Electronic Supplementary Information

For

Ratiometric fluorescent probe for determining Pd^{2+} ions based on coordination reaction

Bo Qiao, Shiguo Sun, Na Jiang, Si Zhang and Xiaojun Peng

State Key Laboratory of Fine Chemicals, Dalian University of Technology, E224 West Campus, No. 2, Linggong Road, Ganjingzi District, 116024 Dalian, China. Fax: +86 411 84986304; Tel: +86 411 84986304; E-mail: shiguo@dlut.edu.cn, pengxj@dlut.edu.cn

Reagents and instruments

All starting materials were purchased and used without further purication. All solvents were analytical grade. The stock solution of **RI** and $PtCl_2$ were prepared in DMSO. The stock solution of $PdCl_2$ was prepared in 3:1 (v/v) MeOH/brine. The stock solution of $RuCl_3$ and $RhCl_3$ were prepared in 1:1 (v/v) MeOH/H_2O. The stock solution of other metal salts used in the experiments were prepared in distilled water. ^{1}H NMR and ^{13}C NMR spectra were obtained by Bruker Avance Ⅱ 400M spectrometer(in DMSO-d or $CDCl_3$, TMS as internal standard). Mass spectrometry data were obtained by HP1100 LC/MSD mass spectrometer or LTQ Orbitrap XL TM mass spectrometer. Fluorescence spectra were obtained by Varian CARY Eclipse fluorescence spectrophotometer. Absorption spectra were obtained by Agilent 8453 UV-Visible spectrophotometer. The pH values were obtained by PHS-3C pH meter model.

Synthesis of R2: Rhodamine B (**RB**, 5 g, 10.4 mmol) and ethanediamine (9 ml, 134.8 mmol) were dissolved in ethanol (50 mL) in a 250 mL flask, then the mixture was heated at reflux for 7 h. After ethanol was removed under vacuum, the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 10:1) to give **R2** as a pale yellow powder (4.7 g, yield: 93%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.94 – 7.86 (m, 1H), 7.50 – 7.38 (m, 2H), 7.14 – 7.03 (m, 1H), 6.43 (dd, J = 8.8, 4.0 Hz, 2H), 6.37 (d, J = 2.6 Hz, 2H), 6.27 (dd, J = 8.9, 2.6 Hz, 2H), 3.42 – 3.24 (m, 8H), 3.19 (t, J = 6.6 Hz, 2H), 2.43 (t, J = 6.6 Hz, 2H), 1.16 (t, J = 7.0 Hz, 12H). ES-API: $[M+H]^+$, calcd: m/z = 485.29, found: m/z = 485.3.

Synthesis of RI: **R2** (300 mg, 0.6 mmol) and isatoic anhydride (100 mg, 0.6 mmol) were add to a 100 mL flask with ethanol (20 ml), heated until they were dissolved. Then kept reflux with vigorous stirring for 2 h. After the mixture cooled to room temperature, white needle solid was precipitated out. Removed ethanol under vacuum, and purified the residue by column chromatography on neutral aluminum oxide (CH_2Cl_2/MeOH, 100:1) to give **RI** as a white powder (136 mg, yield: 37%). ^{1}H NMR (400 MHz, DMSO-d$_6$, δ ppm): 8.06 (t, J = 5.2 Hz, 1H), 7.85 – 7.75 (m, 1H), 7.56 – 7.44 (m, 2H), 7.35 (d, J = 7.8 Hz, 1H), 7.09 (t, J = 7.7 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.63 (d, J = 8.2 Hz, 1H), 6.44 (t, J = 7.5 Hz, 1H), 6.37 (dd, J = 10.1, 7.2 Hz, 6H), 3.31 (dd, J = 14.2, 7.1 Hz, 8H), 3.22 – 3.13 (m, 2H), 2.99 (s, 2H), 1.08 (t, J = 6.9 Hz, 12H). ^{13}C NMR

(100 MHz, DMSO-d_6, δ ppm): 169.08, 168.08, 154.34, 153.07, 150.08, 148.87, 133.22, 132.04, 130.41, 128.53, 124.02, 122.83, 116.76, 114.84, 108.64, 105.28, 97.85, 64.72, 44.14, 38.18, 12.89. HRMS: $[M+H]^+$, calcd: m/z = 604.3288, found: m/z = 604.3268. Elemental analysis, calcd.: C, 73.61; H, 6.84; N, 11.60; Found: C, 73.41; H, 6.77; N, 11.37.

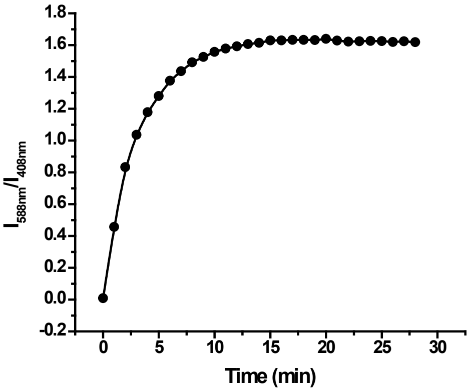

Fig. S1 Time-dependent fluorescent intensities ratio (I_{588nm}/I_{408nm}) change of **RI** (10 μM) with $PdCl_2$ (10 μM) in EtOH/H_2O (1:1, v/v) at room temperature, λ_{ex} = 360 nm.

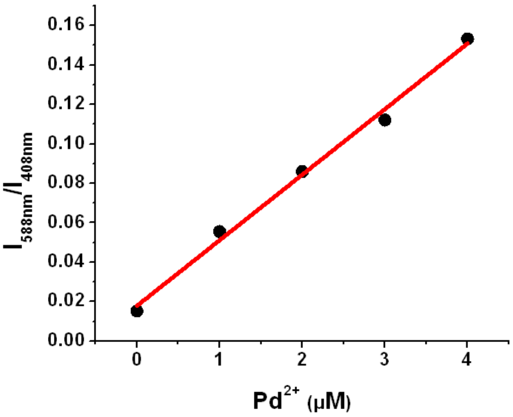

Fig. S2 Changes in fluorescent intensities ratio (I_{588nm}/I_{408nm}) of **RI** (10 μM) in the presence of different concentrations of $PdCl_2$ (0 μM to 4 μM). R^2 = 0.9922.

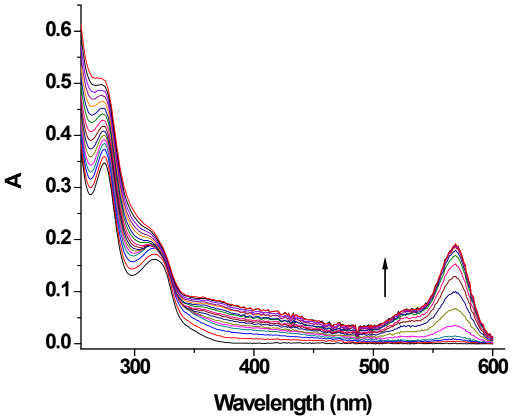

Fig. S3 UV-Vis spectra of **RI** (10 μM) upon titration of Pd^{2+} (30 μM) in EtOH/H_2O (1:1, v/v) at room temperature after incubation of 10 min.

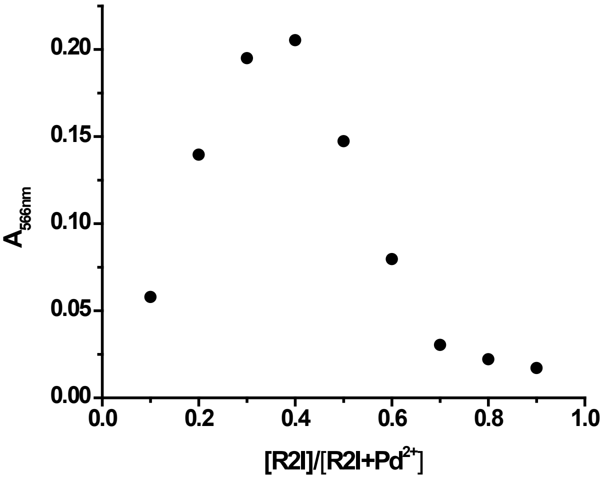

Fig. S4 Job plot of **RI** for Pd^{2+} determined by UV-Vis method (at 566 nm), The total concentration of **RI** and Pd^{2+} was 30 μM.

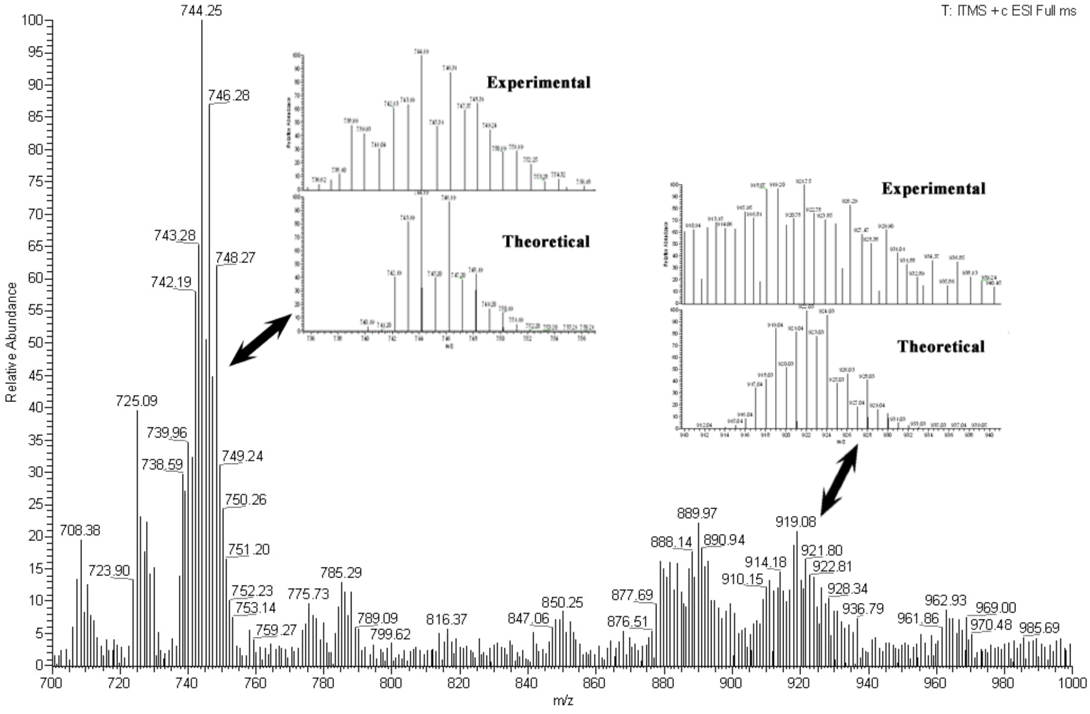

Fig. S5 The ESI Full ms of **RI**/Pd^{2+} in methanol.

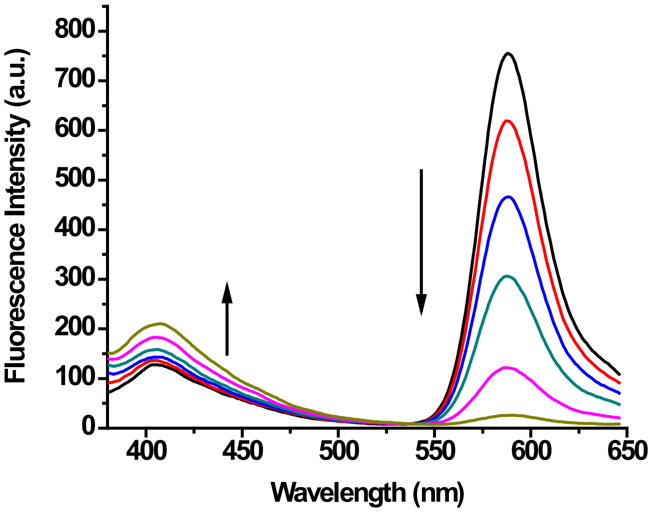

Fig. S6 Fluorescence spectral changes of **RI** (10 μM)/Pd^{2+} (20 μM) upon addition of S^{2-} (0 μM to 25 μM) in EtOH/H_2O (1:1, v/v). λ_{ex} = 360 nm.

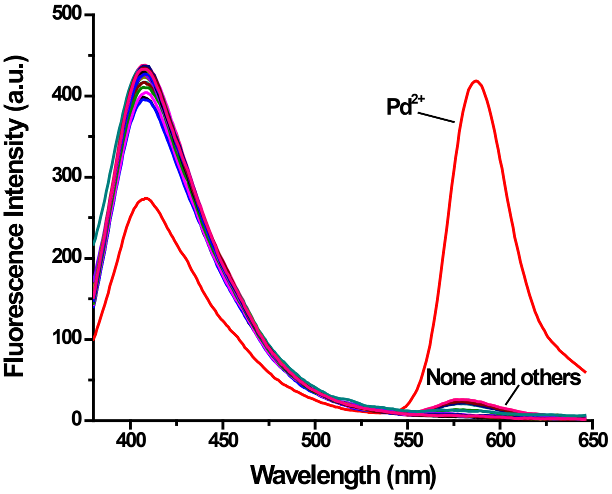

Fig. S7 Fluorescence spectra of **RI** (10 μM) in the presence of different metal ions (10 μM for Pd^{2+} and 20 μM for others) in EtOH/H_2O (1:1, v/v). λ_{ex} = 360 nm.

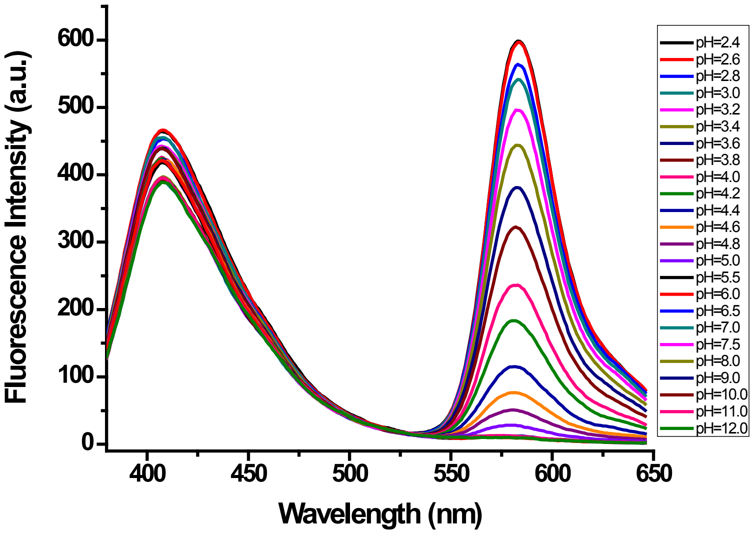

Fig. S8 Fluorescence intensity of **RI** (10 μM) in different pH values (2.4–12) in EtOH/H_2O (1:1, v/v). λ_{ex} = 360 nm.

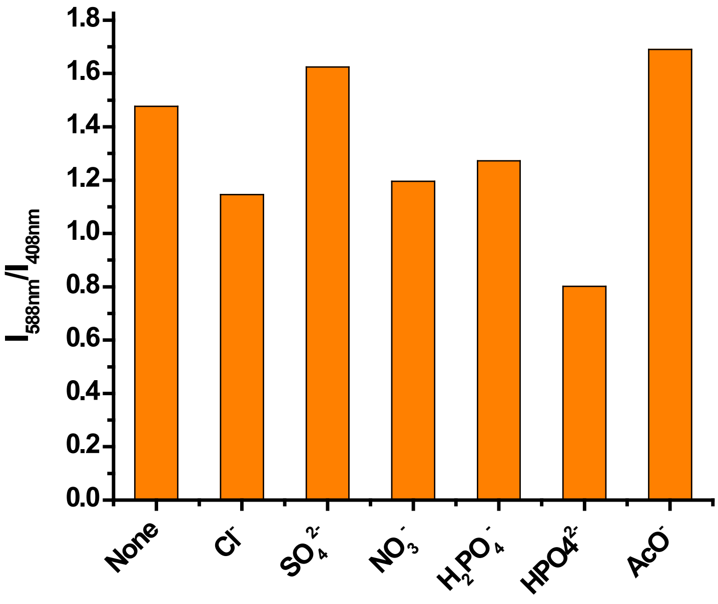

Fig. S9 Fluorescence intensity ratio (I_{588nm}/I_{408nm}) of **RI** (10 μM) after addition of Pd^{2+} (10 μM) in the presence of common anions (20 μM) in EtOH/H_2O (1:1, v/v). λ_{ex} = 360 nm.

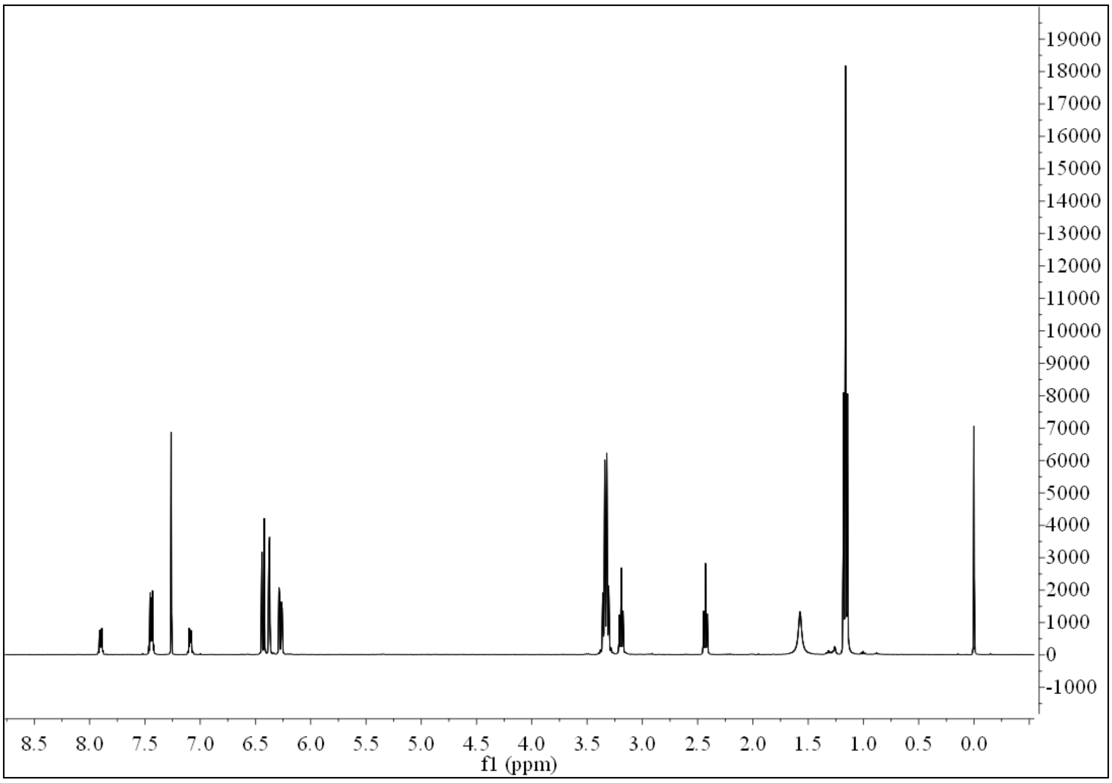

Fig. S10 ^{1}H NMR of **R2**.

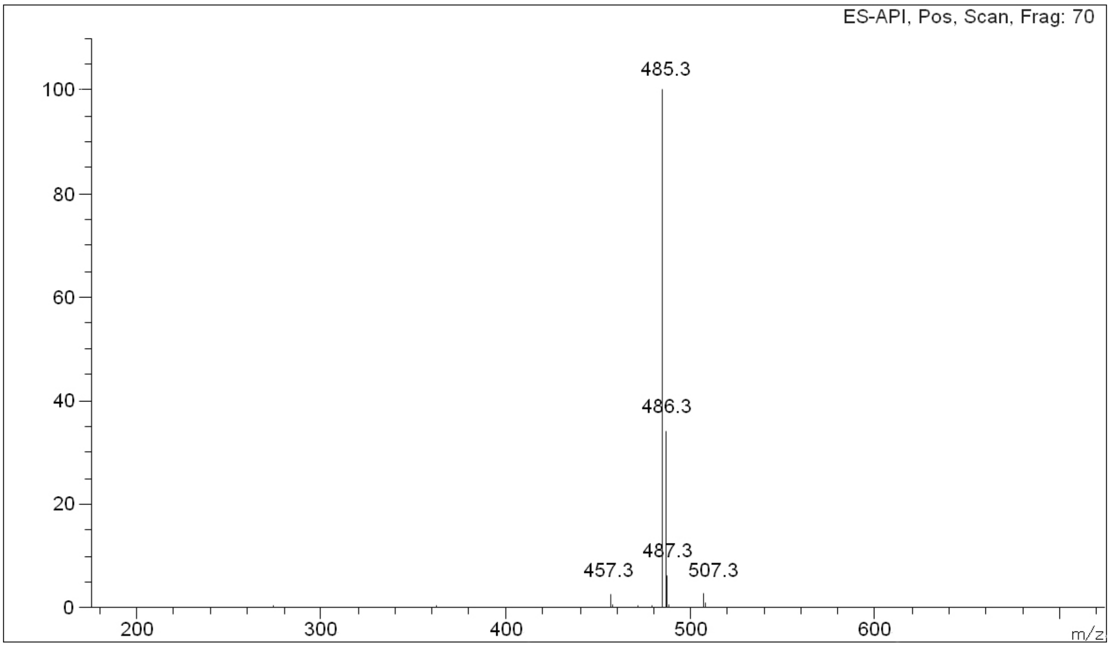

Fig. S11 MS of **R2**.

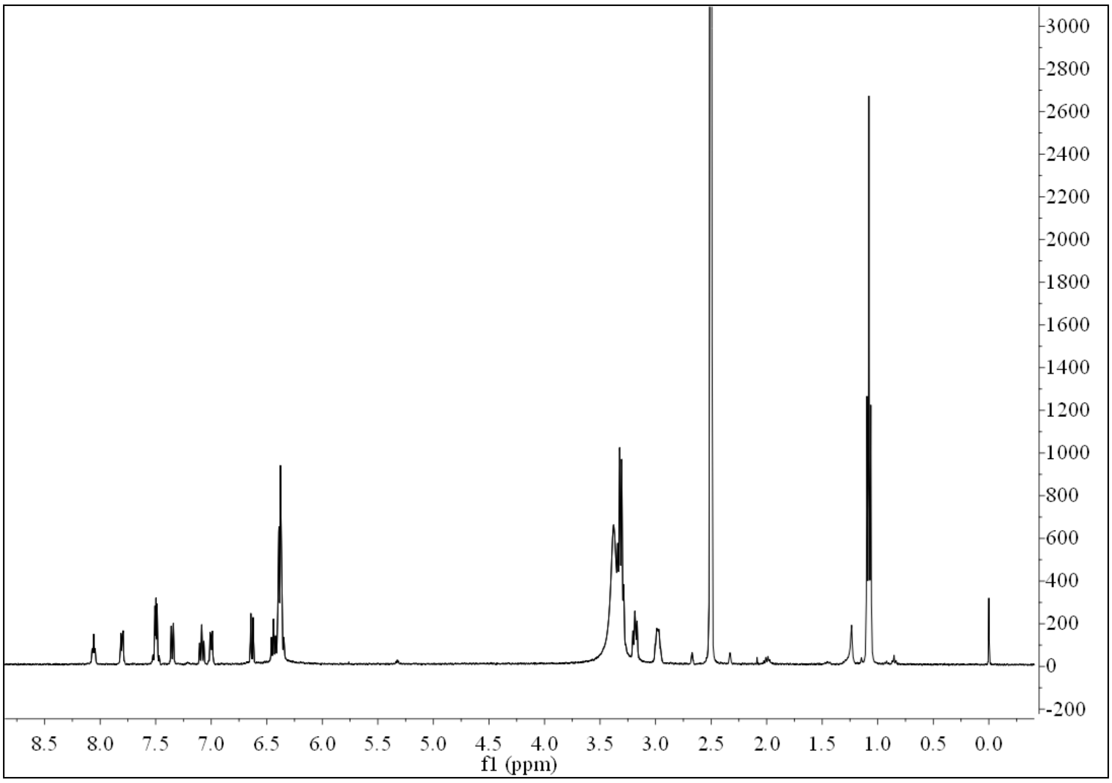

Fig. S12 ^{1}H NMR of **RI**.

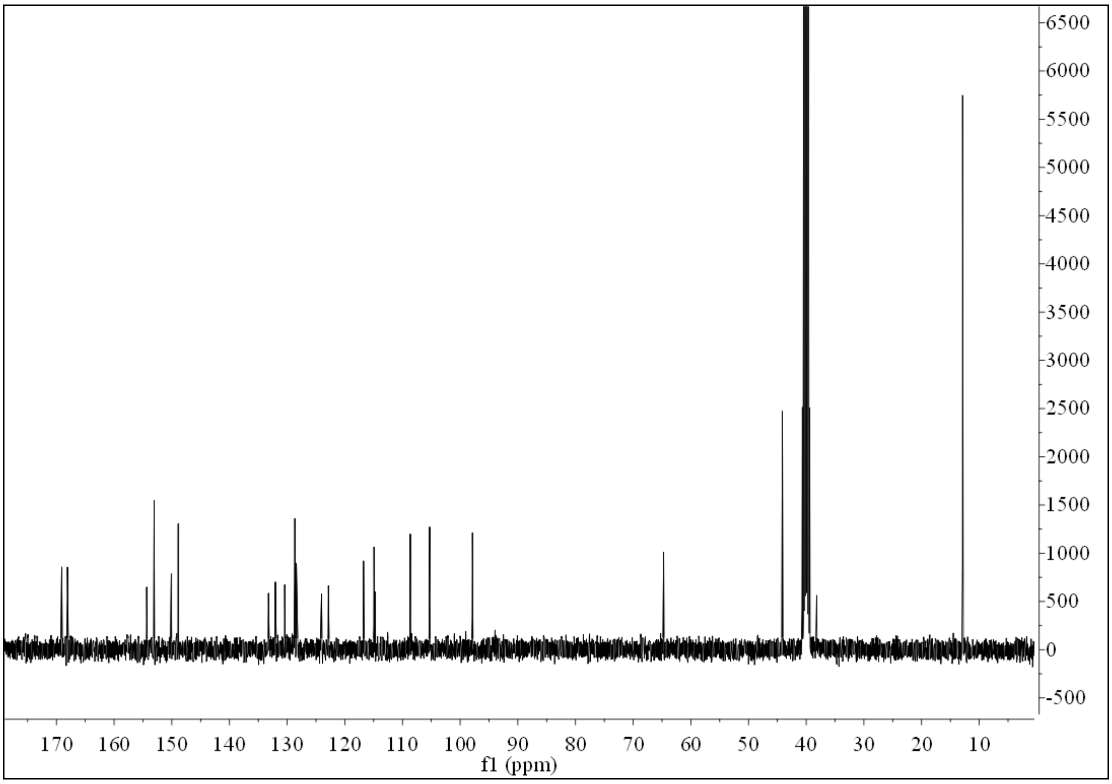

Fig. S13 ^{13}C NMR of **RI**.

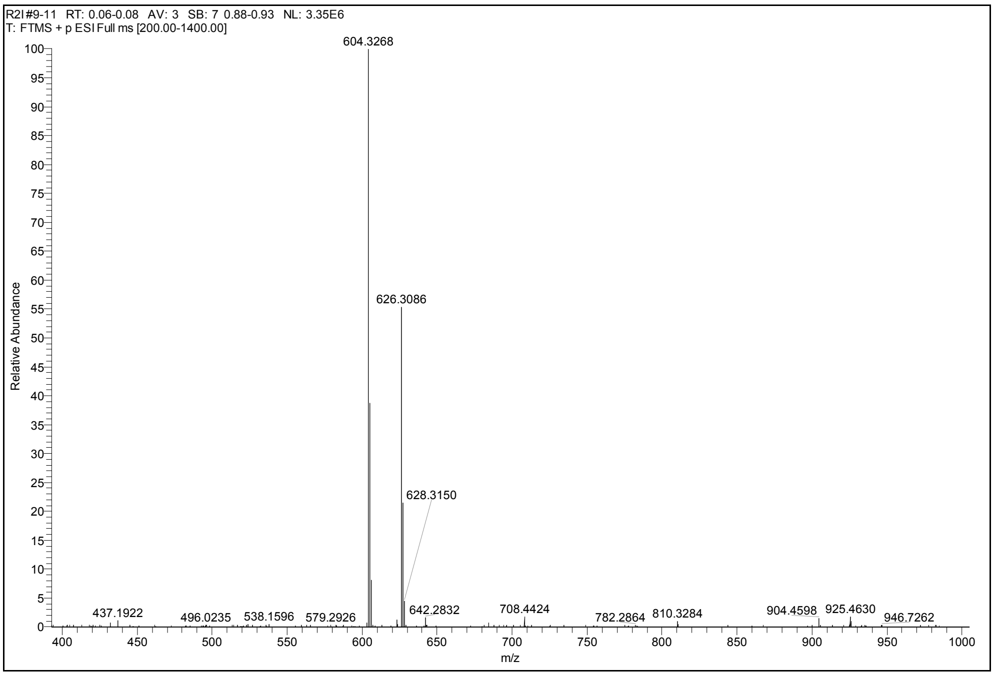

Fig. S14 HRMS of **RI**.