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EXPERIMENTAL PAPER

Access to a Library of Pyrano[3,2-c]quinolines Using $NiFe_2O_4$@SiO_2 Bonded Ionic Liquid

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Pyrans and quinolines are at the core of bioactive materials with interesting pharmacological effects. Several compounds containing quinoline fused to pyrans, such as pyrano[3,2-c]quinolines, have also shown valuable properties. Pyranoquinoline frameworks have been identified in important natural compounds, including oricine, huajiaosimuline and flindersine (Scheme 1). Similar structures have a broad range of such pharmacological properties as anti-inflammatory, antibacterial, antitubercular, antiproliferative and anti-tubulin activities; some are selective σ1 receptor ligands, and some are mitotic kinesin-5 inhibitors.[1–10]

Thus, the synthesis of pyranoquinolines is of considerable interest. Among the different methods used for the preparation of pyranoquinolines, multicomponent reactions of 4-hydroxy-quinolin-2(1H)-one, malononitrile, and aldehydes are simple and practical methods. This approach requires the use of base catalysts and published sources have reported the use of piperidine,[11] triethanolamine,[12] tris-hydroxymethylaminomethane (THAM),[13] Na_2CO_3,[10] and di-*n*-butylamine (DBA).[14]

The reported strategies have been useful in moving the field forward, but up-to-date heterogeneous catalysis may offer improvements in efficiency and convenience. The immobilization of ionic liquids facilitates the separation of the catalyst from the reaction mixture and in addition, increases the selectivity of the catalyst. Several examples of the use of ionic liquids immobilized on magnetic nanoparticles in synthetic organic chemistry have been reported.[15–19] We now report an efficient and facile procedure for the convenient access of functionalized pyrano[3,2-c]quinolines *via* a one-pot, a three-component reaction using $NiFe_2O_4$@SiO_2 bonded 3-methyl-1-(3-(trimethoxysilylpropyl)-1*H*-imidazolium hydrogen sulfate **(A)** as an efficient catalyst (Scheme 2). The Experimental section and the Supplementary Materials provide the details on the preparation and characterization of the catalyst.

As our initial model, we studied the three-component reaction of 4-hydroxyquinolin-2(1H)-one (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol). The process was examined solvent-free and in the presence of different solvents, at different temperatures and with different catalyst doses. The results are summarized in Table 1.

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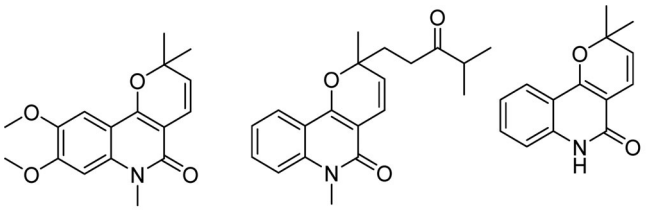
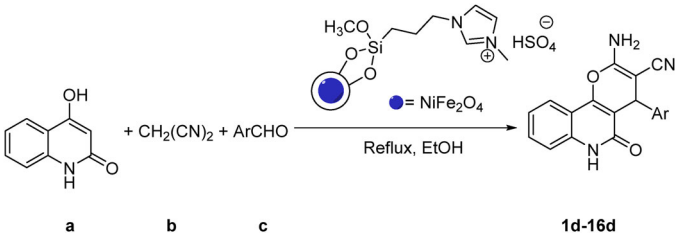


Scheme 1. Structures of the drugs oricine, huajiaosimuline and flindersine.



Scheme 2. Catalytic three-component synthesis of pyrano[3,2-c]quinolines.

Table 1. Optimization of the reaction conditions: Synthesis of **1d.**

Entry	Catalyst (g)	Solvent (3 mL)	Yield (%)[a]
1	0.025	-; 100 °C	35
2	–	EtOH; Reflux	–
3	0.025	EtOH; Reflux	75
4	0.025	CH_2Cl_2; Reflux	–
5	0.025	*n*-Hexane; Reflux	–
6	0.025	EtOAc; Reflux	20
7	0.025	H_2O; Reflux	25
8	0.025	EtOH (50%); Reflux	94
9	0.05	EtOH (50%); Reflux	92
10	0.075	EtOH (50%); Reflux	88
11	0.1	EtOH (50%); Reflux	89
12	0.01	EtOH (50%); Reflux	30

[a]Isolated yields; reaction time 100 min.

The solvent has a significant effect on the product yield. Aqueous ethanol produced high yields. The productivity of the reaction is low in water and under solvent-free condition. No product was obtained when catalyst was absent. Use of 0.025 g of **(A)** as a catalyst and ethanol (50%, at reflux) produced the best yield over a reaction time of 100 min (94%).

With the best reaction conditions having been determined, several derivatives of pyrano[3,2-c]quinoline were prepared, using 4-hydroxyquinolin-2(1H)-one, malononitrile and aromatic aldehydes bearing both electron-withdrawing and electron-donating groups. The results are summarized in Table 2 (products **1d-16d**). Yields were excellent (mean 91%). The reactions were monitored by thin layer chromatography (TLC). It was noted that some aldehydes with electron-withdrawing/halogen groups (NO_2, Cl, Br) achieved TLC completion somewhat faster than those containing electron-donating groups (CH_3, OCH_3). The NMR and elemental analysis data were consistent with the structures proposed for the products.

Table 2. Preparation of **1d-16d** using **(A)** as catalyst.

Product	Aldehyde	Time (min)	Yield (%)*
1d	PhCHO	100	94
2d	4-ClPhCHO	80	96
3d	3-ClPhCHO	80	95
4d	2-ClPhCHO	95	90
5d	4-BrPhCHO	80	97
6d	4-NO_2PhCHO	70	84
7d	4-CH_3PhCHO	120	87
8d	4-CH_3OPhCHO	140	89
9d	2,4-Cl_2PhCHO	90	87
10d	3,5-Cl_2PhCHO	75	96
11d	3-BrPhCHO	150	81
12d	3,4-Cl_2PhCHO	70	96
13d	3-NO_2PhCHO	70	90

*Isolated yields.

Table 3. Reusability of **(A)**.

Run	1	2	3	4	5	6	7	8	9
Yield (%)[a]	94	93	92	89	91	90	89	88	87

[a]Isolated yields; reaction time 100 min.

Thus the ^{1}H-NMR spectrum of compound **1d** showed the amide hydrogen (N-H) located at δ 0.71 as a singlet. The ^{13}C-NMR spectrum of compound **1d** revealed 17 carbon signals, among these the C = O carbon at δ 161.2.

The catalyst could be recovered from the reaction medium by an external magnet (see Experimental section) and then used for new reactions for the preparation of (**1d**), remaining effective through a substantial number of cycles (Table 3).

Summing up, the title catalyst permitted the preparation of pyranoquinolines under mild conditions from 4-hydroxyquinolin-2(1H)-one, malononitrile and substituted benzaldehydes. Yields were excellent. The products were isolated from the reaction mixtures in a simple procedure. The procedure has the advantage of using a recoverable heterogeneous catalyst.

Experimental section

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. The powder X-Ray diffraction patterns were measured with a Bruker D8 Advance diffractometer using Cu-Kα irradiation. The NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). Elemental analysis was performed on a Heraeus CHN-O-Rapid analyzer. FE-SEM coupled with EDAX was taken using a Hitachi S-4160 photograph to examine the shape and metallic composition of the samples. Melting points were obtained on a Electrothermal IA9200 instrument and are uncorrected. Infrared spectra were taken using a Shimadzu IRTracer-100 instrument.

Preparation of $NiFe_2O_4$

$NiCl_2{\cdot}6H_2O$ (molecular weight 237 g/mol, 65 mmol, 15.4 g) and $FeCl_3{\cdot}6H_2O$ (molecular weight 270 g/mol, 130 mmol, 35.1 g), with the molar ratio of 1:2, were dissolved in

200 mL of deionized water under mechanical stirring. The final weight ratio of salts/water was 1/4. A dilute solution of NH_4OH was added dropwise to the mixture until the pH was 11. After precipitation, the solid was filtered, washed with deionized water and calcined in an electric furnace at 700 °C.

Preparation of $NiFe_2O_4$@SiO_2

To a dispersion of $NiFe_2O_4$ nanoparticles (3 g) in 150 mL ethanol, tetraethyl orthosilicate (TEOS) (7 mL) was added and mechanically stirred for 1 h. Afterward the pH of the solution was adjusted to 8.5 with 20% aqueous ammonium hydroxide. After 48 of mechanically stirring the mixture, $NiFe_2O_4$@SiO_2 was separated with an external magnet, washed with water (25 mL) three times, and dried at 100 °C in air.

Preparation of the title nanoparticles (A)

(3-Chloropropyl)trimethoxysilane (3 mmol) was combined with *N*-methyl imidazole (3 mmol) in 20 mL of toluene and the mixture was kept at reflux for 24 h. Next, the mixture was combined with $NiFe_2O_4$@SiO_2 (3 g) and stirred for 24 h at reflux. Finally, the mixture was washed with ethanol (20 mL) twice, dried, and dispersed in 100 mL of $CHCl_3$, to which was added dropwise sulfuric acid (4 mmol, 98%), and the mixture refluxed for 6 h. Next, the resulting solid was separated, washed with diethyl ether (25 mL), and dried. The characterization data for the catalyst are available in the Supplementary Materials of the online version of this article or from the corresponding author upon request.

Preparation of 1d-16d

A mixture of **a**, **b**, **c** (each 1 mmol) and **(A)** (0.025 g) was refluxed in ethanol (50%). After the completion of the reaction (TLC monitoring, (silica gel 60 F_{254}); EtOAc:hexane 10:90 v/v), the solid formed in the reaction mixture was dissolved in hot ethanol. Next, an external magnet was glued to the outer surface of the reaction vessels and the magnetic catalyst adhered to the inner surface of the vessel. The solution phase was filtered, and the crude product was recrystallized from ethanol to afford the desired pure products.

2-Amino-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (1d)

Yield 94%, mp 297-299 °C. IR (KBr, cm^{-1}) 3504, 3401, 3023, 2179, 1679, 1605, 1509, 1388, 1254, 1175, 1121, 1103, 907, 758; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.54 (s, 1H, CH), 7.02 (s, 2H, NH_2), 7.19-7.24 (m, 3H), 7.29-7.39 (m, 4H), 7.63 (t, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 10.71 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 37.1, 58.1, 109.2, 113.7, 115.1, 120.1, 123.2, 126.9, 127.4, 127.8, 128.6, 131.4, 139.2, 147.5, 151.2, 160.1, 161.2 ppm.

Anal. Calcd for $C_{19}H_{13}N_3O_2$: C, 72.37; H, 4.16; N, 13.33. Found: C, 72.29; H, 4.11; N, 13.25.

2-Amino-4-(4-chlorophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (2d)

Yield 96%, mp >300 °C. IR (KBr, cm^{-1}) 3509, 3363, 3165, 2181, 1664, 1593, 1501, 1381, 1258, 1170, 1108, 1032, 819, 753; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.59 (s, 1H, CH), 7.22 (s, 2H, NH_2), 7.28-7.45 (m, 6H), 7.64 (t, J = 8.2 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 11.61 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 37.6, 58.3, 109.4, 114.1, 115.2, 120.2, 122.9, 126.7, 127.6, 129.2, 131.4, 139.1, 142.0, 147.4, 151.1, 160.3, 161.7 ppm.

Anal. Calcd for $C_{19}H_{12}C1N_3O_2$: C, 65.24; H, 3.46; N, 12.01. Found: C, 65.21; H, 3.41; N, 11.94.

2-Amino-4-(3-chlorophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (3d)

Yield 95%, mp >300 °C. IR (KBr, cm^{-1}) 3507, 3401, 3021, 2172, 1660, 1623, 1590, 1251, 1117, 755; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.57 (s, 1H, CH), 7.24-7.42 (m, 8H), 7.61 (t, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 11.41 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 37.2, 58.5, 109.6, 114.3, 115.0, 120.3, 123.1, 126.6, 127.5, 128.9, 129.4, 129.8, 131.5, 139.2, 142.2, 147.6, 151.0, 160.2, 161.5 ppm.

Anal. Calcd for $C_{19}H_{12}C1N_3O_2$: C, 65.24; H, 3.46; N, 12.01. Found: C, 65.31; H, 3.55; N, 11.92.

2-Amino-4-(2-chlorophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (4d)

Yield 90%, mp >300 °C. IR (KBr, cm^{-1}) 3509, 3415, 2171, 1664, 1626, 1591, 1253, 1120, 753; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.62 (s, 1H, CH), 7.26-7.47 (m, 8H), 7.60 (t, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 11.01 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 38.1, 58.2, 109.4, 114.1, 115.2, 120.4, 123.0, 126.8, 127.1, 128.2, 128.7, 129.6, 131.4, 139.4, 143.4, 147.5, 151.2, 160.0, 162.2 ppm.

Anal. Calcd for $C_{19}H_{12}C1N_3O_2$: C, 65.24; H, 3.46; N, 12.01. Found: C, 65.29; H, 3.57; N, 11.94.

2-Amino-4-(4-bromophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (5d)

Yield 97%, mp >300 °C. IR (KBr, cm^{-1}) 3405, 2181, 1666, 1606, 1381, 1250, 1118, 1008, 750; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.59 (s, 1H, CH), 7.22 (s, 2H, NH_2), 7.28-7.45 (m, 6H), 7.64 (t, J = 8.6 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 11.61 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 38.3, 58.6, 109.0, 114.4, 115.0, 119.8, 122.3, 126.8, 129.6, 130.8, 131.6, 139.0, 141.7, 147.0, 151.4, 160.6, 161.4 ppm.

Anal. Calcd for $C_{19}H_{12}C1N_3O_2$: C, 57.89; H, 3.07; N, 10.66. Found: C, 57.99; H, 3.14; N, 10.71.

2-Amino-4-(4-nitrophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (6d)

Yield 84%, mp >300 °C. IR (KBr, cm^{-1}) 3511, 3378, 2180, 1662, 1628, 1531, 1352, 1253, 1120, 903, 764; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.89 (s, 1H, CH), 7.28-7.38 (m, 4H), 7.54 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 8.2 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 8.19 (d, J = 8.0 Hz, 2H), 11.61 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 57.1, 111.3, 114.5, 115.9, 120.1, 122.8, 126.7, 129.1, 130.9, 131.6, 139.6, 146.7, 147.7, 151.8, 161.6, 162.4 ppm.

Anal. Calcd for $C_{19}H_{12}N_4O_4$: C, 63.33; H, 3.36; N, 15.55. Found: C, 63.36; H, 3.44; N, 15.48.

2-Amino-5-oxo-4-(p-tolyl)-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (7d)

Yield 87%, mp >300 °C. IR (KBr, cm^{-1}) 3396, 3342, 3038, 2179, 1668, 1622, 1598, 1379, 1253, 904, 835; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.26 (s, 3H, CH_3), 4.47 (s, 1H, CH), 7.04 (s, 2H, NH_2), 7.09 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 8.2 Hz, 1H), 7.37 (t, J = 8.3 Hz, 1H), 7.61 (t, J = 8.2 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 10.41 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 21.8, 36.5, 57.4, 109.3, 113.1, 115.0, 120.0, 123.1, 126.1, 126.7, 127.5, 131.1, 139.3, 147.2, 151.3, 160.0, 160.9 ppm.

Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.59; N, 12.76. Found: C, 73.04; H, 4.66; N, 12.71.

2-Amino-4-(4-methoxyphenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (8d)

Yield 89%, mp >300 °C. IR (KBr, cm^{-1}) 3501, 3328, 2953, 2186, 1662, 1593, 1502, 1382, 1324, 1259, 1117, 1.35, 817, 764; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.71 (s, 3H, OCH_3), 4.27 (s, 1H, CH), 6.91 (d, J = 7.8 Hz, 2H), 7.08-7.11 (m, 4H), 7.29 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 8.4 Hz, 1H), 7.60 (t, J = 8.3 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 10.11 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 35.8, 55.6, 57.1, 109.3, 113.2, 115.1, 120.0, 123.1, 123.7, 126.1, 126.5, 131.0, 139.3, 147.1, 151.1, 155.4, 160.0, 160.9 ppm.

Anal. Calcd for $C_{20}H_{15}N_3O_3$: C, 69.56; H, 4.38; N, 12.17. Found: C, 69.51; H, 4.41; N, 12.11.

2-Amino-4-(2,4-dichlorophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (9d)

Yield 87%, mp >300 °C. IR (KBr, cm^{-1}) 3501, 3368, 2184, 1669, 1629, 1586, 1264, 1180, 1045, 852, 754; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.76 (s, 1H, CH), 7.31-7.39 (m, 3H), 7.46 (d, J = 7.8 Hz, 1H), 7.51 (s, 2H, NH_2), 7.61-7.65 (m, 2H), 7.96 (d, J = 8.2 Hz, 1H), 11.61 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 58.6, 110.1, 114.3, 115.2, 120.9, 122.9, 126.7, 128.3, 128.9, 131.9, 137.4, 139.6, 144.4, 144.9, 147.8, 151.6, 160.4, 162.1 ppm.

Anal. Calcd for $C_{19}H_{11}C1_2N_3O_2$: C, 59.40; H, 2.89; N, 10.94. Found: C, 59.33; H, 2.85; N, 10.90.

2-Amino-4-(3,5-dichlorophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (10d)

Yield 96%, mp >300 °C. IR (KBr, cm^{-1}) 3401, 3361, 2182, 1663, 1624, 1591, 1258, 1041, 757; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.69 (s, 1H, CH), 7.30 (d, J = 8.4 Hz, 1H), 7.37 (t, J = 8.4 Hz, 1H), 7.48 (s, 2H), 7.55 (s, 2H, NH_2), 7.61 (t, J = 8.4 Hz, 1H), 7.71 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 11.41 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 57.9, 110.0, 114.2, 115.3, 120.8, 123.3, 126.8, 128.7, 131.7, 138.4, 139.5, 143.8, 147.6, 151.2, 160.3, 162.1 ppm.

Anal. Calcd for $C_{19}H_{11}C1_2N_3O_2$: C, 59.40; H, 2.89; N, 10.94. Found: C, 59.46; H, 2.94; N, 10.91.

2-Amino-4-(3-bromophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (11d)

Yield 81%, mp >300 °C. IR (KBr, cm^{-1}) 3339, 3151, 2190, 1677, 1596, 1383, 1260, 1163, 1107, 1045, 998, 852, 756; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.59 (s, 1H, CH), 7.18 (s, 2H, NH_2), 7.26-7.45 (m, 5H), 7.61-7.65 (m, 2H), 7.96 (d, J = 8.4 Hz, 1H), 11.53 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 38.1, 58.5, 109.1, 114.4, 115.0, 119.9, 122.5, 126.8, 127.6, 128.1, 129.6, 130.8, 131.6, 139.0, 141.7, 147.0, 151.4, 160.6, 161.4 ppm.

Anal. Calcd for $C_{19}H_{12}BrN_3O_2$: C, 57.89; H, 3.07; N, 10.66. Found: C, 57.97; H, 3.17; N, 10.60.

2-Amino-4-(3,4-dichlorophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (12d)

Yield 96%, mp >300 °C. IR (KBr, cm^{-1}) 3410, 3028, 2188, 1662, 1257, 1180, 1121, 752; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.73 (s, 1H, CH), 7.29-7.49 (m, 6H), 7.57 (s, 1H), 7.61 (t, J = 8.2 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 11.61 (s, 1H, NH) ppm; 13C-NMR (100 MHz, DMSO-d6): δ = 57.8, 110.2, 114.5, 115.1, 121.0, 123.2, 126.8, 127.8, 128.3, 131.7, 138.6, 139.3, 142.1, 146.3, 147.4, 151.4, 160.1, 161.9 ppm.

Anal. Calcd for $C_{19}H_{11}Cl_2N_3O_2$: C, 59.40; H, 2.89; N, 10.94. Found: C, 59.36; H, 2.86; N, 10.88.

2-Amino-4-(3-nitrophenyl)-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile (13d)

Yield 90%, mp >300 °C. IR (KBr, cm^{-1}) 3501, 3398, 2186, 1689, 1607, 1261, 1043, 850; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.81 (s, 1H, CH), 7.28-7.41 (m, 6H), 7.64 (t, J = 8.2 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.33 (s, 1H), 11.52 (s, 1H, NH) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 57.4, 110.9, 114.2, 115.6, 120.3, 123.2, 126.8, 127.8, 128.1, 129.7, 131.3, 131.7, 139.6, 146.1, 147.6, 151.3, 161.4, 162.3 ppm.

Anal. Calcd for $C_{19}H_{12}N_4O_4$: C, 63.33; H, 3.36; N, 15.55. Found: C, 63.26; H, 3.31; N, 15.51.

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Disclosure statement

There are no competing or conflicts of interest to declare.

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