Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

L-Proline Promoted Fluorescent Sensor for Mg^{2+} Detection in a Multicomponent Sensory System

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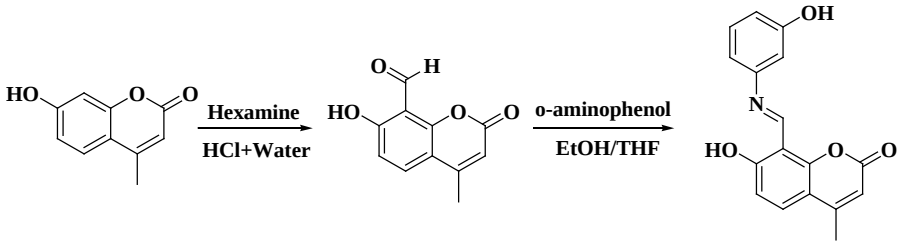
Contents:

ESI 1. Instrumentation and Materials

All solvents and reagents were commercially available and analytical-reagent-grade. THF was purified by distillation from sodium in the presence of benzophenone and Et_3N was newly distilled before using. NMR spectra were collected on a 300-Bruker spectrometer 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR and reported as parts per million (ppm) from the internal standard TMS. MS was determined on a Micromass GCT. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. Fluorescence spectra were obtained from an RF-5301PCspectrometer. Ultraviolet-visible (UV-vis) spectra were obtained using a Shimadzu UV-Vis-NIR spectrophotometer.

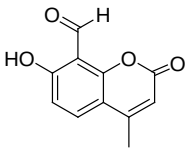
Each metal ion titration experiment was started with a 3.0 mL ligand with a known concentration (1.0×10^{-5} mol/L corresponding to host molecular in CH_3CN solution). $Mg(NO_3)_2$ salt and other various metal salts (nitrate, 1.0×10^{-3} mol/L, H_2O) were used for the titration. Ligand-metal complexes were produced by adding aliquots of a solution of the selected metal salt to a CH_3CN solution of the ligand.

ESI 2. Synthesis procedures of 8-formyl-7-hydroxy-4-methylcoumarin (2), host molecular



Scheme 1 Synthesis procedures of **Host** molecular

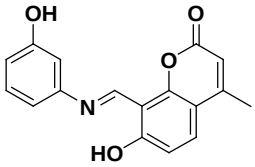
Synthesis of 8-formyl-7-hydroxy-4-methylcoumarin (2) [1]



8-Formyl-7-hydroxy-4-methylcoumarin was prepared according to the literature. [1] 7-Hydroxy-4-methylcoumarin (10g, 56.8mol) and hexamine (19.9g, 142mmol) in glacial acetic acid (90 mL) were heated for 6 h. Then 20% HCl (130 mL) was added in and the mixture was further heated for 40 min, after which the mixture was cooled and extracted with ether twice (50mL× 2). The combined organic layer was concentrated under reduced pressure to afford 8-formyl-7-hydroxy-4-methylcoumarin as light yellow powder. The crude product was recrystallized from ethanol (yield, 15%). m.p. 140-142°C. ^1H NMR (300 MHz, $CDCl_3$): δ12.24 (s, 1H), 10.64 (s, 1H), 7.76-7.73 (d, 1H), 6.94-6.91 (d, 1H), 6.23 (s, 1H), 2.45 (s, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ191.7, 164.0, 160.2, 155.6, 154.0, 133.7, 114.0, 112.2, 111.5, 109.3, 18.8. FT-IR

(KBr, cm^{-1}): 3050, 1720, 1610.

Synthesis of 7-hydroxy-8-((3-hydroxy- phenylimino)methyl)-4-methyl-coumarin [2]



8-formyl-7- hydroxy-4-methylcoumarin (102mg, 0.5mmol) was dissolved in anhydrous THF(8mL) with stiring, then *o*-aminophenol (65.4mg, 0.6mmol) in ethanol was added into the above solution. The obtained solution was stirred at 25-30°C for 5 hour. Solid precipitated and collected by filtering. The obtained solid was washed with ethanol for 5 times. Then the crude product was recrystallized from EtOH (86.0% yield). m.p. 182-184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ14.95 (s, 1H), 9.75 (s, 1H), 9.17(s, 1H), 7.80-7.76 (d, 1H), 7.29-7.26 (d, 1H), 7.00-6.87 (m, 3H), 6.80-6.76 (d, 1H), 6.23 (s, 1H) 2.40 (s, 1H). MS (EI, *m/z*): 295.1 (M^+). ^{13}CNMR (75 MHz, $CDCl_3$): δ166.28, 159.51, 158.94, 156.57, 154.50, 154.32, 147.61, 130.93, 130.85, 115.39, 114.77, 112.86, 111.16, 110.74, 108.00, 106.47, 18.78.

ESI 3. Fluorescence responses of host molecular to various metals in three different system

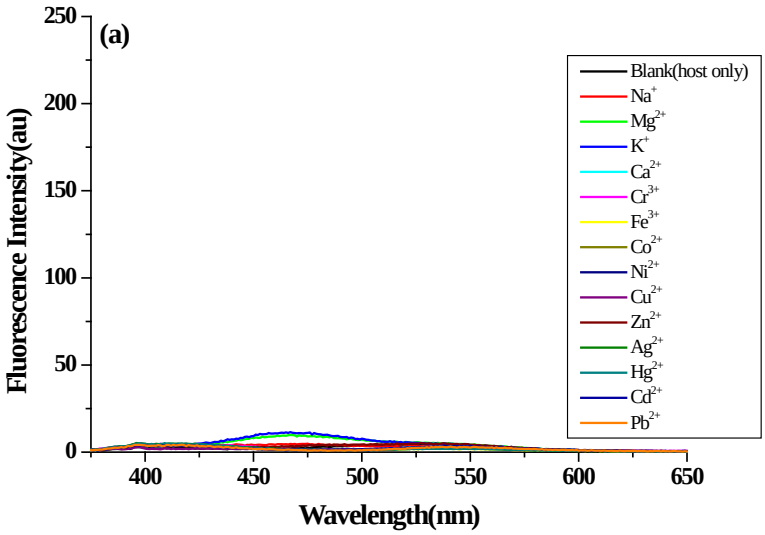


Fig.ESI 3. (**a**) Fluorescence spectra of the host molecular (1.0×10^{-5} mol/L in CH_3CN) in the presence of various metal ions (λ_{ex} = 355 nm)

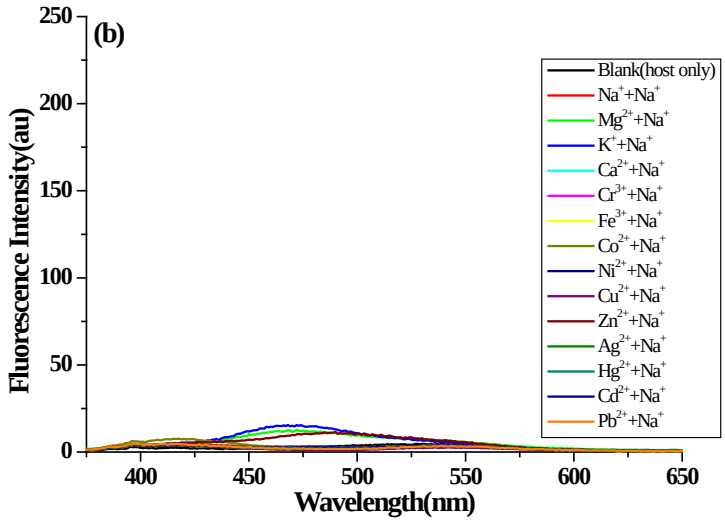


Fig.ESI 3. (**b**) Fluorescence spectra of the host molecular (1.0×10^{-5} mol/L in CH_3CN) in the presence of various metal ions + Na^+ (λ_{ex} = 355 nm)

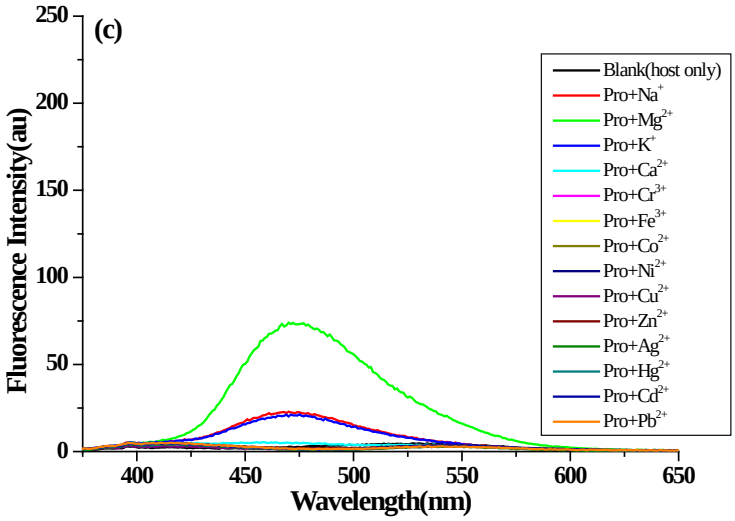


Fig.ESI 3. (**c**) Fluorescence spectra of the host molecular (1.0×10^{-5} mol/L in CH_3CN) in the presence of various metal ions + L-proline (λ_{ex} = 355 nm)

ESI 4. Competition experiment of host molecular towards Mg^{2+} in the multicomponent system

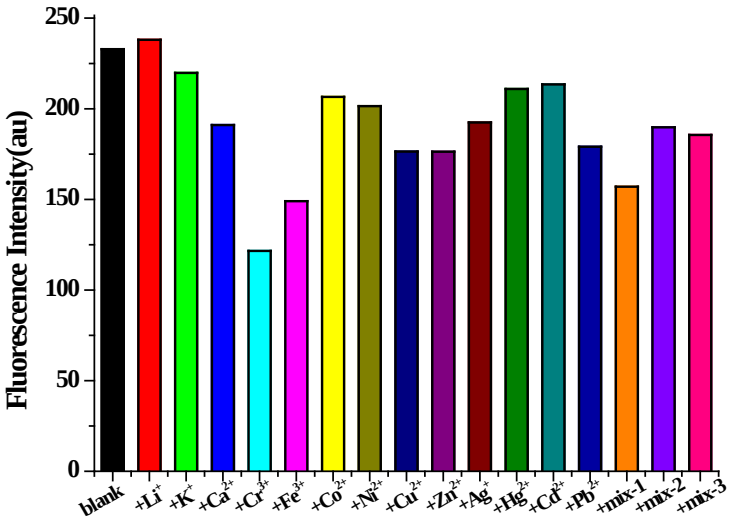


Fig. ESI 4. Fluorescence intensity of the multicomponent system (blank= host molecular + Mg^{2+} + Na^{+} + L-proline) and the multicomponent system with extra 1.0 eq X (X =Li^{+}, K^{+}, Ca^{2+}, Cr^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, mix-1, mix-2 and mix-3). (mix-1 = mixture of K^{+}, Ca^{2+}, Cr^{2+} and Fe^{3+}; mix-2 = mixture of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}; mix-3 = mixture of Ag^{2+}, Hg^{2+}, Cd^{2+} and Pb^{2+})

ESI 5. The promoting effect of Na^{+} and L-proline

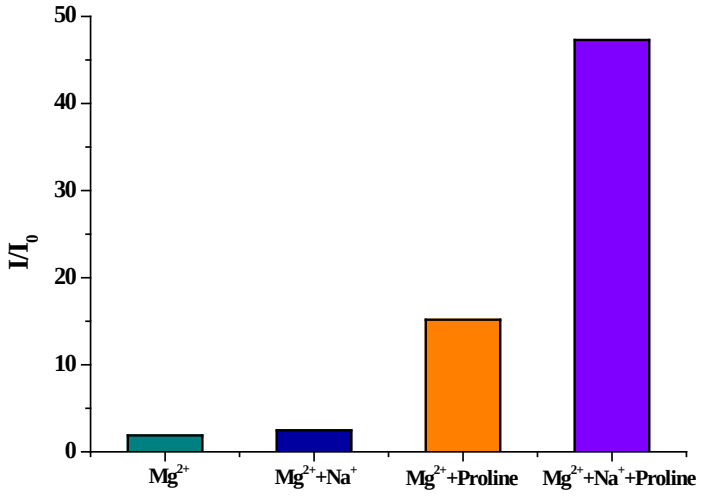


Fig. ESI 5. Relative fluorescence intensity of host molecular in the presence of Mg^{2+}, Mg^{2+}+Na^{+}, Mg^{2+}+L-proline and Mg^{2+}+Na^{+}+ L-proline.

ESI 6. The promoting effect of L-proline, D-proline and racemic proline

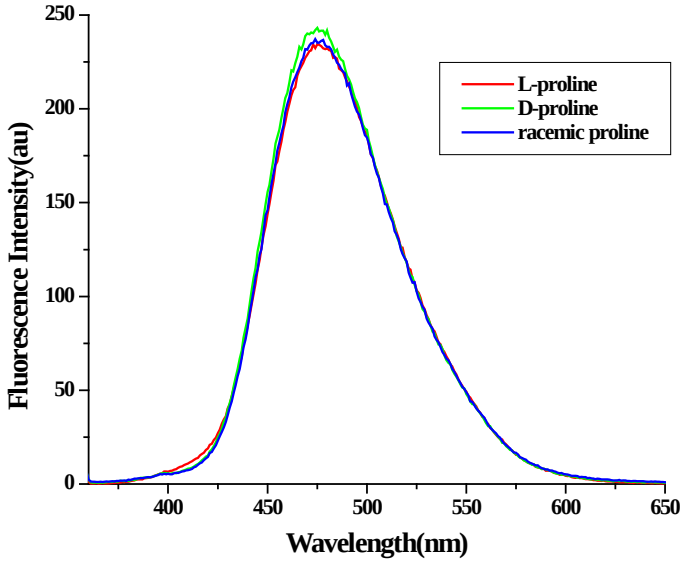


Fig. ESI 6. L-proline, D-proline and racemic proline are used as promoter in the multicomponent system, respectively.

ESI 7. Calculation of the detection limit

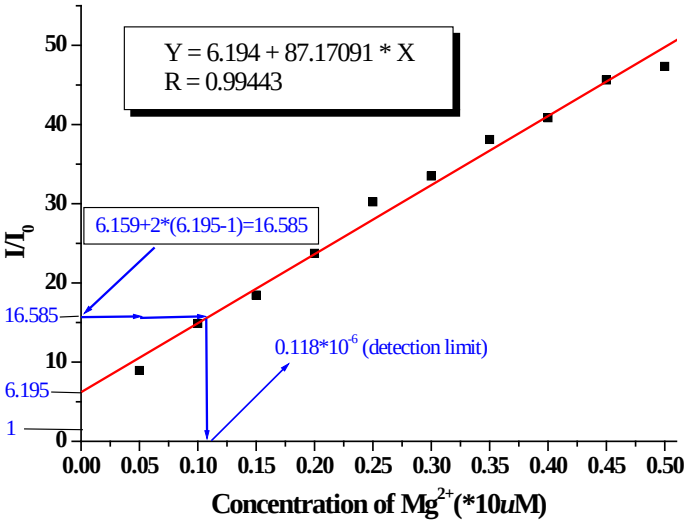
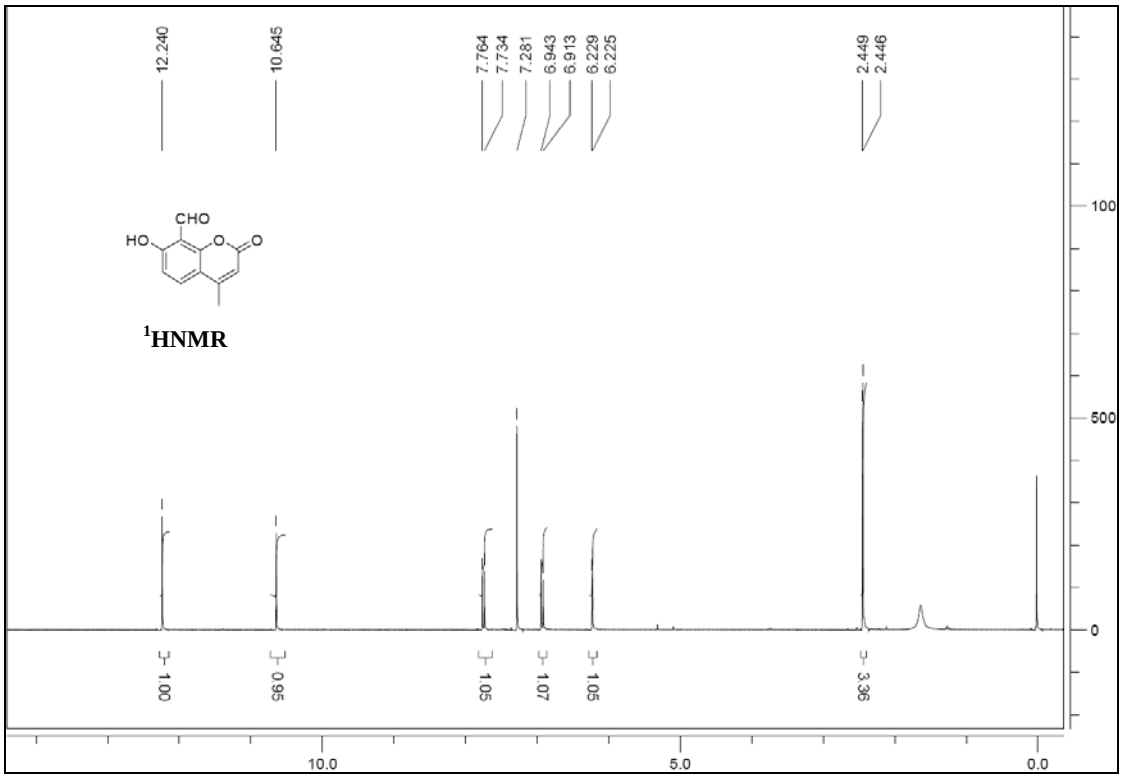
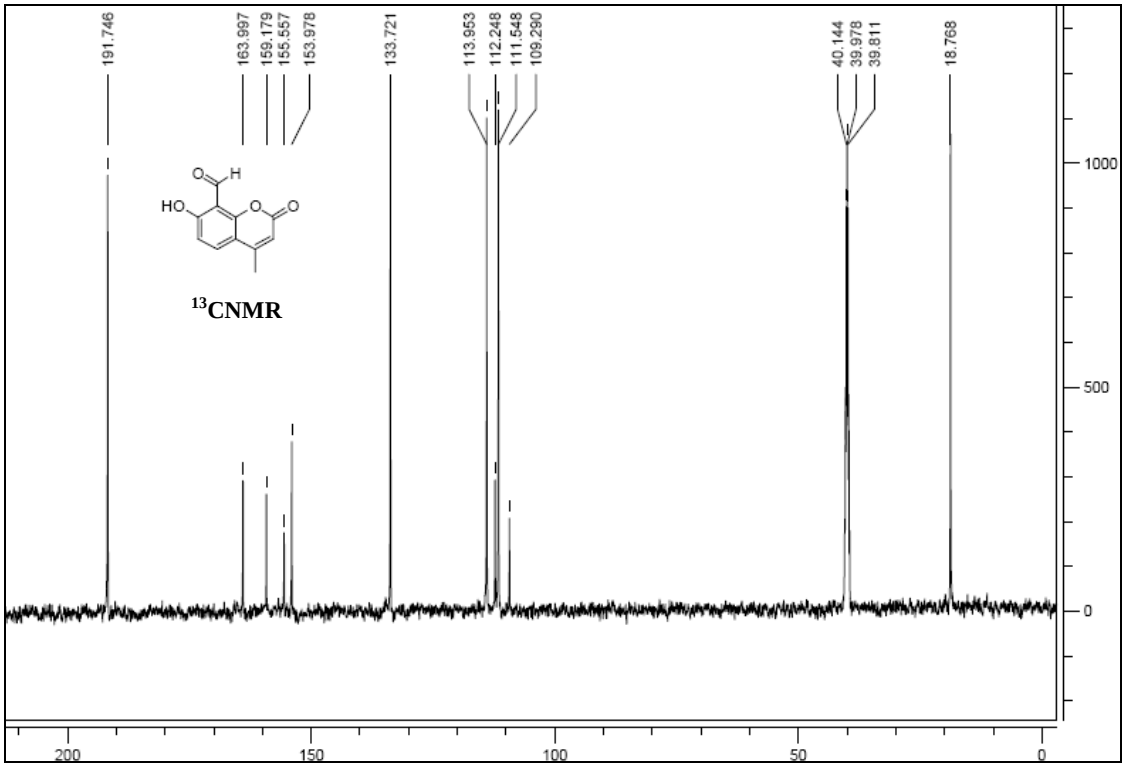


Fig. ESI 7. Calculation process of the detection limit of this system

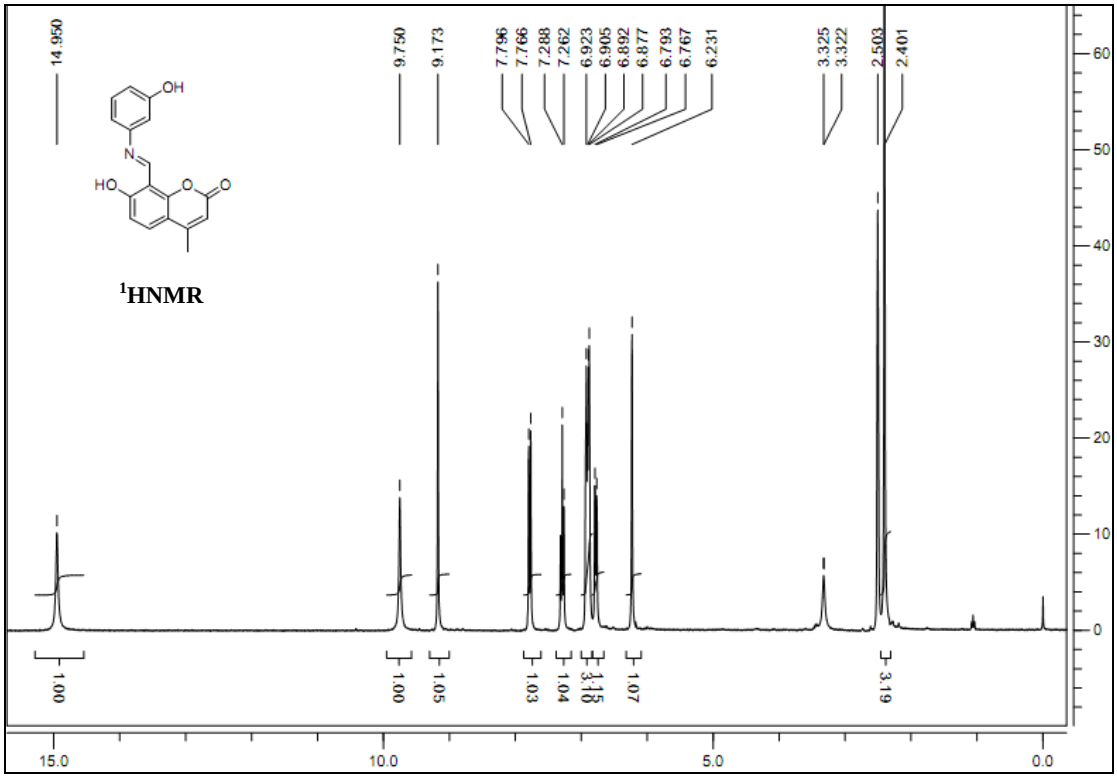
ESI 8. ^{1}H NMR and ^{13}C NMR Spectra



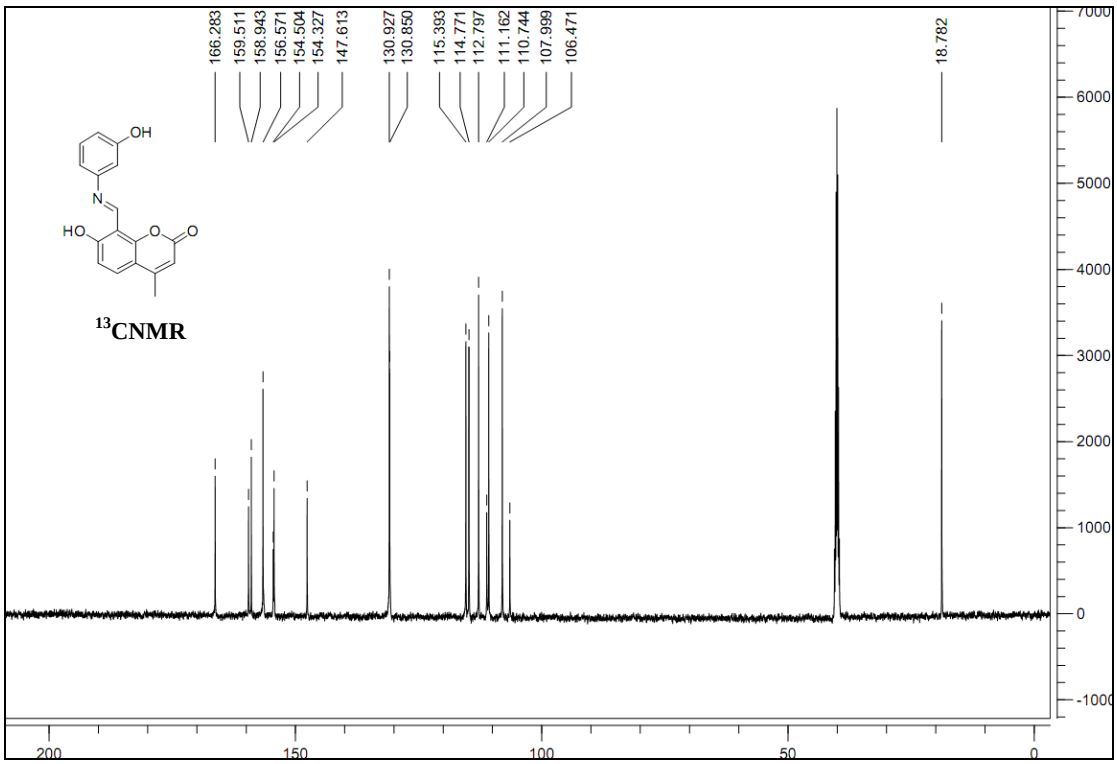
^{1}HNMR



^{13}CNMR

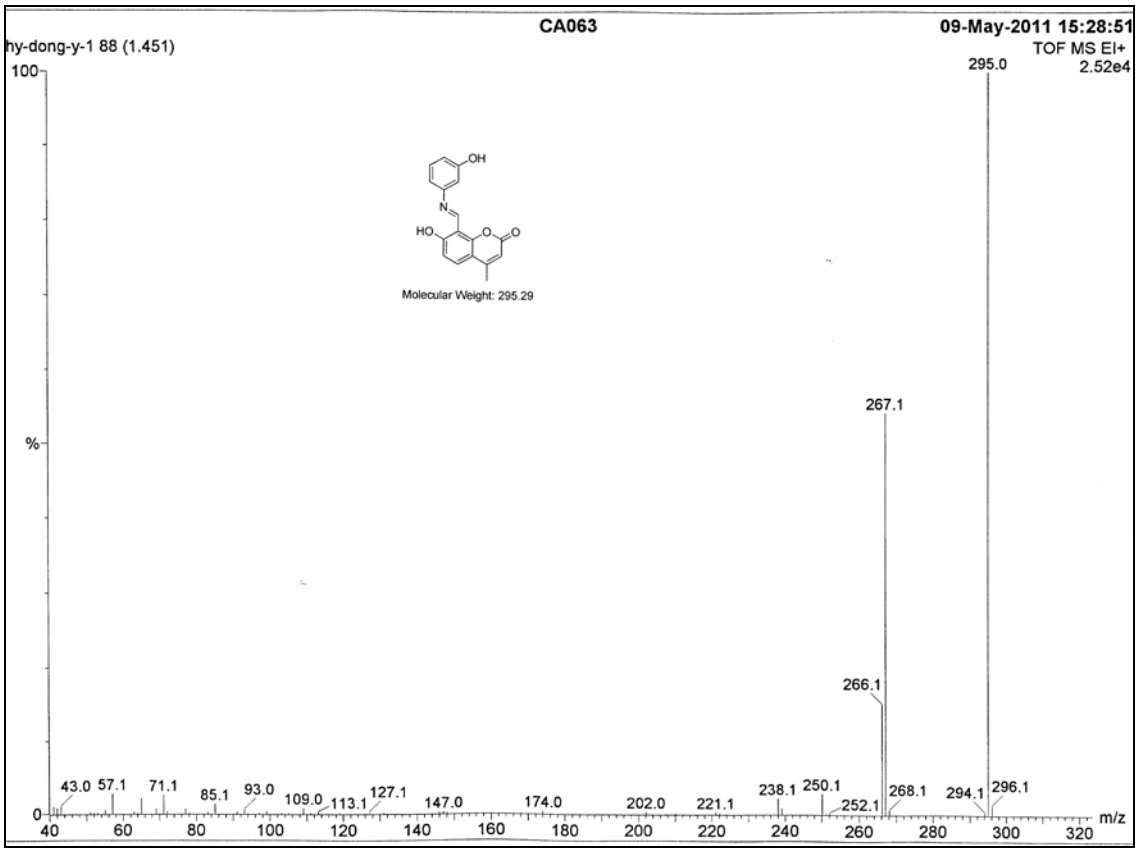


^{1}HNMR



^{13}CNMR

ESI 9. Mass spectrum of host molecular



ESI 10. References

1. (a) A. Kulkarni, S. A. Patil and P. S. Badami, *Eur. J. Med. Chem.* 2009, **44**, 2904-2912; (b) A. D. Kulkarni, G. B. Bagihalli, S. A. Patil, and P. S. Badami, *J. Coord. Chem.* 2009, **62**, 3060 -3072.
2. (a) O. D. Kachkovski, O. I. Tolmachev, L. O. Kobryn, E. E. Bila and M. I. Ganushchak, *Dyes and Pigments* 2004**, 63**, 203-211; (b) Y. Dong, J. F. Li, X. X. Jiang, F. Y. Song, Y. X. Cheng and C. J. Zhu, *Org. Lett.* 2011, **13**, 2252-2255; (c) M. A. Phaniband, S. D. Dhumwad and Pattan, S. R. *Med. Chem. Res.* 2011, **20**, 493-502.