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Enantioselective Michael addition of malonates to α,β -unsaturated ketones catalyzed by 1,2-diphenylethanediamine[†]

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A general and highly enantioselective Michael addition of malonates to cinnamones and chalcones has been developed. The commercially available 1,2-diphenylethanediamine could be directly utilized as the organocatalyst to furnish the desired adducts in satisfactory yield (61–99%) and moderate to excellent enantiopurity (65 to >99% ee). β -Ketoester was also a competent donor and was employed to construct densely functionalized cyclohexenones *via* a tandem Michael-aldol condensation process.

Introduction

The direct Michael addition of stabilized carbon-centered nucleophiles to electron-poor olefins is widely recognized as a highly atom-economic carbon–carbon bond-forming reaction in organic synthesis. Therefore, the development of an enantioselective catalytic protocol for this conversion has constituted an actively pursued field in the past decades.¹ Although significant progress has been achieved with metal complexes,^{1a–c} recently the well-designed organocatalyst has played an impressive role in this field as well.^{1d,1e} Particularly, the organocatalytic Michael addition of malonates to α,β -unsaturated ketones will produce versatile adducts, which can be readily converted to the corresponding δ -ketoesters as useful synthetic building blocks after decarboxylation.² Pioneering work, the first highly enantioselective truly organocatalytic reaction of this type was developed by Jørgensen using an imidazoline catalyst in 2003.^{2a} Subsequently, other organocatalysts such as proline-derived tetrazole,^{2b,3} metal salts of carboxylic acids,⁴ phase-transfer catalysts,⁵ various chiral thio-ureas,⁶ proline-derived guanidines,⁷ primary amines⁸ and their derivatives⁹ have been introduced to catalyze this reaction. Despite excellent enantiopurities having been achieved in a few cases, nevertheless some of the established approaches suffer from several drawbacks to a certain extent, such as narrow substrate scope and restriction to a special combination of nucleophile and electrophile type. Moreover, among all these well-demonstrated organocatalytic Michael reactions, those untransformed and simple molecules are always not the preferred catalysts as a consequence of inferior enantioselectivity and poorer reactivity,

high degrees of optical purity and reactivity need to be achieved in the presence of modified organocatalysts in most cases. As we all know, these employed optimal organocatalysts should usually been prepared from commercially available precursors or naturally occurring compounds after several-step, even multi-step transformation.^{2,3,5a,5b,6–9} The costly preparative procedure hence impairs the synthetic efficiency and practicality to a certain extent. Therefore, the development of highly general asymmetric Michael addition promoted by simple and commercially available molecules is clearly in high demand.¹⁰

In this context, chiral vicinal 1,2-diamines, mainly cyclohexane-1,2-diamines (CHDA)¹¹ and 1,2-diphenylethanediamine (DPEN)¹² emerged as a class of efficient and commercially available primary amine catalysts.¹³ These diamines enabled the stereoselective functionalization of a variety of steric-constraint carbonyl compounds, including aliphatic and aromatic ketones,^{11a–c,12h,12i} α -branched substituted aldehydes,^{11d,11e} and α,β -unsaturated carbonyl compounds.^{11f,12a–g} A range of versatile building blocks were smoothly constructed in a highly enantioenriched fashion *via* enamine,^{11a,11b,11d,12h} iminium,^{11f,12a–f} enamine–iminium^{11c,11e,12g} and dienamine¹²ⁱ activation modes. As part of our continuous efforts in developing asymmetric Michael addition of unactivated α,β -unsaturated ketones,¹⁴ we disclosed herein a highly enantioselective Michael addition of malonates to cinnamones^{2–4,6a–c,8–9} and chalcones^{5,6d–f,8b,15} catalyzed by a structurally simple DPEN.

Results and discussion

Instead of the often-used CHDA, the moisture- and air-stable, commercially inexpensive DPEN was initially utilized to screen the optimal conditions due to its operational simplicity. Gratifyingly, the Michael reaction between β -naphthyl-substituted cinnamone **1a** and diethyl malonate **2a** proceeded smoothly to afford the desired adduct **3aa** with promising enantiopurity (92% ee) in the presence of acetic acid (Table 1, entry 1). In order to

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Table 1 Optimization of reaction conditions^a

$\beta\text{-Nap} = \beta\text{-naphthyl}$

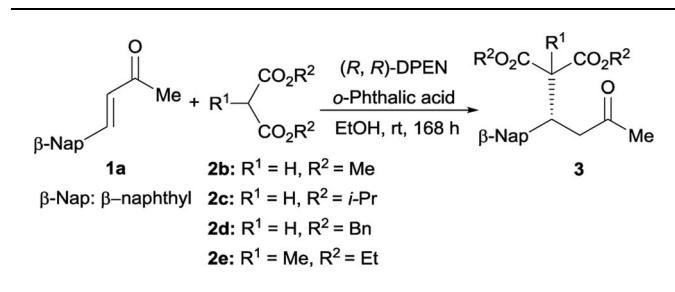
Entry	Additive	Solvent	Time (h)	Yield ^b (%)	ee ^c (%)
1	HOAc	Toluene	168	86	92
2	TFA	Toluene	168	79	96
3	TsOH	Toluene	168	30	97
4	BA	Toluene	168	82	81
5	PNBA	Toluene	168	65	71
6	ONBA	Toluene	168	64	72
7	OFBA	Toluene	168	77	61
8	<i>o</i> -Phthalic acid	Toluene	144	95	95
9	SA	Toluene	168	91	88
10	SA	CHCl ₃	168	91	90
11	SA	Et ₂ O	72	97	90
12	SA	THF	168	91	88
13	SA	EtOH	168	75	96
14	<i>o</i> -Phthalic acid	EtOH	96	95	94
15 ^d	<i>o</i> -Phthalic acid	EtOH	168	99	94
16 ^e		EtOH	168	NR	
17 ^f	<i>o</i> -Phthalic acid		30	99	90

^a Unless otherwise noted, the reaction was performed with 0.2 mmol of **1a**, 4 mmol of malonate **2a**, 20 mol% (*R,R*)-DPEN and 40 mol% acid in 1 mL of solvent at rt. TFA = trifluoroacetic acid, TsOH = *p*-toluenesulfonic acid, BA = benzoic acid, PNBA = *p*-nitrobenzoic acid, ONBA = *o*-nitrobenzoic acid, OFBA = *o*-fluorobenzoic acid, SA = salicylic acid. NR = no reaction. ^b Isolated yield. ^c Determined by chiral HPLC. ^d Conducted with 2 mmol of malonate **2a**. ^e Performed in the absence of acid. ^f 0.6 mL (4 mmol) malonate **2a** was used as the solvent.

Table 2 Substrate scope of Michael addition of malonates to cinnamones and its analogues^a

Entry	R ₁	R ₂	2	3	Time (h)	Yield ^b (%)	ee ^c (%)
1	Ph	Me (1b)	2a	3ab	168	75	91
2	<i>p</i> -FC ₆ H ₄	Me (1c)	2a	3ac	168	99	95
3	<i>o</i> -ClC ₆ H ₄	Me (1d)	2a	3ad	168	99	96
4	<i>m</i> -ClC ₆ H ₄	Me (1e)	2a	3ae	168	99	94
5	<i>p</i> -ClC ₆ H ₄	Me (1f)	2a	3af	168	99	95
6	<i>p</i> -BrC ₆ H ₄	Me (1g)	2a	3ag	168	70	93
7	<i>p</i> -MeC ₆ H ₄	Me (1h)	2a	3ah	168	85	94
8	<i>p</i> -MeOC ₆ H ₄	Me (1i)	2a	3ai	168	92	96
9	1-Naphthyl	Me (1j)	2a	3aj	168	97	96
10	2-Naphthyl	Me (1a)	2a	3aa	96	95	94
11 ^d	2-Furanyl	Me (1k)	2a	3ak	168	84	86
12	2-Thiophenyl	Me (1l)	2a	3al	168	97	92
13	Me	Me (1m)	2a	3am	168	70	86
14 ^d	<i>n</i> -Bu	Me (1n)	2a	3an	168	65	95
15	Ph	Et (1o)	2a	3ao	168	61	91
16 ^e	-(CH ₂) ₃ - (1p)		2a	3ap	168	71	82
17	-(CH ₂) ₄ - (1q)		2a	3aq	96	97	87

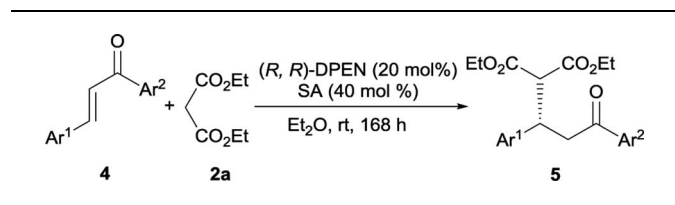
^a Unless otherwise noted, the reaction was performed with 0.2 mmol of **1**, 4 mmol of malonate **2a**, 20 mol% (*R,R*)-DPEN and 40 mol% *o*-phthalic acid in 1 mL of EtOH at rt. ^b Isolated yield. ^c Determined by chiral HPLC. ^d Performed with 40 mol% SA in ether. ^e 2 mmol of malonate **2a** was used.

Table 3 Substrate scope of malonates^a

Entry	2	3	Yield ^b (%)	ee ^c (%)
1	2b	3ba	81	90
2	2c	3ca	65	93
3	2d	3da	92	74
4	2e	3ea	72	95

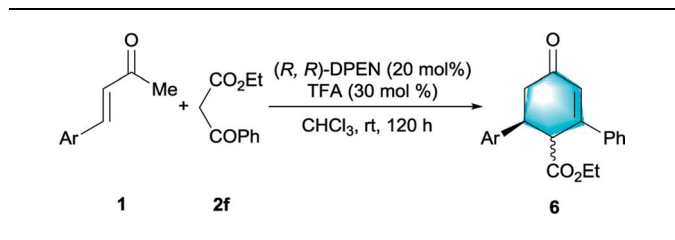
^a Unless otherwise noted, the reaction was performed with 0.2 mmol of **1a**, 4 mmol of malonate **2**, 20 mol% (*R,R*)-DPEN and 40 mol% *o*-phthalic acid in 1 mL of EtOH at rt for 168 h. ^b Isolated yield. ^c Determined by chiral HPLC.

further improve the reactivity, we then turned our attention to examine the effect of other acidic additive. It was revealed that a significant decrease of catalytic capability was observed in the case of stronger acid (entries 2 and 3). Subsequently the model reaction was performed with a range of aromatic carboxylic acids. Although most of aromatic acid furnished **3aa** with diminished yield and optical purity (entries 4–7 vs. entry 1), the enhancement of reactivity was fortunately observed with *o*-phthalic acid and salicylic acid (SA) (entries 8 and 9). In particular, the dicarboxylic acid, *o*-phthalic acid, gave rise to complete conversion after 144 hours, together with 95% ee.^{11e,16} The effect of different solvents was successively investigated with SA (entries 10–13). The protic

Table 4 Substrate scope of the Michael addition of malonate to chalcones^a

Entry	Ar ¹	Ar ²	5	Yield ^b (%)	ee ^c (%)
1	Ph	Ph (4a)	5a	75 (55) ^d	92 (98) ^d
2	<i>p</i> -MeC ₆ H ₄	Ph (4b)	5b	98	98
3	<i>p</i> -ClC ₆ H ₄	Ph (4c)	5c	99	94
4	2-Naphthyl	Ph (4d)	5d	88	94
5	2-Thiophenyl	Ph (4e)	5e	83	65
6	Ph	<i>p</i> -MeC ₆ H ₄ (4f)	5f	99	99
7	Ph	<i>p</i> -ClC ₆ H ₄ (4g)	5g	99	>99
8	Ph	2-Thiophenyl (4h)	5h	65	96
9	<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄ (4i)	5i	99	93

^a Unless otherwise noted, the reaction was performed with 0.2 mmol of **4**, 4 mmol of malonate **2a**, 20 mol% (*R,R*)-DPEN, 40 mol% salicylic acid in 1 mL of ether at rt for 168 h. ^b Isolated yield. ^c Determined by chiral HPLC. ^d Carried out with *o*-phthalic acid in 1 mL of EtOH.

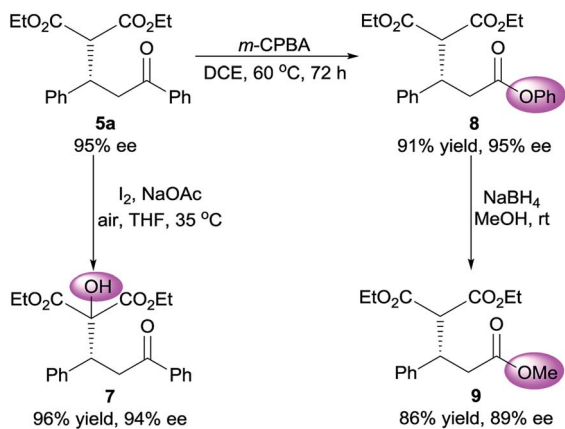
Table 5 Domino reaction for the synthesis of cyclohexenone^a

Entry	Ar	6	Yield ^b (%)	dr ^c	ee ^d (%)
1	Ph (1b)	6a	97	77 : 23	96/97
2	<i>p</i> -ClC ₆ H ₄ (1f)	6b	97	79 : 21	87/87
3	<i>p</i> -BrC ₆ H ₄ (1g)	6c	92	80 : 20	95/97
4	<i>p</i> -MeOC ₆ H ₄ (1i)	6d	99	66 : 34	92/90
5	2-Naphthyl (1a)	6e	99	53 : 47	89/87
6	2-Thiophenyl (1l)	6f	94	60 : 40	92/90

^a Unless otherwise noted, the reaction was performed with 0.2 mmol of **1**, 0.4 mmol of **2f**, 20 mol% (*R,R*)-DPEN and 30 mol% TFA in 1 mL of CHCl₃ at rt for 120 h. ^b Isolated yield of the diastereomeric mixture. ^c Diastereomeric ratio (dr) was determined by ¹H NMR analysis of the crude mixture; major isomer: *trans*. ^d Determined by chiral stationary-phase HPLC.

solvent, EtOH, gave the best enantioselectivity and ether led to a considerable improvement of reaction rate. Meanwhile, the model reaction went to completion after 96 hours with maintained enantiomeric excess when exposed to *o*-phthalic acid in EtOH (entry 14), however, sluggish transformation was detected in ether because of poor solubility of this catalyst system. Moreover, reducing the amount of malonate resulted in substantial decrease of reactivity (entry 15). The model reaction didn't occur in the absence of acidic additive (entry 16). Meanwhile, higher reactivity was observed under neat condition (entry 17).

Once the optimal reaction conditions have been established, the substrate scope of this Michael addition was extended to a variety of cinnamones and malonates. As summarized in Table 2, this catalytic approach was not sensitive to the electronic property of cinnamones. The electron-neutral benzylideneacetone **1b** reacted properly with diethyl malonate **2a** to generate **3ab** in synthetically useful yield and good enantioselectivity (Table 2, entry 1). The electron-deficient α,β -unsaturated ketones **1c–1g** were well tolerated by this catalytic system and enabled access to the expected adducts **3ac–3ag** in a highly enantioselective manner (entries 2–6). Meanwhile, the electron-rich cinnamones **1h** and **1i** are also suitable acceptors for this conversion (entries 7 and 8). On the other hand, the position of substituent on the phenyl ring exerted negligible affect on this titled Michael reaction. Almost identical isolated yields were obtained in the case of the sterically congested *ortho*-substituted enone **1d** in comparison with the *meta*-substituted **1e** and *para*-substituted **1f** (entry 3 vs. entries 4 and 5). In contrast with bulky α -naphthyl-containing **1j**, better catalytic performance in terms of reactivity and enantiocontrol was achieved when β -naphthyl-embedded acceptor **1a** was utilized (entry 9 vs. entry 10). The heteroaromatic substrates **1k** and **1l** served as appropriate acceptors as well, however, a modified condition was required for **1k** to achieve synthetically useful



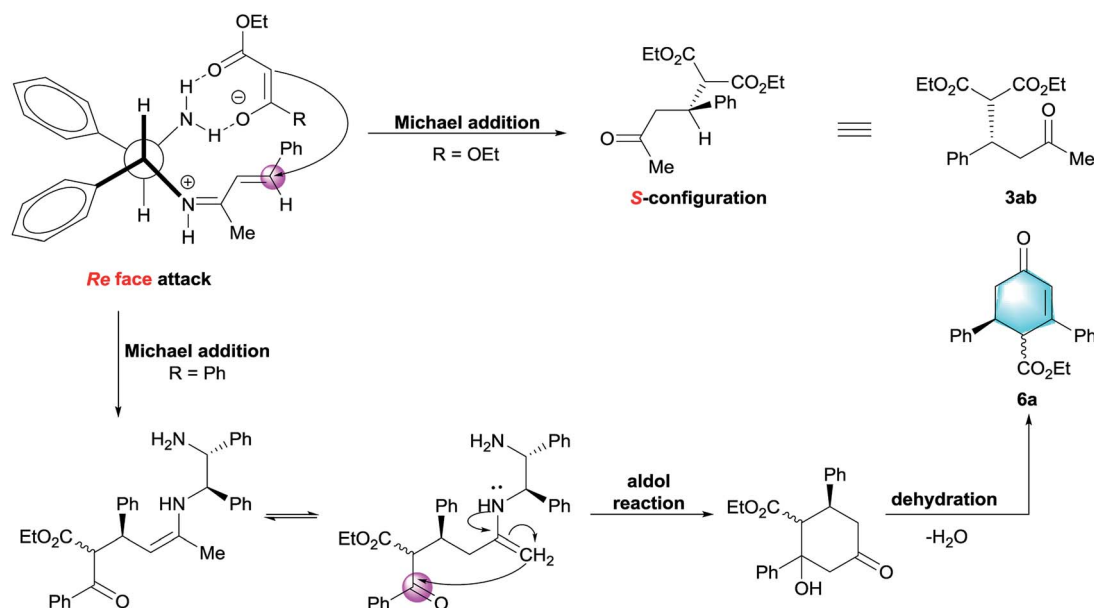
Scheme 1 Synthetic transformation of adduct 5a.

conversion (entries 11 and 12). In addition to aromatic substrates, the aliphatic enones **1m** and **1n** were also compatible with this catalytic strategy, but with slightly poorer reactivity (entries 13 and 14). Notably, variation of R_2 ketone substituent indicated that enone **1o** possessing a sterically more demanding ethyl group also participated in this conjugate addition (entry 15). Cyclic enones^{2b,3,4b,6a,6g,7,17} were suitable acceptors as well, generating the corresponding adducts **3ap** and **3aq** with good enantioselectivities (entries 16 and 17).

With respect to the donor, good enantiomeric excess was obtained for dimethyl ester **2b**, and lower reactivity was detected for diisopropyl ester **2c** but without compromising the optical purity (Table 3, entries 1 and 2). In contrast, dibenzyl malonate **2d** afforded desired adduct **3da** with relatively poorer optical purity (entry 3). Meanwhile, the reaction was totally inert in the case of di-*tert*-butyl malonate. Moreover, methyl-substituted malonate **2e** was also compatible with this catalytic protocol, but relatively lower reactivity was observed (entry 4).

With the exception of cinnamones, our catalytic protocol was also applicable to chalcones, a class of challenging substrates for iminium ion activation.¹⁸ Only moderate isolated yield was obtained when performed with *o*-phthalic acid in EtOH, whereas the reactivity could be effectively improved when conducted with salicylic acid in ether (Table 4, entry 1). Again, this Michael reaction was independent of the electronic nature of substituents on each aromatic ring of chalcones. Both the electron-rich chalcones **4b** and **4f**, and the electron-poor chalcones **4c**, **4g** and **4i** worked smoothly with diethyl malonate **2a**, forming the expected adducts with complete conversion in highly enantioenriched fashion (entries 2, 3, 6, 7 and 9). Only slightly reduced yield was detected for enone **4d** bearing a bulky naphthyl group at the β -site, along with 94% ee (entry 4). The heteroaromatic chalcones **4e** and **4h** underwent clean reactions and gave rise to the desired adducts **5e** and **5h** in acceptable yields and moderate to excellent enantioselectivities (entries 5 and 8). The absolute configuration of **3** and **5** was confirmed to be *S* via comparison of HPLC traces and optical rotation value with that of literatures reported.^{2b,6e}

In addition to malonates, we were pleased to find that β -ketoester was also competent donor for this catalytic protocol.¹⁹ After further optimization of reaction conditions, we found that the cascade Michael-aldol condensation process between cinnamones **1** and ethyl benzoylacetate **2f** readily occurred with 30 mol% of TFA in chloroform, delivering highly functionalized cyclohexenones **6** as an inseparable mixture of diastereomers. (See Table S1 in the ESI[†]). Both the electron-deficient cinnamones and the electron-rich cinnamones were well tolerated (Table 5, entries 2–4). The bulky naphthyl group-containing enone **1a** and the heteroaromatic substrate **1l** were compatible with this catalytic protocol as well, leading to the formation of annulated product **6e** and **6f** with high levels of enantiopurities (entries 5 and 6). The absolute stereochemistry of cyclohexenone **6** was determined to be *S* via conversion of **6a** to



Scheme 2 Proposed reaction pathway.

known compound after a simple decarboxylation (see eqn S(1) in the ESI†).^{19b} Notably, cyclohexenones and their derivatives constituted crucial skeletal components common in enormous natural products and pharmaceutical molecules.²⁰

To demonstrate the synthetic potential of this organo-catalytic asymmetric process, base-controlled chemoselective conversion of Michael adduct **5a** were conducted in the presence of iodine.²¹ α -Hydroxylation of malonate moiety occurred smoothly to provide α -hydroxyl malonate **7** almost without compromise of enantiopurity, when treated with a catalytic amount of NaOAc (Scheme 1). Moreover, the adduct **5a** could be converted to phenyl ester **8** by brief exposure to *meta*-chloroperoxybenzoic acid (*m*-CPBA) without deterioration of optical purity. This Baeyer–Villiger oxidation proceeded with exclusive regioselectivity. Lastly, transesterification of crude **8** worked properly with NaBH₄ in MeOH to afford methyl ester in 86% yield, albeit a slight deterioration of optical purity was detected.

To account for the observed stereochemical outcome of this Michael addition, a bifunctional catalytic model was proposed in Scheme 2.^{12g} Initially, benzylideneacetone **1b** was activated *via* formation of iminium ion with one amino group of vicinal diamine catalyst. Another amino group of DPEN could be engaged in hydrogen-bonding interaction with the carbonyl moiety of ethyl malonate. As a result, the donor was restricted to attack Re face of enone, thereby leading to the generation of *S*-configured adduct **3ab**. In the case of ethyl benzoylacetate, the formation of enamine intermediate allowed the following intramolecular aldol reaction to construct cyclohexanone.^{19b} After final dehydration, the cyclohexenone **6a** was therefore obtained.

Conclusions

In conclusion, we have developed a general and enantioselective Michael addition of malonate to cinnamones and chalcones. The commercially available DPEN could be utilized as the organocatalyst to furnish the desired adducts in satisfactory yield (61–99%) and moderate to excellent enantiopurity (65 to >99% ee). This catalytic protocol was also applicable to β -ketoester and constructed a densely functionalized cyclohexenone *via* a tandem Michael-aldol condensation process. Furthermore, profound synthetic manipulation could be performed on the resulting adduct to construct various optically active building blocks.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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