ESI for

Palladium(II) complexes bearing 1,2,3-triazole based organosulfur/ selenium ligand: synthesis, structure and applications in Heck and Suzuki-Miyaura coupling as catalyst via palladium nanoparticles

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Table S1 Crystal data and structural refinements for Complexes **1** / **2**

Compounds	**1**	**2**
Empirical formula	**C_{16} H_{15} Cl_2 N_3 Pd S**	**C_{16} H_{15} Cl_2 N_3 Pd Se**
Formula wt.	458.68	505.57
Crystal size [mm]	0.34×0.31×0.23	0.48×0.25×0.22
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)/c	P2(1)2(1)2(1)
Unit Cell dimension	a = 8.482(3) Å b= 11.062(4) Å c = 18.913(7) Å α = 90.00° β=92.849(6)° γ = 90.00°	a = 8.8269(19) Å b = 9.289(2) Å c = 20.716(4) Å α = 90.00° β = 90.00° γ = 90.00°
Volume [Å^3]	1772.4(11)	1698.6(6)
Z	4	4
ρ_{calcd} [g/cm^3]	1.719	1.977
μ(Mo$K\alpha$) [mm^{-1}]	1.467	3.551
F(000)	912.0	984.0
θ range [°]	2.13–25.00	1.97 –24.99
Index ranges	$-10 \le h \le 10$ $-13 \le k \le 13$ $-22 \le l \le 22$	$-10 \le h \le 10$ $-11 \le k \le 11$ $-24 \le l \le 24$
Reflections collected	16478	16232
Independent reflections($R_{int.}$)	3116 (0.0363)	2998 (0.0477)
Completeness to max. θ [%]	100	100
Max./min. Transmission	0.610 / 0.717	0.072 / 0.036
Data/restraints/ parameters	3116 / 0 / 208	2998 / 0 / 208
Goodness-of-fit on F^2	1.278	1.147
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0472, wR_2 = 0.0943	R_1 = 0.0355, wR_2 = 0.0782
R indices (all data)	R_1 = 0.0507, wR_2 = 0.0959	R_1 = 0.0389, wR_2 =0.0794
Largest diff. peak/hole[e.Å^{-3}]	0.874 / −0.852	0.979 / −0.483

Table S2 Selected bond lengths [Å] and bond angles [°]

Compounds	Bond length [Å]		Bond angle [°]	
1	N(3)—Pd(1)	2.005(4)	N(3)—Pd(1)—Cl(1)	174.04(11)
	Pd(1)—S(1)	2.2727(14)	N(3)—Pd(1)—Cl(2)	92.72(11)
	Cl(1)—Pd(1)	2.2968(14)	S(1)—Pd(1)—Cl(1)	89.01(5)
	Cl(2)—Pd(1)	2.3003(13)	S(1)—Pd(1)—Cl(2)	177.91(5)
	N(2)—N(3)	1.312(5)	Cl(1)—Pd(1)—Cl(2)	93.09(5)
	C(10)—S(1)	1.826(5)	N(3)—Pd(1)—S(1)	85.18(11)
	C(11)—S(1)	1.786(5)	C(11)—S(1)—C(10)	102.3(3)
	C(9)—N(3)	1.368(6)	C(11)—S(1)—Pd(1)	107.07(17)
			C(10)—S(1)—Pd(1)	99.45(17)
2	Pd(1)—N(3)	2.005(4)	N(3)—Pd(1)—Cl(1)	173.41(14)
	Pd(1)—Cl(1)	2.2799(15)	N(3)—Pd(1)—Cl(2)	95.32(14)
	Pd(1)—Cl(2)	2.3146(16)	Cl(1)—Pd(1)—Cl(2)	91.22(6)
	Pd(1)—Se(1)	2.3693(8)	N(3)—Pd(1)—Se(1)	85.37(13)
	Se(1)—C(10)	1.985(6)	Cl(1)—Pd(1)—Se(1)	88.11(4)
	C(11)—Se(1)	1.942(6)	Cl(2)— Pd(1)—Se(1)	178.20(5)
	N(2)—N(3)	1.326(6)	C(11)—Se(1)—C(10)	98.9(3)
	N(3)—C(9)	1.373(7)	C(11)—Se(1)—Pd(1)	104.41(17)
			C(10)—Se(1)—Pd(1)	96.77(19)

Table S3 Non-covalent interactions C–H···Cl distances [Å] of **1** / **2**

1		**2**	
C(10)–H(10A)···Cl(1)	2.815(2)	C(18)–H(18)···Cl(2)	3.026(2)
C(10)–H(10B)···Cl(1)	3.033(2)	C(16)–H(16)···Cl(2)	3.122(2)
C(12)–H(12)···Cl(2)	2.822(2)	C(10) –H(10A)···Cl(1)	3.328(2)
C(8)–H(8)···Cl(1)	2.883(5)	C(8)–H(8)···Cl(2)	3.051(2)
C(8)–H(8)···Cl(2)	2.635(3)	C(8)–H(8)···Cl(1)	2.790(2)
C(7)–H(7A)···Cl(1)	2.789(2)	C(7)–H(7A)···Cl(2)	2.959(2)
C(7)–H(7B)···Cl(2)	2.932(2)	C(6)–H(6)···Cl(1)	3.150(2)
		C(4)–H(4)···Cl(1)	3.059(2)

Table S4 Selected bond lengths (Å) and angles (°) for **1** / **2** and the values calculated from DFT studies

1			**2**		
Bond length / angle			Bond length / angle		
N(3)—Pd(1)	2.005(4)	2.100	N(3)—Pd(1)	2.005(4)	2.099
S(1)—Pd(1)	2.2727(14)	2.513	Se(1)—Pd(1)	2.3693(8)	2.566
Cl(1) —Pd(1)	2.2968(14)	2.371	Cl(1) —Pd(1)	2.2799(15)	2.328
Cl(2)—Pd(1)	2.3003(13)	2.314	Cl(2)—Pd(1)	2.3146(16)	2.325
S(1)—C(10)	1.826(5)	1.908	Se(1)—C(10)	1.985(6)	2.040
S(1)—C(11)	1.786(5)	1.855	Se(1)—C(11)	1.942(6)	1.971
S(1)—Pd—Cl(1)	177.91(5)	175.35	Se(1)—Pd—Cl(1)	178.20(5)	175.44
N3—Pd—Cl(2)	174.04(11)	173.89	N3—Pd—Cl(2)	173.41(14)	174.76
N3—Pd—Cl(1)	92.72(11)	93.39	N3—Pd—Cl(1)	95.32(14)	93.39
S(1)—Pd— N(3)	85.18(11)	82.59	Se(1)—Pd— N(3)	85.37(13)	82.90
Cl(2)—Pd—Cl(1)	93.09(5)	92.58	Cl(2)—Pd—Cl(1)	91.22(6)	92.30
S(1)—Pd—Cl(2)	89.01(5)	91.50	Se(1)—Pd—Cl(2)	88.11(4)	92.02

Table S5 HOMO-LUMO energy gap of the **1 / 2** Mulliken partial atomic charge

	Mulliken partial atomic charge						
Complex	Energygap (kcal/mol)	Metal	Calcogen	N of triazole			Cl
				N3	N2	N1	
1	78.5641	-0.038	0.465	-0.326	0.007	-0.196	-0.262
2	78.8025	-0.060	0.520	-0.330	0.015	-0.196	-0.279

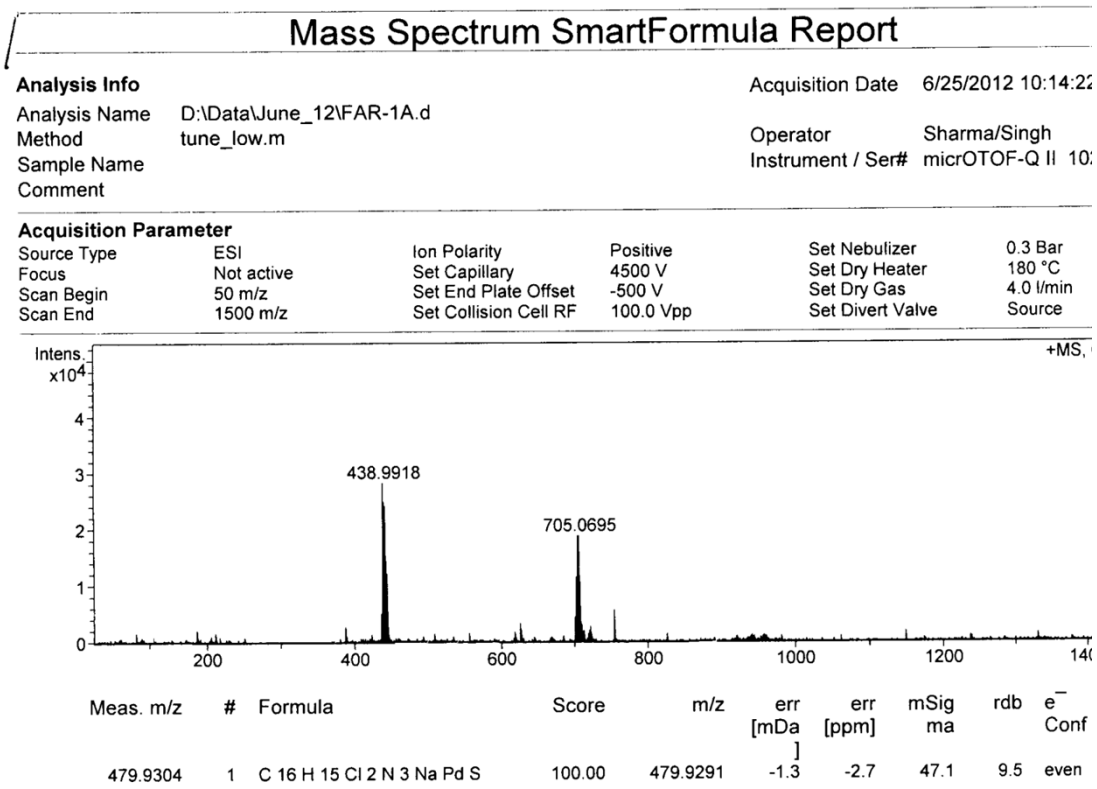


Fig. S1 Mass spectrum of **1**

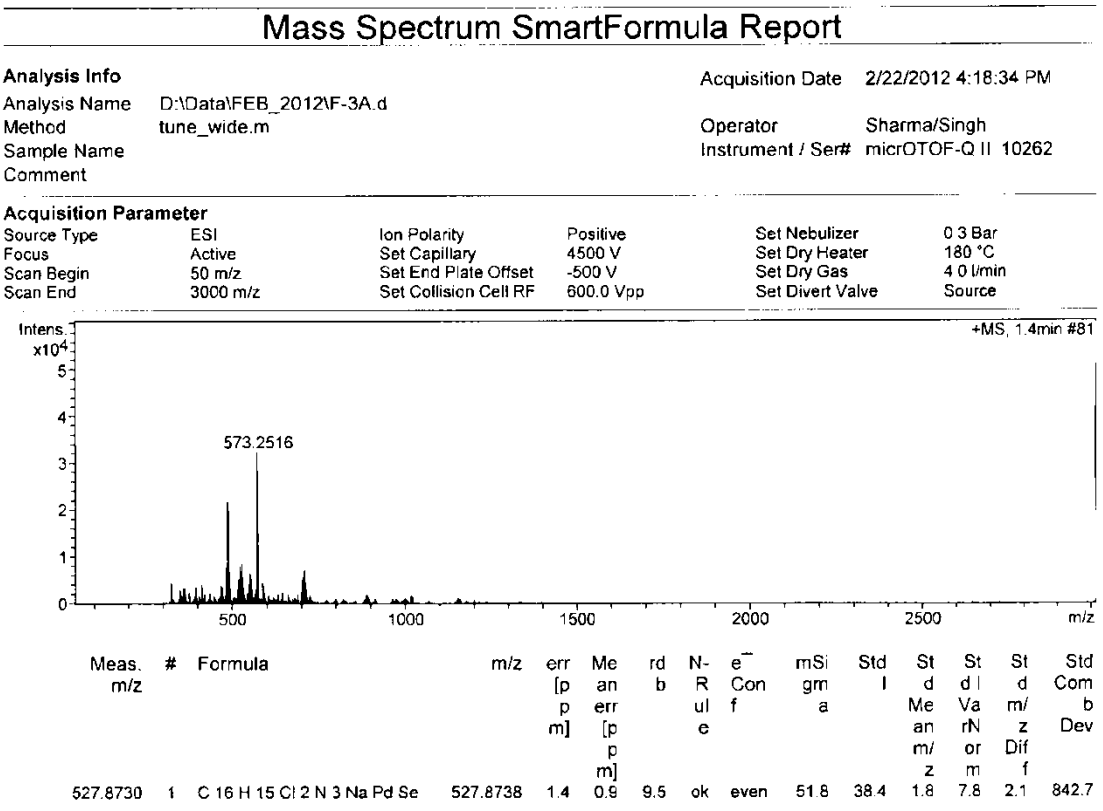


Fig. S2 Mass spectrum of **2**

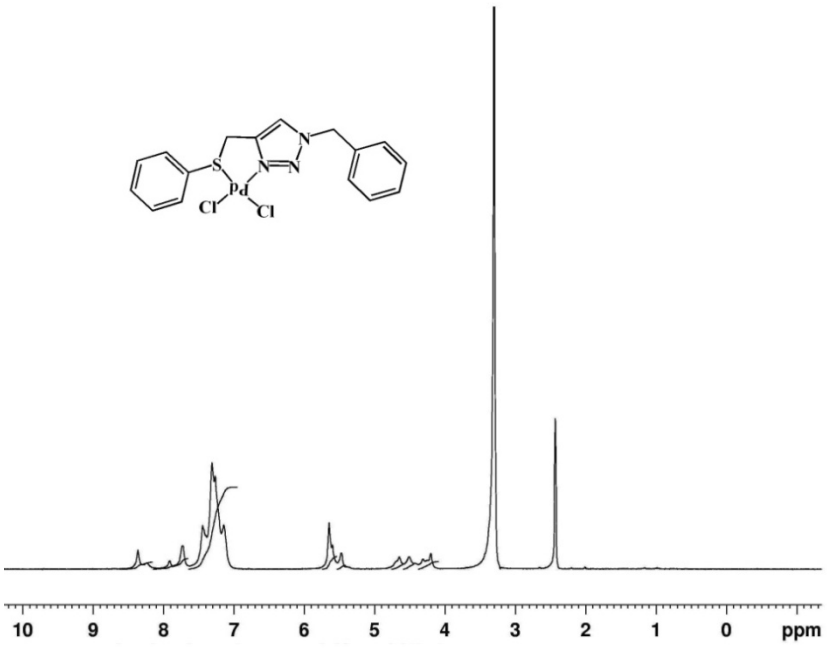


Fig. S3 ^{1}H NMR spectrum of **1**

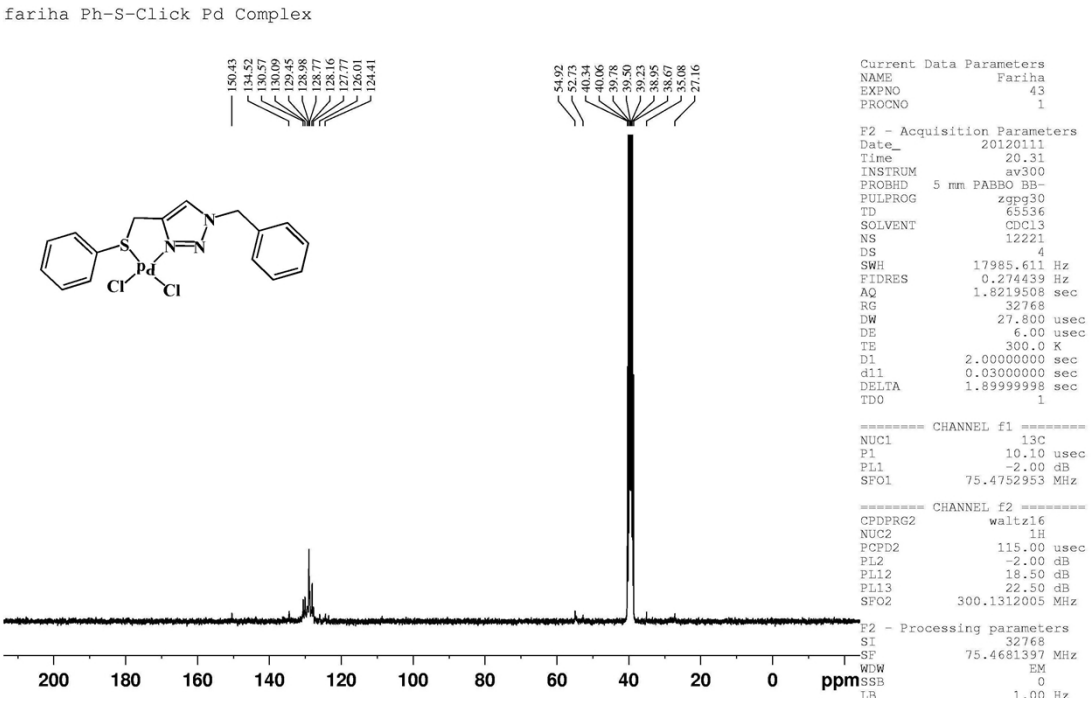
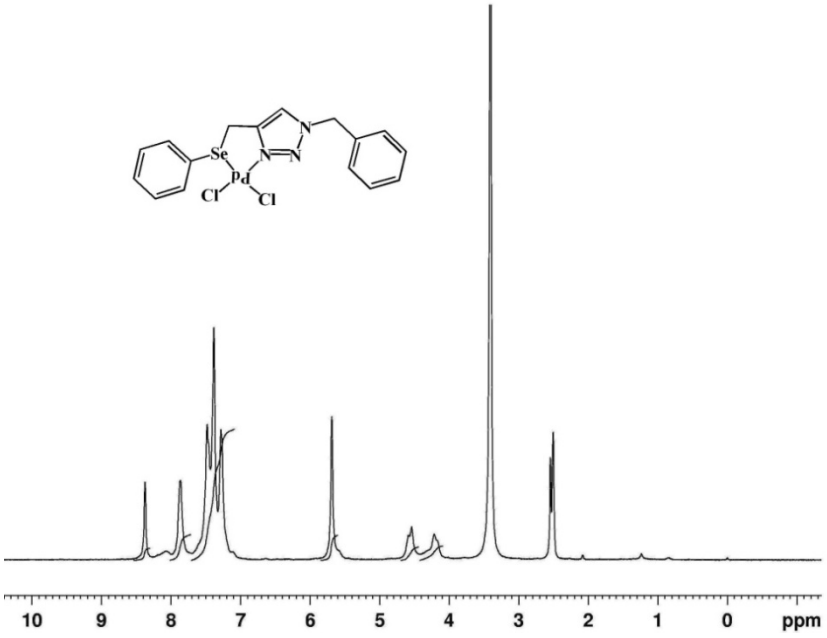


Fig. S4 ^{13}C{^{1}H} NMR spectrum of **1**

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RG                       181
DW                    81.000 usec
DE                     6.00 usec
TE                    300.0 K
D1                 1.00000000 sec
TD0                        1

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PL1                    -2.00 dB
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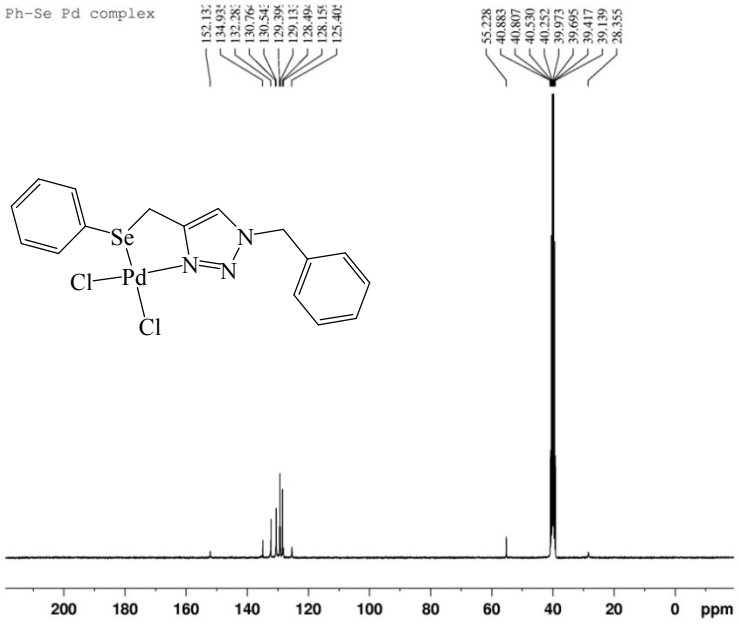
Fig. S5 ^{1}H NMR spectrum of **2**

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TE                    300.0 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1

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P1                     10.10 usec
PL1                    -2.00 dB
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 115.00 usec
PL2                    -2.00 dB
PL12                   18.50 dB
PL13                   22.50 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
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SF                75.4677490 MHz
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GB                            0
PC                         1.40
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Fig. S6 ^{13}C{^{1}H} NMR spectrum of **2**

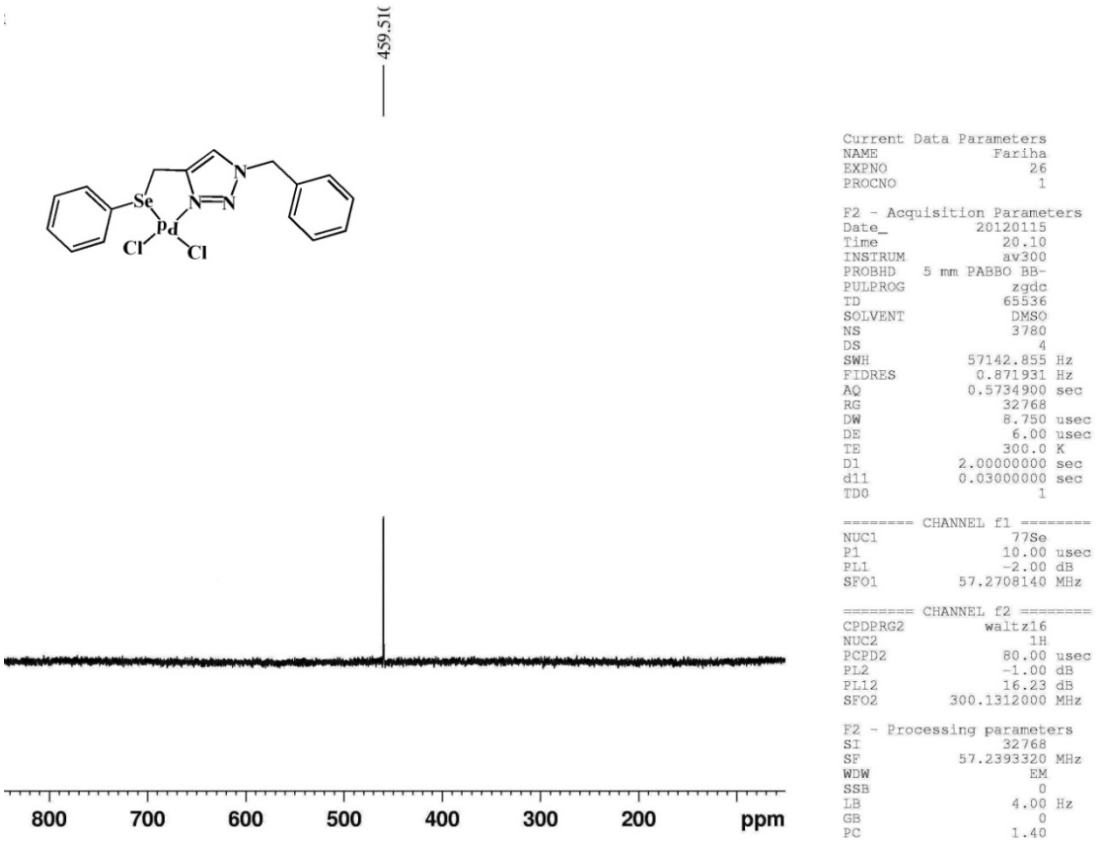


Fig. S7 $^{77}Se\{^{1}H\}$ NMR spectrum of **2**

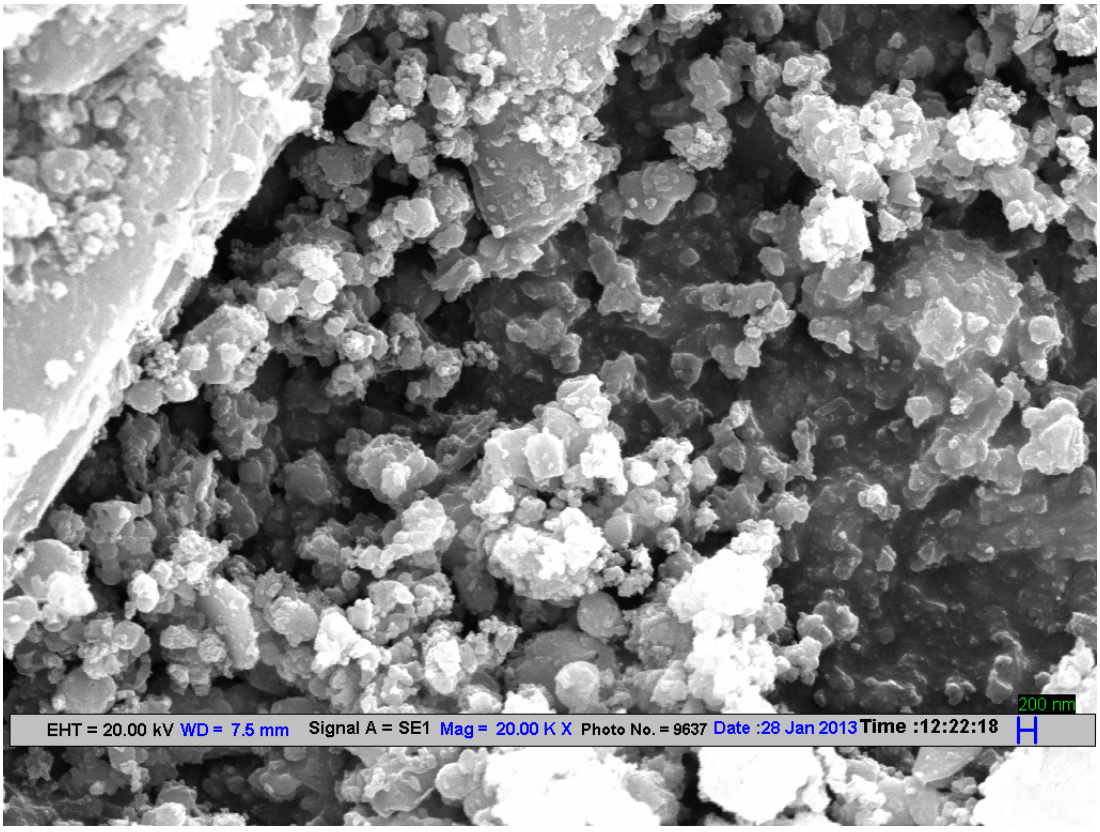


Fig. S8 SEM image of NPs obtained from **1** during Suzuki-Miyaura reaction

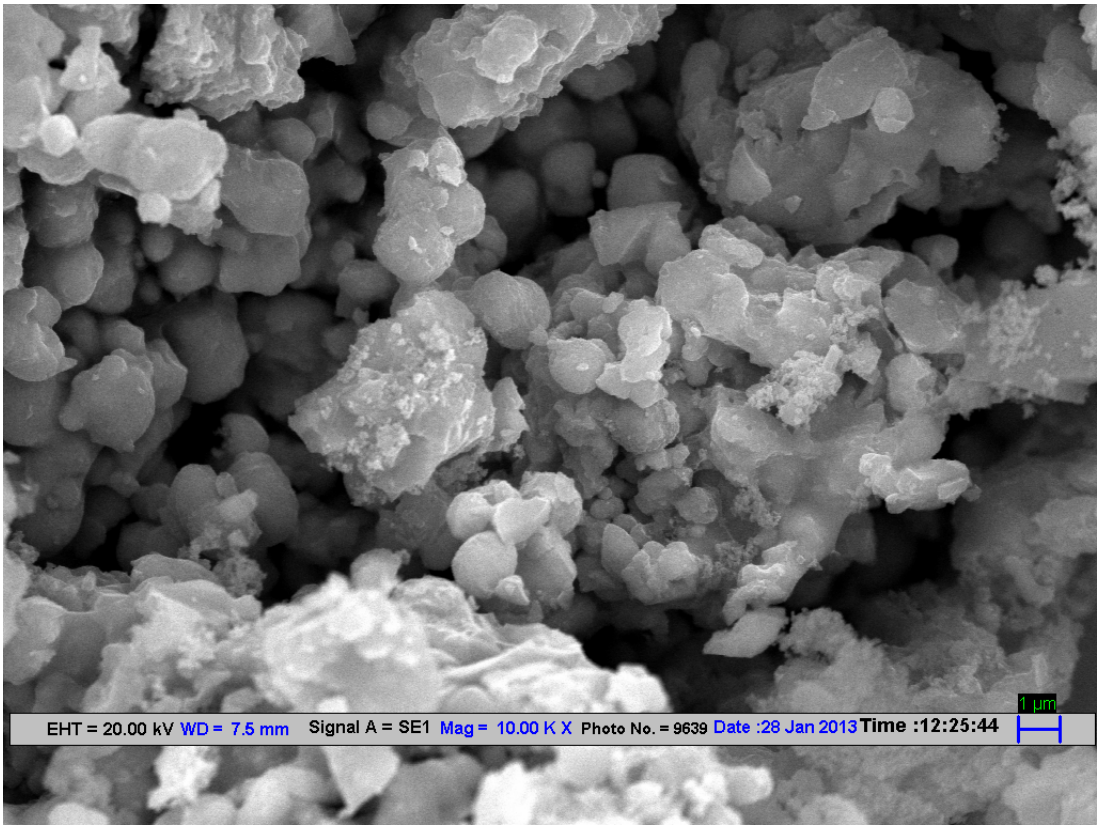


Fig. S9 SEM image of NPs obtained from **2** during Suzuki-Miyaura reaction

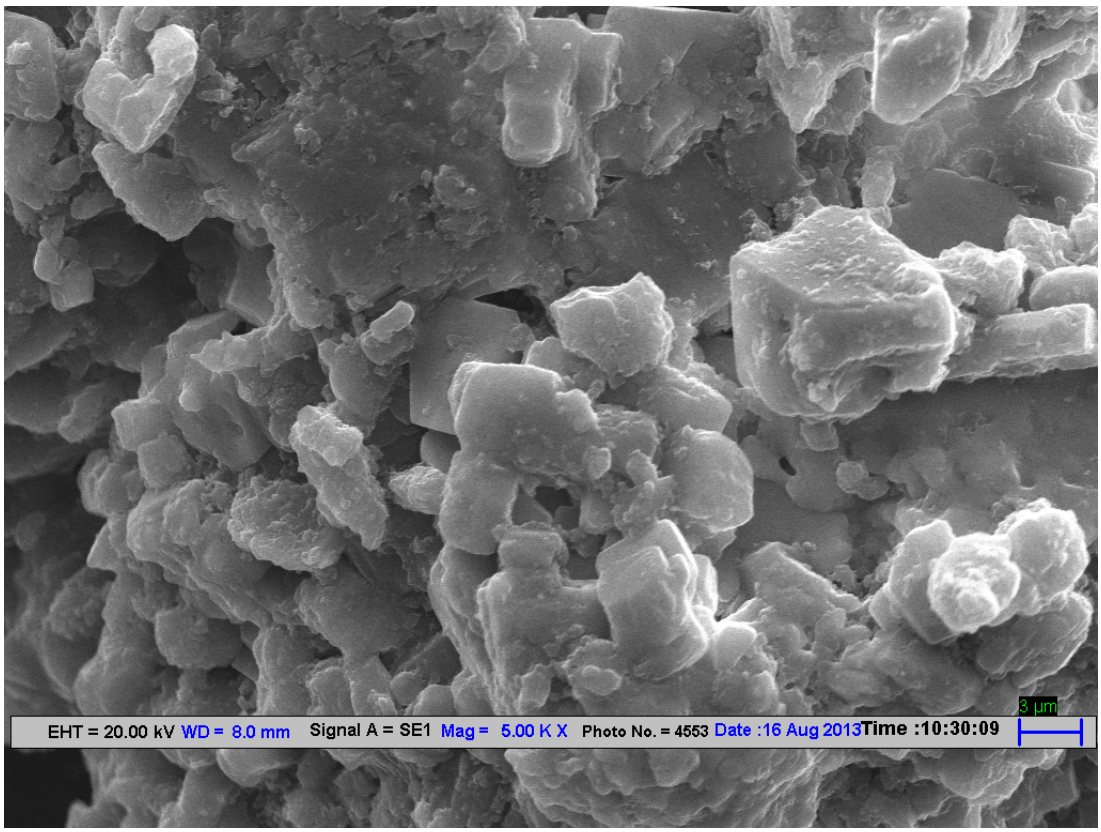


Fig. S10 SEM image of NPs obtained from **1** during Heck reaction

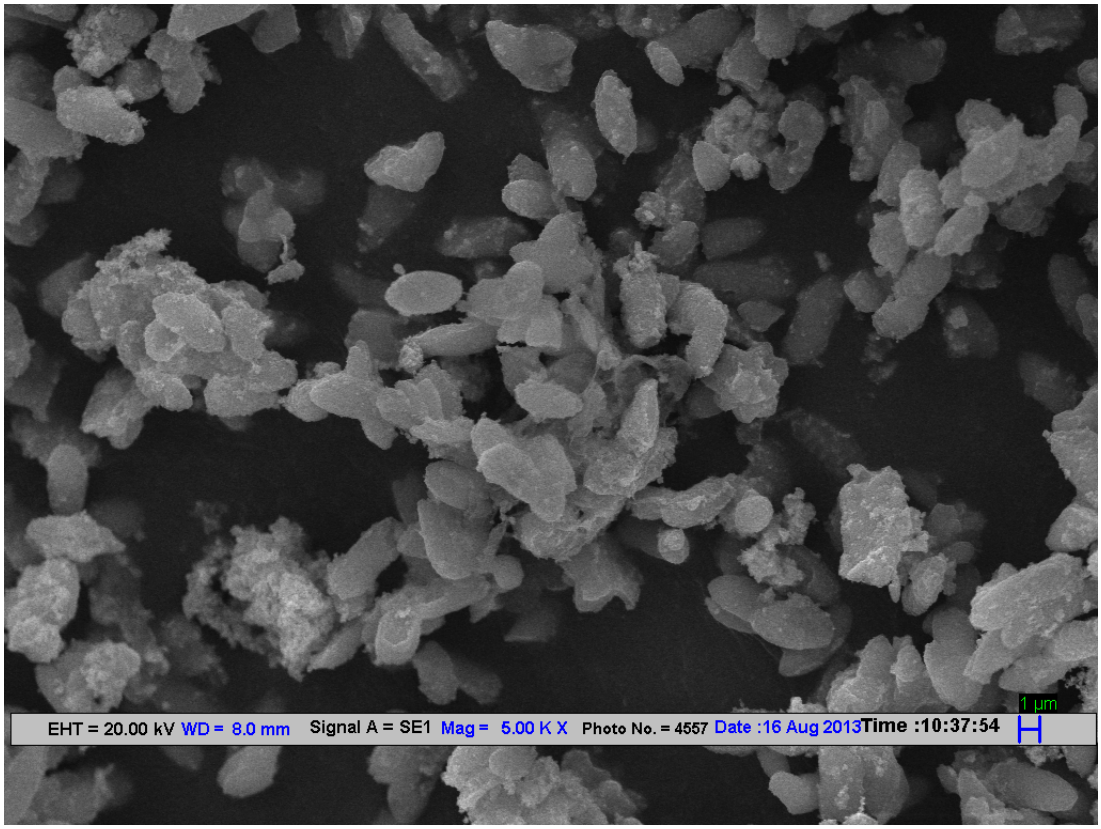
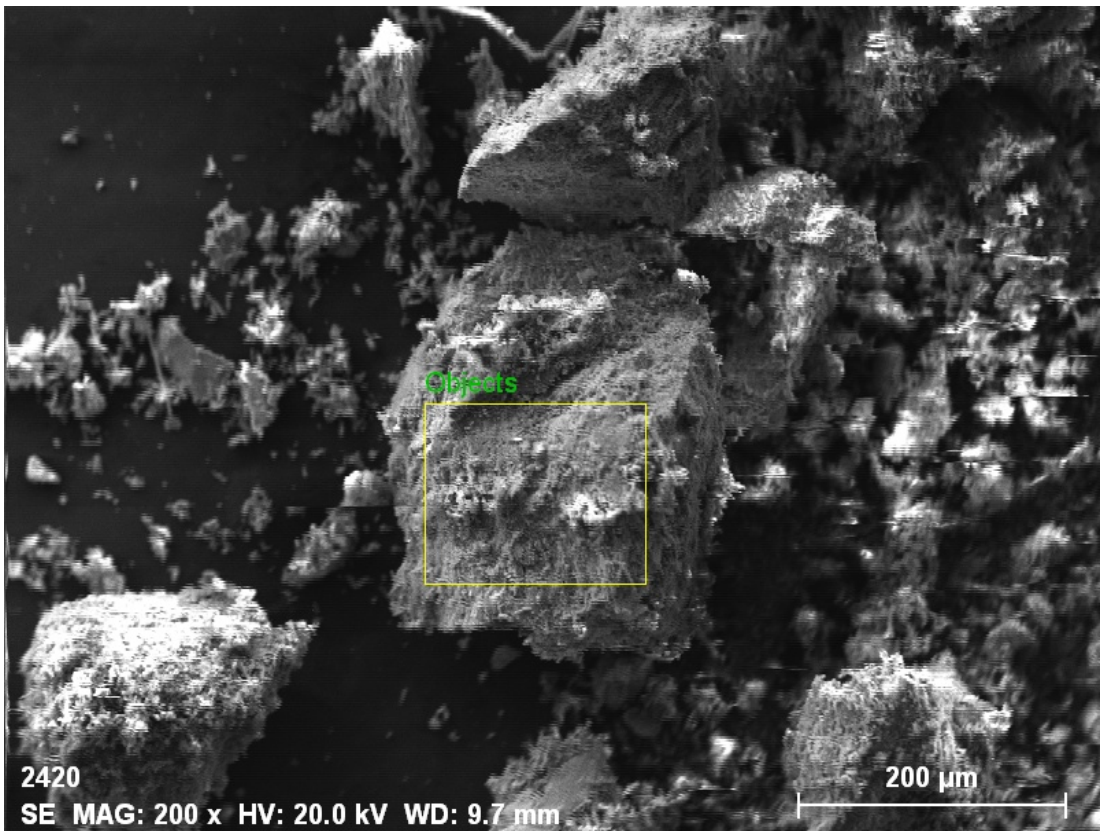


Fig. S11 SEM image of NPs obtained from **2** during Heck reaction



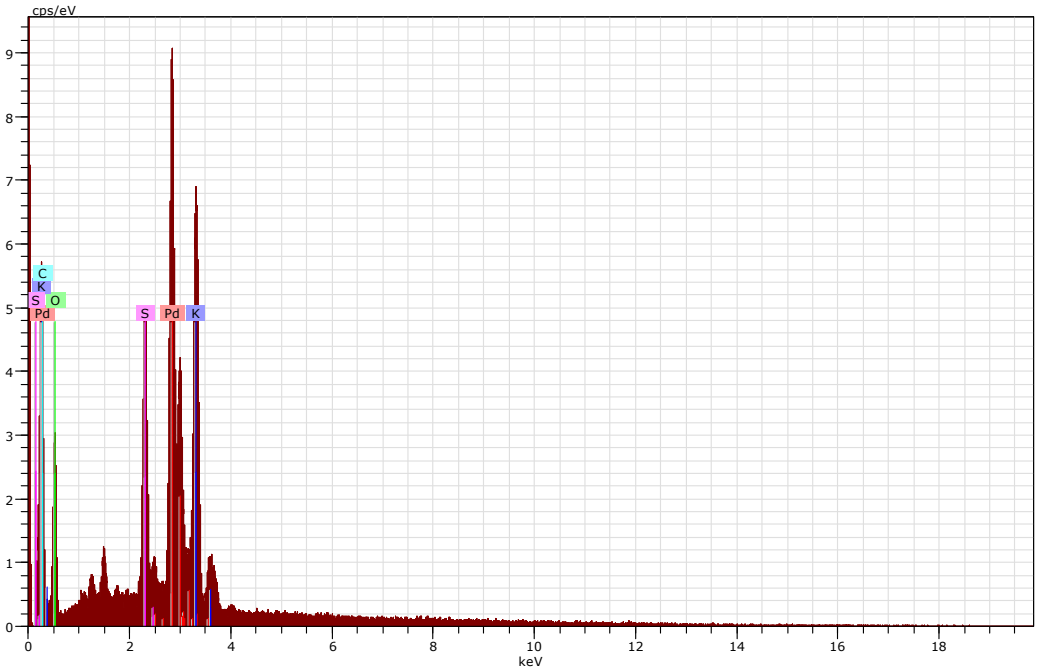
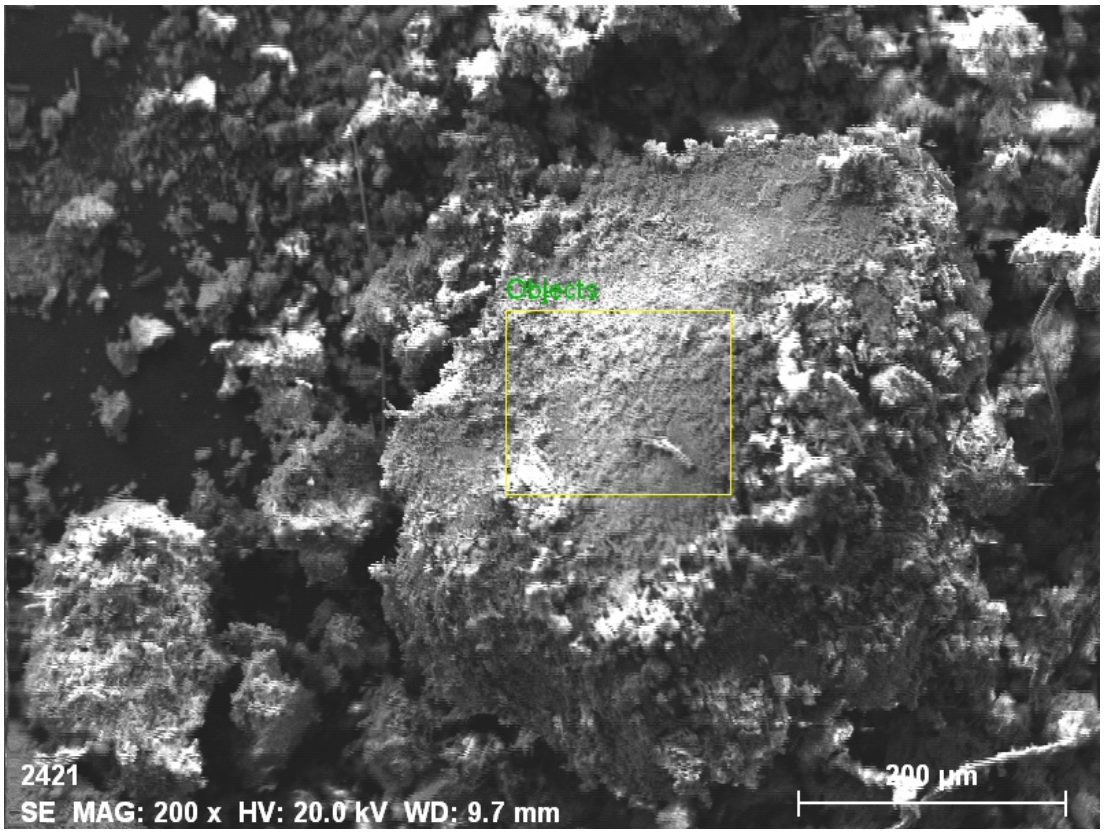


Fig. S12 SEM−EDX image NPs obtained from **1** during Suzuki-Miyaura reaction



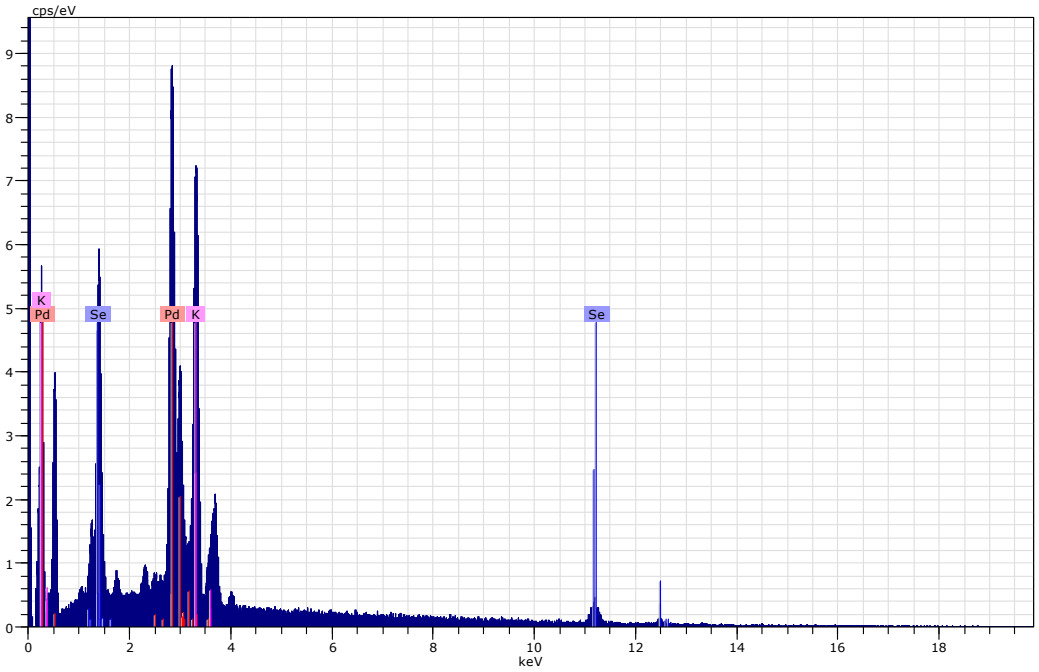
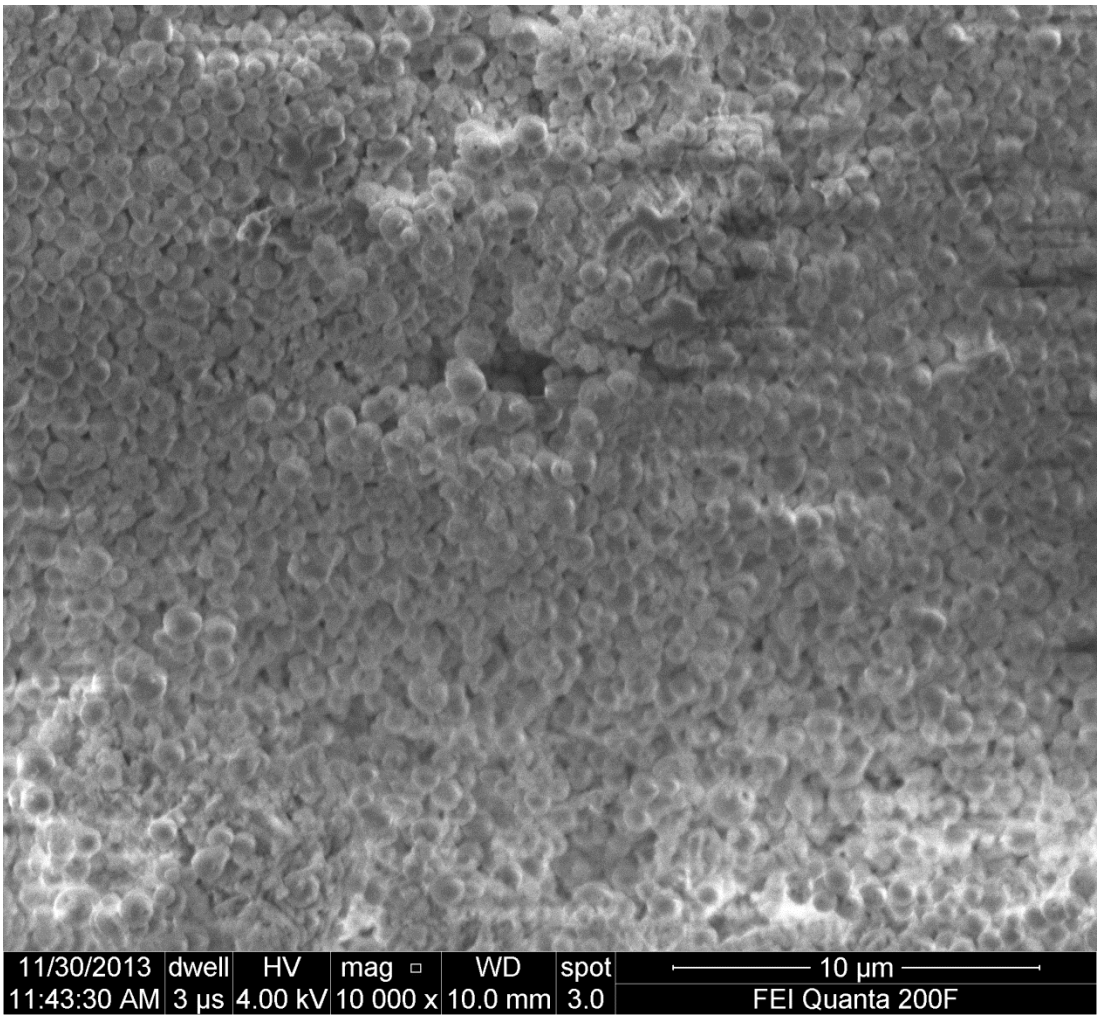


Fig. S13 SEM−EDX image NPs obtained from **2** during Suzuki-Miyaura reaction



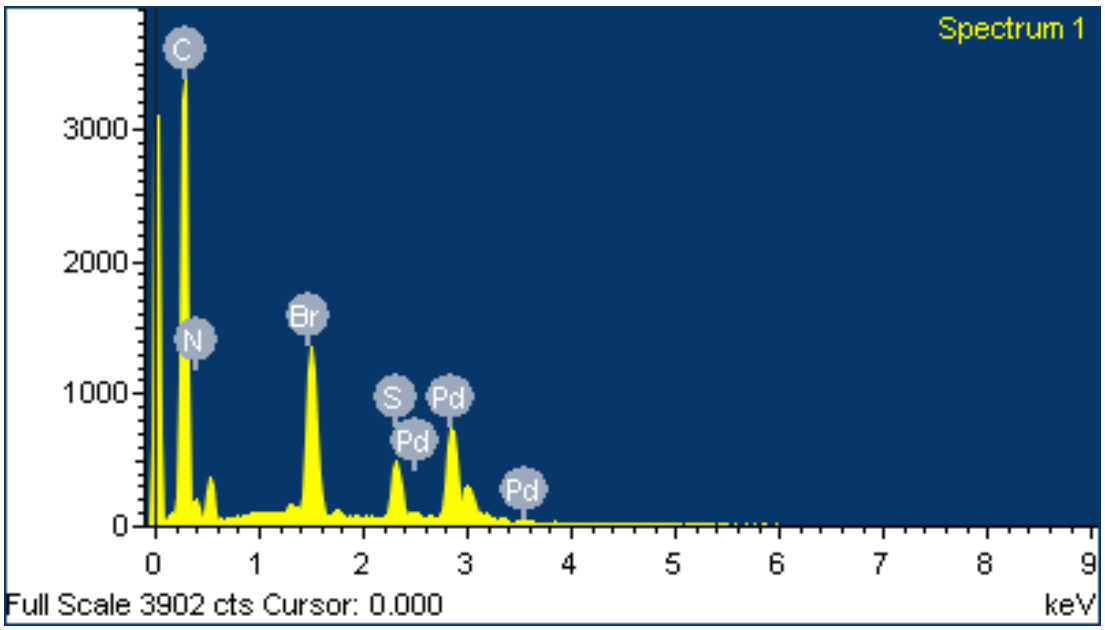
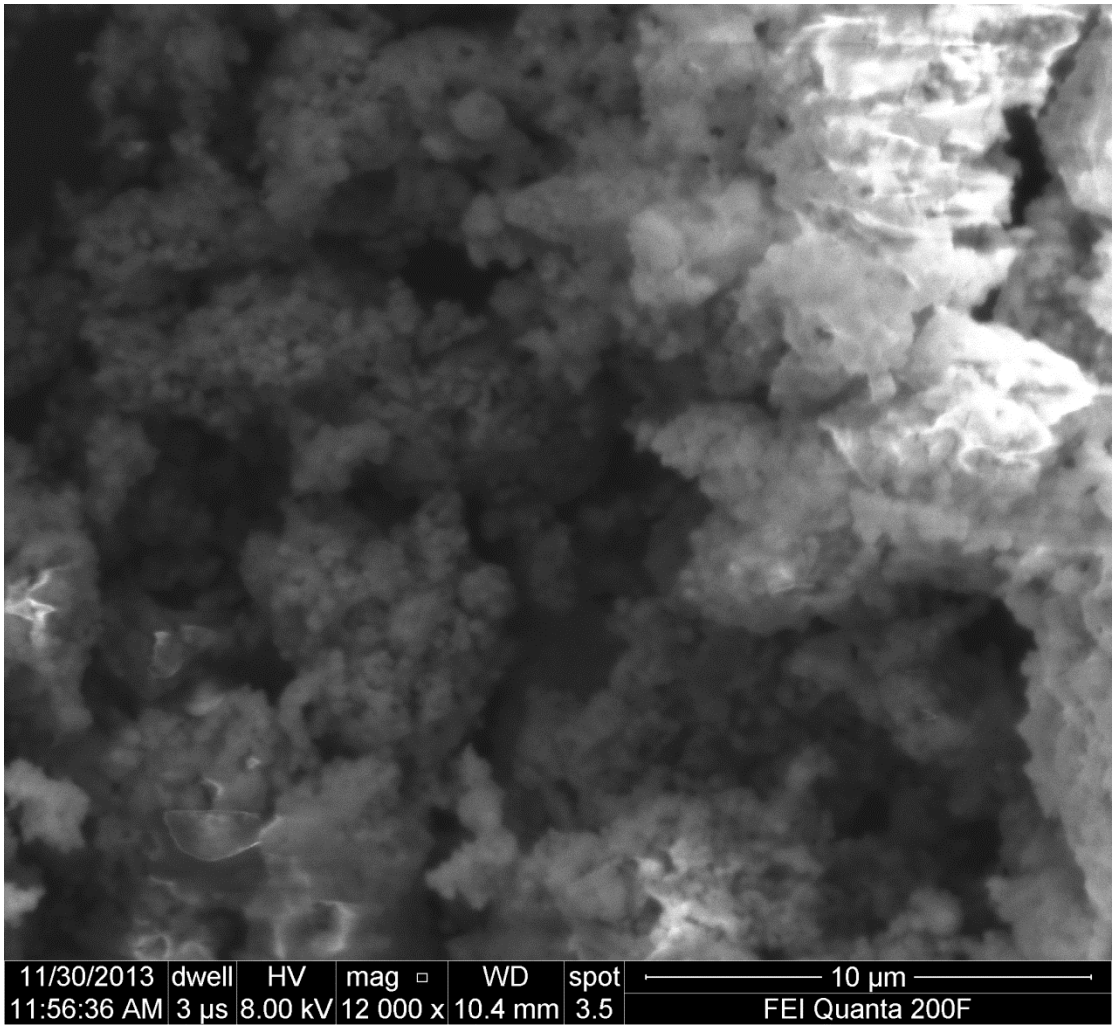


Fig. S14 SEM−EDX image NPs obtained from **1** during Heck reaction



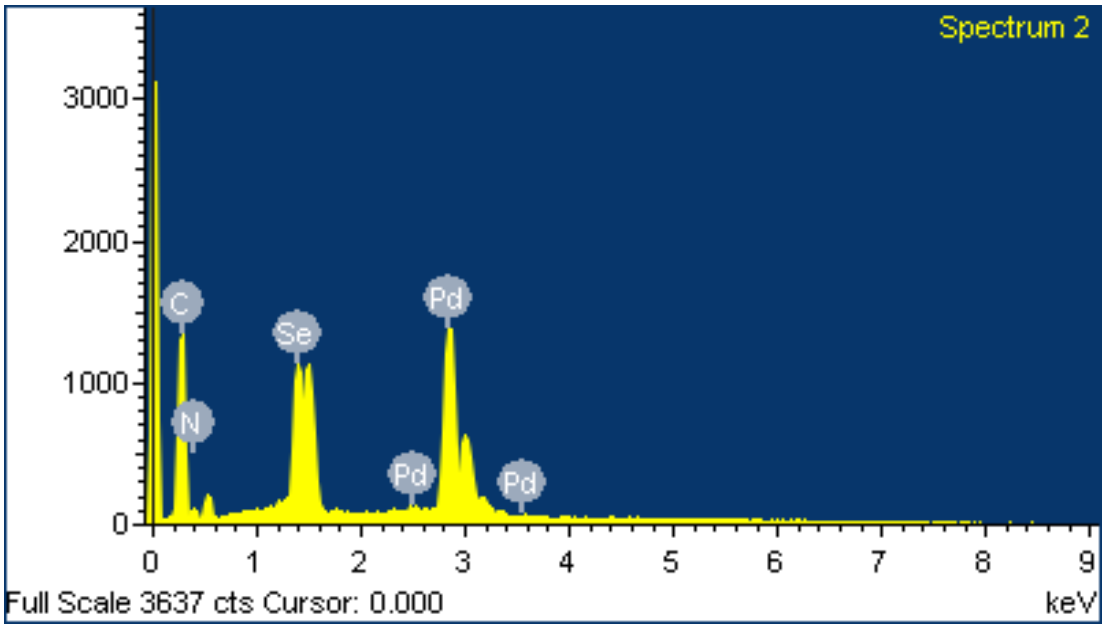


Fig. S15 SEM-EDX image NPs obtained from **2** during Heck reaction

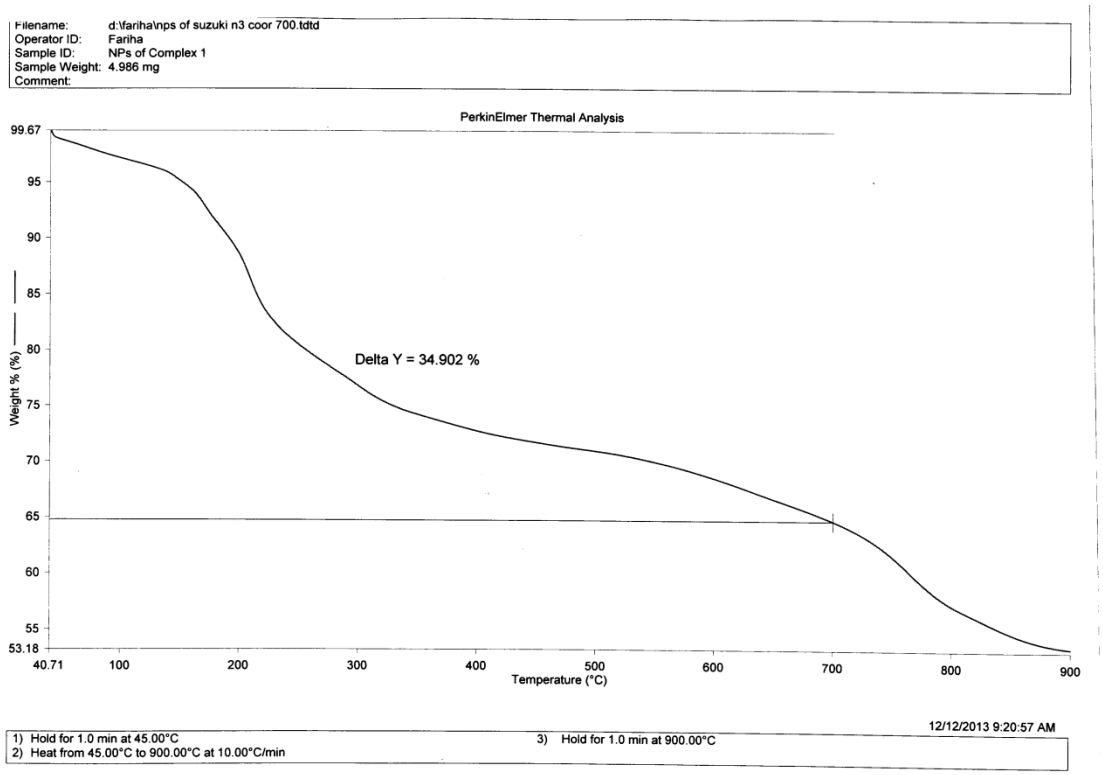


Fig. S16 TGA of NPs obtained from **1** during Suzuki-Miyaura reaction

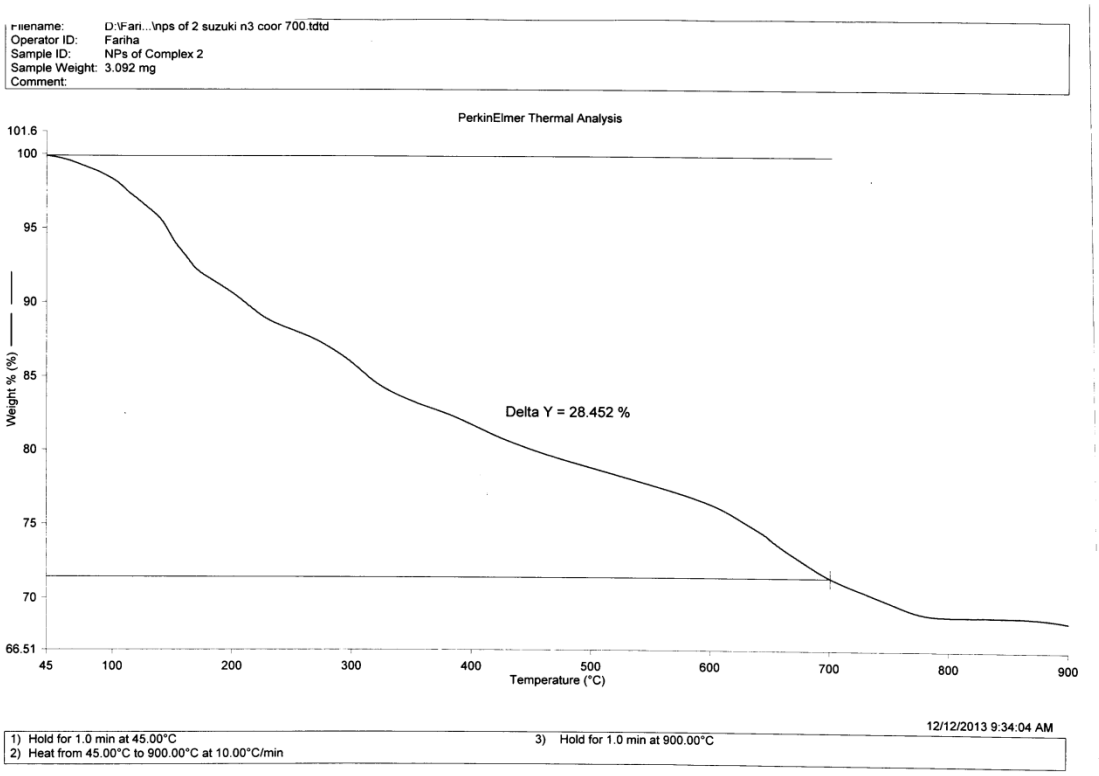


Fig. S17 TGA of NPs obtained from **2** during Suzuki-Miyaura reaction

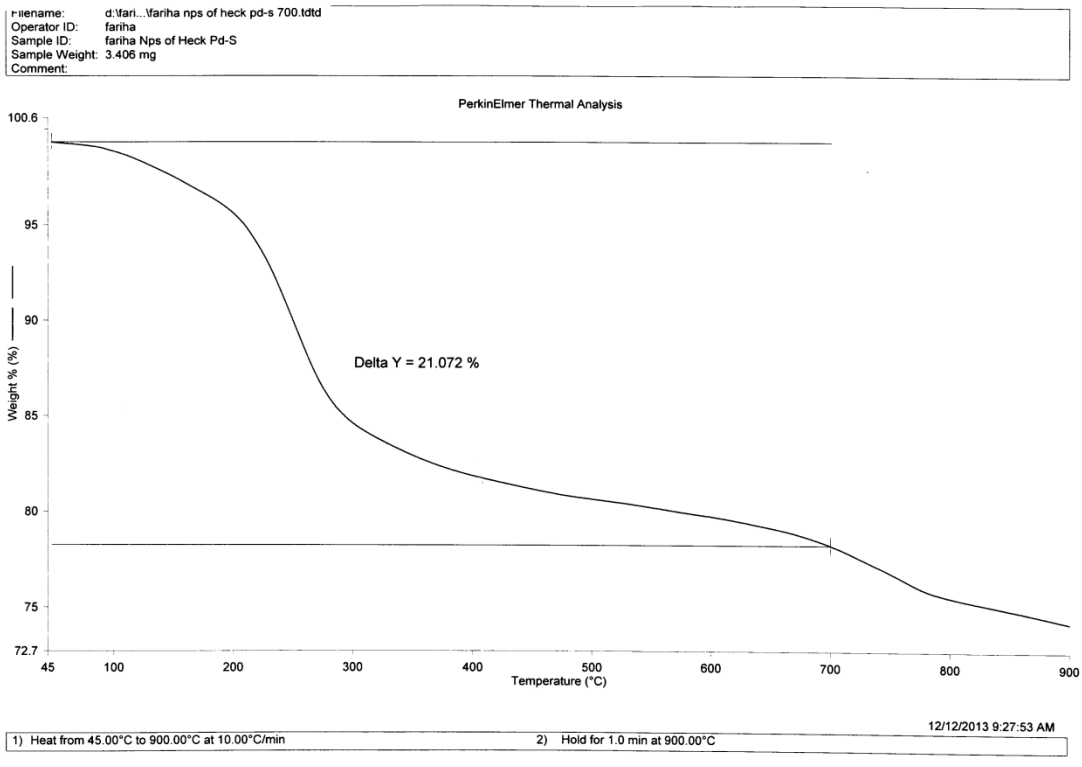


Fig. S18 TGA of NPs obtained from **1** during Heck reaction

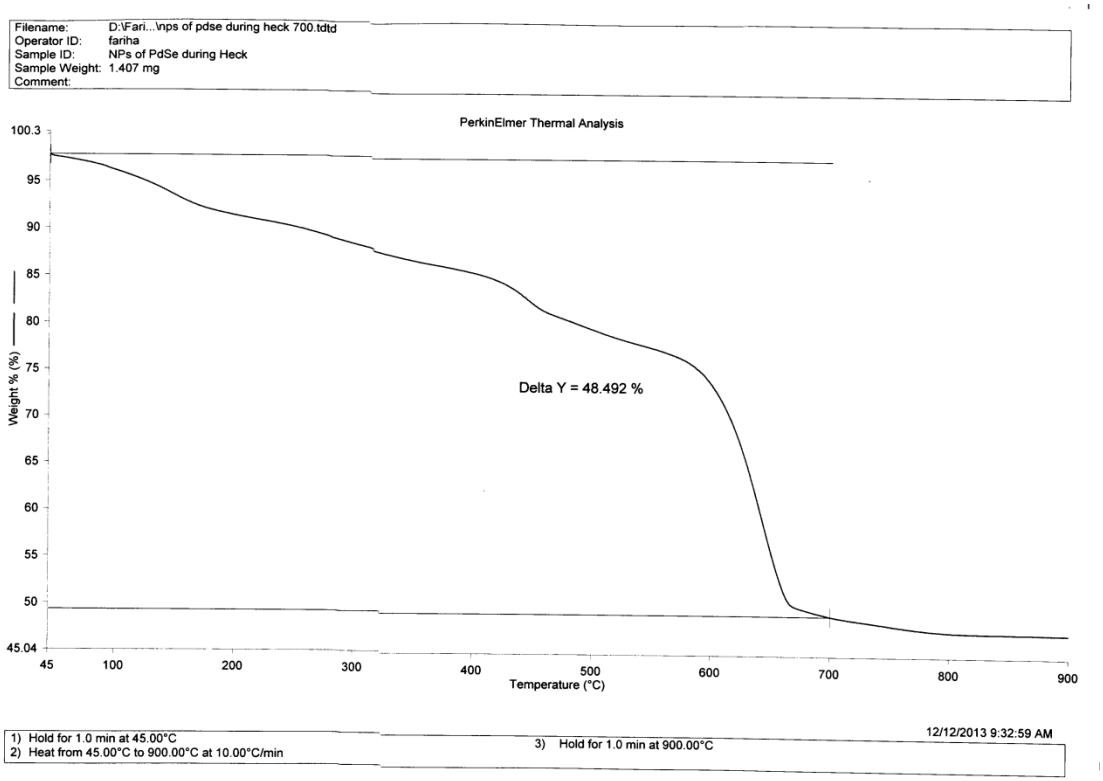


Fig. S19 TGA of NPs obtained from **2** during Heck reaction

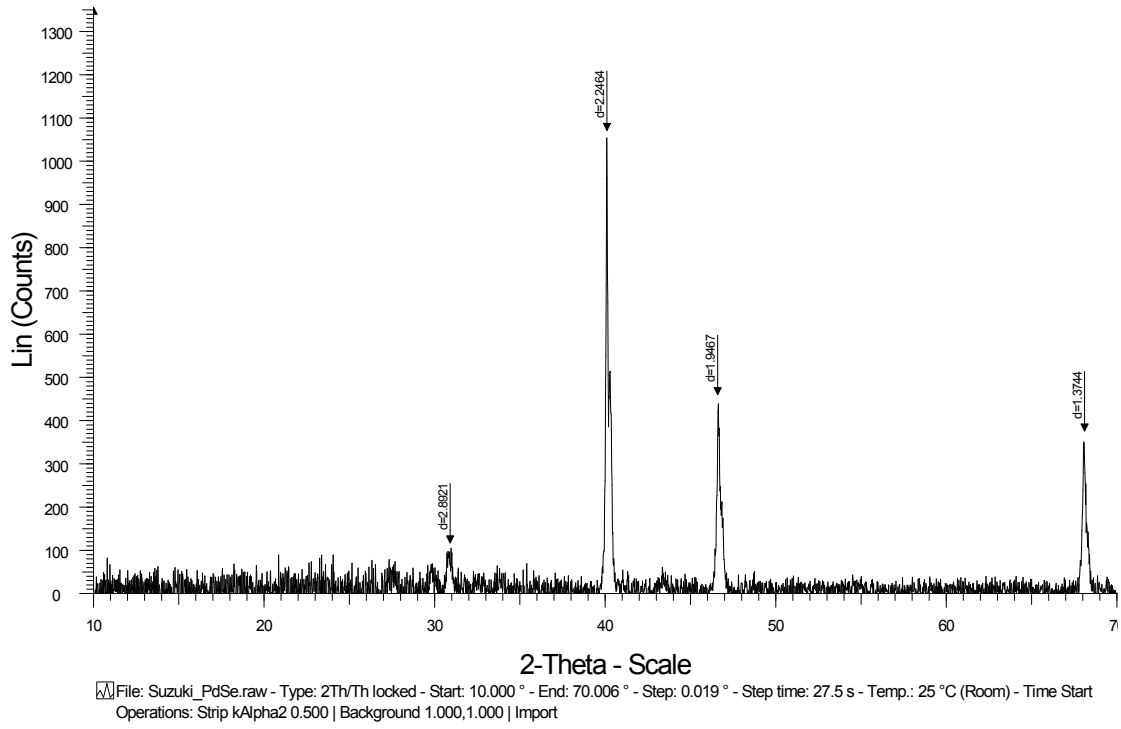


Fig. S20 PXRD of NPs after anneanling obtained from **1** during Suzuki-Miyaura reaction

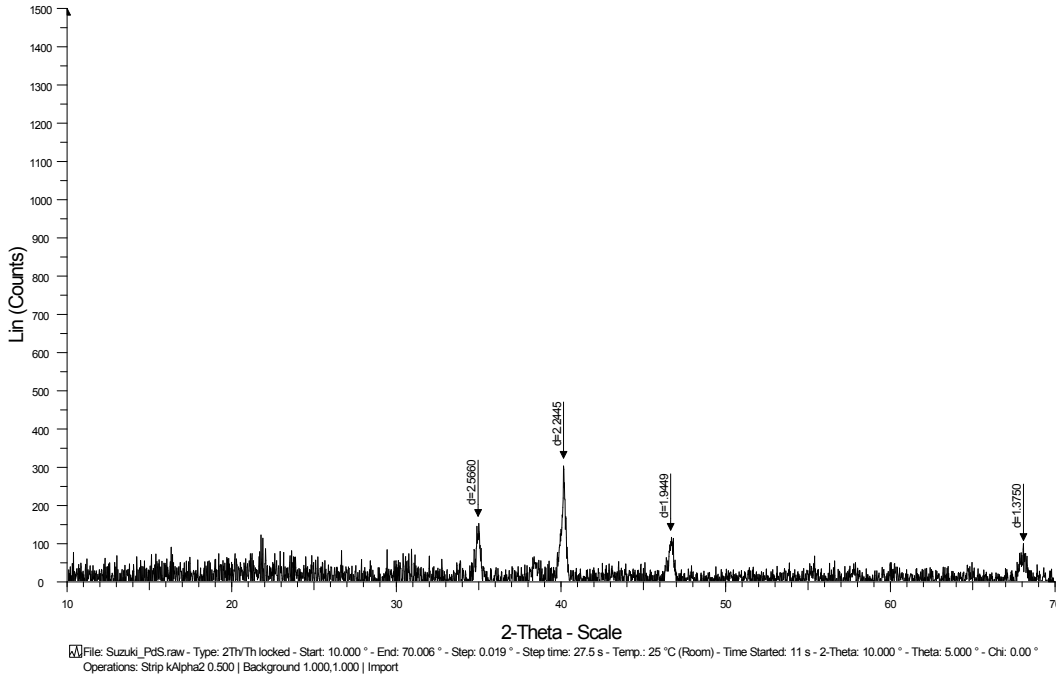


Fig.S21 PXRD of NPs after anneanling obtained from **2** during Suzuki-Miyaura reaction

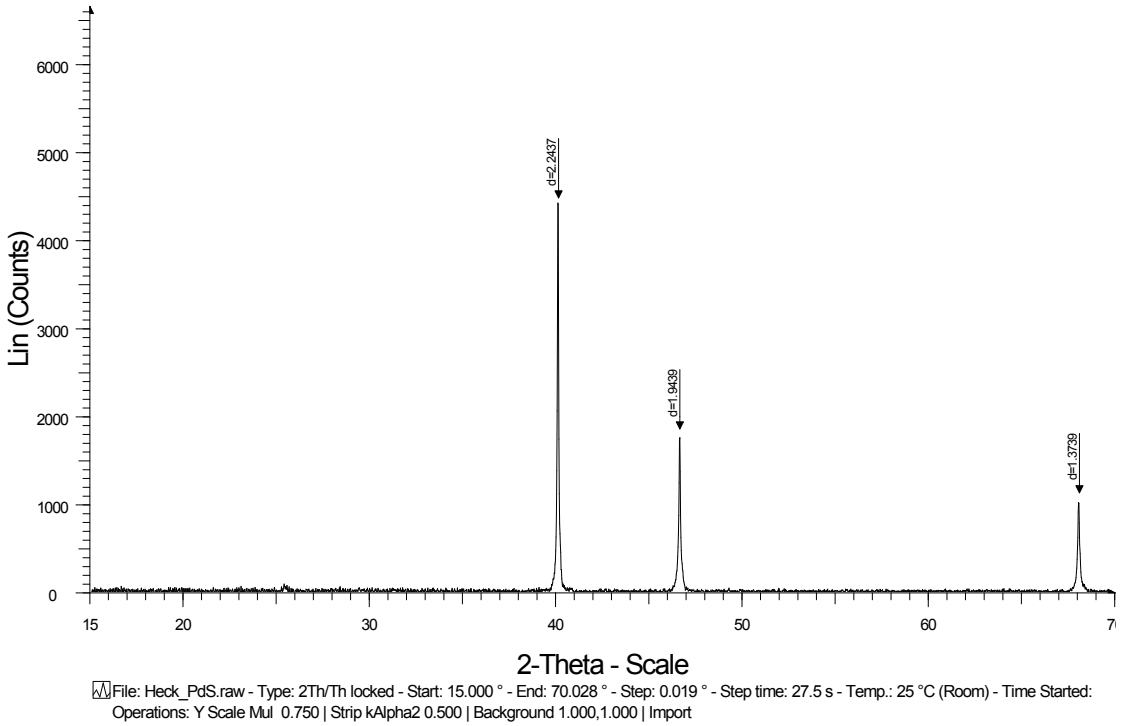


Fig. S22 PXRD of NPs after anneanling obtained from **1** during Heck reaction

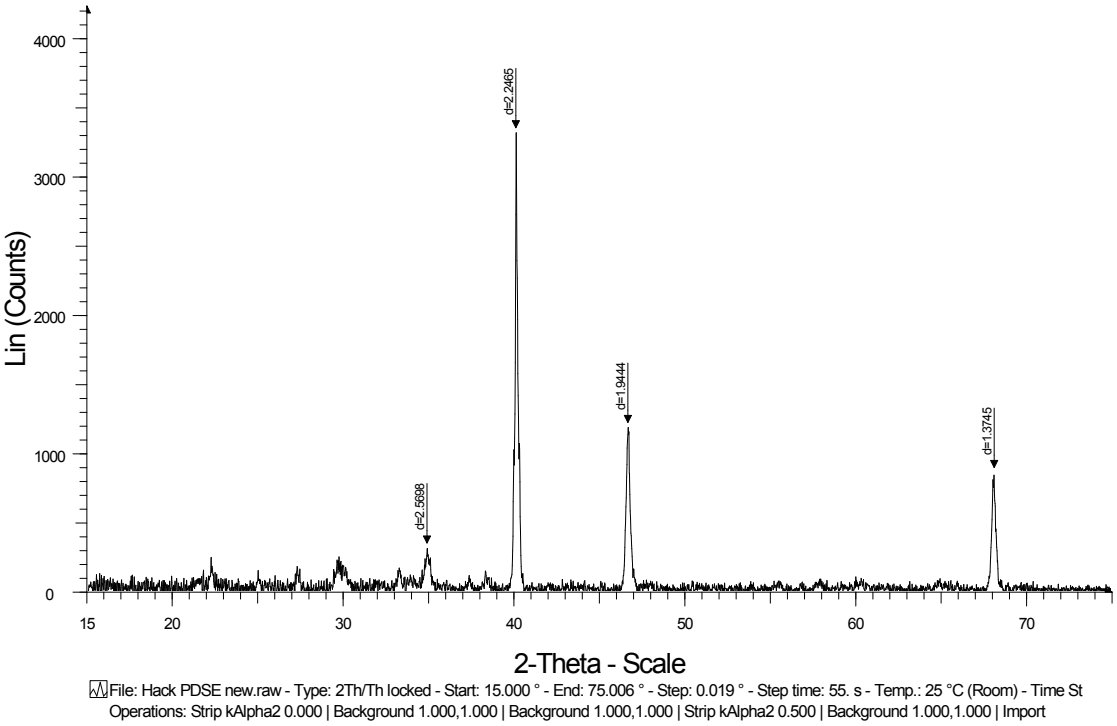


Fig. S23 PXRD of NPs after anneanling obtained from **2** during Heck reaction

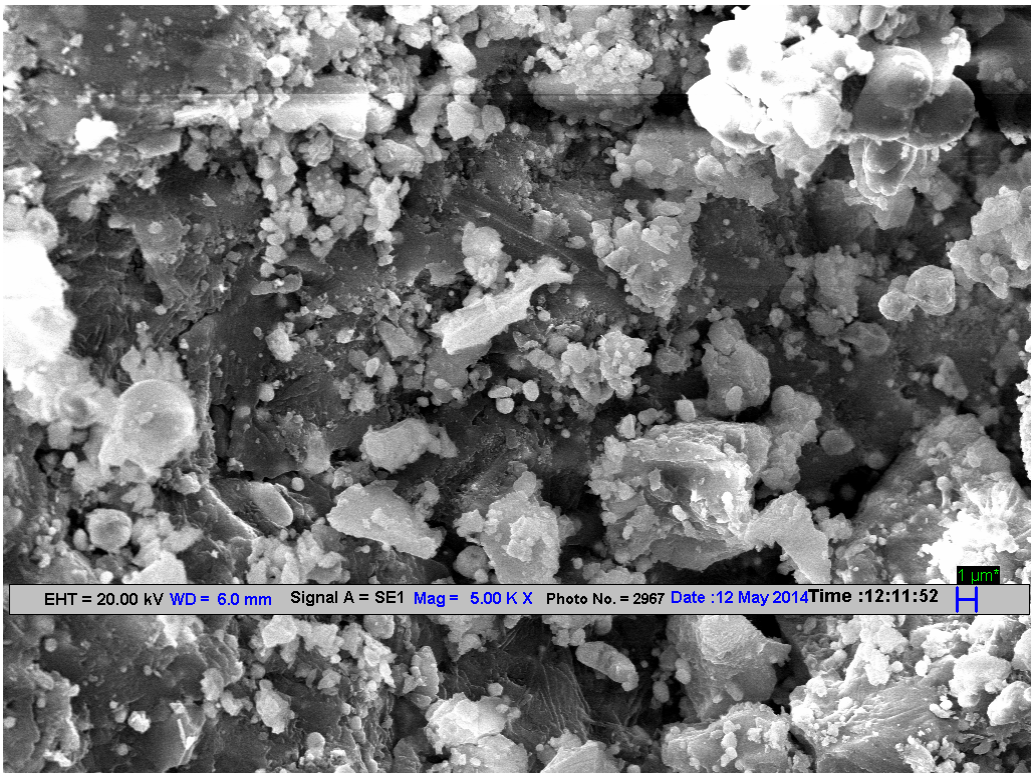


Fig. S24 SEM image of NPs after anneanling obtained from **1** during Suzuki-Miyaura reaction

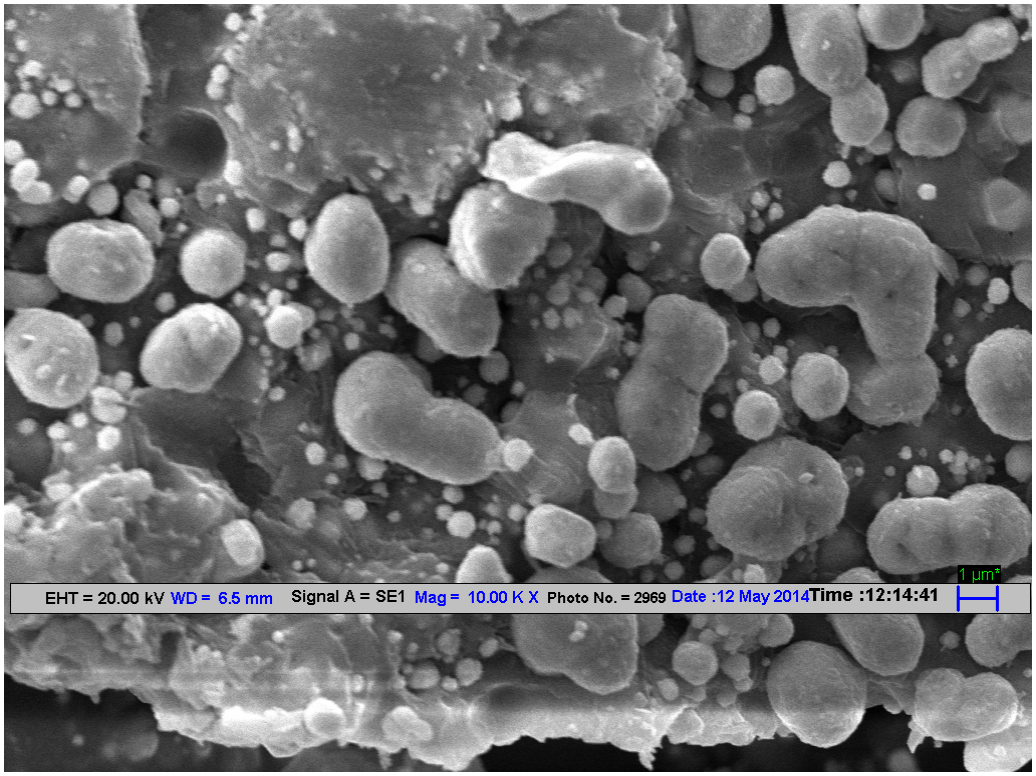


Fig. S25 SEM image of NPs after anneanling obtained from **2** during Suzuki-Miyaura reaction

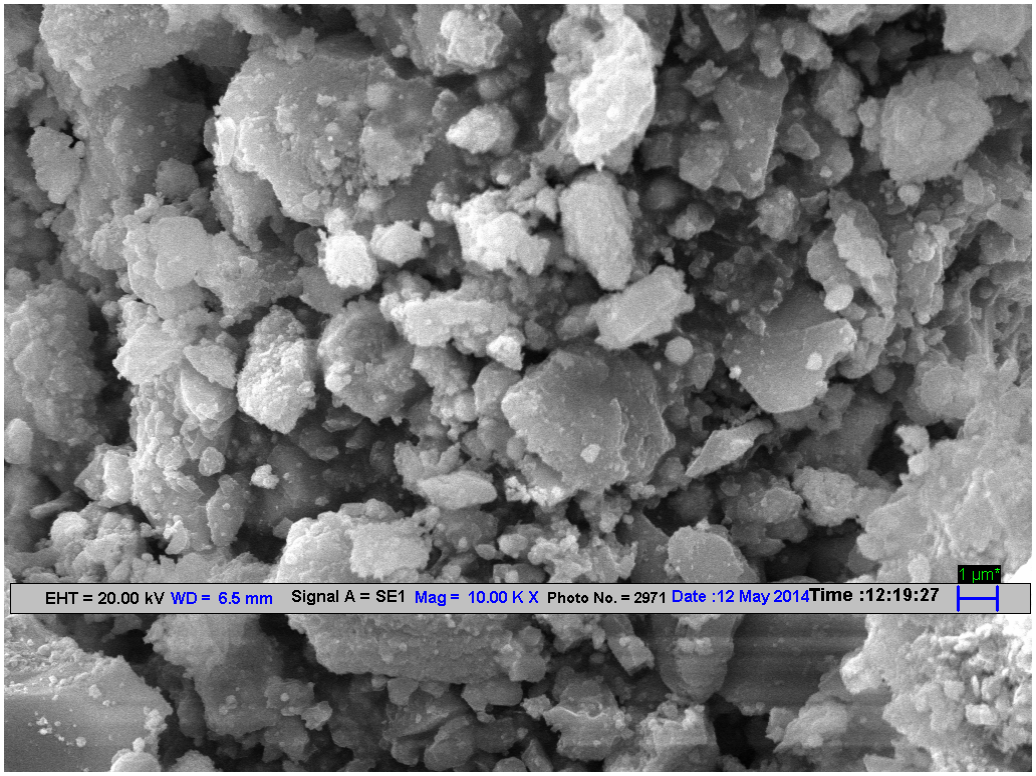


Fig. S26SEM image of NPs after anneanling obtained from **1** during Heck reaction

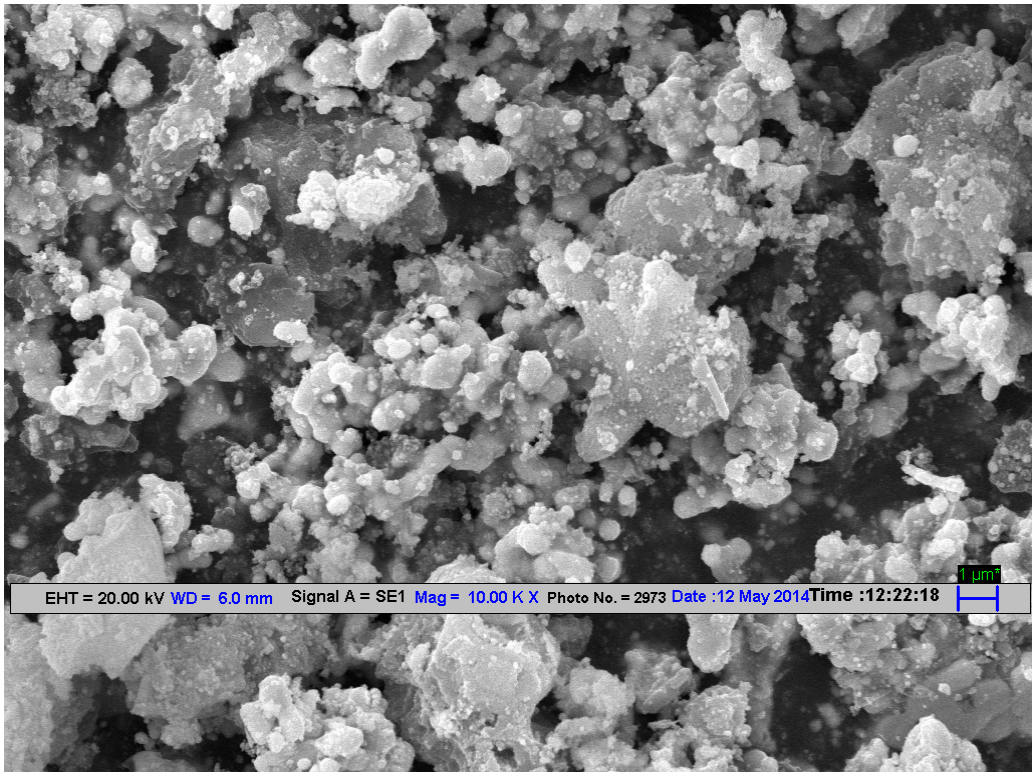
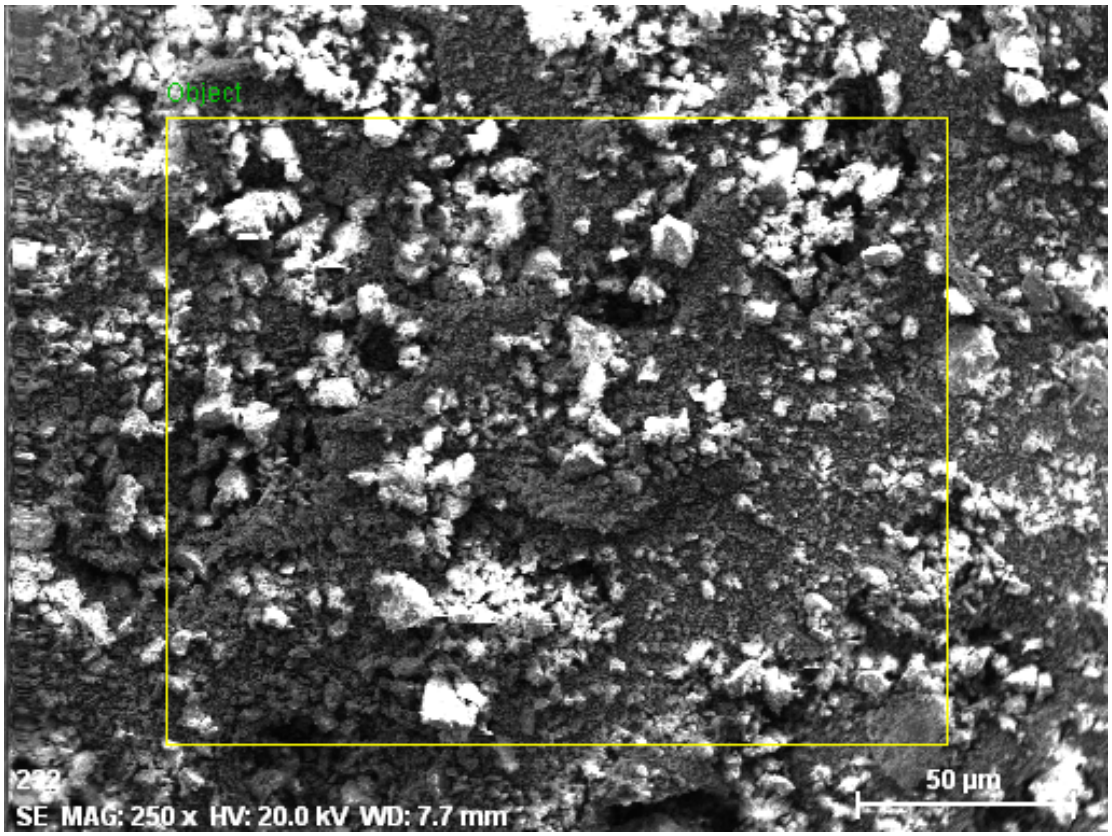


Fig. S27SEM image of NPs after anneanling obtained from **2** during Heck reaction



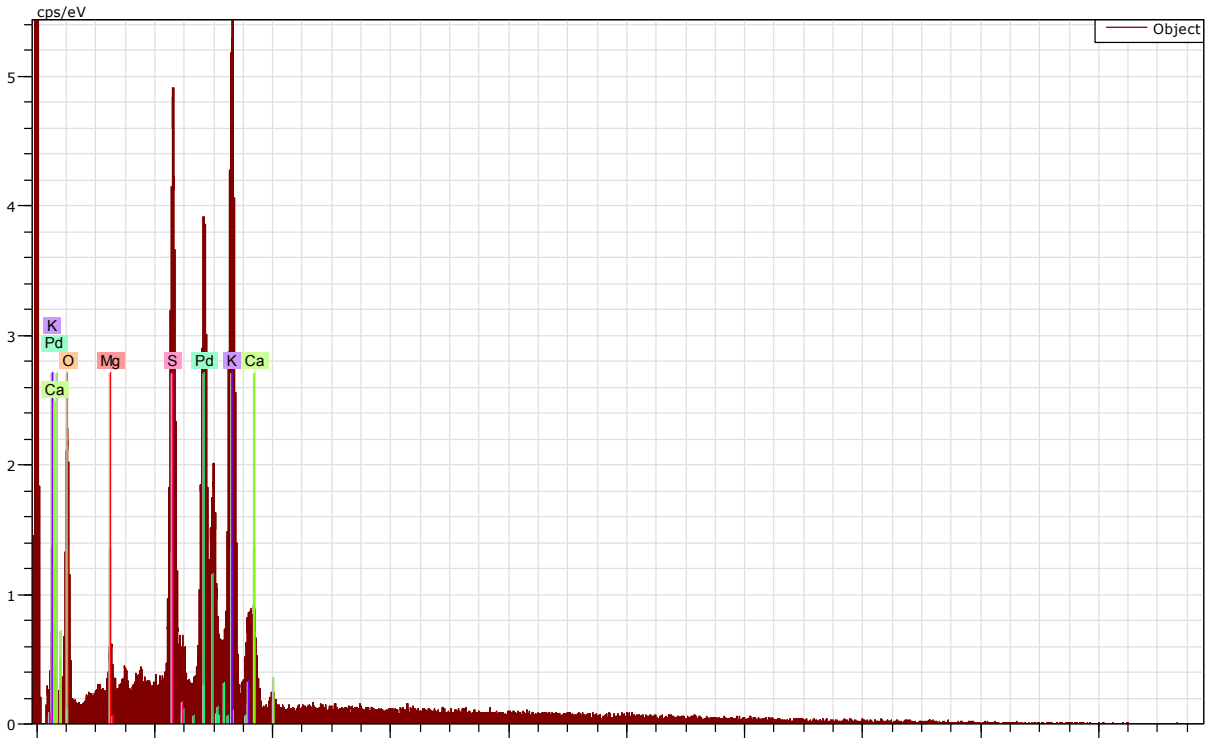
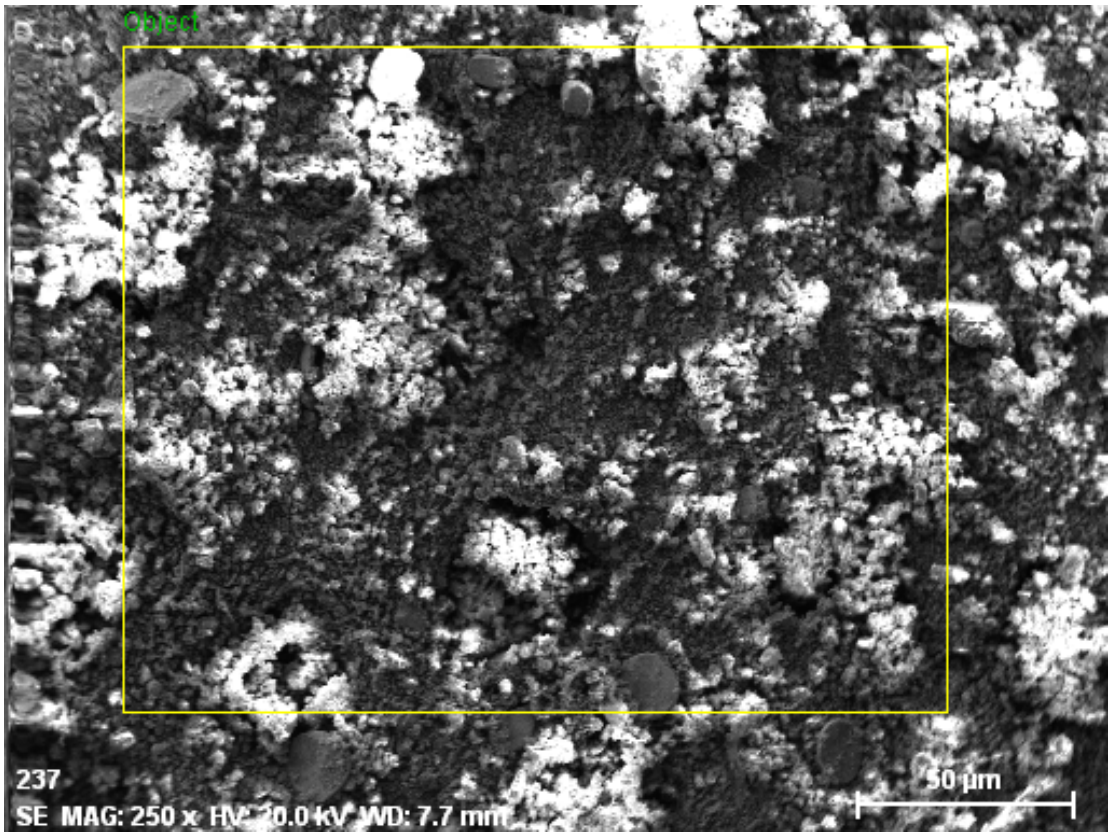


Fig. S28 SEM−EDX image of NPs after annealimg obtained from **1** during Suzuki-Miyaura reaction



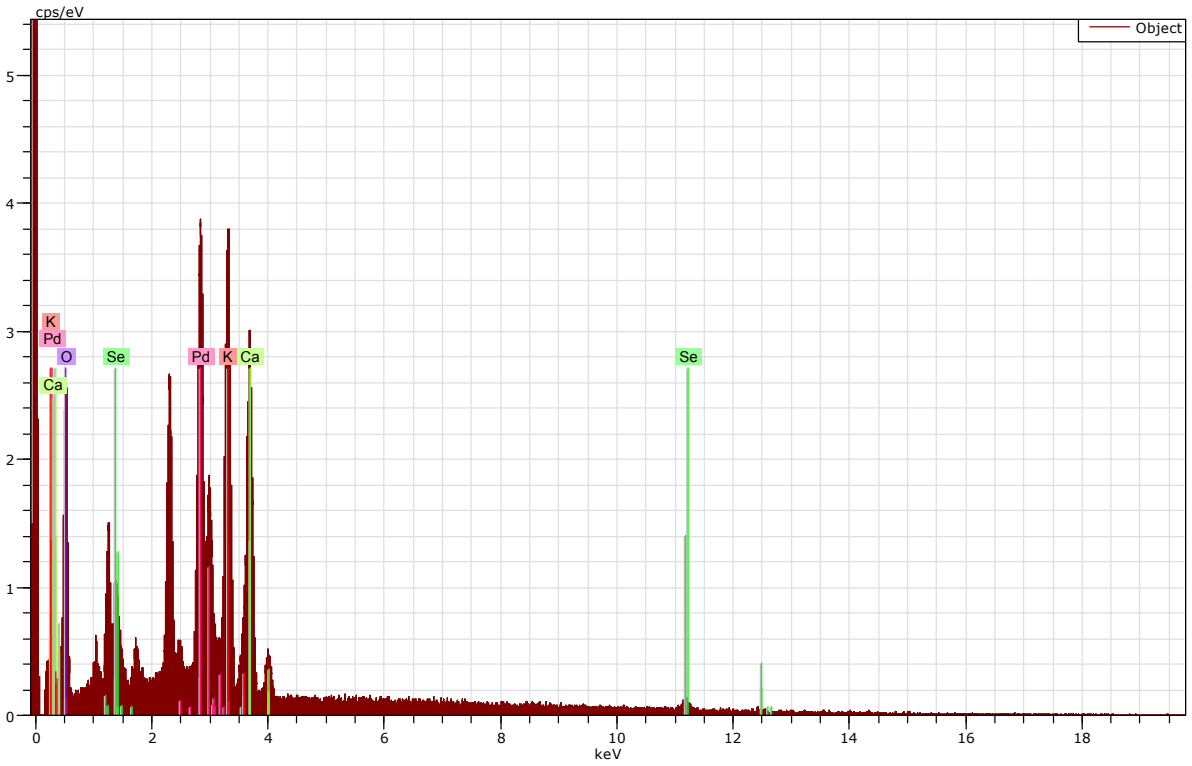
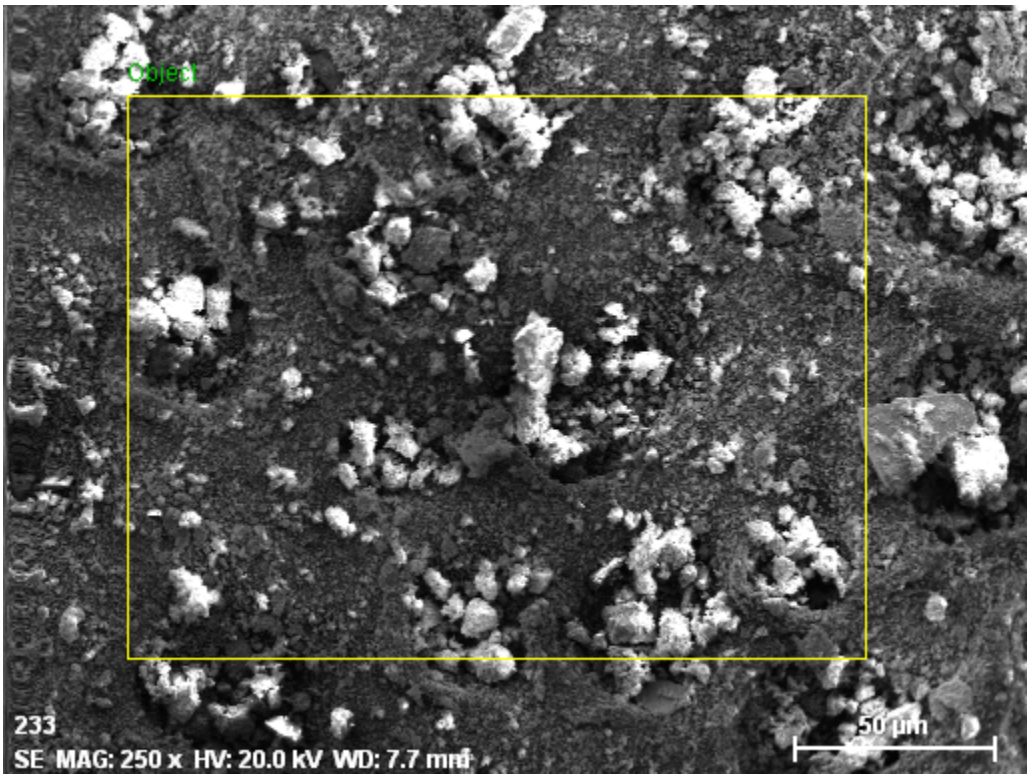


Fig. S29 SEM−EDX image of NPs after annealimg obtained from **2** during Suzuki-Miyaura reaction



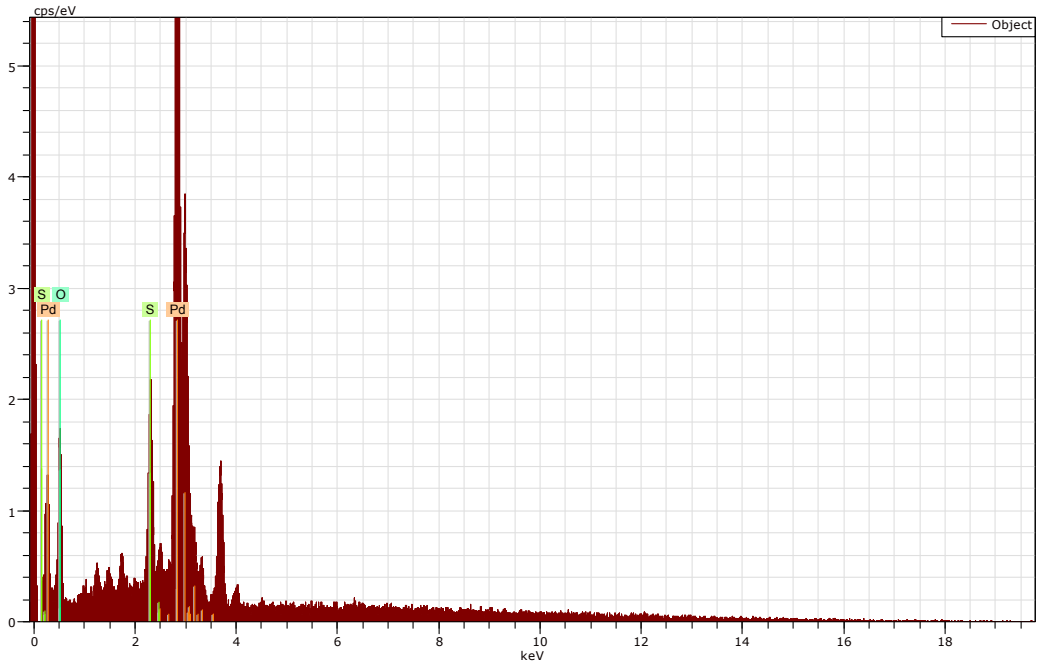
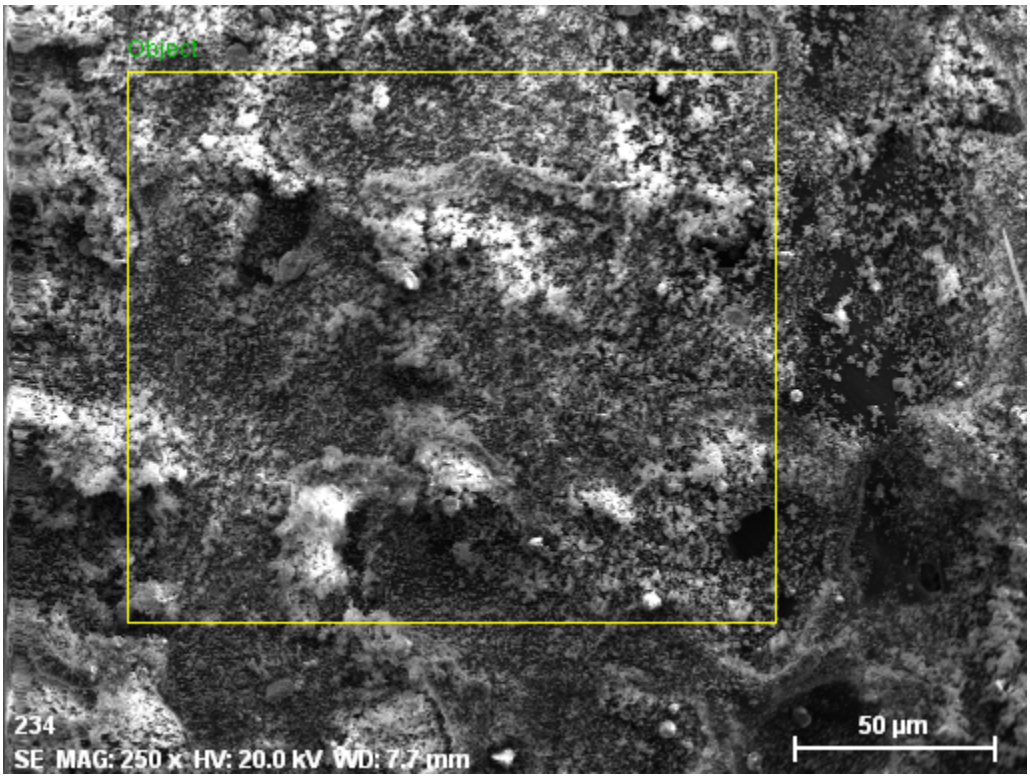


Fig. S30 SEM−EDX image of NPs after annealimg obtained from **1** during Heck reaction



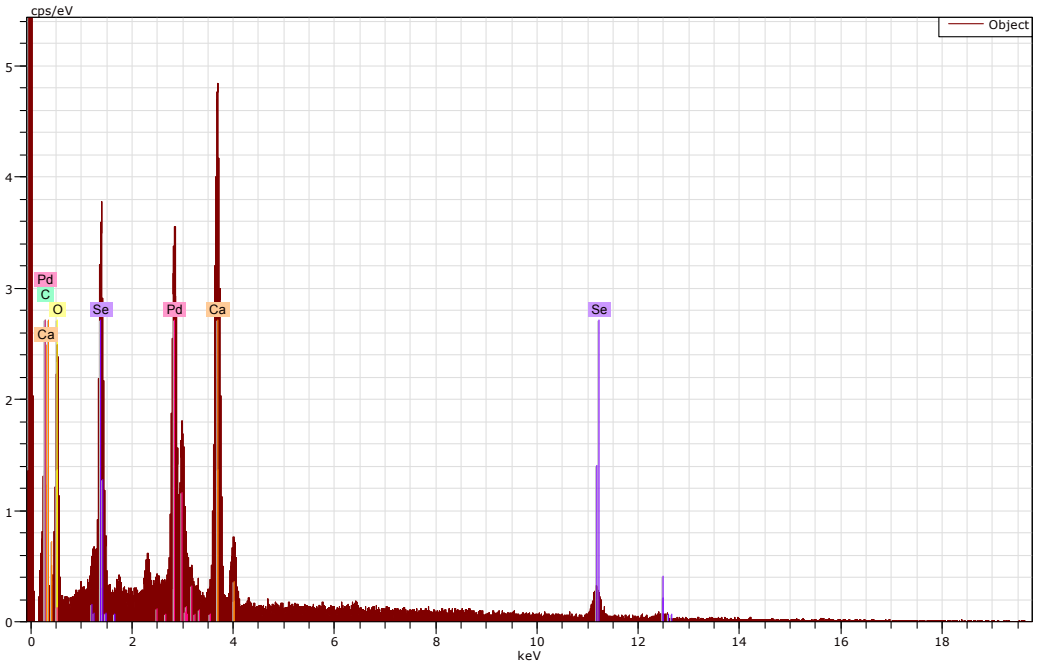


Fig. S31 SEM−EDX image of NPs after annealimg obtained from **2** during Heck reaction