Supporting Information

Novel dithieno-benzo-imidazole-based Pb^{2+} sensors: substituent effects on sensitivity and reversibility

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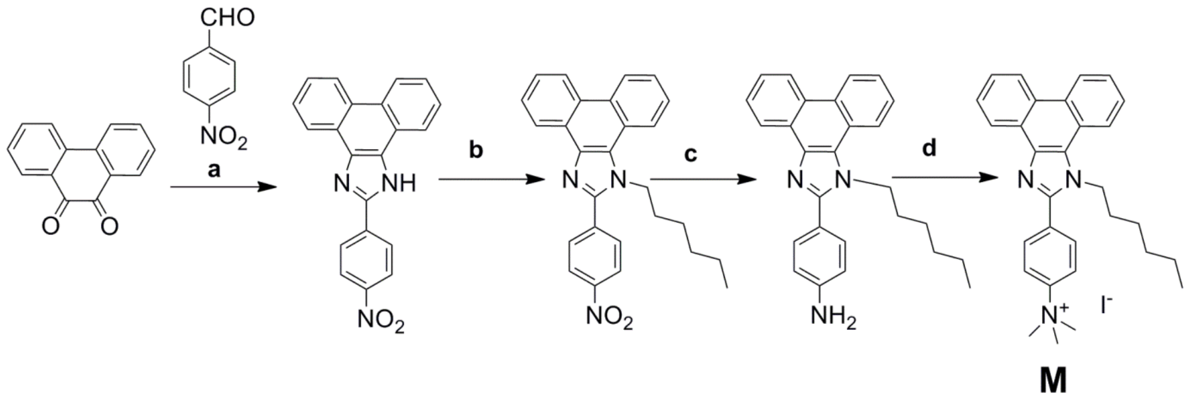
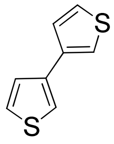
Reagents, measurements and characterizations. All chemicals and solvents were reagent grades and purchased from ACROS, Aldrich, TCI, Fluka, TEDIA, and Lancaster Chemical Co. THF was distilled over sodium/benzophenone to keep anhydrous before use. After distillation over CaH_2, DMF was purified by refluxing with calcium hydride and then distilled. The solvents were degassed by nitrogen 1 h prior to use before reaction. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DX-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometer using $CDCl_3$, D-THF and D_6-DMSO solvents. Elemental analyses were performed on HERAEUS CHN-OS RAPID elemental analyser. A solution of **M1, M2**, and **A2** (1.4×10^{-5} mol/L) were prepared in DMSO and hepes-buffered water (v/v = 1/1) (pH = 7.0). A solution of **A1** (1.4×10^{-3} mol/L) was prepared in THF. This stock solution was further diluted by THF and hepes-buffered water (v/v = 1/1) to afford a final concentration of sample solution 1.4×10^{-5} mol/L (pH = 7.0). The solutions of metal ions (1.4×10^{-3} mol/L) were prepared in DI water. The solutions of **M1**, **M2**, **A1** and **A2** (3.0 mL) were placed in a quartz cell (10.0 mm width) and the fluorescence as well as absorption spectra were recorded. Metal ion sensing experiments were carried out by taking following metal ions as their nitrate salts ($NaNO_3$, KNO_3, $Mg(NO_3)_2\cdot6H_2O$, $Ca(NO_3)_2\cdot4H_2O$, $Ba(NO_3).XH_2O$, $AgNO_3$, $Co(NO_3)_2\cdot6H_2O$, $Ni(NO_3)_2\cdot6H_2O$, $Zn(NO_3)_2\cdot6H_2O$, $Cu(NO_3)_2\cdot3H_2O$, $Pb(NO_3)_2$. Reversibility tests were performed by taking the sodium salts for the desired anions. Anion sensing titrations of compound **4** were tested by taking tetrabutylammonium salts as the desired anions.



Scheme S1 *Reagents and conditions*: (a) NH_4OAc, AcOH, 100°C, overnight; (b) 1-iodohexane, K_2CO_3, DMF, 95°C, overnight, (81.3%); (c) Pd/C, hydrazine monohydrate, reflux, 4 h, 88.1%; (d) iodomethane, THF, reflux, 2 h, 91.3%;

Experimental Section

3,3'Bithiophene (2):

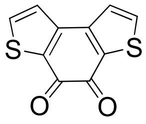


2

3-Bromothiophene (0.122 mole, 20 gm) was dissolved in 100 ml anhydrous diethyl ether. The solution was cooled to -78°C. To it 2.5 molar n-BuLi in hexane (0.122 mole , 48.8 ml) was added dropwise for 40 mins under N_2. The reaction was allowed to stir for 10 mins at -78°C and 20 mins at -60°C. Then, $CuCl_2$ (0.130 mole, 17.42 gm) was added in one portion at -60°C. The reaction was carefully maintained at -60°C for another 1 h. Then, the reaction mixture was slowly warmed to room temperature and continued stirring for another 18 h at room temperature. The reaction mixture was quenched by 30 ml water and filtered to remove inorganic impurity. The organic phase was collected and dried in $MgSO_4$. Solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using hexane as an eluent. Product was obtained as white solids (7.9 gm, 77.9%). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38 (m, 2H), 7.35 (m, 4H). ^{13}C NMR (75

MHz, $CDCl_3$): δ (ppm) 137.0, 126.1, 125.8, 119.6; EI-MS (m/z): Calcd for $C_8H_6S_2$, 165.99; Found 166 (M^+). ^{1}H and ^{13}C NMR spectra were in agreement with the reported literature.[1]

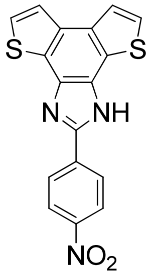
Benzo[1,2-b:4,3-b$^/$]dithiophene-4,5-quinone (3):



3

3,3' Bithiophene (7 gm, 42.10 mmole) was dissolved in 100 ml of 1,2- dichloroethane. To it oxalyl chloride (3 ml , 34.94 mmole) was added slowly, and the solution was turned to orange. The reaction mix was allowed to stir at 90°C for 4 days. The reaction mix was cooled and kept at 0°C overnight. Then, the mixture was filtered. Residue product was washed thoroughly by hexane. After drying, the product obtained was red solids (6 gm, 64.65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.83 (d, 2H, 4.8 Hz), 7.29 (d, 2H, 4.8 Hz). ^{1}H NMR (D_6-DMSO): δ 8.23 (d, 2H, 4.8 Hz), 7.69 (d, 2H, 4.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 173.5, 142.1, 138.2, 134.9, 124.5. EI-MS (m/z): Calcd for $C_{10}H_4O_2S_2$, 219.97; Found 220 (M^+). ^{1}H and ^{13}C NMR spectra were in agreement with the reported literature.[2]

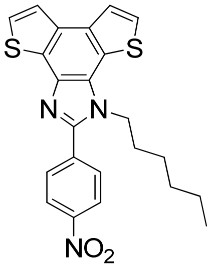
2-(4-Nitrophenyl)-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazole (4):



4

A mixture of 4-nitrobenzaldehyde (2.8 gm, 18.52 mmole), benzo[1,2-b:4,3-b']dithiophene-4,5-quinone (3.7 gm, 16.84 mmole), ammonium acetate (40.64 gm, 527.8 mmole) and acetic acid (150 ml) was heated to 100°C overnight. The green solution was cooled to room temperature, and 50ml water was added to stir for 15 mins at room temperature. The solution was filtered in a Buchner funnel. The red residue was washed thoroughly in water and hexane, dried and taken to the next step without further purification. ^{1}H NMR (D$_6$-DMSO, 300 MHz) δ ppm 13.98 (s, 1H), 8.44 (d, 2H, 9Hz), 8.36 (d, 4H, 8.7Hz), 8.02 (d, 1H, 5.1 Hz), 7.81 (d, 1H, 5.1 Hz). EI-MS (m/z): Calcd for $C_{17}H_9N_3O_2S_2$, 351.01; Found 351 (M^+).

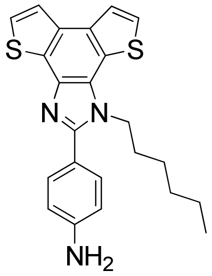
1-Hexyl-2-(4-nitrophenyl)-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazole (5):



5

To a solution of **4** (4.8 gm, 13.65 mmole) in DMF (50 ml), K_2CO_3 (4.54 gm, 32.89 mmole) was added and heated to 95°C for 3 h and then cooled to room temperature. To it 1-iodohexane (2.61 ml, 3.76 gm, 17.73 mmole) was added slowly. Reaction mixture was heated to 95°C overnight. After cooling to room temperature the reaction mixture was poured in 300 ml water. Organic phase was extracted by ethyl acetate via repeated washing in water and dried over $MgSO_4$, Then, the solvent was removed under rotary evaporation. A crude product was purified by silica gel column chromatography (EA: Hexane = 5: 95) to give yellow solids (4.79 gm, 80.4%). ^{1}H NMR (CDCl$_3$, 300 MHz) δ ppm 8.42 (d, 2H, 6.9 Hz,), 8.01 (d, 2H, 6.9 Hz,), 7.89 (d, 1H, 5.4 Hz), 7.81 (d, 2H, 5.4 Hz), 7.59 (d, 2H, 5.4 Hz), 7.55 (d, 2H, 5.2 Hz) 4.54 (t, 2H, 7.9 Hz), 1.94 (m, 2H), 1.34-1.24 (m, 6H), 0.84 (t, 3H, 6.6 Hz). ^{13}C NMR (CDCl$_3$, 75 MHz): δ ppm 149.45, 148.52, 137.15, 137.05, 136.11, 133.50, 132.46, 130.68, 129.39, 128.49, 124.95, 124.38, 123.57, 122.98, 121.15, 47.12, 31.51, 31.37, 26.57, 22.88, 14.31. EI-MS (m/z): Calcd for $C_{23}H_{21}N_3O_2S_2$, 435.11; Found 435 (M^+). Anal. Calcd. for $C_{23}H_{21}N_3O_2S_2$: C, 63.42; H, 4.86; N, 9.65. Found: C, 63.39; H, 4.83; N, 9.63.

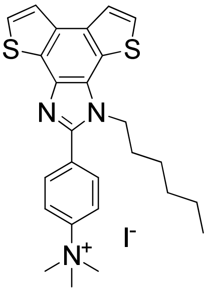
4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)aniline (M1):



M1

A mixture of **5** (2.8 gm, 6.42 mmole) and 50 mg Pd/C (10 %) was dissolved in ethanol and heated to reflux for 20 mins. To it 4.5 ml hydrazine monohydrate was added slowly. The solution mixture was further refluxed for 4 h and filtered. The filtrate was dried and the product was recrystallized to get gray solids (2.33 gm, 89.9%). ^{1}H NMR (D$_6$-DMSO, 300MHz) δ ppm 8.09 (d, 1H, 5.4 Hz), 8.02 (d, 1H, 5.4 Hz), 7.86 (d, 1H, 5.4 Hz), 7.75 (d, 1H, 5.4 Hz), 7.48 (d, 2H, 8.1 Hz), 6.73 (d, 2H, 8.4 Hz), 5.60 (s, broad, 2H) 4.48 (t, 2H, 6.9 Hz), 1.80 (m, 2H), 1.21-1.16 (m, 6H), 0.77 (t, 3H, 6.3 Hz). ^{13}C NMR (D$_6$-DMSO, 75 MHz) δ ppm 154.29, 151.60, 137.15, 136.05, 133.08, 132.47, 131.65, 129.86, 129.18, 128.38, 125.65, 124.78, 121.88, 118.18, 114.96, 47.23, 31.99, 31.88, 26.91, 26.37, 15.20. EI-MS (m/z): Calcd for $C_{23}H_{23}N_3S_2$, 405.13; Found 405 (M$^+$). Anal. Calcd. for $C_{23}H_{23}N_3S_2$: C, 68.11; H, 5.72; N, 10.36. Found C, 68.16; H, 5.77; N, 10.33.

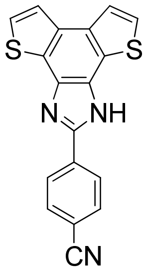
4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)-N,N,N-trimethylbenzenaminium iodide (M2):



M2

M1 (1.7 gm, 4.19 mmole) was dissolved in THF. To it an excess of iodomethane (3 ml) was added dropwise and stirred at 50°C for 24 h. Further, 2ml of iodomethane was added and the reaction was continued for 48 h at 50°C. The reaction was monitored by ESI-MS. The mixture was cooled, filtered, washed with hexane and recrystallized with THF-Et_2O to get white solids (1.47 gm, 61.3%). ^{1}H NMR (D_6-DMSO, 300MHz) δ ppm 8.32 (d, 2H, 4.5 Hz), 8.21 (d, 2H, 7.5 Hz), 7.67 (d, 1H, 9 Hz), 7.50 (d, 1 H, 8.4 Hz), 7.02 (d, 1H, 9.3 Hz), 6.85 (d, 1H, 8.4 Hz), 4.50 (t, 2H, 6.8 Hz), 3.07 (s, 9 H), 1.78-1.72 (m, 2H), 1.21-1.13 (m, 6H), 0.78 (3H, t, 6.4 Hz). ^{13}C NMR (D_6-DMSO, 75 MHz) δ ppm 153.71, 150.16, 137.11, 136.45, 135.31, 133.11, 132.79, 132.60, 131.25, 129.58, 129.35, 127.32, 126.14, 124.47, 124.31, 122.02, 121.12, 54.61, 48.21, 31.56, 31.12, 26.07, 22.69, 14.62. EI-MS (m/z): Calcd for $C_{23}H_{30}IN_3S_2$, 575.09; Found 575 (M^+). Anal. Calcd. for $C_{23}H_{30}IN_3S_2$: C, 54.26; H, 5.25; N, 7.30. Found: C, 54.39; H, 5.19; N, 7.28.

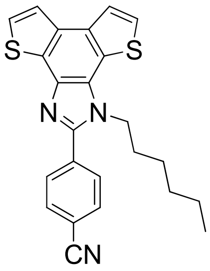
4-(1H-Dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)benzonitrile (6):



6

A mixture of 4-cyanobenzaldehyde (3.2 gm, 24.40 mmole), benzo[1,2-b:4,3-b$^{/}$]dithiophene-4,5-quinone (4.88 gm , 22.18 mmole), ammonium acetate (51.28 gm, 665.40 mmole) and acetic acid (150 ml) was heated to 100°C overnight. The solution was cooled to room temperature, and 50ml water was added to stir for 15 mins at room temperature. The solution was filtered in a Buchner funnel. The green residue was washed thoroughly in water and hexane, dried and taken to the next step without further purification. ^{1}H NMR (D$_6$-DMSO, 300MHz) δ ppm 13.92 (s, 1H), 8.42 (d, 2H, 8.4 Hz), 8.05 (m, 4H), 7.87 (d, 1H, 5.1 Hz), 7.80 (d, 1H, 5.1 Hz). EI-MS (m/z): Calcd for $C_{18}H_9N_3S_2$, 331.02; Found 331 (M^+).

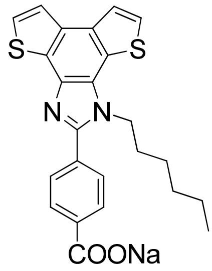
4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)benzonitrile (A1):



A1

To a solution of **6** (5.2 gm, 15.69 mmole) in DMF 50 ml, K_2CO_3 (5.22 gm, 37.81 mmole) was added and heated to 95°C for 3 h, and then cooled to room temperature. To it 1-iodohexane (3.0 ml, 4.32 gm, 20.39 mmole) was added slowly. Reaction mixture was heated to 95°C overnight. After cooling to room temperature, the reaction mixture was poured in 300 ml water. Organic phase was extracted by ethyl acetate via repeated washing in water. Dried over $MgSO_4$, solvent was removed under rotary evaporation. Crude product was purified by silica gel column chromatography (EA:Hexane = 5:95) to give yellow solids (5.37 gm, 82.4%). ^1H NMR ($CDCl_3$, 300 MHz) δ ppm 7.94 (d, 2H, 8.4 Hz), 7.88-7.79 (m, 4H), 7.58 (d, 2H, 5.4 Hz), 7.55 (d, 2H, 5.4 Hz) 4.51 (t, 2H, 7.8 Hz), 1.91 (m, 2H), 1.32-1.23 (m, 6H), 0.84 (t, 3H, 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 149.38, 136.02, 135.26, 133.38, 132.90, 132.38, 130.43, 129.36, 128.34, 127.98, 124.87, 124.26, 123.54, 122.97, 121.17, 118.77, 113.48, 47.00, 31.48, 31.37, 26.54, 22.87, 14.32. EI-MS (m/z): Calcd for $C_{24}H_{21}N_3S_2$, 415.12; Found 415 (M^+). Anal. Calcd. for $C_{24}H_{21}N_3S_2$: C, 69.36; H, 5.09; N, 10.11. Found: C, 69.35; H, 5.07; N, 10.12.

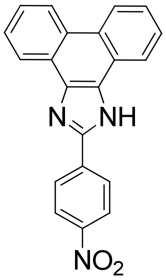
Sodium 4-(1-hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)benzoate (A2):



A2

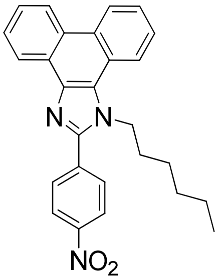
A1 (1.6 gm, 3.85 mmole) was dissolved in ethanol and aqueous NaOH (2 ml, 3 M) was added. The mixture was refluxed for 2 h. After cooling in freezer, the sodium salt was precipitated out. The resulting solution was filtered and the precipitate was dried to afford **A2** as green solids (1.64 gm, 94%). ^1H NMR (D_6-DMSO, 300 MHz) δ ppm 8.15-8.12 (m, 3H), 8.06 (d, 1H, 5.4 Hz), 7.97-7.91 (m, 3H), 7.80 (d, 1H, 5.4 Hz), 4.55 (t, 2H, 7.2 Hz), 1.80 (m, 2H), 1.27-1.19 (m, 6H), 0.77 (t, 3H, 7.3 Hz). ^{13}C NMR (D_6-DMSO, 300 MHz) δ ppm 170.78, 152.22, 136.49, 135.62, 134.19, 133.22, 131.41, 131.19, 130.61, 129.91, 129.71, 129.20, 126.89, 126.50, 125.15, 122.17, 47.57, 32.15, 32.17, 26.31, 23.27, 14.96. EI-MS (m/z): Calcd for $C_{24}H_{21}N_2NaO_2S_2$, 456.09; Found 456 (M^+). Anal. Calcd. for $C_{24}H_{21}N_2NaO_2S_2$: C, 63.14; H, 4.64; N, 6.14. Found: C, 62.44; H, 4.96; N, 5.94.

2-(4-Nitrophenyl)-1H-phenanthro[9,10-d]imidazole:



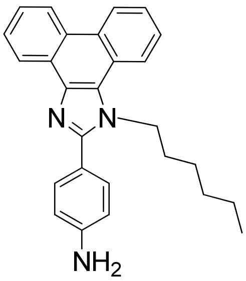
A mixture of 4-nitrobenzaldehyde (2.1 gm, 13.89 mmole), phenanthrene-9,10-dione (2.7 gm, 12.98 mmole), ammonium acetate (30.01 gm, 389.4 mmole) and acetic acid (150 ml) was heated to 100 °C overnight. The green solution was cooled to room temperature, and 50ml water was added to stir for 15 mins at room temperature. The solution was filtered in a Buchner funnel. The red residue was washed thoroughly in water and hexane, dried and taken to the next step without further purification. ^{1}H NMR (D_6-DMSO, 300 MHz) δ ppm 13.78 (s, 1H), 8.87 (d, 2H, 8.1 Hz), 8.58 (d, 2H, 8.4 Hz), 8.55 (d, 2H, 9 Hz), 8.45 (d, 2H, 9 Hz), 7.76 (t, 2H, 7.2 Hz), 7.67 (t, 2H, 7.2 Hz). EI-MS (m/z): Calcd for $C_{21}H_{13}N_3O_2$, 339.10; Found 339 (M^+).

1-Hexyl-2-(4-nitrophenyl)-1H-phenanthro[9,10-d]imidazole:



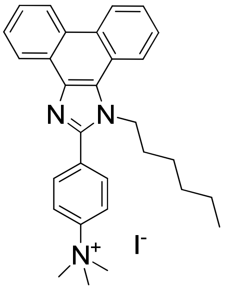
To a solution of 2-(4-nitrophenyl)-1H-phenanthro[9,10-d]imidazole (4.05 gm, 11.93 mmole) in DMF 50ml, K_2CO_3 (5.11 gm, 36.98 mmole) was added and heated to 95 °C for 3 h. Then, it was cooled to room temperature, and 1-iodohexane (2.29 ml, 3.28 gm, 15.50 mmole) was added slowly. Reaction mixture was heated to 95 °C overnight. After cooling to room temperature, the reaction mixture was poured into 300 ml water. Organic phase was extracted by ethyl acetate via repeated washing in water. Dried over $MgSO_4$, the solvent was removed under rotary evaporation. Crude product was purified by silica gel column chromatography (EA: Hexane = 5: 95) to give golden yellow solids (4.1 gm, 81.3%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ ppm 8.84 (d, 1H, 7.6 Hz), 8.76-8.69 (m, 2H), 8.44 (d, 2H, 8.8 Hz), 8.24 (d, 1H, 7.5 Hz), 7.99 (d, 2H, 8.7 Hz), 7.71-7.64 (m, 4H), 4.64 (t, 2H, 7.5 Hz), 1.97-1.92 (m, 2H), 1.24-1.18 (m, 6H), 0.79 (t, 3H, 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ ppm 150.32, 148.38, 138.78, 137.60, 131.11, 129.79, 128.61, 127.78, 127.40, 127.28, 127.16, 126.24, 125.62, 124.85, 124.23, 123.44, 122.80, 121.15, 47.56, 31.30, 30.57, 26.26, 22.69, 14.16. EI-MS (m/z): Calcd for $C_{27}H_{25}N_3O_2$, 423.19; Found 423 (M^+). Anal. Calcd. for $C_{27}H_{25}N_3O_2$: C, 76.57; H, 5.95; N, 9.92. Found: C, 76.51; H, 5.91; N, 9.88.

4-(1-Hexyl-1H-phenanthro[9,10-d]imidazol-2-yl)aniline:



A mixture of 1-hexyl-2-(4-nitrophenyl)-1H-phenanthro[9,10-d]imidazole (2.2 gm, 5.19 mmole) and 47 mg Pd/C (10 %) was dissolved in ethanol and heated to reflux for 20 mins. To it 4.4 ml hydrazine monohydrate was added slowly. The solution mixture was further refluxed for 4 h and filtered. The filtrate was dried and the product was recrystallized to get gray solids (1.79gm, 88.1%). ^{1}H NMR (D_6-DMSO, 300MHz) δ ppm 8.90 (d, 1H, 8.1 Hz), 8.79 (d, 1H, 8.1 Hz), 8.56 (d, 1H, 7.8 Hz), 8.31 (d, 1H, 7.8 Hz), 7.70-7.57 (m, 4H), 7.39 (d, 2H, 8.4 Hz), 6.74 (d, 2H, 8.4 Hz), 5.55 (s, broad, 2H), 4.58 (t, 2H, 6.7 Hz), 1.74-1.68 (m, 2H), 1.05-0.99 (m, 6H), 0.66 (t, 3H, 6.6 Hz). ^{13}C NMR (D_6-DMSO, 75 MHz) δ ppm 154.72, 150.72, 145.67, 137.88, 131.52, 128.71, 127.99, 126.21, 126.15, 125.51, 125.24, 124.28, 123.81, 122.76, 121.69, 118.16, 114.34, 46.97, 31.13, 30.26, 25.92, 22.66, 14.47. EI-MS (m/z): Calcd for $C_{27}H_{27}N3$, 393.22; Found 393 (M^+). Anal. Calcd. for $C_{27}H_{27}N3$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.47; H, 6.88; N, 10.75.

4-(1-Hexyl-1H-phenanthro[9,10-d]imidazol-2-yl)-N,N,N-trimethylbenzenaminium iodide:



M

4-(1-Hexyl-1H-phenanthro[9,10-d]imidazol-2-yl)aniline (1.2 gm, 3.04 mmole) was dissolved in THF. To it an excess of iodomethane (2.5 ml) was added dropwise and stirred at 50°C for 24 h. Further, 2ml of iodomethane was added and the reaction was continued for 48 h. at 50°C. The reaction was monitored by ESI-MS. The mixture was cooled, filtered, washed with hexane and recrystallized with THF-Et_2O to get white solids (0.94 gm, 55.2 %). ^1H NMR (D_6-DMSO, 300MHz) δ ppm 9.01 (d, 1H, 8.6 Hz), 8.94 (d, 1H, 7.8 Hz), 8.56 (d, 1H, 7.5 Hz), 8.46 (d, 1H, 7.6 Hz), 7.87-6.75 (m, 5H), 7.71 (d, 1H, 8.6 Hz), 7.05 (d, 1H, 8.9 Hz), 6.90 (d, 1H, 8.7 Hz), 4.72 (t, 2H, 6.6 Hz), 3.09 (s, 9 H), 1.77-1.71 (m, 2H), 1.37-1.08 (m, 6H), 0.72 (3H, t, 6.3 Hz). ^{13}C NMR (D_6-DMSO, 75 MHz) δ ppm 153.39, 150.68, 145.84, 139.47, 132.98, 132.57, 129.39, 129.28, 129.15, 128.83, 128.04, 125.66, 125.24, 125.01, 122.86, 122.73, 121.58, 121.17, 57.86, 48.29, 31.48, 31.14, 25.96, 22.67, 14.50. EI-MS (m/z): Calcd for $C_{30}H_{34}IN_3$, 563.18; Found 563 (M^+). Anal. Calcd. for $C_{30}H_{34}IN_3$: C, 63.94; H, 6.08; I, 22.52; N, 7.46. Found: C, 63.22; H, 6.78; N, 7.85.

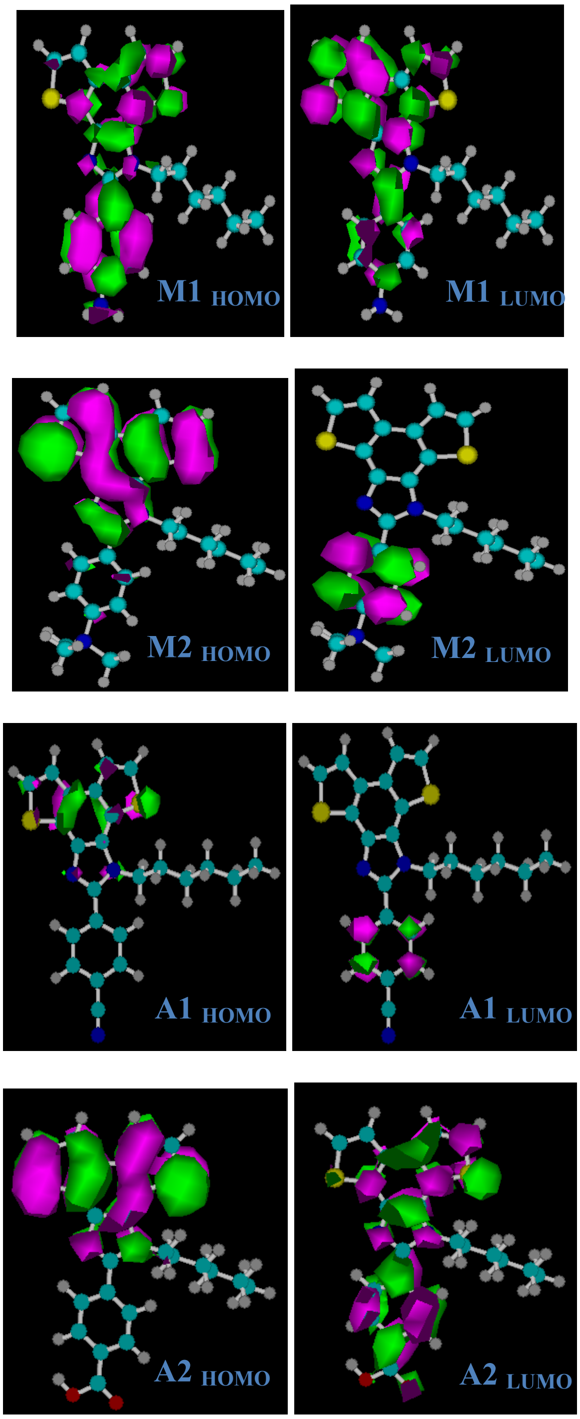


Fig. S1 Computational analysis showing coagulation of HOMO electron clouds in the electron donating part and coagulation of LUMO electron clouds in the electron withdrawing part for compounds **M1, M2**, **A1** and **A2**.

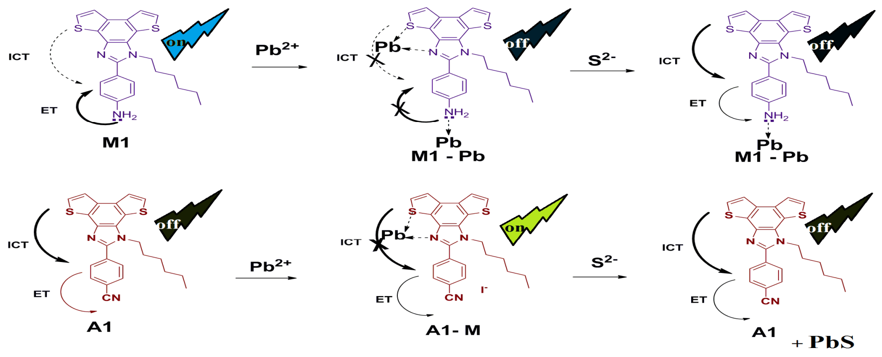


Fig. S2 Schematic representation of the fluorescence on-off-off and off-on-off mechanism for **M1** and **A1**, respectively, as response to Pb^{2+} and S^{2-}.

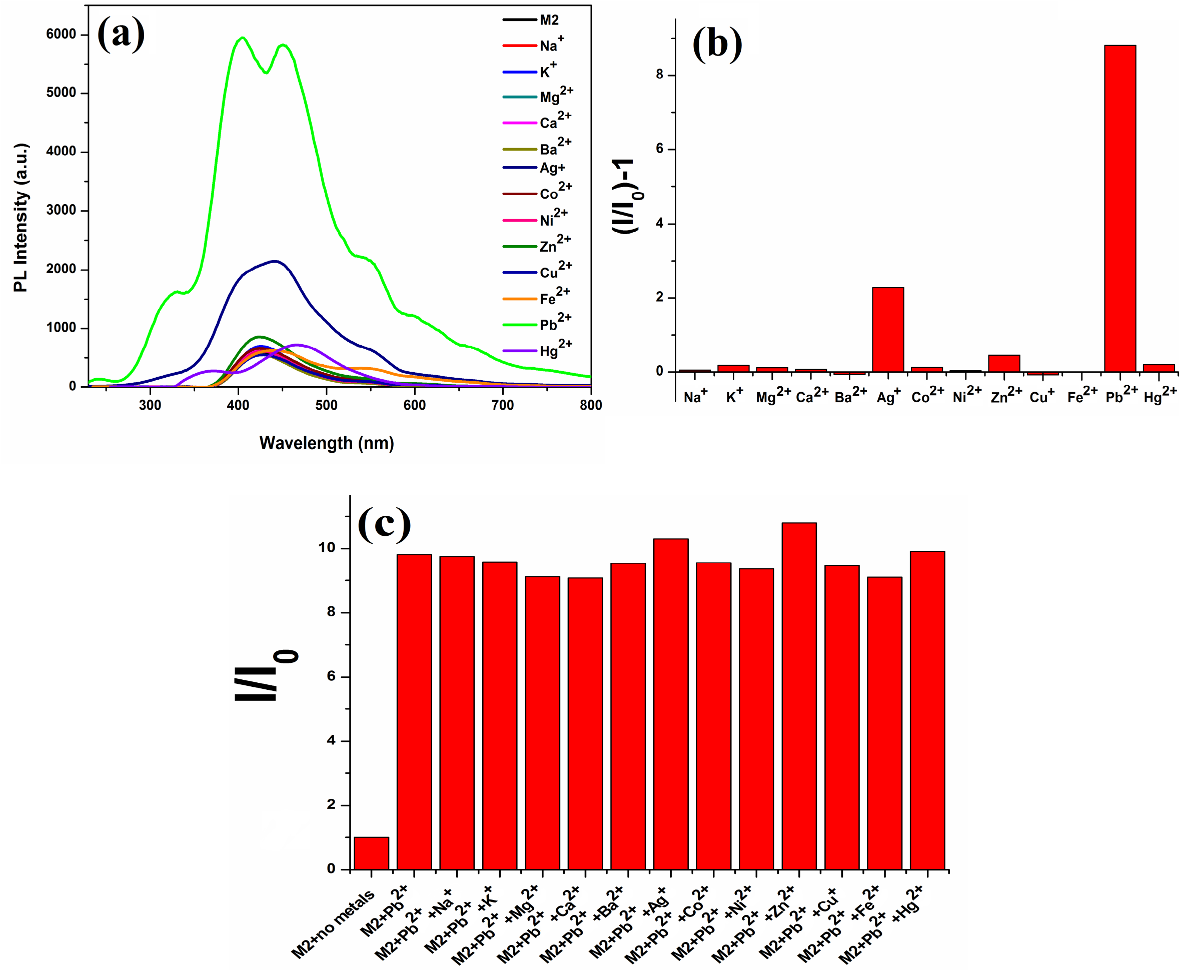


Fig. S3 (a) Fluorescence emission spectra of **M2** (λ_{ex} = 240 nm) upon the addition of various metal ions. The concentration of **M2** (1.4×10^{-5} M) in DMSO/H_2O (1:1), metal ions added (1.5×10^{-3} M) in H_2O. (b) Histogram representing the fluorescence spectral responses of **M2** upon the addition of different metal ions. (c) Histogram representing the emission profiles of **M2** in presence of Pb^{2+} and equivalent amount of other background metal ions (Dual metal system).

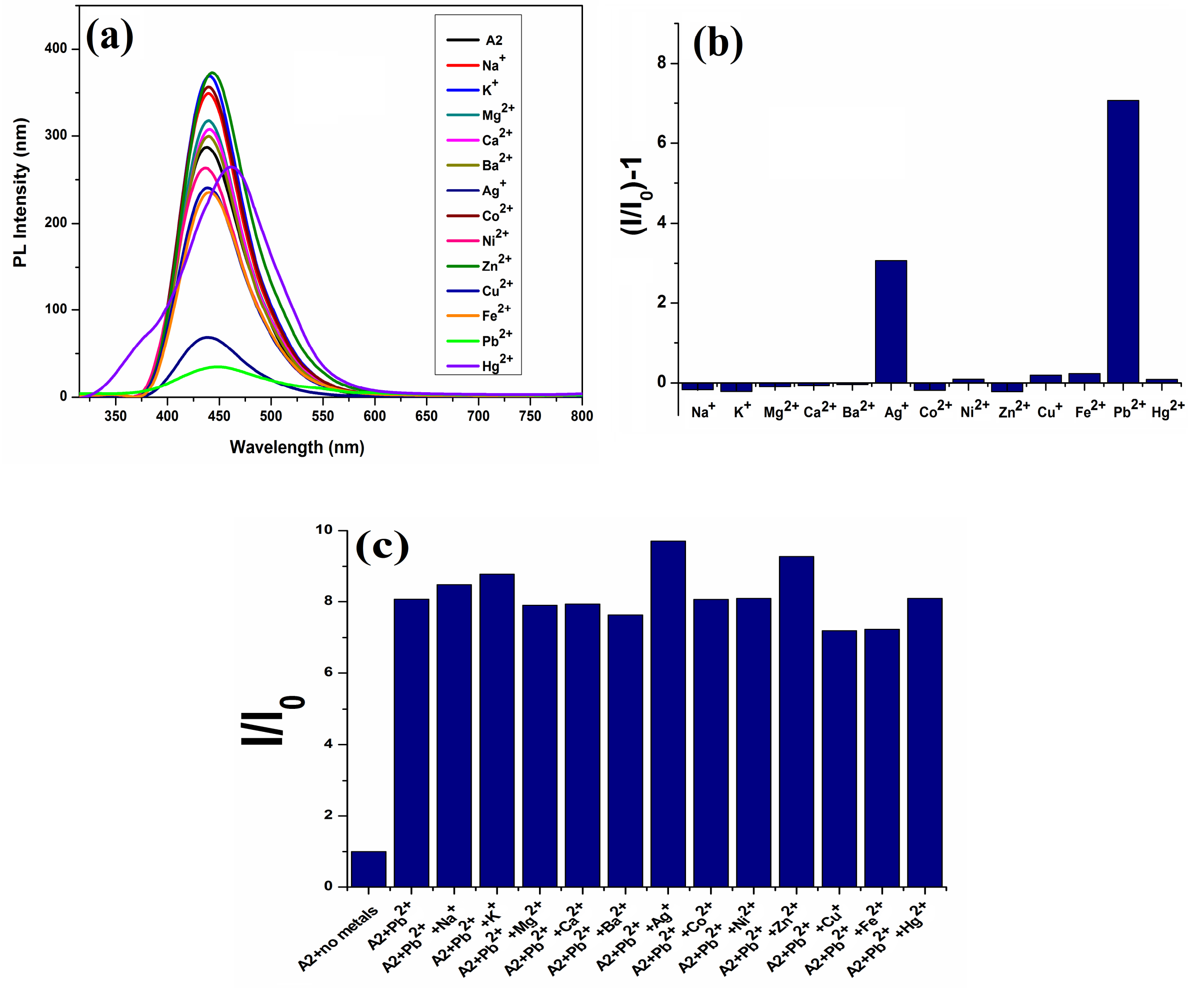


Fig. S4 (a) Fluorescence emission spectra of **A2** (λ_{ex} = 265 nm) upon the addition of various metal ions. The concentration of **A2** (1.4×10^{-5} M) DMSO/H_2O (1:1), metal ions added (1.5×10^{-3} M) in H_2O. (b) Histogram representing the fluorescence spectral responses of **M2** upon the addition of different metal ions. . (c) Histogram representing the emission profiles of **A2** in presence of Pb^{2+} and equivalent amount of other background metal ions (Dual metal system).

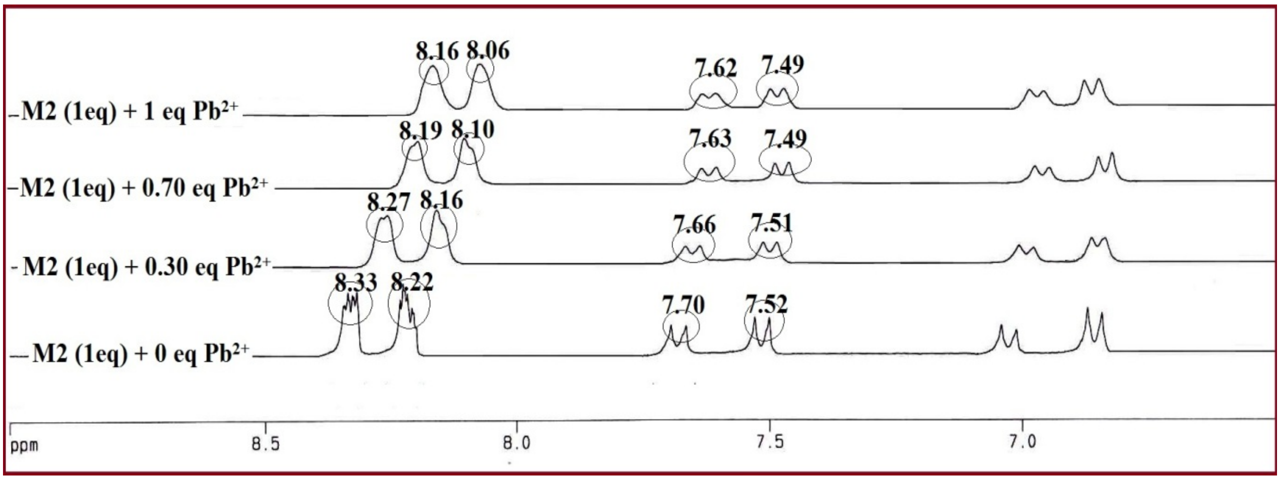


Fig. S5 ^{1}H NMR titration of **M2** upon the addition of 0-1 equiv. of Pb^{2+}.

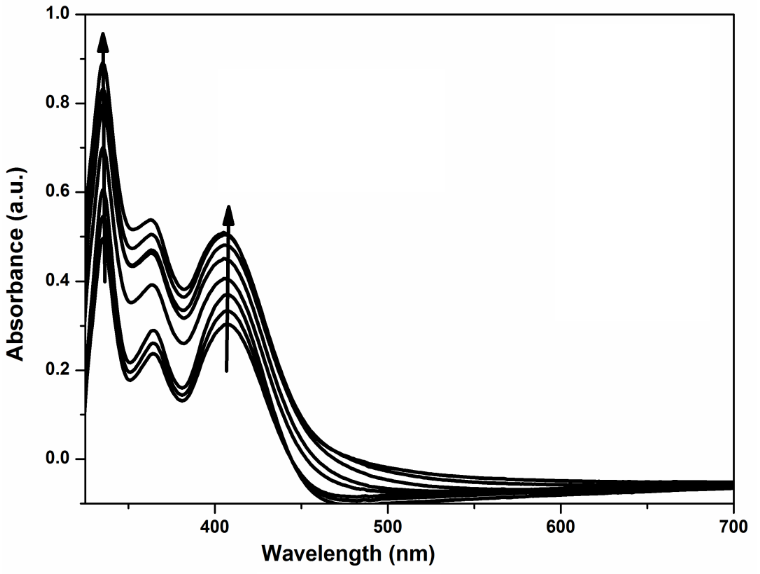


Fig. S6 Absorption spectral titrations of **M2** upon the addition of Pb^{2+} metal ions. The concentration of **M2** (1.4×10^{-5} M) DMSO/H_2O (1:1), Pb^{2+} ions added (1.5×10^{-5} M) in H_2O.

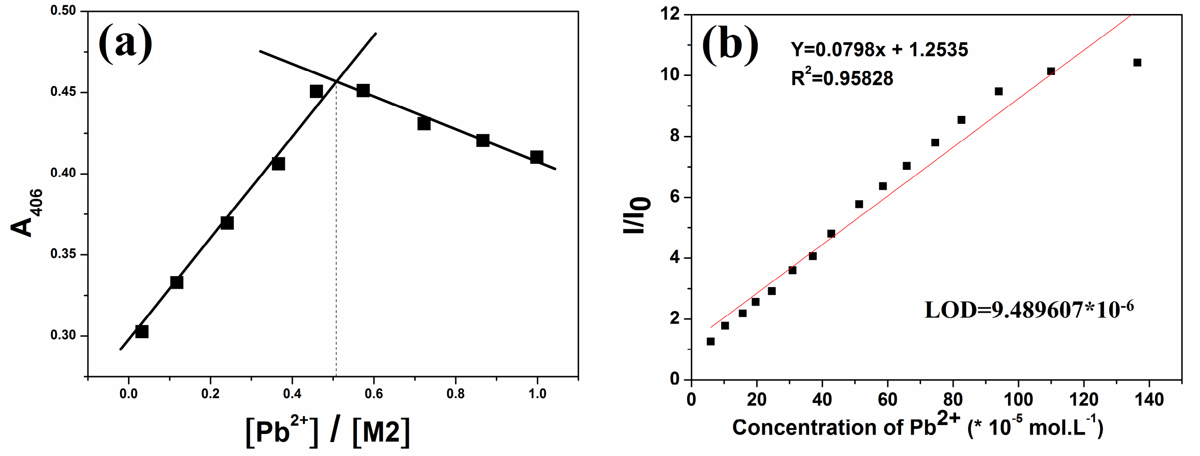


Fig. S7 (a) Job's Plot for **M2** by plotting the variation of the absorption at 406 nm as a function of $[Pb^{2+}]$/[**M2**]. Total concentration of **M2**+Pb^{2+} was kept constant at 14 μM. (b) Calculation of detection limit from the linear fit equation and standard deviation.

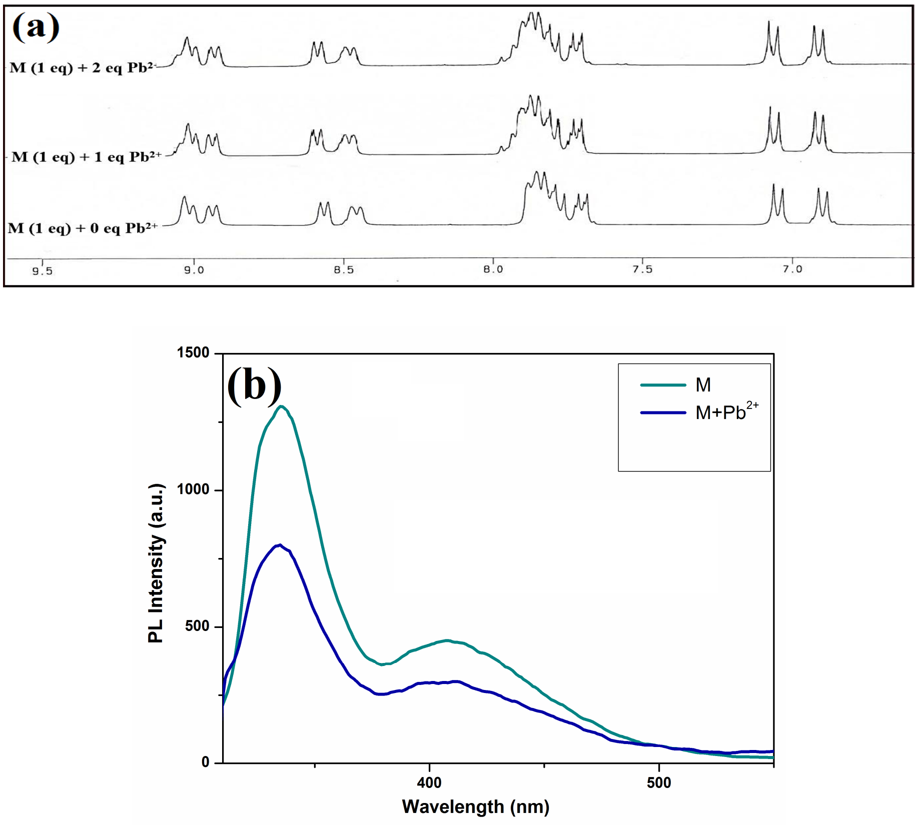


Fig. S8 (a) ^{1}H NMR titration of **M** upon the addition of 0-2 equiv. of Pb^{2+}.(b) Fluorescence spectral changes of **M** (1.4×10^{-5} M) in DMSO/H_2O (1:1) (λ_{ex} = 290 nm) upon the addition of Pb^{2+} (1.5×10^{-3} M) in H_2O.

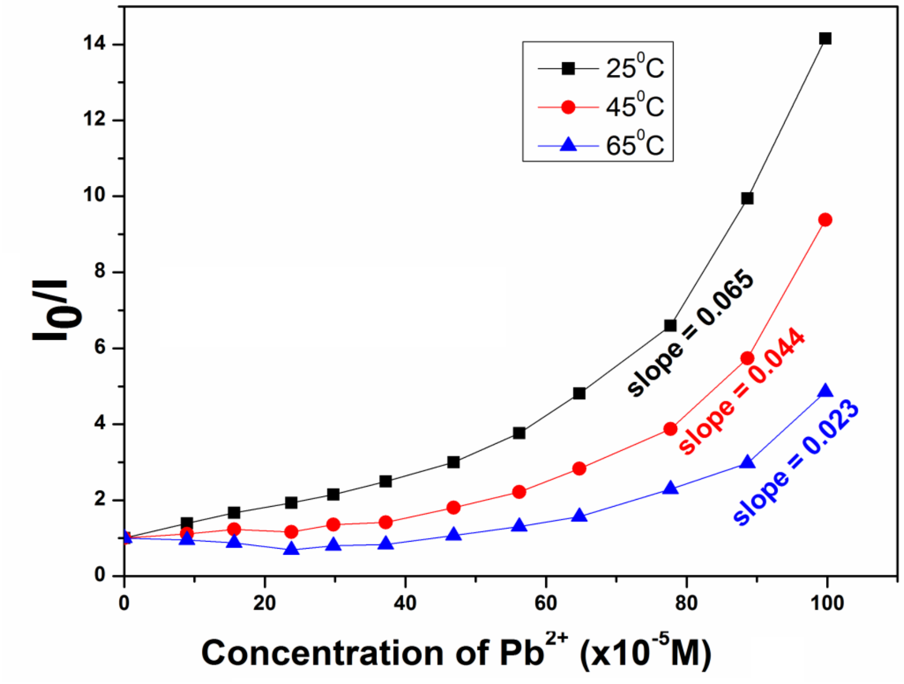


Fig. S9 Stern-Volmer plots for the fluorescence quenching of **A2** by Pb^{2+} at 25°C, 45°C and 65°C.

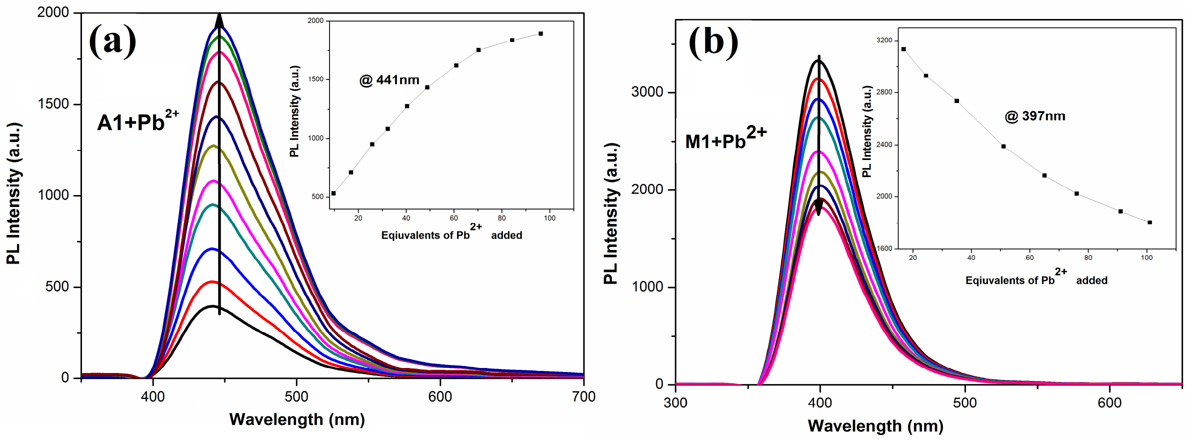


Fig. S10 Fluorescence spectral changes of (a) **A1** (1.4×10^{-5} M) in THF/H_2O (1:1) (λ_{ex} = 240 nm) and (b) **M1** (1.4×0^{-5} M) in DMSO/H_2O (1:1) (λ_{ex} = 245 nm) upon titration with Pb^{2+} (0 - 1.5×10^{-3} M) in H_2O.

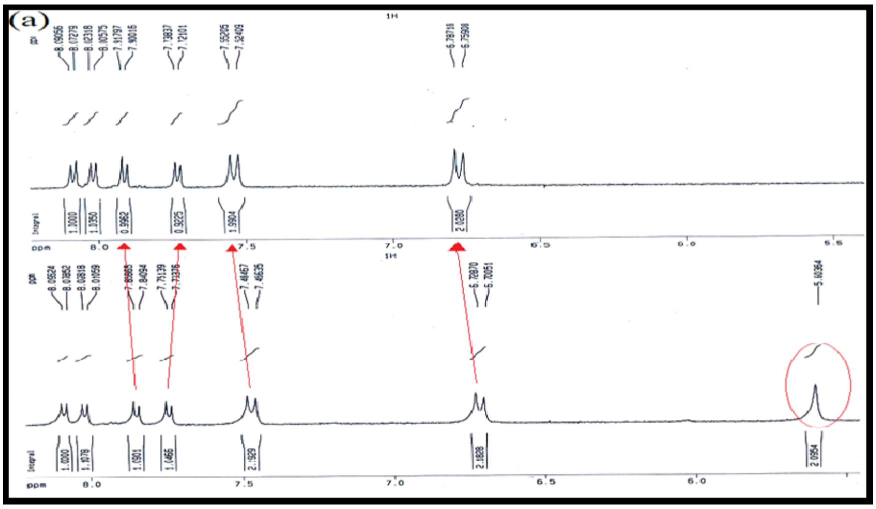


Fig. S11 ^{1}H NMR spectra of **M1** in D_6-DMSO/D_2O=1/1 before (down) and after (up) the addition of 10 equiv. of Pb^{2+} in D_2O.

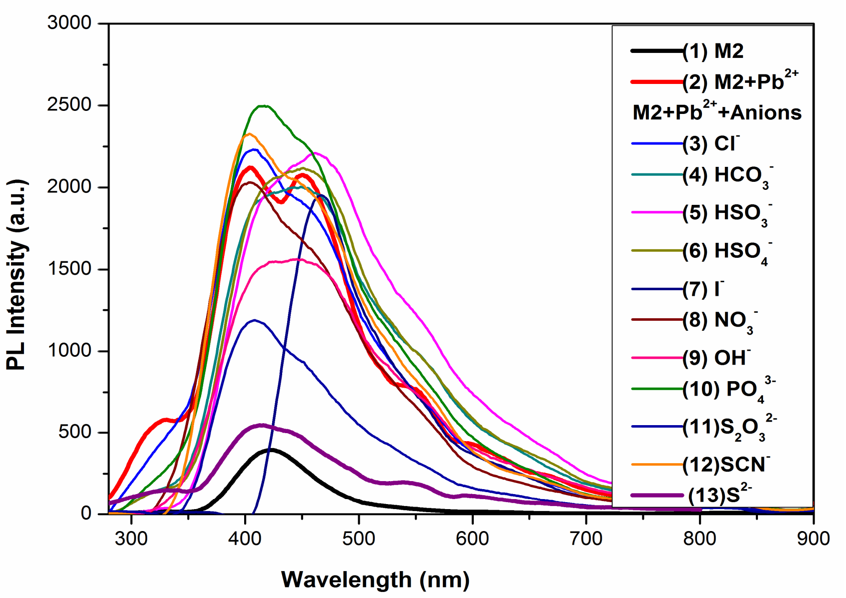


Fig. S12 Fluorescence spectral response of **M2** (1.4×10^{-5} M) in DMSO/H_2O (1:1) (λ_{ex} = 240 nm) upon the addition of S^{2-} (1.4×10^{-6} M) and other anions (1.4×10^{-4} M) in the presence of Pb^{2+} (1.5×10^{-3} M).

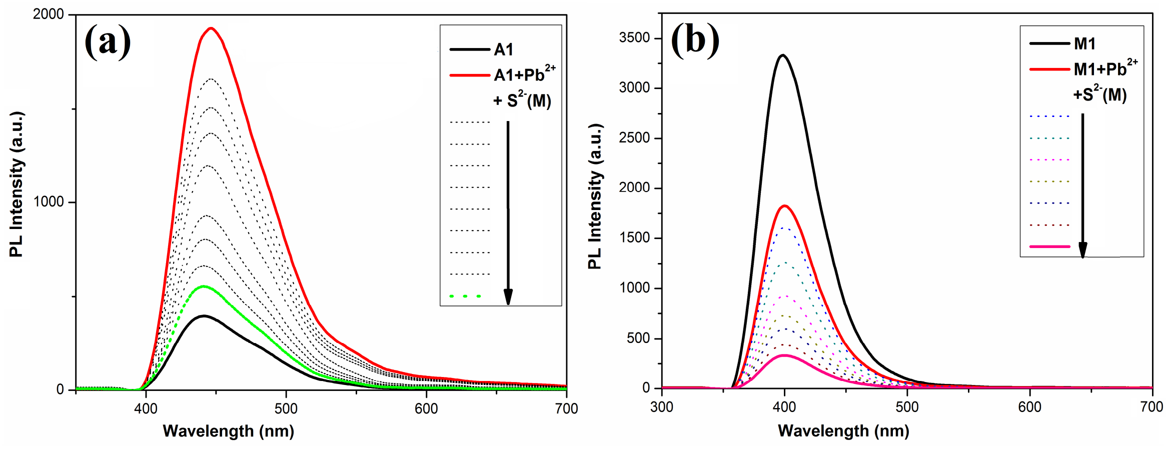


Fig. S13 Fluorescence spectral response of (a) **A1** (1.4×10^{-5} M) in THF/H_2O (1:1) ($\lambda_{ex} = 240$ nm)and (b) **M1** (1.4×10^{-5} M) in DMSO/H_2O (1:1) ($\lambda_{ex} = 245$ nm) upon titration with S^{2-} (0 - 1.4×10^{-6} M) in the presence of Pb^{2+} (1.5×10^{-3} M).

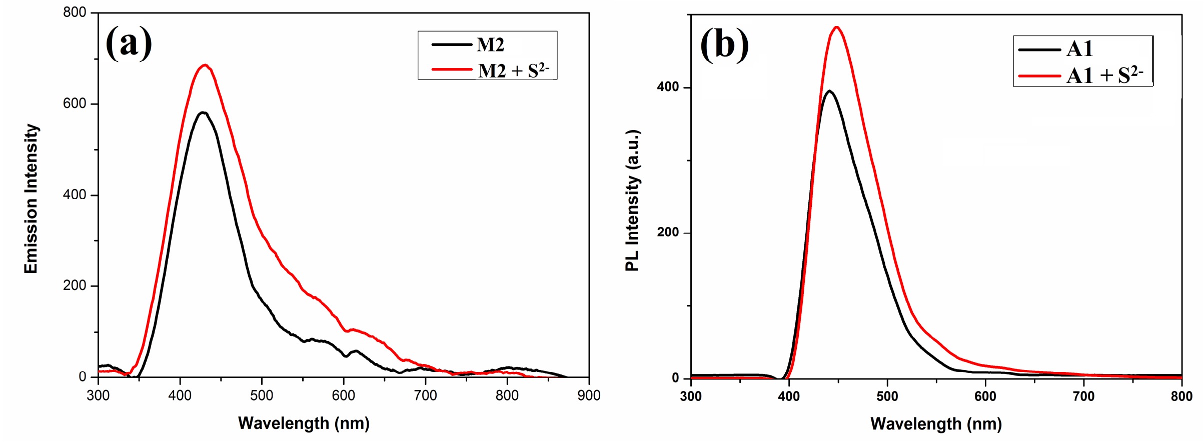


Fig. S14 Fluorescence spectral response of (a) **M2** (1.4×10^{-5} M) in DMSO/H_2O (1:1) ($\lambda_{ex} = 240$ nm) and (b) **A1** (1.4×10^{-5} M) in THF/H_2O (1:1) ($\lambda_{ex} = 240$ nm) upon the addition of S^{2-} (1.4×10^{-5} M) in H_2O.

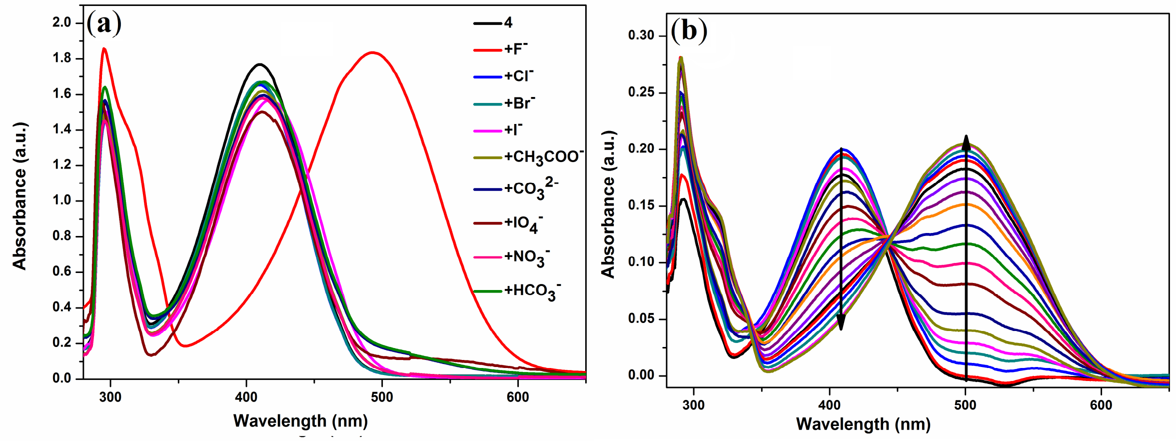
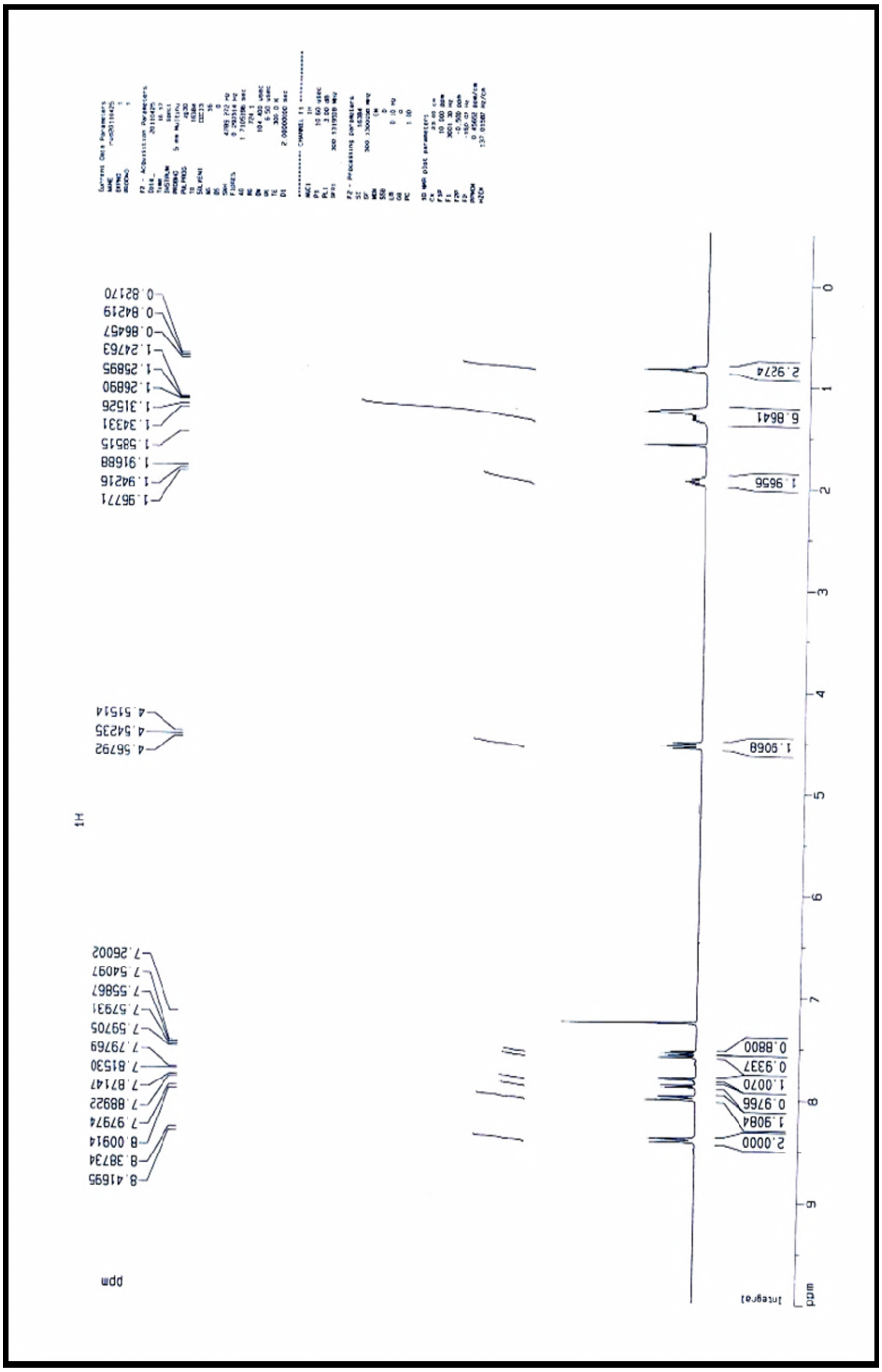
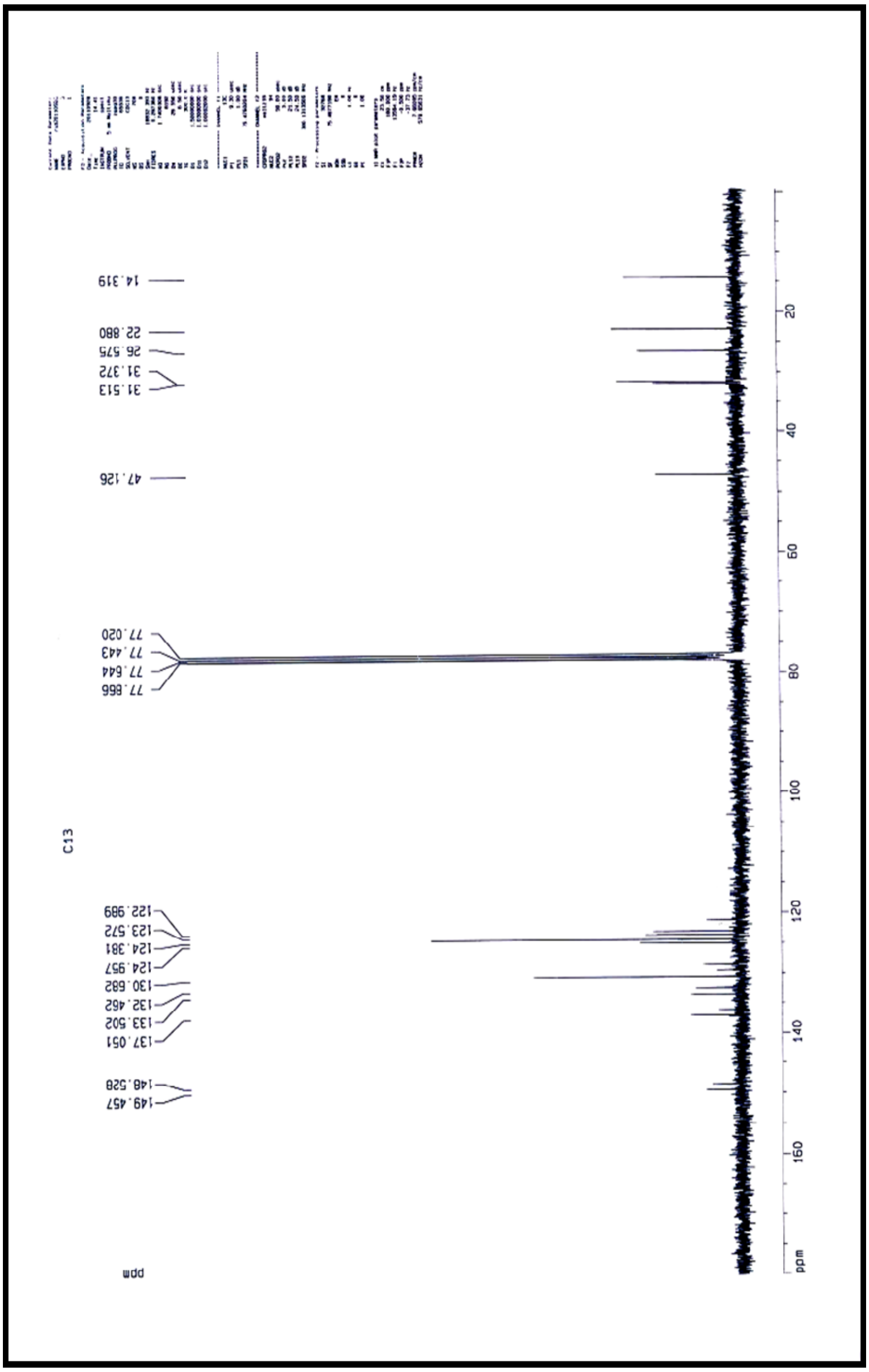


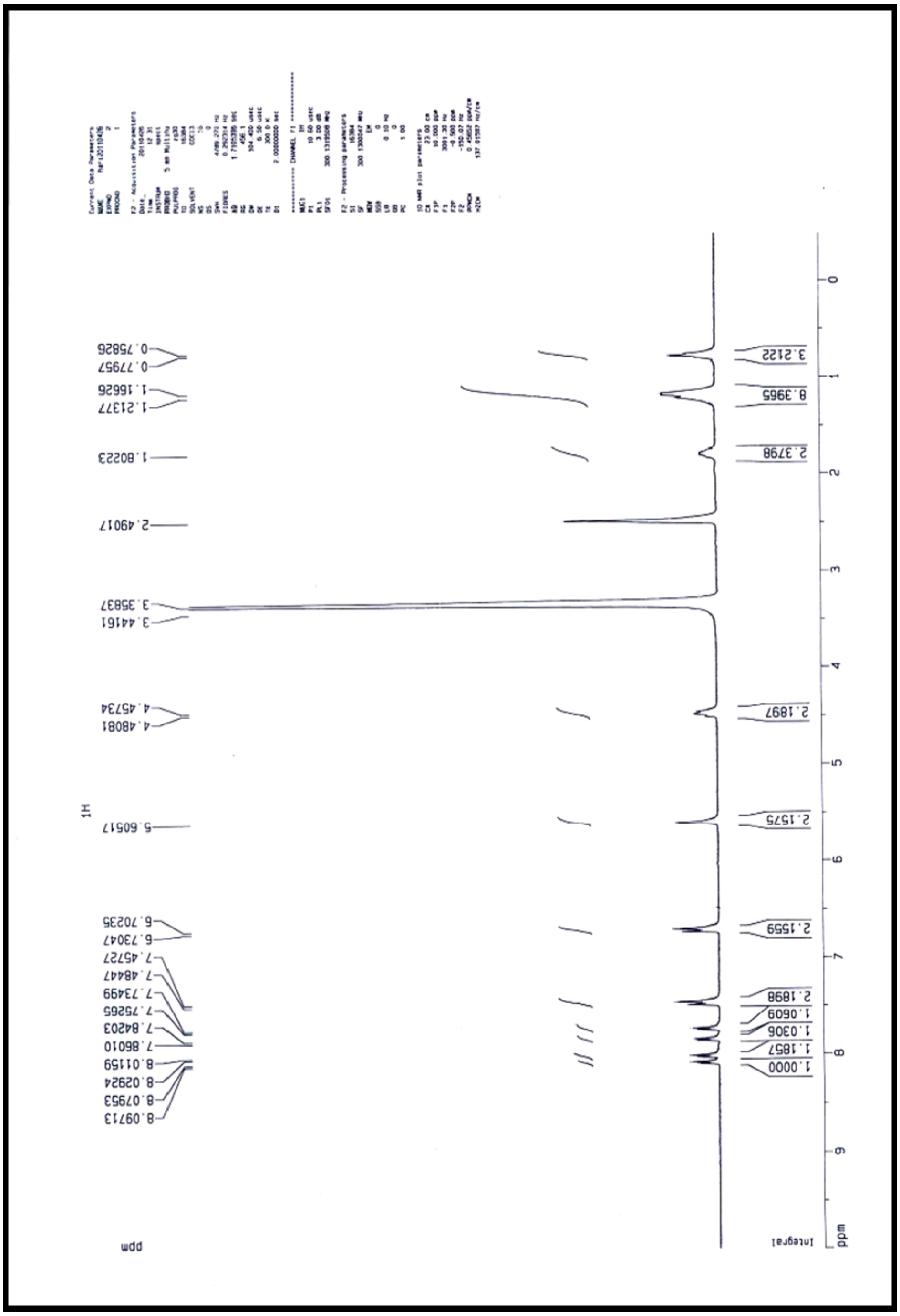
Fig. S15 Absorption spectral response of **4** (1.4×10^{-5} M) (a) upon the addition of 1 equiv. of different anions (b) titration of **4** upon the sequential addition of F^- ions (0 - 1 equiv. w.r.t. **4**).



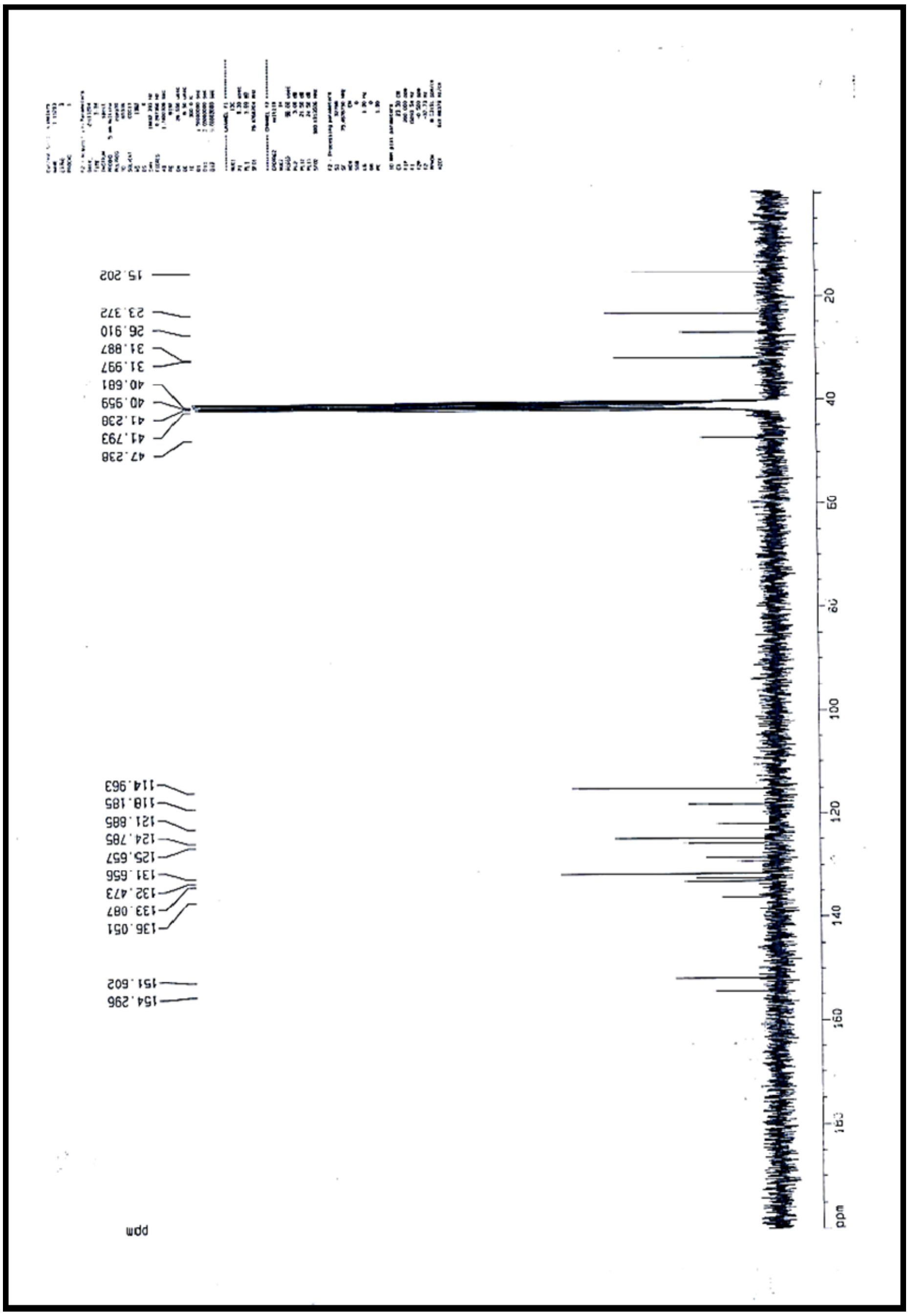
^{1}H-NMR of **1-Hexyl-2-(4-nitrophenyl)-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazole (5)**



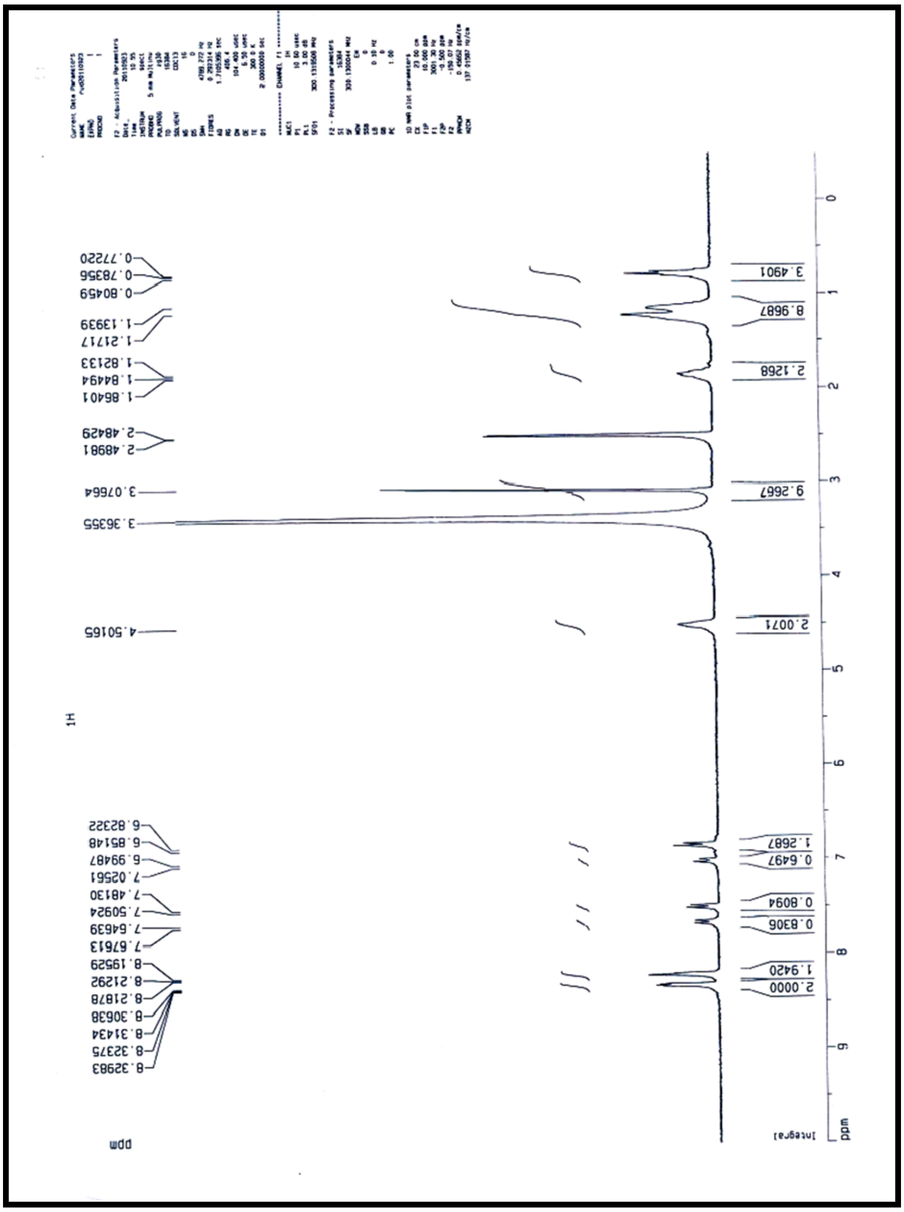
^{13}C-NMR of **1-Hexyl-2-(4-nitrophenyl)-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazole (5)**



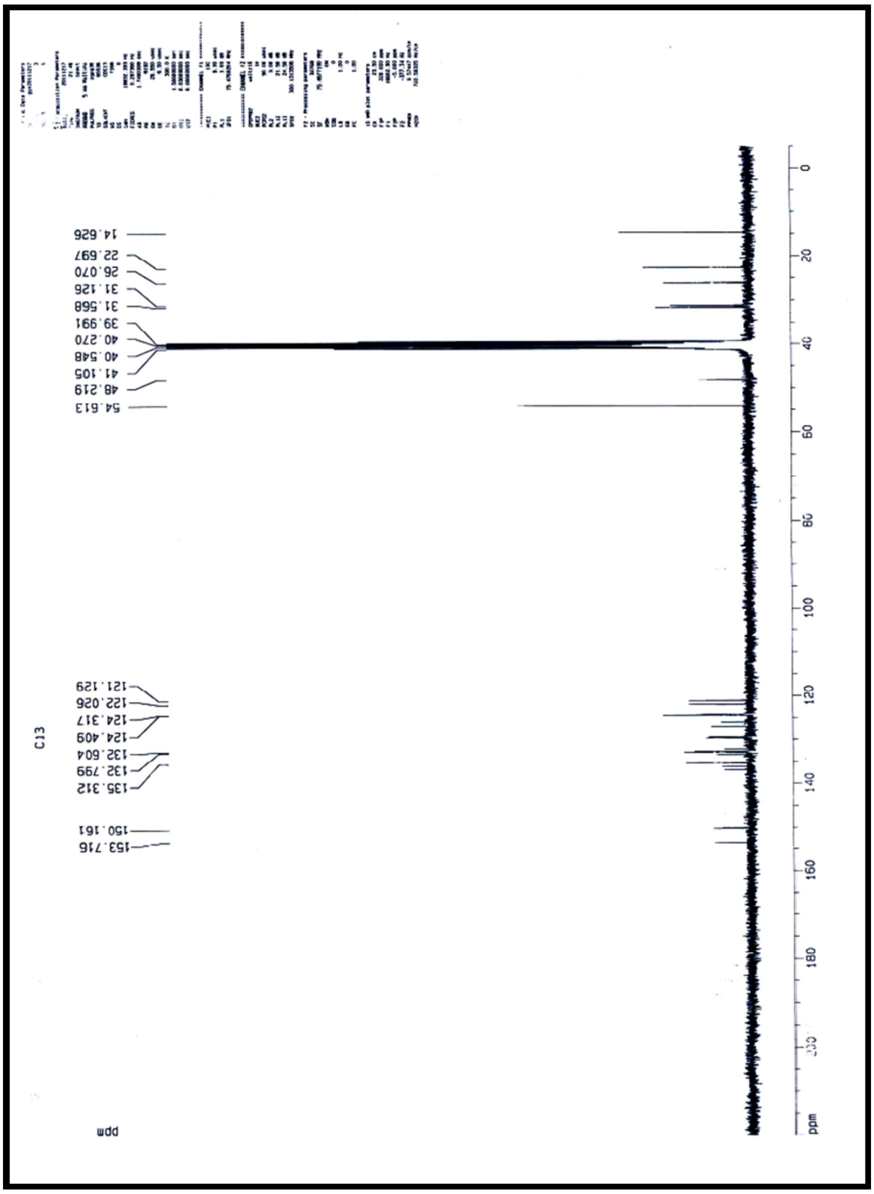
^{1}H-NMR of **4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)aniline (M1)**



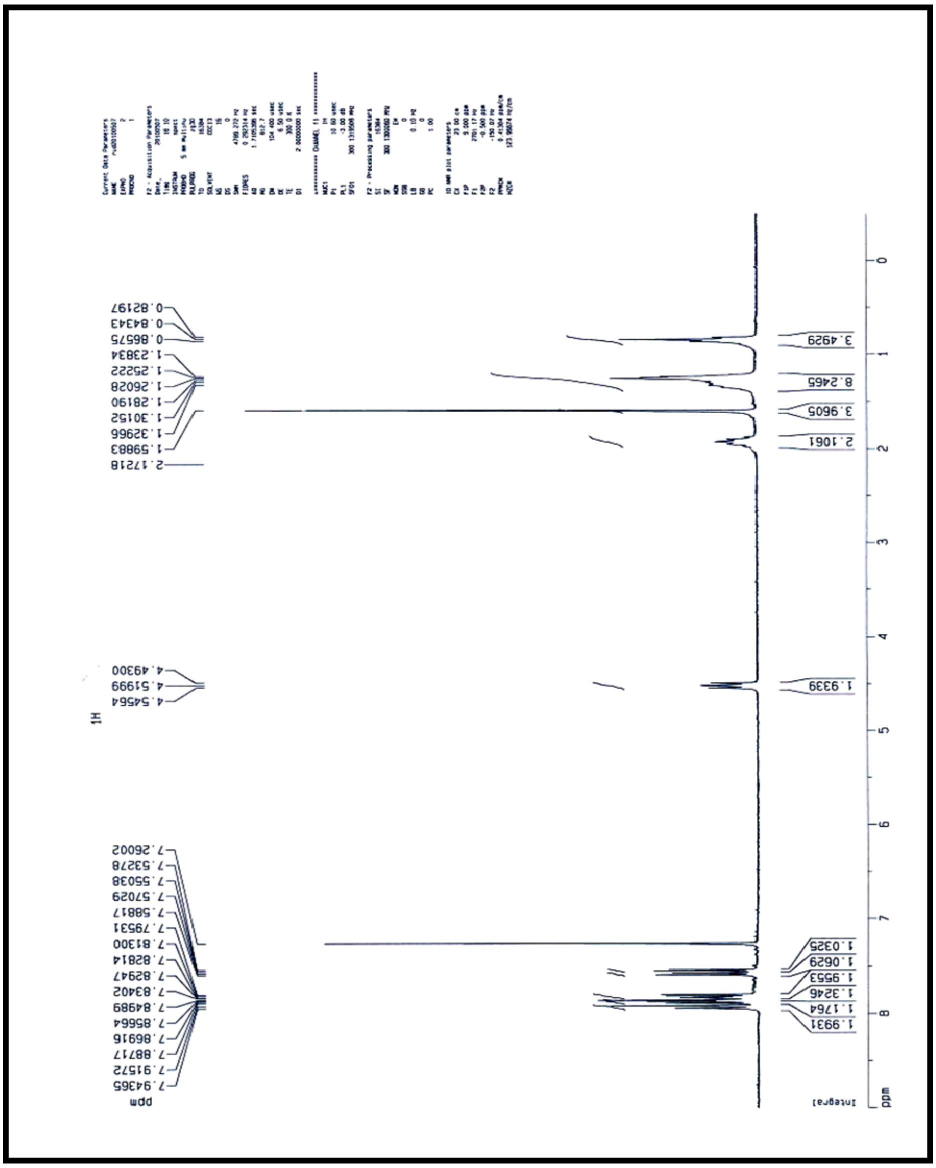
^{13}C-NMR of **4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)aniline (M1)**



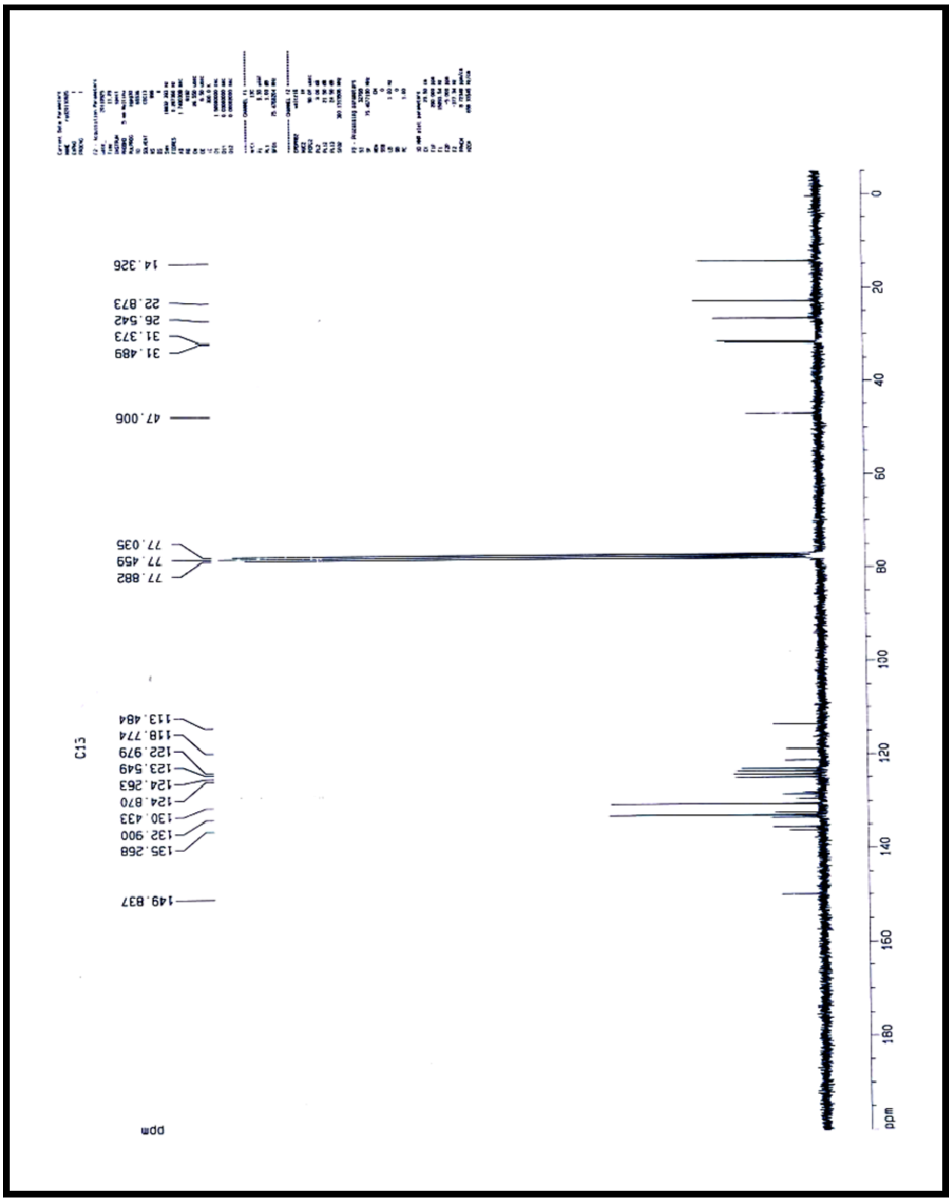
^{1}H-NMR of **4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)-N,N,N-trimethylbenzenaminium iodide (M2)**



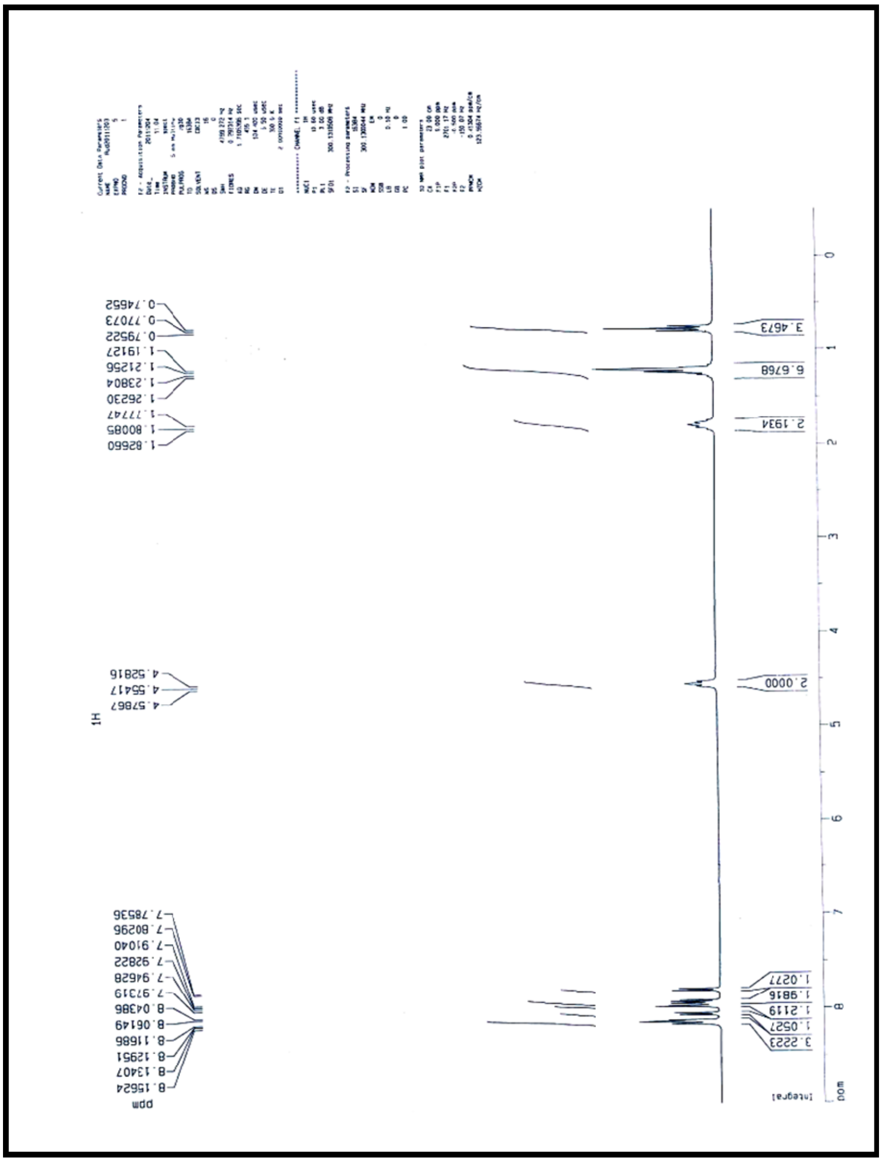
^{13}C-NMR of **4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)-N,N,N-trimethylbenzenaminium iodide (M2)**



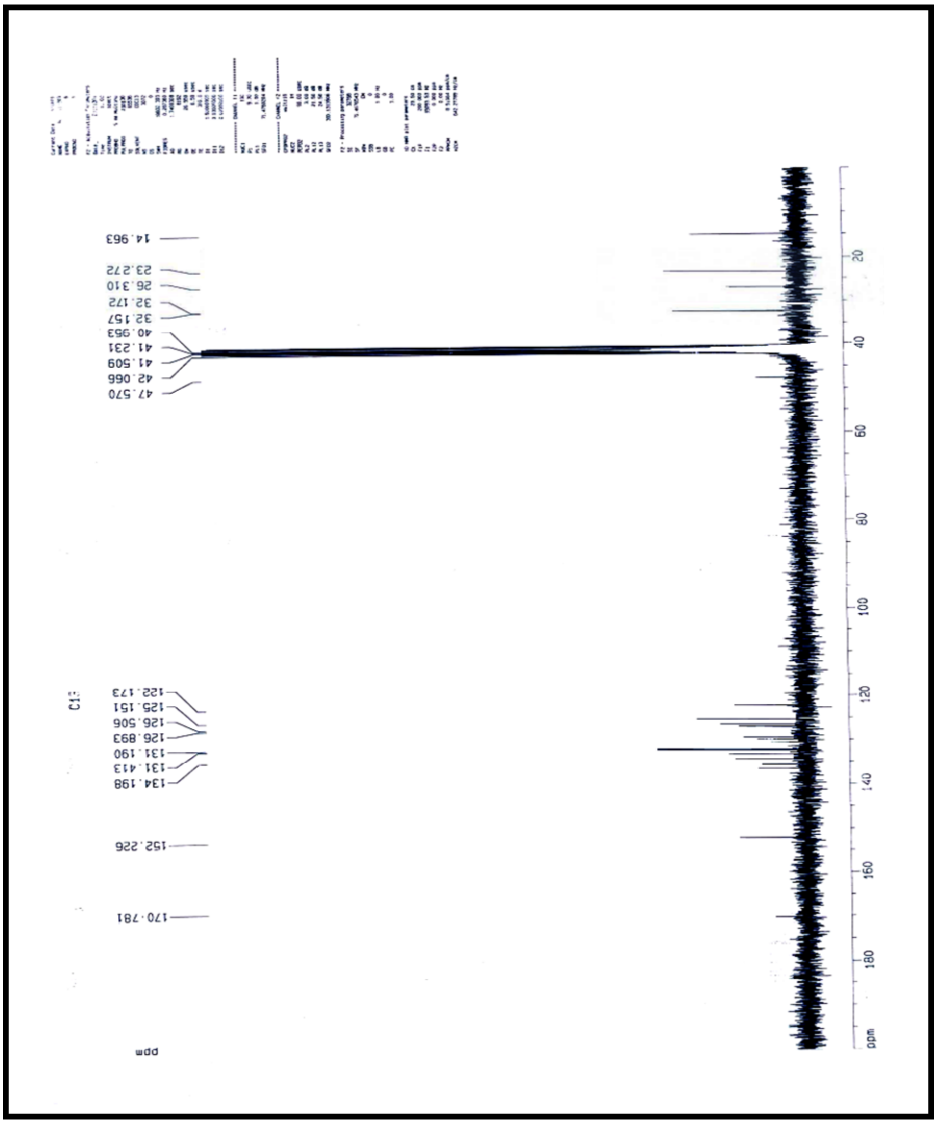
^{1}H-NMR of **4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)benzonitrile (A1)**



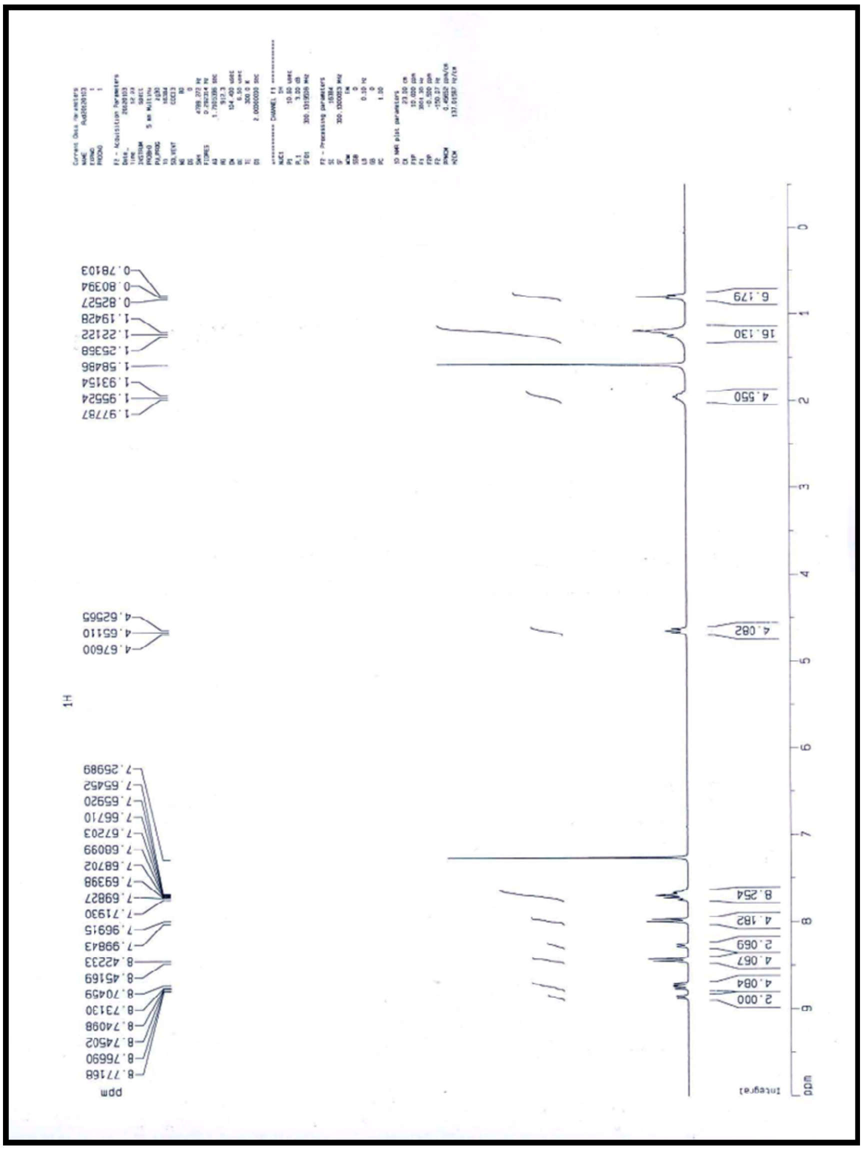
^{13}C-NMR of **4-(1-Hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)benzonitrile (A1)**



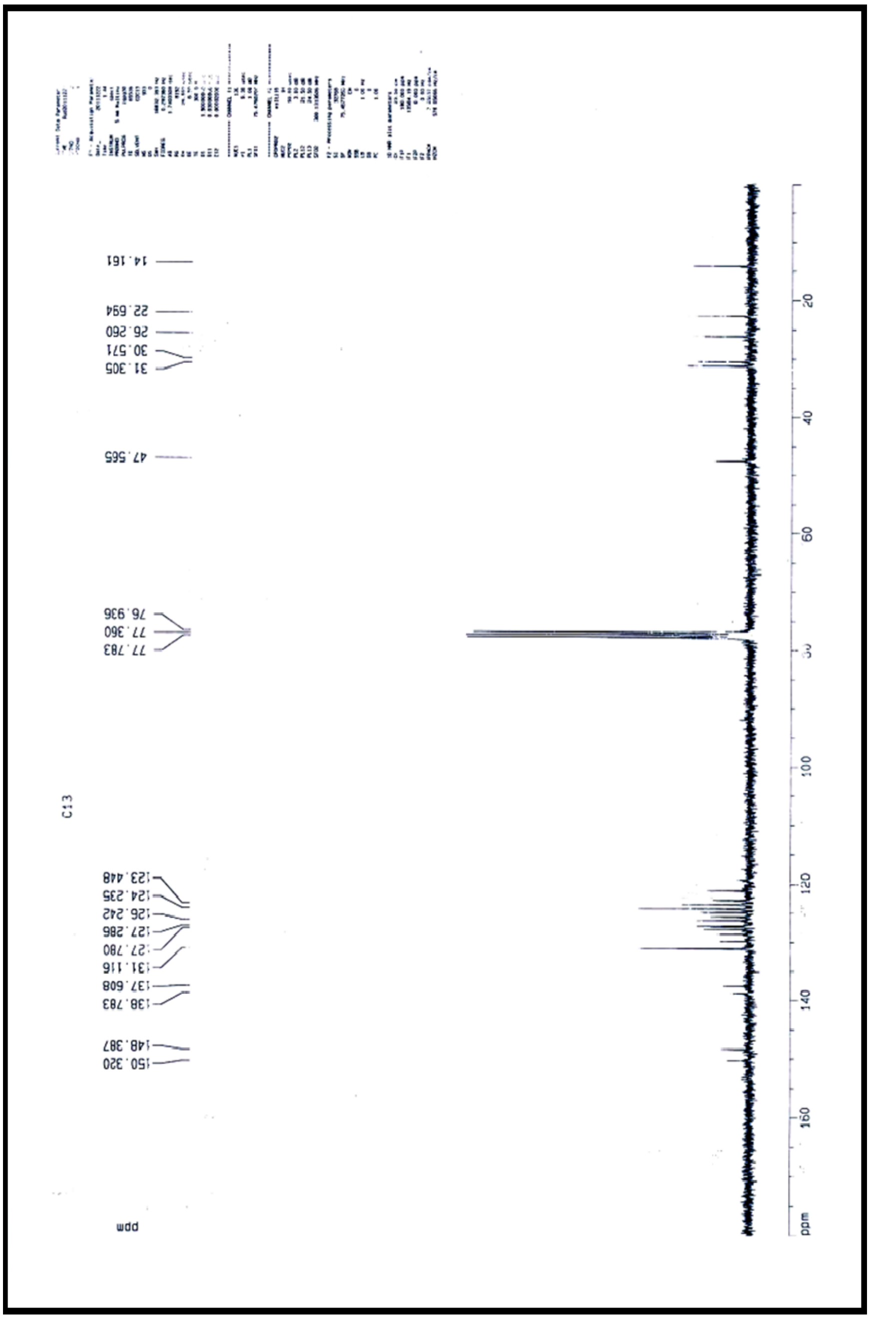
^{1}H-NMR of **Sodium 4-(1-hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)benzoate (A2)**



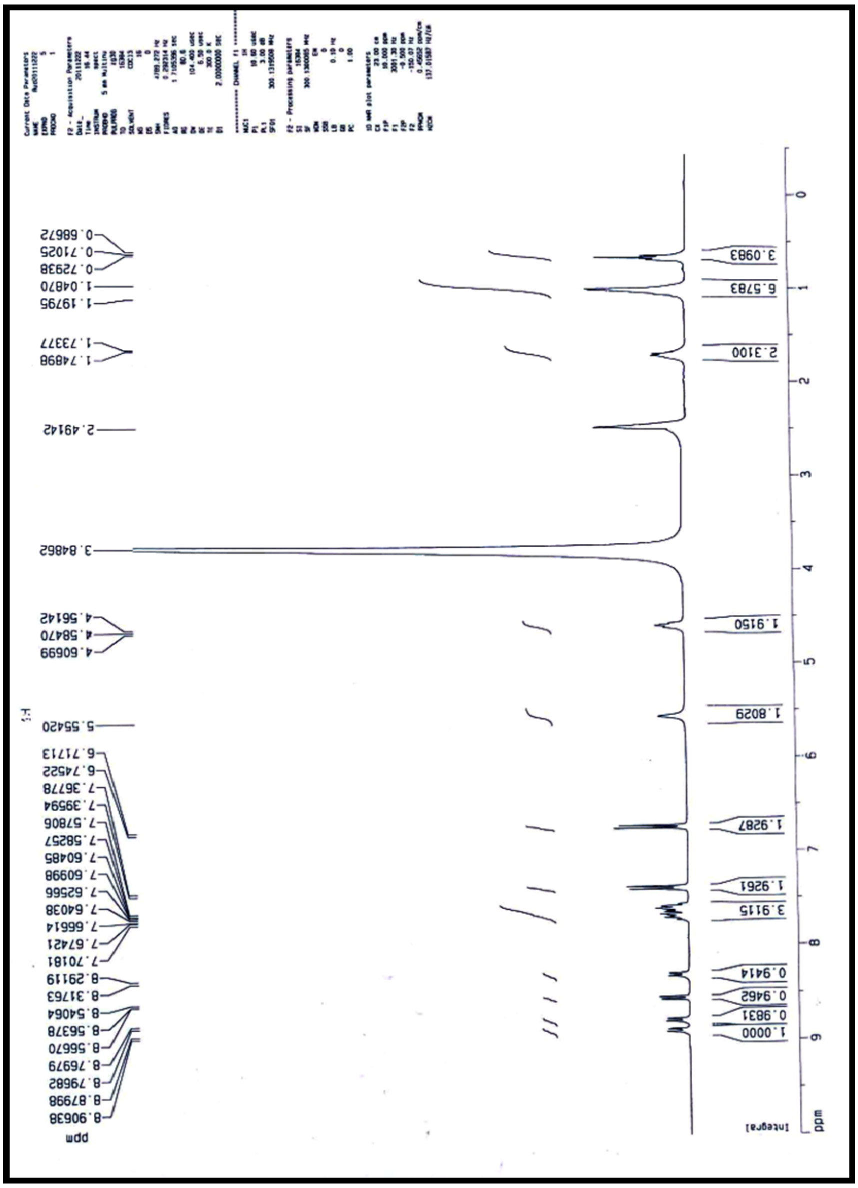
^{13}C-NMR of **Sodium 4-(1-hexyl-1H-dithieno[2',3':3,4;3'',2'':5,6]benzo[1,2-d]imidazol-2-yl)benzoate (A2)**



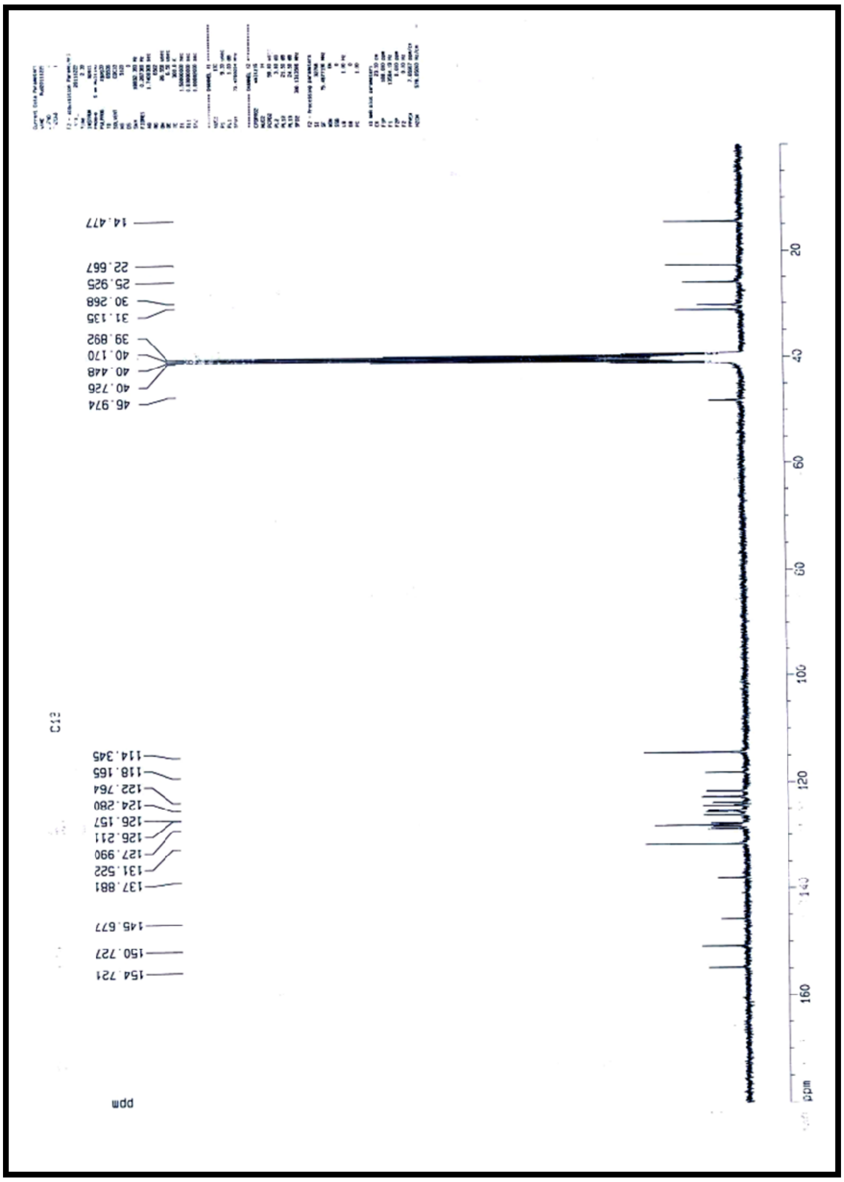
^{1}H-NMR of **1-Hexyl-2-(4-nitrophenyl)-1H-phenanthro[9,10-d]imidazole**



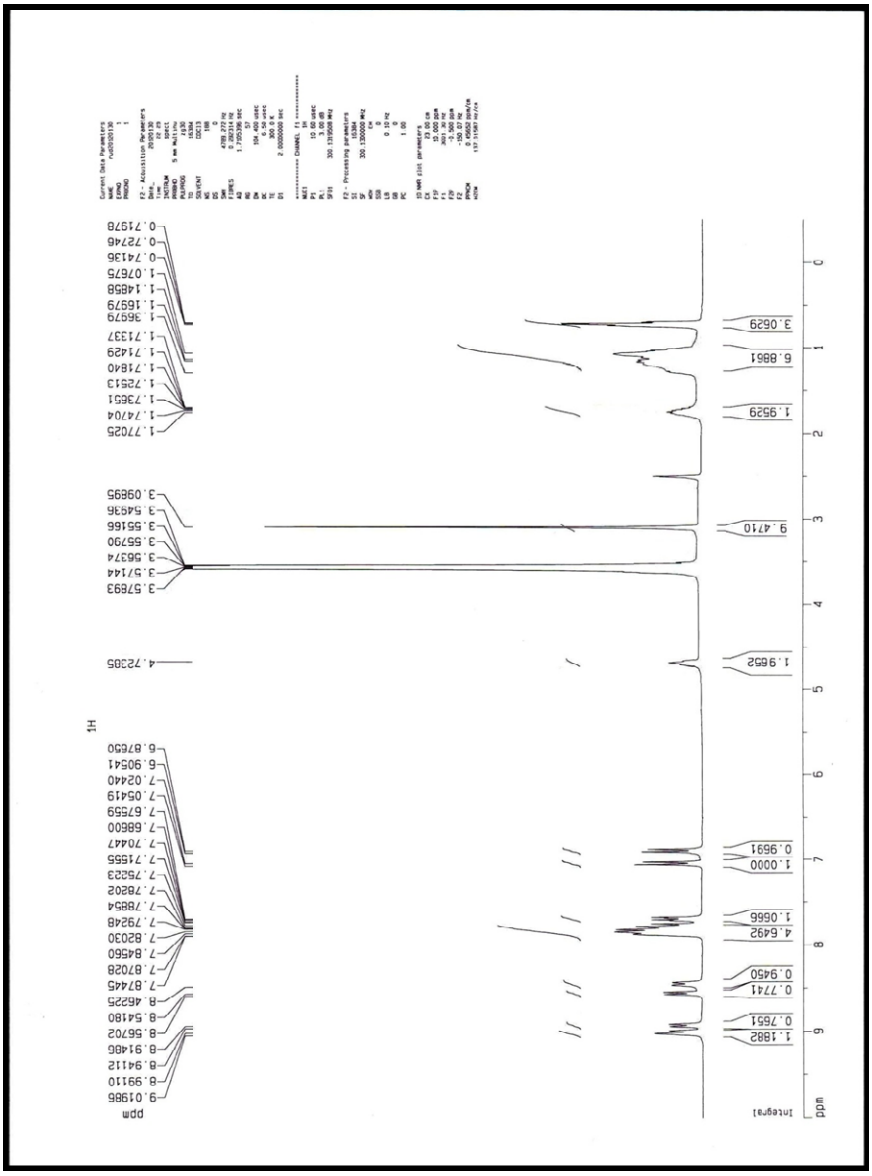
^{13}C-NMR of **1-Hexyl-2-(4-nitrophenyl)-1H-phenanthro[9,10-d]imidazole**



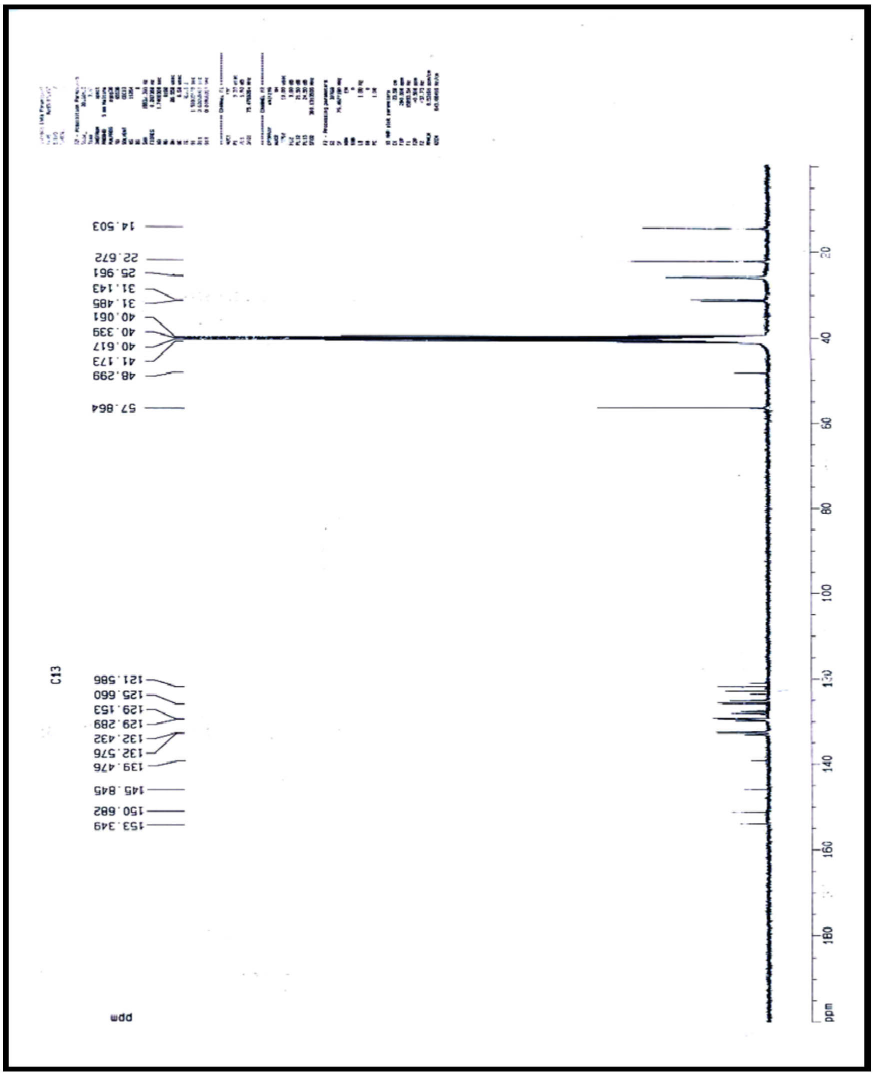
^{1}H-NMR of **4-(1-Hexyl-1H-phenanthro[9,10-d]imidazol-2-yl)aniline**



^{13}C-NMR of **4-(1-Hexyl-1H-phenanthro[9,10-d]imidazol-2-yl)aniline**



^{1}H-NMR of **4-(1-Hexyl-1H-phenanthro[9,10-d]imidazol-2-yl)-N,N,N-trimethylbenzenaminium iodide.**



^{13}C-NMR of **4-(1-Hexyl-1H-phenanthro[9,10-d]imidazol-2-yl)-N,N,N-trimethylbenzenaminium iodide.**

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1. Y. Miyake, M. Wu, M. J. Rahman, Y. Kuwatani and M. Iyoda, *J Org. Chem.*, 2006, **16**, 6110.
2. A. Meyer, E. Sigmund, F. Luppertz, G. Schnakenburg, I. Gadaczek, T. Bredow. S. S. Jester and H. Höger, *Beilstein J. Org. Chem.*, 2010, **6**, 1180.