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A Mechanochemical Approach for the Construction of Carbon–Carbon Double Bonds: Efficient Syntheses of Aryl/Heteroaryl/Aliphatic Acrylates and Nitriles

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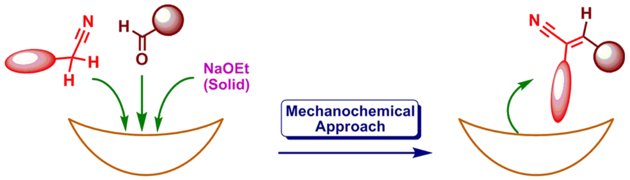
Abstract An efficient method for the construction of carbon–carbon double bond has been developed from aromatic aldehydes and compounds with active methylene moieties in the presence of catalytic amount of solid sodium ethoxide via mechanochemical approach. This capable process provides a diverse range of homoaryl/heteroaryl/aliphatic acrylates and nitriles in good to excellent yields at short reaction period.

Graphical Abstract



Keywords C=C bond formation · Ethyl cyanoacetate · Malononitrile · Sodium ethoxide · Mechanochemical approach

1 Introduction

Despite the availability of various carbon–carbon bond forming reactions, condensation of aldehydes with compounds possessing active methylene scaffold has been one of the vital reactions for the construction of carbon–carbon double bonds in organic synthesis [1, 2] with several applications in the synthesis of biologically important carbocyclic and heterocyclic compounds and fine chemicals [3, 4]. To effect this type of condensation reactions, scientists around the globe have utilized various synthetic protocols [4–47] including the utilization of zeolites [5, 6], metal based/encapsulated nanoparticles [7–10], ionic liquids [7, 11] metal organic frame works [14–19], and mesoporous materials [20–24] as catalysts in addition to other technologies such as microwave etc. [34–47]. Although there are several methods developed for the condensation of aldehydes with compounds having active methylene moiety, most of them require toxic solvents or higher temperatures, expensive catalysts, catalysts preparation, long reaction periods, tedious workup etc. In continuation of our search towards the development of new methods for the construction of biopertinent chemical entities [48–52], we initially tried to develop a new and efficient method for the synthesis of pyrazole based acrylates as one of the compounds from the same family (i.e., compound **13** in Table 1) provided good anti-oxidant property in our preliminary search. The final step of the acrylate synthesis is the formation of carbon–carbon double bond from its corresponding aldehyde. Further, it is known that development of a simple and new method which could be applicable to a diverse range of substrates is highly indispensable. Hence, we decided to develop a new and efficient method to effect the aforementioned condensation reaction to culminate with the formation of diverse range of acrylates. Although numerous technologies are currently available for organic synthesis, mechanochemistry [53–67] plays a unique role as it primarily require no or minimal solvent to achieve specific target molecules. Further, it is mainly promoted by either mechanical milling or hand grinding and is effective as well as advantageous in

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Table 1 Synthesis of aryl acrylates (**1–15**)

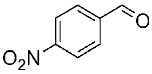
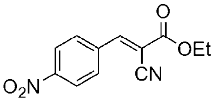
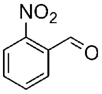
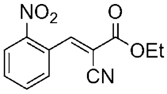
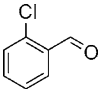
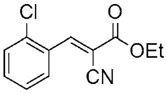
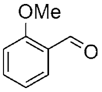
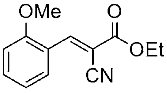
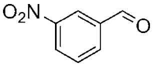
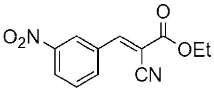
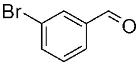
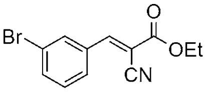
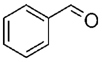
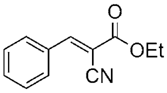
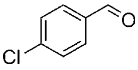
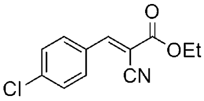
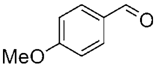
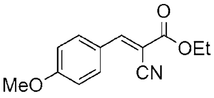
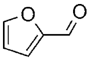
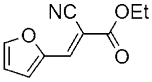
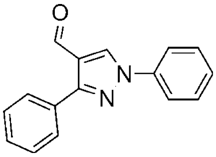
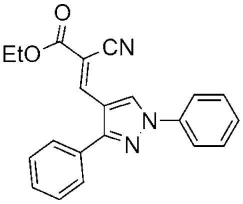
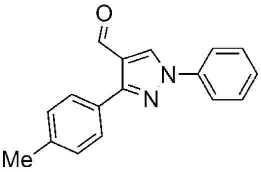
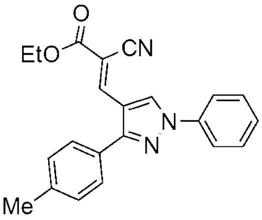
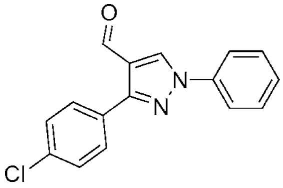
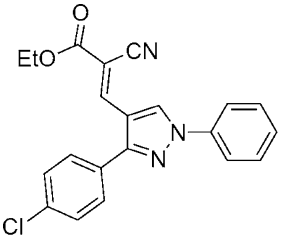
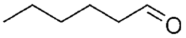
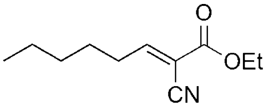
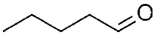
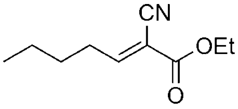
Entry	Reactant	Time (min)	Product	Yield (%)	m.p. (°C)	[Ref.]
1		5	 **(1)**	94	166–167	[68]
2		5	 **(2)**	92	97–98	[68]
3		5	 **(3)**	95	54–55	[69]
4		5	 **(4)**	86	71–72	[68]
5		5	 **(5)**	91	128–129	[70]
6		5	 **(6)**	95	80–81	[71]
7		5	 **(7)**	90	51–52	[72]
8		5	 **(8)**	93	84–85	[68]
9		5	 **(9)**	88	81–82	[73]
10		5	 **(10)**	84	92–93	[73]
11		5	 **(11)**	89	133–135	–
12		5	 **(12)**	86	138–139	–

Table 1 continued

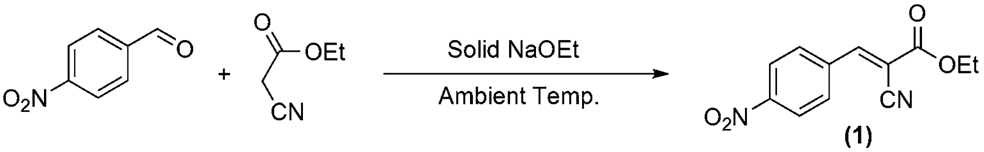
Entry	Reactant	Time (min)	Product	Yield (%)	m.p. (°C)	[Ref.]
13		5	 **(13)**	92	115–116	–
14			 **(14)**	66	–	[74]
15			 **(15)**	63	–	[75]

widening types of synthesis. There are several reports available for the condensation of aldehydes with active methylene compounds under ball milling/hand grinding with or without utilization of catalysts. Recent examples include the condensation of aldehydes with malononitrile/ethyl cyanoacetate using sodium modified hydroxyl apatite [64] or gallium chloride [65] as catalysts under grinding method and the condensation of aldehydes with barbituric acid under ball milling method [54]. Described herein is a simple and efficient method of condensation between various types of aldehydes such as homocyclic, heterocyclic and aliphatic ones with compounds possessing active methylene scaffolds such as ethyl cyanoacetate and malononitrile using a catalytic amount of solid sodium ethoxide (15 mol%) under mechanochemical method.

2 Results and Discussion

We initially screened with various bases and quaternary ammonium salts for the construction of carbon–carbon double bond to deliver a heteroaryl acrylate (compound **13**) from pyrazole based aldehyde (i.e., precursor of compound **13**; see Table 1) and ethyl cyanoacetate by mechanochemical method and found that solid sodium ethoxide is a better option in terms of yield, reactivity and easy handling etc. We then focused our attention towards the development of an efficient method which could be applicable to the synthesis of a diverse range acrylates using solid sodium ethoxide. Hence, reaction between commercially available 4-nitrobenzaldehyde and ethyl cyanoacetate in the presence of solid sodium ethoxide under mechanochemical method was chosen initially as a model reaction and schematic representation of the same is depicted in Scheme 1.

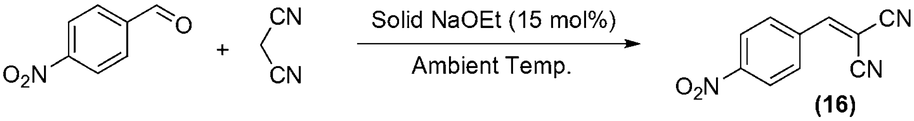
When 1 equivalent of 4-nitrobenzaldehyde, 1.1 equivalent of ethyl cyanoacetate and 1 equivalent of solid sodium ethoxide (i.e., 1:1.1:1 equ., respectively) were ground well using a pestle and mortar at ambient temperature for a couple of minutes, ethyl 2-cyano-3-(4-nitrophenyl)acrylate (**1**) was formed in excellent yield (95 %). This remarkable result provoked us to perform the reaction with lower catalyst load. Hence, we executed the model reaction independently with the catalyst load 50, 25, 20, 15, 10 and 5 mol% in order to recognize superior condition (i.e., better yield with lower catalyst load). Among all the reactions, the one with 15 mol% of the catalyst load provided excellent result in 5 min of grinding as it provided the acrylate product with 94 % yield while further reduction of the catalyst load to 10 and 5 mol % offered comparatively lower yield (82 and 68 %, respectively). Replacing sodium ethoxide by sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate in the model reaction also afforded its corresponding acrylate product albeit in lower yield (up to 83 %). Thus, grinding 1 equivalent of 4-nitrobenzaldehyde and 1.1 equivalent of ethyl cyanoacetate in the presence of 15 mol% of solid sodium ethoxide using pestle and mortar for 5 min was found to be the optimal one. Having a very favourable methodology in hand, reactions between diverse ranges of aromatic, heteroaromatic and aliphatic aldehydes and ethyl cyanoacetate were investigated and the results are furnished in Table 1 (entries 1–15). When ortho-substituted aromatic aldehydes such as 2-nitrobenzaldehyde, 2-chlorobenzaldehyde and 2-methyl benzaldehyde were



(1)

Scheme 1 Synthesis of ethyl 2-cyano-3-(4-nitrophenyl)acrylate (**1**)

Scheme 2 Synthesis of 2-(4-nitrobenzylidene)malononitrile (**16**)



(16)

utilized independently as aldehyde sources in the optimal reaction condition in place of 4-nitrobenzaldehyde, the corresponding aryl acrylate products with the formation of carbon–carbon double bond were obtained with 86–92 % yield (entries 2–4). Among those three, the one with electron releasing methoxy group provided its corresponding acrylate product with lower yield while the other couple of aromatic aldehydes possessing electron withdrawing moieties offered their corresponding aryl acrylate products with comparatively higher yields. A couple of meta-substituted aromatic aldehydes such as 3-nitrobenzaldehyde and 3-bromobenzldehyde in addition to unsubstituted one such as benzaldehyde were also exploited in this optimal reaction and gave excellent results (entries 5–7). Further, employment of other para-substituted aldehydes such as 4-chlorobenzaldehyde and 4-methoxybenzaldehyde also culminated with the formation of their corresponding acrylates in good yields (entries 8 and 9). Utilization of furfuraldehyde, an aldehyde containing oxygen heteroatom in the optimal reaction smoothly provided its corresponding acrylate in good yield despite slightly lower than the others (entry 10). We then shifted to the utilization of a few higher molecular weight heterocyclic aldehydes in the optimal reaction, and particularly pyrazole based aldehydes as one of the aldehydes afforded its corresponding acrylate, which exhibit good anti-oxidant property in our preliminary study as discussed earlier. In our past experimental experience, many of the mechanochemical methods give good results only for liquid substrates/simple and low molecular weight substrates. When we tried for higher molecular weight substrates, the products are formed in many cases but in lower yield. Having this common observation in mind, we tried with the use of three pyrazole based aldehydes, synthesized from their corresponding aralkyl ketones and aryl hydrazines via condensation followed by Vilsmeier–Haack reactions, as substrates in the model reaction with ethyl cyanoacetate in the presence of catalytic amount of solid sodium ethoxide as provided in the optimal reaction. It has to be noted that all the aforementioned three aldehydes offered their corresponding heteroaryl acrylates such as ethyl 3-(1,3-diphenyl-1*H*-pyrazol-4-yl)-2-cyanoacrylate, ethyl 3-[1-phenyl-3-(4-methylphenyl)-1*H*-pyrazol-4-yl]-2-cyanoacrylate and ethyl 3-[3-(4-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl]-2-cyanoacrylate in good yields irrespective of the nature of the substituents though the one possessing electron releasing methyl group gave its corresponding acrylate with slightly lower yield compared to the ones with no substituent and electron with drawing chloro substituent (entries 11–13). As an overall observation of the reactions between various aromatic aldehydes and ethyl cyanoacetate in the presence of catalytic amount of solid sodium ethoxide (15 mol%) under mechanochemical method (i.e., using pestle and mortar), the use of all the aromatic aldehydes irrespective of the nature and position of the substituents as well as homo aromatic, heteroaromatic nature of the rings gave good to excellent yields of the products, however, when comparing the yields of the products obtained from aldehydes with the substituents within the specific position, slightly lower yields were noted in the case of products possessing electron releasing groups while products with electron withdrawing moieties culminated with slightly higher yields of the products. Reactions between aliphatic aldehydes and ethyl cyanoacetate under the experimental condition also provided their corresponding acrylates although in lower yields compared to aromatic aldehydes (entries 14 and 15).

For further exploration of the utility of this method, we then shifted to the employment of malononitrile, another chemical entity with active methylene group in place of ethyl cyanoacrylate in the optimal reaction. Ren et al. [37] studied the condensation reaction between some of the aromatic aldehydes and malononitrile by grinding in the absence of catalysts and solvents. However, the methodology requires longer reaction time (ca. 12 h) and the yields of the products in many cases are ranging from 68 to 88 %. Akin to our previous case, 4-nitrobenzaldehyde was utilized as a model substrate along with malononitrile and catalytic amount of solid sodium ethoxide in this case and the schematic representation for the synthesis of model nitrile (**16**) is furnished in Scheme 2.

Table 2 Synthesis of aryl nitriles (**16–29**)

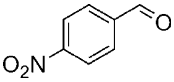
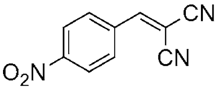
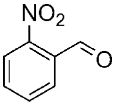
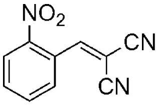
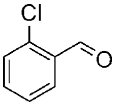
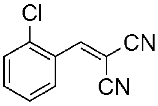
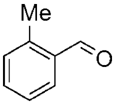
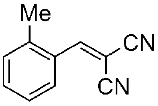
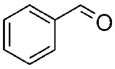
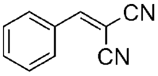
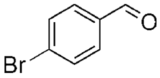
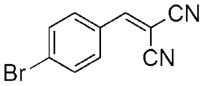
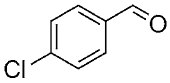
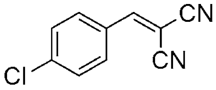
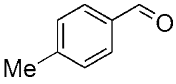
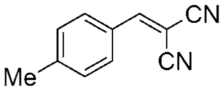
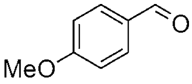
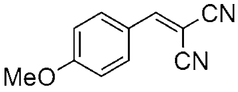
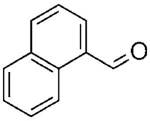
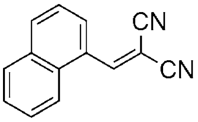
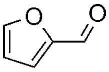
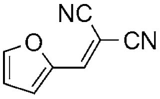
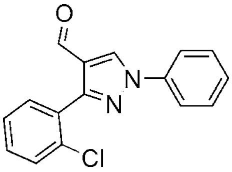
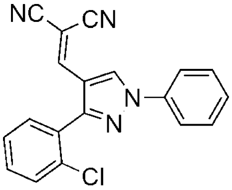
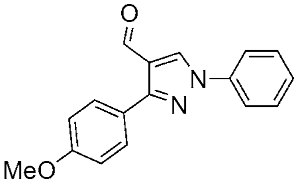
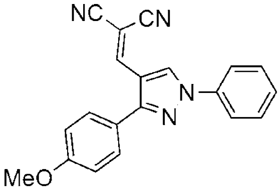
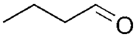
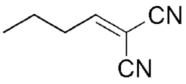
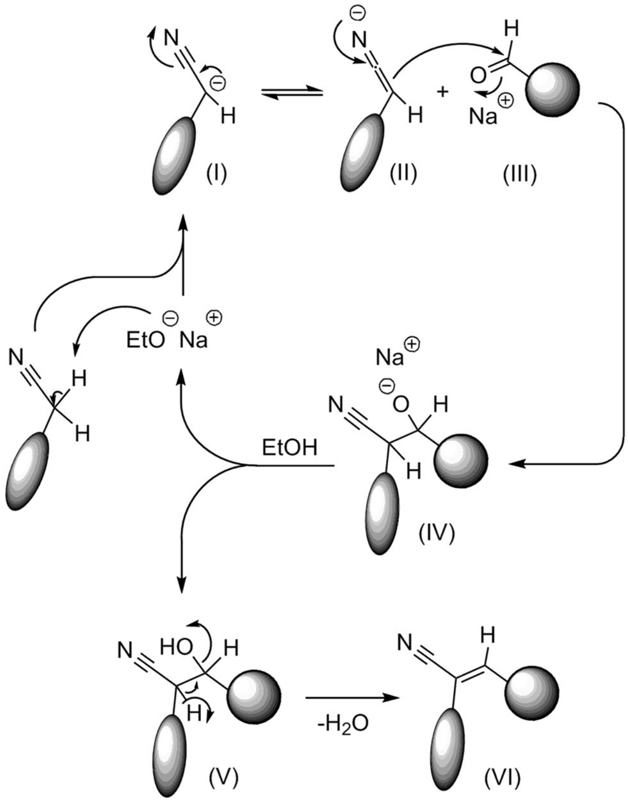
Entry	Reactant	Time (min)	Product	Yield (%)	m.p. (°C)	[Ref.]
1		2	 **(16)**	96	158–159	[76]
2		2	 **(17)**	94	139–140	[23]
3		2	 **(18)**	93	93–94	[37]
4		2	 **(19)**	87	97–98	[10]
5		2	 **(20)**	96	86–87	[77]
6		2	 **(21)**	93	217–218	[78]
7		2	 **(22)**	92	167–168	[77]
8		2	 **(23)**	88	130–131	[79]
9		2	 **(24)**	85	121–122	[16]
10		2	 **(25)**	91	175–176	[33]
11		2	 **(26)**	87	72–73	[73]
12		2	 **(27)**	93	205–206	–
13		2	 **(28)**	95	170–171	–

Table 2 continued

Entry	Reactant	Time (min)	Product	Yield (%)	m.p. (°C)	[Ref.]
14			 **(29)**	72	–	[20]



Scheme 3 Plausible mechanism

When 1 equivalent of 4-nitrobenzaldehyde and 1.1 equivalent of malononitrile in the presence of 15 mol% of solid sodium ethoxide were ground well at ambient temperature, the corresponding product 2-(4-nitrobenzylidene)malononitrile (**16**) was formed in excellent yield (96 %) within less than 2 min (Table 2; entry 1) unlike the synthesis of acrylates, as the time required to achieve acrylate products in good to excellent yields is 5 min. Akin to the previous cases, a diverse range of aryl aldehydes were utilized in place 4-nitrobenzaldehyde and all the reactions were performed with malononitrile and catalytic amount of solid sodium ethoxide by the standard mechanochemical method and the results are provided in Table 2 (entries 2–14). When benzaldehyde and its variants with various electron releasing and electron withdrawing substituents were employed as aldehyde sources in the above reaction, all their corresponding products were obtained in good to excellent yields irrespective of the nature of the substituents in less than just a couple of minutes (entries 2–9), however, on comparing the yields of the products based on within the nature of the substituents, subtle differences were noted, i.e., the products carrying electron withdrawing groups yielded little higher yields while the products containing electron releasing moieties provided little lower yields as in the case of the previous series of compounds. In addition, 1-naphthaldehyde and furfuraldehyde also afforded their corresponding nitriles in good yields under the general reaction conditions (entries 10 and 11). A couple of pyrazole based aldehydes were also employed as aldehyde sources in the general optimal reaction condition and undoubtedly, their corresponding nitrile products were obtained in excellent yields (entries 12 and 13). Eventually, this method is applicable for the aliphatic aldehydes as well as the utilization of n-butyraldehyde produced its corresponding nitrile product in good yield (entry 14).

In an attempt to furnish evidence for the mechanochemical process, FTIR-ATR spectra were recorded before and after the reaction of one of the aldehydes **28** with malononitrile and, eventually after the addition of water followed by recrystallization. The FTIR-ATR spectrum of aldehyde showed an absorption band at 1662 cm^{-1} due to the presence of carbonyl group. However, after grinding with malononitrile, the aforesaid band disappeared and a new band appeared at 2228 cm^{-1}, which corresponds to the nitrile groups of the product. Further, in the case of crystallized product also an absorption band appeared in the same region (i.e., 2230 cm^{-1}) while none appeared in the region 1640–1680 cm^{-1}. These results clearly imply that the reaction proceeds through mechanochemical way.

A plausible mechanistic route for the synthesis of aryl/heteroaryl/aliphatic acrylates/nitriles (**VI**) is depicted in Scheme 3. Abstraction of proton from compound with active methylene moiety (i.e., ethyl cyanoacetate/malononitrile) by ethoxide anion produces a facile nucleophile, 1-cyano-2-ethoxy-2-oxoethan-1-ide/dicyanomethanide (**I**) which is in equilibrium with (**II**). Attack of 1-cyano-2-ethoxy-2-oxoethan-1-ide/dicyanomethanide on carbonyl carbon of aryl/heteroaryl/aliphatic aldehyde (**III**), activated by sodium, affords the intermediate **IV**. The intermediate **IV** upon abstraction of proton from ethanol followed by dehydration eventually generates the target molecules, aryl/heteroaryl/aliphatic acrylates/nitriles malononitrile (**VI**). The ethoxide anion, thus liberated involves in the abstraction of proton from the reactant possessing active methylene scaffold (i.e., ethyl cyanoacetate/malononitrile), thereby completes the catalytic cycle.

3 Conclusions

The expediency of this methodology lies in the fact that the reactions have been carried out in extremely rapid manner using catalytic amount of solid sodium ethoxide to furnish carbon–carbon double bonded molecules such as aryl acrylates and aryl nitriles in good to excellent yields. The methodology could be applicable to a diverse range of aldehydes such as homo/hetero aromatics/aliphatic with various substituents irrespective of the nature of the same as well as diverse range of molecules with active methylene groups. Further, tedious workup is not at all required. In conclusion, the methodology described herein would probably be a general and useful one for the synthesis of an ample variety of aryl/heteroaryl/aliphatic based acrylates and nitriles.

4 Experimental

4.1 General

All the reported melting points were measured in open capillaries and are uncorrected. The solvents and reagents used were either purchased as anhydrous form from standard companies or purified before their use. Silica gel 60 F plates were used for performing thin-layer chromatography (TLC).

4.2 Typical Procedure for the Synthesis of Aryl/Heteroaryl/Aliphatic Acrylates and Nitriles (1–29)

In a mortar, respective aldehydes (1.0 mmol), respective compounds with active methylene moiety (ethyl cyanoacetate/malononitrile) (1.1 mmol), and solid sodium ethoxide (15 mol%) have been taken and ground well using a pestle for 2–5 min at ambient temperature. Distilled water has then been added to the reaction mixture and the solid thus obtained after stirring has been filtered, washed well with water and dried in vacuum. Recrystallization from aqueous ethanol afforded the analytically pure target molecules, aryl/heteroaryl/aliphatic acrylates and nitriles.

Most of the synthesized compounds are reported ones and their physical and spectroscopic data are compared with the literature/authentic samples. Physical and spectroscopic data for the compounds, ethyl 3-(1,3-diphenyl-1*H*-pyrazol-4-yl)-2-cyanoacrylate (**11**), ethyl 3-[1-phenyl-3-(4-methylphenyl)-1*H*-pyrazol-4-yl]-2-cyanoacrylate (**12**), ethyl 3-[3-(4-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl]-2-cyanoacrylate (**13**), 2-[(3-(2-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene]malononitrile (**27**) and 2-[(3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene]-malononitrile (**28**) are furnished below.

4.2.1 *Ethyl 3-(1,3-diphenyl-1H-pyrazol-4-yl)-2-cyanoacrylate (**11**)*

Dirty-white solid; m.p. 133–135 °C; ^{1}H NMR (300 MHz; CDCl$_3$) δ 9.15 (s, 1H), 8.32 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 6.4 Hz, 2H), 7.56–7.50 (m, 5H), 7.42 (t, J = 7.2 Hz, 1H), 4.36–4.33 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz; CDCl$_3$) δ 162.7, 156.4, 146.3, 138.8, 130.8, 129.7, 129.4, 129.3, 129.2, 129.0, 128.5, 119.9, 116.7, 114.9, 99.8, 62.4, 14.2; GC/MS (m/z) 343 (M$^+$); Anal. Calcd for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24, Found: C, 73.50; H, 4.89; N, 12.27.

4.2.2 *Ethyl 3-[1-phenyl-3-(4-methylphenyl)-1H-pyrazol-4-yl]-2-cyanoacrylate (**12**)*

Dirty-white solid; m.p. 138–139 °C; ^{1}H NMR (300 MHz; CDCl$_3$) δ 9.13 (s, 1H), 8.32 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.4 Hz, 4H), 7.41 (t, J = 7.4 Hz, 1H), 7.32 (d, J = 7.6 Hz, 2H), 4.38–4.33 (m, 2H), 2.44 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz; CDCl$_3$) δ 162.7, 156.5, 146.5, 139.4, 138.9, 129.7, 129.6, 129.3, 129.0, 128.1, 127.9, 119.9, 116.8, 114.9, 99.6, 62.4, 21.4, 14.2; GC/MS (m/z) 357 (M$^+$); Anal. Calcd for $C_{22}H_{19}N_3O_2$: C, 73.93; H, 5.36; N, 11.76. Found: C, 74.04; H, 5.44; N, 11.67.

4.2.3 *Ethyl 3-[3-(4-bromophenyl)-1-phenyl-1H-pyrazol-4-yl]-2-cyanoacrylate (**13**)*

Half-white solid; m.p. 115116 °C; ^{1}H NMR (300 MHz; CDCl$_3$) δ 9.14 (s, 1H), 8.25 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.57-7.50 (m, 7H), 7.42 (t, J = 6.8 Hz, 1H), 4.38–4.34 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz; CDCl$_3$) δ 162.6, 155.1, 145.7, 138.8, 135.7, 130.4, 129.7, 129.4, 129.3, 128.3, 120.0, 116.6, 114.9, 100.2, 62.5, 14.2; MS (m/z): 422 (M$^+$). Anal. Calcd. For C, 59.73; H, 3.82; N, 9.95, Found: C, 59.79; H, 3.94; N, 9.88.

4.2.4 *2-[(3-(2-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)methylene]malononitrile (**27**)*

Half-white solid; m.p. 205–206 °C; IR (ν cm^{-1}) 2359.5, 2226.4, 1593.2, 1523.8, 1498.7, 1240.2, 1076.3, 1031.9, 947.1, 939.3, 906.5, 825.5, 756.1, 733.0, 713.7, 680.9, 642.3, 609.5; ^{1}H NMR (300 MHz; CDCl$_3$) δ 9.10 (s, 1H), 7.81(d, J = 7.5 Hz, 2H), 7.59–7.41 (m, 8H); ^{13}C NMR (75 MHz; CDCl$_3$) δ 154.2, 151.1, 138.5, 133.7, 132.3, 131.4, 130.3, 129.8, 129.1, 128.8, 128.7, 127.3, 120.1, 116.1, 113.7, 78.7; GC/MS (m/z) 330 (M$^+$); Anal. Calcd for $C_{19}H_{11}ClN_4$: C, 68.99; H, 3.35; N, 16.94, Found: 69.01; H, 3.39; N, 16.91.

*4.2.5 2-[(3-(4-Methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)methylene]malononitrile (**28**)*

Yellow solid; m.p. 170–171 °C; IR (ν cm^{-1}) 2360.9, 2222.0, 1573.9, 1508.3, 1446.6, 1340.5, 1259.5, 1228.7, 1178.5, 1026.1, 952.8, 902.6, 841.0, 756.1, 684.7, 634.6, 607.6; ^{1}H NMR (300 MHz; CDCl$_3$) δ 9.01 (s, 1H), 7.82–7.78 (m, 3H), 7.56–7.43 (m, 5H), 7.06 (d, J = 8.70 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (75 MHz; CDCl$_3$) δ 161.0, 156.2, 151.3, 138.6, 130.5, 129.8, 129.2, 128.6, 122.5, 120.1, 115.0, 114.7, 114.0, 113.9, 78.1, 55.5; GC/MS (m/z) 326 (M$^+$); Anal. Calcd for $C_{20}H_{14}N_4O$: C, 73.61; H, 4.32; N, 17.17, Found: 73.66; H, 4.30; N, 17.14.

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