

“Carboxylated ‘locking unit’ directed ratiometric probe design, synthesis and application in selective recognition of Fe³⁺/Cu²⁺”

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Supporting Information

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General Information

The solvents and reagents were purchased from commercial sources. The reagents were used without any further purification unless and otherwise stated. The solvents were distilled prior to use, and the spectroscopic grade solvents were used for the spectroscopic measurements. Chloride salts of Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{3+} , Cu^{2+} , Hg^{2+} , Zn^{2+} , Al^{3+} , Cd^{2+} , and Co^{2+} , nitrate salts of Sr^{2+} , Pb^{2+} , Ag^+ , Ba^{2+} , Ni^{2+} and NH_4^+ , and sulphate salt of Fe^{2+} were used during the spectroscopic measurements. TLC was done on Merck silica gel plates (60F254) with a fluorescent indicator. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance II 400 and Bruker Avance 300 MHz spectrometers Spectrometer in CDCl_3 and $\text{DMSO}-d_6$. UV-vis and fluorescence spectra were recorded on a Simadzu UV-2450 spectrophotometer and Cary Eclipse Fluorescence spectrophotometer respectively. The excitation wavelength was fixed at 297 nm ($\lambda_{\text{ex}} = 297 \text{ nm}$) in case of fluorescence measurements at 25 °C in a 1 cm quartz cell with a slit width of 5 nm for both excitation and emission. FT-IR and mass spectra were recorded on a Perkin Elmer Spectrum 2 spectrophotometer and Q-TOF micromass spectrometer respectively. All the spectral measurements were done after 4 hrs of the preparation of solution of compound **1**. (2-formyl-phenoxy)-acetyl acid was prepared following a literature procedure.¹

Preparation of 2-(2-((E)-(9-ethyl-9H-carbazol-3-ylimino)methyl)phenoxy)acetic acid (1): To the methanolic solution of 3-amino-9-ethyl carbazole **4** (421 mg, 2 mmol), (2-formyl-phenoxy)-acetyl acid **3** (360 mg, 2 mmol) was added at room temperature. The mixture was kept stirring at 70 °C. A deep orange product which was precipitated out after 30 min of stirring was isolated by filtration. The isolated product was washed with methanol several times and dried under vacuum. This yielded 521 mg of pure product (70%) which was characterized using common spectroscopic tools like FT-IR, NMR and mass spectrometry (Scheme 1).

Deep orange powder; Melting point: 130 °C; FT-IR (KBr, ν in cm^{-1}): 748, 890, 1059, 1128, 1156, 1236, 1281, 1332, 1369, 1383, 1457, 1474, 1486, 1650, 1718, 1916, 2933, 2978, 3052, 3426; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 1.33 (t, $J = 7.0$ Hz, 3H), 4.45 (q, $J = 6.9$ Hz, 2H), 4.88 (s, 2H), 7.09-7.14 (m, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.45-7.51 (m, 3H), 7.59-7.65 (m, 2H), 8.11-8.13 (m, 2H) 8.22 (d, $J = 7.7$ Hz, 1H), 9.13 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3+\text{DMSO-}d_6$) δ 13.53, 37.15, 65.22, 108.63, 108.79, 112.12, 112.51, 118.55, 119.81, 120.18, 121.16, 122.32, 122.72, 124.96, 125.66, 126.95, 131.86, 138.16, 139.97, 143.71, 153.22, 157.51, 169.89; MS (TOF-ES): m/z calculated for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{MH}]^+$ 373.16, found 373.35.

Preparation of 2-((E)-(9-ethyl-9H-carbazol-3-ylimino)methyl)phenol (5): To a methanolic solution of 3-amino-9-ethyl carbazoleamine (2 mmol, 420.5 mg) was added salicylaldehyde (2 mmol, 244 mg) and left stirring for 30 minutes at room temperature. The yellow coloured solid precipitate was isolated through filtration, washed with ethanol several times and dried under vacuum. 525 mg (83% yield) of pure compound **5** was obtained as yellow powder and the same was characterized using common spectroscopic tools like FT-IR, NMR and mass spectrometry (Scheme 1).

Yellow powder; Melting point: 107 °C; FT-IR (KBr, ν in cm^{-1}): 742, 802, 857, 862, 917, 1147, 1234, 1283, 1321, 1354, 1382, 1453, 1485, 1595, 1617, 2863, 2978, 3049; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.47 (t, $J = 7.3$ Hz, 3H), 4.38 (q, $J = 7.1$ Hz, 2H), 6.99 (t, $J = 7.4$ Hz, 1H), 7.10 (d, $J = 8.2$ Hz, 1H), 7.29 (t, $J = 7.1$, 1H), 7.38 - 7.56 (m, 6H), 8.08 (brs, 1H), 8.16 (d, $J = 7.7$ Hz 1H), 8.79 (s, 1H), 13.79 (s, 1H); $^{13}\text{C-NMR}$ (75MHz, CDCl_3) δ 14.25, 38.14, 109.22, 109.37, 113.04, 117.57, 119.34, 119.56, 120.19, 121.06, 123.33, 123.99, 126.58, 132.29, 132.84, 139.53, 140.58, 141.02, 160.25, 161.48; MS (TOF-ES): m/z calculated for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}$ $[\text{MH}]^+$ 315.15, found 315.63.

Preparation of 2-((9-ethyl-9H-carbazol-3-ylamino)methyl)phenol (6): To a methanolic solution (10 ml) of compound **5** (2 mmol, 628 mg) NaBH₄ (2.4 mmol, 91 mg) was added slowly and the reaction mixture was left stirring for one hour. After completion of the reaction (as judged by the TLC) the solvent was reduced to 1 ml under vacuum and then water (3 ml) was slowly added to the reaction mixture. When the pH of the resulting solution was adjusted to pH 6 by adding dilute HCl, appearance of white precipitate was observed. The precipitate was filtered, washed 6 times (5 ml x 6) with water, and dried under vacuum for several hours. The product was obtained as off-white solid powder (475 mg, 75%) and found to be sufficiently pure for spectroscopic studies.

Off-white powder; Melting point: 138 °C; FT-IR (KBr, ν in cm⁻¹): 747, 813, 862, 977, 966, 1070, 1152, 1207, 1234, 1289, 1311, 1343, 1469, 1485, 1507, 1589, 2901, 2972, 3049, 3322; ¹H-NMR (300 MHz, CDCl₃) δ 1.42 (t, J = 7.2 Hz, 3H), 4.35 (q, J = 7.2 Hz, 2H), 4.56 (s, 2H), 6.91 - 6.96 (m, 2H), 7.08 - 7.50 (m, 7H), 7.64-7.65 (m, 1H), 8.03 (d, J = 7.7 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃) δ 14.24, 37.98, 51.48, 108.36, 109.55, 117.12, 118.85, 120.21, 120.85, 122.90, 123.53, 123.87, 126.18, 128.99, 129.54, 136.27, 139.93, 140.85, 157.86; MS (TOF-ES): m/z calculated for C₂₁H₂₁N₂O [MH]⁺ 317.16, found 317.61.

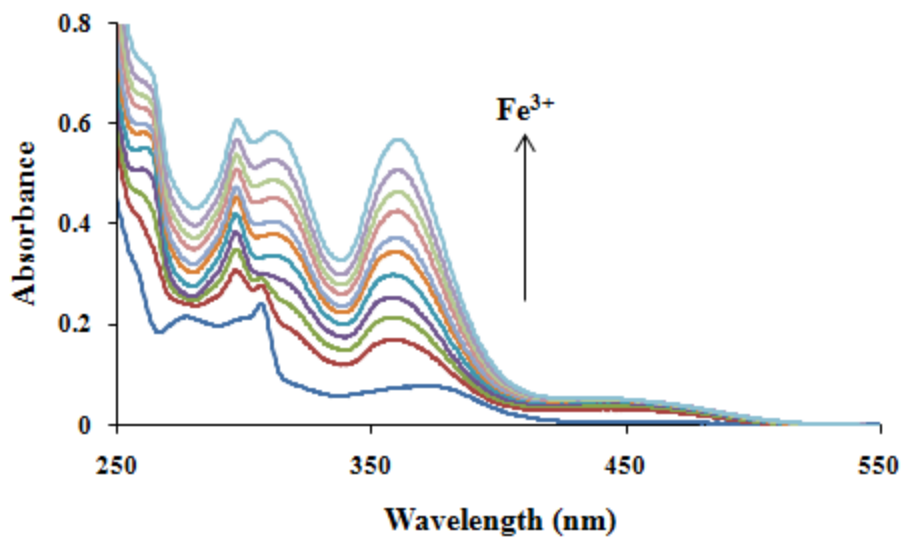


Figure S1: UV-vis absorption titration profile of compound **1** (10 μM) in the presence of 0-20 μM of Fe³⁺ ion.

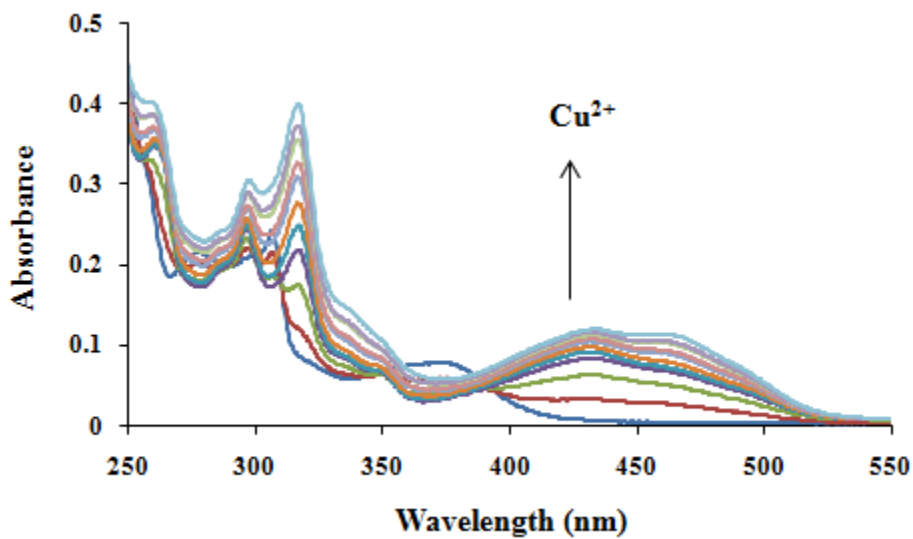
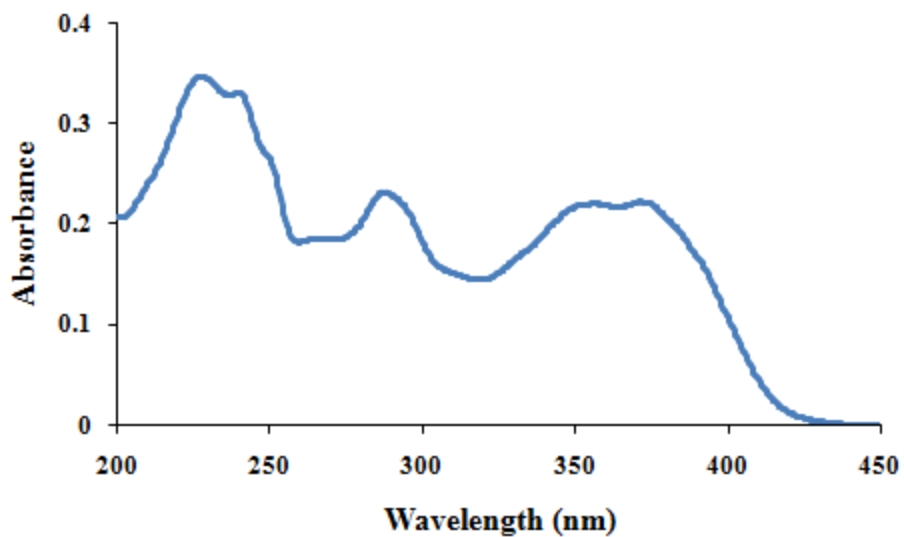
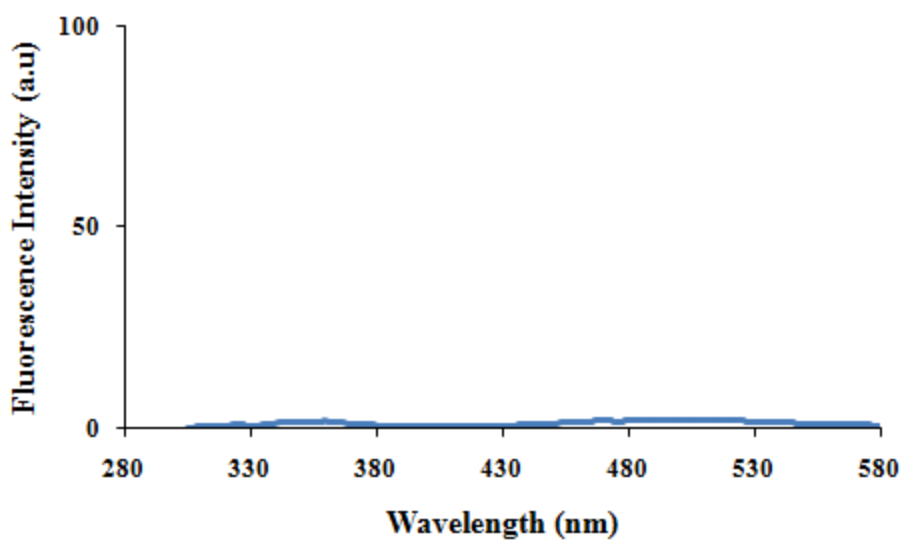


Figure S2: UV-vis absorption titration profile of compound **1** (10 μM) in the presence of 0-20 μM of Cu²⁺ ion.

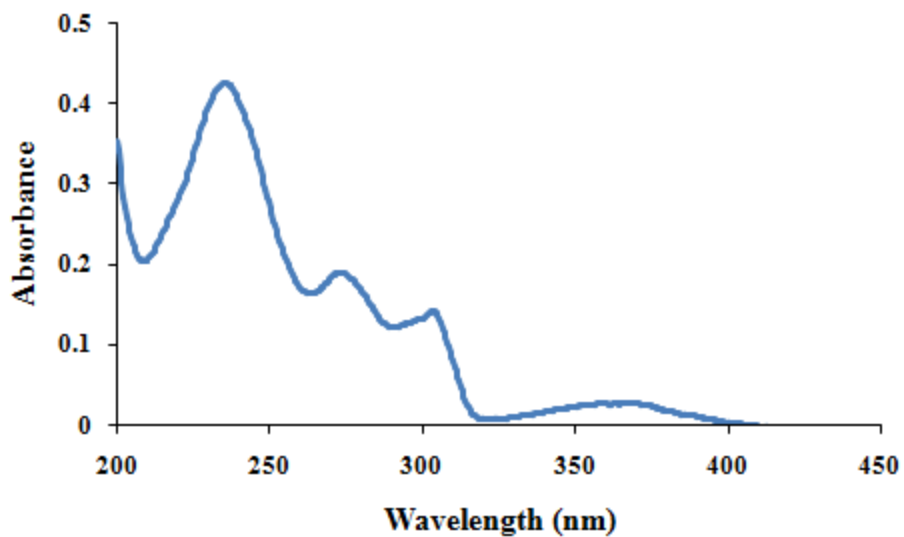


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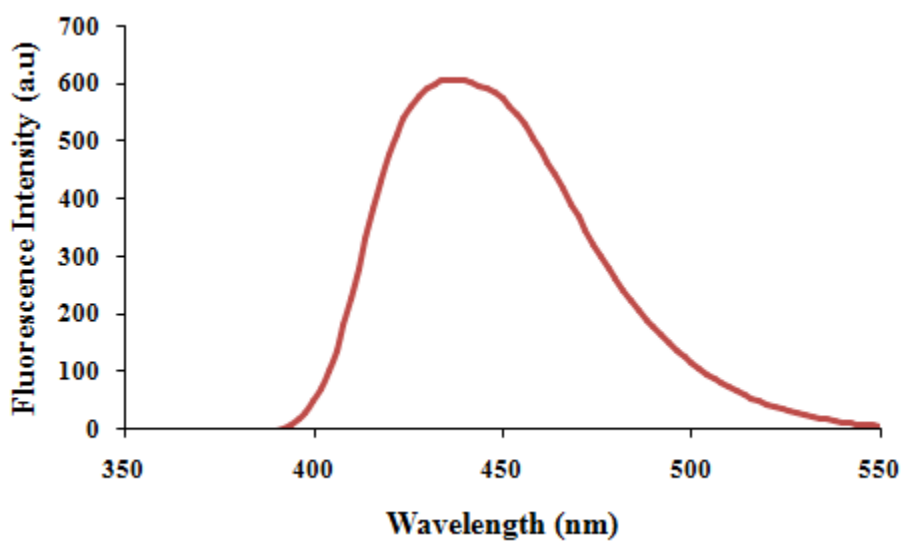


(b)

Figure S3 : (a) Absorption spectra of compound **5**, (b) Emission spectra of compound **5** ($\lambda_{ex} = 297$ nm).

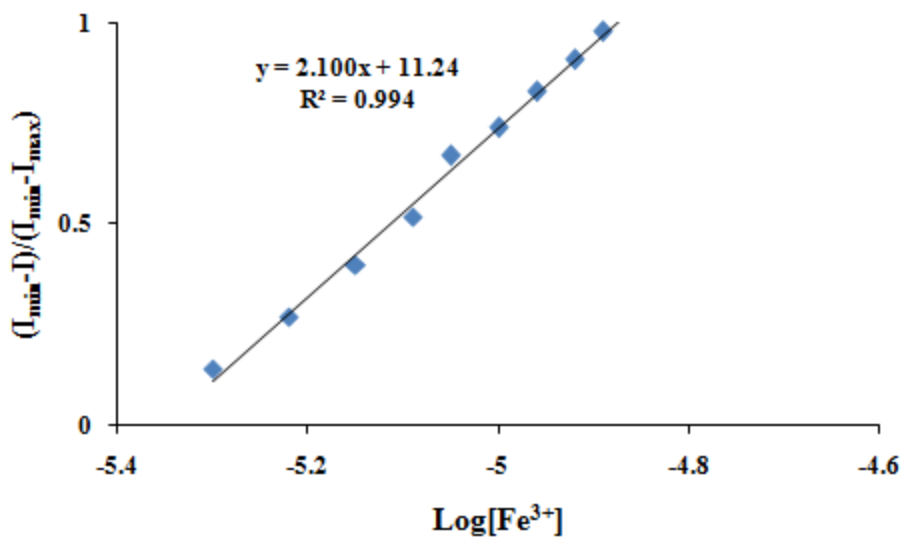


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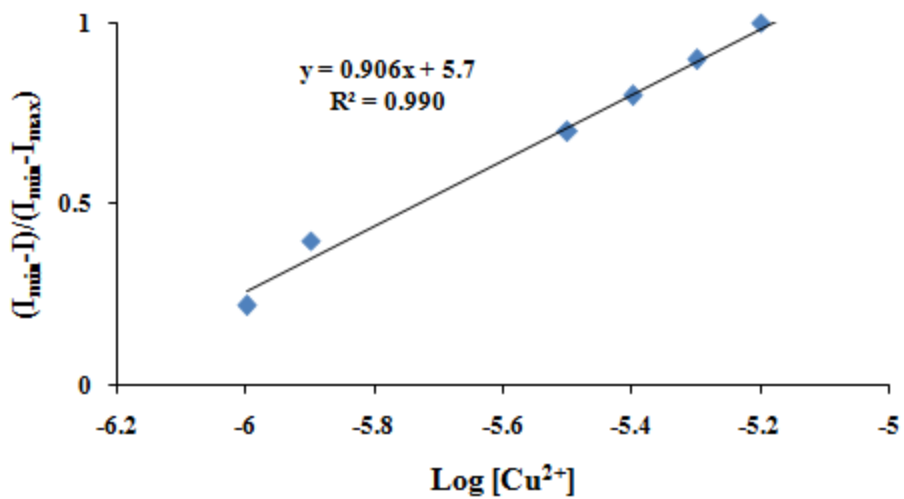


(b)

Figure S4 : (a) Absorption spectra of compound **6**, (b) Emission spectra of compound **6** (λ_{ex} = 297 nm).

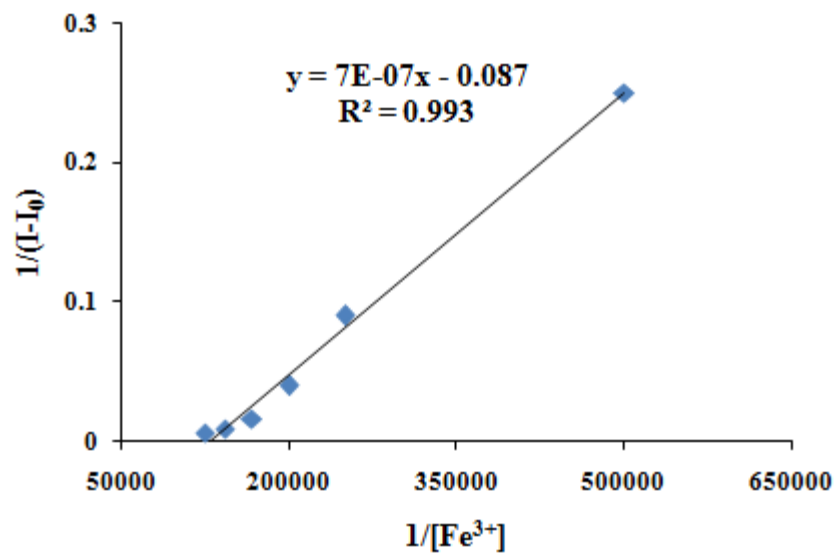


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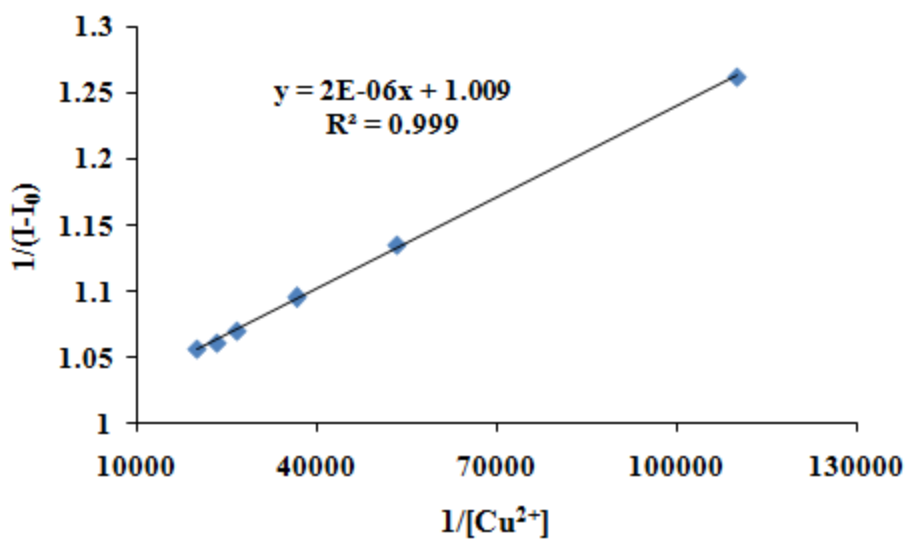


(b)

Figure S5: Limit of detection calculation² for (a) 1-Fe^{3+} and (b) 1-Cu^{2+} .

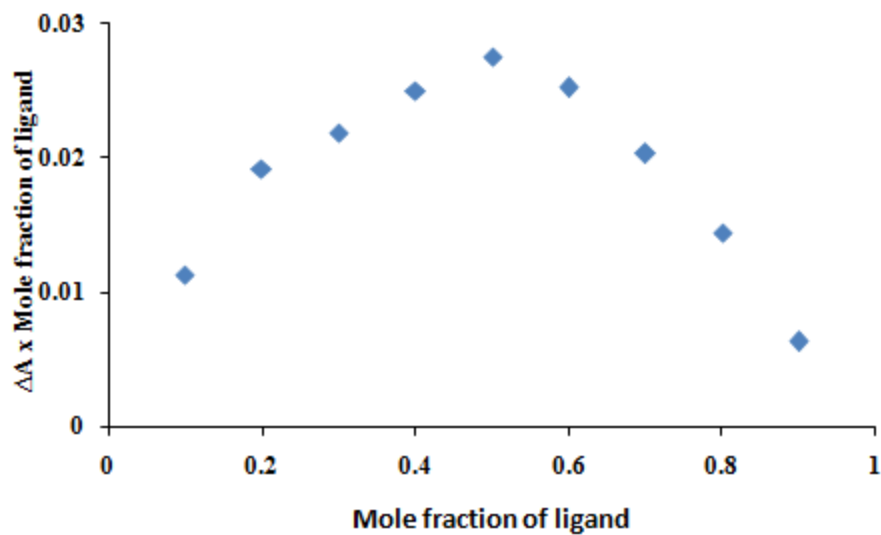


(a)

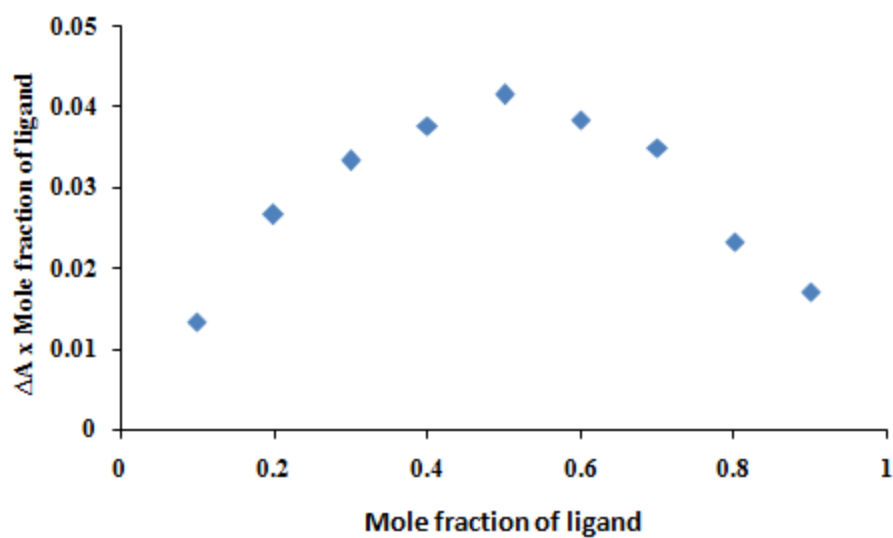


(b)

Figure S6: Binding constants calculation: (a) 1-Fe³⁺ and (b) 1-Cu²⁺ (from spectrofluometric titration using Benesi-Hildebrand equation).³



(a)



(b)

Figure S7: Job's plot ⁴ for (a) **1-Fe³⁺** and (b) **1-Cu²⁺** (absorbance values were recorded at 297 nm).

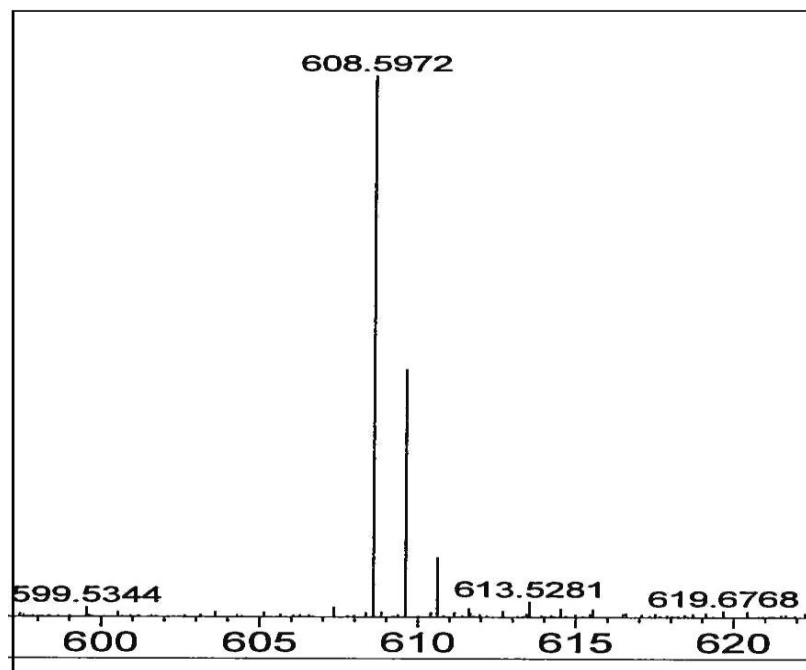


Figure S8(a): ESI- mass spectra of 1-Fe^{3+} complex

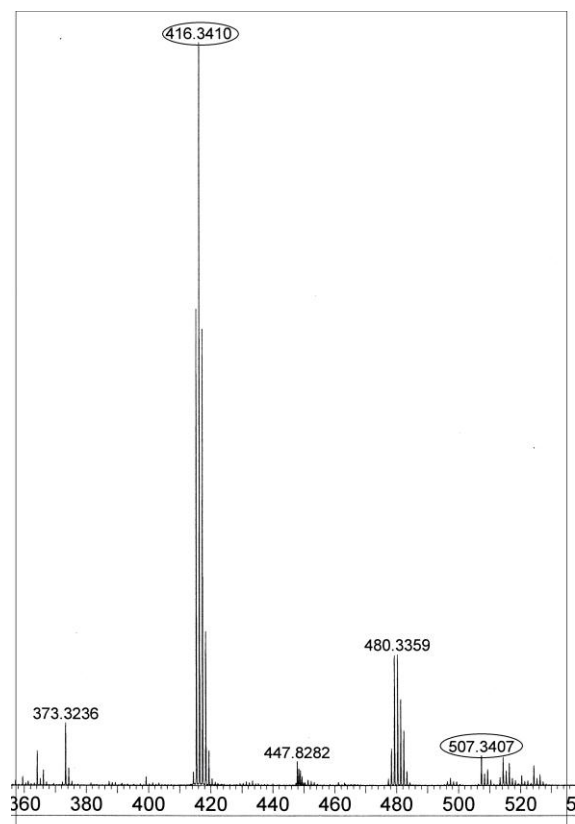


Figure S8(b): ESI- mass spectra of **1**-Cu²⁺ complex.

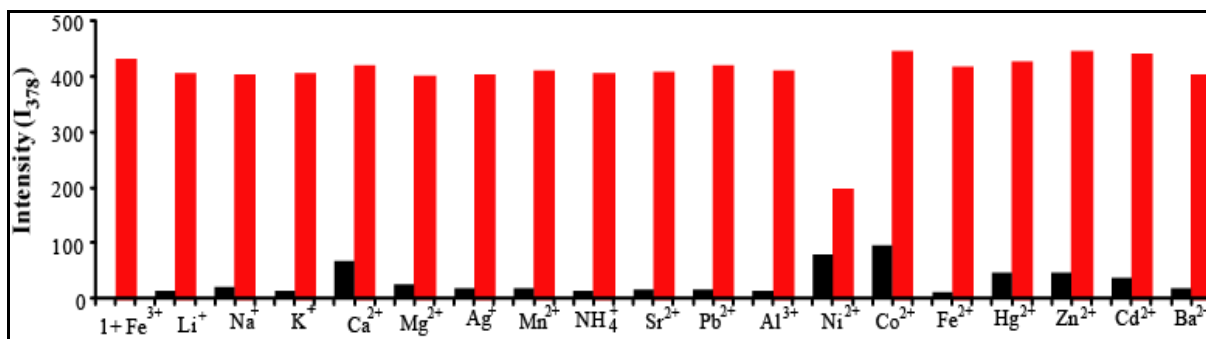


Figure S9a: Fluorescence response of compound **1** towards Fe³⁺ in the presence of excess (100 μM) of other cations. Red bars indicate the addition of Fe³⁺.

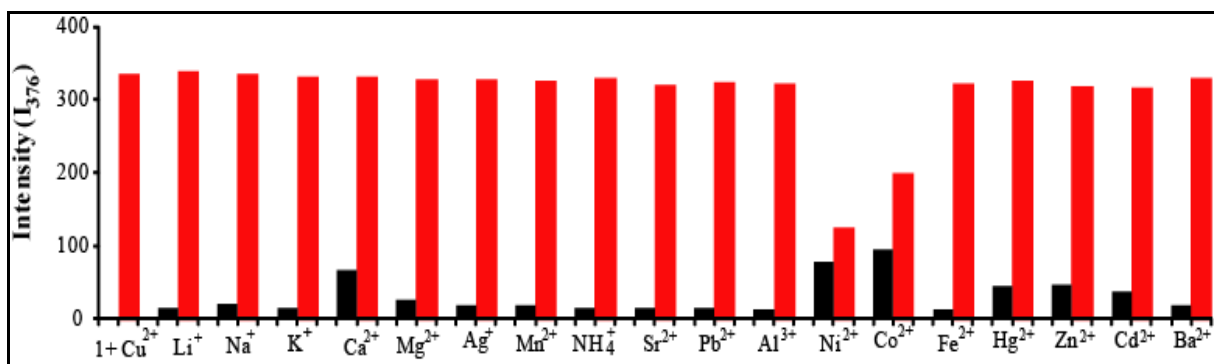


Figure S9b: Fluorescence response of compound **1** towards Cu²⁺ in the presence of excess (100 μM) of other cations. Red bars indicate the addition of Cu²⁺.

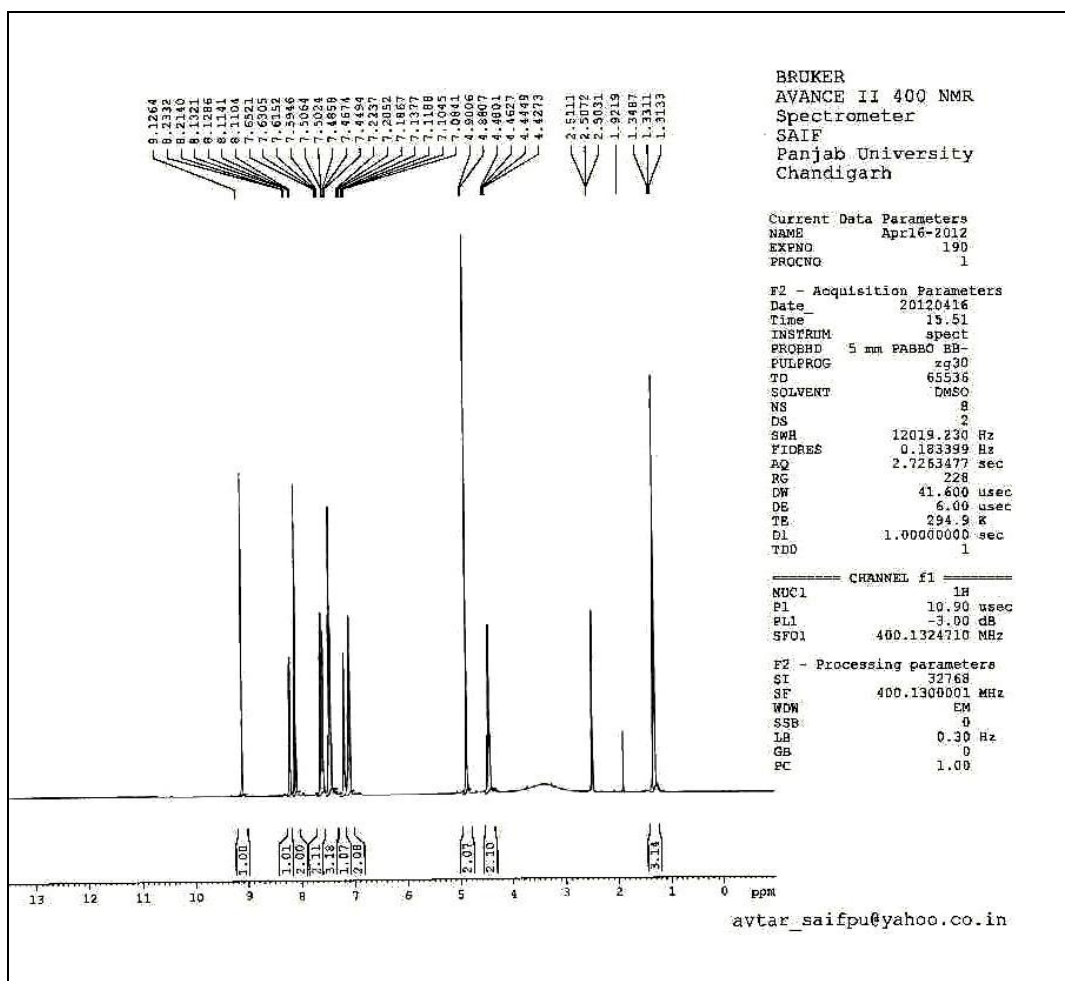


Fig S10: ¹H NMR of compound 1

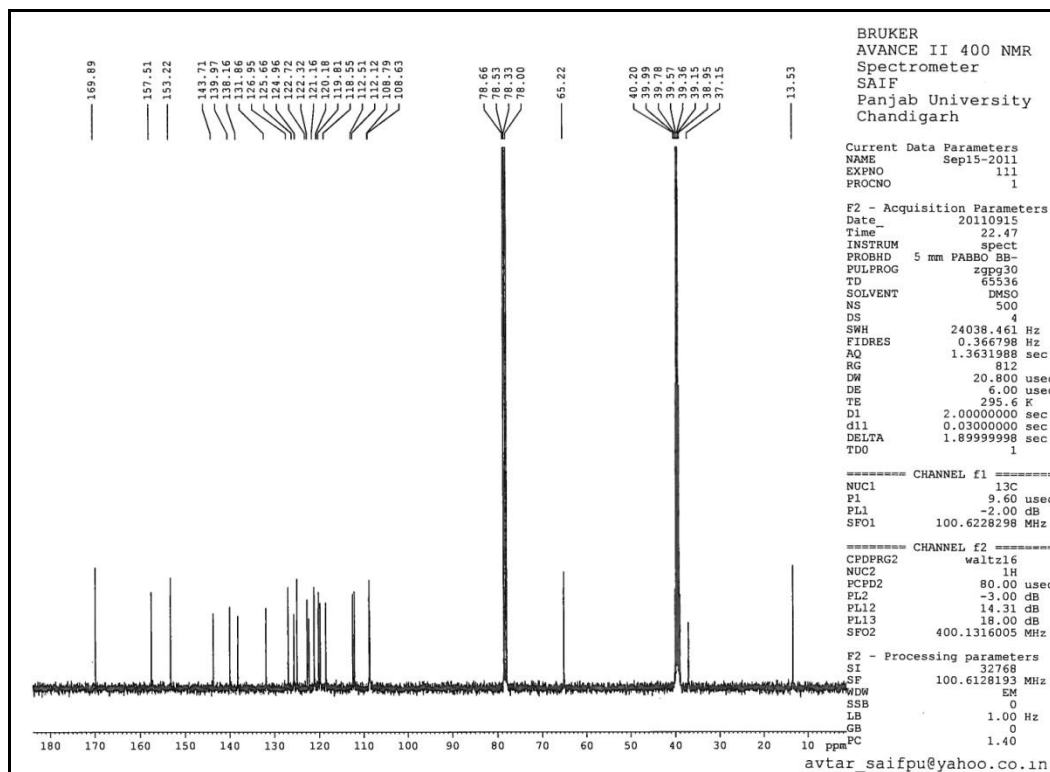


Fig S11: ^{13}C NMR of compound 1

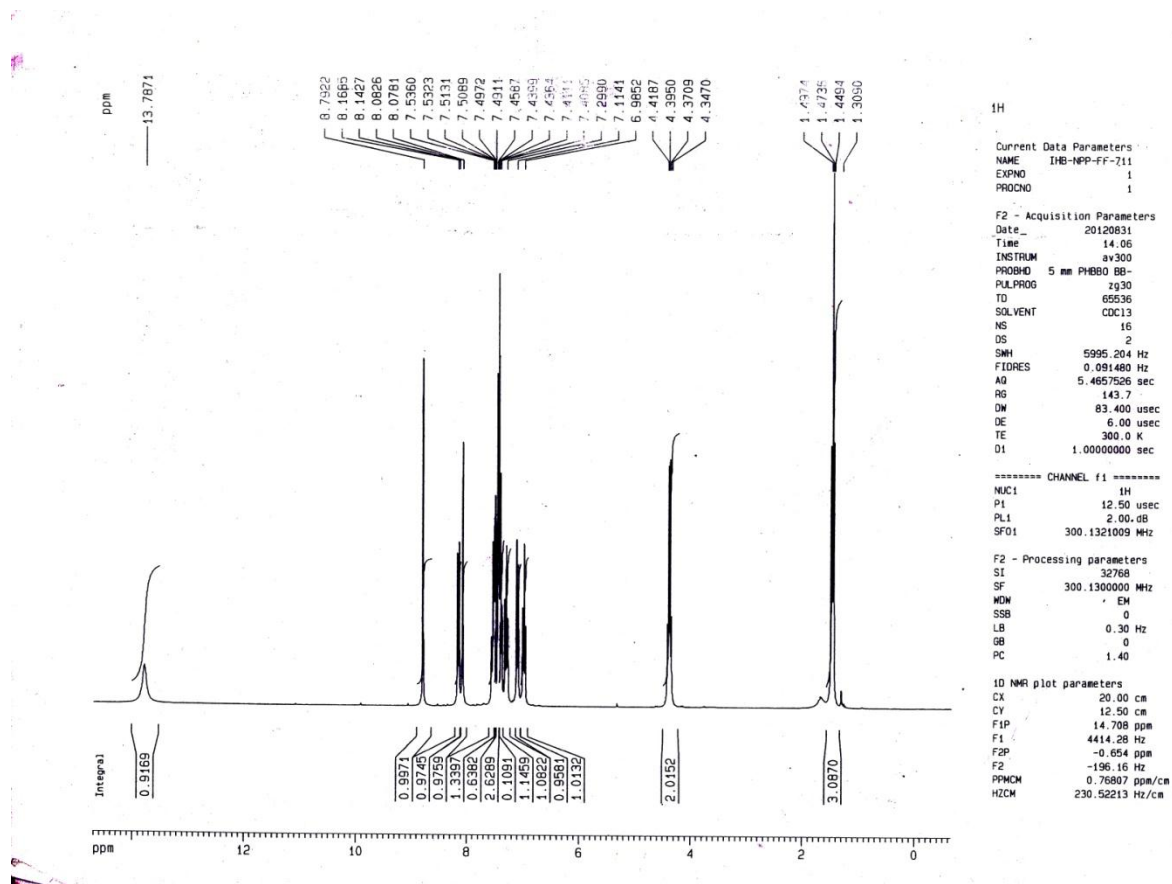
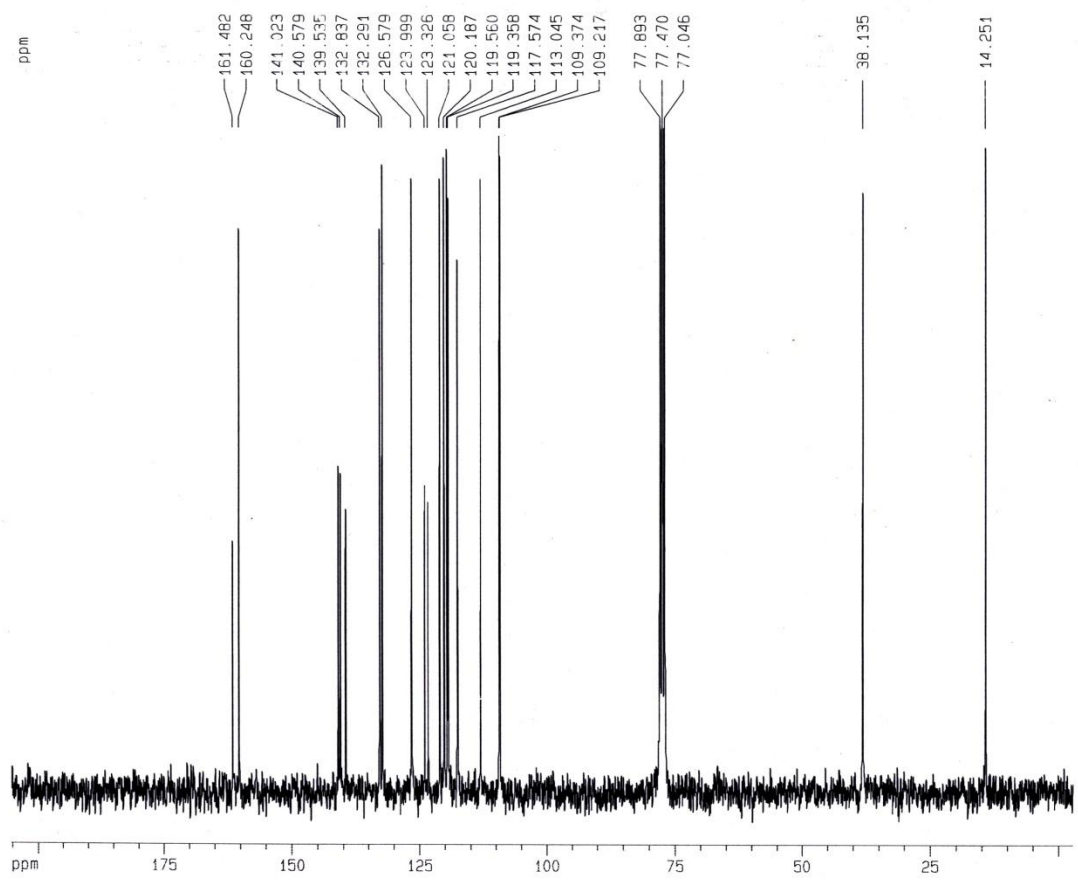


Fig S12: ¹H NMR of compound 5



Current Data Parameters
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EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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Time 14.50
INSTRUM av300
PROBHD 5 mm PHBBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 32768
DW 27.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

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NUC1 13C
P1 9.35 usec
PL1 -5.00 dB
SF01 75.4760204 MHz

===== CHANNEL f2 =====
CPOPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 18.00 dB
PL13 22.00 dB
SF02 300.1312005 MHz

F2 - Processing parameters
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WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
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CY 12.50 cm
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F1 15488.75 Hz
F2P -2.849 ppm
F2 -215.02 Hz
PPMCM 10.40429 ppm/cm
HZCM 785.18829 Hz/cm

Fig S13: ¹³C NMR of compound 5

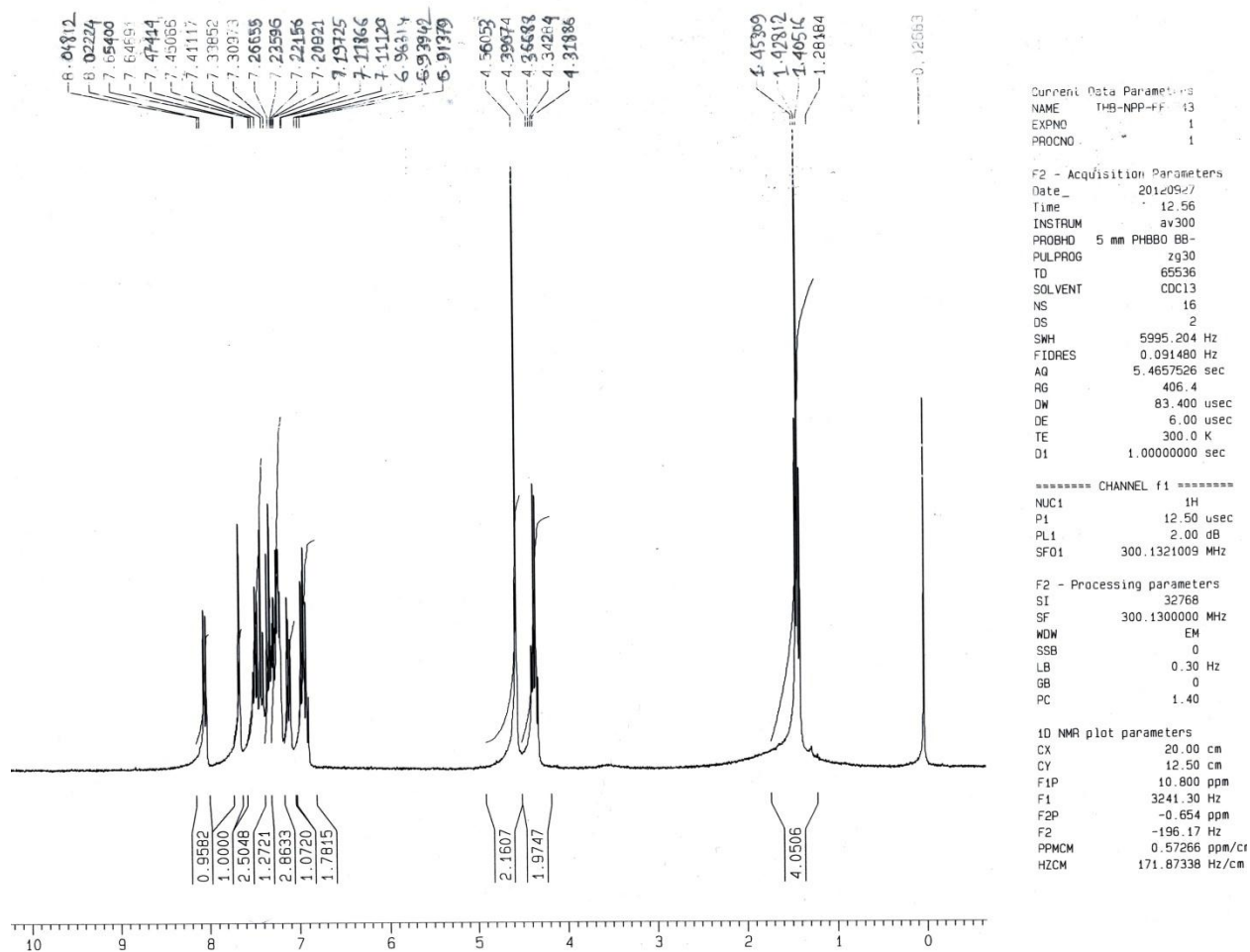


Fig S14: ^1H NMR of compound 6

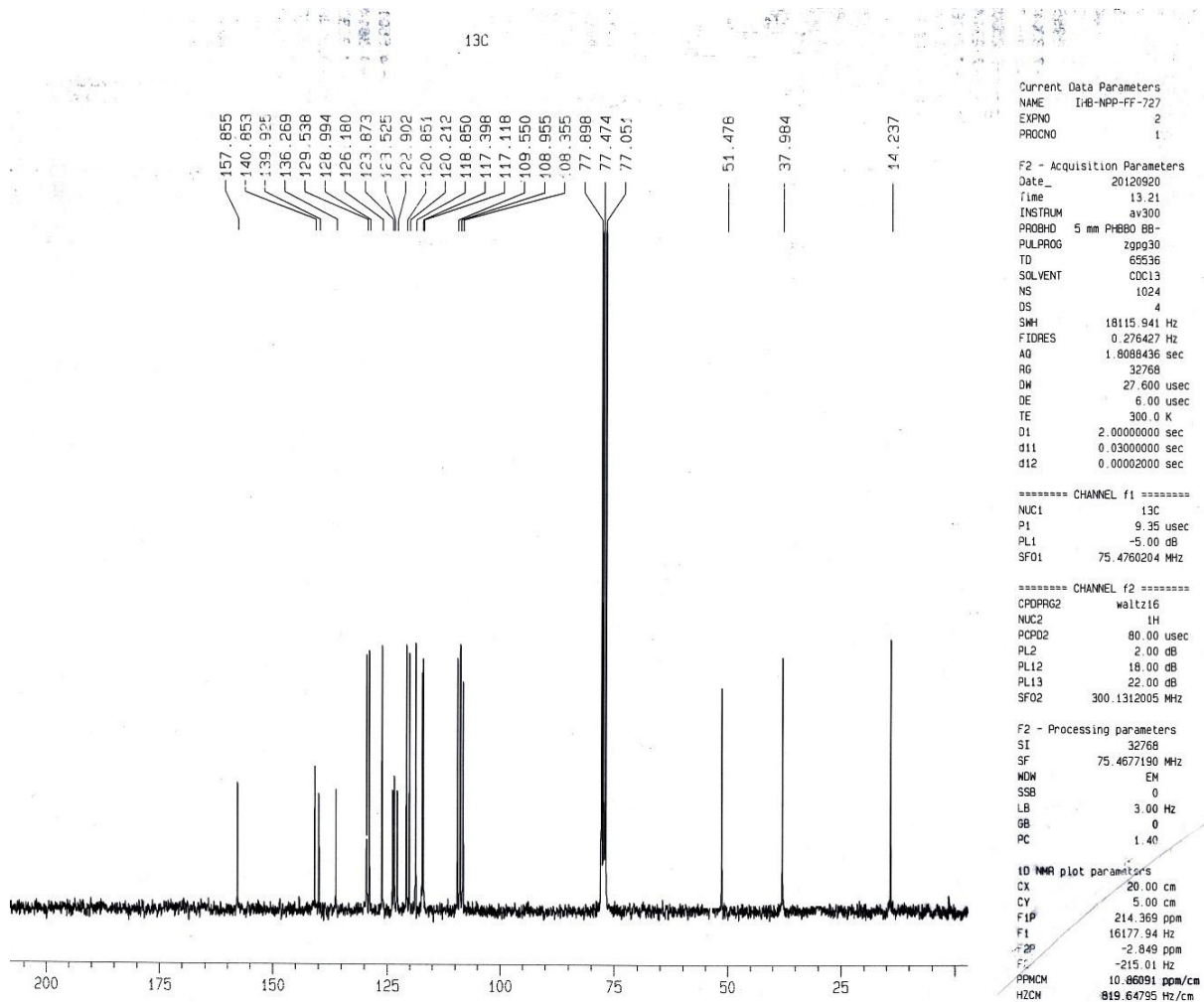


Fig S15: ^{13}C NMR of compound 6

References:

1. H. Liu, X. –B. Shao, M. –X. Jia, X. –K. Jiang, Z. –T. Li, G. –J. *Tetrahedron*, 2005, **61**, 8095-8100.
2. A. Caballero, R. Martinez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tárraga, P. Molina, J. Veciana, *J. Am. Chem. Soc.*, 2005, **127**, 15666-15667.
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