

Ratiometric fluorescent detection of cyanide based a hybrid coumarin-hemicyanine dye: the large emission shift and the high selectivity

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Electronic Supplementary Information (ESI†)

Contents

1. General information and methods

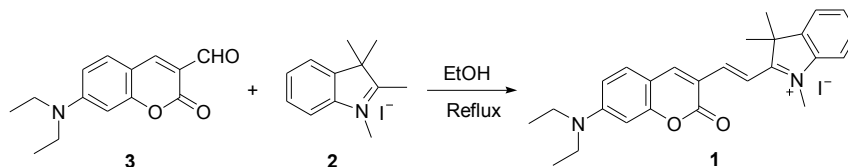
All reagents and solvents were purchased from commercial sources and were of the highest grade. Solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC). Flash chromatography (FC) was performed using silica gel 60 (200–300 mesh). Absorption spectra were taken on an Agilent 8453 spectrophotometer. Fluorescence spectra were taken on HITACHI F-4500 fluorescence spectrometer. The ^1H NMR and ^{13}C NMR spectra were recorded at 600 and 150MHz, respectively. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High resolution mass spectra were obtained on a Varian QFT-ESI mass spectrometer.

2. Procedures of sensing

Deionized water was used throughout all experiments. Cyanide anion was prepared from its potassium, and the other anions were prepared from their sodium salts. A stock solution of **1** (5 mM) was prepared in MeOH. The stock solution of **1** was then diluted to the corresponding concentration (10 μM) with the solution of MeOH–Tris·HCl buffer (10 mM, pH = 9.3, 1:1, v/v). The potassium cyanide stock

solution of 1.0×10^{-1} M was diluted to 1.0×10^{-2} M and 1.0×10^{-3} M with deionized water for spectra titration studies. Spectra data were recorded in an indicated time after the addition.

3. Synthesis



1-Methyl-2,3,3-trimethyl-3H-indolium 2^{S1} and diethylaminocoumarin-aldehyde 3^{S2} were synthesized according to the literature reported procedures. Compound **2** (100 mg, 0.33 mmol) was treated with **3** (81 mg, 0.33 mmol) in anhydrous ethanol (20 mL). The reaction mixture was then refluxed for 12 h, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 100:1) on silica gel to give the product **1** as a purple powder (130 mg, yield: 73%). Mp: 241–242 °C. ^1H NMR (600MHz, CDCl_3) δ 10.08 (s, 1H), 8.60 (d, $J = 15.6$, 1H), 8.14 (d, $J = 9$, 1H), 8.01 (d, $J = 15.6$, 1H), 7.54 (m, 3H), 7.45 (d, $J = 7.8$, 1H), 6.70 (m, 1H), 6.47 (s, 1H), 4.32 (s, 3H), 3.54 (q, $J = 7.2$, 4H), 1.85 (s, 6H), 1.30 (t, $J = 7.2$, 6H); ^1H NMR (600MHz, $\text{DMSO}-d_6$) δ 8.80 (s, 1H), 8.24 (d, $J = 16.2$, 1H), 7.83–7.86 (m, 3H), 7.56–7.62 (m, 3H), 6.92 (d, $J = 6.6$, 1H), 6.73 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 181.3, 161.2, 158.9, 154.6, 150.8, 149.5, 142.7, 141.6, 134.6, 129.3, 128.7, 122.6, 113.3, 112.6, 111.2, 111.0, 108.9, 96.8, 68.2, 51.7, 45.7, 36.0, 27.5, 12.6; ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 181.3, 159.8, 158.1, 154.4, 150.7, 149.7, 143.6, 142.4, 132.8, 129.4, 129.1, 123.2, 114.9, 112.7, 111.7, 110.7, 109.9, 97.1, 55.4, 51.8, 45.3, 34.2, 26.4, 12.9; HRMS [ESI]: m/z , calcd for [M] 401.2229; Found 401.2228.

The **1**–CN adduct could be conveniently synthesized as viscous oil *via* the condensation of compound **1** with 1 equiv. of KCN in DMSO at room temperature (yield: 91%). Note: the product is very unstable, and will decompose when exposed in air. ^1H NMR (600MHz, $\text{DMSO}-d_6$) δ 8.23 (s, 1H), 7.47 (d, $J = 9.0$, 1H), 7.17 (m, 2H), 6.84–6.90 (m, 2H), 6.68–6.76 (m, 3H), 6.58 (s, 1H), 3.45(q, $J = 6.6$, 4H), 2.71 (s, 3H),

1.46 (s, 3H), 1.14 (t, $J = 6.6$, 6H), 1.12 (s, 3H). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 160.2, 155.1, 154.6, 151.2, 146.2, 138.1, 129.1, 128.0, 126.6, 122.4, 121.8, 121.7, 118.4, 114.3, 110.3, 105.4, 97.4, 89.3, 55.4, 44.6, 44.3, 29.1, 27.7, 27.6, 12.7; HRMS [ESI]: m/z , calcd for $[\text{M}+\text{H}]^+$ 428.2338; Found 428.2336.

References

- [S1] M. Tomasulo, S. Sortino, and F. M. Raymo, *J. Org. Chem.*, 2008, **73**, 118.
[S2] J.-S. Wu, W.-M. Liu, X.-Q. Zhuang, F. Wang, P.-F. Wang, S.-L. Tao, X.-H. Zhang, S.-K. Wu, and S.-T. Lee, *Org. Lett.*, 2007, **9**, 33.

4. Supplemental spectra

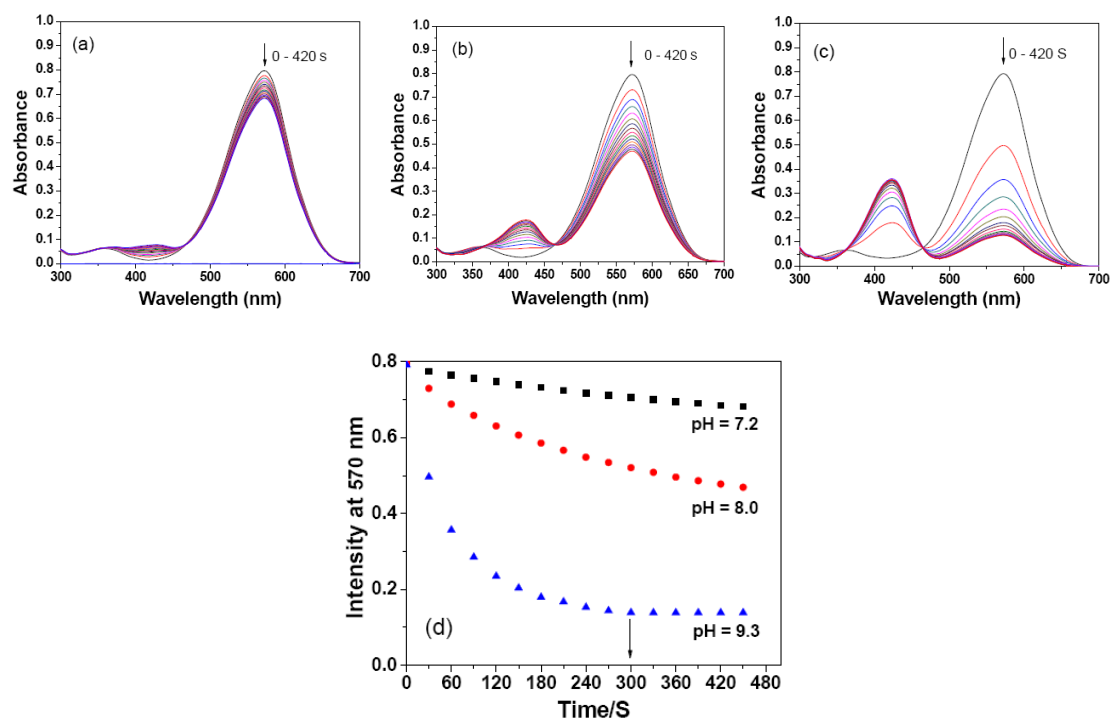


Fig. S1 Time-dependent changes in the absorption spectra of probe **1** (10 μM) upon addition of 5 equiv CN^- in $\text{MeOH-Tris}\cdot\text{HCl}$ buffer (10 mM, 1:1, v/v) with the varied pH value [(a) pH = 7.2; (b) pH = 8.0; (c) pH = 9.3]. (d) Time-dependent absorption intensity of probe **1** at 570 nm in the presence of 5 equiv CN^- in the different pHs.

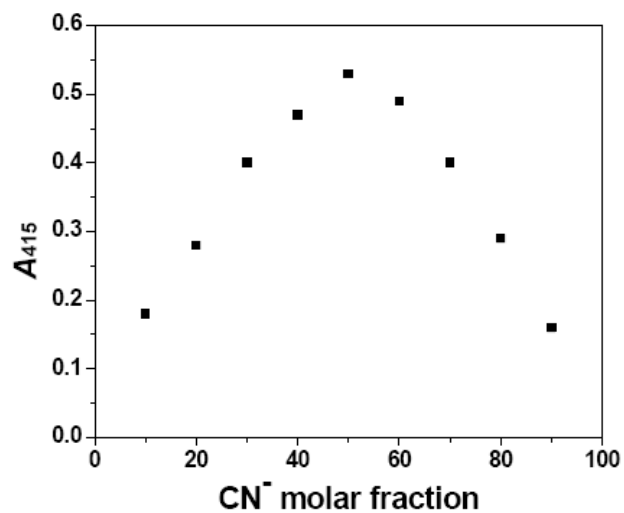


Fig. S2 Job's plots of the complexation between **1** and CN⁻. Total concentration of **1** + CN⁻ was kept constant at 50 μM.

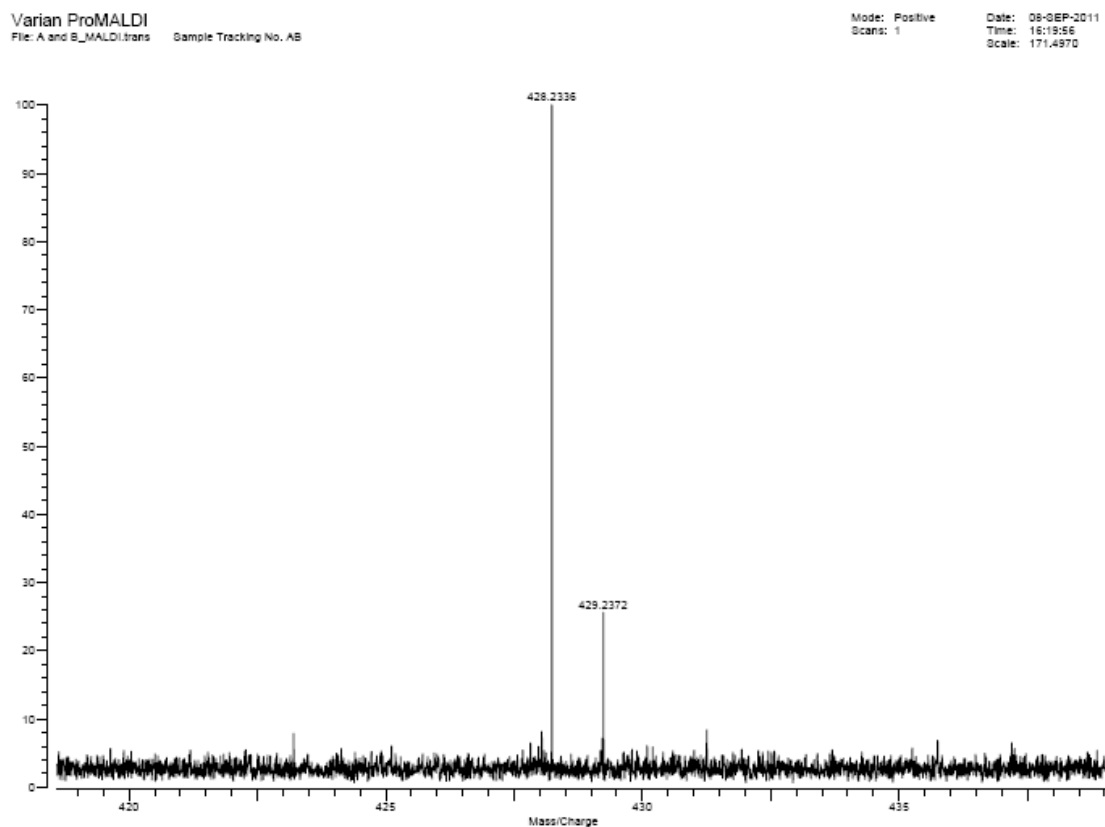


Fig. S3 The HRMS for **1**-CN adduct.

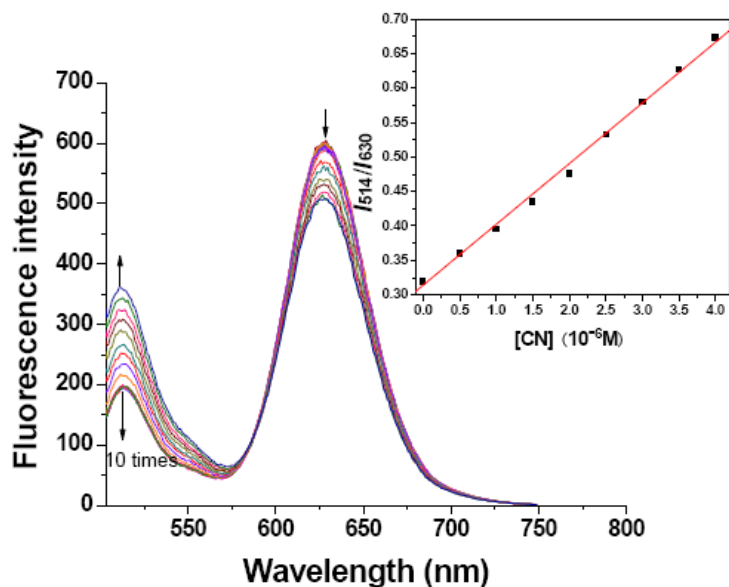


Fig. S4 Fluorescence titration spectra of **1** (10 μM) in MeOH–Tris·HCl buffer (10 mM, pH = 9.3, 1:1, v/v) upon addition of CN⁻ (0–4 μM). Inset: Fluorescence ratio (I_{514}/I_{630}) changes upon gradual addition of CN⁻. λ_{ex} = 490 nm. Slits: 5 nm/10 nm.

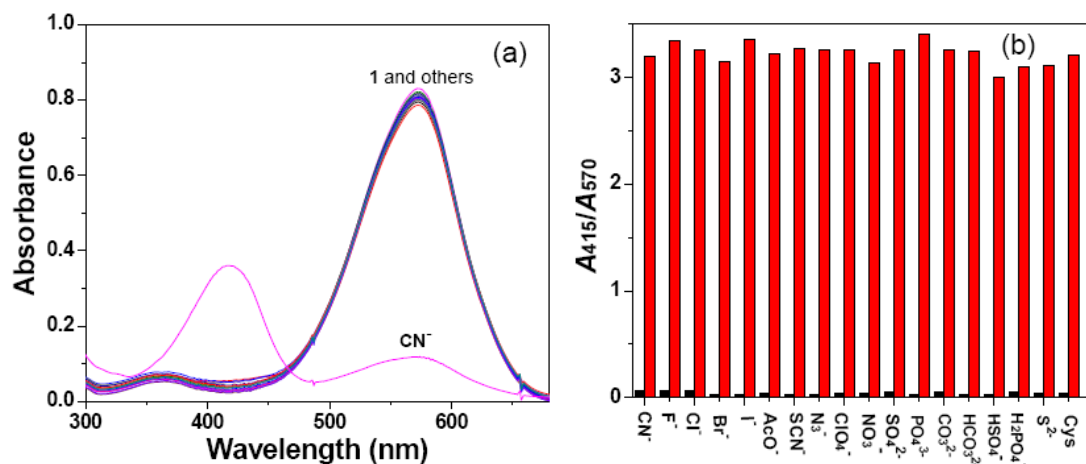


Fig. S5 (a) The absorption spectra of **1** (10 μM) upon addition of 50 μM of various species in MeOH–Tris·HCl buffer (10 mM, pH = 9.3, 1:1, v/v). (b) Absorption ratio (A_{415}/A_{570}) response of **1** (10 μM) to 50 μM of CN⁻ containing 50 μM of various species.

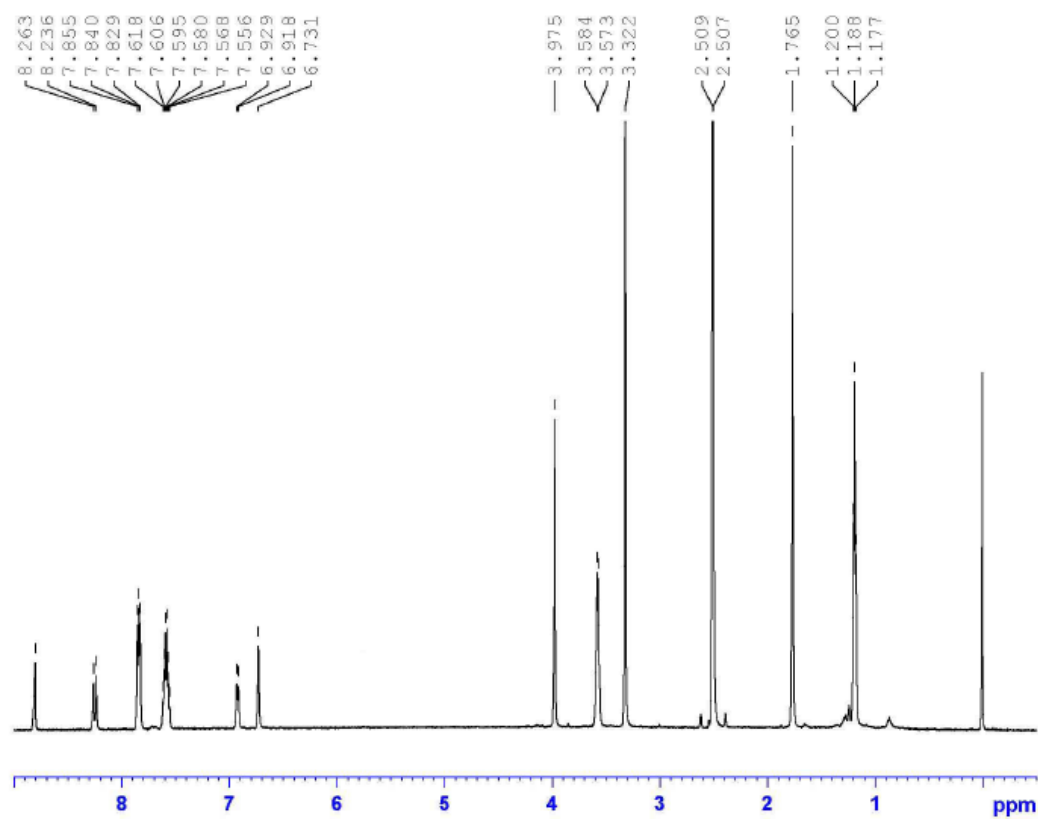
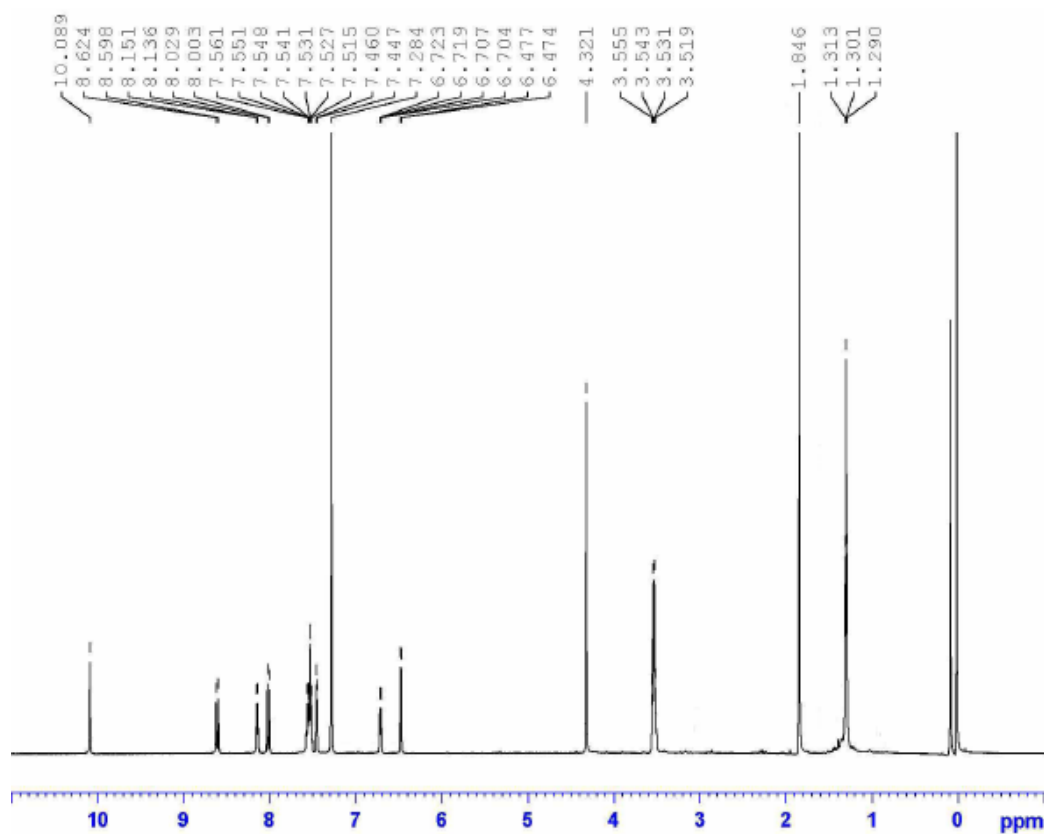


Fig. S6 ^1H NMR charts of **1** in CDCl_3 (top) and $\text{DMSO}-d_6$ (below), respectively.

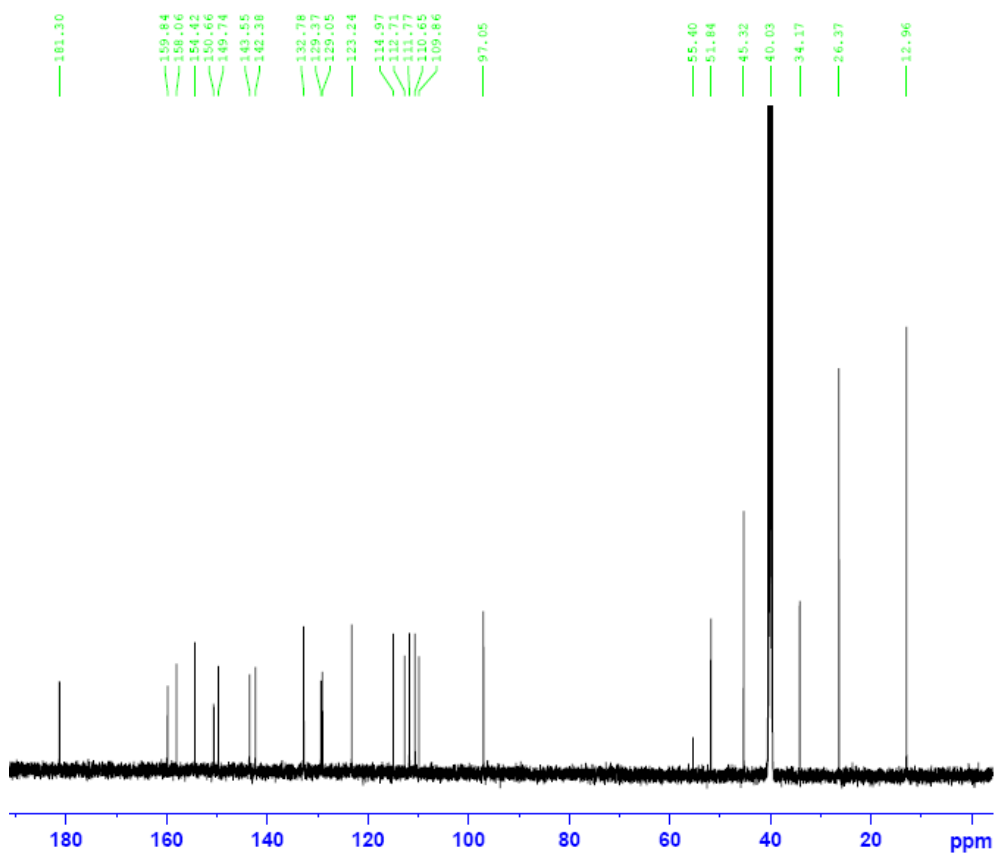
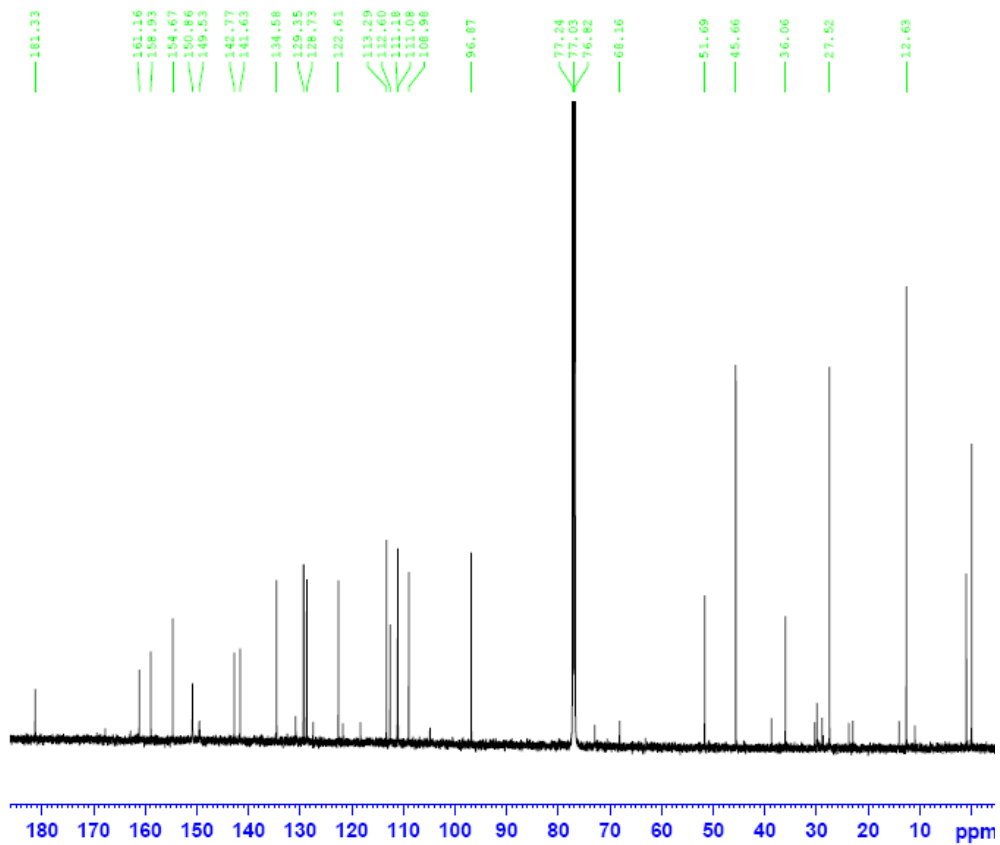


Fig. S7 ¹³C NMR charts of **1** in CDCl₃ (top) and DMSO-*d*₆ (below), respectively.

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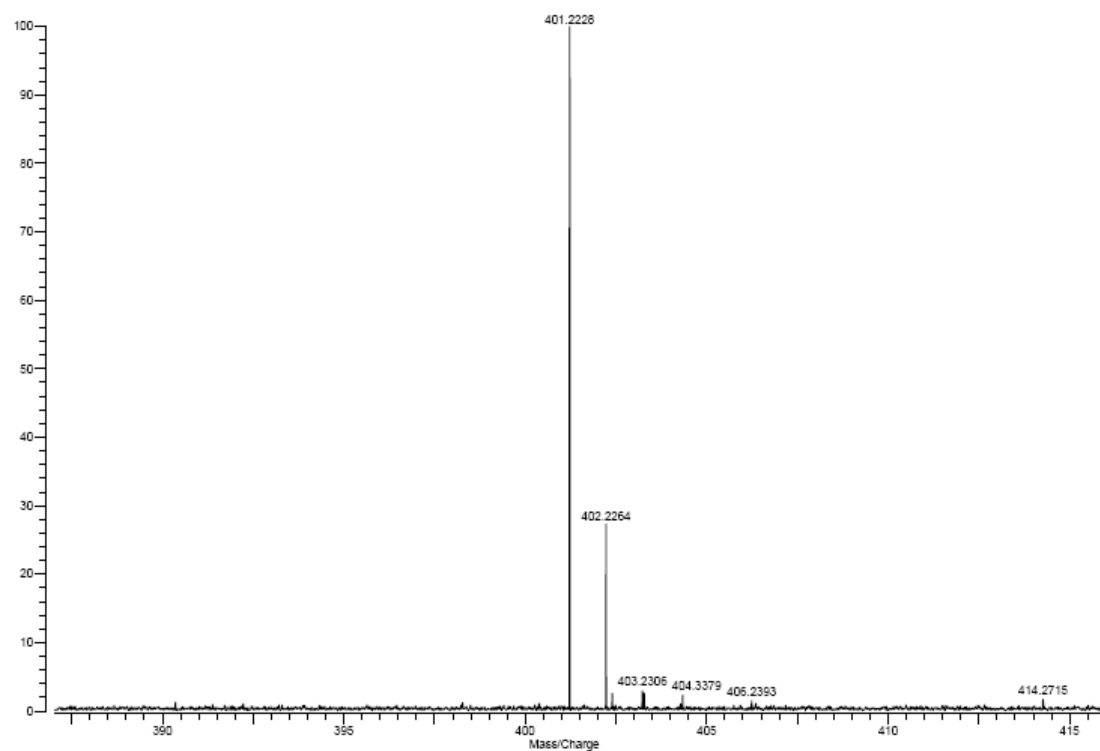


Fig. S8 HRMS chart of **1**.

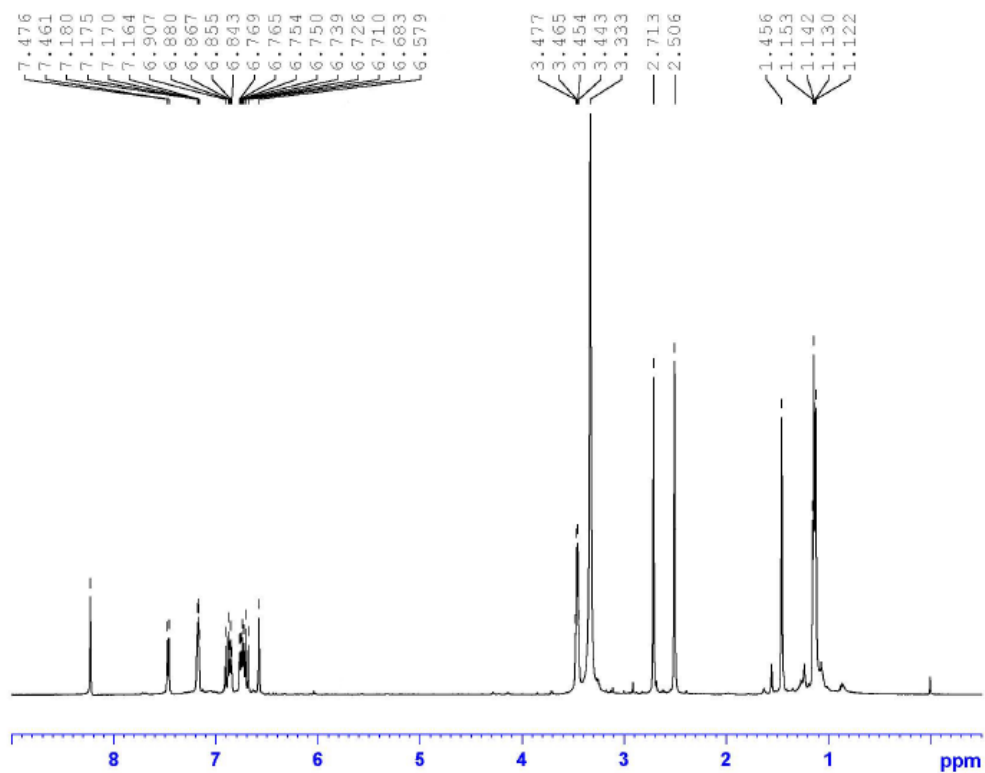


Fig. S9 ^1H NMR chart of **1-CN** adduct ($\text{DMSO-}d_6$).

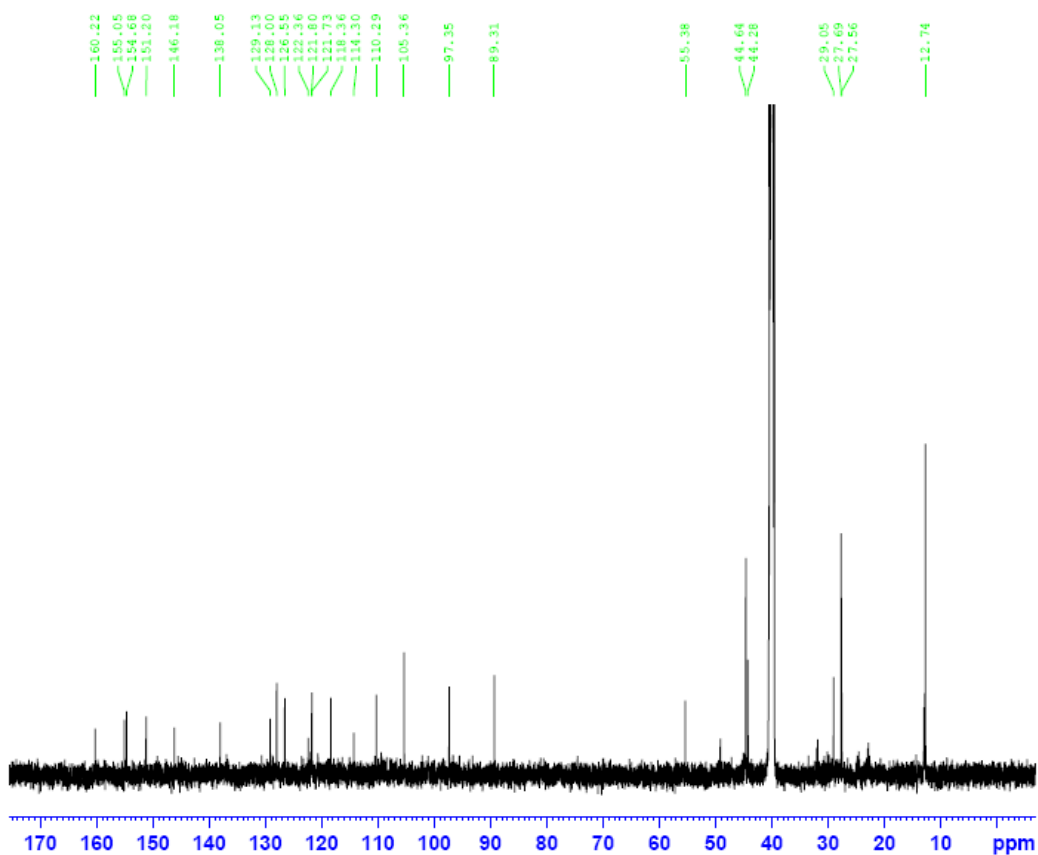


Fig. S10 ^{13}C NMR chart of **1-CN** adduct ($\text{DMSO-}d_6$).