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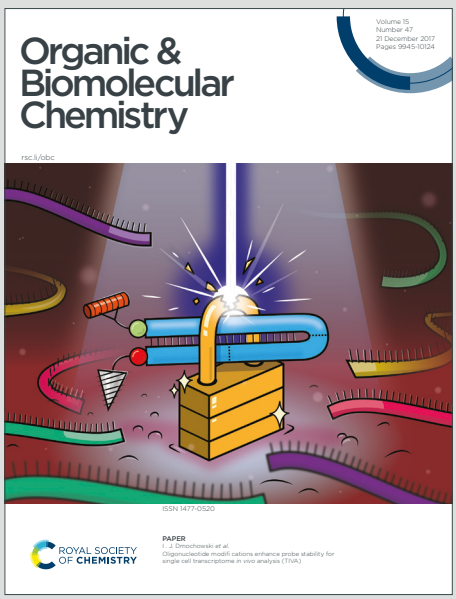

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ARTICLE

$InCl_3$-catalyzed 5-*exo-dig* cyclization/1,6-conjugate addition of *N*-propargylamides with *p*-QMs to construct oxazole derivatives

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An $InCl_3$-catalyzed atom-economic intramolecular 5-*exo-dig* cyclization/1,6-conjugate addition/aromatization of *N*-propargylamides with *p*-QMs to produce oxazoles tethering diarylmethane has been successfully developed. $InCl_3$ not only served as Lewis acid to catalyze the cyclization of propargylic amides but also activated the carbonyl of *p*-QMs to achieve the 1,6-addition process in a one-pot manner. The reaction has attractive features, including mild reaction conditions, broad scope of substrates, good yields, and scalability.

Introduction

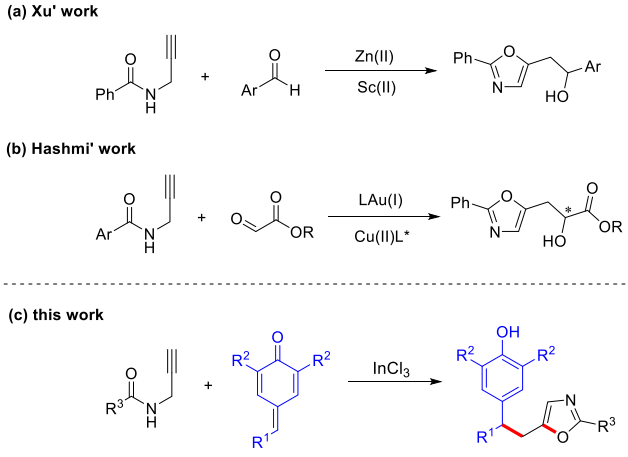
The exploration of privileged structures in drug discovery is a rapidly emerging theme in medicinal chemistry.[1] Among them, oxazoles and their derivatives are important nitrogen containing heterocycles generally endowed with biological properties, making them a privileged scaffold for applications in medicinal chemistry and pharmaceuticals.[2] Additionally, oxazole derivatives are important intermediates in organic synthesis and ligands for metal catalysis.[3] Therefore, continuous efforts have been devoted to the development of novel methods for the synthesis of novel oxazole derivatives.[2]

A rapidly increasing recognition of the rich and fascinating chemistry of *N*-propargylamides as versatile building blocks in organic synthesis has been brought out in the past decades.[4] Various strategies for the construction of oxazoles, particularly by the cyclization reactions of *N*-propargylamides, have been developed by metal catalysis,[5] such as Au, Pd, Cu, Ag, Fe, Zn, Ru, and others.[6] Recently, Xu reported a Zn(II)/Sc(III) bimetallic catalytic approach to construct functionalized oxazole derivatives from easily available *N*-propargylamides (Scheme 1a).[7] Hashmi reported a convenient protocol for the synthesis of oxazole α-hydroxy esters from *N*-propargylamides and alkylglyoxylates (Scheme 1b).[8] On the other hand, *para*-quinone methides (*p*-QMs) are prominent 1,6-acceptors due to the possibility of aromatization after the 1,6-addition.[9] A lot of nucleophiles[10] have been added to *p*-QMs in a 1,6-fashion under a variety of conditions. All the elegant achievements mentioned above in the transformations of *p*-QMs mainly focused on transition metal catalysis.[11]

To the best of our knowledge, no reaction of *N*-propargylamides as nucleophiles with *p*-QMs has been reported so far. On the basis of the above successful examples and our ongoing interest in heterocycle synthesis,[12] we here report an $InCl_3$-catalyzed intramolecular 5-*exo-dig* cyclization/1,6-conjugate addition/aromatization of *N*-propargylamides with *p*-QMs to construct oxazole derivatives bearing a diarylmethane group (Scheme 1c). Herein $InCl_3$ not only served as Lewis acid to catalyze the cyclization of *N*-propargylamides but also activated the carbonyl of *p*-QMs in one pot. In this transformation, all the atoms participating in the reaction enter the product and no by-product are formed. This ene–ene reaction is useful method for carbon–carbon bond formation with high atom-economy.

Results and discussion

Optimization of reaction conditions was carried out using *p*-quinone methide **1a** and *N*-(prop-2-yn-1-yl)benzamide (**2a)** under various conditions, and the results are summarized in Table 1. An initial experiment was conducted in DCE at 70 °C in the presence of 10 mol % $Zn(OTf)_2$, the desired product **3aa** was obtained in 55% yield after 24



Scheme 1 Strategies to construct oxazole derivatives.

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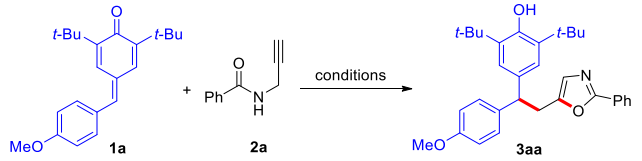
h (Table 1, entry 1). In contrast, the reaction couldn't proceed when no catalyst was employed, indicating a Lewis acid catalyst was crucial to the transformation (Table 1, entry 2). Then other Lewis acids such as $Cu(OTf)_2$, $Al(OTf)_3$, $In(OTf)_3$ were also examined (Table 1, entries 3-5). The results showed $In(OTf)_3$ was the most efficient and gave 85% yield (Table 1, entry 5). Next, $InCl_3$ was tested. Encouragingly, the yield of **3aa** was increased to 90%, and the reaction time also was shortened significantly to 3 h from 24 h (Table 1, entry 6). However, both decreasing and increasing amount of $InCl_3$ decreased the yield of **3aa** (Table 1, entries 7 and 8). No comparative yields were obtained when other solvents such as MeCN and EtOH were used (Table 1, entries 9 and 10). Gratifyingly, the yield of **3aa** increased to 94% when the concentration of **1a** was raised up to 0.2 M (Table 1, entry 11). However, further increasing in concentration didn't give a superior yield (Table 1, entry 12). Screening of the reaction temperature and the ratio of **2a**/**1a** couldn't provide satisfactory results (Table 1, entries 13-16). Taking temperature and reaction time into consideration, the entry 11 was selected as the best reaction conditions.

Having optimized conditions in hand, substrate scope was evaluated using a wide range of *N*-propargylamides **2** with **1a** (Table 2). As shown in Table 2, irrespective of the electronic nature, the aromatic *N*-propargylamides bearing various substituents on the phenyl ring all successfully were transformed to the desired products **3aa**–**3ak** in good to excellent yields. *N*-propargylamides bearing electron-deficient substituents offered higher yields than that bearing electron-rich substituents. Gratifyingly, replacing the aromatic groups R with 2-naphthyl, piperonyl, 2-thienyl and 2-furyl, afforded products **3al**-**3ao** in 54-70% yields. Unfortunately, when alkyl *N*-propargylamides such as Bn, CH_3 and *t*-Bu (**2p-2r**) were employed, the reaction system became sluggish and the corresponding products were hardly observed, which troubled the 1,6-conjugate addition process.

Next, the scope of *p*-QMs was investigated under the standard conditions (Table 3). As shown in Table 3, *p*-QMs bearing both electron-rich and electron-deficient substituents on the phenyl ring were smoothly transformed to their corresponding products (**3ba**–**3ga**) in moderate to excellent yields, except for **3ha** and **3ia** which had only 13% and 18% yields, respectively due to the 2-bromo substituted one with steric hindrance and the special property of

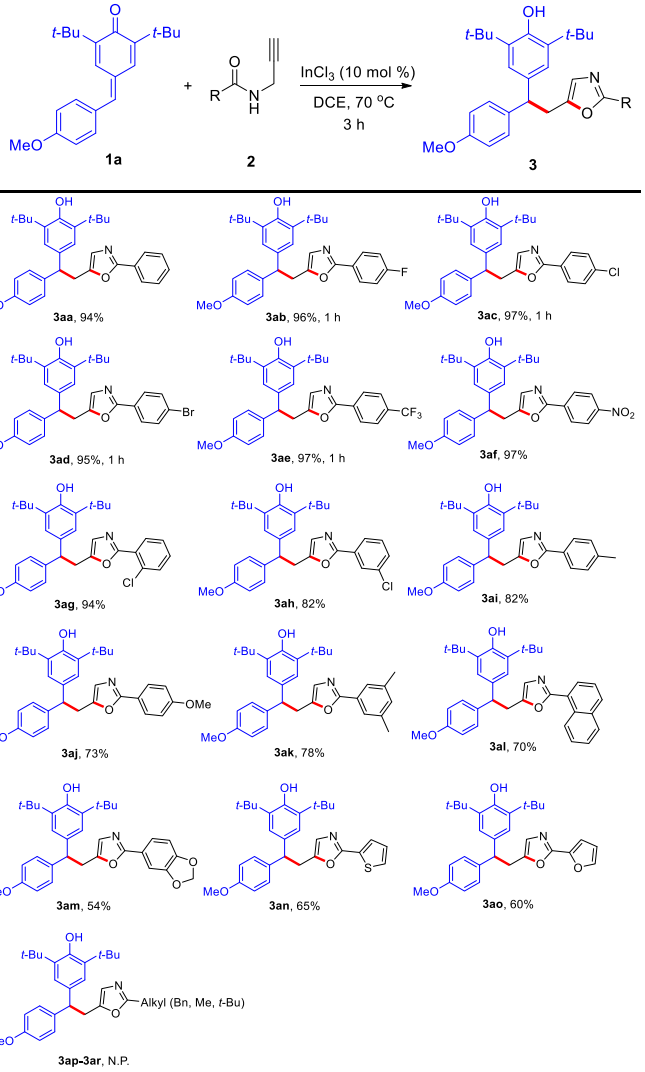
Table 1 Optimization of the reaction conditions[a]



entry	catalyst (mol %)	solvent (mL)	t (°C)	time (h)	yield (%)[b]
1	$Zn(OTf)_2$ (10)	DCE (2)	70	24	55
2	-	DCE (2)	70	24	N.R.
3	$Cu(OTf)_2$ (10)	DCE (2)	70	24	53
4	$Al(OTf)_3$ (10)	DCE (2)	70	24	15
5	$In(OTf)_3$ (10)	DCE (2)	70	24	85
6	$InCl_3$ (10)	DCE (2)	70	3	90
7	$InCl_3$ (5)	DCE (2)	70	3	68
8	$InCl_3$ (20)	DCE (2)	70	3	82
9	$InCl_3$ (10)	MeCN (2)	70	3	63
10	$InCl_3$ (10)	EtOH (2)	70	3	complex
11	**$InCl_3$ (10)**	**DCE (1)**	70	**3**	**94**
12	$InCl_3$ (10)	DCE (0.5)	70	3	82
13	$InCl_3$ (10)	DCE (1)	50	24	92
14	$InCl_3$ (10)	DCE (1)	80	3	88
15[c]	$InCl_3$ (10)	DCE (1)	70	24	86
16[d]	$InCl_3$ (10)	DCE (1)	70	24	80

[a]Unless otherwise noted, all reactions were performed with **1a** (0.2 mmol), **2a** (0.3 mmol). [b]Isolated yield based on **1a**. [c]With 0.24 mmol **2a**. [d]With 0.2 mmol **2a**. N.R. = no reaction

Table 2 Substrate scope of *N*-propargylamides **2**[a, b]



[a]Unless otherwise noted, all reactions were performed with **1a** (0.5 mmol), **2** (0.75 mmol) and $InCl_3$ (0.05 mmol) in DCE (2.5 mL) for 3 h. [b]Isolated yield based on **1a**.

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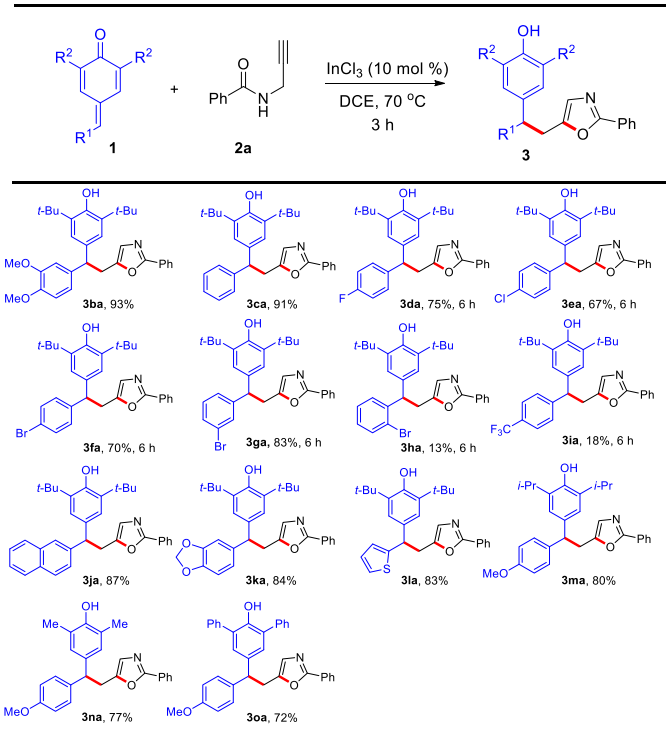
Table 3 Substrate scope of *p*-QMs **1**[a, b]



[a]Unless otherwise noted, all reactions were performed with **1** (0.5 mmol), **2a** (0.75 mmol) and $InCl_3$ (0.05 mmol) in DCE (2.5 mL) for 3 h. [b]Isolated yields based on **1**.

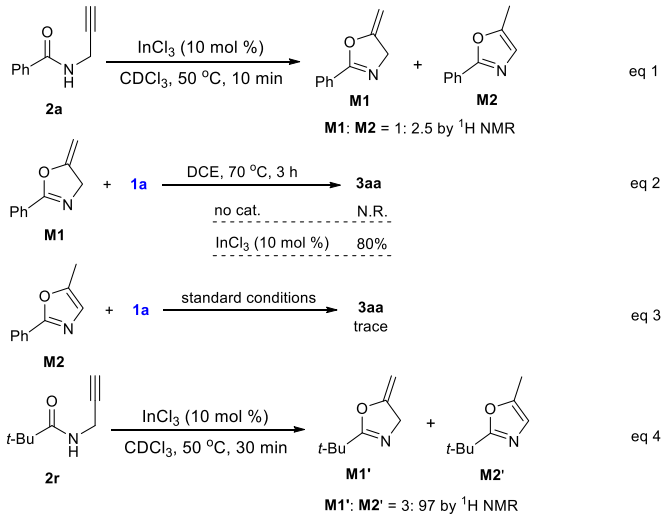
trifluoromethyl group. When R^1 group of *p*-QMs are 2-naphthyl (**3ja**), piperonyl (**3ka**) or 2-thienyl groups (**3la**), the reactions proceeded well, affording products in 83-87% yields. Moreover, the *tert*-butyl group of *p*-QMs were replaced with other alkyl groups such as methyl and isopropyl or phenyl group, the reactions proceeded smoothly, affording the desired products **3ma**-**3oa** in 72-80% yields.

The structures of all new compounds **3** were identified by their IR, ^{1}H NMR, ^{13}C NMR and HRMS spectra, and unequivocally confirmed by X-ray diffraction analysis of single-crystal of **3ad** (see the Supporting Information for details).

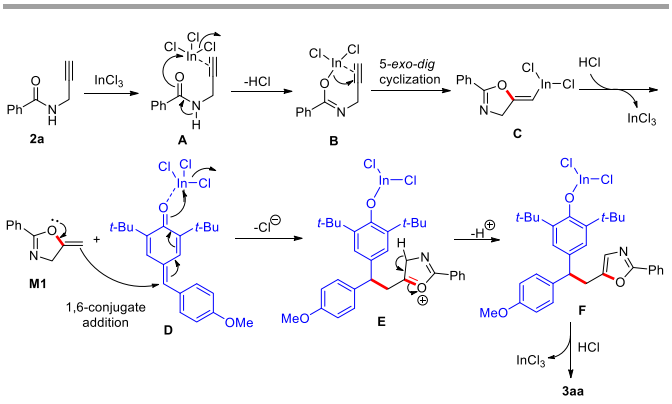
Some control experiments were conducted to elucidate the reaction mechanism. Firstly, to explore the active intermediate, an *in situ* ^{1}H NMR experiment with **2a** was performed, and two cyclization intermediates **M1**[13] and **M2**[14] (1:2.5) were observed (Scheme 1, eq 1). Then **M1** and **M2** were prepared using *N*-propargylamide **2a** in the presence of $Zn(OTf)_2$ or $InCl_3$, respectively (see SI). Next, the isolated **M1** and **M2** were employed to react with **1a**, respectively. The results revealed that without any catalyst the reaction of **M1** with **1a** did not occur, but provided **3aa** in 80% yield by $InCl_3$ catalysis (Scheme 1, eq 2). In contrast, the reaction of **M2** with **1a** afforded only trace **3aa** under the standard conditions (Scheme 1, eq 3), which suggested that *p*-QM **1a** could capture **M1** quickly, preventing the isomeration of **M1** to **M2**. The above experimental results indicate that the real active intermediate is **M1**, and $InCl_3$ not only catalyzes the cyclization of *N*-propargylamides but also promotes the 1,6-conjugate addition process. Additionally, an alkyl *N*-propargylamide substrate **2r** also was investigated by *in situ* ^{1}H NMR (Scheme 1, eq 4), and two cyclization intermediates **M1'** and **M2'**[14] also were observed in a ratio of 3:97. It was found that **M2** was much more than **M1**, which resulted in the alkyl *N*-propargylamides **2p-2r** couldn't provide the corresponding products.

Based on the above experimental results and relevant reports,[4] a plausible mechanism as outlined in Scheme 2 was proposed. Firstly, $InCl_3$ as Lewis acid could activate the triple bond of **2a** to form **B** through **A** losing HCl, followed by regioselective intramolecular 5-*exo-dig* cyclization to give the intermediate **C**[5c,5i,7] which, on hydrolysis with HCl generated *in situ*, resulted in the oxazoline intermediate **M1**. At the same time, $InCl_3$ coordinated with the carbonyl group of *p*-QMs to form an electrophilic intermediate **D**, then 1,6-conjugate addition process of **D** with **M1** *via* **E** gave **F** with losing a proton. Then on hydrolysis with HCl generated *in situ*, **F** produced the final product **3aa** with releasing $InCl_3$.

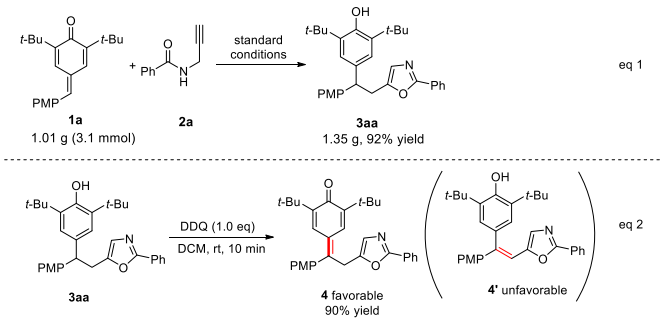
To demonstrate the practicality of this transformation, a scaled-up synthesis was performed under the standard conditions (Scheme 3, eq 1). Gratifyingly, the reaction of 1.01 g (3.1 mmol) *p*-QM 1a with *N*-propargylamide 2a produced the corresponding product 3aa in 92% yield (1.35 g). Additionally, the phenol part of 3aa could be easily oxidized to the formal of quinone in the presence of 1 equiv. of 2,3-



Scheme 2 Control experiments.



Scheme 3 Plausible mechanism.



Scheme 4 Gram-scale and follow-up reactions.

dichloro-5.6-dicyano-1,4-benzoquinone (DDQ) at room temperature within 10 min, affording compound 4 in 90% yield (Scheme 3, eq 2).

Conclusions

In summary, we have successfully developed a novel, simple and economical, environmentally friendly one-pot reaction to synthesize novel functionalized oxazoles tethering diarylmethane in good to excellent yields. It is the first report of preparation of title compounds by use of *N*-propargylamides with *p*-QMs promoted by $InCl_3$ catalysis, in which $InCl_3$ plays dual roles: catalyzing the cyclization of *N*-propargylamides to give oxazoles, and activating the *p*-QMs to achieve the 1,6-addition. The reaction pathway involves intramolecular 5-*exo-dig* cyclization/1,6-conjugate addition/aromatization. The reaction has attractive features, including mild reaction conditions, environmentally friendly, high chemo- and regioselectivities, broad scope of substrates, good yields, and scalability. Undoubtedly, this domino synthetic strategy provides a convenient and green way to construct the target molecules in an atom-economic manner.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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