Electronic Supplementary Material (ESI) for Chemical Communications


# Coumarin-Derived Transformable Fluorescent Probe for $Zn^{2+}$

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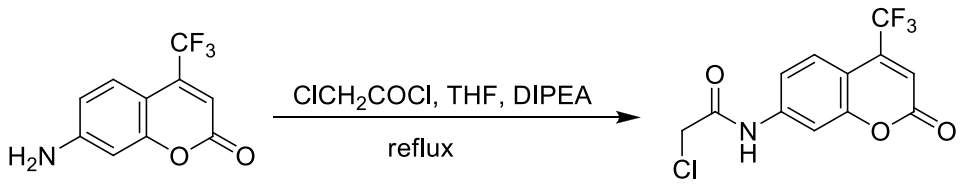
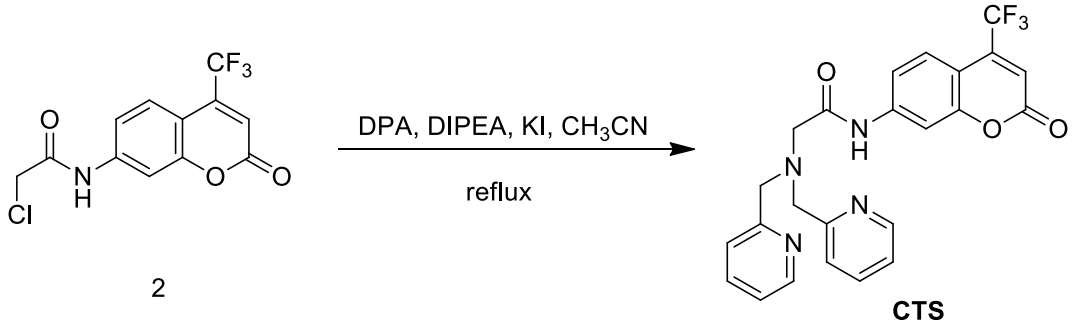
## Synthesis




1 2

A solution of 250 mg (2.2 mmol, 5 eq) of 2-chloroacetyl chloride in 5 ml of dry $CH_2Cl_2$ was added dropwise to a solution of 100 mg (0.44 mmol) **1** in 20 ml of dry $CH_2Cl_2$ stirred at room temperature. After stirred 2 h at 40 $^oC$, the solvent was removed under reduced pressure to give product **13** as a pale-yellow solid without further purification in 97% yield (129 mg). $^1$H-NMR ($CDCl_3$, 400 MHz) δ 4.23 (s, 2H, $CH_2$), 6.73 (s, 1H), 7.46 (d, $J$ = 10.4 Hz, 1H), 7.70 (d, $J$ = 10.4 Hz, 1H), 7.87 (s, 1H), 8.46 (s, 1H, CONH). HRMS (ESI) calcd for $C_{12}H_8ClF_3NO_3$ [$MH^+$] 306.0145, found 306.0150.




2 **CTS**

7-(2-chloroacetayl)amino-4-(trifluoromethyl)coumarin (**2**) (100 mg, 0.33 mmol), di-(2-picolyl)amine (DPA) (70 mg, 0.35 mmol), *N,N*-diisopropylethylamine (DIPEA) (0.5 mL) and potassium iodide (30 mg) were added to acetonitrile (50 mL). After stirred and refluxed for 4 h under nitrogen atmosphere, the mixture was cooled to room temperature and the mixture was removed under reduced pressure to obtain a yellow oil, which was purified by alumina column chromatography ($CH_2Cl_2$:MeOH = 100:2) to afford 7-(2-(di-(2-picolyl)amino)acetayl)amino-4--(trifluoromethyl)coumarin (**CTS**) as semi-solid. Yield: 102 mg (67%). $^1$H-NMR ($CDCl_3$, 400 MHz) δ 3.56 (s, 2H), 3.97 (s, 4H), 6.68 (s, 1H), 7.21-7.28 (m, 4H), 7.65 (t, $J$ = 7.6 Hz, 2H), 7.69 (d, $J$ = 8.4 Hz, 1H), 7.86 (d, $J$ = 8.4 Hz, 1H), 7.98 (s, 1H), 8.67 (d, $J$ = 4.0 Hz, 2H), 11.59 (s, 1H). $^{13}$C-NMR ($CDCl_3$, 100 MHz) δ 58.85, 60.17, 107.31, 109.05, 113.33, 113.38, 116.42, 122.70, 123.26, 125.76, 136.73, 143.30, 144.67, 149.40, 155.30, 157.84, 159.37, 170.86. HRMS (ESI) calcd for $C_{24}H_{20}F_3N_4O_3$ [$MH^+$] 469.1488, found 469.1483.

## Imaging of jurkat cells

Jurkat cells cultured in RPMI 1640 media supplemented with 10% (v/v) fetal bovine Serum, 1% (v/v) 100mM Sodium Pyruvate (Gibco) and 1%(v/v) 1M HEPES buffer (Sigma H0887). The

cells were seeded at $0.3\times10^6$ cells/ml in the culture media, incubated at 37°C, 5% CO2, and pessaged very other day.

10 μM **CTS** in the culture media containing 0.1% (v/v) DMSO was added to the cells and the cells were incubated for 1 h at 37 °C. After washing twice to remove the remaining sensor, the cells were treated with 20 μM $Cd(ClO_4)_2$ for 30 min. Without washing the cells were further treated with 20 μM $Zn(ClO_4)_2$ for 30 min. The treated cells were imaged by fluorescence microscopy.

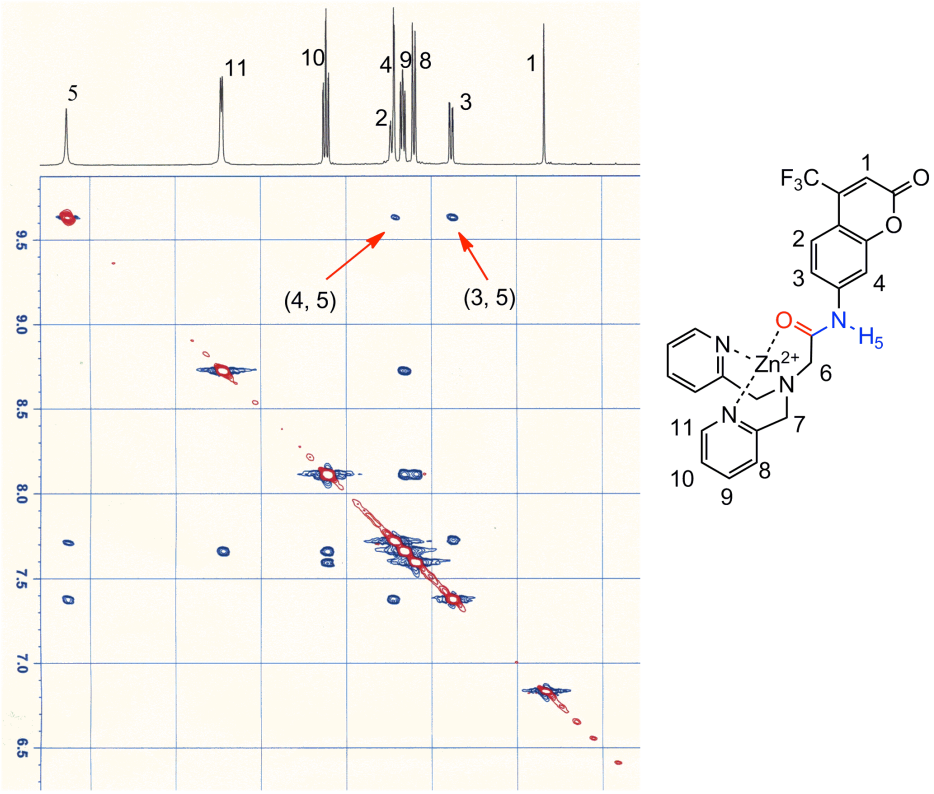



Figure S1. Partial 500 MHz $^1$H-$^1$H NOESY spectra of **CTS**/$Zn^{2+}$ (1:1) in $CD_3CN$.

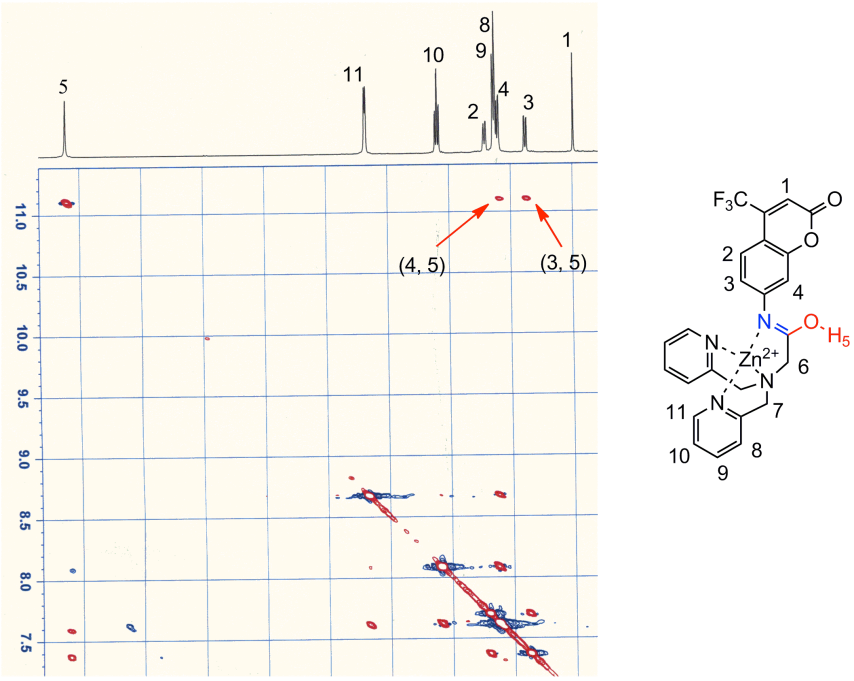



Figure S2. Partial 500 MHz $^{1}$H-$^{1}$H NOESY spectra of **CTS**/$Zn^{2+}$ (1:1) in DMSO-$d_6$.

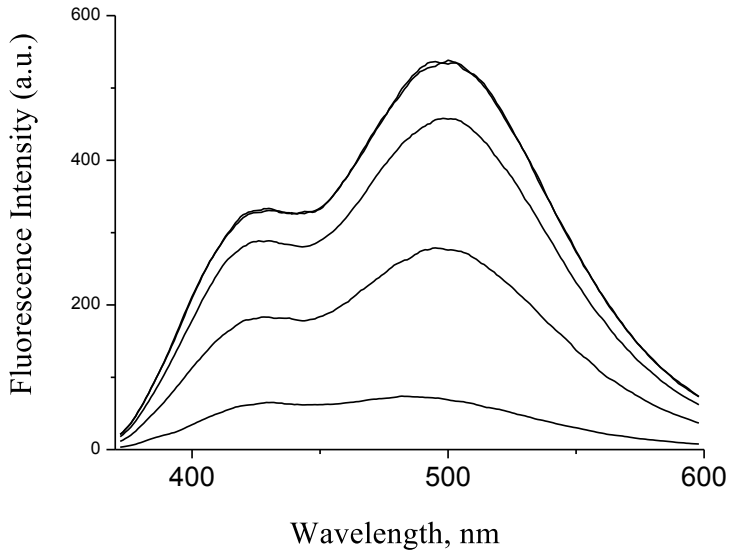



Figure S3. Fluorescence spectra of 10 μM **CTS** in the presence of different concentrations of $Zn^{2+}$.

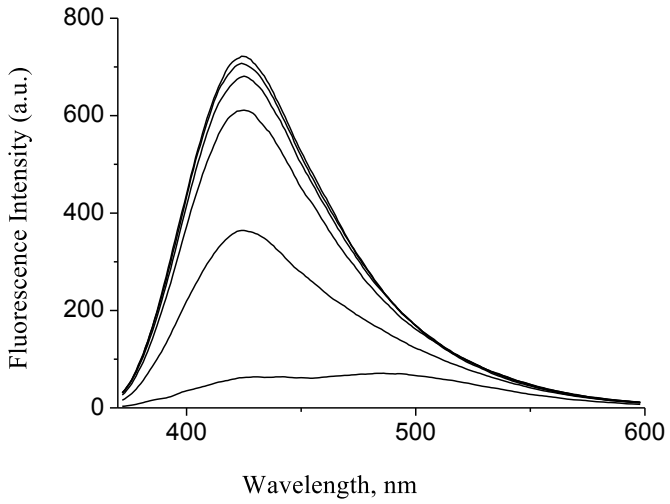



Figure S4. Fluorescence spectra of 10 μM **CTS** in the presence of different concentrations of $Cd^{2+}$.

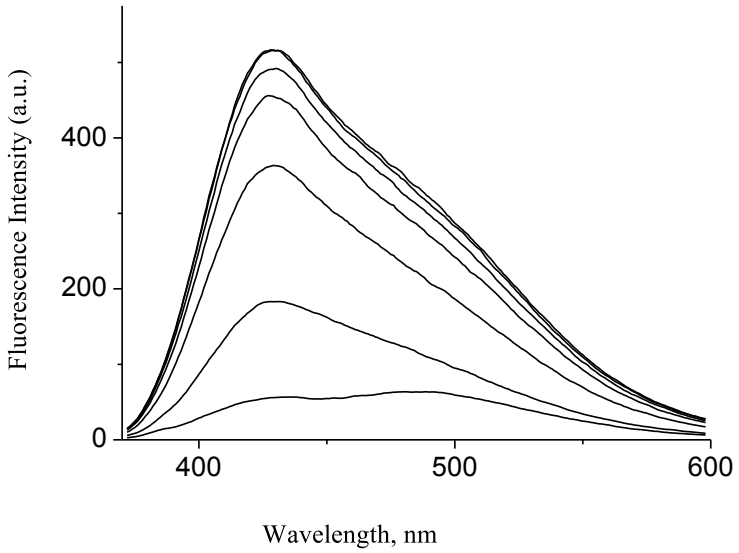



Figure S5. Fluorescence spectra of 10 μM **CTS** in the presence of different concentrations of $Hg^{2+}$.

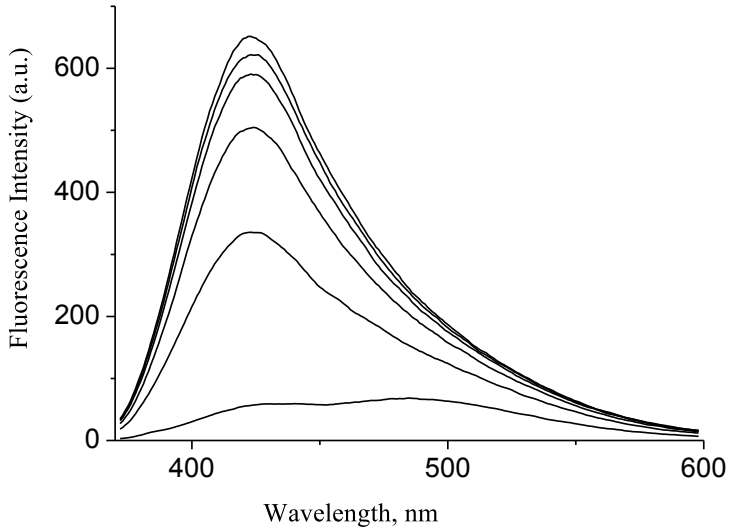



Figure S6. Fluorescence spectra of 10 μM **CTS** in the presence of different concentrations of $Cd^{2+}$.

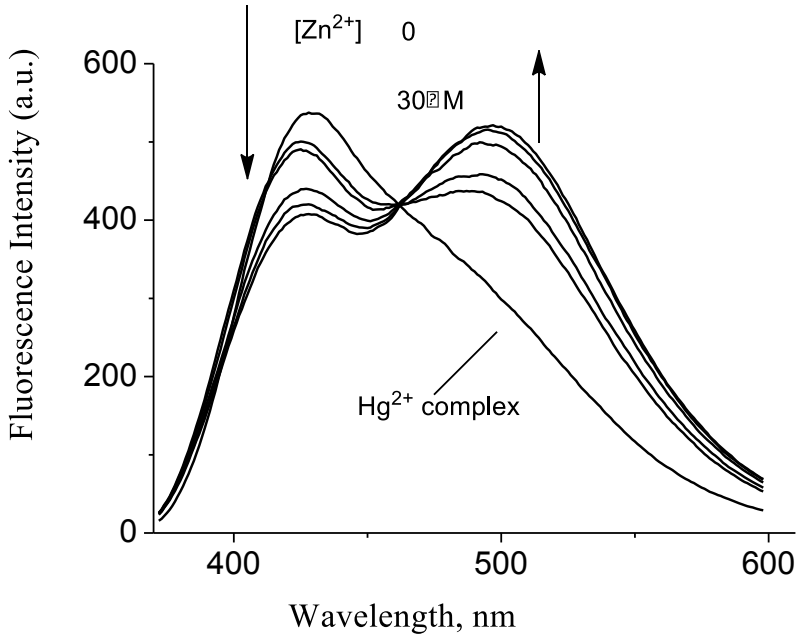



Figure S7. Fluorescence spectra of 10 μM **CTS**/$Hg^{2+}$ in the presence of different concentrations of $Zn^{2+}$ in aqueous solution (DMSO: 0.5 M HEPES (pH 7.4) = 5:95).

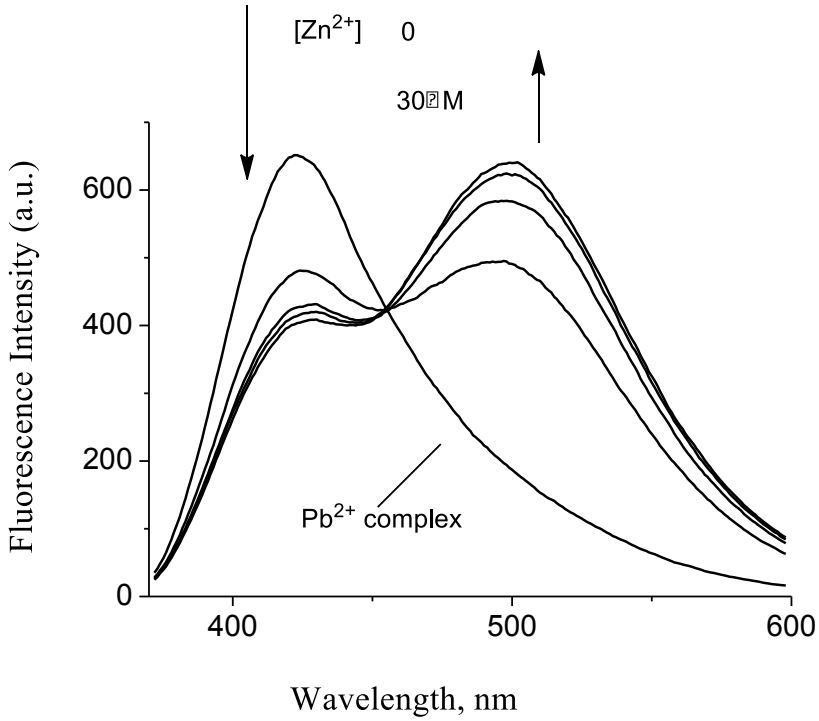



Figure S8. Fluorescence spectra of 10 μM **CTS**/$Pb^{2+}$ in the presence of different concentrations of $Zn^{2+}$ in aqueous solution (DMSO: 0.5 M HEPES (pH 7.4) = 5:95)

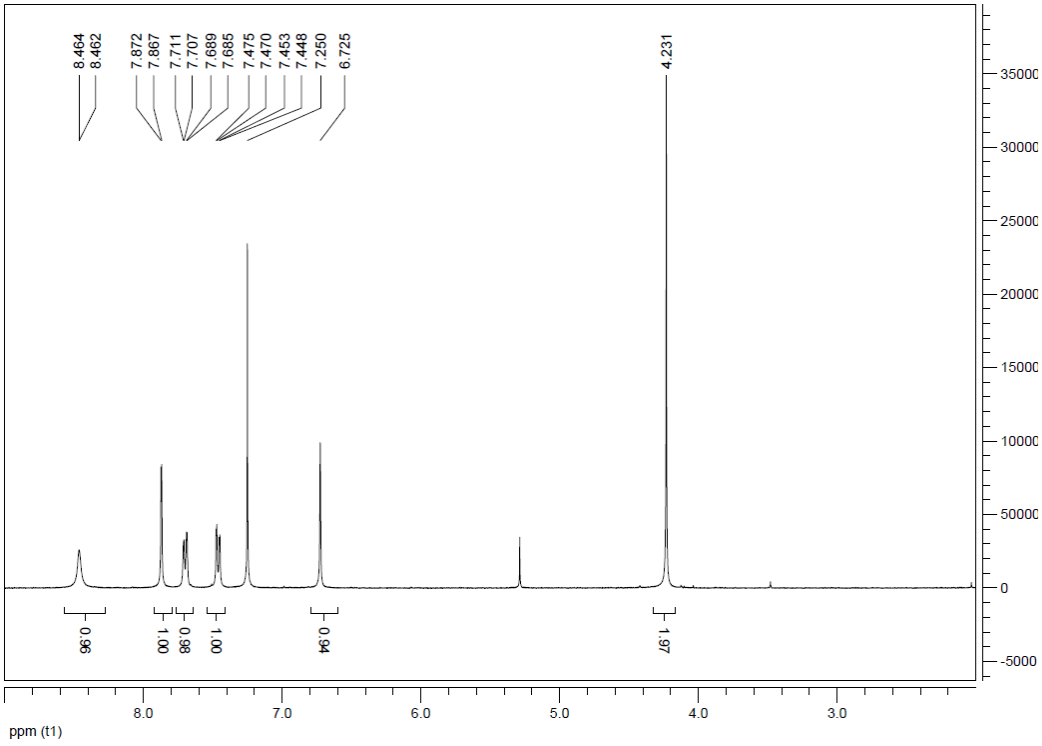



Figure S9. $^{1}$H-NMR spectra of compound **2** in $CDCl_3$.

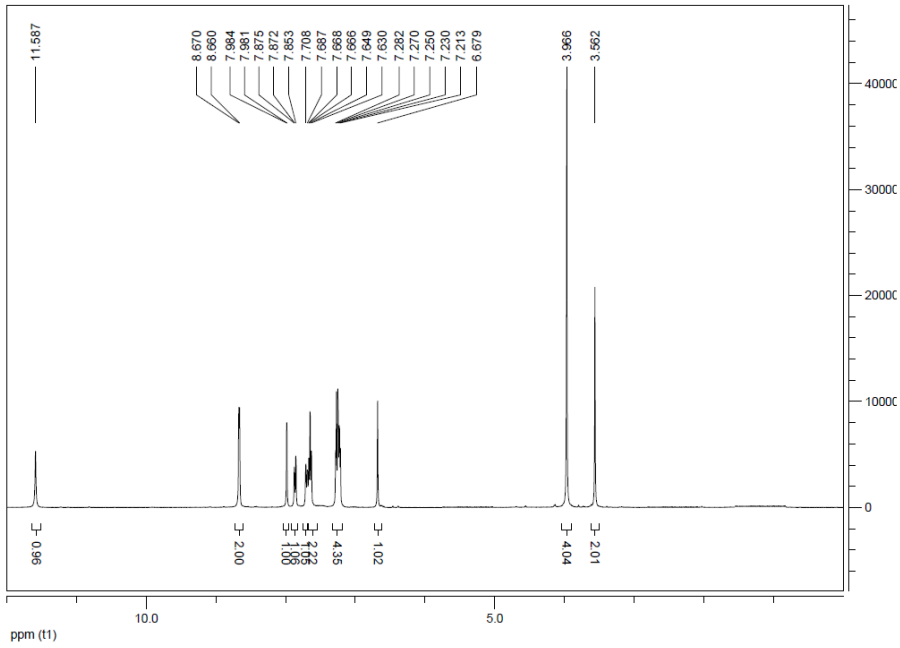



Figure S10. $^{1}$H-NMR spectra of compound **CTS** in $CDCl_3$.

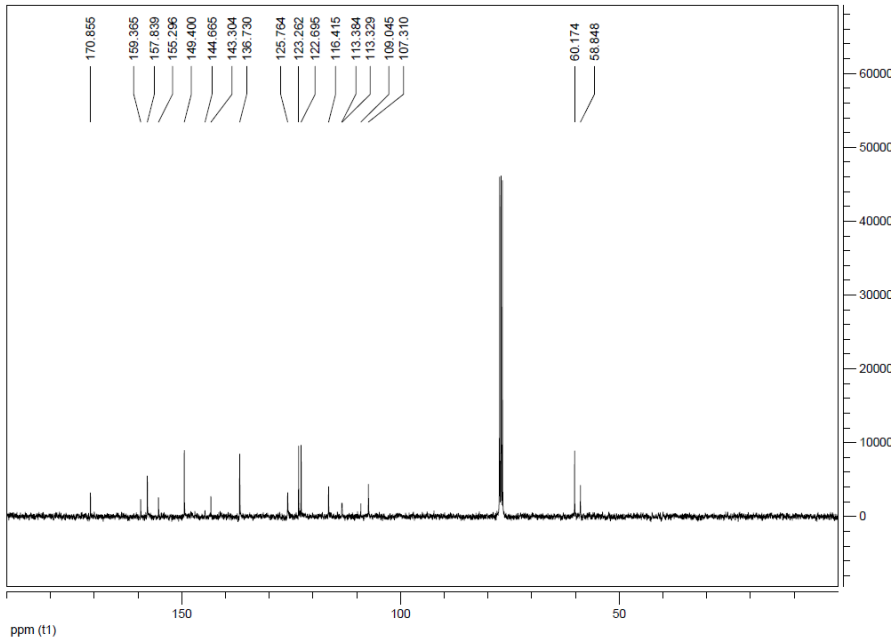



Figure S11. $^{13}$C-NMR spectra of compound **CTS** in $CDCl_3$.

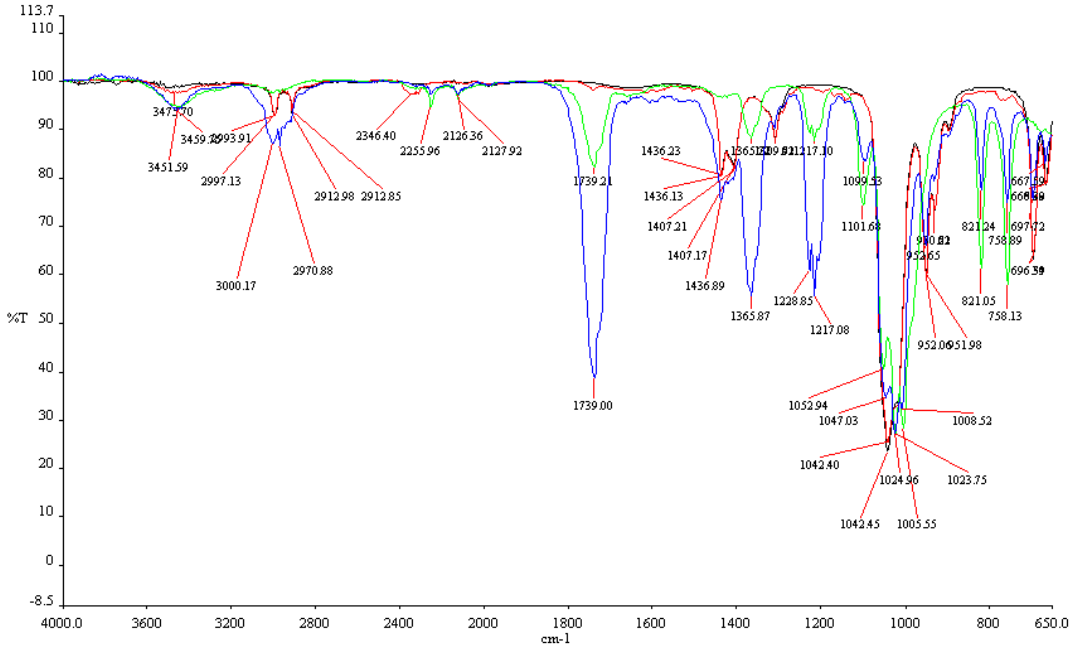



Figure S12. IR spectra of DMSO (black line), **CTS** in DMSO (red line), $Zn^{2+}$ solution in DMSO (green line), and **CTS**/$Zn^{2+}$ (1 : 1) complex in DMSO.