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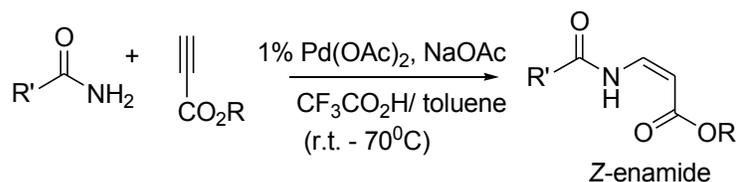


# Stereoselective synthesis of enamides by Pd-catalyzed hydroamidation of electron deficient terminal alkynes

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**Abstract.** Hydroamidation of electron-deficient terminal alkynes by amides in presence of Pd-catalyst has been exploited for the stereoselective synthesis of *Z*-enamides. The possible intramolecular hydrogen bonding between the amido proton and carbonyl oxygen of ester group provides the extra stability to the *Z*-isomer of vinyl-palladium complex, which subsequently undergo protodepalladation and lead to the *Z*-enamide selectively. This process is found to be mild and operationally simple with broad substrate scope.

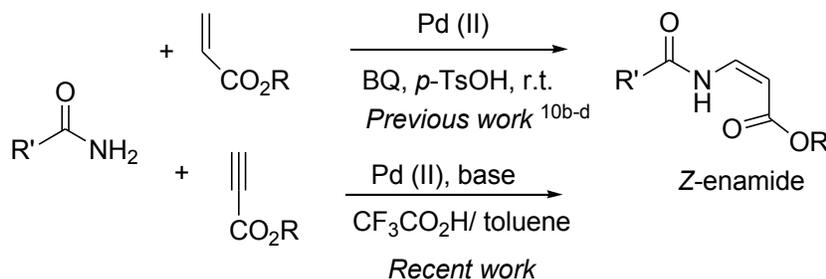
**Keywords:** Enamides; Hydroamidation; amides; terminal alkynes; palladium.

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3 Enamides constitute the core structure of many functional materials<sup>1</sup> and natural products of  
4 biological significance.<sup>2</sup> Furthermore, enamides are proved to be a versatile intermediate for the  
5 synthesis of heterocycles, amino acids and potential drug metabolites.<sup>3</sup> Thus, a number of  
6 methods have been developed for their synthesis.<sup>4</sup> The classical methods include the  
7 condensation of carbonyl derivatives with amides or acylation of imines leads to mixtures with  
8 the *E*-enamide as major isomer.<sup>5-7</sup> In contrast, stereoselective synthesis of thermodynamically  
9 less favorable *Z*-enamide has been rarely explored. Indeed, several elegant methods such as  
10 Curtius rearrangement of  $\alpha$ ,  $\beta$ -unsaturated acyl azides,<sup>8</sup> and elimination of  $\beta$ -hydroxy- $\alpha$ -  
11 silylamides (Peterson reaction),<sup>9</sup> oxidative amidation of conjugated olefins,<sup>10</sup> Pd- and/or Cu-  
12 catalyzed cross-coupling of vinyl derivatives (*viz*, halides,<sup>11</sup> triflates,<sup>12</sup> tosylates,<sup>13</sup> borates,<sup>14</sup>  
13 ethers<sup>15</sup>) with amides have been reported for stereoselective synthesis of enamides. However,  
14 requirement of rigorous reaction conditions and intricacy in starting material preparation often  
15 limits their practical applications.<sup>16</sup>

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35 On the other hand, addition of amides to terminal alkynes, known as hydroamidation, has  
36 been emerged as an appealing atom-economic approach to this substrate class. Evidently,  
37 Watanabe and co-workers<sup>17</sup> reported the ruthenium-complex mediated synthesis of *E*-enamides  
38 at high temperature. Gooßen and co-workers<sup>18</sup> developed ligand-mediated Ru-catalyzed  
39 hydroamidation reactions that allow the *anti*-Markovnikov addition of various N-H nucleophiles  
40 to terminal acetylenes for selective formation of either *E*- or *Z*-configured enamide derivatives.  
41 Takai and co-workers<sup>19</sup> used commercially available rhenium-catalyst (i.e.  $\text{Re}_2(\text{CO})_6$ ) for the  
42 coupling of the cyclic amides with alkyl alkynes to access *E*-enamides. These Ru/Re-catalyzed  
43 hydroamidation reactions so far reported are endowed with: the use of inactivated terminal  
44 alkynes, the formation of doubly vinylated enamides and ligand-dependant stereoselectivity.<sup>20</sup>

Evidently, the enamides synthesized by later methods often undergo double bond isomerization to thermodynamically more stable *E*-enamides.<sup>18b</sup> Moreover, use of electron deficient terminal alkynes as coupling partner in the hydroamidation process was not yet precedent. Therefore, development of mild and efficient methods for stereoselective synthesis of *Z*-enamides from such alkynes is particularly interesting. Based on our present interest on stereoselective synthesis of enamides,<sup>10d</sup> we herein report a mild and efficient Pd-catalyzed hydroamidation protocol for the stereoselective synthesis of *Z*-enamides from the electron deficient terminal alkynes through N-C cross-coupling reactions (Scheme 1). Moreover, this method is found to be very practical and results in the thermodynamically less favored *Z*-enamides selectively from the primary amides. To the best of our knowledge, this is the first report on Pd-catalyzed hydroamidation of alkynes to enamide.

### Scheme 1

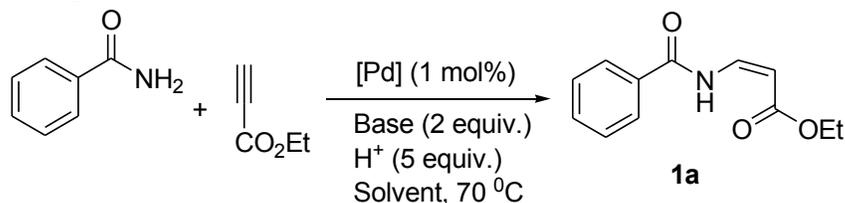


Our strategy originated from the seminal work of Fujiwara<sup>21</sup> and Kitamura.<sup>22</sup> They have described the Pd-catalyzed coupling of ethyl propiolate with electron rich arenes through C-H activation. It occurred to us that the use of amide as nucleophile instead of electron rich arene may leads to vinyl-palladium complex which on subsequent protodepalladation in the presence of Brønsted acid would afford the enamide. Unlike the Fujiwara's report<sup>21</sup> the possible intramolecular hydrogen bonding between the amido proton and carbonyl oxygen of electron deficient alkyne in the vinyl-palladium complex would eventually attribute to the *Z*-selectivity of

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3 the resulting enamide. With this in mind, we began our study using benzamide and ethyl  
4 propiolate as the model substrates. Unfortunately, under similar conditions as reported by  
5 Fujiwara (i.e. Pd(OAc)<sub>2</sub>/CF<sub>3</sub>CO<sub>2</sub>H) no trace of enamide **1a** was obtained even at higher  
6 temperature (70°C) with recovery of starting material (Table 1, entry 1). However, addition of  
7 two equivalents of base such as NaOMe furnished the *Z*-enamide (**1a**) as the major product in  
8 appreciable yield (44 %) at 70°C (entry 2). The appearance of doublets at δ 11.5 (for N-H) and  
9 5.27 (vinylic proton) with coupling constant 8.8 Hz, reveals the formation of *Z*-enamide.<sup>10b</sup>  
10 Optimization studies were then performed that varied the nature of bases, solvents and added  
11 acids. These investigations revealed that the utilization of two equiv. of sodium acetate (NaOAc)  
12 gave **1a** (82 % yield) over a period of 12 h at 70 °C in toluene. No trace of *E*-enamide was  
13 identified from TLC as well as <sup>1</sup>H NMR. Decreasing as well as increasing the temperature led  
14 to poor yield of enamide. Furthermore, polar solvents such as DMF, THF, CH<sub>3</sub>CN and 1,4-  
15 dioxane resulted no or poor yield of isomeric mixture (entries 18-21). A satisfactory result was  
16 obtained when dichloroethane (DCE) was used: enamide was isolated in 72% yield (*Z/E* 2:1  
17 from <sup>1</sup>H NMR) (entry 17). The use of other bases such as <sup>t</sup>BuOK, NaOH, Cs<sub>2</sub>CO<sub>3</sub> resulted in  
18 lower yield. Excess of trifluoroacetic acid (5 equiv.) was found to be essential for the completion  
19 of the reaction. 1 mol % of Pd(OAc)<sub>2</sub> was confirmed to be optimal. An increase in catalyst  
20 concentration from 1 mol % to 5 mol% afforded the product in lower yield due to unwanted  
21 polymerization/decomposition. The catalytic efficiencies of other Pd-catalysts were also  
22 examined and it revealed that among the tested catalysts (i.e. PdCl<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>,  
23 Pd(PPh<sub>3</sub>)<sub>2</sub>(OAc)<sub>2</sub>, Pd(TFA)<sub>2</sub>, Pd(OAc)<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd/C) Pd(OAc)<sub>2</sub> displayed  
24 higher activity under the same experimental conditions (entries 3-10).  
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A plausible pathway for the selective synthesis of Z-enamide (**1a**) is outlined in Scheme 2, although numerous details remain to be elucidated. The reaction of benzamide with ethyl

**Table 1.** Optimization of reaction conditions <sup>a</sup>



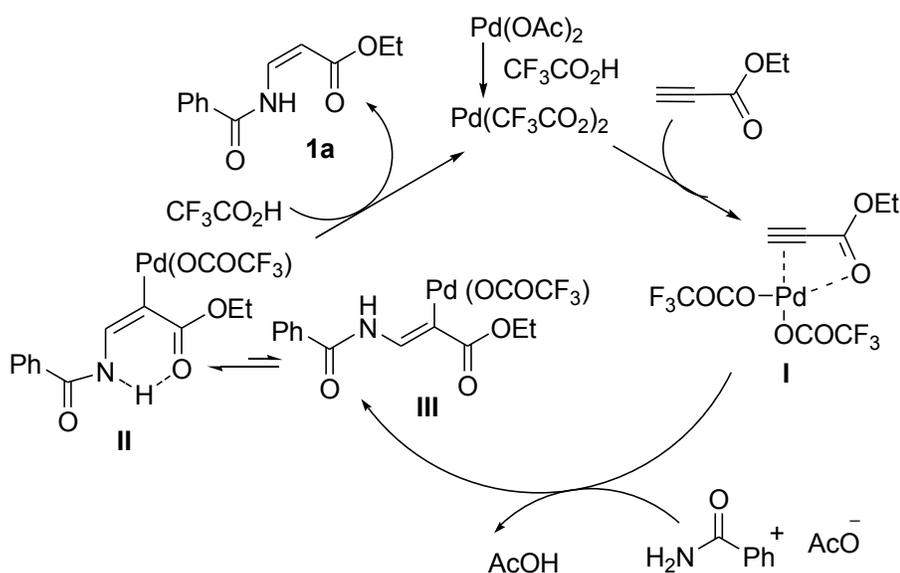
| Entry | catalyst  | acid                                 | solvent            | additive                        | % yield (Z/E) |
|-------|---|--------------------------------------|--------------------|---------------------------------|---------------|
| 1     | Pd(OAc) <sub>2</sub>                                  | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | nil                             | 0             |
| 2     | Pd(OAc) <sub>2</sub>                                  | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOMe                           | 44            |
| 3     | <b>Pd(OAc)<sub>2</sub></b>                            | <b>CF<sub>3</sub>CO<sub>2</sub>H</b> | <b>toluene</b>     | <b>NaOAc</b>                    | <b>82</b>     |
| 4     | PdCl <sub>2</sub>                                     | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOAc                           | 31            |
| 5     | Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>    | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOAc                           | 68            |
| 6     | Pd(PPh <sub>3</sub> ) <sub>2</sub> (OAc) <sub>2</sub> | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOAc                           | 56            |
| 7     | Pd(CF <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub>     | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOAc                           | 72            |
| 8     | Pd(dba) <sub>2</sub>                                  | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOAc                           | 16            |
| 9     | Pd(PPh <sub>3</sub> ) <sub>4</sub>                    | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOAc                           | 0             |
| 10    | Pd/C  | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOAc                           | 0             |
| 11    | Pd(OAc) <sub>2</sub>                                  | CH <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOAc                           | 26            |
| 12    |   | PivOH                                | toluene            | NaOAc                           | <5            |
| 13    |   | nil                                  | toluene            | NaOAc                           | 0             |
| 14    |   | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | <sup>t</sup> BuOK               | <10           |
| 15    |   | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | NaOH                            | 0             |
| 16    |   | CF <sub>3</sub> CO <sub>2</sub> H    | toluene            | Cs <sub>2</sub> CO <sub>3</sub> | 15            |
| 17    |   | CF <sub>3</sub> CO <sub>2</sub> H    | DCE                | NaOAc                           | 72 (2:1)      |
| 18    |   | CF <sub>3</sub> CO <sub>2</sub> H    | dioxane            | NaOAc                           | 39 (1.8:1)    |
| 19    |   | CF <sub>3</sub> CO <sub>2</sub> H    | CH <sub>3</sub> CN | NaOAc                           | 15 (1: 1.2)   |
| 20    |   | CF <sub>3</sub> CO <sub>2</sub> H    | DMF                | NaOAc                           | 0             |
| 21    |   | CF <sub>3</sub> CO <sub>2</sub> H    | THF                | NaOAc                           | 0             |

<sup>a</sup>Reaction conditions: A mixture of benzamide (100 mg, 0.82 mmol), ethyl propiolate (0.12 mL, 1.23 mmol), Pd-catalyst (1 mol %), Brønsted acid (5 equiv) and additive (2 equiv.) in the indicated solvent were heated at 70 °C for 12 h under N<sub>2</sub> atmosphere.

propiolate in absence of trifluoroacetic acid did not result any enamide (entry 13). Furthermore, this cross-coupling in presence of acetic acid resulted only 26% of the enamide (entry 11) where

as the cross-coupling in presence of  $\text{Pd}(\text{CF}_3\text{COO})_2$  afforded 72% yield of enamide (entry 7). It indicates that at optimum reaction conditions like earlier observation of Fujiwara<sup>21</sup> and Kitamura,<sup>22</sup>  $\text{Pd}(\text{OAc})_2$  reacts with  $\text{CF}_3\text{CO}_2\text{H}$  and leads to the more reactive  $\text{Pd}(\text{CF}_3\text{COO})_2$ . Addition of the latter to the activated alkyne leads to the alkyne-palladium complex (**I**). Nucleophilic attack of amide nitrogen to **I** results in vinyl-palladium complex (**II** and/or **III**). As expected, like Chang<sup>10b</sup> and our's<sup>10d</sup> report the possible hydrogen bonding between the carbonyloxygen of alkyne and the N-H of amide ( $\text{C}=\text{O}\dots\text{H}-\text{N}$ ) provides the additional stability to the complex and thus drives the equilibrium towards **II**. This intramolecular H-bonding attributes to the excellent Z-selectivity of the hydroamidation reaction. Furthermore, in presence of excess of Brønsted acid, **II** undergoes protodepalladation<sup>23, 24</sup> readily and affords the Z-enamide selectively.

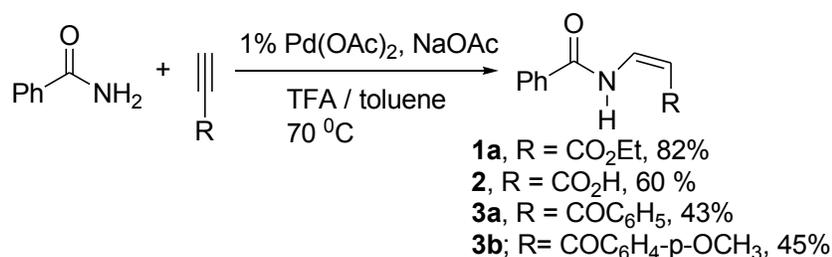
**Scheme 2:** The plausible mechanism



Having the optimal conditions, the scope of alkyne component was explored with different substitutions. It revealed that electron-withdrawing substitutions like  $-\text{COOH}$ ,  $\text{COAr}$  to the

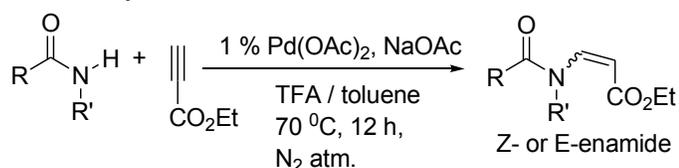
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3 alkyne, resulted *Z*-enamides selectively in modest yield (Scheme 3). Unactivated alkynes such as  
4 phenylacetylene and 1-octyne are inactive to afford the enamide, albeit the homocoupling of  
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6 alkynes were resulted.  
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### 11 Scheme 3



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Next, we investigated the scope and limitation of the catalytic process with various amides and the results are summarized in Table 2. Pleasingly, this catalytic protocol was found to be tolerant to both electron-donating and -withdrawing aryl ring substitutions, and in most cases moderate to good yields of enamides was obtained. As such, electron withdrawing substituents (i.e. -NO<sub>2</sub>, Cl) to the aromatic ring, that decrease the nucleophilicity of amide still participated in cross-coupling with ethyl propiolate and led to the *Z*-enamides in good yield without affecting the selectivity. Heteroaryl amides also afforded the corresponding enamides in good yield with retention of *Z*-selectivity (entries 8, 9). Amides with alkyl group, carbamate and urea are found to be reactive to ethyl propiolate and resulted *Z*-enamides selectively (entries 13, 14). However, when secondary amides were used, tertiary enamides with *E*-selectivity ( $J = 14.4$  Hz) were resulted in modest yield (entries 15-18). Cyclic amides such as pyrrolidinone, ethylene urea were also underwent hydroamidation reaction and furnished the *E*-enamides in appreciable yield. Selective formation of *E*-enamide is due to the lack of intramolecular hydrogen bonding in the vinyl-palladium complex that drives the equilibrium towards the thermodynamically more stable intermediate (e.g. **III**).

**Table 2:** Enamide synthesis<sup>a</sup>

| Entry          | Substrate             | Product   | % Yield | Entry           | Substrate | Product | % Yield |
|----------------|-----------------------|-----------|---------|-----------------|-----------|---------|---------|
| 1              |                       |           | 82      | 14              |           |         | 52      |
| 2              | X = 4-OMe             | <b>1b</b> | 68      | 15 <sup>b</sup> |           |         | 46      |
| 3              | X = 4-Cl              | <b>1c</b> | 62      | 16 <sup>b</sup> |           |         | 54      |
| 4              | X = 2-Cl              | <b>1d</b> | 56      | 17 <sup>b</sup> |           |         | 56      |
| 5              | X = 4-NO <sub>2</sub> | <b>1e</b> | 72      | 18 <sup>b</sup> |           |         | 41      |
| 6              | X = 2-NO <sub>2</sub> | <b>1f</b> | 50      | 19              |           |         | 72      |
| 7              | X = 3-NO <sub>2</sub> | <b>1g</b> | 56      | 20              |           |         | 54      |
| 8 <sup>b</sup> | X = 2-OMe             | <b>1h</b> | 75      |                 |           |         |         |
| 9              | X = 2-OH              | <b>1i</b> | 56      |                 |           |         |         |
| 10             |                       |           | 67      |                 |           |         |         |
| 11             |                       |           | 60      |                 |           |         |         |
| 12             |                       |           | 52      |                 |           |         |         |
| 13             |                       |           | 55      |                 |           |         |         |

<sup>a</sup>Reaction conditions: 100 mg of amide, ethyl propiolate (1.5 equiv.), TFA (5 equiv.), Pd(OAc)<sub>2</sub> (1 mol %), NaOAc (2 equiv.) heated at 70 °C for 12 h under N<sub>2</sub> atmosphere. <sup>b</sup>Reactions were carried out at room temperature over a period of 36 h.

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3 In summary, the first Pd-catalyzed hydroamidation of activated terminal alkynes is  
4 presented. The conditions can be applied to a number of amides as well as electron deficient  
5 alkynes with good functional group tolerance. The reaction is stereoselective: primary amides  
6 give *Z*-enamides whereas secondary amides give *E*-enamides selectively. The high  
7 stereoselectivity is possibly due to the favorable intramolecular hydrogen bonding between the  
8 carbonyl oxygen of alkyne and the N-H of amide in the vinyl palladium complex. This  
9 methodology is simple and allows to access varieties of enamides with high stereoselectivity.  
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## 22 Experimental Section

### 23 24 25 General procedure for enamide synthesis from alkyne

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28 **Method A:** An oven dried round bottom flask was charged with amide (100 mg), Pd(OAc)<sub>2</sub> (1  
29 mol%), trifluoroacetic acid (5 equiv.), NaOAc (2 equiv.), and toluene (4 mL). The reaction  
30 mixture was stirred for 5 minutes under nitrogen atmosphere at room temperature and then ethyl  
31 propiolate (1.5 equiv.) was added dropwise. The reaction mixture was then stirred for 5 min. and  
32 then temperature was raised to 70 °C. After 12 h, the reaction mixture was diluted with ethyl  
33 acetate followed by water. The organic layer was separated and the aqueous layer was extracted  
34 with ethyl acetate. The combined organic layer was dried over brine, anhydrous Na<sub>2</sub>SO<sub>4</sub>, and  
35 then evaporated under reduced pressure. The crude residue was purified by column  
36 chromatography over silica gel using mixture of petroleum ether and ethyl acetate as eluent to  
37 give the pure enamide.  
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53 **Method B:** An oven dried round bottom flask was charged with amide (100 mg), Pd(OAc)<sub>2</sub> (1  
54 mol%), trifluoroacetic acid (5 equiv.), NaOAc (2 equiv.), and toluene (4 mL). The reaction  
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3 mixture was stirred for 5 minutes under nitrogen atmosphere at room temperature and then ethyl  
4 propiolate (1.5 equiv.) was added dropwise. The reaction mixture was stirred for 12 h at room  
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6 temperature (r. t.) and then diluted with ethyl acetate followed by water. The organic layer was  
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8 separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer  
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10 was dried over brine, anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then evaporated under reduced pressure. The crude  
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12 residue was purified by column chromatography over silica gel using mixture of petroleum ether  
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14 and ethyl acetate as eluent to give the pure enamide.  
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21 ***(Z)-Ethyl 3-(benzamido)acrylate (1a)***<sup>10b</sup>  
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24 **1a** was obtained following general procedure (Method A) as a white crystalline solid (179 mg,  
25 82 % yield), mp: 76-77 °C. IR (KBr): 3324, 2955, 1684, 1638, 1581, 1508, 1480 cm<sup>-1</sup>. <sup>1</sup>H NMR  
26 (400 MHz, CDCl<sub>3</sub>): δ 11.54 (d, 1H, *J* = 9.6 Hz), 7.98-7.95 (m, 2H), 7.76 (dd, 1H, *J*<sub>1</sub> = 11.2 Hz,  
27 *J*<sub>2</sub> = 8.8 Hz), 7.64-7.58 (m, 2H), 7.55-7.49 (m, 2H), 5.28 (d, 1H, *J* = 8.8 Hz), 4.25 (q, 2H, *J* = 7.2  
28 Hz), 1.34 (t, 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.6 (s), 164.5 (s), 138.7 (d),  
29 132.9 (d), 132.1 (s), 128.9 (d), 127.7 (d), 97.1 (d), 60.3 (t), 14.2 (q). MS (ESI,-Ve) *m/z* (relative  
30 intensity) 217.90 [M-H]<sup>+</sup>, 100%. Anal. Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>3</sub>: C, 65.74; H, 5.98; N, 6.39. Found:  
31 C, 65.40; H, 5.68; N, 6.09.  
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44 ***(Z)-Ethyl 3-(4-methoxybenzamido)acrylate (1b)***  
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47 **1b** was obtained following general procedure (Method A) as a white crystalline solid (169 mg,  
48 68 % yield), mp: 100-102°C. IR (KBr): 3433, 2998, 2967, 2924, 1670, 1622, 1479, 1369 cm<sup>-1</sup>.  
49 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.45 (d, 1H, *J* = 10.8 Hz), 7.94 (d, 2H, *J* = 8.8 Hz), 7.75 (dd,  
50 1H, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 8.8 Hz), 6.99 (t, 2H, *J*<sub>1</sub> = 6.8 Hz, *J*<sub>2</sub> = 2 Hz), 5.24 (d, 1H, *J* = 9.2 Hz), 4.25  
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(q, 2H,  $J = 6.8$  Hz,  $J = 14.4$  Hz) 3.89 (s, 3H), 1.35 (t, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.7 (s), 163.9 (s), 163.3 (s), 139.0 (d), 129.7 (d), 124.5 (s), 114.1 (d), 96.4 (d), 60.1 (t), 55.4 (t), 14.2(q). MS (ESI,-Ve)  $m/z$  (relative intensity) 248.13 ( $[\text{M-H}]^+$ , 100%). Anal. Calcd for  $\text{C}_{13}\text{H}_{15}\text{NO}_4$ : C 62.64; H 6.07; N 5.62. Found: C 62.69; H 6.00; N 5.53.

**(Z)-Ethyl 3-(4-chlorobenzamido)acrylate (1c)**

**1c** was obtained following general procedure (Method A) as yellow solid (157 mg, 62 % yield), mp: 52-54°C. IR (KBr): 3290, 2932, 1702, 1678, 1639, 1590, 1509, 1486  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.54 (d, 1H,  $J = 10$  Hz), 7.93-7.88 (m, 2H), 7.73 (dd, 1H,  $J_1 = 11.2$  Hz,  $J_2 = 8.8$  Hz), 7.50-7.46 (m, 2H), 5.29 (d, 1H,  $J = 8.8$  Hz), 4.25 (q, 2H,  $J = 7.2$  Hz), 1.35 (t, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.7 (s), 163.4 (s), 139.3 (s), 138.6 (d), 130.6 (s), 129.2 (d), 129.1 (d), 97.5 (d), 60.4 (t), 14.2 (q). MS (ESI, -ve)  $m/z$  (relative intensity) 252.14 ( $[\text{M-H}]^+$ , 100%). Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{ClNO}_3$ : C, 56.81; H, 4.77; N, 5.52. Found: C, 56.78; H, 4.68; N, 5.72.

**(Z)-Ethyl 3-(2-chlorobenzamide)acrylate (1d)**

**1d** was obtained following general procedure (Method A) as a white crystalline solid (141 mg, 56 % yield), mp: 85-87°C. IR (KBr): 3313, 3071, 2981, 2940, 2901, 1723, 1685, 1628, 1592, 1481, 1434, 1379, 1256, 1201, 1139, 1094, 1029  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.18 (d, 1H,  $J = 9.6$  Hz), 7.75-7.66 (m, 2H), 7.52-7.41 (m, 2H), 7.40-7.34 (m, 1H), 5.28 (d, 1H,  $J = 8.8$  Hz), 4.20 (q, 2H,  $J = 7.2$  Hz), 1.32 (t, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.8, 164.4, 137.5, 133.2, 132.4, 131.5, 130.7, 130.5, 127.2, 98.1, 60.3, 14.2. MS (ESI, -ve)  $m/z$  (relative intensity) 252.16 ( $[\text{M-H}]^+$ , 100%). Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{ClNO}_3$ : C 56.81; H 4.77; N 5.52. Found: C 57.02; H 5.00; N 5.92.

**(Z)-Ethyl 3-(4-nitrobenzamido)acrylate (1e)**

**1e** was obtained following general procedure (Method A) as yellow solid (190 mg, 72 % yield), mp: 127-129°C. IR (KBr): 3437, 2990, 2912, 1687, 1670, 1628, 1527, 1477, 1346 cm.<sup>-1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.69 (d, 1H, *J* = 10 Hz), 8.37-8.33 (m, 2H), 8.14-8.10 (m, 2H), 7.72 (dd, 1H, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 8.8 Hz), 5.36 (d, 1H, *J* = 8.8 Hz), 4.25 (q, 2H, *J* = 7.2 Hz), 1.34 (t, 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.6 (s), 162.5 (s), 150.3 (s), 138.0 (d), 137.6 (s), 128.8 (d), 124.0 (d), 98.8 (d), 60.6 (t), 14.2 (q). MS (ES-APCI, +ve) *m/z* (relative intensity) 265 ([M+H]<sup>+</sup>, 100%). Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>: C 54.55; H 4.58; N 10.60. Found: C 54.32; H 4.70; N 10.44.

**(Z)-Ethyl 3-(2-nitrobenzamido)acrylate (1f)**

**1f** was obtained following general procedure (Method A) as a white crystalline solid (132 mg, 50 % yield), mp: 108-109°C. IR (KBr): 3464, 3319, 3071, 2986, 2955, 1687, 1627, 1532, 1353, 1221, 1024 cm.<sup>-1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.71 (d, 1H, *J* = 10.0 Hz), 8.85-8.82 (m, 1H), 8.48-8.44 (m, 1H), 8.27-8.23 (m, 1H), 7.78-7.71 (m, 2H), 5.36 (d, 1H, *J* = 8.8 Hz), 4.30-4.23 (q, 2H), 1.38-1.33 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.5 (s), 162.3 (s), 148.6 (s), 138.1 (d), 134.1 (s), 132.9 (d), 130.1 (d), 127.2 (d), 123.1 (d), 98.7 (d), 60.6 (t), 14.2 (q). MS (ESI, -ve) *m/z* (relative intensity) 262.98 ([M-H]<sup>+</sup>, 100%). Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>: C 54.55; H 4.58; N 10.60. Found: C 54.82; H 4.78; N 10.89.

**(Z)-Ethyl 3-(3-nitrobenzamido)acrylate (1g)**

**1g** was obtained following general procedure (Method A) as yellow solid (147 mg, 56 % yield), mp: 103-105°C. IR (KBr): 3693, 3292, 3063, 2980, 2932, 1682, 1630, 1531, 1379, 1349, 1202

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2  
3 cm.<sup>-1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.92 (d, 1H, *J* = 9.6 Hz), 8.11 (m, 1H), 7.77-7.60 (m, 4H),  
4  
5 5.33 (d, 1H, *J* = 8.8 Hz), 4.22-4.15 (q, 2H), 1.33-1.27 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ  
6  
7 169.1 (s), 163.9 (s), 146.9 (s), 137.4 (d), 133.7 (d), 131.4 (d), 131.4 (s), 128.3 (d), 124.8 (d), 98.5  
8  
9 (d), 60.4 (t), 14.1 (q). MS (ESI, -ve) *m/z* (relative intensity) 263.02 ([M-H]<sup>+</sup>, 100%). Anal. Calcd  
10  
11 for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>: C 54.55; H 4.58; N 10.60. Found: C 54.74; H 4.67; N 11.00.

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16 ***(Z)*-Ethyl 3-(2-methoxybenzamido)acrylate (1h)**

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18  
19 **1h** was obtained following general procedure (Method B) as oil (186 mg, 75 % yield). IR (neat):  
20  
21 3442, 3025, 2979, 2846, 1680, 1621, 1481, 1397cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 12.39 (d,  
22  
23 1H, *J* = 10.4 Hz), 8.27-8.22 (m, 1H), 7.78 (dd, 1H, *J*<sub>1</sub> = 11.2 Hz, *J*<sub>2</sub> = 8.8 Hz), 7.55-7.51 (m,  
24  
25 1H), 7.12-6.99 (m, 1H), 5.21 (d, 1H, *J* = 8.8 Hz), 4.25 (q, 2H, *J* = 7.2 Hz), 4.12 (s, 3H), 1.32 (t,  
26  
27 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.2 (s), 163.6 (s), 158.4 (s), 138.0 (d), 134.2  
28  
29 (d), 132.8 (d), 121.2 (d), 119.8 (s), 111.5 (d), 97.1 (d), 59.7 (t), 55.7 (q), 14.3 (q). MS (ESI, +ve)  
30  
31 *m/z* (relative intensity) 272.02 ([M+Na]<sup>+</sup>, 100%), 521.10 ([2M+Na]<sup>+</sup>, 90%). Anal. Calcd for  
32  
33 C<sub>13</sub>H<sub>15</sub>NO<sub>4</sub>: C 62.64; H 6.07; N 5.62. Found: C 62.48; H 5.90; N 5.38.

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39 ***Ethyl 3-(2-hydroxybenzamido)acrylate (1i)***

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42 **1i** was obtained following general procedure (Method A) as a white crystalline solid (131 mg, 56  
43  
44 % yield), mp: 98-100 °C. IR (KBr): 3311, 2956, 1686, 1661, 1636, 1602, 1517 cm<sup>-1</sup>. <sup>1</sup>H NMR  
45  
46 (400 MHz, CDCl<sub>3</sub>): δ 11.84 (s, 1H), 11.75 (d, 1H, *J* = 9.6 Hz), 7.71 (dd, *J*<sub>1</sub> = 10.8 Hz, *J*<sub>2</sub> = 8.8  
47  
48 Hz), 7.63-7.59 (m, 1H), 7.52-7.39 (m, 1H), 7.09-7.03 (m, 1H), 7.02-6.92 (m, 1H), 5.33 (d, 1H, *J*  
49  
50 = 8.8 Hz), 4.26 (q, 2H, *J* = 7.2 Hz), 1.35 (t, 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ  
51  
52 169.6 (s), 167.8 (s), 162.5 (s), 137.4 (d), 135.7 (d), 126.3 (d), 119.3 (d), 118.7 (d), 113.0 (s), 98.2  
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(d), 60.5 (t), 14.2 (q). MS (ESI, -ve)  $m/z$  (relative intensity) 234.09 ( $[M-H]^+$ , 100%). Anal. Calcd for  $C_{12}H_{13}NO_4$ : C, 61.27; H, 5.57; N, 5.95. Found: C, 61.22; H, 5.74; N, 6.07.

***(Z)*-3-(Benzamido)acrylic acid (2)**

**2** was obtained following general procedure (Method A) as a white crystalline solid (114 mg, 60 % yield), mp: 163-165 °C. IR (KBr): 3327, 3036, 2997, 1697, 1671, 1594, 1402, 1239  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  11.29 (d, 1H),  $J = 10.8$  Hz), 7.98-7.85 (m, 3H), 7.68-7.60 (m, 1H), 7.59-7.50 (m, 2H), 7.09-7.03 (m, 1H), 5.34 (d, 1H,  $J = 9.2$  Hz).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  173.5 (s), 164.5 (s), 141.1 (d), 133.3 (d), 131.9 (s), 129.0 (d), 127.7 (d), 95.7 (d). MS (ESI, -ve)  $m/z$  (relative intensity) 190.04 ( $[M-H]^+$ , 100%). Anal. Calcd for  $C_{10}H_9NO_3$ : C 62.82; H 4.74; N 7.33. Found: C 62.61; H 4.69; N 7.63.

***N*-((*Z*)-3-oxo-3-phenylprop-1-enyl)benzamide (3a)<sup>26</sup>**

**3a** was obtained following general procedure (Method A) as a white crystalline solid (89 mg, 43 % yield), mp: IR (KBr): 3338, 3063, 2912, 2858, 1692, 1638, 1585, 1384, 1234, 1012  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  12.95 (d, 1H,  $J = 9.2$  Hz), 8.07-8.10 (m, 2H), 7.90-8.02 (m, 3H), 7.48-7.66 (m, 6H), 6.43 (d, 1H,  $J = 8.8$  Hz).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  193.2(s), 165.3(s), 140.1(d), 138.1(s), 133.1(d), 132.9(d), 132.0(s), 128.9(d), 128.7(d), 128.0(d), 127.9(d), 100.8(d). MS (ESI, -ve)  $m/z$  (relative intensity) 250.06 ( $[M-H]^+$ , 100%).

***N*-((*Z*)-3-(4-methoxyphenyl)-3-oxoprop-1-enyl)benzamide (3b)**

**3b** was obtained following general procedure (Method A) as a white crystalline solid (104 mg, 45 % yield), mp: 86-88 °C. IR (KBr): 3338, 3063, 2912, 2858, 1692, 1638, 1585, 1384, 1234, 1012  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  12.98 (d, 1H,  $J = 10$  Hz), 8.05-8.13 (m, 2H), 7.96-

1  
2  
3 8.03 (m, 2H), 7.92 (dd, 1H,  $J_1 = 10.8$  Hz,  $J_2 = 8.8$  Hz, 1H), 7.60-7.65 (m, 1H), 7.53-7.58 (m,  
4  
5 2H), 6.98-7.02 (m, 2H), 6.40 (d, 1H,  $J = 8.8$  Hz), 3.90 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$   
6  
7 191.8 (s), 165.3 (s), 163.5 (s), 139.4 (d), 133.0 (d), 132.1 (s), 131.0 (s), 130.2 (d), 128.9 (d),  
8  
9 127.9 (d), 113.9 (d), 100.8 (d), 55.5 (q). MS (ESI, -ve)  $m/z$  (relative intensity) 280.09 ( $[\text{M}-\text{H}]^+$ ,  
10  
11 100%). Anal. Calcd for  $\text{C}_{17}\text{H}_{15}\text{NO}_3$ : C, 72.58; H, 5.37; N, 4.98; O, 17.06. Found: C, 72.65; H,  
12  
13 5.33; N, 5.05.  
14  
15  
16  
17

#### 18 **(Z)-Ethyl 3-(furan-2-carboxamido)acrylate (4)**

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21 **4** was obtained following general procedure (Method A) as a white crystalline solid (140 mg, 67  
22  
23 % yield), mp: 83-85°C. IR (KBr): 3327, 3128, 2978, 2936, 2874, 1725, 1685, 1629, 1587, 1492,  
24  
25 1469  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.38 (d, 1H,  $J = 8.8$  Hz), 7.68-7.58 (m, 2H), 7.31 (m,  
26  
27 1H), 6.59-6.56 (m, 1H), 5.26 (d, 1H,  $J = 8.8$  Hz), 4.25 (q, 2H,  $J = 7.2$  Hz), 1.34 (t, 3H,  $J = 7.2$   
28  
29 Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.1 (s), 155.6 (s), 146.5 (s), 145.6 (d), 137.3 (d), 117.0  
30  
31 (d), 112.6 (d), 97.4 (d), 60.3 (t), 14.2(q). MS (ESI, +ve)  $m/z$  (relative intensity) 210.12 ( $[\text{M}+\text{H}]^+$ ,  
32  
33 100%). Anal. Calcd for  $\text{C}_{10}\text{H}_{11}\text{NO}_4$ : C 57.41; H 5.30; N 6.70. Found: C 57.59; H 5.18; N 6.58.  
34  
35  
36  
37  
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#### 39 **(Z)-Ethyl 3-(thiophene-2-carboxamido)acrylate (5)**

40  
41  
42 **5** was obtained following general procedure (Method A) as a white crystalline solid (135 mg, 60  
43  
44 % yield), mp: 116-118°C. IR (KBr): 3335, 3070, 2952, 1674, 1627, 1525, 1470, 1425  $\text{cm}^{-1}$ .  $^1\text{H}$   
45  
46 NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.40 (d, 1H,  $J = 9.6$  Hz), 7.75-7.72 (m, 1H), 7.68 (dd,  $J_1 = 8.8$  Hz,  
47  
48  $J_2 = 5.6$  Hz), 7.64-7.62 (m, 1H), 7.18-7.15 (m, 1H), 5.25 (d, 1H,  $J = 8.8$  Hz), 4.25 (q, 2H,  $J = 7.2$   
49  
50 Hz), 1.33 (t, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.5 (s), 159.2 (s), 138.3 (d),  
51  
52 137.3 (s), 132.5 (d), 130.0 (d), 128.1 (d), 96.9 (d), 60.3 (t), 14.2 (q). MS (ESI, -ve)  $m/z$  (relative  
53  
54  
55  
56  
57  
58  
59  
60

intensity) 224.06 ( $[M-H]^+$ , 100%). Anal. Calcd for  $C_{10}H_{11}NO_3S$ : C, 53.32; H, 4.92; N, 6.22; S, 14.23. Found: C, 53.48; H, 5.27; N, 6.32; S, 14.42.

**(Z)-Ethyl 3-acetamidoacrylate (6)<sup>10b</sup>**

**6** was obtained following general procedure (Method A) as oil (81 mg, 52 % yield). IR (neat): 3325, 2950, 2925, 2850, 1719, 1686, 1630, 1502, 1398, 1386  $cm^{-1}$ .  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  10.42 (s, 1H), 7.49 (dd, 1H,  $J_1 = 11.2$  Hz,  $J_2 = 8.8$  Hz), 5.12 (d, 1H,  $J = 9.2$  Hz), 4.19 (q, 2H,  $J = 7.2$  Hz), 2.17 (s, 3H), 1.31 (t, 3H,  $J = 7.0$  Hz).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  169.2 (s), 168.4 (s), 137.9 (d), 96.3 (d), 60.2 (t), 23.6 (q), 14.2 (q). MS (ESI, +ve)  $m/z$  (relative intensity) 158.06 ( $[M+H]^+$ , 100%).

**(Z)-Ethyl 3-(acrylamido)acrylate (7)**

**7** was obtained following general procedure (Method A) as oil (93 mg, 55 % yield). IR (neat): 3335, 2981, 2940, 1682, 1630, 1480, 1409, 1376  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  10.68 (bs, 1H), 7.58 (dd, 1H,  $J_1 = 10.4$  Hz,  $J_2 = 9.2$  Hz), 6.45 (d, 1H,  $J = 17.2$  Hz), 6.28-6.18 (m, 1H), 5.86 (d, 1H,  $J = 10.4$  Hz), 5.19 (d, 1H,  $J = 8.8$  Hz), 4.20 (q, 2H,  $J = 6.8$  Hz), 1.30 (t, 3H,  $J = 6.8$  Hz).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  169.2 (s), 163.2 (s), 138.0 (d), 129.9 (d), 129.6 (d), 97.3 (d), 60.2 (t), 14.1 (q). MS (ESI, -ve)  $m/z$  (relative intensity) 168 ( $[M-H]^+$ , 38%). Anal. Calcd for  $C_8H_{11}NO_3$ : C, 56.80; H, 6.55; N, 8.28. Found: C, 56.91; H, 6.38; N, 8.21.

**(2Z)-Ethyl 3-(cinnamamido)acrylate (8)<sup>10b</sup>**

**8** was obtained following general procedure (Method A) as a white crystalline solid (127 mg, 52 % yield), mp: 112-113°C. IR (KBr): 3435, 2986, 2936, 1679, 1627, 1479, 1380  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  10.73 (d, 1H,  $J = 9.2$  Hz), 7.79 (d, 1H,  $J = 15.6$  Hz), 7.67 (dd, 1H,  $J_1 = 8.8$

1  
2  
3 Hz,  $J_2 = 11.2$  Hz), 7.60-7.55 (m, 2H), 7.44-7.39 (m, 3H), 6.54 (d, 1H,  $J = 15.6$  Hz), 5.21 (dd, 1H,  
4  
5  $J = 8.8$  Hz) 4.23 (q, 2H,  $J = 7.2$  Hz), 1.34 (t, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$   
6  
7 169.4 (s), 163.5 (s), 144.4 (d), 138.4 (d), 134.2 (s), 130.5 (d), 128.9 (d), 128.2 (d), 119.2 (d), 96.7  
8  
9 (d), 60.2 (t), 14.2 (q). MS (ESI, -ve)  $m/z$  (relative intensity) 243.88 ( $[\text{M}-\text{H}]^+$ , 100%). Anal. Calcd  
10  
11 for  $\text{C}_{14}\text{H}_{15}\text{NO}_3$ : C, 68.56; H, 6.16; N, 5.71. Found: C, 68.36; H, 6.42; N, 6.08.

### 16 **(Z)-Ethyl 3-ureidoacrylate (9)**

17  
18  
19 **9** was obtained following general procedure (Method B) as oil (72 mg, 46 % yield). IR (neat):  
20  
21 3431, 3384, 2970, 2924, 2851, 1710, 1656, 1632, 1510, 1463, 1366  $\text{cm}^{-1}$   $^1\text{H}$  NMR (400 MHz,  
22  
23  $\text{CDCl}_3$ ):  $\delta$  9.98 (d, 1H,  $J = 10$  Hz), 7.45 (dd, 1H,  $J_1 = 11.4$  Hz,  $J_2 = 8.8$  Hz), 5.03 (d, 1H,  $J = 8.8$   
24  
25 Hz), 5.04 (s, 2H,  $-\text{NH}_2$ ), 4.18 (q, 2H,  $J = 7.2$  Hz), 1.30 (t, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  
26  
27  $\text{CDCl}_3$ ):  $\delta$  169.8 (s), 153.7 (s), 140.7 (d), 93.2 (d), 59.9 (t), 14.2 (q). MS (ESI, +ve)  $m/z$  (relative  
28  
29 intensity) 159 ( $[\text{M}+\text{H}]^+$ , 100%), 316 ( $[\text{M}]^+$ , 30%). Anal. Calcd for  $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_3$ : C, 45.57; H,  
30  
31 6.37; N, 17.71. Found: C, 45.77; H, 6.29; N, 17.92.

### 36 **Butyl (Z)-2-(ethoxycarbonyl)vinylcarbamate (10)**

37  
38  
39 **10** was obtained following general procedure (Method B) as oil (116 mg, 54 % yield). IR (neat):  
40  
41 3716, 3329, 2962, 2874, 1745, 1685, 1633, 1489, 1404, 1370, 1355  $\text{cm}^{-1}$   $^1\text{H}$  NMR (400 MHz,  
42  
43  $\text{CDCl}_3$ ):  $\delta$  9.75 (bs, 1H), 7.27 (m, 1H), 5.03 (d, 1H,  $J = 8.8$  Hz), 4.22-4.12 (m, 4H), 1.69-1.60 (m,  
44  
45 2H), 1.46-1.40 (m, 2H), 1.33 (t, 3H,  $J = 7.2$  Hz), 0.96 (t, 3H,  $J = 6.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  
46  
47  $\text{CDCl}_3$ ):  $\delta$  168.9 (s), 153.6 (s), 140.1 (d), 94.7 (d), 66.0 (t), 59.9 (t), 30.7 (t), 18.9 (t), 14.2 (q),  
48  
49 13.5 (q). MS (ESI, +ve)  $m/z$  (relative intensity) 238.14 ( $[\text{M}+\text{Na}]^+$ , 100%). Anal. Calcd for  
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51  $\text{C}_{10}\text{H}_{17}\text{NO}_4$ : C, 55.80; H, 7.96; N, 6.51. Found: C, 55.85; H, 8.22; N, 6.72.

**Methyl (E)-2-(ethoxycarbonyl)vinylmethylcarbamate (11)**

**11** was obtained following general procedure (Method B) as oil (104 mg, 56 % yield). IR (neat): 3098, 2974, 2958, 1733, 1705, 1629, 1446, 1376, 1360  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.27 (bs, 1H), 5.20 (d, 1H,  $J = 14.4$  Hz), 4.21 (q, 2H,  $J = 7.2$  Hz), 3.86 (s, 3H), 3.13 (s, 3H), 1.28 (q, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.4, 130.1, 128.0, 98.5, 60.0, 54.1, 31.3, 14.3. MS (ESI, +ve)  $m/z$  (relative intensity) 187.07 ( $[\text{M}+\text{H}]^+$ , 100%). Anal. Calcd for  $\text{C}_8\text{H}_{13}\text{NO}_4$ : C, 51.33; H, 7.00; N, 7.48. Found: C, 51.42; H, 7.23; N, 7.42.

**(E)-Ethyl 3-(N-methylformamido)acrylate (12)**

**12** was obtained following general procedure (Method B) as oil (64 mg, 41 % yield). IR (neat): 2980, 2940, 2897, 1711, 1624, 1369  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.48 (s), 7.82 (d, 1H,  $J = 13.6$  Hz), 5.44 (d, 1H,  $J = 14$  Hz), 4.23 (q, 2H,  $J = 8$  Hz), 3.09 (s, 3H), 1.31 (t, 3H,  $J = 8$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.8 (s), 163.1 (d), 143.4 (d), 100.0 (d), 60.4 (t), 27.7 (q), 14.3 (q). MS (ESI, +ve)  $m/z$  (relative intensity) 314.30 ( $[\text{2M}]^+$  100%). Anal. Calcd for  $\text{C}_7\text{H}_{11}\text{NO}_3$ : C, 53.49; H, 7.05; N, 8.91. Found: C, 53.42; H, 7.22; N, 8.82.

**(E)-Ethyl 3-(2-oxopyrrolidin-1-yl)acrylate (13)<sup>25</sup>**

**13** was obtained following general procedure (Method A) as a white crystalline solid (131 mg, 72 % yield), mp: 118-120  $^\circ\text{C}$ . IR (KBr): 3083, 2979, 2905, 1727, 1627, 1460, 1386, 1364, 1326  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.12 (d, 1H,  $J = 14.4$  Hz), 5.28 (d, 1H,  $J = 14.4$  Hz), 4.25 (q, 2H,  $J = 7.2$  Hz), 3.58 (t, 2H,  $J = 7.2$  Hz), 2.58 (t, 2H,  $J = 7.2$  Hz), 2.22-2.17 (m, 2H), 1.31 (t, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  174.1 (s), 167.1 (s), 137.2 (d), 100.8 (d), 60.2

(t), 44.9 (t), 30.9 (t), 17.4 (t), 14.3 (q). MS (ESI, +ve)  $m/z$  (relative intensity) 206.21 ( $[M+Na]^+$ , 100%). Anal. Calcd for  $C_9H_{13}NO_3$ : C, 59.00; H, 7.15; N, 7.65. Found: C, 59.19; H, 7.38; N, 7.72.

**(E)-Ethyl 3-(3-(4-hydroxyphenyl)-2-oxoimidazolidin-1-yl)acrylate (14)**

**14** was obtained following general procedure (Method A) as a white crystalline solid (99 mg, 54 % yield), mp: 72-74°C. IR (KBr): 3402, 2979, 2932, 2901, 1728, 1628, 1480, 1431, 1391, 1368  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.05 (d, 1H,  $J = 13.6$  Hz), 6.03 (bs, 1H), 4.98 (d, 1H,  $J = 13.6$  Hz), 4.19 (q, 2H,  $J = 7.2$  Hz), 3.66 (m, 4H), 1.29 (t, 3H,  $J = 7.2$  Hz).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  167.5 (s), 157.4 (s), 138.8 (d), 96.3 (d), 59.9 (t), 42.0 (t), 37.4 (t), 14.3 (q). MS (ESI, +ve)  $m/z$  (relative intensity) 207.10 ( $[M+Na]^+$ , 100%). Anal. Calcd for  $C_8H_{12}N_2O_3$ : C, 52.17; H, 6.57; N, 15.21. Found: C, 52.38; H, 6.82; N, 15.49.

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**Supporting Information Available.** Copies of NMR ( $^1H$  and  $^{13}C$ ) spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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