

Supporting Information

Synthesis and application of [Zr-UiO-66-PDC-SO₃H]Cl at the preparation of dicyanomethylene pyridines via chemical and electrochemical methods

Amir Mohammad Naseri ^a, Mahmoud Zarei^{*a}, Saber Alizadeh^{*b}, Saeed Babaee ^a, Mohammad Ali Zolfigol^{*a}, Davood Nematollahi^{*b}, Jalal Arjomandi^c, Hu Shi^d

[a] Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Tel: +988138282807, Fax: +988138380709 Iran.

E-Mail: mahmoud8103@yahoo.com , zolfigol@basu.ac.ir & mzolfigol@yahoo.com

[b] Department of Analytical Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran.

E-Mail: s.alizade66@yahoo.com & s.alizadeh93@basu.ac.ir, nemat@basu.ac.ir, nematollahid@gmail.com

[c] Department of Physical Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran.

[d] School of Chemistry and Chemical Engineering, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China.

E-Mail: hshi@sxu.edu.cn.

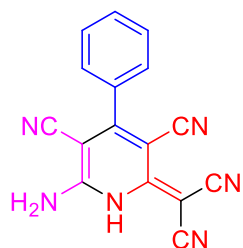
6-Amino-2-(dicyanomethylene)-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (a)	6
6-Amino-4-(4-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (b).....	6
6-Amino-2-(dicyanomethylene)-4-(p-tolyl)-1,2-dihydropyridine-3,5-dicarbonitrile (c).....	6
6-Amino-2-(dicyanomethylene)-4-(3-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (d)	7
6-Amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e).....	7
6-Amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)	7
6-Amino-4-(2-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (g).....	7
6-Amino-2-(dicyanomethylene)-4-(3-ethoxy-4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (h)	8
6-Amino-2-(dicyanomethylene)-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (i)	8
6-Amino-2-(dicyanomethylene)-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (j)	8
6-Amino-2-(dicyanomethylene)-4-(2-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (k)	8
6-Amino-2-(dicyanomethylene)-4-(3,4-dihydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (l).....	9
6-Amino-2-(dicyanomethyl)-4-(3,4-dimethoxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (m)	9
6'-Amino-2'-(dicyanomethylene)-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (n)	9
6-Amino-4-(4-bromophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (o).....	10

6-Amino-2-(dicyanomethylene)-4-(3-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (p).....	10
6-Amino-2-(dicyanomethylene)-4-(4-fluorophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (q)	10
4,4',4''-(((1,3,5-Triazine-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl))tris(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (r)	11
4,4'-(1,4-Phenylene)bis(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (s)	11
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (a)	12
¹ H NMR spectrum of 6-Amino-2-(dicyanomethylene)-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile(a).....	12
6-Amino-2-(dicyanomethylene)-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile(a)	13
FT-IR spectrum of 6-amino-4-(4-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (b)	13
¹ H NMR spectrum of 6-amino-4-(4-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (b)	14
¹³ C NMR spectrum of 6-amino-4-(4-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (b)	14
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(p-tolyl)-1,2-dihydropyridine-3,5-dicarbonitrile (c)	15
¹ H NMR spectrum of 6-Amino-2-(dicyanomethylene)-4-(p-tolyl)-1,2-dihydropyridine-3,5-dicarbonitrile (c).....	15
¹³ C NMR spectrum of 6-Amino-2-(dicyanomethylene)-4-(p-tolyl)-1,2-dihydropyridine-3,5-dicarbonitrile (c).....	16
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (d)	16
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (d)	17
¹³ C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (d)	17
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e).....	18
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e).....	18
¹³ C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e).....	19
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)	20

¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)	20
¹³ C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)	21
FT-IR spectrum of 6-amino-4-(2-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (g)	22
¹ H NMR spectrum of 6-amino-4-(2-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (g)	22
¹³ C NMR spectrum of 6-amino-4-(2-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (g)	23
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-ethoxy-4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (h)	23
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-ethoxy-4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (h)	24
¹³ C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-ethoxy-4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (h)	24
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (i)	25
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (i)	25
¹³ C NMR spectrum of 6-amino-2-(dicyanomethylene)-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (i)	26
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (j)	26
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (j)	27
¹³ C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (j)	27
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(2-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (k)	28
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(2-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (k)	28
¹³ C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(2-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (k)	29
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(3,4-dihydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (l)	29

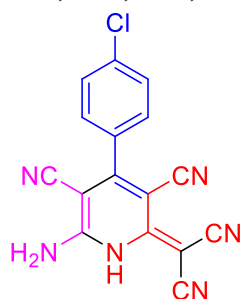
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3,4-dihydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (l)	30
FT-IR spectrum of 6-amino-2-(dicyanomethyl)-4-(3,4-dimethoxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (m)	30
¹ H NMR spectrum of 6-amino-2-(dicyanomethyl)-4-(3,4-dimethoxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (m)	31
¹³ C NMR spectrum of 6-amino-2-(dicyanomethyl)-4-(3,4-dimethoxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (m)	31
FT-IR spectrum of 6'-amino-2'-(dicyanomethylene)-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (n).....	32
¹ H NMR spectrum of 6'-amino-2'-(dicyanomethylene)-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (n)	32
¹³ C NMR spectrum of 6'-amino-2'-(dicyanomethylene)-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (n)	33
FT-IR spectrum of 6-amino-4-(4-bromophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (o)	33
¹ H NMR spectrum of 6-amino-4-(4-bromophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (o)	34
¹³ C NMR spectrum of 6-amino-4-(4-bromophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (o)	34
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (p)	35
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (p)	35
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-fluorophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (q)	36
¹ H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-fluorophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (q)	36
FT-IR spectrum of 4,4',4''-(((1,3,5-triazine-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl))tris(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (r).....	37
¹ H NMR spectrum of 4,4',4''-(((1,3,5-triazine-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl))tris(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (r).....	37
¹³ C NMR spectrum of 4,4',4''-(((1,3,5-triazine-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl))tris(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (r).....	38
FT-IR spectrum of 4,4'-(1,4-phenylene)bis(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (s)	38

¹ H NMR spectrum of 4,4'-(1,4-phenylene)bis(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (s)	39
¹³ C NMR spectrum of 4,4'-(1,4-phenylene)bis(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (s)	39



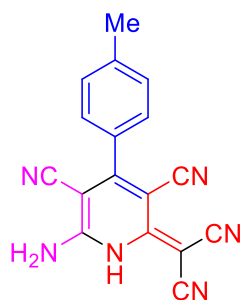
6-Amino-2-(dicyanomethylene)-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (a)

Yellow solid; Yield: 65%(0.185 g); Mp: 280-283 °C; IR (KBr): ν (cm⁻¹) = 3374, 3306, 3215, 2218, 2191, 1642. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.80 (s, 3H), 7.60 – 7.53 (m, 3H), 7.48 (d, *J* = 1.3 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 160.5, 160.4, 157.8, 135.3, 129.7, 128.4, 128.3, 116.2, 115.9, 85.4, 80.7, 43.6.



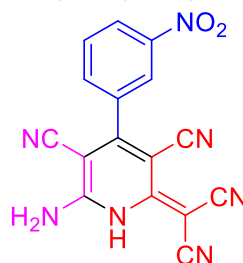
6-Amino-4-(4-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (b)

Yellow solid; Yield: 87%(0.277 g); Mp: 290-262 °C; IR (KBr): ν (cm⁻¹) = 3363, 3302, 3211, 2228, 2217, 2191, 1645. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.52 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 161.6, 159.5, 158.5, 134.9, 134.9, 130.8, 129.1, 116.8, 116.5, 85.6, 81.0, 44.2.



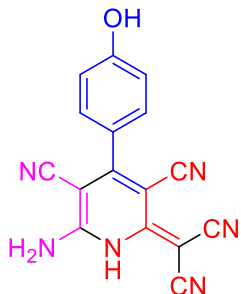
6-Amino-2-(dicyanomethylene)-4-(p-tolyl)-1,2-dihydropyridine-3,5-dicarbonitrile (c)

Yellow solid; Yield: 85%(0.253 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3483, 3371, 3202, 2213, 2200, 2171, 1620. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.29 (s, 4H), 6.87 (s, 2H), 2.38 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.7, 159.7, 158.7, 139.0, 132.8, 128.9, 128.3, 116.9, 116.6, 85.0, 80.3, 20.9.



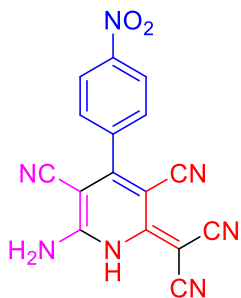
6-Amino-2-(dicyanomethylene)-4-(3-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (d)

Yellow solid; Yield: 77%(0.254 g); Mp: 316-318 °C; IR (KBr): ν (cm⁻¹) = 3438, 3339, 3213, 2197, 2181, 1657, 1556, 1352. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.38 – 8.35 (m, 1H), 8.33 – 8.30 (m, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.05 (s, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 163.0, 159.0, 157.9, 148.0, 137.8, 135.9, 130.8, 124.8, 123.9, 117.1, 116.9, 85.3, 80.7, 44.3.



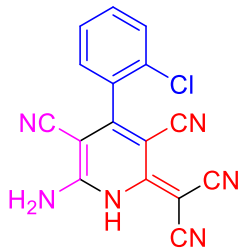
6-Amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e)

Yellow solid; Yield: 82%(0.246 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3342, 3227, 2183, 1652, 1553. ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.85 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.89 – 6.78 (m, 4H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 163.4, 160.1, 159.3, 159.1, 130.6, 126.6, 117.7, 117.3, 115.5, 85.6, 80.7, 43.6. MS = 301



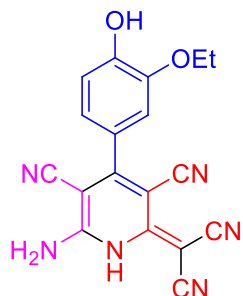
6-Amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)

Yellow solid; Yield: 79%(0.260 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3336, 2196, 1655, 1556, 1508, 1360. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.35 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.05 (s, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 162.9, 159.0, 158.3, 148.5, 142.9, 130.7, 124.1, 116.9, 116.7, 85.0, 80.4, 44.3. MS = 330.



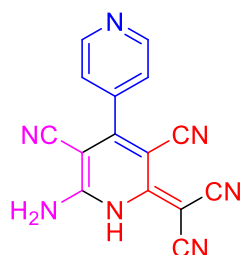
6-Amino-4-(2-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (g)

Yellow solid; Yield: 68%(0.216 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3438, 3342, 3231, 2195, 2164, 1636, 1557. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.61 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.50 (td, *J* = 7.7, 1.9 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.00 (s, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 162.7, 158.9, 157.9, 135.5, 131.6, 131.4, 130.7, 130.0, 128.0, 116.6, 116.3, 86.0, 81.1, 44.0.



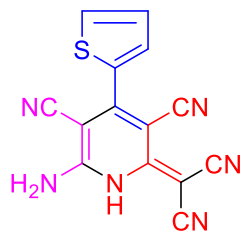
6-Amino-2-(dicyanomethylene)-4-(3-ethoxy-4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (h)

Yellow solid; Yield: 83%(0.286 g); Mp: 333-335 °C; IR (KBr): ν (cm⁻¹) = 3431, 3342, 3236, 2198, 2165, 1649, 1554. ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.38 (s, 1H), 6.97 – 6.94 (m, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.85 – 6.78 (m, 3H), 4.06 (q, *J* = 7.0 Hz, 2H), 1.36 – 1.33 (m, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 163.3, 160.1, 159.3, 148.6, 146.5, 126.8, 122.1, 117.8, 117.4, 115.7, 114.6, 85.6, 80.8, 64.3, 43.6, 15.1.



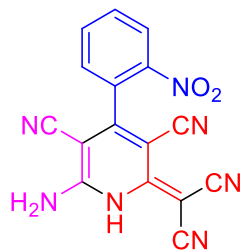
6-Amino-2-(dicyanomethylene)-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (i)

Yellow solid; Yield: 74%(0.211 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3443, 3345, 3224, 2211, 2195, 2175, 1650, 1569. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.72 (d, *J* = 5.7 Hz, 2H), 7.46 (d, *J* = 4.4 Hz, 2H), 7.04 (s, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 162.9, 159.0, 157.7, 150.3, 144.2, 123.6, 116.9, 116.6, 84.7, 80.1, 44.3.



6-Amino-2-(dicyanomethylene)-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (j)

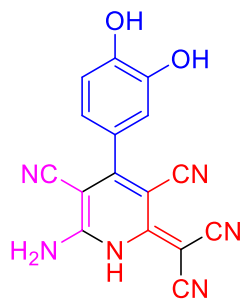
Yellow solid; Yield: 70%(0.203 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3481, 3345, 3211, 2213, 2189, 2163, 1624, 1555. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.82 (d, *J* = 4.9 Hz, 1H), 7.37 (d, *J* = 3.5 Hz, 1H), 7.23 – 7.18 (m, 1H), 6.97 (s, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 163.4, 159.3, 152.2, 135.2, 130.4, 129.6, 127.9, 117.3, 116.9, 85.8, 81.0, 44.2.



6-Amino-2-(dicyanomethylene)-4-(2-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (k)

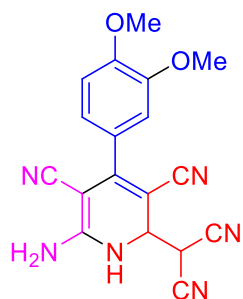
Yellow solid; Yield: 60%(0.197 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3437, 3341, 3230, 2218, 2195, 1637, 1560, 1517, 1351. ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.27 (d, *J* = 8.2 Hz, 1H), 7.92 (t, *J* = 7.5 Hz, 1H), 7.80 (t, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.5 Hz,

1H), 7.05 (s, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 170.8, 162.6, 158.8, 158.1, 147.3, 135.2, 131.8, 131.6, 131.3, 125.4, 116.6, 116.4, 84.9, 80.2, 60.2, 44.1, 21.2, 14.6.



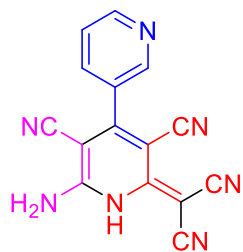
6-Amino-2-(dicyanomethylene)-4-(3,4-dihydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (l)

Yellow solid; Yield: 75%(0.237 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3457, 3334, 3225, 2197, 2168, 1650, 1560. ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.33 (s, 1H), 9.26 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 3H), 6.77 (s, 1H), 6.67 (d, *J* = 8.1 Hz, 1H).



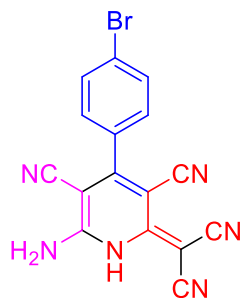
6-Amino-2-(dicyanomethylene)-4-(3,4-dimethoxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (m)

Yellow solid; Yield: 70%(0.242 g); Mp: 332-335 °C; IR (KBr): ν (cm⁻¹) = 3504, 3489, 3374, 2216, 2194, 2172, 1613, 1551. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.07 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 2.1 Hz, 1H), 6.97 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.88 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.7, 159.3, 158.8, 149.6, 148.0, 127.7, 121.3, 117.1, 116.7, 112.2, 111.2, 85.1, 80.3, 55.5, 55.4, 43.1, 40.0,



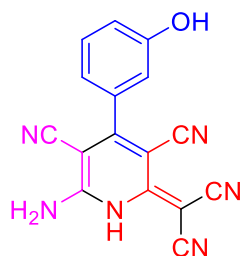
6'-Amino-2'-(dicyanomethylene)-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (n)

Brown solid; Yield: 80%(0.228 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3389, 3317, 3161, 2209, 2189, 2156, 1654, 1577, 1514. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.79 – 8.47 (m, 2H), 7.91 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.55 (dd, *J* = 7.9, 4.9 Hz, 1H), 7.03 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.52, 158.57, 156.38, 150.38, 148.47, 136.39, 131.89, 123.40, 116.65, 116.43, 85.08, 80.40, 40.03.



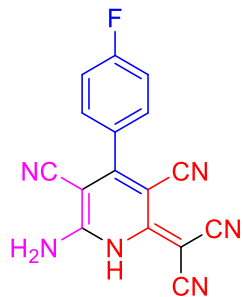
6-Amino-4-(4-bromophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (o)

White solid; Yield: 84%(0.305 g); Mp: 330-332 °C; IR (KBr): ν (cm⁻¹) = 3451, 3339, 3224, 2214, 2194, 2170, 1674, 1572, 1511. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.77 – 7.64 (m, 2H), 7.46 – 7.30 (m, 2H), 6.97 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.5, 158.5, 158.5, 135.0, 131.4, 130.6, 123.0, 116.7, 116.4, 84.8, 80.1, 40.0.



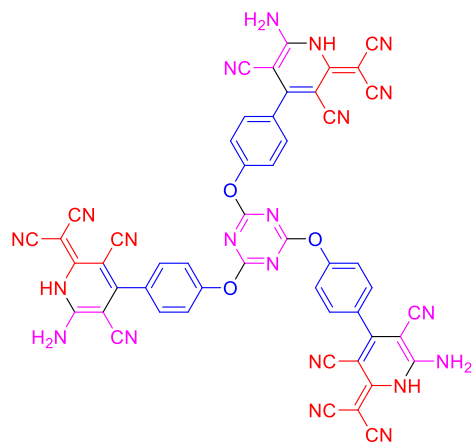
6-Amino-2-(dicyanomethylene)-4-(3-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (p)

Yellow solid; Yield: 85%(0.255 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3476, 3330, 3218, 2202, 2171, 1625, 1548. ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.72 (s, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.94 – 6.84 (m, 3H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.73 (s, 1H).



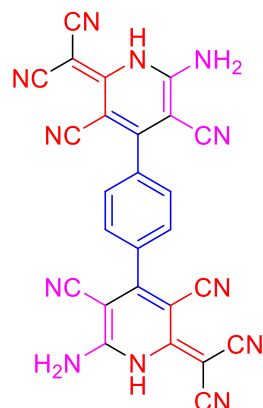
6-Amino-2-(dicyanomethylene)-4-(4-fluorophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (q)

Yellow solid; Yield: 83%(0.251 g); Mp: 324-326 °C; IR (KBr): ν (cm⁻¹) = 3449, 3374, 3309, 3216, 2212, 2194, 2171, 1646. ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.51 – 7.45 (m, 2H), 7.34 (t, *J* = 8.6 Hz, 2H), 6.97 (s, 2H).



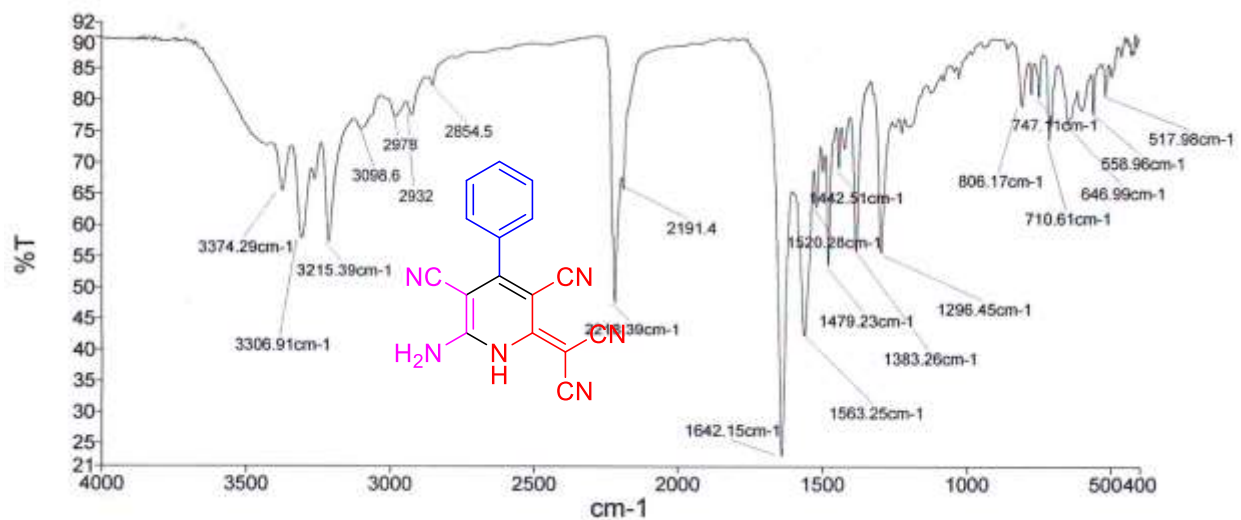
4,4',4''-(((1,3,5-Triazine-2,4,6-triyl)tris(oxy)))tris(benzene-4,1-diyl)tris(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (r)

Yellow solid; Yield: 65%(0.634 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3504, 3374, 3224, 2215, 2194, 2166, 1613, 1551. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.53 (td, *J* = 8.5, 4.3 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.38 (d, *J* = 8.6 Hz, 1H), 6.95 (s, 1H), 6.91 (s, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.3, 163.2, 159.2, 159.1, 153.2, 152.5, 133.9, 132.5, 130.6, 130.1, 122.0, 121.7, 120.6, 117.3, 117.0, 85.5, 80.8, 40.5, 40.3, 40.1.

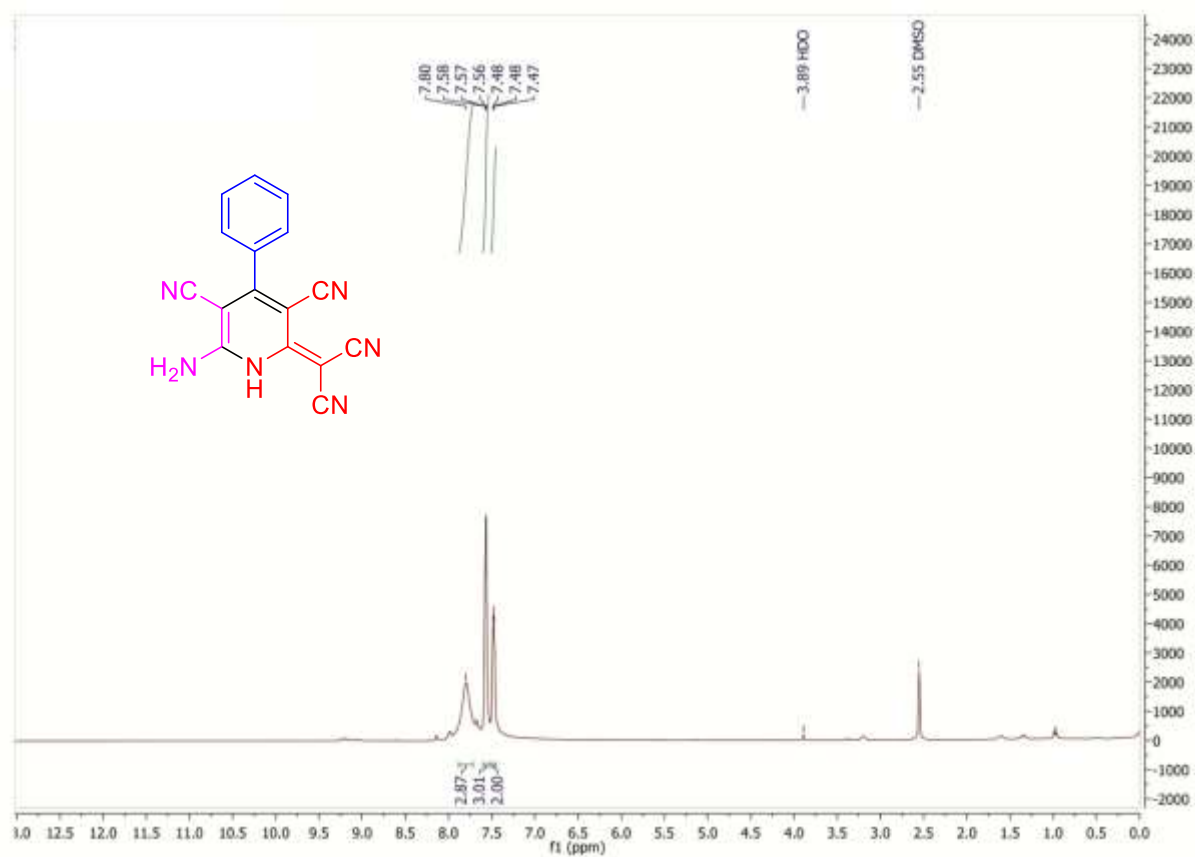


4,4'-(1,4-Phenylene)bis(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (s)

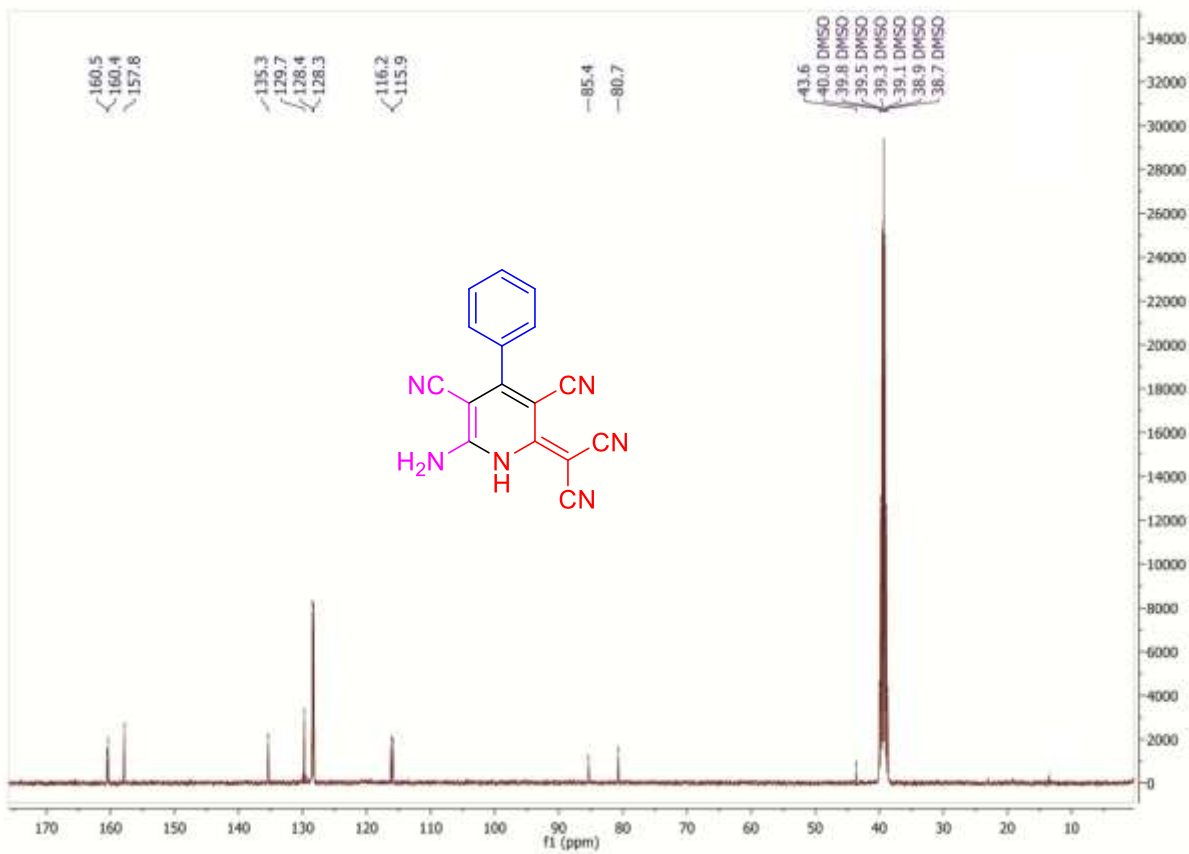
Yellow solid; Yield: 77%(0.377 g); Mp: >350 °C; IR (KBr): ν (cm⁻¹) = 3395, 3334, 3228, 2192, 2158, 1650, 1549, 1429. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.55 (s, 1H), 6.94 (s, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 159.2, 144.3, 139.6, 135.2, 135.0, 134.8, 132.4, 131.5, 129.1, 128.9, 126.5, 126.4, 121.7, 121.2, 120.1, 119.6, 118.4, 116.8, 111.1, 111.0, 110.8, 102.8, 42.3.



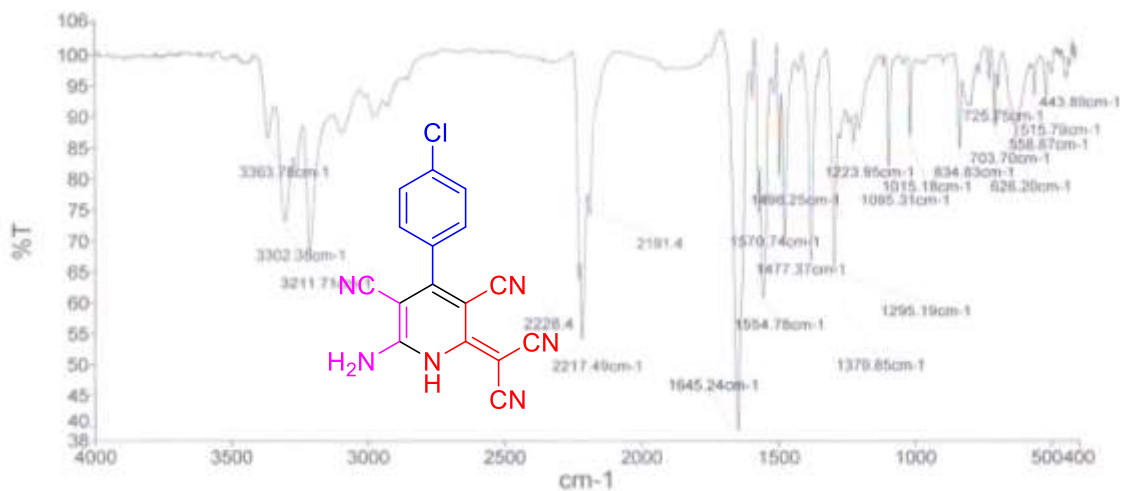
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile (a)



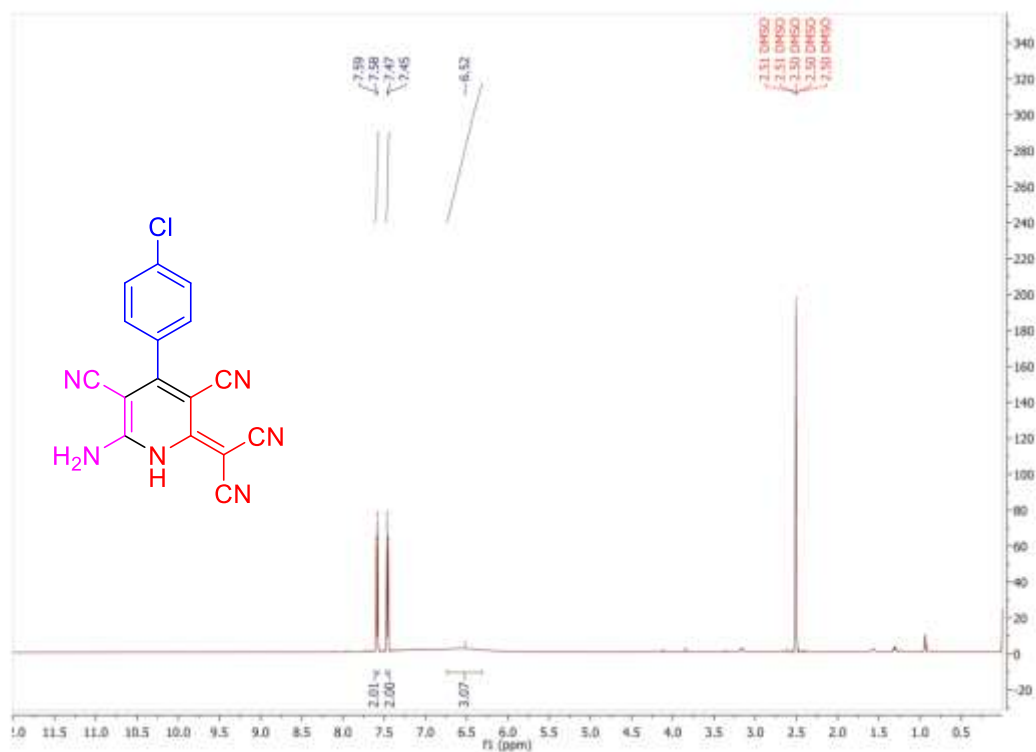
¹H NMR spectrum of 6-Amino-2-(dicyanomethylene)-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile(a)



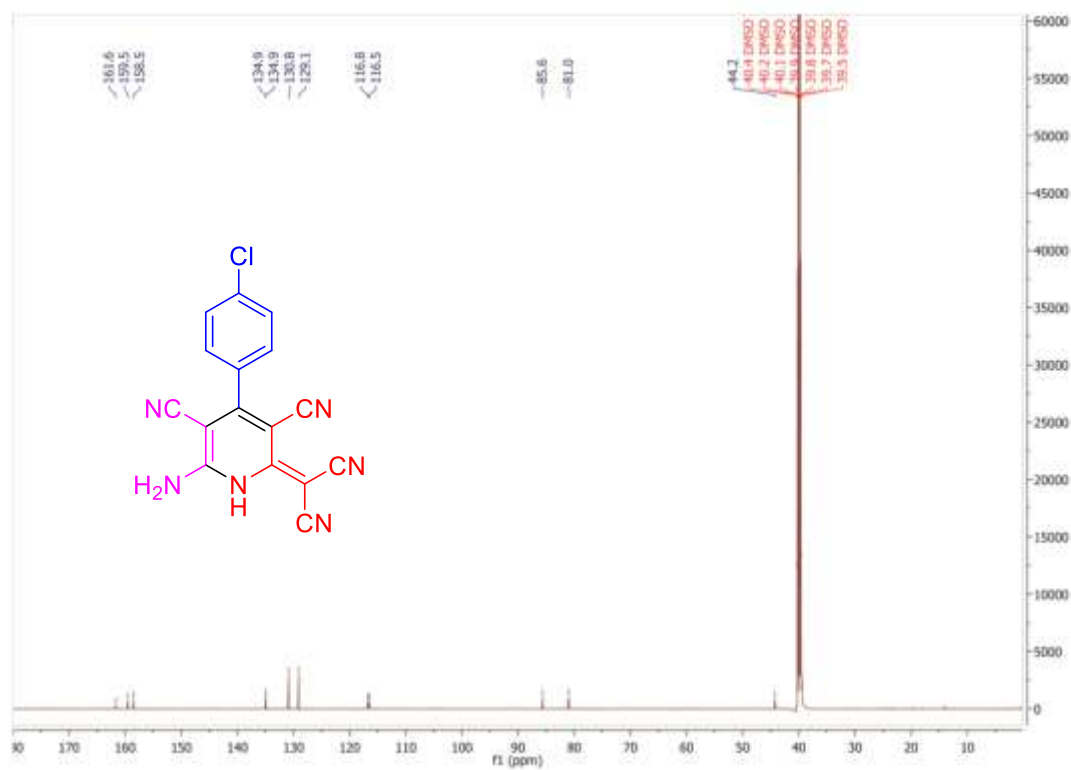
6-Amino-2-(dicyanomethylene)-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile(a)



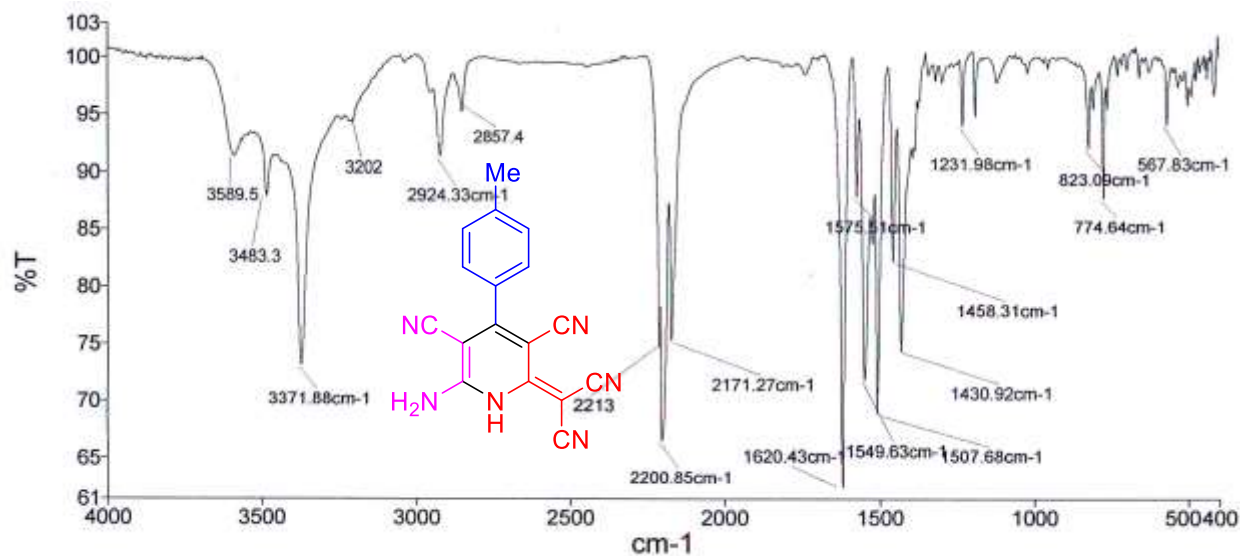
FT-IR spectrum of 6-amino-4-(4-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (b)

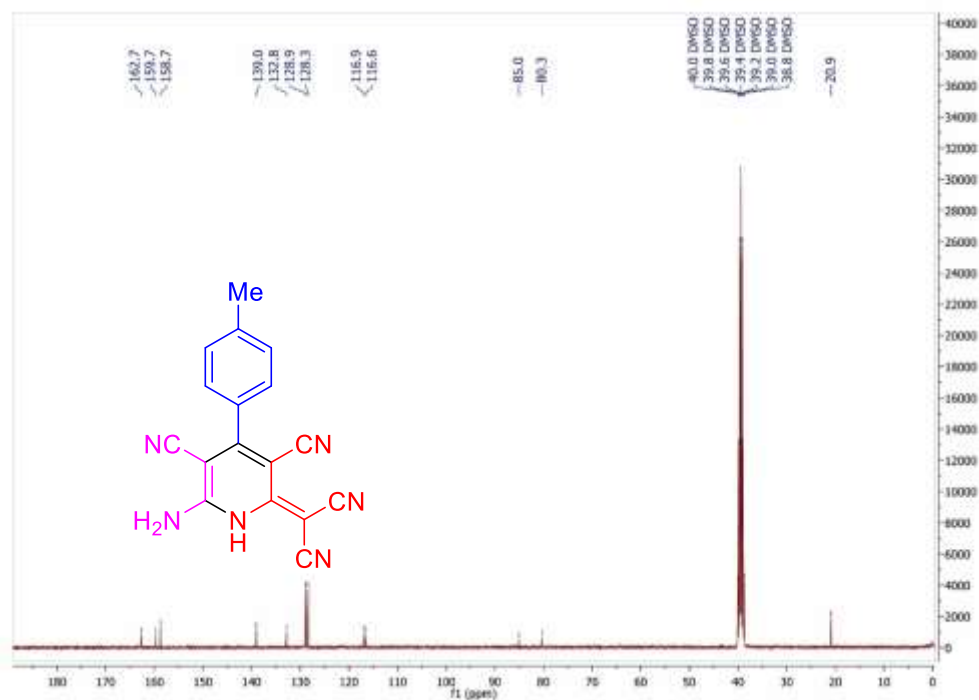


¹H NMR spectrum of 6-amino-4-(4-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (b)

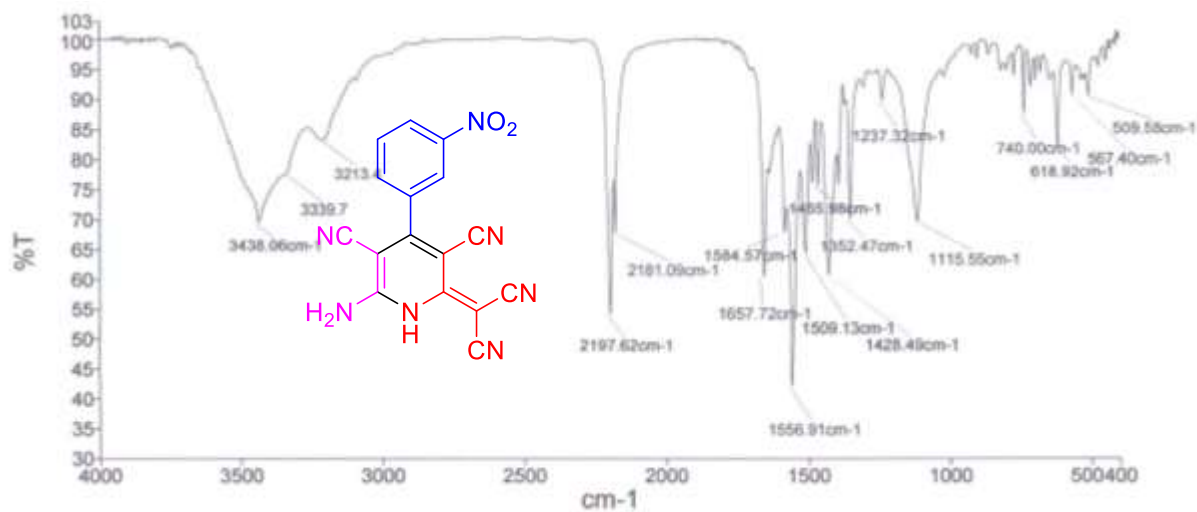


¹³C NMR spectrum of 6-amino-4-(4-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (b)

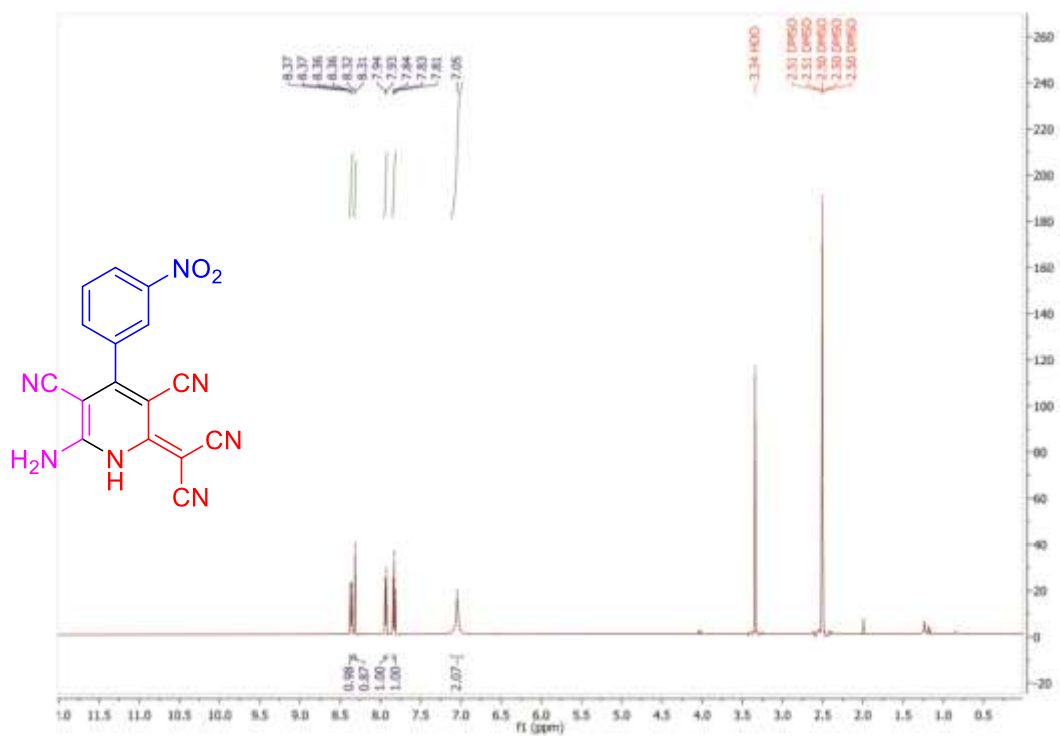




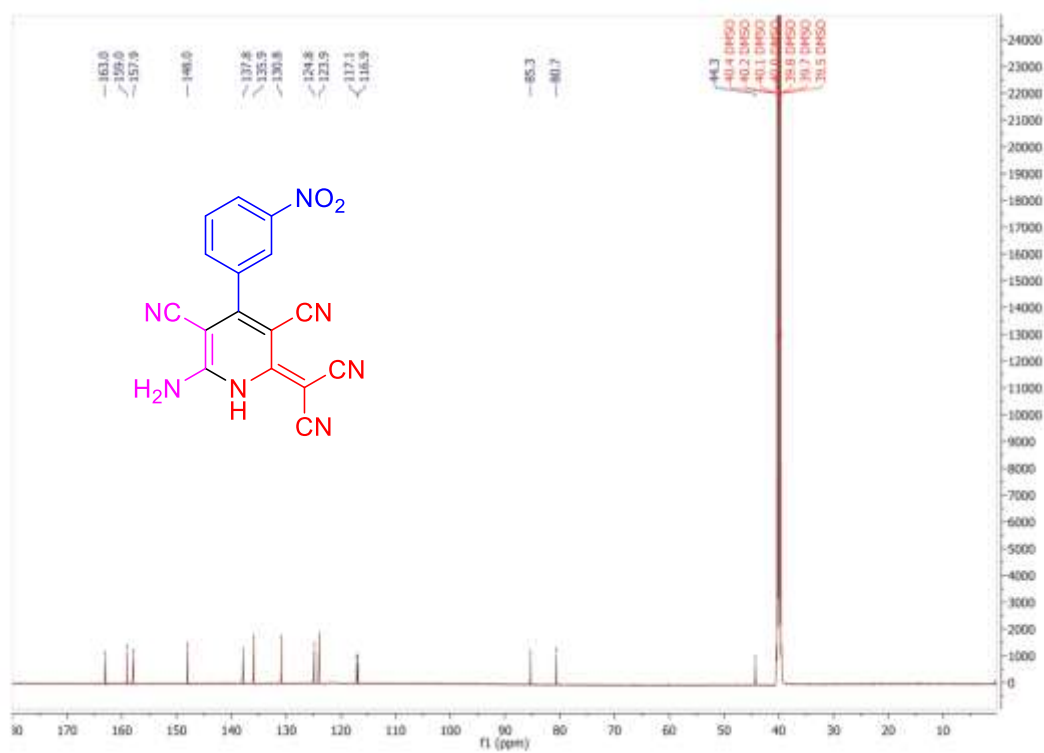
¹³C NMR spectrum of 6-Amino-2-(dicyanomethylene)-4-(p-tolyl)-1,2-dihydropyridine-3,5-dicarbonitrile (c)



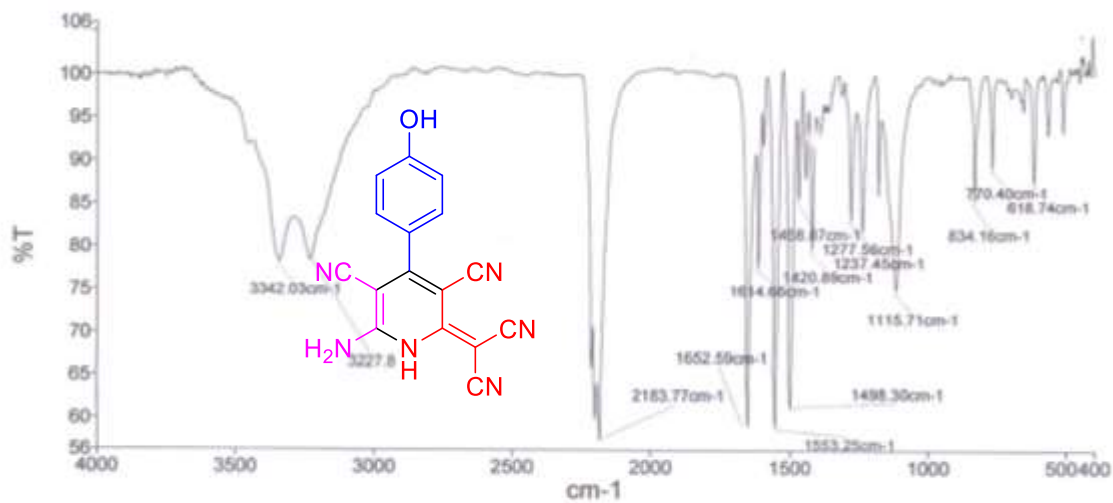
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (d)



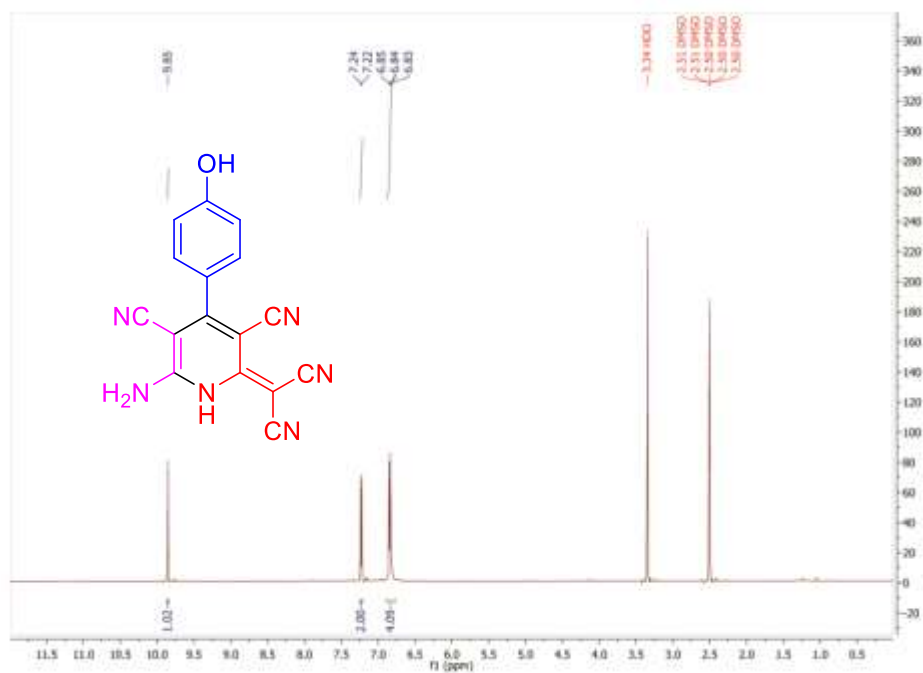
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (d)



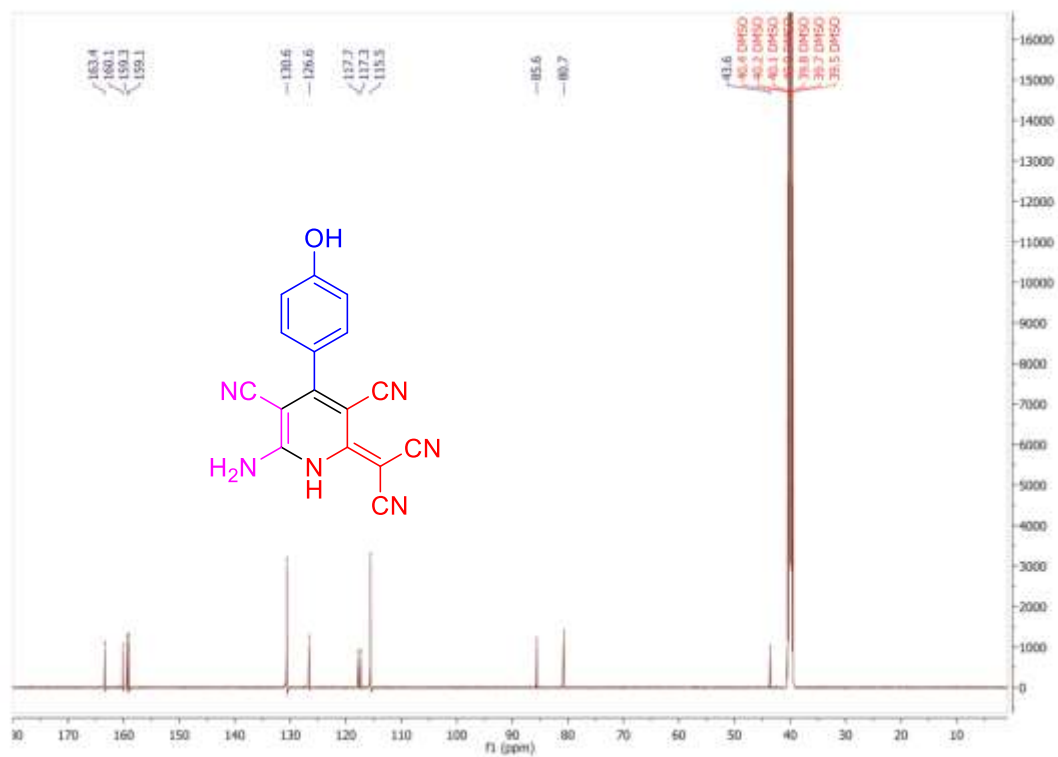
¹³C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (d)



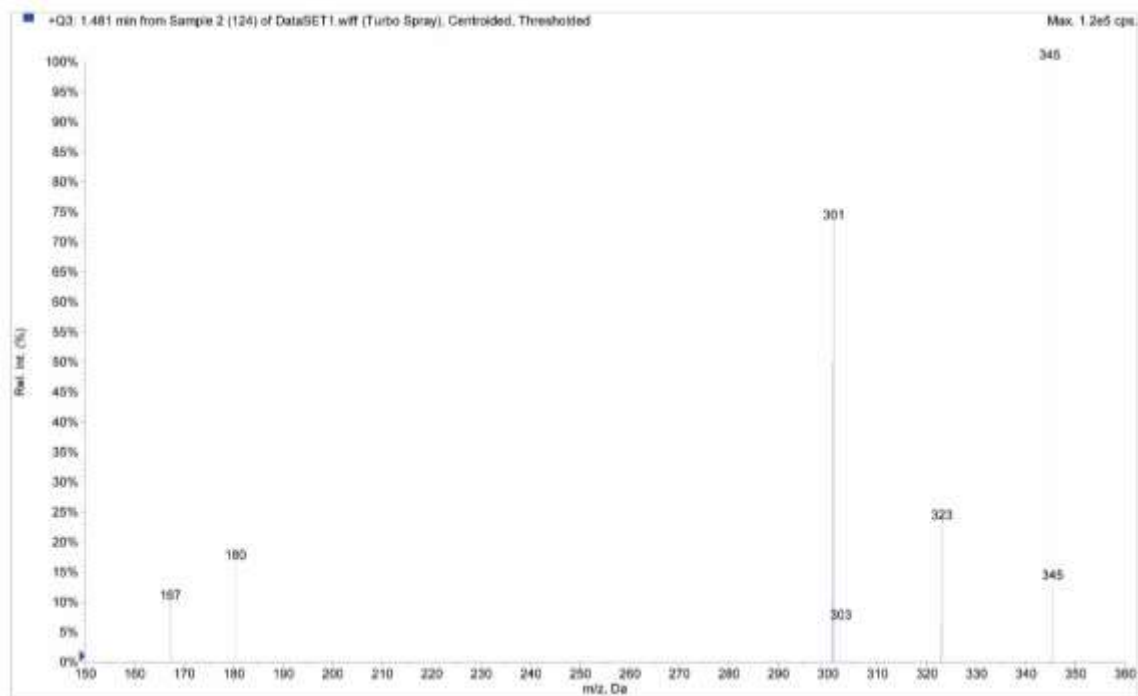
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e)



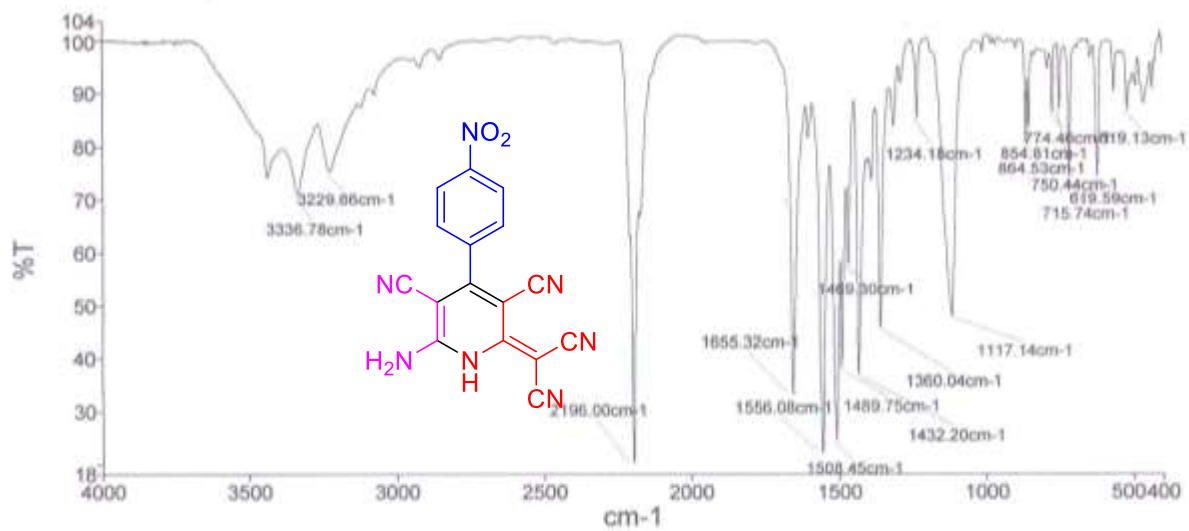
^1H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e)



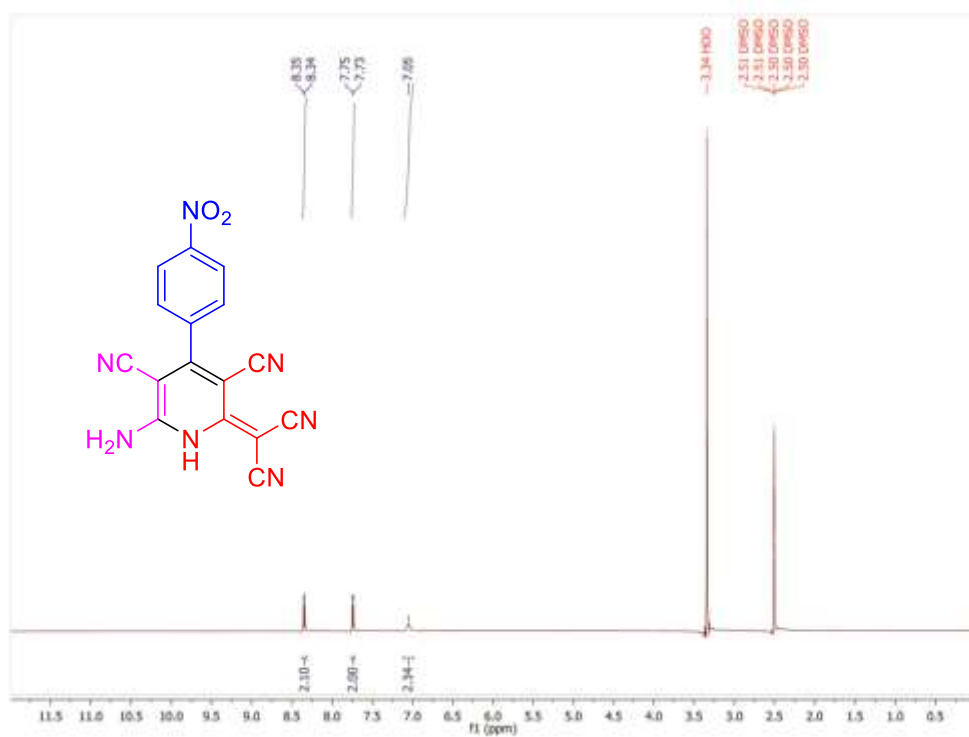
^{13}C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e)



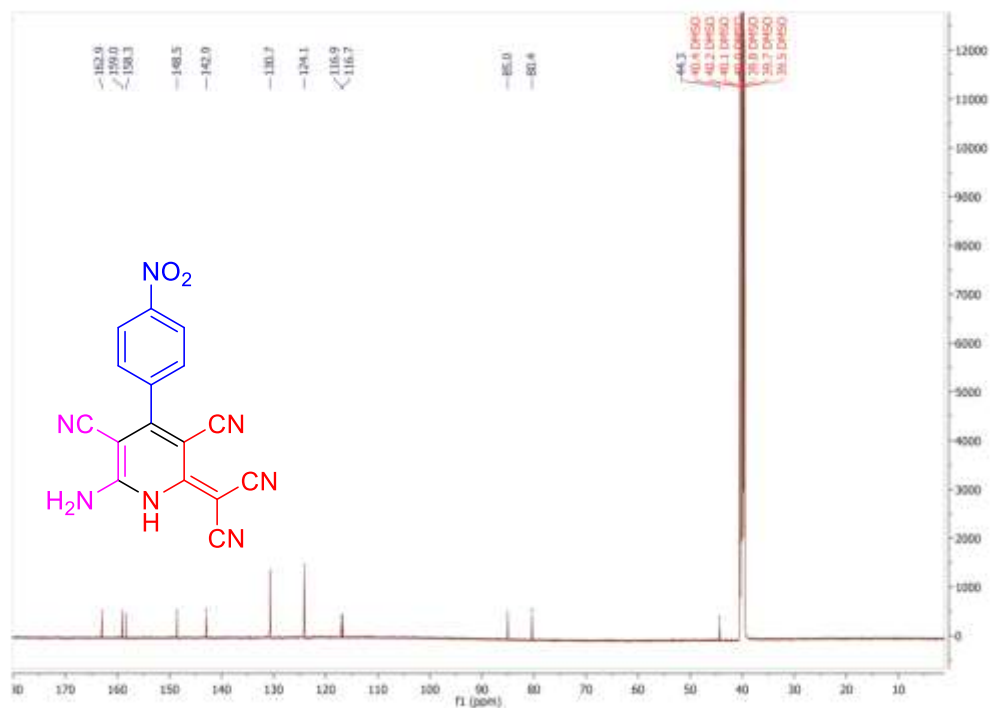
Mass spectrum of 6-amino-2-(dicyanomethylene)-4-(4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (e)



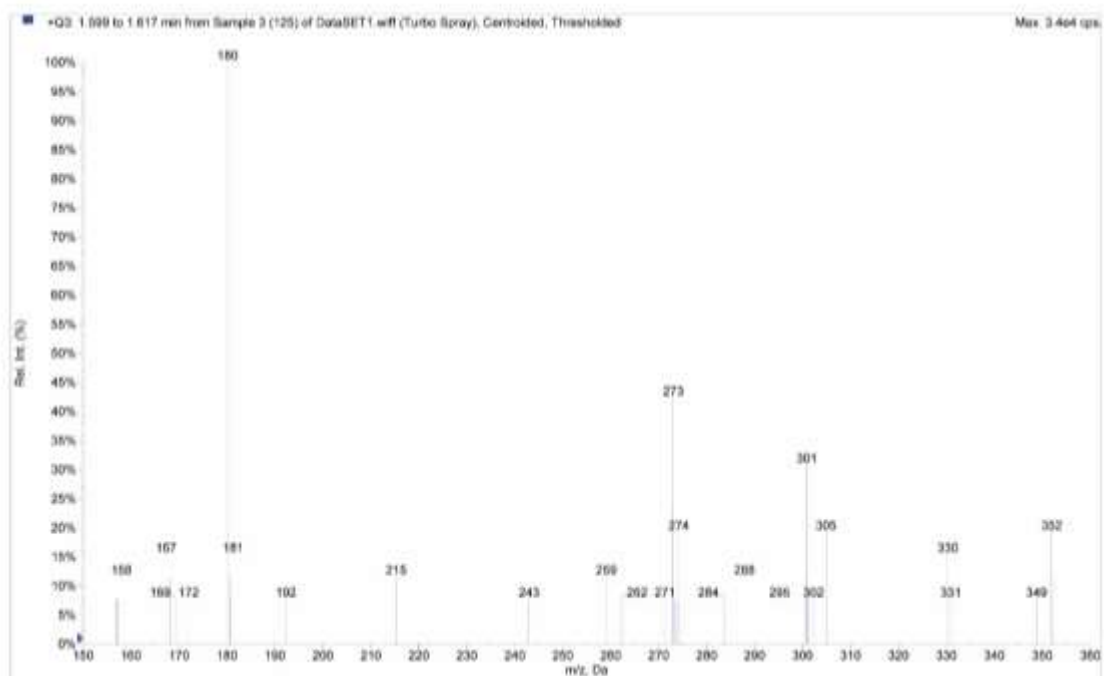
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)



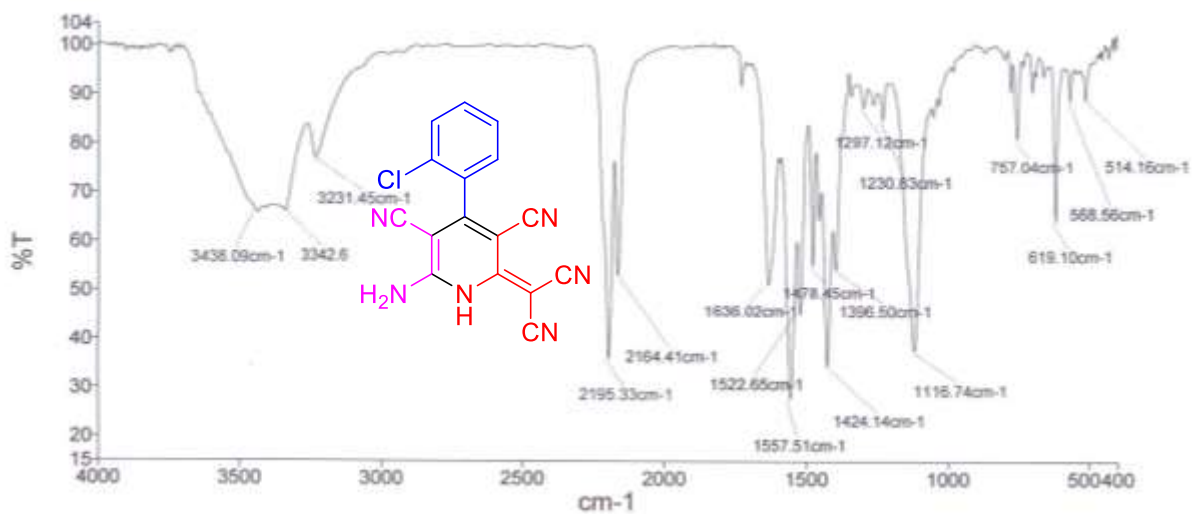
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)



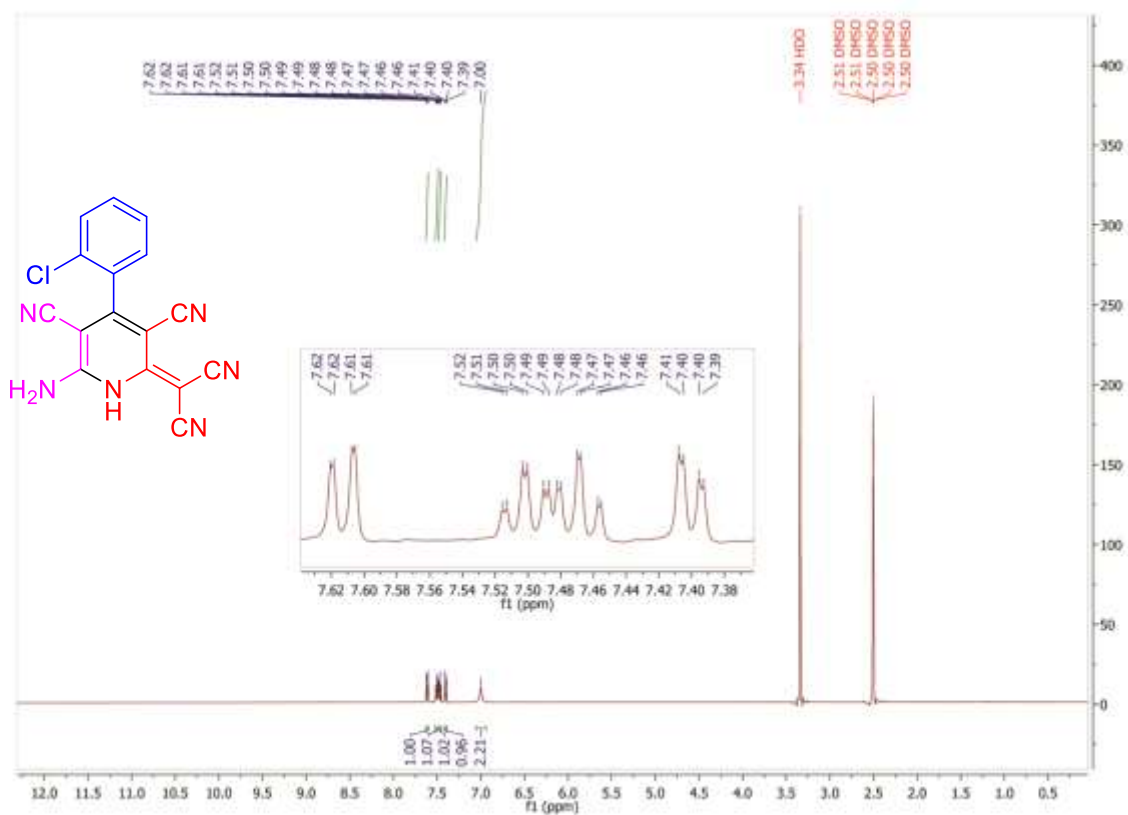
¹³C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)



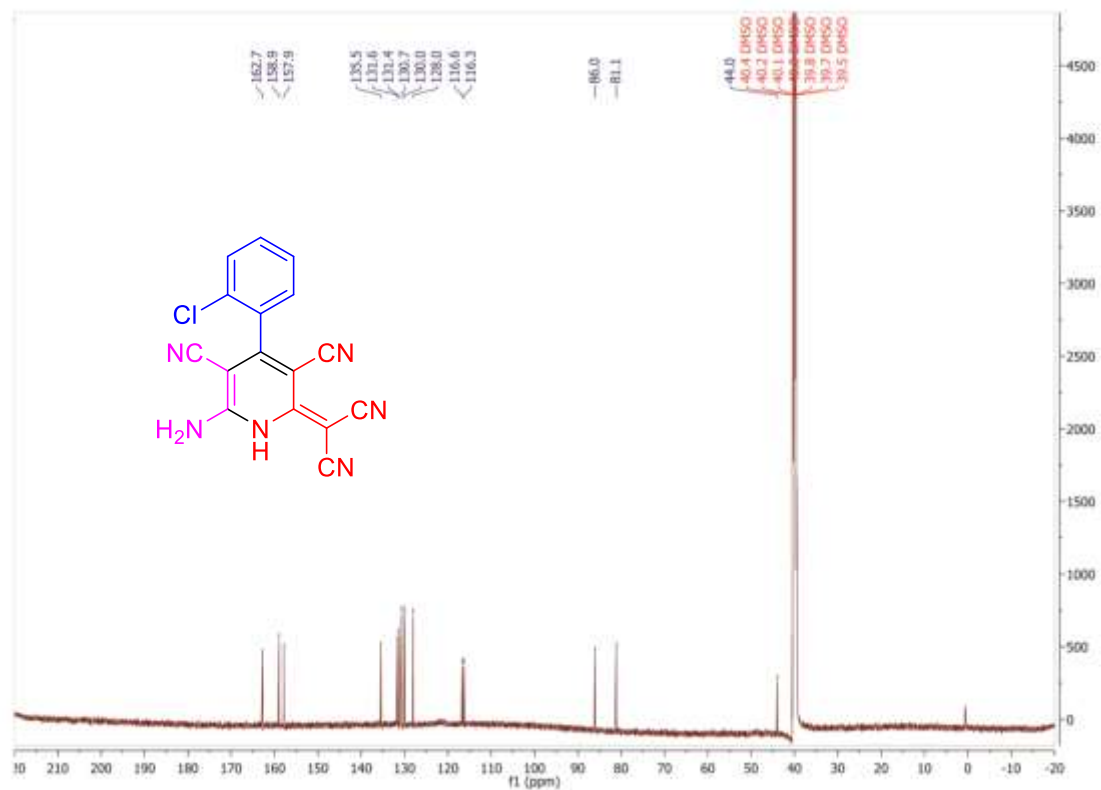
Mass spectrum of 6-amino-2-(dicyanomethylene)-4-(4-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (f)



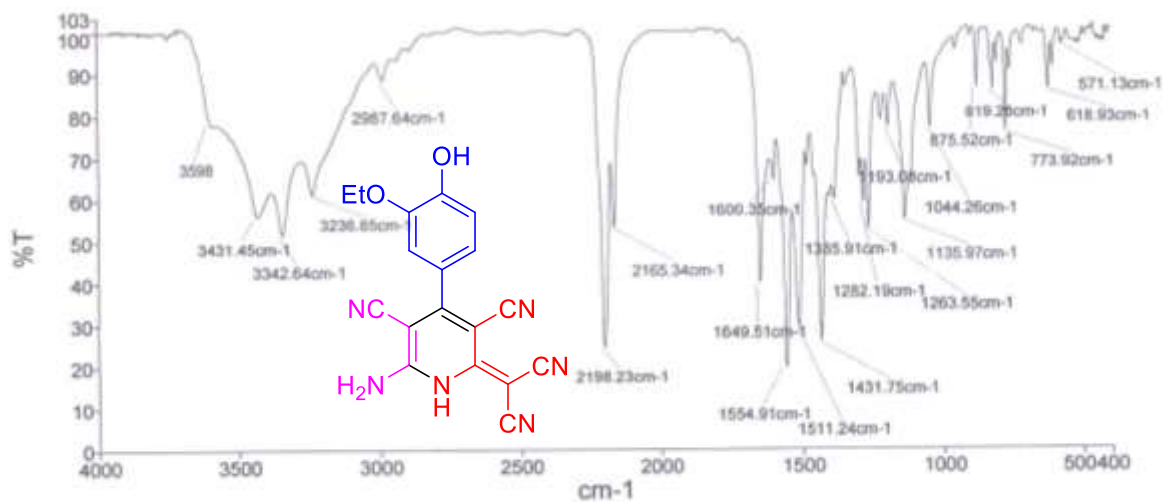
FT-IR spectrum of 6-amino-4-(2-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (g)



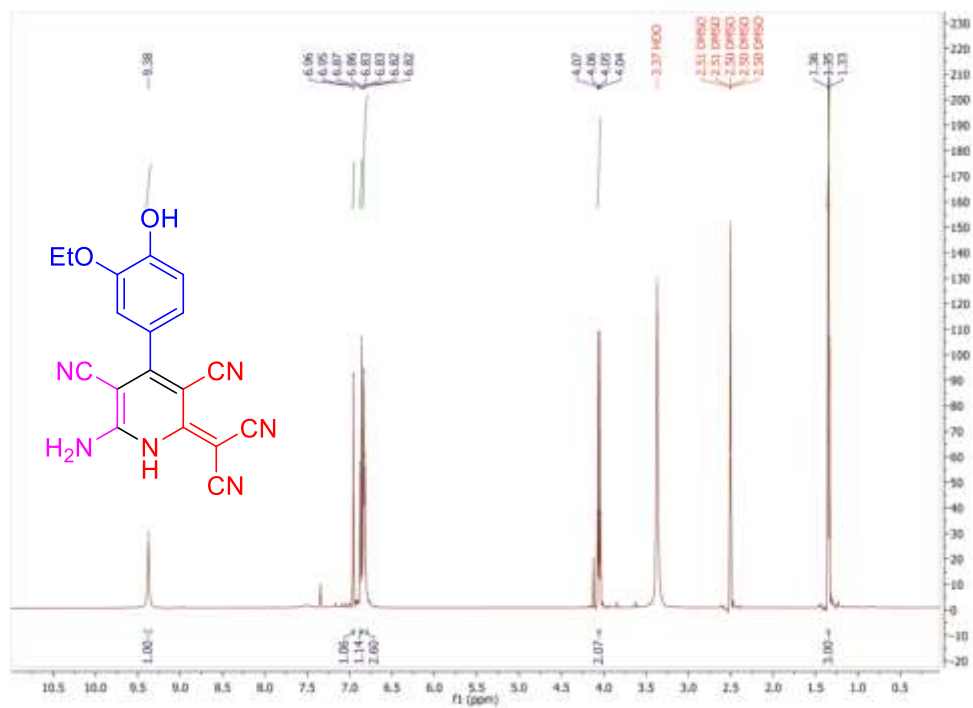
¹H NMR spectrum of 6-amino-4-(2-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (g)



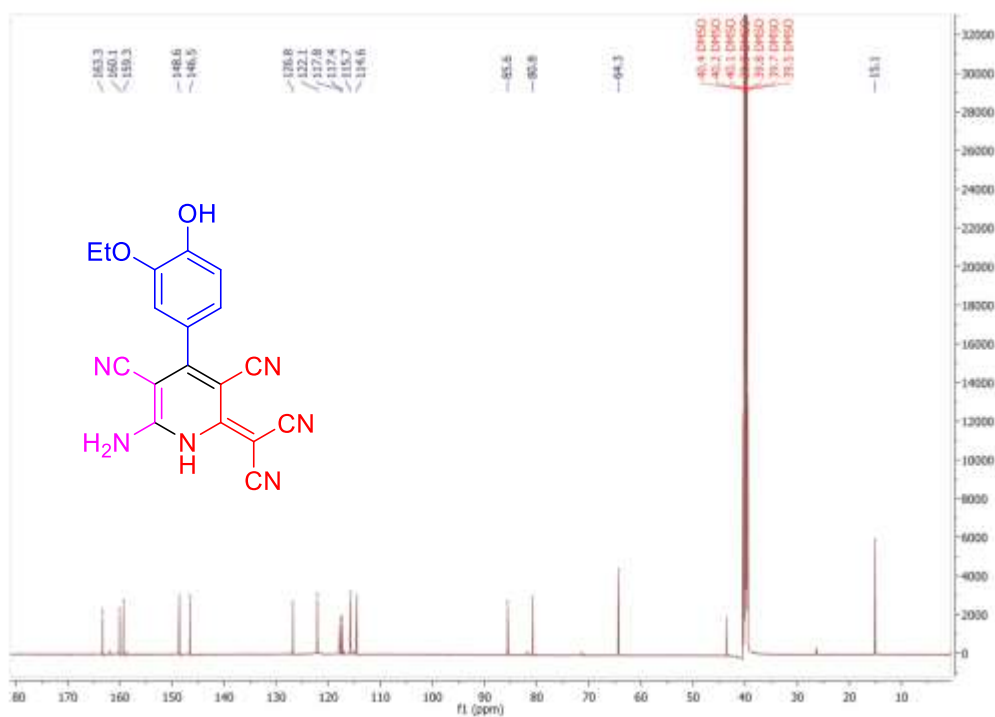
¹³C NMR spectrum of 6-amino-4-(2-chlorophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (g)



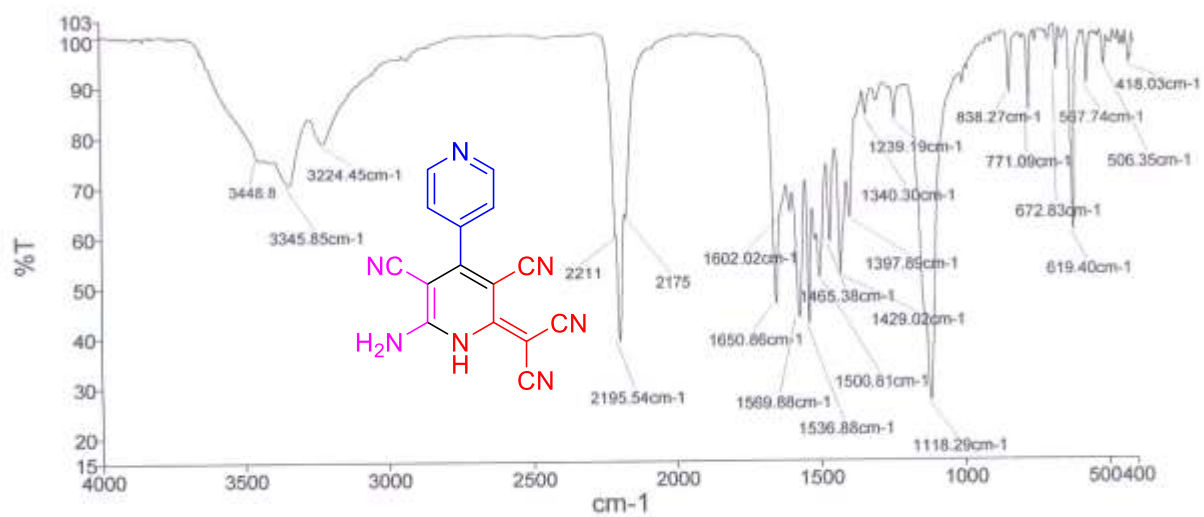
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-ethoxy-4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (h)



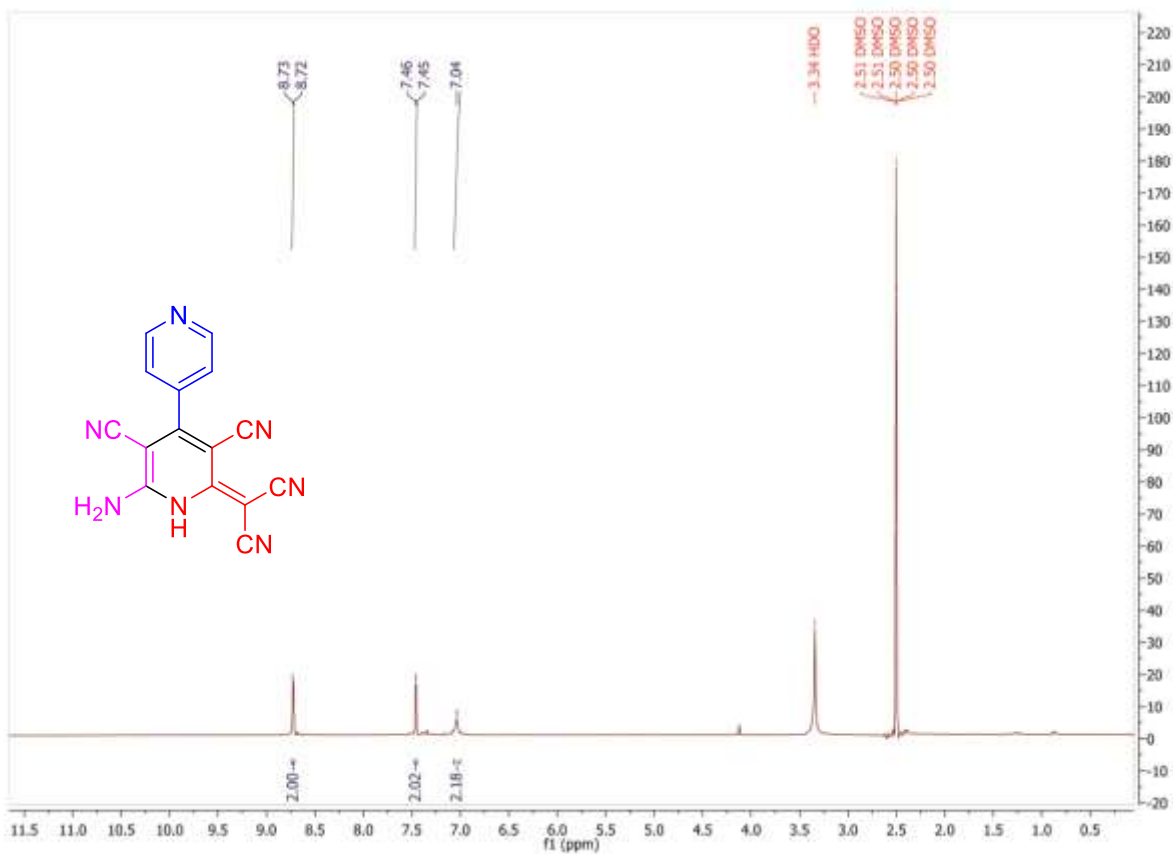
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-ethoxy-4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (h)



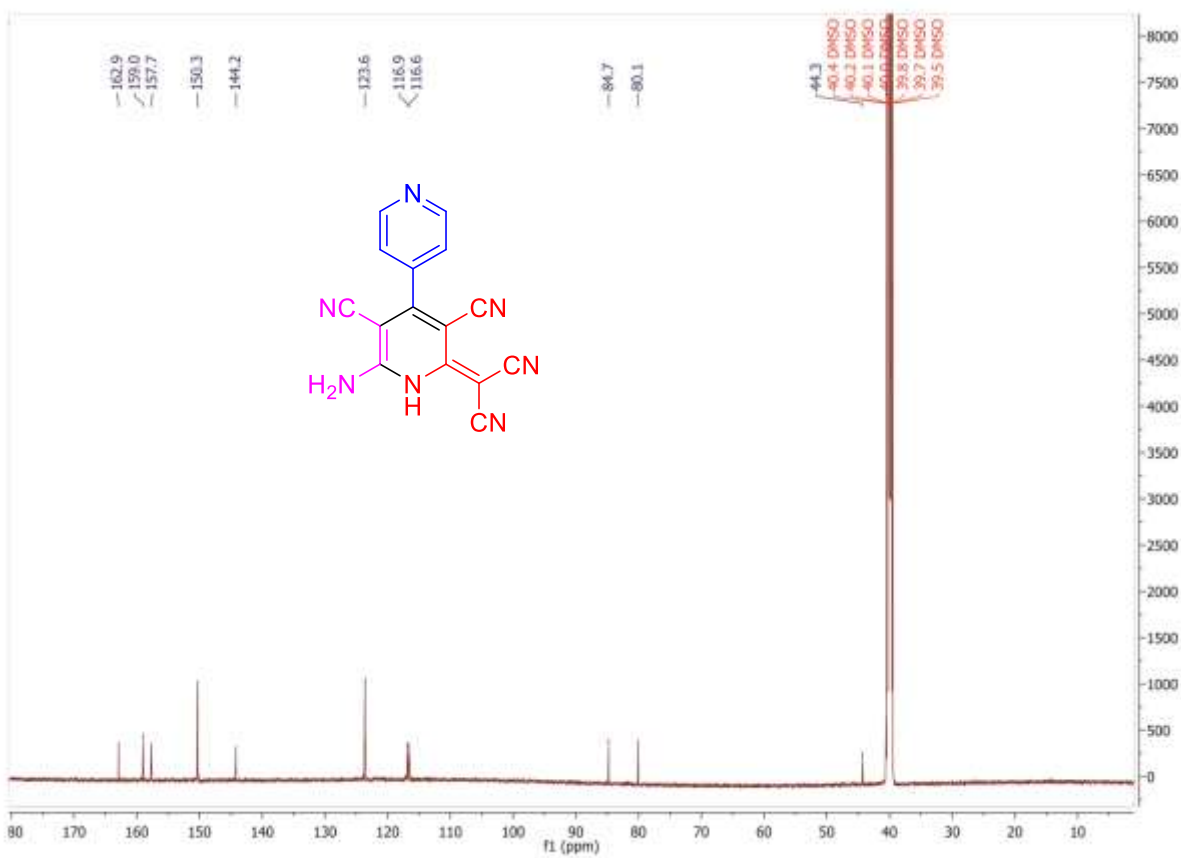
¹³C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-ethoxy-4-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (h)



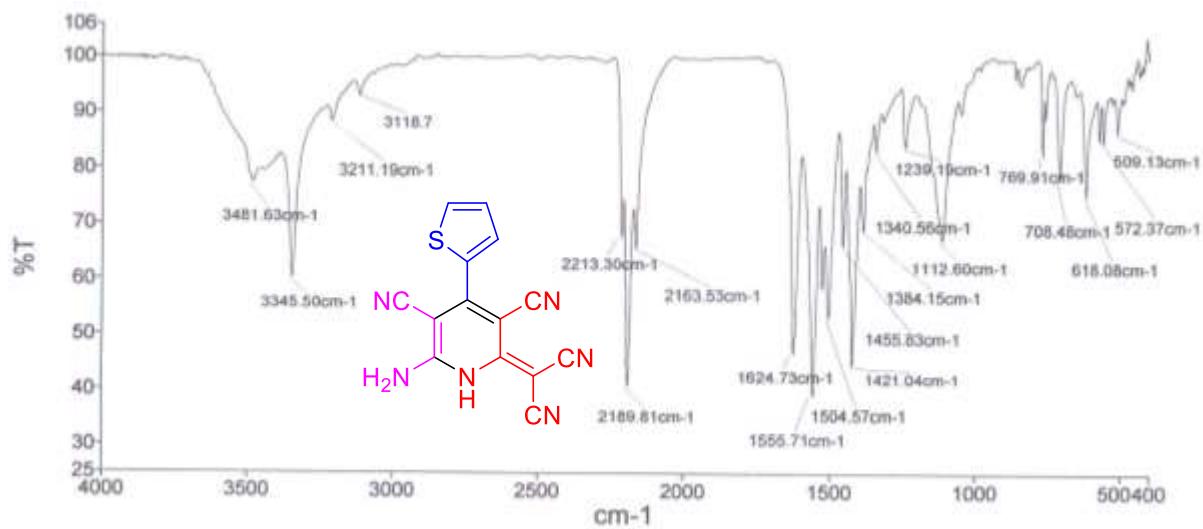
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (i)



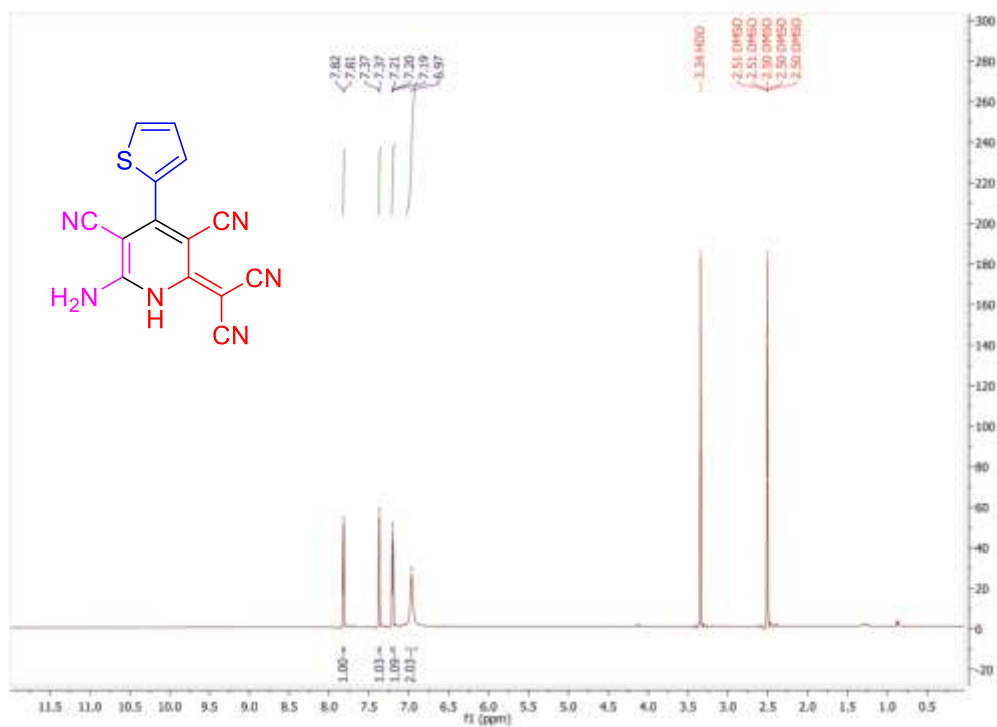
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (i)



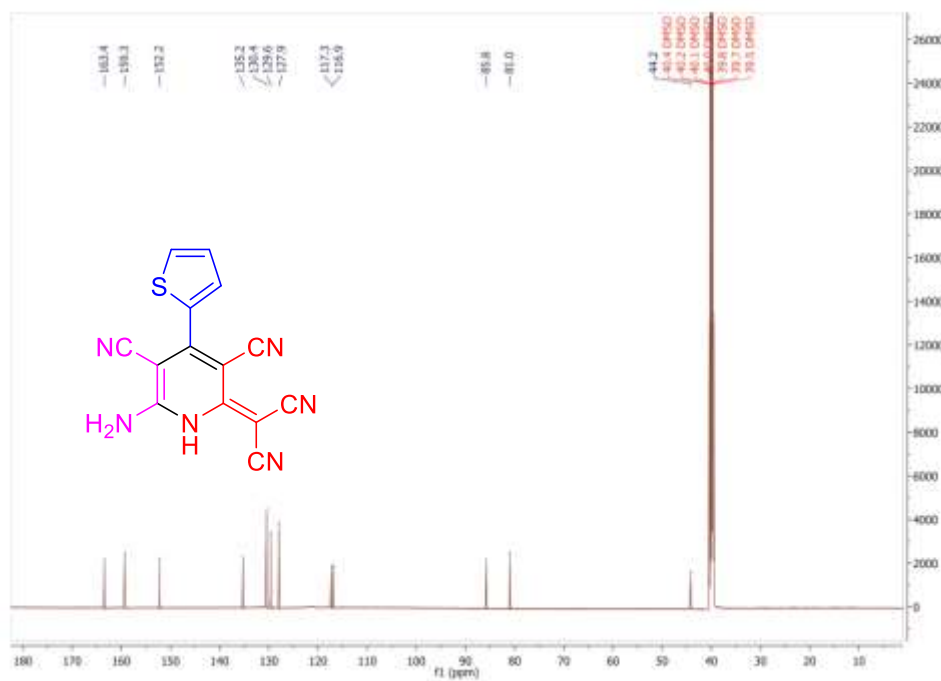
¹³C NMR spectrum of 6-amino-2-(dicyanomethylene)-1,2-dihydro-[4,4'-bipyridine]-3,5-dicarbonitrile (i)



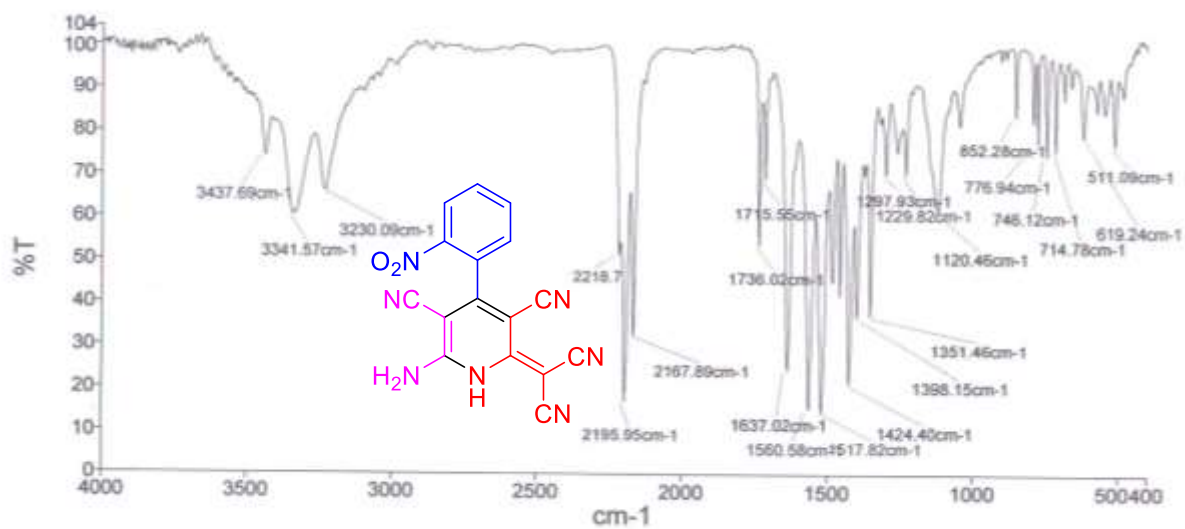
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (j)



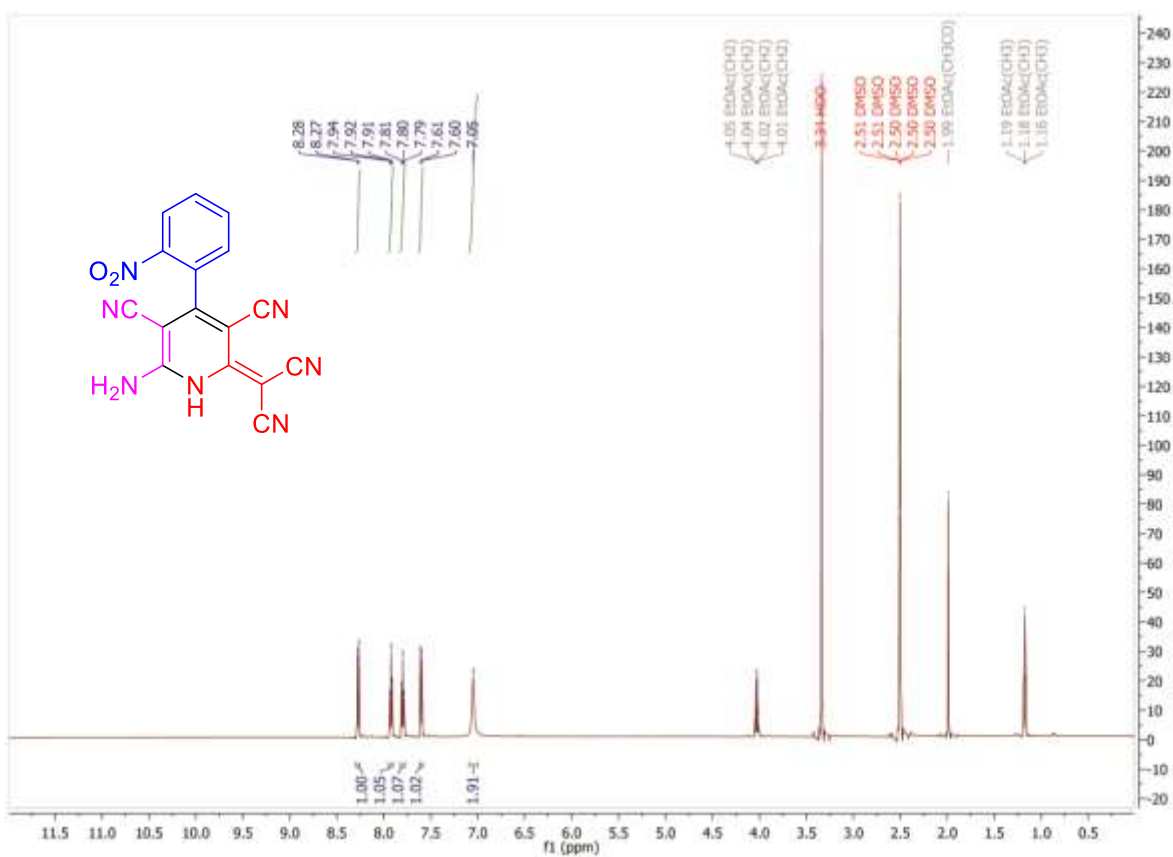
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (j)



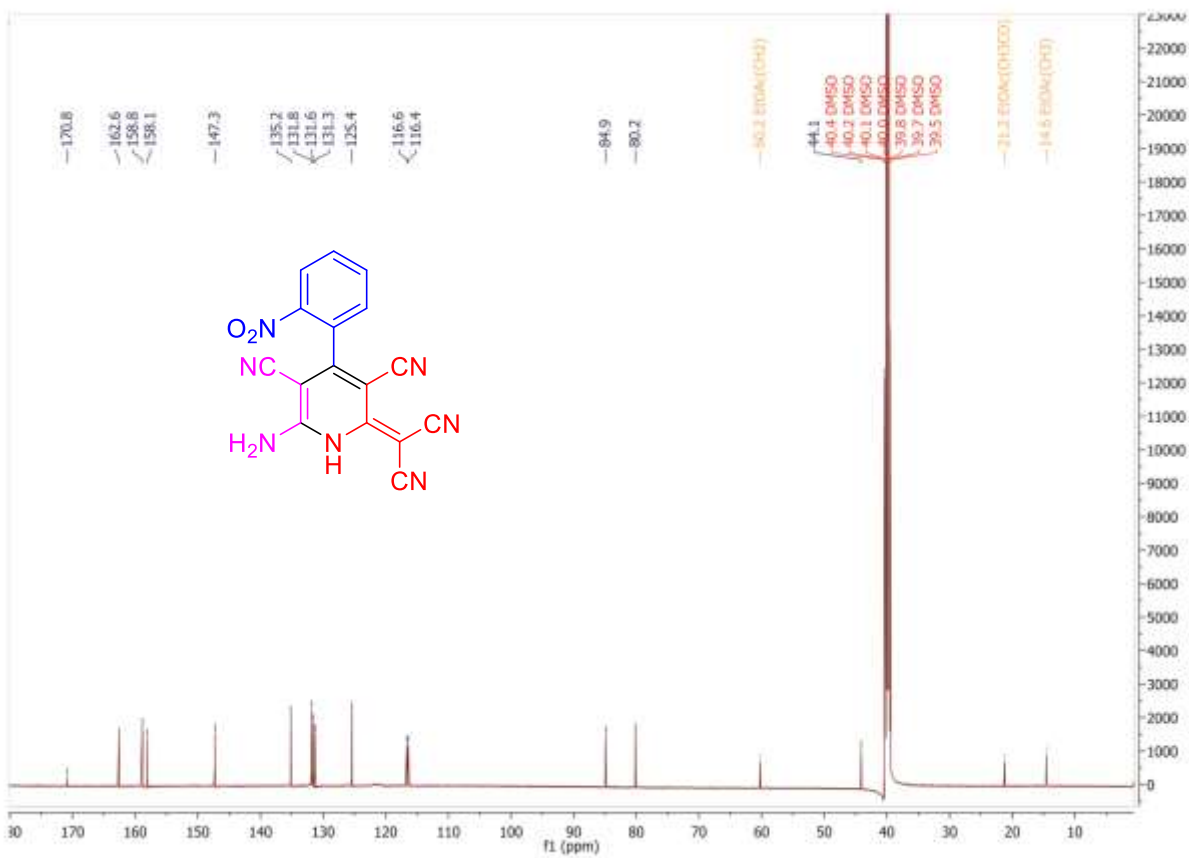
¹³C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(thiophen-2-yl)-1,2-dihydropyridine-3,5-dicarbonitrile (j)



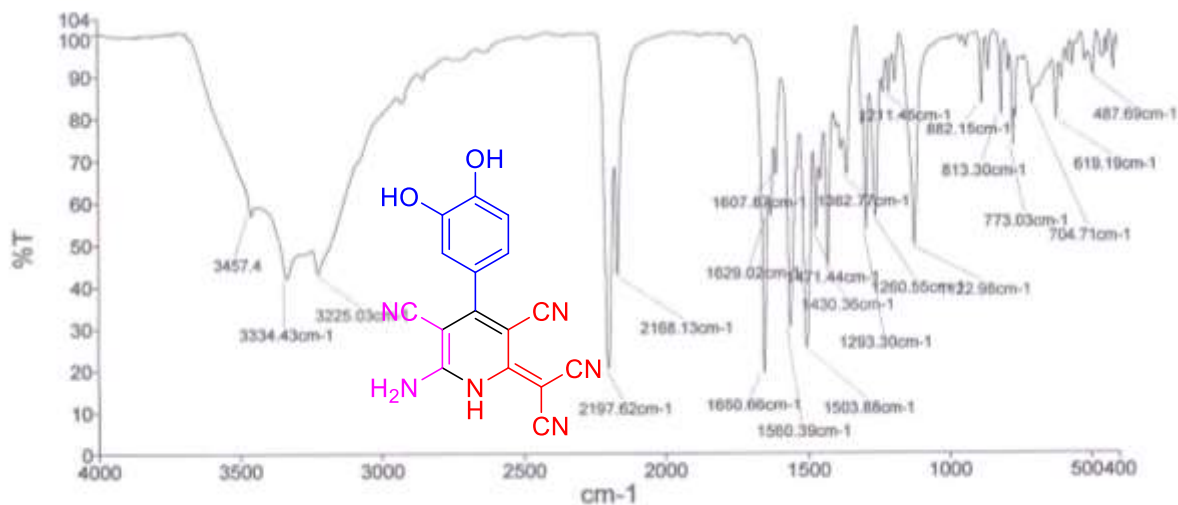
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(2-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (k)



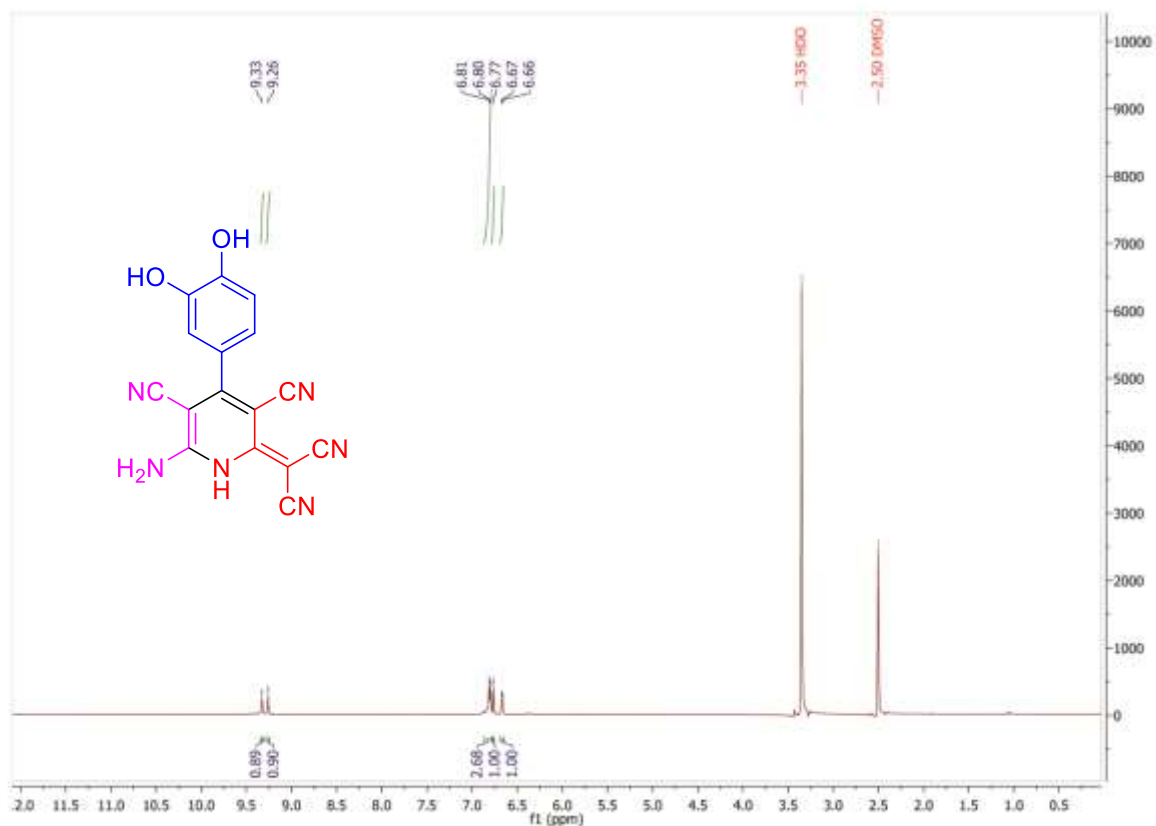
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(2-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (k)



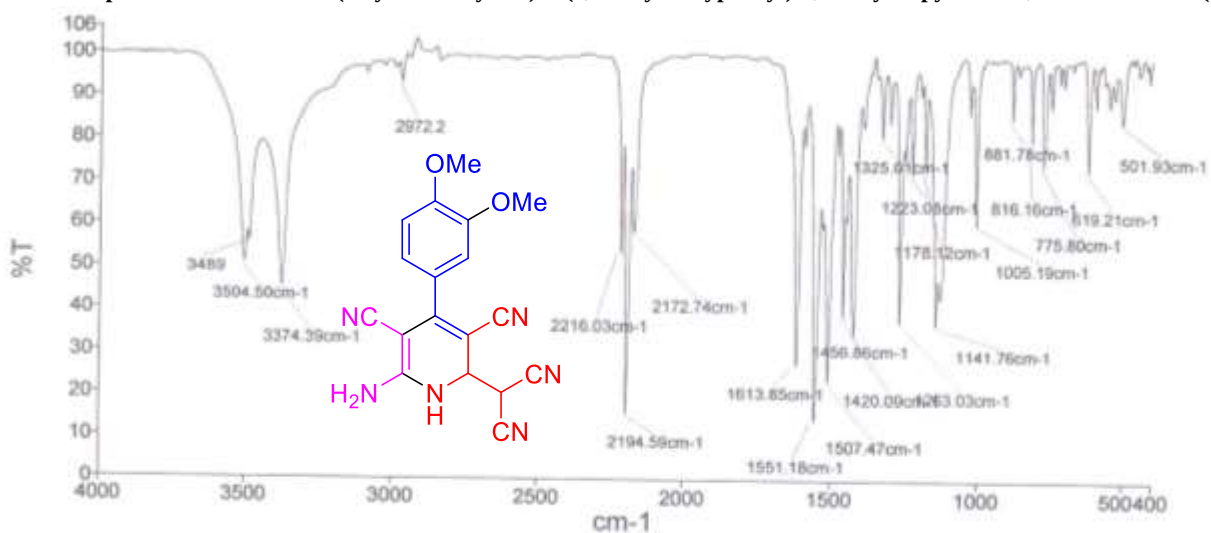
¹³C NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(2-nitrophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (k)



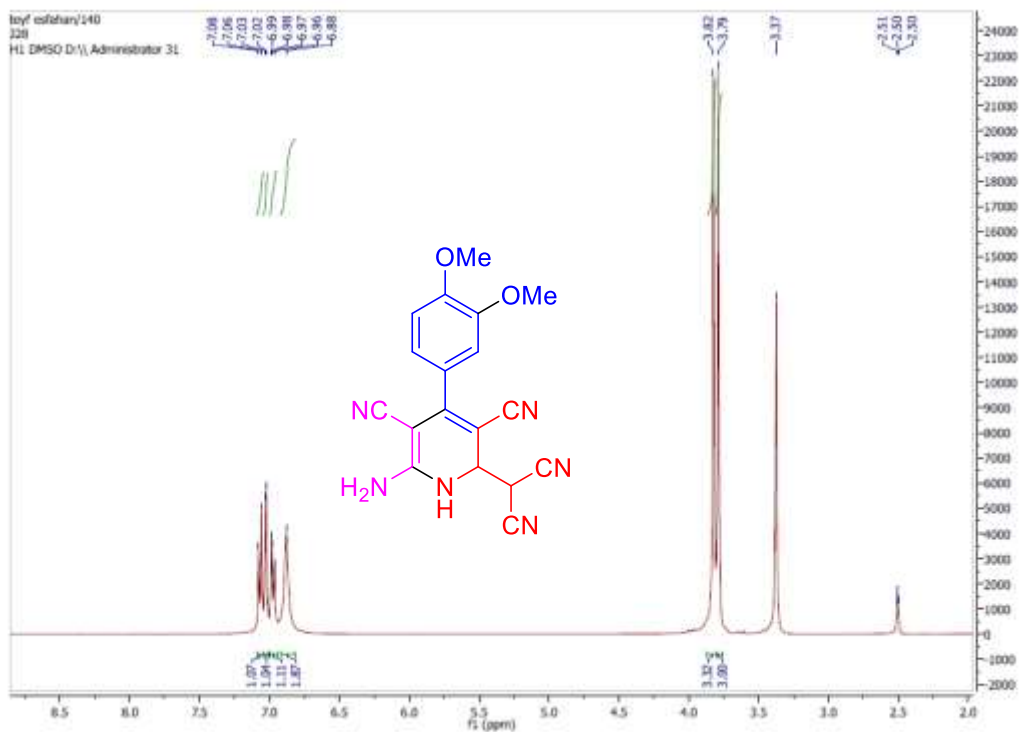
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(3,4-dihydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (l)



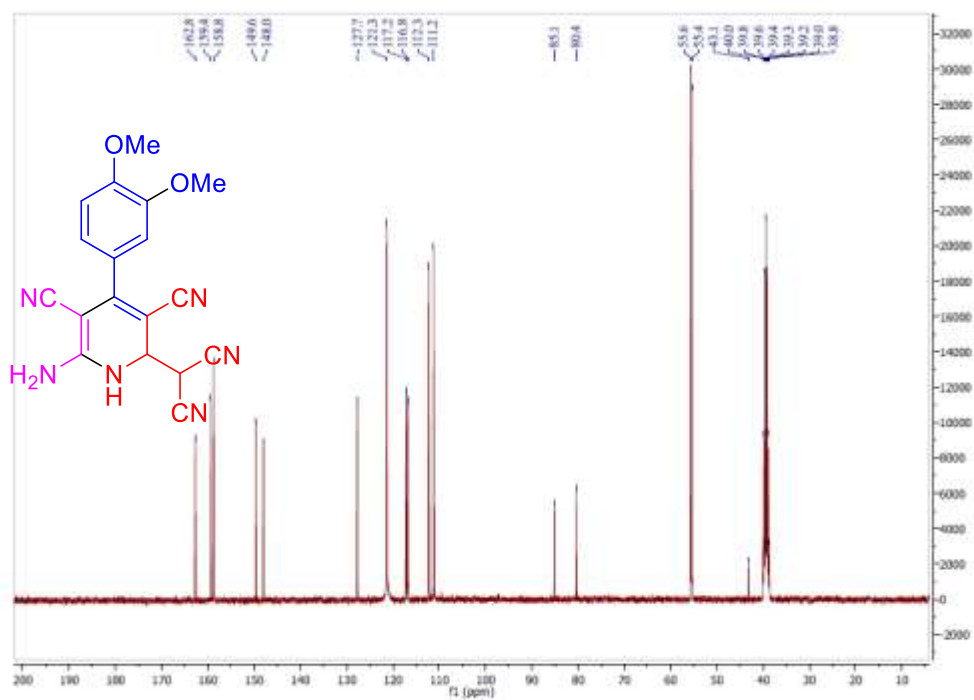
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3,4-dihydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (l)



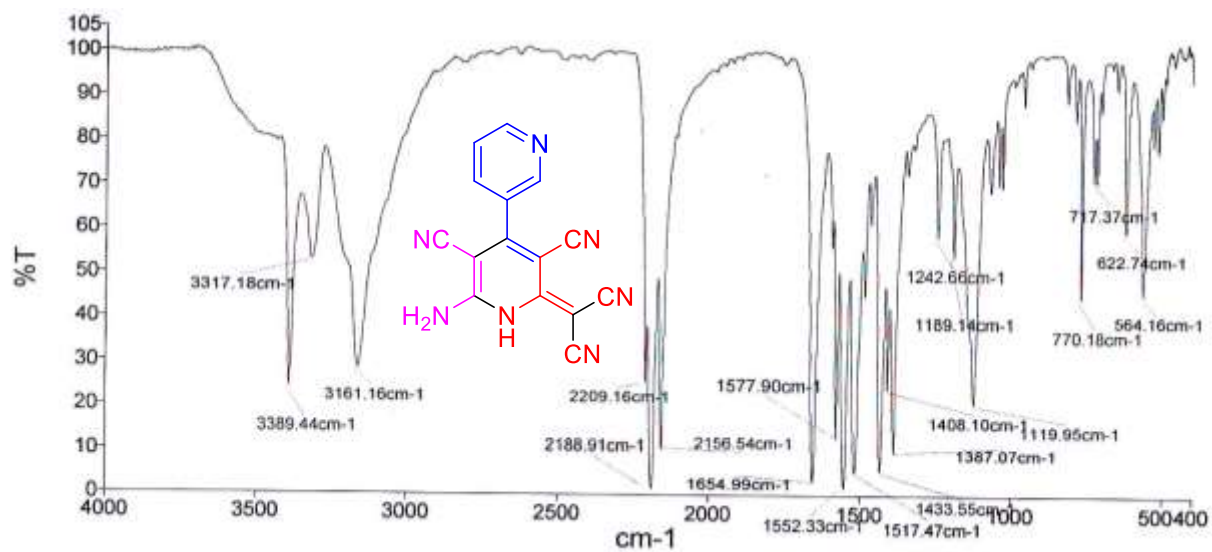
FT-IR spectrum of 6-amino-2-(dicyanomethyl)-4-(3,4-dimethoxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (m)



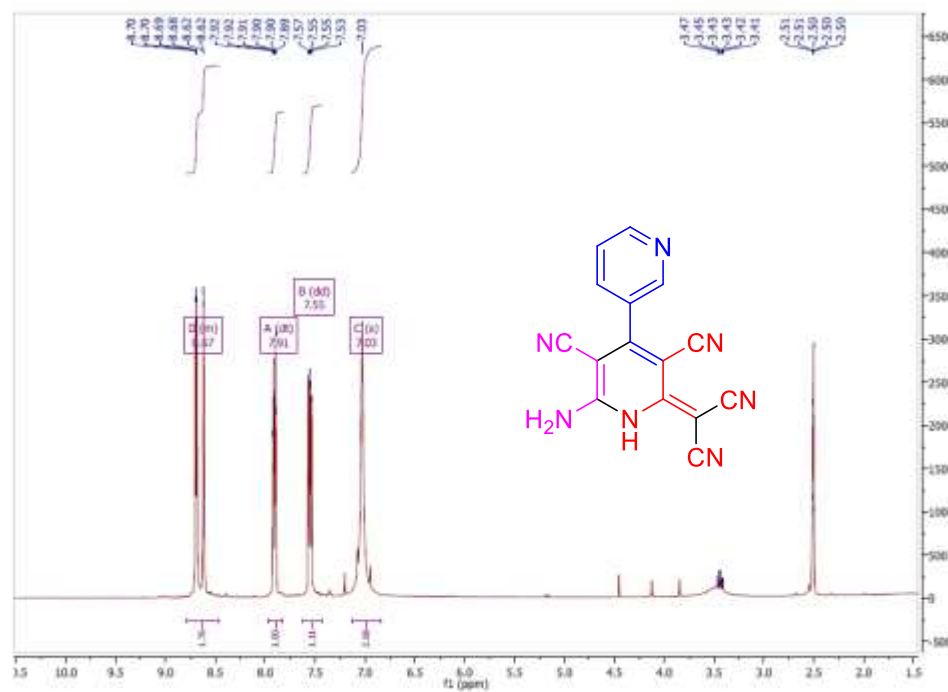
¹H NMR spectrum of 6-amino-2-(dicyanomethyl)-4-(3,4-dimethoxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (m)



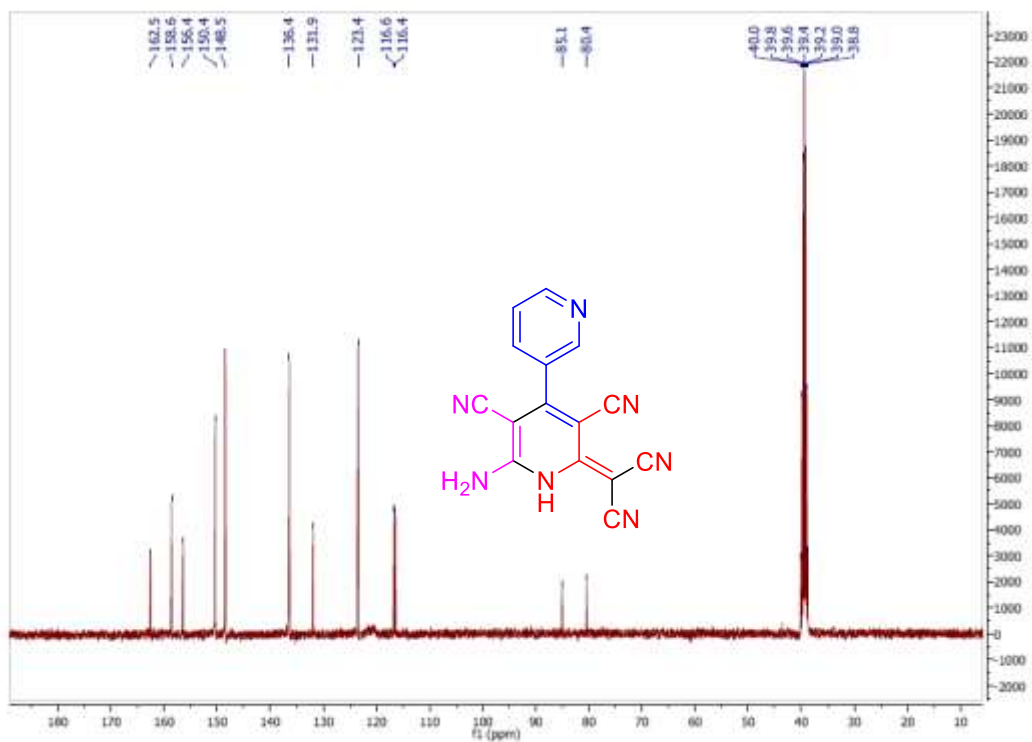
¹³C NMR spectrum of 6-amino-2-(dicyanomethyl)-4-(3,4-dimethoxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (m)



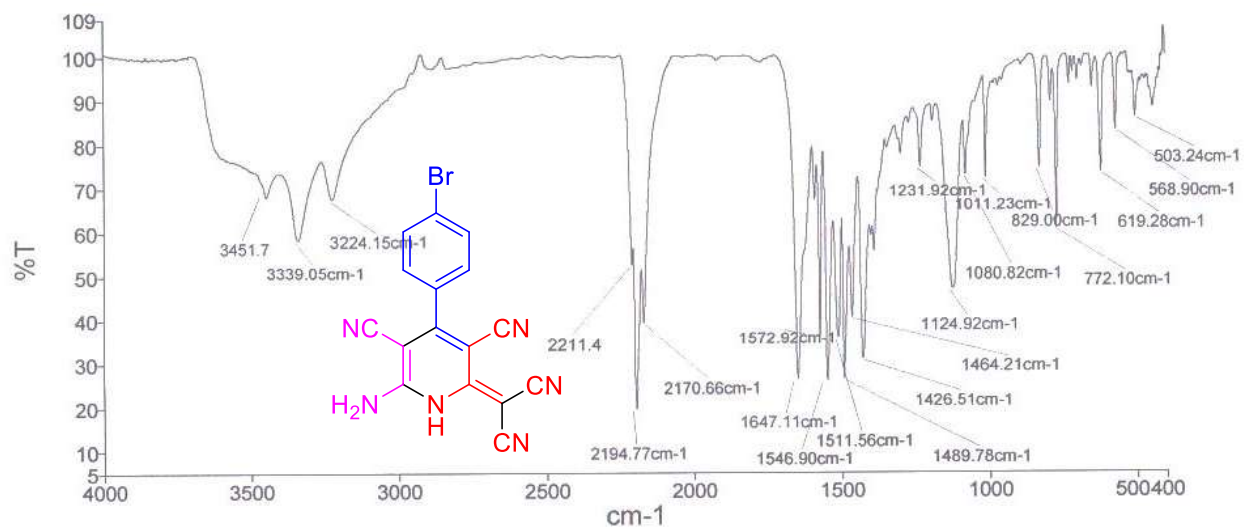
FT-IR spectrum of 6'-amino-2'-(dicyanomethylene)-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (n)



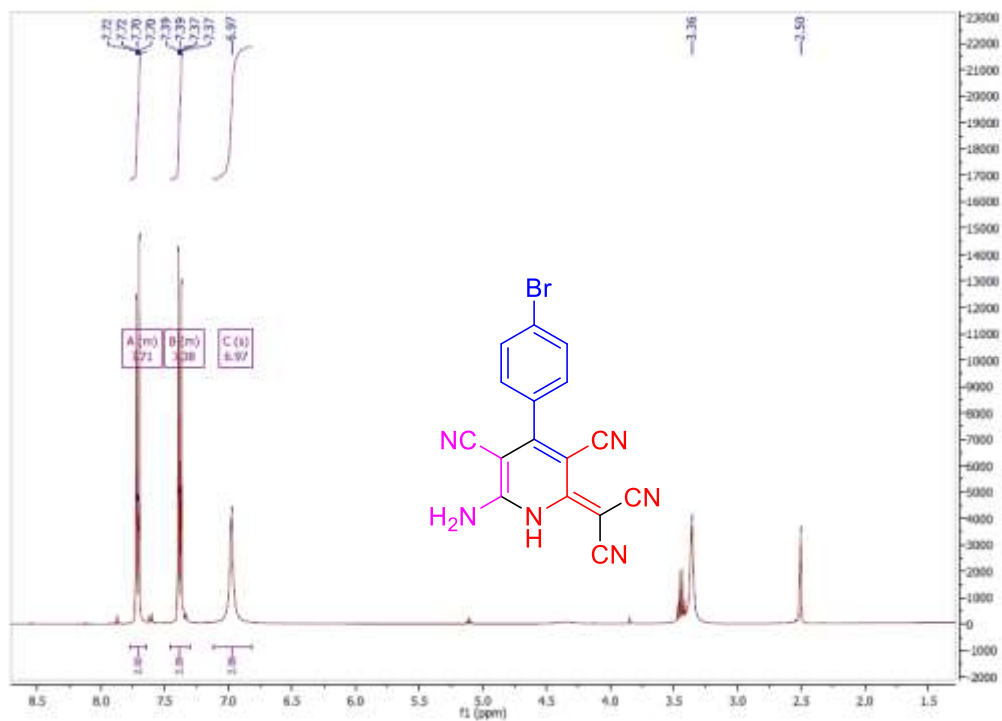
¹H NMR spectrum of 6'-amino-2'-(dicyanomethylene)-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (n)



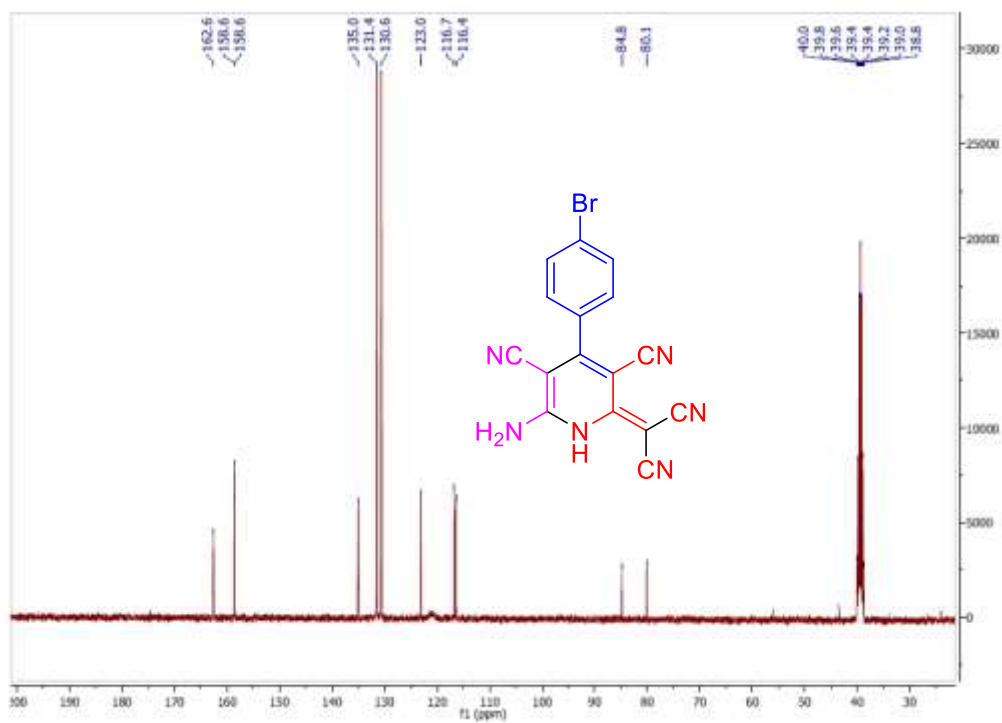
¹³C NMR spectrum of 6'-amino-2'-(dicyanomethylene)-1',2'-dihydro-[3,4'-bipyridine]-3',5'-dicarbonitrile (n)



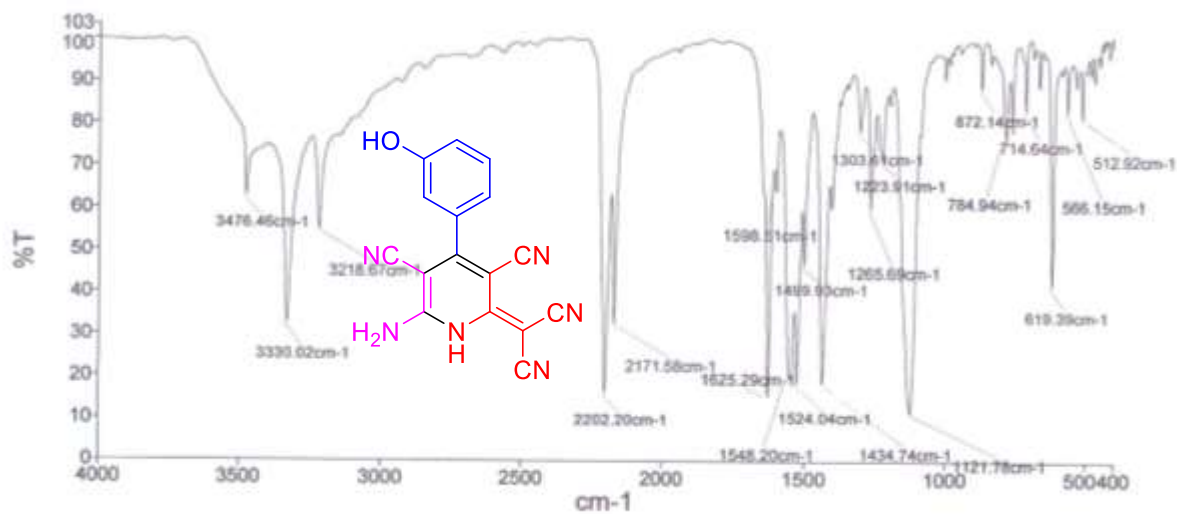
FT-IR spectrum of 6-amino-4-(4-bromophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (o)



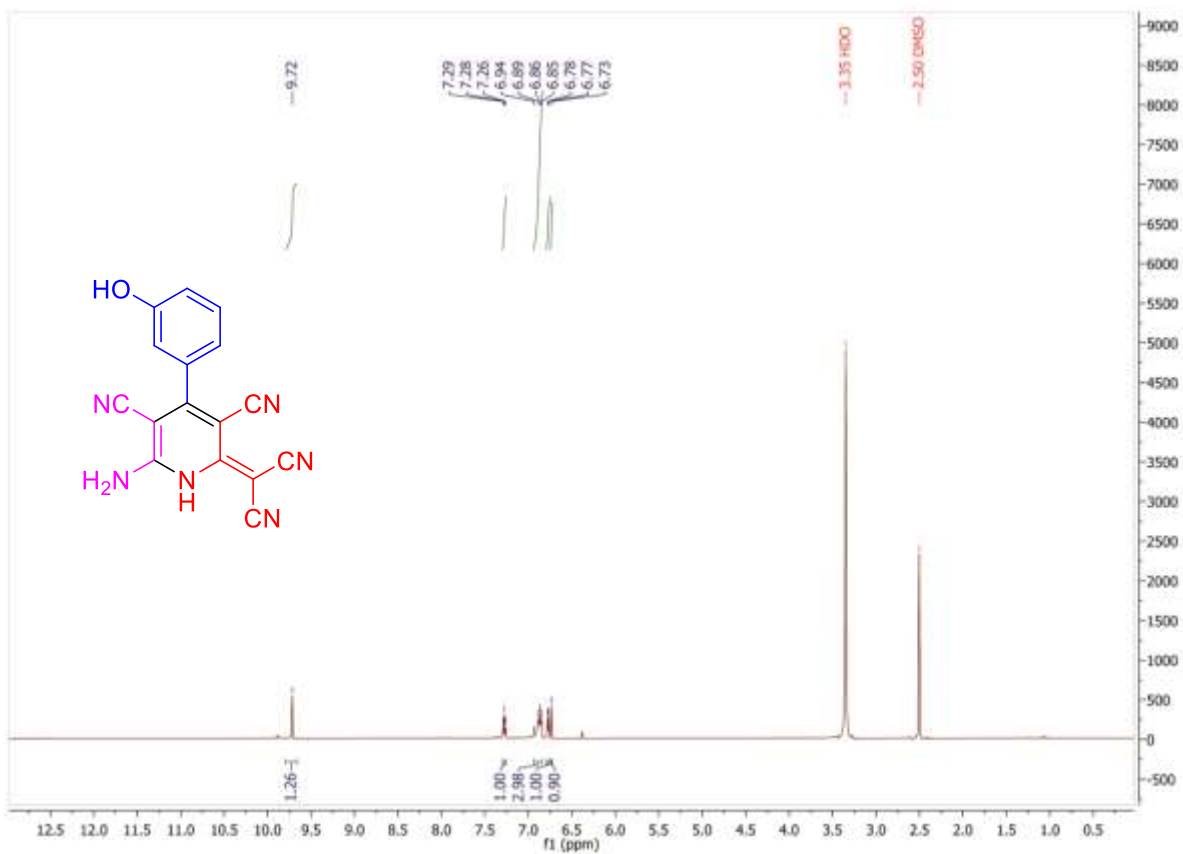
¹H NMR spectrum of 6-amino-4-(4-bromophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (o)



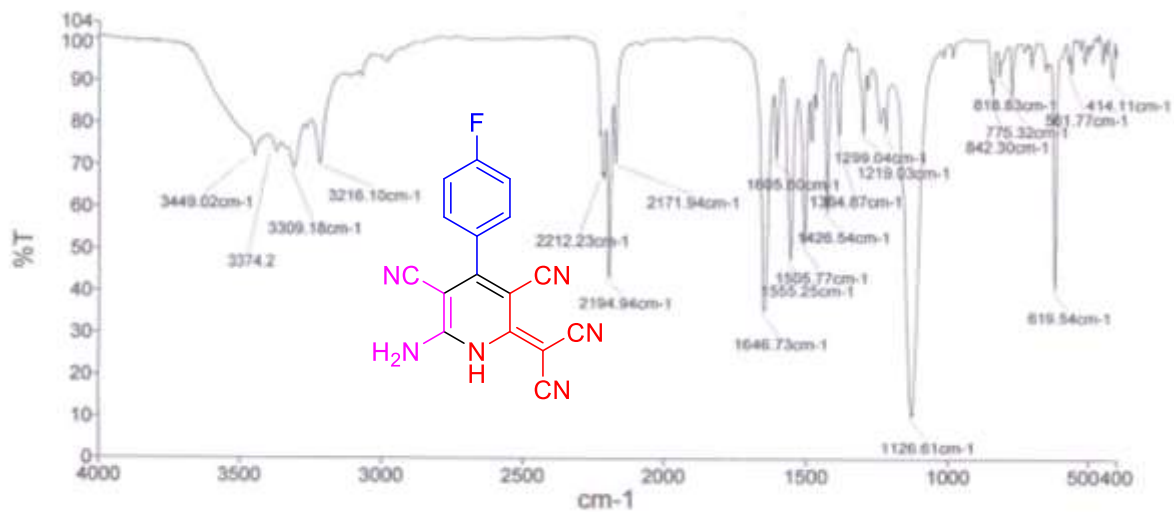
¹³C NMR spectrum of 6-amino-4-(4-bromophenyl)-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile (o)



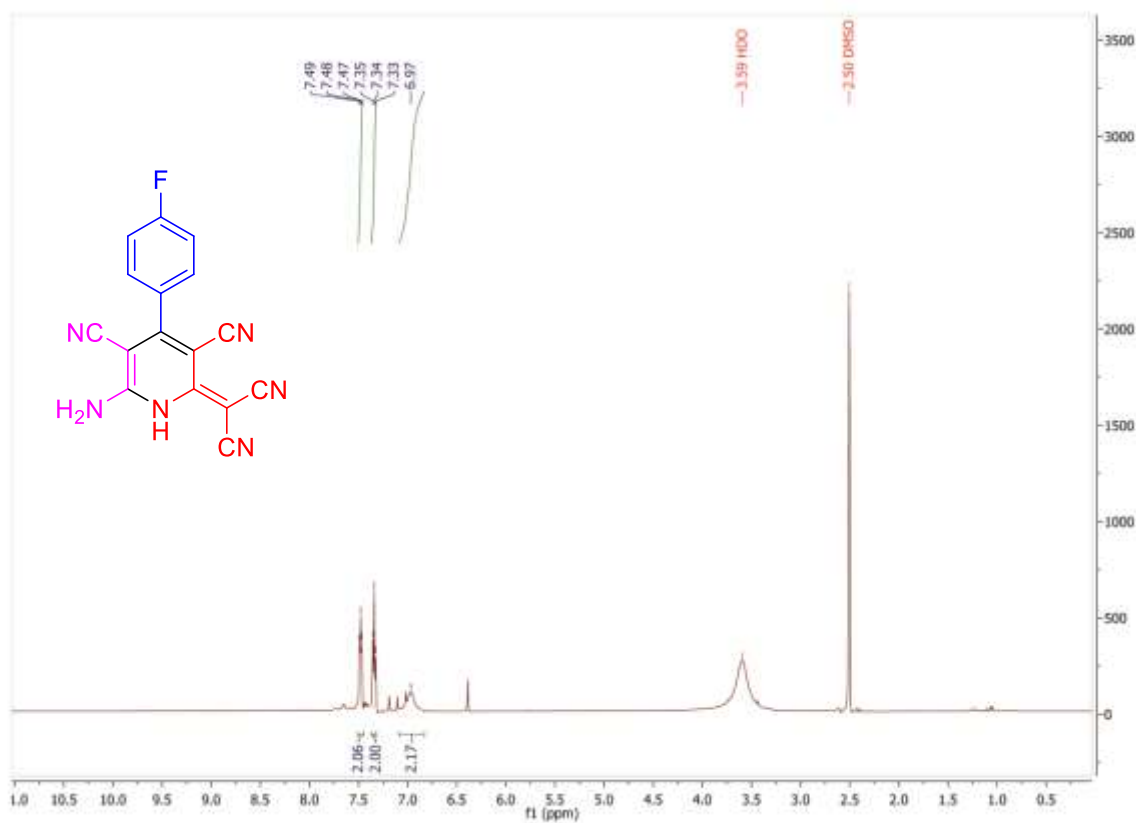
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (p)



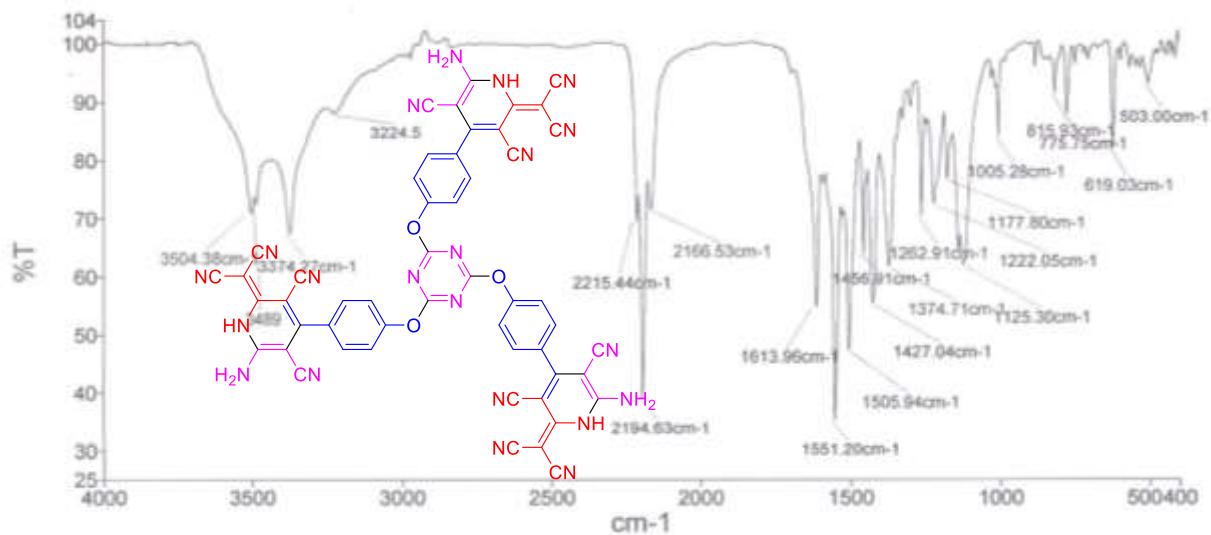
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(3-hydroxyphenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (p)



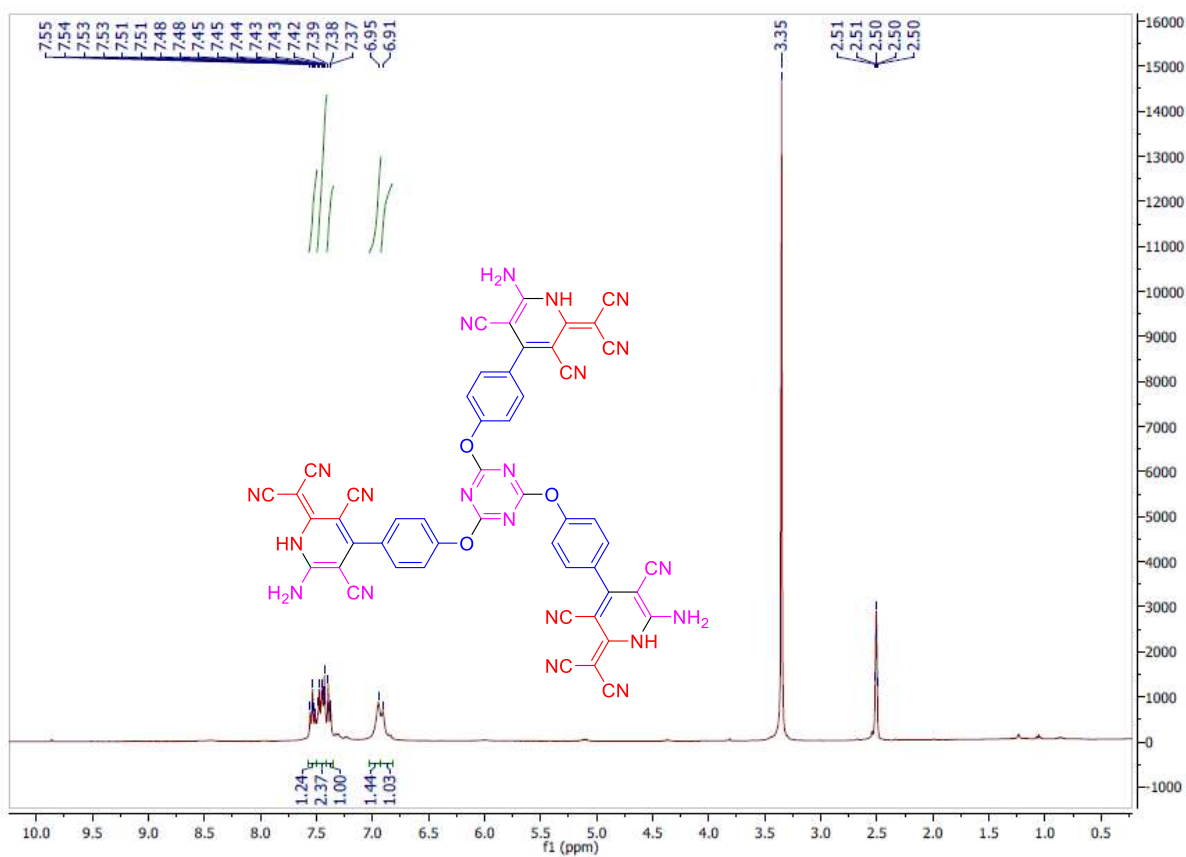
FT-IR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-fluorophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (q)



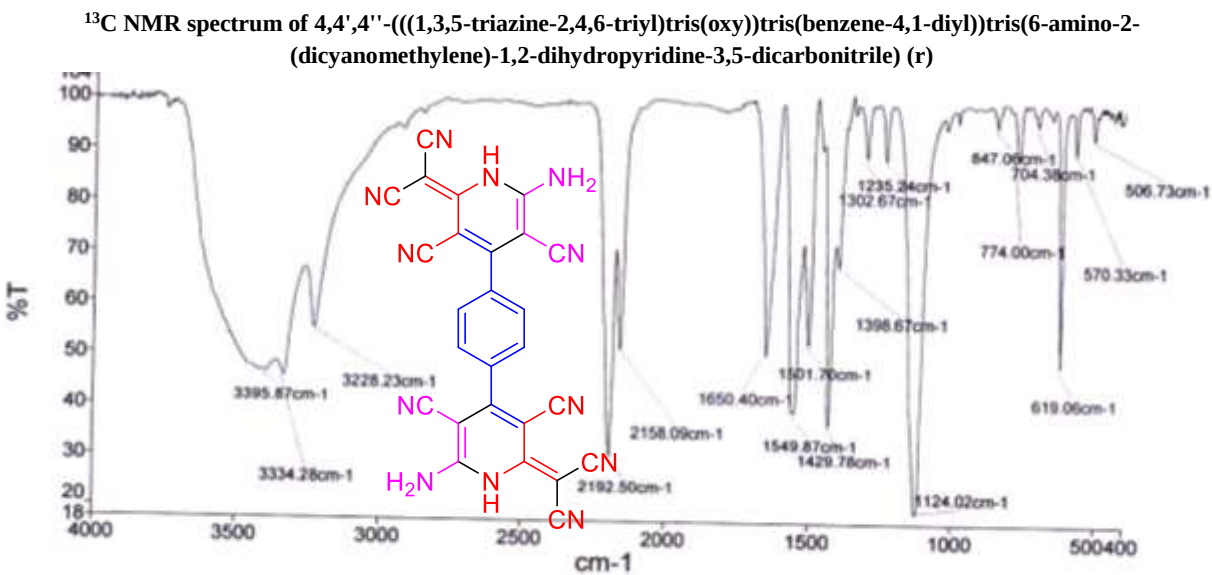
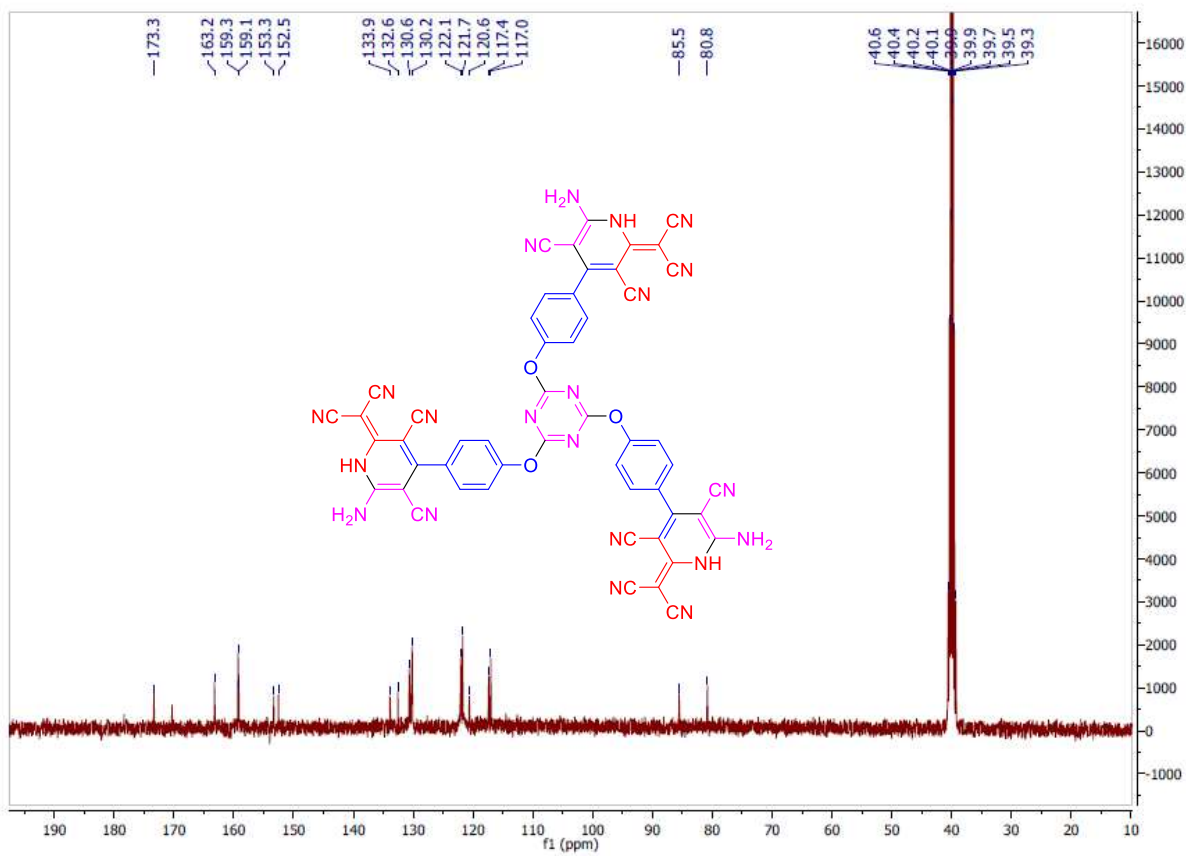
¹H NMR spectrum of 6-amino-2-(dicyanomethylene)-4-(4-fluorophenyl)-1,2-dihydropyridine-3,5-dicarbonitrile (q)



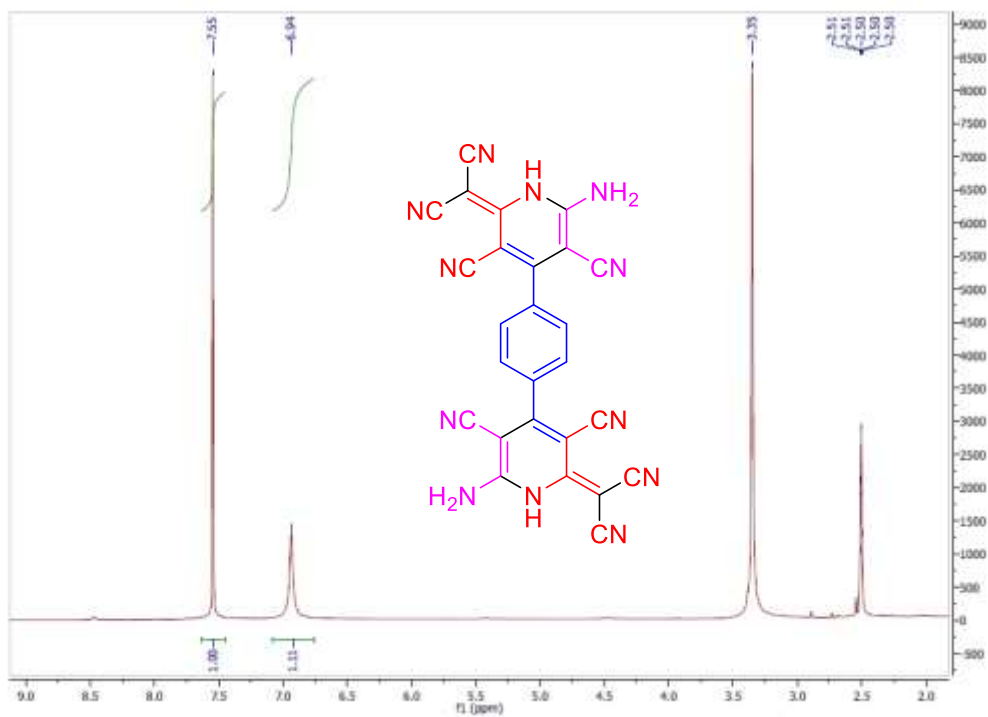
FT-IR spectrum of 4,4',4''-(((1,3,5-triazine-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl))tris(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (r)



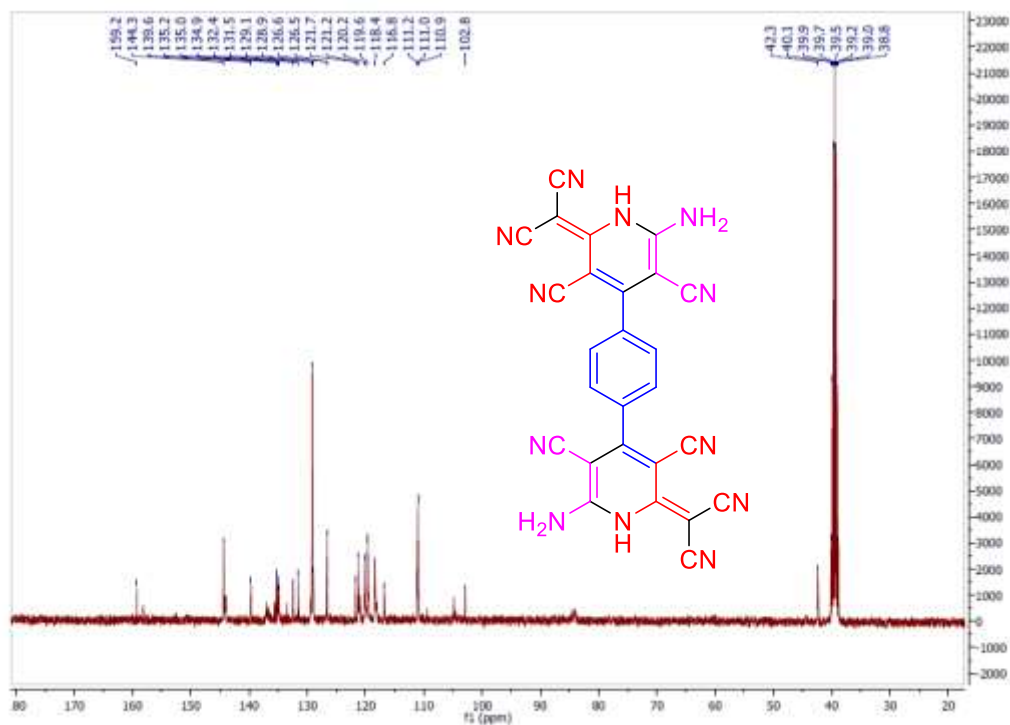
^1H NMR spectrum of 4,4',4''-(((1,3,5-triazine-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl))tris(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (r)



FT-IR spectrum of 4,4'-(1,4-phenylene)bis(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (s)



¹H NMR spectrum of 4,4'-(1,4-phenylene)bis(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (s)



¹³C NMR spectrum of 4,4'-(1,4-phenylene)bis(6-amino-2-(dicyanomethylene)-1,2-dihydropyridine-3,5-dicarbonitrile) (s)