

## Supporting information

### **Fabrication and characterization of mesoporous yolk-shell nanocomposites as an effective reusable heterogeneous base catalyst for the synthesis of ortho-aminocarbonitrile tetrahydronaphthalenes**

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#### **General procedure for synthesis of orthoaminocarbonitrile tetrahydronaphthalenes**

In a round-bottomed flask equipped with a stirrer, cyclohexanon (1 mmol), aromatic aldehydes (1 mmol), malononitrile (2 mmol), and catalyst (5 mg, CaMg@MYS) were stirred in 5 mL ethanol under 70 °C. The progress of the reaction was monitored by Thin-layer chromatography (TLC). Following the completion of the reaction, the precipitate was separated from the filtrate with filter paper and washed with ethanol. The precipitate was then dissolved in ethyl acetate to separate the catalyst. For reuse, the catalyst was washed with acetone and dried at 80 °C. A pure product was obtained by evaporating the solvent under reduced pressure and drying it for 12 h at 60 °C.

### Spectral data for orthoaminocarbonitrile tetrahydro-naphthalene derivatives

2-Amino-4-phenyl-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*)-tricarbonitrile (**4a**); White solid; m.p.: 255-256 °C, (m.p.: 255-257 °C) Lit. <sup>32</sup>, IR (KBr, v, cm<sup>-1</sup>): 3417, 3338, 2931, 2865, 2208, 1646, 1599, 1496, 1391, 1275, 1037, 713, 579; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) (δ, ppm): 7.48-7.62 (m, 2H), 7.43 (s, 3H), 7.38 (s, 2H), 5.73 (t, 1H), 3.54 (d, *J*= 12.0 Hz, 1H), 2.72-2.88 (m, 1H), 2.14-2.25 (m, 1H), 1.98-2.12 (m, 1H), 1.62-1.72 (m, 1H), 1.38-1.52 (m, 2H), 0.81-0.91 (m, 1H).

2-Amino-4-(2-chlorophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*)-tricarbonitrile (**4b**); White solid; m.p.: 282-284 °C, (m.p.: 271-272 °C) Lit. <sup>33</sup>, IR (KBr, v, cm<sup>-1</sup>): 3445, 3355, 2945, 2853, 2216, 1624, 1441, 1390, 1272, 1041, 749, 510; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) (δ, ppm): 7.79 (dd, *J*= 8.0 Hz, 1H), 7.62 (d, *J*=8.0 Hz, 1H), 7.48-7.58 (m, 2H), 7.45 (s, 2H), 5.77 (s, 1H), 3.88 (d, *J*= 12.0 Hz, 1H), 2.80-2.92 (m, 1H), 2.02-2.24 (m, 2H), 1.62-1.70 (m, 1H), 1.33-1.50 (m, 2H), 0.75-0.89 (m, 1H).

2-Amino-4-(2-nitrophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*)-tricarbonitrile (**4c**); Cream solid; m.p.: 244-246 °C, (m.p.: 245-247 °C) Lit. <sup>39</sup>, IR (KBr, v, cm<sup>-1</sup>): 3444, 3356, 2860, 2215, 1626, 1525, 1443, 1354, 1269, 1045, 726, 507; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) (δ, ppm): 8.09 (d, *J*=8.0 Hz, 1H), 8.02 (d, *J*=8.0 Hz 1H), 7.92 (t, 1H), 7.75 (t, 1H), 7.45 (s, 2H), 5.79 (s, 1H), 4.07 (d, *J*= 12Hz, 1H), 2.96-3.08 (m, 1H), 2.04-2.26 (m, 2H), 1.69-1.73 (m, 1H), 1.45-1.52 (m, 2H), 0.98-1.07 (m, 1H).

2-Amino-4-(4-fluorophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*)-tricarbonitrile (**4d**); White solid; m.p.: 264-266 °C, (m.p.: 265-267 °C) Lit. <sup>33</sup>, IR (KBr, v, cm<sup>-1</sup>): 3448, 3356, 2957, 2847, 2212, 1621, 1519, 1448, 1386, 1232, 1119, 931, 823, 507; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) (δ, ppm): 7.84 (d, *J*=12.0 Hz 1H), 7.77-7.82 (m, 1H), 7.59-7.75 (m, 2H), 7.46 (s, 2H), 5.74 (s,

1H), 3.85-3.97 (m, 1H), 2.87-3.03 (m, 1H), 1.59-1.80 (m, 2H), 1.13-1.31 (m, 1H), 0.81 (d,  $J = 12.5$  Hz, 2H), 0.56-0.65 (m, 1H).

2-Amino-4-(4-(dimethylamino)phenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*) tricarbonitrile (**4e**); Yellow solid; m.p.: 262-264 °C, (m.p.: 263-265 °C) Lit. <sup>34</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3447, 3354, 2915, 2213, 1619, 1525, 1444, 1356, 1273, 1170, 948, 818, 520; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.36 (d,  $J = 8.0$  Hz, 1H), 7.33 (s, 2H), 7.19 (d,  $J = 8.0$  Hz, 1H), 6.80 (d,  $J = 8.0$  Hz, 1H), 6.69 (d,  $J = 8.0$  Hz, 1H), 5.70 (s, 1H), 3.30 (s, 1H), 2.93 (s, 6H, N(Me)<sub>2</sub>), 2.64-2.78 (m, 1H), 2.02-2.23 (m, 2H), 1.63-1.72 (m, 1H), 1.49-1.57 (m, 1H), 1.38-1.60 (m, 2H), 0.76-0.91 (m, 1H).

2-Amino-4-(4-methylphenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*)-tricarbonitrile (**4f**); White solid; m.p.: 235-237 °C, (m.p.: 236-238 °C) Lit. <sup>35</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3420, 3334, 3244, 2943, 2866, 2212, 1646, 1600, 1514, 1450, 1391, 1272, 1161, 1037, 828, 587; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.47 (d,  $J = 8.0$  Hz, 1H), 7.36 (s, 2H), 7.30 (d,  $J = 8.0$  Hz, 2H), 7.18-7.24 (m, 1H), 5.72 (s, 1H), 3.47 (d,  $J = 12.0$  Hz, 1H), 2.78 (m, 1H), 2.34 (s, 3H, Me), 2.13-2.23 (m, 1H), 1.98-2.11 (m, 1H), 1.62-1.71 (m, 1H), 1.38-1.52 (m, 2H), 0.78-0.91 (m, 1H).

2-Amino-4-(3-bromophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*)-tricarbonitrile (**4g**); White solid; mp: 251-254 °C, (m.p.: 250-253 °C) Lit. <sup>33</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3417, 3339, 2931, 2864, 2211, 1648, 1602, 1474, 1396, 1278, 1160, 1080, 888, 797, 744, 686, 580; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.79 (s, 1H), 7.57-7.70 (m, 1H), 7.43-7.52 (m, 2H), 7.40 (s, 2H), 5.73 (s, 1H), 3.64 (d,  $J = 12.8$  Hz, 1H), 2.72-2.95 (m, 1H), 2.13-2.27 (m, 1H), 2.00-2.12 (m, 1H), 1.58-1.76 (m, 1H), 1.39-1.56 (m, 2H), 0.78-0.93 (m, 1H).

2-Amino-4-(4-chlorophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*)-tricarbonitrile (**4h**); White solid; m.p.: 247-249 °C (m.p.: 248-250 °C) Lit. <sup>35</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3420, 3343, 3244,

2939, 2867, 2212, 1644, 1602, 1492, 1394, 1274, 1059, 837, 753, 569, 515;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.43-7.65 (m, 4H), 7.39 (s, 2H), 5.72 (s, 1H), 3.65 (dd,  $J=12.0$  Hz, 1H), 2.73-2.87 (m, 1H), 1.99-2.26 (m, 2H), 1.59-1.77 (m, 1H), 1.37-1.53 (m, 2H), 0.78-0.92 (m, 1H).

2-Amino-4-(4-(hydroxy)phenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(*4H*) tricarbonitrile (**4i**); yellow solid; m.p.: 239-240 °C (m.p.: 240-241 °C) Lit. <sup>36</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3450, 3361, 2933, 2862, 2211, 1642, 1517, 1452, 1386, 1271, 1175, 1100, 837, 745, 544;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 9.66 (s, 1H, OH), 7.37 (d,  $J=8.0$  Hz, 1H), 7.34 (s, 2H), 7.20 (d,  $J=8.0$  Hz, 1H), 6.86 (d,  $J=8.0$  Hz, 1H), 6.76 (d,  $J=8.0$  Hz, 1H), 5.70 (s, 1H), 3.37 (d,  $J=12.0$  Hz, 1H), 2.66-2.78 (m, 1H), 2.00-2.24 (m, 2H), 1.60-1.76 (m, 1H), 1.38-1.55 (m, 2H), 0.73-0.91 (m, 1H).

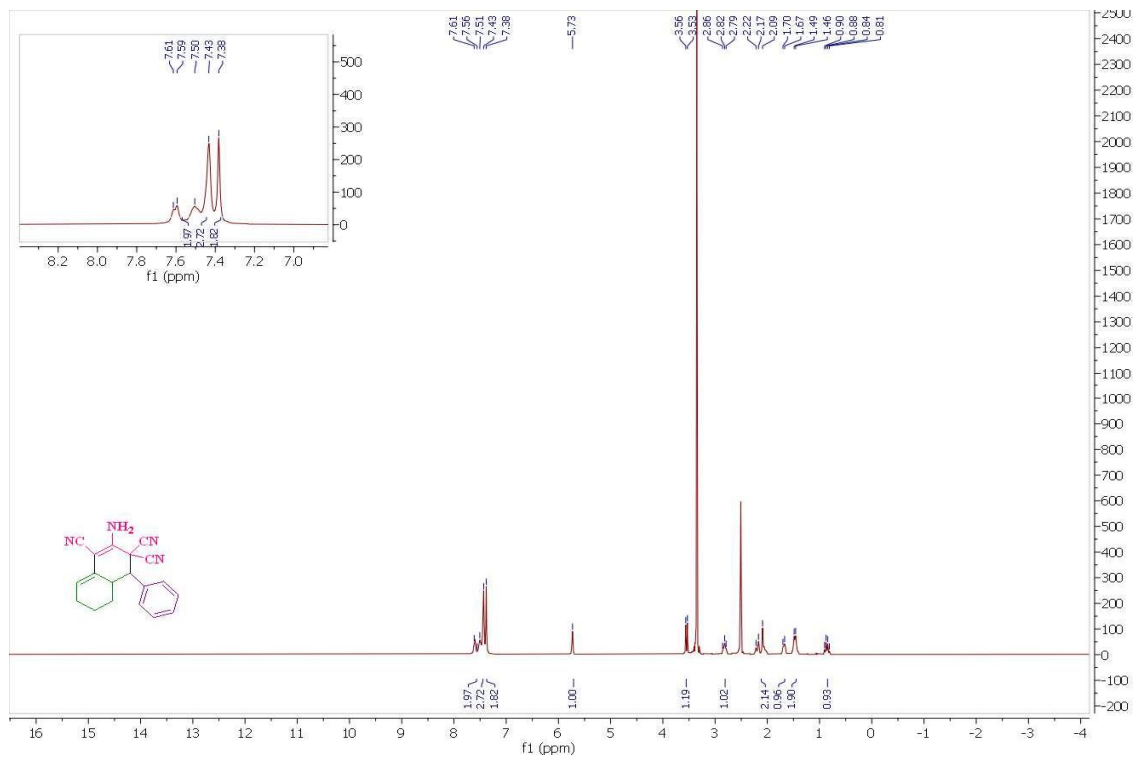
2-Amino-4a,5,6,7-tetrahydro-4-(3,4,5-trimethoxyphenyl)naphthalene-1,3,3(*4H*)-tricarbonitrile (**4j**); Yellow solid; m.p.: 233-235 °C (m.p.: 234-236 °C) Lit. <sup>33</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3438, 3355, 3246, 2938, 2838, 2203, 1640, 1593, 1509, 1462, 1334, 1246, 1127, 1007, 846, 757, 695;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.38 (s, 2H), 6.87 (s, 1H), 6.83 (s, 1H), 5.73 (s, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.48 (s, 2H), 2.82 (s, 1H), 2.15-2.27 (m, 2H), 1.64-1.78 (m, 1H), 1.45-1.61 (m, 2H), 0.83-0.97 (m, 1H).

2-Amino-4a,5,6,7-tetrahydro-4-(3,4-dimethoxyphenyl) naphthalene-1,3,3(*4H*)-tricarbonitrile (**4k**); White solid; mp.: 288-290 °C (m.p.: 289-291 °C) Lit. <sup>36</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3447, 3358, 3253, 3005, 2939, 2872, 2836, 2201, 1640, 1593, 1509, 1469, 1456, 1429, 1349, 1334, 1306, 1275, 1253, 1130, 1008, 967, 845, 804, 756, 698;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.35 (s, 2H), 7.06-7.14 (m, 2H), 6.97 (s, 1H), 5.72 (dd, 1H), 3.76 (d,  $J=15.0$  Hz, 6H, OCH<sub>3</sub>), 3.38-3.53 (t,  $J=12.0$  Hz, 1H), 2.64-2.91 (m, 1H), 1.98-2.26 (m, 2H), 1.53-1.78 (m, 1H), 1.40-1.61 (m, 2H), 0.80-0.96 (m, 1H).

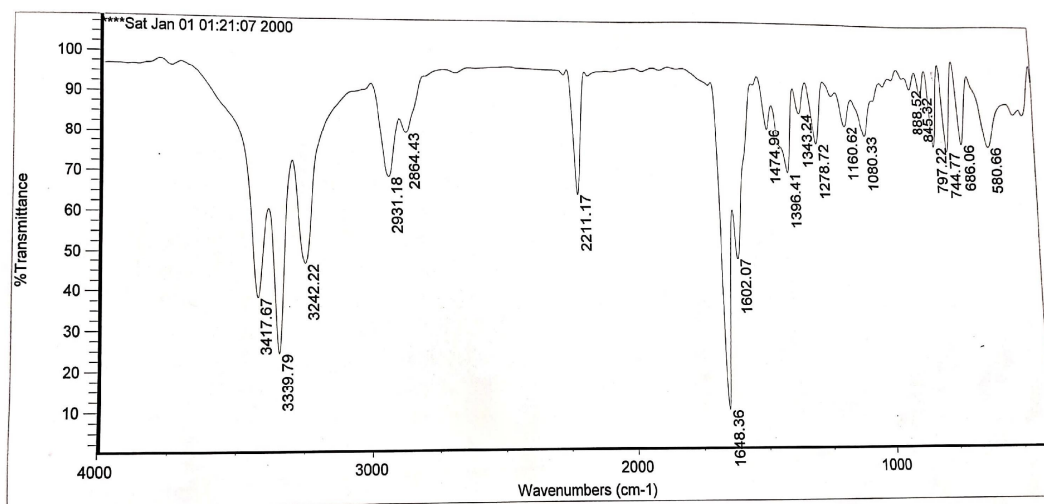
2-Amino-4-(2,4-dichlorophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4*H*)-tricarbonitrile (**4l**); Yellow solid; m.p.: 257-259 °C (m.p.: 256-258 °C) Lit. <sup>36</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3445, 3355, 2926, 2857, 2214, 1624, 1474, 1390, 1269, 1110, 1050, 952, 808, 754, 514; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.74-7.91 (m, 2H), 7.65 (d,  $J=8.0$  Hz, 1H), 7.45 (s, 2H), 5.76 (s, 1H), 3.87 (d,  $J=12.0$  Hz, 1H), 2.78-2.97 (m, 1H), 1.98-2.26 (m, 2H), 1.60-1.74 (m, 1H), 1.30-1.52 (m, 2H), 0.72-0.94 (m, 1H).

2-Amino-4-(4-bromophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4*H*)-tricarbonitrile (**4m**); Yellow solid; m.p.: 264-266 °C (m.p.: 244-246 °C) Lit. <sup>32</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3421, 3344, 2932, 2866, 2210, 1643, 1601, 1489, 1395, 1274, 1077, 1011, 832, 750, 509; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.63-7.76 (m, 1H), 7.51-7.62 (m, 1H), 7.35-7.50 (m, 3H), 5.74 (s, 1H), 3.63 (d,  $J=12.0$  Hz, 1H), 2.73-2.88 (m, 1H), 1.97-2.27 (m, 2H), 1.63-1.75 (m, 1H), 1.38-1.58 (m, 2H), 0.77-0.93 (m, 1H).

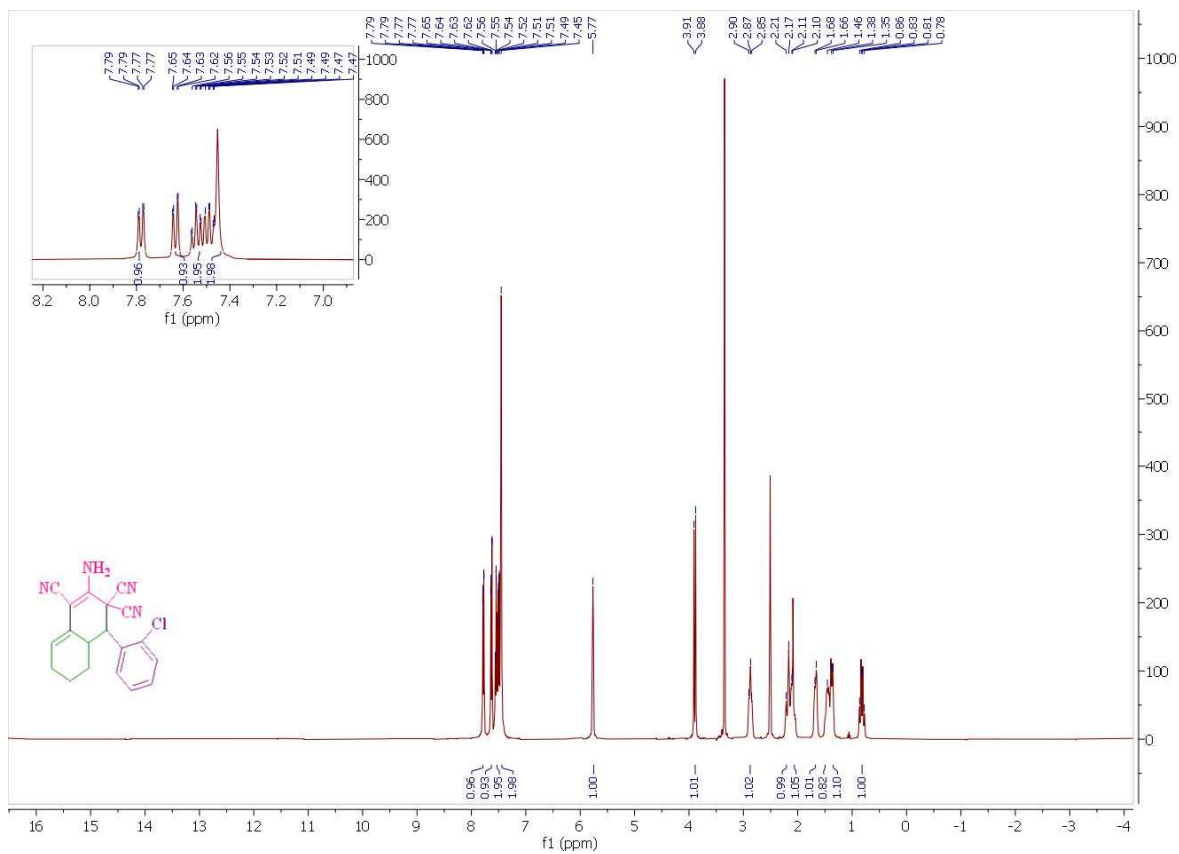
2-Amino-4-(4-isopropylphenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4*H*)-tricarbonitrile (**4n**); Yellow solid; m.p.: 197-199 °C, (m.p.: 196-198 °C) Lit. <sup>41</sup>, IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3446, 3355, 2960, 2213, 1629, 1512, 1398, 1270, 1158, 839, 732, 491; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) ( $\delta$ , ppm): 7.47-7.52 (m, 1H), 7.25-7.41 (m, 5H), 5.72 (s, 1H), 3.47 (d,  $J=12.0$  Hz, 1H), 2.73-2.83 (m, 1H), 2.0-2.24 (m, 2H), 1.63-1.70 (m, 1H), 1.41-1.50 (m, 2H), 1.23 (d,  $J=8.0$  Hz, 6H), 0.77-0.89 (m, 1H).



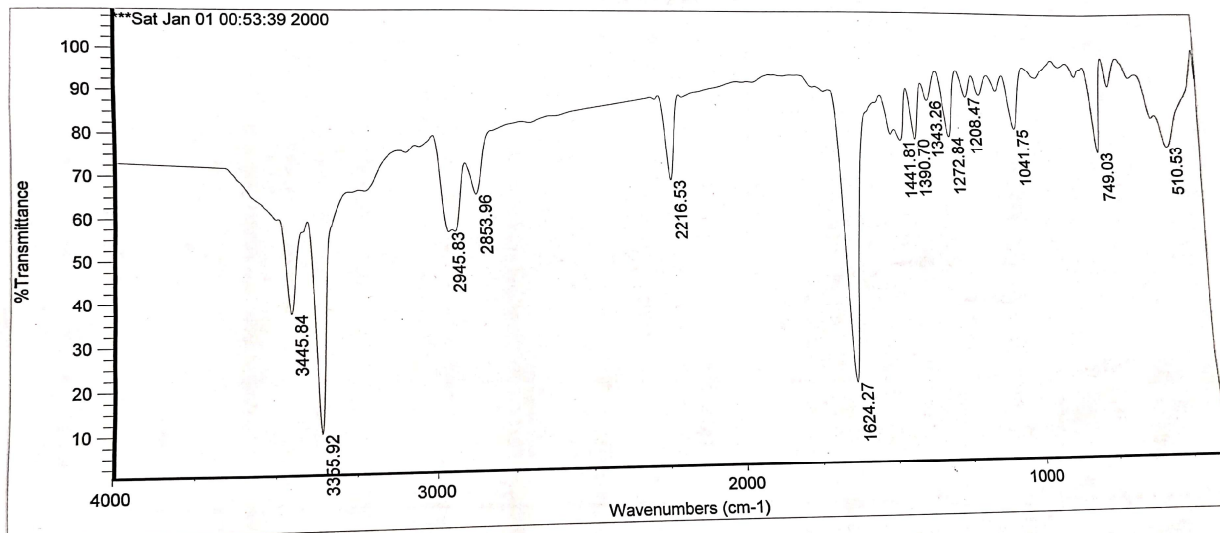
**<sup>1</sup>H NMR of 4a**



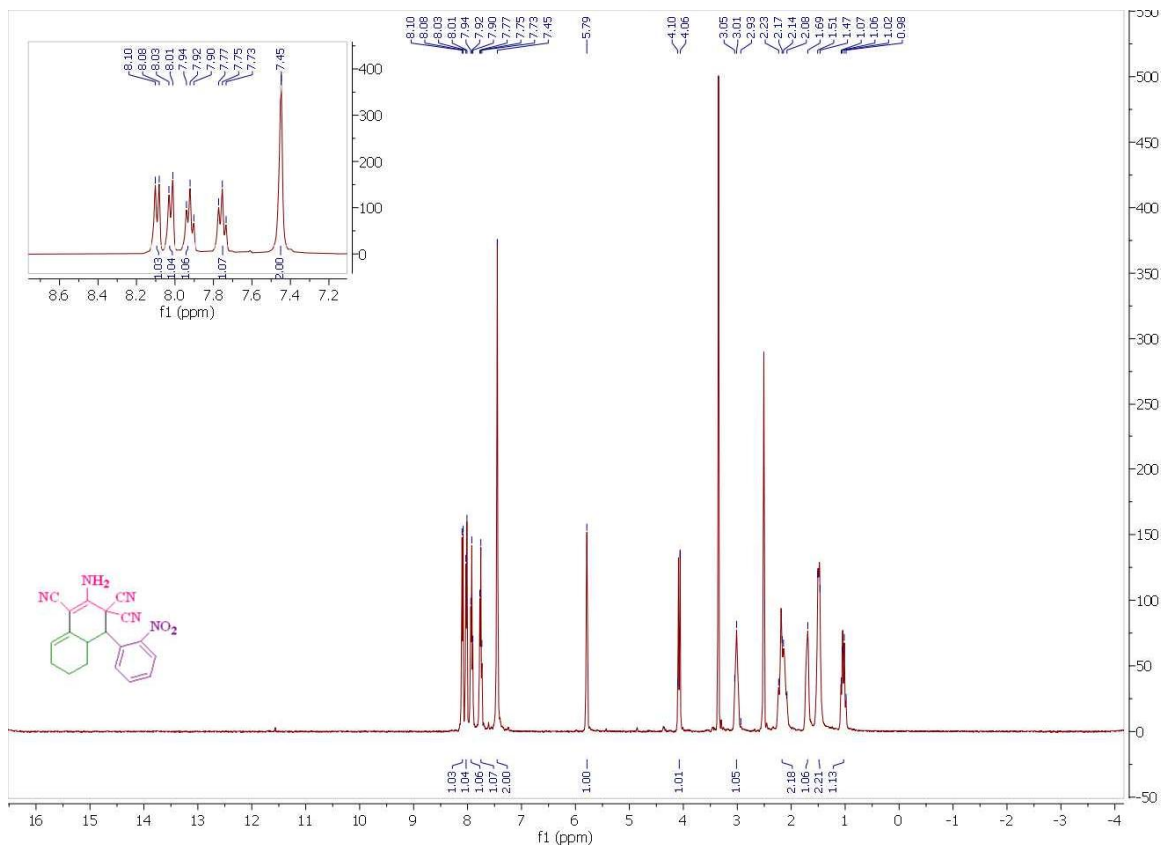
**FT-IR of 4a**



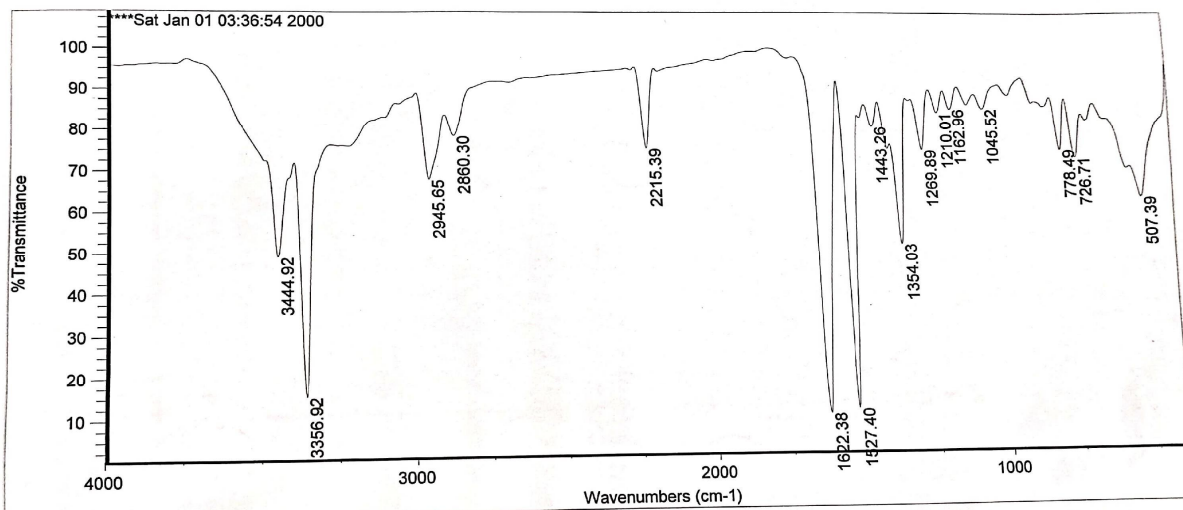
**<sup>1</sup>H NMR of 4b**



**FT-IR of 4b**

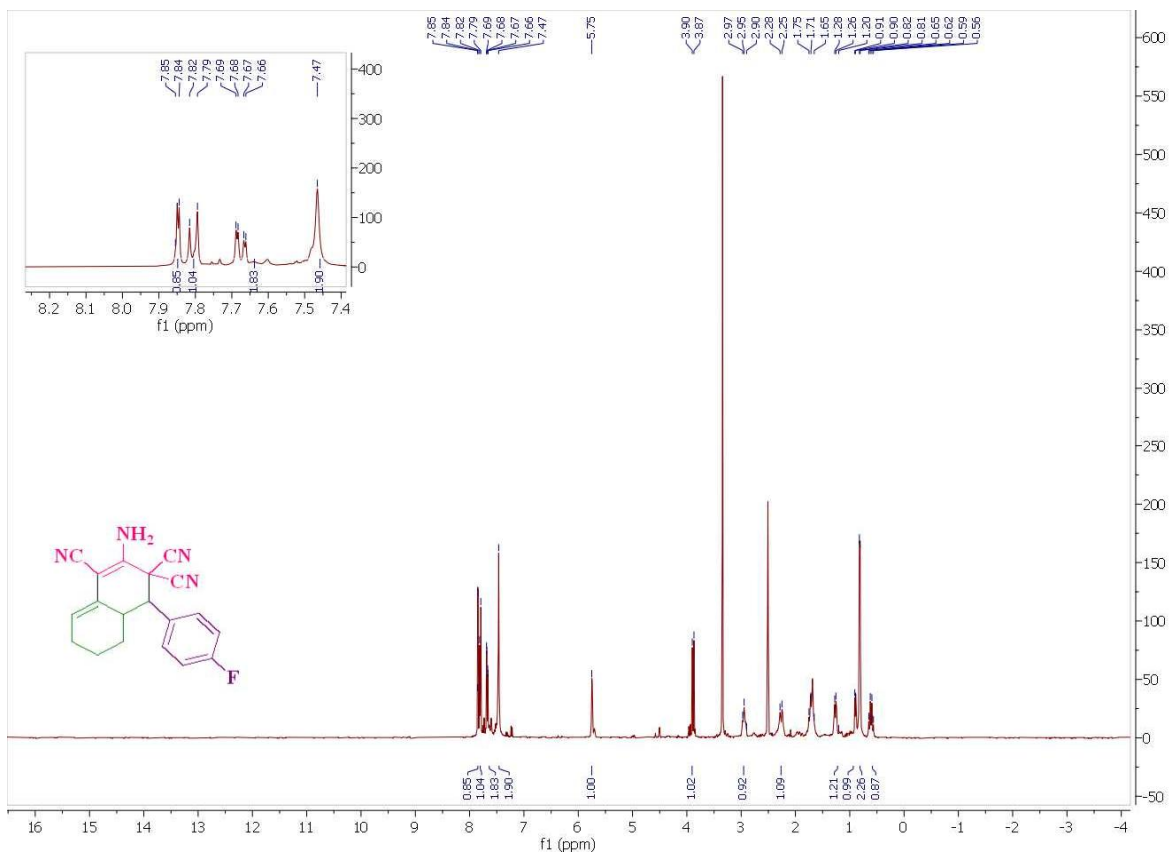


**<sup>1</sup>H NMR of 4c**

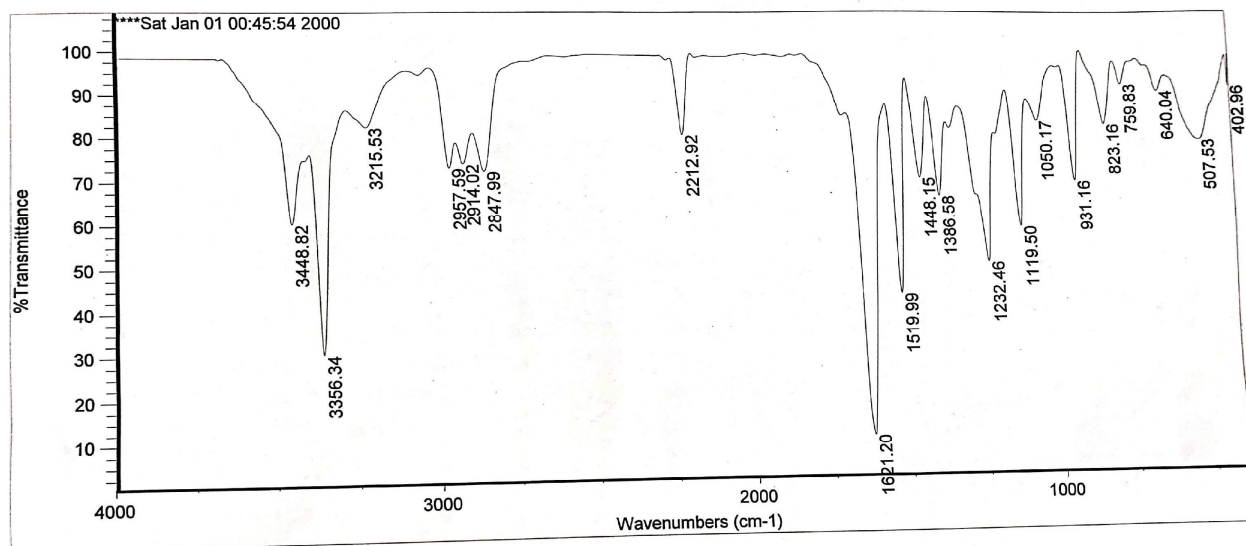


**FT-IR of 4c**

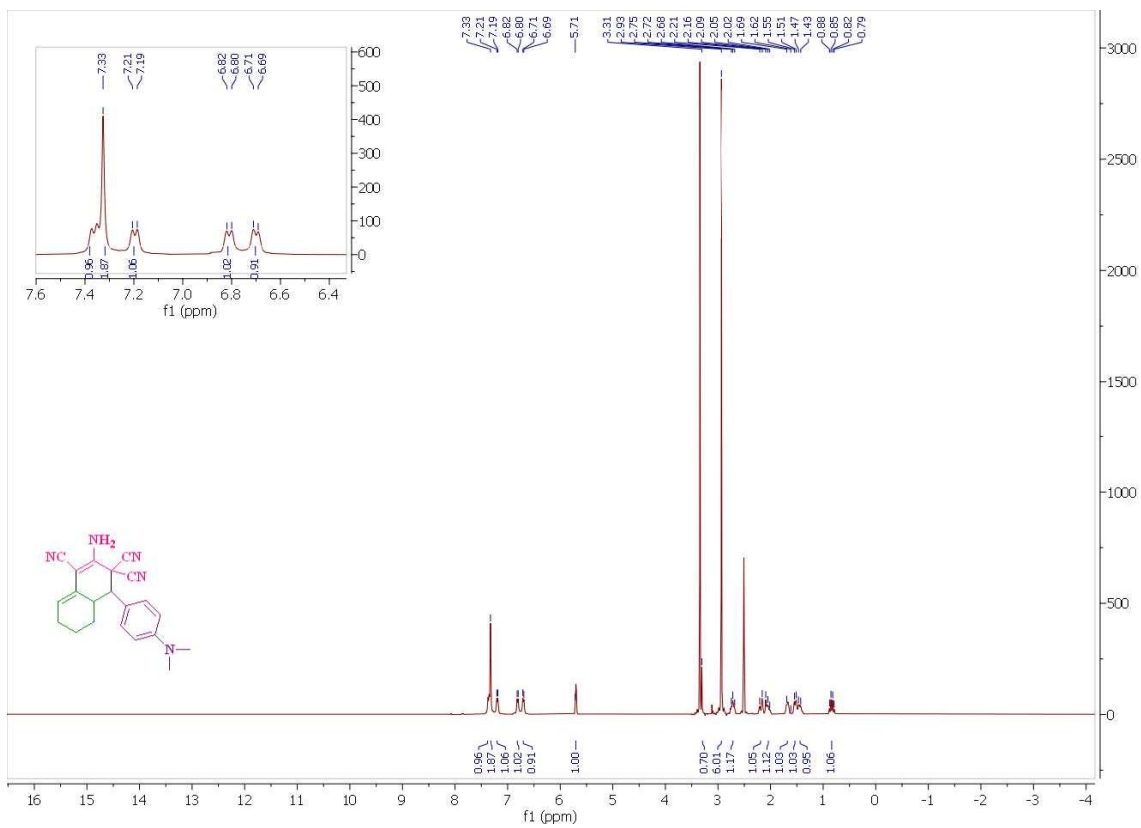




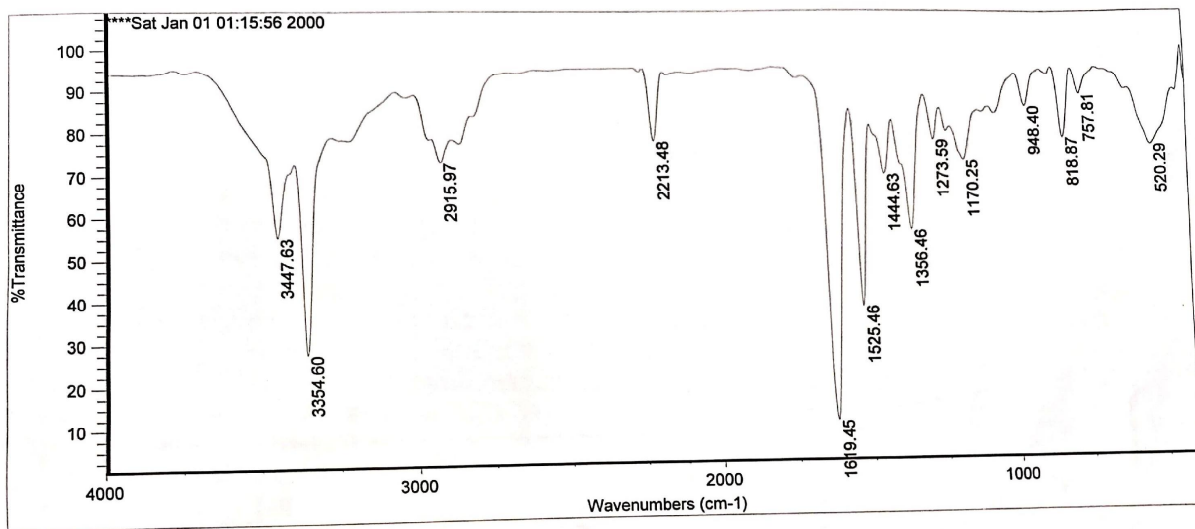
**<sup>1</sup>H NMR of 4d**



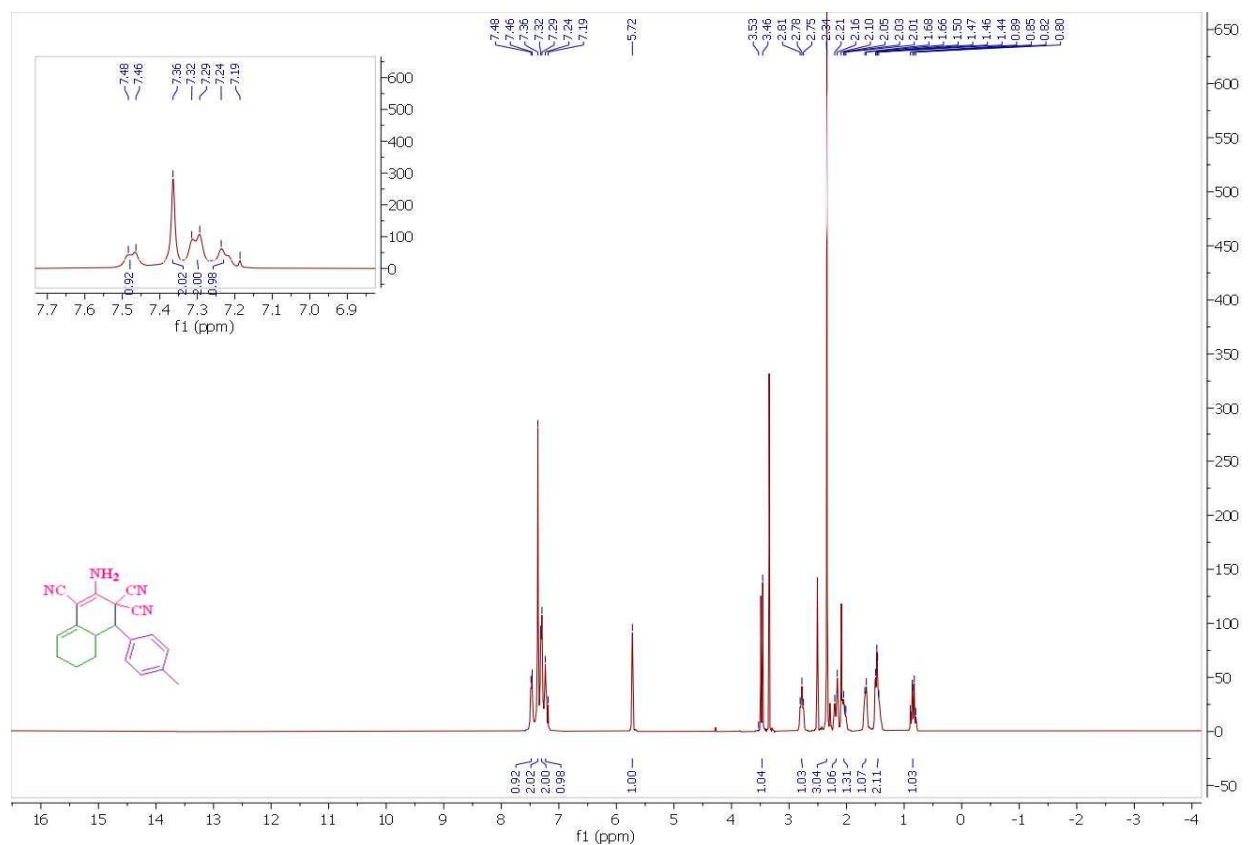
**FT-IR of 4d**



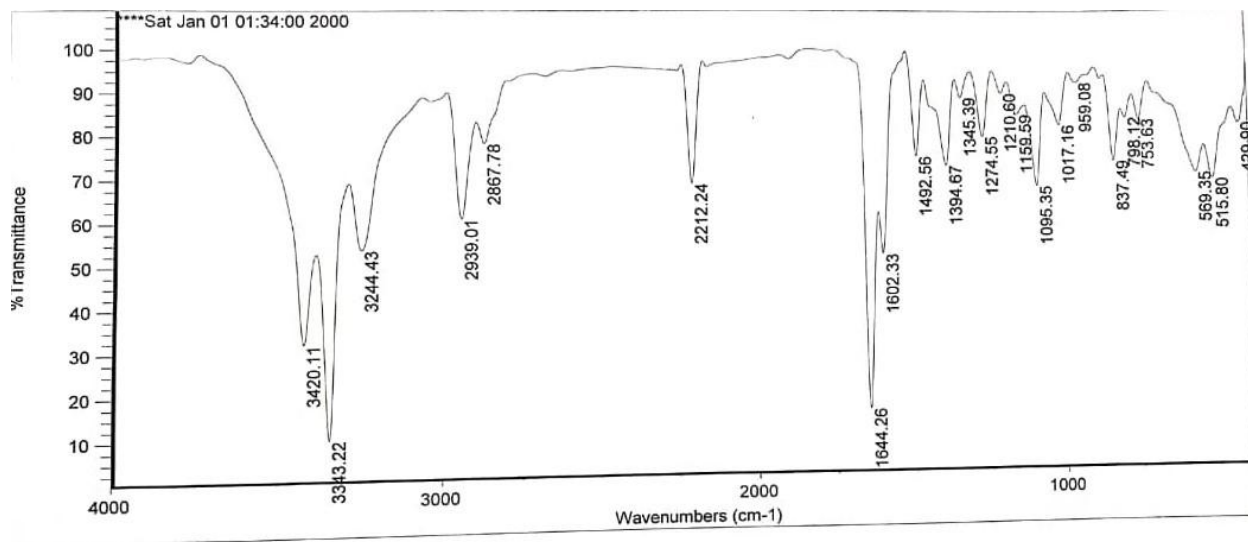
**<sup>1</sup>H NMR of 4e**



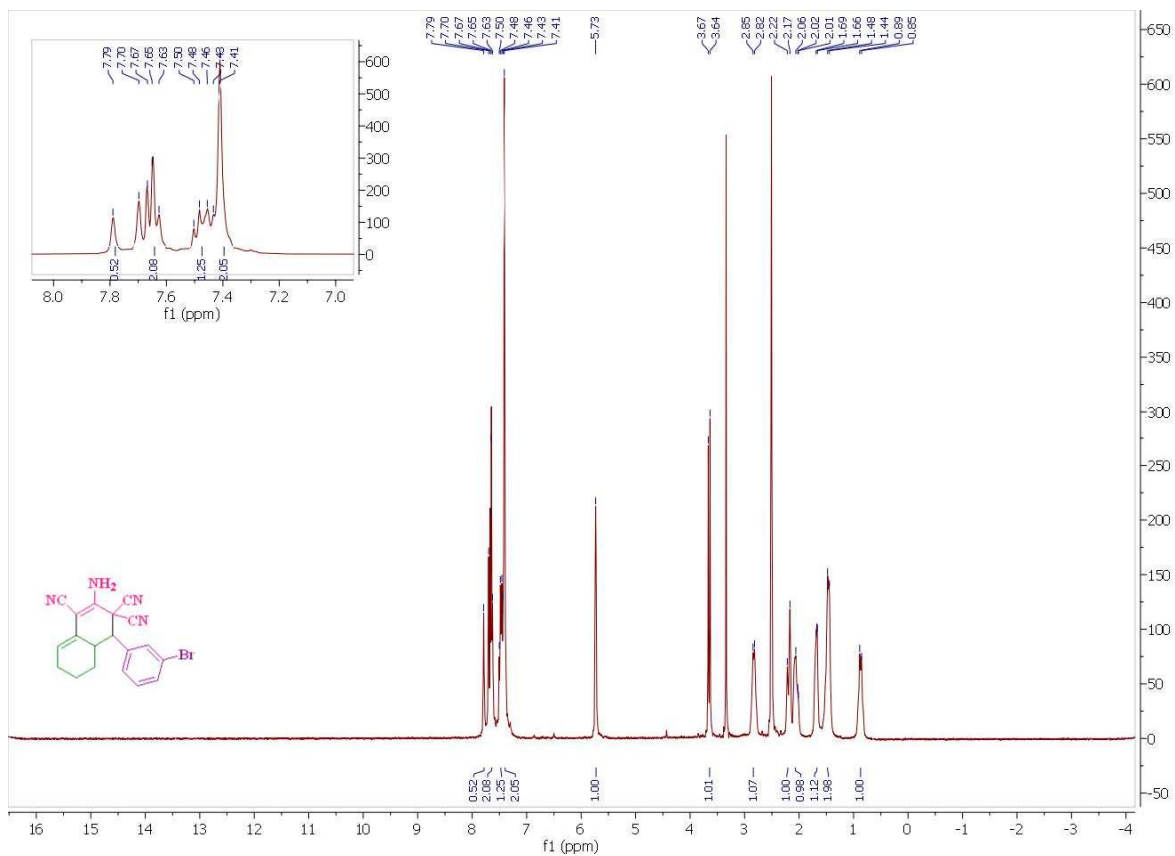
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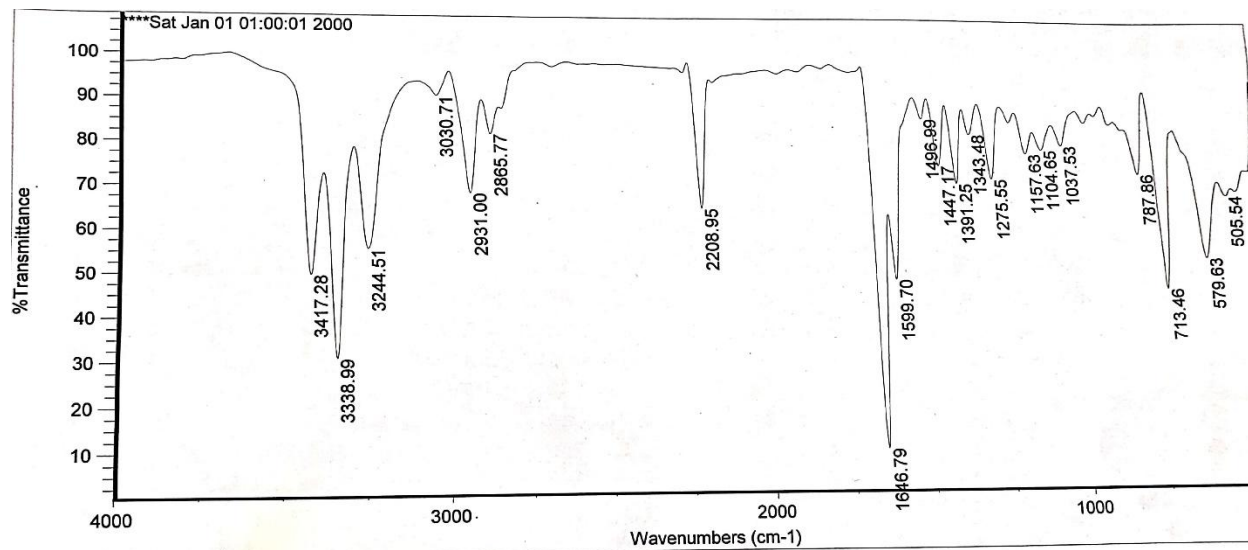
**<sup>1</sup>H NMR of 4f**



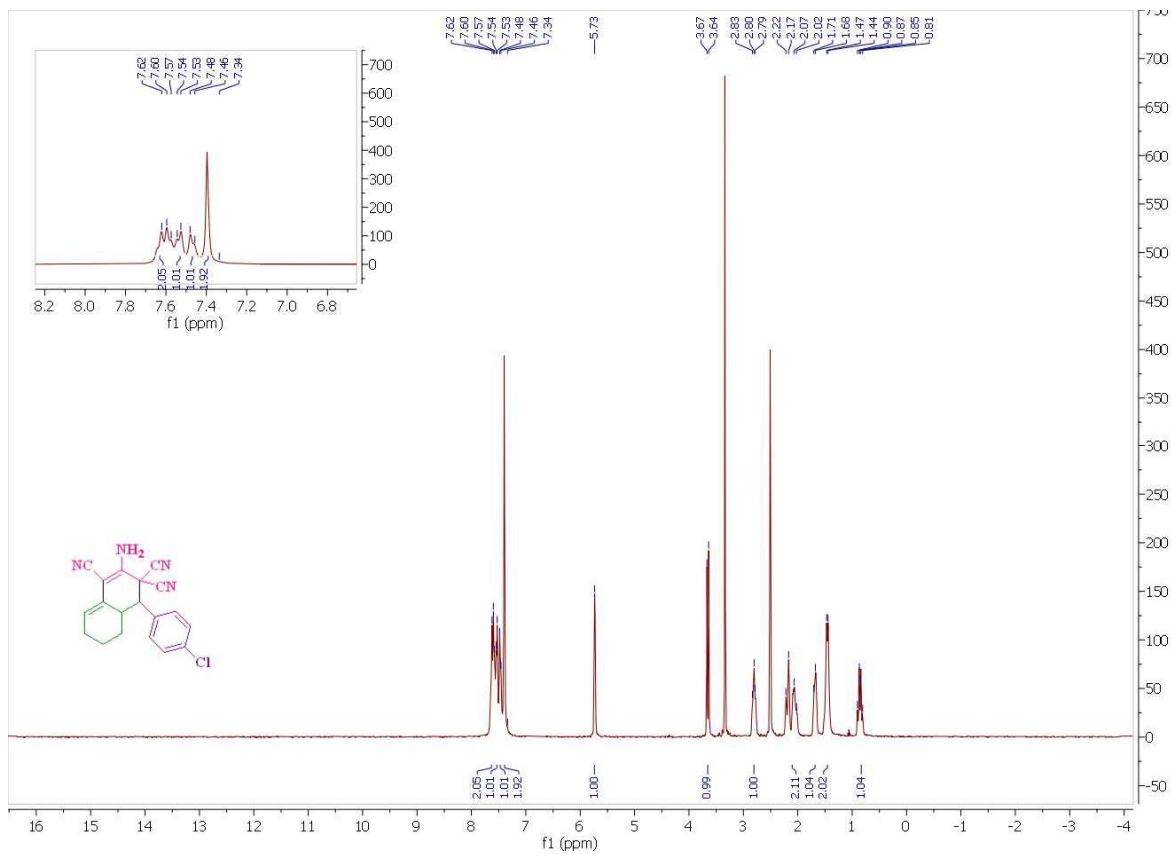
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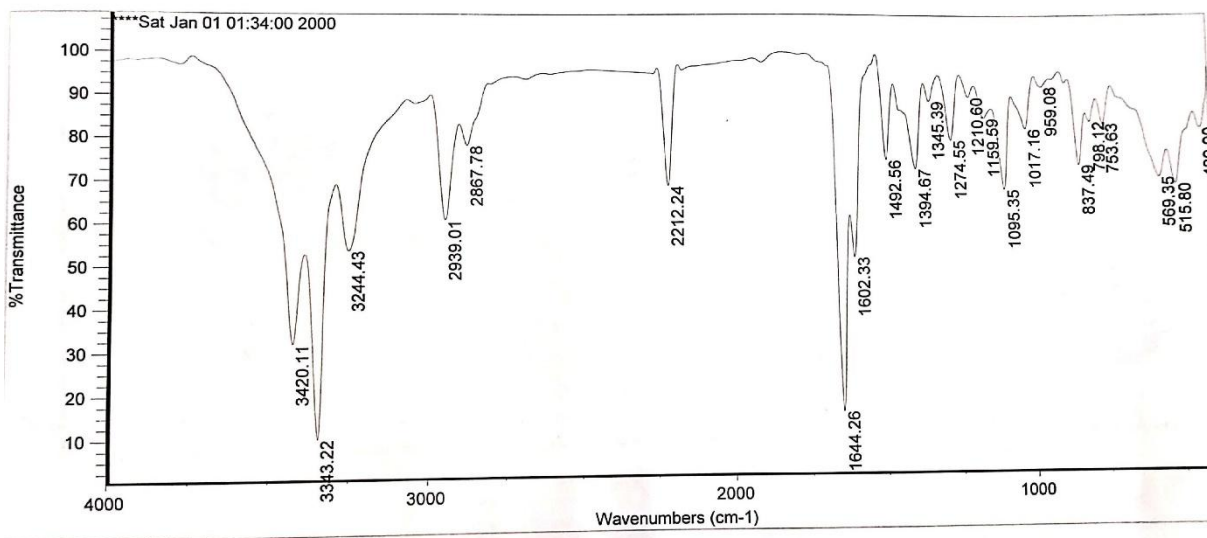
**<sup>1</sup>H NMR of 4g**



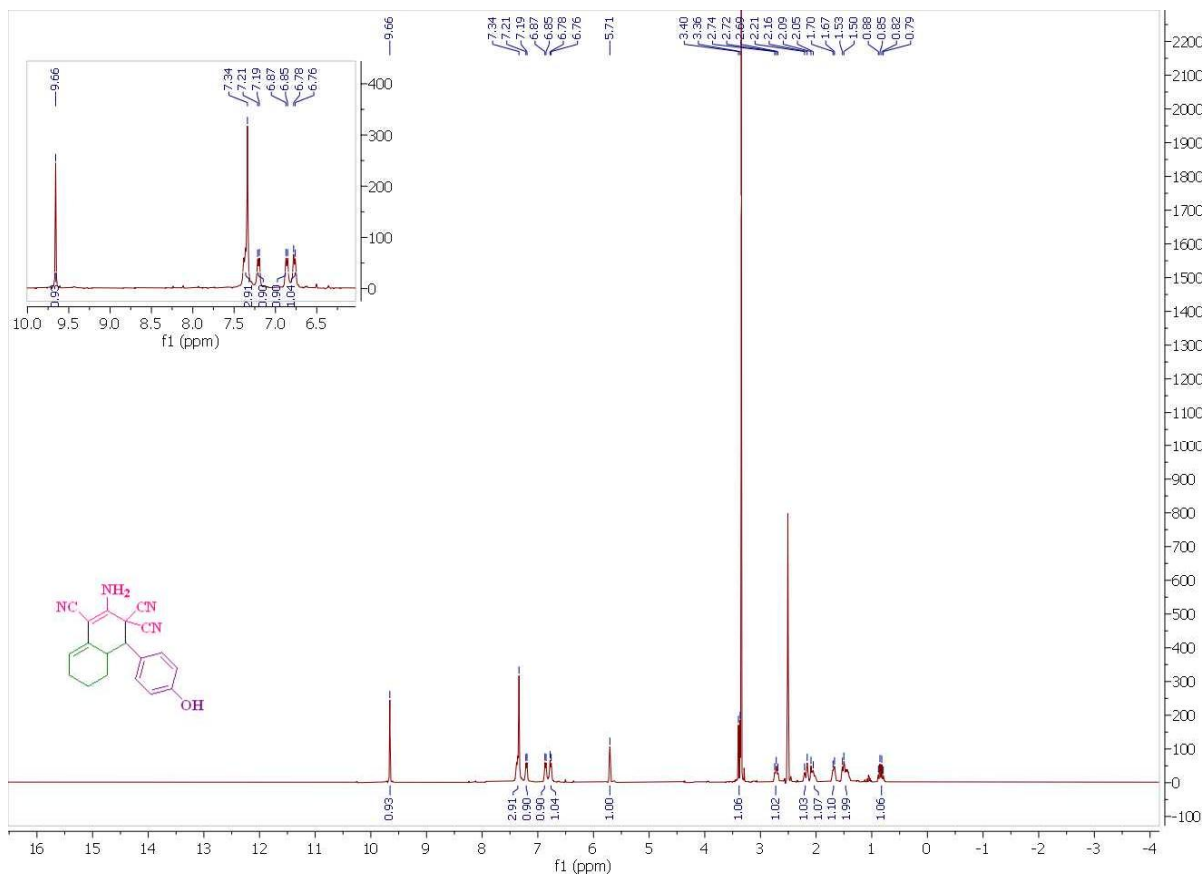
**FT-IR of 4g**



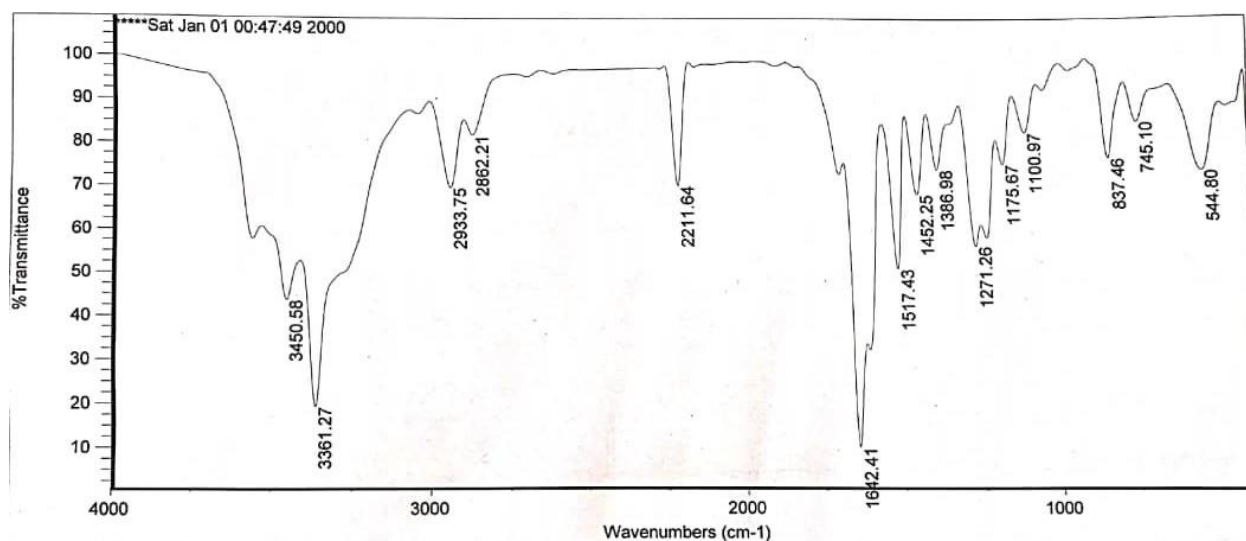
**<sup>1</sup>H NMR of 4h**



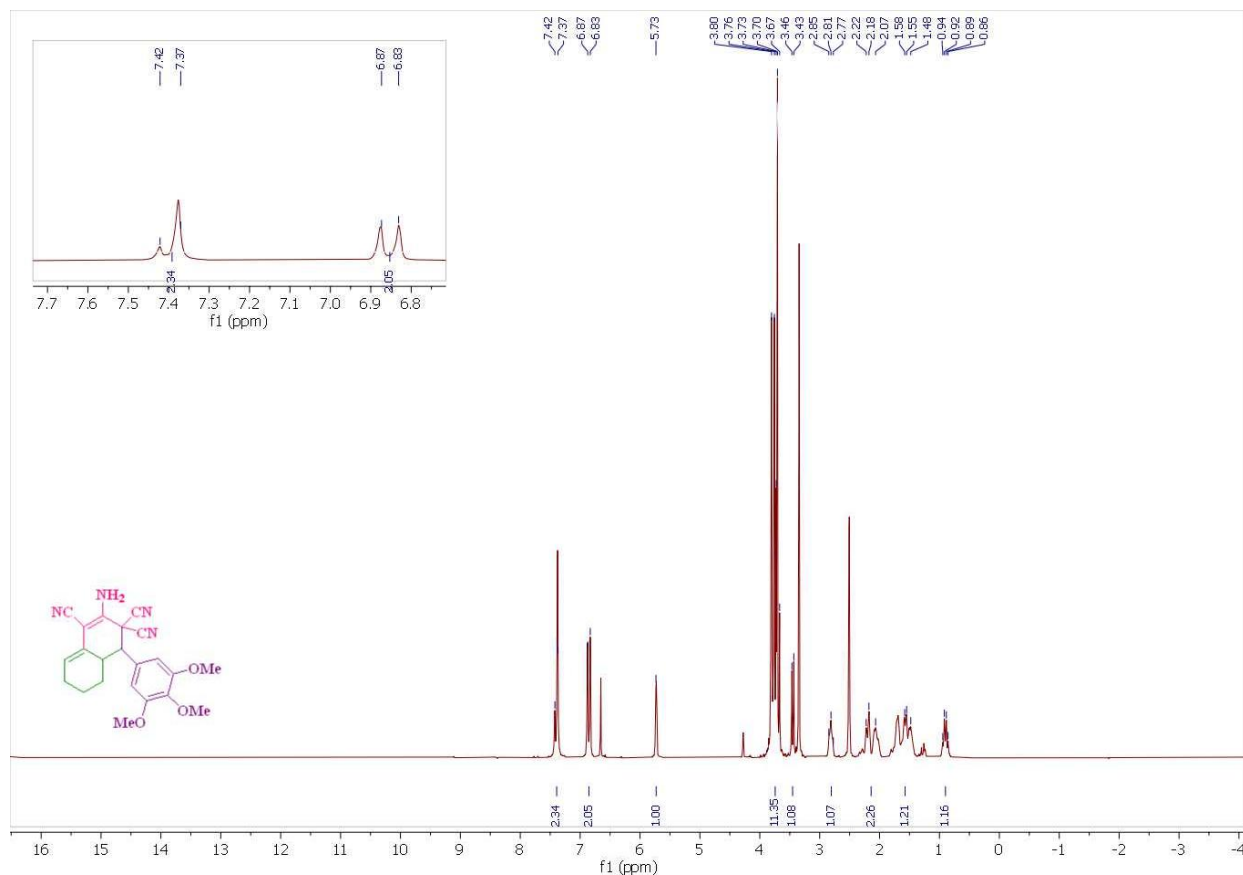
**FT-IR of 4h**



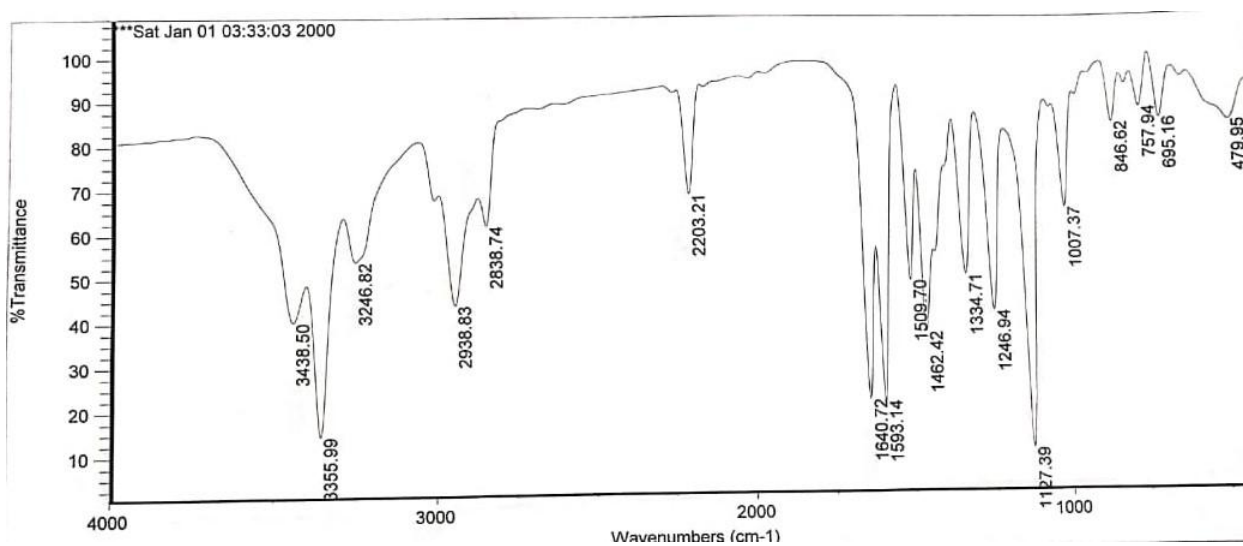
**<sup>1</sup>H NMR of 4i**



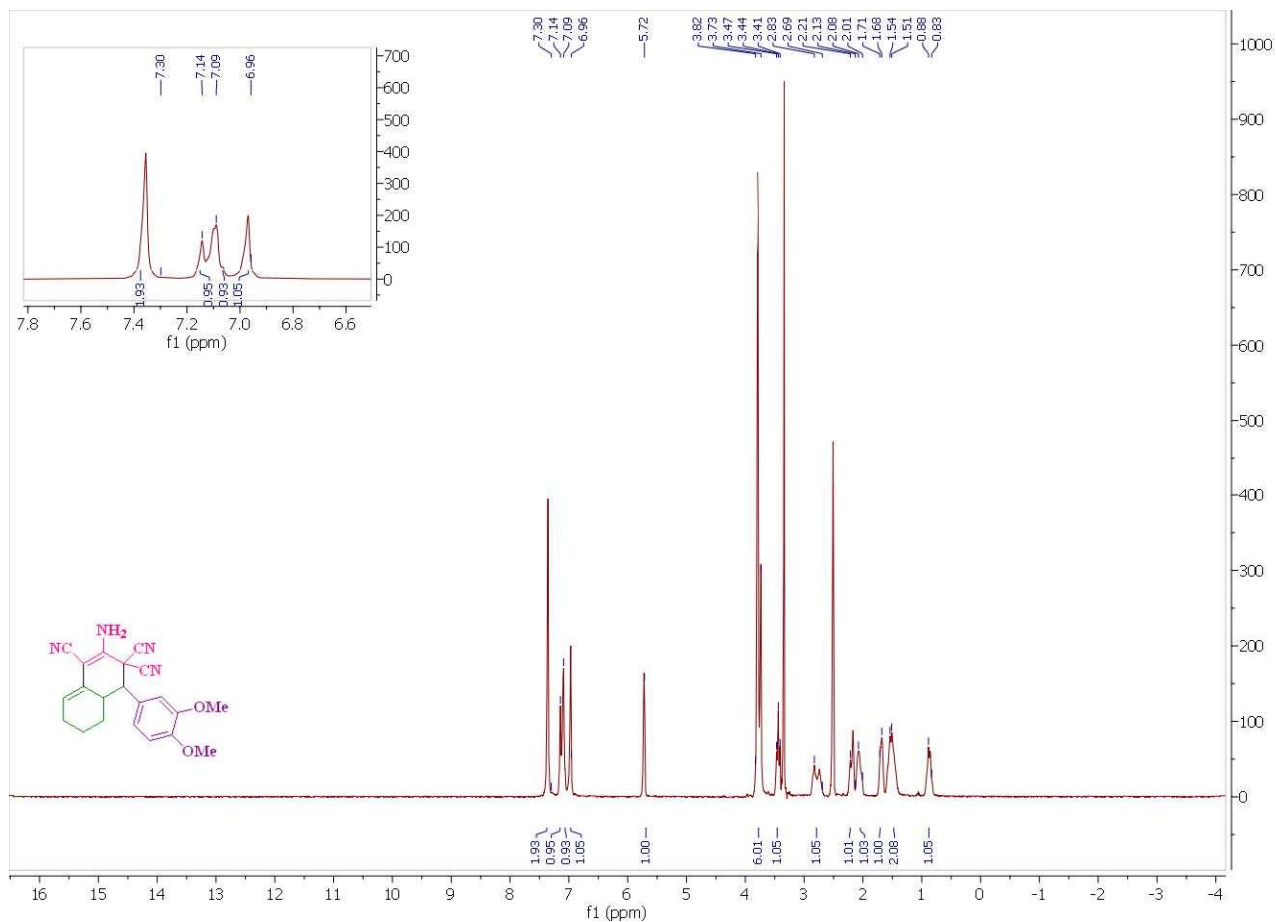
**FT-IR of 4i**



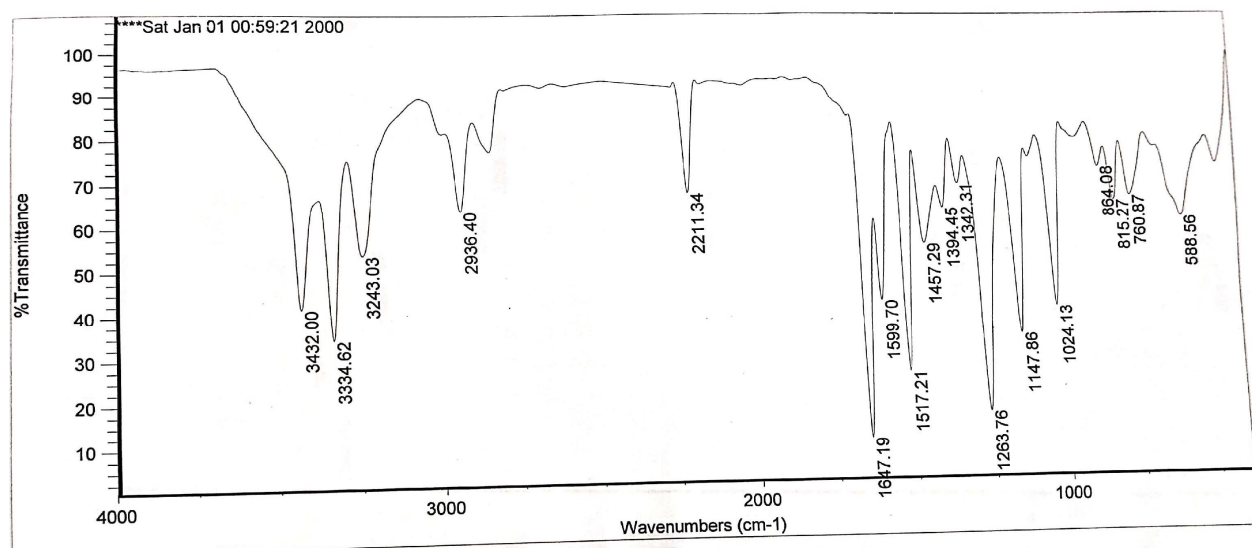
**<sup>1</sup>H NMR of 4j**



**FT-IR of 4j**

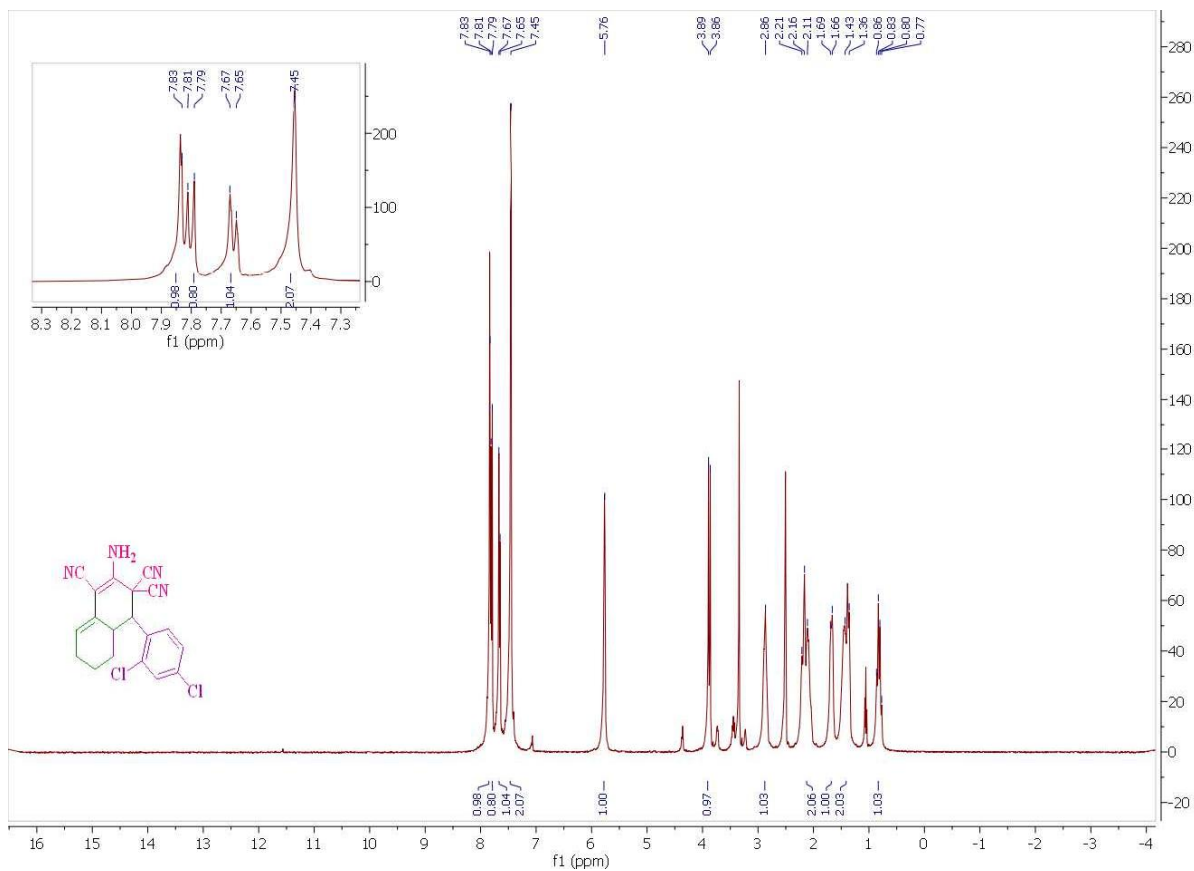


**<sup>1</sup>H NMR of 4k**

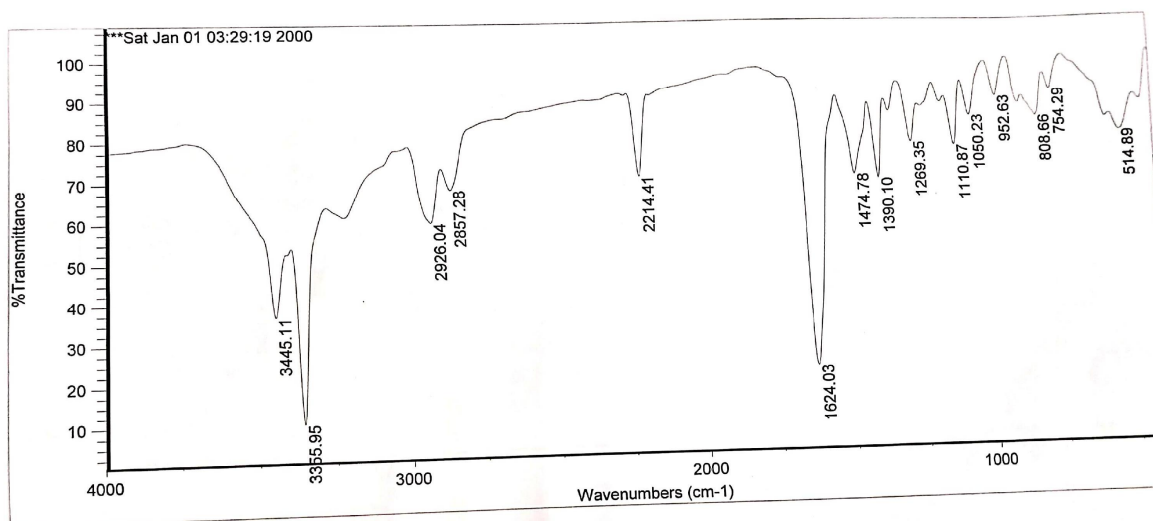


**FT-IR of 4k**

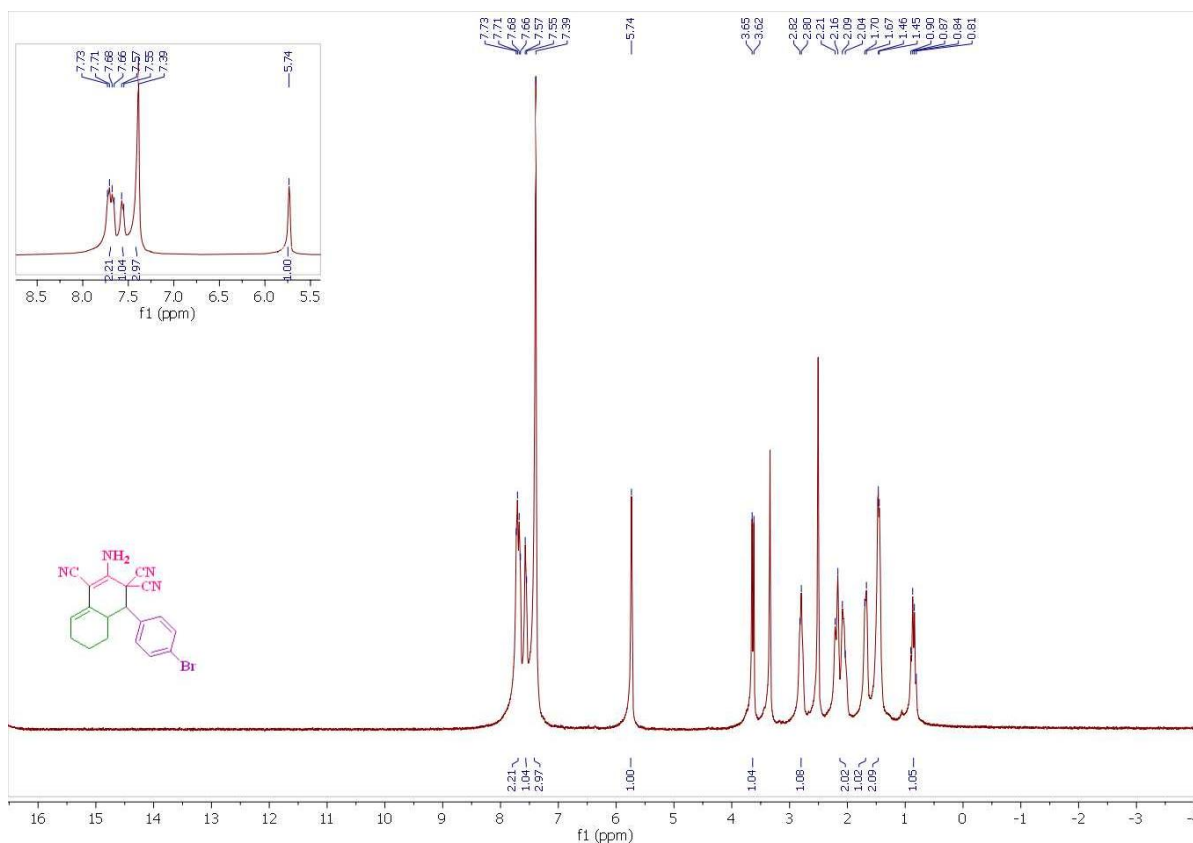




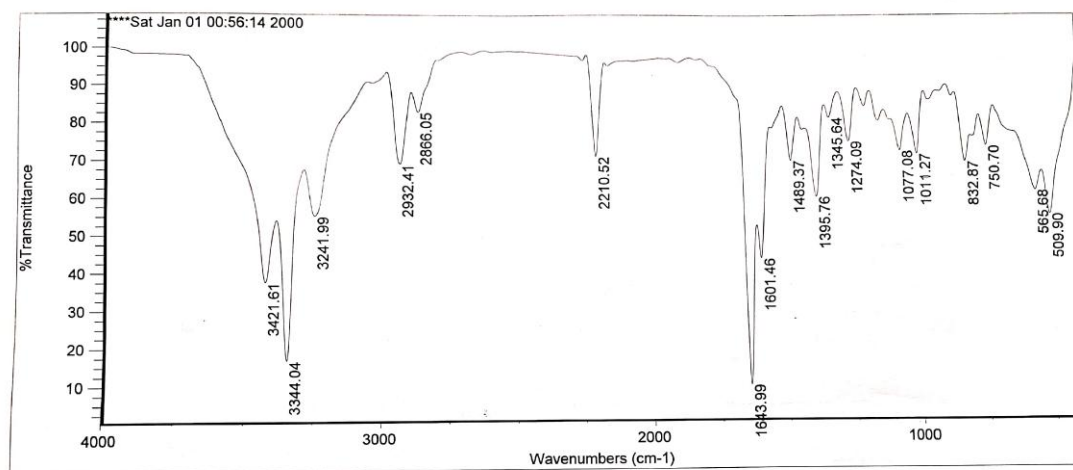
**<sup>1</sup>H NMR of 4I**



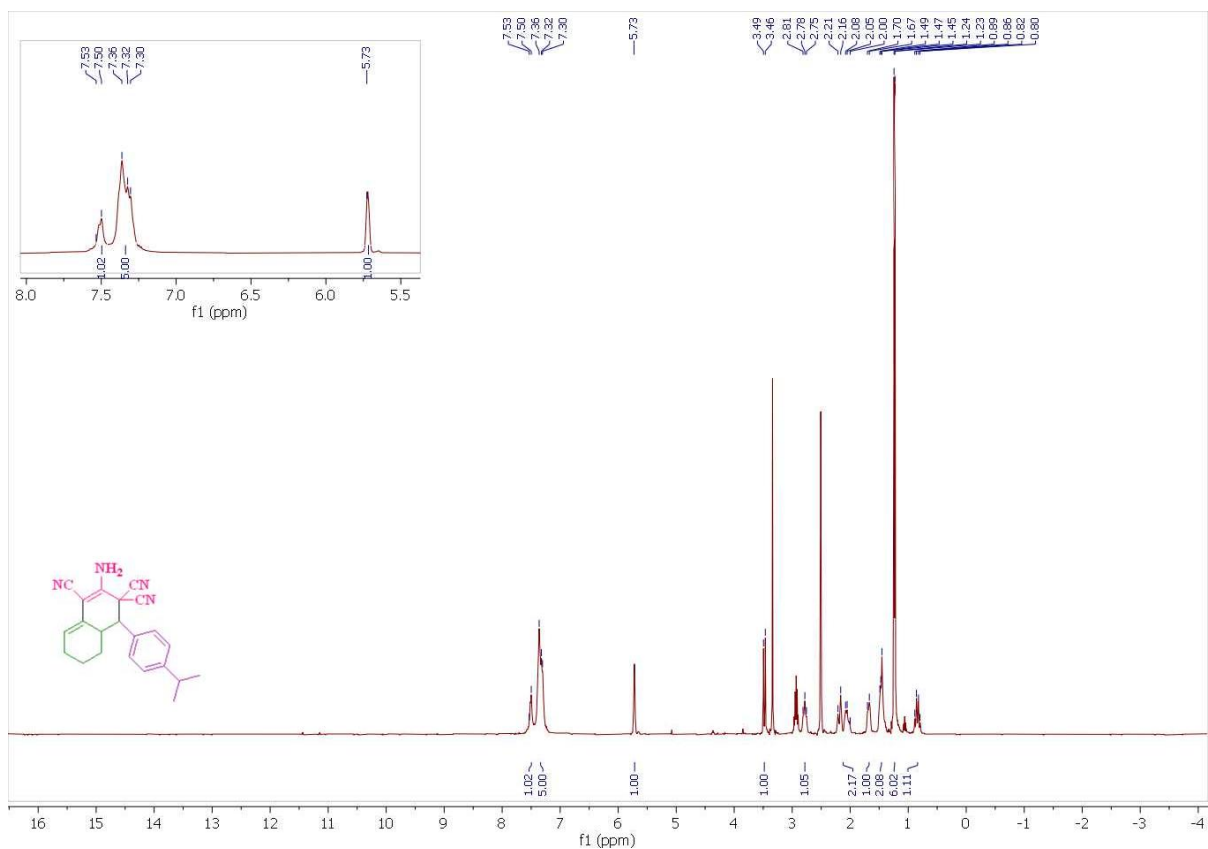
**FT-IR of 4I**



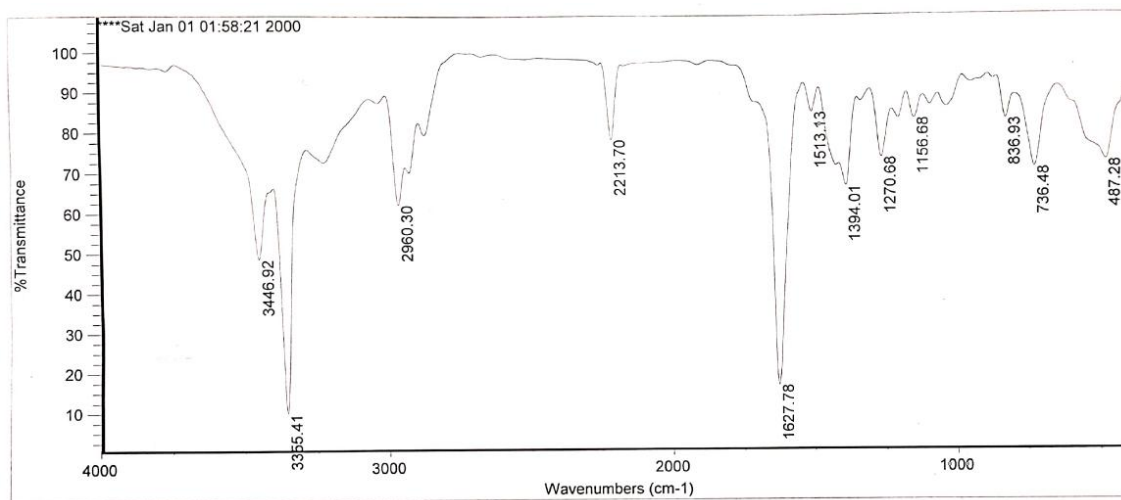
$^1\text{H}$  NMR of **4m**



FT-IR of **4m**



**<sup>1</sup>H NMR of 4n**



**FT-IR of 4n**