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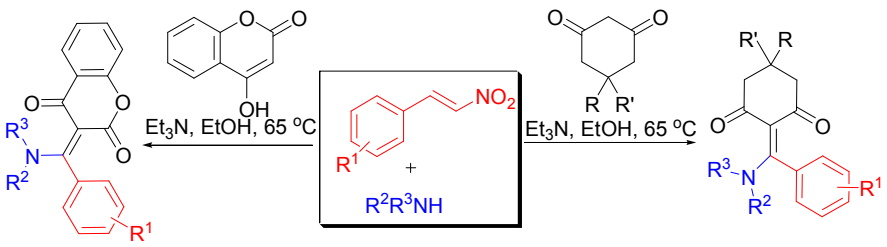

The diversity-oriented synthesis of β-enaminones via three-component reaction between substituted β-nitrostyrenes, β-dicarbonyl compounds and amines has been developed.

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ARTICLE TYPE

Three-Component Reaction between Substituted β-Nitrostyrenes, β-Dicarbonyl Compounds and Amines: Diversity-Oriented Synthesis of Novel β-Enaminones

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An efficient and practical method has been developed for the diversity-oriented synthesis of β-enaminones via three-component reaction between substituted β-nitrostyrenes, β-dicarbonyl compounds and amines for the generation of a wide range of structurally interesting and pharmacologically significant compounds under mild conditions.

Enamino diketone skeleton is a basic structure feature found in a number of important pharmaceutical and agrochemical molecules, including the antimicrobial, antibacterial, anti-inflammatory, antiaggregant, antiischemic, antileukemia[1] and other types of physiological activity. β-Enaminones are also known as effective and ecologically herbicides and safe plant protection agents.[2] (Fig. 1) Additionally, some compounds with enamino diketone skeleton have a great potential for complexation with different metals such as Pd, Ni, and Cu, and the products have different biological activities.[3]

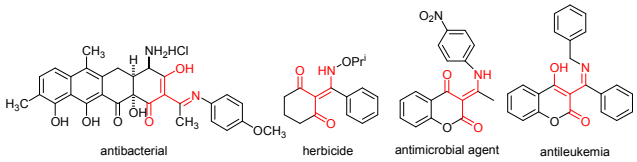


Fig. 1 Examples of bioactive β-enaminones

The variety of chemical reactivity possible with an enamino diketone motif means that they also serve as versatile intermediates in many synthetic routes.[4] This combination of significant pharmacological and biological properties and compelling synthetic utility has resulted in the development of a number of methods for enamino diketone preparation. They are most commonly synthesized either by enamination of the corresponding cyclic 1,3-diketone and triethyl orthoformate with aromatic amines,[5] or by direct nuclophilic addition of the triketones such as 2-benzoyl-1,3-cyclohexanedione with primary or secondary amine.[6] In addition, the condensation of methylketones or ketones with activated methylene with dimethoxy-*N,N*-dimethylmethanamine was usually used to prepare the enaminones.[7] Copper-promoted aminolysis of β-carbonyl 1,3-dithianes with amines was also described to provide an efficient access to β-enaminones.[4d] However, many of the previously developed β-enaminone synthesis possess several disadvantages, including the use of the limited availability of triketone reactants or β-carbonyl 1,3-dithianes.

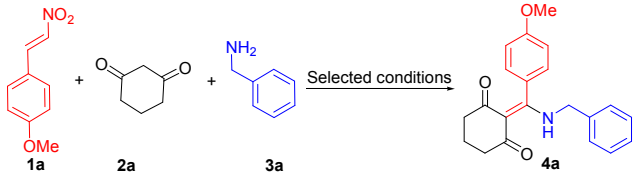
Substituted β-nitrostyrenes are important synthetic intermediates and starting materials for the synthesis of a variety of useful building blocks.[8] In addition, due to the strong electron-withdrawing nature of the NO_2 group, they play a key role in the Michael addition reaction which is an efficient synthetic tool for the formation of C-C bonds.[9] Recently we reported a very straightforward one-pot multicomponent synthesis of polysubstituted piperidines, substituted furo[3,2-c]chromen-4-ones and substituted 4-hydroxybenzofuranes using substituted β-nitrostyrenes as essential building blocks.[10] As a part of our continuous interest directed towards the green and sustainable development of new methodologies using substituted β-nitrostyrenes as essential building blocks for the synthesis of highly functionalized molecules, we report the results of our recent efforts devoted to efficient three-component reaction between substituted β-nitrostyrenes, β-dicarbonyl compounds and amines for the direct formation of β-enaminones under mild conditions.

Initially, we examined the reaction of 1-methoxy-4-(2-nitrovinyl)benzene (**1a**), cyclohexane-1,3-dione (**2a**) with phenylmethanamine (**3a**) using trimethylamine as a catalyst. We were delighted to find that the catalyst trimethylamine gave the desired 2-((benzylamino)(4-methoxyphenyl)methylene)cyclohexane-1,3-dione (**4a**) in 43% yield in the solvent of ethanol at room temperature (Table 1, entry 1). Subsequent experiments with various temperatures revealed that 65-75 °C was the optimal reaction temperature for the three multicomponent reaction, producing the desired product in 65% yield (Table 1, entries 2–5). Low conversion was observed at lower reaction temperature, possibly due to the nucleophilic addition coordination of the amine to C3 of the furan ring with difficulties.

When piperidine was used as the base, it gave no obvious reaction (Table 1, entry 6), indicating the important role of the tertiary amine. When inorganic weak base K_2CO_3 was used, the desired product **4a** was only a minor product (Table 1, entry 7). However, a decisive step-up in the yield of product 4a was achieved when replacing K_2CO_3 with Li_2CO_3 (Table 1, entry 8), which was less effective than triethylamine. As expected, no product **4a** was observed using a strong base NaOH (Table 1, entry 9), possibly due to the difficulty in the formation of

hydroxyl group of the nitrogen. Reducing the amount of triethylamine to half or one equivalent led to decreased yields of product **4a** (Table 1, entries 10 and 11). Further increase of the amount of triethylamine had no significant beneficial effect on the reaction (Table 1, entries 12 and 13). Further experiments revealed that alcohol was confirmed to be the most effective solvent (Table 1, entry 4). Other solvents, such as DMF, THF and 1,4-dioxane, gave lower product yields (Table 1, entries 14, 15 and 16). These optimised reaction conditions employed the same equivalents of 1,3-cyclohexanediones, substituted *β*-nitrostyrene and amine, and 1.5 equivalents of base triethylamine (Table 1, entry 4), and the reaction time for this one-pot process was 6 hours.

Table 1 Optimisation of the reaction conditions[a]

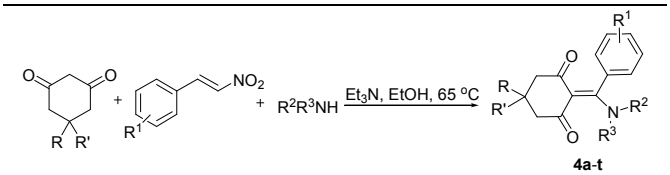


Entry	base/solvent/T(°C)/t(h)	Yield (%)[b]
1	Et_3N (1.5eq)/EtOH/r.t/6	43
2	Et_3N (1.5eq)/EtOH/45/6	49
3	Et_3N (1.5eq)/EtOH/55/6	53
4	Et_3N (1.5eq)/EtOH/65/6	65
5	Et_3N (1.5eq)/EtOH/75/6	64
6	Piperidine (1.5eq)/EtOH/65/6	trace
7	K_2CO_3 (1.5eq)/EtOH/65/ 6	trace
8	Li_2CO_3 (1.5eq)/EtOH/65/ 6	63
9	NaOH(1.5eq)/EtOH/65/ 6	none
10	Et_3N (0.5eq)/EtOH/65/6	59
11	Et_3N (1.0eq)/EtOH/65/6	61
12	Et_3N (2.0eq)/EtOH/65/6	65
13	Et_3N (2.5eq)/EtOH/65/6	65
14	Et_3N (1.5eq)/DMF/65/6	58
15	Et_3N (1.5eq)/THF/65/6	45
16	Et_3N(1.5eq)/1,4-dioxane/65/6	60

[a]Reaction conditions: 3 mmol 1-methoxy-4-(2-nitrovinyl)benzene (**1a**), 3 mmol cyclohexane-1,3-dione (**2a**), 3 mmol phenylmethanamine (**3a**), 15 mL solvent, 6 h. [b]Yields were isolated.

With these reaction conditions identified, our attention turned to examination of the scope of the multicomponent reaction. To determine the scope of the designed protocol, three-component reaction of a number of substituted *β*-nitrostyrenes **1a-n** generated from aromatic aldehydes and nitromethane, commercially available substituted 1,3-cyclohexanediones **2a-c** and amines **3a-j** was carried out under optimized reaction condition, and the results were summarized in Table 2.

Table 2 Synthesis of 2-((alkylamino)(aryl)methylene)cyclohexane-1,3-diones via three-component reaction



Entry	R/R'	R^1	R^2/R^3	Yield%[a]
1	H/H	*p*-MeO	Bn/H	65 (**4a**)
2	H/H	*p*-MeO	$PhCH(CH_3)$/H	78 (**4b**)
3	H/H	*m*-MeO	Bn/H	63 (**4c**)
4	H/H	*o*-MeO	Bn/H	59 (**4d**)
5	Me/Me	*p*-Me	Bn/H	81 (**4e**)
6	Me/Me	*p*-Me	HO_2CCH_2/H	79 (**4f**)
7	Me/Me	*p*-MeO	n-C_4H_9/H	87 (**4g**)
8	Me/Me	*p*-Me	n-C_8H_{17}/H	84 (**4h**)
9	Me/Me	*p*-Me	n-$C_{10}H_{21}$/H	86 (**4i**)
10	Me/Me	*p*-Me	n-$C_{14}H_{29}$/H	81 (**4j**)
11	Me/Me	*p*-Me	n-$C_{16}H_{33}$/H	80 (**4k**)
12	Me/Me	*p*-Cl	Bn/H	80 (**4l**)
13	Me/Me	*m*-MeO	Bn/H	87 (**4m**)
14	Me/Me	*o*-MeO	Bn/H	78 (**4n**)
15	Me/Me	*m*-Br	Bn/H	76 (**4o**)
16	Me/Me	*p*-MeO	Bn/H	83 (**4p**)
17	Me/Me	*p*-MeO	$HO_2CCH(CH_3)$/H	64 (**4q**)
18	Me/Me	*p*-MeO	n-C_6H_{13}/n-C_6H_{13}	55 (**4r**)
19	Me/Me	*p*-NO_2	Bn/H	51 (**4s**)
20	^{i}Pr/H	*p*-Cl	Bn/H	62 (**4t**)

[a] isolated yield

The substrate scope for this reaction was found to be broad for a variety of 1,3-cyclohexanediones, substituted *β*-nitrostyrenes and amines (Table 2). As shown in Table 2, 1,3-cyclohexanediones were found to afford the expected product, whereas 5,5-dimethyl-1,3-cyclohexanedione proved to be good substrates. 1,3-Cyclopentanedione was also tested as a starting material in the reaction, however, 1,3-cyclopentanedione was incompatible with this multicomponent reaction. This is because the intermediate cyclopentane[*a*]furan skeleton was formed difficultly. In general, reaction yields were good for substituted *β*-nitrostyrenes, regardless of the electronic nature and substitution pattern on the aryl moiety. In particular, the reaction was found to afford good to excellent yields for the desired *β*-enaminones for a variety of electron-rich *β*-nitrostyrenes.

In terms of the amine component, this assembly process enjoyed the wide aliphatic primary amines. A variety of functional groups, such as acid and aryl groups, were tolerated and installed. The reaction was also tolerant of higher fatty amine and secondary amine (Table 2, entries 8-11 and 18), furnishing the *β*-enaminone product in good yield. However, aromatic amines were incompatible with this multicomponent reaction due to their weak nucleophilicity. *β*-Enaminones **4a–t** were fully characterized by spectroscopic methods and were confirmed by single-crystal X-ray diffraction studies performed for two representative compounds **4f** and **4l** (Fig. 2). As a similar reaction, Qi and co-workers have reported the *L*-proline-dependent chemoselective reactions of cyclohexane-1,3-dione and nitroolefins with aromatic amines in water, and for the generation of tetrahydro-4*H*-indol-4-one derivatives.[11a] In this domino reaction, the Michael addition of cyclohexanedione to 2-nitrovinylbenzene formed 2-(1-aryl-2-nitroethyl)-cyclohexane-1,3-dione ion, which is followed by *L*-proline -promoting deprotonation to form a resonance-stabilized N-oxide, and a stable Schiff base also was yielded from the carbonyl of cyclohexane-1,3-dione and aromatic amine in the presence of *L*-proline. Finally, an intramolecular cyclization followed by nucleophilic addition of an intermediate enamine to N-oxide oxime afforded the desired tetrahydro-4*H*-indol-4-one. In addition, Saito et al. also reported one-pot synthesis of 2-amino-

3-arylbenzofuran derivatives from cyclohexane-1,3-dione and nitroolefins.[11b,11c]

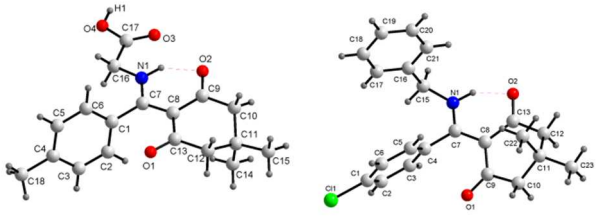
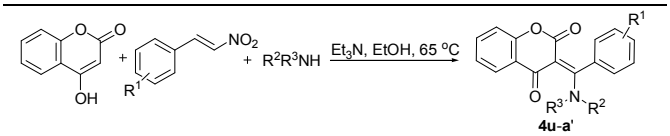


Fig. 2. Molecular structure of *β*-enaminones **4f** and **4l**[12]

In particular, we were pleased to see that our conditions allowed for a highly efficient route to (*E*)-3-((alkylamino)(aryl)methylene) chroman-2,4-diones, and the results are summarized in Table 3. It was found that the three-component reaction showed broad tolerance for various R^1, R^2 and R^3 groups of substrates. All selected substrates, *β*-nitrostyrenes bearing electron-rich (entries 1, 2, 6), electron deficient (entries 3, 4, 5) R^1 groups, reacted smoothly with fatty amines and secondary amine, and 4-hydroxy-2H-chromen-2-one to give the corresponding polysubstituted (*E*)-3-((alkylamino)(aryl)methylene)chroman-2,4-diones **4u**-**4y** in high yields at 65 °C for 6 h. In addition, in the case of *β*-nitrostyrene, the three-component reaction also worked well, yielding the desired product **4a'** in 70% yield (Table 3, entry 7).

All the prepared compounds have been characterized by spectral and analytical data. The structure of **4x** was shown in Fig. 3.[12] X-ray crystallographic analysis determined that product **4x** possess *E* exocyclic double bond at C(2) of *β*-dicarbonyl compound. On the basis of spectroscopic evidence the structure of compound **4u**-**4a**' was identified as (*E*)-3-((alkylamino)(aryl)methylene) chroman-2,4-dione. The exocyclic double-bond *E* configuration seemed to be thermodynamically favorable because an intermolecular hydrogen bond was observed on the basis of their X-ray crystallographic data.

Table 3 Synthesis of (*E*)-3-((alkylamino)(aryl)methylene)chroman-2,4-diones via three-component reaction



Entry	R^1	R^2/R^3	Yield%[a]
1	*p*-Me	Bn/H	89 (**4u**)
2	*o*-MeO	Bn/H	84 (**4v**)
3	*p*-NO_2	4-$MeOC_6H_4CH_2$/H	72 (**4w**)
4	*p*-Cl	4-$MeOC_6H_4CH_2$/H	85 (**4x**)
5	*p*-Cl	$PhCH(CH_3)$/H	84 (**4y**)
6	*p*-Me	n-C_4H_9/H	82 (**4z**)
7	H	n-C_6H_{13}/n-C_6H_{13}	70 (**4a'**)

[a] isolated yield

On the basis of the above results, a possible mechanism for the Et_3N-promoted three component reaction from substituted *β*-nitrostyrenes, *β*-dicarbonyl compounds and amines is tentatively proposed as depicted in Scheme 1 (with the three component reaction of 1-methoxy-4-(2-nitrovinyl)benzene, *β*-cyclohexanedione and benzylamine as an example).

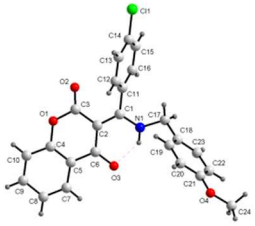
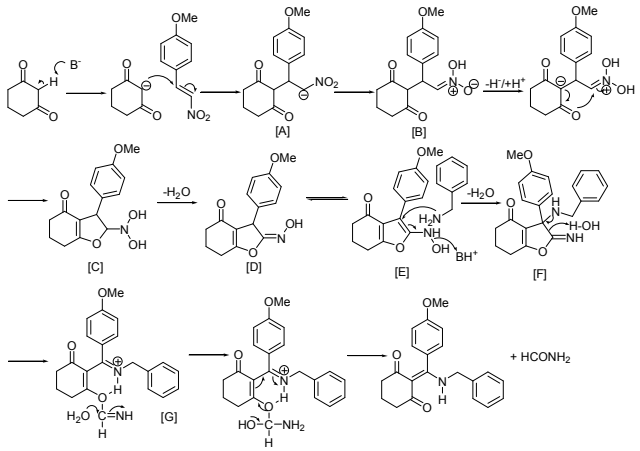


Fig. 3. Molecular structure of (*E*)-3-((4-methoxybenzylamino)(4-chlorophenyl) methylene)chroman-2,4-dione (**4x**)[12]

Initially, the Michael addition of cyclohexanedione to 1-methoxy-4-(2-nitrovinyl) benzene formed 2-(1-(4-methoxyphenyl)-2-nitroethyl)- cyclohex- ane-1,3-dione ion (Scheme 1, **A**), which is followed by base-promoting deprotonation to form a resonance-stabilized N-oxide oxime (Scheme 1, **B**) and a cyclic enolate. Next, intermediate enolate nucleophilic addition to N-oxide oxime (Scheme 1, **B**) gave an intermediate N-oxide hydroxylamine (Scheme 1, **C**), following dehydration yielded furan oxime (Scheme 1, **D**). Subsequently, the intermediate **E**, generated via C=N double bond isomerization of intermediate **D** under basic conditions, undergoes nucleophilic addition from an amine, followed by dehydration to afford the furan imine intermediate **F**. Finally, the ring opening of the furan imine intermediate **F** produces the iminium **G**, which undergoes an intramolecular keto-enol tautomerism to give the *β*-enaminone product (Scheme 1).



Scheme 1 Tentative reaction mechanism.

In summary, we have shown that a wide range of *β*-enaminones can be successfully synthesised using an one-pot three-component system that combines substituted *β*-nitrostyrenes and *β*-dicarbonyl compounds with amines. The reaction proceeds with easily accessible for substituted *β*-nitrostyrenes bearing electron-rich and electron-poor groups, and triethylamine as non-expensive promoter. Due to the described usefulness of *β*-enaminone derivatives, such simple reaction conditions and functional group tolerance are offering a new attractive method for access to such structures. Therefore, from these results, it can be envisioned that this procedure will find many applications in organic synthesis.

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Notes and references

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Electronic supplementary information (ESI) available: Reaction conditions and spectra. CCDC 965964, 959044 and 990835. For ESI and crystallographic data in CIF or other electronic format see DOI:

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12 Crystallographic data for β-enaminones **4f**, **4l** and **4x** have been deposited with the Cambridge Crystallographic Data Centre with the deposition number CCDC 965964, 959044 and 990835.

