

Electronic Supplementary Information

An efficient and chemoselective synthesis of N-substituted 2-aminopyridines via microwave-assisted multicomponent reaction

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Characterization data of compounds **4** and **5** are as follows:

2-((S)-1-phenylethylamino)-4-(4-chlorophenyl)-6-(4-methoxyphenyl)pyridine-3-carbonitrile (4a)

IR (KBr, ν , cm^{-1}): 3342, 3026, 2973, 2207, 1597, 1488, 1368, 1238, 1093, 1015, 821, 698.

^1H NMR (DMSO- d_6) (δ , ppm): 8.04 (d, $J = 8.8$ Hz, 2H, ArH), 7.68 (d, $J = 8.8$ Hz, 2H, ArH), 7.63 (d, $J = 8.8$ Hz, 2H, ArH), 7.53 (d, $J = 7.6$ Hz, 2H, ArH), 7.40 (d, $J = 7.2$ Hz, 1H, ArH), 7.33 (t, $J = 7.6$ Hz, 2H, ArH), 7.23 (s, 1H, ArH), 7.20 (t, $J = 7.2$ Hz, 1H, NH), 7.01 (d, $J = 8.8$ Hz, 2H, ArH), 5.47–5.43 (m, 1H, CH), 3.82 (s, 3H, OCH₃), 1.59 (d, $J = 6.8$ Hz, 3H, CH₃).

Anal. calcd. for C₂₇H₂₂ClN₃O; C, 73.71; H, 5.04; N, 9.55; found C, 73.54; H, 5.18; N, 9.69.

2-((S)-1-phenylethylamino)-4-(4-bromophenyl)-6-(4-methoxyphenyl)pyridine-3-carbonitrile (4b)

IR (KBr, ν , cm^{-1}): 3352, 3026, 2971, 2831, 2208, 1576, 1485, 1368, 1239, 1036, 1011, 821, 698.;

^1H NMR (DMSO- d_6) (δ , ppm): 8.04 (d, $J = 8.8$ Hz, 2H, ArH), 7.77 (d, $J = 8.4$ Hz, 2H, ArH), 7.61 (d, $J = 8.4$ Hz, 2H, ArH), 7.53 (d, $J = 7.2$ Hz, 2H, ArH), 7.41 (d, $J = 7.6$ Hz, 1H, ArH), 7.33 (t, $J = 7.6$ Hz, 2H, ArH), 7.22 (s, 1H, ArH), 7.20 (t, $J = 7.2$ Hz, 1H, NH), 7.01 (d, $J = 8.8$ Hz, 2H, ArH), 5.51–5.47 (m, 1H, CH), 3.82 (s, 3H, OCH₃), 1.59 (d, $J = 7.6$ Hz, 3H, CH₃).

Anal. calcd. for C₂₇H₂₂BrN₃O, C, 66.95; H, 4.58; N, 8.67; found C, 66.74; H, 4.68; N, 8.57.

2-((S)-1-phenylethylamino)-4,6-bis(4-methoxyphenyl)pyridine-3-carbonitrile (4c)

IR (KBr, ν , cm^{-1}): 3376, 3068, 3029, 2931, 2836, 2208, 1607, 1498, 1439, 1291, 1235, 1019, 829, 698, 628.

^1H NMR (DMSO- d_6) (δ , ppm): 8.03 (d, $J = 8.8$ Hz, 2H, ArH), 7.63 (d, $J = 8.4$ Hz, 2H, ArH), 7.53 (d, $J = 7.6$ Hz, 2H, ArH), 7.33 (t, $J = 7.6$ Hz, 2H, ArH), 7.41 (d, $J = 7.6$ Hz, 1H, ArH), 7.20 (t, $J = 7.2$ Hz, 1H, NH), 7.19 (s, 1H, ArH), 7.10 (d, $J = 8.8$ Hz, 2H, ArH), 7.00 (d, $J = 8.8$ Hz, 2H, ArH), 5.46–5.41 (m, 1H, CH), 3.84 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 1.59 (d, $J = 6.8$ Hz, 3H, CH₃).

Anal. calcd. for C₂₈H₂₅N₃O₂, C, 77.22; H, 5.79; N, 9.65; found C, 77.46; H, 5.87; N, 9.84.

2-((S)-1-phenylethylamino)-6-(4-chlorophenyl)-4-(4-methoxyphenyl)pyridine-3-carbonitrile (4d)

IR (KBr, ν , cm^{-1}): 3334, 3028, 2971, 2931, 2208, 1603, 1578, 1501, 1451, 1296, 1256, 1155, 1030, 825, 766, 702.

^1H NMR (DMSO- d_6) (δ , ppm): 8.12 (dd, $J_1 = 8.8$ Hz, $J_2 = 5.6$ Hz, 2H, ArH), 7.65 (d, $J = 8.4$ Hz, 2H, ArH), 7.53 (d, $J = 8.0$ Hz, 2H, ArH), 7.37–7.29 (m, 5H, ArH), 7.26 (s, 1H, ArH), 7.20 (t, $J = 7.2$ Hz, 1H, NH), 7.11 (d, $J = 8.8$ Hz, 2H, ArH), 5.45–5.41 (m, 1H, CH), 3.84 (s, 3H, OCH₃), 1.59 (d, $J = 7.6$ Hz, 3H, CH₃).

Anal. calcd. for C₂₇H₂₂ClN₃O, C, 73.71; H, 5.04; N, 9.55; found C, 73.94; H, 4.91; N, 9.71.

2-((R)-1-phenylethylamino)-6-(4-chlorophenyl)-4-(4-methoxyphenyl)pyridine-3-carbonitrile (4e)

IR (KBr, ν , cm^{-1}): 3338, 2998, 2896, 2210, 1601, 1535, 1494, 1306, 1156, 1038, 826.

^1H NMR (DMSO- d_6) (δ , ppm): 8.13 (d, $J = 8.8$ Hz, 2H, ArH), 7.68 (d, $J = 8.4$ Hz, 2H, ArH), 7.51 (d, $J = 8.4$ Hz, 2H, ArH), 7.37–7.33 (m, 3H, ArH), 7.30 (d, $J = 8.8$ Hz, 2H, ArH), 7.27 (s, 1H, ArH), 7.19 (t, $J = 7.6$ Hz, 1H, NH), 7.11 (d, $J = 8.8$ Hz, 2H, ArH), 5.44–5.39 (m, 1H, CH), 3.83 (s, 3H, OCH₃), 1.60 (d, $J = 7.6$ Hz, 3H, CH₃).

Anal. calcd. for C₂₇H₂₂ClN₃O, C, 73.71; H, 5.04; N, 9.55; found C, 73.92; H, 4.89; N, 9.68.

2-((R)-1-phenylethylamino)-4-(4-chlorophenyl)-6-(4-methoxyphenyl)pyridine-3-carbonitrile (4f)

IR (KBr, ν , cm^{-1}): 3341, 3026, 3029, 2932, 2207, 1604, 1578, 1488, 1406, 1260, 1169, 821, 698.

^1H NMR (DMSO- d_6) (δ , ppm): 8.06 (d, $J = 8.8$ Hz, 2H, ArH), 7.68 (d, $J = 8.8$ Hz, 2H, ArH), 7.63 (d, $J = 7.6$ Hz, 2H, ArH), 7.53 (d, $J = 7.6$ Hz, 2H, ArH), 7.35–7.31 (m, 3H, Ar), 7.23 (s, 1H, ArH), 7.20 (t, $J = 7.2$ Hz, 1H, NH), 7.03 (d, $J = 8.8$ Hz, 2H, ArH), 5.50–5.45 (m, 1H, CH), 3.82 (s, 3H, OCH₃), 1.60 (d, $J = 6.8$ Hz, 3H, CH₃).

Anal. calcd. for $C_{27}H_{22}ClN_3O$, C, 73.71; H, 5.04; N, 9.55; found C, 73.89; H, 4.94; N, 9.75.

4-(4-chlorophenyl)-2-(cyclohexylamino)-6-(4-methoxyphenyl)pyridine-3-carbonitrile (4g)

IR (KBr, ν , cm^{-1}): 3378, 2932, 2853, 2209, 1578, 1511, 1486, 1366, 1243, 1089, 823, 778, 668.

1H NMR (DMSO- d_6) (δ , ppm): 8.14 (d, $J = 8.8$ Hz, 2H, ArH), 7.69 (d, $J = 8.4$ Hz, 2H, ArH), 7.63 (d, $J = 8.4$ Hz, 2H, ArH), 7.23 (s, 1H, ArH), 7.06 (d, $J = 8.8$ Hz, 2H, ArH), 6.62 (d, $J = 7.6$ Hz, 1H, NH), 4.19–4.12 (m, 1H, CH), 3.83 (s, 3H, OCH₃), 1.95 (d, $J = 10.4$ Hz, 2H, CH₂), 1.78 (d, $J = 12.4$ Hz, 2H, CH₂), 1.63–1.20 (m, 6H, CH₂).

Anal. calcd. for $C_{25}H_{24}ClN_3O$, C, 71.85; H, 5.79; N, 10.05; found C, 71.99; H, 5.53; N, 10.21.

4-(4-bromophenyl)-2-(cyclohexylamino)-6-(4-fluorophenyl)pyridine-3-carbonitrile (4h)

IR (KBr, ν , cm^{-1}): 3330, 2926, 2853, 2211, 1599, 1573, 1507, 1488, 1361, 1228, 1155, 1074, 819.

1H NMR (DMSO- d_6) (δ , ppm): 8.22 (dd, $J_1 = 8.8$ Hz, $J_2 = 5.6$ Hz, 2H, ArH), 7.77 (d, $J = 8.8$ Hz, 2H, ArH), 7.63 (d, $J = 8.8$ Hz, 2H, ArH), 7.35 (t, $J = 8.8$ Hz, 2H, ArH), 7.30 (s, 1H, ArH), 6.71 (d, $J = 7.6$ Hz, 1H, NH), 4.16–4.09 (m, 1H, CH), 3.83 (s, 3H, OCH₃), 1.97 (d, $J = 11.2$ Hz, 2H, CH₂), 1.77 (d, $J = 12.4$ Hz, 2H, CH₂), 1.63–1.34 (m, 5H, CH₂), 1.20–1.08 (m, 1H, CH₂).

Anal. calcd. for $C_{24}H_{21}BrFN_3$, C, 64.01; H, 4.70; N, 9.33; found C, 64.23; H, 4.56; N, 9.58

6-(4-chlorophenyl)-2-(cyclohexylamino)-4-(4-methoxyphenyl)pyridine-3-carbonitrile (4i)

IR (KBr, ν , cm^{-1}): 3369, 2932, 2852, 2201, 1584, 1510, 1488, 1252, 1235, 1182, 1011, 824.

1H NMR (DMSO- d_6) (δ , ppm): 8.19 (d, $J = 8.8$ Hz, 2H, ArH), 7.66 (d, $J = 8.8$ Hz, 2H, ArH), 7.58 (d, $J = 8.8$ Hz, 2H, ArH), 7.29 (s, 1H, ArH), 7.12 (d, $J = 8.8$ Hz, 2H, ArH), 6.61 (d, $J = 7.6$ Hz, 1H, NH), 4.18–4.08 (m, 1H, CH), 3.85 (s, 3H, OCH₃), 1.97 (d, $J = 10.4$ Hz, 2H, CH₂), 1.77 (d, $J = 12.4$ Hz, 2H, CH₂), 1.62–1.37 (m, 5H, CH₂), 1.22–1.09 (m, 1H, CH₂).

Anal. calcd. for $C_{25}H_{24}ClN_3O$, C, 71.85; H, 5.79; Cl, 8.48; N, 10.05; found C, 72.03; H, 5.61; N, 10.26.

4-(4-bromophenyl)-6-(4-methoxyphenyl)-2-(phenylamino)pyridine-3-carbonitrile (4j)

IR (KBr, ν , cm^{-1}): 3324, 2936, 2215, 1607, 1579, 1540, 1496, 1238, 1009, 821.

1H NMR (DMSO- d_6) (δ , ppm): 9.17 (s, 1H, NH), 8.11 (d, $J = 8.8$ Hz, 2H, ArH), 7.81 (d, $J = 8.8$ Hz, 2H, ArH), 7.69–7.66 (m, 4H, ArH), 7.53 (s, 1H, ArH), 7.38 (t, $J = 7.6$ Hz, 2H, ArH), 7.07–7.04 (m, 3H, ArH), 3.83 (s, 3H, OCH₃).

Anal. calcd. for $C_{25}H_{18}BrN_3O$, C, 65.80; H, 3.98; N, 9.21; found C, 65.57; H, 4.12; N, 9.35.

4,6-bis(4-methoxyphenyl)-2-(phenylamino)pyridine-3-carbonitrile (4k)

IR (KBr, ν , cm^{-1}): 3323, 2933, 2215, 1606, 1582, 1498, 1237, 1171, 1031, 825.

1H NMR (DMSO- d_6) (δ , ppm): 9.07 (s, 1H, NH), 8.11 (d, $J = 8.8$ Hz, 2H, ArH), 7.71 (d, $J = 8.8$ Hz, 2H, ArH), 7.68 (d, $J = 8.8$ Hz, 2H, ArH), 7.49 (s, 1H, ArH), 7.35 (t, $J = 8.0$ Hz, 2H, ArH), 7.15 (d, $J = 8.8$ Hz, 2H, ArH), 7.07–7.04 (m, 3H, ArH), 3.87 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃).

Anal. calcd. for $C_{26}H_{21}N_3O_2$, C, 76.64; H, 5.19; N, 10.31; found C, 76.38; H, 5.47; N, 10.49.

6-(4-chlorophenyl)-4-(4-methoxyphenyl)-2-(phenylamino)pyridine-3-carbonitrile (4l)

IR (KBr, ν , cm^{-1}): 3329, 3046, 3004, 2953, 2214, 1608, 1541, 1491, 1367, 1253, 1090, 1010, 823, 742.

1H NMR (DMSO- d_6) (δ , ppm): 9.18 (s, 1H, NH), 8.16 (d, $J = 8.8$ Hz, 2H, ArH), 7.73 (d, $J = 8.8$ Hz, 2H, ArH), 7.67 (d, $J = 8.8$ Hz, 2H, ArH), 7.57 (s, 1H, ArH), 7.57 (d, $J = 8.8$ Hz, 2H, ArH), 7.37 (t, $J = 7.8$ Hz, 2H, ArH), 7.16 (d, $J = 8.8$ Hz, 2H, ArH), 7.08 (t, $J = 7.8$ Hz, 1H, ArH), 3.87 (s, 3H, OCH₃).

Anal. calcd. for $C_{25}H_{18}ClN_3O$, C, 72.90; H, 4.40; N, 10.20; found C, 73.18; H, 4.21; N, 10.34.

6-(2,4-dichlorophenyl)-4-(4-chlorophenyl)-2-(phenylamino)pyridine-3-carbonitrile (4m)

IR (KBr, ν , cm^{-1}): 3350, 2968, 2220, 1616, 1573, 1543, 1496, 1377, 1097, 818, 746.

1H NMR (DMSO- d_6) (δ , ppm): 9.31 (s, 1H, NH), 7.77 (d, $J = 8.4$ Hz, 2H, ArH), 7.74 (s, 1H, ArH), 7.69–7.68 (m, 3H, ArH), 7.63 (d, $J = 8.4$ Hz, 2H, ArH), 7.57 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H, ArH), 7.30 (t, $J = 7.8$ Hz, 2H, ArH), 7.26 (s, 1H, ArH), 7.04 (t, $J = 7.8$ Hz, 1H, ArH).

Anal. calcd. for $C_{24}H_{14}Cl_3N_3$, C, 63.95; H, 3.13; N, 9.32; found C, 63.74; H, 3.01; N, 9.54.

4-(4-methoxyphenyl)-2-(phenylamino)-6-(pyridin-2-yl)pyridine-3-carbonitrile (4n)

IR (KBr, ν , cm^{-1}): 3321, 3055, 2836, 2209, 1606, 1579, 1497, 1248, 1180, 835, 740.

1H NMR (DMSO- d_6) (δ , ppm): 9.23 (s, 1H, NH), 8.71 (d, $J = 4.4$ Hz, 1H, Py-H), 8.20 (d, $J = 8.0$ Hz, 1H, Py-H), 8.01–7.97 (m, 1H, Py-H), 7.94 (s, 1H, Py-H), 7.69 (d, $J = 8.4$ Hz, 4H, ArH), 7.53–7.50 (m, 1H, Py-H), 7.40 (t, $J = 7.8$ Hz, 2H, ArH), 7.17 (d, $J = 8.4$ Hz, 2H, ArH), 7.10 (t, $J = 7.8$ Hz, 1H, ArH), 3.87 (s, 3H, OCH₃).

Anal. calcd. for $C_{24}H_{18}N_4O$, C, 76.17; H, 4.79; N, 14.81; found C, 76.01; H, 4.98; N, 14.68.

4-(4-chlorophenyl)-2-(phenylamino)-6-(pyridin-2-yl)pyridine-3-carbonitrile (4o)

IR (KBr, ν , cm^{-1}): 3322, 3042, 2211, 1606, 1578, 1440, 1249, 1090, 794, 743.

¹H NMR (DMSO-*d*₆) (δ , ppm): 9.30 (s, 1H, NH), 8.72 (d, J = 4.0 Hz, 1H, Py-H), 8.20 (d, J = 8.0 Hz, 1H, Py-H), 8.02–7.98 (m, 1H, Py-H), 7.93 (s, 1H, Py-H), 7.75 (d, J = 8.4 Hz, 2H, ArH), 7.70–7.68 (m, 4H, ArH), 7.54–7.51 (m, 1H, Py-H), 7.41 (t, J = 7.8 Hz, 2H, ArH), 7.12 (t, J = 7.8 Hz, 1H, ArH).

Anal. calcd. for C₂₃H₁₅ClN₄, C, 72.16; H, 3.95; N, 14.63; found C, 72.51; H, 3.67; N, 14.48.

2-(*p*-tolylamino)-4-(4-chlorophenyl)-6-(4-methoxyphenyl)pyridine-3-carbonitrile (4p)

IR (KBr, ν , cm⁻¹): 3330, 2926, 2853, 2211, 1599, 1573, 1507, 1488, 1361, 1228, 1155, 1074, 819.

¹H NMR (DMSO-*d*₆) (δ , ppm): 9.06 (s, 1H, NH), 8.10 (d, J = 9.2 Hz, 2H, ArH), 7.75 (d, J = 8.8 Hz, 2H, ArH), 7.67 (d, J = 8.8 Hz, 2H, ArH), 7.55 (d, J = 8.4 Hz, 2H, ArH), 7.49 (s, 1H, ArH), 7.18 (d, J = 8.4 Hz, 2H, ArH), 7.05 (d, J = 9.2 Hz, 2H, ArH), 3.83 (s, 3H, OCH₃), 2.32 (s, 3H, CH₃).

Anal. calcd. for C₂₆H₂₀ClN₃O, C, 73.32; H, 4.73; N, 9.87; found C, 73.14; H, 4.55; N, 9.69.

2-(*p*-tolylamino)-4-(4-bromophenyl)-6-(4-methoxyphenyl)pyridine-3-carbonitrile (4q)

IR (KBr, ν , cm⁻¹): 3329, 3016, 2913, 2837, 2212, 1609, 1577, 1510, 1448, 1239, 1009, 818.

¹H NMR (DMSO-*d*₆) (δ , ppm): 9.06 (s, 1H, NH), 8.10 (d, J = 8.8 Hz, 2H, ArH), 7.81 (d, J = 8.4 Hz, 2H, ArH), 7.67 (d, J = 8.4 Hz, 2H, ArH), 7.55 (d, J = 8.4 Hz, 2H, ArH), 7.49 (s, 1H, ArH), 7.18 (d, J = 8.4 Hz, 2H, ArH), 7.04 (d, J = 8.4 Hz, 2H, ArH), 3.82 (s, 3H, OCH₃), 2.32 (s, 3H, CH₃).

Anal. calcd. for C₂₆H₂₀BrN₃O, C, 66.39; H, 4.29; N, 8.93; found C, 66.26; H, 4.49; N, 8.76

2-(*p*-tolylamino)-4,6-bis(4-methoxyphenyl)pyridine-3-carbonitrile (4r)

IR (KBr, ν , cm⁻¹): 3321, 3001, 2932, 2836, 2215, 1606, 1540, 1370, 1251, 1170, 825.

¹H NMR (DMSO-*d*₆) (δ , ppm): 8.96 (s, 1H, NH), 8.10 (d, J = 8.8 Hz, 2H, ArH), 7.70 (d, J = 8.8 Hz, 2H, ArH), 7.56 (d, J = 8.4 Hz, 2H, ArH), 7.45 (s, 1H, ArH), 7.17 (d, J = 8.4 Hz, 2H, ArH), 7.14 (d, J = 8.8 Hz, 2H, ArH), 7.04 (d, J = 8.4 Hz, 2H, ArH), 3.86 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 2.31 (s, 3H, CH₃).

Anal. calcd. for C₂₇H₂₃N₃O₂, C, 76.94; H, 5.50; N, 9.97; found C, 77.12; H, 5.67; N, 9.79.

2-(*p*-tolylamino)-6-(4-chlorophenyl)-4-(4-methoxyphenyl)pyridine-3-carbonitrile (4s)

IR (KBr, ν , cm⁻¹): 3324, 2954, 2216, 1608, 1511, 1491, 1419, 1254, 1012, 821.

¹H NMR (DMSO-*d*₆) (δ , ppm): 9.07 (s, 1H, NH), 8.15 (d, J = 8.8 Hz, 2H, ArH), 7.72 (d, J = 8.4 Hz, 2H, ArH), 7.57 (d, J = 8.8 Hz, 2H, ArH), 7.55 (s, 1H, ArH), 7.54 (d, J = 8.4 Hz, 2H, ArH), 7.16 (t, J = 8.6 Hz, 4H, ArH), 3.87 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 2.31 (s, 3H, CH₃).

Anal. calcd. for C₂₆H₂₀ClN₃O, C, 73.32; H, 4.73; N, 9.87; found C, 73.59; H, 4.56; N, 9.59.

2-(*p*-tolylamino)-6-(4-chlorophenyl)-4-(thiophen-2-yl)pyridine-3-carbonitrile (4t)

IR (KBr, ν , cm⁻¹): 3312, 3076, 2915, 2219, 1608, 1575, 1509, 1329, 1170, 1032, 819, 719.

¹H NMR (DMSO-*d*₆) (δ , ppm): 9.03 (s, 1H, NH), 8.09 (d, J = 8.8 Hz, 2H, ArH), 7.93–7.90 (m, 2H, thiophenyl-H), 7.54 (d, J = 8.8 Hz, 2H, ArH), 7.53 (s, 1H, ArH), 7.46–7.21 (m, 1H, thiophenyl-H), 7.18 (d, J = 8.4 Hz, 2H, ArH), 7.06 (d, J = 8.4 Hz, 2H, ArH), 3.83 (s, 3H, OCH₃), 2.32 (s, 3H, CH₃).

Anal. calcd. for C₂₃H₁₆ClN₃S, C, 68.73; H, 4.01; N, 10.46; S, 7.98; found C, 68.95; H, 4.21; N, 10.29; S, 7.84

2-(*p*-tolylamino)-4-(4-methoxyphenyl)-6-(pyridin-2-yl)pyridine-3-carbonitrile (4x)

IR (KBr, ν , cm⁻¹): 3327, 2915, 2217, 1608, 1578, 1510, 1247, 1031, 836.

¹H NMR (DMSO-*d*₆) (δ , ppm): 9.12 (s, 1H, NH), 8.71 (d, J = 4.0 Hz, 1H, Py-H), 8.19 (d, J = 8.0 Hz, 1H, Py-H), 8.01–7.97 (m, 1H, Py-H), 7.90 (s, 1H, Py-H), 7.69 (d, J = 8.4 Hz, 2H, ArH), 7.57 (d, J = 8.4 Hz, 2H, ArH), 7.52–7.49 (m, 1H, Py-H), 7.20 (d, J = 8.4 Hz, 2H, ArH), 7.16 (d, J = 8.4 Hz, 2H, ArH), 3.87 (s, 3H, OCH₃), 2.32 (s, 3H, CH₃).

Anal. calcd. for C₂₅H₂₀N₄O, C, 76.51; H, 5.14; N, 14.28; found C, 76.69; H, 5.03; N, 14.35.

2-(*p*-tolylamino)-4-(4-chlorophenyl)-6-(pyridin-2-yl)pyridine-3-carbonitrile (4y)

IR (KBr, ν , cm⁻¹): 3323, 2948, 2218, 1611, 1578, 1545, 1411, 1249, 1091, 794.

¹H NMR (DMSO-*d*₆) (δ , ppm): 9.20 (s, 1H, NH), 8.71 (d, J = 4.0 Hz, 1H, Py-H), 8.19 (d, J = 7.6 Hz, 1H, Py-H), 8.02–7.98 (m, 1H, Py-H), 7.90 (s, 1H, Py-H), 7.75 (d, J = 8.4 Hz, 2H, ArH), 7.68 (d, J = 8.0 Hz, 2H, ArH), 7.57 (d, J = 8.0 Hz, 2H, ArH), 7.53–7.50 (m, 1H, Py-H), 7.21 (d, J = 8.4 Hz, 2H, ArH), 2.32 (s, 3H, CH₃).

Anal. calcd. for C₂₄H₁₇ClN₄, C, 72.63; H, 4.32; N, 14.12; found C, 72.49; H, 4.47; N, 14.01.

3-(4-chlorophenyl)-5-(4-methoxyphenyl)-2,6-dicyanoanilines (5a)

IR (KBr, ν , cm⁻¹): 3466, 3363, 3241, 2986, 2216, 1645, 1578, 1562, 1464, 1297, 1180, 1093, 1030, 822.

¹H NMR (DMSO-*d*₆) (δ , ppm): 7.68 (d, J = 8.4 Hz, 2H, ArH), 7.62–7.60 (m, 4H, ArH), 7.09 (d, J = 8.4 Hz, 2H, ArH), 6.84 (s, 2H, NH₂), 6.79 (s, 1H, ArH), 3.83 (s, 3H, OCH₃).

Anal. calcd. for C₂₁H₁₄ClN₃O, C, 70.10; H, 3.92; N, 11.68; found C, 70.34; H, 3.71; N, 11.61.

3-(4-bromophenyl)-5-(4-methoxyphenyl)-2,6-dicyanoanilines (5b)

IR (KBr, ν , cm⁻¹): 3458, 3361, 2214, 1638, 1559, 1518, 1458, 1242, 1029, 820;

¹H NMR (DMSO-*d*₆) (δ, ppm): 7.74 (d, *J* = 8.4 Hz, 2H, ArH), 7.62–7.59 (m, 4H, ArH), 7.09 (d, *J* = 8.4 Hz, 2H, ArH), 6.85 (s, 2H, NH₂), 6.79 (s, 1H, ArH), 3.83 (s, 3H, OCH₃).

Anal. calcd. for C₂₁H₁₄BrN₃O, C, 62.39; H, 3.49; N, 10.39; found C, 62.57; H, 3.34; N, 10.26

3-(4-bromophenyl)-5-(4-fluorophenyl)-2,6-dicyanoanilines (5c)

IR (KBr, ν, cm⁻¹): 3463, 3359, 3244, 2218, 1646, 1576, 1515, 1240, 1162, 1010, 823.

¹H NMR (DMSO-*d*₆) (δ, ppm): 7.75 (d, *J* = 8.4 Hz, 2H, ArH), 7.73–7.69 (m, 2H, ArH), 7.61 (d, *J* = 8.4 Hz, 2H, ArH), 7.38 (t, *J* = 8.8 Hz, 2H, ArH), 6.92 (s, 2H, NH₂), 6.82 (s, 1H, ArH).

Anal. calcd. for C₂₀H₁₁BrFN₃, C, 61.24; H, 2.83; N, 10.71; found C, 61.51; H, 2.92; N, 10.83.

3-(4-chlorophenyl)-5-(4-methoxyphenyl)-2,6-dicyanoanilines (5d)

IR (KBr, ν, cm⁻¹): 3468, 3364, 3241, 2216, 1644, 1578, 1548, 1464, 1286, 1259, 1181, 1014, 822.

¹H NMR (DMSO-*d*₆) (δ, ppm): 7.68 (d, *J* = 8.4 Hz, 2H, ArH), 7.63–7.60 (m, 4H, ArH), 7.09 (d, *J* = 8.4 Hz, 2H, ArH), 6.84 (s, 2H, NH₂), 6.79 (s, 1H, ArH), 3.83 (s, 3H, OCH₃).

Anal. calcd. for C₂₁H₁₄ClN₃O, C, 70.10; H, 3.92; N, 11.68; found C, 70.36; H, 4.01; N, 11.79.

3-(4-chlorophenyl)-5-phenyl-2,6-dicyanoanilines (5e)

IR (KBr, ν, cm⁻¹): 3467, 3365, 3241, 2215, 1643, 1499, 1286, 1095, 829, 696.

¹H NMR (DMSO-*d*₆) (δ, ppm): 7.69 (d, *J* = 8.4 Hz, 2H, ArH), 7.66–7.63 (m, 2H, ArH), 7.61 (d, *J* = 8.4 Hz, 2H, ArH), 7.55–7.53 (m, 3H, ArH), 6.87 (s, 2H, NH₂), 6.82 (s, 1H, ArH).

Anal. calcd. for C₂₀H₁₂ClN₃, C, 72.84; H, 3.67; N, 12.74; found C, 72.59; H, 3.79; N, 12.58.

3-(2,4-dichlorophenyl)-5-(4-methoxyphenyl)-2,6-dicyanoanilines (5f)

IR (KBr, ν, cm⁻¹): 3468, 3390, 3236, 3089, 3006, 2838, 2210, 1624, 1576, 1461, 1248, 1031, 830.

¹H NMR (DMSO-*d*₆) (δ, ppm): 8.27 (d, *J* = 8.8 Hz, 2H, ArH), 8.23 (s, 1H, ArH), 7.91–7.86 (m, 2H, ArH), 7.11 (d, *J* = 8.8 Hz, 2H, ArH), 6.94 (s, 2H, NH₂), 6.82 (s, 1H, ArH), 3.83 (s, 3H, OCH₃).

Anal. calcd. for C₂₁H₁₃Cl₂N₃O, C, 63.98; H, 3.32; N, 10.66; found C, 64.24; H, 3.41; N, 10.74.

3-(4-methoxyphenyl)-5-(3-nitrophenyl)-2,6-dicyanoanilines (5g)

IR (KBr, ν, cm⁻¹): 3464, 3354, 3243, 2215, 1652, 1609, 1532, 1347, 1253, 1177, 806.

¹H NMR (DMSO-*d*₆) (δ, ppm): 8.48 (s, 1H, ArH), 8.37 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, 1H, ArH), 8.13 (d, *J* = 8.0 Hz, 1H, ArH), 7.84 (t, *J* = 8.0 Hz, 1H, ArH), 7.64 (d, *J* = 8.4 Hz, 2H, ArH), 7.10 (d, *J* = 8.4 Hz, 2H, ArH), 6.92 (s, 2H, NH₂), 6.91 (s, 1H, ArH), 3.84 (s, 3H, OCH₃).

Anal. calcd. for C₂₁H₁₄N₄O₃, C, 68.10; H, 3.81; N, 15.13; found C, 68.41; H, 3.72; N, 15.04.

2-(1-(4-bromophenyl)-3-(4-methoxyphenyl)-3-oxopropyl)malononitrile (6b)

Mp: 123–124 °C; IR (KBr, ν, cm⁻¹): 3014, 2967, 2905, 2250, 1671, 1602, 1574, 1488, 1369, 1223, 1075, 836, 810.

¹H NMR (DMSO-*d*₆) (δ, ppm): 7.96 (d, *J* = 8.8 Hz, 2H, ArH), 7.59 (d, *J* = 8.8 Hz, 2H, ArH), 7.36 (d, *J* = 8.8 Hz, 2H, ArH), 6.98 (d, *J* = 8.8 Hz, 2H, ArH), 4.69 (d, *J* = 5.2 Hz, 1H, CH), 3.93–3.96 (m, 1H, ArH), 3.88 (s, 3H, OCH₃), 3.53–3.73 (m, 2H, CH₂).

Anal. calcd. for C₁₉H₁₅BrN₂O₂, C, 59.55; H, 3.95; N, 7.31; found C, 59.68; H, 3.79; N, 7.46.