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Asymmetric Catalysis

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Catalytic Asymmetric 1,3-Dipolar Cycloaddition of Two Different Ylides: Facile Access to Chiral 1,2,4-Triazinane Frameworks**

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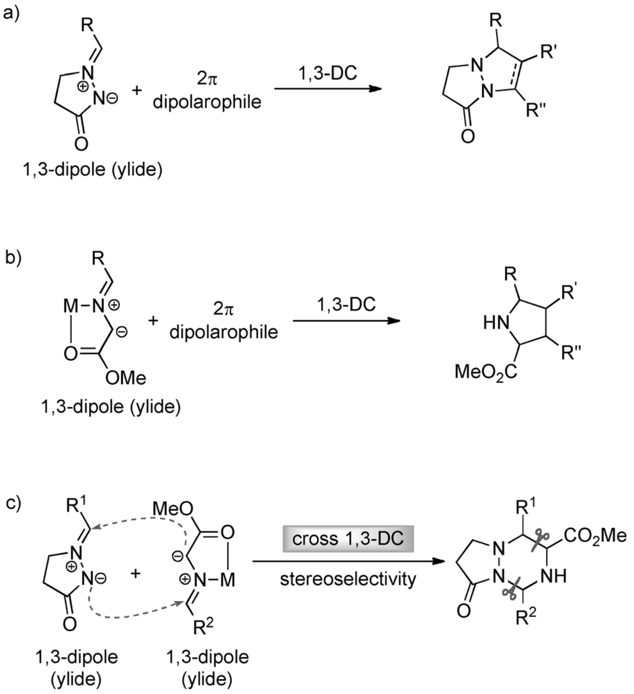
Heterocyclic structures are the core moieties in many natural alkaloids, important pharmaceuticals, and building blocks in organic synthesis as well.[1–3] Much attention has been paid to developing efficient protocols for the design and synthesis of novel heterocyclic compounds over the past decades.[4] 1,3-Dipolar cycloaddition reactions (1,3-DC) are one of the most powerful tools for the convergent construction of heterocyclic frameworks.[5] Pyrazolidinium ylides[6,7] and in situ formed azomethine ylides[8] serve as commonly used three-atom dipoles in 1,3-DCs with 2π dipolarophiles, and have been well-documented in the construction of five-membered nitrogen heterocycles, such as N,N-bicyclic pyrazolidinone and pyrrolidine derivatives (Scheme 1 a and b).

Nevertheless, it is surprising that limited progress has been made so far on the 1,3-dipolar cycloaddition (cross-1,3-DC) of two different ylides for the synthesis of six-membered heterocycles. We believe this cross-cycloaddition represents a significant challenge considering the possible dimerization[9] and concomitant synthetic difficulties associated with regio-, diastereo-, and enantioselectivity control. Hence, a catalytic asymmetric cross-1,3-DC of different ylides for the straightforward construction of structurally diverse six-membered nitrogen heterocycles is highly desirable from the view point of synthetic efficiency (Scheme 1 c). Herein, we report the first copper(I)-catalyzed cross-1,3-DC between pyrazolidinium ylides and in situ formed azomethine ylides to give highly substituted 1,2,4-triazinane frameworks with exclusive diastereoselectivity and excellent enantioselectivity. The importance of this unprecedented cross-1,3-DC not only resides in the diversification of existing 1,3-dipolar cycloadditions but also in the access to 1,2,4-triazinane[10] and hexahydropyridazine[11] skeletons, which are found in several biologically active molecules.



Scheme 1. a) Well-documented 1,3-dipolar cycloaddition of pyrazolidinium ylide for the construction of pyrazolidinone/pyrazolones. b) Well-documented 1,3-dipolar cycloaddition of azomethine ylide for the construction of pyrrolidines. c) Unknown cross 1,3-dipolar cycloaddition of pyrazolidinium ylide and azomethine ylide for the construction of 1,2,4-triazinane skeletons

Initially, our investigation began with the reaction of the pyrazolidinium ylide **1a**, which was readily synthesized from pyrazolidin-3-one and benzaldehyde,[12] with the imino ester **2a** to test our hypothesis on the cross-1,3-DC. We reasoned that the in situ formed N-metalated azomethine ylide is crucial to realizing this elusive cross-cycloaddition, and different metal salts and various commonly used chiral ligands were first studied (see the Supporting Information for detailed information). In most cases, only trace amounts of a cycloadduct were detected. However, to our delight, the cross-cycloadduct **3aa** was obtained in good yield with exclusive diastereoselectivity (> 20:1 d.r.) when commercially available (S,S_p)-*i*Pr-Phosferrox[13] (**L1**) was employed as the chiral ligand: both AgOAc and $Cu(CH_3CN)_4BF_4$ salts efficiently promoted this transformation and the desired adduct was isolated with 32 and 81 % *ee*, respectively (Table 1, entries 1 and 2). Control experiments demonstrated that no cross-cycloaddition occurred without a metal precursor and the chiral ligand *t*Bu-Phosferrox. Then, a series of Phosferrox ligands was synthesized and subsequently screened to establish optimal reaction conditions, and the representative results are summarized in Table 1. These results demonstrated that the substituent on oxazoline ring was crucial, and

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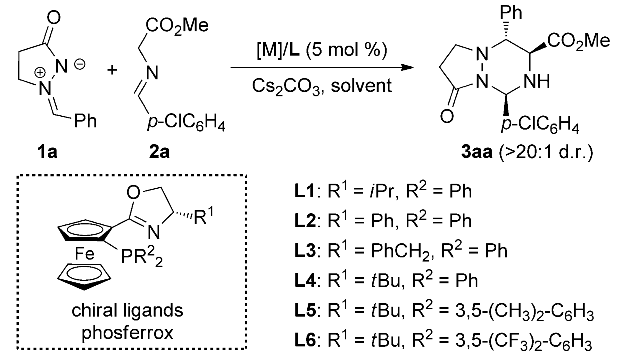
Table 1: Optimization of the metal-catalyzed cross-cycloaddition of **1a** with **2a**.[a]



L1: R^1 = *i*Pr, R^2 = Ph
L2: R^1 = Ph, R^2 = Ph
L3: R^1 = PhCH$_2$, R^2 = Ph
L4: R^1 = *t*Bu, R^2 = Ph
L5: R^1 = *t*Bu, R^2 = 3,5-(CH$_3$)$_2$-C$_6$H$_3$
L6: R^1 = *t*Bu, R^2 = 3,5-(CF$_3$)$_2$-C$_6$H$_3$

Entry	L	[M]	Solvent	*T* [°C]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**L1**	AgOAc	CH$_2$Cl$_2$	10	12	81	32
2	**L1**	CuBF$_4$	CH$_2$Cl$_2$	10	12	84	81
3	**L2**	CuBF$_4$	CH$_2$Cl$_2$	10	12	75	33
4	**L3**	CuBF$_4$	CH$_2$Cl$_2$	10	18	63	73
5	**L4**	CuBF$_4$	CH$_2$Cl$_2$	10	12	85	91
6	**L5**	CuBF$_4$	CH$_2$Cl$_2$	10	12	80	87
7	**L6**	CuBF$_4$	CH$_2$Cl$_2$	10	20	78	82
8	**L4**	CuBF$_4$	PhMe	10	24	76	72
9	**L4**	CuBF$_4$	MeCN	10	12	63	50
10	**L4**	CuBF$_4$	THF	10	15	59	70
11	**L4**	CuBF$_4$	(CH$_2$Cl)$_2$	10	12	81	85
12	**L4**	CuBF$_4$	CH$_2$Cl$_2$	0	16	88	93
13	**L4**	CuBF$_4$	CH$_2$Cl$_2$	−20	20	85	96

[a] All reactions were carried out with 0.2 mmol of **1a** and 0.3 mmol of **2a** in 1.0 mL of solvent. [b] Yield of isolated product. [c] The *ee* value was determined by HPLC analysis. The >20:1 d.r. was determined by ^{1}H NMR analysis of the crude reaction mixture. THF = tetrahydrofuran.

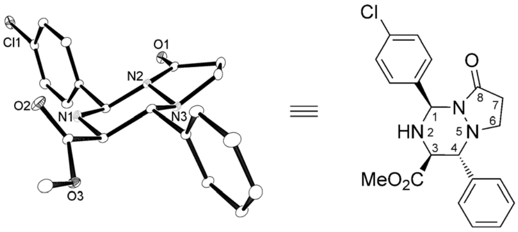
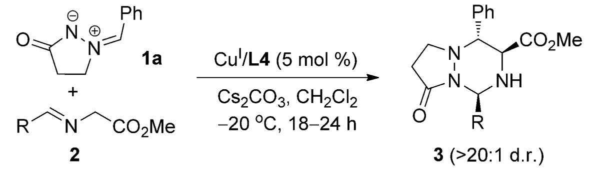
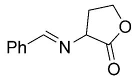
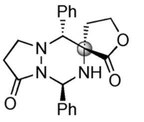


Figure 1. X-ray structure of (1*R*,3*S*,4*R*)-**3aa**. Thermal ellipsoids shown at 10% probability.

L4, bearing a *tert*-butyl group on the oxazoline ring, exhibited the better performance in terms of the reaction rate and enantioselectivity in comparison with those ligands bearing isopropyl (**L1**), phenyl (**L2**) and benzyl (**L3**) groups, and thus delivered the desired cross-cycloadduct **3aa** as the sole isomer in good yield with high enantioselectivity (entry 5). These results indicated that the steric congestion on the oxazoline ring in those ferrocenyl ligands was beneficial to the enhancement of asymmetric induction without affecting the catalytic activity. When the phenyl group on the phosphorus atom of the (*S*,*S*$_p$)-*t*Bu-Phosferrox ligand **L4** was replaced by a more sterically hindered and electron-donating xylyl group (**L5**), the catalytic activity and high level of diastereoselectivity remained albeit with the decreased enantioselectivity (entry 6). The ligand **L6**, containing the bulky and electron-withdrawing 3,5-bis(trifluoromethyl)phenyl group on the phosphorus atom, displayed a similar deleterious effect on the enantioselectivity (entry 7). Encouraged by these results, further optimization with respect to solvent and reaction temperature was carried out for this cross-cycloaddition (entries 8–13). The originally used solvent CH$_2$Cl$_2$ was found to be the optimal solvent, and the yields or enantioslectivities were significantly decreased when other solvents were used. Further enhancement of the enantioselectivity was fulfilled through reducing the reaction temperature, and 93 and 96% *ee* were achieved upon completion of the reaction when the temperature was lowered to 0°C and −20°C, respectively (entries 12 and 13). The absolute configuration of **3aa** was unequivocally determined as (1*R*,3*S*,4*R*) by X-ray diffraction analysis (Figure 1).[14]

Table 2: Substrate scope of copper(I)-catalyzed cross-cycloaddition of **1a** with various azomethine ylides (**2**).[a]



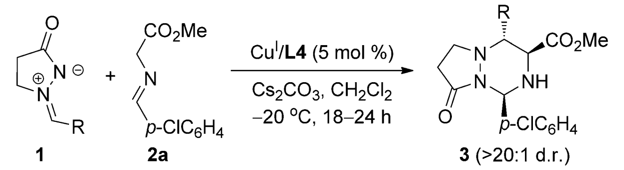
Entry	R	3	Yield [%][b,c]	*ee* [%][d]
1	p-ClC$_6$H$_4$ (**2a**)	**3aa**	85	96
2	p-BrC$_6$H$_4$ (**2b**)	**3ab**	87	95
3	m-BrC$_6$H$_4$ (**2c**)	**3ac**	84	94
4	p-NO$_2$C$_6$H$_4$ (**2d**)	**3ad**	94	96
5	p-CF$_3$C$_6$H$_4$ (**2e**)	**3ae**	82	95
6	Ph (**2f**)	**3af**	88	97
7	p-MeC$_6$H$_4$ (**2g**)	**3ag**	84	95
8	O-MeC$_6$H$_4$ (**2h**)	**3ah**	86	97
9	2-naphthyl (**2i**)	**3ai**	81	97
10	3-pyridyl (**2j**)	**3aj**	73	91
11	nPr (**2k**)	**3ak**	80	90
12	 (**2l**)	 **3al**	82	94

[a] All reactions were carried out with 0.2 mmol of **1a** and 0.3 mmol of **2** in 1.0 mL of CH$_2$Cl$_2$. [b] Yield of the isolated product. [c] The *ee* value was determined by HPLC analysis. A minor diastereomer was not detected by ^{1}H NMR analysis of the crude reaction mixture.

With the optimal reaction conditions in hand, various imino esters (**2**) were explored to investigate the generality of this cross-cycloaddition with respect to the in situ formed azomethine ylides. The results are tabulated in Table 2. In general, a wide range of aryl imino esters which bear various functional groups on the phenyl ring were competent in this cross-cycloaddition, thus giving rise to the desired cycloadducts in good yields (81–94%) with exclusive diastereoselectivity (>20:1 d.r.) and excellent enantioselectivities (94–97% *ee*; Table 2, entries 1–9). Substituent groups, with different electronic properties (e.g., electron-neutral, electron-rich, or electron-deficient), on the phenyl ring are all compatible with this catalytic system. Little influence was exhibited by the different substitution patterns (e.g., *para*, *meta*, or *ortho*) on the yields and stereoselectivities. It is worth mentioning that the heteroaryl imino ester **2j** derived from 3-pyridyl aldehyde was also tolerated in this reaction and provided the corresponding adduct **3aj** with 91 % *ee* (entry 10). Notably, the less reactive alkyl imino ester **2k** also worked well, thus leading to the expected adduct **3ak** in good yield with 90 % *ee* (entry 11). Remarkably, the cyclic imino ester **2l** derived from (±)-homoserine was also a viable precursor of an azomethine ylide for this cyclization process, and good yield and excellent stereoselectivity were observed for the expected spiroadduct **3al** bearing one spiro-quaternary and two tertiary stereogenic centers (entry 12).

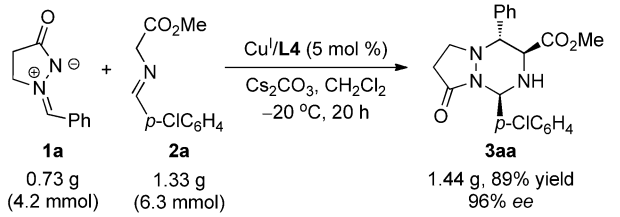
Next, the potential of this cross-cycloaddition with respect to pyrazolidinium ylides was further evaluated. The cross-cycloaddition tolerated all the tested pyrazolidinium ylides derived from aryl aldehydes with different electron properties and substituent patterns (Table 3). The expected adducts (**3aa–ia**) were isolated in high yields and excellent enantioselectivities (entries 1–9). Additionally, pyrazolidinium ylides with fused-ring substituents (**1j**) and a heteroaromatic 3-pyridyl group (**1k**) also worked well in this catalytic system, thus leading to the expected cycloadducts in good yields with excellent enantioselectivities (entries 10 and 11). Notably, the aliphatic pyrazolidinium ylide **1l** could also be incorporated in the current catalytic system as a viable substrate, thus affording the product **3la** in good yield, albeit with moderate enantioselectivity (entry 12).

Table 3: Substrate scope of copper(I)-catalyzed cross-cycloaddition of various pyrazolidinium ylides (**1**) with **2a**.[a]



Entry	R	3	Yield [%][b,c]	*ee* [%][d]
1	Ph (**1a**)	**3aa**	85	96
2	*p*-MeC$_6$H$_4$ (**1b**)	**3ba**	86	95
3	*m*-MeC$_6$H$_4$ (**1c**)	**3ca**	83	96
4	*o*-MeC$_6$H$_4$ (**1d**)	**3da**	81	95
5	*p*-MeOC$_6$H$_4$ (**1e**)	**3ea**	79	97
6	*p*-ClC$_6$H$_4$ (**1f**)	**3fa**	89	97
7	*m*-ClC$_6$H$_4$ (**1g**)	**3ga**	93	96
8	*o*-ClC$_6$H$_4$ (**1h**)	**3ha**	88	98
9	*p*-CNC$_6$H$_4$ (**1i**)	**3ia**	90	96
10	2-naphthyl (**1j**)	**3ja**	87	96
11	3-pyridyl (**1k**)	**3ka**	85	96
12	*n*-pentyl (**1l**)	**3la**	67	74

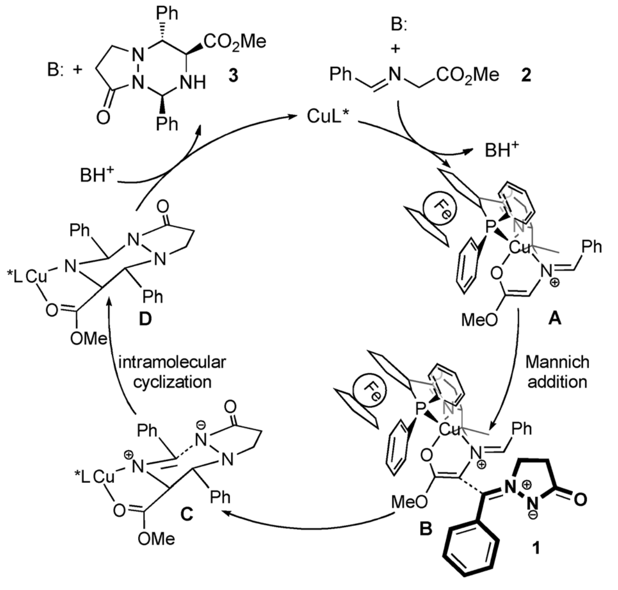
[a] All reactions were carried out with 0.2 mmol of **1** and 0.3 mmol of **2a** in 1.0 mL of CH$_2$Cl$_2$. [b] Yield of the isolated product. [c] The *ee* value was determined by HPLC analysis. A minor diastereomer was not detected by ^{1}H NMR analysis of the crude reaction mixture.



Scheme 2. Scale-up of the cross-cycloaddition reaction.

To test the synthetic utility of the present cross-cycloaddition, **3aa** was prepared on gram scale under the optimized reaction conditions (Scheme 2). With the 5 mol % Cu^I/*t*Bu-Phosferrox (**L4**) complex as the catalyst, the cross-cycloaddition proceeded smoothly and the corresponding adduct was obtained as a single diastereomer in 89 % yield and 96 % *ee*.

Based on the absolute configuration of (*S*)-**3aa**, we proposed a plausible stepwise mechanism to rationalize the stereoselectivity of this cross-cycloaddition (Scheme 3). The in situ formed azomethine ylide is coordinated to the Cu^I/*t*Bu-Phosferrox (**L4**) complex in a distorted tetrahedral geometry leading to the catalytically active species **A**, which has been supported by a recent DFT calculation study reported by Hou and co-workers.[15a] The back side of the metalloazomethine ylide is shielded by the bulky *tert*-butyl group in the oxazoline ring of the Phosferrox ligand, and blocks the approach of the pyrazolidinium ylide **1** from the underside. A preferential *exo* approach of the pyrazolidinium ylide to the metalloazomethine ylide occurrs, and the *endo* approach is inhibited probably because of the unfavored steric repulsion between the phenyl group in pyrazolidinium ylide and the diphenylphosphine group in chiral *t*Bu-Phosferrox ligand. Then, the



Scheme 3. Proposed mechanism for the cross-cycloaddtion of a pyrazolidinium ylide and azomethine ylide.

initial Mannich addition of the metalloazomethine ylide **A** to the *Si* face of **1** through the gauche conformation (**B**) gives rise to the zwitterionic intermediate **C**, which should be the crucial step for the stereochemistry. Subsequent intermolecular cyclization delivers the species **D**, which contains the chiral 1,2,4-triazinane framework, with excellent stereoselectivity control via a chairlike six-membered transition state, in which the two substituent groups of the azomethine ylide and the phenyl group, and the skeleton of five-membered pyrazolidinone ring are all arranged at the equatorial positions. A final protonation step gives the heterocyclic 1,2,4-triazinane with regeneration of the catalyst. The postulated catalytic cycle is compatible with the observed stereochemical outcome, and further investigations to explore the mechanism are underway.

In conclusion, we have presented the first cross-1,3-DC between pyrazolidinium ylides and azomethine ylides employing the Cu^{I}/*t*Bu-Phosferrox complex as the catalyst. A wide range of 1,2,4-triazinane derivatives having a diversity of functional groups were realized in generally high yield with excellent stereocontrol. The application of this cross-cycloaddition in the asymmetric construction of bioactive molecules and further exploration of the cross-cycloaddition of other ylides are currently being investigated in our laboratory.

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[14] CCDC 946767 (**3aa**) 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.

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