Supporting Information

Silver, Gold, Palladium, and Platinum N-heterocyclic Carbene Complexes Containing a Selenoether-Functionalized Imidazol-2-ylidene Moiety

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I Single crystal X-ray structure analysis

Table S1. Crystallographic data and data refinement of compound 2, 3a, 3b, 4, and 5.

Compound	2	3a	3b	4·1/2 ACN	5·1/2 ACN
CCDC-No.	1572749	1572750	1572751	1572752	1572753
Empirical formula	$C_{11}H_{12}AgClN_2Se$	$C_{11}H_{12}AuClN_2Se$	$C_{11}H_{12}AuClI_2N_2Se$	$2(C_{11}H_{12}Cl_2N_2PdSe)\cdot CH_3CN$	$2(C_{11}H_{12}Cl_2N_2PtSe)$ CH_3CN
M (g·mol-1)	394.51	483.60	737.40	898.02	1075.40
Crystal size (mm3)	0.05 × 0.05 × 0.05	0.10 × 0.10 × 0.03		0.03 x 0.03 x 0.04	0.20 × 0.10 × 0.10
T (K)	100	100	100	140	140
Θ (°) (completeness)	2.97-35.65 (99.9 %)	2.50-34.71 (99.7 %)	2.39-40.48 (99.8 %)	2.59-27.51 (99.7 %)	2.95-27.59 (99.4 %)
h, k, l range	±15, ±11, -18, 17	±29, ±11, -16, 18	±10, ±12, ±16	±17, ±11, -26, 27	±17, ±11, ±27
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	P21/c	C2/c	$P\bar{1}$	C2/c	C2/c
a (Å)	11.3831(8)	22.565(4)	7.8455(14)	14.4803(10)	14.6518(13)
b (Å)	8.9871(6)	8.7963(13)	9.1574(16)	9.3822(6)	9.3451(8)
c (Å)	13.6832(10)	13.7733(19)	12.295(2)	22.6206(15)	22.571(2)
α (°)	90	90	97.297(8)°	90	90
β (°)	111.035(4)	105.928(7)	95.050(8)°	94.894(3)	95.596(5)
γ (°)	90	90	109.229(8)°	90°	90°
V (Å^3)	1306.52(16)	2628.8(7)	819.3(3)	3062.0(4)	3075.7(5)
Z	4	8	2	4	4
Dcalc (g·cm^{-3})	2.006	2.444	2.989	1.948	2.322
μ (Mo Kα) (mm^{-1})	4.507	14.139	15.116	3.925	11.825
F(000)	760	1776	656	1736	1992
Max./min. transmission	0.7471/ 0.5441	0.7471/ 0.5441	0.7479/ 0.3854	1.0000/ 0.9069	0.7456/ 0.4759
Reflections collected	30727	21902	23115	27642	24826
Independent reflections	3144	3169	3942	2821	2838
(R_{int})	(0.0677)	(0.0322)	(0.0551)	(0.0356)	(0.0343)
Data/ restraints/ parameters	3144/ 0/ 146	3169/ 0/ 146	3942/ 0/ 164	2821/ 12/ 171	2838/ 0/ 170
Max./min. Δρ (e· Å^{-3})a	0.762/ -0.681	1.348/-0.663	1.070/-1.470	1.065/ -0.858	2.743/ -0.983
R_1/wR_2 [I>2σ (I)]b	0.0223/ 0.0518	0.0183/ 0.0450	0.0213/ 0.0543	0.0424/ 0.1031	0.0324/ 0.0756
R_1/wR_2 (all data)b	0.0260/ 0.0506	0.0208/ 0.0443	0.0226/ 0.0537	0.0467/ 0.1015	0.0356/ 0.0744
Goodness-of-fit (GOF) on F^{2c}	1.040	1.085	1.039	1.201	1.245

[a] Largest difference peak and hole; [b] $R_1 = [\Sigma(||Fo| - |Fc||)/\Sigma |Fo|]$; $wR_2 = [\Sigma [w(Fo^2 - Fc^2)^2]/\Sigma [w(Fo^2)^2]]^{1/2}$; [c] Goodness-of-fit = $[\Sigma [w(Fo^2 - Fc^2)^2]/(n-p)]^{1/2}$; [d] Absolute structure parameter.[1]

Compound 2

Table S2. Bond lengths [Å] of compound 2.

Ag—C4	2.084(2)	N2—C5	1.449(3)
Ag—Cl	2.3599(6)	C2—C3	1.335(3)
Se—C6	1.917(2)	C6—C7	1.388(3)
Se—C5	1.954(2)	C6—C11	1.391(3)
N1—C4	1.354(3)	C7—C8	1.390(4)
N1—C2	1.385(3)	C8—C9	1.378(4)
N1—C1	1.466(3)	C9—C10	1.387(4)
N2—C4	1.354(3)	C10—C11	1.383(4)
N2—C3	1.387(3)		

Table S3. Angles and torsion angles [°] of compound 2.

C4—Ag—Cl	172.69(6)	N2—C4—Ag	127.57(15)
C6—Se—C5	95.69(10)	N1—C4—Ag	128.34(16)
C4—N1—C2	111.20(19)	N2—C5—Se	113.00(15)
C4—N1—C1	124.06(18)	C7—C6—C11	119.8(2)
C2—N1—C1	124.74(18)	C7—C6—Se	119.32(19)
C4—N2—C3	111.17(18)	C11—C6—Se	120.88(18)
C4—N2—C5	124.14(18)	C6—C7—C8	119.6(3)
C3—N2—C5	124.69(19)	C9—C8—C7	120.5(3)
C3—C2—N1	106.84(19)	C8—C9—C10	119.8(3)
C2—C3—N2	106.70(19)	C11—C10—C9	120.1(3)
N2—C4—N1	104.09(18)	C10—C11—C6	120.1(2)
C4—N1—C2—C3	-0.2(2)	C1—N1—C4—Ag	0.3(3)
C1—N1—C2—C3	-179.94(19)	C4—N2—C5—Se	-111.0(2)
N1—C2—C3—N2	0.3(2)	C3—N2—C5—Se	69.3(2)
C4—N2—C3—C2	-0.2(2)	C11—C6—C7—C8	0.8(4)
C5—N2—C3—C2	179.53(19)	Se—C6—C7—C8	-178.85(19)
C3—N2—C4—N1	0.1(2)	C6—C7—C8—C9	-1.3(4)
C5—N2—C4—N1	-179.67(18)	C7—C8—C9—C10	0.7(4)
C3—N2—C4—Ag	179.56(15)	C8—C9—C10—C11	0.3(4)
C5—N2—C4—Ag	-0.2(3)	C9—C10—C11—C6	-0.8(4)
C2—N1—C4—N2	0.1(2)	C7—C6—C11—C10	0.2(4)
C1—N1—C4—N2	179.81(18)	Se—C6—C11—C10	179.86(18)
C2—N1—C4—Ag	-179.39(15)		

Table S4. Hydrogen-bond geometry [Å, º] of compound 2.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···Cl^{i}	0.98	2.92	3.817(2)	153
C5—H5A···Cl^{ii}	0.99	2.67	3.539(2)	147
C5—H5B···Cl^{iii}	0.99	2.79	3.636(2)	144

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, -*y*+1/2, *z*-1/2; (iii) -*x*, -*y*, -*z*+1.

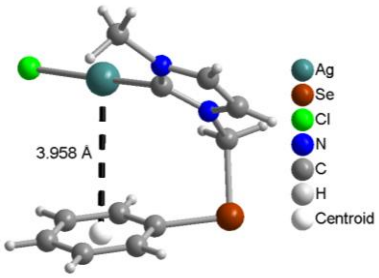

Figure S1. Silver-π-contact in compound **2**, labeled with the centroid-metal distance as black dashed line.

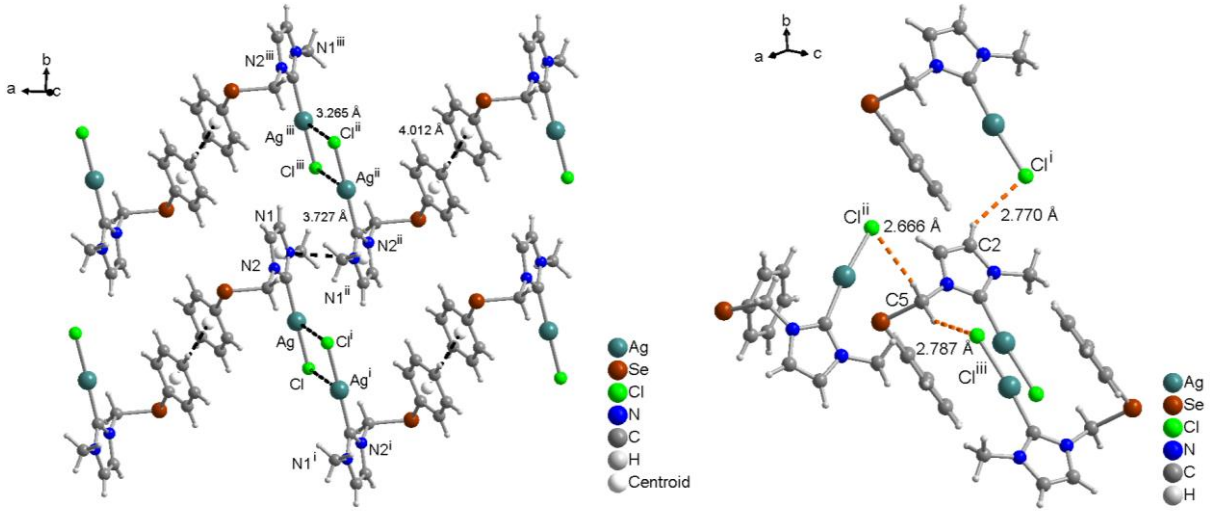

Figure S2. Left: Section of the packing diagram of compound **2** showing the π-stacking interactions along the *a*-direction for the imidazole rings and along *bc*-direction for the phenyl rings as black dashed lines (labeled with the centroid-centroid distances) and short Ag···Cl intermolecular contacts as black dashed lines (labeled with their Ag-Cl distance). Right: Packing diagram showing the C–H···Cl interactions as orange dashed lines (labeled with the C–H···Cl distances).

Compound 3a

Table S5. Bond lengths [Å] of compound 3a.

Au—C4	1.986(3)	N2—C3	1.388(4)
Au—Cl	2.2913(9)	N2—C5	1.449(4)
Au—Au^{i}	3.2537(5)	C2—C3	1.343(5)
Se—C6	1.917(4)	C6—C11	1.392(5)
Se—C5	1.956(3)	C6—C7	1.398(5)
N1—C4	1.349(4)	C7—C8	1.379(6)
N1—C2	1.387(4)	C8—C9	1.388(7)
N1—C1	1.461(4)	C9—C10	1.382(8)
N2—C4	1.345(4)	C10—C11	1.380(6)

Table S6. Angles and torsion angles [°] of compound 3a.

C4—Au—Cl	177.50(9)	N2—C4—N1	105.3(3)
C4—Au—Au^{i}	84.29(9)	N2—C4—Au	127.4(2)
Cl—Au—Au^{i}	95.40(3)	N1—C4—Au	127.2(2)
C6—Se—C5	95.42(15)	N2—C5—Se	113.2(2)
C4—N1—C2	110.5(3)	C11—C6—C7	120.4(4)
C4—N1—C1	124.5(3)	C11—C6—Se	119.3(3)
C2—N1—C1	125.0(3)	C7—C6—Se	120.3(3)
C4—N2—C3	110.8(3)	C8—C7—C6	119.6(4)
C4—N2—C5	124.6(3)	C7—C8—C9	120.3(4)
C3—N2—C5	124.6(3)	C10—C9—C8	119.6(4)
C3—C2—N1	106.9(3)	C11—C10—C9	121.3(5)
C2—C3—N2	106.6(3)	C10—C11—C6	118.8(4)
C4—N1—C2—C3	0.5(4)	C1—N1—C4—Au	-2.4(5)
C1—N1—C2—C3	179.1(3)	C4—N2—C5—Se	112.5(3)
N1—C2—C3—N2	-0.4(4)	C3—N2—C5—Se	-69.6(4)
C4—N2—C3—C2	0.2(4)	C11—C6—C7—C8	-1.9(6)
C5—N2—C3—C2	-178.0(3)	Se—C6—C7—C8	178.6(3)
C3—N2—C4—N1	0.1(4)	C6—C7—C8—C9	2.1(6)
C5—N2—C4—N1	178.3(3)	C7—C8—C9—C10	-0.7(6)
C3—N2—C4—Au	-176.4(2)	C8—C9—C10—C11	-0.9(7)
C5—N2—C4—Au	1.7(5)	C9—C10—C11—C6	1.1(6)
C2—N1—C4—N2	-0.4(4)	C7—C6—C11—C10	0.3(6)
C1—N1—C4—N2	-179.0(3)	Se—C6—C11—C10	179.8(3)
C2—N1—C4—Au	176.2(2)		

Table S7. Hydrogen-bond geometry [Å, º] of compound 3a.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1C···Cl^{ii}	0.98	2.77	3.673(3)	153
C2—H2···Cl^{ii}	0.95	2.78	3.565(4)	141
C5—H5B···Cl^{iii}	0.99	2.78	3.586(4)	140

Symmetry codes: (ii) *x*, *y*+1, *z*; (iii) *x*, -*y*+1, *z*+1/2.

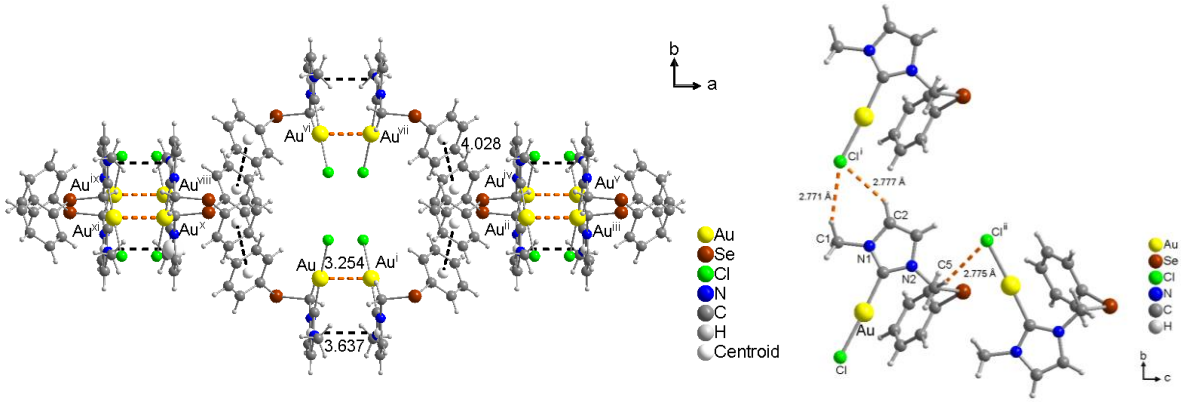

Figure S3. Left: Section of the packing diagram of compound **3a** showing the π-stacking interactions along the *ac*-direction for the imidazole rings as black dashed lines (labeled with the centroid-centroid distance) and metal–metal interactions as orange dashed lines (labeled with the metal–metal distance). Right: Section of the packing diagram of compound **3a** showing the potential hydrogen bonds C–H···Cl as orange dashed lines (labeled with their distances).

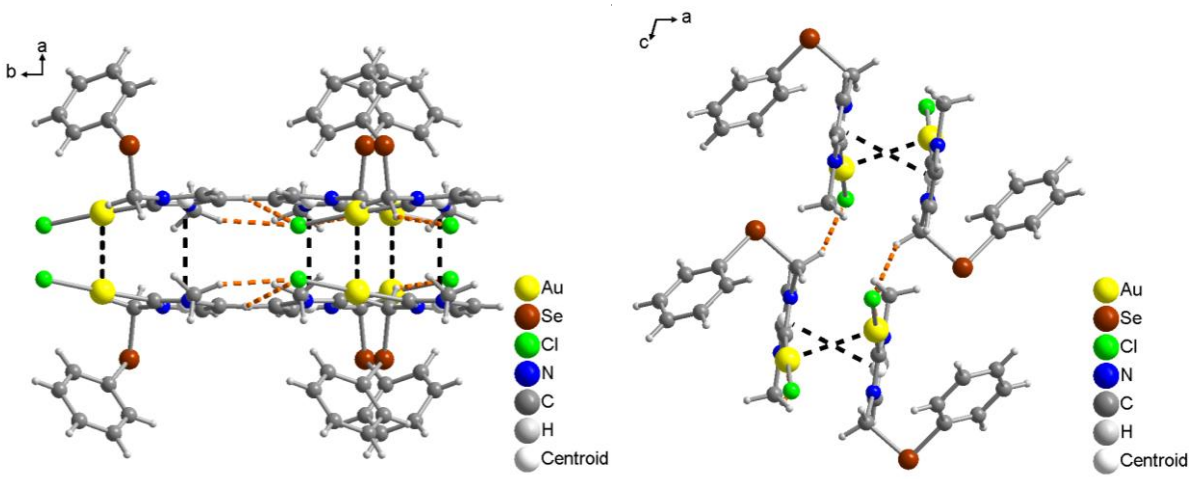

Figure S4. Sections of the packing diagram of compound **3a** showing π-stacking interactions along the *ac*-direction for the imidazole rings, metal-metal interactions as black dashed lines and the potential hydrogen bonds C–H···Cl as orange dashed lines along the *c*-plane.

Compound 3b

Table S8. Bond lengths [Å] of compound 3b.

Au—C4	1.996(4)	C2—C3	1.354(5)
Au—Cl	2.3372(9)	N2—C3	1.391(4)
Au—I1	2.6098(5)	N2—C5	1.458(4)
Au—I2	2.6109(5)	C6—C7	1.390(5)
Se—C6	1.920(3)	C6—C11	1.392(5)
Se—C5	1.936(4)	C7—C8	1.390(5)
N1—C4	1.342(4)	C8—C9	1.386(5)
N1—C2	1.379(5)	C9—C10	1.387(6)
N1—C1	1.459(5)	C10—C11	1.390(5)
N2—C4	1.334(5)		

Table S9. Angles and torsion angles [°] of compound 3b.

C4—Au—Cl	179.75(10)	C3—C2—N1	107.1(3)
C4—Au—I1	85.26(9)	N2—C4—N1	107.0(3)
Cl—Au—I1	94.50(3)	N2—C4—Au	125.7(3)
C4—Au—I2	87.32(9)	N1—C4—Au	127.2(3)
Cl—Au—I2	92.93(3)	N2—C5—Se	115.0(2)
I1—Au—I2	172.534(10)	C7—C6—C11	120.6(3)
C6—Se—C5	98.00(15)	C7—C6—Se	118.7(3)
C4—N1—C2	109.7(3)	C11—C6—Se	120.6(3)
C4—N1—C1	125.1(3)	C8—C7—C6	119.8(3)
C2—N1—C1	125.2(3)	C9—C8—C7	119.4(4)
C4—N2—C3	109.8(3)	C8—C9—C10	121.0(4)
C4—N2—C5	123.2(3)	C9—C10—C11	119.8(4)
C3—N2—C5	126.6(3)	C10—C11—C6	119.4(3)
I1—Au—C4—N1	-94.5(3)	C3—N2—C4—Au	-177.7(3)
I1—Au—C4—N2	96.6(3)	C3—N2—C4—N1	-0.1(4)
I2—Au—C4—N1	86.3(3)	C5—N2—C4—Au	-4.4(5)
I2—Au—C4—N2	96.6(3)	C5—N2—C4—N1	173.2(3)
C6—Se—C5—N2	-70.0(3)	C3—N2—C5—Se	-42.6(4)
C5—Se—C6—C7	-100.2(3)	C4—N2—C5—Se	145.3(3)
C5—Se—C6—C11	82.1(3)	N1—C2—C3—N2	-0.5(4)
C1—N1—C2—C3	179.8(3)	Se—C6—C7—C8	-178.2(3)
C4—N1—C2—C3	0.5(4)	C11—C6—C7—C8	-0.5(5)
C1—N1—C4—Au	-2.1(5)	Se—C6—C11—C10	179.6(3)
C1—N1—C4—N2	179.6(3)	C7—C6—C11—C10	1.9(5)
C2—N1—C4—Au	177.3(3)	C6—C7—C8—C9	-1.7(6)
C2—N1—C4—N2	-0.2(4)	C7—C8—C9—C10	2.6(6)
C4—N2—C3—C2	0.4(4)	C8—C9—C10—C11	1.2(7)
C5—N2—C3—C2	-172.6(3)	C9—C10—C11—C6	1.1(6)

Table S10. Hydrogen-bond geometry [Å, °] of compound 3b.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*C*···Cl^{i}	0.98	2.72	3.688(4)	172
C2—H2···I2^{i}	0.95	3.24	4.081(4)	149
C5—H5*A*···I1^{ii}	0.99	3.12	3.885(4)	135
C5—H5*B*···Cl^{ii}	0.99	2.73	3.581(4)	145

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) -*x*, -*y*+1, -*z*+1.

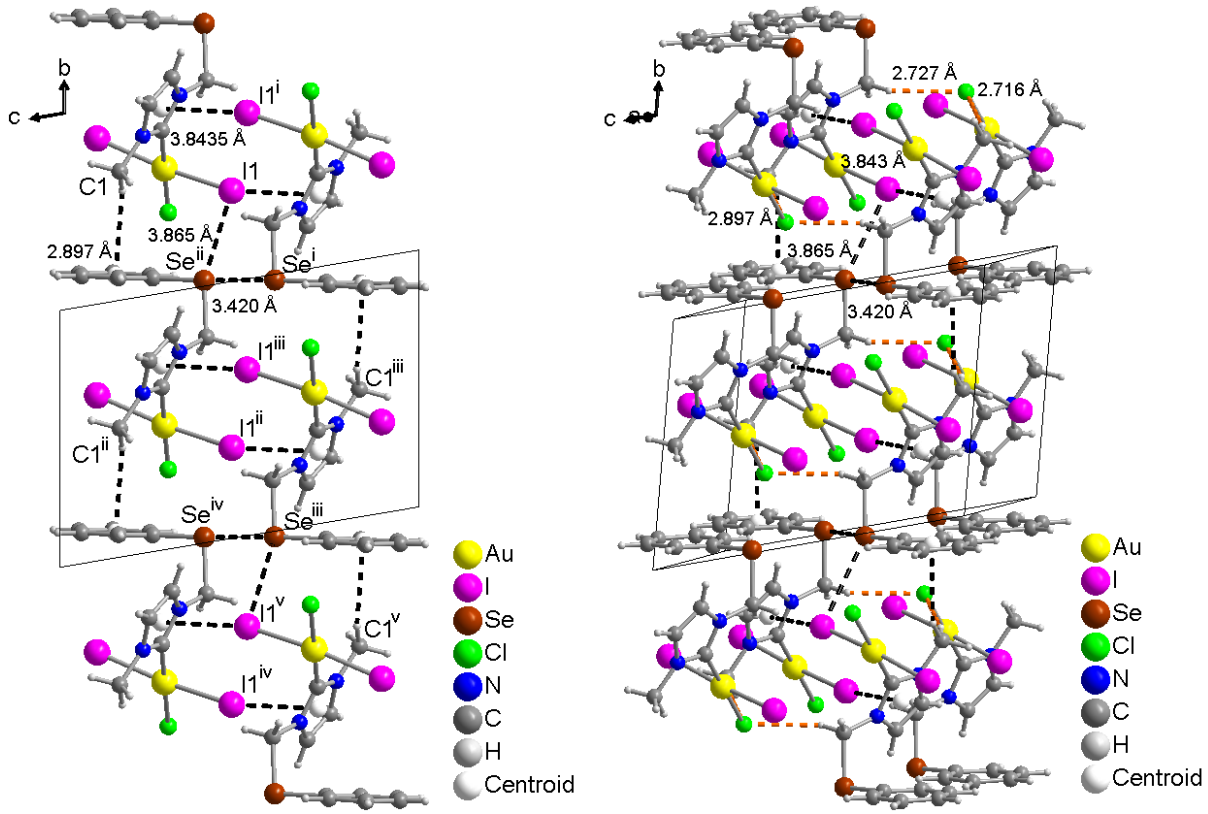

Figure S5. Left: Section of the packing diagram of compound **3b** showing significant C–H··· π-stacking and Au–I···π interactions as black dashed lines (labeled with their hydrogen atom–centroid distance and their Au–I···centroid distance). Right: Section of the packing diagram of compound **3b** showing significant C–H···π–stacking and Au–I···π interactions as black dashed lines (labeled with their hydrogen atom–centroid distance and their Au–I···centroid distance), Se···Se and Se···I distances as black dashed lines (labeled with the distance), and the potential hydrogen bonds C–H···Cl as orange dashed lines (labeled with their C–H···Cl distances). The sum of the van der Waals radii is 2 × Se = 3.80 Å, Se + I = 3.88 Å, 2 × I = 3.96 Å.

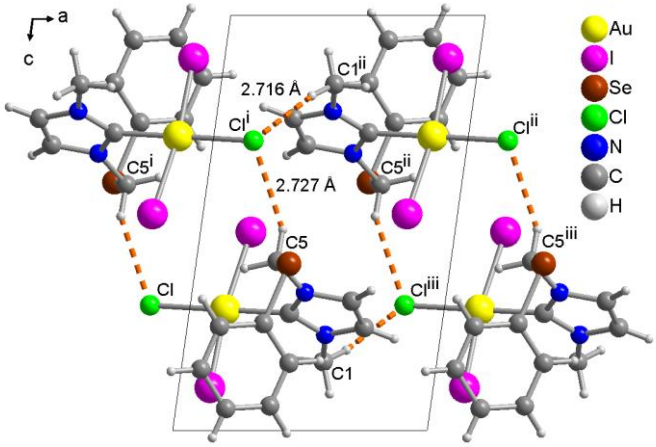

Figure S6. Section of the packing diagram of compound **3b** showing the potential hydrogen bonds C–H···Cl as orange dashed lines along the *a*- and *c*-direction (labeled with their C–H···Cl distances).

Compound 4

Table S11. Bond lengths [Å] of compound 4.

Pd—C4	2.000(7)	N2—C3	1.374(9)
Pd—Cl1	2.3202(16)	N2—C5	1.431(10)
Pd—Cl2	2.3546(16)	C6—C11	1.353(11)
Pd—Se	2.3637(8)	C6—C7	1.356(12)
C1—N1	1.474(11)	C7—C8	1.408(15)
Se—C5	1.929(7)	C8—C9	1.371(15)
Se—C6	1.932(7)	C9—C10	1.312(13)
C2—C3	1.338(12)	C10—C11	1.389(11)
C2—N1	1.378(10)	N3—C13	1.08(2)
N1—C4	1.311(10)	C12—C13	1.41(3)
N2—C4	1.370(9)		

Table S12. Angles and torsion angles [°] of compound 4.

C4—Pd—Cl1	96.1(2)	C3—N2—C5	125.1(6)
C4—Pd—Cl2	172.4(2)	N1—C4—N2	105.4(6)
Cl1—Pd—Cl2	91.40(6)	N1—C4—Pd	135.9(5)
C4—Pd—Se	86.6(2)	N2—C4—Pd	118.6(5)
Cl1—Pd—Se	177.35(5)	C2—C3—N2	106.7(7)
Cl2—Pd—Se	85.98(5)	N2—C5—Se	110.5(5)
C5—Se—C6	97.9(3)	C11—C6—C7	119.8(7)
C5—Se—Pd	96.1(2)	C11—C6—Se	123.2(5)
C6—Se—Pd	102.9(2)	C7—C6—Se	117.0(6)
C3—C2—N1	106.9(7)	C6—C7—C8	119.0(10)
C4—N1—C2	111.3(7)	C9—C8—C7	120.1(10)
C4—N1—C1	128.3(6)	C10—C9—C8	119.1(9)
C2—N1—C1	120.3(7)	C9—C10—C11	121.6(9)
C4—N2—C3	109.7(6)	C6—C11—C10	120.0(8)
C4—N2—C5	125.0(6)	N3—C13—C12	180.000(11)
C3—C2—N1—C4	0.3(10)	C5—N2—C3—C2	-175.0(7)
C3—C2—N1—C1	-177.5(9)	C4—N2—C5—Se	17.4(8)
C2—N1—C4—N2	-0.3(9)	C3—N2—C5—Se	-168.4(5)
C1—N1—C4—N2	177.2(9)	C11—C6—C7—C8	1.5(19)
C2—N1—C4—Pd	-179.1(6)	Se—C6—C7—C8	-176.3(11)
C1—N1—C4—Pd	-1.6(14)	C6—C7—C8—C9	-5(2)
C3—N2—C4—N1	0.2(8)	C7—C8—C9—C10	7(2)
C5—N2—C4—N1	175.2(6)	C8—C9—C10—C11	-5.3(18)
C3—N2—C4—Pd	179.3(5)	C7—C6—C11—C10	-0.1(15)
C5—N2—C4—Pd	-5.8(9)	Se—C6—C11—C10	177.6(7)
N1—C2—C3—N2	-0.1(9)	C9—C10—C11—C6	2.0(15)
C4—N2—C3—C2	-0.1(9)		

Table S13. Hydrogen-bond geometry [Å, °] of compound 4.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···Cl2	0.98	2.62	3.602(9)	177
C3—H3···Cl1^{i}	0.95	2.52	3.350(9)	146
C5—H5B···Cl1^{iii}	0.99	2.75	3.528(7)	136

Symmetry codes: (i) 1/2+x,-1/2+y,z; (iii) -x,2-y,-z

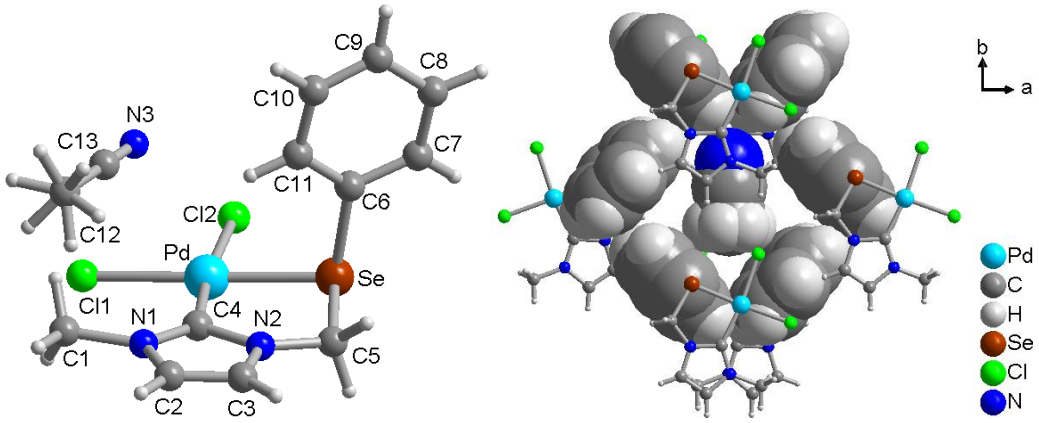

Figure S7. Left: Molecular structure of compound **4** with acetonitrile solvent molecule. Right: Section of the packing diagram of compound **4** showing the acetonitrile within a void formed by six molecules (acetonitrile and phenyl groups are shown in the space filling mode to illustrate the extent of the cavity). Both compounds **4** and **5** (cf. Figure S8) crystallize with a slightly disordered acetonitrile solvent molecule at a special position within a void, which is formed by the phenyl groups from six molecules.

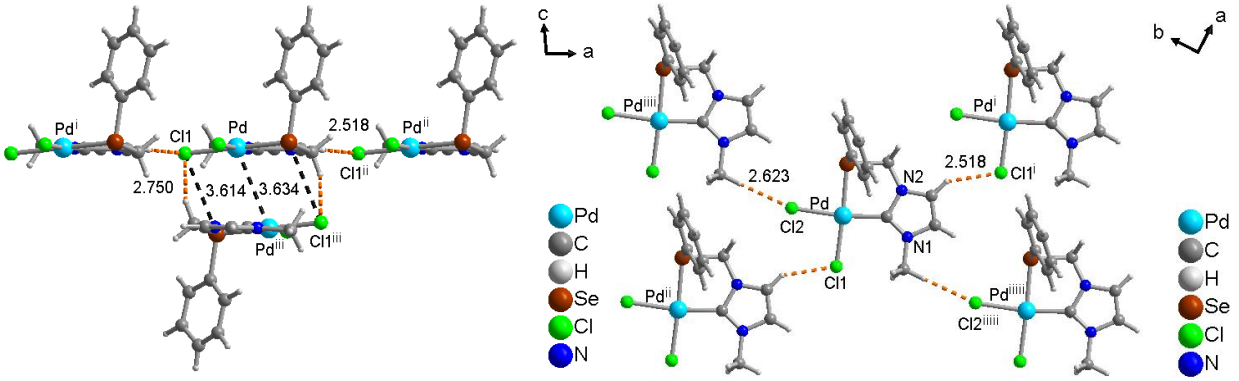

Figure S8. Left and right: Sections of the packing diagram of compound **4** showing the potential hydrogen bonds C–H···Cl as orange dashed lines along the *ab*-plane and *c*-direction as well as short Se···Cl and metal–metal distances along the *ac*-plane as black dashed lines.

Compound 5

Table S14. Bond lengths [Å] of compound 5.

Pt—C4	1.990(7)	N2—C4	1.375(9)
Pt—Cl2	2.3280(17)	N2—C5	1.425(10)
Pt—Se	2.3598(8)	C6—C11	1.353(11)
Pt—Cl1	2.3615(18)	C6—C7	1.360(11)
Se—C6	1.933(7)	C11—C10	1.390(11)
Se—C5	1.957(8)	C10—C9	1.328(14)
C1—N1	1.477(12)	C9—C8	1.359(15)
C2—C3	1.332(13)	C8—C7	1.404(14)
C2—N1	1.386(10)	N3—C13	1.13(2)
N1—C4	1.307(10)	C12—C13	1.47(3)
N2—C3	1.375(10)		

Table S15. Angles and torsion angles [°] of compound 5.

C4—Pt—Cl2	96.4(2)	C4—N2—C5	126.3(6)
C4—Pt—Se	86.79(19)	N1—C4—N2	106.0(6)
Cl2—Pt—Se	176.51(5)	N1—C4—Pt	135.6(5)
C4—Pt—Cl1	173.8(2)	N2—C4—Pt	118.4(5)
Cl2—Pt—Cl1	89.72(6)	C2—C3—N2	106.7(7)
Se—Pt—Cl1	87.11(5)	N2—C5—Se	109.0(5)
C6—Se—C5	97.8(3)	C11—C6—C7	120.7(7)
C6—Se—Pt	104.5(2)	C11—C6—Se	122.4(6)
C5—Se—Pt	96.3(2)	C7—C6—Se	116.9(6)
C3—C2—N1	107.5(8)	C6—C11—C10	119.2(8)
C4—N1—C2	110.5(7)	C9—C10—C11	121.6(9)
C4—N1—C1	128.4(6)	C10—C9—C8	119.1(9)
C2—N1—C1	121.0(7)	C9—C8—C7	120.8(9)
C3—N2—C4	109.4(7)	C6—C7—C8	118.4(9)
C3—N2—C5	124.1(6)	N3—C13—C12	180.0
C3—C2—N1—C4	1.3(9)	C5—N2—C3—C2	-175.6(7)
C3—C2—N1—C1	-176.5(9)	C3—N2—C5—Se	-168.0(5)
C2—N1—C4—N2	-1.2(8)	C4—N2—C5—Se	17.2(8)
C1—N1—C4—N2	176.4(9)	C7—C6—C11—C10	0.5(14)
C2—N1—C4—Pt	-179.3(6)	Se—C6—C11—C10	177.5(7)
C1—N1—C4—Pt	-1.7(14)	C6—C11—C10—C9	1.7(15)
C3—N2—C4—N1	0.7(8)	C11—C10—C9—C8	-4.4(18)
C5—N2—C4—N1	176.2(6)	C10—C9—C8—C7	5(2)
C3—N2—C4—Pt	179.2(5)	C11—C6—C7—C8	0.1(17)
C5—N2—C4—Pt	-5.3(9)	Se—C6—C7—C8	-177.1(10)
N1—C2—C3—N2	-0.8(9)	C9—C8—C7—C6	-3(2)
C4—N2—C3—C2	0.1(8)		

Table S16. Hydrogen-bond geometry (Å, º) of compound 5.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···Cl2	0.98	2.62	3.596(10)	178
C3—H3···Cl1^{i}	0.95	2.55	3.396(9)	148
C5—H5B···Cl1^{iii}	0.99	2.75	3.567(8)	136

Symmetry codes: (i) 1/2+x,-1/2+y,z; (iii) -x,2-y,-z

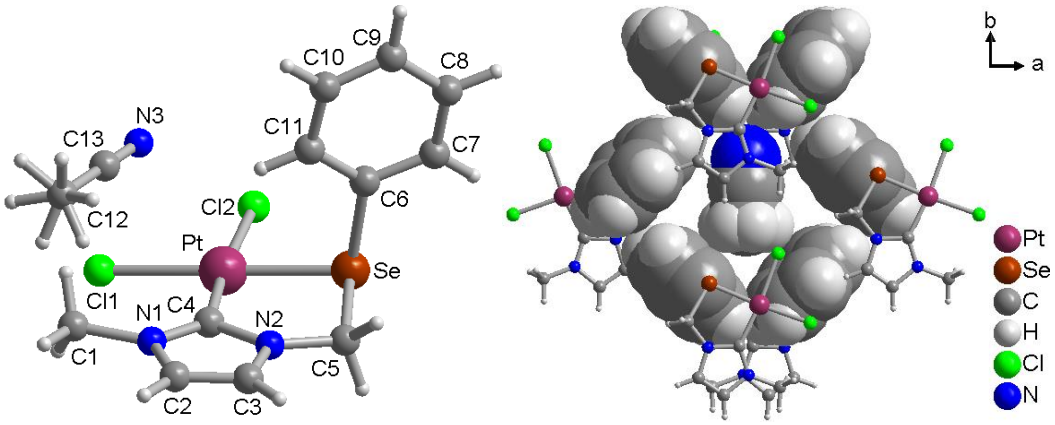

Figure S9. Left: Molecular structure of compound **5** with acetonitrile solvent molecule. Right: Section of the packing diagram of compound **5** showing the acetonitrile within a void formed by six molecules (acetonitrile and phenyl groups are shown in the space filling mode to illustrate the extent of the cavity). Both compounds **4** (cf. Figure S6) and **5** crystallize with a slightly disordered acetonitrile solvent molecule at a special position within a void, which is formed by the phenyl groups from six molecules.

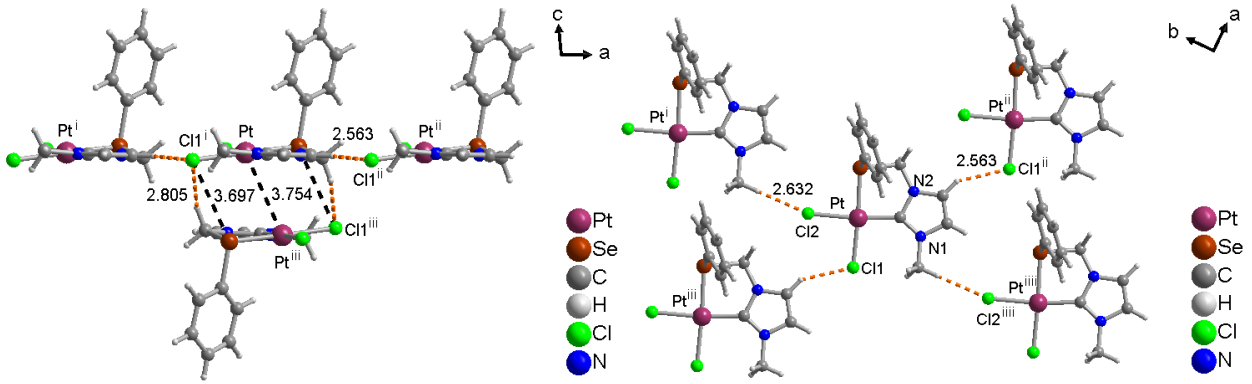

Figure S10. Left and right: Sections of the packing diagram of compound **5** showing the potential hydrogen bonds C–H···Cl as orange dashed lines along the *ab*-plane and *c*-direction as well as short Se···Cl and metal–metal distances along the *c*-plane as black dashed lines.

II NMR and mass-spectra of the compounds

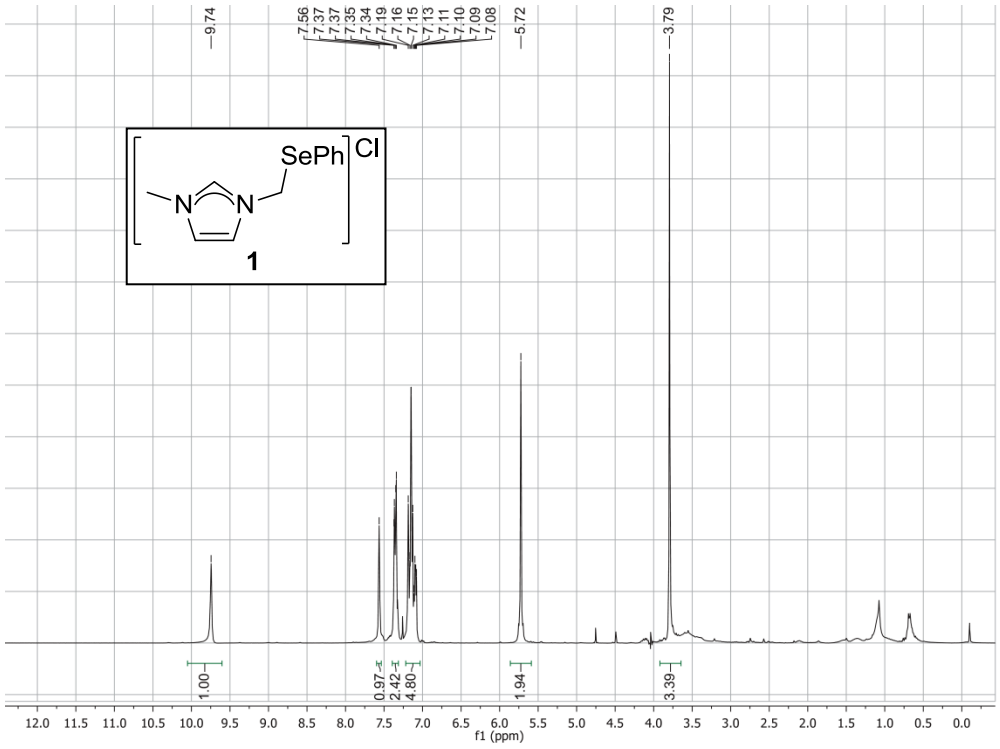

Figure S11. ^{1}H-NMR-sprectrum of compound **1** in $CDCl_3$.

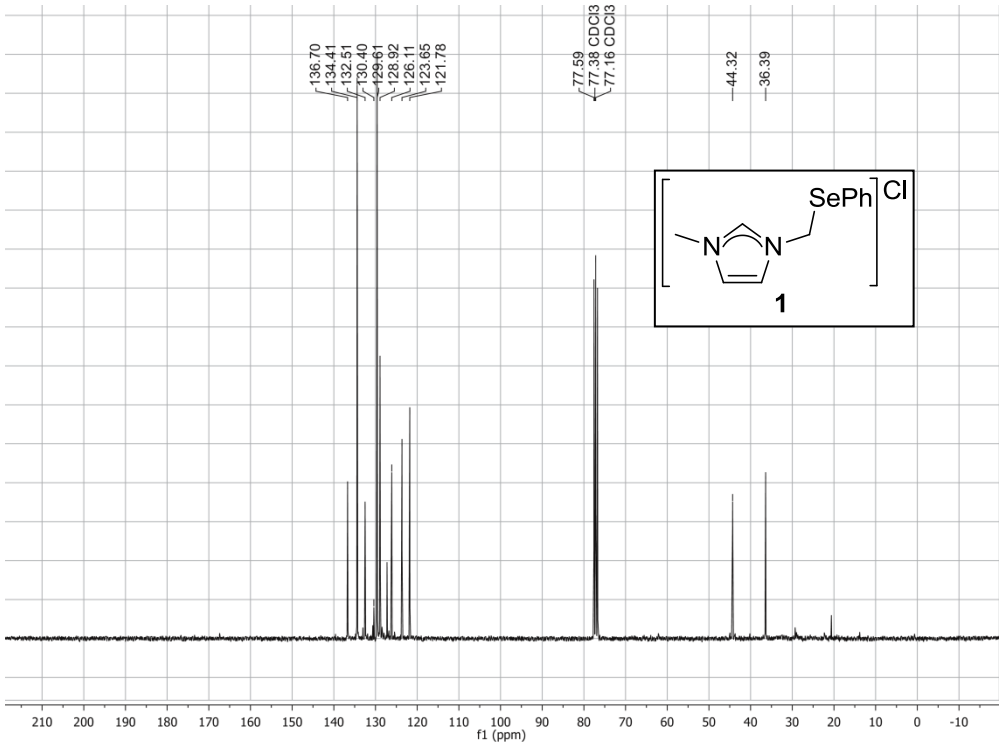

Figure S12. ^{13}C-NMR-spectrum of compound **1** in $CDCl_3$.

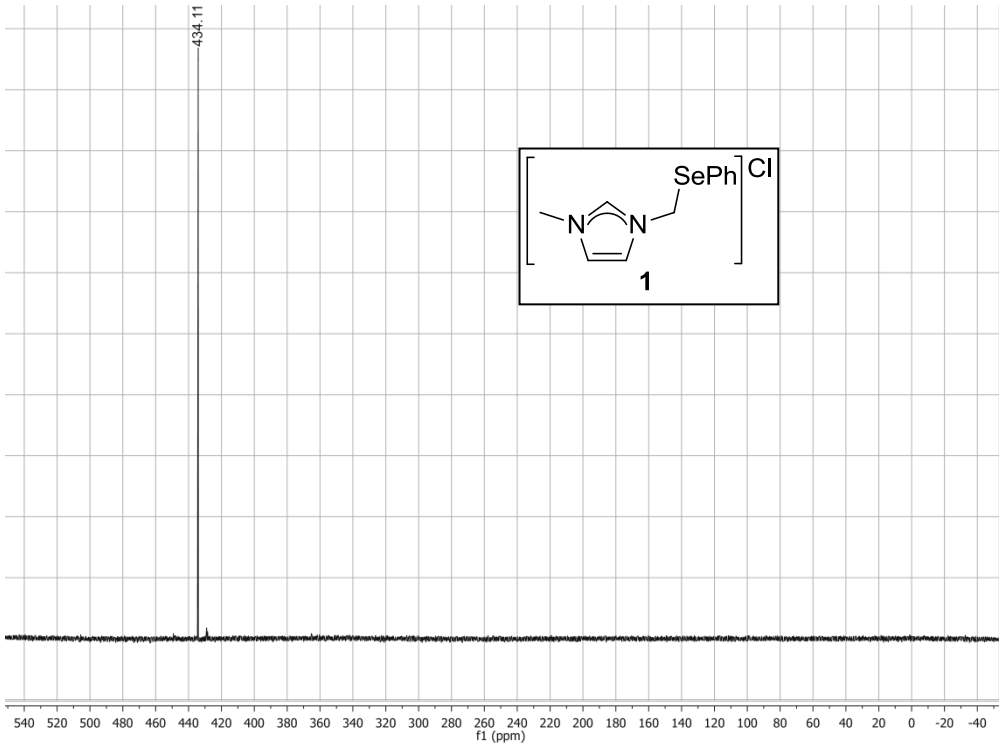

Figure S13. ^{77}Se-NMR-spectrum of compound **1** in $CDCl_3$.

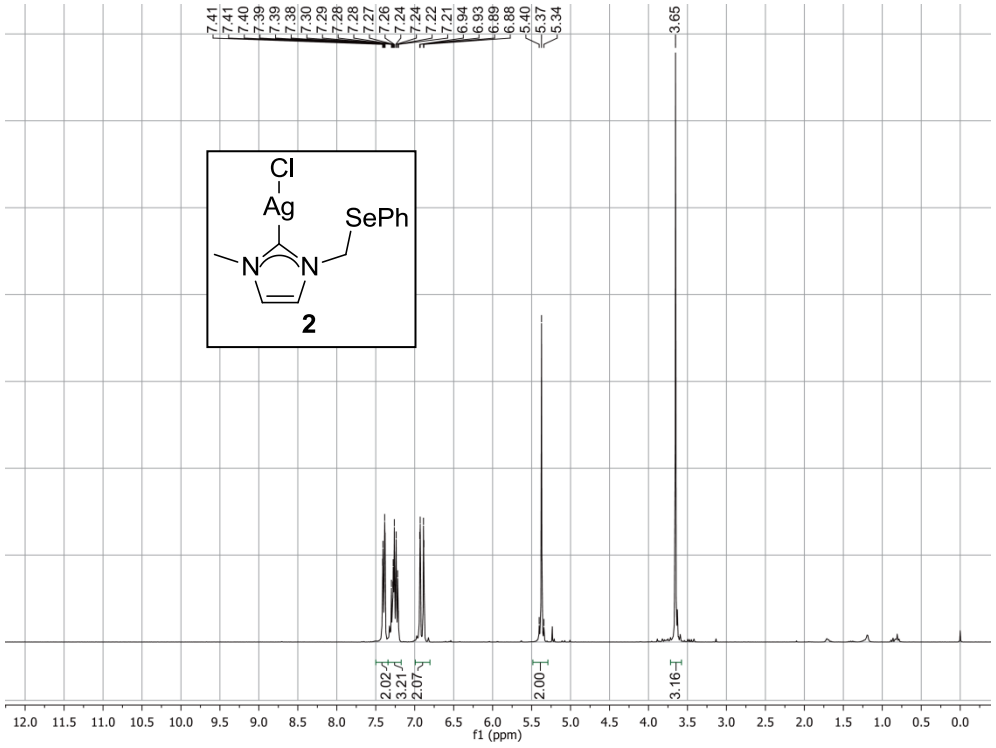

Figure S14. ^{1}H-NMR-spectrum of compound **2** in $CDCl_3$.

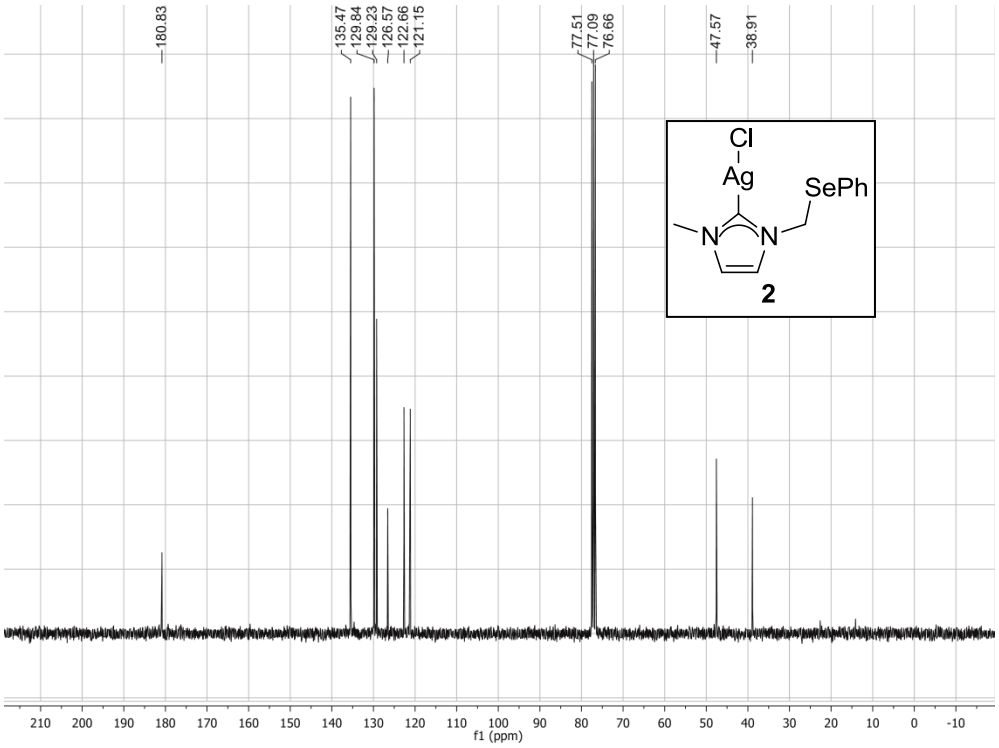

Figure S15. ^{13}H-NMR-spectrum of compound **2** in $CDCl_3$.

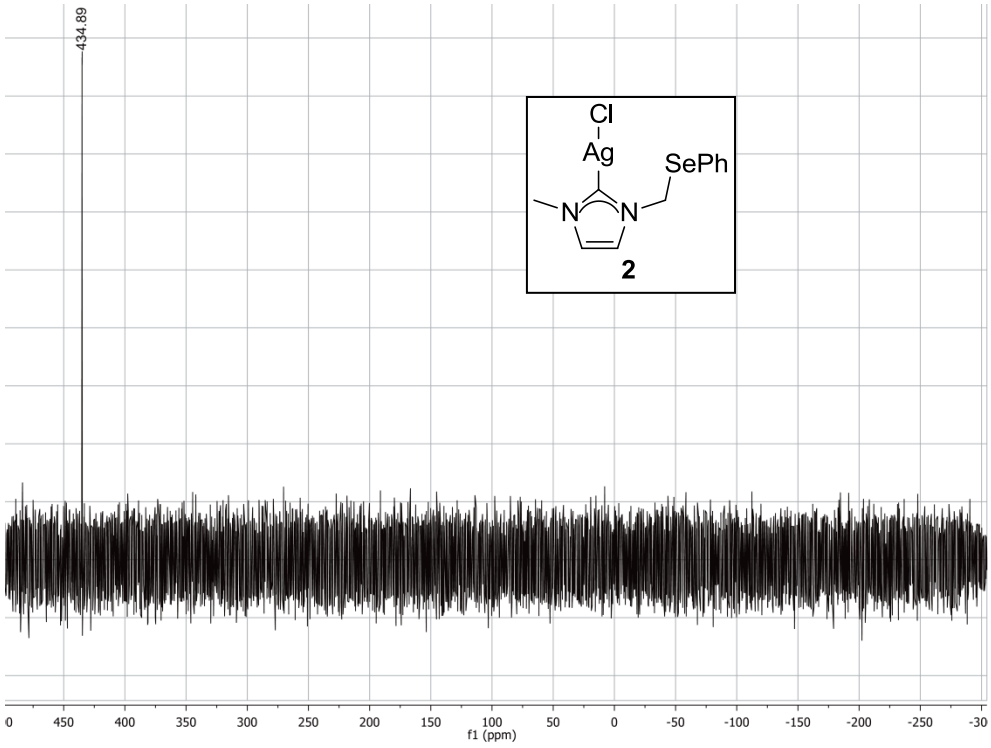

Figure S16. ^{77}Se-NMR-spectrum of compound **2** in $CDCl_3$.

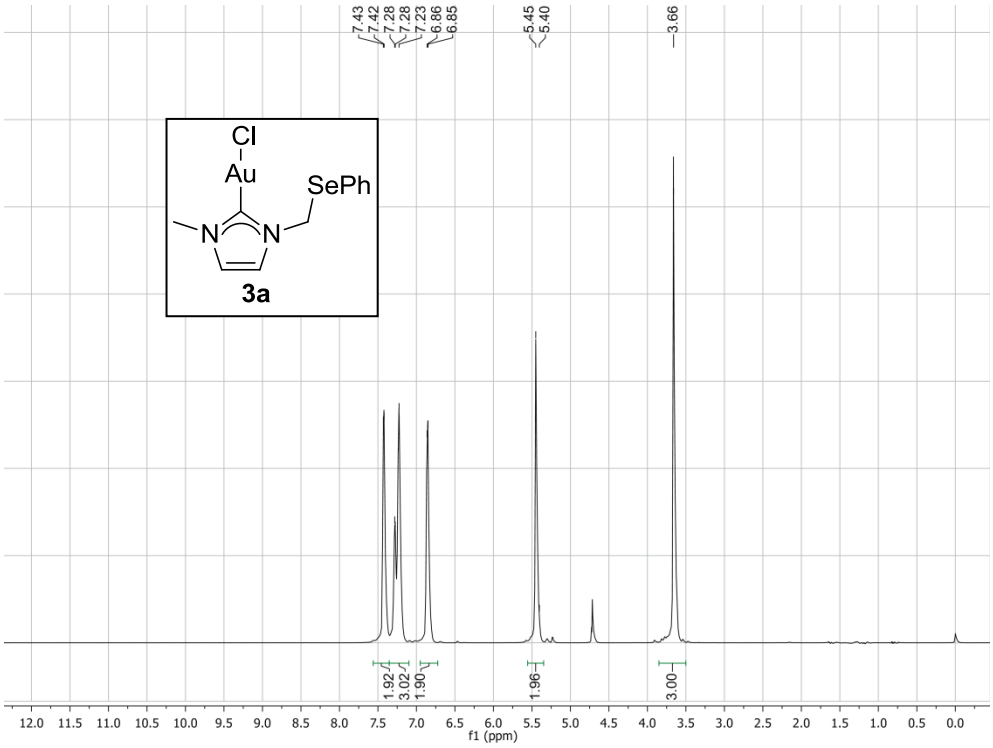

Figure S17. ^{1}H-NMR-spectrum of compound **3a** in $CDCl_3$.

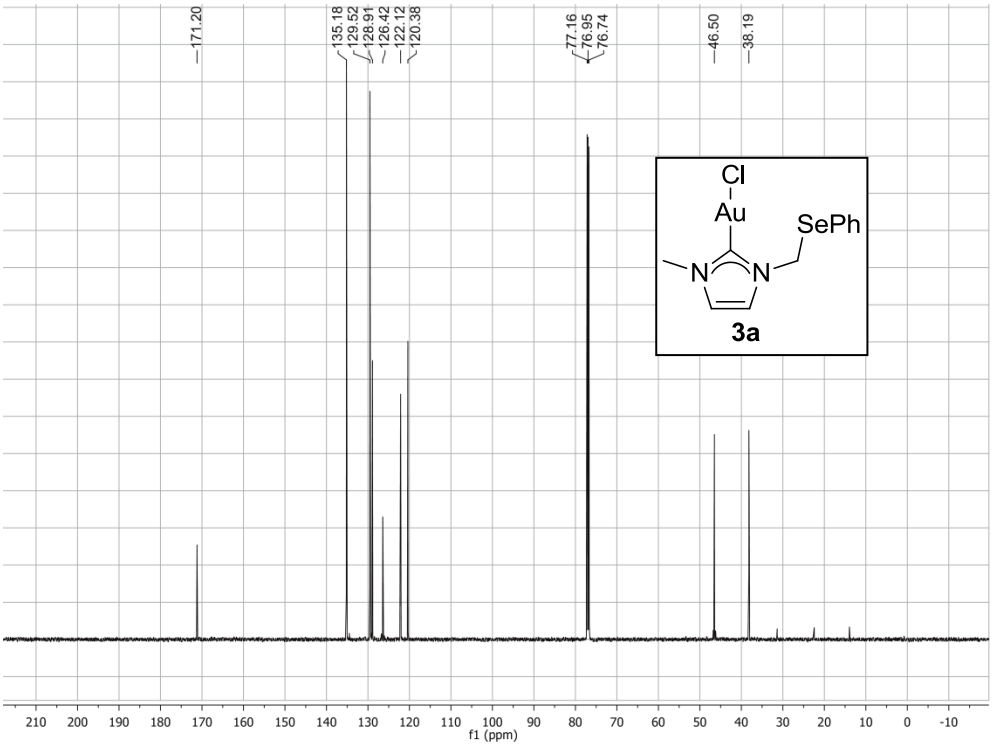

Figure S18. ^{13}C-NMR-spectrum of compound **3a** in $CDCl_3$.

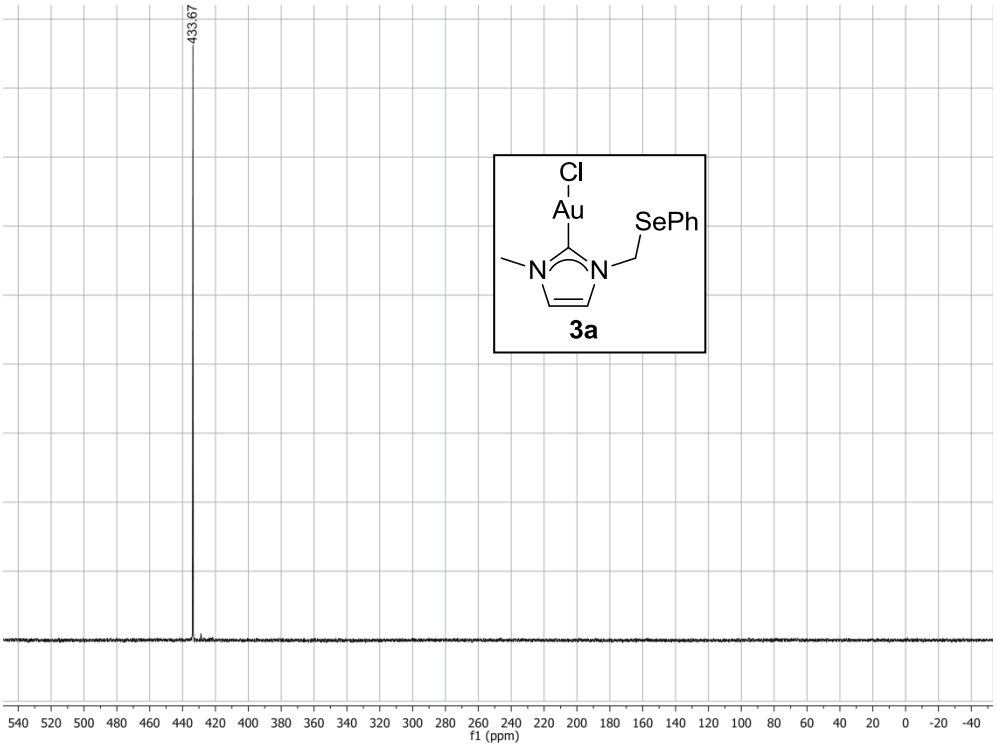

Figure S19. ^{77}Se-NMR-spectrum of compound **3a** in $CDCl_3$.

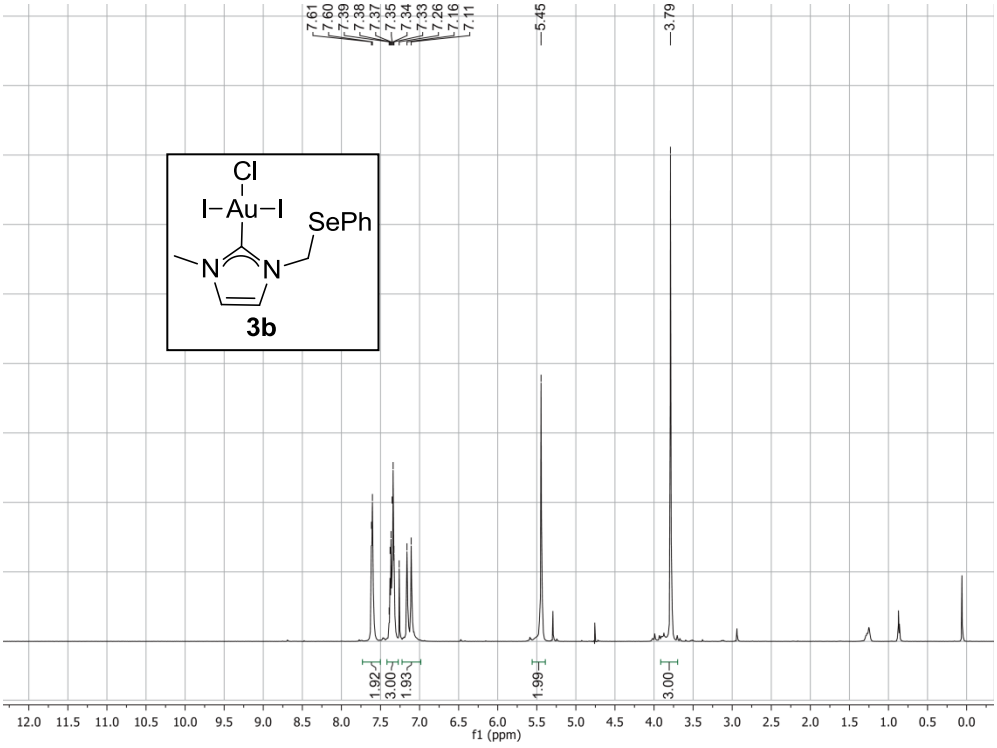

Figure S20. ^{1}H-NMR-spectrum of compound **3b** in $CDCl_3$.

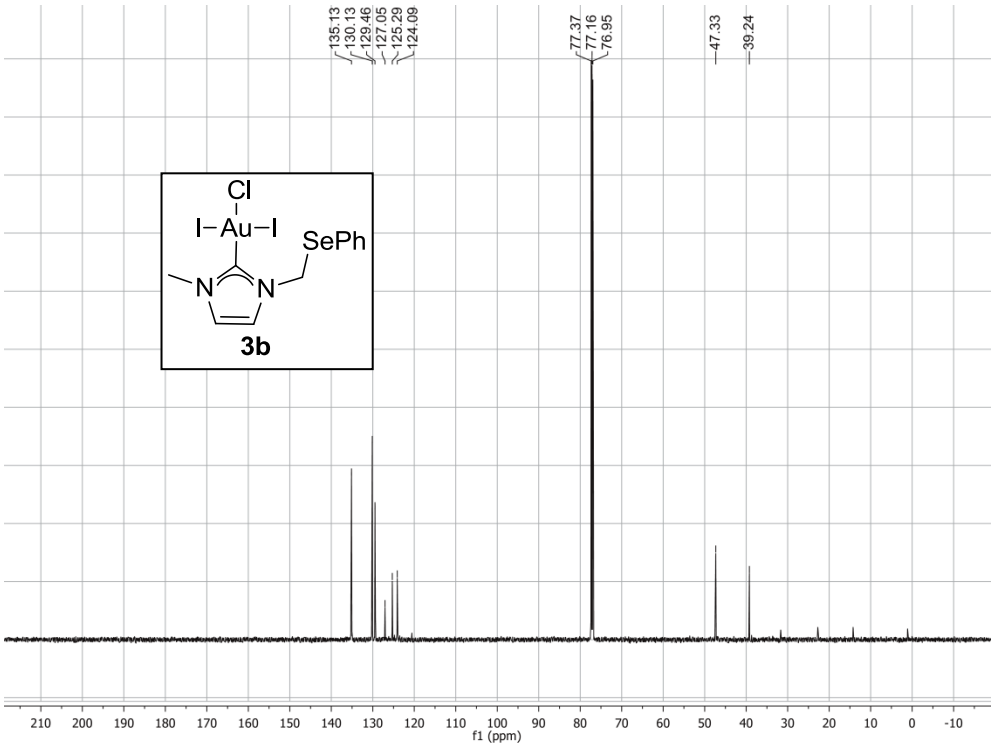

Figure S21. ^{13}C-NMR-spectrum of compound **3b** in $CDCl_3$.

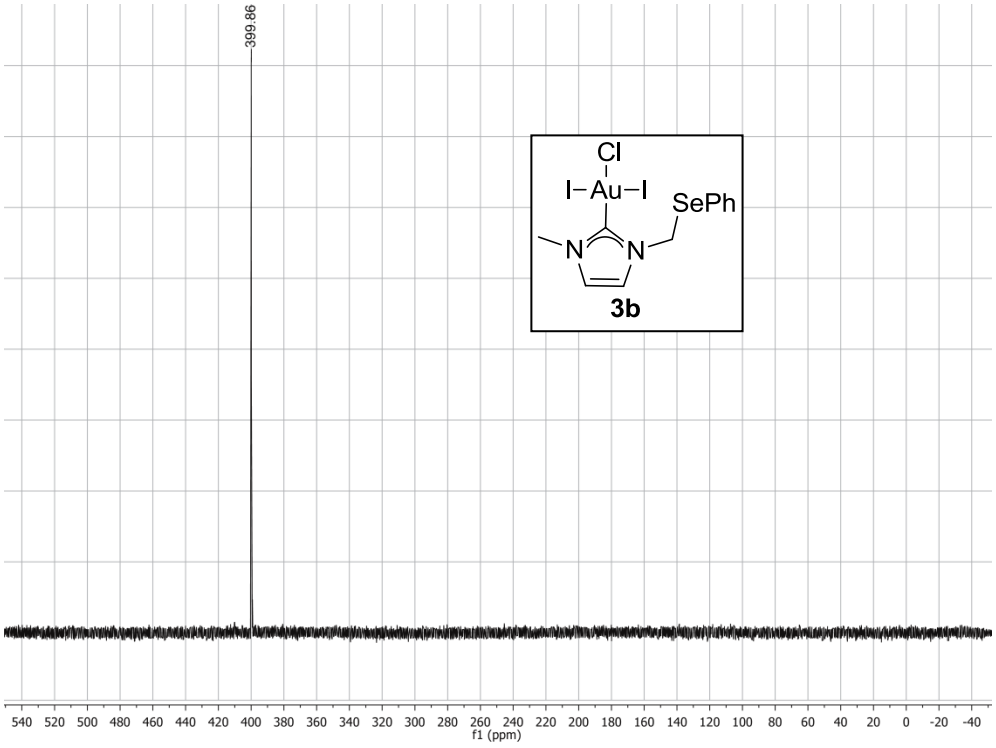

Figure S22. ^{77}Se-NMR-spectrum of compound **3b** in $CDCl_3$.

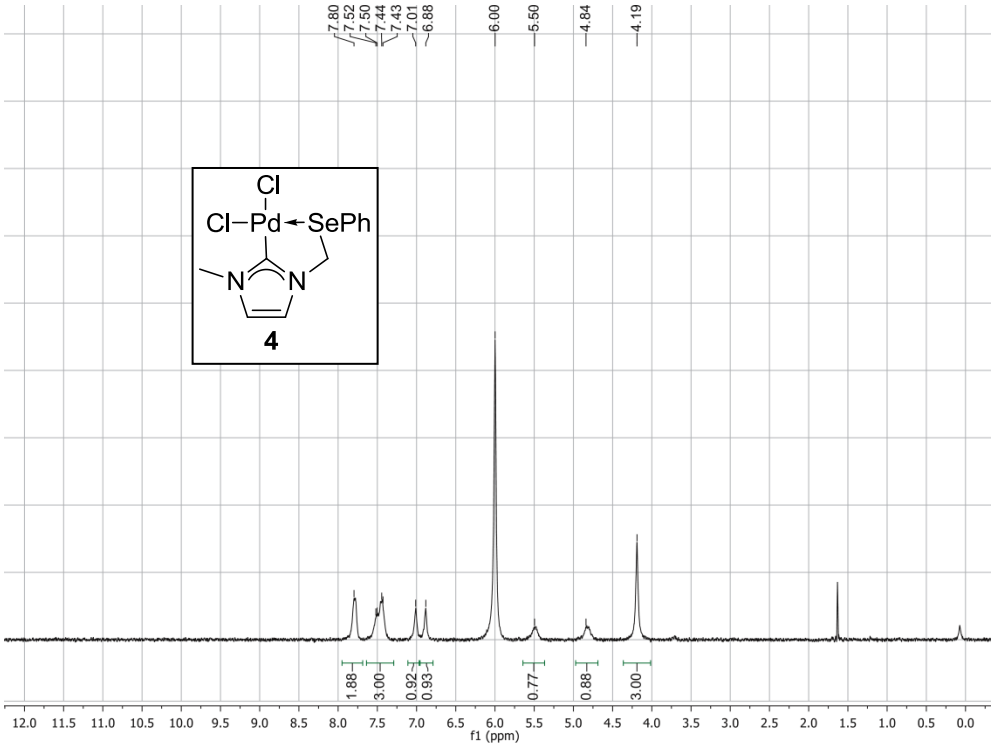

Figure S23. ^{1}H-NMR-spectrum of compound **4** in $C_2D_2Cl_4$.

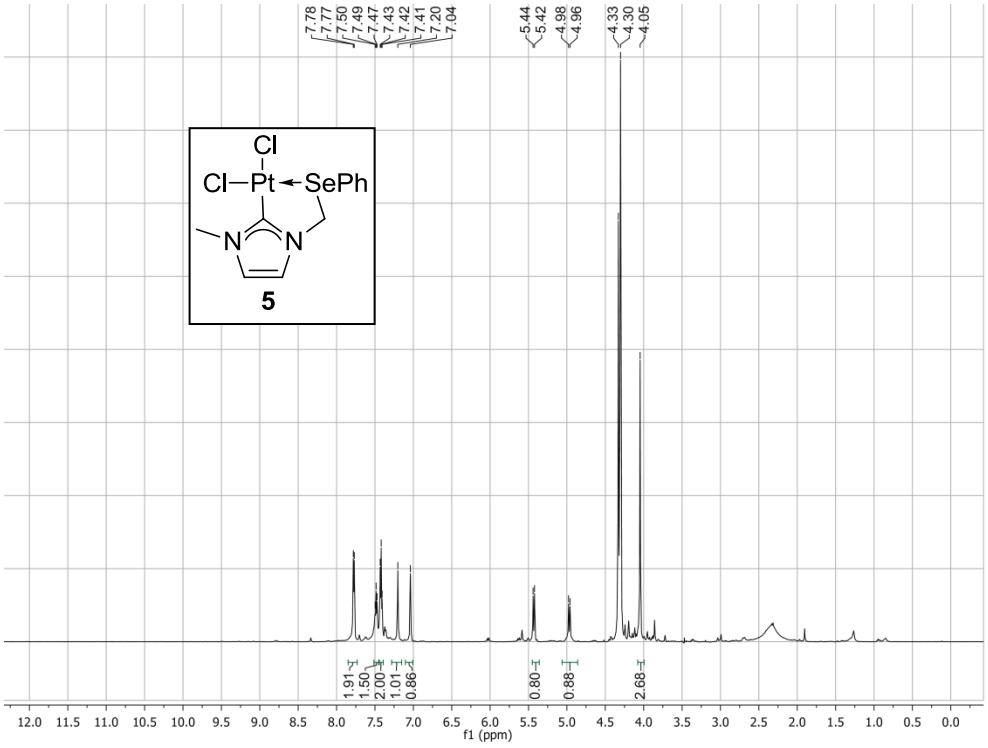

Figure S24. ^{1}H-NMR-spectrum of compound **5** in CD_3NO_2.

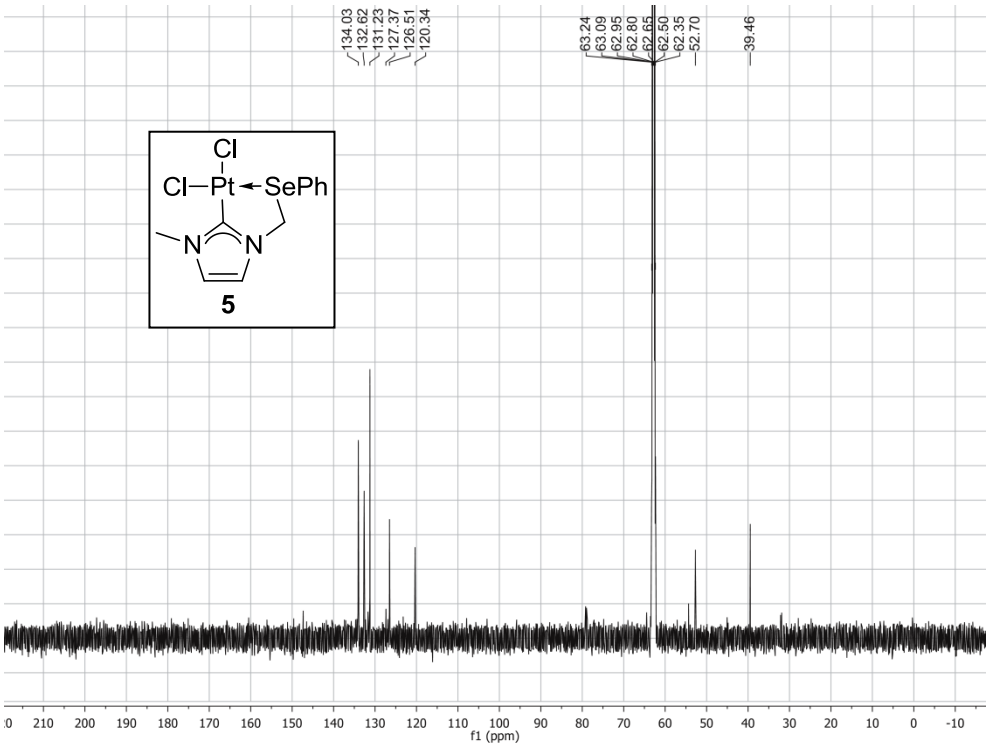

Figure S25. ^{13}C-NMR-spectrum of compound **5** in CD_3NO_2.

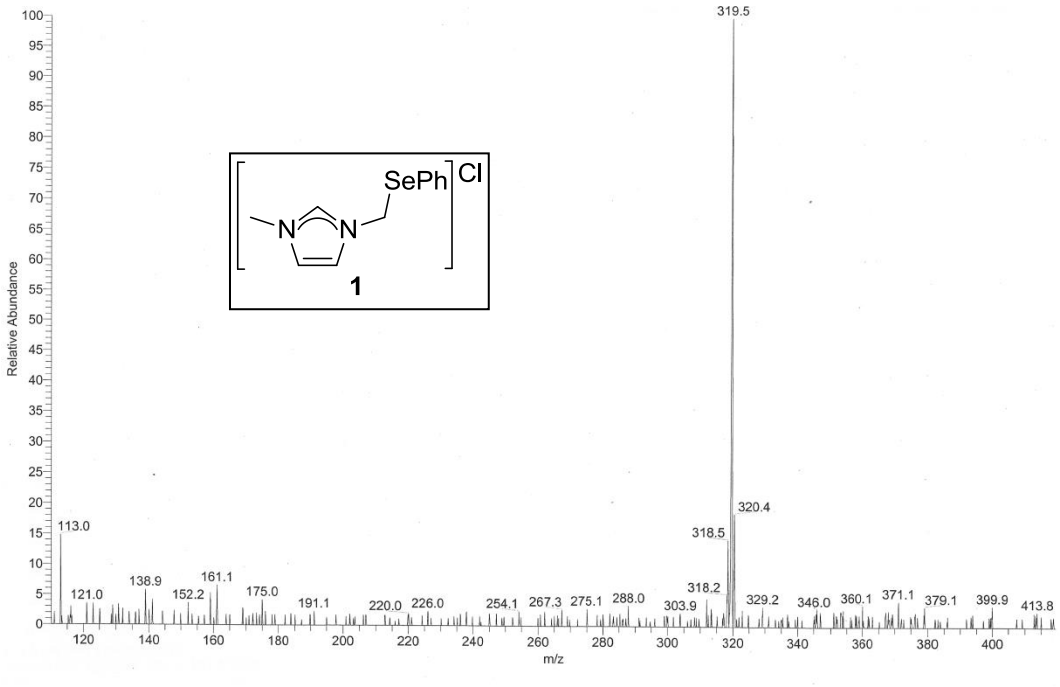

Figure S26. ESI-MS of the *N*-butyl-*N'*-[(Phenylseleno)methylene)]imidazolium cation.

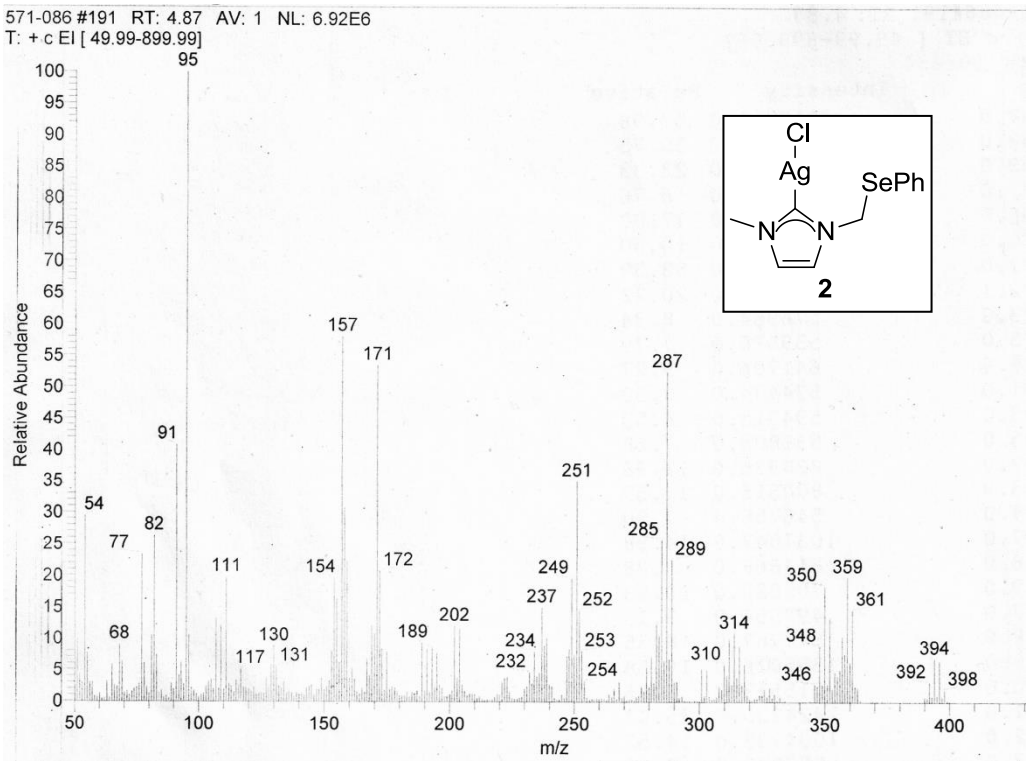

Figure S27. EI-MS of compound **2**.

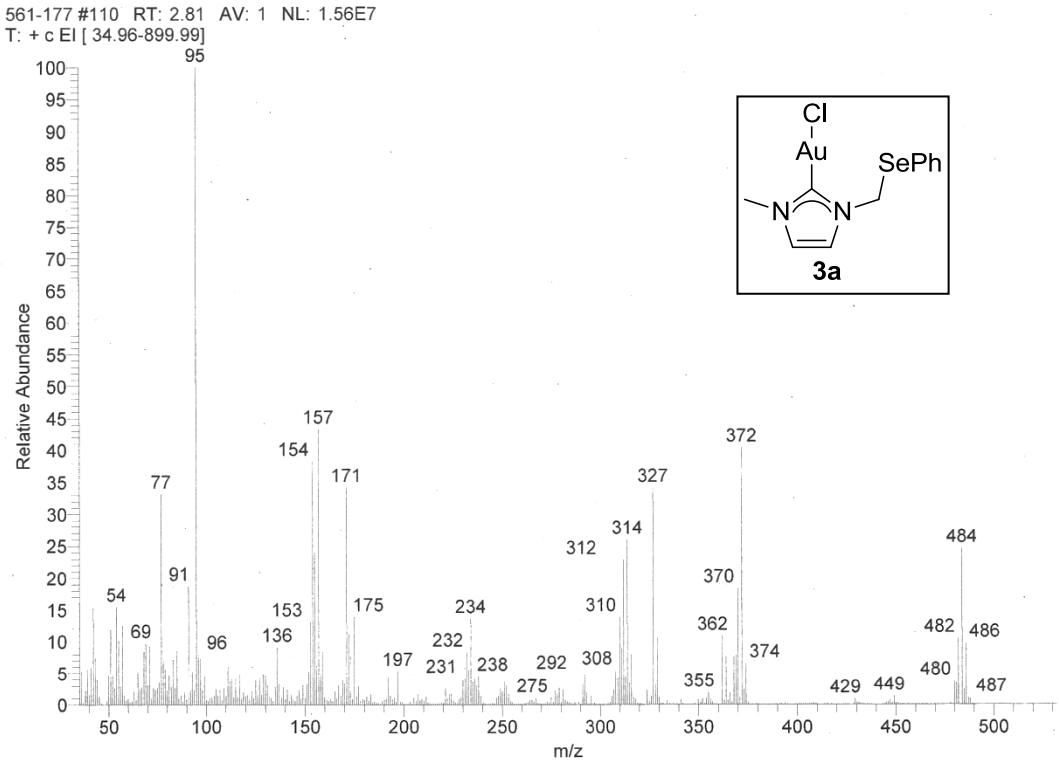

Figure S28. EI-MS of compound **3a**.

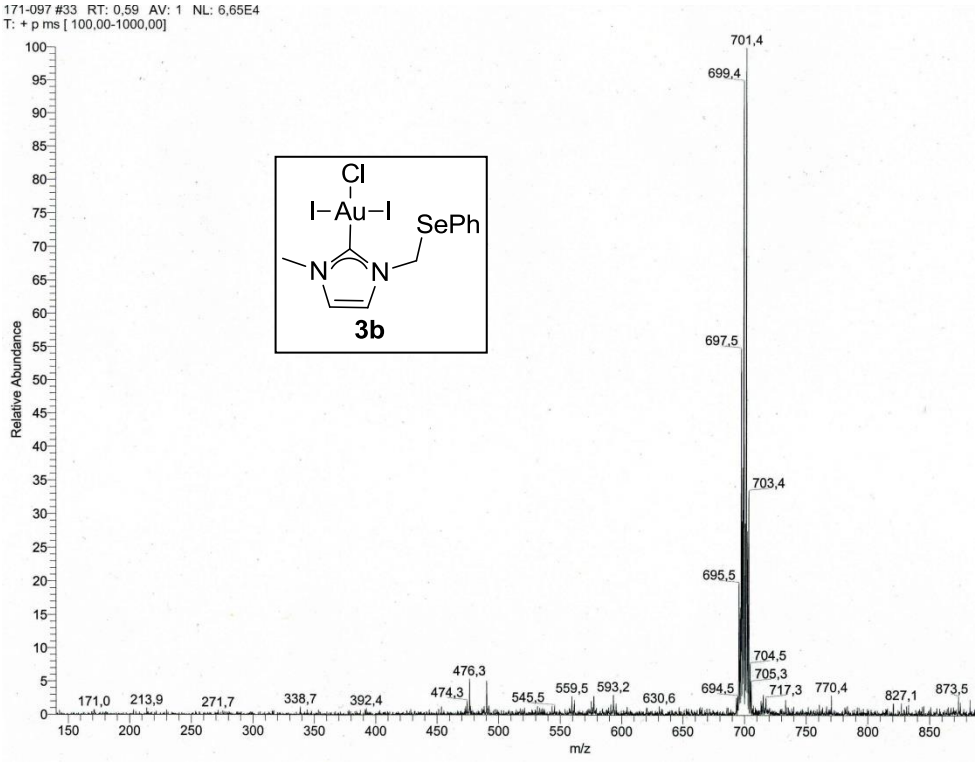

Figure S29. ESI-MS of compound **3b**.

III Nanoparticle synthesis

$Pd_{17}Se_{15}$ nanoparticles

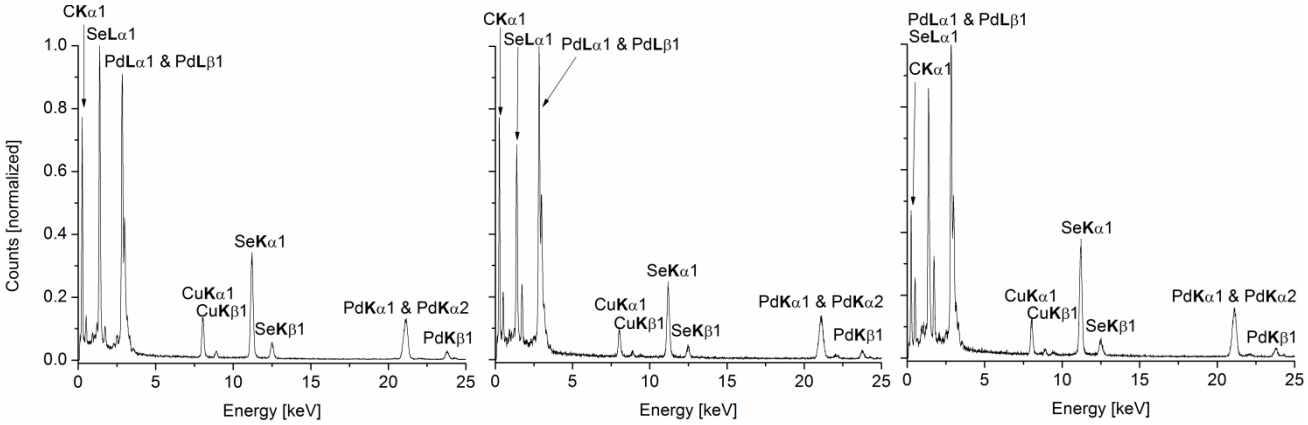

Figure S30 EDX-spectra of the $Pd_{17}Se_{15}$ nanoparticles obtained from compound **4** in $[BMIm]NTf_2$ at three different positions on the TEM-grid of the same sample.

Table S17. Atomic ratio of Se and Pd from the TEM-EDX-spectra of the $Pd_{17}Se_{15}$ nanoparticles obtained from compound **4** in $[BMIm]NTf_2$ for three different regions on the TEM-grid of the same sample.

	Measurement 1	Measurement 2	Measurement 3	Average value
Se(K) [At-%]	36	37	41	38
Pd(K) [At-%]	64	63	59	62

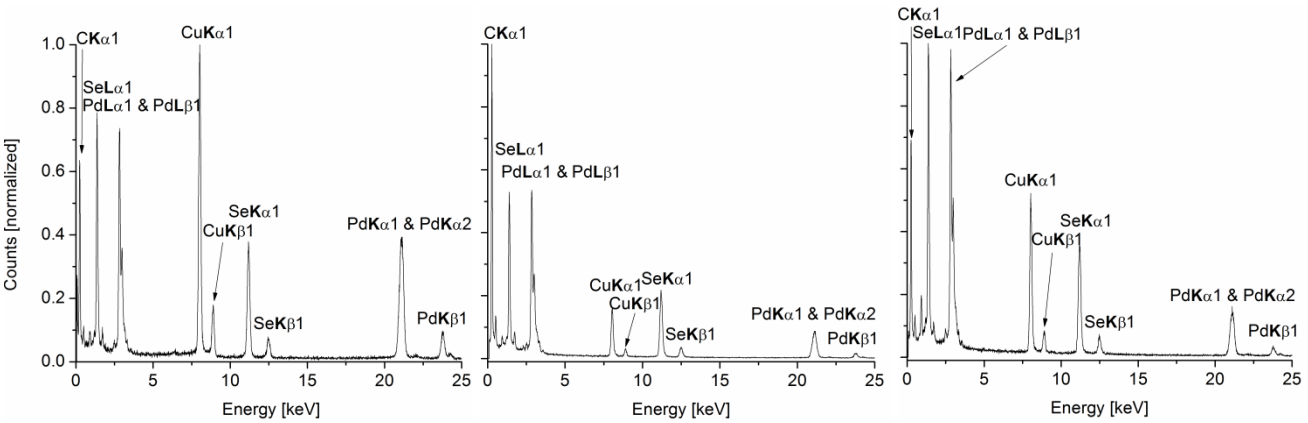

Figure S31. EDX-spectra of the $Pd_{17}Se_{15}$ nanoparticles obtained from compound **4** in propylene carbonate at three different spots on the TEM-grid of the same sample.

Table S18. Atomic ratio of Se and Pd from the TEM-EDX-spectra of the $Pd_{17}Se_{15}$ nanoparticles obtained from compound **4** in propylene carbonate for three different regions on the TEM-grid of the same sample.

	Measurement 1	Measurement 2	Measurement 3	Average value
Se(K) [At-%]	46	45	44	45
Pd(K) [At-%]	54	55	56	55

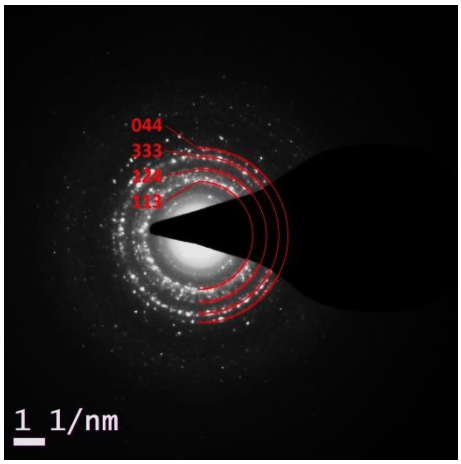

Figure S32. SAED-image of the $Pd_{17}Se_{15}$ nanoparticles obtained from compound **4** in propylene carbonate.

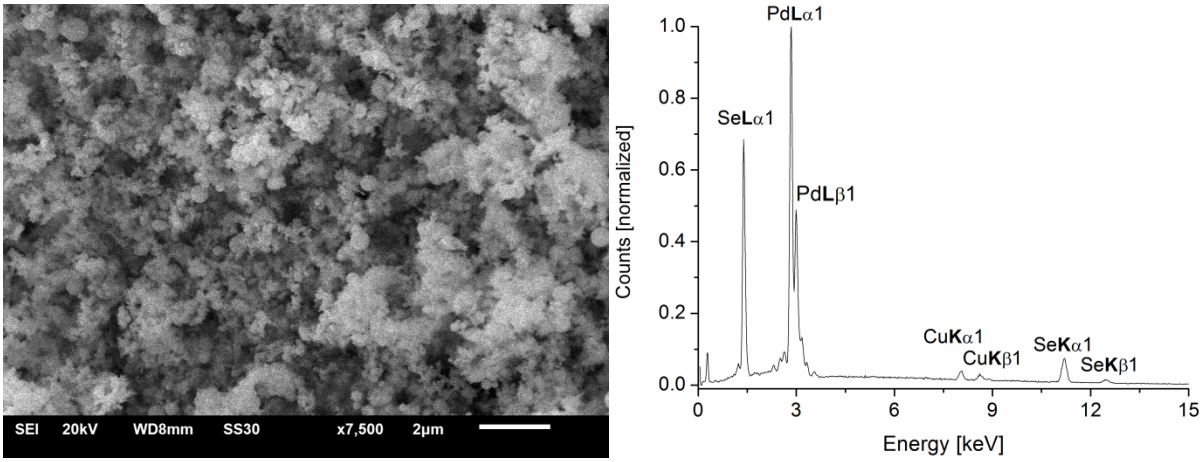

Figure S33. SEM image (left) and SEM-EDX spectrum of the $Pd_{17}Se_{15}$ nanoparticles obtained from compound **4** in $[BMIm]NTf_2$ (right) gave a Pd:Se ratio of 60:40.

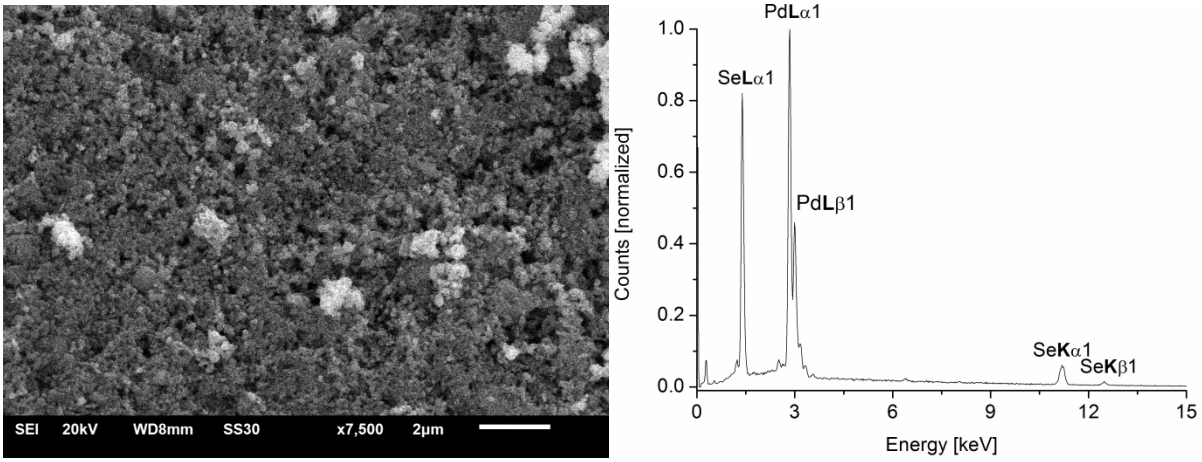

Figure S34. SEM image (left) and SEM-EDX spectrum of the $Pd_{17}Se_{15}$ nanoparticles obtained from compound **4** in PC (right) gave a Pd:Se ratio of 56:44.

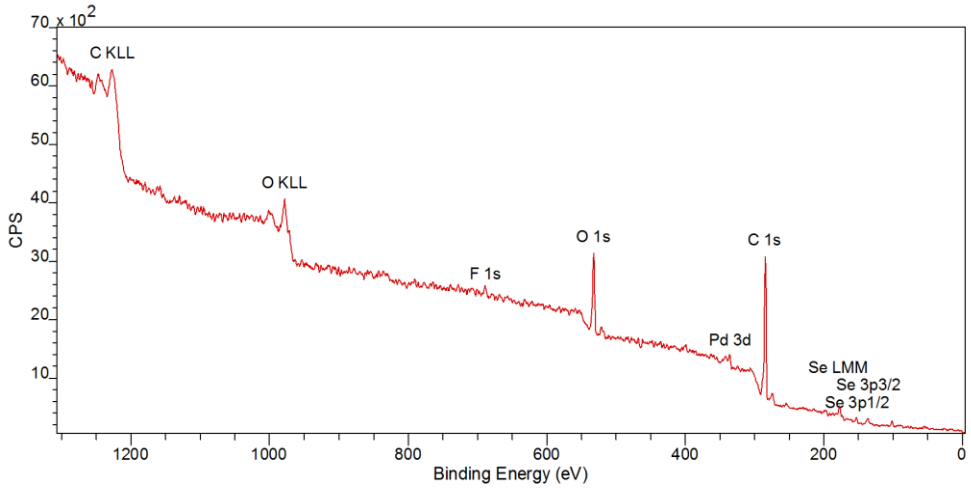

Figure S35. Overview XP spectrum of Pd/Se ($Pd_{17}Se_{15}$) nanoparticle sample obtained from compound **4** in [BMIm]NTf_2.

Pt clusters/nanoparticles

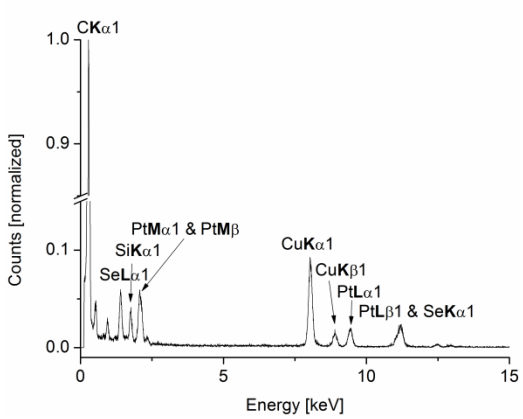

Figure S36. EDX-spectrum of the nanoclusters obtained from compound **5** in [BMIm]NTf_2 showing the presence of selenium and platinum in the sample.

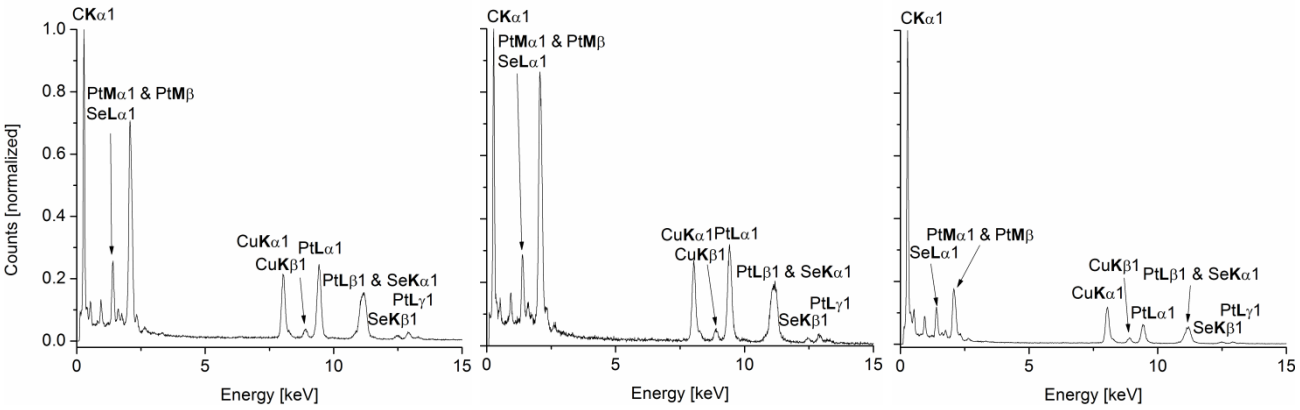

Figure S37. EDX-spectra of the $Pt_{17}Se_{15}$ nanoparticles obtained from compound **5** in propylene carbonate at three different spots on the TEM-grid of the same sample.

Table S19. Atomic ratio of Se and Pt from the TEM-EDX-spectra of the Pt/Se nanoparticles obtained from compound **5** in $[BMIm]NTf_2$ at three different spots on the TEM-grid of the same sample.

	Measurement 1	Measurement 2	Measurement 3	Average value
Se(L) [At-%]	47	57	46	50
Pt(L) [At-%]	53	43	54	50

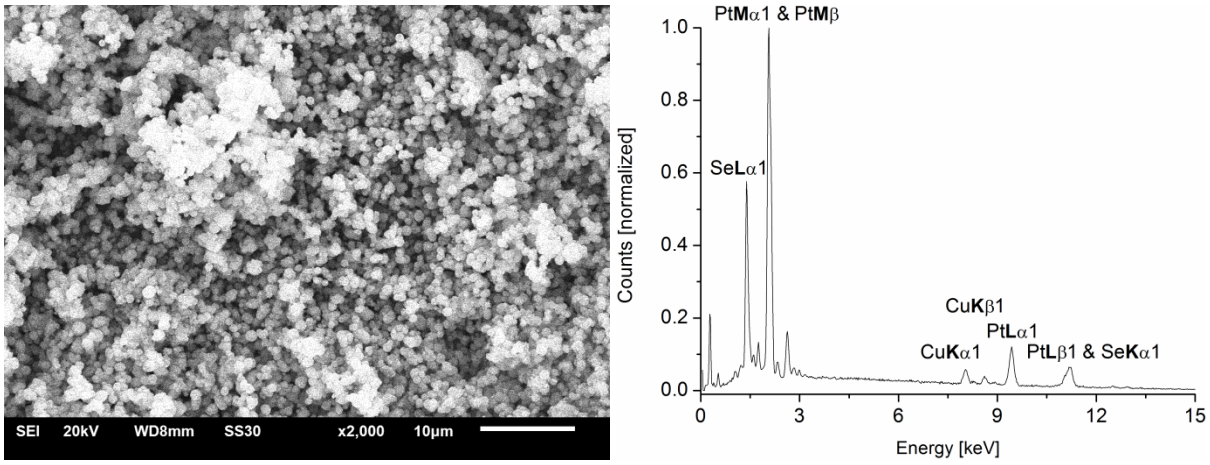

Figure S38. SEM image (left) and SEM-EDX spectrum of the Pt/Se sample obtained from compound **5** in $[BMIm]NTf_2$ (right) gave a Pt:Se ratio of 56:44.

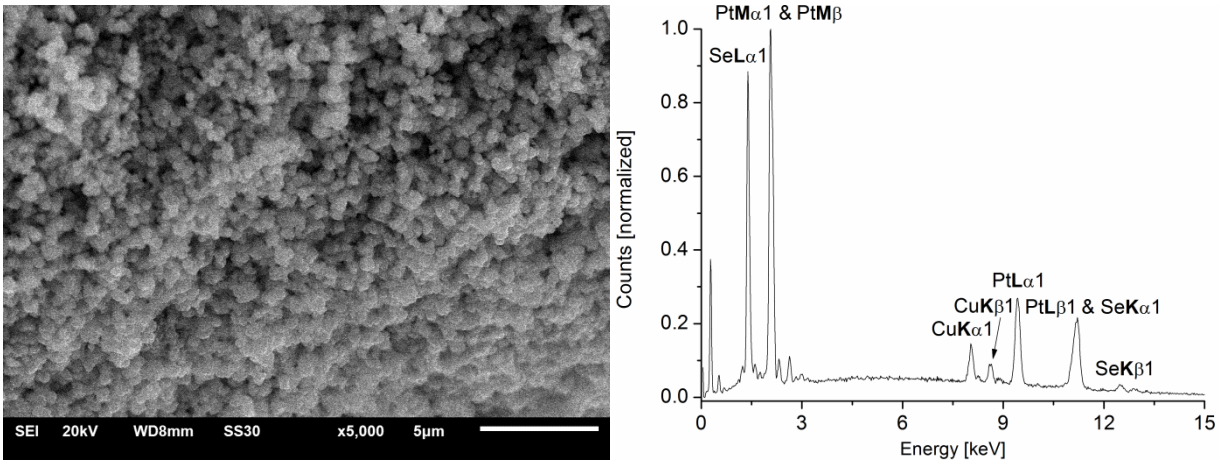

Figure S39. SEM image (left) and SEM-EDX spectrum of the Pt/Se sample obtained from compound **5** in PC (right) gave a Pt:Se ratio of 54:46.

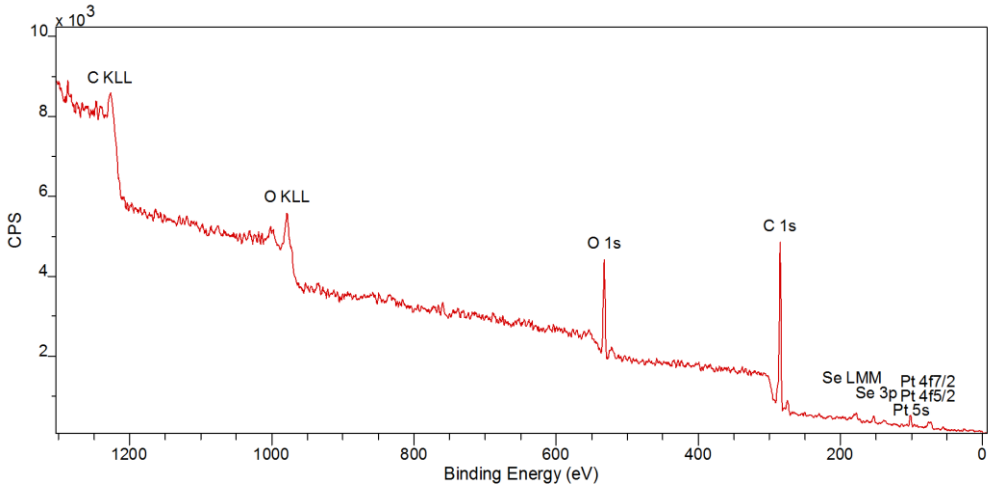

Figure S40. Overview XP spectrum of the Pt sample obtained from compound **5** in PC.

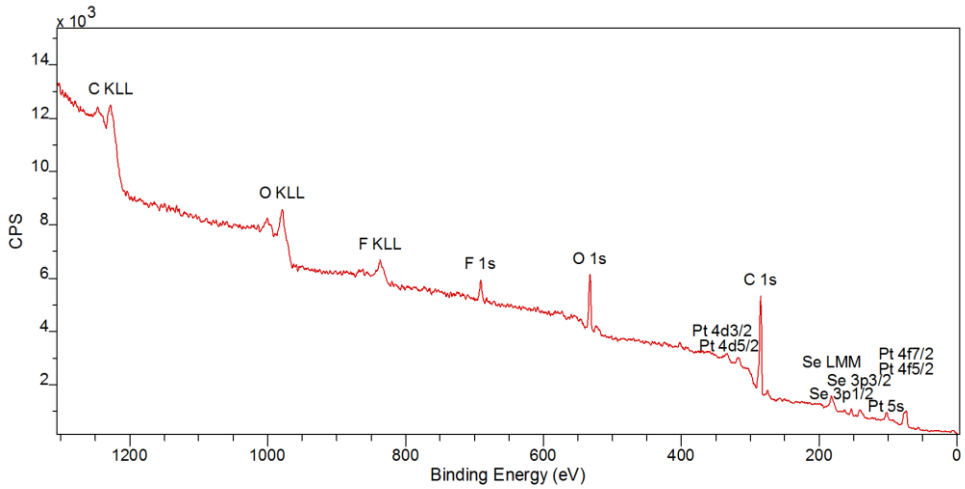

Figure S41. Overview XP spectrum of the Pt sample obtained from compound **5** in [BMIm]NTf_2.

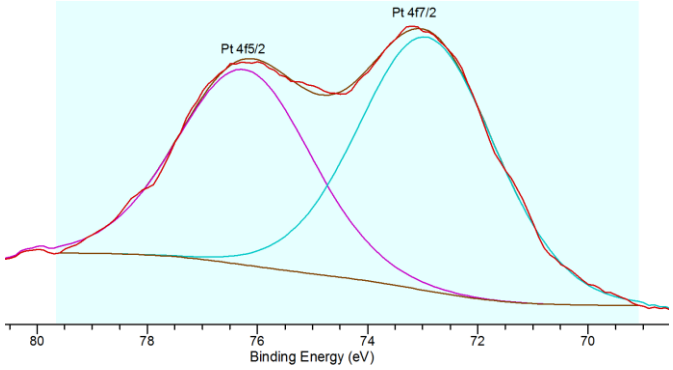

Figure S42. HR-XP spectrum of the Pt sample obtained from the decomposition of compound **5** in [BMIm]NTf_2.

IV Catalysis

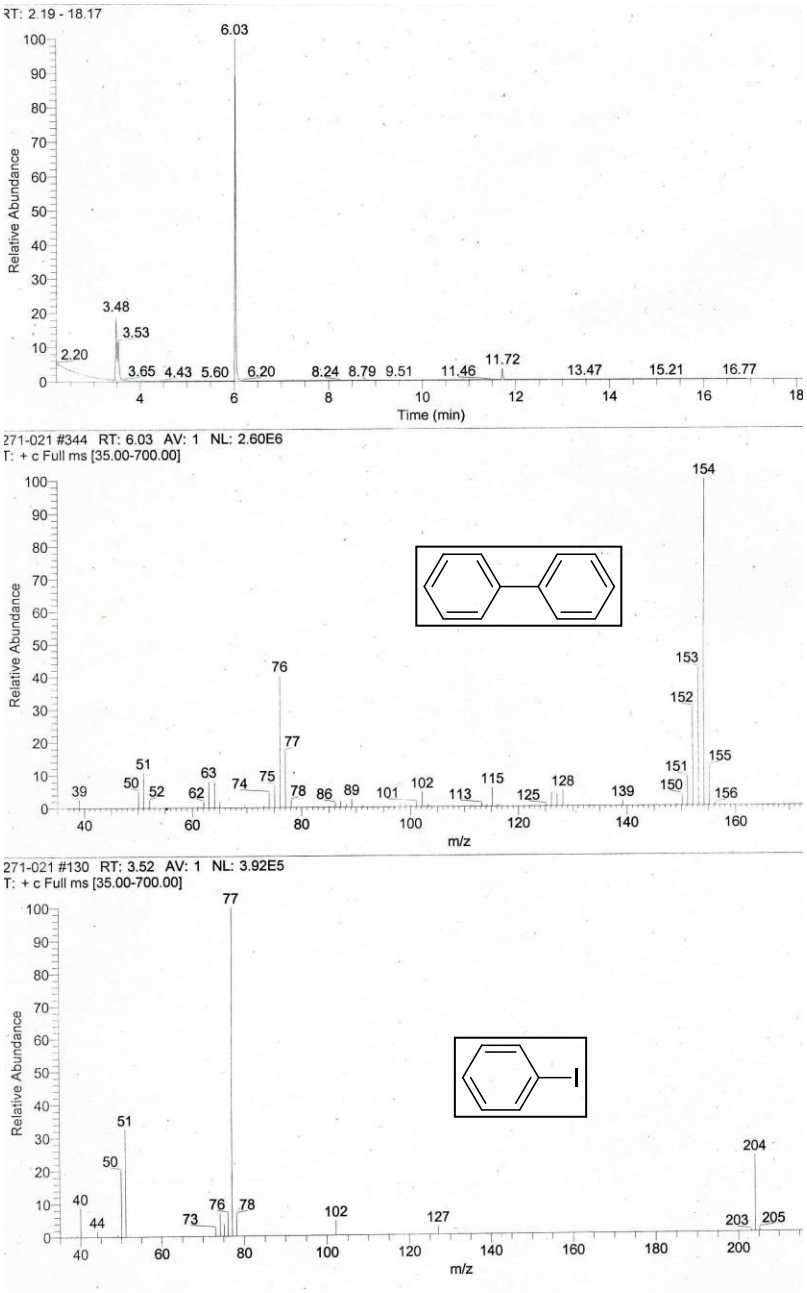

Figure 43. Results of the GC-MS analysis of the reaction mixture of the Suzuki coupling reaction using the $Pd_{17}Se_{15}$ nanoparticles from the IL.

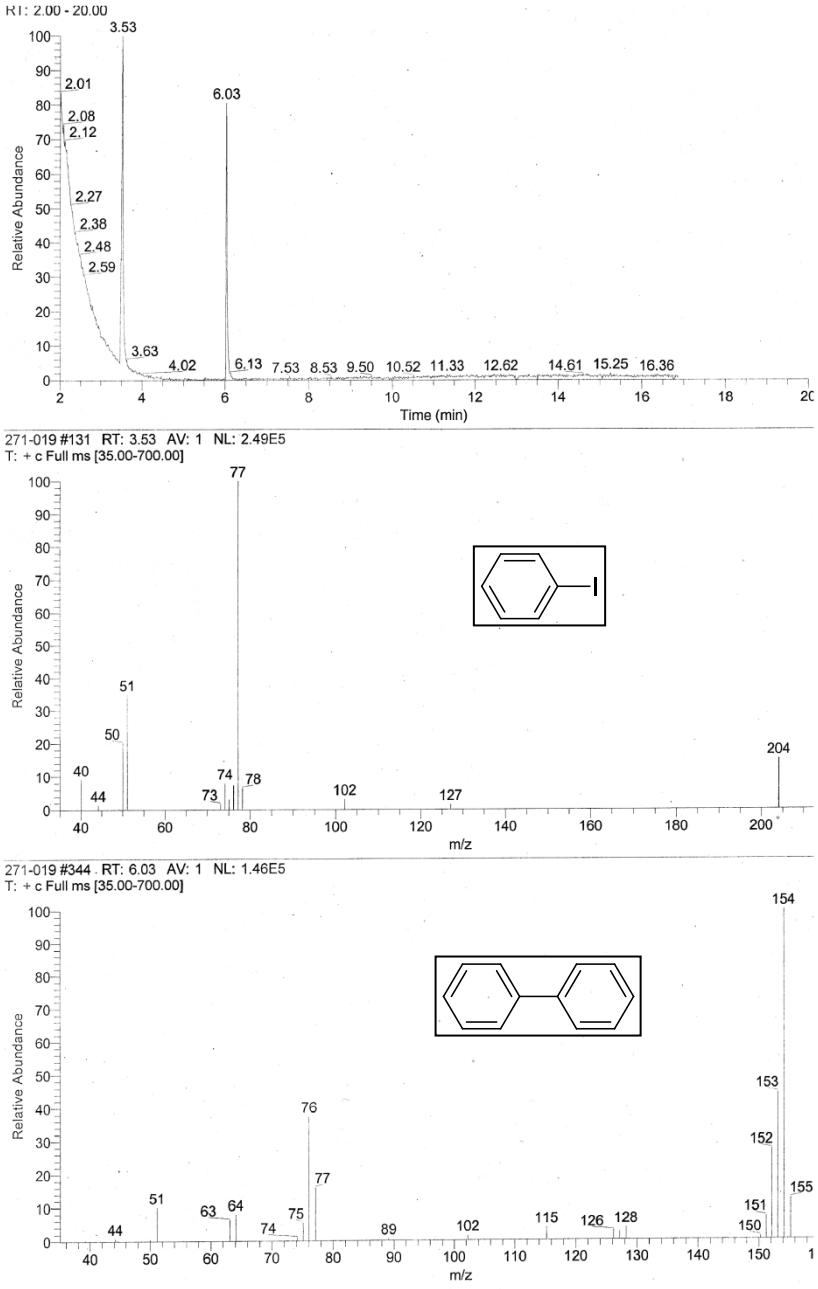

Figure 44. Results of the GC-MS analysis of the reaction mixture of the Suzuki coupling reaction using the $Pd_{17}Se_{15}$ nanoparticles from PC.

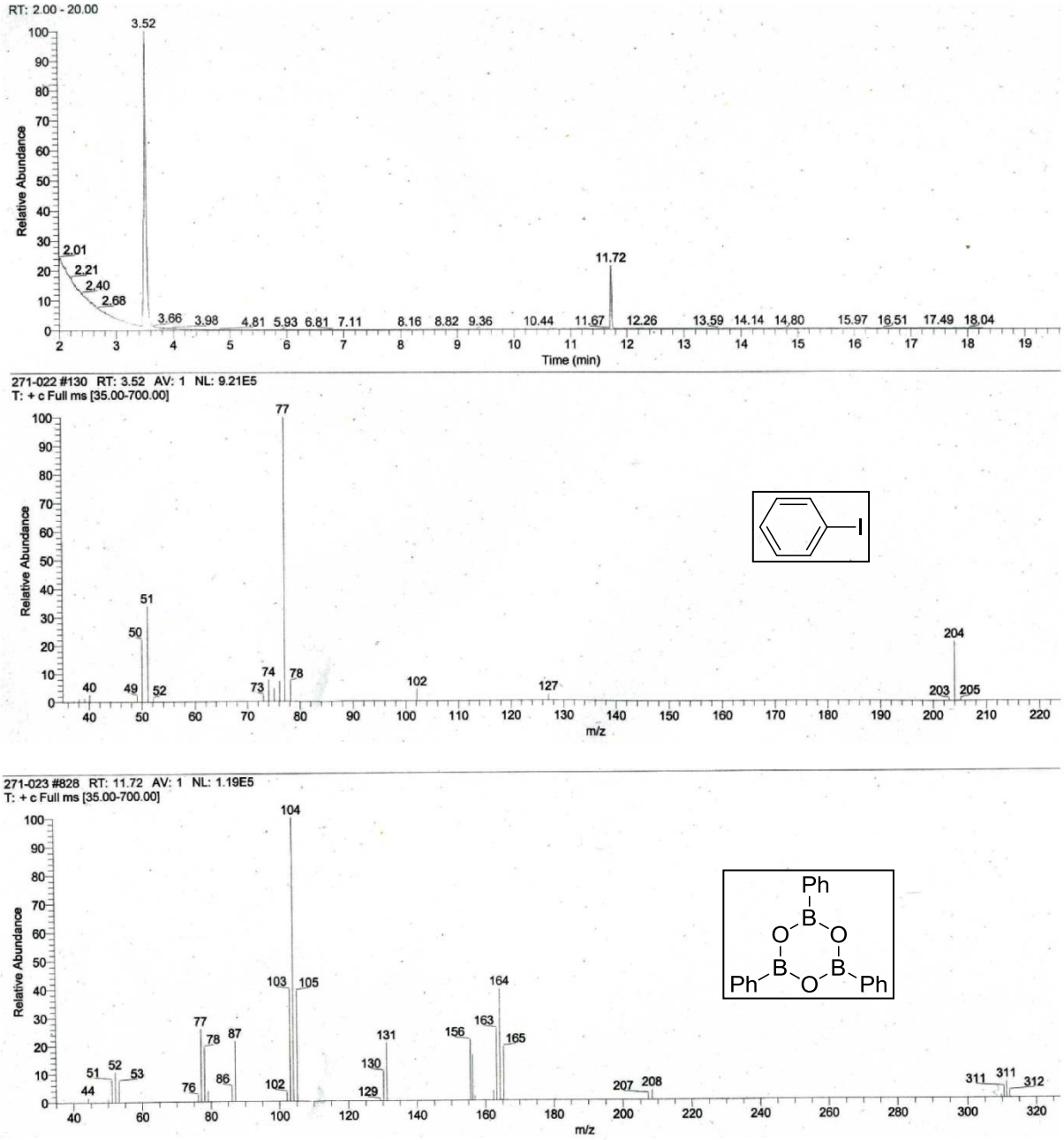

Figure S45. Results of the GC-MS analysis of the reaction mixture of the Suzuki coupling reaction using the Pt clusters from the IL.

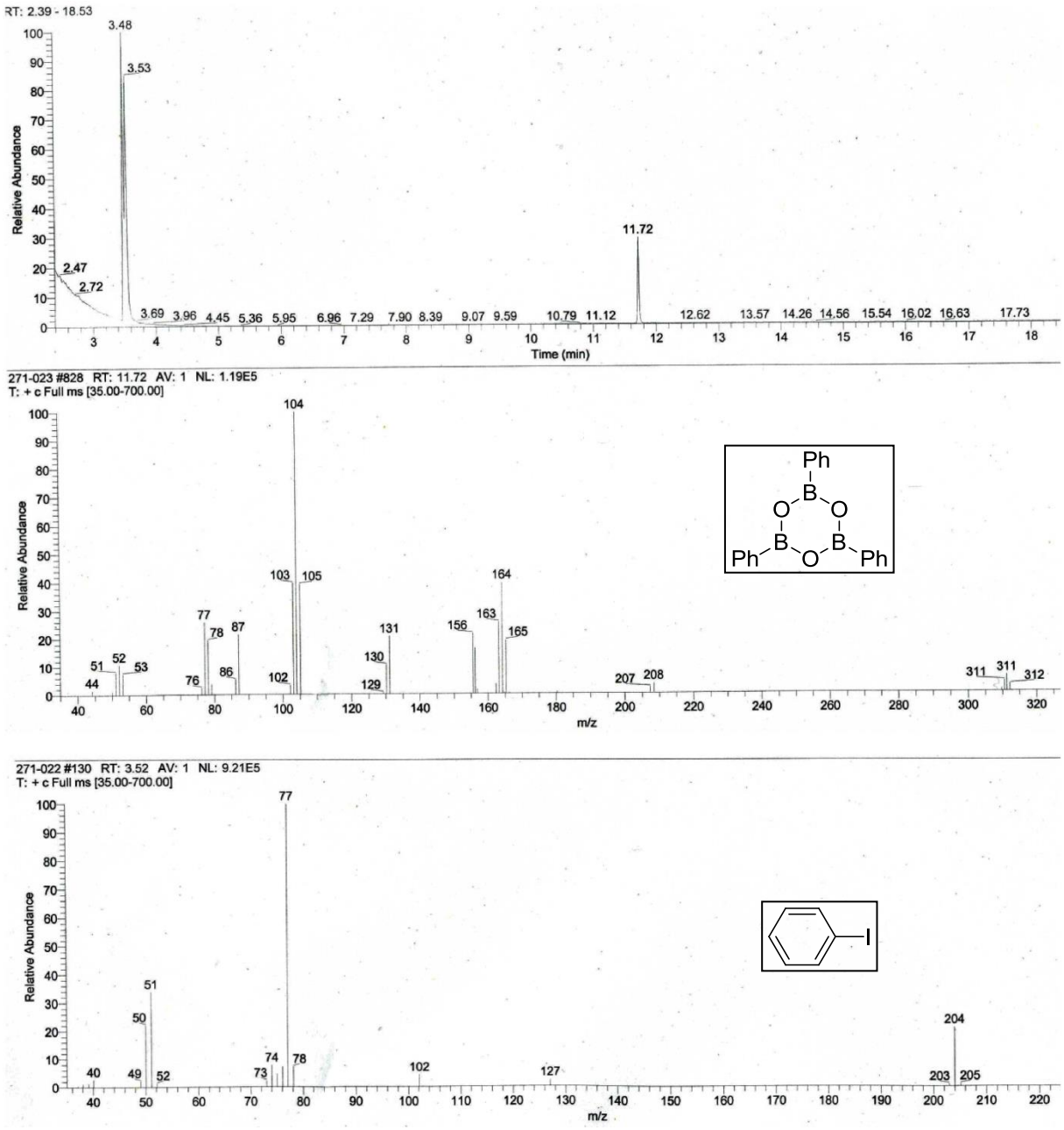

Figure S46. Results of the GC-MS analysis of the reaction mixture of the Suzuki coupling reaction using the Pt nanoparticles from the PC.

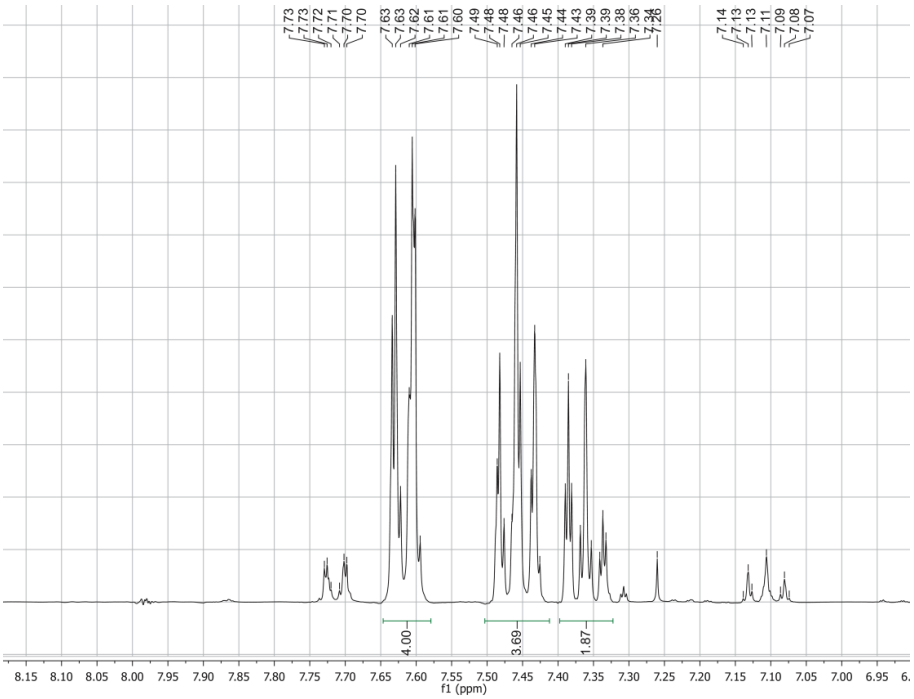

Figure S47. ^{1}H-NMR-spectrum of biphenyl obtained from the Suzuki coupling reaction using the $Pd_{17}Se_{15}$ nanoparticles from the IL.

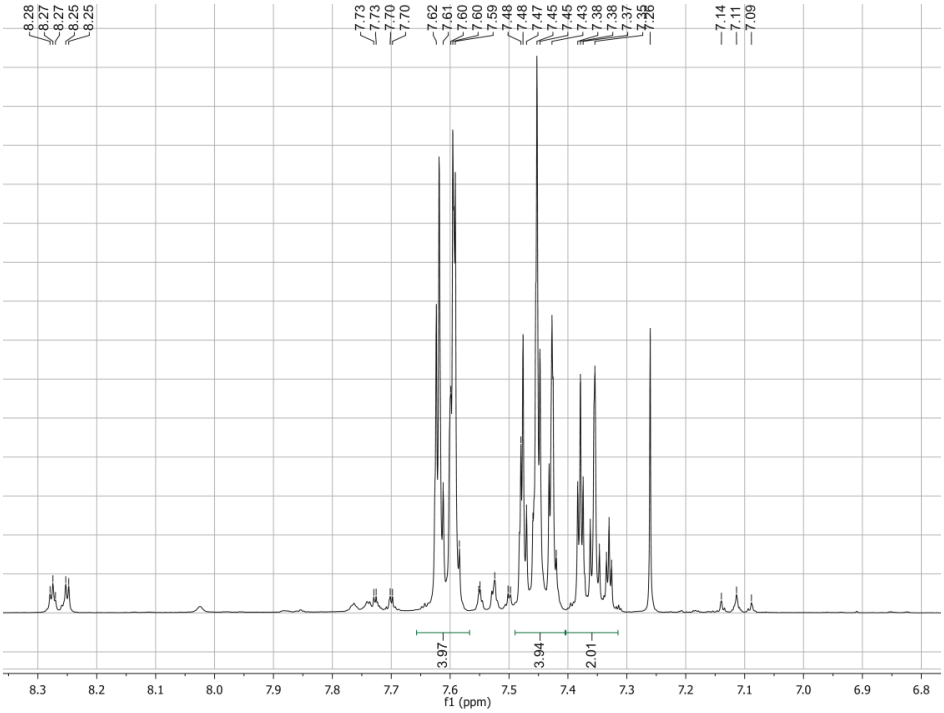

Figure S48. ^{1}H-NMR-spectrum of biphenyl obtained from the Suzuki coupling reaction using the $Pd_{17}Se_{15}$ nanoparticles from PC.

(1) (a) Flack, H. D.; Sadki, M.; Thompson, A. L.; Watkin, D. J. *Acta Cryst., Sect. A* **2011**, *67*, 21–34. (b) Flack, H. D.; Bernardinelli, G. *Chirality* **2008**, *20*, 681–690. (c) Flack, H. D.; Bernardinelli, G. *Acta Cryst.*, Sect. A **1999**, *55*, 908–915. (d) Flack, H. D. *Acta Cryst.*, *Sect. A* **1983**, *39*, 876–881.