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A one-pot multicomponent K-10 clay catalyzed synthesis of 2-Amino-3,5-dicarbonitrile-6-thiopyridines

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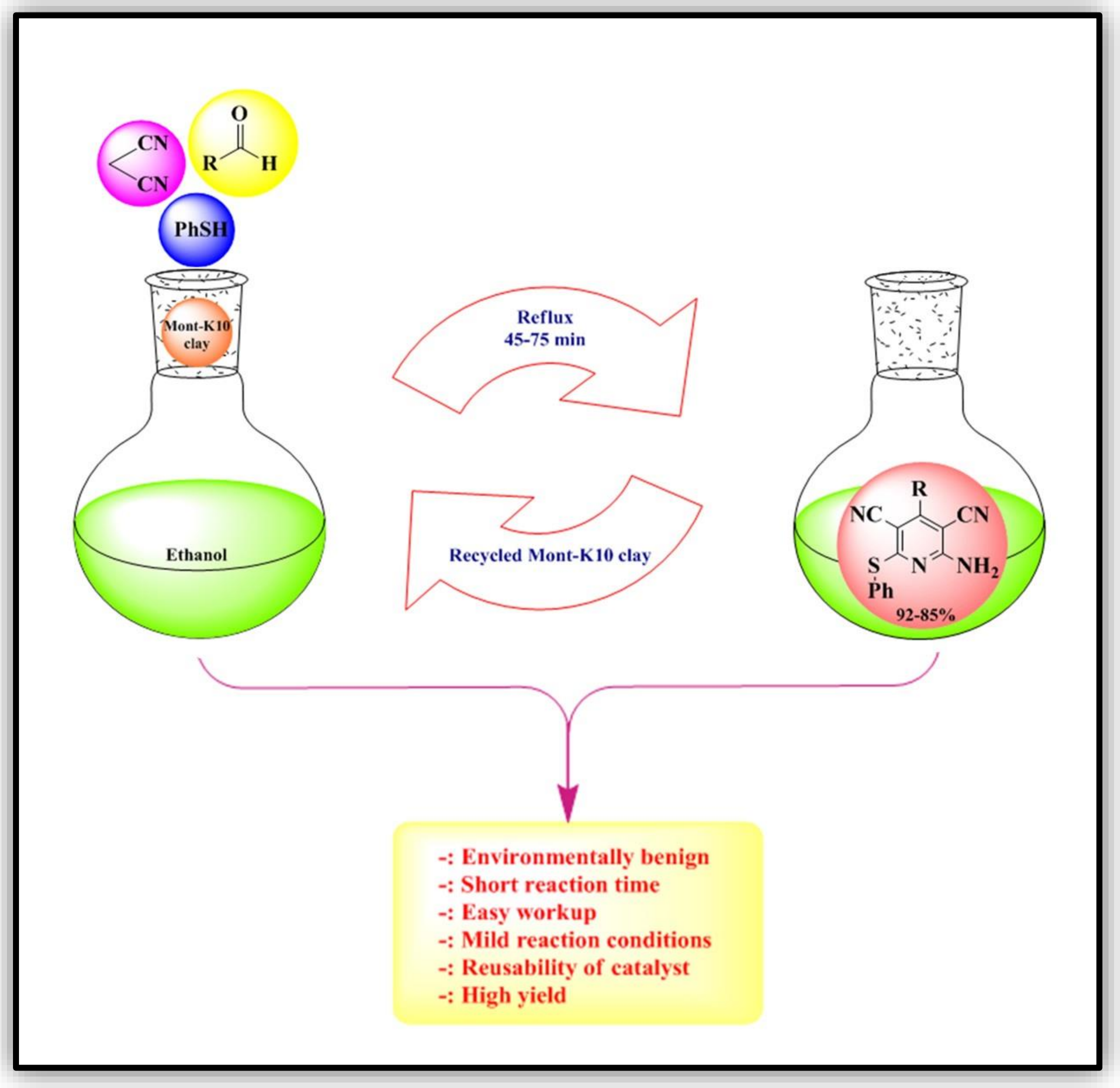
Abstract

2-Amino-3,5-dicarbonitrile-6-thiopyridines occupy a prominent place among the physiologically and biologically active scaffolds owing to their therapeutic applications in the treatment of Parkinson's disease, asthma, urinary incontinence, kidney disease, the Hepatitis B Foundation infections, Creutzfeldt–Jacob disease, cancer, hypoxia⁄ischemia and epilepsy. A one-pot, multicomponent condensation of aldehydes, malononitrile and thiophenol catalyzed by Montmorillonite K-10 clay afforded 2-amino-3,5-dicarbonitrile-6-thiopyridines in good to excellent yields. All the products could be well characterized on the basis of spectral studies. The catalyst could be recycled three times without affecting the yields and even in the fourth recycling of the catalyst, the yield decreases marginally. This approach manifests environmentally benign feasibility in contexts of enhanced yields, milder conditions, short reaction times and reusability of the catalyst.

Keywords

Multicomponent reaction; Montmorillonite K-10 clay catalysis; 2-Amino-3,5-dicarbonitrile-6-thiopyridines; Catalyst recycling; Green chemistry

Graphical Abstract



Introduction

Green chemistry's core objective is to reduce, if not eliminate, waste in the manufacturing of chemicals and related products: "prevention is better than cure". In view of this, there are ongoing efforts to create new procedures for recognized synthesis employing better catalysts [1]. Multicomponent reactions (MCRs) have been widely recognized as an efficient synthetic methodology to obtain highly diverse and complex structures under economical and green chemistry conditions [2]. In recent years, MCRs have attained prominent place in combinatorial chemistry with the possibility of gaining access to vast libraries of biologically pertinent molecules and natural products desirable in the realms of agrochemicals and pharmaceuticals [3-6]. Pyridine ring system and its analogues show a broad spectrum of physiological and biological activities [7]. Among these, 2-Amino-3,5-dicarbonitrile-6-thiopyridine occupies a prominent place as 'privileged scaffold' owing to its latent therapeutic applications in the treatment of Parkinson's disease, asthma, urinary incontinence, kidney disease, the Hepatitis B Foundation infections, Creutzfeldt–Jacob disease, cancer, hypoxia/ischemia and epilepsy [8,9]. In addition, they are often used as anti-bacterial and anti-prion agents [10] (Figure 1).

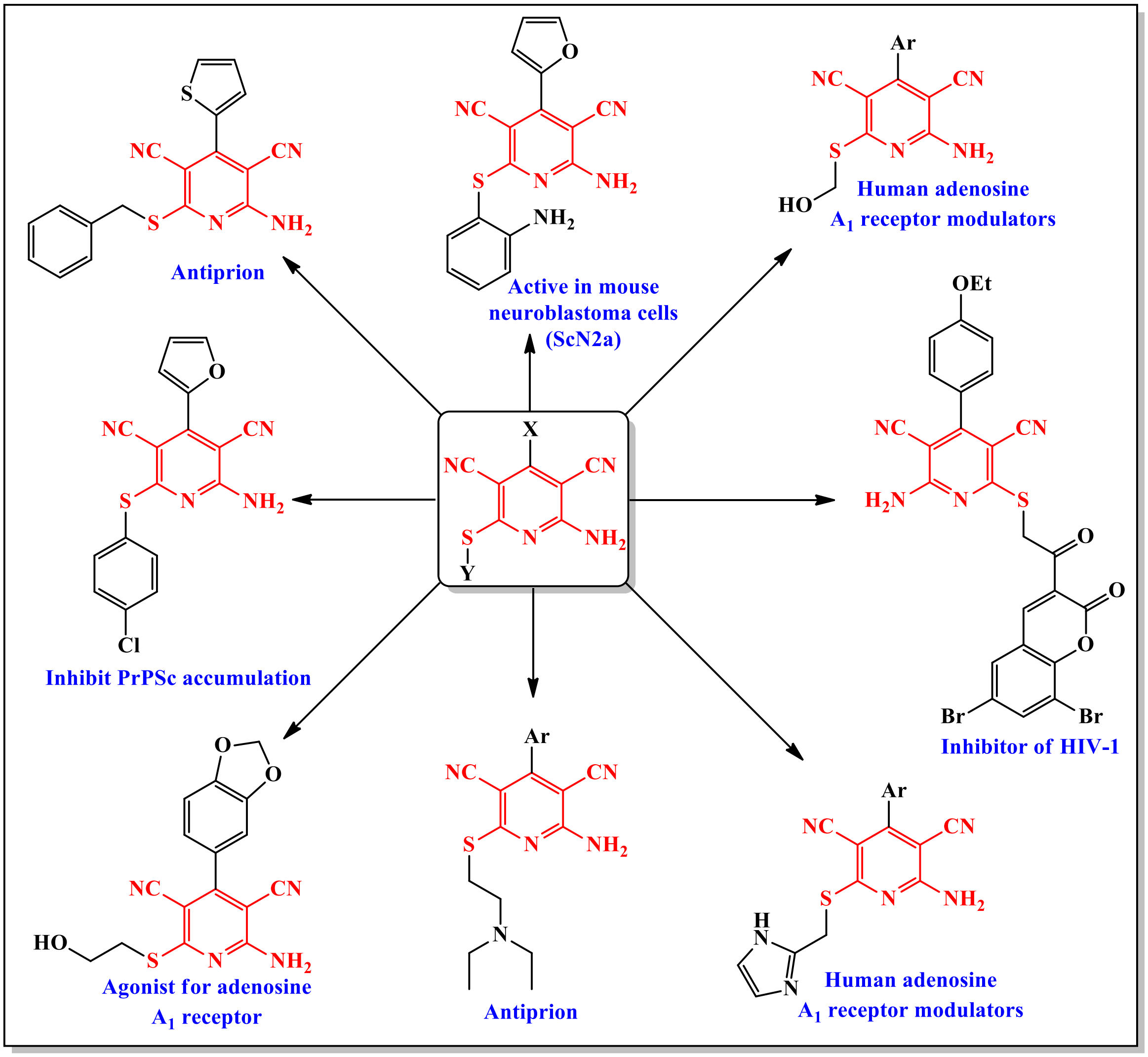


Figure 1: Some bioactive compounds containing 2-Amino-3,5-dicarbonitrile-6-thio-pyridine scaffold.

The multicomponent condensation of aldehyde, malononitrile, and thiol has been accomplished by using various organocatalysts such as Et_3N [11], diethylamine [12], deep eutectic solvent (DES) [13], Baker's yeast [14], water extract of banana [15], tetra-

n-butylammonium fluoride [16]**,** o-Iodoxybenzoic acid [17]**,** diethylamine [18]**,** piperidine [19], imidazole [20], L-Arginine [21], *N,N'*-Di(1*H*-tetraazol-5-yl)-6H,12*H*-5,11-ethanedibenzo[*b,f*][1,5]diazocine-3,9-dicarboxamide [22], choline methoxide [23] procuring target pyridines in 80–98% yields.

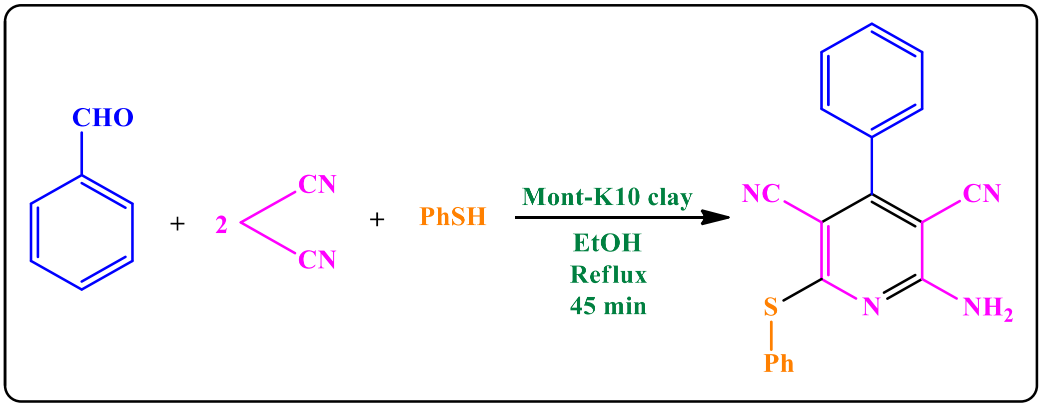
Apart from organocatalysts, various nanomaterial-based catalysts have also been employed [24-33]. However, these methods suffered from prolonged reaction times and poor yields. Apart from these, Bronsted, Lewis acids and basic catalysts have also been used with limited success [34-50].

In addition to the aforementioned catalysts, heterogeneous catalysts as well as ionic liquids have also been used [51-63]. The majority of these protocols had some limitations such as protracted reaction times, formation of inevitable side products, low yields, tedious workup, etc. Therefore, there is always scope to develop an efficient protocol incorporating a mild, potent, and an eco-friendly catalyst for synthesizing highly substituted pyridines.

Recent progresses in heterogeneous catalysis demonstrate the utility of K10 clay as a suitable solid acid catalyst or support for simple organic transformations namely Fries rearrangement, Fischer-Hepp rearrangement, Orton rearrangement and many more [64]. Mont K-10 clay is an economically feasible, non-corrosive solid catalyst exhibiting numerous benefits, including easier handling and workup, strong acidity, low cost, milder reaction conditions, excellent yields, high selectivity and regeneration [65-69]. We herein report a facile multicomponent reaction of aldehyde, malononitrile and thiophenol catalyzed by Mont - K10 clay to afford 2-Amino-3,5-dicarbonitrile-6-thiopyridines in moderate to high yields.

Results and Discussion

With a view to find optimum reaction conditions, we investigated the multicomponent reaction of benzaldehyde, malononitrile and thiophenol in the presence of varying amounts of Mont - K10 clay using ethanol as the solvent (Scheme 1). The results are presented in Table 1.



Scheme 1: Optimized reaction of benzaldehyde, malononitrile and thiophenol in the presence of Mont-K10 clay.

No product was formed on carrying out the reaction in the absence of a catalyst even on refluxing in ethanol for 10 hrs. (Table 1, Entry 1). On the other hand, reaction was complete in 45 min. on refluxing in ethanol in the presence of 20 mol% of Mont-K10 clay affording the product in high yield (92%; Table 1, Entry 5). The plateau effect was observed on increasing the concentration of the catalyst further (Table 1, Entry 6).

Table 1: Effect of concentrations of catalyst.^{a}

Entry	Mont-K10 (mol %)	Time (h)	Yield (%)^{b}
1	0	10	Nil
2	5	6	23
3	10	3	43
4	15	1.5	60
5	20	0.75	92
6	25	0.75	92

^{a}Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), thiophenol (1 mmol); catalyst: K-10 clay (x mol%); solvent: ethanol (5 mL);
^{b}Isolated yields

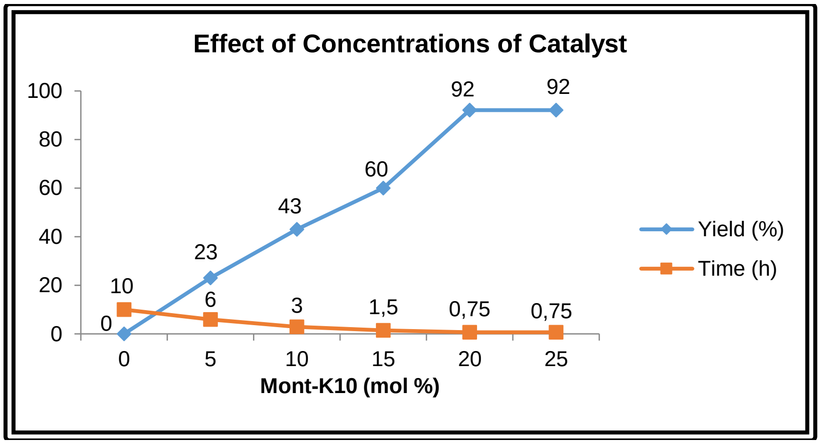


Figure 2: Graphical representation of Table 1 findings.

Furthermore, to assess the feasibility of the procedure we carried out the reaction at altering temperatures. It was observed that the reaction proceeded smoothly at 78°C and the desired product was isolated in 92% yield within 45 min. (Table 2, Entry 4).

Table 2: Effect of temperature on the reaction.^{a}

Entry	Temp (°C)	Time (h)	Yield (%)[b]
1	RT	3	Nil
2	55	1.5	60
3	65	1	79
4	78	0.75	92

[a]Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), thiophenol (1 mmol); catalyst: K-10 clay (20 mol%); solvent: ethanol (5 mL);
[b]Isolated yields

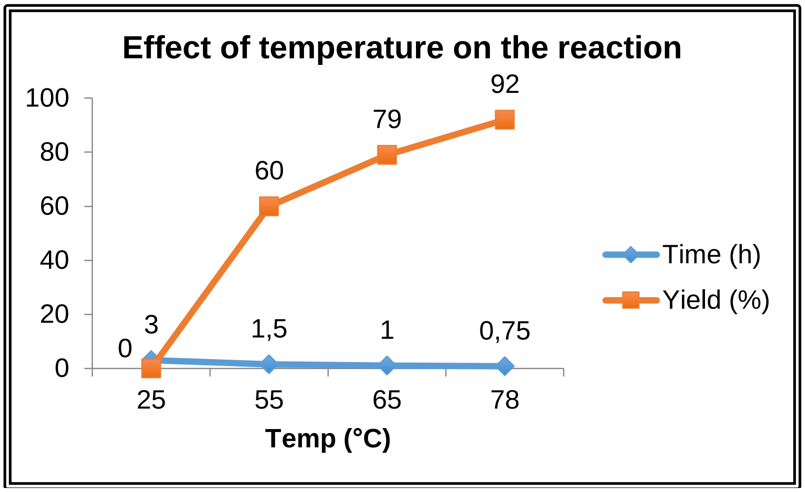
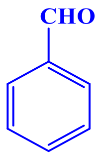
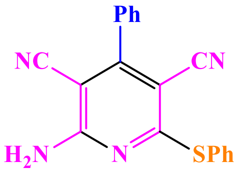
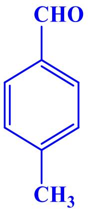
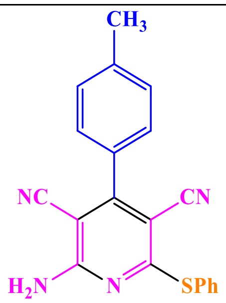
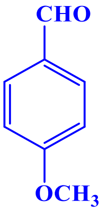
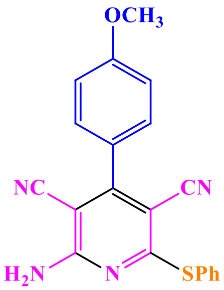
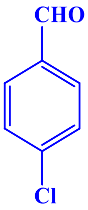
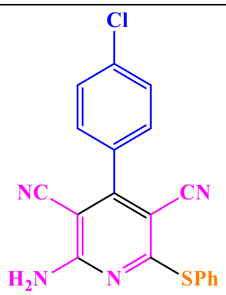
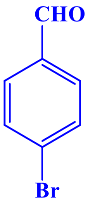
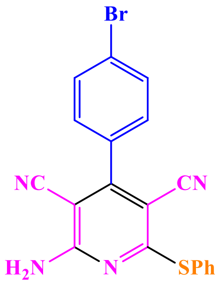


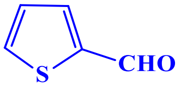
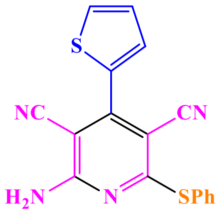
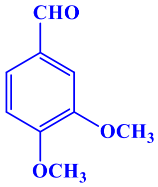
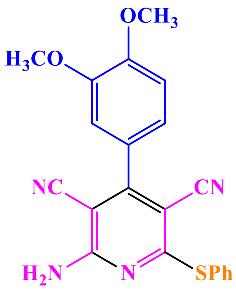
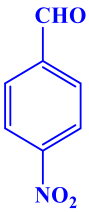
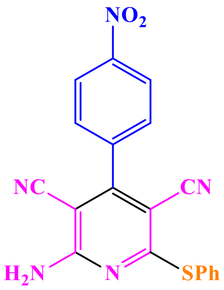
Figure 3: Graphical representation of Table 2 findings.

After developing optimum reaction conditions, the multicomponent condensation was carried out with an array of aldehydes (Table 3). Aromatic aldehydes comprising varied functionalities, like Me, OMe, Cl and Br were inferred to be compliant under optimal reaction conditions (Table 3, entries 2-5). Heteroaromatic aldehyde such as thiophene-2-carbaldehyde was equally amenable to these conditions (Table 3, entry 6). Hence, it is concluded that, aromatic aldehydes possessing electron-donating or electron-withdrawing groups condensed very conveniently with malononitrile and thiols, affording the subsequent 2-Amino-3,5-dicarbonitrile-6-thio-pyridines within a short reaction time (45-75 min) and good to excellent yields (92-85%).

Table 3: K-10 clay catalyzed multicomponent synthesis of substituted 2-Aminopyridines.[a]

Entry	R-CHO	Product	Yield (%)[b]	Time (min)

1			92	45
2			92	45
3			91	50
4			90	60
5			88	60

6			86	75
7			85	75
8			85	60

[a]Reaction conditions: aromatic aldehydes (4 mmol), malononitrile (8 mmol), thiophenol (4 mmol); catalyst: K-10 clay (20 mol%); solvent: ethanol (15 mL)
[b]Isolated yields

All the products could be well characterized on the basis of IR, ^{1}H and ^{13}C NMR studies. In the IR spectrum, the absorption bands at 2218-2213 cm^{-1} resulted due to C≡N stretching vibration. Besides, two absorption bands at 3465-3453 cm^{-1} and 3328-3322 cm^{-1} were observed due to N-H stretching vibrations of the amino group. In the ^{1}H-NMR spectra, the NH_2 protons gave a singlet (2H) at 7.9-7.7 ppm and aromatic ring protons were observed as a multiplet at 8.5-7.1 ppm. In the ^{13}C NMR spectra, all aromatic carbon atoms showed signals at 115-166 ppm.

Next, the catalytic activity of the recycled Mont - K10 clay was examined. All the reactions were complete within 45 min and the products could be isolated in pure state. The catalyst was recovered and reused in consecutive reactions over four runs (Table 4). It may be noted that the catalyst could be reused up to 3rd run without affecting the yield. However in the 4th run, the yield decreased marginally.

Table 4: Recycling studies of Mont-K10 clay.[a]

No. of cycles	Native	Run 1	Run 2	Run 3	Run 4
Yield (%)[b]	92	92	92	91	89
Time (min)	45	45	45	45	45

[a]Reaction conditions: benzaldehyde (1 mmol), malononitrile (2 mmol), thiophenol (1 mmol); catalyst: K-10 clay (20 mol%); solvent: ethanol (5mL)
[b]Isolated yields

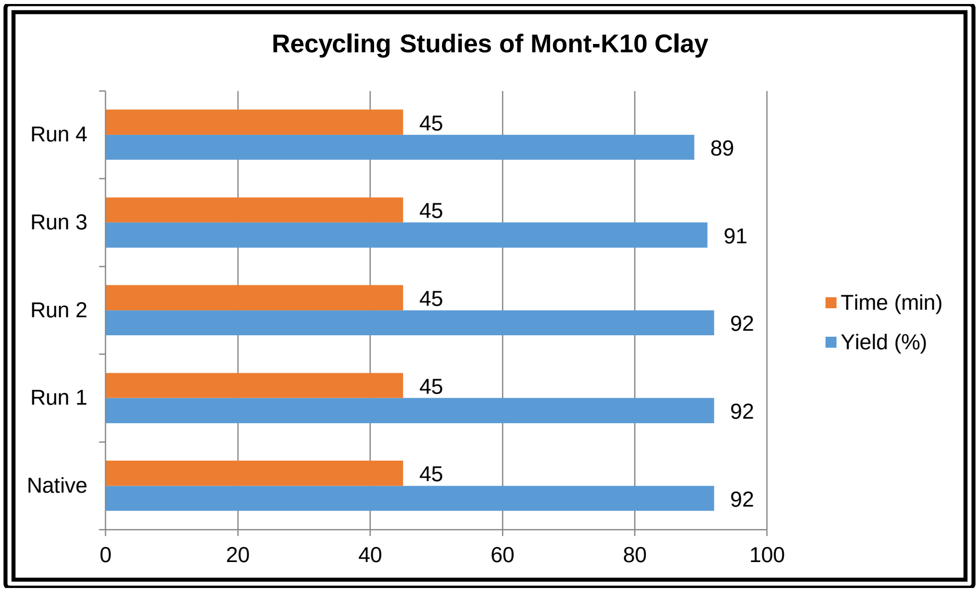


Figure 4: Graphical representation of recycling studies of Mont-K10 clay.

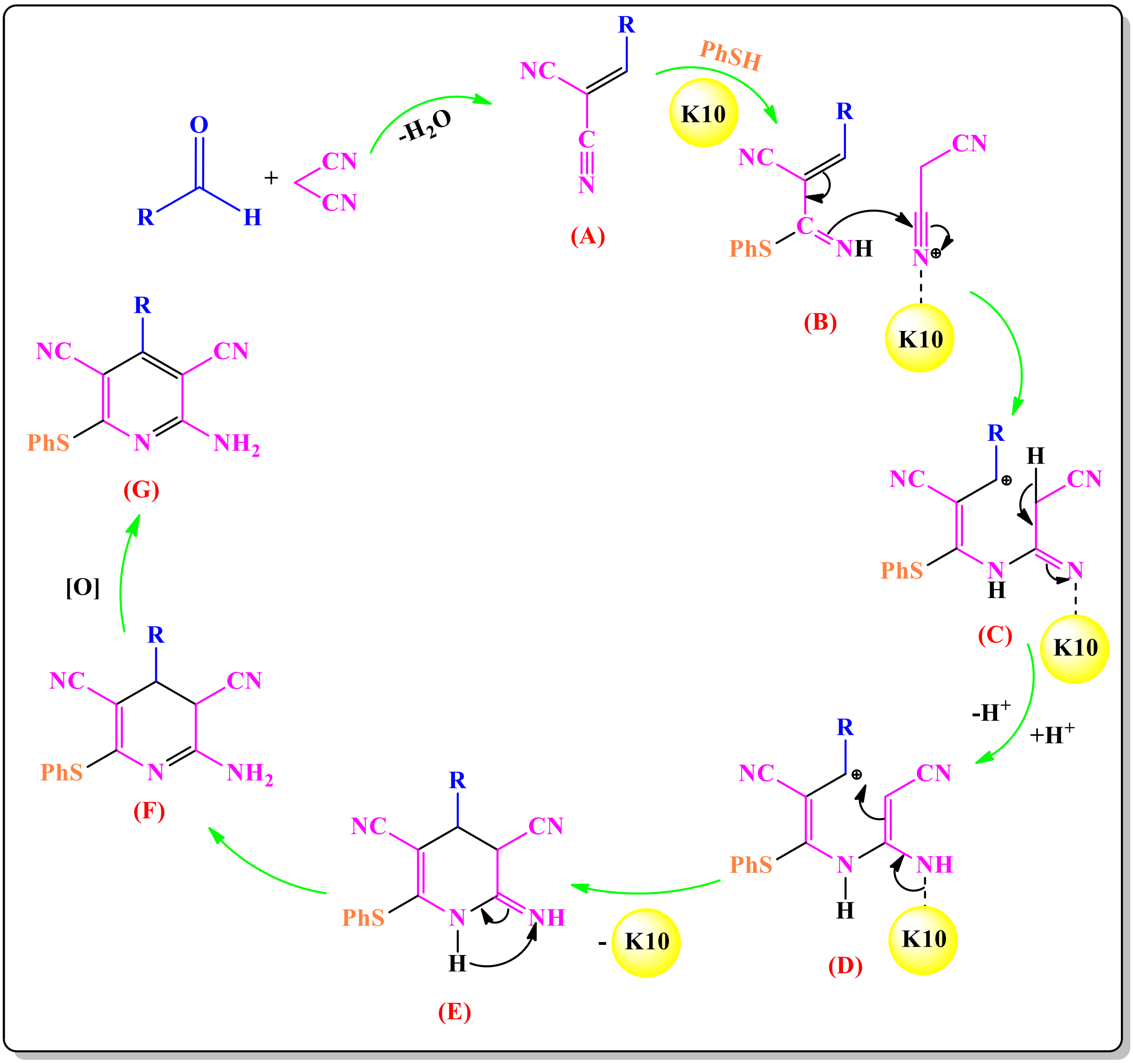
Furthermore, the efficacy of the current approach was contrasted with the acid catalyzed protocols mentioned in the literature (Table 5). This strategy was ascertained to be the best in pursuit of economical, eco-friendly and efficiency aspects as it lead to excellent yields, short reaction timing, ease of workup and reusability of catalyst.

Table 5: Comparison of the present protocol with the reported methods using acid catalyst.[a]

Entry	Catalyst	mol %	Yield (%)[b]	Time (hr)	Reusability of catalyst
1.	Iodoxybenzoic acid (IBX)[d] [17]	10	80	1.5	No
2.	$ZnCl_2$[c] [34]	20	65	2	No
3.	Boric acid[c] [36]	10	90	0.6	No
4.	Phosphotungstic acid[c] [37]	2	86	0.6	No
5.	Scandium triflate[c] [44]	5	85	2	No
6.	Mont-K10 clay[c]	20	92	0.7	Yes

[a] Reaction conditions: benzaldehyde, malononitrile, thiophenol (1:2:1)
[b] Isolated yields
[c] Reflux
[d] Stirred at 70°C

The mechanism for Knoevenagel condensation in the presence of $ZnCl_2$ was delineated by Sridhar et al. [37], indicating that the Lewis acid moiety activates the aldehyde and nitrile of the Knoevenagel product. As a result, K-10 clay appears to play the same role, first initiating the condensation of aldehyde with malononitrile followed by the Michael addition of thiophenol to the initially formed adducts. The resulting product reacts with the second molecule of malononitrile, which is catalysed by K-10, and is then followed by intramolecular cyclization, proton shift, and oxidation. Scheme 2 depicts the entire series of reactions.



Scheme 2: Proposed mechanism for the Mont-K10 clay catalyzed synthesis of 2-Amino-3,5-dicarbonitrile-6-thiopyridines.

Conclusion

It has been possible to accomplish multicomponent reaction of aldehyde, malononitrile and thiophenol in the presence of K-10 clay as catalyst under milder conditions to obtain 2-Amino-3,5-dicarbonitrile-6-thiopyridines in high yields. The catalyst could be recycled at least for three times without affecting its activity. The easy workup, short reaction time, recyclability of the catalyst, high yield and benign reaction conditions make this approach a viable alternative to the other methodologies reported in literature.

Supporting Information

Supporting Information File 1: Experimental details, Characterization and Spectral data.

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