Electronic Supporting Information (ESI) for

Highly Selective Colorimetric Sensing Pyrophosphate in Water by A NBD-phenoxo-bridged Dinuclear Zn(II) Complex

Shengjun Yang,[a] Guoqiang Feng*[a] and Nicholas H. Williams[b]

[a]*Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China.*
[b]*Centre for Chemical Biology, Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK.*
E-mail: gf256@mail.ccnu.edu.cn

1. Job's plot examined for PPi and ATP with 1·2Zn

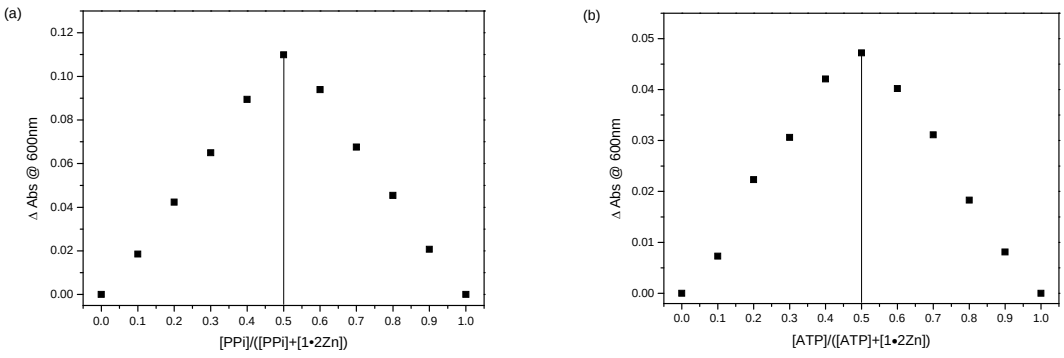


Fig. S1 (a) Job's plot examined between **1**·2**Zn** and PPi, [**1**·2**Zn**] + [PPi] = 50 μM. (b) Job's plot examined between **1**·2**Zn** and ATP, [**1**·2**Zn**] + [ATP] = 50 μM. All the spectra were measured in pure aqueous solution of 50 mM HEPES buffer (pH 7.4) at 25℃.

2. Selectivity of sensor 1·2Zn for PPi over Pi, ADP and ATP.

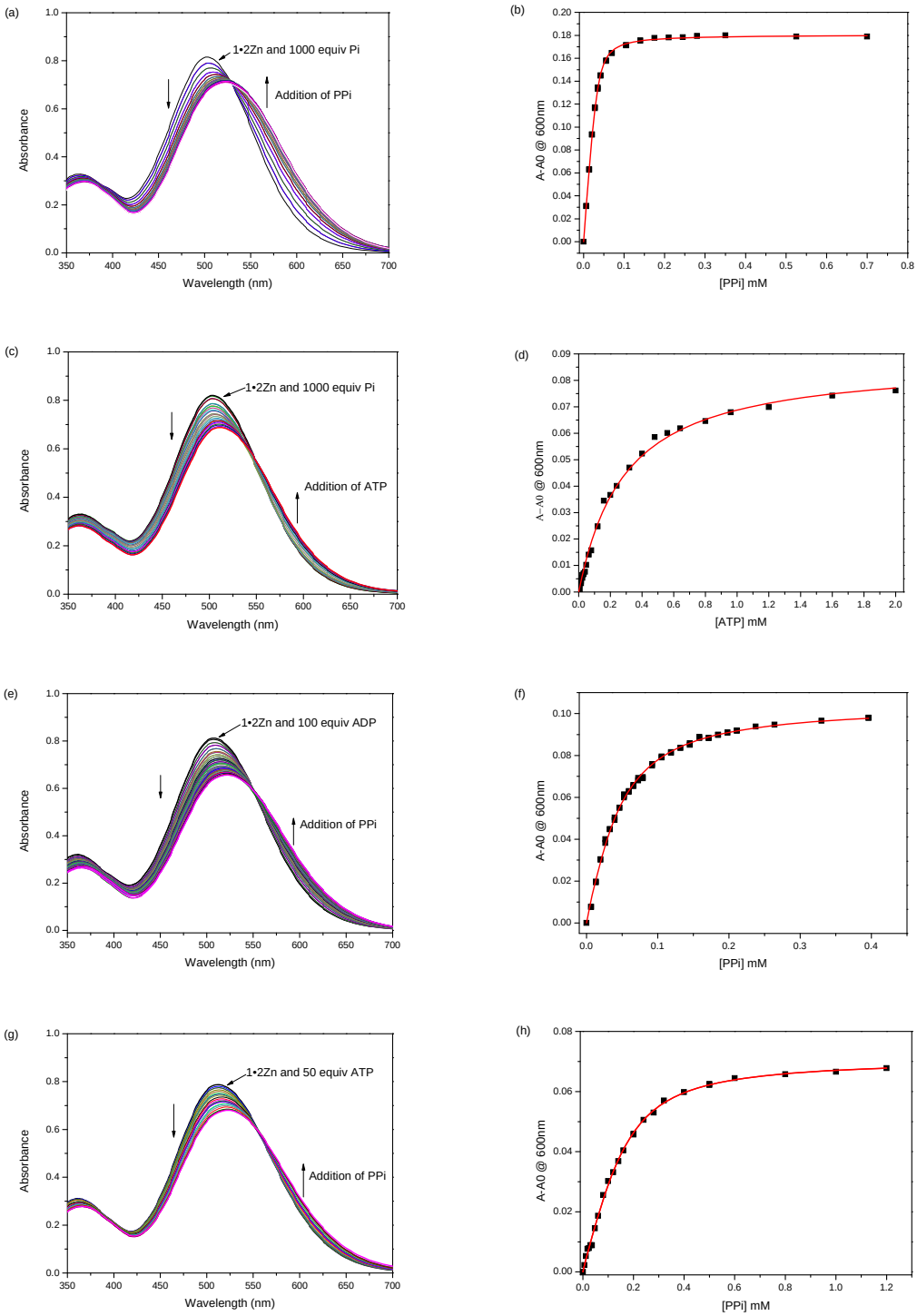
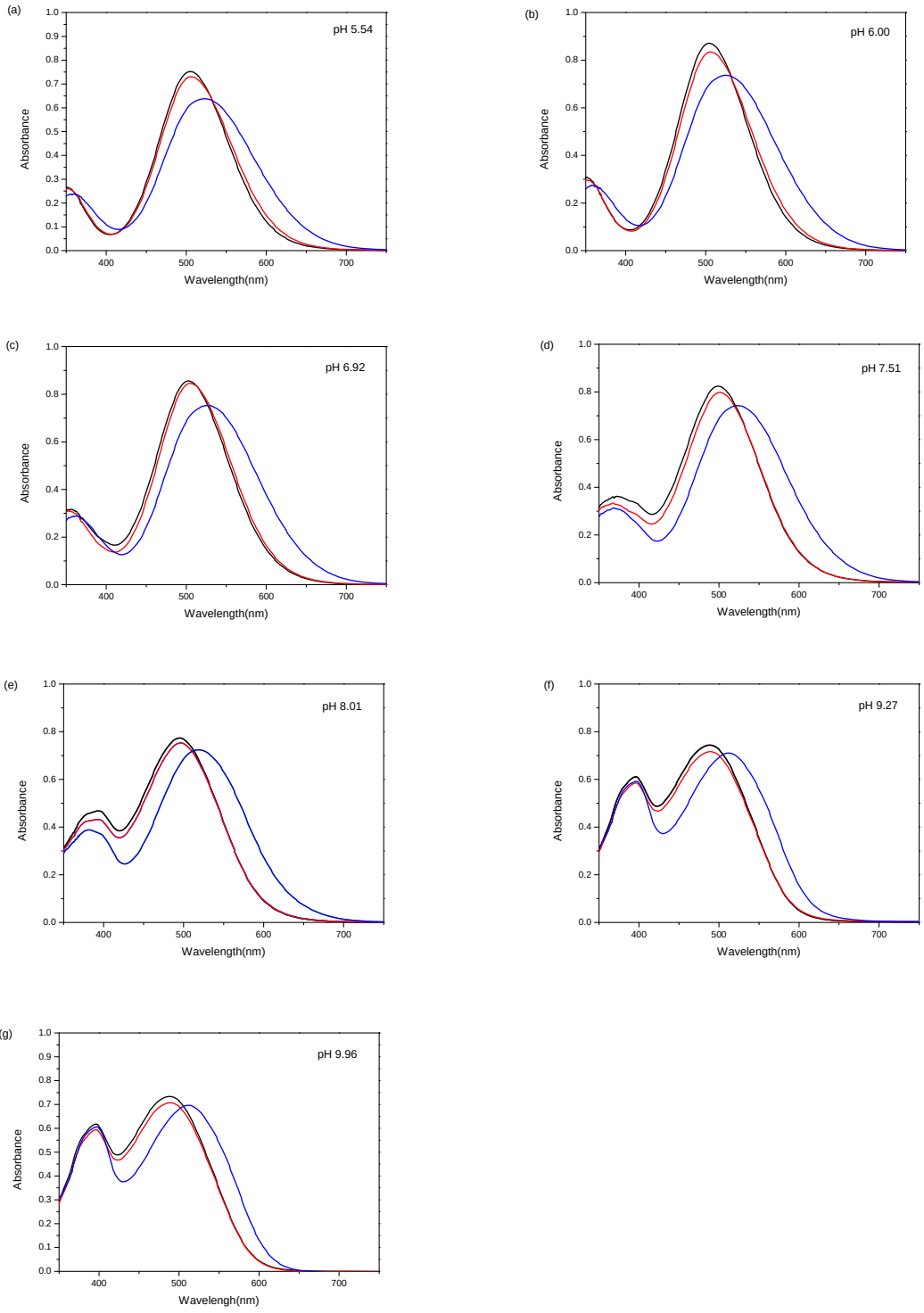


Fig. S2 (a) UV-vis spectra changes of sensor **1·2Zn** (35 μM) in the presence of 1000 equiv HPO_4^{2-} (Pi) upon addition PPi (0-70 μM). (b) Plot of absorbance changes (A-A0) at 600 nm against PPi concentration. (c) UV-vis spectra changes of sensor **1·2Zn** (35 μM) in the presence of 1000 equiv Pi upon addition ATP (0-2 mM). (d) Plot of absorbance changes (A-A0) at 600 nm against ATP concentration. (e) UV-vis spectra changes of sensor **1·2Zn** (35 μM) in the presence of 100 equiv ADP upon addition PPi (0-0.4 mM). (f) Plot of absorbance changes (A-A0) at 600 nm against PPi concentration. (g) UV-vis spectra changes of sensor **1·2Zn** (35 μM) in the presence of 50 equiv ATP upon addition PPi (0-1.2 mM). (f) Plot of absorbance changes

(A-A0) at 600 nm against PPi concentration. All titrations were measured in pure aqueous solution of 50 mM HEPES buffer (pH 7.4) at 25℃. The red line in (b), (d), (f) and (h) are a nonlinear curve fitting of the titration data using a competitive binding scheme. These experiments showed high selectivity of sensor **1**·2**Zn** for PPi over Pi, ADP and ATP.

3. Sensing PPi at different pH.



pH	**1**·2**Zn** λ_{max} (nm)	**1**·2**Zn** + PPi λ_{max} (nm)	$\Delta\lambda_{max}$ (nm)
5.54	504	522	18
6.00	504	526	22
6.92	503	528	25
7.51	499	524	25
8.01	495	519	24
9.27	488	512	24
9.96	487	512	25

Fig. S3 UV-vis spectra of sensor **1**·2**Zn** (35 μM, **black** line), in the presence of a mixture of various anions $H_2PO_4^-$, F^-, Cl^-, Br^-, $CH_3CO_2^-$, NO_3^-, HCO_3^-, ClO_4^- N_3^-, HPO_4^{2-} (Pi), SO_4^{2-}, $S_2O_7^{2-}$, Citrate and PO_4^{3-} (70 μM of each anion, **red** line) and after add PPi (35 μM, **blue** line) in the presence of a mixture of various anions (70 μM of each anion) in pure aqueous solution of 50 mM buffer at 25℃. (a) MES, pH 5.54. (b) MES, pH 6.00. (c) HEPES, pH 6.92. (d) HEPES, pH 7.51. (e) HEPES, pH 8.01. (f) CHES, pH 9.27. (g) CAPS, pH 9.96.

4. Studies on 2·Zn

Color changes of sensor **2·Zn** (50 μM) in 50 mM aqueous HEPES buffer solution (pH 7.4). Anions (1 mM) from left to right: none, PPi, AMP, ADP, ATP, PO_4^{3-}, HPO_4^{2-}, PhPi, F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, HCO_3^-, $CH_3CO_2^-$, Citrate, N_3^-, $S_2O_7^{2-}$, ClO_4^- .

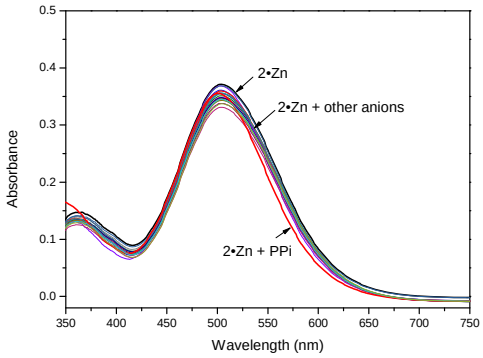
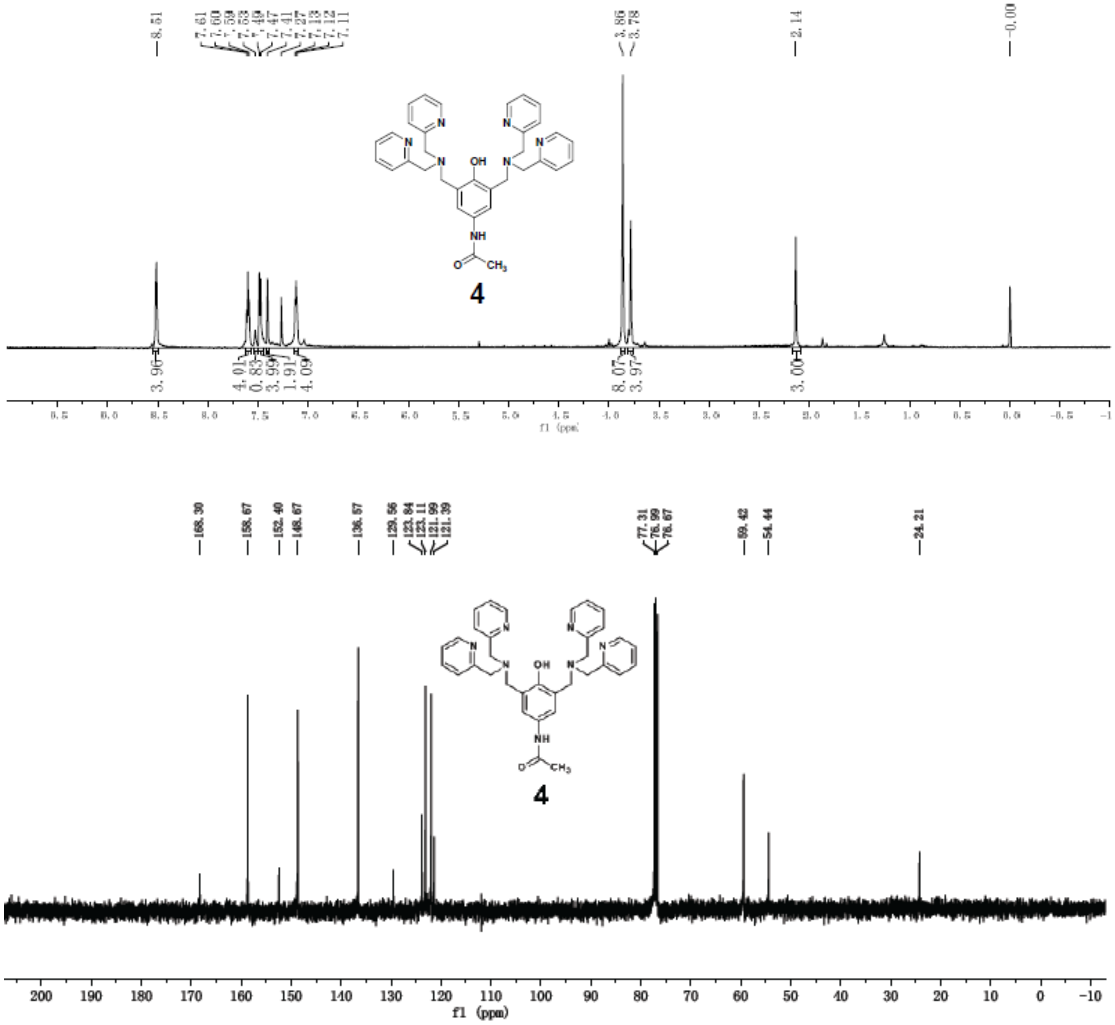
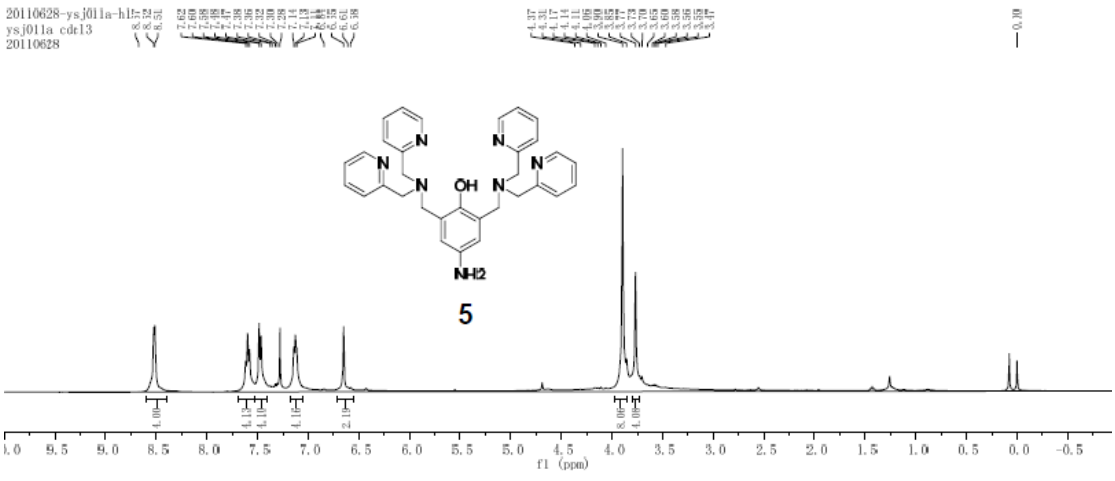


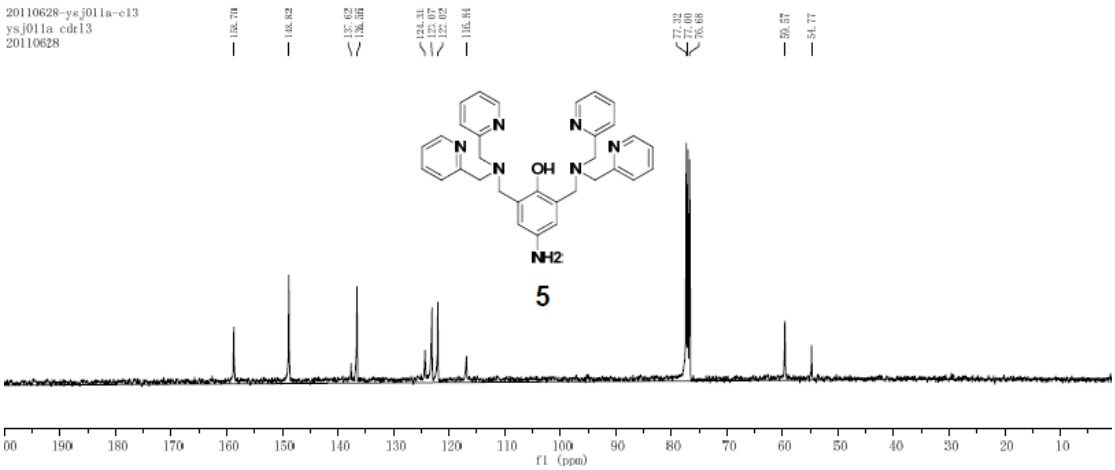
Fig. S4 UV-vis spectra of **2·Zn** (50 μM) in the absence and presence of 20 equiv of various anions in pure aqueous solution of 50 mM HEPES buffer at pH 7.4. Other anions are AMP, ADP, ATP, PO_4^{3-}, HPO_4^{2-} (Pi), $H_2PO_4^-$, PhPi, F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, HCO_3^-, $CH_3CO_2^-$, Citrate, N_3^-, $S_2O_7^{2-}$, ClO_4^-.

7. ^{1}H NMR and ^{13}C NMR spectra of compound 4, 5, 1 and 6, 7, 2, and Mass spectra of 1 and 2.

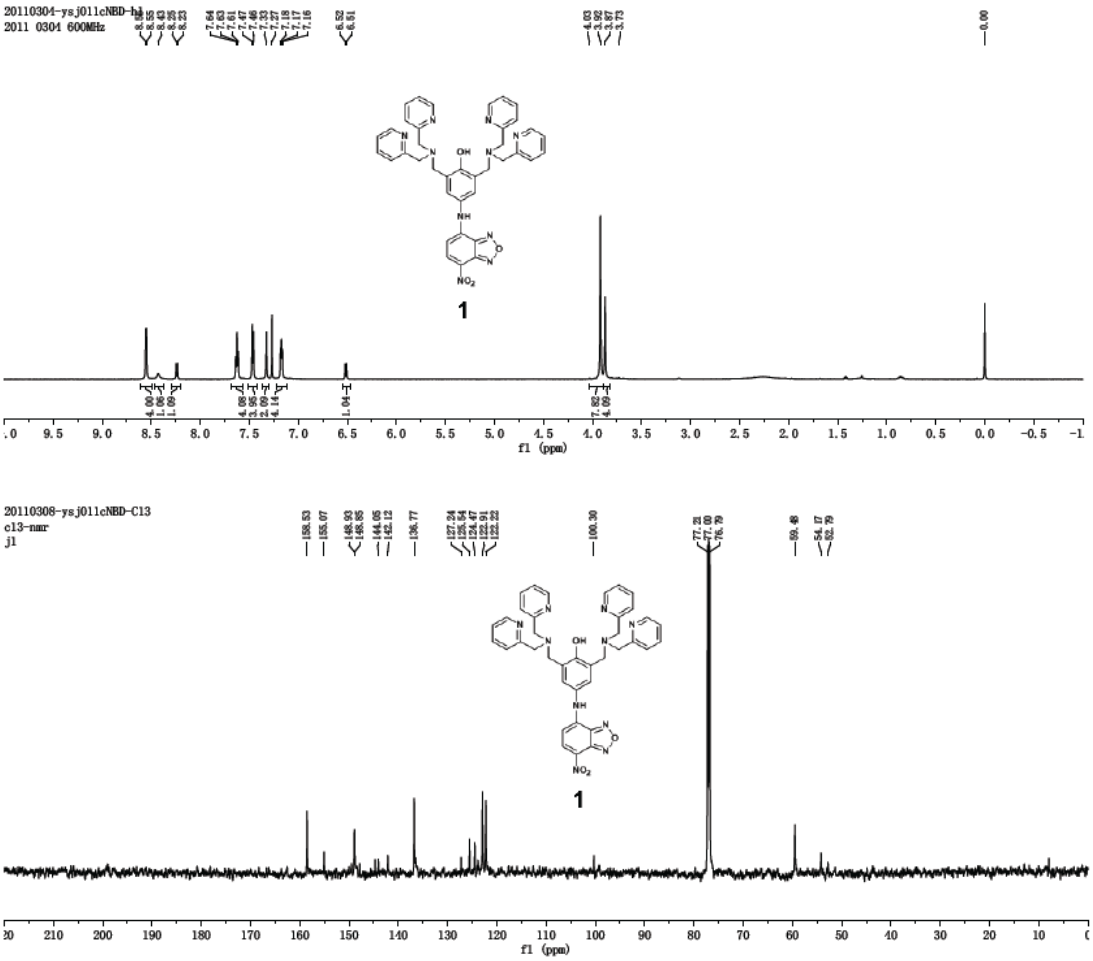


^{1}H NMR and ^{13}C NMR of compound **4** recorded in $CDCl_3$.

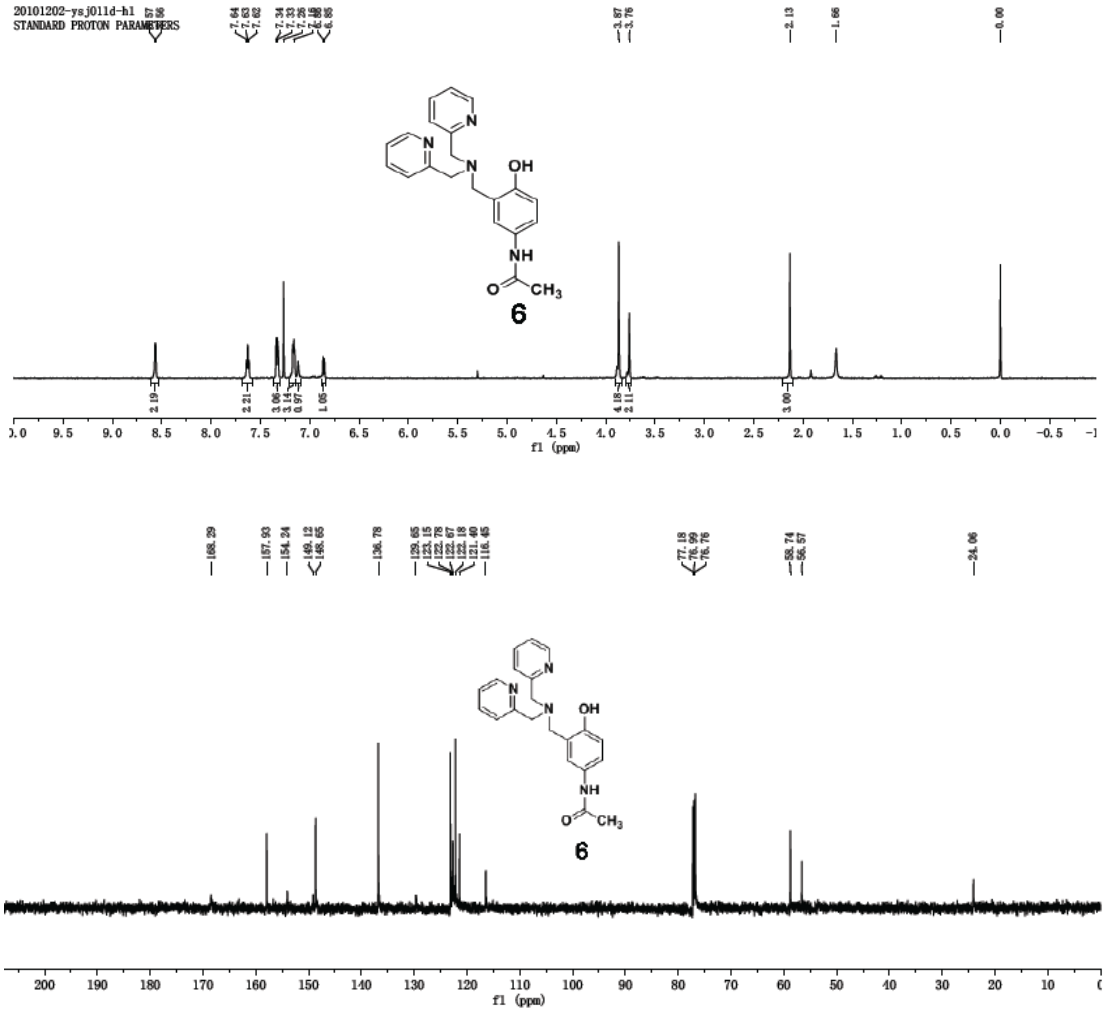




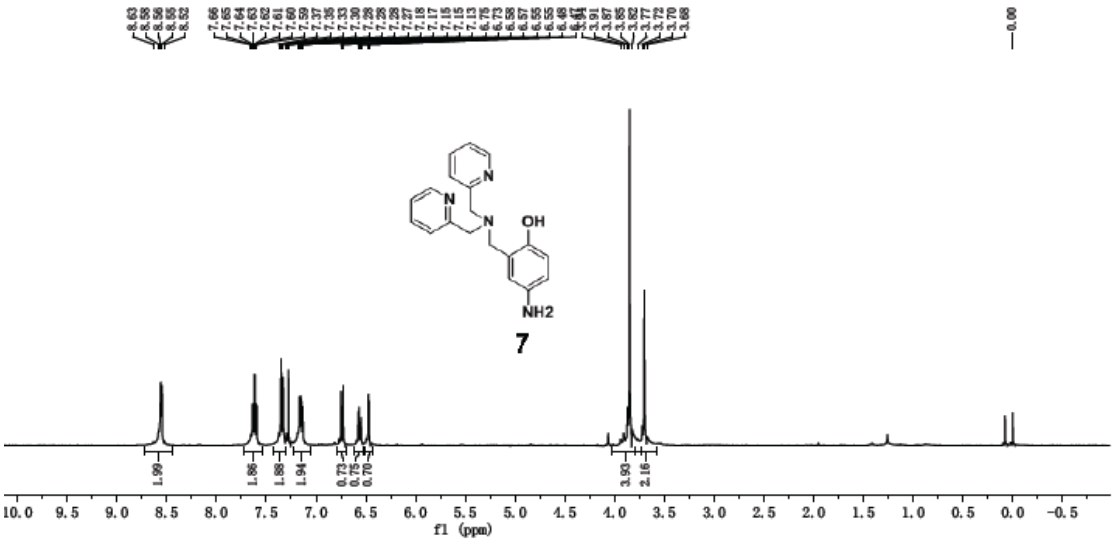
^{1}H NMR and ^{13}C NMR of compound **5** recorded in $CDCl_3$.

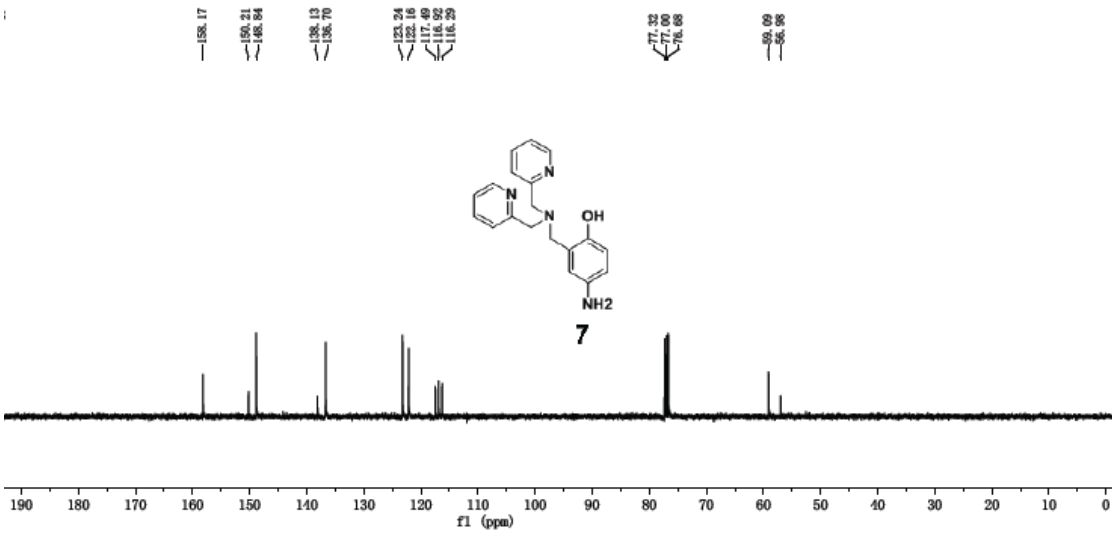


^{1}H NMR and ^{13}C NMR of compound **1** recorded in $CDCl_3$.

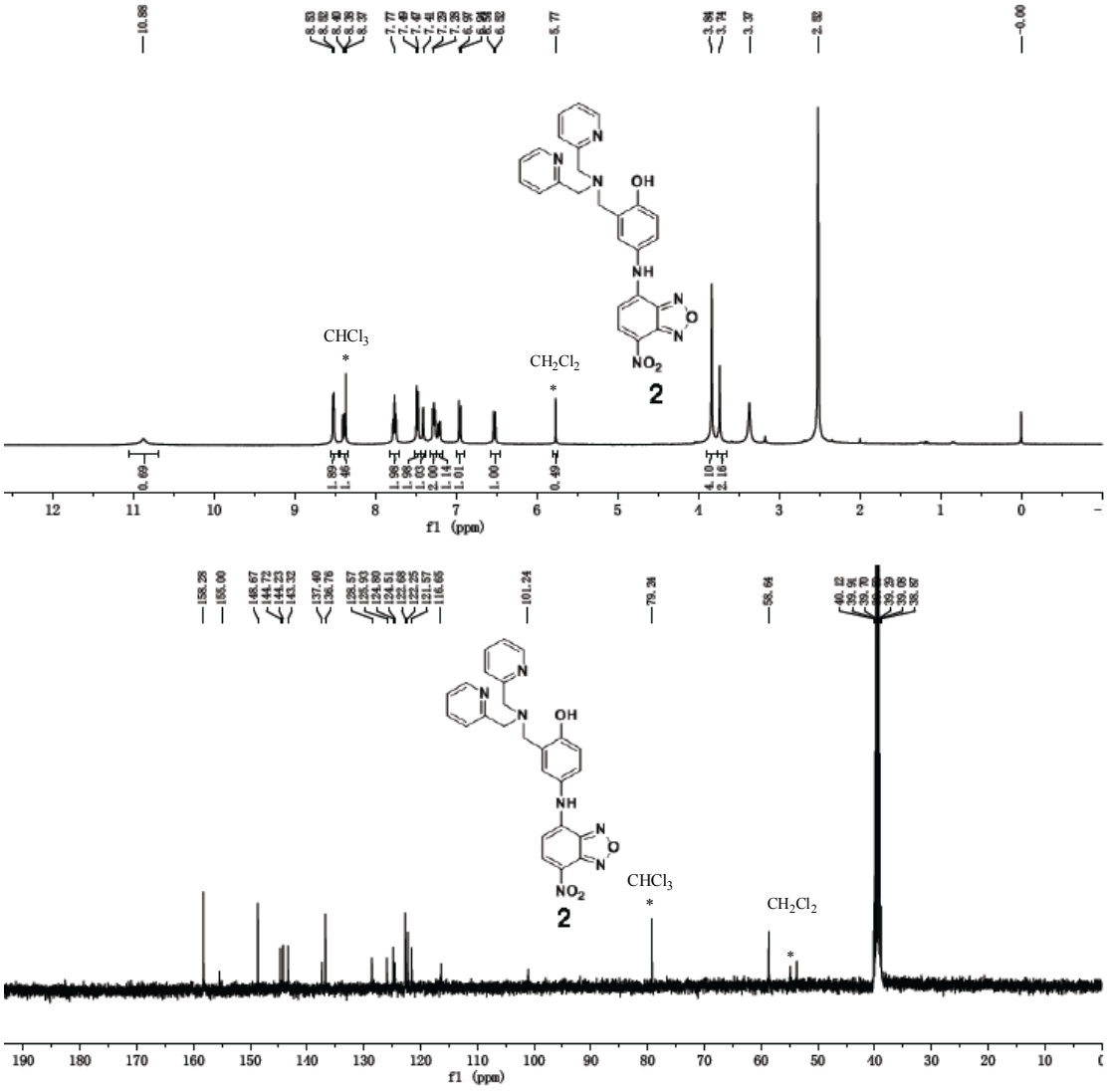


^{1}H NMR and ^{13}C NMR of compound **6** recorded in $CDCl_3$.

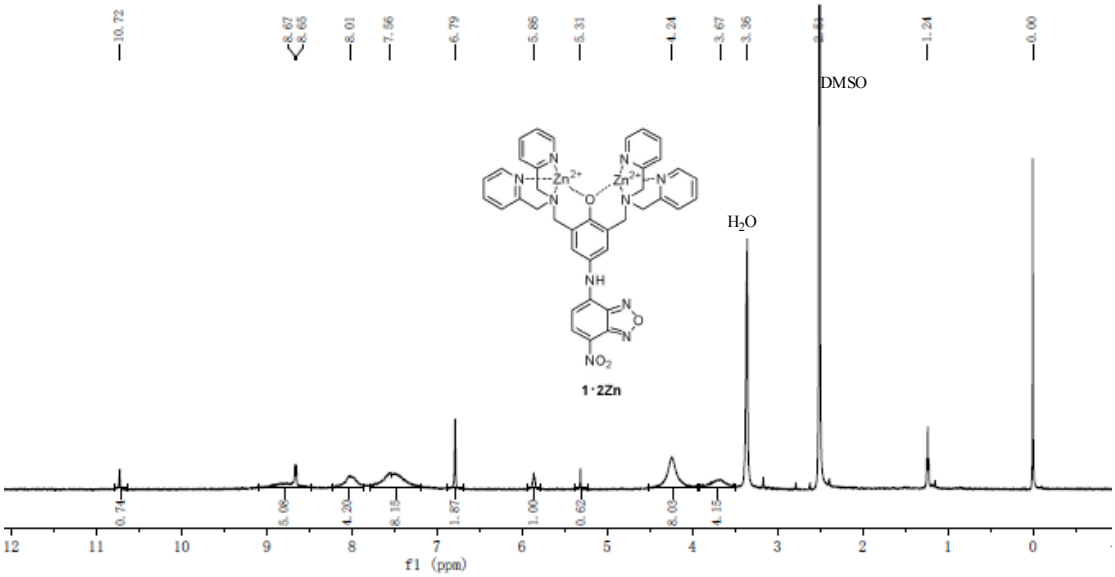




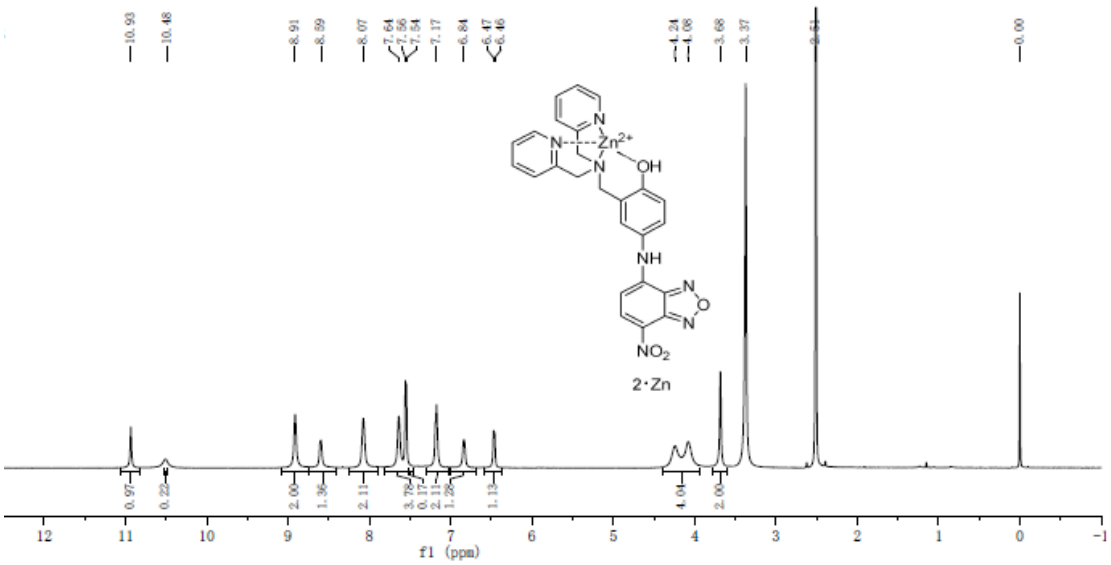
^{1}H NMR and ^{13}C NMR of compound **7** recorded in $CDCl_3$.



^{1}H NMR and ^{13}C NMR of compound **2** recorded in DMSO-d_6 and $CDCl_3$.

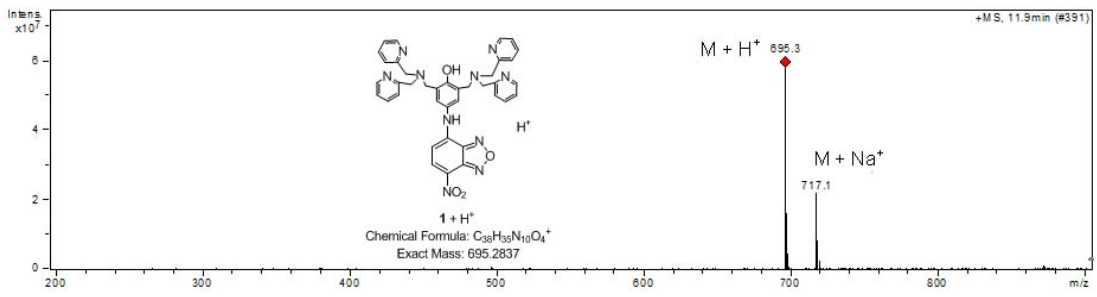


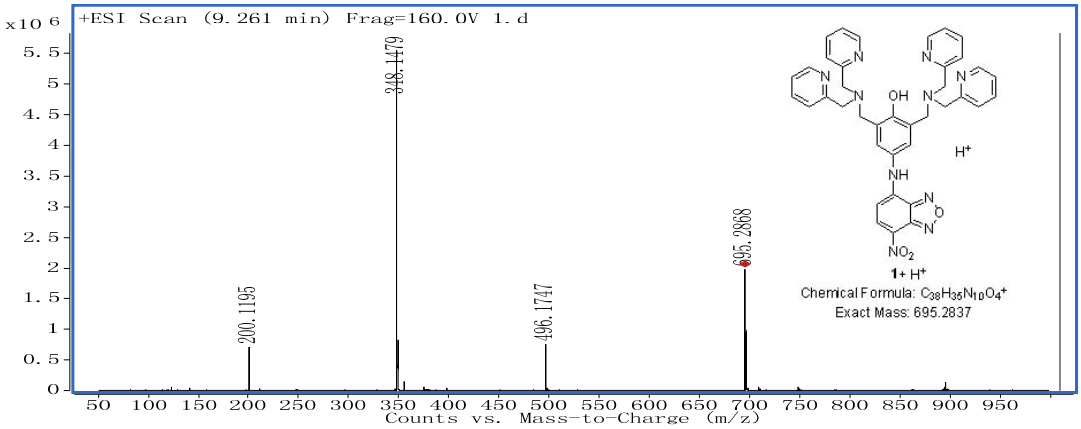
^{1}H NMR of compound **1·2Zn** recorded in DMSO-*d6*.



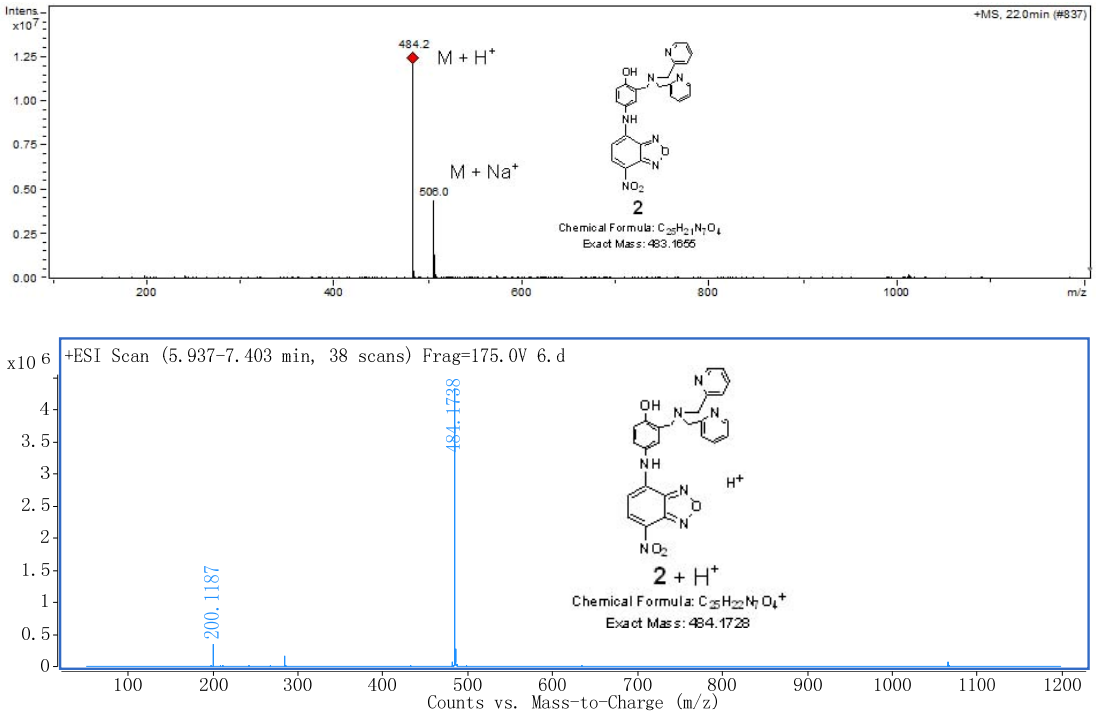
^{1}H NMR of compound **2·Zn** recorded in DMSO-*d6*.

ESI-MS and HR-MS of compound 1 and 2





ESI-MS and HR-MS of compound **1.**



ESI-MS and HR-MS of compound **2.**