Supporting Information For

A Bimodal Multianalyte Simple Molecule Chemosensor for Mg^{2+}, Zn^{2+}, and Co^{2+}

Yiran Li, Jiang Wu, Xiaojie Jin, Jianwei Wang, Shuai Han, Wenyu Wu, Jun Xu, Weisheng Liu, Xiaojun Yao, and Yu Tang*

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, P. R. China

Fax: (+86) 931-891-2582; E-mail: tangyu@lzu.edu.cn

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to an acetonitrile solution of **HL** (50 μM) in the presence of Mg^{2+} (25 μM). λ_{em} = 546 nm, [Metal] = 100 μM, [Ca^{2+}] = 500 μM, [K^+] = 500 μM, [Na^+] = 500 μM, [Al^{3+}] = 500 μM.

Fig. S5 Competition experiments. The black bars (A) represent the addition of an excess of metal ions to an acetonitrile/Tris-HCl (50 mM, pH 7.40) (9:1, v/v) solution of **HL**(50 μM), and the red bars (B) represent the subsequent addition of 50 μM Zn^{2+} ions to the foregoing solution. λ_{em} = 558 nm.

Fig. S6 The linear dynamic response of **HL** for Zn^{2+} and the determination of the detection limit (LOD) for Zn^{2+} in an acetonitrile/Tris-HCl (50 mM, pH 7.40) (9:1, v/v) solution.

Fig. S7 Absorbance Job's plot for **HL** with Co^{2+} in an acetonitrile/Tris-HCl (50 mM, pH 7.40) (9:1, v/v) solution.

Fig. S8 ESI-MS spectrum of **CoL_2** complex.

Fig. S9 The linear fitting (absorbance at 476 nm) of **CoL_2**.

Fig. S10 Competition experiments (absorbance at 476 nm). The black bars (A) represent the addition of an excess of metal ions to an acetonitrile/Tris-HCl (50 mM, pH 7.40) (1:1, v/v) solution of **HL**(50 μM), and the chromatic bars (B) represent the subsequent addition of 25 μM Co^{2+} ions to the foregoing solution.

Fig. S11 The different metal salts toward **HL** for sensing Mg^{2+}, Zn^{2+}, and Co^{2+}.

Fig. S12 ^{1}H-NMR spectrum of **HL** (d_6-DMSO) at room temperature.

Fig. S13 ^{13}C-NMR spectrum of **HL** (d_6-DMSO) at room temperature.

References

Determination of binding constants for Mg^{2+} and Zn^{2+}.

The association constant and stoichiometry for the formation of the complex were evaluated using the Benesi-Hildebrand (B-H) plot [Eq. (1)].[1]

$$\frac{1}{F - F_0} = \frac{1}{K^{0.5}(F_{\max} - F_0)[\mathrm{M}^{n+}]^{0.5}} + \frac{1}{F_{\max} - F_0} \qquad (1)$$

Binding stoichiometry for the complex formation is confirmed from experimental data. In the case of evaluation of the binding constant from the results of fluorescence titration, a modified B-H equation [Eq. (1)] is used, where F_0, $F_{\max}$, and F represent the emission intensity of **HL**, the maximum emission intensity observed in the presence of Mg^{2+} or Zn^{2+}, and intensity at a certain concentration of the metal ion, respectively. K is the association constant (M^{-2}) and was determined from the slope of the linear plot, and $[M^{n+}]$ is the concentration of the Mg^{2+} or Zn^{2+} ion added during titration studies.

Determination of binding constants for Co^{2+}.[2]

Assuming a 1: n stoichiometry for interaction between L and Co^{2+}, the equilibrium is given by the following equation:

$$\mathrm{L} + n\mathrm{Co}^{2+} \xrightleftharpoons{K} \mathrm{LCo}_n^{2+} \qquad (2)$$

The association constant, K, is therefore expressed as:

$$K = \frac{[\mathrm{LCo}_n^{2+}]}{[\mathrm{L}][\mathrm{Co}^{2+}]^n} = \frac{[\mathrm{LCo}_n^{2+}]}{([\mathrm{L}]_0 - [\mathrm{LCo}_n^{2+}])([\mathrm{Co}^{2+}]_0 - n[\mathrm{LCo}_n^{2+}])^n} \qquad (3)$$

$[LCo^{2+}{}_n]$, $[L]$, and $[Co^{2+}]$ represent the equilibrium concentrations of the complex, free L, and free Co^{2+}, respectively. $[L]_0$ and $[Co^{2+}]_0$ are the initial concentrations of L and Co^{2+}, respectively. If $[Co^{2+}]_0 >> [LCo^{2+}{}_n]$, the equation 3 can be simplified as follows:

$$K = \frac{[\mathrm{LCo}_n^{2+}]}{([\mathrm{L}]_0 - [\mathrm{LCo}_n^{2+}])([\mathrm{Co}^{2+}]_0)^n} \qquad (4)$$

Then it can be transformed to:

$$K[\mathrm{Co}^{2+}]_0^n = \frac{[\mathrm{LCo}_n^{2+}]}{[\mathrm{L}]_0 - [\mathrm{LCo}_n^{2+}]} \qquad (5)$$

Absorbance intensity is given by following equations:

$$\frac{A-A_{\min}}{A_{\max}-A}=\frac{[\mathrm{LCo}_n^{2+}]}{[\mathrm{LCo}_n^{2+}]_{\max}-[\mathrm{LCo}_n^{2+}]}=\frac{[\mathrm{LCo}_n^{2+}]}{[\mathrm{L}]_0-[\mathrm{LCo}_n^{2+}]} \qquad (6)$$

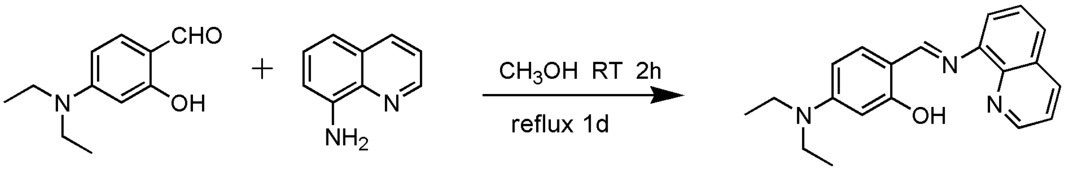
$A_{\min}$ is the absorbance intensity of L without cations, A is the absorbance intensity of L obtained with Co^{2+}, $A_{\max}$ is the absorbance intensity of L in the presence of excess amount of Co^{2+}. In the presence of excess amount of Co^{2+}, $[LCo^{2+}{}_n]_{\max}$ is almost equal to $[L]_0$. Using equations 5 and 6, the following equation is given:

$$\frac{A-A_{\min}}{A_{\max}-A}=K[\mathrm{Co}^{2+}]_0^n \qquad (7)$$

$$\lg\frac{A-A_{\min}}{A_{\max}-A}=\lg K+n\lg[\mathrm{Co}^{2+}]_0 \qquad (8)$$

When assuming the 2:1 stoichiometry (n = 0.5), equation 1 is obtained.

$$\lg\frac{A-A_{\min}}{A_{\max}-A}=\lg K+0.5\lg[\mathrm{Co}^{2+}] \qquad (1)$$



HL

Scheme S1 Synthetic route to **HL**

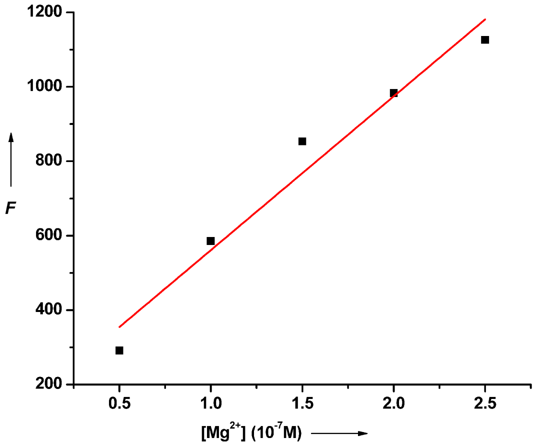


Fig. S1 The linear dynamic response of **HL** for Mg^{2+} and the determination of the detection limit (LOD) for Mg^{2+} in CH_3CN.

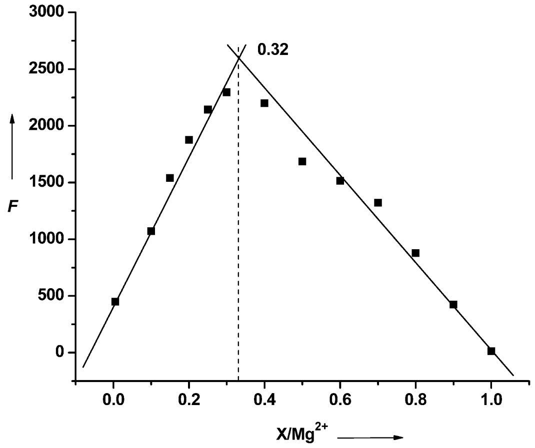


Fig. S2 Fluorescence Job's plot for **HL** with Mg^{2+} in CH_3CN. The total [**HL**] + [Mg^{2+}] = 100 μM.

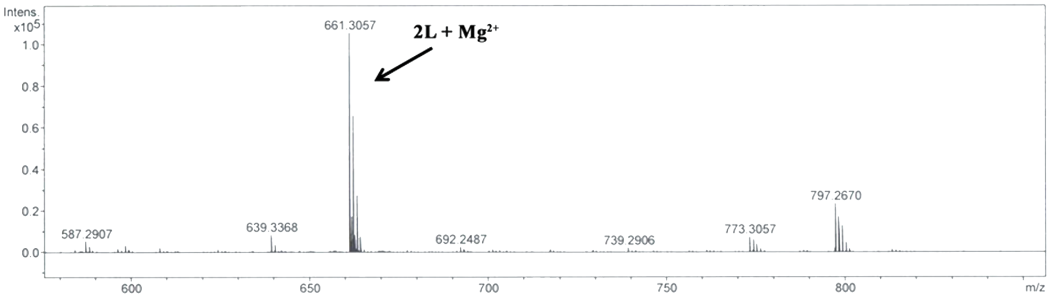


Fig. S3 ESI-MS spectrum of **MgL$_2$** complex.

ESI-MS exhibited the formation of a complex between two deprotonated **HL** and an Mg^{2+} [m/z 661.3057 (2**L**+Mg^{2+}); calcd for $C_{40}H_{40}MgN_6O_2$ m/z 661.09].

The physiologically important cations, such as K$^+$, Na$^+$, Ca^{2+}, and Al^{3+}, which exist at high concentrations in living cells, have negligible interference for forming the Mg-complex. In addition, Cd^{2+} and Hg^{2+} quenched the fluorescence intensity due to the heavy metal effect. Even though some biologically relevant metal ions, like Zn^{2+}, Cu^{2+} and so on, showed various extend responses in the fluorescence intensity, these cations would have little influence, since they exist at low concentrations[3] compared to Mg^{2+}. These results suggested **HL** could be a fluorescence sensor for Mg^{2+} without interference of other physiologically important cations.

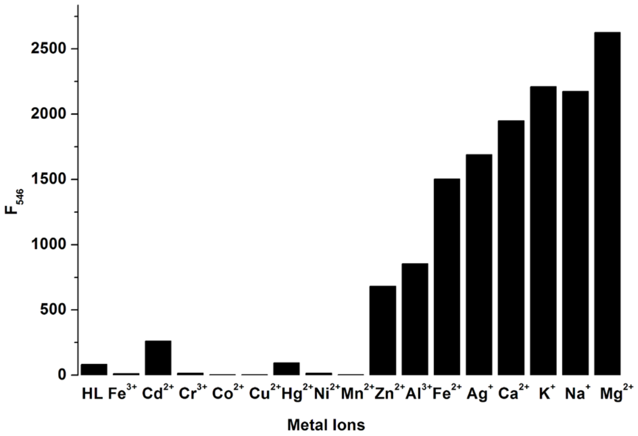


Fig. S4 Competition experiments. The black bars represent the addition of an excess of metal ions to an acetonitrile solution of **HL** (50 μM) in the presence of Mg^{2+} (25 μM). λ_{em} = 546 nm, [Metal] = 100 μM, [Ca^{2+}] = 500 μM, [K$^+$] = 500 μM, [Na$^+$] = 500 μM, [Al^{3+}] = 500 μM.

Via monitoring the fluorescence intensity at 558 nm, zinc ions could be distinguished from other metal ions, such as: Na^+, K^+, Ag^+, Fe^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, Fe^{3+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, and Mn^{2+}, indicating excellent selectivity for Zn^{2+} over these competing cations. But Ni^{2+}, Cu^{2+} and Co^{2+} had some extent the influence on the F_{558nm} value of the zinc complex, which indicated that Ni^{2+}, Cu^{2+}, and Co^{2+} could form complexes with **HL** and thus quenched the fluorescence. There were many other Zn^{2+} sensors, which had exhibited similarly depressed responses due to the competition from these ions. However, these free cations would have little influence in vivo because they exist at a very low concentration.[4]

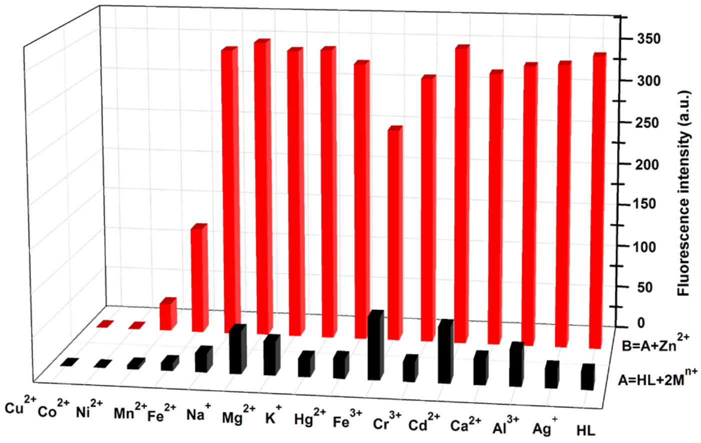


Fig. S5 Competition experiments. The black bars (A) represent the addition of an excess of metal ions to an acetonitrile/Tris-HCl (50 mM, pH 7.40) (9:1, v/v) solution of **HL**(50 μM), and the red bars (B) represent the subsequent addition of 50 μM Zn^{2+} ions to the foregoing solution. λ_{em} = 558 nm.

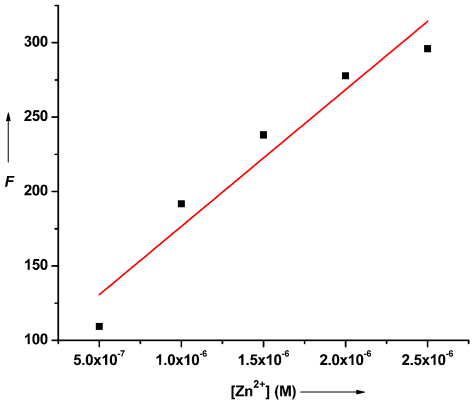


Fig. S6 The linear dynamic response of **HL** for Zn^{2+} and the determination of the detection limit (LOD) for Zn^{2+} in an acetonitrile/Tris-HCl (50 mM, pH 7.40) (9:1, v/v) solution.

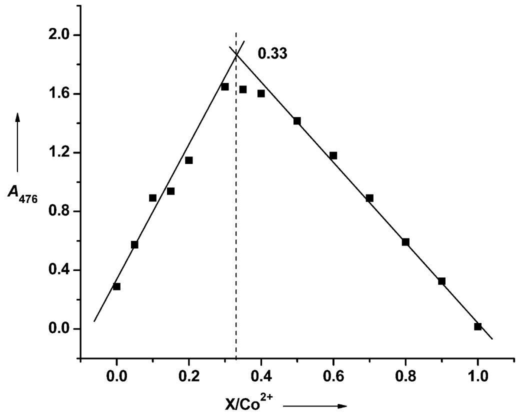


Fig. S7 Absorbance Job's plot for **HL** with Co^{2+} in an acetonitrile/Tris-HCl (50 mM, pH 7.40) (9:1, v/v) solution. The total [**HL**] + [Co^{2+}] = 100 μM.

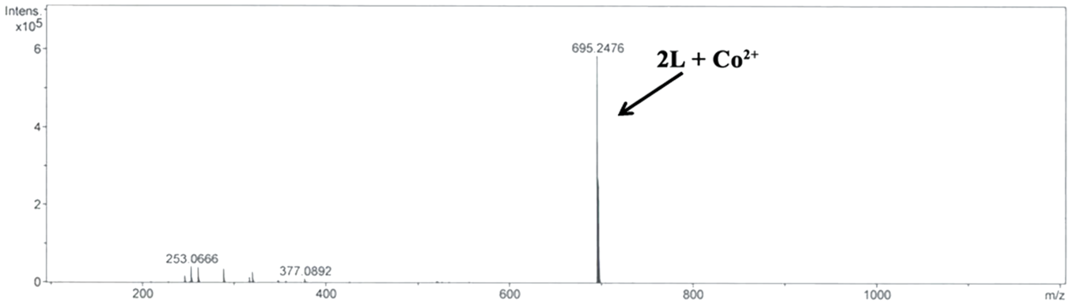


Fig. S8 ESI-MS spectrum of **CoL_2** complex.

ESI-MS exhibited the formation of a complex between two deprotonated **HL** and a Co^{2+} [m/z 695.2476 (2L+Co^{2+}); calcd for $C_{40}H_{40}CoN_6O_2$ m/z 695.25].

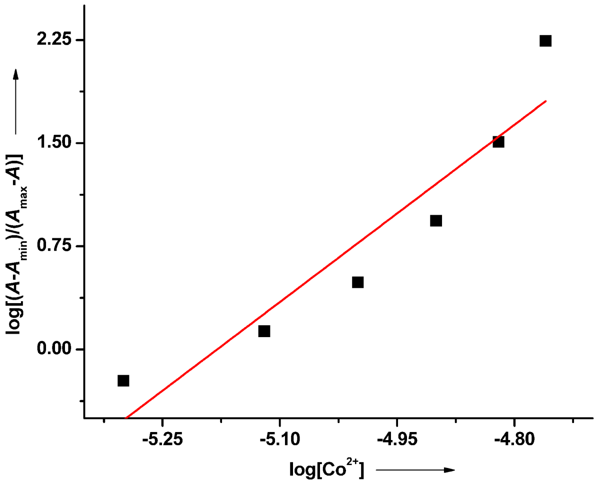


Fig. S9 The linear fitting (absorbance at 476 nm) of complexes. $\log[(A - A_{\min})/(A_{\max} - A)] = \log K + \log[Co^{2+}]$. K is the stability constant, $A_{\min}$ is absorbance of **HL** without any cations, A is absorbance of **HL** obtained with Co^{2+}, $A_{\max}$ is absorbance of **HL** in the presence of excess amount of Co^{2+}.

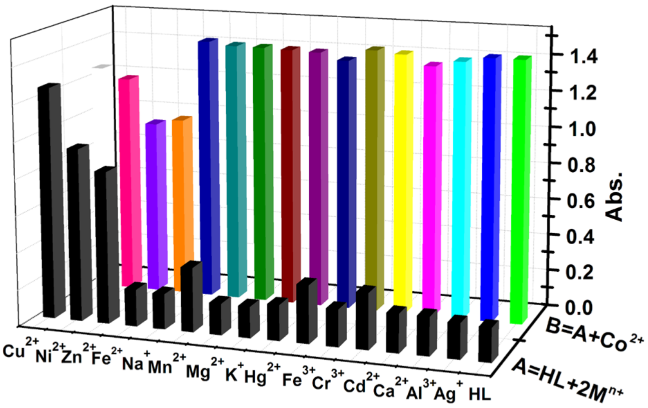


Fig. S10 Competition experiments (absorbance at 476 nm). The brown bars (A) represent the addition of an excess of metal ions to an acetonitrile/Tris-HCl (50 mM, pH 7.40) (1:1, v/v) solution of **HL**(50 µM), and the chromatic bars (B) represent the subsequent addition of 25 µM Co^{2+} ions to the foregoing solution.

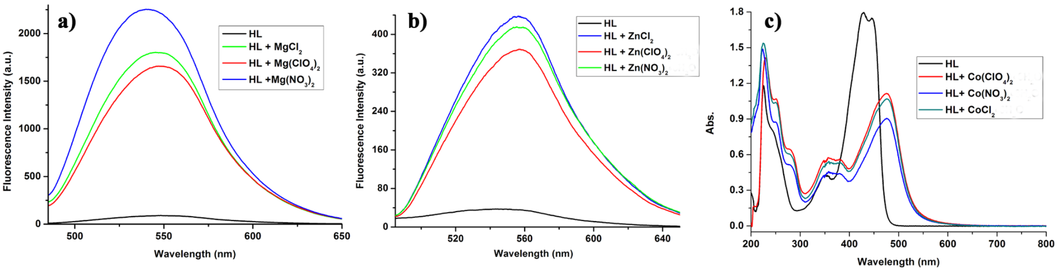


Fig. S11 The different metal salts toward **HL** for sensing Mg^{2+}, Zn^{2+}, and Co^{2+}. (a) Fluorescent (λ_{ex} = 470 nm) spectral changes of **HL** (1.0 µM) upon titration with $MgCl_2$, $Mg(ClO_4)_2$, and $Mg(NO_3)_2$ in CH_3CN. (b) Fluorescence (λ_{ex} = 470 nm) responses of **HL** (50 µM) in the presence of $ZnCl_2$, $Zn(ClO_4)_2$, and $Zn(NO_3)_2$ in an acetonitrile/Tris-HCl (50 mM, pH 7.40) (9:1, v/v) solution. (c) UV/Vis absorption spectra of **HL** (50 µM) in the presence of $CoCl_2$, $Co(ClO_4)_2$, and $Co(NO_3)_2$ in an acetonitrile/Tris-HCl (50 mM, pH 7.40) (1:1, v/v) solution.

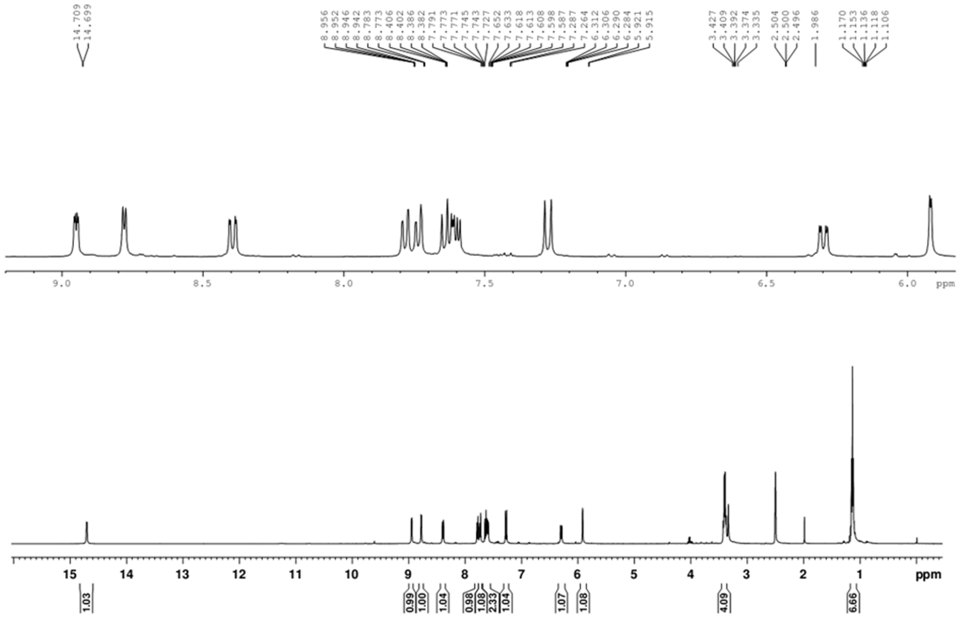


Fig. S12 ^{1}H-NMR spectrum of **HL** (d_6-DMSO) at room temperature.

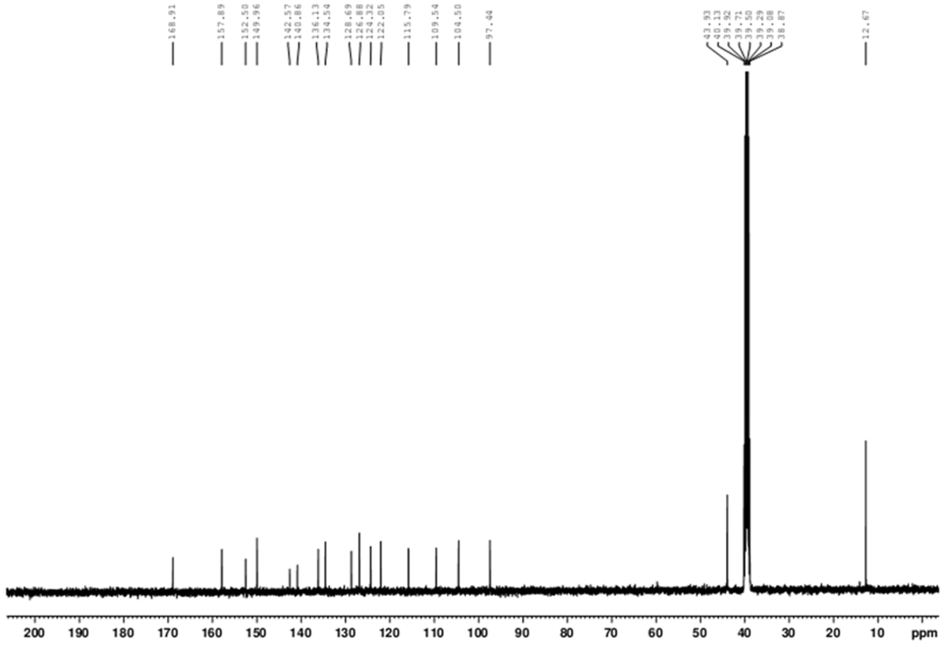


Fig. S13 ^{13}C-NMR spectrum of **HL** (d_6-DMSO) at room temperature.

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