

## Supplementary Information

### **A colorimetric and ratiometric fluorescence probe for detection of palladium in the red light region**

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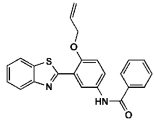
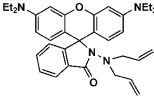
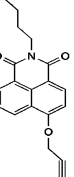
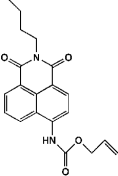
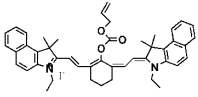
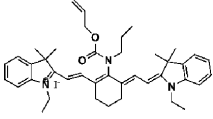
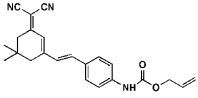
Key Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China. E-mail: [baozhutian@ecust.edu.cn](mailto:baozhutian@ecust.edu.cn); [jlzhang@ecust.edu.cn](mailto:jlzhang@ecust.edu.cn).

Table S1. Photophysical data of probe 1 and compound 2

Compound	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	$\Phi^{\text{a}}$
Probe 1	420	570	31000	0.003
Compound 2	472	643	36000	0.016

<sup>a</sup>The fluorescent quantum yields were determined using rhodamine 6G as a reference dye ( $\Phi = 0.94$  in EtOH).

Table S2. Comparison of determined detection limit with those of some literatures.

Probe	$\lambda_{\text{ex}}/\lambda_{\text{em}}$ (nm)	Linear range ( $\mu\text{M}$ )	Detection limit	Reference
	350/550	1–8	5.2 nM	Anal. Chim. Acta. 2013, 786, 139-145.
	530/580	0–33.3	185 nM	Chem. Commun. 2010, 46, 1079–1081.
	410/480 410/553	0–7	70 nM	Chem. Commun. 2011, 47, 8656–8658
	403/498 403/524	0–1	6.1 nM	Org. Lett. 2011, 13 (18), 4922-4925.
	740/805 545/655	0–50	2.47 nM	Chem. Commun. 2014, 50, 13525-13528.
	640/750	0–1	3.8 nM	Analyst, 2013, 138, 3667-3672.
	472/570 472/643	0–1	24.2 nM	This Work

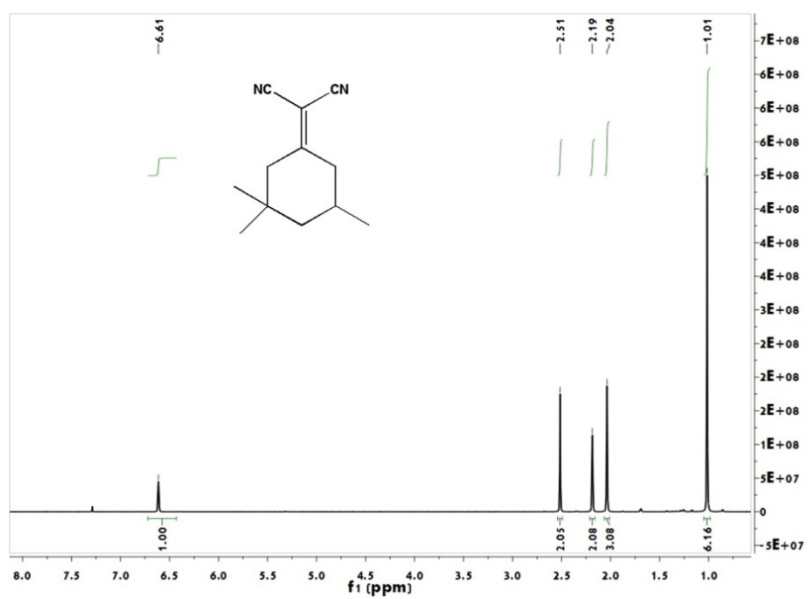


Fig. S1.  $^1\text{H}$  NMR spectrum of compound 3 in  $\text{CDCl}_3$

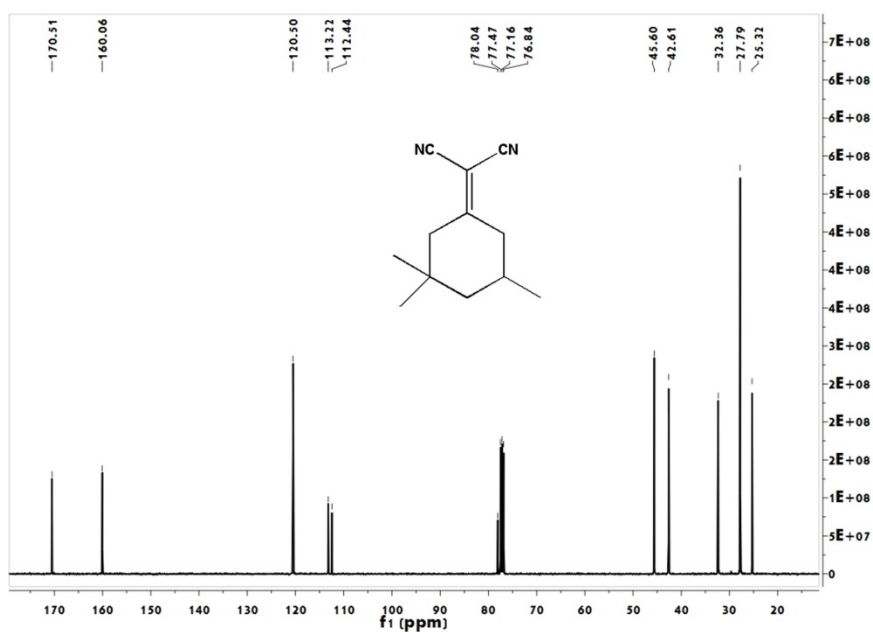
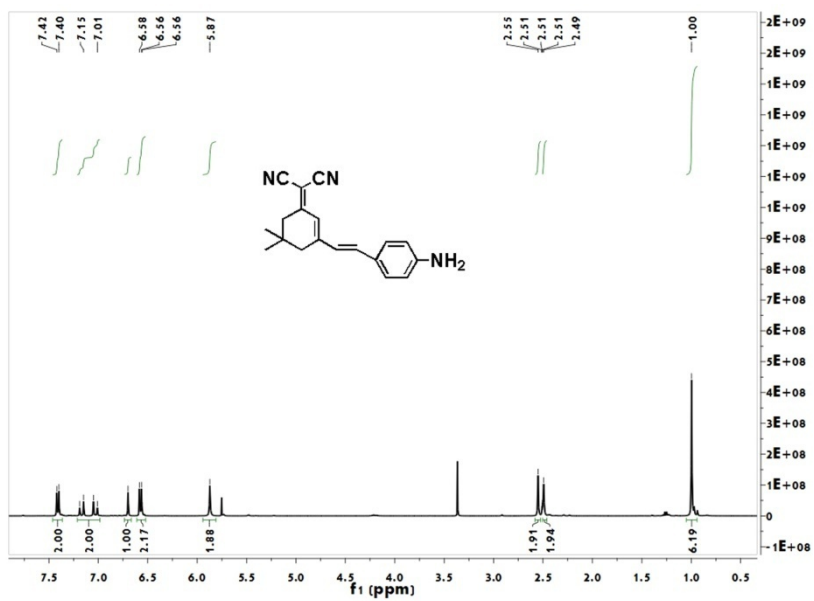
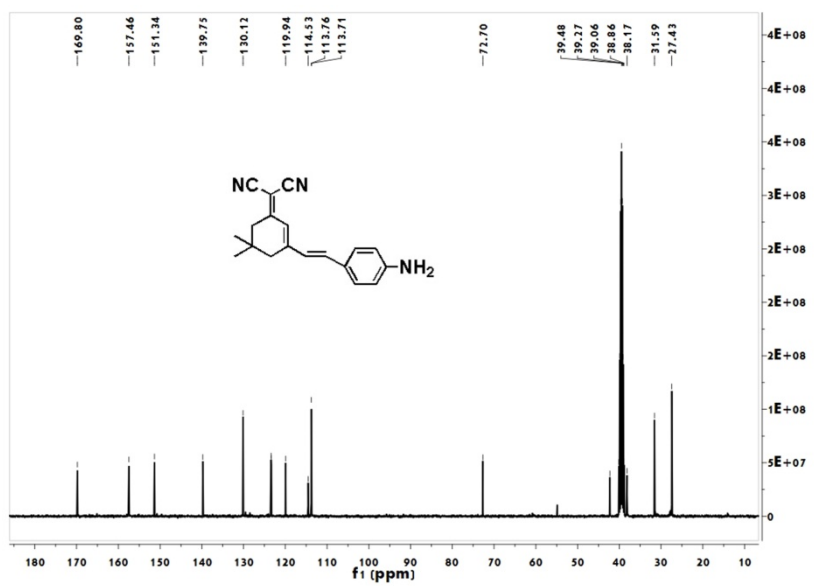


Fig. S2.  $^{13}\text{C}$  NMR spectrum of compound 3 in  $\text{CDCl}_3$



**Fig. S3.**  $^1\text{H}$  NMR spectrum of compound 2 in  $\text{CDCl}_3$ .



**Fig. S4.**  $^{13}\text{C}$  NMR spectrum of compound 2 in DMSO.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions  
18 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:  
C: 0-45 H: 0-80 N: 0-3

ZHANG-JL

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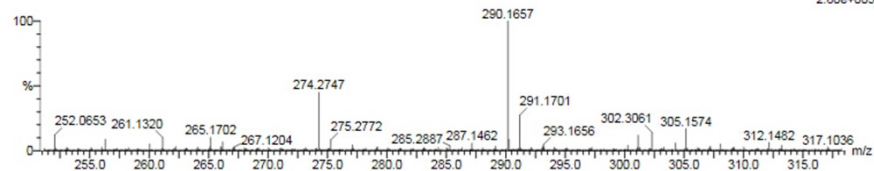
14-Nov-2014

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2.80e+003

ZJ-XKQ-04 14 (0.520) Cm (9:19)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
290.1657	290.1657	0.0	0.0	11.5	205.6	0.0	C19 H20 N3

Fig. S5. HRMS spectrum of compound 2.

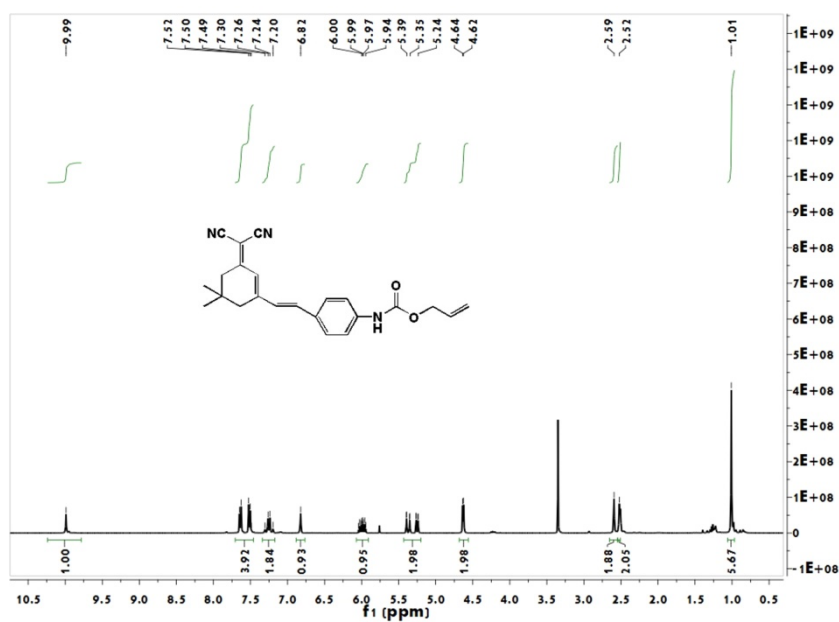


Fig. S6. <sup>1</sup>H NMR spectrum of Probe 1 in DMSO.

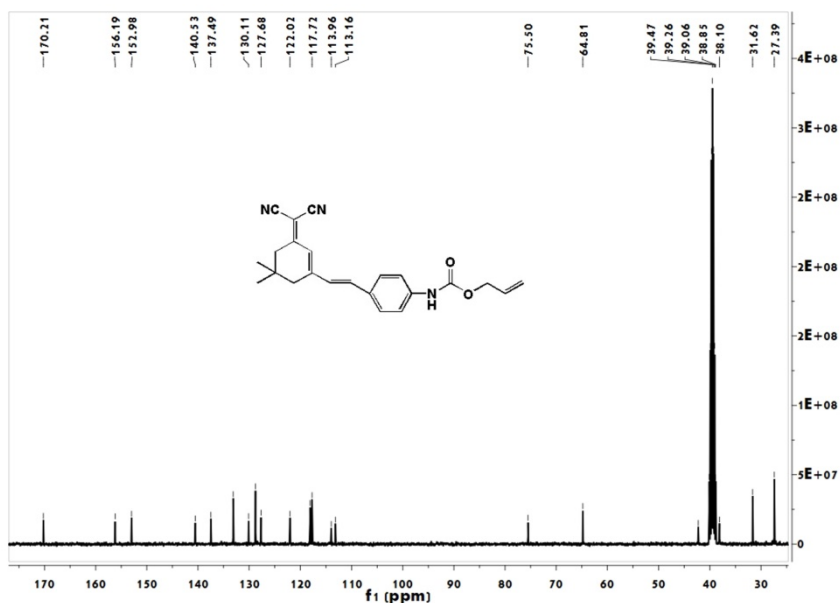


Fig. S7.  $^{13}\text{C}$  NMR spectrum of Probe 1 in DMSO.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

131 formula(e) evaluated with 9 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-45 H: 0-80 N: 0-3 O: 0-6

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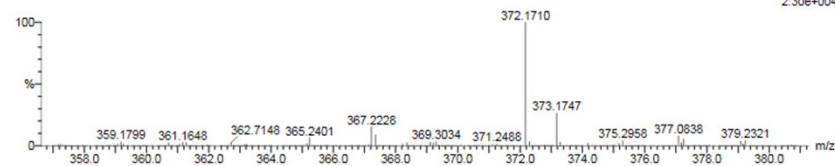
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ZJ-XKQ-06 13 (0.383) Cm (10.16)

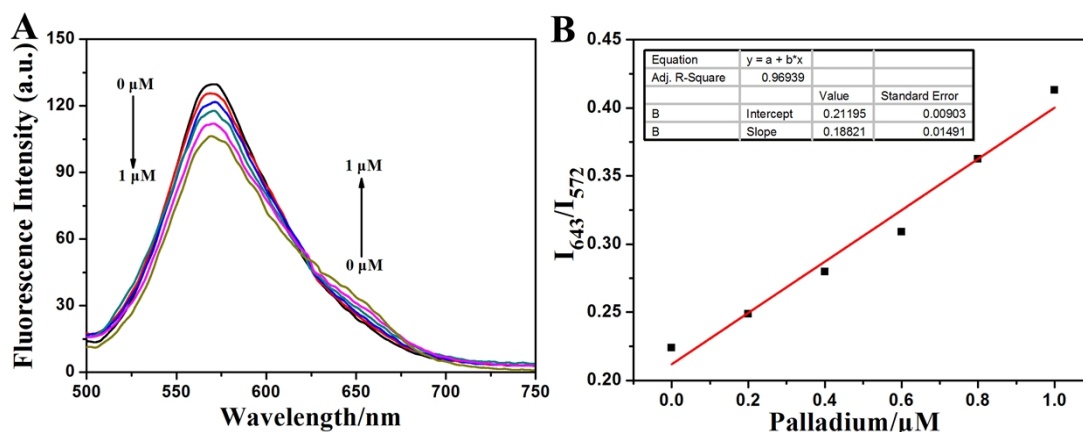


Minimum:

Maximum: 30.0 50.0 -1.5 100.0

Mass	Calc. Mass	mDa	PFM	DBE	i-FIT	i-FIT (Norm)	Formula
372.1710	372.1712	-0.2	-0.5	14.5	186.9	0.0	C23 H22 N3 O2

Fig. S8. HR-MS spectrum of Probe 1



**Fig. S9.** Fluorescence (A) spectra of Probe 1 (10 $\mu$ M) towards palladium (0) at different concentrations (0-1  $\mu$ M) in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20mM). B) Ratiometric calibration curve ( $I_{643}/I_{570}$ ) as a function of Pd (0) concentration.  $\lambda_{ex}$  = 472 nm. Slit: 5 nm/5 nm. Note: Pd represents palladium (0).

The detection limit was calculated with the following equation [1-3]:

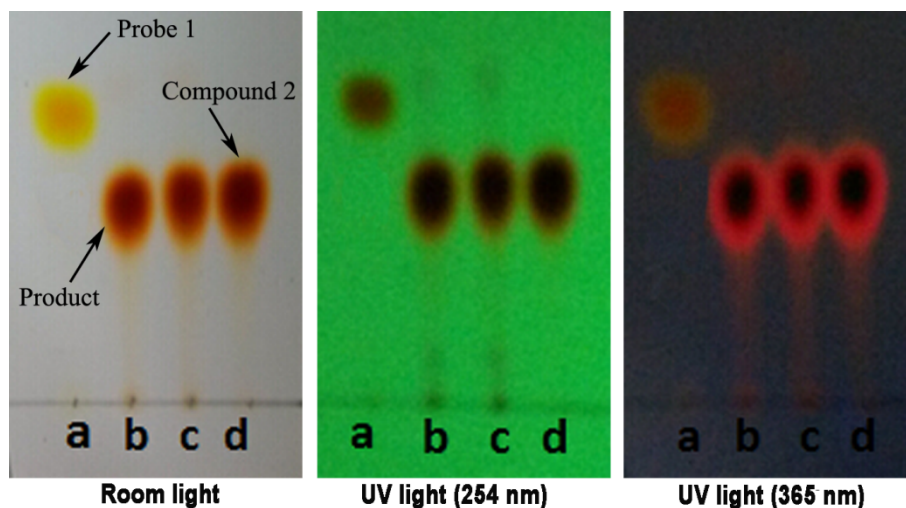
$$\text{Detection limit} = 3\sigma/S$$

Where,  $\sigma$  represents the standard deviation and S is the slope of the fitted straight line (Origin software). Here, the standard deviation  $\sigma$  was estimated by according to five times of blank measurement. The  $I_{643}/I_{570}$  values of five blank measurements for Probe 1 were 0.204, 0.204, 0.205, 0.207, and 0.203, respectively.  $\sigma = 0.001517\mu\text{M}$ ;  $S = 0.18821$ . The detection limit was calculated to be 24.2 nM ( $3\sigma/S$ ).

[1] M. Cigáň, K. Jakusová, J. Donovalová, et al. *RSC Adv.*, 2014, **4**, 54072-54079

[2] B. C. Zhu, C. C. Gao, Y. Z. Zhao, et al. *Chem. Commun.*, 2011, **47**, 8656-8658.

[3] C. Hu, W. Sun, J. Cao, et al. *Org. Lett.* 2013, **15**, 4022-4025.



**Fig. S10.** Pictures of the thin layer chromatography (TLC) plates under different light used to compare Probe 1, the reference sample compound 2, reaction mixture Probe 1 with Pd(PPh<sub>3</sub>)<sub>4</sub>. Spots on the TLC plate: (a) Probe 1; (b) Reaction product of Probe 1 and Pd(PPh<sub>3</sub>)<sub>4</sub>; (c) mixture of b and compound 2; (d) Compound 2. The eluent for TLC: Petroleum ether/ethyl acetate = 5:2 (v/v).

#### Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

18 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-45 H: 0-80 N: 0-3

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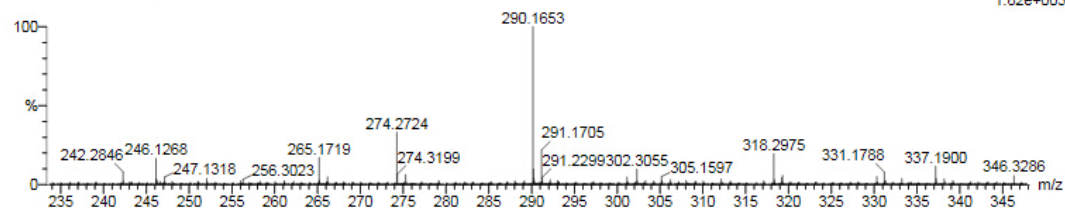
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1.82e+003

ZJ-XKQ-07 37 (1.234) Cm (34:40)



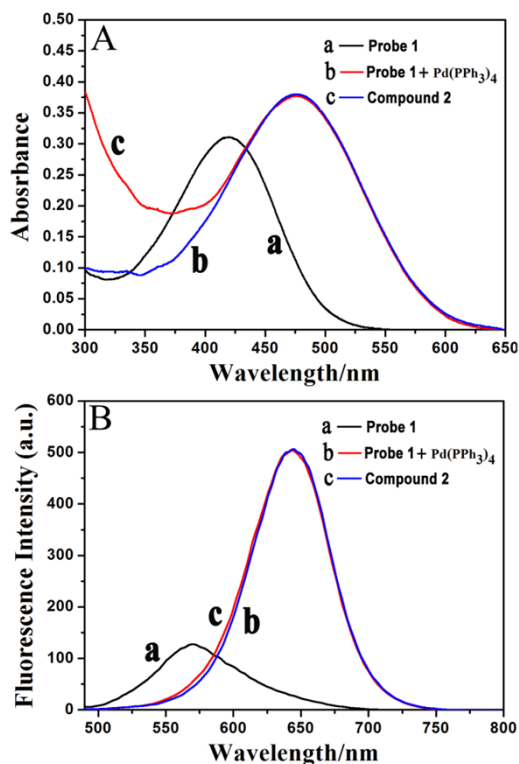
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Maximum: 30.0 50.0 -1.5 100.0

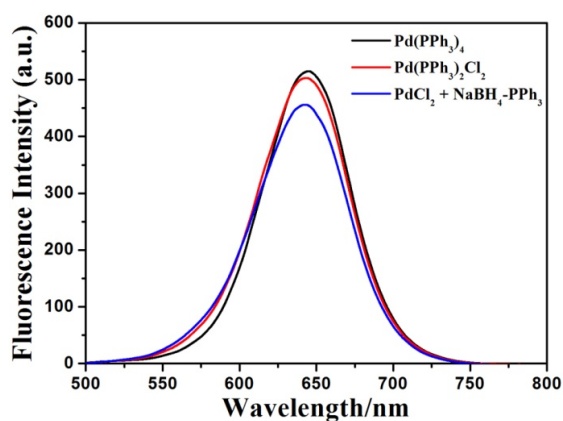
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
290.1653	290.1657	-0.4	-1.4	11.5	176.2	0.0	C19 H20 N3

**Fig. S11.** HRMS spectra of Probe 1 after upon addition of palladium (0).

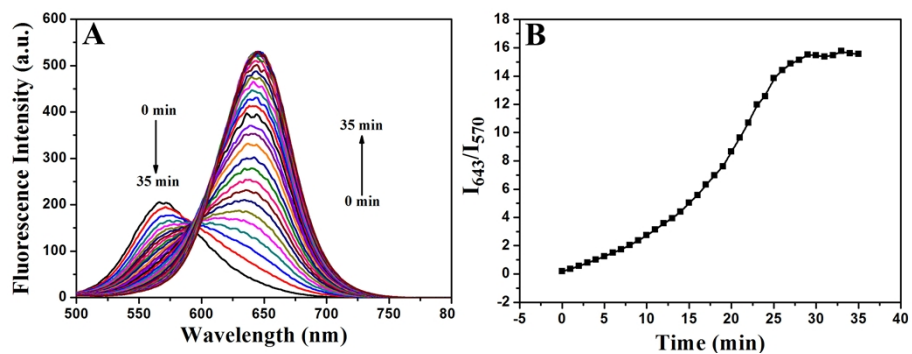




**Fig. S12.** UV-vis absorption and fluorescence spectra of Probe 1, compound 2, and the reaction product of Probe 1 and palladium (0). All spectra were recorded in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM).  $\lambda_{\text{ex}} = 472$  nm. Slit: 5 nm/5 nm.



**Fig. S13.** Fluorescence spectra of Probe 1 (10  $\mu\text{M}$ ) in DMSO/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM) after addition of different kinds of palladium species (50  $\mu\text{M}$ ).  $\lambda_{\text{ex}} = 472$  nm. Slit: 5 nm/5 nm. All measures were carried out after palladium species and Probe reacted for 30 min.



**Fig. S14.** (A) Time dependent fluorescence spectra and (B)  $I_{643}/I_{570}$  evolution of Probe 1 upon addition of  $\text{PdCl}_2(\text{II})$  ( $50 \mu\text{M}$ ).  $\lambda_{\text{ex}} = 472 \text{ nm}$ . Slit:  $5 \text{ nm}/5 \text{ nm}$ .