Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A green and clean pathway: One pot, multicomponent, visible light assisted synthesis of pyrano[2,3-c]pyrazoles under catalyst-free and solvent-free conditions

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Experimental Section

General Information:

Reagents were obtained from commercial suppliers and used without further purification unless otherwise specified by a reference. All reactions were performed using oven-dried glassware. Organic solutions were concentrated using a Buchi rotary evaporator. TLC was performed using silica gel GF254 (Merck) plates. Melting points were determined by open glass capillary method and are uncorrected. IR spectra in KBr were recorded on a Perkin-Elmer 993 IR spectrophotometer, ^{1}HNMR spectra were recorded on a Bruker AVII 400 spectrometer in $CDCl_3$, DMSO-d_6 using TMS as internal reference with chemical shift value being reported in ppm. All coupling constants (J) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded on the same instrument at 100 MHz in $CDCl_3$ and DMSO-d_6 and TMS was used as internal reference.

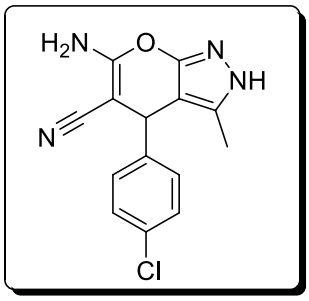
General method

We took 1.0 mmol of ethylacetoacetate (**1**) or diethyl acetylene dicarboxylate (**6**) and hydrazine hydrate (**2**) in round bottom flask. The mixture was irradiated with 22 W CFL stirring at rt for 1–5 min. After the completion of the reaction (monitored by TLC), aromatic aldehyde (**3**) and malononitrile (**4**) was added. On completion of the reaction (monitored by TLC) water was added and the compound was filtered. Solid was washed with water and the resulting crude product was purified by recrystalization and some of them are purified by column

chromatography by using ethyl acetate and hexane as eluent. A yield of 56-88% (**5a-m**) and 63-90% (**7a-h**) was obtained. The product was confirmed by IR, ^{1}H and mass spectra. All the compounds that were obtained are known and were characterized by comparison of their spectral data with those reported in literature.[18a, 18b, 18d, 20, 22, 23, 24a, 24b.]

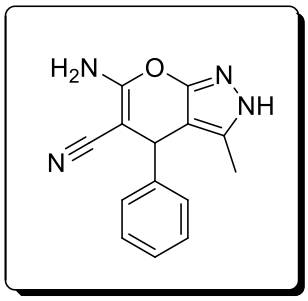
**Cautionary note: Before using hydrazine hydrate we must use laboratory glasses, gloves and mask.*

Spectral data of synthesized compounds:



5 (a) 6-amino-4-(4-chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

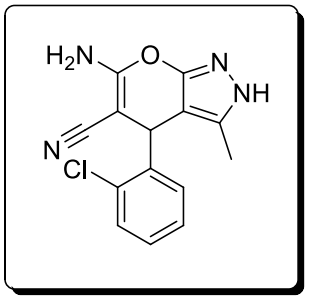
IR (KBr) ν (cm^{-1}): 871, 1260, 1388, 1588, 1635, 2935, 3020, 3419; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.93 (s, 3H), 5.16 (s, 1H), 6.93 (s, 2H), 7.10-7.78 (m, 4H), 12.42 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*: 10.1, 36.8, 57.8, 98.8, 121.7, 127.0, 127.9, 129.2, 136.8, 143.9, 155.1, 161.2; MS (ESI) *m/z*: 286.



5 (b) 6-amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

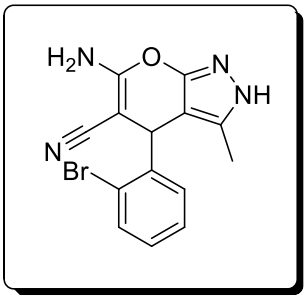
IR (KBr) ν (cm^{-1}): 1040, 2198, 3177, 3316, 3380; ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 1.79 (s, 3H), 4.56 (s, 1H), 6.87 (s, 2H), 7.17-7.24 (m, 3H), 7.27-7.31 (m, 2H), 12.06 (s, 1H); ^{13}C NMR

(100 MHz, DMSO-d_6) δ: 9.8, 36.2, 57.3, 97.8, 120.8, 126.9, 127.6, 128.9, 135.8, 144.7, 154.9, 161.0; MS (ESI) *m/z*: 252.



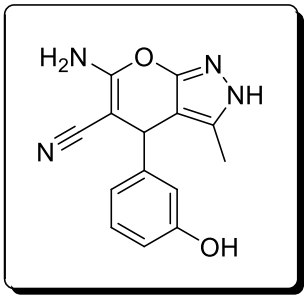
5 (c) 6-amino-4-(2-chorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr) ν (cm^{-1}): 764, 1060, 1418, 1498, 1609, 1658, 2195, 3165, 3395; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ: 1.95 (s, 3H), 5.08 (s, 1H), 6.77 (s, 2H), 7.07-7.34 (m, 3H), 7.74-7.81 (m, 1H), 12.19 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 10.2, 36.5, 57.4, 98.6, 121.1, 127.2, 127.5, 127.6, 128.0, 129.5, 136.1, 144.0, 155.9, 161.3; MS (ESI) *m/z*: 286.



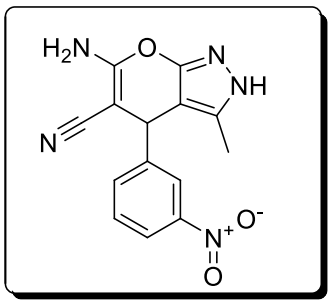
5 (d) 6-amino-4-(2-bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr) ν (cm^{-1}): 556, 1057, 2195, 3150, 3314, 3397; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.76 (s ,3H), 5.08 (s, 1H), 6.96 (s, 2H), 7.14-7.17 (m, 2H), 7.33 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 12.14 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 9.8, 35.6, 55.7, 96.7, 120.4, 122.5, 128.4, 128.6, 130.7, 132.3, 133.5, 135.6, 154.5, 161.4; MS (ESI) *m/z*: 330.



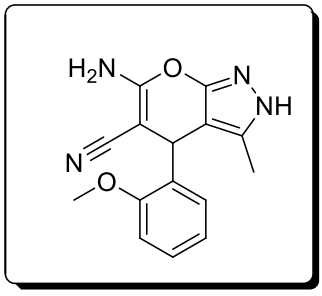
5 (e) 6-Amino-4-(3-hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile*:*

IR (KBr) ν (cm^{-1}): 1068, 1270, 1409, 1485, 1605, 1658, 2189, 3173, 3372; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.79 (s, 3H), 4.49 (s, 1H), 6.54 (s, 1H), 6.71 (m, 2H), 6.84 (s, 2H), 7.06 (t, J = 8.2 Hz, 1H), 9.34 (s, 1H), 12.07 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 14.7, 41.5, 62.6, 102.7, 119.2, 119.5, 123.7, 126.3, 134.4, 140.6, 151.3, 160.0, 162.8, 166.3; MS (ESI) *m/z*: 268.



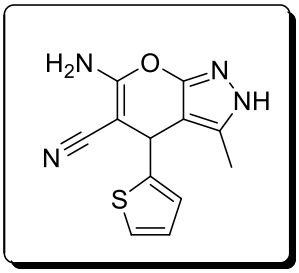
5 (f) 6-amino-3-methyl-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr) ν (cm^{-1}): 1073, 1340, 1402, 1533, 1605, 1658, 2192, 2936, 3112, 3214, 3465; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ: 1.93 (s, 3H), 4.77 (s, 1H), 6.22 (s, 2H), 7.57 (t, 1H, J = 8.2 Hz), 7.64 (d, 1H, J = 7.6 Hz), 8.02–8.04 (m, 2H), 11.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ: 9.6, 29.4, 56.9, 112.8, 120.4, 123.4, 128.6, 128.8, 135.9, 141.5, 146.8, 151.6, 154.8, 160.7; MS (ESI) *m/z*: 297.



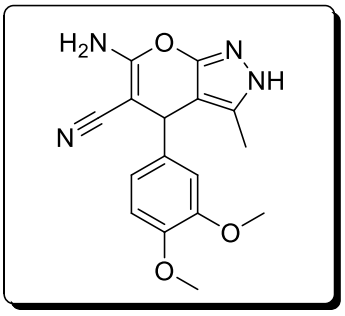
5 (g) 6-amino-4-(2-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr) ν (cm^{-1}): 1045, 2190, 2833, 3156, 3317, 3369; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.77 (s, 3H), 3.76 (s, 3H), 4.98 (s, 1H), 6.79 (s, 2H), 6.89-6.93 (m, 1H), 6.97-7.01 (m, 2H), 7.19- 7.22 (m, 1H), 12.00 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 9.6, 29.2, 55.7, 56.6, 97.4, 111.4, 120.9, 120.6, 127.9, 128.3, 132.3, 134.7, 155.3, 156.5, 161.5; MS (ESI) *m/z*: 282.



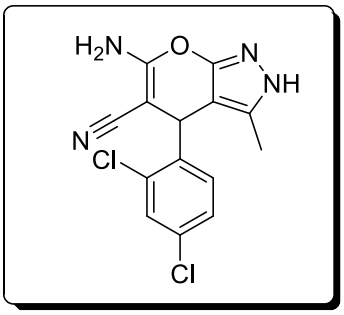
5 (h) 6-amino-3-methyl-4-(thiophen-2-yl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr) ν (cm^{-1}): 1046, 2191, 3170, 3309, 3359; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.87 (s, 3H), 4.93 (s, 1H), 6.85-6.93 (m, 4H), 7.30-7.31 (m, 1H), 12.07 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 9.8, 31.5, 57.7, 97.7, 120.8, 124.5, 124.7, 126.6, 136.5, 149.5, 154.0, 160.9; MS (ESI) *m/z*: 258.



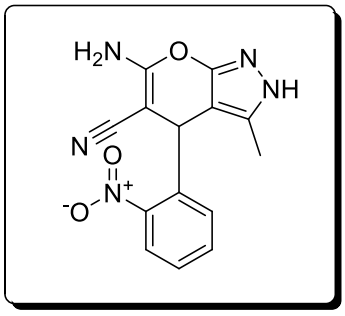
5 (i) 6-amino-4-(3,4-dimethoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile:

IR (KBr) ν (cm^{-1}): 1040, 1406, 1509, 1605, 1641, 2194, 2894, 3133, 3260, 3382; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ: 1.77 (s, 3H), 3.56 (s, 3H), 3.67 (s, 3H), 4.48 (s, 1H), 5.97 (s, 2H), 6.65 (d, *J* = 6.7 Hz, 1H), 6.72 (s, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 11.23 (s, 1H); ^{13}C NMR (DMSO-d_6 + $CDCl_3$, 100 MHz) δ: 10.0, 36.8, 55.7, 55.8, 60.2, 97.0, 104.3, 104.6, 104.8, 120.8, 135.6, 139.4, 152.7, 152.8, 155.0, 160.6; MS (ESI) *m/z*: 312.



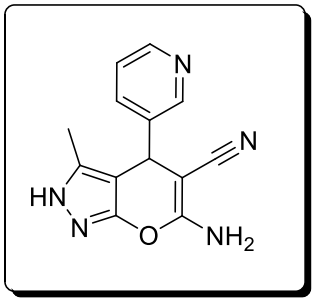
5 (j) 6-Amino-4-(2,4-dichlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr) ν (cm^{-1}): 1066, 1402, 1495, 1605, 1635, 2194, 3195, 3482; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.79 (s, 3H), 5.07 (s, 1H), 7.02 (s, 2H), 7.22 (d, J = 8.2 Hz, 1H), 7.36 (dd, J = 2.2 Hz, 8.2 Hz, 1H), 7.58 (d, J = 2.2 Hz, 1H), 11.26 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 9.7, 36.0, 55.4, 96.5, 120.4, 126.5, 128.6, 132.8, 132.3, 132.6, 135.6, 140.2, 145.4, 161.2; MS (ESI) *m/z*: 320.



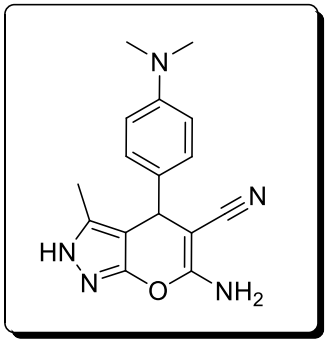
5 (k) 6-amino-4-(2-nitrophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr) ν (cm^{-1}): 1042, 1162, 1353, 1405, 1496, 1520, 1641, 2191, 2875, 2925, 2960, 3162, 3318, 3370, 3415; ^{1}H NMR (400 MHz, CD_3OD) δ: 1.88 (s, 3H), 5.28 (s, 1H), 6.24 (s, 2H), 7.36 (d, J = 8.2 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 11.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ: 10.4, 29.2, 56.3, 99.2, 118.2, 120.5, 128.3, 129.2, 130.6, 135.4, 138.4, 155.0, 161.4, 165.3; MS (ESI) *m/z*: 297.



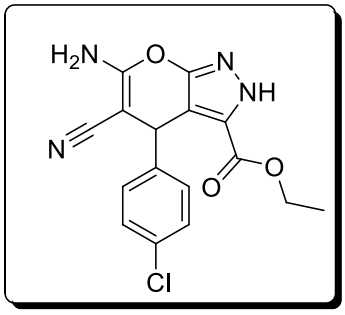
5 (l) 6-Amino-3-methyl-4-(pyridin-3-yl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr): 1051, 1420, 1500, 1602, 1640, 2208, 3172, 3356, 3390 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.74 (s, 3H), 4.65 (s, 1H), 6.95 (s, 2H), 7.26 (dd, J = 3.4 Hz,12.2 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 8.35 (s, 1H), 8.36 (d, J = 2.6 Hz, 1H), 12.14 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 9.9, 33.8, 56.4, 96.9, 120.8, 124.0, 135.4, 135.5, 139.9, 148.4, 148.5, 154.9, 161.4; MS (ESI) *m/z*: 253.



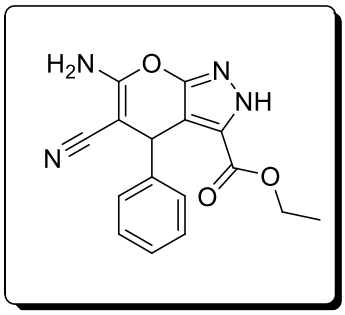
5 (m) 6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile:

IR (KBr) ν_{max}(cm^{-1}): 1060, 2184, 3177, 3308, 3382,. ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 1.76 (s, 3H), 3.36 (s, 6H), 4.46 (s, 1H), 6.67 (d, J = 8.2 Hz, 2H), 6.75 (s ,2H), 6.97 (d, J = 8.2 Hz, 2H), 12.04 (s, 1H); ^{13}CNMR (100 MHz, DMSO-d_6) δ: 9.6, 35.4, 57.7, 98.3, 112.4, 120.4, 127.5, 132.2, 135.6, 149.3, 154.9, 160.7; MS (ESI) *m/z*: 295.



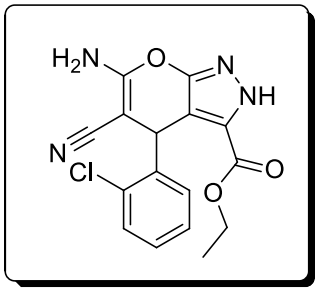
(7a) Ethyl-6-amino-4-(4-chlorophenyl)-5-cyano-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate:

IR (KBr) ν (cm^{-1}): 1636, 1732, 2190, 2980, 3465; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.96 (t, J= 6.2 Hz, 3H), 4.04 (q, J = 6.2 Hz, 2H), 4.73 (s, 1H), 7.04 (s, 2H), 7.08 (d, J = 9.2 Hz, 2H), 7.27 (d, J = 9.2 Hz, 2H), 13.75 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 14.8, 36.2, 57.4, 61.8, 103.8, 120.8, 128.0, 129.9, 129.0, 131.8, 144.8, 155.0, 158.6, 160.9; MS (ESI) *m/z*: 344.



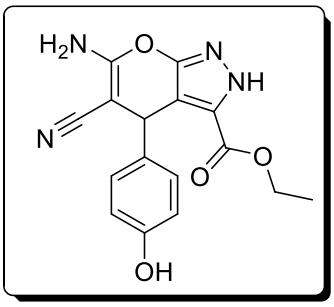
(7b) Ethyl-6-amino-5-cyano-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate:

IR (KBr) ν (cm^{-1}): 1640, 1712, 2190, 2367, 3308, 3415; ^{1}HNMR (400 MHz, DMSO-d_6) δ: 1.10 (t, J = 6.1 Hz, 3H), 4.13 (q, J = 6.2 Hz, 2H), 4.83(s, 1H), 6.10 (s, 2H), 7.28–7.15 (m, 5H), 13.79 (s, 1H); ^{13}C NMR(100 MHz, DMSO-d_6) δ: 13.8, 36.2, 60.0, 60.8, 103.5, 119.2, 126.6, 126.2, 127.9, 129.6, 144.0, 155.8, 158.5, 160.0; MS (ESI) *m/z*: 310.



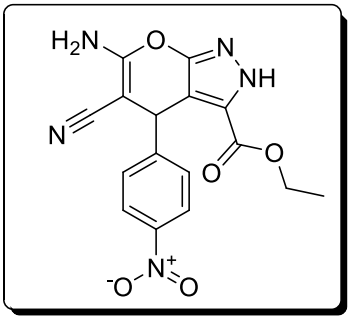
(7c) Ethyl-6-amino-4-(2-chlorophenyl)-5-cyano-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate:

IR (KBr) ν (cm^{-1}): 1648, 1692, 2190, 2985, 3468; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.95 (t, J= 6.2 Hz, 3H), 4.06 (q, J = 6.1 Hz, 2H), 5.28 (s, 1H), 7.07 (s, 2H), 7.40–7.28 (m, 4H), 13.78 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 13.0, 34.8, 56.6, 60.1, 102.7, 119.2, 127.5, 128.6, 130.0, 129.7, 130.8, 131.8, 132.5, 141.8, 157.3, 160.7; MS (ESI) *m/z*: 344.



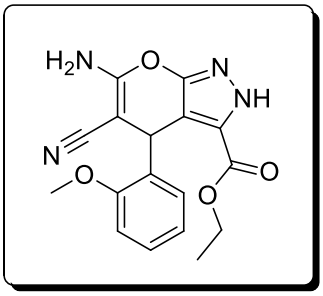
(7d) Ethyl-6-amino-5-cyano-4-(4-hydroxyphenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate:

IR (KBr) ν (cm^{-1}): 1646, 1708, 2196, 2988, 3453; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.07 (t, J = 6.2 Hz, 3H), 4.12 (q, J= 6.2 Hz, 2H), 4.64 (s, 1H), 6.62 (d, J = 6.2 Hz, 2H), 6.85(d, J= 6.2 Hz, 2H), 6.93 (s, 2H), 9.24 (s, 1H), 13.65 (s, 1H); ^{13}C NMR(100 MHz, DMSO-d_6) δ: 13.3, 36.6, 58.9, 70.0, 104.9, 115.0, 120.9, 128.8, 135.9, 128.2, 155.0, 156.0, 158.8, 160.0; MS (ESI) *m/z*: 326.



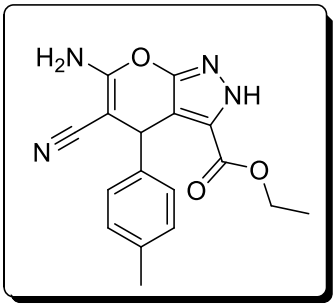
(7e) Ethyl-6-amino-5-cyano-4-(4-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate:

IR (KBr) ν (cm^{-1}): 1640, 1730, 2205, 2991, 3496; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.06 (t, J= 6.2 Hz, 3H), 4.07 (q, J= 6.2 Hz, 2H), 4.93 (s, 1H), 7.17 (s, 2H), 7.37 (d, J= 9.1 Hz, 2H), 8.18 (d, J= 9.1 Hz, 2H), 13.88 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 13.8, 36.6, 56.6, 60.0, 101.8, 119.5, 123.8, 128.0, 128.3, 146.2, 151.2, 155.5, 157.9, 159.2; MS (ESI) *m/z*: 355.



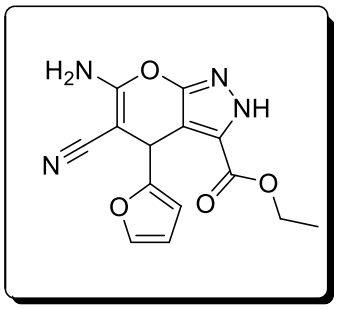
(7f) Ethyl-6-amino-5-cyano-4-(2-methoxyphenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate:

IR (KBr) ν (cm^{-1}): 1638, 1712, 2198, 2996, 3446; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.04 (t, J= 7.4 Hz, 3H), 3.75 (s, 3H), 4.06 (q, J= 7.2 Hz, 2H), 5.15 (s, 1H), 6.22 (s, 2H), 6.96–6.75 (m, 3H), 7.15 (d, J= 6.3, Hz, 1H), 13.81 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 13.8, 31.8, 55.6, 58.7, 60.8, 103.8, 110.2, 119.2, 120.4, 127.8, 128.8, 128.3, 132.6, 156.6, 156.7, 158.6, 160.8; MS (ESI) *m/z*: 340.



(7g) Ethyl-6-amino-5-cyano-4-(p-tolyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate:

IR (KBr) ν (cm^{-1}): 1640, 1735, 2190, 2927, 3280, 3452; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.16 (t, J= 6.3 Hz, 3H), 2.33 (s, 3H), 4.19 (q, J= 6.2 Hz, 2H), 7.44 (s, 2H), 4.85 (s, 1H), 7.08–7.05 (d, J = 9.3 Hz, 2H), 7.13–7.10 (d, J = 9.3 Hz, 2H), 13.77 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 13.9, 20.2, 36.9, 60.8, 60.2, 103.9, 120.5, 127.5, 128.0, 129.8, 135.2, 141.5, 155.0, 158.8, 159.0; MS (ESI) *m/z*: 324.



(7h) Ethyl-6-amino-5-cyano-4-(furan-2-yl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate:

IR (KBr) ν (cm^{-1}): 1642, 1712, 2190, 2928, 3404; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.25 (t, J = 9.2 Hz, 3H), 4.26 (q, J = 9.2 Hz, 2H), 4.96 (s, 1H), 6.08 (d, J = 6.2 Hz, 1H), 6.12 (s, 2H), 6.26 (s, 1H), 7.62 (d, J = 6.3 Hz, 1H), 13.44 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 12.1, 30.6, 55.9, 60.0, 100.8, 104.0, 109.0, 119.9, 128.2, 140.8, 144.2, 155.0, 157.9, 160.6; MS (ESI) *m/z*: 300.

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