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An efficient catalyst-free one-pot synthesis of primary amides from aldehydes of Baylis-Hillman Reaction

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A facile and efficient method for the preparation of allyl amides from the aldehyde of Baylis-Hillman adducts has been developed using hydroxylamine/methanol system under catalyst-free condition. The effect of solvents, temperature effect on the reaction and substituents on the phenyl ring have been examined. This method is best demonstrated by its advantages like operational simplicity, moderate to excellent yields, short reaction time and simple reaction procedure. Most importantly, the reaction proceeds smoothly in the absence of a catalyst and external oxidant.

Introduction

The amide is a ubiquitous functionality of numerous biologically active molecules and forms an essential integral part of many natural products, functional materials and pharmaceutical drugs (Fig. 1).[1] These are significant intermediates in the modern organic synthesis and used as raw materials for engineering plastics, detergent manufacturing, pesticides, lubricants, anti-block reagents, intensifiers of perfume, natural products, proteins, peptides, bio-molecules and materials science.[2] Furthermore, the important advantage properties of amides, such as good stability, high polarity and conformational diversity, make it one of the most reliable and popular functional groups in organic chemistry. Particularly, α,β-unsaturated primary amides are synthetically important key intermediates and useful precursors for various biologically active compounds and pharmaceuticals.[3-5]

Traditionally, the most common and basic methodology for the synthesis of the primary amide is ammonolysis of carboxylic acid derivatives such as acids, acyl halides, anhydrides and esters.[6] Another attractive method for the preparation of amide is the amino carbonylation of olefins in the presence of transition metal catalysts.[7] Carbonyl compounds such as aldehydes, ketones, and oximes are imperative intermediates in the synthesis of amides.[8] However, the applications of these existing methods are still inadequate due to some flaws, such as harsh reaction conditions, poor atom-efficiency, longer reaction time, use of hazardous reagents, tedious workup, and generation of wastes.

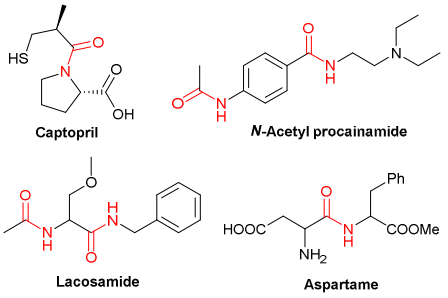

Fig. 1 Amide bond in pharmaceutical drugs.

To overcome these problems, numerous synthetic approaches have been reported such as Beckmann rearrangement,[9] Staudinger reaction,[10] Aube-Schmidt reaction,[11] amino carbonylation of haloarenes,[12] iodonium-promoted α-bromonitroalkane with amine coupling,[13] direct amide from alcohols with nitroarenes or amines,[14] hydroamination of alkynes,[15] amidation of thioacids in the presence of azides,[16] from primary amides by transamidation,[17] from organonitriles by hydration[18] and *N*-formylation of amines by aerobic oxidation.[19] Importantly, oxidative amidation of aldehydes via C-H activation of aldehyde is one of the elegant approaches that have been used as less hazardous than those traditional methods.[20] Several methods for oxidative amidation of aldehydes with amines have been reported using stoichiometric amounts of oxidant/catalyst such as NBS,[21] iodine,[22] *tert*-butyl hydroperoxide (TBHP),[23] 3,3,5,5-tetra-*tert*-

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butyldiphenoquinone,[24] *N*-heterocyclic carbene (NHC),[25] lanthanides[26] and transition metals.[27] In fact, to the best of our knowledge, there are few methodologies explored for the direct conversion of aldehydes into primary amides using $NH_2OH.HCl$ in the presence of catalyst.[28]

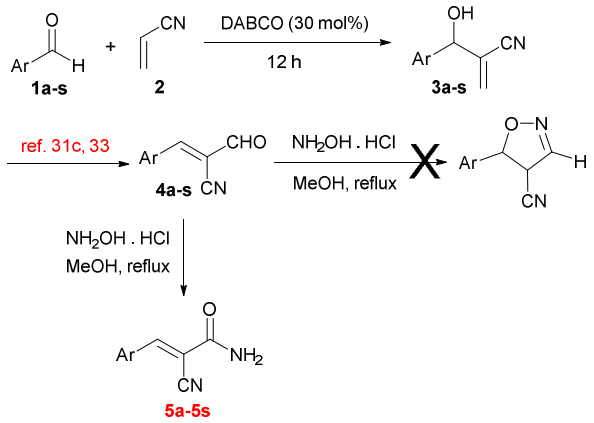
In above cases, significant results were obtained but the use of expensive metal catalysts and utilisation of other co-reagents were restricted for large scale reactions. Therefore, the development of a simple, efficient and promising method to access primary amides remains highly desirable. In this context, the novel and practical methods for the synthesis of primary amide, whether catalyst-free or waste-free are in great demand.

In recent years, the Baylis-Hillman reaction has attracted the attention of many organic chemists, because it is a simple, straightforward method for the generation of attractive densely functional molecules.[29] During the past few years, a lot of our efforts have been devoted to Baylis-Hillman chemistry and its applications towards the synthesis of new heterocyclic compounds.[30] Some of our synthesized compounds even displayed good biological activity.[31]

Our research into new methodologies for environmentally benign processes[32] prompted us to investigate the direct transformation of cyanocinnamaldehydes into primary amides. Herein, we described the use of hydroxylamine as an excellent reagent for the easy and mild adaptation of Baylis–Hillman adducts into the corresponding allyl amides under a catalyst-free condition in methanol. This reaction is fast, smooth, clean and high yielding.

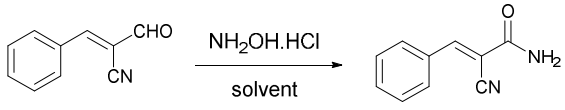
Results and discussion

The synthesis of substituted (*E*)-2-cyano-3-phenylacrylamide (**5a**-**s**) as outlined in Scheme 1 commenced with the Baylis-Hillman (BH) reaction of a series of substituted aromatic aldehydes (**1a-s**) with acrylonitrile (**2**) using a catalytic amount of DABCO at room temperature under solvent-free condition.[31c] The synthesized Baylis-Hillman adducts (**3a-s**) were converted into corresponding substituted (*E*)-α-cyanocinnamaldehydes (**4a-s**) using the well know procedure.[31c,33] At this stage, our initial attempt was made to synthesis of 2,3-dihydroisoxazoles from (*E*)-α-cyanocinnamaldehydes using $NH_2OH.HCl$. However, to our surprise, an unexpected cinnamylamide (**5a**) was obtained in 30% yield instead of 2,3-dihydroisoxazole when the reaction was carried out in the presence of 1 equivalent $NH_2OH.HCl$ in methanol at room temperature using **4a** as a substrate (Table 1, entry 1). Pleasingly, reaction yield could be increased up to 49% with 2 equivalents of $NH_2OH.HCl$ (Table 1, entry 2). It could be found that the amount of $NH_2OH.HCl$ had a noteworthy influence on the formation of the product **5a**. In this sense, to improve the yield of the reaction, we started our investigations by testing various solvent systems with 2 equivalents of $NH_2OH.HCl$ at room temperature or reflux temperature, using model substrate **4a**. Different polar and non-polar solvents were used for standardization of the reaction conditions and the best results were realized in methanol/ethanol system (Table 1, entries 2 and 3). Notably, the reaction was smoothly performed in both methanol and ethanol underwent effortlessly and no change in the yield as wells as the time of the reaction at reflux temperature (Table 1, entry 4 and 5).



Scheme 1 Synthesis of amides.

Table 1 Optimization of the reaction conditions[a]



4a 5a

Entry	Solvent (Temp)	Time (h)	Yield (%)[b]
1	MeOH (rt)	5	30[c]
2	MeOH (rt)	5	49
3	EtOH (rt)	5	50
4	MeOH (reflux)	2	84
5	EtOH (reflux)	2	84
6	MeOH/EtOH (4 Å MS, reflux)	2	-
7	Aq. MeOH	24	-
8	CH_3CN (rt)	24	-
9	Toluene (rt)	24	-
10	AcOH (rt)	24	-
11	DCM (rt)	24	-
12	THF (rt)	24	-
13	AcOH (reflux)	24	40
14	Toluene (reflux)	24	30

[a]Reaction conditions: **4a** (0.4 mmol), $NH_2OH.HCl$ (2 equiv), solvent (2 mL). [b]Isolated yields. [c]$NH_2OH.HCl$ (1 equiv).

No amide could be obtained when the reaction was performed in methanol or ethanol using molecular sieves under identical conditions (Table 1, entry 6). Importantly, when aqueous methanol was used as a solvent the desired product **5a** was not obtained (Table 1, entry 7). It was noticed that the reaction was not initiated with some organic solvents such as CH_3CN,

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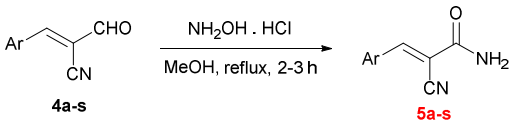
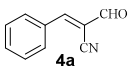
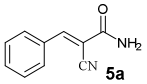
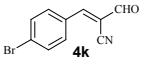
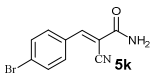
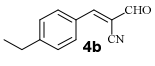
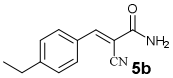
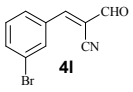
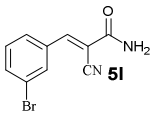
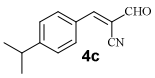
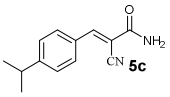
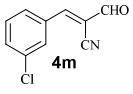
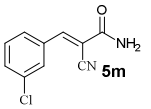
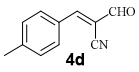
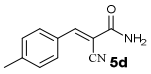
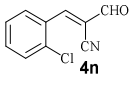
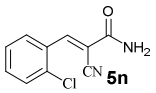
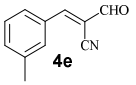
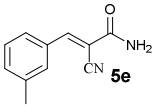
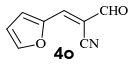
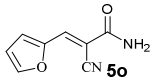
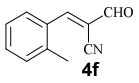
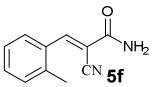
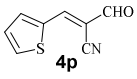
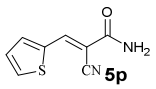
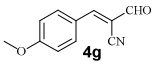
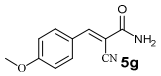
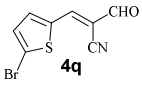
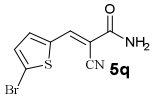
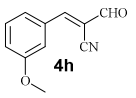
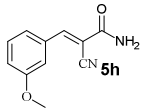
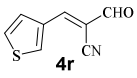
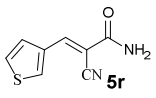
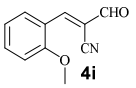
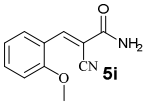
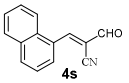
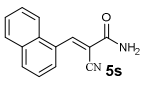
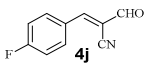
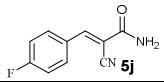
toluene, acetic acid, DCM and THF at room temperature (Table 1, entries 8-12). However, when the reaction was carried out at reflux temperature in acetic acid or toluene the desired product **5a** was obtained in lower yields (entry 13 and 14). From Table 1, it could also be found that the reaction was indolent at room temperature and absolute conversion could be occurred at reflux temperature within short period of time (2 h) when the reaction was carried out in methanol.

Having optimized reaction conditions in hand, to further probe the scope and limitations of this method a variety of substituted cinnamaldehydes could be effectively renewed into the corresponding amides (**5a-s**) in good to excellent yields as listed in Table 2. Therefore, phenyl group containing the electron-donating as well as withdrawing groups at different positions have been employed efficiently in this protocol irrespective of the steric and electronic character of a substituent on the phenyl ring. To our delight, this method could also be applied to the transformation of hetero-atom containing cinnamaldehydes, such as 2-furyl, 2-thienyl, 3-thienyl and 5-bromo-2-thienyl as well as extended aromatics, such as naphthyl cinnamaldehyde could be tolerated well under the optimal conditions, and smoothly afforded the corresponding amides, in good yields.

Table 2 Direct synthesis of primary amides from aldehydes under catalyst-free condition[a]



Entry	Aldehyde	Amide	Time (h)	Yield (%)[b]	Entry	Aldehyde	Amide	Time (h)	Yield (%)[b]
1	 4a	 5a	2	87	11	 4k	 5k	2	81
2	 4b	 5b	2.8	77	12	 4l	 5l	2	76
3	 4c	 5c	2.5	75	13	 4m	 5m	2	82
4	 4d	 5d	2.5	77	14	 4n	 5n	2	76
5	 4e	 5e	3	76	15	 4o	 5o	2	74
6	 4f	 5f	3	81	16	 4p	 5p	2.5	84
7	 4g	 5g	2.5	82	17	 4q	 5q	3	78
8	 4h	 5h	3	85	18	 4r	 5r	3	81
9	 4i	 5i	2.6	85	19	 4s	 5s	2.5	85
10	 4j	 5j	2	78					

[a]The reaction was conducted with **4** (1 mmol) and $NH_2OH.HCl$ (2 mmol) in 5 mL of methanol at reflux temperature.

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[b]Isolated yield.

On the other hand, to further investigate the practical application of this alteration in organic synthesis, the gram-scale reaction of **4a** was performed under standard reaction conditions. Interestingly, compound **5a** was smoothly afforded in 90% yield without any decrease when compared to the small-scale reaction (Table 2, entry 1). The cyanoacrylamide scaffolds play significant role in the field of synthetic organic chemistry and medicinal community, and they also possess fluorescent properties.[34]

The spectral data (^{1}H NMR, ^{13}C NMR, Mass, and IR) of the synthesized compounds are in full agreement with proposed structures. The ^{1}H NMR of spectra of the compound **5a** showed two broad singlets at 6.34 and 5.94 ppm corresponding to exchangeable amide (NH_2) hydrogens. Further, signals of the corresponding aromatic and aliphatic protons were present as well. The ^{13}C NMR spectra exhibited signal at 115 ppm corresponding to the nitrile group, the signal appeared at downfield region 160 ppm corresponding to the amide group (C=O). In addition, IR spectra of products showed a signal at 2220 cm^{-1}, due to the presence of nitrile group and signal at 1690 cm^{-1} corresponding to the carbonyl amide (NH_2) group. Furthermore, the structure of compound **5a** was fully established by a single crystal X-ray diffraction analysis (**Fig. 2**).

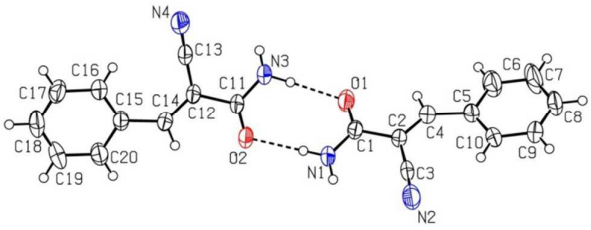
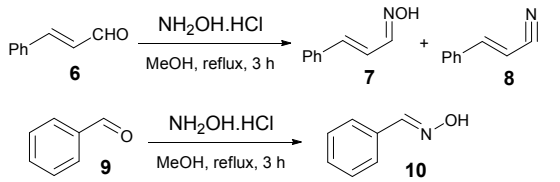


Fig. 2 ORTEP diagram of compound **5a** with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.



Scheme 2

We also tried to use simple aldehydes such as *trans*-cinnamaldehyde and benzaldehyde. The reaction of *trans*-cinnamaldehyde (**6**) with $NH_2OH.HCl$ under optimal reaction conditions gave a mixture of oxime (**7**) and nitrile (**8**) with 9:1 ratio respectively. On the other hand, the benzaldehyde (**9**) provided oxime (**10**) as the only product in 94% yield (Scheme 2).

Conclusions

In this paper, we disclosed a novel, efficient and useful pathway for the synthesis of primary amide derivatives under simple reaction conditions. Baylis-Hillman adducts were used in the synthesis of new amide derivatives and characterized by spectral analyses. Application of this strategy to the preparation of new heterocyclic entities from allyl amides is currently being pursued. Moreover, this pathway has advantages like oxidant-free and catalyst-free conditions as well. Further studies on the mechanism and synthetic applications are ongoing in our research group.

Experimental section

General

All commercially available chemicals were used without further purification. Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra were recorded using a Thermo Nicolet Nexus 670 FTIR spectrometer. The NMR spectra were recorded on Bruker Avance 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C, respectively, using TMS as an internal standard. The chemical shifts are expressed as δ values in parts per million (ppm) and the coupling constants (*J*) are given in Hertz (Hz). ESI-MS was obtained on Thermo-Finnigan MAT-1020B instrument. Column chromatography was performed on silica gel (60-120 mesh, Acme, India).

General procedure for the synthesis of Baylis-Hillman adducts (3a-s)[31c]

Aromatic aldehydes (**1a-s**) (5 mmol), acrylonitrile (**2**) (10 mmol) and DABCO (30 mol% with respect to aldehyde) were mixed and allowed to stir at room temperature until completion of the reaction (10-12 h) was monitored by TLC. After that, the reaction mixture was diluted with water (15 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography using 10% EtOAc in hexane as eluent to afford pure Baylis-Hillman adducts (**3a-s**) in 80-90% yield. The spectroscopic and analytical data of all the synthesized compounds were in good agreement with those reported in the literature.[31c,29]

General procedure for the synthesis of [E]-α-cyanocinnamaldehyde (4a-s)

A stirred solution of BH adduct **3a-s** (1 mmol) and $NaNO_3$ (1 mmol) in 1 mL of $[Hmim]HSO_4$ was heated at 80 °C for 1–2 h. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The resulting crude product was purified by column chromatography using 10% EtOAc in hexane as eluent to afford pure [*E*]-α-cyanocinnamaldehyde derivatives (**4a-s**). The characterization

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data of the newly synthesized compounds were given below.[31c,33]

(*E*)-2-Formyl-3-(3-methoxyphenyl)acrylonitrile (4h)

White solid; Yield: 71%; mp: 80-83 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.83 (s, 1H), 7.69-7.67 (m, 1H), 7.50-7.40 (m, 2H), 7.16-7.12 (m, 1H), 3.89 (s, 3H); ESI-MS (*m/z*) 188 $[M+H]^+$.

(*E*)-3-(3-Chlorophenyl)-2-formylacrylonitrile (4m)

White solid; Yield: 62%; mp: 92-94 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (s, 1H), 8.00-7.95 (m, 2H), 7.85 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H). ESI-MS (*m/z*) 209 $[M+NH_4]^+$.

General procedure for the synthesis of (*E*)-2-cyano-3-phenylacrylamide (5a-s)

To a magnetically stirred suspension of (*E*)-α-cinnamaldehyde **4a-s** (1 mmol) in methanol (5 mL) was added hydroxylamine hydrochloride (2 mmol) in one portion and stir the reaction mixture under reflux for the appropriate time, the reaction evolution was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography to afford pure [*E*]-α-acrylamide (**5a-5s**) as white solid. Other amide derivatives were prepared in a similar way. All compounds were characterised by ^{1}H NMR, ^{13}C NMR, IR and Mass and compared with the reported data.[34]

(*E*)-2-Cyano-3-phenylacrylamide (5a)

White solid; Yield: 87%; mp: 115-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.98-7.93 (m, 2H), 7.59-7.47 (m, 3H), 6.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 153.9, 132.9, 131.5, 130.7, 129.1, 116.9, 103.1; MS (ESI) m/z (%): 173 $[M+H]^+$.

(*E*)-2-Cyano-3-(4-ethylphenyl)acrylamide (5b)

White solid; Yield: 77%; mp: 129-130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.34 (brs, 1H), 5.94 (brs, 1H), 2.76-2.69 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4, 153.8, 150.4, 131.0, 129.1, 128.7, 117.2, 101.6, 29.0, 14.9; IR (KBr, cm^{-1}): 3378, 3314, 3166, 2967, 2932, 2220, 1694, 1586, 1507, 1370, 1212, 1180; MS (ESI) m/z (%): 201 $[M+H]^+$.

(*E*)-2-Cyano-3-(4-isopropylphenyl)acrylamide (5c)

White solid; Yield: 75%; mp: 112-114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.36 (brs, 1H), 6.06 (brs, 1H), 3.05-2.91 (m, 1H), 1.28 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 162.6, 153.2, 150.2, 130.1, 129.4, 126.9, 116.4, 105.1, 33.4, 23.2; IR (KBr, cm^{-1}): 3417, 3202, 2958, 2212, 1690, 1590, 1461, 1378, 1283, 1212; MS (ESI) m/z (%): 215 $[M+H]^+$.

(*E*)-2-Cyano-3-p-tolylacrylamide (5d)

White solid; Yield: 77%; mp: 150-152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.34 (brs, 1H), 5.93 (brs, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 162.4, 150.4, 142.5, 129.9, 129.3, 128.8, 116.3, 104.5, 21.0; IR (KBr, cm^{-1}): 3386, 3156, 2924, 2217, 1695, 1590, 1373, 1211, 1180; MS (ESI) m/z (%): 187 $[M+H]^+$.

(*E*)-2-cyano-3-m-tolylacrylamide (5e)

White solid; Yield: 76%; mp: 145-146 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.74 (s, 1H), 7.42-7.35 (m, 2H), 6.36 (brs, 1H), 5.97 (brs, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.2, 149.3, 137.8, 130.6, 130.0, 129.6, 126.8, 125.1, 115.3, 106.3, 18.5; IR (KBr, cm^{-1}): 3492, 3384, 3182, 2920, 2223, 1694, 1594, 1391, 1300, 1245; MS (ESI) m/z (%): 187 $[M+H]^+$.

(*E*)-2-Cyano-3-o-tolylacrylamide (5f)

White solid; Yield: 81%; mp: 139-140 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.46-7.39 (m, 1H), 7.36-7.28 (m, 2H), 6.38 (brs, 1H), 6.02 (brs, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.7, 149.9, 138.4, 131.2, 130.6, 130.2, 127.4, 125.7, 115.9, 106.8, 19.1; IR (KBr, cm^{-1}): 3410, 3313, 3170, 2924, 2221, 1699, 1594, 1480, 1382, 1293, 1225; MS (ESI) m/z (%): 187 $[M+H]^+$.

(*E*)-2-Cyano-3-(4-methoxyphenyl)acrylamide (5g)

White solid; Yield: 82%; mp: 210-212 °C; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 8.26 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.28 (brs, 1H), 5.68 (brs, 1H), 3.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.3, 161.0, 148.8, 130.8, 122.8, 115.4, 112.9, 100.8, 53.8; IR (KBr, cm^{-1}): 3445, 3303, 3170, 2927, 2205, 1697, 1582, 1508, 1386, 1361, 1260, 1176; MS (ESI) m/z (%): 203 $[M+H]^+$.

(*E*)-2-Cyano-3-(3-methoxyphenyl)acrylamide (5h)

White solid; Yield: 85%; mp: 145-147 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.52 (m, 1H), 7.51-7.49 (m, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.12-7.09 (m, 1H), 6.34 (brs, 1H), 5.92 (brs, 1H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 162.1, 159.1, 150.4, 132.7, 129.6, 122.5, 117.8, 116.0, 114.1, 106.0, 54.8; IR (KBr, cm^{-1}): 3394, 3312, 3176, 2997, 2222, 1717, 1672, 1597, 1487, 1461, 1378, 1259; MS (ESI) m/z (%): 203 $[M+H]^+$.

(*E*)-2-Cyano-3-(2-methoxyphenyl)acrylamide (5i)

White solid; Yield: 85%; mp: 132-134 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.18 (dd, *J* = 7.7, 1.5 Hz, 1H) 7.53-7.49 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.34 (brs, 1H), 6.01 (brs, 1H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 162.1, 158.1, 145.9, 133.5, 128.0, 120.3, 120.1, 116.3, 110.9, 104.9, 55.2; IR (KBr, cm^{-1}): 3399, 3261, 3207, 3001, 2934, 2208, 1667, 1578, 1489, 1461, 1379, 1303, 1253, 1161; MS (ESI) m/z (%): 203 $[M+H]^+$.

(*E*)-2-Cyano-3-(4-fluorophenyl)acrylamide (5j)

White solid; Yield: 78%; mp: 147-149 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.02-7.96 (m, 2H), 7.20 (t, *J* = 8.4 Hz, 2H), 6.33 (brs, 1H), 5.86 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 165.8, 162.4, 161.7, 150.2, 132.4 (d), 127.7, 116.1, 115.9 (d), 104.0; IR (KBr, cm^{-1}): 3468, 3367, 3303, 3164, 2213, 1700, 1587, 1501, 1412, 1234, 1161; MS (ESI) m/z (%): 213 $[M+Na]^+$.

(*E*)-3-(4-Bromophenyl)-2-cyanoacrylamide (5k)

Pale yellow solid; Yield: 81%; mp: 220-222 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 6.33 (brs, 1H), 5.76 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.8, 149.2, 131.7, 131.2, 130.5, 125.9, 115.7, 106.3; IR (KBr, cm^{-1}): 3437, 3144, 2924, 2853, 2211, 1699, 1599, 1576, 1483, 1397, 1373, 1275; MS (ESI) m/z (%): 252 $[M+H]^+$.

(*E*)-3-(3-Bromophenyl)-2-cyanoacrylamide (5l)

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White solid; Yield: 76%; mp: 136-138 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.03 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 6.34 (brs, 1H), 5.77 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.1, 149.9, 134.5, 133.2, 132.2, 130.1, 128.1, 122.3, 115.6, 105.9; IR (KBr, cm^{-1}): 3468, 3371, 2924, 2208, 1690, 1592, 1554, 1468, 1374, 1291, 1200; MS (ESI) m/z (%):252 $[M+H]^+$.

(*E*)-3-(3-Chlorophenyl)-2-cyanoacrylamide (5m)

White solid; Yield: 82%; mp: 131-133 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.89 (t, *J* = 1.8 Hz, 1H), 7.87-7.84 (m, 1H), 7.54-7.51 (m, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 6.35 (brs, 1H), 5.82 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.6, 148.9, 133.9, 133.3, 131.3, 130.1, 129.0, 127.9, 115.5, 107.2; IR (KBr, cm^{-1}): 3471, 3331, 3215, 2922, 2210, 1692, 1595, 1563, 1421, 1373, 1204; MS (ESI) m/z (%): 207 $[M+H]^+$.

(*E*)-3-(2-Chlorophenyl)-2-cyanoacrylamide (5n)

White solid; Yield: 76%; mp: 150-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.15 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.48 (td, *J* = 8.0, 1.5 Hz, 1H), 7.41 (td, *J* = 7.7, 1.3 Hz, 1H), 6.34 (brs, 1H), 5.92 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.2, 146.9, 134.4, 132.4, 130.0, 129.6, 129.0, 126.9, 115.2, 109.4; IR (KBr, cm^{-1}): 3470, 3376, 3148, 2923, 2214, 1707, 1601, 1467, 1437, 1379, 1280, 1208; MS (ESI) m/z (%):206 $[M]^+$.

(*E*)-2-Cyano-3-(furan-2-yl)acrylamide (5o)

Light brown solid; Yield: 74%; mp: 140-142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.75 (d, *J* = 1.5 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 6.65-6.64 (dd, *J* = 3.6, 1.5 Hz, 1H), 6.29 (brs, 1H), 5.76 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6):δ162.0, 148.2, 147.3, 135.9, 120.0, 115.8, 113.1, 100.8; IR (KBr, cm^{-1}): 3408, 3311, 3203, 2923, 2212, 1696, 1595, 1468, 1380, 1321, 1256, 1157; MS (ESI) m/z (%): 163 $[M+H]^+$.

(*E*)-2-Cyano-3-(thiophen-2-yl)acrylamide (5p)

White solid; Yield: 84%; mp: 150-152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.79-7.78 (m, 1H), 7.77-7.76 (m, 1H), 7.23-7.21 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.26 (brs, 1H), 5.89 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 162.1, 143.2, 136.2, 135.6, 133.7, 127.8, 116.2, 101.5; IR (KBr, cm^{-1}): 3465, 3360, 3137, 2924, 2203, 1699, 1579, 1412, 1376, 1349, 1299, 1211; MS (ESI) m/z (%): 179 $[M+H]^+$.

(*E*)-3-(5-Bromothiophen-2-yl)-2-cyanoacrylamide (5q)

Light yellow solid; Yield: 78%; mp: 148-150 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.48 (d, J = 4.1 Hz, 1H), 7.19 (d, J = 4.1 Hz, 1H), 6.19 (brs, 1H), 5.68 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.8, 142.5, 137.5, 137.3, 131.2, 120.7, 116.2, 102.3; IR (KBr, cm^{-1}): 3420, 3308, 3038, 2210, 1681, 1593, 1415, 1384, 1288, 1237; MS (ESI) m/z (%): 258 $[M+H]^+$.

(*E*)-2-Cyano-3-(thiophen-3-yl)acrylamide (5r)

White solid; Yield: 81%; mp: 125-126 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.12 (d, *J* = 3.0 Hz, 1H), 7.83-7.81 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.47-7.45 (dd, *J* = 5.2, 3.0 Hz, 1H), 6.30 (brs, 1H), 5.98 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 161.8, 144.5, 133.8, 133.6, 126.7, 126.1, 116.3, 102.1; IR (KBr, cm^{-1}): 3469, 3410, 3177, 2924, 2213, 1695, 1589, 1373, 1327, 1249, 1160; MS (ESI) m/z (%): 179 $[M+H]^+$.

(*E*)-2-Cyano-3-(naphthalen-1-yl)acrylamide (5s)

White solid; Yield: 85%; mp: 191-192 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.65-7.58 (m, 3H), 6.40 (brs, 1H), 5.92 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 162.2, 148.1, 132.8, 131.5, 130.7, 129.0, 128.4, 127.0, 126.8, 126.3, 125.0, 123.2, 115.7, 110.5; IR (KBr, cm^{-1}): 3404, 3312, 3169, 2922, 2221, 1696, 1590, 1382, 1351, 1242; MS (ESI) m/z (%): 223 $[M+H]^+$.

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