Chemical Papers
https://doi.org/10.1007/s11696-019-00838-2

ORIGINAL PAPER

Highly efficient and facile synthesis of β-enaminones catalyzed by diphenylammonium triflate

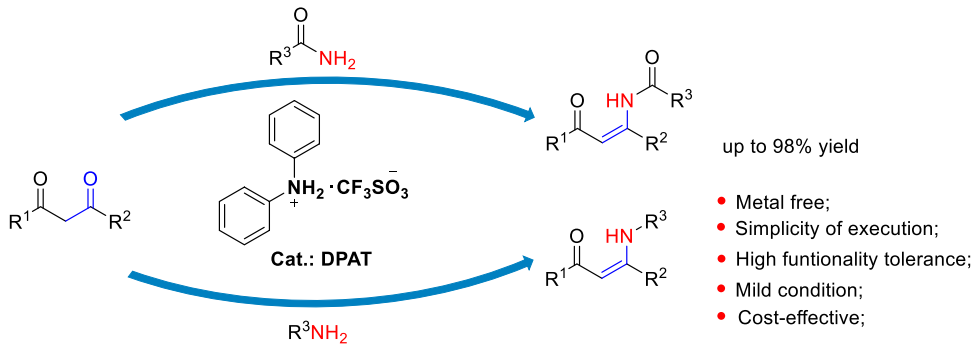
Ting-Ting Zhao[1] · Jiang-Long Song[1] · Feng-Qing Hong[2] · Jian-Sheng Xia[2] · Jian-Jun Li[1]

Received: 7 March 2019 / Accepted: 28 May 2019

Abstract

The catalytic performance of diphenylammonium triflates as an organocatalyst in the synthesis of β-enaminones from various substituted β-diketones and amides (or amines) were evaluated. A wide range of β-enaminones were efficiently synthesized in good to excellent yields under mild reaction conditions. Applying diphenylammonium triflate (DPAT) as catalyst makes this protocol cost-effective, low corrosive and easy to handle.

Graphic abstract



Keywords Ammonium triflates · Diphenylammonium triflate · β-enaminones · Organocatalyst

Introduction

β-enaminones are important precursors for the construction of a variety of pharmaceutical compounds, including anti-convulsivant, anti-inflammatory agents, anti-cancer agents, and quinoline antibacterials (Edafiogho et al. 2006; Tabatabaeian et al. 2014; Zhang et al. 2014). In addition, substituted β-enaminones are commonly used as intermediates in the synthesis of heterocycles, such as pyridines (Chen et al. 2017), indoles (Li et al. 2018), pyrroles (Zhao et al. 2017) and isoxazole derivatives (Fatima and Adel 2005). Due to the extensive application of β-enaminones in organic synthesis and drug development, much attention has been given to development of facile, green, and practical methods for the preparation of β-enaminones. The classical method to synthesize β-enaminones synthesis involves direct

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11696-019-00838-2) contains supplementary material, which is available to authorized users.

✉ Jian-Jun Li
lijianjun@zjut.edu.cn

[1] National Engineering Research Center for Process Development of Active Pharmaceutical Ingredients, College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

[2] TianTai YiSheng Biochemical Co., Ltd, 197 Fengze Road, Tiantai 317299, People's Republic of China

Published online: 03 June 2019

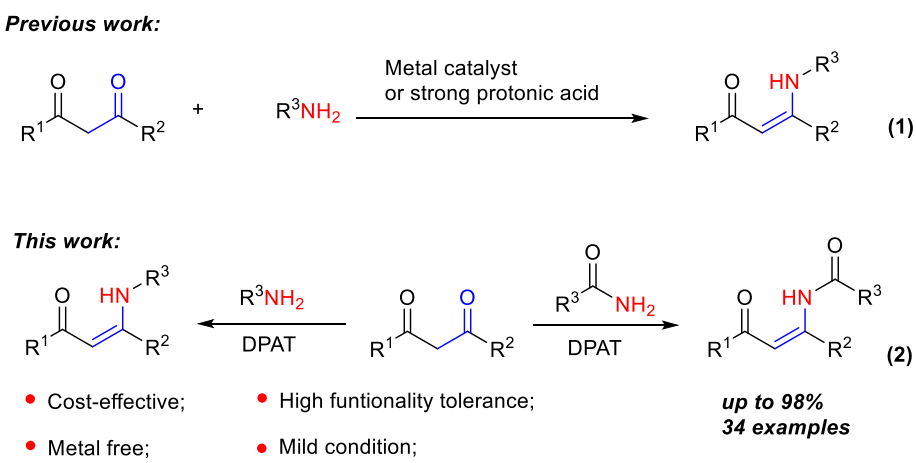
condensation of corresponding amine with 1,3-dicarbonyl compounds via catalysis of strong protonic acid (Baraldi et al. 1983; Martin et al. 1961). Subsequently, greener methods which employed the metal as catalysts such as $NaAuCl_4$ (Arcadi et al. 2003), $Zn(ClO_4)_2{\cdot}6H_2O$ (Bartoli et al. 2004), $Er(OTf)_3$ (Dalpozzo et al. 2006), $Zn[aminoacid]_2$ (Winck et al. 2014) and $Ca(CF_3COO)_2$ (Harrad et al. 2010), to prepare β-enaminones were developed. Although great progress has been achieved in past decades, most of them suffer from one or more of limitations, such as unsatisfactory yields, the use of expensive or less easily available reagents, highly corrosive, and longer reaction time. Until now, studies on the synthesis of β-enaminones involved the condensation of β-ketoesters with less active amides has rarely been reported (Ovenden and Capon 1999; Guin et al. 2007; Klapars et al. 2005). Consequently, developing the green and highly efficient methods for synthesis of a wide range of β-enaminones under less hazardous conditions is of prime importance.

Ammonium triflates have been used as a novel type of organocatalyst in a variety of reactions (Wakasugi et al. 2000; Mercs et al. 2007; Li et al. 2012; Mahjoob and Montazeri 2012; Li and Gui 2014; Jiang et al. 2018) and have displayed great catalytic activity and efficiency. Compared with strong protonic acid or metal catalyst, it has the advantages of reusable, cost-effective, operational simplicity and low corrosive. Despite the considerable success that has been achieved, we wished to expand the application of ammonium triflate to the preparation of β-enaminones. Herein, we report a green, mild and efficient method for the condensation of β-ketoesters with amines or amides (sulfonamides) to synthesize a variety of β-enaminones in good to excellent yields, catalyzed by DPAT (Scheme 1).

Results and discussion

To begin our study, we chose benzamide and ethyl acetoacetate as model reactants to examine and optimized the conditions of this condensation. The transformation was initially carried out in toluene under refluxing for 6 h without adding any catalyst and the experimental result showed that no desired product was detected. A variety of ammonium triflates (Fig. 1, Table 1) such as piperidinium triflate (PT), morpholinium triflate (MorT), (1-ethylpyrrolidin-2-yl)methanaminium triflate (EPMAT), *p*-methoxyanilinium triflate (*p*-MOAT), *p*-nitroanilinium triflate (*p*-NAT), 1-phenylethan-1-aminium triflate (1-PEAT), tributylaminium triflate (TBAT) and diphenylammonium triflate (DPAT) were then tested for this reaction. To our delight, DPAT showed an excellent catalytic activity and the corresponding product was obtained in 96% yield. Subsequently, we also explored whether the amounts of DPAT would affect the efficiency of this reaction. It was observed that increasing or decreasing the amount of DPAT all led to a slight decrease in the yield (Table 1, entries 10, 11). Furthermore, various commonly used solvents including CH_3CH_2OH, THF, CH_3CN, cyclohexane, methylcyclohexane and *p*-xylene (Table 1, entries 13–18) were examined. However, none of them gave a better result than toluene.

On the basis of the screening of the reaction conditions, it was concluded that this condensation should be performed in toluene by employing DPAT as catalyst (10 mol%) under refluxing for 6 h. To demonstrate the generality of this method, the scope of the reaction was investigated under the optimized conditions, and the results are summarized in Table 2. This method was found to be applicable to a wide range of β-diketones (β-ketoesters) and amides, delivering the desired product in moderate to excellent yields. Moreover, β-diketones (β-ketoesters) and amides resulted (*Z*)-β-enaminones with high stereoselectivity (*Z*/*E* > 20:1, determined by ^{1}H NMR spectroscopy of the crude reaction



Scheme 1 Different strategies for the synthesis of β-enaminones

Fig. 1 Ammonium triflates

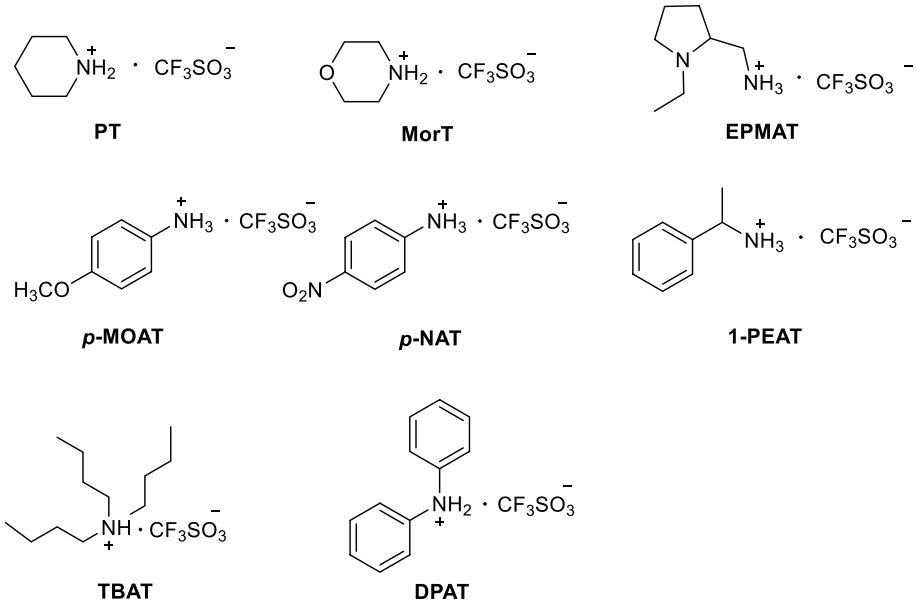
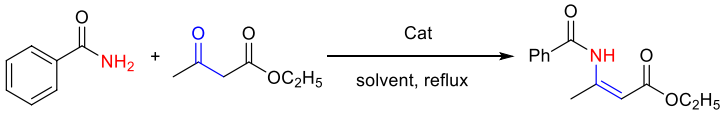


Table 1 Optimization of the reaction conditions



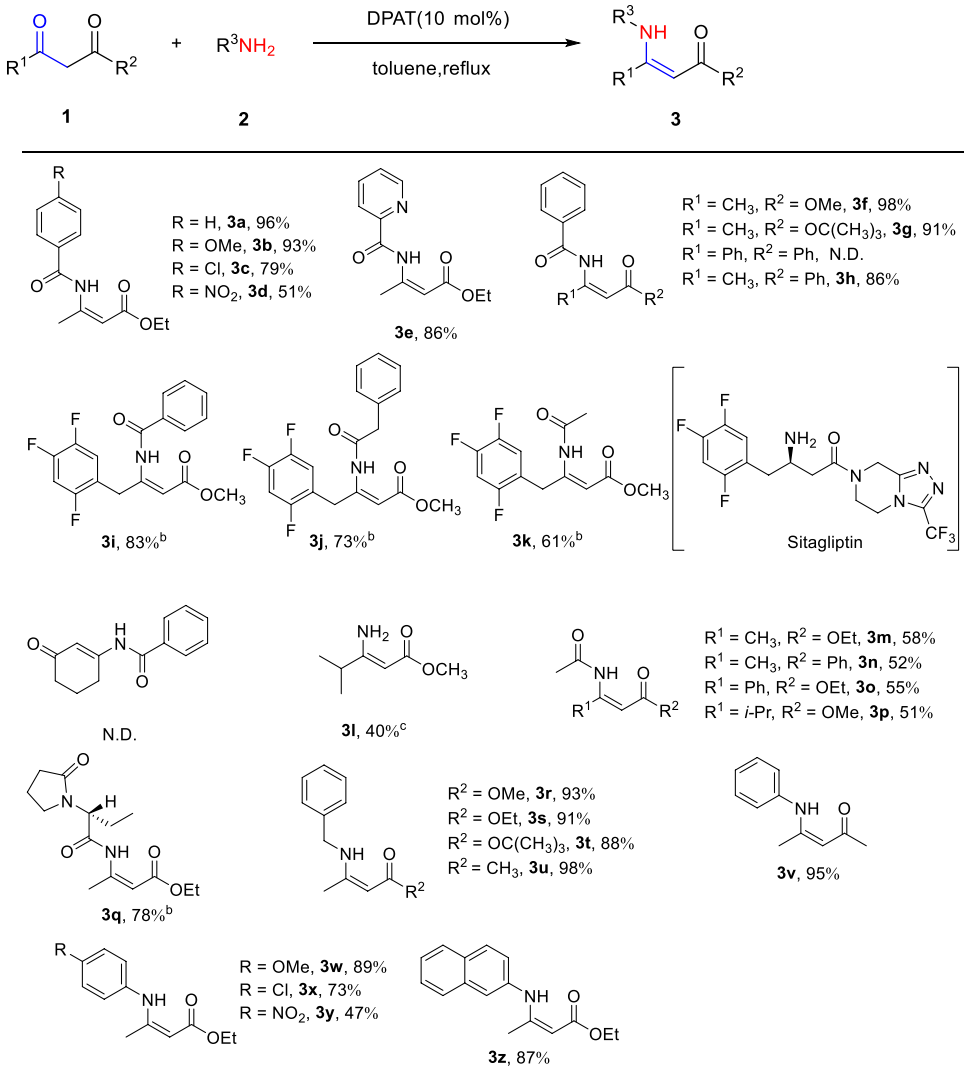
Entry	Catalyst (mol%)	Solvent	Yield (%)[a]
1	None	Toluene	Trace
2	PT(10)	Toluene	Trace
3	MorT(10)	Toluene	Trace
4	EPMAT(10)	Toluene	Trace
5	*p*-MOAT(10)	Toluene	11
6	*p*-NAT(10)	Toluene	17
7	1-PEAT(10)	Toluene	9
8	TBAT(10)	Toluene	Trace
9	DPAT(10)	Toluene	96
10	DPAT(5)	Toluene	92
11	DPAT(15)	Toluene	93
12[b]	DPAT(10)	Toluene	68
13	DPAT(10)	C_2H_5OH	56
14	DPAT(10)	THF	51
15	DPAT(10)	CH_3CN	64
16	DPAT(10)	Cyclohexane	91
17	DPAT(10)	Methylcyclohexane	92
18	DPAT(10)	*p*-xylene	87

Reaction conditions: benzamide (0.6 mmol), ethyl acetoacetate (0.5 mmol) in refluxing solvent (2 mL), catalyst (5-15 mol %), 6 h

[a]Isolated yields after column chromatography based on ethyl acetoacetate

[b]At 80 °C

Table 2 Synthesis of β-enaminones catalyzed by DPAT[a]



[a]Reaction conditions: amides or amines (0.6 mmol), β-dicarbonyl compounds (0.5 mmol), and DPAT (0.05 mmol), all reactions were stirred in refluxing toluene (2 mL), 6 h

[b]8 h

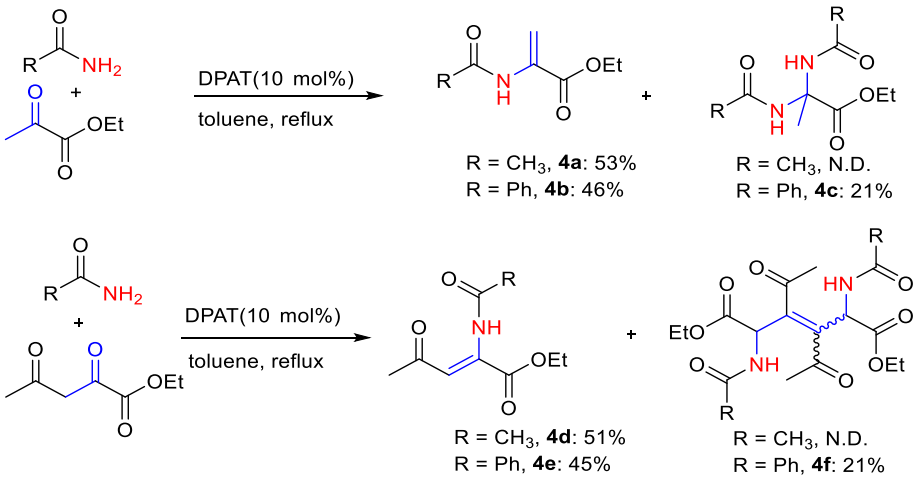
[c]Urea (0.6 mmol), β-dicarbonyl compounds (0.5 mmol), under optimized conditions

mixture). The occurrence of (*Z*)-selectivity was probably due to feasible hydrogen-bond formation between (N)H and O(=C). For example, the screened β-ketoesters were all effective substrates examined, which could proceed this condensation well with aromatic amides or aliphatic amides to gave the corresponding products in 51–98% yields. Aromatic amides bearing electron-donating groups at 4-position of aromatic ring such as methoxy **2b** provided the desired products in 93% yield. The electron-withdrawing substituents at 4-position of aryl group such as chloro or nitro, seem to disfavor this transformation, as the yield was reduced to 79%, 51%. β-Diketone substrate was also tolerated well for this transformation and provided the desired product **3h** in 86% yield. However, it failed to give the product when 1,3-cyclohexanedione or 1,3-diphenylpropane-1,3-dione was used as β-diketone substrate mainly due to their steric hindrance and inherent low reactivity (Table 2). Satisfactorily, amides substrate including the aromatic amides, aliphatic amide and benzylamide were all compatible for this protocol, providing a series of products β-enaminones via condensation with β-diketones (β-ketoesters) (Table 2). Furthermore, an unprotected β-amino product was observed when urea was used as substrate. Urea successfully functions as a latent scaffold for amino group. Products **3i**, **3j** and **3k**, the intermediates for synthesis of sitagliptin that is an active ingredient of antidiabetic drug used in the treatment of type 2 diabetes mellitus (T2DM) (Enguzel-Alperen et al. 2018), could be synthesized via the condensation with amides under optimized conditions in satisfied yields. Furthermore, aromatic amines and benzylamine were investigated

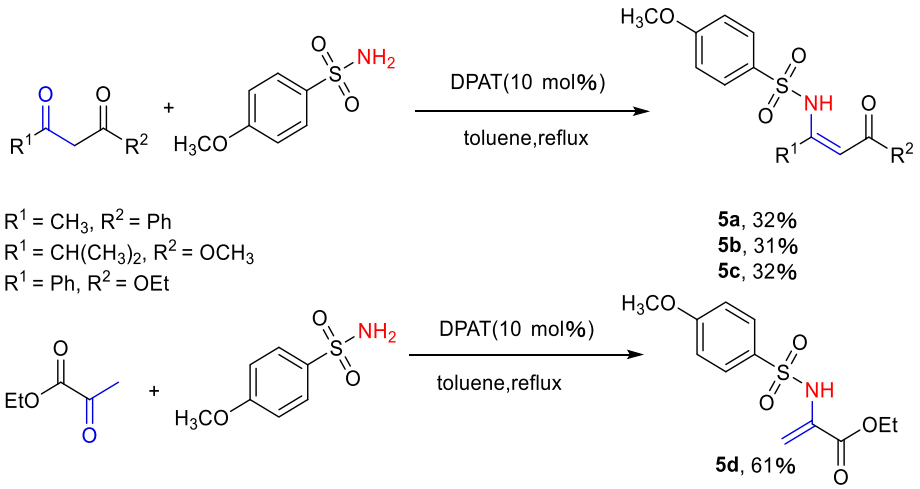
for this reaction and the results are given in Table 2. Screening revealed that the reactions between aromatic amines and 1,3-diketones or β-ketoesters could proceeded smoothly and provided the desired products **3v**–**3z** in 47–95% yields. The general applicability of our method was then extended to the condensation of α-ketoesters with acetamide or benzamide (Scheme 2). α-Ketoesters with acetamide only led to the synthesis of desired products **4a** and **4d** in moderate yields. Moreover, it only selectively gave the product **4d** when the condensation between acetamide and ethyl 2,4-dioxopentanoate was proceeded under optimized conditions. To our surprise, except for the desired product **4b** (46%), an unexpected bis(benzamide) byproduct **4c** was also obtained between the condensation of benzamide with ethyl pyruvate in 21% yield (Scheme 2). Interestingly, a similar result was obtained when using 2,4-dioxovalerate as substrate instead of ethyl pyruvate. Besides the isolation of the desired product **4e** in a yield of 45%, the coupling product **4f** was isolated in 21% yield. Finally, it was delight to find that this approach was also applicable to sulfonamides though its activity was inferior to amides, such as 4-methoxybenzenesulfonamide, giving the corresponding products in 31 to 61% yields (Scheme 3, **5a**–**5d**).

To gain mechanistic insight into the transformation of **4c**, the control experiment was carried out (Scheme 4).

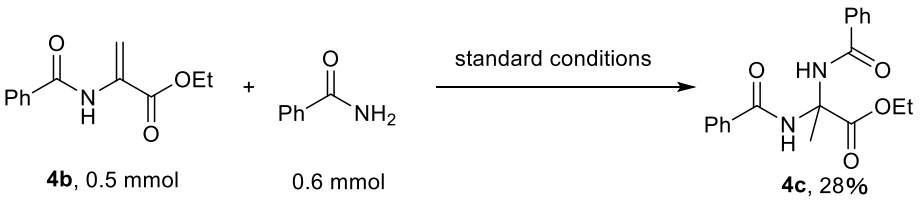
Scheme 2 Reaction between acetamide (benzamide) and α-ketoester



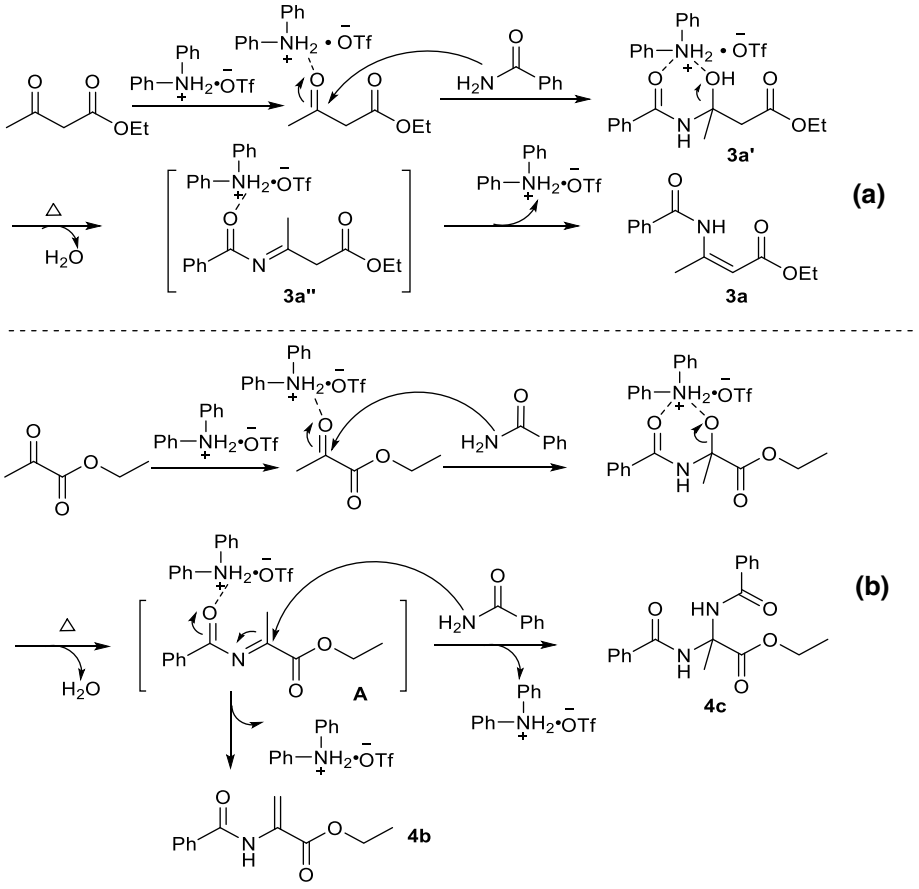
Scheme 3 Condensation reaction between 4-methoxybenzenesulfonamide and α- and β-keto compounds



Scheme 4 Control experiment



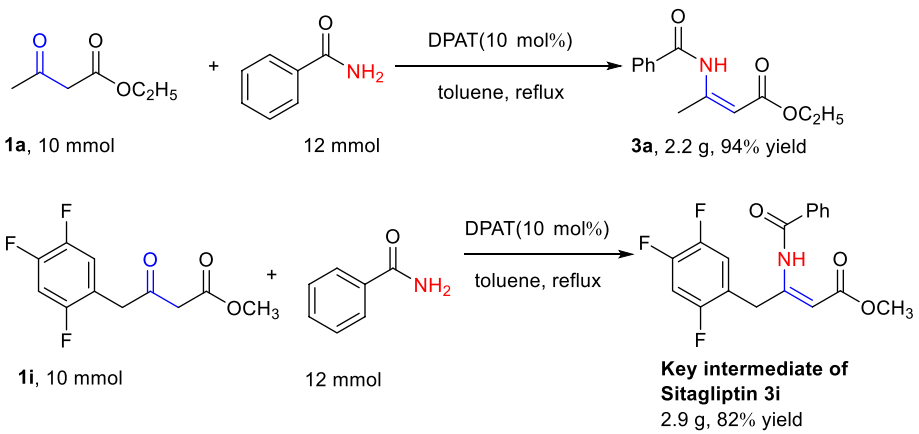
Scheme 5 Proposed mechanism



The condensation of benzamide with **4b** was conducted and provided the desired product **4c** in 28% yield.

According to the above mentioned observations, a possible mechanism for the DPAT-catalyzed synthesis of **3a** and **4c** has been proposed in Scheme 5. Initially, the **3a′** is formed after condensation between benzamide and ethyl acetoacetate in the presence of DPAT, followed by elimination of a molecule of H_2O to generate the imine intermediate **3a″**. After removing the catalyst DPAT, the **3a″** is transformed into the desired product **3a** (Scheme 5a). Similarly, the imine **A** is generated after the condensation of benzamide with ethyl pyruvate in the presence of DPAT. Subsequently, the imine **A** is attacked by the benzamide to form the coupling product **4c**. Meanwhile, **A** is also transformed into the more stable product **4b** by removing the catalyst DPAT (Scheme 5b). In addition, no bis-addition product was detected between the reaction of acetamide with α-ketoesters (Scheme 2), suggesting that the imine intermediate formed by acetamide and α-ketoesters is probably unstable due to lack of large conjugated system.

Scheme 6 Gram-scale synthesis of product **3a** and **3i**



To further demonstrate the practicality of this transformation, a gram-scale experiment of **1a** and **1i** were carried out. The result is shown in the Scheme 6, **3a** and **3i** was obtained in 94% and 82% yields, respectively, which indicated the easy scale up of this transformation.

Conclusions

DPAT is widely used as organocatalyst in various chemical transformations (Wakasugi et al. 2000; Li et al. 2012). In this work, we have developed a novel method for the synthesis of β-enaminones using DPAT as the metal-free catalyst. This protocol featured by its environmentally benign, simple work-up procedure, easy manipulation and highly efficient, which make it an attractive and useful addition to the existing methods for the synthesis of β-enaminones. Notably, this reaction can be run on the gram-scale, giving the desired products in 94% and 82% yields. Moreover, the amides and sulfonamides were well compatible for this protocol. Further applications of DPAT are ongoing in our laboratory.

Experimental

All reagents were purchased from commercial suppliers and used without further purification. The flash column chromatography was carried out over silica gel (200–400 mesh), purchased from Qingdao Haiyang Chemical Co., Ltd. Melting points were determined on a Büchi B-540 capillary melting point apparatus and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at VARIAN-400, using DMSO-d_6 or $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz. Mass spectra were measured with Thermo Finnigan LCQ-Advantage. High resolution mass spectral (HRMS) analyze were measured on an Agilent 6210 TOF LC/MS and Q-Exactuve(Thermo USA) UHPLC-Q-Orbitrap using ESI techniques.

General procedures for the synthesis of β-enaminones

A mixture of amides (amines) (0.6 mmol), 1,3-dicarbonyl compounds (0.5 mmol), and DPAT (0.05 mmol) was stirred in refluxing toluene for 6 h. After completion of the reaction (Reaction progress was monitored by TLC), the mixture was washed with water (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated. Purification by column chromatography on silica gave the product **3**, **4**, **5**.

(*Z*)-Ethyl 3-benzamidobut-2-enoate (3a)

White solid; m.p.: 47.3–47.6 °C. (lit. of Aberhart and Lin 1981)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (s, 1H), 7.92–7.90 (m, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 5.00 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 165.0, 155.1, 133.8, 132.1, 128.6, 127.4, 97.2, 59.9, 22.1, 14.4.

MS (ESI): *m/z* = 234.1 $[M+H]^+$.

(*Z*)-Ethyl 3-(4-methoxybenzamido)but-2-enoate (3b)

White solid; m.p.: 108.5–109.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (s, 1H), 7.97 (d, *J* = 9.2 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 2H), 5.02 (d, *J* = 0.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 2.54 (d, *J* = 0.8 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 164.9, 162.9, 155.7, 129.7, 126.3, 114.1, 96.8, 59.9, 55.4, 22.1, 14.3.

HRMS (ESI): $C_{14}H_{17}NNaO_4$ $[M+Na]^+$; calculated: 286.1050, found: 286.1050.

(*Z*)-Ethyl 3-(4-chlorobenzamido)but-2-enoate (3c)

White solid; m.p.: 88.3–89.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.17 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 5.07 (d, *J* = 0.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.54 (d, *J* = 0.8 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 164.2, 155.2, 138.8, 132.4, 129.1, 129.0, 97.7, 60.1, 22.0, 14.3.

HRMS (ESI): $C_{13}H_{14}ClNNaO_3$ $[M+Na]^+$; calculated: 290.0554 found: 290.0566.

(*Z*)-Ethyl 3-(4-nitrobenzamido)but-2-enoate (3d)

Yellow solid; m.p.: 122.3–123.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.36 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 5.13 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 163.2, 154.7, 150.0, 139.5, 128.8, 124.0, 98.7, 60.3, 21.9, 14.3.

HRMS (ESI): $C_{13}H_{14}N_2NaO_5$ $[M+Na]^+$; calculated: 301.0795 found: 301.0797.

(*Z*)-Ethyl 3-(picolinamido)but-2-enoate (3e)

White solid; m.p.: 76.7–77.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.00 (s, 1H), 8.77 (d, *J* = 4.4 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.91–7.87 (m, 1H),

7.52–7.46 (m, 1H), 5.09 (s, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.56 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 163.4, 153.4, 149.9, 148.8, 137.4, 126.6, 122.9, 98.9, 59.9, 22.1, 14.4.

HRMS (ESI): $C_{12}H_{14}N_2NaO_3$ $[M+Na]^+$; calculated: 257.0897 found: 257.0911.

(*Z*)-Methyl 3-benzamidobut-2-enoate (3f)

White solid; m.p.: 55.2–55.7 °C. (lit. of Holz et al. 2003)

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.08 (s, 1H), 7.98–7.95 (m, 2H), 7.56–7.52 (m, 1H), 7.50–7.46 (m, 2H), 5.04 (s, 1H), 3.74 (s, 3H), 2.54 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.1, 155.4, 133.8, 132.2, 128.7, 127.5, 96.8, 51.2, 22.2.

MS (ESI): m/z = 242.4 $[M+Na]^+$.

(*Z*)-*Tert*-butyl 3-benzamidobut-2-enoate (3g)

White solid; m.p.: 80.2–80.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (s, 1H), 7.97–7.95 (m, 2H), 7.54–7.47 (m, 3H), 4.95 (s, 1H), 2.50 (s, 3H), 1.50 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.2, 154.0, 134.0, 132.1, 128.6, 127.5, 99.2, 80.4, 28.4, 22.1.

HRMS (ESI): $C_{15}H_{20}NO_3$ $[M+H]^+$; calculated: 262.1438, found: 262.1435.

(*Z*)-*N*-(4-oxo-4-phenylbut-2-en-2-yl)benzamide (3h)

Yellow solid; m.p.: 108.6–109.2 °C. (lit. of Sugiura et al. 2009)

^{1}H NMR (600 MHz, $CDCl_3$) δ 13.87 (s, 1H), 8.14–8.13 (m, 2H), 7.99–7.98 (m, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.59–7.55 (m, 3H), 7.50 (t, J = 7.8 Hz, 2H), 6.21 (s, 1H), 2.71 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 166.2, 158.2, 138.8, 133.8, 132.7, 132.5, 129.0, 128.6, 128.1, 127.7, 102.6, 22.8.

MS (ESI): m/z = 288. 1 $[M+Na]^+$.

(*Z*)-Methyl 3-benzamido-4-(2,4,5-trifluorophenyl) but-2-enoate (3i)

Yellow solid; m.p.: 119.8–120.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.04 (s, 1H), 7.91–7.89 (m, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.10–7.04 (m, 1H), 6.92–6.86 (m, 1H), 4.91 (s, 1H), 4.29 (s, 2H), 3.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 165.0, 156.0 (dm, J_F = 247.0 Hz), 155.0, 149.0 (dm, J_F = 246.0 Hz), 146.5 (dm, J_F = 242.0 Hz), 133.4, 132.5, 128.8, 127.6, 120.4 (dm, J_F = 15.0 Hz), 118.4 (dm, J_F = 20.0 Hz), 105.5 (tm, J_F = 24.0 Hz), 98.1 (d, J_F = 4.0 Hz), 51.5, 32.7.

HRMS (ESI): $C_{18}H_{13}F_3NO_3$ $[M-H]^-$; calculated: 348.0853, found: 348.0861.

(*Z*)-Methyl 3-(2-phenylacetamido)-4-(2,4,5-trifluorophenyl) but-2-enoate (3j)

White solid; m.p.: 104.2–104.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.35–7.25 (m, 5H), 6.99–6.93 (m, 1H), 6.91–6.84 (m, 1H), 4.80 (s, 1H), 4.11 (s, 2H), 3.66 (s, 3H), 3.63 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.7, 155.8 (dm, J_F = 244.0 Hz), 154.1, 148.9 (dm, J_F = 235.0 Hz), 146.5 (dm, J_F = 241.0 Hz), 133.4, 129.1, 128.7, 127.3, 120.1 (dm, J_F = 20.0 Hz), 118.1 (dm, J_F = 20.0 Hz), 105.4 (tm, J_F = 19.0 Hz), 98.0, 51.3, 45.6, 32.5.

HRMS (ESI): $C_{19}H_{15}F_3NO_3$ $[M-H]^-$; calculated: 362.1010, found: 362.0998.

(*Z*)-Methyl 3-acetamido-4-(2,4,5-trifluorophenyl) but-2-enoate (3k)

White solid; m.p.: 102.6–102.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 7.03–6.96 (m, 1H), 6.89–6.83 (m, 1H), 4.78 (s, 1H), 4.11 (s, 2H), 3.68 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.6, 155.8 (dm, J_F = 243.0 Hz), 154.4, 149.0 (dm, J_F = 248.0 Hz), 146.5 (dm, J_F = 241.0 Hz), 120.2 (dt, J_F = 19.0, 5.0 Hz), 118.2 (dt, J_F = 19.0, 5.0 Hz), 105.4 (tm, J_F = 26.0 Hz), 97.2 (d, J_F = 4.0 Hz), 51.3, 32.4, 25.3.

HRMS (ESI): $C_{13}H_{11}F_3NO_3$ $[M-H]^-$; calculated: 286.0697, found: 286.0691.

(*Z*)-Methyl 3-amino-4-methylpent-2-enoate (3l)

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.53 (s, 1H), 3.61 (s, 3H), 2.30 (m, 1H), 1.12 (d, J = 7.8 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 169.7, 80.3, 50.0, 34.8, 21.1.

HRMS (ESI): $C_7H_{14}NO_2$ $[M+H]^+$; calculated: 144.1019, found: 144.1021.

(*Z*)-Ethyl 3-acetamidobut-2-enoate (3m)

White solid; m.p.: 63.1–63.6 °C. (lit. of Lee and Zhang 2002)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 4.88 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.14 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 168.6, 154.8, 96.3, 59.8, 25.3, 22.0, 14.4.

MS (ESI): $m/z = 172.0\ [M+H]^+$.

(*Z*)-*N*-(4-oxo-4-phenylbut-2-en-2-yl)acetamide (3n)

Yellow solid; m.p.: 97.8–98.9 °C. (lit. of Sugiura et al. 2009)

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.82 (s, 1H), 7.92 (d, $J = 7.0$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 8.0$ Hz, 2H), 6.05 (s, 1H), 2.53 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.4, 169.9, 157.6, 138.7, 132.4, 128.6, 127.6, 101.6, 25.5, 22.5.

MS (ESI): $m/z = 226.1\ [M+Na]^+$

(*Z*)-Ethyl 3-acetamido-3-phenylacrylate (3o)

White solid; m.p.: 42.5–44.8 °C. (lit. of Lee and Zhang 2002)

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.43–7.36 (m, 5H), 5.30 (s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 2.19 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 168.4, 154.5, 135.9, 129.6, 128.0, 127.1, 101.1, 60.3, 24.8, 14.3.

MS (ESI): $m/z = 256.2\ [M+Na]^+$

(*Z*)-Methyl 3-acetamido-4-methylpent-2-enoate (3p)

Yellow oil. (lit. of Wu et al. 2011)

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.15 (s, 1H), 5.07 (s, 1H), 3.87 (m, 1H), 3.71 (s, 3H), 2.15 (s, 3H), 1.12 (d, $J = 6.6$ Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 168.4, 165.7, 92.3, 51.1, 29.3, 25.6, 21.3.

MS (ESI): $m/z = 208.1\ [M+H]^+$.

(*Z*)-Ethyl 3-(2-(2-oxopyrrolidin-1-yl)butanamido) but-2-enoate (3q)

White solid; m.p.: 60.2–60.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 4.92 (d, $J = 1.0$ Hz, 1H), 4.66 (dd, $J_1 = 10.8$ Hz, $J_2 = 4.8$ Hz, 1H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.42–3.32 (m, 2H), 2.66–2.59 (m, 1H), 2.51–2.41 (m, 1H), 2.36 (d, $J = 1.0$ Hz, 3H), 2.22–2.00 (m, 4H), 1.25 (t, $J = 7.2$ Hz, 3H), 0.92 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 169.6, 168.9, 154.0, 98.2, 60.2, 57.7, 43.8, 31.0, 22.1, 21.3, 18.3, 14.7, 11.2.

HRMS (ESI): $C_{14}H_{21}N_2O_4$ $[M+H]^+$; calculated: 281.1507, found: 281.1493.

(*Z*)-Methyl 3-(benzylamino)but-2-enoate (3r)

White solid; m.p.: 35.2–35.6 °C. (lit. of Hebbache et al. 2008).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.34–7.23 (m, 5H), 4.53 (s, 1H), 4.42 (d, $J = 6.4$ Hz, 2H), 3.63 (s, 3H), 1.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 161.6, 138.5, 128.6, 127.2, 126.5, 82.8, 50.0, 46.8, 19.4.

MS (ESI): $m/z = 206.1\ [M+H]^+$.

(*Z*)-Ethyl 3-(benzylamino)but-2-enoate (3s)

White solid; m.p.: 22.1–22.6 °C. (lit. of Hebbache et al. 2008).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.34–7.23 (m, 5H), 4.52 (s, 1H), 4.42 (d, $J = 6.4$ Hz, 2H), 4.08 (q, $J = 7.2$ Hz, 2H), 1.91 (s, 3H), 1.26 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 161.5, 138.6, 128.6, 127.2, 126.5, 83.2, 58.4, 46.8, 19.4, 14.7.

MS (ESI): $m/z = 220.4\ [M+H]^+$.

(*Z*)-*Tert*-butyl 3-(benzylamino)but-2-enoate (3t)

Yellow oil. (lit. of Hebbache et al. 2008)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.34–7.22 (m, 5H), 4.45 (s, 1H), 4.40 (d, $J = 6.4$ Hz, 2H), 1.87 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.2, 138.9, 128.6, 127.1, 126.6, 85.0, 77.9, 46.8, 28.8, 19.4.

MS (ESI): $m/z = 248.2\ [M+H]^+$.

(*Z*)-4-(benzylamino)pent-3-en-2-one (3u)

White solid; m.p.: 25.1–25.3 °C. (lit. of Chen et al. 2010)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (s, 1H), 7.34–7.22 (m, 5H), 5.03 (s, 1H), 4.45 (d, $J = 6.4$ Hz, 2H), 2.03 (s, 3H), 1.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 162.8, 137.8, 128.6, 127.2, 126.5, 95.8, 46.7, 28.9, 18.9.

MS (ESI): $m/z = 190.0\ [M+H]^+$.

(*Z*)-4-(phenylamino)pent-3-en-2-one (3v)

White solid; m.p.: 50.3–50.7 °C. (lit. of Chen et al. 2010).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.44 (s, 1H), 7.32 (t, $J = 8.0$ Hz, 2H), 7.17 (t, $J = 7.6$ Hz, 1H), 7.11–7.06 (m, 2H), 5.18 (s, 1H), 2.10 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 159.9, 138.6, 128.9, 125.3, 124.6, 97.5, 29.2, 19.9.

MS (ESI): $m/z = 176.2\ [M+H]^+$.

(*Z*)-Ethyl 3-((4-methoxyphenyl)amino)but-2-enoate (3w)

White solid; m.p.: 40.6–41.2 °C. (lit. of Zhang et al. 2006)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.04 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 4.67 (s, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.82 (s, 3H), 1.90 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 160.0, 157.4, 132.2, 126.8, 114.2, 84.7, 58.6, 55.5, 20.1, 14.6.

MS (ESI): $m/z = 236.2\ [M+H]^+$.

(*Z*)-Ethyl 3-((4-chlorophenyl)amino)but-2-enoate (3x)

White solid; m.p.: 51.0–52.0 °C. (lit. of Zhang et al. 2006)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.34–7.28 (m, 2H), 7.03 (d, $J = 8.8$ Hz, 2H), 4.73 (s, 1H), 4.17 (q, $J = 7.2$ Hz, 2H), 2.00 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 158.4, 138.0, 130.3, 129.2, 125.5, 86.9, 58.9, 20.2, 14.6.

MS (ESI): $m/z = 240.1\ [M+H]^+$.

(*Z*)-Ethyl 3-((4-nitrophenyl)amino)but-2-enoate (3y)

Green solid; m.p.: 112.0–112.8 °C. (lit. of Zhang et al. 2006)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.96 (s, 1H), 8.23 (d, $J = 8.8$ Hz, 2H), 7.17 (d, $J = 8.8$ Hz, 2H), 4.93 (s, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.26 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 155.7, 145.8, 142.8, 125.3, 120.6, 91.6, 59.5, 21.0, 14.4.

MS (ESI): $m/z = 251.1\ [M+H]^+$.

(*Z*)-Ethyl 3-(naphthalen-2-ylamino)but-2-enoate (3z)

Yellow oil; (lit. of Chen et al. 2010)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.10 (d, $J = 7.6$ Hz, 1H), 7.93–7.91 (m, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.62–7.54 (m, 2H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.36–7.32 (m, 1H), 4.86 (s, 1H), 4.26 (q, $J = 7.2$ Hz, 2H), 1.90 (s, 3H), 1.38 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 160.5, 135.4, 134.3, 130.5, 128.2, 126.7, 126.6, 126.4, 125.3, 123.6, 122.8, 85.7, 58.8, 20.0, 14.7.

MS (ESI): $m/z = 256.2\ [M+H]^+$.

Ethyl 2-acetamidoacrylate (4a)

Yellow oil. (lit. of Yamashita et al. 2014)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H, NH), 6.46 (s, 1H, =CH), 5.77 (d, $J = 1.0$ Hz, 1H, =CH), 4.18 (q, $J = 7.0$ Hz, 2H), 2.03 (s, 3H), 1.23 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 163.8, 131.0, 108.1, 61.8, 24.2, 13.8.

MS (ESI): $m/z = 158.0\ [M+H]^+$.

Ethyl 2-benzamidoacrylate (4b)

Yellow oil. (lit. of Yang et al. 2018)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H, NH), 7.84–7.81 (m, 2H), 7.55–7.51 (m, 1H), 7.49–7.44 (m, 2H), 6.77 (s, 1H, =CH), 5.99 (d, $J = 1.6$ Hz, 1H, =CH), 4.33 (q, $J = 7.2$ Hz, 2H), 1.38 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.0, 134.2, 131.8, 131.1, 128.6, 126.8, 108.4, 62.3, 14.2.

MS (ESI): $m/z = 220.1\ [M+H]^+$.

Ethyl 2,2-bis(benzamido)propanoate (4c)

White solid; m.p.: 132.0–133.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.78–7.75 (m, 4H), 7.50–7.46 (m, 2H), 7.39 (t, $J = 7.6$ Hz, 4H), 4.35 (q, $J = 7.2$ Hz, 2H), 2.08 (s, 3H), 1.32 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 168.7, 133.5, 131.8, 128.4, 127.1, 67.3, 62.9, 23.8, 14.2.

HRMS (ESI): $C_{19}H_{20}N_2O_4Na\ [M+Na]^+$; calculated: 363.1315, found: 363.1316.

(*Z*)-Ethyl 4-acetamido-2-oxopent-3-enoate (4d)

Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.18 (s, 1H), 5.75 (s, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 2.27 (s, 3H), 2.18 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 168.4, 163.9, 142.7, 106.3, 62.3, 31.0, 23.4, 13.8.

HRMS (ESI): $C_9H_{12}NO_4\ [M\text{-}H]^-$; calculated: 198.0772, found: 198.0777.

(*Z*)-Ethyl 2-benzamido-4-oxopent-2-enoate (4e)

Yellow solid; m.p.: 107.2–107.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 7.95–7.93 (m, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 2H), 5.85 (s, 1H), 4.39 (q, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 1.37 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 165.7, 163.1, 143.5, 133.0, 132.6, 128.8, 128.0, 106.5, 62.6, 29.8, 14.2.

HRMS (ESI): $C_{14}H_{16}NO_4\ [M+H]^+$; calculated: 262.1074, found: 262.1075.

Diethyl 3,4-diacetyl-2,5-bis(benzamido) hex-3-enedioate (4f)

Yellow solid; m.p.: 103.2–103.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.32 (s, 2H), 8.06 (d, J = 7.6 Hz, 4H), 7.59 (t, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 4H), 6.28 (s, 2H), 4.36 (q, J = 7.2 Hz, 4H), 2.68 (s, 6H), 1.41 (t, J = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 164.6, 163.9, 143.6, 133.0, 131.5, 128.8, 128.0, 62.5, 31.2, 22.9, 14.1.

HRMS (ESI): $C_{28}H_{30}N_2O_8Na$ $[M + Na]^+$; calculated: 545.1894, found: 545.1902.

(*Z*)-4-methoxy-*N*-(4-oxo-4-phenylbut-2-en-2-yl) benzenesulfonamide (5a)

Yellow solid; m.p.: 70.8–72.0 °C. (lit. of Lee et al. 2017)

^{1}H NMR (600 MHz, $CDCl_3$) δ 13.34 (s, 1H), 7.93–7.88 (m, 4H), 7.55 (t, J = 7.8 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 6.05 (s, 1H), 3.89 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 191.1, 163.4, 156.3, 138.0, 132.6, 132.0, 129.5, 128.6, 127.7, 114.6, 100.5, 55.7, 20.2.

MS (ESI): m/z = 354.3 $[M + H]^+$.

(*Z*)-Methyl 3-((4-methoxyphenyl) sulfonamido)-4-methylpent-2-enoate (5b)

Yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.01 (s, 1H), 7.82 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 5.04 (s, 1H), 3.88 (s, 3H), 3.72 (s, 3H), 3.13 (dt, J = 13.2, 7.2 Hz, 1H), 1.02 (d, J = 6.6 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 164.4, 163.3, 129.3, 128.3, 114.4, 93.9, 55.7, 51.3, 29.4, 21.8.

HRMS (ESI): $C_{14}H_{18}NO_5S$ $[M-H]^-$; calculated: 312.0911, found: 312.0906.

(*Z*)-Ethyl 3-((4-methoxyphenyl) sulfonamido)-3-phenylacrylate (5c)

Yellow solid; m.p.: 76.6–78.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.46 (m, 3H), 7.36–7.30 (m, 4H), 6.86 (d, J = 9.0 Hz, 2H), 5.22 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 163.2, 155.0, 134.0, 131.0, 130.5, 129.7, 128.9, 127.9, 113.9, 102.1, 60.5, 55.6, 14.2.

HRMS (ESI): $C_{18}H_{18}NO_5S$ $[M-H]^-$; calculated: 360.0911, found: 360.0909.

Ethyl 2-((4-methoxyphenyl)sulfonamido)acrylate (5d)

Yellow solid; m.p.: 96.1–97.9 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 9.0 Hz, 2H), 7.13 (s, 1H), 6.98 (d, J = 8.4 Hz, 2H), 5.66 (s, 2H), 4.22 (q, J = 7.2 Hz, 2H), 3.88 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.4, 163.2, 131.1, 129.9, 129.8, 114.2, 106.6, 62.5, 55.7, 14.0.

HRMS (ESI): $C_{12}H_{14}NO_5S$ $[M-H]^-$; calculated: 284.0598, found: 284.0605.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Nos. 21776254 and 21406203).

Compliance with ethical standards

Conflict of interest There is no conflict of interest.

References

Aberhart DJ, Lin HJ (1981) Synthesis of geometrical isomers of β-arylamidoacrylic esters. J Org Chem 46:3749–3751. https://doi.org/10.1021/jo00331a041

Arcadi A, Bianchi G, Giuseppe SD, Marinelli F (2003) Gold catalysis in the reactions of 1,3-dicarbonyls with nucleophiles. Green Chem 5:64–67. https://doi.org/10.1039/b210165c

Baraldi PG, Simoni D, Manfredini S (1983) An improved preparation of enaminones from 1,3-diketones and ammonium acetate or amine acetates. Synthesis 11:902–903. https://doi.org/10.1055/s-1983-30557

Bartoli G, Bosco M, Locatelli M, Marcantoni E, Melchiorre P, Sambri R (2004) $Zn(ClO_4)_2{\cdot}6H_2O$ as a powerful catalyst for the conversion of β-ketoesters into β-enamino esters. Synlett 2:239–242. https://doi.org/10.1055/s-2003-44974

Chen JX, Zhang CF, Gao WX, Jin HL, Ding JC, Wu HY (2010) B_2O_3/Al_2O_3 as a new, highly efficient and reusable heterogeneous catalyst for the selective synthesis of β-enamino ketones and esters under solvent-free conditions. J Braz Chem Soc 21:1552–1556. https://doi.org/10.1590/S0103-50532010000800021

Chen G, Wang Z, Zhang XY, Fan XS (2017) Synthesis of functionalized pyridines via Cu(II)-catalyzed one-pot cascade reactions of inactivated saturated ketones with electrondeficient enamines. J Org Chem 82:11230–11237. https://doi.org/10.1021/acs.joc.7b01901

Dalpozzo R, Nino AD, Nardi M, Russo B, Procopio A (2006) Erbium(III) triflate: a valuable catalyst for the synthesis of aldimines, ketimines, and enaminone. Synthesis 7:1127–1132. https://doi.org/10.1055/s-2006-926378

Edafiogho IO, Ananthalakshmi KVV, Kombian SB (2006) Anticonvulsant evaluation and mechanism of action of benzylamino enaminones. Bioorg Med Chem 14:5266–5272. https://doi.org/10.1016/j.bmc.2006.03.049

Enguzel-Alperen C, Unal F, Yuzbasioglu D (2018) Investigation of in vitro genotoxic effects of an anti-diabetic drug sitagliptin.

Food Chem Toxicol 112:235–241. https://doi.org/10.1016/j.fct.2018.01.003
Fatima A, Adel A (2005) Heterocyclic synthesis via enaminones: novel synthesis of (1H)-pyridin-2-one, pyrazolo[1,5-a]pyrimidine and isoxazole derivatives incorporating a *N*-methylphthalimide and their biological evaluation. J Heterocycl Chem 42:307–311. https://doi.org/10.1002/jhet.5570420222
Guin J, Mück-Lichtenfeld C, Grimme S, Studer A (2007) Radical transfer hydroamination with aminated cyclohexadienes using polarity reversal catalysis: scope and limitations. J Am Chem Soc 129:4498–4503. https://doi.org/10.1021/ja0692581
Harrad MA, Outtouch R, Ali MA, Firdoussi LE, Karim A, Roucoux A (2010) $Ca(CF_3COO)_2$: an efficient Lewis acid catalyst for chemo- and regio-selective enamination of β-dicarbonyl compounds. Catal Commun 11:442–446. https://doi.org/10.1016/j.catcom.2009.11.019
Hebbache H, Hank Z, Boutamine S, Meklati M, Bruneau C, Renaud JL (2008) Iron salts catalyzed synthesis of β-*N*-substituted aminoacrylates. C R Chimie 11:612–619. https://doi.org/10.1016/j.crci.2007.12.004
Holz J, Monsees A, Jiao HJ et al (2003) Synthesis of a new chiral bisphospholane ligand for the Rh(I)-catalyzed enantioselective hydrogenation of isomeric β-Acylamido acrylates. J Org Chem 68:1701–1707. https://doi.org/10.1021/jo020453h
Jiang J, Zhang M, Wu WB, Lu HB, Shi YL, Li JJ (2018) L-Phenylalanine triflate as organocatalyst for divergent approaches to trisubstituted hexahydroimidazo[1,2-a]pyridine and 1,4-diazepane derivatives. Synlett 29:246–250. https://doi.org/10.1055/s-0036-1589115
Klapars A, Campos KR, Chen CY, Volante RP (2005) Preparation of enamides via palladium-catalyzed amidation of enol tosylates. Org Lett 7:1185–1188. https://doi.org/10.1021/ol050117y
Lee SG, Zhang YJ (2002) Rh(I)-catalyzed enantioselective hydrogenation of (E)- and (Z)-β-(acylamino)acrylates using 1,4-bisphosphine ligands under mild conditions. Org Lett 4:2431–2492. https://doi.org/10.1021/ol0261884
Lee D, Kim SM, Hirao H, Hong SK (2017) Gold(I)/Gold(III)-catalyzed selective synthesis of *N*-sulfonyl enaminone isomers from sulfonamides and ynones via two distinct reaction pathways. Org Lett 19:4734–4737. https://doi.org/10.1021/acs.orglett.7b02022
Li JJ, Gui XX (2014) L-ProT catalyzed highly regioselective *N*-alkoxyalkylation of purine rings with vinyl ethers. Chin Chem Lett 25:1341–1345. https://doi.org/10.1016/j.cclet.2014.04.023
Li JJ, He P, Yu CM (2012) DPTA-catalyzed one-pot regioselective synthesis of polysubstituted pyridines and 1,4-dihydropyridines. Tetrahedron 68:4138–4144. https://doi.org/10.1016/j.tet.2012.03.104
Li Y, Peng JS, Chen X et al (2018) Copper-catalyzed synthesis of multisubstituted indoles through tandem Ullmann-type C–N formation and cross-dehydrogenative coupling reactions. J Org Chem 83:5288–5294. https://doi.org/10.1021/acs.joc.8b00353
Mahjoob S, Montazeri N (2012) Highly efficient and easy synthesis of 2,4,6-triarylpyridines catalyzed by pentafluorophenylammonium triflate (PFPAT) as a new recyclable solid acid catalyst in solvent-free conditions. Chin Chem Lett 23:419–422. https://doi.org/10.1016/j.cclet.2012.01.035
Martin DF, Janusonis GA, Martin BB (1961) Stabilities of bivalent metal complexes of some β-ketoimines. J Am Chem Soc 83:73–75. https://doi.org/10.1021/ja01462a015
Mercs L, Pozzi G, Quici S (2007) Efficient condensation of carboxylic acids with alcohols catalyzed by fluorous ammonium triflates. Tetrahedron Lett 48:3053–3056. https://doi.org/10.1016/j.tetlet.2007.02.117
Ovenden SPB, Capon RJ (1999) Amphilactams A–D: novel nematocides from southern Australian marine sponges of the genus amphimedon. J Org Chem 64:1140–1144. https://doi.org/10.1021/jo981377e
Sugiura M, Kumahara M, Nakajima M (2009) Asymmetric synthesis of 4H-1,3-oxazines: enantioselective reductive cyclization of *N*-acylated β-amino enones with trichlorosilane catalyzed by chiral lewis bases. Chem Commun. https://doi.org/10.1039/b905102c
Tabatabaeian N, Shojaei AF, Shirini F, Hejazi SZ, Rassa M (2014) A green multicomponent synthesis of bioactive pyrimido[4,5-b]quinolone derivatives as antibacterial agents in water catalyzed by $RuCl_3{\cdot}_XH_2O$. Chin Chem Lett 25:308–312. https://doi.org/10.1016/j.cclet.2013.10.021
Wakasugi K, Misaki T, Yamada K, Tanabe Y (2000) Diphenylammonium triflate (DPAT): efficient catalyst for esterification of carboxylic acids and for transesterification of carboxylic esters with nearly equimolar amounts of alcohols. Tetrahedron Lett 41:5249–5252. https://doi.org/10.1016/S0040-4039(00)00821-2
Winck CR, Darbem MP, Gomes RS, Rinaldi AW, Domingues NL (2014) $Zn[aminoacid]_2$ hybrid materials applied as heterogeneous catalysts in the synthesis of β-enaminones. Tetrahedron Lett 55:4123–4125. https://doi.org/10.1016/j.tetlet.2014.05.122
Wu Y, Qi SB, Wu FF et al (2011) Synthesis of β-amino acid derivatives via copper-catalyzed asymmetric 1,4-reduction of β-(acylamino) acrylates. Org Lett 13:1754–1757. https://doi.org/10.1021/ol200287z
Yamashita T, Matoba H, Kuranaga T, Inoue M (2014) Total syntheses of nobilamides B and D: application of traceless Staudinger ligation. Tetrahedron 70:7746–7752. https://doi.org/10.1016/j.tet.2014.05.091
Yang T, Fan X, Zhao X, Yu W (2018) Iron-catalyzed acyl migration of tertiary α-azidyl ketones: synthetic approach toward enamides and isoquinolones. Org Lett 20:1875–1879. https://doi.org/10.1021/acs.orglett.8b00409
Zhang ZH, Yin L, Wang YM (2006) A general and efficient method for the preparation of β-enamino ketones and esters catalyzed by indium tribromide. Adv Synth Catal 348:184–190. https://doi.org/10.1002/adsc.200505268
Zhang JP, Huang J, Liu C et al (2014) Discovery of a series of pyridopyrimidine derivatives as potential topoisomerase I inhibitors. Chin Chem Lett 25:1025–1028. https://doi.org/10.1016/j.cclet.2014.05.048
Zhao XY, Zhang Y, Deng J, Zhang-Negrerie D, Du YF (2017) TBHP/TBAI-mediated oxidative cascade reaction consisting of dimerization, cyclization, and 1,2-aryl migration: metal-free synthesis of pyrrolin-4-ones and highly substituted pyrroles. J Org Chem 82:12682–12690. https://doi.org/10.1021/acs.joc.7b02491