Supporting information

β-carboline-Imidazopyridine hybrid: A selective and sensitive optical sensor for sensing of copper and fluoride ions

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General procedure for the synthesis of compound 3:

To a stirred solution of L-tryptophan methyl ester **1** (5.0 g, 1.0 mmol) in DCM (methylene chloride) (40 mL), dimethoxy glyoxal (3.55 mL, 2.0 mmol) was added at room temperature. Thereafter in resulting reaction mixture, a solution of TFA 2.5 mL in 10mL DCM was added in small portions with help of dropping funnel and the reaction was continued at room temperature. Successive completion of the reaction (5 h) as monitored by TLC, the reaction mixture was poured into 10% aqueous $NaHCO_3$ solution under stirring with glass rod. As pH was adjusted to slight basic (7.3) the organic layer was separated and the aqueous layer was further extracted with $CHCl_3$ at least three times. Finally the organic layers were combined and washed with brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated to yield the product (9.0 g from 5.00 g) which was utilized for the next step without any purification.

General procedure for the synthesis of compound 4:

To a stirred solution of **3** (9.0 g, 1 mmol) in dry THF (80 mL), powdered $KMnO_4$ (13.5 g) was added in small portions and stirred vigorously at room temperature for 15 h. After completion of the reaction as observed with TLC, the dark blackish reaction mixture was filtered through a bed of celite under suction to obtain a colorless filtrate. The available residue over celite was further washed with THF (6 × 30 mL). The filtrate was concentrated *in vacuum* to yield the product which was finally washed with hexane to obtain a white solid product (8.5 g from 9.0 g).

General procedure for the synthesis of compound 5:

A mixture of **4** (6.50 g), in glacial acetic acid (10 mL) and water (15 mL), was reflux for 30 min at 100 ^{o}C. After completion of the reaction as monitored by TLC, the reaction mixture cooled down and added small portion of crushed ice. On adding crushed ice yellow precipate formed, in which excess of water was added and filtered the precipate followed by washing with aq. $NaHCO_3$ (10% solution) and dried in air to yield **5** as a yellow solid (93%; 5.22 g from 6.50 g). IR (KBr):ν_{max} 1703, 1691, 3533 cm^{-1}; (400 MHz, $CDCl_3$): δ 4.04 (S, 3H, CH_3), δ 7.33 (m, 1H, ArH), δ 7.56 (broad S, 2H, ArH), δ 8.14 (d, 1H, J= 8.1 Hz, ArH), δ 9.0 (s, 1H, ArH), δ 10.24 (broad S, 1H, NH), δ 10.37 (s, 1H, CHO); ^{13}C NMR (100 MHz, DMSO) δ 53.8, 113.19, 122.68, 130.9, 133.09, 135.65, 136.93, 138.93, 142.22, 166.50, 196.44.

General procedure for the synthesis of S1-S2:

To a stirred solution of **5** (methyl 1-formyl-9H-carbazole-3-carboxylate) (1 mmol) and 2-aminopyridine (1 mmol) in absolute ethanol (5 ml), $In(OTf)_3$ (10 mol%) was added under anhydrous conditions. Thereafter *t*-butylisocyanate/ethylisocynoacetate (1.1 mmol) was added to the reaction mixture and refluxes the content at 80-90 ^{o}C till the completion of the reaction. After the successive completion of the reaction as monitored by TLC a small portion of crushed ice was added, which resulting a yellow precipitation, thereafter to the reaction mixture excess water added and extracted the content with EtOAc (3 x 20 mL). Finally the organic layers were combined, washed with 10% $NaHCO_3$ (10 ml) and brine (10 ml). Combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum which resulting yellow solid of products (S1 & S2).

Compound S1: Yellow solid; yield (90%); mp 170°C; IR (KBr):ν_{max} 1401, 3133 cm^{-1}; TOF-MS ES+ m/z Calcd: 413.19. Found:428.14 . (M+CH_3); ^{1}H NMR (400 MHz, DMSO): δ 1.15 (S, 9H, *t*-butyl), δ 3.94 (s, 3H, $COOCH_3$), δ 6.03 (S, 1H, -NH), δ 6.93 (t, 1H, J =6.4 Hz, ArH), δ 7.28 (m, 2H, ArH), δ 7.58 (t, 1H, J = 8.4Hz, ArH), δ 7.64 (d, 1H, J= 8.4 Hz, ArH), δ 7.94 (d, 1H, J = 8.4Hz, ArH), δ 8.37 (d, 1H, J = 8.4Hz, ArH), δ 8.39 (d, 1H, J = 6.4 Hz, ArH), δ 8.84 (s, 1H, ArH), δ 12.0 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO) δ 30.24, 57.69, 61.15, 113.82, 116.15, 117.74, 121.66, 129.25, 130.19, 133.55, 134.84, 136.36, 138.45, 141.59, 141.75, 165.90.

Compound S2: Yellow solid; yield (92%); mp 176°C; IR (KBr): ν_{max} 1629, 1730, 3136 cm^{-1}; TOF-MS ES+ m/z Calcd: 443.16; Found: 458.12 ($M+CH_3$); ^1H NMR (400 MHz, DMSO): δ 1.3 (t, 3H, J = 8.0 Hz, $COOCH_2CH_3$), δ 3.89 (q, 2H, J =8.4 Hz, $COOCH_2CH_3$), δ 4.36 (m, 5H, $COOCH_3$+ -CH_2COO-), δ 6.87 (t, 1H, J =6.8Hz, -NH), δ 6.95 (m, 1H, ArH), δ 7.28 (m, 2H, ArH), δ 7.57 (m, 1H, ArH), δ 7.63 (d, 1H, J=8.4 Hz, ArH), δ 7.93 (d, 1H, J = 8.0 Hz, ArH), δ 8.36 (d, 1H, J= 8.4 Hz, ArH), δ 8.44 (d, 1H, J = 8.4 Hz, ArH), δ 8.79 (s, 1H, ArH), δ 11.92 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO) δ 14.79, 48.27, 60.67, 61.23, 112.64, 114.01, 115.77, 117.78, 120.80, 121.49, 122.38, 124.36, 128.89, 128.93, 131.83, 134.41, 136.11, 138.21, 140.12, 141.55, 166.06.

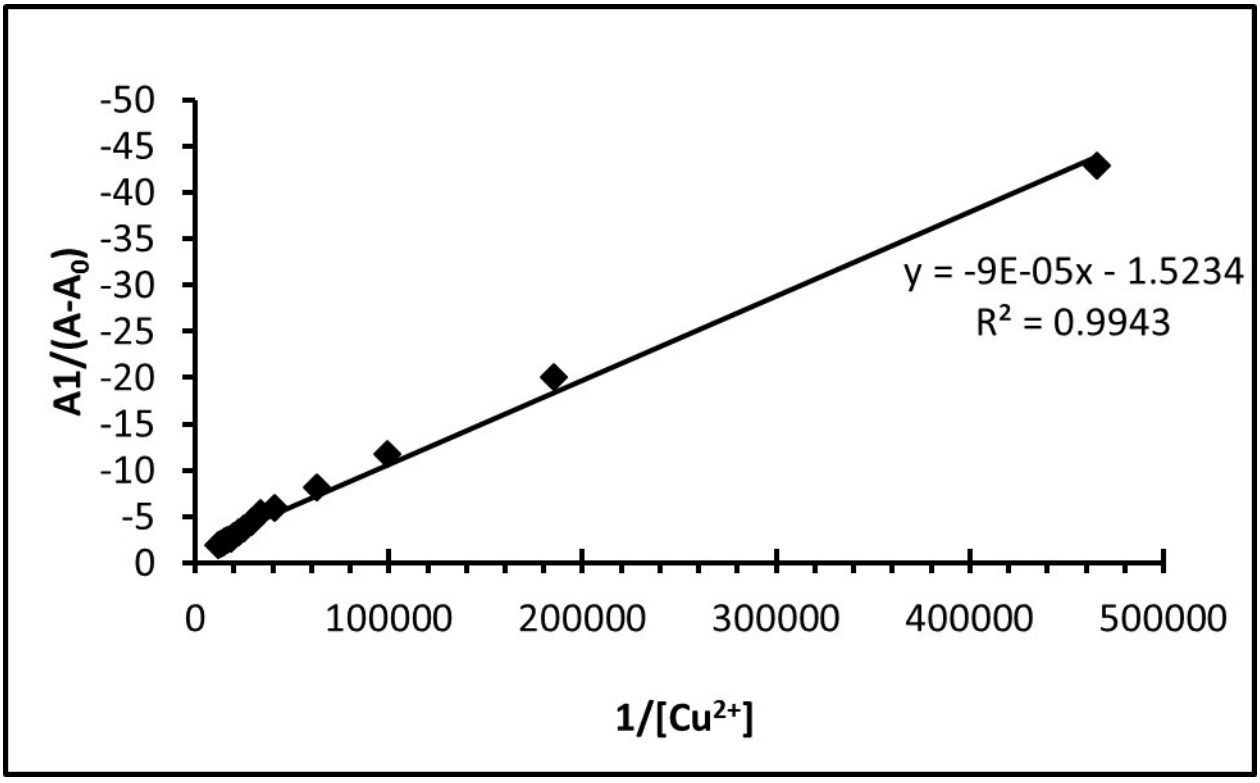


Figure S1. Benesi–Hildebrand plot of **S1** with Cu^{2+} ion+ (Binding constant, K= 1.67×10^4 M^{-1}).

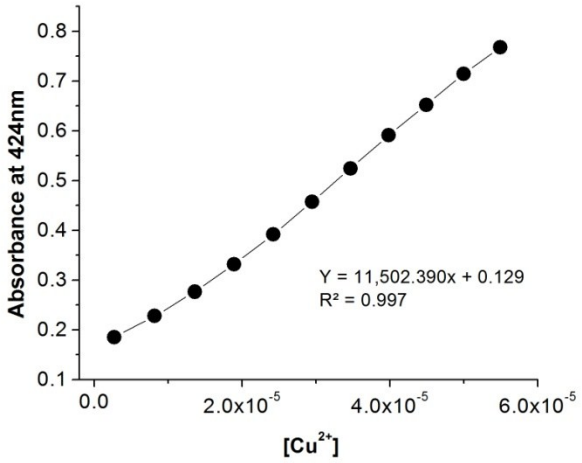


Figure S2. Determination of detection limit for Cu^{2+} ion. Absorbance Vs. Cu^{2+} concentration plot in **S1** solution.

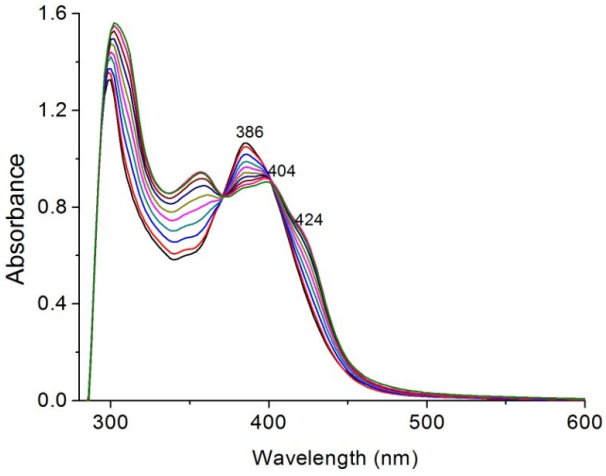


Figure S3. UV-visible titration of **S2** (8.3×10^{-5} M) with 0.0-2.0 equiv. of Cu^{2+} ion

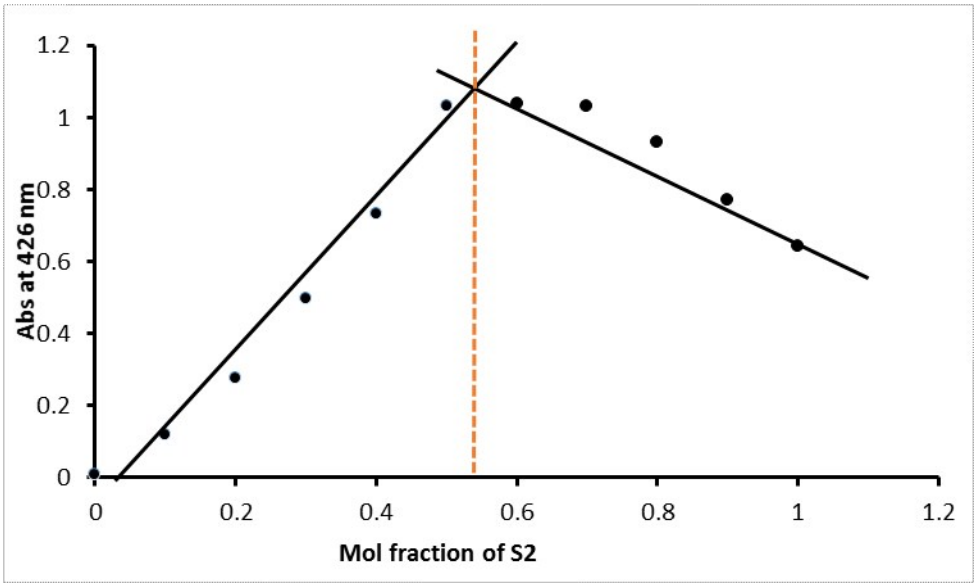


Figure S4. Job's plot titration for **S2** with Cu^{2+} ion (80 μM)

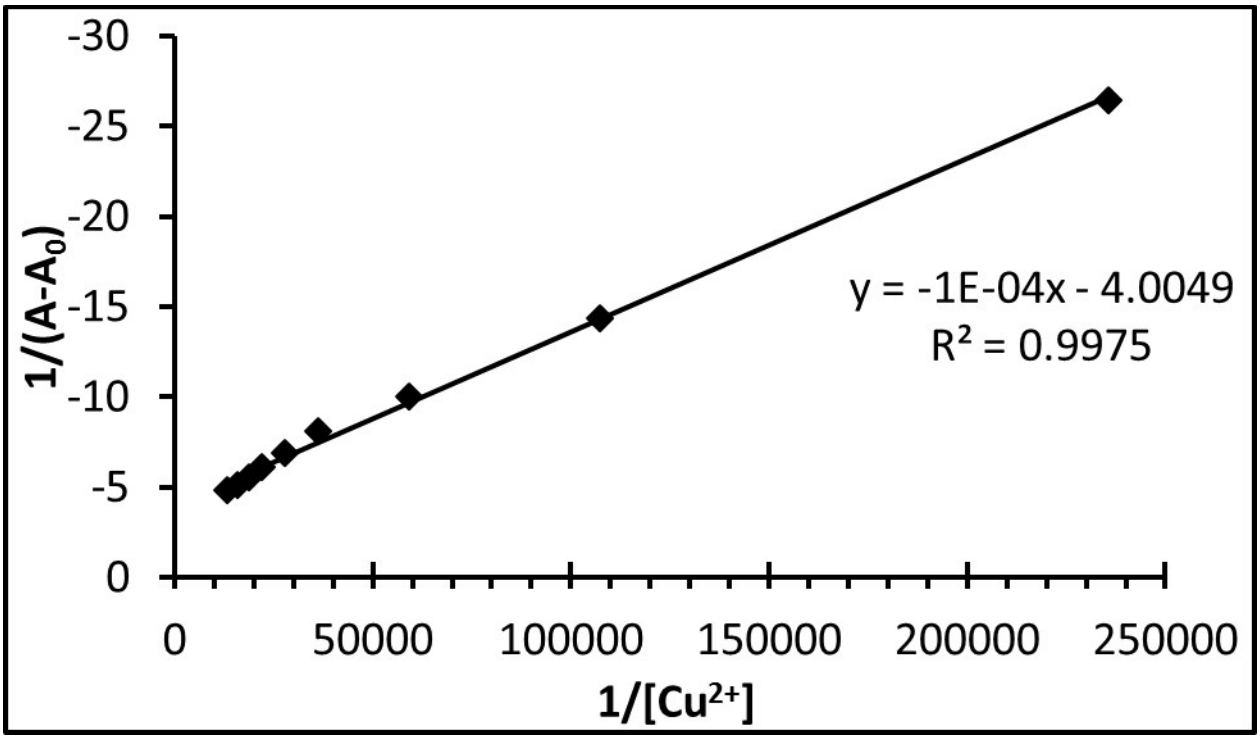


Figure S5. Benesi–Hildebrand plot **S2**-Cu^{2+} ion (Binding constant, K= 4.17×10^4 M^{-1}).

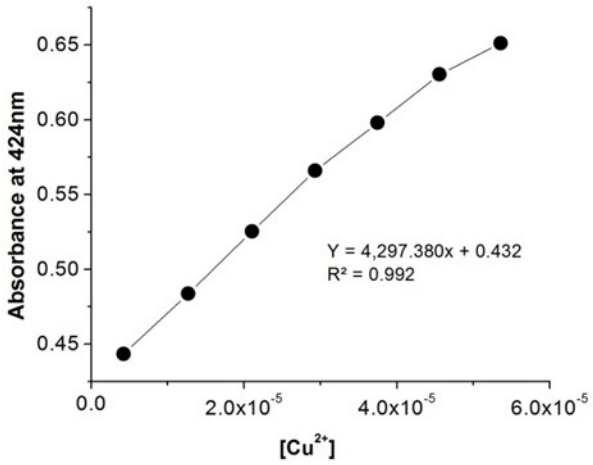


Figure S6. Determination of detection limit for Cu^{2+} ion. Absorbance Vs. Cu^{2+} concentration plot in **S2** solution.

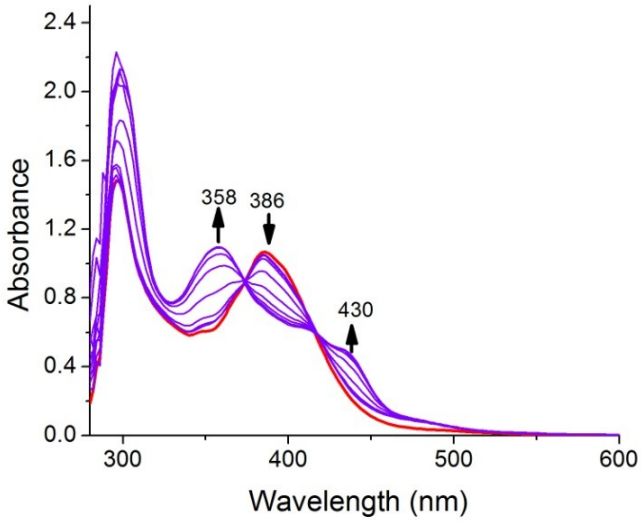


Figure S7. UV-Visible titration experiments of **S2** with F^- ion

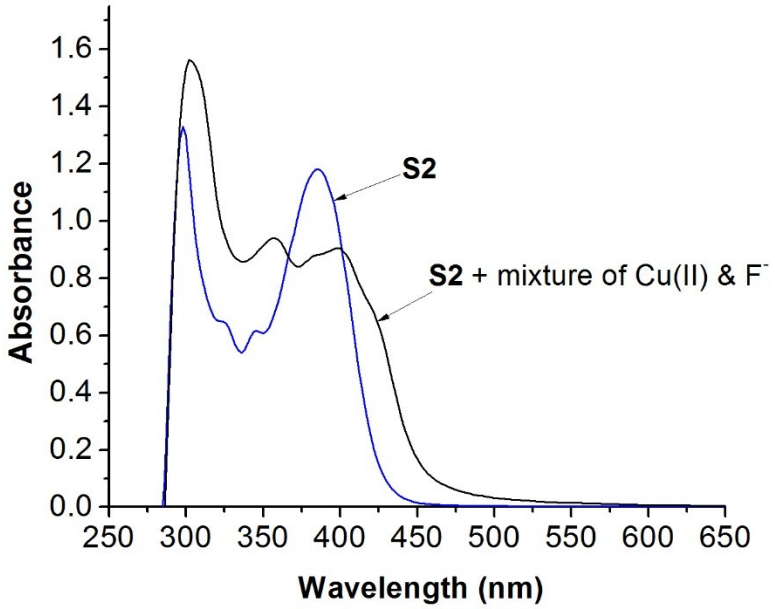


Figure S8. UV-Visible titration experiments of **S2** with mixture of Cu^{2+} and F^- ion

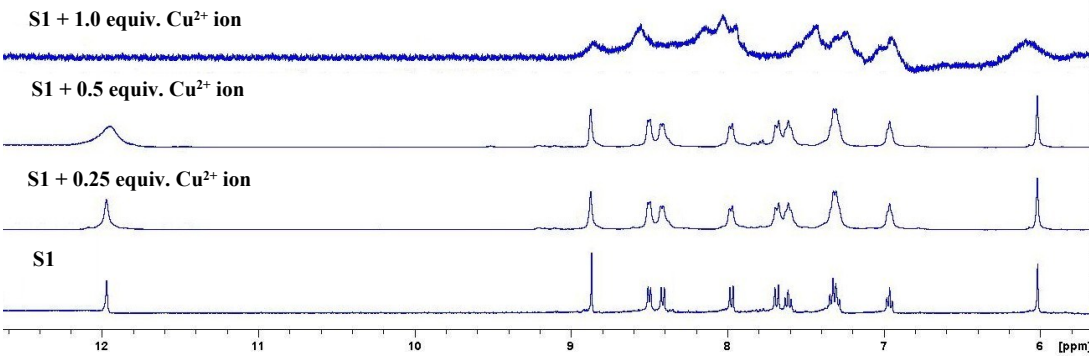


Figure S9. ^{1}H NMR titration of **S1** with various equivalent of Cu^{2+} ion

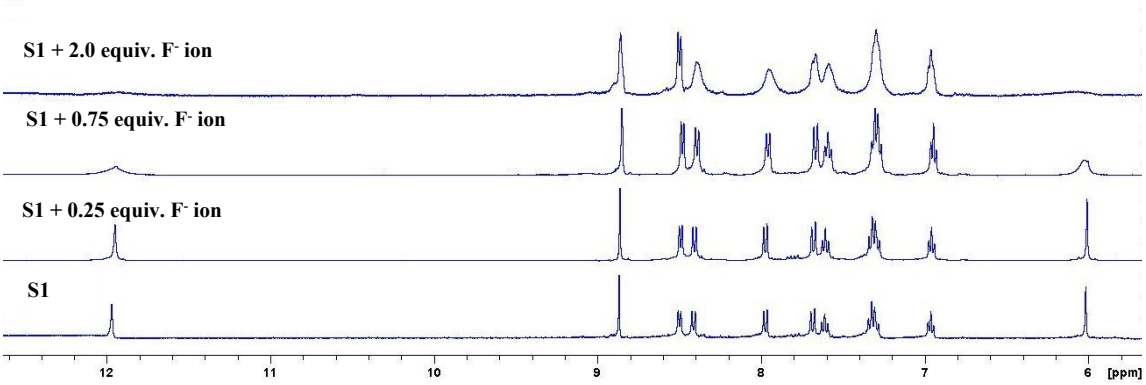


Figure S10. ^{1}H NMR titration of **S1** with various equivalent of F^{-} ion

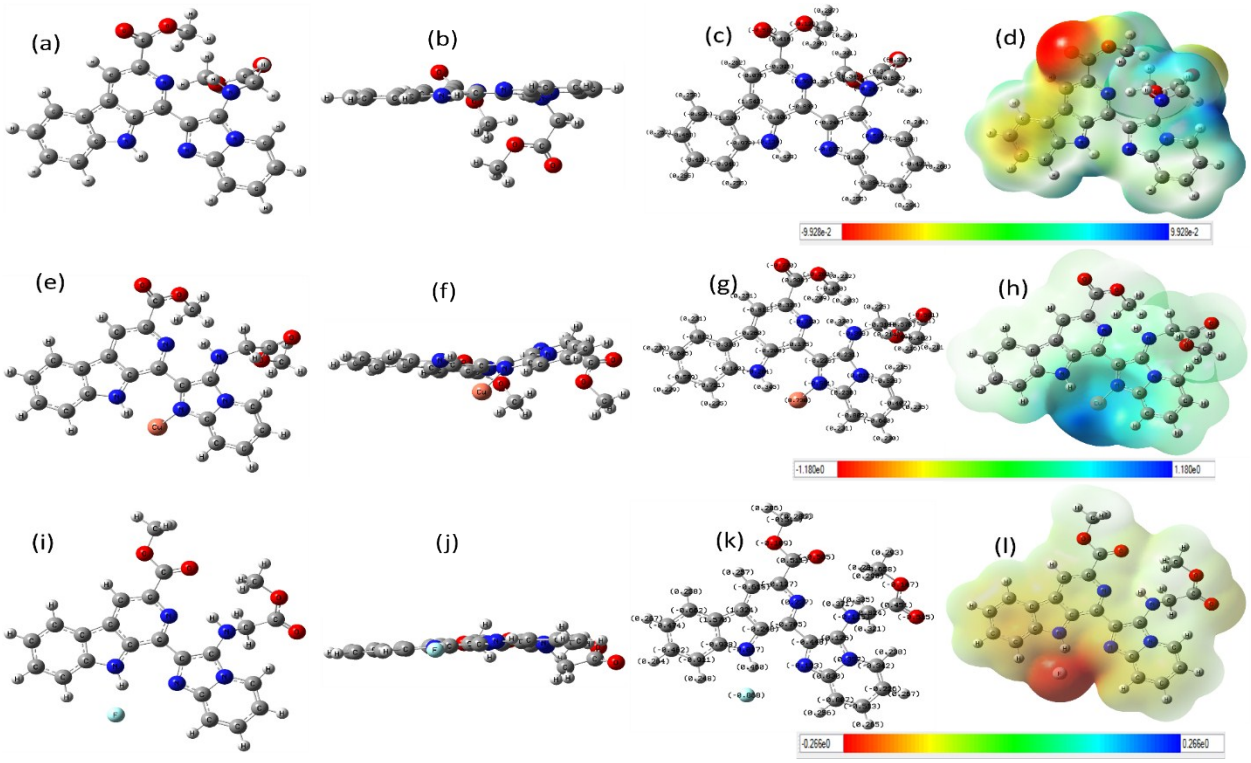
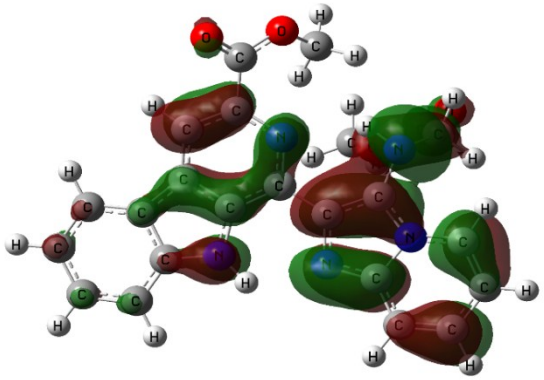
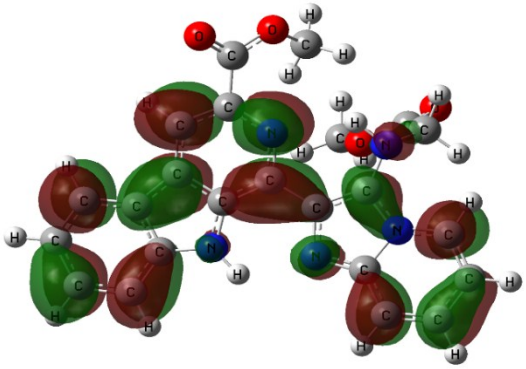


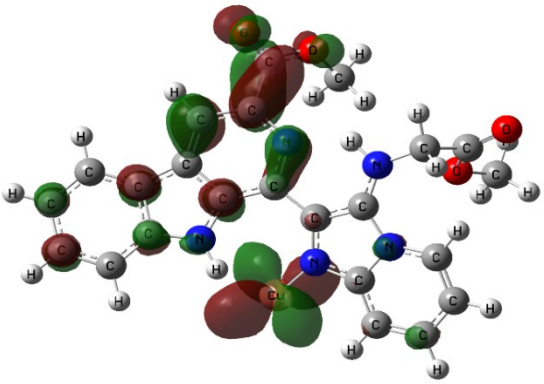
Figure S11. Optimized structures (**S2**: a, b; **S2**+Cu^{+2}: e, f; S2+F^{-}: i, j), Mulliken Charge analysis (c, g, and k), MEP map (d, h, and l) of **S2** **S**2+Cu^{+2} complex, **S2**+F^{-} complex respectively in acetonitrile solvent phase.



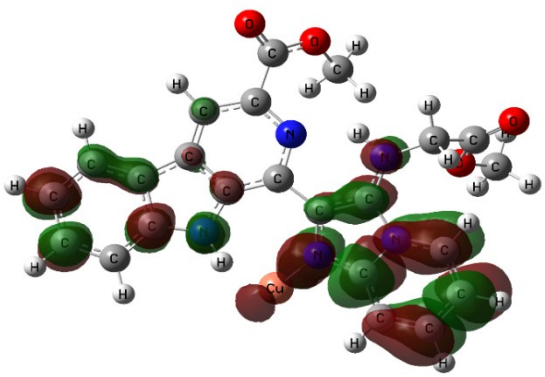
HOMO: S2



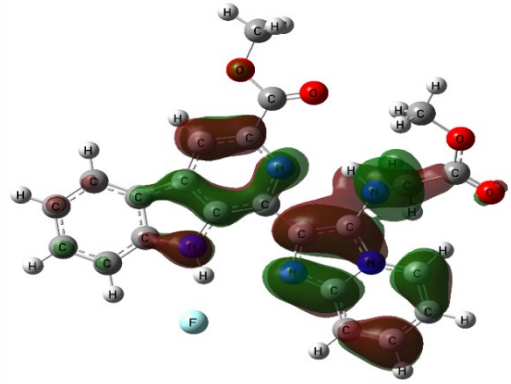
LUMO: S2



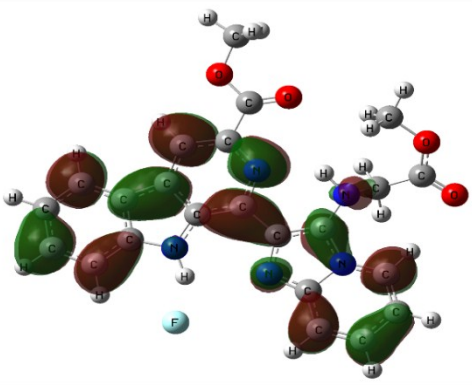
HOMO: S2+Cu^{+2}



LUMO: S2+Cu^{+2}



HOMO: S2+F^{-}



LUMO: S2+F^{-}

Figure S12. Frontier Molecular orbitals **S1** and complexes in solvent phase

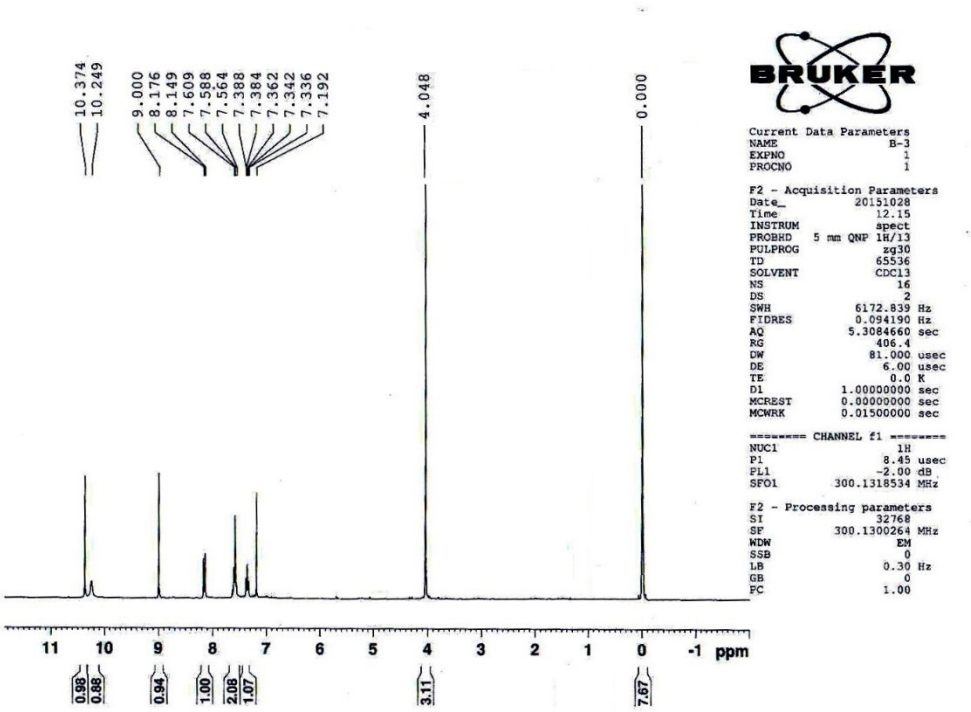


Figure S13. ^{1}H NMR spectrum of **5**

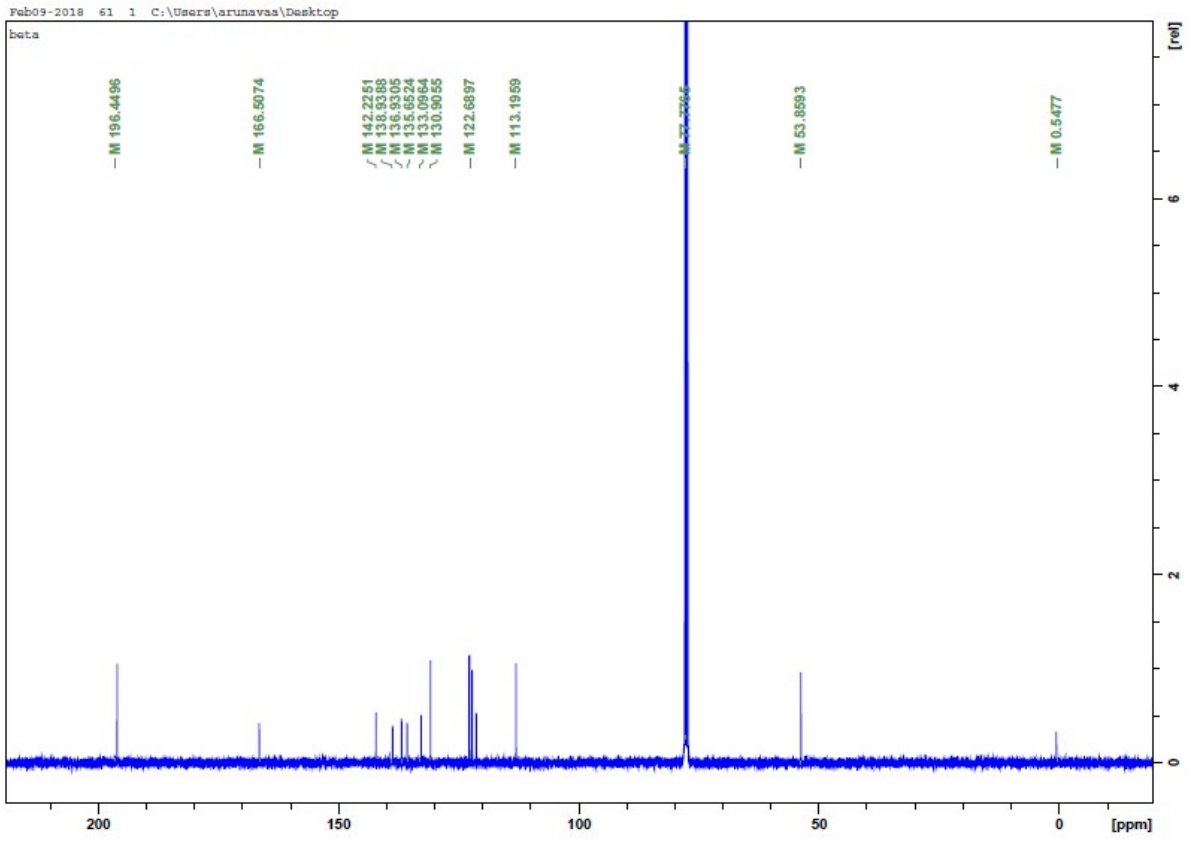


Figure S14. ^{13}C NMR spectrum of **5**

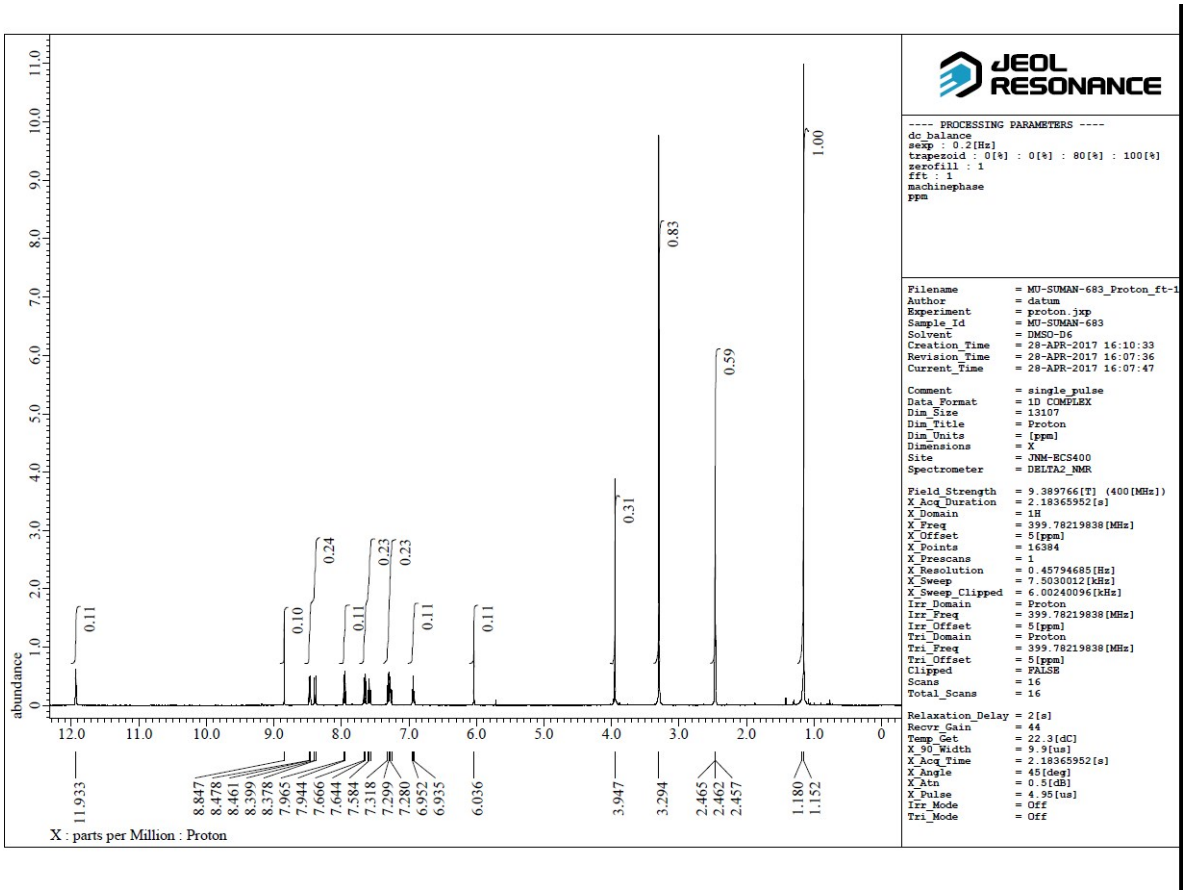


Figure S15. ^{1}H NMR spectrum of **S1**

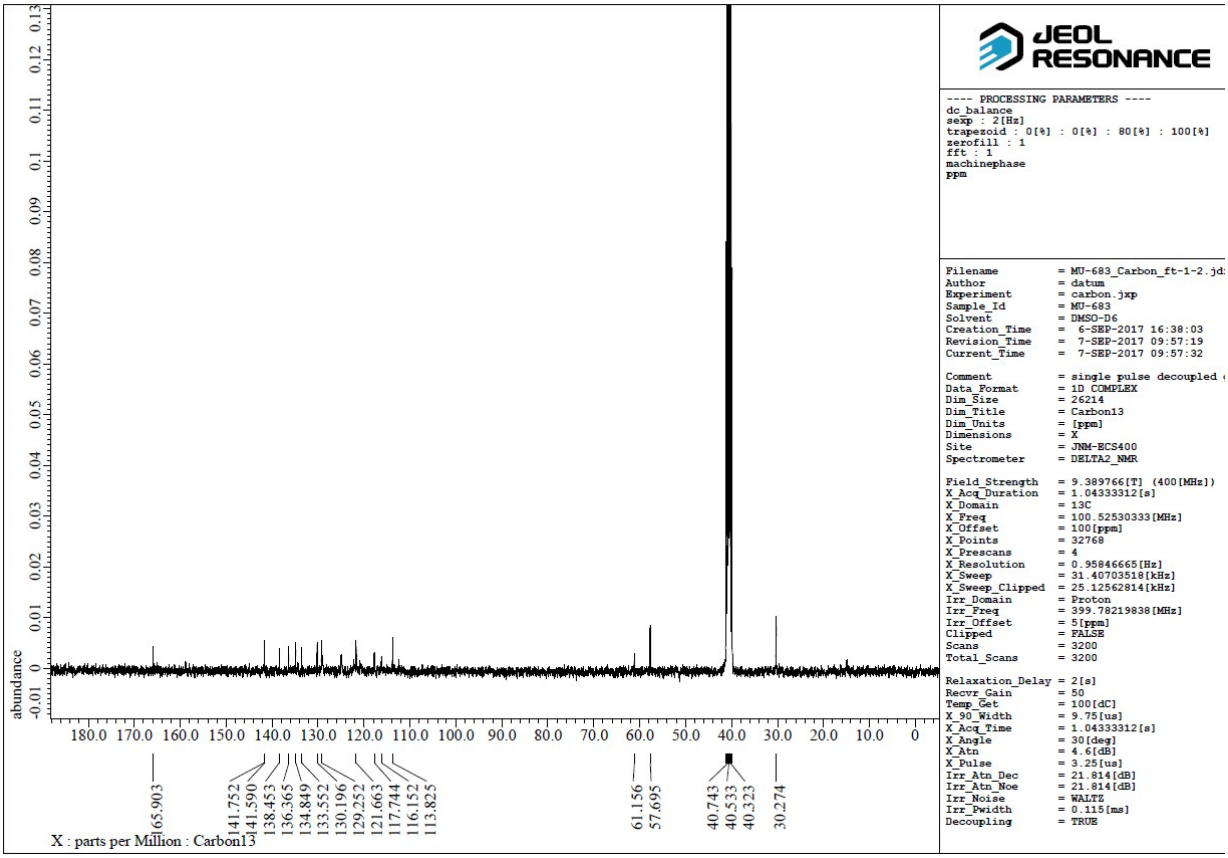


Figure S16. ^{13}C NMR spectrum of **S1**

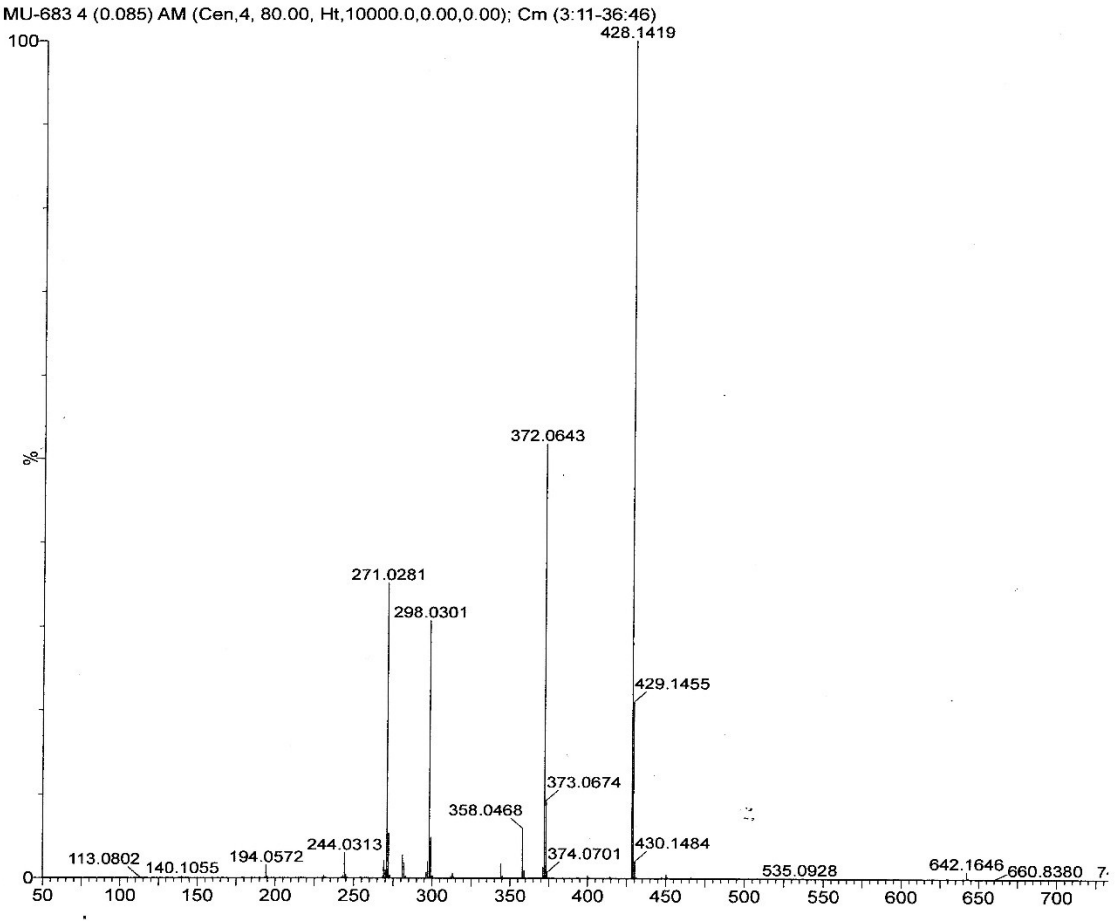


Figure S17. Mass spectrum of **S1**

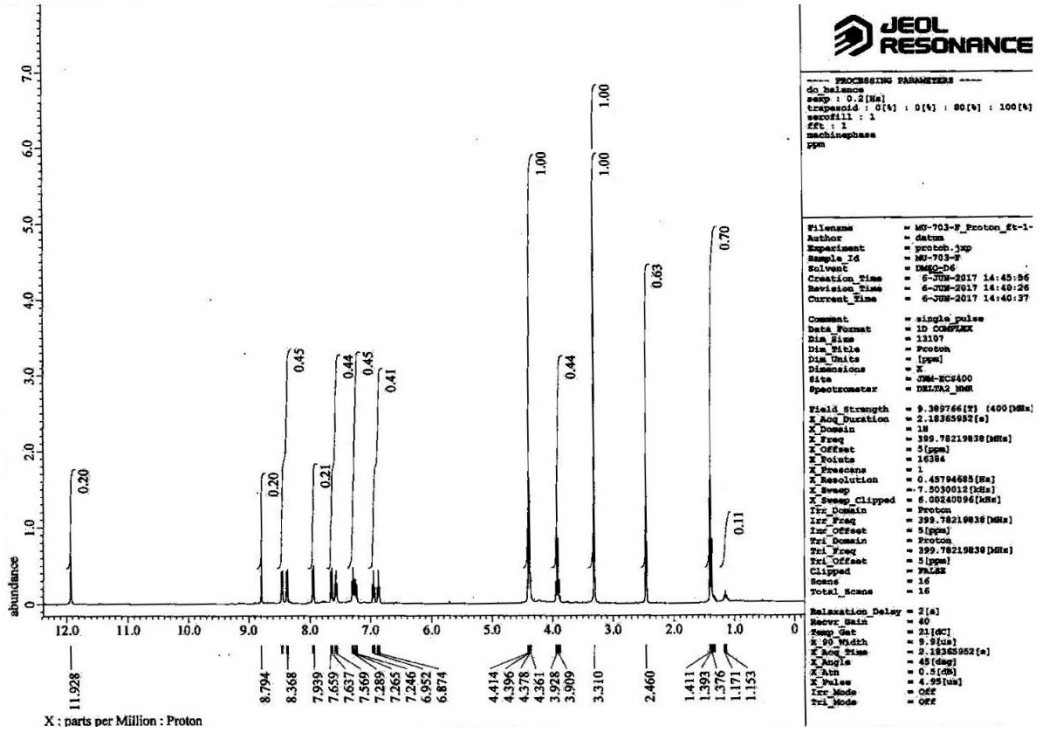


Figure S18. ^{1}H NMR spectrum of **S2**

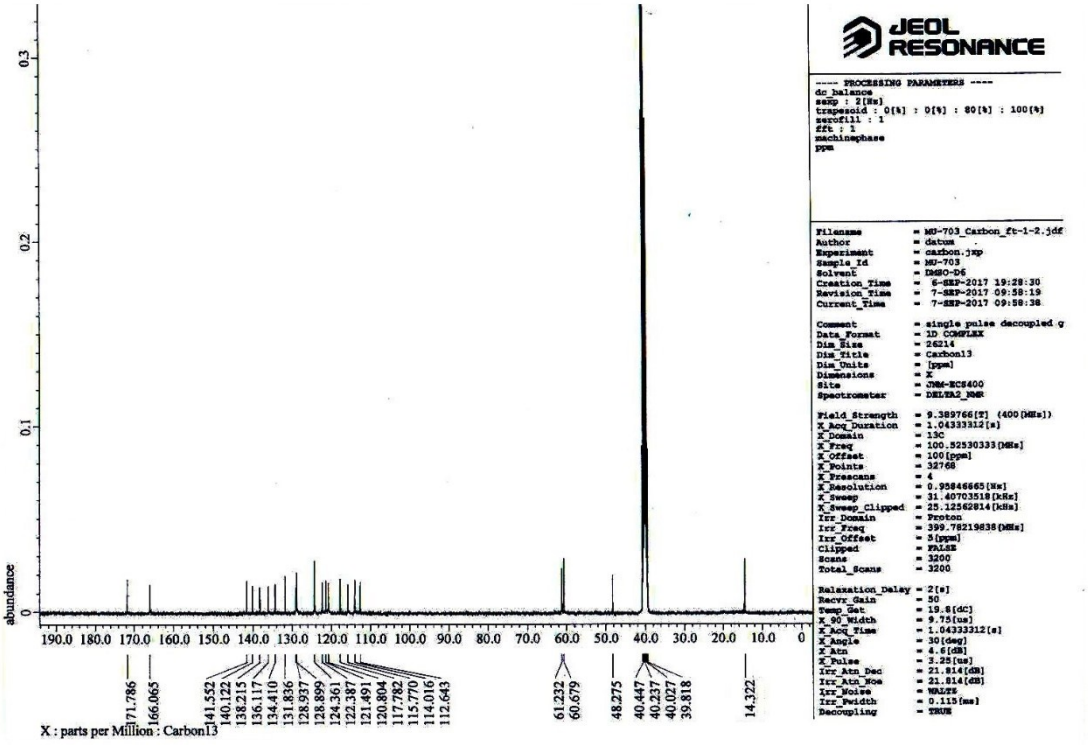


Figure S19. ^{13}C NMR spectrum of **S2**

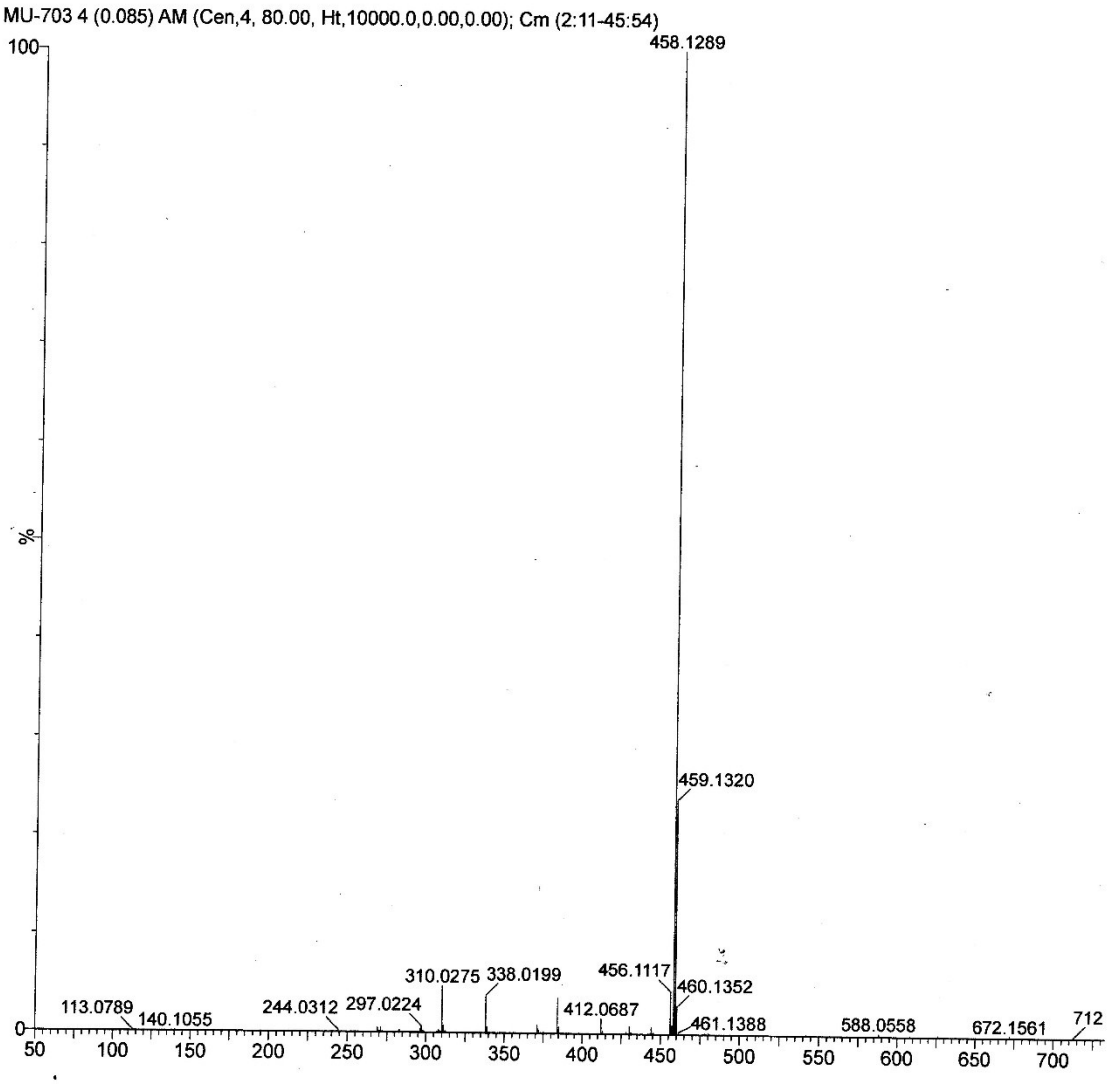


Figure S20. Mass spectrum of **S2**