Electronic supplementary information

For

A Heptamethine cyanine -Based Colorimetric and Ratiometric Fluorescent Chemosensor for Selective Detection of Ag^+ in an Aqueous Medium

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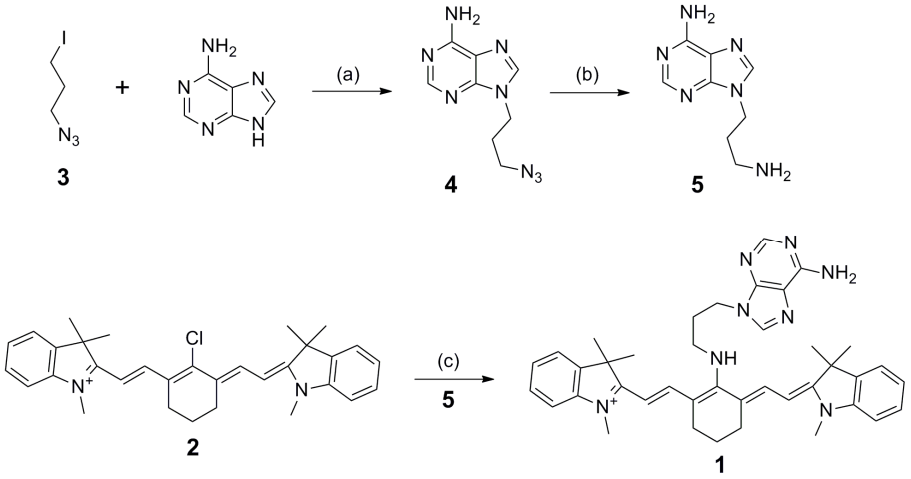
Instruments and Materials

NMR spectra were recorded on Bruker AV400 NMR and Bruker AV300 NMR. Mass spectra were measured with a JEOL JMS-T100LC mass spectrometer (ESI+). HR-MS spectra were measured with a Bruker En Apex ultra 7.0T FT-MS mass spectrometer. Uncorrected fluorescence emission spectra were conducted on a Hitachi F-4500 luminescence spectrometer. Absorption spectra were determined on a Varian CARY 300 spectrometer. Doubly distilled water was used throughout the experiments. All the materials for synthesis were purchased from commercial suppliers and used without further purification.

General detection procedures. Compound **1** was dissolved in CH_3OH to make a 1.0×10^{-3} M stock solution, which was further diluted to required concentration for measurement. Silver nitrate was dissolved in water to make a 1.0×10^{-3} M stock solution of silver ion.

To 10-mL glass tubes containing 1.0 mL of 200 mM succinic acid — NaOH buffer solution (pH 5.4) and different amounts of silver ions, added the redistilled water to the full scale, the resulting solution were mixed thoroughly. Then 0.20 mL of 1.0 $\times 10^{-3}$ M stock solution of compound **1** was added directly with a micropipette and the solutions were mixed again. The absorption and fluorescence sensing of Ag^{+} were run after 40 minutes.



(a) DMF (extra dry), K_2CO_3, N_2 atmosphere, rt, 36 hs, (b) Triphenyl phosphine, dry CH_3OH, refluxed for 2 hs, N_2 atmosphere, (c) 1,8-Bis (dimethylamino) naphtalene, CH_3OH, refluxed for 6 hs, N_2 atmosphere.

Compound **2** and **3** were synthesized according to the references [S1, S2].

Synthesis of compound **4**. A mixture of **3** (0.3 g, 1.42 mmol), adenine (0.48 g, 3.55 mmol), and K_2CO_3 (0.89 g, 7.1 mmol) in anhydrous DMF (15 mL) was stirred under N_2 atmosphere at room temperature for 36 hs. Then the resulting mixture was added to the saturated NaCl solution, then extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, and the solvents were evaporated in vacuum. The residue was chromatographed on silica gel with CH_3OH /CH_2Cl_2 (1:10, v/v) as eluent to give 0.41 g (54.5%) of **4** as white solid.

^{1}H NMR (d_6-DMSO, 400 MHz) δ(ppm):8.16 (s, 2H), 7.24 (s, 2H), 4.22 (t, J = 6.8 Hz, 2H), 3.39 (t, J = 6.4 Hz, 2H), 2.08 (penta, J = 6.8 Hz, 2H).

^{13}C NMR (d_6-DMSO, 100 MHz) δ(ppm): 156.44 , 152.89 , 150.04 , 141.28 , 119.23 , 48.56 , 40.96 , 29.09.

ESI mass spectrometry, m/z: 219.0 $(M+H)^+$

Synthesis of compound **5**. A mixture of **4** (0.3 g, 1.38 mmol) and triphenyl phosphine (0.54 g, 2.06mmol) in dry CH_3OH (9 mL) was stirred and refluxed under N_2 atmosphere for 2 hs. Then the resulting mixture were evaporated in vacuum. The residue was recrystalized in CH_3OH to give 0.14 g (53%) of **5** as white solid.

^1H NMR (d_6-DMSO, 400 MHz) δ(ppm):8.13 (s, 2H), 7.19 (s, 2H), 4.19 (t, J = 6.8 Hz, 2H), 2.47 (t, J = 6.4 Hz, 2H), 1.84 (penta, J = 6.8 Hz, 2H).

^{13}C NMR (d_6-DMSO, 100 MHz) δ(ppm):156.41, 152.79, 150.03，141.37, 119.19, 41.02, 38.90, 33.70.

ESI mass spectrometry, m/z: 193.1 $(M+H)^+$

HRMS: m/z: Calcd. for $C_8H_{12}N_6$, $(M+H)^+$: 193.12017, found: 193.12042.

Synthesis of compound **1**. A mixture of **2** (0.1 g, 0.16 mmol), **5** (0.038 g, 0.2 mmol) and 1,8-Bis (dimethylamino) naphthalene (0.042 g, 0.2 mmol) in dry CH_3OH (10 mL) was stirred and refluxed under N_2 atmosphere for 6 hs. Then the resulting mixture were evaporated in vacuum. The residue was chromatographed on silica gel with CH_3OH /CH_2Cl_2 (1:25, v/v) as eluent to give 0.057 g (45%) of **1** as blue solid.

^1H NMR ($CDCl_3$,400MHz) δ (ppm)：8.48 (s, 1H), 8.26 (s, 1H), 8.12 (s, 1H), 7.73 (bs, 2H), 7.270-7.291 (dd, J = 7.6, 0.8 Hz, 2H), 7.24 (d, J = 7.6 Hz, 2H), 7.05 (t, J = 7.5 Hz, 2H), 6.88 (d, J = 7.9 Hz, 2H), 5.99 (s, 2H), 5.51 (d, J = 12.8 Hz, 2H), 4.45 (t, J = 6.8 Hz, 2H), 3.91 – 3.82 (m, 2H), 3.41 (s, 6H), 2.72 – 2.56 (m, 2H), 2.46 (t, J = 6.2 Hz, 4H), 1.85 – 1.76 (m, 2H), 1.61 (s, 12H).

^{13}C NMR ($CDCl_3$,100MHz) δ (ppm):169.66 , 168.05 , 155.46 , 152.70 , 150.06 , 143.62, 141.14, 138.01, 128.10, 122.78 , 122.04 , 120.44 , 119.42 , 108.26 , 94.20 , 77.27 , 47.75, 46.62 , 41.24 , 31.51 , 28.98 , 25.41 , 22.69 , 21.40.

ESI mass spectrometry, m/z: 639.2 $(M)^+$

HRMS: m/z: Calcd. for $C_{40}H_{47}N_8$, $(M)^+$:639.39237, found: 639.39129

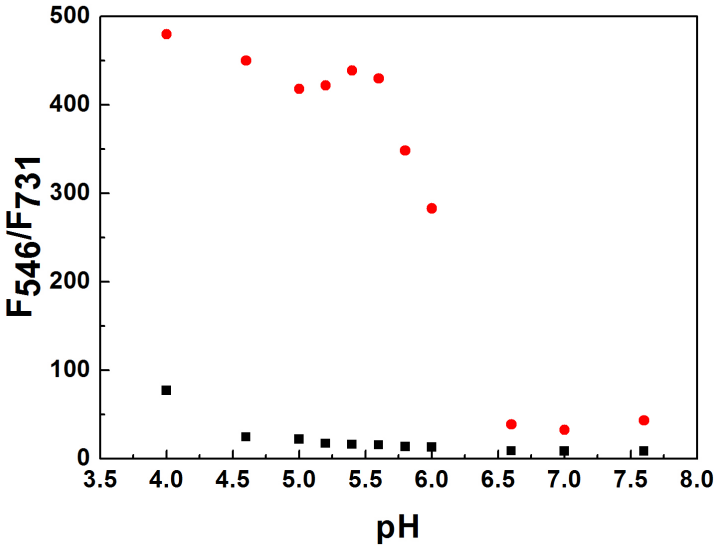


Fig. S1 Effect of different pH on the ratiometric fluorescent response of 1 to Ag^+ ion.

[**1**] = 20.0 μmol/L, [Ag^+] = 10.0 μmol/L, under the different pH with MeOH-H_2O (1/4, V/V) solutions. Dots in red represents the fluorescent ratiometric value (F_{546}/F_{731}) of **1**+Ag^+ solution; dots in black represents the ratiometric value (F_{546}/F_{731}) of **1** solution.

Fig. S2 Visual color changes of 1 upon addition of Ag^+

[**1**] = 20.0 μmol/L, pH 5.40 (succinic acid-NaOH buffer). Concentration of Ag^+, from left to right (μmol/L): 0.0, 0.6, 1.0, 3.0, 5.0, 7.0, 8.0, 9.0, 10.

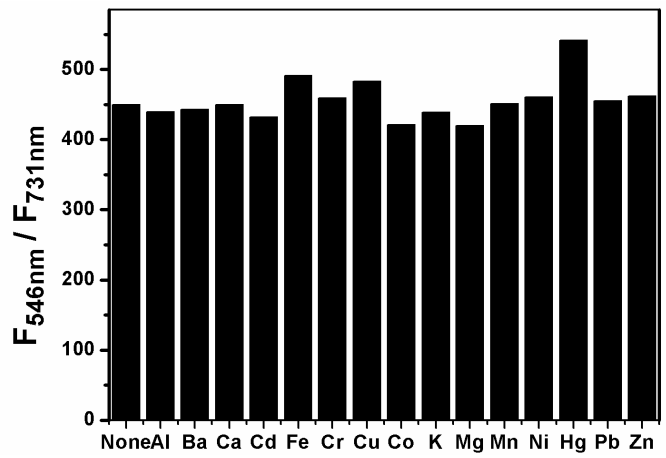


Fig. S3 Fluorimetric response of 1 to Ag^+ in the presence of competitive cations

[**1**] =20.0 μmol/L, [Ag^+] = 10.0 μmol/L, pH 5.40 (succinic acid-NaOH buffer) in MeOH-H_2O (1/5, V/V) solution. Cd^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+}, each of 5 equiv. of Ag^+; Al^{3+}, Ba^{2+}, Ca^{2+}, Mg^{2+} and K^+, each of 10 equiv. of Ag^+, respectively.

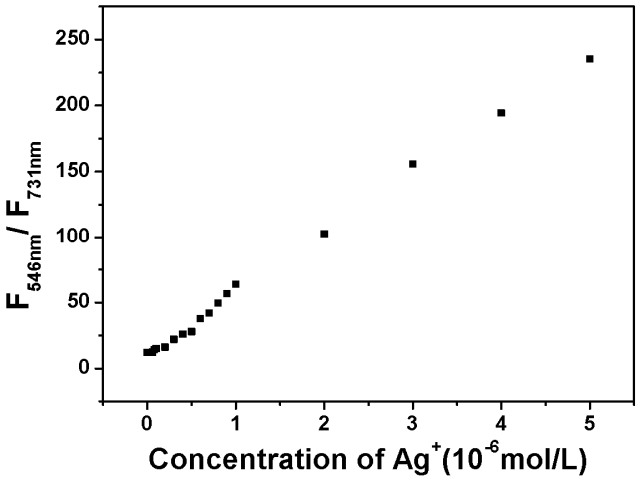


Fig. S4 Relative Fluorescence intensity of 1 versus the Ag^+ concentrationin

[**1**] =20.0 μmol/L, pH 5.40 (succinic acid-NaOH buffer) in H_2O-MeOH (5/1, V/V) solution. λex / λem = 512 / 546 nm,731 nm; slit: ex / em = 10.0/20.0 nm.

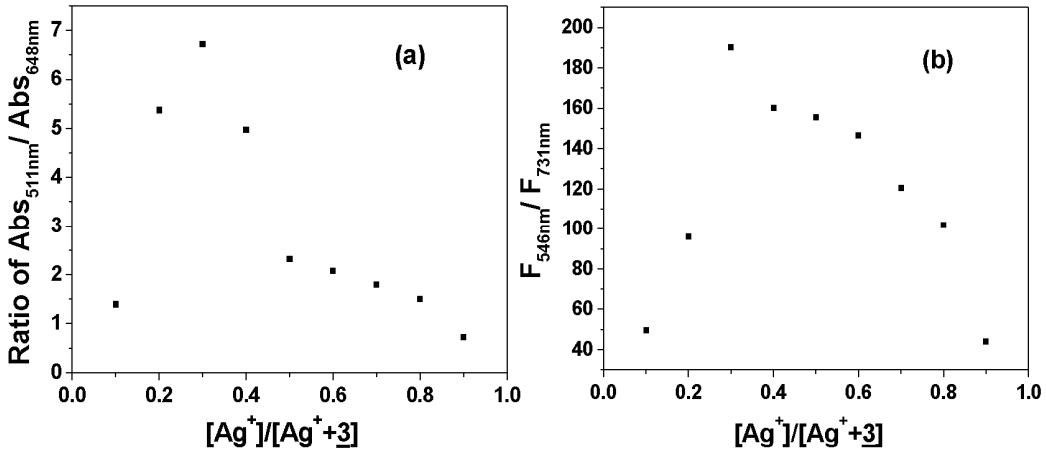


Fig. S5 Job's plot of the complexation between 1 and Ag^+

(a) by absorption spectroscopy; (b) by fluorescence spectroscopy;

[**1**]+[Ag^+] = 20.0 μmol/L, pH 5.40 (succinic acid-NaOH buffer) in MeOH-H_2O (1/5, V/V) solution.

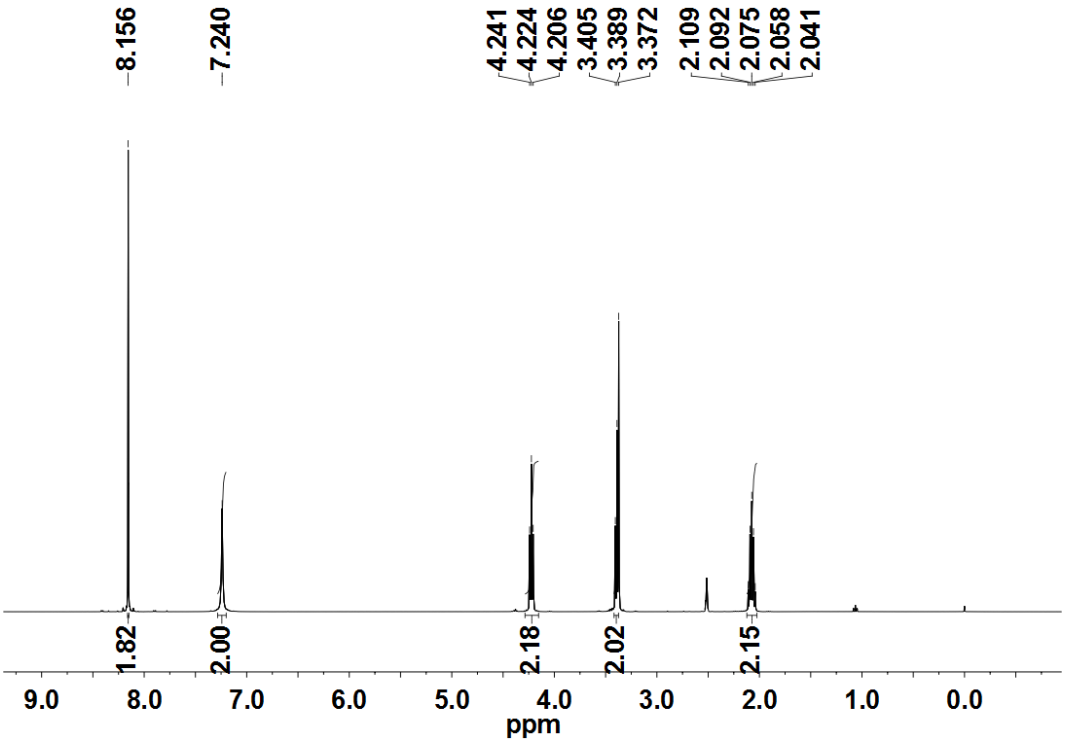


Fig. S6 ^{1}H NMR spectra of **4** in DMSO-d6

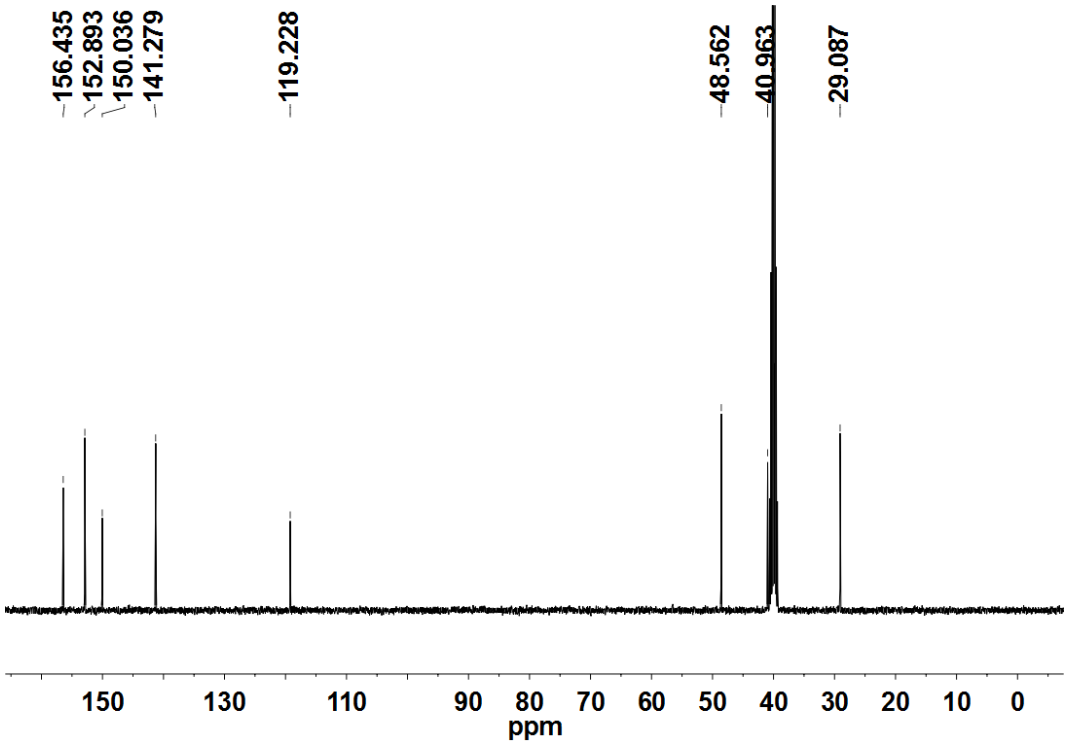


Fig. S7 ^{13}C NMR spectra of **4** in DMSO-d6

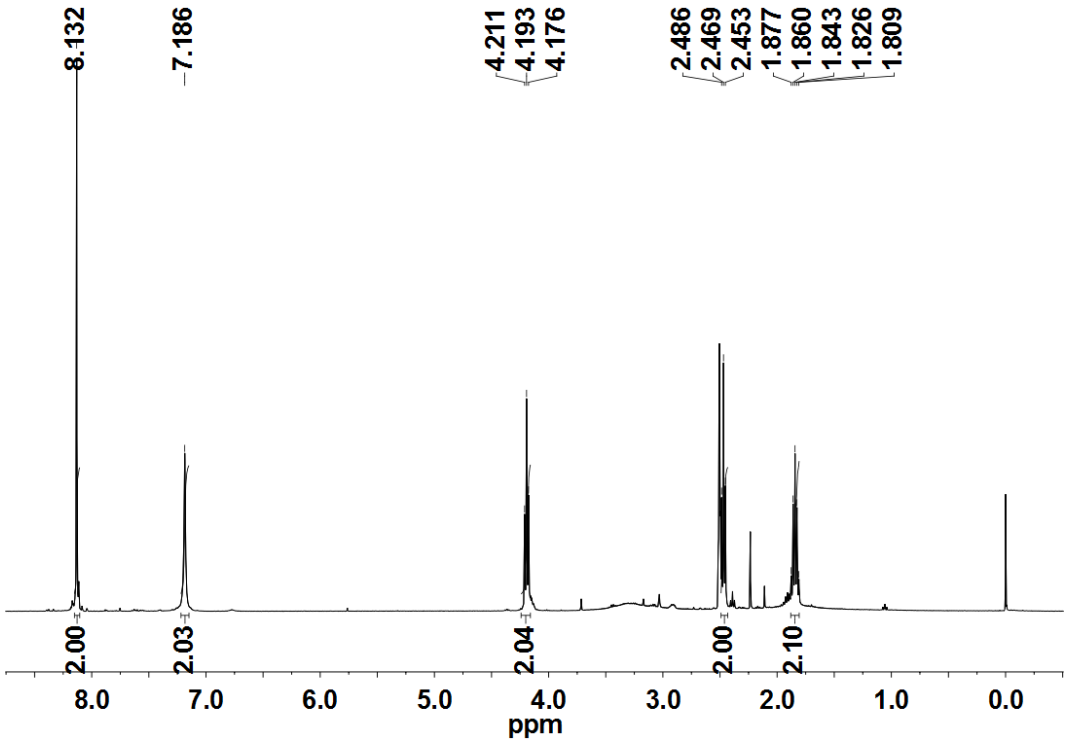


Fig. S8 ^{1}H NMR spectra of **5** in DMSO-d6

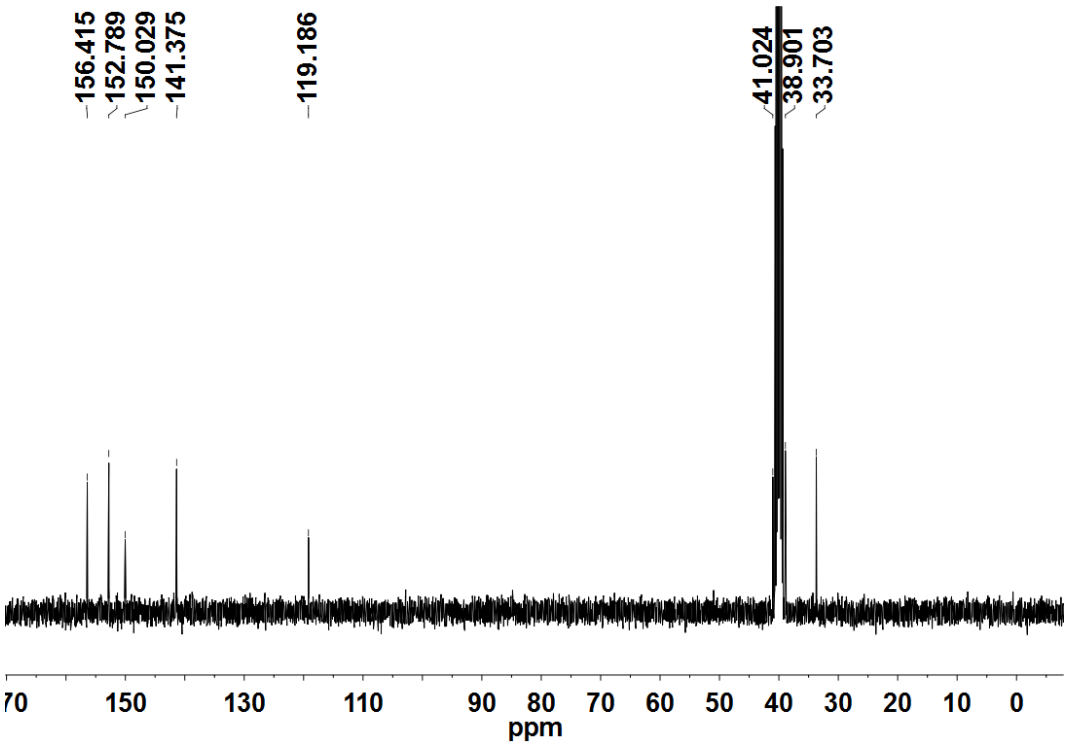


Fig. S9 ^{13}C NMR spectra of **5** in DMSO-d6

Display Report

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Sample Name		Instrument	apex-Ultra
Comment			

Acquisition Parameter

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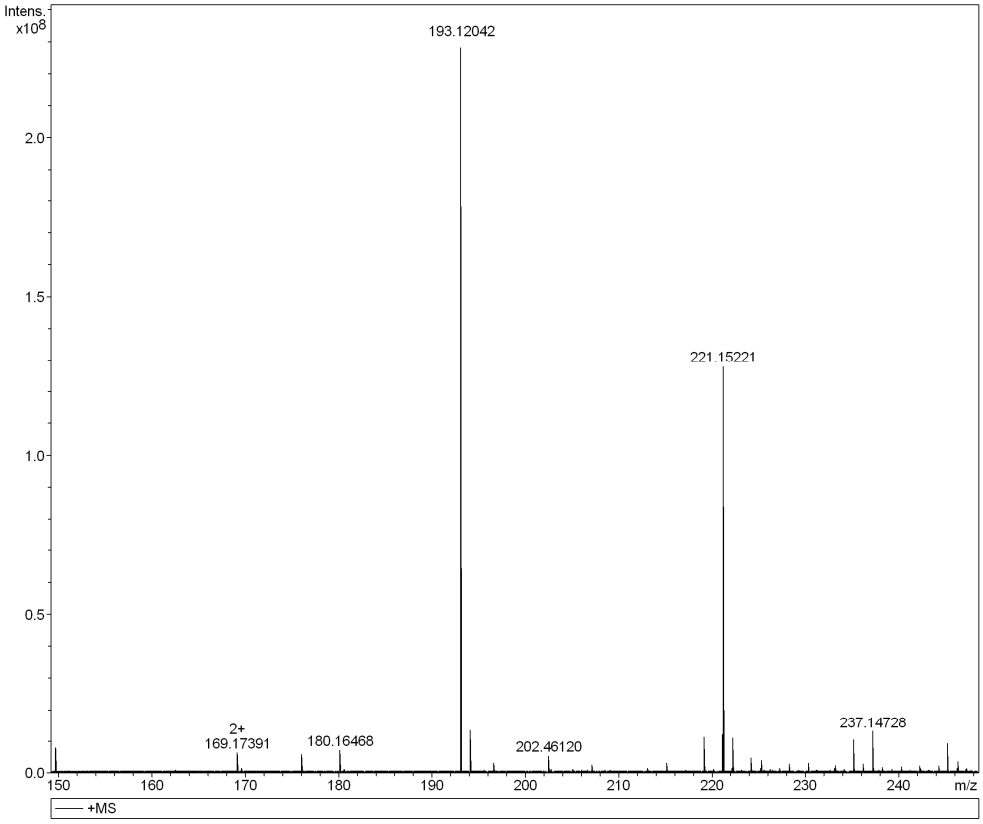

Bruker Compass DataAnalysis 4.0 printed: 11/3/2011 08:23:47 Page 1 of 2

Fig.S10 HR-MS spectra of **5**

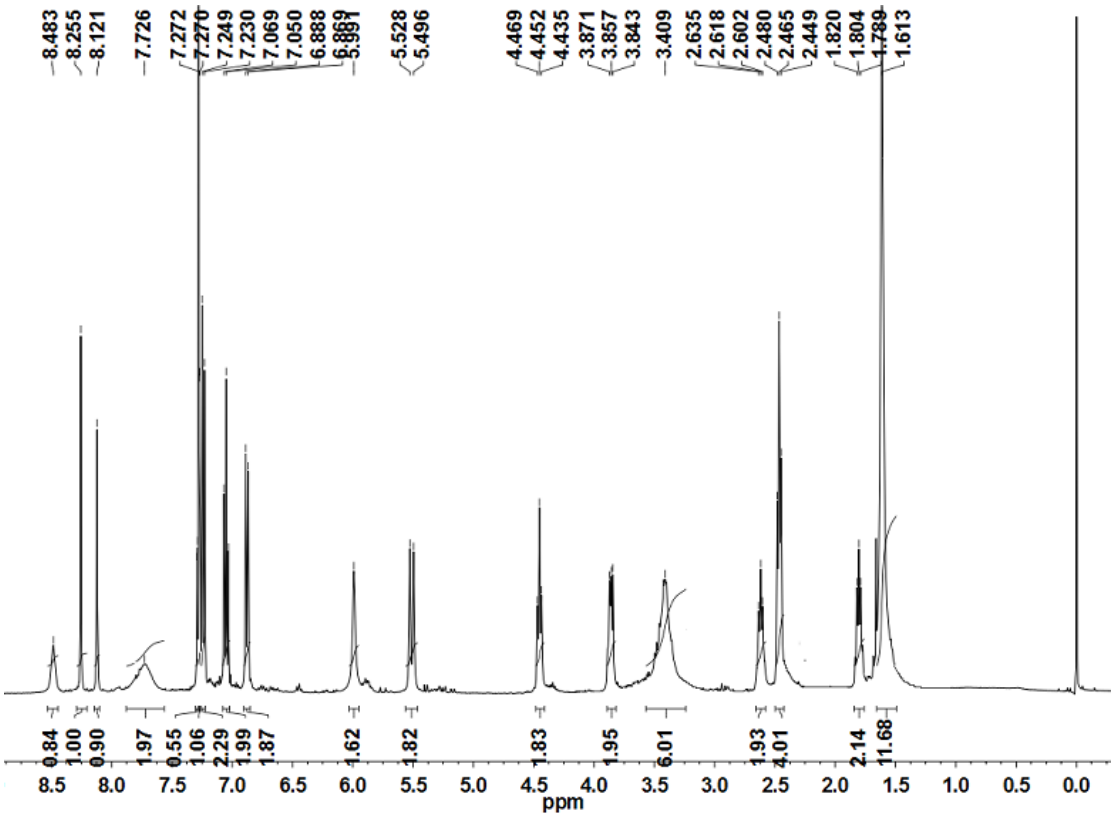

Fig. S11 ^{1}H NMR spectra of **1** in $CDCl_3$

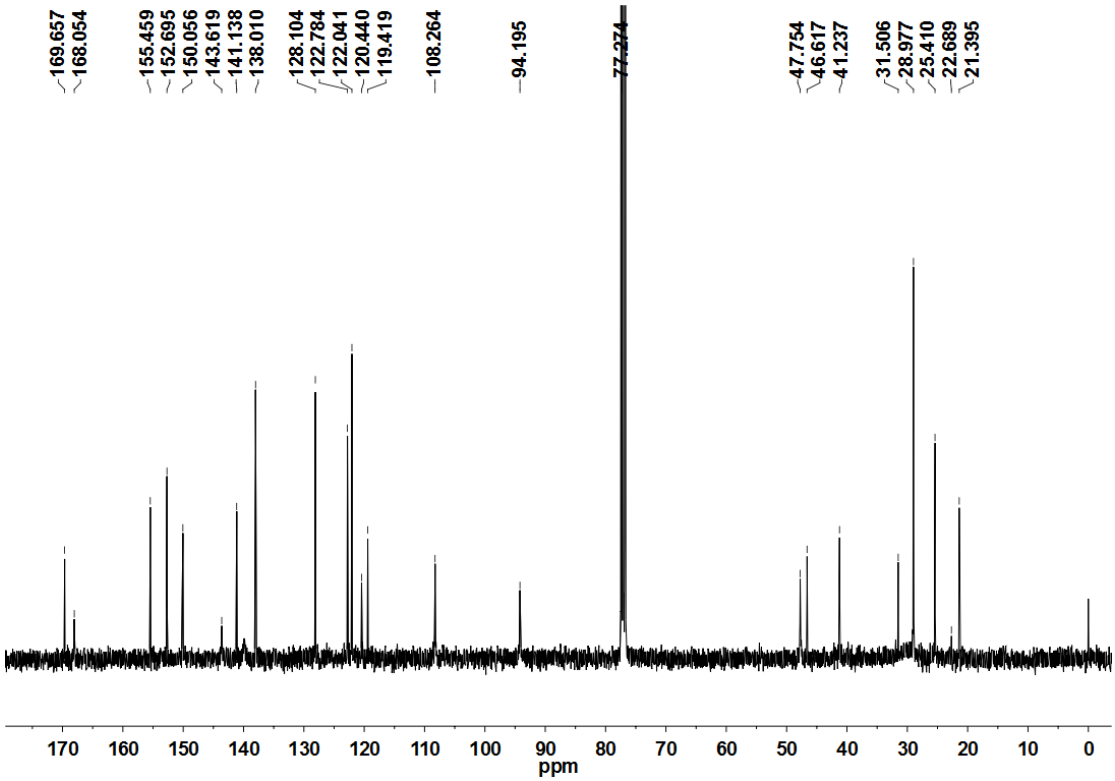

Fig. S12 ^{13}C NMR spectra of **1** in $CDCl_3$

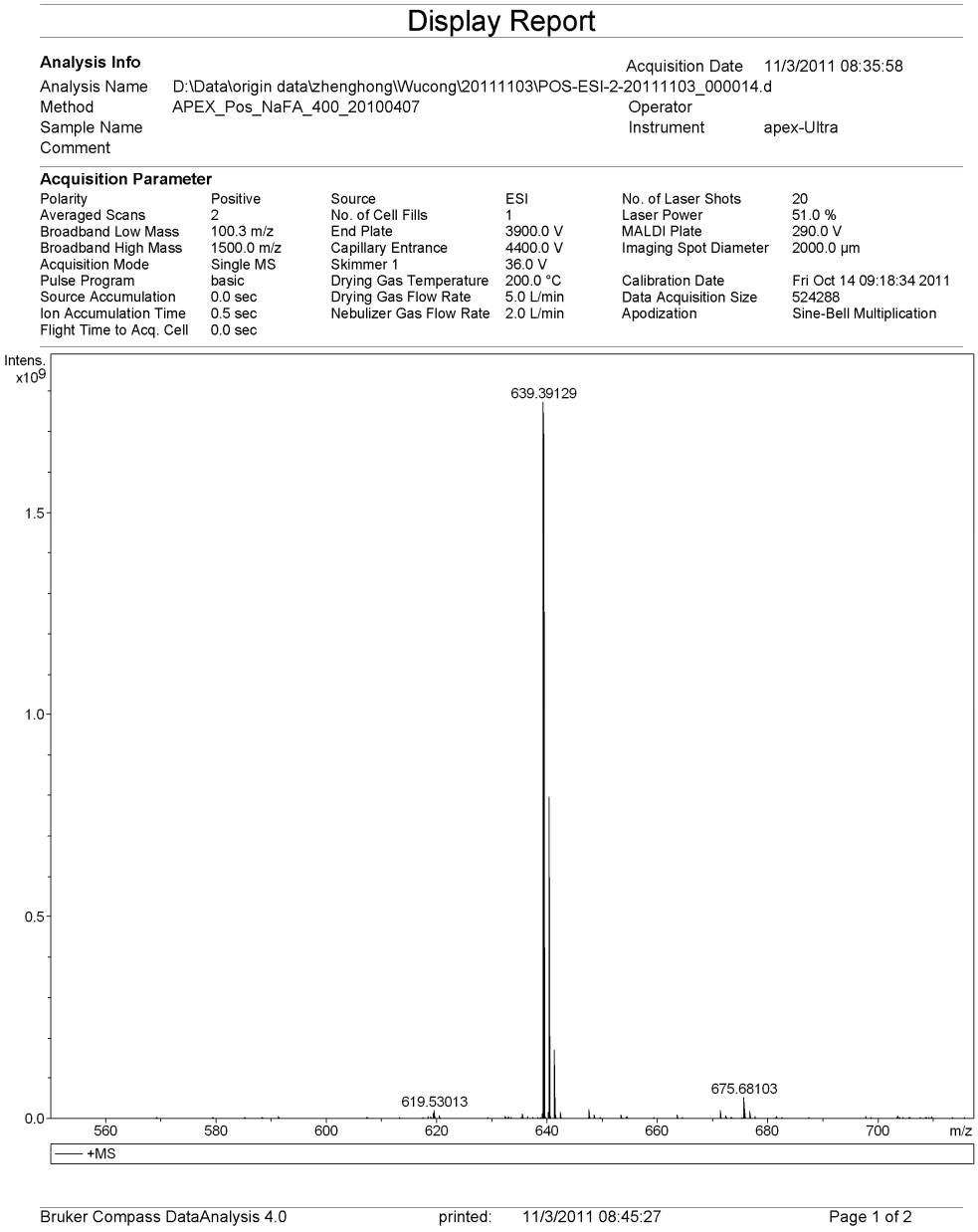

Fig. S13 HR-MS spectra of **1**

References:

S1. T. Gorecki, G. Patonay and L. Strekowski, *J. Heterocyclic. Chem.*, 1996, **33**: 1871-1876.

S2. L. Yao, B.T. Smith and J. Aube, *J. Org. Chem.*, 2004, **69**: 1720-1722.