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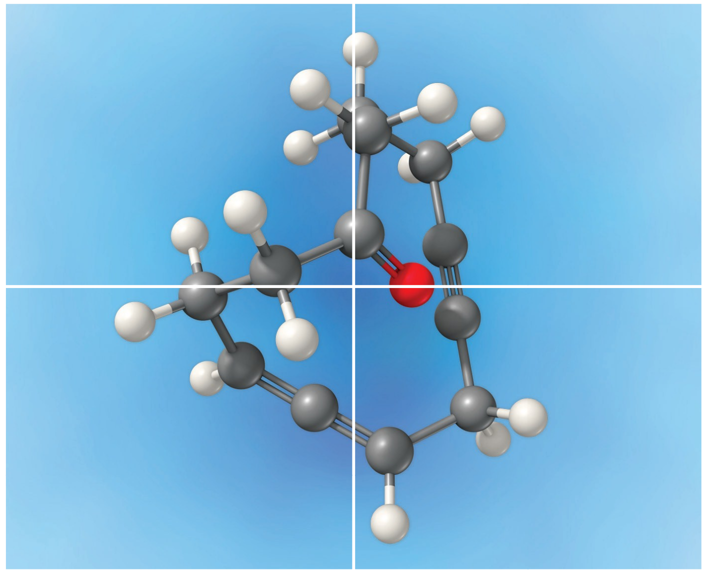

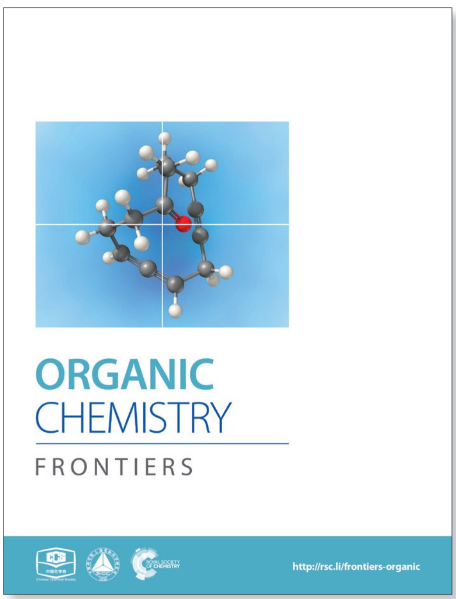

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Efficient Catalytic Enantioselective Nazarov Cyclizations of Divinyl Ketoesters

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Zhou Xu[a,b], Hai Ren[a], Lijia Wang[a] *and Yong Tang[a] *

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An efficient catalytic enantioselective Nazarov cyclization of divinyl ketoesters was developed using a chiral BOX/Cu(II) complex, which provides a facile access to a variety of optically active multi-substituted cyclopent-2-enone esters in 78-95% yields with 78-90% ee.

Multi-substituted five membered carbocyclic skeletons are widely found in natural products and other biologically active compounds.[1] Nazarov cyclization reaction[2-4] represents one of the most effective methods for the construction of five membered carbocyclic rings, and it has been applied in the total synthesis of many useful natural products.[5] However, the asymmetric catalytic Nazarov reaction, which has attracted increasing attention from chemists, is quite difficult to achieve high enantioselectivity. Only a few successful examples have been reported.[6-9] In 2004, Trauner et al. developed the first highly efficient scandium-pybox catalyzed asymmetric Nazarov reactions of divinyl ketones bearing an oxygen at the α-position of the vinyl nucleophile (Type A, Figure 1).[6b] In 2013, Rawal et al. documented the Cr(III)/Salen promoted enantioselective Nazarov cyclizations of dienones (Type A, Figure 1), giving rise to cyclopentenoids in 80−96% ee.[6f] In 2010, an elegant bifunctional thiourea promoted organocatalytic asymmetric

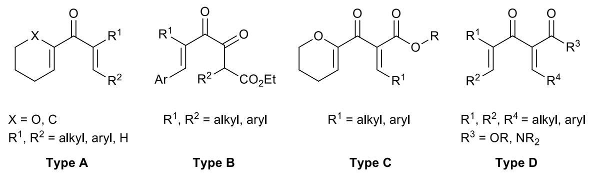
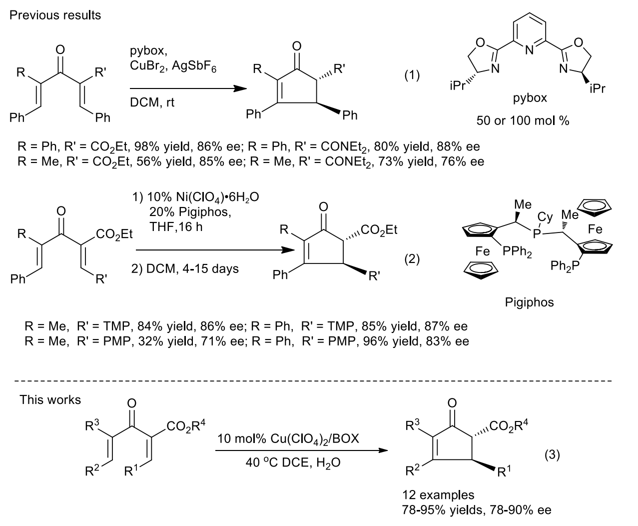


Figure 1. Representative substrate types used in Nazarov reaction.

Nazarov cyclization of diketoesters (Type B, Figure 1) was realized by Tius et al., affording the α-hydroxycyclopentenones in 42-95% yields with 80-97% ee.[7a] In the same year, our group reported a highly regio-, diastereo-, and enantioselective Nazarov reaction of alkoxy divinyl ketoesters (Type C, Figure 1) catalyzed by chiral trisoxazoline/ Copper(II) system.[8]

Scheme 1. Asymmetric Nazarov cyclization of divinyl ketoesters (Type D).



On the other hand, for acyclic divinyl ketoesters (Type D, Figure 1) as substrates,[10d, 10e] the racemic studies on the Nazarov cyclization[10] have achieved important breakthrough in recent years, however, successful examples of asymmetric

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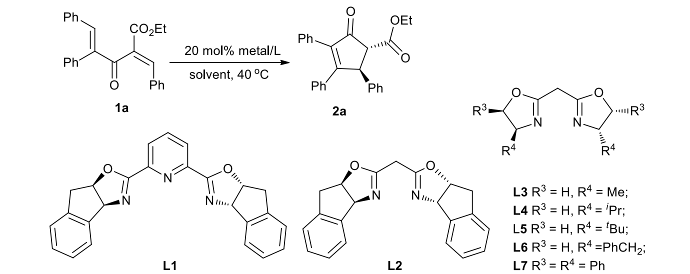
version are still limited. , In 2003, Aggarwal et al. developed the first asymmetric Nazarov cyclization promoted by stoichiometric or semi-stoichiometric chiral Cu(II)-pybox complexes, achieving up to 88% enantiomeic excess (eq. 1, Scheme 1).[9a] Togni et al. reported a chiral tridentate phosphine Pigiphos/Ni(II) catalyzed process of divinyl ketoesters containing activated trimethoxyphenyl (TMP) group or 4-methoxyphenyl (PMP) group, affording the products in 32-97% yields with 45-88% ee after 4-15 days (eq. 2, Scheme 1).[9b] Despite these great efforts, challenging problems, such as reactivity, stereoselectivity and substrate scope generality in this process have not been well resolved yet. Recently, we have developed an efficient catalytic enantioselective Nazarov cyclizations of divinyl ketoesters, which provide a facile access to the optically active multi-substituted cyclopent-2-enones in high yields with good to excellent ee values (eq. 3, Scheme 1). In this communication, we wish to report the preliminary results.

Initially, the enantioselective Nazarov cyclization of substrate **1a** was carried out with 20 mol% of copper complex in a chloroform solution at 40 °C. The pyridyl bisoxazolines were documented as effective chiral ligands in the asymmetric Nazarov reactions. [6b, 6e 9a, 9c] However, as to substrate **1a**[11], with **L1** the reaction could not occur (entry 1, table 1). Then we tried to use BOX ligand **L2,** and found that the cyclization proceeded smoothly producing **2a** in 86% yield with 51% ee (entry 2). Changing the solvent to 1,2-dichloroethane (DCE) led to a better level of enantioselectivity (61% ee, entry 3). Next, we turned to investigate a series of BOX ligand bearing various chiral backbones.[12] With the L-Ala derived BOX ligand **L3**, the product **2a** was obtained in 84% yield with 47% ee (entry 4). A more hindered ^{i}Pr group was beneficial to the enantioselectivity (67% ee, entry 5). However, continuing to increase the hindrance, **L5** resulted in a dramatic drop of the enantioselectivity (23% ee entry 6). Meanwhile, when the L-Phe derived BOX ligand **L6** was employed, the **2a** was produced in 93% yield with 58% ee (entry 7). Under optimal conditions, we finally found chiral ligand **L7** could promote the reaction very efficiently, affording the **2a** in 92% yield with 90% ee after 10 h (entry 8), better than the pybox/Cu(SbF_6)2 in both selectivity and catalysts loading. We also examined the counter ion effect of this reaction. As shown in entries 8-10, ClO_4^- proved to be the best one. However, when the catalyst loading was further reduced to 10 mmol%, the ee value was fall to 84% ee (entry 11). In order to raise the efficiency of this reaction system, additives were examined. Interestingly, 4Å molecular sieve destroyed the reaction, while a trace amount of water could promoted the reaction to give 92% yield and 90% ee (entry 12 vs. 13). [13]

Under the optimized reaction conditions (entry 8, table 1), we next investigated the substrate scope (table 2). Divinyl ketoesters **1b-d** bearing R[1] group with -Br substituted at the para-, meta- and ortho- position underwent cyclization with

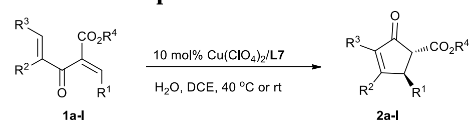
Table 1. Reaction Optimization.



entry	metal salts	L	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	$Cu(ClO_4)_2\ 6H_2O$	**L1**	$CHCl_3$	24	0	-
2	$Cu(ClO_4)_2\ 6H_2O$	**L2**	$CHCl_3$	17	86	51
3	$Cu(ClO_4)_2\ 6H_2O$	**L2**	DCE	14	90	62
4	$Cu(ClO_4)_2\ 6H_2O$	**L3**	DCE	12	84	47
5	$Cu(ClO_4)_2\ 6H_2O$	**L4**	DCE	14	90	67
6	$Cu(ClO_4)_2\ 6H_2O$	**L5**	DCE	16	95	23
7	$Cu(ClO_4)_2\ 6H_2O$	**L6**	DCE	14	93	58
8	$Cu(ClO_4)_2\ 6H_2O$	**L7**	DCE	10	92	90
9	$Cu(SbF_6)_2$	**L7**	DCE	8	94	89
10	$Cu(OTf)_2$	**L7**	DCE	10	86	88
11[d]	$Cu(ClO_4)_2\ 6H_2O$	**L7**	DCE	14	91	84
12[d,e]	$Cu(ClO_4)_2\ 6H_2O$	**L7**	DCE	24	0	-
13[d,,f]	$Cu(ClO_4)_2\ 6H_2O$	**L7**	DCE	24	92	90

[a] Reactions were carried out with metal salts (0.04 mmol), ligand (0.04 mmol) and **1a** (0.2 mmol) in solvent (4.0 mL) under Ar atmosphere; [b] Isolated yield; [c] Determined by chiral HPLC; [d] The reaction was carried out with 10 mol% catalyst loading; [e] 4Å molecular sieve was added. [f] H_2O (0.12 mmol, 2.3 uL) was added.

Table 2. Substrate Scope[a].



entry	R^1; R^2; R^3; R^4	2	time (h)	yield (%)[b]	ee (%)[c]
1	Ph; Ph; Ph; Et	**2a**	24	92	90 [e]
2	4-BrC_6H_5; Ph; Ph; Et	**2b**	45	81	88
3	3-BrC_6H_5; Ph; Ph; Et	**2c**	55	80	85
4	2-BrC_6H_5; Ph; Ph; Et	**2d**	60	78	86
5	4-PhC_6H_5; Ph; Ph; Et	**2e**	22	92	84(88)[d]
6	4-$CF_3C_6H_5$; Ph; Ph; Et	**2f**	72	83	84
7	1-Naphthyl; Ph; Ph; Et	**2g**	24	89	86
8	2-Naphthyl; Ph; Ph; Et	**2h**	24	93	87
9[f]	Ph; 4-$MeOC_6H_5$; Ph; Et	**2i**	2	91	78
10[f]	Ph;4-$MeOC_6H_5$;4-$MeOC_6H_5$;Et	**2j**	2	90	82
11	Ph; Ph; Ph; Me	**2k**	20	95	90
12	4-IC_6H_5; Ph; Ph; Me	**2l**	30	87	90

[a] Reactions were carried out with $Cu(ClO_4)_2\ 6H_2O$ (0.02 mmol), **L7** (0.02 mmol), **1** (0.2 mmol) and H_2O (0.12 mmol) in DCE (4.0 mL) under Ar atmosphere; [b] Isolated yield; [c] Determined by chiral HPLC; [d] The reaction was carried out with 20 mol% catalyst loading; [e] The absolute configuration of the major enantiomer is (1*R*,5*S*) by the comparison of the reported data;[9c] [f] The reaction was carried out at rt.

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high enantioselectivity (85-88% ee) and a decline of the reactivity (entries 2-4). When R^1 was 4-PhC_6H_5- group, 20% catalyst loading was required to produce the cyclization product **2e** in 92% yield with 88% ee (entry 5). Cyclic enones products **2g** and 2**h** bearing both 1- and 2- naphthyl group could be easily accessed in 89% yield with 86% ee, and in 93% yield with 87% ee, respectively (entries 7 and 8).The catalyst system was even competent with electron deficient substrate **1f**, affording the product **2f** in 83% yield with 84% ee (entry 6). As to the electron-rich substrates **1i** and **1j**, the reactions proceeded very fast and finished within 2 h at room temperature, giving the corresponding products **2i** and **2j** in high yields with good enantioselectivities (entries 9 and 10). Thus, the current catalyst system is tolerated for both electron rich and poor substrates. In addition, changing the ester group from ethyl to methyl, both the reactivity and the enantioselectivity are maintained (entry 11). Moreover, for the 4-IC_6H_5 substituted divinyl ketoester **1l**, a pleasing result of 87% yield with 90% ee was obtained (entry 12).

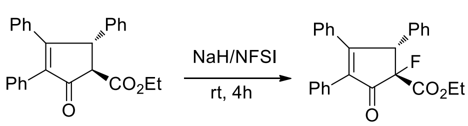
Interestingly, when substrate **1a'** was employed with the current catalytic system, the absolute configuration of the major enantiomer reversed to (1*S*, 5*R*), leading to the product **2a'** in 72% ee (Scheme 2). Thus, under the same catalyst system, both the two enantiomers could be obtainedin terms of changing the Z/E configuration of substrates.

Scheme 2. Control experiment of 1a'.

(2Z, 4E) **1a'** (1S, 5R) **2a'**

Fluorine-containing chiral cyclic ketoesters are potential useful building blocks for the synthesis of natural products and medicines. Ma et al. reported an elegant copper-catalyzed tandem Nazarov cyclization–electrophilic fluorination reaction in the stereoselective synthesis of highly substituted indanones.[14] We found that under mild reaction conditions, compound **2a** was easily transferred to fluorine substituted ketoester **3a** in 87% yield without loss of optical purity with stereospecific diastereoselectivity (Scheme 3).[7, 9c]

Scheme 3. Product transformation.



2a 90% ee **3a** 87% yield, 90% ee

Conclusions

In conclusion, we have developed an efficient catalytic enantioselective Nazarov cyclizations of divinyl ketoesters by a chiral BOX/Cu(II) complex, which provide a facile access to the optically active cyclopent-2-enone esters with functional diversity in 78-95% yields with 78-90% ee. There are several remarkable features of the method, such as mild reaction conditions, highly catalytic efficiency and simple procedure, that make the current reaction practically useful. Study on the application of this method to total synthesis of natural product is ongoing in our lab.

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[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China. E-mail: tangy@mail.sioc.ac.cn; wanglijia@sioc.ac.cn

[b] Xuzhou Medical College, 209Tongshan Road, Xuzhou 221004, China

Electronic Supplementary Information (ESI) available: Experimental procedures and the characterization data of new compounds. See DOI: 10.1039/c000000x/

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11 CCDC 1029676 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See the Supporting Information.

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