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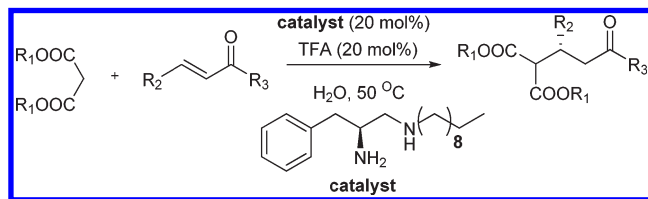
Water-Compatible Iminium Activation: Highly Enantioselective Organocatalytic Michael Addition of Malonates to α,β -Unsaturated Enones

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The highly enantioselective Michael addition of malonates to α,β -unsaturated ketones in water was reported to be catalyzed by a primary–secondary diamine catalyst containing a long alkyl chain. This asymmetric Michael addition process was found to be effective for a variety of α,β -unsaturated ketones.

Over the past few decades, reactions in which water is used as the solvent have received a great deal of attention.¹ In all

the reported water-containing organocatalytic systems,² nitroalkenes and enals are the most frequently used substrates in the Michael reactions,³ but to the best of our knowledge, research aimed at using enones as Michael acceptors in an aqueous system remains a more significant challenge.⁴ Recently, primary amine salts have successfully been applied in the iminium catalysis of enones,⁵ however, no success has been met in aqueous system.

Many kinds of catalysts such as proline salts,⁶ chiral metal compounds,⁷ chiral ionic liquids,⁸ phase-transfer catalysts,⁹ and other organocatalysts¹⁰ have been developed for the Michael reaction of malonates with enones. Although great success has been achieved over the past few years in these important reactions, all of them were performed in organic media or in neat condition. Thus, the development of organocatalytic version of this Michael reaction in water is a highly desirable topic in organic synthesis. Moreover, chalcones are

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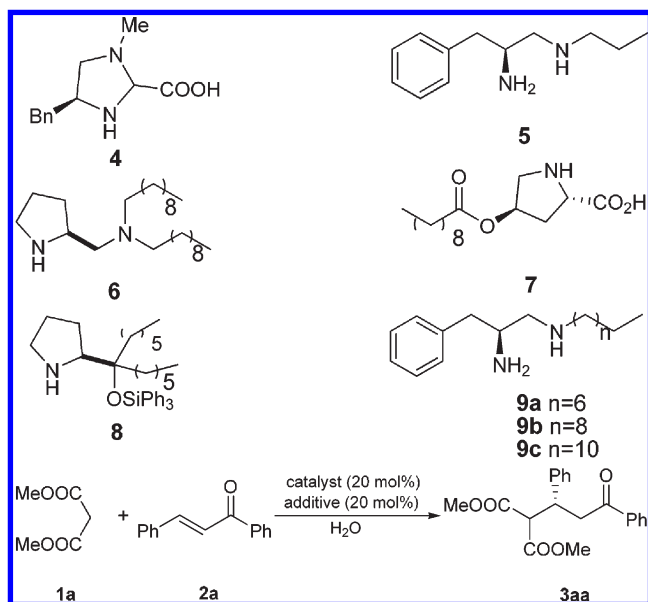
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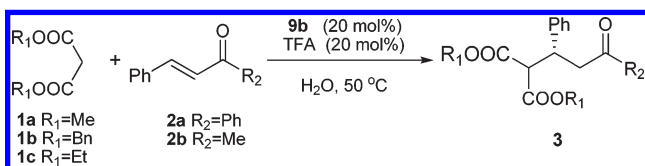
TABLE 1. Screening of Catalysts for the Asymmetric Michael Addition of Dimethyl Malonate **1a** to Chalcone **2a**^a

entry	catalyst	additive	<i>t</i> (h)	<i>T</i> (°C)	yield (%) ^b	ee (%) ^c
1	4	none	60	25	0	—
2	5	TFA	60	25	9	94
3	9a	TFA	60	25	55	97
4	9b	TFA	60	25	76	97
5	9c	TFA	60	25	76	95
6	9b	PhCOOH	60	25	53	95
7	9b	<i>p</i> -TsOH	60	25	70	97
8	9b	TFA	40	40	82	97
9	9b	TFA	40	50	90	96
10	9b	TFA	40	60	88	95

^aReaction conditions: **2a** (1.0 equiv, 0.25 mmol), **1a** (2.0 equiv, 0.5 mmol), catalyst (20 mol %), H₂O (0.5 mL). ^bYield of the isolated product after column chromatography. ^cThe ee value was determined by HPLC on a chiral phase.

still challenge substrates in the Michael reactions in the field of organocatalysis. Herein, we report a system for the highly enantioselective Michael addition of malonates to enones by designing a class of water-compatible primary–secondary diamine catalysts, which is applicable to a broad range of enone substrates (including chalcones).

Initially, the Michael reaction of dimethyl malonate **1a** (2.0 equiv) with chalcone **2a** (1.0 equiv) was selected as a model reaction performed in water with several putative organocatalysts (20 mol %, 60 h, Table 1). When imidazolidine catalyst **4**^{10a} which was a good asymmetric catalyst for the Michael addition of malonates to enones reported by Jørgensen was used as the catalyst in water, no product was afforded after 60 h (Table 1, entry 1). Zhao recently reported several primary–secondary diamine catalysts^{10f,11} for these important reactions through iminium activation with excellent results. So we tried **5** as the catalyst in water. Unfortunately, the reaction proceeded slowly to give low yield (9%); however, the ee was high (94%). We suspected that the low yield might be ascribed to insufficient mixing of reagents in

TABLE 2. Enantioselective Michael Reactions of Malonates **1** with Enones **2** in Water^a

entry	R ₁	R ₂	product	<i>t</i> (h)	yield (%) ^b	ee (%) ^c
1	Me 1a	Ph	3aa	40	90	96
2	Bn 1b	Ph	3ba	40	86	76
3	Et 1c	Ph	3ca	40	88	96
4	Me 1a	Me	3ab	40	49	85
5	Bn 1b	Me	3bb	40	78	92
6	Et 1c	Me	3cb	40	68	89

^aReaction conditions: **2** (1.0 equiv, 0.25 mmol), **1** (2.0 equiv, 0.5 mmol), **9b**/TFA (20 mol %), H₂O (0.5 mL). ^bYield of the isolated product after column chromatography. ^cThe ee value was determined by HPLC on a chiral phase.

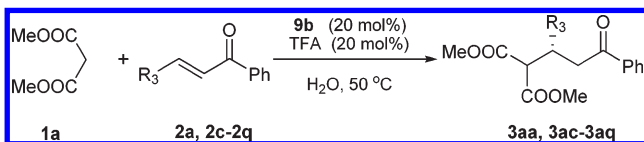
water. Barbas and Hayashi recently independently reported organocatalysts **6**^{2f} and **7**^{2c} for aldol reactions in water. Palomo also designed prolinol-based catalyst **8**^{2p} which enabled iminium-type catalysis of enals in aqueous system. We found that the common feature of these catalysts was that they all contained long alkyl chains in their structures which have been proved to play an important role in assembling with hydrophobic reactants in water and sequestering the transition state from water.^{2f}

Inspired by these excellent works mentioned above, we tried to introduce a long alkyl chain to catalyst **5**. We expected that it might be able to promote the Michael reaction in water. So the new catalysts **9** were prepared in three steps from Boc-L-phenylalanine to evaluate their activities with water as the sole solvent.

Next, catalyst **9b** (20 mol %) bearing a long decyl amine moiety was examined. We were pleased to see that by using this catalyst in aqueous media with TFA (CF₃COOH) (20 mol %) as the acidic additive, an emulsion was formed. The reaction proceeded very well and resulted in good yield (76%) with excellent enantioselectivity (97%) (Table 1, entry 4). Considering that the chain length might affect the yield, we tried other two catalysts **9a** and **9c** containing a shorter and a longer alkyl chain, respectively. However, they both gave inferior results (Table 1, entries 3 and 5). We also tested other acidic additives, but no better results could be found (Table 1, entries 6 and 7). Finally, we carried out the reactions at higher temperature (40, 50, and 60 °C). To our delight, the reactions proceeded completely in 40 h and also gave excellent enantioselectivities (Table 1, entries 8–10). We chose 50 °C as the optimal reaction temperature because up to 90% yield could be obtained.

The generality of the reactions was next investigated under the optimized reaction conditions using water as the sole solvent. First, we examined the effect of the ester substituents (R₁) of the malonates (Table 2). When chalcone **2a** was used as the Michael acceptor, reactions proceeded smoothly with **1a** and **1c** to afford excellent enantioselectivities (Table 2, entries 1 and 3, but in the case of **1b**, selectivity decreased dramatically (Table 2, entry 2). In contrast, when we tested benzylideneacetone **2b**, dibenzyl malonate was found to be the best Michael donor in these reactions, the corresponding product **3bb** was obtained in 78% yield and 92% ee (Table 2, entries 4–6).

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TABLE 3. Enantioselective Michael Reactions of Dimethyl Malonate **1a** with Enones **2** in Water ^a

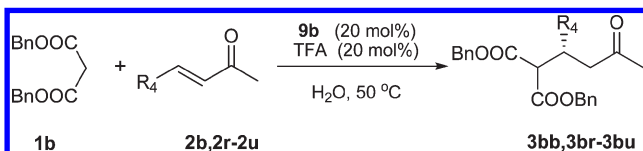
entry	R ₃	product	<i>t</i> (h)	yield (%) ^b	ee (%) ^c
1	Ph, 2a	3aa	40	90	96
2	1-naphthyl, 2c	3ac	42	85	97
3	4-FC ₆ H ₄ , 2d	3ad	42	86	96
4	2-FC ₆ H ₄ , 2e	3ae	42	98	97
5 ^d	2-FC ₆ H ₄ , 2e	3ae	54	78	98
6 ^e	2-FC ₆ H ₄ , 2e	3ae	54	88	97
7 ^f	2-FC ₆ H ₄ , 2e	3ae	54	76	97
8	4-ClC ₆ H ₄ , 2f	3af	54	80	95
9	2-ClC ₆ H ₄ , 2g	3ag	40	92	97
10 ^d	2-ClC ₆ H ₄ , 2g	3ag	54	85	98
11	4-BrC ₆ H ₄ , 2h	3ah	54	56	97
12	2-BrC ₆ H ₄ , 2i	3ai	40	86	96
13	4-MeC ₆ H ₄ , 2j	3aj	64	72	96
14	3-MeC ₆ H ₄ , 2k	3ak	40	91	98
15 ^d	3-MeC ₆ H ₄ , 2k	3ak	54	96	97
16	2-MeC ₆ H ₄ , 2l	3al	40	78	97
17	4-MeOC ₆ H ₄ , 2m	3am	64	91	97
18	3-MeOC ₆ H ₄ , 2n	3an	64	95	95
19 ^d	3-MeOC ₆ H ₄ , 2n	3an	64	88	97
20	2-MeOC ₆ H ₄ , 2o	3ao	42	88	96
21	2-furyl, 2p	3ap	60	64	96
22	isopropyl, 2q	3aq	60	39	96

^aReaction conditions: **2** (1.0 equiv, 0.25 mmol), **1** (2.0 equiv, 0.5 mmol), **9b**/TFA (20 mol %), H₂O (0.5 mL). ^bYield of the isolated product after column chromatography. ^cThe ee value was determined by HPLC on a chiral phase. ^d**9b**/TFA (10 mol %), **1a** (2 equiv, 0.5 mmol). ^e**9b**/TFA (20 mol %), **1a** (1.2 equiv, 0.3 mmol). ^f**9b**/TFA (10 mol %), **1a** (1.2 equiv, 0.3 mmol).

Then the scope of the Michael reactions of dimethyl malonate **1a** (2 equiv) with a variety of chalcones **2a**, **2c–2q** was explored. As summarized in Table 3, in most cases, high yields and excellent enantioselectivities (95–98%) were observed, irrespective of the electronic nature or position of the substituents on the phenyl ring (Table 3, entries 1–20). It is noteworthy that, when the amount of catalyst was decreased to 10 mol %, excellent enantioselectivities could still be achieved without much erosion of the yields (Table 3, entries 5, 10, 15, 19).

Furan enone **2p** was also found to react in water to give the desired product in 70% yield and 96% ee (Table 3, entry 21). When sterically hindered alkyl-substituted enone **2q** was used, a lower yield was obtained but an excellent enantioselectivity was maintained (Table 3, entry 22).

Less reactive chalcones with methyl group on the carbonyl were also surveyed, and the results were presented in Table 4. Gratifyingly, the reactions of dibenzyl malonate with various enones **2b**, **2r–2u** proceeded smoothly to give high yielding and enantioselective (92–93%) products. Both electro-withdrawing (Table 4, entries 3 and 4) and –donating substituents (Table 4, entry 2) were introduced on the aromatic ring without compromising the yields or enantioselectivities of the reactions. It should be mentioned that alkyl substituted enone **2u** also gave excellent

TABLE 4. Enantioselective Michael Reactions of Dibenzyl Malonate **1b** with Enones **2** in Water ^a

entry	R ₄	product	<i>t</i> (h)	yield (%) ^b	ee (%) ^c
1	Ph, 2b	3bb	40	78	92
2	3-MeOC ₆ H ₄ , 2r	3br	60	87	92
3	2-ClC ₆ H ₄ , 2s	3bs	60	71	92
4	2-FC ₆ H ₄ , 2t	3bt	60	92	93
5	pentyl, 2u	3bu	60	51	92

^aReaction conditions: **2** (1.0 equiv, 0.25 mmol), **1** (2.0 equiv, 0.5 mmol), **9b**/TFA (20 mol %), H₂O (0.5 mL). ^bYield of the isolated product after column chromatography. ^cThe ee value was determined by HPLC on a chiral phase.

enantioselectivity (92%) albeit with low yield (51%). Finally, 2-cyclohexenone **2v** was also tested, and gave moderate yield (67%) and good enantioselectivity (80% ee).

In conclusion, we have developed an organocatalyst for the Michael addition of malonates to unsaturated enones in water. The catalyst used herein is simple and easily prepared. The broad scope of this reaction makes this procedure highly attractive for practical use.

Experimental Section

Typical Procedure for the Enantioselective Organocatalytic Michael Addition of Malonate **1a to Chalcone **2a** in Water.** To a mixture of enone **2a** (0.25 mmol), catalyst **9b** (0.05 mmol), and TFA (0.05 mmol) in H₂O (0.5 mL) was added malonate **1a** (0.5 mmol). After 40 h of stirring at 50 °C, the reaction mixture was extracted with EtOAc three times. The combined organic extracts were dried over Na₂SO₄, filtered, and concentrated, and the residue was directly purified by flash chromatography (petroleum ether/ethyl acetate, 7/1) to afford the product **3aa**, 90% yield, 96% ee,

[α]_D²⁰ = –12 (*c* = 1.0 in CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 7.92–7.88 (m, 2H), 7.56–7.50 (m, 1H), 7.45–7.39 (m, 2H), 7.29–7.13 (m, 5H), 4.24–4.16 (m, 1H), 3.86 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.62–3.43 (m, 2H), 3.50 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 197.4, 168.7, 168.1, 140.4, 136.7, 133.0, 128.5, 128.4, 128.0, 127.2, 57.2, 52.6, 52.4, 42.3, 40.7; IR (CHCl₃): 3061, 2953, 1731, 1681, 1596, 1434, 1301, 1238, 1159, 1024, 749, 690 cm^{–1}; HRMS (ESI): C₂₀H₂₀O₅ + H, Calc: 341.1384, Found: 341.1387; HPLC: DAICEL CHIRALCEL AD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, retention time: *t*_{major} = 20.9, *t*_{minor} = 31.2, 96% ee.

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Supporting Information Available: Experimental details on the syntheses and analyses of the presented compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.