Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Sulfide-selective chemosignaling by a Cu^{2+} complex of dipicolylamine appended fluorescein

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Experimental Details.

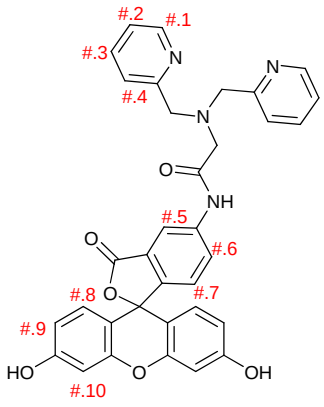
Experimental Details.

5-Aminofluorescein and di-(2-picolyl)amine were purchased from Aldrich Chemical Co. All solvents were purchased from Aldrich Chemical Co. as 'anhydrous' or 'spectroscopic grade'. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a Varian gemini 2000 spectrometer and referenced to the residual solvent signals. UV-Vis spectra were recorded with a Jasco V-550 spectrophotometer equipped with a Peltier temperature controller. Fluorescence spectra was measured on an Aminco-Bowman Series 2 Spectrophotometer. Mass spectra were obtained on a JMS-AX505WA (JEOL).

Preparation of 2

Fluorescein-chloroacetamide **2** was prepared by following a slightly modified procedure of the reported method for the preparation of fluorescein acetamide.[1] Fluorescein chloroacetamide **2** (yield 90%); ^{1}H NMR (300 MHz, methanol-d_4) δ 8.62 (d, J = 2.1 Hz, 1H), 8.16 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H), 7.49 (d, J = 9.3 Hz, 2H), 7.43 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 2.1 Hz, 2H), 7.16 (dd, J_1 = 9.3 Hz, J_2 = 2.1 Hz, 1H), 4.30 (s, 2H); ^{13}C NMR (75 MHz, methanol-d_4) δ 171.68, 168.14, 167.88, 160.33, 142.24, 133.97, 132.74, 131.53, 125.03, 124.99, 123.06, 120.66, 117.92, 103.44, 97.55, 44.20; HRMS (FAB-); *m/z* calcd for $C_{22}H_{14}ClNO_6$ $[M-H]^-$: 423.0510, found 423.0515.

Preparation of 1



Compound.1

Fluorescein-chloroacetamide **2** (0.047 g, 0.11 mmol) was dispersed in THF/methanol (1:1, v/v) solution, and sodium bicarbonate (0.008 g, 0.1 mmol) and sodium iodide (0.015 g, 0.1 mmol) were added to the reaction mixture at room temperature. After 12 h, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The product was purified by preparative TLC (silica gel, CH_3OH). Fluorescein-DPA **1**

(0.041 g, yield 70%); ^{1}H NMR (300 MHz, methanol-d_4) δ 8.61 (d, *J* = 4.8 Hz, 2H, *H*-1), 8.23 (s, 1H, *H*-5), 8.00 (d, *J* = 10.8 Hz, 1H, *H*-6), 7.77 (m, 2H, *H*-3), 7.49 (d, *J* = 7.5 Hz, 2H, *H*-4), 7.29 (m, 2H, *H*-2), 7.15 (m, 3H, *H*-7 and *H*-8), 6.56 (m, 2H, *H*-9), 6.53 (br d, 2H, *H*-10), 3.98 (s, 4H, Pyr-*H*), 3.51 (s, 2H, COC*H*$_2$N); ^{13}C NMR (75 MHz, methanol-d_4) δ 181.39, 173.94, 172.36, 160.15, 159.35, 150.34, 142.52, 140.38, 138.73, 132.63, 131.41, 130.08, 125.28, 124.20, 123.66, 123.02, 121.95, 121.35, 114.04, 104.35, 61.66, 59.82; HRMS (FAB); *m/z* calcd for $C_{34}H_{27}N_4O_6$ $[M+H]^+$: 587.1931, found 587.1921.

Preparation of 1-Cu^{2+} complex

To a methanol solution of fluorescein-DPA **1** was added $Cu(ClO_4)_2$ in water. After stirring for 10 min., the precipitate formed was filtered and the solid was washed with distilled water. It was recrystallized from aqueous ethanol to yield dark-brown colored solid of **1**-Cu^{2+} complex. Yield: 84%. HRMS (FAB); *m/z* calcd for $C_{34}H_{26}CuN_4O_6$ $[M-H+Cu]^+$: 649.1148, found 649.1157. Anal. Calcd for $C_{34}H_{27}N_4O_6 \cdot CuClO_4 \cdot H_2O$: C, 53.20; H, 3.68; N, 7.30. Found: C, 53.01; H, 3.81; N, 7.50. Attempts to measure well resolved NMR spectra were failed, and only featureless broad spectra were obtained due to the presence of paramagnetic Cu^{2+} ions.

Detection limit

Detection limit was calculated from a plot of the fluorescence changes as a function of log[sulfide] following the procedure of literature.[2] A linear regression curve was fitted to the intermediate values of the sigmoidal plot. The point at which this line crossed the ordinate axis was taken as the detection limit.

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1) S. S. Gupta, K. S. Raja, E. Kaltgrad, E. Strable and M. G. Finn, *Chem. Commun.*, **2005**, 4315.

2) M. Shortreed, R. Kopelman, M. Kuhn and B. Hoyland, *Anal. Chem.*, 1996, **68**, 1414.

Figure S1. Changes in fluorescence spectra of **1** in the presence of various metal ions in 10 mM hepes buffer solution at pH 7.0. [**1**] = 5.0×10^{-6} M, [M^{n+}] = 5.0×10^{-4} M, λ_{ex} = 470 nm.

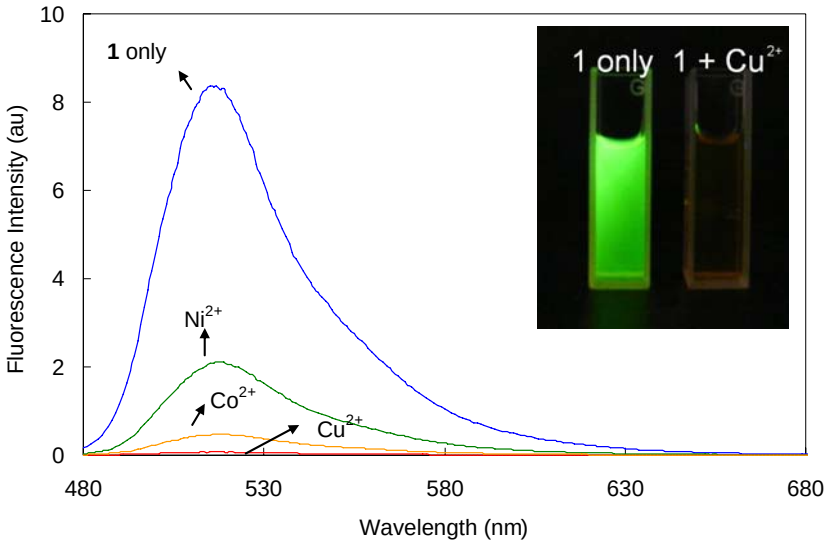

Figure S2. Job's plot for **1**-Cu^{2+} complex. [**1**] + [Cu^{2+}] = 5.0×10^{-6} M in 10 mM hepes buffer solution at pH 7.0. λ_{ex} = 470 nm.

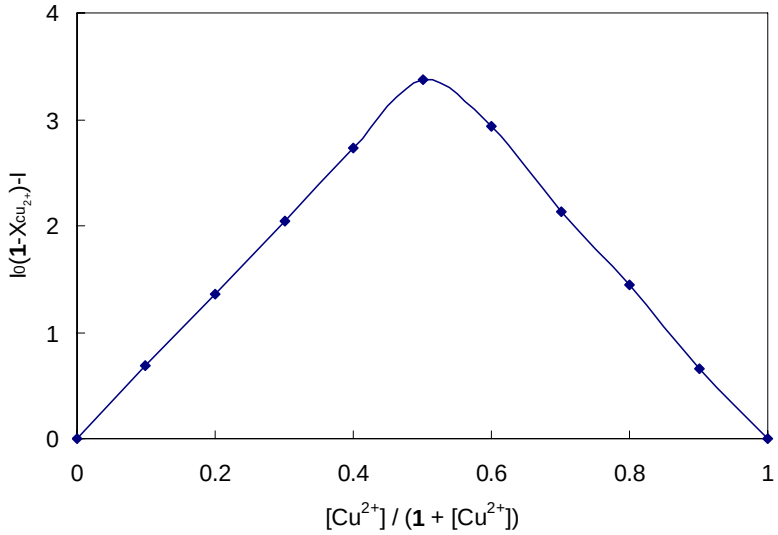

Figure S3. Ratio of $I_{(1 + Cu^{2+} + anion)}$ / $I_{(1 + Cu^{2+})}$ at 517 nm of the **1**-Cu^{2+} system in the presence of various anions in 10 mM hepes buffer solution at pH 7.0. [**1**] = 5.0×10^{-6} M, $[Cu^{2+}] = 5.0 \times 10^{-6}$ M, $[A^{n-}] = 1.0 \times 10^{-3}$ M, λ_{ex} = 470 nm.

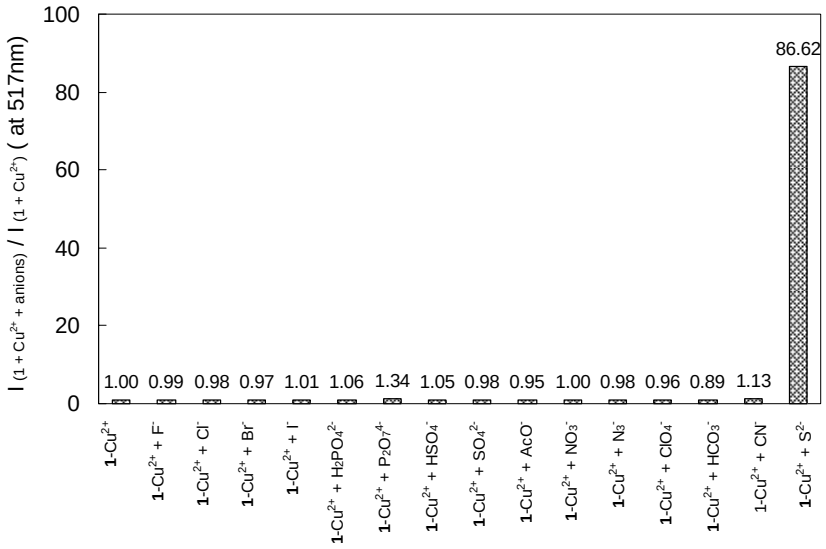

Figure S4. Signaling of S^{2-} ions by the **1**-Cu^{2+} system in the presence of 100 equiv of possibly interfering anions as background in 10 mM hepes buffer solution at pH 7.0. [**1**] = 1.0×10^{-5} M, $[Cu^{2+}] = 1.0 \times 10^{-5}$ M, $[S^{2-}] = 1.0 \times 10^{-4}$ M, $[A^{n-}] = 1.0 \times 10^{-3}$ M, λ_{ex} = 470 nm.

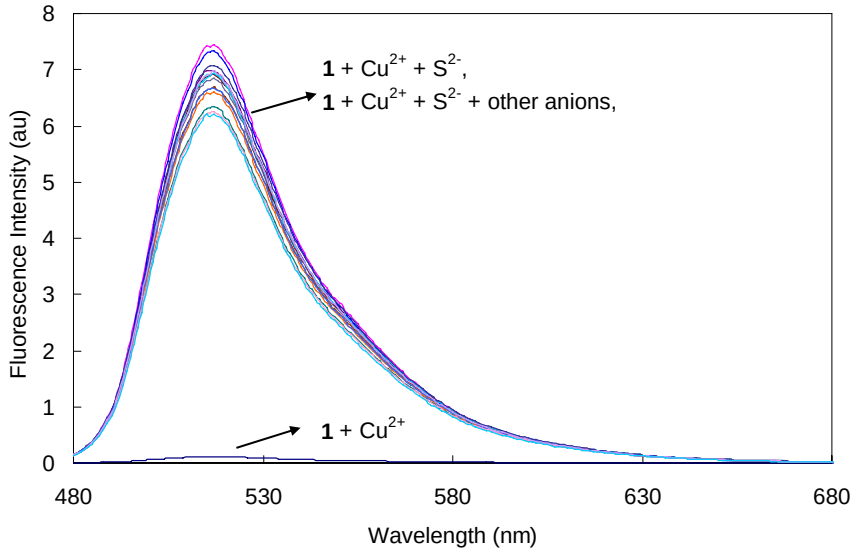

Figure S5. Changes in fluorescence spectra of the **1**-Cu^{2+} system upon treatment with 2 equiv of S^{2-} ions and **1** in 10 mM hepes buffer solution at pH 7.0. [**1**] = 5.0×10^{-6} M, [Cu^{2+}] = 5.0×10^{-6} M, [S^{2-}] = 1.0×10^{-5} M, λ_{ex} = 470 nm.

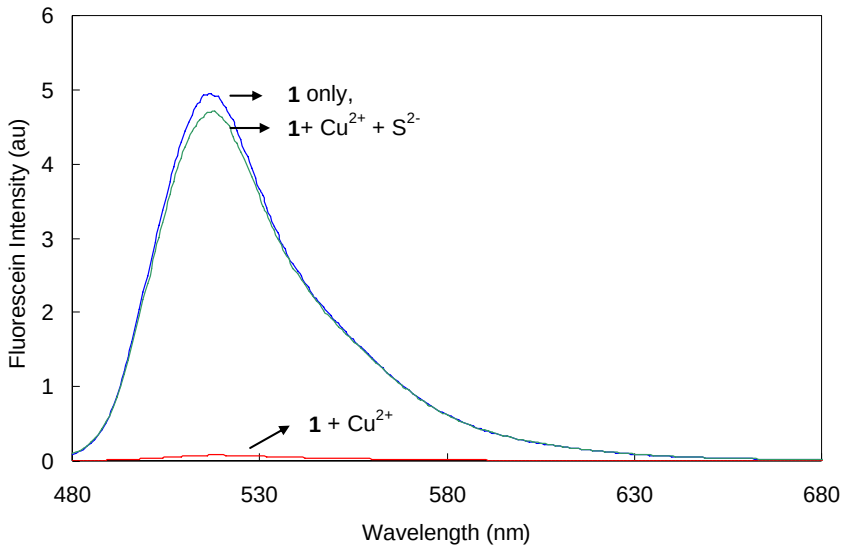

Figure S6. Partial ^{1}H NMR spectra of **1** only, **1**-Cu^{2+} system, and **1**-Cu^{2+} system upon treatment with S^{2-} ions in methanol-d_4. [**1**] = 2.0×10^{-2} M, [Cu^{2+}] = 2.0×10^{-2} M, [S^{2-}] = 4.0×10^{-2} M.

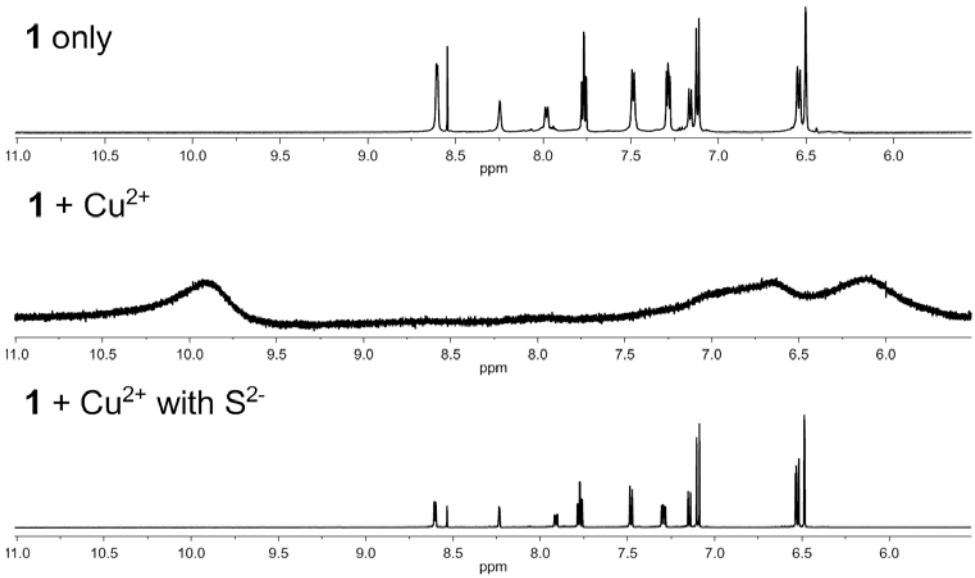

Figure S7. ^{1}H-NMR spectrum of **1** in methanol-d_4.

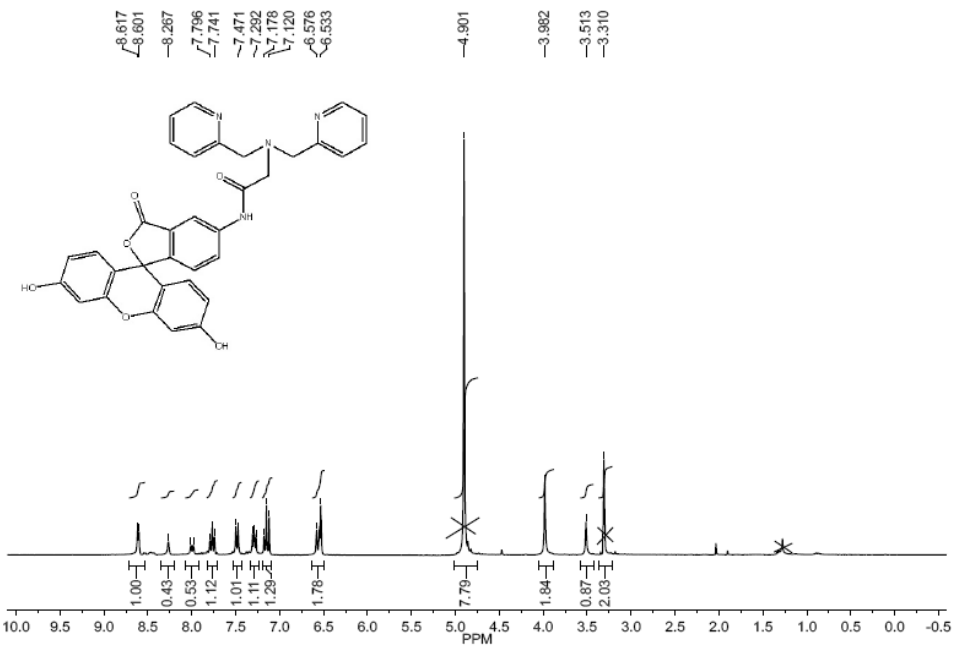

Figure S8. ^{13}C-NMR spectrum of **1** in methanol-d_4.

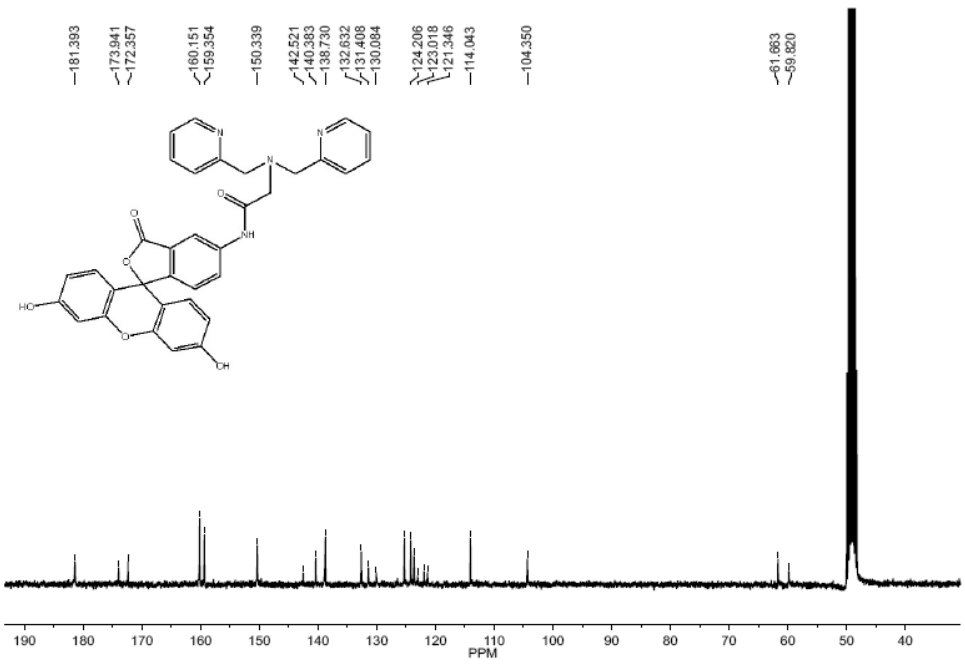

Figure S9. ^{1}H-NMR spectrum of **2** in methanol-d_4.

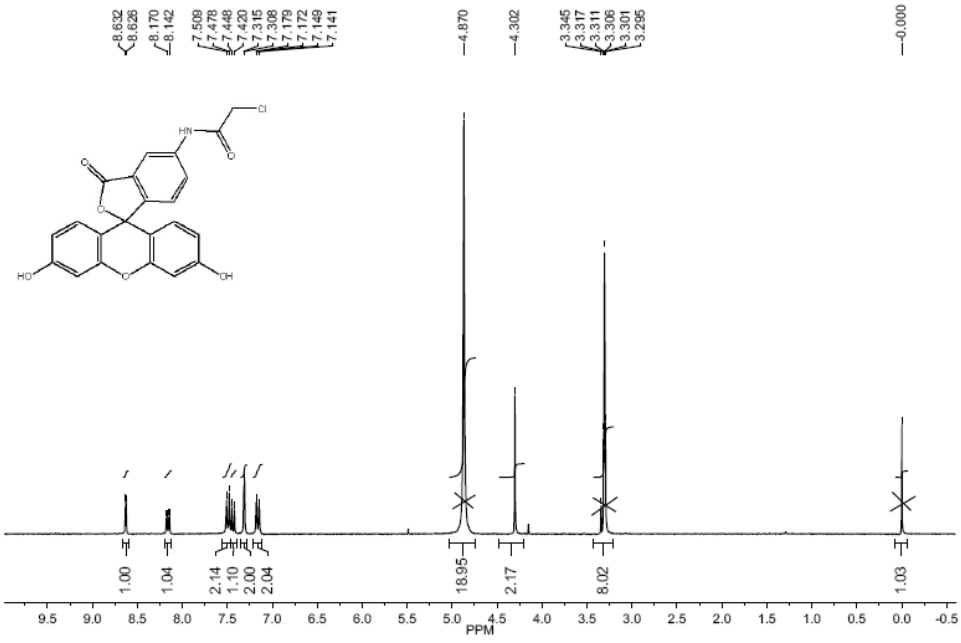

Figure S10. ^{13}C-NMR spectrum of **2** in methanol-d_4.

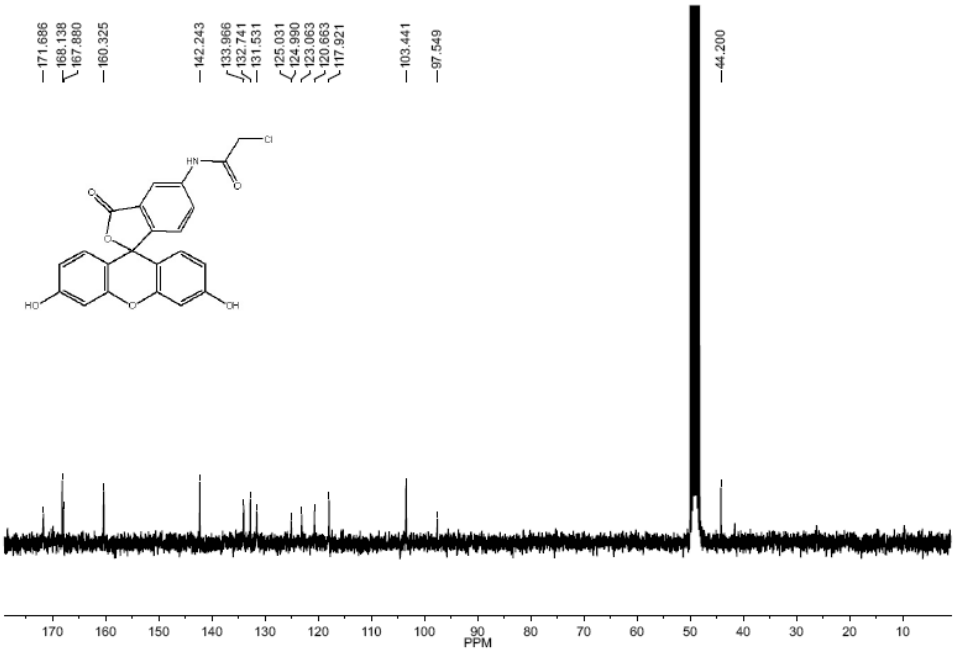

Figure S11. 2D NMR spectrum of **1** in methanol-d_4.