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Enantioselective [3 + 2] Cycloaddition Reaction of Ethynylethylene Carbonates with Malononitrile Enabled by Organo/Metal Cooperative Catalysis

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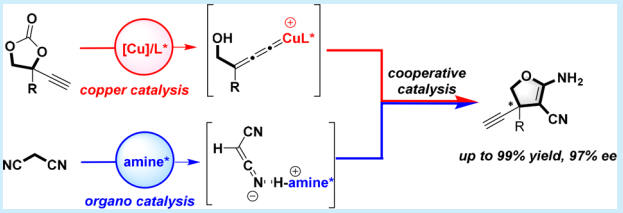
Supporting Information

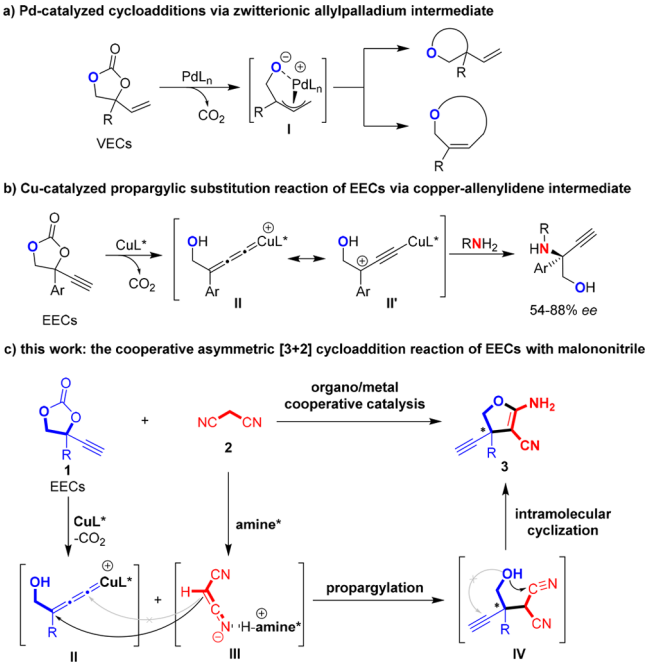
ABSTRACT: The first catalytic asymmetric decarboxylative [3 + 2] cycloaddition reaction of ethynylethylene carbonates with malononitrile has been developed successfully by an organo/copper cooperative system. This strategy led to a series of optically active polysubstituted dihydrofurans in good yields with high levels of enantioselectivities (up to 99% yield, 97% ee). The presence of the terminal alkynyl and the cyano group in the dihydrofuran products provides a wide scope for further structural transformations. More importantly, this organo/metal cooperative catalytic system will broaden the substrate scope and enable fundamentally new reactions.



Transition-metal-catalyzed asymmetric cycloaddition reactions have become powerful strategies for the construction of structurally diverse chiral heterocyclic compounds.[1] Particularly, vinylethylene carbonates (VECs) have been employed as alternatives for the generation of zwitterionic π-allyl-Pd intermediate **I** and were applied successfully in palladium-catalyzed asymmetric decarboxylative cycloaddition reactions. Moreover, this strategy provides valuable access to diverse oxygen-containing heterocycles (Scheme 1a).[2] Over the past decades, copper-catalyzed propargylic substitution and cycloaddition reactions via copper−allenylidene complexes have emerged as the most powerful strategy for the construction of complex molecules.[3,4] The role of the ethynylethylene carbonates (EECs) serving as synthons in asymmetric reactions for the construction of quaternary stereocenters has never been investigated until most recently. The group of Zhang reported an elegant and efficient copper-catalyzed asymmetric decarboxylative propargylic substitution reaction via copper−allenylidene complex **II** (**II′**) for the enantioselective construction of β-amino alcohols (Scheme 1b).[5] The development of methods for the cycloaddition reactions of EECs would be of significant value, providing access to distinct chiral oxygen-containing heterocycles with terminal alkynes for further transformations. To realize the application of EECs as 1,3-dipole precursors in copper-catalyzed asymmetric cycloaddition reactions, a suitable reaction partner possessing both the nucleophilic and electrophilic sites is highly desired. In this context, malononitrile attracted our attention because of its high reactivity as a 1,2-dipole surrogate in the presence of amine catalysts.[6]

2,3-Dihydrofurans have emerged as useful synthetic intermediates for organic synthesis and one of the most commonly observed classes of structural units in natural and synthetic products with diverse and well-documented biological activities (e.g., aflatoxin B_1 and clerodin).[7] Cycloaddition approaches that assemble the heterocyclic core are particularly attractive for dihydrofuran synthesis. Developing catalytic asymmetric methods to access these frameworks is

Scheme 1. Design of Catalytic Enantioselective [3 + 2] Cycloaddition Reaction of EECs



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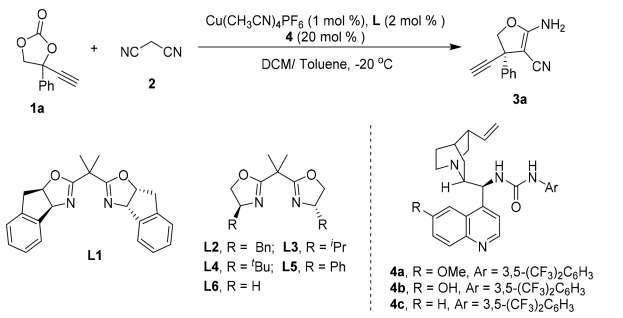
therefore a topic of continued interest for synthetic chemists.[8] Based on recent advances on the copper-catalyzed cycloaddition reaction via copper−allenylidene intermediates and our ongoing efforts toward the development of cooperative catalysis systems,[4,5,9] we designed the asymmetric [3 + 2] cycloaddition reactions of EECs with malononitrile in the cooperative catalysis of copper and amine[10] for the enantioselective construction of polysubstituted dihydrofurans (Scheme 1c). As proposed in Scheme 1c, copper-mediated decarboxylation of EECs **1** would lead to the copper−allenylidene intermediate **II**. Meanwhile, the nucleophilic intermediate **III** was generated from the chiral amine catalyst and malononitrile **2**. The asymmetric propargylic substitution reaction between intermediates **II** and **III** will afford intermediate **IV**. The final chemoselective intramolecular cyclization step would furnish 2-amino-3-cyano-dihydrofurans **3**. Herein, we will report the first asymmetric [3 + 2] cycloaddition reaction of EECs with malononitrile enabled by a cooperatively catalytic copper/amine system.

The feasibility of our design was initially examined by the reaction of EEC **1a** and malononitrile **2** under the cooperative catalysis of ligand-bound copper(I) complex and urea-cinchona alkaloid **4** (Table 1). We were delighted to find that the designed [3 + 2] cycloaddition reaction, indeed, occurred in the presence of 1 mol % $Cu(CH_3CN)_4PF_6$, 2 mol % bis(oxazoline) (box) ligand **L1**, and 20 mol % **4a** and

Table 1. Optimization of Reaction Conditions[a]



entry	[Cu]	L	4	yield (%)[b]	ee (%)[c]
1	$Cu(CH_3CN)_4PF_6$	**L1**	**4a**	50	80
2	$Cu(CH_3CN)_4PF_6$	**L2**	**4a**	50	62
3	$Cu(CH_3CN)_4PF_6$	**L3**	**4a**	90	68
4	$Cu(CH_3CN)_4PF_6$	**L4**	**4a**	10	66
5	$Cu(CH_3CN)_4PF_6$	**L5**	**4a**	95	57
6	$Cu(CH_3CN)_4PF_6$	**L6**	**4a**	35	8
7	$Cu(CH_3CN)_4PF_6$	**L1**	**4b**	38	76
8	$Cu(CH_3CN)_4PF_6$	**L1**	**4c**	62	89
9[d]	$Cu(CH_3CN)_4PF_6$	**L1**	**4c**	90	95
10[d]	$Cu(CH_3CN)_4PF_6$		**4c**	75	92
11[d]			**4c**	n.d.	
12[d]	$Cu(CH_3CN)_4PF_6$	**L1**		n.d.	
13[d]	$Cu(CH_3CN)_4PF_6$	*ent*-**L1**	**4c**	50	53
14[d]	$Cu(CH_3CN)_4PF_6$	**L6**	**4c**	65	22
15[d]	$Cu(CH_3CN)_4PF_6$	**L1**	DMAP	63	4

[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.6 mmol), $Cu(CH_3CN)_4PF_6$ (1 mol %), **L** (2 mol %), and **4** (20 mol %) in DCM (1.0 mL)/ toluene (2.0 mL) at −20 °C for 48 h. [b]Isolated yield. [c]The ee value was determined by HPLC. [d]With **1a** (0.6 mmol), **2** (0.3 mmol), $Cu(CH_3CN)_4PF_6$ (1 mol %), **L1** (2 mol %), **4c** (20 mol %), and $MgSO_4$ (100 mg) in DCM (2.0 mL)/ *m*-xylene (4.0 mL) at −10 °C for 48 h.

produced the corresponding polysubstituted dihydrofuran **3a** in moderate yield and enantioselectivity (50% yield, 80% ee, entry 1). Encouraged by this result, we next evaluated a series of chiral ligands **L2**−**L5** and an achiral ligand **L6** and identified chiral ligand **L1** as a uniquely effective catalyst delivering the desired product **3a** (entries 2−6 vs entry 1). Furthermore, a survey of urea-cinchona catalysts **4b** and **4c** (entries 7 and 8) revealed that **4c** was the optimal organocatalyst in terms of reactivity and enantioselection when employed in concert with a copper catalyst. Further improvements in reaction efficiency were realized via the change of the stoichiometric ratio of reactants in combination with the addition of $MgSO_4$ as a reaction supplement to deliver the desired adduct **3a** in 90% yield and 95% ee (entry 9). All other deviations from the optimal conditions led to a decrease of the enantioselectivity, and in some cases even the yield (see Supporting Information, Tables S1 and S2) and the standard conditions were obtained as $Cu(CH_3CN)_4PF_6$ (1 mol %), box ligand **L1** (2 mol %), urea-cinchona catalyst **4c** (20 mol %), EEC **1a** (0.6 mmol), malononitrile **2** (0.3 mmol), and $MgSO_4$ (100 mg) in DCM (2.0 mL)/*m*-xylene (4.0 mL) at −10 °C for 48 h (entry 9). A survey of control experiments were carried out to gain more insight into the cooperative catalytic system (entries 10−15). While the use of $Cu(CH_3CN)_4PF_6$ without ligands resulted in diminished yield and enantioselectivity, the box ligand **L1** was found to be a competent catalyst (entry 10 vs 9). The use of the individual catalysts completely failed to promote the cycloaddition reaction, thus suggesting that the cooperative catalytic system plays a crucial role in this reaction (entries 11 and 12). The use of box ligand *ent*-**L1**, achiral ligand **L6**, and 4-dimethylaminopyridine (DMAP) would dramatically affect both the efficiency and enantioselectivity of this reaction (entries 13−15), and all these results would imply that the matched chirality of the ligand and amine catalyst plays an irreplaceable role in the asymmetric [3 + 2] cycloaddition reactions.

Under the optimal reaction conditions, we evaluated the substrate scope of the EECs **1** in the catalytic asymmetric [3 + 2] cycloaddition reactions. As shown in Figure 1, this protocol was applicable to a wide range of EECs **1** with either electron-withdrawing or electron-donating substituents on the benzene ring (**1a**−**1q**), delivering chiral 2-amino-3-cyano-dihydrofurans **3a**−**3q** in generally high yields (up to 96% yield) and excellent enantioselectivities (up to 97% ee). In short, the substrates **1b**, **1i**, and **1n**, which, respectively, possess a methoxy substituent at the 4-, 3-, and 2-positions, all participated in this transformation successfully and resulted in excellent enantioselectivities (**3b**, **3i**, and **3n**, 90−96% ee). Moreover, the presence of halogen atom functionalities on the benzene ring does not have a deleterious impact on the reaction performance (**3e**−**g**, **3j**−**l**). Disubstituted substrates were also tolerated to provide the desired products with excellent enantioselectivities (**3p** and **3q**). Notably, substrates **1r**−**1u** bearing naphthyl and heteroaryl groups could also participate in the [3 + 2] cycloaddition reaction to give the corresponding product **3r**−**3u** in excellent stereoselectivity (91%−96% ee). Nevertheless, this method can also be extended to aliphatic-substituted EEC **1v** and ethynyl oxazolidinone **1w**, affording products **3v** and **3w** with moderate stereoselectivity. The absolute configuration of the cycloadduct **3i** (>99% ee after recrystallization) was assigned by single-crystal X-ray diffraction analysis.

In order to demonstrate the utility of this catalytic asymmetric [3 + 2] cycloaddition reaction, a gram-scale

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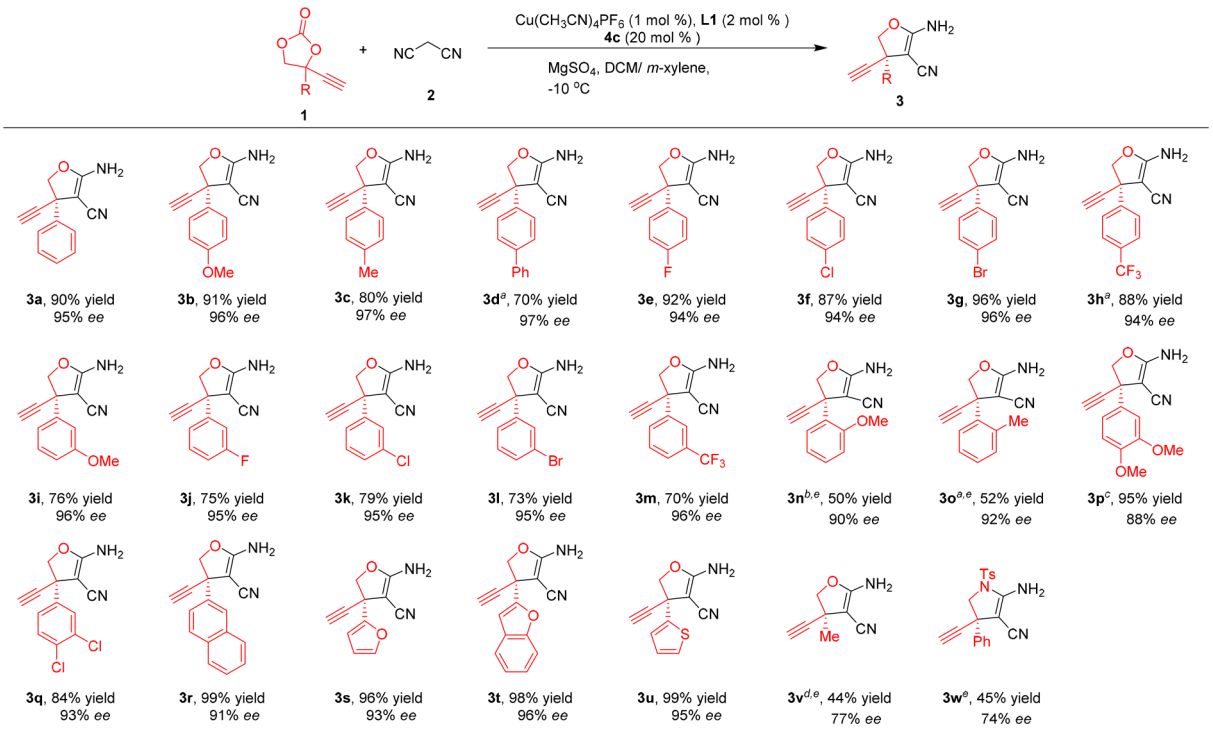
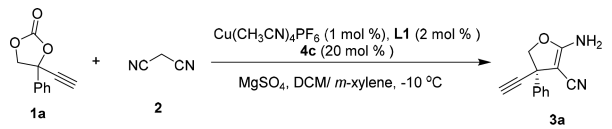


Figure 1. Expansion of substrate scope for the reaction of various ethynylethylene carbonates (EECs) **1** with malononitrile **2**. Reaction conditions: **1** (0.6 mmol), **2** (0.3 mmol), $Cu(CH_3CN)_4PF_6$ (1 mol %), **L1** (2 mol %), **4c** (20 mol %), $MgSO_4$ (100 mg) in DCM (2.0 mL)/*m*-xylene (4.0 mL) at −10 °C for 48 h. Isolated yield. The ee value was determined by HPLC. [a]For 5 days. [b]$Cu(CH_3CN)_4PF_6$ (3 mol %), **L1** (6 mol %), **4c** (20 mol %), for 5 days. [c]$Cu(CH_3CN)_4PF_6$ (5 mol %), **L1** (10 mol %), **4c** (20 mol %) at 0 °C. [d]$Cu(CH_3CN)_4PF_6$ (10 mol %), **4c** (20 mol %) at 30 °C for 7 days. [e]On the average of 10−20% of starting materials was recovered, and trace amounts of unknown products were obtained.

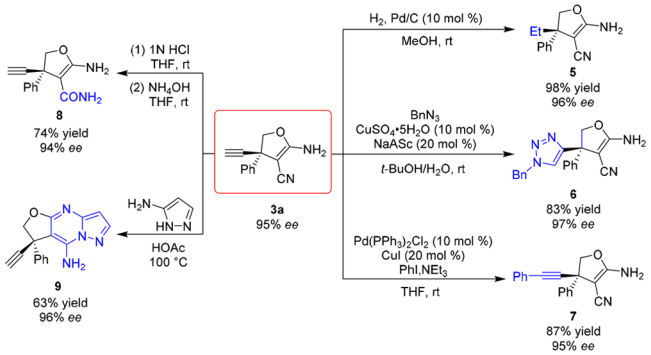
synthesis of dihydrofuran **3a** was conducted under the standard reaction conditions (Scheme 2). To our great pleasure, the reaction proceeded well, and the desired product was isolated in a very good yield of 87% (1.10 g) and excellent stereoselectivity (93% ee).

Scheme 2. Gram-Scale Reaction



Synthetic transformations starting from dihydrofuran **3a** were performed to demonstrate the applicability of this reaction. As shown in Scheme 3, hydrogenation of the alkyne group using a Pd/C catalyst leads to alkyl-substituted product **5** with maintained enantioselectivity. A copper-catalyzed click reaction of **3a** with BnN_3 produced 1,2,3-triazole-substituted chiral dihydrofuran **6** in 83% yield, again without loss of optical purity. Taking advantage of the Sonagashira coupling of **3a** with iodobenzene, we obtained compound **7** in 87% yield and 95% ee. The hydrolysis of the cyano group of **3a** occurred to afford the corresponding amide **8** with excellent stereoselectivity. Treatment of **3a** with 3-aminopyrazole in HOAc gave 6,7-dihydro-5*H*-cyclopenta[d]pyrazolo[1,5-*a*]pyrimidine **9** in 63% yield.

Scheme 3. Synthetic Transformations of 3a



In conclusion, a convenient and efficient catalytic asymmetric [3 + 2] cycloaddition reaction of EECs with malononitrile has been established for the synthesis of 2-amino-3-cyano-dihydrofuran derivatives in good yields and enantioselectivities (up to 99% yield, 97% ee) under mild conditions. Control experiments suggest that chiral copper complexes and the urea-cinchona organocatalyst, respectively, play a crucial role to exhibit the high reactivity and enantioselectivity of this [3 + 2] cycloaddition reaction. Moreover, the reaction is compatible with a variety of functionalities and is amenable to be scaled up to a gram scale. Further investigations into this organo/metal cooperative catalytic process are currently being pursued in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03454.

Experimental details and characterization data (PDF)

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Accession Codes

CCDC 1871659 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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