

## Supporting Information

### **Multisulfonate hyperbranched polyglycerol functionalized graphene oxide as an efficient reusable catalyst for green synthesis of benzo[a]pyrano-[2,3-c]phenazines under solvent-free conditions**

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## Data of compounds

### 3-amino-1-phenyl-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6a)

Yellow solid, mp: 300-303 °C (lit. [25]: 298-300 °C); IR (KBr, v,  $\text{cm}^{-1}$ ): 3443, 3312, 3174, 3055, 2188, 1659, 1623, 1593, 1493, 1397;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 5.49 (s, 1H), 7.08 (t,  $J^3=8.0$  Hz, 1H), 7.21 (t,  $J^3=8.0$  Hz, 2H), 7.28 (m,  $\text{NH}_2$ ), 7.39 (d,  $J^3=8.0$  Hz, 2H), 7.90-7.94 (m, 3H), 7.98 (t,  $J^3=8.0$  Hz, 1H), 8.13-8.15 (m, 1H), 8.24-8.26 (m, 1H), 8.43 (d,  $J^3=8.0$  Hz, 1H), 9.21 (d,  $J^3=8.0$  Hz, 1H).

### 3-amino-1-(4-(dimethylamino)phenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6b)

Orange solid, mp: 259-263 °C (lit. [25]: 261-263 °C); IR (KBr, v,  $\text{cm}^{-1}$ ): 3463, 3310, 3061, 2208, 1628, 1594, 1533, 1458, 1351;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 3.38 (s, 6H), 6.84 (m,  $\text{NH}_2$ ), 7.19 (s, 1H), 7.80-7.91 (m, 6H), 8.15 (d,  $J^3=8.0$  Hz, 1H), 8.28 (d,  $J^3=8.0$  Hz, 1H), 8.30-8.32 (m, 2H), 9.25-9.27 (m, 1H), 11.55 (s, 1H).

### 3-amino-1-(2-chlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6c)

Yellow solid, mp: 300-304 °C; IR (KBr, v,  $\text{cm}^{-1}$ ): 3464, 3312, 3170, 3057, 2191, 1658, 1623, 1590, 1470, 1387;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 5.92 (s, 1H), 7.08-7.10 (m, 2H), 7.18-7.19 (m, 1H), 7.33 (m,  $\text{NH}_2$ ), 7.38-7.40 (m, 1H), 7.89-8.02 (m, 5H), 8.22-8.24 (m, 1H), 8.44 (d,  $J^3=8.0$  Hz, 1H), 9.21 (d,  $J^3=8.0$  Hz, 1H).

### 3-amino-1-(4-chlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6d)

Yellow solid, mp: 285-290 °C (lit. [25]: 288-291 °C); IR (KBr, v,  $\text{cm}^{-1}$ ): 3464, 3311, 3173, 3057, 2188, 1659, 1623, 1593, 1489, 1402, 1385;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 5.45 (s, 1H), 7.26 (d,  $J^3=8.0$  Hz, 2H), 7.32 (s,  $\text{NH}_2$ ), 7.41 (d,  $J^3=8.0$  Hz, 2H), 7.89-7.93 (m, 2H), 7.96-8.0 (m, 2H), 8.08-8.10 (m, 1H), 8.22-8.23 (m, 1H), 8.41 (d,  $J^3=8.0$  Hz, 1H), 9.18 (d,  $J^3=8.0$  Hz, 1H).

### 3-amino-1-(2,4-dichlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6e)

Brown solid, mp: 307-310 °C (lit. [31]: 308-310 °C); IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3478, 3313, 3168, 3069, 2186, 1659, 1624, 1589, 1468, 1403, 1385;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 5.84 (s, 1H), 7.14 (d,  $J^3=8.0$  Hz, 1H), 7.20 (d,  $J^3=8.0$  Hz, 1H), 7.40 (s,  $\text{NH}_2$ ), 7.54 (s, 1H), 7.88-8.0 (m, 5H), 8.21-8.23 (m, 1H), 8.41 (d,  $J^3=8.0$  Hz, 1H), 9.19 (d,  $J^3=8.0$  Hz, 1H).

**3-amino-1-(2-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6f)**

Brown solid, mp: 284-286 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3464, 3311, 3169, 3055, 2191, 1659, 1623, 1589, 1467, 1387;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 5.88 (s, 1H), 6.97-7.01 (m, 1H), 7.10 (m, 2H), 7.36 (s,  $\text{NH}_2$ ), 7.57 (d,  $J^3=8.0$  Hz, 1H), 7.87-7.89 (m, 2H), 7.93 (t,  $J^3=8.0$  Hz, 2H), 7.99-8.01 (m, 1H), 8.18-8.20 (m, 1H), 8.42 (d,  $J^3=8.0$  Hz, 1H), 9.17 (d,  $J^3=8.0$  Hz, 1H).

**3-amino-1-(3-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6g)**

Brown solid, mp: 268-269 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3486, 3302, 3171, 3060, 2197, 1662, 1627, 1591, 1471, 1385;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 5.51 (s, 1H), 7.19-7.23 (m, 1H), 7.29-7.33 (m, 1H), 7.40-7.44 (m, 1H), 7.46-7.49 (m,  $\text{NH}_2$ ), 7.61-7.63 (m, 1H), 7.95-8.02 (m, 4H), 8.14-8.17 (m, 1H), 8.27-8.31 (m, 1H), 8.43-8.48 (m, 1H), 9.22-9.26 (m, 1H).

**3-amino-1-(4-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6h)**

Yellow solid, mp: 280-285 °C (lit. [25]: 283-285 °C); IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3467, 3320, 3173, 3056, 2187, 1660, 1623, 1591, 1485, 1401, 1384;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 5.44 (s, 1H), 7.35 (d,  $J^3=8.0$  Hz, 2H), 7.40 (d,  $J^3=8.0$  Hz, 2H), 7.43 (s,  $\text{NH}_2$ ), 7.92-7.98 (m, 4H), 8.09-8.10 (m, 1H), 8.22-8.23 (m, 1H), 8.42 (d,  $J^3=8.0$  Hz, 1H), 9.19 (d,  $J^3=8.0$  Hz, 1H).

**3-amino-1-(2-fluorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6i)**

Yellow solid, mp: 270-272 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3449, 3312, 3058, 2189, 1661, 1625, 1591, 1490, 1406, 1387;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 5.75 (s, 1H), 7.0-7.16 (m, 2H), 7.26-7.34 (m, 2H), 7.38 (s,  $\text{NH}_2$ ), 7.90-8.0 (m, 4H), 8.26-8.29 (m, 1H), 8.32-8.36 (m, 1H), 8.46 (d,  $J^3=8.0$  Hz, 1H), 9.24 (d,  $J^3=8.0$  Hz, 1H).

**3-amino-1-(4-fluorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6j)**

Yellow solid, mp: 275-280 °C (lit. [25]: 274-276 °C); IR (KBr, v, cm<sup>-1</sup>): 3459, 3315, 3174, 3052, 2190, 1660, 1623, 1593, 1502, 1402, 1385; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 5.49 (s, 1H), 7.03 (t, *J*<sup>3</sup> = 8.0 Hz, 2H), 7.41-7.45 (m, 2H-Ar and 2H-NH<sub>2</sub>), 7.91-8.0 (m, 4H), 8.12-8.14 (m, 1H), 8.23-8.26 (m, 1H), 8.42 (d, *J*<sup>3</sup> = 8.0 Hz, 1H), 9.20 (d, *J*<sup>3</sup> = 8.0 Hz, 1H).

**3-amino-1-(2-nitrophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6k)**

Brown solid, mp: 279-283 °C; IR (KBr, v, cm<sup>-1</sup>): 3437, 3063, 2194, 1664, 1629, 1594, 1526, 1388, 1351; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 6.11 (s, 1H), 7.31 (t, *J*<sup>3</sup> = 8.0 Hz, 1H), 7.40 (d, *J*<sup>3</sup> = 8.0 Hz, 1H), 7.47 (t, *J*<sup>3</sup> = 8.0 Hz, 1H), 7.52 (s, NH<sub>2</sub>), 7.86-7.98 (m, 4H), 8.19 (d, *J*<sup>3</sup> = 8.0 Hz, 1H), 8.24-8.26 (m, 1H), 8.28-8.31 (m, 1H), 8.42 (d, *J*<sup>3</sup> = 8.0 Hz, 1H), 9.13 (d, *J*<sup>3</sup> = 8.0 Hz, 1H).

**3-amino-1-(4-nitrophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6l)**

Yellow solid, mp: 277-280 °C (lit. [25]:281-283°C); IR (KBr, v, cm<sup>-1</sup>): 3440, 3318, 3204, 3068, 2197, 1672, 1628, 1593, 1514, 1385, 1346; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 5.61 (s, 1H), 7.53-7.55 (m, NH<sub>2</sub>), 7.67-7.71 (m, 2H), 7.93-8.01 (m, 4H), 8.08-8.12 (m, 2H), 8.25-8.29 (m, 2H), 8.44-8.46 (m, 1H), 9.21-9.24 (m, 1H).

**3-amino-1-(3-methoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6m)**

Yellow solid, mp: 238-243 °C (lit.[31]: 240-242 °C); IR (KBr, v, cm<sup>-1</sup>): 3420, 3340, 3215, 2193, 1666, 1596, 1492, 1385; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 3.67 (s, 3H), 5.48 (s, 1H), 6.67 (d, *J*<sup>3</sup> = 8.0 Hz, 1H), 6.91 (d, *J*<sup>3</sup> = 8.0 Hz, 1H), 7.01 (s, 1H), 7.13 (t, *J*<sup>3</sup> = 8.0 Hz, 1H), 7.40 (s, NH<sub>2</sub>), 7.93-7.94(m, 2H), 7.99 (t, *J*<sup>3</sup> = 8.0 Hz, 2H), 8.15-8.18 (m, 1H), 8.25-8.28 (m, 1H), 8.43 (d, *J*<sup>3</sup> = 8.0 Hz, 1H), 9.21 (d, *J*<sup>3</sup> = 8.0 Hz, 1H).

**3-amino-1-(4-methoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6n)**

Yellow solid, mp: 270-272 °C; IR (KBr, v, cm<sup>-1</sup>): 3431, 3314, 3194, 3047, 2194, 1667, 1596, 1508, 1386; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) (δ, ppm): 3.61 (s, 3H), 5.50 (s, 1H), 6.77 (d, *J*<sup>3</sup> = 8.0 Hz, 2H), 7.19-7.21 (m, NH<sub>2</sub>), 7.33 (d, *J*<sup>3</sup> = 8.0 Hz, 2H), 7.95-8.0 (m, 4H), 8.20-8.22 (m, 1H), 8.30-8.31(m, 1H), 8.46 (d, *J*<sup>3</sup> = 8.0 Hz, 1H), 9.26 (d, *J*<sup>3</sup> = 8.0 Hz, 1H).

**3-amino-1-(2,3-dimethoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6o)**

Yellow solid, mp: 287-291 °C (lit. [25]: 292-294°C); IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3426, 3312, 3174, 3051, 2187, 1659, 1624, 1592, 1491, 1387;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 3.84 (s, 3H), 3.88 (s, 3H), 5.83 (s, 1H), 6.73(t,  $J^3=8.0$  Hz, 1H), 6.95 (d,  $J^3=8.0$  Hz, 1H), 7.05-7.11 (m, 1H), 7.19 (s,  $\text{NH}_2$ ), 7.89-8.02 (m, 5H), 8.25-8.27 (m, 1H), 8.46 (d,  $J^3=8.0$  Hz, 1H), 9.24 (d,  $J^3=8.0$  Hz, 1H).

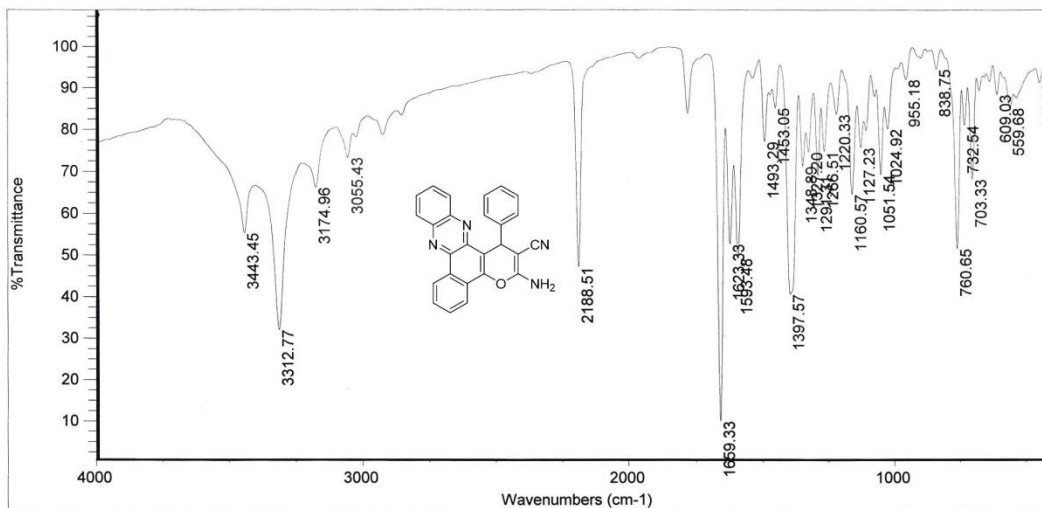
**3-amino-1-(o-tolyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6p)**

Yellow solid, mp: 256-260 °C; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3486, 3309, 3174, 3061, 2194, 1662, 1627, 1595, 1386;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 2.18 (s, 3H), 5.44 (s, 1H), 6.89 (d,  $J^3=8.0$  Hz, 1H), 7.10 (t,  $J^3=8.0$  Hz, 1H), 7.19 (m, 2H), 7.36 (s,  $\text{NH}_2$ ), 7.91-7.92 (m, 2H), 7.97-8.0 (m, 2H), 8.13-8.14 (m, 1H), 8.23-8.25(m, 1H), 8.43 (d,  $J^3=8.0$  Hz, 1H), 9.20 (d,  $J^3=8.0$  Hz, 1H).

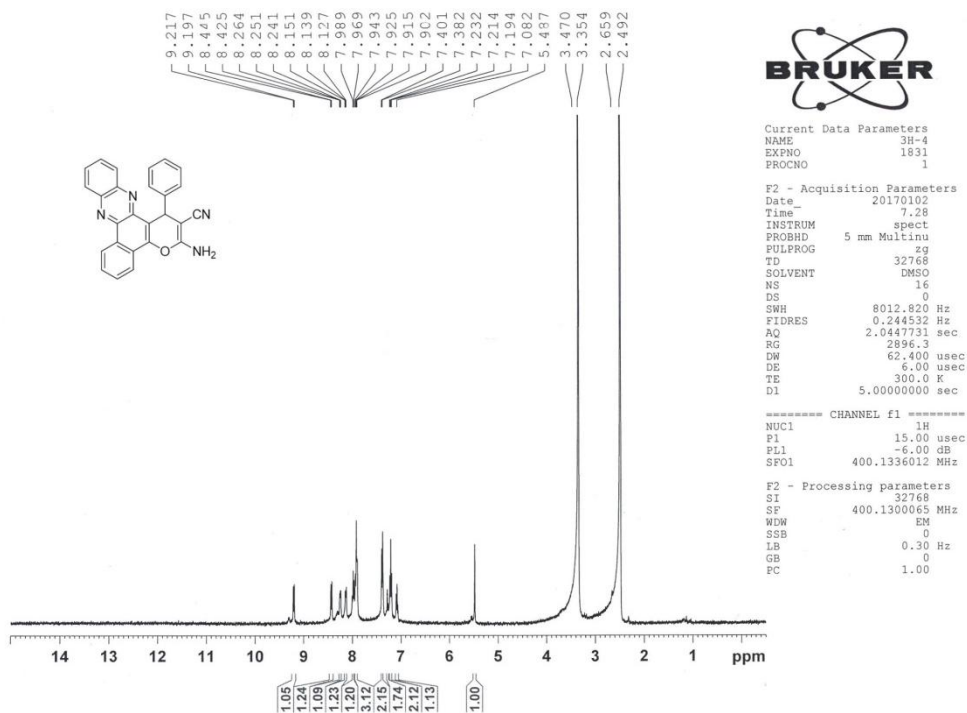
**3-amino-1-(p-tolyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6q)**

Yellow solid, mp: 295-297 °C (lit. [25]: 293-294 °C); IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3441, 3311, 3177, 3054, 2187, 1659, 1623, 1594, 1496, 1387;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) ( $\delta$ , ppm): 2.13 (s, 3H), 5.45 (s, 1H), 7.01 (d,  $J^3=8.0\text{Hz}$ , 2H), 7.27 (d,  $J^3=8.0$  Hz, 2H), 7.34 (m,  $\text{NH}_2$ ), 7.91-8.0 (m, 4H), 8.14-8.16 (m, 1H), 8.25-8.27 (m, 1H), 8.43 (d,  $J^3=8.0$  Hz, 1H), 9.22 (d,  $J^3=8.0$  Hz, 1H).

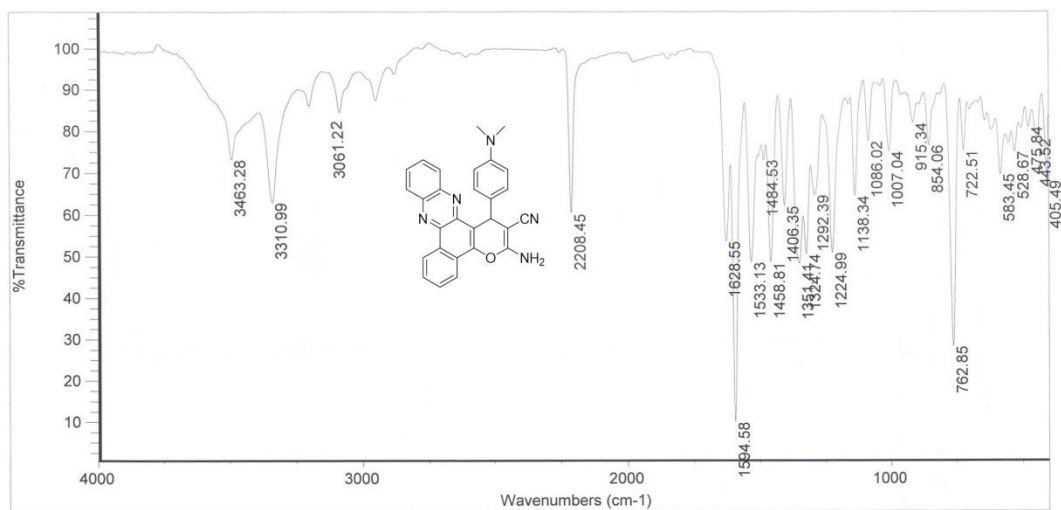
## NMR and IR spectra of compounds:



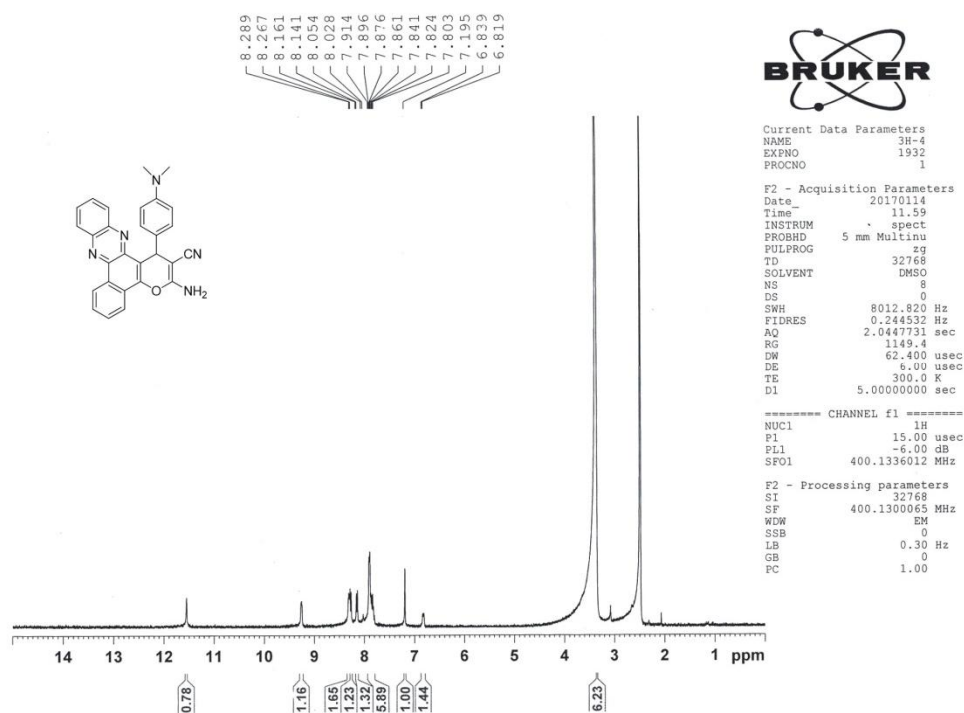
IR of 3-amino-1-phenyl-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6a)



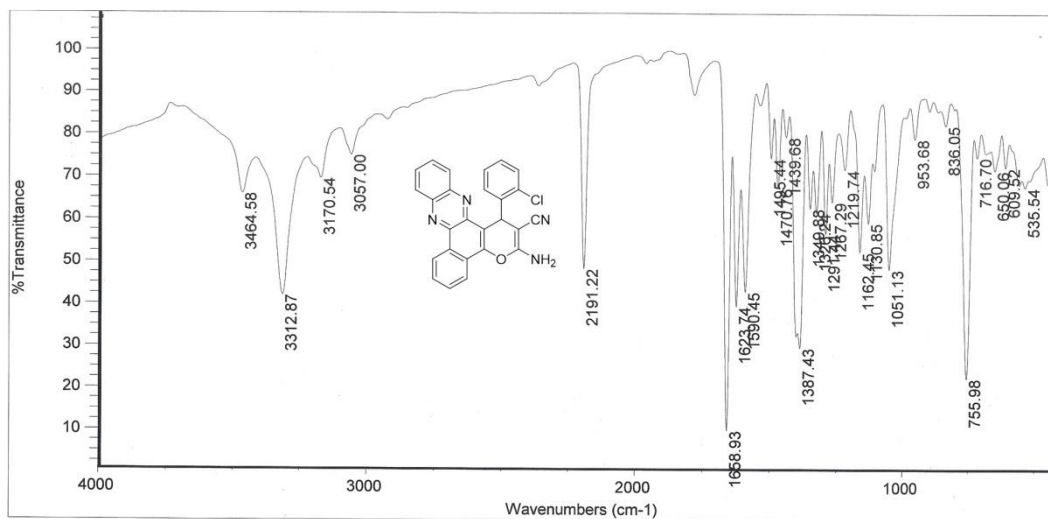
$^1\text{H}$  NMR of 3-amino-1-phenyl-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6a)



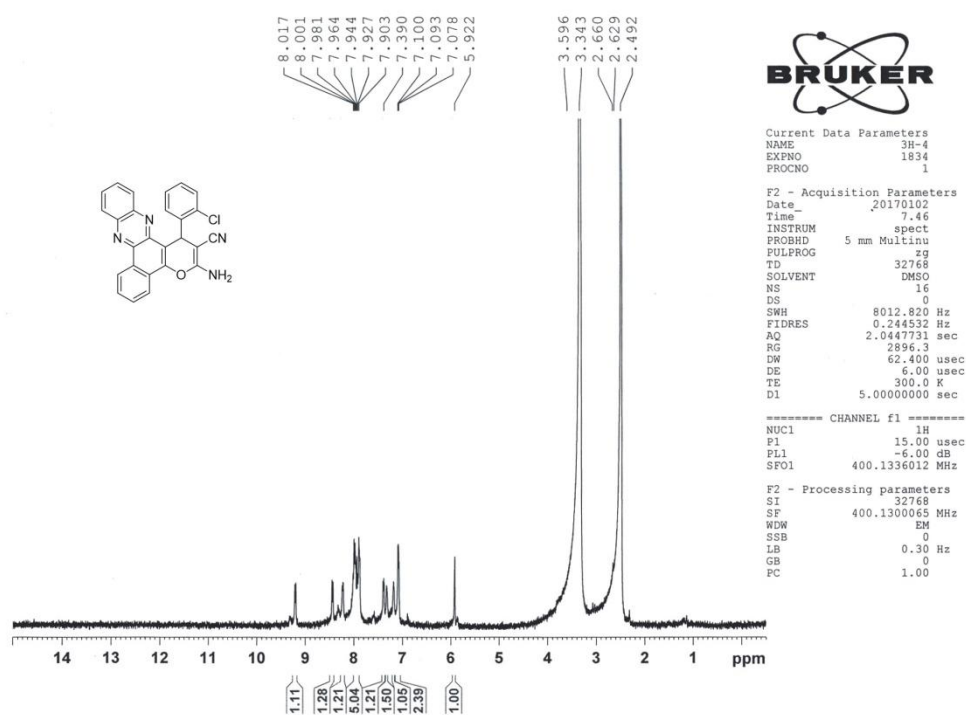
IR of 3-amino-1-(4-(dimethylamino)phenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6b)



<sup>1</sup>H NMR of 3-amino-1-(4-(dimethylamino)phenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6b)

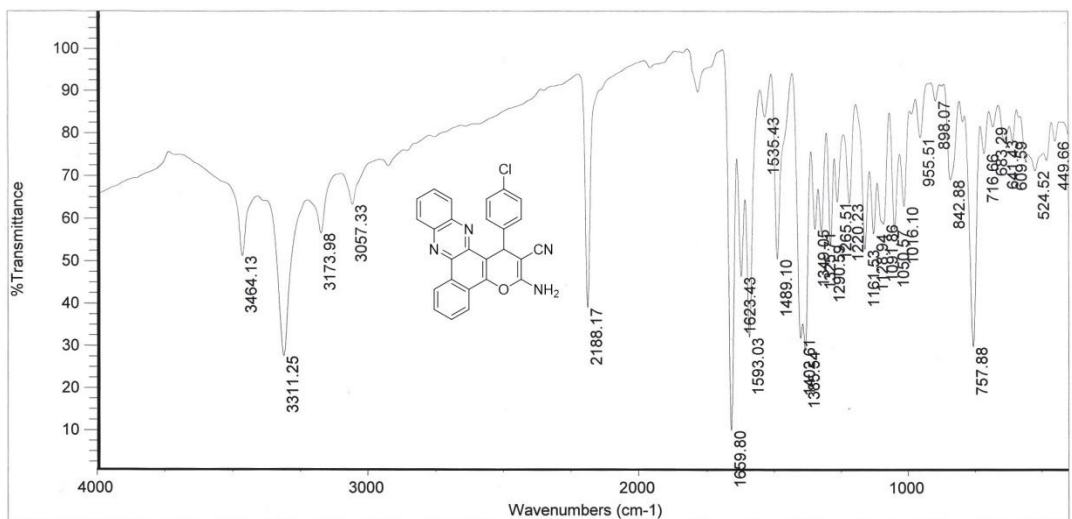


IR of 3-amino-1-(2-chlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6c)

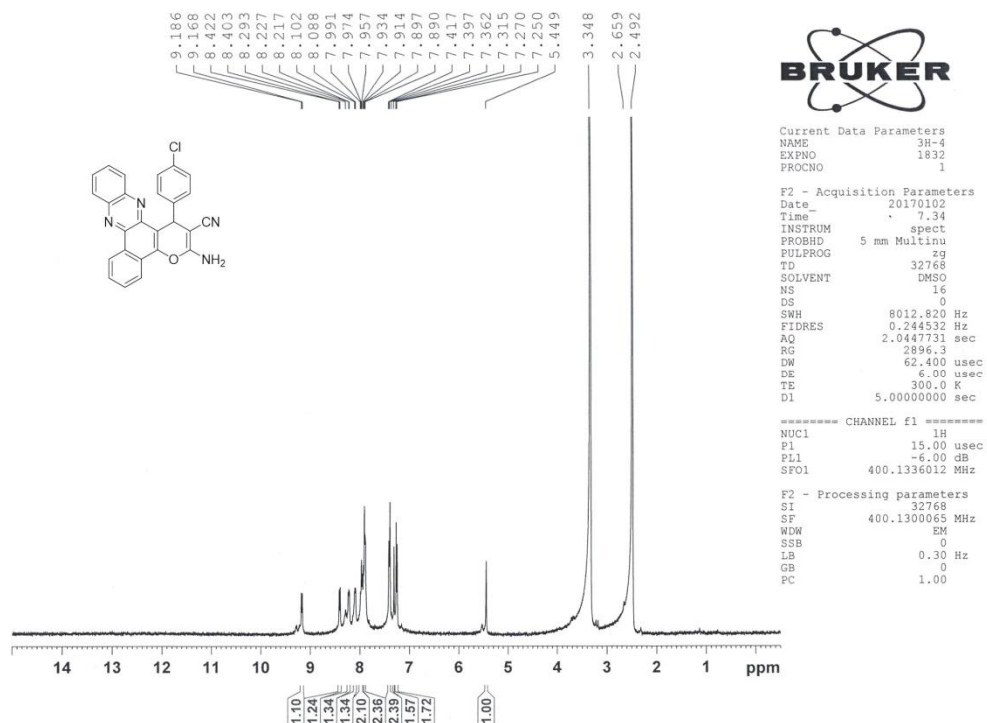


<sup>1</sup>H NMR of 3-amino-1-(2-chlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6c)

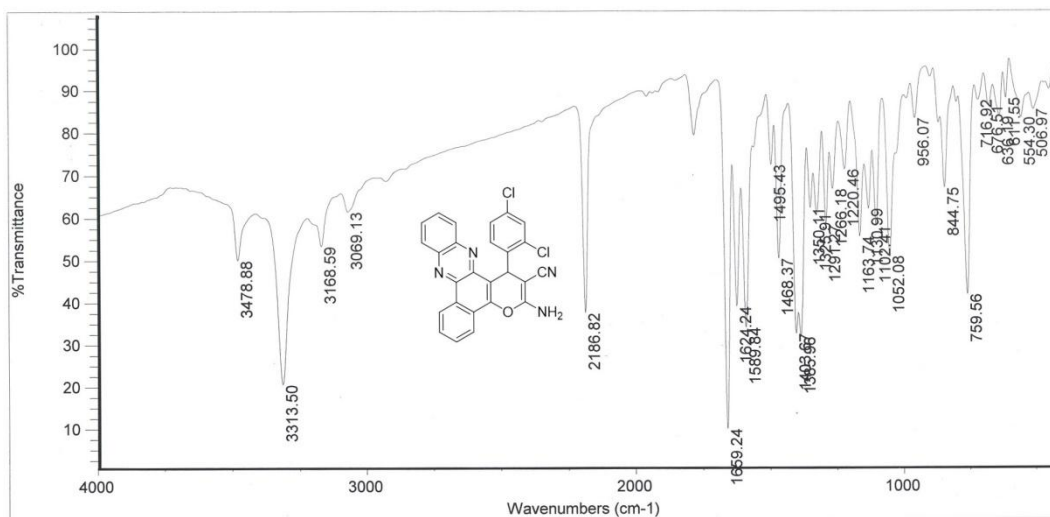




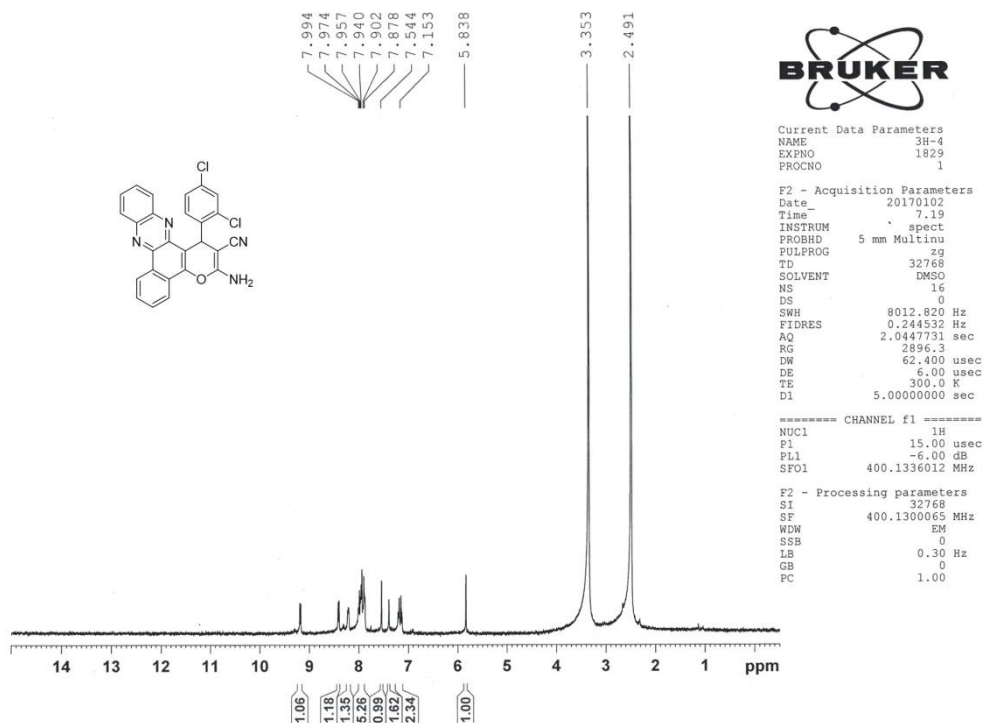
IR of 3-amino-1-(4-chlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6d)



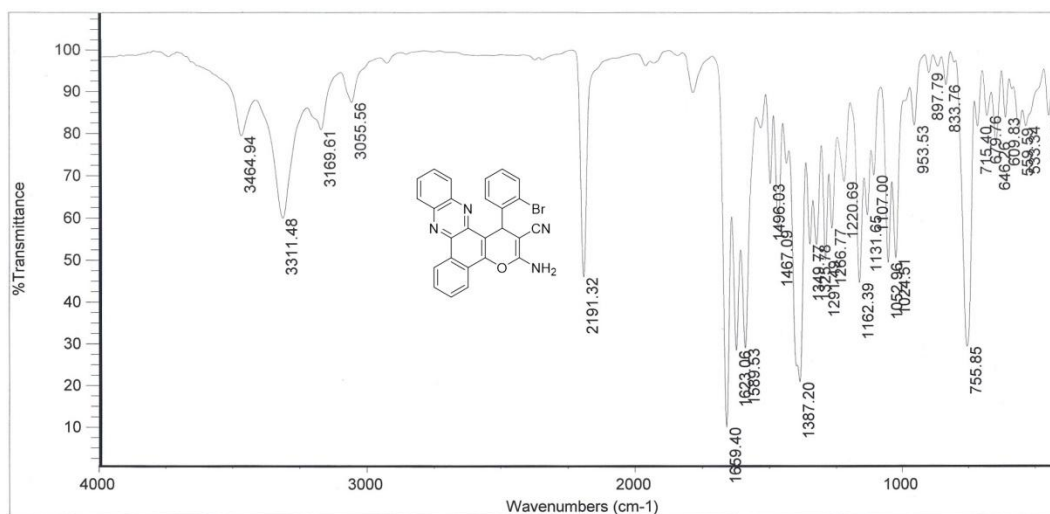
$^1\text{H}$  NMR of 3-amino-1-(4-chlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6d)



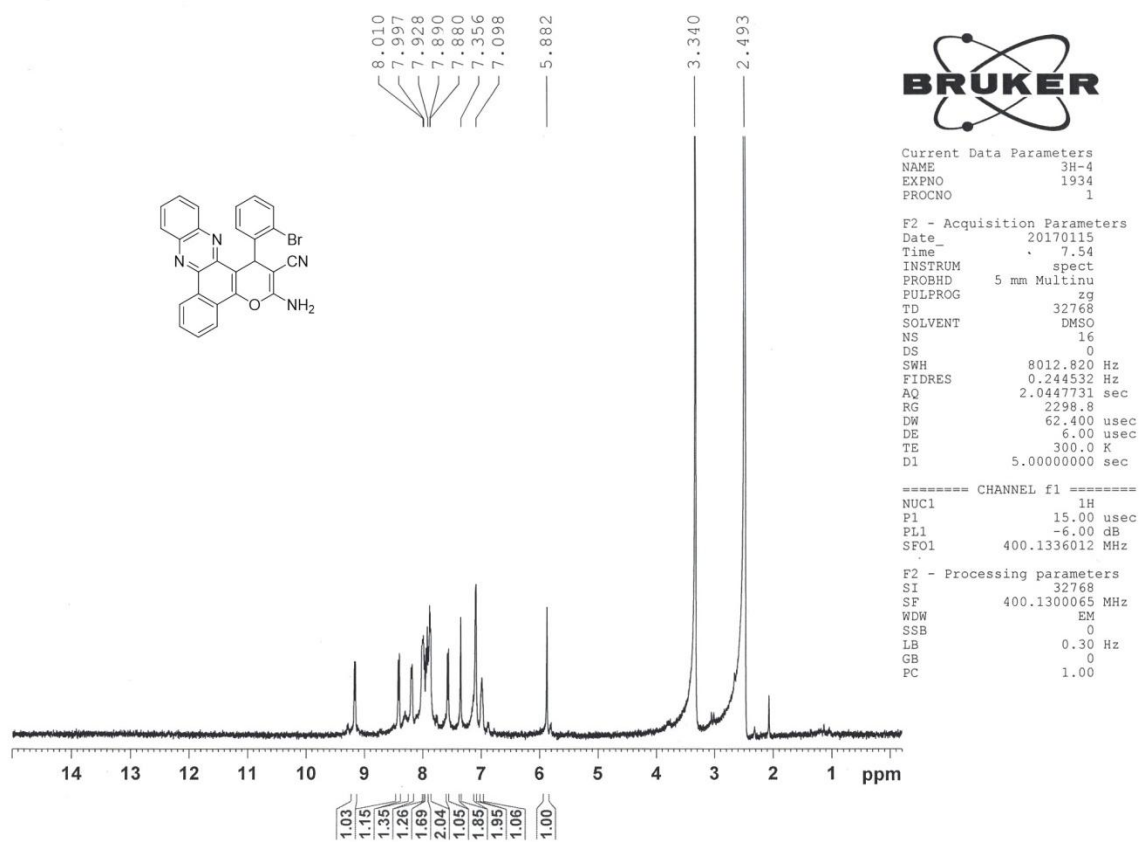
IR of 3-amino-1-(2,4-dichlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6e)



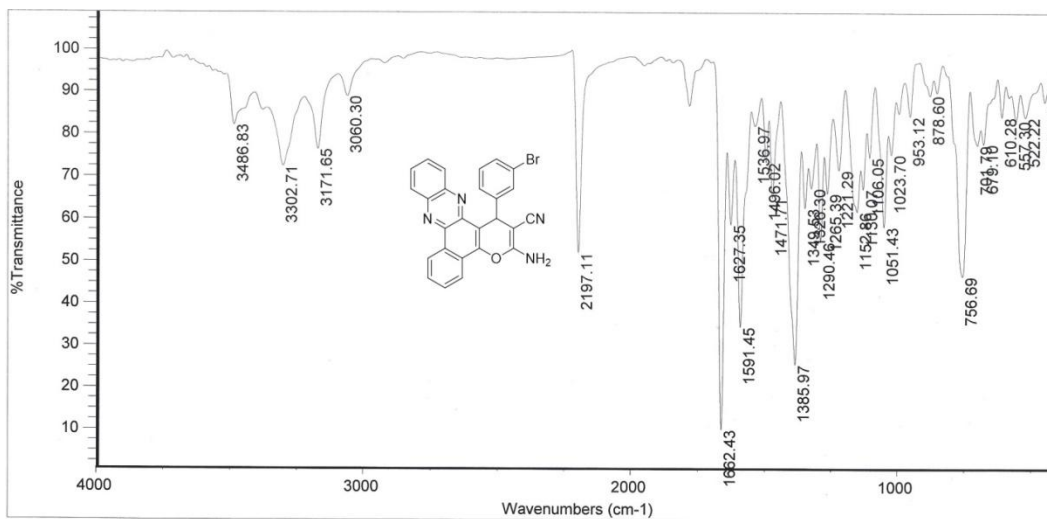
<sup>1</sup>H NMR of 3-amino-1-(2,4-dichlorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6e)



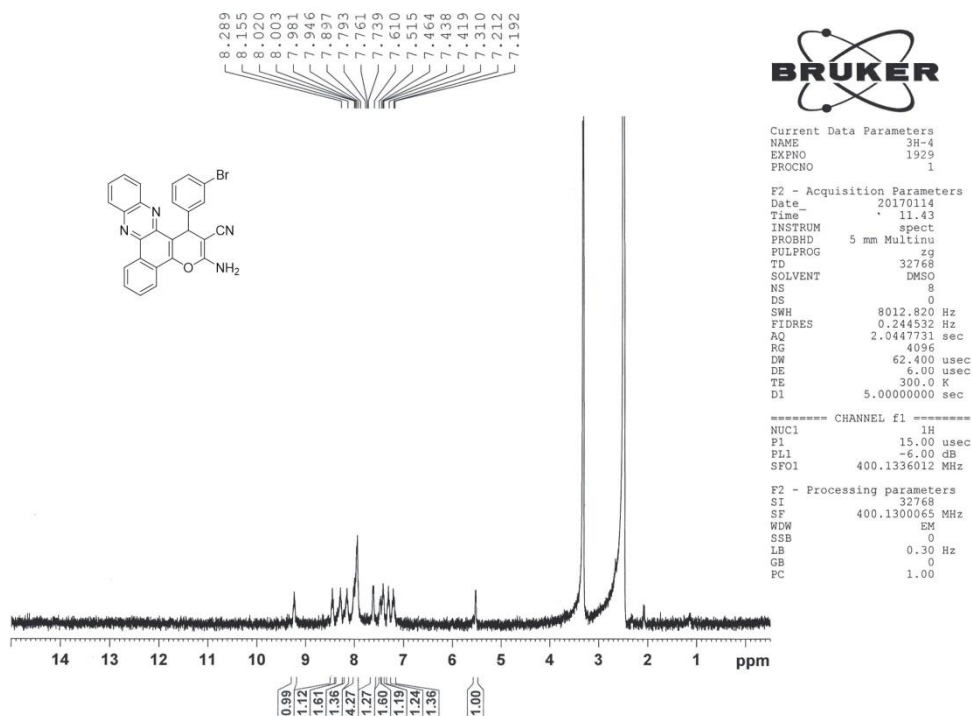
IR of 3-amino-1-(2-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6f)



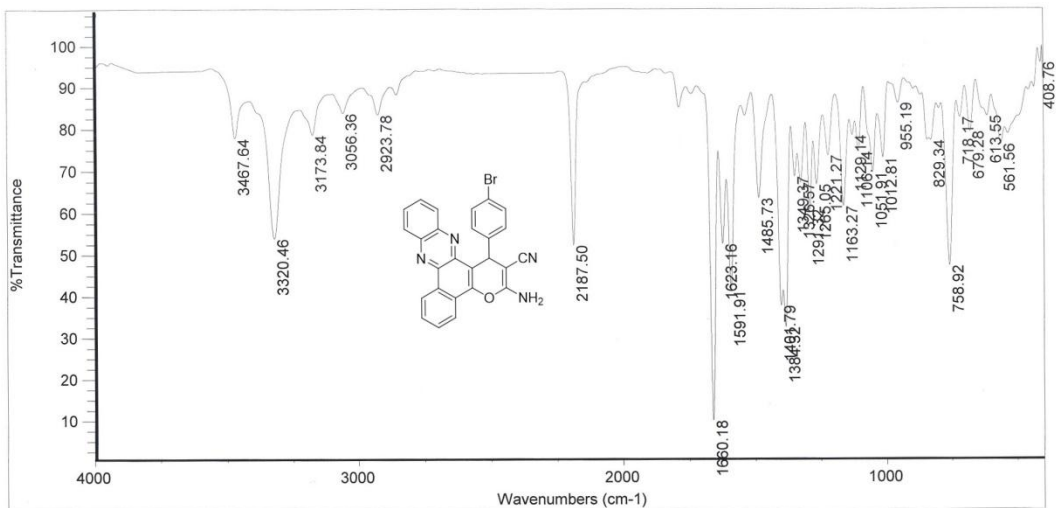
<sup>1</sup>H NMR of 3-amino-1-(2-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6f)



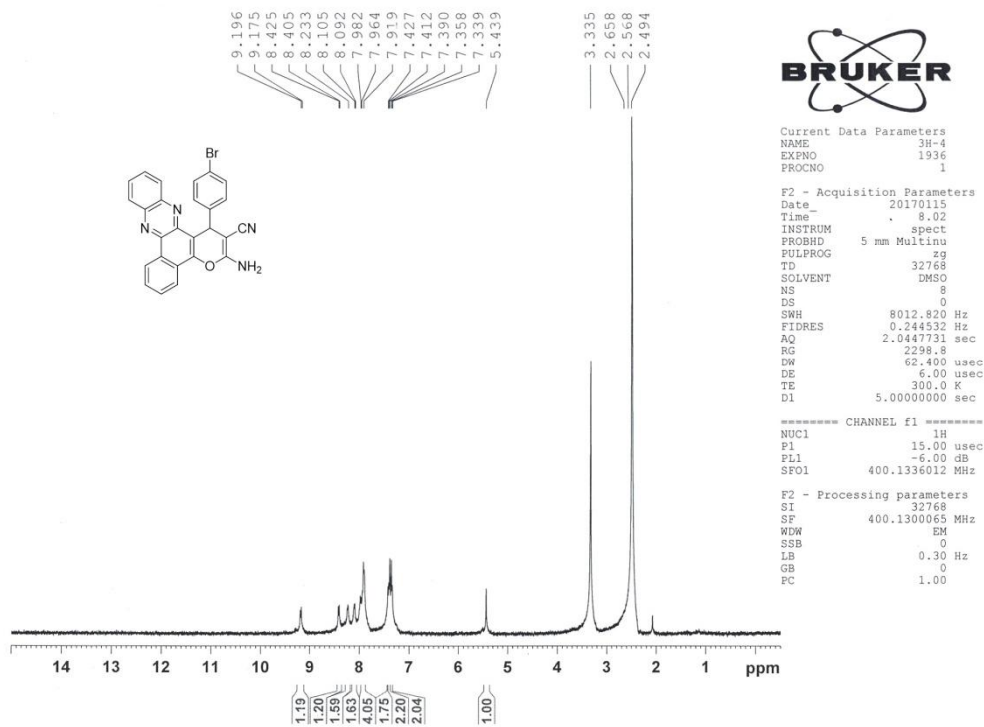
IR of 3-amino-1-(3-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6g)



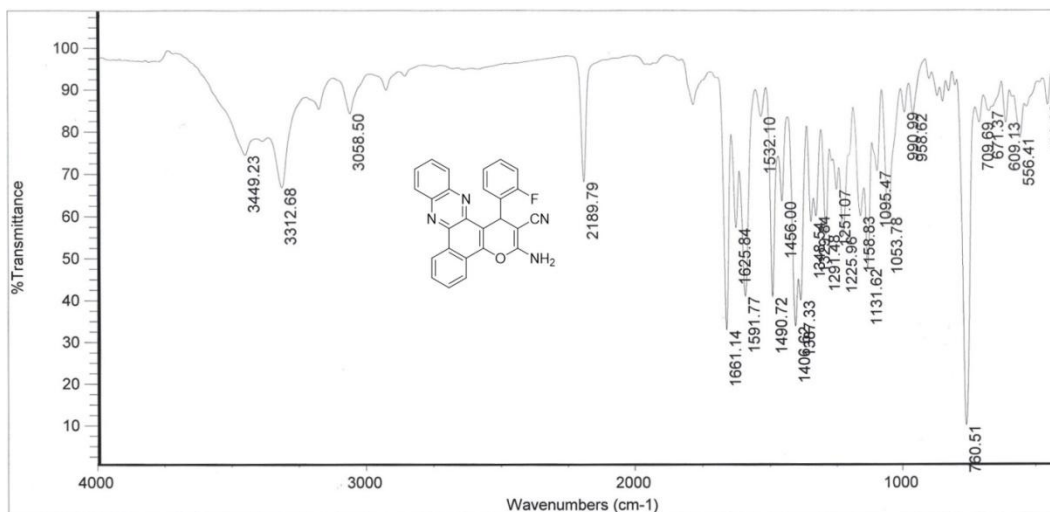
<sup>1</sup>H NMR of 3-amino-1-(3-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6g)



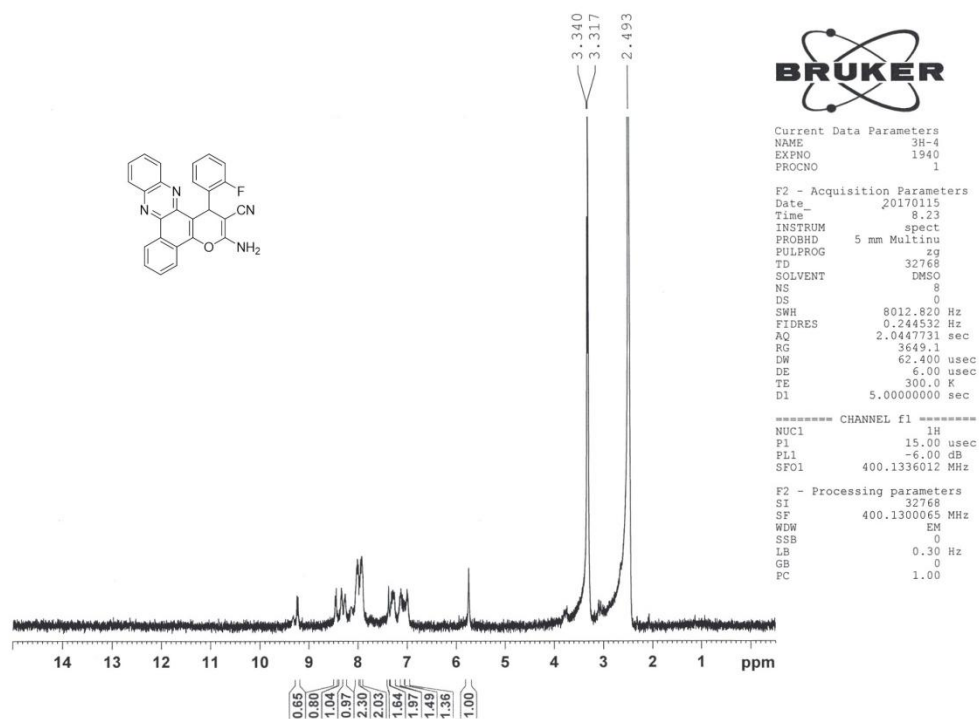
IR of 3-amino-1-(4-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6h)



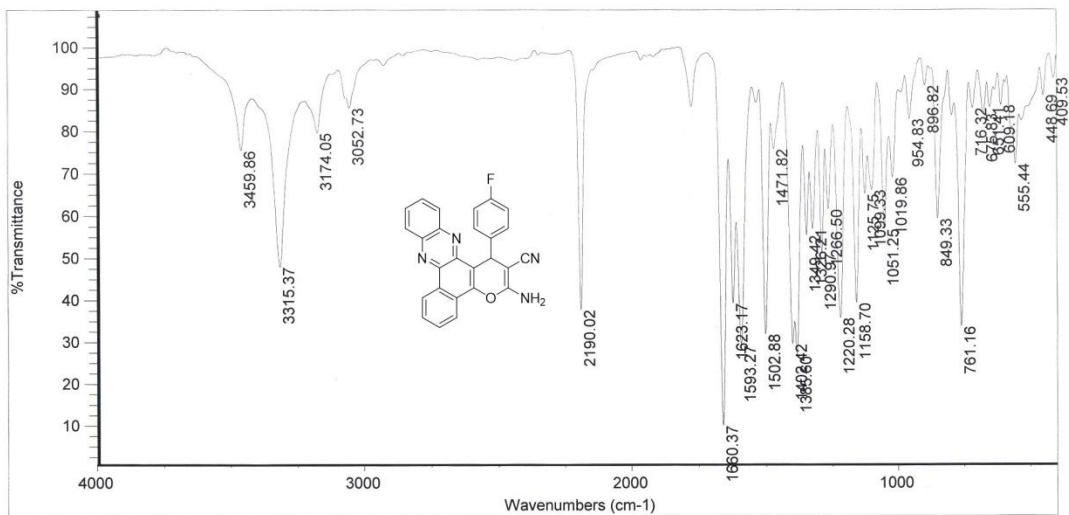
<sup>1</sup>H NMR of 3-amino-1-(4-bromophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6h)



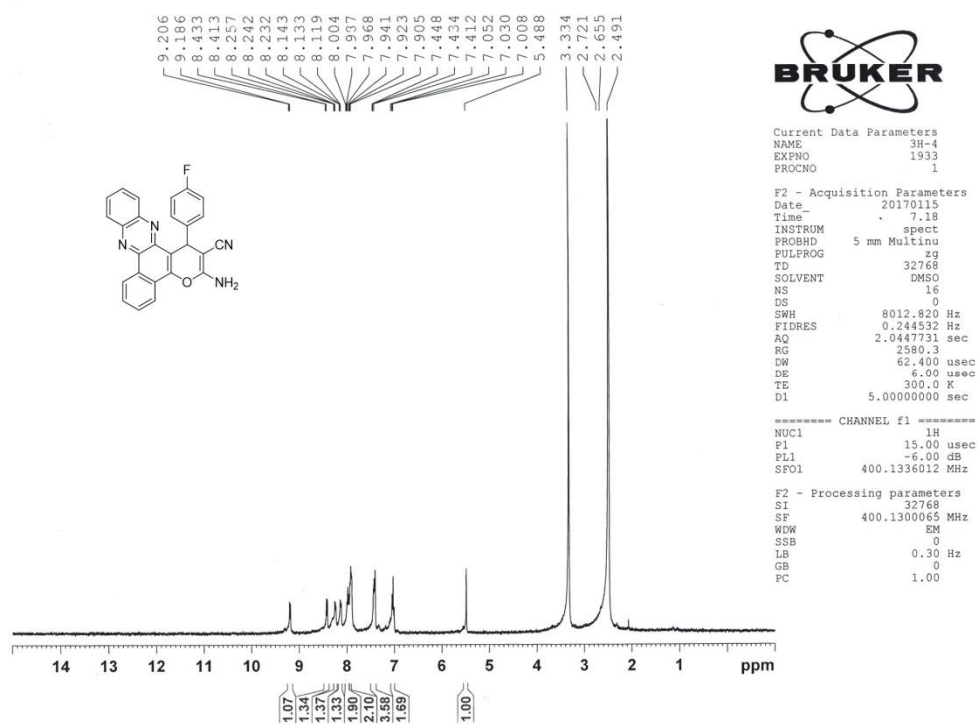
IR of 3-amino-1-(2-fluorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6i)



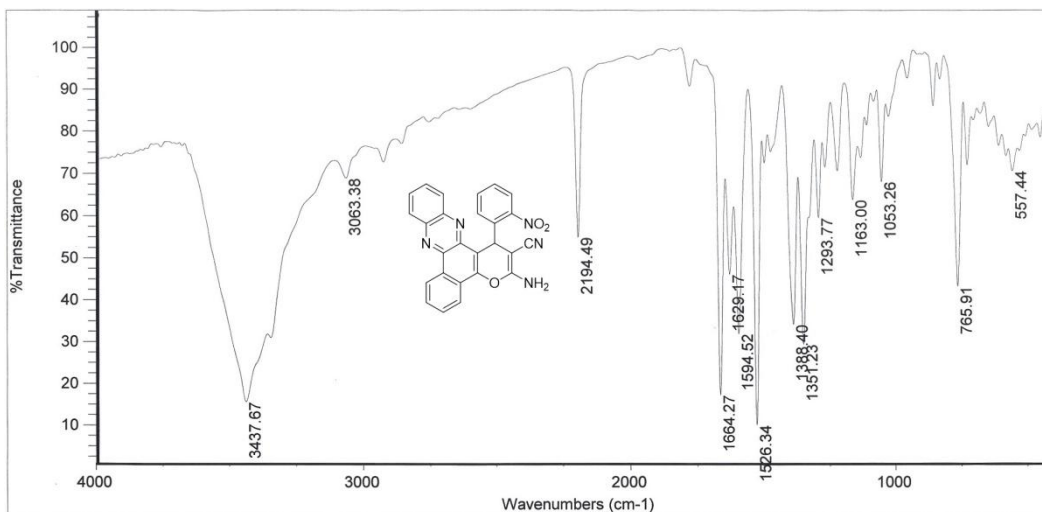
<sup>1</sup>H NMR of 3-amino-1-(2-fluorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6i)



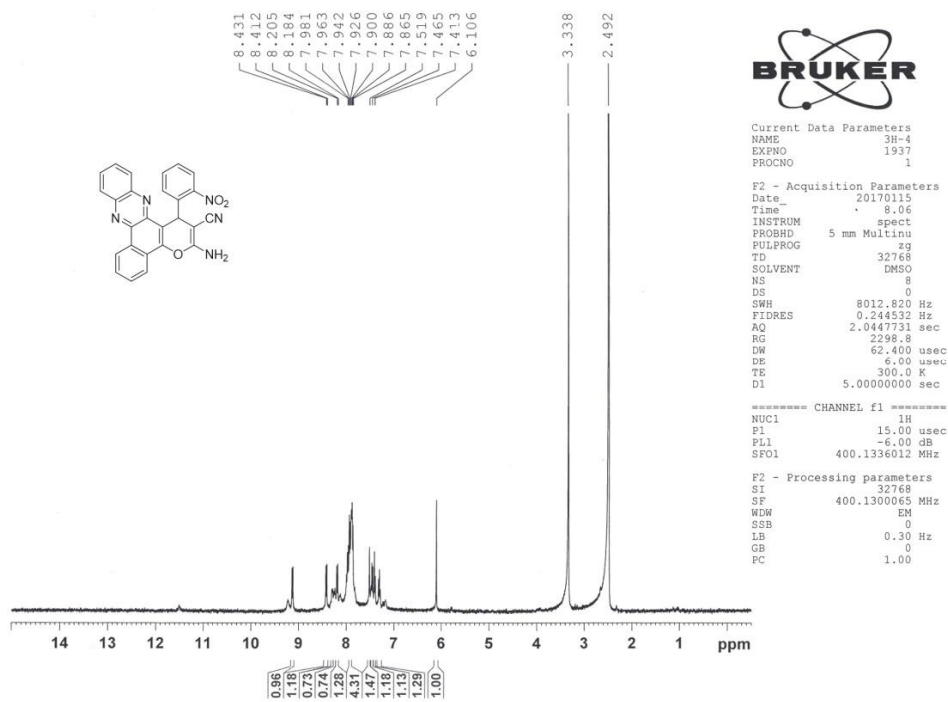
IR of 3-amino-1-(4-fluorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6j)



<sup>1</sup>H NMR of 3-amino-1-(4-fluorophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6j)

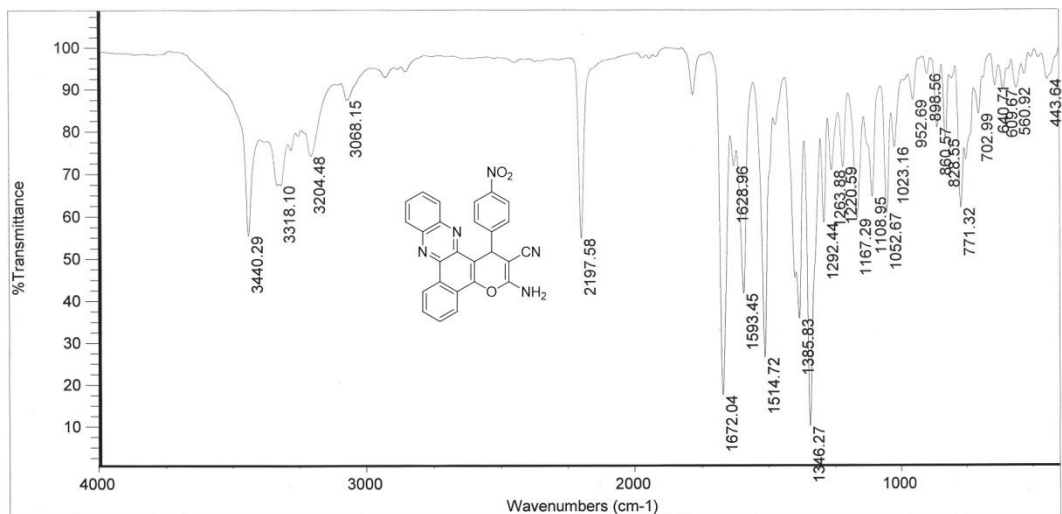


IR of 3-amino-1-(2-nitrophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6k)

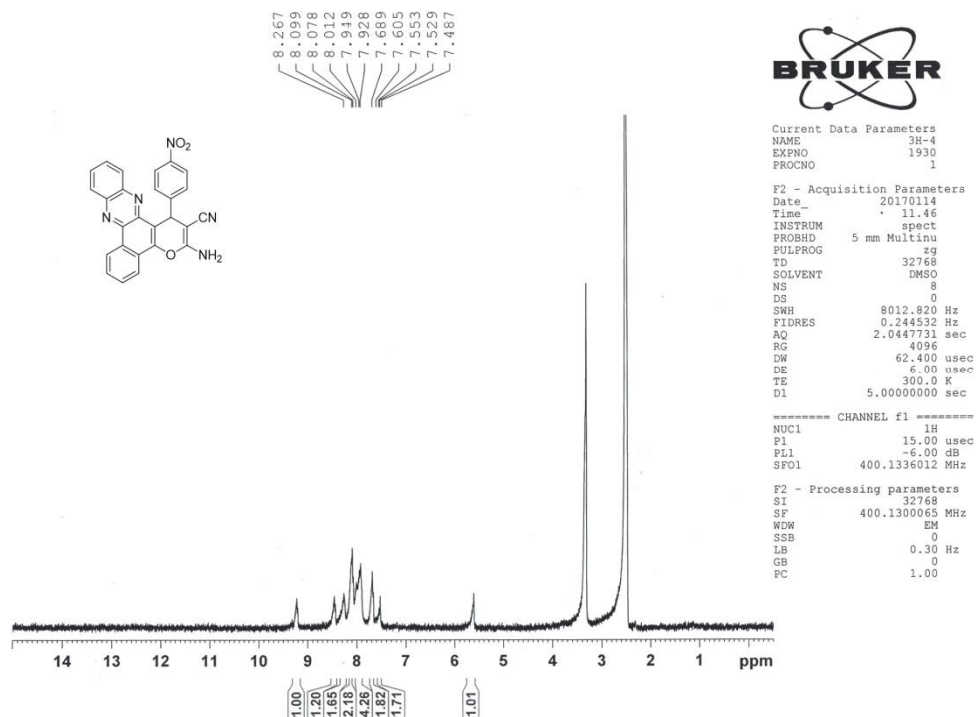


<sup>1</sup>H NMR of 3-amino-1-(2-nitrophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6k)

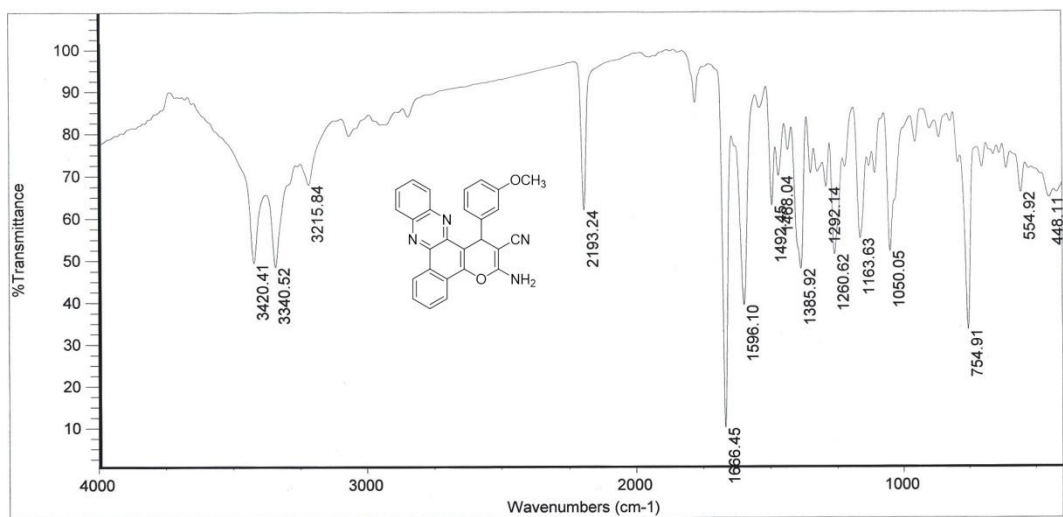




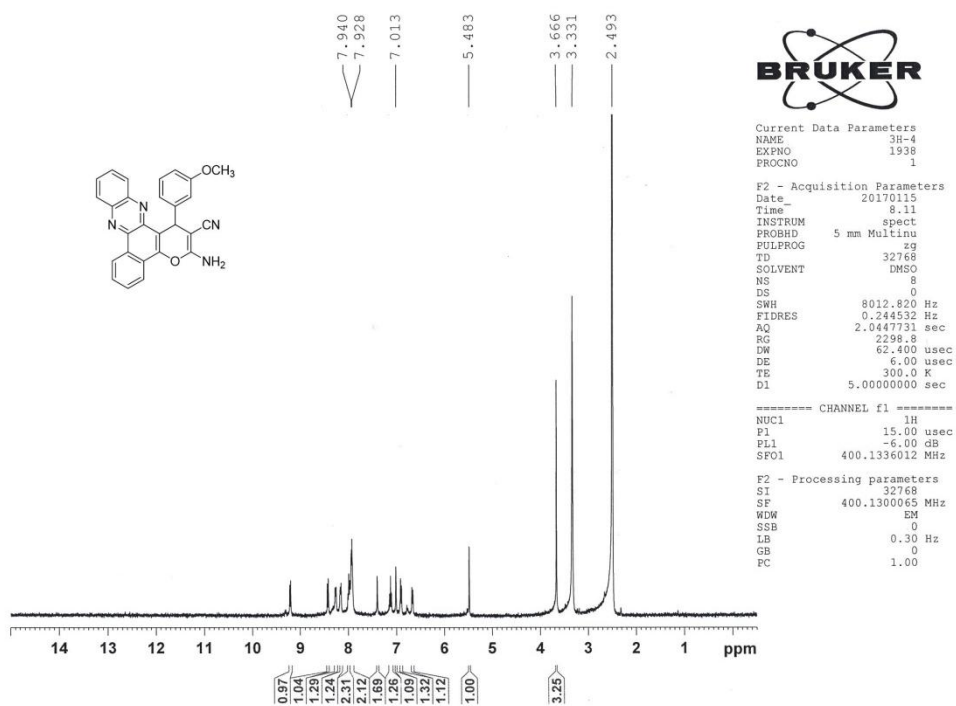
IR of 3-amino-1-(4-nitrophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6l)



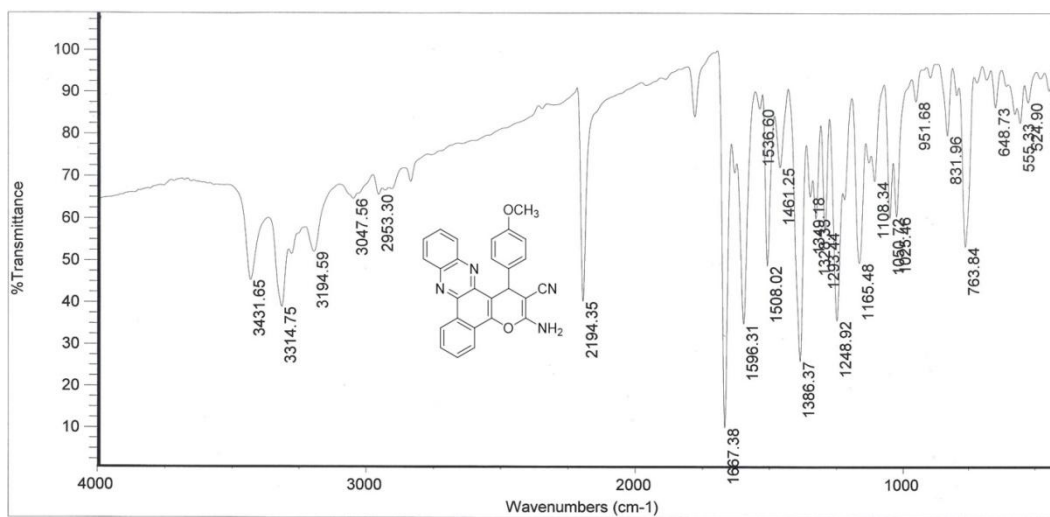
$^1\text{H}$  NMR of 3-amino-1-(4-nitrophenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6l)



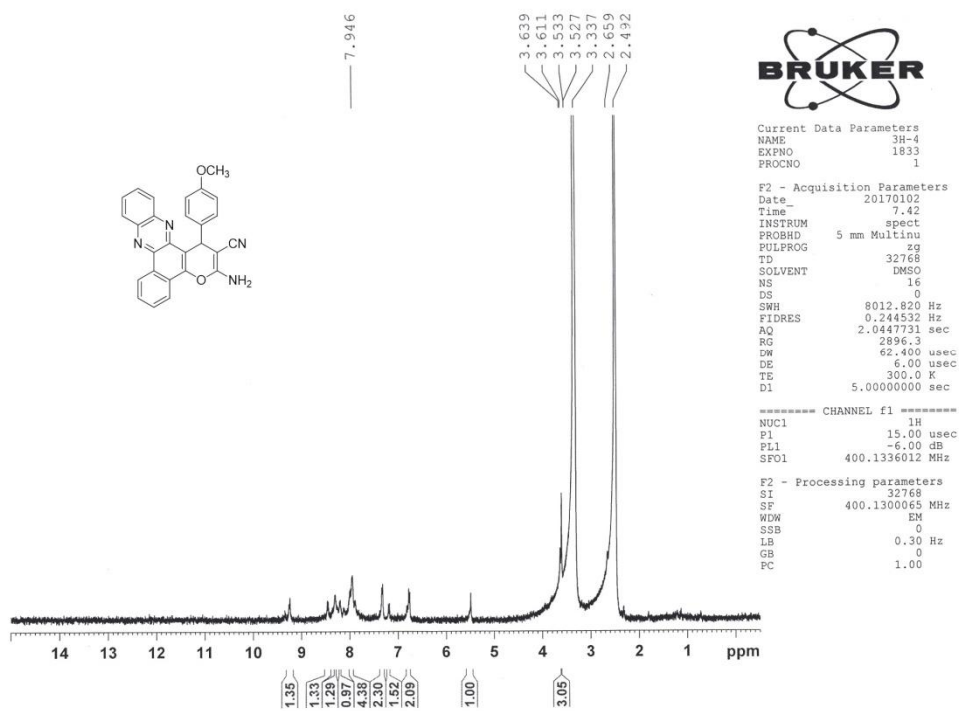
IR of 3-amino-1-(3-methoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6m)



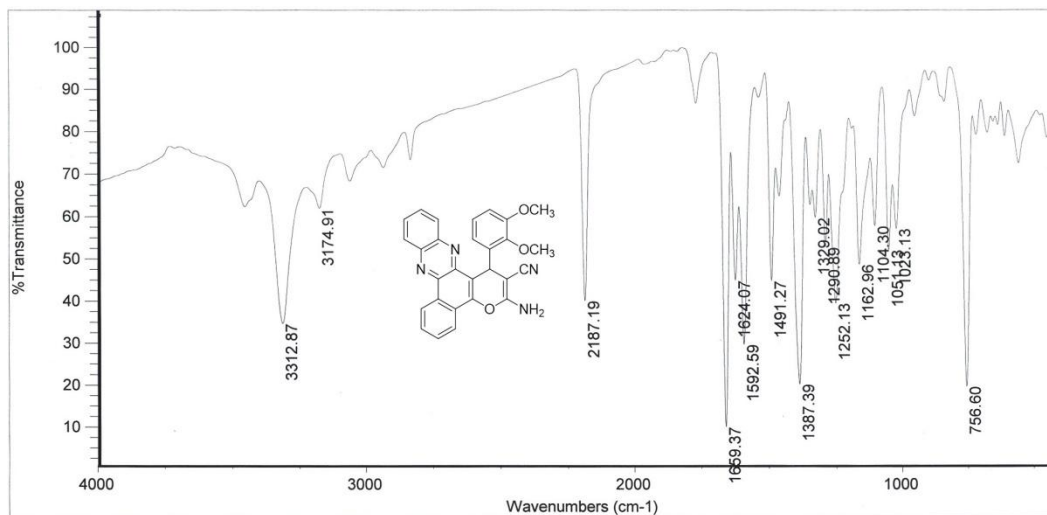
<sup>1</sup>H NMR of 3-amino-1-(3-methoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6m)



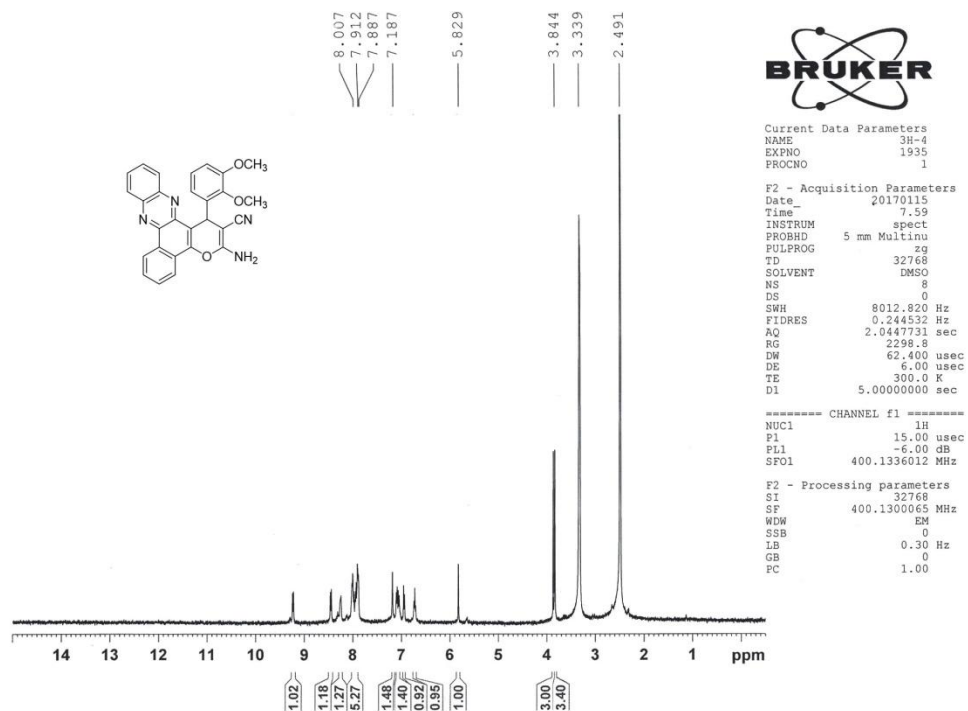
IR of 3-amino-1-(4-methoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6n)



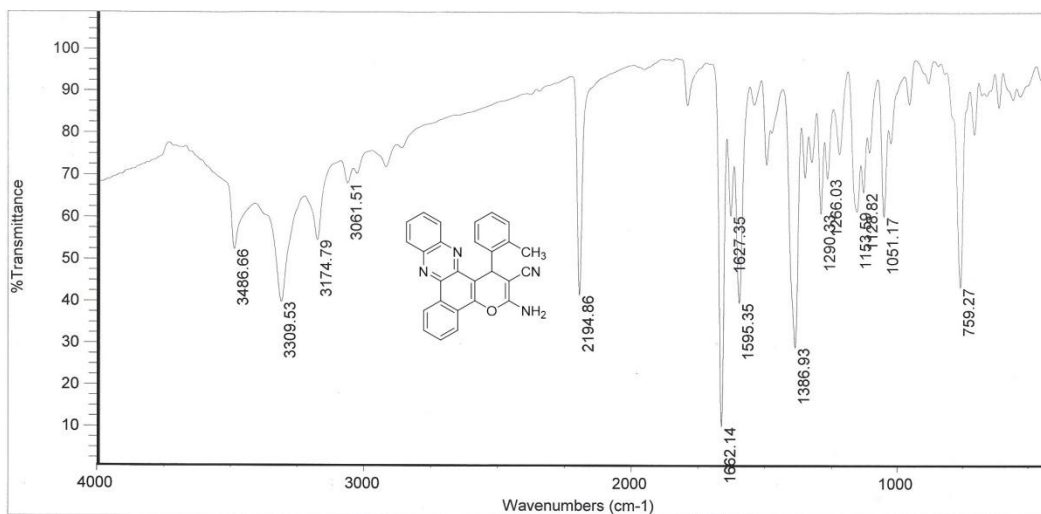
<sup>1</sup>H NMR of 3-amino-1-(4-methoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6n)



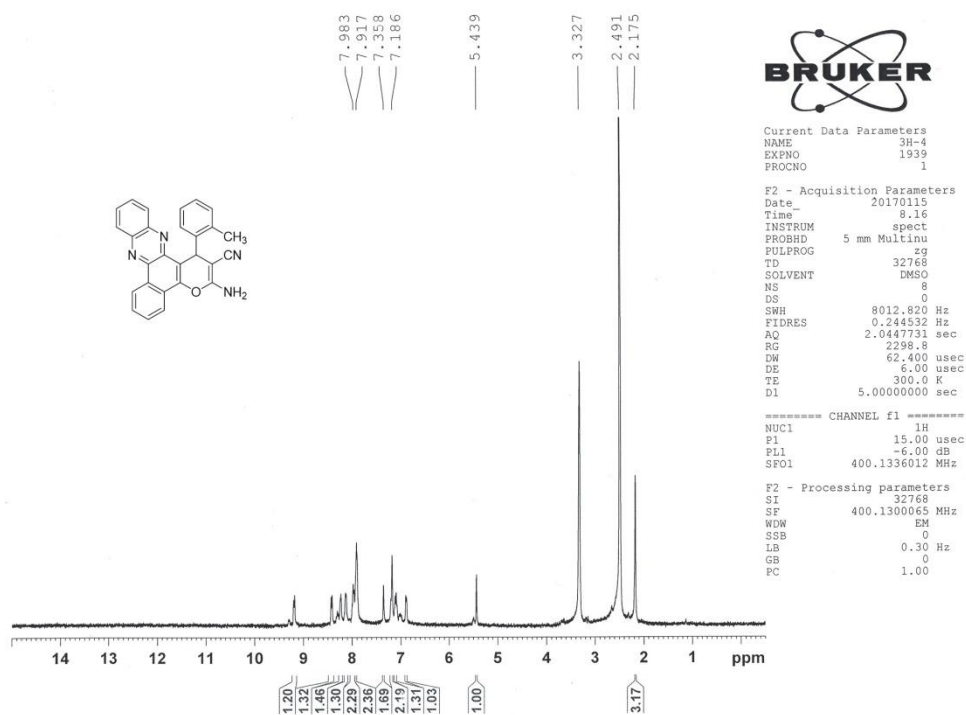
IR of 3-amino-1-(2,3-dimethoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6o)



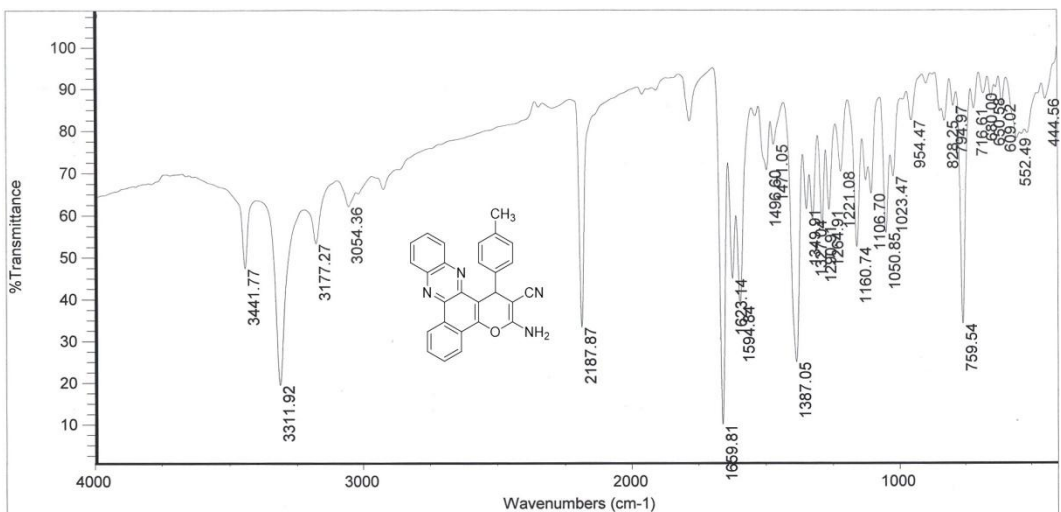
<sup>1</sup>H NMR of 3-amino-1-(2,3-dimethoxyphenyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6o)



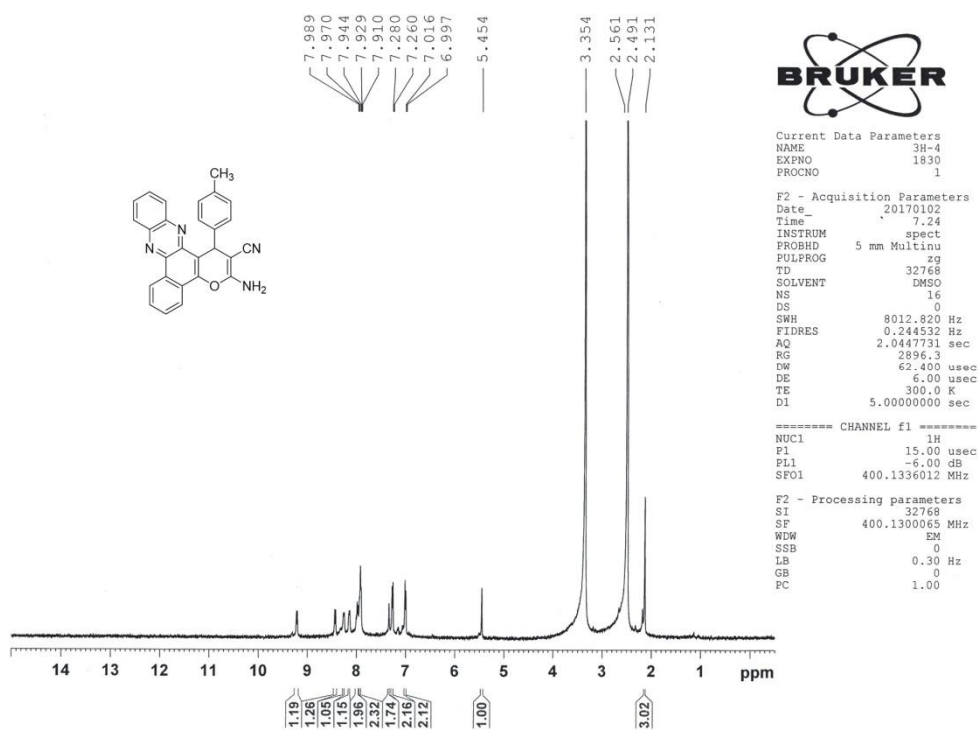
IR of 3-amino-1-(o-tolyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6p)



<sup>1</sup>H NMR of 3-amino-1-(o-tolyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6p)



IR of 3-amino-1-(p-tolyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6q)



<sup>1</sup>H NMR of 3-amino-1-(p-tolyl)-1H-benzo[a]pyrano[2,3-c]phenazine-2-carbonitrile (6q)