Supporting Information

Tetrasubstituted olefinic xanthene dyes: synthesis *via* palladium-catalyzed *6-exo-dig* cyclization/*C-H* activation of 2-bromobenzyl-*N*-propargylamines and solid state fluorescence properties

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General Information:

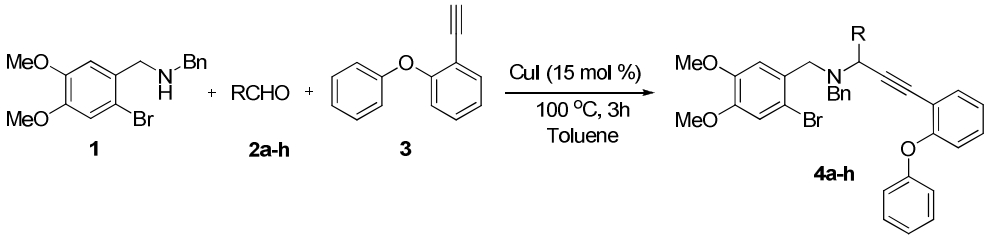
Reagents and solvents were purchased from commercial sources (Aldrich and Merck). Reagents were used without further purification unless otherwise noted. Column chromatography was performed on silica gel (100–200 mesh, SRL. India). Analytical TLC was performed on pre-coated aluminium sheets of silica gel $60F_{254}$ of 0.2 mm thickness (Merck, Germany). Melting points were determined in capillary tubes and are uncorrected. Infrared (IR) spectra were recorded on a Perkin–Elmer FTIR spectrophotometer. ^{1}H NMR (500 MHz) and ^{13}C (75 MHz and 125 MHz) spectra were recorded in $CDCl_3$ solution with TMS as internal standard on a JEOL spectrometer. Mass spectra were recorded using a Thermo Finnigan LCQ Advantage MAX 6000 ESI mass spectrometer. High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer. Elemental analyses were recorded using a Thermo Finnigan FLASH EA 1112 CHN analyzer. Solution state UV-Visible spectra were measured using a ANALYTIK JENA-SPECORD 200 plus UV-Visible spectrophotometers and DRS spectra were measured using a VARIAN-CARY-100 Conc. Solution state fluorescence spectra were measured using a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer.

Solid state fluorescence spectra were recorded in HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer using front-face detection method. In the front-face technique, the excitation light is focused to the front surface of the sample and then fluorescence emission was collected from the same region at 45° angle that minimizes reflected and scattered light.

Compound preparation:

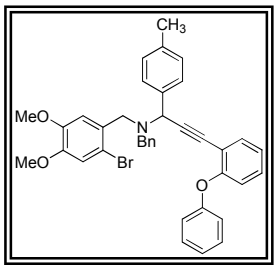
Alkyne **3** was synthesized using the known protocol reported in Tietze, L. F.; Hungerland, T.; Dufert, A.; Objartel, I.; Stalke, D. *Chem. Eur. J.* **2012,** *18*, 3286.

General Procedure for synthesis of Propargyl amines (4a-h):

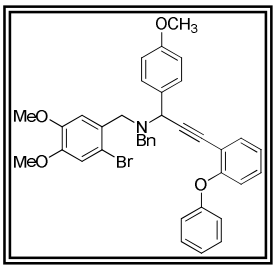


A mixture of CuI (15 mol-%), amine (0.50 mmol), aldehyde (0.55 mmol) and phenylacetylene (0.75 mmol) in toluene (3mL) was heated at 100 ^{o}C for 3 h. Then the reaction mixture was filtered through Celite and washed with ethyl acetate. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate as eluent, affording compound in good yields.

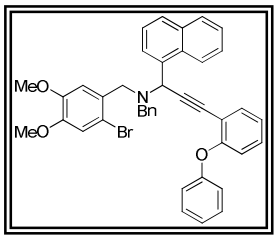
Spectral data of compounds (4a- h):



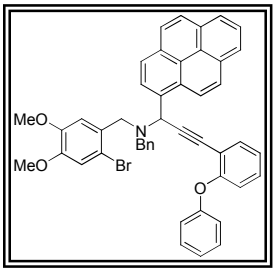
N-benzyl-*N*-(2-bromo-4,5-dimethoxybenzyl)-3-(2-phenoxyphenyl)-1-*p*-tolylprop-2-yn-1-amine (**4a**):Yellow liquid, IR (KBr): 749, 1031, 1158, 1221, 1254, 1447, 1496, 1592, 2844, 2926, 3021 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.30 (s, 3H, -CH_3), 3.41 (d, J = 13.00 Hz, 1H, -CH_2), 3.46 (d, J = 14.00 Hz, 1H, -CH_2), 3.61 (d, J = 13.00 Hz, 1H, -CH_2), 3.75 (d, J = 14.00 Hz, 1H, -CH_2), 3.81 (s, 3H, -OCH_3), 3.82 (s, 3H, -OCH_3), 4.81 (s, 1H, -C*H*), 6.91 (s, 1H, Ar-*H*), 7.04-7.08 (m, 7H, Ar-*H*), 7.17-7.20 (m, 2H, Ar-*H*), 7.23-7.29 (m, 4H, Ar-*H*), 7.31-7.36 (m, 3H, Ar-*H*),7.43 (d, J = 8.00 Hz, 2H, Ar-*H*), 7.68 (d, J = 7.50 Hz, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 21.1, 53.4, 54.6, 55.9, 56.1, 56.2, 83.8, 90.1, 113.4, 114.3, 115.1, 116.6, 117.6, 120.1, 122.8, 123.9, 126.9, 128.1, 128.2, 128.7, 129.0, 129.6, 129.7, 130.7, 133.9, 135.8, 137.0, 139.4, 148.2, 148.3, 157.0, 157.8. MS (ESI): *m/z* 632 $[M+H]^+$, 634 $[(M+H)+2]^+$.



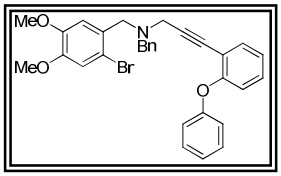
N-benzyl-*N*-(2-bromo-4,5-dimethoxybenzyl)-1-(4-methoxyphenyl)-3-(2-phenoxyphenyl)prop-2-yn-1-amine (**4b**): Yellow liquid, IR (KBr): 749, 1033, 1162, 1250, 1448, 1502, 1596, 2838, 2935, 3002, 3063 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.39 (d, *J* = 13.00 Hz, 1H, -CH_2), 3.46 (d, *J* = 15.00 Hz, 1H, -CH_2), 3.61 (d, *J* = 13.00 Hz, 1H, -CH_2), 3.72 (d, *J* = 15.00 Hz, 1H, -CH_2), 3.77 (s, 3H, -OCH_3), 3.82 (s, 6H, -OCH_3), 4.79 (s, 1H, -C*H*), 6.78 (d, *J* = 8.50 Hz, 2H, Ar-*H*), 6.91 (s, 1H, Ar-*H*), 7.02-7.08 (m, 5H, Ar-*H*), 7.19 (t, *J* = 8.00 Hz, 2H, Ar-*H*), 7.23-7.28 (m, 4H, Ar-*H*), 7.31-7.37 (m, 3H, Ar-*H*), 7.44 (d, *J* = 8.50 Hz, 2H, Ar-*H*), 7.68 (d, *J* = 8.00 Hz, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ53.4, 54.6, 55.2, 55.9(2), 56.1, 83.8, 90.2, 113.3, 113.4, 114.3, 115.0, 116.6, 117.5, 120.2, 122.7, 124.0, 126.9, 128.1, 128.9, 129.5, 129.7(2), 130.7, 130.9, 133.9, 139.4, 148.2, 148.3, 157.0, 157.8, 158.8. MS (ESI): *m*/*z* 648 $[M+H]^+$, 650 $[(M+H)+2]^+$.



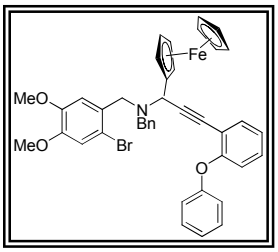
N-benzyl-*N*-(2-bromo-4,5-dimethoxybenzyl)-1-(naphthalen-1-yl)-3-(2-phenoxyphenyl)prop-2-yn-1-amine (**4c**): Yellow liquid, IR (KBr): 748, 796, 1032, 1159, 1221, 1255, 1447, 1496, 1593, 1680, 2841, 2933, 3057 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.35 (s, 3H, -OCH_3), 3.49 (d, *J* = 14.00 Hz, 1H, -CH_2), 3.58 (d, *J* = 13.00 Hz, 1H, -CH_2), 3.66 (d, *J* = 13.00 Hz, 1H, -CH_2), 3.74 (d, *J* = 14.00 Hz, 1H, -CH_2), 3.77 (s, 3H, -OCH_3), 5.52 (s, 1H, -C*H*), 6.45 (s, 1H, Ar-*H*), 6.85 (s, 1H, Ar-*H*), 7.06-7.10 (m, 4H, Ar-*H*), 7.20-7.30 (m, 8H, Ar-*H*), 7.33-7.39 (m, 4H, Ar-*H*),7.66 (d, *J* = 8.50 Hz, 1H, Ar-*H*), 7.69 (d, *J* = 8.00 Hz, 1H, Ar-*H*), 7.75 (d, *J* = 8.50 Hz, 2H, Ar-*H*),7.85 (d, *J* = 7.50 Hz, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 53.1, 54.5, 55.3, 55.8, 56.0, 84.6, 90.1, 113.7, 113.9, 114.5, 116.6, 117.6, 120.2, 122.8, 124.0, 124.9, 125.0, 125.1, 125.2, 127.3, 127.7, 127.9, 128.3, 128.6, 129.8, 130.1, 130.8, 131.3, 133.7, 133.8, 133.9, 138.5, 147.9, 148.0, 157.1, 157.8. MS (ESI): *m*/*z* 668 $[M+H]^+$, 670 $[(M+H)+2]^+$.



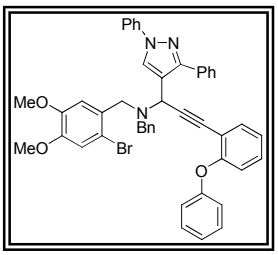
N-benzyl-*N*-(2-bromo-4,5-dimethoxybenzyl)-3-(2-phenoxyphenyl)-1-(pyren-1-yl)prop-2-yn-1-amine (**4d**): Yellow liquid, IR (KBr): 749, 846, 1159, 1254, 1447, 1494, 1592, 1736, 2839, 2934, 3038 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.26 (s, 3H, -OCH_3), 3.48 (d, J = 14.00 Hz, 1H, -CH_2), 3.62 (d, J = 13.00 Hz, 1H, -CH_2), 3.69 (d, J = 13.00 Hz, 1H, -CH_2), 3.75 (s, 3H, -OCH_3), 3.82 (d, J = 14.00 Hz, 1H, -CH_2), 5.79 (s, 1H, -CH), 6.52 (s, 1H, Ar-H), 6.85 (s, 1H, Ar-H), 7.10-7.16 (m, 4H, Ar-H), 7.23-7.28 (m, 6H, Ar-H), 7.37-7.42 (m, 3H, Ar-H), 7.80-7.84 (m, 2H, Ar-H), 7.88 (d, J = 9.00 Hz, 1H, Ar-H), 7.94-8.00 (m, 4H, Ar-H), 8.10 (d, J = 7.50 Hz, 1H, Ar-H), 8.12 (d, J = 7.50 Hz, 1H, Ar-H), 8.41 (d, J = 8.50 Hz, 1H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 53.2, 54.9, 55.3, 55.6, 56.0, 85.0, 90.3, 113.8, 114.1, 114.6, 116.6, 117.7, 120.2, 122.9, 124.0, 124.1, 124.4, 124.5, 124.8, 124.9, 125.1, 125.8, 126.5, 127.3, 127.7, 128.0, 128.9, 129.8, 130.1, 130.5, 130.6, 131.1, 131.6, 133.9, 138.6, 148.0, 148.1, 157.2, 157.8. MS (ESI): *m/z* 742 $[M+H]^+$, 744 $[(M+H)+2]^+$.



N-benzyl-*N*-(2-bromo-4,5-dimethoxybenzyl)-3-(2-phenoxyphenyl)prop-2-yn-1-amine (**4e**): Yellow liquid, IR (KBr): 749, 1160, 1221, 1254, 1447, 1494, 1594, 1735, 2838, 2929, 3028, 3062 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.40 (s, 2H, -CH_2), 3.60 (s, 2H, -CH_2), 3.67 (s, 2H, -CH_2), 3.81 (s, 3H, -OCH_3), 3.84 (s, 3H, -OCH_3), 6.97-7.02 (m, 4H, Ar-H), 7.04-7.08 (m, 2H, Ar-H), 7.12 (t, J = 7.50 Hz, 1H, Ar-H), 7.21-7.27 (m, 4H, Ar-H), 7.29-7.33 (m, 4H, Ar-H), 7.55 (d, J = 7.50 Hz, 1H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 41.9, 55.9, 56.1, 57.0, 57.1, 81.4, 89.4, 113.5, 114.7, 115.4, 116.3, 117.9, 119.6, 122.9, 123.6, 127.0, 128.1, 129.1, 129.4, 129.7, 130.1, 133.7, 138.7, 148.1, 148.4, 157.2, 157.5. MS (ESI): *m/z* 542 $[M+H]^+$, 544$[(M+H)+2]^+$.

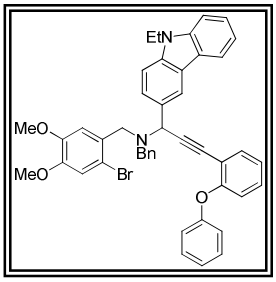


N-benzyl-*N*-(2-bromo-4,5-dimethoxybenzyl)-3-(2-phenoxyphenyl)-1-(ferrocen-1-yl)prop-2-yn-1-amine (**4f**): Yellow liquid, IR (KBr): 747, 804, 1031, 1157, 1253, 1446, 1493, 1594, 2842, 2929, 3085 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.44 (d, *J* = 13.50 Hz, 1H, -CH_2), 3.57(d, *J* = 15.00 Hz, 1H, -CH_2), 3.62 (d, *J* = 13.50 Hz, 1H, -CH_2), 3.68 (d, *J* = 15.00 Hz, 1H, -CH_2), 3.80 (s, 3H, -OCH_3), 3.82 (s, 3H, -OCH_3), 4.04 (s, 6H, -fc-C*H*), 4.08 (s, 1H, -fc-C*H*),4.19 (s, 1H, -fc-C*H*),4.34 (s, 1H, -fc-C*H*), 4.66 (s, 1H, -C*H*), 6.91 (s, 1H, Ar-*H*), 7.02-7.08 (m, 5H, Ar-*H*), 7.16-7.19 (m, 2H, Ar-*H*), 7.22-7.25 (m, 4H, Ar-*H*), 7.33 (t, *J* = 8.00 Hz, 3H, Ar-*H*), 7.66 (dd, *J* = 1.50 Hz, *J* = 7.50 Hz, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ53.1, 53.5, 54.5, 55.8, 56.0, 67.4, 68.2, 68.5, 69.0, 69.2, 80.8, 85.9, 91.4, 112.9, 113.7, 114.8, 116.6, 117.7, 119.9, 122.8, 123.8, 126.7, 128.0, 128.6, 129.5, 129.7, 131.0, 133.8, 139.7, 148.0, 148.1, 157.0, 157.6. MS (ESI): *m/z* 726 $[M+H]^+$, 728 $[(M+H)+2]^+$.



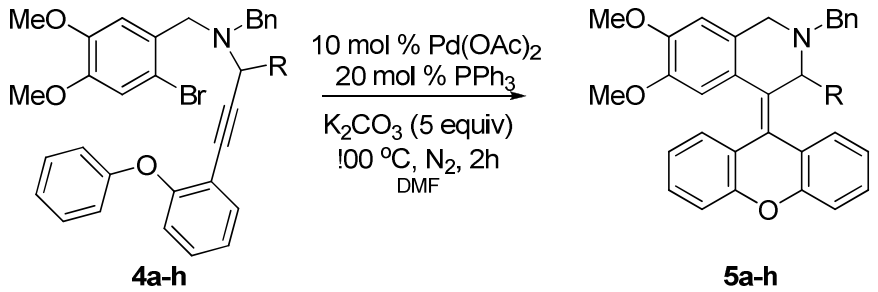
N-benzyl-*N*-(2-bromo-4,5-dimethoxybenzyl)-1-(1,3-diphenyl-1*H*-pyrazol-4-yl)-3-(2-phenoxyphenyl)prop-2-yn-1-amine (**4g**): White solid, mp: 70-72 ^{o}C; IR (KBr): 693, 752, 958, 1158, 1217, 1251, 1446, 1497, 1596, 2839, 2930, 3058 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.40 (s, 3H, -OCH_3), 3.58 (d, *J* = 12.50 Hz, 1H, -CH_2), 3.71-3.80 (m, 6H, -OCH_3, -CH_2), 5.18 (s, 1H, -C*H*), 6.70 (s, 1H, Ar-*H*), 6.85 (s, 1H, Ar-*H*), 7.01 (d, *J* = 8.00 Hz, 1H, Ar-*H*), 7.07-7.12 (m, 3H, Ar-*H*), 7.16-7.24 (m, 10H, Ar-*H*), 7.34(t, *J* = 7.50 Hz, 5H, Ar-*H*), 7.58 (d, *J* = 8.00 Hz, 2H, Ar-*H*), 7.68 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 7.73 (d, *J* = 6.50 Hz, 2H, Ar-*H*), 8.19 (s, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ49.2, 53.1, 55.4, 55.7, 56.0, 82.3, 90.5, 113.4, 114.0, 114.6, 115.7, 118.4, 118.8, 119.2(2), 123.4, 123.6, 126.1, 127.2, 127.6, 127.7, 128.0, 128.2, 129.2, 129.8,

129.9, 130.0, 130.5, 133.0, 133.7, 138.2, 139.6, 148.1, 150.1, 157.2, 157.8. MS (ESI): *m/z* 760 $[M+H]^+$, 762 $[(M+H)+2]^+$.



N-benzyl-*N*-(2-bromo-4,5-dimethoxybenzyl)-1-(9-ethyl-9*H*-carbazol-3-yl)-3-(2-phenoxyphenyl)prop-2-yn-1-amine (**4h**): Yellow liquid, IR (KBr): 746, 1030, 1157, 1251, 1332, 1489, 1596, 2840, 2931, 3059 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ1.38 (t, *J* = 8.00 Hz, 3H, -C*H*$_3$), 3.49 (d, *J* = 13.00 Hz, 1H, -C*H*$_2$), 3.56 (d, *J* = 13.50 Hz, 1H, -C*H*$_2$), 3.70 (d, *J* = 13.50 Hz, 1H, -C*H*$_2$), 3.78 (s, 3H, -OC*H*$_3$), 3.79 (d, *J* = 13.50 Hz, 1H, -C*H*$_2$), 3.82 (s, 3H, -OC*H*$_3$), 4.31 (q, *J* = 7.50 Hz, 2H, -C*H*$_2$), 5.07 (s, 1H, -C*H*), 6.90 (s, 1H, Ar-*H*), 7.05-7.09 (m, 3H, Ar-*H*), 7.12-7.14 (m, 2H, Ar-*H*), 7.16-7.21 (m, 3H, Ar-*H*), 7.24-7.30 (m, 3H, Ar-*H*), 7.32-7.36 (m, 6H, Ar-*H*), 7.42 (t, *J* = 8.00 Hz, 1H, Ar-*H*), 7.66 (d, *J* = 8.50 Hz, 1H, Ar-*H*), 7.75 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 7.93 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 8.40 (s, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 13.8, 37.5, 53.3, 54.7, 55.8, 56.0, 56.6, 83.9, 90.5, 107.8, 108.4, 113.3, 114.2, 114.9, 116.5, 118.1, 118.6, 119.7, 120.2, 120.4, 122.4, 122.8, 123.0, 123.7, 125.4, 126.2, 126.9, 128.1, 129.0, 129.2, 129.6, 129.8, 130.9, 133.9, 139.3, 139.6, 140.1, 148.1(2), 157.4, 157.6. MS (ESI): *m/z* 735 $[M+H]^+$, 737 $[(M+H)+2]^+$.

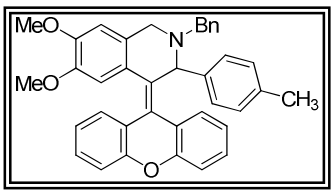
General procedure for synthesis of Tetrasubstituted olefins (5a- h):



$Pd(OAc)_2$(10 mol %), PPh_3(20 mol %) and K_2CO_3(5 equiv) were added into a two-neck round bottom flask. The flask was evacuated and flushed with nitrogen. Propargylamine **4** (0.3 mmol)

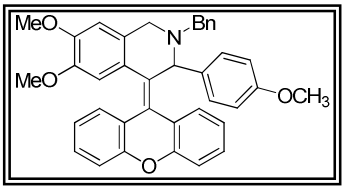
dissolved in DMF was added to the flask and heated to 100 ^{o}C for two hours under N_2 atmosphere, coolled to rt and quenched by the addition of saturated NH_4Cl (aq.) solution. The aqueous layer was extracted with EtOAc. The organic phase was washed with brine, dried (anhydrous Na_2SO_4) and concentrated under reduced pressure. The crude product was chromatographed.

Spectral data of compounds (5a- h):



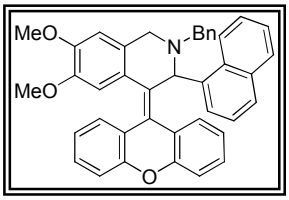
2-Benzyl-6,7-dimethoxy-3-*p*-tolyl-4-(9*H*-xanthen-9-ylidene)-1,2,3,4-tetrahydroisoquinoline (**5a**): Yellow solid; mp: 90-92 ^{o}C; IR (KBr): 748, 1053, 1146, 1218, 1256, 1450, 1509, 1602, 2842, 2925, 3025 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.18 (s, 3H, -C*H*$_3$), 3.31 (s, 3H, -OC*H*$_3$), 3.78 (s, 3H, -OC*H*$_3$), 3.88 (d, *J* = 16.00 Hz, 1H, -C*H*$_2$), 3.96 (d, *J* = 16.00 Hz, 1H, -C*H*$_2$), 4.06 (d, *J* = 14.00 Hz, 1H, -C*H*$_2$), 4.27 (d, *J* = 14.00 Hz, 1H, -C*H*$_2$), 5.74 (s, 1H, -C*H*), 6.38 (s, 1H, Ar-*H*), 6.39 (s, 1H, Ar-*H*), 6.83 (t, *J* = 7.50 Hz, 1H, Ar-*H*), 6.89 (t, *J* = 9.5 Hz, 2H, Ar-*H*), 6.94 (t, *J* = 7.50 Hz, 3H, Ar-*H*),7.12-7.15 (m, 2H, Ar-*H*), 7.17-7.24 (m, 3H, Ar-*H*), 7.30 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 7.34 (t, *J* = 7.50 Hz, 1H, Ar-*H*), 7.40 (t, *J* = 7.00 Hz, 2H, Ar-*H*), 7.55 (d, *J* = 7.50 Hz, 2H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 20.9, 50.8, 54.9, 55.5, 59.2, 60.2, 107.9, 112.7, 116.8(2), 122.8, 123.1, 123.4, 125.4, 126.0, 126.4, 126.7, 127.2, 127.5, 127.9, 128.5, 128.6, 128.8, 128.9, 129.4, 129.6, 130.5, 136.0, 137.2, 139.4, 145.9, 148.6, 154.6, 154.9. MS (ESI): *m*/*z* 552 $[M+H]^+$. HRMS calculated for ($C_{38}H_{33}NO_3$ + H) : 552.2539, found : 552.2538.

2-Benzyl-6,7-dimethoxy-3-(4-methoxyphenyl)-4-(9*H*-xanthen-9-ylidene)-1,2,3,4-

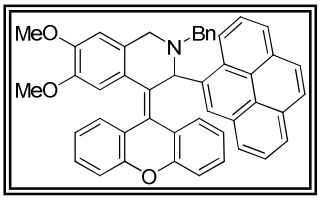


tetrahydroisoquinoline (**5b**): Yellow solid; mp: 98-100 ^{o}C; IR (KBr): 762, 1032, 1250, 1450, 1508, 1603, 2836, 2928 cm^{-1}; ^{1}H

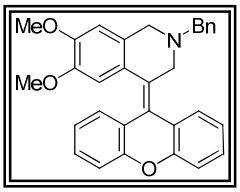
NMR (500 MHz, $CDCl_3$): δ 3.31 (s, 3H, -OCH_3), 3.66 (s, 3H, -OCH_3), 3.79 (s, 3H, -OCH_3), 3.87 (d, J = 16.00 Hz, 1H, -CH_2), 3.93 (d, J = 16.00 Hz, 1H, -CH_2), 4.03 (d, J = 14.00 Hz, 1H, -CH_2), 4.25 (d, J = 14.00 Hz, 1H, -CH_2), 5.71 (s, 1H, -CH), 6.40 (s, 2H, Ar-H), 6.62 (d, J = 8.00 Hz, 2H, Ar-H), 6.84 (t, J = 7.50 Hz, 1H, Ar-H), 6.92-6.96 (m, 3H, Ar-H), 7.12-7.25 (m, 5H, Ar-H), 7.31 (d, J = 7.50 Hz, 1H, Ar-H), 7.34 (d, J = 6.50 Hz, 1H, Ar-H), 7.40 (t, J = 7.00 Hz, 2H, Ar-H),7.55 (d, J = 7.50 Hz, 2H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ50.8, 54.9, 55.0, 55.5, 59.1, 59.8, 107.8, 112.7, 113.2, 116.8(2), 122.8, 123.1, 123.3, 125.4, 126.0, 126.4, 126.7, 127.2, 127.5, 127.9, 128.5, 128.7, 128.9, 129.4, 129.6, 130.5, 132.2, 139.3, 145.9, 148.6, 154.6, 154.8, 158.1. MS (ESI): m/z 568 $[M+H]^+$. Anal. Calcd for $C_{38}H_{33}NO_4$: C 80.40 H 5.86 N 2.47. Found: C 80.57 H 5.90 N 2.52.



2-Benzyl-6,7-dimethoxy-3-(naphthalen-1-yl)-4-(9*H*-xanthen-9-ylidene)-1,2,3,4-tetrahydroisoquinoline (**5c**): Yellow solid; mp: 118-120 ^{o}C; IR (KBr): 759, 1055, 1145, 1215, 1257, 1449, 1507, 1598, 2839, 2926, 3052 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.36 (s, 3H, -OCH_3), 3.59(d, J = 16.00 Hz, 1H, -CH_2), 3.76 (d, J = 16.00 Hz, 1H, -CH_2), 3.79 (s, 3H, -OCH_3), 3.90 (d, J = 13.00 Hz, 1H, -CH_2), 4.12 (d, J = 13.00 Hz, 1H, -CH_2), 6.22 (s, 1H, -CH), 6.37 (s, 1H, Ar-H), 6.72 (s, 1H, Ar-H), 6.76 (t, J = 7.50 Hz, 1H, Ar-H), 7.00 (td, J = 1.50 Hz, J = 6.75 Hz,1H, Ar-H), 7.11-7.31 (m, 10H, Ar-H), 7.35-7.41 (m, 3H, Ar-H), 7.44 (t, J = 8.00 Hz, 1H, Ar-H), 7.52 (d, J = 8.00 Hz, 1H, Ar-H), 7.64 (d, J = 7.50 Hz, 1H, Ar-H), 7.79 (d, J = 8.00 Hz, 1H, Ar-H),8.07 (d, J = 8.50 Hz, 1H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ49.7, 54.9, 55.6, 58.5, 60.6, 108.9, 112.4, 116.6, 117.1, 123.0, 123.1, 124.1, 124.8(2), 125.2, 125.5, 126.1, 126.3(2), 127.2, 127.7, 127.8, 128.2, 128.3, 128.5, 128.7, 129.2, 129.6, 129.9, 132.0, 134.0, 137.5, 138.9, 146.2, 148.7, 154.3, 154.5. MS (ESI): m/z 588 $[M+H]^+$. HRMS calculated for ($C_{41}H_{33}NO_3$ + H) : 588.2539, found : 588.2559.

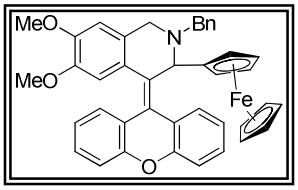


2-Benzyl-6,7-dimethoxy-3-(pyren-4-yl)-4-(9*H*-xanthen-9-ylidene)-1,2,3,4-tetrahydroisoquinoline (**5d**): Yellow solid; mp: 100-102 ^{o}C; IR (KBr): 749, 844, 1056, 1145, 1215, 1256, 1448, 1506, 1597, 2838, 2925, 3031 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.36 (s, 3H, -OC*H*$_3$), 3.67 (d, *J* = 15.00 Hz, 1H, -C*H*$_2$), 3.80 (s, 3H, -OC*H*$_3$), 3.80 (d, *J* = 15.50 Hz, 1H, -C*H*$_2$), 3.95 (d, *J* = 14.00 Hz, 1H, -C*H*$_2$), 4.19 (d, *J* = 13.00 Hz, 1H, -C*H*$_2$), 6.42 (s, 1H, -C*H*), 6.50 (s, 1H, Ar-*H*), 6.72 (s, 1H, Ar-*H*), 6.76 (t, *J* = 7.50 Hz, 1H, Ar-*H*),7.00 (t, *J* = 7.00 Hz, 1H, Ar-*H*),7.13 (t, *J* = 7.5 Hz, 1H, Ar-*H*),7.20-7.41 (m, 9H, Ar-*H*), 7.55 (d, *J* = 8.00 Hz, 1H, Ar-*H*), 7.82-7.97 (m, 6H, Ar-*H*), 8.10 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 8.15 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 8.19 (d, *J* = 9.50 Hz, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ50.2, 55.0, 55.6, 58.7, 60.8, 108.9, 112.4, 116.6, 117.1, 123.0, 123.1, 124.1(2), 124.2, 124.7, 124.8, 124.9, 125.1, 125.7, 126.1, 126.3(2), 126.4, 126.8, 127.0(2), 127.2, 127.3, 127.8, 128.2, 128.3, 129.0, 129.2, 129.4, 129.5, 130.1, 130.4, 130.7, 131.2, 136.0, 138.9, 146.4, 148.8, 154.4, 154.5. MS (ESI): *m/z* 662 $[M+H]^+$. HRMS calculated for ($C_{47}H_{35}NO_3$ + H) : 662.2695, found : 662.2685.

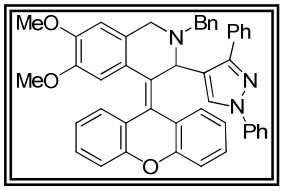


2-Benzyl-6,7-dimethoxy-4-(9*H*-xanthen-9-ylidene)-1,2,3,4-tetrahydroisoquinoline (**5e**): white solid; mp: 152-154 ^{o}C; IR (KBr): 756, 866, 1060, 1213, 1253, 1450, 1509, 1601, 2783, 2931, 3011 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.33 (s, 3H, -OC*H*$_3$), 3.57 (s, 2H, -C*H*$_2$), 3.72 (s, 2H, -C*H*$_2$), 3.84 (s, 3H, -OC*H*$_3$), 3.90 (s, 2H, -C*H*$_2$), 6.52 (s, 1H, Ar-*H*), 6.55 (s, 1H, Ar-*H*), 6.73 (t, *J* = 6.50 Hz, 1H, Ar-*H*), 6.78 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 6.91 (t, *J* = 7.00 Hz, 1H, Ar-*H*), 7.11-7.21 (m, 4H, Ar-*H*), 7.33 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 7.38-7.43 (m, 3H, Ar-*H*), 7.48 (d, *J* = 6.50 Hz, 2H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 53.4, 54.7, 55.6, 57.3, 62.3, 108.5, 111.3, 116.2, 116.9, 120.6, 122.7, 122.9, 126.1, 126.4, 126.8, 127.1, 127.5, 127.8, 128.5, 128.8, 129.7, 130.0, 137.8, 145.8, 148.5,

154.6, 155.1; MS (ESI): *m/z* 462 $[M+H]^+$. HRMS calculated for ($C_{31}H_{27}NO_3$ + H) : 462.2069, found : 462.2063.

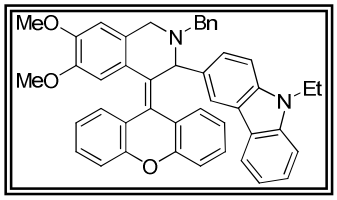


2-Benzyl-6,7-dimethoxy-3-(ferrocen-1-yl)-4-(9*H*-xanthen-9-ylidene)-1,2,3,4-tetrahydroisoquinoline (**5f**): Yellow solid; mp: 148-150 ^oC; IR (KBr): 739, 761, 843, 1048, 1121, 1237, 1350, 1508, 1596, 2831, 2923, 3000, 3073 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.90 (s, 1H, -fc-C*H*), 3.38 (s, 3H, -OCH_3),3.44 (d, *J* = 15.50 Hz, 1H, -CH_2), 3.60 (s, 5H, -fc-C*H*), 3.68(d, *J* = 13.00 Hz, 1H, -CH_2), 3.74 (d, *J* = 13.00 Hz, 1H, -CH_2), 3.79 (s, 1H, -fc-C*H*),3.83 (s, 3H, -OCH_3), 3.98 (s, 2H, -fc-C*H*), 4.04 (d, *J* = 15.50 Hz, 1H, -CH_2), 5.41 (s, 1H, -C*H*), 6.44 (s, 1H, Ar-*H*), 6.51 (s, 1H, Ar-*H*),6.79 (t, *J* = 8.50 Hz, 1H, Ar-*H*), 6.84 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 6.95 (t, *J* = 7.00 Hz, 1H, Ar-*H*), 7.18 (t, *J* = 8.00 Hz, 3H, Ar-*H*), 7.23 (d, *J* = 7.50 Hz, 1H, Ar-*H*), 7.34 (d, *J* = 6.50 Hz, 1H, Ar-*H*), 7.42 (d, *J* = 7.00 Hz, 1H, Ar-*H*) 7.47 (t, *J* = 7.00 Hz, 2H, Ar-*H*) 7.62 (d, *J* = 7.50 Hz, 2H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 52.3, 54.9, 55.2, 55.6, 58.5, 66.6, 67.4, 67.7, 68.4, 70.7, 81.7, 107.6, 112.1, 116.7, 116.9, 118.8, 122.7, 123.1, 125.7, 126.4, 126.7, 127.1, 127.4, 127.7, 128.5, 129.7, 129.8, 130.2, 132.2, 138.8, 145.8, 148.6, 155.1, 155.4. MS (ESI): *m/z* 646 $[M+H]^+$. HRMS calculated for ($C_{41}H_{35}FeNO_3$ + H) : 646.2045, found 646.2044.

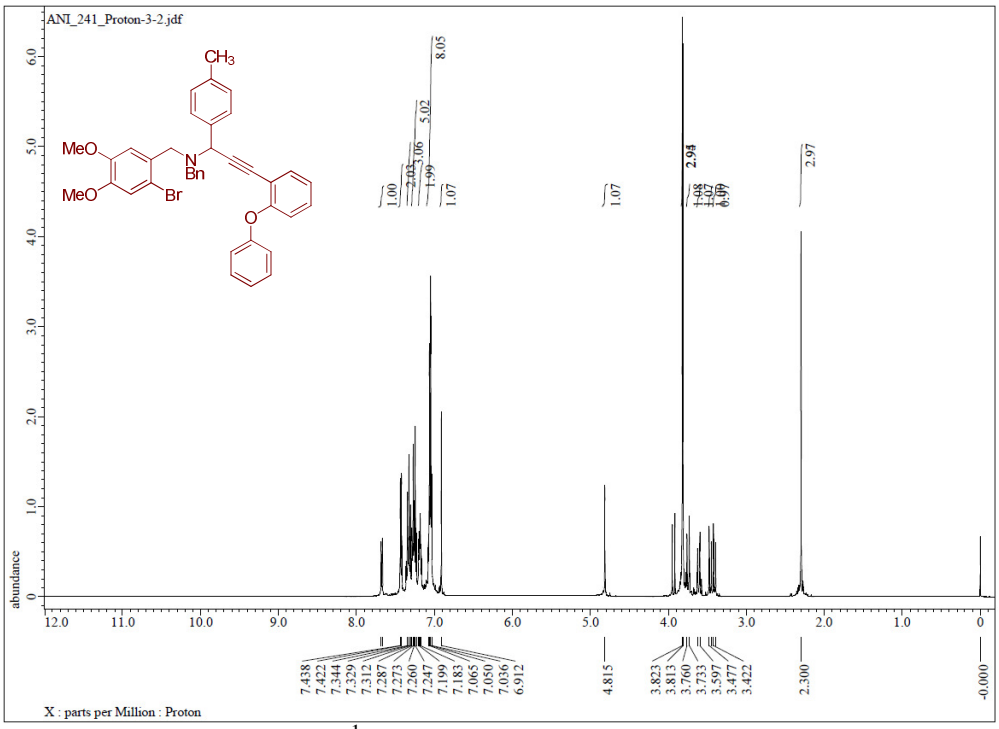


2-Benzyl-3-(1,3-diphenyl-1*H*-pyrazol-4-yl)-6,7-dimethoxy-4-(9*H*-xanthen-9-ylidene)-1,2,3,4-tetrahydroisoquinoline (**5g**): Yellow solid; mp: 178-180 ^oC; IR (KBr): 694, 759, 1059, 1133, 1237, 1353, 1447, 1507, 1596, 2735, 2840, 2922, 3055 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.39 (s, 3H, -OCH_3), 3.53(d, *J* = 14.00 Hz, 1H, -CH_2), 3.60 (d, *J* = 14.00 Hz, 1H, -CH_2), 3.67(d, *J* = 17.00 Hz, 1H, -CH_2), 3.90 (s, 3H, -OCH_3), 4.11 (d, *J* = 17.00 Hz, 1H, -CH_2), 5.84 (s, 1H, -C*H*), 6.56 (s, 1H, Ar-*H*), 6.58 (s, 1H, Ar-*H*), 6.71 (s, 1H, Ar-*H*), 6.72-6.75 (m, 1H, Ar-*H*), 6.93-6.96 (m, 2H, Ar-*H*),

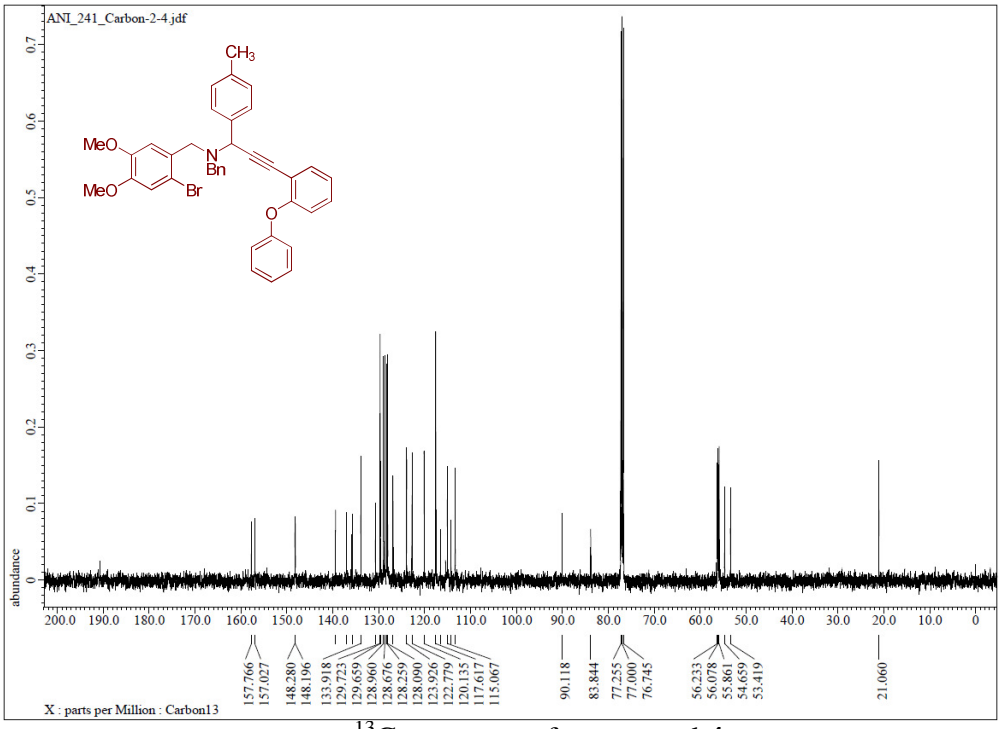
7.13 (d, *J* = 7.50 Hz, 2H, Ar-*H*), 7.16-7.25 (m, 11H, Ar-*H*), 7.30-7.39 (m, 7H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ 51.3, 52.1, 55.0, 55.8, 58.5, 107.8, 112.7, 116.2, 116.6, 117.0, 118.7, 120.5, 122.6, 123.7, 125.6, 126.0, 126.1, 126.3, 127.0, 127.2, 127.2, 127.5, 127.6, 127.9, 128.2, 128.5, 129.1, 129.2, 129.3, 129.5, 129.7, 130.8, 133.4, 138.5, 139.7, 146.1, 149.1, 154.3, 154.9, 155.4. MS (ESI): *m*/*z* 680 $[M+H]^+$. HRMS calculated for ($C_{46}H_{37}N_3O_3$ + H) : 680.2913, found : 680.2907.



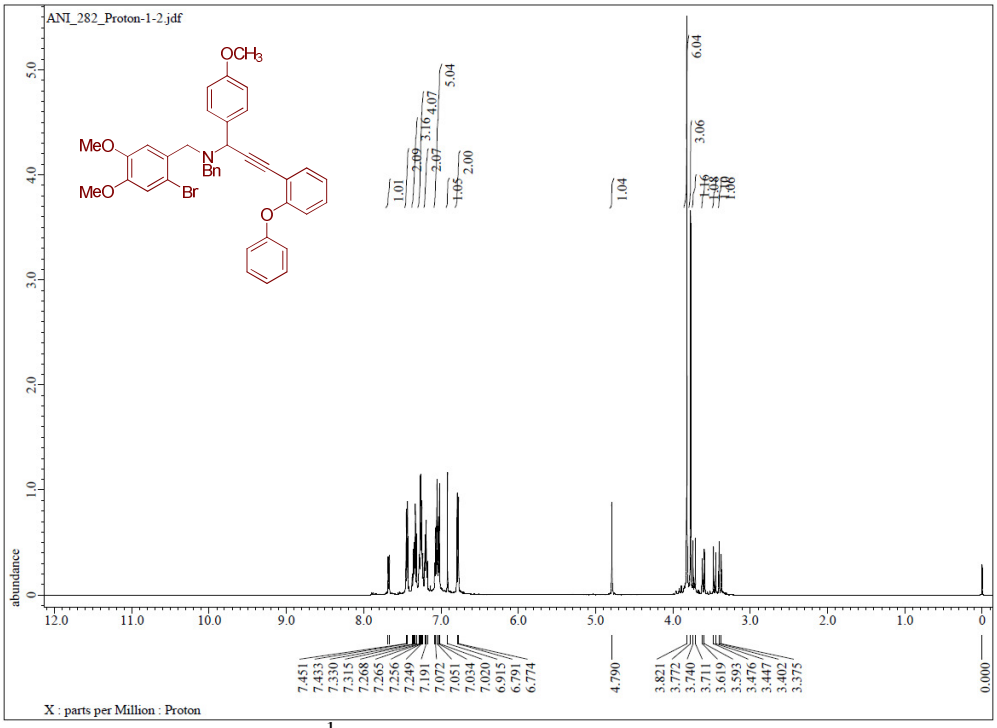
3-(2-Benzyl-6,7-dimethoxy-4-(9*H*-xanthen-9-ylidene)-1,2,3,4-tetrahydroisoquinolin-3-yl)-9-ethyl-9*H*-carbazole (**5h**): Yellow solid; mp: 98-100 ^{o}C; IR (KBr): 746, 861, 1054, 1146, 1230, 1255, 1337, 1452, 1506, 1600, 2929, 3055 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.33 (t, *J* = 7.50 Hz, 3H, -CH_3), 3.33 (s, 3H, -OCH_3), 3.77 (s, 3H, -OCH_3), 3.91 (d, *J* = 16.00 Hz, 1H, -CH_2), 4.02 (d, *J* = 16.00 Hz, 1H, -CH_2), 4.09 (d, *J* = 14.00 Hz, 1H, -CH_2), 4.22 (q, *J* = 7.50 Hz, 2H, -CH_2), 4.30 (d, *J* = 14.00 Hz, 1H, -CH_2), 5.95 (s, 1H, -C*H*), 6.41 (s, 1H, Ar-*H*), 6.47 (s, 1H, Ar-*H*), 6.87 (t, *J* = 7.50 Hz, 1H, Ar-*H*), 6.94 (t, *J* = 7.50 Hz, 1H, Ar-*H*),7.09-7.24 (m, 8H, Ar-*H*), 7.30 (d, *J* = 8.00 Hz, 1H, Ar-*H*),7.33-7.38 (m, 3H, Ar-*H*), 7.42 (t, *J* = 7.50 Hz, 2H, Ar-*H*), 7.59 (d, *J* = 7.00 Hz, 2H, Ar-*H*),7.79 (s, 1H, Ar-*H*), 7.91 (d, *J* = 8.00 Hz, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$)**:**δ13.8, 37.4, 50.9, 55.0, 55.5, 59.1, 60.8, 107.8, 108.0, 108.2, 112.8, 116.8, 116.9, 118.4, 119.4, 120.2, 122.4, 122.8, 122.9, 123.1, 123.4, 125.3, 125.6, 125.7, 126.1, 126.6, 126.8, 127.2, 127.5, 127.9, 128.5, 129.0, 129.6, 129.7, 130.8, 131.2, 138.9, 139.5, 140.0, 146.0, 148.6, 154.6, 154.8. MS (ESI): *m*/*z* 655 $[M+H]^+$. HRMS calculated for ($C_{45}H_{38}N_2O_3$ + H) : 655.2961, found : 655.2949.



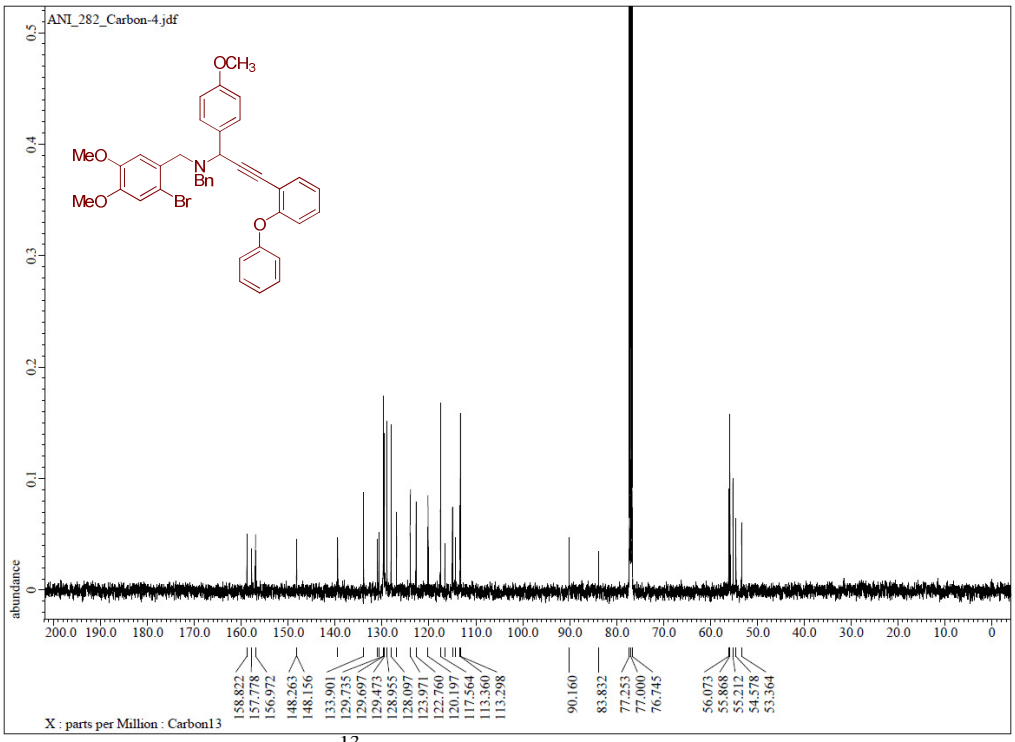
^{1}H spectrum of compound **4a**



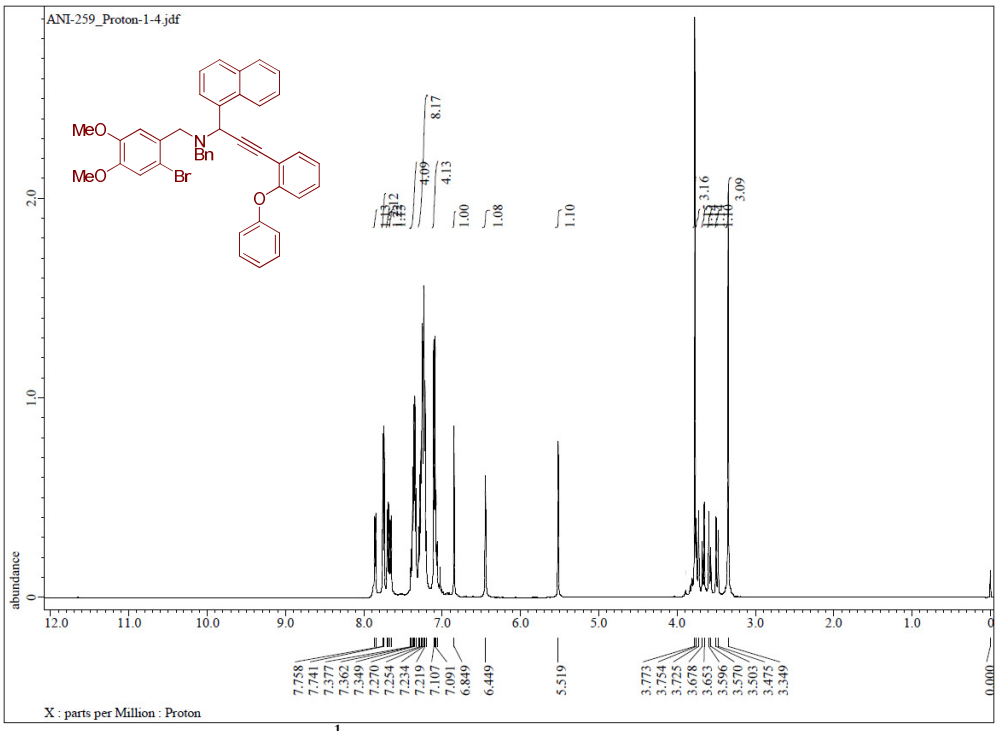
^{13}C spectrum of compound **4a**



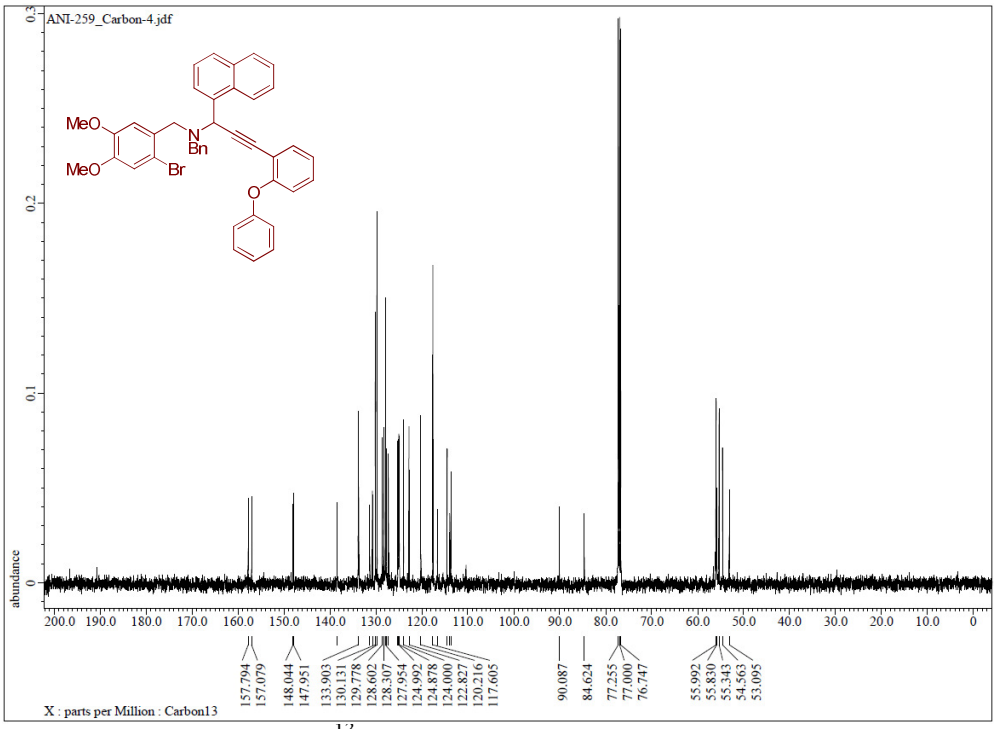
^{1}H spectrum of compound **4b**



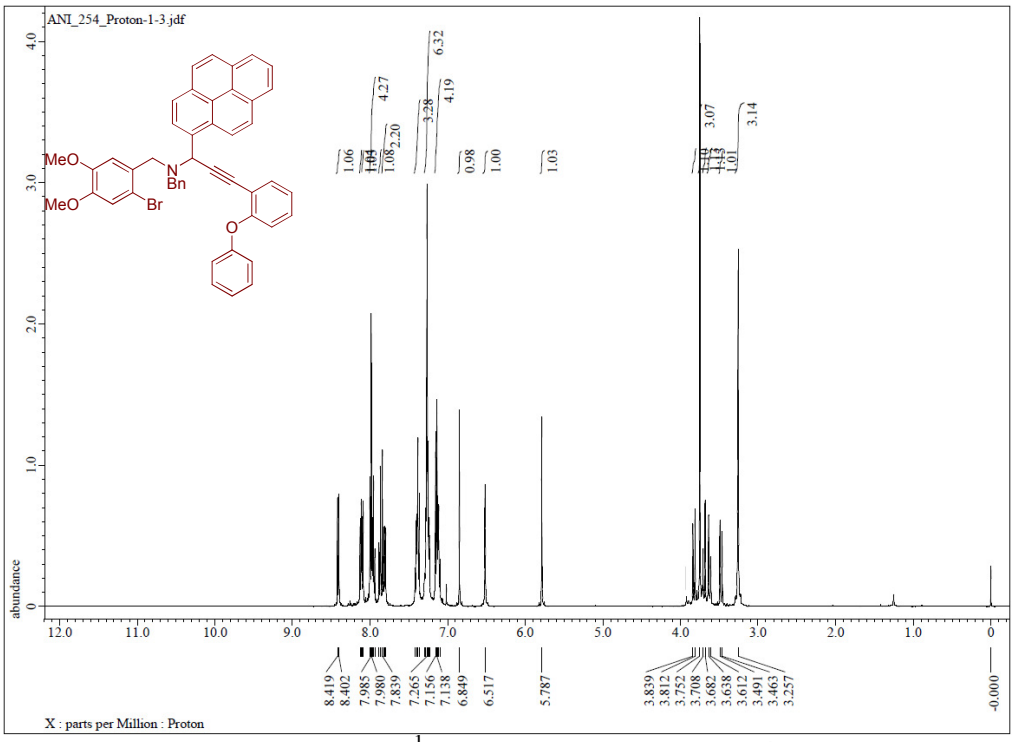
^{13}C spectrum of compound **4b**



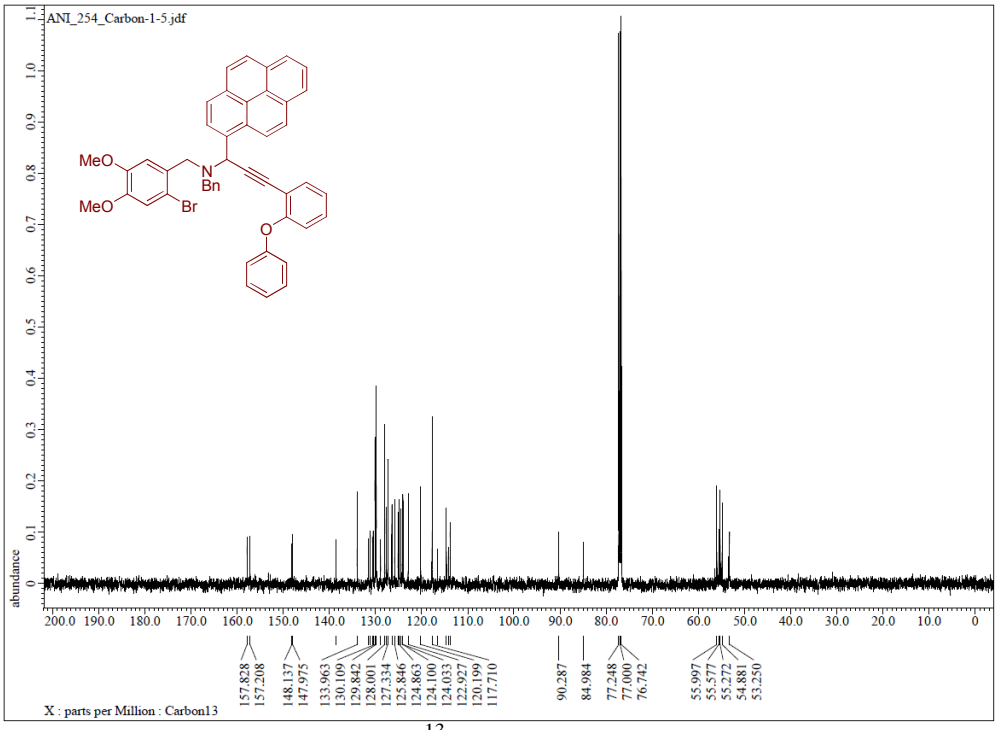
^{1}H spectrum of compound **4c**



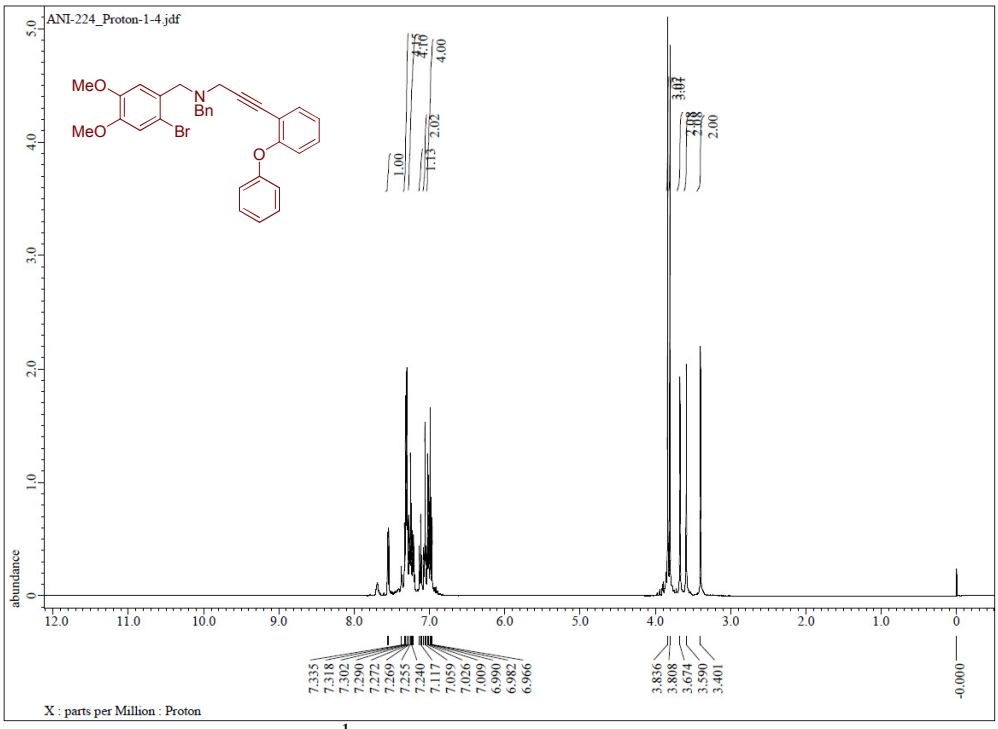
^{13}C spectrum of compound **4c**



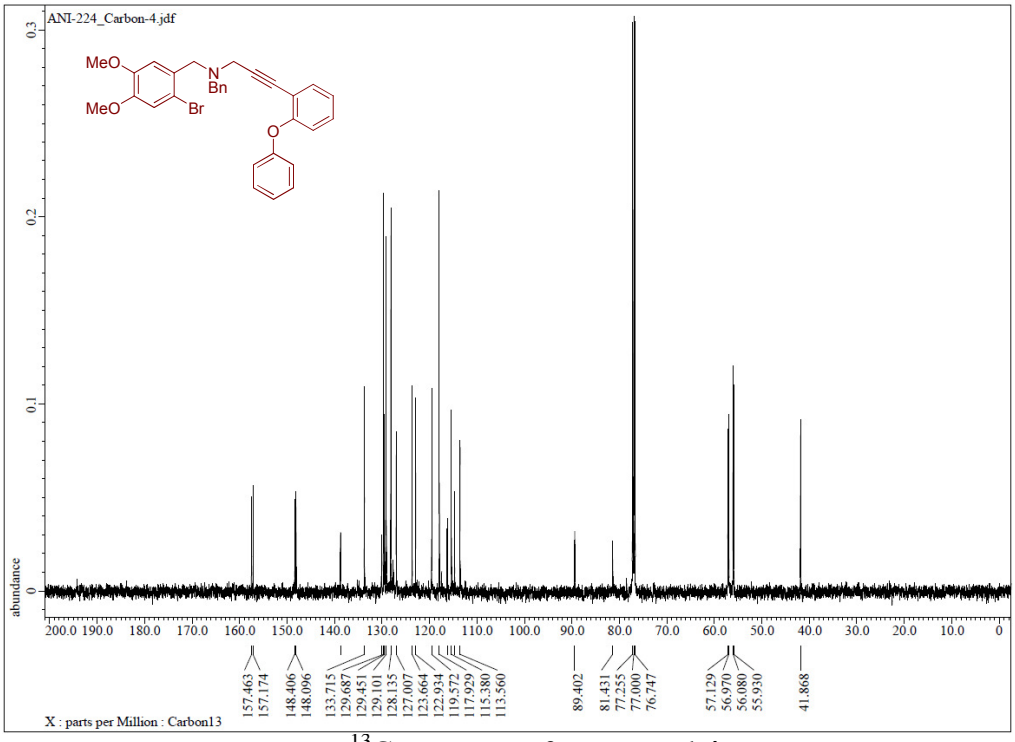
^{1}H spectrum of compound **4d**



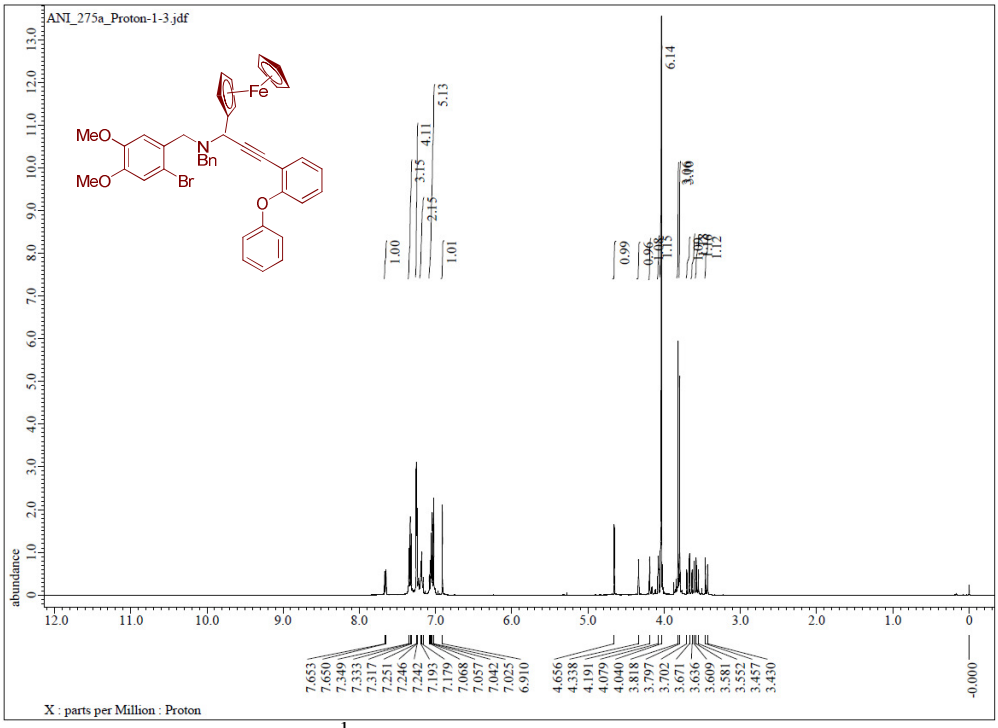
^{13}C spectrum of compound **4d**



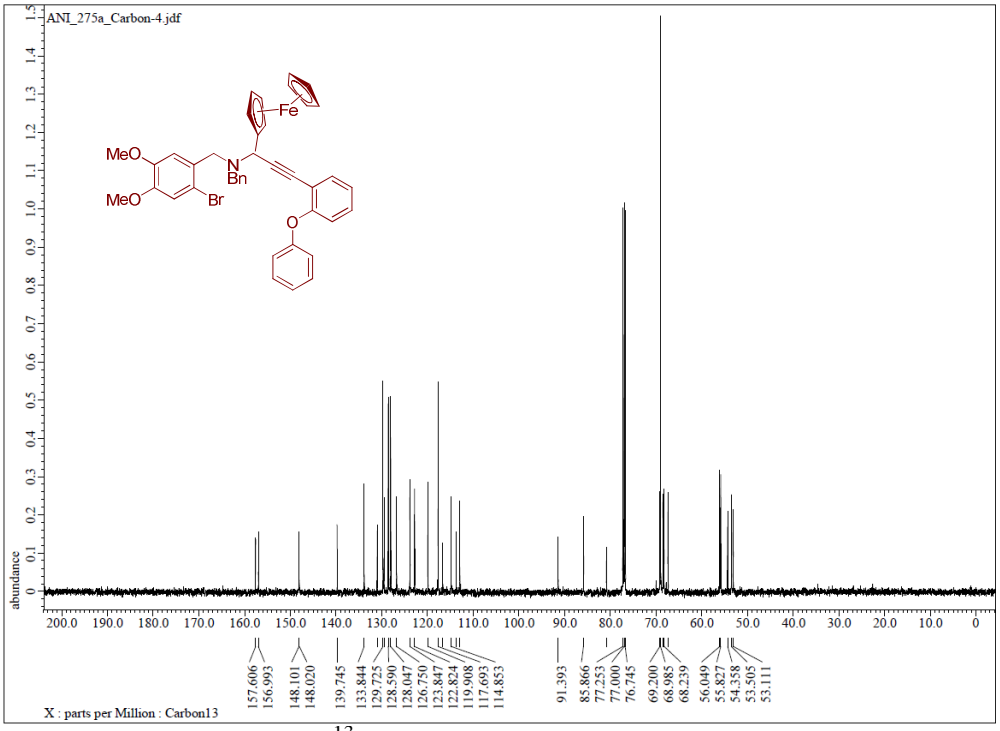
^{1}H spectrum of compound **4e**



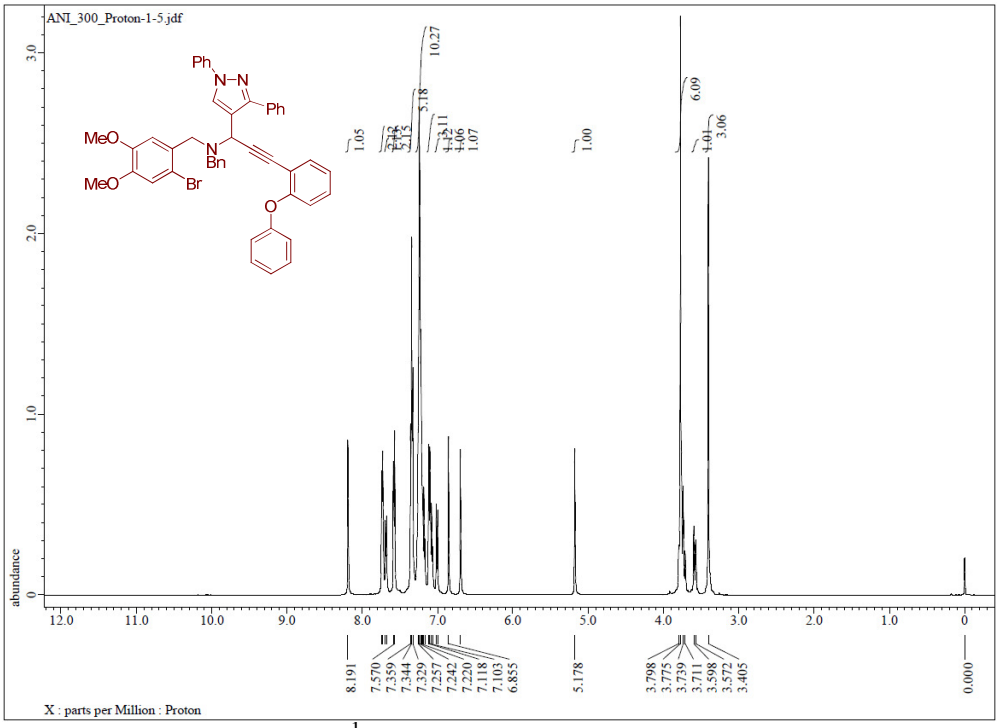
^{13}C spectrum of compound **4e**



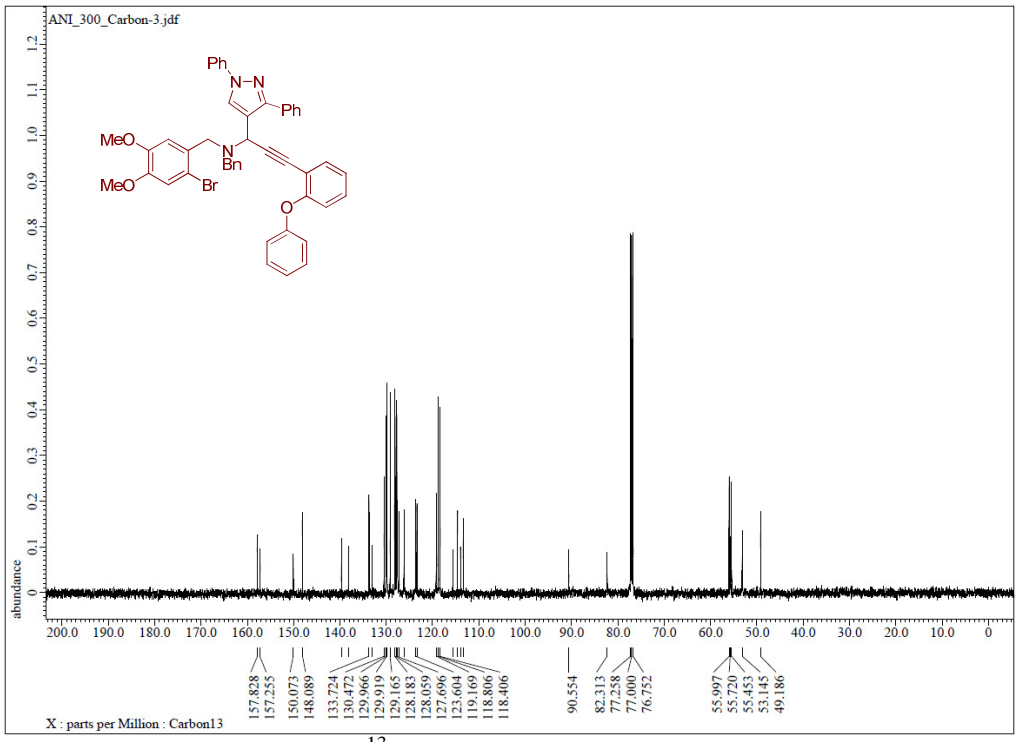
^{1}H spectrum of compound **4f**



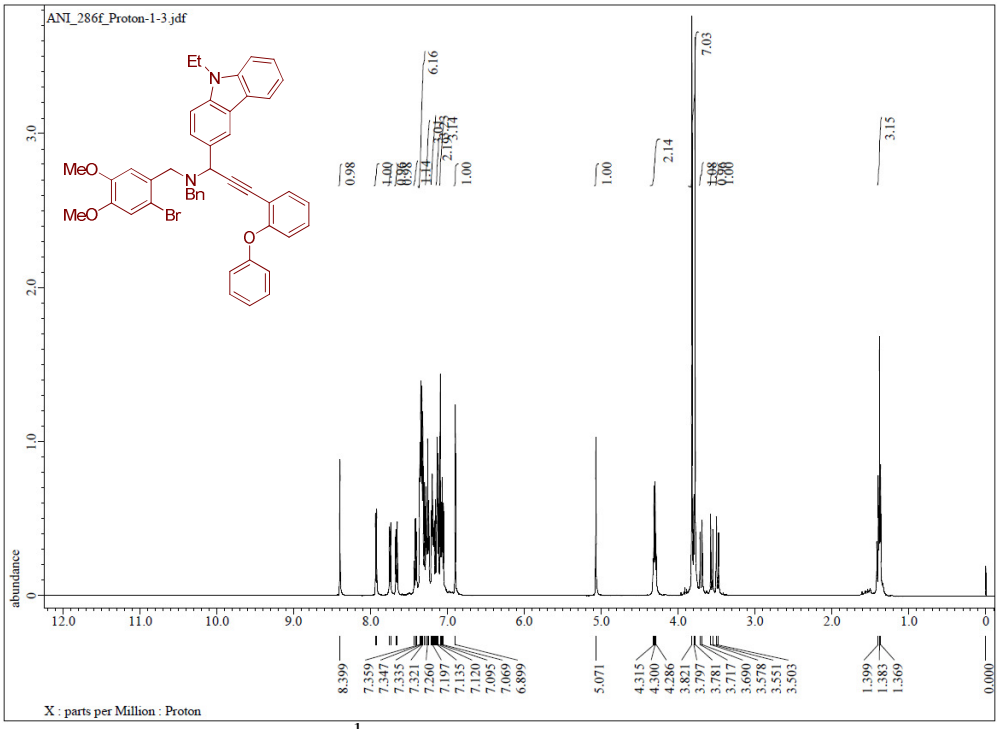
^{13}C spectrum of compound **4f**



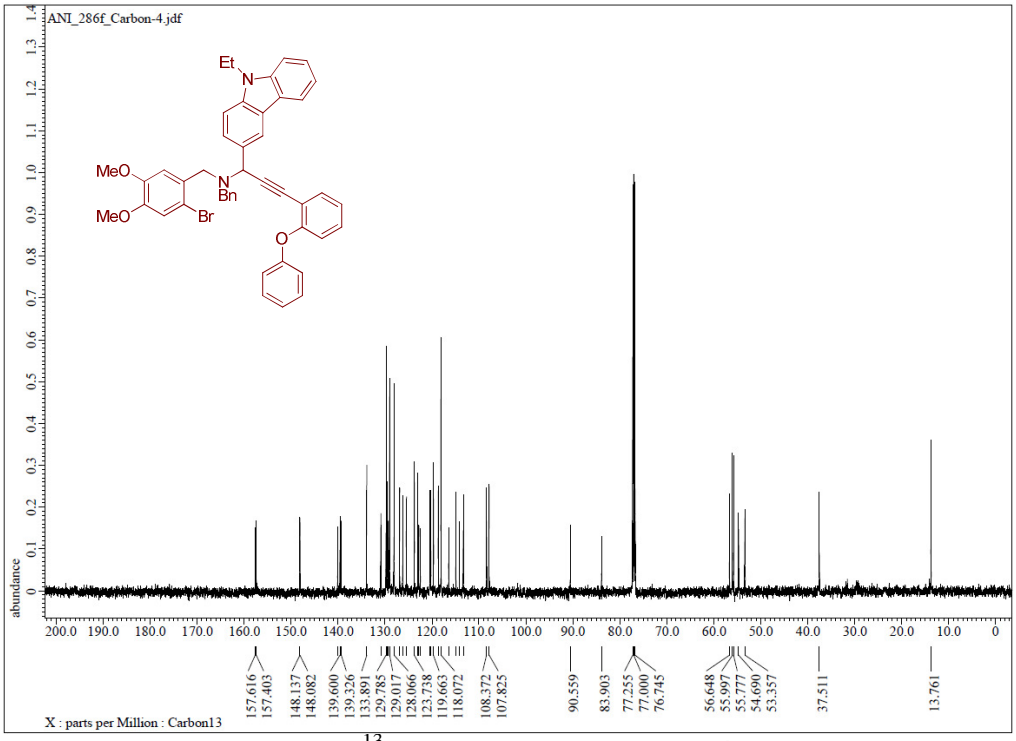
^{1}H spectrum of compound **4g**



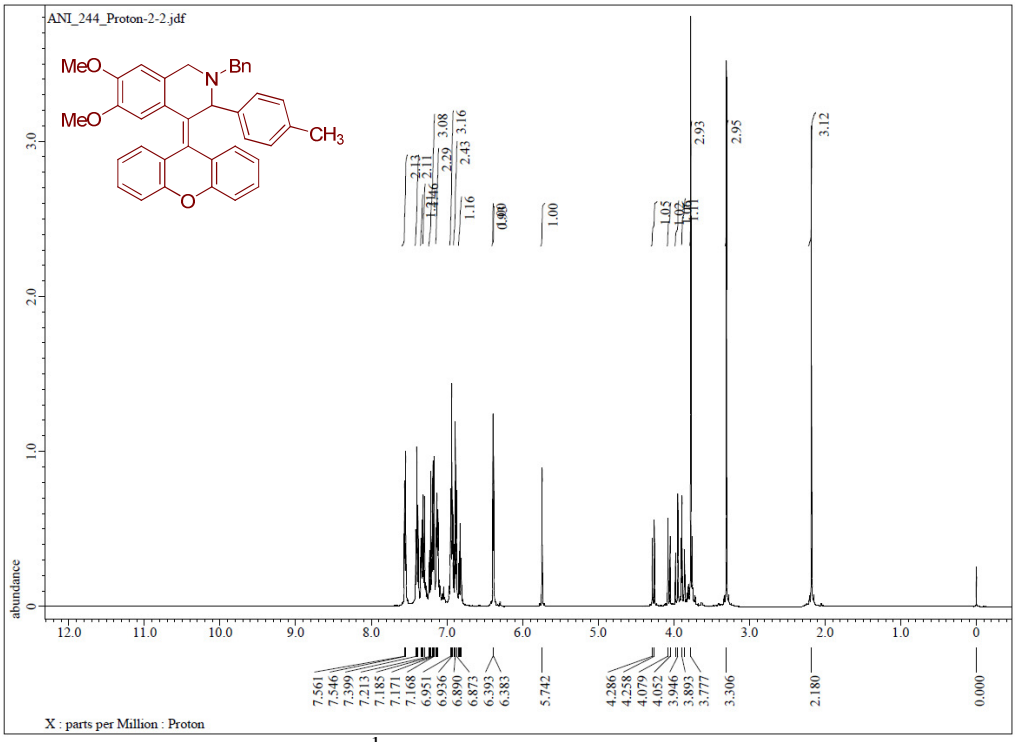
^{13}C spectrum of compound **4g**



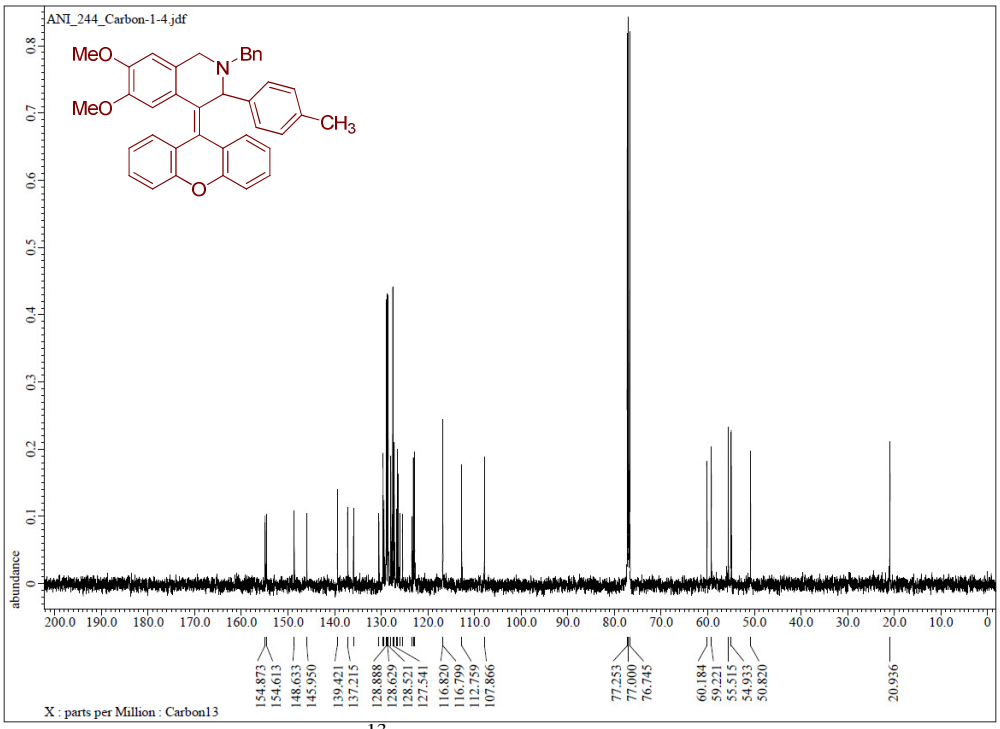
^{1}H spectrum of compound **4h**



^{13}C spectrum of compound **4h**



^{1}H spectrum of compound **5a**



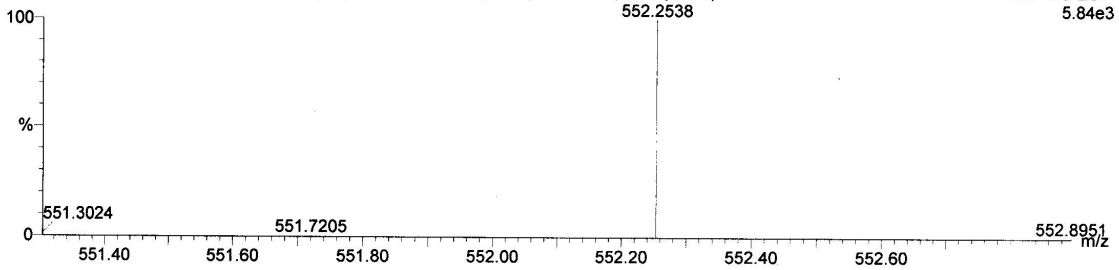
^{13}C spectrum of compound **5a**

Elemental Composition Report **Page 1**

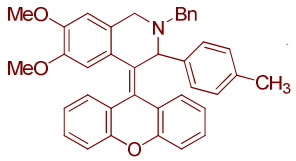
Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

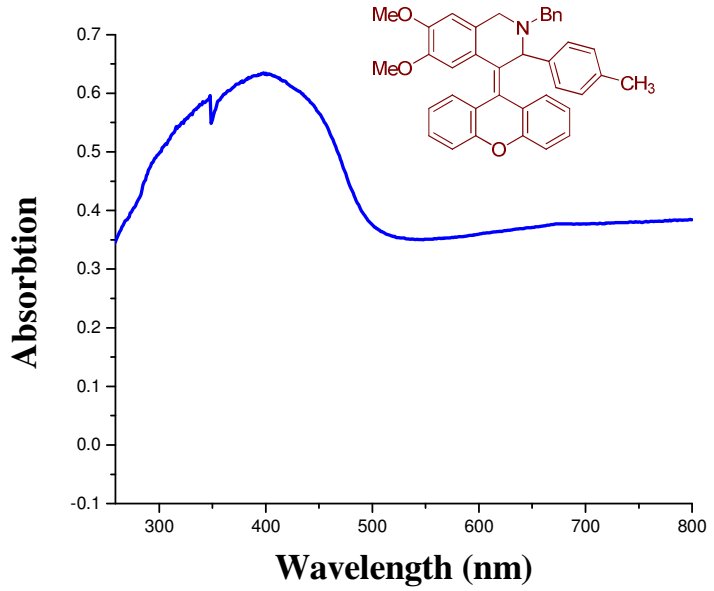
QTOF MICRO DEPARTMENT OF CHEMISTRY IITM 27-Dec-201211:37:49
GSK-IN-244 74 (1.383) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x4.00); Cm (58:75) TOF MS ES+
5.84e3



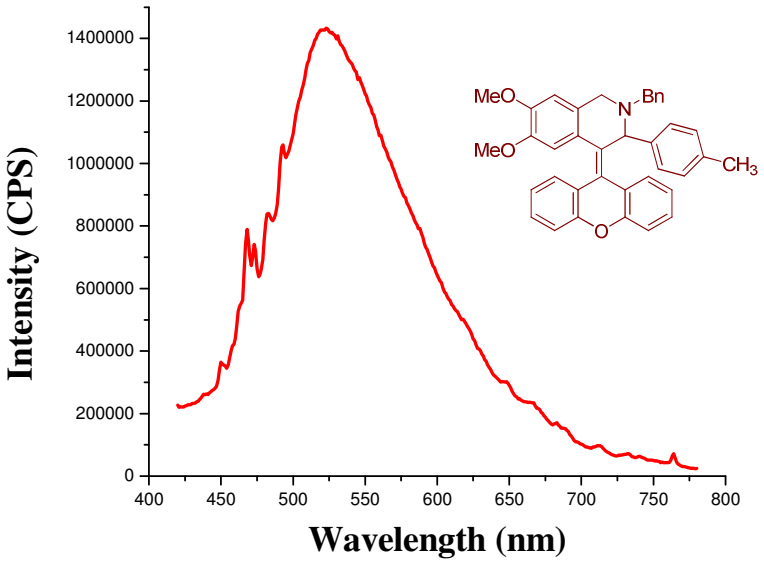
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
552.2538	552.2539	-0.1	-0.2	22.5	1	C38 H34 N O3



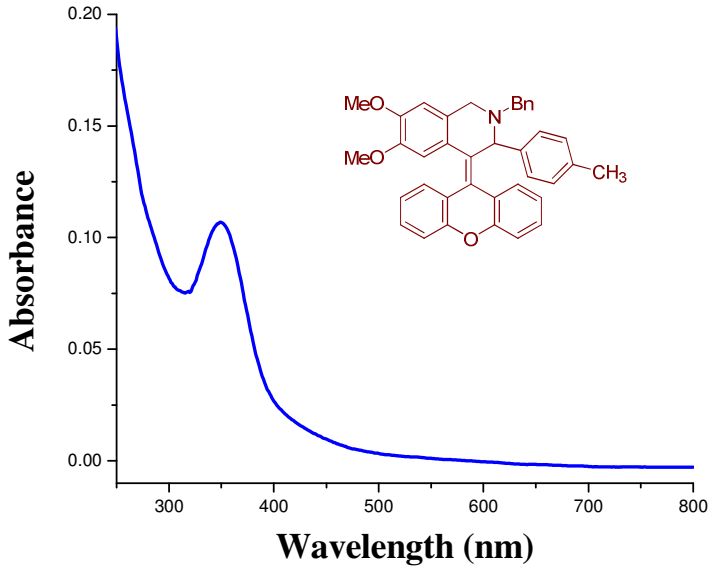
HRMS spectrum of compound **5a**



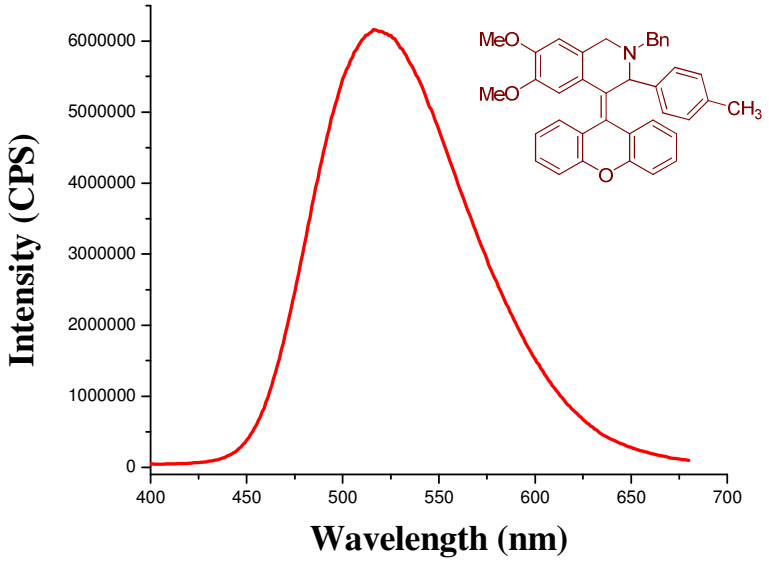
UV-Visible spectrum (DRS) of compound **5a**



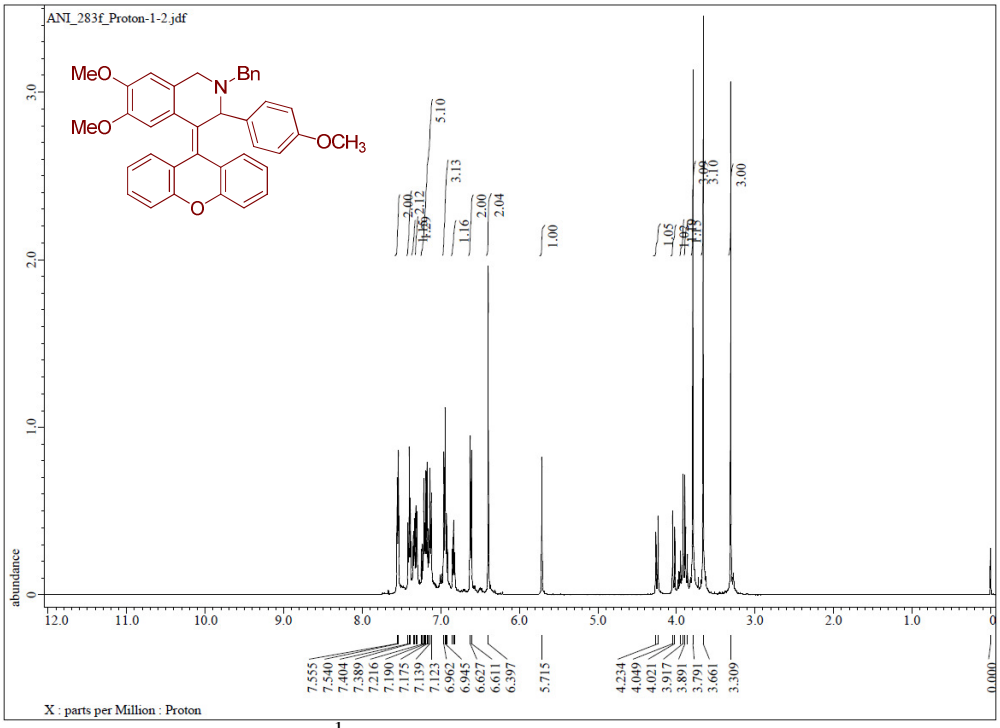
Solid state emission spectrum of compound **5a**



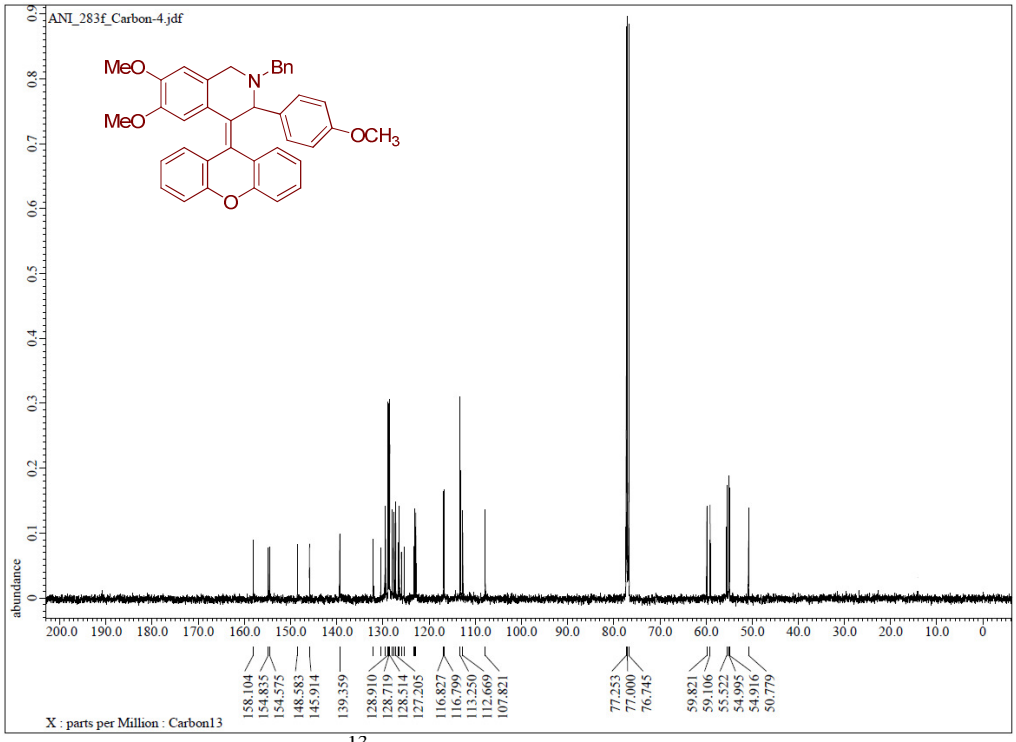
UV-Visible spectrum of **5a** in 99% H_2O/CH_3CN mixture



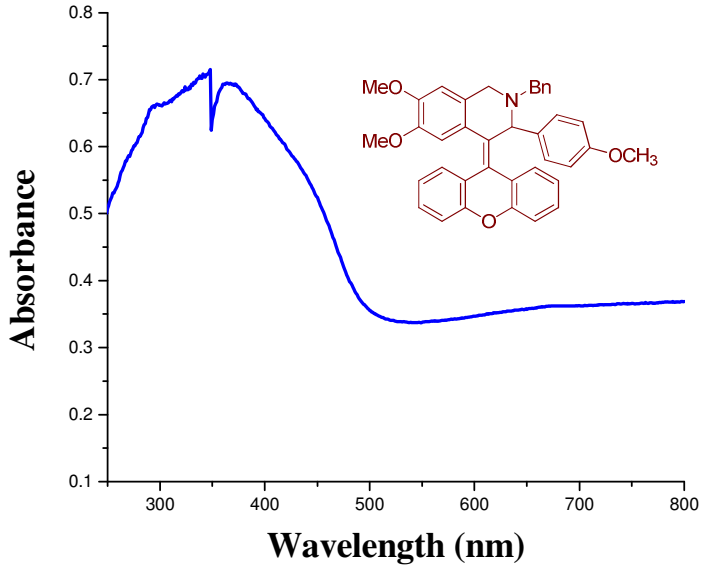
Emission spectrum of **5a** in 99% H_2O/CH_3CN mixture



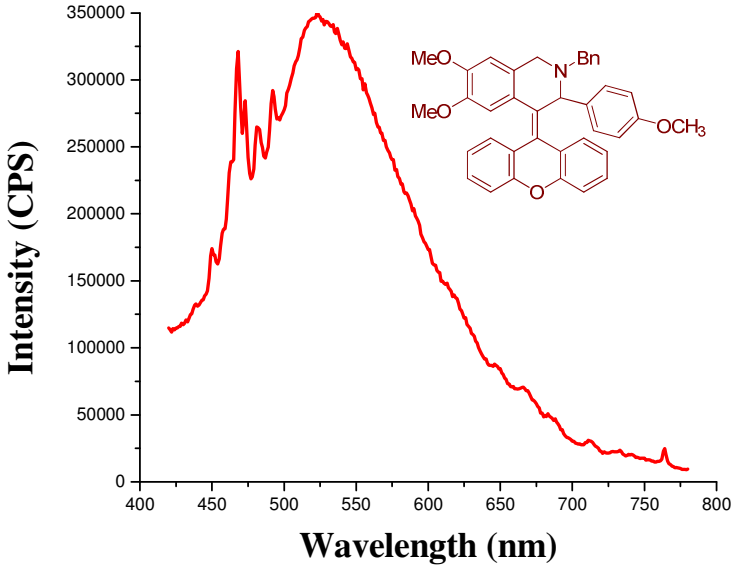
^{1}H spectrum of compound **5b**



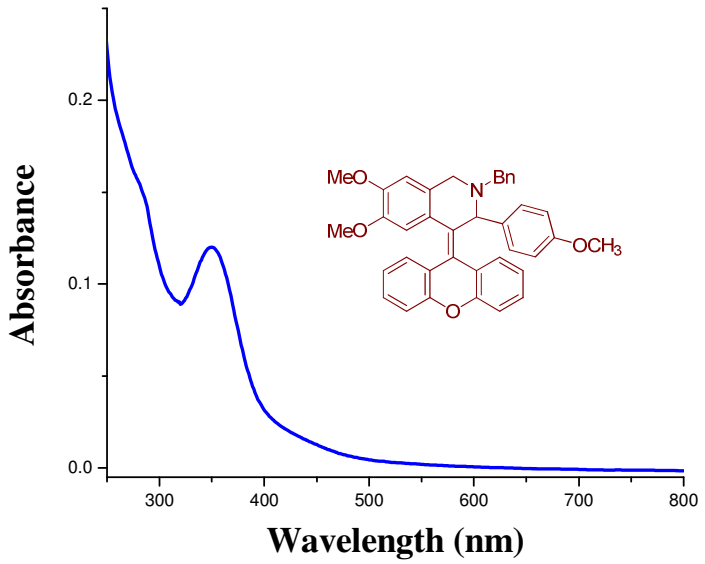
^{13}C spectrum of compound **5b**



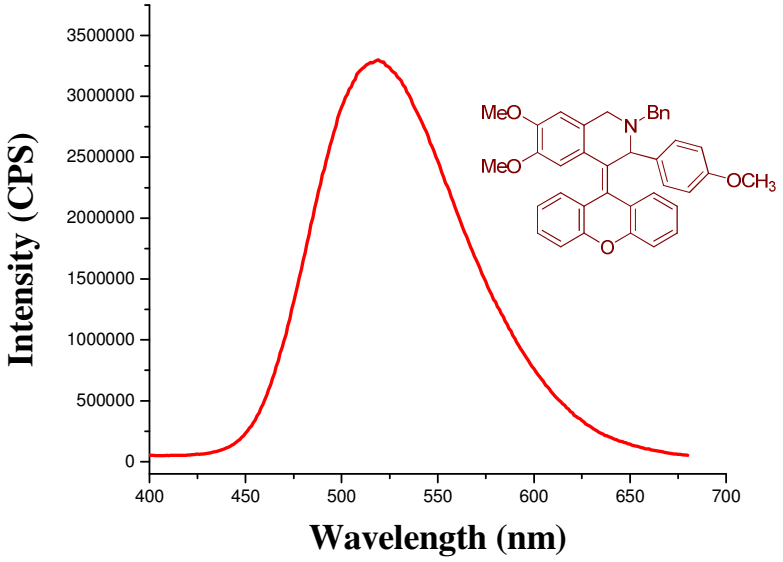
UV-Visible spectrum (DRS) of compound **5b**



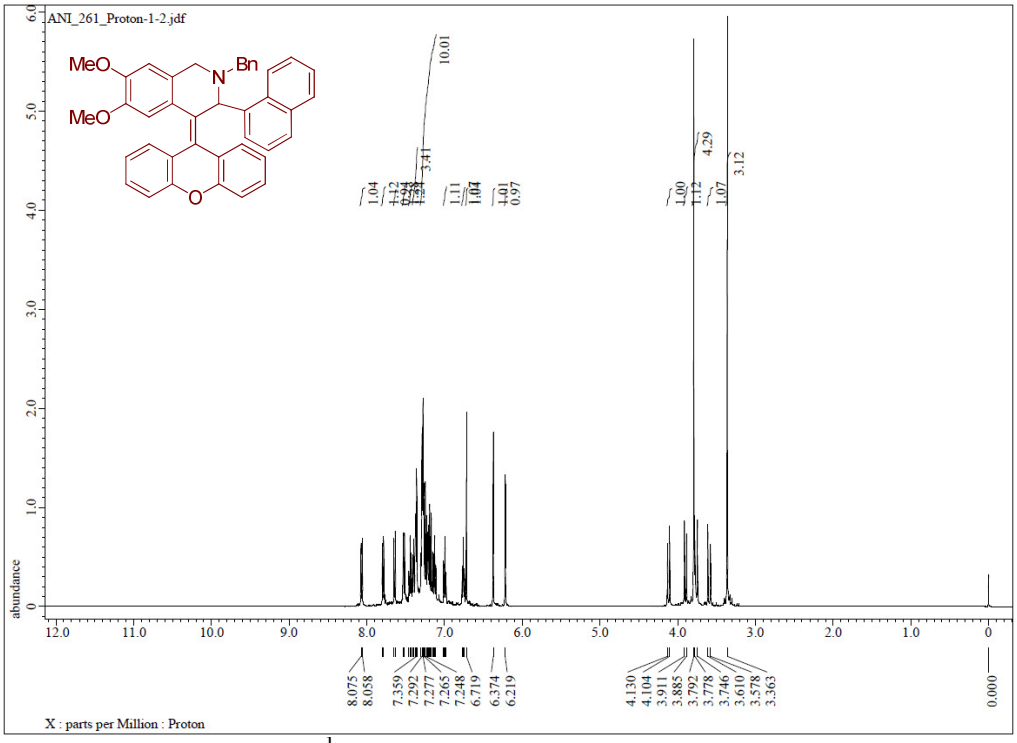
Solid state emission spectrum of compound **5b**



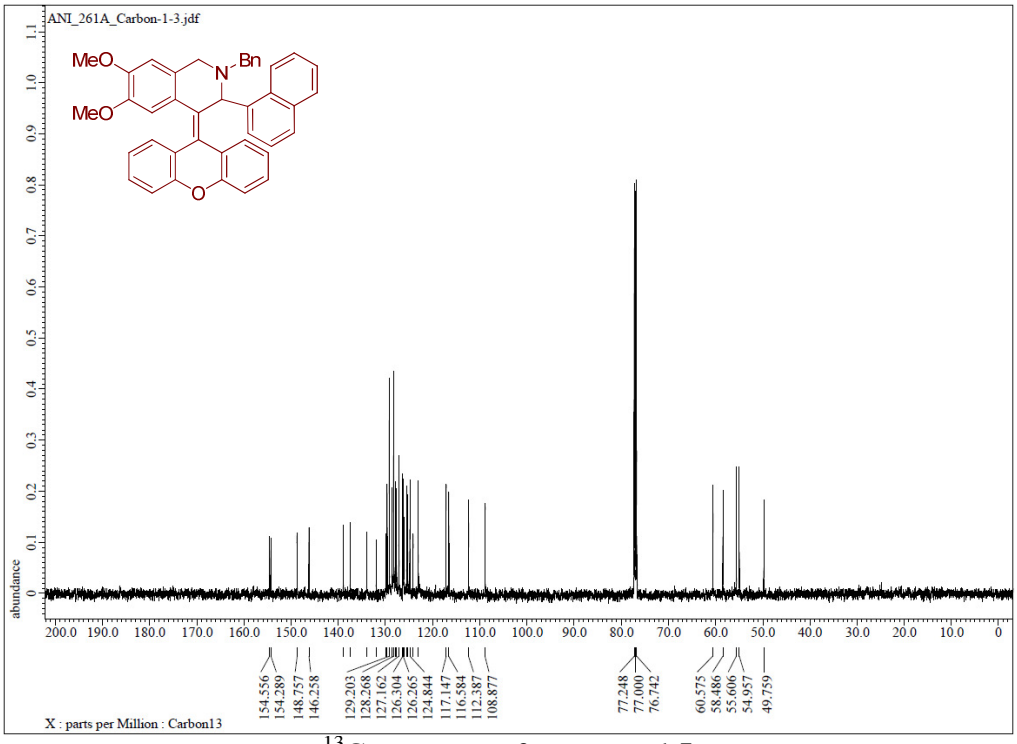
UV-Visible spectrum of **5b** in 99% H_2O/CH_3CN mixture



Emission spectrum of **5b** in 99% H_2O/CH_3CN mixture



^{1}H spectrum of compound **5c**



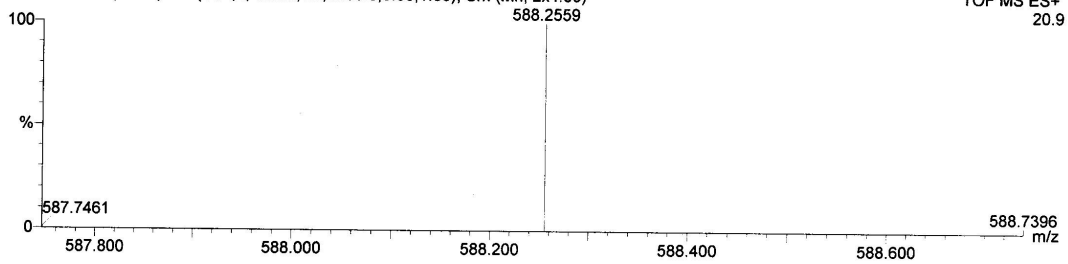
^{13}C spectrum of compound **5c**

Elemental Composition Report **Page 1**

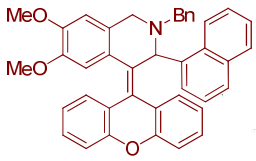
Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

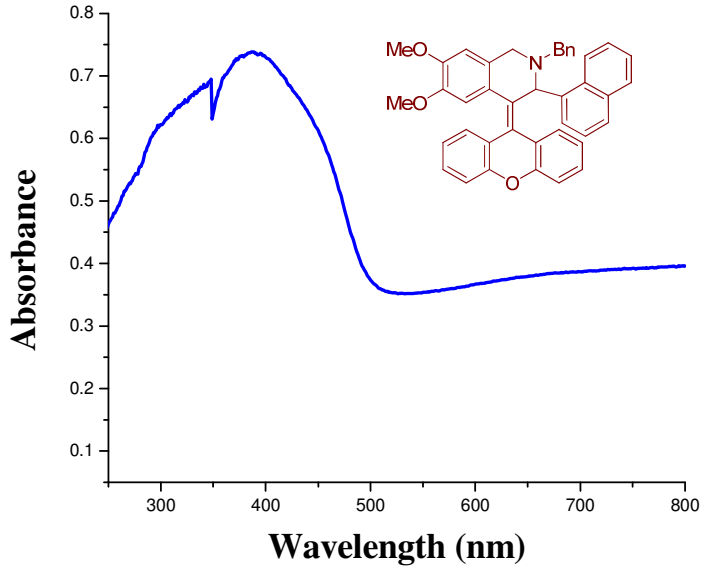
QTOF MICRO DEPARTMENT OF CHEMISTRY IITM 28-Dec-201213:06:11
SB-SP-261 15 (0.279) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x4.00) TOF MS ES+
20.9



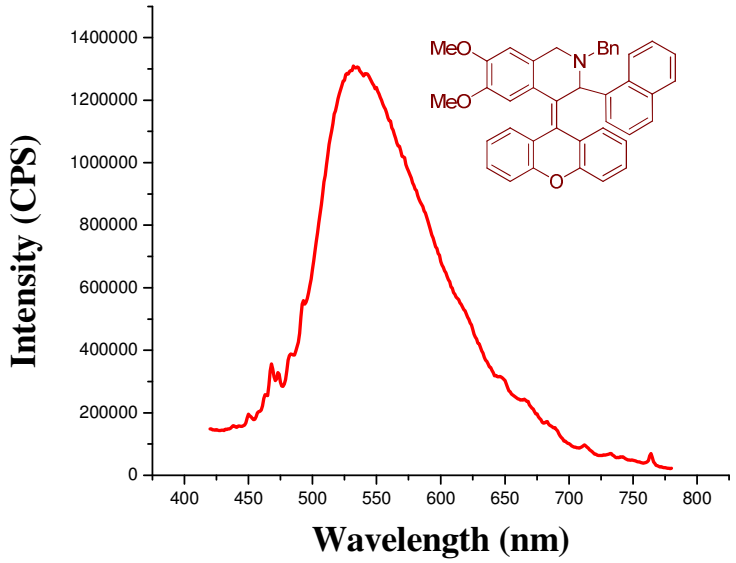
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
588.2559	588.2539	2.1	3.5	25.5	1	C41 H34 N O3



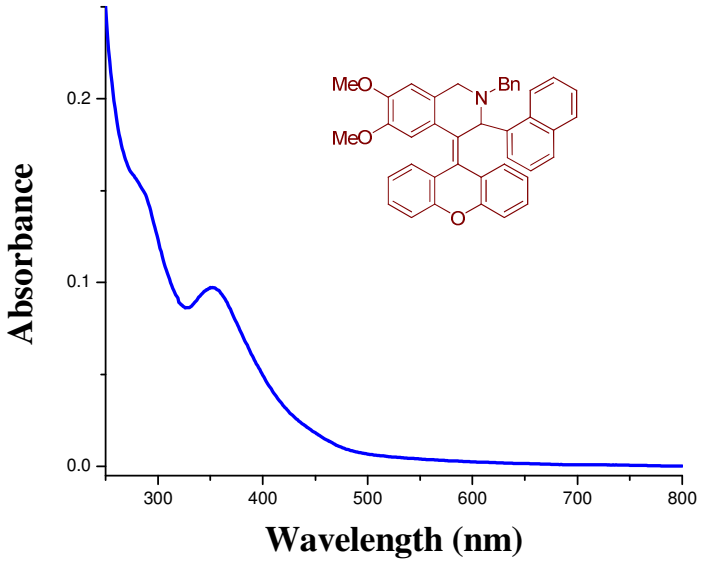
HRMS spectrum of compound **5c**



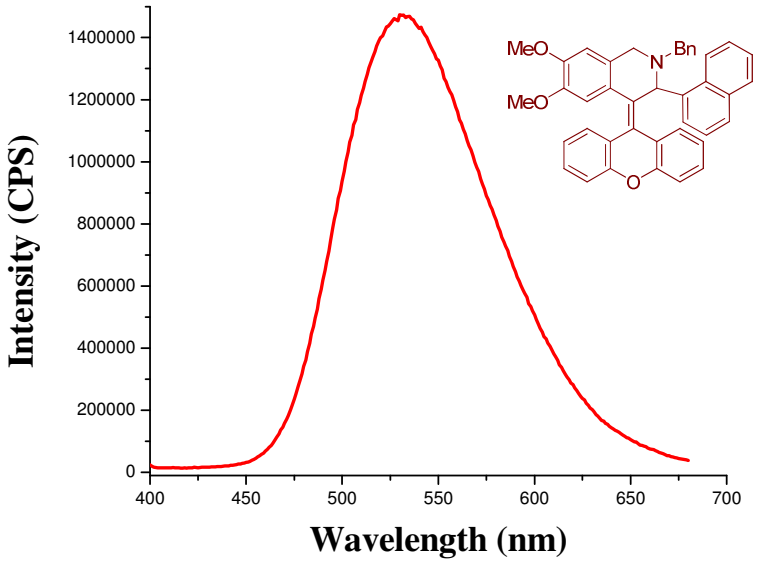
UV-Visible spectrum (DRS) of compound **5c**



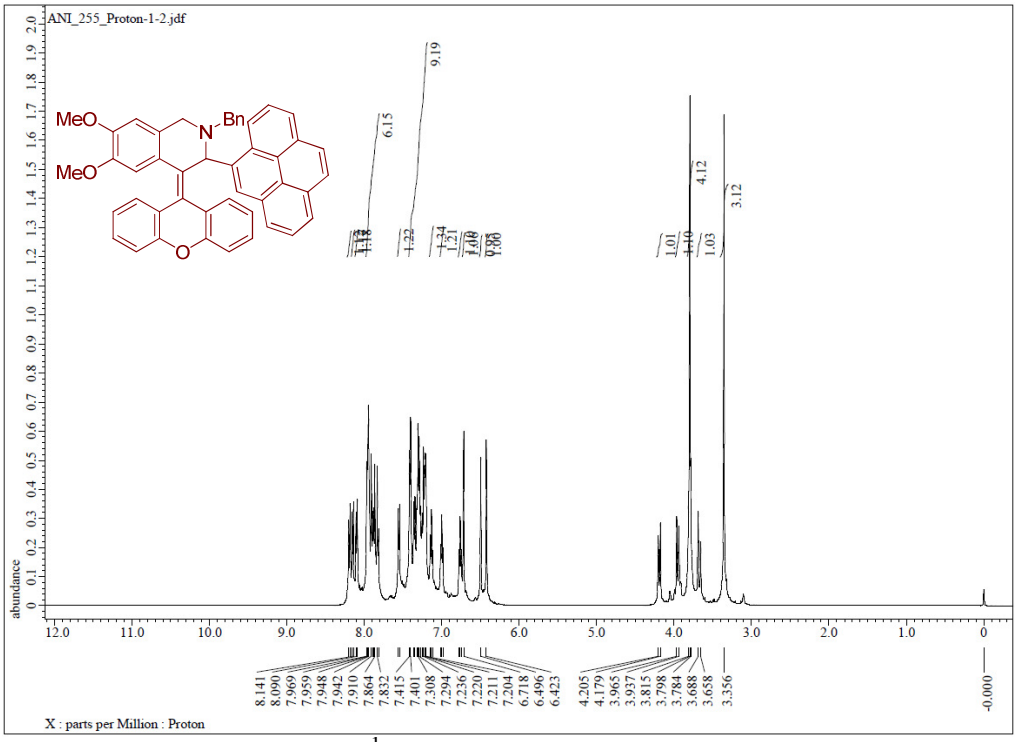
Solid state emission spectrum of compound **5c**



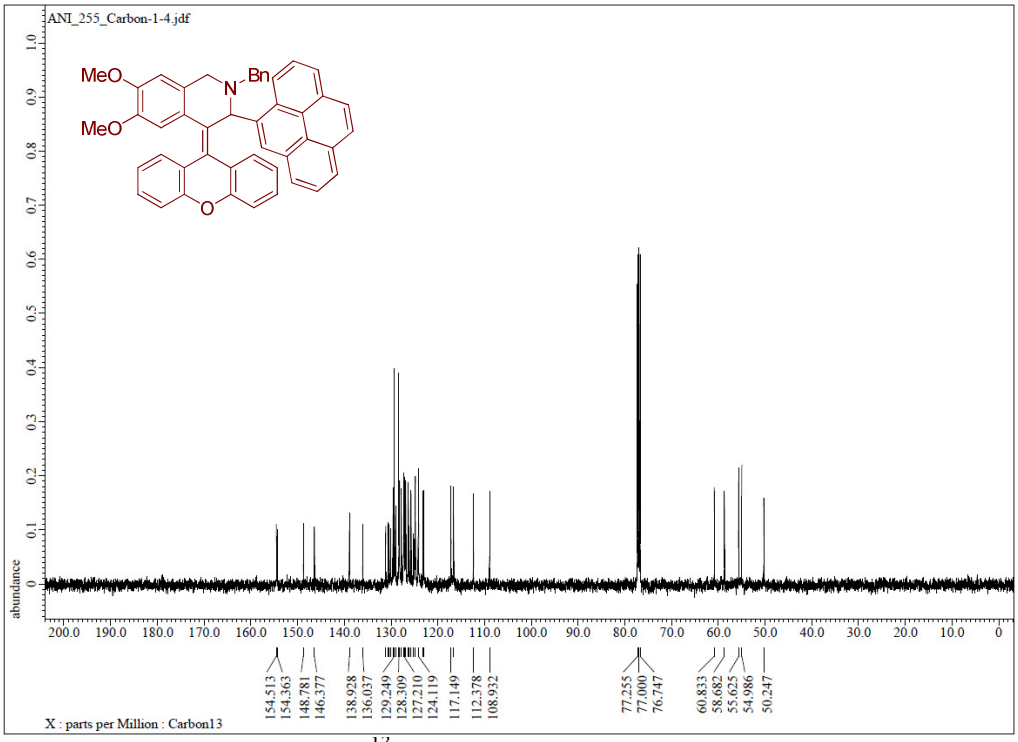
UV-Visible spectrum of **5c** in 99% H_2O/CH_3CN mixture



Emission spectrum of **5c** in 99% H_2O/CH_3CN mixture



^{1}H spectrum of compound **5d**



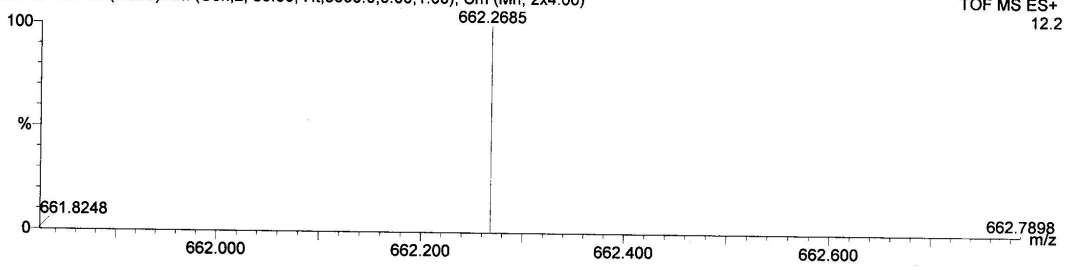
^{13}C spectrum of compound **5d**

Elemental Composition Report **Page 1**

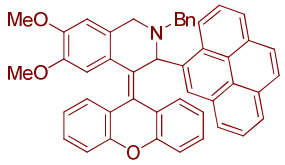
Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

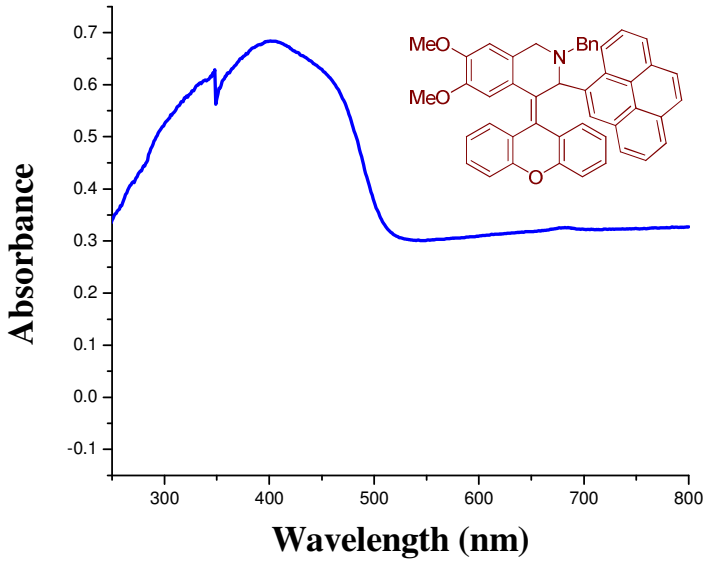
QTOF MICRO DEPARTMENT OF CHEMISTRY IITM 28-Dec-201212:16:41
SB-SP-291 48 (0.896) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x4.00) TOF MS ES+
12.2



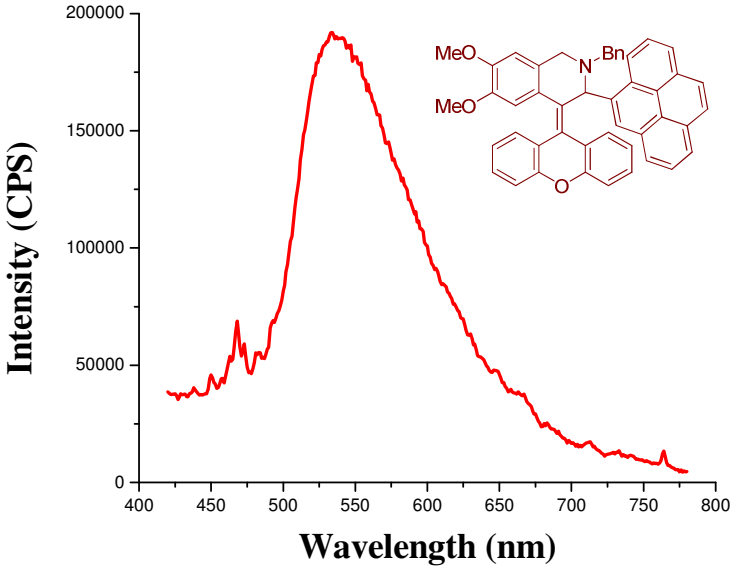
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
662.2685	662.2695	-1.0	-1.5	30.5	1	C47 H36 N O3



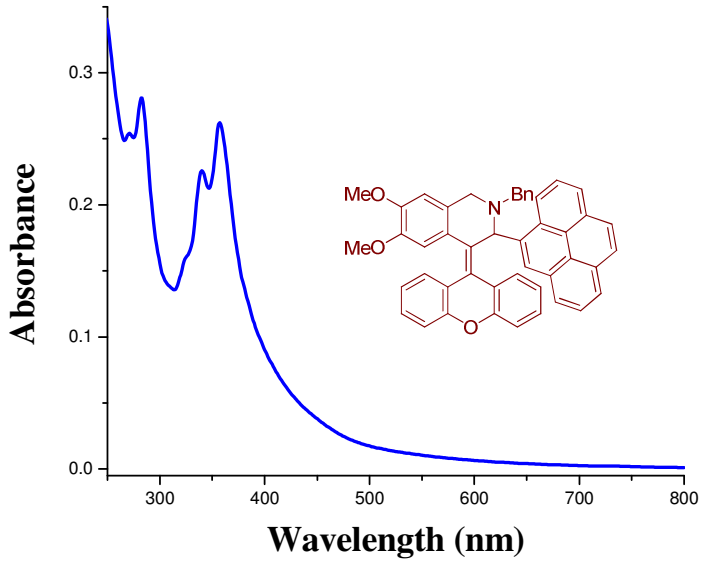
HRMS spectrum of compound **5d**



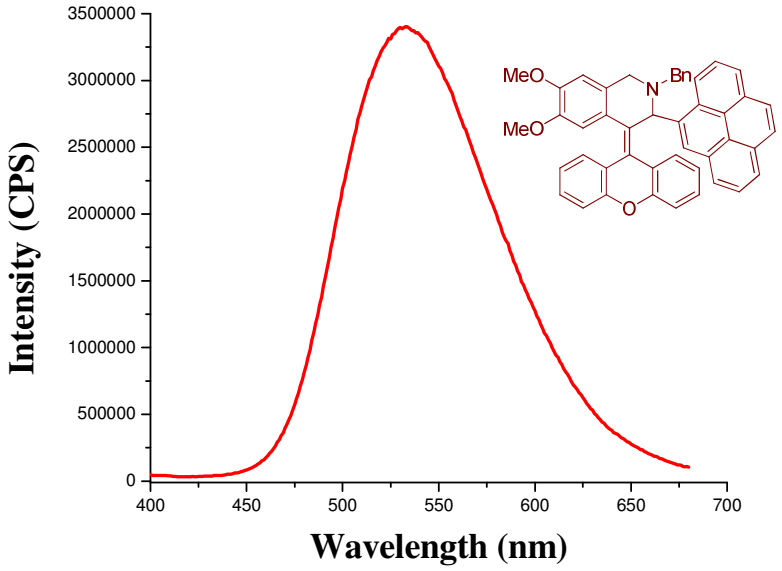
UV-Visible spectrum (DRS) of compound **5d**



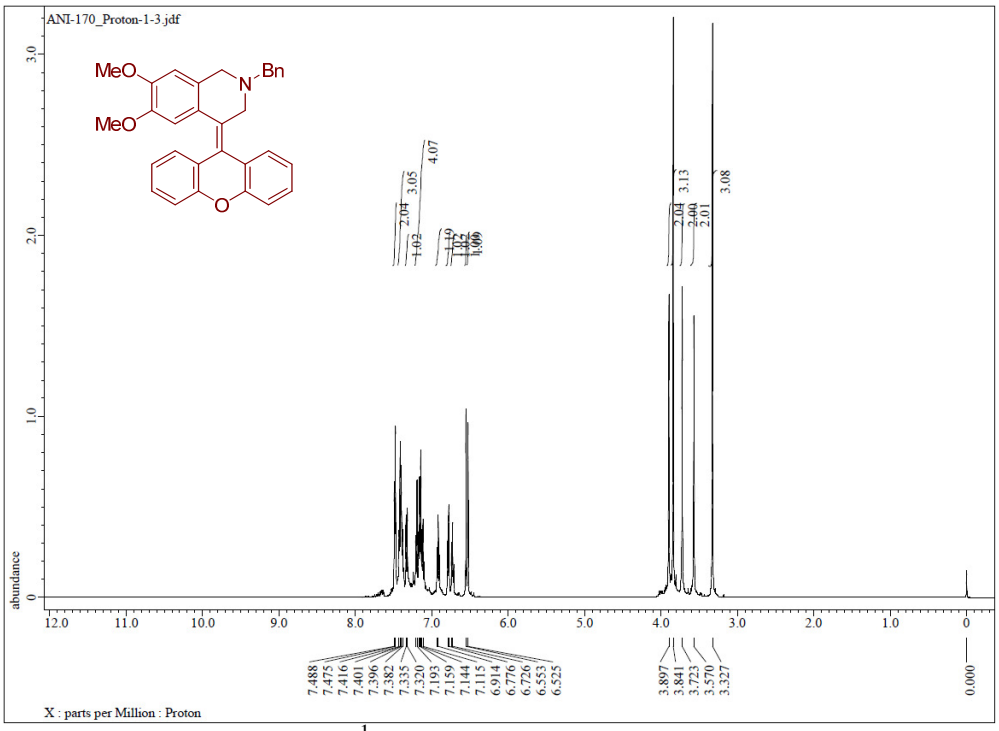
Solid state emission spectrum of compound **5d**



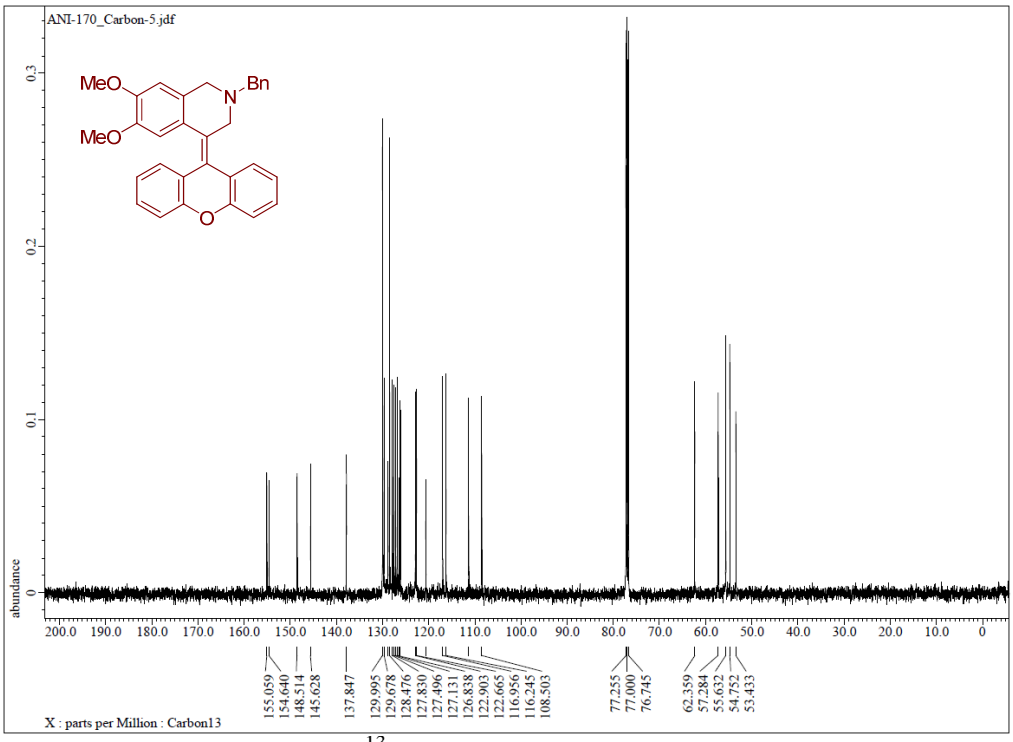
UV-Visible spectrum of **5d** in 99% H_2O/CH_3CN mixture



Emission spectrum of **5d** in 99% H_2O/CH_3CN mixture



^{1}H spectrum of compound **5e**



^{13}C spectrum of compound **5e**

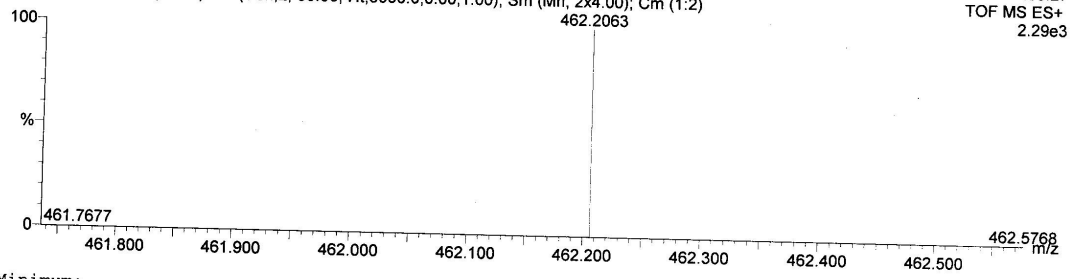
Elemental Composition Report

Page 1

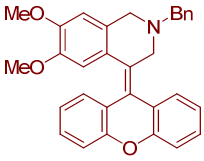
Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

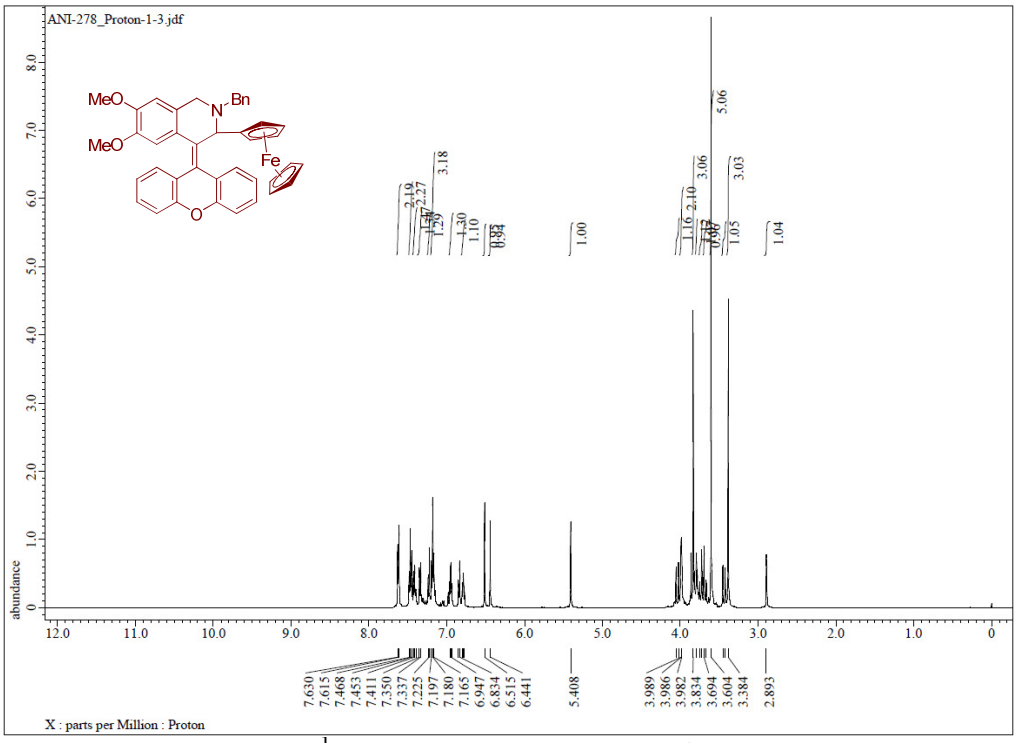
QTOF MICRO
GSK-SRG-IN-170 2 (0.037) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x4.00); Cm (1:2)
DEPARTMENT OF CHEMISTRY IITM
01-Jan-201312:03:27
TOF MS ES+
2.29e3



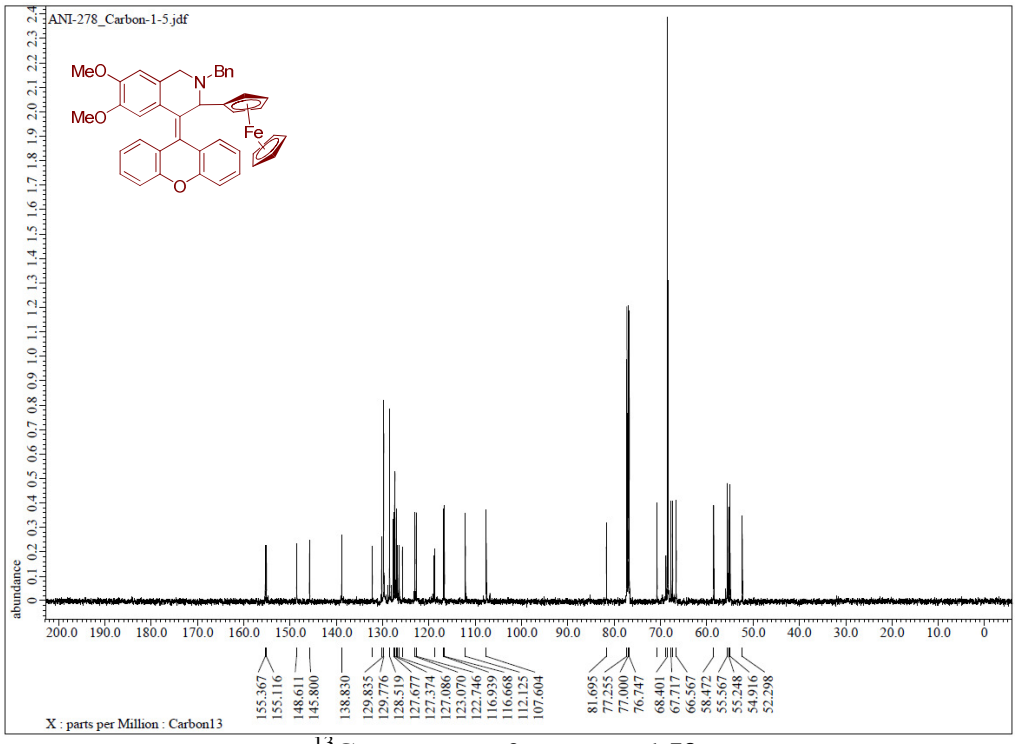
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
462.2063	462.2069	-0.6	-1.3	18.5	1	C31 H28 N O3



HRMS spectrum of compound **5e**



^{1}H spectrum of compound **5f**



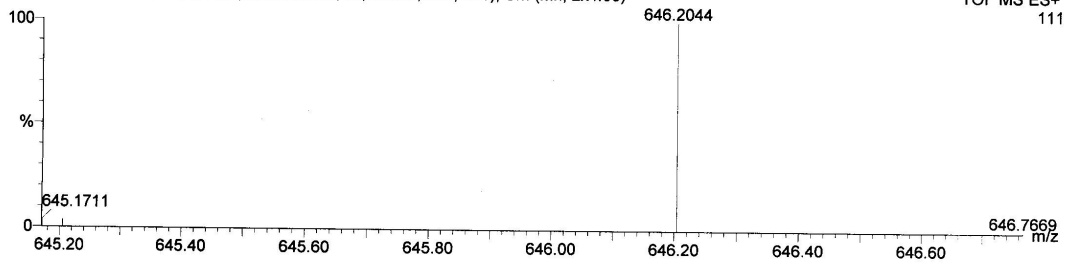
^{13}C spectrum of compound **5f**

Elemental Composition Report **Page 1**

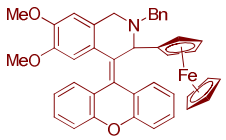
Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
9 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

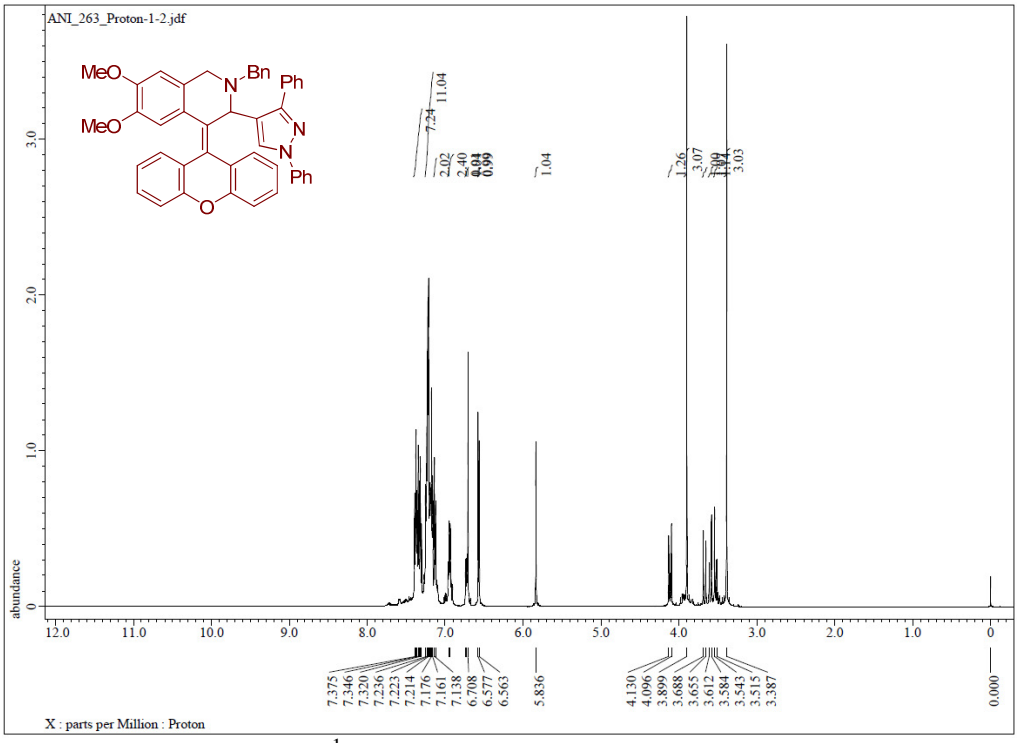
QTOF MICRO DEPARTMENT OF CHEMISTRY IITM 01-Jan-201312:16:40
GSK-SRG-IN-278 7 (0.150) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x4.00) TOF MS ES+
111



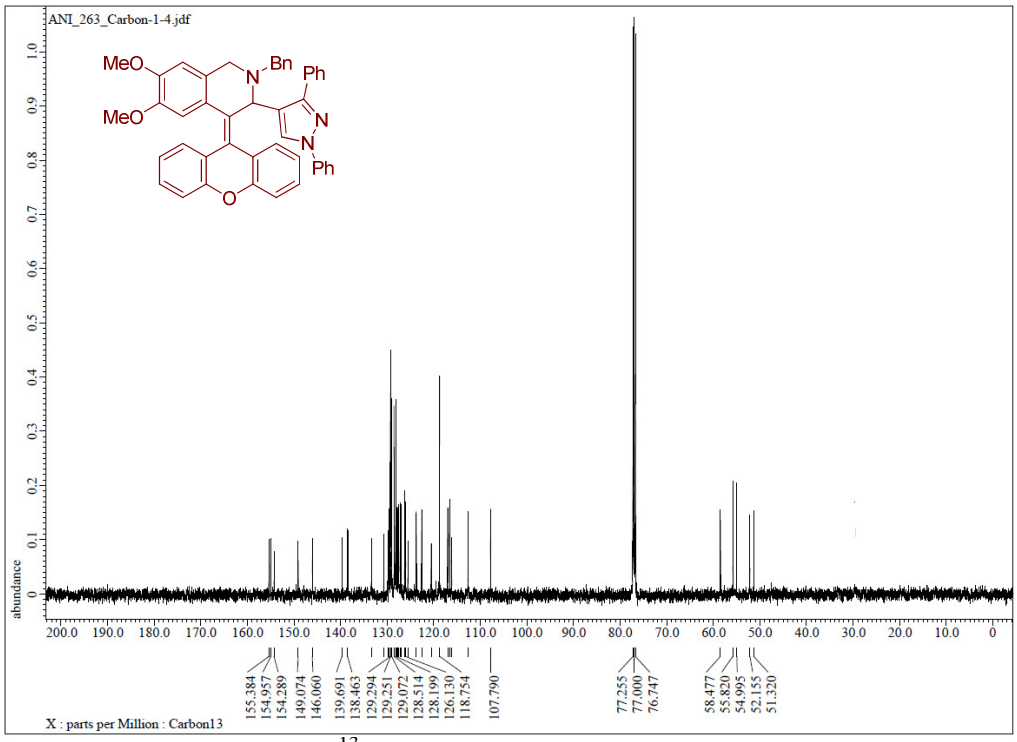
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
646.2044	646.2045	-0.1	-0.1	24.5	1	C41 H36 N O3 Fe



HRMS spectrum of compound **5f**



^{1}H spectrum of compound **5g**



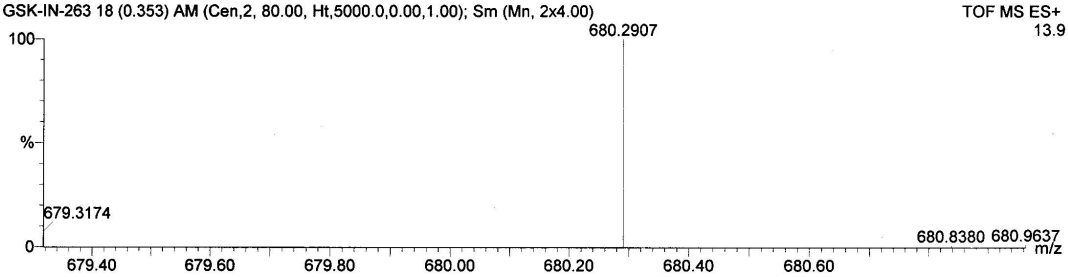
^{13}C spectrum of compound **5g**

Elemental Composition Report **Page 1**

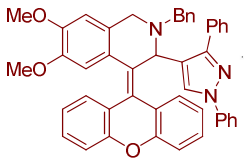
Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

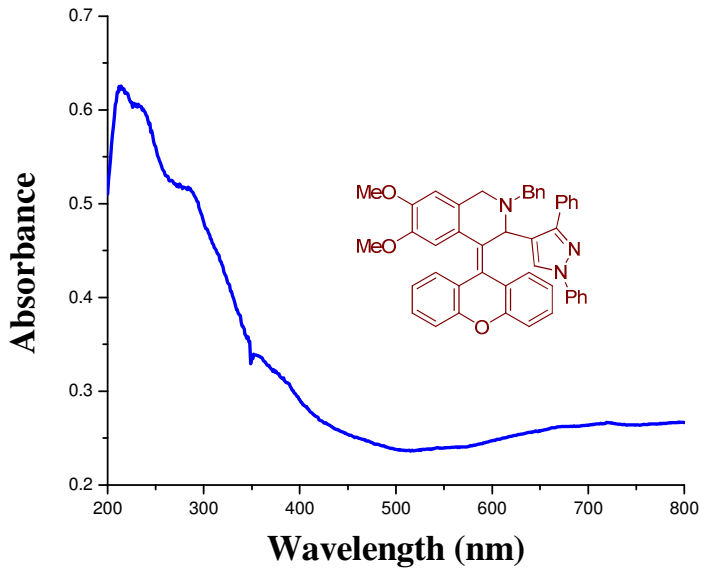
QTOF MICRO DEPARTMENT OF CHEMISTRY IITM 27-Dec-201211:49:22
GSK-IN-263 18 (0.353) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x4.00) TOF MS ES+
13.9



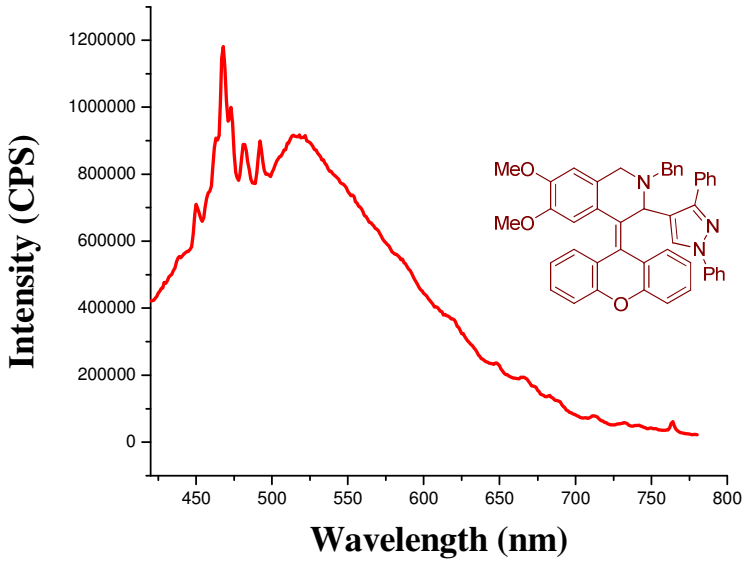
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
680.2907	680.2913	-0.6	-0.9	29.5	1	C46 H38 N3 O3



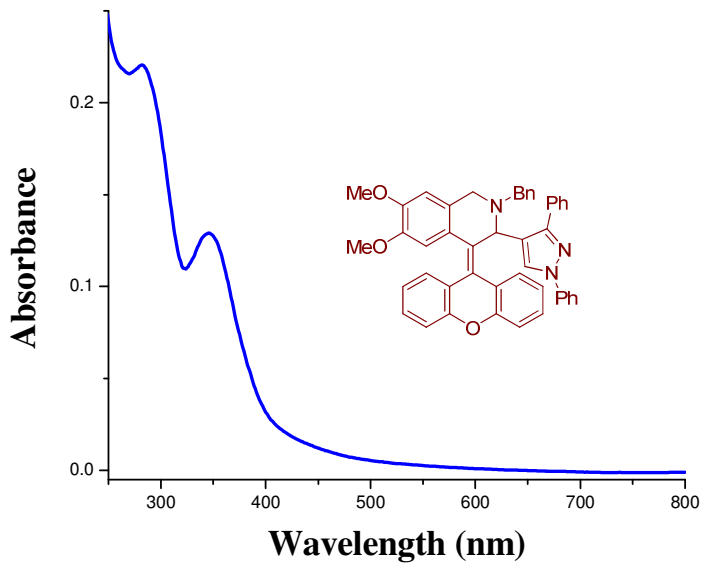
HRMS spectrum of compound **5g**



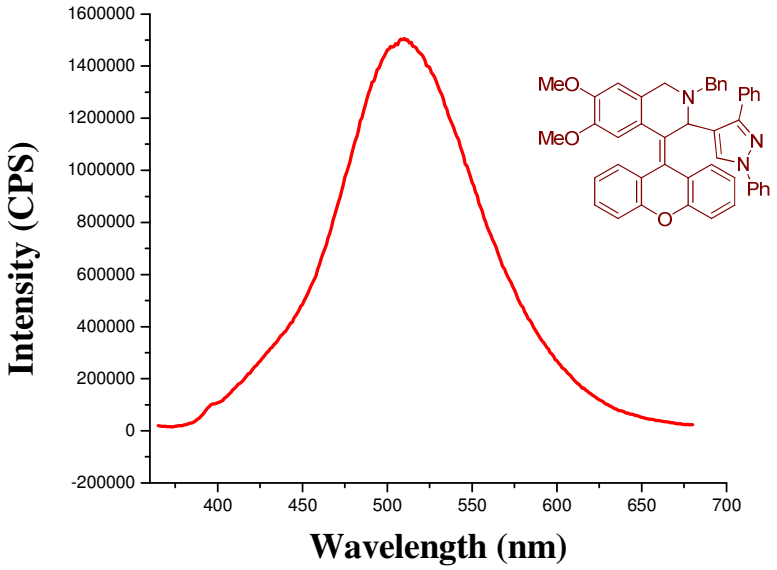
UV-Visible spectrum (DRS) of compound **5g**



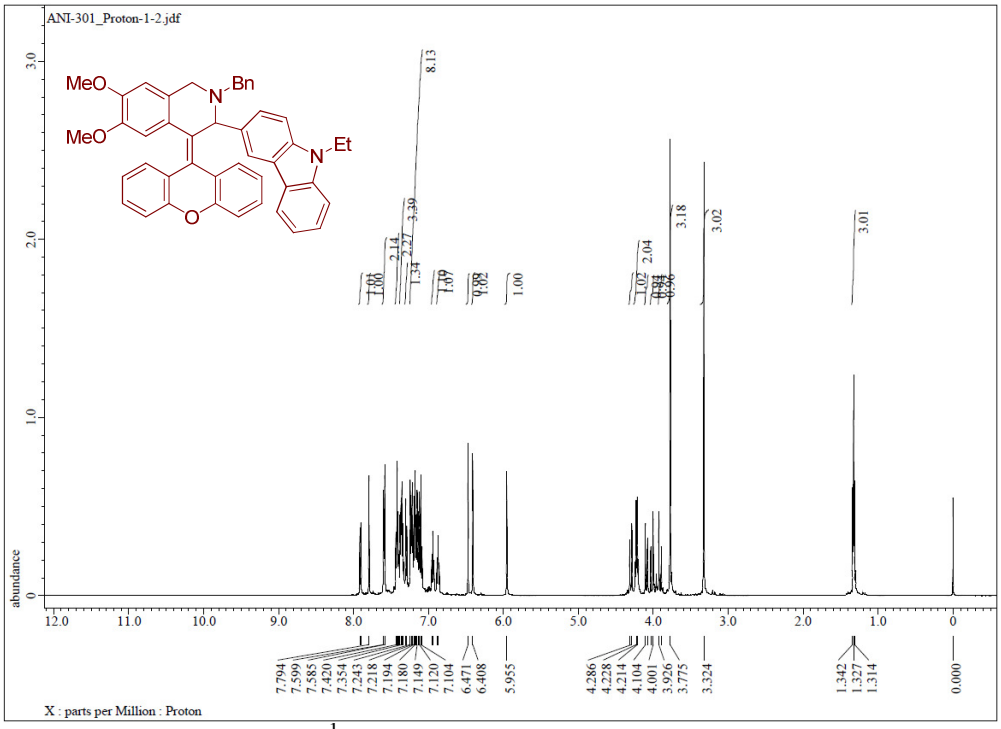
Solid state emission spectrum of compound **5g**



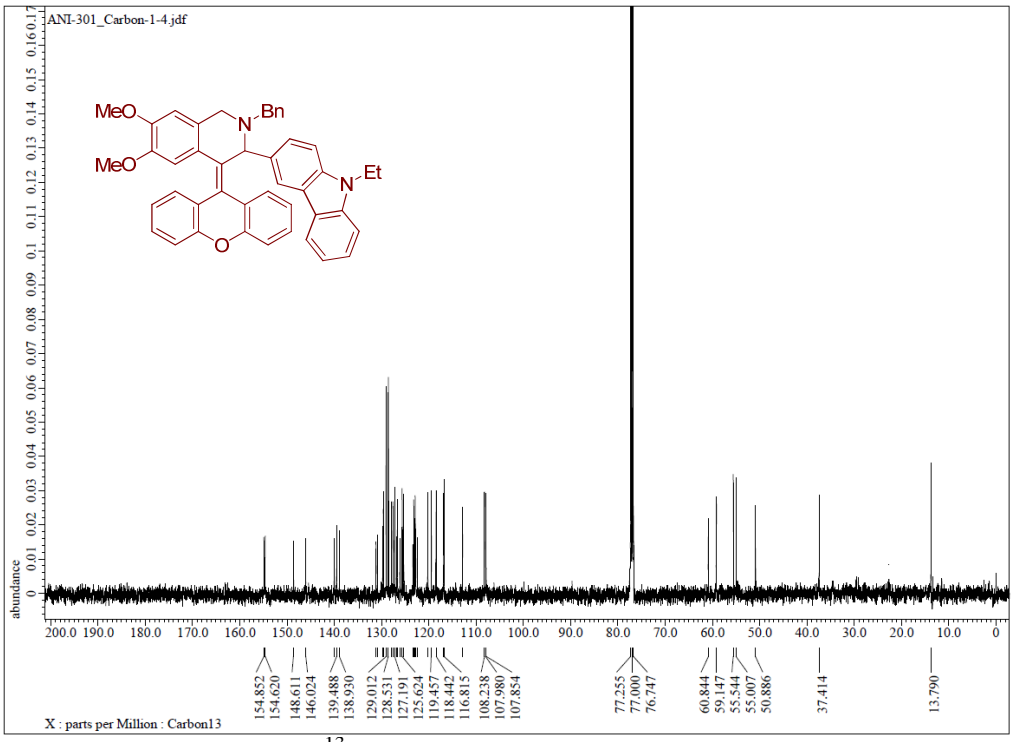
UV-Visible spectrum of **5g** in 99% H_2O/CH_3CN mixture



Emission spectrum of **5g** in 99% H_2O/CH_3CN mixture



^{1}H spectrum of compound **5h**



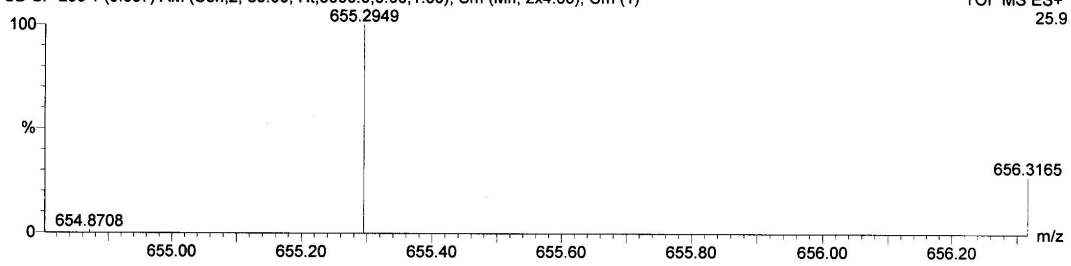
^{13}C spectrum of compound **5h**

Elemental Composition Report **Page 1**

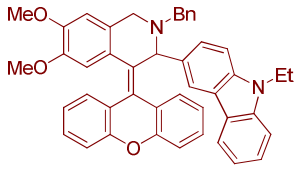
Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

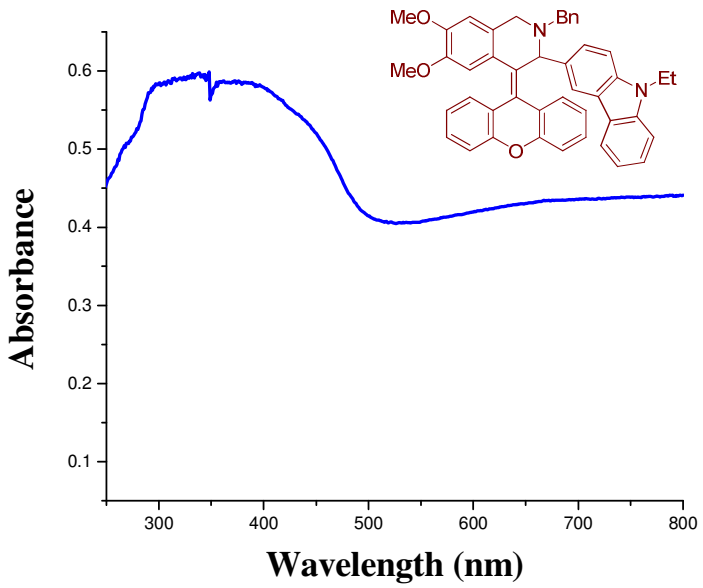
QTOF MICRO DEPARTMENT OF CHEMISTRY IITM 28-Dec-201212:13:41
SB-SP-290 1 (0.037) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x4.00); Cm (1) TOF MS ES+
25.9



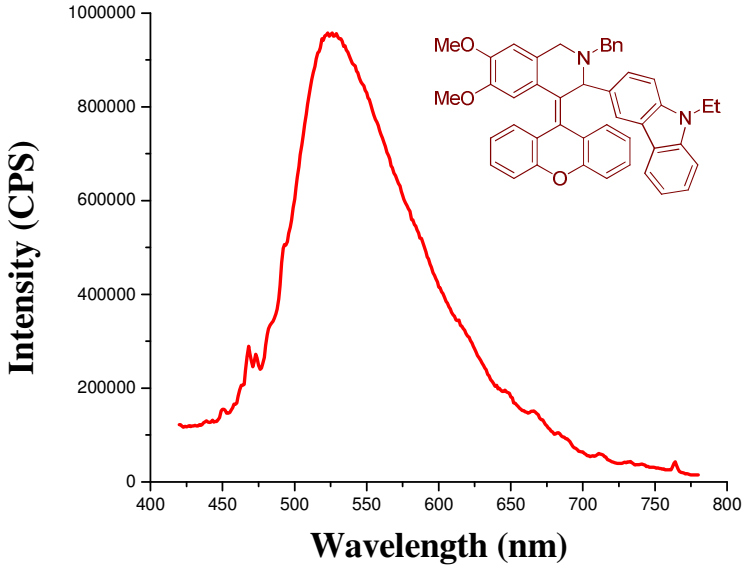
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
655.2949	655.2961	-1.2	-1.8	27.5	1	C45 H39 N2 O3



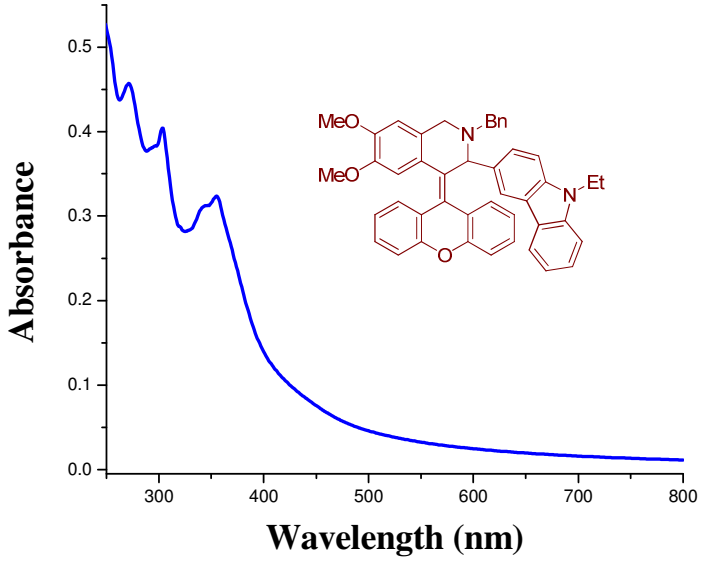
HRMS spectrum of compound **5h**



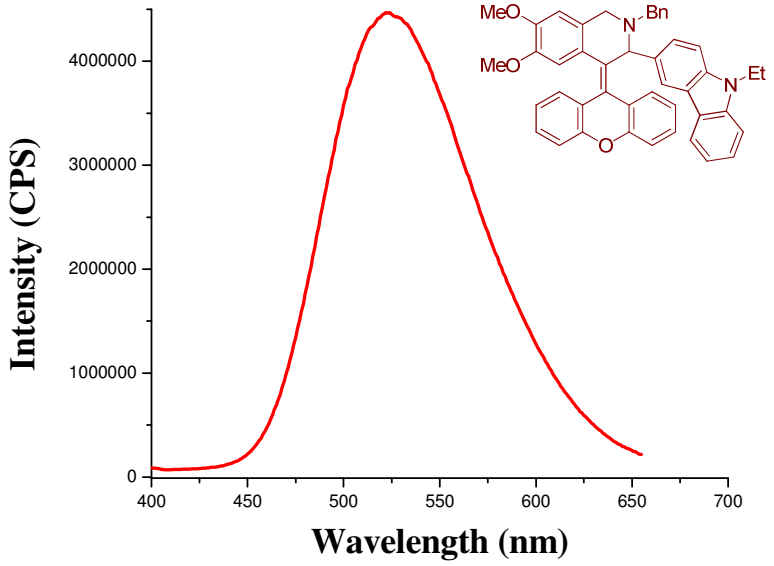
UV-Visible spectrum (DRS) of compound **5h**



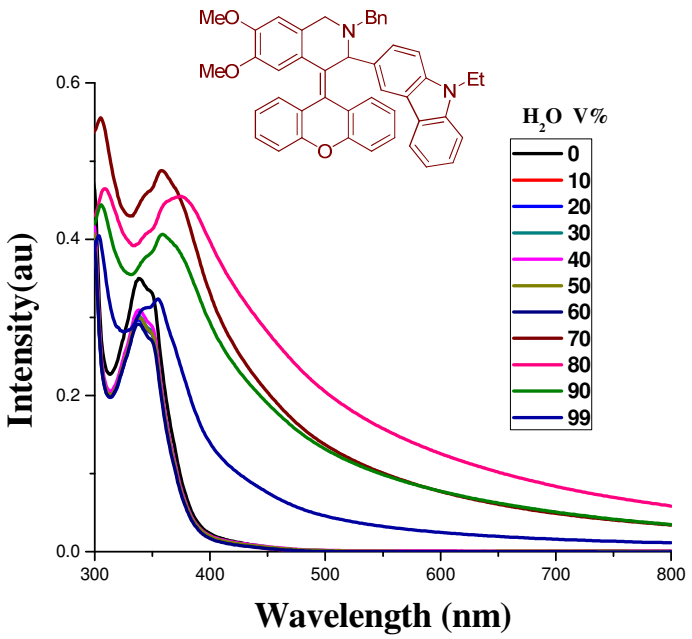
Solid state emission spectrum of compound **5h**



UV-Visible spectrum of **5h** in 99% H_2O/CH_3CN mixture

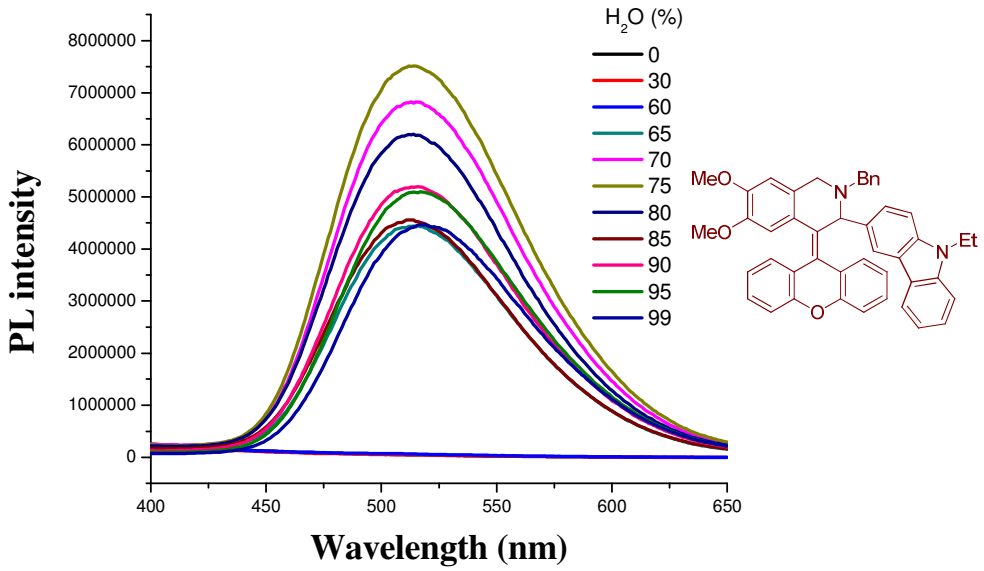


Emission spectrum of **5h** in 99% H_2O/CH_3CN mixture



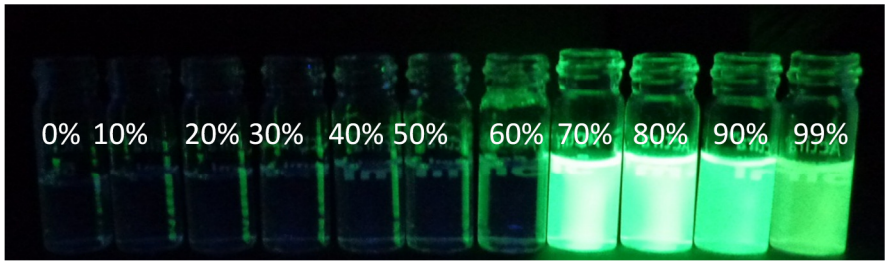
Absorption spectra of **5h** in CH_3CN/H_2O mixtures with different water fraction (f_w),

Concentration (μM): 10.



PL spectra of **5h** in CH_3CN/H_2O mixtures with different water fraction (f_w), Concentration (μM): 10;

excitation wavelength (nm): 350.



Photos of **5h** in CH_3CN/H_2O mixtures (water volume fraction (f_w) = 0-99%) taken under UV luminescent.

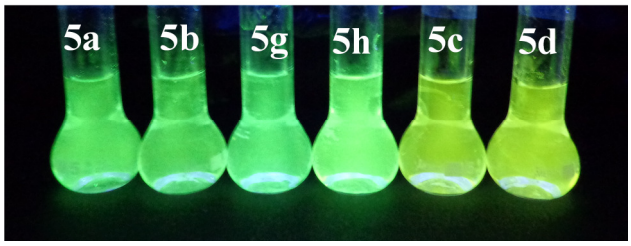


Photo of compounds (**5a-d, 5g-h**) in 99%H_2O/CH_3CN mixture taken under UV luminescent.

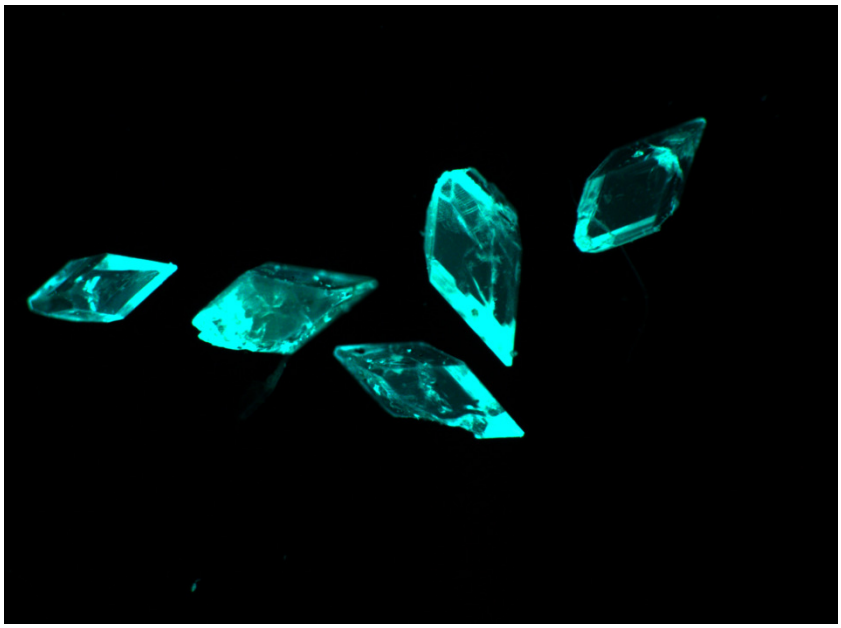
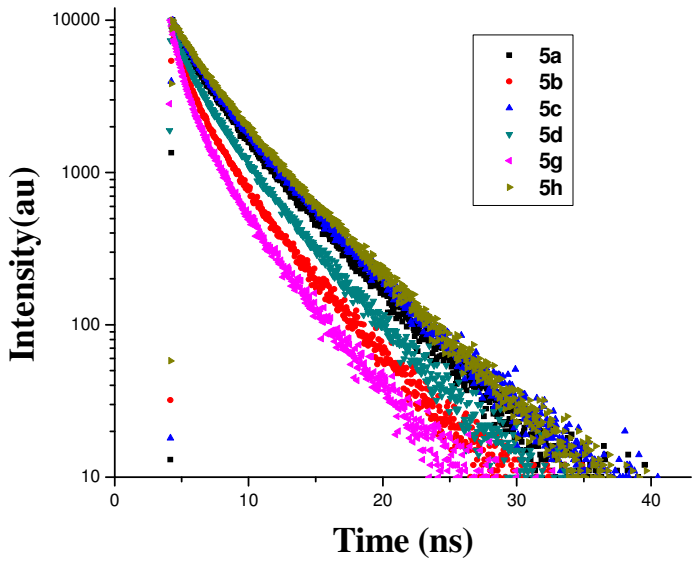
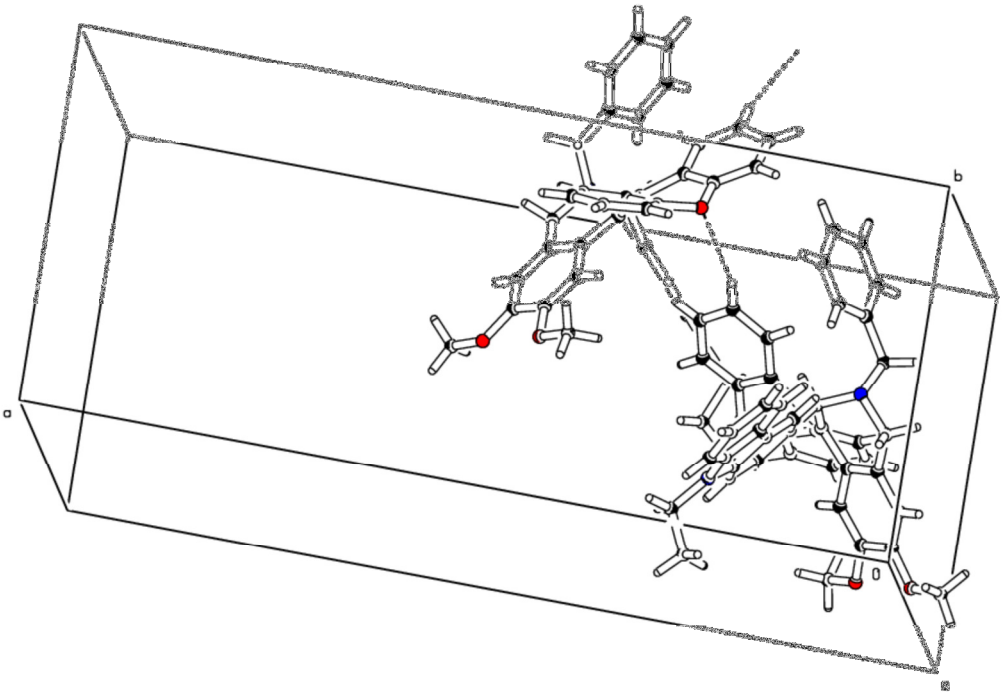


Photo of microscopic image of **5h** in crystal state



Solid state fluorescent life time of compounds (**5a-d, 5g&5h**)



Moecular packing and C-H···O hydrogen bond (dotted ilnes) formed between the adjacent molecules of **5h** in crystal state