Supporting information

Rational Design of a Reusable Chemodosimeter for the Selective Detection of Hg^{2+}

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1 apparatus and reagents

All cations in the form of perchloride salts were purchased from Sigma-Aldrich and used without further purification. The solutions of anions were prepared from their sodium salts. All solvents used for spectroscopic test are spectrostropic grade. A JASCO FP-6300 spectrofluorimeter was used for fluorescence measurements. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE-400 spectrometer. Mass spectra were measured on an Agilent 6310 MS spectrometer and a Q-TOF MS spectrometer.

2． Synthesis and structural characterization of 2（4- Allyloxy-N-butyl-1,8-naphthalimide）

4-Hydroxy-N-butyl-1, 8-naphthalimide **1** (1.4 g, 4.7mmol) and K_2CO_3 (0.94 g, 6.8mmol) was suspended in acetone (30 ml). Then, the mixture was refluxed for 12 h under Ar. After cooled, inorganic salt was filtrated off. After evaporation of the filtrate, the product was purified with silica gel chromatography, eluted with CH_2Cl_2 and petroleum ether (1:3) to afford **2** as pure white solid in 69% yield.(1.0 g) :^{1}H NMR (400 Hz,$CDCl_3$) δ: 8.59 (d, *J* = 8 Hz , 2H), 8.52(d, *J* = 8 Hz , 1H), 7.68-7.72 (m, 1H), 7.02(d, *J* = 8 Hz , 1H), 6.13-6.23 (m, 1H), 5.41-5.57 (m, 2H), 4.85(d, *J* = 4 Hz , 2H), 4.15-4.18 (m, 2H), 1.67-1.73 (m, 2H), 1.42-1.48 (m, 2H), 0.90-1.00 (m, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ:13.89, 20.42, 30.27, 40.10, 69.55, 106.20, 115.20, 118.73, 122.46, 123.56, 125.92, 128.62, 129.40, 131.51,131.87,133.26,159.61,163.92,164.52 ； HRMS (ESI) m/z calcd for $C_{19}H_{19}NO_3Na$ $[M+Na]^+$:332.1263; found,332.1269.

2． Synthesis of compound AHNA（2-allyl-4-hydroxy-N-butyl-1,8-naphthalimide）

4- Allyloxy-N-butyl-1, 8-naphthalimide **2**(1.0 g, 3.32mmol) was dissolved in N-methylpyrrolidone (10 mL) and refluxed for 3 h at 220 ºC under Ar. After evaporation of the solvent, the product was purified with silica gel chromatography，eluted with ethyl acetate and petroleum ether (1:15) to afford **AHNA** as dark yellow solid in 22% yield (0.22g). : ^{1}H NMR (400 Hz,$CDCl_3$) δ: 8.51-8.59 (m, 2H), 8.40 (s, 1H), 7.69-7.73 (m, 1H), 6.49(s, 1H), 6.06 -6.14 (m, 1H),5.37(d, *J* = 12 Hz , 2H), 4.16-4.19 (m,

2H),3.70 (d, *J* = 4 Hz , 2H), 1.67-1.73 (m, 2H), 1.42-1.47 (m, 2H), 0.95-0.99 (m, 3H); ^{13}C NMR (400 MHz, CDCl3) δ:13.89, 20.41, 30.28,35.58, 40.15, 115.04, 118.43, 119.68, 122.42, 122.81, 125.99, 128.35, 128.78, 131.23, 134.98,135.00,156.27,164.10,164.60； HRMS (ESI) m/z calcd for $C_{19}H_{18}NO_3$ $[M-H]^+$:308.1287; found,308.1281.

2. Synthesis of compound Hg-AHNA

2-Allyl-4-hydroxy-N-butyl-1,8-naphthalimide （ 60mg ， 0.19mmol ） was dissolved in Dimethylsulfoxide (5ml) and 4995ml Tris-HCl buffer solution(pH=7.4), then $HgCl_2$ (0.515mg, 1.9mmol) was added. After stirring overnight, the solution was extracted with dichloromethane. After evaporation of the solvent, the product was recrystallized from ethyl acetate to yield dark yellow crystals of **Hg-AHNA** in 40% yield (0.42g): ^{1}H NMR (400 Hz,$CDCl_3$) δ: 8.58 (d, J = 8 Hz , 1H), 8.45 (s, 1H), 8.26 (d, *J* = 8 Hz , 1H), 7.68-7.72 (m, 1H), 5.56-5.63 (m, 1H), 4.15-4.18 (m, 2H), 3.70-3.76 (m, 1H),3.06-3.12 (m, 1H), 2.55-2.59(m, 1H), 2.42 -2.46(m, 1H), 1.67-1.75 (m, 2H),1.42-1.47 (m, 2H), 0.96-0.99 (m, 3H); ^{13}C NMR (400 MHz, DMSO-d_6) δ:13.89, 20.41, 30.28,35.58, 40.15, 115.04, 118.43, 119.68, 122.42, 122.81, 125.99, 128.35, 128.78, 131.23, 134.98,135.00,156.27,164.10,164.60； HRMS (ESI) m/z calcd for $C_{19}H_{19}NO_3ClHg$ $[M+H]^+$:546.0760; found,546.0734.

3. General procedure for Hg^{2+} detection

A stock solution of probe **AHNA** (10^{-2} mol/ L^{-1}) was prepared by dissolving the requisite amount of **AHNA** in DMSO, and solutions of various metal ions were prepared by dissolving their salts in water. All measurements were made according to the following procedure. In a small cell, 40 μ L**AHNA** of the stock solution of **AHNA** and 3940 μ L Tris-HCl buffer solution(pH=7.4) were mixed, followed by addition of an appropriate volume of metal ions solution, then the fluorescence sensing of different metal ions was run.

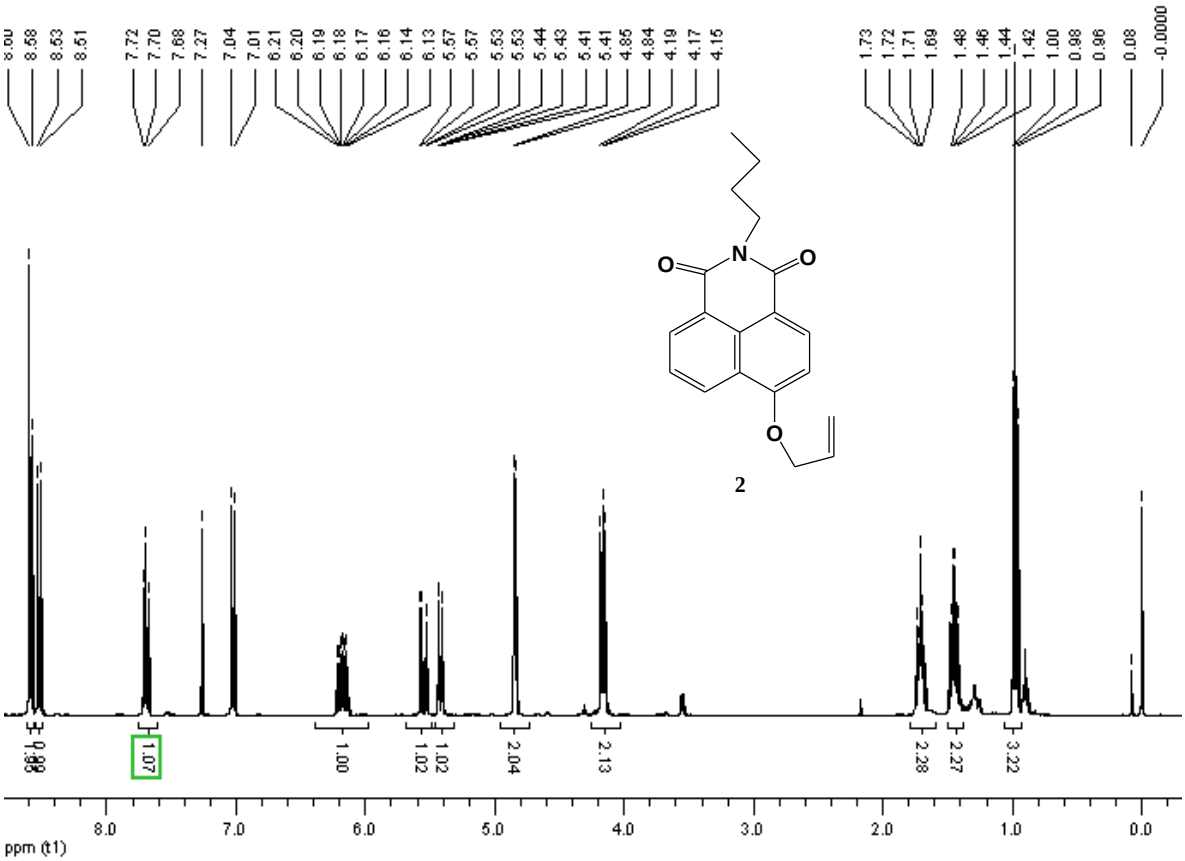

Figure S1. ^{1}H NMR for compound **2** in $CDCl_3$

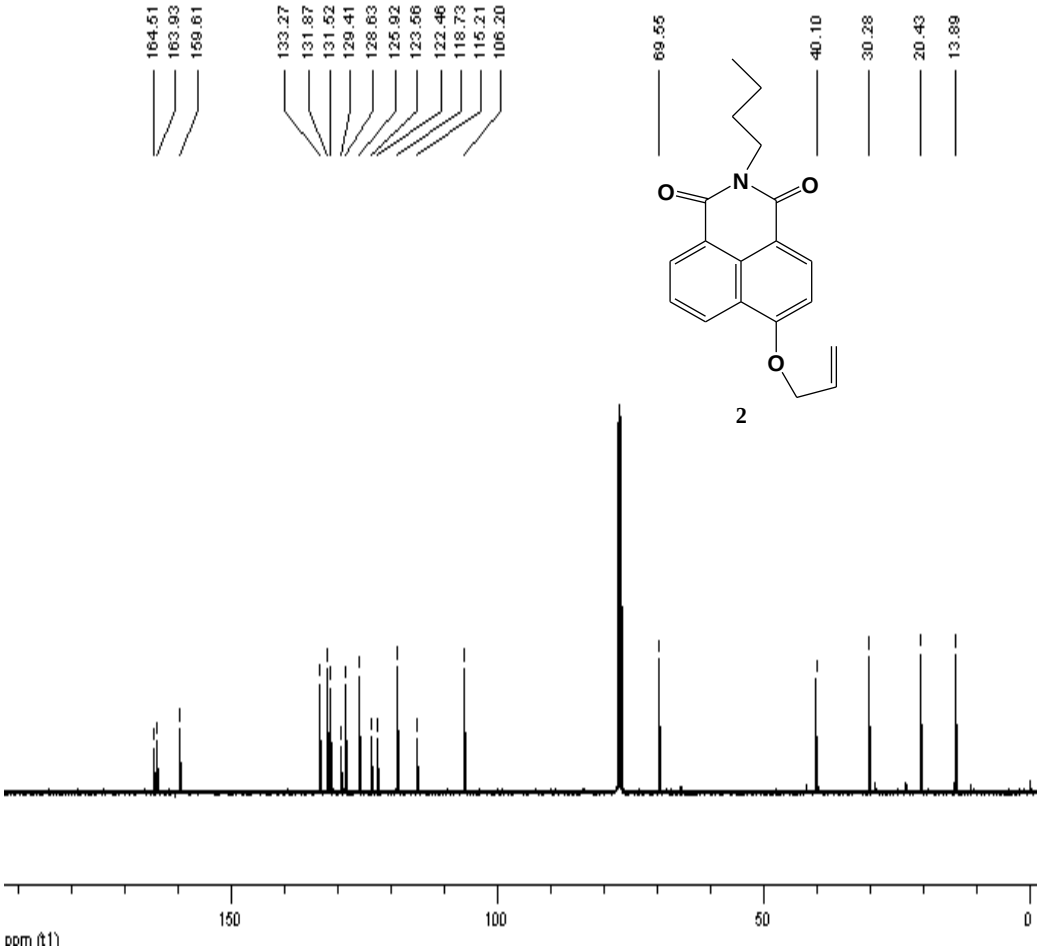

Figure S2. ^{13}C NMR for compound **2** in $CDCl_3$

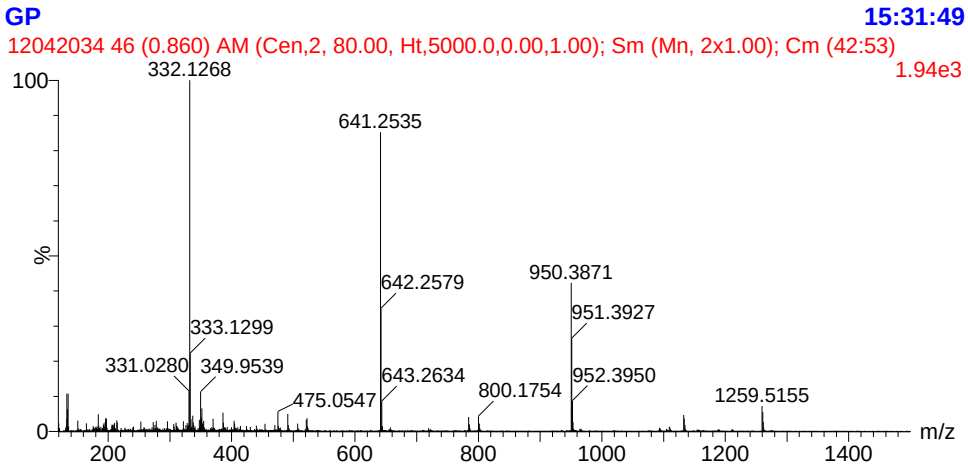

Figure S3. HRMS spectrum of compound **2**

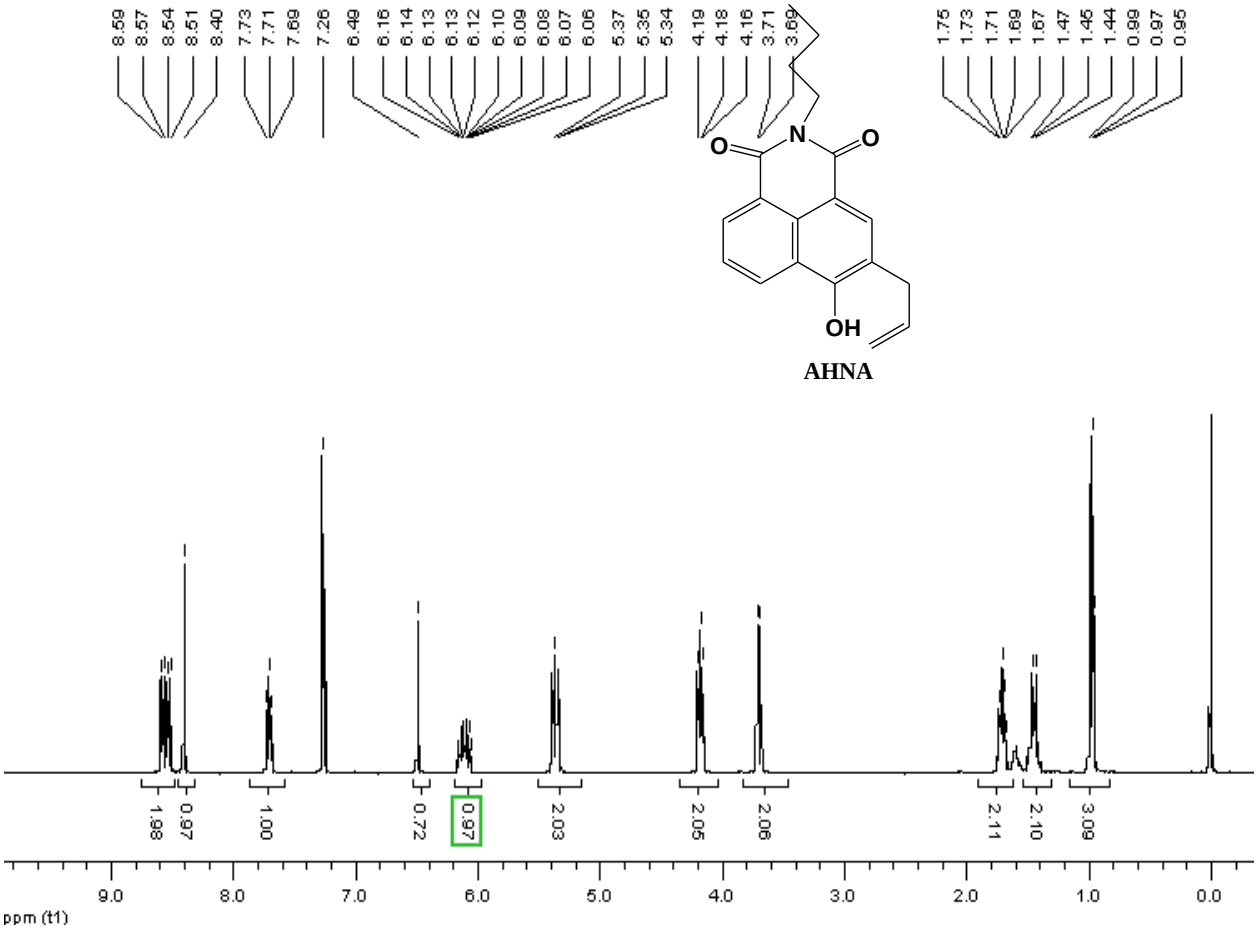

Figure S4. ^{1}H NMR for compround **AHNA** in $CDCl_3$.

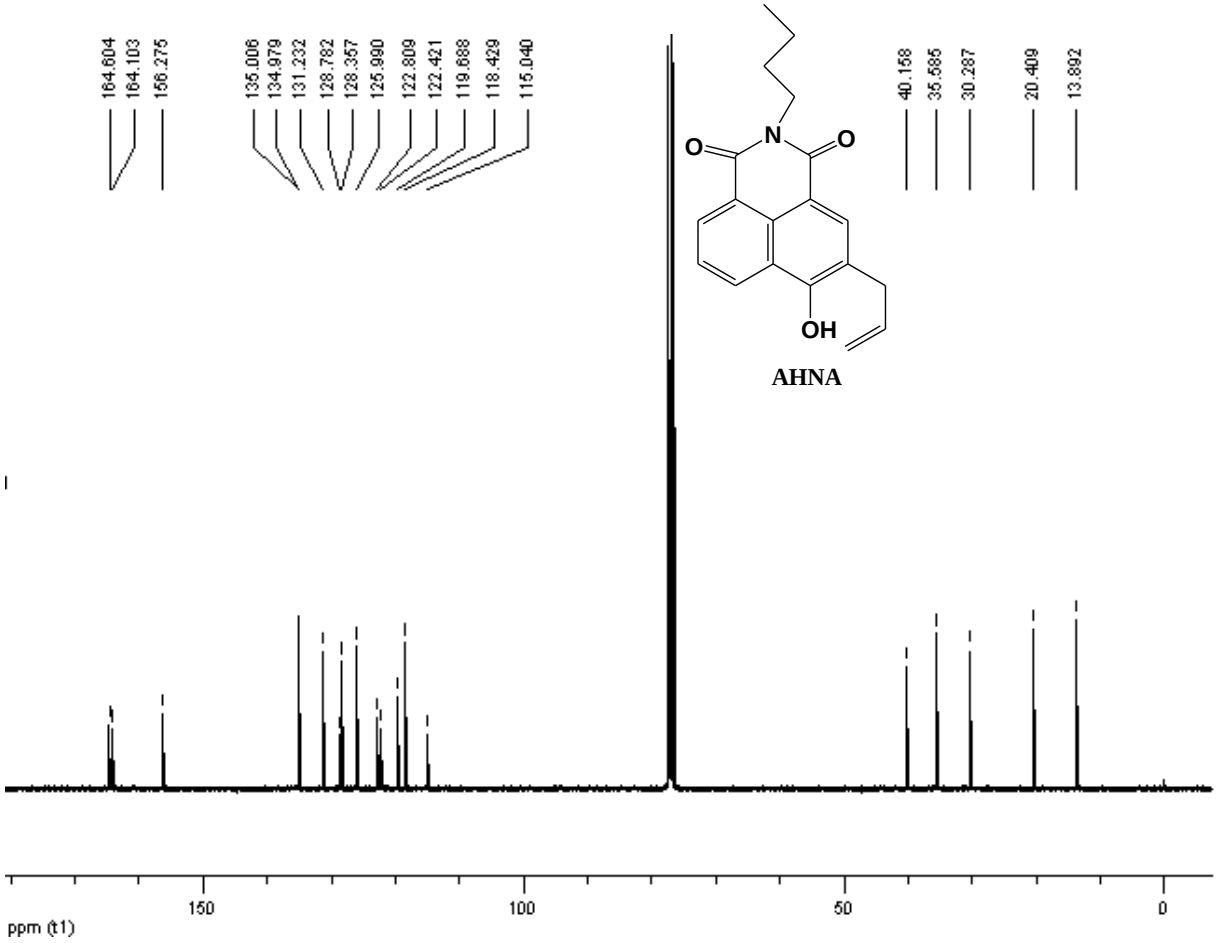

Figure S5. ^{13}C NMR for compround **AHNA** in $CDCl_3$.

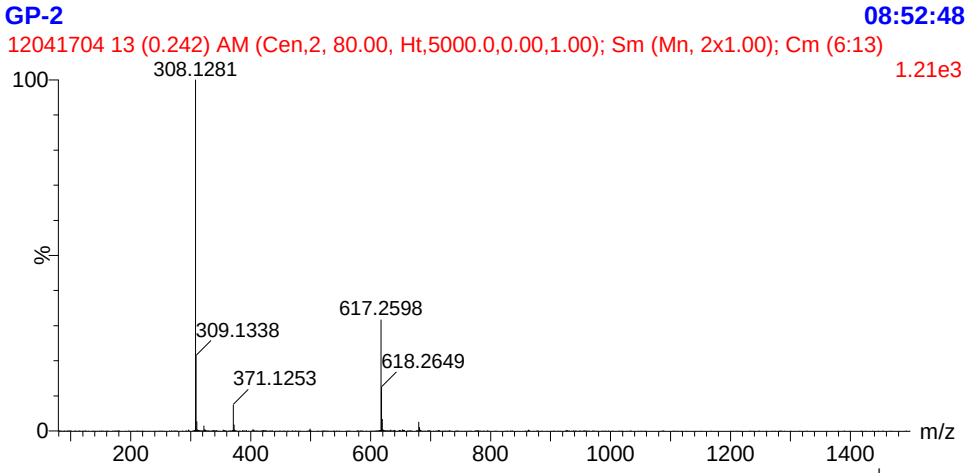

Figure S6. HRMS spectrum of compound **AHNA** $[M-H]^+$

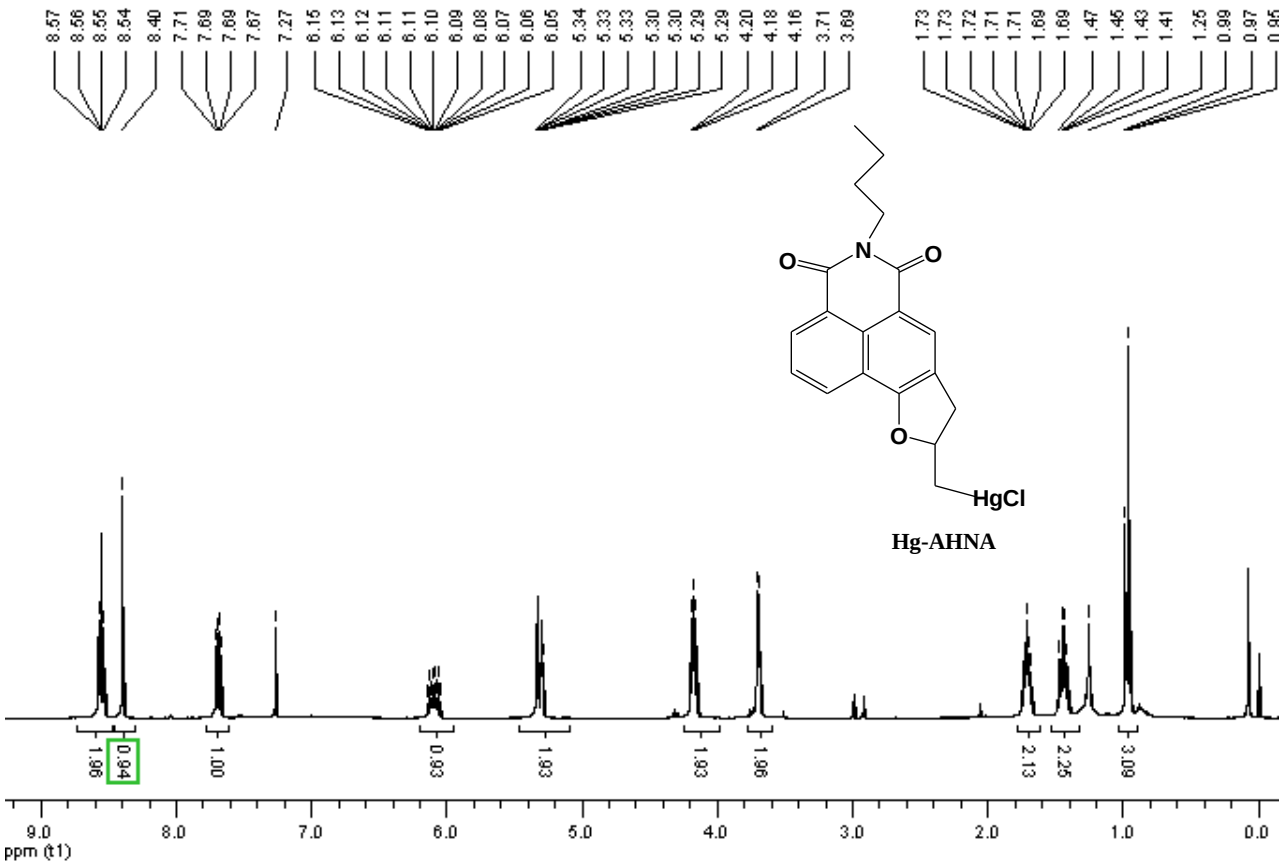

Figure S7. ^{1}H NMR for compround **Hg-AHNA** in $CDCl_3$

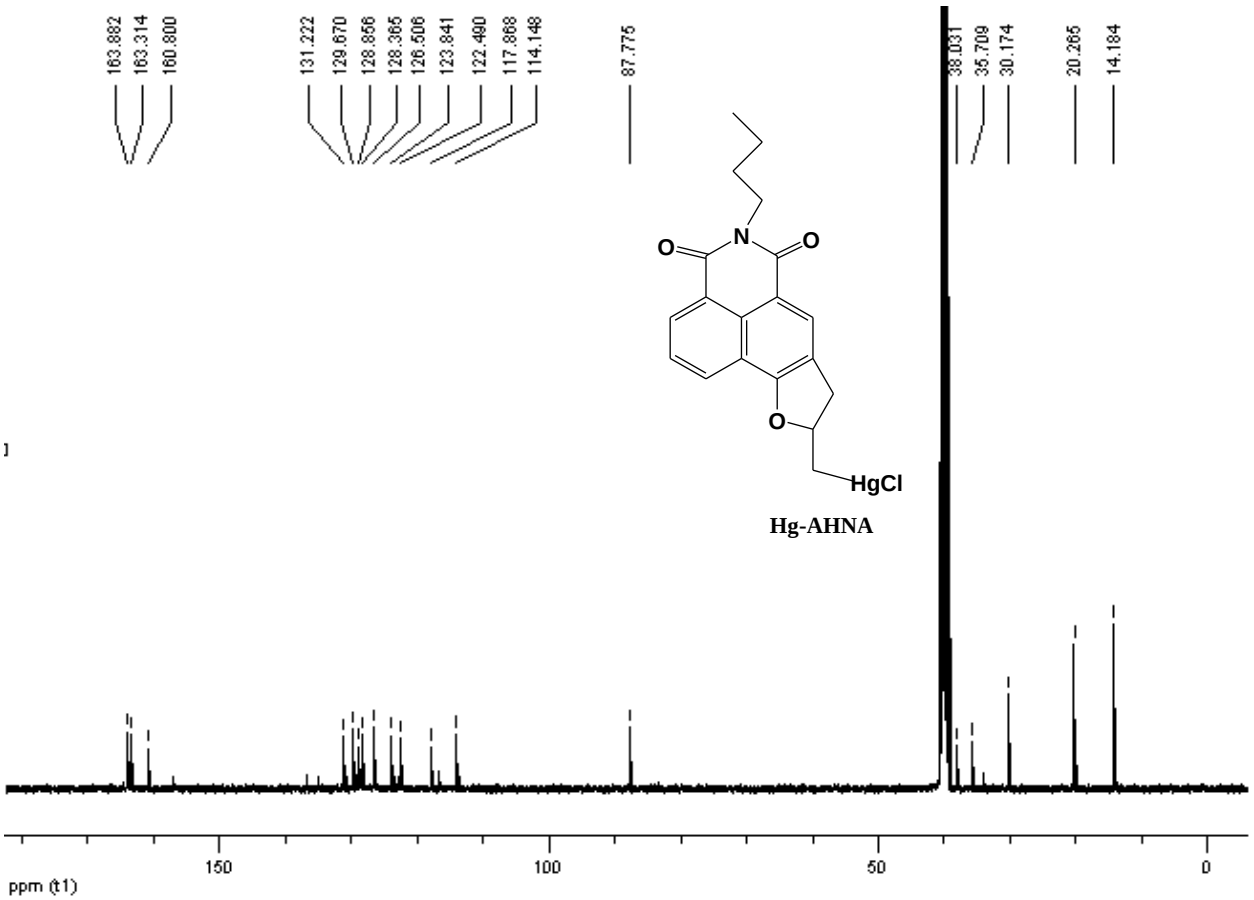

Figure S8. ^{13}C NMR for compround **Hg-AHNA** in DMSO-d_6

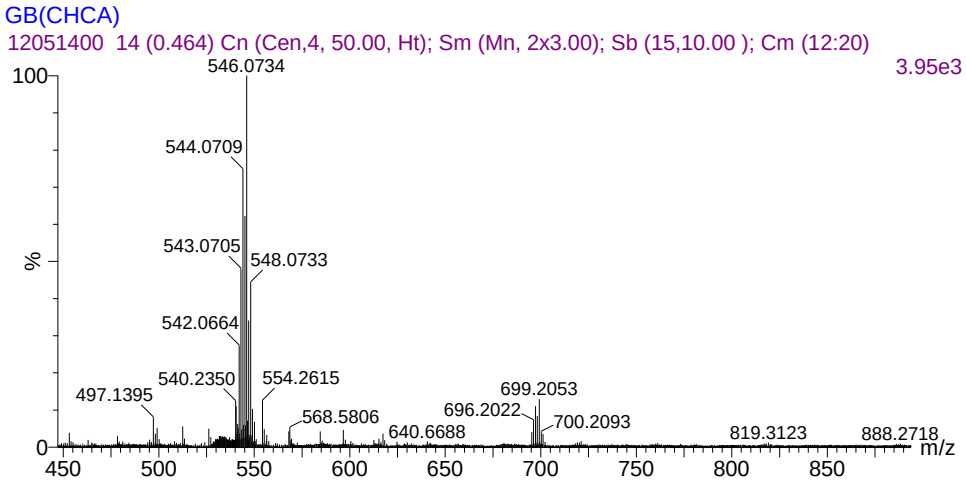

Figure S9. HRMS spectrum of compround **Hg-AHNA**

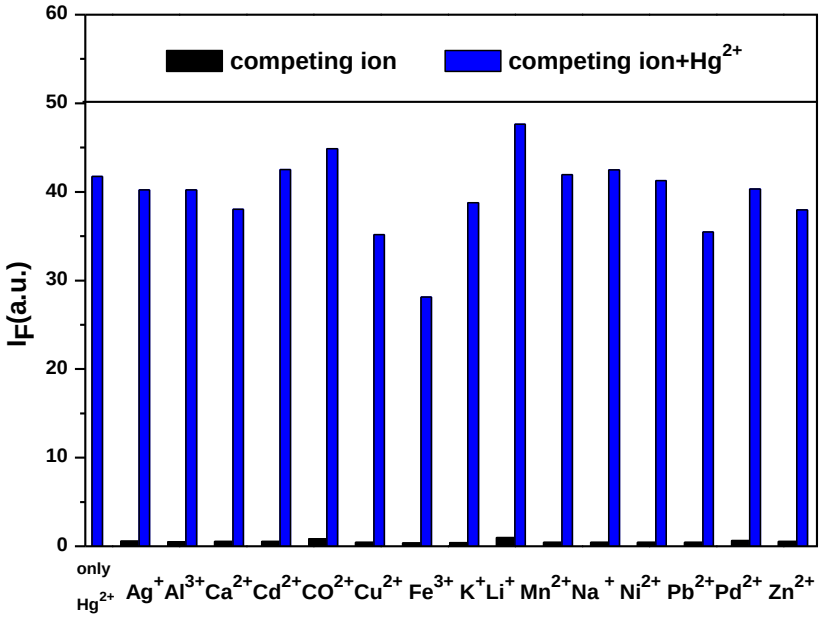

Figure S10. Changes in fluorescence of **AHNA** (10 μ M in Tris-HCl buffer solution containing1%DMSO,pH =7.4) upon addition of Hg^{2+} (5 equiv.) with various metal ions (5 equiv.)

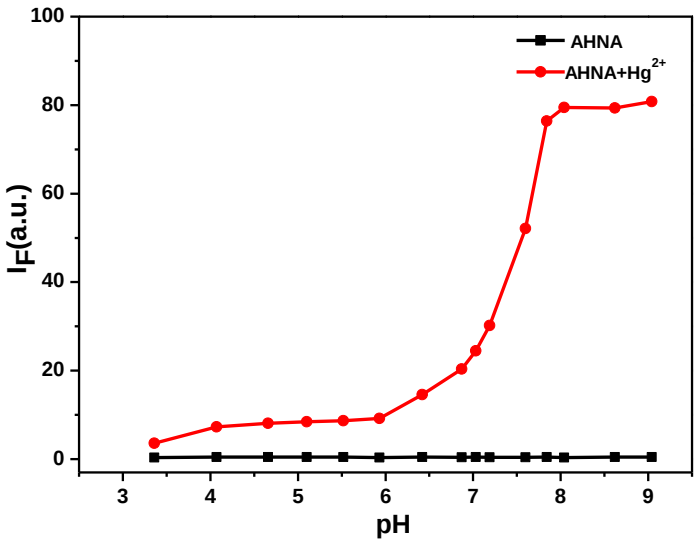

Figure S11. Changes in fluorescence of **AHNA** (black) and **AHNA** with Hg^{2+}(red) in buffer solution with different pH (10 μ M in Tris-HCl buffer solution containing1%DMSO,pH =7.4, excitation at 400nm,and emission was integrated at 500nm).

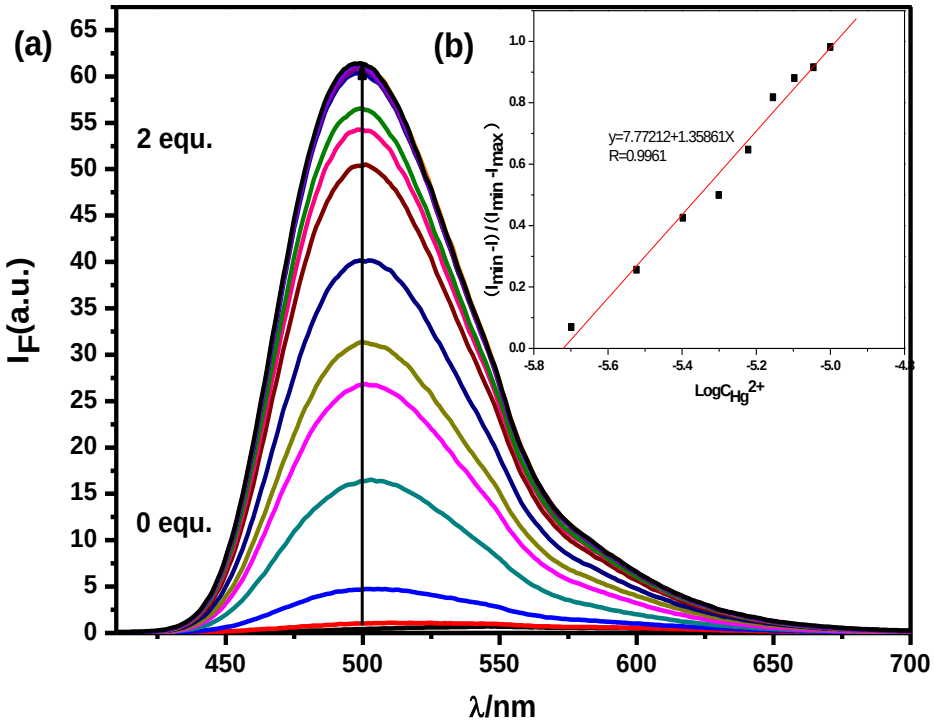

Figure S12. (a) Fluorescence emission spectra of **AHNA**（10 μM in Tris-HCl buffer solution containing1%DMSO,pH =7.4）responding to different concentrations of Hg^{2+}(0-2 equiv., excitation at 400nm). (b) Normalized response of fluorescence signal to changing Hg^{2+} concentrations in Tris-HCl buffer solution (10 μM containing1%DMSO,pH =7.4). (Ex.400 nm; Em.500 nm).

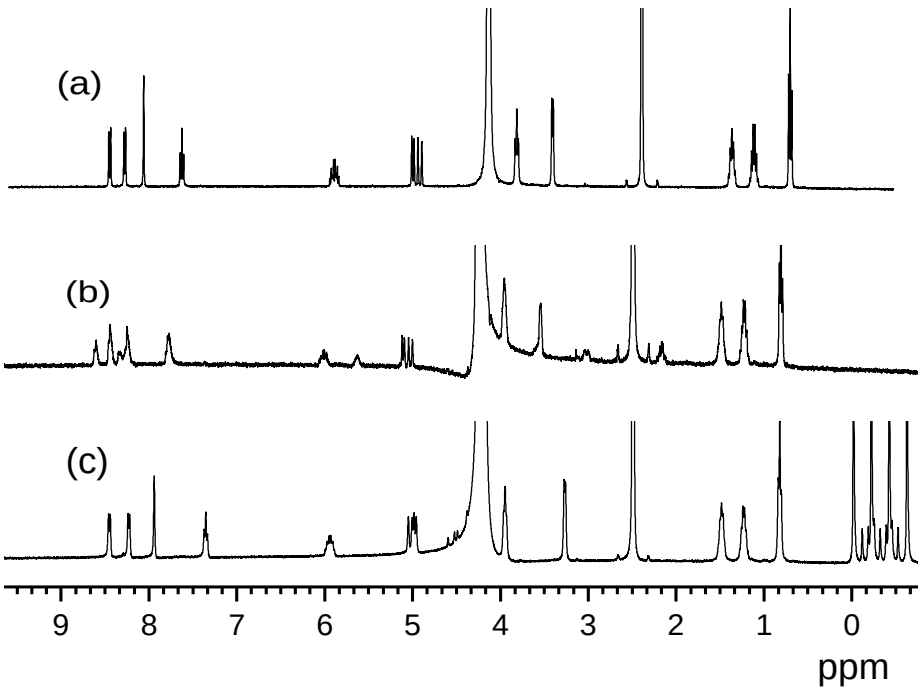

Figure S13. ^{1}H NMR spectra for (a) **AHNA**, (b) **AHNA** +$HgCl_2$ (5.0quiv.) and (c) **AHNA** +$HgCl_2$ + $NaBH_4$ in DMSO-d6 containing 30% D_2O

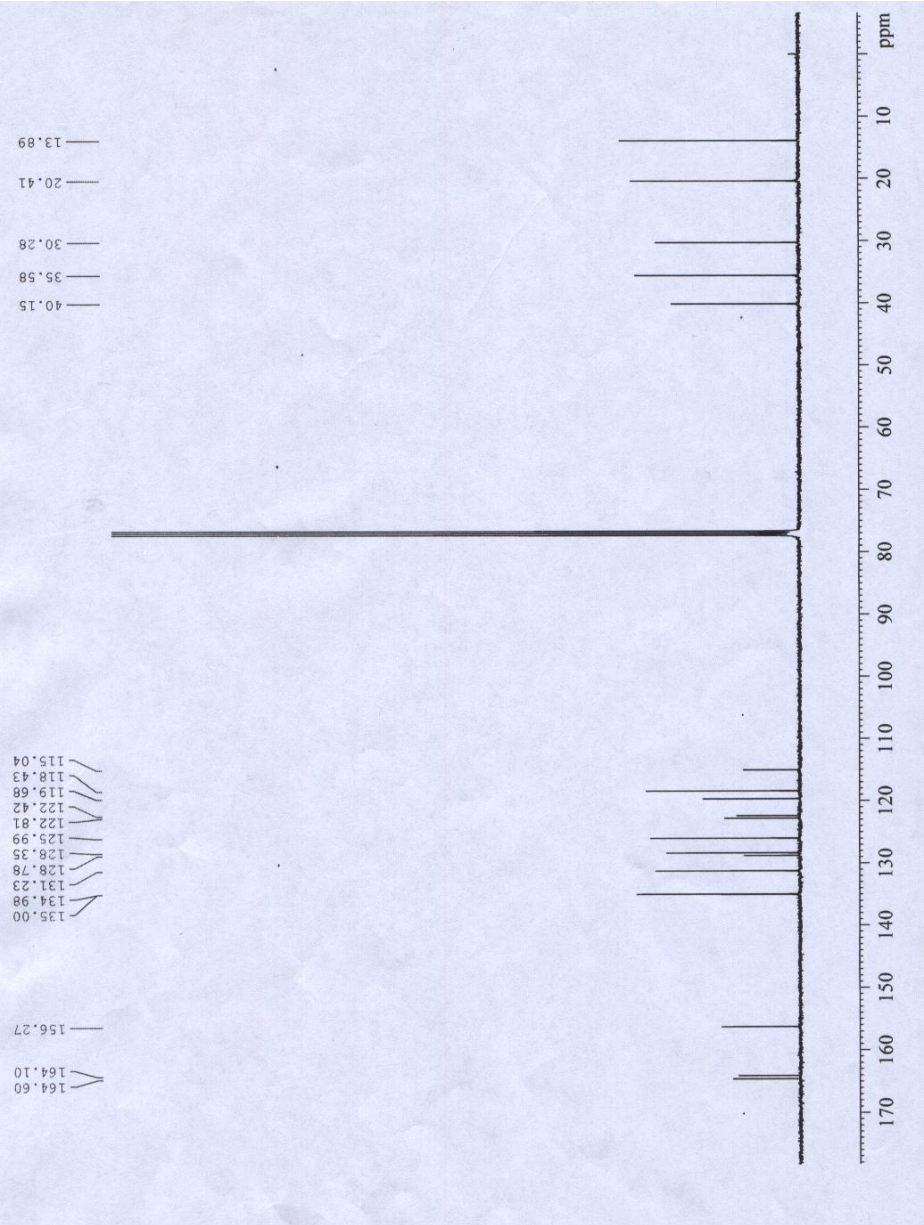

Figure S14. ^{13}C NMR spectrum of compround recycled **AHNA**

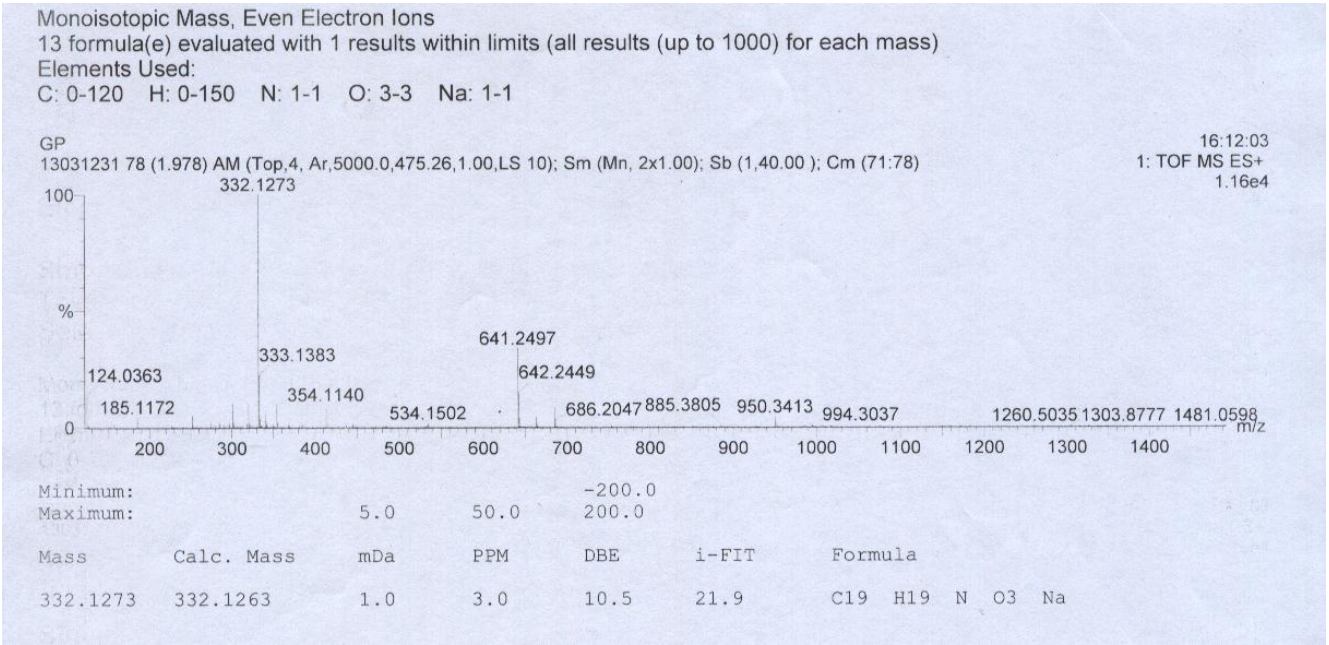

Figure S15. HRMS spectrum of compround recycled **AHNA** $[M+Na]^+$

Table 1. Crystallographic Data and Structure Refinements for single crystals of compounds **AHNA** and **Hg-AHNA**.

Compound reference	AHNA	Hg-AHNA
Chemical formula	$C_{19}H_{19}NO_3$	$C_{19}H_{18}ClHgNO_3$
CCDC Number	917431	917432
Formula Mass	309.35	544.38
Crystal system	Monoclinic	Tetragonal
a/Å	4.9619(4)	23.616(3)
b/Å	13.1060(14)	23.616(3)
c/Å	12.2014(9)	6.9313(15)
α/°	90.00	90.00
β/°	91.684(6)	90.00
γ/°	90.00	90.00
Unit cell volume/Å3	793.12(12)	3865.6(10)
Temperature/K	296(2)	296(2)
Space group	P2(1)	P4(2)/mbc
No. of formula units per unit cell, Z	2	8
No. of reflections measured	4293	20463
No. of independent reflections	2456	1863
Rint	0.0164	0.0742
Final R1 values (I > 2σ(I))	0.0439	0.0436
Final wR(F2) values (I > 2σ(I))	0.1161	0.1004
Final R1 values (all data)	0.0584	0.0825
Final wR(F2) values (all data)	0.1252	0.1107

$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]^2\}^{1/2}$