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Highly enantioselective direct allylic alkylation of butenolides with Morita–Baylis–Hillman carbonates catalyzed by chiral squaramide-phosphine†

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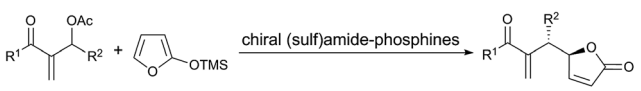
An efficient asymmetric vinylogous allylic alkylation of β,γ-butenolides with Morita–Baylis–Hillman carbonates has been developed. With a chiral cyclohexane-based squaramide-phosphine catalyst **5e**, optically active γ,γ-disubstituted butenolides containing adjacent quaternary and tertiary chiral centers have been constructed in good-to-excellent yields (up to 98%) and excellent stereoselectivities (87 : 13–99 : 1 dr, 96–99% ee).

β,γ-Unsaturated butenolides have attracted great attention recently due to their utility for the direct construction of γ,γ-disubstituted butenolide derivatives, which are important motifs in biologically active natural compounds and pharmaceutically useful molecules.[1–3] Many endeavors have been devoted towards developing efficient protocols to access optically active γ,γ-disubstituted butenolides in the past decade.[4] In 2010, Chen and co-workers[4a] have developed the first direct asymmetric allylic alkylation of γ-substituted β,γ-butenolides with Morita–Baylis–Hillman (MBH) carbonates to access γ,γ-disubstituted butenolides containing adjacent quaternary and tertiary chiral centers, catalyzed by cinchona alkaloid derivatives. Since Chen's pioneering work, various direct vinylogous reactions with β,γ-butenolides as the nucleophiles have been reported, and the electrophiles involve α,β-unsaturated carbonyl compounds,[4b,f–k] nitroolefins,[4e,l] aldimines[4c] and MBH carbonates.[4a,d] It is worth noting that the progress has been mainly focused on Michael reactions. To the best of our knowledge, enantioselective vinylogous allylic alkylation has been rarely described.[4a,d,5] Therefore, the development of a simplified protocol to allow easy access to diverse γ,γ-disubstituted butenolides from β,γ-unsaturated butenolides *via* vinylogous allylic alkylation is still challenging.

Recently, the enantioselective allylic alkylation with MBH adducts catalyzed by Lewis basic tertiary amines or phosphines has emerged as a powerful strategy to deliver multifunctional compounds.[6] Among these examples, the asymmetric vinylogous reaction involving MBH carbonates catalyzed by tertiary phosphines has not been well developed.[7] To the best of our knowledge, the only example is the reaction between 2-trimethylsilyloxy furan and MBH carbonates reported by Shi's group (Scheme 1).[5a] Despite their ability to render γ,γ-stereogenic quaternary centers, which are challenging motifs in organic synthesis, the application of γ-substituted β,γ-butenolides in the asymmetric allylic alkylation is still in its infancy[4a,d] probably due to the low reactivity. Considering the higher nucleophilicity of tertiary phosphines than the corresponding amines, we envisioned that chiral tertiary phosphines could be more effective for the direct vinylogous allylic alkylation between γ-substituted butenolides and MBH carbonates. Herein, we report the first direct asymmetric vinylogous allylic alkylation of butenolides with MBH carbonates to access γ,γ-disubstituted butenolides using chiral tertiary phosphine as organocatalyst.[8]

We began our investigation with the vinylogous allylic alkylation of β,γ-butenolide **1a** with MBH carbonate **2a** in the presence of 10 mol% *rac*-**4a** in CH_2Cl_2 at ambient temperature. To our delight, the vinylogous reaction completed in 4 hours and the regioselective γ,γ-disubstituted butenolide was obtained with excellent diastereoselectivity in 92% yield. Then we examined the chiral cyclohexane-based bifunctional phosphine organocatalysts at 25 °C (Fig. 1), and the results are summarized in Table 1.[9] In general, the aliphatic thioureas provided higher yields than the aromatic thioureas with a similar diastereoselectivity (entries 1–4 *vs.* entries 5 and 6). The



Scheme 1 Previous work with chiral phosphine catalysts.

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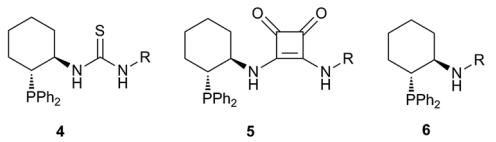


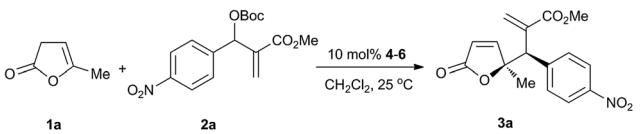
4 5 6

Fig. 1 Structures of the chiral bifunctional phosphines screened.

bifunctional phosphines with an additional chiral group could enhance the enantioselectivity, and a chirality match existed between the chiral backbone and the additional group (entries 3 and 4). To improve the stereoselectivity, chiral phosphines with other H-bonding donators were examined. Squaramide **5c** gave better enantioselectivity but lower yield than the corresponding thiourea **4c** (entry 9 *vs.* entry 3). Therefore squaramide-phosphines[10] containing different scaffolds were evaluated (entries 7–11). Organocatalyst **5e** bearing aromatic scaffold exhibited better yield and enantioselectivity than **5b** and **5c** bearing aliphatic scaffold. Using **6a** with NH_2 group as the H-bonding donor, the vinylogous reaction rate was increased, but poor enantioselectivity obtained. Amide-phosphine **6b** with a single H-bonding donator exhibited a lower reactivity, albeit producing the same level of enantioselectivity as the squaramide-phosphines (entry 13). Therefore squaramide-phosphine **5e** was selected as the chiral organocatalyst to further optimize the reaction conditions.

Subsequently, the optimization of other reaction parameters (solvent, ratio of substrates, temperature and substrate concentration) was carried out with squaramide-phosphine **5e**.

Table 1 Screening of the chiral bifunctional phosphine organocatalysts[a]



1a 2a 3a

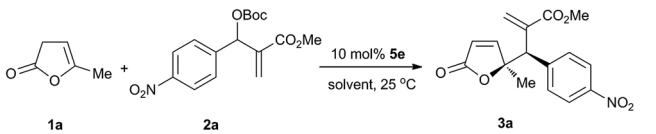
Entry	Catalyst	Time (h)	Yield[b] (%)	dr[c]	ee[c] (%)
1	**4a** (R = Bn)	4	94	97 : 3	59
2	**4b** (R = *n*-$C_{12}H_{25}$)	24	72	97 : 3	73
3	**4c** (R = (*S*)-1-phenylethyl)	12	93	97 : 3	82
4	**4d** (R = (*R*)-1-phenylethyl)	12	52	97 : 3	60
5	**4e** (R = Ph)	144	27	97 : 3	82
6	**4f** (R = 3,5-$(CF_3)_2C_6H_3$)	24	Complex	nd[d]	nd
7	**5a** (R = Bn)	24	NR[e]	nd	nd
8	**5b** (R = *n*-$C_{12}H_{25}$)	3	97	97 : 3	97
9	**5c** (R = (*S*)-1-phenylethyl)	36	84	97 : 3	90
10	**5d** (R = Ph)	48	31	97 : 3	95
11	**5e** (R = 3,5-$(CF_3)_2C_6H_3$)	12	97	98 : 2	98
12	**6a** (R = H)	3	83	96 : 4	44
13	**6b** (R = Bz)	72	85	91 : 9	92

[a] The reactions were performed with 0.3 mmol of **1a**, 0.2 mmol of **2a**, and 10 mol% of catalyst in 1 mL CH_2Cl_2 at 25 °C. [b] Isolated yield. [c] The dr and ee values were based on chiral HPLC analysis, and the given ee data were for **3a**. [d] Not determined. [e] No reaction.

As shown in Table 2, in halogenated solvents γ,γ-disubstituted butenolides **3a** could be obtained in excellent yield, diastereoselectivity and enantioselectivity (entries 1–3). Lower yields were produced with other polar solvents surveyed due to the low conversion of the substrates (entries 4–6). Change of the ratio of **1a**/**2a** from 2 : 1 to 1 : 1.5 led to higher reaction rate with a similar yield, but the enantioselectivity was slightly lower (entries 2 and 7–9). It was found that higher reaction temperature resulted in an increase of reaction rate with a decrease of diastereoselectivity, without compromising the enantioselectivity (entries 2, 10 and 11). Change of substrate concentration in $CHCl_3$ did not affect the yield and diastereoselectivity. Meanwhile, a slightly higher enantioselectivity was achieved by proceeding the reaction in a lower concentration (entries 2 and 12–15). Further decrease of the concentration from 0.1 M to 0.025 M had no significant impact on stereoselectivity. The decrease of catalyst loading from 10 mol% to 5 mol% led to a significant decrease in yield due to a lower conversion (entry 2 *vs.* entry 16). Therefore, the optimal reaction conditions have been identified as follows: 1.5 equiv. of β,γ-butenolide **1** and MBH carbonate **2** in $CHCl_3$ (0.1 M) at 25 °C using 10 mol% of squaramide-phosphine **5e** as the chiral catalyst.

Under the optimized reaction condition, the substrate scope of the vinylogous allylic alkylation using a simple γ-methyl-substituted butenolide **1a** and differently substituted MBH carbonates was examined (Table 3, entries 1–16). Excellent enantioselectivities were observed for MBH carbonates derived

Table 2 Optimization of the reaction conditions[a]



1a 2a 3a

Entry	Solvent	Ratio (**1a**/**2a**)	Conc. (M)	Time (h)	Yield[b] (%)	dr[c]	ee[c] (%)
1	CH_2Cl_2	1.5 : 1	0.2	12	97	98 : 2	98
2	$CHCl_3$	1.5 : 1	0.2	12	98	98 : 2	98
3	$ClCH_2CH_2Cl$	1.5 : 1	0.2	12	92	97 : 3	98
4	THF	1.5 : 1	0.2	96	52	29 : 1	96
5	EtOAc	1.5 : 1	0.2	96	57	34 : 1	97
6	CH_3CN	1.5 : 1	0.2	96	Trace	nd[d]	nd
7	$CHCl_3$	1 : 1.5	0.2	3	98	98 : 2	96
8	$CHCl_3$	1 : 1	0.2	9	95	98 : 2	98
9	$CHCl_3$	2 : 1	0.2	24	97	98 : 2	98
10[e]	$CHCl_3$	1.5 : 1	0.2	4	98	97 : 3	98
11[f]	$CHCl_3$	1.5 : 1	0.2	48	98	99 : 1	98
12	$CHCl_3$	1.5 : 1	0.4	12	98	98 : 2	97
13	$CHCl_3$	1.5 : 1	0.1	12	98	98 : 2	99
14	$CHCl_3$	1.5 : 1	0.05	12	98	98 : 2	99
15	$CHCl_3$	1.5 : 1	0.025	12	98	98 : 2	99
16[g]	$CHCl_3$	1.5 : 1	0.2	96	37	98 : 2	99

[a] Unless otherwise noted the reactions were performed with **1a**, **2a**, and 10 mol% of **5e** in the solvent at 25 °C. [b] Isolated yield. [c] The dr and ee values were based on chiral HPLC analysis, and the given ee data were for **3a**. [d] Not determined. [e] At 40 °C. [f] At 0 °C. [g] The catalyst loading was 5 mol%.

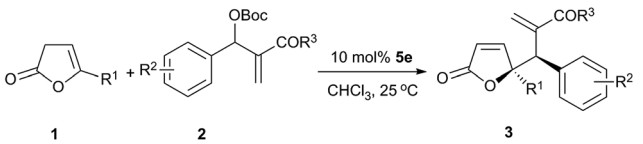
from different alkyl acrylates and methyl vinyl ketone, while *n*-butyl acrylate and *t*-butyl acrylate provided lower yields probably due to the steric effect (entries 1–5). MBH carbonates with a strong electron-withdrawing group at the 4- and 3-position of aromatic ring gave better yields than those with a weak electron-withdrawing group or without substituent (entries 1 and 6–14). MBH carbonates bearing two electron-withdrawing groups at both 3- and 4-positions of phenyl also afforded the desired products in good yields and enantioselectivities (entries 15 and 16). The MBH carbonate with substituent at the 2-position of phenyl failed to produce the desired product probably due to an *ortho* effect. To our disappointment, MBH carbonates with an electron-donating group such as methyl and methoxyl at phenyl ring, and MBH carbonates of alkyl aldehydes are unreactive substrates under the typical reaction condition.

Further exploration of the substrate scope has been focused on the β,γ-butenolides bearing different γ-aryl groups. Considering the reaction rate, excess MBH carbonate (1.5 equiv.) was used, and the vinylogous reaction was accomplished within 3 hours attaining the same enantiocontrol (entry 18 *vs.* entry 17). To our delight, the reaction tolerated all the β,γ-butenolides bearing different γ-aryl groups with either an electron-withdrawing or an electron-donating group, affording the corresponding adducts **3** in excellent yields, diastereo- and enantioselectivities (Table 3, entries 17–22).

To determine the absolute configuration, a vinylogous allylic alkylation was performed with $DHQD(PYR)_2$ as chiral catalyst, according to the literature report.[4a] Compound **3p** was assigned as (*R*,*S*) by comparing the HPLC spectra and optical rotation values with the product resulting from $DHQD(PYR)_2$ catalysis. The absolute configurations of other products were assigned by analogy.

In conclusion, we have developed the first chiral phosphine-organocatalyzed enantioselective vinylogous allylic alkylation of MBH carbonates with β,γ-butenolides. In the presence of 10 mol% chiral cyclohexane-based squaramide-phosphine **5e**, the corresponding γ,γ-disubstituted butenolides containing adjacent quaternary and tertiary stereogenic centers were obtained in up to 98% yield with excellent diastereo- and enantioselectivities. This asymmetric reaction provides an efficient approach toward the synthesis of chiral γ,γ-disubstituted butenolides.

Table 3 Substrate scope of the direct asymmetric allylic alkylation of β,γ-butenolides with MBH carbonates[a]



Entry	R^1	R^2	R^3	Time (h)	Yield[b] (%)	dr[c]	ee[c] (%)
1	Me	4-NO_2	OMe	12	**3a**, 98	98 : 2	99
2	Me	4-NO_2	OEt	12	**3b**, 92	98 : 2	99
3	Me	4-NO_2	O^{n}Bu	120	**3c**, 56	99 : 1	99
4	Me	4-NO_2	O^{t}Bu	120	**3d**, 52	99 : 1	99
5	Me	4-NO_2	Me	6	**3e**, 95	99 : 1	99
6	Me	3-NO_2	OMe	12	**3f**, 98	87 : 13	98
7	Me	4-CN	OMe	12	**3g**, 91	97 : 3	98
8	Me	3-CN	OMe	12	**3h**, 93	90 : 10	98
9	Me	4-CF_3	OMe	72	**3i**, 94	96 : 4	98
10	Me	3-CF_3	OMe	72	**3j**, 87	90 : 10	97
11	Me	4-Br	OMe	120	**3k**, 72	96 : 4	98
12	Me	4-Cl	OMe	96	**3l**, 81	96 : 4	98
13	Me	4-F	OMe	120	**3m**, 74	97 : 3	97
14[d]	Me	H	OMe	120	**3n**, 67	96 : 4	96
15	Me	3,4-Cl_2	OMe	12	**3o**, 92	94 : 6	98
16	Me	3,4-F_2	OMe	48	**3p**, 91	94 : 6	98
17	C_6H_5	4-NO_2	OMe	14	**3q**, 94	88 : 12	99
18[e]	C_6H_5	4-NO_2	OMe	3	**3q**, 94	88 : 12	99
19[e]	4-FC_6H_4	4-NO_2	OMe	3	**3r**, 97	93 : 7	98
20[e]	4-ClC_6H_4	4-NO_2	OMe	6	**3s**, 78	98 : 2	98
21[e]	4-MeC_6H_4	4-NO_2	OMe	2	**3t**, 98	91 : 9	99
22[e]	4-$MeOC_6H_4$	4-NO_2	OMe	3	**3u**, 94	94 : 6	98

[a] Unless otherwise noted, the reactions were performed with 0.3 mmol of **1**, 0.2 mmol of **2**, 10 mol% of **5e** in 2 mL $CHCl_3$ at 25 °C. [b] Isolated yield. [c] The dr and ee values were based on chiral HPLC analysis, and the given ee data were for **3**. [d] The catalyst loading was 20 mol%. [e] With 0.2 mmol of **1** and 0.3 mmol of **2**.

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