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Green synthesis of novel 5-amino-bispyrazole-4-carbonitriles using Fe_3O_4@SiO_2@vanillin@thioglycolic acid nano-catalyst

Mohammad Nikpassand*, Leila Zare Fekri, Rajender S. Varma, Lida Hassanzadi, Farhad Sedighi Pashaki

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Material and methods

Chemicals were purchased from Merck and Fluka and used as purchased. Melting points were measured on an Electro-thermal 9100 apparatus and are uncorrected. FT-IR spectra were recorded on a Shimadzu FT-IR-8400S spectrometer. Elemental analyses were recorded on a Carlo-Erba EA1110CNNO-S analyzer. ^1H and ^{13}C NMR spectra were determined on a Bruker DRX 500 Avance spectrometer at 500 and 125 MHz in DMSO-d_6 as solvent and with TMS as internal standard. Elemental analyses were recorded on a Carlo-Erba EA1110CNNO-S analyser. Nanostructures were detected using a Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuKα, radiation, λ=0.154056), at a scanning speed of 2°/min from 10° to 80° (2θ). Transmission electron microscopy (TEM) measurements were carried out on a Zeiss-EM10C-100 KV instrument.

Synthesis of silica-coated Fe_3O_4 (Fe_3O_4@SiO_2@vanillin@thioglycolic acid MNPs)

The synthetized Fe_3O_4 & Fe_3O_4@SP-Cl MNPs were synthesized by research group, et al. .[20, 21]

Then Fe_3O_4@SP-Cl MNPs (0.2 g), Vanillin (0.2 g), NaOH 10% (5 mL), and distilled H_2O (15 mL) were added. It was stirred for 24 hours. Then thioglycolic acid (1.5 mL) was added. After 5 h, Et_3N (5 mL) was added, and after stirring with the magnet, separation was performed and incubated in oven at 50 °C for 24 h (Figure 1). The structure of the nanocatalysts obtained was confirmed by TEM, FE-SEM, TGA-DTG, XRD, EDX, VSM, Zeta Potential and FT-IR spectroscopy (Figures 2-9).

The morphology and size of the Fe_3O_4@SiO_2@vanillin@thioglycolic acid MNPs was investigated by TEM spectrum as shown in Figure 2. In order to investigate the reusing performance of Fe_3O_4@SiO_2@vanillin@thioglycolic acid MNPs, the recyclability of catalyst was tested in **4a**.

General procedure for preparation of novel new azo-linked 5-amino-pyrazole-4-carbonitriles 4a-k or pyrazolyl-5-amino-pyrazole-4-carbonitriles 6a-j

A mixture of synthetized azo-linked salicylaldehyde (1mmol) or synthetized pyrazolecarbaldehyde (1mmol), phenylhydrazine or *p*-tolylhydrazine (1mmol), malononitrile (1 mmol) and Fe_3O_4@SiO_2@vanillin@thioglycolic acid (0.1 g) were mixed at room temperature for the required reaction time according to Tables 4 and 5. The progress of the reaction was investigated by thin layer chromatography (TLC; TLC Silica gel 60 F_{254}, ethyl acetate: *n*-hexane 1: 2). After completion of the reaction, the resulting mixture was dissolved in hot ethanol (20 mL) and the catalyst separated by a 1.4 Tesla external magnet and washed with hot distilled water (5 mL) and ethanol (5 mL) two times. The resulting novel 5-amino-pyrazole-4-carbonitriles was isolated and purified using a column chromatography (ethyl acetate: *n*-hexane 2: 3).

The physical properties and spectral data of compounds

5-amino-3-(5-((4-chlorophenyl)diazenyl)-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (4a)

Yellow solid, m.p.: 235–237°C; FT-IR (KBr, cm^{-1}): 3292 (N-H stretch), 3064 (C-H stretch), 2390 (C≡N stretch), 1602 (N=N stretch), 1566, 1544 and 1492 (C=C stretch), 1276 (C-N stretch), 1255 (C-O stretch), 1002 (C-Cl stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 6.82 (t, J = 7.2 Hz, 1H), 7.04-7.11 (m, 4H), 7.28 (t, J = 7.5 Hz, 2H), 7.66 (dd, J = 6.3, 2.1 Hz, 2H), 7.80 (dd, J = 8.7, 2.4 Hz, 1H), 7.90 (dd, J = 6.3, 2.1 Hz, 2H), 8.25 (s, 2H, NH_2), 10.60 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 112.3, 117.2, 119.6, 122.2, 122.3, 123.9, 124.4, 129.7, 129.9, 134.4, 135.1, 135.5, 142.6, 143.2, 145.1, 145.7, 151.1, 159.2; Anal. calcd for $C_{22}H_{15}ClN_6O$: C, 63.69; H, 3.64; N, 20.26. Found: C, 63.72; H, 3.63; N, 20.25.

5-amino-3-(5-((2-chlorophenyl)diazenyl)-2-

hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (4b)

Yellow solid, m.p.: 176–178°C; FT-IR (KBr, cm^{-1}): 3288 (N-H stretch), 2390 (C ≡ N stretch), 1602 (N=N stretch), 1566 and 1494 (C=C stretch), 1276 (C=N stretch), 1255 (C-O stretch), 1029 (C-Cl stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 4.50 (s, 2H, NH_2), 6.80 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 7.8 Hz, 1H), 7.27 (t, J = 7.5 Hz, 2H), 7.36-7.55 (m, 2H), 7.68 (dd, J = 7.5, 1.2 Hz, 2H), 7.80 (dd, J = 7.8, 2.4 Hz, 1H), 8.28 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 112.3, 112.5, 117.3, 118.00, 119.6, 122.3, 123.2, 123.6, 128.4, 129.7, 130.2, 131.1, 132.2, 133.8, 135.0, 145.2, 146.1, 148.5, 159.5; Anal. calcd for $C_{22}H_{15}ClN_6O$: C, 63.69; H, 3.64; N, 20.26. Found: , 63.67; H, 3.65; N, 20.28.

5-amino-3-(2-hydroxy-5-((2-methyl-4-nitrophenyl)diazenyl)phenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (4c)

Yellow solid, m.p.: 193–195°C; FT-IR (KBr, cm^{-1}): 3421 and 3330 (N-H stretch), 2196 (C ≡ N stretch), 1683 (N=N stretch), 1600 and 1564 (C=C stretch), 1519 (NO_2 stretch), 1492 (C=C stretch), 1334 (NO_2 stretch), 1255 (C-O stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 2.42 (s, 3H, CH_3), 6.81 (t, J = 7.2 Hz, 1H), 7.04-7.10 (m, 3H), 7.27 (t, J = 8.1 Hz, 2H), 7.68 (d, J = 9.0 Hz, 1H), 7.80 (dd, J = 9.0, 2.7 Hz, 1H), 8.12 (dd, J = 8.7, 2.7 Hz, 1H), 8.22 (s, 1H), 8.26 (d, J = 2.1 Hz, 1H), 10.61 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 25.51, 112.3, 117.0, 117.3, 118.4, 119.6, 122.3, 122.5, 122.9, 123.7, 123.8, 126.6, 129.7, 134.9, 138.5, 144.5, 145.1, 146.4, 148.0, 154.0, 154.0, 159.9; Anal. calcd for $C_{23}H_{17}N_7O_3$: C, 62.87; H, 3.90; N, 22.31. Found: C, 62.87; H, 3.89; N, 22.33.

5-amino-3-(2-hydroxy-5-((4-nitrophenyl)diazenyl)phenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (4d)

Yellow solid, m.p.: 149–151°C; FT-IR (KBr, cm^{-1}): 3461 (N-H stretch), 3307 (N-H stretch), 2189 (C ≡ N stretch), 1662 (N=N stretch), 1641, 1598 and 1566 (C=C stretch), 1515 and 1340 (NO_2 stretch), 1251 (C-O stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 6.78-7.30 (m, 6H), 7.49-7.54 (m, 1H), 7.96-8.02 (m, 2H), 8.16 (s, 1H), 8.23-8.25 (m, 1H), 8.34-8.39 (m, 1H), 10.27 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 112.1, 112.3, 116.3, 117.6, 119.4, 119.8, 119.9, 120.8,

123.5, 125.3, 127.8, 129.6, 129.7, 136.8, 137.8, 145.0, 145.1, 156.1; Anal. calcd for $C_{22}H_{15}N_7O_3$: C, 62.11; H, 3.55; N, 23.05. Found: C, 62.09; H, 3.57; N, 23.06.

5-amino-3-(5-((4-bromophenyl)diazenyl)-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (4e)

Red solid, m.p.: 218–220°C; FT-IR (KBr, cm^{-1}): 3433 (N-H stretch), 3321 (N-H stretch), 2190 (C ≡ N stretch), 1683 (N=N stretch), 1658 and 1568 (C=C stretch), 1255 (C-O stretch), 1002 (C-Br stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 6.79 (t, J = 6.9 Hz, 1H), 7.04-7.11 (m, 2H), 7.28 (t, J = 5.8 Hz, 2H), 7.76-7.84 (m, 5H), 8.24-8.26 (m, 2H), 10.60 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 112.1, 112.3, 117.2, 119.6, 122.2, 122.4, 123.9, 124.6, 124.8, 129.7, 132.8, 133.1, 135.3, 145.1, 145.7, 151.4, 156.1, 159.2; Anal. calcd for $C_{22}H_{15}BrN_6O$: C, 57.53; H, 3.29; N, 18.30. Found: C, 57.55; H, 3.30; N, 18.29.

5-amino-3-(2-hydroxy-5-((4-methoxyphenyl)diazenyl)phenyl)-1-phenyl-1H-pyrazole-4-carbonitrile (4f)

Red solid, m.p.: 184–186°C; FT-IR (KBr, cm^{-1}): 3419 (N-H stretch), 3315 (N-H stretch), 2189 (C ≡ N stretch), 1686 (N=N stretch), 1647, 1600 and 1577 (C=C stretch), 1244 (C-O stretch).; ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 3.85 (s, 3H, CH_3O), 6.82 (t, J = 7.2 Hz, 1H), 7.09-7.20 (m, 5H), 7.29 (t, J = 7.6 Hz, 2H), 7.71-7.77 (m, 1H), 7.88 (d, J = 8.4 Hz, 2H), 8.19-8.29 (m, 1H), 10.61 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 55.9, 112.3, 114.9, 115.1, 115.6, 117.1, 119.6, 121.8, 122.1, 123.4, 124.1, 124.6, 129.7, 130.7, 136.1, 145.1, 145.8, 146.7, 158.4; Anal. calcd for $C_{23}H_{18}N_6O_2$: C, 67.31; H, 4.42; N, 20.48. Found: C, 67.33; H, 4.41; N, 20.50.

5-amino-3-(5-((4-chlorophenyl)diazenyl)-2-hydroxyphenyl)-1-(p-tolyl)-1H-pyrazole-4-carbonitrile (4g)

Red solid, m.p.: 234-236°C; FT-IR (KBr, cm^{-1}): 3292 (N-H stretch), 2339 (C≡N stretch), 1602 (N=N stretch), 1566, 1544 and 1452 (C=C stretch), 1276 (C-N stretch), 1255 (C-O stretch), 1002 (C-Cl stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 2.25 (s, 3H, CH_3), 6.94 (d, J = 8.4 Hz, 2H), 7.08-7.11 (m, 4H), 7.66 (dt, J = 8.4, 3.0 Hz, 2H), 7.78 (dd, J = 8.6, 2.4 Hz, 1H), 7.91 (dt, J = 8.4, 3.0 Hz,

2H), 8.21-8.22 (s, 2H), 10.49 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 20.7, 112.4, 117.1, 122.3, 122.4, 123.3, 123.7, 124.3, 128.2, 129.9, 130.2, 132.5, 134.7, 135.5, 137.6, 142.8, 145.7, 151.1, 159.1; Anal. calcd for $C_{23}H_{17}ClN_6O$: C, 64.41; H, 4.00; N, 19.60. Found: C, 64.39; H, 3.99; N, 19.63.

5-amino-3-(2-hydroxy-5-((2-methyl-4-nitrophenyl)diazenyl)phenyl)-1-(p-tolyl)-1H-pyrazole-4-carbonitrile (4h)

Red solid, m.p.: 190-192°C; FT-IR (KBr, cm^{-1}): 3328 and 3218 (N-H stretch), 2268 (C ≡ N stretch), 1681 (N=N stretch), 1664 (C=N stretch), 1618, 1583 and 1564 (C=C stretch), 1515 and 1340 (NO_2 stretch), 1255 (C-O stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 2.33 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 4.51 (s, 2H, NH_2), 6.94 (d, J = 8.4 Hz, 2H), 7.06-7.18 (m, 3H), 7.66 (d, J = 8.4 Hz, 1H), 7.78 (dd, J = 8.7 2.4 Hz, 1H), 8.15 (dd, J = 8.7, 2.7 Hz, 1H), 8.20 (s, 1H), 8.24 (d, J = 2.4 Hz, 1H), 10.19 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 17.4, 20.6, 112.4, 112.5, 112.7, 117.0, 117.3, 122.4, 122.5, 123.4, 123.7, 124.4, 126.6, 128.2, 130.1, 134.4, 138.5, 142.9, 146.4, 148.0, 154.1, 159.9; Anal. calcd for $C_{24}H_{19}N_7O_3$: C, 63.57; H, 4.22; N, 21.62. Found: C, 63.59; H, 4.20; N, 21.63.

5-amino-3-(5-((2-chlorophenyl)diazenyl)-2-hydroxyphenyl)-1-(p-tolyl)-1H-pyrazole-4-carbonitrile (4i)

Red solid, m.p.: 172-174°C; FT-IR (KBr, cm^{-1}): 3218 (N-H stretch), 3035 (O-H stretch), 2290 (C≡N stretch), 1667 (N=N stretch), 1664, 1612 and 1581 (C=C stretch), 1247 (C-O stretch), 1056 (C-Cl stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 2.23 (s, 3H, CH_3), 7.53 (s, 2H, NH_2), 6.92-7.10 (m, 5H), 7.46-7.56 (m, 3H), 7.68-7.78 (m, 2H), 8.22 (s, 1H), 10.23 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 20.7, 112.3, 112.5, 115.3, 118.0, 122.4, 123.6, 128.2, 128.4, 128.5, 129.7, 130.1, 131.0, 131.1, 133.7, 134.3, 134.5, 142.9, 146.1, 148.1, 159.5; Anal. calcd for $C_{23}H_{17}ClN_6O$: C, 64.41; H, 4.00; N, 19.60. Found: C, 64.39; H, 4.01; N, 19.59.

5-amino-3-(2-hydroxy-5-((4-nitrophenyl)diazenyl)phenyl)-1-(p-tolyl)-1H-pyrazole-4-carbonitrile (4j)

Yellow solid, m.p.: 131-133°C; FT-IR (KBr, cm^{-1}): 3477 and 3309 (N-H stretch), 2360 (C≡N stretch),

1614 (N=N stretch), 1589, 1564 and 1488 (C=C stretch), 1402 (NO_2 stretch), 1271 (C-O stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 12.23 (s, 3H, CH_3), 4.52 (s, 2H, NH_2), 6.87-6.98 (m, 1H),7.05-7.09 (m, 1H), 7.14-7.20 (m, 1H), 7.37 (s, 1H), 7.49-7.54 (m, 2H), 7.80-7.84 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 8.14 (s,1H), 8.23-8.27 (m, 1H), 8.40 (d, *J* = 8.6 Hz, 1H), 8.92 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 20.7, 112.2, 112.4, 112.5, 116.3, 119.7, 120.9, 122.6, 123.5, 125.4, 127.7, 128.0, 129.4, 130.1, 137.3, 142.9, 145.9, 148.3, 156.1; Anal. calcd for $C_{23}H_{17}N_7O_3$: C, 62.87; H, 3.90; N, 22.31. Found: C, 62.85; H, 3.88; N, 22.33.

5-amino-3-(5-((4-bromophenyl)diazenyl)-2-hydroxyphenyl)-1-(p-tolyl)-1H-pyrazole-4-carbonitrile (4k)

Brown solid, m.p.: 180-183°C; FT-IR (KBr, cm^{-1}): 3218 (N-H stretch), 3037 (O-H stretch), 2366 (C≡N stretch), 1668 (N=N stretch), 1573, 1517 and 1483 (C=C stretch), 1280 (C-O stretch), 1006 (C-Br stretch); ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 2.22 (s, 3H, CH_3), 4.56 (s, 2H, NH_2), 6.93-6.98 (m, 3H),7.05-7.09 (m, 3H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.27-7.81 (m, 2H), 8.17 (d, *J* = 2.4 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ_C (ppm) 20.6, 112.4, 112.5, 115.3, 117.2, 122.3, 124.5, 126.1, 128.1, 129.7, 130.1, 130.8, 132.8, 134.6, 142.9, 143.6, 145.6, 151.4, 159.3; Anal. calcd for $C_{23}H_{17}BrN_6O$: C, 58.36; H, 3.62; N, 17.76. Found: C, 58.34; H, 3.63; N, 17.77.

5-amino-1,1',3'-triphenyl-1H,1'H-[3,4'-bipyrazole]-4-carbonitrile (6a)

Brown solid, m.p.: 134–136°C, FT-IR (KBr, cm^{-1}): 3439 (N-H stretch), 3052 (C-H, Ar stretch), 2224 (C≡N stretch), 1643, 1599 and 1499 (C=C stretch) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 6.41 (t, *J* = 6.3 Hz, 1H, Ar-H), 7.06 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.22 (t, *J* = 8.4 Hz, 2H, Ar-H), 7.36 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.52-7.61 (m, 5H, Ar-H), 7.83 (dt, *J* = 9.0, 2.4 Hz, 2H, Ar-H), 8.01 (d, *J* = 6.0 Hz, 2H, Ar-H), 8.05 (s, 1H, Ar-H), 8.91 (s, 1H, NH), 10.39 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 112.3, 118.9, 119.0, 120.3, 127.1, 127.1, 129.0, 129.4, 129.5, 130.0, 130.4, 130.5, 131.2, 132.1, 133.5, 139.6, 145.9, 149.4 ppm. Anal. calcd for $C_{25}H_{18}N_6$: C, 74.61; H, 4.51; N, 20.88. Found: C, 74.63; H, 4.49; N, 20.90.

5-amino-3'-(3-nitrophenyl)-1,1'-diphenyl-1H,1'H-[3,4'-bipyrazole]-4-carbonitrile (6b)

Red solid, m.p.: 148–150°C, FT-IR (KBr, cm^{-1}): 3308 and 3441 (N-H stretch), 2825 and 3100 (C-H stretch), 1938 (C≡N stretch), 1599 (C=N stretch), 1493 (C=C stretch), 1344 and 1531 (NO_2 stretch) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 6.91 (tt, J = 7.5, 0.9 Hz, 1H, Ar-H), 7.06 (dd, J = 8.4, 0.6 Hz, 2H, Ar-H), 7.26-7.33 (m, 2H, Ar-H), 7.36-7.42 (m, 1H, Ar-H), 7.51-7.57 (m, 2H, Ar-H), 7.66 (t, J = 8.1 Hz, 1H, Ar-H), 7.81-7.85 (m, 3H, Ar-H), 8.18 (dq, J = 7.2, 0.9 Hz, 1H, Ar-H), 8.29 (dq, J = 9.0, 1.2 Hz, 1H, Ar-H), 8.38 (s, 1H, Ar-H), 8.68 (s, 1H, NH), 10.12 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 112.6, 118.3, 119.2, 120.2, 123.0, 123.4, 126.3, 127.3, 128.7, 129.3, 129.5, 129.6, 129.8, 134.6, 134.8, 139.4, 144.5, 148.4, 148.7 ppm. Anal. calcd for $C_{25}H_{17}N_7O_2$: C, 67.11; H, 3.83; N, 21.91. Found: C, 67.09; H, 3.81; N, 21.93.

5-amino-3'-(4-nitrophenyl)-1,1'-diphenyl-1H,1'H-[3,4'-bipyrazole]-4-carbonitrile (6c)

Red solid, m.p.: 154–156°C, FT-IR (KBr, cm^{-1}): 3442 and 3320 (N-H stretch), 2959 and 2928 (C-H stretch), 2180 (C≡N stretch), 1598 (N=N stretch), 1544 and 1355 (NO_2 stretch) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 6.75 (t, J = 7.1 Hz, 1H, Ar-H), 7.05 (d, J = 7.8 Hz, 2H, Ar-H), 7.21 (t, J = 8.1 Hz, 2H, Ar-H), 7.36-7.41 (m, 2H, Ar-H), 7.56 (t, J = 7.8 Hz, 2H, Ar-H), 6.12-7.99 (m, 5H), , 8.35 (d, J = 8.7 Hz, 2H, Ar-H), 8.94 (s, 1H, NH), 10.40 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 112.3, 119.0, 119.1, 119.7, 124.1, 127.4, 127.8, 129.0, 129.5, 129.7, 130.0, 139.4, 139.9, 145.8, 147.4, 148.2 ppm. Anal. calcd for $C_{25}H_{17}N_7O_2$: C, 67.11; H, 3.83; N, 21.91. Found: C, 67.12; H, 3.84; N, 21.89.

1,1'-diphenyl-3'-(p-tolyl)-1H,1'H-[3,4'-bipyrazol]-5-amine (6d)

Brown solid, m.p.: 112–114°C, FT-IR (KBr, cm^{-1}): 3405 (N-H stretch), 2960 and 2828 (C-H stretch), 2222 (C≡N stretch), 1657 (C=N stretch), 1599, 1498 (C=C stretch) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 2.52 (s, 3H, CH_3), 6.73 (t, J = 6.91 Hz, 1H, Ar-H), 6.97 (dd, J = 8.7, 3.9 Hz, 2H, Ar-H), 7.06 (d, J = 7.5 Hz, 1H, Ar-H), 7.12 (t, J = 7.5 Hz, 1H, Ar-H), 7.32-7.38 (m, 2H, Ar-H), 7.51-7.61 (m, 3H, Ar-H), 7.95-8.0 (m, 3H, Ar-H),8.85 (s, 1H, NH), 10.3 (s, 1H, NH) ppm. ^{13}C

NMR (125 MHz, DMSO-d_6): δ_C (ppm): 34.5 (CH_3), 112.2, 115.9, 116.4, 118.5, 118.7, 118.8, 123.8, 126.2, 126.8, 128.8, 129.5, 130.0, 130.03, 130.2, 130.3, 139.8, 146.0, 151.1, 158.2 ppm. Anal. calcd for $C_{25}H_{21}N_5$: C, 76.70; H, 5.41; N, 17.89. Found: C, 76.72; H, 5.39; N, 17.87.

3'-(4-methoxyphenyl)-1,1'-diphenyl-1H,1'H-[3,4'-bipyrazol]-5-amine (6e)

Red solid, m.p.: 152–154°C, FT-IR (KBr, cm^{-1}): 3440, 3308 (N-H stretch), 3045 and 2932 (C-H. Ar stretch), 2198 (C≡N stretch), 1601 (C=N stretch), 1642, 1504, 1433 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 3.85 (s, 3H, OCH_3), 6.73 (t, J = 8.7 Hz, 1H, Ar-H), 7.04-7.12 (m, 4H, Ar-H), 7.22 (t, J = 8.4 Hz, 2H, Ar-H), 7.36 (t, J = 7.2 Hz, 1H, Ar-H), 7.55 (t, J = 7.5 Hz, 2H, Ar-H), 7.71 (dd, J = 6.9, 2.1 Hz, 2H, Ar-H), 7.99 (dd, J = 3.0, 0.9 Hz, 2H, Ar-H), 8.02 (d, J = 1.2 Hz, 1H, Ar-H), 8.88 (s, 1H, NH), 10.22 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 55.7 (OCH_3), 112.3, 114.5, 114.9, 118.6, 118.8, 118.845, 120.2, 125.6, 126.4, 126.9, 129.5, 129.9, 130.0, 130.1, 130.8, 139.7, 145.9, 150.7, 159.9 ppm. Anal. calcd for $C_{25}H_{21}N_5O$: C, 73.69; H, 5.19; N, 17.19. Found: C, 73.72; H, 5.16; N, 17.21.

5-amino-3'-(3-chlorophenyl)-1,1'-diphenyl-1H,1'H-[3,4'-bipyrazole]-4-carbonitrile (6f)

Yellow solid, m.p.: 148–150°C, FT-IR (KBr, cm^{-1}): 3218 and 3362 (N-H stretch), 2928 and 3592 (C-H stretch), 2084 (C≡N stretch), 1604 (C=N stretch), 1537 and 1528 (C=C stretch) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 6.94 (t, J = 7.8 Hz, 1H, Ar-H), 7.12 (d, J = 8.2 Hz, 2H, Ar-H), 7.22-7.35 (m, 2H, Ar-H), 7.39-7.53 (m, 3H, Ar-H), 7.61-7.67 (m, 1H, Ar-H), 7.78-7.83 (m, 3H, Ar-H), 8.17-8.23 (m, 2H, Ar-H), 8.32 (s, 1H, Ar-H), 8.72 (s, 1H, NH), 10.09 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 111.7, 119.0, 119.2, 119.8, 121.7, 123.1, 123.7, 127.5, 128.0, 129.0, 129.5, 129.6, 131.1, 131.8, 133.3, 134.2, 139.9, 142.3, 146.9, 148.7 ppm. Anal. calcd for $C_{25}H_{17}ClN_6$: C, 68.73; H, 3.92; N, 19.24. Found: C, 68.72; H, 3.94; N, 19.21.

5-amino-3'-(4-chlorophenyl)-1,1'-diphenyl-1H,1'H-[3,4'-bipyrazole]-4-carbonitrile (6g)

Yellow solid, m.p.: 139–141°C, FT-IR (KBr, cm^{-1}): 3372 and 3404 (N-H stretch), 3093 and 2943 (CH stretch), 2183 (C≡N stretch), 1583 (C=N stretch), 1558 and 1527 (C=C stretch) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 6.72 (t, J = 7.8 Hz,

1H, Ar-H), 7.07 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.31 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.42 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.59-7.63 (m, 2H, Ar-H), 7.78-7.89 (m, 4H, Ar-H), 8.02 (s, 2H, Ar-H), 8.09 (s, 1H, Ar-H), 8.96 (s, 1H, NH), 10.52 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 111.7, 112.4, 118.3, 118.5, 119.6, 122.4, 127.3, 127.8, 128.3, 128.7, 129.4, 130.1, 130.5, 133.2, 133.4, 134.2, 138.3, 146.2, 148.4 ppm. Anal. calcd for $C_{25}H_{17}ClN_6$: C, 68.73; H, 3.92; N, 19.24. Found: C, 68.72; H, 3.94; N, 19.27.

5-amino-3'-(4-iodophenyl)-1,1'-diphenyl-1H,1'H-[3,4'-bipyrazole]-4-carbonitrile (6h)

Yellow solid, m.p.: 157–159°C, FT-IR (KBr, cm^{-1}): 3377 and 3309 (N-H stretch), 3104 and 2998 (CH stretch), 2185 (C≡N stretch), 1593 (C=N stretch), 1550 and 1512 (C=C stretch) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 6.78 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.11 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.27 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.39 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.58 (t, *J* = 7.80 Hz, 2H, Ar-H), 7.72-7.83 (m, 3H, Ar-H), 7.92-7.98 (m, 3H, Ar-H), 8.08 (s, 1H, Ar-H), 8.78 (s, 1H, NH), 10.09 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 111.9, 113.7, 118.5,119.3, 119.9, 121.3, 128.5, 128.9, 129.3, 129.7, 130.4,131.4, 133.0, 133.5, 135.8, 138.5, 145.4, 149.8 ppm. Anal. calcd for $C_{25}H_{17}IN_6$: C, 56.83; H, 3.24; N, 15.91. Found: C, 56.85; H, 3.21; N, 15.89.

5-amino-3'-(3-bromophenyl)-1,1'-diphenyl-1H,1'H-[3,4'-bipyrazole]-4-carbonitrile (6i)

Yellow solid, m.p.: 141–143°C, FT-IR (KBr, cm^{-1}): 3326 and 3421 (N-H stretch), 2963 and 3105 (C-H stretch), 1987 (C≡N stretch), 1573 (C=N stretch), 1485 (C=C stretch) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 6.97 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.06 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.33-7.55 (m, 5H, Ar-H), 7.68 (t, *J* = 8.2 Hz, 1H, Ar-H), 7.84-7.92 (m, 3H, Ar-H), 8.18 (d, *J* = 7.9 Hz, 1H, Ar-H), 8.31 (d, *J* = 7.9 Hz, 1H, Ar-H), 8.42 (s, 1H, Ar-H), 8.78 (s, 1H, NH), 10.21 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 112.6, 118.3, 119.0, 119.6, 121.3, 123.2, 123.9, 125.6, 127.6, 128.3, 129.2, 129.7, 130.1, 130.3, 131.3, 133.1, 133.4, 138.5, 142.8, 148.6, 149.6 ppm. Anal. calcd for $C_{25}H_{17}BrN_6$: C, 62.38; H, 3.56; N, 17.46. Found: C, 62.41; H, 3.53; N, 17.48.

5-amino-3'-(4-bromophenyl)-1,1'-diphenyl-1H,1'H-[3,4'-bipyrazole]-4-carbonitrile (6j)

Yellow solid, m.p.: 153–255°C, FT-IR (KBr, cm^{-1}): 3439 and 3316 (N-H stretch), 3050 and 2961 (CH stretch), 2200 (C≡N stretch), 1599 (C=N stretch), 1539 and 1499 (C=C stretch) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm): 6.75 (t, J = 7.2 Hz, 1H, Ar-H), 7.05 (d, J = 8.1 Hz, 2H, Ar-H), 7.22 (t, J = 7.5 Hz, 2H, Ar-H), 7.37 (t, J = 6.6 Hz, 1H, Ar-H), 7.55 (t, J = 7.5 Hz, 2H, Ar-H), 7.74-7.79 (m, 4H, Ar-H), 7.99 (s, 2H, Ar-H), 8.02 (s, 1H, Ar-H), 8.92 (s, 1H, NH), 10.25 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm): 112.3, 118.9, 119.0, 122.1, 127.1, 127.2, 129.4, 129.5, 130.0, 130.8, 132.0, 132.5, 139.6, 145.9, 149.5 ppm. Anal. calcd for $C_{25}H_{17}BrN_6$: C, 62.38; H, 3.56; N, 17.46. Found: C, 62.40; H, 3.54; N, 17.48.