**Supporting Information**

for

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

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**1. Experimental Procedure :-**

Chemicals were procured from Sigma Aldrich and were used as such without further purification. Solvents were freshly dried and distilled. Mont-K10 clay was preheated every time prior to conducting the reaction. The progress of the reaction was monitored by TLC using EtOAc : hexane (20% +80% ) as the developing solvent. Melting points were determined on a KGX apparatus in open capillary and are uncorrected.

IR spectra were recorded on Bruker FT IR spectrometer ALPHA II in KBr pellet. 1H NMR and 13C NMR spectra were recorded on Jeol Resonance 400 MHz spectrometer, at a frequency of 399.78 MHz and 100 MHz respectively in CDCl3 using TMS as internal standard. The values of chemical shifts are reported in parts per million (*δ* ppm) and coupling constants (*J*) are given in Hertz.

*General procedure for the synthesis of 2-Amino-3,5-dicarbonitrile-6-thiopyridine derivatives:-*

The aldehyde (4 mmol), malononitrile (8 mmol, 528 mg), thiophenol (4 mmol, 440 mg), and mont - K10 clay (20 mol %) were suspende in ethanol (15 mL) taken in a 25-mL round-bottomed flask provided with a condenser and the mixture was refluxed with 15-mL of ethanol. The reaction was kept in open to air during reflux and the progress of the reaction was monitored with TLC. After completion of the reaction, the reaction mixture was allowed to cool at r.t., then the Mont- K10 clay was filtered off and the solvent of the filtrate was removed at under reduced pressure. The solid product was then washed with ethyl acetate (3 x 10 mL) and dried *in vacuo*. The crude product was purified by recrystallization from ethanol.

The filtered K-10 clay was washed with ethanol (2 x 10 mL) and ethyl acetate (2 x 10

mL), dried overnight in oven and reused in the subsequent reactions.

All the synthesized products were stable solids and their structures were established

on the basis of their spectral analysis (IR, 1H NMR and 13C NMR).

**2. Characterisation Data:-**

The structure of all the synthesized compounds were unambiguously inferred with the help of IR, 1H NMR and 13C NMR spectral studies.



**2-Amino-4-phenyl-6-phenylsulfanyl-pyridine-3,5-dicarbonitrile (Entry 1, Table 3):**

Colourless solid; mp 216-218˚C [54]; yield 92%; IR (KBr) νmax/cm-1: 3454 (N-H str.), 3348 (N-H str.), 3239, 2214 (C≡N str.), 1646 (C=C str.), 1562, 1511, 1349, 1283, 1108, 849, 760 (C-S str.).

1H NMR (400 MHz, DMSO-*d*6, δ ppm, *J* Hz): 8.52 (s, 1H, Ar–H), 7.92 (bs**,** 2H, NH2), 7.66 (d, *J* = 8Hz, 3H, Ar–H), 7.60 (t, *J* = 8Hz, 6H, Ar–H).

13C NMR (100 MHz, CDCl3, δ ppm): 154.4, 150.6, 148.3, 148.0, 144.1, 137.6, 130.6, 130.0, 129.1, 129.0, 124.1, 119.0, 95.6, 94.4.



**2-Amino-6-phenylsulfanyl-4-p-tolyl-pyridine-3,5-dicarbonitrile (Entry 2, Table 3):**

White solid; mp 225-226˚C [37]; yield 92%; IR (KBr) νmax/cm-1: 3455 (N-H str.), 3348 (N-H str.), 3239, 2213 (C≡N str.), 1646 (C=C str.), 1562, 1510, 1348, 1282, 1108, 848, 759 (C-S str.), 695.

1H NMR (400 MHz, CDCl3, δ ppm, *J* Hz): 7.79 (bs, 2H, NH2), 7.70 (s, 1H, Ar–H), 7.50 (s, 1H, Ar–H), 7.33-7.21 (m, 5H, Ar–H), 7.10 (s, 1H, Ar–H), 2.43 (s, 3H, CH3).

13C NMR (100 MHz, CDCl3, δ ppm): 159.8, 146.4, 132.3, 131.0, 130.4, 129.9, 129.2, 129.1, 128.8, 128.5, 114.1, 112.9, 81.3, 60.1, 22.1, 21.2.



**2-Amino-4-(4-methoxy-phenyl)-6-phenylsulfanyl-pyridine-3,5-dicarbonitrile (Entry**

**3, Table 3):**

Colourless solid; mp 238-240˚C [54]; yield 91%; IR (KBr) νmax/cm-1: 3353 (N-H str.), 3221 (N-H str.), 3031, 2262 (C≡N str.), 2215 (C≡N str.), 1660 (C=C str.), 1603, 1540, 1428, 1315, 1183, 1076, 966, 810, 700 (C-S str.).

1H NMR (400 MHz, CDCl3, δ ppm, *J* Hz): 8.36 (s, 1H, Ar-H), 7.92 (bs, 2H, NH2), 7.25-7.16 (m, 7H, Ar-H), 6.06 (s, 1H, Ar-H), 3.84 (s, 3H, OCH3).

13C NMR (100 MHz, DMSO-*d6*, δ ppm): 161.1, 154.9, 149.2, 127.8, 124.6, 115.3, 114.5, 112.5, 112.3, 77.1, 56.5, 55.9.



**2-Amino-4-(4-chloro-phenyl)-6-phenylsulfanyl-pyridine-3,5-dicarbonitrile (Entry 4,**

**Table 3):**

White solid; mp 222-224˚C [16]; yield 90%; IR (KBr) νmax/cm-1: 3454 (N-H str.), 3347 (N-H str.), 3238, 2214 (C≡N str.), 1645 (C=C str.), 1561, 1510, 1440, 1348, 1283, 1109, 850, 761 (C-S str.), 696.

1H NMR (400 MHz, CDCl3, δ ppm, *J* Hz): 7.86-7.83 (m, 4H, Ar-H), 7.71 (bs, 2H, NH2), 7.52-7.49 (m, 4H, Ar-H), 7.24 (d, *J* = 1.2 Hz, 1H, Ar-H).

13C NMR (100 MHz, DMSO-*d6*, δ ppm): 154.6, 150.6, 148.3, 148.0, 144.1, 137.6, 134.1, 130.6, 130.0, 129.1, 129.0, 128.5, 124.1, 119.0, 95.5, 94.3.



**2-Amino-4-(4-bromo-phenyl)-6-phenylsulfanyl-pyridine-3,5-dicarbonitrile (Entry 5,**

**Table 3):**

Colourless solid; mp 254–256˚C [16]; yield 88%; IR (KBr) νmax/cm-1: 3353 (N-H str.), 3222 (N-H str.), 3031, 2262 (C≡N str.), 2215 (C≡N str.), 1660 (C=C str.), 1603, 1540, 1429, 1315, 1183, 1076, 966, 810, 702 (C-S str.).

1H NMR (400 MHz, CDCl3, δ ppm, *J* Hz): 7.77-7.75 (m, 5H, Ar-H), 7.74 (t, *J* = 8 Hz, 2H, NH2), 7.68-7.65 (m, 4H, Ar-H).

13C NMR (100 MHz, CDCl3, δ ppm): 159.2, 158.5, 133.1, 133.0, 132.1, 131.9, 131.8, 130.1, 130.0, 129.7, 129.6, 113.5, 112.4, 83.5.



**2-Amino-6-phenylsulfanyl-4-thiophen-2-yl-pyridine-3,5-dicarbonitrile (Entry 6,**

**Table 3):**

Yellow solid; mp 206-208˚C [54]; yield 86%; IR (KBr) νmax/cm-1: 3455 (N-H str.), 3347 (N-H str.), 3240, 2213 (C≡N str.), 1647 (C=C str.), 1563, 1511, 1443, 1349, 1283, 1109, 849, 758 (C-S str.), 698.

1H NMR (400 MHz, CDCl3, δ ppm, *J* Hz): 7.87 (d, *J* = 4 Hz, 4H, Ar-H), 7.79 (d, *J* = 4 Hz, 3H, Ar-H), 7.26 (t, *J* = 4 Hz, 3H, Ar-H).

13C NMR (100 MHz, CDCl3, δ ppm): 148.7, 141.0, 134.7, 130.5, 130.4, 130.3, 129.7, 129.4, 124.5, 110.7, 110.2, 52.6, 29.8.



**2-Amino-4-(3,4-dimethoxyphenyl)-6-phenylsulfanyl-pyridine-3,5-dicarbonitrile (Entry 7, Table 3):**

Light yellow solid; mp 262-264˚C [37]; yield 85%; IR (KBr) νmax/cm-1: 3355 (N-H str.), 3222 (N-H str.), 3032, 2916, 2853, 2265 (C≡N str.), 2216 (C≡N str.), 1660 (C=C str.), 1604, 1541, 1429, 1316, 1184, 1076, 968, 853, 810, 771 (C-S str.), 703.

1H NMR (400 MHz, DMSO-*d6*, δ ppm, *J* Hz): 8.29 (s, 1H, Ar-H), 7.58 (bs, 2H, NH2), 7.56-7.53 (m, 6H, Ar-H), 7.17 (d, *J* = 8 Hz, 1H, Ar-H), 3.84 (s, 3H, OCH3), 3.71 (s, 3H, OCH3).

13C NMR (100 MHz, DMSO-*d6*, δ ppm): 165.3, 161.4, 159.8, 135.4, 134.3, 131.7, 131.5, 130.0, 129.9, 128.1, 125.1, 116.1, 114.7, 77.8, 56.9, 56.4, 56.0.



**2-Amino-4-(4-nitro-phenyl)-6-phenylsulfanyl-pyridine-3,5-dicarbonitrile (Entry 8,**

**Table 3):**

Yellow solid; mp 287-289˚C [54]; yield 85%; IR (KBr) νmax/cm-1: 3454 (N-H str.), 3348 (N-H str.), 3239, 2214 (C≡N str.), 1646 (C=C str.), 1562 (N-O str.), 1511 (N-O str.), 1441, 1349, 1283, 1108, 849, 760 (C-S str.), 696.

1H NMR (400 MHz, CDCl3, δ ppm, *J* Hz): 8.30-8.27 (m, 2H, Ar–H), 7.63 (bs, 2H, NH2), 7.50 (d, *J* = 4Hz, 2H, Ar–H), 7.42-7.40 (m, 3H, Ar–H), 4.61 (d, *J =* 4Hz, 1H, Ar-H), 4.06 (d, *J =* 4Hz, 1H, Ar-H).

13C NMR (100 MHz, DMSO-*d*6, δ ppm): 154.5, 150.7, 148.4, 148.1, 144.2, 137.7, 130.7, 130.1, 129.2, 129.2, 129.1, 124.2, 119.0, 94.4.

**3. Spectral Data:-**











