **F**, which next undergoes C–O bond formation to give **3**, could not be excluded at the present stage (path b).

Alcohols are intrinsically less coordinative toward metal than carboxylates and poorer hydrogen-bonding donors than ureas, both of which render alcohols inapplicable in previously reported conditions.[4a,b,5] In this study, we have capitalized on a conceptually novel strategy with achiral pyridine

as the ancillary ligand to achieve the first asymmetric radical oxytrifluoromethylation of alkenes with alcohols. This transformation offers a unique and direct approach to a wide range of trifluoromethyl-substituted tetrahydrofurans bearing an α-tertiary stereocenter with excellent efficiency, remarkable enantioselectivity, good substrate scope and excellent functional group tolerance. In addition, a series of mechanistic experiments suggest that achiral pyridine may act as a coordinative ligand on copper metal to stabilize the loosely alcohol-binded transient Cu/CPA complexes, thus playing an unusually significant role in asymmetric induction.

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Conflict of interest

The authors declare no conflict of interest.

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