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Copper(II)-Catalyzed Enantioselective Intramolecular Cyclization of *N*-Alkenylureas

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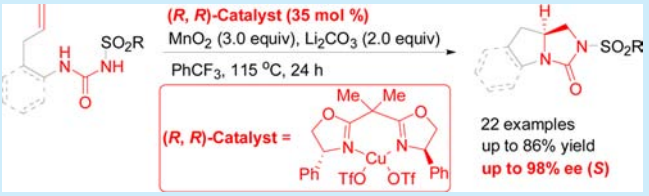
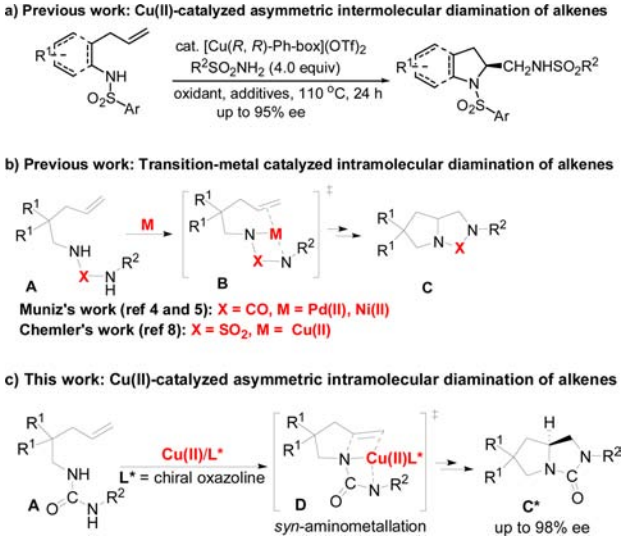
Supporting Information

ABSTRACT: The first Cu(II)-catalyzed highly enantioselective intramolecular cyclization of *N*-alkenylureas was developed for the concise assembly of chiral vicinal diamino bicyclic heterocycles. Facile removal of carbonyl group of the carbamido moiety allowed for ready access to enantioenriched cyclic vicinal diamines.



Vicinal diamine-containing heterocycles are commonly encountered in natural products and many biologically active molecules.[1] Direct diamination of alkenes presents a powerful tool to construct such 1,2-diamine motifs.[1a,c,d] In recent years, much significant progress toward developing intermolecular diamination processes has been achieved.[2] Notably, the Shi, Chemler, and Michael groups have successively employed diaziridinones,[2l] sulfonylamides,[2o] and *N*-fluorobenzenesulfonimides[2n] as nitrogen sources, in combination with Pd or a copper salt/chiral ligand catalytic system, to realize the more challenging asymmetric intermolecular diamination of olefins. Meanwhile, transition-metal-catalyzed fully intramolecular diamination (FID) of alkenes has also attracted great interest because this transformation provides an atom- and step-economic strategy for rapidly assembling a complex polycyclic nucleus. Compounds containing chiral vicinal diamino polycyclic units have already demonstrated distinctive bioactivity.[3] In this context, transition-metal Pd(II),[4] Ni(II),[5] Au(I,)[6] and Cu(I)[7] catalysts have been employed to enable the FID of various functionalized alkenes by Muñiz and Chiba, respectively. Moreover, Chemler and co-workers found that stoichiometric copper(II) acetate could also efficiently promote the FID of alkenyl sulfamides.[8] However, in comparison with the Cu(II)-catalyzed asymmetric intramolecular carbonamination[9] and Cu(II)-catalyzed asymmetric intermolecular diamination (Scheme 1a)[2o] of monoamide-containing alkenes, transition-metal-catalyzed intramolecular asymmetric diamination of olefins has not achieved any breakthrough up to now, possibly due to two inherent vicinal amino anchors (−NHXNH−, X = CO or SO_2) from alkene molecules easily forming cyclometal complexes such as **B** (Scheme 1b),[10] thereby inhibiting the external chiral ligand-induced enantioselectivity to some degree. Nevertheless, considering that transition-metal-catalyzed FID of alkenes involved a key *syn*-aminometalation process[4b,6,8] in which the stereochemistry-determining C−N bond-forming step occurred,[9,11] we believe that a proper chiral ligand on central metal ions can play remarkably enantionselective induction by microcontrolling electronic and steric environments around the 1,2-diamine-reactive centers. Herein we describe the first highly enantioselective intramolecular diamination of alkenes using cheap and readily available chiral bis(oxazoline) copper(II) catalyst (Scheme 1c).

Scheme 1. Metal-Catalyzed Diamination of Alkenes



Considering the fact that chiral *N*-heterocyclic carbenes and bidentate nitrogen ligands have already been successfully applied to asymmetric intermolecular diamination[2p] and intramolecular carboamination[9,11,12] of alkenes, respectively, we initially screened 2,2′-bipyridine (L_1) and crowned imidazole (L_2) to trace the achiral ligand type which could possibly realize $Cu(OTf)_2$-catalyzed intramolecular diamination of alkenes with various vicinal diamino groups under the MnO_2 (3.0 equiv)/Li_2CO_3 (2.0 equiv) conditions at 115 °C for 24 h.

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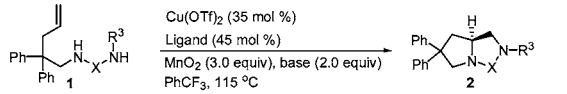
To our delight, we quickly found bipyridine L_1 (45 mol %) could enhance the intramolecuar diamination of *N*-tosylcarbamido-substituted alkene (**1d**) in the presence of a catalytic amount of $Cu(OTf)_2$ (35 mol %) to afford 40% yield of the desired **2d** (Table 1, compare entries 1−3 with 4). Disappointingly, no enhancement was achieved with regard to the crowned imidazole L_2, although its crown-ether ring (N15C5) can complex with alkali metal cations and play a role in phase-transfer catalyst.

With a promising achiral ligand type in hand, we then directly turned our attention to screening various chiral nitrogen-containing ligands by employing alkene **1d** as the model substrate. At first, we evaluated chiral N,P-chelating ligands (L_3 and L_4) and found (*R*,*R*)-L_3 could afford 23% yield of the diamination product **2d** with an enantiomeric excess (ee) of 8% (entry 6 vs 7). Although the enantioselectivity of **2d** was very poor, this positive result encouraged us to further investigate the chiral induction of chiral *N*,*N*-chelating bidentate oxazoline ligands with different backbones (entries 8−18). Gratifyingly, among the tested chiral ligands, (*R*,*R*)-L_{15} was the most effective ligand which furnished **2d** in 73% yield with an excellent ee value (90%) (entry 18); other substituted alkenes were prepared in order to investigate the generality of the reaction. As shown in Table 2, the reactivity of substrates **1** was partly dependent on the bisoxazoline ligands such as (*R*,*R*)-L_{11} and (*S*,*S*)-L_{14} afforded **2d** with moderate to good enantioselectivity (61−79% ee) (entries 14 and 17). Of particular note is that alkali metal lithium carbonates exerted significantly enhanced enantioselective catalytic performance compared with Na_2CO_3, and $NaHCO_3$, etc. (compare entries 19−22 with 18).[13] Especially for Cs_2CO_3, basically no desired **2d** was observed (entry 22). Moreover, employing the $AgSbF_6$ (70 mol %) could increase the yield of **2d** to 95%, but with the enantioselectivity of **2d** dropping to 29% ee (entry 23). Finally, reducing the amount of copper catalyst $Cu(OTf)_2$ and chiral ligand L_{15} led to poorer yield and ee value (entry 24) (see the Supporting Information for the more details about screening of reaction conditions).

With these optimized conditions in hand, a representative selection of *N*-sulfonylcarbamido-substituted alkenes was prepared in order to investigate the generality of the reaction. The intramolecular diamination of *N*-arylsulfonyl-substituted substrates **1d**−**n** consistently produced the desired optically active bicyclic compounds (**2d**−**n**) in moderate to good yields with excellent enantioselectivity (entry 1, 61−79% yield, 89−96% ee). *Para*- or *meta*-substitution of *N*-sulfonyl phenyl rings with electron-donating (Me, MeO) or electron-withdrawing (CF_3, NO_2, halogen, etc.) groups does not significantly affect the yield and enantioselectivity. Moreover, *N*-methyl, *N*-(2-thienyl), and *N*-(1-naphthyl) sulfonyl group substituted alkenes (**1o**−**q**) could also exhibit good reactivity with excellent 90−98% ee (**2o**−**q**), no matter whether the *N*-sulfonyl moiety varies in size. Besides the *δ*,*δ*-diphenyl substituted alkenes, *δ*,*δ*-dimethyl substituted olefin (**1s**) was also compatible for this reaction and provided the diamination products **2s** (71% yield) with 86% ee (entry 3). However, *N*-(2-allylphenyl)urea derivative **1r** and 1-allyl-1-carbamidomethylcyclohexane **1t** afforded the corresponding cyclization products in 67% and 72% yield with a moderate enantioselectivity (49% ee for **2r** and 65% ee for **2t**) probably owing to their conformation rigidity and steric reasons (entries 2 and 4). Unfortunately, in the absence of *δ*-substitution, alkene **1u** could not furnish the desired product **2u** due to the lack of a Thorpe−Ingold effect,[14]

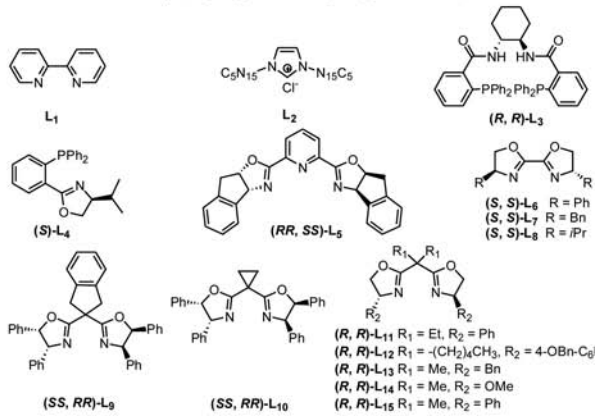
Table 1. Optimization for Reaction Conditions[a]



1a, X = SO_2, R^3 = CO_2Et
1b, X = SO_2, R^3 = Bn
1c, X = CO, R^3 = PhCO
1d, X = CO, R^3 = Ts

2a, X = SO_2, R^3 = CO_2Et
2b, X = SO_2, R^3 = Bn
2c, X = CO, R^3 = PhCO
2d, X = CO, R^3 = Ts

entry	1	L	base	2, yield [%][b]	ee [%][c]
1	**1a**	L_1	Li_2CO_3	**2a**, nr[d]	–
2	**1b**	L_1	Li_2CO_3	**2b**, nr[d]	–
3	**1c**	L_1	Li_2CO_3	**2c**, dec[e]	–
4	**1d**	L_1	Li_2CO_3	**2d**, 40	–
5	**1d**	L_2	Li_2CO_3	**2d**, nr[d]	–
6	**1d**	(*R*, *R*)-L_3	Li_2CO_3	**2d**, 23	8
7	**1d**	(*S*)-L_4	Li_2CO_3	**2d**, <5	nd[f]
8	**1d**	(*RR*, *SS*)-L_5	Li_2CO_3	**2d**, trace	nd[f]
9	**1d**	(*S*, *S*)-L_6	Li_2CO_3	**2d**, trace	nd[f]
10	**1d**	(*S*, *S*)-L_7	Li_2CO_3	**2d**, trace	nd[f]
11	**1d**	(S, *S*)-L_8	Li_2CO_3	**2d**, trace	nd[f]
12	**1d**	(SS, *RR*)-L_9	Li_2CO_3	**2d**, 10	30
13	**1d**	(*SS*, *RR*)-L_{10}	Li_2CO_3	**2d**, trace	nd[f]
14	**1d**	(*R*, *R*)-L_{11}	Li_2CO_3	**2d**, 25	61
15	**1d**	(*R*, *R*)-L_{12}	Li_2CO_3	**2d**, 24	35
16	**1d**	(*S*, *S*)-L_{13}	Li_2CO_3	**2d**, 25	26
17	**1d**	(*S*, *S*)-L_{14}	Li_2CO_3	**2d**, 37	79
18	**1d**	(*R*, *R*)-L_{15}	Li_2CO_3	**2d**, 73	90
19	**1d**	(*R*, *R*)-L_{15}	Na_2CO_3	**2d**, 44	18
20	**1d**	(*R*, *R*)-L_{15}	$NaHCO_3$	**2d**, 45	25
21	**1d**	(*R*, *R*)-L_{15}	K_2CO_3	**2d**, 37	21
22	**1d**	(*R*, *R*)-L_{15}	Cs_2CO_3	**2d**, <5	nd[f]
23	**1d**	(*R*, *R*)-L_{15}	Li_2CO_3	**2d**, 95	29[g]
24	**1d**	(*R*, *R*)-L_{15}	Li_2CO_3	**2d**, 62	67[h]



[a]All the reactions were carried out using alkenes (**1**) (0.10 mmol) and L_{15} (45 mol %) with $Cu(OTf)_2$ (35 mol %) in the presence of MnO_2 (3.0 equiv) and Li_2CO_3 (2.0 equiv) in $PhCF_3$ (2.0 mL) at 115 °C for 24 h under Ar in a sealed reaction tube, followed by flash chromatography on SiO_2. [b]Isolated yield. [c]Determined by HPLC using a Phenomenex Lux 15u cellulose-1 Chiralpak. [d]nr = no reaction. [e]Decomposed. [f]Not determined. [g]$CuBr_2$ (35 mol %)/$AgSbF_6$ (70 mol %) system was used. [h]$Cu(OTf)_2$ (20 mol %) and L_{15} (25 mol %) was used.

and the starting material **1u** was recovered completely (entry 5). Finally, we were gratified to find that this transformation is not limited to *δ*,*δ*-geminal disubstituted alkenes; the racemic *δ*-

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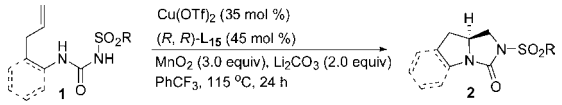
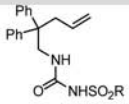
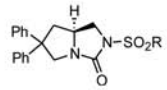
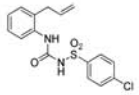
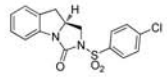
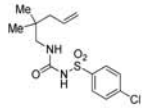
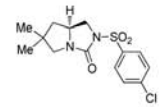
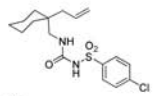
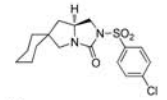
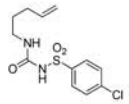
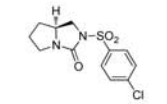
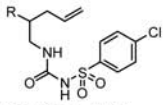
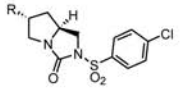
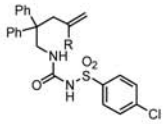
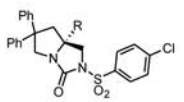
Table 2. Substrate Scope[a]



entry	substrate	product	yield (%)[b]	ee (%)[c]
1				
	1d, R = 4-Me-Ph	**2d**	73	90
	1e, R = C_6H_5	**2e**	67	90
	1f, R = 4-MeO-Ph	**2f**	79	89
	1g, R = 4-F-Ph	**2g**	76	92
	1h, R = 3-F-Ph	**2h**	67	95
	1i, R = 4-Cl-Ph	**2i**	78	94
	1j, R = 3-Cl-Ph	**2j**	75	96
	1k, R = 4-Br-Ph	**2k**	67	95
	1l, R = 4-I-Ph	**2l**	72	90
	1m, R = 4-CF_3-Ph	**2m**	74	90
	1n, R = 4-NO_2-Ph	**2n**	61	92
	1o, R = Me	**2o**	68	93
	1p, R = 2-thienyl	**2p**	86	90
	1q, R = 1-naphthyl	**2q**	78	98
2			67	49
	1r	**2r**		
3			71	86
	1s	**2s**		
4			72	65
	1t	**2t**		
5			nr[d]	–
	1u	**2u**		
6				
	1v, R = n-Amyl	**2v**	42	53[e]
	1w, R = Ph	**2w**	46	90[e]
7				
	1x, R = Me	**2x**	69	93
	1y, R = Ph	**2y**	49	n.d.[f]

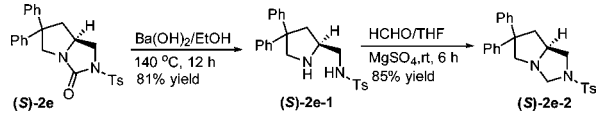
[a]All the reactions were carried out using alkenes (**1**) (0.10 mmol) and $\mathbf{L_{15}}$ (45 mol %) with $Cu(OTf)_2$ (35 mol %) in the presence of MnO_2 (3.0 equiv) and Li_2CO_3 (2.0 equiv) in $PhCF_3$ (2.0 mL) at 115 °C for 24 h under Ar in a sealed reaction tube, followed by flash chromatography on SiO_2. [b]Isolated yield. [c]Determined by HPLC using a Phenomenex Lux 15u cellulose-1 Chiralpak. [d]nr = no reaction. [e]No diastereoisomer was observed from the ^1H NMR spectrum of the chiral product; [f]Not determined. The enantiomers could not be separated by HPLC on a chiral stationary phase.

monoalkyl- and δ-monoaryl-substituted alkenes (**1v** and **1w**) could also participate successfully in the enantioselective intramolecular diamination and provided **2v** (42% yield) and **2w** (46% yield) with 53% ee and 90% ee (entry 6), respectively.[15] More importantly, the reaction system still enabled β-methyl- or β-phenyl-substituted alkenes **1x** and **1y** to furnish the chiral quaternary carbon-containing diamination product **2x** (69% yield with 93% ee) and **2y** (49% yield), respectively (see entry 7).

Finally, we determined the absolute configuration of these optically active bicycles via X-ray analysis of **2l**, which proved to be the 2-(4-iodobenzenesulfonyl)-6,6-diphenylhexahydro-(*S*)-pyrrolo[1, 2-*c*]imidazo-3-one.[16] Hence, the other remaining cyclization products in Table 2 were also assigned *S* stereochemistry by assuming an analogous reaction pathway.

To demonstrate the utility of the optically active bicycles, we were subsequently able to remove the carbonyl group of the carbamido moiety of the product (***S***)-**2e** by treatment with $Ba(OH)_2 \cdot 8H_2O$/aq EtOH at 140 °C for 12 h to give 81% yield of (*S*)-pyrrolidine **2e-1**, which could be further condensed with formaldehyde to furnish the (*S*)-hexahydropyrrolo[1,2-c]-imidazole **2e-2** in 85% yield with 90% ee (Scheme 2).

Scheme 2. Synthetic Application for This Transformation



In summary, we have developed the first example of Cu(II)-catalyzed asymmetric intramolecular cyclization of *N*-alkenylureas, which provides a useful method for the rapid assembly of chiral vicinal diamino bicyclic heterocycles in moderate to good yields with high to excellent enantioselectivity (up to 98% ee). The readily available *N*,*N*-chelating bidentate oxazoline ligand in conjunction with alkali metal lithium carbonates plays a key role for obtaining high enantioselectivity. Further applications of this transformation toward the synthesis of bioactive chiral vicinal diamines are underway.

■ ASSOCIATED CONTENT

Supporting Information

Analytical data for all isolated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) It is interesting that substrate **1w** would lead to the formation of racemic diasteroisomer **2w** and **2w-1** (**2w**/**2w-1** = 2.3:1) in 77% overall yield using Muñiz's Pd-catalytic conditions (see ref 6), and **2w-1** was already isolated and characterized by its corresponding ^{1}H NMR and ^{13}C NMR spectrum (see the Supporting Information). On the other hand, only chiral **2w** was detected by using TLC and ^{1}H NMR methods under our Cu(II)/(*R*, *R*)-$\mathbf{L}_{15}$ conditions, and no diasteroisomer **2w-1** was observed.

(16) For X-ray analysis details, see the Supporting Information.

NOTE ADDED AFTER ASAP PUBLICATION

The toc/abstract, Scheme 1, and Table 2 graphics were corrected on February 20, 2015.

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