

# Didocosyl selenide stabilized recyclable Pd(0) nanoparticles and coordinated palladium(II) as efficient catalysts for Suzuki-Miyaura coupling

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## S1 General Experimental Section

$^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{77}\text{Se}\{^1\text{H}\}$  spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13, 75.47 and 57.24 MHz respectively with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane.  $^{13}\text{C}$  DEPT NMR was used routinely to determine the number of hydrogen atoms linked to carbon atoms. Elemental analyses were carried out with a Perkin–Elmer 2400 Series II C, H, N analyzer. Estimation of palladium in nanoparticles was carried out on an AA7000 Series atomic absorption spectrophotometer (Lab India).

TEM studies were carried out with a Technai G<sup>2</sup> 20 electron microscope operated at 200 kV. The specimens for TEM were prepared by dispersing the powder in chloroform by ultrasonic treatment, dropping slurry onto a porous carbon film supported on a copper grid, and then drying in air. Powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 Advance diffractometer with Ni-filtered  $\text{CuK}\alpha$  radiation using a scan speed of 1 s and scan step of 0.02 °.

Melting points were determined in an open capillary and reported as such. The progress of the ligand's synthesis was monitored by TLC plate coated with an appropriate grade silica gel. Iodine was used for visualizing the spots. The products of catalytic reactions were separated and purified (if required) by column chromatography using silica gel (60–120 mesh) as the solid support. *n*-Hexane and its mixtures with chloroform/ethyl acetate in variable proportions were used as eluent. The products of Suzuki reactions were authenticated by matching their spectroscopic data with those reported in the literature. Commercially available reagents were used as received without further purification. The solvents viz. chloroform, DMF, hexane, MeOH and EtOH were dried by the standard methods. All reactions were carried out in glassware dried in an oven, under ambient conditions, except the synthesis of Ligand **L1**. The commercial nitrogen gas was used after passing it successively

through traps containing solutions of alkaline anthraquinone-sodium dithionite, alkaline pyrogallol, conc. H<sub>2</sub>SO<sub>4</sub> and KOH pellets. Nitrogen atmosphere if required was created using Schlenk techniques.

To use complex **1** as a catalyst at low concentration, appropriate aliquots (in  $\mu\text{L}$ ) of its solutions ( $2 \times 10^{-2}$  to  $1.5 \times 10^{-5}$  M) prepared in chloroform by successive dilution (See Table 1) were used. When 1 to 5 mol% of **1** was used, its calculated amount (15.73 mg, 1 mol%; 31.46 mg, 2 mol% and 78.65 mg, 5 mol%) was dissolved in 5 mL of chloroform.

**Table 1**

$1.5 \times 10^{-5}$ M, 20 $\mu\text{L}$ , $3 \times 10^{-7}$ mmol, $3 \times 10^{-5}$ mol%
$2 \times 10^{-4}$ M, 50 $\mu\text{L}$ , $10^{-6}$ mmol, $10^{-4}$ mol%
$2 \times 10^{-4}$ M, 50 $\mu\text{L}$ , $10^{-5}$ mmol, $10^{-3}$ mol%
$2 \times 10^{-2}$ M, 50 $\mu\text{L}$ , $10^{-3}$ mmol, $10^{-1}$ mol%

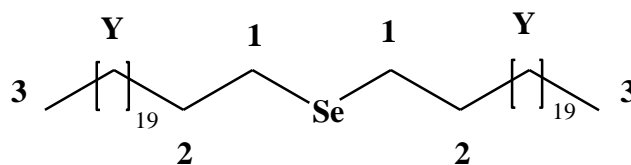
## **S2 Starting Materials and Syntheses of Ligand, Palladium complex and Palladium Nano-Particles**

Selenium powder, NaBH<sub>4</sub>, 1-bromodocosane, sodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>), potassium carbonate, cesium carbonate and all aryl halides were procured from Aldrich (USA).

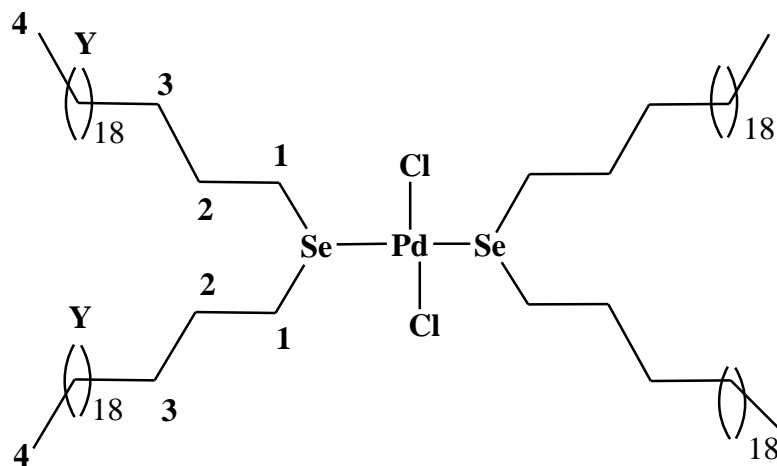
### **General Procedure for Syntheses of L1, its Pd(II) Complex and L1-Stabilized Pd(0) Nanoparticles 2–4**

**L1 (*n*-C<sub>22</sub>H<sub>45</sub>)<sub>2</sub>Se:** Selenium powder (0.169 g, 2.0 mmol) was stirred in dry ethanol (20 mL) at 60 °C for 1 h. Saturated aqueous solution of NaBH<sub>4</sub> with one pellet of NaOH (0.200 g) was added drop wise to the reaction mixture under nitrogen atmosphere. After the complete decolorization of solution 1-bromodocosane (1.552 g, 4 mmol) was added as solid with stirring. The mixture was stirred further at 60 °C for 10 h. The precipitate was filtered and washed three times with ethanol. The resulting residue was dried in *vacuo*. Yield: (1.212 g) 86%; m.p. 67 °C. Anal. Found: C, 75.64; H, 13.01%. Calc. for C<sub>44</sub>H<sub>90</sub>Se: C, 75.70; H, 12.99%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  (ppm): 0.886 (t, *J* = 6.6 Hz, 6H), 1.216–1.397 (m, 76H), 1.575–1.653 (m, 4H), 2.493 (t, *J* = 7.5 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 14.10, 22.71,

23.91, 29.20, 29.39, 29.57–29.73, 29.99, 30.70, 31.95.  $^{77}\text{Se}\{^1\text{H}\}$  NMR (57 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 163.65.



**1:** The  $\text{Na}_2[\text{PdCl}_4]$  (0.147 g, 0.5 mmol) was dissolved in 10 mL of methanol. The solution of ligand **L1** [(0.698 g), 1 mmol] made in 1:1 mixture of 20 mL of chloroform and hexane was added to it with vigorous stirring. The mixture was further stirred for 2 h. The solution was reduced to 10 mL on rotary evaporator. The yellow precipitate was filtered and washed several times with methanol. The resulting residue was dried in *vacuo*. Yield: (0.613 g) 78%; m.p. 64 °C. Anal. Found: C, 67.21; H, 11.49%. Calc. for  $\text{C}_{88}\text{H}_{180}\text{Cl}_2\text{PdSe}_2$ : C, 67.17; H, 11.53%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  (ppm): 0.881 (t,  $J = 6.3$  Hz, 12H,  $\text{H}_4$ ), 1.215–1.455 (m, 136H), 1.888–1.935 (m, 16H), 2.588–2.625 (m, 8H), 2.921–2.984 (m, 8H).



$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 14.12, 22.69, 28.81, 29.12, 29.36–29.83, 31.08, 31.92.  $^{77}\text{Se}\{^1\text{H}\}$  NMR (57 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 257.18.

**Pd(0) NPs 2–4:** The  $\text{Na}_2[\text{PdCl}_4]$  (0.147 g, 0.5 mmol) was dissolved in 50 mL of methanol. The solution of ligand **L1** [1.396 g, 2 mmol (Pd:L = 1:4) for **2**; (0.349 g, 0.5 mmol (Pd:L = 1:1) for **3**; (0.036 g, 0.125 mmol (Pd:L = 4:1) for **4**] made in 100 mL of 1:1 mixture of chloroform and hexane was added to it with vigorous stirring. The mixture was further stirred for 1 h. The solution of  $\text{NaBH}_4$  (0.057 g, 1.5 mmol) in methanol was added drop wise over a period of 45 minutes to the reaction mixture.

The mixture was further stirred for 2 h. The solvent was reduced to 20 mL on rotary evaporator. The residue was centrifuged and washed three times with methanol. The resulting residue was dried in *vacuo*.

### S3 Procedure for Catalytic Reactions

#### S3.1. General Procedure for Suzuki Miyaura C–C Coupling Reaction Catalyzed by **1**

An oven-dried flask was charged with aryl halides (1.0 mmol), phenylboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mol) and DMF/H<sub>2</sub>O (2.0 ml/1.0 ml). An appropriate amount of complex **1** as solution made in chloroform was added. The flask was placed on an oil bath at 100 °C. Progress of reaction was monitored by TLC. Mixture of ethylacetate and hexane (20:80) was used as mobile phase for TLC development. After completion of reaction the mixture was extracted with 10 mL diethylether. The extract was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent of the extract was removed with rotary evaporator and the resulting residue purified by a column chromatography on silica gel using either chloroform–hexane mixture (5:95 to 20:80) or ethylacetate–hexane mixture (5:95 to 20:80).

#### S3.2. General Procedure for the Suzuki Reaction of Aryl bromides with Phenylboronic acid Catalyzed by Nanoparticles (**2**, **3** and **4**)

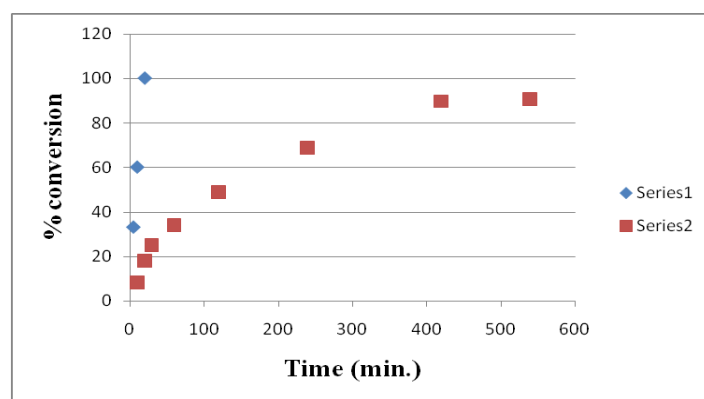
An oven-dried flask was charged with aryl halide (5.0 mmol), phenylboronic acid (6.0 mmol), K<sub>2</sub>CO<sub>3</sub> (8.0 mmol) and DMF/H<sub>2</sub>O (9 mL/3 mL). Nanoparticles **2**, **3** or **4** (Pd ~0.5, 1 and 1.5 mol %) was added. Progress of reaction was monitored by NMR. After the maximum conversion, the reaction mixture was cooled to room temperature and mixed with 5 ml of hexane. The mixture was further stirred for 10 minutes. Hexane layer containing Pd NPs was separated and washed with 5 ml of acetone water mixture (1:1). Hexane was evaporated off under reduced pressure. The residue was dried in *vacuo* and used as such in next reaction cycle. DMF, water layer was extracted with 10 mL diethylether. The extract was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent of the extract was evaporated off with rotary evaporator and residue was subjected to proton NMR for estimating conversions. For each subsequent catalytic cycles aryl halide (5.0 mmol), phenylboronic acid (6.0 mmol), K<sub>2</sub>CO<sub>3</sub> (10.0 mol) and DMF/H<sub>2</sub>O (5 mL/2 mL) were added to the

nanoparticles recovered and stirred at 100 °C. The conversions were evaluated by proton NMR as described above. After completion of fifth catalytic cycle, the reaction the mixture was extracted with 50 mL diethylether. The extract was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent of the extract was removed with rotary evaporator and the resulting residue purified by a column chromatography on silica gel.

## S4 Hot Filtration Hg Poisoning Test

### S4.1. Hot Filtration Test

The reaction with catalyst **3** was subjected to hot filtration test. The reaction mixture of Suzuki coupling reaction of phenylboronic acid (1.2 mmol) with 4-bromobenzaldehyde (1.0 mmol) catalyzed with 1 mol % of **3** under optimal reaction conditions was filtered hot through G-4 crucible containing 1 g celite, when 60% conversion (monitored by <sup>1</sup>H NMR spectroscopy) was obtained (~ after 10 min of reaction). The conversion monitored in filtrate with time, continued and reached maximum (90%) after 7 h. This indicates that some of the palladium was leached from NPs which continued the catalytic reaction. The palladium leaching estimated by AAS, was found to be 0.5% of initial catalyst loading. In the hot filtrate 4-bromobenzaldehyde (1.0 mmol), phenylboronic acid (1.2 mmol), and K<sub>2</sub>CO<sub>3</sub> (2.0 mol) were further added. After 24 h total conversion was only 54% indicating leached palladium was almost rendered inactive.



Series 1: Without Hot Filtration

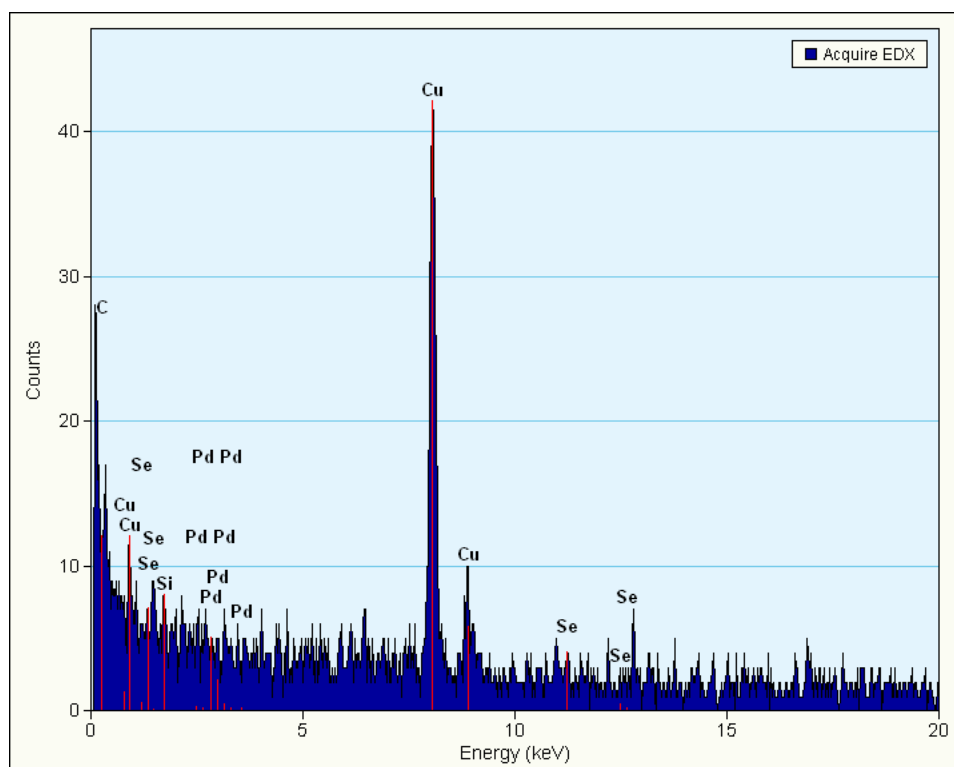
Series 2: After Hot Filtration

#### *S4.2. Hg Poisoning Test*

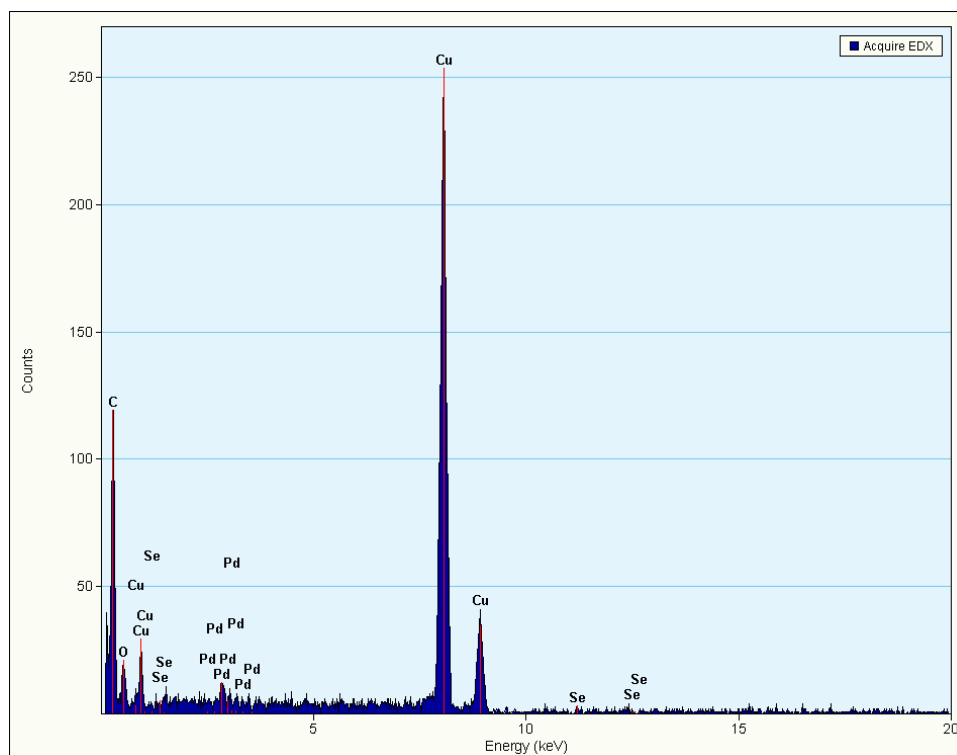
For mercury poisoning test poison excess of Hg (Hg : Pd; 400 : 1) was taken in the reaction flask before the addition of reactants. Thereafter coupling reaction of 4-bromoanisole with phenylboronic acid using **1** (0.1 mol%) or **3** (1 mol%) under optimal conditions was carried out in the flask. The product biaryl derivative was obtained in ~100% yield (when **1** was used as catalyst), even in the presence of excess of Hg. Thus it is unlikely that Pd nanoparticles acted as the active catalyst in our protocol. When NPs **3** were used as catalyst under optimal reaction conditions only 18% product was obtained after reaction of 5 h. The coupling reaction of 4-bromoanisole with phenylboronic acid in the presence of 1 mol% of **3** under optimal reaction condition was carried out. When 61% conversion took place 400 equivalents of Hg (for 1 equivalent of Pd) were added to the reaction mixture. After continuing reaction further for 24 h at 100 °C only 67 % conversion could be reached.

#### *S4.3. PPh<sub>3</sub> Poisoning Test*

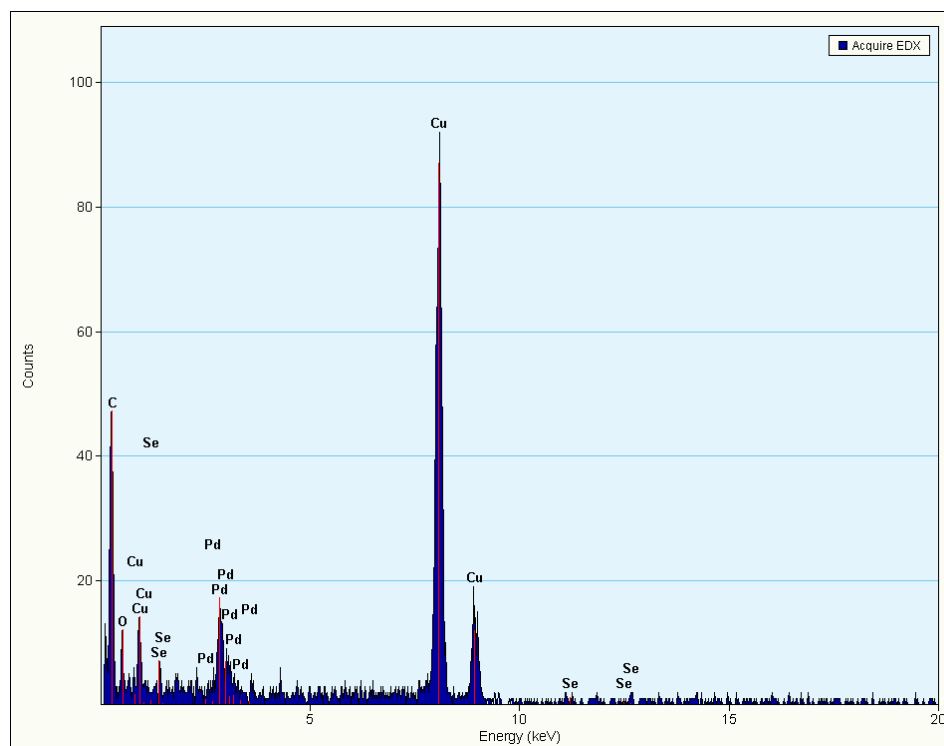
To the coupling reaction of 4-bromoanisole with phenylboronic acid using **3** (1 mol%) as a catalyst, PPh<sub>3</sub> (2 mol%) was added under optimal conditions. After 24 h of reaction cross coupling product 4-biphenylcarboxyldehyde was not obtained. This observation is as expected for NPs.



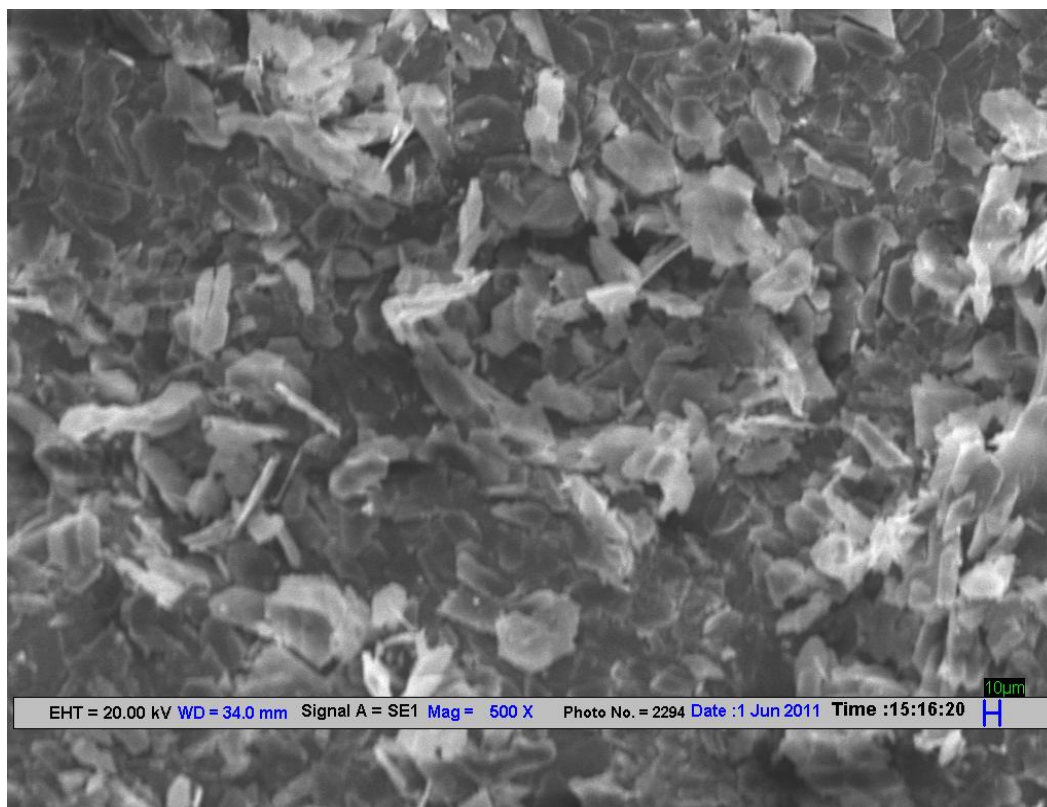
**Figure S1.** TEM–EDX of Pd NPs stabilized by  $\text{Se}(\text{C}_{22}\text{H}_{45})_2$  (metal:ligand = 1:4) (2)



**Figure S2.** TEM–EDX of Pd NPs stabilized by  $\text{Se}(\text{C}_{22}\text{H}_{45})_2$  (metal:ligand = 1:1) (3)

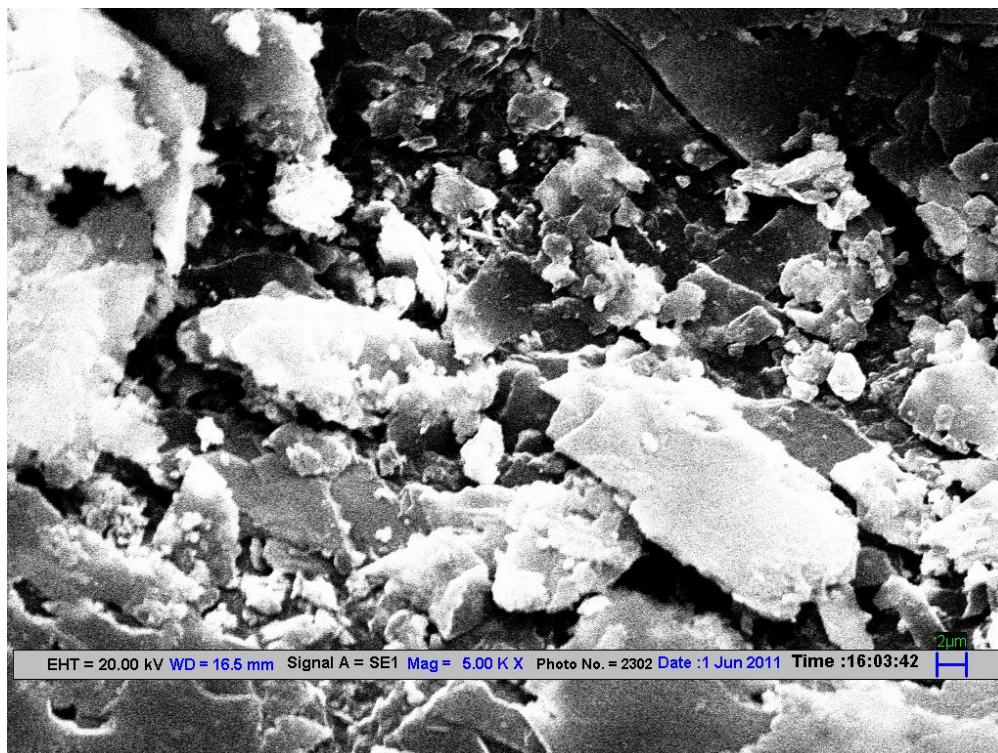


**Figure S3.** TEM-EDX of Pd NPs stabilized by  $\text{Se}(\text{C}_{22}\text{H}_{45})_2$  (metal:ligand = 4:1) (4)

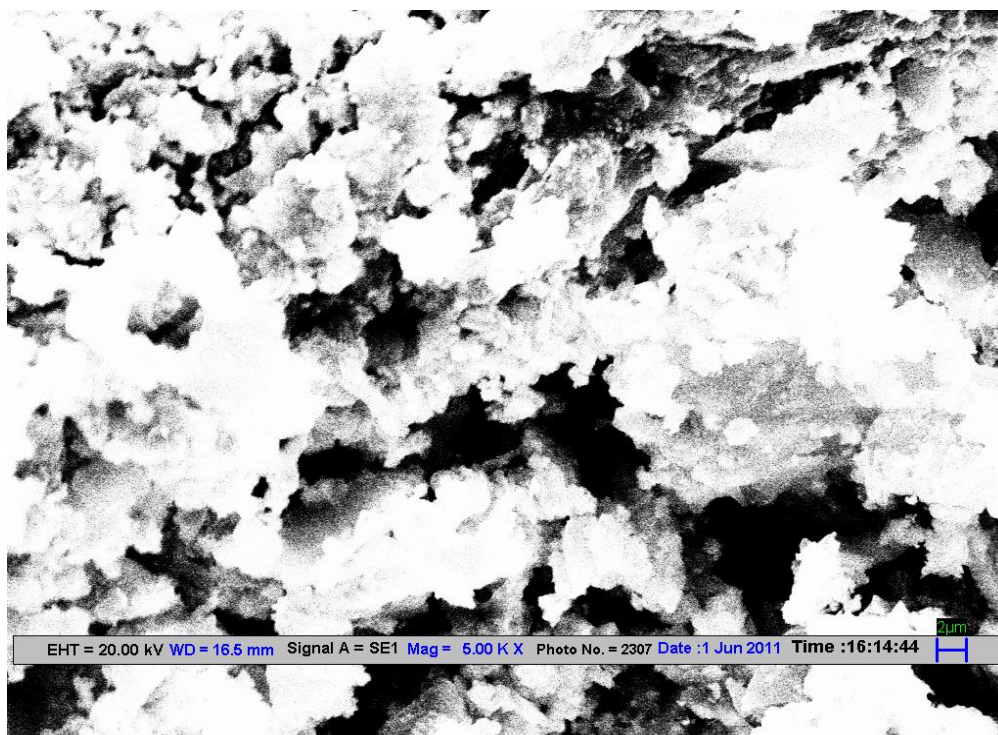


**Figure S4.** SEM image Pd NPs stabilized by  $\text{Se}(\text{C}_{22}\text{H}_{45})_2$  (metal:ligand = 1:4) (2)

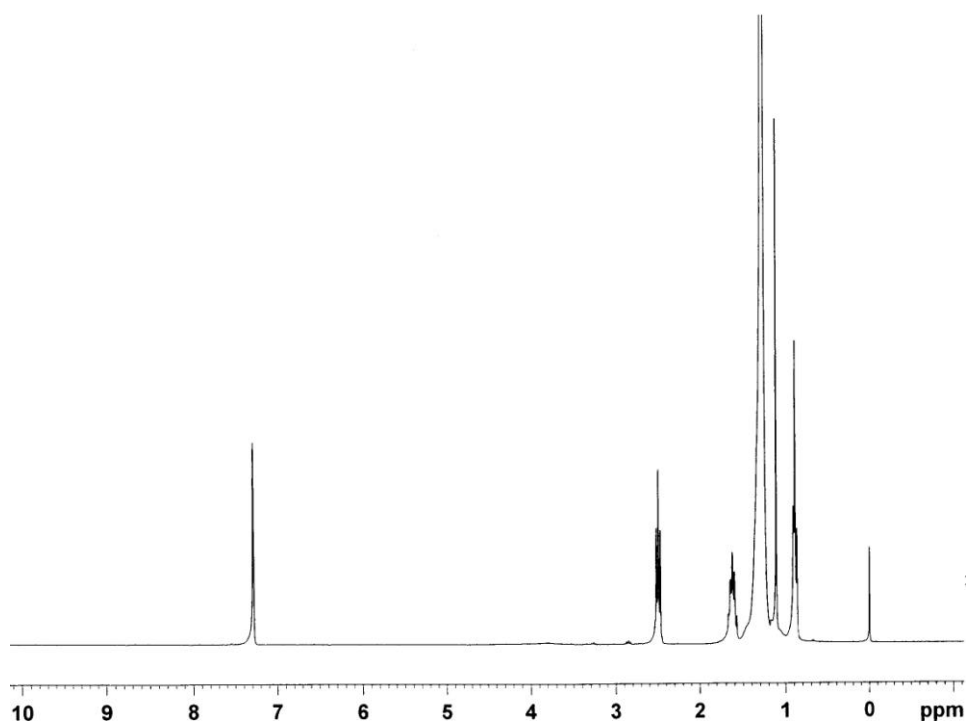




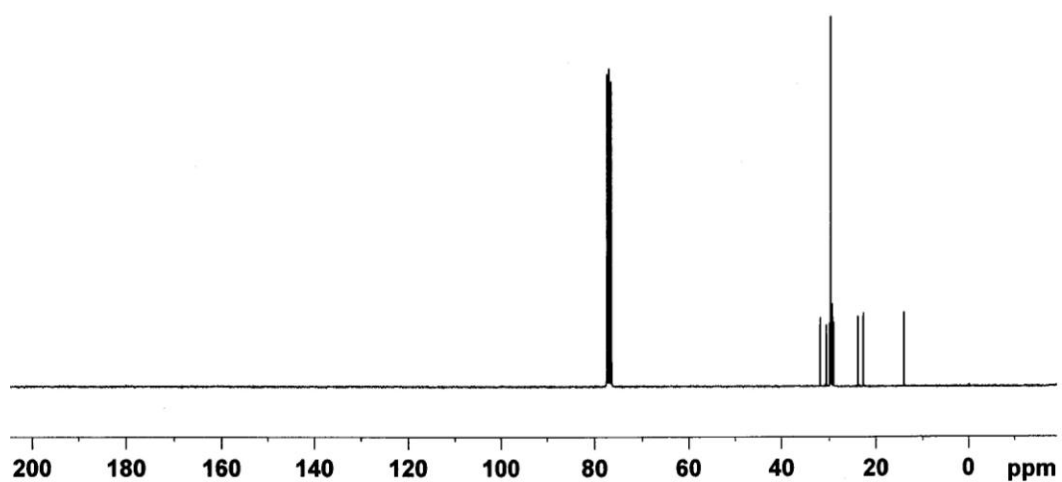
**Figure S5.** SEM image Pd NPs stabilized by  $\text{Se}(\text{C}_{22}\text{H}_{45})_2$  (metal:ligand = 1:1) (3)



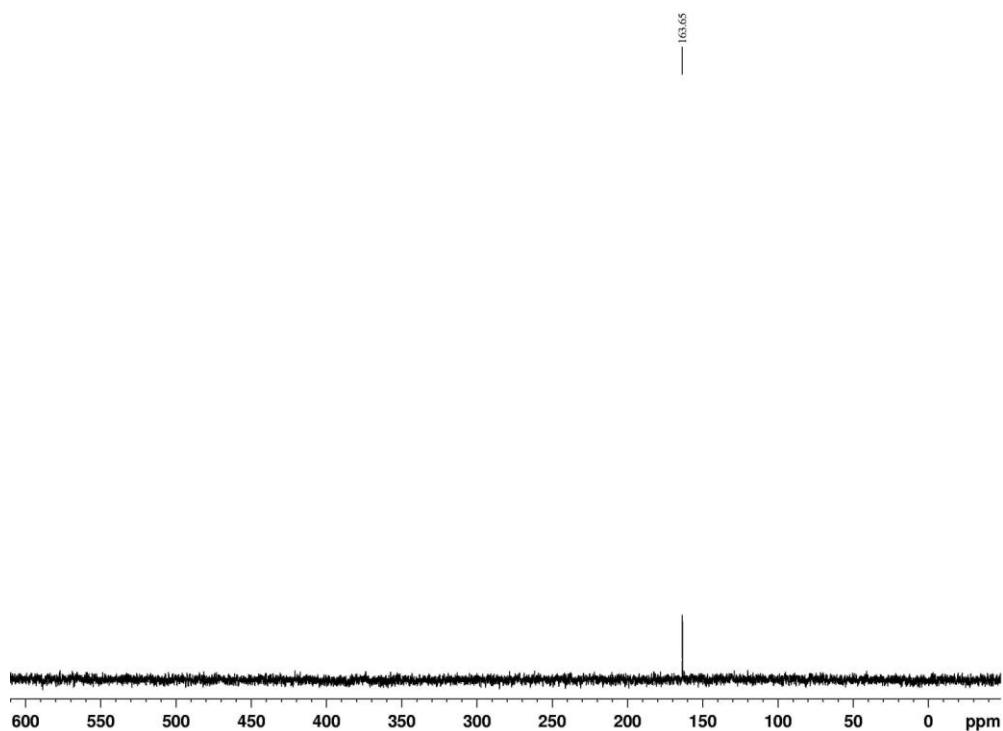
**Figure S6.** SEM image Pd NPs stabilized by  $\text{Se}(\text{C}_{22}\text{H}_{45})_2$  (metal:ligand = 4:1) (4)



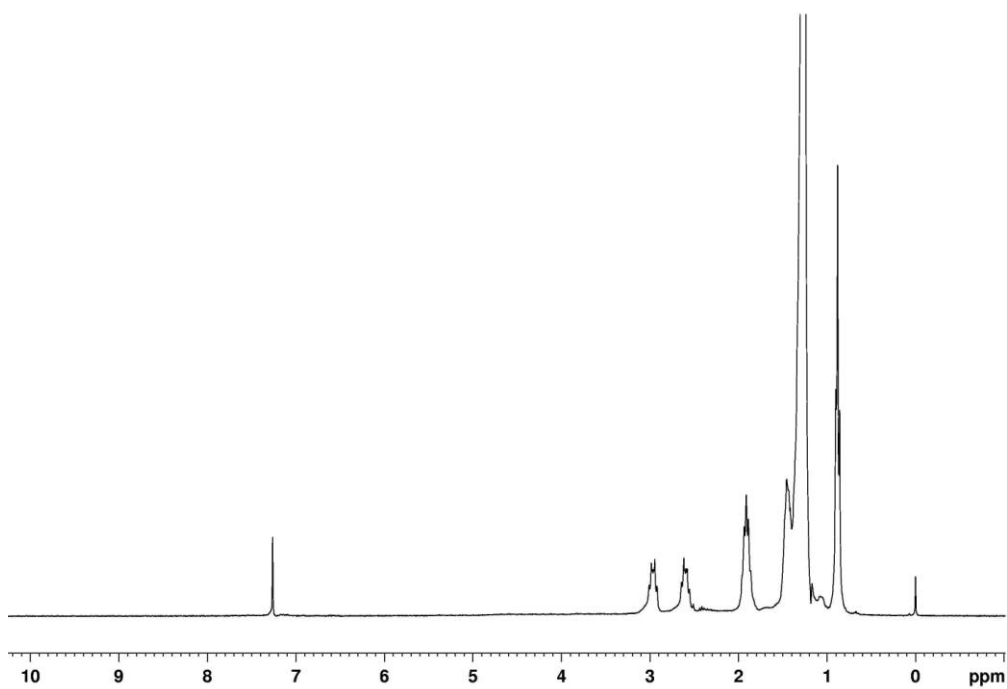
**Figure S7.**  $^1\text{H}$  NMR Spectrum of Ligand (L1)



**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Ligand (L1)



**Figure S9.**  $^{77}\text{Se}\{^1\text{H}\}$  NMR Spectrum of Ligand (L1)



**Figure S10.**  $^1\text{H}$  NMR Spectrum of  $\text{Pd}[\text{Se}(\text{C}_{22}\text{H}_{45})_2]_2\text{Cl}_2$  (1)

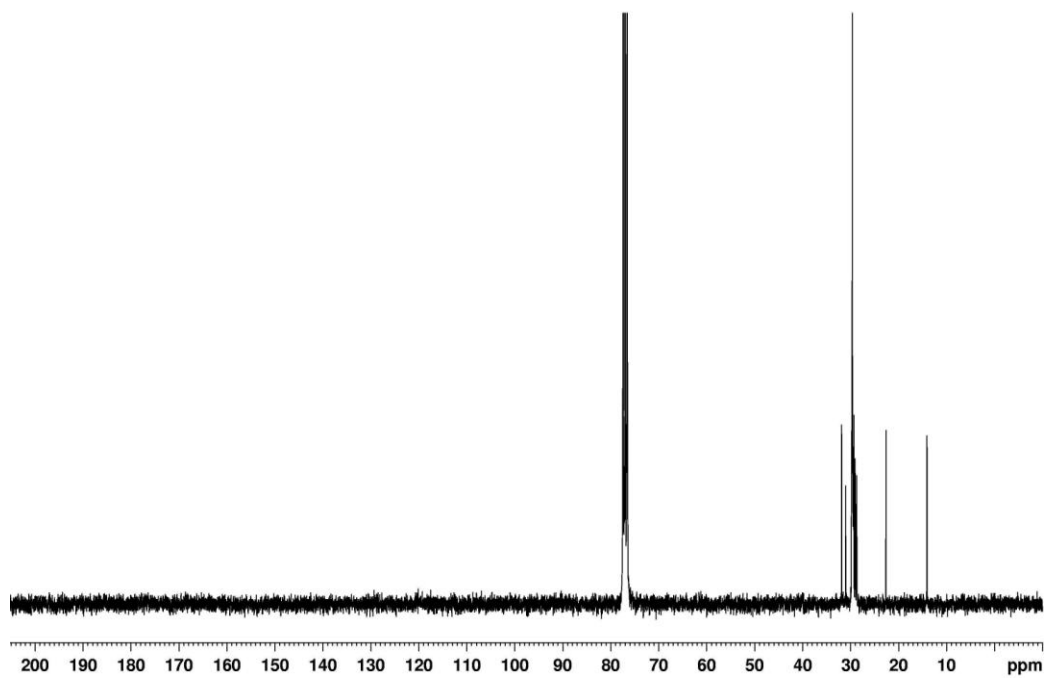


Figure S11.  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of  $\text{Pd}[\text{Se}(\text{C}_{22}\text{H}_{45})_2]_2\text{Cl}_2$  (1)

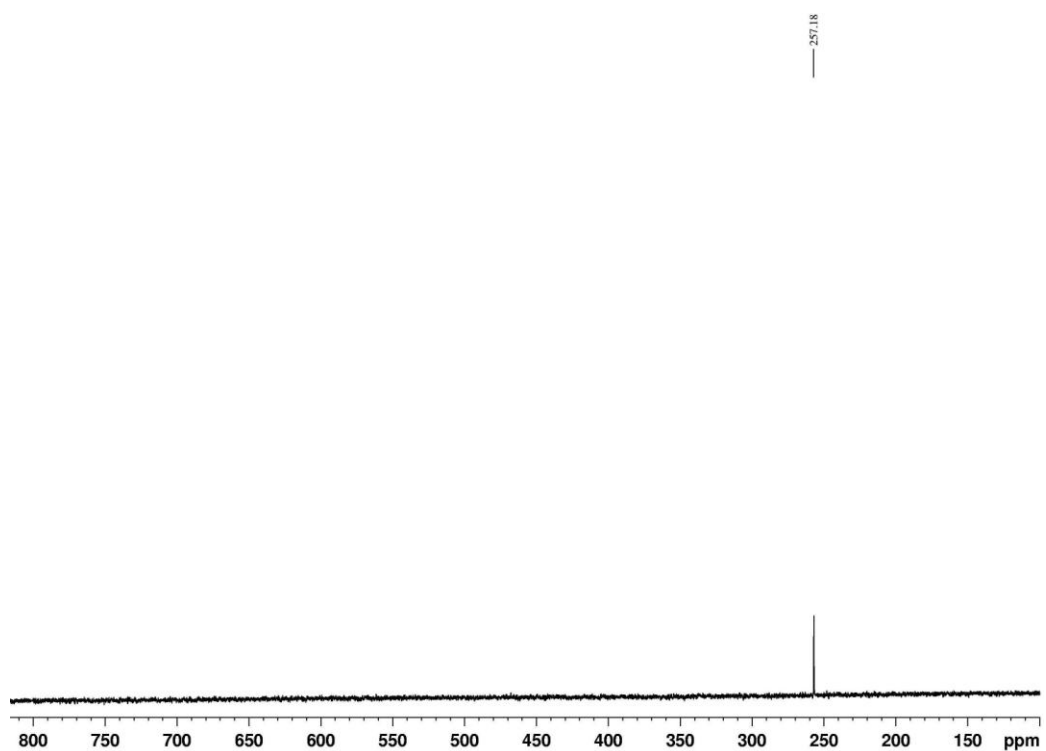
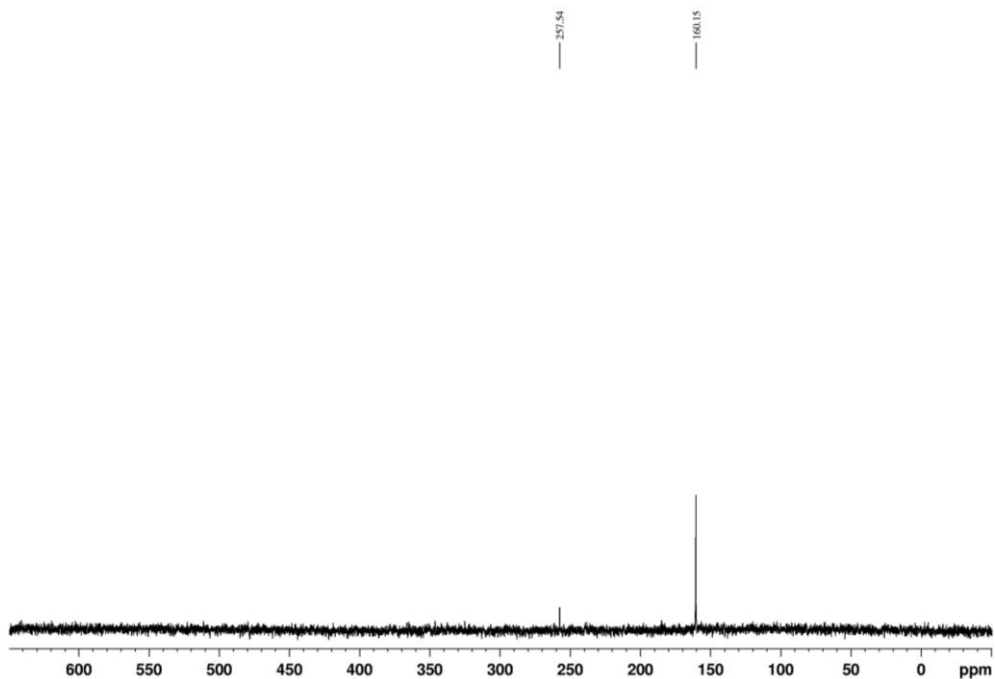
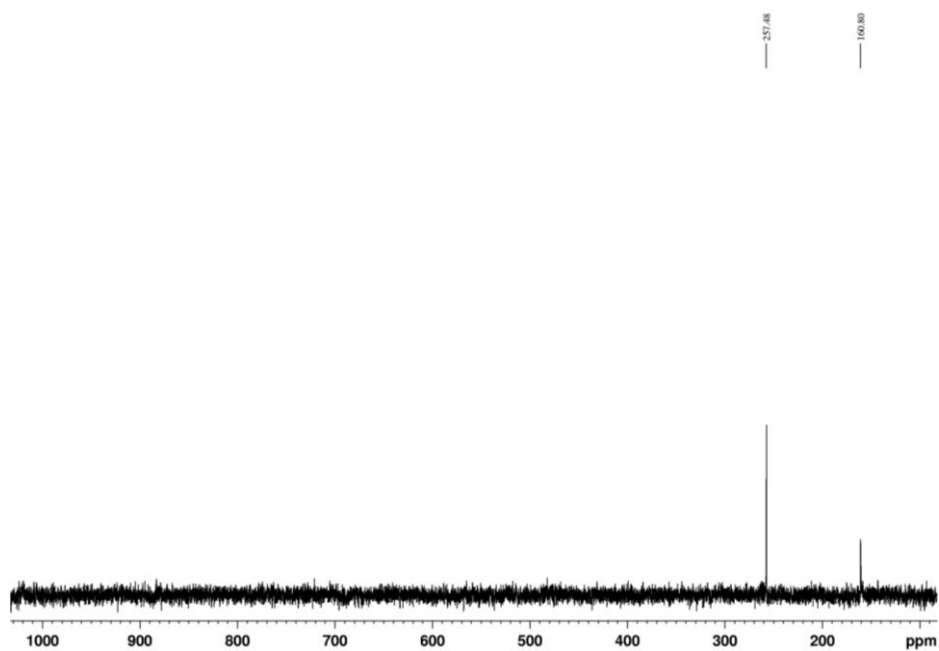


Figure S12.  $^{77}\text{Se}\{^1\text{H}\}$  NMR Spectrum of  $\text{Pd}[\text{Se}(\text{C}_{22}\text{H}_{45})_2]_2\text{Cl}_2$  (1)



**Figure S13.**  $^{77}\text{Se}\{^1\text{H}\}$  NMR Spectrum of **2**



**Figure S14.**  $^{77}\text{Se}\{^1\text{H}\}$  NMR Spectrum of **3**

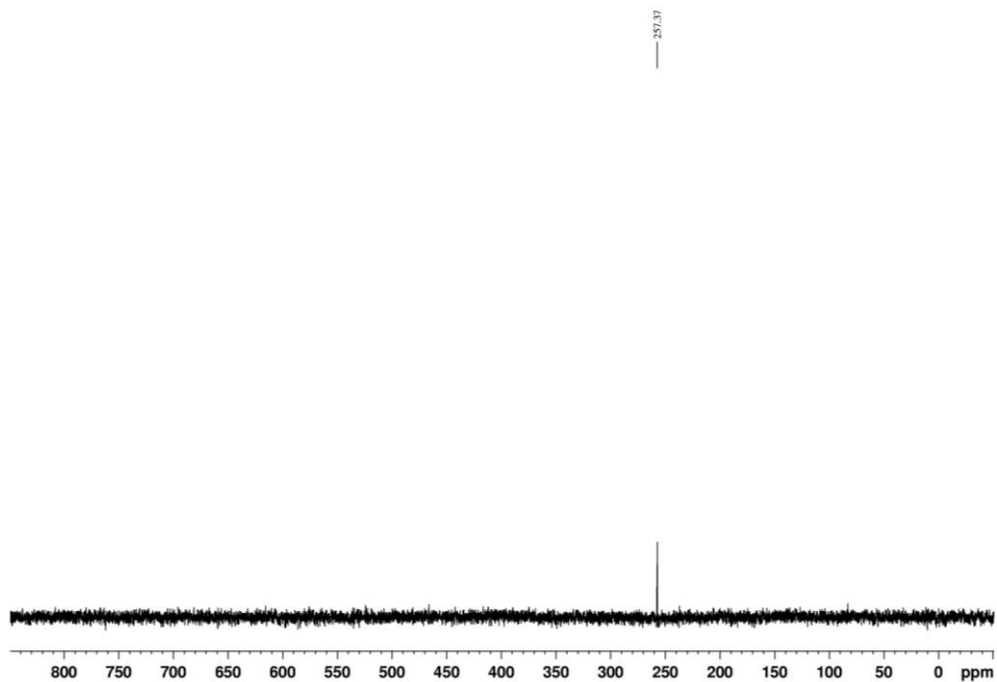


Figure S15.  $^{77}\text{Se}\{^1\text{H}\}$  NMR Spectrum of **4**

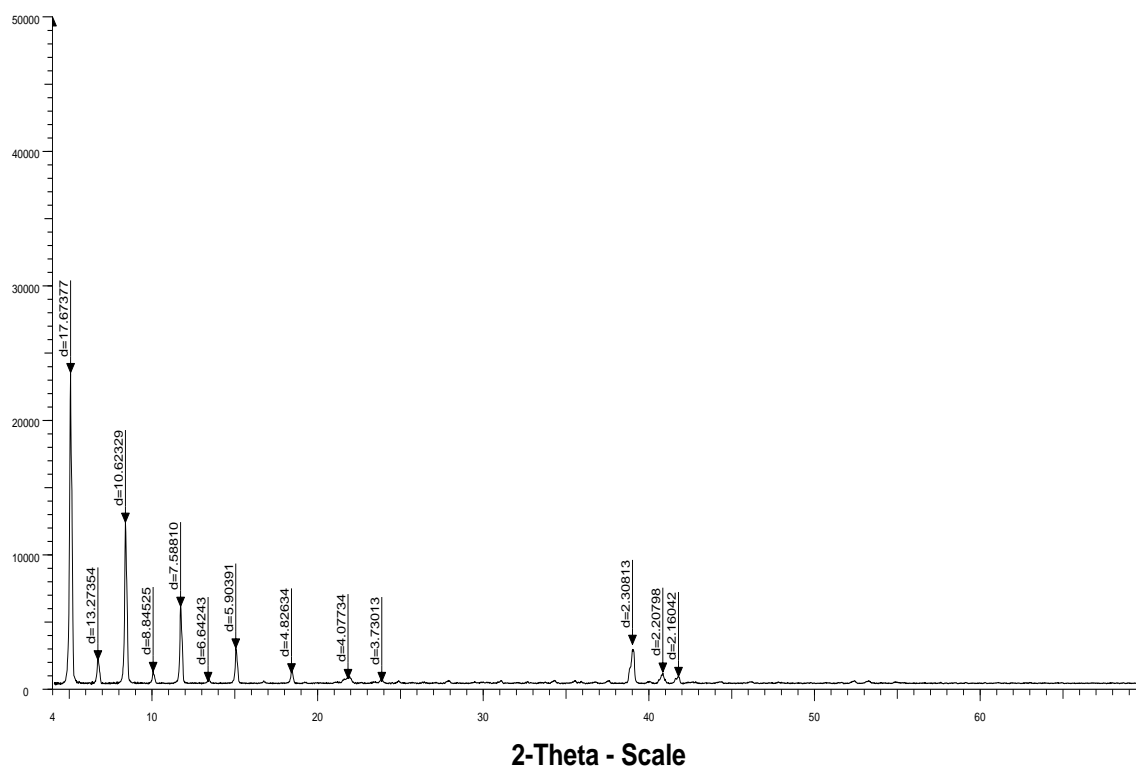


Figure S16. Powder XRD pattern of ligand (**L1**)

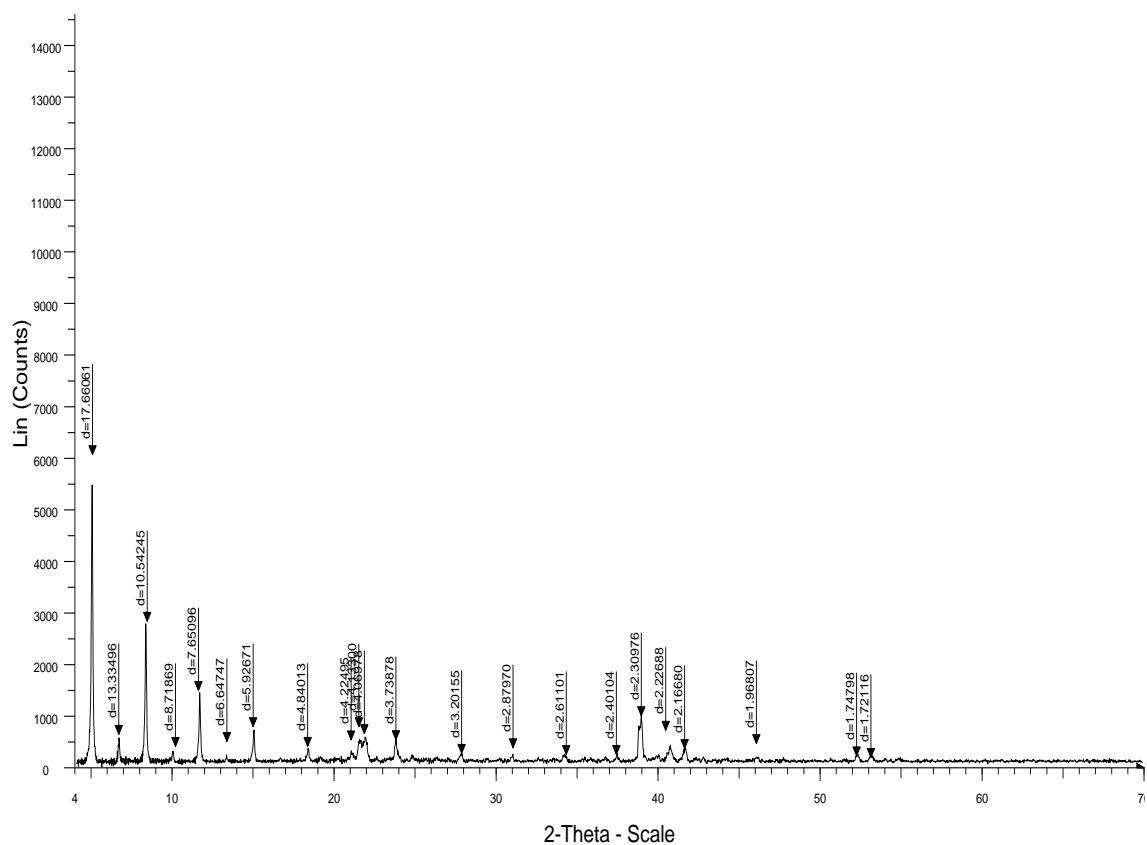


Figure S17. Powder XRD pattern of **2**

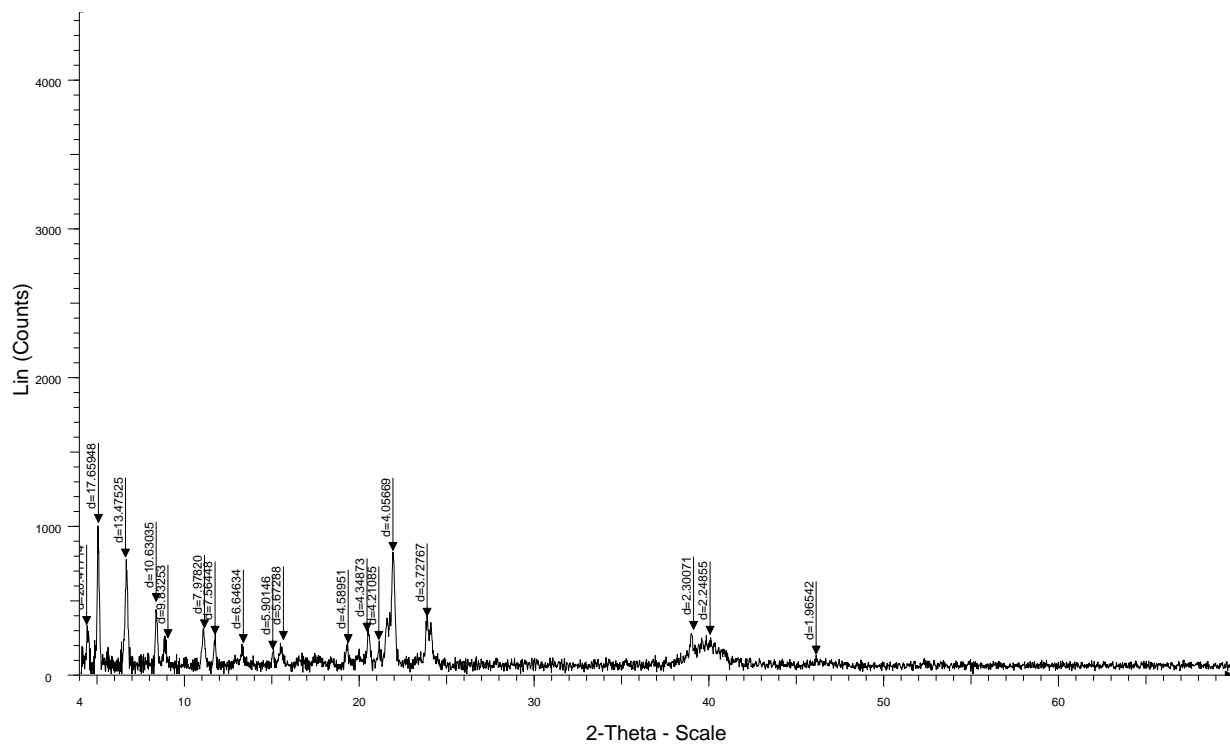
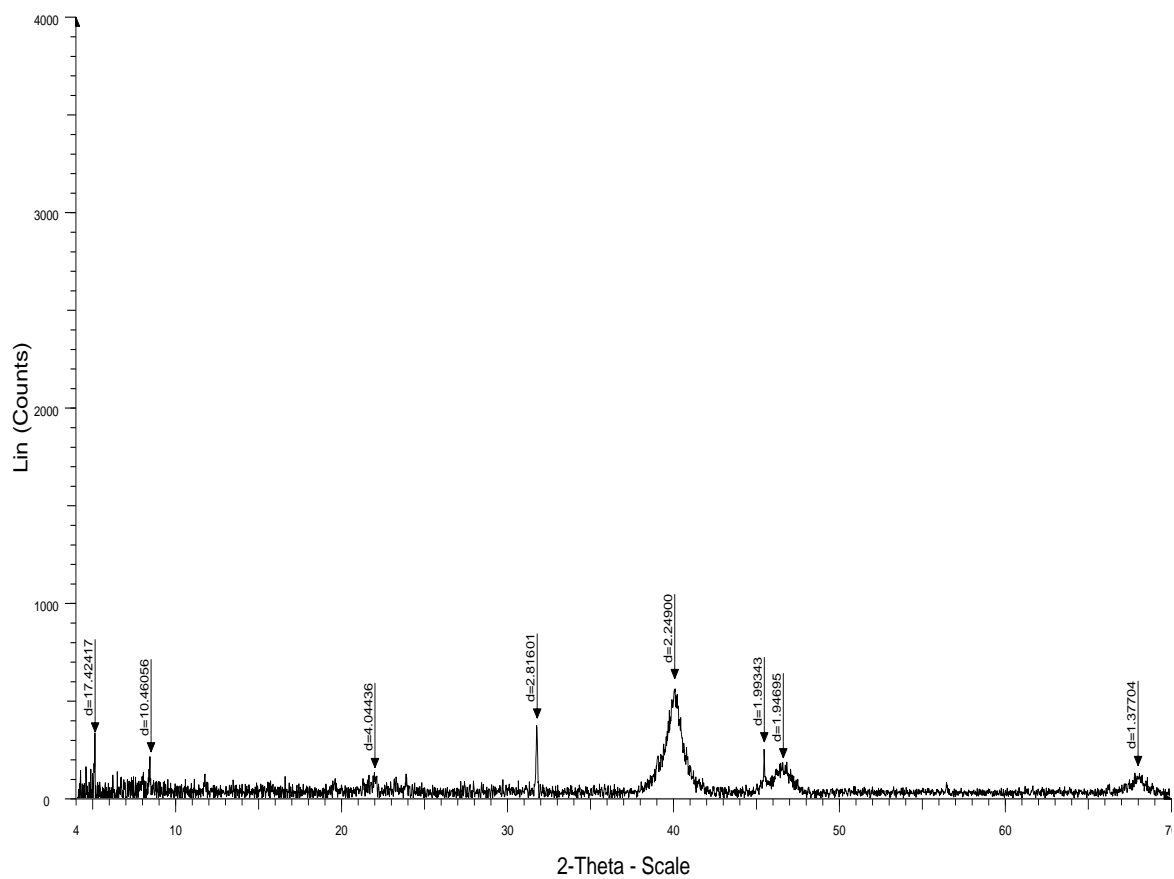
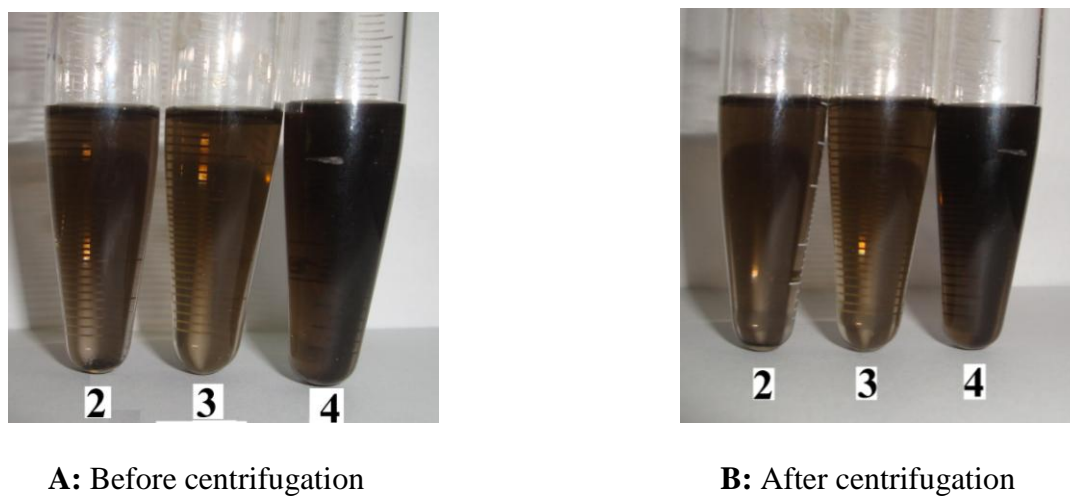


Figure S18. Powder XRD pattern of **3**



**Figure S19.** Powder XRD pattern of **4**



**A:** Before centrifugation

**B:** After centrifugation

**Figure S20.** Images of solutions of Pd NPs in  $\text{CHCl}_3$