Electronic Supporting Information (ESI) for

Rapid and selective detection of fluoride in aqueous solution by a new hemicyanine-based colorimetric and fluorescent chemodosimeter

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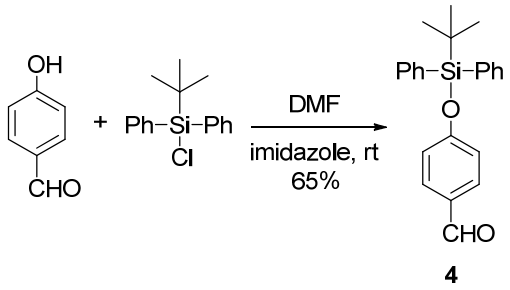
Synthesis of 4-(*tert*-butyldiphenylsilyloxy)benzaldehyde 4

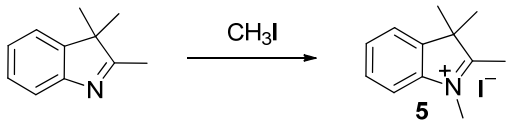


4

Compound **4** was prepared according to a previously published procedure[1]: to a solution of *p*-hydroxybenzaldehyde (1.22 g, 10 mmol) and imidazole (816 mg, 12 mmol) in dry DMF (20 mL), *tert*-butylchlorodiphenylsilane (2.75 g, 10 mmol) was dropped under ice-water bath. After stirring 12 h at room temperature, the volatiles were evaporated under reduced pressure to oil. The residue was purified by flash chromatography (silica gel column) using petroleum ether and ethyl acetate (v/v = 10/1) to afford **4** as a white solid in 65% yield. Mp: 94-97˚C; ^{1}H NMR (400 MHz, $CDCl_3$): 1.11 (9H, s, *t*-Bu), 6.86 (2H, t, ArH), 7.36-7.46 (6H, m, ArH), 7.63-7.71 (6H, m, ArH), 7.41 (2H, s, ArH), 9.80 (1H, s, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): 19.4,

26.3, 120.2, 127.9, 130.2, 131.7, 131.8, 135.3, 161.1, 190.8. IR (KBr, cm^{-1}): 2951, 2857, 1696, 1599, 1511, 1276, 1163, 1114, 904, 746; MS (EI): Calcd for $C_{23}H_{24}O_2Si^+$ (M^+) 360.15; Found 360.03.

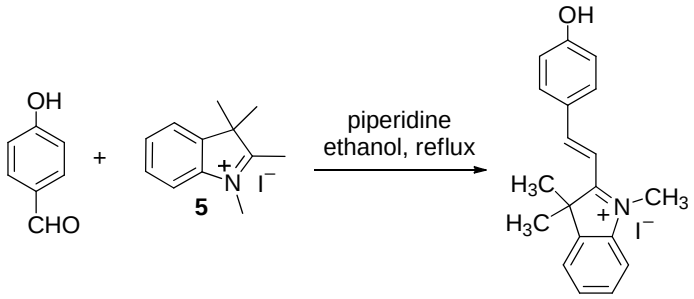
Synthesis of compound 5



5

Compound **5** was prepared as a light purple solid from 2,3,3-trimethylindolenine and iodomethane by a previously reported method.[2] Mp: > 300˚C. ^{1}H NMR (600 MHz, DMSO-d_6): 1.53 (6H, s, $2CH_3$), 2.80 (3H, s, CH_3), 3.99 (3H, s, CH_3), 7.61 (2H, m, ArH), 7.84 (1H, t, J = 6.0 Hz, ArH), 7.92 (1H, t, ArH); ^{13}C NMR (150 MHz, DMSO-d_6): 196.0, 142.1, 141.6, 129.3, 128.8, 123.4, 115.2, 54.0, 35.0, 21.7, 14.5; IR (KBr, cm^{-1}): 3448, 2964, 1630, 1608, 1481, 1457, 1020, 778; MS (EI): Calcd for $C_{12}H_{16}N^+$ $[M - I]^+$ 174.13; Found 173.14.

Synthesis of the reference sample of 2



5 **2**

The reference sample of **2** was prepared according to a previously published procedure.[3] To a solution of **5** (301 mg, 1 mmol) in ethanol (10 mL), 4-hydroxybenzaldehyde (122 mg, 1 mmol) and piperidine (10 μL) was added. The reaction mixture was heated to reflux for 1 h with stirring and then cooled to room temperature. A red solid precipitated and filtered to give the desired product in 58% yield. Mp: 255-257 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6): 1.77 (6H, s, $2CH_3$), 4.08 (3H, s, NCH_3), 6.96 (2H, d, J = 8.4 Hz, ArH), 7.46 (1H, d, J = 16 Hz, CH), 7.59 (2H, t, J = 7.6 Hz, ArH), 7.84 (2H, d, J = 7.2 Hz, ArH), 8.12 (2H, d, J = 8.0 Hz, ArH), 8.36 (1H,

d, J = 16 Hz, CH), 10.85 (1H, s, OH). ^{13}C NMR (100 MHz, DMSO-d_6): 181.3, 163.1, 153.6, 143.1, 141.8, 133.6, 128.8, 125.9, 122.7, 116.3, 114.6, 109.3, 51.7, 34.3, 25.7. MS (EI): Calcd. for $C_{19}H_{20}NO$ [M – HI] 277.36; Found 277.28.

References:

1. B. Zhu, F. Yuan, R. Li, Y. Li, Q. Wei, Z. Ma, B. Du and X. Zhang, *Chem. Commun.*, 2011, **47**, 7098.
2. Y. Ueno, J. Jose, A. Loudet, C. Pérez-Bolívar, P. Anzenbacher, Jr. and K. Burgess, *J. Am. Chem. Soc.*, 2011, **133**, 51.
3. S.-P. Wang, W.-J. Deng, D. Sun, M. Yan, H. Zheng and J.-G. Xu, *Org. Biomol. Chem.*, 2009, **7**, 4017.

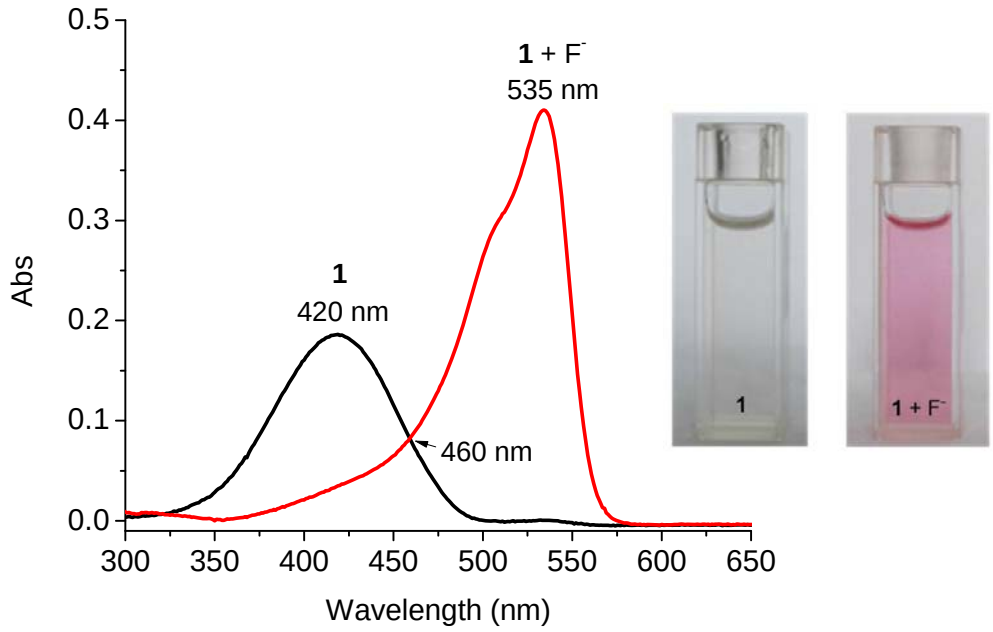


Fig. S1 Absorption and colour changes of chemodosimeter **1** (5 μM) upon addition of F^- (40 mM) in PBS (20 mM, pH 7.4) solution (ethanol/water = 3/7, v/v) at 25˚C. The UV-vis spectrum (red line) was obtained 5 min after F^- addition.

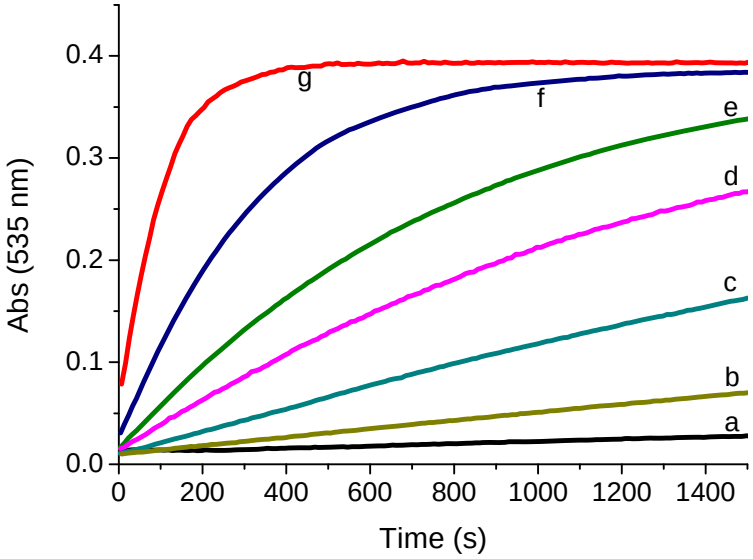


Fig. S2 Time-dependent of absorption kinetics spectra of chemodosimeter **1** (5 μM) upon addition of different concentrations of F^- in PBS (20 mM, pH 7.4) solution (ethanol/water = 3/7, v/v) at 25˚C. The reaction is monitored at 535 nm. [F^-] from a to g: 0, 0.1, 0.5, 1, 2, 6 and 20 mM, respectively.

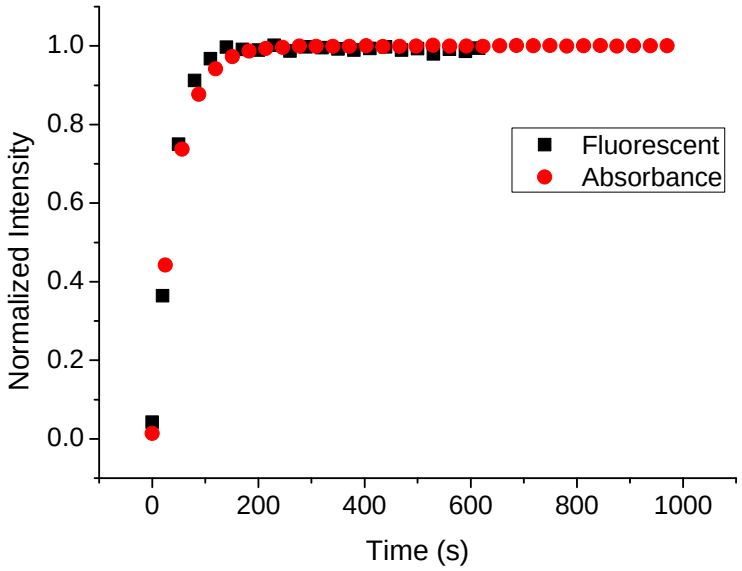


Fig. S3 A comparison of kinetics of chemodosimeter **1** (5 μM) upon addition of 40 mM F^- in PBS (20 mM, pH 7.4) solution (ethanol/water = 3/7, v/v) at 25˚C measured by absorbance intensity changes at 535 nm (●) and fluorescent intensity changes at 558 nm (■). Both absorbance intensity and fluorescent intensity are normalized to make a clear comparison.

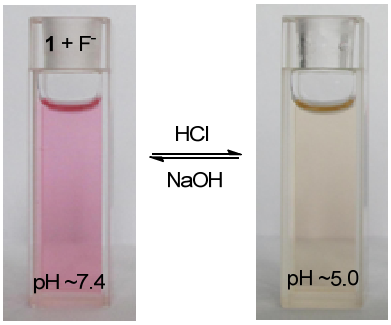


Fig. S4 The reversible colour changes of the reaction mixture (**1** + F^-) upon subsequent addition of HCl acid and aqueous NaOH.

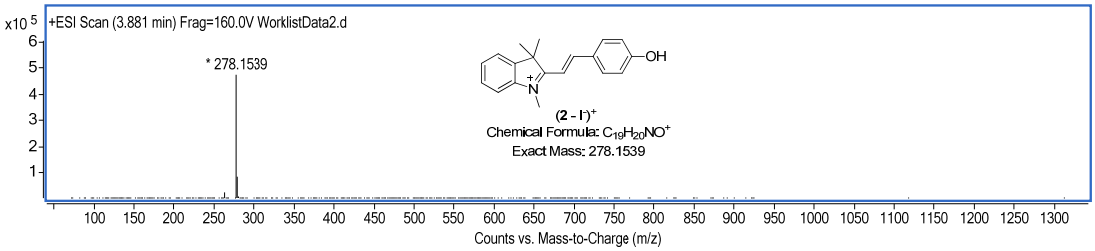


Fig. S5 HR-MS spectrum of the reaction product of chemodosimeter **1** with F^-

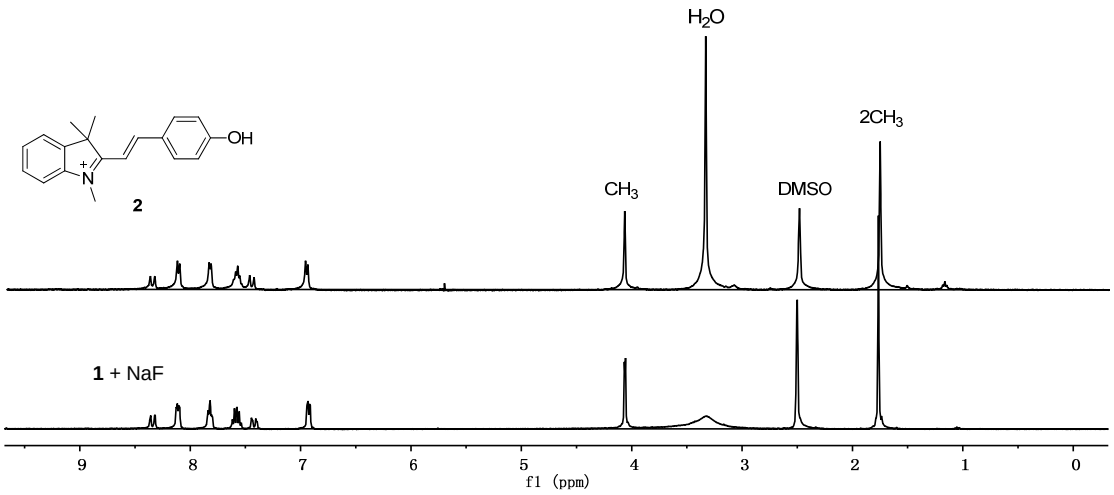


Fig. S6 Comparison of the ^{1}H NMR spectra between the reference sample of **2** and the reaction product of chemodosimeter **1** with F^-.

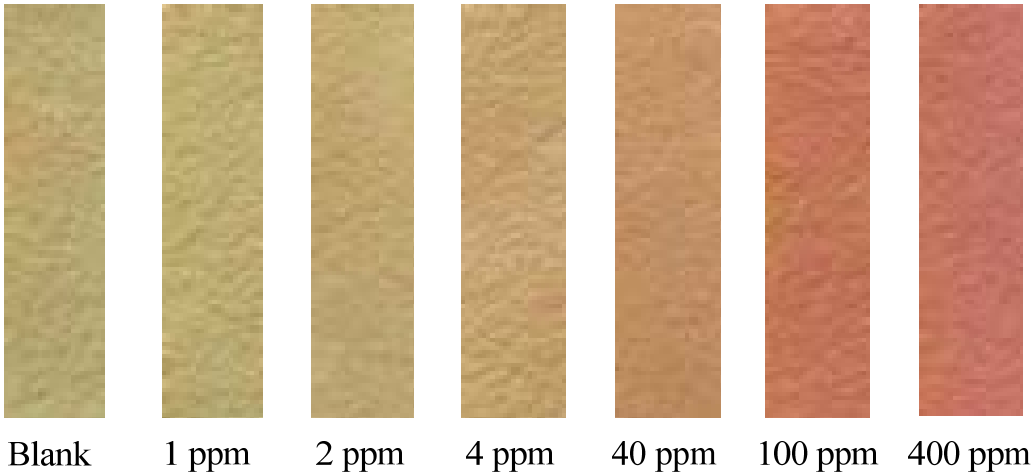
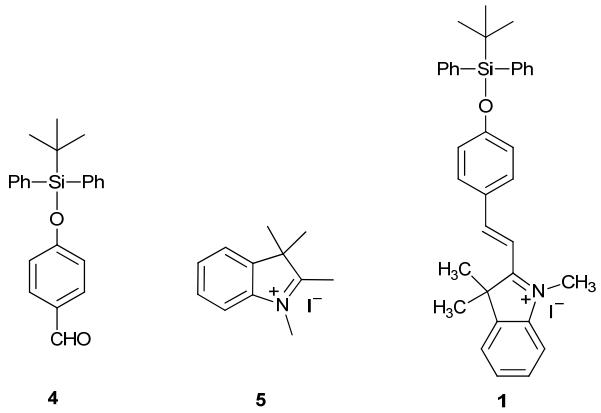
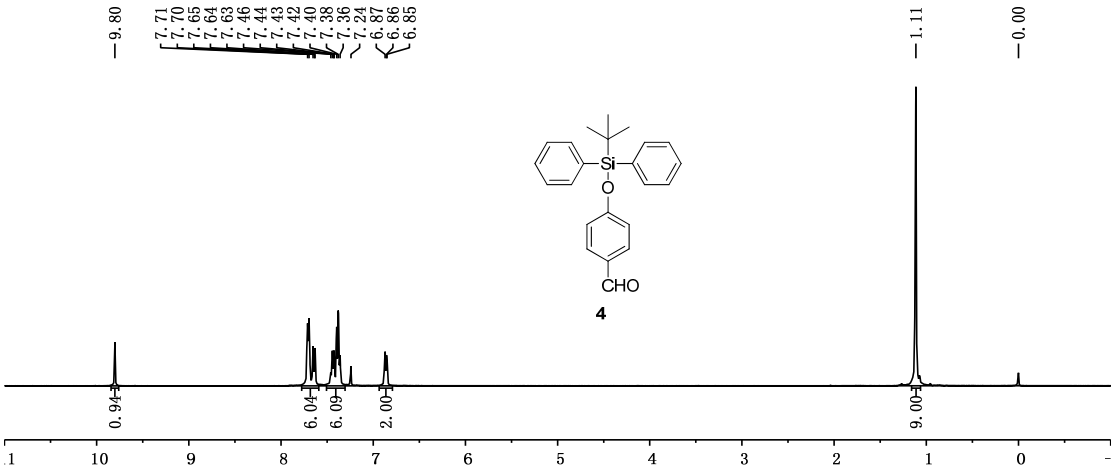


Fig. S7 Colour changes of test paper containing chemodosimeter **1** with different concentration of F^- in water.

NMR and MS spectra for the following compounds:





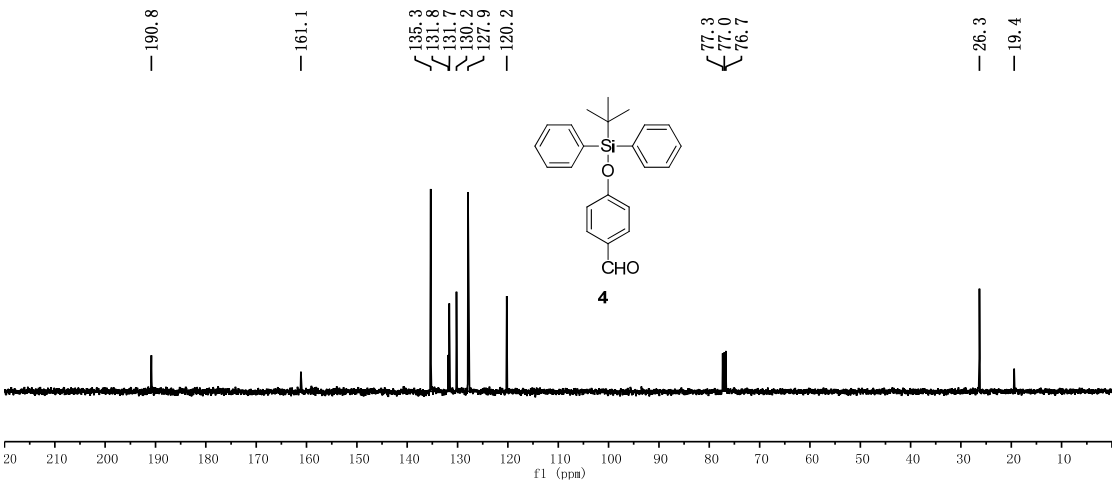


Fig. S8 ^{1}H NMR and ^{13}C NMR spectra of compound **4** recorded in $CDCl_3$.

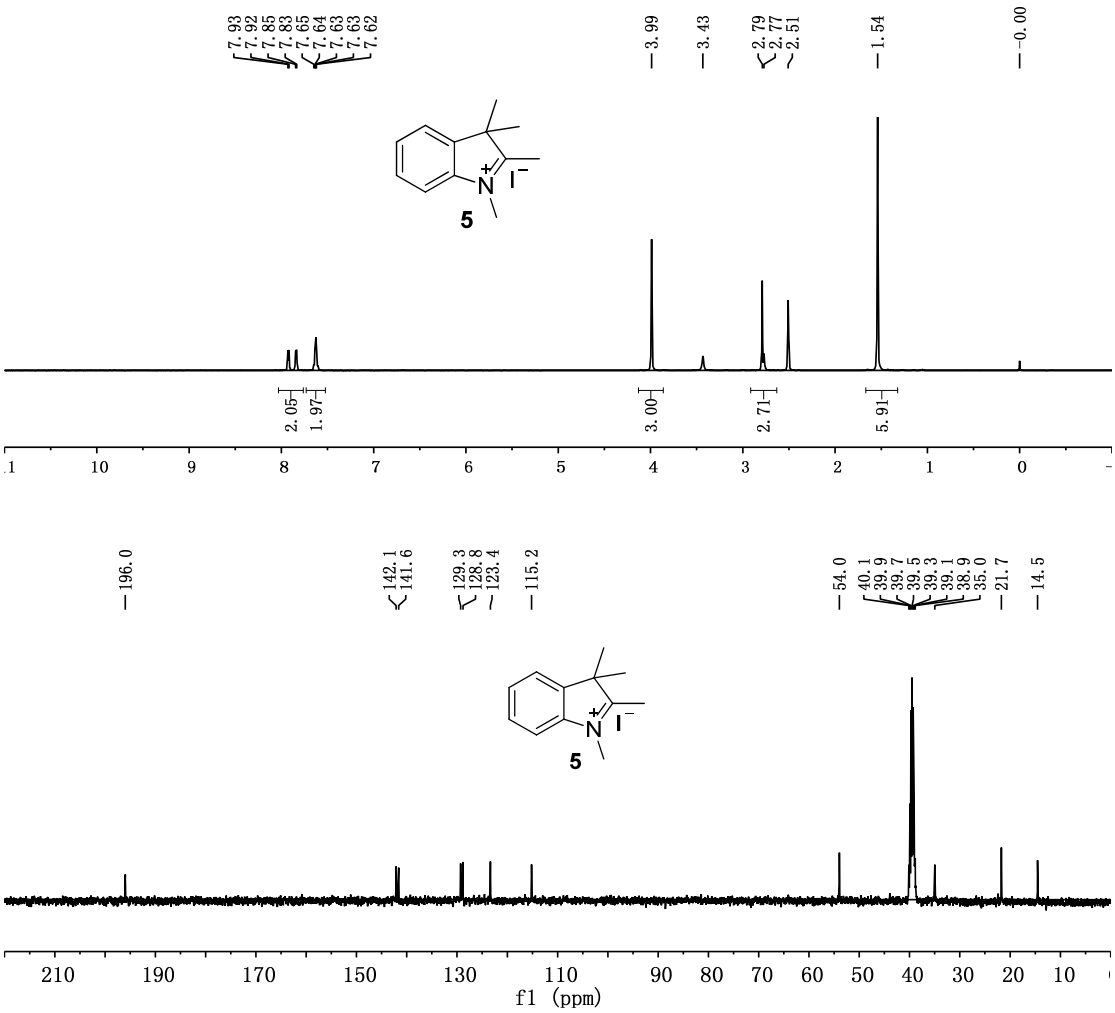


Fig. S9 ^{1}H NMR and ^{13}C NMR spectra of compound **5** recorded in DMSO-d_6.

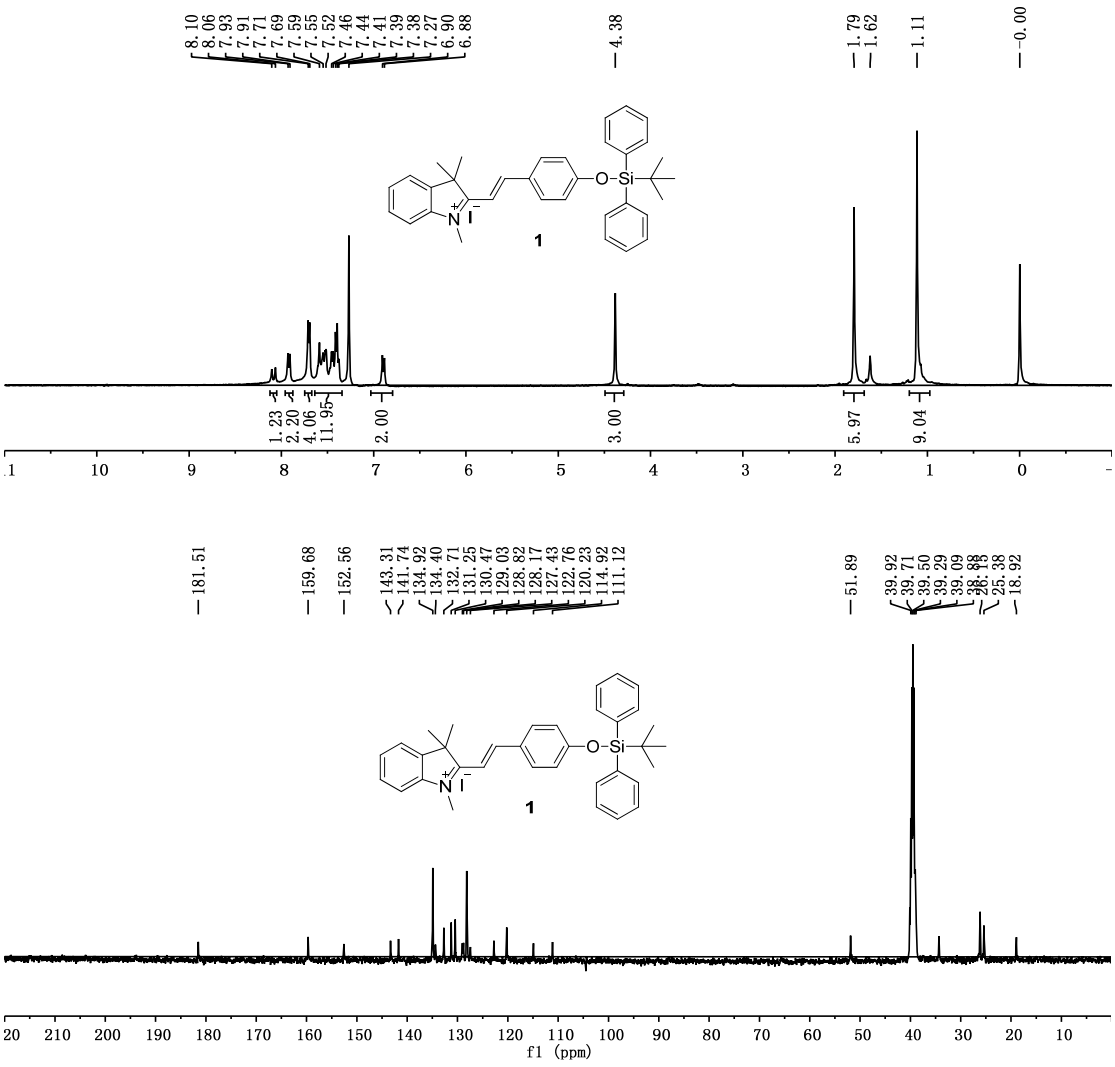


Fig. S10 ^{1}H NMR and ^{13}C NMR spectra of compound **1** recorded in $CDCl_3$ and DMSO-d_6, respectively.

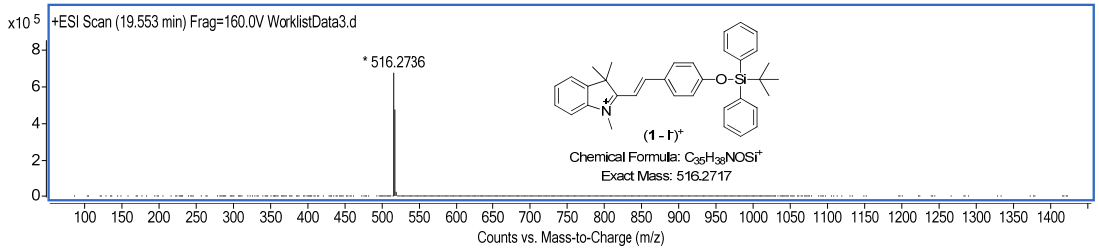


Fig. S11 HR-MS spectrum of chemodosimeter **1**