Organic LETTERS

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Asymmetric Construction of 3,4-Diamino Pyrrolidines via Chiral *N,O*-Ligand/Cu(I) Catalyzed 1,3-Dipolar Cycloaddition of Azomethine Ylides with *β*-Phthalimidonitroethene

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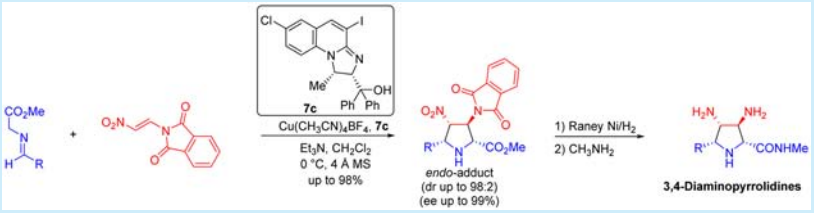
Supporting Information



ABSTRACT: A series of chiral *N,O*-ligands derived from a 1,2-dihydroimidazo[1,2-*a*]quinolone motif have been evaluated for the asymmetric 1,3-dipolar cycloaddition of azomethine ylides with a novel dipolarophile *β*-phthalimidonitroethene. A newly designed DHIPOH ligand **7c** bearing 1-methyl and 4-iodo substituents was found to have significant "synergistic steric effects" and consequently afforded the corresponding 4-nitro-3-aminopyrrolidines with excellent diastereo- (dr up to 98:2) and enantio selectivities (ee up to 99%). Subsequent Raney Ni-catalyzed reduction and deprotection of phthalyl led to the structurally and biologically important 3,4-diaminopyrrolidines in a straightforward and efficient pathway.

In biology-oriented synthesis (BIOS),[1] compound collections are derived from or inspired by natural products. Biological relevance is employed as the key criterion to generate hypotheses for the design and synthesis of natural product-inspired compound collections. Among them, optically pure 3,4-diaminopyrrolidine[2] is a significant scaffold in medicinal chemistry and highly valuable synthetic building block in organic synthesis (Figure 1).[3]

The general method for the preparation of chiral 3,4-diaminopyrrolidine often requires multistep transformations from commercially available D/L-tartaric acid via the azide substitution and reduction of pyrrolidine-3,4-diol as key steps.[3] On the other hand, the catalytic asymmetric 1,3-dipolar cycloaddition[4,5] of azomethine ylides to a wide variety of electron-deficient alkene dipolarophiles is conceptually an extremely powerful and atom-economical strategy for the asymmetric synthesis of highly functionalized chiral pyrrolidines. Of particular interest is the 1,3-dipolar cycloaddition between azomethine ylides and nitroalkenes[6] to form pyrrolidines with an additional nitro functionality. The first highly enantioselective [3 + 2] cycloaddition of azomethine ylide and nitroalkene for the construction of *exo*-selective chiral pyrrolidines was reported by Carretero's group[7] in 2005. Hou and co-workers[8] then implemented a more systematic study on this type of asymmetric reaction utilizing a Cu(I)/chiral ferrocenyl *P,N*-ligand complex. The *endo*/*exo* selectivity could be easily switched by tuning the electron density of the chiral ligand. Subsequently, Arai,[9] Oh,[10] Waldmann,[11] Cossío,[12] Xu[13] et al. devoted their independent efforts for the development of the catalytic asymmetric 1,3-dipolar cycloaddition of azomethine ylides to various nitroalkenes. However, compared with the commonly utilized *β*-alkyl or *β*-aryl substituted nitroalkenes, the heteroatom modified nitroalkenes have rarely been explored (Scheme 1a).[14] Retrosynthetically, using *β*-amino nitroalkene as the dipolarophile would provide a straightforward way to construct structurally novel highly functionalized chiral 4-nitro-3-aminopyrrolidines, which could then easily be converted to the important 3,4-diaminopyrrolidines by Raney Ni reduction and deprotection of phthalyl (Scheme 1b).

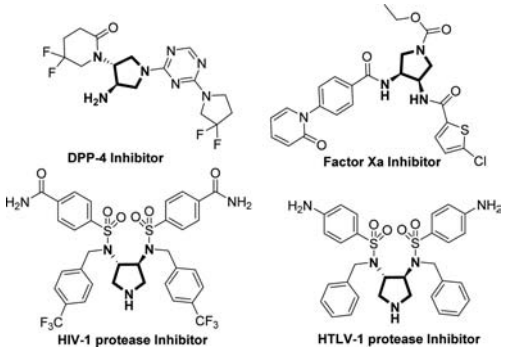
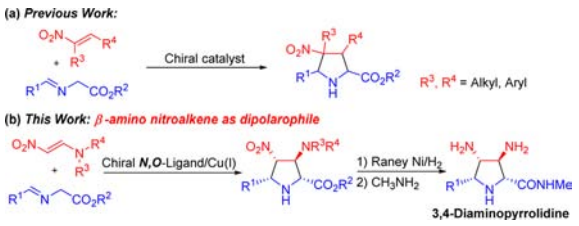


Figure 1. Biologically active molecules with 3,4-diaminopyrrolidine skeletons.

Received: August 22, 2015
Published: September 29, 2015

DOI: 10.1021/acs.orglett.5b02431
Org. Lett. 2015, 17, 4988–4991

Scheme 1. Catalytic Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides with Nitroalkenes

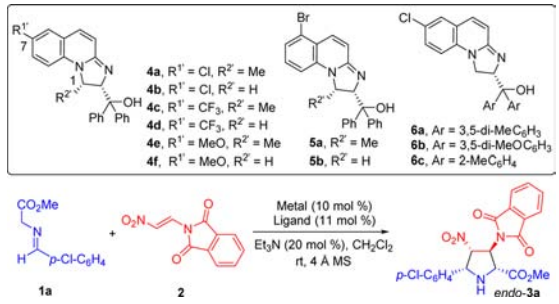


We have recently established a library of newly designed DHIPOH-based *N,O*-ligands with successful applications to catalytic asymmetric reactions.[15] Among them, the first catalytic asymmetric 1,3-dipolar cycloadditions of azomethine ylides to α-phthalimidoacrylates catalyzed by both a Ag(I) and Cu(II) system were reported. Notably, this catalytic system provides an efficient access to the useful quaternary α-amino acid containing pyrrolidines with excellent diastereo- and enantioselectivities.[15d,g] Herein, we would like to describe our further elaborative manipulation on the DHIPOH motif and their applications for the asymmetric synthesis of 4-nitro-3-aminopyrrolidines via Cu(I)-catalyzed 1,3-dipolar cycloaddition. A newly designed 4-iodo-DHIPOH ligand **7c** allows the successful catalytic cycloaddition of azomethine ylides with β-phthalimidonitroethene in excellent diastereo- (dr up to 98:2) and enantioselectivities (ee up to 99%). A practical utility of this protocol was demonstrated by subsequent H_2 reduction of corresponding cycloadducts in the presence of Raney Ni and deprotection of phthalyl, affording the important 3,4-diaminopyrrolidines in good yields.

We began our studies by choosing glycine methyl ester **1a** and β-phthalimidonitroethene **2** as the model substrates, with $Cu(OAc)_2{\cdot}H_2O$ (10 mol %)/chiral *N,O*-ligand **4a** (11 mol %) as the catalytic system in the presence of 20 mol % of Et_3N as the base in CH_2Cl_2 at rt (Table 1, entry 1). To our delight, the reaction proceeded smoothly to afford the desired 4-nitro-3-aminopyrrolidine *endo*-**3a** in 72% yield with 90:10 dr and 86% ee. It is notable that using $Cu(CH_3CN)_4ClO_4$ instead of $Cu(OAc)_2{\cdot}H_2O$ led to improvements in both yield (81%) and stereoselectivity (dr = 94:6, ee = 89%) (entry 2). Encouraged by this result, a series of chiral *N,O*-ligands **4**–**6** were investigated. According to our previous work,[15] we have demonstrated that the substituent $R^{2'}$ on the imidazole ring plays a critical role in the enantioselectivities. When ligand **4b**, which lacks the steric repulsion of the methyl group on the imidazole ring, was employed, the yield and enantioselectivity decreased obviously (entry 3). This observation was also found in other *N,O*-ligands **4c**–**f**, **5**, and **6** (entries 4–12). The electronic effect of the substituents on the quinoline backbone was also tested. Methyl appended *N,O*-ligand **4c**, **4e**, and **5a** with either electron-withdrawing or -donating groups on the quinoline backbone gave similar enantioselectivities (entries 4, 6, 8).

Note that, in our previous work, the steric and electronic effects of substituents on the quinoline backbone of *N,O*-ligands on the reaction stereoselectivity have been investigated; however, the steric effect of the 4-substituent has not been studied. It is also worth noting that the 4-substituent is spatially close to the reactive center, and we envisaged that installation of a bulky group at the 4-position would have a positive steric effect on this new 1,3-dipolar cycloaddition. With this consideration in mind, an 4-iodo substituted DHIPOH ligand **7a** was first synthesized to test this idea. As expected, the use of ligand **7a** led to dramatic improvements in both yield and enantioselectivity (from 68% to 87% ee) compared to ligand **4b** (Scheme 2). Next, since it has been proven that ligand **4a** bearing a chiral methyl group gave higher enantioselectivity than that obtained from ligand **4b**, we further envisioned whether the steric hindrance of the 4-substituent and chiral methyl matched each other; thus, the stereoselectivity could be further improved. Consequently, two novel chiral *N,O*-ligands **7b** and **7c** were synthesized for the optimization of the catalytic system (details in Supporting Information (SI)). To our delight, both ligand **7b** and **7c** bearing the methyl group and 4-iodo group were found to be better ligands to give *endo*-**3a** with excellent enantioselectivities.

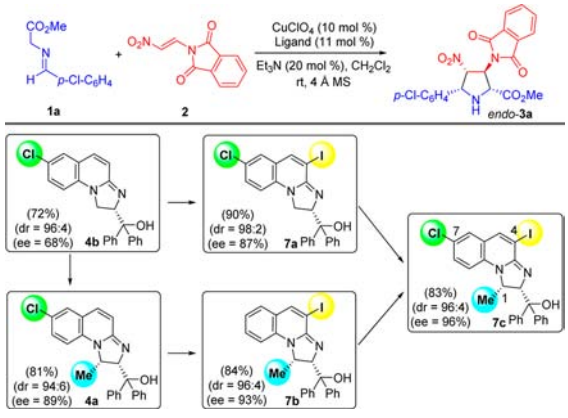
Table 1. Catalysts Screening for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylide 1a with β-Phthalimidonitroethene 2[a]



entry	metal	ligand	yield (%)[b]	dr[c]	ee (%)[c]
1	$Cu(OAc)_2{\cdot}H_2O$	**4a**	72	90:10	86
2	$CuClO_4$	**4a**	81	94:6	89
3	$CuClO_4$	**4b**	72	96:4	68
4	$CuClO_4$	**4c**	92	94:6	85
5	$CuClO_4$	**4d**	90	95:5	60
6	$CuClO_4$	**4e**	91	94:6	84
7	$CuClO_4$	**4f**	92	93:7	64
8	$CuClO_4$	**5a**	79	93:7	86
9	$CuClO_4$	**5b**	60	93:7	67
10	$CuClO_4$	**6a**	89	94:6	75
11	$CuClO_4$	**6b**	88	94:6	61
12	$CuClO_4$	**6c**	93	90:10	77

[a]All reactions were carried out with 0.2 mmol of **1a** and 0.1 mmol of **2** in 1 mL of CH_2Cl_2 at rt. $CuClO_4$ = $[Cu(CH_3CN)_4ClO_4]$. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

Scheme 2. Ligands Screening for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylide 1a with β-Phthalimidonitroethene 2 in the Presence of $Cu(CH_3CN)_4ClO_4$



DOI: 10.1021/acs.orglett.5b02431
Org. Lett. 2015, 17, 4988–4991

Moreover, **7c** gave the optimal enantioselectivity up to 96% (Scheme 2). It indicated that the increased steric hindrance of the 4-substituent could exert enhanced enantioselectivity via cooperative steric effects with the chiral methyl group.

With this optimal ligand **7c**, other metal salts were examined and $Cu(CH_3CN)_4BF_4$ gave an improved yield (93%) with a maintained enantioselectivity (ee = 96%). The use of a highly reactive **7c**/$Cu(CH_3CN)_4BF_4$ catalytic system also allowed a lower catalyst loading (5 mol %) and temperature (0 °C), providing the corresponding cycloadduct *endo*-**3a** without any loss of yield (93%) and diastereoselectivity (dr = 96:4), and a slightly higher enantioselectivity (ee = 97%) (details in SI).

Under the optimal reaction conditions [$Cu(CH_3CN)_4BF_4$ (5 mol %), *N*,*O*-ligand **7c** (5.5 mol %), Et_3N (20 mol %), CH_2Cl_2, 4 Å MS, 0 °C], the generality and substrate scope of this asymmetric 1,3-dipolar cycloaddition were investigated, and the results are summarized in Table 2. Azomethine ylides **1** derived from aryl aldehydes bearing electron-deficient (Table 2, entries 1−7), electron-rich (entries 8−13), and electron-neutral substituents (entries 14−15) on the aryl rings proceeded smoothly in this transformation, providing the corresponding products **3a**−**3o** in excellent yields (89−98%), high diastereoselectivities (dr = 93:7−98:2), and excellent enantioselectivities (ee = 90−99%). It is noteworthy that sterically hindered *ortho*-methyl imino ester **1h** and 2,4-dimethyl imino ester **1k** were tolerated in this reaction, affording the corresponding products in high yields and high diastereoselectivities, albeit in slightly lower enantioselectivities (entries 8 and 11). Additionally, the heteroaryl imino ester **1p** derived from 2-furylaldehyde gave cycloadduct *endo*-**3p** in 93% yield, 97:3 dr, and 95% ee (entry 16). Remarkably, less reactive alkyl substituted imino ester **1q** worked well in the presence of 10 mol % catalyst and 2 equiv of Et_3N with high diastereo-/enantioselectivity despite a lower yield (entry 17).

To demonstrate the synthetic utility of this catalytic system, the model reaction was carried out on a gram scale, affording **3a** in 94% yield, 96:4 dr, and 97% ee (Scheme 3).

Table 2. Scope of Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides 1 with *β*-Phthalimidonitroethene 2 Catalyzed by a $Cu(CH_3CN)_4BF_4$/7c System[a]

entry	1, R	3	yield (%)[b]	dr[c]	ee (%)[c]
1	**1a**, *p*-ClC_6H_4	**3a**	93	96:4	97(99[e])
2	**1b**, *o*-ClC_6H_4	**3b**	96	98:2	96
3	**1c**, *m*-ClC_6H_4	**3c**	90	96:4	95
4	**1d**, 2,4-diClC_6H_4	**3d**	92	98:2	95(99[e])
5	**1e**, *p*-BrC_6H_4	**3e**	97	96:4	95
6	**1f**, *p*-$CF_3C_6H_4$	**3f**	98	98:2	96
7	**1g**, *p*-$CO_2MeC_6H_4$	**3g**	94	97:3	96
8	**1h**, *o*-MeC_6H_4	**3h**	95	98:2	90(99[e])
9	**1i**, *m*-MeC_6H_4	**3i**	93	97:3	95
10	**1j**, *p*-MeC_6H_4	**3j**	89	98:2	97
11	**1k**, 2,4-diMeC_6H_4	**3k**	92	97:3	91
12	**1l**, *p*-$MeOC_6H_4$	**3l**	89	97:3	97
13	**1m**, *p*-^{t}BuC_6H_4	**3m**	96	93:7	97
14	**1n**, Ph	**3n**	89	97:3	96
15	**1o**, 2-naphthyl	**3o**	90	93:7	99
16	**1p**, 2-furyl	**3p**	93	97:3	95
17[d]	**1q**, ^{i}Bu	**3q**	76	94:6	90

[a]All reactions were carried out with 0.4 mmol of **1** and 0.2 mmol of **2** in 2 mL of CH_2Cl_2. $CuBF_4$ = $[Cu(CH_3CN)_4BF_4]$. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]10 mol % catalyst and Et_3N (2 equiv) was used at rt. [e]The ee values given in parentheses were determined after simple recrystallization.

Scheme 3. Gram Scale Cataytic Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylide 1a with *β*-Phthalimidonitroethene 2

The excellent diastereo- and enantioselectivities observed in this asymmetric 1,3-dipolar cycloaddition can be rationalized by the proposed transition state **I** shown in Figure 2. According to our previous report, the 1,3-dipolar cycloaddition is proposed to favor an *endo* cycloaddition mode. The two phenyl groups adjacent to the oxygen in the ligand block the dipolarophile's approach from the "bottom" face, forming *endo*-**3a** through approach from the "top" face. The 4-iodo substituent reinforces the block of the phthalimido group's approach from the "bottom" face. The unique "synergistic steric effects" from both 1-methyl and 4-iodo groups lead to a higher level of diastereo- and enantioselectivity. The relative and absolute configuration of the major diastereoisomer of **3a** was assigned as *endo*-(2*R*,3*S*,4*S*,5*R*) by single-crystal X-ray crystallographic analysis (details in SI), which could be applied to all cycloadducts.

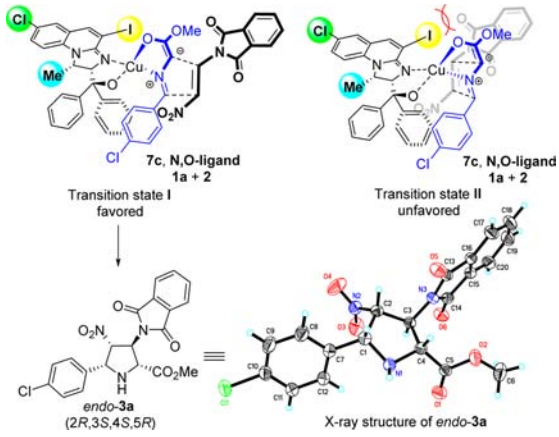
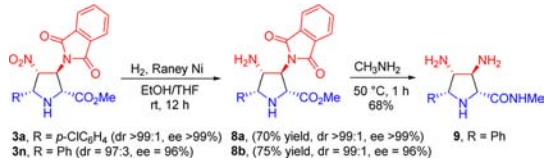


Figure 2. Proposed transition state leading to the major product *endo*-**3a**.

Raney Ni-catalyzed reduction of 4-nitro-3-aminopyrrolidines **3** afforded **8** in good yields, without loss of stereochemical integrity allowing ready conversion to 3,4-diaminopyrrolidine **9** in 68% yield from **8b** via deprotection of phthalyl in the presence of methylamine (Scheme 4). As a result, **9** in high optical purity could be generated efficiently in only 3 steps: catalytic asymmetric 1,3-dipolar cycloaddition, Raney Ni-catalyzed reduction, and deprotection of phthalyl which shows great potential utility in organic synthesis and medicinal chemistry.

DOI: 10.1021/acs.orglett.5b02431
Org. Lett. 2015, 17, 4988−4991

Scheme 4. Reduction and Deprotection of 4-Nitro-3-aminopyrrolidines 3 to 3,4-Diaminopyrrolidine 9



In conclusion, the first highly efficient catalytic asymmetric 1,3-dipolar cycloaddition of azomethine ylides with β-phthalimidonitroethene was developed. The newly designed 4-iodo-DHIPOH ligand **7c**/$Cu(CH_3CN)_4BF_4$ complex was demonstrated as an optimal catalytic system with "synergistic steric effects" derived from the chiral 1-methyl and 4-iodo groups for inducing asymmetry in the synthesis of 4-nitro-3-amino-pyrrolidines with excellent diastereo- (dr up to 98:2) and enantioselectivities (ee up to 99%). The synthetic utility of this protocol was illustrated by a gram scale reaction and subsequent Raney Ni-catalyzed reduction and deprotection of phthalyl, affording the structurally and biologically important 3,4-diaminopyrrolidines in a straightforward and efficient pathway. Further development of novel dipolarophiles for this asymmetric catalytic system and their applications are ongoing 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.5b02431.

Experimental details; characterization of new compounds; NMR and HPLC spectra (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by The Fundamental Research Funds for the Central Universities, the National Natural Science Foundation of China (No. 21172068), Shanghai Pujiang Program (No. 14PJD013), and Shanghai Yangfan Program (No. 14YF1404600).

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DOI: 10.1021/acs.orglett.5b02431
Org. Lett. 2015, 17, 4988−4991