

Synthesis of metal-organic frameworks MIL-101(Cr)-NH₂ containing phosphorous acid functional groups: Application for the synthesis of *N*-amino-2-pyridone and pyrano [2,3-*c*]pyrazole derivatives *via* a cooperative vinylogous anomeric based oxidation

Saeed Babae,^a Mahmoud Zarei,^{*a} Hassan Sepehrmansourie,^a Mohammad Ali Zolfigol,^{*a} Sadegh Rostamnia^{*b}

^a Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Tel: +988138282807, Fax: +988138380709 Iran. E-Mail: zolfi@basu.ac.ir&mzolfigol@yahoo.com.

^b Organic and Nano Group (ONG), Department of Chemistry, Faculty of Science, University of Maragheh, PO Box 55181-83111, Maragheh, Iran. E-Mail: srostamnia@gmail.com.

1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (6a).....	4
1,6-diamino-4-(4-hydroxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6f).....	4
1,6-diamino-2-oxo-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (6g).....	4
1',6'-diamino-2'-oxo-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (6h).....	4
1,6-diamino-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (6i).....	5
1,6-diamino-4-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6k)	5
1,6-diamino-4-(1H-indol-3-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6l)	5
6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5- carbonitrile (7g)	5
6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5- carbonitrile (7m)	6
Figure S1: FT-IR spectrum of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5- dicarbonitrile (6a).....	7
Figure S2: ¹ H NMR spectrum of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5- dicarbonitrile (6a).....	8
Figure S3: FT-IR spectrum of 1,6-diamino-4-(4-hydroxyphenyl)-2-oxo-1,2-dihydropyridine- 3,5-dicarbonitrile (6f).....	9
Figure S4: ¹ H NMR spectrum of 1,6-diamino-4-(4-hydroxyphenyl)-2-oxo-1,2- dihydropyridine-3,5-dicarbonitrile (6f).....	10
Figure S5: ¹³ C NMR spectrum of 1,6-diamino-4-(4-hydroxyphenyl)-2-oxo-1,2- dihydropyridine-3,5-dicarbonitrile (6f).....	11
Figure S6: FT-IR spectrum of 1,6-diamino-2-oxo-1,2-dihydro-[4,4'-bipyridine]-3,5- dicarbonitrile (6g)	12
Figure S7: ¹ H NMR spectrum of 1,6-diamino-2-oxo-1,2-dihydro-[4,4'-bipyridine]-3,5- dicarbonitrile (6g)	13
Figure S8: ¹³ C NMR spectrum of 1,6-diamino-2-oxo-1,2-dihydro-[4,4'-bipyridine]-3,5- dicarbonitrile (6g)	14
Figure S9: FT-IR spectrum of 1',6'-diamino-2'-oxo-1',2'-dihydro-[3,4'-bipyridine]-3',5'- dicarbonitrile (6h)	15
Figure S10: ¹ H NMR spectrum of 1',6'-diamino-2'-oxo-1',2'-dihydro-[3,4'-bipyridine]-3',5'- dicarbonitrile (6h)	16
Figure S11: ¹³ C NMR spectrum of 1',6'-diamino-2'-oxo-1',2'-dihydro-[3,4'-bipyridine]-3',5'- dicarbonitrile (6h)	17
Figure S12: FT-IR spectrum of 1,6-diamino-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5- dicarbonitrile (6i)	18

Figure S13: ¹ H NMR spectrum of 1,6-diamino-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (6i)	19
Figure S14: ¹³ C NMR spectrum of 1,6-diamino-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (6i)	20
Figure S15: FT-IR spectrum of 1,6-diamino-4-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6k)	21
Figure S16: ¹ H NMR spectrum of 1,6-diamino-4-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6k)	22
Figure S17: ¹³ C NMR spectrum of 1,6-diamino-4-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6k)	23
Figure S18: FT-IR spectrum of 1,6-diamino-4-(1H-indol-3-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6l)	24
Figure S19: ¹ H NMR spectrum of 1,6-diamino-4-(1H-indol-3-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6l)	25
Figure S20: ¹³ C NMR spectrum of 1,6-diamino-4-(1H-indol-3-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6l)	26
Figure S21: FT-IR spectrum of 6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-1,4-dihydropyran[2,3-c]pyrazole-5-carbonitrile (7g)	27
Figure S22: ¹ H NMR spectrum of 6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-1,4-dihydropyran[2,3-c]pyrazole-5-carbonitrile (7g)	28
Figure S23: ¹³ C NMR spectrum of 6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-1,4-dihydropyran[2,3-c]pyrazole-5-carbonitrile (7g)	29
Figure S24: FT-IR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1,4-dihydropyran[2,3-c]pyrazole-5-carbonitrile (7m)	30
Figure S25: ¹ H NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1,4-dihydropyran[2,3-c]pyrazole-5-carbonitrile (7m)	31
Figure S26: ¹³ C NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1,4-dihydropyran[2,3-c]pyrazole-5-carbonitrile (7m)	32

1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (6a)

White solid; Mp: 237-240 °C; FT-IR (KBr): ν (cm⁻¹) = 3446, 2400, 3308, 3248, 2218, 2206, 1639, 1617, 1599. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.24 (s, 2H), 7.41 – 7.29 (m, 5H), 5.49 (s, 2H).

1,6-diamino-4-(4-hydroxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6f)

White solid; Mp: 325-327 °C; FT-IR (KBr): ν (cm⁻¹) = 3447, 3310, 3209, 2213, 2195, 1696, 1606. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.61 (s, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.68 (s, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 159.6, 159.4, 159.2, 156.6, 129.8, 124.8, 116.7, 115.8, 115.2, 115.2, 86.1, 74.1.

1,6-diamino-2-oxo-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (6g)

White solid; Mp: 337-339 °C; FT-IR (KBr): ν (cm⁻¹) = 3530, 3345, 3291, 3213, 3102, 2219, 1683, 1653, 1460. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.87 (dd, *J* = 4.4, 1.6 Hz, 2H), 8.51 (s, 2H), 7.61 (dd, *J* = 4.4, 1.6 Hz, 2H), 5.78 (s, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 159.0, 156.9, 156.6, 150.1, 142.3, 122.5, 115.8, 115.0, 85.9, 73.8.

1',6'-diamino-2'-oxo-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (6h)

White solid; Mp: 311-312 °C; FT-IR (KBr): ν (cm⁻¹) = 3334, 3286, 3170, 3064, 2228, 2209, 1681, 1622. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.84 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.80 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.49 (s, 2H), 8.08 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.70 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1H), 5.79 (s, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 159.0, 156.6, 156.3, 151.1, 148.0, 136.0, 130.7, 123.5, 116.2, 115.3, 86.6, 74.5.

1,6-diamino-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (6i)

White solid; Mp: 300 °C; FT-IR (KBr): ν (cm⁻¹) = 3397, 3306, 3250, 2210, 1639, 1614, 1091. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.37 (s, 2H), 7.99 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.58 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.33 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.72 (s, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 159.2, 156.7, 151.6, 133.3, 130.7, 130.3, 127.7, 116.4, 115.6, 86.4, 74.2.

1,6-diamino-4-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6k)

White solid; Mp: 249-251 °C; FT-IR (KBr): ν (cm⁻¹) = 3379, 3314, 3263, 2185, 3017, 2214, 2191, 1643, 1603. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.29 (s, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.71 (s, 2H), 3.10 (s, 6H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 159.6, 159.5, 156.8, 151.5, 129.5, 120.4, 117.1, 116.2, 111.1, 85.4, 73.6, 39.6.

1,6-diamino-4-(1H-indol-3-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6l)

White solid; Mp: >350 °C; FT-IR (KBr): ν (cm⁻¹) = 3435, 3359, 3318, 3270, 3127, 2210, 1654, 1628. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 11.93 (s, 1H), 8.34 (s, 2H), 7.90 (s, 1H), 7.58 – 7.52 (m, 2H), 7.29 (td, *J* = 8.4, 1.2 Hz, 1H), 7.20 (td, *J* = 8.4, 1.2 Hz, 1H), 5.71 (s, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 159.7, 156.9, 153.6, 136.0, 127.6, 124.5, 122.1, 120.0, 120.0, 117.2, 116.3, 112.2, 108.8, 86.1, 74.3.

6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7g)

White solid; Mp: 168-170 °C; FT-IR (KBr): ν (cm⁻¹) = 3385, 3305, 3172, 2918, 2189, 1645. ¹H

NMR (400 MHz, DMSO-*d*₆) δ (ppm): 7.65 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 10.7 Hz, 3H), 6.66 (d, *J* = 8.2 Hz, 2H), 4.46 (s, 1H), 2.87 (s, 6H), 1.79 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 160.5, 159.8, 154.7, 151.9, 149.2, 135.5, 132.0, 129.5, 127.9, 120.9, 112.3, 111.6, 98.1, 58.0, 40.1, 35.3, 9.7.

6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7m)

White solid; Mp: 228-230 °C; FT-IR (KBr): ν (cm⁻¹) = 3498, 3272, 3321, 3245, 3002, 2190,

1661. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 11.19 (s, 1H), 9.46 (s, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.85 (s, 2H), 6.71 (d, *J* = 7.7 Hz, 1H), 4.74 (s, 1H), 3.94 (s, 3H), 2.10 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 160.0, 146.6, 137.8, 124.1, 123.9, 120.9, 120.0, 110.0, 104.9, 55.5, 54.9, 28.7, 9.8.

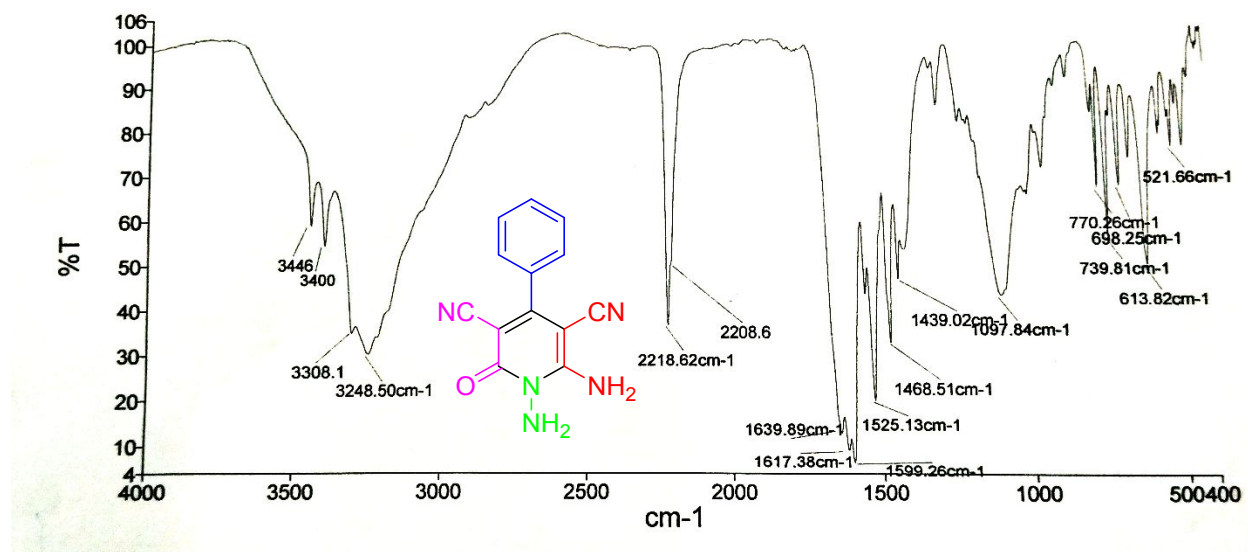


Figure S1: FT-IR spectrum of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (6a)

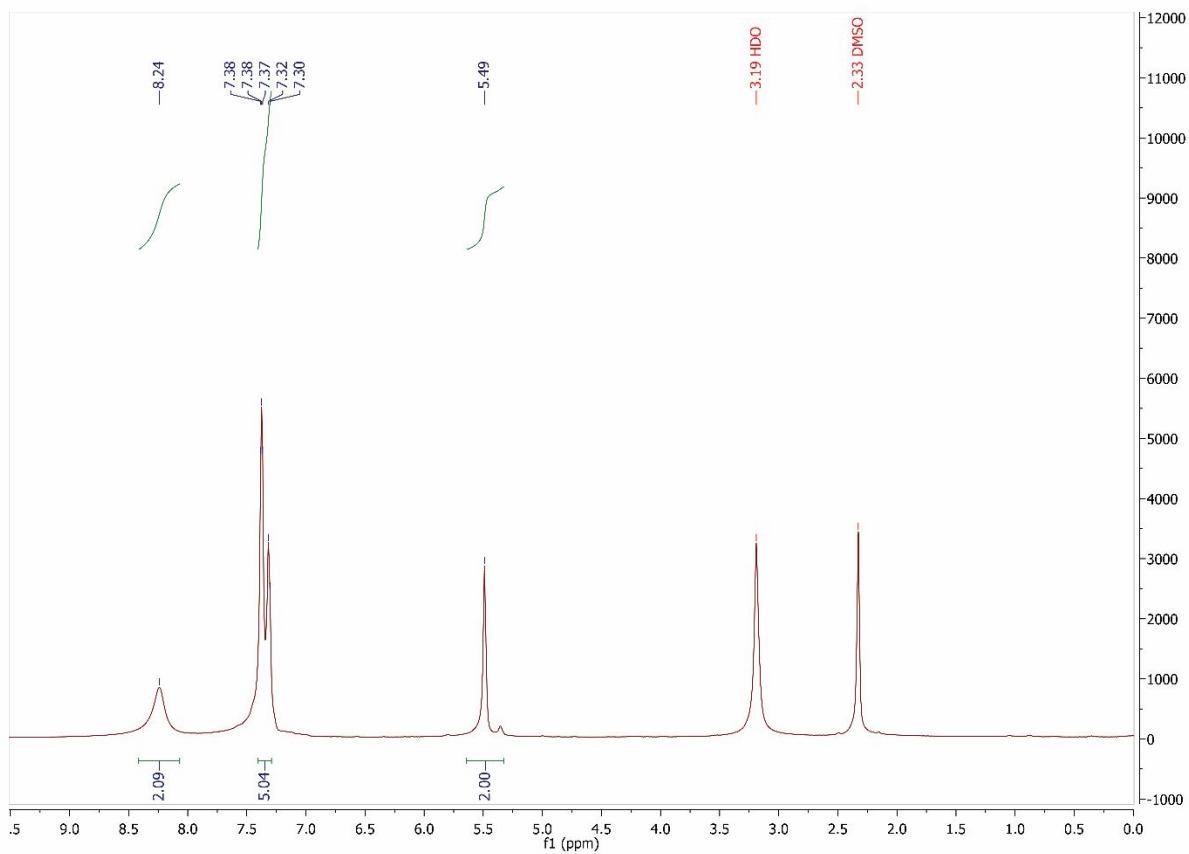


Figure S2: ¹H NMR spectrum of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (6a)

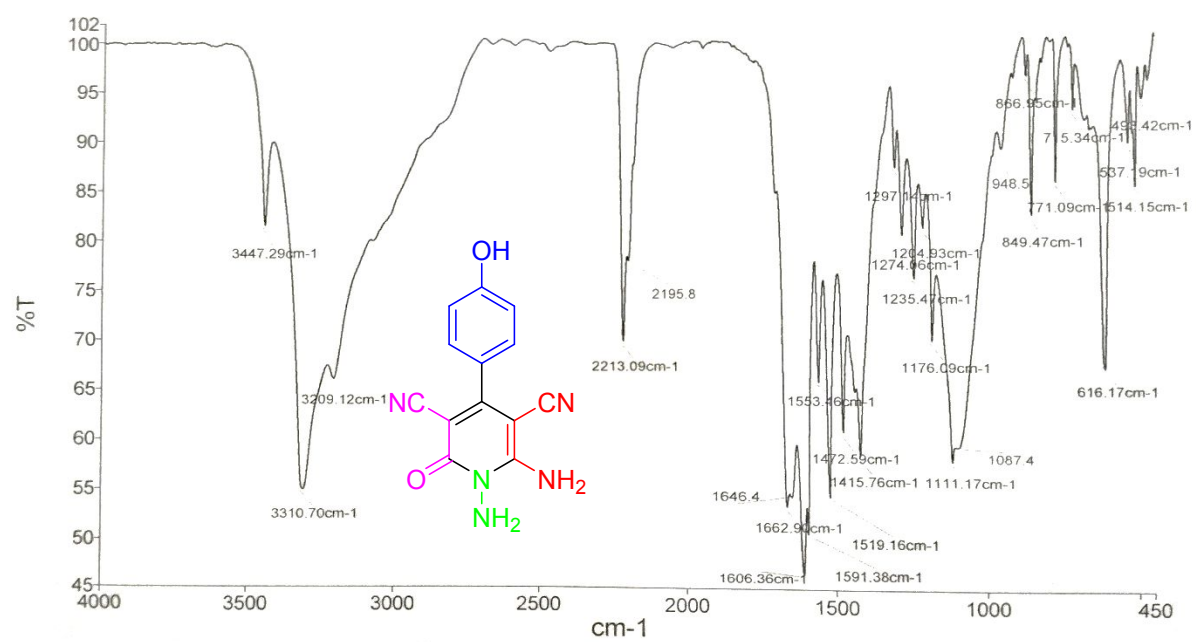


Figure S3: FT-IR spectrum of 1,6-diamino-4-(4-hydroxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6f)

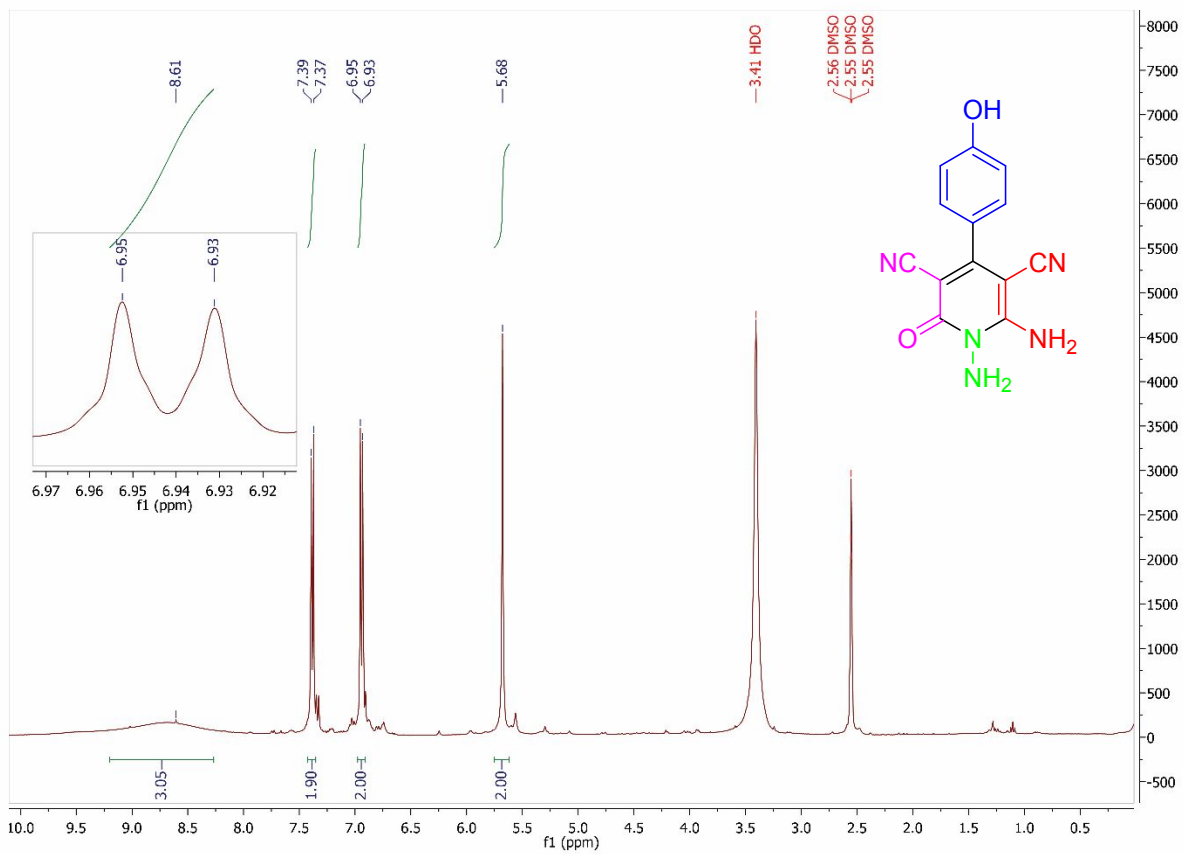


Figure S4: ¹H NMR spectrum of 1,6-diamino-4-(4-hydroxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6f)

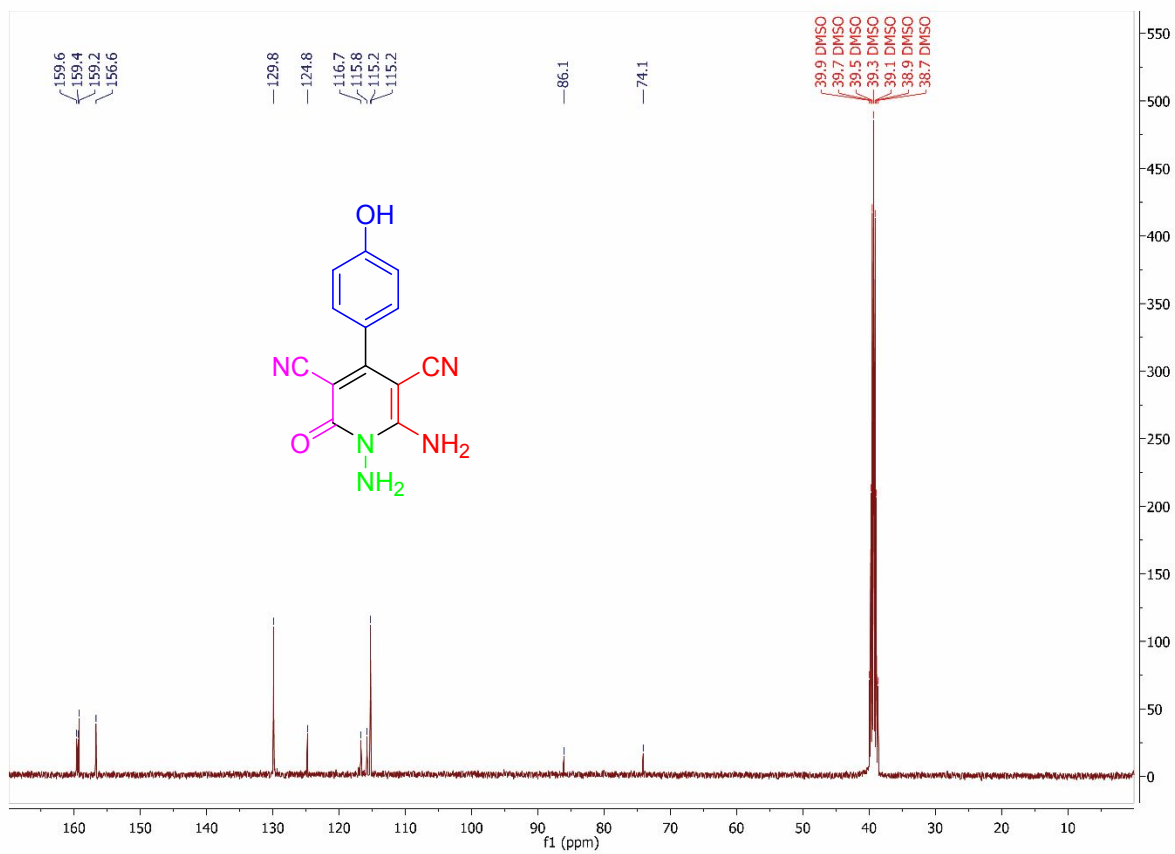


Figure S5: ^{13}C NMR spectrum of 1,6-diamino-4-(4-hydroxyphenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6f)

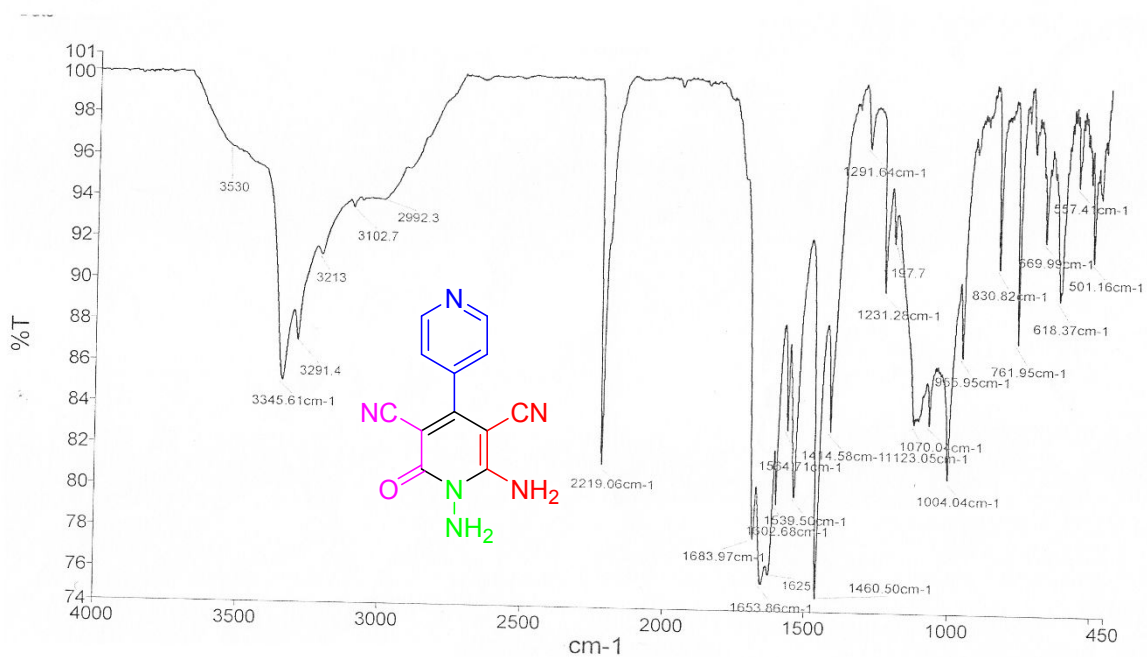


Figure S6: FT-IR spectrum of 1,6-diamino-2-oxo-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (6g)

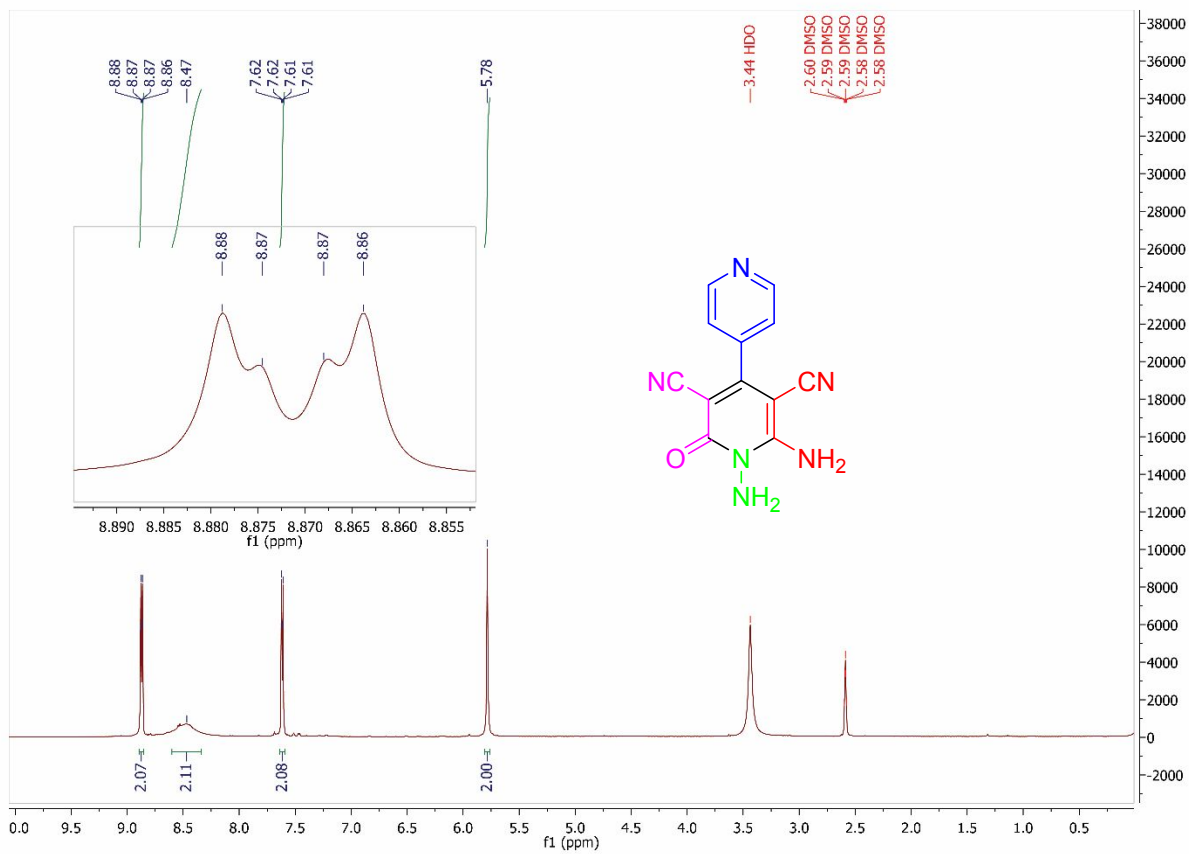


Figure S7: ^1H NMR spectrum of 1,6-diamino-2-oxo-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (6g)

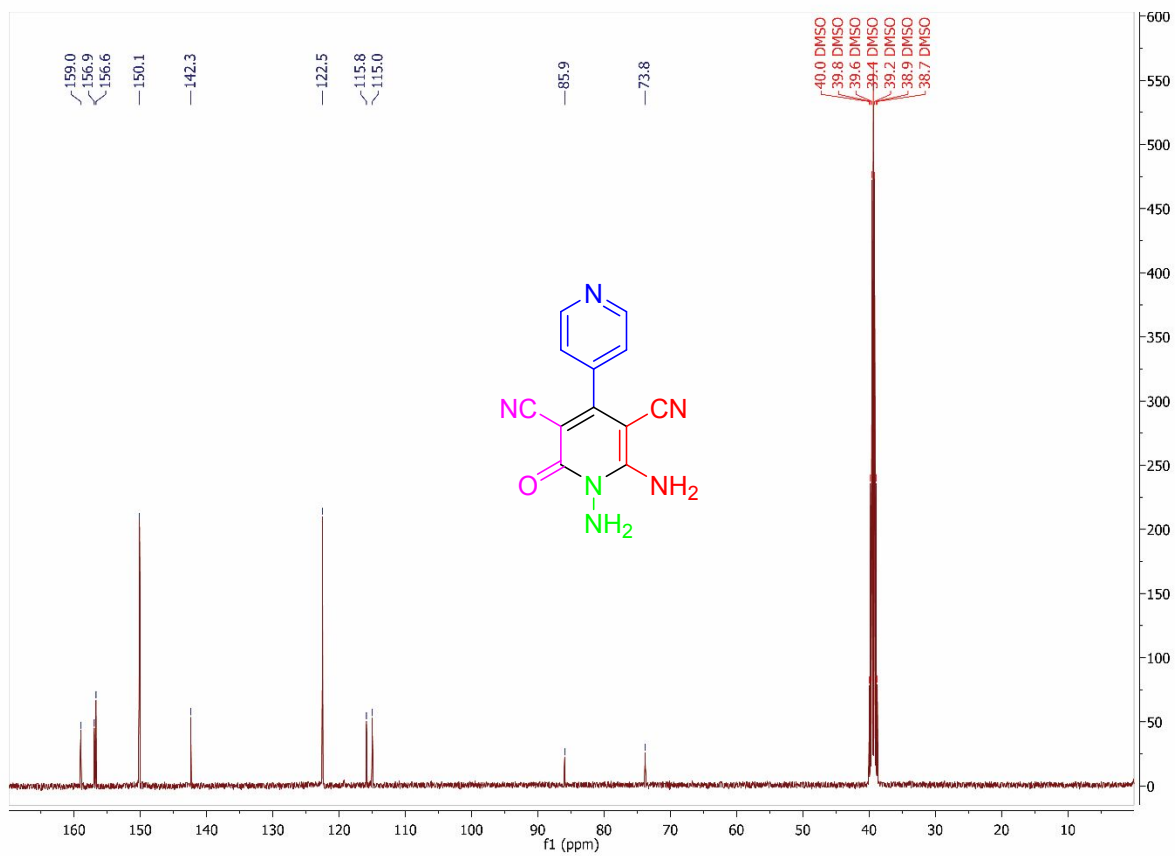


Figure S8: ^{13}C NMR spectrum of 1,6-diamino-2-oxo-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (6g)

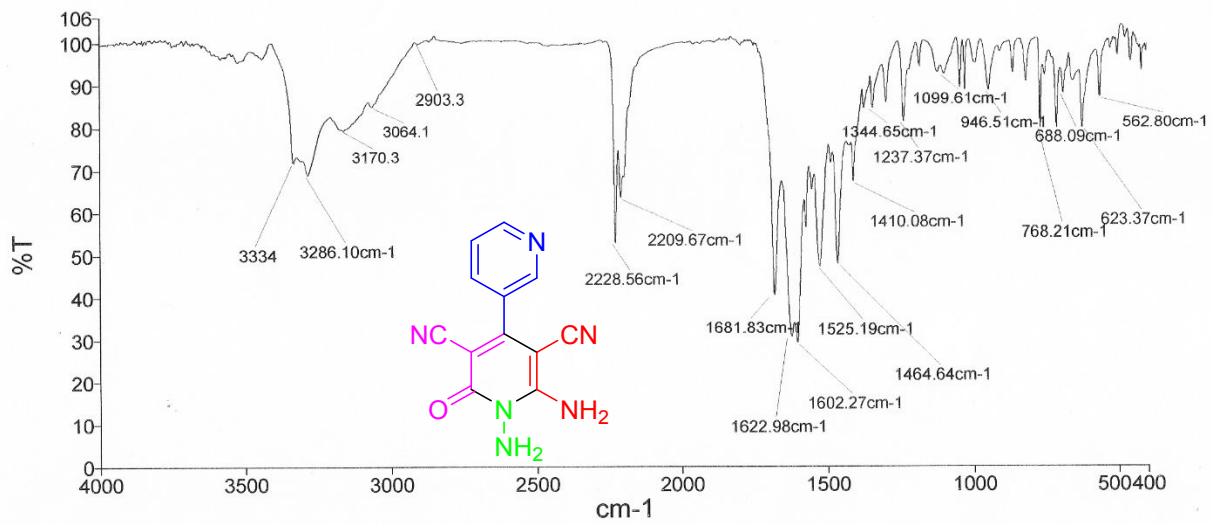


Figure S9: FT-IR spectrum of 1',6'-diamino-2'-oxo-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (6h)

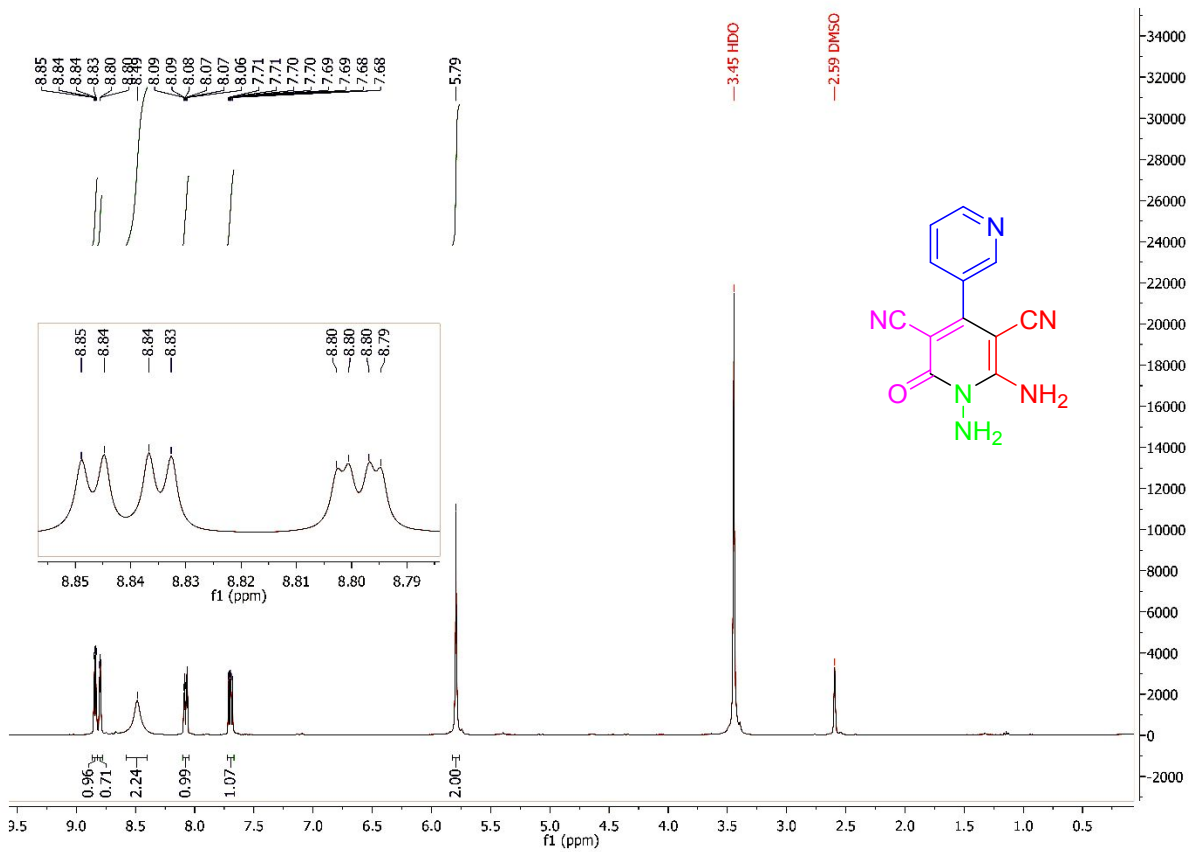


Figure S10: ^1H NMR spectrum of 1',6'-diamino-2'-oxo-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (6h)

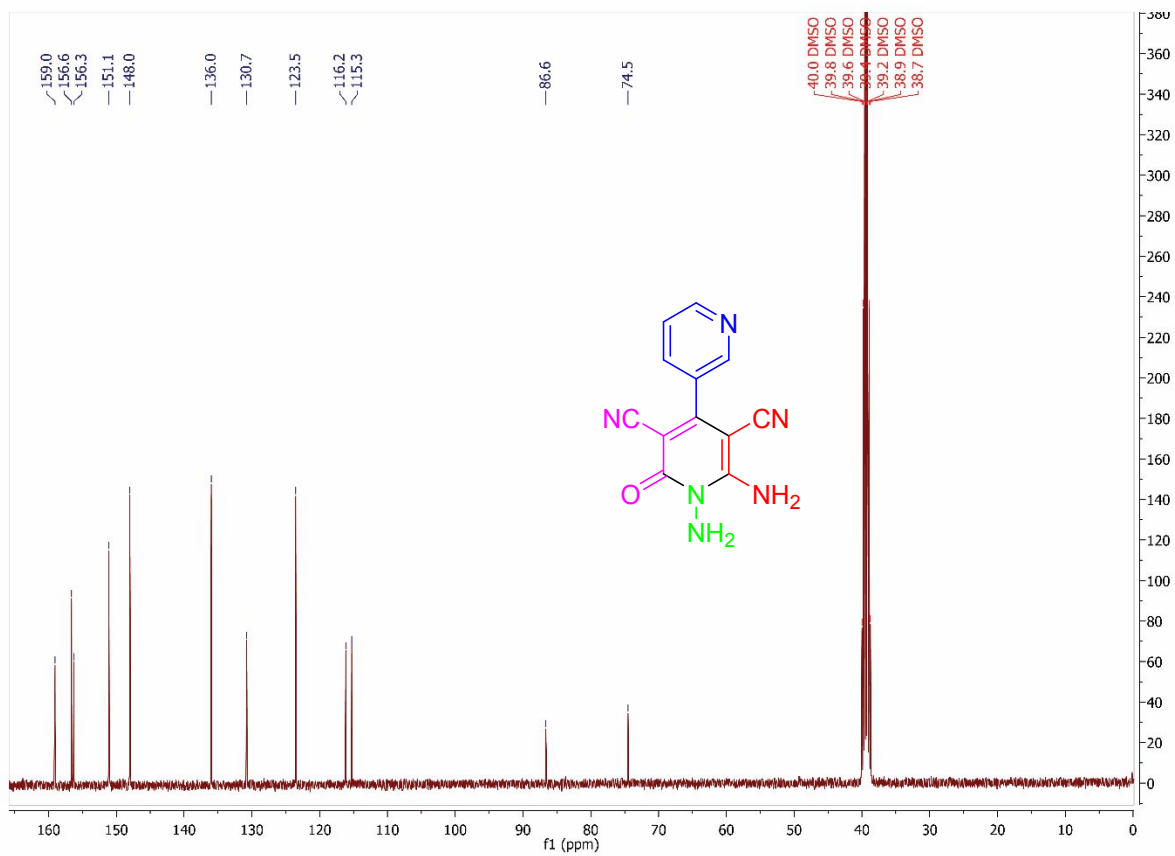


Figure S11: ¹³C NMR spectrum of 1',6'-diamino-2'-oxo-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (6h)

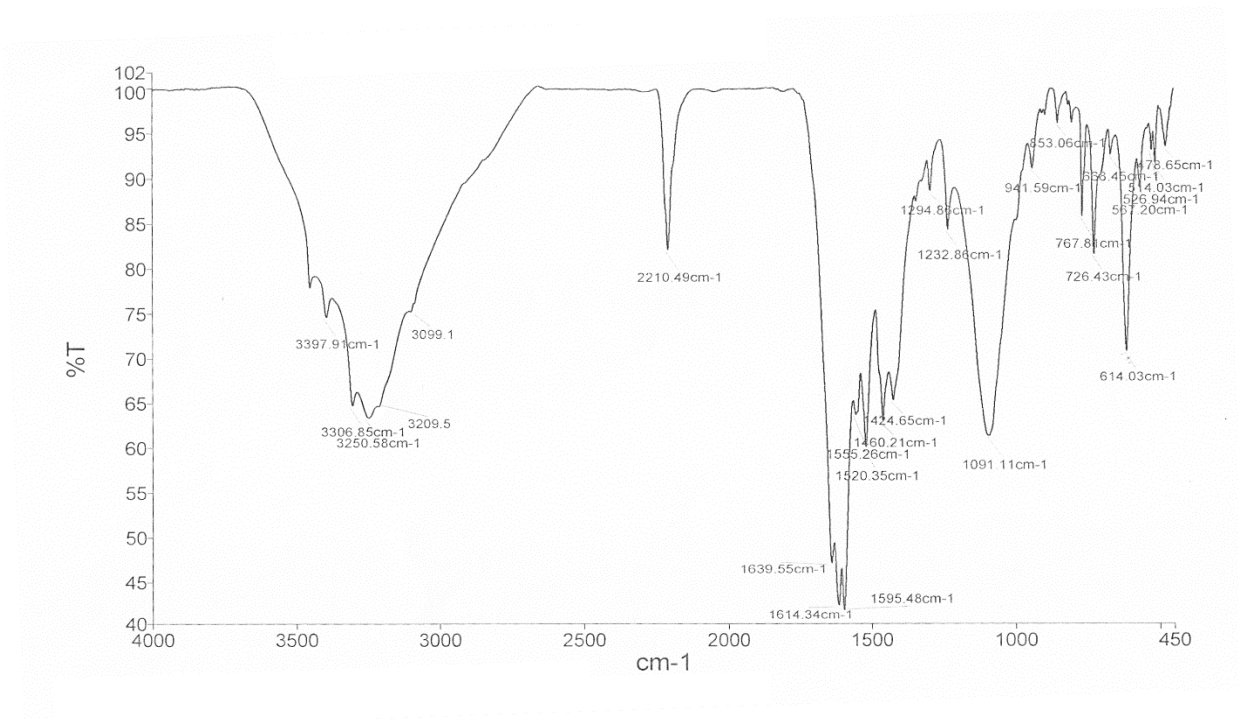


Figure S12: FT-IR spectrum of 1,6-diamino-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (6i)

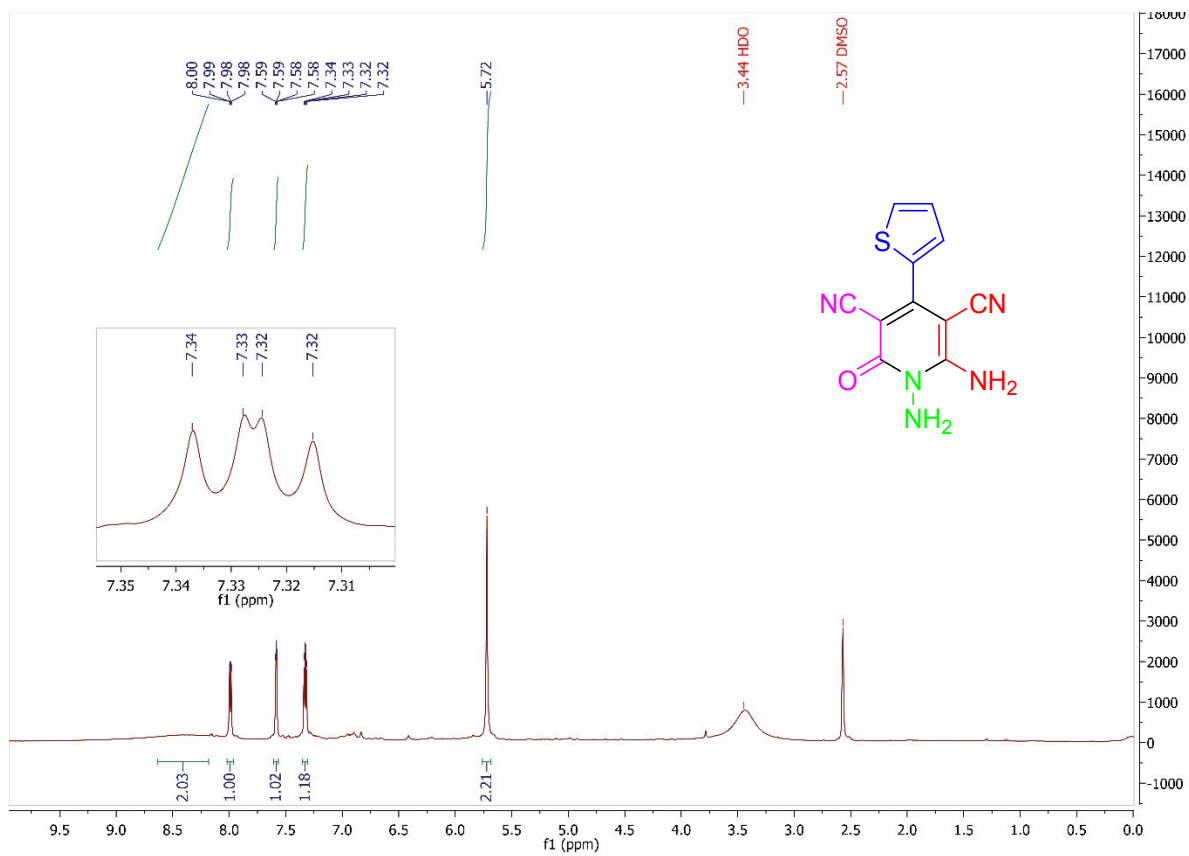


Figure S13: ¹H NMR spectrum of 1,6-diamino-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (6i)

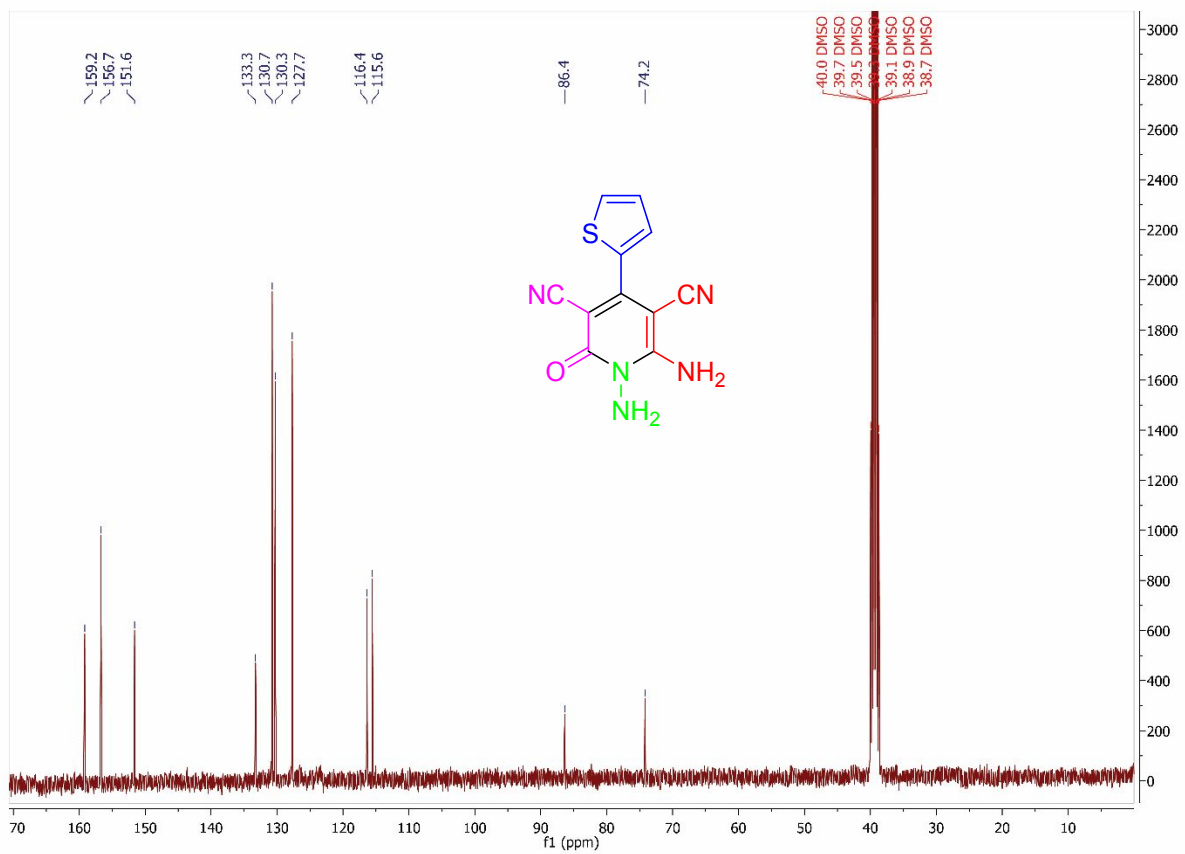


Figure S14: ^{13}C NMR spectrum of 1,6-diamino-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (6i)

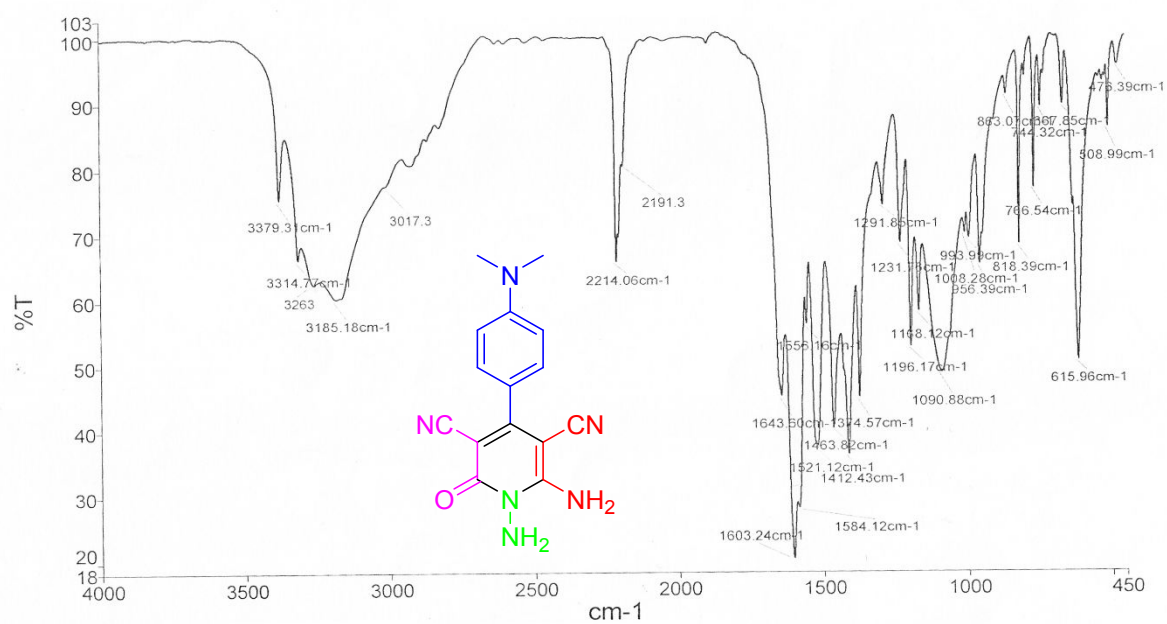


Figure S15: FT-IR spectrum of 1,6-diamino-4-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6k)

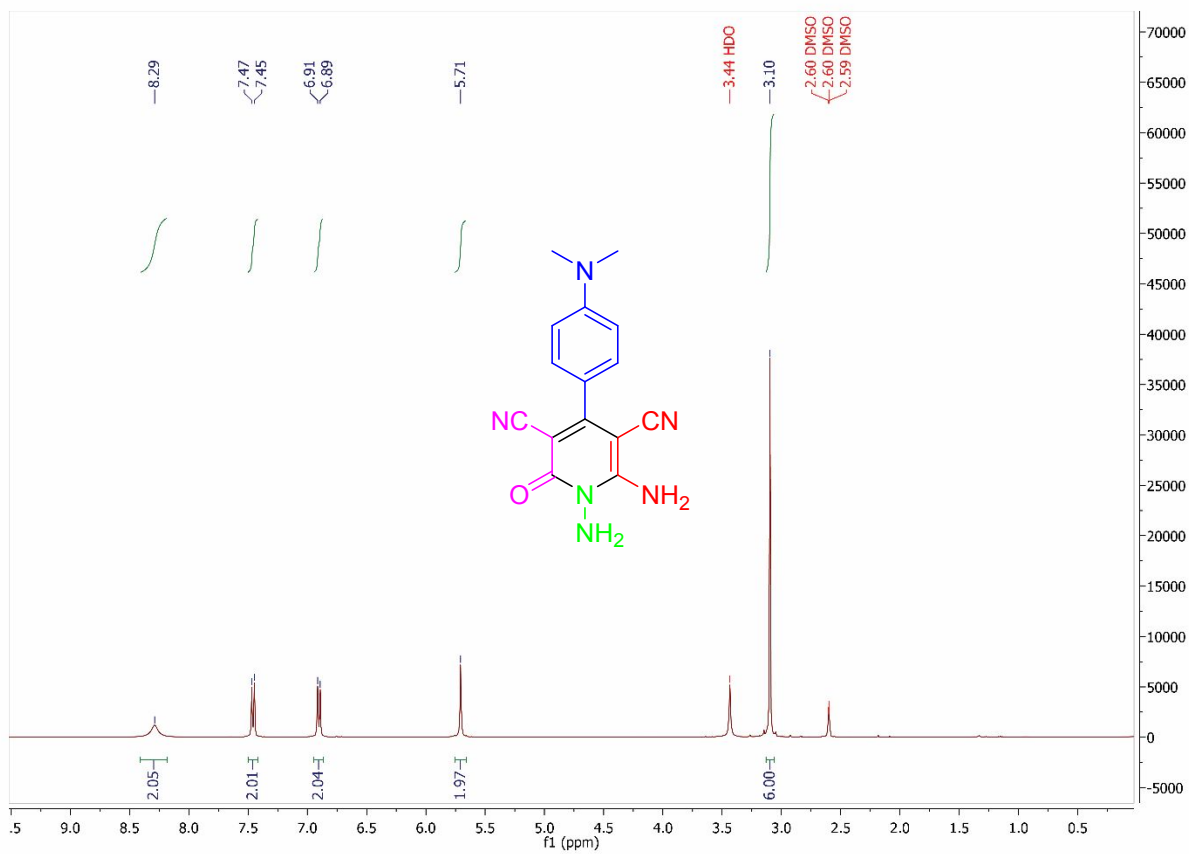


Figure S16: ¹H NMR spectrum of 1,6-diamino-4-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6k)

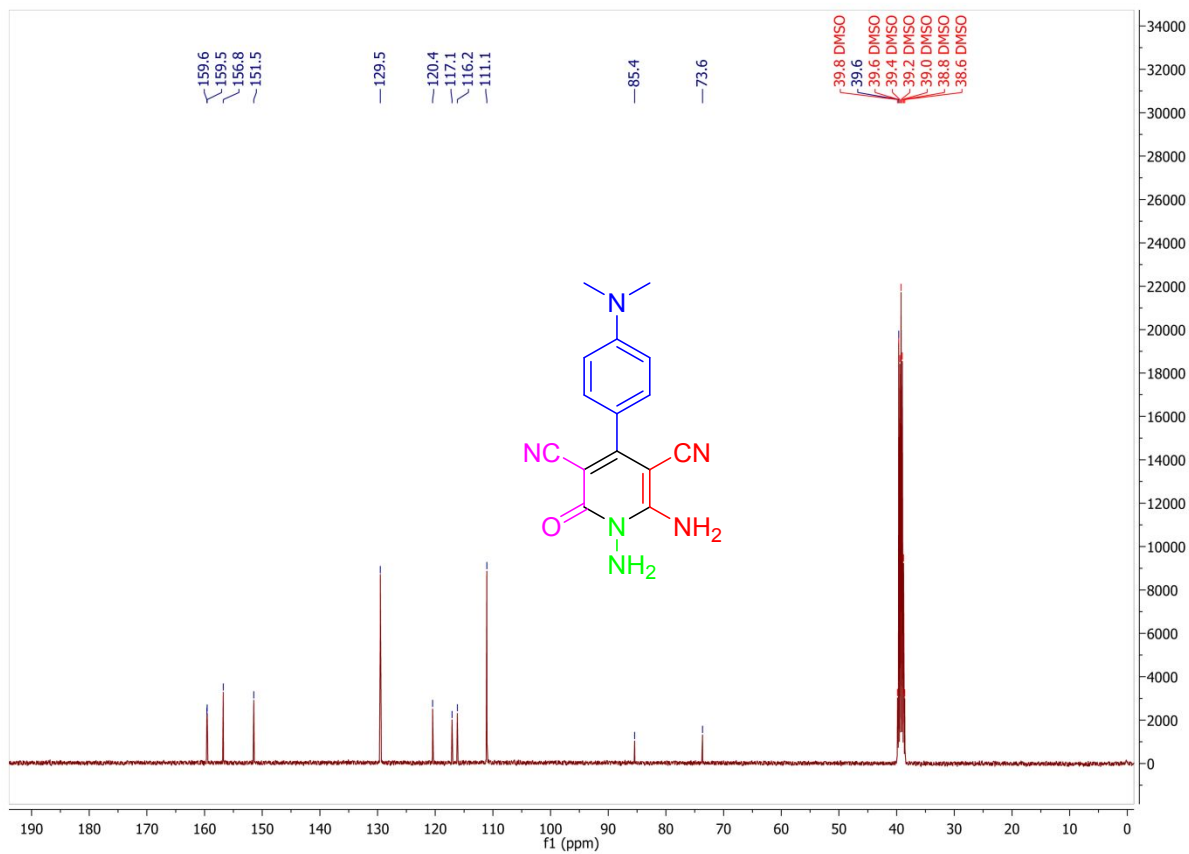


Figure S17: ¹³C NMR spectrum of 1,6-diamino-4-(4-(dimethylamino)phenyl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6k)

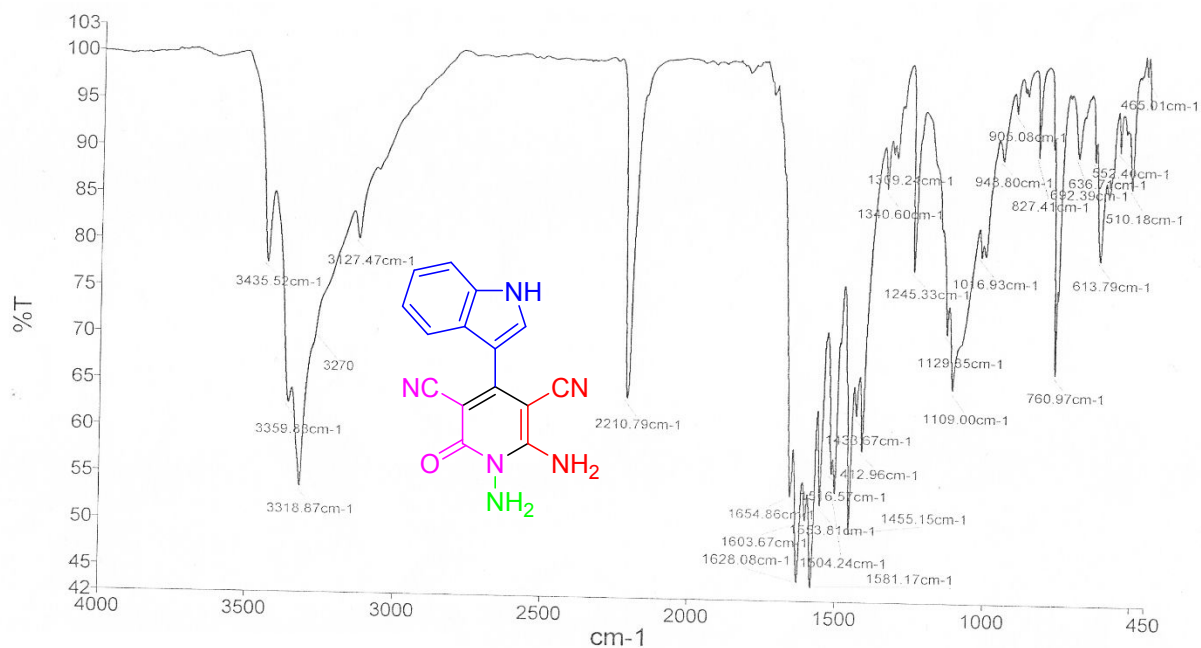


Figure S18: FT-IR spectrum of 1,6-diamino-4-(1H-indol-3-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6l)

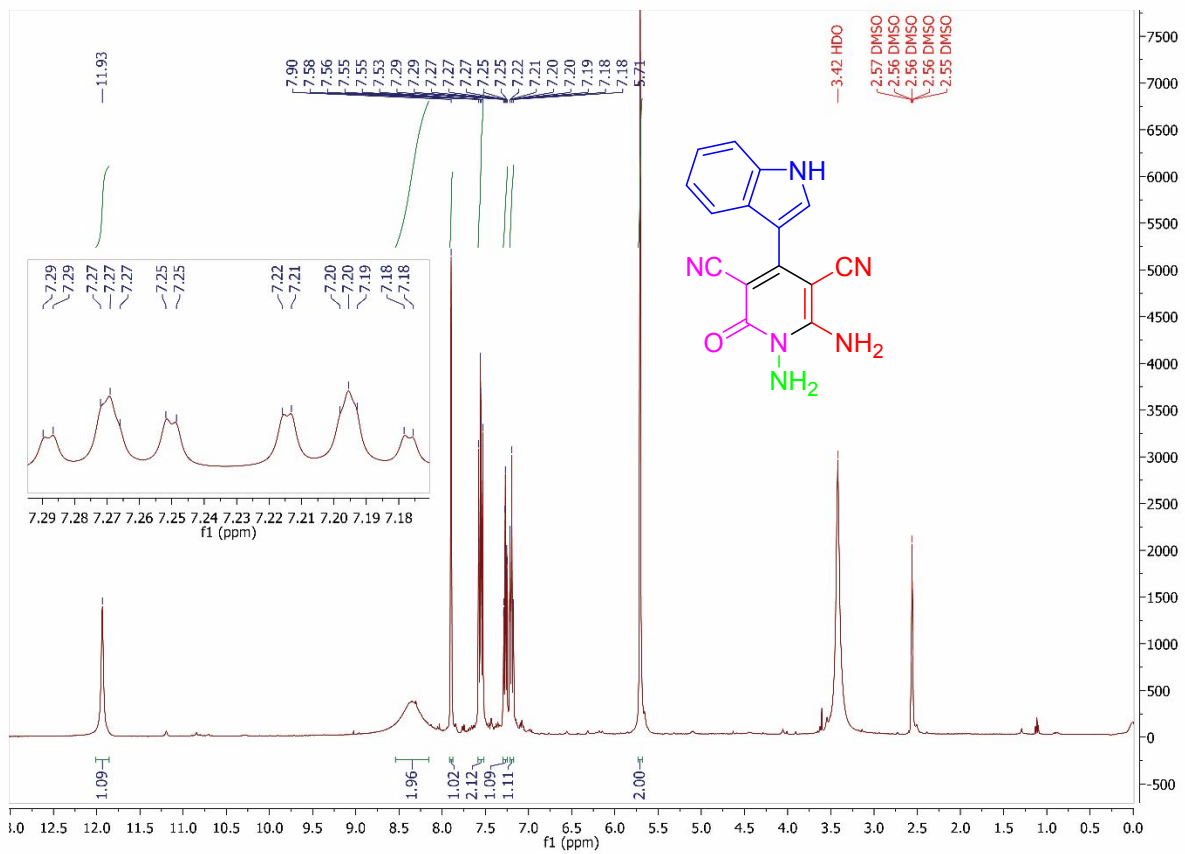


Figure S19: ¹H NMR spectrum of 1,6-diamino-4-(1H-indol-3-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6l)

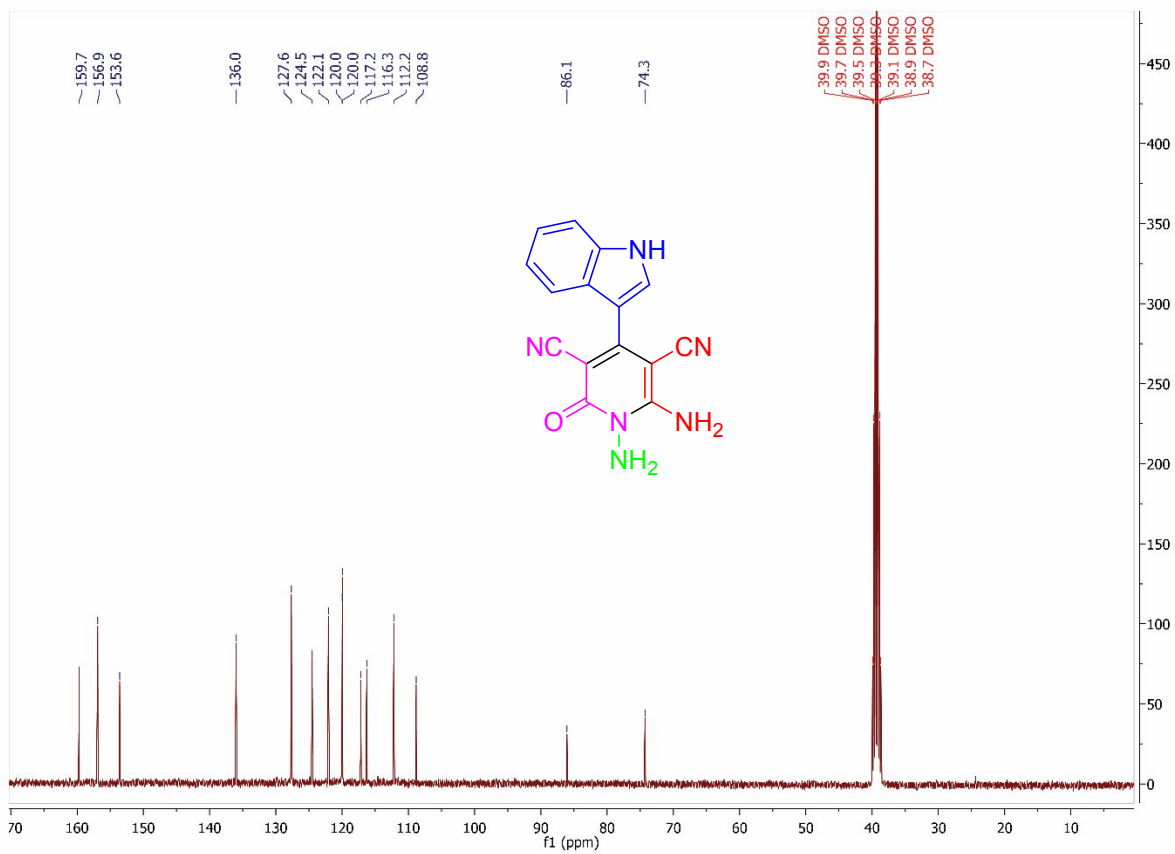


Figure S20: ¹³C NMR spectrum of 1,6-diamino-4-(1H-indol-3-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (6l)

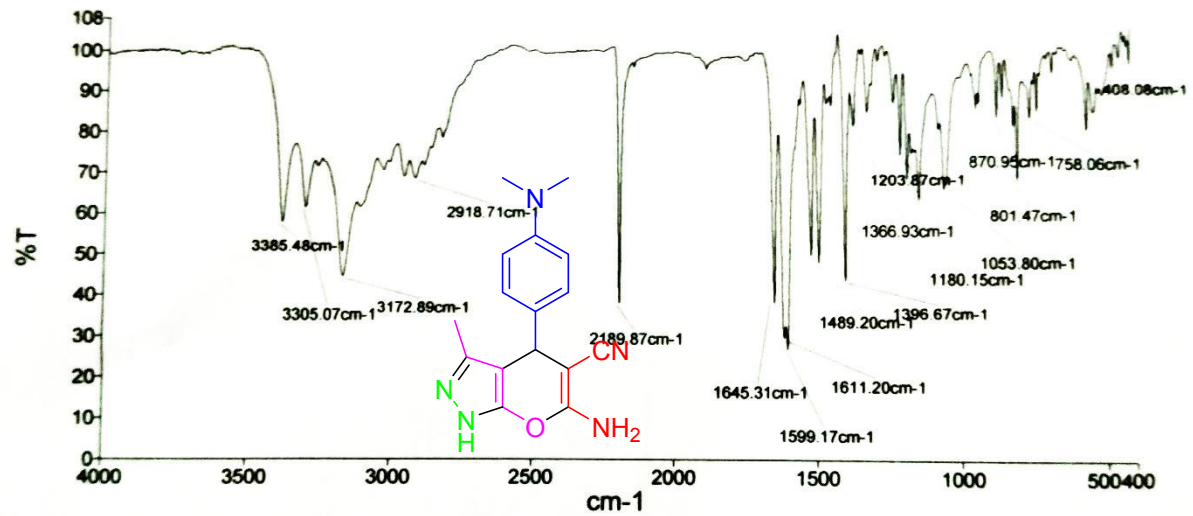


Figure S21: FT-IR spectrum of 6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7g)

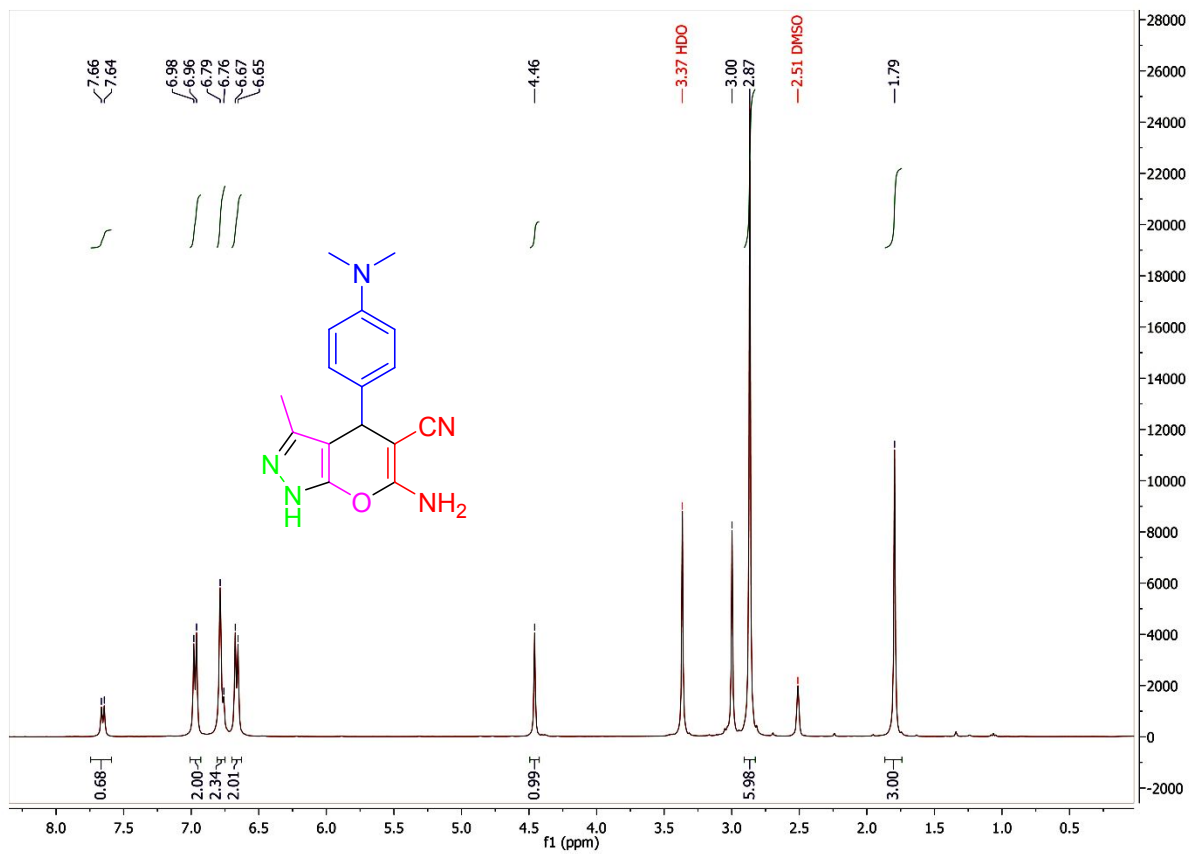


Figure S22: ¹H NMR spectrum of 6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7g)

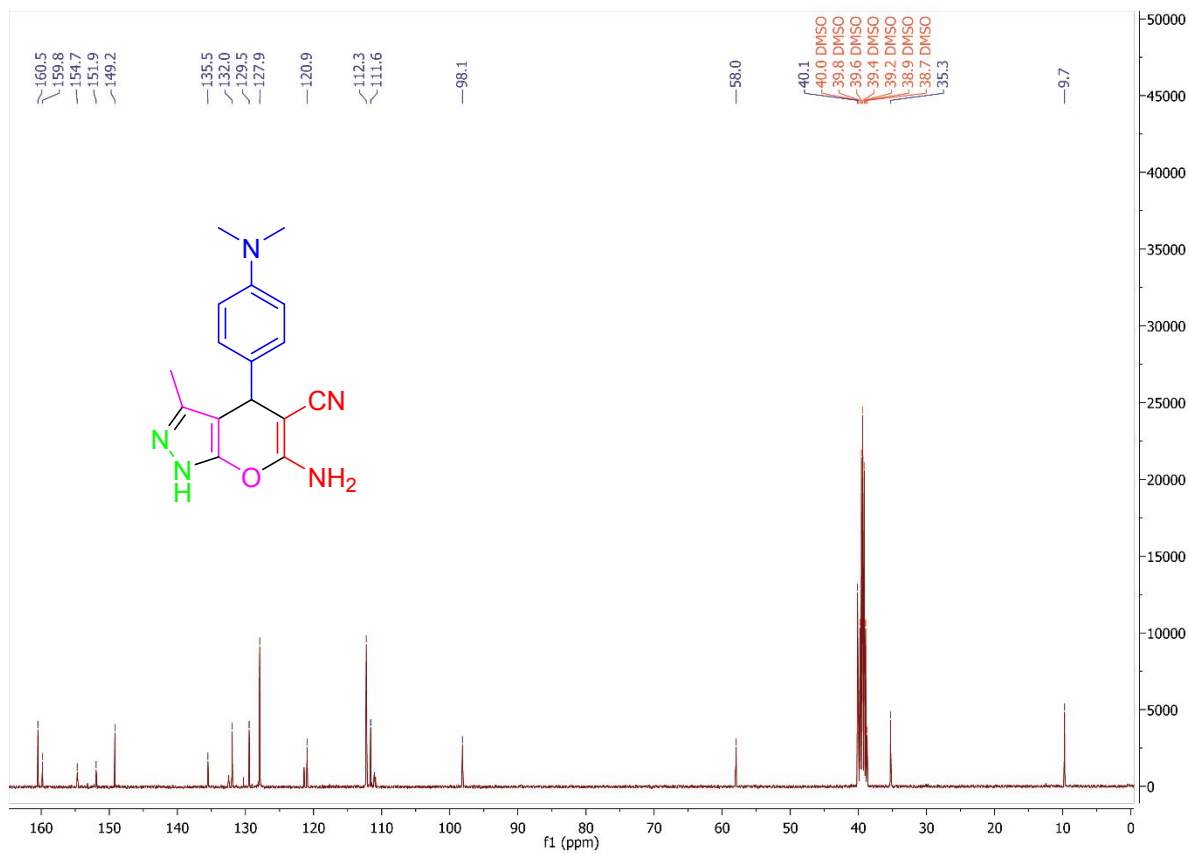


Figure S23: ¹³C NMR spectrum of 6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-1,4-dihydropyranopyrazole-5-carbonitrile (7g)

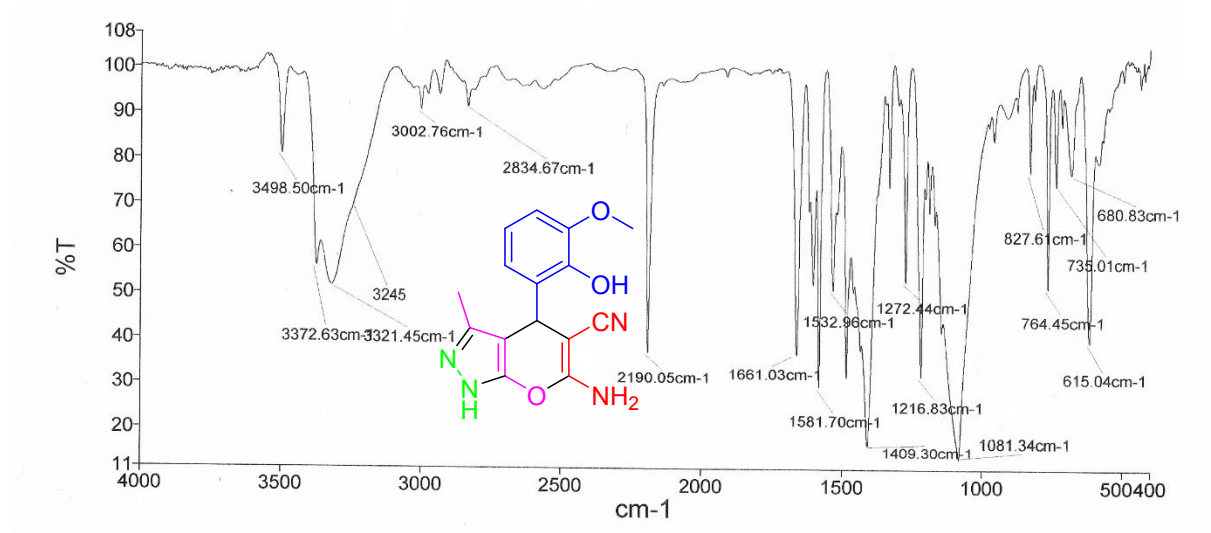


Figure S24: FT-IR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7m)

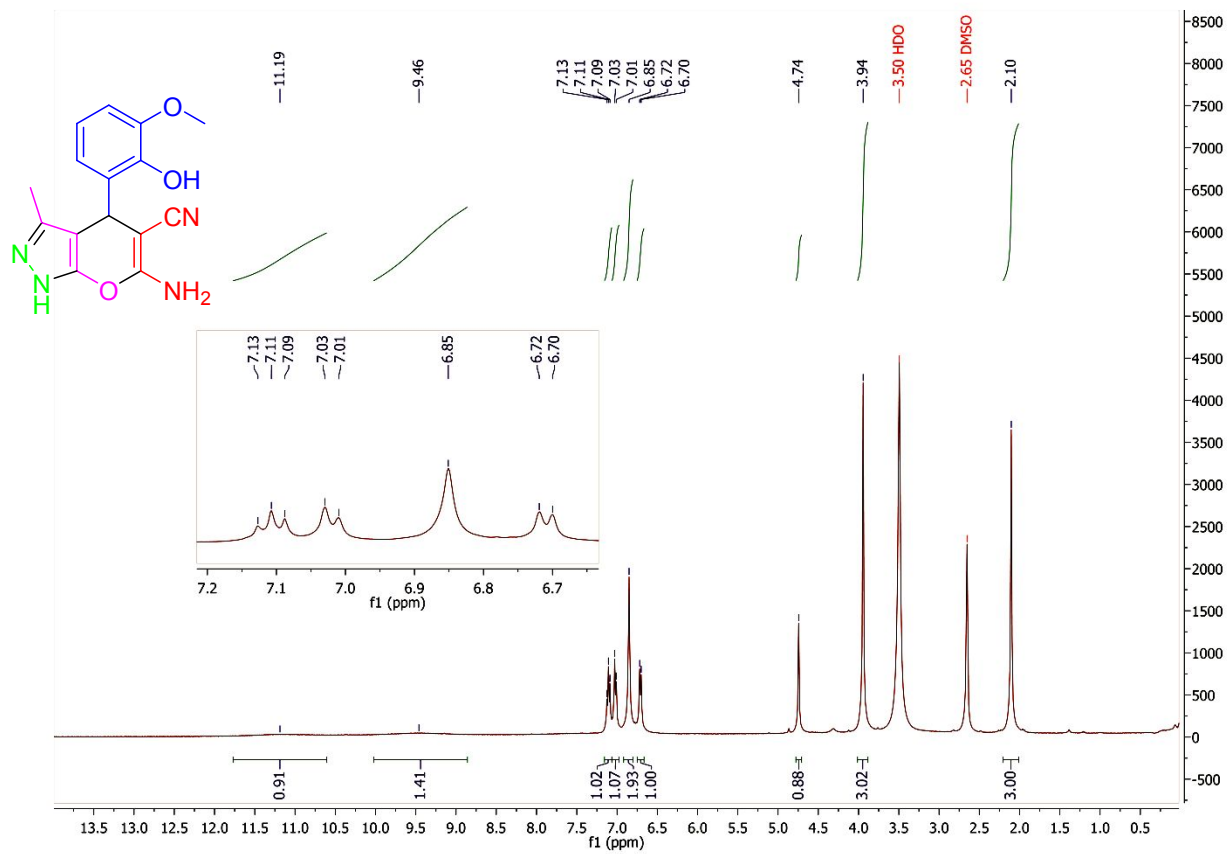


Figure S25: ¹H NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7m)

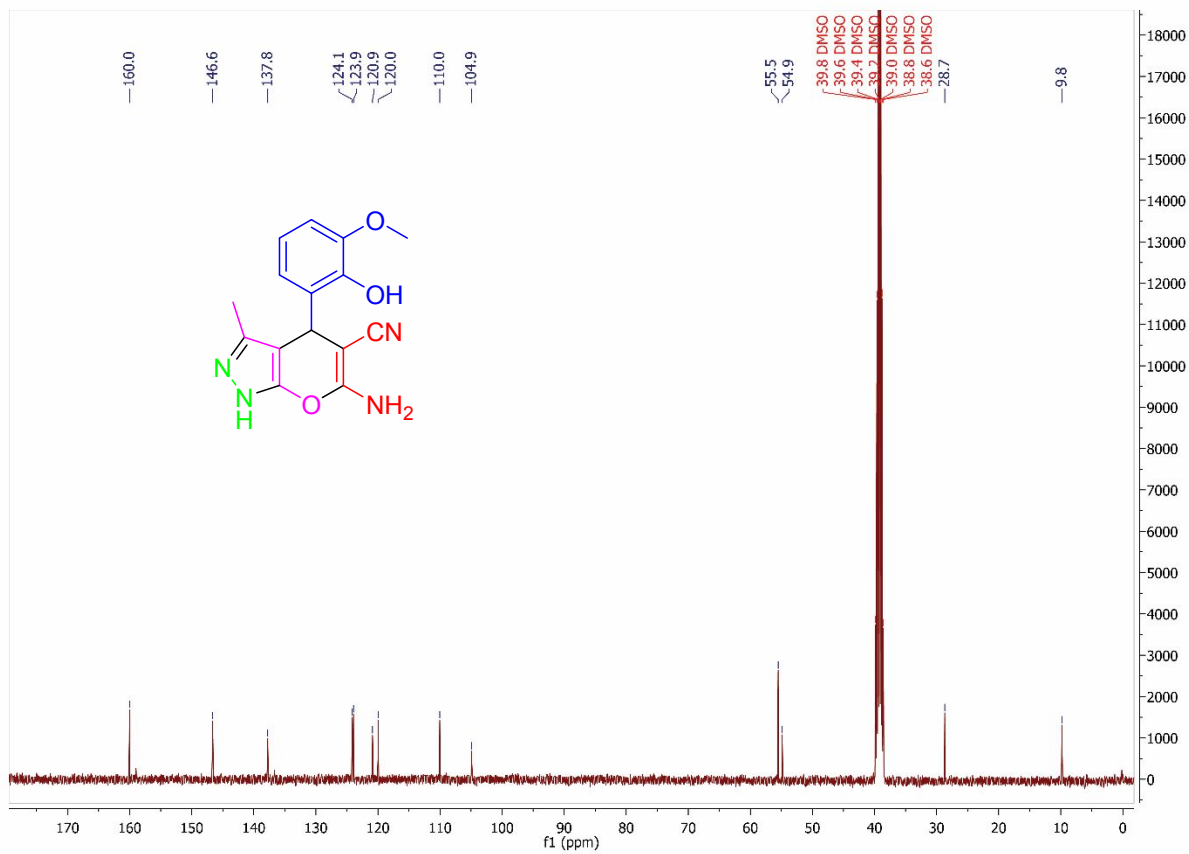


Figure S26: ¹³C NMR spectrum of 6-amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7m)