

Supporting Information

A Facile Naphthalene-Based Fluorescent Chemodosimeter for Mercury Ions in Aqueous Solution

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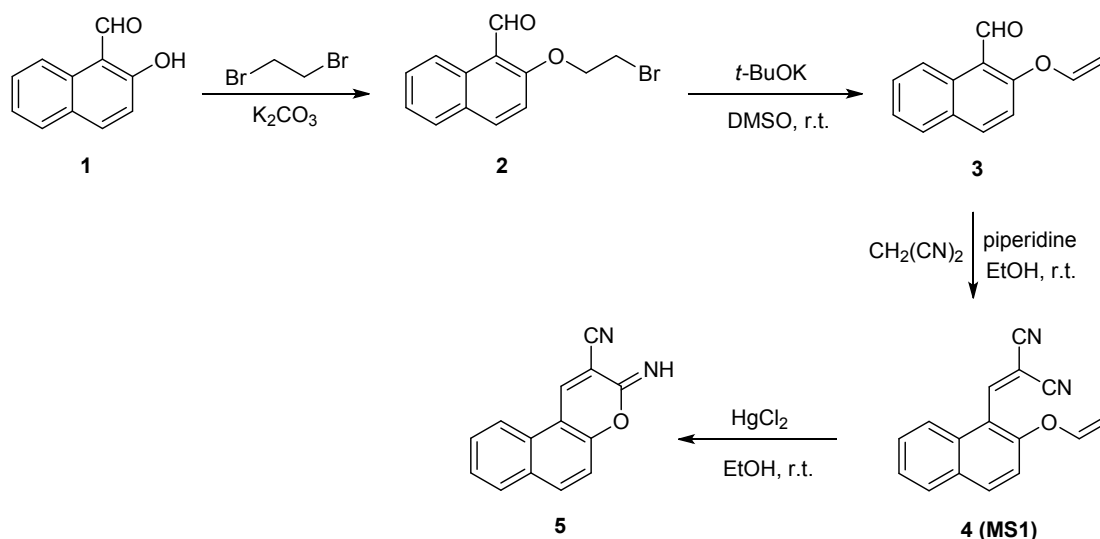
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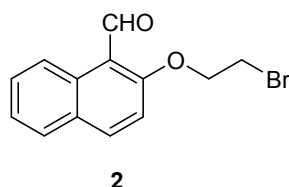
Materials and general methods

All the solvents were of analytic grade. NMR experiments were carried out on a Bruker AV-400 NMR spectrometer with chemical shifts reported in ppm (in CDCl₃, d₆-DMSO, or TMS as an internal standard). All pH measurements were made with a Sartorius basic pH-Meter PB-10. Fluorescence spectra were determined on a PerkinElmer LS55 Fluorescence spectrophotometer. Absorption spectra were determined on a Shimadzu UV 2501(PC)S UV-Visible spectrophotometer. The excitation and emission widths for **MS1** were all 5.

Synthesis and characterization



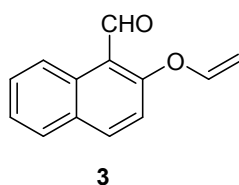
Scheme S1 Synthesis of probes **4 (MS1)** and **5**.



2-(2-bromoethoxy)-1-naphthaldehyde (2): 2-hydroxy-1-naphthaldehyde (500 mg, 2.9 mmol) and potassium carbonate (400 mg, 2.9 mmol) were dissolved in acetone (20 mL) under nitrogen atmosphere, then 1, 2-dibromoethane (1.3 mL, 15.1 mmol) was added and the solution was refluxed for 3 h until all starting material got consumed which was monitored by TLC analysis.

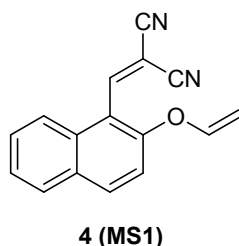
The reaction mixture was washed with water (100 mL), extracted with ether acetate (3 × 40 mL). The extract was dried over sodium sulfate and then concentrated under vacuum. The product was purified by flash chromatography using petroleum ether/ethyl acetate (10:1, v/v) as eluant to give **3** (0.5 g, 62%) as a pale yellow gum;

¹H NMR (400 MHz, CDCl₃) δ 10.77 (s, 1H), 9.12 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 6.7 Hz, 1H), 7.28 (t, *J* = 6.5 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 4.32 (brs, 2H), 3.54 (brs, 2H).



2-(vinylloxy)-1-naphthaldehyde (3): Potassium *tert*-butoxide (242 mg, 2.2 mmol) was dissolved in anhydrous DMSO (0.5 mL) and then added dropwise into a 10 mL bottom flask containing a DMSO solution (3.0 mL) of **2** (500 mg, 1.8 mmol) under nitrogen atmosphere and the mixture was stirred overnight at room temperature. Water (100 mL) was then added to the reaction solution. The mixture was extracted with ether acetate (3 × 40 mL), dried over sodium sulfate and then concentrated under vacuum. The product was purified by flash chromatography using petroleum ether/ethyl acetate (20:1, v/v) as eluant to give **3** (164 mg, 46%) as a pale yellow solid;

¹H NMR (400 MHz, CDCl₃) δ 10.75 (s, 1H), 9.21 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 9.5 Hz, 1H), 6.71 (dd, *J* = 13.6, 5.5 Hz, 1H), 4.76 (d, *J* = 13.7 Hz, 1H), 4.56 (d, *J* = 5.4 Hz, 1H).



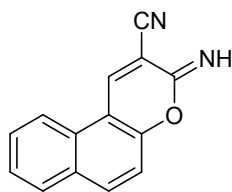
2-((2-(vinylloxy)naphthalen-1-yl)methylene)malononitrile (4, MS1): **3** (100 mg, 0.5 mmol) and malononitrile (40 mg, 0.6 mmol) were dissolved in ethanol (5 mL) under nitrogen atmosphere, then one drop of piperidine was added and the solution was stirred at room temperature for 1 h

until all starting material got consumed. Water (50 mL) was then added to the reaction solution. The mixture was extracted with ether acetate (3 × 15 mL), dried over sodium sulfate and then concentrated under vacuum. The product was purified by flash chromatography using petroleum ether/ethyl acetate (5:1, v/v) as eluant to give **4 (MS1)** (59 mg, 48%) as a pale yellow solid;

¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.1 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 6.73 (dd, *J* = 13.5, 5.4 Hz, 1H), 5.02 (d, *J* = 13.6 Hz, 1H), 4.73 (d, *J* = 5.2 Hz, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 155.37, 153.47, 146.36, 135.01, 131.06, 129.54, 129.06, 128.85, 125.78, 123.12, 116.21, 115.05, 113.55, 112.03, 99.14, 90.57.

HR-MS (ESI): Calcd. For [M+H]⁺ = 247.0871; Found, 247.0873.



5

3-imino-3H-benzo[f]chromene-2-carbonitrile (5): To a stirred solution of **4** (30 mg, 0.12 mmol) in ethanol (15 mL) was added HgCl₂ (98 mg, 0.36 mmol) in water (1.0 mL) at room temperature. The mixture was stirred for 1 h, and the precipitate was formed. The precipitated solid was filtered, washed with water, ethanol, and dried under vacuum to afford compound **5** as a white solid (23 mg, 86%);

¹H NMR (400 MHz, DMSO) δ 9.18 (s, 1H), 8.80 (s, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 1H).

¹³C NMR (100 MHz, DMSO) δ 153.93, 143.11, 135.44, 129.62, 128.93, 128.81, 125.98, 122.16, 116.15, 115.54, 111.19.

HR-MS (ESI): Calcd. For [M+H]⁺ = 221.0715; Found, 221.0712.

Photophysical properties of MS1

Table S1 Photophysical properties of the probe.

entry	λ_{ab} (nm)	λ_{em} (nm)	Φ^{a}	$\varepsilon / \text{M}^{-1} \text{cm}^{-1}$
MS1	538	470	0.002	5156
MS1+Hg²⁺	399	470	0.183 ^b	8856

(a) The quantum yield (Φ) of **MS1** and **MS1-Hg²⁺** system were determined according to the literature.¹ (b) Φ was determined in the present of 5.0 equiv. of Hg²⁺.

$$\Phi_{\text{Sample}} = \frac{\Phi_{\text{QS}} \cdot A_{\text{QS}} \cdot F_{\text{Sample}} \cdot \lambda_{\text{exQS}} \cdot \eta_{\text{Sample}}^2}{A_{\text{Sample}} \cdot F_{\text{QS}} \cdot \lambda_{\text{exSample}} \cdot \eta_{\text{QS}}^2}$$

Where Φ is quantum yield; A is absorbance at the excitation wavelength; F is integrated area under the corrected emission spectra; λ_{ex} is the excitation wavelength; η is the refractive index of the solution; the Sample and QS refer to the sample and the standard, respectively. We chose quinine sulfate in 0.1N H₂SO₄ as standard, which has the quantum yield of 0.546.²

Additional spectral of MS1

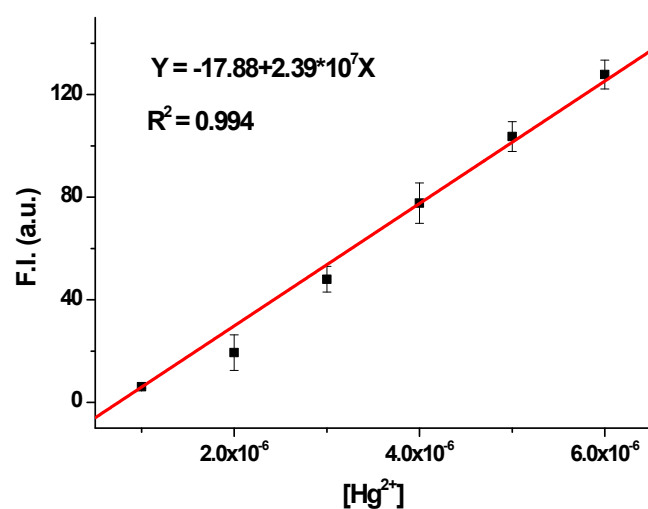


Fig. S1 Calibration curve of **MS1** (10 μ M) with Hg^{2+} (10 mM PBS buffer solution, pH 7.4, containing 1% CH_3CN , $\lambda_{\text{ex}} = 395$ nm). The detection limit (DL) of Hg^{2+} ions using **MS1** was determined from the following equation: ³

$$\text{DL} = 3 * \sigma / K$$

Where σ is the standard deviation of the blank solution; K is the slope of the calibration curve.

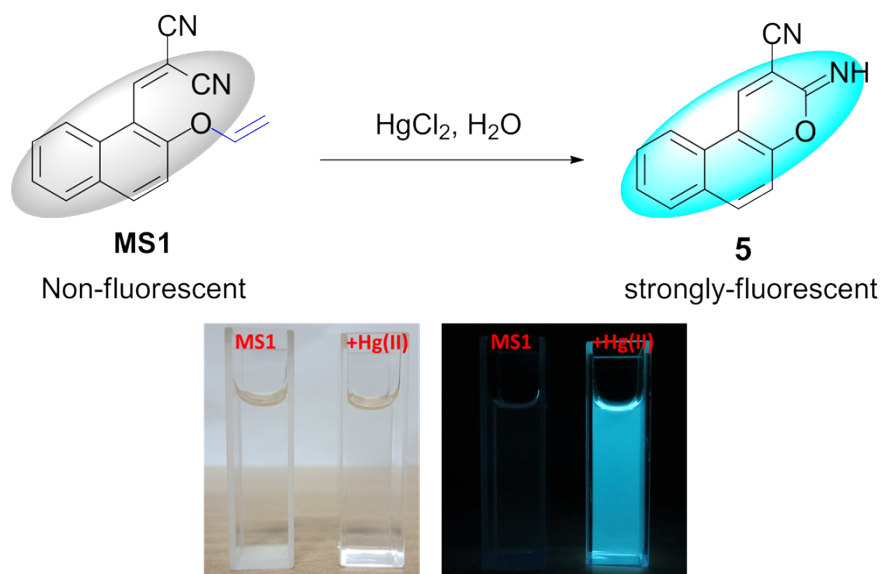
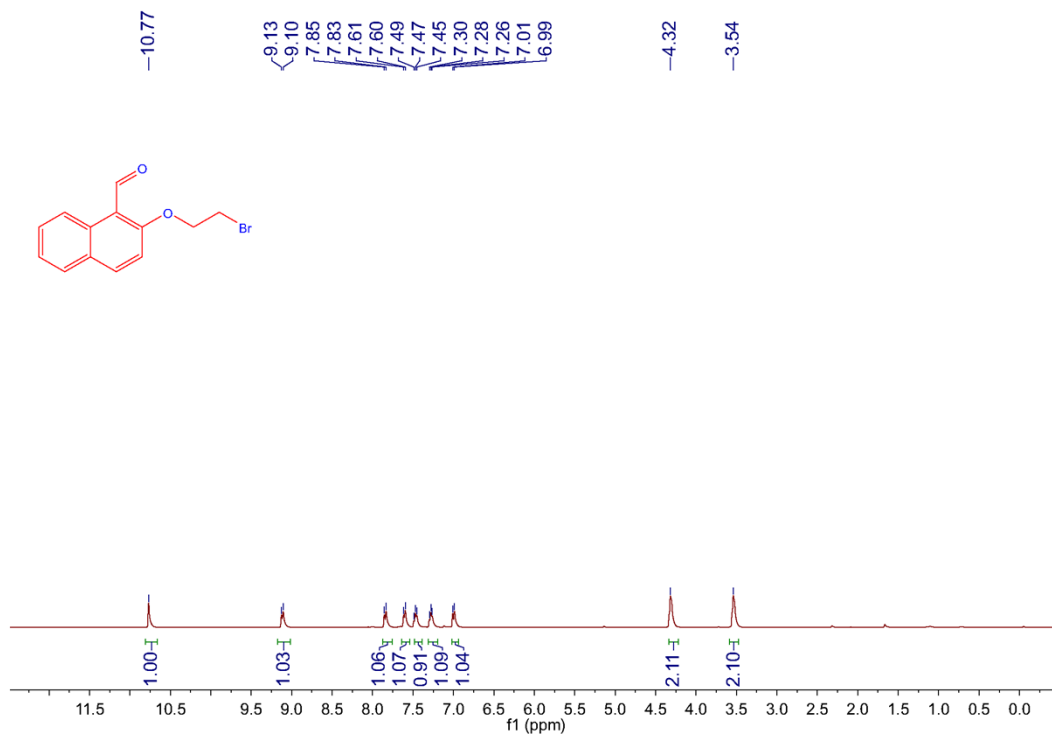


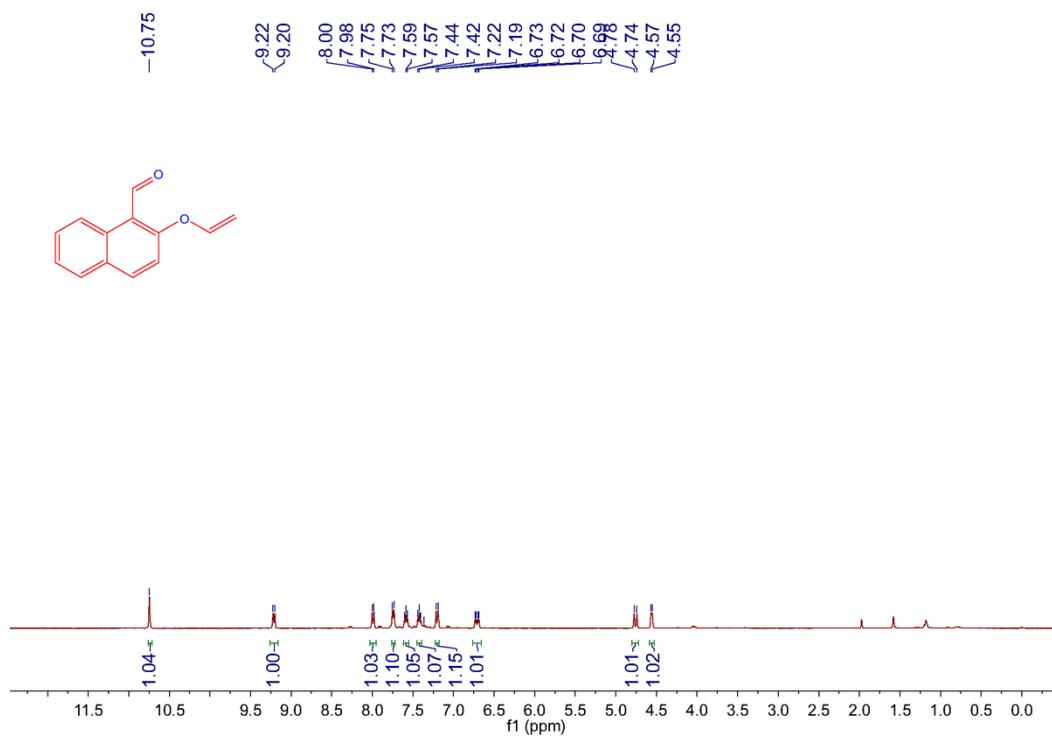
Fig. S2 The color changes of **MS1** in the absence and presence of Hg^{2+}

The characterization data of compounds

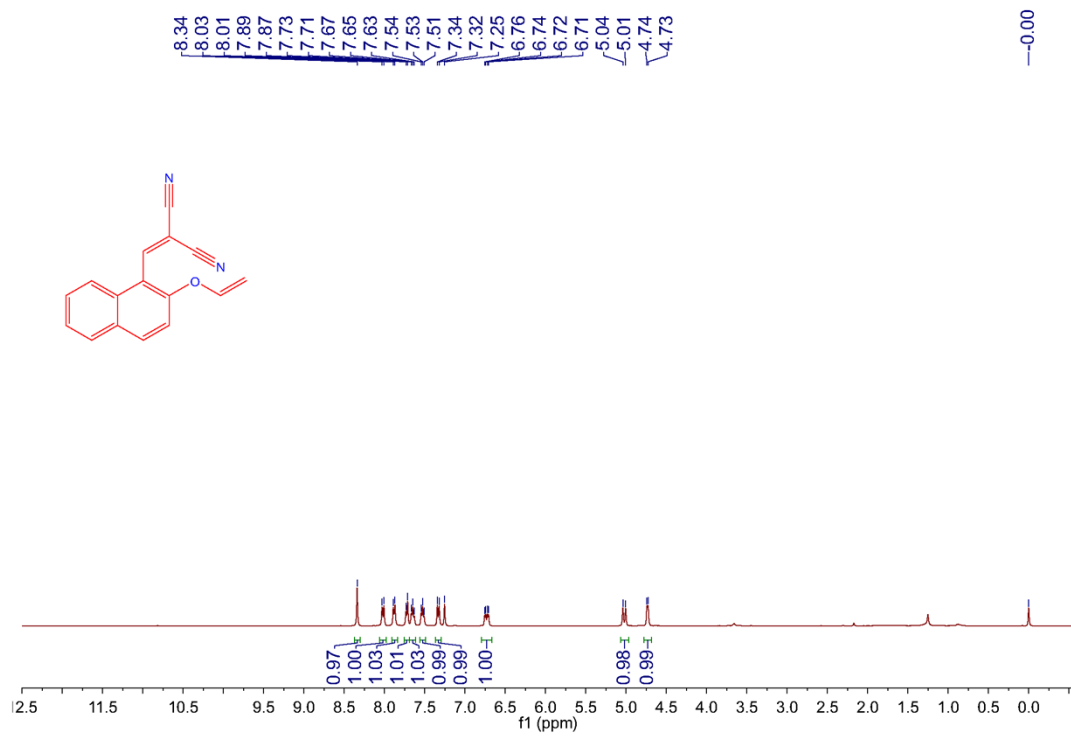
¹H NMR of compound 2



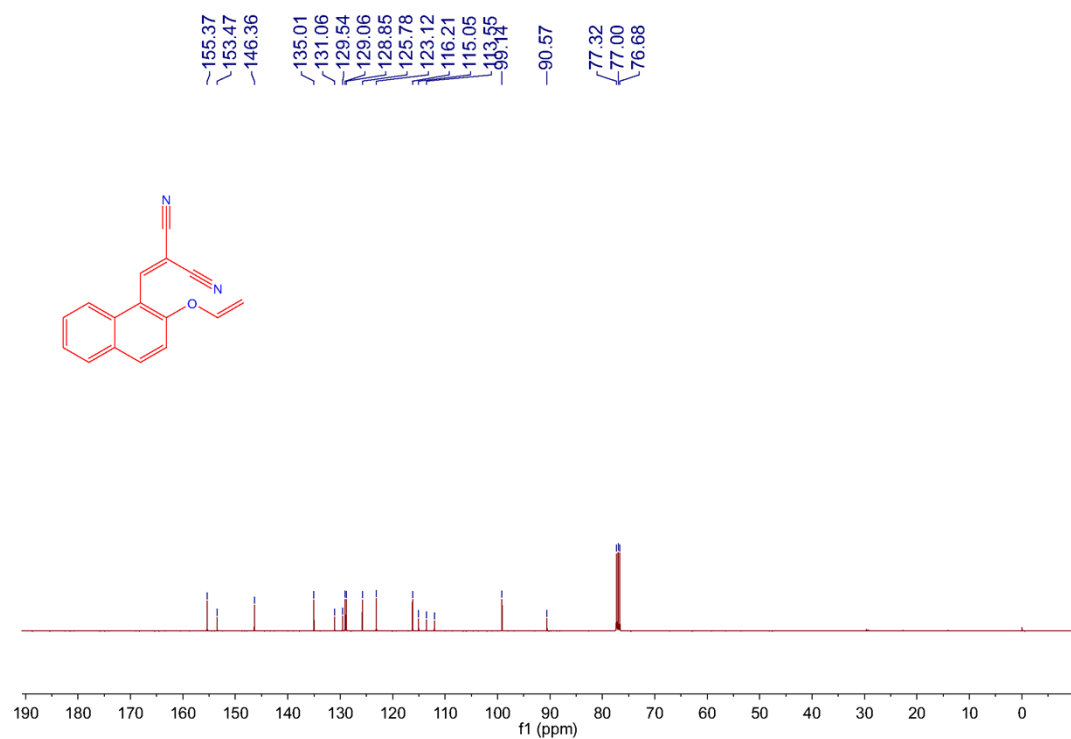
¹H NMR of compound 3



¹H NMR of compound 4 (MS1)

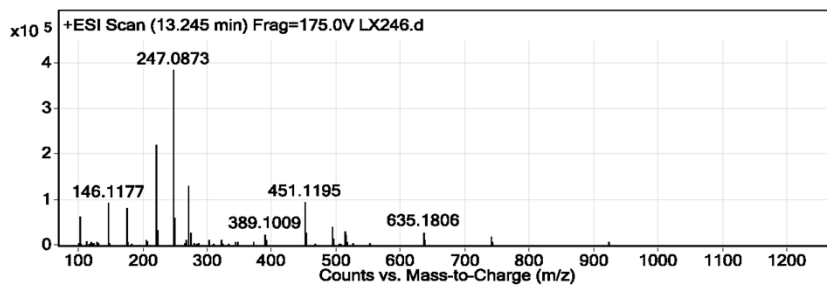


¹³C NMR of compound 4 (MS1)



HR-MS (ESI) of compound 4 (MS1)

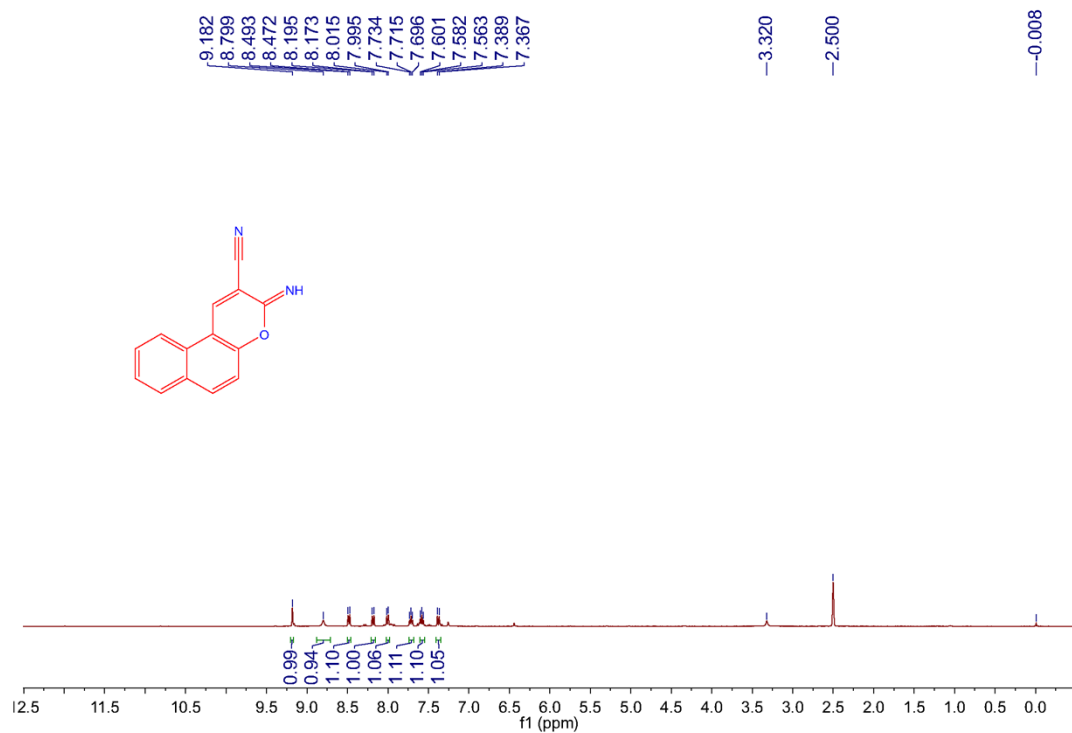
Qualitative Analysis Report



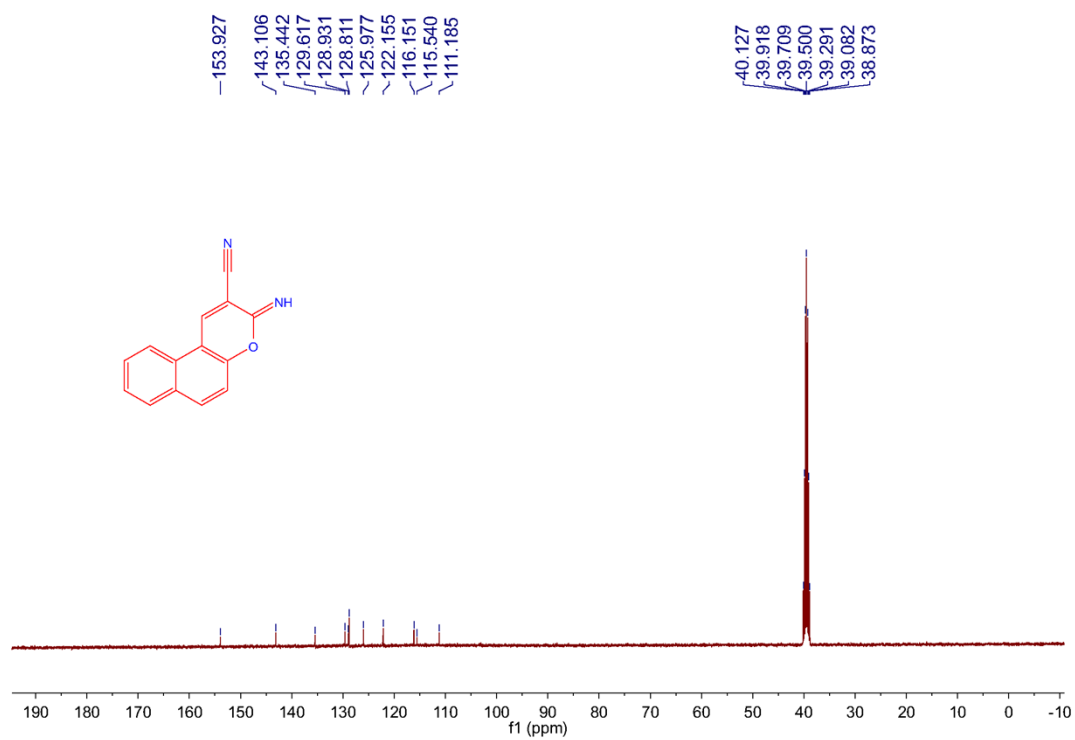
Peak List

<i>m/z</i>	<i>z</i>	Abund
102.1281		64553.6
146.1177		94111.2
174.1125		84271.9
221.0715	1	222635.1
222.0744	1	33855.1
247.0873	1	386131.5
248.0902	1	63490.9
269.0691	1	132529
451.1195	1	96029.7
493.1668		42509.4

¹H NMR of compound 5

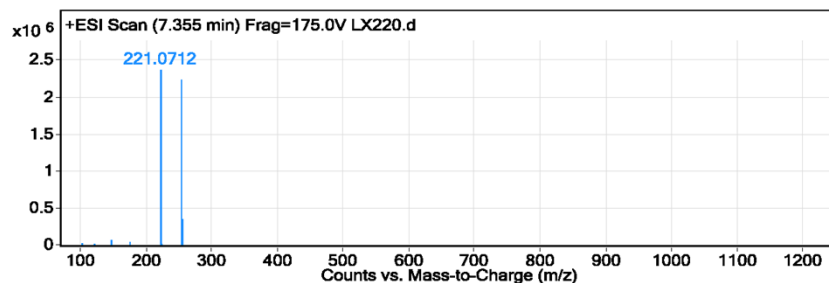


¹³C NMR of compound 5



HR-MS (ESI) of compound 5

Qualitative Analysis Report



Peak List

<i>m/z</i>	<i>z</i>	Abund
221.0712	1	2381011
222.0742	1	359219.8
253.0975	1	2253223.3
254.1006	1	372054.7

References

- 1 R. A. Velapoldi, H. H. Tønnesen, *J. Fluoresc.*, 2004, **14**, 465-472.
- 2 D. F. Eaton, *Pure Appl. Chem.*, 1988, **60**, 1107-1114.
- 3 (a) J. T. Yeh, P. Venkatesan and S. P. Wu, *New J. Chem.*, 2014, **38**, 6198. (b) A. Roy, D. Kand, T. Saha and P. Talukdar, *Chem. Commun.*, 2014, **50**, 5510.