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# L-Proline-catalyzed multicomponent synthesis of 3-indole derivatives

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## ABSTRACT

A green one-pot multicomponent reaction for the synthesis of 3-indole derivatives was developed via L-proline-catalyzed condensation between indoles, aldehydes, and malononitrile. The process was carried out in ethanol at room temperature, and the desired products were obtained in good to excellent yields of up to 98%. Pyrrole as the nucleophile and 2,2,2-trifluoroacetophenone as the electrophile can also work in this transformation. The salient features of this protocol were environmental friendliness, simplicity of the procedure, ready accessibility of the catalyst, high yield, and mild reaction conditions.

## 1. Introduction

Multicomponent reactions (MCRs), owing to the obvious advantages of atom economy, automatable procedure, time-saving, inherent exploratory power and minimization of chemical waste, have gained much attention in synthetic organic chemistry.[1] Moreover, this strategy has proved to be a particularly valuable and efficient methodology in the section of synthetic chemistry.[2]

The indole is probably one of the most ubiquitous moieties in nature.[3] A vast number of natural and synthetic indole derivatives have been found a venerable value in pharmaceutical and medical applications since they are able to bind with high affinity to many receptors.[4] Among them, 3-substituted indole derivatives have attracted much attention because they exist in many natural products, and their simple structure with broad scope of potent biological activities.[5]

Due to the inherent advantages, MCRs have proved to some traditional reactions that require two or three steps to synthesize the structurally complex molecules, such as carbon-carbon bond formation reaction in the field of alkylation of indoles. In 1978, Yonemitsu et al. first reported the successful multicomponent-based synthesis of 3-substituted indoles with Meldrum's acid, aldehydes, and different indoles.[6] Up to now, the Yonemitsu reaction has been largely applied to the synthesis of complex indole alkaloid precursors.[7] And Zhou group reported a method to obtain 3-substituted indole frameworks by a chiral thiourea catalyst.[8] 3-Substituted indole derivatives have also been obtained via L-proline catalyzed similar reactions based on dimedone,[9a–d] Meldrum's acid[9e] and even ketones.[9f] In other instances, this structure is also effectively obtained by the reaction between indoles, aldehydes and active methylene compounds when different kinds of catalyst are applied, like Ti(IV)/Et$_3$N,[10a–c] Sc(OTf)$_3$,[10d] and molecular sieves[10e] etc. And Perumal group reported InCl$_3$-catalyzed three-component reaction between salicylaldehydes, malononitrile and indoles in 2007.[11] It is even extended to cascade reactions recently to afford 3-substituted indoles.[12]

The three-component reaction between indoles, aldehydes and malononitrile is a unique type of reaction for the synthesis of 3-substituted indole derivatives. There are some reports about this reaction. Recently Zhou and co-workers reported this type of reaction catalyzed by a copper(II) sulfonato Salen complex with KH$_2$PO$_4$ as an additive in water at 60 °C.[13] Arjan and co-workers reported an extensive investigation using Zn(II)/Salen complexes as mediators in the presence of base.[14] However, the Salen ligand needs to be synthesized through several additional steps. And in the same year, Wan and co-workers used polyethylene glycol (PEG-200)-promoted this reaction in the presence of KH$_2$PO$_4$.[15] After that, Grée and co-workers reported that this three-component reaction could be conducted using Cu(OAc)$_2$ as a ligand-free catalyst and KH$_2$PO$_4$ as an additive in PEG-400 at 70 °C.[16] Also, Singh group used tetrabutyl ammonium fluoride trihydrate (TBAF·3H$_2$O) to catalyze this reaction in 2013.[17]

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0040-4020/

In consideration of the importance of this three-component reaction, there still remains a necessity to develop new environmentally friendly methodology to realize this important transformation for the preparation of potential medicinal scaffolds. And L-proline has been effectively used as a versatile organocatalyst for carbon–carbon bond formation in various organic transformations.[18] So we wish report the synthesis of 3-substituted-alkylated indoles via the three-component reaction of indole (or pyrrole), aldehyde (or 2,2,2-trifluoroacetophenone) and malononitrile in ethanol at room temperature, using L-proline as an inexpensive and environmentally benign catalyst.

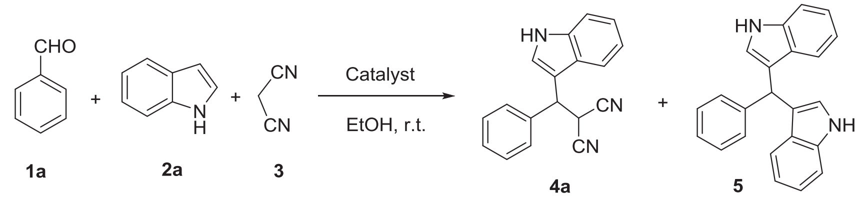
## 2. Results and discussion

During the course of our initial investigation, the three-component reaction of indole, benzaldehyde and malononitrile was used as a model reaction for the catalyst screening in ethanol (Table 1). The control experiment in the absence of catalyst was first carried out, and the desired product **4a** was only obtained in a yield of 8% (Table 1, entry 1). When some Brønsted acids such as trifluoroacetic acid (TFA), acetic acid, decanoic acid ($C_9H_{19}COOH$) and *p*-toluenesulfonic acid were tested as catalysts, no desired product **4a** was obtained, but bis(indolyl)methane (BIM) **5** was received instead (Table 1, entries 2–5). Some organic and inorganic bases were also screened, but none of them showed to be efficient to catalyze the formation of **4a** in a satisfied yield (Table 1, entries 6–11). When pyrrolidine was used as a catalyst, the desired product **4a** was only obtained in a very low yield of 13% (Table 1, entry 6), but a by-product was observed, which was formed by pyrrolidine itself with benzaldehyde and indole via a Mannich-type reaction as we described in the previous research.[19] The model reaction with salt $KH_2PO_4$ or NaOAc only gave the desired product **4a** in low yields (Table 1, entries 12 and 13). Some natural amino acids were also tested as catalysts (Table 1, entries 14–20). The desired product **4a** was obtained in low yields when L-methionine, L-histidine, L-serine, L-leucine, and L-threonine were used (Table 1, entries 14–18). A moderate yield was obtained with L-cysteine (Table 1, entry 19). Moreover, to our delight, when L-proline was applied as a catalyst, the desired product **4a** was isolated in a good yield of 91% with a trace amount of BIM **5** as a by-product (Table 1, entry 20). As a comparison, protected L-proline derivative, 1-(*tert*-butoxycarbonyl)pyrrolidine-2-carboxylic acid (*N*-Boc-L-proline) was also used as a catalyst, which gave **4a** in a low yield of 28% (Table 1, entry 21), indicating that imino group was necessary for L-proline to display its catalytic activity in the reaction. We hypothesized that L-proline catalyzes the reaction by the formation of an iminium ion intermediate with benzaldehyde, which facilitates the attack of nucleophile malononitrile to form the Knoevenagel adduct. And then Michael addition of indole to the adduct furnishes the desired product **4a**. Although pyrrolidine possesses the imino group similar to L-proline, pyrrolidine itself participates in the reaction failing to act as a catalyst. It seems that carboxyl group gives L-proline unique properties so that it can work as a catalyst instead of a reactant like pyrrolidine in the model reaction. Therefore, L-proline was chosen as an appropriate catalyst.

Next, the catalyst loading was investigated (Table 1, entries 20, 22 and 23), and it was found that 10 mol % of L-proline was sufficient for the model reaction to obtain the desired product **4a** in a good yield of 91% (Table 1, entry 22). Thus, 10 mol % of L-proline was selected as an optimal catalyst loading for further investigation.

Next, several solvents were tested for the L-proline-catalyzed reaction of benzaldehyde, indole and malononitrile. As shown in Table 2, when the reaction was carried out in solvents like MTBE, isopropyl ether, THF, 1,4-dioxane, $CH_2Cl_2$, $CHCl_3$, *n*-butyl acetate,

**Table 1**
Catalyst screening for the multicomponent synthesis of 3-alkylated indole[a]



| Entry | Catalyst | Yield of 4a[b] (%) |
|---|---|---|
| 1 | None | 8 |
| 2 | Trifluoroacetic acid | 0 |
| 3 | Acetic acid | 0 |
| 4 | Decanoic acid | Trace |
| 5 | *p*-Toluenesulfonic acid | 0 |
| 6 | Pyrrolidine | 13 |
| 7 | Piperidine | 11 |
| 8 | Dimethylamine | 17 |
| 9 | Triethylamine | 23 |
| 10 | NaOH | 19 |
| 11 | $NaHCO_3$ | 15 |
| 12 | $KH_2PO_4$ | 16 |
| 13 | NaOAc | 15 |
| 14 | L-Methionine | 26 |
| 15 | L-Histidine | 18 |
| 16 | L-Serine | 19 |
| 17 | L-Leucine | 23 |
| 18 | L-Threonine | 24 |
| 19 | L-Cysteine | 48 |
| 20 | L-Proline | 91 |
| 21 | *N*-Boc-L-proline | 28 |
| 22 | L-Proline (10 mol %) | 91 |
| 23 | L-Proline (5 mol %) | 85 |

[a] Unless otherwise noted, reaction conditions: benzaldehyde (1.0 mmol), indole (1.0 mmol), malononitrile (1.0 mmol), catalyst (20 mol %) in ethanol (1.0 mL) at rt for 48 h.

[b] Isolated yield after silica gel column chromatography.

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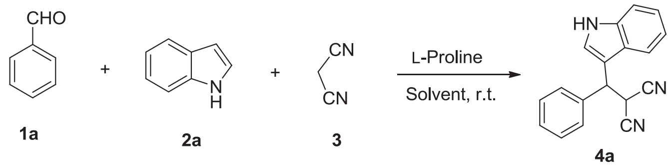
**Table 2**
Optimization of reaction conditions[a]



| Entry | Solvent | Time (h) | Yield[b] (%) |
|---|---|---|---|
| 1 | MTBE | 72 | 21 |
| 2 | Isopropyl ether | 72 | 45 |
| 3 | THF | 72 | 39 |
| 4 | 1,4-Dioxane | 72 | 38 |
| 5 | $CH_2Cl_2$ | 72 | 50 |
| 6 | $CHCl_3$ | 72 | 30 |
| 7 | *n*-Butyl acetate | 72 | 41 |
| 8 | DMSO | 72 | 39 |
| 9 | $H_2O$ | 72 | 52 |
| 10 | Solvent-free | 72 | 51 |
| 11 | MeOH | 72 | 85 |
| 12 | EtOH | 48 | 91 |
| 13 | *n*-Propanol | 72 | 75 |
| 14 | Isopropanol | 72 | 82 |
| 15 | EtOH (15 °C) | 48 | 83 |
| 16 | EtOH (35 °C) | 48 | 90 |
| 17 | EtOH (50 °C) | 48 | 76 |

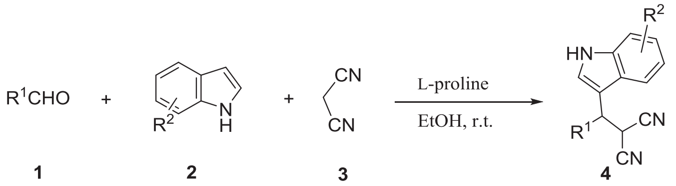
[a] Unless otherwise noted, reaction conditions: benzaldehyde (1.0 mmol), indole (1.0 mmol), malononitrile (1.0 mmol), L-proline (10 mol %) in solvent (1.0 mL) at rt.
[b] Isolated yield after silica gel column chromatography.

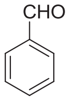
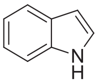
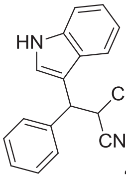
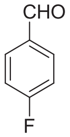
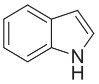
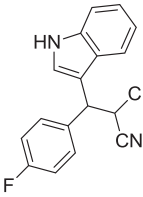
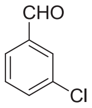
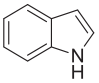
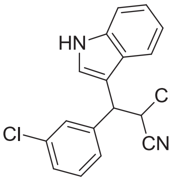
DMSO and $H_2O$ at rt for 72 h, the desired product **4a** was only obtained in yields of 39–52 % (Table 2, entries 1–9). The model reaction under solvent-free conditions gave product in a moderate yield of 51% (Table 2, entry 10). Some alcohols such as MeOH, EtOH, *n*-propanol and isopropanol were also tested as solvents. The reaction in alcohol solvents gave better yields than in other tested solvents. The best yield of 91% was received in EtOH at rt after 48 h (Table 2, entry 12). Lower yields were obtained in other alcohols even after 72 h (Table 2, entries 11, 13 and 14). Thus, EtOH was selected as an optimal solvent for the reaction.

The effects of temperature were also investigated (Table 2, entries 15–17). Rising temperature to 50 °C did not lead to an increase of the yield, but on the contrary a lower yield was obtained (Table 2, entry 14) due to the formation of the by-product bis(indolyl) methane (BIM) **5** at a higher temperature. Therefore, rt (approximately 25 °C) was chosen as a suitable temperature for the reaction.

Finally, a number of structurally different aldehydes and indoles were tested to explore the scope and generality of this methodology under the optimized reaction conditions. As shown in Table 3, aromatic aldehydes with electron-withdrawing and neutral groups afforded the respective addition products in good yields of 89–97% (Table 3, entries 1–9), while the aromatic aldehydes containing an electron-donating groups gave the products in a moderate yield after longer reaction time (Table 3, entries 10–13). And aliphatic aldehydes could also react with indole to afford the desired products with moderate yields (Table 3, entries 14, 15). Moreover, indoles with either electron-withdrawing or electron-donating group could react with various aromatic aldehydes smoothly to give the

**Table 3**
Scope of the L-proline-catalyzed three-component reaction[a]



| Entry | Aldehyde | Indole | Product | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 |  |  |  **4a** | 48 | 90 |
| 2 |  |  |  **4b** | 42<br>72 | 86<br>89 |
| 3 |  |  |  **4c** | 36 | 94 |

(*continued on next page*)

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**Table 3** *(continued)*

| | | | | | |
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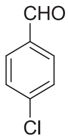
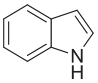
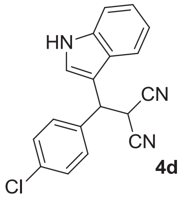
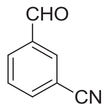
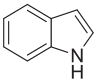
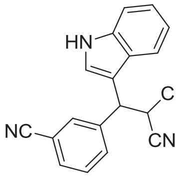
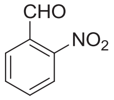
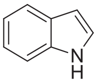
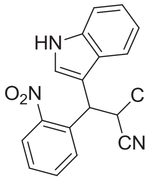
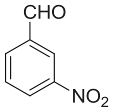
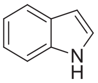
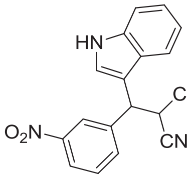
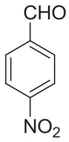
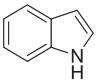
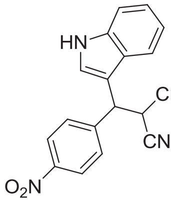
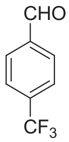
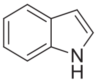
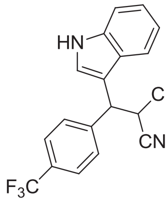
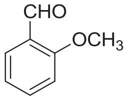
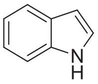
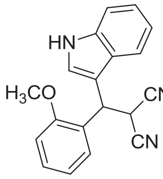
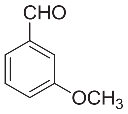
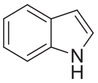
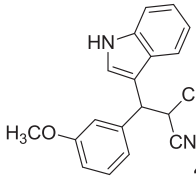
| 4 |  |  |  **4d** | 62 | 92 |
| 5 |  |  |  **4e** | 48 | 93 |
| 6 |  |  |  **4f** | 36 | 92 |
| 7 |  |  |  **4g** | 32 | 95 |
| 8 |  |  |  **4h** | 48 | 97 |
| 9 |  |  |  **4i** | 48<br>72 | 83<br>89 |
| 10 |  |  |  **4j** | 72 | 79 |
| 11 |  |  |  **4k** | 72 | 78 |

**Table 3** *(continued)*

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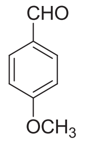
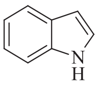
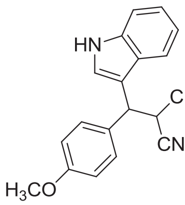
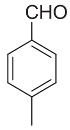
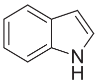
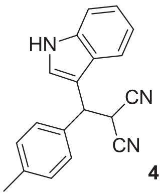
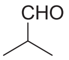
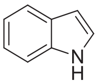
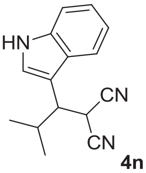
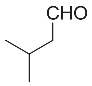
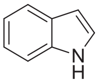
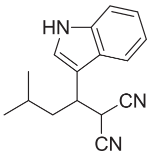
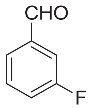
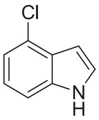
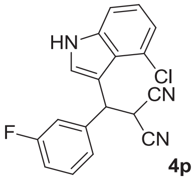
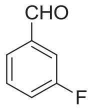
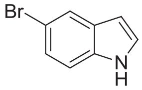
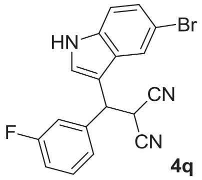
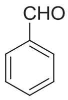
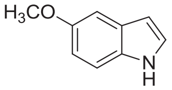
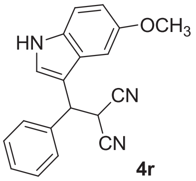
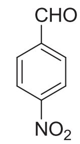
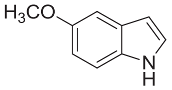
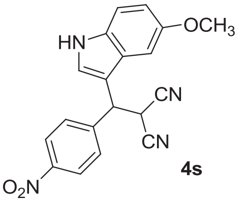
| 12 |  |  | <br>**4l** | 72 | 73 |
| 13 |  |  | <br>**4m** | 72 | 65 |
| 14 |  |  | <br>**4n** | 72 | 63 |
| 15 |  |  | <br>**4o** | 70 | 58 |
| 16 |  |  | <br>**4p** | 72 | 85 |
| 17 |  |  | <br>**4q** | 72 | 79 |
| 18 |  |  | <br>**4r** | 48 | 96 |
| 19 |  |  | <br>**4s** | 30 | 98 |

(*continued on next page*)

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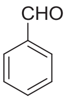
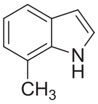
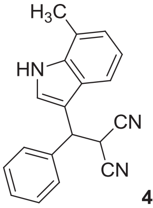
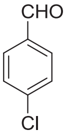
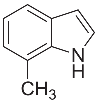
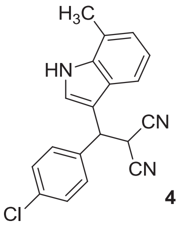
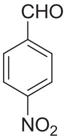
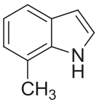
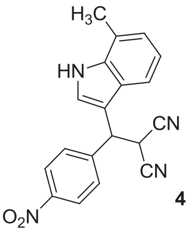
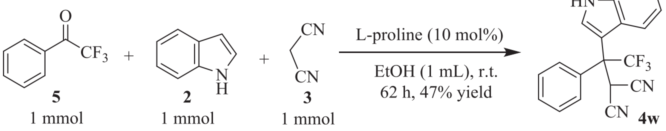
**Table 3** *(continued)*

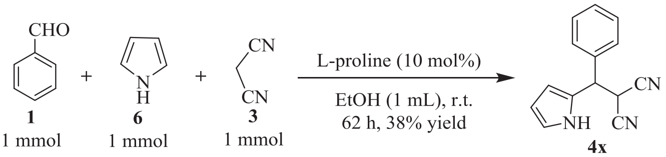
| | | | | | |
|---|---|---|---|---|---|
| 20 |  |  |  **4t** | 42 | 95 |
| 21 |  |  |  **4u** | 38 | 93 |
| 22 |  |  |  **4v** | 38<br>72 | 82<br>83 |

[a] Reaction conditions: aldehyde (1.0 mmol), indole (1.0 mmol), malononitrile (1.0 mmol), L-proline (10 mol%) in ethanol (1.0 mL) at r.t.. [b] Isolated yield after silica gel column chromatography.

corresponding products in good yields of 79–98% (Table 3, entries 16–22). When 2,2,2-trifluoroacetophenone instead of benzaldehyde was used as an electrophile to the reaction, the yield of 47% was obtained after 62 h (Scheme 1). Moreover, electron-rich heterocycles, such as pyrrole, furan, thiophene and trimethoxybenzene (1, 2, 3-, 1, 3, 5-, and 1, 2, 3-), also were used to react with benzaldehyde and malononitrile, but only pyrrole could work for this transformation, affording the desired product in 38% yield (Scheme 2). All the reactions were monitored by thin layer chromatography (TLC). When judged as completion or no more in obvious progress, the reaction was terminated and the product was isolated by silica gel column chromatography. For several examples (Table 3, entries 2, 9 and 22), relatively lower yields were obtained when the reactions were terminated according to the TLC monitoring (less than 48 h). As a comparison, the reaction time for these examples was then prolonged to 72 h, but no obvious increase in yield was observed. In total, nine new compounds were obtained, and characterized by $^1$H NMR, $^{13}$C NMR, IR and HRMS. Unfortunately, there was no obvious enantiomeric excess of the products observed by the chiral HPLC analysis.



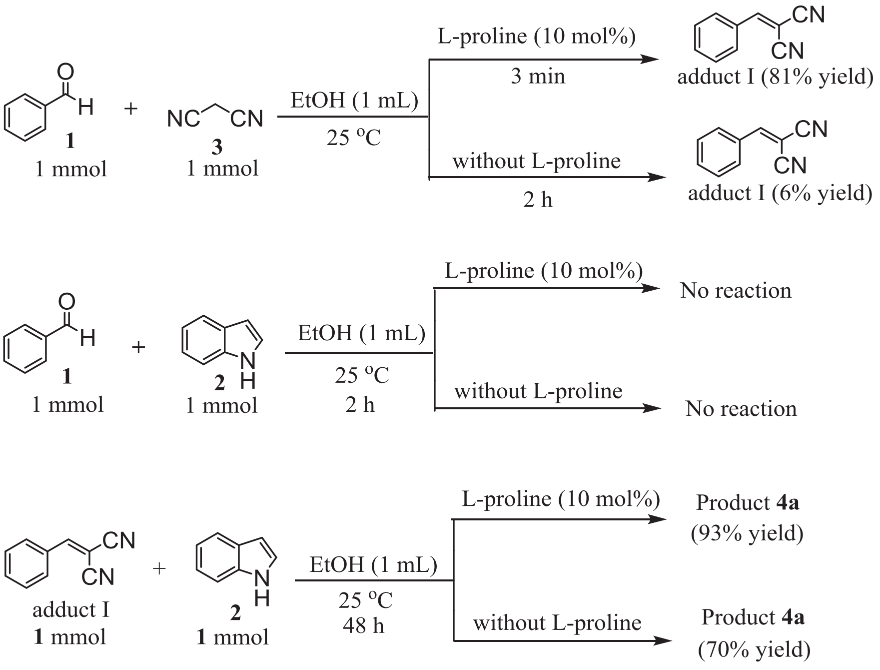
**Scheme 1.** L-Proline catalyzed reaction using 2,2,2-trifluoroacetophenone as the electrophile.



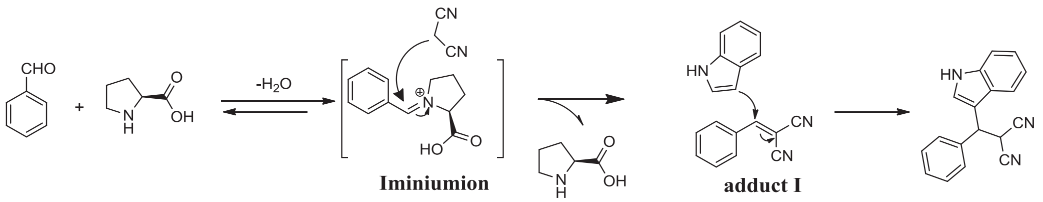
**Scheme 2.** L-Proline catalyzed reaction using pyrrole as the nucleophile.

In order to explore the mechanism of this reaction, we performed several control experiments (Scheme 3). In the first series experiments, benzaldehyde treated with malononitrile in the presence of L-proline (10 mol %) gave Knoevenagel adduct I in an excellent yield of 81% after less than 3 min. The same reaction in the absence of L-proline gave the Knoevenagel adduct I with a yield of 6% after 2 h. The results revealed that L-proline greatly accelerated the formation of Knoevenagel adduct I. Then benzaldehyde was treated with indole in the absence of L-proline under the same reaction conditions, and almost no new material was generated after 2 h. Also no reaction was observed when L-proline (10 mol %) was added to the mixture of benzaldehyde and indole for 2 h. These results suggested that the malononitrile instead of indole first reacts with benzaldehyde under the catalysis of L-proline. Moreover, to verify if L-proline catalyzes the Michael addition of indole with Knoevenagel adduct I to form the final products, some more control experiments were performed (Scheme 3). When treated with L-proline (10 mol %), the reaction of indole and Knoevenagel adduct I gave the desired product **4a** in a good yield of 93% in EtOH for 48 h. Meanwhile, the same reaction carried out in the absence of L-proline gave product **4a** in a lower yield of 70%. The results indicated that the Michael addition of indole with Knoevenagel adduct I can take place without catalyst, however the reaction can still be promoted by L-proline.

Thus a plausible pathway for L-proline-catalyzed alkylation of 3-indole was proposed (Scheme 4). Firstly, the reaction commences with the formation of an iminium ion intermediate from benzaldehyde and L-proline. Then, adduct **I** forms through Knoevenagel



**Scheme 3.** Control experiments.



**Scheme 4.** A possible pathway for L-proline-catalyzed alkylation of indole.

condensation between imine intermediate and nucleophilic malononitrile. Finally, Michael addition of indole with adduct **I** furnishes the desired product.

## 3. Conclusion

In summary, we developed an L-proline-catalyzed multicomponent reaction of aldehydes (or 2,2,2-trifluoroacetophenone), malononitrile and indoles (or pyrrole) for the synthesis of 3-alkylated indole derivatives in EtOH at room temperature. The desired products were obtained in good to excellent yields of up to 98%. L-proline was used as a readily available, inexpensive and metal-free catalyst. The procedure was simple, and the reaction conditions were mild. Moreover, this multicomponent reaction was highly atom-economic. 3-Alkylated indole derivatives could be prepared in high yields using 1:1:1 M ratio of reactants by loss of a molecule of water in total. These advantages make the methodology a rather attractive process for the synthesis of 3-alkylated indole derivatives.

## 4. Experimental

### 4.1. General procedure for the L-proline-catalyzed multicomponent reaction

The aldehyde (or 2,2,2-trifluoroacetophenone) (1.0 mmol), malononitrile (1.0 mmol), indole (or pyrrole) (1.0 mmol), L-proline (10 mol%) and ethanol (1.0 mL) were added sequentially into a round-bottom flask to form a clear yellow solution. The resultant mixture was stirred at rt for a specific time. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.10.027.

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