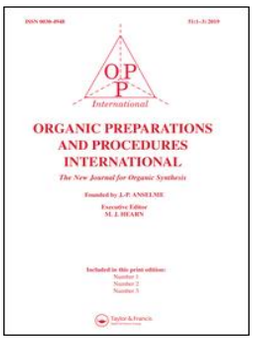

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OPPI BRIEF

Nano-Co_3S_4 as a Retrievable and Robust Catalyst for the Synthesis of 2-Oxo-pyridines and 5-Oxo-[1,2,4]triazolo[2,3-a]pyridines

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Pyridones possess many biological properties such as antibacterial,[1] anti-inflammatory,[2] antiproliferative,[3] antitumor,[4] antihepatitis B,[5] and anti-HIV-1 activities.[6] Finding effective methods for the preparation of pyridones is a principal challenge. Recently, reports have appeared on the synthesis of pyridones using such catalysts as [bmim]BF_4,[7] [$RuCl_2$(*p*-cymene)$]_2$,[8] [TMG][Lac] (1,1,3,3-tetramethylguanidine lactate),[9] sodium ethoxide,[10] piperidine,[11] and bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$).[12]

Despite the use of these procedures, there remains a need for further new methods for the preparation of pyridones. Nanoscale heterogeneous catalysts present high surface areas, which are mainly responsible for their catalytic activity.[13–15] Among diverse nanoparticles, metal sulfide nanoparticles have received substantial attention due to their unique properties and possible applications in numerous fields.[16–17] As part of our ongoing interest in the use of nanoscale heterogeneous catalysts for the preparation of heterocyclic systems,[18–19] we now wish to report the use of Co_3S_4 nanoparticles as an efficient catalyst for the preparation of 2-oxo-pyridines by the four-component reaction of hydrazine hydrate, ethyl cyanoacetate, malononitrile and aldehydes under reflux conditions in ethanol. We have also prepared 5-oxo-[1,2,4]triazolo[2,3-a]pyridines through the reaction of 2-oxo-pyridines with acetyl chloride in the presence of Co_3S_4 nanoparticles under reflux conditions in dimethylformamide (DMF) (*Scheme 1*).

We initially attempted a four-component condensation of hydrazine hydrate, ethyl cyanoacetate, malononitrile and 4-chlorobenzaldehyde as a model reaction under different conditions. Yields were determined in the presence of ZrO_2, NiO, SnO, CoO, CoS and Co_3S_4 nanoparticles and the results are shown in *Table 1*. Nano-Co_3S_4 gave the best yields in the shortest time and a very good yield of 92% was obtained with 0.4 mol%, which was not improved by increasing to 0.6 mol%. Our nano-Co_3S_4 was

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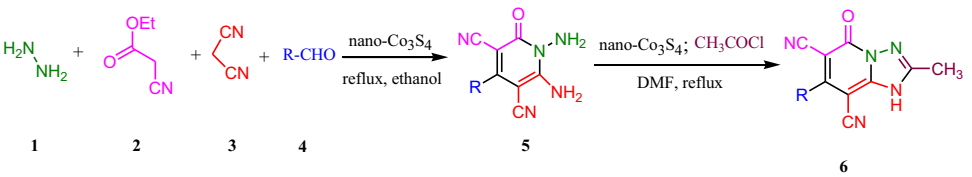


Scheme 1. Synthesis of 2-oxo-pyridines and 5-oxo-[1,2,4]triazolo[2,3-a]pyridines using Co_3S_4 nanoparticles.

Table 1
Optimization of Reaction Conditions using Different Catalysts and Solvents[a]

Entry	solvent (reflux)	Catalyst (mol%)	Time (min)	Yield[b]%
1	EtOH	———	250	12
2	EtOH	nano-ZrO_2 (2)	100	48
3	EtOH	nano-NiO (3)	100	39
4	EtOH	nano-SnO (3)	150	30
5	EtOH	nano-CoO (0.8)	45	55
6	EtOH	nano-CoS (0.8)	45	67
7	EtOH	nano-Co_3S_4 (0.2)	30	88
8	EtOH	nano-Co_3S_4 (0.4)	30	92
9	EtOH	nano-Co_3S_4 (0.6)	30	92
10	CH_3CN	nano-Co_3S_4 (0.4)	30	82
11	DMF	nano-Co_3S_4 (0.4)	30	70
12	water	nano-Co_3S_4 (0.4)	30	62

[a]Hydrazine hydrate (2 mmol), ethyl cyanoacetate (2 mmol), malononitrile (2 mmol), 4-chloro benzaldehyde (2 mmol).
[b]Isolated yield.

characterized (see Experimental Section), and the data were submitted for review. A reaction run in the absence of any catalyst gave a yield of only 12% (entry 1). EtOH was a better solvent than MeCN, DMF and water. This work established the optimum conditions.

We next turned to the efficacy of the catalyst using different aldehydes, and the results are summarized in *Table 2*. We found our method to be compatible with such aldehydes as acetaldehyde, propionaldehyde, 4-bromobenzaldehyde, 4-methoxybenzaldehyde, 4-nitrobenzaldehyde, and 4-isopropylbenzaldehyde. The products were isolated in very good to excellent yields under reflux conditions in ethanol. Aldehydes containing electron-withdrawing groups generally gave yields of the corresponding 2-oxo-pyridines of 90-94% in 30 min (entries 3, 4, 7, 8, 10), but those with electron-donating groups gave slightly lower yields of 83-86% in a longer reaction time of 45 min (entries 5, 6, 9, 11, 12, 13).

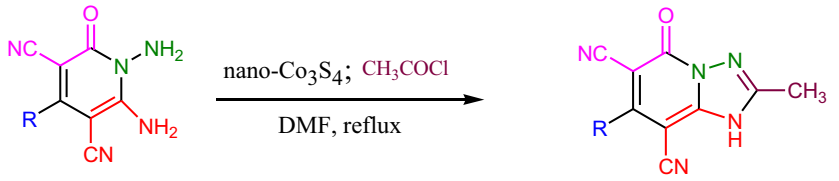
In continuation of our work on the synthesis of pyridones, a series of 5-oxo[1,2,4]-triazolo [2,3-a] pyridines has been prepared through the reaction of 2-oxo-pyridines with acetyl chloride in the presence of Co_3S_4 nanoparticles under reflux conditions in DMF (*Scheme 2*).

In this reaction, a plausible mechanism involves Knoevenagel condensation, Michael addition and cyclization to form the 2-oxo-pyridines.

Table 2
Synthesis of 2-oxo-pyridines using Nano-Co_3S_4[a]

Entry	R (aldehyde)	product	Time (min)	Yield[b] %	mp°C (found)	mp°C (reported) (ref)
1	CH_3-	**5a**	55	75	202-204	———
2	CH_3CH_2-	**5b**	55	78	209-211	———
3	4-NO_2-C_6H_4	**5c**	30	94	226-227	226-228 (12)
4	4-Cl-C_6H_4	**5d**	30	92	243-244	242-243 (12)
5	4-OMe-C_6H_4	**5e**	45	85	224-226	222-224 (12)
6	4-OH-C_6H_4	**5f**	45	83	242-245	——
7	4-Br-C_6H_4	**5g**	30	92	234-236	234-236 (19)
8	3-NO_2-C_6H_4	**5h**	30	90	218-220	——
9	3-OH-C_6H_4	**5i**	40	86	232-235	——
10	2-Cl-C_6H_4	**5j**	30	90	239-241	——
11	4-isopropyl-C_6H_4	**5k**	45	85	212-214	——
12	4-CH_3-C_6H_4	**5l**	45	86	239-241	238-240 (12)
13	4-$N(CH_3)_2$-C_6H_4	**5m**	45	84	230-232	——
14	C_6H_5	**5n**	35	88	237-239	237-239 (12)

[a]Hydrazine hydrate (2 mmol), ethyl cyanoacetate (2 mmol), malononitrile (2 mmol), benzaldehydes (2 mmol) under reflux conditions in ethanol using nano-Co_3S_4.
[b]Isolated yield.



5 **6**

R= CH_3, 4-Cl-C_6H_4, 4-CH_3-C_6H_4

Scheme 2. Synthesis of 5-oxo[1,2,4]triazolo [2,3-a]pyridines using nano-Co_3S_4.

We also considered the reusability of the nano-Co_3S_4 as catalyst for the synthesis of product **5d** and it was found that product yields only reduced to a negligible extent on each reuse (runs 1-5: 92, 92, 91, 91, 90%). After completion of the reaction (TLC), acetone was added. The catalyst was insoluble in acetone, and it could therefore be recycled by an easy filtration. The solvent was then evaporated and the solid obtained recrystallized from ethanol to afford the 2-oxo-pyridines. The recovered nano-Co_3S_4 was washed five to seven times with ethanol and dried at room temperature for 20 h.

In this study, we have described a simple and highly efficient procedure for the synthesis of 2-oxo-pyridines and 5-oxo-[1,2,4]triazolo[2,3-a]pyridines using nano-Co_3S_4 as a retrievable catalyst. High yields, low reaction times, atom economy, reusability of the catalyst and low catalyst loading are some of the significant advantages of the present method.

Experimental Section

The products were isolated and characterized by physical and spectral data. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as internal standard. The progress of the reactions was monitored by thin-layer chromatography (TLC) on Riedel-de Haen plates coated with silica gel 60 F254. The IR spectra were recorded on FT-IR Magna 550 apparatus using KBr plates. Melting points were determined on Electro thermal 9200, and are not corrected. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips X'pert diffractometer with monochromatized Cu Kα radiation (λ= 1.5406 Å). Microscopic morphology of products was visualized by SEM (MIRA 3 TESCAN). The XRD patterns of Co_3S_4 nanoparticles agreed well with the reported pattern (JCPDS No. 73-1703). Our SEM image showed particles with diameters in the nanometer range. Energy Dispersive Spectroscopy (EDS) confirmed the presence of Co and S. XRD, SEM and EDS data were submitted for review by the Editors and are available from the author upon request.

Preparation of Co_3S_4 Nanoparticles

Co_3S_4 nanoparticles were prepared according to the technique reported in the literature.[20] In a typical preparation, molar ratios (1:3) of $Co(CH_3COO)_2{\cdot}4H_2O$ to thioglycolic acid were mixed in 200 mL distilled water with stirring. After 30 min stirring the final solution was sealed in a 250 mL Teflon-lined stainless steel autoclave and heated at 150 °C for 48 h in an electric oven. The autoclave was allowed to cool to room temperature and the product was washed with distilled water and absolute ethanol several times to remove excessive reactants and by-products, followed by drying in an electric oven at 70 °C for 12 h.

General Procedure for the Preparation of 2-oxo-pyridines (5)

A mixture of hydrazine hydrate (2 mmol), ethyl cyanoacetate (2 mmol), malononitrile (2 mmol), aldehyde (2 mmol) and 0.4 mol% of nano-Co_3S_4 in ethanol (5 mL) was refluxed with stirring for the specified time (*Table 2*). The reaction was monitored by TLC (*n*-hexane/ethyl acetate 8:2). After cooling, the reaction mixture was dissolved in acetone and the mixture stirred for 2 min. The suspended solution was filtered and the heterogeneous catalyst was recovered. The acetone was evaporated and the solid that separated out was filtered and recrystallized with ethanol to get pure product. The structures of the products were fully established on the basis of their ^{1}H NMR, ^{13}C NMR, FT-IR spectra and melting points. The novel compounds gave satisfactory elemental analyses.

General Procedure for the Preparation of 5-Oxo-[1,2,4]triazolo[2,3-a]pyridines (6)

A mixture of 2-oxo-pyridines **5** (1 mmol) and acetyl chloride (1 mmol) and 0.4 mol% of nano-Co_3S_4 in DMF (5 ml) was heated under reflux for 60 min, cooled and poured onto ice. The solid obtained was filtered off and recrystallized with ethanol to get pure product **6**. The structures of the products were fully established on the basis of their ^{1}H NMR, ^{13}C NMR and FT-IR spectra. The structure of compound **5e** was confirmed by ^{1}H-^{1}H COSY.

1,6-Diamino-4-methyl-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5a)

White solid, mp 202-204 °C, IR (KBr): ν_{max} 3406, 3450 (NH_2), 3303, 3334 (NH_2), 2218, 2224 (CN), 1644 (C=O), 1602 (C=C) cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 2.06 (s, 3H, CH_3), 5.45 (s, 2H, NH_2), 8.31 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.18, 72.5, 88.9, 115.4, 115.7, 157.2, 159.2, 160.1 ppm.

Anal. Calcd for $C_8H_7N_5O$: C, 50.79; H, 3.73; N, 37.02. Found: C, 50.67; H, 3.63; N, 37.00.

1,6-Diamino-4-ethyl-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5b)

White solid, mp 209-211 °C, IR (KBr): ν_{max} 3407, 3453 (NH_2), 3305, 3338 (NH_2), 2219, 2225 (CN), 1651(C=O), 1608 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.09 (CH_3, t, $J = 7.6$ Hz, 3H), 2.04 (CH_2, m, 2H,), 5.53 (s, 2H, NH_2), 8.34 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.5, 17.10, 71.4, 87.6, 115.3, 115.5, 157.7, 159.4, 160.3 ppm.

Anal. Calcd for $C_9H_9N_5O$: C, 53.20; H, 4.46; N, 34.47. Found: C, 53.14; H, 4.35; N, 34.37.

1,6-Diamino-4-(4-nitrophenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5c)

Yellow solid, mp 226-228 °C, IR (KBr): ν_{max} 3284, 3393 (NH_2), 3318, 3328 (NH_2), 2218, 2223 (CN), 1675 (C=O), 1629 (C=C) cm^{-1},^{1}H NMR (400 MHz, DMSO-d_6): δ 5.73 (s, 2H, NH_2), 7.84 (d, 2H, $J = 8.8$ Hz, CH_{Ar}), 8.39 (d, 2H, $J = 8.8$ Hz, CH_{Ar}), 8.84 (s, 2H, NH_2) ppm; ^{13}C NMR (100MHz, DMSO-d_6): δ 74.3, 86.2, 115.3, 115.5, 124.2, 129.3, 140.8, 148.7, 156.7, 157.4, 158.6 ppm. MS (EI) (*m/z*): 296.

Anal. Calcd for $C_{13}H_8N_6O_3$: C, 52.71; H, 2.72; N 28.37. Found: C, 52.65; H, 2.82; N 28.30.

1,6-Diamino-4-(4-chlorophenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5d)

White solid, mp 243-245°C, IR (KBr): ν_{max} 3392, 3416 (NH_2), 3294, 3303 (NH_2), 2214 (CN), 1674 (C=O), 1608 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.65 (s, 2H, NH_2), 7.54 (d, 2H, $J = 8$ Hz, CH_{Ar}), 7.65 (d, 2H, $J = 8$ Hz, CH_{Ar}), 8.57 (s, 2H, NH_2) ppm; ^{13}C NMR(100 MHz, DMSO-d_6): δ 74.5, 86.5, 115.2, 116.4, 128.5, 130.2, 133.1, 135.2, 156.5, 158.4, 159.3 ppm. MS (EI) (*m/z*): 285 (is due to the ^{35}Cl) and 287 (is due to the ^{37}Cl).

Anal. Calcd for $C_{13}H_8N_5OCl$: C, 54.65; H, 2.82; N, 24.51; Found: C, 54.62; H, 2.93; N, 24.42.

1,6-Diamino-4-(4-methoxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5e)

Cream solid, mp 222-224 °C, IR (KBr): ν_{max} 3453, 3392 (NH_2), 3270, 3222 (NH_2), 2216, 2128 (CN), 1669 (C=O), 1643 (C=C) cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.84 (s, 3H, OCH_3), 5.97 (s, 2H, NH_2), 7.12 (d, 2H, $J = 7.8$ Hz, CH_{Ar}), 7.28 (d, 2H, $J = 7.8$ Hz, CH_{Ar}), 8.45 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.3,

74.4, 87.3, 113.8, 115.6, 116.6, 126.4, 129.8, 156.5, 159.2, 159.4, 160.2 ppm. MS (EI) (*m/z*): 281.

Anal. Calcd. for $C_{14}H_{11}N_5O_2$: C, 59.78; H, 3.94; N, 24.89. Found: C, 59.72; H, 3.96; N, 24.73.

1,6-Diamino-4-(4-hydroxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5f)

White solid, mp 242-245 °C, IR (KBr): ν_{max} 3481, 3394 (NH_2), 3274, 3226 (NH_2), 2208, 2128 (CN), 1669 (C=O), 1645 (C=C) cm^{-1},^{1}H NMR (400 MHz, DMSO-d_6): δ 5.60 (s, 2H, NH_2), 6.89 (d, 2H, $J = 7.8$ Hz, CH_{Ar}), 7.33 (d, 2H, $J = 7.8$ Hz, CH_{Ar}), 8.34 (s, 2H, NH_2), 10.12 (s, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 74.1, 86.0, 115.2, 115.8, 116.7, 124.7, 129.8, 156.6, 159.5, 159.6, 160.4 ppm.

Anal. Calcd. for $C_{13}H_9N_5O_2$: C, 58.43; H, 3.39; N, 26.21. Found: C, 58.35; H, 3.32; N, 26.17.

1,6-Diamino-4-(4-bromophenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5g)

Brown crystals, mp 234-236 °C, IR (KBr): ν_{max} 3384, 3412 (NH_2), 3292, 3307 (NH_2), 2214 (CN), 1666 (C=O), 1609 (C=C) cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.67 (s, 2H, NH_2), 7.60-7.98 (m, 4H, CH_{Ar}), 8.55 (s, 2H, NH_2) ppm; ^{13}C NMR (100MHz, DMSO-d_6): δ 74.4, 86.5, 115.2, 116.4, 128.6, 130.1, 133.3, 135.3, 156.5, 158.5, 159.2 ppm. MS (EI) (*m/z*): 329 (is due to ^{79}Br) and 331 (is due to ^{81}Br).

Anal. Calcd. for $C_{13}H_8N_5OBr$: C, 47.29; H, 2.44; N, 21.21. Found: C, 47.19; H, 2.33; N, 21.25.

1,6-Diamino-4-(3-nitrophenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5h)

Yellow solid, mp 218-220 °C, IR (KBr): ν_{max} 3285, 3396 (NH_2), 3316, 3323 (NH_2), 2215, 2225 (CN), 1673 (C=O), 1625 (C=C) cm^{-1},^{1}H NMR (400 MHz, DMSO-d_6): δ 5.76 (s, 2H, NH_2), 7.92-8.04 (m, 4H, CH_{Ar}), 8.64 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 74.4, 86.6, 115.2, 116.0, 122.2, 124.9, 130.6, 134.8, 136.8, 147.8, 156.7, 157.1, 158.6 ppm. MS (EI) (*m/z*): 296.

Anal. Calcd. for $C_{13}H_8N_6O_3$: C, 52.71; H, 2.72; N 28.37. Found: C, 52.63; H, 2.84; N 28.28.

1,6-Diamino-4-(3-hydroxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5i)

White solid, mp 232-235 °C, IR (KBr): ν_{max} 3486, 3397 (NH_2), 3270, 3224 (NH_2), 2203, 2127(CN), 1669 (C=O), 1642 (C=C) cm^{-1},^{1}H NMR (400 MHz, DMSO-d_6): δ 5.62 (s, 2H, NH_2), 6.80-7.34 (m, 4H, CH_{Ar}), 8.34 (s, 2H, NH_2), 10.14 (s, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 74.3, 86.5, 115.6, 115.9, 116.8, 124.8, 125.3, 126.7, 129.9, 156.4, 159.1, 159.2, 160.6 ppm.

Anal. Calcd. for $C_{13}H_9N_5O_2$: C, 58.43; H, 3.39; N, 26.21. Found: C, 58.30; H, 3.30; N, 26.15.

1,6-Diamino-4-(2-chlorophenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5j)

White solid, mp 239- 241˚C, IR (KBr): ν_{max} 3390, 3413 (NH_2), 3292, 3306 (NH_2), 2216 (CN), 1673 (C=O), 1608 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 5.67 (s, 2H, NH_2), 7.50 -7.65 (m, 4H, CH_{Ar}), 8.53 (s, 2H, NH_2) ppm; ^{13}C NMR(100 MHz, DMSO-d_6): δ 74.4, 86.3, 115.1, 116.2, 127.4, 128.4, 129.7, 130.5, 133.5, 135.5, 156.4, 158.5, 159.4 ppm. MS (EI) (*m/z*): 285 (is due to the ^{35}Cl) and 287 (is due to the ^{37}Cl).

Anal. Calcd. for $C_{13}H_8N_5OCl$: C, 54.65; H, 2.82; N, 24.51. Found: C, 54.60; H, 2.91; N, 24.40.

1,6-Diamino-4-(4-isopropylphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5k)

White solid, mp 212-214 °C, IR (KBr): ν_{max} 3404, 3450 (NH_2), 3304, 3332 (NH_2), 2216, 2220 (CN), 1640 (C=O), 1603 (C=C) cm^{-1},^1H NMR (400 MHz, DMSO-d_6): δ 1.28 (d, $J = 7.6$ Hz, $2CH_3$), 3.08-3.14 (m, CH), 5.63 (s, 2H, NH_2), 7.28 (d, 2H, $J = 8.0$ Hz, CH_{Ar}), 7.39 (d, 2H, $J = 8.0$ Hz, CH_{Ar}), 8.52 (s, 2H, NH_2) ppm; ^{13}C NMR(100 MHz, DMSO-d_6): δ 21.5, 34.5, 74.7, 86.7, 115.2, 116.4, 127.5, 128.7, 131.4, 140.7, 156.4, 159.5, 159.7 ppm.

Anal. Calcd. for $C_{16}H_{15}N_5O$: C, 65.52; H, 5.15; N, 23.88. Found: C, 65.48; H, 5.10; N, 23.80.

1,6-Diamino-4-(4-methylphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5l)

White solid; mp 238-240 °C, IR (KBr): ν_{max} 3400, 3454 (NH_2), 3305, 3334 (NH_2), 2219, 2221 (CN), 1640 (C=O), 1605 (C=C) cm^{-1},^1H NMR (400 MHz, DMSO-d_6): δ 2.27 (s, 3H, CH_3), 5.65 (s, 2H, NH_2), 7.30 (d, 2H, $J = 8.0$ Hz, CH_{Ar}), 7.35 (d, 2H, $J = 8.0$ Hz, CH_{Ar}), 8.49 (s, 2H, NH_2) ppm; ^{13}C NMR(100 MHz, DMSO-d_6):δ 21.1, 74.4, 86.9, 115.5, 116.2, 127.3, 128.5, 131.2, 140.6, 156.3, 159.1, 159.6 ppm. MS (EI) (*m/z*): 265.

Anal. Calcd. for $C_{14}H_{11}N_5O$: C, 63.39; H, 4.18; N, 26.40. Found: C, 63.14; H, 4.27; N, 26.32.

1,6-Diamino-4-(4-n,n-dimethylaminophenyl)-2-oxo-1,2-dihydropyridine-3,5 dicarbonitrile (5m)

White solid, mp 230-232 °C, IR (KBr): ν_{max} 3405, 3458 (NH_2), 3302, 3337 (NH_2), 2215, 2220 (CN), 1642 (C=O), 1608 (C=C) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.80 (s, 6H, $N(CH_3)_2$), 5.63 (s, 2H, NH_2), 7.34 (d, 2H, $J = 7.8$ Hz, CH_{Ar}), 7.47 (d, 2H, $J = 7.8$ Hz, CH_{Ar}), 8.52 (s, 2H, NH_2) ppm; ^{13}C NMR(100 MHz, DMSO-d_6):δ 39.7, 74.1, 86.5, 115.3, 116.7, 127.4, 128.7, 131.8, 148.3, 156.3, 159.2, 159.7 ppm.

Anal. Calcd. For $C_{15}H_{14}N_6O$: C, 61.21; H, 4.79; N, 28.55. Found: C, 61.15; H, 4.71; N, 28.46.

1,6-Diamino-4-phenyl-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (5n)

White solid; mp 237-239 °C, IR (KBr,): ν_{max} 3448, 3353 (NH_2), 3242, 3315 (NH_2), 2224 (CN), 1645 (C=O), 1606 (C=C) cm^{-1}, ^1H NMR (400 MHz, DMSO-d_6): δ 5.64

(s, 2H, NH_2), 7.46-7.56 (m, 5H, CH_{Ar}), 8.48 (s, 2H, NH_2) ppm; ^{13}C NMR (100MHz, DMSO-d_6): δ 74.3, 86.2, 115.5, 1116.4, 127.8, 128.4, 130.2, 134.5, 156.6, 159.2, 159.5 ppm. MS (EI) (*m/z*): 251.

Anal. Calcd. for $C_{13}H_9N_5O$: C, 62.15; H, 3.61; N, 27.87. Found: C, 62.09; H, 3.54; N, 27.78.

7-Methyl-5-oxo-1H-4,5-dihydro-2-methyl[1,2,4]triazolo[2,3-a]pyridine-6,8-dicarbonitrile (6a)

White solid, mp 262-264 °C, IR (KBr,): ν_{max} 3205 (NH), 2215 (CN), 1698 (C=O), 1625 (C=C) cm^{-1}, ^1H NMR (400 MHz, DMSO-d_6): δ 1.84 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.55 (s, 1H, NH), ppm; ^{13}C NMR (100MHz, DMSO-d_6): δ 14.3, 24.2, 74.4, 86.5, 115.8, 115.9, 146.4, 156.7, 159.5, 160.1 ppm.

Anal. Calcd. for $C_{10}H_7N_5O$: C, 56.34; H, 3.31; N, 32.85. Found: C, 56.28; H, 3.25; N, 32.78.

7-(4-Chlorophenyl)-5-oxo-1H-4,5-dihydro-2-methyl[1,2,4]triazolo[2,3-a]pyridine-6,8-dicarbonitrile (6b)

White solid, mp 282-285 °C, IR (KBr,): ν_{max} 3207 (NH), 2219 (CN), 1695 (C=O), 1625 (C=C) cm^{-1}, ^1H NMR (400 MHz, DMSO-d_6): δ 2.02 (s, 3H, CH_3), 3.54 (s, 1H, NH), 7.30-8.20 (m, 4H, CH_{Ar}) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 24.2, 75.8, 88.7, 115.7, 115.9, 127.8, 129.3, 131.5, 133.6, 147.5, 156.4, 159.8, 161.2 ppm.

Anal. Calcd. for $C_{15}H_8ClN_5O$: C, 58.17; H, 2.60; N, 22.61; Found: C, 58.10; H, 2.53; N, 22.54.

7-(4-Methylphenyl)-5-oxo-1H-4,5-dihydro-2-methyl[1,2,4]triazolo[2,3-a]pyridine-6,8-dicarbonitrile (6c)

White solid, mp 272-275 °C, IR (KBr,): ν_{max} 3212 (NH), 2215(CN), 1690 (C=O), 1623 (C=C) cm^{-1}, ^1H NMR (400 MHz, DMSO-d_6): δ 2.02 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.54 (s, 1H, NH), 7.30-8.20 (m, 4H, CH_{Ar}) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 22.8, 24.4, 75.7, 88.5, 115.6, 115.8, 126.3, 129.6, 130.2, 135.3, 147.8, 155.9, 159.7, 161.5 ppm.

Anal. Calcd. for $C_{16}H_{11}N_5O$: C, 66.43; H, 3.83; N, 24.21. Found: C, 66.38; H, 3.76; N, 24.15.

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