Electronic Supporting Information

for

Palladium(II)-selenoether complexes as new single source precursors: First synthesis of Pd_4Se and Pd_7Se_4 nanoparticles

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S1. General Experimental Section.

^{1}H, $^{13}C\{^{1}H\}$ and $^{77}Se\{^{1}H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13, 75.47 and 57.24 MHz respectively. The chemical shifts are reported in ppm relative to the residual deuterated solvent or the internal standard (tetramethylsilane in case of ^{1}H, / $^{13}C\{^{1}H\}$ NMR and Me_2Se for $^{77}Se\{^{1}H\}$ NMR). Elemental analyses were carried out with a Perkin–Elmer 2400 Series II C, H, N analyzer. Yields refer to isolated yields of compounds which appear pure by ^{1}H−NMR. All reactions were carried out in glassware dried in an oven and under N_2 atmosphere except the syntheses of Schiff base of $H_2N(CH_2)_3SePh$ and its reduced derivative carried out under ambient conditions.

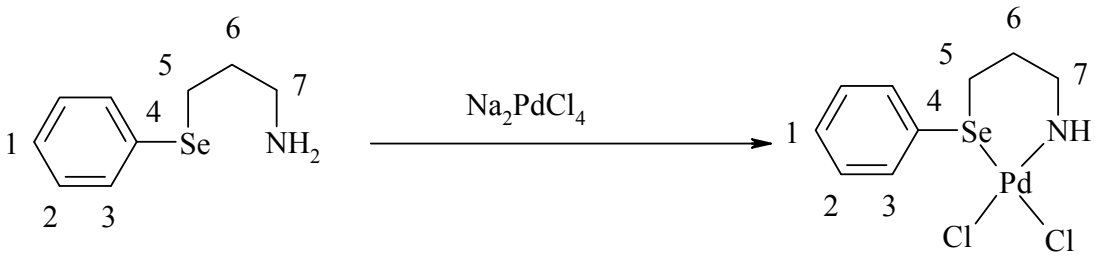
The morphologies of nano-sized phases were studied with a Carl ZEISS EVO5O scanning electron microscope (SEM). Sample was mounted on a circular metallic sample holder with a sticky carbon tape. Elemental composition of these phases has been obtained by associated EDX system Model QuanTax 200, which is based on the SDD technology and provides an energy resolution of 127 eV at Mn K alpha. Sample was mounted on a circular metallic sample holder with a sticky carbon tape.

Powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 Advance diffractometer using Ni-filtered Cu*Kα* radiation, scan speed of 1 s and scan step of 0.05º. Transmission electron microscopic (TEM) studies were carried out using a JEOL JEM 200CX TEM instrument operated at 200 kV. The specimens for these studies were prepared by dispersing the powdered sample in ethanol by ultrasonic treatment, and then a few drops were put onto a porous carbon film supported on a copper grid, and dried in air.

DLS studies were carried out using a Zeta Nano Sizer (Nano-series) Nano ZS−90 fitted with a 633 nm laser.

S2. Starting Materials and Synthesis of 1 and 2.

Diphenyldiselenide, $NaBH_4$, 3-chloropropylamine hydrochloride, 2-hydroxybenzophenone, sodium tetrachloropalladate (Na_2PdCl_4) and TOP were procured from Aldrich. Palladium (II) complex (**1**) was synthesized (Scheme S 2.1) by the reaction of selenated amine[1] and Na_2PdCl_4.



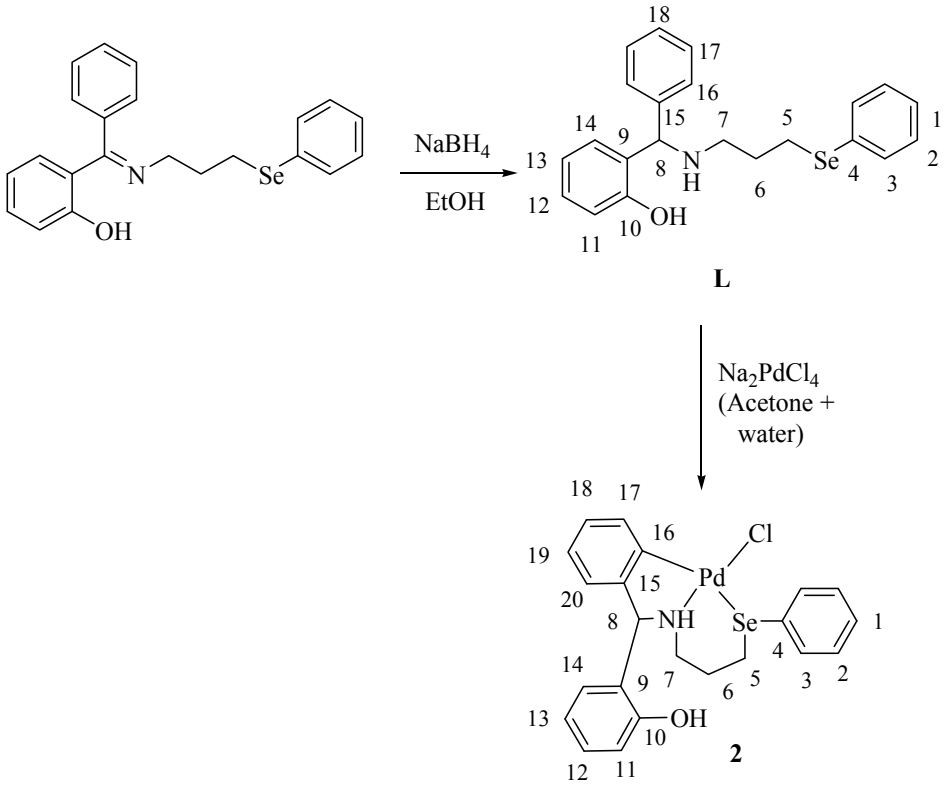
Scheme S 2.1 Methodology for Syntheses of **1**

Selenated Schiff base 2−OH−C_6H_4−C(Ph)=N−$(CH_2)_3$−Se−C_6H_5 was synthesized (Scheme S2.2) according the previously published procedure.[2]

Reduced Schiff Base (**L**):[3] The C_6H_5Se−$(CH_2)_3$−N=C(Ph)C_6H_4−2−OH (0.395 g, 1 mmol) prepared by reported method[1b] and $NaBH_4$ (0.0416 g, 1.1 mmol) were refluxed for 15 h in 100 mL dry ethanol. The solution was cooled and its solvent was removed on a rotary evaporator. The ligand was leached into dry chloroform. The solvent was removed under vacuum. The **L** was obtained as light yellow liquid. Yield: 0.333 g (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.434 (s, 2H, NH + OH), 1.921−2.078 (m, 2H, H_6), 2.785−3.041 (m, 4H, H_5 + H_7), 4.952 (s, 1H, H_8), 6.843 (t, J = 7.5 Hz, 1H, H_{13}), 6.934 (d, J = 7.5 Hz, 1H, H_{14}), 6.986 (d, J = 8.1 Hz, 1H, H_{11}), 7.280 (t, J = 8.1 Hz, 1H, H_{12}), 7.322−7.428 (m, 8H, H_1 + H_2 + H_{16} + H_{17} + H_{18}), 7.554−7.585 (m, 2H, H_3); ^{13}C (75 MHz): δ 24.87 (C_6), 29.61 (C_5), 47.41 (C_7), 67.54 (C_8), 116.80 (C_{11}), 119.00 (C_{13}), 124.46 (C_9), 126.80 (C_1), 127.11 (C_{17}), 127.67 (C_{18}), 128.56 (C_{12}), 128.73 (C_{16}), 128.85 (C_{14}), 128.91 (C_2), 129.54 (C_4), 132.56 (C_3), 141.34 (C_{15}), 157.41 (C_{10}). ^{77}Se NMR (57 MHz): δ 293.63.

[PdCl(2−HO−C_6H_4−CH(Ph)−NH−$(CH_2)_3$−SeC_6H_5)] (**2**):[3] The $Na_2[PdCl_4]$ (0.294 g, 1 mmol) was dissolved in 5 mL of water. The solution of ligand **L** (0.397 g, 1 mmol) made in 10 mL of acetone was added to it with vigorous stirring. The mixture was further stirred for 2 h. The

orange red solution was extracted with chloroform. The chloroform layer was washed with water, dried with anhydrous Na_2SO_4 and evaporated to dryness under vacuum to obtain **2** as an orange colored powder.



Scheme S2.2 Synthesis of Reduced Schiff Base Ligand (**L**) and Palladium Complex (**2**).

Yield (0.381 g) 71%; m.p. 159 °C (d). Anal. Found: C, 44.16; H, 4.19; N, 2.29%. Calc. for $C_{22}H_{25}BClNO_4PdSe$: C, 44.11; H, 4.21; N, 2.34%. NMR: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.728 (m, 1H), 2.199−2.276 (m, 1H), 2.679–3.021 (m, 4H), 3.316 (s, 1H, CH), 5.365 (bs, 1H), 6.089 (d, J = 6.9 Hz, 1H), 6.783−6.922 (m, 5H), 7.189 (t, J = 6.9 Hz, 1H), 7.271 (d, J = 6.6 Hz, 1H), 7.436−7.437 (m, 3H), 7.605 (d, J = 7.5 Hz, 1H), 8.053−8.150 (m, 2H). ^{13}C (75 MHz): δ 17.69 (C_6), 31.85 (C_5), 53.24 (C_7), 66.56 (C_8), 113.80 (C_{11}), 118.83 (C_{13}), 124.26 (C_9), 127.29, 128.21, 128.37, 128.44, 128.56, 129.56, 129.68, 129.93, 129.99, 132.98, 133.53, 139.36, 161.39. ^{77}Se NMR (57 MHz, $CDCl_3$): δ 266.07.

S3. Dynamic Light Scattering (DLS) Analysis.

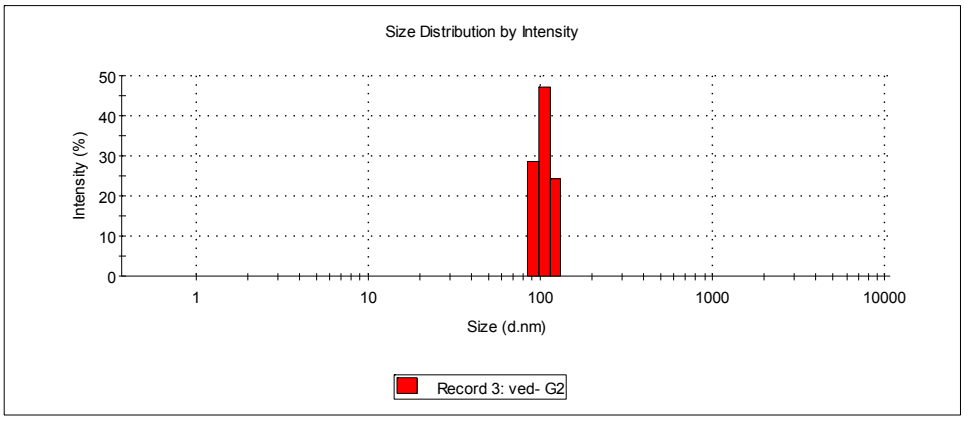


Figure S3.1 DLS Analysis of Pd_4Se Nanoparticles

Size (d.nm)	91.28	105.7	122.4
Intensity (%)	28.6	47.1	24.3

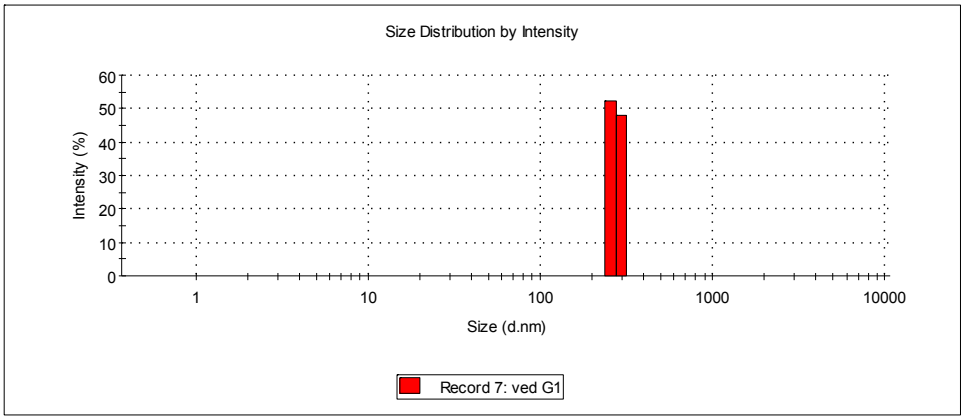


Figure S3.2 DLS Analysis of Pd_7Se_4 Nanoparticles

Size (d.nm)	255.0	295.3
Intensity (%)	52.1	47.9

S4. Powder XRD and SEM−EDX Studies of Pd_4Se and Pd_7Se_4 Nanoparticles

The powder X-ray diffraction pattern of these nanoparticles was indexes on the basis of a primitive tetragonal unit cell (JCPDS #11−0498) with the refined lattice parameter = 10.87 Å and d values (*hkl*): 2.69 (022), 2.57 (200), 2.42 (102), 2.36 (201), 2.32 (210), 2.24 (112), 2.11(211), 1.99 (211), 1.91 (202), 1.85 (220), 1.57 (302), 1.51 (320), 1.42 (104), 1.32 (431), 1.28 (322), 1.25 (204), 1.24 (213) for Pd_4Se and orthorhombic unit cell (JCPDS # 31−0939) with refined parameter = 9.39 Å and d values (*hkl*): 5.68 (101), 4.74 (011), 4.23 (110), 4.08 (102), 3.90 (111), 3.69 (012), 3.42 (200), 3.25 (201), 3.03 (103), 2.89 (210), 2.86 (013), 2.84 (202), 2.78 (211), 2.64 (113), 2.59 (021), 2.54 (004), 2.51 (212), 2.43 (121), 2.38 (104), 2.29 (014), 2.29 (014), 2.24 (122), 2.23 (301), 2.19 (213), 2.17 (114), 2.11 (220), 2.10 (023), 2.08 (302), 2.07 (221), 2.06 (311), 2.04 (204), 2.01 (123), 1.95 (222), 1.90 (214), 1.84 (024), 1.83 (115), 1.79 (030), 1.76 (031), 1.71 (321), 1.70 (131), 1.69 (401), 1.66 (215), 1.64 (322), 1.63 (410), 1.62 (402), 1.61 (411), 1.57 (125) for Pd_7Se_4. The SEM−EDX studies have suggested that the composition of Pd−Se nanoparticles (wt %) which is given in Table 1 (Pd_4Se) and Table 2 (Pd_7Se_4) and very close to the initial loaded stoichiometry.

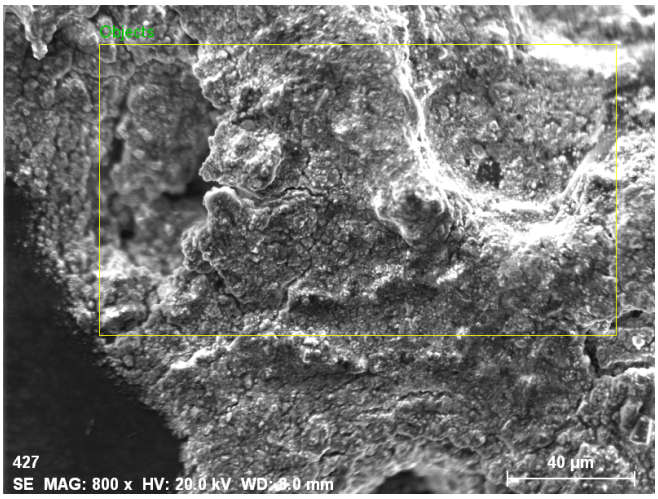


Figure S4.1 SEM Image of Pd_4Se Nanoparticles

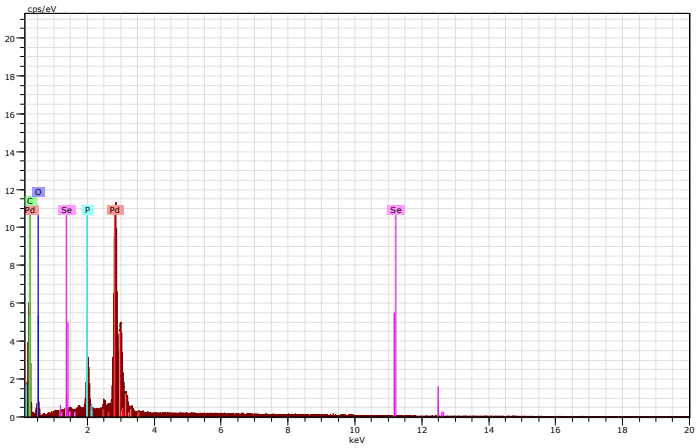


Figure S4.2 SEM–EDX of Pd_4Se Nanoparticles

Spectrum: Objects

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
Pd	46	L-series	45.51	55.29	14.47	1.5
C	6	K-series	22.10	26.85	62.25	3.0
O	8	K-series	8.58	10.43	18.15	1.6
P	15	K-series	3.79	4.60	4.14	0.2
Se	34	K-series	2.33	2.83	1.00	0.2
		Total:	82.31	100.00	100.00	

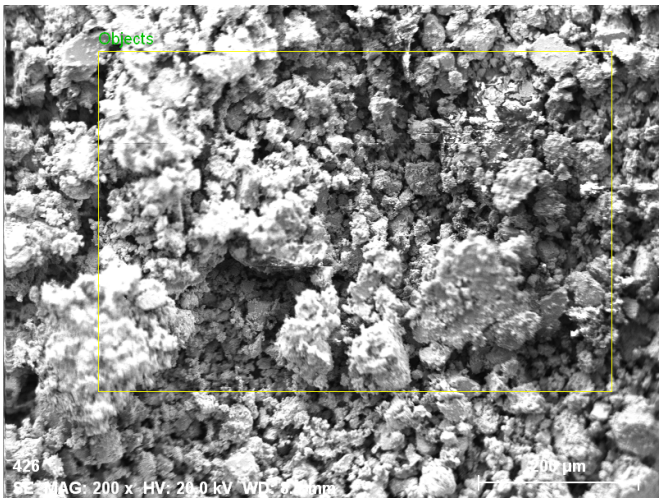


Figure S4.3 SEM Image of Pd_7Se_4 Nanoparticles

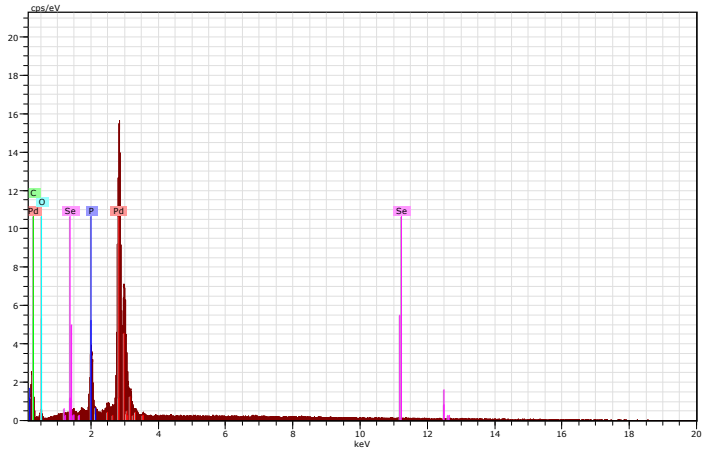


Figure S4.4 SEM–EDX of Pd_7Se_4 Nanoparticles

Spectrum: Objects

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
Pd	46	L-series	56.38	72.26	29.98	1.8
C	6	K-series	9.82	12.58	46.24	1.5
P	15	K-series	4.25	5.45	7.76	0.2
Se	34	K-series	3.82	4.90	2.74	0.2
O	8	K-series	3.75	4.81	13.28	0.8
		Total:	78.02	100.00	100.00	

S5. NMR Spectra

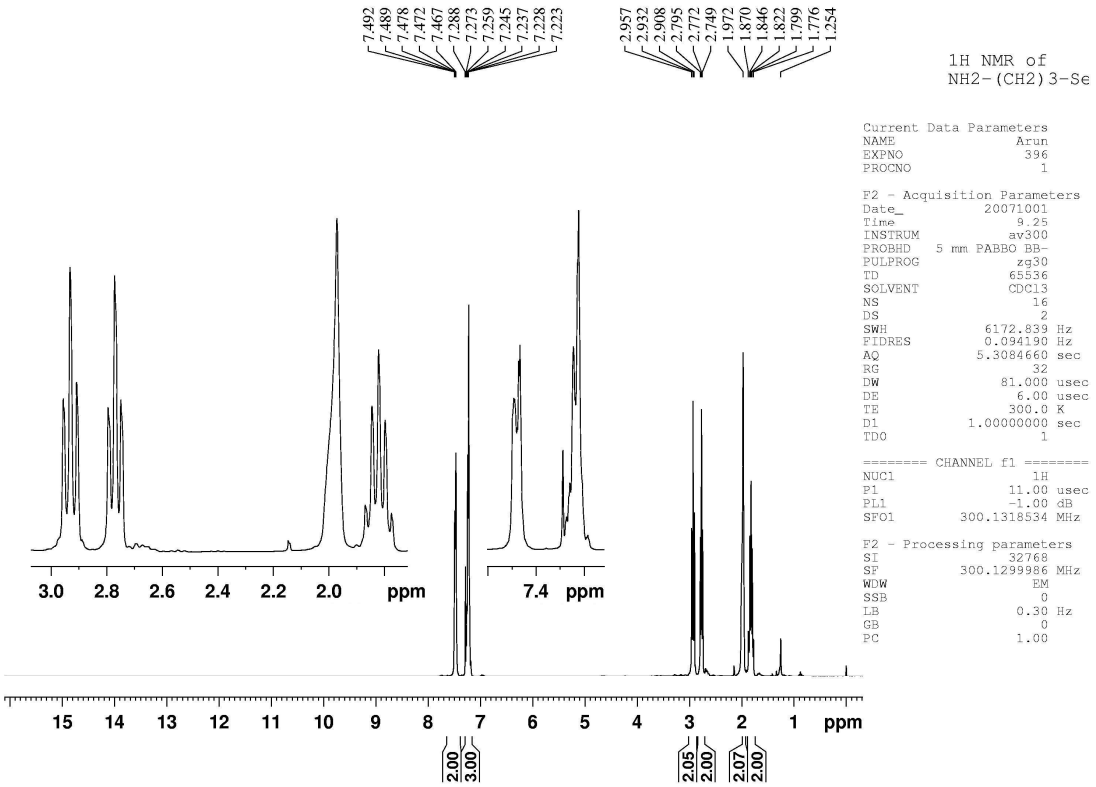


Figure S5.1 ^{1}HNMR Spectrum of PhSe–$(CH_2)_3$–NH_2

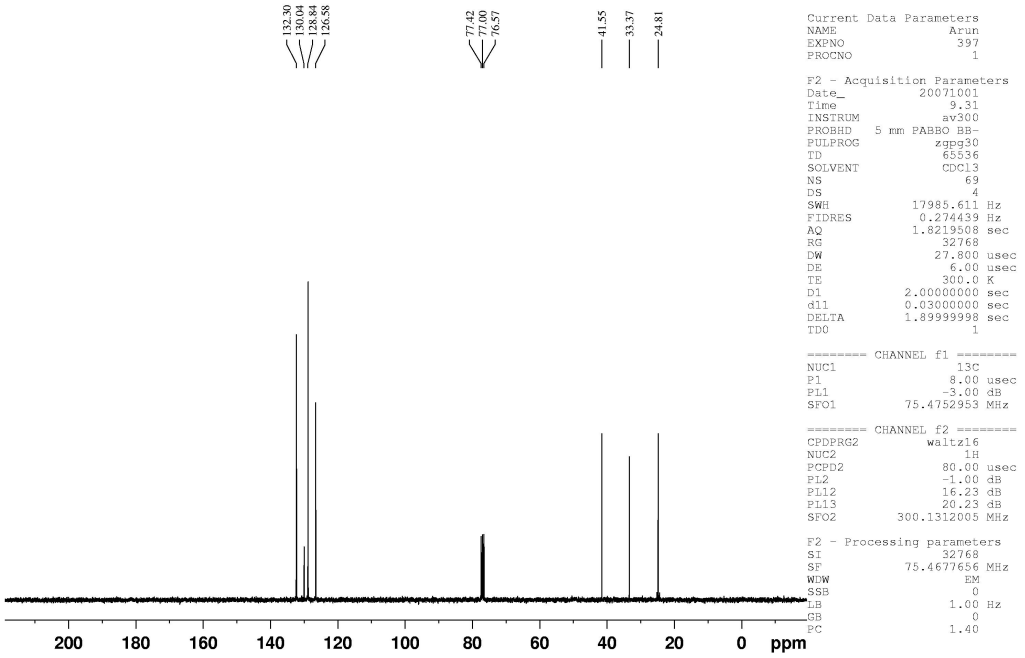


Figure S5.2 $^{13}C\{^{1}H\}$NMR Spectrum of PhSe–$(CH_2)_3$–NH_2

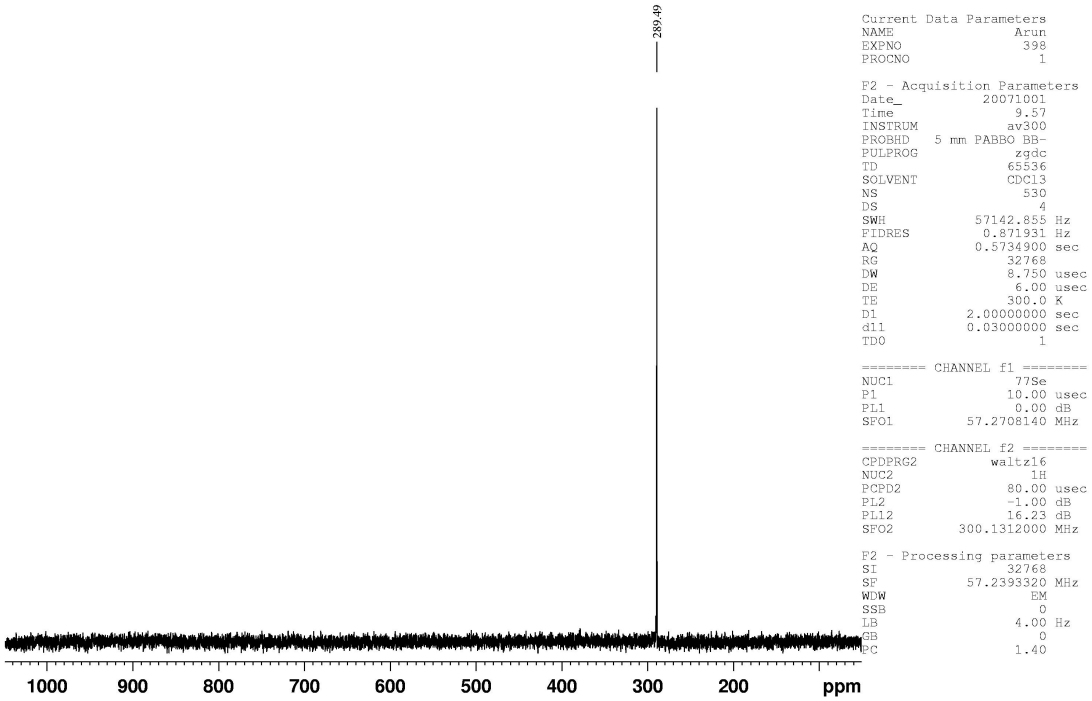


Figure S5.3 $^{77}Se\{^{1}H\}$NMR Spectrum of PhSe–$(CH_2)_3$–NH_2

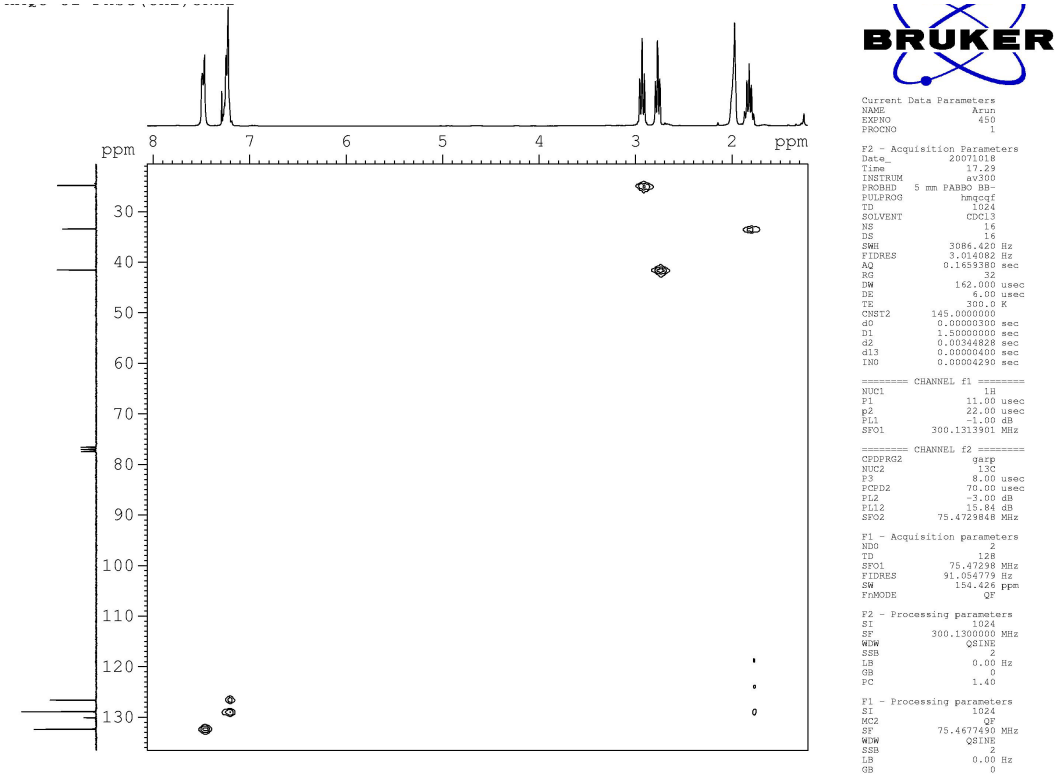


Figure S5.4 HMQC NMR Spectrum of PhSe–$(CH_2)_3$–NH_2

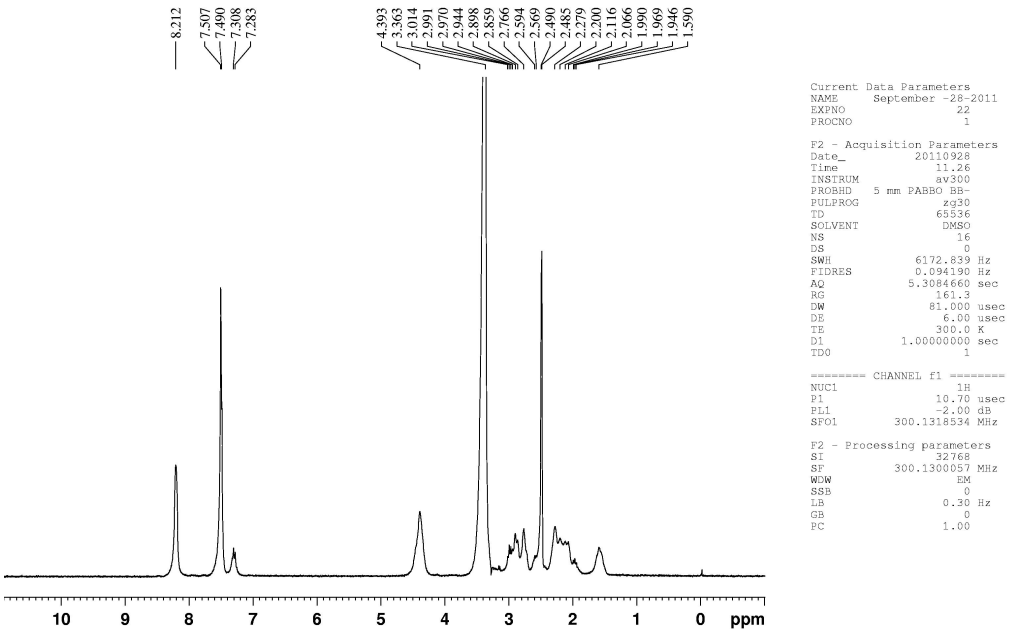


Figure S5.5 ^{1}H NMR Spectrum of [$PdCl_2${PhSe−$(CH_2)_3$−NH_2}]

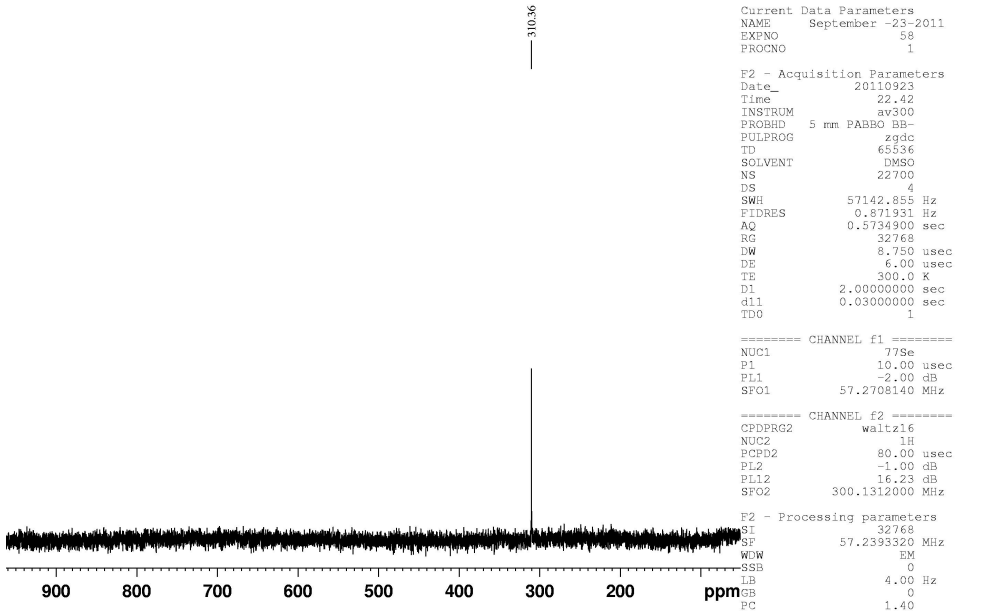


Figure S5.6 ^{77}Se{^{1}H} NMR Spectrum of [$PdCl_2${PhSe−$(CH_2)_3$−NH_2}]

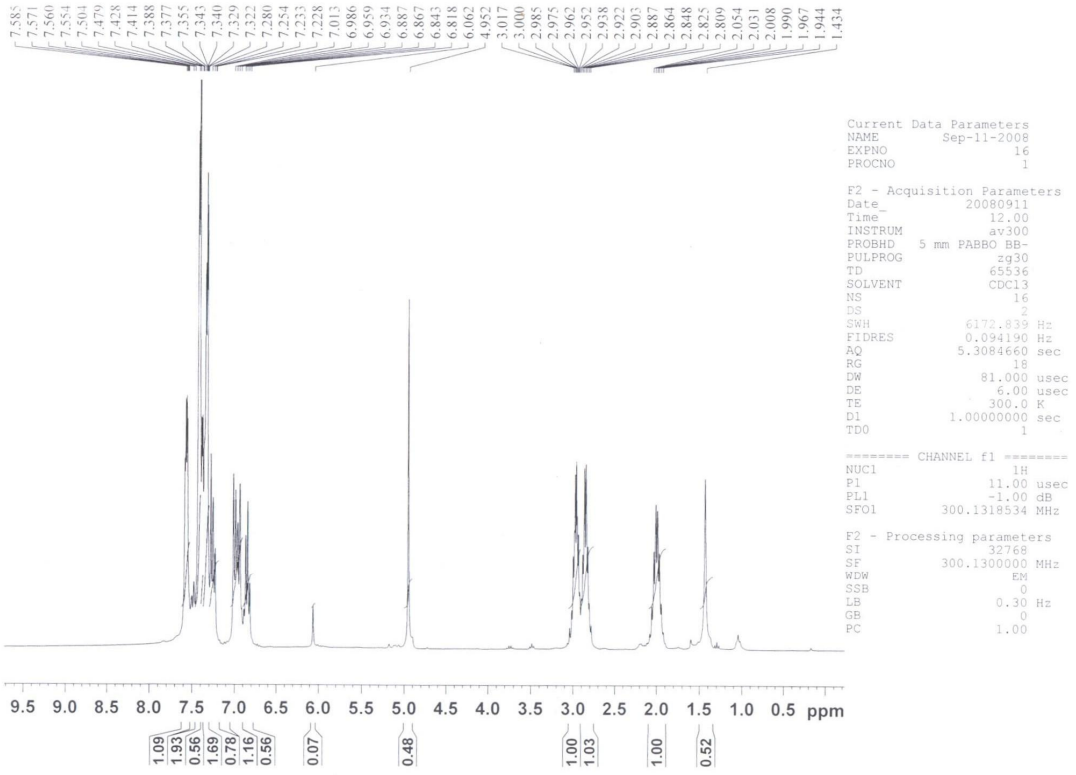


Figure S5.7 ^{1}H NMR Spectrum of PhSe−$(CH_2)_3$−NH−CH(Ph)−C_6H_4−2−OH

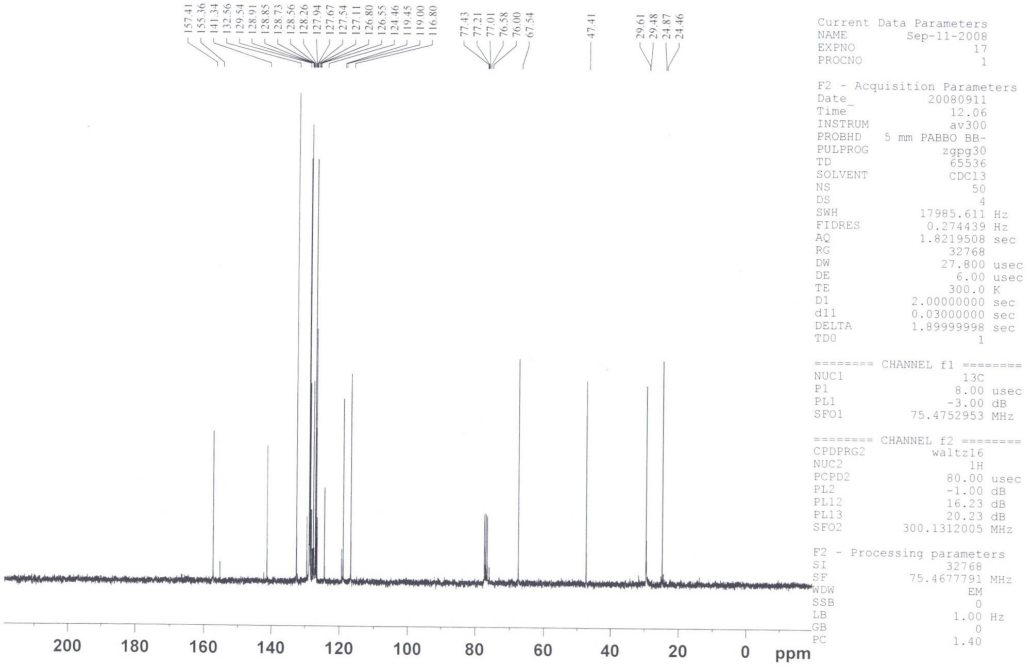


Figure S5.8 ^{13}C{^{1}H} NMR Spectrum of PhSe−$(CH_2)_3$−NH−CH(Ph)−C_6H_4−2−OH

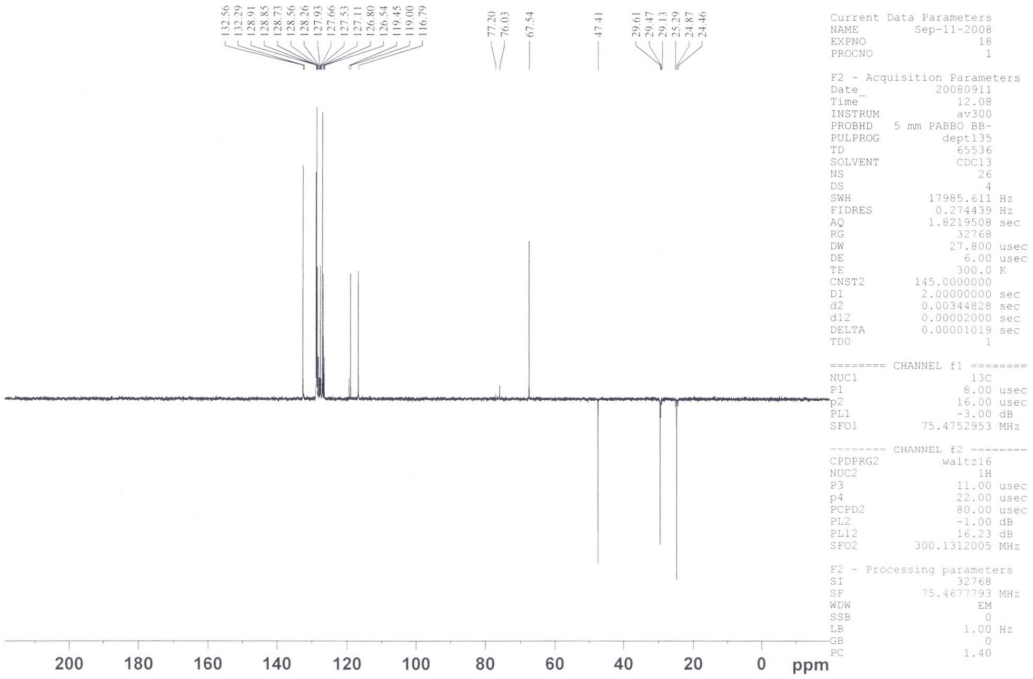


Figure S5.9 DEPT−135 NMR Spectrum of PhSe−$(CH_2)_3$−NH−CH(Ph)−C_6H_4−2−OH

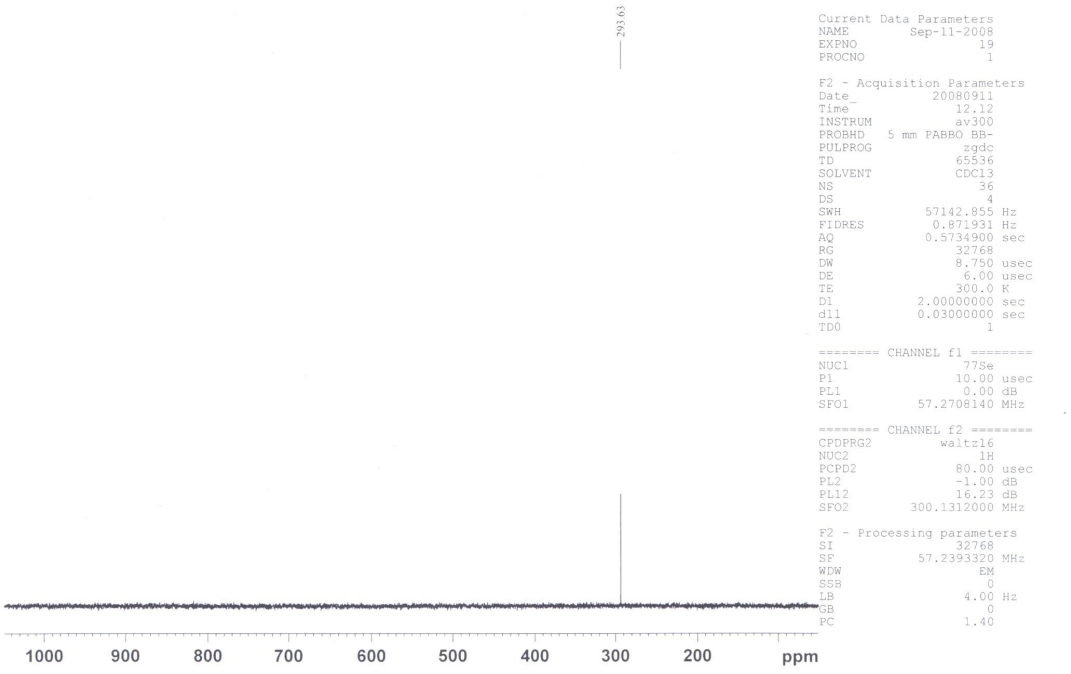


Figure S5.10 $^{77}Se\{^1H\}$ NMR Spectrum of PhSe−$(CH_2)_3$−NH−CH(Ph)−C_6H_4−2−OH

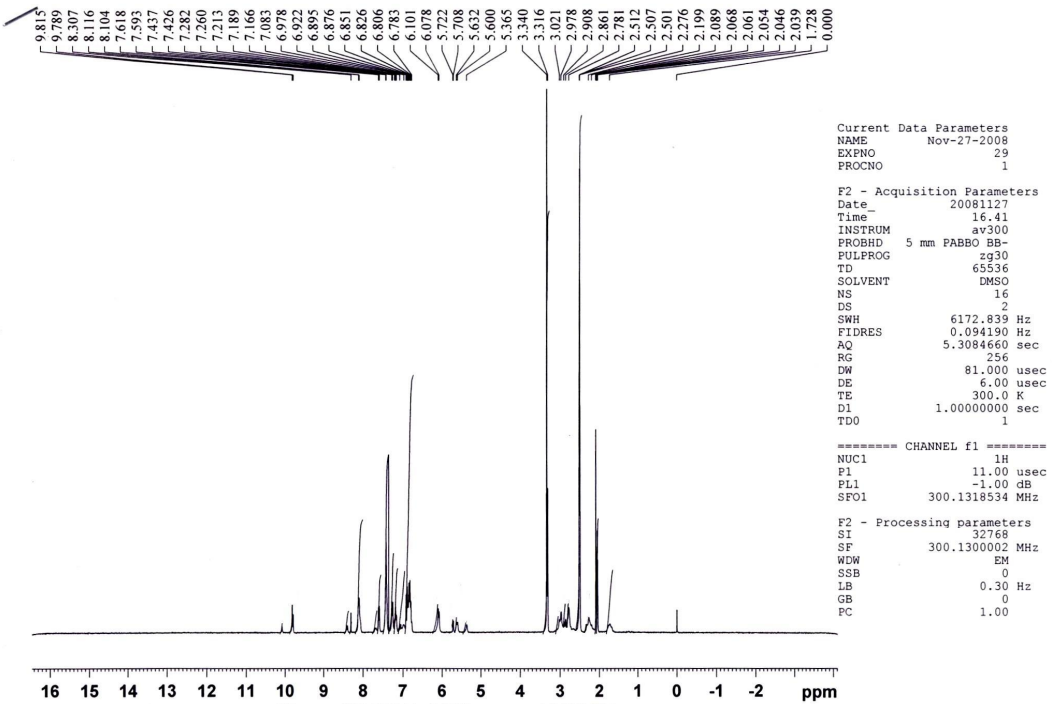


Figure S5.11 ^{1}H NMR Spectrum of [PdCl{PhSe−$(CH_2)_3$−NH−CH(C_6H_4)−C_6H_4−2−OH}] (**2**)

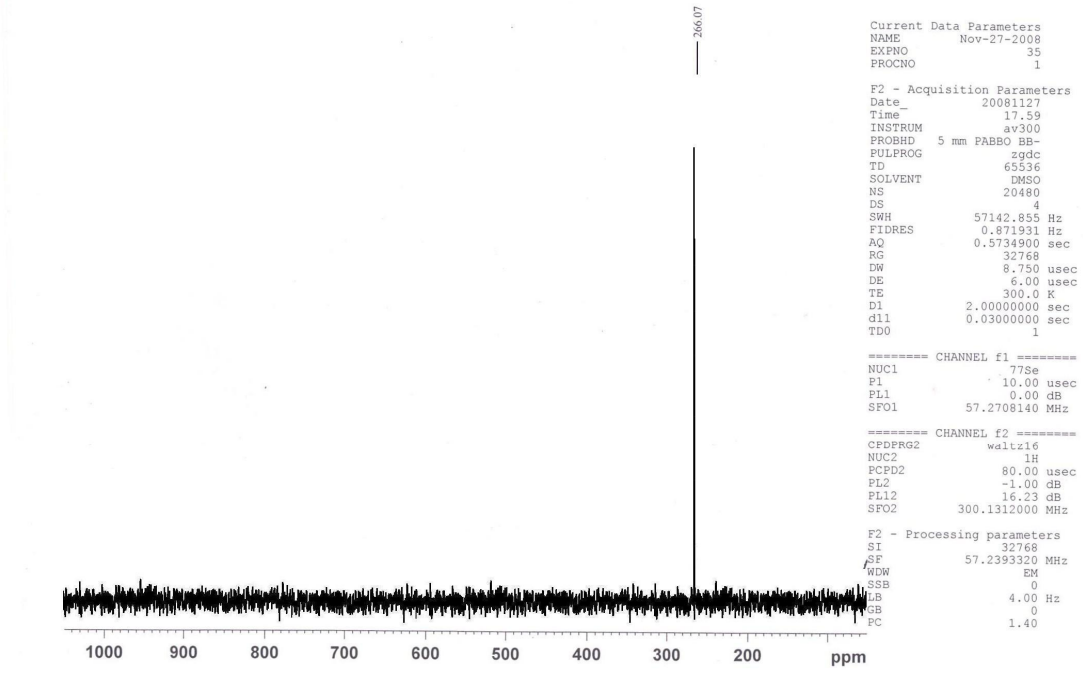


Figure S5.12 ^{77}Se{^{1}H} NMR Spectrum of [PdCl{PhSe−$(CH_2)_3$−NH−CH(C_6H_4)−C_6H_4−2−OH}] (**2**)