Supporting information

Ratiometric sensing of Hg^{2+} based on calix[4]arene of *partial cone* conformation possessing a dansyl moiety

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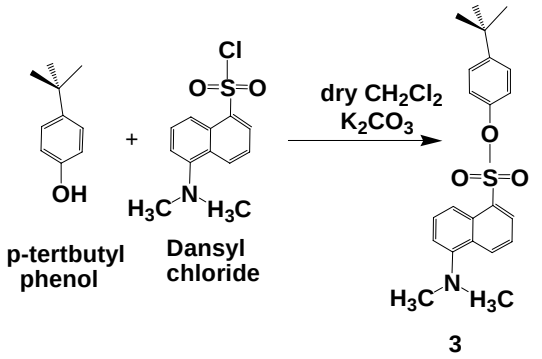
General Information. The melting points were determined in capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on JEOL 300 MHz (300 MHz ^{1}H; 75 MHz ^{13}C). Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet), coupling constants (Hz), integration, and interpretation. Silica Gel 60 (60-120 mesh). UV-vis spectra were recorded by using SHIMADZU-UV-2450 spectrophotometer, and fluorescence spectra were recorded on SHIMADZU- RF-5301PC.

Synthesis of 1. To be published elsewhere.

Synthesis of 2. Dansyl Chloride (182 mg, 0.672 mmol) was added dropwise to the stirred solution of **1** (500 mg, 0.611 mmol) and Et_3N (68 mg, 0.672 mmol) in 50ml dry dichloromethane. The reaction was stirred at room temperature for 6 h. After the completion of reaction, the reaction mixture was washed with water. The organic layer was separated, dried over anhydrous sodium sulfate and distilled under reduced pressure to give a crude residue. The pure compound **2** was obtained in 30% yield after column Chromatography on silica gel (Dichloromethane). mp, 220ºC, IR ν_{max} (KBr pellet, cm^{-1}) 3311 cm^{-1} (N-H stretching), ^1H NMR(300 MHz, $CDCl_3$): δ 1.12 [s, 18H, $C(CH_3)_3$], δ 1.22 [s, 9H, $C(CH_3)_3$], δ 1.35 [s, 9H, $C(CH_3)_3$], δ 0.92 [t, *J*=6.75, 6H, CH_3], δ 1.75 -1.81 [m, 4H, CH_2], δ 1.97 [t, *J*=6.0, 2H, NCH_2], δ 2.73 [s, 6H, NCH_3], δ 3.19 [d, *J*=15, 2H, CH_2], δ 3.36 [d, *J*=15.0, 2H, CH_2], δ 3.67 [d, *J*=15.0, 2H, CH_2], δ 4.13 [d, *J*=15, 2H, CH_2], δ 3.46-3.49 [m, 2H, OCH_2], δ 3.76-3.79 [m, 4H, OCH_2], δ 4.22 [s, 1H, NH], δ 6.77 [d, 2H, ArH], δ 6.85 [s, 2H, ArH], δ 6.96 [d, 2H, ArH], δ 6.70 [s, 2H, ArH], 6.78[s,1H ArOH], δ 7.46-7.556 [m, 2H, ArH], δ 7.11 [d, 1H, ArH], δ 8.12 [d, *J*=9, 1H, ArH], δ 8.26 [d, *J*=9, 1H, ArH], δ .8.41 [d, *J*=9, 1H, ArH]; ^{13}C NMR(300 MHz, $CDCl_3$): δ 10.21 [CH_3], δ 22.78 [CH_2], δ 31.27 [CH_3], δ 31.34 [CH_3], δ 31.56 [C], δ 31.59 [C], δ 33.81 [CH_2], δ 33.95 [CH_2], δ 38.50 [CH_2], δ 43.42 [CH_2], δ 45.34 [CH_3], δ 68.12 [CH_2], δ 75.47 [CH_2], δ 114.90 [ArC], δ 118.98 [ArC], δ 122.91 [ArC], δ 124.54 [ArC], δ 126.20 [ArC], δ 127.28 [ArC], δ 128.11[ArC] , δ 128.96 [ArC], δ 129.89 [ArC], δ 133.10 [ArC], δ 133.44 [ArC], δ 134.58 [ArC], δ 135.135[ArC], δ 142.18 [ArC], δ 144.24 [ArC], δ 146.26[ArC], δ 149.15 [ArC], δ 151.83 [ArC], δ 152.65 [ArC], δ 152.98 [ArC]; FAB-MS: *m/z* 1009$(M+2)^+$. Anal cal. for $C_{64}N_2H_{83}S_1O_6$ C, 76.27 %; H, 8.24 %; N, 2.78% , Found: C, 76.20%; H, 8.15 %; N, 2.57%.

Synthesis of 3



Synthetic Scheme -2

Dansyl chloride (268 mg, 0.99 mmol) was added dropwise to the stirred solution of *p-tert*-butyl phenol (100 mg, 0.66 mmol) and K_2CO_3 (455 mg, 3.3mmol) in 50 ml dry dichloromethane. The reaction was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was washed with water. The organic layer was separated, dried over anhydrous sodium sulfate and distilled under reduced pressure to give a crude residue. The residue was crystallized in MeOH to obtain a pure compound **3** in 35% yield. mp, 110ºC, IR ν_{max} (KBr pellet, cm^{-1}) 1360 cm^{-1} (S=O stretching), ^{1}H NMR(300 MHz, $CDCl_3$); δ 1.22 [s, 9H, $C(CH_3)_3$], δ 2.91 [s, 6H, NCH_3], δ 6.80 [d, *J*=6.0, 1H, ArH], δ 7.18 [d, *J*=6.0, 1H, ArH], δ 7.24 [d, *J*=9.0, 1H, ArH], δ 7.47 [t, *J*=9.0, 1H, ArH], δ 7.66 [t, *J*=9.0, 1H, ArH], δ 8.09 [d, *J*=6.0, 1H, ArH], δ 8.46 [d, *J*=9.0, 1H, ArH], δ 8.59 [d, *J*=6.0, 1H, ArH]; ^{13}C NMR(300 MHz, $CDCl_3$): δ 31.65 [CH_3], δ 34.87 [CH_3], δ 45.85 [CH_3], δ 115.96 [ArC], δ 115.96 [ArC], δ 120.01 [ArC], δ 121.77 [ArC], δ 123.38 [ArC], δ 126.85 [ArC], δ 129.31 [ArC], δ 130.14 [ArC], δ 130.48 [ArC], δ 131.50 [ArC], δ 131.69 [ArC], δ 132.19 [ArC], δ 147.76 [ArC], δ 150.39 [ArC], δ 152.25 [ArC]; ESI-MS: *m/z* 406 (M+ Na^+).

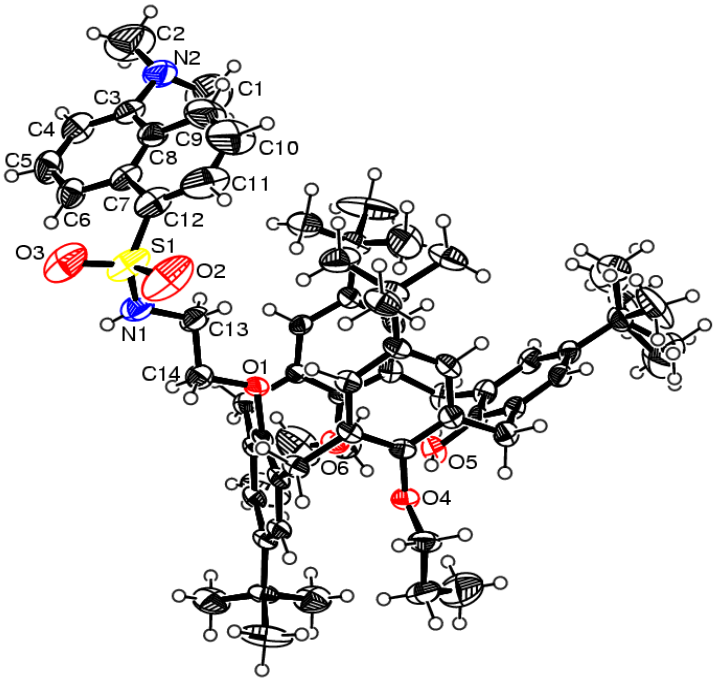


Figure S1. ORTEP diagram of **2** in partial cone conformation.

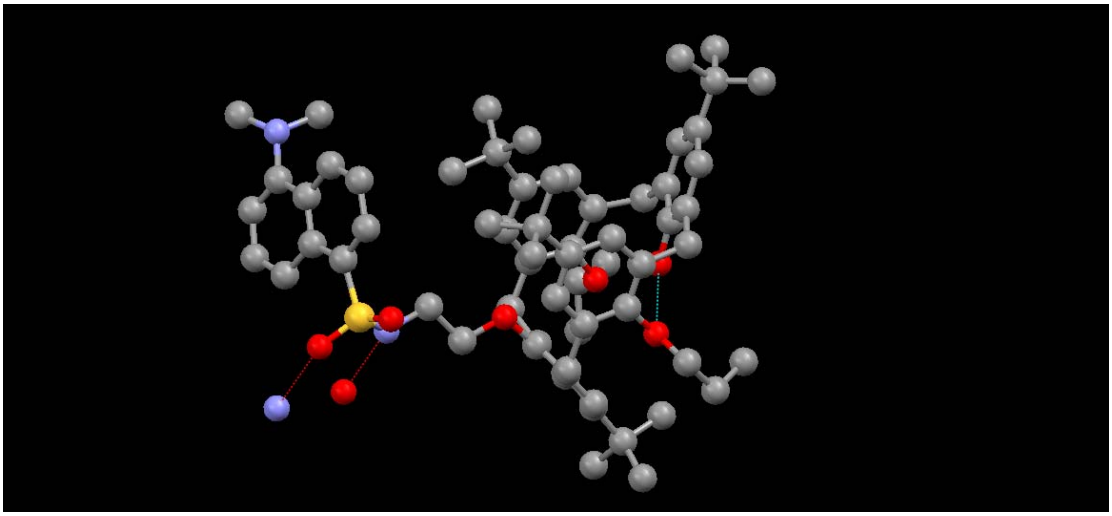


Figure S2. Ball and Stick structure of **2** in partial cone conformation showing intramolecular hydrogen bonding between phenolic hydrogen and oxygen atom of propyl chain on adjacent benzene ring.

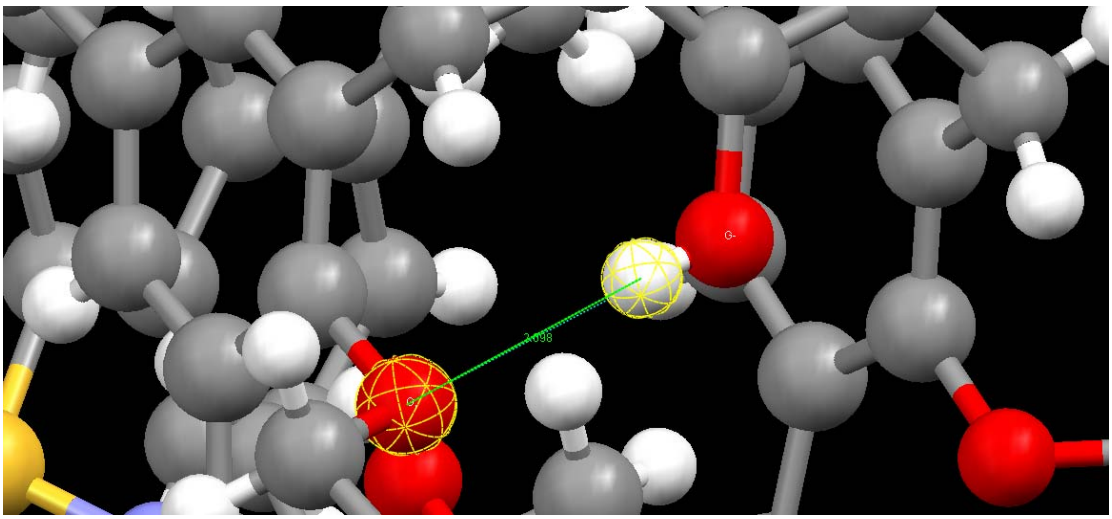


Figure S3. Hydrogen bonding between phenolic hydrogen and oxygen atom of propyl chain *(closer view).*

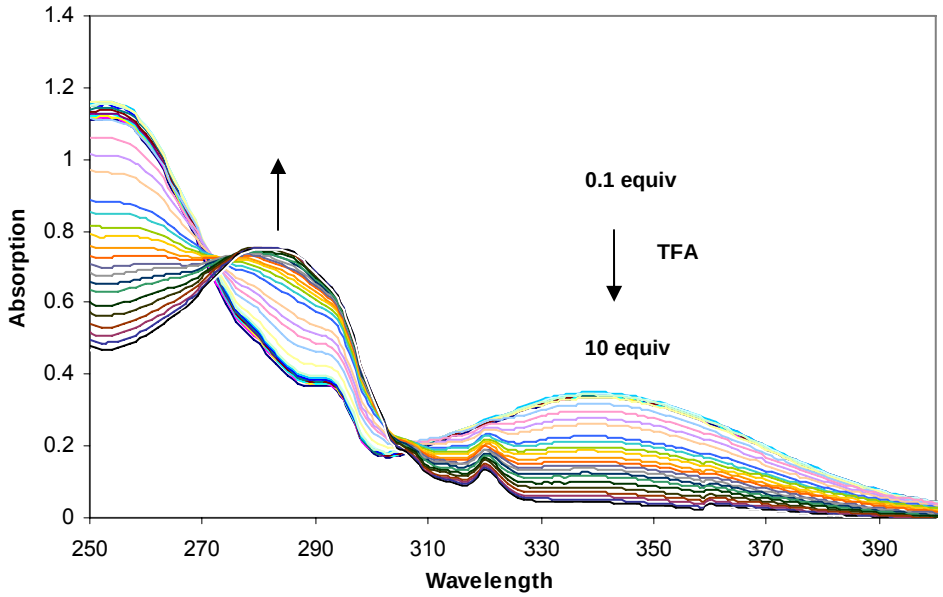


Figure S3. UV/visible spectra of **2** (5 x 10^{-5} M) in the presence of trifluoroacetic acid (0.1 equiv to 10 equiv), THF:H_2O (9:1,v/v) buffered with HEPES, pH = 7.0.

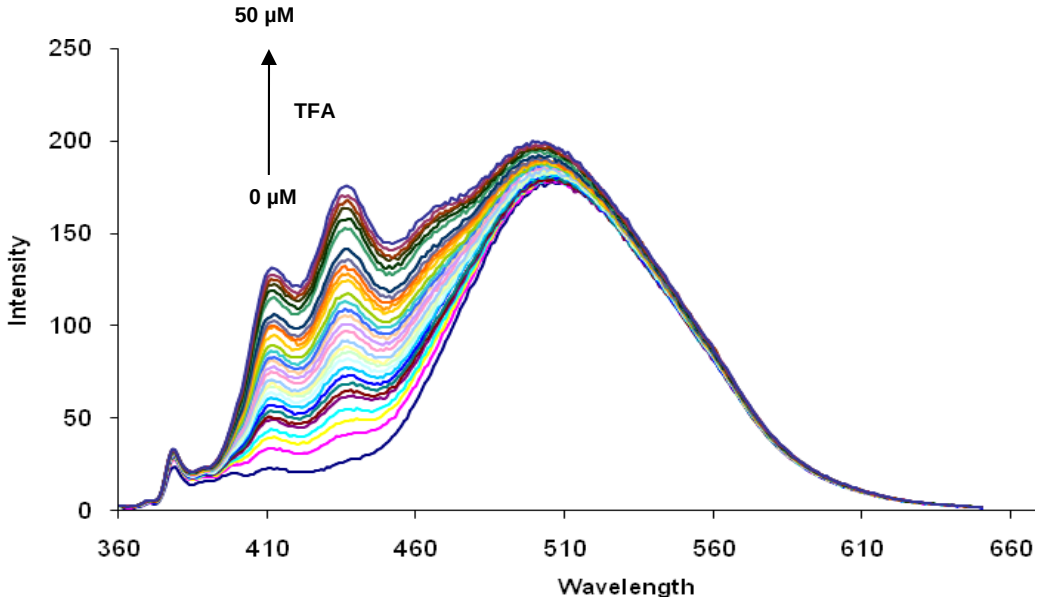


Figure S4. Fluorescence spectra of **2** (1µM) in the presence of trifluoroacetic acid (50 µM), THF: H_2O (9:1,v/v) buffered with HEPES, pH = 7.0 ; λ_{ex} = 338 nm.

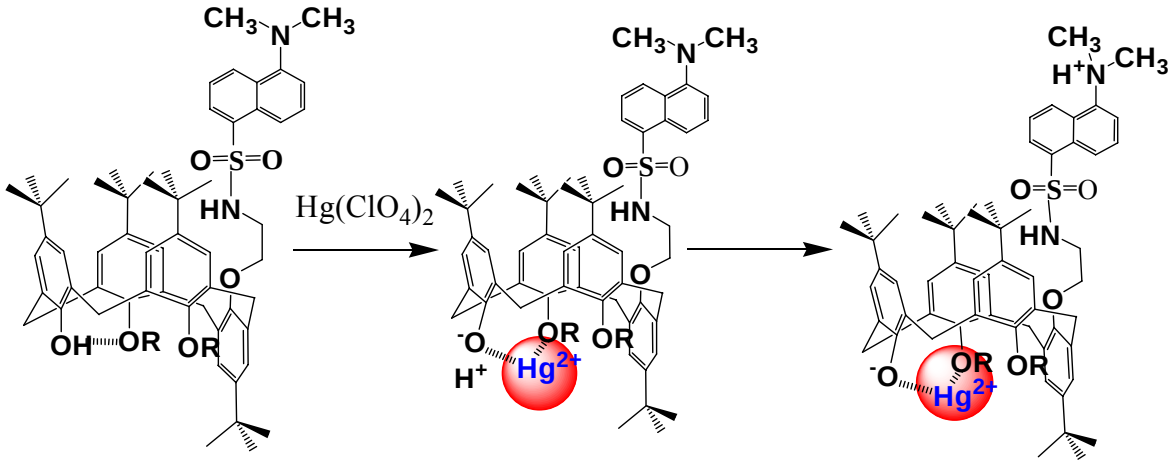


Figure S5. Mechanism of displacement of proton in presence of Hg^{2+}

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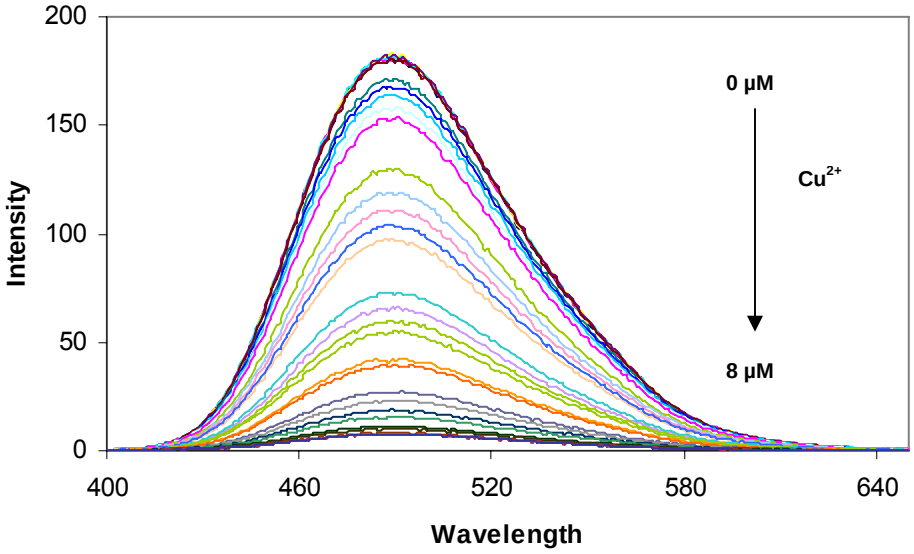


Figure S6. Fluorescence spectra of **2** (1 μM) in response to the presence of **Cu^{2+}** (8 μM) ions in THF: H_2O (9:1,v/v) buffered with HEPES, pH = 7.0 ; λ_{ex} = 338 nm.

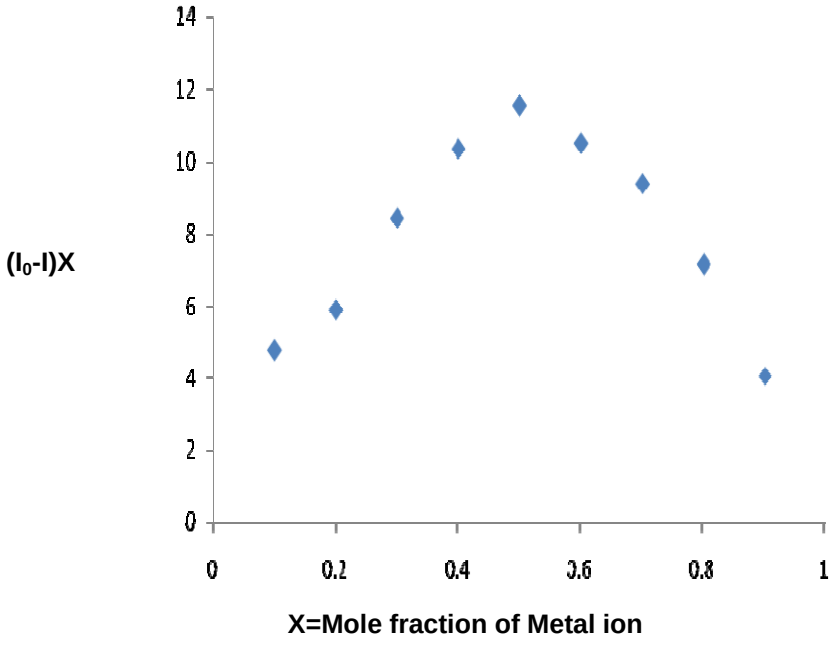


Figure S7. Job plot for Hg^{2+}.

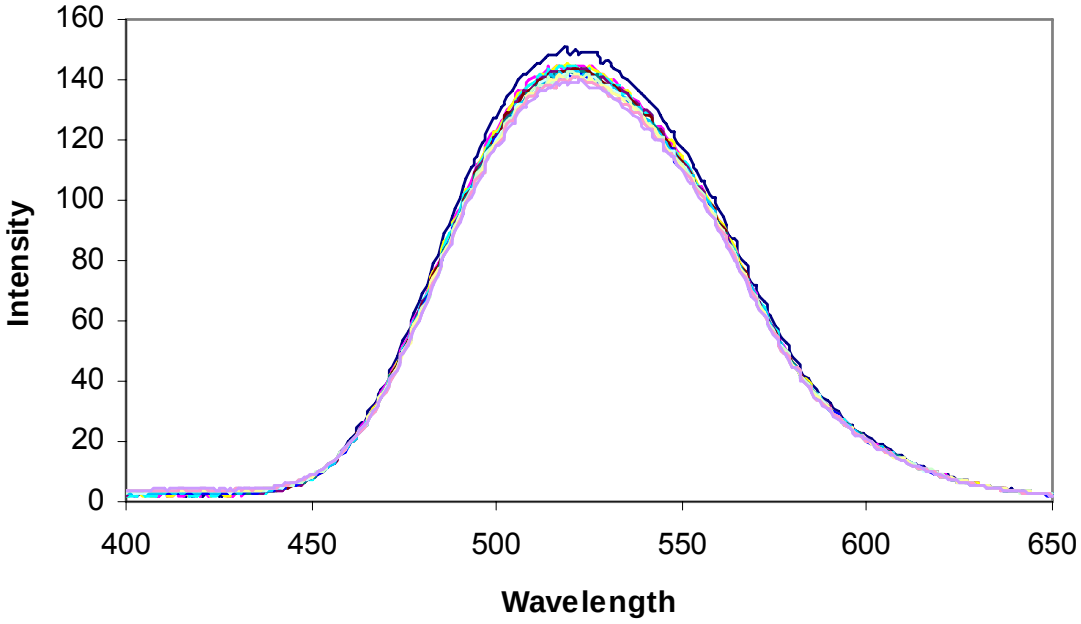
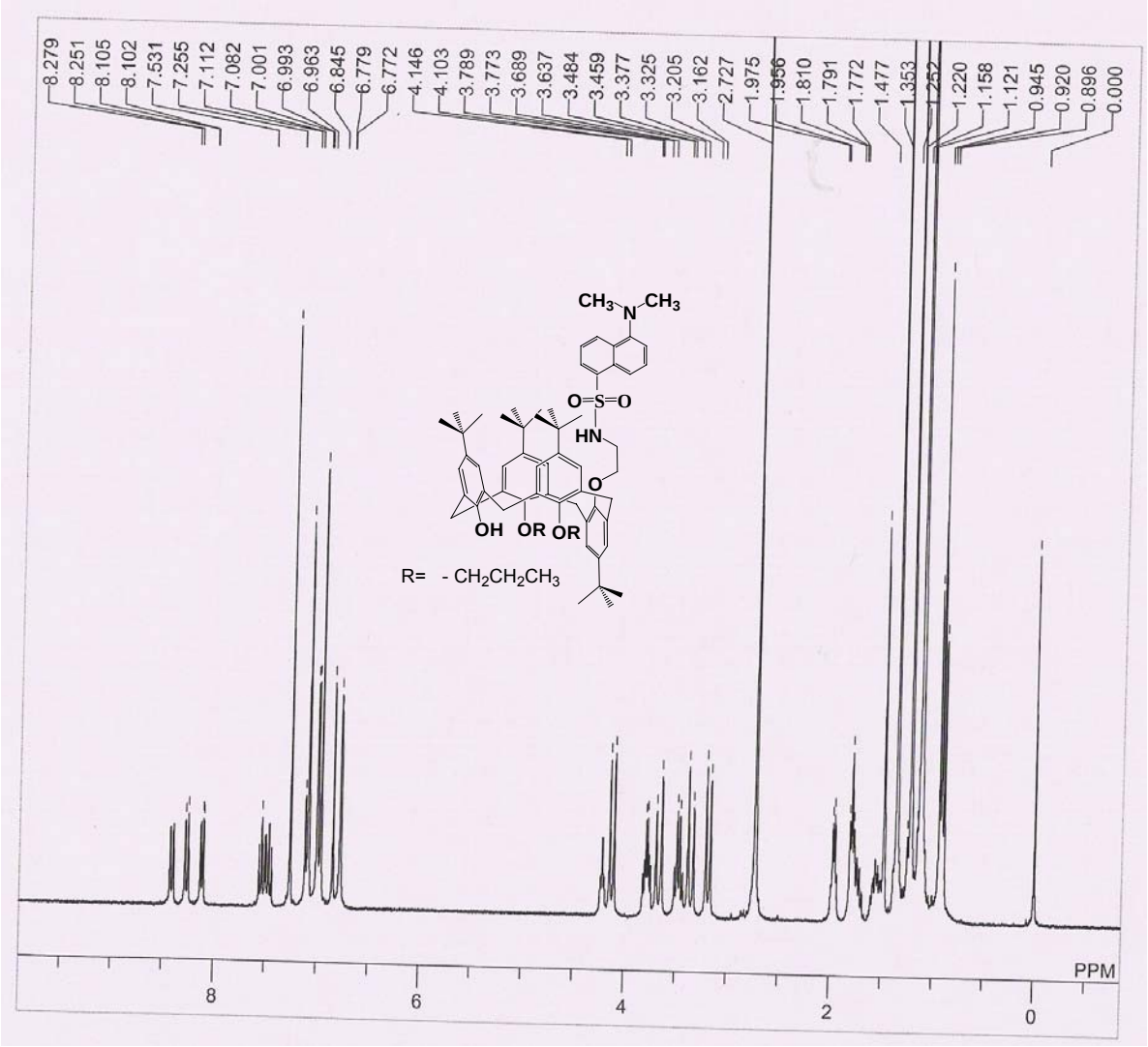
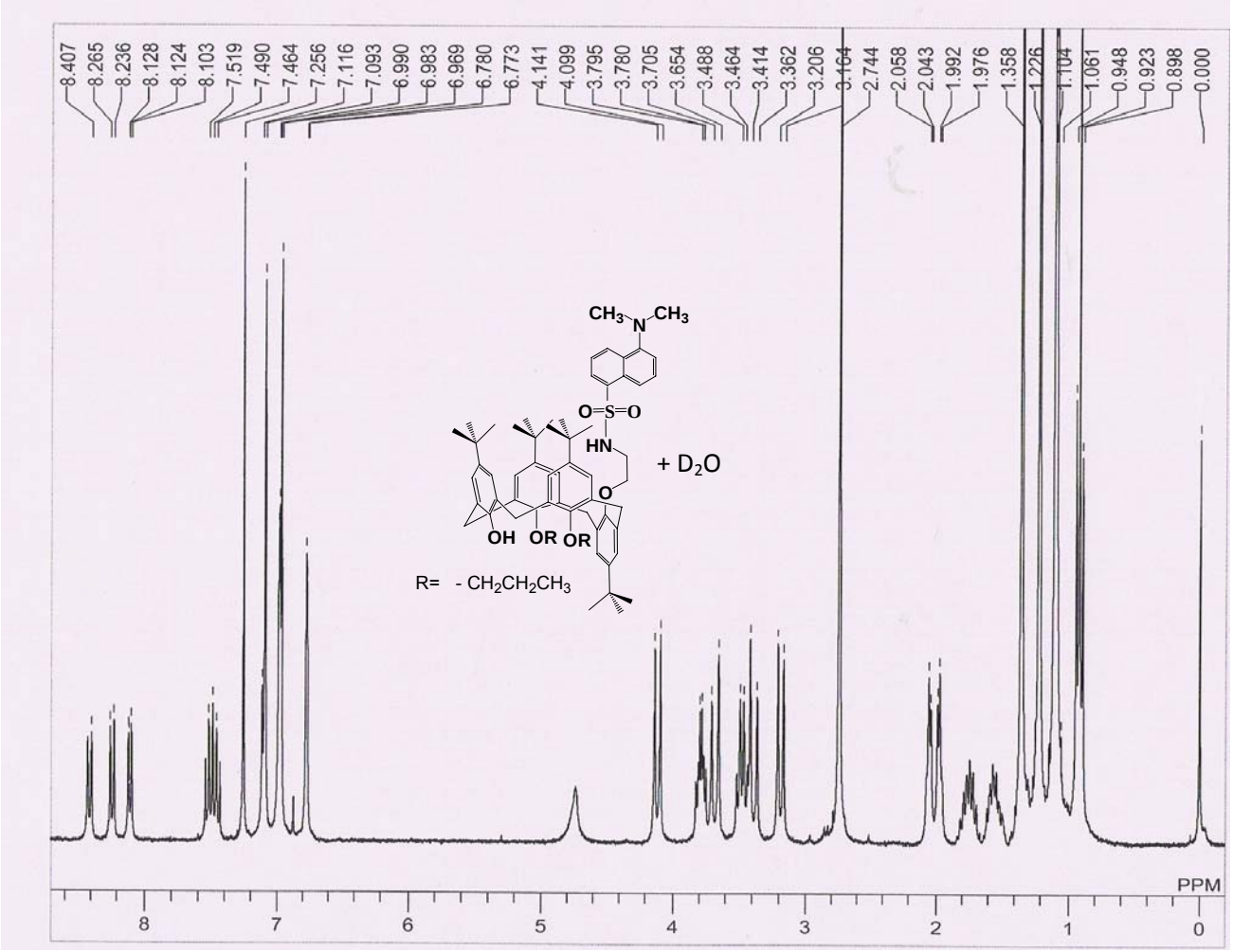


Figure S8. Fluorescence spectra of **3** (1 μM) in response to the presence of **Hg^{2+}** (20 μM) ions in THF: H_2O (9:1,v/v) buffered with HEPES, pH = 7.0 ; λ_{ex} = 338 nm.

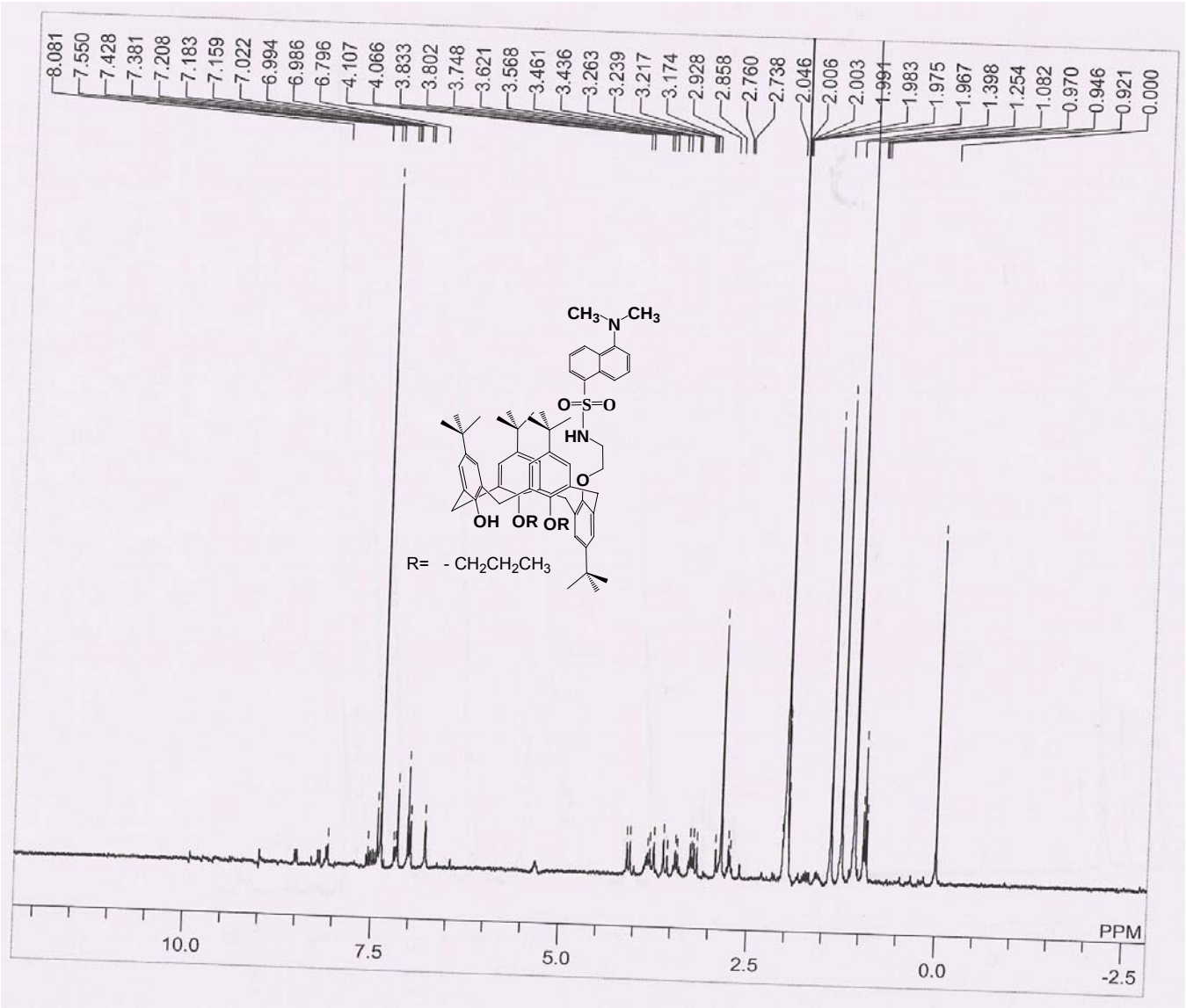
^{1}H NMR spectrum of receptor 2



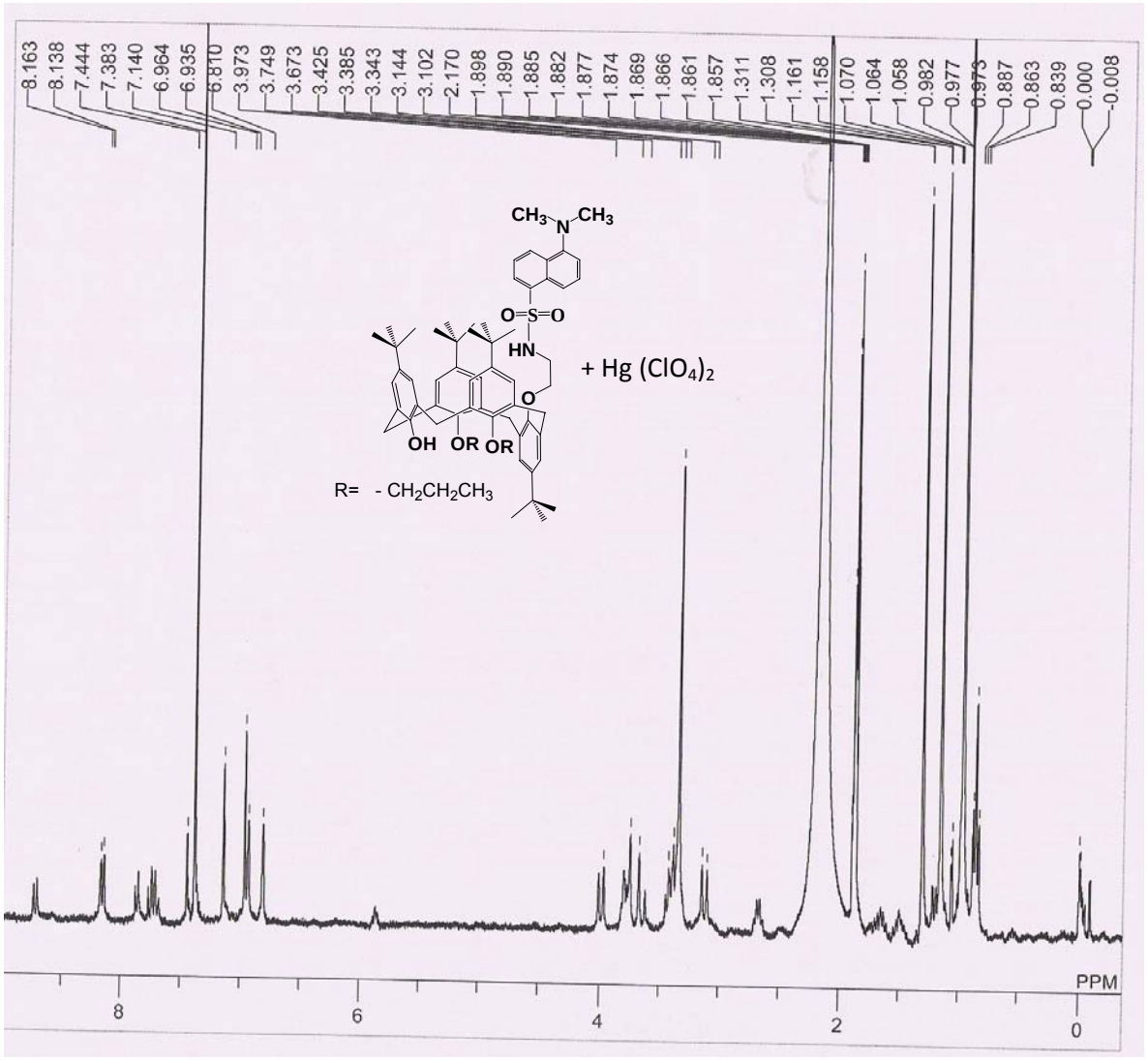
^{1}H NMR spectrum of receptor 2+ D_2O



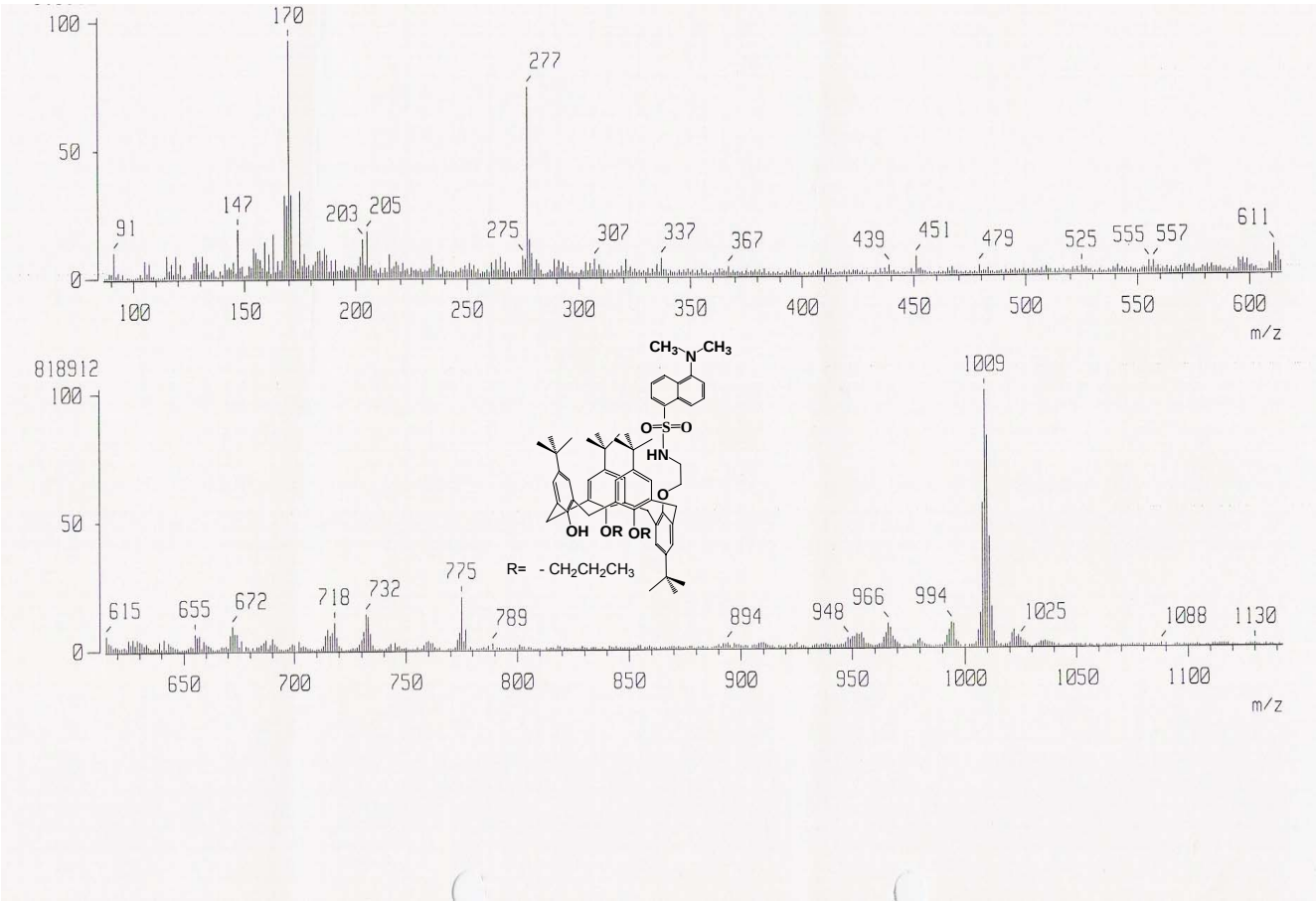
^{1}H NMR spectrum of receptor 2 in $CDCl_3$:CD_3CN in (8:2)



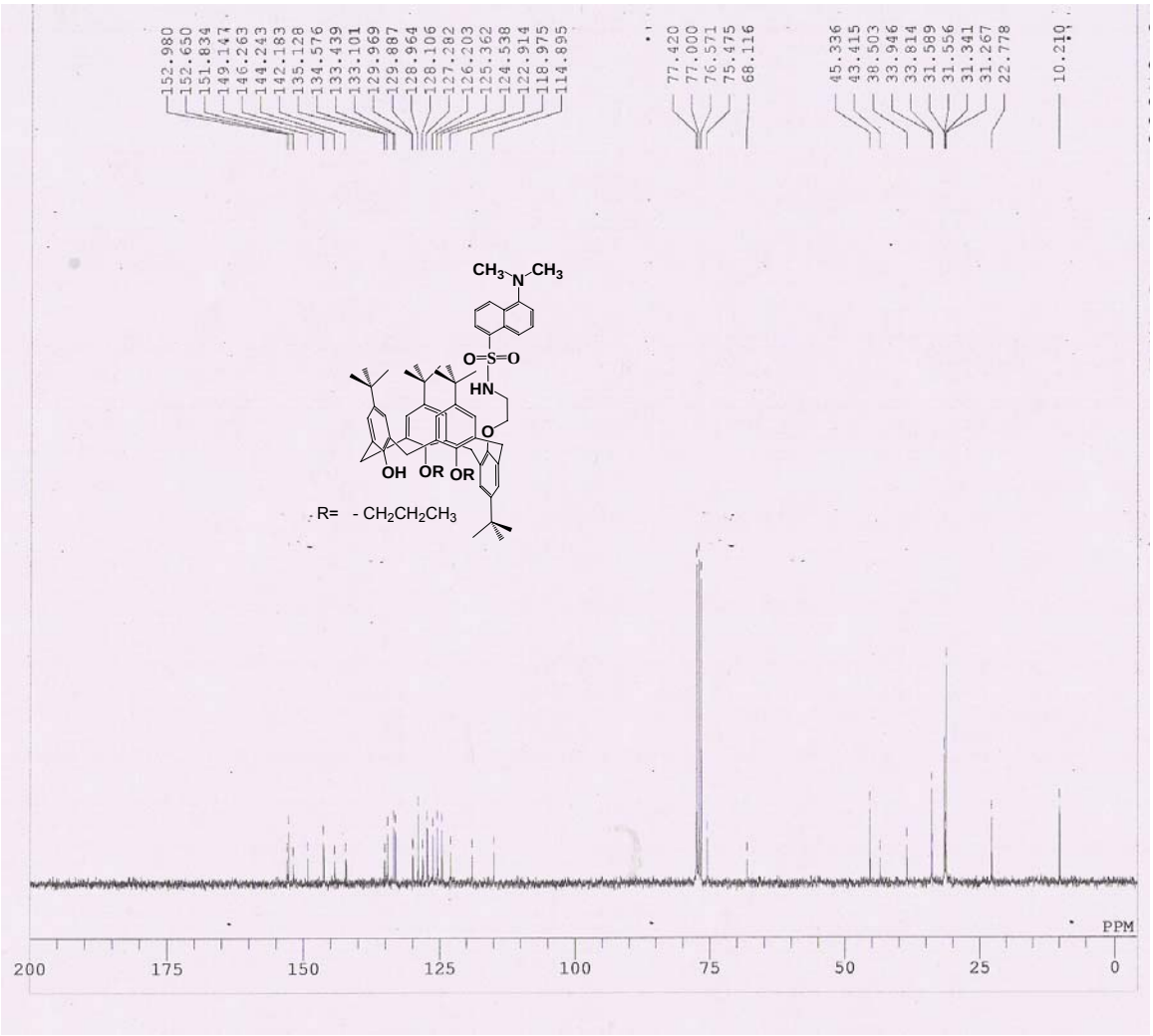
^{1}H NMR spectrum of receptor 2+ Hg^{2+} in $CDCl_3$:CD_3CN in (8:2)



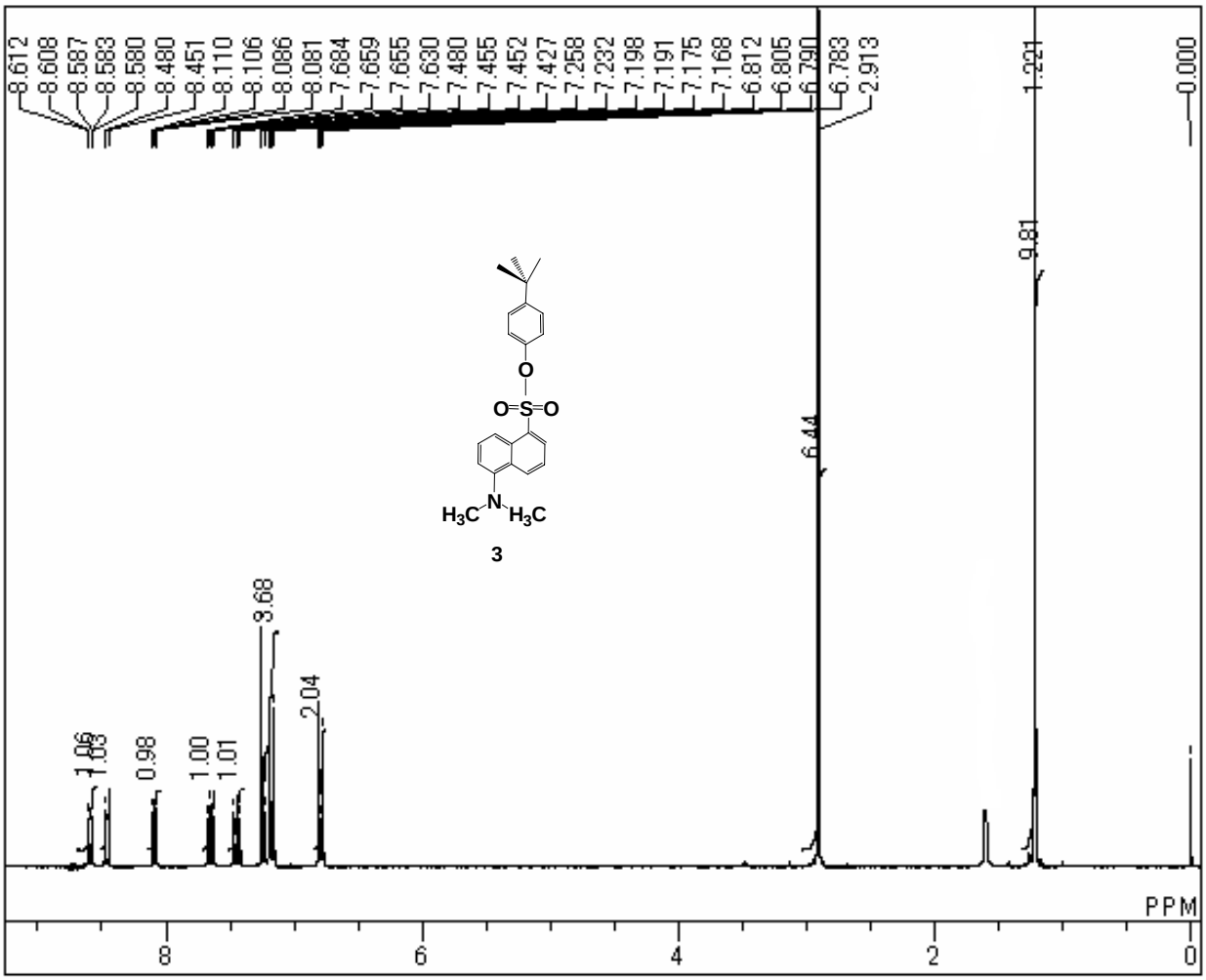
FAB mass spectrum of receptor 2



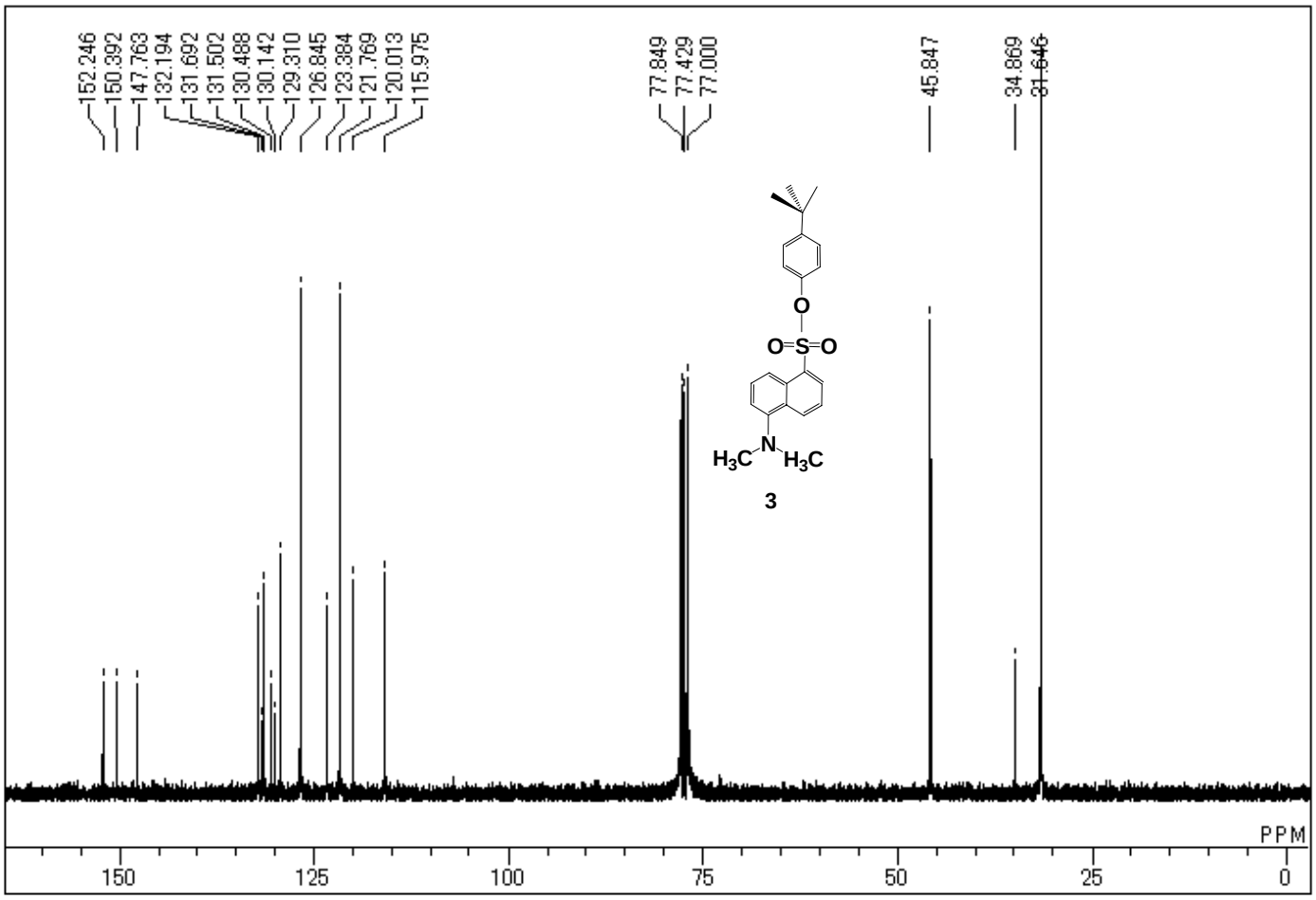
^{13}C spectrum of receptor 2



^{1}H NMR spectrum of receptor 3



^{13}C spectrum of receptor 3



ESI-MS spectrum of receptor 3