Supplementary Information

An efficient one-pot four-component synthesis of 1*H*-pyrazolo[1,2-*b*] phthalazine-5,10-dione derivatives catalyzed by proline

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1. General information

All reactions were carried out under argon atmosphere using oven-dried reaction vessels. Unless otherwise noted, all commercially available compounds were used as purchased without further purification. All aldehydes were purified either by distillation or washing with $NaHCO_3$ after dissolving in ether before use. ^{1}H NMR spectra were recorded as solutions in DMSO-d_6. Chemical shifts are expressed in parts per million (ppm, δ) with reference to the residual chloroform in DMSO-d_6 (δ = 3.35 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals in ^{1}H NMR include: s = singlet, bs = broad

singlet, d = doublet, t = triplet, m = multiplet and dd = doublet of doublets. ^{13}C NMR spectra were recorded in DMSO-d_6 solution with complete proton decoupling. High-Resolution Mass Spectra (HRMS) were performed with a Qtof Micro YA263 spectrometer. IR (infrared spectroscopy) was recorded in an FT-IR spectrometer; the IR spectra of solid compounds were recorded in KBr pallet. The reactions were monitor routinely with precoated silica gel on aluminum plates (Merck), which were analyzed with $KMnO_4$ solution. Solvents, reagents and chemicals were purchased from Aldrich, Merck, SRL, Spectrochem and Process Chemicals.

2. General procedure for the Synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones (5)

A mixture of phthalimide (1.0 mmol) and hydrazine hydrate (1.0 mmol) in ethanol (1.0 mL) was stirred under reflux for 1 h. Then aromatic aldehyde (1.0 mmol), malononitrile, or ethyl cyanoacetate (1.0 mmol) and proline (10 mol %) in mixed solvent of ethanol and water (2.0 mL, ratio 1:1) were added, and the mixture was refluxed for a specified time. Progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. The residue precipitated during the process was filtered, and the filter cake was washed with ethanol and residue was recrystallized from ethanol to afford the pure product **5**.

3. Spectral data of the compounds

3-Amino-5,10-dioxo-1-phenyl-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5a)

Yellow powder solid, Yield: 90 %, M.p.: 275-277 °C; IR (KBr): 3360, 2198, 1651, 1567, 1439, 1384, 1248, 1167, 1028, 955, 784, 703, 691 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.11 (s, 1H), 7.28-7.37 (m, 3H), 7.43-7.45 (m, 2H), 7.94-7.97 (m, 2H), 8.05-8.09 (m, 3H), 8.23-8.26 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 61.9, 63.5, 116.5, 127.2, 127.3, 127.8, 128.8, 129.0, 129.1,

129.3, 134.2, 135.1, 138.9, 151.1, 154.1, 157.1; HRMS (ES^+): calcd for $[C_{18}H_{12}N_4O_2]Na^+$: 339.0853; found: 339.0856.

3-amino-1-(4-cyanophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5b)

Yellow powder solid, Yield: 96 %, M.p.: 275-277 °C; IR (KBr): 3363, 2202, 1650, 1573, 1438, 1376, 1250, 1176, 1031, 945, 776, 701, 695 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.21 (s, 1H), 7.70 (d, J = 8 Hz, 2H), 7.84 (d, J = 8 Hz, 2H), 7.96-7.98 (m, 2H), 8.05-8.09 (m, 1H), 8.14 (bs, 2H), 8.24-8.26 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 60.9, 62.8, 111.5, 116.3, 119.1, 127.2, 127.8, 128.2, 128.9, 129.5, 133.1, 133.4, 134.3, 135.1, 144.4, 151.4, 154.3, 157.2; HRMS (ES^+): calcd for $[C_{19}H_{11}N_5O_2]$ Na^+: 364.0805; found: 364.0803.

3-amino-1-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5c)

Yellow powder solid, Yield: 95 %, M.p.: 226-227 °C; IR (KBr): 3434, 3323, 3075, 2198, 1681, 1657, 1516, 1432, 1379, 1277, 1144, 1027, 833, 715, 694 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.28 (s,1H), 7.78-7.81 (m, 2H), 7.94-7.98 (m , 2H), 8.06-8.09 (m , 1H), 8.17 (bs , 2H), 8.20-8.23 (m, 2H), 8.25-8.28 (m , 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 60.9, 62.6, 116.2, 124.3, 127.2, 127.8, 128.6, 128.9, 129.5, 134.4, 135.2, 146.3, 147.9, 151.4, 154.3, 157.2; HRMS (ES^+): calcd for $[C_{18}H_{11}N_5O_4]$ Na^+: 384.0704; found: 384.0703.

3-amino-1-(3-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5d)

Light yellowish powder solid, Yield: 93 %, M.p.: 266-268 °C; IR (KBr): 3365, 3246, 2201, 1683, 1668, 1537, 1407, 1375, 1280, 1170, 1084, 792, 696 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.33 (s, 1H), 7.67 (t, J = 8 Hz, 1H), 7.92-8.01 (m, 3H), 8.04-8.09 (m, 1H), 8.17 (bs, 2H), 8.19-8.20 (m, 1H), 8.24-8.27 (m, 1H), 8.40-8.42 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 60.8, 62.6,

116.3, 122.4, 123.8, 127.2, 127.7, 129.0, 129.5, 130.6, 134.3, 135.1, 141.2, 148.5, 151.6, 154.4, 157.3; HRMS (ES^+): calcd for $[C_{18}H_{11}N_5O_4]$ Na^+: 384.0704; found: 384.0702.

3-amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5e)

Yellow powder solid, Yield: 88 %, M.p.: 268-269 °C; IR (KBr): 3375, 2201, 1652, 1558, 1438, 1380, 1277, 1136, 1016, 832, 736, 696 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 6.15 (s, 1H), 7.43 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.97-7.98 (m, 2H), 8.08-8.10 (m, 1H), 8.11 (bs, 2H), 8.26-8.28 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 61.0, 62.3, 116.0, 126.7, 127.3, 128.5, 128.6, 128.9, 132.9, 133.8, 134.7, 137.5, 150.8, 153.7, 156.7; HRMS (ES^+): calcd for $[C_{18}H_{11}ClN_4O_2]Na^+$: 373.0463; found: 373.0464.

3-amino-1-(3-chlorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5f)

Light yellowish powder solid, Yield: 82 %, M.p.: 268-270 °C; IR (KBr): 3361, 3260, 2194, 1652, 1568, 1441, 1385, 1278, 1167, 1028, 873, 792, 727, 694 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 6.16 (s, 1H), 7.40-7.46 (m, 3H), 7.64 (s, 1H), 7.97-7.99 (m, 2H), 8.10-8.13 (m, 1H), 8.13 (bs, 2H), 8.26-8.28 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 61.3, 62.8, 116.4, 126.1, 127.2, 127.7, 128.8, 129.0, 129.5, 130.9, 133.7, 134.2, 135.1, 141.5, 151.3, 154.3, 157.2; HRMS (ES^+): calcd for $[C_{18}H_{11}ClN_4O_2]Na^+$: 373.0463; found: 373.0462.

3-amino-1-(2,5-dichlorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5g):

Yellow powder solid, Yield: 83 %, M.p.: 238-240 °C; IR (KBr): 3357, 3176, 2204, 85, 1652, 1563, 1471, 1384, 1281, 1141, 1053, 852, 787, 694 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.43 (s, 1H), 7.40-7.42 (m, 1H), 7.65-7.69 (m, 2H), 7.96-7.99 (m, 2H), 8.06-8.09 (m, 1H), 8.17 (bs, 2H), 8.25-8.28 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 59.8, 60.6, 116.0, 127.2, 127.8, 128.5, 128.8, 129.3, 129,6, 132.8, 134.1, 134.4, 135.0, 135.2, 151.7, 154.1, 157.2; HRMS (ES^+): calcd for $[C_{18}H_{10}Cl_2N_4O_2]Na^+$: 407.0074; found: 407.0077.

3-amino-1-(5-chloro-2-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5h):

Dark yellowish powder solid, Yield: 86 %, M.p.: 265-267 °C; IR (KBr): 3376, 3179, 2212, 1683, 1657, 1528, 1412, 1380, 1275, 1141, 1031, 844, 722, 698 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.56 (s, 1H), 7.67 (dd, J = 8.8Hz, 2.2Hz, 1H), 7.95-7.98 (m, 2H), 8.04-8.10 (m, 3H), 8.21 (bs, 2H), 8.26-8.28 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 58.5, 59.5, 116.1, 126.9, 127.1, 127.7, 128.7, 129.1, 129.8, 130.3, 134.4, 135.1, 136.0, 139.7, 147.4, 152.3, 154.5, 157.3; HRMS (ES^+): calcd for $[C_{18}H_{10}ClN_5O_4]Na^+$: 418.0314; found: 418.0313.

3-amino-1-(4-bromophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5i)

Yellow powder solid, Yield: 90 %, M.p.: 266-268 °C; IR (KBr): 3374, 3263, 2200, 1662, 1563, 1438, 1277, 1136, 1012, 830, 696 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.12 (s, 1H), 7.44 (d, J = 8.4Hz, 2H), 7.55 (d, J = 8.4Hz, 2H), 7.94-7.98 (m, 2H), 8.04-8.08 (m, 1H), 8.10 (bs, 2H), 8.23-8.26 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 61.4, 62.9, 116.4, 121.9, 127.1, 127.7, 129.0, 129.3, 129.6, 131.9, 134.2, 135.1, 138.4, 151.2, 154.2, 157.1; HRMS (ES^+): calcd for $[C_{18}H_{11}BrN_4O_2]Na^+$: 416.9958; found: 416.9955.

3-amino-1-(3-bromophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5j)

Light yellowish powder solid, Yield: 93 %, M.p.: 270-272 °C; IR (KBr): 3365, 3256, 3190, 2193, 1652, 1564, 1438, 1386, 1278, 1164, 1028, 997, 859, 724, 692 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): 6.12 (s, 1H), 7.32 (t, J = 7.8Hz, 1H), 7.49 (t, J = 8.1Hz, 2H), 7.75 (s, 1H), 7.94-7.97 (m, 2H), 8.07-8.10 (m, 1H), 8.11 (bs, 2H), 8.23-8.26 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 61.3, 62.8, 116.4, 122.3, 126.5, 127.2, 127.7, 129.0, 129.5, 130.0, 131.2, 131.7, 134.2, 135.1, 141.7, 151.3, 154.2, 157.2; HRMS (ES^+): calcd for $[C_{18}H_{11}BrN_4O_2]Na^+$: 416.9958; found: 416.9960.

3-amino-1-(4-fluorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5k)

Light yellowish powder solid, Yield: 94 %, M.p.: 265-266 °C; IR (KBr): 3850, 3364, 2191, 1652, 1514, 1372, 1279, 1162, 1026, 827, 784, 694 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.14 (s, 1H), 7.17 (t, J = 8.8Hz, 2H), 7.52 (dd, J = 8.4Hz, 5.5Hz, 2H), 7.93-7.98 (m, 2H), 8.06-8.08 (m,

1H), 8.09 (bs, 2H), 8.23-8.26 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 61.7, 62.8, 115.6, 115.9, 116.4, 127.1, 127.7, 129.1, 129.3, 129.6, 129.7, 134.2, 135.1, 151.2, 154.2, 157.1, 160.8, 164.1; HRMS (ES^+): calcd for $[C_{18}H_{11}BrN_4O_2]$ Na^+: 357.0759; found: 357.0761.

3-amino-5,10-dioxo-1-(p-tolyl)-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5l)

Yellow powder solid, Yield: 87 %, M.p.: 254-256 °C; IR (KBr): 3362, 3262, 2198, 1682, 1652, 1567, 1439, 1386, 1279, 1167, 1027, 825, 784, 700, 692 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.28 (s, 3H), 6.07 (s, 1H), 7.14 (d, J = 7.9Hz, 2H), 7.32 (d, J = 7.9Hz, 2H), 7.92-7.97 (m, 2H), 8.06-8.08 (m, 3H), 8.23-8.26 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.2, 62.0, 63.3, 116.1, 127.1, 127.3, 127.7, 129.2, 129.5, 134.2, 135.1, 135.9, 138.1, 151.1, 154.0, 157.1; HRMS (ES^+): calcd for $[C_{19}H_{14}N_4O_2]Na^+$: 353.1009; found: 353.1010.

3-amino-1-(4-methoxyphenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5m)

Yellow powder solid, Yield: 91 %, M.p.: 193-195 °C; IR (KBr): 3370, 3266, 3009, 2191, 1660, 1567, 1439, 1385, 1275, 1164, 1032, 833, 693 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.76 (s, 3H), 6.10 (s, 1H), 6.92 (d, J = 8.7Hz, 2H), 7.39 (d, J = 8.6Hz, 2H), 7.94-7.99 (m, 2H), 8.08 (bs, 2H), 8.09-8.11 (m, 1H), 8.23-8.27 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 55.6, 56.5, 61.9, 63.1, 114.3, 116.6, 127.1, 127.7, 128.9, 129.2, 130.6, 134.2, 135.1, 151.0, 154.1, 157.1, 159.8; HRMS (ES^+): calcd for $[C_{19}H_{14}N_4O_3]Na^+$: 369.0959; found: 369.0959.

3-amino-1-(3,4-dimethoxyphenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5n)

Light yellowish powder solid, Yield: 77 %, M.p.: 150-152 °C; IR (KBr): 3372, 3264, 2841, 2186, 1682, 1659, 1520, 1438, 1381, 1270, 1139, 1023, 808, 691 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.71 (s, 3H), 3.73 (s, 3H), 6.06 (s, 1H), 6.90 (d, J = 8Hz, 1H), 6.97 (d, J = 8Hz, 1H), 7.03 (s, 1H), 7.93-7.96 (m, 2H), 8.05-8.10 (m, 3H), 8.23-8.26 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 56.0, 56.2, 61.9, 63.5, 111.4, 112.2, 116.6, 120.0, 127.1, 127.7, 129.3, 131.0, 134.1, 135.1, 149.2, 149.4, 151.0, 154.2, 157.2; HRMS (ES^+): calcd for $[C_{20}H_{16}N_4O_4]$ Na^+: 399.1064; found: 399.1062.

3-amino-5,10-dioxo-1-(3,4,5-trimethoxyphenyl)-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5o)

Light yellowish powder solid, Yield: 89 %, M.p.: 246-248 °C; IR (KBr): 3374, 3257, 2189, 1657, 1592, 1433, 1388, 1275, 1129, 1006, 788, 694 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 3.64 (s, 3H), 3.73 (s, 6H), 6.05 (s, 1H), 6.75 (s, 2H), 7.94-7.97 (m, 2H), 8.06 (bs, 2H), 8.08-8.11 (m, 1H), 8.24-8.27 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 56.5, 60.4, 61.8, 63.8, 104.8, 116.6, 127.2, 127.7, 129.2, 129.4, 134.1, 134.5, 135.0, 137.8, 151.1, 153.4, 154.4, 157.2; HRMS (ES^+): calcd for $[C_{21}H_{18}N_4O_5]$ Na^+: 429.1170; found: 429.1169.

3-amino-1-(2,6-dichlorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5p)

Light yellowish powder solid, Yield: 66 %, M.p.: 267-269 °C; IR (KBr): 3399, 3271, 2200, 1683, 1652, 1560, 1414, 1374, 1279, 1144, 1030, 787, 706, 696 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 6.91 (s, 1H), 7.39-7.44 (m, 2H), 7.60-7.62 (m, 1H), 8.00-8.03 (m, 2H), 8.10-8.11 (m, 1H), 8.26 (bs, 2H), 8.29-8.32 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 56.9, 59.8, 115.7, 127.3, 128.0, 128.3, 128.8, 129.5, 129.6, 130.7, 131.0, 131.3, 133.1, 134.6, 135.6, 135.6, 152.5, 153.8, 157.1; HRMS (ES^+): calcd for $[C_{18}H_{10}Cl_2N_4O_2]Na^+$: 407.0074; found: 407.0076.

3-amino-1-(naphthalen-1-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5q)

Dark yellowish powder solid, Yield: 62 %, M.p.: 181-183 °C; IR (KBr): 3363, 3232, 2199, 1656, 1544, 1478, 1372, 1265, 1147, 1037, 956, 788, 700, 697 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): 6.98 (s, 1H), 7.44-7.49 (m, 1H), 7.54-7.64 (m, 3H), 7.89-8.06 (m, 5H), 8.11 (bs, 2H), 8.29-8.32 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 62.3, 116.4, 123.3, 126.2, 126.4, 126.9, 127.2, 127.9, 129.0, 129.3, 130.5, 133.9, 134.3, 135.3, 151.2, 157.3; HRMS (ES^+): calcd for $[C_{22}H_{15}N_4O_2]^+$: 367.1190; found: 367.1190.

3-amino-1-cyclohexyl-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (5r)

Yellow powder solid, Yield: 83 %, M.p.: 274-275 °C; IR (KBr): 3364, 2929, 2188, 1652, 1381, 1276, 1163, 1029, 954, 894, 786, 691 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 1.07-1.74 (m, 10H), 2.25-2.29 (m, 1H), 5.17 (s, 1H), 7.95-7.99 (m, 4H), 8.19-8.21 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 26.2, 26.4, 26.5, 28.6, 56.2, 64.6, 117.6, 127.3, 127.7, 128.8, 129.2, 134.1, 135.2, 152.6, 154.4, 157.0; HRMS (ES^+): calcd for $[C_{18}H_{19}N_4O_2]^+$: 323.1503; found: 323.1502.

Ethyl 3-amino-1-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b] phthalazine-2-carboxylate (5s)

Yellow powder solid, Yield: 79 %, M.p.: 228-230 °C; IR (KBr): 3443, 3331, 1704, 1651, 1520, 1346, 1106, 1012, 951, 839, 797, 704, 684 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): 1.04 (t, J = 7 Hz, 3H), 3.96-3.98 (m, 2H), 6.20 (s, 1H), 7.76 (d, J = 8 Hz, 2H), 7.97-8.01 (m, 2H), 8.07-8.11 (m, 1H), 8.16 (d, J = 8 Hz, 2H), 8.28-8.32 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.6, 59.3, 63.1, 81.3, 123.6, 127.2, 127.8, 129.1, 129.3, 129.4, 134.3, 135.2, 147.4, 147.8, 150.5, 153.9, 157.4, 164.3; HRMS (ES^+): calcd for $[C_{20}H_{16}N_4O_6]Na^+$: 431.0963; found: 431.0965.

Ethyl 3-amino-1-(3-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b] phthalazine-2-carboxylate (5t)

Light yellowish powder solid, Yield: 75 %, M.p.: 237-238 °C; IR (KBr): 3250, 1694, 1652, 1532, 1403, 1348, 1264, 1160, 1096, 1023, 970, 813, 782, 702, 671 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): 1.01 (t, J = 7 Hz, 3H), 3.94-3.99 (m, 2H), 6.23 (s, 1H), 7.60 (t, J = 8 Hz, 1H), 7.94-7.99 (m, 4H), 8.07-8.15 (m, 3H), 8.28-8.31 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4, 59.2, 63.2, 81.2, 122.8, 123.1, 125.3, 127.2, 127.6, 127.7, 129.1, 129.5, 130.0, 134.2, 134.6, 135.1, 142.6, 148.0, 148.5, 150.5, 154.0, 157.4, 164.3; HRMS (ES^+): calcd for $[C_{20}H_{16}N_4O_6]Na^+$: 431.0963; found: 431.0963.

Ethyl 3-amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylate (5u)

Yellow powder solid, Yield: 79 %, M.p.: 239-241 °C; IR (KBr): 3451, 3338, 2983, 1707,1661, 1621, 1517, 1431, 1395, 1287, 1131, 1014, 830, 703, 692 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): 1.01 (t, J = 7 Hz, 3H), 3.93-3.97 (m, 2H), 6.05 (s, 1H), 7.32 (d, J = 8 Hz, 2H), 7.43 (d, J = 8 Hz,

2H), 7.93-7.96 (m, 2H), 8.05-8.08 (m, 1H), 8.23-8.26 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.6, 59.2, 63.1, 81.7, 127.2, 127.7, 128.3, 129.2, 129.3, 129.8, 132.6, 134.1, 135.1, 139.3, 150.3, 153.7, 157.3, 164.4; HRMS (ES$^+$): calcd for $[C_{20}H_{16}ClN_3O_4]Na^+$: 420.0722; found: 420.0723.

Ethyl 3-amino-1-(5-chloro-2-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylate (5v)

Yellow powder solid, Yield: 81 %, M.p.: 250-252 °C; IR (KBr): 3436, 3324, 1705, 1665, 1651, 1621, 1531, 1438, 1360, 1287, 1133, 1023, 845, 695 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96-0.99 (m, 3H), 3.94-3.98 (m, 2H), 6.23 (s, 1H), 6.96 (s, 1H), 7.60-7.62 (m, 1H), 7.70-7.77 (m, 1H), 7.92-8.10 (m, 5H), 8.29-8.31 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.6, 59.2, 80.4, 126.5, 127.2, 127.7, 129.0, 129.5, 129.7, 134.2, 135.1, 138.7, 148.1, 151.1, 154.0, 157.5, 164.1; HRMS (ES$^+$): calcd for $[C_{20}H_{15}ClN_4O_6]Na^+$: 465.0573; found: 465.0574.

4. ^{1}H and ^{13}C NMR spectra of the compounds

Figure S1: ^{1}H spectra of 3-amino-5,10-dioxo-1-phenyl-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5a)

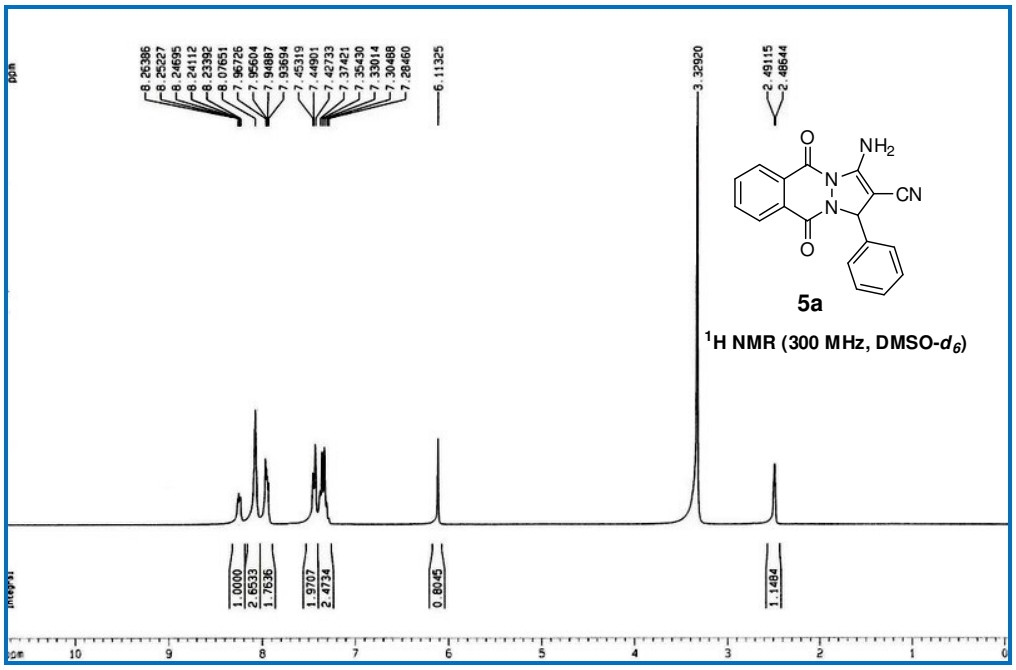

Figure S2: ^{13}C spectra of 3-amino-5,10-dioxo-1-phenyl-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile(5a)

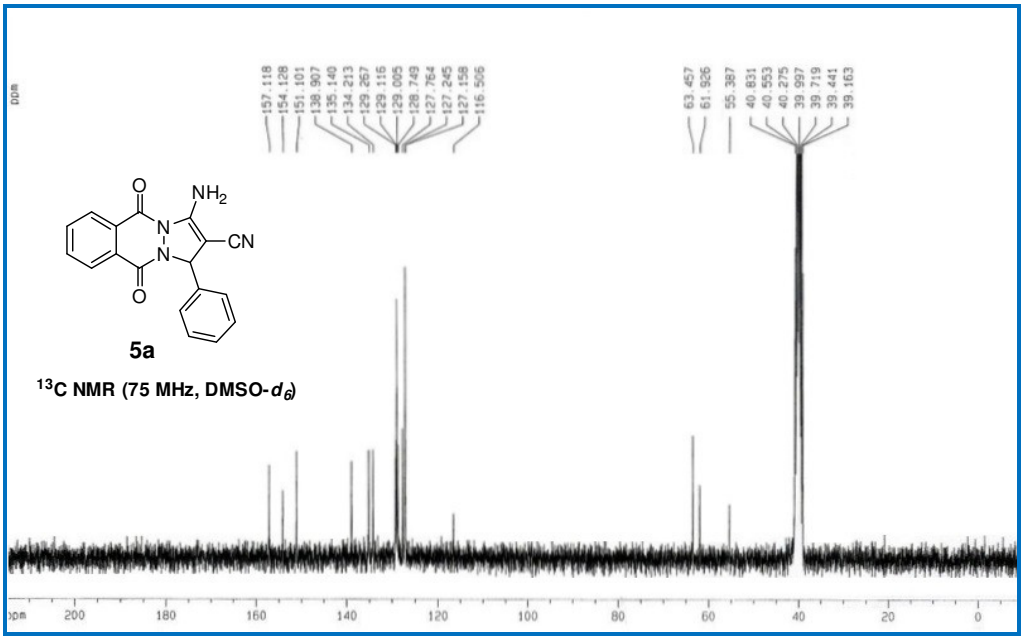

Figure S3: ^{1}H spectra of 3-amino-1-(4-cyanophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5b)

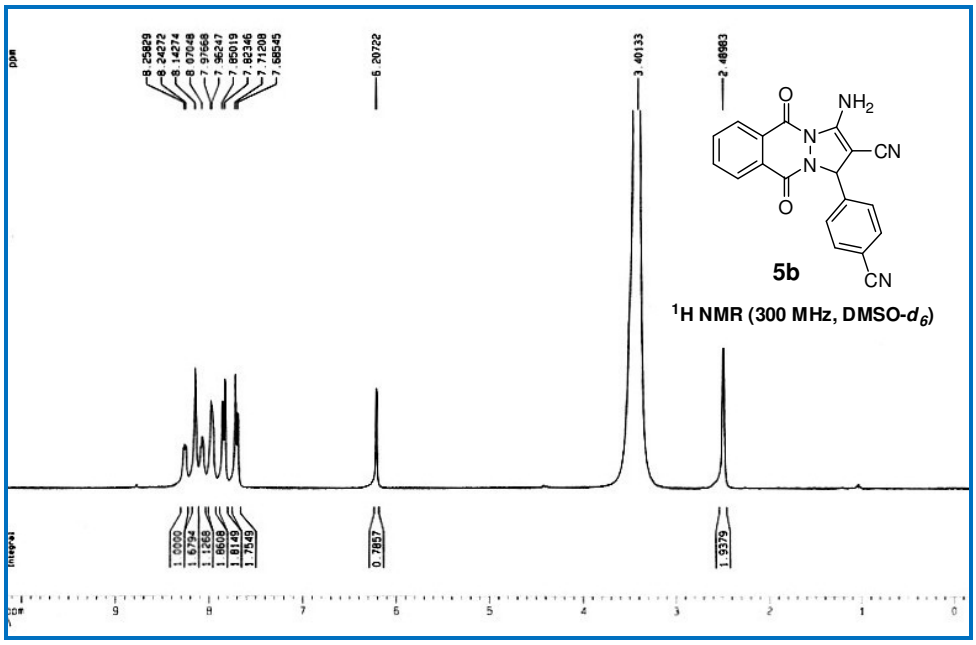

Figure S4: ^{13}C spectra of 3-amino-1-(4-cyanophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5b)

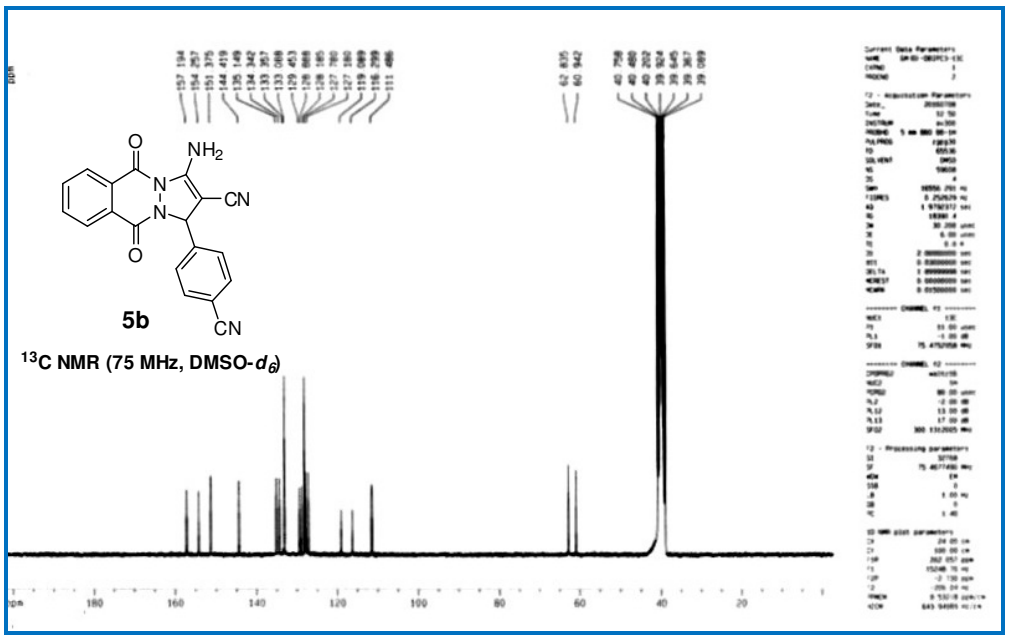

Figure S5: ^{1}H spectra of 3-amino-1-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5c)

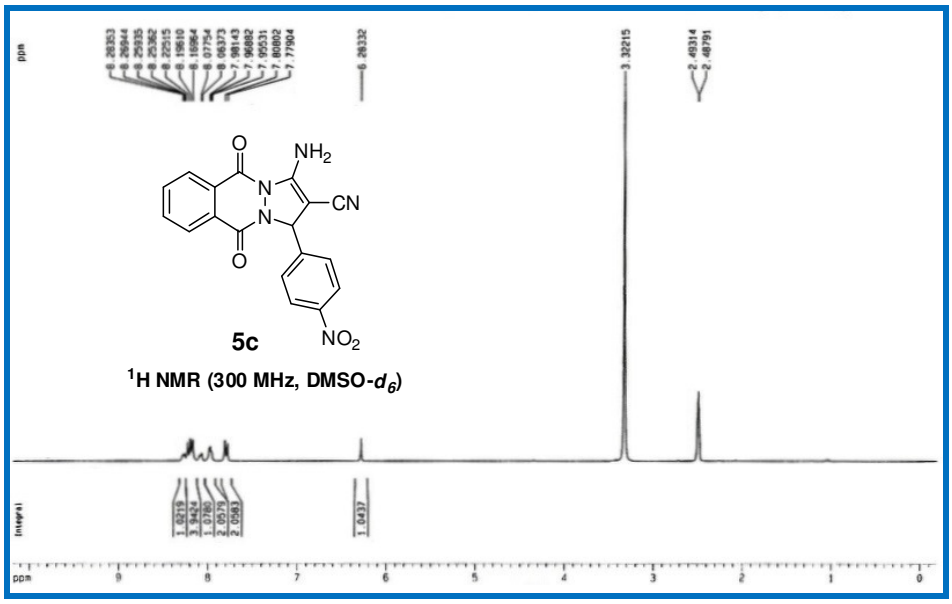

Figure S6: ^{13}C spectra of 3-amino-1-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5c)

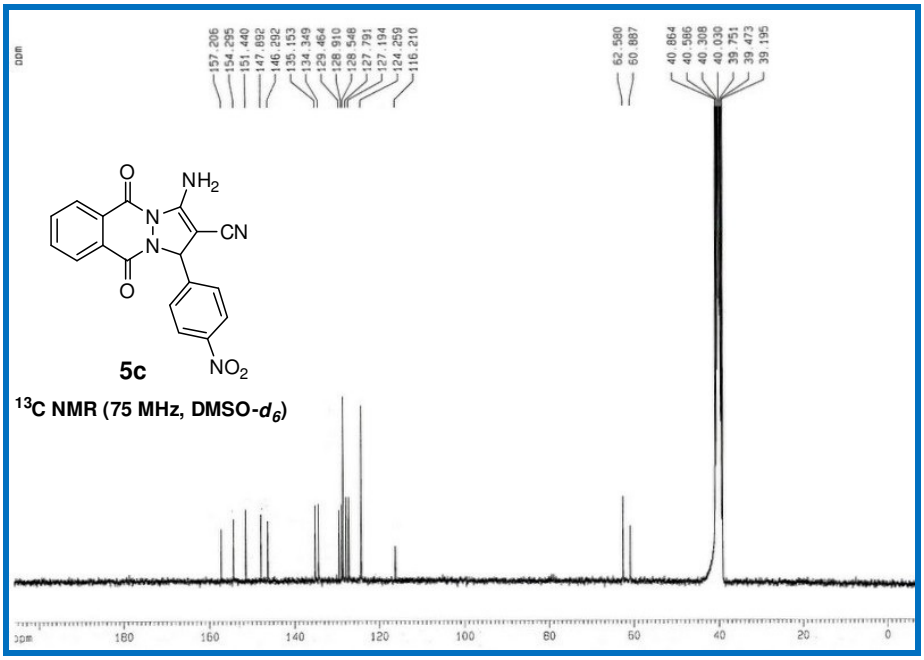

Figure S7: ^{1}H spectra of 3-amino-1-(3-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5d)

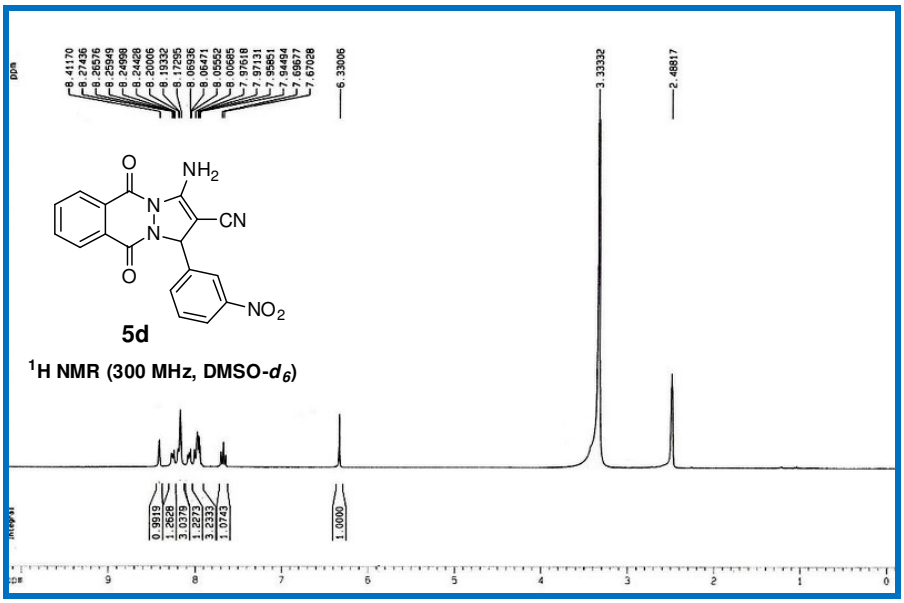

Figure S8: ^{13}C spectra of 3-amino-1-(3-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5d)

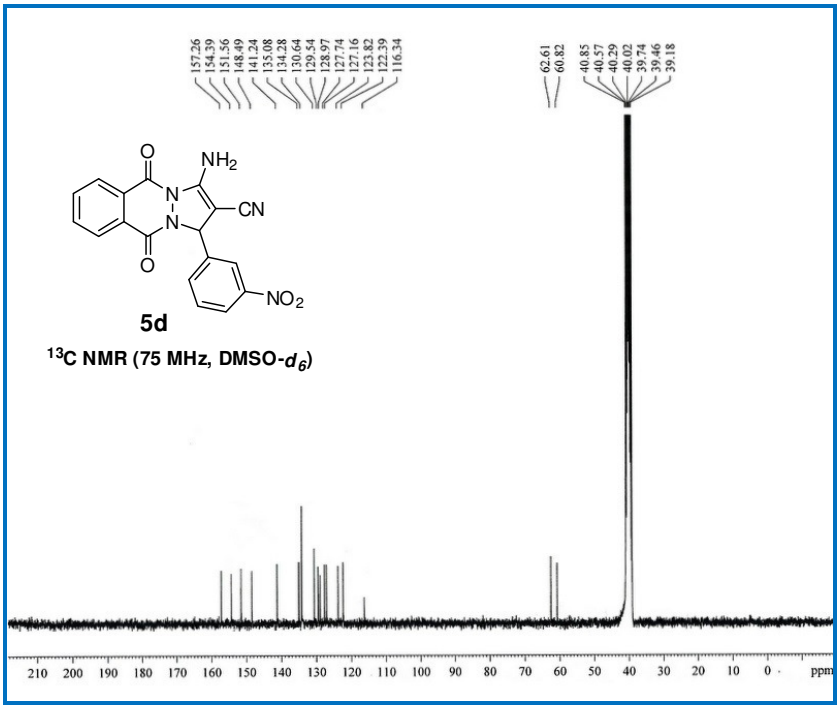

Figure S9: ^{1}H spectra of 3-amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5e)

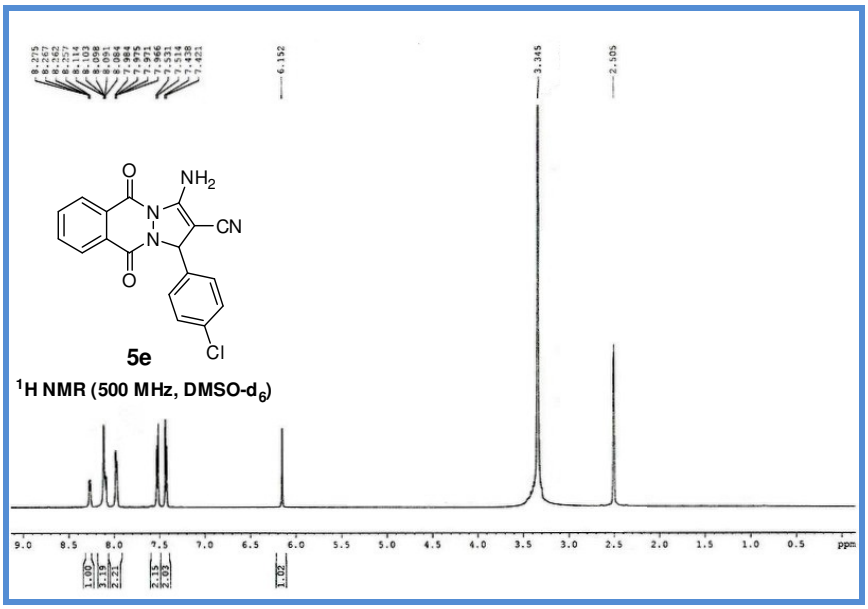

Figure S10:^{13}C spectra of 3-amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5e)

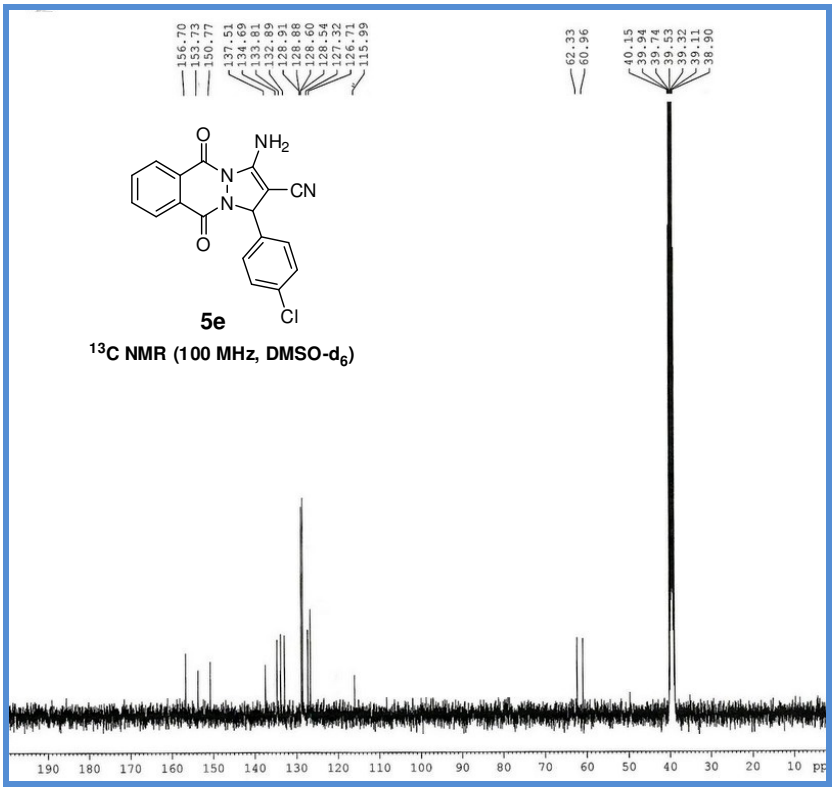

Figure S11: ^{1}H spectra of 3-amino-1-(3-chlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5f)

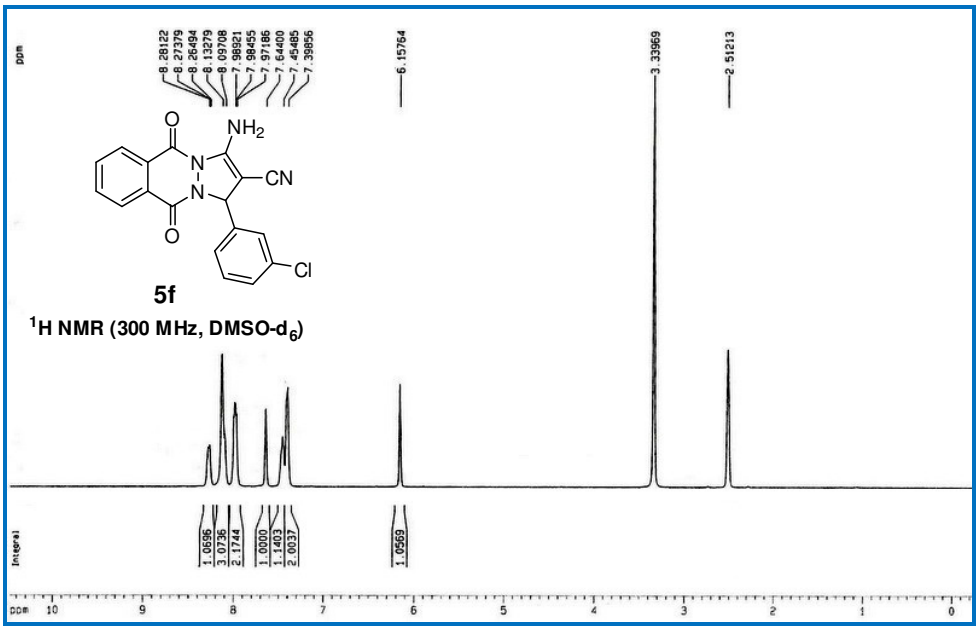

Figure S12: ^{13}C spectra of 3-amino-1-(3-chlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5f)

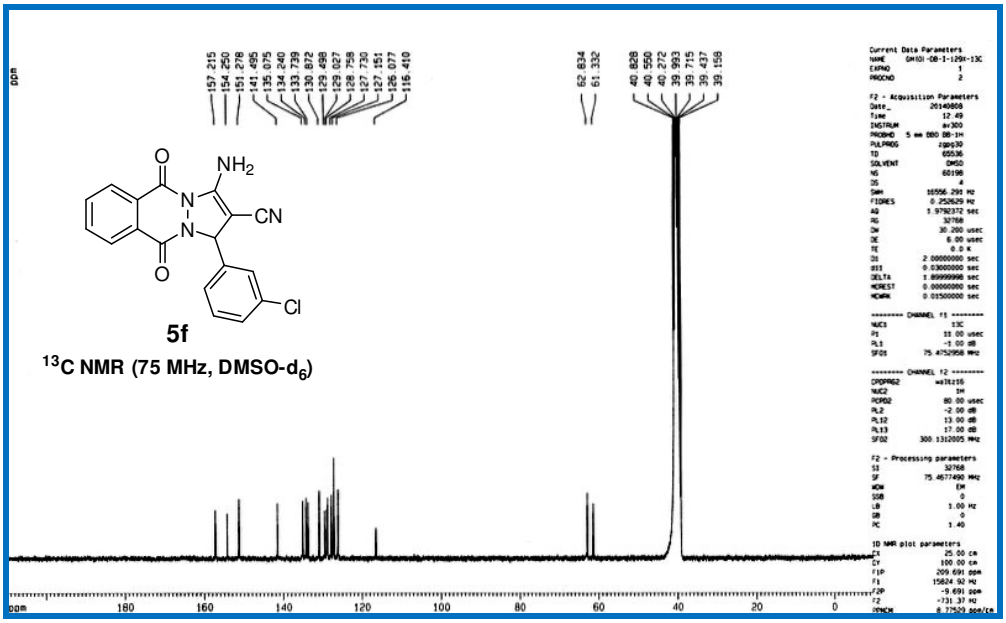

Figure S13: ^{1}H spectra of 3-amino-1-(2,5-dichlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5g)

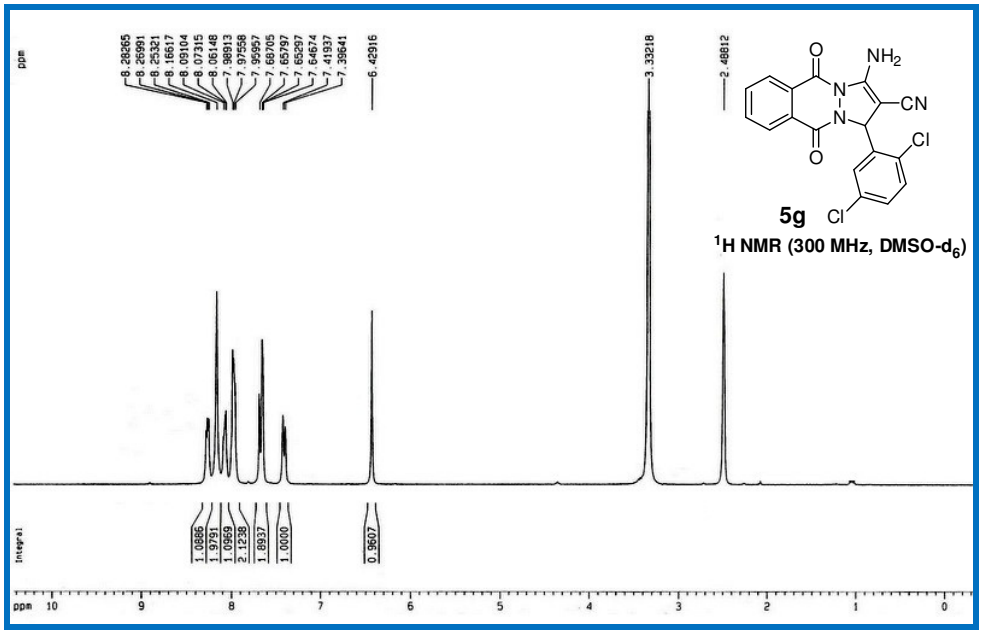

Figure S14: ^{13}C spectra of 3-amino-1-(2,5-dichlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5g)

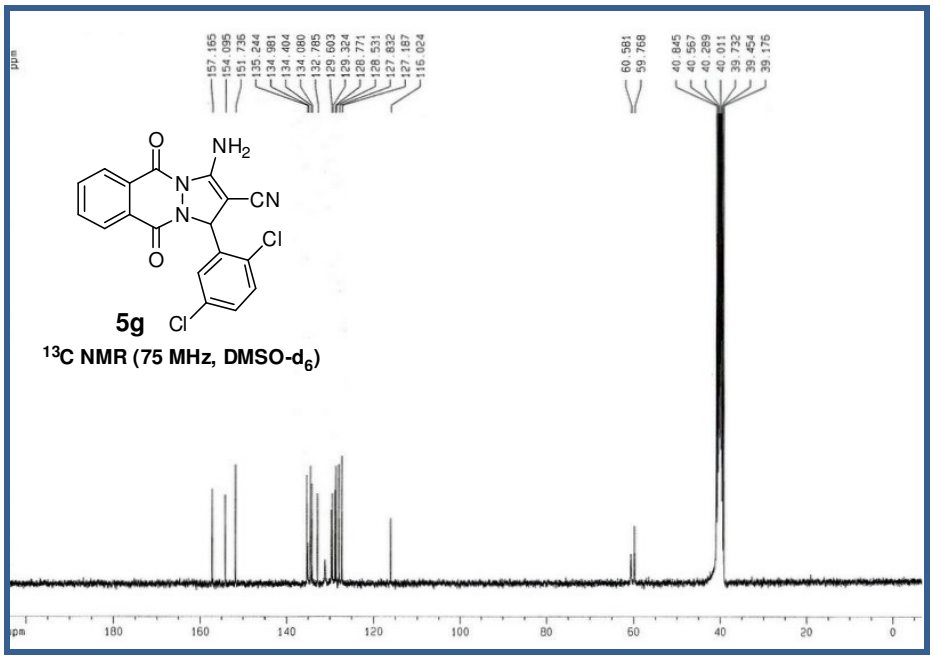

Figure S15: ^{1}H spectra of 3-amino-1-(5-chloro-2-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5h)

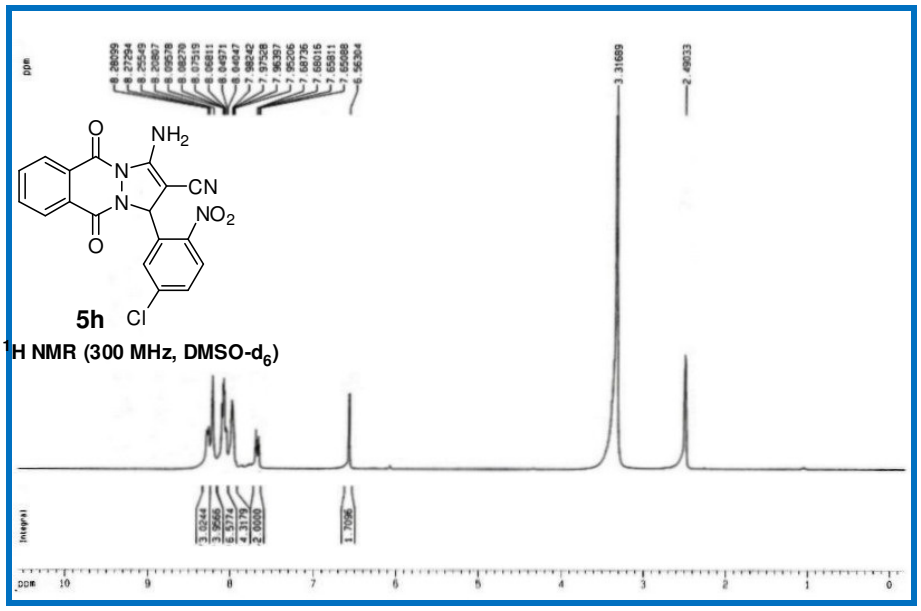

Figure S16: ^{13}C spectra of 3-amino-1-(5-chloro-2-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5h)

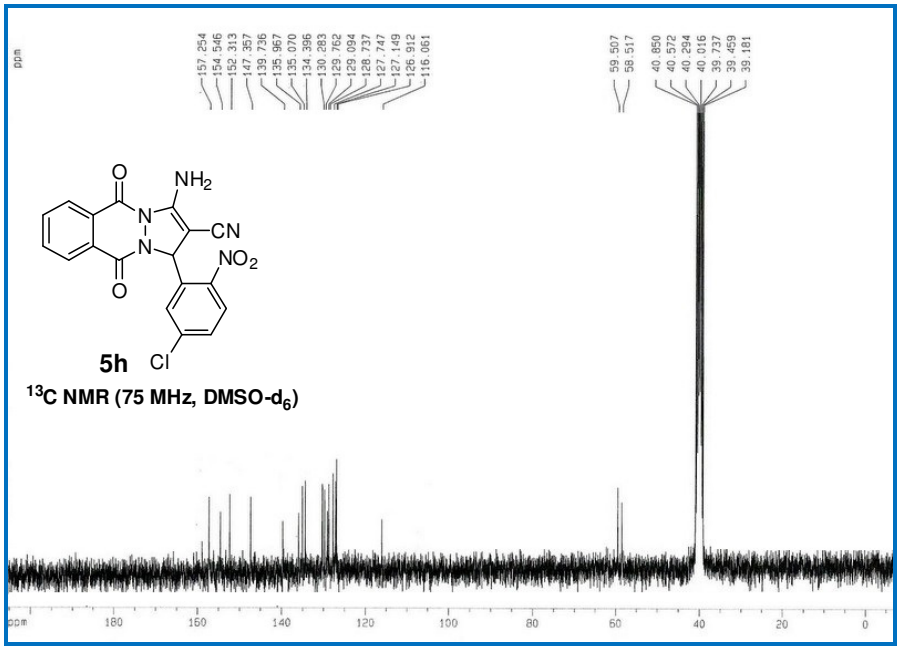

Figure S17: ^{1}H spectra of 3-amino-1-(4-bromophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5i)

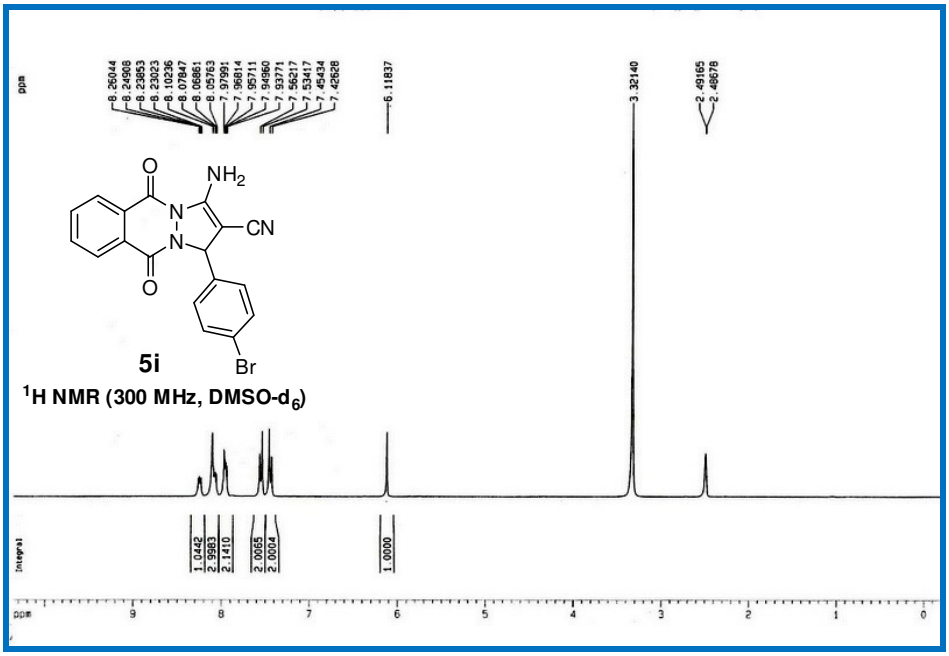

Figure S18: ^{13}C spectra of 3-amino-1-(4-bromophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5i)

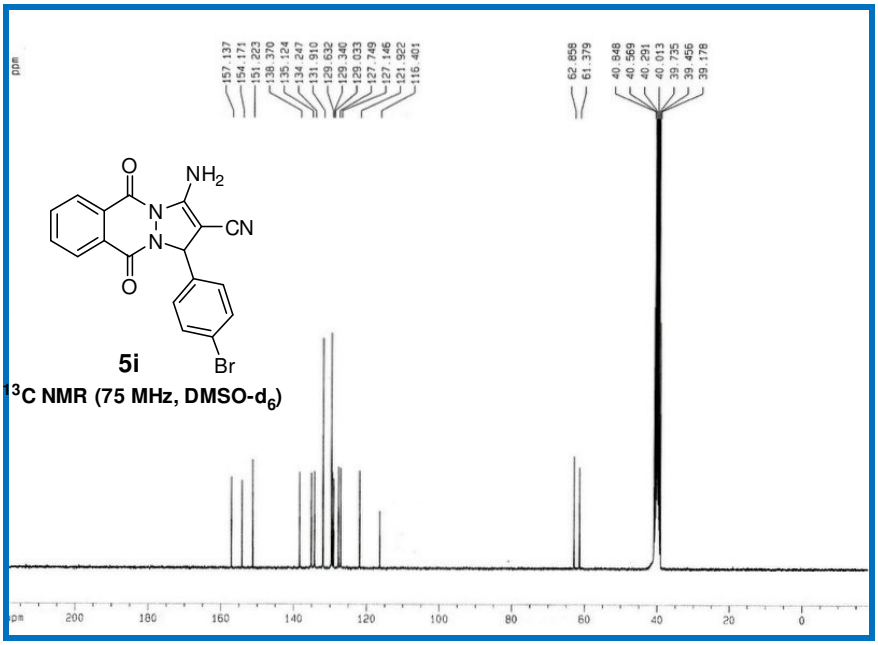

Figure S19: ^{1}H spectra of 3-amino-1-(3-bromophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5j)

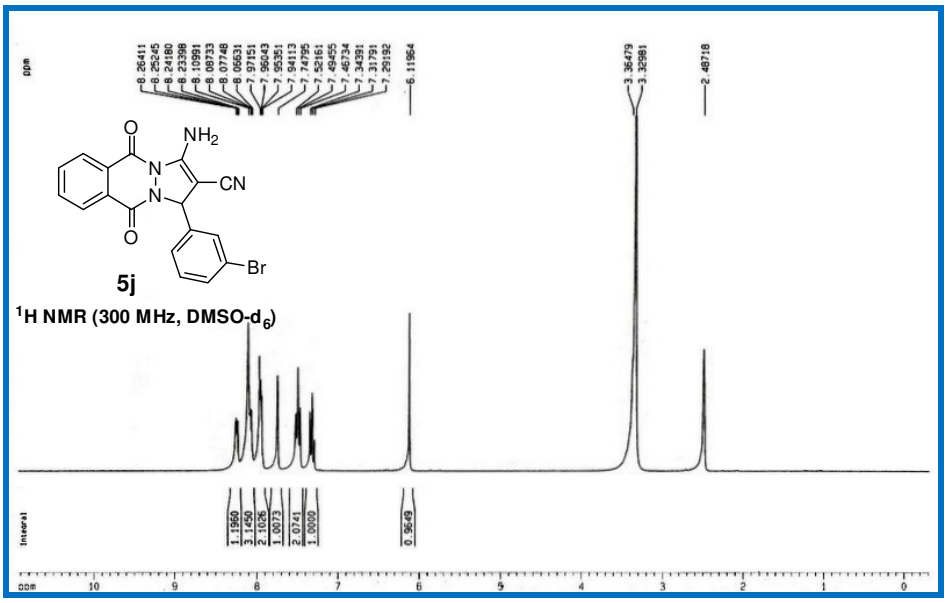

Figure S20: ^{13}C spectra of 3-amino-1-(3-bromophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5j)

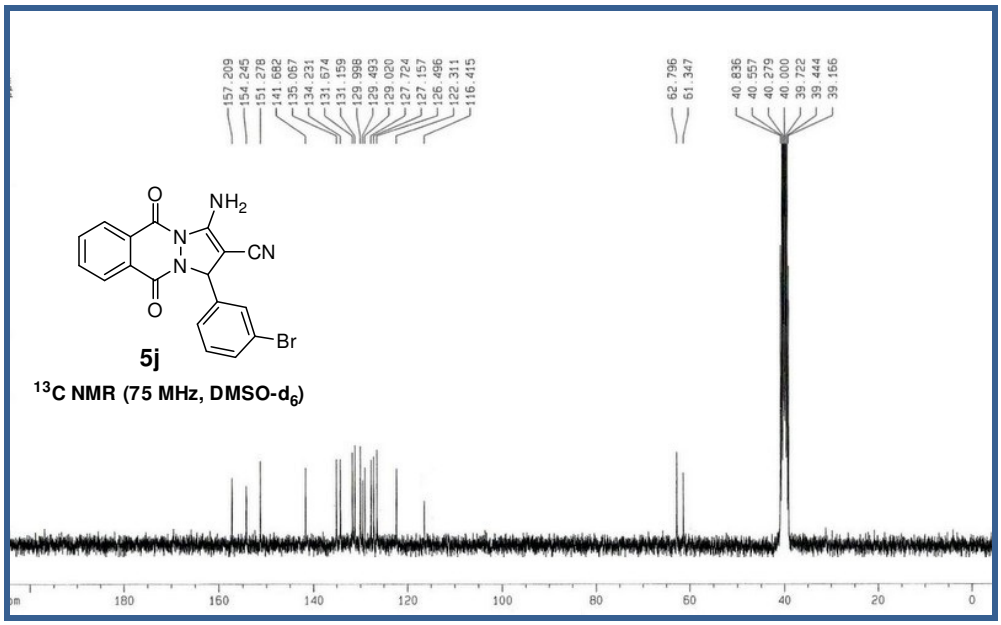

Figure S21: ^{1}H spectra of 3-amino-1-(4-fluorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5k)

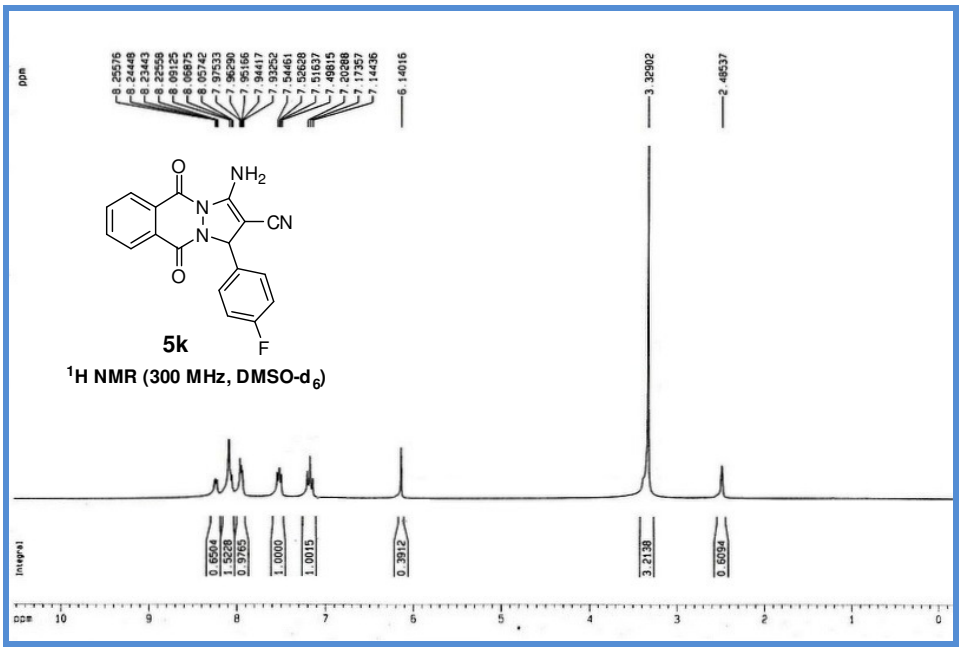

Figure S22: ^{13}C spectra of 3-amino-1-(4-fluorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5k)

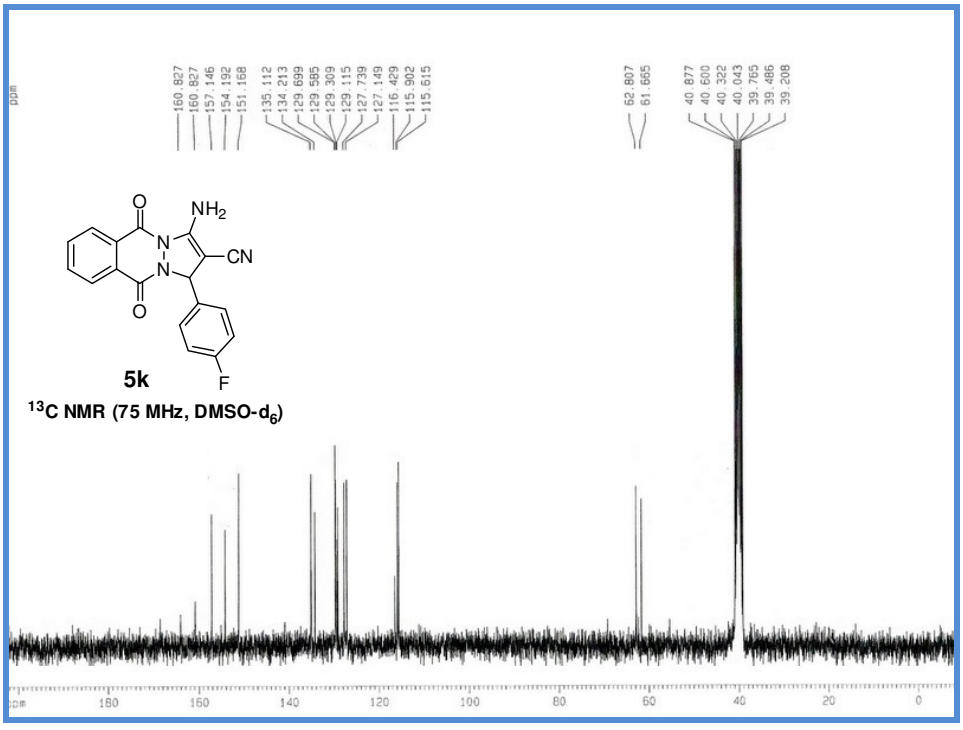

Figure S23: ^{1}H spectra of 3-amino-5,10-dioxo-1-(p-tolyl)-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5l)

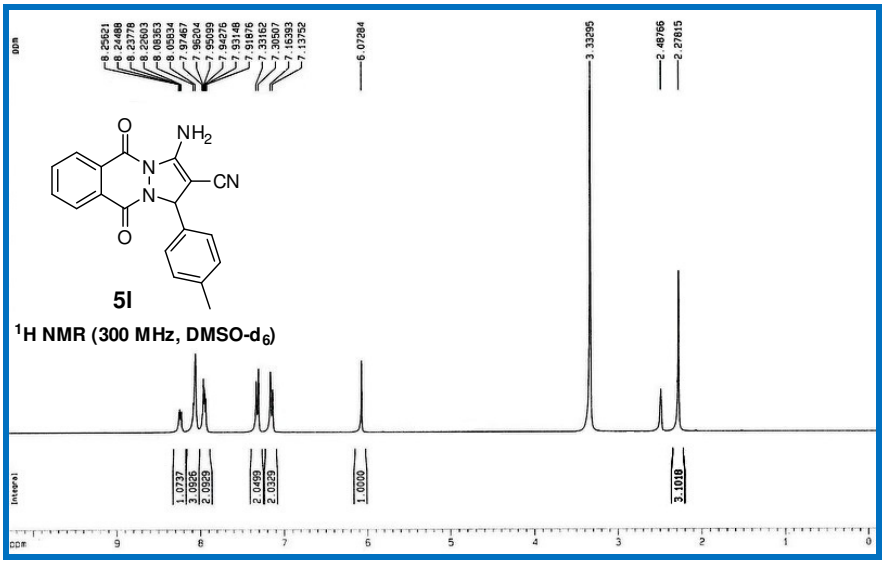

Figure S24: ^{13}C spectra of 3-amino-5,10-dioxo-1-(p-tolyl)-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5l)

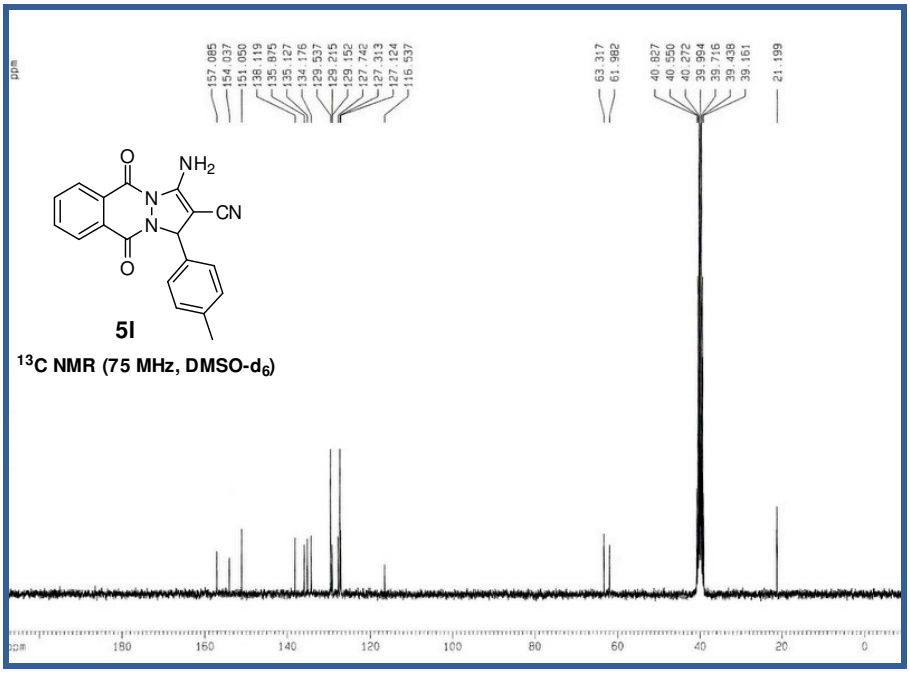

Figure S25: ^{1}H spectra of 3-amino-1-(4-methoxyphenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5m)

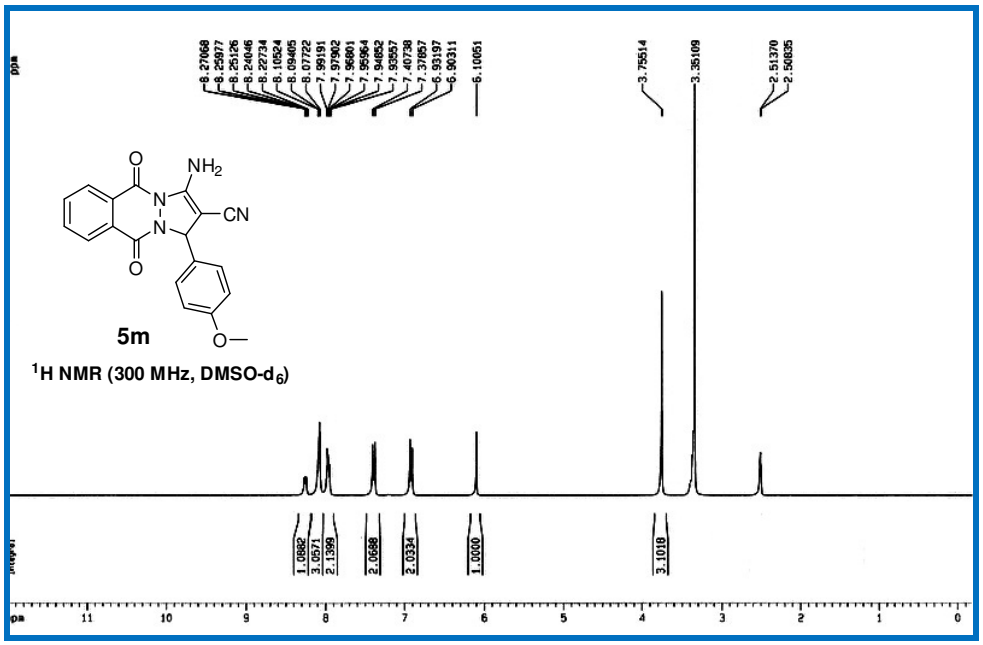

Figure S26: ^{13}C spectra of 3-amino-1-(4-methoxyphenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5m)

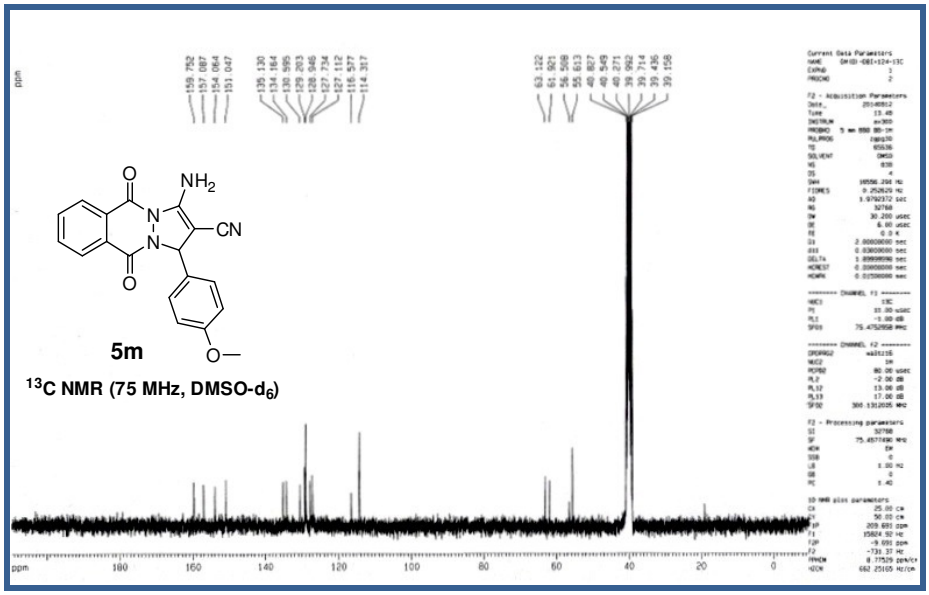

Figure S27: ^{1}H spectra of 3-amino-1-(3,4-dimethoxyphenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5n)

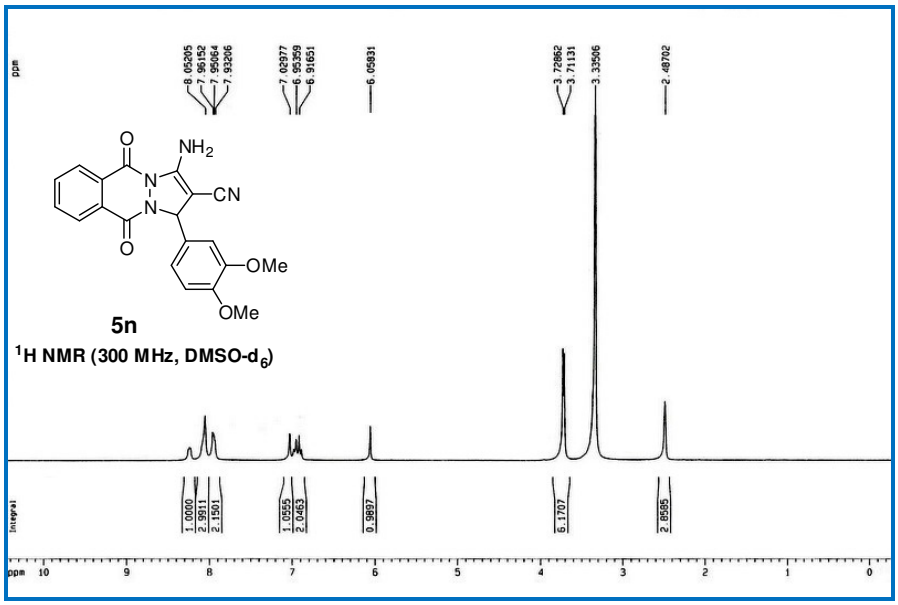

Figure S28: ^{13}C spectra of 3-amino-1-(3,4-dimethoxyphenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5n)

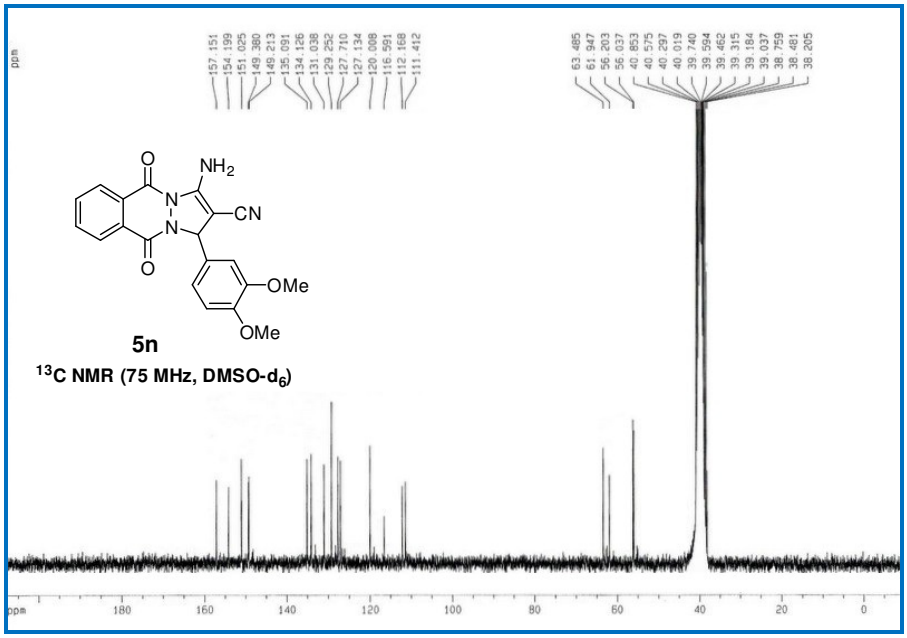

Figure S29: ^{1}H spectra of 3-amino-5,10-dioxo-1-(3,4,5-trimethoxyphenyl)-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5o)

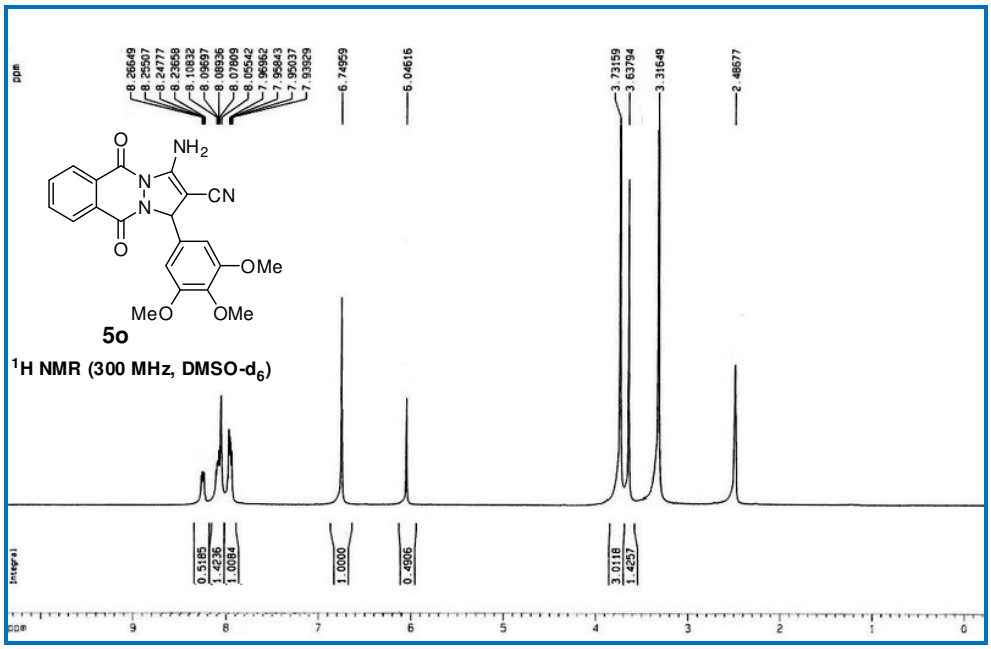

Figure S30: ^{13}C spectra of 3-amino-5,10-dioxo-1-(3,4,5-trimethoxyphenyl)-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5o)

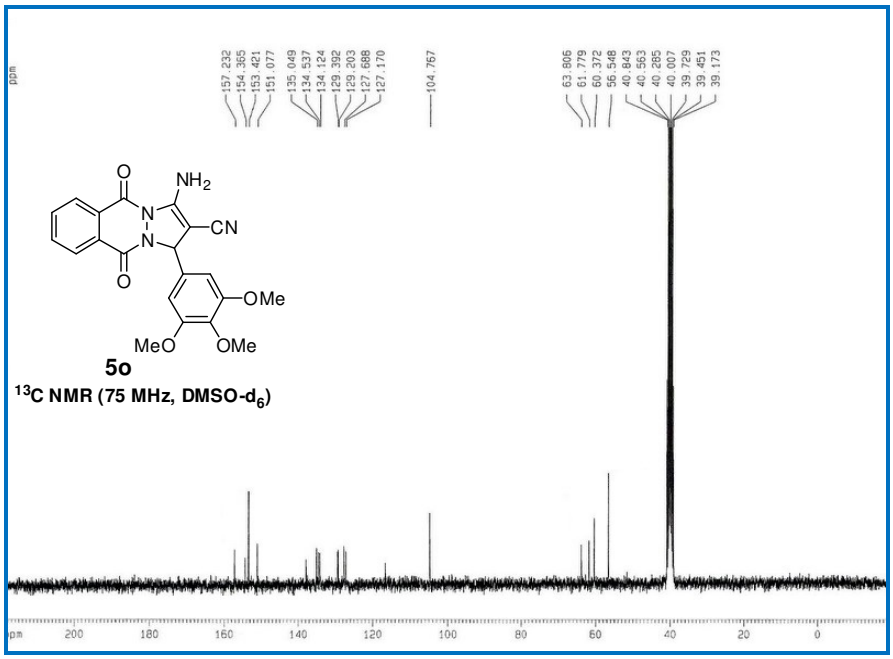

Figure S31: ^{1}H spectra of 3-amino-1-(2,6-dichlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5p)

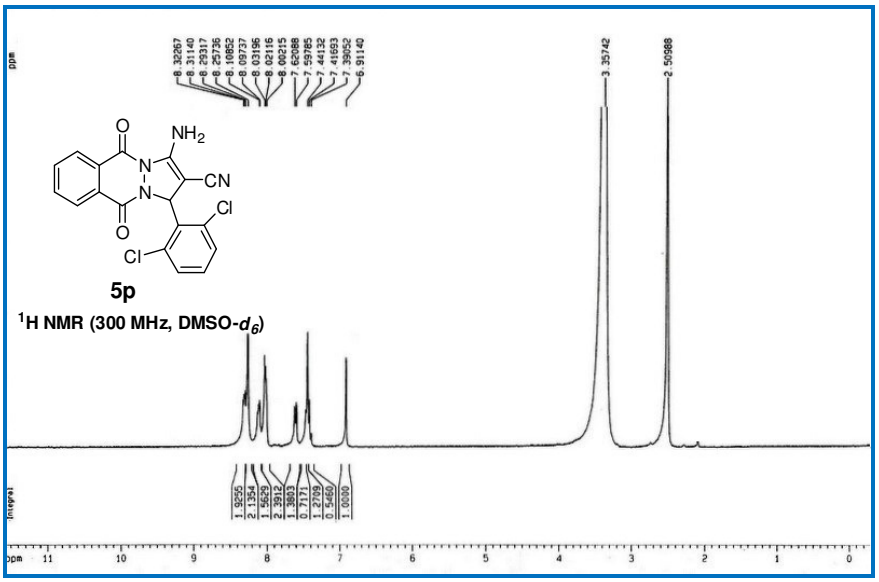

Figure S32: ^{13}C spectra of 3-amino-1-(2,6-dichlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5p)

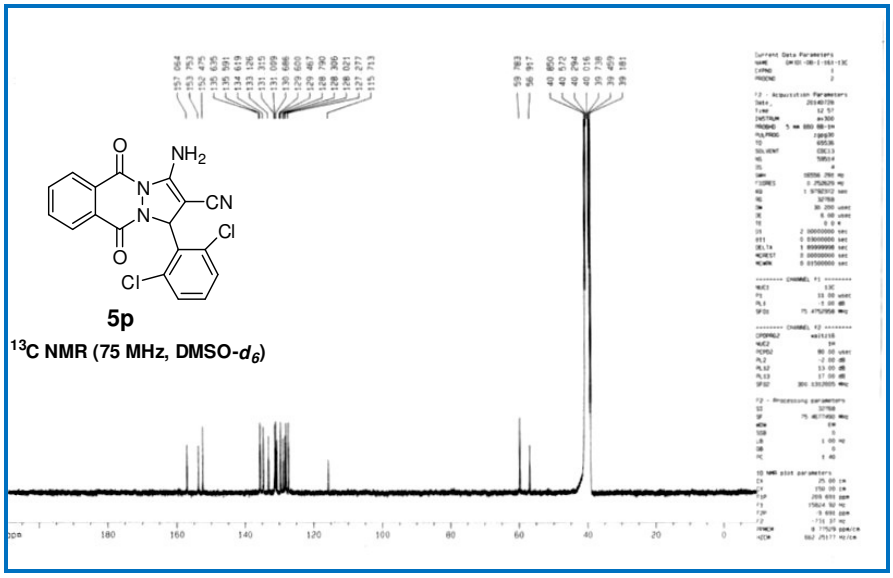

Figure S33: ^{1}H spectra of 3-amino-1-(naphthalen-1-yl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5q)

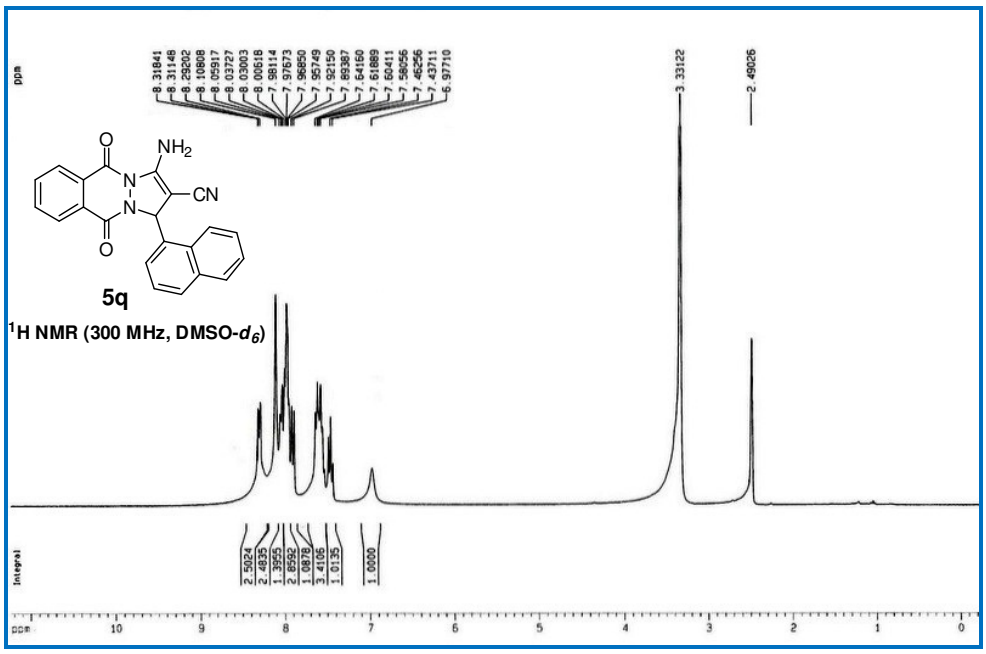

Figure S34: ^{13}C spectra of 3-amino-1-(naphthalen-1-yl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5q)

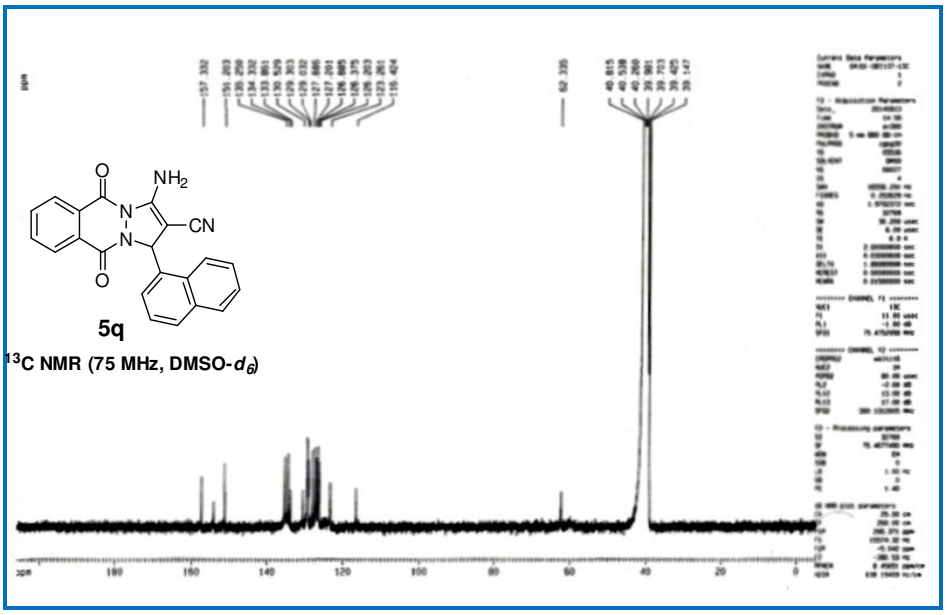

Figure S35: ^{1}H spectra of 3-amino-1-cyclohexyl-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5r)

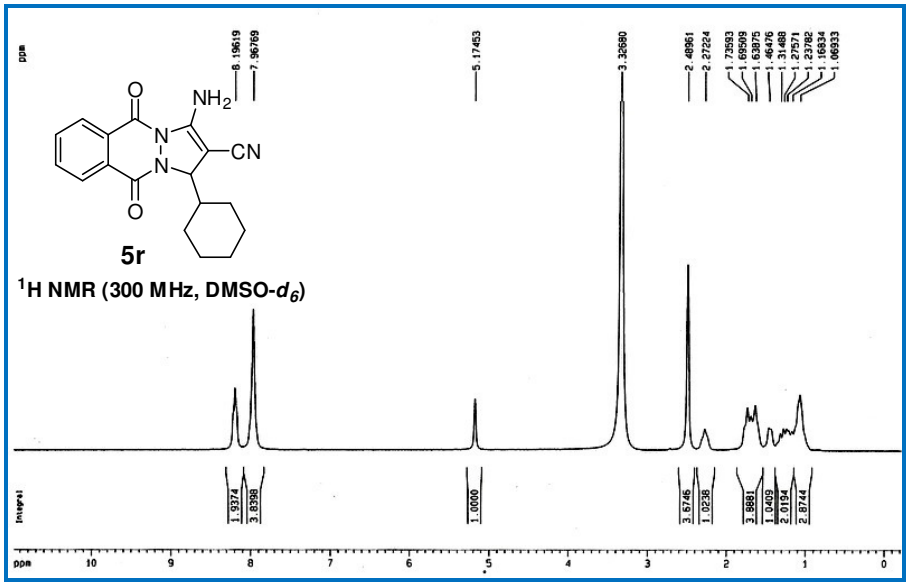

Figure S36: ^{13}C spectra of 3-amino-1-cyclohexyl-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carbonitrile (5r)

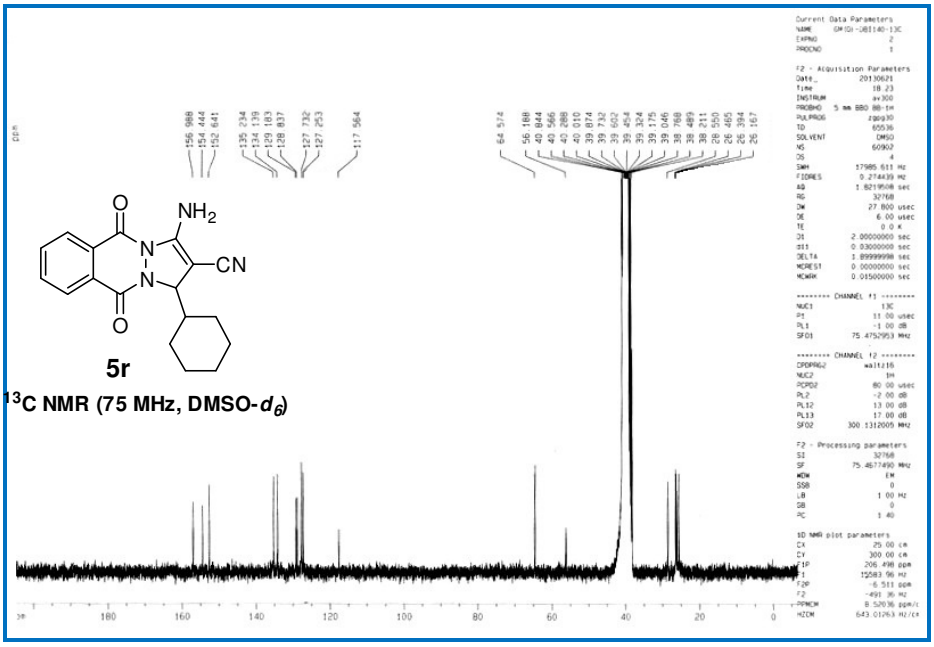

Figure S37: ^{1}H spectra of Ethyl 3-amino-1-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carboxylate (5s)

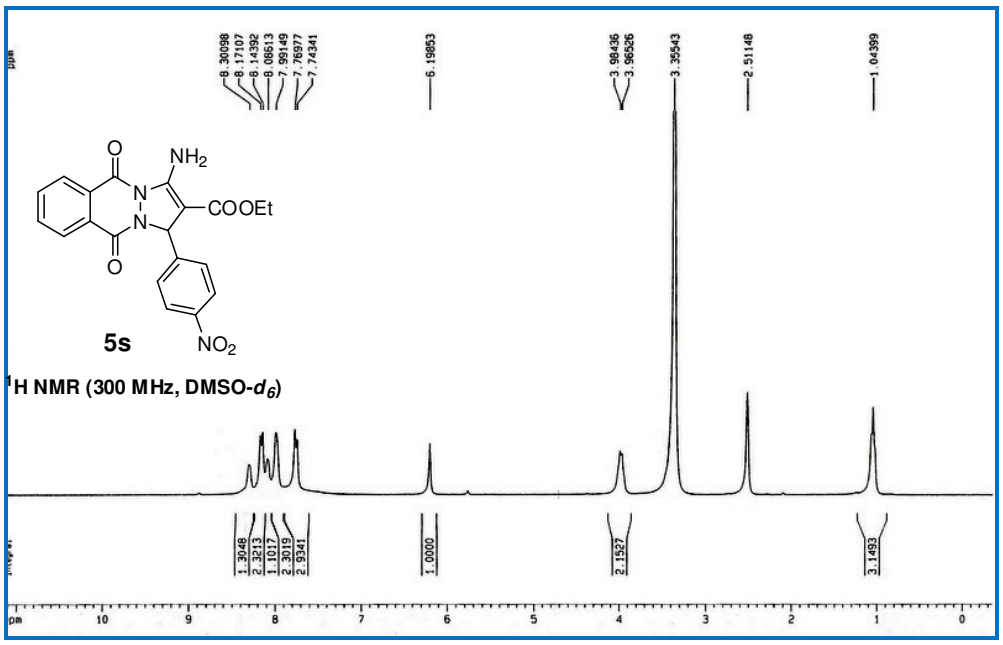

Figure S38: ^{13}C spectra of Ethyl 3-amino-1-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carboxylate (5s)

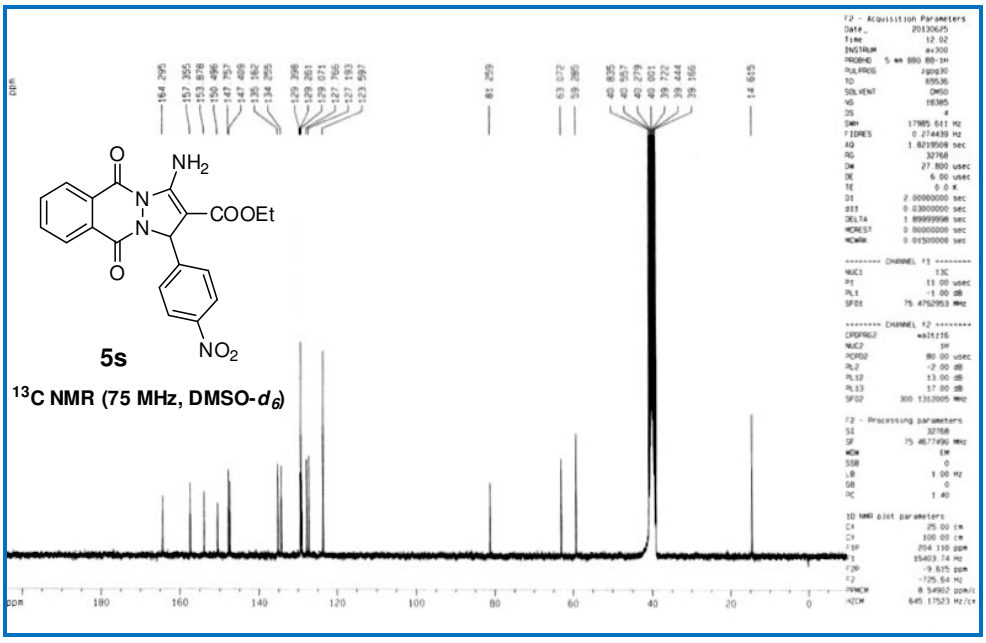

Figure S39: ^{1}H spectra of Ethyl 3-amino-1-(3-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carboxylate (5t)

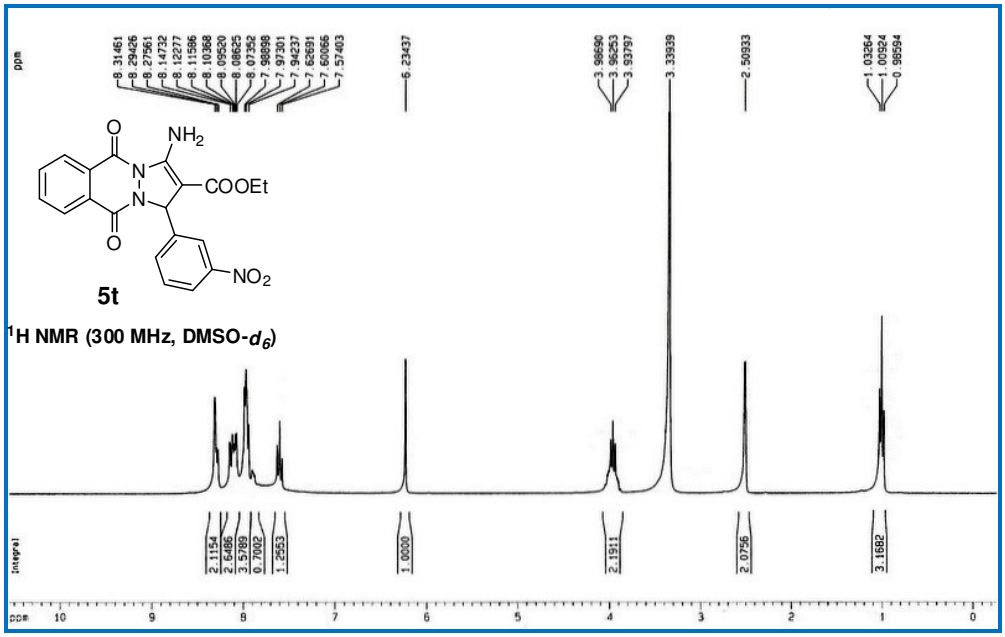

Figure S40: ^{13}C spectra of Ethyl 3-amino-1-(3-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carboxylate (5t)

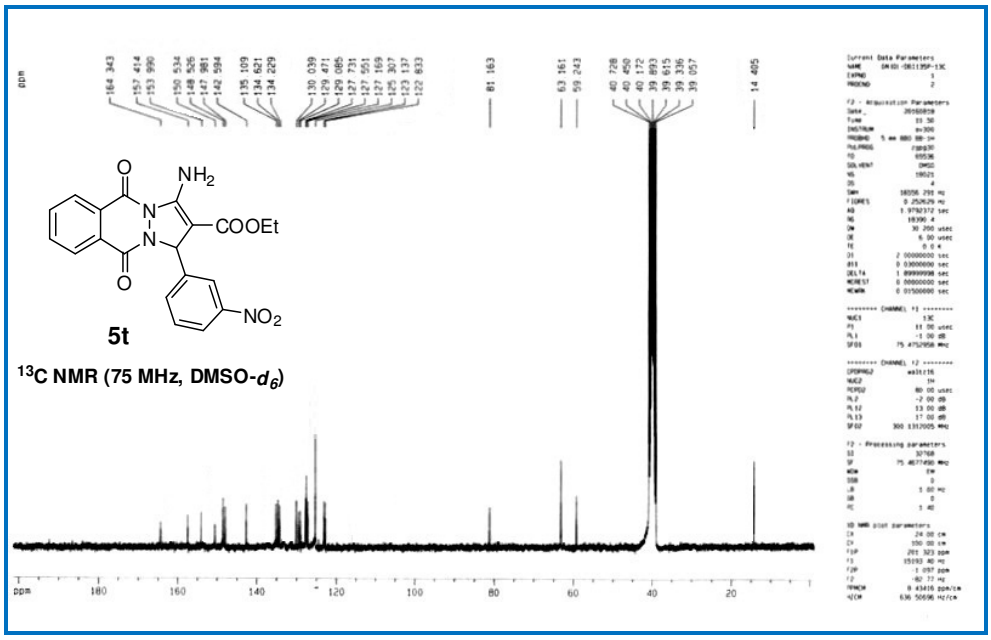

Figure S41: ^{1}H spectra of Ethyl 3-amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carboxylate (5u)

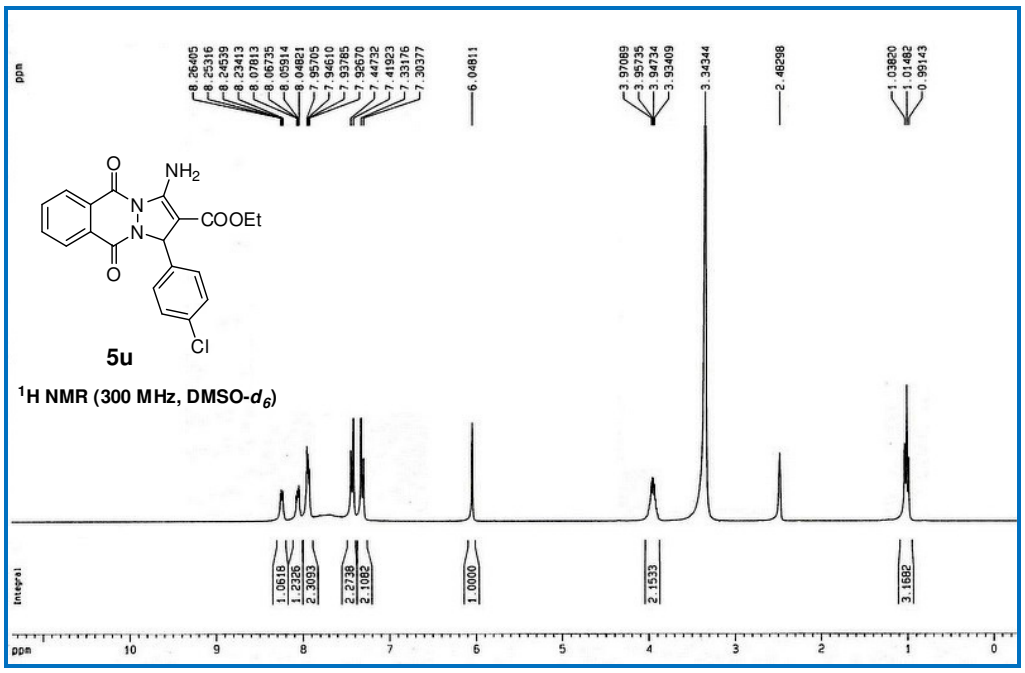

Figure S42: ^{13}C spectra of Ethyl 3-amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carboxylate (5u)

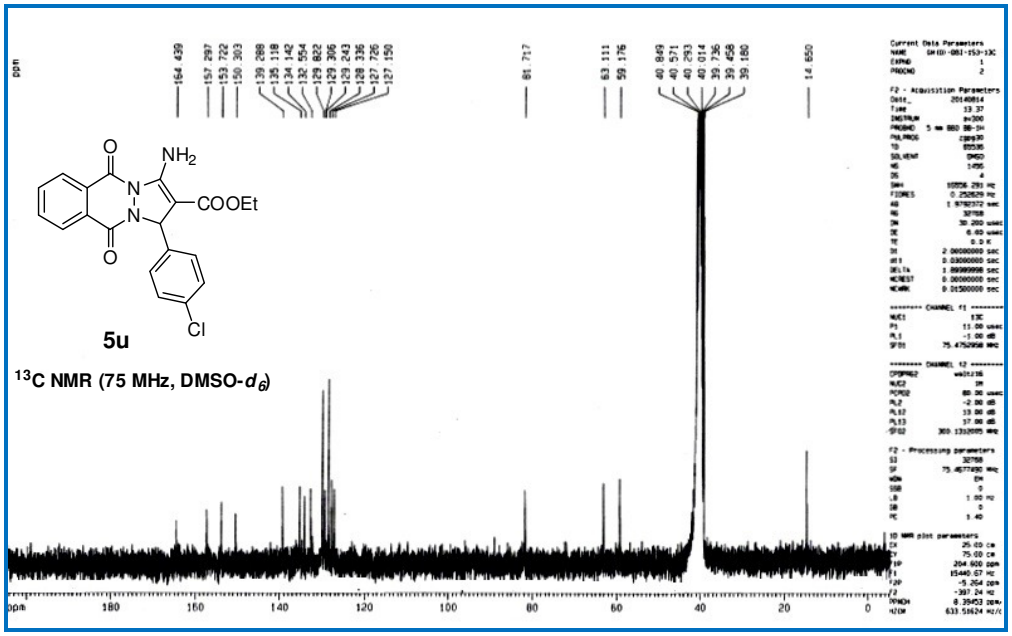

Figure S43: ^{1}H spectra of Ethyl 3-amino-1-(5-chloro-2-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carboxylate (5v)

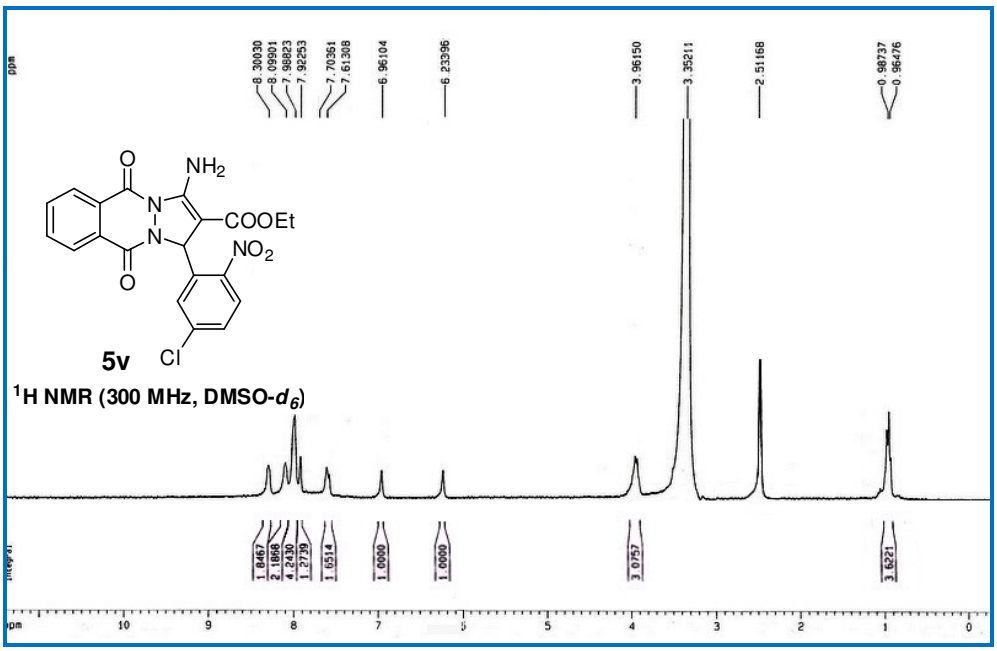

Figure S44: ^{13}C spectra of Ethyl 3-amino-1-(5-chloro-2-nitrophenyl)-5,10-dioxo-5,10-dihydro-1*H*-pyrazolo[1,2-*b*]phthalazine-2-carboxylate (5v)