Supporting Information for:

Highly Activated Michael Acceptor by an Intramolecular Hydrogen Bond as a Fluorescence Turn-On Probe for Cyanide

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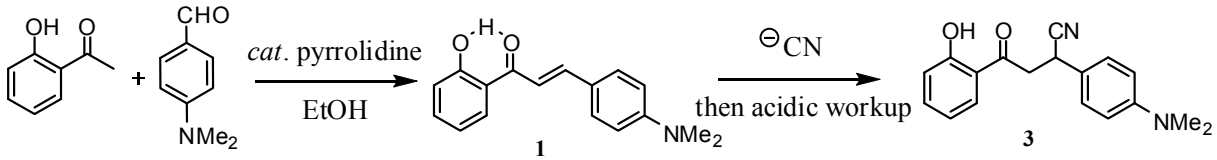
Contents

1. Instruments and reagents

All fluorescence and UV-vis absorption spectra were recorded in FP 6500 fluorescence spectrometer and HP 8453 absorption spectrometer, respectively. The ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz NMR spectroscopy. Mass spectra were recorded on G6401A MS-spectrometer. All experiments were carried out with commercially available reagents and solvents, and used without further purification, unless otherwise noted.

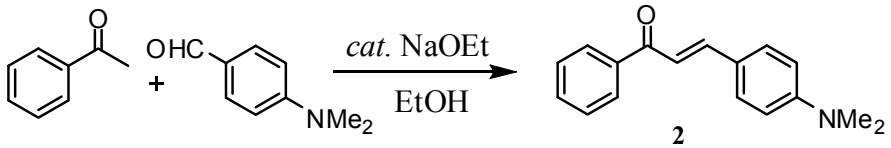
2. Synthesis of **1** and **3**



Probe 1. 2-(Hydroxy)acetophenone (120 μL, 1.00 mmol), 4-(Dimethylamino)benzaldehyde (150mg , 1.00 mmol), pyrrolidine (83 μL, 1.0 mmol) were dissolved in 3 mL EtOH in a flask. The reaction mixture was stirred overnight at room temperature to afford probe **1** as red precipitates. The solid was filtered, and dried in vacuum (180mg, yield 67%).
^{1}H NMR ($CDCl_3$, 300 MHz): 13.23 (br s, 1H), 7.93(d, ^{3}J = 15 Hz, 1H), 7.91 (d, ^{3}J = 5.1 Hz, 1H), 7.58 (d, ^{3}J = 9.0 Hz, 2H), 7.48 (d, ^{3}J = 5.1 Hz, 1H), 7.46 (d, ^{3}J = 15 Hz, 1H), 7.01 (d, ^{3}J = 7.8 Hz, 1H), 6.93(t, ^{3}J = 8.1 Hz, 1H), 6.71 (d, ^{3}J = 9.0 Hz, 2H), 3.07(s, 6H).
^{13}C NMR ($CDCl_3$, 75 MHz): 193.52, 163.50, 152.35, 146.58, 135.67, 130.89, 129.39, 122.34, 120.42, 118.60, 118.50, 114.27, 111.82, 40.14 (14 carbon peaks).

Probe 3. Probe **1** (101 mg, 0.30 mmol), TBACN (100 equiv) were dissolved in 30mL ACN in a flask. The reaction mixture was stirred 5h at room temperature and then the solvent was removed under the reduced pressure and the residue was extracted with CH_2Cl_2 (30 mL × 3) from acidic aqueous solvent and purified by column chromatography using CH_2Cl_2 (R_f = 0.50) afforded the desired probe **3** as a yellow-orange solid (102.7mg, yield 92 %).
^{1}H NMR ($CDCl_3$, 300 MHz): 11.92 (s, 1H), 7.65(dd, ^{3}J = 8.1 Hz, ^{4}J = 1.5 Hz, 1H), 7.51 (td, ^{3}J = 8.4 Hz, ^{4}J = 1.5 Hz, 1H), 7.28 (d, ^{3}J = 8.7 Hz, 2H), 7.01 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.2 Hz, 2H), 6.91 (td, ^{3}J = 8.4 Hz, ^{4}J = 1.2 Hz, 1H), 6.73 (d, ^{3}J = 8.7 Hz, 2H), 4.45(dd, ^{3}J = 8.1 Hz, ^{3}J = 6.0 Hz, 1H), 3.72 (dd, ^{3}J = 8.1 Hz, ^{2}J = 18 Hz, 1H) 3.51 (dd, ^{3}J = 6.0 Hz, ^{2}J = 18 Hz, 1H) 2.98 (s, 6H).
^{13}C NMR ($CDCl_3$, 75 MHz): 200.76, 162.51, 150.46, 137.03, 129.45, 128.20, 121.81, 120.97, 119.23, 118.78,112.78, 44.18, 40.42, 30.83 (14 carbon peaks).
HRMS (FAB^+, m-NBA): *m/z* obs'd 294.1363 ($[M]^+$, cal'd 294.1368 for $C_{18}H_{18}O_2N_2$).

3. Synthesis of **2**



Probe 2. Acetophenone (146 mg, 1.20 mmol), 4-(dimethylamino)benzaldehyde (182 mg , 1.20 mmol), NaOEt (41.5 mg, 0.60 mmol) were dissolved in 3 mL EtOH in a flask. The reaction mixture was stirred overnight at room temperature to afford probe **1** as an orange precipitate (241.1 mg, yield 80%). The solid was filtered and dried in vacuum.
^{1}H NMR ($CDCl_3$, 200 MHz): 8.05(d, ^{3}J = 8.0 Hz, 1H), 7.86(d, ^{3}J = 15.4 Hz, 1H), 7.61-7.51 (m, 5H), 7.40 (d, ^{3}J =15.4 Hz, 1H), 6.74 (d, ^{3}J = 15.4 Hz, 1H), 1.60 (s, 6H).

4. NMR spectra of **1**, **2** and **3**

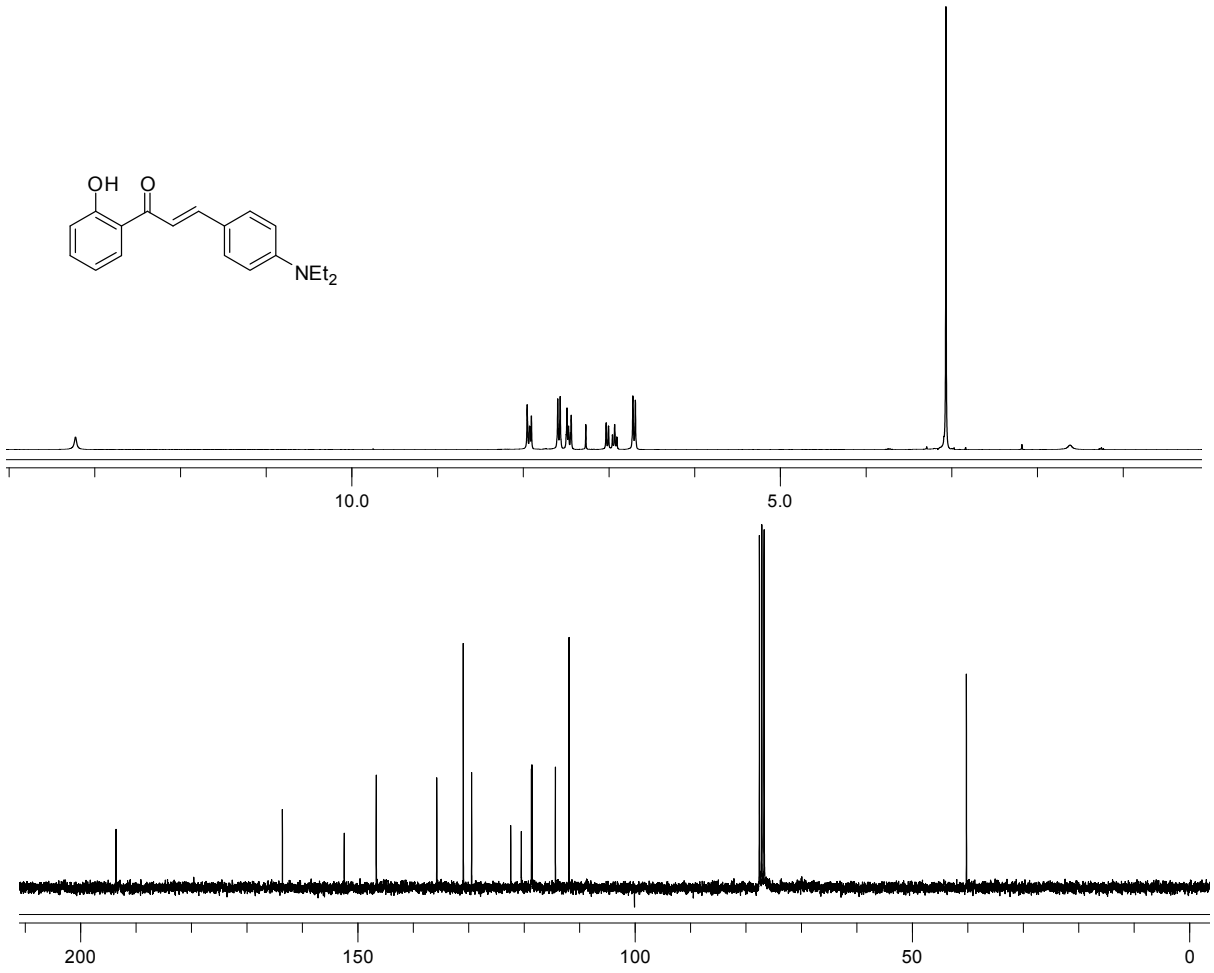


Fig. S1. ^{1}H and ^{13}C NMR spectra of **1** in $CDCl_3$.

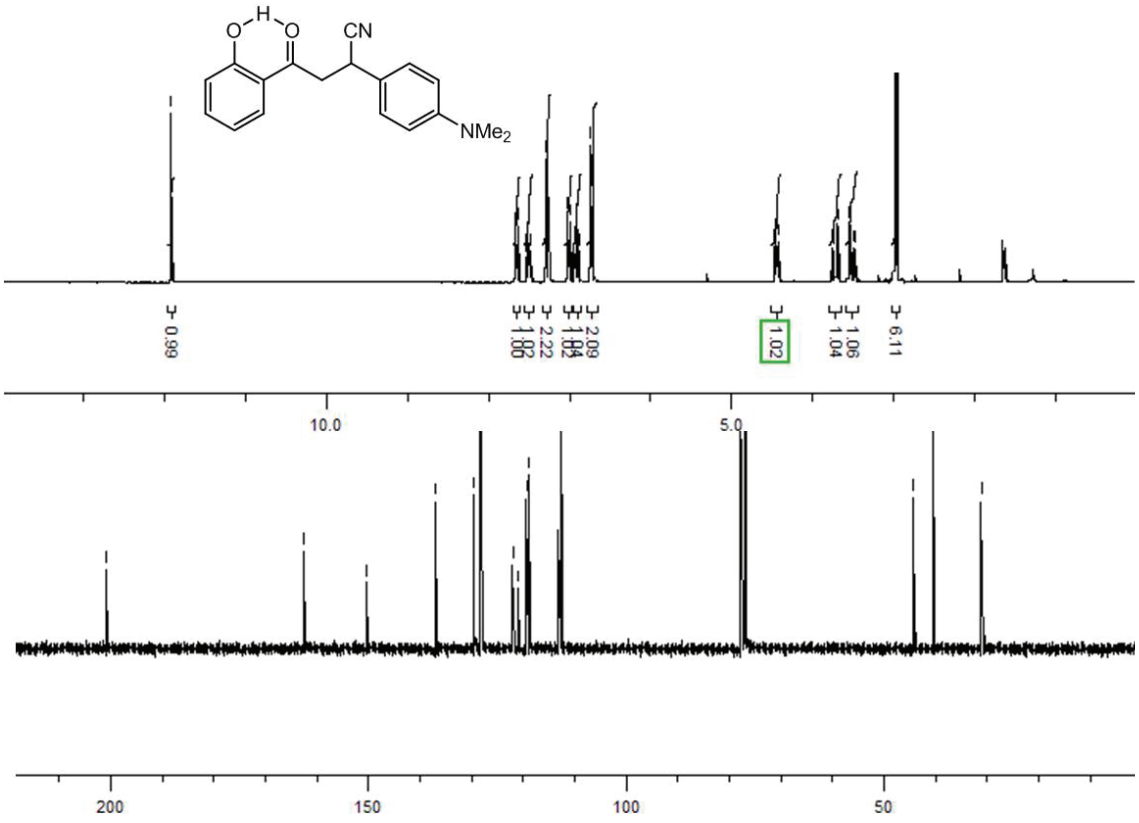


Fig. S2. ^{1}H and ^{13}C NMR spectra of **3** in $CDCl_3$.

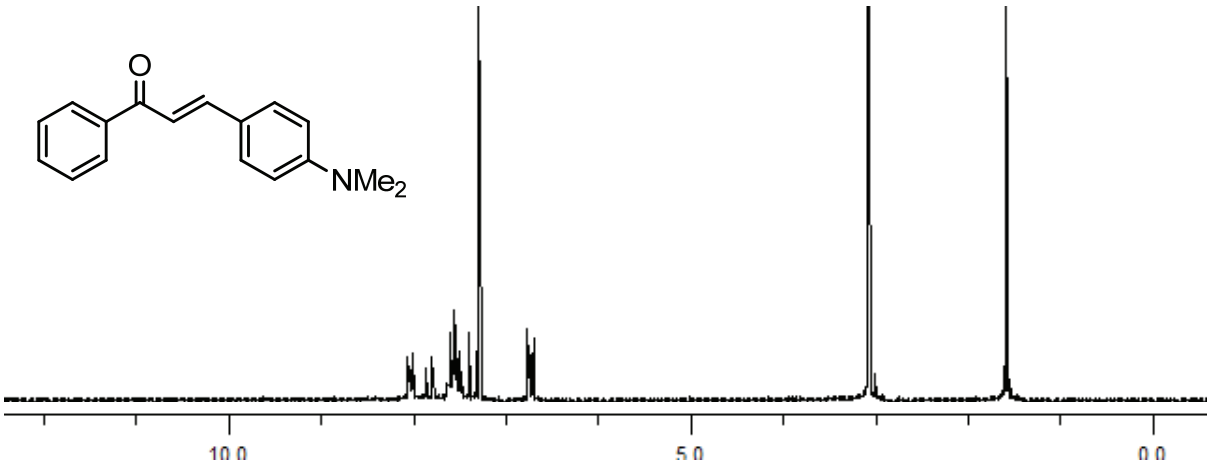


Fig. S3. ^{1}H NMR spectra of **2** in $CDCl_3$.

5. UV-vis kinetics of **2**

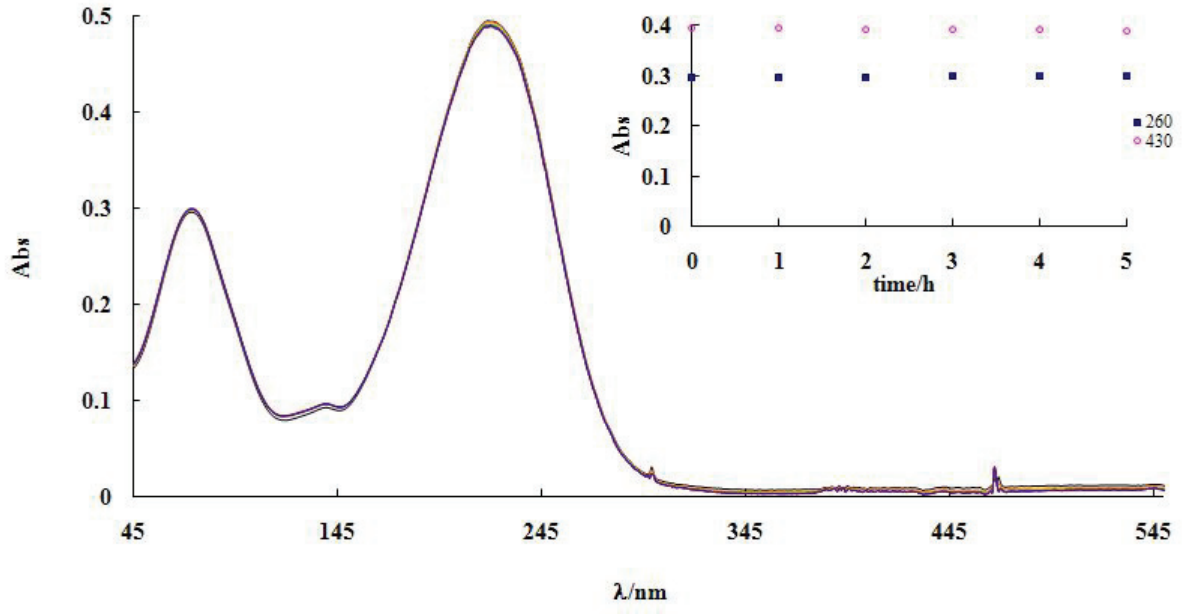


Fig. S4 UV-vis kinetics between **2** (10μM in ACN) and with CN^- ions (100 equiv).

6. Fluorescence intensities of **1** in the presence of various competitive anions.

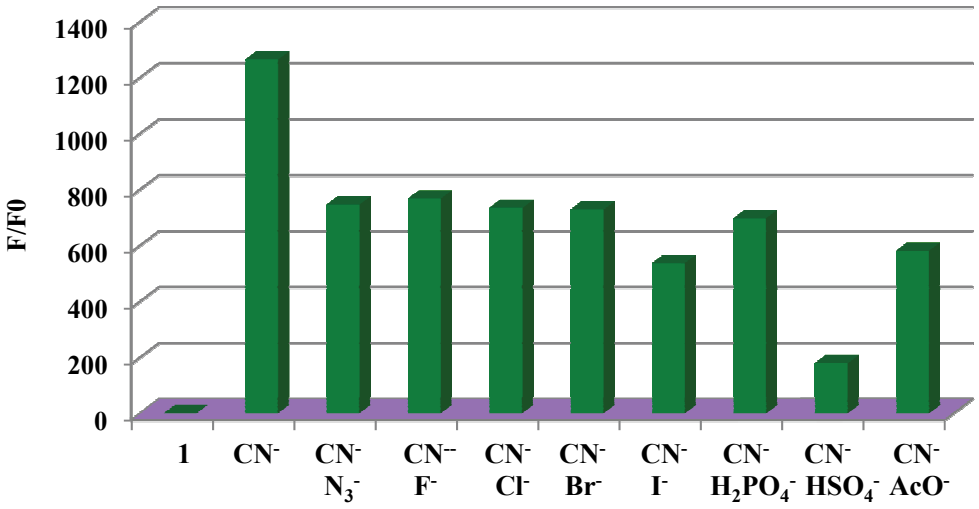


Fig. S5. Fluorescence intensities of chemodosimeter **1** (10 μM, ACN) in the presence of competitive anions (100 equiv) together with CN^- ions (100 equiv), where λ_{ex} = 272 nm, λ_{em} = 469 nm. Notice that the Michael addition of cyanide anion is possibly affected by the acidity of anions such as hydrogen sulfate (HSO_4^-).

7. Fluorometric determination of limit of cyanide detection

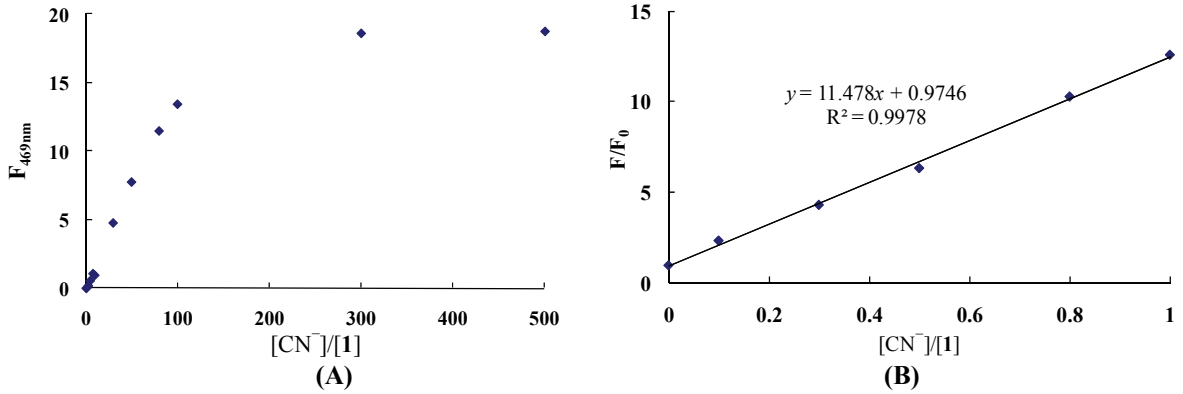


Fig. S6. Fluorometric determination of limit of cyanide detection after stepwise addition of cyanide to **1** (10 μM in ACN), where λ_{ex} = 272 nm, λ_{em} = 469 nm.

8. Job′s plot

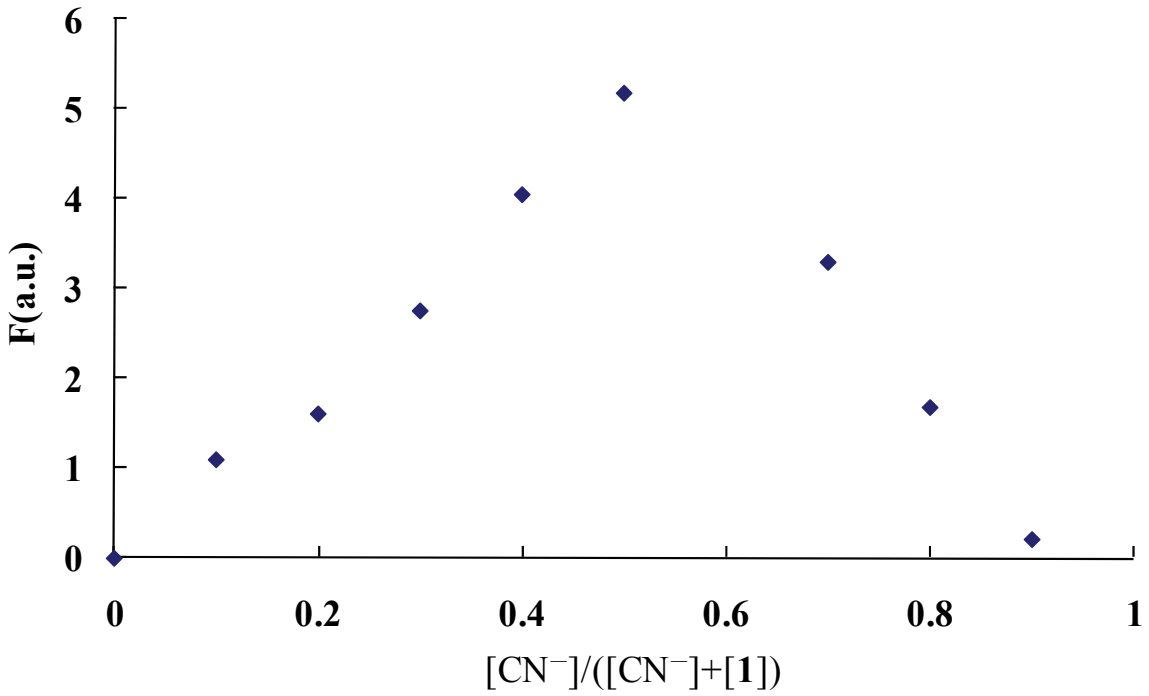
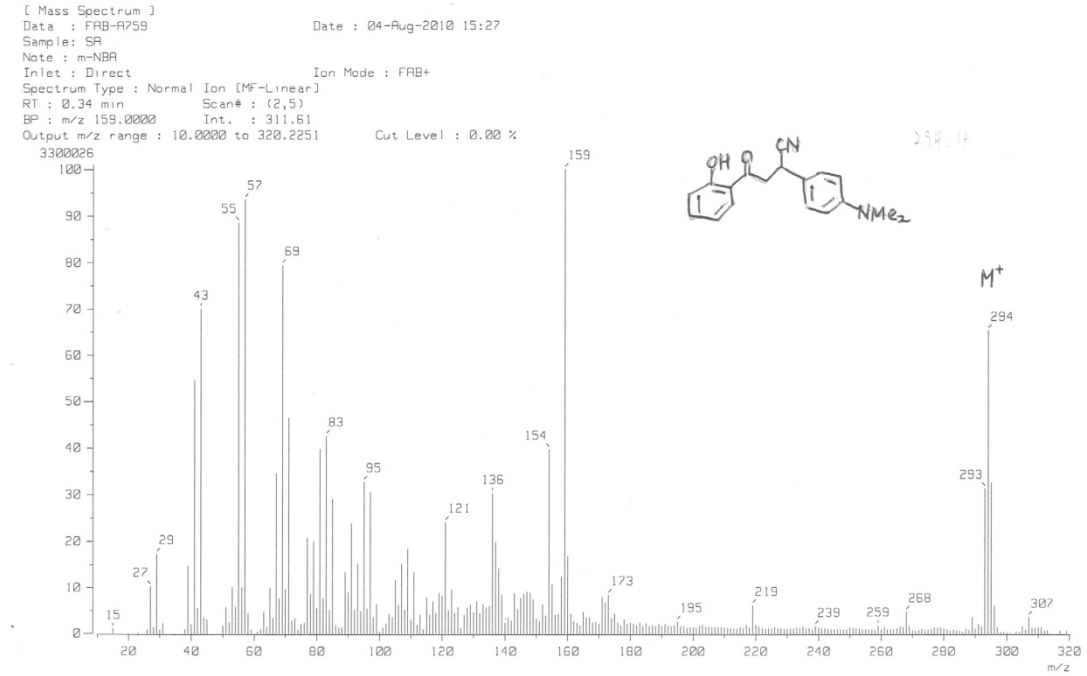


Fig. S7. Job′s plot between **1** and cyanide, [**1**] + [CN^-] = 20 μM in CAN. Fluorescence intensities at 357 nm are monitored after λ_{ex} 272 nm is applied. The plot indicates one to one binding stoichiometry between **1** and cyanide.

9. Mass spectral data

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[ Theoretical Ion Distribution ]                                    Page: 1
Molecular Formula : C18 H18 N2 O2
                (m/z   294.1368, MW   294.3531, U.S. 11.0)
Base Peak :   294.1368, Averaged MW :   294.3516(a),   294.3523(w)

    m/z       INT.
  294.1368 100.0000 ************************************************************
  295.1400  20.8311 ************
  296.1428   2.4579 *
  297.1454   0.2114
  298.1480   0.0142
  299.1507   0.0008

 [ Elemental Composition ]
 Data  : FAB-A781                      Date : 06-Aug-2010 15:30
 Sample: SA
 Note : m-NBA
 Inlet : Direct                        Ion Mode : FAB+
 RT : 0.27 min                         Scan#: (8,9)
 Elements : C 100/0, H 100/0, N 10/0, O 10/0
 Mass Tolerance      : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5
 Unsaturation (U.S.) : 0.0 - 100.0

 Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
   294.1363   100.0    -15.6 /  -4.6   15.0  C 23 H 18
                        +7.2 /  +2.1   12.0  C 14 H 14 N 8
                        +2.6 /  +0.8   11.5  C 16 H 16 N 5 O
                        -1.9 /  -0.6   11.0  C 18 H 18 N 2 O 2
                       +16.3 /  +4.8    7.5  C 11 H 16 N 7 O 3
                       +11.7 /  +3.5    7.0  C 13 H 18 N 4 O 4
                        +7.2 /  +2.1    6.5  C 15 H 20 N O 5
                       -12.8 /  -3.8    3.0  C 7 H 18 N 8 O 5
                       +16.3 /  +4.8    2.0  C 12 H 22 O 8
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Fig. S8. Low and high resolution mass spectra of **3**.