

## Electronic Supplementary Information

Confinement of Au-*N*-heterocyclic carbene in Pd<sub>6</sub>L<sub>12</sub> metal-organic cage

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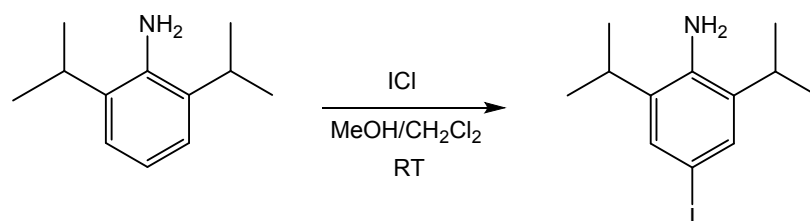
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## Additional experimental section

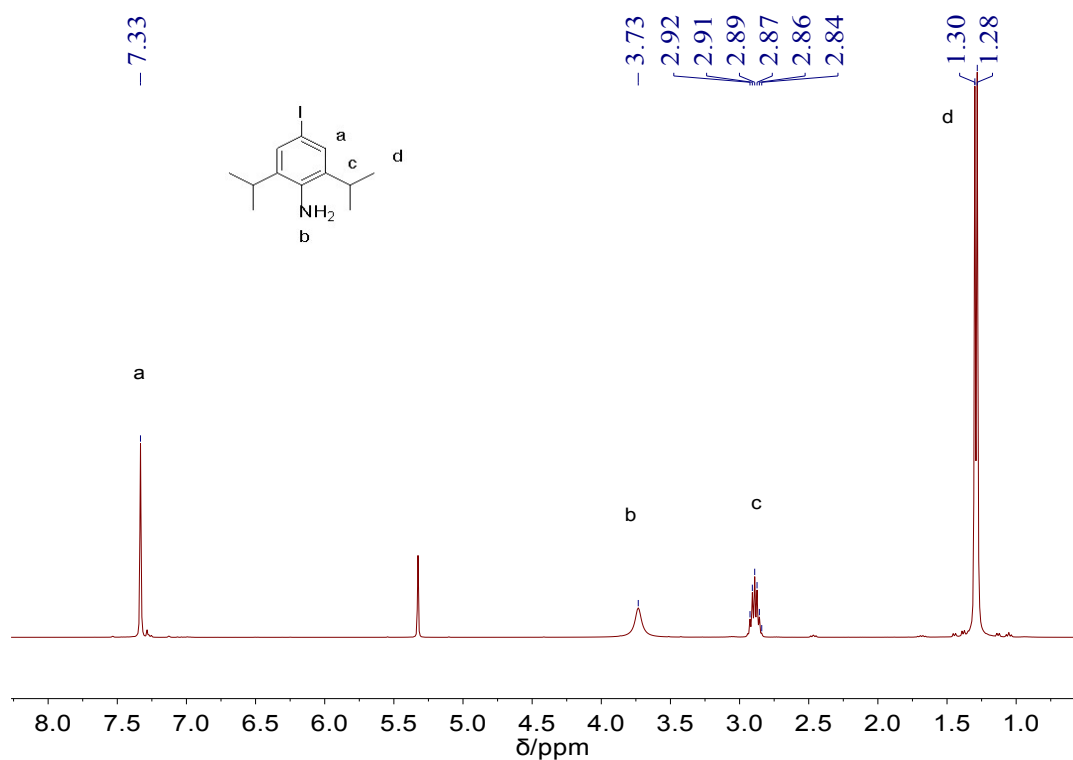
### General methods

All commercial chemicals and solvents were purchased without further purification, unless otherwise specified.  $^1\text{H}$  NMR,  $^{11}\text{B}$  NMR,  $^{19}\text{F}$  NMR,  $^{31}\text{P}$  NMR,  $^1\text{H}$ - $^1\text{H}$  COSY and  $^1\text{H}$ - $^1\text{H}$  NOESY spectra were recorded on a Bruker Avance III 400MHz NMR spectrometer.  $^1\text{H}$  DOSY spectrum was recorded on a Bruker Avance III 600MHz NMR spectrometer. ESI-TOF mass spectra were performed on a timsTOF from Bruker equipped with an auto-sample injection system. Detection was in positive-ion mode and the capillary voltage was 3500 V, dry temperature was held at 200 °C, dry gas was 4.5 L min<sup>-1</sup>, and Nebulizer was 0.6 bar. For cyclic voltammetry the working electrode was glassy carbon electrode 3 mm in diameter, a platinum wire was counter electrode, and an Ag/AgCl (3.0 mol L<sup>-1</sup> KCl) electrode or Ag wire as reference electrode. All electrochemical experiments were carried out in dry DMSO solutions of n-Bu<sub>4</sub>NPF<sub>6</sub> (0.10 mol L<sup>-1</sup>) as supporting electrolyte, which was freed of oxygen by bubbling through high-purity nitrogen before experiments. The concentration was 3.0 μmol L<sup>-1</sup> for **L** and 0.25 μmol L<sup>-1</sup> for Pd<sub>6</sub>L<sub>12</sub>.

### Synthesis of 4-iodo-2,6-diisopropylaniline

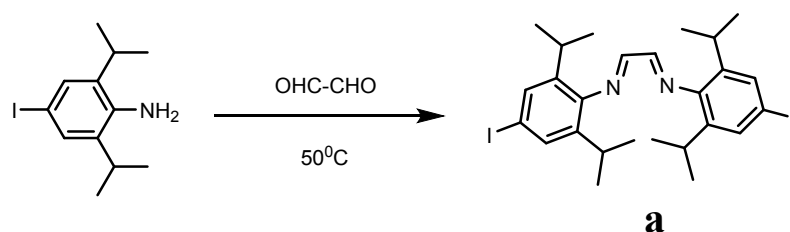


Synthesized according to the reported procedure.<sup>S1</sup> 2,6-Diisopropylaniline (9.399 g, 53.1 mmol) was dissolved in a mixture of methanol and dichloromethane (60 mL, v/v 1:1). Iodochloride (9.464 g, 58.4 mmol, excess) dissolved in a mixture of methanol-dichloromethane (60 mL, v/v 1:1) was added into the solution of 2,6-diisopropylaniline. The resultant mixture was stirred at room temperature for 12 h. At the end of the reaction the solvent was evaporated out. The resulting crude solid product was treated with 60 mL saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The resulting mixture was stirred at room temperature for 0.5 h and then extracted with dichloromethane (3 × 20 mL). After drying over sodium sulfate, the solvent was evaporated out. Brown oil was eventually obtained after distillation under reduced pressure (15.149 g, 94%).  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 (s, 2H), 3.73 (s, 2H), 2.89 (m, 2H), 1.29 (d,  $J$  = 6.9 Hz, 12H).

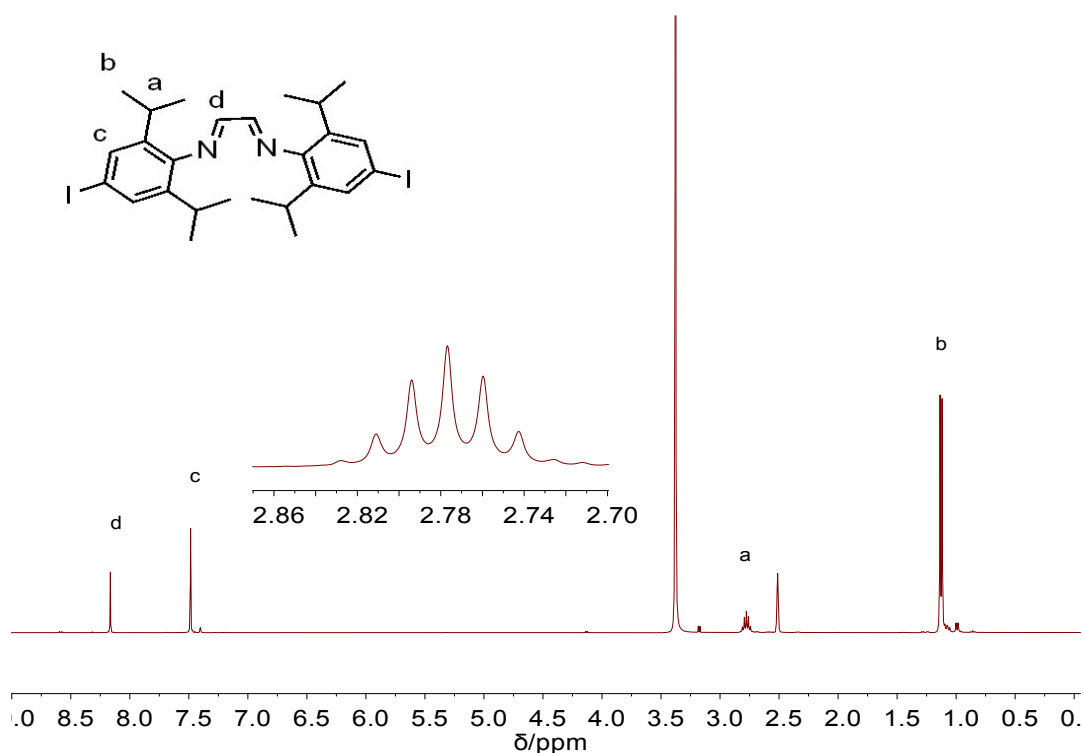


**Fig. S1** <sup>1</sup>H NMR spectrum of 4-iodo-2,6-diisopropylaniline (400 MHz, CDCl<sub>3</sub>).

#### Synthesis of bis(4-iodo-2,6-diisopropylphenyl)diazabutadiene (**a**)

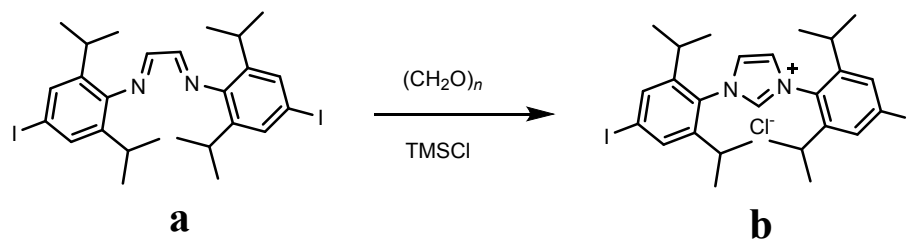


Synthesized according to the reported procedure.<sup>S1</sup> Glyoxal (5.257 g, 40 wt% in water, 36.3 mmol) was added dropwise into 4-iodo-2,6-diisopropylaniline (21.969 g, 72.5 mmol) in methanol (36 mL), 362 μL acetic acid was added in the system as catalyst. The reaction mixture was stirred for 7 h at 50 °C. The yellow solid was achieved by filtration and washed with methanol (3 × 10 mL), leading to the yellow product (13.939 g, 61%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.06 (s, 2H), 7.49 (s, 4H), 2.86 (m, 4H), 1.20 (d, *J* = 6.9 Hz, 24H).



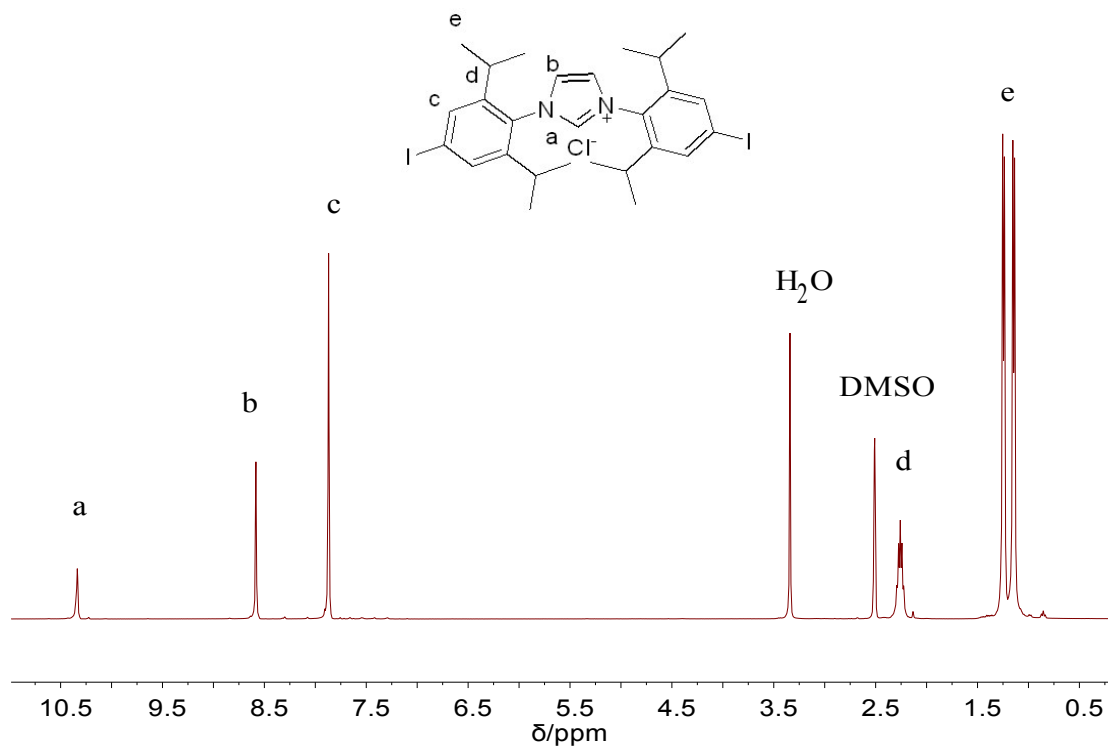
**Fig. S2**  $^1\text{H}$  NMR spectrum of bis(4-iodo-2,6-diisopropylphenyl)diazabutadiene (400 MHz,  $\text{DMSO-}d_6$ ).

**Synthesis of  $N,N'$ -1,3-bis(4-iodo-2,6-diisopropylphenyl)imidazolium chloride (b)**

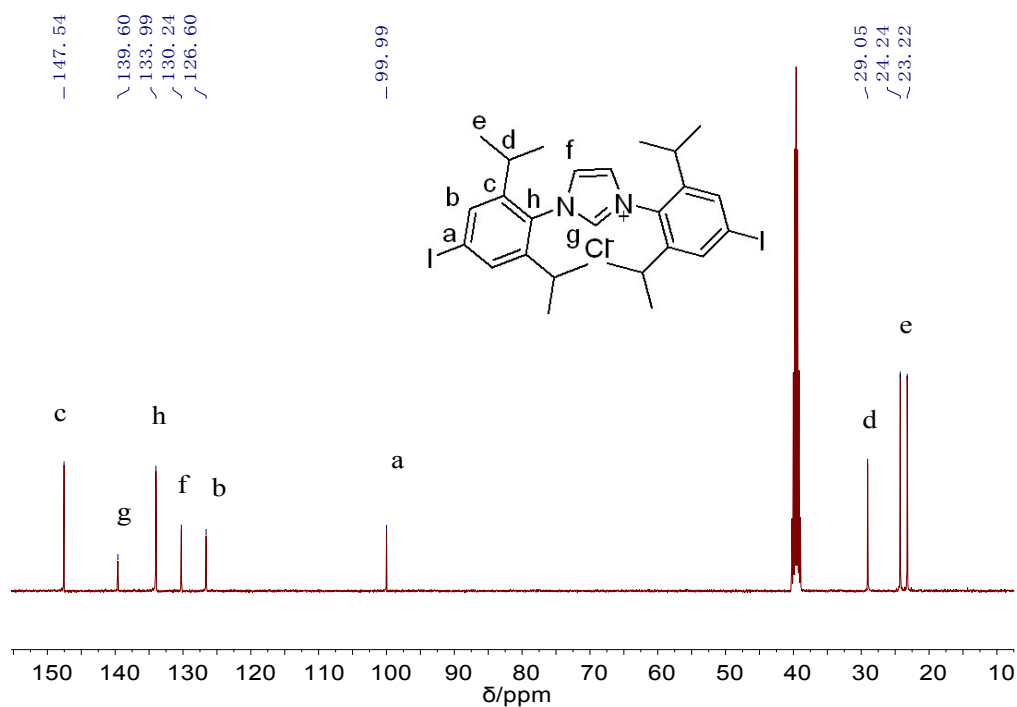


A 250 mL round-bottom flask equipped with a magnetic stirring bar and a stopper was charged with ethyl acetate (100 mL) and heated in an oil bath at 70 °C. To the warm solvent bis(4-iodo-2,6-diisopropylphenyl)diazabutadiene (6.910 g, 11 mmol) and paraformaldehyde (0.360 g, 12 mmol, excess) were added. Next, a solution of chlorotrimethylsilane (1.5 mL) in ethyl acetate (2.5 mL) was added dropwise over 45 min with vigorous stirring. The resulting yellow-orange suspension was further stirred for 4 h at 70 °C. The color turned to black-brown. The suspension was filtered through a funnel and the white precipitate was rinsed twice with ethyl acetate ( $3 \times 10$  mL) to obtain the product (7.264 g, 62%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  10.34 (s, 1H), 8.58 (s, 2H), 7.87 (s, 4H), 2.26 (m, 4H), 1.24 (d,  $J = 6.8$  Hz, 12H), 1.14 (d,  $J = 6.8$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  147.54 (s), 139.60 (s), 133.99 (s), 130.24 (s), 126.60 (s), 99.99 (s), 29.05

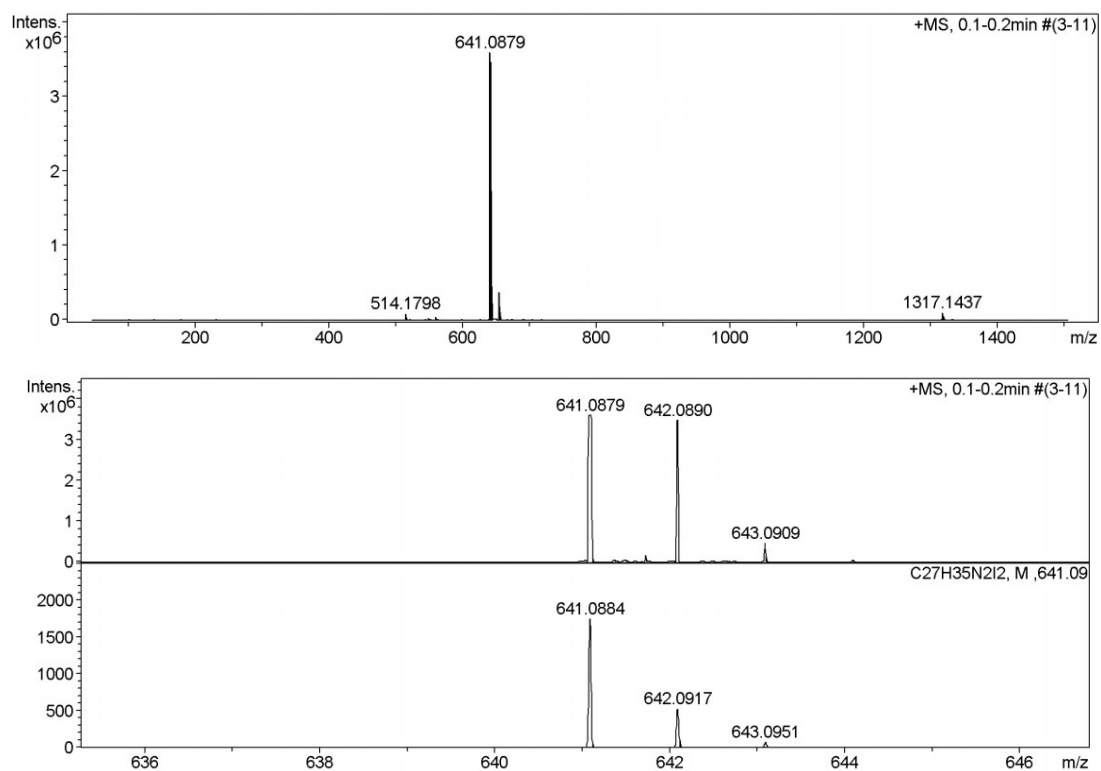
(s), 24.24 (s), 23.22 (s). FT-IR ( $\text{cm}^{-1}$ , KBr): 1623 (w) (C=N), 1568 (m), 1532 (m), 1464 (m), 1328 (m), 1205 (s), 1107 (w), 949 (s), 862 (s), 787 (w), 769 (w), 686 (w), 565 (w). TOF-MS (ESI<sup>+</sup>):  $m/z$  found (calcd.) for  $[\text{M}-\text{Cl}]^+ [\text{C}_{27}\text{H}_{35}\text{N}_2\text{I}_2]^+ = 641.0879 (641.0884)$ .



**Fig. S3** <sup>1</sup>H NMR spectrum of 1,3-bis(4-iodo-2,6-diisopropylphenyl)imidazolium chloride (400 MHz, DMSO-*d*<sub>6</sub>).



**Fig. S4**  $^{13}\text{C}$  NMR spectrum of 1,3-bis(4-iodo-2,6-diisopropylphenyl)imidazolium chloride (100 MHz,  $\text{DMSO-}d_6$ ).



**Fig. S5** ESI-MS spectrum of 1,3-bis(4-iodo-2,6-diisopropylphenyl)imidazolium chloride in  $\text{CH}_3\text{CN}$ , and isotopic distribution and simulation of  $[\text{M}-\text{Cl}]^+ [\text{C}_{27}\text{H}_{35}\text{N}_2\text{I}_2]^+$ .

### Synthesis of (1,3-bis(4-iodo-2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene)gold(I) chloride (c)

Synthesized according to modified literature method.<sup>S2</sup> Compound **b** (2.57 mmol, 1.737 g), Na<sub>2</sub>CO<sub>3</sub> (25.7 mmol, 2.724 g) and HAuCl<sub>4</sub>·4H<sub>2</sub>O (2.57 mmol, 1.058 g) were added to a dry Schlenk vial equipped with a magnetic stirring bar under argon atmosphere. Then 3-chloropyridine (12.26 g, 108 mmol) was added dropwise, and the reaction mixture was stirred at 80 °C for 24 h. After completion of reaction, the solution was cooled to room temperature and 250 mL dichloromethane was added to dissolve the product, then the mixture was filtered through celite. The combined organic phase was evaporated to dryness under reduced pressure. The residue was washed with MeOH and dried under vacuum to give **c** as light yellow solid (1.424 g, 63%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.62 (s, 4H), 7.17 (s, 2H), 2.47 (p, *J* = 6.8 Hz, 4H), 1.34 (d, *J* = 6.8 Hz, 12H), 1.22 (d, *J* = 6.8 Hz, 12H). TOF-MS (ESI<sup>+</sup>): *m/z* found (calcd.) for [M+Na]<sup>+</sup> [C<sub>27</sub>H<sub>34</sub>AuClN<sub>2</sub>I<sub>2</sub>Na]<sup>+</sup> = 895.0048 (895.0058).

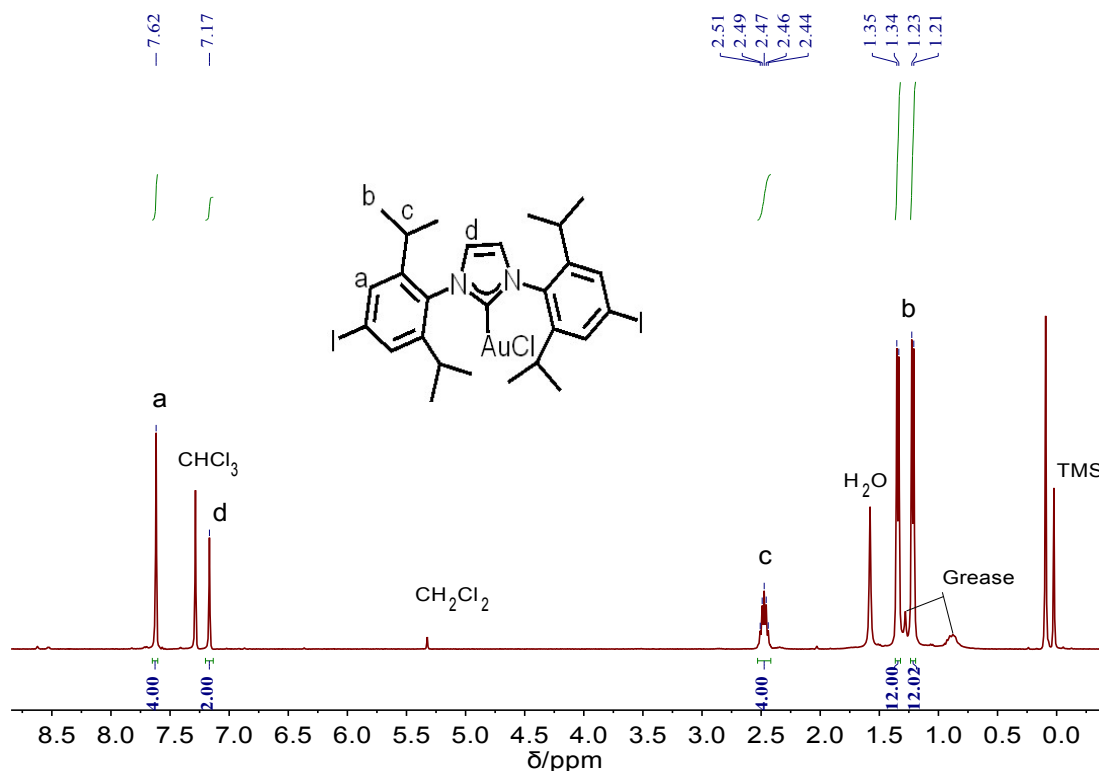
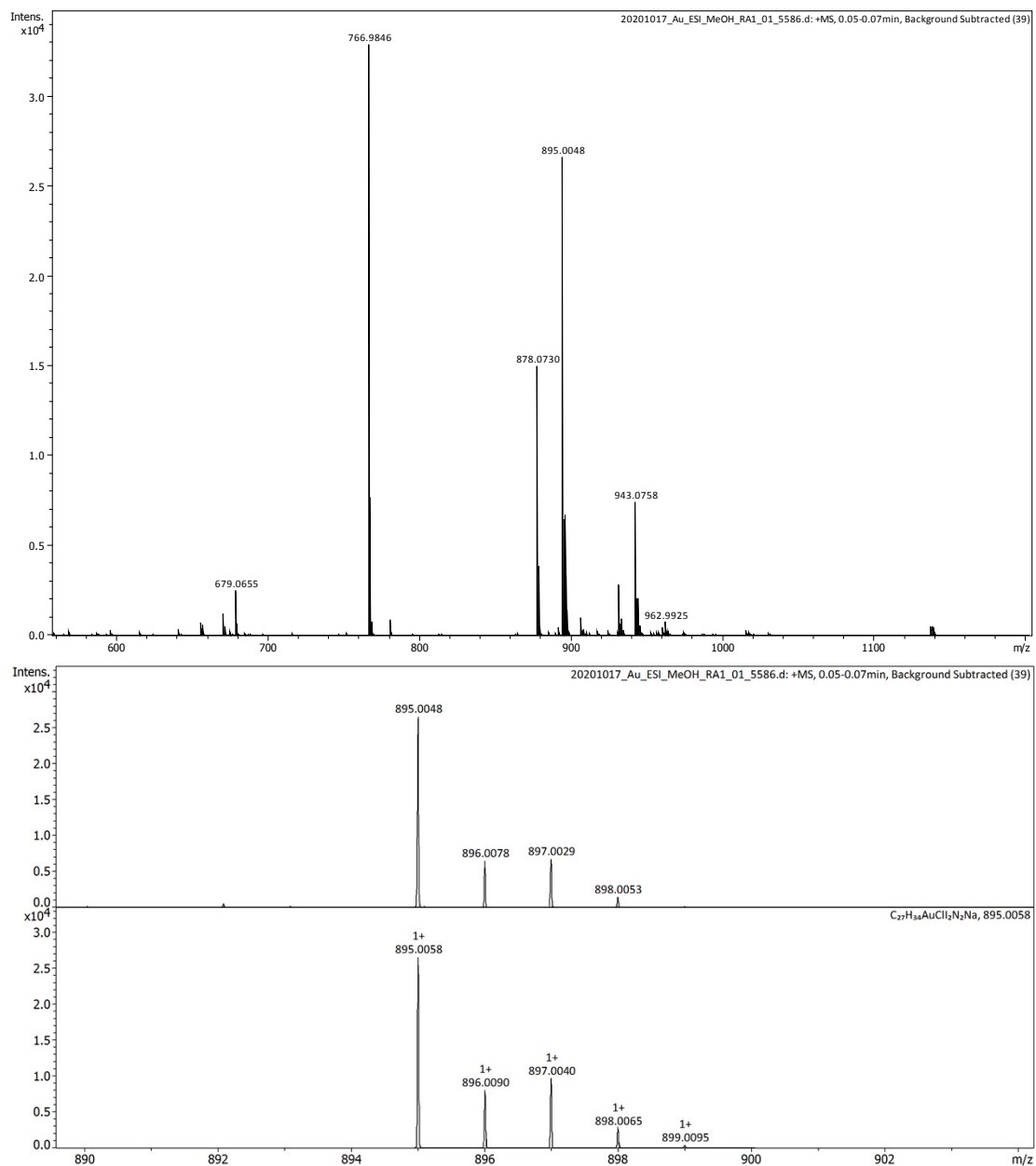
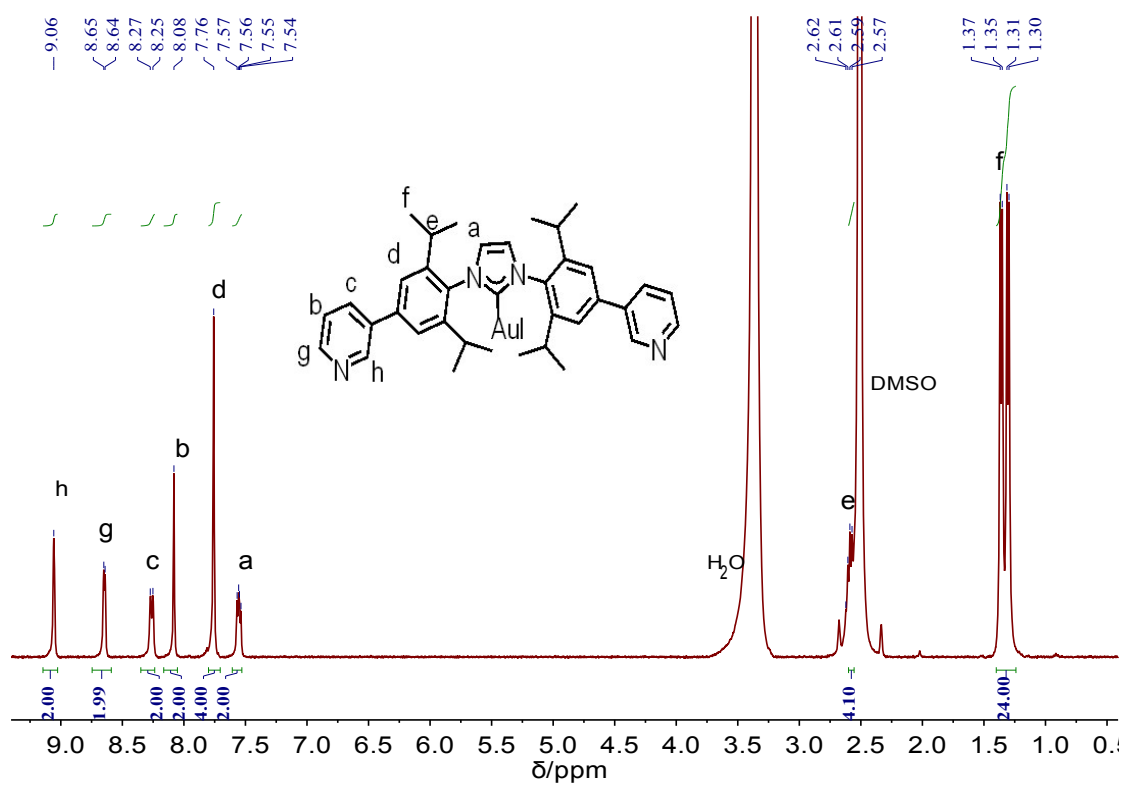


Fig. S6 <sup>1</sup>H NMR spectrum of **c** in CDCl<sub>3</sub> (400 MHz, 298 K).

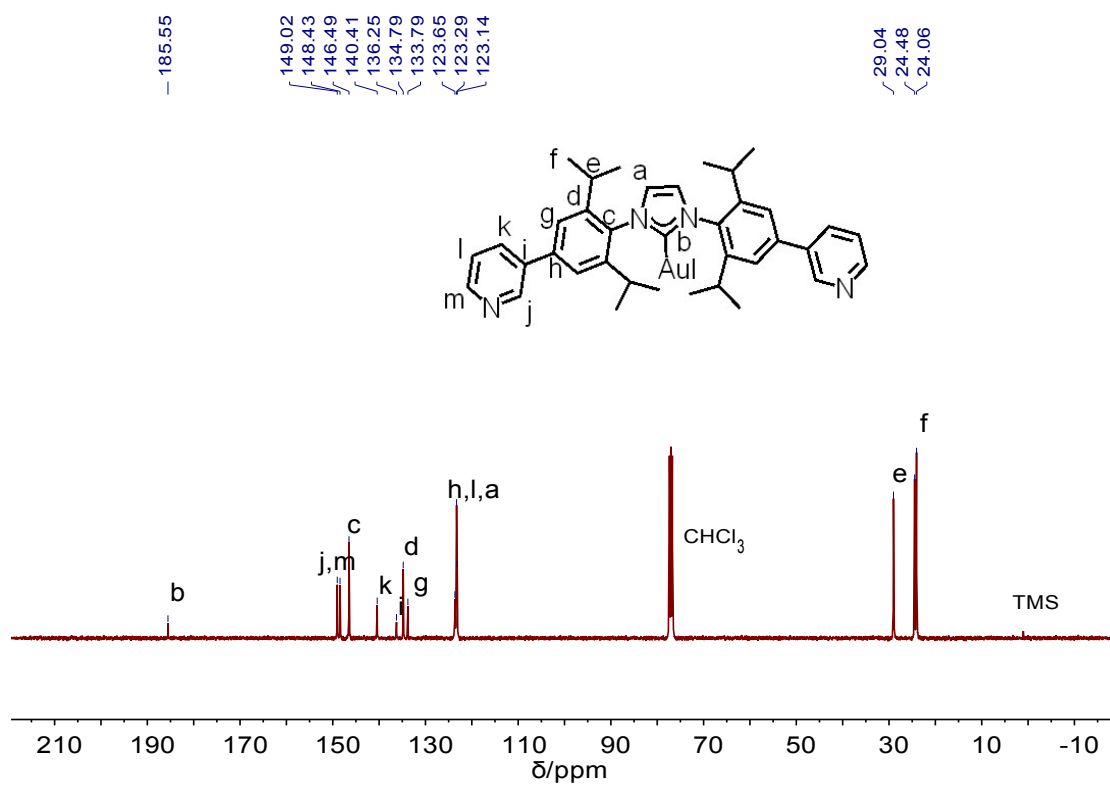


**Fig. S7** ESI-MS spectrum of **c** in CH<sub>3</sub>OH, and isotopic distribution and simulation of [M+Na]<sup>+</sup> [C<sub>27</sub>H<sub>34</sub>AuClI<sub>2</sub>N<sub>2</sub>Na]<sup>+</sup>.

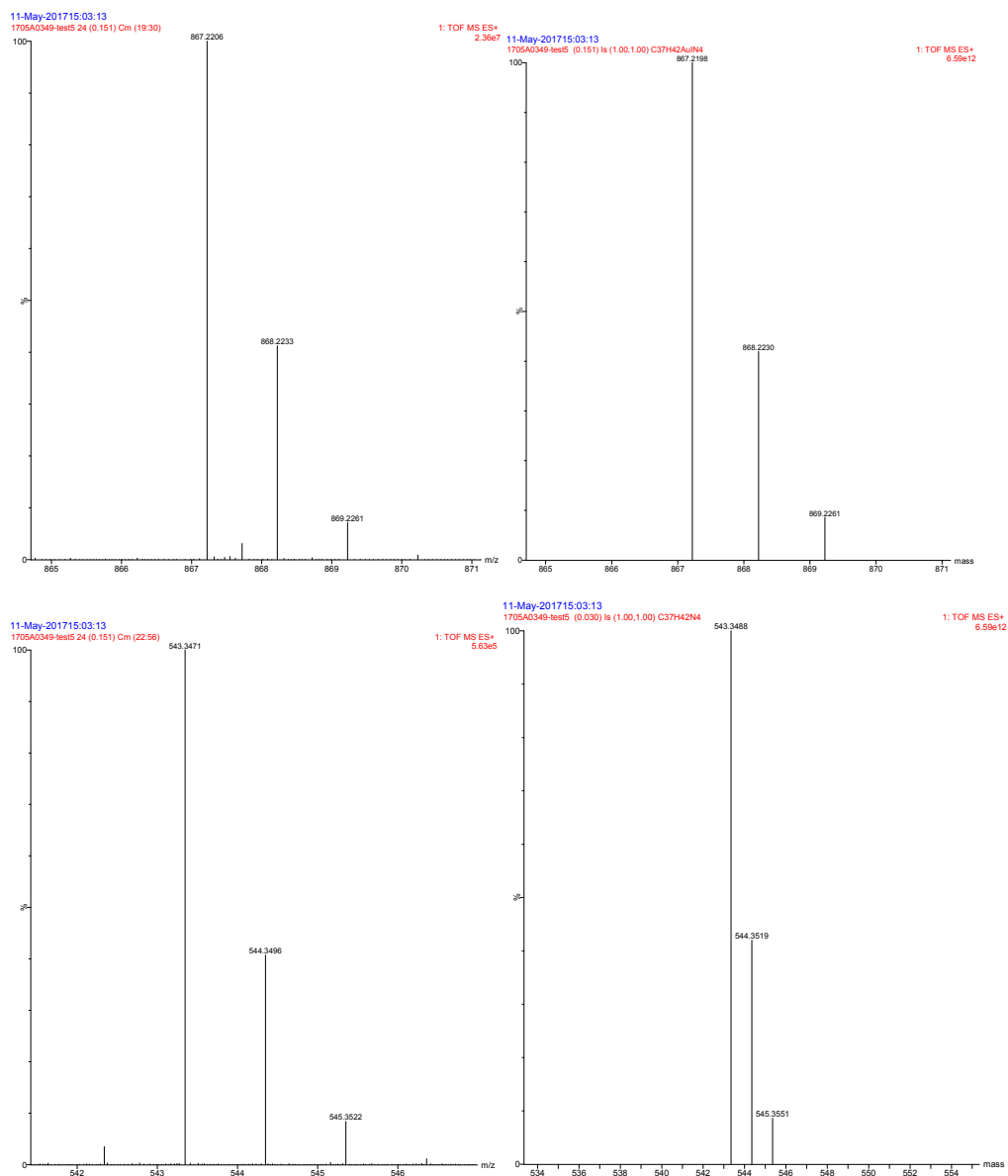




**Fig. S8**  $^1\text{H}$  NMR spectrum of **L** in  $\text{DMSO-}d_6$  (400 MHz, 293 K).



**Fig. S9**  $^{13}\text{C}$  NMR spectrum of **L** in  $\text{CDCl}_3$  (100 MHz, 298 K).



**Fig. S10** Q-TOF-MS spectrum of **L** in MeCN, and isotopic distribution and simulation of  $[M+H]^+$   $[C_{37}H_{42}N_4AuI+H]^+$  found (calcd.) for 867.2206 (867.2198) and  $[M-AuI+H]^+$   $[C_{41}H_{44}N_2O_2+H]^+$  found (calcd.) for 543.3471 (543.3488).

## References

- S1 H. Yang, G. Li, Z. Ma, J. Chao and Z. Guo, *J. Catal.*, 2010, **276**, 123-133.  
 S2 W. Wang, A. Zheng, P. Zhao, C. Xia and F. Li, *ACS Catal.*, 2014, **4**, 321-327.

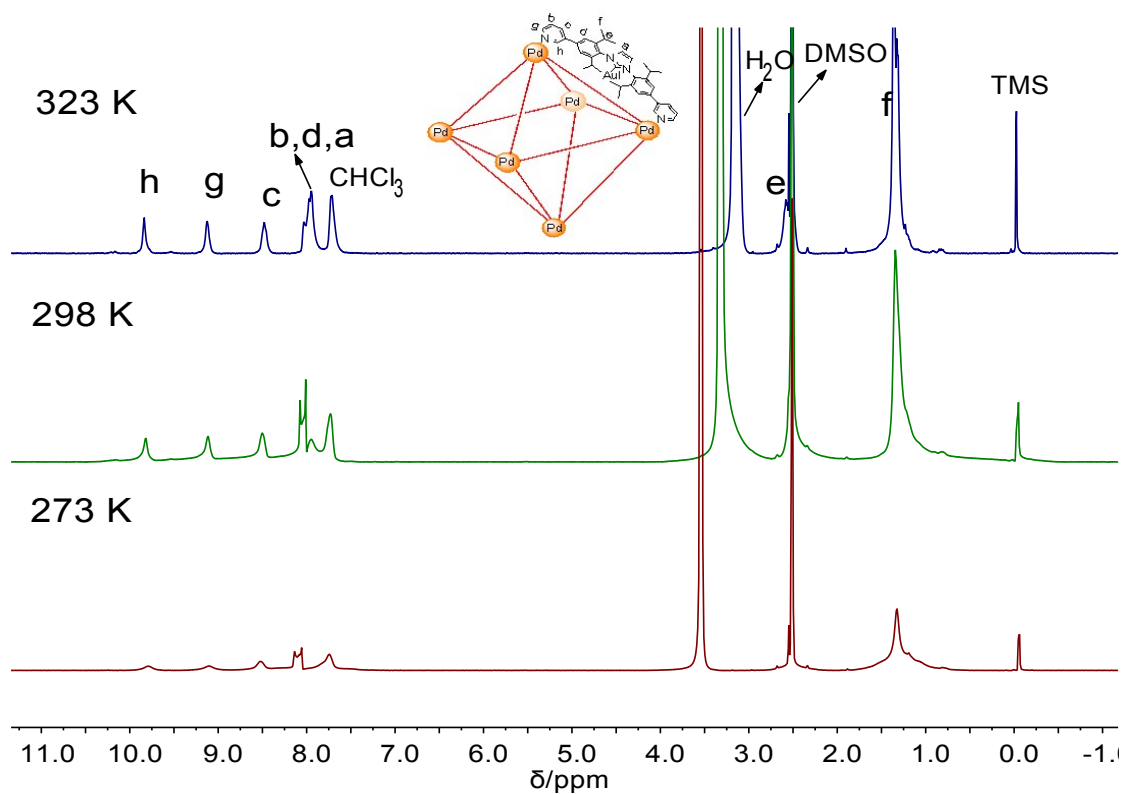


Fig. S11 VT  $^1\text{H}$  NMR spectra of  $\text{Pd}_6\text{L}_{12}$  in  $\text{CDCl}_3$ - $\text{DMSO-}d_6$  solvent mixture (v/v 1:1) (400 MHz).

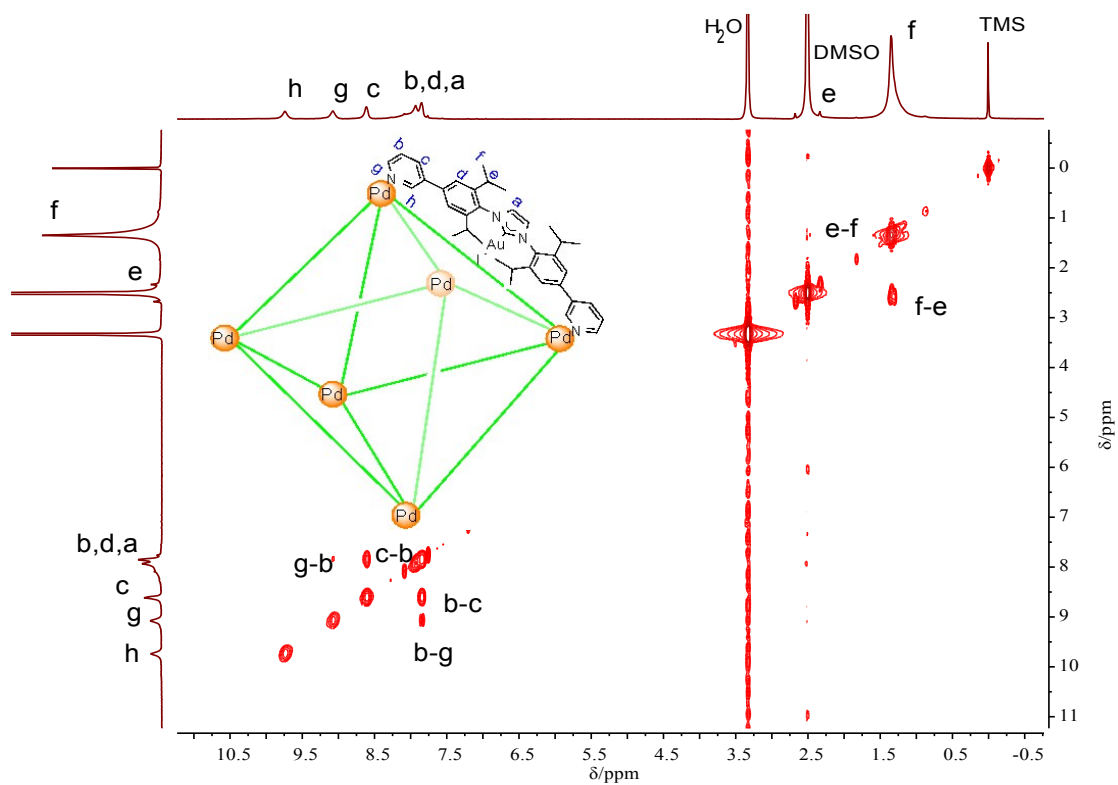


Fig. S12  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of  $\text{Pd}_6\text{L}_{12}$  in  $\text{DMSO-}d_6$  (400 MHz, 298 K).

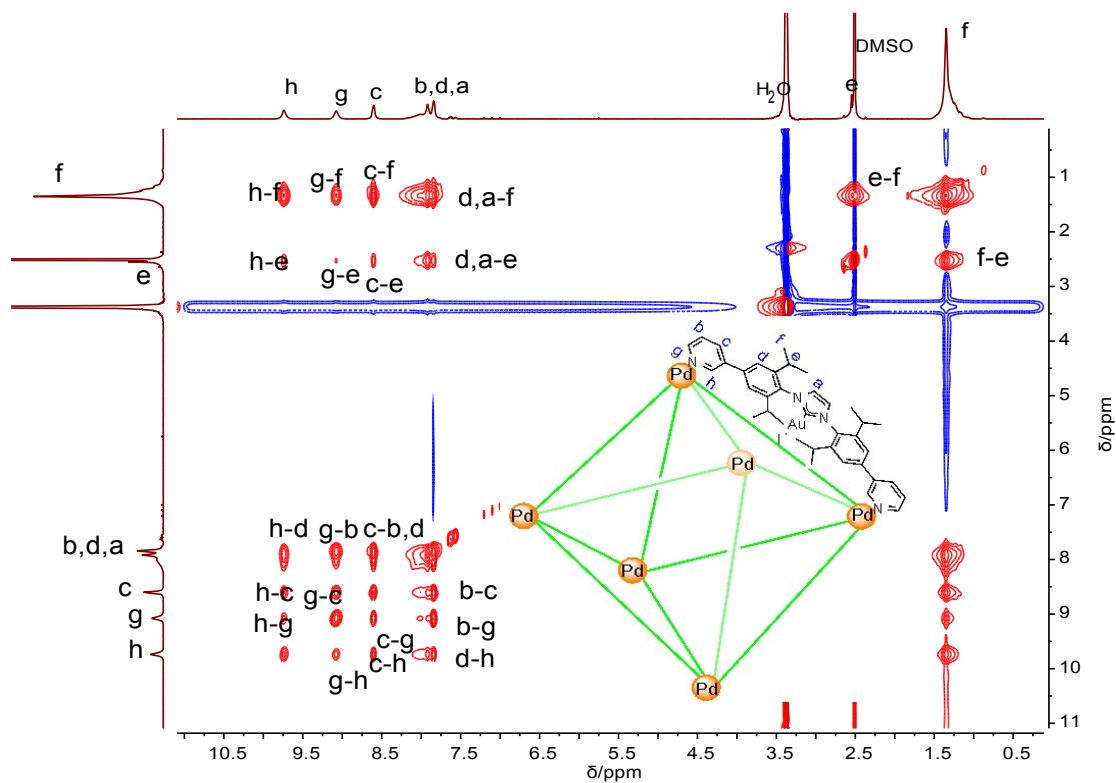


Fig. S13  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum of  $\text{Pd}_6\text{L}_{12}$  in  $\text{DMSO-}d_6$  (500 MHz, 298 K).

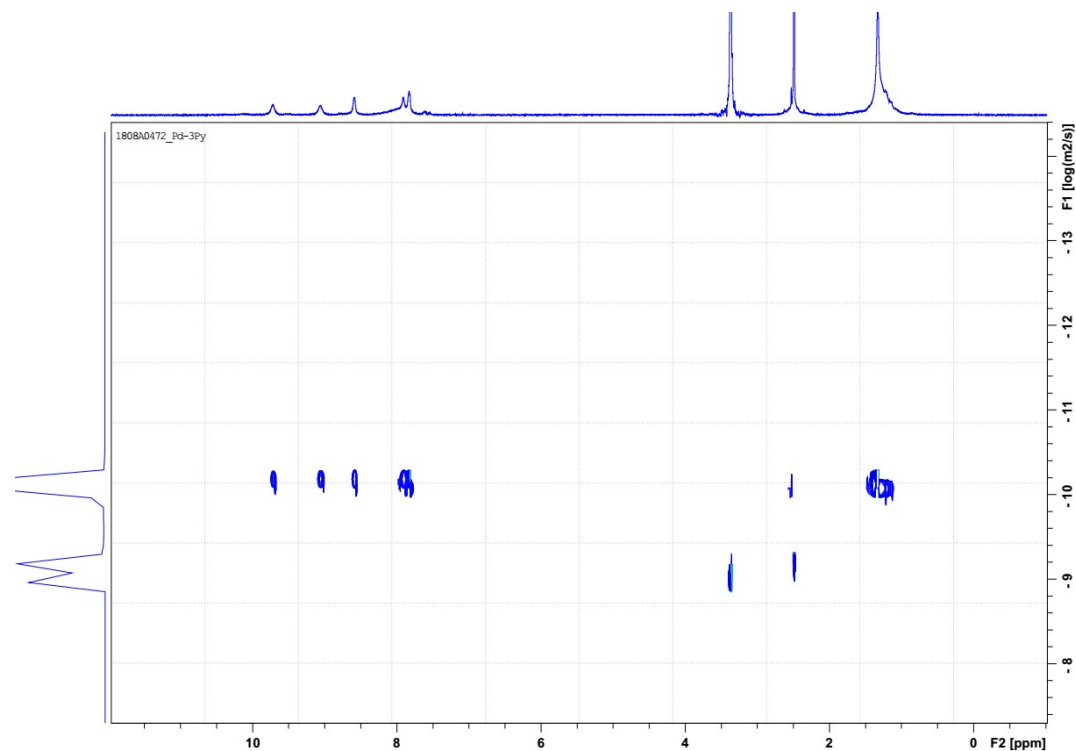
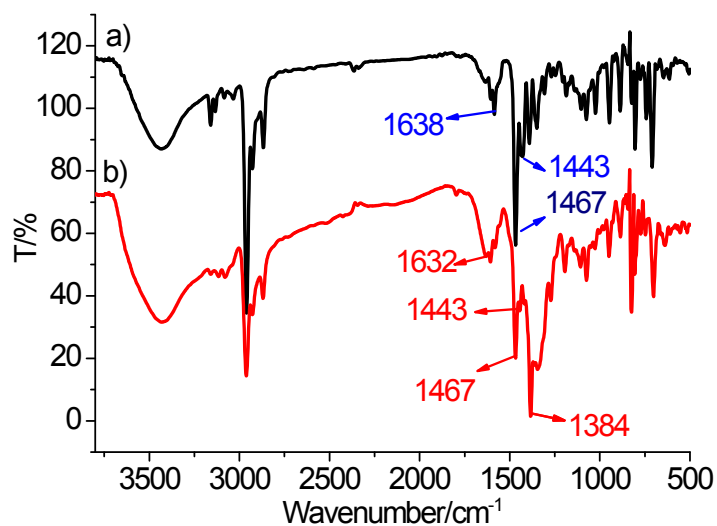


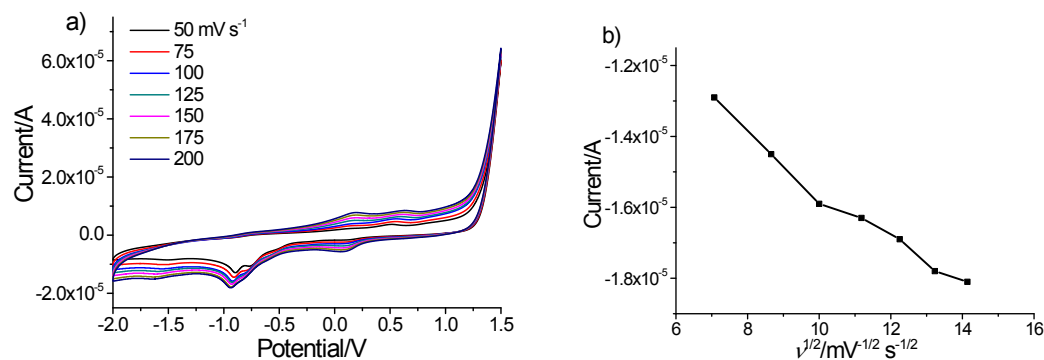
Fig. S14  $^1\text{H}$  DOSY spectrum of  $\text{Pd}_6\text{L}_{12}$  in  $\text{DMSO-}d_6$  (500 MHz, 298 K). The diffusion coefficient

is  $5.75 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ , the dynamic diameter is 19.0 Å. Stokes-Einstein equation:  $D = \frac{k_b T}{6\pi\eta r}$  was applied to estimate the dynamic radius, with  $D$  is diffusion values ( $5.75 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ) obtained from DOSY spectrum,  $k_b$  is Boltzmann constant ( $1.38 \times 10^{-23} \text{ N m K}^{-1}$ ),  $T$  is absolute temperature

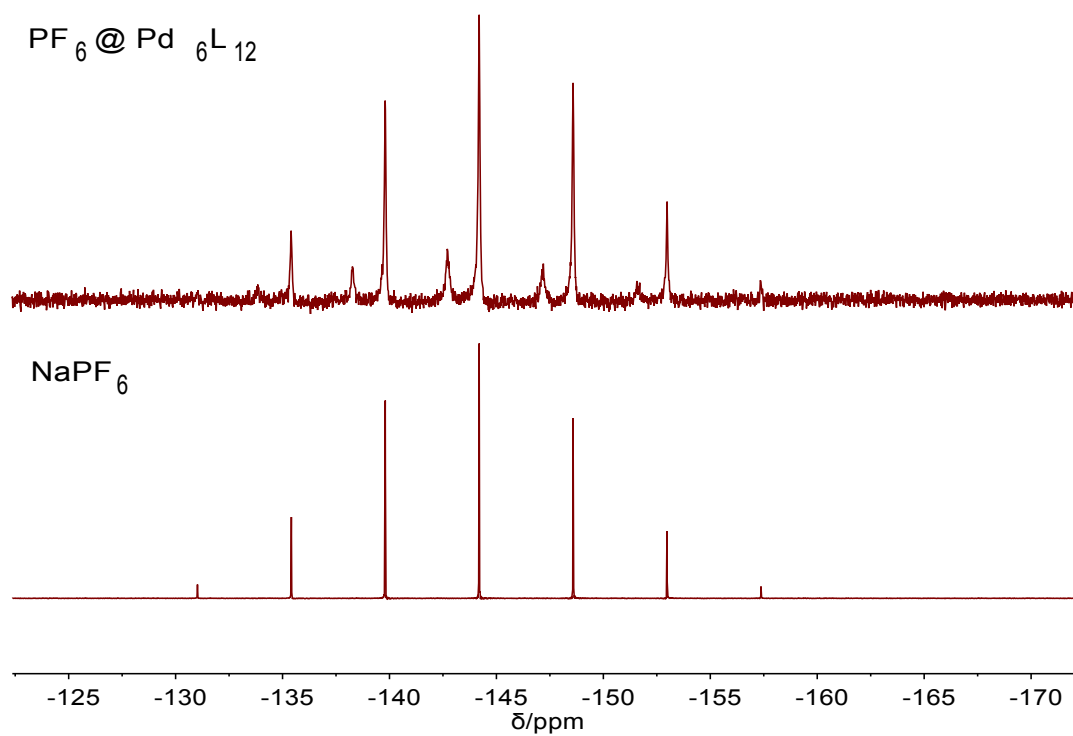
(298 K),  $\eta$  is dynamic viscosity of DMSO- $d_6$ ,  $1.996 \text{ mPa s}^{-1}$ , and  $r$  is the estimated dynamic radius. According to the Stokes-Einstein equation, it could be calculated that the molecular radius of  $\text{Pd}_6\text{L}_{12}$  was  $19.0 \text{ \AA}$ .



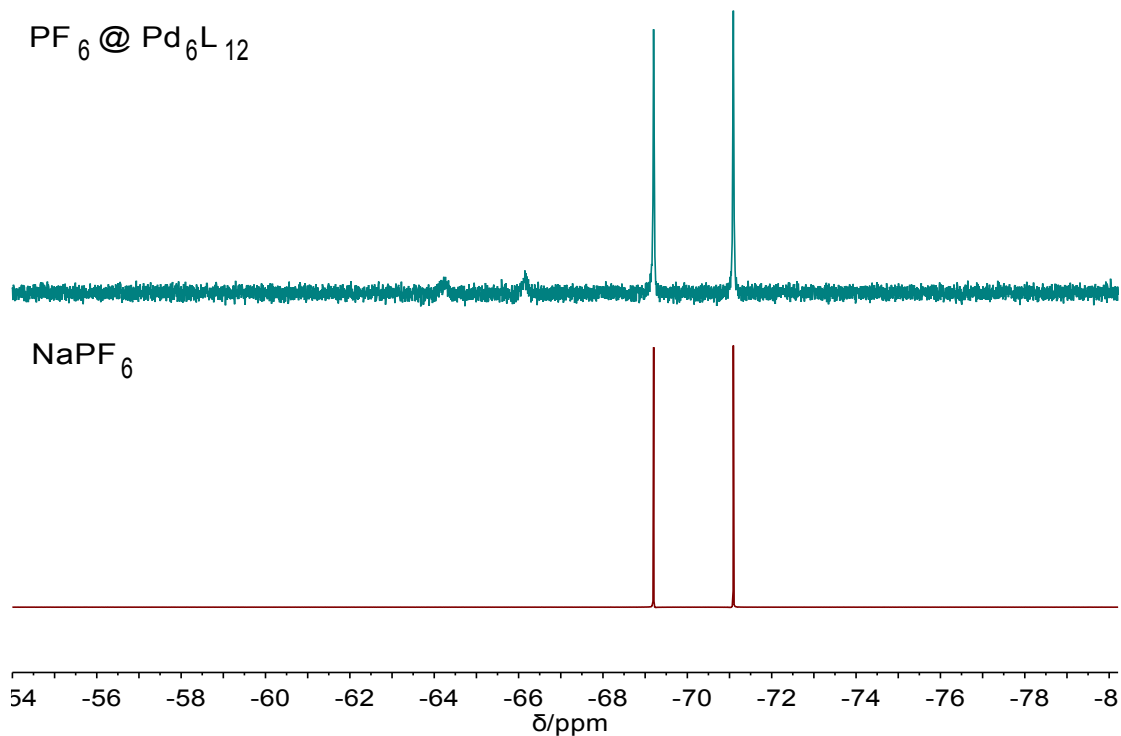
**Fig. S15** FT-IR spectra of a) L and b)  $\text{Pd}_6\text{L}_{12}$ .



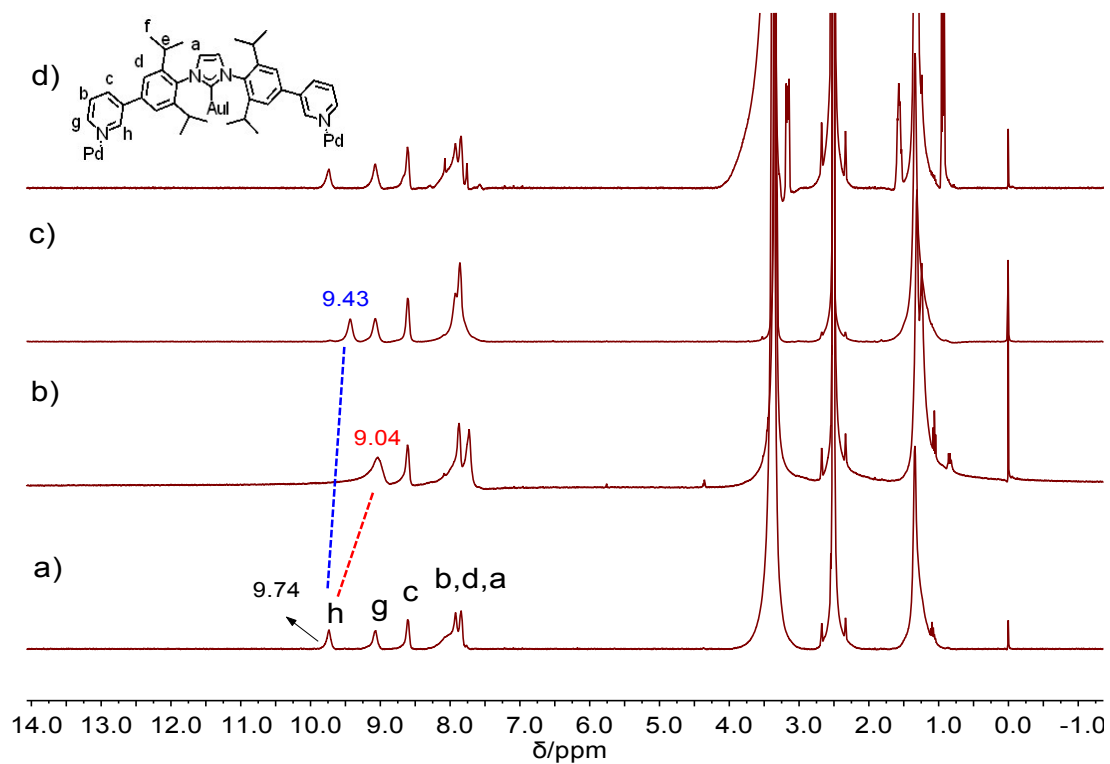
**Fig. S16** (a) Cyclic voltammograms of  $0.25 \mu\text{mol L}^{-1} \text{Pd}_6\text{L}_{12}$  in DMSO at scan rates of 50, 75, 100, 125, 150, 175 and 200  $\text{mV s}^{-1}$ , and (b) plot of the reduction current versus the square root of the scan rate ( $v^{1/2}$ ).



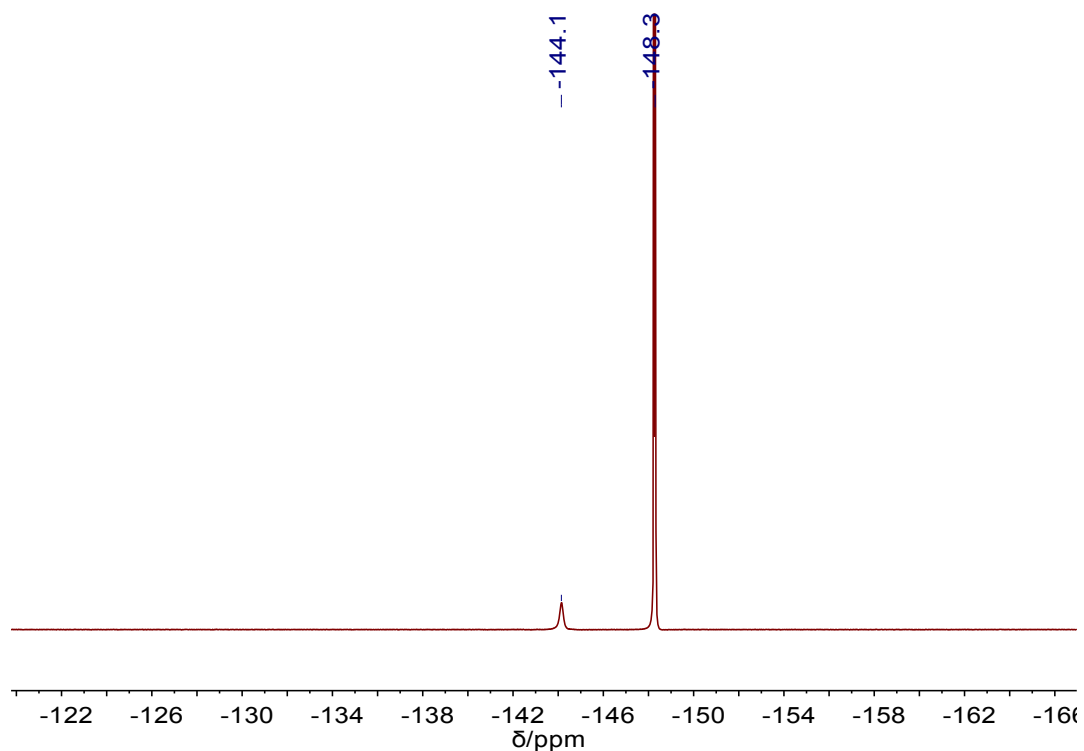
**Fig. S17**  $^{31}\text{P}$  NMR spectra of  $\text{PF}_6^- @ \text{Pd}_6\text{L}_{12}$  (top) and  $\text{NaPF}_6$  (down) in  $\text{DMSO}-d_6$  (162 MHz, 298 K).



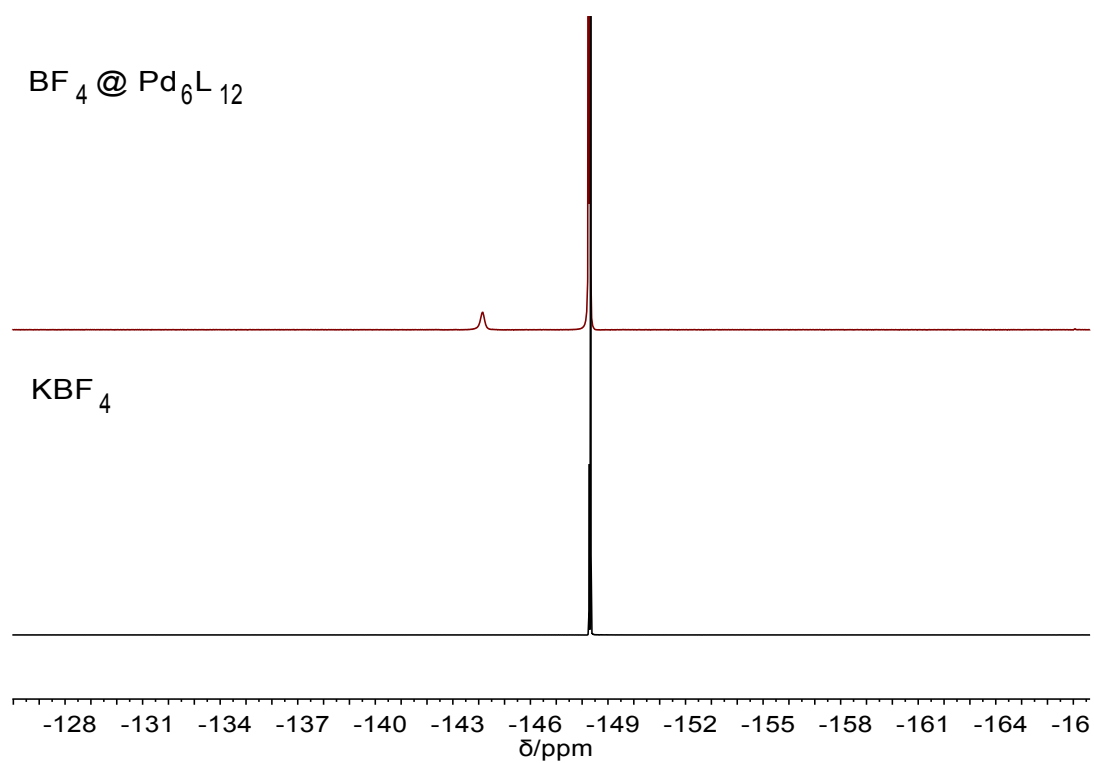
**Fig. S18**  $^{19}\text{F}$  NMR spectra of  $\text{PF}_6^- @ \text{Pd}_6\text{L}_{12}$  (top) and  $\text{NaPF}_6$  (down) in  $\text{DMSO}-d_6$  (376 MHz, 298 K).



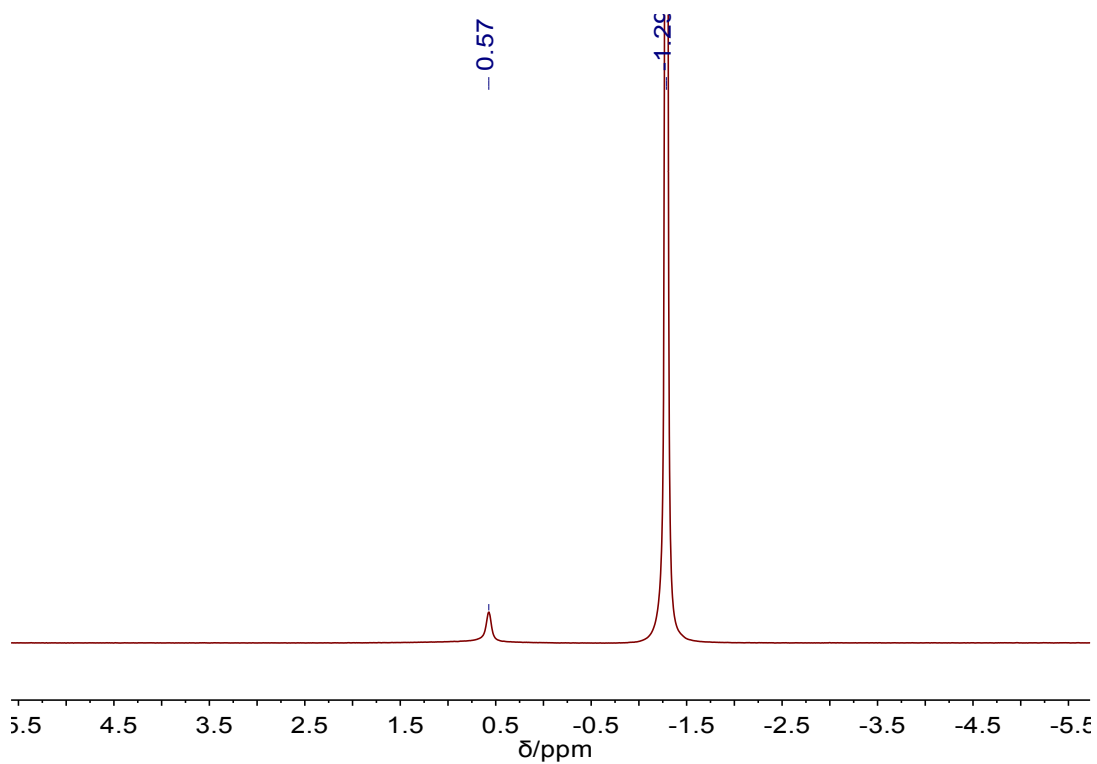
**Fig. S19**  $^1\text{H}$  NMR spectra of (a)  $\text{Pd}_6\text{L}_{12}$ , (b)  $\text{PF}_6^-@Pd_6L_{12}$ , (c)  $\text{BF}_4^-@Pd_6L_{12}$ , (d)  $\text{OTf}@Pd_6L_{12}$  in  $\text{DMSO-}d_6$  (400 MHz, 298 K).



**Fig. S20**  $^{19}\text{F}$  NMR spectrum of  $\text{BF}_4^-@Pd_6L_{12}$  in  $\text{DMSO-}d_6$  (376 MHz, 298 K).

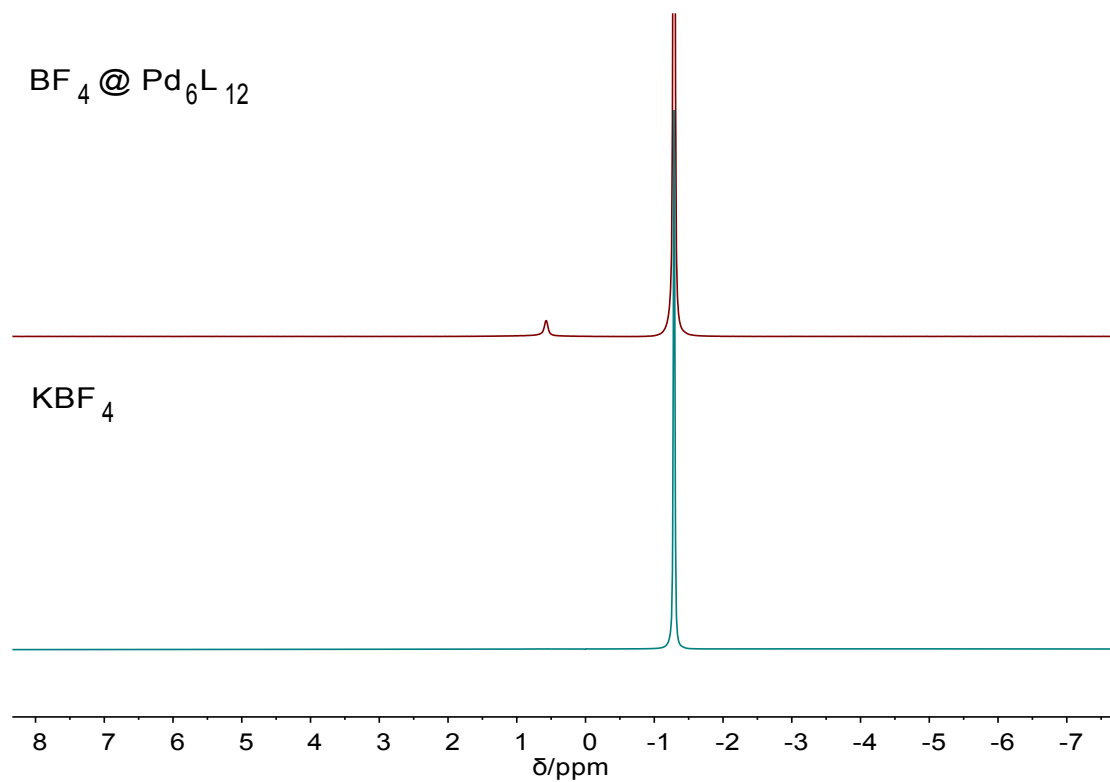


**Fig. S21**  $^{19}\text{F}$  NMR spectra of  $\text{BF}_4^- @ \text{Pd}_6\text{L}_{12}$  (top) and  $\text{KBF}_4$  (down) in  $\text{DMSO-}d_6$  (376 MHz, 298 K).

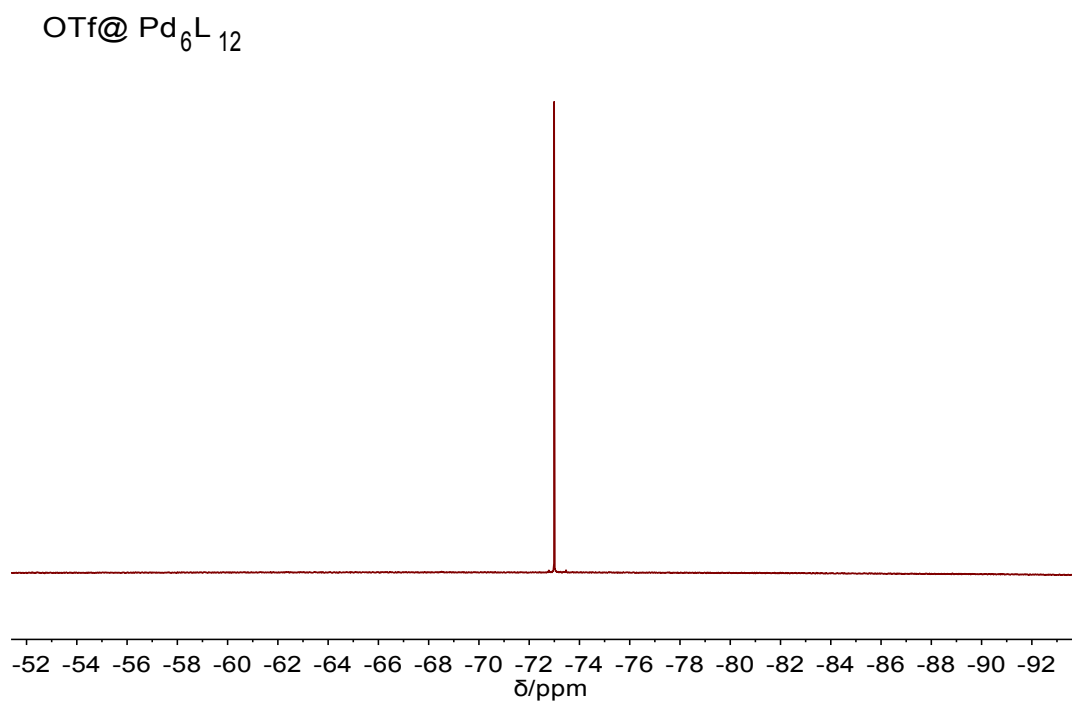


**Fig. S22**  $^{11}\text{B}$  NMR spectrum of  $\text{BF}_4^- @ \text{Pd}_6\text{L}_{12}$  in  $\text{DMSO-}d_6$  (128 MHz, 298 K).





**Fig. S23**  $^{11}\text{B}$  NMR spectra of  $\text{BF}_4^- @ \text{Pd}_6\text{L}_{12}$  (top) and  $\text{KBF}_4$  (down) in  $\text{DMSO-}d_6$  (128 MHz, 298 K).



**Fig. S24**  $^{19}\text{F}$  NMR spectrum of  $\text{OTf} @ \text{Pd}_6\text{L}_{12}$  in  $\text{DMSO-}d_6$  (376 MHz, 298 K).

**Table S1** Selected bond lengths (Å) and bond angles (°) for Pd<sub>6</sub>L<sub>12</sub>.

Au(1)-I(1)	2.488(4)	Pd(1)-N(4)	1.981(12)
Au(1)-C(18)	1.979(15)	Pd(1)-N(1) <sup>1</sup>	1.99(2)
Au(2)-I(2)	2.514(3)	Pd(1)-N(5)	2.023(19)
Au(2)-C(55)	1.966(14)	Pd(1)-N(8) <sup>2</sup>	1.96(12)
C(18)-Au(1)-I(1)	176.3(6)	N(4)-Pd(1)-N(1) <sup>1</sup>	86.8(8)
C(55)-Au(2)-I(2)	179.4(5)	N(4)-Pd(1)-N(5)	176.8(7)
C(36)-N(4)-Pd(1)	119.7(9)	N(1) <sup>1</sup> -Pd(1)-N(5)	90.9(9)
C(37)-N(4)-Pd(1)	119.9(9)	N(8) <sup>2</sup> -Pd(1)-N(4)	90(6)
C(7BA)-N(1)-Pd(1) <sup>3</sup>	118.5(15)	N(8) <sup>2</sup> -Pd(1)-N(1) <sup>1</sup>	176(5)
C(5)-N(1)-Pd(1) <sup>3</sup>	119.9(16)	N(8) <sup>2</sup> -Pd(1)-N(5)	93(6)

<sup>1</sup> $x - y + 1/3, x - 1/3, -z + 2/3$ ; <sup>2</sup> $-x + y + 1, -x + 1, z$ ; <sup>3</sup> $y + 1/3, -x + y + 2/3, -z + 2/3$ ; <sup>4</sup> $-y + 1, x - y, z$ .