ChemComm

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Cite this: *Chem. Commun.*, 2017, **53**, 8192

Received 20th April 2017,
Accepted 29th June 2017

DOI: 10.1039/c7cc03034g

rsc.li/chemcomm

Copper-catalyzed intermolecular asymmetric propargylic dearomatization of phenol derivatives†

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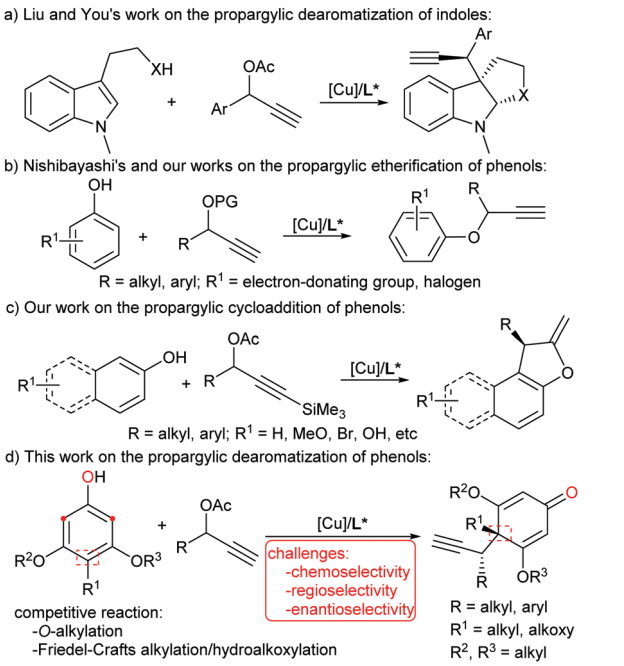
A copper-catalyzed intermolecular asymmetric propargylic dearomatization of phenol derivatives has been realized. Under the catalysis of Cu(OTf)·1/2C_6H_6 decorated with a chiral tridentate ketimine P,N,N-ligand, the dearomatization reaction proceeded smoothly with excellent control of chemo-, regio-, and enantioselectivities, thus providing a variety of optically active cyclohexadienone derivatives with up to >99% ee.

Catalytic asymmetric dearomatization of phenol derivatives has been recognized as a powerful transformation for the generation of cyclohexadienones that are popular structure motifs in various complex molecules and natural products.[1] In the past several years, significant efforts have been devoted to the development of various strategies for catalytic asymmetric dearomatization of phenol derivatives.[1–3] In spite of many impressive advances in this area, asymmetric dearomatization of phenol derivatives under non-oxidative conditions, especially in an intermolecular pathway, has remained underdeveloped.[4] The successful examples are limited to halogenation,[4a,c] allylation,[4b,l,m] alkylation,[4d–g] amination,[4j,k] and spiroannulation.[4h,i] Therefore, further exploration of new types of intermolecular catalytic asymmetric dearomatization of phenol derivatives is still a highly desirable and challenging task.

In the past decade, copper-catalyzed asymmetric propargylic transformation has attracted increasing attention due to its high potential in the stereoselective construction of C–C and C-heteroatom bonds.[5–7] In particular, Liu and You[8] have recently demonstrated the compatibility of this methodology with the dearomatization process by a tandem propargylic dearomatization/cyclization of indoles (Scheme 1a). It is then envisioned that this methodology should also be suitable for the intermolecular propargylic dearomatization of phenol derivatives. However,



Scheme 1 Intermolecular asymmetric propargylic dearomatization of phenols: possibility and challenge.

the challenge for the realization of such a process is obvious, as phenols are known to undergo a propargylic *O*-alkylation (Scheme 1b),[9] as well as a sequential Friedel–Crafts alkylation/intramolecular hydroalkoxylation process (Scheme 1c)[10] in the presence of a copper catalyst. Consequently, no example of propargylic dearomatization of phenol derivatives has been reported thus far. Herein we wish to report the first copper-catalyzed intermolecular asymmetric propargylic dearomatization of phenol derivatives with excellent control of chemo-, regio- and enantioselectivities.

The success of this dearomatization relies on the discovery of a system that could efficiently inhibit the propargylic *O*-alkylation and facilitate the dearomatization over the competitive

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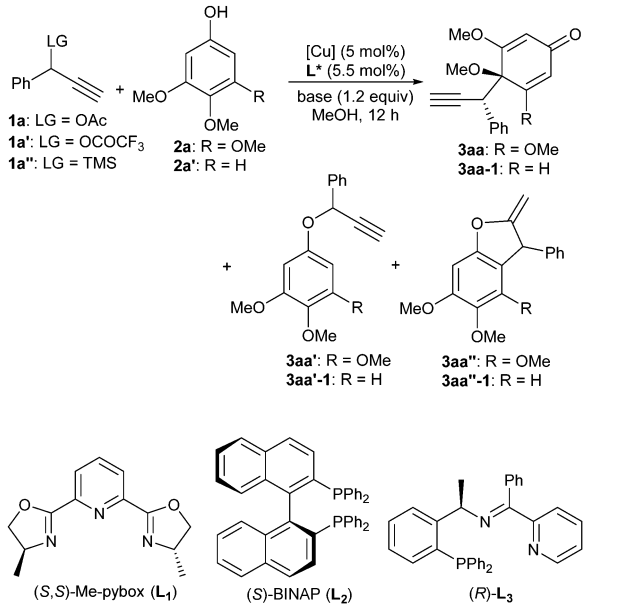
† Electronic supplementary information (ESI) available. CCDC 1537514. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc03034g

Friedel–Crafts-type reaction. For this purpose, 3,4,5-trimethoxyphenol **2a** was initially selected as the standard substrate to examine the possibility of the propargylic dearomatization with 1-phenyl-2-propynyl acetate **1a**, as we have reported recently that electron-rich phenols preferentially underwent Friedel–Crafts-type reaction rather than propargylic *O*-alkylation.[10] Not surprisingly, initial attempts of the reaction led to the complex mixture. $Pd(PPh_3)_4$ and AuCl didn't catalyze the reaction at all. To our delight, however, when $Cu(OAc)_2{\cdot}H_2O$ combined with (*S*,*S*)-Me-pybox (**L$_1$**) was used in the reaction, the dearomatization product **3aa** was detected and successfully separated from the reaction mixture after a careful column chromatography, accompanied by Friedel–Crafts-type cycloadduct **3aa″** but without any *O*-alkylation product **3aa′** (Table 1, entry 1). Although the result was still far from satisfactory, it indicated the feasibility of the intermolecular propargylic dearomatization of phenols. We then set out to improve the dearomatization outcome by optimizing the reaction conditions. Firstly, different chiral ligands were tested. As shown in Table 1, the ligand structure showed significant influence on the reactivity and enantioselectivity, and chiral tridentate ketimine P,N,N-ligand (*R*)-**L$_3$** was identified as the most promising ligand in terms of yield and enantioselectivity (entries 1–3). Base additives proved to be crucial for the reaction since no dearomatization product was detected in its absence (entry 4). The best base additive was Et_3N, with which 59% yield and 95% ee were obtained (entry 6). Subsequent screening of Cu salts identified $Cu(OTf){\cdot}1/2C_6H_6$ as the best choice (entry 9). The solvent screening disclosed that the protic solvent was favourable to the reaction, and MeOH proved to be the best one, presumably facilitating the formation of Cu–allenylidene intermediates (entries 11 and 12).[6k] Lowering the reaction temperature could significantly inhibit various competitive reactions, therefore dramatically improving the yield and enantioselectivity of dearomatization products (entries 13 and 14). When the reaction was performed at −20 °C, Friedel–Crafts-type reaction was completely suppressed, and the dearomatization product was exclusively obtained in 91% yield and with >99% ee (entry 14). Replacing the OAc group of **1a** with $OCOCF_3$ (**1a′**) or TMS (**1a″**) didn't result in the dearomatization product (entries 15 and 16). Both methoxy groups in 3- and 5-positions proved to be necessary for the dearomatization since no dearomatization product **3aa–1** was detected with 3,4-dimethoxyphenol (**2a′**) as the substrate (entry 17).

With the optimized reaction conditions in hand, we examined the applicability of propargylic acetates **1** in the propargylic dearomatization of 3,4,5-trimethoxyphenol **2a**, and the results are summarized in Table 2. In all cases, only dearomatization products were observed. The reaction was sensitive to the substitution pattern on the phenyl ring. Thus, reactions with propargylic acetates containing the 3-Cl or the 4-Cl group (**1c** and **1d**) proceeded smoothly to give the desired products (**3ca** and **3da**) in high yields and with excellent enantioselectivity (>99% ee), while substrate **1b** with a 2-Cl substituent led to an obvious decrease in the yield although high enantioselectivity was maintained (entries 1–3). The electronic properties of the substituent at the *para*-position of the phenyl ring showed little influence on the reactivity and enantioselectivity, and all substrates **1d–i** gave rise to the corresponding dearomatization products in good yields (85–93% yield) and with excellent enantioselectivities (97–>99% ee) (entries 3–8). 2-Naphthyl-substituted substrate **1j** was a suitable reaction partner, giving **3ja** in 92% yield and with >99% ee (entry 9). Heterocyclic substrate **1k** served well for the reaction, producing **3ka** in 88% yield and with 97% ee (entry 10). Aliphatic substrate **1l** also worked in the reaction, giving rise to the dearomatization product **3la** in a high enantioselectivity of 95% ee although a reduced yield was observed (entry 11).

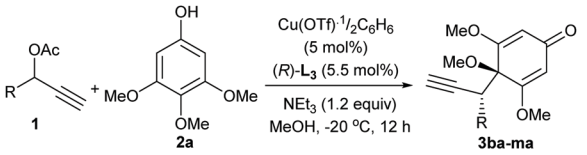
Table 1 Optimization of the reaction[a]

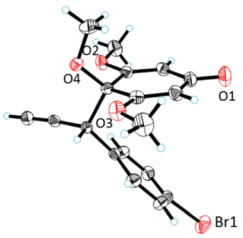


Entry	[Cu]	L	2	Base	T (°C)	Yield[b] (%)	ee[c] (%)
1[d]	$Cu(OAc)_2{\cdot}H_2O$	**L1**	**2a**	$^iPr_2NEt$	rt	38	−71
2	$Cu(OAc)_2{\cdot}H_2O$	**L2**	2a	$^iPr_2NEt$	rt	<10	—
3	$Cu(OAc)_2{\cdot}H_2O$	**L3**	2a	$^iPr_2NEt$	rt	58	92
4	$Cu(OAc)_2{\cdot}H_2O$	**L3**	2a	—	rt	—	—
5	$Cu(OAc)_2{\cdot}H_2O$	**L3**	2a	K_3PO_4	rt	53	88
6	$Cu(OAc)_2{\cdot}H_2O$	**L3**	2a	NEt_3	rt	59	95
7	$Cu(MeCN)_4BF_4$	**L3**	2a	NEt_3	rt	55	96
8	CuI	**L3**	2a	NEt_3	rt	50	93
9	$Cu(OTf){\cdot}1/2C_6H_6$	**L3**	2a	NEt_3	rt	64	97
10	$Cu(OTf)_2$	**L3**	2a	NEt_3	rt	63	96
11[e]	$Cu(OTf){\cdot}1/2C_6H_6$	**L3**	2a	NEt_3	rt	—	—
12[f]	$Cu(OTf){\cdot}1/2C_6H_6$	**L3**	2a	NEt_3	rt	27	93
13	$Cu(OTf){\cdot}1/2C_6H_6$	**L3**	2a	NEt_3	0	79	98
14	$Cu(OTf){\cdot}1/2C_6H_6$	**L3**	2a	NEt_3	−20	91	>99
15[g]	$Cu(OTf){\cdot}1/2C_6H_6$	**L3**	2a	NEt_3	−20	—	—
16[h]	$Cu(OTf){\cdot}1/2C_6H_6$	**L3**	2a	NEt_3	−20	—	—
17[i]	$Cu(OTf){\cdot}1/2C_6H_6$	**L3**	2a′	NEt_3	−20	—	—

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), [Cu] (0.015 mmol, 5 mol%), **L*** (0.0165 mmol, 5.5 mol%), and base (0.36 mmol, 1.2 equiv.) in 3 mL of MeOH at indicated reaction temperature for 12 h. [b] Yield of the isolated product of **3aa**. [c] ee of **3aa** determined by HPLC using a chiral stationary phase. [d] The reaction resulted in **3aa** (38% yield) and **3aa″** (8% yield) but without any *O*-alkylation product **3aa′**. [e] Using CH_2Cl_2 as the solvent. [f] Using EtOH as the solvent. [g] **1a′** was used instead of **1a**, in which the corresponding propargylic alcohol was recovered. [h] **1a″** was used instead of **1a**, resulting in the complex mixture. [i] **2a′** was used instead of **2a**, exclusively generating cycloadduct **3aa″–1** in 41% yield and with 92% ee.

Table 2 Scope with respect to propargylic acetates[a]





(*S*)-**3fa**

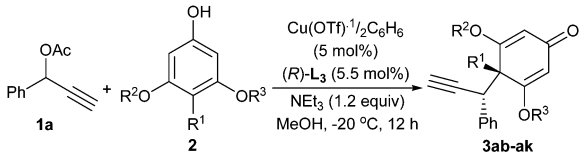
Entry	Substrate (R)	Product (3)	Yield[b] (%)	ee[c] (%)
1	**1b**: R = 2-ClC_6H_4	**3ba**	72	98
2	**1c**: R = 3-ClC_6H_4	**3ca**	90	>99
3	**1d**: R = 4-ClC_6H_4	**3da**	93	>99
4	**1e**: R = 4-FC_6H_4	**3ea**	87	99
5	**1f**: R = 4-BrC_6H_4	**3fa**	87	>99
6	**1g**: R = 4-MeC_6H_4	**3ga**	85	99
7	**1h**: R = 4-$MeOC_6H_4$	**3ha**	89	97
8	**1i**: R = 4-$CF_3C_6H_4$	**3ia**	90	>99
9	**1j**: R = 2-naphthyl	**3ja**	92	>99
10	**1k**: R = 2-furyl	**3ka**	88	97
11[d]	**1l**: R = Me	**3la**	54	95
12[d]	**1m**: R = H	**3ma**	—	—

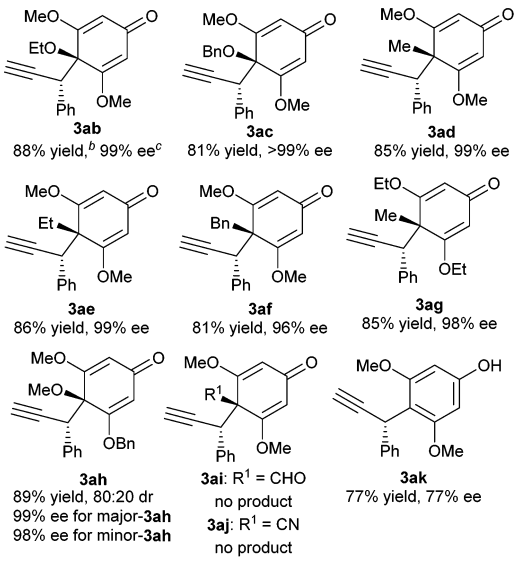
[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.36 mmol), Cu(OTf)·1/2C_6H_6 (0.015 mmol, 5 mol%), (*R*)-**L**$_3$ (0.0165 mmol, 5.5 mol%), and NEt_3 (0.36 mmol, 1.2 equiv.) in 3 mL of MeOH at −20 °C for 12 h. [b] Yield of the isolated product. [c] Determined by HPLC using a chiral stationary phase. [d] The reaction was performed at 0 °C with $^iPr_2NEt$ instead of Et_3N as the base additive.

However, propynyl acetate **1m** didn't lead to the formation of the dearomatization product **3ma** (entry 12). The absolute configuration of the dearomatization product was unambiguously established to be *S* by X-ray crystallographic analysis of **3fa**.[11]

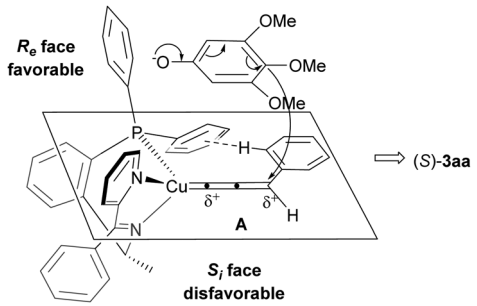
The scope with regard to phenol derivatives was next investigated, and the results are listed in Table 3. In all cases, only dearomatization products were observed. Alkoxy groups on the 4-position such as ethoxy and benzyloxy groups, as well as aliphatic groups on the 4-position such as methyl, ethyl, and benzyl groups were well tolerated, and the corresponding dearomatization products (**3ab–af**) were obtained in good yields (81–88%) and with excellent enantioselectivity (96–>99% ee). In addition, 3,5-diethoxy-4-methylphenol **2g** was also a suitable substrate, affording the dearomatization product **3ag** in 85% yield and with 98% ee. It was noteworthy that substrate **2h** bearing different substituents on the 3,5-position, which would lead to the generation of a new quaternary carbon stereocenter in the cyclohexadienone framework, also underwent the asymmetric dearomatization reaction well, giving the corresponding product **3ah** in 89% yield and 80/20 dr with a major diastereomer in 99% ee. However, the introduction of electron-withdrawing groups at the 4-position such as a formyl or a cyano group completely inhibited the dearomatization process, not giving any dearomatization product

Table 3 Scope with respect to phenol derivatives[a]





[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.36 mmol), Cu(OTf)·1/2C_6H_6 (0.015 mmol, 5 mol%), (*R*)-**L**$_3$ (0.0165 mmol, 5.5 mol%), and NEt_3 (0.36 mmol, 1.2 equiv.) in 3 mL of MeOH at −20 °C for 12 h. [b] Yield of the isolated product. [c] Determined by HPLC using a chiral stationary phase.



Scheme 2 Proposed mechanistic pathway for observed stereochemistry.

3ai or **3aj**. When 3,5-dimethoxyphenol **2k** was used as the substrate, a Friedel–Crafts alkylation product **3ak** was obtained in moderate enantioselectivity. 2,4,6-Trimethoxyphenol didn't serve as the suitable substrate, not leading to the dearomatization product.

Based on the previous reports[6,7] and the experimental results, a transition state of the Cu–allenylidene complex with (*R*)-**L**$_3$ is proposed to account for the observed stereochemistry as shown in Scheme 2.

In conclusion, we have developed a copper-catalyzed intermolecular propargylic dearomatization of phenol derivatives. With the support of a sterically hindered ketimine P,N,N-ligand, an array of electron-rich 4-substituted 3,5-dialkoxyphenols could

be dearomatized in highly chemo-, regio- and enantioselective forms, therefore leading to optically active cyclohexadienone derivatives with up to >99% ee. Further extension of the reaction scope and synthetic application are currently underway.

Support for this research from the National Natural Science Foundation of China (21572226) is gratefully acknowledged.

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11 CCDC 1537514 [(*S*)-**3fa**] contains the supplementary crystallographic data for this paper†.