Supporting Information

ONE-POT FOUR COMPONENT REACTION FOR THE SYNTHESIS OF 1-(1*H*-INDOL-2-YL)-1*H*-PYRAZOLO[1,2-*b*]PHTHALAZINE-5,10-DIONE DERIVATIVES BY SELF-CATALYSIS

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3-amino-1-(1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile 5a: Yield = 3.01 gm; M. P.: >220 ^{o}C; IR (KBr) : 3116-3440 cm^{-1} (broad, medium, -NH- group), 2218 (sharp, strong, -CN- group), 1669 cm^{-1} (sharp, strong, -CO- of amide group), 1686 cm^{-1} (sharp, strong, -CO-of amide group) ; ^{1}H- NMR (DMSO-d$_6$, 400 MHz): δ 5.67 (s, 1H, -C**H**), 7.26-8.68 (m, 11H, Ar-**H &** N**H$_2$**), δ 11.87 (s, 1H, -N**H, D$_2$O exchangeable**); ^{13}C-NMR (DMSO-d$_6$, 100 MHz): δ 61.0, 69.0, 110.1, 111.5, 115.9, 119.2, 122.9, 123.9, 127.3, 134.6, 135.8, 138.4, 144.6, 145.8, 161.0, 164.5; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 355.09650. Found: 355.09380.

3-amino-1-(1-methyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile 5b: Yield = 3.13 gm; M. P.: >220 ^{o}C; IR (KBr) 2210 (sharp, strong, -CN- group), 1667 cm^{-1} (sharp, strong, -CO- of amide group), 1680 cm^{-1} (sharp, strong, -CO-of amide group) ; ^{1}H- NMR (DMSO-d$_6$, 400 MHz): δ 2.2 (s, 3H, -C**H$_3$**), 6.07 (s, 1H, -C**H**), 7.14-8.25 (m, 11H, Ar-**H &** N**H$_2$**); ^{13}C-NMR (DMSO-d$_6$, 100 MHz): δ 50.5, 73.3, 111.5, 112.7, 114.8, 115.0, 116.5, 119.0, 127.0, 127.3, 128.0, 128.8, 135.7, 137.5, 138.8, 143.3, 151.7, 155.7; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 369.19850. Found: 355.19400.

3-amino-1-(1-ethyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile 5c: Yield = 3.06 gm; M. P.: >220 ^{o}C; IR (KBr) 2215 (sharp, strong, -CN- group), 1661 cm^{-1} (sharp, strong, -CO- of amide group), 1675 cm^{-1} (sharp, strong, -CO-of amide group) ; ^{1}H- NMR (DMSO-d$_6$, 400 MHz): δ 1.4 (t, 3H, C**H$_3$)** 4.4 (q, 2H, -C**H$_2$**), 6.06 (s, 1H, -C**H**), 7.3-8.6 (m, 11H, Ar-**H &** N**H$_2$**); ^{13}C-NMR (DMSO-d$_6$, 100 MHz):

δ 14.8, 41.9, 69.0, 74.0, 110.1, 115.9, 119.2, 122.9, 123.9, 127.3, 134.6, 135.7, 140.6, 143.7, 151.6, 155.1; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 383.25862. Found: 383. 25512.

3-amino-1-(1-butyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile 5d: Yield = 3.28 gm; M. P.: >220 ^oC; IR (KBr) 2211 (sharp, strong, -CN- group), 1664 cm^{-1} (sharp, strong, -CO- of amide group), 1679 cm^{-1} (sharp, strong, -CO-of amide group) ; ^1H- NMR (DMSO-d_6, 100 MHz): δ 1.2-2.5 (m, 9H, -C**H₂**-C**H₂**-C**H₂**-C**H₃)**, 6.10 (s, 1H, -C**H**), 7.10-8.08 (m, 11H, Ar-**H &** N**H₂**); ^{13}C-NMR (DMSO-d_6, 400 MHz): δ 15.1, 16.2, 18.3,23.3, 61.3, 68.4, 111.1, 111.4, 114.1, 118.1, 122.3, 123.3, 127.0, 133.1, 134.2, 138.1, 144.1, 145.4, 161.2, 164.7; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 411.16822. Found: 411. 16383.

3-amino-1-(1-benzyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile 5e: Yield = 3.33 gm; M. P.: >220 ^oC; IR (KBr) 2230 (sharp, strong, -CN- group), 1659 cm^{-1} (sharp, strong, -CO- of amide group), 1680 cm^{-1} (sharp, strong, -CO-of amide group) ; ^1H- NMR (DMSO-d_6, 400 MHz): δ 2.3 (s, 2H, -C**H₂)**, 6.12 (s, 1H, -C**H**), 7.11-8.09 (m, 16H, Ar-**H &** N**H₂**); ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 23.0, 61.2, 68.5, 111.2, 111.3, 113.2, 114.5, 114.6, 115.3, 115.9, 116.3, 117.8, 118.4, 122.0, 123.1, 126.2, 133.4, 134.1, 138.3, 144.2, 145.9, 161.9, 163.3; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 445.23821. Found: 445.23462.

3-amino-1-(1-phenylsulfonyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile 5f: Yield = 3.71 gm; M. P.: >220 ^oC; IR (KBr) 2232 (sharp, strong, -CN- group), 1653 cm^{-1} (sharp, strong, -CO- of amide group), 1683 cm^{-1} (sharp, strong, -CO-of amide group), 1305 cm^{-1} (sharp, strong, -SO_2- group) ; ^1H- NMR (DMSO-d_6, 400 MHz): δ 5.88 (s, 1H, -C**H**), 7.10-8.23 (m, 16H, Ar-**H &** N**H₂**); ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 60.1, 67.4, 111.1, 111.5, 113.1, 114.0, 114.4, 115.7, 115.9, 116.0, 117.5, 118.5, 122.1, 123.0, 126.4, 133.7, 134.0, 138.5, 144.1, 145.8, 161.8, 163.7; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 495.03008. Found: 495. 03458.

Ethyl-3-amino-1-(1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylate 5g: Yield = 3.21 gm; M. P.: >220 ^oC; IR (KBr) : 3110-3450 cm^{-1} (broad, medium, -NH- group), 2203 (sharp, strong, -CN- group), 1666 cm^{-1} (sharp, strong, -CO- of amide group), 1670 cm^{-1} (sharp, strong, -CO-of amide group) ; ^1H- NMR (DMSO-d_6, 400 MHz): δ 1.23 (t, 3H, -C**H₃**), 4.16 (q, 2H, -C**H₂**), 5.90 (s, 1H, -C**H**), 7.20-8.69 (m, 11H, Ar-**H &** N**H₂**), δ 11.79 (s, 1H, -N**H, D₂O exchangeable**); ^{13}C-NMR (DMSO-

d_6, 100 MHz): δ 15.3, 55.2, 60.5, 68.1, 110.3, 111.4, 115.0, 117.2, 122.0, 123.5, 127.2, 133.0, 134.9, 137.3, 142.5, 144.5, 160.1, 162.4; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 402.14340. Found: 402.14600.

Ethyl-3-amino-1-(1-methyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylate 5h: Yield = 3.32 gm; M. P.: >220 ^oC; IR (KBr) 2213 (sharp, strong, -CN- group), 1664 cm^{-1} (sharp, strong, -CO- of amide group), 1683 cm^{-1} (sharp, strong, -CO-of amide group) ; ^1H- NMR (DMSO-d_6, 400 MHz): δ 1.12 (t, 3H, -C**H₃**), 2.24 (s, 3H, -C**H₃**), 4.00 (q, 2H, -C**H₂**), 5.89 (s, 1H, -C**H**), 7.22-8.64 (m, 11H, Ar-**H &** N**H₂**); ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 15.3, 22.5, 56.3, 61.4, 67.0, 111.4, 113.5, 114.7, 118.0, 122.0, 122.7, 125.0, 132.4, 134.6, 138.0, 144.1, 143.5, 160.2, 163.5; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 416.23842. Found: 416.23582.

Ethyl-3-amino-1-(1-ethyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylate 5i: Yield = 3.44 gm; M. P.: >220 ^oC; IR (KBr) 2212 (sharp, strong, -CN- group), 1660 cm^{-1} (sharp, strong, -CO- of amide group), 1678 cm^{-1} (sharp, strong, -CO-of amide group) ; ^1H- NMR (DMSO-d_6, 400 MHz): δ 1.16 (t, 3H, -C**H₃**), 1.61 (t, 3H, C**H₃)** 3.92 (q, 2H, -C**H₂**), 4.12 (q, 2H, -C**H₂**), 6.01 (s, 1H, -C**H**), 7.20-8.90 (m, 11H, Ar-**H &** N**H₂**); ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 15.2, 19.4, 23.6, 54.3, 60.2, 68.4, 111.5, 111.7, 114.0, 118.1, 122.3, 124.1, 126.8, 133.4, 134.9, 138.1, 144.2, 145.5, 161.6, 164.6; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 430.01340. Found: 430.01810.

Ethyl-3-amino-1-(1-butyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylate 5j: Yield = 3.66 gm; M. P.: >220 ^oC; IR (KBr) 2210 (sharp, strong, -CN- group), 1668 cm^{-1} (sharp, strong, -CO- of amide group), 1676 cm^{-1} (sharp, strong, -CO-of amide group) ; ^1H- NMR (DMSO-d_6, 400 MHz): δ 1.21 (t, 3H, -C**H₃**), 1.3-2.4 (m, 9H, -C**H₂**-C**H₂**-C**H₂**-C**H₃)**, 4.13 (q, 2H, -C**H₂**), 5.92 (s, 1H, -C**H**), 7.12-8.00 (m, 11H, Ar-**H &** N**H₂**); ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 14.8, 16.2, 16.3, 17.0, 20.1, 54.0, 60.2, 67.3, 110.3, 111.2, 113.8, 117.2, 120.2, 122.4, 126.2, 132.6, 134.5, 137.0, 143.8, 145.2, 161.3, 164.0; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 458.60013. Found: 458.60470.

Ethyl-3-amino-1-(1-benzyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylate 5k: Yield = 3.69 gm; M. P.: >220 ^oC; IR (KBr) 2240 (sharp, strong, -CN- group), 1679 cm^{-1} (sharp, strong, -CO- of amide group), 1690 cm^{-1} (sharp, strong, -CO-of amide group) ; ^1H- NMR (DMSO-d_6, 400 MHz): δ 1.25 (t, 3H, -C**H₃**), 2.21 (s, 2H, -C**H₂)**, 4.16 (q, 2H, -C**H₂**), 5.92 (s, 1H, -C**H**), 7.21-8.29 (m, 16H, Ar-**H &** N**H₂**); ^{13}C-

NMR (DMSO-d_6, 100 MHz): δ 14.9, 23.1, 55.4, 62.0, 65.4, 110.1, 111.2, 114.2, 114.4, 114.6, 115.1, 115.5, 116.3, 116.7, 118.0, 122.1, 123.4, 126.5, 133.3, 134.1, 138.3, 144.0, 145.9, 162.8, 163.8; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 492.92601. Found: 492.92461.

Ethyl-3-amino-1-(1-phenylsulfonyl-1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylate 5l: Yield = 4.06 gm; M. P.: >220 ^oC; IR (KBr) 2231 (sharp, strong, -CN- group), 1652 cm^{-1} (sharp, strong, -CO- of amide group), 1684 cm^{-1} (sharp, strong, -CO-of amide group), 1303 cm^{-1} (sharp, strong, -SO_2- group) ; ^{1}H- NMR (DMSO-d_6, 400 MHz): δ 1.23 (t, 3H, -C**H$_3$**), 5.99 (s, 1H, -C**H**), 4.15 (q, 2H, -C**H$_2$**), 7.10-8.24 (m, 16H, Ar-**H &** N**H$_2$**); ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 14.9, 54.7, 60.2, 67.3, 111.0, 111.0, 113.2, 114.1, 114.3, 115.6, 115.9, 116.0, 117.4, 118.5, 122.6, 123.1, 126.3, 133.5, 134.1, 138.5, 144.1, 145.4, 161.6, 163.8; HRMS calcd for $C_{20}H_{13}N_5O_2$ $[M+H]^+$: 542.23048. Found: 542.23403.

Figures:

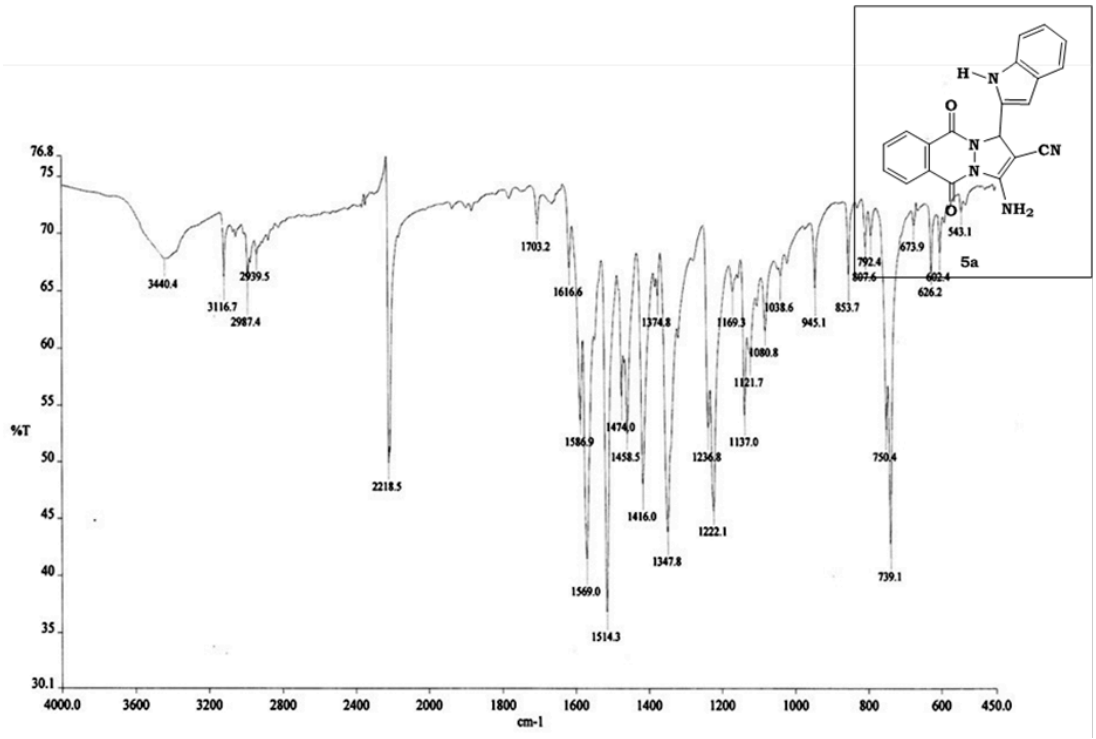

Figure-S1: FTIR spectrum of 3-amino-1-(1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile.

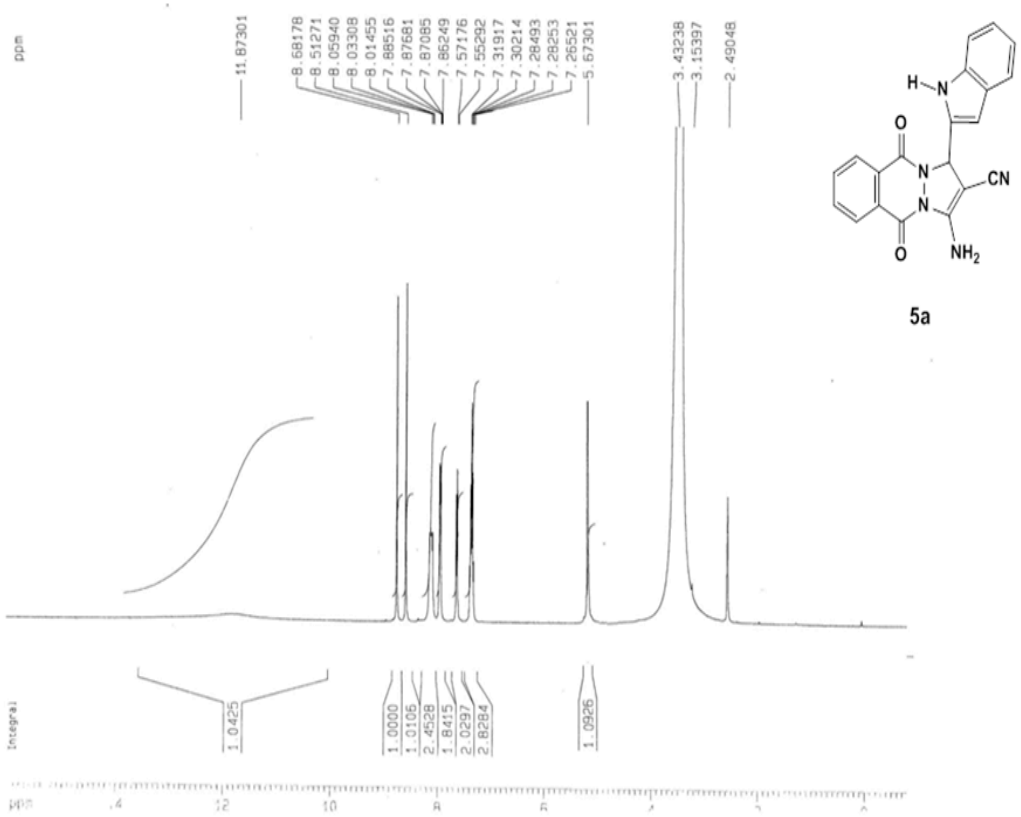

Figure-S2: [1]H NMR spectrum of 3-amino-1-(1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile.

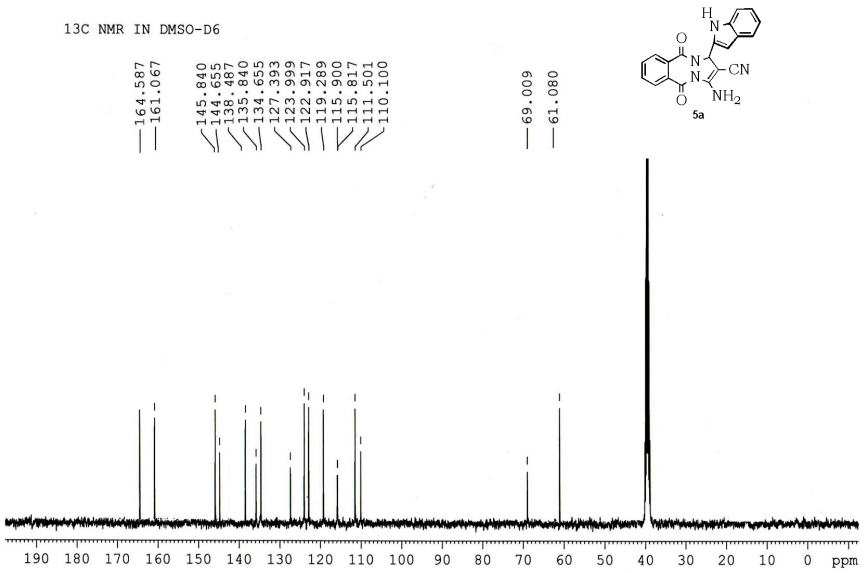

Figure-S3: [13]H NMR spectroscopy for the 3-amino-1-(1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile.

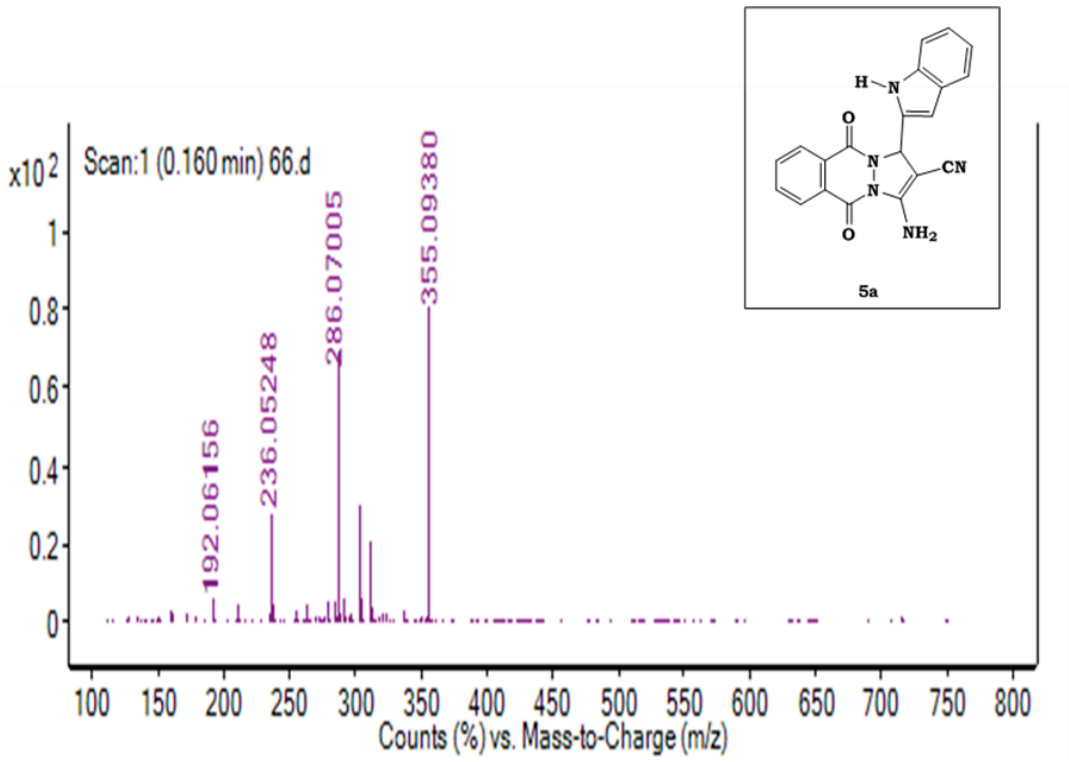

Figure-S4: Mass spectrometric image for the 3-amino-1-(1H-indol-2-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile.