Supporting Information

Reactive Probes for Ratiometric Detection of Co^{2+} and Cu^{+} Based on ESIPT Mechanism

Debabrata Maity, Vikash Kumar and T. Govindaraju*

New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P.O., Bangalore-560064, India. Fax: +91 80 22082627; Tel: +91 80 22082969.

E-mail: tgraju@jncasr.ac.in.

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General experimental procedure

All the solvents and reagents were obtained from Sigma-Aldrich and used as received unless otherwise mentioned. The solutions of metal ions were prepared from $Al(ClO_4)_3 \cdot 9H_2O$, $LiClO_4 \cdot 3H_2O$, $NaClO_4$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, $Ba(ClO_4)_2$, $Mn(ClO_4)_2 \cdot 6H_2O$, $Fe(ClO_4)_2 \cdot H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot H_2O$, $Ag(ClO_4)_2$, $Hg(ClO_4)_2$, $Pb(ClO_4)_2$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $[Cu(CH_3CN)_4]PF_6$ and $Zn(ClO_4)_2 \cdot 6H_2O$ respectively in CH_3CN. ^1H and ^{13}C NMR were recorded on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (in *$CDCl_3$*, tetramethylsilane as internal standard). HRMS were recorded on Agilent 6538 UHD Accurate-Mass Q-TOF LC/MS analyzer. Fluorescence spectra were recorded on a Perkin Elmer LS 55 spectrophotometer.

Synthesis of HBTCo and HBTCu

Synthesis of HBTCo. A mixture of 2-hydroxybenzothiazole (65 mg, 0.28 mmol) and **N_3O** ligand[1] (100 mg, 0.34 mmol) was dissolved in DMF (10 mL). K_2CO_3 (400 mg, 2.8 mmol) was added and the resulting mixture was heated at 90 °C for overnight. After cooling to room temperature, solvent was evaporated in vacuo. The residue in H_2O (50 mL) was extracted with of CH_2Cl_2 (3×20 mL). This organic layer was washed with brine, dried over Na_2SO_4, solvent was evaporated in vacuo and the residue was purified on basic alumina column (solvent. CH_2Cl_2/MeOH: 95/5) to obtain the product as light yellow oil (121 mg, yield 88%). ^1H NMR (400 MHz, *$CDCl_3$*) δ 2.90 (2H, t, *J* = 5.2 Hz), 3.69 (2H, t, *J* = 5.2 Hz), 3.96 (4H, d, *J* = 4 Hz), 5.47 (2H, s), 7.11-7.16 (3H, m), 7.27-7.31 (2H, m), 7.34-7.43 (2H, m), 7.47-7.51 (2H, m), 7.54-7.58 (1H, td, *J* = 6 Hz, 1.6 Hz), 7.63 (1H, t, *J* = 7.6 Hz), 7.88 (1H, d, *J* = 8 Hz), 8.09 (1H, d, *J* = 8 Hz), 8.51-8.55 (2H, m) (*Note: HBTCo contains one exchangeable alcoholic proton. Therefore the signal for this proton not appeared in the spectrum*). ^{13}C NMR (400 MHz, *$CDCl_3$*) δ 56.8, 59.7, 60.0, 60.1, 71.4, 113.1, 120.2, 121.2, 121.6, 122.1, 122.2, 122.7, 122.8, 123.0, 124.6, 125.9,

129.9, 131.8, 136.0, 136.5, 137.4, 149.0, 152.2, 155.8, 155.9, 159.1, 159.2, 163.0. HRMS: observed m/z = 505.1667 $[M + Na]^+$ and calculated m/z = 505.1674 for $C_{28}H_{26}N_4NaO_2S$.

Synthesis of HBTCu. A mixture of 2-hydroxybenzothiazole (80 mg, 0.35 mmol) and **N_4** ligand[2] (143 mg, 0.42 mmol) was dissolved in DMF (10 mL). K_2CO_3 (490 mg, 3.5 mmol) was added and the resulting mixture was heated at 90 °C for overnight. After cooling to room temperature, the solvent was evaporated in vacuo. The residue in H_2O (50 mL) was extracted with of CH_2Cl_2 (3×20 mL). This organic layer was washed with brine, dried over Na_2SO_4, evaporated in vacuo and the residue was purified on neutral alumina column (solvent. ethyl acetate) to obtain the product as light yellow oil (168 mg, yield 90%). ^{1}H NMR (400 MHz, *CDCl₃*) δ 3.92 (4H, s), 3.93 (2H, s), 5.46 (2H, s), 7.08-7.16 (4H, m), 7.33-7.39 (2H, m), 7.46-7.49 (2H, m), 7.50-7.70 (6H, m), 7.86 (1H, d, *J* = 7.6 Hz), 8.08 (1H, d, *J* = 8 Hz), 8.50 (1H, dd, *J* = 6.4 Hz, 1.6 Hz), 8.53 (2H, d, *J* = 4.4 Hz). ^{13}C NMR (400 MHz, *CDCl₃*) δ 59.0, 59.2, 70.6, 76.1, 112.0, 119.0, 120.2, 120.5, 121.0, 121.1, 121.6, 121.8, 121.9, 123.6, 124.9, 128.8, 130.7, 135.0, 135.4, 136.3, 148.1, 151.2, 154.7, 154.9, 158.1, 158.3, 162.0. HRMS: observed m/z = 530.2014 $[M + H]^+$ and calculated m/z = 530.2015 for $C_{32}H_{28}N_5OS$.

General method for measurements of photophysical properties

Fluorescence spectra were recorded on a Perkin Elmer model LS 55 spectrophotometer. 1 cm cells were used for emission titration. For fluorescence titrations stock solution of ligands **HBTCo** and **HBTCu** were prepared (c = 2000 μM) in CH_3CN. The solutions of guest cations were prepared in CH_3CN in the order of 10^{-3} M. Working solutions of **HBTCo** and **HBTCu** and metal ions were prepared from the stock solutions. Excitation was carried out at 350 nm for **HBTCo** and **HBTCu** with 10 nm excitation and 10 nm emission slit widths.

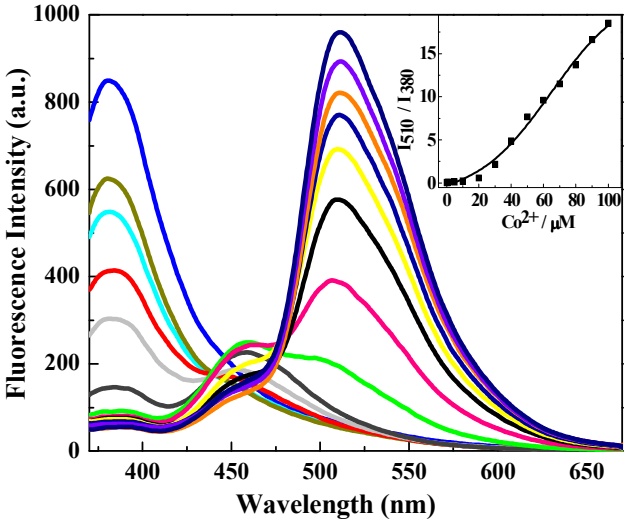


Figure S1. Fluorescence responses of **HBTCo** (20.0 μM) upon addition of 0.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0 μM of Co^{2+} after 2 h in aqueous solution (50 mM HEPES, pH 7.2, 2 mM GSH) (λ_{ex} = 350 nm).

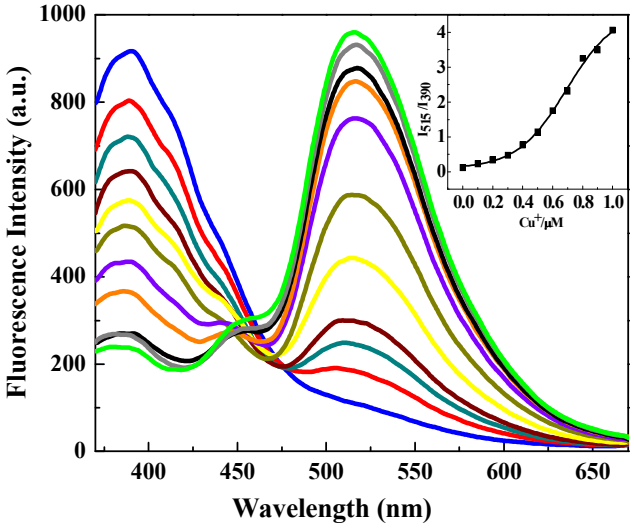


Figure S2. Fluorescence responses of **HBTCu** (20.0 μM) upon addition of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 μM of Cu^+ after 2 h in aqueous solution (50 mM HEPES, pH 7.2, 2 mM GSH) (λ_{ex} = 350 nm).

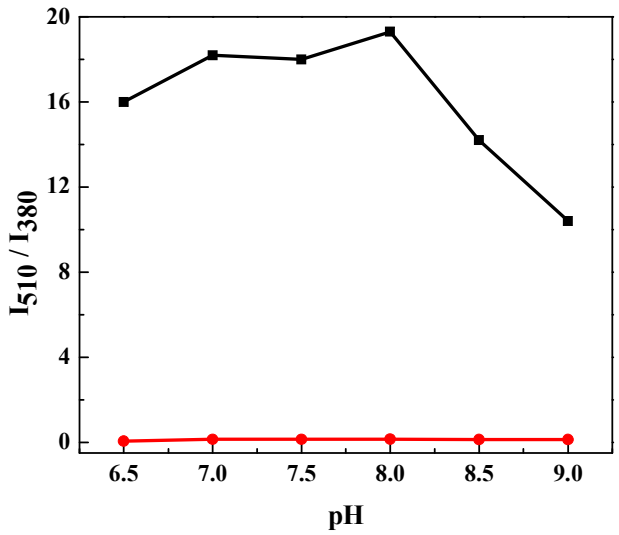


Figure S3. Effect of pH on the ratiometric fluorescence emission of **HBTCo**. **HBTCo** (20.0 μM) with 100.0 μM of Co^{2+} after 2 h in aqueous solution (50 mM HEPES, pH 7.2). Black trace: with 2 mM GSH and red trace: without GSH in the buffer.

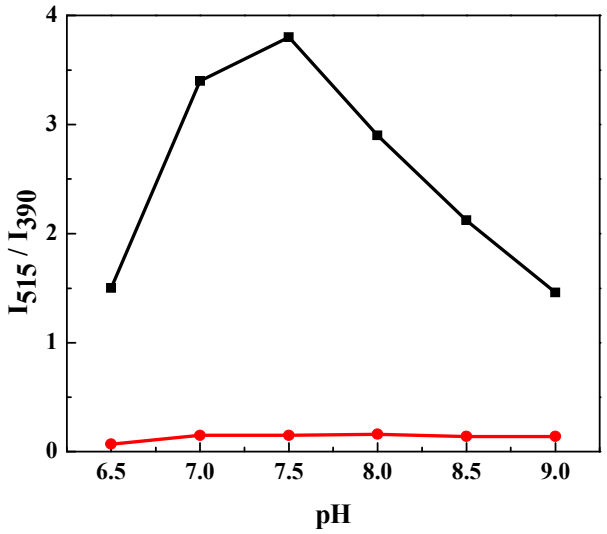
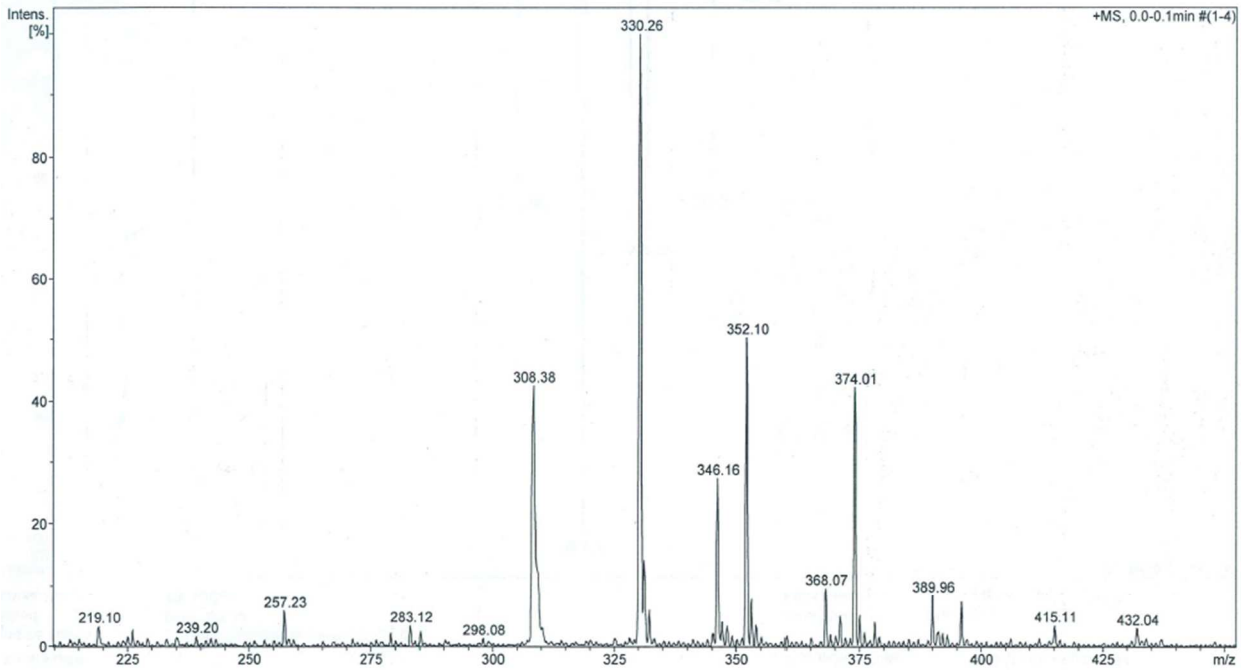
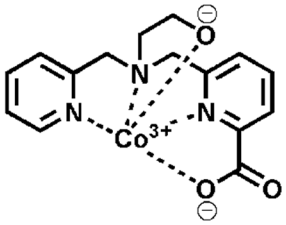


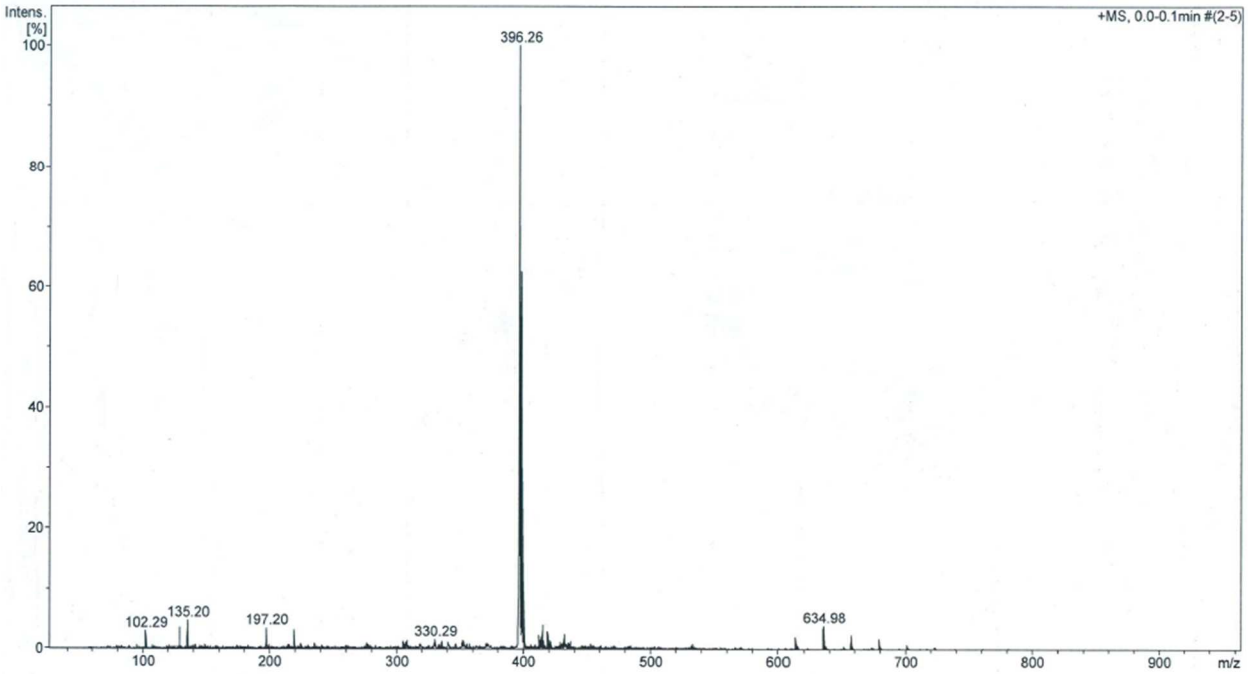
Figure S4. Effect of pH on the ratiometric emission of **HBTCu**. **HBTCu** (20.0 μM) with 1.0 μM of Cu^+ after 2 h in aqueous solution (50 mM HEPES, pH 7.2). Black trace: with 2 mM GSH and red trace: without GSH in the buffer.

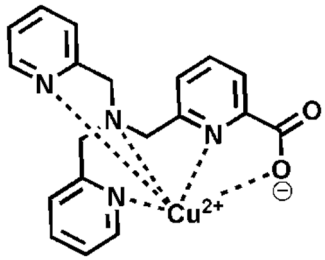




Calculated m/z = 344:04 for $C_{15}H_{16}CoN_3O_3$ (**N_3O**-Co complex)

Figure S5. ESI mass spectra (positive ion mode) for the reaction of 20.0 μM **HBTCo** with 100.0 μM Co^{2+} in water in presence of 100.0 μM GSH. Mass peaks observed at 346.16 ($[M + 2H]^+$), 368.07 ($[M + H+ Na]^+$) and 389.96 ($[M + 2Na]^+$) are corresponds to **N_3O**-Co complex $C_{15}H_{16}CoN_3O_3$. Mass peaks observed at 308.38 ($[M + H]^+$), 330.26 ($[M + Na]^+$), 352.10 ($[M + 2Na-H]^+$) and 374.01($[M + 3Na-2H]^+$) are corresponds to GSH.





Calculated m/z = 396.06 for $C_{19}H_{17}CuN_4O_2$ (**N_4**-Cu complex)

Figure S6. ESI mass spectra (positive ion mode) for the reaction of 20.0 μM **HBTCu** with 10.0 μM Cu^+ in water in presence of 100.0 μM GSH. Mass peaks observed at 396.26 ($[M + H]^+$) is corresponds to **N_4**-Cu complex $C_{19}H_{17}CuN_4O_2$. Mass peaks observed at 330.29 ($[M + Na]^+$) is corresponds to GSH.

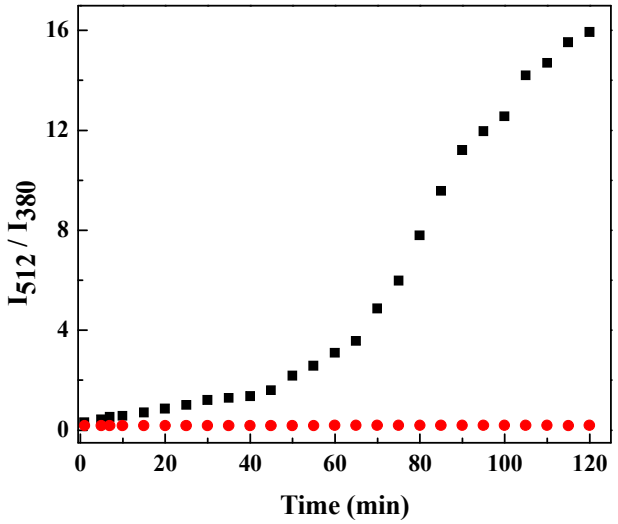


Figure S7. Time dependent ratiometric study of 20.0 μM **HBTCo** incubated with 100 μM of Co^{2+} in aqueous solution (50 mM HEPES, pH 7.2) with (**black trace**) and without (**red trace**) 2 mM GSH.

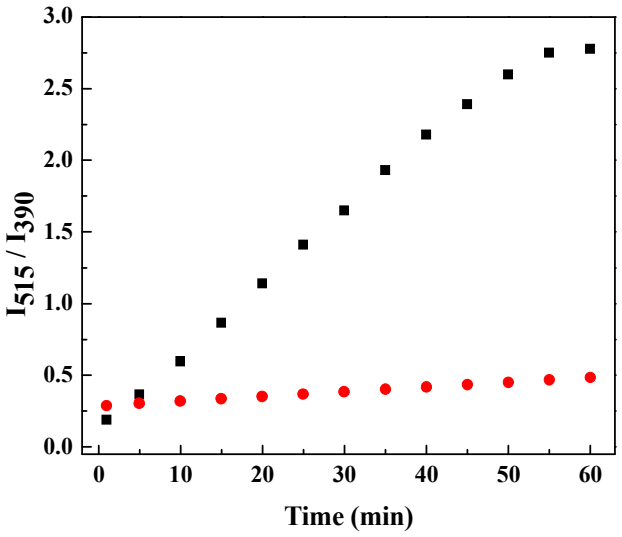


Figure S8. Time dependent ratiometric study of 20.0 μM **HBTCu** incubated with 1.0 μM of Cu^+ in aqueous solution (50 mM HEPES, pH 7.2) with (**black trace**) and without (**red trace**) 2 mM GSH.

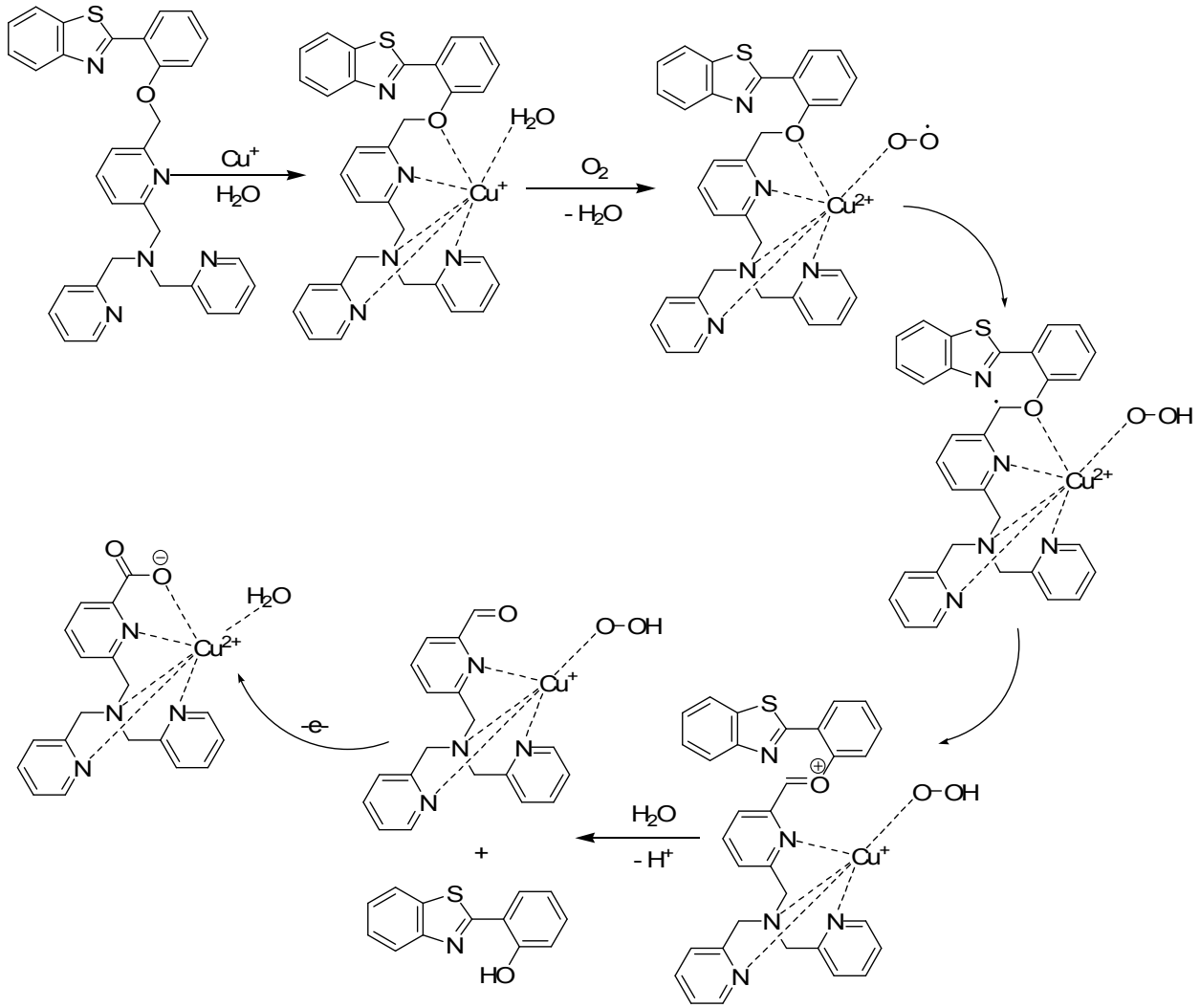


Figure S9. Proposed mechanism for oxidative cleavage of benzylic ether bond in **HBTCu**

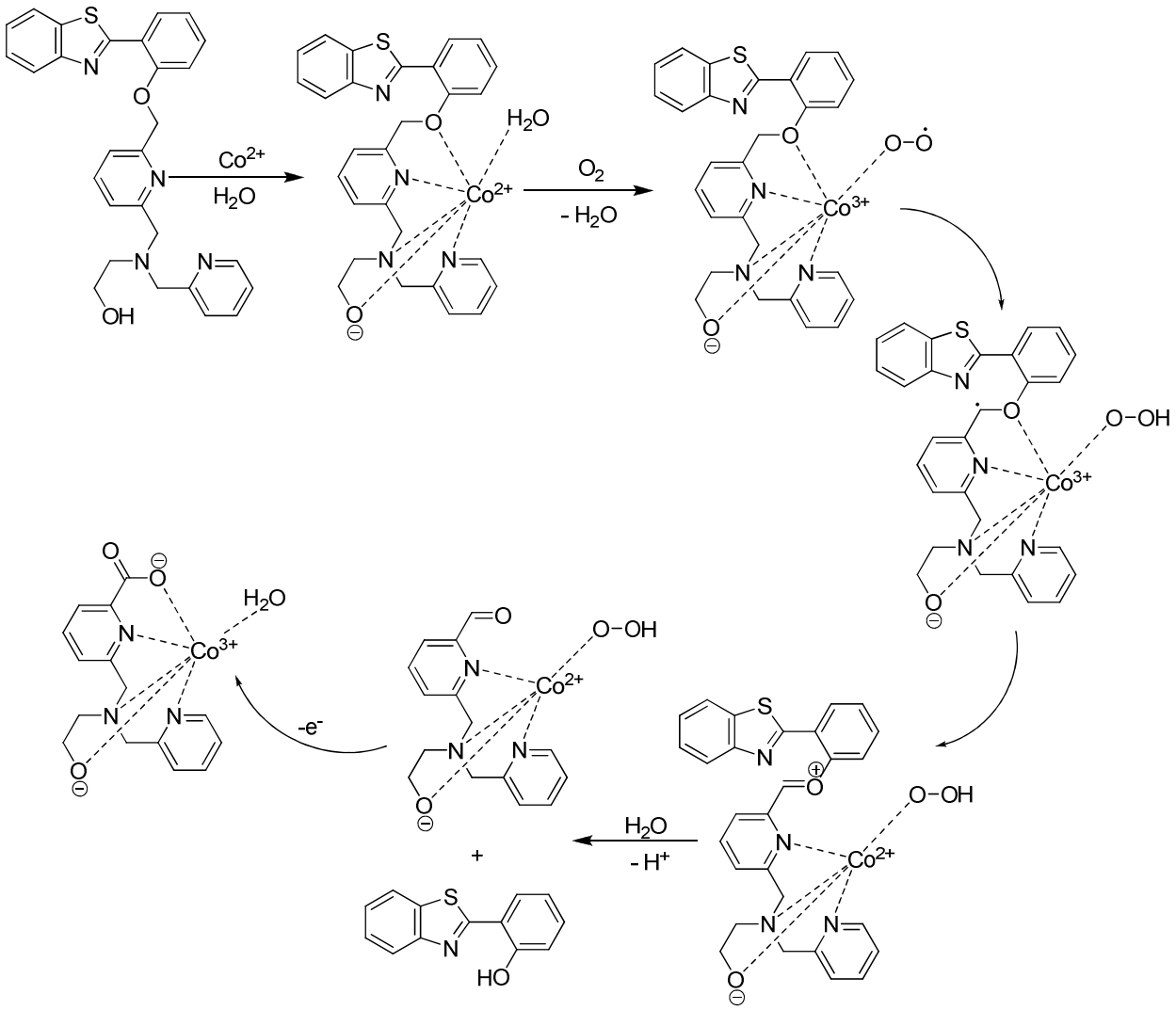


Figure S10. Proposed mechanism for oxidative cleavage of benzylic ether bond in **HBTCo**

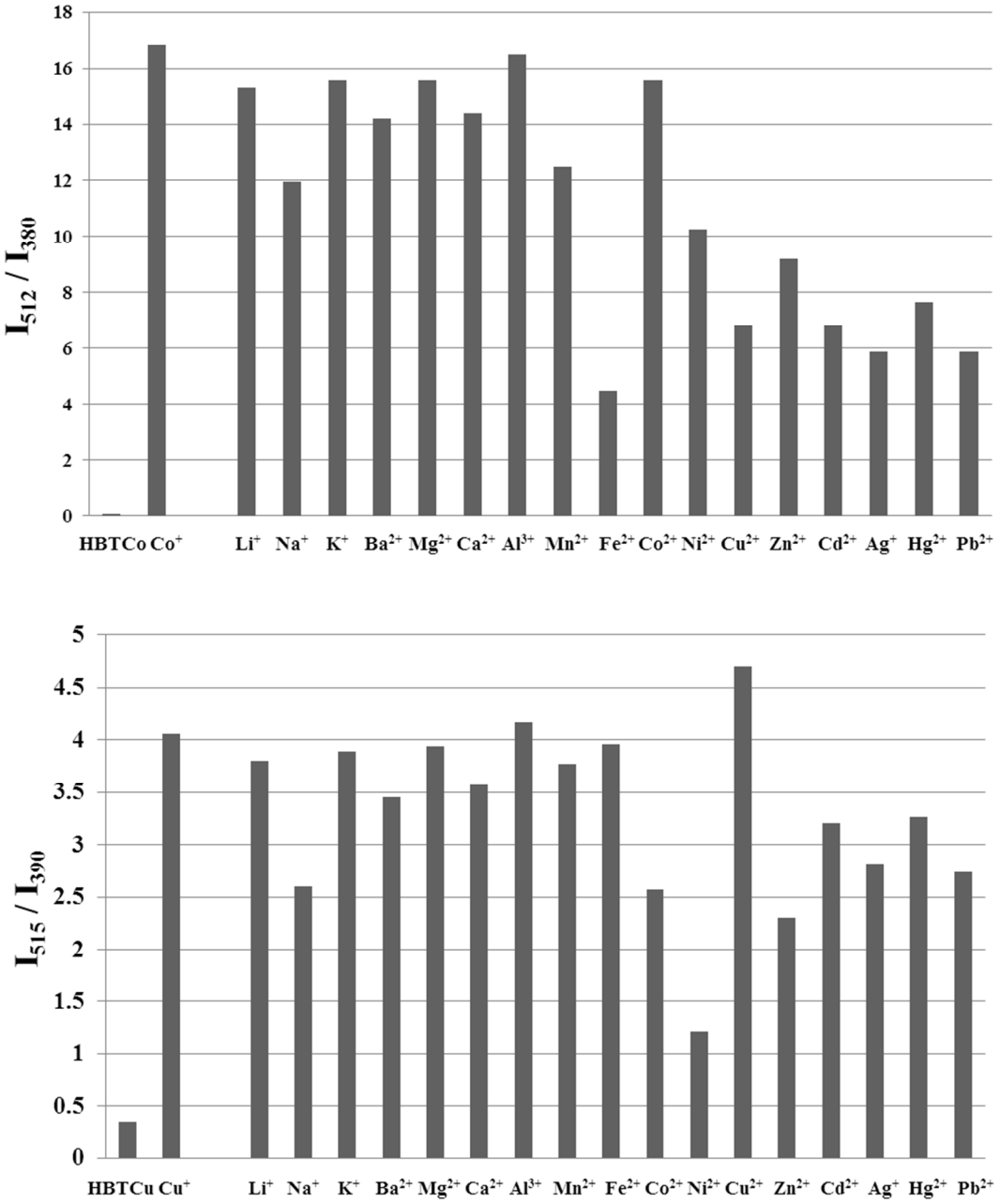
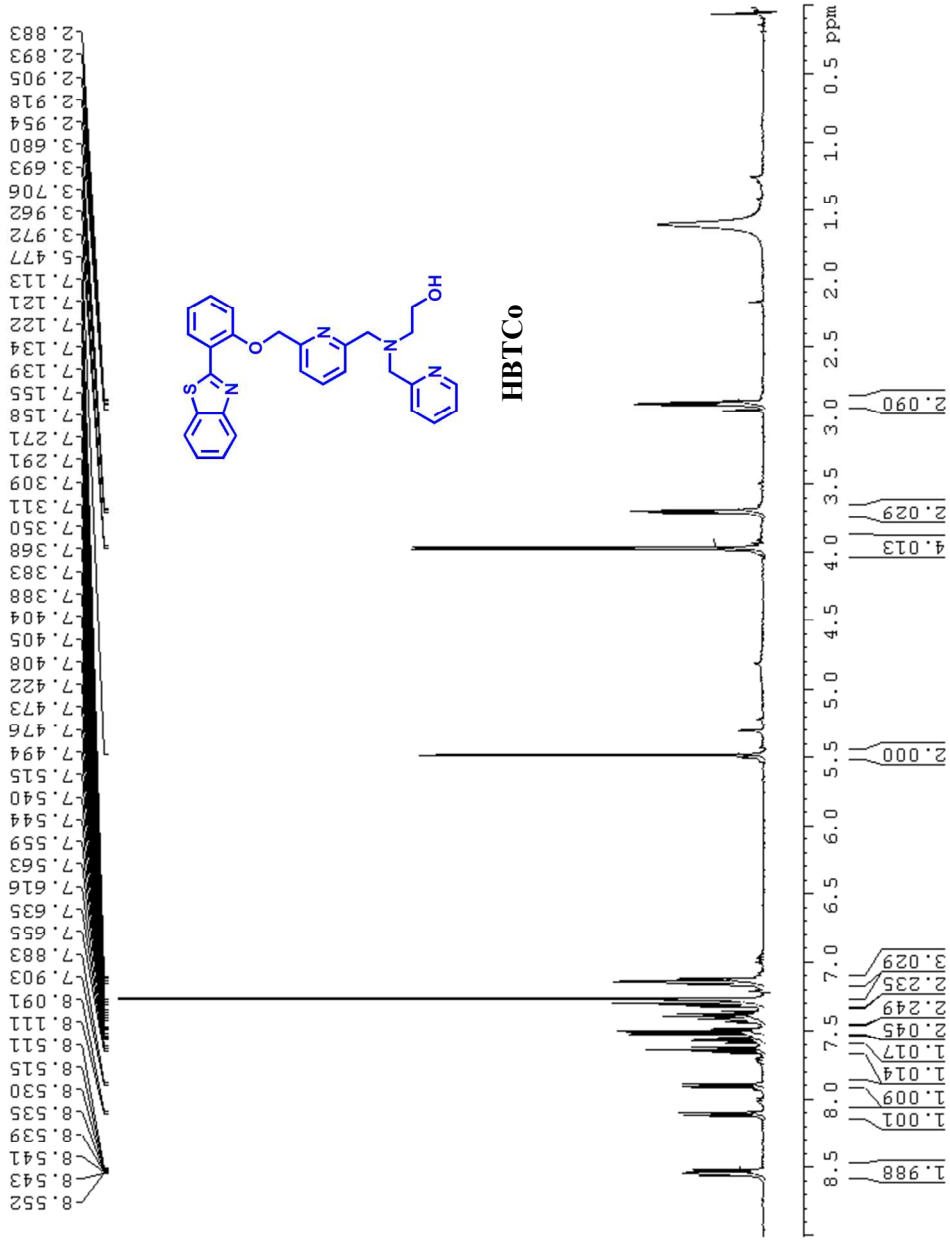


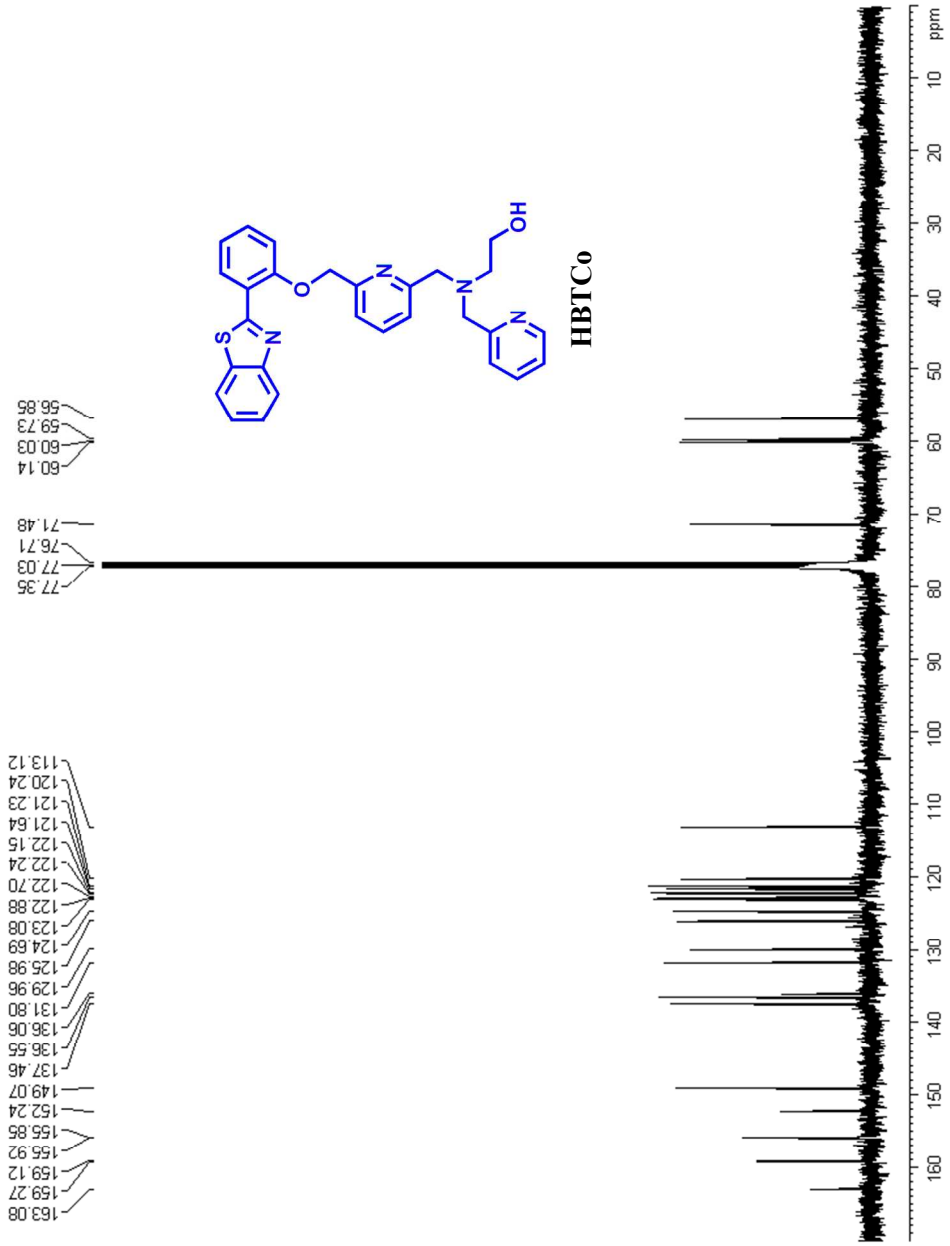
Figure S11. Competitive experiment for the detection of Co^{2+} and Cu^{+} using 20.0 μM **HBTCo** and **HBTCu** respectively. Top: 100.0 μM Co^{2+} is mixed with100.0 μM of corresponding metal ions. Bottom: 100.0 μM Cu^{+} is mixed with100.0 μM of corresponding metal ions. Left two bars are control response of the corresponding probe and only metal ion.

NMR spectra

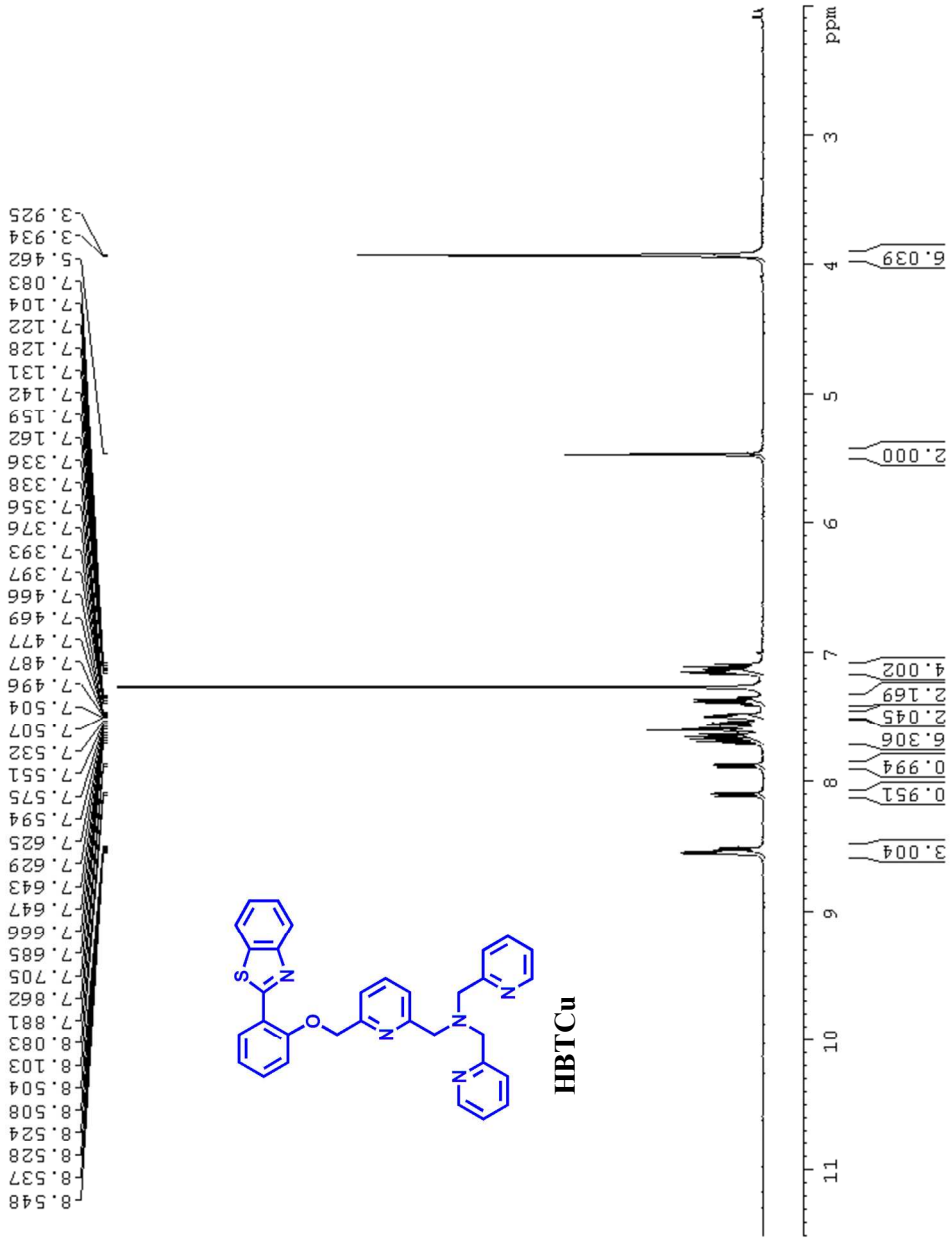
^{1}H NMR spectrum of HBTCo



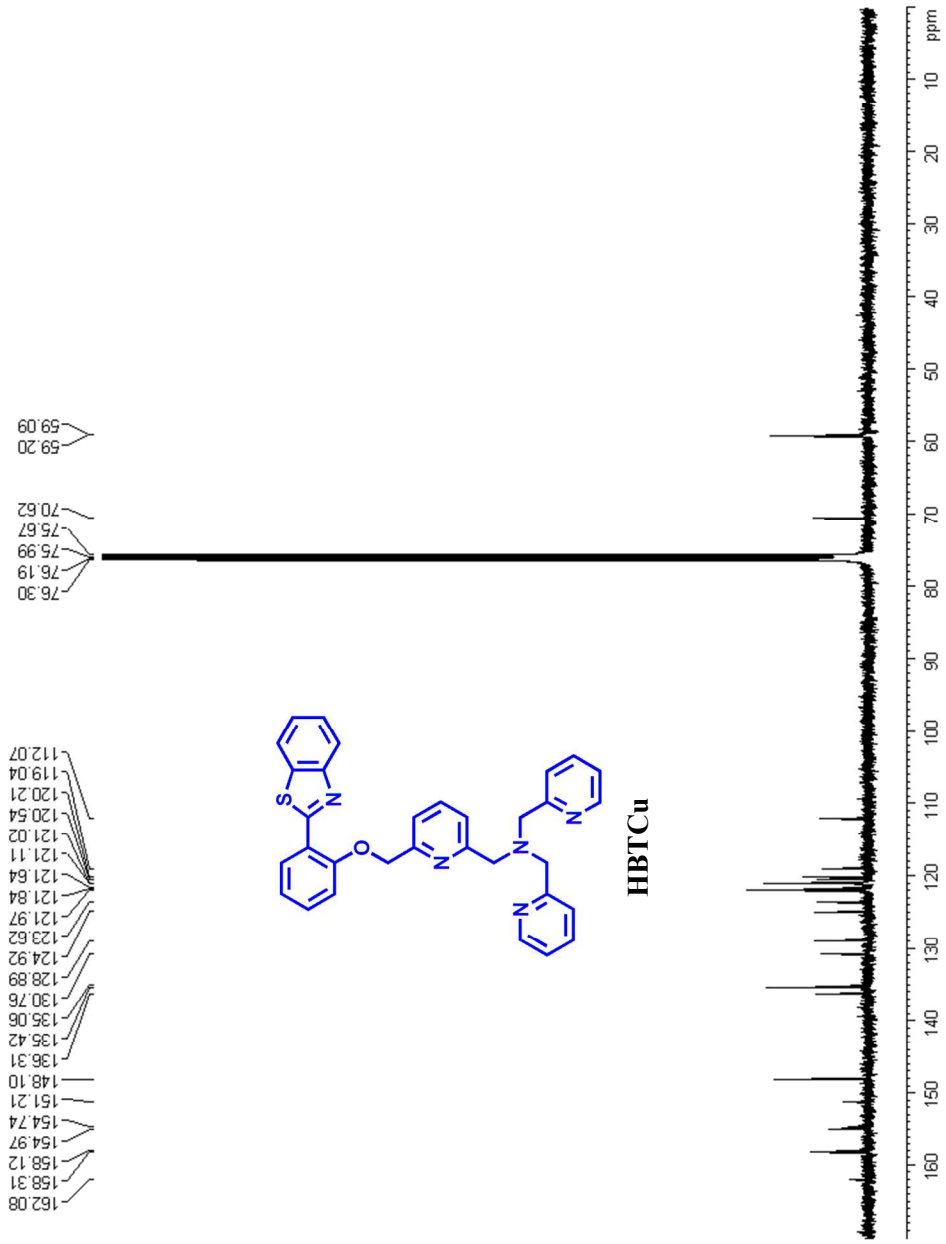
^{13}C NMR spectrum of HBTCo



^{1}H NMR spectrum of HBTCu



^{13}C NMR spectrum of HBTCo



HRMS spectra

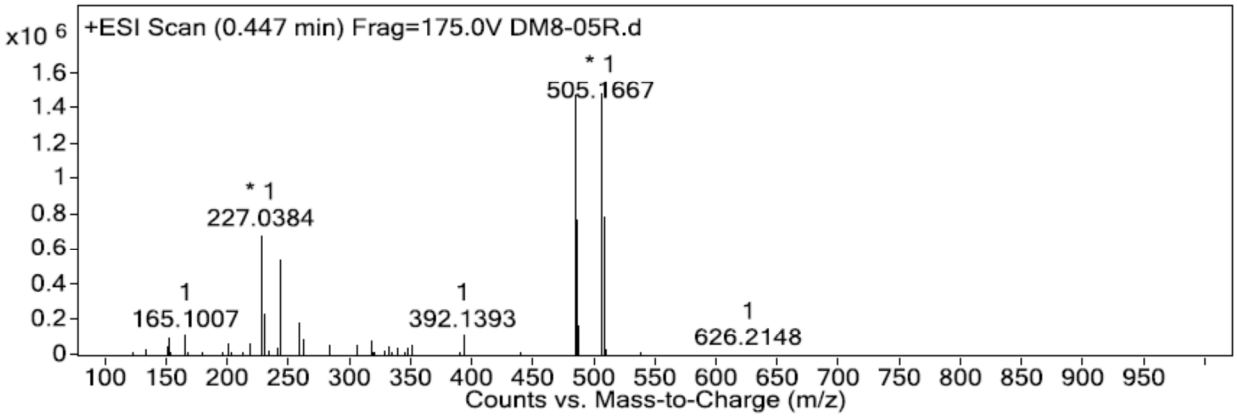


Figure S12. HRMS spectra of **HBTCo.** Observed m/z = 505.1667 $[M + Na]^+$ and calculated m/z = 505.1674 for $C_{28}H_{26}N_4NaO_2S$.

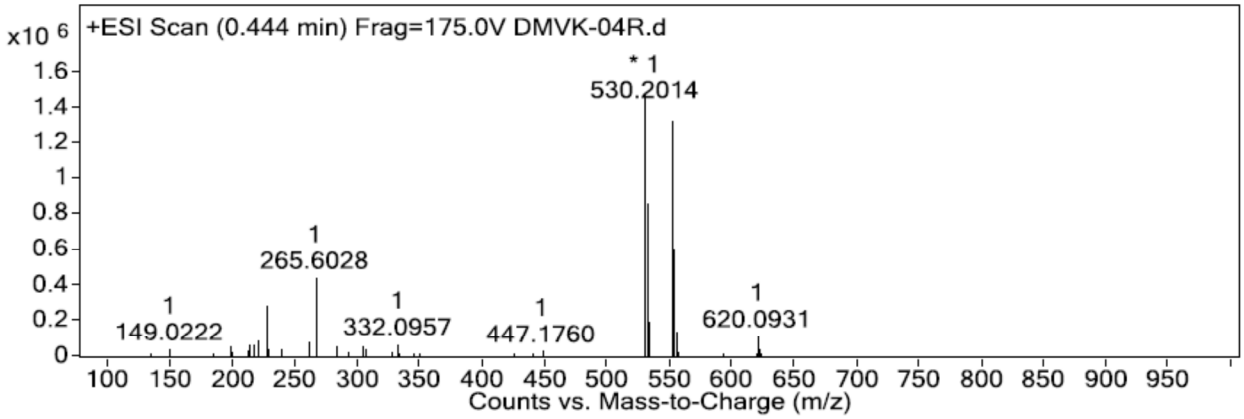


Figure S13. HRMS spectra of **HBTCu.** HRMS: observed m/z = 530.2014 $[M + H]^+$ and calculated m/z = 530.2015 for $C_{32}H_{28}N_5OS$.

References

(1) Au-Yeung H. Y.; New E. J.; Chang C. J. *Chem. Commun.* **2012**, *48*, 5268.

(2) Lucchese B.; Humphreys K. J.; Lee D.; Incarvito C. D.; Sommer R. D.; Rheingold A. L.; Karlin K. D. *Inorg. Chem.* **2004**, *43*, 5987.