Electronic Supplementary Information For

A Fluorescent and Colorimetric Probe Specific for Palladium Detection

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Materials and general methods:

All solvents used were of analytical grade. Analyte solutions were prepared from KCl, NaCl, NH_4Cl, $CaCl_2$, $BaCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, $CdCl_2{\cdot}2.5H_2O$, $FeCl_3{\cdot}6H_2O$, $CrCl_3{\cdot}6H_2O$, $MnCl_2{\cdot}5H_2O$, $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $PbCl_2$, $LaCl_3{\cdot}7H_2O$, $HgCl_2$, $Cu(NO_3)_2{\cdot}2.5H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ by separately dissolved in distilled water, 2.5 mM for $PbCl_2$ and $HgCl_2$, 25.0 mM for other cations. A 10.0 mM solution of **RPd1** (26.8 mg, 0.05 mmol) was prepared in DMSO (5 mL) and stored in a refrigerator for use. A 100 mM solution of PPh_3 (262.3 mg, 1.00 mmol) was prepared in DMSO (10 mL). A 5.0 mM stock solution of $PdCl_2$ (8.9 mg, 0.05 mmol) was prepared in 75:25 MeOH/brine (10 mL). Further dilution of the 5.0 mM stock solution of $PdCl_2$ with MeOH was done to prepare the 1.0 mM and 100.0 μM stock solutions. A 50.0 μM solution of $PtCl_2$ (3.32 mg, 0.0125 mmol) was prepared in EtOH/H_2O (1 : 1, v/v, 250 mL) solution, directly used for analysis. A 5.0 mM solution of $Pd(OAc)_2$ (5.61 mg, 0.025 mmol) was prepared in acetone (5mL). A 1.0 mM solution of $Pd(PPh_3)_4$ (11.6 mg, 0.010 mmol, freshly synthesized from $PdCl_2$, with colour of light yellow) was prepared in 95 : 5 MeOH/DMF (10 mL). Measurements were done after addition of different cations to **RPd1** solutions overnight.

^{1}H-NMR, ^{13}C-NMR and ^{1}H-^{1}H COSY spectras were recorded on a VARIAN INOVA-400 spectrometer chemical shifts reported as ppm (in $CDCl_3$, TMS as internal standard). Mass spectrometry data were obtained with a HP1100LC/MSD mass spectrometer and a LC/Q-TOF MS spectrometer. Fluorescence measurements were performed on a VAEIAN CARY Eclipse Fluorescence Spectrophotometer (Serial No. FL0812-M018) and the slit width was 5 nm for excitation and 2.5 nm for emission. All pH measurements were made with a Model PHS-3C meter.

The quantum yield of **RPd1, RPd1**-Pd^{2+} and **RPd1**-Pd^0/PPh_3 were determined according to the method bellow.

$$\varphi_u = \frac{(\varphi_s)(FA_u)(A_s)(\lambda_{exs})(\eta_u^{\,2})}{(FA_s)(A_u)(\lambda_{exu})(\eta_s^{\,2})}$$

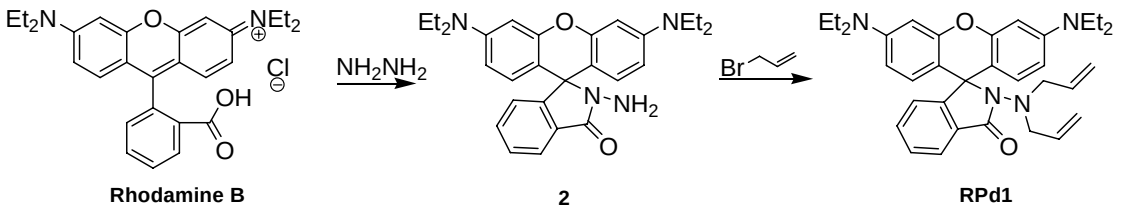
Where φ is fluorescence quantum yield; FA is integrated area under the corrected emission spectra; A is the absorbance at the excitation wavelength; λ_{ex} is the excitation wavelength; η is the refractive index of the solution; the subscripts u and s refer to the unknown and the standard, respectively. We chose rhodamine B as standard, which has the fluorescence quantum yield of 0.49 in ethanol.[1]

Reactors contamination experimental procedure.

To four 10 mL round-bottom flasks were added K_2CO_3 (10 mg) and THF (3 mL). To three of the four flasks were then added $PdCl_2$, $Pd(AcO)_2$ and $Pd(PPh_3)_4$ (10 mg respectively). The mixtures in the three flasks were stirred at room temperature for 1 h, and then all chemicals were removed. The four flasks were brushing with detergent, washing with water and acetone three times.

To the four washed flasks were added 5 mL of **RPd1** aqueous solution (10 μM). The solutions were stirred at room temperature overnight, then fluorescence measurements were performed (Slit width was 5 nm both for excitation and emission).

Synthetic procedures:



Rhodamine B **2** **RPd1**

Scheme S1. Synthesis of **RPd1.**

Synthesis of 2

Rhodamine hydrazide (**2**) was synthesized from rhodamine B by the procedure published in literature.[2]

Synthesis of RPd1

2 (300.0 mg, 0.66 mmol), K_2CO_3 (96.6 mg, 0.7 mmol) was dissolved in 20 mL acetic ether in a 50-mL flask. 1.0 mL (excess) 3-bromopropene was then added dropwises with vigorous stirring. The mixture was refluxed overnight. After removal of acetic ether under vacuum, the residue was purified by flash chromatography with CH_2Cl_2/acetic ether as eluent to give the white powder **RPd1** (159.3 mg, yield: 45.0%) . TLC analysis: R_f = 0.6 in 5.0% acetic ether in CH_2Cl_2.

^{1}H-NMR (400 MHz, $CDCl_3$), δ_H (ppm): 7.88 (d, 1H, *J* = 7.6 Hz, C_6H_4), 7.51 (m, 2H, *J*

= 4.8 Hz, C_6H_4), 7.21 (d, 1H, *J* = 6.8 Hz, C_6H_4), 6.44 (s, 2H, Xanthene-H), 6.36 (d, 2H, *J* = 8.8 Hz, Xanthene-H), 6.26 (d, 2H, *J* = 6.8 Hz, Xanthene-H), 5.09 (m, 2H,CH), 4.85 (d, 2H, *J* = 16.8 Hz, CH_2), 4.72 (d, 2H, *J* = 10.0 Hz, CH_2), 3.50 (s, 2H, CH_2), 3.35 (q, 8H, *J* = 7.2 Hz, CH_2), 3.31 (s, 2H, CH_2), 1.15 (t, 12H, *J* = 7.2 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$), δ_C (ppm): 165.97, 155.01, 149.30, 149.15, 135.89, 133.85, 132.80, 129.31, 128.35, 124.44, 122.63, 116.67, 107.75, 107.18, 98.50, 66.15, 58.58, 45.05, 12.36; **Q-TOF MS**: $[M+H]^+$ 537.3230; found 537.3223.

Experimental procedures

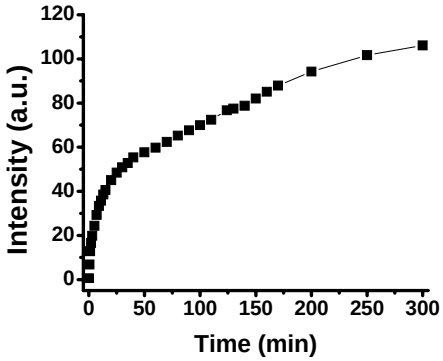


Fig. S1. Time dependent fluorescence intensity (at 580 nm) changes of **RPd1** (10 μM) with 1.0 equiv of Pd^{2+} in ethanol/H_2O (1:1, v/v, 25 °C), λ_{ex} = 530 nm.

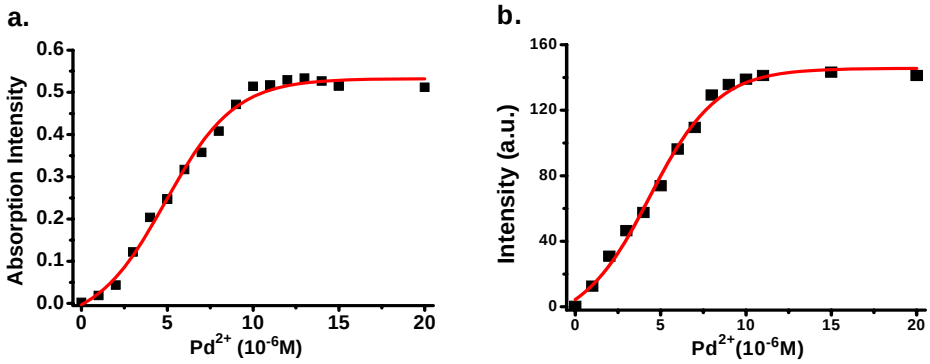


Fig. S2. Absorption (a, at 560 nm) and fluorescence (b, at 580 nm) intensities of **RPd1** (10 μM) upon addition of Pd^{2+} (0-20 μM). Condition: ethanol/H_2O (1:1, v/v, 25 °C) solution, λ_{ex} = 530 nm.

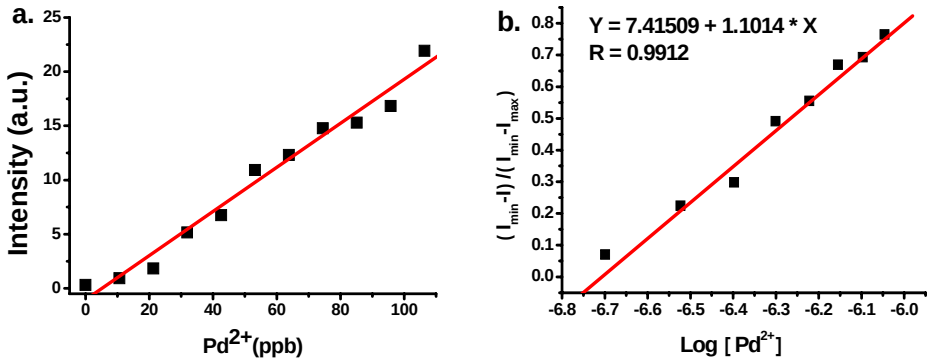


Fig. S3. a, fluorescence intensity at 580 nm of **RPd1** (10 μM) upon addition of Pd^{2+} (0-106.4 ppb, 1.0 μM of Pd^{2+} in the form of $PdCl_2$ is equal to 106.4 ppb of Pd^{2+}). b, normalized response of the fluorescence signal to changing Pd^{2+} concentrations. A linear regression curve was then fitted to these normalized fluorescence intensity data, and the point at which this line crossed the ordinate axis was considered as the detection limit (1.85×10^{-7} M).[3] Y = 7.41509 + 1.1014 * X, R = 0.9912.

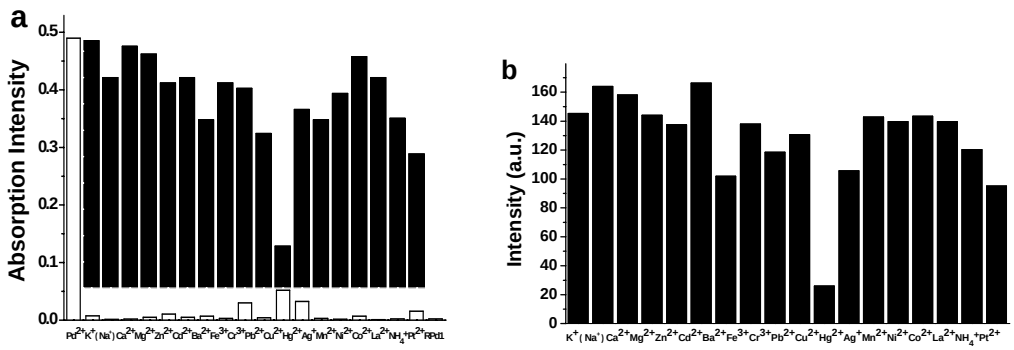


Fig. S4. Absorption (a, at 560 nm) and fluorescence (b, 580 nm) responses of **RPd1** (10 μM) to miscellaneous cations. White bars represent **RPd1** only and **RPd1** + cations; Black bas represent **RPd1** + Pd^{2+} in the presence of other cations (10 μM for Pd^{2+} and 50 μM for others). Condition: ethanol/H_2O (1:1, v/v, 25 °C) solution, λ_{ex} = 530 nm.

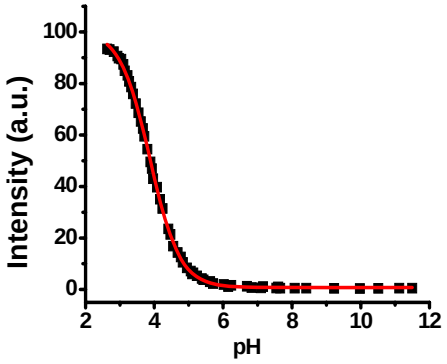


Fig. S5. Influence of pH on fluorescence at 580 nm for **RPd1** (10 μM) in ethanol

aqueous solution, λ_{ex} = 530 nm. The pH of solution was adjusted by aqueous solution of NaOH (1 M) or HCl (1 M).

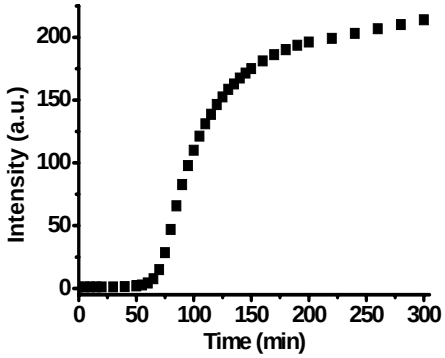


Fig. S6. Time dependent fluorescence intensity (at 580 nm) changes of **RPd1** (10 μM) with 1.0 equiv of Pd^{2+} in ethanol/H_2O (1:1, v/v, contained 100 μM PPh_3, 25 °C), λ_{ex} = 530 nm.

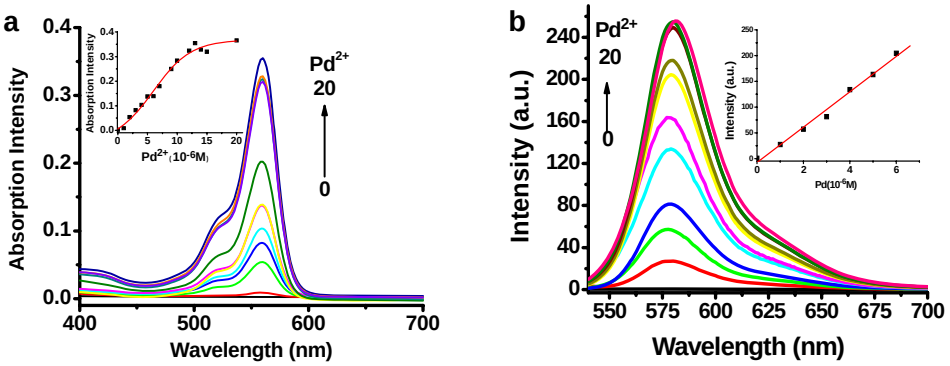


Fig. S7. Absorption (a) and fluorescence (b) spectral changes of **RPd1** (10 μM) upon addition of Pd^{2+} (0-20 μM). Inset: a, absorption intensity at 560 nm (0-20 μM); b, fluorescence intensity at 580 nm (0-6 μM). Condition: ethanol/H_2O (1:1, v/v, contained 100 μM PPh_3, 25 °C) solution, λ_{ex} = 530 nm.

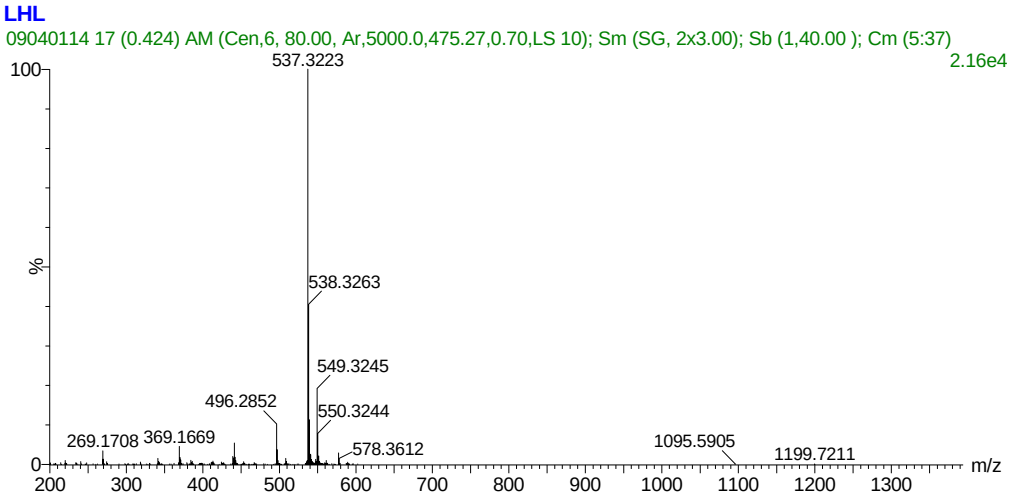


Fig. S8. TOF-MS of **RPd1.**

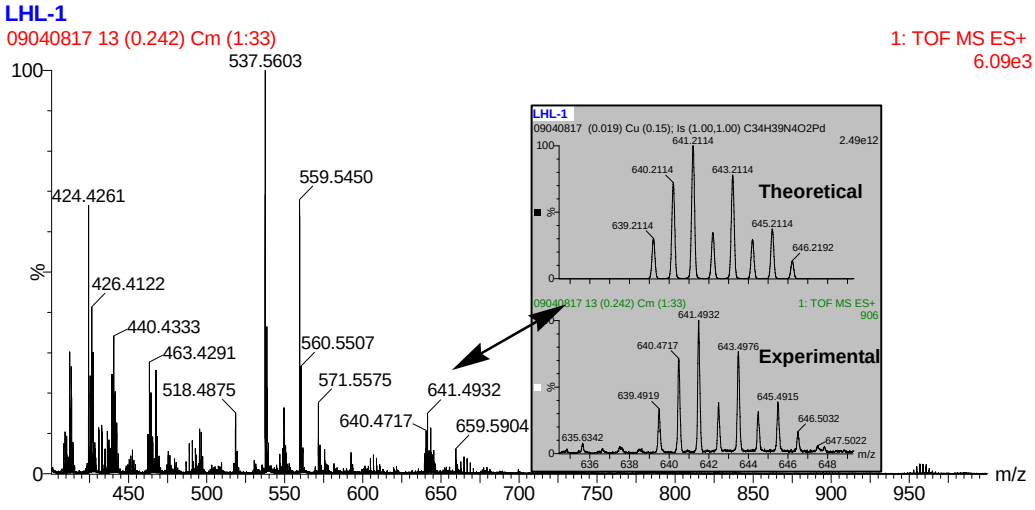


Fig. S9. TOF-MS of **RPd1** + $PdCl_2$: [**RPd1** + Pd^{2+} - H^+]$^+$.

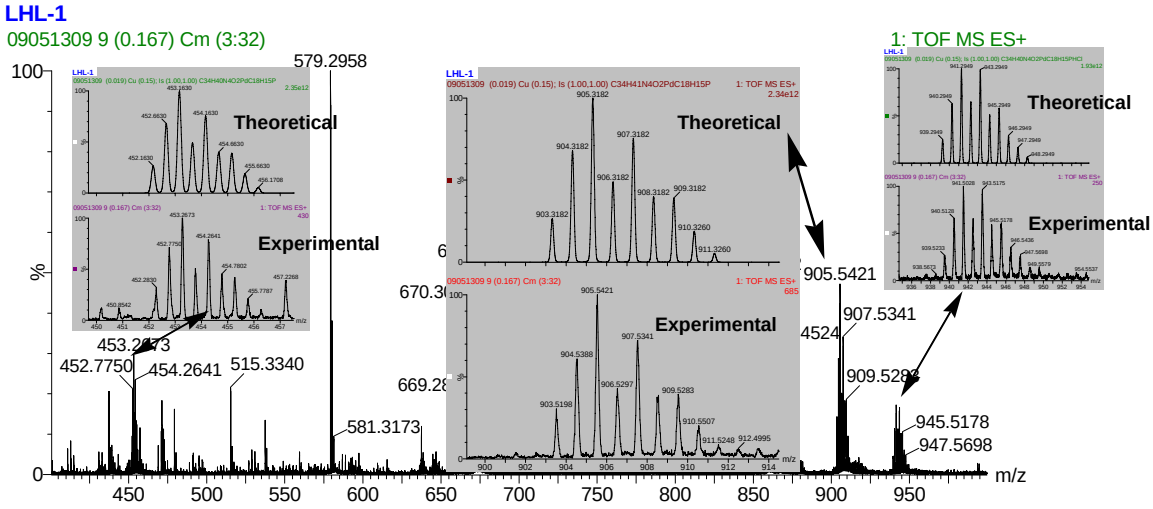


Fig. S10. TOF-MS of **RPd1** + $PdCl_2$ + PPh_3: [**RPd1** + Pd^0 + PPh_3 + $2H^+$]$^{2+}$, [**RPd1** + Pd^0 + PPh_3 + H^+]$^+$, [**RPd1** + Pd^0 + PPh_3 + HCl + H^+]$^+$.

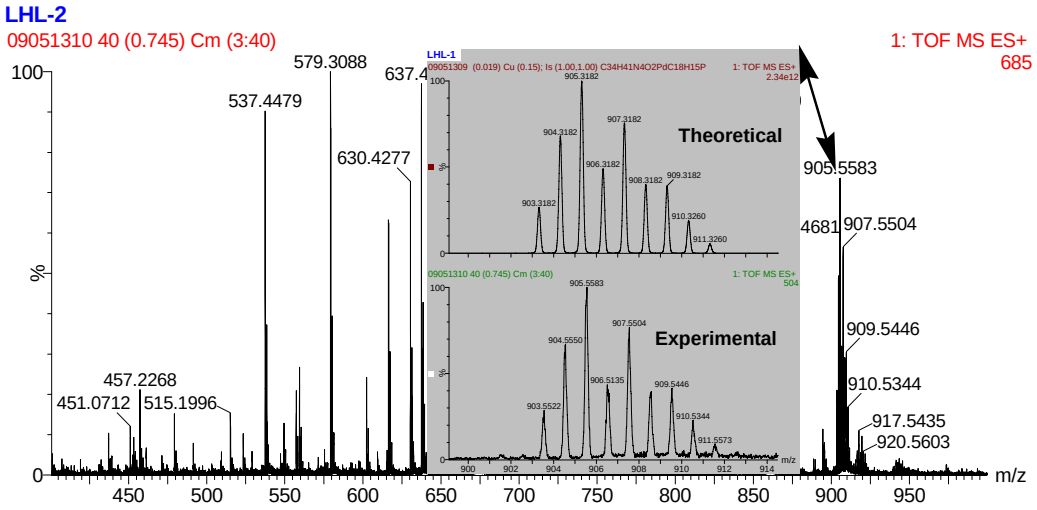


Fig. S11. TOF-MS of **RPd1** + $Pd(PPh_3)_4$: [**RPd1** + Pd^0 + PPh_3 + H^+]$^+$.

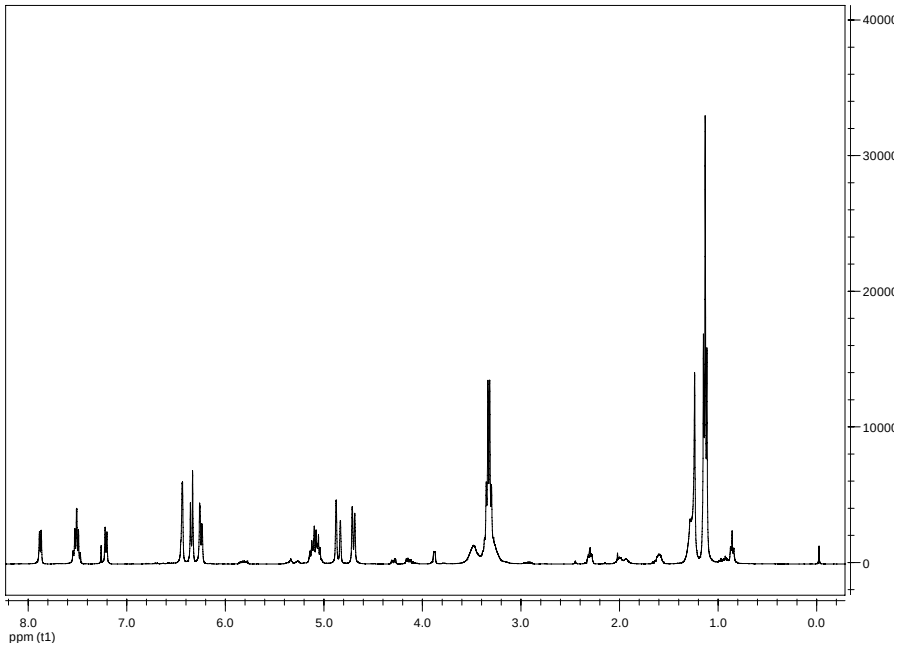


Fig. S12. ^{1}H-NMR of **RPd1.**

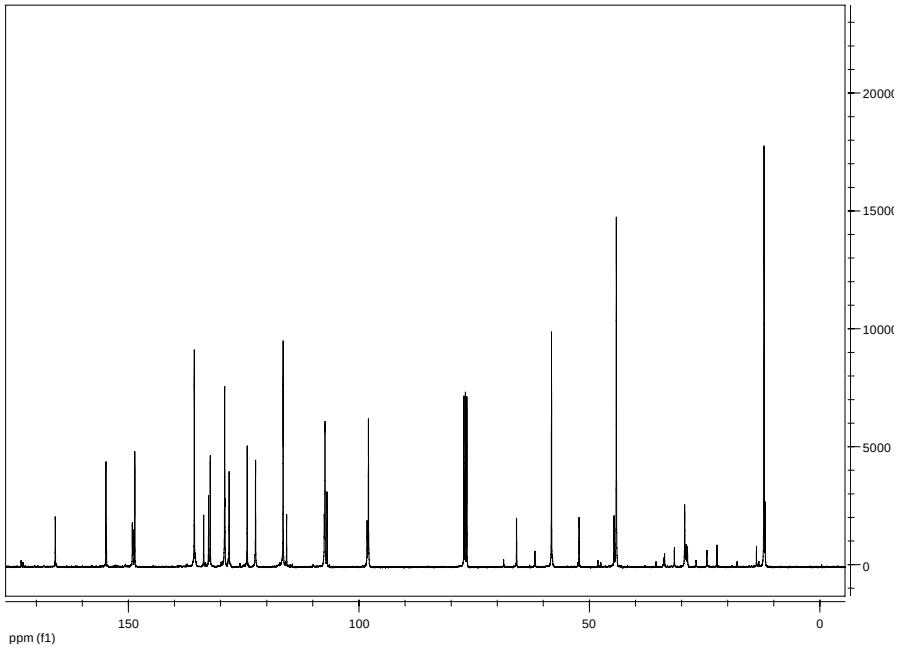


Fig. S13. ^{13}C-NMR of **RPd1.**

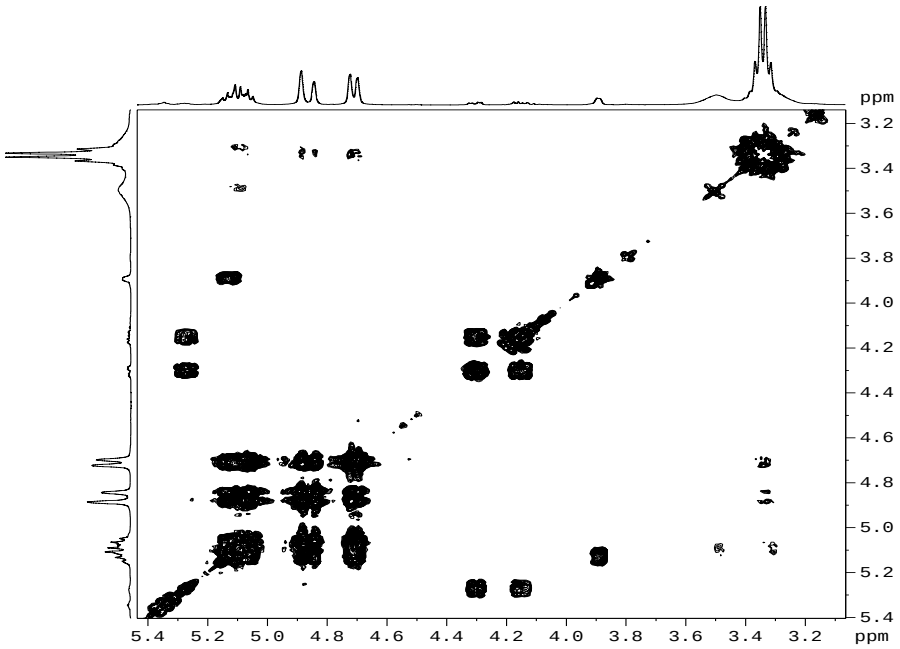


Fig. S14. ^{1}H-^{1}H COSY of **RPd1.**

References:

1. K. G. Casey and E. L. Quitevis, *J. Phys. Chem*., 1988, **92**, 6590.
2. X. F. Yang, X. Q. Guo and Y. B. Zhao, *Talanta*, 2002, **57**, 883.
3. M. Shortreed, R. Kopelman, M. Kuhn and B. Hoyland, *Anal. Chem*., 1996, **68**, 1414.