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Organocatalytic enantioselective decarboxylative Michael addition of β-ketoacids to α,β-unsaturated ketones†

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Enantioselective decarboxylative Michael addition reactions promoted by chiral primary amine organocatalysts have been developed, allowing the facile synthesis of the corresponding chiral 1,5-diketones with excellent enantioselectivity (up to 97% ee). The method reported represents a valuable approach of utilizing β-ketoacids as synthetic equivalents of aryl methyl ketones.

The Michael addition reaction is one of the most important and powerful methods for the formation of C–C bonds in organic synthesis,[1] and the development of an asymmetric version of this reaction has been a subject of intense study.[2] The organocatalytic asymmetric version of this reaction can afford key chiral intermediates from the reaction of a series of Michael donors and acceptors.[3,4] Among them, the enantioselective organocatalytic conjugate addition reaction of 1,3-dicarbonyl compounds to α,β-unsaturated carbonyl compounds represents a direct and highly appealing approach to chiral 1,5-dicarbonyl compounds that are versatile intermediates for further transformations in organic synthesis.[5] Extensive studies have been devoted to the development of asymmetric conjugate addition of 1,3-dicarbonyl compounds to Michael acceptors.[6] Particularly, a number of reactions of β-keto esters as carbon nucleophiles have been reported.[7] Recently, the enantioselective decarboxylative additions of malonic acid half-thioesters as ester enolate equivalents have received much attention.[8] Although a number of reactions of malonic acid half-thioesters as carbon nucleophiles to various electrophiles have been reported,[9] the corresponding β-ketoacids have received relatively little attention as carbon nucleophiles. There are a few reported examples of the catalytic enantioselective decarboxylative reactions of β-ketoacids such as Michael addition to nitroalkenes in the presence of chiral Ni(II) complexes and aldol-type reactions with trifluoromethyl ketones and isatins using organocatalysts.[10] However, the catalytic enantioselective decarboxylative Michael addition of β-ketoacids to α,β-unsaturated ketones has not been reported so far. Chiral 1,5-diketones are among the most important synthetic feedstocks for constructing valuable molecules including chiral cyclohexenones.[11] Recently, chiral 6-aryl-2,6-hexanediione derivatives were obtained by kinetic resolution of racemic compounds by the Luo and Cheng group.[12] To the best of our knowledge, there is no report for the catalytic enantioselective synthesis of 6-aryl-2,6-hexanediione derivatives.

As part of a research program related to the development of synthetic methods for the enantioselective construction of stereogenic carbon centers,[13] we recently reported the enantioselective Michael additions of active methylenes and methines.[14] Herein, we wish to describe the direct enantioselective decarboxylative Michael addition of β-ketoacids to α,β-unsaturated ketones catalyzed by chiral primary amine organocatalysts.

To determine suitable reaction conditions for the catalytic enantioselective decarboxylative Michael addition reaction of β-ketoacids, we initially investigated the reaction mechanisms with benzoylacetic acid (**1a**) and (*E*) 4-phenylbut-3-en-2-one (**2a**) in the presence of 20 mol% of catalyst in toluene at room temperature. We first examined the impact of the structure of catalysts **I–VII** (Fig. 1) on the enantioselectivities (3–83% ee, Table 1, entries 1–7). The binaphthyl-modified primary amine catalyst **VI** and thiourea organocatalyst **VII** were less effective (3 and 35% ee, Table 1, entries 6 and 7), whereas the cinchona-alkaloid-derived organocatalyst **I–V** effectively promoted the addition reaction in high yields and with high enantioselectivities (61–83% ee, Table 1, entries 1–5). The best results were obtained with catalyst **III** (83% ee, Table 1, entry 3). Different solvents were then tested in the presence of 20 mol% of catalyst **III** together with benzoylacetic acid (**1a**) and (*E*) 4-phenyl-3-en-2-one (**2a**) in order to improve the selectivity of the reaction further. A survey of the reaction media indicated that many common solvents such as THF, dichloromethane, diethyl ether, ethyl acetate, acetonitrile, and xylene (Table 1, entries 3 and 8–13) were well tolerated in this conjugate addition without significant decreases in enantioselectivity. Among the solvents probed, the best results (79% yield and 83% ee) were achieved when the reaction was conducted in toluene (Table 1, entry 3). Based on the exploratory studies, we

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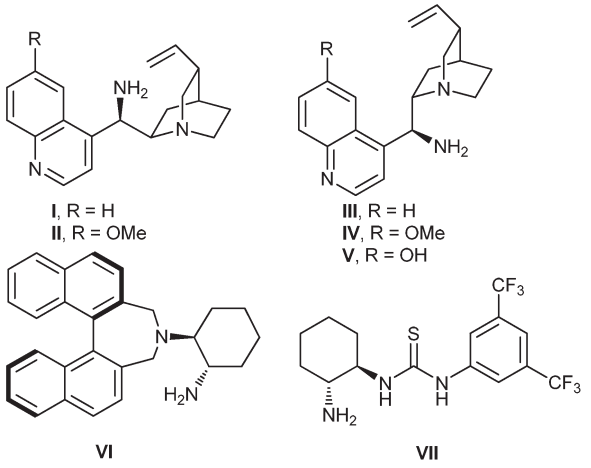


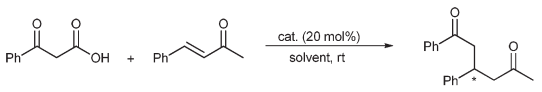
Fig. 1 Structures of chiral organocatalysts.

examined the reactivity and selectivity with organocatalyst **III** in the presence of different acids, such as trifluoroacetic acid, *p*-toluenesulfonic acid, and amino acid derivatives as additives (entries 14–20). Among the additives used, the best results (84% yield and 95% ee) were achieved when the reaction was conducted in L-phenylglycine (entry 17). The present catalytic system tolerates catalyst loading down to 10 or 5 mol% without compromising the yield or the enantioselectivity (Table 1, entries 21–23). In the presence of catalyst **I** and L-phenylglycine, the Michael addition of benzoylacetic acid (**1a**) to (*E*) 4-phenylbut-3-en-2-one (**2a**) afforded the opposite enantiomer (*S*)-**3a** with moderate yield and excellent enantioselectivity (94% ee, Table 1, entry 24).

To examine the generality of the catalytic enantioselective decarboxylative Michael addition reaction of the benzoylacetic acid derivatives **1** by using chiral primary amine organocatalyst **III**, we studied the Michael addition of various benzoylacetic acid derivatives **1** with (*E*) 4-phenylbut-3-en-2-one (**2a**). As seen from the results summarized in Table 2, the corresponding chiral 1,5-diketones **3a–f** were obtained in excellent yields and with excellent enantioselectivities. A range of electron-donating and electron-withdrawing substitutions on the aryl ring of the benzoylacetic acid derivatives **1b–e** provided reaction products in high yields and excellent enantioselectivities (90–97% ee, Table 2, entries 1–5). The naphthyl-substituted β-ketoacid **1f** provided the products with high selectivity (81% ee, Table 2, entry 6).

With the optimal reaction conditions in hand, we then carried on evaluating the generality of this protocol. The results of a representative selection of α,β-unsaturated ketones for the conjugate addition reaction are summarized in Table 3. A range of electron-donating and electron-withdrawing substituents on the aryl ring of the (*E*) 4-arylbut-3-en-2-one **2b–d** provided the reaction products in high yields (78–90%) and with excellent enantioselectivities (91% ee, Table 3, entries 1–3). The heteroaryl- and naphthyl-substituted α,β-unsaturated ketones **2e–f** provided the products with high selectivities (Table 3, entries 4 and 5). Furthermore, (*E*) 5-phenylpent-4-en-3-one (**2g**), (*E*) hex-4-en-3-one (**2h**), and cyclohexenone (**2i**) were also effective substrates for the process (entries 6–8). The absolute configuration of the adducts **3**

Table 1 Optimization of the reaction conditions[a]

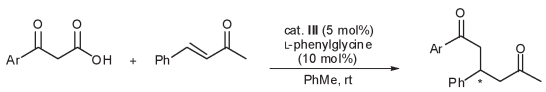


1a 2a 3a

Entry	Cat.	Solvent	Time (h)	Yield (%)[b]	ee (%)[c]
1	**I**	PhMe	16	74	73 (*S*)
2	**II**	PhMe	5	71	61 (*S*)
3	**III**	PhMe	5	79	83 (*R*)
4	**IV**	PhMe	5	72	81 (*R*)
5	**V**	PhMe	5	78	81 (*R*)
6	**VI**	PhMe	5	63	3 (*R*)
7	**VII**	PhMe	5	51	35 (*R*)
8	**III**	THF	5	57	77 (*R*)
9	**III**	CH_2Cl_2	5	75	71 (*R*)
10	**III**	Et_2O	5	71	69 (*R*)
11	**III**	EtOAc	5	77	67 (*R*)
12	**III**	MeCN	5	70	51 (*R*)
13	**III**	*p*-xylene	5	70	81 (*R*)
14[d]	**III**	PhMe	8	62	51 (*R*)
15[e]	**III**	PhMe	8	64	59 (*R*)
16[f]	**III**	PhMe	8	64	77 (*R*)
17[g]	**III**	PhMe	1	84	95 (*R*)
18[h]	**III**	PhMe	1	92	89 (*R*)
19[i]	**III**	PhMe	1	79	85 (*R*)
20[j]	**III**	PhMe	1	84	85 (*R*)
21[k]	**III**	PhMe	3	88	95 (*R*)
22[l]	**III**	PhMe	5	86	95 (*R*)
23[m]	**III**	PhMe	13	67	80 (*R*)
24[g]	**I**	PhMe	9	61	94 (*S*)

[a] Reaction conditions: benzoylacetic acid (**1a**, 0.24 mmol), (*E*) 4-phenylbut-3-en-2-one (**2a**, 0.2 mmol) catalyst (0.04 mmol) at room temperature. [b] Isolated yield. [c] Enantiopurity was determined by HPLC analysis using chiralpak IC column. [d] 40 mol% TFA loading. [e] 40 mol% *p*-TsOH loading. [f] 40 mol% D-tartaric acid loading. [g] 40 mol% L-phenylglycine loading. [h] 40 mol% *N*-Boc- L-phenylglycine loading. [i] 40 mol% L-phenylalanine loading. [j] 40 mol% L-histidine loading. [k] 10 mol% catalyst and 20 mol% L-phenylglycine loading. [l] 5 mol% catalyst and 10 mol% L-phenylglycine loading. [m] 2.5 mol% catalyst and 5 mol% L-phenylglycine loading.

Table 2 Variation of the benzoylacetic acids **1**[a]



1 2a 3

Entry	**1**, Ar	Time (h)	Yield (%)[b]	ee (%)[c]
1	**1a**, Ph	5	**3a**, 86	95 (*R*)
2	**1b**, 4-MeC_6H_4	5	**3b**, 79	93
3	**1c**, 4-$MeOC_6H_4$	6	**3c**, 80	90
4[d]	**1d**, 2-ClC_6H_4	15	**3d**, 84	97
5[d]	**1e**, 4-BrC_6H_4	15	**3e**, 87	90 (*R*)
6	**1f**, 2-naphthyl	6	**3f**, 86	81

[a] Reaction conditions: β-ketoacids (**1**, 0.24 mmol), (*E*) 4-phenylbut-3-en-2-one (**2a**, 0.2 mmol), catalyst (**III**, 0.04 mmol), and L-phenylglycine (0.08 mmol) at room temperature. [b] Isolated yield. [c] Enantiopurity was determined by HPLC analysis using chiralpak IC (for **3a** and **3b**), IA (for **3c**, **3d**, and **3f**), and chiralcel OD-H (for **3e**) columns. [d] This reaction carried out using catalyst **IV** at 0.025 M solution in THF/PhMe (1 : 1).

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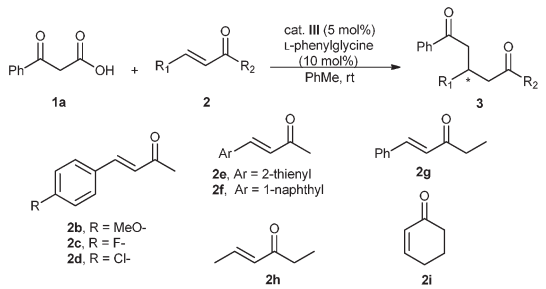
Table 3 Variation of the α,β-unsaturated ketones **2**[a]



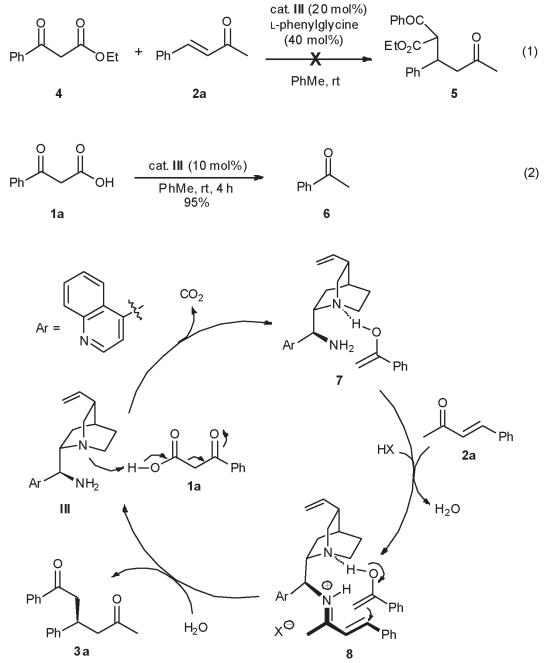
Entry	2	Time (h)	Yield (%)[b]	ee (%)[c]
1[c]	**2b**	13	**3g**, 88	91 (*R*)
2	**2c**	4	**3h**, 90	91
3[c]	**2d**	13	**3i**, 78	91 (*R*)
4[d]	**2e**	6	**3j**, 82	95
5	**2f**	3	**3k**, 89	93
6	**2g**	5	**3l**, 78	97
7[d]	**2h**	15	**3m**, 76	95
8[e]	**2i**	6	**3n**, 78	91

[a] Reaction conditions: benzoylacetic acid (**1a**, 0.24 mmol), α,β-unsaturated ketones (**2**, 0.2 mmol), catalyst (**III**, 0.04 mmol), and L-phenylglycine (0.08 mmol) at room temperature. [b] Isolated yield. [c] Enantiopurity was determined by HPLC analysis using chiralpak IA (for **3g–j**), IC (for **3l–n**), and AS-H (for **3k**) columns. [d] This reaction carried out at 0.025 M solution in PhMe. [e] This reaction carried out using catalyst **IV**.

were determined for some derivatives by comparison of their optical and HPLC properties with literature values.[12]

To find some evidence for the reaction mechanism, we evaluated the reactivity of an analogous reaction and the stability of benzoylacetic acid **1a** under reaction conditions. The Michael addition of β-keto ester **4** to α,β-unsaturated ketone **2a** was conducted in the presence of catalyst **III** (20 mol%) and L-phenylglycine (40 mol%), and the Michael adduct **5** was not found (Scheme 1, eqn 1). When **1a** was exposed to catalyst **III** (10 mol%) in toluene for 4 h, acetophenone **6** was isolated quantitatively (Scheme 1, eqn 2). Based on the above results, we propose a plausible mechanism as described in Scheme 1. The tertiary amine of catalyst **III** deprotonates benzoylacetic acid **1a**, followed by the decarboxylation to afford the enol intermediate **7**. The enantioselective Michael addition of an enol to the iminium intermediate **8** afforded the chiral 1,5-diketone **3a**.

In conclusion, we have developed a highly efficient catalytic enantioselective decarboxylative Michael addition reaction of benzoylacetic acids **1** to α,β-unsaturated ketones **2** using a cinchonidine-derived chiral primary amine organocatalyst. The desired 1,5-diketones were obtained in good to high yields, and excellent enantioselectivities (up to 97% ee) were observed for all the substrates examined in this work. We believe that the present method provides the first practical entry for the preparation of chiral 6-aryl-2,6-hexanedione derivatives. Further study of this catalytic enantioselective decarboxylative addition reaction of β-ketoacids with various carbon electrophiles is in progress.



Scheme 1 Possible reaction mechanism.

Acknowledgements

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