

## Preparation of GO/SiO<sub>2</sub>/PEA as a new solid base catalyst for the green synthesis of some spirooxindole derivatives

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### 6'-amino-3'-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile (5a)

M.p. 232-234 °C. FTIR (KBr)  $\nu$  max: 3337 (NH), 3132 (NH), 2182 (C=N), 1711 (C=O), 1496 (C-H, Ar)  $\text{Cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta_{\text{H}}$ : 1.51 (3H, s, CH<sub>3</sub>), 6.88 (1H, d,  $J=7.0$  Hz, ArH), 6.96 (2H, m, ArH), 7.22 (2H, s, NH<sub>2</sub>), 7.24 (1H, s, ArH), 10.59 (1H, s, NH), 12.27 (1H, s, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 12.5, 47.1, 58.5, 111.1, 112.5, 116.2, 122.1, 125.6, 127.7, 140.7, 162.6, 166.9, 175.3 ppm. Anal. Calcd. For C<sub>15</sub>H<sub>11</sub>N<sub>5</sub>O<sub>2</sub>: C, 61.43; H, 3.78; N, 23.88 %. Found: C, 61.36; H, 3.75; N, 23.82 %.

### 6'-amino-3'-methyl-2-oxo-1'H-spiro[5-Nitro-indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile(5b)

M.p. 226-228 °C. FTIR (KBr)  $\nu$  max: 3419-3337 (NH), 3174 (NH), 2187 (C=N), 1720 (C=O), 1498 (C-H, Ar)  $\text{Cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta_{\text{H}}$ : 1.57 (3H, s, CH<sub>3</sub>), 7.12 (1H, d,  $J=7.0$  Hz, ArH), 7.41 (2H, s, NH<sub>2</sub>), 7.90 (1H, s, ArH), 8.21 (1H, d,  $J=8.0$  Hz, ArH), 11.36 (1H, s, NH), 12.40 (1H, s, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta_{\text{C}}$ : 9.8, 48.3, 55.4, 95.2, 110.8, 119.8, 121.6, 127.3, 134.6, 136.5, 144.5, 148.9, 156.7, 164.1, 178.9 ppm; Anal. Calcd. For C<sub>15</sub>H<sub>10</sub>N<sub>6</sub>O<sub>4</sub>: C, 53.25; H, 2.96; N, 24.85 %. Found: C, 53.22; H, 3.12; N, 24.79 %.

### 6'-amino-3'-methyl-2-oxo-1'H-spiro[5-Fluoro-indoline-3,4'-pyrano[2,3-c]pyrazole]-5' carbonitrile(5c)

M.p. 262-265 °C. FTIR (KBr)  $\nu$  max: 3409(NH), 3220(NH), 2186(C=N), 1706(C=O), 1490 (C-H, Ar)  $\text{Cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta_{\text{H}}$ : 1.56 (3H, s, CH<sub>3</sub>), 6.90 (1H, s, ArH), 6.97 (1H, d,  $J=6.0$  Hz, ArH), 7.07 (1H, d,  $J=7.0$  Hz, ArH), 7.28 (2H, s, NH<sub>2</sub>), 10.62 (1H, s, NH), 12.31 (1H, s, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta_{\text{C}}$ : 9.4, 48.3, 55.3, 95.4, 111.0, 116.2, 119.1, 134.9, 135.2, 138.3, 147.6, 155.8, 157.8, 163.3, 178.2 ppm; Anal. Calcd. For C<sub>15</sub>H<sub>10</sub>FN<sub>5</sub>O<sub>2</sub>: C, 57.82; H, 3.21; N, 22.49 %. Found: C, 57.79; H, 3.23; N, 22.51 %.

### 6'-amino-3'-methyl-2-oxo-1'H-spiro[5-chloro-indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile (5d)

M.p. 232-234 °C. FTIR (KBr)  $\nu$  max: 3346 (NH), 3137 (NH), 2182 (C=N), 1714 (C=O), 1487 (C-H, Ar)  $\text{Cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta_{\text{H}}$ : 1.57 (3H, s, CH<sub>3</sub>), 6.90 (1H, d,  $J=6.0$  Hz, ArH), 7.12 (1H, d,  $J=7.0$  Hz, ArH), 7.29 (1H, s, ArH), 7.29 (2H, s, NH<sub>2</sub>), 10.74 (1H, s, NH), 12.33 (1H, s, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta_{\text{C}}$ : 9.4, 48.1, 55.1, 95.2, 112.0, 119.1, 125.1, 127.1, 129.5, 135.6, 141.3, 155.7, 163.3, 177.9 ppm; Anal. Calcd. For C<sub>15</sub>H<sub>10</sub>ClN<sub>5</sub>O<sub>2</sub>: C, 54.88; H, 3.05; N, 21.34 %. Found: C, 54.89; H, 3.09; N, 21.41 %.

### 6'-amino-3'-methyl-2-oxo-1'H-spiro[5-Bromo-indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile(5e)

M.p. 248-250 °C. FTIR (KBr)  $\nu$  max: 3346 (NH), 3141 (NH), 2182 (C=N), 1713 (C=O), 1498 (C-H, Ar)  $\text{Cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$ : 1.56 (3H, s, CH<sub>3</sub>), 6.86 (1H, d,  $J=6.0$  Hz, ArH), 7.22 (1H, s, ArH), 7.30 (2H, s, NH<sub>2</sub>), 7.41 (1H, d,  $J=7.0$  Hz, ArH), 10.76 (1H, s, NH), 12.34 (1H, s, NH) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$ : 9.4, 48.0, 55.0, 95.2, 112.2, 114.7, 119.5, 128.0, 132.2, 135.2, 135.5, 141.3, 155.6, 163.1, 178.2 ppm; Anal. Calcd. for C<sub>15</sub>H<sub>10</sub>BrN<sub>5</sub>O<sub>2</sub>: C, 48.41; H, 2.71; N, 18.82 %. Found: C, 48.44; H, 2.65; N, 18.74 %.

**7'-amino-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6a)**

M.p. 281-283 °C. FTIR (KBr)  $\nu$  max: 3321 (NH<sub>2</sub>), 2197 (C=N), 1679 (C=O amide), 1249 (C=O)  $\text{Cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$ : 6.77(1H, d,  $J=6.0$  Hz, ArH), 6.88 (1H, t,  $J=6.0$  Hz ArH), 7.16 (2H, t,  $J=7.0$  Hz, ArH), 7.45(2H s, NH<sub>2</sub>), 10.56 (1H, s, NH), 12.51 (1H, s, NH) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$ : 45.1, 57.5, 85.2, 112.4, 119.6, 123.7, 124.3, 129.1, 133.7, 142.6, 163.9, 166.1, 167.9, 176.6, 183.2 ppm; Anal. Calcd. for C<sub>15</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>S: C, 45.79; H, 2.29; N, 17.81 %. Found: C, 45.81; H, 2.27; N, 17.92 %.

**7'-amino-5-fluoro-1,1',2,2',3',4'-hexahydro-2,4'-dioxo-2'-thioxospiro[indole-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6b)**

M.p. 299-301 °C. FTIR (KBr)  $\nu$  max: 3367 (NH<sub>2</sub>), 3163 (NH), 2199 (C=N), 1684 (C=O amide), 1258 (C=O), 1485(C=C), 1184-1341 (C-O)  $\text{Cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$ : 6.76(1H, t,  $J=6.0$  Hz ArH), 6.95 (1H, t,  $J=6.0$  Hz, ArH), 7.18 (1H, d,  $J=7.0$  Hz, ArH), 7.44(2H s, NH<sub>2</sub>), 10.53 (1H, s, NH), 12.40 (1H, s, NH) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$ : 47.1, 57.0, 91.2, 110.0, 112.3, 115.1, 116.8, 134.7, 138.4, 152.9, 157.1, 158.2, 159.2, 174.1, 177.4 ppm; Anal. Calcd. for C<sub>15</sub>H<sub>8</sub>FN<sub>5</sub>O<sub>3</sub>S: C, 50.42; H, 2.24; N, 19.61 %. Found: C, 50.44; H, 2.22; N, 19.59 %.

**7'-amino-5-Chloro-1,1',2,2',3',4'-hexahydro-2,4'-dioxo-2'-thioxospiro[indole-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6c)**

M.p. 289-291 °C. FTIR (KBr)  $\nu$  max: 3357 (NH<sub>2</sub>), 2197 (C=N), 1681 (C=O amide), 1222 (C=O), 1476 (C=C), 1302-1172 (C-O)  $\text{Cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$ : 6.77 (1H, d,  $J=6.0$  Hz, ArH), 7.19 (1H, d,  $J=7.0$  Hz, ArH), 7.36 (1H, s, ArH), 7.45(2H s, NH<sub>2</sub>), 10.63 (1H, s, NH), 12.39 (1H, s, NH) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{C}}$ : 48.3, 56.8, 91.0, 110.8, 116.9, 124.4, 126.1, 128.6, 135.2, 141.1, 153.3, 158.3, 160.1, 174.3, 177.1 ppm; Anal. Calcd. for C<sub>15</sub>H<sub>8</sub>ClN<sub>5</sub>O<sub>3</sub>S: C, 48.15; H, 2.14; N, 18.72 %. Found: C, 48.14; H, 2.18; N, 18.81 %.

**7'-amino-5-bromo-1,1',2,2',3',4'-hexahydro-2,4'-dioxo-2'-thioxospiro[indole-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6d)**

M.p. 238-240 °C. FTIR (KBr)  $\nu$  max: 3350 (NH<sub>2</sub>), 2199 (C=N), 1691 (C=O amide), 1213 (C=O), 1339-1169 (C-O) Cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ <sub>H</sub>: 6.74 (1H, d, *J*=6.0 Hz, ArH), 7.32 (1H, t, *J*=7.0 Hz, ArH), 7.50 (1H, s, ArH), 7.50 (2H s, NH<sub>2</sub>), 10.68 (1H, s, NH), 12.54 (1H, s, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ <sub>C</sub>: 47.3, 57.3, 91.5, 111.7, 114.1, 117.3, 127.5, 131.8, 137.1, 142.5, 153.8, 158.8, 160.0, 174.8, 177.5 ppm; Anal. Calcd. for C<sub>15</sub>H<sub>8</sub>BrN<sub>5</sub>O<sub>3</sub>S: C, 43.06; H, 1.91; N, 16.74 %. Found: C, 43.11; H, 1.89; N, 16.69 %.

**2-amino-6,8-dimethyl-5,7-dioxospiro[5'-chloro-(3'H)-indol-3',4,4(H)-5,6,7,8-tetrahydropyrano(2,3-d)pyrimidine]-(1'H)-2'-one-3-carbonitrile (6e)**

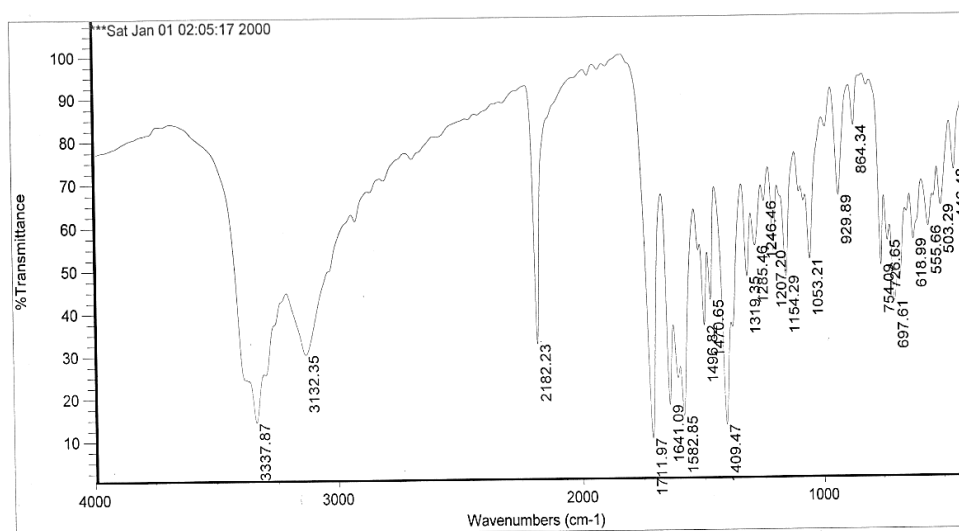
M.p. 248-250 °C. FTIR (KBr)  $\nu$  max: 3407(NH<sub>2</sub>), 2197(C=N), 1681(C=O amide), 1245(C=O), 1499(C=C), 1302-1172(C-O) Cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ <sub>H</sub>: 3.02 (3H, s, CH<sub>3</sub>), 3.35 (3H, s, CH<sub>3</sub>), 6.79 (1H, d, *J*=6.0 Hz, ArH), 7.18 (1H, d, *J*=7.0 Hz, ArH), 7.27(1H s, ArH), 7.64 (2H, s, NH<sub>2</sub>), 10.63 (1H, s, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ <sub>C</sub>: 28.2, 29.7, 48.1, 56.9, 86.1, 113.5, 117.2, 118.0, 126.4, 130.6, 136.3, 140.6, 151.1, 152.6, 157.9, 165.9, 178.1 ppm; Anal. Calcd. for C<sub>17</sub>H<sub>12</sub>ClN<sub>5</sub>O<sub>4</sub>: C, 31.10; H, 3.11; N, 18.13 %. Found: C, 31.12; H, 3.09; N, 18.15 %.

**2-amino-6,8-dimethyl-5,7-dioxospiro[5'-Fluoro-(3'H)-indol-3',4,4(H)-5,6,7,8-tetrahydropyrano(2,3-d)pyrimidine]-(1'H)-2'-one-3-carbonitrile (6f)**

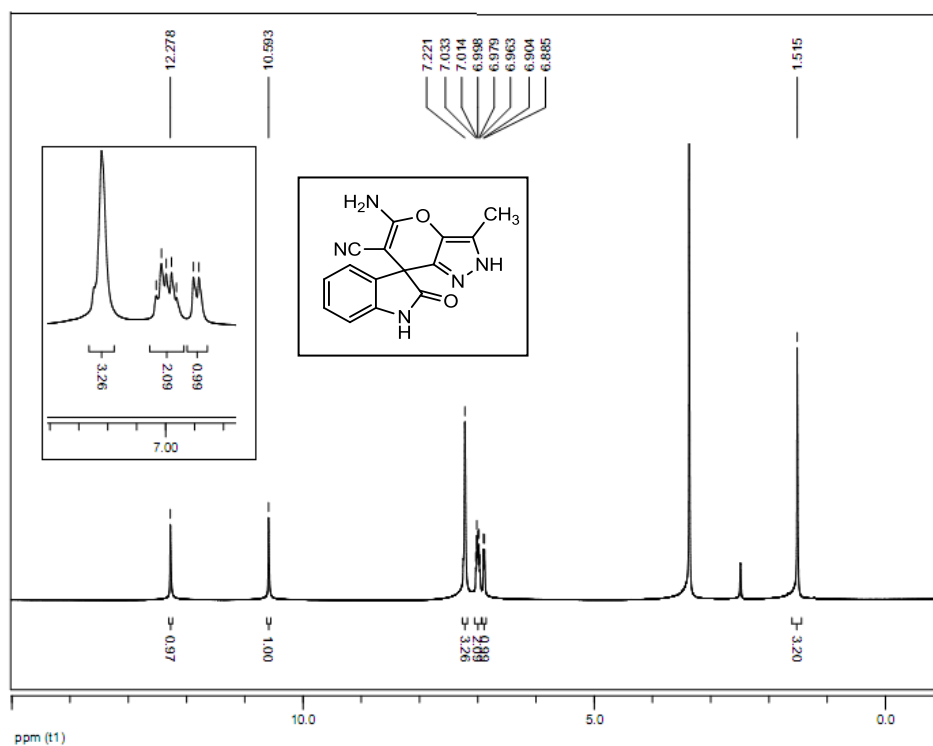
M.p. 276-278 °C. FTIR (KBr)  $\nu$  max: 3484(NH<sub>2</sub>), 2197(C=N), 1681(C=O amide), 1288(C=O), 1486 (C=C) Cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ <sub>H</sub>: 3.01 (3H, s, CH<sub>3</sub>), 3.46 (3H, s, CH<sub>3</sub>), 6.77 (1H, m, ArH), 6.97 (1H, t, *J*=6.0 Hz ArH), 7.07 (1H, s, ArH), 7.62 (2H, s, NH<sub>2</sub>), 10.52 (1H, s, NH), 12.50 (1H, s, NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ <sub>C</sub>: 28.2, 30.1, 47.8, 56.9, 85.4, 87.1, 112.3, 117.2, 132.6, 136.9, 137.5, 142.3, 150.1, 153.1, 159.1, 161.0, 178.3 ppm; Anal. Calcd. for C<sub>17</sub>H<sub>12</sub>FN<sub>5</sub>O<sub>4</sub>: C, 32.49; H, 3.24; N, 18.95 %. Found: C, 32.46; H, 3.28; N, 18.91 %.

**7'-amino-1,1',2,2',3',4'-hexahydro-1',3'-dimethyl-2,2',4'-trioxospiro[indole-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6g)**

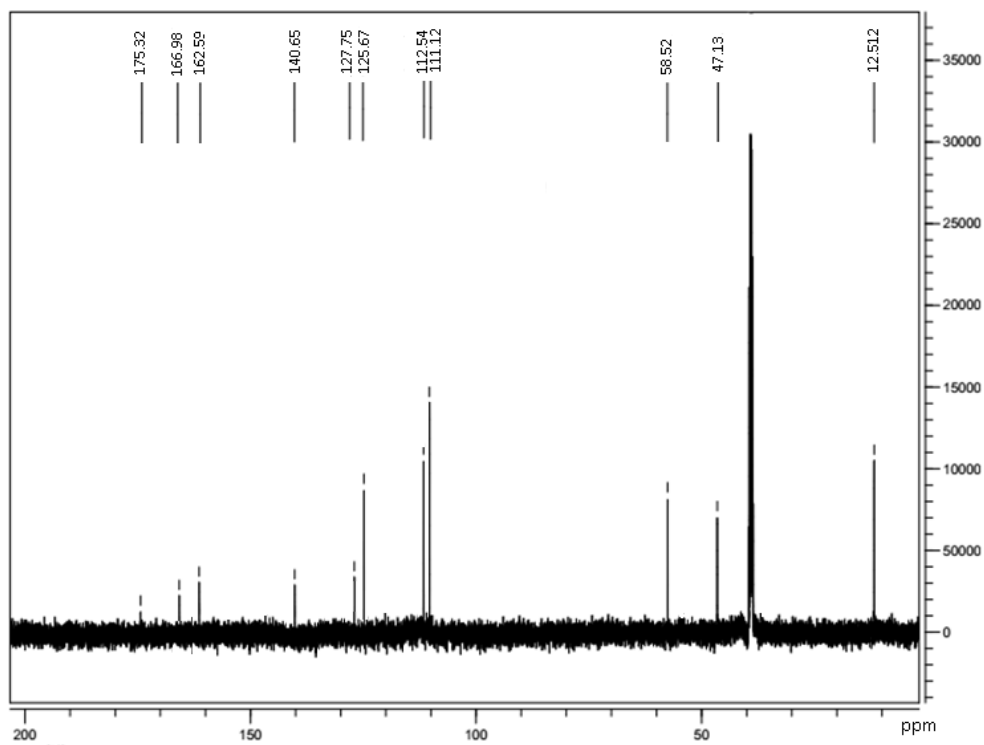
M.p. 299-301°C. FTIR (KBr)  $\nu$  max: 3428 (NH<sub>2</sub>), 3317 (NH), 2924 (CH<sub>2</sub>), 2000 (C=N), 1693 (C=O amide), 1652 (C=O) Cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ <sub>H</sub>: 3.01 (3H, s, CH<sub>3</sub>), 3.71 (3H, s, CH<sub>3</sub>), 6.95 (1H, d, *J*=6.0 Hz ArH), 7.28 (2H, t, *J*=7.0 Hz, ArH), 7.43 (1H, t, *J*=7.0 Hz, ArH), 7.13 (2H, s, NH<sub>2</sub>) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ <sub>C</sub>: 27.4, 29.6, 48.0, 57.5, 87.3, 109.6, 117.0, 121.8, 123.9, 128.4, 133.5, 142.2, 150.0, 152.1, 158.3, 159.2, 177.5 ppm; Anal. Calcd. for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>O<sub>4</sub>: C, 34.16; H, 3.70; N, 19.94 %. Found: C, 34.14; H, 3.73; N, 19.97 %.



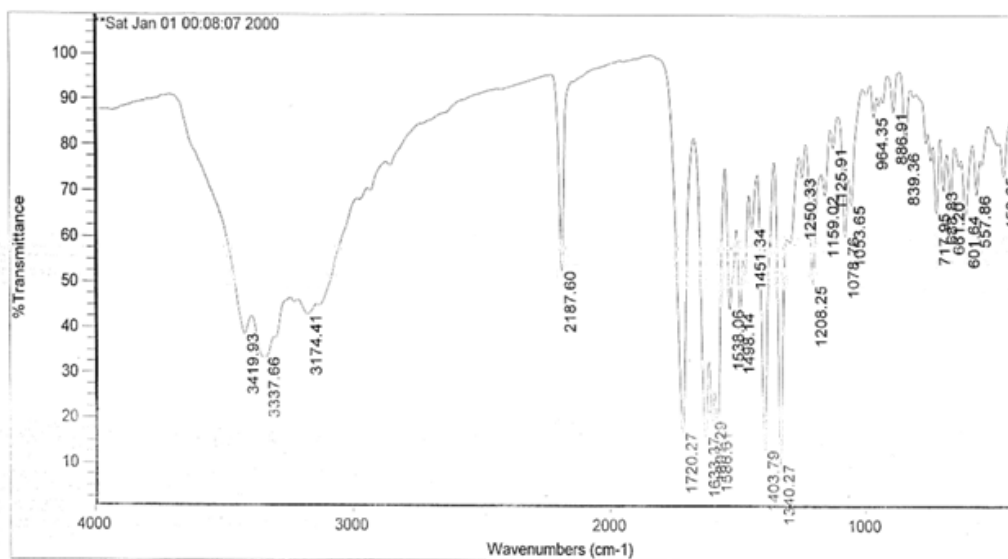
FTIR of 5a



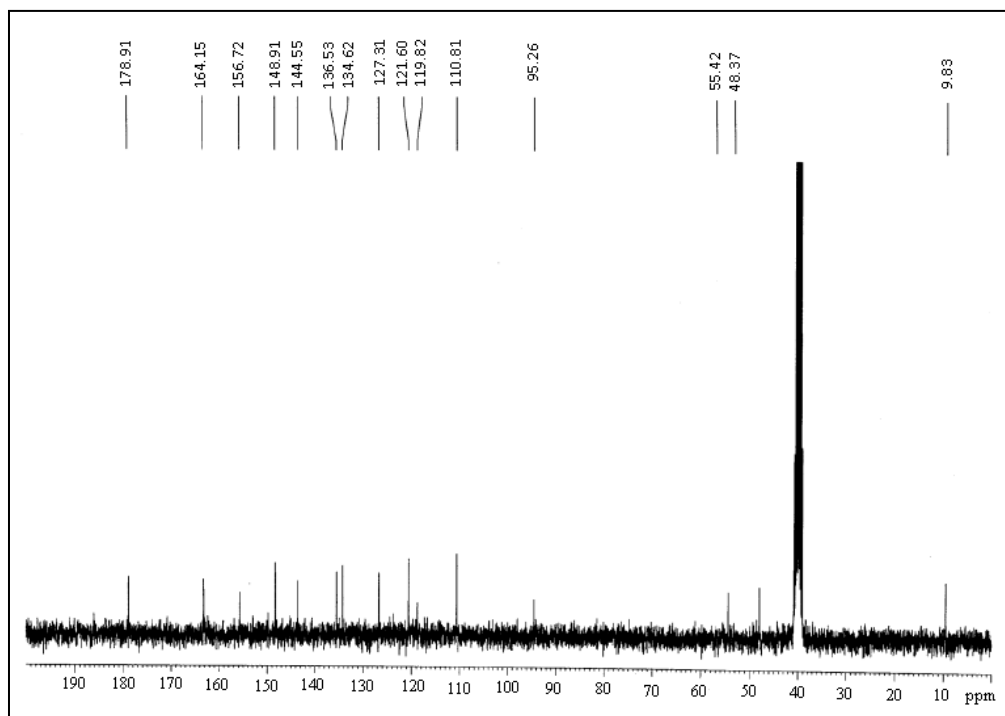
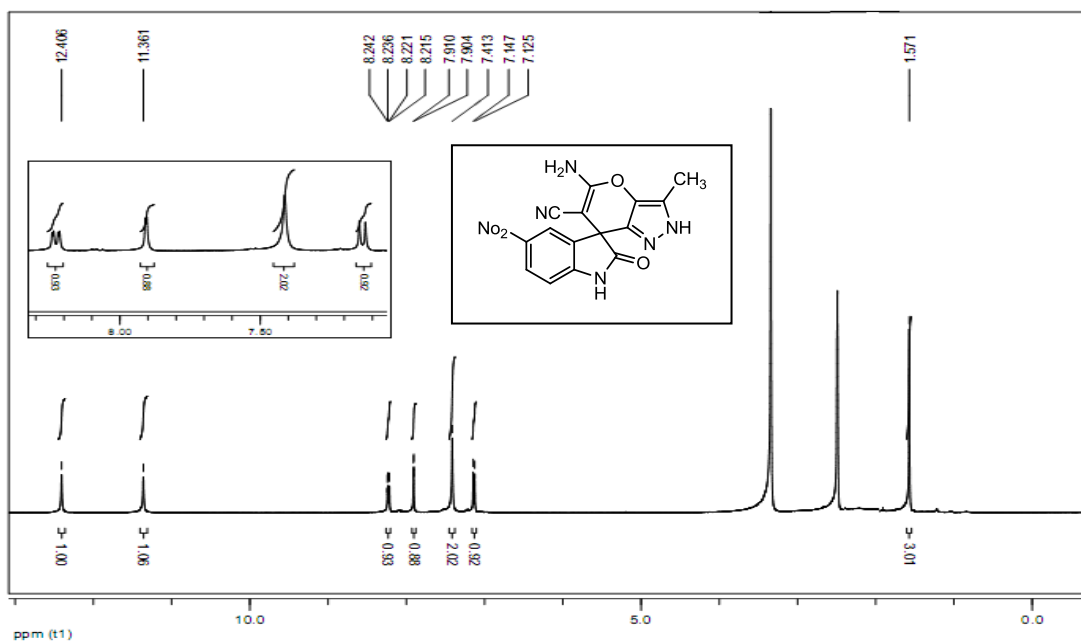
<sup>1</sup>H NMR of 5a

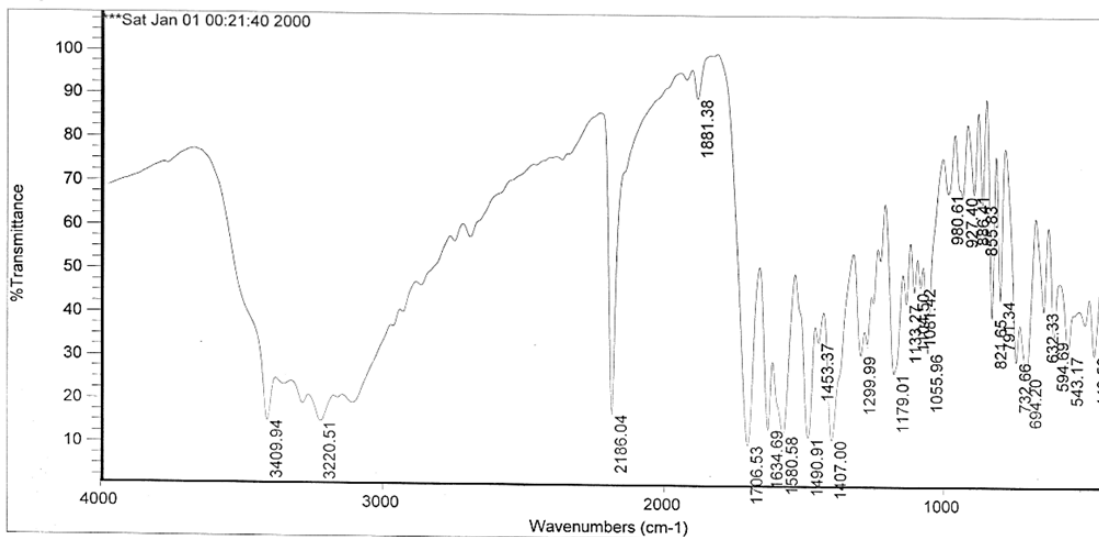


<sup>13</sup>C NMR of 5a

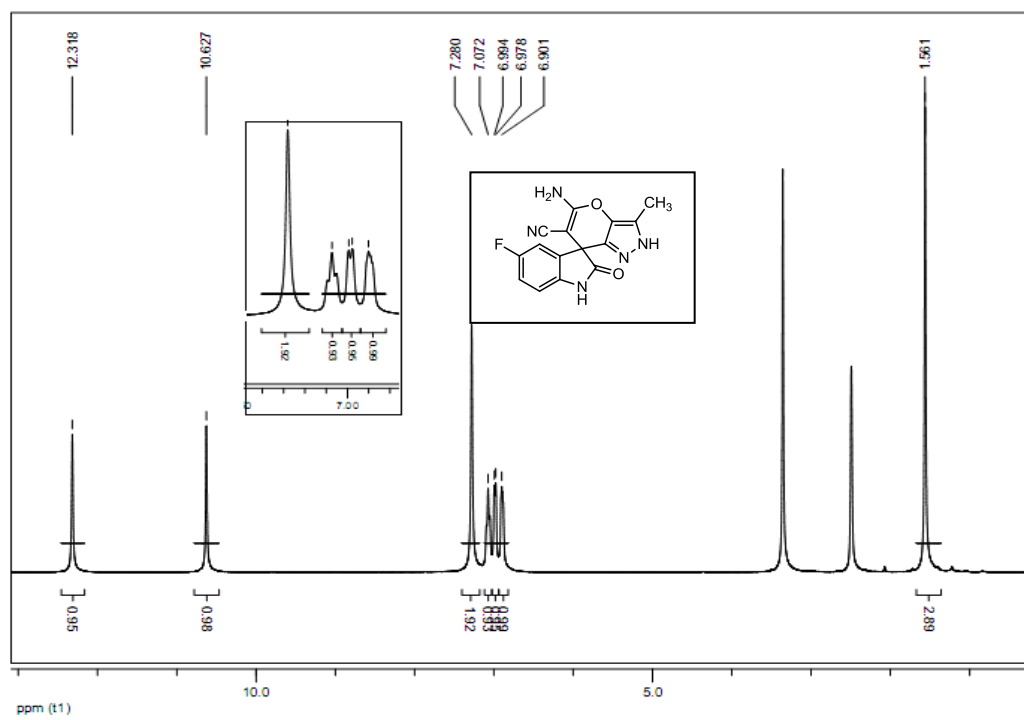


FTIR of 5b

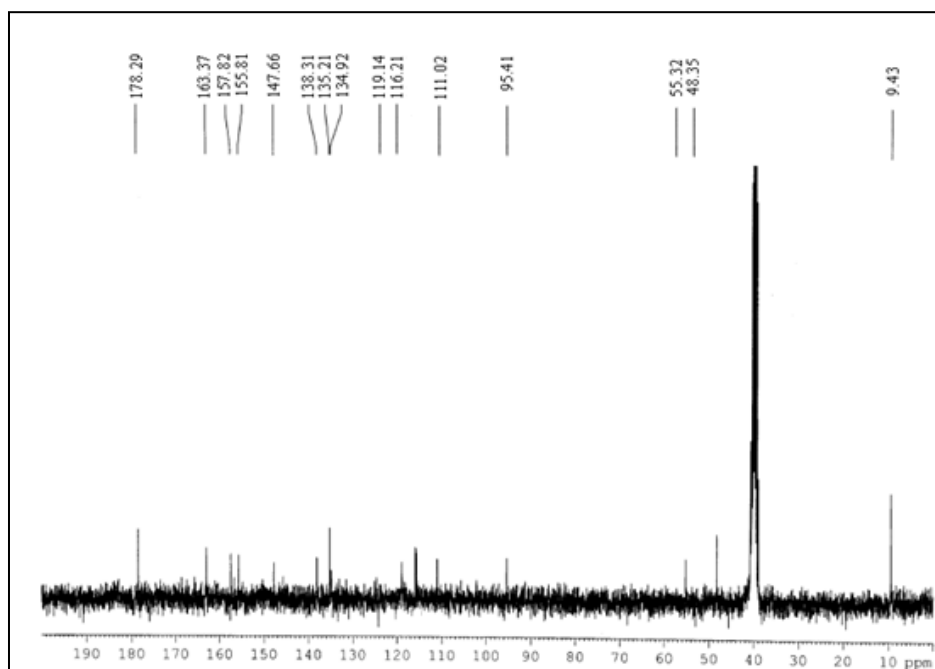




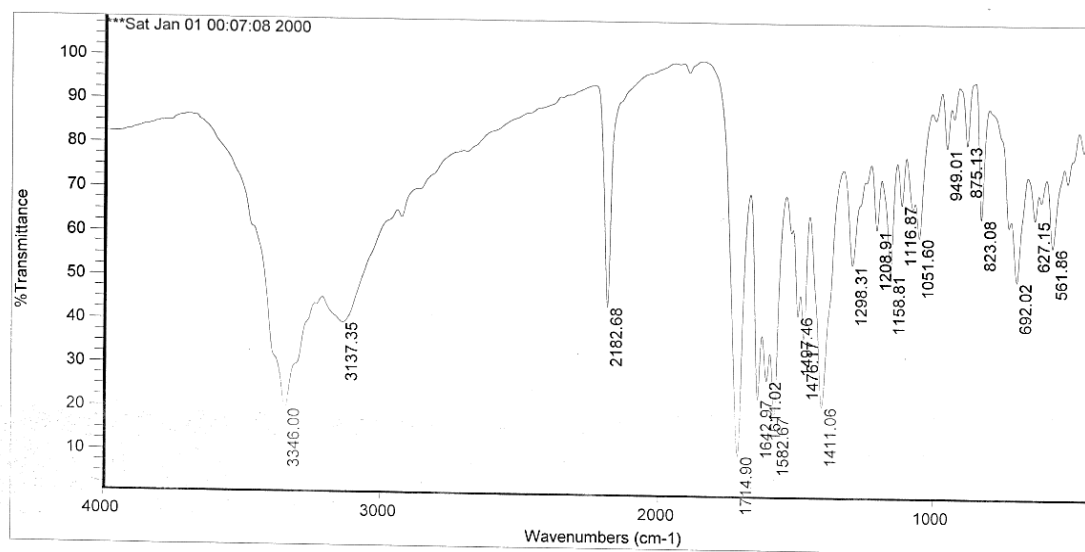
FTIR of 5c



<sup>1</sup>H NMR of 5c

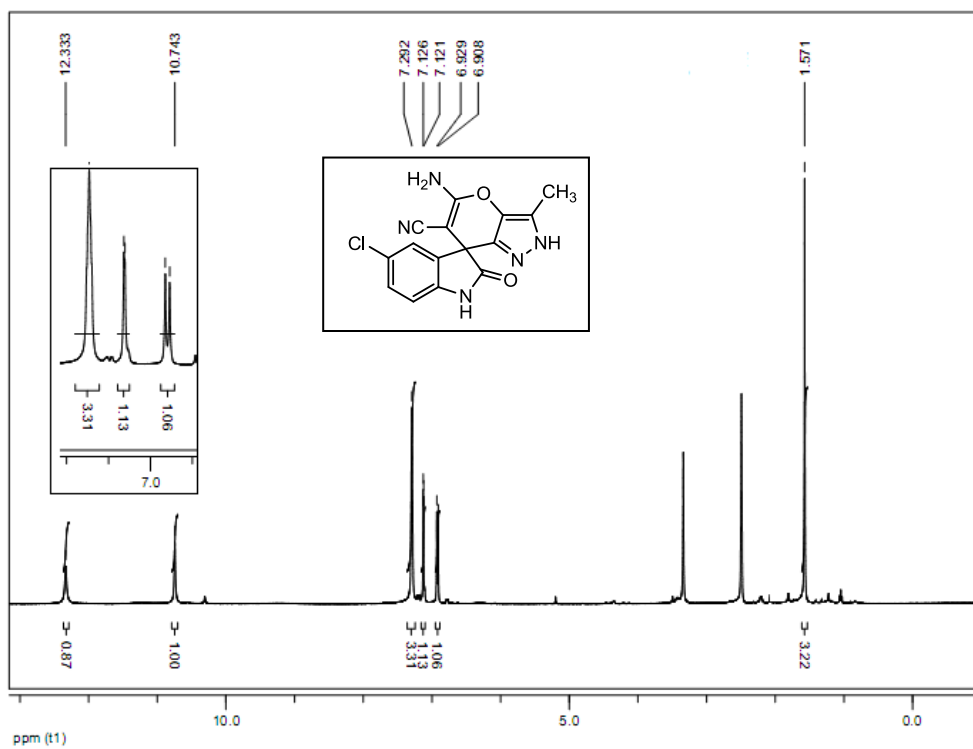


$^{13}\text{C}$  NMR of 5c

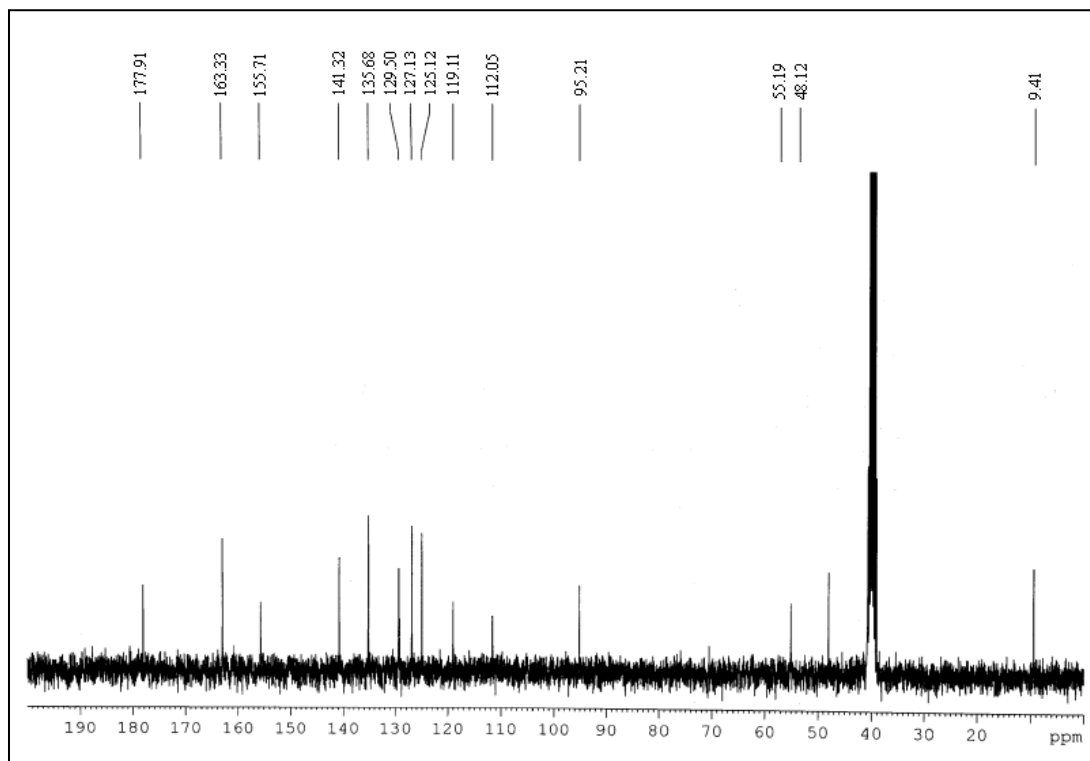


FTIR of 5d

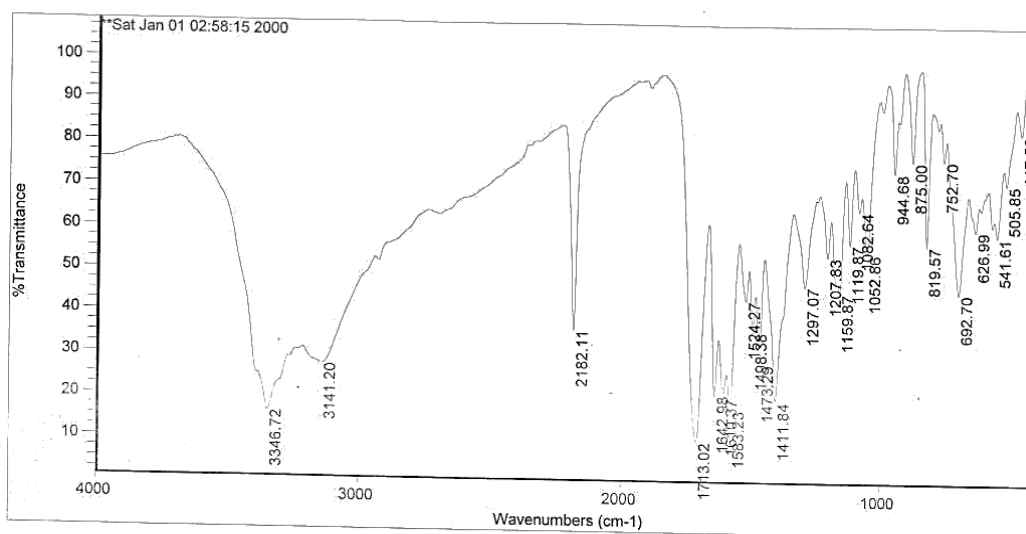




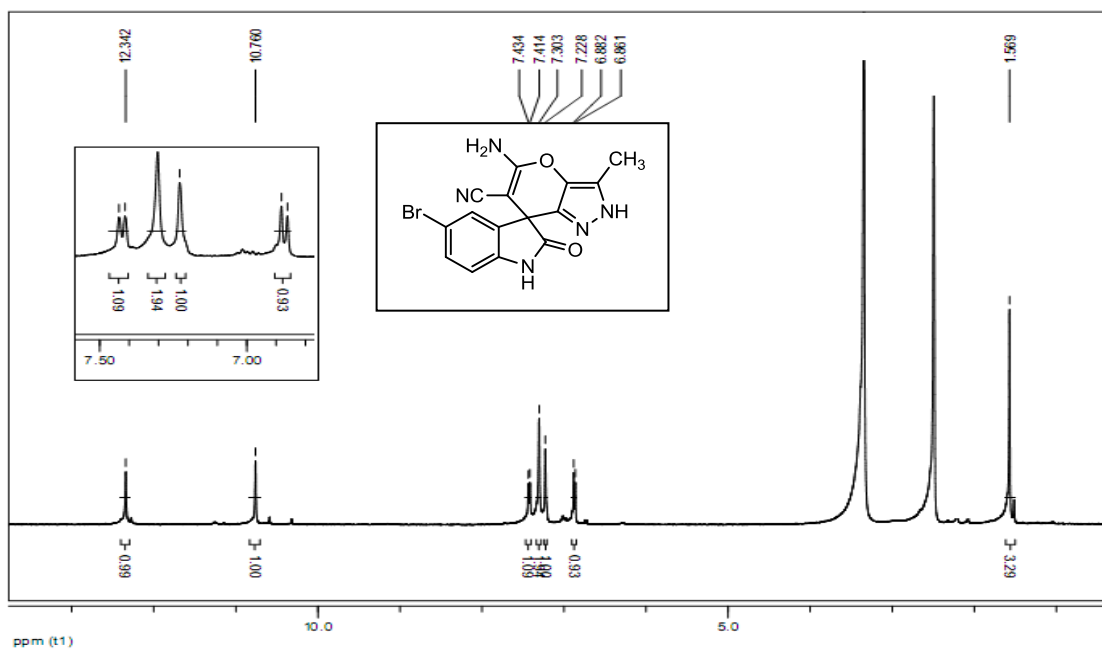
<sup>1</sup>H NMR of 5d



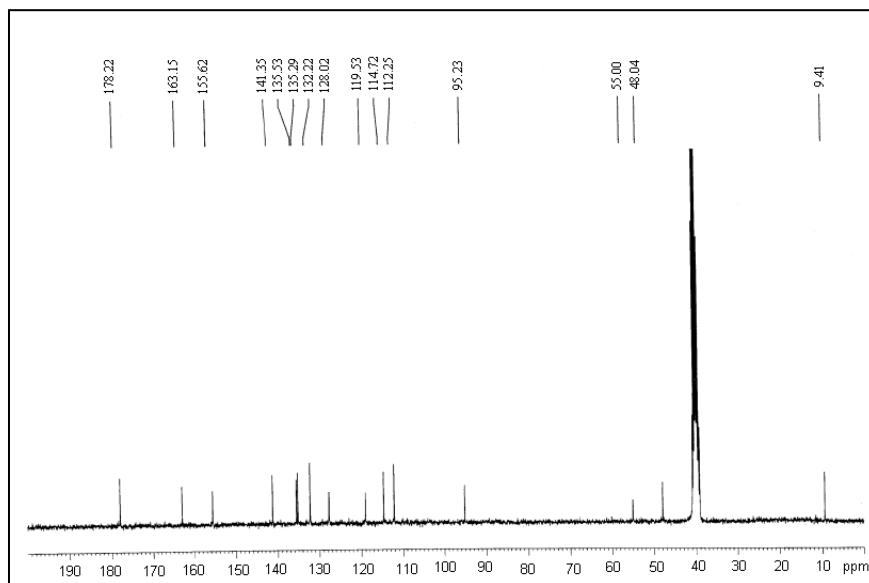
<sup>13</sup>C NMR of 5d



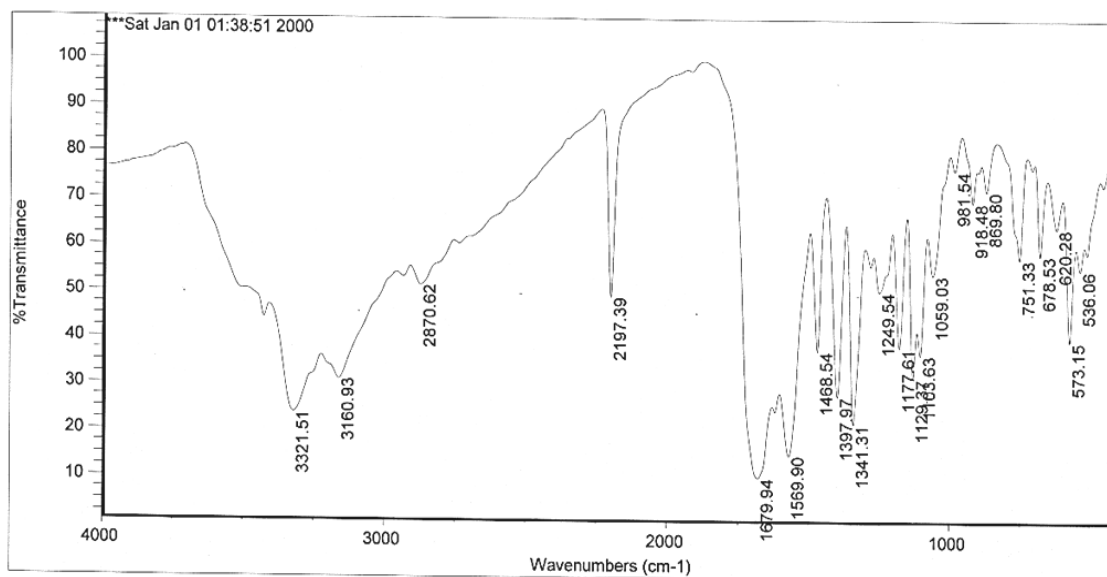
FTIR of 5e



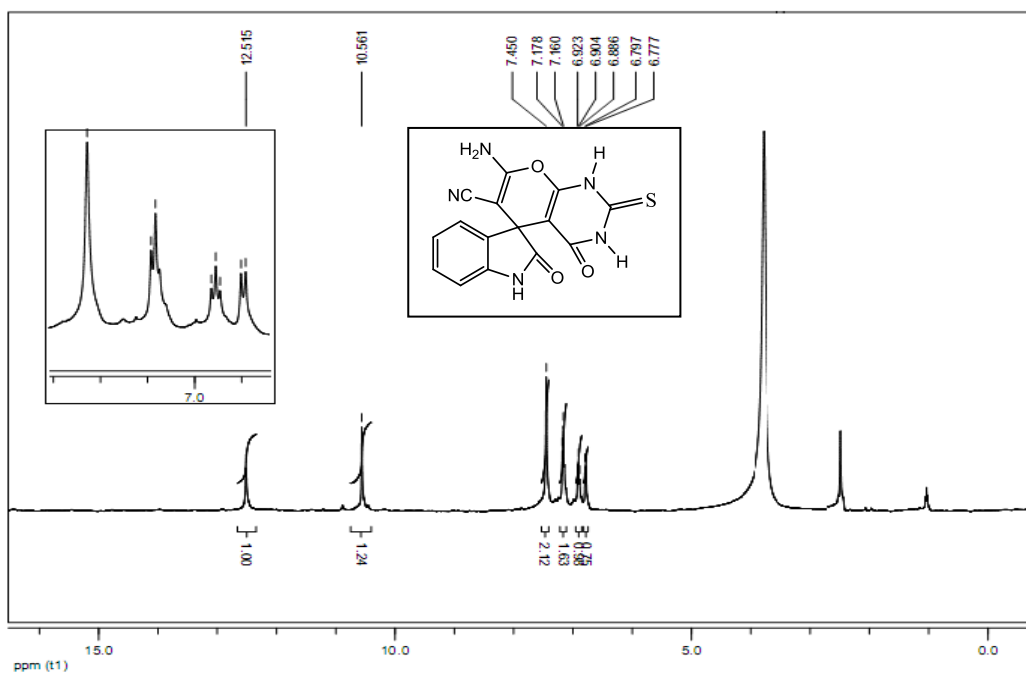
<sup>1</sup>H NMR of 5e



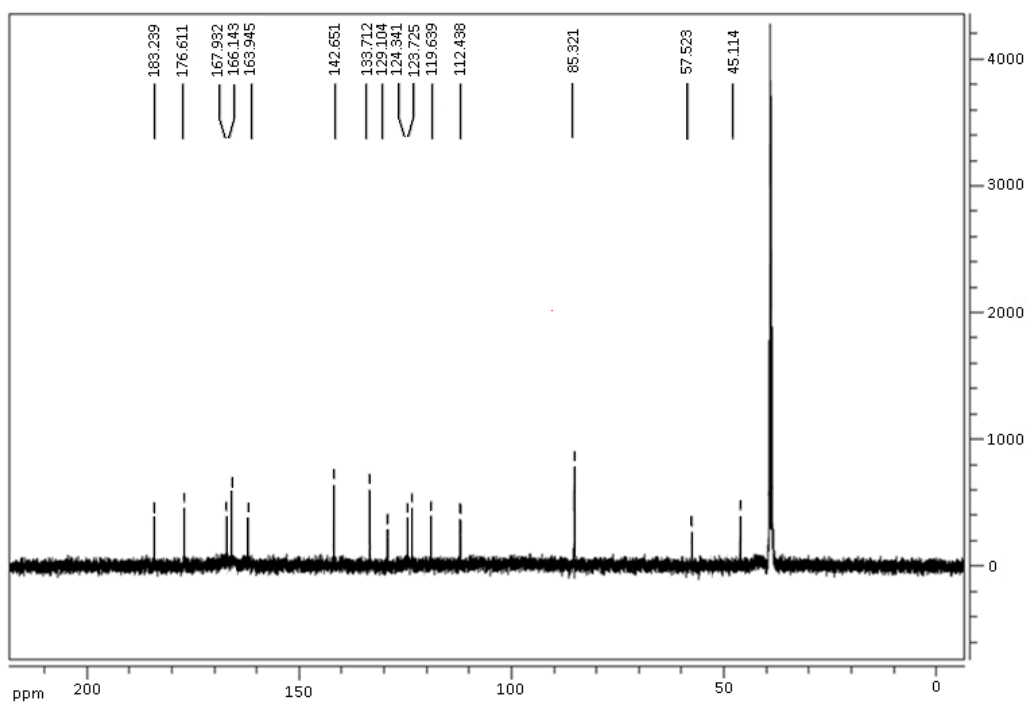
<sup>13</sup>C NMR of 5e



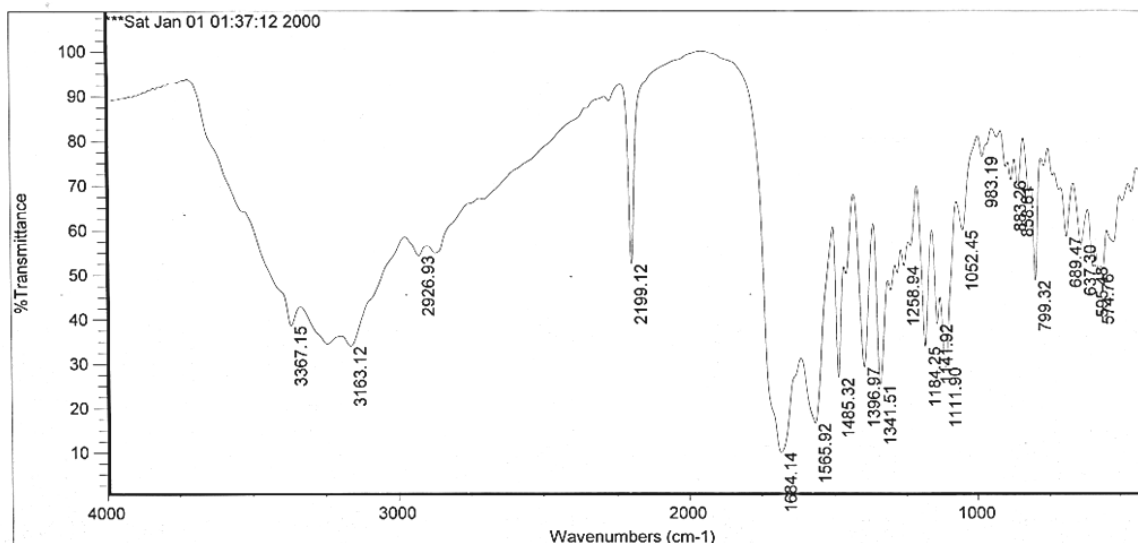
FTIR 6a



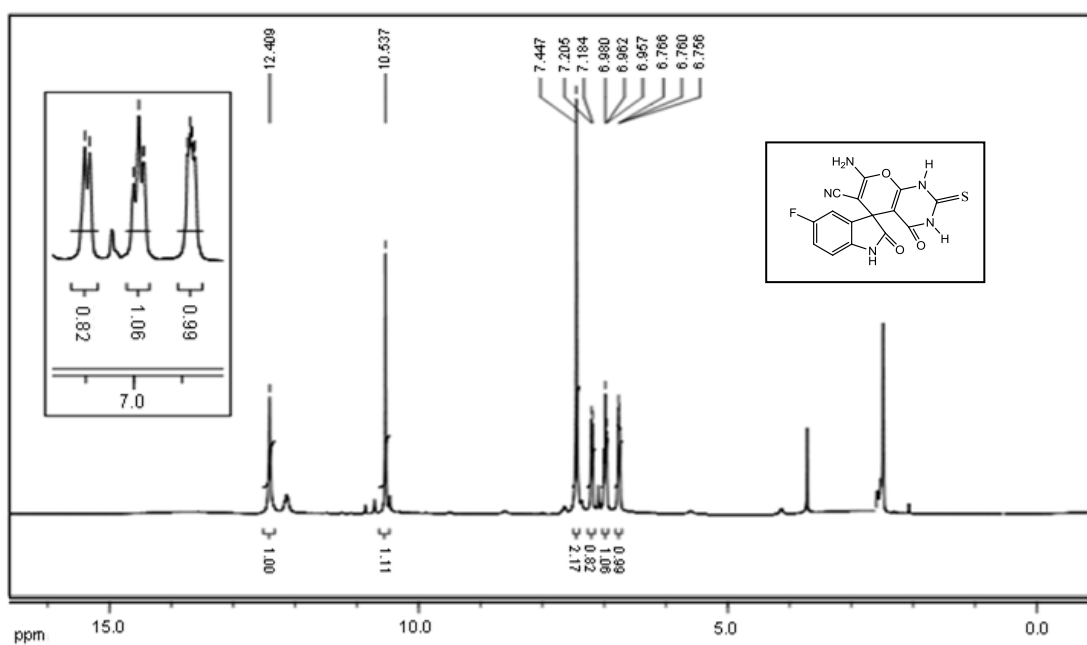
$^1\text{H}$ NMR of 6a



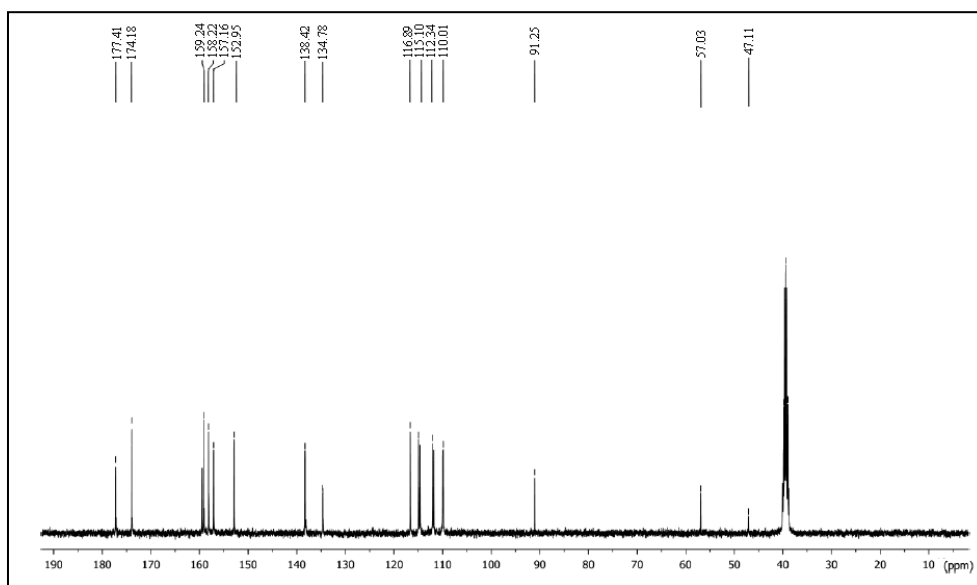
$^{13}\text{C}$  NMR of 6a



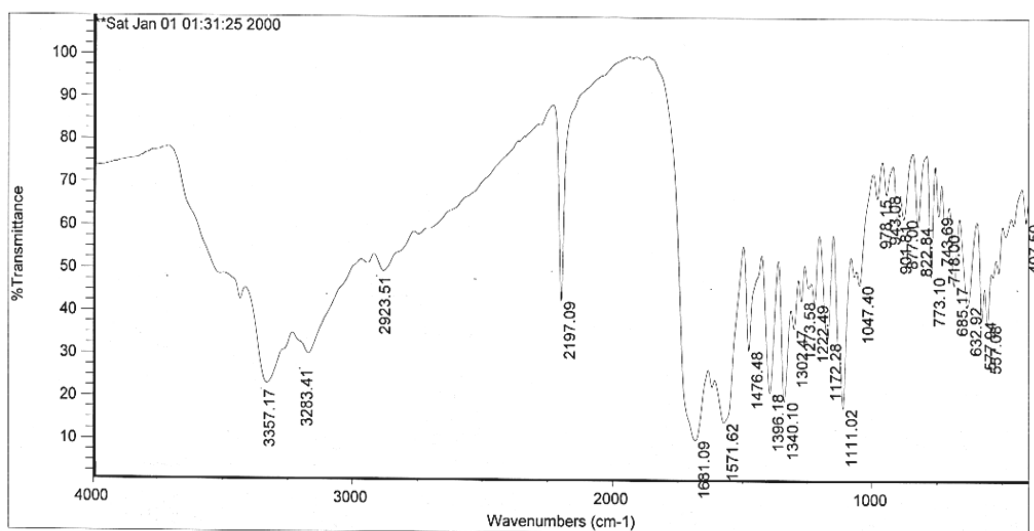
FTIR of 6b



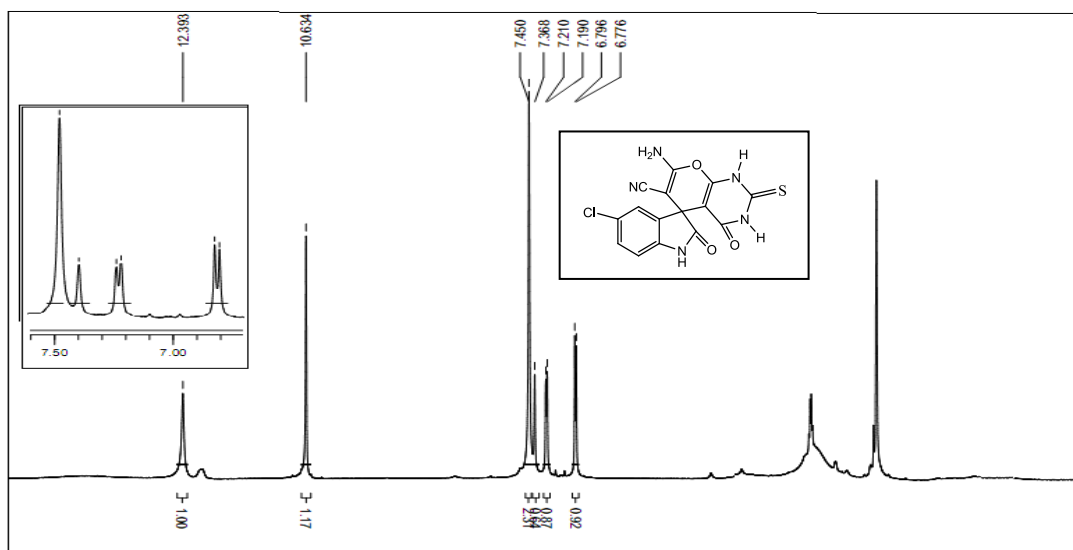
<sup>1</sup>H NMR of 6b



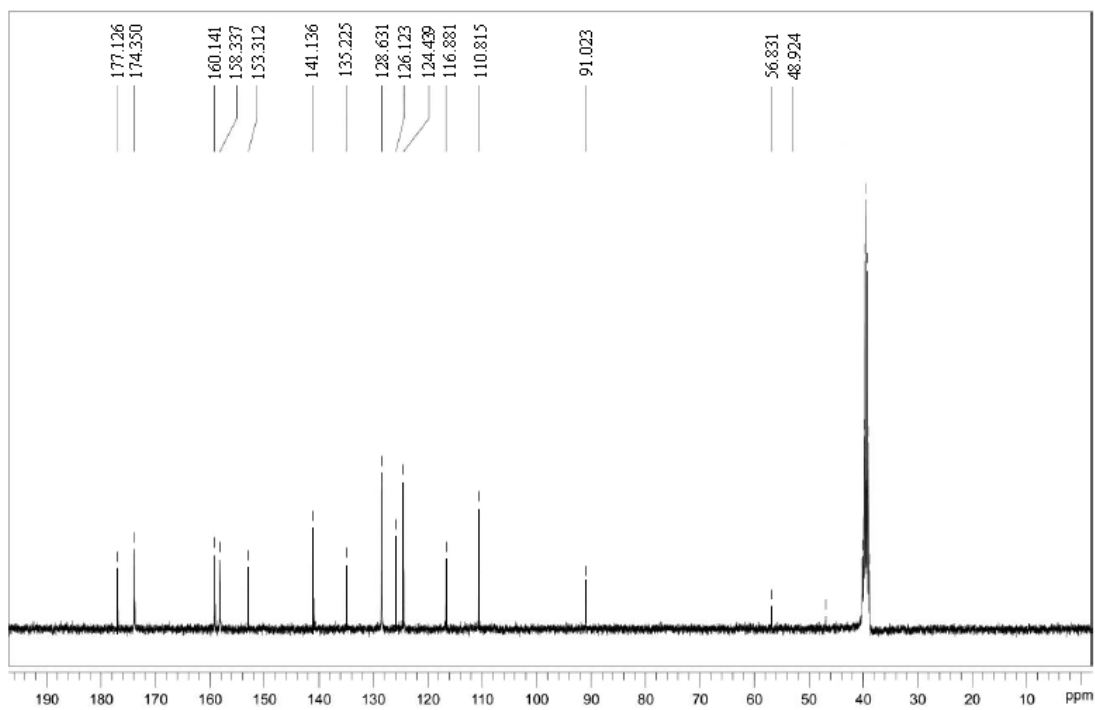
$^{13}\text{C}$  NMR of 6b



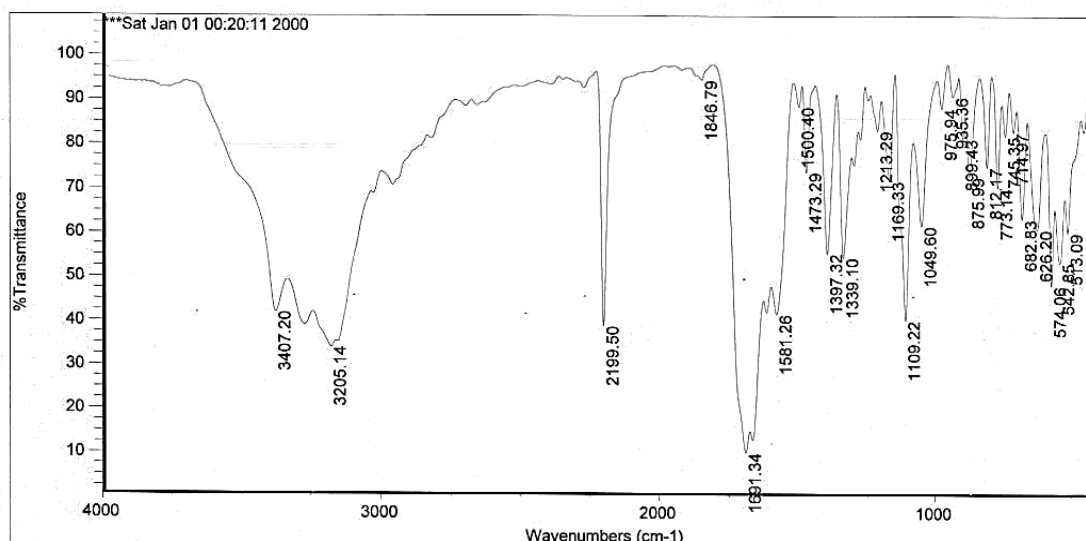
FTIR of 6c



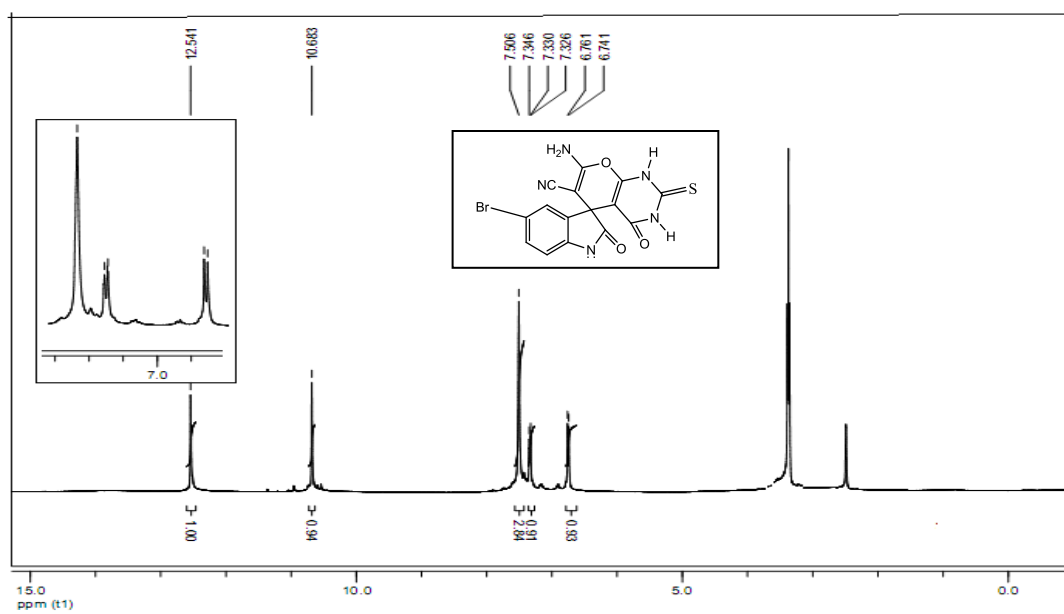
$^1\text{H}$ NMR of 6c



$^{13}\text{C}$  NMR of 6c

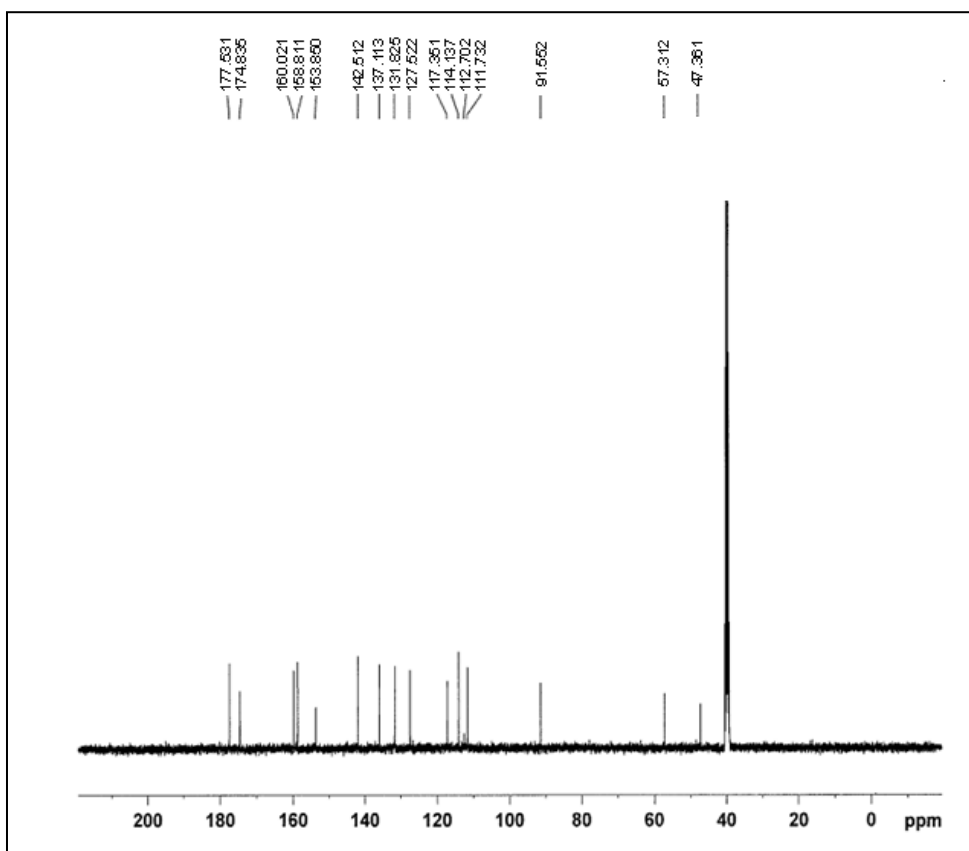


FTIR of 6d

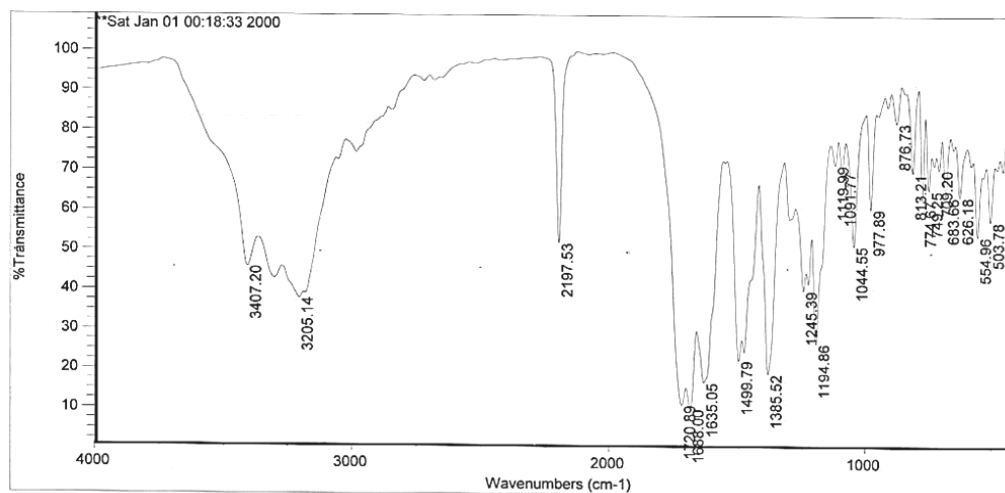


<sup>1</sup>H NMR of 6d

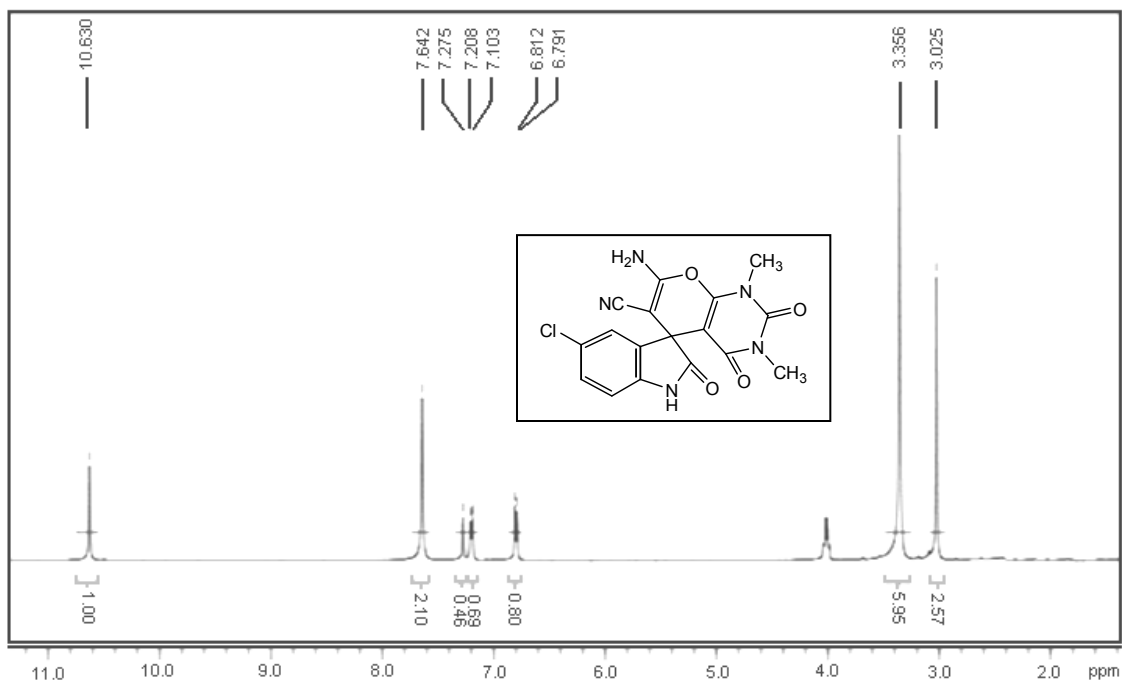




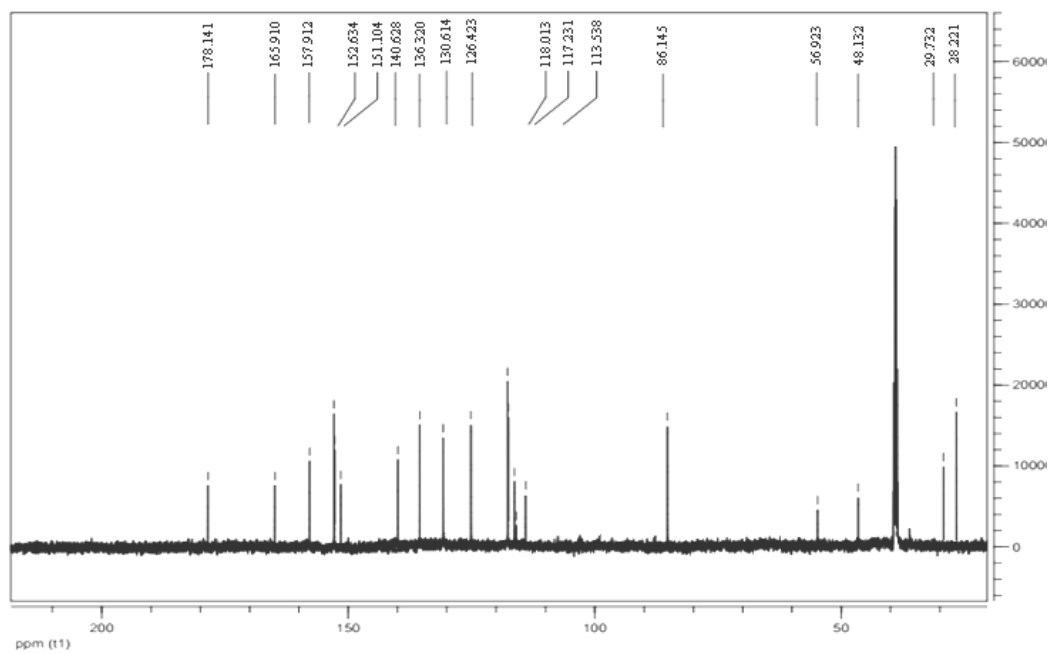
$^{13}\text{C}$  NMR of 6d



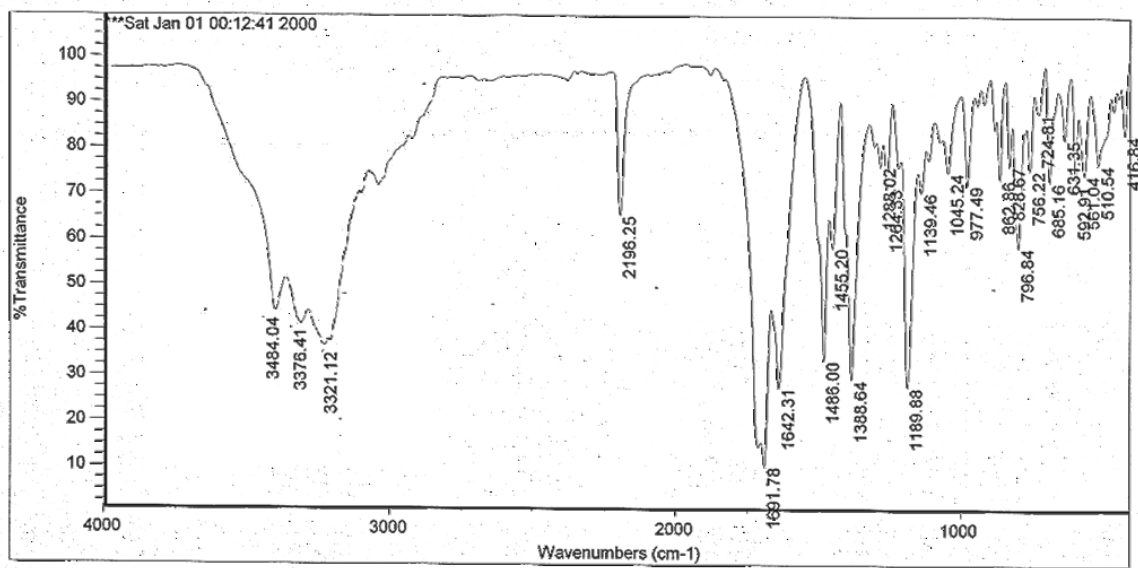
FTIR of 6e



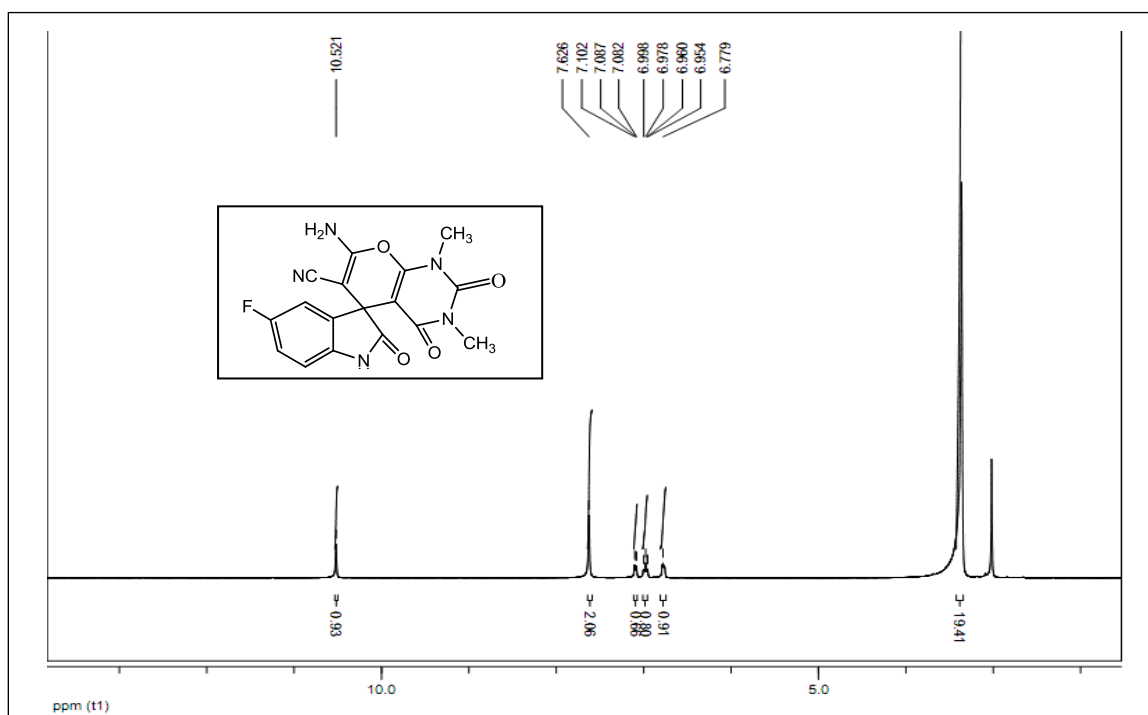
$^1\text{H NMR}$  of 6e



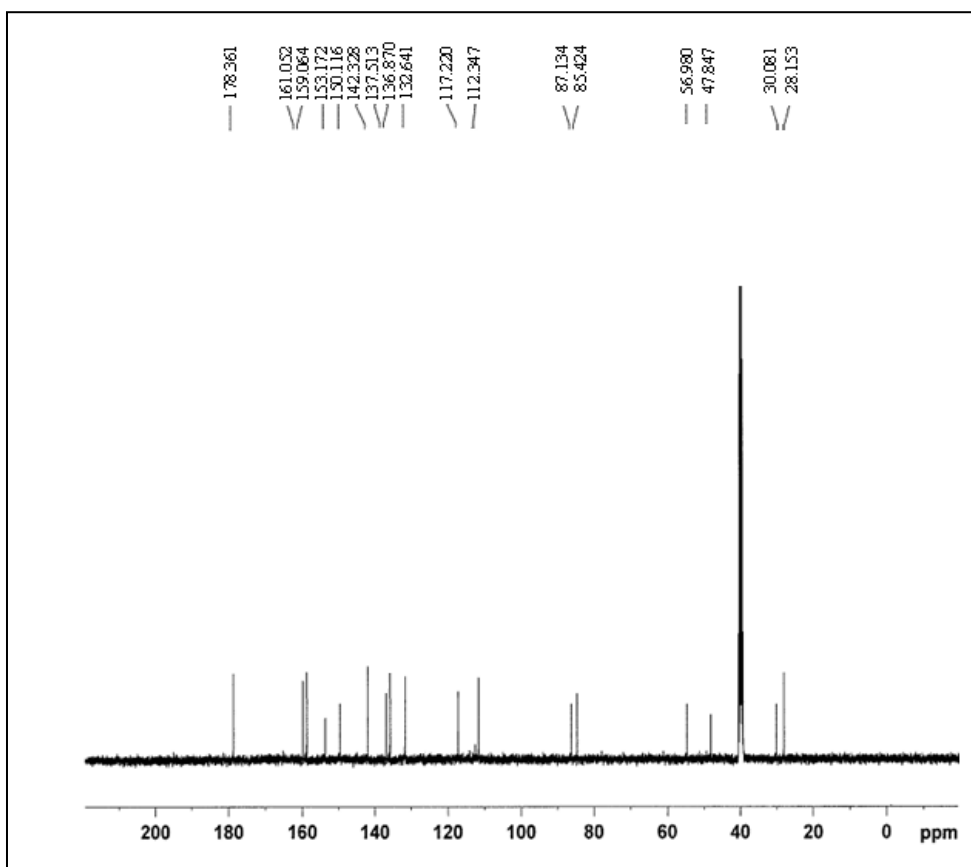
$^{13}\text{C NMR}$  of 6e



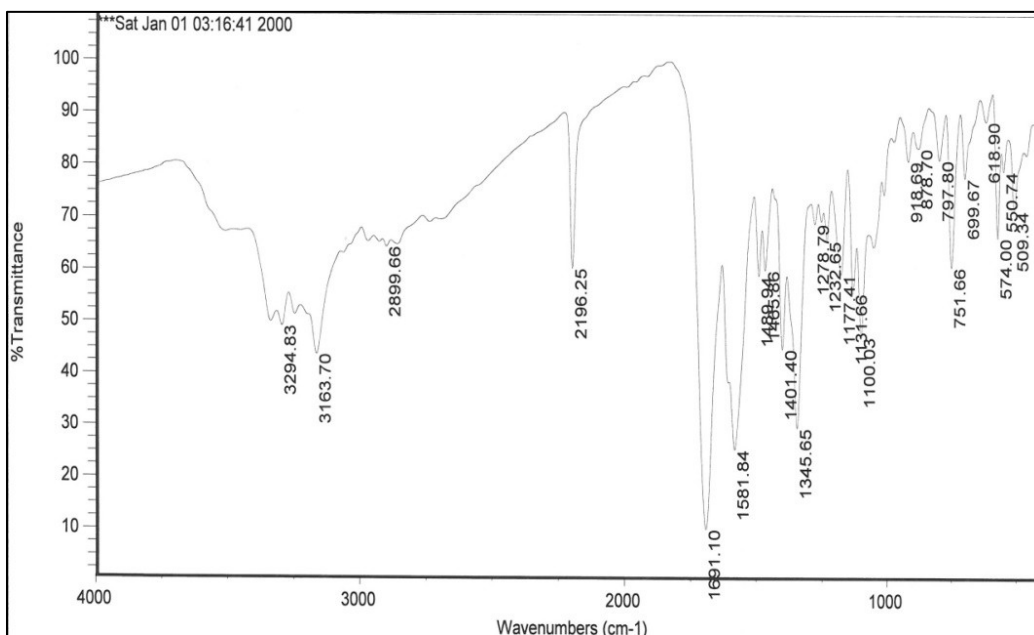
FTIR of 6f



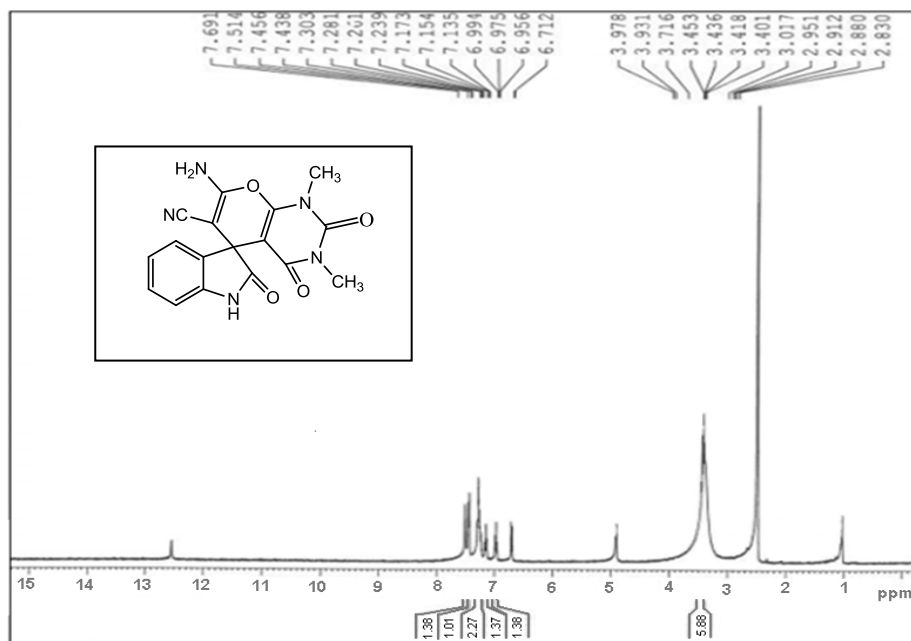
<sup>1</sup>H NMR of 6f



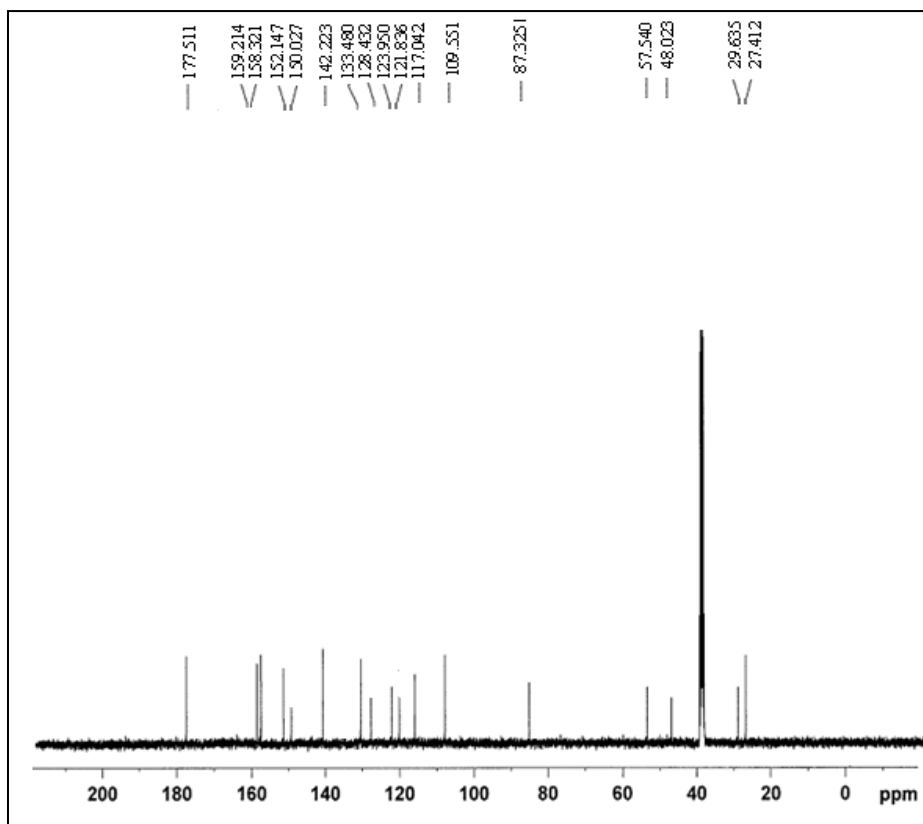
<sup>13</sup>C NMR of 6f



FTIR of 6g



$^1\text{H NMR}$  of 6g



$^{13}\text{C NMR}$  of 6g