Electronic Supplementary Information (ESI†)

Ratiometric fluorescent detection of CN^- based on CN^-- promoted interruption of the π-conjugation of a coumarin-containing Michael receptor

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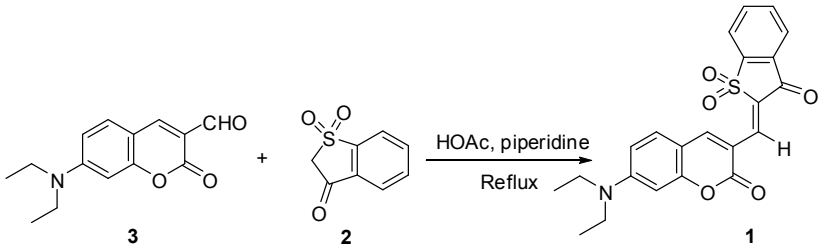
1. General information and methods

All reagents and solvents were purchased from commercial sources (Aladdin Reagent Company, Shanghai, China) and were of the highest grade. Solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Qingdao Yuminyuan Chemicals GF254 silica gel coated plates. Flash chromatography (FC) was performed using silica gel 60 (200–300 mesh) obtained from the Qingdao Ocean Chemicals. Absorption spectra were taken on an Agilent 8453 spectrophotometer using a 1-cm quartz cell. Fluorescence spectra were taken on Varian Cary Eclipse fluorescence spectrometer. High resolution mass spectra were obtained on a Varian QFT-ESI mass spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker ARX300 nuclear magnetic resonance spectrometer at 300 and 75 MHz, respectively (TMS as internal standard). The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad.

2. Procedures of sensing

Cyanide anion and the other anions were prepared from n-Bu_4N salts. A stock solution of **1** (10 mM) was prepared in DMF. The stock solution of **1** was then diluted to the corresponding concentration (10 μM) with the solution of CH_3CN. The tetrabutylammonium cyanide stock solution of 1.0×10^{-1} M was diluted to 1.0×10^{-2} M and 1.0×10^{-3} M with CH_3CN for spectra titration studies. Spectral data were recorded in an indicated time after the addition.

3. Synthesis[S1]



To a solution of coumarin aldehyde **3**[S2] (245 mg, 1.00 mmol) and benzo[b]thiophene-3(2H)-one 1,1-dioxide **2** (218 mg, 1.20 mmol) in glacial acetic

acid (10 mL) was added 3 drops of piperidine. The reaction mixture was then refluxed for 1 h, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography (dichloromethane / acetone, 100:1) on silica gel to give the product **1** as a darkblue solid (299 mg, yield: 73%). Mp: 227–228 ^{o}C.^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 8.93 (s, 1H), 8.49 (s, 1H), 8.11 (d, *J* = 7.5, 1H), 8.03 (d, *J* = 7.5, 1H), 7.80-7.93 (m, 2H), 7.49 (d, *J* = 7.5, 1H), 6.66 (d, *J* = 9.0, 1H), 6.47 (s, 1H), 3.50 (q, *J* = 6.6, 4H), 1.27 (t, *J* = 6.3, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.29, 30.42, 46.25, 97.87, 110.38, 110.46, 121.90, 125.464, 128.264, 133.75, 134.92, 136.71, 139.76, 144.30, 149.79, 154.79, 159.30, 161.84, 178.66; ESI-MS *m/z* 432.0878 (100%, $[M + Na]^+$), $[M+Na]^+$ calculated 432.0876.

References

[S1] J. Griffiths, V. Millar, G. S. Bahra, *Dyes and Pigments*, 1995; **28**, 327–39.

[S2] J.-S. Wu, W.-M. Liu, X.-Q. Zhuang, F. Wang, P.-F. Wang, S.-L. Tao, X.-H. Zhang, S.-K. Wu, S.-T. Lee, Org. Lett. 2006; **9**: 33–36.

4. Supplemental spectra

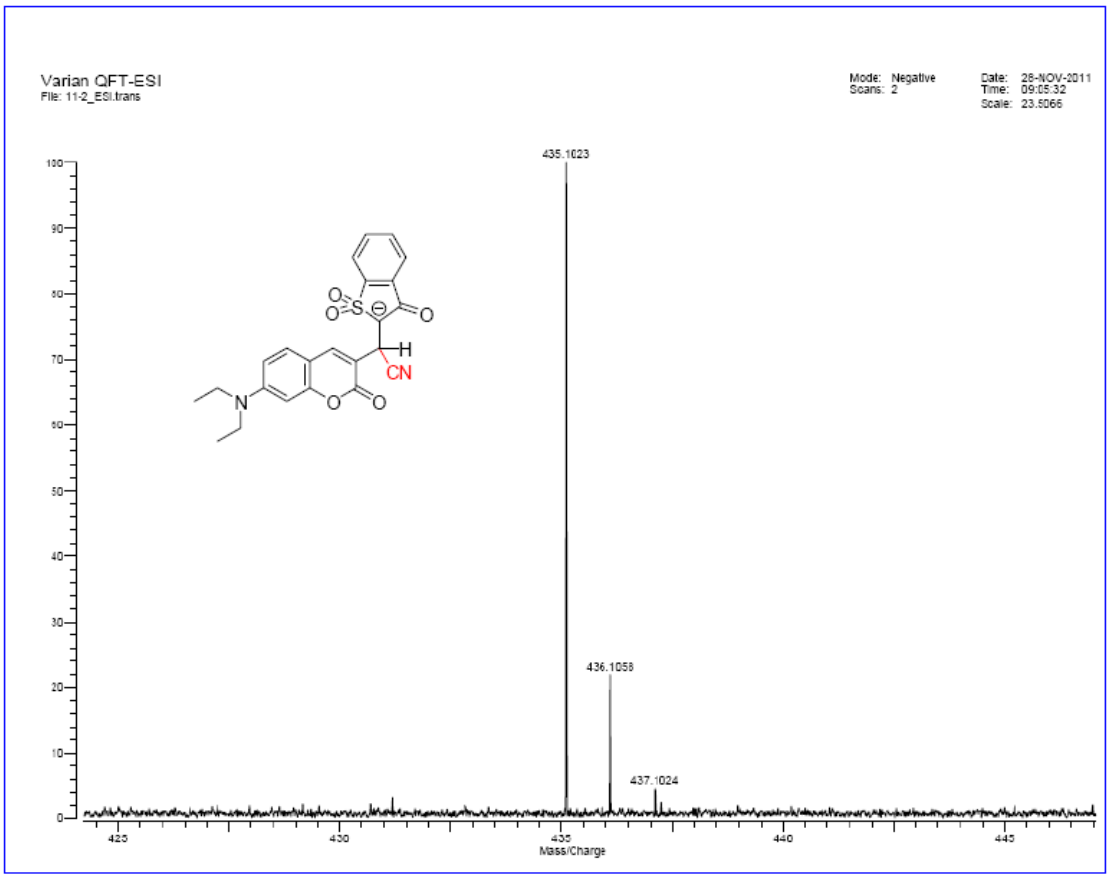


Figure S1 The HRMS for **1**-CN adduct.

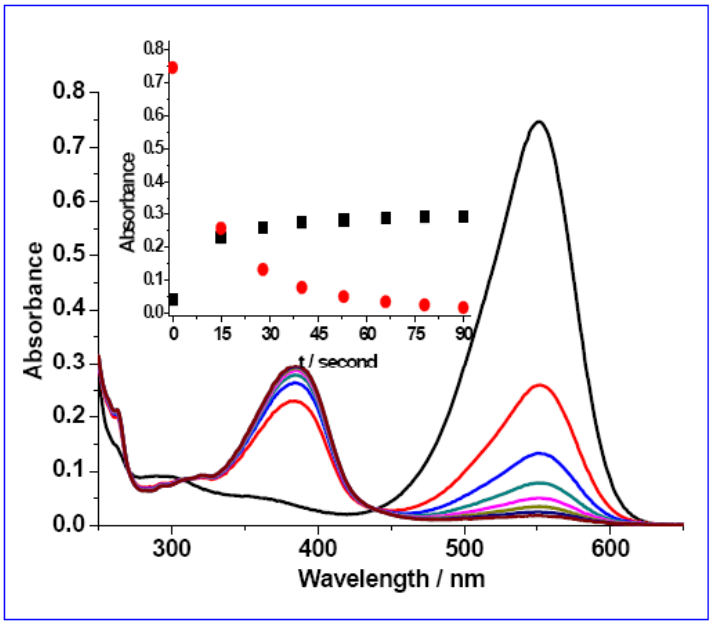


Figure S2 The kinetic study of the response of the probe **1** to CN^- at 25 ^oC in CH_3CN.

Condition: [**1**] = 10 μM, [CN] = 20 μM.

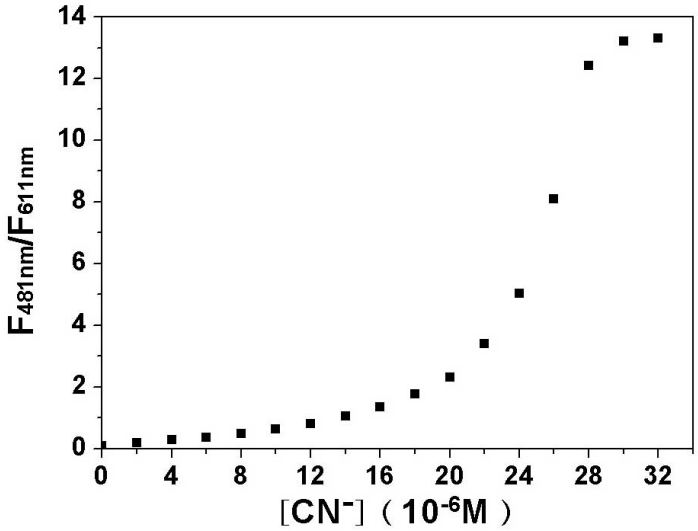


Figure S3 Fluorescence intensity ratio changes (F_{481}/F_{611}) of **1** upon gradual addition of CN^-. λex = 440 nm. Slits: 5 nm/10 nm.

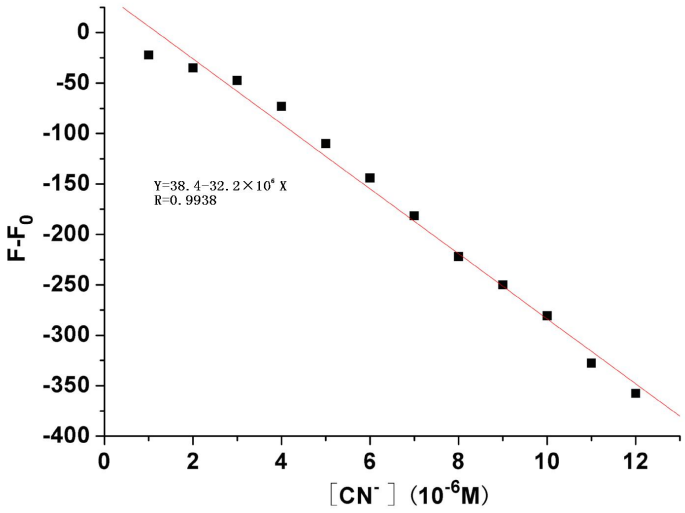


Figure S4 Linear concentration range of CN^- (**1**: 10.0 μM) in CH_3CN (λ_{ex} = 440 nm, F_0: Fluorescence intensity at 611 nm in the absence of CN^-, F: Fluorescence intensity at 611 nm in the presence of CN^-).

The corresponding quantitative analytical data (linear concentration range, LOD) were determined using a reported procedure (C. Tong, G. Xiang, *J. Lumin.*, 2007, **126**, 575–580. C. Tong, G. Xiang, *J. Lumin.*, 2007, **126**, 575–580; and Y. Peng, A.J. Zhang, M. Dong and et al. Chem. Commun., 2011,47, 4505-4507).

The result of the analysis as follows:

Linear Equation: $Y = 38.4 - 32.2 \times X$ R=0.9938, $S=38.42177 \times 10^6$

$$\delta = \sqrt{\frac{\sum (F_0 - \overline{F}_0)^2}{N-1}} = 4.227068231 \quad N=10 \quad K=3$$

$LOD=K \times \delta / S=3.30 \times 10^{-7}$ M

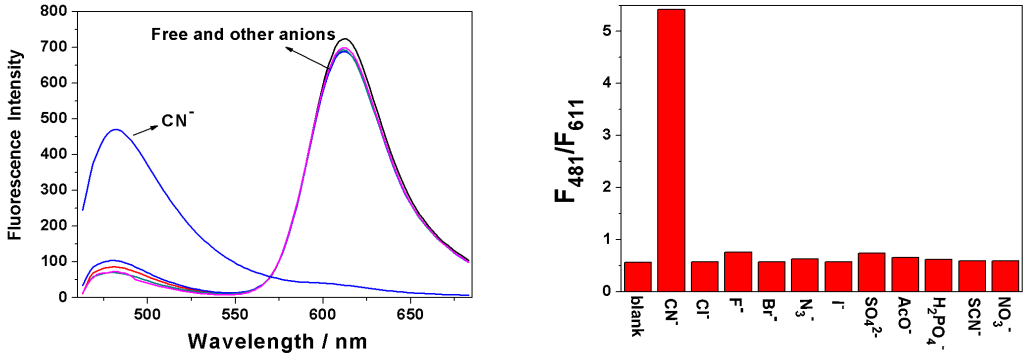


Figure S5 The fluorescence spectra of **1** (10 μM) upon addition of various anions (30 μM) in MeCN。

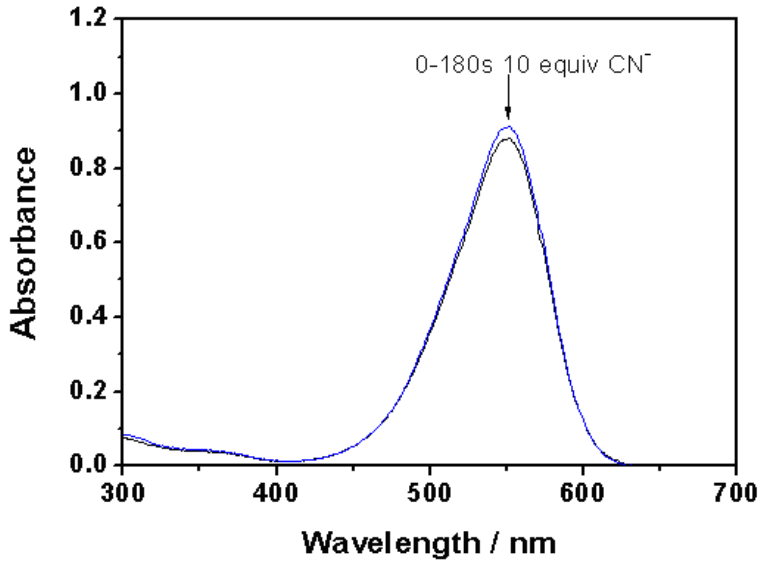


Figure S6 Changes in absorption spectra of **1** (10 μM) measured in 9:1 CH_3CN-HEPES buffer (10 mM, pH = 7.4) at 25℃ upon addition of 100 μM n-Bu_4NCN

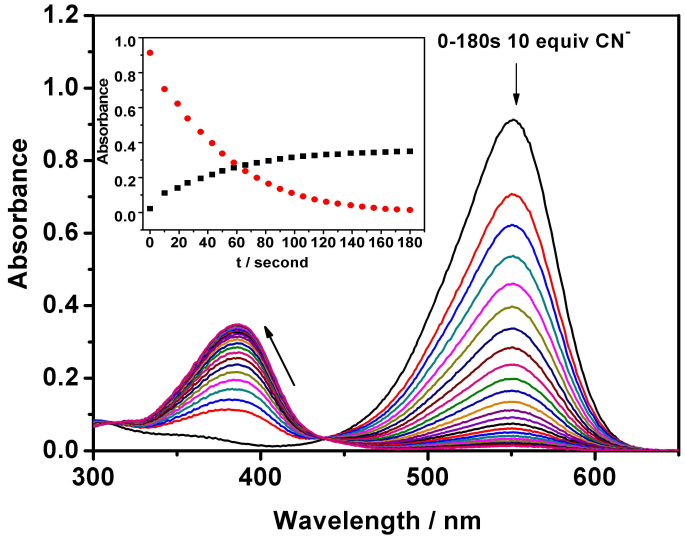


Figure S7 Changes in absorption spectra of **1** (10 μM) measured in 9:1 CH_3CN-HEPES buffer (10 mM, pH = 7.4) at 50℃ upon addition of 100 μM n-Bu_4NCN. Inset: Absorbance intensity *vs* time change of **1** at 550 nm (red dot) and 384 nm (black dot) upon addition of 100 μM n-Bu_4NCN. λex = 440 nm. Slits: 5 nm/10 nm.

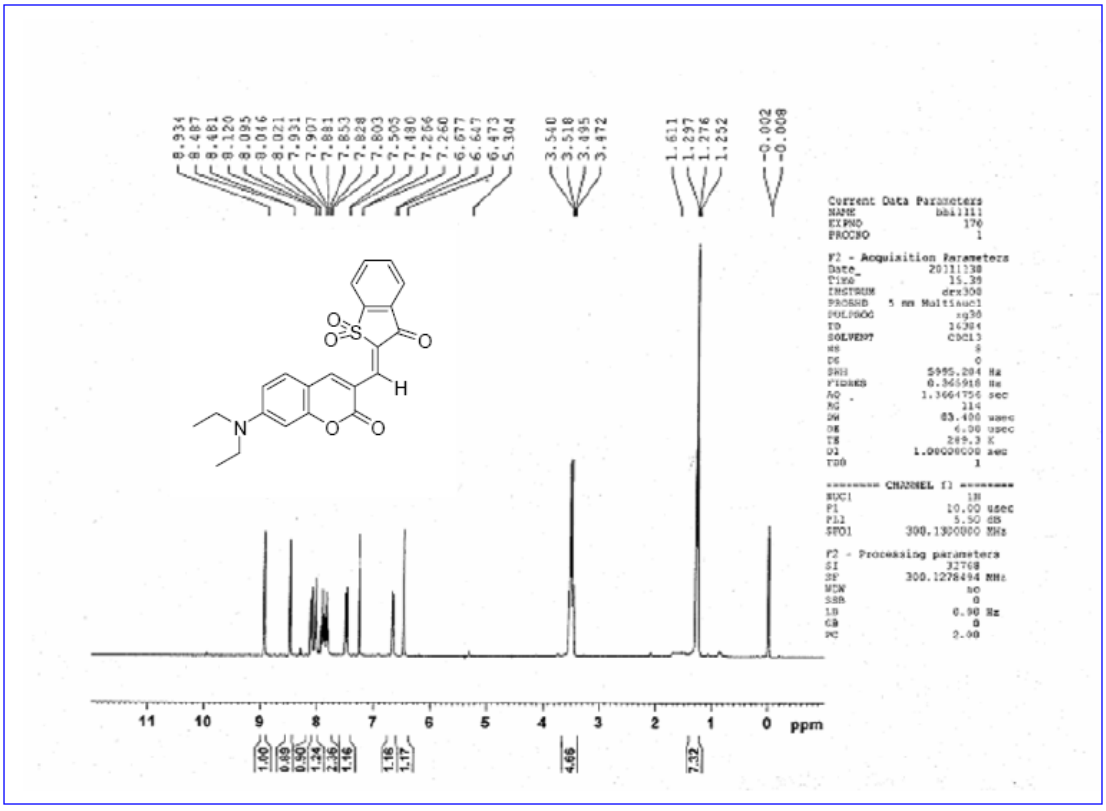


Figure S8 ^1H NMR charts of **1** ($CDCl_3$).

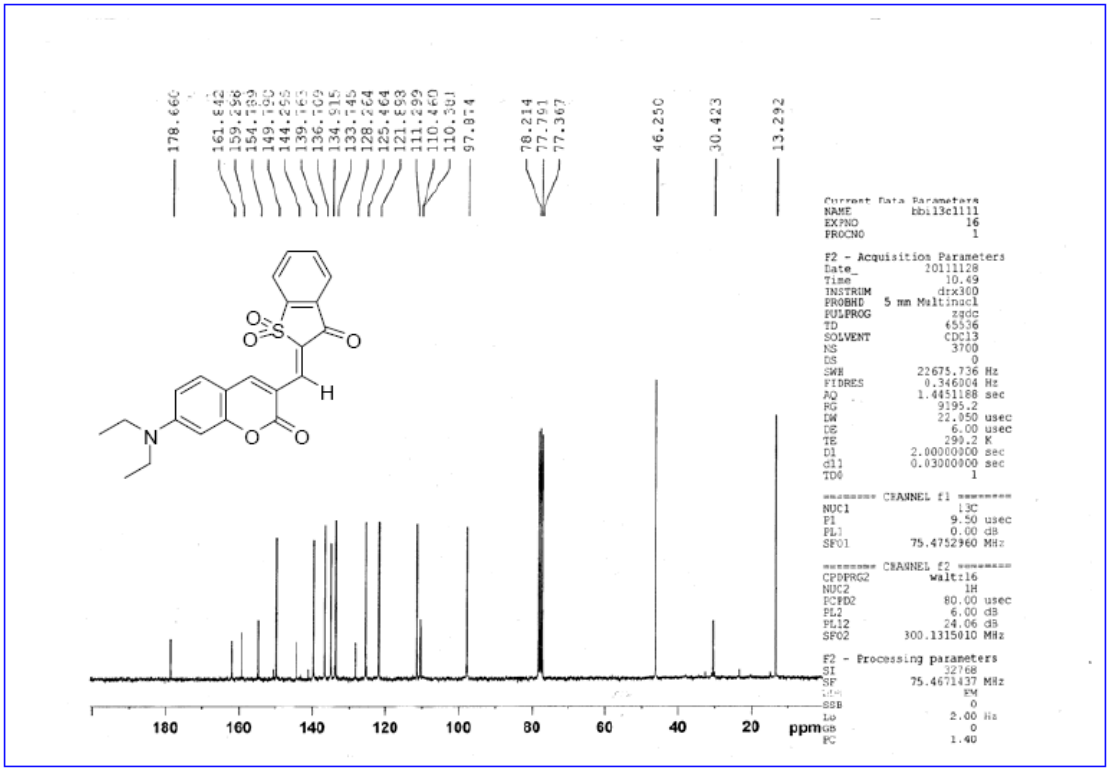


Figure S9 ^{13}C NMR charts of **1** ($CDCl_3$).

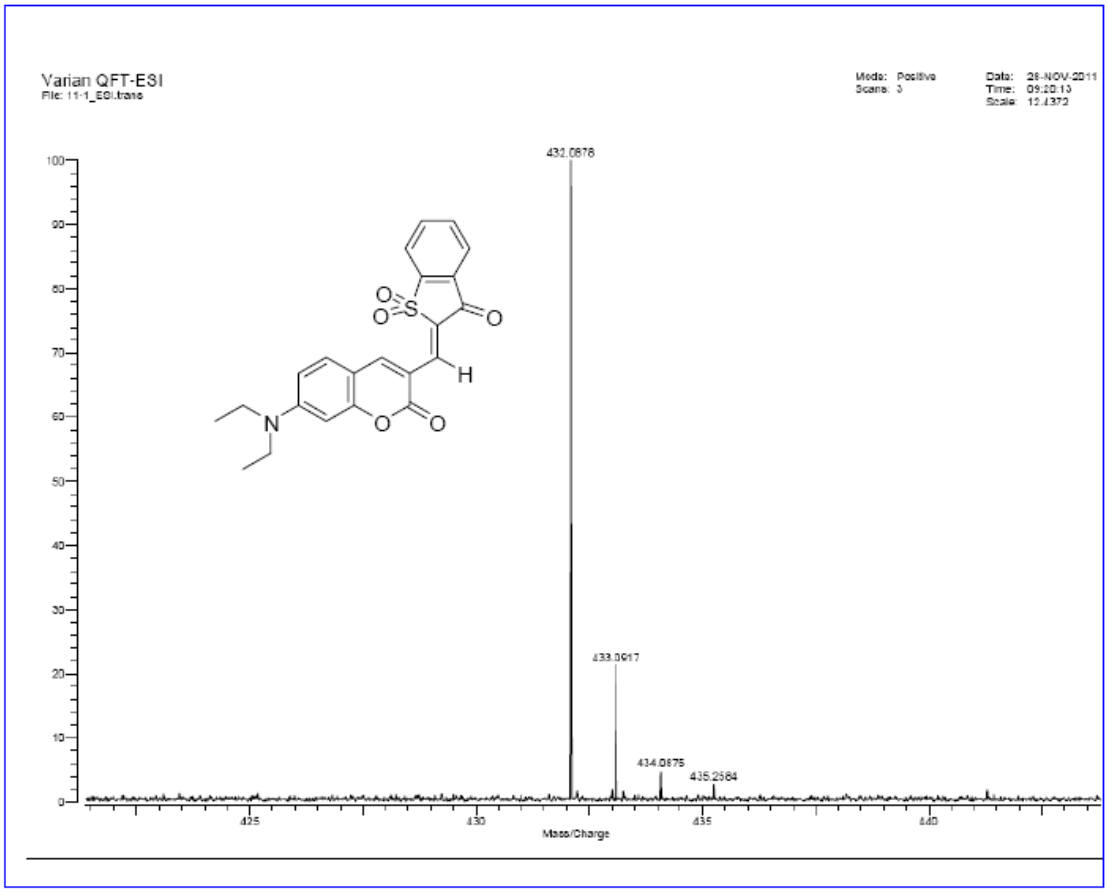


Figure S10 HRMS chart of **1**.

5. Z-matrix and total energy of 1 and 1-CN^-

1: SCRF-B3LYP/6-311++G(d,p)

Charge = 0 Multiplicity = 1

SCF Done: E(RB3LYP) = -1679.169338 a.u.

Number of Imaginary frequencies: n.a.

Symbolic Z-matrix:

C						
C	1	B1				
C	2	B2	1	A1		
C	3	B3	2	A2	1	D1
C	4	B4	3	A3	2	D2
C	1	B5	2	A4	3	D3
H	3	B6	2	A5	1	D4
H	4	B7	3	A6	2	D5
H	5	B8	4	A7	3	D6
H	6	B9	1	A8	2	D7
C	2	B10	1	A9	6	D8
S	1	B11	6	A10	5	D9
C	11	B12	2	A11	1	D10
O	11	B13	2	A12	1	D11
O	12	B14	1	A13	6	D12
O	12	B15	1	A14	6	D13
C	13	B16	11	A15	2	D14
H	17	B17	13	A16	11	D15
C	17	B18	13	A17	11	D16
C	19	B19	17	A18	13	D17
C	19	B20	17	A19	13	D18
C	20	B21	19	A20	17	D19
O	21	B22	19	A21	17	D20
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H	20	B24	19	A23	17	D22
O	21	B25	19	A24	17	D23
C	22	B26	20	A25	19	D24
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N	30	B33	29	A32	24	D31
C	34	B34	30	A33	29	D32
H	35	B35	34	A34	30	D33
H	35	B36	34	A35	30	D34

C	34	B37	30	A36	29	D35
H	38	B38	34	A37	30	D36
H	38	B39	34	A38	30	D37
C	35	B40	34	A39	30	D38
H	41	B41	35	A40	34	D39
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H	41	B43	35	A42	34	D41
C	38	B44	34	A43	30	D42
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H	45	B46	38	A45	34	D44
H	45	B47	38	A46	34	D45

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B32	1.07976597

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1-CN: SCRF-B3LYP/6-311++G(d,p)

Charge = -1 Multiplicity = 1

SCF Done: E(RB3LYP) =-1772.188231 a.u.

Number of Imaginary frequencies: n.a.

Symbolic Z-matrix:

C						
C	1	B1				
C	2	B2	1	A1		
C	3	B3	2	A2	1	D1
C	4	B4	3	A3	2	D2
C	1	B5	2	A4	3	D3
H	3	B6	2	A5	1	D4
H	4	B7	3	A6	2	D5
H	5	B8	4	A7	3	D6
H	6	B9	1	A8	2	D7
C	2	B10	1	A9	6	D8
S	1	B11	6	A10	5	D9
C	11	B12	2	A11	1	D10
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B11	1.80039545

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D22	-1.75604830
D23	3.12192725
D24	-179.25360428
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D27	179.37193182
D28	-0.36054489
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