Electronic Supplementary Information

for

A New Strategy for Highly Selective Fluorescent Sensing of F^- and Zn^{2+} with Dual Output Modes

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Contents

1. Materials and Methods.

Cationic compounds such as NaCl, KCl, $MgCl_2$, $CaCl_2$, $ZnCl_2$, $CdCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $AgNO_3$ and anionic compounds such as $[Bu_4N]^+Cl^-$, $[Bu_4N]^+Br^-$, $[Bu_4N]^+I^-$, $[Bu_4N]^+ClO_4^-$, $[Bu_4N]^+HSO_4$, NaCN, NaOAc and NaH_2PO_4 were purchased from Shanghai Chemical Co., $[Bu_4N]^+F^-$ was purchased from J&K Chemical Co. and 2-methyl-8-hydroxyquinoline was a Alfa Aesar Co. product. They were used without further purification. 5-bromo-8-tert-butyldimethylsilyloxy-2-methyl-quinoline were prepared according to the literature[1]. Et_3N and 1,4-Dioxane were freshly distilled over appropriate drying agents. All the other reagents were purchased and used without further purification.

Fluorescence spectra measurements were performed on a Shimadzu RF-5301PC spectroflurophotometer. Absorption spectra were determined on a Pgeneral UV-Vis TU-1901 Spetrophotometer. ^1H and ^{13}C NMR spectra were taken on a Bruker AVANCE Ⅱ spectrometer with TMS as an internal standard and $CDCl_3$ or DMSO-d6 as solvent. MS were performed on a ProteomeX-LTQ spectrometer. All spectra were recorded at room temperature(temperature controlled at 25 ± 3 °C).

2. Synthesis and characterization.

5-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-*tert*-butyldimethylsilyloxy-2-methylquinoline (2)

5-bromo-8-tert-butyldimethylsilyloxy-2-methyl-quinoline (0.9 g, 2.56 mmol), pinacolborane (0.6 mL, 3.8 mmol), Et_3N (1.1 mL, 7.5 mmol) and $PdCl_2(dppf)$ (0.04 g, 0.049 mmol) were dissolved in anhyd 1,4-dioxane (9 mL) under Ar atmosphere and the solution was stirred overnight at 90 °C. After cooling to room temperature, the mixture was poured into water (50 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and chromatographed on silica gel (petroleum ether: ethyl acetate = 20: 1, v/v). Then the resulting light yellow solid was purified by recrystallization from hexane to give **4** (0.71 g) as white solid, yield: 79%. ^1H NMR (400 MHz, CDCl3): δ= 8.95(m, 1H), 7.97(d, 1H, *J*=7.6Hz), 7.28(m, 1H), 7.14(d, 1H, *J*=7.2Hz), 2.73(s, 3H), 1.39(s, 12H), 1.07(s, 9H), 0.28(s, 6H). ^{13}C NMR

(100 MHz, CDCl3): δ= 156.5, 155.5, 141.3, 136.6, 136.3, 131.9, 125.9, 122.2, 121.9, 117.4, 83.5, 25.9, 24.9, 24.7, 18.9, -3.8. MS: *m/z* = 399.28.

5-(4-aldehyde)-8- *tert*-butyldimethylsilyloxy-2-methylquinoline (1)

5-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-*tert*-butyldimethylsilyloxy-2-methylquinoline (0.56 g, 1.4 mmol), 4-bromobenzaldehyde (0.28 g, 1.5 mmol), $Pd(PPh_3)_4$ (0.04 g, 0.034 mmol),and Na_2CO_3 (1.48 g, 14 mmol) were added to a flask under Ar atmosphere. A solvent mixture of toluene (23 mL), water (14 mL), and ethanol (7 mL) was degassed and added to the reaction mixture. The resulting mixture was refluxed with vigorous stirring for 24 h. After cooling to room temperature, the mixture was poured into water (50 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried (Na_2SO4) and chromatographed on silica gel (petroleum ether: ethyl acetate = 5: 1, v/v) to give **1** (0.37 g) as light yellow solid, yield: 70%. ^1H NMR (400 MHz, $CDCl_3$): δ= 10.10(s, 1H), 8.08(d, 1H, *J*=8.4Hz), 8.00(d, 2H, *J*=8.0Hz), 7.62(d, 1H, *J*=8.0Hz), 7.36 (d, 1H, *J*=8.0Hz), 7.24 (d, 2H, *J*=8.4Hz), 1.09(s, 9H), 0.34(s, 6H). ^{13}C NMR (100MHz, $CDCl_3$): δ=157.24, 152.64, 146.42, 135.10, 133.70, 131.25, 130.78, 130.67, 129.95, 129.83, 127.09, 125.53, 122.30, 117.53, 25.94, 24.76, 18.97, -3.81. MS: *m/z* = 377.33.

References:

1. N. Jotterand, D. A. Pearce, B. Imperiali, *J. Org. Chem.* 2001, **66**, 3224.

3. UV-visible Absorbance Analysis.

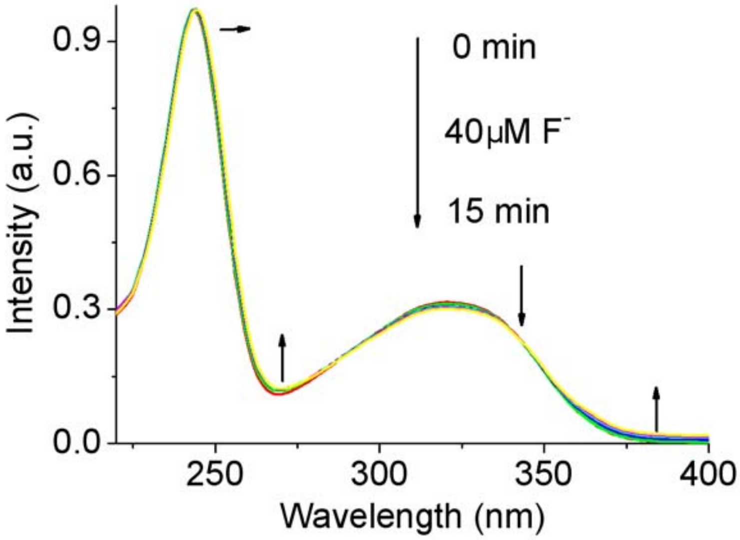


Fig. S1. Time-dependent UV-vis spectra of **1** in CH_3CN upon addition of 2.0 equiv F^- ions. [**1**] = 20 μM.

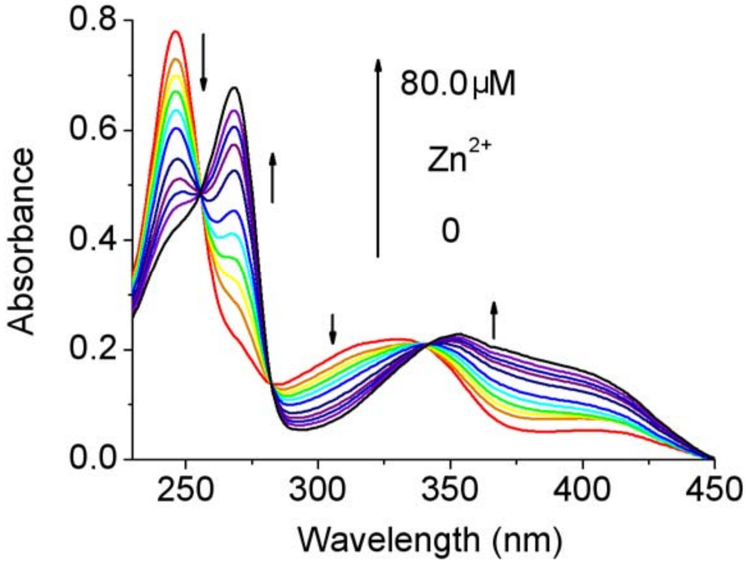


Fig. S2 UV-vis spectra of the system [**1** + F^-] + Zn^{2+} in CH_3CN in the presence of increasing Zn^{2+} concentrations. [**1**] = 20 μM.

4. ^{1}H NMR Analysis.

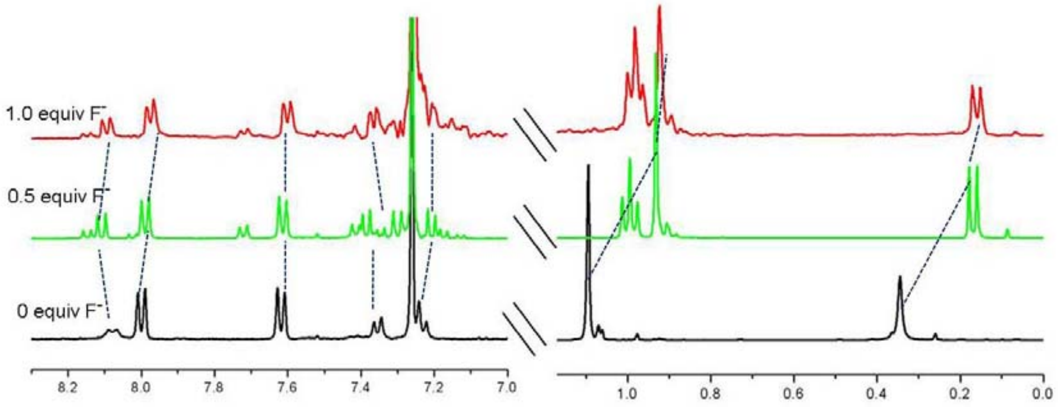


Fig. S3. ^{1}H NMR spectrum of **1** (bottom) and **1**+ F$^-$ (top) taken in $CDCl_3$.

5. Fluorometric Analysis.

The quantum yields of sensor **1** in different solvents were determined according to the following equation:

$$\Phi_u = \Phi_s \frac{F_u A_s n_u^2}{F_s A_u n_s^2}$$

Where Φ is quantum yield; *F* is integrated area under the corrected emission spectra; *A* is absorbance at the excitation wavelength; *n* is the refractive index of the solution; the subscripts *u* and *s* refer to the unknown and the standard, respectively. Quinine bisulfate in 0.05 M H_2SO_4 solution was used as the standard, which has a quantum yield of 0.55.

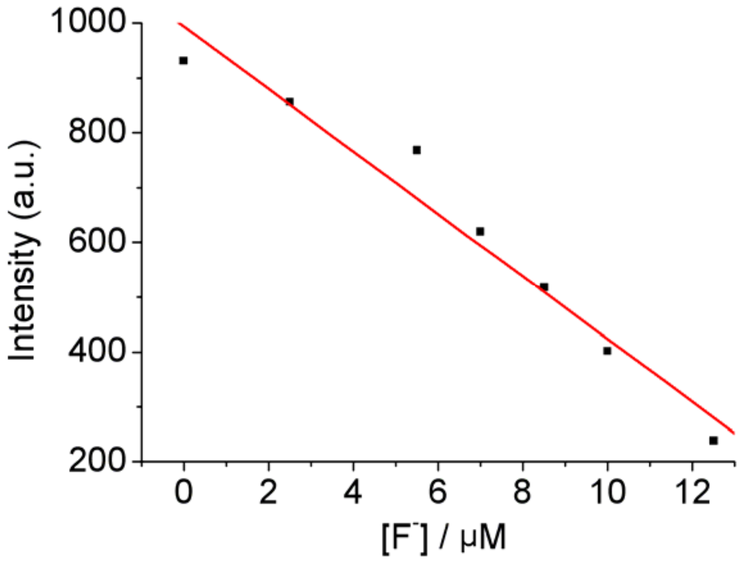


Fig. S4. Fluorescence emission changes of sensor **1** at 458 nm vs TBAF concentration form 0 to 12.5 μM. [**1**] = 20 μM. λ_{ex} = 340 nm.

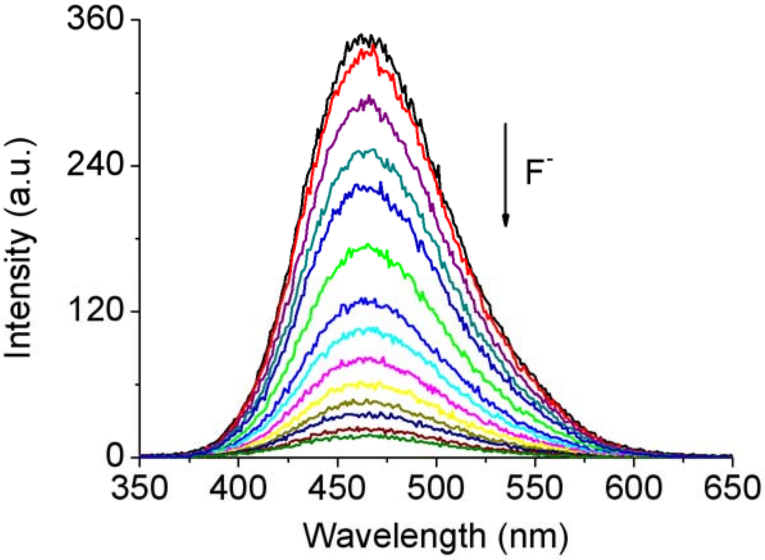


Fig. S5. Time-dependent fluorescence spectra of **1** in CH_3CN upon addition of 1.0 equiv F^- ions. [**1**] = 20 μM. λ_{ex} = 340 nm.

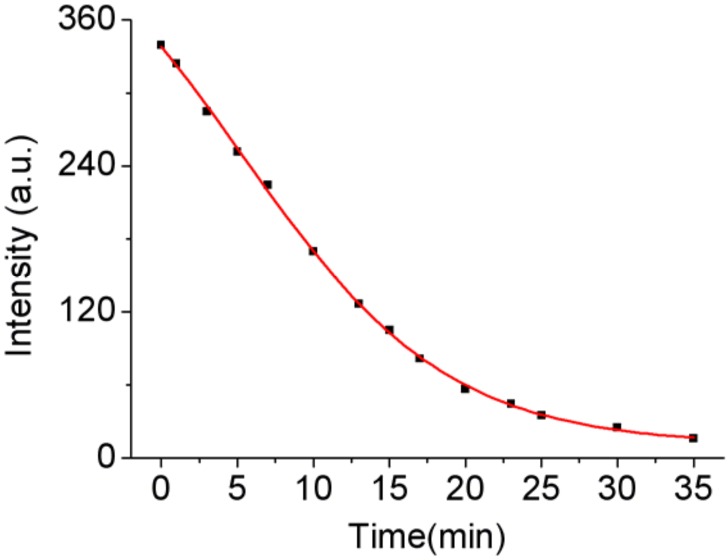


Fig. S6. Emission intensity at 458 nm of sensor **1** as a function of time upon addition of 1.0 equiv F^- ions. [**1**] = 20 μM. λ_{ex} = 340 nm. The equilibrium time was about 35 min.

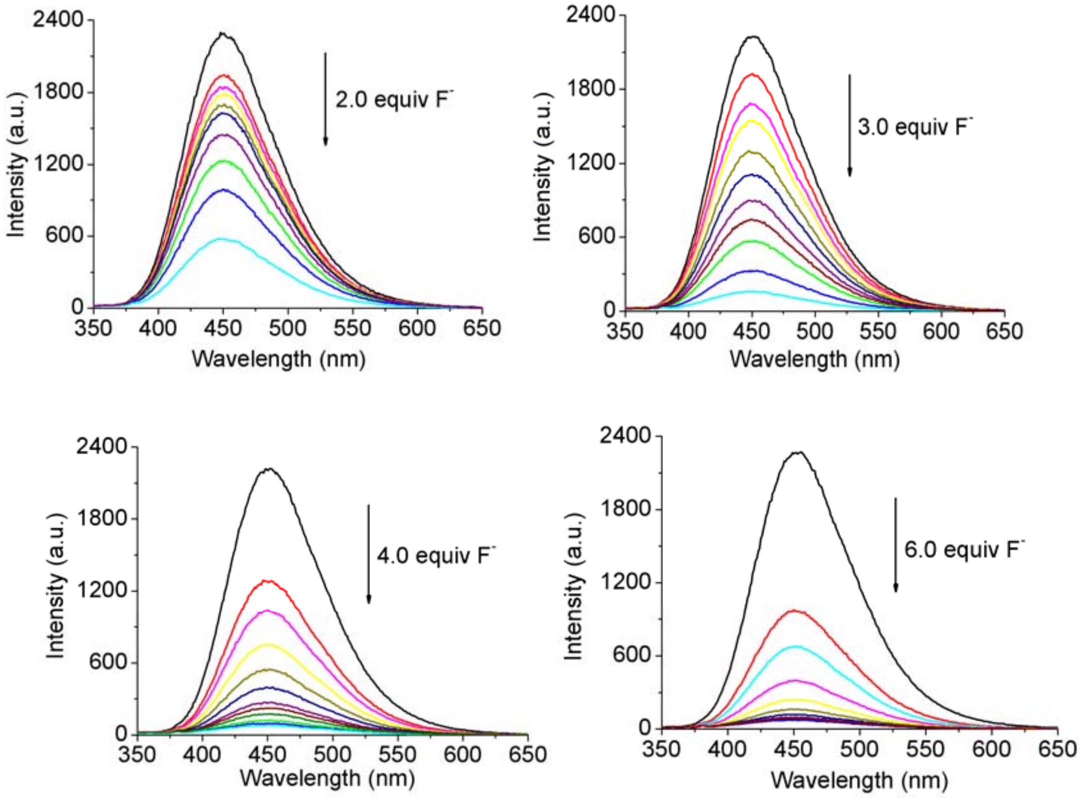


Fig. S7. Time-dependent (0-15 min) fluorescence spectra of **1** in CH_3CN upon addition of 2.0, 3.0, 4.0, and 6.0 equiv F^- ions. [**1**] = 20 μM. λ_{ex} = 340 nm. The equilibrium times were about 25min, 18min, 12 min, and 8 min, respectively.

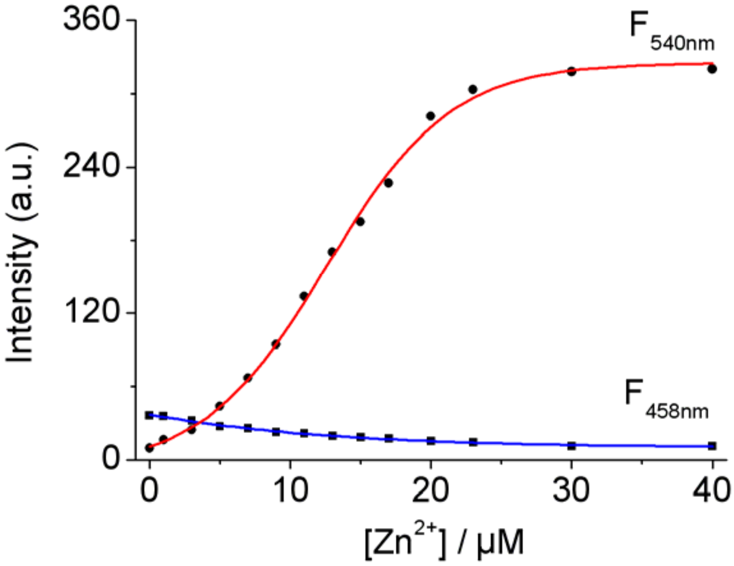


Fig. S8. Fluorescence emission changes of sensor **1** vs Zn^{2+} concentration at 458 and 540 nm in CH_3CN. [**1**] = 20 μM. λ_{ex} = 340 nm.

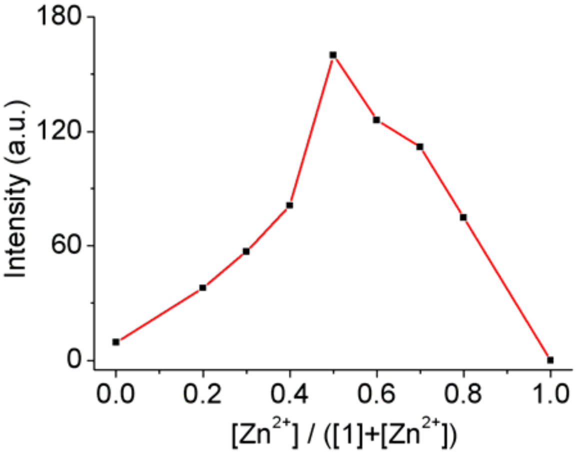


Fig. S9. Job' plots of changes in fluorescence intensity at 540nm at varying mole ratios of **1** and Zn^{2+} in CH_3CN. [**1**] = 20 μM. λ_{ex} = 340 nm.

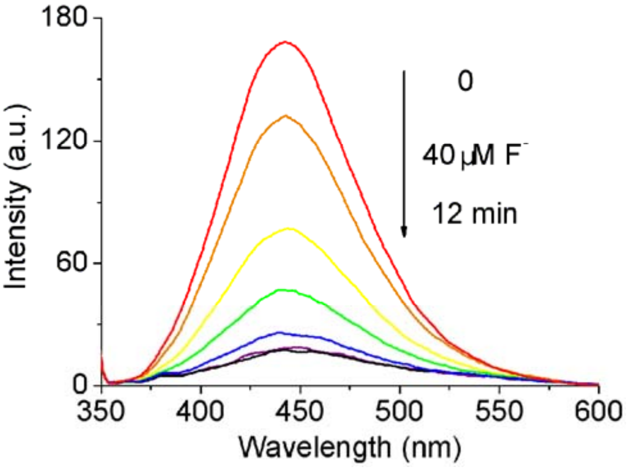


Fig. S10. Time-dependent fluorescence spectra of **1** in acetone upon addition of 2.0 equiv F^- ions. [**1**] = 20 μM. λ_{ex} = 340 nm.

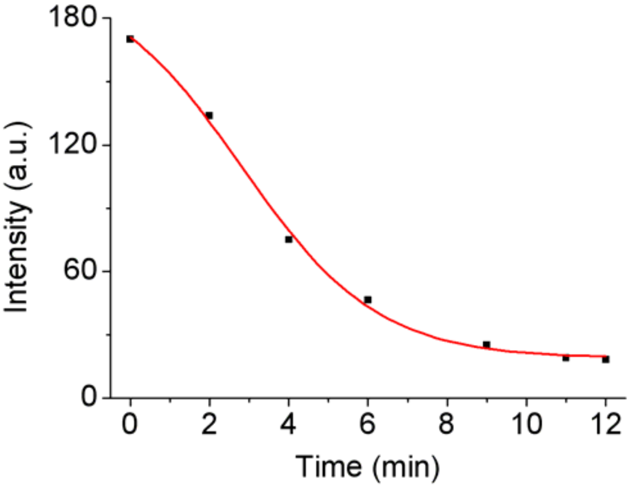


Fig. S11. Emission intensity at 440 nm of sensor **1** as a function of time upon addition of 2.0 equiv F^- ions. [**1**] = 20 μM. λ_{ex} = 340 nm.

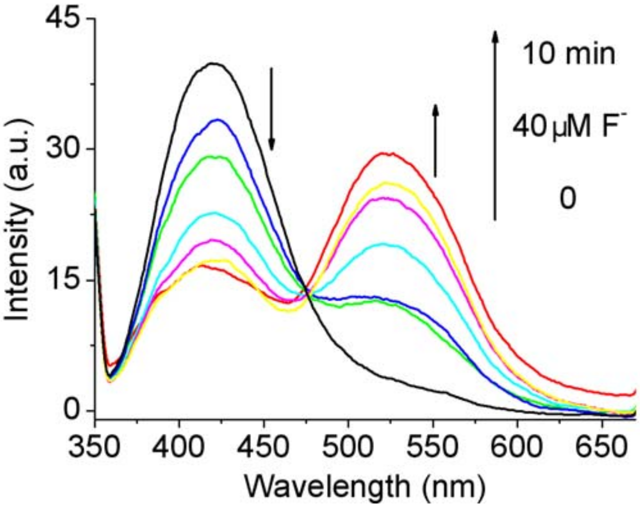


Fig. S12. Time-dependent fluorescence spectra of **1** in THF upon addition of 2.0 equiv F^- ions. [**1**] = 20 μM. λ_{ex} = 340 nm.

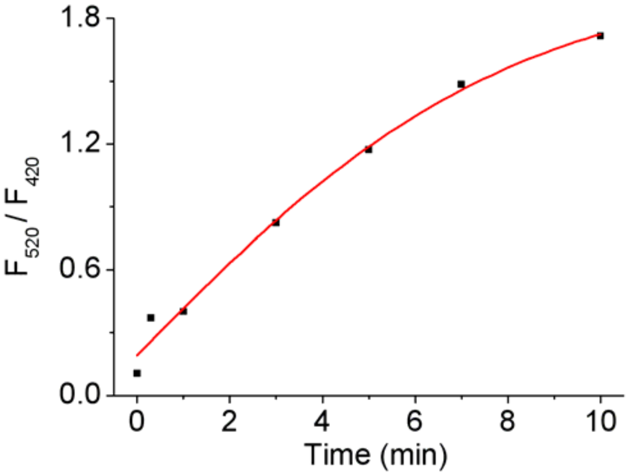


Fig. S13. Emission intensity ratio (F_{520}/F_{420}) of sensor **1** as a function of time upon addition of 2.0 equiv F^- ions. [**1**] = 20 μM. λ_{ex} = 340 nm.

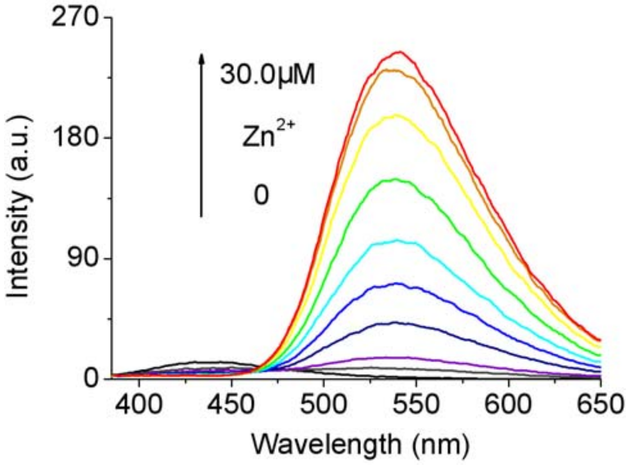


Fig. S14 Fluorescence spectra of the system [**1** + F^-] + Zn^{2+} in acetone in the presence of increasing Zn^{2+} concentrations in acetone. [**1**] = 20 μM. λ_{ex} = 340 nm.

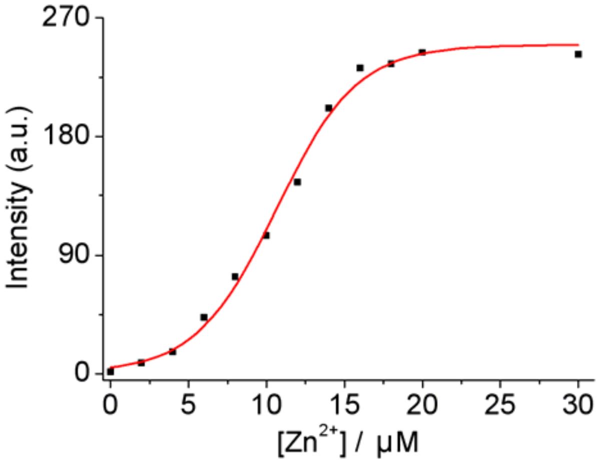


Fig. S15. Fluorescence emission changes of the system [**1** + F$^-$] vs Zn^{2+} concentration at 540 nm in acetone. [**1**] = 20 μM. λ_{ex} = 340 nm.

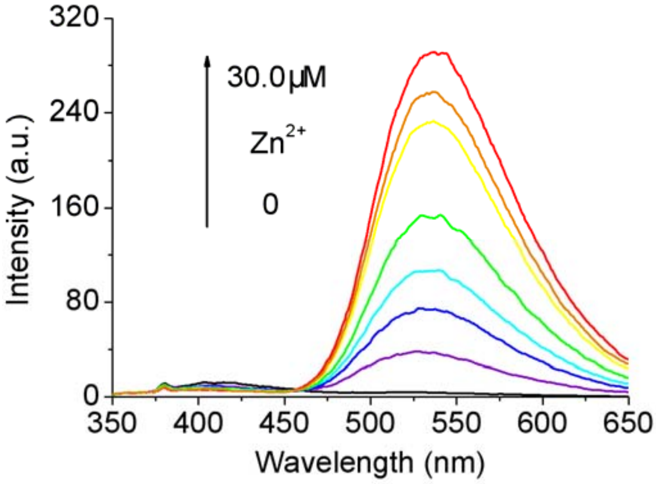


Fig. S16. Fluorescence spectra of the system [**1** + F$^-$] + Zn^{2+} in acetone in the presence of increasing Zn^{2+} concentrations in THF. [**1**] = 20 μM. λ_{ex} = 340 nm.

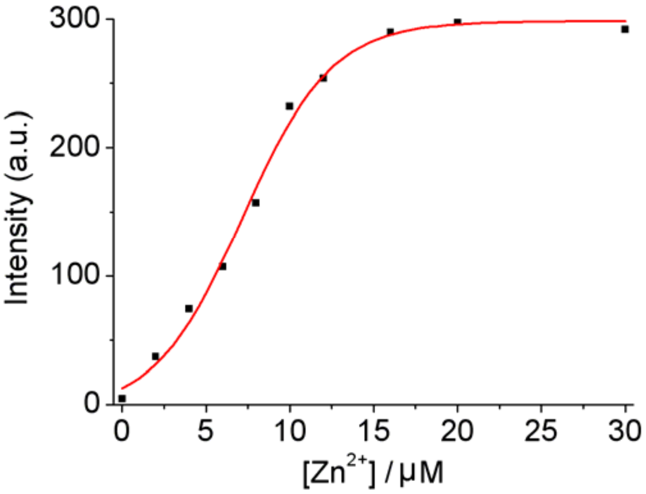


Fig. S17. Fluorescence emission changes of the system [**1** + F$^-$] vs Zn^{2+} concentration at 540 nm in THF. [**1**] = 20 μM. λ_{ex} = 340 nm.

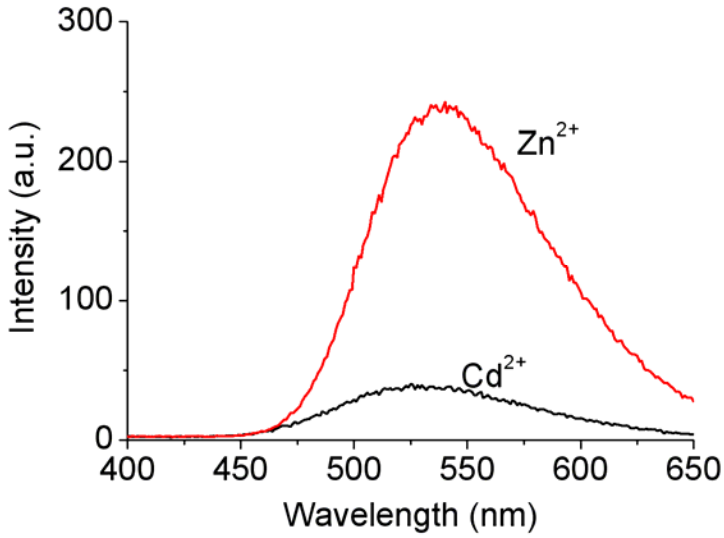


Fig. S18. Fluorescence spectra of the system [**1** + F$^-$] in the presence of 3 equiv Zn^{2+} and Cd^{2+} in acetone. [**1**] = 20 μM. λ_{ex} = 340 nm.

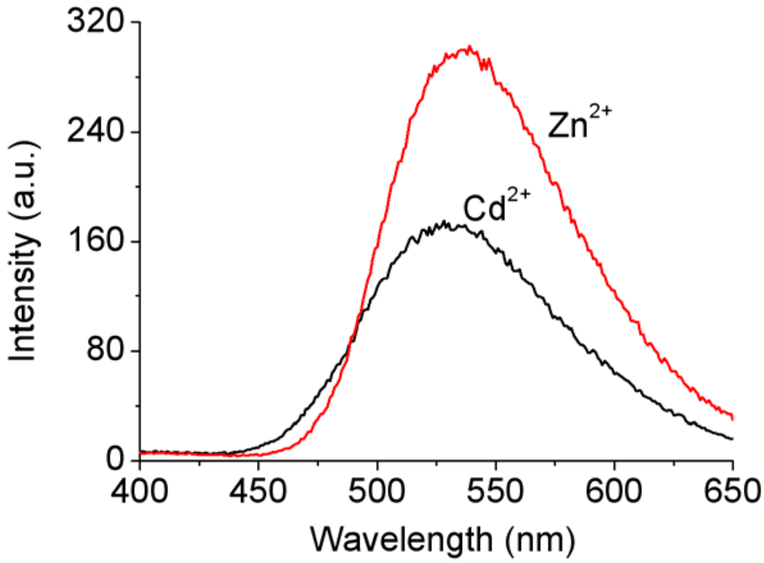


Fig. S19. Fluorescence spectra of the system [**1** + F$^-$] in the presence of 3 equiv Zn^{2+} and Cd^{2+} in THF. [**1**] = 20 μM. λ_{ex} = 340 nm.

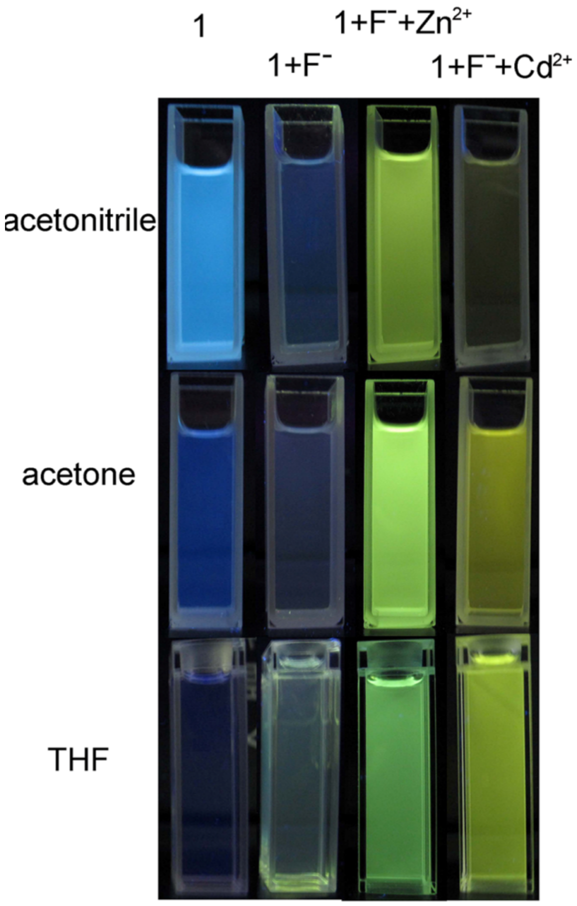
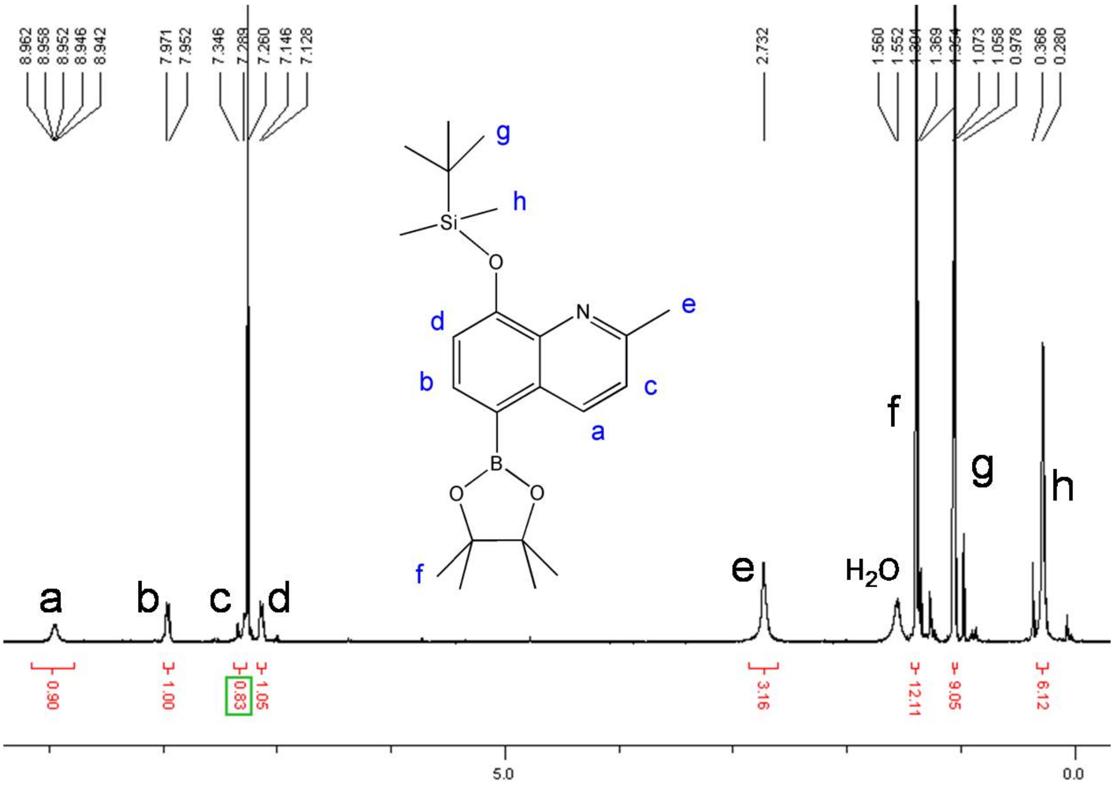


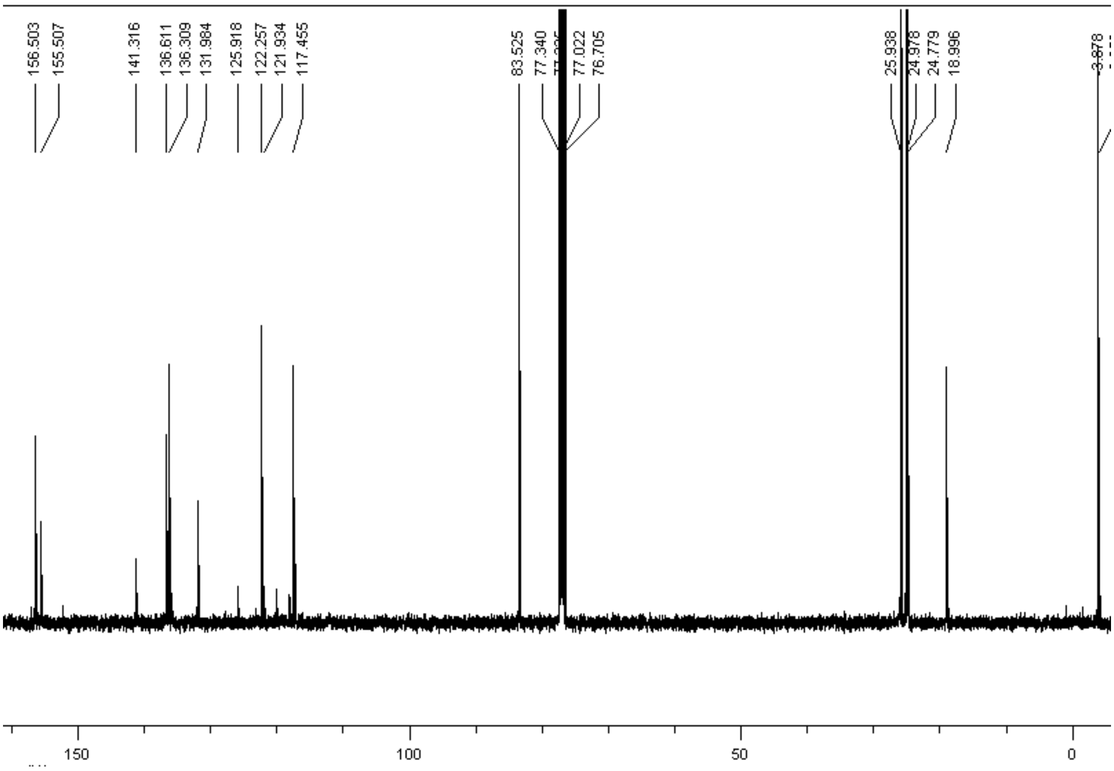
Fig. S20. Naked eye fluorescent color changes under UV lamp observed for **1** upon addition of F^-, Zn^{2+} and Cd^{2+} in CH_3CN, acetone, and THF. [**1**] = 20 μM. λ_{ex} = 340 nm.

6. NMR and MS Data.

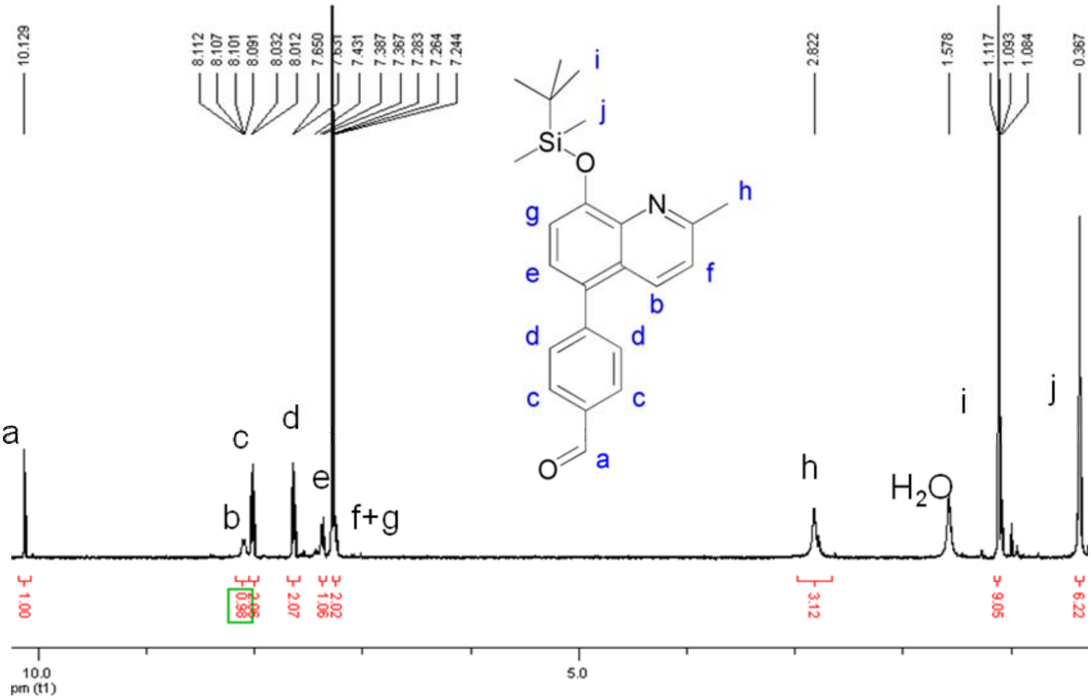
^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of **2**



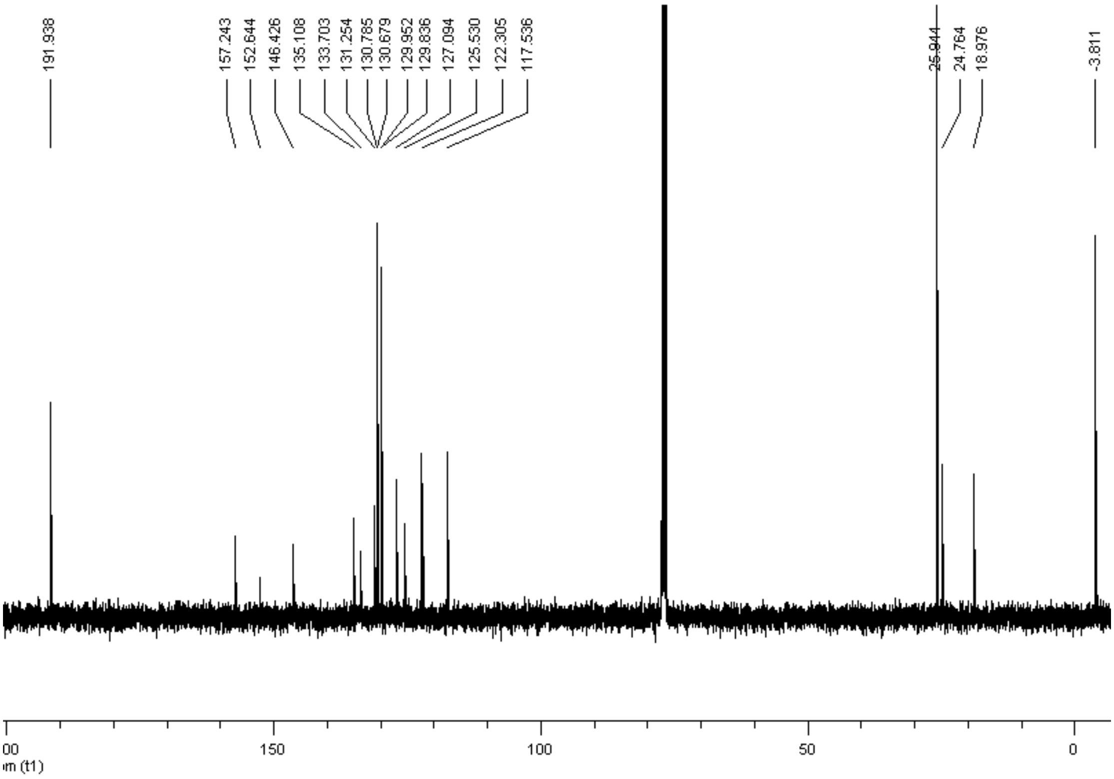
^{13}C NMR (CDCl$_3$, 100 MHz) spectrum of **2**



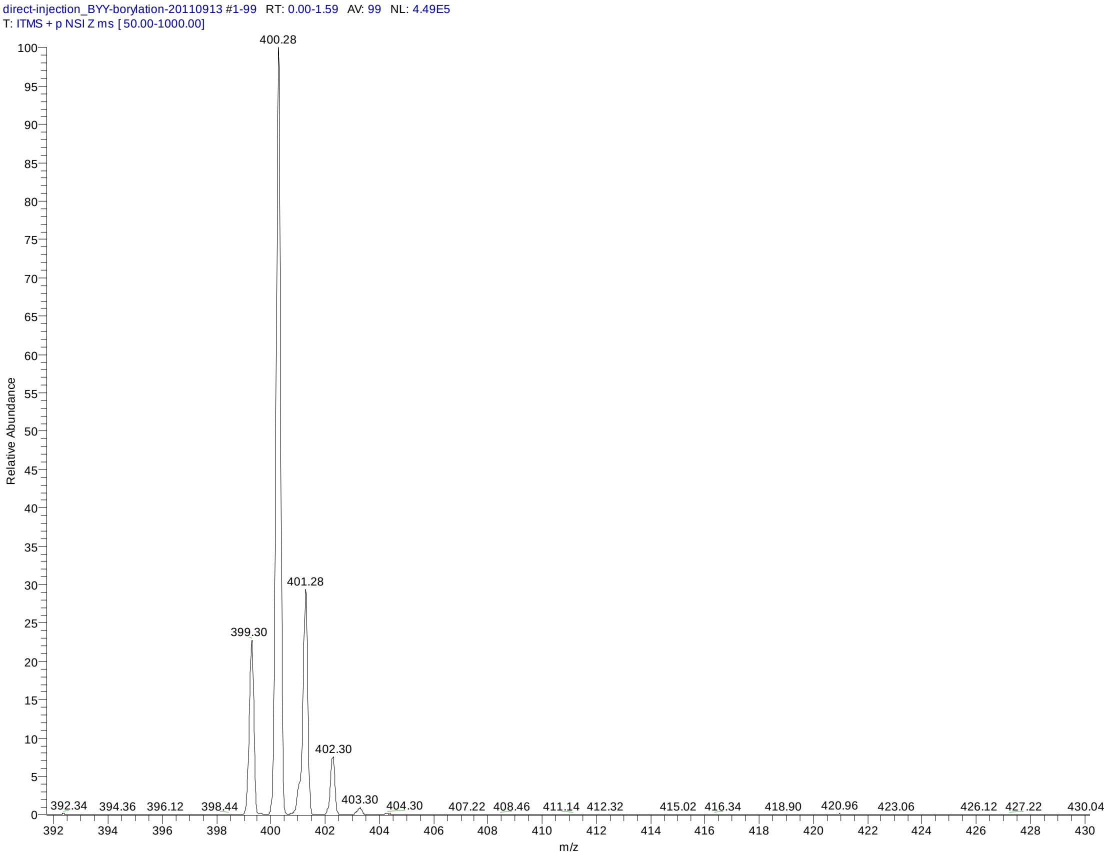
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **1**



^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **1**



MS spectrum of **2**



MS spectrum of **1**