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Diastereo- and Enantioselective Direct Vinylogous Michael Addition of γ -Substituted Butenolides to 2-Enoylpyridines Catalyzed by Chiral Bifunctional Amine-Squaramides

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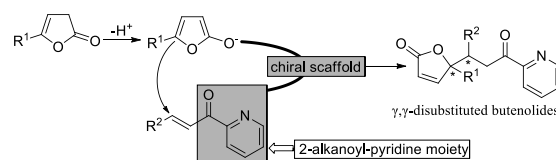
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The diastereo- and enantioselective direct vinylogous Michael addition reaction of γ -substituted butenolides to 2-enoylpyridines has been achieved. A range of γ,γ -disubstituted butenolide derivatives, bearing two consecutive tri- and tetrasubstituted stereogenic centers, were readily obtained in good yields with excellent stereoselectivities (up to >99:1 dr and >99% ee).

γ,γ -Disubstituted butenolide skeletons represent a structural type of both synthetic and biological importance. A great number of biologically active natural products and pharmaceutically relevant molecules contain the special butenolide motifs.¹ Much attention has been devoted to the synthesis of diverse γ,γ -disubstituted butenolide compounds by synthetic chemists.² In this research area, the most common synthetic methods for the optically active butenolides mainly confined to the catalytic asymmetric Mukaiyama-type reactions by using the preformed silyloxyfurans.^{2,3} However, alternative approaches involving γ -substituted butenolides as pronucleophiles by functionalization at the γ -position for generating enantiomerically pure γ,γ -disubstituted butenolides recently have received more attention due to atom and step economy. In this respect, various transformations, such as the direct asymmetric allylic alkylation,⁴ vinylogous Mannich,⁵ and vinylogous Michael addition reactions⁶ of γ -substituted butenolides, have been well documented. Even so, considering the ubiquitous nature of butenolides in natural products and medicinally important agents, developing new strategies for the efficient construction of the useful γ,γ -disubstituted butenolide compounds is still desirable.

Asymmetric organocatalysis employing hydrogen bonding for substrate activation has been demonstrated to be an effective and versatile strategy in facilitating a variety of organic transformations.⁷ In this realm, chiral amine-squaramide catalysts, possessing a squaramide moiety as a powerful hydrogen bond donor and a tertiary amine moiety as the basic site, have been identified as a family of chiral bifunctional catalysts for a range of asymmetric transformations.⁸ Meanwhile, we noticed that 2-enoylpyridines, featuring α,β -unsaturated carbonyls attached to a pyridine group, were excellent substrates for highly enantioselective conjugated addition reactions.⁹ In particular, the 2-alkanoyl-pyridine moiety has been shown to be efficient template for high reactivity and stereoselectivity due to readily coordination to hydrogen bonding (Scheme 1).^{9a} However, an asymmetric addition of γ -substituted butenolides to 2-enoylpyridines has not been reported yet, despite the popularity of γ -substituted butenolides as versatile nucleophiles. Therefore, as our continuing program of research in asymmetric organocatalysis,¹⁰ herein, we document a highly efficient methodology for the diastereo- and enantioselective direct vinylogous Michael addition reaction of γ -substituted butenolides to 2-enoylpyridines with chiral bifunctional amine-squaramide (Scheme 1), allowing the generation of γ,γ -disubstituted butenolides possessing consecutive tri- and tetrasubstituted stereogenic centers.



Scheme 1 Diastereo- and Enantioselective Direct Vinylogous Michael Addition Reaction of γ -Substituted Butenolides to 2-Enoylpyridines.

We started our studies with the reaction of γ -phenyl-substituted butenolide **1a** and 2-enoylpyridine **2a** in the presence of various chiral bifunctional organocatalysts **A-E** in dichloromethane (Table 1). The reaction gave product **3a** in moderate yield and 77:23 diastereomeric ratio (dr) and 63% ee.

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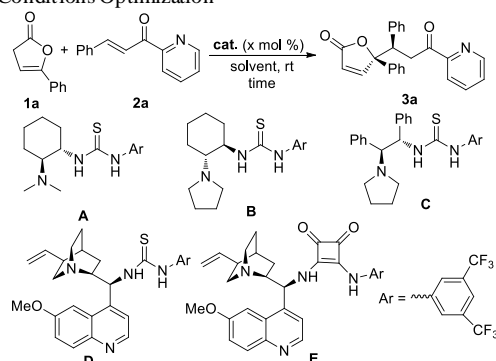
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with catalyst **A** (entry 1). Similar to catalyst **A**, bifunctional thiourea-tertiary amine catalysts **B** and **C**, possessing chiral 1,2-diamine skeleton, also afforded mediocre results (entries 2 and 3). Another thiourea-tertiary amine catalyst **D** derived from quinine could finish the reaction in 29 h to provide **3a** in 78% yield with 91:9 dr and 80% ee (entry 4). To our delight, the reaction proceeded to completion with chiral bifunctional quinine amine-squaramide catalyst **E** in 7 h, affording **3a** in 75% yield with up to 98:2 dr and 98% ee (entry 5). Having identified catalyst **E** as the strongest candidate, we undertook a screen of solvents with 10 mol % catalyst dosage at room temperature (entries 6-9). By comparison, excellent reaction rate and stereochemistry control could be obtained when 1,2-dichloroethane (DCE) was used as a solvent (entry 7). Subsequently, we screened reaction temperature and catalyst loading. At 0 °C, **3a** was obtained in 85% yield with 99:1 dr and >99% ee after 6 h (entry 10). Further decreasing temperature to -10 °C, no any improvement on reaction rate was observed (entry 11). With 5 mol % **E**, the reaction could complete in 8 h and furnish **3a** in 82% yield and excellent stereoselectivity (entry 12). However, with 1 mol % **E**, a set of slightly worse results were observed (entry 13). Notably, when the reaction was carried out on a scale up to 30-fold increase, there was no change in reactivity and stereoselectivity, this suggests that this method is amenable to large scale production (entry 14).

Table 1 Conditions Optimization^a



Entry	cat.	x	Solvent	Time (h)	Yield (%) ^b	dr ^c	ee (%) ^d
1	A	10	CH ₂ Cl ₂	42	45	77:23	63
2	B	10	CH ₂ Cl ₂	42	60	78:22	57
3	C	10	CH ₂ Cl ₂	42	51	73:27	72
4	D	10	CH ₂ Cl ₂	29	78	91:9	80
5	E	10	CH ₂ Cl ₂	7	75	98:2	98
6	E	10	CHCl ₃	20	56	97:3	88
7	E	10	DCE	4	75	99:1	99
8	E	10	toluene	20	63	99:1	99
9	E	10	Et ₂ O	46	78	97:3	97
10	E	10	DCE	6	85	99:1	>99 ^e
11	E	10	DCE	10	83	99:1	>99 ^f
12	E	5	DCE	8	82	99:1	99 ^e
13	E	1	DCE	22	74	98:2	98 ^e
14	E	5	DCE	13	76	>99:1	99 ^{e,g}

^a Unless noted, the reactions were carried out with **1a** (0.1 mmol), **2a** (0.15 mmol), and a specified amount catalyst in 2.0 mL of solvent at room temperature. ^b Isolated yields. ^c Determined by ¹H NMR analysis of crude reaction mixture. ^d Ee of major diastereomer was determined by chiral HPLC analysis. ^e Run at 0 °C. ^f Run at -10 °C. ^g Scale-up reaction with 30-fold increase was carried out.

Under the optimized experimental conditions, we then examined a variety of γ -substituted butenolides **1** and 2-enolpyridines **2** to establish the general utility of the asymmetric direct vinylogous Michael addition reaction (Table 2). We were pleased to find that a wide range of aromatic 2-enolpyridines underwent reactions with **1a** in high reactivities and excellent diastereo- and enantioselectivities (entries 1-13). Firstly, the Michael acceptors with electron-withdrawing groups furnished the desired products in 73-88% yields and with up to >99:1 dr and >99% ee values regardless of the kind and position of the substituents in the benzene ring (entries 1-9). Similarly, a series of satisfactory results could be readily obtained with the 2-enolpyridine possessing various electron donating substitutions on the phenyl group (entries 10-13). Fused aromatic 2-enolpyridine **2o** also reacted efficiently with **1a** giving **3o** in 65% yield and 98:2 dr and 98% ee (entry 14). Nevertheless, as highlighted in entries 15 and 16, the 2-enolpyridines bearing a heteroaromatic substituent also were proven to be suitable reaction partner for giving corresponding adducts **3p** and **3q** in excellent results. In addition, not only aliphatic substituted but also ester group substituted 2-enolpyridine could participate in the reaction and furnish the expected adducts **3r** and **3s** in good yields and excellent stereoselectivities (entries 17 and 18). On the other hand, the substrate scope for γ -substituted butenolide component was also investigated. Excellent diastereo- and enantioselectivities and good yields were able to be readily obtained with butenolides **1b-e** bearing different γ -aromatic substituents having an electron nature ranging from electron-withdrawing to electron-donating (entries 19-22). Afterwards, a 2-naphthyl-based butenolide also gave rise to the corresponding adduct **3x** in 85% yield with 97:3 dr and 99% ee (entry 23). Unfortunately, in the case of aliphatic substituted butenolide as a substrate, the catalyst system was inefficient and no reaction occurred (entry 24).

Table 2 Substrate Scope of Direct Vinylogous Michael Addition Reaction between γ -Substituted Butenolides and 2-Enolpyridines^a

Reaction scheme: 1a-g + 2a-s $\xrightarrow[\text{DCE, 0 °C}]{\text{E (5 mol \%)}}$ 3b-x

1a-g: 1a: R¹ = Ph, 1b: R¹ = 4-FC₆H₄, 1c: R¹ = 4-ClC₆H₄, 1d: R¹ = 4-BrC₆H₄, 1e: R¹ = 4-MeC₆H₄, 1f: R¹ = 2-naphthyl, 1g: R¹ = Me

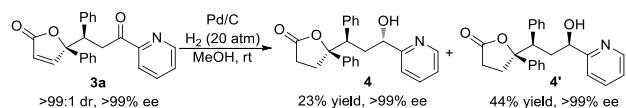
Entry	1	R ²	Time (h)	3/yield (%) ^b	dr ^c	ee (%) ^d
1	1a	2-FC ₆ H ₄ (2b)	12	3b /85	>99:1	>99
2	1a	3-FC ₆ H ₄ (2c)	12	3c /74	99:1	>99
3	1a	4-FC ₆ H ₄ (2d)	11	3d /86	94:6	98
4	1a	2-ClC ₆ H ₄ (2e)	12	3e /76	99:1	>99
5	1a	4-ClC ₆ H ₄ (2f)	11	3f /73	96:4	97
6	1a	2-BrC ₆ H ₄ (2g)	15	3g /74	>99:1	>99
7	1a	3-BrC ₆ H ₄ (2h)	12	3h /87	>99:1	98
8	1a	4-BrC ₆ H ₄ (2i)	11	3i /75	98:2	99
9	1a	4-NO ₂ C ₆ H ₄ (2j)	11	3j /88	>99:1	99
10	1a	3-MeC ₆ H ₄ (2k)	24	3k /84	>99:1	>99
11	1a	4-MeC ₆ H ₄ (2l)	23	3l /61	>99:1	99
12	1a	4-MeOC ₆ H ₄ (2m)	18	3m /71	92:8	96
13	1a	4-BnOC ₆ H ₄ (2n)	34	3n /72	>99:1	99

14	1a	1-naphthyl (2o)	11	3o /65	98:2	98
15	1a	2-furyl (2p)	13	3p /78	>99:1 ^e	>99
16	1a	2-thienyl (2q)	13	3q /85	96:4	97
17	1a	Me (2r)	13	3r /84	97:3	>99
18	1a	CO ₂ Et (2s)	12	3s /85	>99:1	>99
19	1b	Ph (2a)	10	3t /83	98:2	99
20	1c	Ph (2a)	9	3u /86	98:2	99
21	1d	Ph (2a)	9	3v /77	97:3	98
22	1e	Ph (2a)	13	3w /81	98:2	99
23	1f	Ph (2a)	13	3x /85	97:3	99
24	1g	Ph (2a)	72	nr	nr	nr

^a Unless noted, the reactions were carried out with **1** (0.1 mmol), **2** (0.15 mmol), and catalyst **E** (5 mol %) in 2.0 mL of DCE at room temperature. ^b Isolated yields. ^c Determined by ¹H NMR analysis of crude reaction mixture. ^d Ee of major diastereomer was determined by chiral HPLC analysis. ^e This dr value was determined by HPLC analysis.

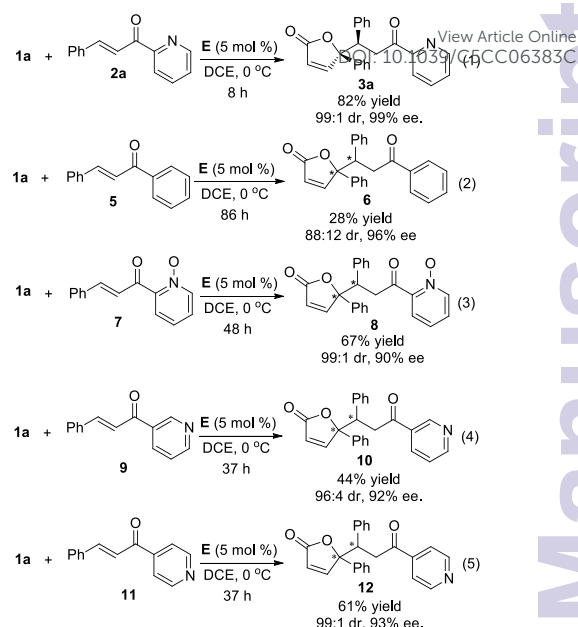
The absolute configuration of the major isomer **3q** was unambiguously determined to be (4*S*, 11*S*) by single-crystal X-ray analysis (See Supporting Information).¹¹ Assuming a common reaction pathway for the catalyst **E**-catalyzed direct vinylogous Michael addition reaction of γ -substituted butenolides and 2-enoylpyridines, the configurations of the other products were assigned by analogy.

The Michael adduct can undergo the further transformation. As shown in Scheme 2, the product **3a** could be hydrogenated by Pd/C in methanol. The double bond and the carbonyl group were both reduced, giving access to a pair of epimerides **4** and **4'** possessing three stereogenic centers with excellent ee values. Importantly, **4** and **4'** could be readily separated with simple column chromatography in 23% and 44% yield, respectively.¹²



Scheme 2 Reduction of Product **3a**.

As the above-listed in Table 1, entry 12, the reaction of **1a** and **2a** could give **3a** in 82% yield with 99:1 dr and 99% ee after 8 h (Scheme 3, (1)). However, under the standard conditions, the addition reaction of **1a** and chalcone **5** exhibited very low reactivity, product **6** was observed only in 28% yield with 88:12 dr and up to 96% ee even for 86 h (Scheme 3, (2)). Similarly, the corresponding product **8** of **1a** addition to 2-enoylpyridine-*N*-oxide **7** could be obtained 67% yield with 99:1 dr and 90% ee after the time for 48 h (Scheme 3, (3)). Furthermore, it was found that the nitrogen atom in different positions of the pyridine also obviously affected the reactivity and stereoselectivity (Scheme 3, (4) and (5)). By comparison the results of these reactions, it revealed that the pyridyl group of **2a** and the position of nitrogen atom in pyridine were crucial to the direct vinylogous Michael addition of γ -substituted butenolides and 2-enoylpyridines, especially in the enhancement of the reactivity and stereoselectivity. These results suggest that the powerful hydrogen-bonding interactions between the squaramide unit of catalyst **E** and the 2-alkanoyl-pyridine moiety of the 2-enoylpyridines play a very important role in the substrate activation.



Scheme 3 Contrast Experiments with **1a** and Different Types of Substrates.

Based on the aforementioned clues and the well-documented activation mode involving chiral bifunctional amine-squaramide catalysts,⁸ a plausible transition state model is proposed to account for the observed stereoselectivity. As shown in Fig. 1, the tertiary amine moiety of chiral amine-squaramide catalyst **E** deprotonates from γ -substituted butenolide to generate an ammonium ion and an enolate. Simultaneously, dual hydrogen bonding from squaramide unit of catalyst **E** to the 2-alkanoylpyridine moiety of the 2-enoylpyridines not only contributes to reducing its LUMO energy, but also directs the 2-enoylpyridine for a face-selective nucleophilic attack. Preferentially, the Michael attack of enolates from the *Si* face to the *Re* face of 2-enoylpyridines thus leads to the formation of the major stereoisomer.

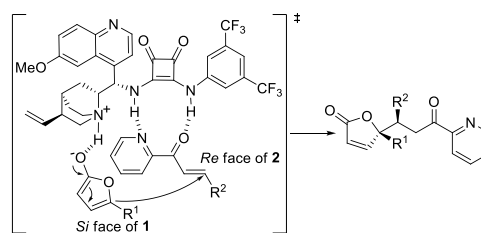


Fig. 1 A proposed transition state for the direct vinylogous Michael addition reaction.

In conclusion, we have developed a highly efficient methodology for the diastereo- and enantioselective direct vinylogous Michael addition reaction of γ -substituted butenolides and 2-enoylpyridines with a chiral bifunctional amine-squaramide as a catalyst. With the developed protocol, a range of γ,γ -disubstituted butenolide derivatives, bearing two consecutive tri- and tetrasubstituted stereogenic centers, were readily obtained in good yields with almost diastereo- and enantiomeric purities (up to 88% yield, >99:1 dr and >99% ee). This catalytic system is well suitable for a wide scope of β -substituted 2-enoylpyridines and γ -aryl-substituted butenolides. The further transformation of the obtained adduct was also

demonstrated. Preliminary experiments revealed that the pyridyl group of the Michael acceptors is crucial to promoting this direct vinylogous Michael addition reaction with high reaction activity and stereoselectivity.

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- CCDC-1057095 (**3q**) 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.
- As to the procedure and the determination of configuration, see the Supporting Information for details.