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Organocatalyzed Highly Enantioselective and *anti*-Selective Construction of γ-Butenolides through Vinylogous Mukaiyama Aldol Reaction

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Abstract: The formation of chiral γ-butenolides has been achieved with good yields (up to 90%), high enantioselectivity (up to 91%) and diastereoselectivity (up to 9/1, *anti*-selective) through an organocatalyzed vinylogous Mukaiyama aldol reaction of 2-(trimethylsilyloxy)furan and aldehydes. A wide range of chiral γ-butenolides was obtained under mild conditions by this methodology.

Keywords: butenolides; diastereoselectivity; enantioselectivity; organocatalysis; vinylogous Mukaiyama aldol reaction

The butenolide ring system represents one of the most ubiquitous structural motifs found in diverse natural products.[1] Consequently, γ-substituted butenolides are useful building blocks for the synthesis of biologically active products, such as the metabolite from *Acremonium sp*, (−)-muricatacin, nakiterpiosin, (−)-*iso*-cladospolide B, and so on (Figure 1).[2] The

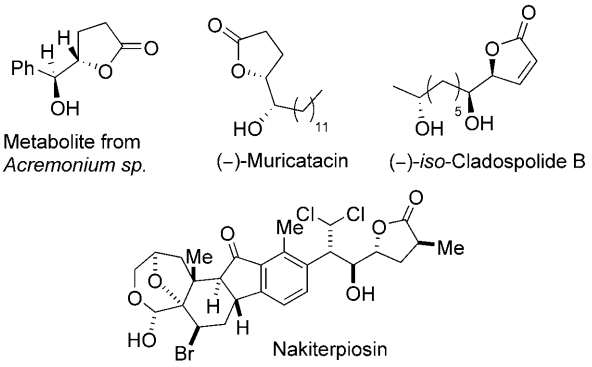


Figure 1. Typical butenolide-containing natural products.

biological activities of these natural products and their analogues depend on the absolute configuration of the stereogenic centers. Thus, many efforts have been directed towards the enantio- and diastereoselective synthesis of the building blocks, i.e., chiral γ-butenolides.[3] With respect to this issue, the asymmetric vinylogous Mukaiyama aldol (VMA) reaction[4,5] of 2-(trimethylsilyloxy)furan (TMSOF) and aldehydes is a very effective strategy. Accordingly, several chiral Lewis acids have been developed as effective catalysts for the synthesis of γ-chiral butenolides *via* VMA reactions.[6–11] For example, Evans et al. reported C_2-symmetrical copper(II) complexes serving as catalysts for asymmetric aldol addition of TMSOF to benzyloxyacetaldehyde with high enantio- and diastereoselectivity.[6] Szlosek et al. described a titanium-BINOL complex which could catalyze the VMA reaction of TMSOF and aldehydes with high enantioselectivity and moderate diastereoselectivity.[7,8] Katsuki and co-workers exploited a Cr(salen) complex as VMA catalyst and investigated the effect of water and alcohol on the enantioselectivity of the reaction products.[9] Scettri and co-workers applied $SiCl_4$ and a chiral Lewis base system to promote a VMA reaction in which high enantioselectivity and moderate diastereoselectivity could be achieved.[10] Recently, Frings et al. developed a chiral copper complex which could catalyze the VMA reaction with controlled enantioselectivity and diastereoselectivity.[11]

On the other hand, organocatalysis is one of the most rapidly growing and fruitful research areas in synthetic organic chemistry during the last decade.[12] Complementing biocatalysis and metal catalysis, asymmetric organocatalysis covers a wide range of organic processes and methodologies, providing efficient and environmentally friendly access to enantiomerically pure compounds including many drugs and bioactive natural products. In terms of VMA reactions

catalyzed by organocatalysts, however, only very few reports could be found in the literature. Utilizing the concept of hydrogen-bonding catalysis, Rawal and co-workers were the first who applied metal-free hydrogen-bonding catalysts, e.g., 1-naphthyl-TADDOL, in asymmetric VMA reactions.[13] Villano et al. realized the enantioselective VMA reaction of Chan's diene catalyzed by hydrogen-bonding catalysts.[14] Soriente and co-workers identified that hydrogen-bonding donors are efficient catalysts for the diastereoselective organocatalytic addition of TMSOF to carbonyl compounds.[15] Besides, Mukaiyama and co-workers reported the asymmetric and *syn*-selective synthesis of butenolide derivatives *via* VMA reactions of aldehydes and 4-methyl-2-(trimethylsilyloxy)furan by using a cinchonidine-derived quaternary ammonium phenoxide.[16] When the non-substituted TMSOF, i.e., 2-(trimethylsilyloxy)furan, was examined, however, the enantioselectivity of the butenolide product was not satisfactory.

Herein, we present our contribution to the efficient synthesis of chiral γ-butenolides *via* asymmetric organocatalysis and report the first examples of bifunctional alkaloid thiourea catalysts[17] as hydrogen-bonding donors for highly enantio- and diastereoselective VMA reactions of TMSOF and aldehydes.

As shown in Figure 2, our initial examination was carried out by using *p*-nitrobenzaldehyde (**1a**) and TMSOF (**2a**) as substrates in the presence of chiral hydrogen-bonding-donor catalysts (**C1–C5**). The obtained results are summarized in Table 1. Toluene was initially chosen as the solvent since most of the reactions mediated by hydrogen-bonding donors proceed smoothly in toluene. Different reactivities were obtained in toluene for the **C1–C5** catalysts (20 mol%) in terms of conversion and selectivity (Table 1, entries 1–5). The quinine-thiourea catalyst (**C4**) proved to be the most efficient catalyst that affords the VMA product (**3a**) with good yield (76%), diastereoselectivity (4/1 *dr*), and enantioselectivity (77% *ee*) after the reaction had been conducted for 18 h (Table 1, entry 4). The quinidine-thiourea catalyst (**C3**) shows the same diastereoselectivity (4/1 *dr*) as **C4**, but with the reverse enantioselectivity (−77% *ee*, Table 1, entry 3).

To optimize the reaction conditions further, the solvent effect was investigated with the use of catalyst **C4** (Table 1, entries 6–10). $CHCl_3$ was confirmed as the best solvent for this asymmetric VMA reaction (Table 1, entry 8). When the reaction was performed in THF, the enantioselectivity of **3a** (73% *ee*) was good, but a lower yield (47%) was obtained (Table 1, entry 6). A similar result was also observed in CCl_4 (Table 1, entry 9). In comparison with the case in $CHCl_3$, a lower diastereoselectivity of **3a** (4/1 *dr*) was obtained in CH_2Cl_2 (Table 1, entry 7). When 2-propanol (*i*-PrOH) was applied as the solvent, a better yield (79%) and higher *ee* (93%) could be reached, but the diastereoselectivity (3/2 *dr*) was poor (Table 1,

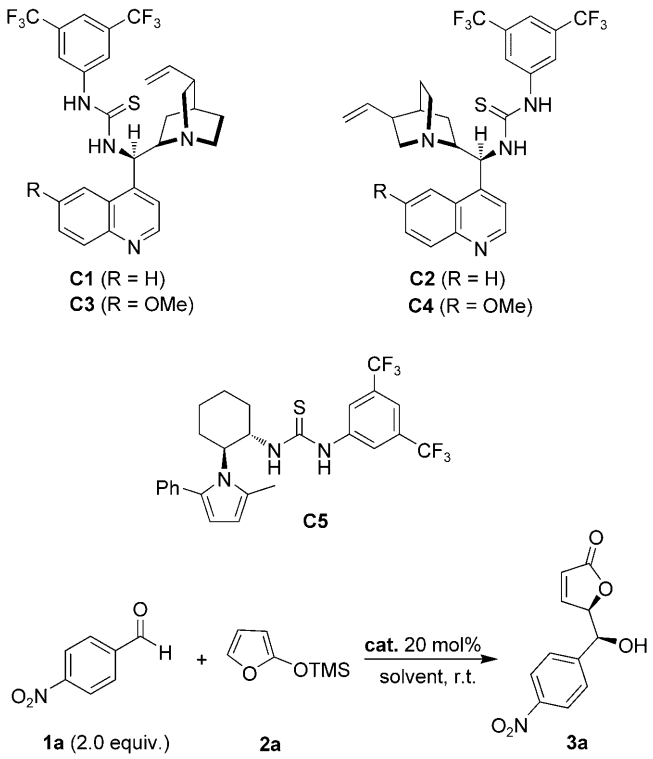


Figure 2. Chiral hydrogen-bonding donors (**C1–C5**) as asymmetric organocatalysts for the asymmetric vinylogous Mukaiyama aldol (VMA) reactions of *p*-nitrobenzaldehyde (**1a**) and TMSOF (**2a**).

Table 1. Screening of catalysts (**C1–C5**) and solvents for the asymmetric vinylogous Mukaiyama aldol (VMA) reactions by using *p*-nitrobenzaldehyde (**1a**) and TMSOF (**2a**) as substrates.

Entry[a]	Catalyst	Solvent	Yield [%][b]	*anti/syn*[c]	*ee* [%][c]
1	**C1**	PhMe	50	80/20	−73
2	**C2**	PhMe	60	78/22	74
3	**C3**	PhMe	75	80/20	−77
4	**C4**	PhMe	76	80/20	77
5	**C5**	PhMe	65	25/75	57
6	**C4**	THF	47	80/20	73
7	**C4**	CH_2Cl_2	75	80/20	75
8	**C4**	$CHCl_3$	77	88/12	79
9	**C4**	CCl_4	69	80/20	70
10	**C4**	*i*-PrOH	79	60/40	93
11	**C4**	$CHCl_3$	78	88/12	91[d]

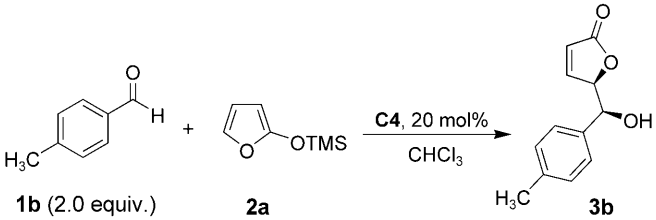
[a] *Reaction conditions:* **1a** (0.30 mmol) and **2a** (0.15 mmol) in solvent at room temperature for 18 h.
[b] Isolated yields after silica gel column chromatography.
[c] Determined by HPLC (Daicel chiral AD-H column). The diastereoisomeric ratio was determined according to refs.[7,8]
[d] *Reaction conditions:* **1a** (0.30 mmol) and **2a** (0.15 mmol) in $CHCl_3$ at −20 °C for 6 h and then at 0 °C for 60 h.

entry 10). Eventually, we found that the best result (78% yield, 91% *ee*, and 88/12 *dr*) was produced after the reaction was conducted in $CHCl_3$ at −20 °C for 6 h and then at 0 °C for 60 h (Table 1, entry 11). A lower yield (51%) was, however, obtained when −20 °C was applied throughout the reaction.

It is well known that water is an efficient additive in Lewis acid-catalyzed VMA reactions.[9,18] We, therefore, investigated the influence of water and other additives on the asymmetric VMA reactions catalyzed by the above-mentioned organocatalysts. The investigation was first carried out by using *p*-methylbenzaldehyde (**1b**) and TMSOF (**2a**) as substrates in the presence of catalyst **C4**. The obtained results are summarized in Table 2.

In the absence of water, the VMA product **3b** was obtained with 83% yield, 89/11 *dr*, and 88% *ee* (Table 2, entry 1). With the addition of 10 mol% water, a higher yield (90%) but slightly lower enantio- and diastereoselectivities (87/13 *dr* and 87% *ee*) were obtained (Table 2, entry 2). Increasing the amount of water to 30 mol% did not cause any additional improvement (83% yield, 86/14 *dr*, and 87% *ee*, Table 2, entry 3). When more water (50 mol%) was added, a lower yield of 30%, *dr* of 80/20 and *ee* of 74% were obtained (Table 2, entry 4). Similar results, i.e., higher conversion and lower stereoselectivity, were observed when 2-propanol was added (Table 2, entries 5 and 6).

Table 2. Effect of water and other additives on the asymmetric vinylogous Mukaiyama aldol (VMA) reactions by using *p*-methyl-benzaldehyde (**1b**) and TMSOF (**2a**) as substrates.



1b (2.0 equiv.) **2a** **3b**

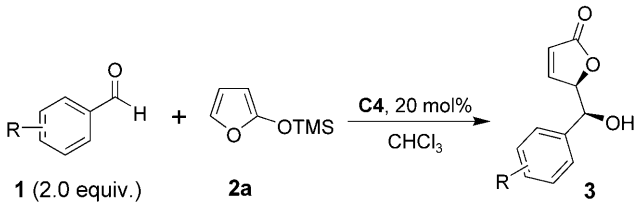
Entry[a]	Additive (mol%)	Yield [%][b]	*anti/syn*[b]	*ee* [%][c]
1	None	83	89/11	88
2	H_2O (10)	90	87/13	87
3	H_2O (30)	83	86/14	87
4	H_2O (50)	30	80/20	74
5	*i*-PrOH (10)	87	84/16	84
6	*i*-PrOH (50)	79	80/20	84
7	4 Å MS[d]	85	75/25	67
8	DIPEA (10)	78	90/10	racemic

[a] *Reaction conditions:* **1b** (0.30 mmol) and **2a** (0.15 mmol) in $CHCl_3$ at −20 °C for 6 h and then at 0 °C for 60 h.
[b] Isolated yields after silica gel column chromatography.
[c] Determined by HPLC (Daicel chiral AD-H column). The diastereoisomeric ratio was determined according to refs.[7,8]
[d] 30 mg of 4 Å MS.

Schneider and co-workers have observed the quantitative formation of silanol in organocatalyzed vinylogous Mukaiyama–Mannich reactions in aqueous solvent.[19] The effects of water or alcohol on the organocatalyzed VMA reaction in our study may be similar to those[19] that Schneider and co-workers proposed. A small amount of water or alcohol in the reaction would trap the TMS species to silanol or silyl ether, which could regenerate the organocatalyst and, therefore, improve the yield. On the contrary, more water or alcohol (≥50 mol%) would deactivate the double hydrogen-bonding catalyst. The addition of 4 Å MS (30 mg) gave a lower *ee* (67%, Table 2, entry 7), while 10 mol% of DIPEA gave the racemic products (Table 2, entry 8).

On the basis of the optimization efforts presented above, the substrate scope of asymmetric VMA reactions catalyzed by organocatalyst **C4** was further investigated (Table 3). In general, all the examined substrates could furnish the desired products in good yields and high selectivities. A variety of aromatic aldehydes bearing either electron-donating or electron-withdraw groups underwent the asymmetric VMA reaction to afford high enantioselectivities ranging from 82 to 91% *ee* (Table 3, entries 1–5). Both the *ortho*-

Table 3. Asymmetric vinylogous Mukaiyama aldol (VMA) reactions catalyzed by the organocatalyst **C4**.



1 (2.0 equiv.) **2a** **3**

Entry[a]	Electrophile	R	Yield [%][b]	*anti/syn*[b]	*ee* [%][c]
1	**1a**	4-NO_2	78	88/12	91
2	**1b**	4-Me	83	89/11	88
3	**1c**	4-Cl	80	90/10	87
4	**1d**	4-OMe	72	60/40	82
5	**1e**	H	78	89/11	86
6	**1f**	2-NO_2	75	90/10	85
7	**1g**	3-Me	80	87/13	85
8	**1h**	4-CN	77	85/15	86
9	**1i**	2,4-Cl_2	82	82/18	85
10	**1j**	3,4-Me_2	82	86/14	86
11	**1k**	4-F	77	89/11	87
12	**1l**	4-Br	75	88/12	84
13	**1m**	2-naph	90	90/10	89

[a] *Reaction conditions:* **1** (0.30 mmol) and **2a** (0.15 mmol) in $CHCl_3$ at −20 °C for 6 h and then at 0 °C for 60 h.
[b] Isolated yields after silica gel column chromatography.
[c] Determined by HPLC (Daicel chiral AD-H column). The diastereoisomeric ratio was determined according to refs.[7,8]

and *meta*-substituted benzaldehydes resulted in high enantioselectivities (85% *ee*, Table 3, entries 6–7). More strikingly, disubstituted benzaldehydes also gave satisfactory results (Table 3, entries 9–10). 2-Naphthaldehyde resulted in high yield (90%), enantioselectivity (89% ee) and diastereoselectivity (9/1) as well (Table 3, entry 13).

In conclusion, we have developed an asymmetric, organocatalyzed vinylogous Mukaiyama aldol (VMA) reaction of 2-(trimethylsilyloxy)furan (TMSOF) and aldehydes, which gives the desired products with high enantioselectivities and *anti*-selectivities. This is the first example of asymmetric VMA reactions of TMSOF and aldehydes catalyzed by bifunctional alkaloid thiourea organocatalysts. Accordingly, a wide range of chiral γ-butenolides could be obtained in good yields and high enantioselectivities. The catalytic system we have developed might be an efficient methodology for the construction of the enantioselective γ-butenolides that exist in many biologically active natural products. For example, Gao et al. achieved very recently the total synthesis of nakiterpiosin, in which the construction of butenolides was indeed realized by vinylogous Mukaiyama aldol reactions.[20] Our further studies will focus on the development of new methodologies for the synthesis of different kinds of chiral γ-butenolides *via* organocatalysis.

Experimental Section

Typical Procedure for the Asymmetric Vinylogous Mukaiyama Aldol (VMA) Reactions Catalyzed by Organocatalysts (C1–C5) as Hydrogen-Bonding Donors

A solution of aldehyde **1** (0.3 mmol) and organocatalyst **C4** (0.03 mmol) in $CHCl_3$ (0.2 mL) was stirred at −20 °C for 10 min, then **2a** (0.15 mmol) was added. The reaction mixture was stirred at −20 °C for 6 h and then at 0 °C for 60 h. TFA (0.5 mL) was added to the reaction mixture thereafter. The solution was then warmed to room temperature and stirred for 1 h after the desilylation was completed. The solution was diluted with ethyl acetate and a saturated aqueous solution of $NaHCO_3$ was added dropwise until the evolution of gas ceased. The organic layer was separated, washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography to afford product **3**.

Acknowledgements

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