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Copper-catalyzed enantioselective allylic oxidation of acyclic olefins

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ABSTRACT

A copper-catalyzed asymmetric allylic oxidation of acyclic olefins has been developed. By using the complexes of copper and chiral spiro bisoxazoline ligands as catalysts, the oxidation of various acyclic olefins was accomplished with excellent regioselectivity (>20:1 in most cases) and up to 67% ee under mild reaction conditions, which represents one of the best results for the enantioselective allylic oxidation of acyclic olefins.

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Introduction

The direct functionalization of C–H bonds is one of the most valuable and challenging tasks in organic synthesis.[1] Allylic oxidation of olefins is a typical C–H bond functionalization reaction. Such reaction can convert simple olefins, the industrial feedstocks, into allylic alcohols, which are very useful building blocks for the synthesis of complex molecules and key intermediates in the productions of many fine chemicals. The copper-catalyzed allylic oxidation of olefins with peresters, known as Kharasch–Sosnovsky reaction, represents a powerful tool for direct C–H bond functionalization at the allylic position of olefins.[2] Although the asymmetric Kharasch–Sosnovsky reaction of cyclic olefins has been developed with high enantioselectivities,[3] the results for acyclic olefins are unsatisfied. Not only the enantioselectivity, but also the regioselectivity (the ratio of branched product **3** and linear product **3′**, *b*/*l*, Scheme 1) of the Kharasch–Sosnovsky reaction of acyclic olefins is a difficult issue.[4] To date, the highest enantioselectivity for the Kharasch–Sosnovsky reaction of acyclic olefins is 40% ee with very low regioselectivity (R = Ph, *b*/*l* = 47:53).[4c] In addition to Kharasch–Sosnovsky reaction, other allylic oxidation reactions of acyclic olefins also lack efficient catalysts. For example, in the palladium-catalyzed asymmetric allylic oxidation of acyclic olefins the enantioselectivity (63% ee) and the regioselectivity (*b*/*l* = 4.4:1) are only moderate.[5] Therefore, the development of efficient allylic oxidation reaction of acyclic olefins with high selectivity is highly desired.

Recently we developed a copper-catalyzed asymmetric allylic oxidation, Kharasch–Sosnovsky reaction, of cyclic olefins with high reactivity and good enantioselectivity.[6] Herein, we report an enantioselective Kharasch–Sosnovsky reaction of acyclic olefins catalyzed by the copper complexes of chiral spiro bisoxazoline ligands. The reaction exhibited as high as 20:1 of *b*/*l* regioselectivity and up to 67% ee of enantioselectivity, which represents one of the best results for the catalytic enantioselective allylic oxidation of acyclic olefins.

Results and discussion

The asymmetric allylic oxidation of *n*-decene (**1a**) was first studied with *tert*-butyl perbenzoate (TBPB, **2a**) as oxidant in the presence of copper(I) catalyst generated in situ from $Cu(MeCN)_4PF_6$ and chiral spiro bisoxazoline ligand (R_a,*S*,*S*)-**4a** (Table 1). To our delight, the reaction ran smoothly in acetone at 30 °C to afford the branched allylic ester product **3a** as almost the only oxidation product. However, the enantioselectivity was only 22% ee (entry 1). Various chiral spiro bisoxazoline ligands having different substituents at 4-position of oxazoline rings were then examined in the reaction (entries 2–8).[7] Most of the ligands with aliphatic substituents at 4-position of oxazoline rings gave excellent regioselectivities (**3a**/**3a′** > 20:1) and higher enantioselectivities than the ligand with phenyl groups (((R_a,*S*,*S*)-**4a**), with (R_a,*S*,*S*)-**4f** being the best ligand (52% yield and 54% ee, entry 6). The ligand (R_a,*S*,*S*)-**4e** bearing bulky isopropyl groups on oxazoline rings gave much lower yield and enantioselectivity (entry 5). The ligand (S_a,*S*,*S*)-**4f** gave very low enantioselectivity comparing with its diastereoisomer (R_a,*S*,*S*)-**4f**, implying that the configurations in the ligand (S_a,*S*,*S*)-**4f** are mismatched for controlling the enantioselectivity of the reaction (entry 9).

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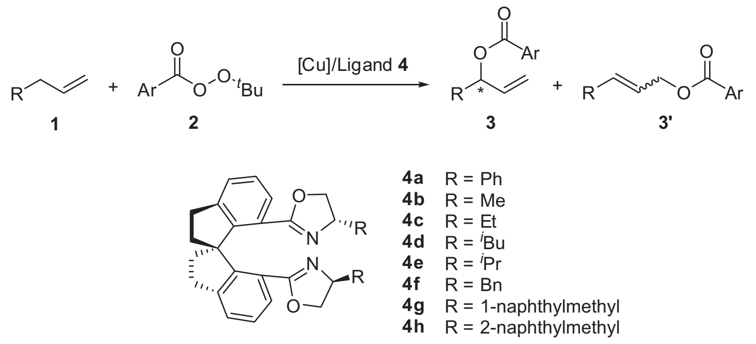
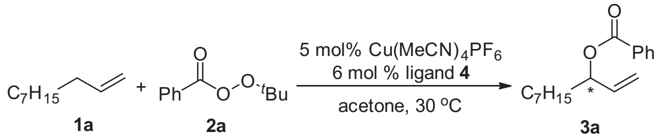


Scheme 1. Copper-catalyzed allylic oxidation of acyclic olefins with peresters.

Table 1
Copper-catalyzed asymmetric allylic oxidation of *n*-decene: ligands evaluation[a]



Entry	Ligand **4**	Yield[b] (%)	ee[c] (%)
1	(R_a,S,S)-**4a**	51	22 (*S*)
2	(R_a,S,S)-**4b**	47	47 (*R*)
3	(R_a,S,S)-**4c**	43	30 (*R*)
4	(R_a,S,S)-**4d**	40	47 (*R*)
5[d]	(R_a,S,S)-**4e**	21	13 (*R*)
6	(R_a,S,S)-**4f**	52	54 (*R*)
7	(R_a,S,S)-**4g**	50	46 (*R*)
8	(R_a,S,S)-**4h**	46	33 (*R*)
9	(S_a,S,S)-**4f**	30	9 (*S*)

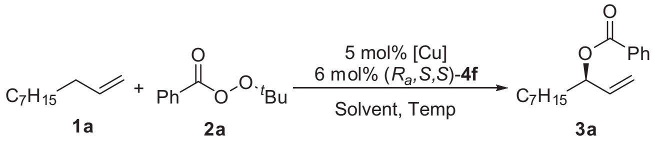
[a] Reaction conditions: $Cu(MeCN)_4PF_6$/ligand/**1a**/**2a** = 0.01:0.012:2:0.2 mmol, in 2 ml acetone at 30 °C for 3 days.

[b] Isolated yields based on the oxidant **2a**. In all cases, **3a**/**3a**′ are >20:1 according to ^1H NMR analysis.

[c] Determined by chiral HPLC using a Chiralcel OD-H column. The absolute configuration of the product was assigned through the comparison of the specific rotation with literature data.

[d] The oxidant **2a** cannot be fully consumed at 30 °C in 3 days.

Table 2
Copper-catalyzed asymmetric allylic oxidation of *n*-decene: reaction conditions investigation[a]



Entry	[Cu]	Solvent	Temp. (°C)	**1a**/**2a**	Yield[b] (%)	ee (%)
1	$Cu(MeCN)_4PF_6$	Acetone	30	10:1	52	54 (*R*)
2	$Cu(MeCN)_4PF_6$	Acetone	30	5:1	38	52 (*R*)
3	$Cu(MeCN)_4PF_6$	Acetone	30	20:1	51	52 (*R*)
4	$Cu(MeCN)_4PF_6$	Acetone	10	10:1	40	38 (*R*)
5	$Cu(MeCN)_4PF_6$	Acetone	60	10:1	25	11 (*R*)
6	$Cu(MeCN)_4PF_6$	MeCN	30	10:1	49	45 (*R*)
7	$Cu(MeCN)_4PF_6$	DCE	30	10:1	36	33 (*R*)
8	$Cu(MeCN)_4PF_6$	DCM	30	10:1	39	30 (*R*)
9	$Cu(MeCN)_4ClO_4$	Acetone	30	10:1	52	48 (*R*)
10	$(CuOTf)_2\cdot$toluene	Acetone	30	10:1	52	47 (*R*)
11[c]	CuCl	Acetone	30	10:1	54	43 (*R*)
12[d]	$Cu(OTf)_2$	Acetone	30	10:1	37	24 (*R*)

[a] The reaction conditions and analysis are the same as those of Table 1, entry 6.

[b] In all cases, **3a**/**3a**′ are >20:1 according to ^1H NMR analysis.

[c] 6 mol % $NaBAr_f\cdot 3H_2O$ was added.

[d] 6 mol % $PhNHNH_2$ was added.

By using (R_a,S,S)-**4f** as ligand, other parameters of the reaction were investigated. When the ratio of olefin to oxidant was reduced to 5:1, the yield of the reaction decreased (Table 2, entries 1–3). The reaction is also sensitive to temperature. Both the yield and the enantioselectivity of the reaction dropped when the reaction was carried out at 10 °C and 60 °C (entries 4 and 5 vs entry 1). The solvent remarkably affected the reactivity and enantioselectivity of the reaction (entries 6–8). The reaction can be performed in acetone, acetonitrile (MeCN), 1,2-dichloroethane (DCE), and dichloromethane (DCM), with acetone being the solvent of choice. However, other solvents such as benzene, toluene, dimethylsulfoxide (DMSO), and tetrahydrofuran (THF) impeded the reaction (data not shown). Various copper salts were also evaluated as catalyst precursors. The ionic copper(I) salts $Cu(MeCN)_4ClO_4$ and CuOTf gave almost the same level of yield and enantioselectivity as $Cu(MeCN)_4PF_6$ (entries 9 and 10). The covalent copper(I) salt CuCl was inert to the reaction, but became active after exchanging the anion to BAr_f^- (tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate) (entry 11). The copper(II) salt $Cu(OTf)_2$ can be a catalyst precursor only in the presence of reductant such as $PhNHNH_2$ (entry 12).

Different peresters were tested in the copper-catalyzed asymmetric allylic oxidation of *n*-decene. The substituents on the phenyl group of the oxidant *tert*-butyl perbenzoates **2** remarkably affected the reactivity and enantioselectivity of the reaction. The oxidants having an electron-donating group at the *para*-position such as *tert*-butyl 4-methylbenzoperoxoate (**2b**) and *tert*-butyl 4-methoxybenzoperoxoate (**2c**) exhibited almost the same level of reactivity and enantioselectivity as those of oxidant **2a** (Table 3, entries 1–3). However, the oxidant with a strong electron-withdrawing group (**2d**) and the bulky oxidant, *tert*-butyl 2,6-dimethylbenzoperoxoate (**2h**) showed very low reactivity and enantioselectivity, and the reaction could not complete at 30 °C in 3 days (entries 4 and 8). The peresters bearing substituents at *ortho*-position, regardless electron-donating or electron-withdrawing, gave lower yield and lower enantioselectivity (entries 5–7). In addition to the perbenzoates, the benzoyl peroxide (BPO, **2i**) can also be used as an oxidant for the reaction albeit the yield and enantioselectivity were lower than those of **2a** (entry 9).

A variety of acyclic olefins were investigated in copper-catalyzed asymmetric allylic oxidation under the optimal reaction conditions. All the tested olefins afforded allylic oxidation products with excellent regioselectivities except for allylcyclohexane (**1c**), which gave a very low ratio of **3**/**3**′ (3:1, Table 4, entry 3). The electronic properties of the substituents of 1-allylarenes markedly affect the reactivity and selectivity of the reaction (entries 4–6). The electron-donating substituent (4-MeO, **1e**) decreased both

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