An efficient solvent-free synthesis of bis(indolyl)methane-based naked eye chemosensor for Cu^{2+} ion from β-chloro-α,β-unsaturated aldehydes using PMA-Cellulose as solid phase reusable catalyst

Arijit Kundu[a], Aniruddha Ganguly[b], Kaliprasanna Dhara[b*], Prasanta Patra[c] and Nikhil Guchhait[b]

[a] *Department of Chemistry, Maulana Azad College, Kolkata-700013, India*

[b] *Department of Chemistry, University College of Science and Technology, University of Calcutta, Kolkata-700009, India*.

[c] *Department of Chemistry, Jhargram Raj College, Paschim Mednipur-721507, India*.

Supplementary Information

1. Experimental

General methods

Melting points were determined in open capillary tubes on Kofler block apparatus and are uncorrected. IR spectra were recorded in cm^{-1} using KBr discs with a Perkin Elmer RXI FTIR spectrophotometer. NMR spectra (^{1}H, ^{13}C) were recorded in $CDCl_3$ or DMSO-D_6 solution in 5 mm BBO probe fitted with a pulse field gradient and working with Topsin 1.3 programme in a Bruker AV-300 Supercon NMR spectrometer (chemical shifts in δ ppm and J in Hz). Hitachi UV-vis U-3501 spectrometer was used for recording UV/VIS spectra in HPLC grade Acetonitrile solution in the order of 10^{-5} mol L^{-1}concentration at room temperature. Perkin-Elmer LS-55 was used for recording fluorescence spectra using aforesaid solution with similar concentration. Field emission scanning electron microscopy (FESEM) was used to observe the surface morphology (both unused and used PMA-Cellulose) and elemental detection of PMA-Cellulose . Previously, the samples were coated with a thin layer of gold to avoid electrical charging during examination. Zeiss Auriga instrument was used for FESEM study. X-ray diffraction analysis of cellulose, phosphomolybdic acid and PMA-Cellulose were performed at room temperature by X-PERT-PRO Pan analytical diffractometer using Cu Kα (λ= 1.5406) as X-ray source of current 30 mA at a generator voltage of 40 kV. The rate of scanning was 1° min^{-1}. ICP-Mass data was collected from Geological survey of India, Central Chemical Laboratory, Kolkata. X-ray crystallographic data were taken on a Bruker Smart Apex 2 diffractometer equipped with a CCD area detector with graphite monochromatized Mo K_{α} radiation. Further information on the crystal structure investigations may be obtained from Cambridge Crystallographic Data Center CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax (+44-(0)1223-336033 or email: (deposit@ccdc.cam.ac.uk) on quoting the depository numbers 986120 for C_{25} H_{18} Br_1 Cl_1 N_2 **(3b)**.

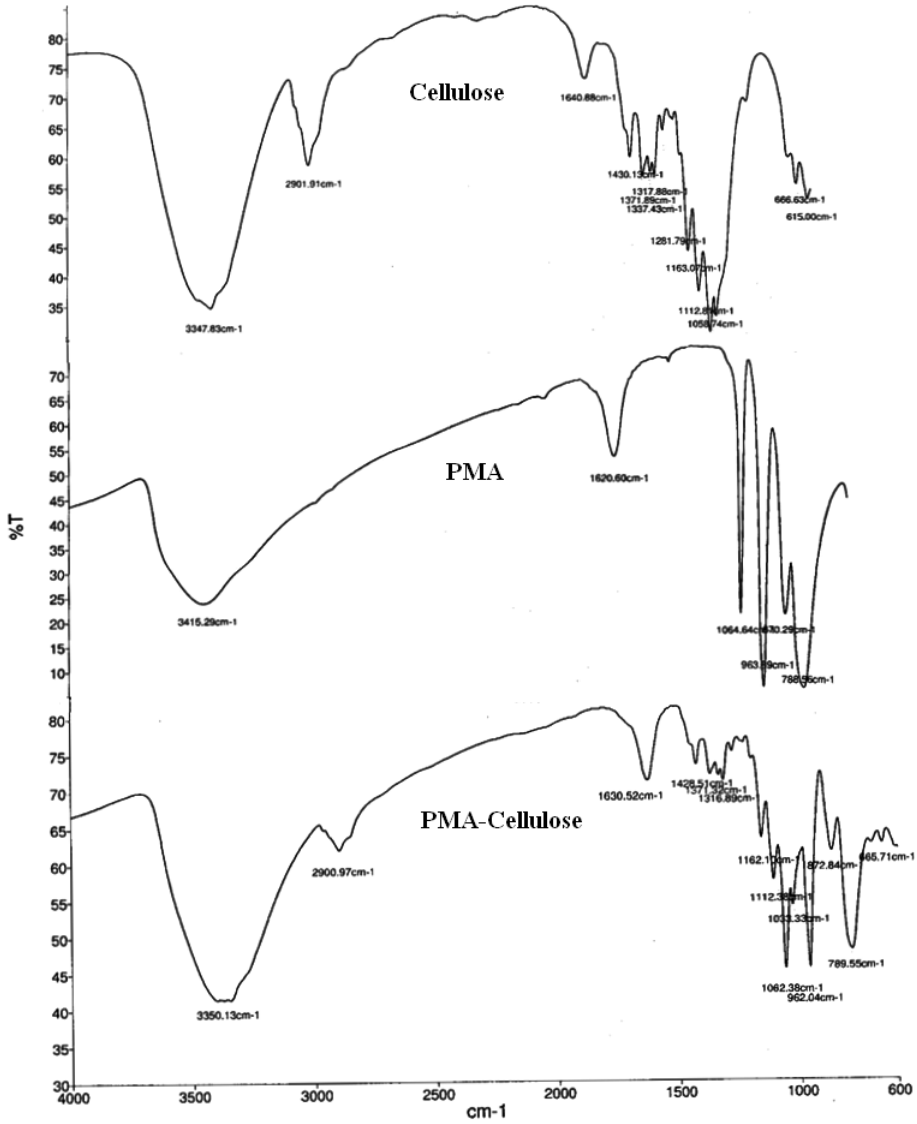


Figure S1: Comparative IR patterns of Cellulose, Phosphomolybdic Acid (PMA), PMA-Cellulose

Table S1: Frequency of bands assigned to catalyst PMA as observed in both PMA and PMA-Cellulose

Assignment	PMA	PMA-Cellulose
ν_4 P-O	1064	1062
ν_3 Mo=O terminal	963	962
ν_2 Mo-O-Mo-O Corner	870	872
ν_1 Mo-o-Mo axis	788	789

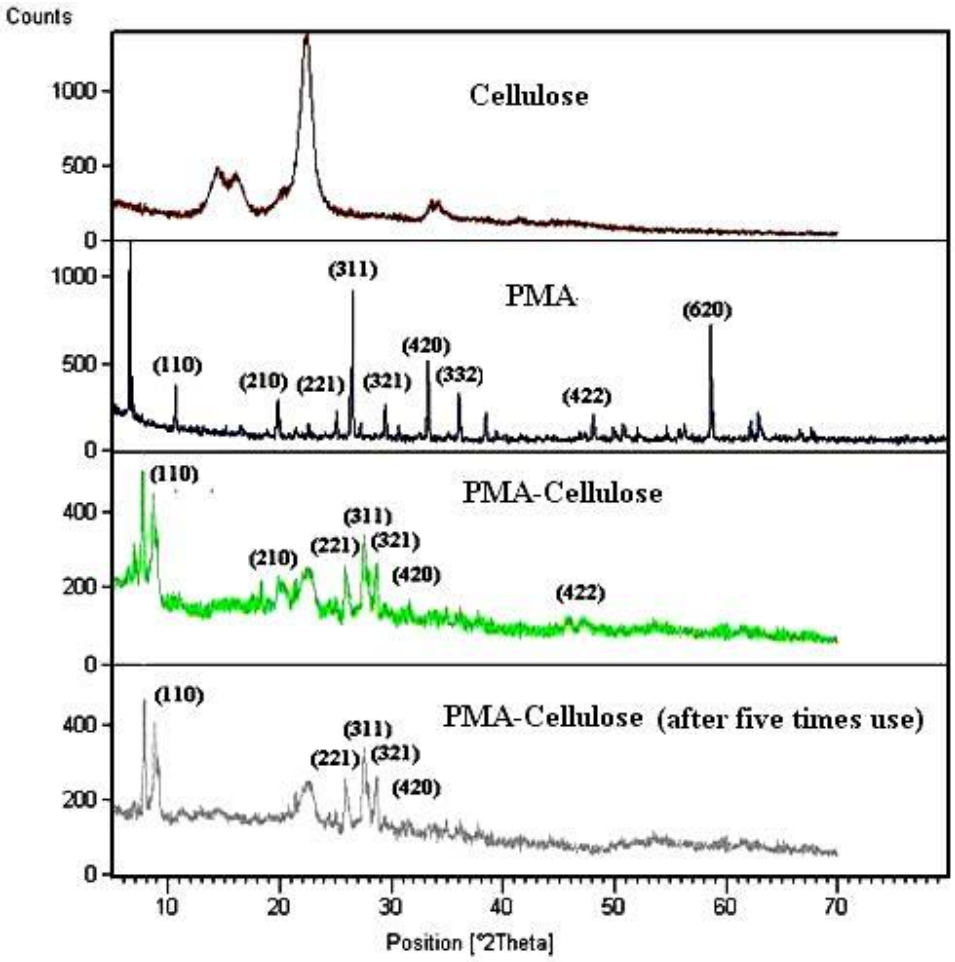


Figure S2: Comparative XRD patterns of Cellulose, PMA, PMA-Cellulose and reused PMA-Cellulose

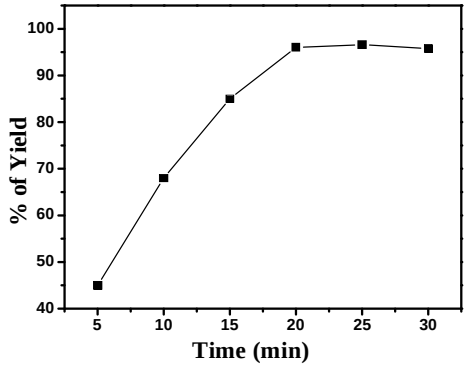
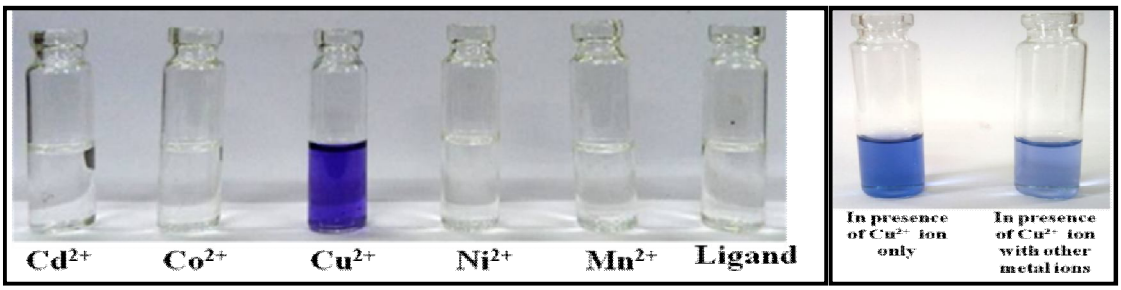


Figure S3: Kinetic measurement graph between reaction time and % of yield of the product



(a) **(b)**

Fig S4 (a): Colour change of compound **4e** in presence of different metal ions (**4d** also give similar observation). **(b)** Study of the interference of other metal ions in presence of Cu^{2+} ion

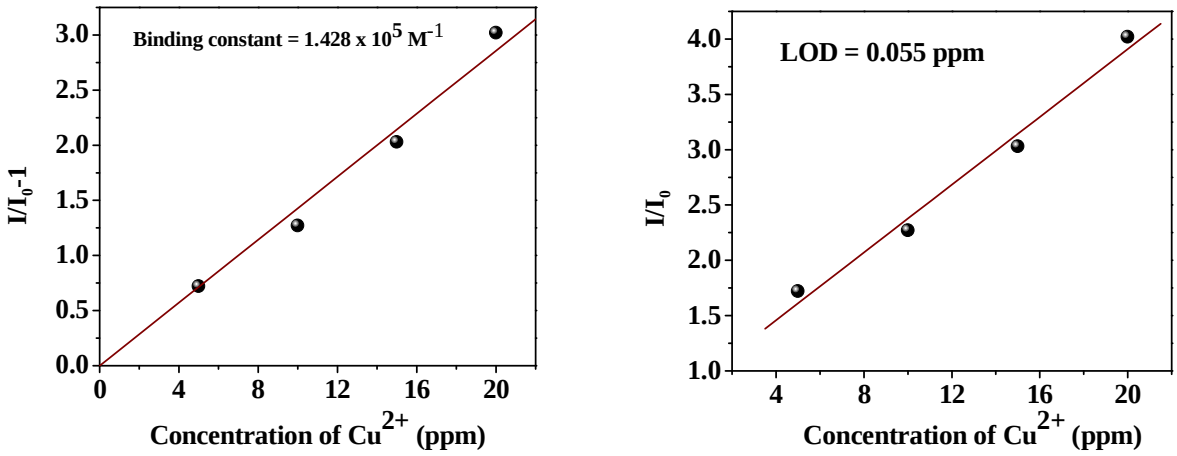


Fig S5 : (a) The Binding constant curve with K_b = 1.428 x 10^5 M^{-1} of compound **4e**

(b) The Limit of detection curve with LOD= 0.055 ppm of compound **4e**

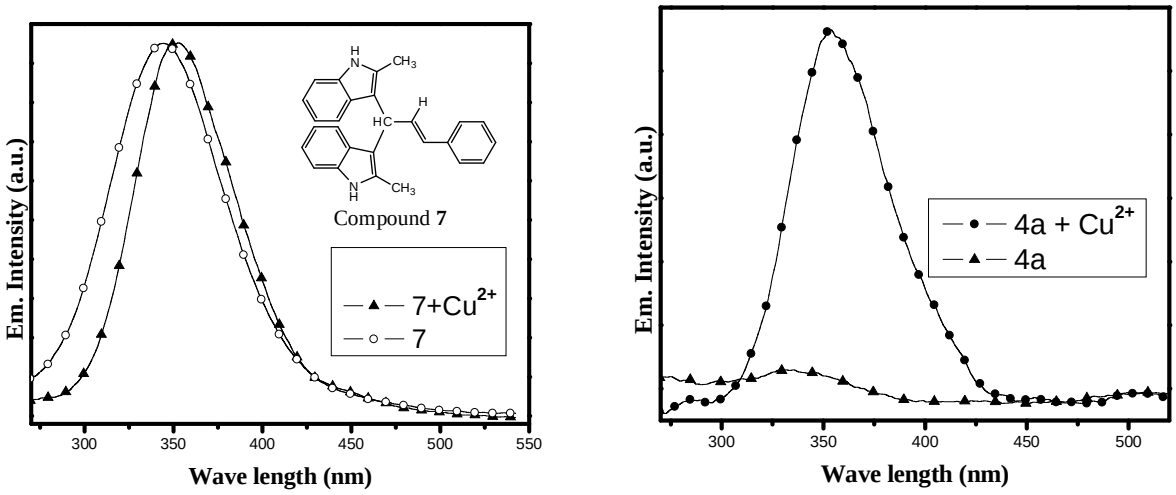


Fig S6: **(a)** Emission spectra of compound **7** in presence and absence of Cu^{2+} ion (λ_{max}= 350 nm)

(b) Emission spectra of compound **4a** in presence and absence of Cu^{2+} ion (λ_{max}= 336 nm)

(Z)-3, 3'-(3-chloro-3-phenylprop-2-ene-1,1-diyl)bis(1H-indole) (3a)

Yield: 96%, (0.366 g); m.p. 60–62°C characteristics: white solid; IR υ_{max} (KBr) 3455, 1507, 1454, 1386; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.89 (1H, d, J=10.2 Hz), 6.72 (1H, d, J= 9.6 Hz), 6.93-6.95(2H, m), 7.05-7.13 (2H, m), 7.17-7.24 (2H, m), 7.29-7.40 (5H, m), 7.58-7.69 (4H, m), 7.93 (2H, s); ^{13}C NMR (75MHz, $CDCl_3$) δ_C 34.9, 60.1, 110.7, 110.8, 119.0, 119.4, 119.6, 121.6, 121.8, 123.8, 126.3, 126.6, 127.9, 128.1, 128.3, 128.5, 128.9, 129.4,129.1, 136.3; analysis calculated for $C_{25}H_{19}ClN_2$: C: 78.42; H: 5.00; N: 7.32% found C: 78.40; H, 5.02; N: 7.31%.

(Z)-3,3'-(3-chloro-3-(4-chlorophenyl)prop-2-ene-1,1-diyl)bis(1H-indole) (3c)

Yield: 90%, (0.375 g); m.p. 155–156°C characteristics: white crystalline solid (from Pet. Ether Chloroform mix); IR υ_{max} (KBr) 3453, 1483, 1455, 1416, 1338, 1237, 1087, 1011, 755, 740; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.87 (1H, d, J=9.6 Hz), 6.70 (1H, d, J= 9.5 Hz), 6.93-6.95 (2H, m), 7.06-7.14 (2H, m), 7.18-7.22 (2H, m), 7.24-7.30 (2H, m), 7.38 (2H, d, J=8.1 Hz), 7.48-7.56 (2H, m), 7.65 (2H, d, J= 7.9 Hz), 7.90 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 35.4, 111.2, 117.3, 119.5, 122.1, 126.8, 127.9, 128.0, 128.5, 130.8, 134.3, 136.7; analysis calculated for $C_{25}H_{18}Cl_2N_2$: C: 71.95; H: 4.35; N: 6.71% found C: 71.96; H: 4.33; N: 6.72%.

(Z)-3,3'-(3-chloro-3-(4-methoxyphenyl)prop-2-ene-1,1-diyl)bis(1H-indole) (3d)

Yield: 92%, (0.379 g); m.p. 146–147°C characteristics: white solid; IR υ_{max} (KBr) 3446, 1601, 1508, 1455, 1418, 1337, 1254 1180, 1093, 1029, 831, 755; ^{1}H NMR (300 MHz, DMSO-D_6) δ_H 3.76(3H, s), 5.74 (1H,d, J= 9.9 Hz), 6.90-6.96 (5H, m), 7.06 (2H, t, J= 7.6 Hz), 7.23-7.24 (2H, m), 7.37 (2H, d, J=8.1 Hz), 7.54-7.61 (4H, m), 10.89 (2H, s); ^{13}C NMR (75MHz, $CDCl_3$) δ_C 34.9, 55.3, 111.6, 113.8, 113.9, 116.3, 118.4, 119.0, 121.0, 122.7, 126.5, 127.7, 127.8, 128.9, 129.8, 129.9, 136.7, 159.6; analysis calculated for $C_{26}H_{21}ClN_2O$: C: 75.63; H: 5.13; N: 6.78% found C: 75.62; H: 5.12; N: 6.80%.

(Z)-3,3'-(3-chloro-3-(4-nitrophenyl)prop-2-ene-1,1-diyl)bis(1H-indole) (3e)

Yield: 95%, (0.406 g); m.p. 160–162°C characteristics: yellow solid; IR υ_{max} (KBr) 3434, 3057, 2346, 1593, 1512, 1485; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.76 (1H, d, J= 9.6 Hz), 6.78-6.95 (5H,m), 7.01-7.05 (2H, m), 7.20-7.28 (2H, m), 7.46-7.60 (4H, m), 7.99 (2H, d, J= 7.5 Hz), 9.32 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 35.6, 115.9, 118.9, 120.0, 122.0, 122.4, 122.7, 124.3, 126.6, 127.8, 129.1, 134.4, 136.8, 144.1, 147.2; analysis calculated for $C_{25}H_{18}ClN_3O_2$: C: 70.18; H: 4.24; N: 9.82% found C: 70.17; H: 4.23; N: 9.81%.

(Z)-3,3'-(3-chloro-3-(3-nitrophenyl)prop-2-ene-1,1-diyl)bis(1H-indole) (3f)

Yield: 96%, (0.410 g); m.p. 107–108°C characteristics: yellow solid; IR υ_{max} (KBr) 3049, 1721, 1617, 1527, 1455, 1416, 1348; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 5.86 (1H, d, J=9.3 Hz), 6.80 (1H, d, J= 9.6 Hz), 6.83-6.88 (2H, m), 7.03-7.09 (2H, m), 7.13-7.21 (3H, m), 7.26-7.38 (3H, m), 7.60 (2H. d, J=7.8 Hz), 7.73-7.78 (1H, m), 7.90 (2H, s), 8.01-8.08 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 37.4, 102.4, 111.0, 111.3, 116.6, 119.2, 119.4, 119.6, 119.9, 120.1, 120.6, 120.8, 121.3, 121.4, 121.5, 121.8, 122.1, 122.3, 122.5, 122.7, 122.9, 123.3, 123.4, 124.1, 125.2, 126.2, 126.6, 128.2, 128.9, 129.2, 129.3, 129.8, 130.2, 132.2, 132.8, 134.8, 135.2, 136.6, 139.6, 147.8, 148.1; analysis calculated for $C_{25}H_{18}ClN_3O_2$: C: 70.18; H: 4.24; N: 9.82% found C: 70.20; H: 4.23; N: 9.80%.

(Z)-3,3'-(3-chloro-3-(p-tolyl)prop-2-ene-1,1-diyl)bis(1H-indole) (3g)

Yield: 90%, (0.356 g); m.p. 118–120 ℃ characteristics: white solid; IR υ_{max} (KBr) 3455, 3402, 1507, 1454, 1416, 1336, 1246, 1093, 1011; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.34 (3H,s), 5.87 (1H, d, J= 9.6 Hz), 6.67 (1H, d, J= 9.48 Hz), 6.94 (2H, s), 7.05-7.26 (9H, m), 7.34-7.38 (1H,m), 7.50 (1H, d, J= 7.27 Hz), 7.64 (1H, d, J= 7.96 Hz), 7.92 (2H, br.s.); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 20.7, 34.9, 102.2, 110.6, 110.8, 117.3, 118.9, 119.4, 119.7, 120.3, 121.6, 121.8, 126.2, 126.6, 128.5, 128.9, 131.6, 136.3, 138.0; analysis calculated for $C_{26}H_{21}ClN_2$: C: 78.68; H: 5.33; N: 7.06% found C: 78.67; H: 5.32; N: 7.08%.

(Z)-3,3'-(3-chloro-2-methyl-3-phenylprop-2-ene-1,1-diyl)bis(1H-indole) (3h)

Yield: 94%, (0.372g); m.p. 128–129 °C characteristics: white solid; IR υ_{max} (KBr) 3416, 3054, 2367, 1617, 1454, 1416, 1386, 1216, 1092, 1011; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.00 (3H, s), 5.58 (1H, s), 6.84 (2H, s), 7.00-7.03 (2H, t, J= 7.6 Hz), 7.13-7.37 (9H,m), 7.44-7.46 (2H, m), 7.94 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.3, 39.3, 112.2, 117.3, 118.9, 120.3, 120.9, 122.0, 122.2, 124.4, 126.9, 127.8, 128.2, 129.4, 129.8, 135.6, 136.5, 138.9; analysis calculated for $C_{26}H_{21}ClN_2$: C: 78.68; H: 5.33; N: 7.06% found C: 78.66; H: 5.31; N: 7.07%.

(Z)-3,3'-(3-chloro-3-phenylprop-2-ene-1,1-diyl)bis(2-methyl-1H-indole) (4a)

Yield: 97%, (0.398g); m.p. 118-119°C characteristics: white solid; IR υ_{max} (KBr) 3437, 3406, 1456, 1443, 1296, 1240, 1016, 893; ^{1}H NMR (300 MHz, DMSO-D_6) δ_H 2.13 (6H, s), 5.59 (1H, d, J= 9.6 Hz), 6.61 (2H, t, J= 7.4 Hz), 6.74 (2H, t, J= 7.4 Hz), 6.93 (1H, d, J= 9.6 Hz), 7.04-7.17 (7H, m), 7.43 (2H, d, J= 7.2 Hz), 10.59 (2H, s); ^{13}C NMR (75MHz, DMSO-D_6) δ_C 12.8, 35.5, 111.0, 111.3, 118.7, 118.8, 120.3, 126.5, 128.3, 129.0, 129.1, 129.9, 131.3, 132.1, 135.7, 137.6; analysis calculated for $C_{27}H_{23}ClN_2$: C: 78.91; H: 5.64; N: 6.82% found C: 78.90; H: 5.66; N: 6.81%.

(Z)-3,3'-(3-(4-bromophenyl)-3-chloroprop-2-ene-1,1-diyl)bis(2-methyl-1H-indole) (4b)

Yield: 95%, (0.465g); m.p. 180-181°C characteristics: red solid; IR υ_{max} (KBr) 3445, 3397, 1484, 1462, 1294, 1006, 738;^{1}H NMR (300 MHz, DMSO-D_6) δ_H 2.29 (6H, s), 5.72 (1H, d, J= 9.3 Hz), 6.76-6.80 (2H, m), 6.90-6.94 (2H, m), 7.16-7.26 (5H, m), 7.57 (4H, s), 10.79 (2H, s); ^{13}C NMR (75MHz, $CDCl_3$) δ_C 12.1, 34.9, 109.9, 111.0, 112.0, 117.7, 119.2, 119.3, 119.6, 119.7, 121.3, 121.4, 122.1, 122.2, 127.4, 128.2, 128.8, 129.6, 131.0, 132.1, 133.1, 135.6, 136.7; analysis calculated for $C_{27}H_{22}BrClN_2$ for C: 66.20; H: 4.53; N: 5.72% found C: 66.22; H: 4.51; N: 5.71%.

(Z)-3,3'-(3-chloro-3-(4-chlorophenyl)prop-2-ene-1,1-diyl)bis(2-methyl-1H-indole) (4c)

Yield: 96%, (0.427g); m.p. 172-173°C characteristics: white crystalline solid (from Pet. Ether Chloroform mix); IR υ_{max} (KBr) 3380, 2919, 2368, 1485, 1459, 1340, 1303, 1242, 1092, 1009, 829, 750 ;^{1}H NMR (300 MHz, DMSO-D_6) δ_H 2.31 (6H, s), 5.75 (1H, d, J= 9.3 Hz), 6.79 (2H, t, J= 7.2 Hz), 6.94 (2H, t, J= 7.2 Hz), 7.17-7.28 (4H, m), 7.43 (2H, d, J= 7.2 Hz), 7.67 (2H, d, J= 7.2 Hz), 10.80 (2H, s); ^{13}C NMR (75MHz, DMSO-D_6) δ_C 12.7, 35.5, 56.5, 110.9, 111.1, 118.6, 118.7, 120.3, 128.1, 128.2, 128.7, 129.1, 132.1, 133.6, 135.6, 136.3; analysis calculated for $C_{27}H_{22}Cl_2N_2$: C, 72.81; H, 4.98; Cl, 15.92; N, 6.29% found C: 72.83; H: 4.97; N: 6.28%.

(Z)-3,3'-(3-chloro-3-(4-methoxyphenyl)prop-2-ene-1,1-diyl)bis(2-methyl-1H-indole) (4d)

Yield: 97%, (0.428g); m.p. 162-163°C characteristics: bluish grey solid; IR υ_{max} (KBr) 3394, 2346, 1601, 1507, 1460, 1289, 1251, 1178, 1023, 834, 739; ^{1}H NMR (300 MHz, DMSO-D_6) δ_H 2.23 (6H, s), 3.66 (3H, S), 5.65 (1H, d, J= 9.6 Hz), 6.71 (2H, t, J= 7.5 Hz), 6.83-6.92 (5H, m), 7.14-7.21 (4H, m), 7.49 (2H, d, J= 8.7 Hz), 10.70 (2H, s); ^{13}C NMR (75MHz, DMSO-D_6) δ_C 12.7, 35.4, 55.7, 110.9,

111.5, 114.4, 118.7, 120.2, 127.7, 127.8, 127.9, 129.3, 129.6, 130.1, 131.9, 135.6, 159.93; analysis calculated for $C_{28}H_{25}ClN_2O$: C: 76.26; H: 5.71; N: 6.35% found C: 76.24; H: 5.73; N: 6.34%.

(Z)-3,3'-(3-chloro-3-(4-nitrophenyl)prop-2-ene-1,1-diyl)bis(1H-indole) (4e)

Yield: 96%, (0.438g); m.p. 130-131°C characteristics: yellow solid; IR υ_{max} (KBr) 3381, 1593, 1513, 1459, 1343, 849, 747; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.25 (6H, s), 5.84 (1H, d, J= 9.3 Hz), 6.93 (2H, t, J= 7.9 Hz), 7.06 (2H, t, J= 7.8 Hz), 7.18 (1H, d, J= 9.4 Hz), 7.26 (3H, d, J= 7.7 Hz), 7.37 (2H, d, J= 8 Hz), 7.71-7.80 (4H, m), 8.13 (1H, s), 8.16 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 18.4, 35.8, 58.5, 110.3, 111.5, 118.9, 119.4, 120.9, 123.6, 127.1, 128.3, 134.6, 135.2, 144.0; analysis calculated for $C_{27}H_{22}ClN_3O_2$: C: 71.13; H: 4.86; N: 9.22% found C: 71.14; H: 4.84; N: 9.21%.

(Z)-3,3'-(3-chloro-3-(3-nitrophenyl)prop-2-ene-1,1-diyl)bis(2-methyl-1H-indole) (4f)

Yield: 93%, (0.423g); m.p. 126-127°C characteristics: yellow solid; IR υ_{max} (KBr) 3387, 1527, 1459, 1347, 740 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.30 (6H, s), 5.88 (1H, d, J=9.6 Hz), 6.92-7.00 (2H, m), 7.05-7.18 (3H, m), 7.28-7.31 (2H, m), 7.4 (2H, d, J=7.8 Hz), 7.46-7.54 (2H, m), 7.83 (1H, s), 7.88-7.95 (1H, m), 8.10-8.18 (1H, m), 8.46-8.51 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 12.6, 35.7, 111.6, 119.4, 120.9, 128.3, 131.3, 135.2, 138.6, 148.7; analysis calculated for $C_{27}H_{22}ClN_3O_2$. C: 71.13; H: 4.86; N: 9.22% found C: 71.11; H: 4.88; N: 9.23%.

(Z)-3,3'-(3-chloro-3-(p-tolyl)prop-2-ene-1,1-diyl)bis(2-methyl-1H-indole) (4g)

Yield: 92%, (0.390g); m.p. 110-111°C characteristics: white solid; IR υ_{max} (KBr) 3380, 2919, 2368, 1485, 1459, 1303, 1092, 1009, 829; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.27 (6H, s), 2.43 (3H, s), 5.84 (1H, d, J= 9.6 Hz), 6.91-6.95 (2H, m), 7.03-7.13 (4H, m), 7.22-7.29 (3H, m), 7.32-7.50 (4H, m), 7.51-7.77 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 12.4, 13.8, 41.3, 109.8, 111.8, 120.2, 125.1, 125.9, 128.1, 128.4, 128.5, 128.6, 128.7, 129.2, 129.4, 130.9, 134.8, 134.9, 137.2, 137.7; analysis calculated for $C_{28}H_{25}ClN_2$: C: 79.14; H: 5.93; N: 6.59% found C: 79.15; H: 5.91; N: 6.57%.

(Z)-3,3'-(3-chloro-2-methyl-3-phenylprop-2-ene-1,1-diyl)bis(2-methyl-1H-indole) (4h)

Yield: 95%, (0.402g); m.p. 92-93°C characteristics: white solid; IR υ_{max} (KBr) 3399, 2917, 1711, 1617, 1459, 1373, 1332, 1300, 1231, 1014; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.05 (6H, S), 2.20-2.26 (3H, m), 5.62 (1H, s), 7.03-7.13 (2H, m), 7.20-7.27 (3H, m), 7.33- 7.38 (5H, m), 7.42-7.56 (3H, m), 7.76 (2H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.1, 13.6, 40.1, 109.2, 109.3, 111.4, 112.3, 118.3, 118.5, 119.7, 120.3, 121.7, 121.8, 127.3, 128.0, 128.7, 129.1, 129.3, 129.4, 130.0, 131.9, 135.2, 136.2, 136.7, 139.3, 139.4, 139.6; analysis calculated for $C_{28}H_{25}ClN_2$: C: 79.14; H: 5.93; N: 6.59% found C: 79.14; H: 5.92; N: 6.60%.

3,3'-((1-chloro-3,4-dihydronaphthalen-2-yl)methylene)bis(1H-indole) (5a)

Yield: 95%, (0.388g); m.p. 154-155°C characteristics: reddish white solid; IR υ_{max} (KBr) 3441, 3419, 1614, 1480, 1455, 1411, 1338, 1216, 1094, 1061, 957, 742; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.27-2.36 (2H, m), 2.66-2.72 (2H, m), 6.30 (1H, s), 6.85 (2H, s), 7.00-7.08 (3H, m), 7.11- 7.20 (3H, m), 7.33-7.35 (3H, m), 7.59 (2H, d, J= 7.9 Hz), 7.73 (1H, d, J= 7.6 Hz), 7.9 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 18.4, 26.6, 28.2, 38.2, 58.5, 111.1, 116.2, 119.2, 119.3, 119.4, 119.4, 120.0, 120.1, 122.1, 123.1, 124.1, 124.7, 125.9, 126.6, 126.9, 127.1, 127.2, 127.5, 133.8, 136.1, 136.6, 138.4; analysis calculated for $C_{27}H_{21}ClN_2$: C: 79.30; H: 5.18; N: 6.85% found C: 79.30; H: 5.17; N: 6.84%.

3,3'-((1-chloro-5-methoxy-3,4-dihydronaphthalen-2-yl)methylene)bis(1H-indole) (5b)

Yield: 92%, (0.403g); m.p. 132-133°C characteristics: gray solid; IR υ_{max} (KBr) 3416, 3379, 1573, 1459, 1433, 1336, 1355, 1291, 1266, 1221, 1094, 1009, 752; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.20-2.26 (2H, m), 2.63-2.69 (2H, m), 3.73 (3H, s), 6.23 (1H, s), 6.75 (1H, d, J= 8.15 Hz), 6.85 (2H, s), 6.98 (3H, t, J= 7.3 Hz), 7.08-7.17 (3H, m), 7.27-7.36 (4H, m), 7.51 (1H, s), 7.54 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 20.1, 26.1, 38.2, 55.7, 110.3, 111.0, 116.3, 117.6, 119.3, 120.1, 123.0, 124.3, 125.8, 126.6, 127.2, 134.9, 136.5, 138.4, 155.6; analysis calculated for $C_{28}H_{23}ClN_2O$: C: 76.61; H: 5.28; N: 6.38% found C: 76.62; H: 5.26; N: 6.37%.

3,3'-((1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)methylene)bis(1H-indole) (5c)

Yield: 97%, (0.425g); m.p. 134-135°C characteristics: gray solid; IR υ_{max} (KBr) 3411, 1605, 1496, 1457, 1421, 1338, 1278, 1105, 1093, 1009, 1025, 885, 741; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.32-2.37 (2H, m), 2.69-2.74 (2H, m), 3.82 (3H, s), 6.31 (1H, s), 6.66 (1H, s), 6.80-6.83 (1H, m), 6.92 (2H, br.s), 7.08 (2H, t, J= 7.2 Hz), 7.22 (2H, t, J= 7.2 Hz), 7.38 (2H, d, J= 8.1 Hz), 7.41 (2H, d, J= 7.8 Hz), 7.68 (1H, d, J= 8.2 Hz), 7.94 (2H, br.s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 26.5, 28.6, 37.9, 55.3, 111.1, 113.1, 116.4, 119.3, 120.1, 122.0, 123.0, 125.6, 126.0, 126.9, 127.2, 135.5, 136.6, 137.8, 159.1; analysis calculated for $C_{28}H_{23}ClN_2O$: C: 76.61; H: 5.28; N: 6.38% found C: 76.60; H: 5.28; N: 6.37%.

3,3'-((3-chloro-1H-inden-2-yl)methylene)bis(1H-indole) (5d)

Yield: 90%, (0.354g); m.p. 143-144°C characteristics: brown solid; IR υ_{max} (KBr); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.07-2.11 (2H, m), 6.16 (1H, s), 6.77 (2H, d, J= 2.1 Hz), 7.03-7.10 (2H, m), 7.18-7.28 (4H,m), 7.29-7.35 (3H, m), 7.44-7.60 (3H, m), 7.87 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 13.8, 33.1, 38.1, 60.2, 110.8, 110.9, 116.2, 116.7, 118.5, 118.8, 118.9, 119.1, 119.2, 119.4, 119.5, 119.6, 121.5, 121.7, 121.8, 122.5, 122.6, 123.3, 123.9, 125.1, 126.3, 126.5, 126.6, 127.9, 128.8, 130.1, 136.2, 136.3, 140.6, 142.3, 144.1; analysis calculated for $C_{26}H_{19}ClN_2$: C: 79.08; H: 4.85; N: 7.09% found C: 79.06; H: 4.86; N: 7.08%.

3,3'-((1-chloro-3,4-dihydronaphthalen-2-yl)methylene)bis(2-methyl-1H-indole) (6a)

Yield: 95%, (0.414g); m.p. 156-157°C characteristics: White solid; IR υ_{max} (KBr) 3418, 3378, 2924, 1614, 1423, 1484, 1461, 1423, 1338, 1295, 1244, 1219, 1010, 957, 752, 741; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.02 (6H, s), 2.26-2.31 (2H, m), 2.60-2.63 (2H, m), 5.96 (1H, s), 6.63-6.68 (2H, m), 6.80-6.89 (3H, m), 6.95-7.10(5H, m), 7.19 (1H, br.s), 7.46 (1H, br.s), 8.84 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 12.2, 27.0, 27.8, 109.8, 110.6, 118.1, 118.4, 119.9, 123.7, 125.4, 126.8, 127.3, 127.8, 128.6, 132.4, 132.9, 135.2, 135.4, 139.8; analysis calculated for $C_{29}H_{25}ClN_2$: C: 79.71; H: 5.77; N: 6.41% found C: 79.70; H: 5.78; N: 6.41%.

3,3'-((1-chloro-5-methoxy-3,4-dihydronaphthalen-2-yl)methylene)bis(2-methyl-1H-indole) (6b)

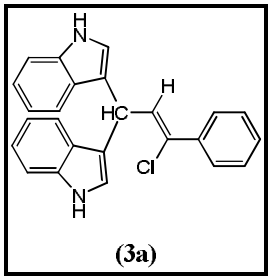
Yield: 90%, (0.420g); m.p. 139-140°C characteristics: White solid; IR υ_{max} (KBr) 3852, 2946, 2368, 1740, 1705, 1635, 1588, 1552, 1506, 1390 ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.12 (6H, s), 2.33-2.39 (2H, m), 2.72-2.77 (2H, m), 3.73 (3H, s), 6.08 (1H, s), 6.73 (1H, d, J= 8.1 Hz), 6.81(2H, t, J= 7.2 Hz), 6.97 (3H, t, J= 7.2 Hz), 7.09-7.29 (5H, m), 7.70 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 12.6, 19.8, 27.3, 38.8, 55.7, 109.9, 110.2, 111.3, 117.3, 119.2, 120.7, 123.8, 126.5, 129.1, 131.8, 134.7, 135.0, 138.8, 155.7; analysis calculated for $C_{30}H_{27}ClN_2O$: C: 77.16; H: 5.83; N: 6.00% found C: 77.18; H: 5.81; N: 6.00%.

3,3'-((1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)methylene)bis(2-methyl-1H-indole) (6c)

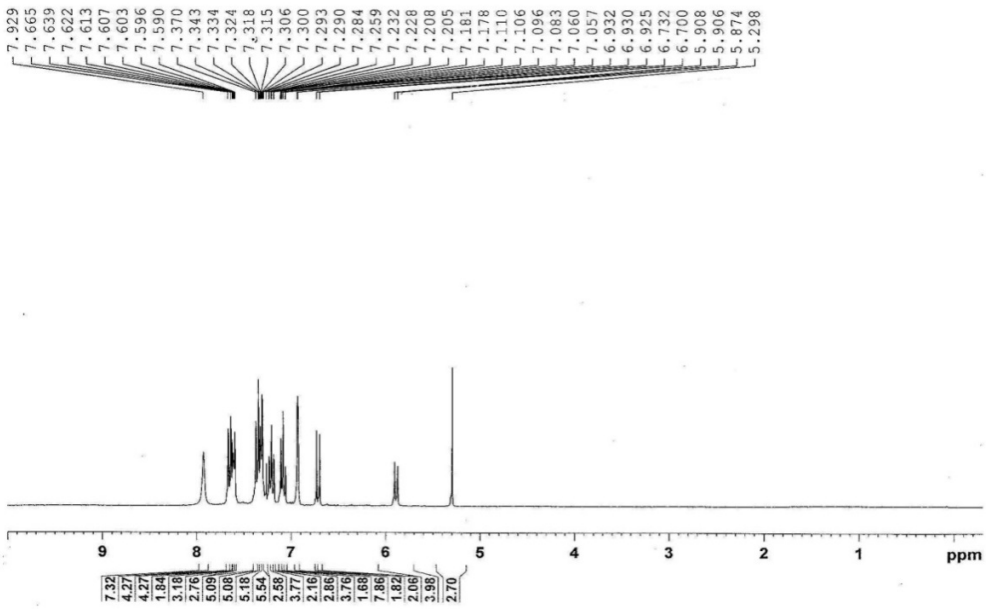
Yield: 96%, (0.448g); m.p. 144-145°C characteristics: White solid; IR υ_{max} (KBr) 3855, 2944, 2367, 1742, 1701, 1631, 1586, 1555, 1508, 1389 ;^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.11 (6H, s), 2.27-2.30 (2H, m), 2.66-2.69 (2H, m), 3.67 (3H, s), 5.94 (1H, s), 6.67-6.77 (3H, m), 6.87 (3H, t, J= 7.5 Hz), 7.00 (2H, d, J= 7.8 Hz), 7.12 (2H, d, J= 7.8 Hz), 7.41 (1H, d, J= 8.7Hz), 10.73 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 12.3, 18.8, 27.5, 27.7, 56.4, 110.1, 110.7, 111.7, 113.4, 118.3, 118.5, 119.3, 120.0, 125.1, 125.3, 126.0, 128.7, 132.4, 135.3, 136.8, 137.4, 159.1; analysis calculated for $C_{30}H_{27}ClN_2O$: C: 77.16; H: 5.83; N: 6.00% found C: 77.16; H: 5.82; N: 6.01%.

3,3'-((3-chloro-1H-inden-2-yl)methylene)bis(2-methyl-1H-indole) (6d)

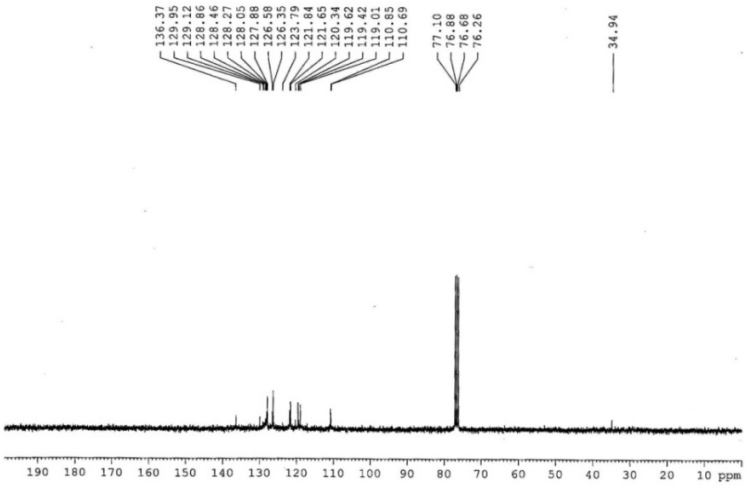
Yield: 97%, (0.410g); m.p. 168-169°C characteristics: White solid; IR υ_{max} (KBr) 3403, 3385, 1458, 1423, 1386, 1337, 1305, 1281, 1242, 973, 753, 727; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.04 (6H, s), 3.27-3.30 (2H, m), 5.93 (1H, s), 6.62-6.67 (2H, m), 6.83- 6.92 (4H, m), 7.04- 7.09 (1H, m), 7.14-7.19 (3H, m), 7.22-7.30 (2H, m), 9.70 (2H, brs); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 11.5, 32.7, 109.6, 110.5, 117.7, 119.3, 122.9, 124.5, 125.5, 125.8, 127.7, 131.3, 134.6, 139.9, 141.8, 144; analysis calculated for $C_{28}H_{23}ClN_2$: C: 79.51; H: 5.48; N: 6.62% found C: 79.50; H: 5.49; N: 6.62%.



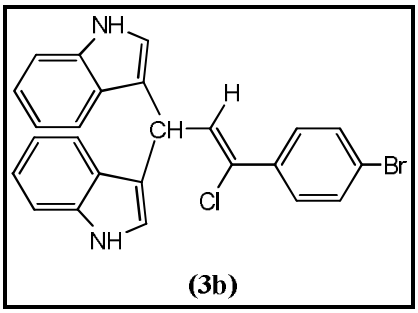
(3a)



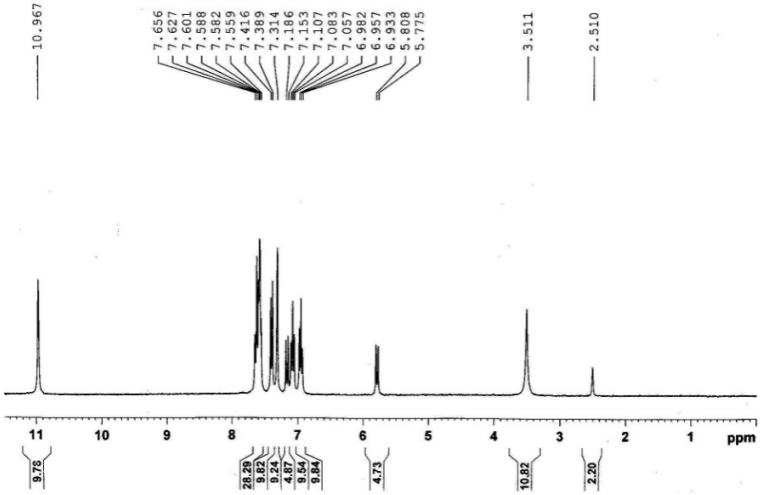
^{1}H NMR, 300 MHz, $CDCl_3$



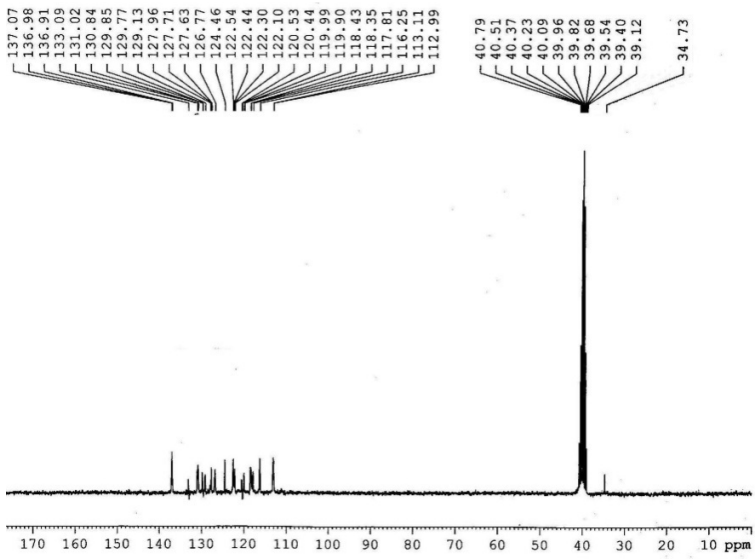
^{13}C NMR, 75MHz, $CDCl_3$



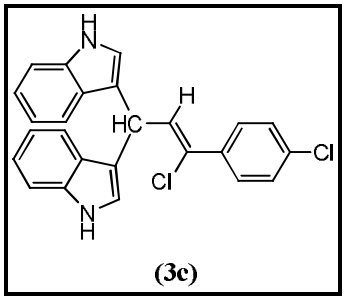
(3b)



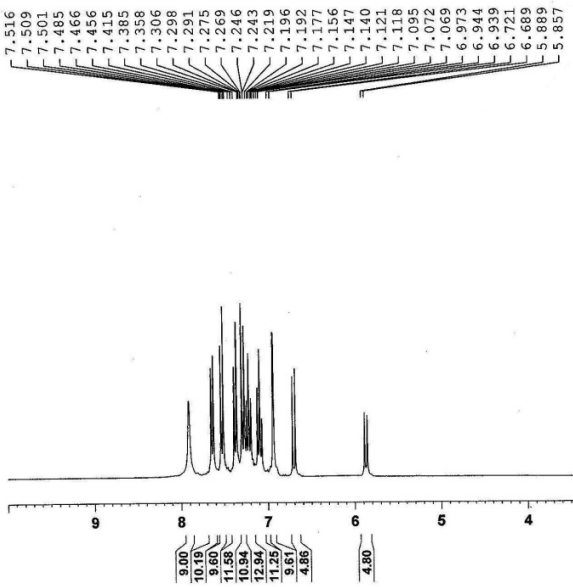
^{1}H NMR, 300 MHz, DMSO-D_6



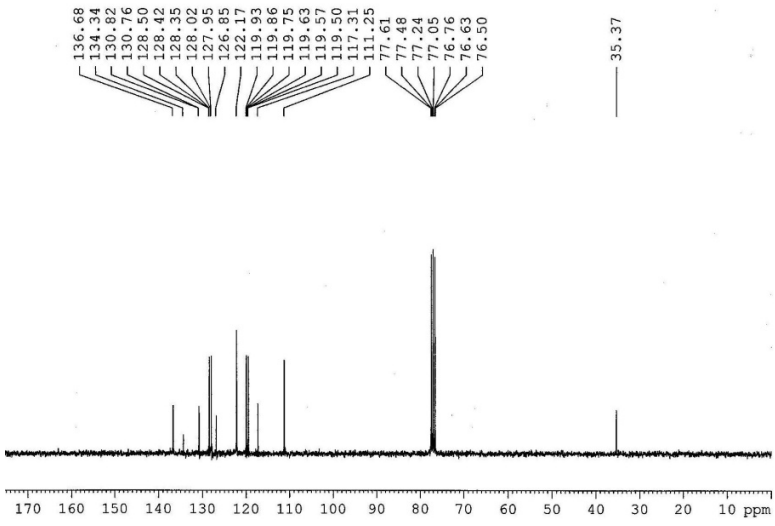
^{13}C NMR, 75MHz, DMSO-D_6



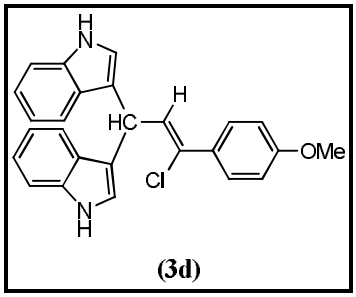
(3c)



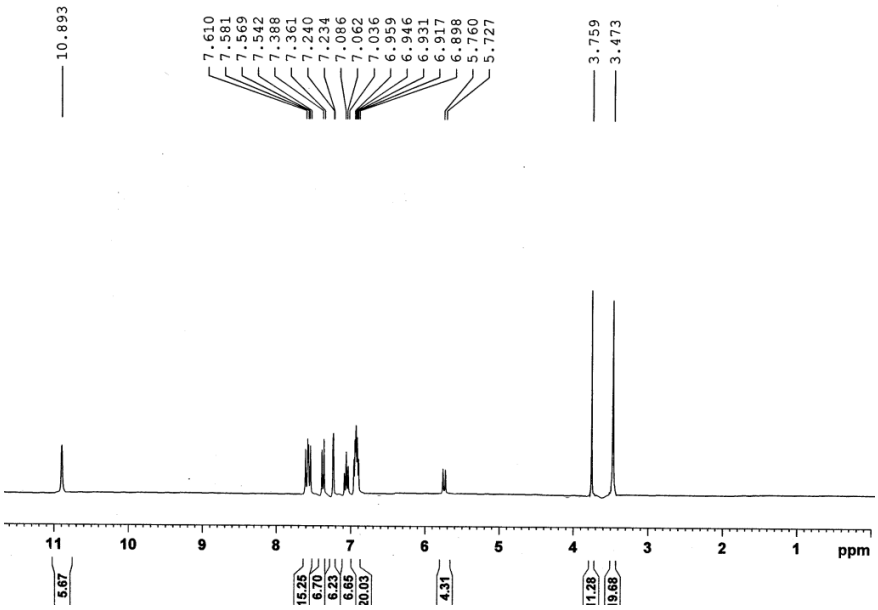
^{1}H NMR, 300 MHz, $CDCl_3$



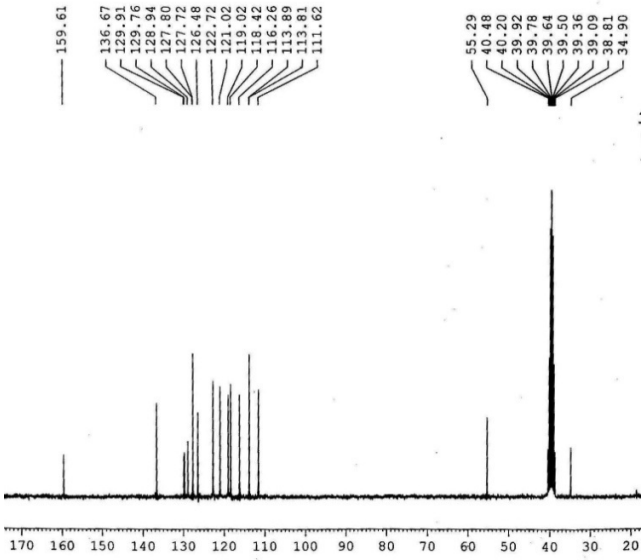
^{13}C NMR, 75MHz, $CDCl_3$



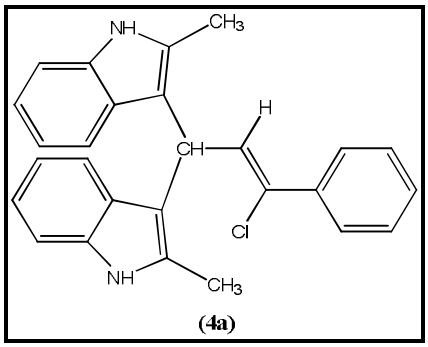
(3d)



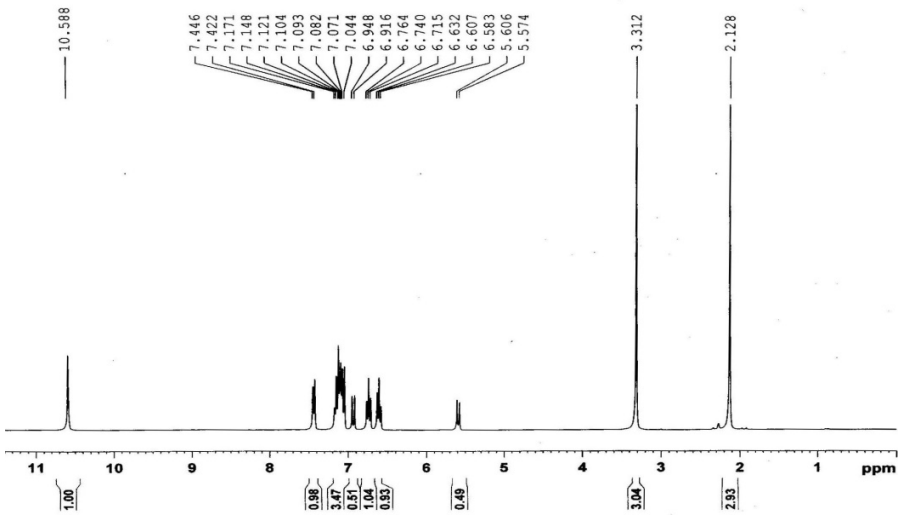
^{1}H NMR, 300 MHz, DMSO-D_6



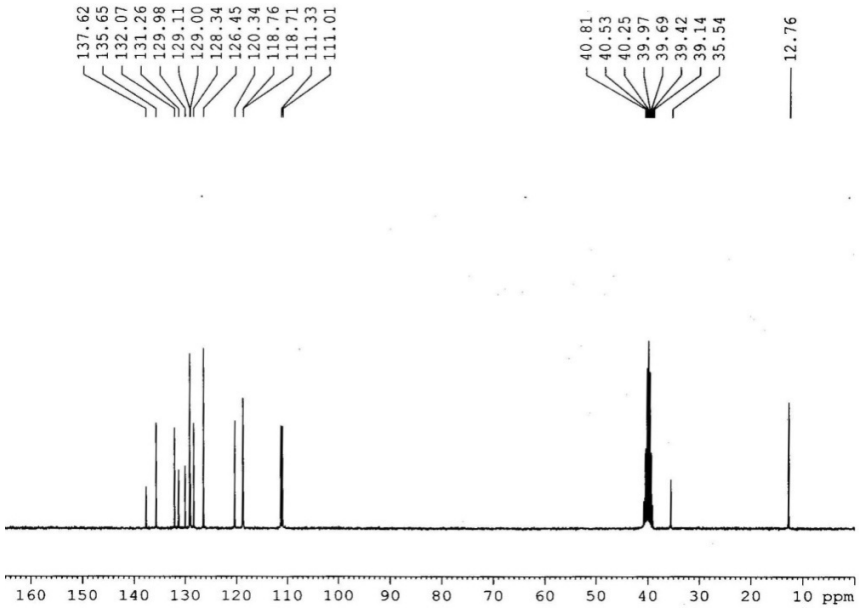
^{13}C NMR, 75MHz, DMSO-D_6



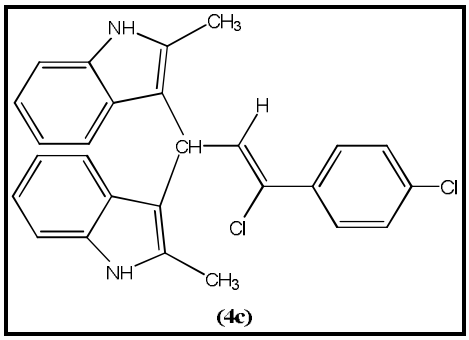
(4a)



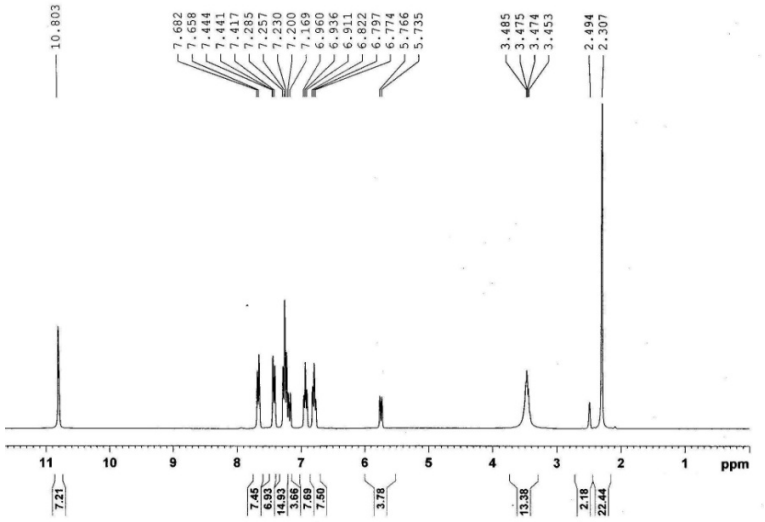
^{1}H NMR, 300 MHz, DMSO-D_6



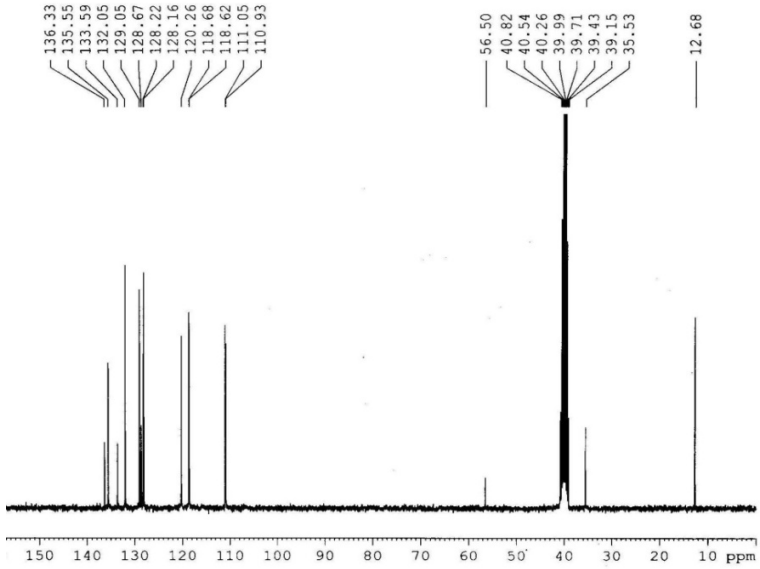
^{13}C NMR, 75MHz, DMSO-D_6



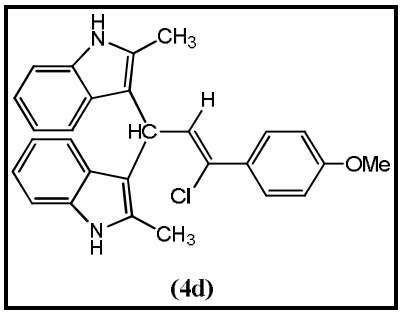
(4c)



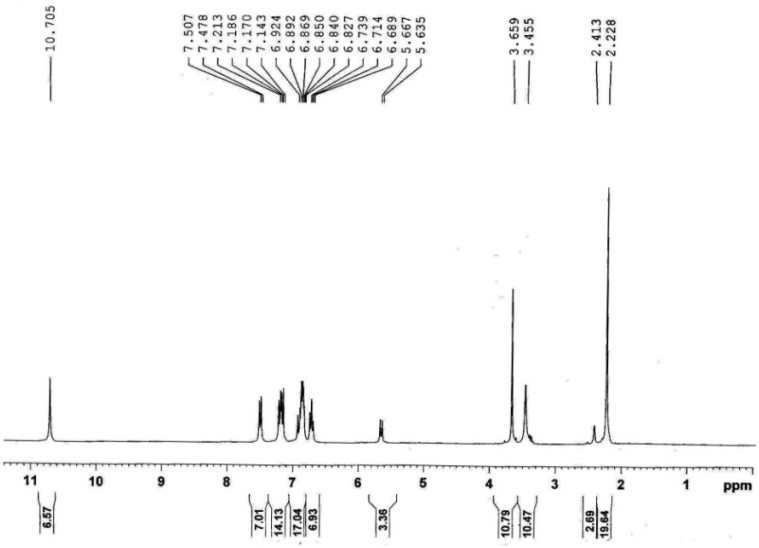
^{1}H NMR, 300 MHz, DMSO-D_6



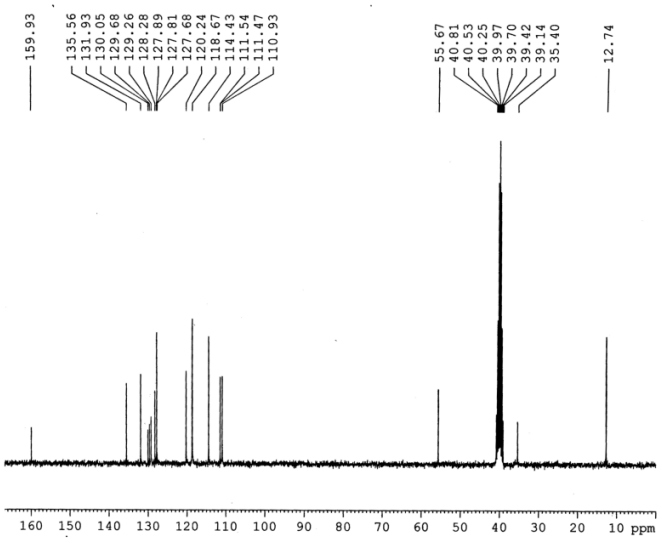
^{13}C NMR, 75MHz, DMSO-D_6



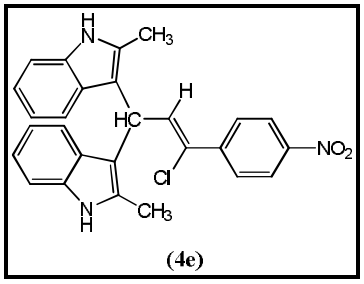
(4d)



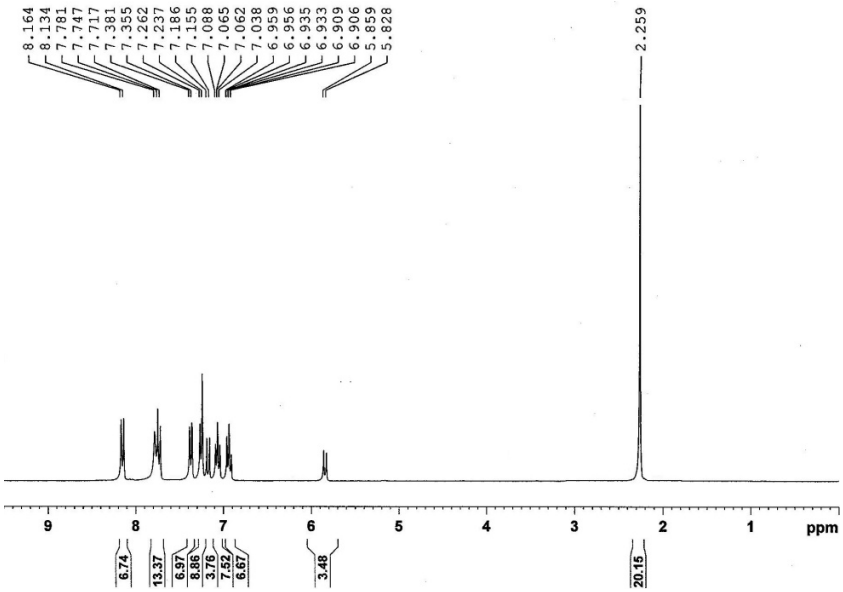
^{1}H NMR, 300 MHz, DMSO-D_6



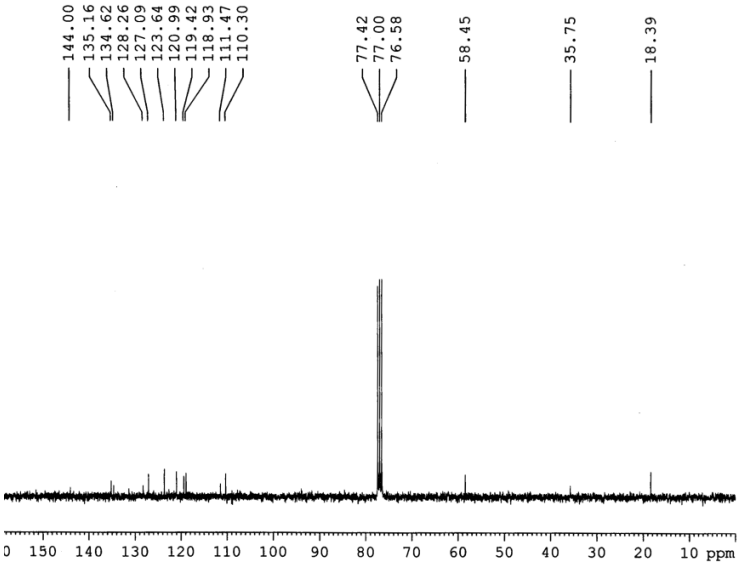
^{13}C NMR, 75MHz, DMSO-D_6



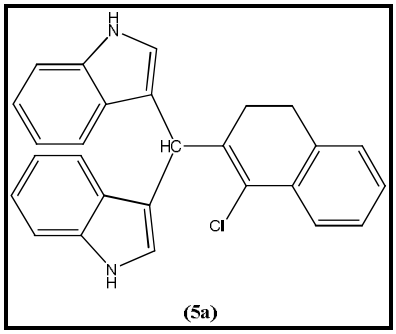
(4e)



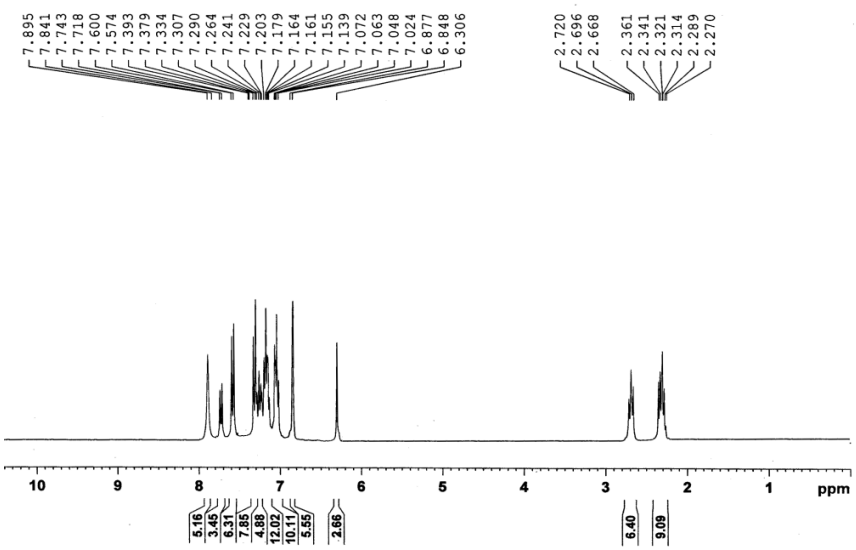
^{1}H NMR, 300 MHz, $CDCl_3$



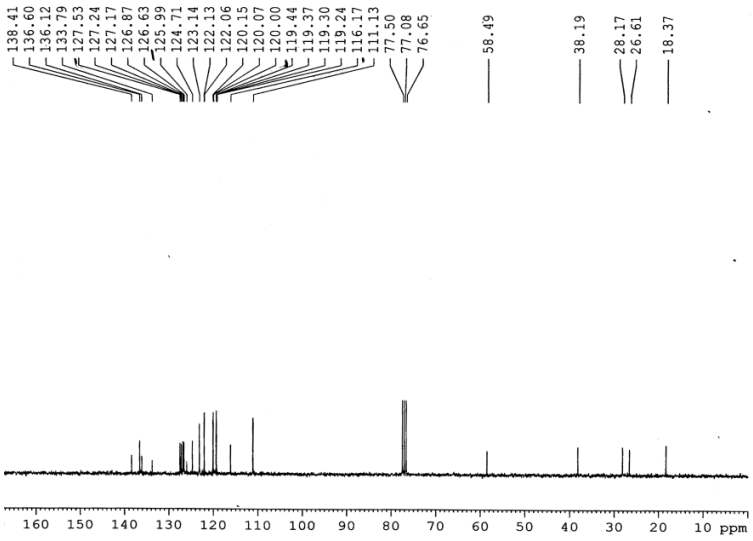
^{13}C NMR, 75 MHz, $CDCl_3$



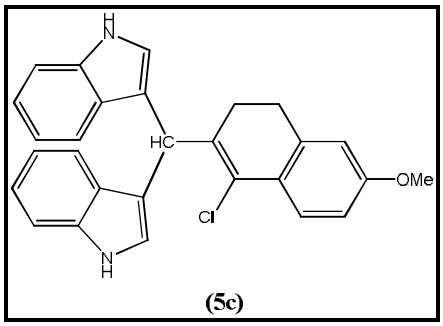
(5a)



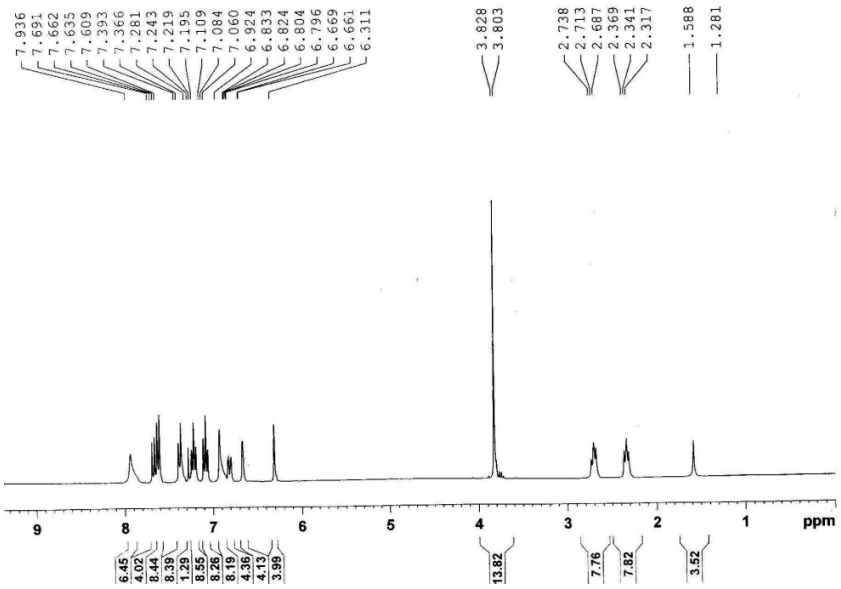
^{1}H NMR, 300 MHz, $CDCl_3$



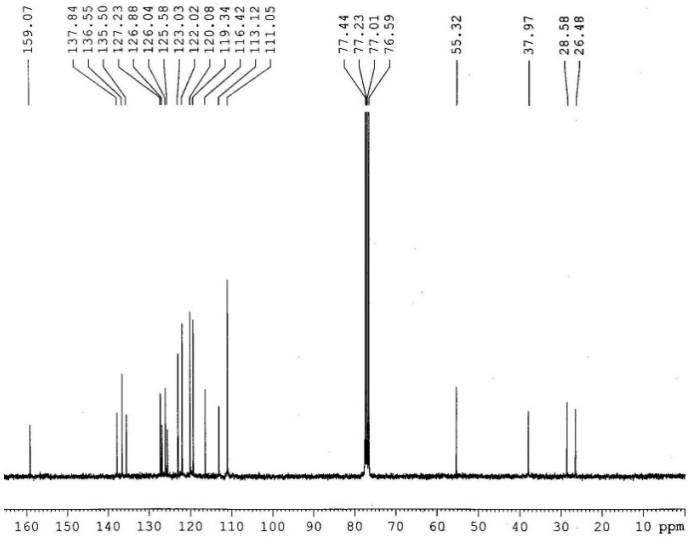
^{13}C NMR, 75 MHz, $CDCl_3$



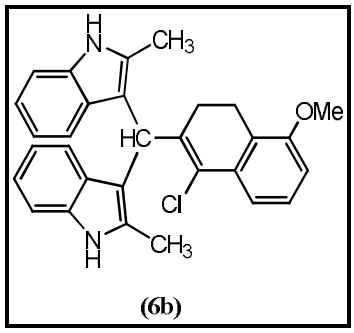
(5c)



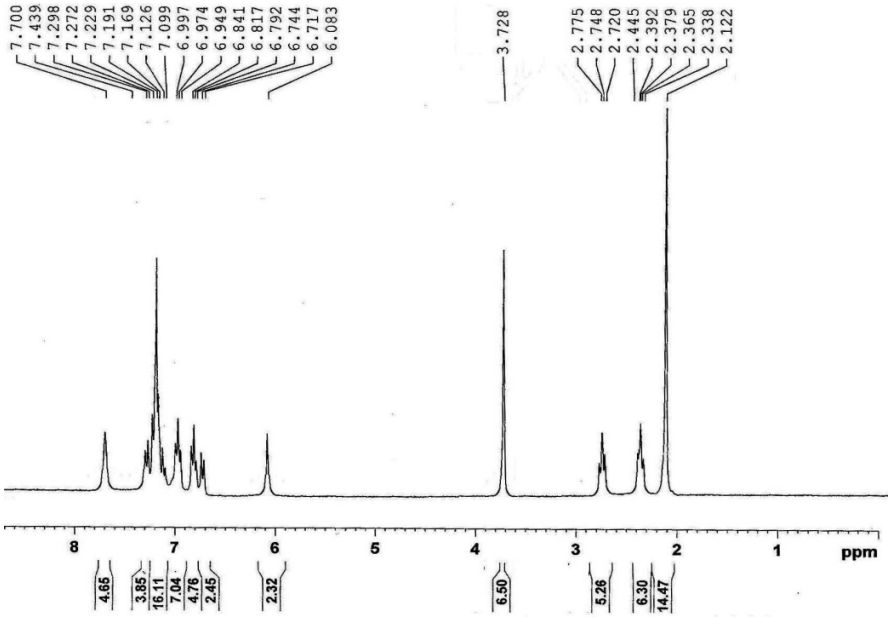
^{1}H NMR, 300 MHz, $CDCl_3$



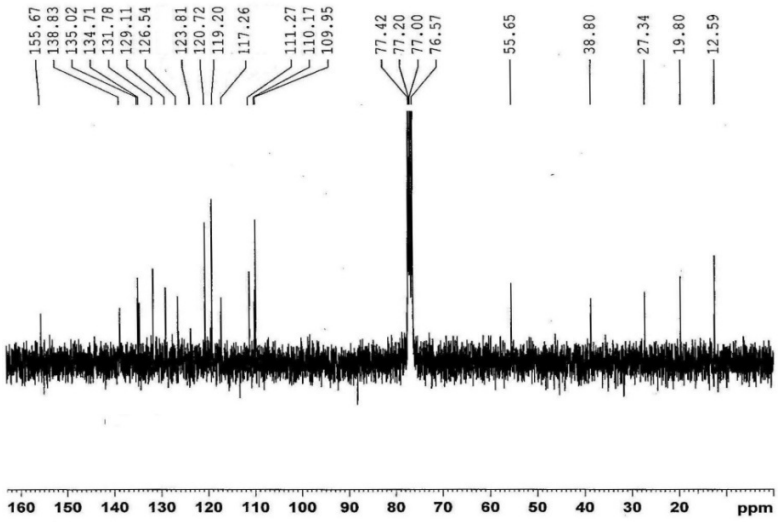
^{13}C NMR, 75 MHz, $CDCl_3$



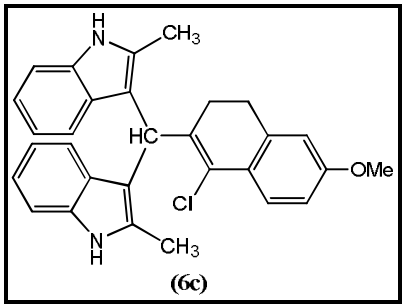
(6b)



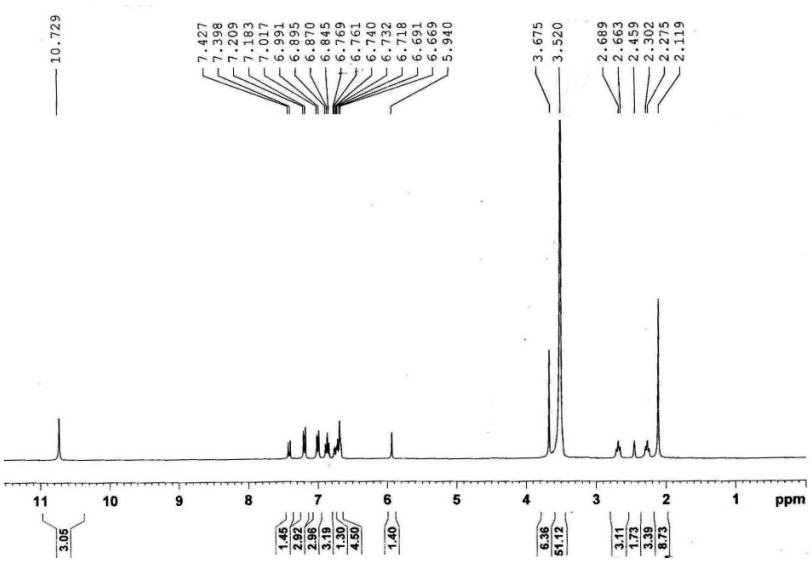
^{1}H NMR, 300 MHz, $CDCl_3$



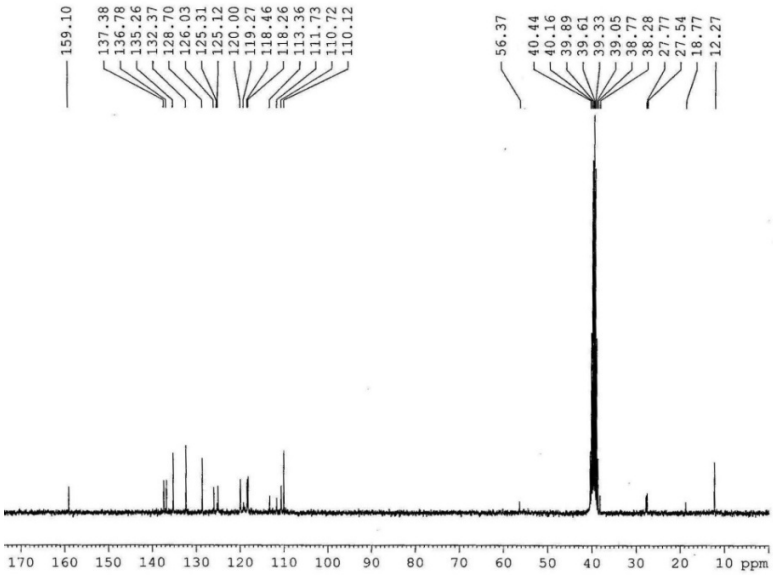
^{13}C NMR, 75 MHz, $CDCl_3$



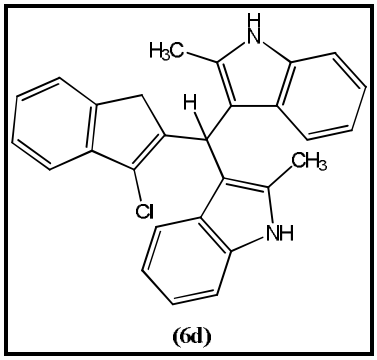
(6c)



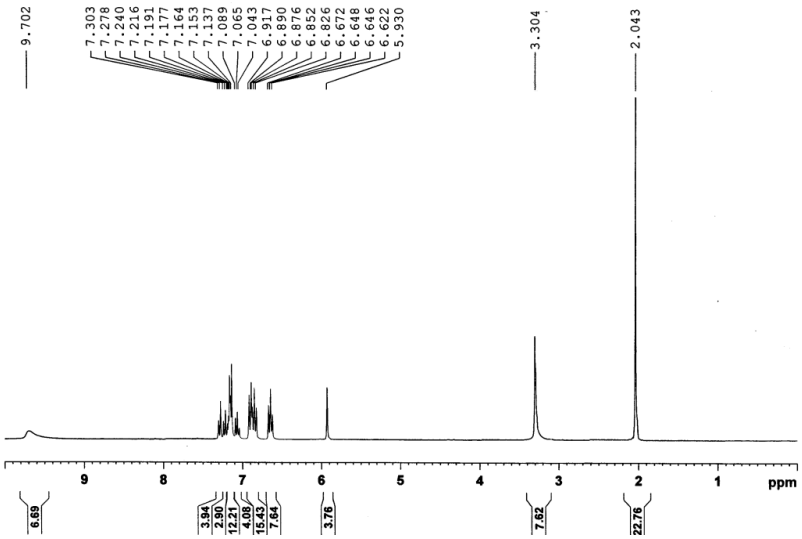
^{1}H NMR, 300 MHz, DMSO-D_6



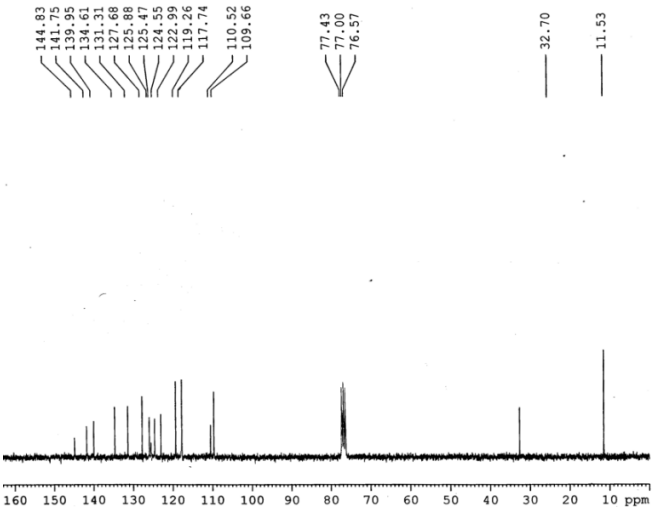
^{13}C NMR, 75MHz, DMSO-D_6



(6d)



^{1}H NMR, 300 MHz, $CDCl_3$



^{13}C NMR, 75 MHz, $CDCl_3$