Electronic Supplementary Material

A turn-on fluorescent chemosensor based on acylhydrazone for sensing of Mg^{2+} with low detection limit

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1. General methods

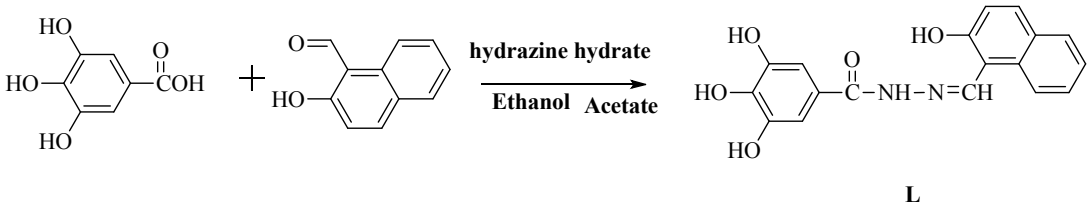
Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury–400BB at 400 MHz spectra. ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. Photoluminescence spectra were performed on a Shimadzu RF–5301 fluorescence spectrophotometer. Melting points were measured on an X–4 digital melting-point apparatus. The infrared spectra were performed on a Digilab FTS–3000 FT–IR spectrophotometer.

All fluorescence spectroscopy was carried out just after the addition of perchlorate salts in DMSO/H_2O (7:3, v/v, 0.01 M HEPES, pH = 8.5) solution, while keeping the ligand concentration constant (2.0×10^{-5} M) on a Shimadzu RF-5301spectrometer. The solution of anions were prepared from the perchlorate salts (Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}). The excitation wavelength was 378 nm

For ^{1}H NMR titrations, the sensor of stock solutions was prepared in DMSO–d_6, the Mg^{2+} was prepared in distilled D_2O. Aliquots of the two solutions were mixed directly in NMR tubes

2. Synthesis of sensor **L**

3, 4, 5-trihydroxybenzoic acid (0.34 g, 2 mmol)and hydrazine hydrate(0.98 g, 2 mmol) were dissolved in 10 mL of ethanol under reflux for 4 h at 80℃. And add 2-hydroxy-1-napthaldehyde (0.344g, 2 mmol) into this solution. The solution was stirred under reflux for 8 h at 80℃. After cooling to room temperature, the yellow precipitate was filtered, washed three times with absolute ethanol, and recrystallized with absolute ethanol to get yellow powder product of **L** in 73.4% yield (m.p. 275-278℃). Anal. Calc. for $C_{18}H_{14}N_2O_5$: C, 63.90; H, 4.17; N, 8.28; O, 23.65 %. Found: C, 63.78; H, 4.06; N, 8.32; O, 23.84. ^{1}H NMR (DMSO-d_6, 400MHz) δ: 12.96 (s, 1H, -OH), 11.92 (s, 1H, -NH), 9.49 (s, 1H, Ar-OH), 9.29 (s, 2H, Ar-OH), 9.0 (s, 1H, -CH), 8.14 (d, 1H), 7.92 (t, 2H), 7.62 (t, 1H), 7.42 (t, 1H), 7.24 (d, 1H), 7.0 (s, 2H); ^{13}C-NMR (DMSO-d_6, 100MHz) δ: 167.57, 162.84, 110.77, 142.42, 137.40, 136.63, 133.98, 132.79, 132.67, 128.49, 127.55, 125.37, 123.96, 113.60, 112.20. IR (KBr,) *v*: 1545 cm^{-1} (CH＝N), 1622 cm^{-1} (C＝O), 3391 cm^{-1} (OH). ESI-MS m/z (M+H) $^+$: calcd. 339.09; found, 339.08.



L

Scheme S1 Synthesis of receptor **L**.

3. ^{1}H NMR spectra of **L**.

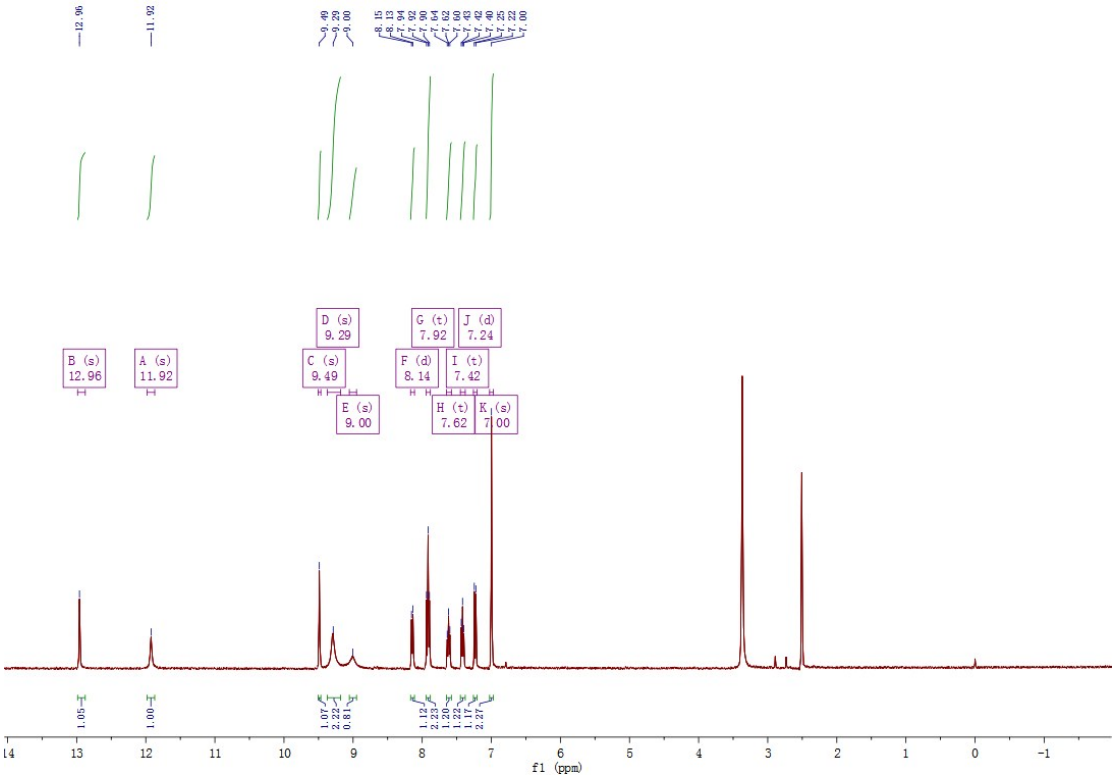


Fig. S1 ^{1}H NMR spectra of **L**.

4. ESI-MS spectra of **L**

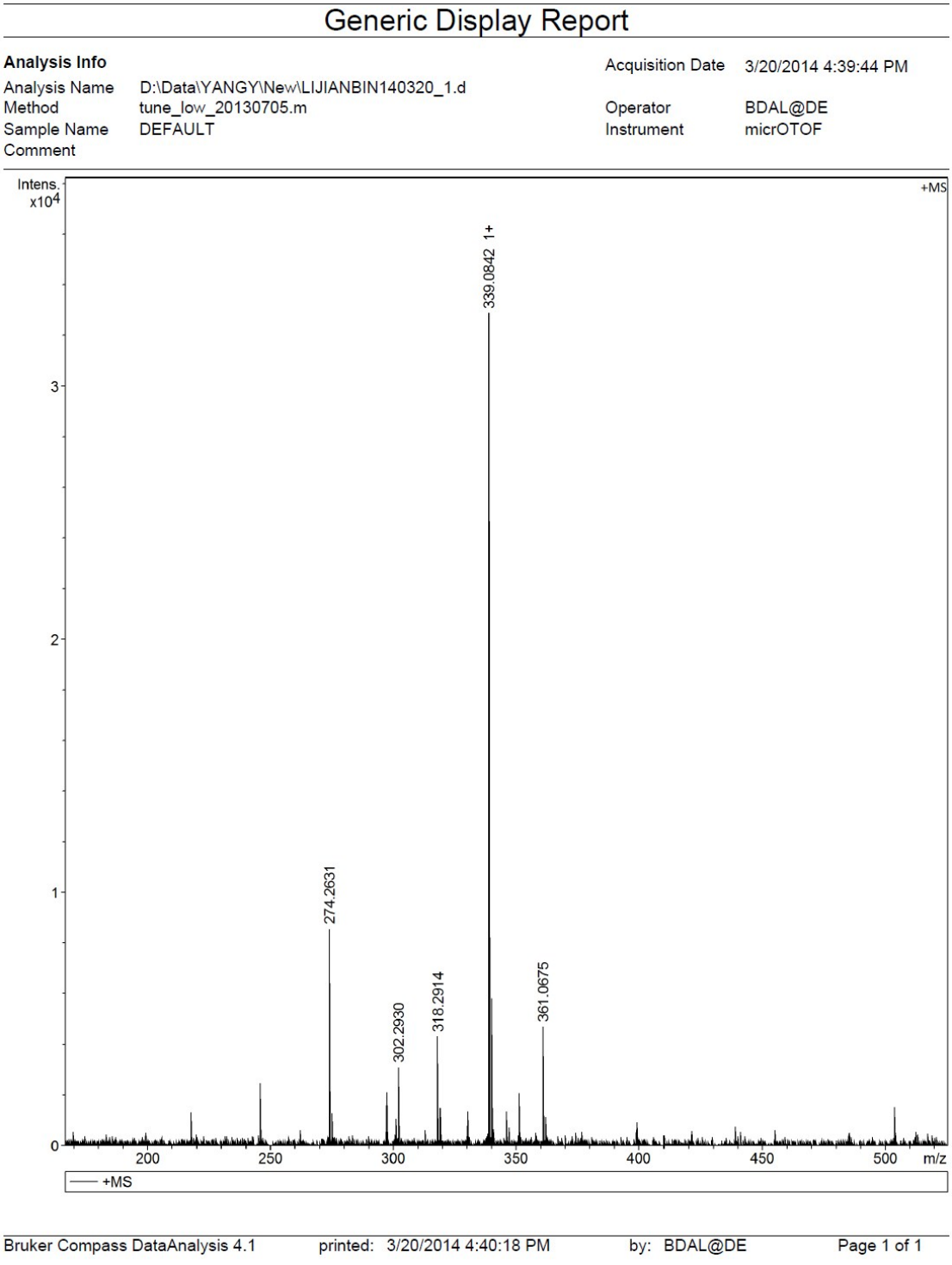


Fig. S2 ESI-MS spectra of **L**.

5. The fluorescence emission of Mn (II)

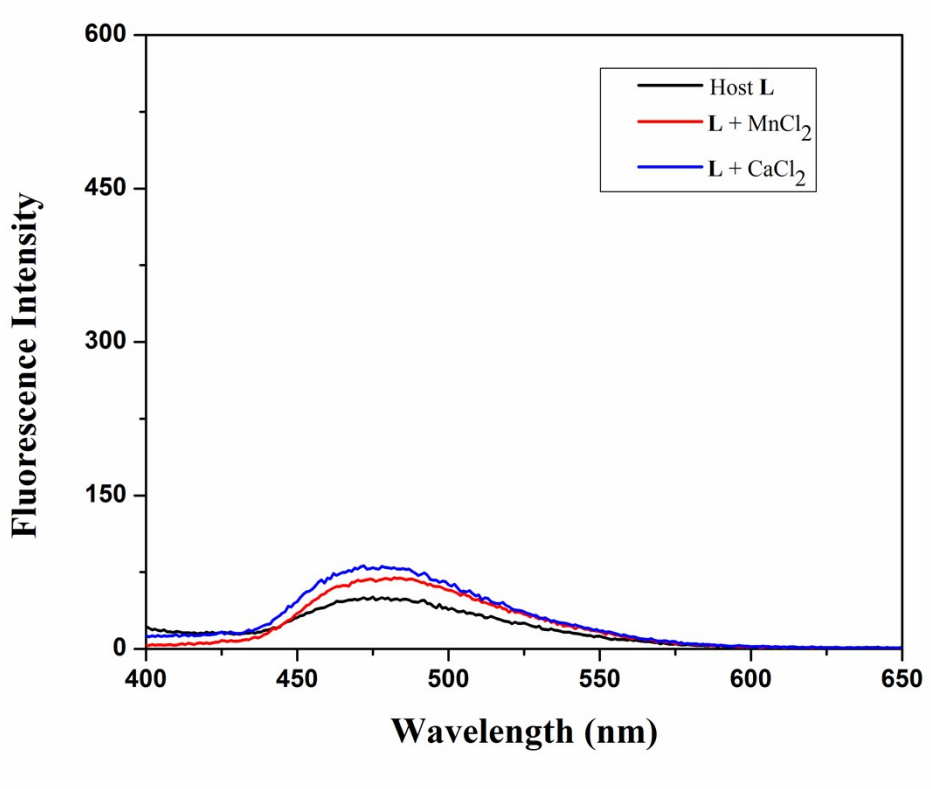


Fig. S3 Fluorescence spectra response of **L** (2.0×10^{-5} M) in DMSO/H_2O (7:3, v/v, 0.01 M HEPES, pH = 8.5) upon addition of 20 equiv. of Mn^{2+} and Ca^{2+}.

6. Absorption spectroscopy

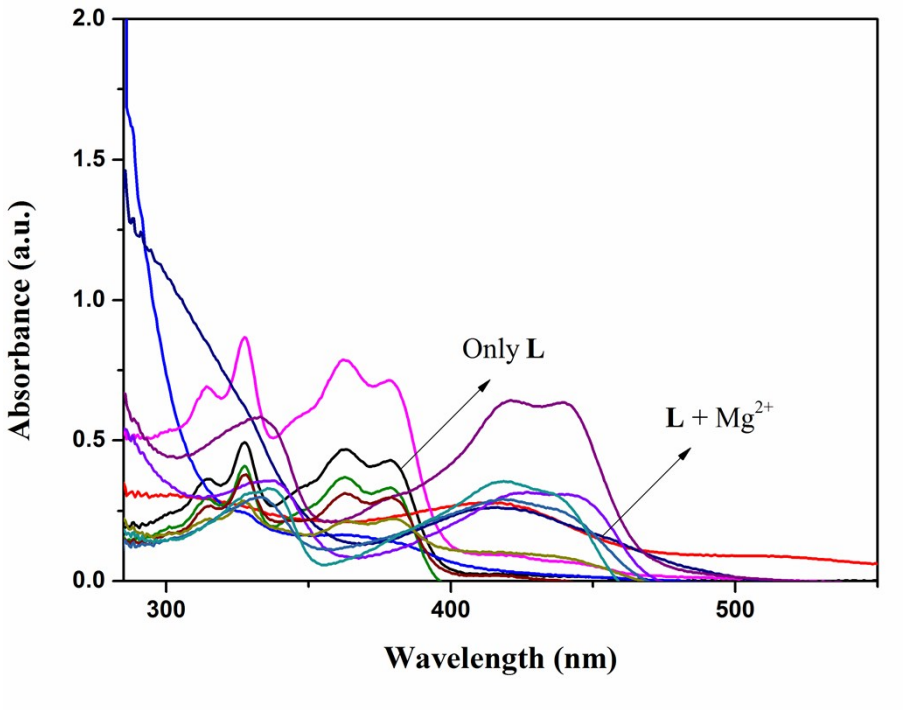


Fig. S4 The absorption spectra of **L** (2×10^{-5} M) and in the presence of various metal ions.

7. pH-dependence

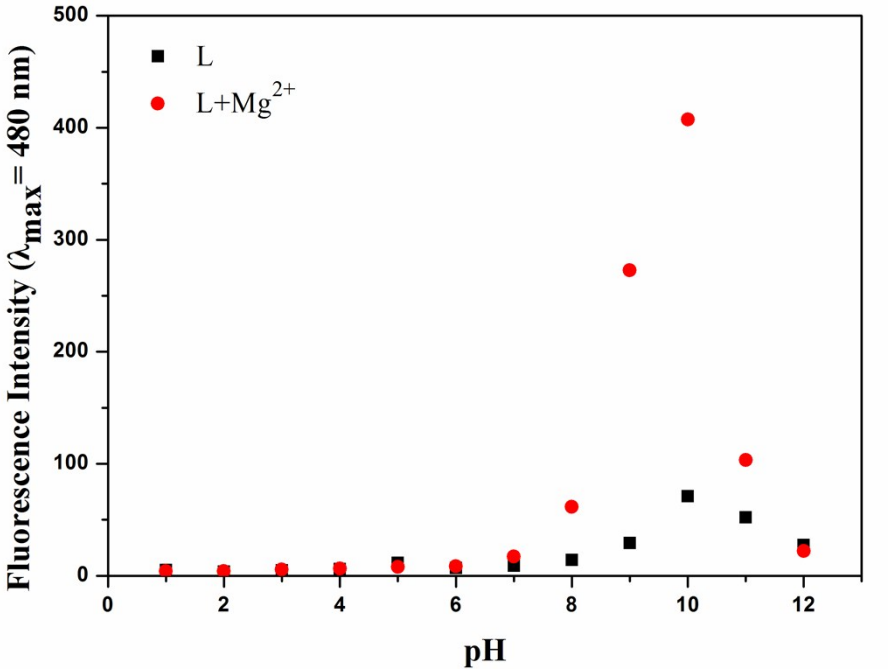


Fig. S5 pH-dependence of **L** (2.0×10^{-5} M) and **L** + Mg^{2+} in DMSO/H_2O (7:3, v/v, 0.01 M HEPES, pH = 8.5) system.

8. IR spectra of **L** and **L**-Mg^{2+}

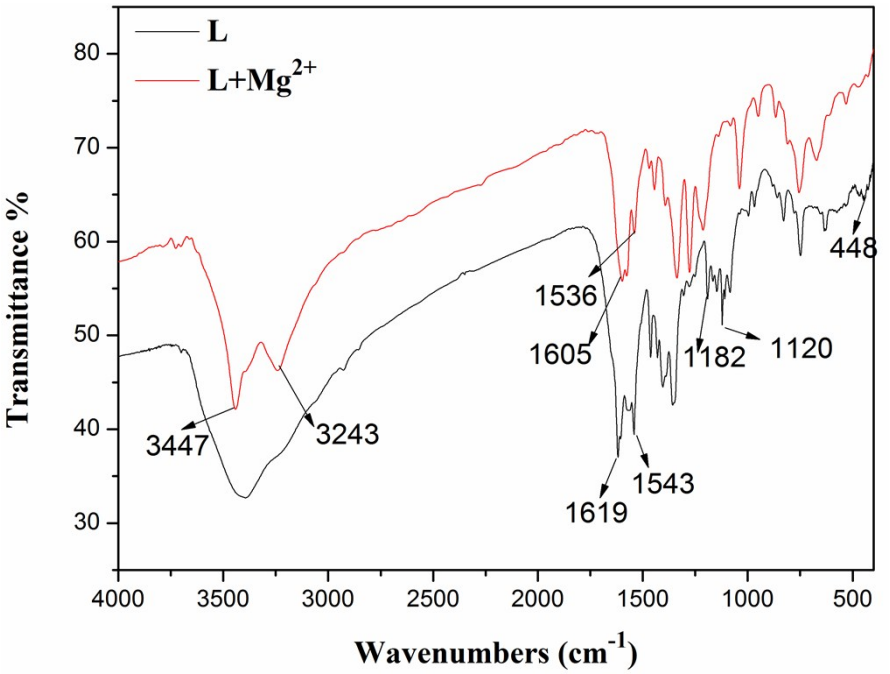


Fig. S6 IR spectra of **L** and **L-Mg^{2+}**.

9. ESI-MS spectra of **L**-Mg^{2+}

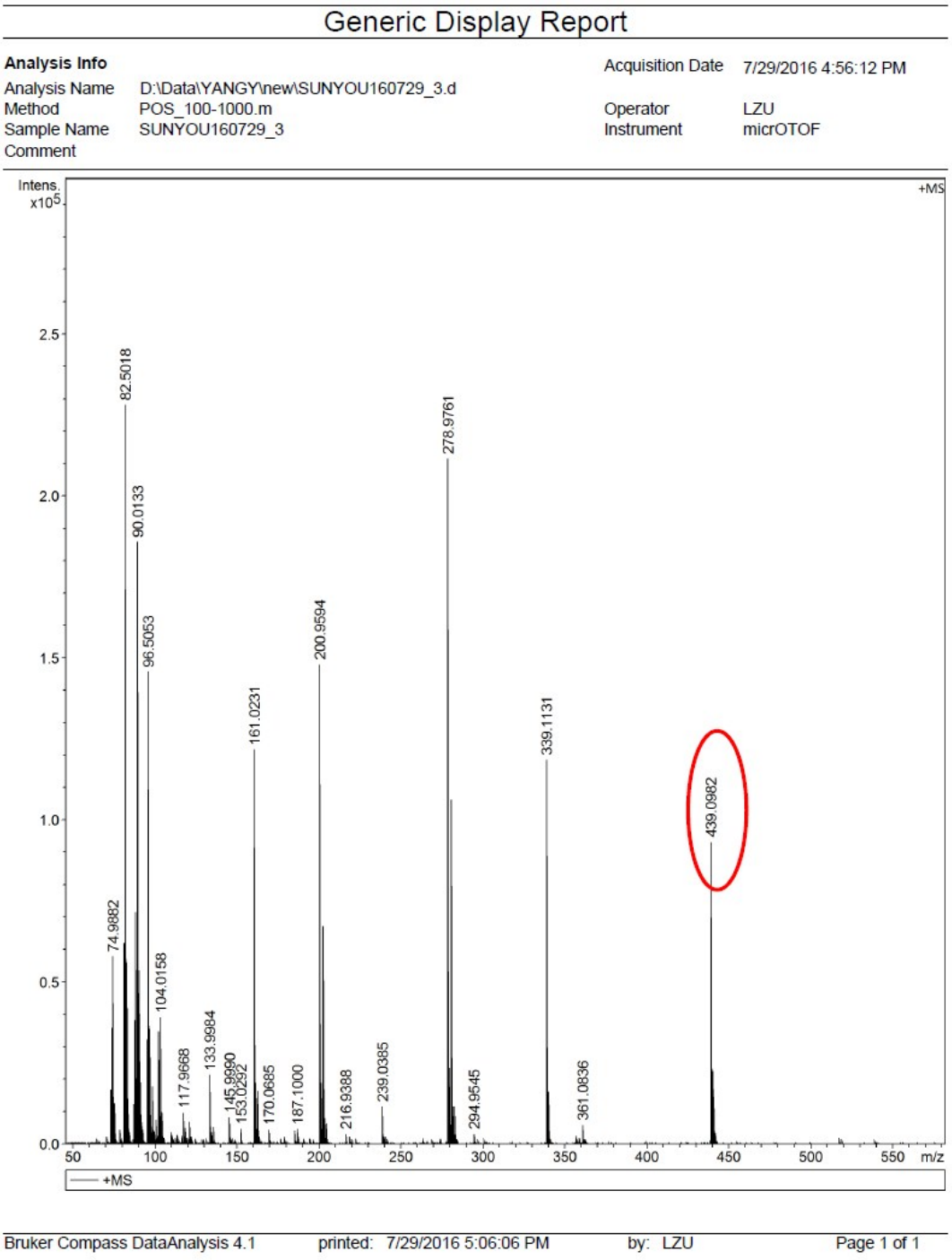


Fig. S7 ESI-MS spectra of **L**-Mg^{2+}.

10. ^{13}C NMR spectra of **L**

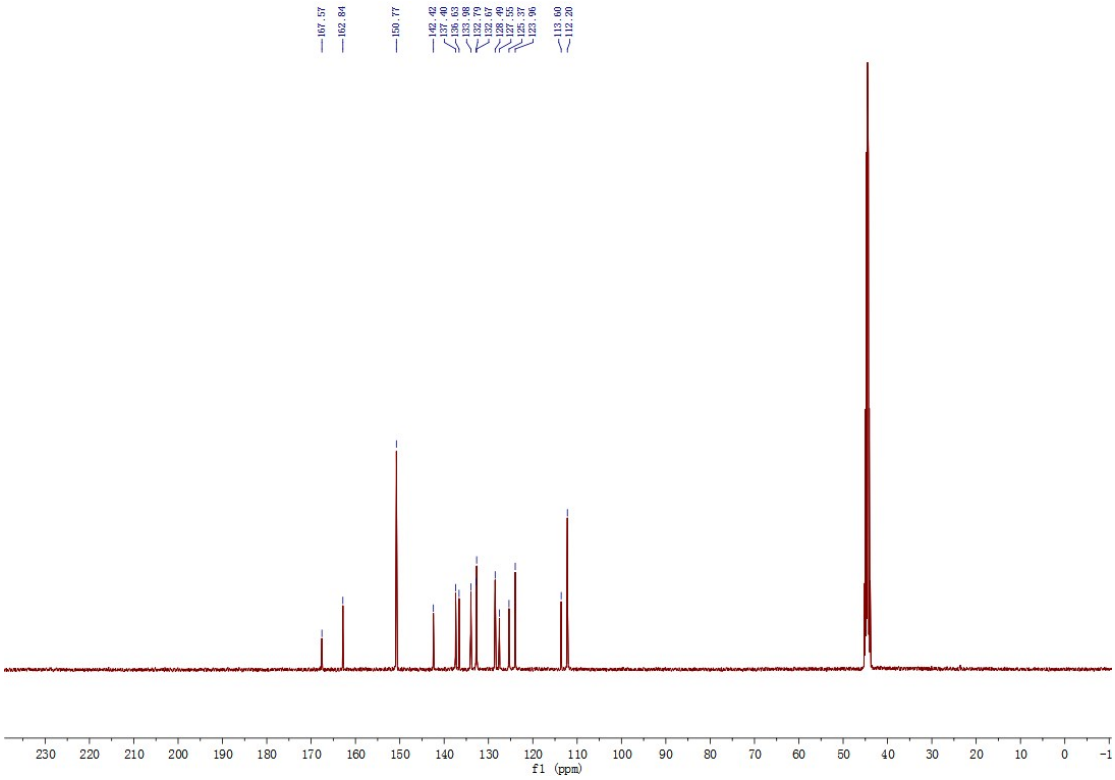


Fig. S8 ^{13}C NMR spectra of **L**.

11. Determination of the detection limit

The limit of detection (LOD) of **L** for Mg^{2+} was obtained by $3S_B/S$, where S_B is the standard deviation of the blank measurements and S is the slope of the calibration curve.