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rsc.li/njc

DOI: 10.1039/C7NJ05169G

Journal Name

ARTICLE

Triflic Acid Catalyzed Metal-Free Synthesis of (*E*)-2-Cyanoacrylamides and 3-Substituted Azetidine-2,4-diones

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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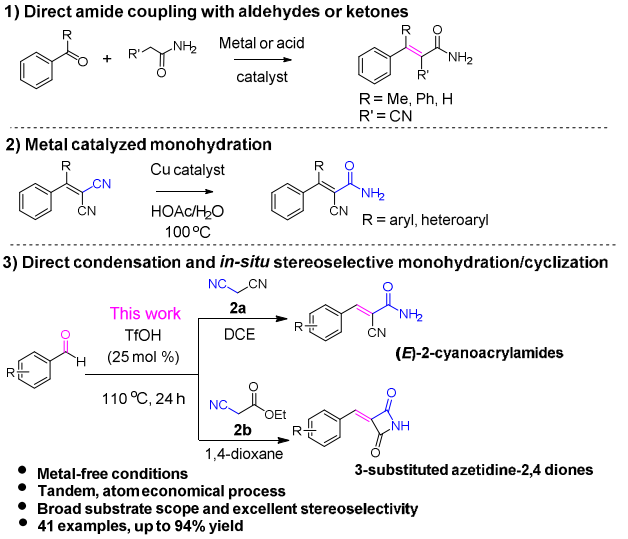
A TfOH-catalyzed highly efficient synthesis of biologically active (*E*)-2-cyanoacrylamides and 3-substituted azetidine-2,4-diones has been reported in 64-94% yields under metal-free condition. The reaction proceeds through sequential knoevenagel condensation/stereoselective in-situ monohydration of nitrile or C-N cyclization protocol in one-pot. The attractive features of this tandem process are moderate reaction conditions, high atom economy, broad substrate scope, gram scale reaction and easy operation.

Introduction

Highly substituted 2-cyanoacrylamides and its derivatives are not only the distinctive structural frameworks but also shows significant biological activities such as protein kinase inhibitors,[1a] GTPase inhibitory activity,[1b] Galactokinase inhibitors,[1c] and diverse pre-functionalized cyanoacrylamides has shown promising inhibitor activities in MSK/RSK-family kinase.[1d] However, multi functionalized azetidines and its derivatives serves as a markedly active drugs against influenza A H2N2 virus,1 anti-HIV-1, anti-HSV-1 and HSV-2 potential.[2] Amides and nitriles are not only the synthetically important moietys but also productive functional groups in chemistry for the key chemical transformations such as amines, carboxylic acids, esters, aldehydes and alcohols etc.[3] In general, the conventional methods for the synthesis of 2-cyanoacrylamides are well-known knoevenagel condensation of aromatic aldehydes or ketones with 2-cyanoacetamide (Scheme 1, eq. 1)[3a,3b] and other methods include use of strong acid or base catalysis,[2] microwave assisted condensation,[4] Titanium tetrachloride and MgO,[5] heterogeneous catalysis,[6] and use of ionic liquids.[7] However, the reported methods known in the literature for the synthesis of 2-cyanoacrylamides have some drawbacks such as they are limited to condensation of only active methylene compounds and having readily available NH_2, $CONH_2$ and CN functional groups in the starting material. In the past decades, worldwide researchers have attracted considerable attention towards hydration of nitriles to amides and the traditional methods for hydration of nitriles is well documented over base catalysis.[8] The main challenge associated in the hydrolysis of nitrile to amide is that it's very difficult to stop the reaction at the amide stage because it undergoes further hydrolysis to give acid. Both homogenous metal catalysts[9] and heterogeneous catalysts such as (Au/TiO_2),[10a] ($Ru(OH)_x/Al_2O_3$),[10b] (Ag/HAP),[10c] KF/Al_2O_3,[10d] KF/phosphate,[10e] MnO_2/SiO_2[10f] Ru-substituted hydroxyapatite ($(RuCl)_2Ca_8(PO_4)_6(OH)_2$)[10] have been reported for the selective conversion of nitriles to amides. However, these reactions often require inert atmosphere and harsh reaction conditions such as the use of high temperature and expensive metal salts.



Scheme 1. Strategies for the synthesis of 2-cyanoacrylamides

Dong and co-workers described an alternative route for the homogeneous and stereoselective monohydration of 2-methylenemalononitriles to 2-cyanoacrylamides by using Cu (II) in acetic acid (Scheme 1, eq. 2)[11a] and more recently rode *et al* reported a direct method for the synthesis of 2-cyanoacrylamides by the condensation and selective

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† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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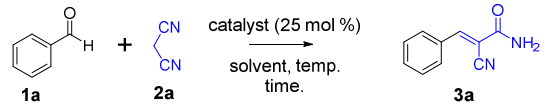
DOI: 10.1039/C7NJ05169G

monohydration of nitriles starting from aldehyde and acetal with malononitrile in the presence of solid acid ferrite catalyst.[11b] To the best of our knowledge, there is no direct metal-free method for the synthesis of (*E*)-2-cyanoacrylamides as well as for 3-substituted azetidine-2,4-diones. Considering the importance of 2-cyanoacrylamides along with 3-substituted azetidine-2,4-diones and as a part of our ongoing research in the development of new synthetic methodologies and organic transformations over heterogeneous catalyst,[12] we herein, disclose for the first time, a one pot TfOH-catalyzed synthesis of (*E*)-2-cyanoacrylamides and 3-substituted azetidine-2,4-diones *via* knoevenagel condensation of aromatic aldehydes with malononitrile/ethyl cyanoacetate under moderate reaction conditions in good to excellent yields.

Results and discussion

Initially, we carried out the reaction between benzaldehyde **1a** with malononitrile **2a** in the presence of Zinc (II) chloride as a catalyst in DCE solvent at 110 °C for 16 h. To our delight, the expected product **3a** was obtained in 60% yield (Table 1, entry **1**).

Table 1.Optimization of the reaction conditions [a]



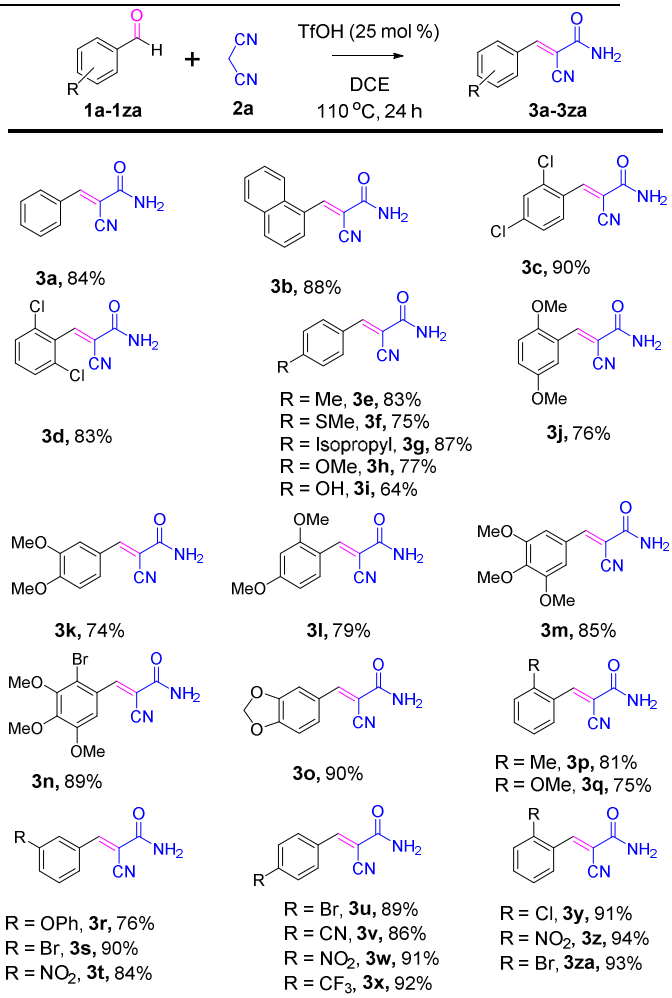
1a 2a 3a

entry	catalyst	solvent	temp. °C	time (h)	yield[b] (%)
1	$ZnCl_2$	DCE	110	16	60
2	$FeCl_3$	DCE	110	16	N.R
3	$AlCl_3$	DCE	110	16	N.R
4	$MgCl_2$	DCE	110	16	N.R
5	$TiCl_4$	DCE	110	16	N.R
6	$AgCOCF_3$	DCE	110	16	Trace
7	$BF_3.Et_2O$	DCE	110	16	Trace
8	TFA	DCE	110	16	Trace
9	$(CF_3SO_2)_2O$	DCE	110	16	N.R
10	TFAA	DCE	110	16	53
11	TfOH	DCE	110	24	84
12	TsOH	DCE	110	16	79
13	TfOH	PhMe	110	24	36
14	TfOH	DMSO	110	24	41
15	TfOH	dioxane	110	24	47
16	TfOH	THF	70	24	31
17	TfOH	EtOH	80	24	46
18	TfOH	MeCN	90	24	70
19	TfOH	IPA	110	24	N.R
20	TfOH	DMF	110	24	N.R
21[c]	TfOH	DCE	110	24	78

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), catalyst (25 mol%), solvent (5 mL), 70-110 °C for 16-24 h. [b]Isolated yields. [c] Catalyst TfOH (20 mol%). N.R = No reaction.

This initial result inspired us to investigate the optimized reaction condition for the formation of **3a**. Several Lewis acid catalysts were screened, such as $FeCl_3$, $AlCl_3$, $MgCl_2$, $TiCl_4$, and $AgCOCF_3$ but unfortunately the reaction failed to give the desired product **3a** (Table 1, entries **2-6**). Next, we examined a series of Brønsted acid catalyst (Table 1, entries **7-12**). Only the TFAA, TfOH and TsOH catalysts were provided the desired product **3a** in 53 to 86% yield. Next, we performed various solvents study (Table 1, entries **13-20**). After careful evaluation, we found that toluene, DMSO, dioxane, THF and EtOH were found to be less effective in the reaction to afford the corresponding product **3a** in 31 to 47% yield. However, acetonitrile as a solvent provided the high yields of desired product in 70% yield and solvents such as IPA and DMF were unsuccessful to produce the corresponding required product (Table 1, entries **18-20**).

Table 2. Substrate scope of aromatic aldehydes **1a-1za** for the synthesis of (*E*)-2-cyanoacrylamides [a]



[a] Reaction conditions: **1a-1za** (1 mmol), **2a** (1.2 mmol), TfOH (25 mol%) in DCE (5 mL) at 110 °C for 24 h.

The catalyst loading 20 mol% was afforded less yield of the product **3a** as compare to 25 mol% of the catalyst (Table 1, entry **21**). After detailed optimization study, we were pleased to find that reaction proceeded very well with TfOH (25 mol %) in DCE solvent (Table 1, entry **11**). After having the optimized

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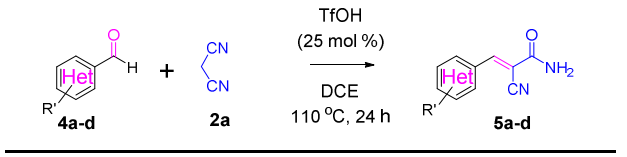
reaction condition in hand, next we explored the substrate scope of the present reaction, by treating various substituted aryl aldehydes **1a-1za** with **2a** (Table 2, entry **3a-3za**). Initially, various unsubstituted aromatic aldehydes **1a-1b** were reacted with **2a** under the optimized reaction condition, to provide the desired 2-cyanoacrylamides product in good yields (Table 2, entries **3a-3b**). This reaction was practically remarkable with aromatic aldehydes bearing both electron-donating and electron-withdrawing substituents on the aryl ring. Consequently, different aryl aldehydes **1c-1za** reacted smoothly to produce the corresponding 2-cyanoacrylamides with good to excellent yields (Table 2, entries **3c-3za**). A variety of functional groups such as Me, OMe, OH, OPh, SMe present at the ortho, meta and para positions of the aromatic aldehydes, mono and disubstituted aldehydes were well tolerated under the optimized reaction condition giving excellent yields of the desired substituted 2-cyanoacrylamides. The *(E)*- stereoselectivity of product 2-cyanoacrylamides were confirmed using NOESY experiment of substrate 3n (see SI).

The substrates having electron-withdrawing substituent on the aromatic ring of aldehydes for example, NO_2, Cl, Br, F and CF_3 groups were efficiently reacted to produce the substituted 2-cyanoacrylamides in slightly higher yield (Table 2, entries **3s-za**). This tandem reaction shows good compatibility with most of the substrates and good functional group tolerance. The success in the synthesis of various (*E*)-2-cyanoacrylamides **3a-3za** and key chemical transformation over Brønsted acid catalyst under metal-free condition prompted us to further extend the substrate scope. Also because of the great potential applications of the nitrile and amide functionality for redox-economy in organic synthesis, we were interested in the synthesis of substituted 2-cyanoacrylamides.[13] Thus, different unsubstituted heterocyclic aldehydes such as **4a-b** and substituted heterocyclic aldehydes such as **4c-d** were subjected to our optimized reaction condition and the results are shown in Table 3.

Table 3. Substrate scope of the heterocyclic aldehydes **4a-d** for the synthesis of (*E*)-2-cyanoacrylamides[a]

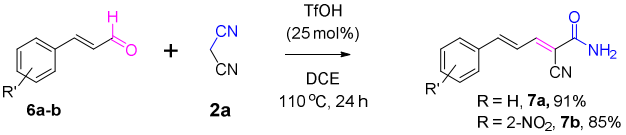


4a-d **2a** **5a-d**

5a, 89% **5b,** 87% **5c,** 94% **5d,** 84%

[a]Reaction conditions: **4a-4d** (1 mmol), **2a** (1.2 mmol), TfOH (25 mol %), in DCE (5 mL) at 110 °C for 24 h.

To our delight, furfuraldehyde, 2-Thiophene carboxaldehyde, 5-bromothiophene-2-carbaldehyde and 3-methylthiophene-2-carbaldehyde were reacted under the standard reaction conditions giving excellent yields of the desired products (Table 3, entries **5a-d**). Motivated by the above results for achieving the monohydration reaction in one-pot, next we thought to investigate the application of present methodology on others substrates like *α,β*-unsaturated aldehydes. Hence, we screened different unsaturated aldehydes such as **6a-b** under optimized reaction condition. The reaction was successfully afforded the desired substituted 2-cyanoacrylamides in 85 and 91% yields (Scheme 2, entry **7a** and **7b**).

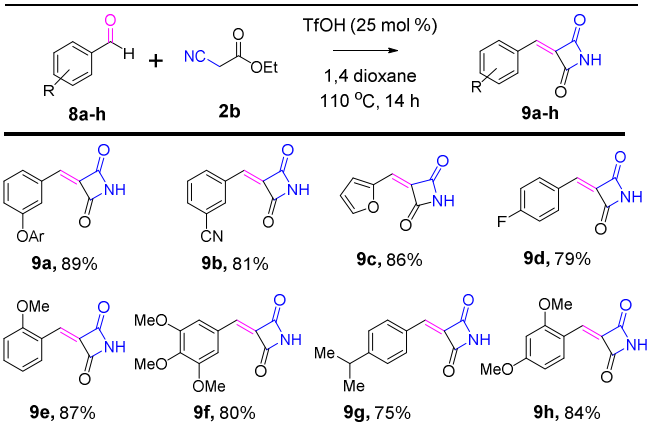


6a-b **2a**

Scheme 2. Substrate scope of the *α,β*-unsaturated aldehydes **6a-b**

Recently, we reported a novel Sn(II)-catalyzed tandem cyclization reaction of aromatic aldehydes with ethyl cyanoacetate for the synthesis of 3-substituted azetidine-2,4-diones.[14] Therefore, we thought to use ethyl cyanoacetate **2b** as the reaction partner instead of malononitrile **2a** in our previously optimized reaction condition.

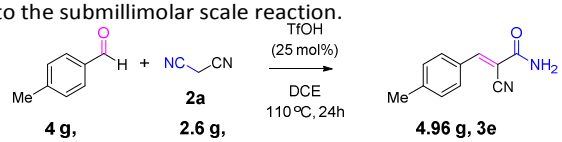
Table 4. Substrate scope of aromatic aldehydes **8a-h** for the 3-substituted azetidine-2,4-diones[a]



8a-h **2b** **9a-h**

[a]Reaction conditions: **8a-h** (1 mmol), **2b** (1.2 mmol), TfOH (25 mol %), in 1,4-dioxane (5 mL) at 110 °C for 14 h.

As depicted in Table 4, the reaction proceeded smoothly with several substituted aromatic aldehydes **8a-h** giving excellent yields of the desired 3-substituted azetidine-2,4-diones and was not found to be much dependent upon the electronic nature of the substituents (Table 4, entry **9a-h**). In this substrate study, both electron donating and withdrawing functional groups on the aromatic aldehydes were found to be very effective. To further demonstrate the significant practicality and efficiency of the developed reaction sequence, a gram scale reaction was performed. The synthesis of (*E*)-2-cyano-3-(p-tolyl)acrylamide (**3e**, 4.96 g) could be achieved in 80% yield from 4-methylbenzaldehyde as the starting material (Scheme 3). The obtained yield of gram scale reaction is similar to the submillimolar scale reaction.



4 g, 33.3 mmol **2a** **2.6 g,** 39.6 mmol **4.96 g, 3e** 26.6 mmol (80 %)

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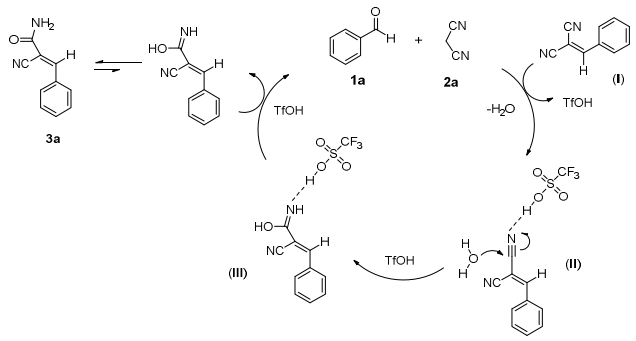
DOI: 10.1039/C7NJ05169G

Scheme 3. Gram scale synthesis of (*E*)-2-cyano-3-(p-tolyl)acrylamide **3e**

Based on the results obtained together with the literature precedence[15] and previous work on triflic acid catalysis, we proposed a possible reaction mechanism for the formation of (*E*)-2-cyanoacrylamides **3a** *via* direct condensation / stereoselective *in-situ* monohydration of nitrile/cyclization reaction (Scheme 4). Initially, benzaldehyde **1a** and malononitrile **2a** undergoes knoevenagel condensation reaction to generate methylenemalononitriles (**I**). The hydration then commences from the coordination of methylenemalononitriles (**I**) with the triflic acid to afford the intermediate (**II**). The anti-cyano group of (**I**) with reference to aryl group is favoured to coordinate to the triflic acid due to both electronic and steric effects.



Scheme 4. Plausible reaction mechanism

The nucleophilic attack of H_2O on the carbon atom of the nitrile of (**II**) afforded intermediate (**III**). The intermediate (**III**) an iminol then undergoes tautomerization to give the corresponding (*E*)-2-cyanoacrylamide (**3a**).

Conclusions

In summary, we have developed for the first time, a novel one-pot metal free method for the synthesis of substituted (*E*)-2-cyanoacrylamides and 3-substituted azetidine-2,4-diones *via* TfOH-catalyzed knoevenagel condensation/stereoselective monohydration and *in-situ* cyclization of aromatic aldehydes and malononitrile/ethyl cyanoacetate. The attractive features of this protocol includes metal-free reaction, good atom economy, broad substrate scope, good functional group tolerance, and practically remarkable in terms of yields and scalability. Further applications of the present methodology are currently ongoing in our laboratory.

Experimental Section

General information:

Unless otherwise specified, all reactions were carried out under an open atmosphere in solvent at reflux condition and reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. All reagents and solvents were obtained from commercial suppliers and Aldrich, Merck Millipore, Alfa Aesar and Avra Synthesis. Aldehydes were purified either by distillation or washing with $NaHCO_3$ after dissolving in ether, prior to use and all AR grade solvents were used without further purification.

Petroleum ether of boiling range 60–80 °C was used. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on AC-200, 400, 500 MHz NMR spectrometers. Deuterated solvent $CDCl_3$+ CCl_4 (70:30) were used as internal standard and singlet at 96.1 ppm in ^{13}C NMR corresponds to carbon of CCl_4. HRMS data for all new compounds were recorded using Orbitrap mass analyzer associated with Accela 1250 pump. Purification was done using column chromatography (100-200 mesh). The reactions were monitored by TLC visualized by UV (254 nm) and/or with iodine. Coupling constants are given in hertz (Hz) and the classical abbreviations are used to describe the signal multiplicities.

General procedure for the optimization of reaction conditions: In a 25 mL round bottom flask benzaldehyde **1a** (1 mmol), malanonitrile **2a** (1.2 mmol), catalyst (20-25 mol %) and solvent (5 mL) were added. The round bottom flask was equipped with condenser and the resultant reaction mixture was refluxed at 70-110 °C for 24 h (Table 1) and the progress of the reaction was monitored by TLC. Upon completion of the reaction, reaction mixture was dried under vacuum. Then the crude reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of silica gel and eluted with EtOAc (20 mL). The solvent was evaporated and the crude residue was preadsorbed on silica gel and purified by column chromatography to afford the corresponding compound **3a** in moderate to good yields.

General procedure for the synthesis of compound 3a-3za and 5a-d: In a 25 mL round bottom flask aldehydes **1a-1za** (1 mmol) or **4a-d** (1 mmol), malononitrile **2a** (1.2 mmol), catalyst TfOH (25 mol%) and DCE (5 mL) were taken. The round bottom flask was equipped with condenser and the resultant reaction mixture was refluxed at 110 °C for 24 h and progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was dried under vacuum. Then the crude reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of silica gel and eluted with EtOAc (20 mL). The solvent was evaporated and the crude residue was preadsorbed on silica gel and purified by column chromatography to afford the corresponding (*E*)-2-cyanoacrylamides **3a-3za** and **5a-d** in good to excellent yields.

General procedure for the synthesis of compounds 7a and 7b: Compound **7a** and **7b** was prepared by using similar reaction procedure as above used for the synthesis of **3a-3za** and **5a-d**.

General procedure for the synthesis of 3-substituted azetidine-2,4-diones 9a-h: In a 10 mL round bottom flask equipped with a magnetic stir bar was added the aldehyde **8a-h** (1 mmol), ethyl cyanoacetate **2b** (1.2 mmol), TfOH (25 mol %) and 1,4-dioxane (5 mL). Then the resultant reaction mixture was kept in stirring at 110 °C for 14 h. Upon completion of the

DOI: 10.1039/C7NJ05169G

reaction, the reaction mixture was dried under vacuum. Then the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water. The solvent was evaporated and the crude residue was preadsorbed on silica gel and purified by column chromatography to afford the corresponding 3-substituted azetidine-2,4-diones **9a-h** in 75-89% yields.

General procedure for the gram scale synthesis of 3e: Following the general procedure as described above for the synthesis of (*E*)-2-cyanoacrylamides, a flame-dried flask was charged with 4-methylbenzaldehyde (4 g, 33.3 mmol), malononitrile **2a** (2.6 g, 39.6 mmol), catalyst TfOH (1.25 g, 0.0083 mmol) and 1,4-dioxane (35 mL). The round bottom flask was equipped with condenser and the resultant reaction mixture was refluxed at 110 °C for 24 h. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was dried under vacuum. Then the crude reaction mixture was diluted with ethyl acetate (50 mL) and filtered through a pad of silica gel and eluted with EtOAc (600 mL). The solvent was evaporated and the crude residue was preadsorbed on silica gel and purified by column chromatography with eluted solvent (pet.ether + ethyl aceate 65:35) to afford the corresponding (*E*)-2-cyano-3-(p-tolyl)acrylamide derivate **3e** in (4.96 g, 80%) yield.

(*E*)-2-cyano-3-phenylacrylamide (3a): R_f : 0.42 (Pet. Ether / EtOAc = 60/40); Yield: 136 mg, 84%; White solid; mp: 130 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 7.46 (br. s., 3H) 7.78 - 7.95 (m, 2H) 8.06-8.22 (m, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm: 103.1 117.0, 129.2, 130.8, 131.6, 133.1, 154.0, 162.1; HRMS (ESI) calculated $[M + H]^+$ for $C_{10}H_9ON_2$: 173.0709; found: 173.0706.

(*E*)-2-cyano-3-(naphthalen-1-yl)acrylamide (3b): R_f : 0.38 (Pet. ether / EtOAc = 65/35); Yield: 125 mg, 88%; White solid; mp: 168 °C; **^{1}H NMR** (500 MHz, *DMSO-d*$_6$) δ ppm: 7.66 (br. s., 3H), 7.86 (br. s., 1H), 8.05 (br. s., 2H), 8.15 (br. s., 2H), 8.20 (br. s., 1H), 8.87 (br. s., 1H); **^{13}C NMR** (101 MHz, *DMSO-d*$_6$) δ ppm: 111.4, 116.4,123.9, 125.6, 127.1,127.4, 127.7, 129.1,129.6, 131, 132.1, 133.2, 148.7, 162.9; HRMS (ESI) calculated $[M+H]^+$ for $C_{14}H_{11}ON_2$: 223.0866; found: 223.0860.

(*E*)-2-cyano-3-(2,4-dichlorophenyl)acrylamide (3c): R_f : 0.43 (Pet. ether / EtOAc = 60/40); Yield: 113 mg, 90%; White solid; mp: 125 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 7.5 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.6 (d, *J* = 2.1 Hz, 1H), 7.8 (br. s., 2H), 8.0 (d, *J* = 8.7 Hz, 1H), 8.3 (s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 110.4, 115.2, 127.7 , 129.1, 129.5 , 130.3, 135.5, 137.2, 145.7, 161.2; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_7ON_2Cl_2$: 240.9930; found: 204.9928

(*E*)-2-cyano-3-(2,6-dichlorophenyl)acrylamide (3d): R_f : 0.42 (Pet. ether / EtOAc = 55/45); Yield: 122 mg, 83%; White solid; mp : 125-128 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 7.4-7.5 (m, 4H), 7.8 (br. s., 1H), 7.9 (br. s., 1H), 8.1 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm : 163.1, 161.8, 150.9, 132.7, 122.8, 117.2, 116.0, 100.5, 95.6; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_7ON_2Cl_2$: 240.9930; found: 204.9928.

(*E*)-2-cyano-3-(p-tolyl)acrylamide (3e): R_f : 0.41 (Pet. ether / EtOAc = 70/30); Yield: 129 mg, 83%; White solid; mp: 136 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 2.4 (s, 3H), 6.4 (br.s., 2H), 7.3 (d, *J* = 8.2 Hz, 2H), 7.9 (d, *J* = 8.2 Hz, 2H), 8.3(s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm: 21.2, 105.3, 116.7, 129.2, 129.9, 130.1, 143.0, 150.5, 162.9; HRMS (ESI) calculated $[M + H]^+$ for $C_{11}H_{11}ON_2$: 187.0866; found: 187.0862.

(*E*)-2-cyano-3-(4-(methylthio)phenyl)acrylamide (3f): R_f : 0.32 (Pet. ether / EtOAc = 60/40); Yield: 108 mg, 75%; White solid; mp: 153 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 2.55 (s, 3H), 6.17 (br. s., 1H), 6.33 (br. s., 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 2H), 8.27 (s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm: 13.4, 102.2, 116.0, 124.3, 126.9, 129.7, 144.6, 150.2, 161.6; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_{11}ON_2S$: 219.0587; found: 219.0581.

(*E*)-2-cyano-3-(4-isopropylphenyl)acrylamide (3g): R_f : 0.41 (Pet. ether / EtOAc = 65/35); Yield: 126 mg, 87%; Yellow solid; mp: 136-138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm : 0.81 (d, *J* = 6.71 Hz, 7H) 5.67 (br. s., 1H) 5.88 (br. s., 1H) 6.88 (m, *J* = 8.24 Hz, 2H) 7.41 (m, *J* = 8.24 Hz, 2H) 7.81 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 23.7, 34.5, 101.8, 117.3, 127.5, 129.4, 131.2, 153.9, 154.9, 162.2; HRMS (ESI) calculated $[M+H]^+$ for $C_{13}H_{15}ON_2$: 215.1179; found: 215.1177.

(*E*)-2-cyano-3-(4-methoxyphenyl)acrylamide (3h): R_f : 0.35 (Pet. ether / EtOAc = 60/40); Yield: 114 mg, 77%; Yellow solid; mp: 207-209 °C; **^{1}H NMR** (400 MHz, *DMSO-d*6) δ ppm: 3.85 (br. s., 3H) 7.13 (d, *J* = 7.32 Hz, 2H) 7.67 (br. s., 1H) 7.80 (br. s., 1H) 7.96 (d, *J* = 7.32 Hz, 2H) 8.11 (br. s., 1H);**^{13}C NMR** (101 MHz, *DMSO-d*6) δ ppm: 55.6, 102.9, 114.83,117.09, 124, 132.47,150.1,162.59, 163.13;HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_{11}O_2N_2$: 203.0815; found: 203.0814.

(*E*)-2-cyano-3-(4-hydroxyphenyl)acrylamide (3i): R_f : 0.50 (Pet. ether / EtOAc = 70/30); Yield: 99 mg, 64%; White solid; mp: 242-243 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 6.85 (m, *J* = 8.7 Hz, 2H) 7.37 (br. s., 2 H) 7.79 (m, *J* = 8.7 Hz, 2H) 8.00 (s, 1H) 10.26 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm : 100.5, 116.0, 117.2, 122.8, 132.7, 150.9, 161.8, 163.1; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_9O_2N_2$: 189.0659; found: 189.0658.

(*E*)-2-cyano-3-(2,5-dimethoxyphenyl)acrylamide (3j): R_f : 0.41 (Pet. ether / EtOAc = 60/40); Yield: 108 mg, 76%; Yellow; mp: 165 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 3.7 (s, 3H), 3.7 (s, 3H), 6.5-6.7 (m, 2H), 6.8 (d, *J* = 9.1 Hz, 1H), 7.0 (dd, *J* = 9.1, 3.0 Hz, 1H), 7.6 (d, *J* = 2.9 Hz, 1H), 8.6 (s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 55.5, 56.3, 106.6, 112.8, 113.1, 116.6, 119.8, 120.8, 145.4, 152.7, 152.8, 162.6; HRMS (ESI) calculated $[M+H]^+$ for $C_{12}H_{13}O_3N_2$: 233.0921; found: 233.0915.

(*E*)-2-cyano-3-(3,4-dimethoxyphenyl)acrylamide (3k): R_f : 0.38 (Pet. ether / EtOAc = 65/35); Yield: 103 mg, 74%; White solid; mp: 195-196 °C; ^{1}H NMR (200 MHz, *DMSO-d*$_6$) δ ppm 3.81 (3 H, s), 3.86 (3 H, s), 7.14 (1 H, d, *J*=8.6 Hz), 7.56 (1 H, dd,

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J=8.5, 1.9 Hz), 7.66 (1 H, s), 7.68 - 7.89 (2 H, m), 8.06 - 8.19 (1 H, m); **^{13}C NMR** (50 MHz, *DMSO-d_6*) δ ppm : 55.4, 55.80, 102.8, 111.8, 112.2, 117.2, 124.4, 125.5, 148.7, 150.6, 152.5, 163.1 HRMS (ESI) calculated $[M+H]^+$ for $C_{12}H_{13}O_3N_2$: 233.0921; found: 233.0915.

(*E*)-2-cyano-3-(2,4-dimethoxyphenyl)acrylamide (3l): R_f : 0.39 (Pet. ether / EtOAc = 60/40); Yield: 110 mg, 79%; White solid; mp : 168-169 °C ; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 3.9 (s, 3H) 3.8 (s, 3H) 7.0 (d, *J* = 8.34 Hz, 1H) 7.2-7.5 (m, 3H) 7.6 (d, *J* = 2.02 Hz, 1H) 8.0 (s, 1 H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 55.3, 55.5, 95.5, 101.9, 111.0, 111.4, 117.0, 124.4, 126.0, 148.6, 150.9, 152.4, 162.6; HRMS (ESI) calculated $[M+H]^+$ for $C_{12}H_{13}O_3N_2$: 233.0921; found: 233.0915.

(*E*)-2-cyano-3-(3,4,5-trimethoxyphenyl)acrylamide (3m): R_f : 0.35 (Pet. ether / EtOAc = 70/30); Yield: 113 mg, 85%; White solid; mp : 113-114 °C ; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm : 3.77 (s, 3H) 3.88 (s, 3H) 3.89 (s, 3H) 7.03 (d, *J* = 9.05 Hz, 1H) 7.69 (br. s., 1H) 7.85 (br. s., 1H) 7.91 (d, *J* = 9.05 Hz, 1H) 8.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm : 56.3, 60.6, 62.0, 104.4, 108.4, 117.0 , 118.3, 123.7, 141.5, 144.9, 153.6, 157.4, 163.0; HRMS (ESI) calculated $[M+H]^+$ for $C_{13}H_{15}O_4N_2$: 263.1026; found: 263.1024.

(*E*)-3-(2-bromo-3,4,5-trimethoxyphenyl)-2-cyanoacrylamide (3n): R_f : 0.39 (Pet. ether / EtOAc =60/40); Yield: 111 mg, 89%; Pale Yellow; mp: 221 °C; **^{1}H NMR**(500 MHz, *DMSO-d_6*) δ ppm: 3.82 (br. s., 3H) 3.86 (br. s., 3H) 3.88 (br. s., 3H) 7.55 (br. s., 1H) 7.87 (br. s., 1H) 8.00 (br. s., 1 H) 8.29 (br. s., 1H);**^{13}C NMR**(126 MHz, *DMSO-d_6*) δ ppm 56.2, 60.9, 109.1,109.6, 111.8, 115.8,127.1, 145.3, 149.3,150.5, 152.3,161.8; HRMS (ESI) calculated $[M+H]^+$ for $C_{13}H_{14}O_4N_2Br$: 341.0131; found: 341.0124.

(*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylamide (3o): R_f : 0.38 (Pet. ether / EtOAc = 65/35); Yield: 130 mg, 90%; white solid; mp: 204-206 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 6.1 (s, 2H), 6.9 (d, *J* = 8.2 Hz, 1H), 7.2-7.5 (m, 3H), 7.6 (s, 1H), 8.0 (s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 101.8, 102.4, 107.7, 108.4, 116.6, 125.8, 128.1, 148.0, 150.4 , 150.9 , 162.4; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_9O_3N_2$: 217.0608; found: 217.0606.

(*E*)-2-cyano-3-(o-tolyl)acrylamide (3p): R_f : 0.42 (Pet. ether / EtOAc = 65/35); Yield: 125 mg, 81%; White solid; mp: 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm : 2.48 (s, 3H) 6.35 (br. s., 1H) 6.41 (br. s., 1H) 7.27-7.47 (m, 4H) 8.07 (d, *J* = 7.78 Hz, 1H) 8.63 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm : 20.0, 104.8, 116.8, 126.7, 128.3, 130.9, 131.1, 132.6, 139.8, 152.1, 161.9; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_{11}ON_2$: 187.0866; found: 187.0862.

(*E*)-2-cyano-3-(2-methoxyphenyl)acrylamide (3q): R_f : 0.35 (Pet. ether / EtOAc = 60/40); Yield: 111 mg, 75%; White solid; mp : 146-148 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 3.85 (s, 3H), 6.97-7.22 (m, 1H), 7.32- 7.50 (m, 3H), 7.53 (br. s., 2H), 8.16 (s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 54.8, 105.7, 114.1, 116.2, 118.1, 122.7, 129.7, 132.8, 150.9, 159.3, 162.0; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_{11}O_2N_2$: 203.0815; found: 203.0814.

(*E*)-2-cyano-3-(4-phenoxyphenyl)acrylamide (3r): R_f : 0.44 (Pet. ether / EtOAc = 60/40); Yield: 110 mg, 76%; White solid; mp : 112-114 °C ; ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm : 6.40 (br. s., 1H) 6.56 (br. s., 1H) 7.01-7.09 (m, 2H) 7.13-7.26 (m, 2H) 7.34 - 7.52 (m, 4H) 7.69 (d, *J* = 7.83 Hz, 1H) 8.26 (s, 1H): ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 161.6, 150.6, 133.1, 132.3, 131.2, 128.6, 127.2, 127.1, 126.4, 124.9, 122.8, 118.5, 116.4, 107.2; HRMS (ESI) calculated $[M+H]^+$ for $C_{16}H_{13}O_2N_2$: 265.0972; found: 265.0969.

(*E*)-3-(3-bromophenyl)-2-cyanoacrylamide (3s): R_f : 0.4 (Pet. ether / EtOAc = 60/40); Yield: 122 mg, 90%; White solid; mp: 131-134 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 7.4-7.5 (m, 1H), 7.6-7.8 (m, 3H), 7.9 (d, *J* = 7.8 Hz, 1H), 8.0 (s, 1H), 8.1 (s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 107.9, 115.8, 122.2, 128.6, 130.8, 132.2, 134.0, 134.4, 148.8, 162.0; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_8ON_2Br$: 250.9815; found: 250.9808.

(*E*)-2-cyano-3-(3-nitrophenyl)acrylamide (3t): R_f : 0.34 (Pet. ether / EtOAc = 65/35); Yield: 137 mg, 84%; Brown solid; mp: 210-211 °C ; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 8.2 (s, 1H), 7.7-7.9 (m, 4H), 7.2 (t, *J* = 8.0 Hz, 1H), 6.8 (s, 1H), 6.9 (s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 160.8, 148.2, 147.4, 134.7, 132.6, 129.6, 125.3, 123.7, 114.9, 107.8; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_8O_3N_3$: 218.0560; found: 218.0555.

(*E*)-3-(4-bromophenyl)-2-cyanoacrylamide (3u): R_f : 0.41 (Pet. ether / EtOAc = 65/35); Yield: 121 mg, 89%; White Solid; mp: 198 °C ; **^{1}H NMR** (500 MHz, *DMSO-d_6*) δ ppm : 7.72 (d, *J*=8.01 Hz, 2 H) 7.77 (br. s., 1 H) 7.82 (d, *J*=8.01 Hz, 2 H) 7.93 (br. s., 1 H) 8.11 (s, 1 H); **^{13}C NMR** (126 MHz, *DMSO-d_6*) δ ppm : 107.51, 116.4, 126.2, 131.2, 131.9, 132.5, 149.7, 162.8; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_8ON_2Br$: 250.9815; found: 250.9808

(*E*)-2-cyano-3-(4-cyanophenyl)acrylamide (3v): R_f : 0.35 (Pet. ether / EtOAc = 60/40); Yield: 126 mg, 86%; White solid; mp: 146-148 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 7.44 (s, 1H), 7.36 (s, 1H), 7.68-7.85 (m, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 8.19 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm : 110.0, 113.8, 115.8, 118.2, 130.3, 133.0, 136.3, 148.7, 162; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_8ON_3$: 198.0662; found: 198.0658.

(*E*)-2-cyano-3-(4-nitrophenyl)acrylamide (3w): R_f : 0.41 (Pet. ether / EtOAc = 60/40); Yield: 131 mg, 91%; Yellow solid; mp: 198-200 °C ; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm : 7.91 (br. s., 1H) 8.06 (br. s., 1H) 8.12 (m, *J* = 8.80 Hz, 2H) 8.29 (s, 1H) 8.38 (m, *J* = 8.80 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm : 110.7, 115.8, 124.2, 131.0, 138.1, 148.3, 148.8, 162.1; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_8O_3N_3$: 218.0560; found: 218.0556.

(*E*)-2-cyano-3-(4-(trifluoromethyl)phenyl)acrylamide (3x): R_f : 0.39 (Pet. ether / EtOAc = 70/30); Yield: 127, 92%; Light Brown;

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mp: 172 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm : 6.53 (br. s., 2H), 7.76 (d, *J* = 8.3 Hz, 3H), 8.04 (d, *J* = 8.2 Hz, 2H), 8.38 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm : 106.0, 116.2 , 120.6 , 126.1 - 126.3 (q, *J* =3.66 and 7.32 Hz), 130.7, 134.3, 134.6, 152.1, 161.5; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_8ON_2F_3$: 241.0583; found: 241.0577.

(*E*)-3-(2-chlorophenyl)-2-cyanoacrylamide (3y): R_f : 0.41 (Pet. ether / EtOAc = 65/35); Yield: 133 mg, 91%; off white solid; mp: 143 °C ; **^{1}H NMR** (500 MHz, *METHANOL-d_4*) δ ppm 7.4 (1 H, br. s.), 7.5 - 7.6 (3 H, m), 7.8 (1 H, d, *J*=7.2 Hz), 8.1 (1 H, d, *J*=7.6 Hz), 8.5 (1 H, s); ^{13}C NMR (126 MHz, *METHANOL-d_4*) δ ppm; 100.8, 106.9, 119.08, 121.27, 121.8, 124.9, 127.1, 140.07, 154.8, 159.5; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_8ON_3$: 198.0662; found: 198.0658.

(*E*)-2-cyano-3-(2-nitrophenyl)acrylamide (3z): R_f : 0.43 (Pet. ether / EtOAc = 60/40); Yield: 135 mg, 94%; White solid; mp: 168-169 °C; ^{1}H NMR (200 MHz, *DMSO-d_6*) δ ppm 7.5 - 7.9 (2 H, m), 7.9 - 7.9 (2 H, m), 8.0 (1 H, br. s.), 8.3 (1 H, d, *J*=8.0 Hz), 8.7 (1 H, s) ^{13}C NMR (50 MHz, *DMSO-d_6*) δ ppm: 108.7, 114.7, 125.1, 128.4, 130.6, 132.3, 134.7, 147.2, 154.1, 162.4; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_8O_3N_3$: 218.0560; found: 218.0555.

(*E*)-3-(2-bromophenyl)-2-cyanoacrylamide (3za): R_f : 0.4 (Pet. ether / EtOAc = 65/35); Yield: 126 mg, 93%; White solid; mp: 178 °C ; ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm : 6.17 (br. s., 1H), 6.37 (br. s., 1H), 7.36 - 7.52 (m, 3H), 7.67-7.75 (m, 1H), 8.09 (dd, *J* = 7.6, 1.8 Hz, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 108.2, 114.5, 124.2, 126.7, 128.5, 131.0, 131.8, 132.1, 149.4, 160.4; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_8ON_2Br$: 250.9815; found: 250.9808.

(*E*)-2-cyano-3-(furan-2-yl)acrylamide (5a): R_f : 0.35 (Pet. ether / EtOAc = 60/40); Yield: 150 mg, 89%; Yellow solid; mp: 148-150 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm : 6.49-6.55 (m, 1H), 6.60 (br. s., 1H), 6.70 (br. s., 1H), 7.13 (d, *J* = 3.4 Hz, 1H), 7.63 (s, 1H), 7.93 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm : 99.8 , 113.2 , 116.4 , 120.5 , 137.4 , 147.3 , 148.8 , 161.8; HRMS (ESI) calculated $[M+H]^+$ for $C_8H_7O_2N_2$: 163.0502; found: 163.0501.

(*E*)-2-cyano-3-(thiophen-2-yl)acrylamide (5b): R_f : 0.39 (Pet. ether / EtOAc = 70/30); Yield: 138 mg, 87%; Dark Brown; mp: 221 °C ; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 7.10-7.32 (m, 1H), 7.59 (br. s., 2H), 7.78 (br. s., 1H), 7.83-8.00 (m, 1H), 8.33 (s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 102.1, 116.7, 128.6, 134.9, 135.8, 137.8, 143.6, 162.6; HRMS (ESI) calculated $[M+H]^+$ for $C_8H_7ON_2S$: 179.0274; found:179.0270.

(*E*)-3-(5-bromothiophen-2-yl)-2-cyanoacrylamide (5c): R_f : 0.35 (Pet. ether / EtOAc = 65/35); Yield: 117 mg, 94%; Pale Yellow; mp: 168 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm : 6.01 (br. s., 1H), 6.24 (br. s., 1H), 7.19 (d, *J* = 4.0 Hz, 1H), 7.41-7.60 (m, 1H), 8.31 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm : 103.02, 117.7, 121.7, 132.34, 137.93, 139.16, 143.45, 162.67; HRMS (ESI) calculated $[M + H]^+$ for $C_8H_6ON_2BrS$: 258.9358; found: 258.9349.

(*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylamide (5d): R_f : 0.36 (Pet. ether / EtOAc = 60/40); Yield: 128 mg, 84%; Dark Brown; mp: 155 °C ; ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm : 2.47 (s, 3H), 5.91-6.46 (m, 2H), 7.02 (d, *J* = 5.2 Hz, 1H), 7.66 (d, *J* = 4.8 Hz, 1H), 8.53 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm : 102.6, 116.6, 121.2, 131.9, 137.5, 138.7, 142.9, 162.2; HRMS (ESI) calculated $[M+H]^+$ for $C_9H_9ON_2S$: 193.0430; found: 193.0426.

(2*E*,4*E*)-2-cyano-5-phenylpenta-2,4-dienamide (7a): R_f : 0.30 (Pet. ether / EtOAc = 50/50); Yield: 136 mg, 91%; Orange solid; mp: 150-152 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm : 7.96-8.03 (m, 1H) 7.60-7.62 (m, 2H) 7.40-7.50 (m, 5H) 7.30-7.34 (m, 1H) 7.15-7.21 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm : 167.4, 156.5, 151.6, 150.9, 139.9, 135.4, 135.1, 133.9, 133.0, 128.1, 120.4, 112.7, 100.8; HRMS (ESI) calculated $[M+H]^+$ for $C_{12}H_{11}ON_2$: 199.0866; found: 199.0865.

(2*E*,4*E*)-2-cyano-5-(2-nitrophenyl)penta-2,4-dienamide (7b): R_f : 0.32 (Pet. ether / EtOAc = 60/40); Yield: 116 mg, 85%; White solid; mp: 207-209 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ ppm : 7.1 (dd, *J* = 15.1, 11.3 Hz, 1H), 7.2-7.8 (m, 5H), 7.9 (d, *J* = 6.7 Hz, 1H), 8.0 (d, *J* = 8.7 Hz, 2H);^{13}C NMR (50 MHz, DMSO-d_6) δ ppm : 110.3,114.7, 124.5,127.2, 128.7, 129.9, 130.4, 133.5, 140.2, 147.9, 149.8, 162.0; HRMS (ESI) calculated $[M+H]^+$ for $C_{12}H_{10}O_3N_3$: 244.0717; found: 244.0717.

3-(3-phenoxybenzylidene)azetidine-2,4-dione (9a): R_f : 0.32 (Pet. ether / EtOAc = 60/40); Yield: 119 mg, 89%; White solid; mp: 207-209 °C; ^{1}H NMR (500 MHz, *CHLOROFORM-d*) δ ppm: 6.94 - 7.02 (m, 2H), 7.07 - 7.17 (m, 2H), 7.29 - 7.36 (m, 2H), 7.40 (t, *J*= 8.12 Hz, 1H), 7.46 (s, 1H), 7.68 (d, *J*= 7.70 Hz, 1H), 8.10 (s, 1 H), 9.41 (br. s., 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm : 163.8, 158.0, 156.0, 153.6, 133.2, 130.5, 130.0, 125.0, 124.1, 122.7, 120.2, 119.4, 115.5, 104.9; HRMS (ESI) calculated [M+H]+ for $C_{16}H_{12}NO_3$: 266.0812, found: 266.0810.

3-((2,4-dioxoazetidin-3-ylidene)methyl)benzonitrile (9b): R_f : 0.4 (Pet. ether / EtOAc = 50/50); Yield: 122 mg, 81%; White solid; mp: 170 °C; ^{1}H NMR (500 MHz, *CHLOROFORM-d*) δ ppm : 7.58 (t, *J*=8.01 Hz, 1H), 7.74 (d, *J*=7.63 Hz, 1H), 8.08 (s, 1H), 8.12 (s, 1H), 8.16 (d, *J*=8.01 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 163.0, 151.3, 135.3, 133.9, 133.8, 132.8, 130.2, 117.4, 115.0, 113.7, 107.2; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_7N_2O_2$: 198.1820, found: 198.1818.

3-(furan-2-ylmethylene)azetidine-2,4-dione (9c): R_f : 0.34 (Pet. ether / EtOAc = 60/40); Yield: 145 mg, 86%; White solid; mp: 146-148 °C; ^{1}H NMR (500 MHz, *DMSO-d*6) δ ppm: 6.62 (br. s., 1H), 7.29 (br. s., 1H), 7.77 (br. s., 1H), 7.90 (br. s., 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ ppm : 162.6, 147.1, 137.7, 120.4, 114.5, 112.6, 98.3; HRMS (ESI) calculated $[M+H]^+$ for $C_8H_6NO_3$: 163.1310, found: 163.1312.

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DOI: 10.1039/C7NJ05169G

3-(4-fluorobenzylidene)azetidine-2,4-dione (9d): R_f : 0.32 (Pet. ether / EtOAc = 60/40); Yield: 121 mg, 79%; White solid; mp: 160-164 °C; ^{1}H NMR (500 MHz, *DMSO-d*$_6$) δ ppm: 7.09 (t, *J*=8.58 Hz, 2H), 7.85 - 7.95 (m, 2H), 8.08 (s, 1H), 8.48 (br. s., 1H);^{13}C NMR (125 MHz, $CDCl_3$) δ ppm : 165.7, 163.6, 152.2, 132.9, 132.9, 127.8, 116.2, 116.0, 115.6, 103.7; HRMS (ESI) calculated $[M+H]^+$ for $C_{10}H_7NO_2F$: 192.0455, found: 192.0456.

3-(2-methoxybenzylidene)azetidine-2,4-dione (9e): R_f : 0.31 (Pet. ether / EtOAc = 60/40); Yield: 120 mg, 87%; White solid; mp: 176-178 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ ppm : 8.62 (1H, s), 8.17 (1H, d, *J* = 7.3 Hz), 7.42 (1H, t, *J* = 7.6 Hz), 6.83-7.04 (2H, m), 3.81 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm : 163.9, 158.5, 148.7, 134.2, 128.6, 120.3, 115.8, 110.7, 102.8, 55.2; HRMS (ESI) calculated $[M+H]^+$ for $C_{11}H_9NO_3Na$: 226.0475, found: 226.0478.

3-(3,4,5-trimethoxybenzylidene)azetidine-2,4-dione (9f): R_f : 0.35 (Pet. ether / EtOAc = 70/30); Yield: 107 mg, 80%; White solid; mp: 210 °C; ^{1}H NMR (500 MHz, *CHLOROFORM-d*) δ ppm: 3.77 - 3.87 (m, 9H), 7.14 - 7.27 (m, 2H), 8.02 (br. s., 1H);^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 164.0, 153.9, 152.9, 142.1, 126.5, 116.1, 108.2, 102.1, 60.7, 55.9, 40.0; HRMS (ESI) calculated $[M+H]^+$ for $C_{13}H_{13}NO_5Na$: 286.0686, found: 286.0690.

3-(4-isopropylbenzylidene)azetidine-2,4-dione (9g): R_f : 0.37 (Pet. ether / EtOAc = 60/40); Yield: 108 mg, 75%; White solid; mp: 246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm : 8.30 (1H, s), 7.99 (2H, m, *J* = 7.9 Hz), 7.40 (2H, m, *J* = 7.9 Hz), 2.94-3.07 (1H, m), 1.26-1.31 (7H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm : 163.5, 154.5, 154.3, 131.0, 129.3, 127.4, 116.3, 102.6, 33.7, 23.4; HRMS (ESI) calculated $[M+H]^+$ for $C_{13}H_{14}NO_2$: 216.1019, found: 216.1022.

3-(2,4-dimethoxybenzylidene)azetidine-2,4-dione (9h): R_f : 0.3 (Pet. ether / EtOAc = 60/40); Yield: 117 mg, 84%; White solid; mp: 216 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm : 8.57 (1H, s), 8.28 (1H, d, *J* = 8.8 Hz), 6.39 (1H, d, *J* = 2.3 Hz), 3.77-3.84 (7H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm : 164.99, 164.49, 160.7, 147.6, 130.22, 116.65, 113.37, 105.67, 98.52, 97.43, 56.31, 55.17; HRMS (ESI) calculated $[M+H]^+$ for $C_{12}H_{12}NO_4$: 234.0761, found: 234.0766.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Authors are highly thankful to CSIR & UGC-New Delhi for the award of fellowship. We also thank to Dr S. S. Tambe, chair of the Chemical Engineering and Process Development Division (CSIR-NCL) for their constant support.

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View Article Online
DOI: 10.1039/C7NJ05169G

Triflic Acid Catalyzed Metal-Free Synthesis of (*E*)-2-Cyanoacrylamides and 3-Substituted Azetidine-2,4-diones

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