

## Electronic Supplementary Information

for

A “naked eyes” and ratiometric fluorescent chemosensor for rapid detection of fluoride based on combination of desilylation reaction and excited state proton transfer

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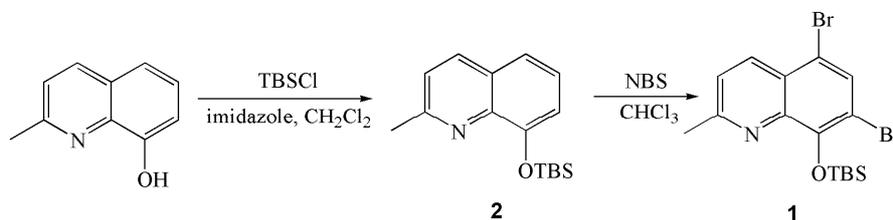
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## 1. Materials and Methods.

Anionic compounds such as  $[\text{Bu}_4\text{N}]^+\text{Cl}^-$ ,  $[\text{Bu}_4\text{N}]^+\text{Br}^-$ ,  $[\text{Bu}_4\text{N}]^+\text{ClO}_4^-$ ,  $[\text{Bu}_4\text{N}]^+\text{HSO}_4^-$ ,  $\text{NaNO}_3$ ,  $\text{NaOAc}$  and  $\text{NaH}_2\text{PO}_4$  were purchased from Shanghai Chemical Co.,  $[\text{Bu}_4\text{N}]^+\text{F}^-$  was purchased from J&K Chemical Co. and 2-methyl-8-hydroxyquinoline was a Alfa Aesar Co. product. They were used without further purification.  $\text{CH}_2\text{Cl}_2$  was purchased from Shanghai Chemical Co. and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . 8-*tert*-butyldimethylsilyloxy-2-methylquinoline<sup>1</sup> was prepared according to the literature. All the other reagents were purchased and used without further purification.

Fluorescence spectra measurements were performed on a Shimadzu RF-5301PC spectrofluorophotometer. Absorption spectra were determined on a Pgeneral UV-Vis TU-1901 Spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Bruker AVANCE II spectrometer with TMS as an internal standard and  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  as solvent. MS were performed on a ProteomeX-LTQ spectrometer. All spectra were recorded at room temperature (temperature controlled at  $25 \pm 3$  °C).

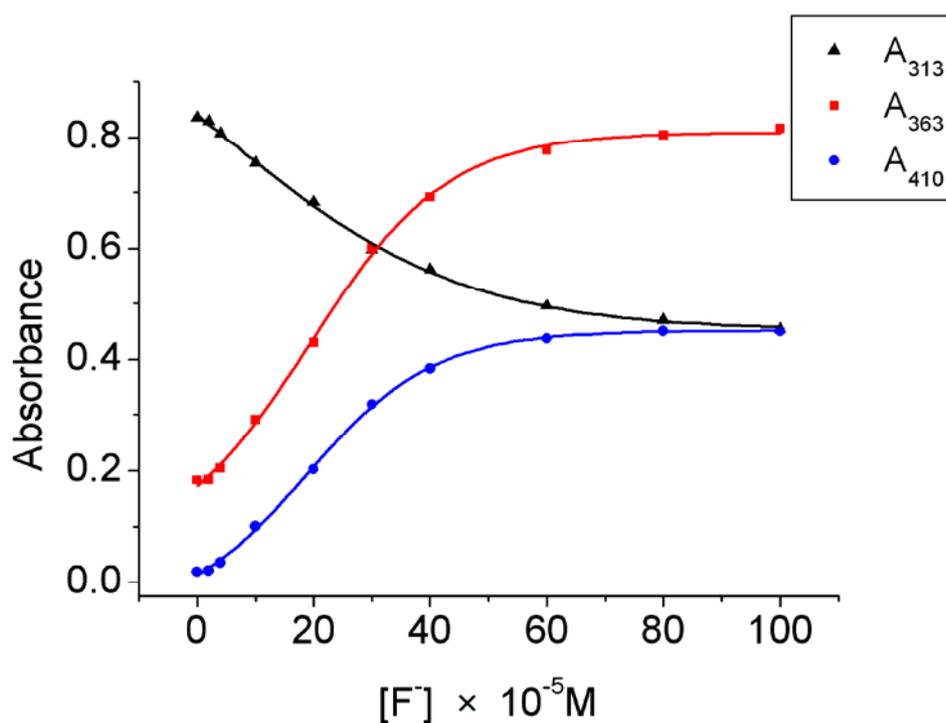
## 2. Synthesis and characterization.



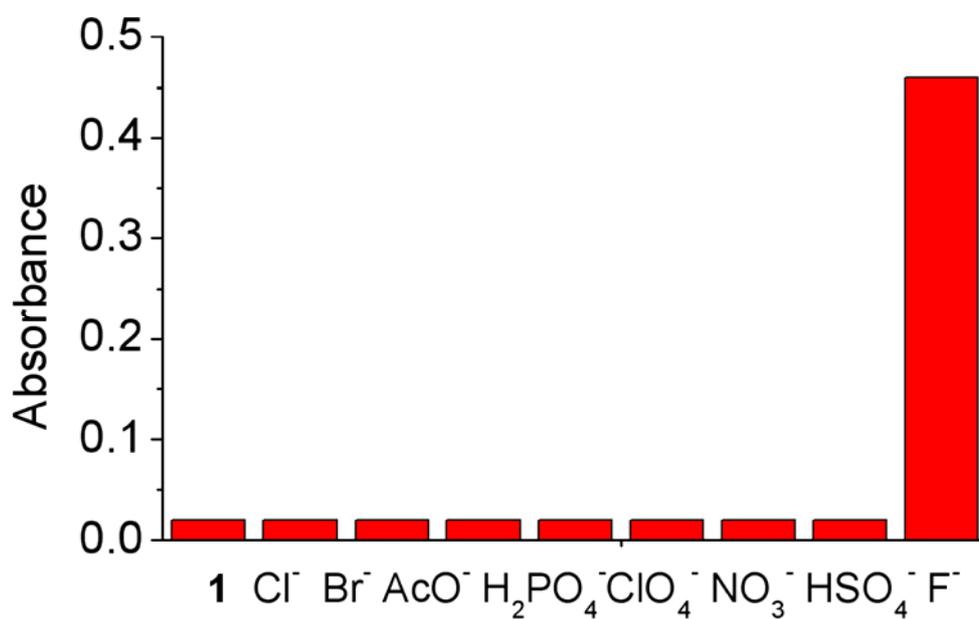
### 5,7-Dibromo-8-*tert*-butyldimethylsilyloxy-2-methylquinoline(**1**)

To a round-bottom flask were added a solution of 8-*tert*-butyldimethylsilyloxy-2-methylquinoline(**2**) (1.27 g, 4.65 mmol) and NBS (1.65 g, 9.30 mmol) in  $\text{CHCl}_3$  (15 ml). The solution was stirred overnight at room temperature. Then it was poured into distilled water (40 ml), and the resulting mixture was extracted three times with  $\text{CH}_2\text{Cl}_2$ . The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under vacuum. Compound (**1**) was isolated using a silica gel chromatographic column eluted with petroleum ether/ethyl acetate (v/v, 12:1), resulting a light yellow solid in 53% yield. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.29(d, 1H,  $J$ =8.8Hz), 7.86(s, 1H), 7.34(d, 1H,  $J$ =8.8Hz), 2.75(s, 3H), 1.10(s, 9H), 0.38(s, 6H). <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.1, 150.1, 141.3, 135.8, 133.1, 126.1, 123.4, 112.3, 111.5, 26.3, 24.3, 19.7, -2.5. MS:  $m/z$ : Calcd: 429.9759  $[\text{M}+\text{H}]^+$ , Found: 429.96  $[\text{M}+\text{H}]^+$ .

### 3. UV-visible Absorbance Analysis.



**Fig. S1.** UV-vis absorbance changes of sensor **1** vs TBAF concentration at 313, 363 and 410 nm.  $[1] = 200 \mu M$ .



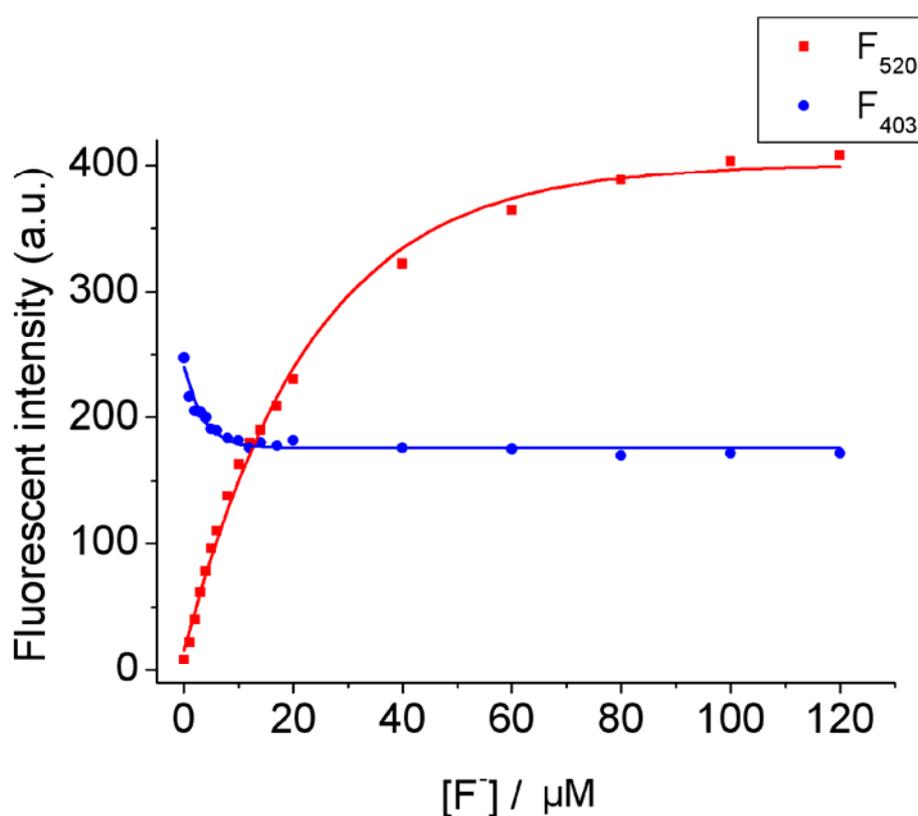
**Fig. S2.** UV-vis absorbance of the sensor **1** at 410 nm in the presence of 10 equivalents of different anions in THF.  $[1] = 200 \mu M$ .

#### 4. Fluorometric Analysis.

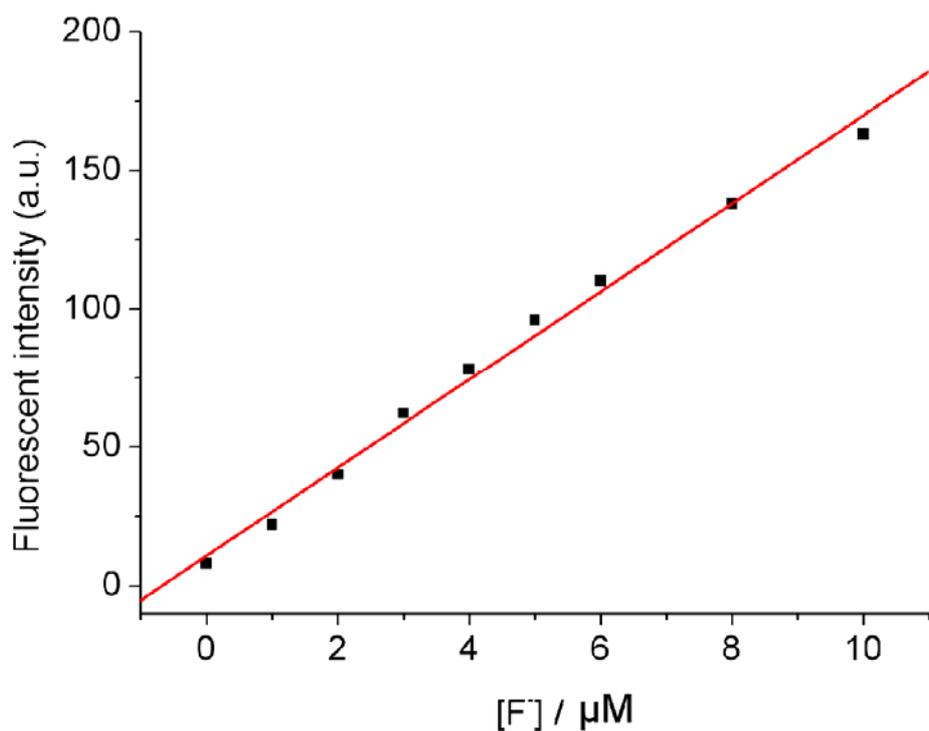
The quantum yields of sensor **1** in different solvents were determined according to the following equation:

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

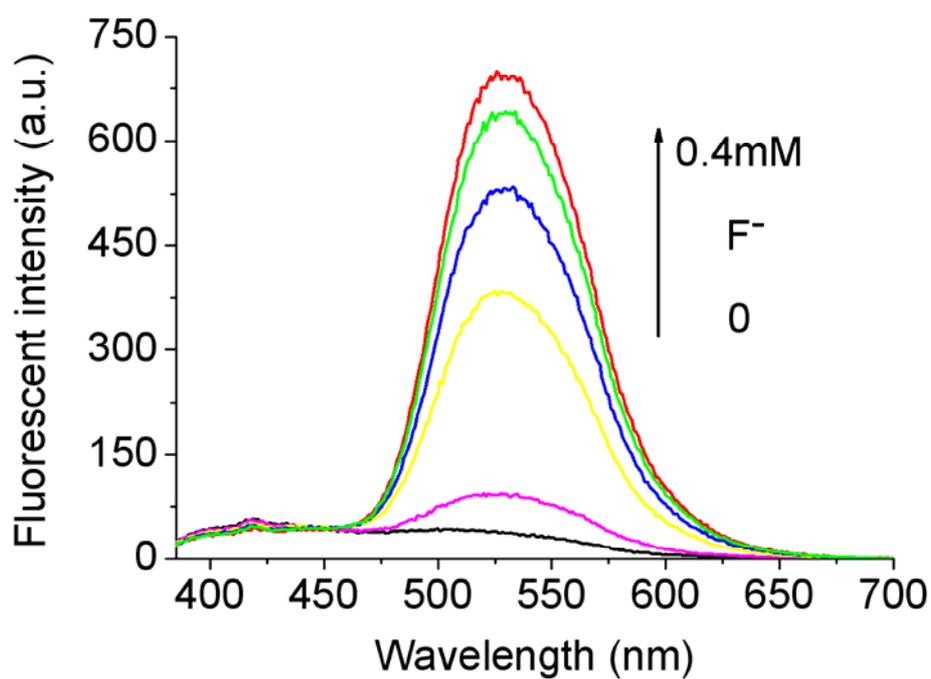
Where  $\Phi$  is quantum yield;  $F$  is integrated area under the corrected emission spectra;  $A$  is absorbance at the excitation wavelength;  $n$  is the refractive index of the solution; the subscripts  $u$  and  $s$  refer to the unknown and the standard, respectively. Quinine bisulfate in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution was used as the standard, which has a quantum yield of 0.55.



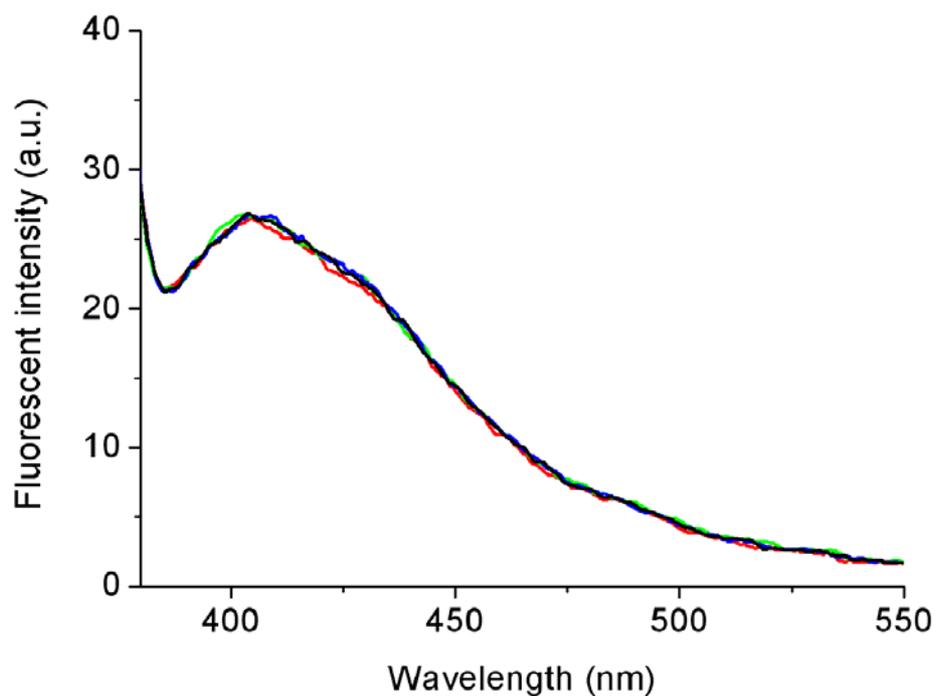
**Fig. S3.** Fluorescence emission changes of sensor **1** vs TBAF concentration at 403 and 520 nm in THF. [1] = 20 μM.  $\lambda_{\text{ex}} = 338$  nm.



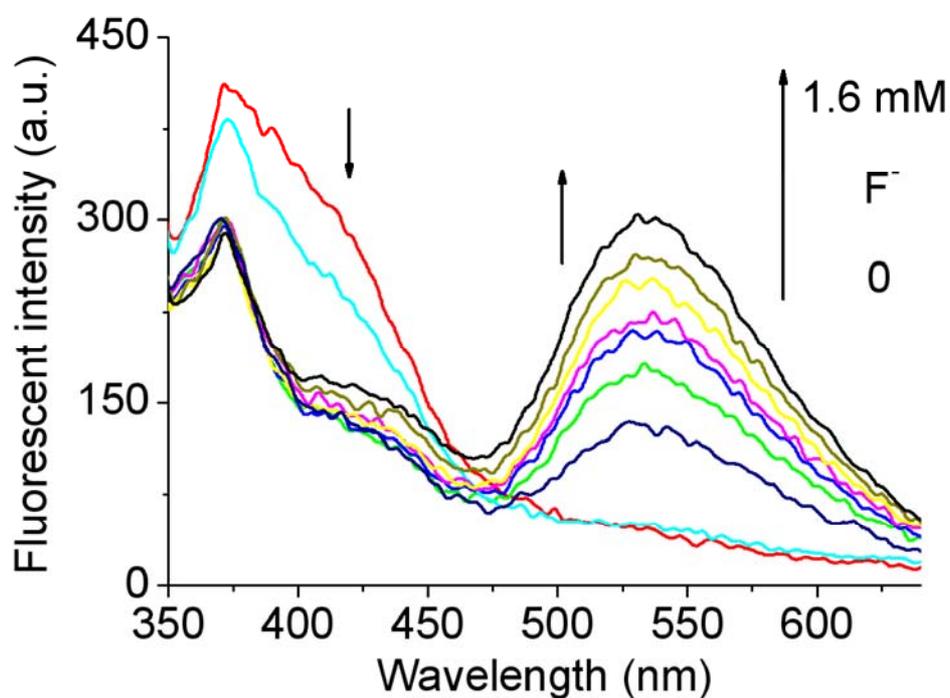
**Fig. S4.** Fluorescence emission changes of sensor **1** at 520 nm vs TBAF concentration form 0 to 10  $\mu\text{M}$ .  $[\mathbf{1}] = 20 \mu\text{M}$ .  $\lambda_{\text{ex}} = 338 \text{ nm}$ .



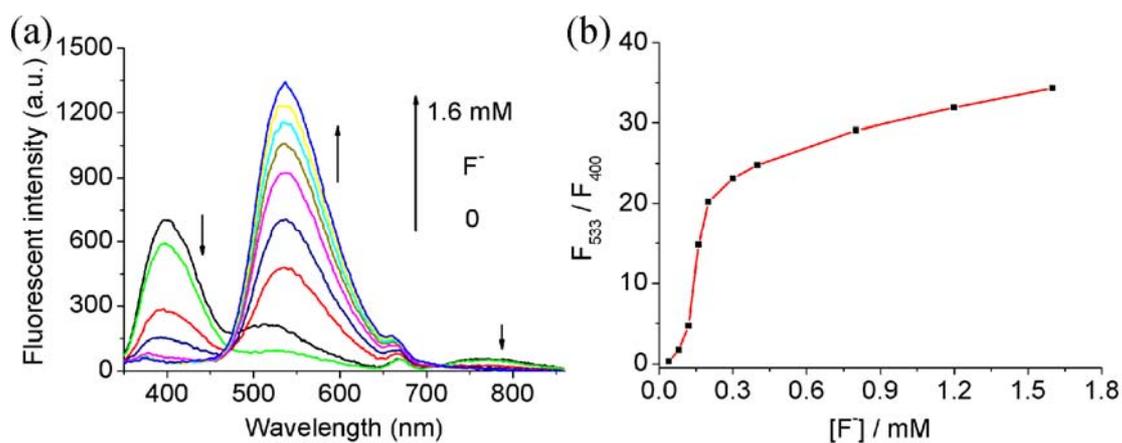
**Fig. S5.** Fluorescence spectra of 5,7-dibromo-8-hydroxyquinoline ( $20\mu\text{M}$ ) + TBAF in THF in the presence of increasing  $\text{F}^-$  concentrations.  $\lambda_{\text{ex}} = 360 \text{ nm}$ .



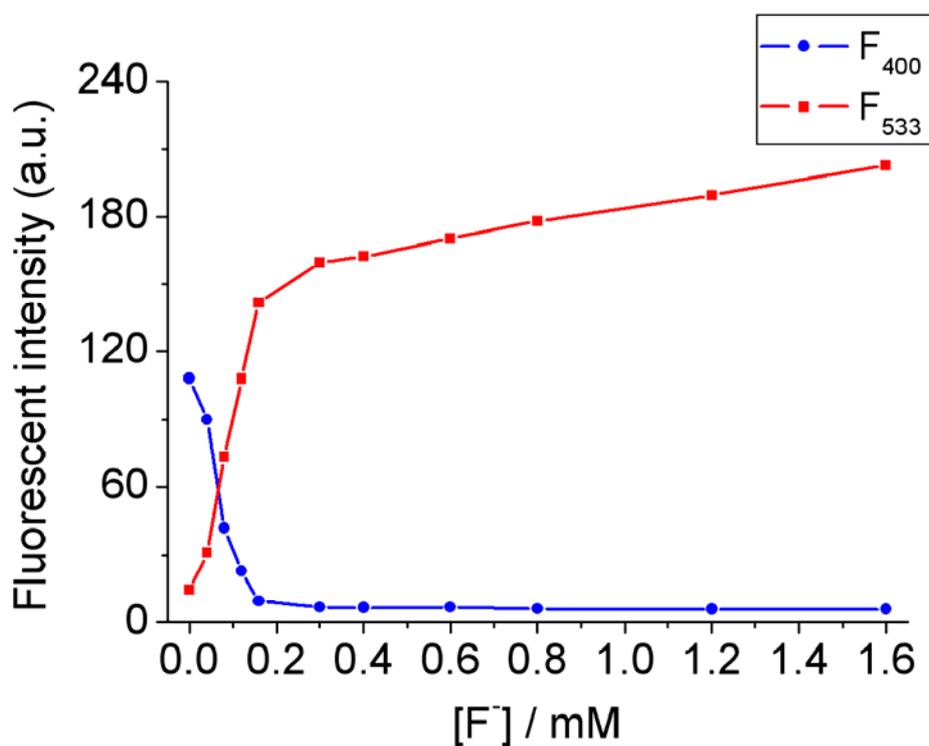
**Fig. S6.** Fluorescence spectra of 8-*tert*-butyldimethylsilyloxy-2-methylquinoline (20  $\mu$ M) + TBAF (0, 0.08 mM, 0.16 mM, 0.4 mM) in THF.  $\lambda_{\text{ex}} = 360$  nm.



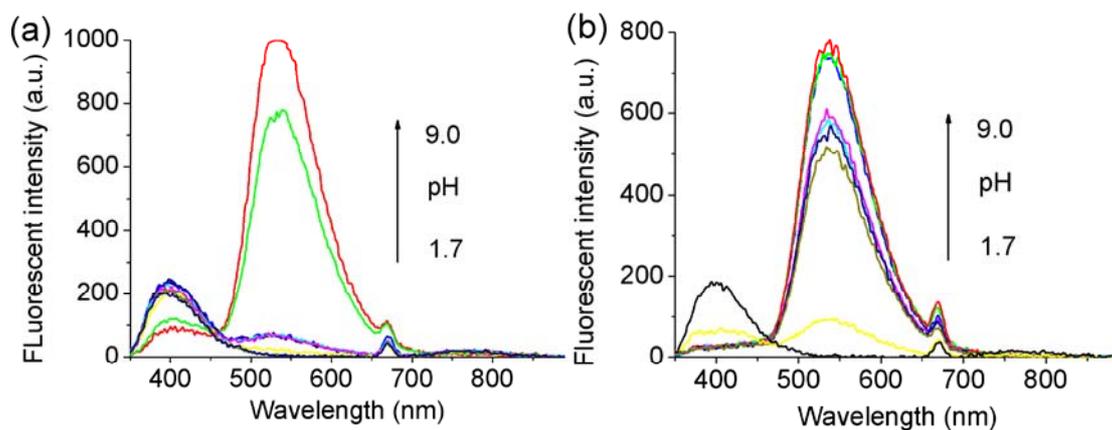
**Fig. S7.** Fluorescence spectra of sensor 1 + TBAF in DMF/H<sub>2</sub>O (95:5, v/v) in the presence of increasing F<sup>-</sup> concentrations. [1] = 20  $\mu$ M.  $\lambda_{\text{ex}} = 335$  nm.



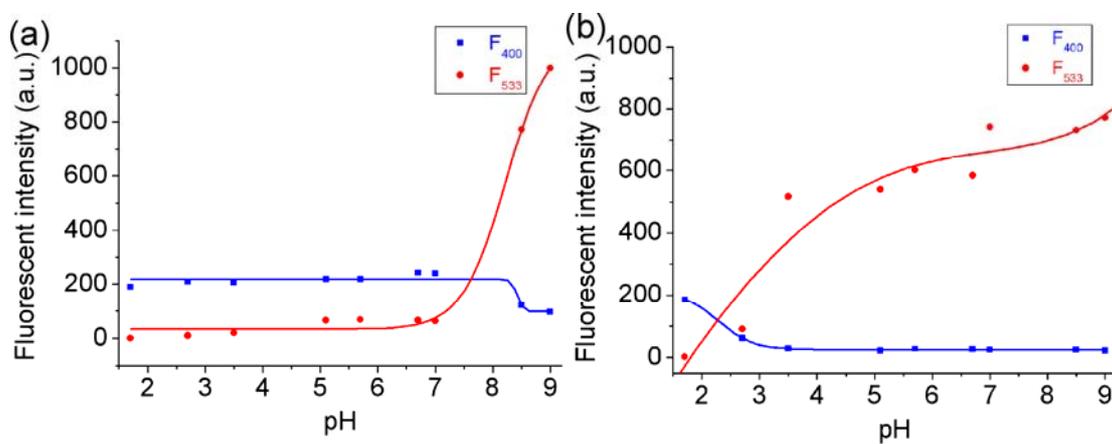
**Fig. S8** (a) Fluorescence spectra of sensor **1** + TBAF in DMF/H<sub>2</sub>O (95:5, v/v) in the presence of increasing  $F^-$  concentrations. (b) Ratiometric calibration curves  $F_{533\text{nm}}/F_{403\text{nm}}$  as a function of  $F^-$  concentrations.  $[1] = 200 \mu\text{M}$ .  $\lambda_{\text{ex}} = 335 \text{ nm}$ .



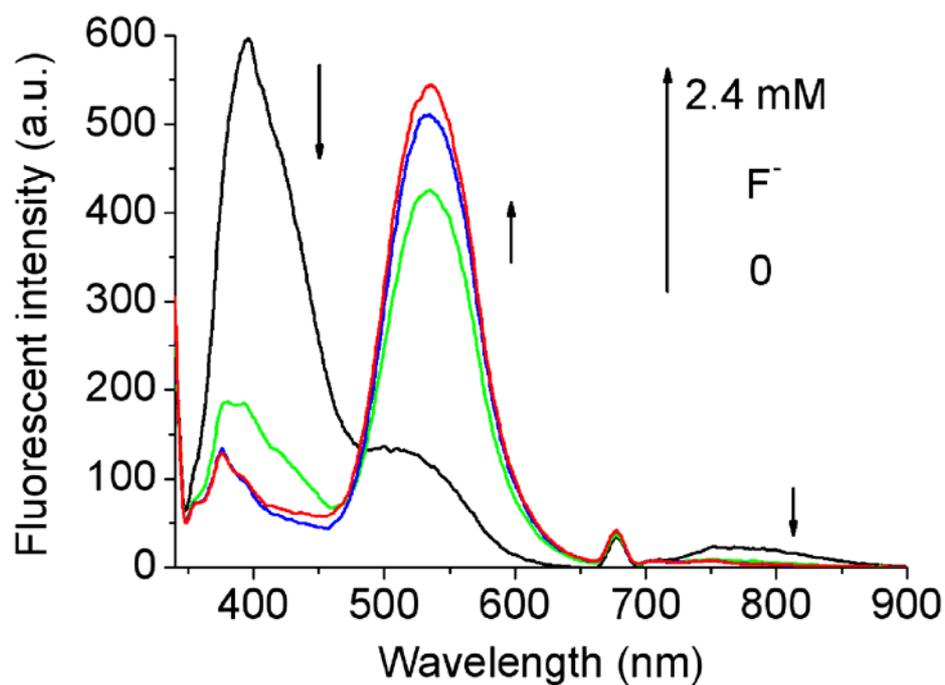
**Fig. S9**. Fluorescence emission changes of sensor **1** vs TBAF concentration at 400 and 533 nm in DMF/H<sub>2</sub>O (95:5, v/v).  $[1] = 200 \mu\text{M}$ .  $\lambda_{\text{ex}} = 335 \text{ nm}$ .



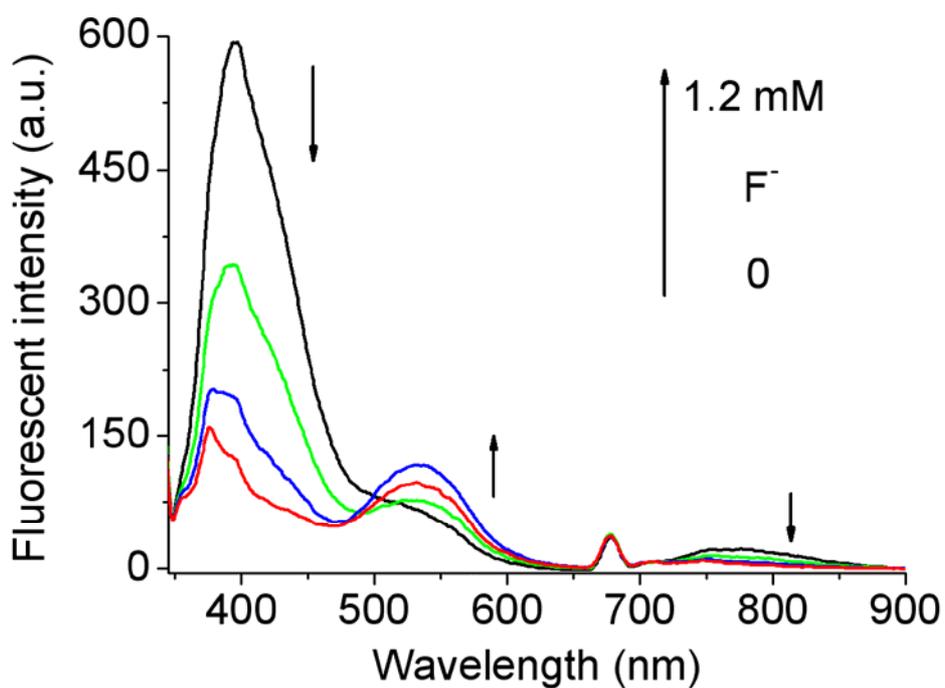
**Fig. S10.** (a) Fluorescence spectra of sensor **1** and (b) sensor **1** + 2.0 equiv F<sup>-</sup> at various pH values in DMF/H<sub>2</sub>O (95:5, v/v). [**1**] = 200 μM. λ<sub>ex</sub> = 335 nm.



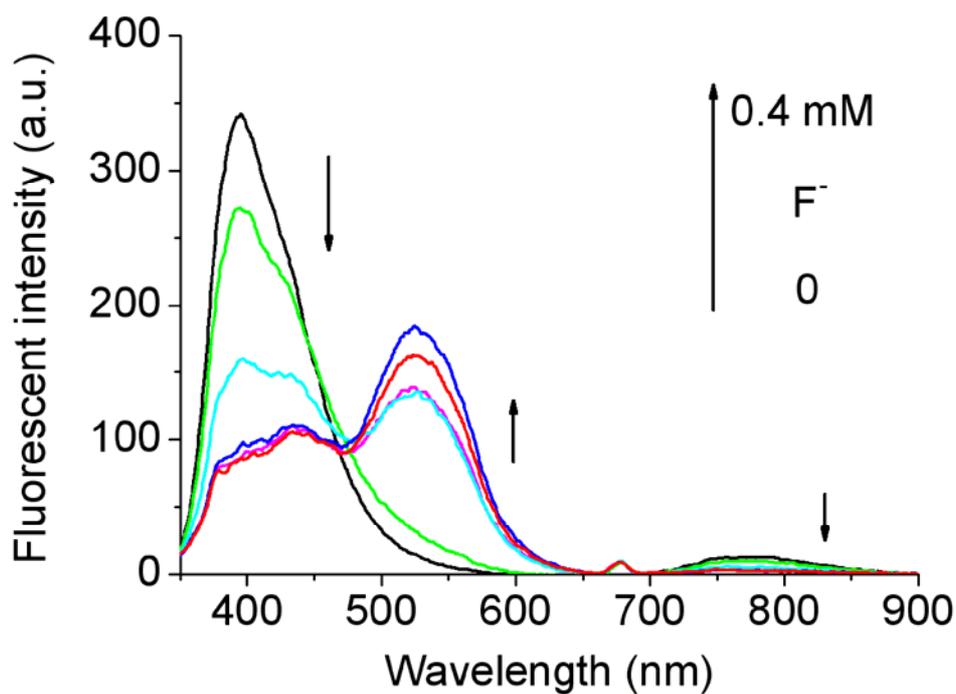
**Fig. S11.** (a) Fluorescence intensity of **1** and (b) sensor **1** + 2.0 equiv F<sup>-</sup> at 400 nm and 533 nm recorded at various pH values in DMF/H<sub>2</sub>O (95:5, v/v). [**1**] = 200 μM. λ<sub>ex</sub> = 335 nm.



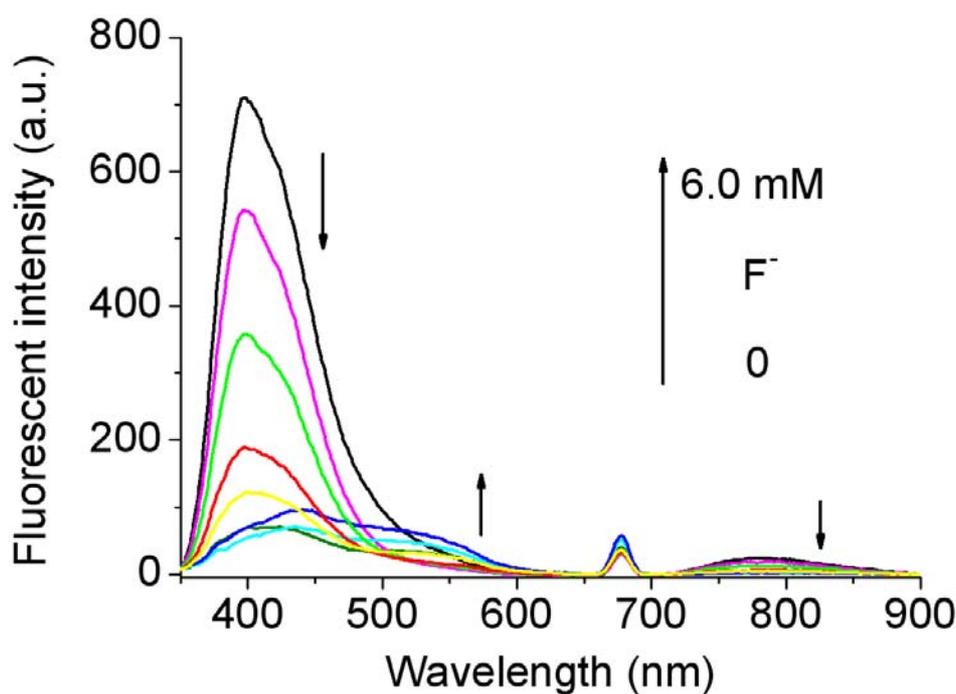
**Fig. S12.** (a) Fluorescence spectra of sensor **1** + TBAF in DMF/H<sub>2</sub>O (90:10, v/v) in the presence of increasing F<sup>-</sup> concentrations. [1] = 200 μM. λ<sub>ex</sub> = 335 nm.



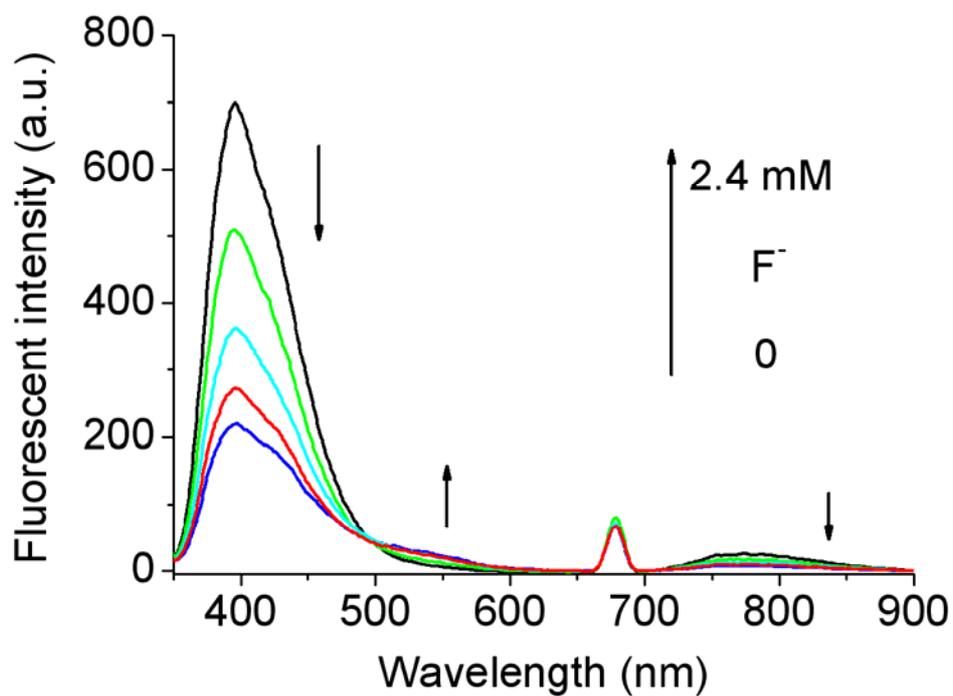
**Fig. S13.** (a) Fluorescence spectra of sensor **1** + TBAF in DMF/H<sub>2</sub>O (80:20, v/v) in the presence of increasing F<sup>-</sup> concentrations. [1] = 200 μM. λ<sub>ex</sub> = 335 nm.



**Fig. S14.** (a) Fluorescence spectra of sensor **1** + TBAF in THF/H<sub>2</sub>O (95:5, v/v) in the presence of increasing F<sup>-</sup> concentrations. [1] = 200 μM. λ<sub>ex</sub> = 338 nm.

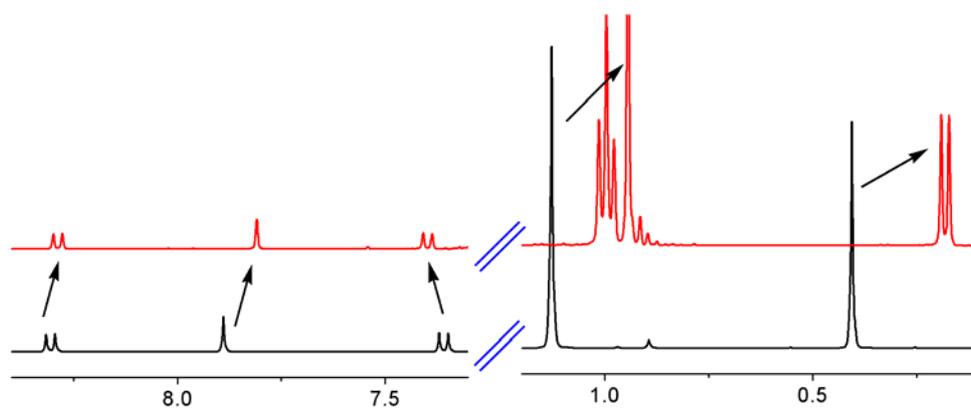


**Fig. S15.** (a) Fluorescence spectra of sensor **1** + TBAF in CH<sub>3</sub>CN/H<sub>2</sub>O (95:5, v/v) in the presence of increasing F<sup>-</sup> concentrations. [1] = 200 μM. λ<sub>ex</sub> = 335 nm.



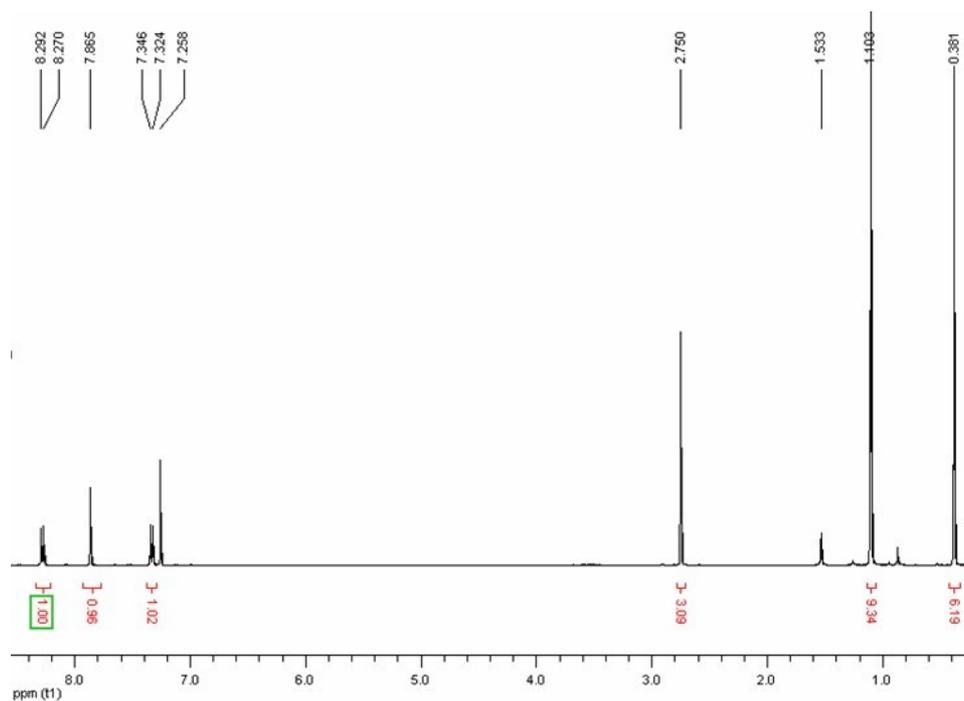
**Fig. S16.** (a) Fluorescence spectra of sensor **1** + TBAF in dioxane/H<sub>2</sub>O (95:5, v/v) in the presence of increasing F<sup>-</sup> concentrations. [1] = 200 μM. λ<sub>ex</sub> = 335 nm.

## 5. <sup>1</sup>H NMR Analysis

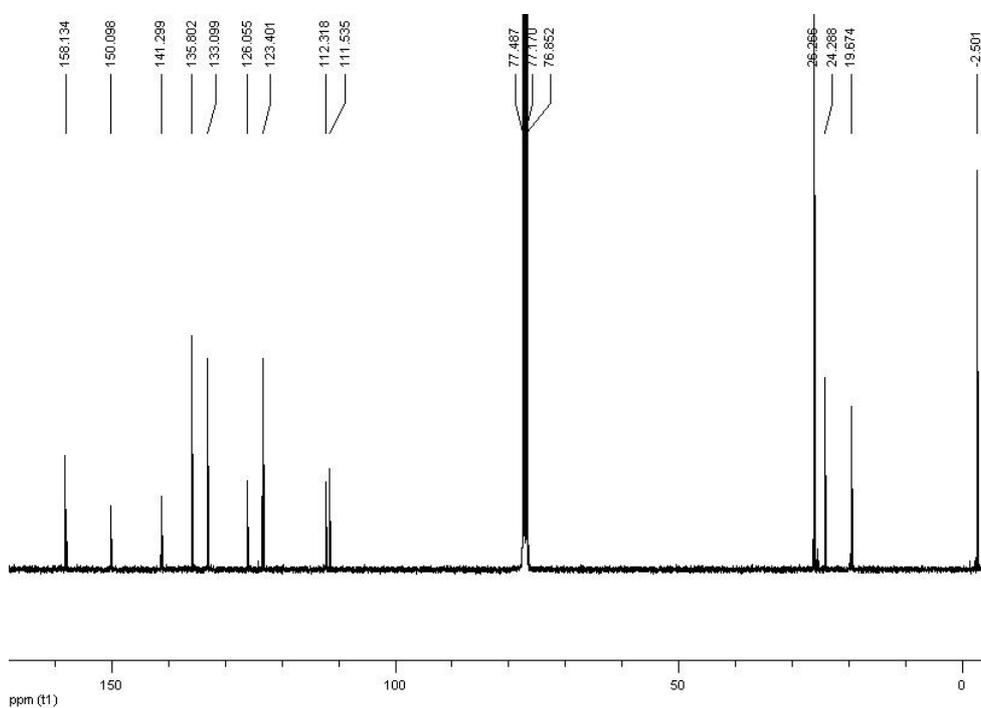


**Fig. S17.** <sup>1</sup>H NMR spectrum of **1** (bottom) and **1**+1.0 equivalent F<sup>-</sup> (top) taken in CDCl<sub>3</sub>.

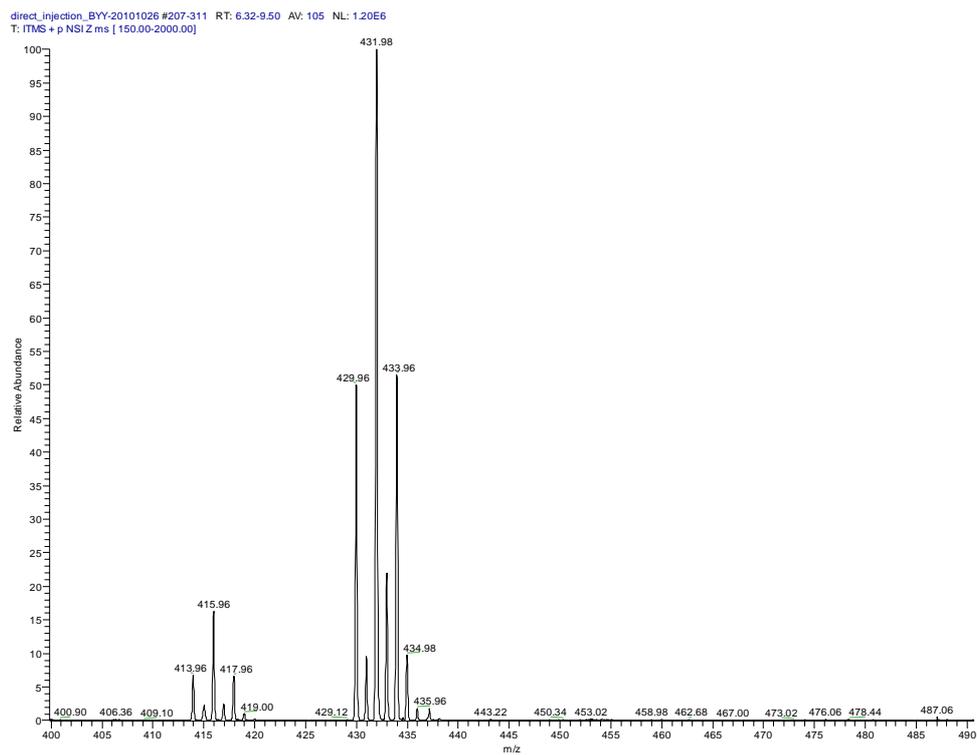
## 6. NMR and MS Data.



**Fig. S18.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **1**.



**Fig. S19.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectrum of **1**.



**Fig. S20.** Mass spectrum of **1**.

## References

1. N. Jotterand, D. A. Pearce, and B. Imperiali, *J. Org. Chem.* 2001, 66, 3224.
2. Olmsted, J. *J. Phys. Chem.* **1979**, 83, 2581.