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Stereoselective Synthesis of Enamides by Pd-Catalyzed Hydroamidation of Electron Deficient Terminal Alkynes

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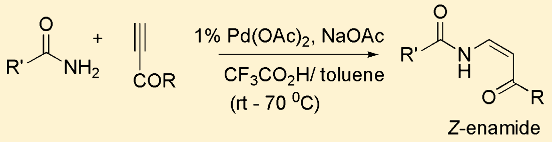
Supporting Information

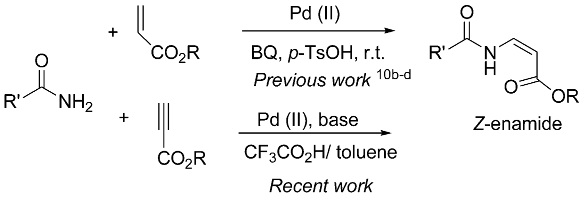
ABSTRACT: Hydroamidation of electron-deficient terminal alkynes by amides in presence of Pd-catalyst has been exploited for the stereoselective synthesis of *Z*-enamides. The possible intramolecular hydrogen bonding between the amido proton and carbonyl oxygen of ester group provides the extra stability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



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

On the other hand, addition of amides to terminal alkynes, known as hydroamidation, has emerged as an appealing atom-economic approach to this substrate class. Evidently, Watanabe and co-workers[17] reported the ruthenium-complex-mediated synthesis of *E*-enamides at high temperature. Gooßen and co-workers[18] developed ligand-mediated Ru-catalyzed hydroamidation reactions that allow the *anti*-Markovnikov addition of various N−H nucleophiles to terminal acetylenes for selective formation of either *E*- or *Z*-configured enamide derivatives. Takai and co-workers[19] used commercially available rhenium catalyst (i.e., $Re_2(CO)_6$) for the coupling of the cyclic amides with alkyl alkynes to access *E*-enamides. These Ru/Re catalyzed hydroamidation reactions so far reported are endowed with the use of inactivated terminal alkynes, the formation of doubly vinylated enamides and ligand-dependent stereoselectivity.[20] Evidently, the enamides synthesized by later methods often undergo double bond isomerization to thermodynamically more stable *E*-enamides.[18b] 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. On the basis of our present interest on stereoselective synthesis of enamides,[10d] 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[21] and Kitamura.[22] 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 lead to vinyl−palladium complex, which on subsequent protodepalladation in the presence of Brønsted acid would afford the enamide. Unlike Fujiwara's report,[21] 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 the resulting enamide. With this in mind, we began our study using benzamide and ethyl propiolate as the model substrates. Unfortunately, under

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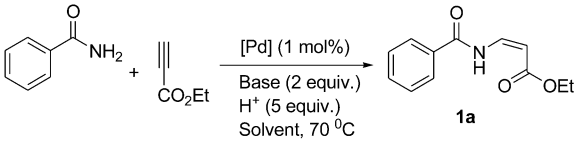
Table 1. Optimization of Reaction Conditions[a]



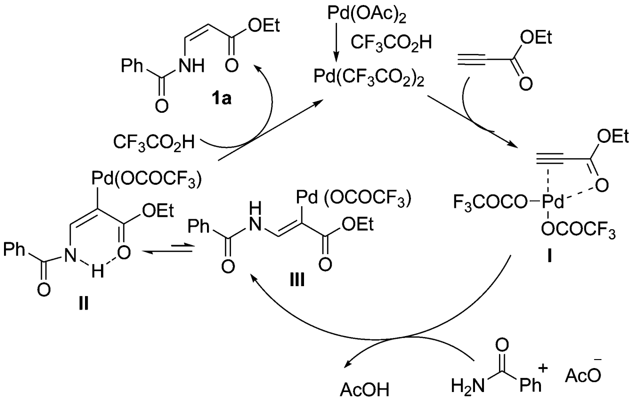
entry	catalyst	acid	solvent	additive	% yield (*Z*/*E*)
1	$Pd(OAc)_2$	CF_3CO_2H	toluene	nil	0
2	$Pd(OAc)_2$	CF_3CO_2H	toluene	NaOMe	44
3	**$Pd(OAc)_2$**	**CF_3CO_2H**	**toluene**	**NaOAc**	**82**
4	$PdCl_2$	CF_3CO_2H	toluene	NaOAc	31
5	$Pd(PPh_3)_2Cl_2$	CF_3CO_2H	toluene	NaOAc	68
6	$Pd(PPh_3)_2(OAC)_2$	CF_3CO_2H	toluene	NaOAc	56
7	$Pd(CF_3CO_2)_2$	CF_3CO_2H	toluene	NaOAc	72
8	$Pd(dba)_2$	CF_3CO_2H	toluene	NaOAc	16
9	$Pd(PPh_3)_4$	CF_3CO_2H	toluene	NaOAc	0
10	Pd/C	CF_3CO_2H	toluene	NaOAc	0
11	$Pd(OAc)_2$	CH_3CO_2H	toluene	NaOAc	26
12		PivOH	toluene	NaOAc	<5
13		nil	toluene	NaOAc	0
14		CF_3CO_2H	toluene	^{t}BuOK	<10
15		CF_3CO_2H	toluene	NaOH	0
16		CF_3CO_2H	toluene	Cs_2CO_3	15
17		CF_3CO_2H	DCE	NaOAc	72 (2:1)
18		CF_3CO_2H	dioxane	NaOAc	39 (1.8:1)
19		CF_3CO_2H	CH_3CN	NaOAc	15 (1:1.2)
20		CF_3CO_2H	DMF	NaOAc	0
21		CF_3CO_2H	THF	NaOAc	0

[a] 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_2 atmosphere.

similar conditions as reported by Fujiwara (i.e., $Pd(OAc)_2/CF_3CO_2H$) no trace of enamide **1a** was obtained even at higher temperature (70 °C) with recovery of starting material (Table 1, entry 1). However, addition of 2 equiv of base such as NaOMe furnished the *Z*-enamide (**1a**) as the major product in appreciable yield (44%) at 70 °C (entry 2). The appearance of doublets at δ 11.5 (for N−H) and 5.27 (vinylic proton) with coupling constant 8.8 Hz, reveals the formation of *Z*-enamide.[10b] Optimization studies were then performed that varied the nature of bases, solvents and added acids. These investigations revealed that the utilization of two equiv of sodium acetate (NaOAc) gave **1a** (82% yield) over a period of 12 h at 70 °C in toluene. No trace of *E*-enamide was indentified from TLC as well as ^{1}H NMR. Decreasing as well as increasing the temperature led to poor yield of enamide. Furthermore, polar solvents such as DMF, THF, CH_3CN and 1,4-dioxane resulted no or poor yield of isomeric mixture (entries 18−21). A satisfactory result was obtained when dichloroethane (DCE) was used: enamide was isolated in 72% yield (*Z*/*E* 2:1 from ^{1}H NMR) (entry 17). The use of other bases such as ^{t}BuOK, NaOH, Cs_2CO_3 resulted in lower yield. Excess of trifluoroacetic acid (5 equiv) was found to be essential for the completion of the reaction. 1 mol % of $Pd(OAc)_2$ was confirmed to be optimal. An increase in catalyst concentration from 1 to 5 mol % afforded the product in lower yield due to unwanted polymerization/decomposition. The catalytic efficiencies of other Pd-catalysts were also examined, and it revealed that among the tested catalysts (i.e., $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_2(OAC)_2$, $Pd(TFA)_2$, $Pd(OAc)_2$, $Pd_2(dba)_3$, $Pd(PPh_3)_4$ and Pd/C), $Pd(OAc)_2$ displayed higher activity under the same experimental conditions (entries 3−10).

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 propiolate in absence of trifloroacetic 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), whereas the cross-coupling in presence of $Pd(CF_3COO)_2$ afforded 72% yield of enamide (entry 7). It indicates that at optimum reaction conditions, like earlier observations of Fujiwara[21] and Kitamura,[22] $Pd(OAc)_2$ reacts with CF_3CO_2H and leads to the more reactive $Pd(CF_3COO)_2$. 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**).

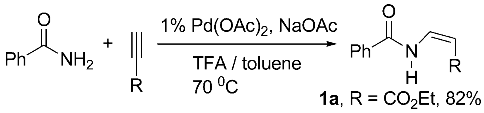
Scheme 2. Plausible Mechanism



As expected, like Chang's[10b] and our[10d] report, the possible hydrogen bonding between the carbonyl oxygen of alkyne and the N—H of amide (C═O···H—N) provides the additional stability to the complex and thus drives the equilibrium toward **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 proto-depalladation[23,24] readily and affords the *Z*-enamide selectively.

Having the optimal conditions, the scope of alkyne component was explored with different substitutions. It revealed that electron-withdrawing substitutions like −COOH, COAr to the alkyne, resulted *Z*-enamides selectively in modest yield (Scheme 3). Unactivated alkynes such as phenylacetylene and 1-octyne are inactive to afford the enamide, albeit the homocoupling of alkynes were resulted.

Scheme 3



1a, R = CO_2Et, 82%
2, R = CO_2H, 60 %
3a, R = COC_6H_5, 43%
3b; R= COC_6H_4-p-OCH_3, 45%

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 were obtained. As such, electron-withdrawing substituents (i.e., $-NO_2$, 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 12−16). However, when secondary amides were used, tertiary enamides with *E*-selectivity (J = 14.4 Hz) were resulted in modest yield (entries 17−20). 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 toward the thermodynamically more stable intermediate (e.g., **III**).

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

■ EXPERIMENTAL SECTION

General Procedure for Enamide Synthesis from Alkyne. Method A: An oven-dried round-bottom flask was charged with amide (100 mg), $Pd(OAc)_2$ (1 mol %), trifluoroacetic acid (5 equiv), NaOAc (2 equiv), and toluene (4 mL). The reaction mixture was stirred for 5 min under nitrogen atmosphere at room temperature, and then ethyl propiolate (1.5 equiv) was added dropwise. The reaction mixture was then stirred for 5 min, and then temperature was raised to 70 °C. After 12 h, the reaction mixture was diluted with ethyl acetate followed by water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over brine, anhydrous Na_2SO_4, and then evaporated under reduced pressure. The crude residue was purified by column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the pure enamide.

Method B: An oven-dried round-bottom flask was charged with amide (100 mg), $Pd(OAc)_2$ (1 mol %), trifluoroacetic acid (5 equiv), NaOAc (2 equiv), and toluene (4 mL). The reaction mixture was stirred for 5 min under nitrogen atmosphere at room temperature, and then ethyl propiolate (1.5 equiv) was added dropwise. The reaction mixture was stirred for 36 h at room temperature (rt) and then diluted with ethyl acetate followed by water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over brine, anhydrous Na_2SO_4, and then evaporated under reduced pressure. The crude residue was purified by column chromatography over silica gel using mixture of petroleum ether and ethyl acetate as eluent to give the pure enamide.

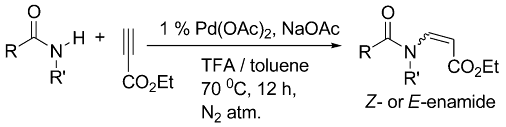
(Z)-Ethyl 3-(benzamido)acrylate (1a).[10b] **1a** was obtained following general procedure (Method A) as a white crystalline solid (179 mg, 82% yield): mp 76−77 °C; IR (KBr) 3324, 2955, 1684, 1638, 1581, 1508, 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.54 (d, 1H, J = 9.6 Hz), 7.98−7.95 (m, 2H), 7.76 (dd, 1H, J_1 = 11.2 Hz, J_2 = 8.8 Hz), 7.64−7.58 (m, 2H), 7.55−7.49 (m, 2H), 5.28 (d, 1H, J = 8.4 Hz), 4.25 (q, 2H, J = 7.2 Hz), 1.34 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (s), 164.5 (s), 138.7 (d), 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 intensity) 217.90 ($[M - H]^+$, 100%). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.40; H, 5.68; N, 6.09.

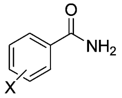
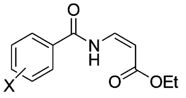
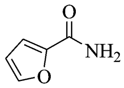
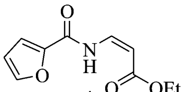
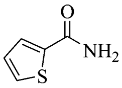
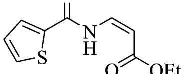
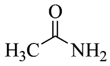
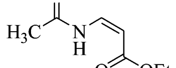
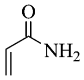
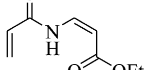
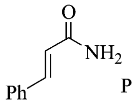
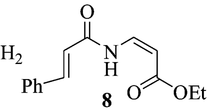
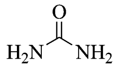
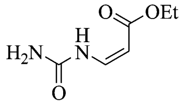
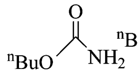
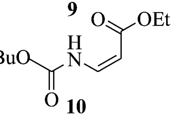
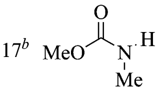
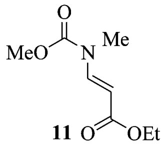
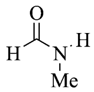
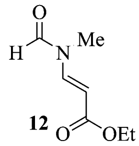
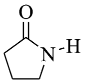
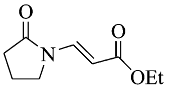
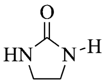
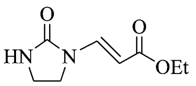
(Z)-Ethyl 3-(4-methoxybenzamido)acrylate (1b). **1b** was obtained following general procedure (Method A) as a white crystalline solid (169 mg, 68% yield): mp 100−102 °C; IR (KBr) 3433, 2998, 2967, 2924, 1670, 1622, 1479, 1369 cm.$^{-1}$ ^1H NMR (400 MHz, $CDCl_3$) δ 11.46 (d, 1H, J = 10.8 Hz), 7.94 (d, 2H, J = 8.8 Hz), 7.75 (dd, 1H, J_1 = 11.2 Hz, J_2 = 8.8 Hz), 6.99 (d, 2H, J = 8.8 Hz), 5.24 (d, 1H, J = 9.2 Hz), 4.25 (q, 2H, J = 6.8 Hz) 3.89 (s, 3H), 1.35 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 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 (q), 14.2 (q); MS (ESI, −Ve) m/z (relative intensity) 248.13 ($[M - H]^+$, 100%). Anal. Calcd for $C_{13}H_{15}NO_4$: 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 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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 ($[M - H]^+$, 100%). Anal. Calcd for $C_{12}H_{12}ClNO_3$: 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 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.15 (d, 1H, J = 8.8 Hz), 7.75−7.66 (m, 2H), 7.52−7.41 (m, 2H), 7.40−7.34 (m, 1H), 5.27 (d, 1H, J = 9.2 Hz), 4.20 (q, 2H, J = 7.2 Hz), 1.29 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (s), 164.3 (s), 137.4 (d), 133.2 (s), 132.3 (d), 131.5 (s), 130.7 (d), 130.5 (d), 127.1 (d), 98.1 (d), 60.2 (t), 14.2 (q); MS (ESI, −ve) m/z (relative intensity)

Table 2. Enamide Synthesis[a]



Entry	Substrate	Product	% Yield
			
1	X= H	**1a**	82
2	X = 4-OMe	**1b**	68
3	X= 4-Cl	**1c**	62
4	X = 2-Cl	**1d**	56
5	X = 4-NO$_2$	**1e**	72
6	X = 2-NO$_2$	**1f**	50
7	X = 3-NO$_2$	**1g**	56
8[b]	X = 2-OMe	**1h**	75
9	X = 2-OH	**1i**	56
10		 **4**	67
11		 **5**	60
12		 **6**	52
13		 **7**	55
14		 **8**	52
15[b]		 **9**	46
16[b]		 **10**	54
17[b]		 **11**	56
18[b]		 **12**	41
19		 **13**	72
20		 **14**	54

[a]Reaction conditions: 100 mg of amide, ethyl propiolate (1.5 equiv), TFA (5 equiv), Pd(OAc)$_2$ (1 mol %), NaOAc (2 equiv) heated at 70 °C for 12 h under N$_2$ atmosphere. [b]Reactions were carried out at room temperature over a period of 36 h.

252.16 ([M − H]$^+$, 100%). Anal. Calcd for $C_{12}H_{12}ClNO_3$: 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.$^{-1}$ ^{1}H NMR (400 MHz, CDCl$_3$) 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_1= 10.8 Hz, J_2= 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); ^{13}C NMR (100 MHz, CDCl$_3$) 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]$^+$, 100%). Anal. Calcd for $C_{12}H_{12}N_2O_5$: 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.$^{-1}$ ^{1}H NMR (400 MHz, CDCl$_3$) 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), 4.27 (q, 2H, J = 7.2 Hz), 1.35 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) 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]$^+$, 100%). Anal. Calcd for $C_{12}H_{12}N_2O_5$: 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 cm.$^{-1}$ ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.92 (d, 1H, J = 9.6 Hz), 8.11 (m, 1H), 7.77−7.60 (m, 4H), 5.33 (d, 1H, J = 8.8 Hz), 4.18 (q, 2H, J = 7.2 Hz), 1.30 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.1 (s), 163.9 (s), 146.9 (s), 137.4 (d), 133.7 (d), 131.4 (d), 131.1 (s), 128.3 (d), 124.8 (d), 98.5 (d), 60.4 (t), 14.1 (q); MS (ESI, −ve) m/z (relative intensity) 263.02 ([M − H]$^+$, 100%). Anal. Calcd for $C_{12}H_{12}N_2O_5$: C 54.55; H 4.58; N 10.60. Found: C 54.74; H 4.67; N 11.00.

*(Z)-Ethyl 3-(2-methoxybenzamido)acrylate (**1h**).* **1h** was obtained following general procedure (Method B) as oil (186 mg, 75% yield): IR (neat) 3442, 3025, 2979, 2846, 1680, 1621, 1481, 1397 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.40 (d, 1H, J = 9.6 Hz), 8.27−8.22 (m, 1H), 7.78 (dd, 1H, J_1 = 11.2 Hz, J_2 = 8.8 Hz), 7.55−7.51 (m, 1H), 7.12−6.99 (m, 1H), 5.21 (d, 1H, J = 9.2 Hz), 4.25 (q, 2H, J = 7.2 Hz), 4.12 (s, 3H), 1.32 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.4 (s), 163.6 (s), 158.4 (s), 138.0 (d), 134.2 (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) m/z (relative intensity) 272.02 ([M + Na]$^+$, 100%), 521.10 ([2M + Na]+, 90%). Anal. Calcd for $C_{13}H_{15}NO_4$: C 62.64; H 6.07; N 5.62. Found: C 62.48; H 5.90; N 5.38.

*Ethyl 3-(2-hydroxybenzamido)acrylate (**1i**).* **1i** was obtained following general procedure (Method A) as a white crystalline solid (131 mg, 56% yield): mp 98−100 °C; IR (KBr) 3311, 2956, 1686, 1661, 1636, 1602, 1517 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.84 (s, 1H), 11.75 (d, 1H, J = 9.6 Hz), 7.71 (dd, J_1 = 10.8 Hz, J_2 = 8.8 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 = 8.8 Hz), 4.26 (q, 2H, J = 7.2 Hz), 1.35 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 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 (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}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 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$_3$) δ 173.9 (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**).[26] **3a** was obtained following general procedure (Method A) as a white crystalline solid (89 mg, 43% yield): mp 102−104 °C; IR (KBr) 3338, 3063, 2912, 2858, 1692, 1638, 1585, 1384, 1234, 1012 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.95 (d, 1H, J = 9.2 Hz,), 8.10−8.07 (m, 2H), 8.02−7.90 (m, 3H), 7.66−7.48 (m, 6H), 6.43 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 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}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.98 (d, 1H, J = 10 Hz), 8.13−8.05 (m, 2H), 8.03−7.96 (m, 2H), 7.92 (dd, 1H, J_1 = 10.8 Hz, J_2 = 8.8 Hz, 1H), 7.65−7.60 (m, 1H), 7.58−7.53 (m, 2H), 7.02−6.98 (m, 2H), 6.40 (d, 1H, J = 8.8 Hz), 3.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 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), 127.9 (d), 113.9 (d), 100.8 (d), 55.5 (q); MS (ESI, −ve) m/z (relative intensity) 280.09 ([M − H]$^+$, 100%). Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98; O, 17.06. Found: C, 72.65; H, 5.33; N, 5.05.

(Z)-Ethyl 3-(furan-2-carboxamido)acrylate (**4**). **4** was obtained following general procedure (Method A) as a white crystalline solid (140 mg, 67% yield): mp 83−85 °C; IR (KBr) 3327, 3128, 2978, 2936, 2874, 1725, 1685, 1629, 1587, 1492, 1469 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.38 (d, 1H, J = 8.8 Hz), 7.68−7.58 (m, 2H), 7.31 (m, 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 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.1 (s), 155.6 (s), 146.5 (s), 145.6 (d), 137.3 (d), 117.0 (d), 112.6 (d), 97.4 (d), 60.3 (t), 14.2(q); MS (ESI, +ve) m/z (relative intensity) 210.12 ([M + H]$^+$, 100%). Anal. Calcd for $C_{10}H_{11}NO_4$: C 57.41; H 5.30; N 6.70. Found: C 57.59; H 5.18; N 6.58.

(Z)-Ethyl 3-(thiophene-2-carboxamido)acrylate (**5**). **5** was obtained following general procedure (Method A) as a white crystalline solid (135 mg, 60% yield): mp 116−118 °C; IR (KBr) 3335, 3070, 2952, 1674, 1627, 1525, 1470, 1425 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.40 (d, 1H, J = 9.6 Hz), 7.75−7.72 (m, 1H), 7.68 (dd, J_1 = 8.8 Hz, 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 Hz), 1.33 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.5 (s), 159.2 (s), 138.3 (d), 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 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**).[10b] **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}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.42 (s, 1H), 7.49 (dd, 1H, J_1 = 11.2 Hz, J_2 = 8.8 Hz), 5.09 (d, 1H, J = 9.2 Hz), 4.15 (q, 2H, J = 7.2 Hz), 2.17 (s, 3H), 1.26 (t, 3H, J = 7.2 Hz); ^{13}CNMR (100 MHz, CDCl$_3$) δ 169.1 (s), 168.5 (s), 137.8 (d), 96.4 (d), 60.1 (t), 23.5 (q), 14.1 (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.$^{-1}$ ^{1}H NMR (400 MHz, CDCl$_3$) δ 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$_3$) δ 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**).[10b] **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.$^{-1}$ ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.73 (d, 1H, J = 9.2 Hz), 7.79 (d, 1H, J = 15.6 Hz), 7.67 (dd, 1H, J_1 = 8.8 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, J = 8.8 Hz) 4.23 (q, 2H, J = 7.2 Hz), 1.34 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 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 (d), 60.2 (t), 14.2 (q); MS (ESI, −ve) m/z (relative intensity) 243.88 ([M − H]$^+$, 100%). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.36; H, 6.42; N, 6.08.

(Z)-Ethyl 3-ureidoacrylate (**9**). **9** was obtained following general procedure (Method B) as oil (72 mg, 46% yield): IR (neat) 3431, 3384, 2970, 2924, 2851, 1710, 1656, 1632, 1510, 1463, 1366 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 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 Hz), 5.04 (s, 2H, *-NH*$_2$), 4.18 (q, 2H, J = 7.2 Hz), 1.30 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ169.8 (s), 153.7 (s), 140.7 (d), 93.2 (d), 59.9 (t), 14.2 (q); MS (ESI, +ve) m/z (relative intensity) 159 ([M + H]$^+$, 100%), 316 ([2M]$^+$, 30%). Anal. Calcd for $C_6H_{10}N_2O_3$: C, 45.57; H, 6.37; N, 17.71. Found: C, 45.77; H, 6.29; N, 17.92.

Butyl (Z)-2-(ethoxycarbonyl)vinylcarbamate (**10**). **10** was obtained following general procedure (Method B) as oil (116 mg, 54% yield): IR (neat) 3716, 3329, 2962, 2874, 1745, 1685, 1633, 1489, 1404, 1370, 1355 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 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, 2H), 1.46−1.40 (m, 2H), 1.33 (t, 3H, J = 7.2 Hz), 0.96 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 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), 13.5 (q); MS (ESI, +ve) m/z (relative intensity) 238.14 ([M + Na]$^+$, 100%). Anal. Calcd for $C_{10}H_{17}NO_4$: 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 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 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}C NMR (100 MHz, CDCl$_3$) δ 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 ([M + H]$^+$, 100%). Anal. Calcd for $C_8H_{13}NO_4$: 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 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.48 (s, 1H), 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}C NMR (100 MHz, CDCl$_3$) δ 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 ([2M]$^+$ 100%). Anal. Calcd for $C_7H_{11}NO_3$: C, 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**).[25] **13** was obtained following general procedure (Method A) as a white crystalline solid (131 mg, 72% yield): mp 118−120 °C; IR (KBr) 3083, 2979, 2905, 1727, 1627, 1460, 1386, 1364, 1326 cm.$^{-1}$ ^{1}H NMR (400 MHz,

$CDCl_3$) δ 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}C NMR (100 MHz, $CDCl_3$) δ 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} ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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Notes

The authors declare no competing financial interest.

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