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Enantioselective [2 + 2] cycloaddition of *N*-allenamides with cyclic *N*-sulfonylketimines: access to polysubstituted azetidines bearing quaternary stereocenters†

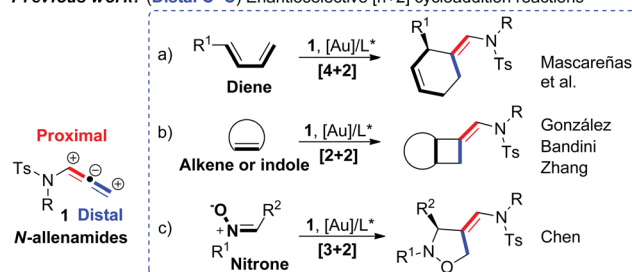
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A Ni(ClO₄)₂-catalyzed enantioselective [2 + 2] cycloaddition of *N*-allenamides with cyclic *N*-sulfonylketimines was developed, which regioselectively occurred at the proximal C=C bonds of the *N*-allenamides. Broad substrate scope of *N*-allenamides and cyclic *N*-sulfonylketimines was observed. A range of fused polysubstituted azetidines bearing quaternary stereocenters were afforded in good yields and with excellent enantioselectivities (up to 99%).

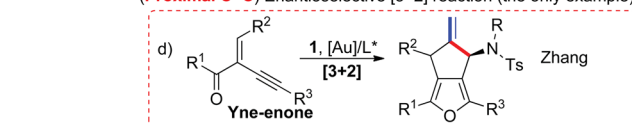
N-Allenamides are readily available allenic scaffolds and valuable building blocks in organic synthesis, and therefore have received considerable attention in the past decades.^{1,2} Significant effort has been devoted to the cycloaddition reactions of *N*-allenamides,³ and several enantioselective [*n* + 2] reactions have been explored as reliable approaches to synthesise a diverse array of carbo- or heterocyclic substructures (Scheme 1).^{4–6} Mascareñas *et al.* developed an elegant enantioselective intermolecular [4 + 2] cycloaddition reaction between *N*-allenamides and dienes using a gold/chiral carbene catalyst (Scheme 1a).⁴ González's and Zhang's groups disclosed [2 + 2] cycloadditions of *N*-allenamides with olefins, leading to optically active cyclobutanes with excellent enantioselectivities (Scheme 1b).^{5a,c} Interestingly, in the latter case a dearomative [4 + 2] reaction of 3-styrylindoles was observed by varying indolic *N*-substituents.^{5c} A dearomative [2 + 2] cycloaddition reaction of *N*-allenamides with indoles was realized by Bandini's group as a powerful route to access cyclobutane-fused indolines with excellent enantioselectivities.^{5b} The [3 + 2] reaction was also developed by Chen and co-workers in an enantioselective cycloaddition of *N*-allenamides with nitrones (Scheme 1c).^{6a} It should be noted that all of the above reactions mainly relied on *N*-allenamide activation to form an α,β -unsaturated imine intermediate and hence regioselectively occurred at its distal C=C bond. In sharp contrast, the reactivity of *N*-allenamide at the proximal C=C bond has remained rarely studied.⁷ The only enantioselective example was reported by

Zhang's group in an asymmetric [3 + 2] reaction involving *in situ* annulation of yne-enones (Scheme 1d).^{6b} Meanwhile, all of the precedent examples exclusively relied on chiral noble gold catalysts. Moreover, despite these advances, no example of cycloaddition of *N*-allenamides with imines has appeared for the synthesis of nitrogen-bearing four-membered heterocycles even in their racemic version.^{1a} Therefore, the development of

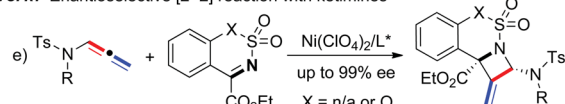
Previous work: (Distal C=C) Enantioselective [*n*+2] cycloaddition reactions



(Proximal C=C) Enantioselective [3+2] reaction (the only example)



This work: Enantioselective [2+2] reaction with ketimines



- **Valuable product:** polysubstituted azetidines, quaternary stereocenters, fused tricyclic
- **Non-noble catalyst:** chiral Ni(ClO₄)₂/Box complex
- **Excellent regioselectivity:** proximal C=C bonds

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Scheme 1 Reactivity of *N*-allenamides in enantioselective cycloaddition reactions.

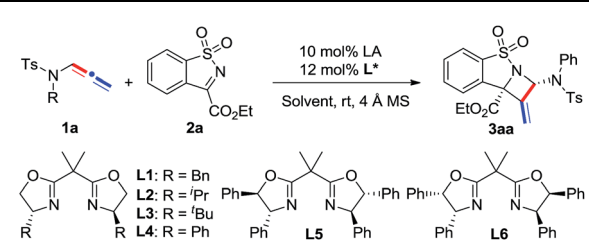
new cycloaddition reactions of *N*-allenamides and a new catalyst system to synthesize important heterocyclic cores is highly attractive.

Azetidine derivatives are important entities in organic chemistry and are frequently occurring scaffolds in natural products and bioactive molecules. Enantioselective [2 + 2] reaction of imines provides a straightforward route to such strained four-membered heterocycles, including β -lactams.^{8,9} However, as a unique building block, *N*-allenamide has not been utilized in the [2 + 2] cycloaddition with imines. We envisioned that an enantioselective [2 + 2] cycloaddition of *N*-allenamides with imines might occur *via* an imine activation strategy using a chiral Lewis acid catalyst, where *N*-allenamide acts as a nucleophile (like enamide) to attack the imine at its more electron-rich proximal C=C bond and hence delivers highly substituted azetidines through the cyclization that follows.¹⁰ Herein, we report the first enantioselective [2 + 2] cycloaddition reaction of *N*-allenamides with cyclic *N*-sulfonyl α -ketiminoesters¹¹ to afford fused polysubstituted chiral azetidines bearing quaternary stereocenters with excellent enantioselectivities (Scheme 1e). A non-noble chiral nickel catalyst was applied for the first time in the cycloaddition reactions of *N*-allenamides.

Our study began with the model reaction between *N*-allenamide **1a** and cyclic α -ketiminoester **2a**. Pleasingly, an initial test revealed that the complex of Ni(ClO₄)₂·6H₂O/chiral bisoxazoline **L1** smoothly promoted the reaction in DCE and in the presence of 4 Å molecular sieves at room temperature, resulting in the desired product **3aa** in 83% yield, albeit with a poor ee value (Table 1, entry 1). Subsequent ligand examination implied that chiral substituents of oxazoline were critical to enantioselectivity (entries 2–7). Ligands **L2**–**L3** bearing isopropyl or *tert*-butyl substituents led to poor enantioselectivities (entries 2 and 3), while **L4**, containing phenyl substituents, was the best choice to give **3aa** in 99% ee and 82% yield (entry 4).¹² Inferior results were obtained when **L5** and **L6** bearing *trans*- or *cis*-diphenyl substituents were used (entries 5 and 6). Phosphine ligand **L7** led to **3aa** with a moderate yield and ee value (entry 7). Solvent investigation showed that excellent enantioselectivities with relatively lower yields were observed in CH₂Cl₂, THF, and toluene (entries 8–10). Either poor yield or poor enantioselectivity was obtained in Et₂O or MeCN (entries 11 and 12). Changing the Lewis acid to Cu(OTf)₂ or Mg(OTf)₂ resulted in an almost racemic product (entries 13 and 14), while Zn(OTf)₂ led to a relatively lower ee (entry 15). Other perchlorate metallic salts, such as Mg(ClO₄)₂, Zn(ClO₄)₂·6H₂O, and Cu(ClO₄)₂·6H₂O, were also tested and inferior results were obtained (entries 16–18). Finally, a poor yield was obtained in the absence of 4 Å MS due to the decomposition of *N*-allenamide **1a** (entry 19). It is noteworthy that only one isomer was detected in these reactions.

With the optimal reaction conditions found, we then investigated the scope of *N*-allenamides **1** and *N*-sulfonyl α -ketiminoesters **2**. As shown in Table 2, α -ketiminoesters **2a**–**2d**, bearing different ester groups, were first evaluated. Good yields and enantioselectivities were afforded in these reactions in spite of a slightly decreased ee value for the iso-propyl substrate **2b**

Table 1 Optimization of the reaction conditions^a



Entry	L*	LA	Solvent	Yield ^b (%)	ee ^c (%)
1	L1	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	83	18
2	L2	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	75	15
3	L3	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	69	11
4	L4	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	82	99
5	L5	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	62	92
6	L6	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	65	93
7	L7	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	70	60
8	L4	Ni(ClO ₄) ₂ ·6H ₂ O	CH ₂ Cl ₂	57	96
9	L4	Ni(ClO ₄) ₂ ·6H ₂ O	THF	51	99
10	L4	Ni(ClO ₄) ₂ ·6H ₂ O	Toluene	60	95
11	L4	Ni(ClO ₄) ₂ ·6H ₂ O	Et ₂ O	23	91
12	L4	Ni(ClO ₄) ₂ ·6H ₂ O	CH ₃ CN	90	10
13	L4	Cu(OTf) ₂	DCE	65	7
14	L4	Mg(OTf) ₂	DCE	75	<5
15	L4	Zn(OTf) ₂	DCE	70	85
16	L4	Mg(ClO ₄) ₂	DCE	70	28
17	L4	Zn(ClO ₄) ₂ ·6H ₂ O	DCE	55	46
18	L4	Cu(ClO ₄) ₂ ·6H ₂ O	DCE	Trace	—
19 ^d	L4	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	45	99

^a Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), LA (10 mol%), ligand (12 mol%), and 4 Å molecular sieves (100 mg) in solvent (1.0 M) at room temperature; **L7**: (*S*)-BINAP. ^b Isolated yield. ^c Determined by chiral HPLC. ^d Without 4 Å MS.

(entries 1–4). Substituents attached at the C5–C7 position of the α -ketiminoesters were then investigated (entries 5–14). The substituted groups, such as halide, –CF₃, –OCF₃, –OMe, and alkyl groups, were well tolerated to afford the corresponding products with excellent enantioselectivities and modest to good yields. The reaction yields of the α -ketiminoesters containing electron-donating substituents were slightly higher than those of the α -ketiminoesters bearing electron-deficient substituents (entries 5–7 vs. 8–11).

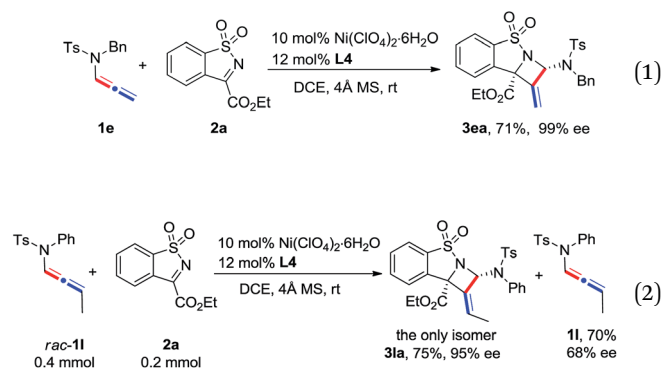
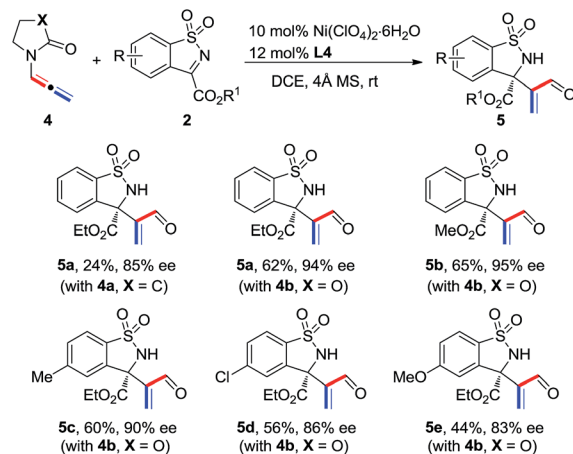


Table 2 Substrate scope of the [2 + 2] reaction^a

Entry	1 (R ² /R ³)	2 (R/R ¹)	Yield ^b (%)	ee ^c (%)
1	1a (4-Me/H)	2a (H/Et)	82 (3aa)	99
2	1a (4-Me/H)	2b (H/ ⁱ Pr)	75 (3ab)	90
3	1a (4-Me/H)	2c (H/Me)	76 (3ac)	99
4	1a (4-Me/H)	2d (H/ ⁿ Bu)	80 (3ad)	98
5	1a (4-Me/H)	2e (5-OMe/Et)	77 (3ae)	99
6	1a (4-Me/H)	2f (5-Me/Et)	73 (3af)	97
7	1a (4-Me/H)	2g (5- ^t Bu/Et)	70 (3ag)	98
8	1a (4-Me/H)	2h (5-Cl/Et)	64 (3ah)	99
9	1a (4-Me/H)	2i (5-F/Et)	70 (3ai)	95
10	1a (4-Me/H)	2j (5-CF ₃ /Et)	52 (3aj)	99
11	1a (4-Me/H)	2k (5-OCF ₃ /Et)	55 (3ak)	98
12	1a (4-Me/H)	2l (7-Cl/Et)	64 (3al)	94
13	1a (4-Me/H)	2m (7-OCF ₃ /Et)	76 (3am)	93
14	1a (4-Me/H)	2n (6,7-(CH ₃) ₄ /Et)	70 (3an)	94
15	1b (4-Me/4-Me)	2a (H/Et)	75 (3ba)	99
16	1c (4-Me/4-Br)	2a (H/Et)	67 (3ca)	97
17	1d (4-Me/3-OMe)	2a (H/Et)	78 (3da)	99
18	1f (H/H)	2a (H/Et)	70 (3fa)	99
19	1g (4- ^t Bu/H)	2a (H/Et)	80 (3ga)	99
20	1h (4-OMe/H)	2a (H/Et)	70 (3ha)	94
21	1i (4-CF ₃ /H)	2a (H/Et)	66 (3ia)	99
22	1j (3,4-(CH ₃) ₄ /H)	2a (H/Et)	80 (3ja)	94
23	1k (4-Cl/H)	2a (H/Et)	72 (3ka)	98
24	1k (4-Cl/H)	2e (5-OMe/Et)	75 (3ke)	99
25	1k (4-Cl/H)	2h (5-Cl/Et)	90 (3kh)	98
26	1b (4-Me/4-Me)	2e (5-OMe/Et)	85 (3be)	98

^a Reaction conditions are identical to those in entry 4 in Table 1.^b Isolated yield of the only isomer. ^c Determined by chiral HPLC.

The scope of *N*-allenamide **4** was also evaluated. By varying the aryl substituents and the sulfonyl groups, a number of substituted *N*-allenamides were tested and afforded the expected products in good yields and with excellent ee values (entries 15–26). It is worth noting that the reaction of *N*-benzyl substrate **1e** also produced the desired azetidine **3ea** in 71% yield and 99% ee (eqn (1)). Moreover, a racemic 3-substituted *N*-allenamide **1l** was also used in this reaction to give the desired product **3la** in 75% yield and 95% ee (eqn (2)). Interestingly, a kinetic resolution process of *N*-allenamide **1l** was observed and the remaining starting material was isolated in 70% yield and 68% ee, which represents a promising route to chiral *N*-allenamide.¹³ In addition, *N*-allenyl pyrrolidinone **4a** and oxazolidinone **4b** were also tested as substrates in this transformation, however, acrylaldehyde **5a** was isolated as the major product instead of the desired cycloaddition adduct (Scheme 2). Although a poor yield of **5a** was obtained for the reaction of **4a**, the yield and ee were both remarkably improved by employing *N*-oxazolidinone **4b** as the substrate. Several other α -ketiminoesters were then examined in the reactions with **4b**

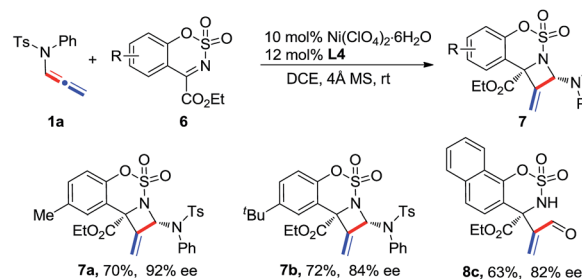
Scheme 2 Reaction of *N*-allenyl pyrrolidinone **4a** and oxazolidinone **4b** with α -ketiminoesters.

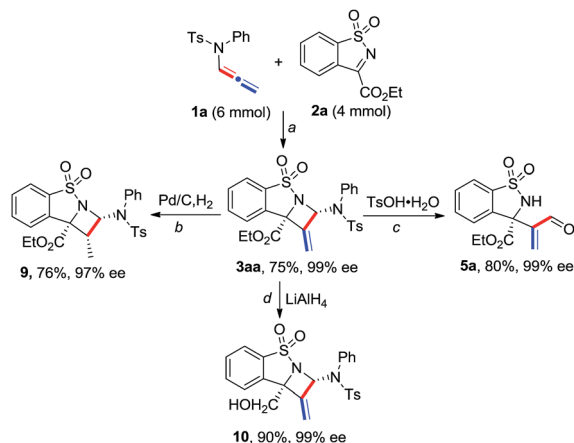
to afford the corresponding acrylaldehydes **5b–5e** in acceptable yields and with good to excellent enantioselectivities.

Cyclic six-membered *N*-sulfonyl α -ketimines were also examined as substrates in this reaction. The desired [2 + 2] adducts **7a** and **7b** were afforded with good yields and enantioselectivities (Scheme 3). In the case of a naphthyl-ketimine substrate, the pure adduct could not be obtained; however, acrylaldehyde **8c** was isolated in 63% yield and with 82% ee by treating the mixture with 10 mol% TsOH after the reaction.

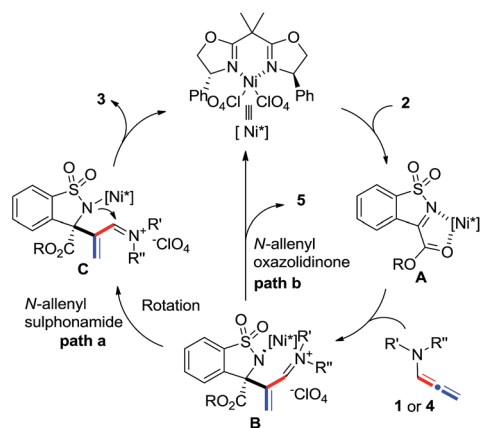
A gram-scale reaction of **1a** with **2a** was carried out to afford product **3aa** in 75% yield and 99% ee, showing good reliability of the present process (Scheme 4). Synthetic transformations of **3aa** were then performed. A Pd/C-catalyzed hydrogenation of **3aa** afforded saturated azetidine **9** as a single isomer in 76% yield and 97% ee. Reduction of **3aa** in the presence of LiAlH₄ led to homoallylic alcohol **10** in 90% yield and 99% ee. TsOH-catalyzed hydrolysis of **3aa** afforded acrylaldehyde **5a** in 80% yield without any loss of enantioselectivity.

A tentative stepwise mechanism that accounts for the [2 + 2] reaction is proposed in Scheme 5. α -Ketiminoester **2** is firstly activated by the chiral nickel catalyst in a 1,4-binding coordination fashion to form intermediate **A**. Subsequent enantioselective nucleophilic addition of *N*-allenamide **1** or **4** to **A** generates intermediate **B**. The [2 + 2] product **3** was then regioselectively formed by the intramolecular cyclization of the

Scheme 3 Reaction of *N*-allenamide **1a** with cyclic six-membered *N*-sulfonylketimines **6**.



Scheme 4 Gram-scale reaction and synthetic transformations of product **3aa**. ^a Conditions are identical to those in entry 4 in Table 1; ^b Pd/C (10 mol%), H₂ (1 atm) in MeOH (0.1 M) at 25 °C for 1 h; ^c TsOH·H₂O (10 mol%) in DCE (0.2 M) at 60 °C for 3 h; ^d LiAlH₄ (2.0 equiv.) in THF (0.1 M) at 25 °C for 1 h.



Scheme 5 Proposed reaction pathway.

amide with iminium (path a) and the catalyst was released simultaneously. The formation of acrylaldehyde **5** instead of the [2 + 2] adduct is probably owing to the hydrolysis of intermediate **B** when employing *N*-allenyl oxazolidinone **4b** as the substrate (path b).

Conclusions

In summary, we have developed a novel catalytic enantioselective [2 + 2] cycloaddition reaction of *N*-allenamides with cyclic *N*-sulfonyl α -ketiminoesters, which delivered a range of polysubstituted chiral azetidines bearing quaternary stereocenters as valuable bioactive compounds in good yields and with excellent enantioselectivities. The complex of Ni(ClO₄)₂ with commercially available chiral bisoxazoline ligands was utilized for the first time as a chiral catalyst in the cycloaddition reaction of *N*-allenamides. Broad substrate scope was observed for allenamides and cyclic *N*-sulfonylketimines. It is noteworthy

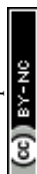
that acrylaldehyde products were obtained when employing *N*-allenyl oxazolidinones as substrates.

Acknowledgements

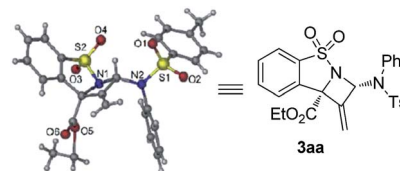
We are grateful for the financial support from the National Natural Science Foundation of China (21372202, 21402175, 21522207, and 21502169) and the Natural Science Foundation of Zhejiang Province (LR14B020001 and LQ15B020003). Y.-X. Jia dedicates this work to Professor Qi-Lin Zhou on the occasion of his 60th birthday.

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