Supporting Information Part I for

Zinc titanate nanopowder: an advanced nanotechnology based recyclable heterogeneous catalyst for the one-pot selective green synthesis of self-aggregated low-molecular mass acceptor-donor-acceptor-acceptor systems and acceptor-donor-acceptor triads

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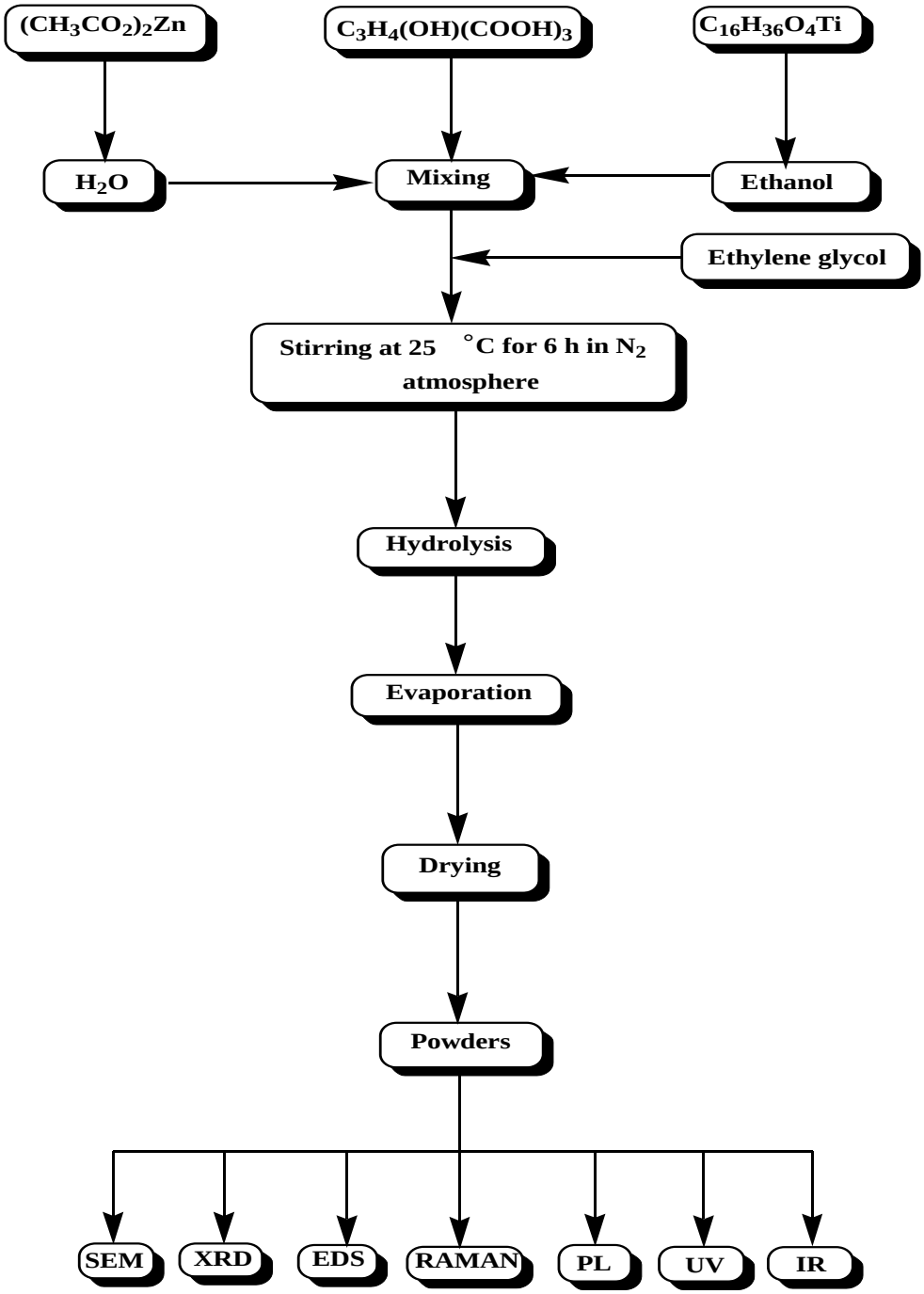
Materials and Methods

All solvents were dried by standard methods. Chemicals were purchased from Aldrich and Spectrochem and used without further purification. TLC was done on glass sheets pre-coated with silica gel (with binder, 300 mesh, Spectrochem). The ^{1}H- and ^{13}C-NMR spectra were taken in d_6 – DMSO with TMS as an internal reference and in one case $CDCl_3$. The chemical shifts were reported as δ values (ppm) relative to TMS. IR spectra were recorded in KBr pellets. The C-H-N-analyses were carried out on a 2400 Series II CHNS Analyzer, Perkin Elmer USA. SEM images were obtained from a Hitachi S-3400N microscope at an operating voltage of 15Kv. The sample was coated with gold for effective imaging before being charged. UV and fluorescence spectra of the samples were recorded in spectrophotometers using standard 1 cm quartz cuvets in dilute solution and also using solid sample holder for powder solid samples. X-ray powder diffraction study was carried out on a Philips PW-1830 X-Ray diffractometer at a voltage of 35 Kv and current 25Ma at scanning rate of 0.2^{o} /minute in the 2θ range $10\text{-}50^{o}$. Raman spectra was taken in LabRAM HR, using a wavelength of 632.8 nm He-Ne laser, with maximum output power of the laser kept at 17 mW. The photoluminescence measurements were taken using HORIBA Jobin Yvon combined Raman/PL system. The 325 nm excitation wavelength of an Ag-Cd laser was used, with maximum output power of the laser kept at 26 mW. The exposure time of the sample was 10 sec. The AFM was taken in VEECO multimode system with Nonoscope IIIa controller. Scanning was done in trapping mode with RTESP tip at resonance frequency 286.57 kHz. The software used was Nanoscope Software version 5.3.



SCHEME S1. Schematic flow-chart of the synthesis of $ZnTiO_3$ nanopowders by sol–gel technique.

Characterization of catalyst

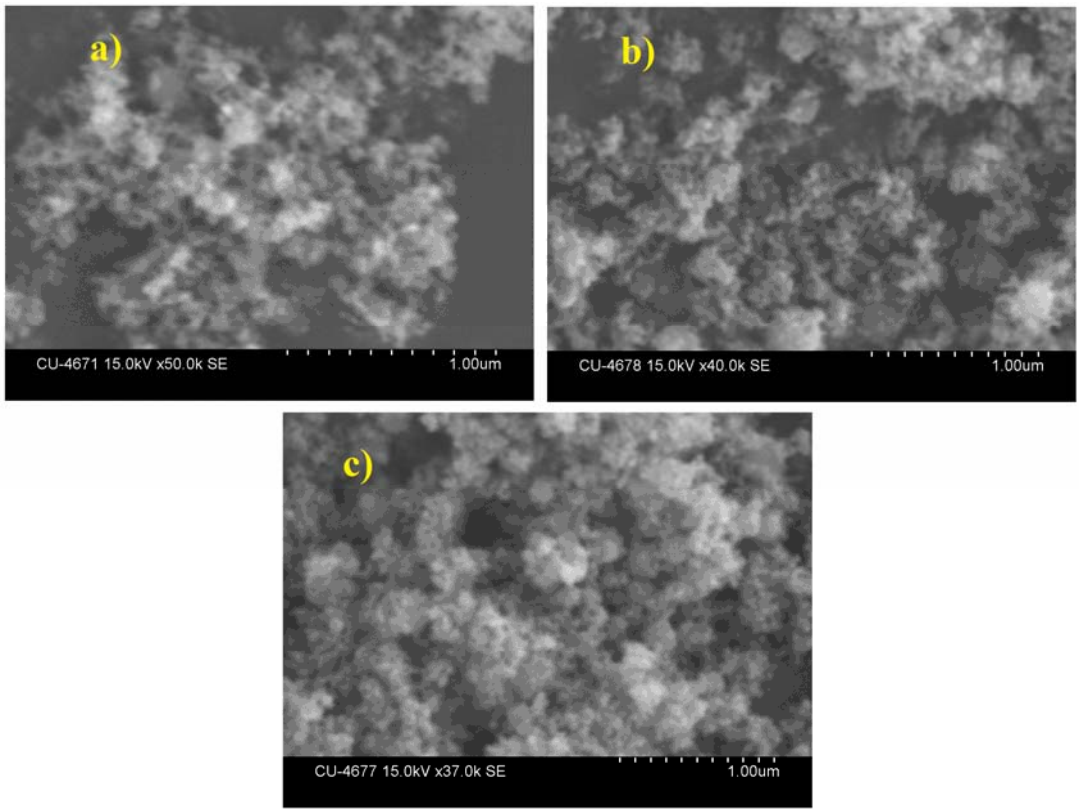


Figure S2. SEM micrographs of $ZnTiO_3$ nanopowders calcinated at different temperatures for 6 h (a) 200 °C (b) 500 °C and (c) 800 °C.

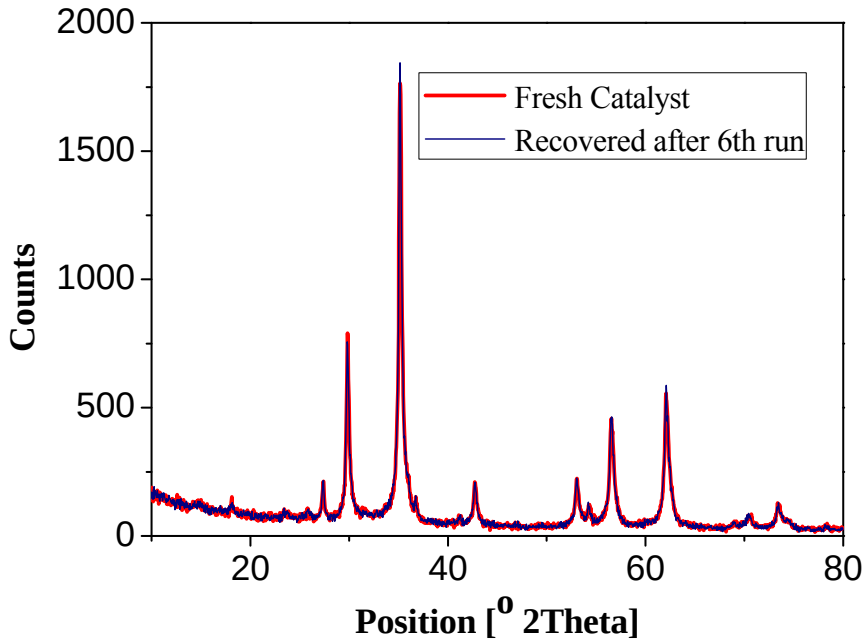


Figure S3. (a) X-ray diffraction profiles of $ZnTiO_3$ nanopowder derived from $ZnTiO_3$ precursor solution after heat treatment at 800 °C. (b) Six-times reused catalyst.

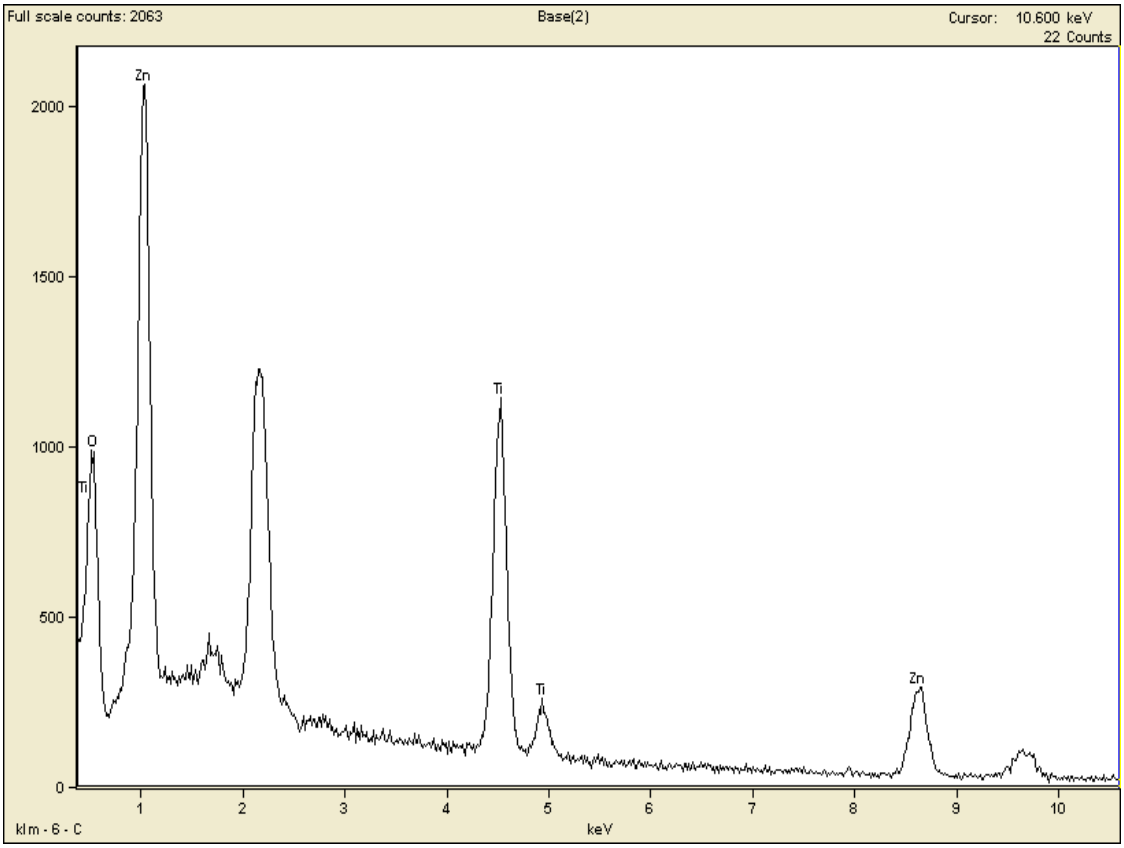


Figure S4. EDX spectra of $ZnTiO_3$ nanopowder calcinated at 800 °C attesting the presence of Zn, Ti and O.

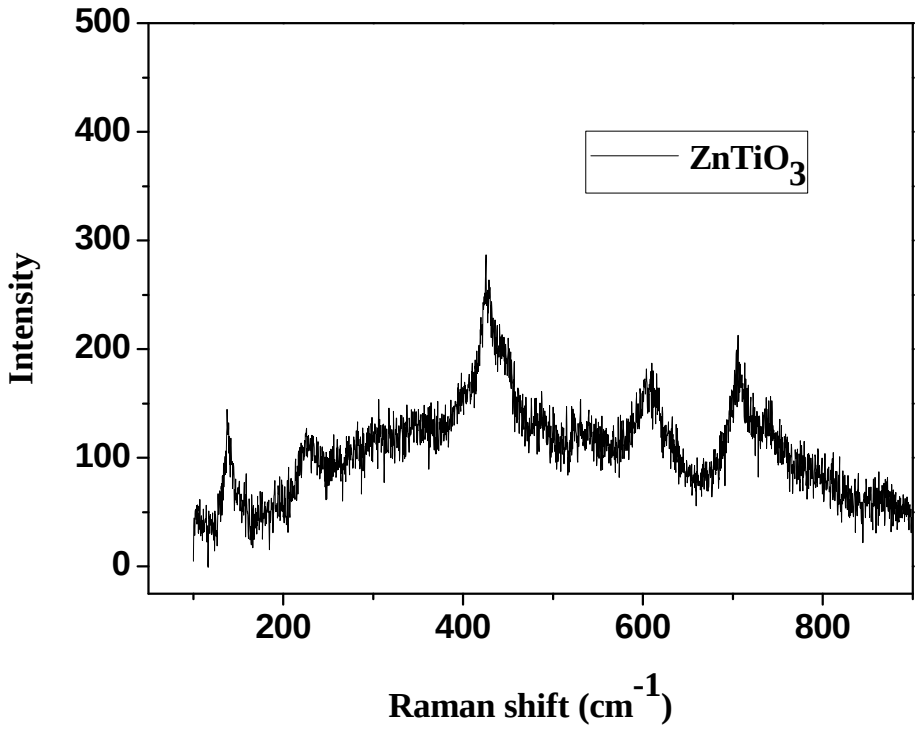


Figure S5. Raman spectra of $ZnTiO_3$ nanopowder calcinated at 800 °C.

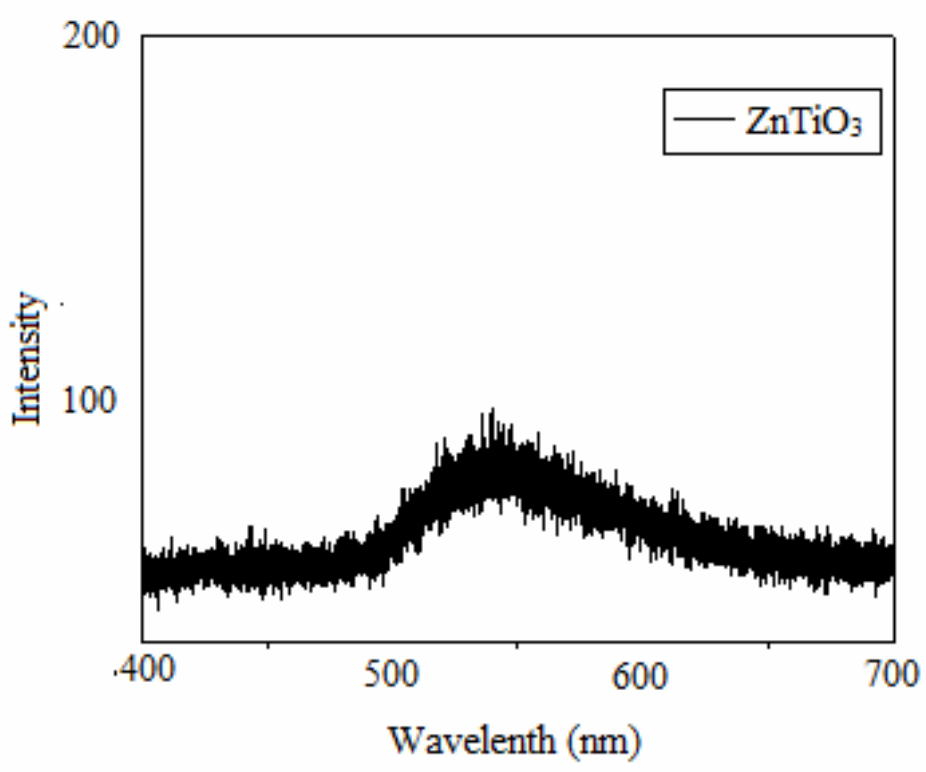


Figure S6. PL spectra of $ZnTiO_3$ nanopowder calcinated at 800 °C.

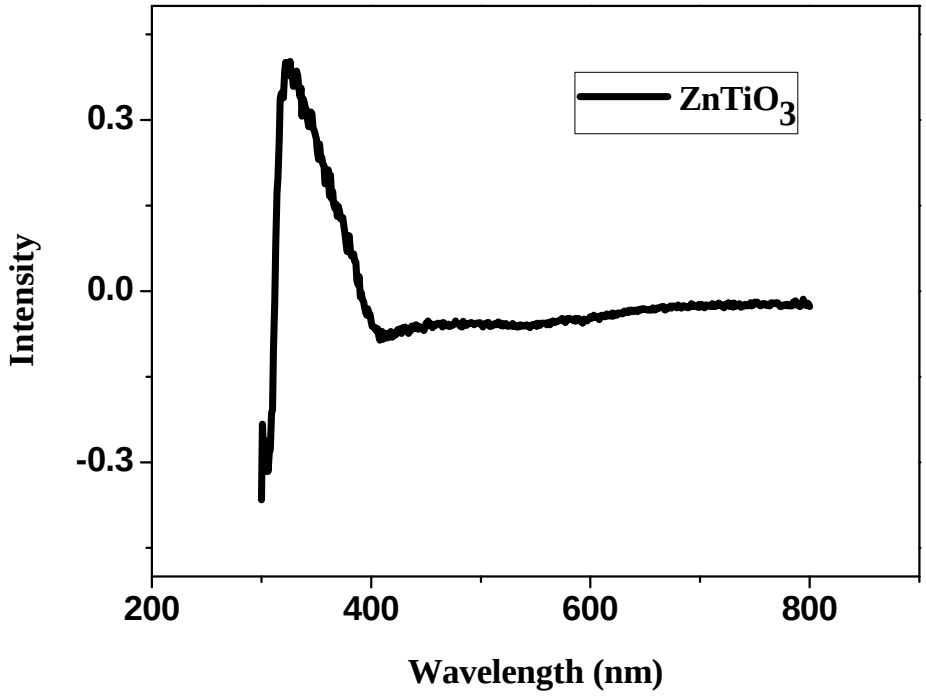


Figure S7. UV absorption spectra of solid $ZnTiO_3$ nanopowder calcinated at 800 °C.

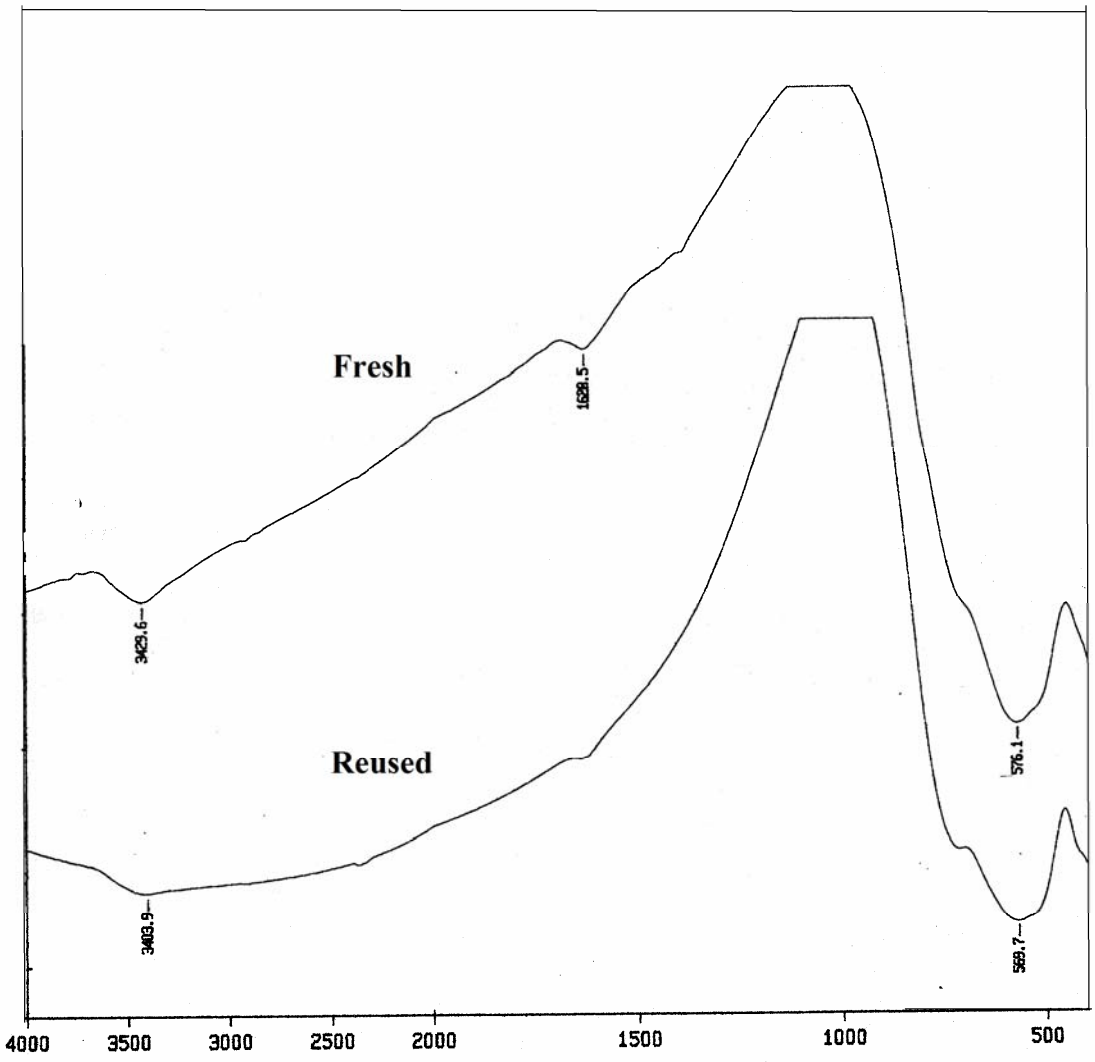


Figure S8. FT-IR spectrum for the comparison of the fresh catalyst and the six-times reused catalyst.

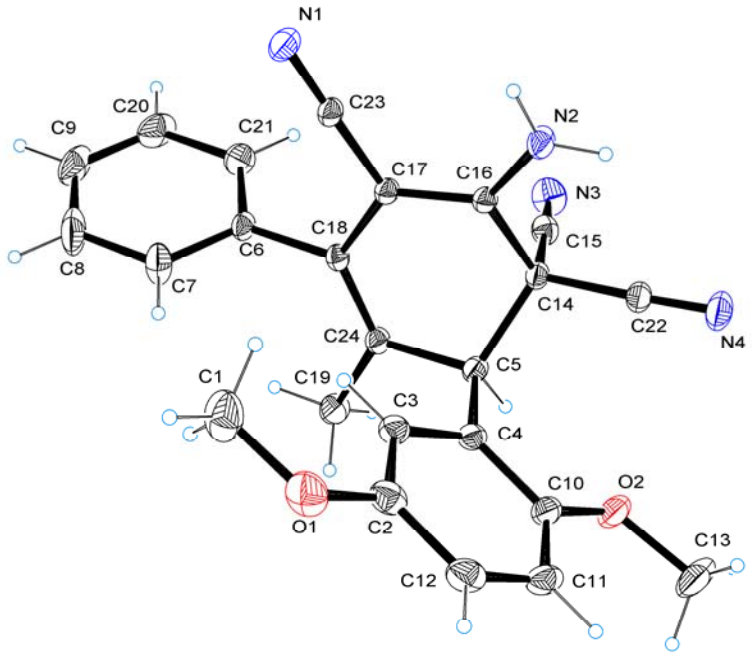


Figure S9: ORTEP DIAGRAM for **4ie** (**CCDC 855039**)

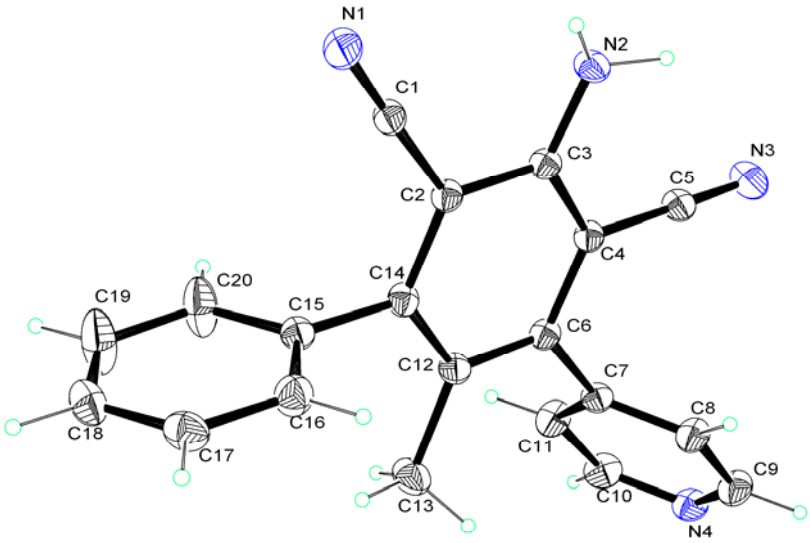


Figure S10: ORTEP DIAGRAM for **5io** (**CCDC 855038**)

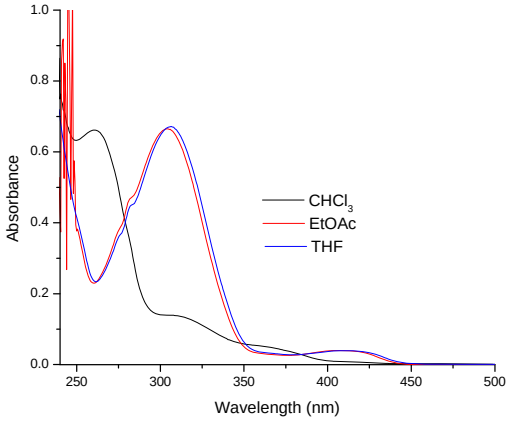


Figure S11: Normalized absorption spectra of (6.29×10^{-5}) mol.dm^{-3} **4ba** in three different solvents.

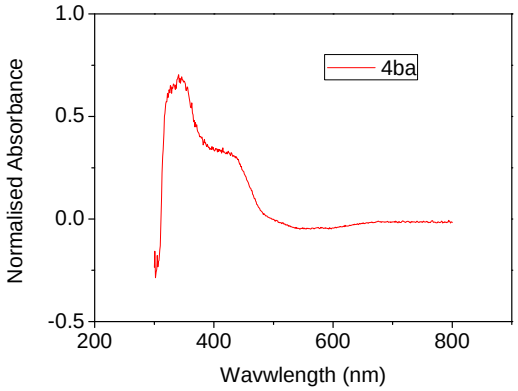


Figure S12: UV-vis spectra of the solid nanostructured materials generated from **4ba**

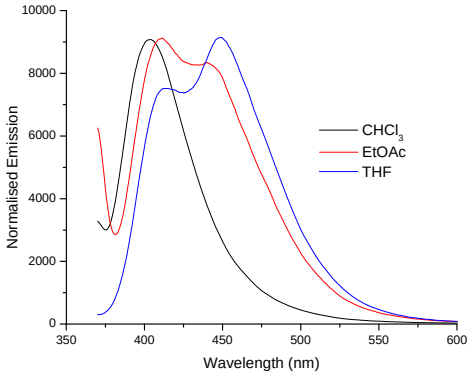
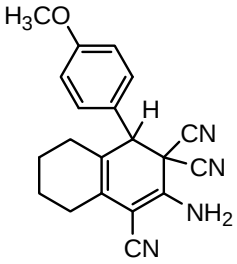


Figure S13: Emission spectra of **4ba** for 360 nm excitation**.**

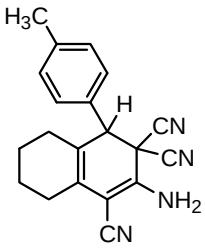
Spectroscopic characterization of the non-aromatic products (A-D-A-A system) 4aa-4jm

2-Amino-4-(4-methoxy-phenyl)-5,6,7,8-tetrahydro-4H-napathalene-1,3,3-tricarbonitrile (4aa):



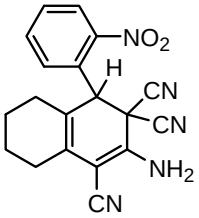
Yellow solid; Yield: 601 mg, 91 %; m.p. 245-247 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{20}H_{18}N_4O$: C, 72.71; H, 5.49; N, 16.96 %. Found: C, 72.91; H, 5.54; N, 17.01 %; IR (KBr) cm^{-1}: 3413, 3335, 3246, 2951, 2853, 2218, 1659, 1595, 1513, 1458, 1389, 1257, 1179, 1031, 840, 809, 601, 534; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.80 (1H, q, *J* = 12.6 Hz, CH), 1.43-1.46 (2H, m, CH_2), 1.63 (1H, br s, CH), 2.04-2.17 (2H, m, CH_2), 2.71 (1H, br s, CH), 3.43 (1H, d, *J* = 12.6 Hz, CH), 3.75 (3H, s, $0CH_3$), 5.67(1H, s, CH), 6.95-7.02 (2H, m, arom.), 7.30 (3H, s, arom. and NH_2), 7.44-7.47 (1H, m, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 21.1, 24.9, 27.1, 43.2, 50.1, 55.2, 81.6, 112.6, 112.7, 116.2, 120.3, 126.4, 129.0, 143.7, 159.6.

2-Amino-4-p-tolyl-5,6,7,8-tetrahydro-4H-napathalene-1,3,3-tricarbonitrile (4ab):



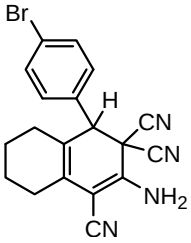
White solid; Yield: 585 mg, 93 %; m.p. 252-254 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82 %. Found: C, 76.51; H, 5.81; N, 17.94 %; IR (KBr) cm^{-1}: 3421, 3336, 3246, 2945, 2866, 2213, 1646, 1600, 1452, 1391, 1272, 1160, 1037, 830, 748, 587, 517, 464; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.80 (1H, q, *J* = 12.0 Hz, CH), 1.42-1.46 (2H, m, CH_2), 1.61 (1H, br s, CH), 2.02-2.17 (2H, m, CH_2), 2.30 (2H, s, CH_3), 2.73-2.76 (1H, m, CH), 3.42 (1H, d, *J* = 12.6 Hz, CH), 5.68 (1H, s, CH), 7.20-7.42 (6H, m, arom. and NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 20.8, 21.0, 24.9, 27.0, 34.0, 43.0, 50.4, 81.6, 112.5, 112.6, 116.2, 117.7, 120.3, 129.0, 129.2, 131.6, 132.4, 138.4, 143.6.

2-Amino-4-(2-nitro-phenyl)-5,6,7,8-tetrahydro-4H-napathalene-1,3,3-tricarbonitrile (4ag):



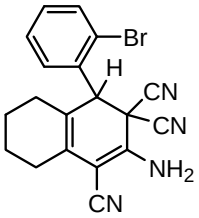
Light orange solid; Yield: 635 mg, 92 %; m.p. 231-233 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{15}N_5O_2$: C, 66.08; H, 4.38; N, 20.28 %. Found: C, 66.19; H, 4.40; N, 20.41 %; IR (KBr) cm^{-1}: 3445, 3357, 2948, 2865, 2216, 1624, 1527, 1353, 1270, 1253, 1209, 1163, 1053, 778, 724, 506; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.99 (1H, q, *J* = 12.3 Hz, CH), 1.43-1.46 (2H, m, CH_2), 1.65 (1H, br s, CH), 2.13 (2H, br s, CH_2), 2.96 (1H, br s, CH), 4.03 (1H, d, *J* = 12.3 Hz, CH), 5.74 (1H, s, CH), 7.38 (2H, s, NH_2), 7.71 (1H, t, *J* = 7,8 Hz, arom.), 7.86 (1H, t, *J* = 7.2 Hz, arom.), 7.97 (1H, d, *J* = 7.5 Hz, arom.), 8.06 (1H, d, *J* = 8.1 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 20.8, 24.8, 26.6, 34.3, 42.1, 45.0, 81.6, 111.9, 112.0, 115.9, 117.7, 121.3, 125.5, 127.8, 128.2, 129.7, 130.7, 133.6, 143.2, 150.9.

2-Amino-4-(4-bromo-phenyl)-5,6,7,8-tetrahydro-4H-napathalene-1,3,3-tricarbonitrile (4ah):



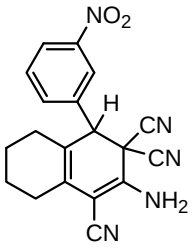
White solid; Yield: 705 mg, 93 %; m.p. 252-254 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{15}BrN_4$: C, 60.17; H, 3.99; N, 14.77 %. Found: C, 60.26; H, 4.00; N, 14.86 %; IR (KBr) cm^{-1}: 3422, 3344, 3245, 2936, 2868, 2211, 1644, 1489, 1394, 1274, 1159, 1076, 1011, 834, 751, 565, 510; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.83 (1H,t, *J* = 12.0 Hz, CH), 1.40 (2H, br s, CH_2), 1.61 (1H, br s, CH), 2.03-2.17 (2H, m, CH_2), 2.75 (1H, br s, CH), 3.58 (1H, d, *J* = 12.0 Hz, CH), 5.69 (1H, s, CH), 7.35 (s, 3H, arom. and NH_2), 7.53 (1H, br s, arom.), 7.65 (2H, br s, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 21.0, 24.9, 27.0, 33.7, 42.7, 49.8, 81.7, 112.3, 112.4, 116.2, 120.6, 122.5, 128.7, 129.3, 131.7, 134.1, 134.5, 143.4.

***2-Amino-4-(2-bromo-phenyl)-5, 6, 7 ,8-tetrahydro-4H-napathalene-1,3,3-tricarbonitrile (4al)*:**



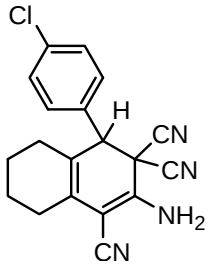
White solid; Yield: 675 mg, 89 %; m.p. 256-258 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{15}BrN_4$: C, 60.17; H, 3.99; N, 14.77 %. Found: C, 60.38; H, 4.02; N, 14.83 %; IR (KBr) cm^{-1}: 3445, 3355, 3203, 2949, 2851, 2216, 1623, 1471, 1440, 1390, 1271, 1025, 746, 558, 511; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.78 (2H, q, *J* = 12.9 Hz, CH_2), 1.30-1.46 (1H, m, CH), 1.62-1.65 (1H, m, CH), 1.99-2.18 (2H, m, CH_2), 2.83 (1H, t, *J* = 9.9 Hz, CH), 3.82 (1H, d, *J* = 12.3 Hz, CH), 5.73 (1H, s, CH), 7.33-7.40 (3H, m, arom. and NH_2), 7.54, (1H, t, *J* = 7.2 Hz, arom.), 7.74 (2H, dt, ^3J = 8.4 Hz and ^4J = 1.2Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 20.8, 24.8, 26.8, 34.8, 41.7, 49.3, 81.5, 111.5, 112.3, 116.0, 120.9, 126.6, 128.4, 128.6, 129.2, 131.0, 133.5, 133.6, 143.5.

2-Amino-4-(3-nitro-phenyl)-5,6,7,8-tetrahydro-4H-napathalene-1,3,3-tricarbonitrile (4aj):



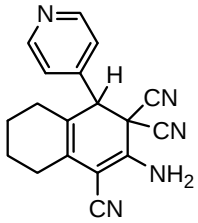
Yellow solid; Yield: 622 mg, 90 %; m.p. 159-161 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{15}N_5O_2$: C, 66.08; H, 4.38; N, 20.28 %. Found: C, 66.21; H, 4.41; N, 20.39 %; IR (KBr) cm^{-1}: 3417, 3332, 3231, 2932, 2210, 1654, 1531, 1350, 1102, 819, 727, 622, 464; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.82-0.87 (1H, m, CH), 1.41 (2H, br s, CH_2), 1.63 (1H, br s, CH), 2.20-2.27 (2H, m, CH_2), 2.87 (1H, br s, CH), 3.91 (1H, d, *J* = 12.0 Hz, CH), 5.72 (1H, s, CH), 7.38 (2H, s, NH_2), 7.46 (1H, s, arom.), 7.68-7.70 (1H, m, arom.), 8.28 (1H, d, *J*= 7.8 Hz, arom.), 8.37 (1H, s, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 22.0, 26.6, 27.8, 41.5, 49.1, 79.0, 111.5, 113.3, 116.4, 117.8, 120.3, 124.2, 124.4, 125.5, 130.7, 135.8, 143.4, 147.9.

2-Amino-4-(4-chloro-phenyl)-5,6,7,8-tetrahydro-4H-napathalene-1,3,3-tricarbonitrile (4ak):



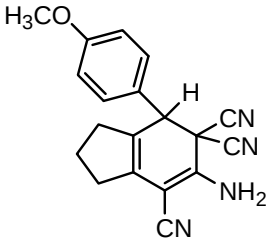
White solid; Yield: 609 mg, 91 %; m.p. 240-242 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{15}ClN_4$: C, 68.16; H, 4.52; N, 16.73 %. Found: C, 68.25; H, 4.54; N, 16.86 %; IR (KBr) cm^{-1}: 3419, 3342, 3245, 2939, 2869, 2211, 1643, 1491, 1390, 1272, 1094, 836, 568, 513, 427; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.81 (1H, q, *J* = 12.6 Hz, CH), 1.39-1.42 (2H, m, CH_2), 1.62(1H, br s, CH), 1.95-2.18 (2H, m, CH_2), 2.76 (1H, t, *J* = 10.2 Hz, CH), 3.60 (1H, d, *J* = 12.3 Hz, CH), 5.69 (1H, s, CH), 7.34 (2H, s, NH_2), 7.43-7.57 (4H, m, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 21.0, 24.9, 27.0, 33.8, 42.7, 49.8, 54.9, 81.7, 112.3, 112.4, 116.1, 120.5, 128.7, 133.7, 133.8, 134.2, 143.4.

2-Amino-4-pyridin-4-yl-5,6,7,8-tetrahydro-4H-napathalene-1,3,3-tricarbonitrile (4ao):



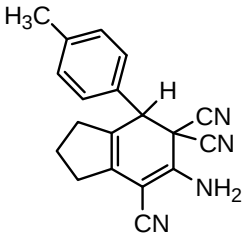
Pink solid; Yield: 554 mg, 92 %; m.p. 227-229 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{18}H_{15}N_5$: C, 71.74; H, 5.02; N, 23.24 %. Found: C, 71.90; H, 5.06; N, 23.35 %; IR (KBr) cm^{-1}: 3339, 3181, 2944, 2208, 1642, 1604, 1421, 1392, 1271, 1165, 1068, 838, 715, 642, 526; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.83 (1H, q, *J* = 12.3 Hz, CH), 1.41-1.37 (2H, m, CH_2), 1.63 (1H, br s, CH), 1.97-2.19 (2H, m, CH_2), 2.82-2.85 (1H, m, CH), 3.65 (1H, d, *J* = 12.3 Hz, CH), 5.71 (1H, s, CH), 7.37-7.54 (4H, m, arom.), 8.64 (2H, s, NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 20.9, 24.8, 26.9, 33.3, 42.1, 49.6, 81.7, 112.1, 112.2, 116.1, 117.8, 120.8, 128.4, 143.1, 143.5, 150.1.

5-Amino-7-(4-methoxy-phenyl) -1,2,3,7-tetrahydro-indene-4,6,6-tricarbonitrile (4ba):



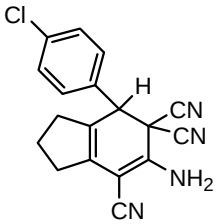
Light yellow solid; Yield: 569 mg, 90 %; m.p. 209-211 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{16}N_4O$: C, 72.13; H, 5.10; N, 17.71 %. Found: C, 72.32; H, 5.12; N, 17.84 %; IR (KBr) cm^{-1}: 3414, 3335, 3244, 2957, 2856, 2218, 1652, 1590, 1515, 1458, 1393, 1257, 1180, 1030, 840, 805, 611, 535; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.09-1.15 (1H, m, CH), 1.81-1.85 (1H, m, CH), 2.28 (2H, br s, CH_2), 3.23-3.29 (1H, m, CH), 3.52 (1H, d, *J*= 12.6 Hz, CH), 3.75 (3H, s, OCH_3), 5.44 (1H, s, CH), 6.97 (2H, d, *J*= 8.4 Hz, arom.), 7.41 (2H, d, *J*= 8.4 Hz, arom.), 7.61 (2H, s, NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 29.8, 31.4, 40.4, 43.1, 44.5, 50.8, 55.6, 77.5, 112.8, 112.9, 114.4, 116.4, 119.7, 126.8, 131.3, 135.8, 143.9, 146.6, 160.2, 162.3.

5-Amino-7-p-tolyl-1,2,3,7-tetrahydro-indene-4,6,6-tricarbonitrile (4bb):



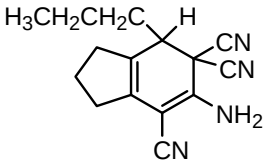
Yellowish white solid; Yield: 559 mg, 93 %; m.p. 179-181 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65 %. Found: C, 76.14; H, 5.40; N, 18.80 %; IR (KBr) cm^{-1}: 3419, 3331, 3241, 2956, 2860, 2216, 1650, 1588, 1393, 1277, 1160, 1042, 828, 612, 514; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.09-1.19 (1H, m, CH), 1.79-1.87 (1H, m, CH), 2.20-2.41 (5H, m, CH_3 and CH_2), 3.53 (1H, d, *J*= 12.6 Hz, CH), 5.45 (1H, s, CH), 7.22 (2H, d, *J*= 7.8 Hz, arom.), 7.38 (2H, d, *J*= 8.1Hz, arom.), 7.62 (2H, s, NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 21.2, 29.8, 31.4, 43.0, 44.3, 51.1, 77.5, 112.7, 112.9, 116.4, 118.2, 119.8, 129.6, 129.9, 132.0, 135.7, 139.0, 146.6, 162.3.

5-Amino-7-(4-chloro-phenyl)-1,2,3,7-tetrahydro-indene-4,6,6-tricarbonitrile (4bk):



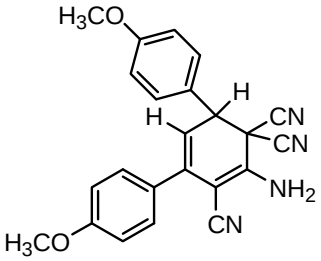
Yellow solid; Yield: 603 mg, 94 %; m.p. 209-211 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{18}H_{13}ClN_4$: C, 67.40; H, 4.08; N, 17.47 %. Found: C, 67.57; H, 4.09; N, 17.57 %; IR (KBr) cm^{-1}: 3411, 3337, 3243, 2947, 2858, 2213, 1647, 1548, 1491, 1457, 1392, 1266, 1089, 883, 512; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.16-1.20 (1H, m, CH), 1.79-1.90 (1H, m, CH), 2.21-2.29 (2H, m, CH_2), 3.30 (1H, s, CH), 3.96 (1H, d, *J*= 12.6 Hz, CH), 5.45 (1H, s, CH), 7.52 (4H, s, arom.), 7.66 (2H, s, NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 29.2, 31.0, 42.4, 43.6, 50.13, 77.2, 112.1, 112.3, 115.9, 119.6, 128.7, 130.4, 131.5, 133.6, 134.0, 135.0, 145.9.

5-Amino-7-(4-propyl-phenyl)-1,2,3,7-tetrahydro-indene-4,6,6-tricarbonitrile (4bh):



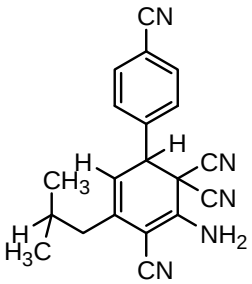
White solid; Yield: 620 mg, 90 %; m.p. 145-147 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{22}H_{24}N_4$: C, 76.71; H, 7.02; N, 16.27 %. Found: C, 76.87; H, 7.06; N, 16.42 %; IR (KBr) cm^{-1}: 3418, 3332, 3244, 2955, 2863, 2215, 1647, 1580, 1391, 1265, 1157, 1041, 825, 602, 511; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.89 (3H, t, *J* = 6.9 Hz, CH_3), 1.09-1.15 (1H, m, CH), 1.40-1.52 (2H, m, CH_2), 1.81-1.85 (1H, m, CH), 2.28 (2H, br s, CH_2), 2.69 (2H, t, *J* = 7.5 Hz, CH_2), 3.23-3.29 (1H, m, CH), 3.52 (1H, d, *J*= 12.6 Hz, CH), 5.44 (1H, s, CH), 7.61 (2H, s, NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 20.8, 22.6, 29.8, 31.4, 34.9, 43.1, 44.5, 50.8, 77.5, 112.8, 112.9, 116.5, 119.7, 131.7.

2-Amino-4,6-bis-(4-methoxy-phenyl)-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4fa):



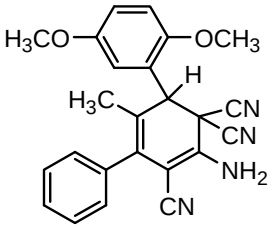
Light yellow solid; Yield: 711 mg, 93 %; m.p. 190-192 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{23}H_{18}N_4O_2$: C, 72.24; H, 4.74; N, 14.65 %. Found: C, 72.37; H, 4.76; N, 14.73 %; IR (KBr) cm^{-1}: 3418, 3330, 3243, 3211, 2935, 2835, 2206, 1636, 1581, 1493, 1452, 1390, 1264, 1221, 1040, 824, 764, 705, 464; δ_H ppm (300 MHz; DMSO-D6; TMS) 3.78 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 4.25 (1H, d, *J* = 3.6 Hz, CH), 5.79 (1H, d, *J* = 4.5 Hz, CH), 6.97 (2H, d, *J* = 8.7 Hz, arom.), 7.03 (2H, dd, *J*= 2.7 Hz and *J*= 8.7 Hz, arom.), 7.63 (2H, s, NH_2), 7.80 (2H, d, *J*= 8.7 Hz, arom.), 8.11 (2H, dd, *J*= 2.7 Hz and *J*= 9.3 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 44.7, 51.3, 55.2, 56.2, 79.7, 111.4, 112.9, 113.1, 113.8, 114.0, 115.0, 116.6, 120.8, 121.1, 127.9, 128.5, 128.7, 128.8, 130.4, 137.0, 143.9, 147.6, 151.7.

2-Amino-6-(4-cyano-phenyl)-4-isobutyl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4hm):



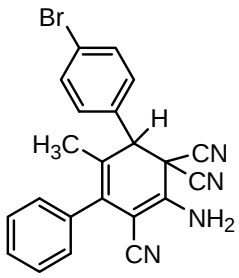
Wlite solid; Yield: 596 mg, 91 %; m.p. 175-177 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{20}H_{17}N_5$: C, 73.37; H, 5.23; N, 21.39 %. Found: C, 73.57; H, 5.25; N, 21.49 %; IR (KBr) cm^{-1}: 3411, 3335, 3242, 2947, 2859, 2212, 1649, 1546, 1491, 1456, 1393, 1267, 1088, 882, 512; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.91 (3H, s, CH_3), 0.93 (3H, s, CH_3), 1.90-1.99 (1H, m, CH), 2.41 (2H, d, *J* = 7.2 Hz, CH_2), 4.27 (1H, d, *J* = 4.2 Hz, CH), 5.79 (1H, d, *J* = 4.5 Hz, CH), 7.22 (2H, s, NH_2), 7.77 (2H, d, *J* = 8.4 Hz, arom.), 7.94 (2H, d, *J* = 8.4 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 22.1, 29.3, 43.6, 77.5, 112.0, 112.1, 115.4, 115.8, 118.4, 118.9, 129.6, 131.3, 132.6, 142.1, 147.5, 151.8, 153.6.

2-Amino-6-(2,5-dimethoxy-phenyl)-5-methyl-4-phenyl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4ie):



Light yellow solid; Yield: 729 mg, 92 %; m.p. 198-200 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{24}H_{20}N_4O_2$: C, 72.71; H, 5.08; N, 14.13 %. Found: C, 72.77; H, 5.11; N, 14.16 %; IR (KBr) cm^{-1}: 3420, 3329, 3245, 3210, 2935, 2834, 2203, 1639, 1582, 1497, 1452, 1392, 1265, 1221, 1038, 818, 765, 705, 465; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.47 (3H, s, CH_3), 3.67 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 4.67 (1H, s, CH), 6.80 (1H, d, *J*= 3.0 Hz, arom.), 6.98 (1H, d, *J*= 3.3 Hz, arom.), 7.04 (1H, s, arom.), 7.14 (2H, d, *J*= 6.9 Hz, arom.), 7.35 (1H, d, *J*= 6.9 Hz, arom.), 7.41 (2H, d, *J*= 7.2Hz, arom.), 7.52 (2H, s, NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 18.6, 44.7, 55.2, 56.2, 79.7, 111.4, 112.9, 113.1, 113.8, 114.0, 115.1, 116.6, 120.7, 121.1, 128.0, 128.5, 128.6, 128.8, 130.4, 137.1, 144.0, 147.6, 151.7, 153.2.

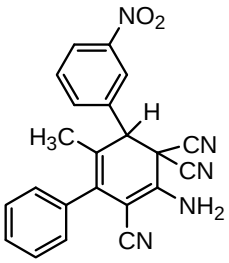
2-Amino-6-(4-bromo-phenyl)-5-methyl-4-phenyl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4ih):



Light yellow solid; Yield: 772 mg, 93 %; m.p. 227-229 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{22}H_{15}BrN_4$: C, 63.63; H, 3.64; N, 13.49 %. Found: C, 63.79; H, 3.65; N, 13.61 %; IR (KBr) cm^{-1}: 3439, 3341, 3210, 2919, 2856, 2207, 1637, 1583, 1486, 1442, 1391, 1263, 1215, 1072, 1011, 828, 763, 701, 514; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.48 (3H, s, CH_3), 4.65 (1H, s, CH), 7.17 (2H, d, *J*= 6.9 Hz, arom.), 7.29-7.34 (2H, m, arom.), 7.36-7.42 (2H, m, arom.), 7.51 (2H, s, NH_2), 7.66 (2H, d, *J*= 9.3 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 18.6, 41.6, 50.2, 79.9, 111.4, 113.6, 116.6, 122.9, 128.0, 128.4,

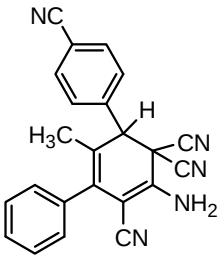
128.5, 128.7, 128.9, 130.3, 130.8, 131.0, 131.6, 131.7, 132.0, 132.1, 136.96, 137.03, 143.9.

2-Amino-5-methyl-6-(3-nitro-phenyl)-4-phenyl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4ij):



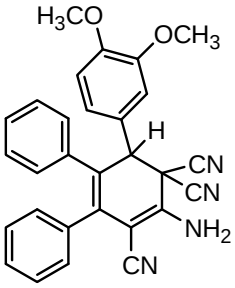
Light yellow solid; Yield: 725 mg, 95 %; m.p. 114-116 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{22}H_{15}N_5O_2$: C, 69.28; H, 3.96; N, 18.36 %. Found: C, 69.47; H, 3.94; N, 18.27 %; IR (KBr) cm^{-1}: 3424, 3322, 3239, 3203, 2920, 2201, 1639, 1580, 1530, 1349, 1215, 1090, 736, 898; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.47 (s, 3H, CH_3), 4.89 (1H, s, CH), 7.15-7.17 (2H, m, 2H, arom.), 7.32-7.42 (m, 3H, arom.), 7.54 (2H, s, NH_2), 7.69-7.75 (m, 1H, arom.), 7.82 (br s, 1H, arom.), 8.23 (1H, d, *J*= 8.1 Hz, arom.), 8.31 (1H, s, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 18.6, 41.6, 49.6, 79.9, 111.3, 113.3, 116.4, 120.2, 124.4, 124.5, 128.1, 128.6, 128.9, 130.9, 131.0, 134.7, 136.0, 136.8, 143.8, 148.0.

2-Amino-6-(4-cyano-phenyl)-5-methyl-4-phenyl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4im):



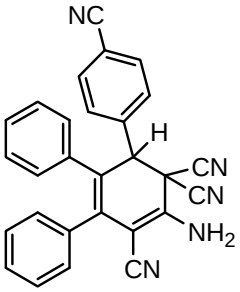
Yellowish white solid; Yield: 679 mg, 94 %; m.p. 180-182 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{23}H_{15}N_5$: C, 76.44; H, 4.18; N, 19.38 %. Found: C, 76.31; H, 4.19; N, 19.50 %; IR (KBr) cm^{-1}: 3338, 3210, 3062, 2924, 2209, 1639, 1581, 1498, 1441, 1391, 1263, 1022, 701, 558; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.48 (3H, s, CH_3), 4.80 (1H, s, CH), 7.18 (2H, d, *J*= 6.9 Hz, arom.), 7.37-7.46 (3H, m, arom.), 7.57 (2H, s, NH_2), 7.63 (2H, d, *J*= 8.4 Hz, arom.), 7.91 (2H, d, *J*= 8.4 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 17.4, 18.6, 41.5, 50.3, 80.0, 97.6, 111.3, 112.3, 113.4, 116.5, 118.4, 120.1, 127.5, 128.1, 128.4, 128.6, 128.8, 128.9, 129.8, 130.5, 130.8, 132.6, 132.7, 133.0, 136.9, 138.3, 142.7, 143.9, 150.9.

2-Amino-6-(3,4-dimethoxy-phenyl)-4,5-diphenyl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4je):



Yellow solid; Yield: 862 mg, 94 %; m.p. 198-200 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{29}H_{22}N_4O_2$: C, 75.97; H, 4.84; N, 12.22 %. Found: C, 76.13; H, 4.85; N, 12.09 %; IR (KBr) cm^{-1}: 3331, 3204, 3060, 2932, 2204, 1641, 1578, 1512, 1450, 1259, 1142, 1022, 700; δ_H ppm (300 MHz; DMSO-D6; TMS) 3.67 (3H, s, OCH_3), 3.71 (3H, s, OCH_3), 4.92 (1H, s, CH), 6.74-6.77 (2H, m, arom.), 6.98-7.01 (3H, m, arom.), 7.08-7.11 (3H, m, arom.), 7.13-7.14 (2H, m, arom.), 7.19-7.24 (2H, m, arom.), 7.34 (1H, s, arom.), 7.70 (2H, s, NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 43.18, 51.31, 55.78, 55.88, 79.0, 79.4, 79.9, 80.5, 111.8, 112.4, 113.8, 114.1, 116.9, 122.6, 124.2, 125.3, 126.0, 127.2, 128.2, 128.6, 128.8, 128.9, 129.5, 130.0, 133.3, 137.6, 139.4, 146.1, 148.9, 149.9.

2-Amino-6-(4-cyano-phenyl)-4,5-diphenyl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (4jm):

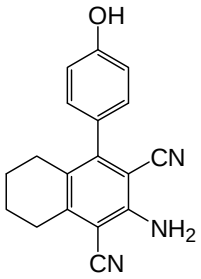


Yellow solid; Yield: 788 mg, 93 %; m.p. 202-204 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{28}H_{17}N_5$: C, 79.42; H, 4.05; N, 16.54 %. Found: C, 79.36; H, 4.06; N, 16.64 %; IR (KBr) cm^{-1}: 3336, 3225, 3058, 2930, 2859, 2210, 1638, 1566, 1496, 1442, 1397, 1257, 700; δ_H ppm (300 MHz; DMSO-D6; TMS) 5.26 (1H, s, CH), 6.71-6.74 (2H, m, arom.), 6.99-7.01 (3H, m, arom.), 7.11-7.13 (2H, m, arom.), 7.20-7.24 (m, 3H, arom.), 7.72 (2H, d, *J*= 8.4 Hz, arom.), 7.83 (2H, s, NH_2), 7.90 (2H, d, *J*= 8.2 Hz, arom.);

δ_C ppm (75 MHz, DMSO-d_6, TMS) 42.1, 49.9, 80.2, 110.9, 112.2, 113.2, 115.3, 116.2, 118.2, 123.5, 126.5, 126.9, 127.1, 127.5, 127.7, 127.9, 128.1, 128.3, 128.5, 128.7, 129.0, 129.5, 130.3, 130.4, 130.8, 131.1, 132.8, 133.7, 136.3, 136.8, 138.3, 142.4, 145.2, 150.2, 151.7.

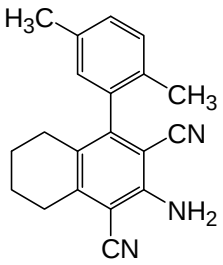
Spectroscopic characterization of the aromatic products (A-D-A system) 5ac-5kk

2-Amino-4-(4-hydroxy-phenyl)-5,6,7,8-tetrahydro-naphthalene-1,3-dicarbonitrile (5ac):



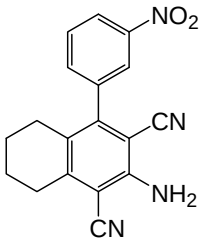
Light yellow solid; Yield: 515 mg, 89 %; m.p. 269-271 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52 %. Found: C, 74.92; H, 5.24; N, 14.30 %; IR (KBr) cm^{-1}: 3467, 3373, 3244, 2939, 2211, 1638, 1563, 1517, 1449, 1267, 1201, 1175, 825, 547, 422; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.19-1.21 (2H, m, CH_2), 1.35 (2H, br s, CH_2), 1.83 (2H, t, J = 5.4 Hz, CH_2), 2.14 (1H, s, CH), 2.98 (1H, s, CH), 5.95 (2H, s, NH_2), 6.49 (2H, d, J = 8.4 Hz, arom.), 6.70 (2H, d, J = 8.2 Hz, arom.), 9.34 (1H, s, OH); δ_C ppm (75 MHz, DMSO-d_6, TMS) 21.5, 22.2, 27.0, 29.1, 95.4, 96.0, 115.4, 115.6, 116.1, 117.8, 124.8, 127.7, 129.7, 146.2, 150.5, 150.8, 157.7, 162.0, 188.4.

2-Amino-4-(2,5-dimethyl-phenyl)-5,6,7,8-tetrahydro-naphthalene-1,3-dicarbonitrile (5ad):



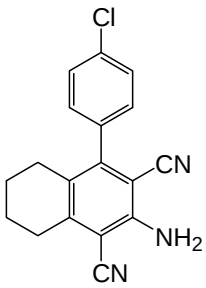
White solid; Yield: 542 mg, 90 %; m.p. 206-208 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94 %. Found: C, 79.84; H, 6.36; N, 14.02 %; IR (KBr) cm^{-1}: 3473, 3344, 3235, 2934, 2219, 1635, 1564, 1450, 1277, 1170, 807, 507, 464; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.52-1.54 (2H, m, CH_2), 1.60-1.67 (2H, m, CH_2), 1.90 (3.48H, s), 2.01-2.11 (1.52H, m), 2.25 (3H, s, CH_3), 2.80 (2H, t, J = 6.3 Hz, CH_2), 6.36 (2H, s, NH_2), 6.82 (1H, s, arom.), 7.11 (1H, d, J = 7.8 Hz, arom.), 7.20 (1H, d, J = 7.8 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 18.5, 20.6, 21.5, 21.9, 26.4, 29.0, 95.4, 95.7, 115.4, 115.5, 124.2, 128.2, 129.3, 130.2, 131.3, 135.3, 136.9, 147.0, 150.0, 150.8.

2-Amino-4-(3-nitro-phenyl)-5,6,7,8- tetrahydro-naphthalene-1,3-dicarbonitrile (5af):



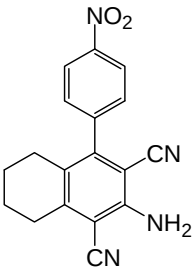
Yellow solid; Yield: 586 mg, 92 %; m.p. 192-194 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{18}H_{14}N_4O_2$: C, 67.91; H, 4.43; N, 17.60 %. Found: C, 68.10; H, 4.44; N, 17.75 %; IR (KBr) cm^{-1}: 3415, 3345, 3247, 2936, 2217, 1653, 1567, 1525, 1459, 1347, 1274, 1167, 1090, 806, 714, 532, 472; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.53 (2H, br s, CH_2), 1.67 (br 2H, s, CH_2), 2.10 (2H, br s, CH_2), 2.80-2.82 (2H, m, CH_2), 6.51 (2H, br s, NH_2), 7.77 (2H, br s, arom.), 8.14 (1H, br s, arom.), 8.28 (1H, br s, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 21.3, 22.0, 26.8, 29.1, 95.3, 96.5, 115.3, 115.7, 123.4, 123.6, 124.2, 130.6, 135.4, 138.9, 147.5, 147.9, 150.8.

2-Amino-4-(4-chloro-phenyl)-5,6,7,8-tetrahydro-naphthalene-1,3-dicarbonitrile (5ak):



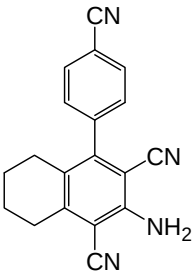
Yellow solid; Yield: 579 mg, 94 %; m.p. 246-248 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{18}H_{14}ClN_3$: C, 70.24; H, 4.58; N, 13.65 %. Found: C, 70.38; H, 4.59; N, 13.75 %; IR (KBr) cm^{-1}: 3341, 3235, 2932, 2216, 1638, 1563, 1452, 1269, 1084, 818; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.52-1.54 (2H, m, CH_2), 1.65-1.69 (2H,m, CH_2), 2.10 (2H, t, J = 6.3 Hz, CH_2), 2.79 (2H, t, J = 6.3 Hz, CH_2), 6.43 (2H, s, NH_2), 7.27 (2H, d, J = 8.4 Hz, 2H, arom.), 7.52 (2H, d, J = 8.4 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 21.4, 22.0, 26.9, 29.1, 95.4, 96.1, 115.8, 124.2, 128.8, 130.4, 133.5, 136.2, 147.1, 148.9, 150.8.

2-Amino-4-(4-nitro-phenyl)-5,6,7,8-tetrahydro-naphthalene-1,3-dicarbonitrile (5al):



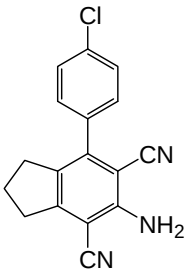
Yellow solid; Yield: 598 mg, 94 %; m.p. 310-312 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{18}H_{14}N_4O_2$: C, 67.91; H, 4.43; N, 17.60 %. Found: C, 68.07; H, 4.44; N, 17.68 %; IR (KBr) cm^{-1}: 3416, 3305, 3139, 2943, 2214, 1646, 1559, 1522, 1346, 1248, 1100, 842, 705, 550, 471; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.55-1.57 (2H, m, CH_2), 1.70 (br s, 2H, CH_2), 2.13 (2H, br s, CH_2), 2.68 (2H, br s, CH_2), 6.66 (2H, s, NH_2), 7.59 (2H, d, J = 8.1 Hz, arom.), 8.31 (2H, d, J = 8.1 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 22.0, 22.3, 25.7, 32.9, 123.8, 130.0, 142.4, 143.2, 147.6, 157.9, 161.5.

2-Amino-4-(4-cyano-phenyl)-5,6,7,8- tetrahydro-naphthalene-1,3-dicarbonitrile (5am):



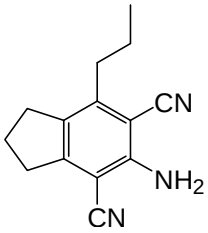
White solid; Yield: 555 mg, 93 %; m.p. 257-259 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{14}N_4$: C, 76.49; H, 4.73; N, 18.78 %. Found: C, 76.66; H, 4.74; N, 18.90 %; IR (KBr) cm^{-1}: 3438, 3336, 3238, 2924, 2221, 1643, 1563, 1456, 1271, 1166, 825, 558, 511, 452; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.52-1.53 (2H, m, CH_2), 1.67 (2H, br s, CH_2), 2.07 (2H, br s, CH_2), 2.80 (2H, br s, CH_2), 6.49 (2H, s, NH_2), 7.49 (2H, d, J = 7.8 Hz, arom.), 7.95 (2H,d, J = 7.8 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 21.3, 21.9, 26.8, 29.1, 96.4, 111.6, 115.3, 115.5, 117.8, 118.5, 123.8, 129.7, 132.7, 142.3, 147.4, 148.3, 150.8, 161.9.

5-Amino-7-(4-chloro-phenyl)-indan-4,6-dicarbonitrile (5bk):



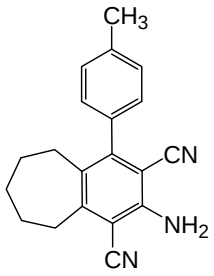
Yellow solid; Yield: 541 mg, 92 %; m.p. 198-200 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{17}H_{12}ClN_3$: C, 69.51; H, 4.12; N, 14.30 %. Found: C, 69.64; H, 4.11; N, 14.38 %; IR (KBr) cm^{-1}: 3415, 3350, 3250, 2957, 2215, 1651, 1567, 1456, 1263, 1089, 1012, 829, 751, 516, 470; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.93 (2H, t, *J* = 6.9 Hz, CH_2), 2.55 (2H, t, *J* = 6.9 Hz, CH_2), 2.95 (2H, t, *J* = 6.9 Hz, CH_2), 6.55 (2H, s, NH_2), 7.40 (2H, d, *J* = 7.4 Hz, arom.), 7.52 (2H, d, *J* = 8.1 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 24.1, 31.0, 31.3, 33.6, 92.7, 94.1, 115.5, 116.0, 116.3, 125.5, 128.7, 128.8, 130.5, 130.9, 133.1, 135.2, 135.4, 135.6, 142.8, 144.5, 152.4, 153.7, 155.2.

5-Amino-7-propyl-indan-4,6-dicarbonitrile (5bh):



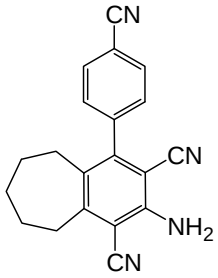
Cream colored solid; Yield: 410 mg, 91 %; m.p. 149-151 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65 %. Found: C, 74.80; H, 6.72; N, 18.66 %; IR (KBr) cm^{-1}: 3410, 3344, 3243, 2963, 2927, 2871, 2214, 1648, 1574, 1457, 1270, 1085, 545; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.89 (3H, t, *J* = 6.9 Hz, CH_3), 1.40-1.52 (2H, m, CH_2), 1.90-2.00 (2H, m, CH_2), 2.53 (2H, t, *J* = 7.8 Hz, CH_2), 2.69 (2H, t, *J* = 7.5 Hz, CH_2), 2.85 (2H, t, *J* = 7.5 Hz, CH_2), 6.30 (2H, s, NH_2); δ_C ppm (75 MHz, DMSO-d_6, TMS) 20.8, 22.61, 24.1, 30.6, 31.6, 33.8, 34.9, 91.4, 95.0, 116.02, 116.6, 131.7, 147.7, 152.6, 154.8.

2-Amino-4-p-tolyl-6,7,8,9-tetrahydro-5H-benzocycloheptene-1,3-dicarbonitrile (5cb):



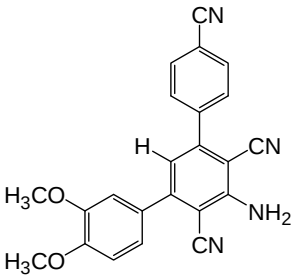
White solid; Yield: 561 mg, 93 %; m.p. 179-181 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94 %. Found: C, 79.88; H, 6.34; N, 13.99 %; IR (KBr) cm^{-1}: 3414, 3348, 3248, 2934, 2858, 2214, 1652, 1558, 1453, 1286, 1196, 962, 819, 512, 467; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.43-1.46 (2H, m, CH_2), 1.71-1.78 (4H, m), 2.39 (s, 3H, CH_3), 2.46-2.50 (2H, m, CH_2), 3.04-3.08 (2H, m, CH_2), 6.02 (2H, br s, NH_2), 7.07 (2H, d, *J* = 8.1 Hz, arom.), 7.25 (2H, d, *J* = 9.0 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 20.9, 26.5, 27.0, 29.8, 30.8, 33.9, 95.4, 96.0, 115.4, 115.6, 116.1, 117.8, 124.8, 127.7, 129.7, 146.6, 150.5, 150.8, 157.7, 162.0.

2-Amino-4-(4-cyano-phenyl)-6,7,8,9-tetrahydro-5H-benzocycloheptene-1,3-dicarbonitrile (5cm):



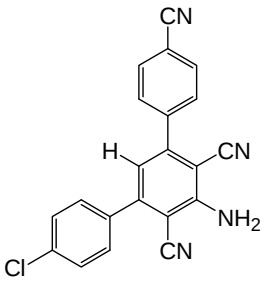
White solid; Yield: 575 mg, 92 %; m.p. 226-228 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{20}H_{16}N_4$: C, 76.90; H, 5.16; N, 17.94 %. Found: C, 71.07; H, 5.17; N, 18.02 %; IR (KBr) cm^{-1}: 3415, 3353, 3254, 2930, 2220, 1657, 1562, 1456, 1293, 1198, 966, 835, 559, 513, 475; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.35 (2H, br s, CH_2), 1.62-1.67 (m, 4H), 2.27-2.30 (2H, m, CH_2), 2.97-2.99 (2H, m, CH_2), 6.52 (2H, s, NH_2), 7.46 (2H, d, *J* = 7.8 Hz, arom.), 7.96 (2H, d, *J* = 7.8 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 26.5, 27.0, 29.8, 30.8, 33.9, 94.2, 97.0, 111.6, 115.7, 115.8, 118.6, 129.8, 129.9, 132.7, 143.0, 146.9, 151.0, 153.9.

2-Amino-6-(3,4-dimethoxy-phenyl)-4-(4-cyano-phenyl)benzene-1,3-dicarbonitrile (5dm):



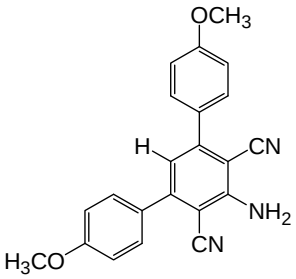
Yellow solid; Yield: 708 mg, 93 %; m.p. 237-239 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{23}H_{16}N_4O_2$: C, 72.62; H, 4.24; N, 14.73 %. Found: C, 72.77; H, 4.25; N, 14.81 %; IR (KBr) cm^{-1}: 3482, 3390, 3238, 2964, 2925, 2844, 2214, 1623, 1572, 1517, 1467, 1414, 1262, 1136, 1016, 839, 798, 766, 555, 491; δ_H ppm (300 MHz; DMSO-D6; TMS) 3.77 (3H, s, OCH_3), 3.78 (s, 3H, OCH_3), 6.84 (3H, s, CN and NH_2), 7.06 (1H, d, *J*= 9.0 Hz, arom.), 7.18 (2H, d, *J*= 6.9 Hz, arom.), 7.80 (2H, d, *J*= 8.1 Hz, arom.), 7.98 (2H, d, *J*= 8.1 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 55.71, 55.74, 93.3, 94.8, 111.7, 112.1, 112.4, 115.8, 116.2, 117.8, 118.4, 121.5, 129.5, 129.8, 132.6, 142.2, 147.9, 148.7, 150.05, 150.11, 154.2.

2-Amino-6-(4-chloro-phenyl)-4-(4-cyano-phenyl)benzene-1,3-dicarbonitrile (5em):



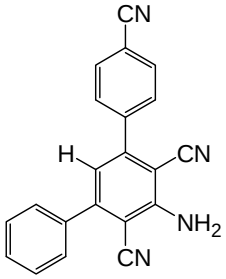
Yellow solid; Yield: 667 mg, 94 %; m.p. 233-235 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{21}H_{11}ClN_4$: C, 71.09; H, 3.13; N, 15.79 %. Found: C, 71.22; H, 3.14; N, 15.90 %; IR (KBr) cm^{-1}: 3464, 3349, 3243, 2222, 1646, 1577, 1499, 1286, 1092, 1014, 829, 554; δ_H ppm (300 MHz; DMSO-D6; TMS) 6.82 (1H, s, CH), 6.95 (2H, s, NH_2), 7.56 (2H, d, *J*= 8.7 Hz, arom.), 7.64 (2H, d, *J*= 8.4 Hz, arom.), 7.81 (2H, d, *J*= 8.1 Hz, arom.), 7.98 (2H, d, *J*= 8.1 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 94.3, 94.9, 112.2, 115.7, 115.8, 117.8, 118.5, 128.3, 128.8, 129.3, 130.1, 130.4, 131.2, 132.4, 133.0, 134.6, 136.1, 142.0, 148.2, 148.9, 154.1, 162.0.

2-Amino-4,6-bis(4-methoxy-phenyl)benzene-1,3-dicarbonitrile (5fa):



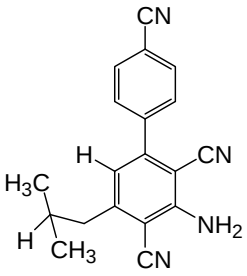
Yellow solid; Yield: 675 mg, 95 %; m.p. 235-237 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.82 %. Found: C, 74.25; H, 4.82; N, 11.83 %; IR (KBr) cm^{-1}: 3462, 3347, 3240, 2217, 1647, 1576, 1509, 1285, 1091, 1012, 828, 544; δ_H ppm (300 MHz; DMSO-D6; TMS) 3.78 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 6.84 (3H, s, CH and NH_2), 6.97 (2H, d, *J*= 8.7 Hz, arom.), 7.12 (2H, d, *J*= 10.2 Hz, arom.), 7.44 (2H, d, *J*= 9.3 Hz, arom.), 7.64 (2H, d, *J*= 8.7 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 55.7, 55.8, 93.2, 94.8, 112.1, 112.4, 115.9, 116.2, 117.8, 118.4, 121.5, 129.1, 129.2, 129.6, 129.8, 132.6, 142.3, 147.9, 148.7, 150.05, 150.12, 154.2.

2-Amino-4-(4-cyano-phenyl)-6-phenylbenzene-1,3-dicarbonitrile (5gm):



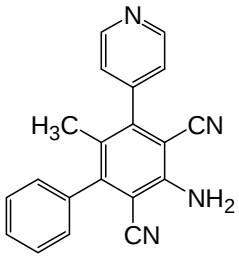
Yellow solid; Yield: 596 mg, 93 %; m.p. 172-174 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{21}H_{12}N_4$: C, 78.73; H, 3.78; N, 17.49 %. Found: C, 78.86; H, 3.79; N, 17.59 %; IR (KBr) cm^{-1}: 3464, 3352, 3236, 3067, 2217, 1633, 1575, 1510, 1424, 1284, 1128, 839, 768, 698, 619, 554, 498; δ_H ppm (300 MHz; DMSO-D6; TMS) 6.81 (1H, s, CH), 6.91 (2H, s, NH_2), 7.48-7.50 (m, 3H, arom.), 7.59-7.62 (m, 2H, arom.), 7.81 (2H, d, *J*= 8.1 Hz, arom.), 7.97 (2H, d, *J*= 8.1 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 94.0, 95.0, 112.2, 115.7, 115.9, 118.5, 127.6, 128.7, 128.8, 129.1, 129.2, 129.5, 129.6, 129.8, 132.0, 137.3, 142.0, 146.1, 148.1, 150.2, 154.1, 170.2.

2-Amino-4-isobutyl-6-phenylbenzene-1,3-dicarbonitrile (5hm):



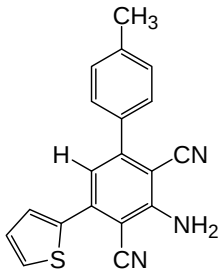
White solid; Yield: 547 mg, 91 %; m.p. 179-181 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65 %. Found: C, 76.13; H, 5.36; N, 18.66 %; IR (KBr) cm^{-1}: 3426, 3352, 3248, 2956, 2218, 1644, 1575, 1434, 1297, 839, 548; δ_H ppm (300 MHz; DMSO-D6; TMS) 0.89 (3H, s, CH_3), 0.91 (3H, s, CH_3), 1.93-1.97 (1H, m, CH), 2.62 (2H, d, *J* = 7.2 Hz, CH_2), 6.73 (1H, s, CH), 6.78 (2H, s, NH_2), 7.74 (2H, d, *J* = 8.1 Hz, arom.), 7.99 (2H, d, *J* = 8.4 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 22.2, 29.4, 43.5, 92.8, 96.8, 112.0, 115.4, 115.8, 118.4, 119.0, 129.6, 132.6, 142.2, 147.6, 151.8, 153.5.

3-Amino-6-methyl-5-pyridin-4-yl-biphenyl-2,4-dicarbonitrile (5io):



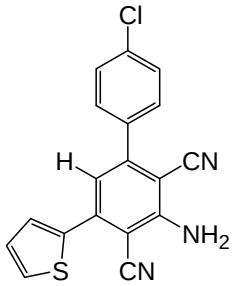
Cream colored solid; Yield: 583 mg, 94 %; m.p. 279-281 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05 %. Found: C, 77.55; H, 4.55; N, 18.18 %; IR (KBr) cm^{-1}: 3373, 3171, 2218, 1659, 1560, 1447, 1414, 1264, 1218, 1000, 827, 764, 695, 647, 570, 534; δ_H ppm (300 MHz; DMSO-D6; TMS) 1.55 (3H, s, CH_3), 6.66 (2H, s, NH_2), 7.31 (2H, d, *J*= 6.6 Hz, arom.), 7.40 (d, J= 6.4 Hz, 3H), 7.48 (2H,d, *J*= 8.1 Hz, arom.), 8.71 (2H,d, *J*= 4.95 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 17.3, 96.0, 97.7, 115.4, 115.5, 122.1, 123.5, 128.4, 128.6, 128.8, 137.5, 145.7, 147.5, 150.1, 150.8, 150.9.

3-Amino-4'-methyl-5-thiophen-2-yl-biphenyl-2,4-dicarbonitrile (5kb):



Yellowish white solid; Yield: 574 mg, 91 %; m.p. 227-229 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{19}H_{13}N_3S$: C, 72.36; H, 4.15; N, 13.32 %. Found: C, 72.50; H, 4.15; N, 13.41 %; IR (KBr) cm^{-1}: 3439, 3345, 3239, 2208, 1636, 1577, 1495, 1442, 1369, 1259, 1077, 752, 699, 473; δ_H ppm (300 MHz; DMSO-D6; TMS) 2.34 (3H, s, CH_3), 6.79 (1H, s, CH), 6.83 (2H, s, NH_2), 7.22 (2H, t, *J*=7.8 Hz, 2-Acetyl thiophene), 7.30 (2H, d, *J*= 8.4 Hz, 2H, arom.), 7.47 (2H, d, *J*= 7.8 Hz, arom.), 7.70 (1H, d, *J*= 3.6 Hz, 2-Acetyl thiophene), 7.80 (1H,d, *J*= 4.8 Hz, 2-Acetyl thiophene); δ_C ppm (75 MHz, DMSO-d_6, TMS) 20.9, 92.1, 94.0, 116.1, 116.3, 117.7, 128.4, 129.3, 129.4, 129.7, 129.7, 134.5, 138.3, 139.4, 141.6, 150.2, 154.6.

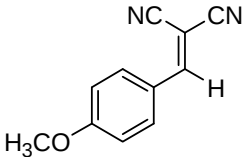
3-Amino-4'-chloro-5-thiophen-2-yl-biphenyl-2,4-dicarbonitrile (5kk):



Light yellow solid; Yield: 618 mg, 92 %; m.p. 279-281 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{18}H_{10}ClN_3S$: C, 64.38; H, 3.00; N, 12.51 %. Found: C, 64.39; H, 3.00; N, 12.60 %; IR (KBr) cm^{-1}: 3464, 3355, 3246, 3113, 2216, 1647, 1569,1498, 1428, 1291, 1247, 1092, 823, 707, 503; δ_H ppm (300 MHz; DMSO-D6; TMS) 6.86 (3H, br s, CH and NH_2), 7.44 (1H, br s, 2-Acetyl thiophene), 7.60 (br s, 4H, arom.), 7.71 (1H, br s, 2-Acetyl thiophene), 7.82 (1H, br s, 2-Acetyl thiophene); δ_C ppm (75 MHz, DMSO-d_6, TMS) 117.7, 128.4, 128.8, 129.4, 129.9, 130.5, 134.5, 136.1, 141.7, 154.5, 161.9.

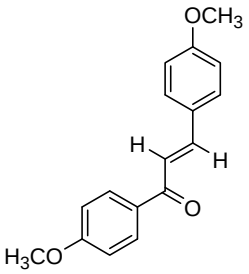
Spectroscopic characterization of the intermediates 6, 9 and 10

2-(4-Methoxy-benzylidene)-malononitrile (6):



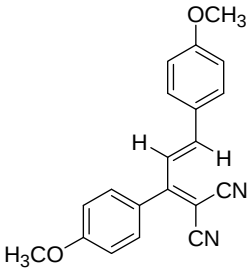
Light yellow solid; Yield: 357 mg, 97 %; m.p. 111-113 °C (recrystallized from EtOAc/DCM); Anal. Calcd for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.21 %. Found: C, 71.74; H, 4.38; N, 15.20 %; IR (KBr) cm^{-1}: 2214, 1603, 1565, 1504, 1272, 1178, 1014, 830, 609; δ_H ppm (300 MHz; $CDCl_3$; TMS) 3.89 (3H, s, OCH_3), 6.99 (2H, dd, *J*= 3.0 Hz and *J*= 11.7 Hz, arom.), 7.63 (1H, s, CH), 7.89 (2H, dd, *J*= 3.0 Hz and *J*= 11.9 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 55.8, 78.6, 113.4, 114.4, 115.2, 124.1, 133.5, 158.9, 164.9.

1,3-Bis-(4-methoxy-phenyl)-propenone (9):



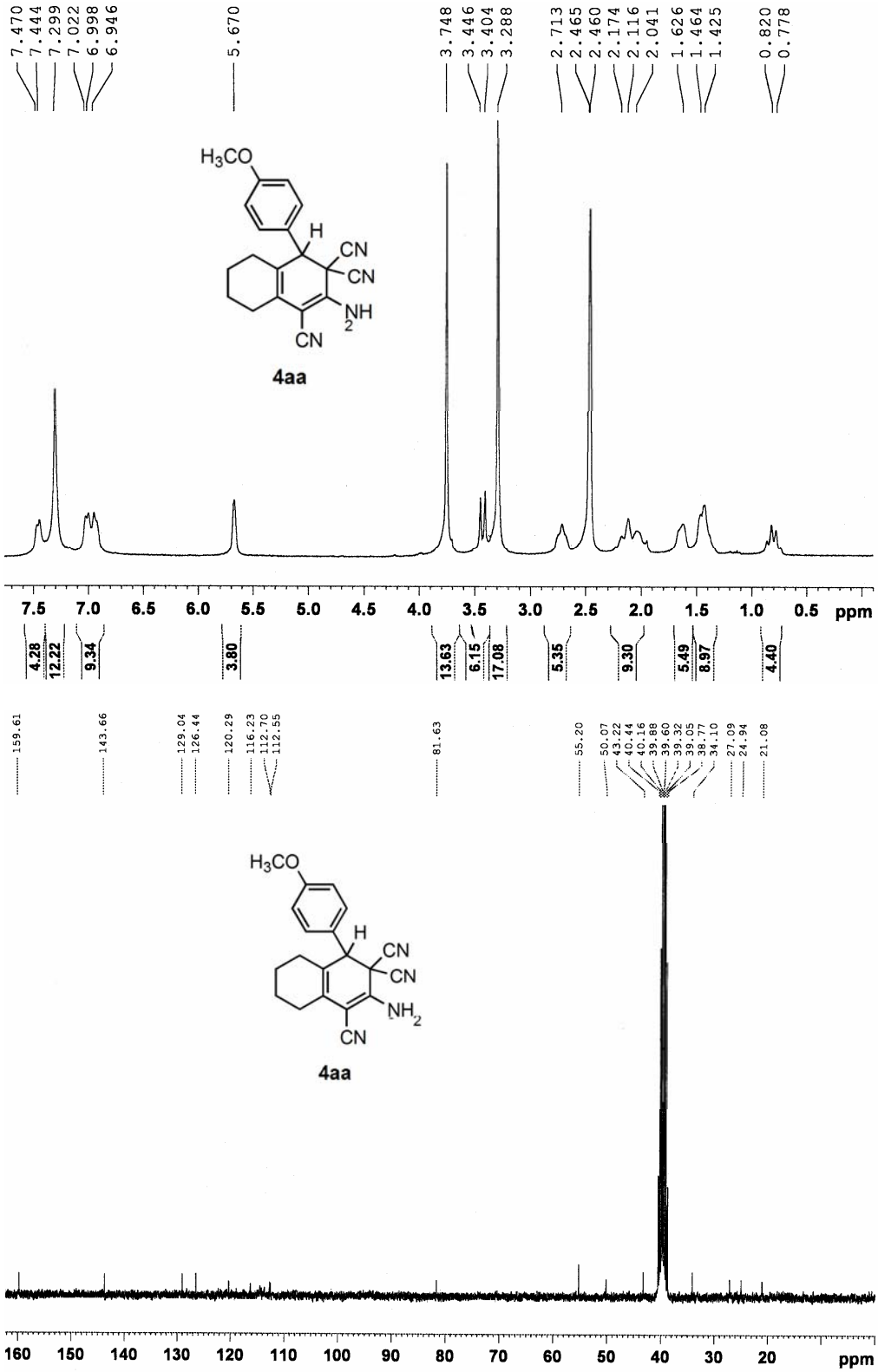
White solid; Yield: 515 mg, 96 %; m.p. 94-96 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01 %. Found: C, 76.11; H, 6.01 %; IR (KBr) cm^{-1}:1597, 1507, 1251, 1169, 1020, 818, 524; δ_H ppm (300 MHz, DMSO-d_6, TMS) 3.78 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 6.97 (2H, d, *J*= 8.8 Hz, arom.), 7.03 (2H, dd, *J*= 2.7 Hz and *J*= 8.7 Hz, arom.), 7.64 (1H, d, *J*= 15.5 Hz, CH), 7.77 (1H, d, *J*= 15.3 Hz, CH), 7.80 (2H, d, *J*= 8.7 Hz, arom.), 8.11 (2H, dd, *J*= 2.7 Hz and *J*= 9.3 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 55.4, 55.6, 114.0, 114.4, 119.6, 127.5, 130.7, 130.8, 143.1, 161.3, 163.1, 187.3.

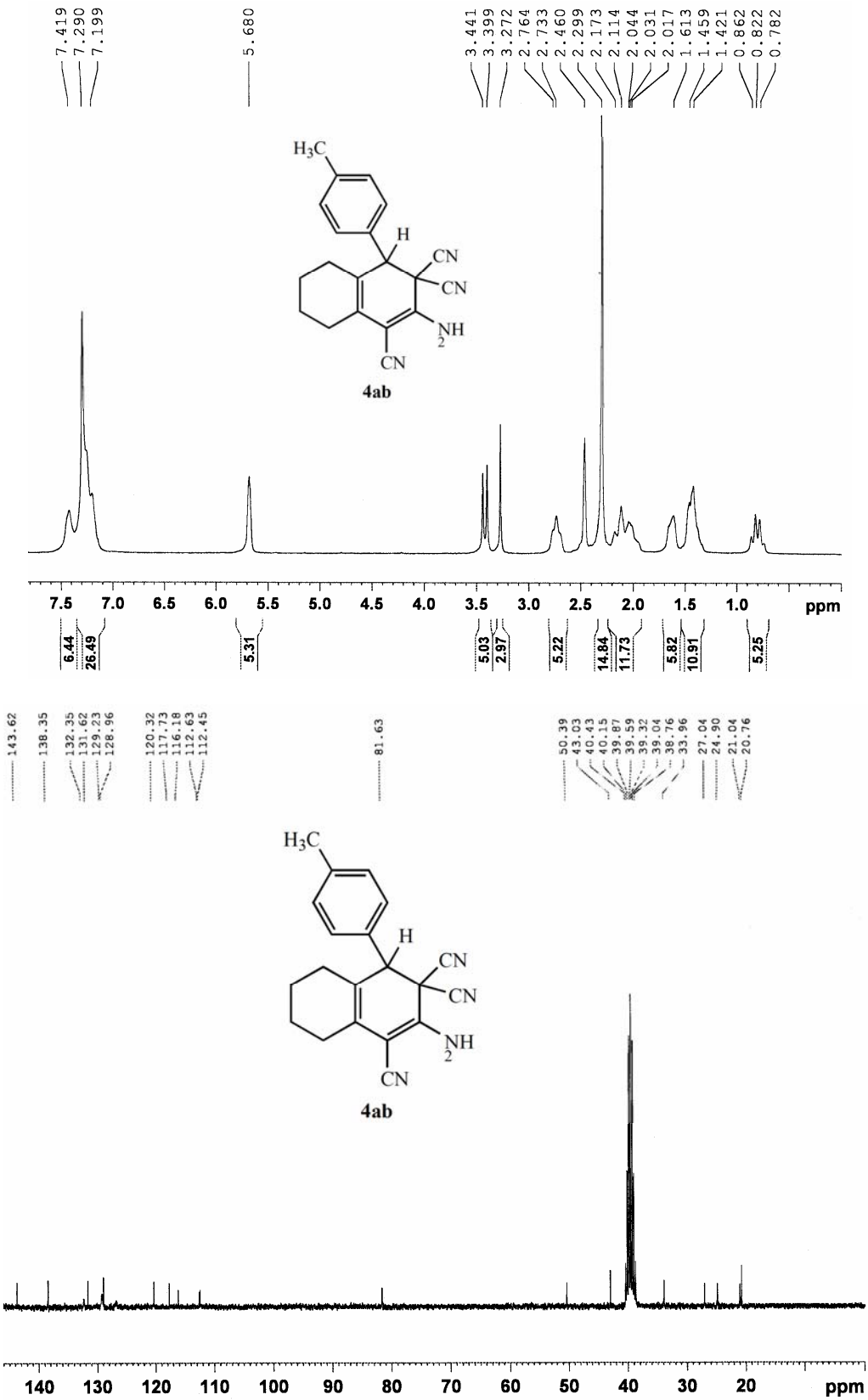
2-[1,3-Bis-(4-methoxy-phenyl)-allylidene]-malononitrile (10):

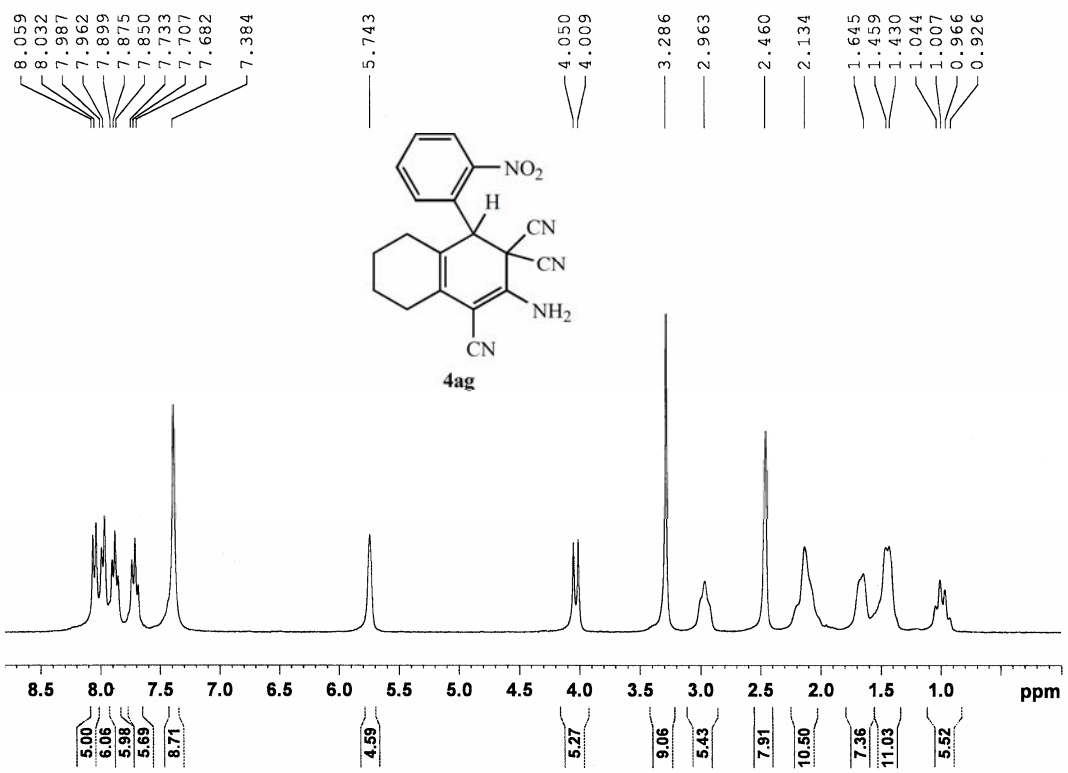


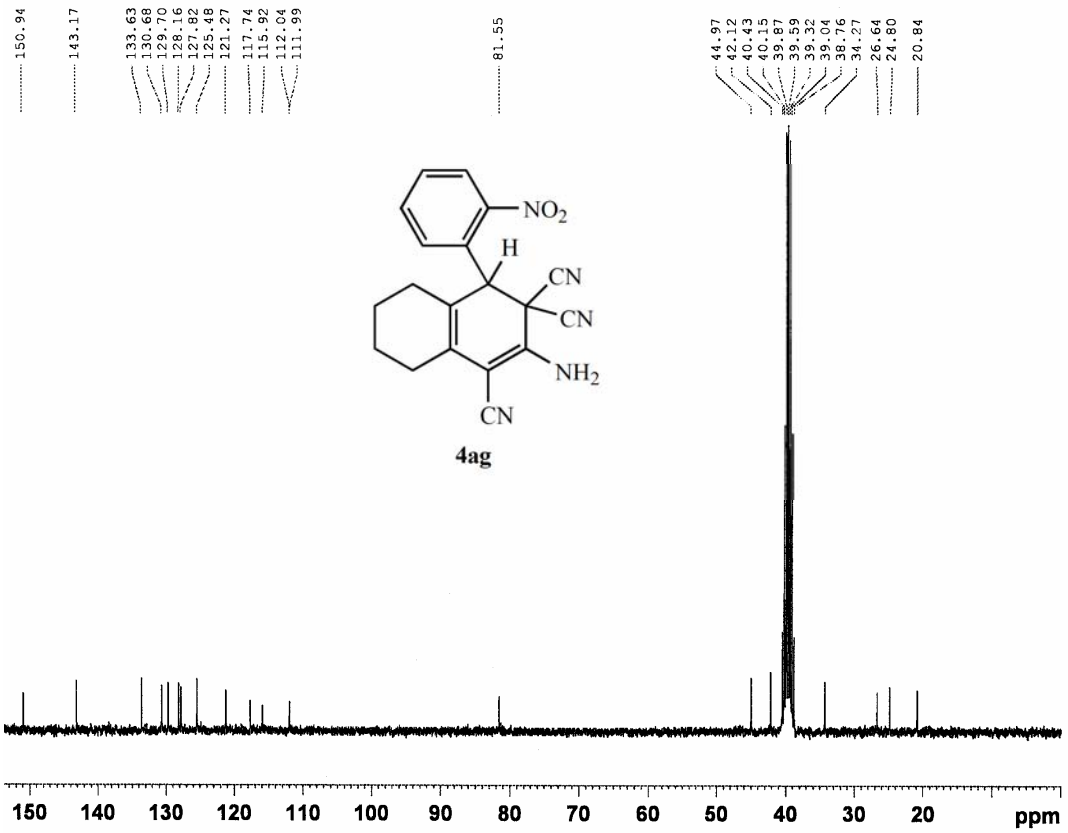
Yellow solid; Yield: 607 mg, 96 %; m.p. 104-106 °C (recrystallized from EtOAc/Pet ether); Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86 %. Found: C, 75.94; H, 5.10; N, 8.99 %; IR (KBr) cm^{-1}: 2212, 1600, 1494, 1256, 1173, 1021, 824, 533; δ_H ppm (300 MHz, DMSO-d_6, TMS) 3.78 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 6.92 (1H, d, *J*= 15.6 Hz, CH), 6.97 (2H, d, *J*= 8.7 Hz, arom.), 7.10 (2H, d, *J*= 8.7 Hz, arom.), 7.36 (1H, d, *J*= 15.3 Hz, CH), 7.44 (2H, d, *J*= 8.7 Hz, arom.), 7.64 (2H, d, *J*= 8.7 Hz, arom.); δ_C ppm (75 MHz, DMSO-d_6, TMS) 55.5, 55.6, 78.3, 113.8, 114.2, 114.4, 114.7, 114.9, 122.1, 125.2, 127.1, 130.1, 131.1, 131.3, 148.8, 161.7, 161.9, 162.3, 171.0.

Spectral Data of non-aromatic products (A-D-A-A system) 4aa-4jm









Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information-Part II for

Zinc titanate nanopowder: an advanced nanotechnology based recyclable heterogeneous catalyst for the one-pot selective green synthesis of self-aggregated low-molecular mass acceptor-donor-acceptor-acceptor systems and acceptor-donor-acceptor triads

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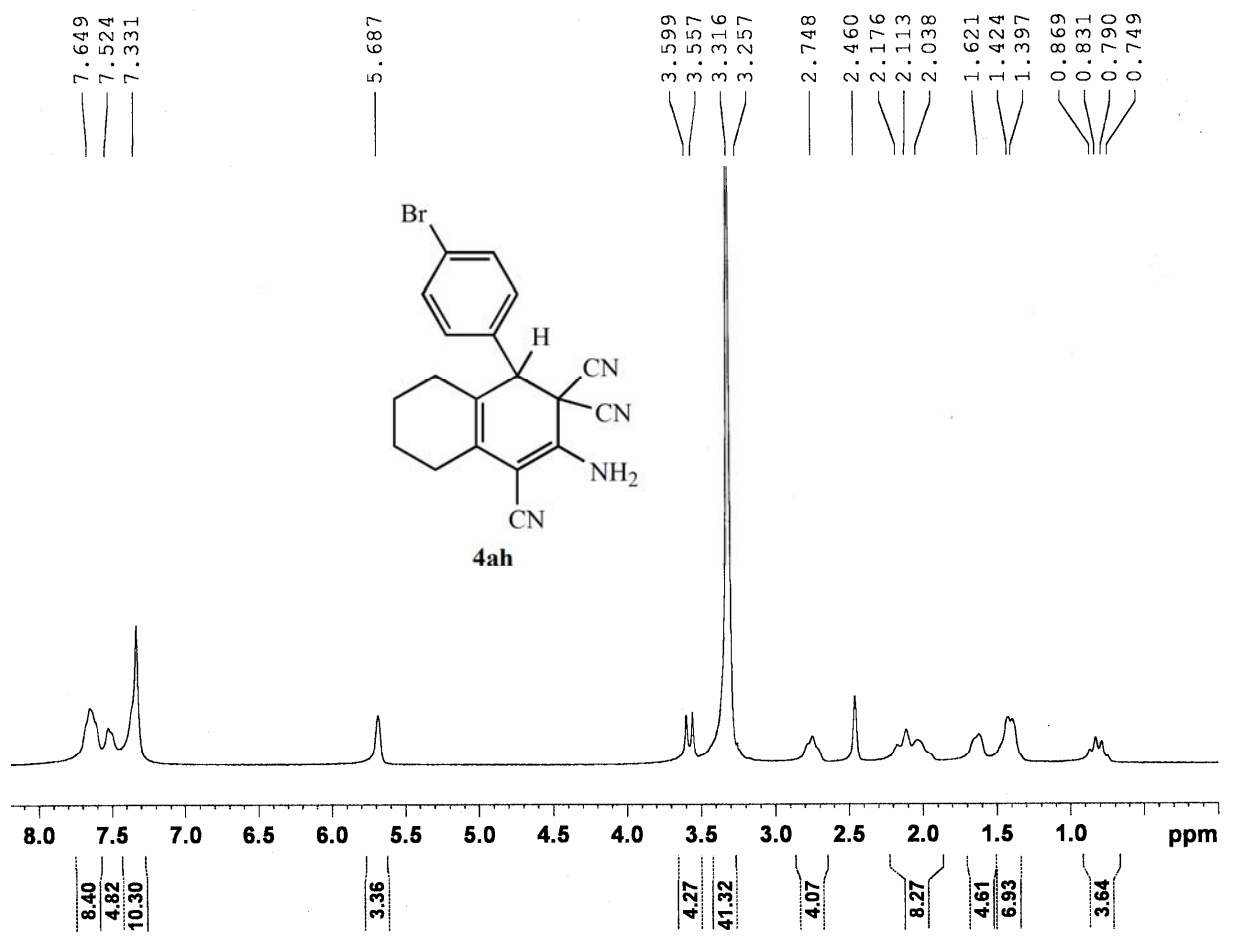
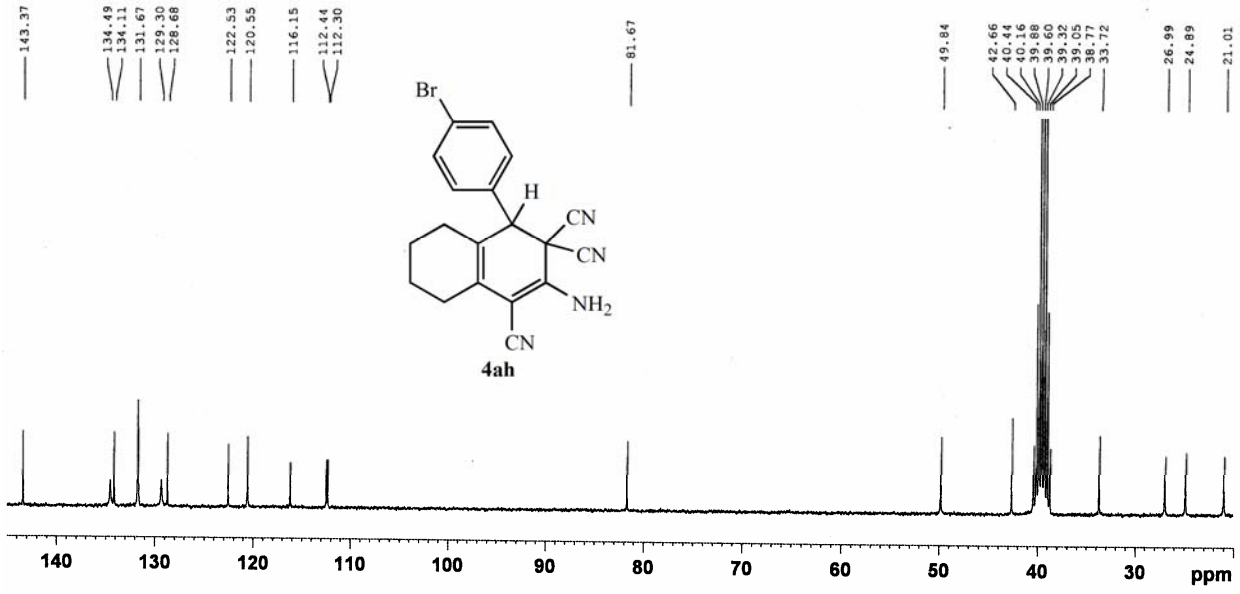
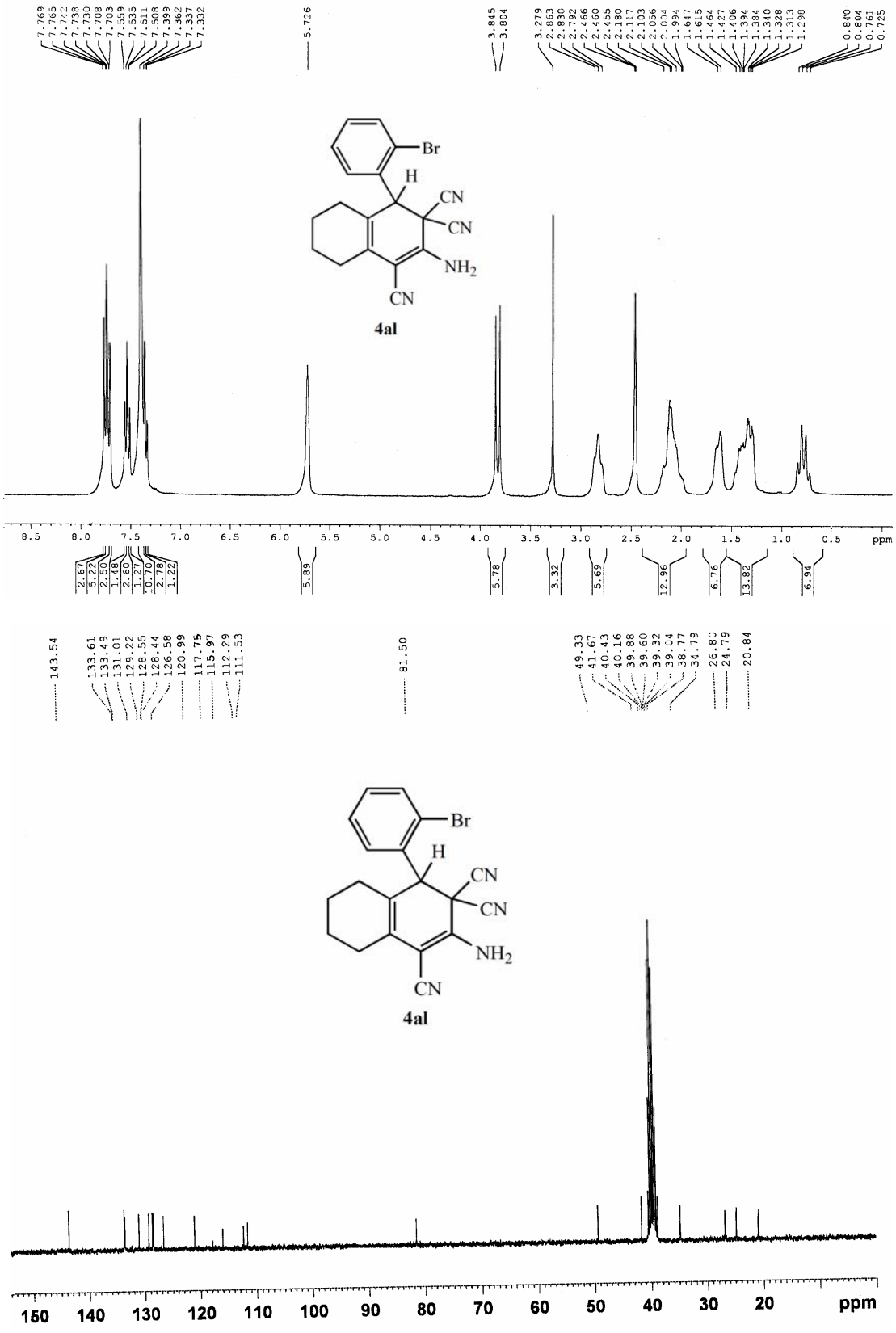
b: Department of Chemistry, Howard University, Washington DC 20059, USA

cmukhop@yahoo.co.in



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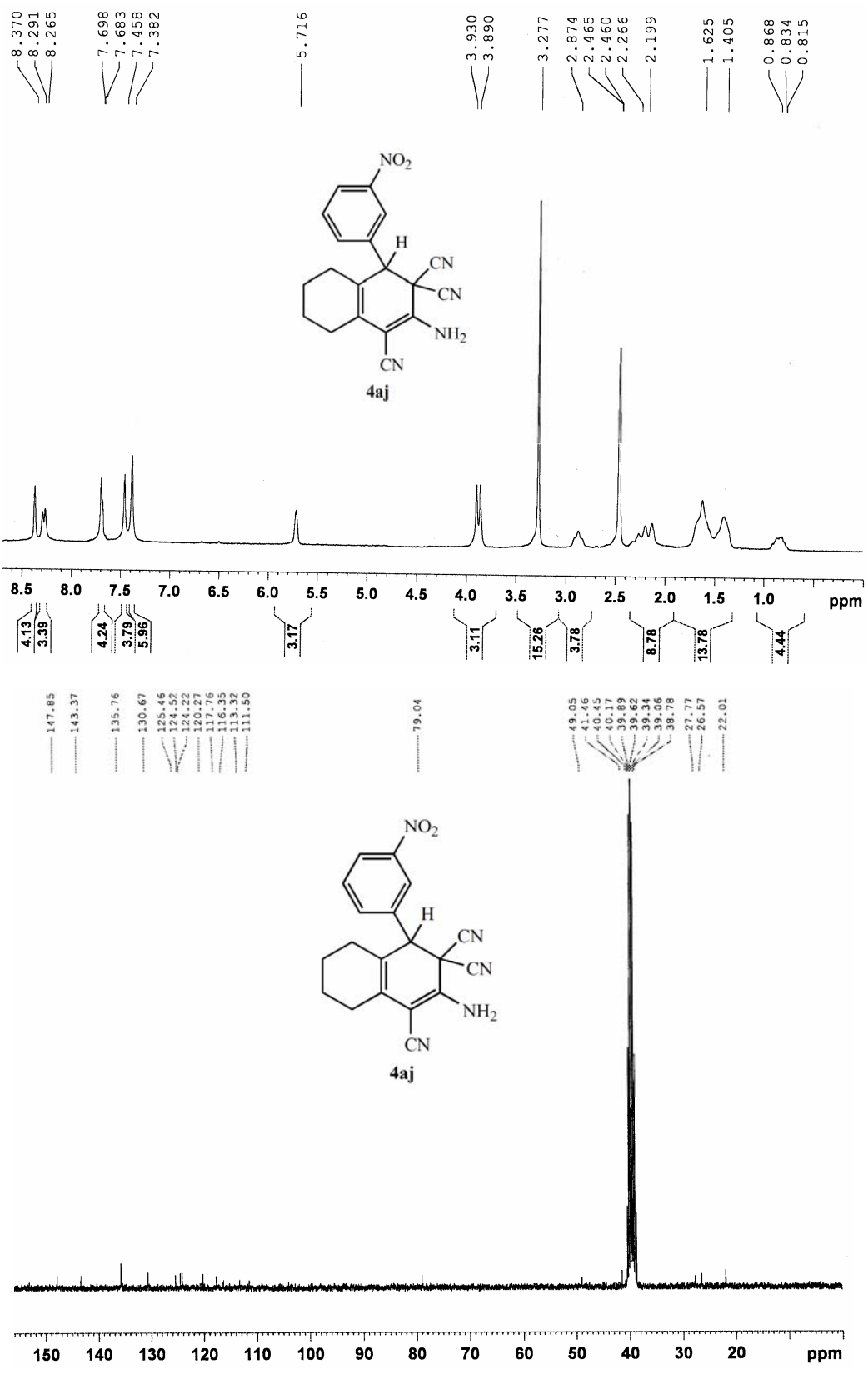
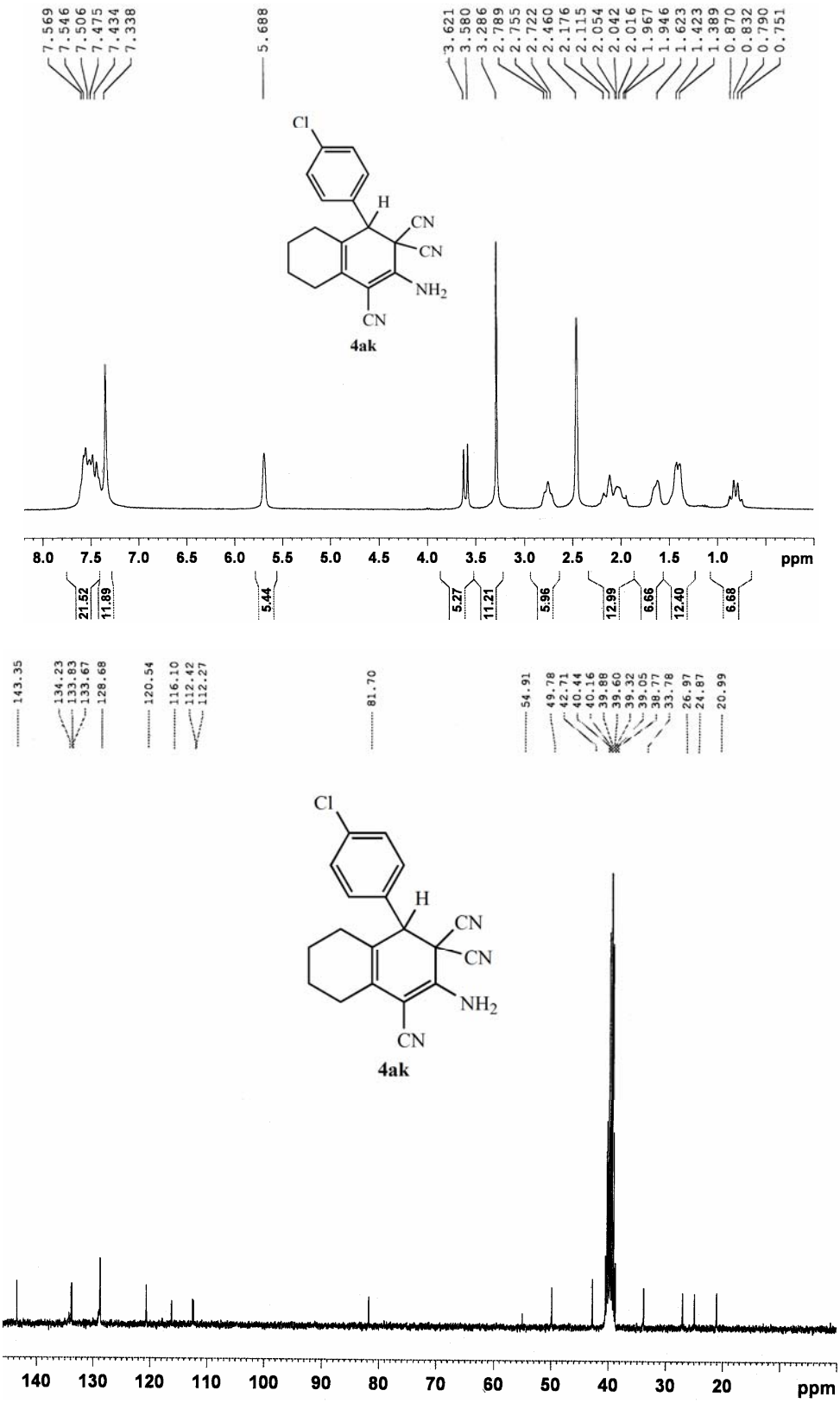
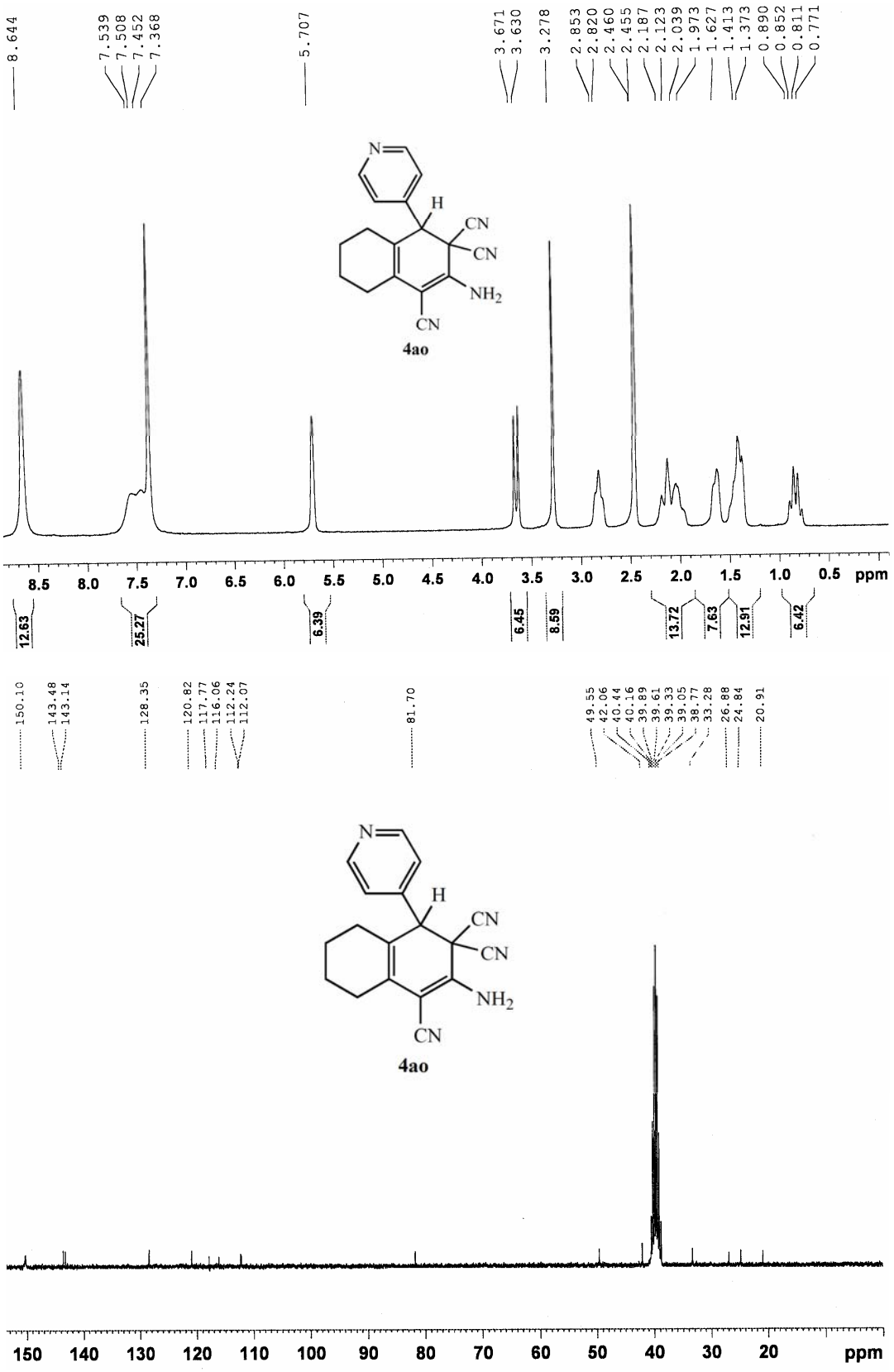
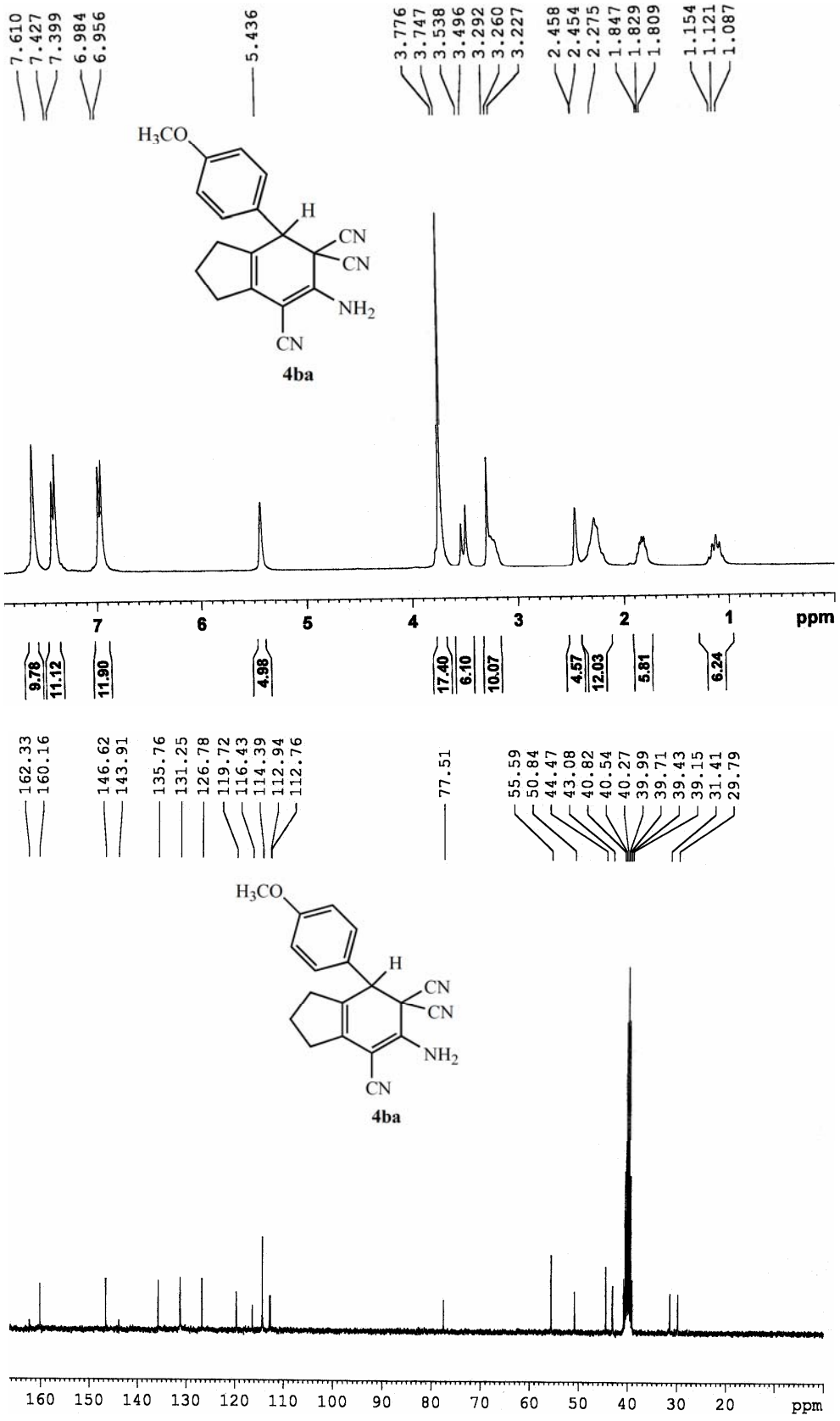
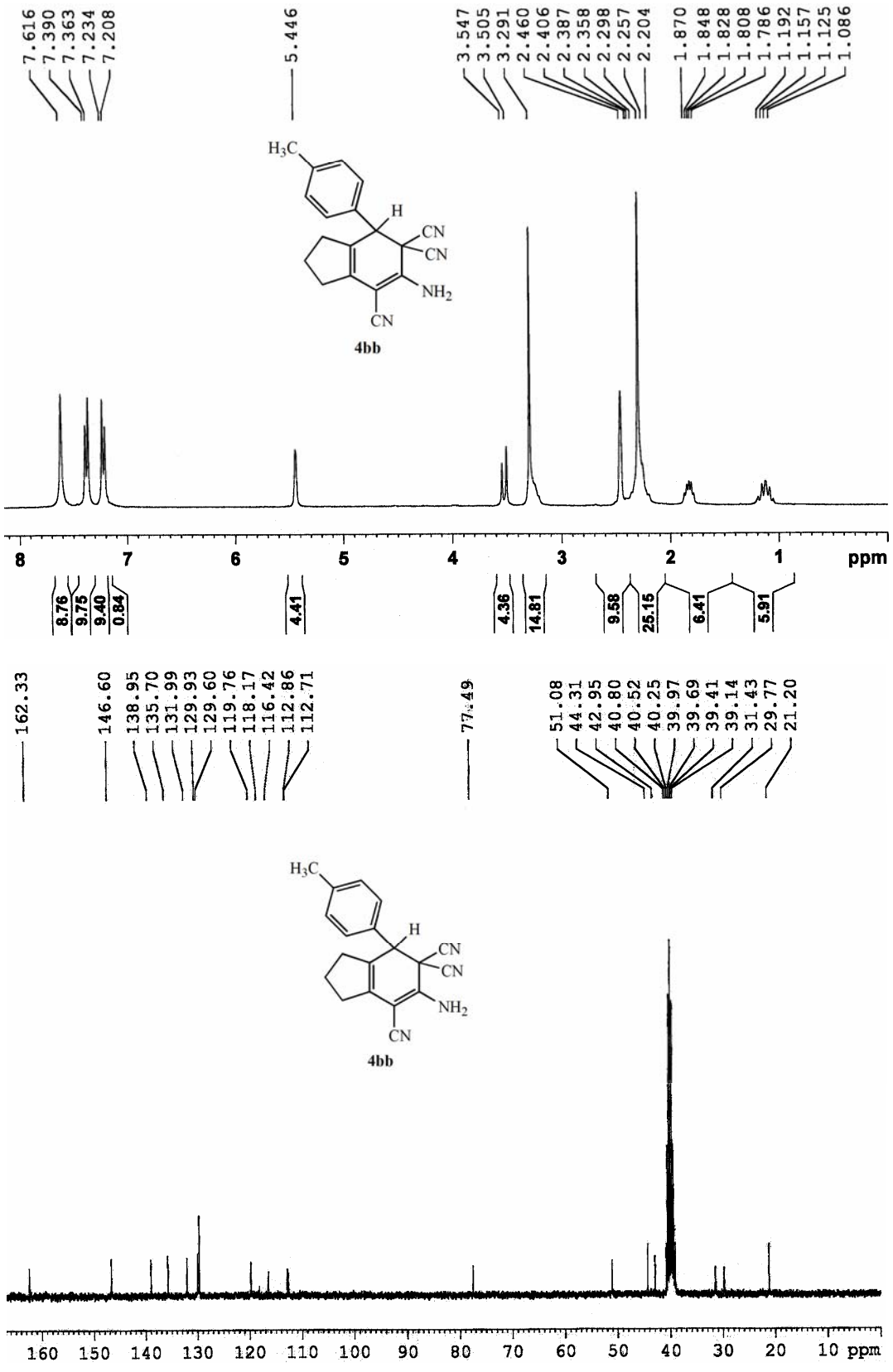
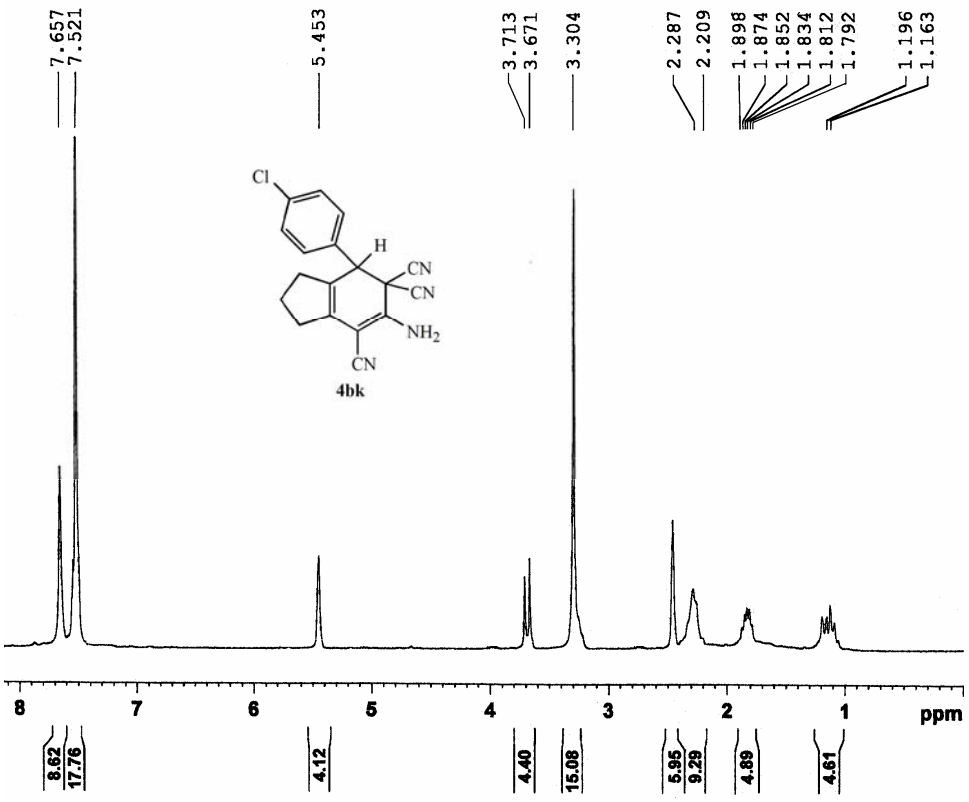


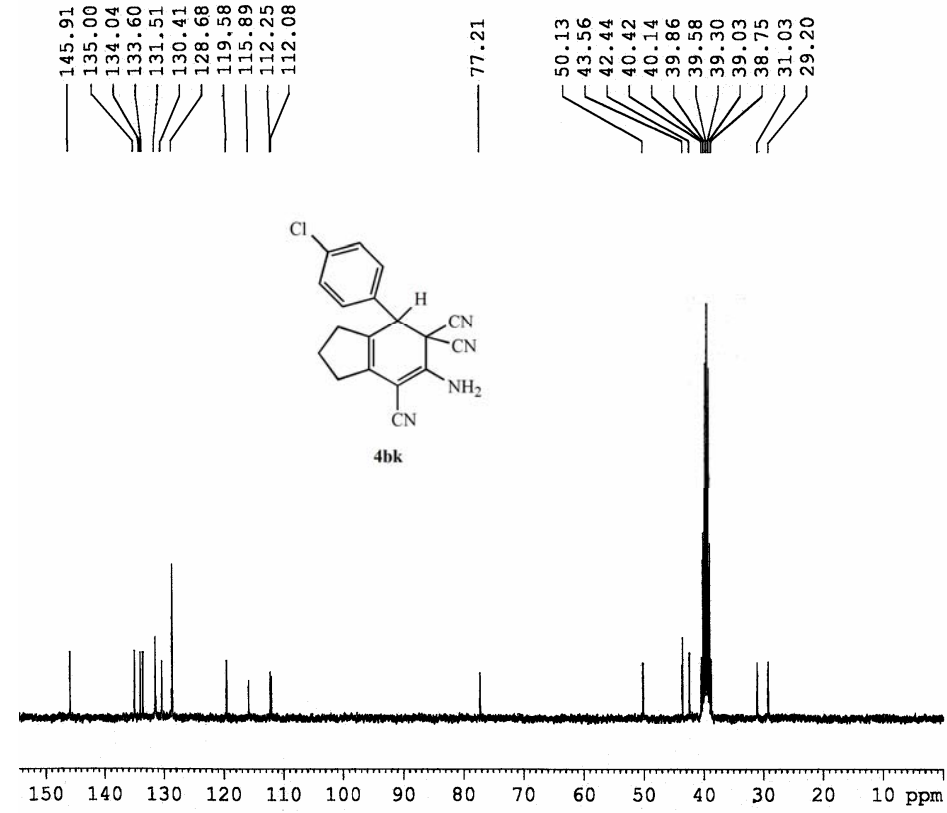


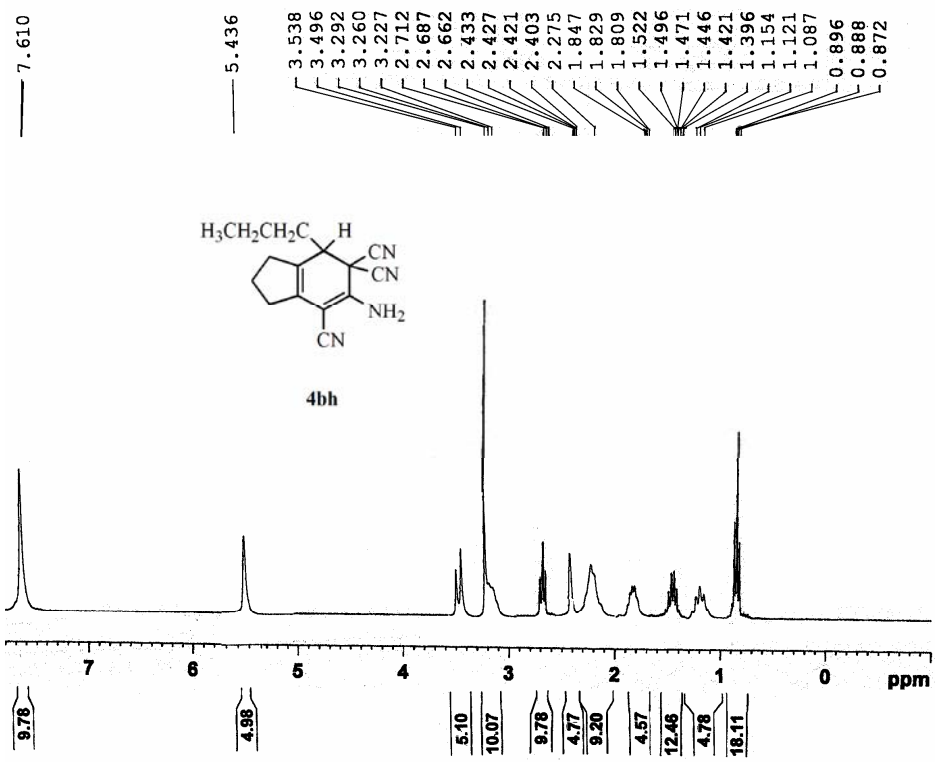


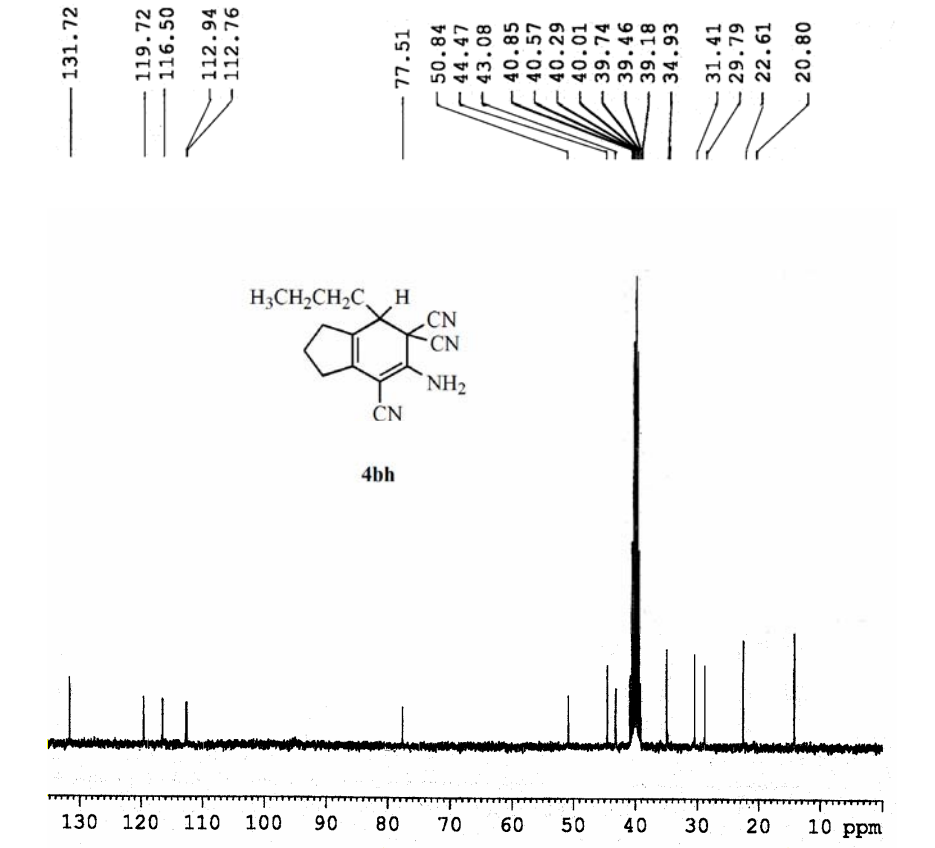


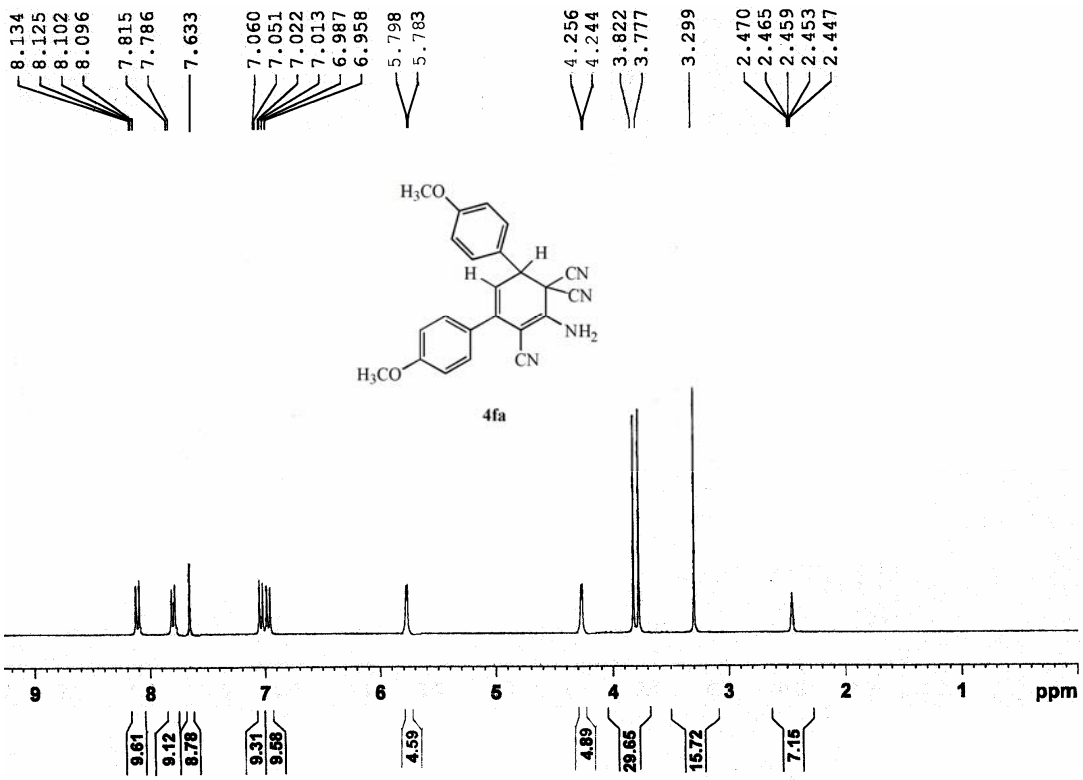


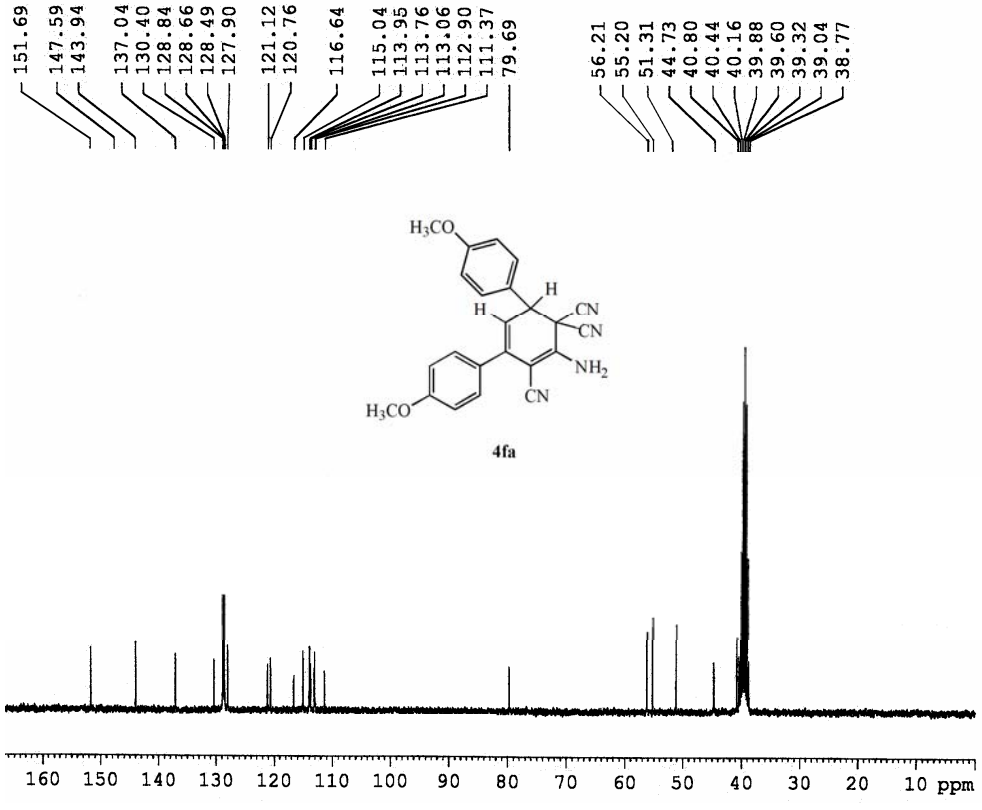


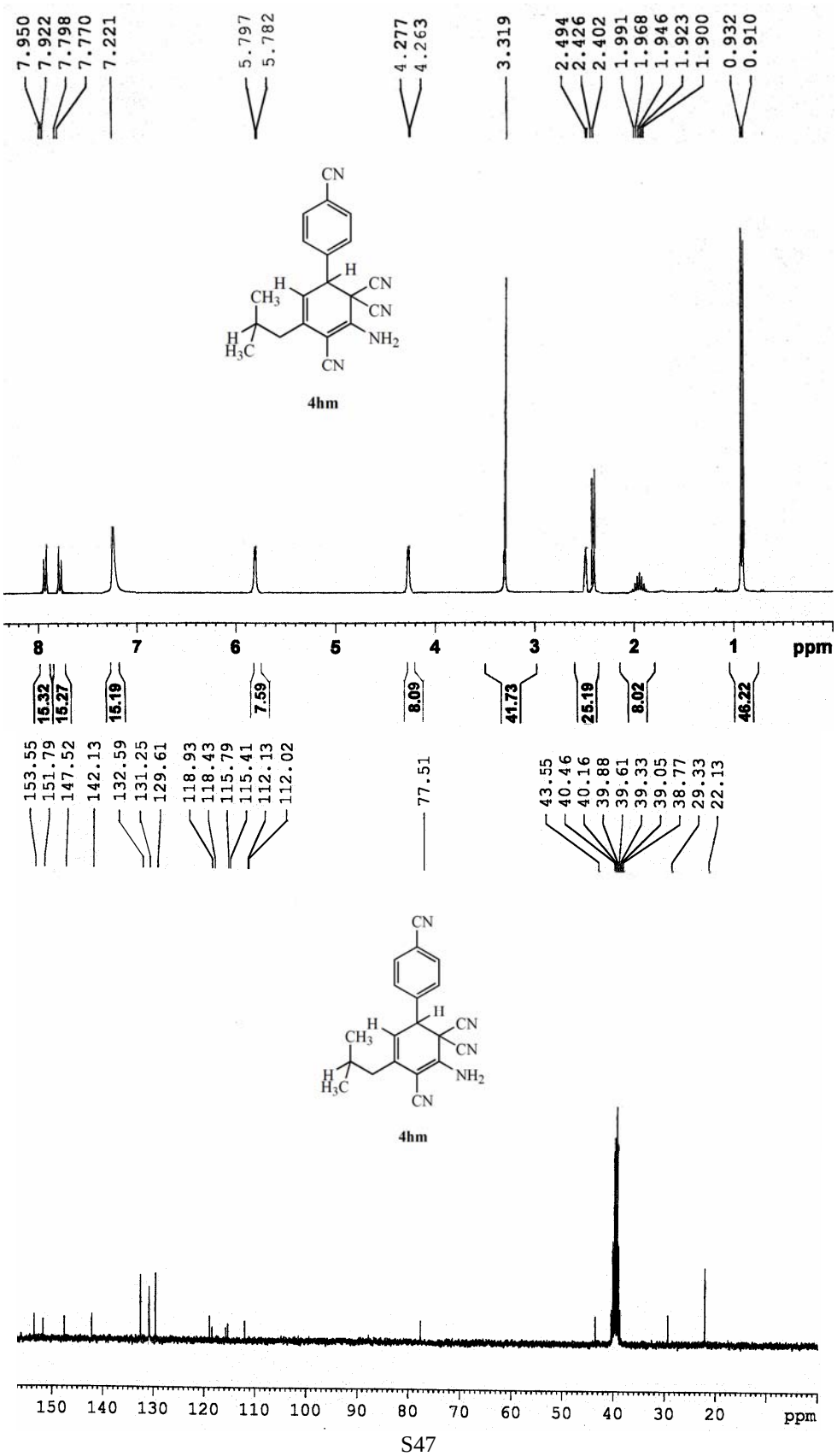


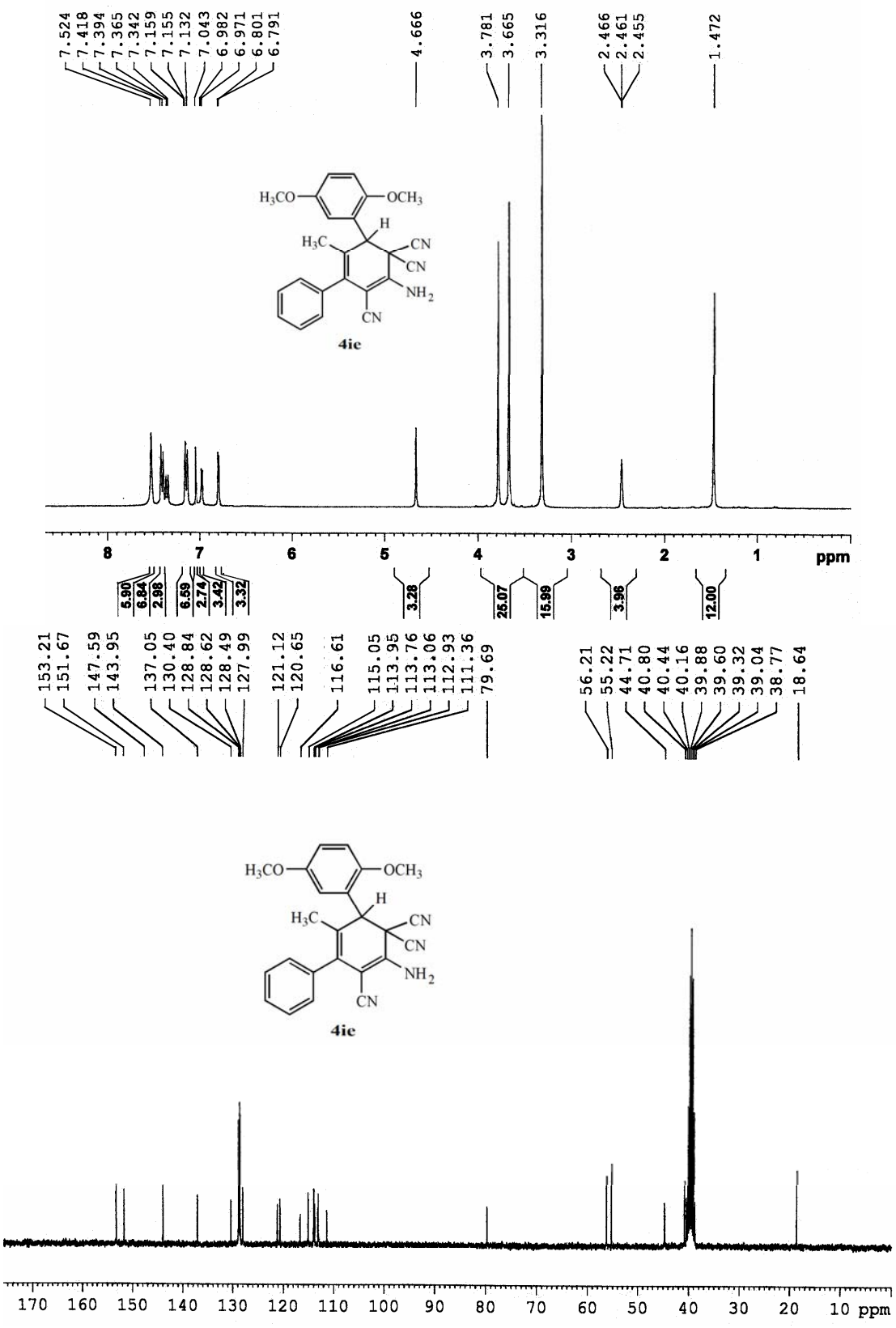


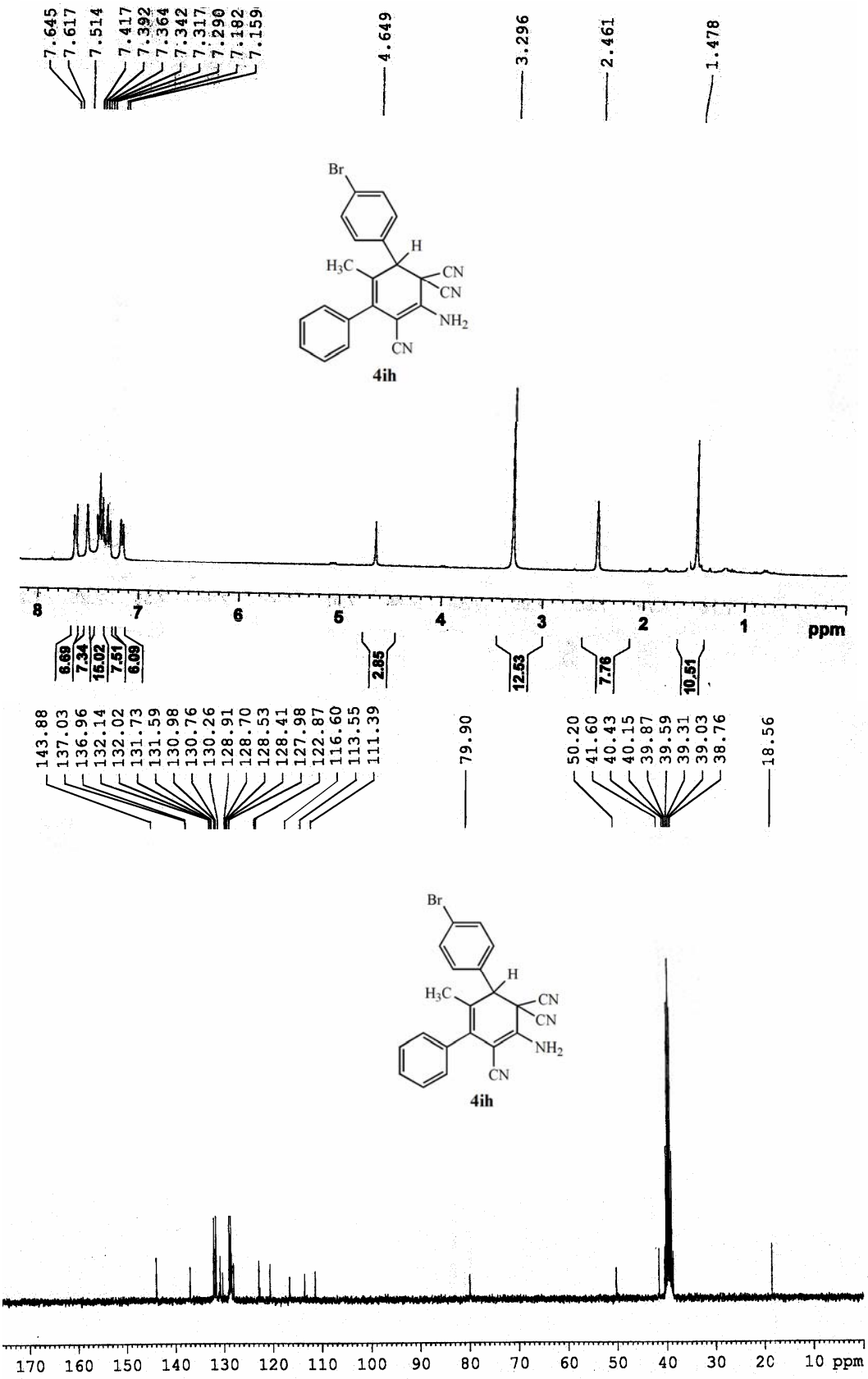


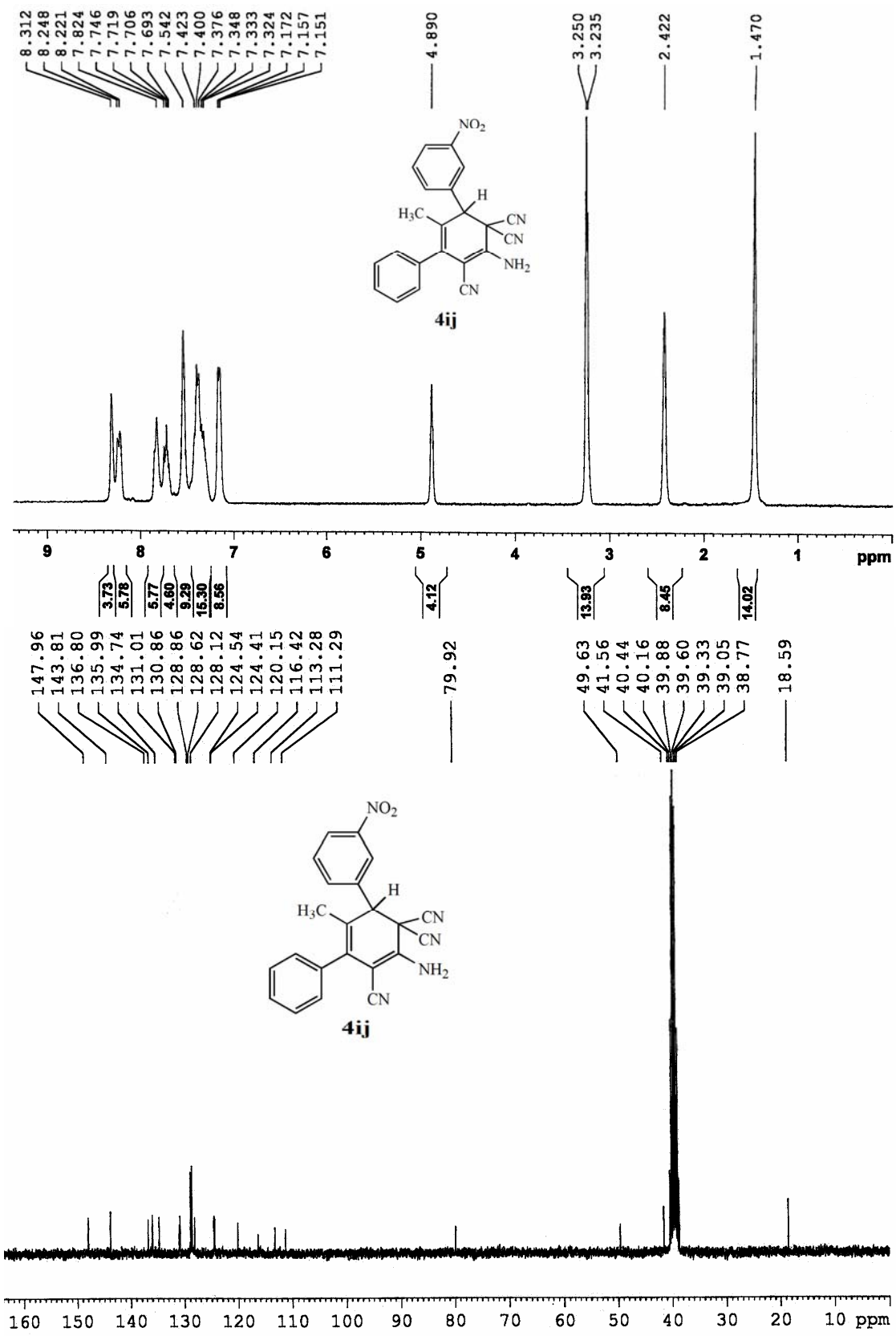


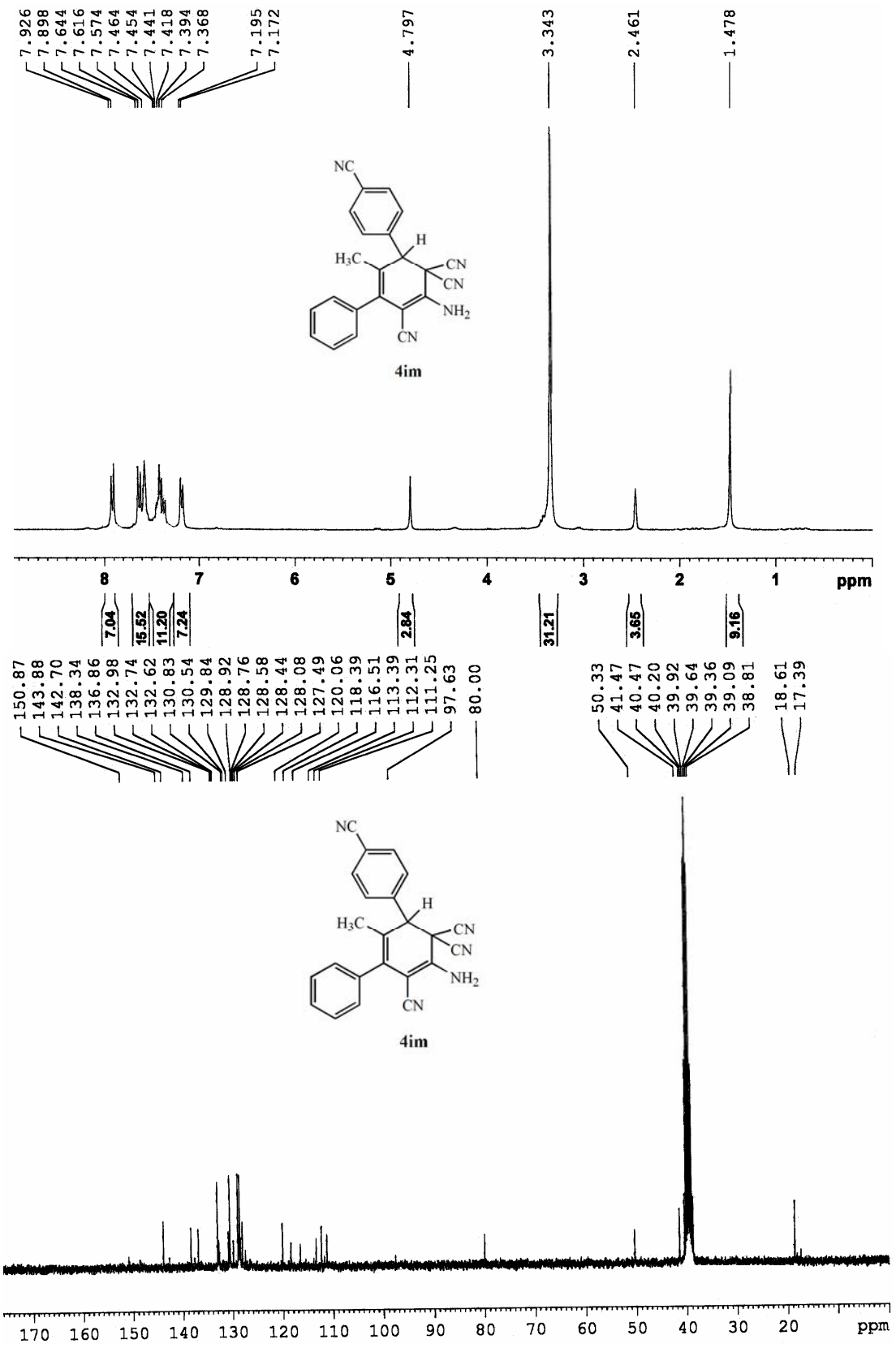


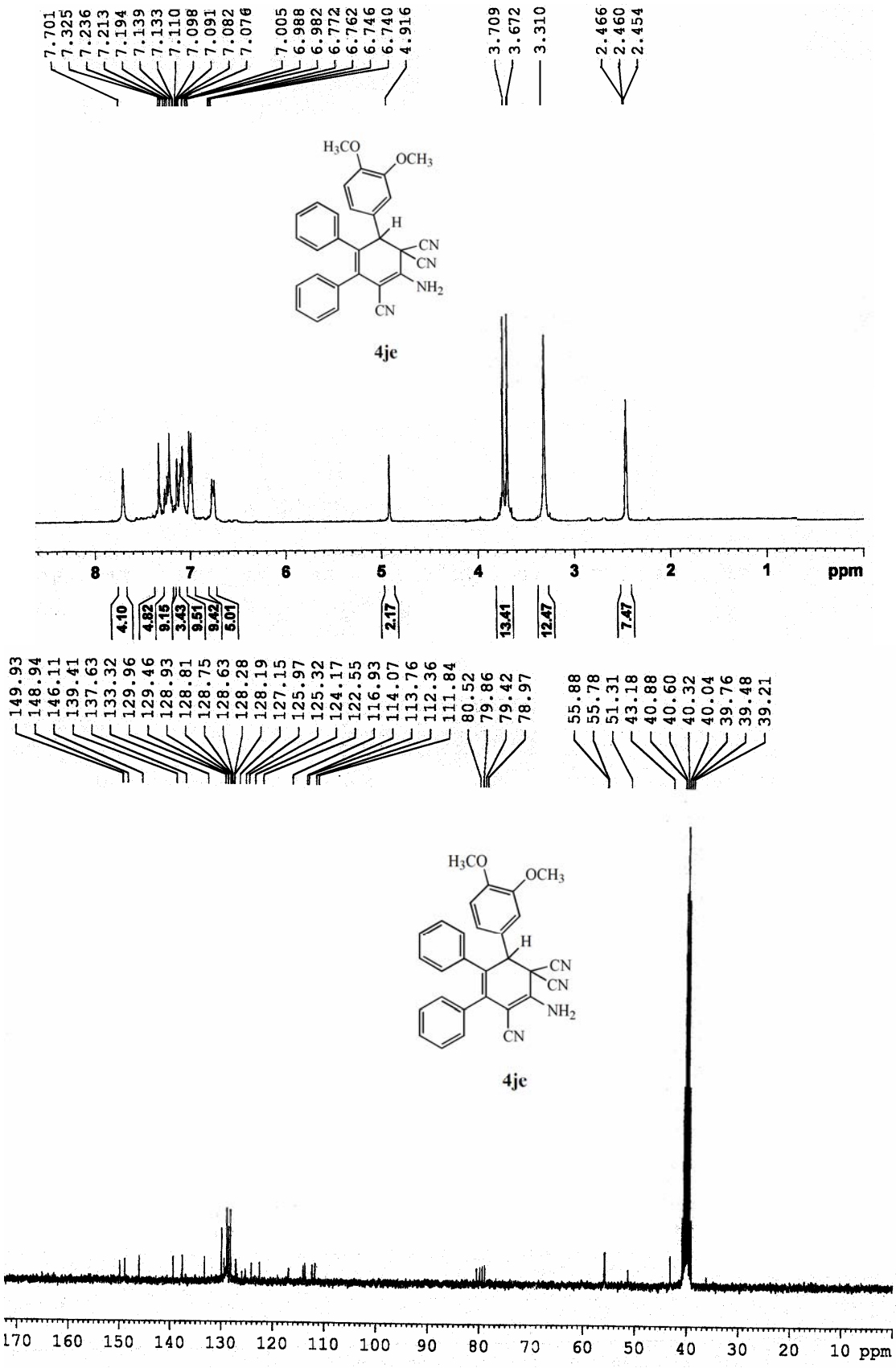


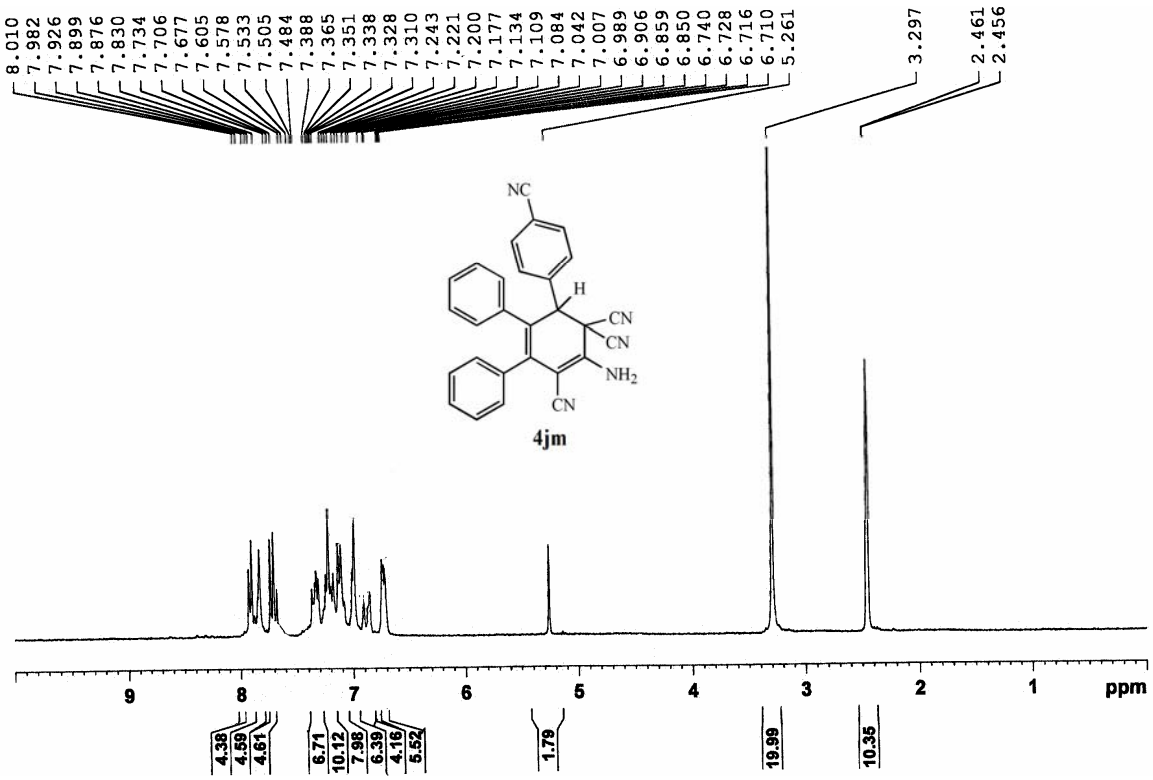


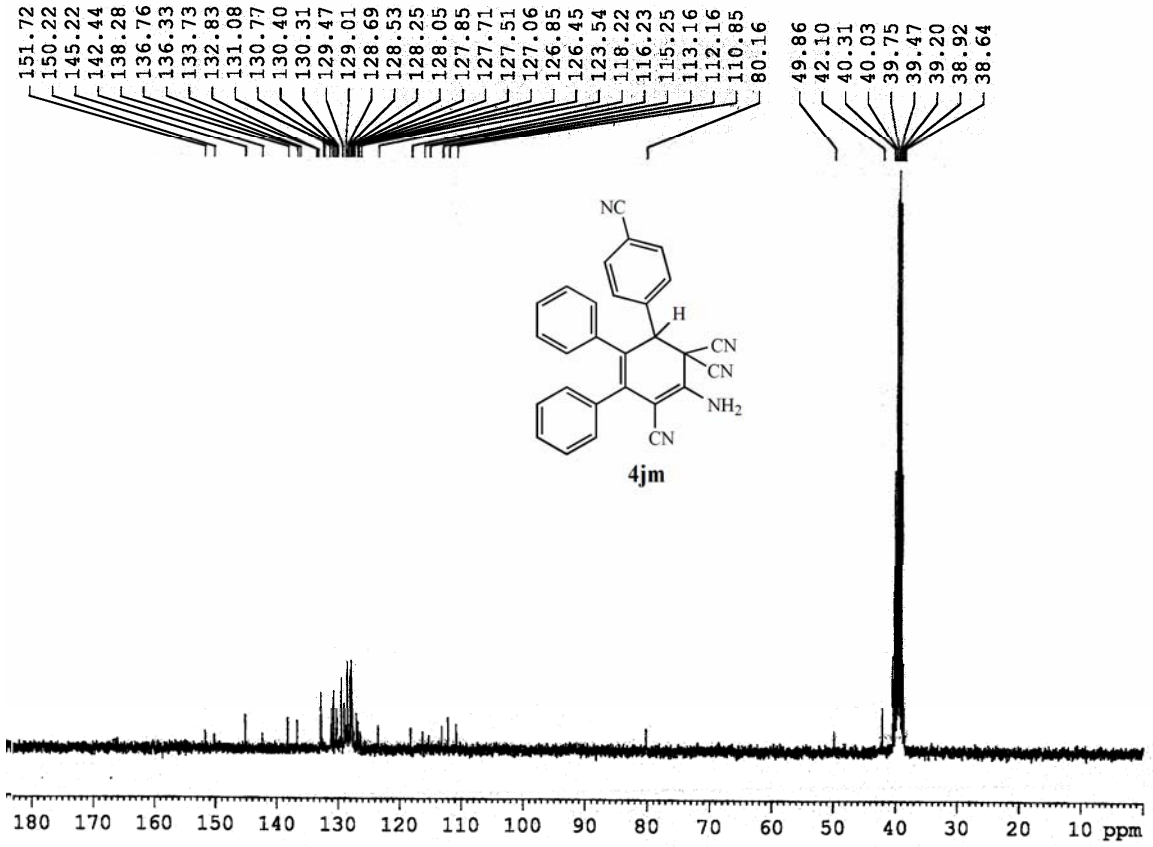












Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information-Part III for

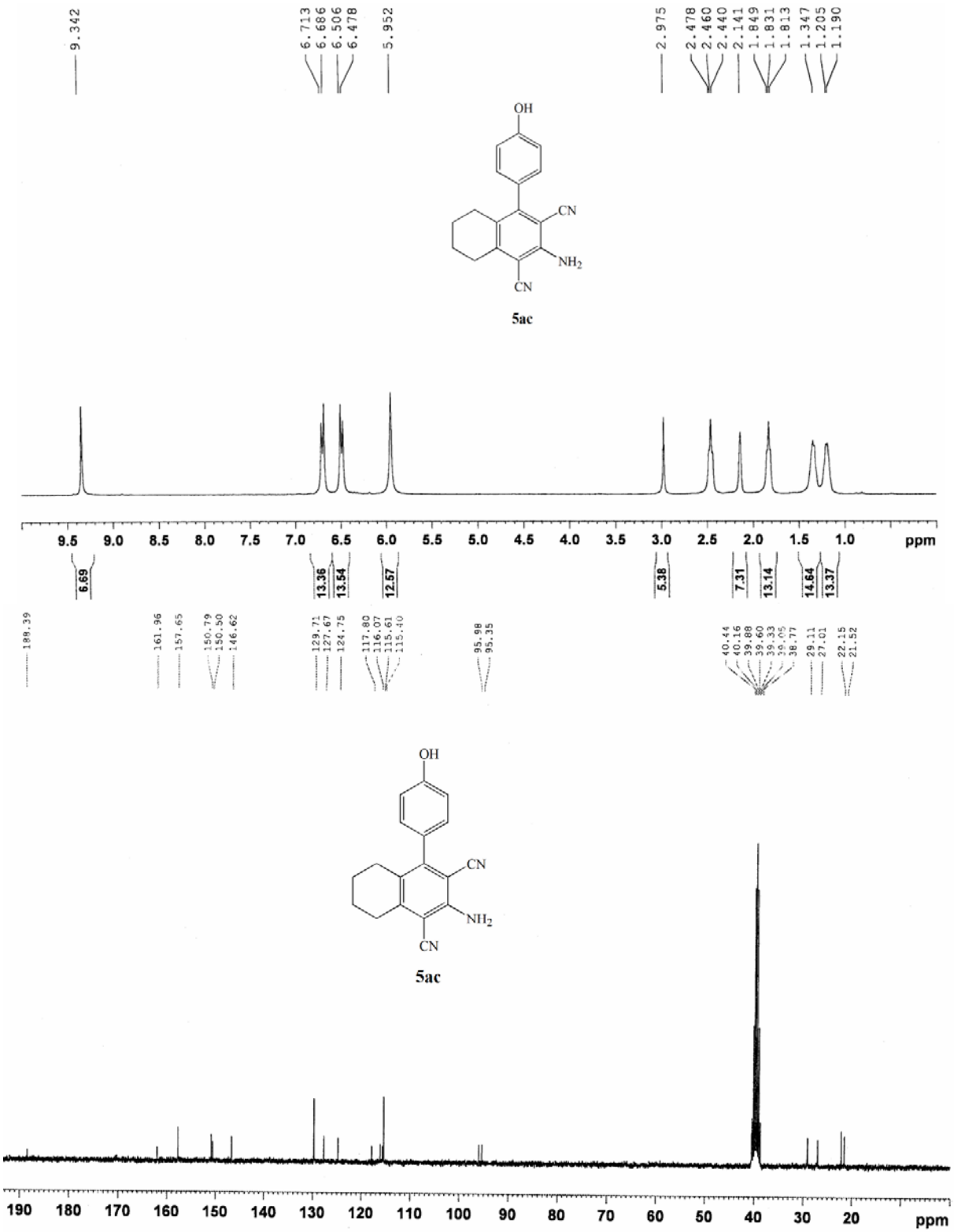
Zinc titanate nanopowder: an advanced nanotechnology based recyclable heterogeneous catalyst for the one-pot selective green synthesis of self-aggregated low-molecular mass acceptor-donor-acceptor-acceptor systems and acceptor-donor-acceptor triads

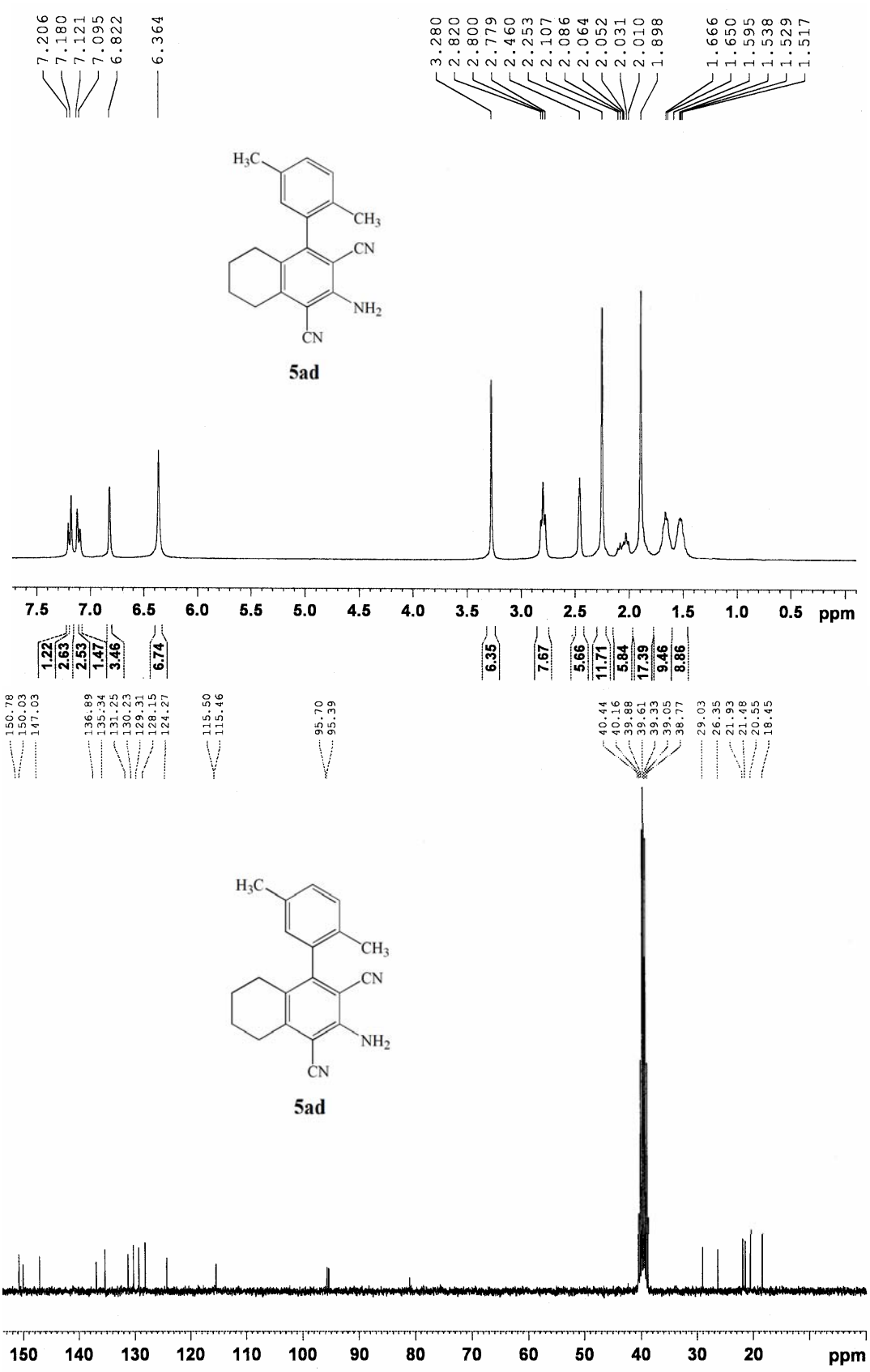
Paramita Das[a], Ray J. Butcher[b] and Chhanda Mukhopadhyay[a]*

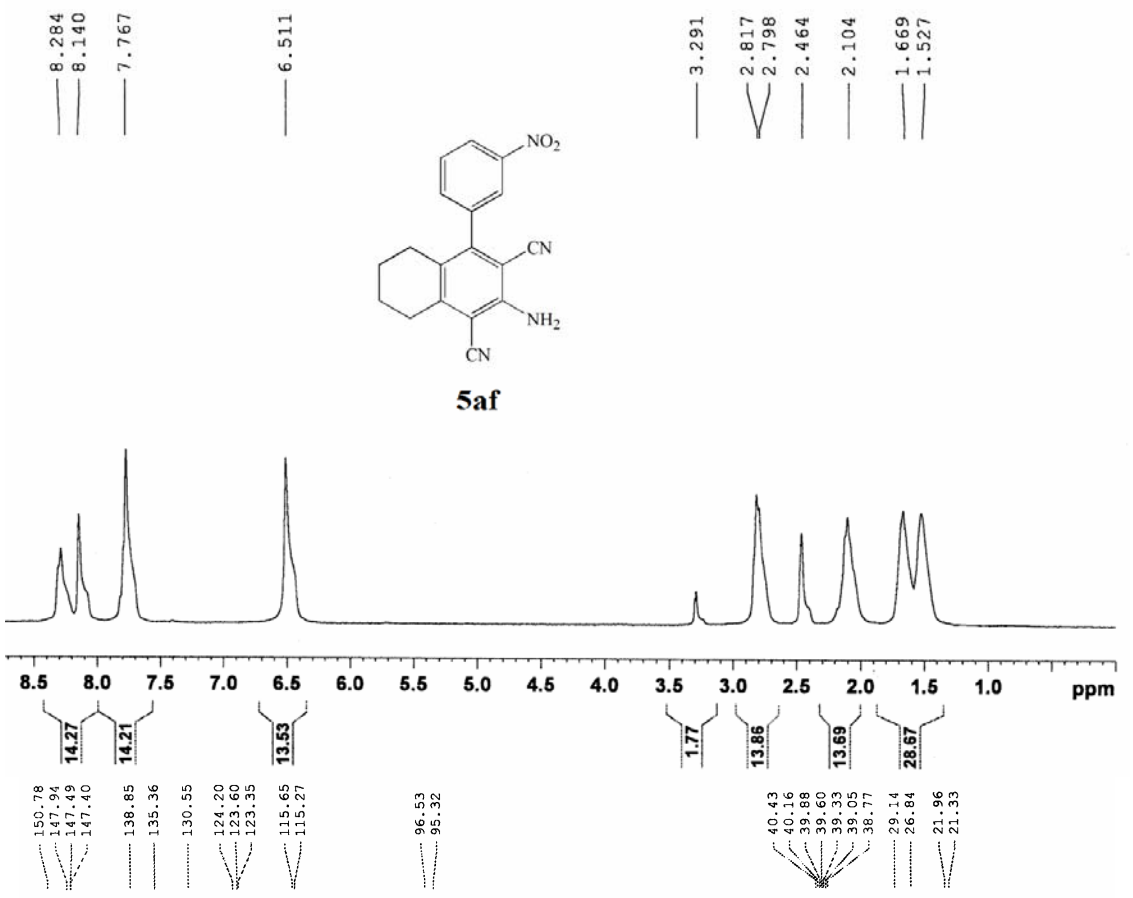
a: Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata-700009, India
b: Department of Chemistry, Howard University, Washington DC 20059, USA

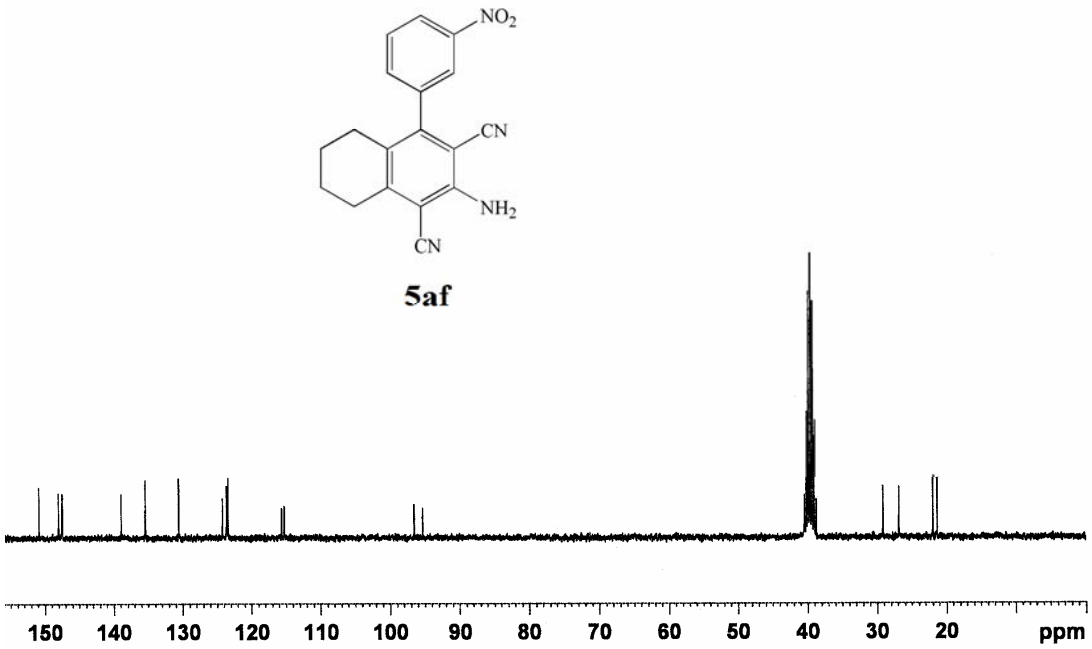
cmukhop@yahoo.co.in

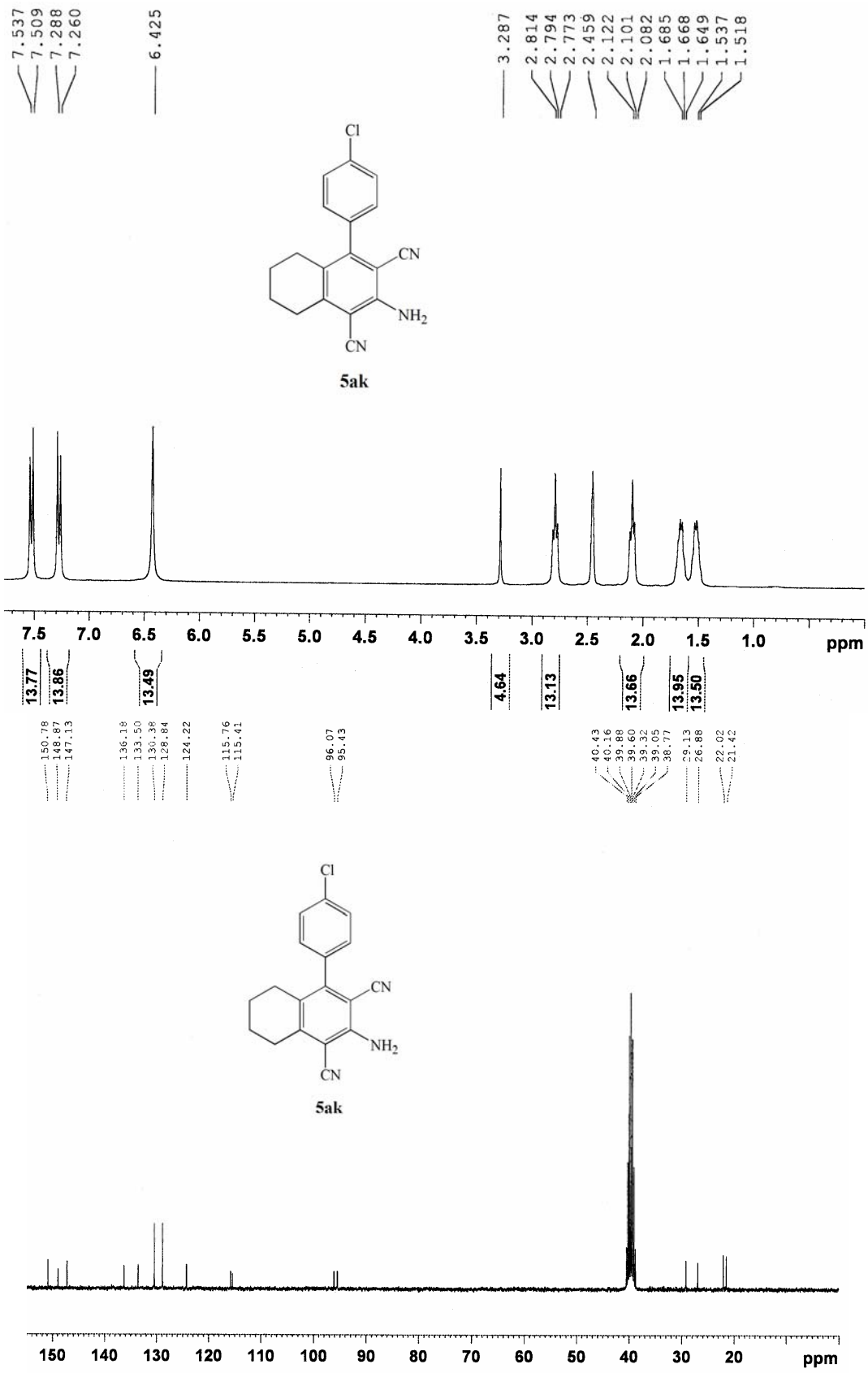
Spectral Data of aromatic products (A-D-A system) 5ac-5kk

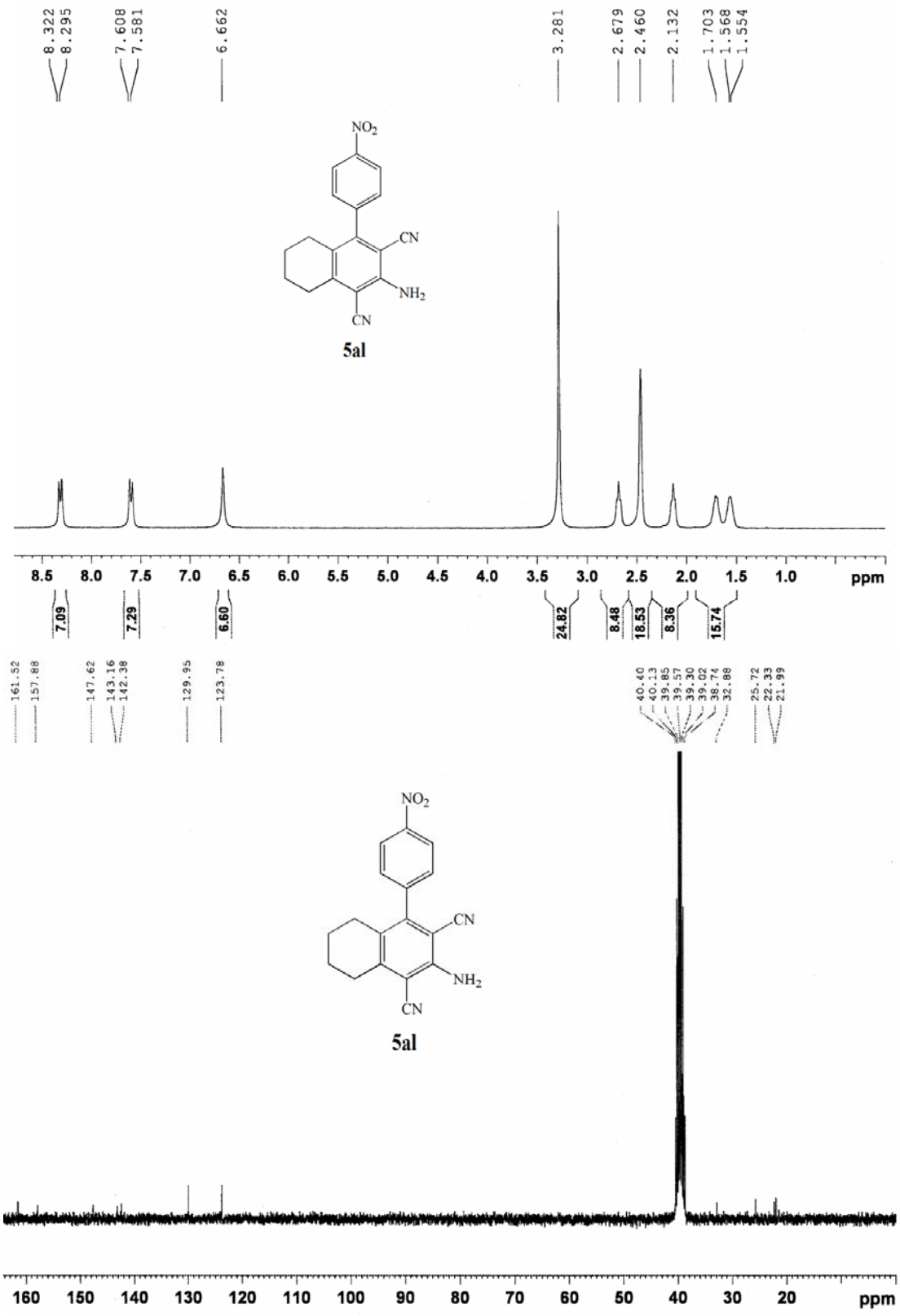


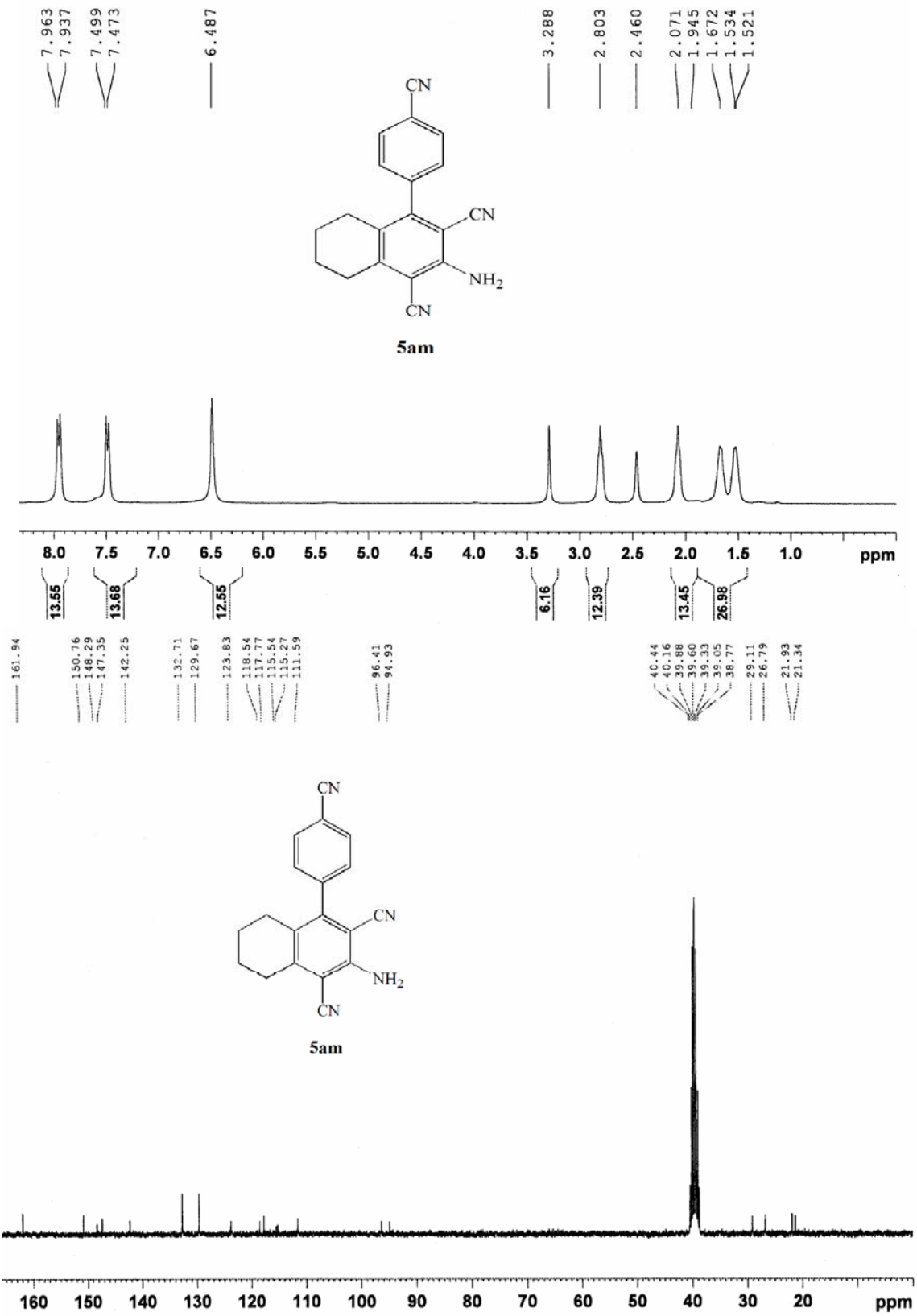


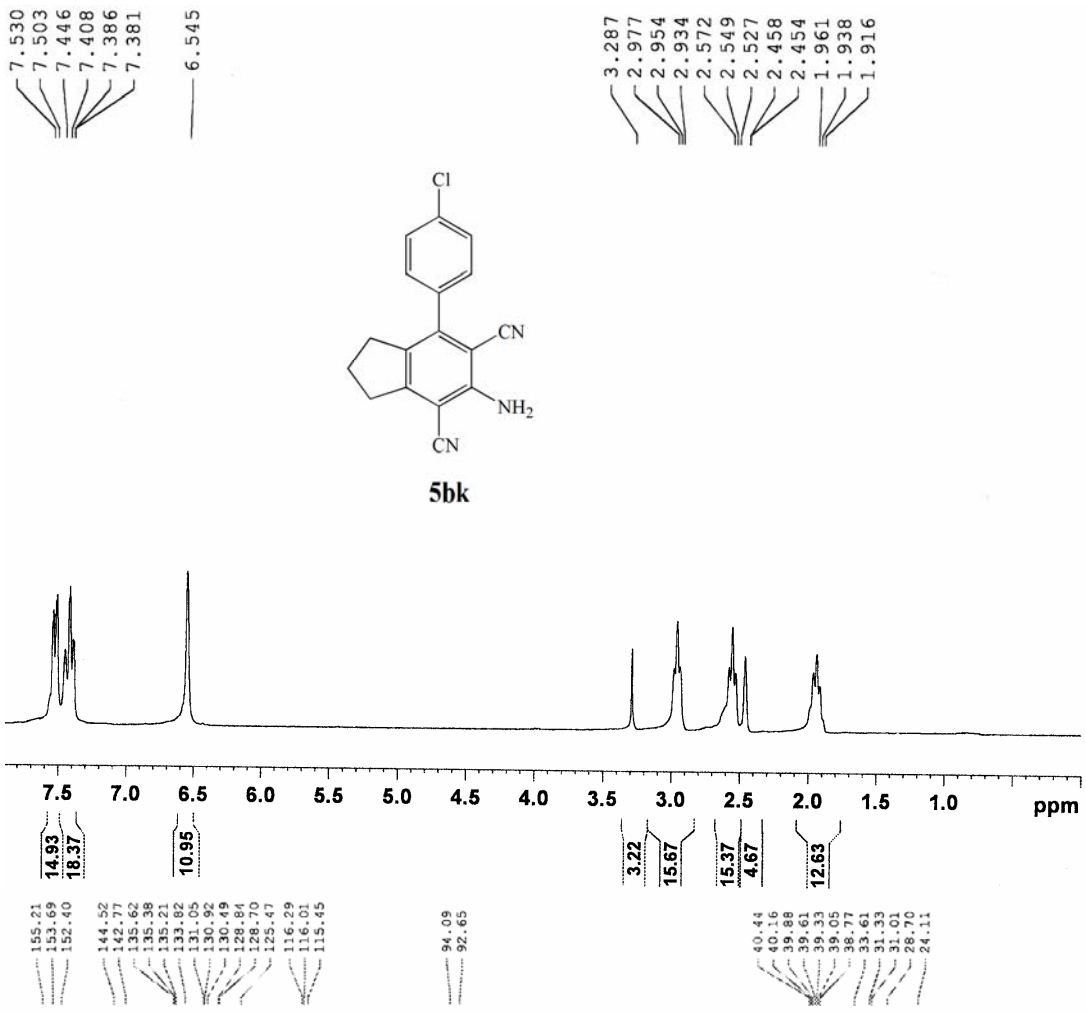












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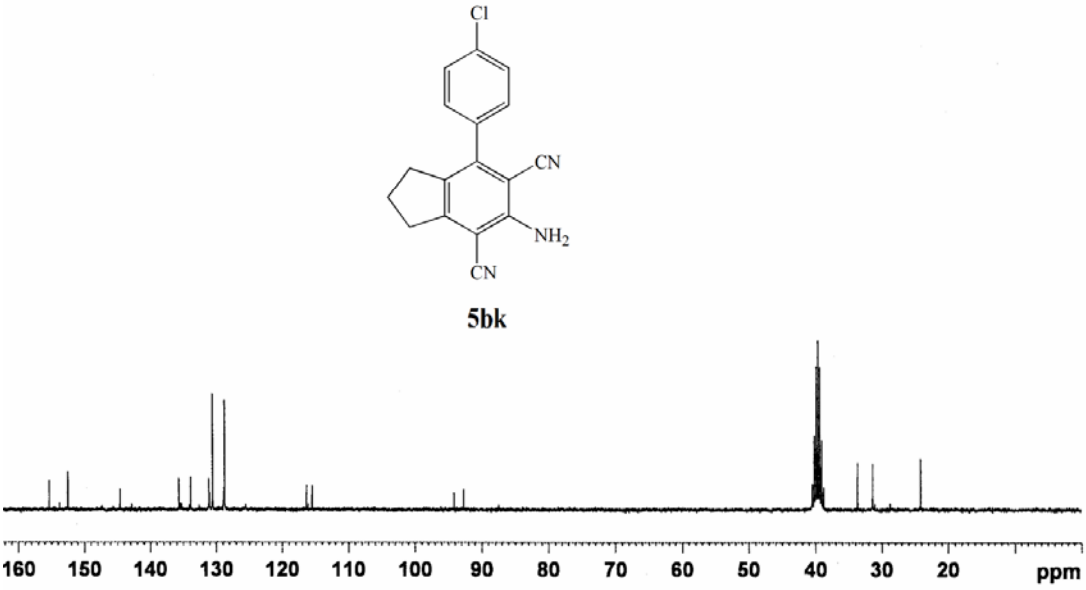

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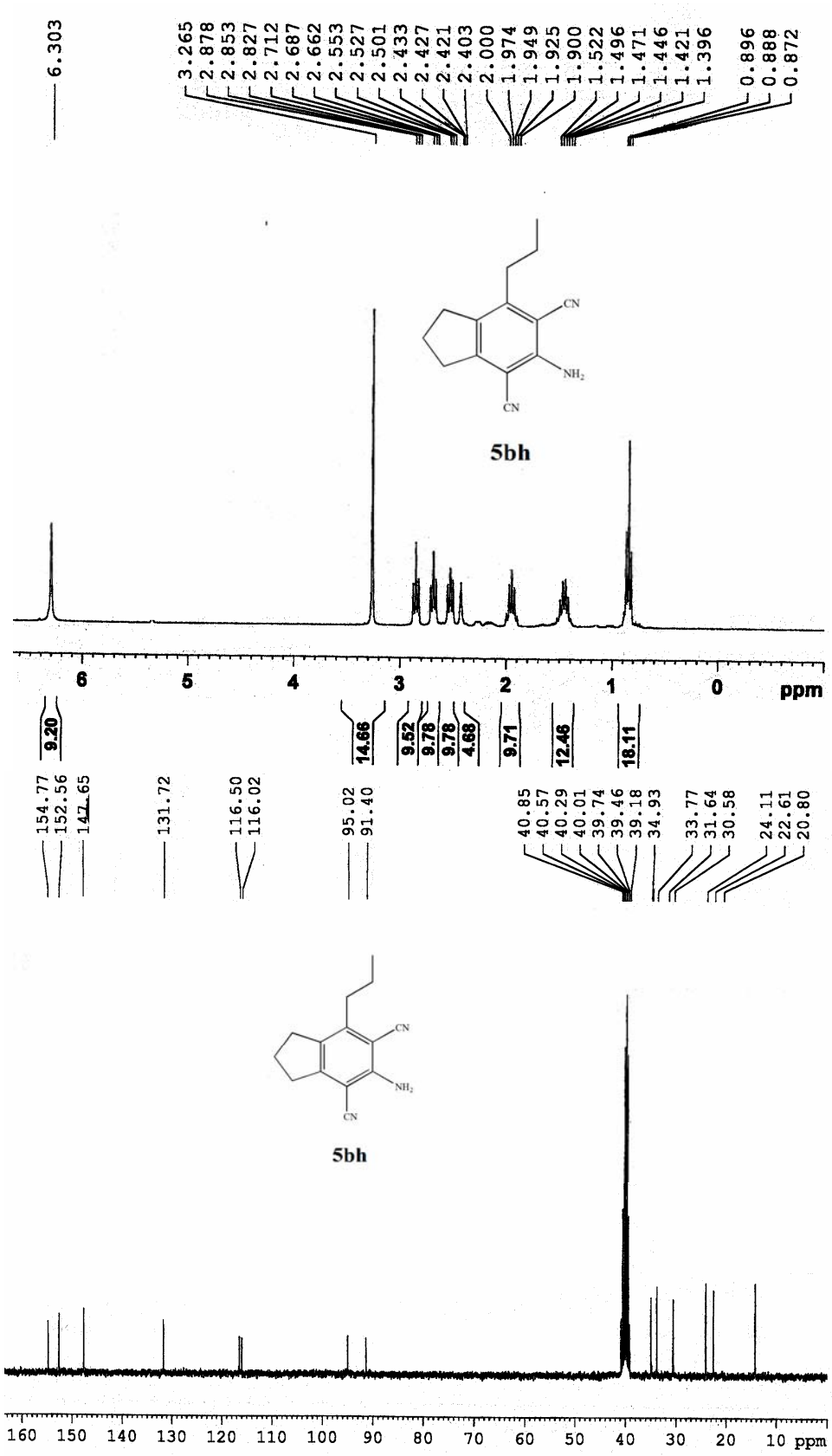
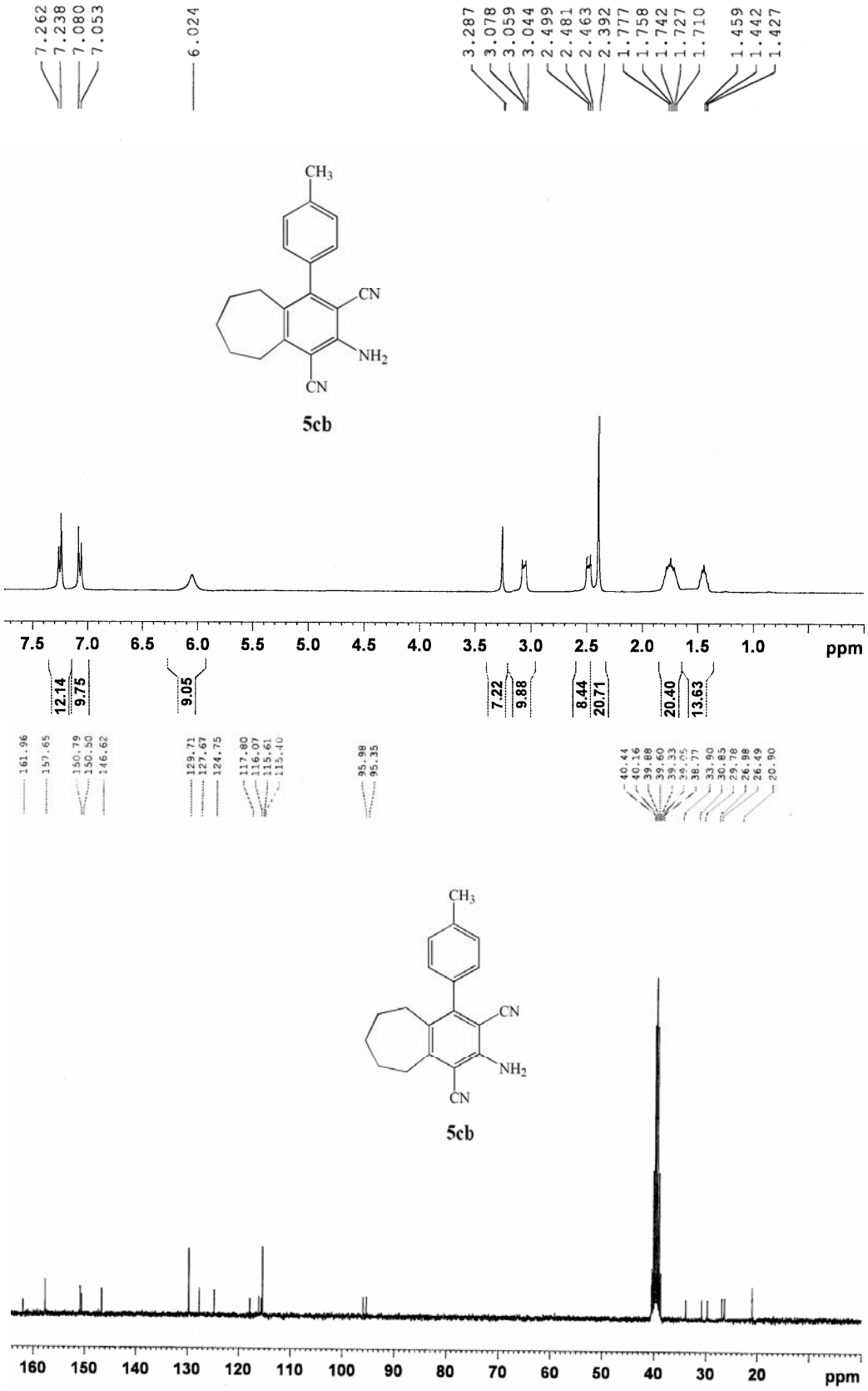
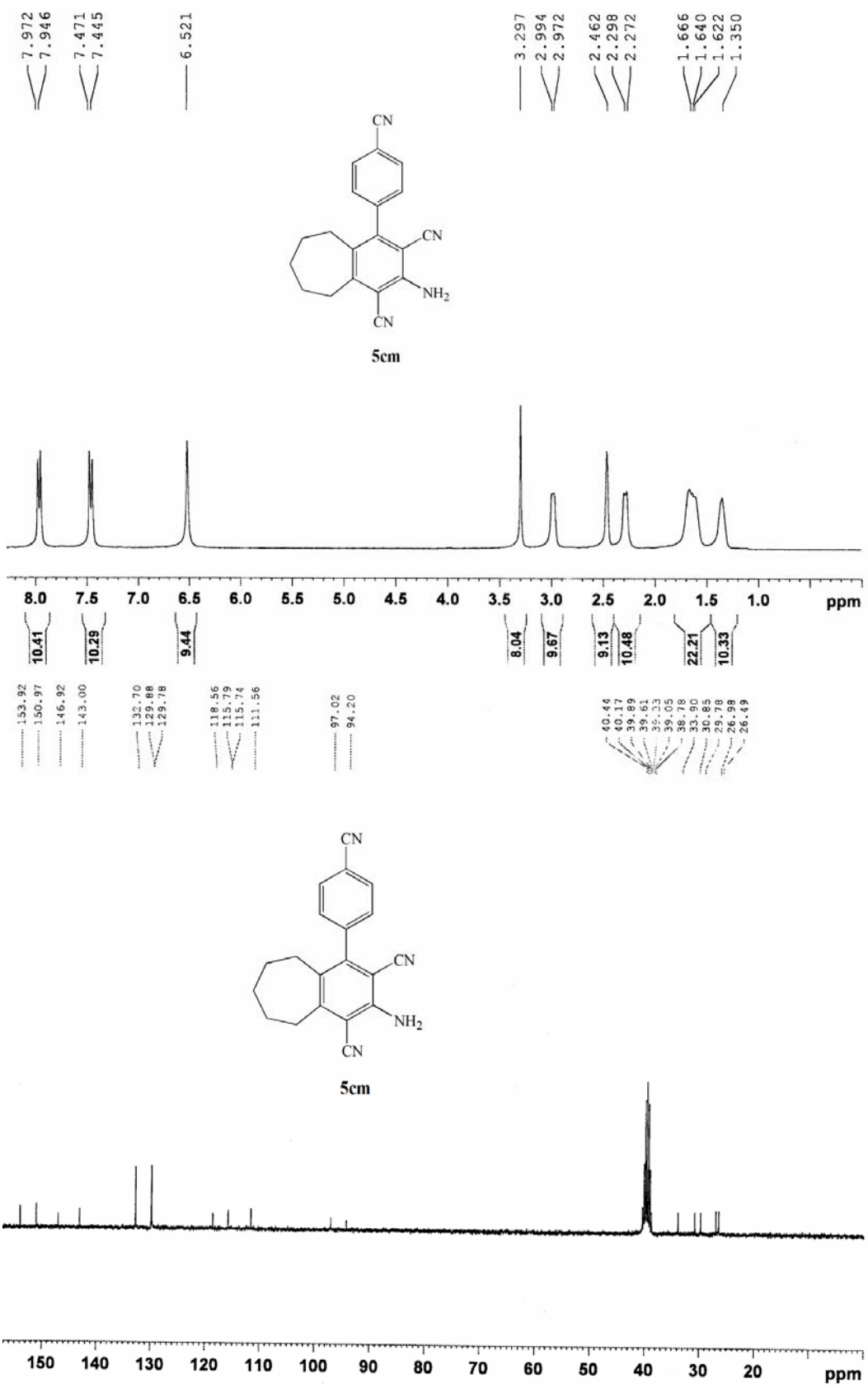
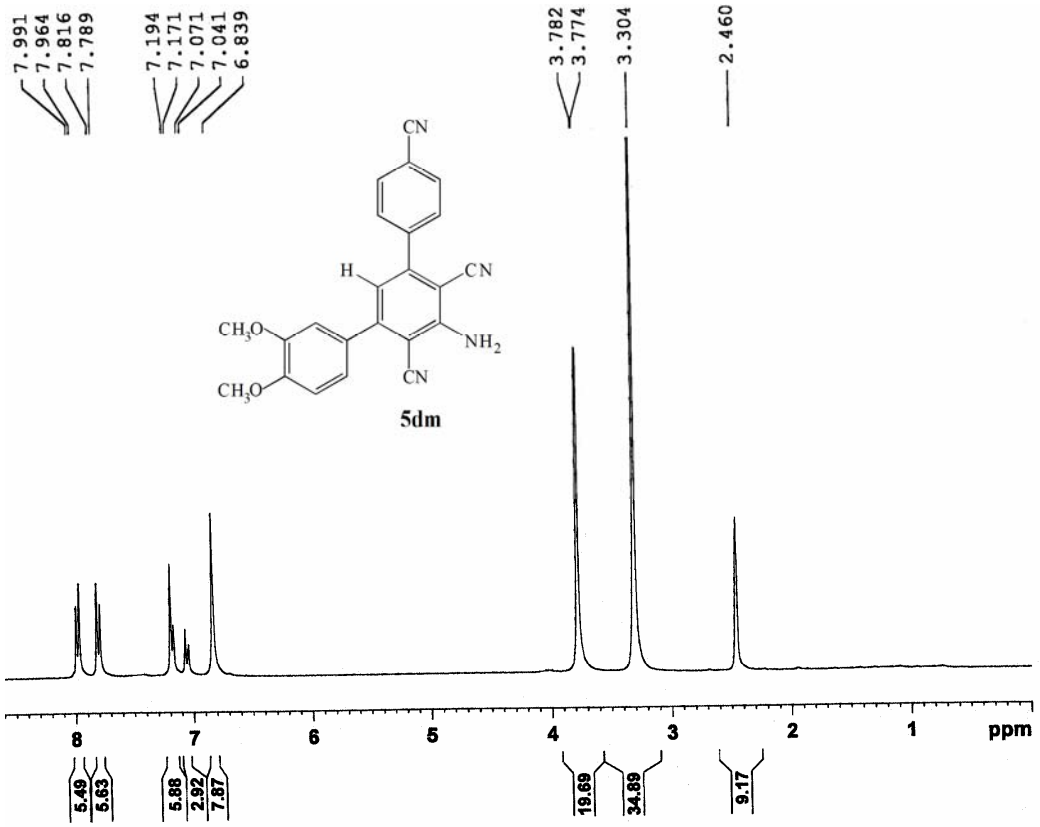
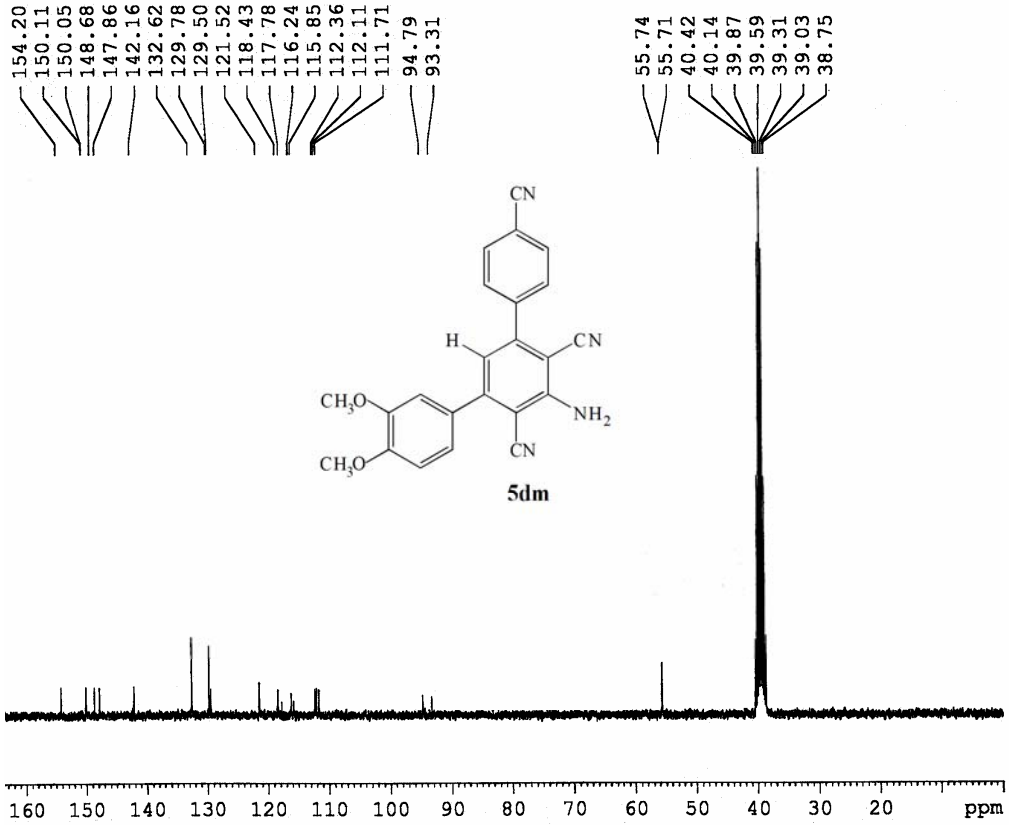
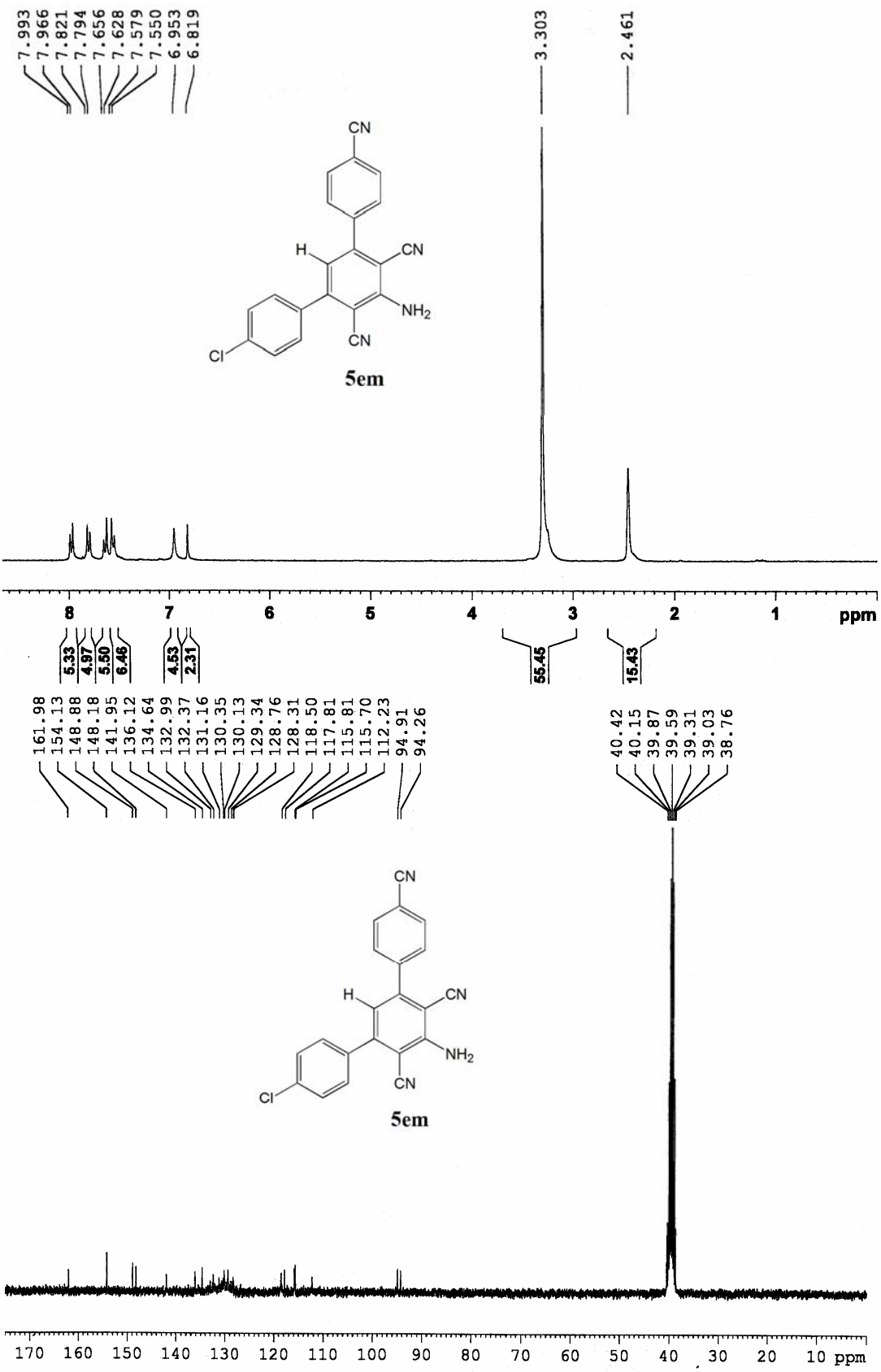


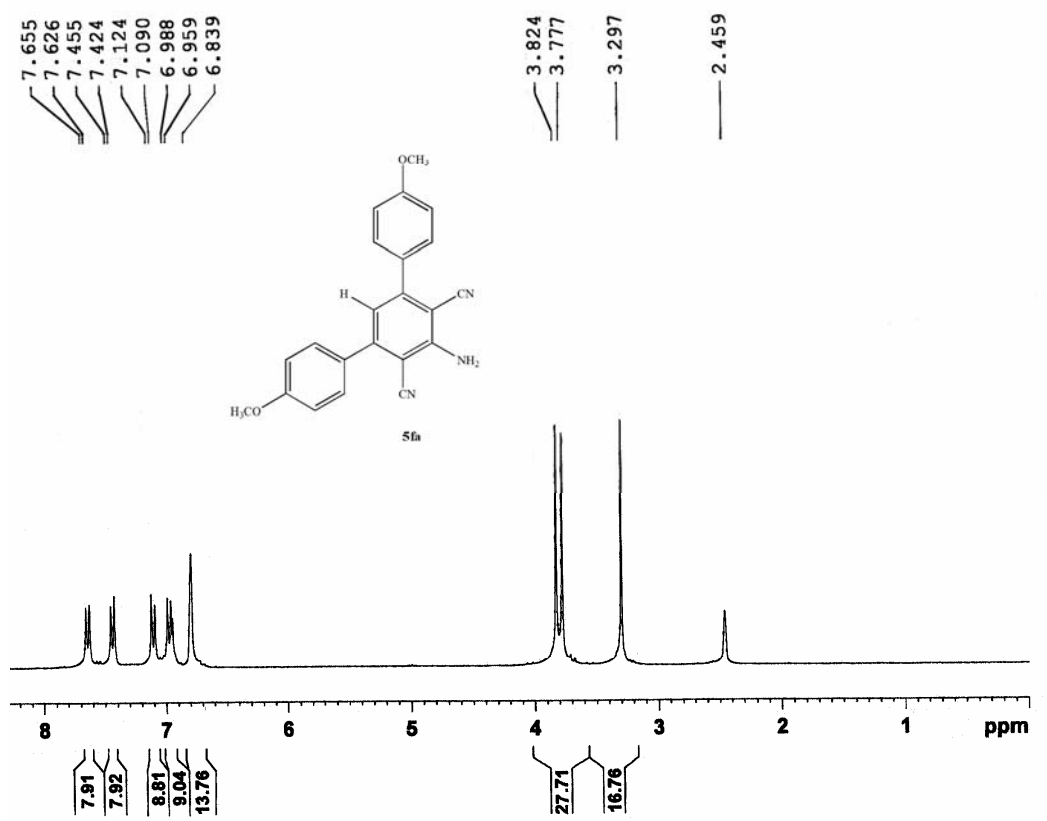


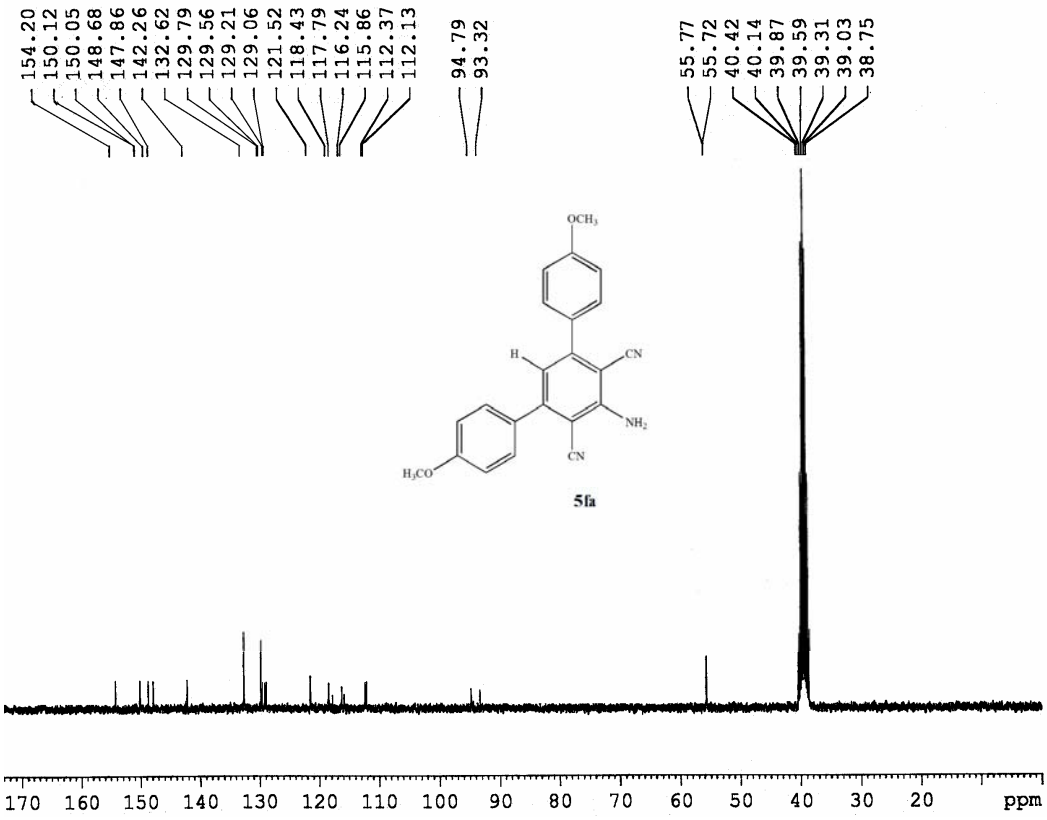


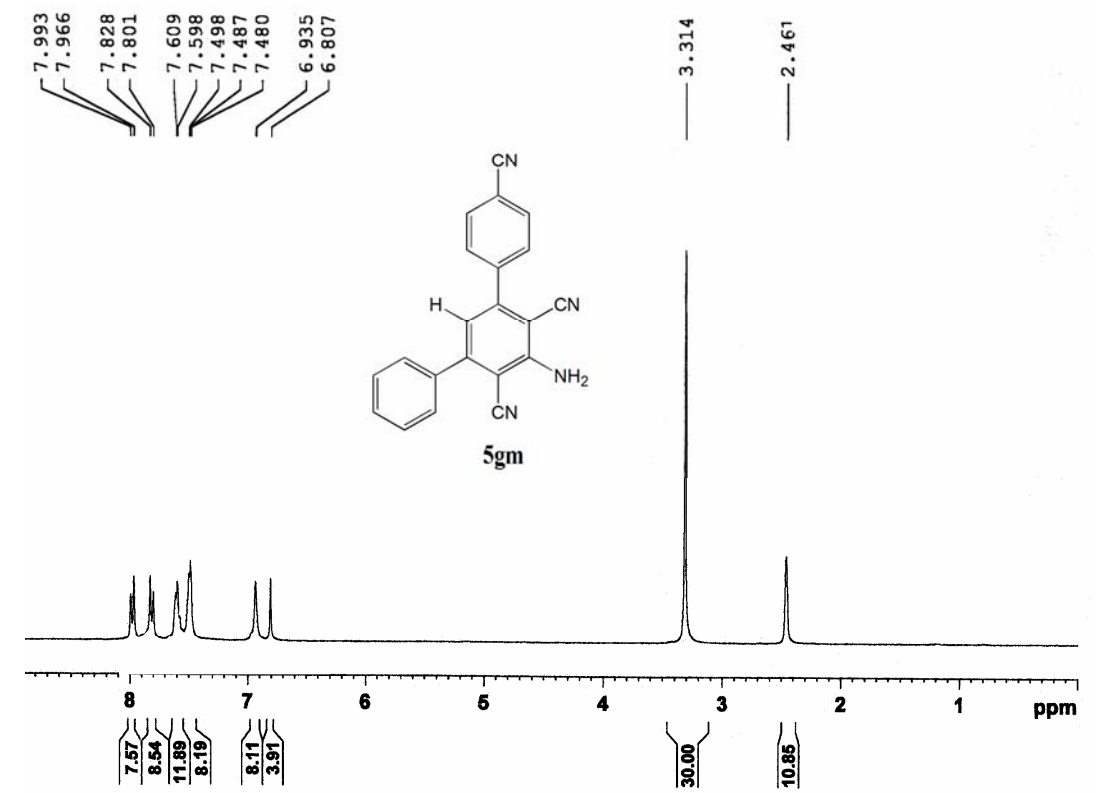


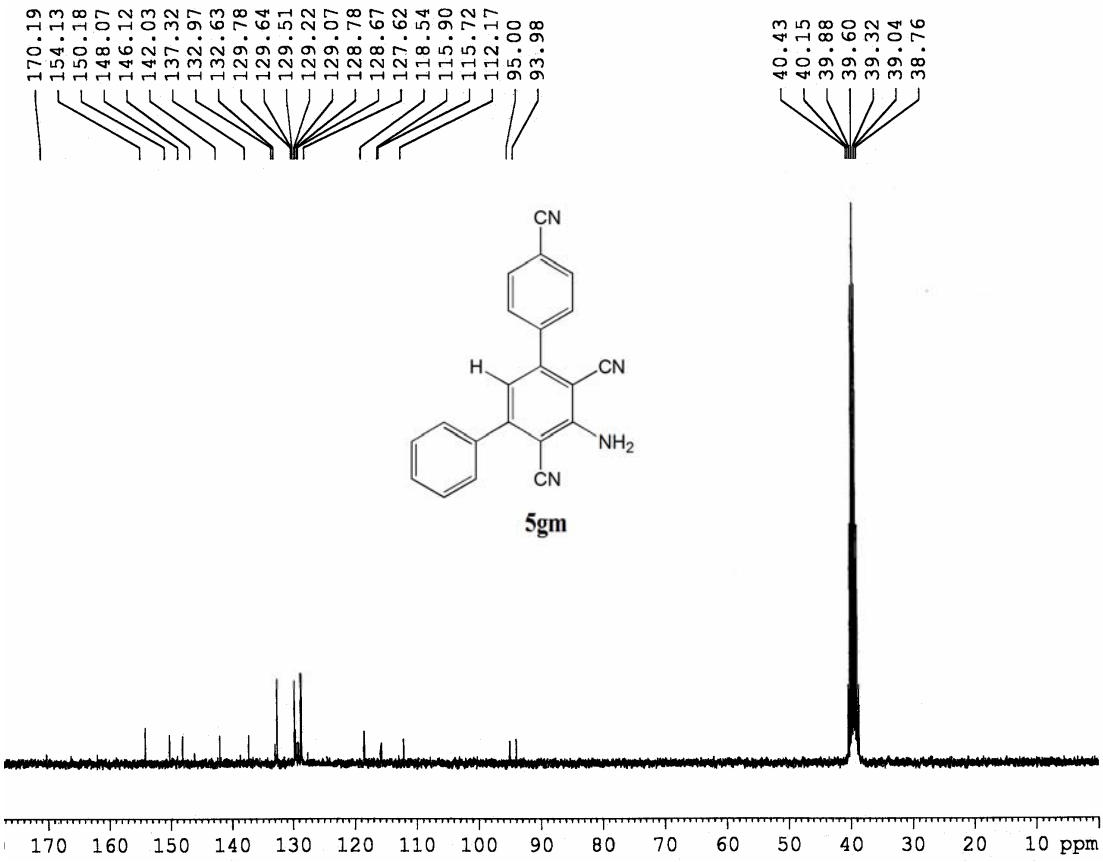


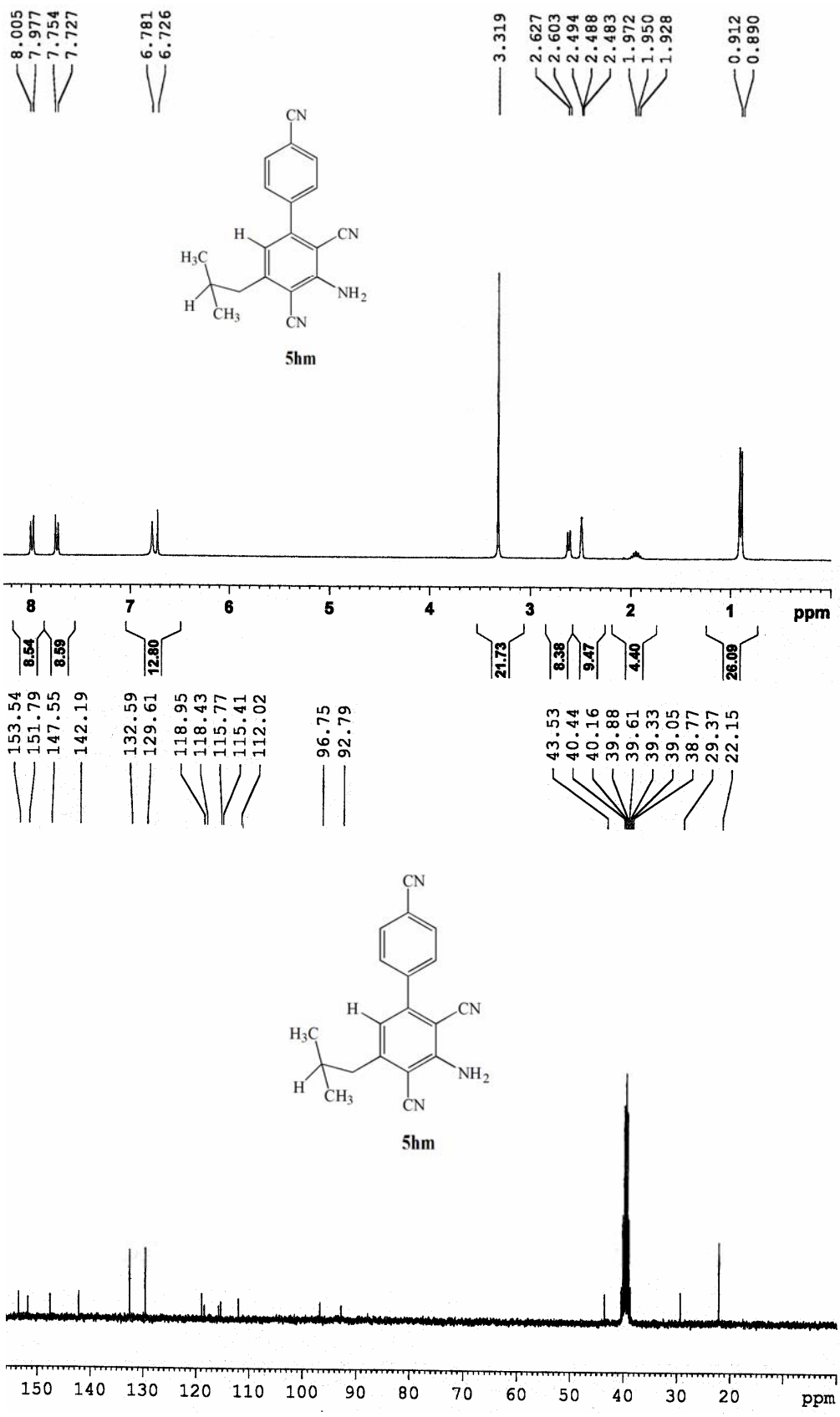


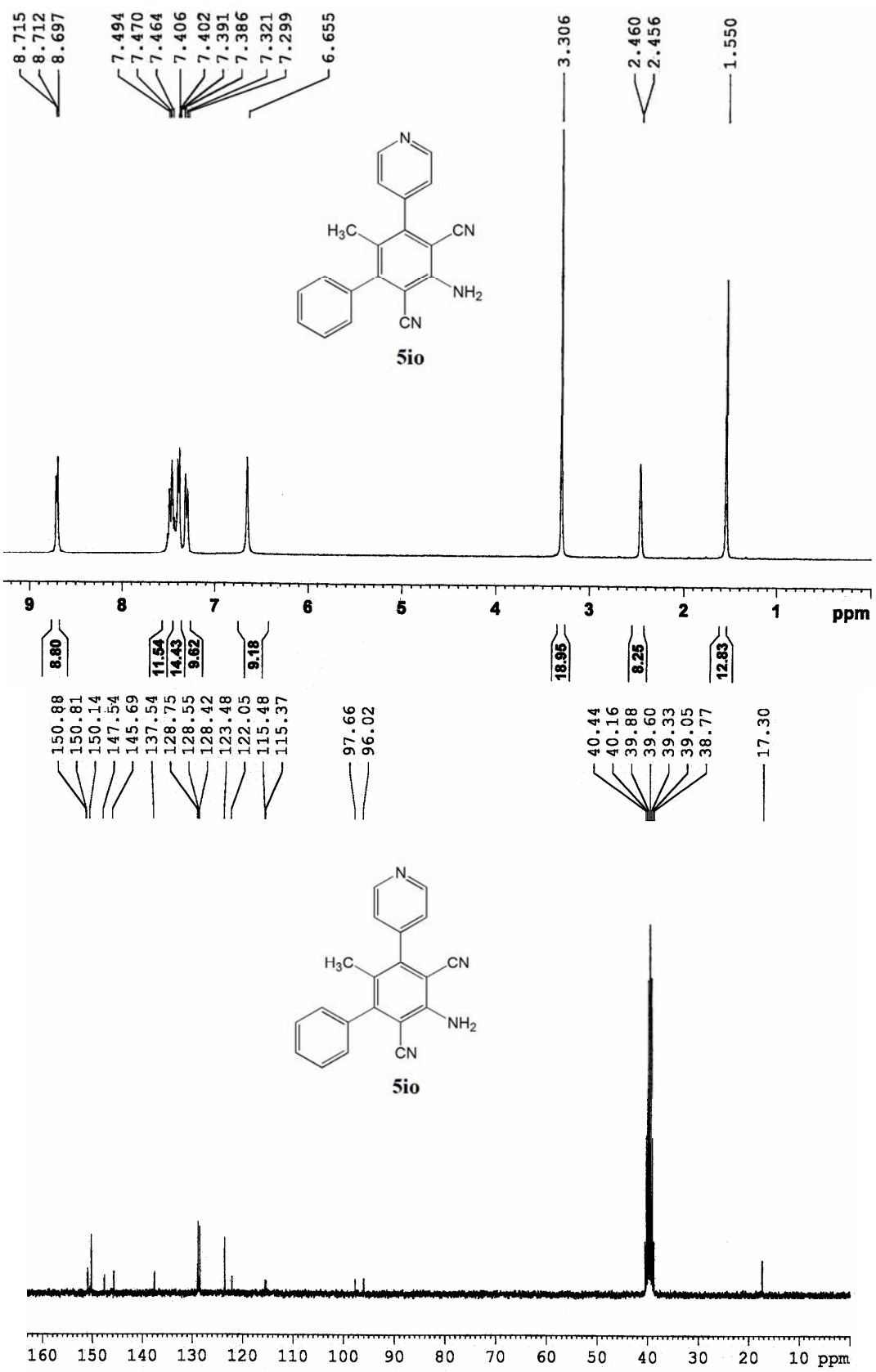


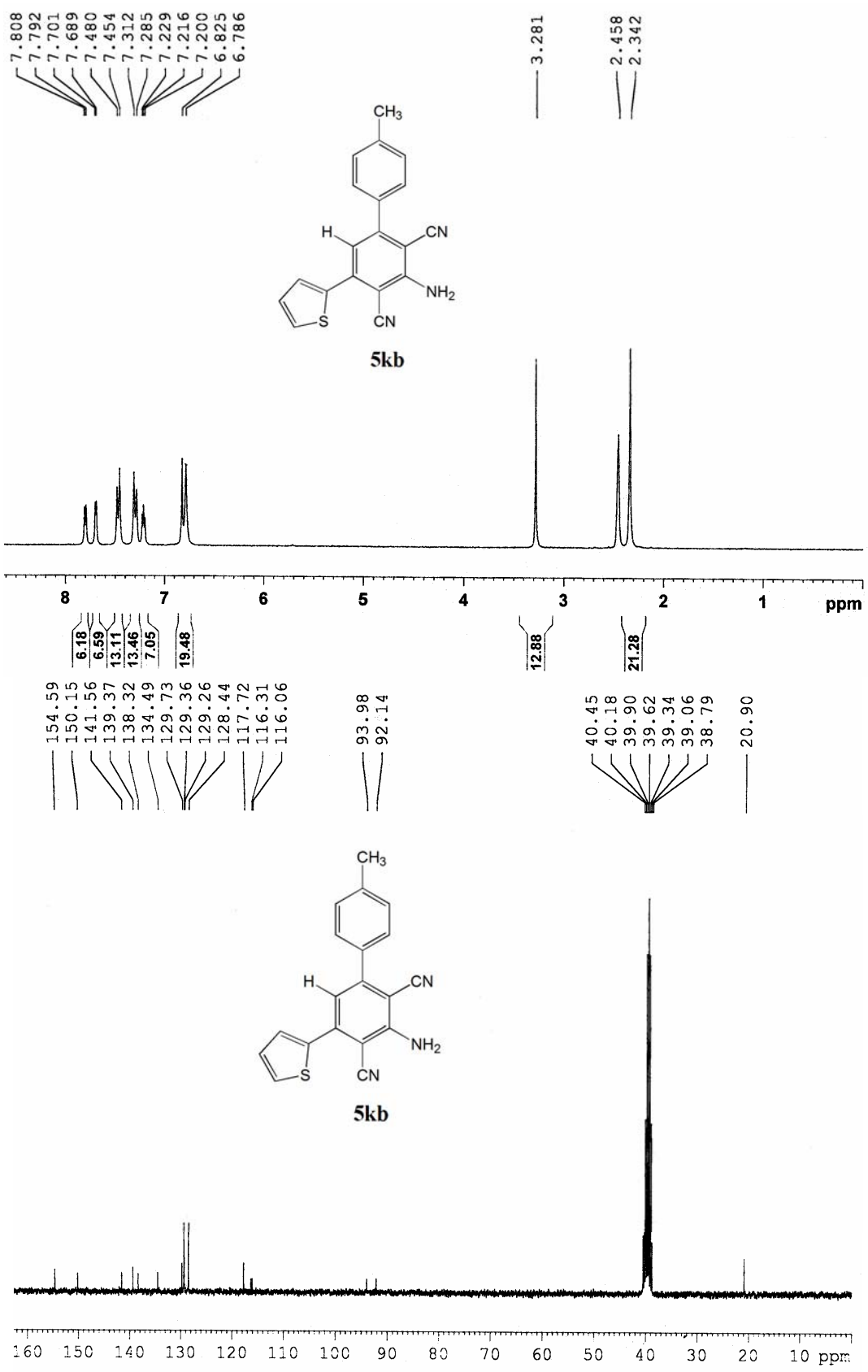


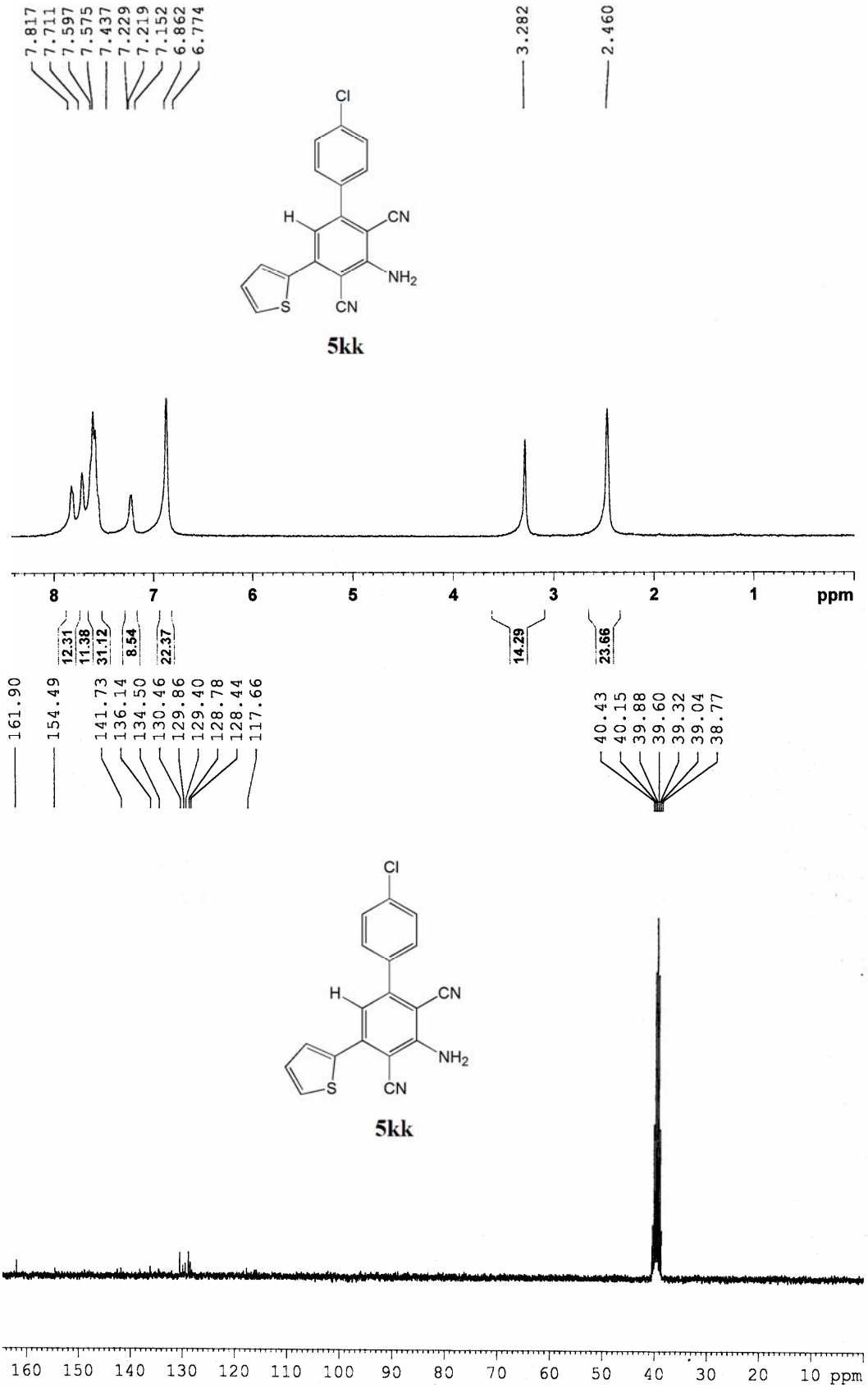




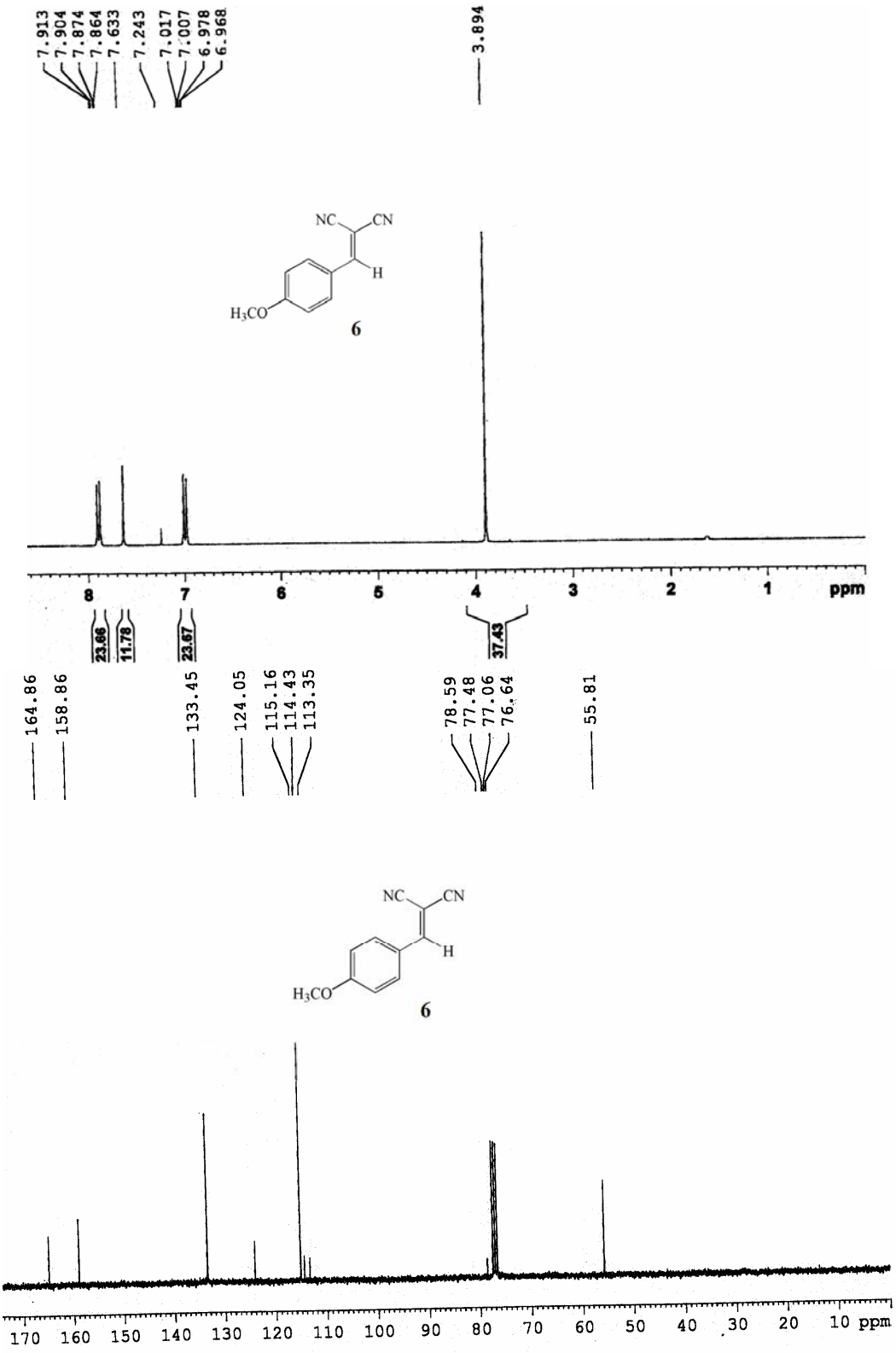


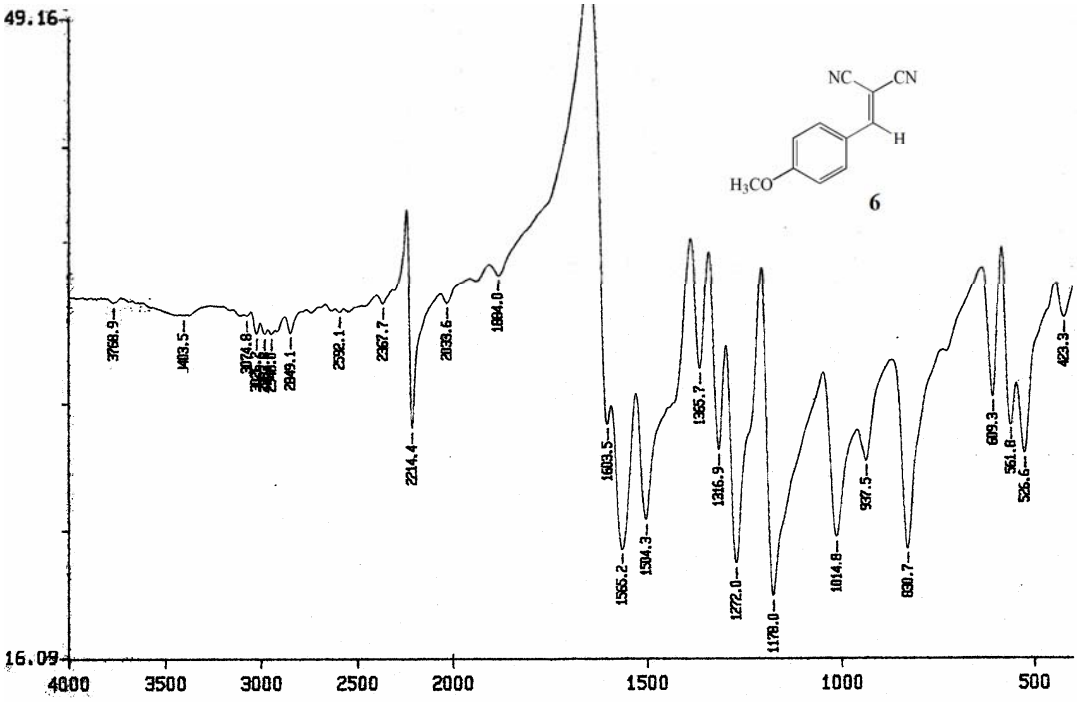




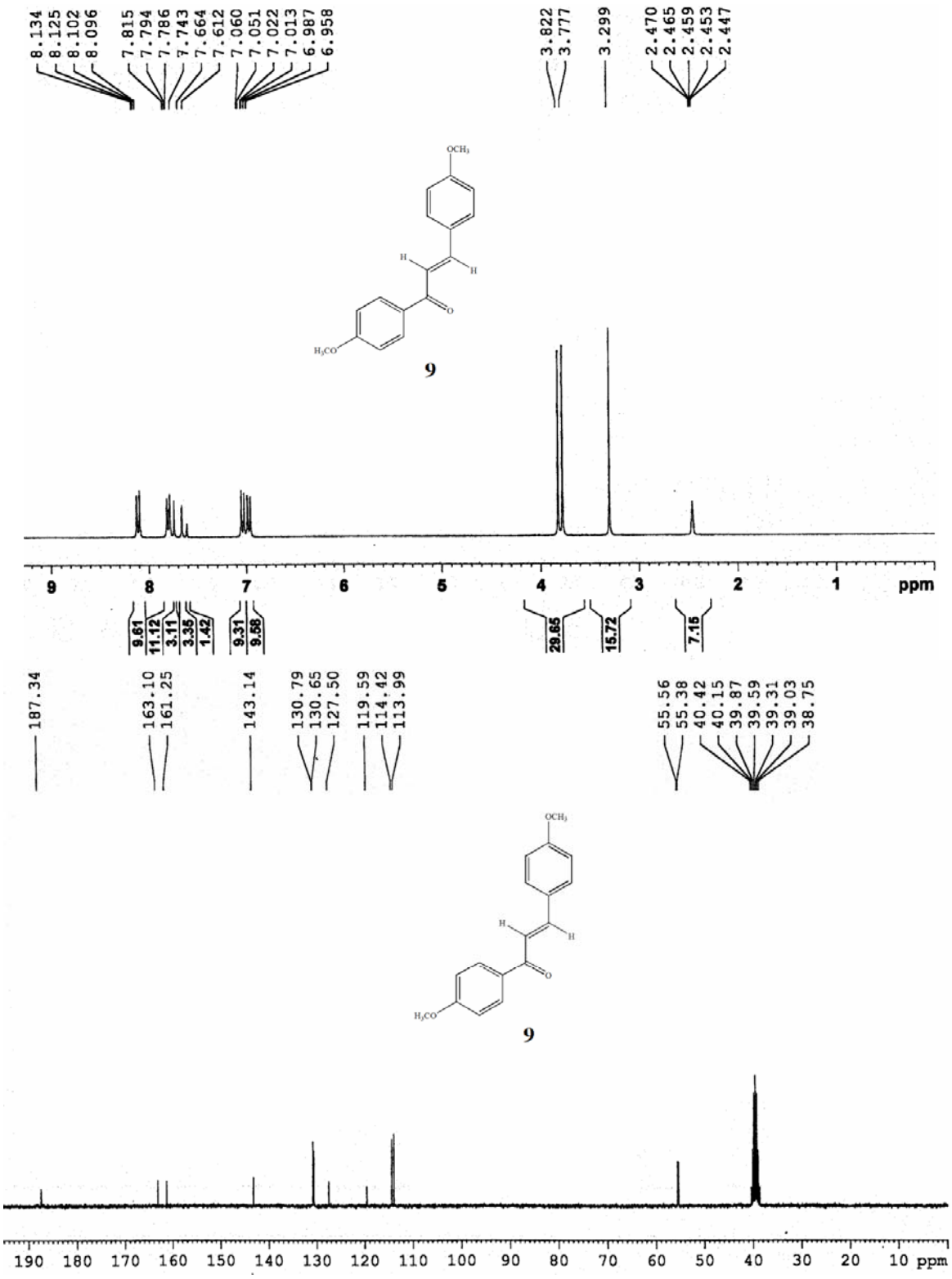


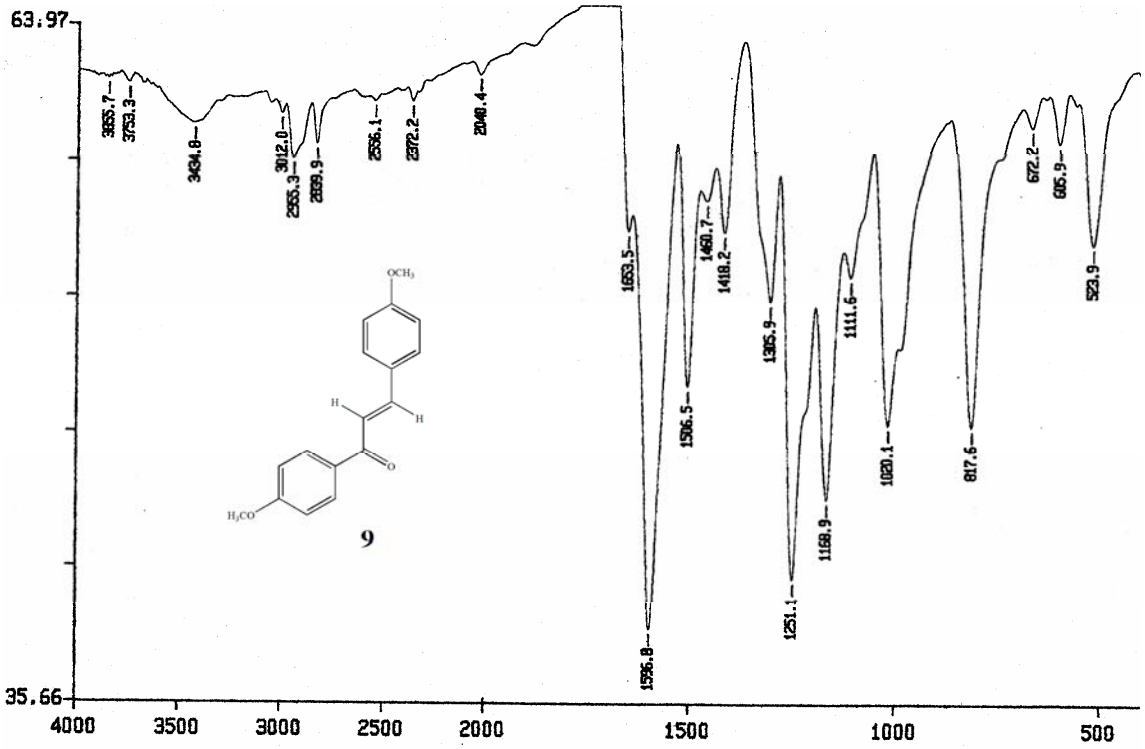
Spectral Data of intermediate 6





Spectral Data of intermediate 9





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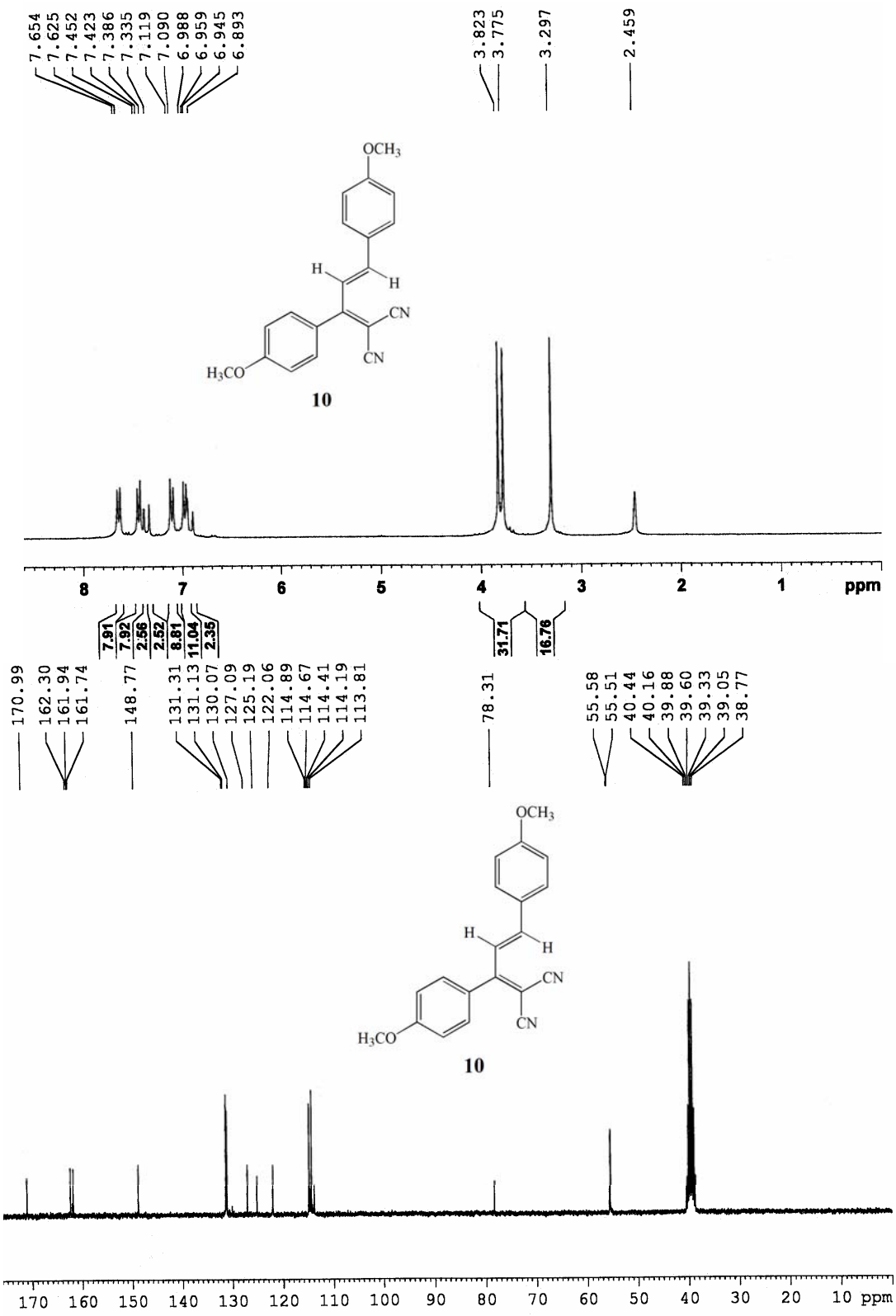
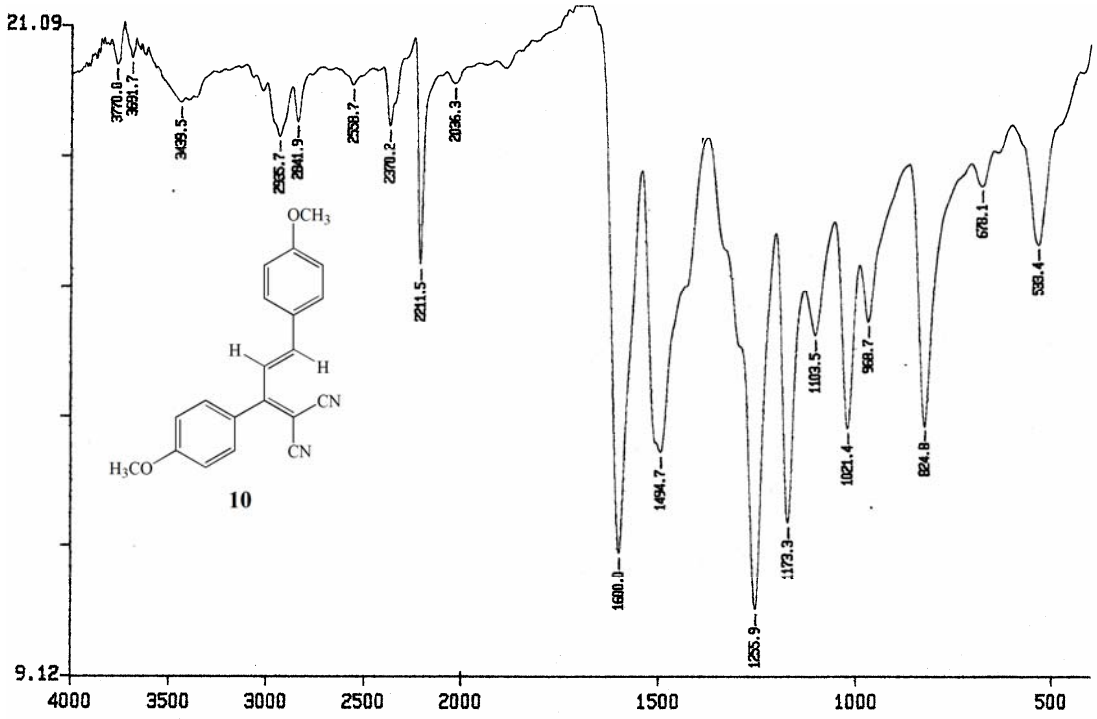
Spectral Data of intermediate 10





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