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"Electronic Supplementary Information (ESI) to be published electronically"

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FOR

Palladium(II) complexes of *N*, *N*-diphenylacetamide based thio/selenoethers and flower shaped $Pd_{16}S_7$ and prismatic $Pd_{17}Se_{15}$ nano-particles tailored as catalysts for C−C and C−O coupling

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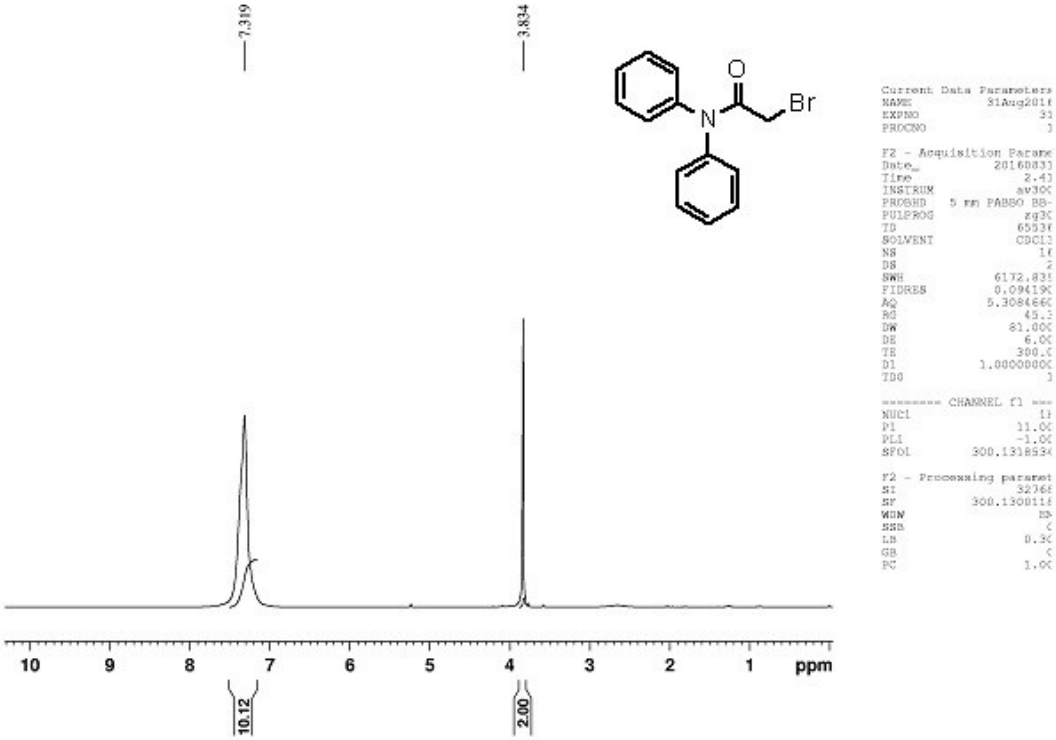

Figure S1. ^{1}H NMR

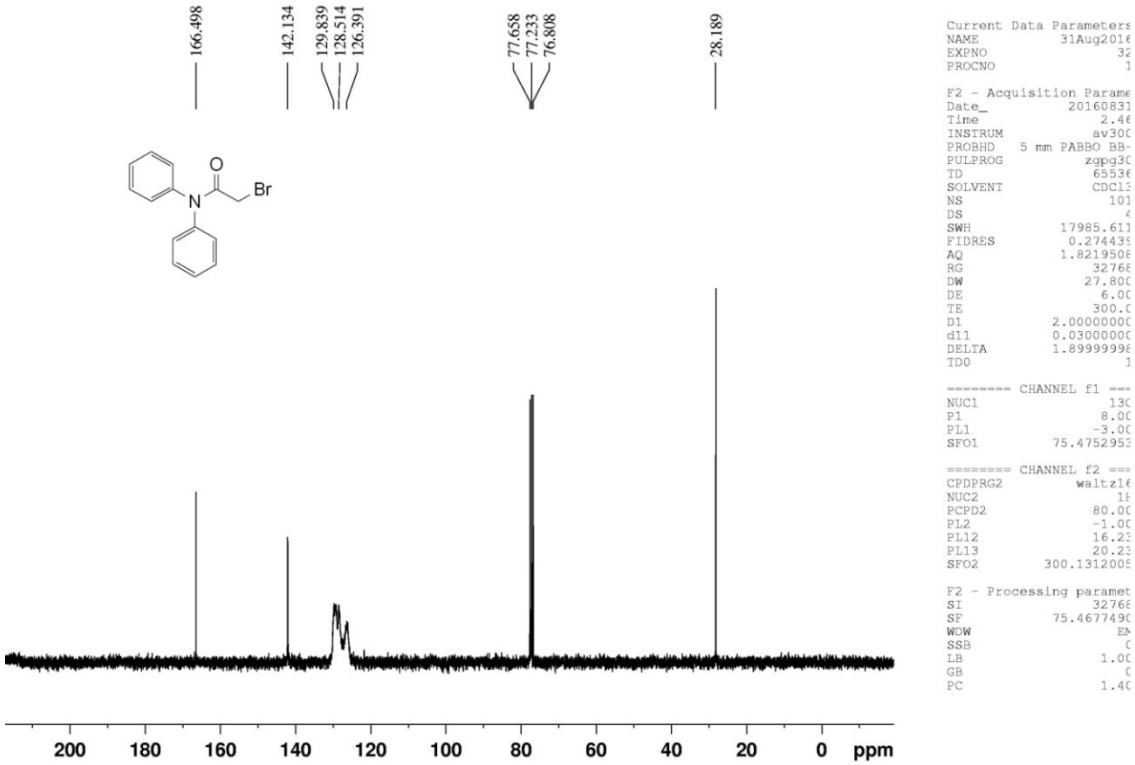

Figure S2. ^{13}C{^{1}H} NMR of P1

Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name		Instrument	micrOTOF-Q II 228888.10262
Comment			

Acquisition Parameter

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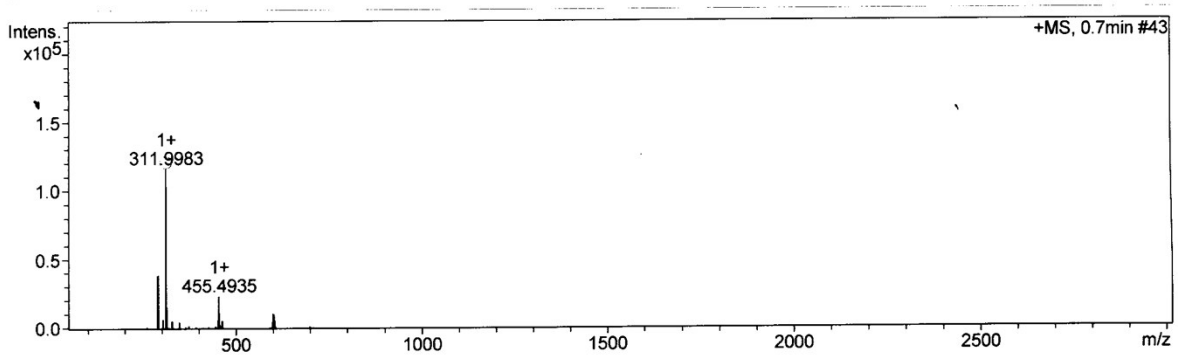

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Figure S3. Mass Spectrum of P1

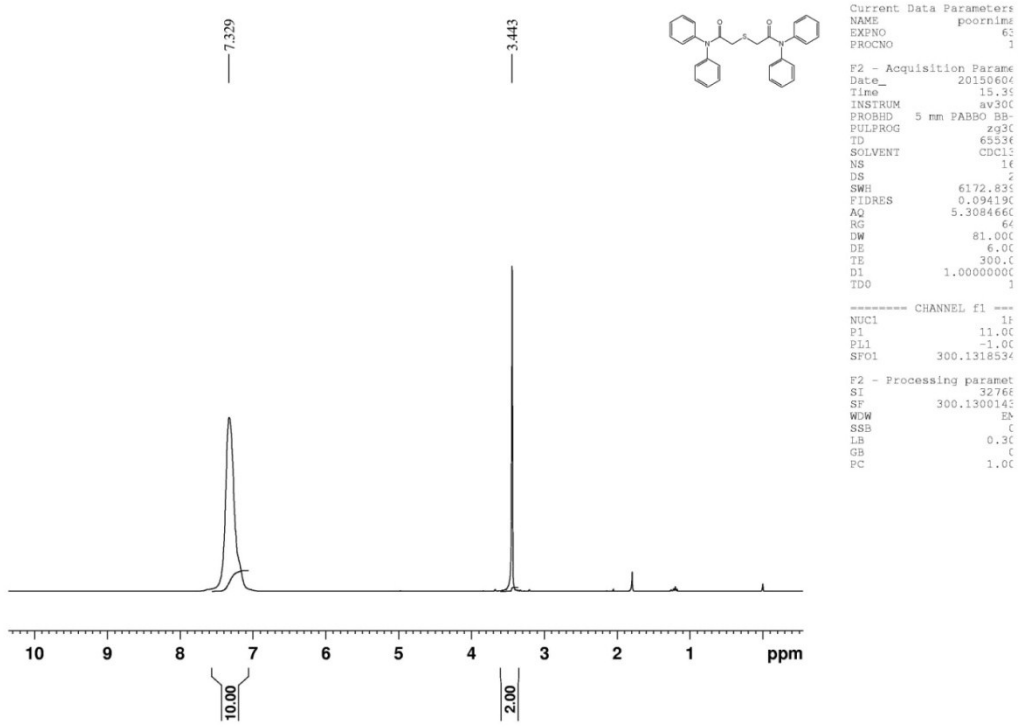

Figure S4. ^{1}H NMR of L1

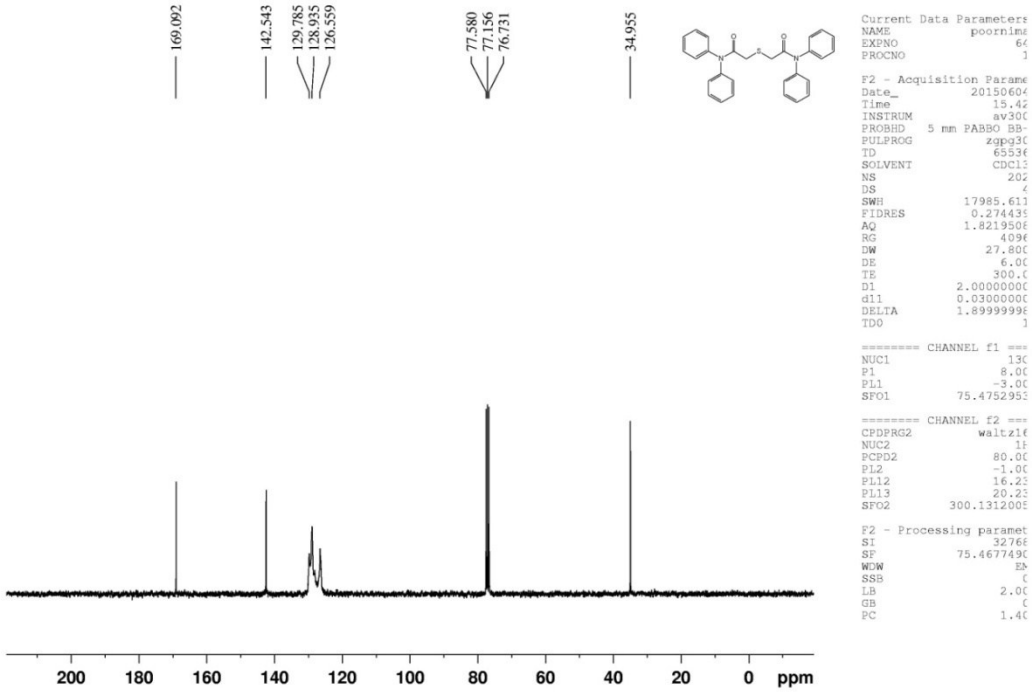

Figure S5. ^{13}C{^{1}H} NMR of L1

Mass Spectrum SmartFormula Report

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Sample Name	P1D	Instrument	micrOTOF-Q II 228888.10262
Comment			

Acquisition Parameter

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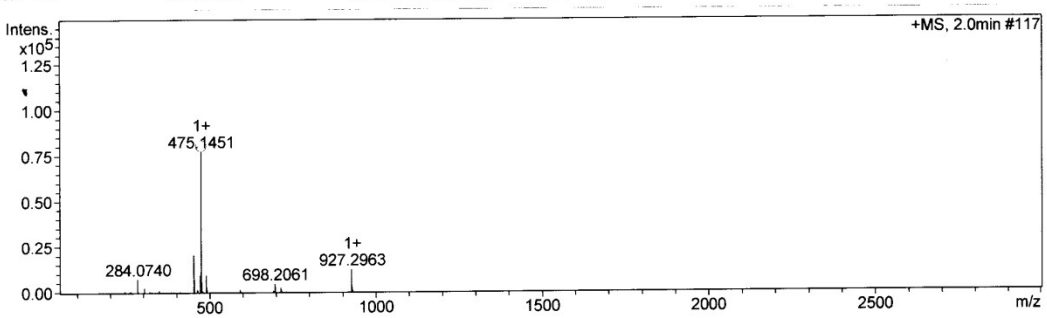

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475.145083	1	C28H24N2NaO2S	475.145070	0.0	0.4	17.5	ok	even	26.9	47.4	0.5	15.4	1.0	842.7

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Figure S6. Mass Spectrum of L1

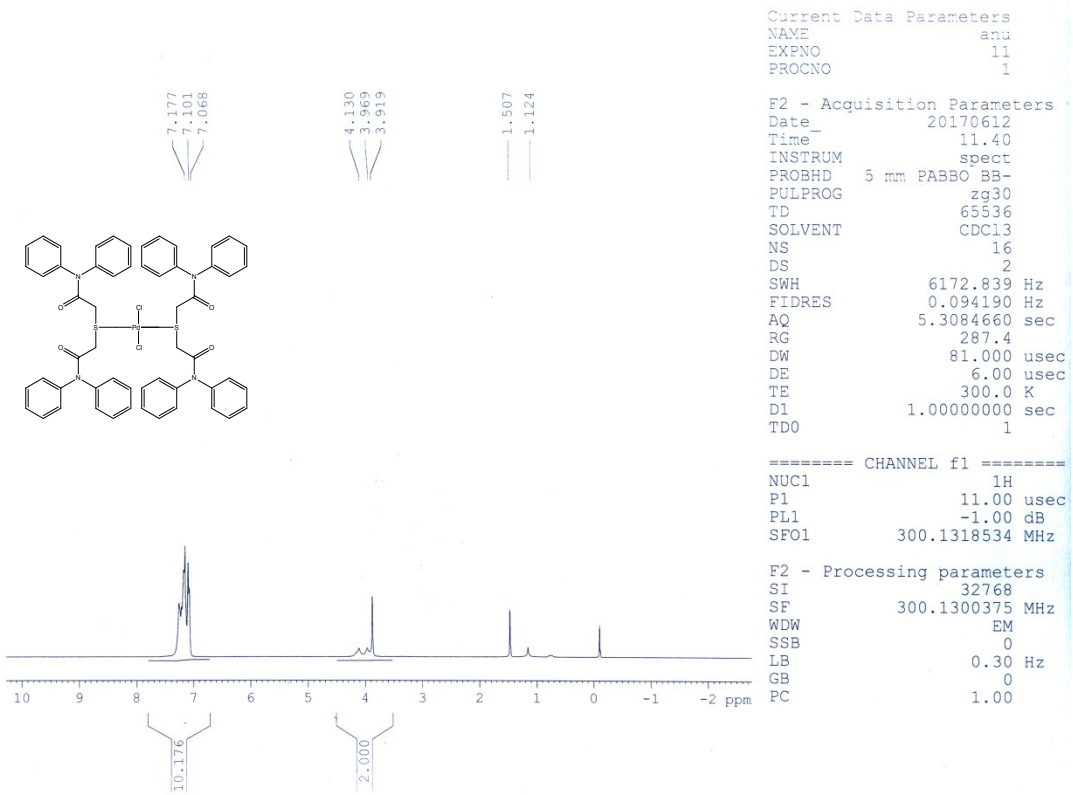

Figure S7. ^{1}H NMR of C1

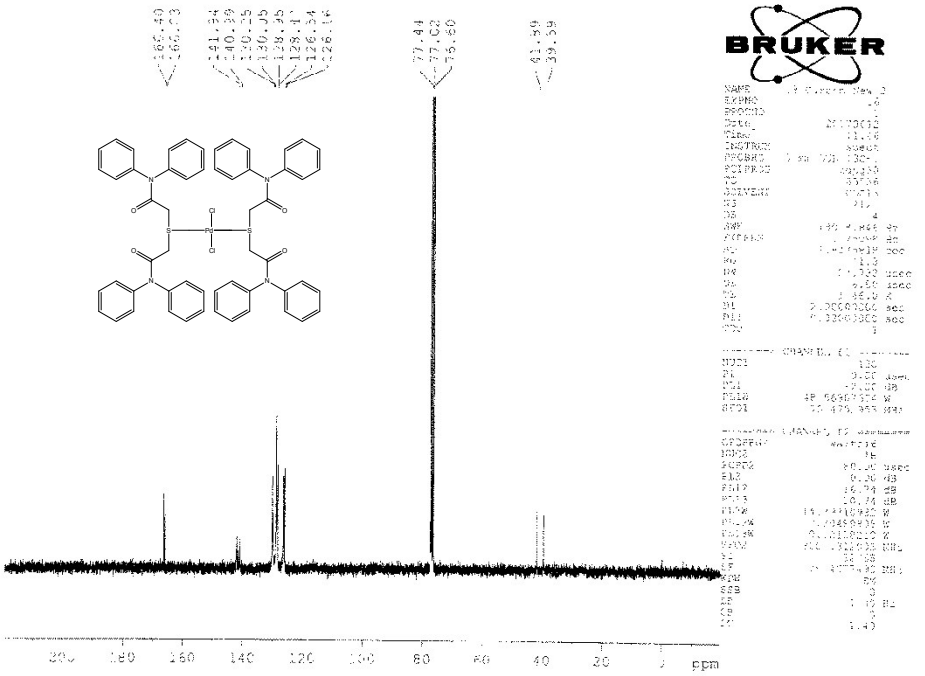

Figure S8. ^{13}C{^{1}H} NMR of C1

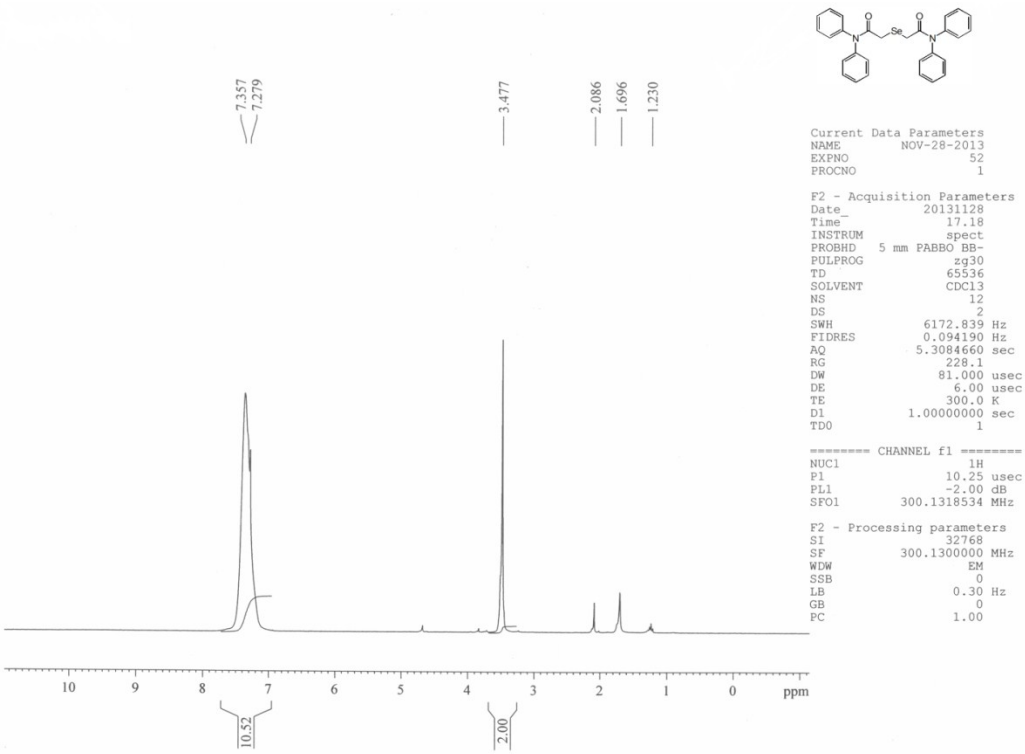

Figure S9. ^{1}H NMR of L2

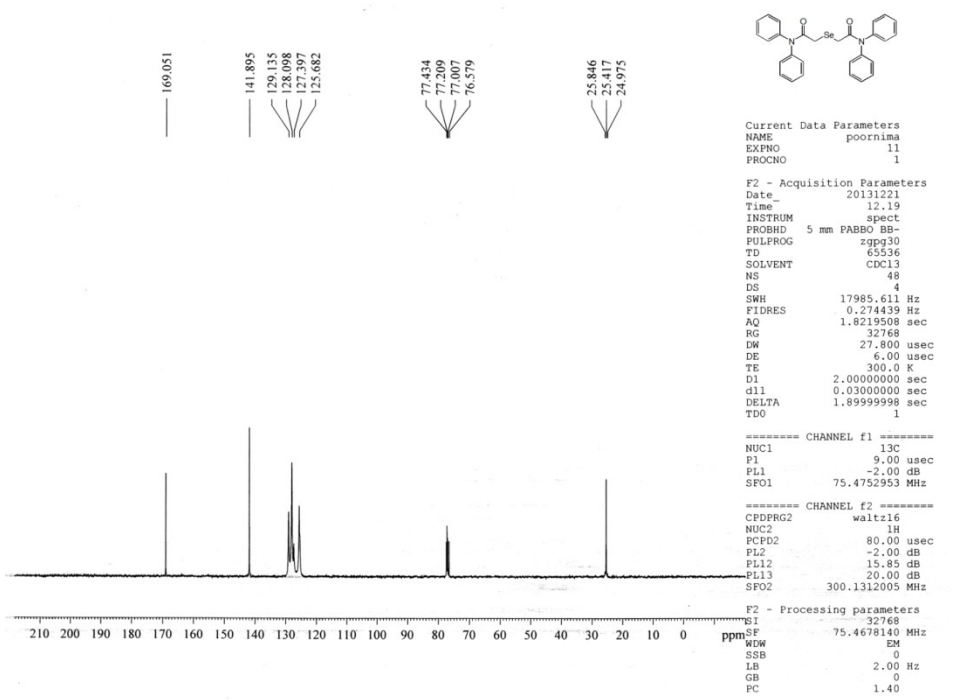

Figure S10. ^{13}C{^{1}H} NMR of L2

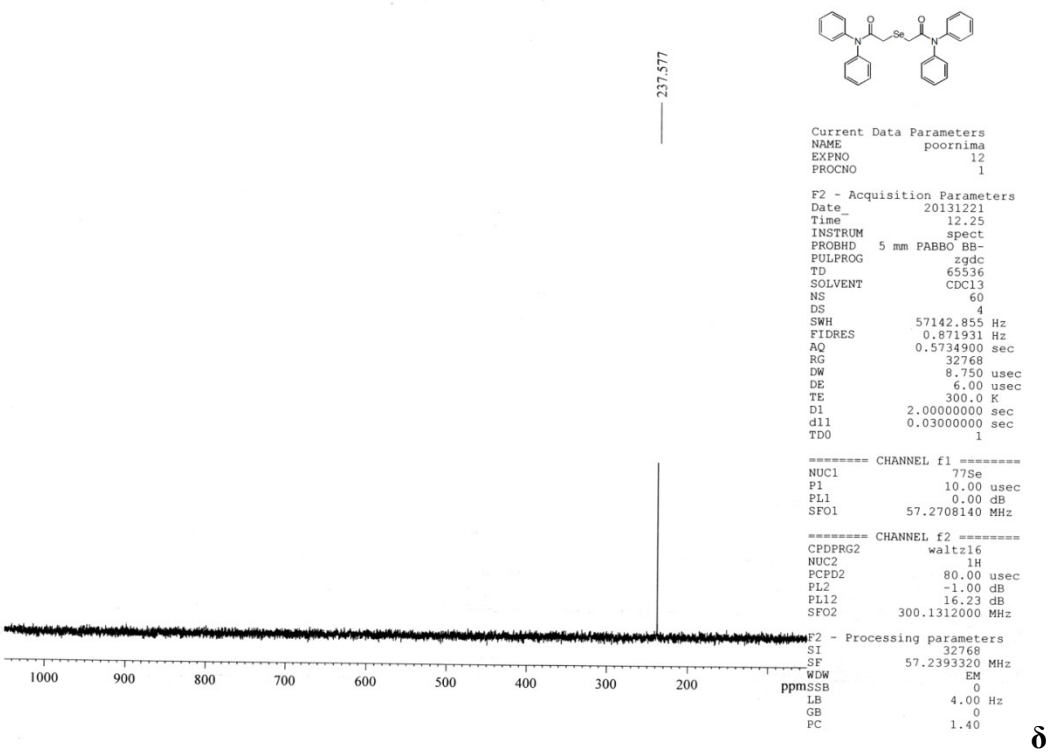

Figure S11. $^{77}Se\{^{1}H\}$ NMR of L2

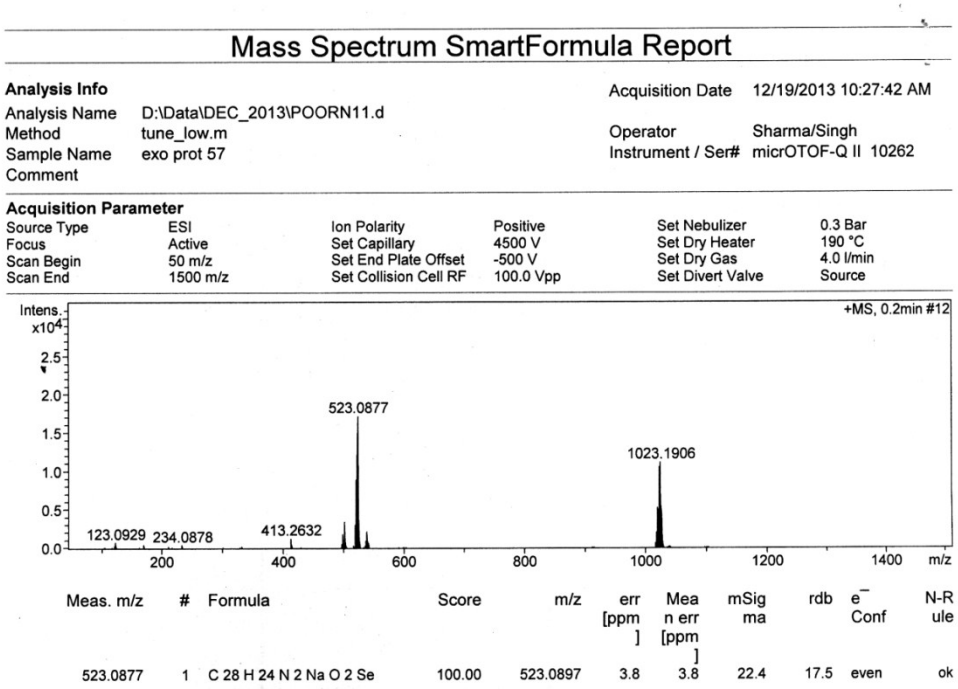

Figure S12. Mass Spectrum of L2

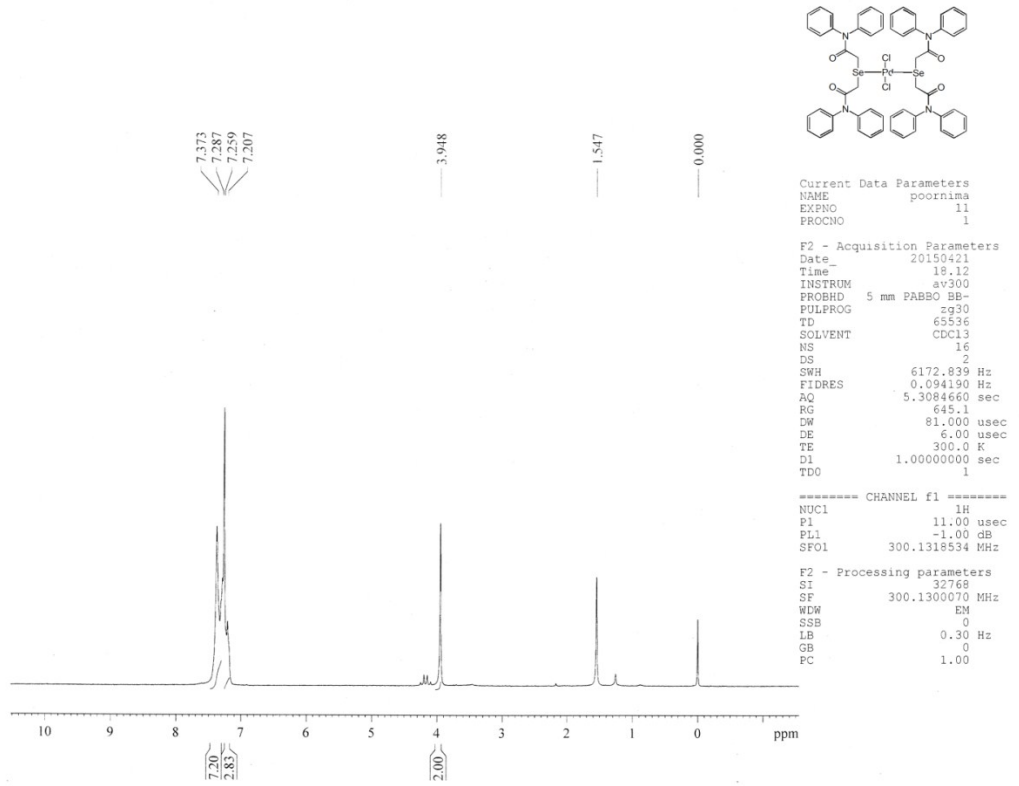

Figure S13. ^{1}H NMR of C2

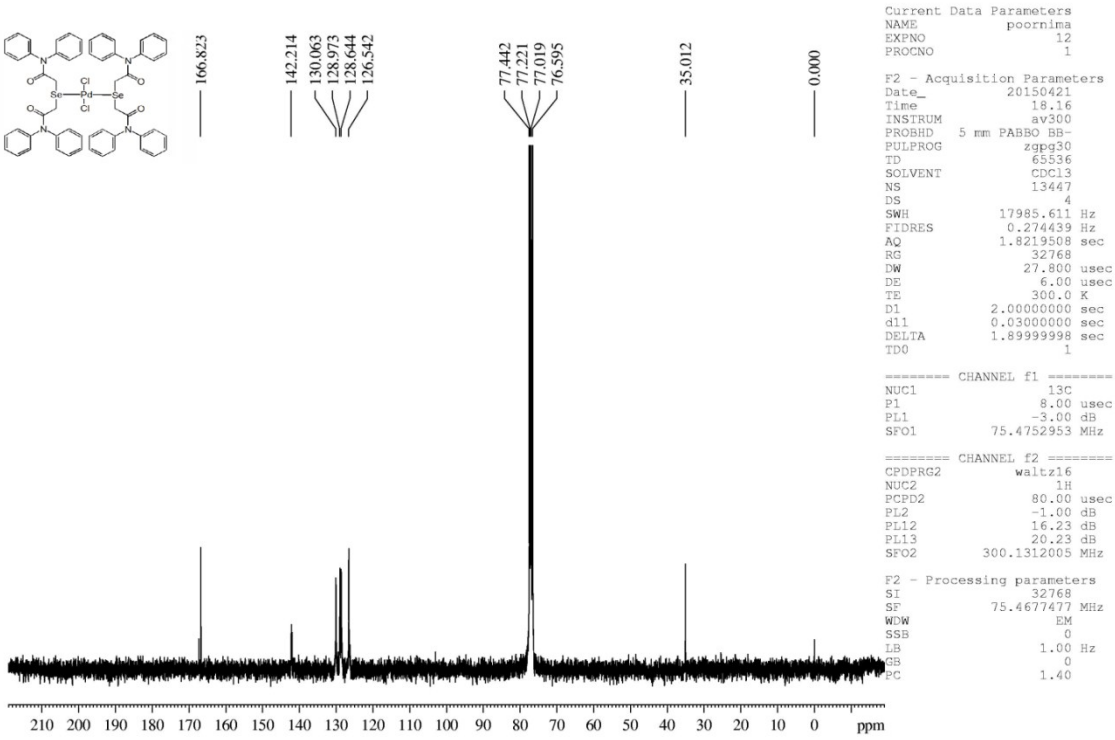

Figure S14. ^{13}C{^{1}H} NMR of C2

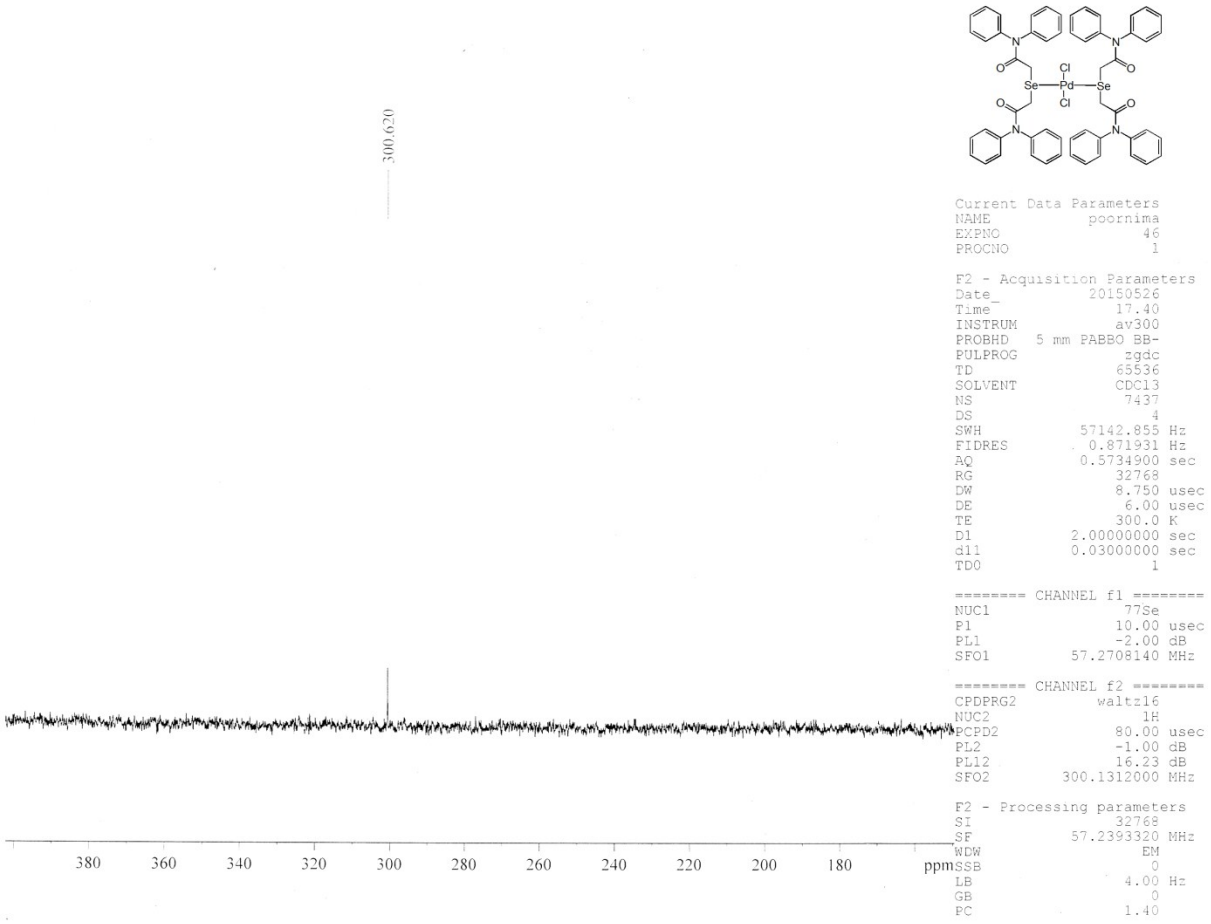

Figure S15. $^{77}Se\{^{1}H\}$ NMR C2

Table S1.

Elemental analyses of bulk sample of flower shaped $Pd_{16}S_7$ nanoparticles.

Element	Weight %	Weight % σ	Atomic %
Carbon	32.602	4.281	69.1317
Nitrogen	2.3462	3.3178	4.0341
Oxygen	3.9223	1.4253	6.2331
Phosphorus	0.6396	0.1535	0.5284
Sulfur	8.6761	0.7095	7.0383
Chlorine	0.5959	0.1999	0.437
Palladium	51.2178	3.8891	12.5976

Table S2.

Elemental analyses of bulk sample of prismatic $Pd_{17}Se_{15}$ nanoparticles

Element	Weight %	Weight % σ	Atomic %
Carbon	5.9232	3.5214	29.921
Nitrogen	0	0	0
Oxygen	1.1975	0.6882	4.6914
Phosphorus	0.0896	0.1092	0.1821
Chlorine	0.784	0.784	1.398
Selenium	43.5885	1.7622	34.9394
Palladium	48.4174	1.9563	28.8682

Table S3
Crystal Data and Structure Refinement Details for Precursor (P1), Ligands (L1, L2) and Complexes (C1, C2)

	P1	**L1**	**C1**	**L2**	**C2**
Empirical formula	$C_{14}H_{12}BrNO$	$C_{28}H_{24}N_2O_2S$	$C_{56}H_{48}Cl_2N_4O_4PdS_2$, $2(CHCl_3)$	$C_{28}H_{24}N_2O_2Se$	$C_{56}H_{48}Cl_2N_4O_4PdSe_2$, $2(C_2H_3N)$
Formula mass (g mol^{-1})	290.15	452.55	1321.14	499.45	1258.31
Temperature (K)	298(2)	298(2)	298(2)	298(2)	298(2)
Wavelenth, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Crystal size (mm^3)	0.29 x 0.27 x 0.25	0.33 x 0.31 x 0.28	0.31 x 0.29 x 0.27	0.32 x 0.31 x 0.29	0.33 x 0.31 x 0.29
Space group	P 2_1/n	C2	P -1	P2_1/n	P -1
a (Å)	9.398(3)	17.766(7)	11.700(4)	9.341(6)	9.430(2)
b (Å)	13.898(4)	5.557(2)	12.284(4)	20.608(13)	10.752(3)
c (Å)	10.247(3)	13.792(5)	12.639(4)	13.101(8)	14.940(4)
α (deg)	90	90	96.477(7)	90	81.965(4)
β (deg)	112.460(6)	120.633(8)	114.035(6)	109.33(1)	89.092(5)
γ (deg)	90	90	106.735(6)	90	68.046(4)
V (Å^3)	1236.9(6)	1171.5(8)	1532.8(9)	2380	1390.1(6)
Z	4	2	1	4	1
ρ_{calcd} (Mg m^{-3})	1.558	1.283	1.431	1.394	1.503
Absorption coefficient (mm^{-1})	3.305	0.166	0.767	1.605	1.792
F(000)	584	476	672	1024	636
h, k, l ranges collected	–11→11	–20→20	–13→13	–11→11	–11→8
	–16→16	–6→6	–14→14	–24→24	–12→12
	–12→12	–16→16	–15→15	–15→15	–15→17
Reflection collected	11687	5687	14795	22425	5997
Independent reflections	2175 [R(int) = 0.0625]	2058 [R(int) = 0.0717]	5395 [R(int) = 0.0452]	4166 [R(int) = 0.0618]	4899 [R(int) = 0.0202]
θ range (°)	2.50–25.00	2.66–24.95	2.05–25.00	1.92–25.00	2.31–25.00
Completeness to θ_{max} (%)	99.9	99.7	99.4	99.6	98.9
Absorption correction	Semi-empirical from equivalents				
Max., min. transmission	0.432, 0.403	0.958, 0.946	0.810, 0.791	0.626, 0.602	0.598, 0.556
Refinement method	Full-matrix least-squares on F2				
Data/restraints /parameters	2173 / 0 / 154	2058 / 1 / 150	5395 / 0 / 349	4166 / 0 / 298	4504 / 0 / 341
Goodness of fit on F^2	1.024	1.082	1.108	1.010	1.023
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0468, wR2 = 0.0965	R1 = 0.0804, wR2 = 0.1166	R1 = 0.0655, wR2 = 0.1624	R1 = 0.0416, wR2 = 0.0937	R1 = 0.0447, wR2 = 0.1382
R indices (all data)	R1 = 0.0879, wR2 = 0.1100	R1 = 0.1168, wR2 = 0.1283	R1 = 0.0771, wR2 = 0.1689	R1 = 0.0723, wR2 = 0.1137	R1 = 0.0590, wR2 = 0.1651
Largest diff peak/hole (e Å^{-3})	0.545 / -0.465	0.292/–0.191	0.747/–0.711	0.316/–0.337	0.625 /–0.568
Extinction coefficient		–	–	–	–

Table S4

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

Compounds	Bond length [Å]		Bond angle [°]	
P1	Br(1)-C(14)	1.941(4)	C(13)-N(1)-C(6)	121.2(3)
	O(1)-C(13)	1.215(4)	C(13)-N(1)-C(7)	122.6(3)
	N(1)-C(13)	1.377(5)	C(6)-N(1)-C(7)	116.1(3)
	N(1)-C(6)	1.434(4)	C(12)-C(7)-C(8)	119.4(4)
	N(1)-C(7)	1.443(4)	C(12)-C(7)-N(1)	119.4(3)
	C(7)-C(12)	1.370(5)	C(8)-C(7)-N(1)	121.1(3)
	C(7)-C(8)	1.372(5)	C(5)-C(6)-C(1)	119.9(4)
	C(6)-C(5)	1.378(5)	C(5)-C(6)-N(1)	119.7(3)
	C(6)-C(1)	1.379(5)	C(1)-C(6)-N(1)	120.3(3)
	C(13)-C(14)	1.501(6)	O(1)-C(13)-N(1)	122.3(4)
			O(1)-C(13)-C(14)	120.1(4)
			N(1)-C(13)-C(14)	117.5(4)
			C(13)-C(14)-Br(1)	107.8(3)
L1	S(1)-C(14)	1.781(5)	C(14)-S(1)-C(14)#1	102.0(4)
	S(1)-C(14)#1	1.781(5)	C(13)-N(1)-C(7)	121.7(4)
	N(1)-C(13)	1.374(5)	C(13)-N(1)-C(2)	121.8(4)
	N(1)-C(7)	1.438(5)	C(7)-N(1)-C(2)	116.3(4)
	N(1)-C(2)	1.449(5)	O(1)-C(13)-N(1)	122.2(5)
	C(13)-O(1)	1.220(5)	O(1)-C(13)-C(14)	122.8(4)
	C(13)-C(14)	1.511(6)	N(1)-C(13)-C(14)	114.9(4)
			C(8)-C(7)-N(1)	119.6(4)
			C(12)-C(7)-N(1)	121.2(4)
			C(13)-C(14)-S(1)	115.5(3)
			C(1)-C(2)-N(1)	120.9(5)
			C(3)-C(2)-N(1)	118.6(5)
L2	Se(1)-C(14)	1.950(3)	C(14)-Se(1)-C(15)	96.99(15)
	Se(1)-C(15)	1.959(4)	O(1)-C(13)-N(1)	122.0(3)
	C(13)-O(1)	1.222(4)	O(1)-C(13)-C(14)	120.3(3)
	C(13)-N(1)	1.372(4)	N(1)-C(13)-C(14)	117.7(3)
	C(13)-C(14)	1.502(4)	C(16)-N(2)-C(17)	121.6(3)
	N(2)-C(16)	1.375(4)	C(16)-N(2)-C(23)	121.3(3)
	N(2)-C(17)	1.440(4)	C(17)-N(2)-C(23)	117.1(3)
	N(2)-C(23)	1.446(4)	C(24)-C(23)-N(2)	121.3(3)
	N(1)-C(6)	1.440(4)	C(28)-C(23)-N(2)	118.9(3)
	N(1)-C(7)	1.443(4)	C(13)-N(1)-C(6)	120.3(3)
	C(16)-O(2)	1.217(4)	C(13)-N(1)-C(7)	123.5(3)
			C(6)-N(1)-C(7)	116.1(2)
			C(8)-C(7)-N(1)	121.0(3)
			C(12)-C(7)-N(1)	119.5(3)
			C(5)-C(6)-N(1)	119.0(3)
			C(1)-C(6)-N(1)	121.4(3)
			O(2)-C(16)-N(2)	121.5(3)
			O(2)-C(16)-C(15)	120.8(3)
			N(2)-C(16)-C(15)	117.7(3)
			C(18)-C(17)-N(2)	119.1(3)
			C(22)-C(17)-N(2)	121.5(3)
			C(16)-C(15)-Se(1)	109.9(2)
			C(13)-C(14)-Se(1)	109.7(2)
C1	Pd(1)-Cl(1)#1	2.2892(15)	Cl(1)#1-Pd(1)-Cl(1)	180.000(1)
	Pd(1)-Cl(1)	2.2892(15)	Cl(1)#1-Pd(1)-S(1)	94.79(5)

	Pd(1)-S(1)	2.3235(14)	Cl(1)-Pd(1)-S(1)	85.21(5)
	Pd(1)-S(1)#1	2.3235(14)	Cl(1)#1-Pd(1)-S(1)#1	85.21(5)
	S(1)-C(14)	1.819(5)	Cl(1)-Pd(1)-S(1)#1	94.79(5)
	S(1)-C(15)	1.830(5)	S(1)-Pd(1)-S(1)#1	180.00(6)
	O(2)-C(16)	1.218(6)	C(14)-S(1)-C(15)	98.4(2)
	N(2)-C(16)	1.365(6)	C(14)-S(1)-Pd(1)	110.65(18)
	N(2)-C(23)	1.438(6)	C(15)-S(1)-Pd(1)	104.24(18)
	N(2)-C(17)	1.439(7)	C(16)-N(2)-C(23)	123.6(4)
	O(1)-C(13)	1.213(6)	C(16)-N(2)-C(17)	118.9(4)
	N(1)-C(13)	1.359(7)	C(23)-N(2)-C(17)	117.3(4)
	N(1)-C(6)	1.441(7)	C(13)-N(1)-C(6)	122.6(4)
	N(1)-C(7)	1.443(6)	C(13)-N(1)-C(7)	121.4(4)
			C(6)-N(1)-C(7)	115.9(4)
			C(16)-C(15)-S(1)	107.7(4)
			O(2)-C(16)-N(2)	123.1(5)
			O(2)-C(16)-C(15)	120.6(4)
			N(2)-C(16)-C(15)	116.2(4)
			C(5)-C(6)-N(1)	119.0(5)
			C(1)-C(6)-N(1)	120.6(5)
			C(28)-C(23)-N(2)	118.7(5)
			C(24)-C(23)-N(2)	120.4(5)
			C(13)-C(14)-S(1)	108.6(4)
			C(12)-C(7)-N(1)	119.0(5)
			C(8)-C(7)-N(1)	120.6(5)
			O(1)-C(13)-N(1)	124.3(5)
			O(1)-C(13)-C(14)	121.5(5)
			N(1)-C(13)-C(14)	114.2(5)
			C(22)-C(17)-N(2)	120.7(5)
			C(18)-C(17)-N(2)	119.9(5)
C2	C(6)-N(1)	1.438(7)	C(1)-C(6)-N(1)	121.2(5)
	C(7)-N(1)	1.420(7)	C(5)-C(6)-N(1)	117.2(5)
	C(13)-O(1)	1.234(6)	C(12)-C(7)-N(1)	119.2(5)
	C(13)-N(1)	1.361(7)	C(8)-C(7)-N(1)	120.8(5)
	C(14)-Se(1)	1.955(5)	O(1)-C(13)-N(1)	122.6(5)
	C(15)-Se(1)	1.974(5)	O(1)-C(13)-C(14)	119.0(5)
	C(16)-O(2)	1.222(6)	N(1)-C(13)-C(14)	118.4(5)
	C(16)-N(2)	1.363(7)	C(13)-C(14)-Se(1)	106.5(3)
	C(17)-N(2)	1.408(7)	C(16)-C(15)-Se(1)	107.4(3)
	C(23)-N(2)	1.449(7)	O(2)-C(16)-N(2)	120.4(5)
	C(29)-N(3)	1.086(11)	O(2)-C(16)-C(15)	122.3(5)
	Cl(1)-Pd(1)	2.2736(16)	N(2)-C(16)-C(15)	117.3(4)
	Pd(1)-Cl(1)#1	2.2736(16)	C(18)-C(17)-N(2)	121.0(5)
	Pd(1)-Se(1)	2.4151(7)	N(2)-C(17)-C(22)	120.2(5)
	Pd(1)-Se(1)#1	2.4151(7)	C(24)-C(23)-N(2)	119.4(5)
			C(28)-C(23)-N(2)	119.9(5)
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			C(13)-N(1)-C(7)	124.1(4)
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			C(7)-N(1)-C(6)	117.4(4)
			C(16)-N(2)-C(17)	120.5(4)
			C(16)-N(2)-C(23)	122.2(4)
			C(17)-N(2)-C(23)	117.0(4)
			Cl(1)-Pd(1)-Cl(1)#1	180.00(3)
			Cl(1)-Pd(1)-Se(1)	87.18(4)
			Cl(1)#1-Pd(1)-Se(1)	92.82(4)
			Cl(1)-Pd(1)-Se(1)#1	92.82(4)

		Cl(1)#1-Pd(1)-Se(1)#1 87.18(4) Se(1)-Pd(1)-Se(1)#1 180.0 C(14)-Se(1)-C(15) 97.6(2) C(14)-Se(1)-Pd(1) 103.57(15) C(15)-Se(1)-Pd(1) 107.27(16)

Secondary interactions:

The intermolecular C–H···O interactions present in the crystal of **P1**, resulting supramolecular structure are shown in Fig. S16. The strong intermolecular H-bonding between O–H is present in **L2**. The centrosymmetric dimeric units that are formed *via* reciprocatory C(5)−H(5)···O2 and C(8)−H(8)···O1 H-bonding interactions, self-assemble, in the crystal lattice of **L2** as shown in Fig. S17.[1]

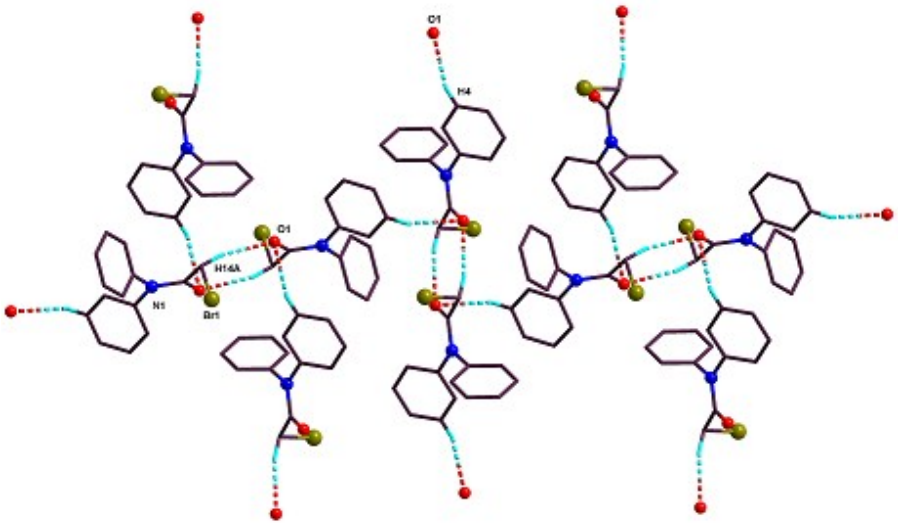


Figure S16. Supramolecular structure due to C–H···O interactions in the crystal lattice of **P1**.

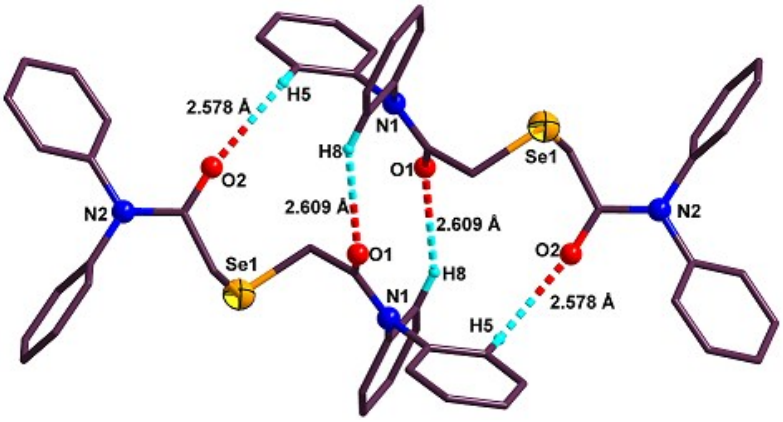


Figure S17. C–H···O interactions in the crystal lattice of **L2.**

In **C1**, intermolecular C(24)–H(24)···O2 and C(12)–H(12)···O1 H-bonding interactions result in supramolecular structure (Figs. S18 and S19). In **C2**, centrosymmetric dimeric units are formed by intermolecular C(12)–H(12)···O2 interactions in conjunction with intramolecular C(15)–H(15A)···O1, C14–H14A···Cl1 and C15–H15B···Cl1 H-bonding as shown in Fig. S20. The presence of intermolecular C(8)–H(8)···O1 interaction and intramolecular H-bonding (C(15)–H(15A)···O1), results in supramolecular structure of **C2** as shown in Figs. S20 and S21.

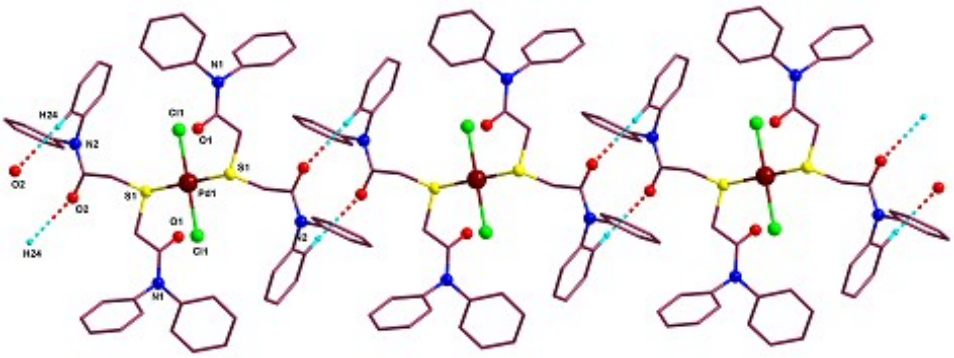


Figure S18. Supramolecular structure due to intermolecular C–H···O interactions in **C1**.

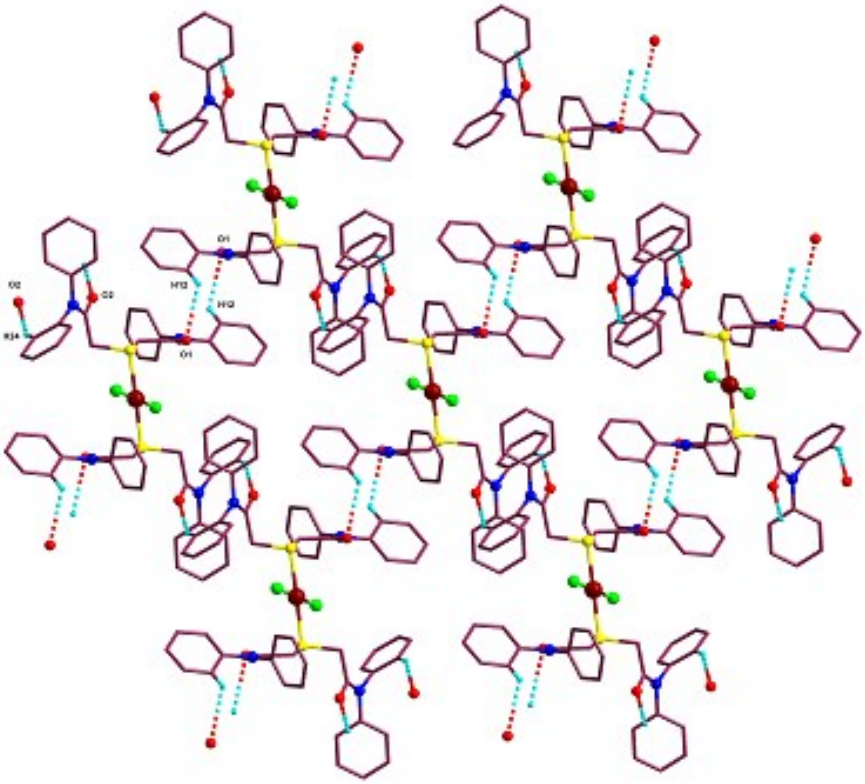


Figure S19. Supramolecular structure due to intermolecular C–H···O interactions in the crystal of **C1**.

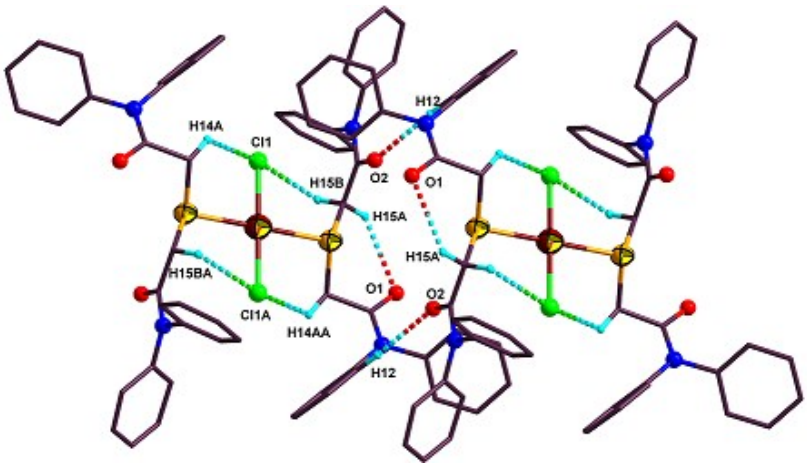


Figure S20. C–H···O and C–H···Cl interactions in the crystal lattice of **C2**.

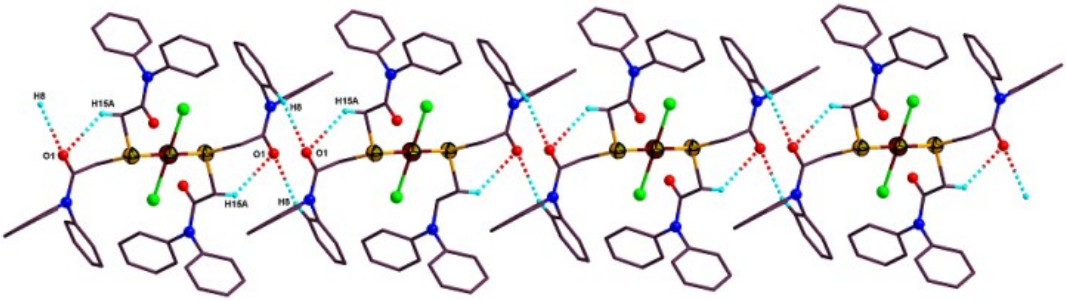


Figure S21. C–H···O interactions in the crystal of **C2**.

Table S5.

Parametric details of D–H···A interactions.

	D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)	Symmetry operation
P1	C(14)–H(14A)···O1	0.97	2.411	3.361(5)	166.2	2-x, -y, 2-z
	C(4)–H(4)···O1	0.93	2.666	3.340(6)	129.9	-1/2+x,1/2-y,-1/2+z
C1	C(24)–H(24)···O2	0.93	2.617	3.450(9)	149.3	x, -1+y, z
	C(12)–H(12)···O1	0.93	2.711	3.340(8)	125.7	1+x, y, 1+z
L2	C(5)–H(5)···O2	0.93	2.578	3.257(5)	130.3	-x,-y,1-z
	C(8)–H(8)···O1	0.93	2.609	3.430(4)	147.6	-x,-y,1-z
C2	C(14)–H(14A)···Cl(1)	0.97	2.734	3.372(6)	123.8	-x,1-y,1-z
	C(15)–H(15B)···Cl(1A)	0.97	2.871	3.244(5)	103.9	-x,1-y,1-z
	C(15)–H(15A)···O(1)	0.97	2.616	3.285(6)	126.3	-x, 1-y, 1-z
	C(12)–H(12)···O(2)	0.93	2.508	3.436(9)	175.5	-x, 1-y, 1-z

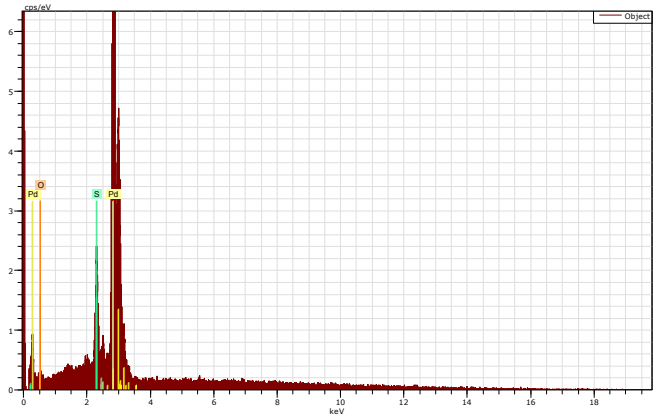


Figure S22. EDX pattern of the prismatic $Pd_{16}S_7$ nanoparticles.

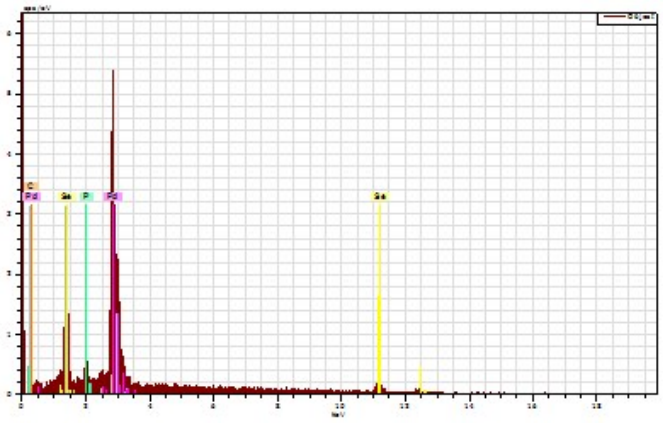
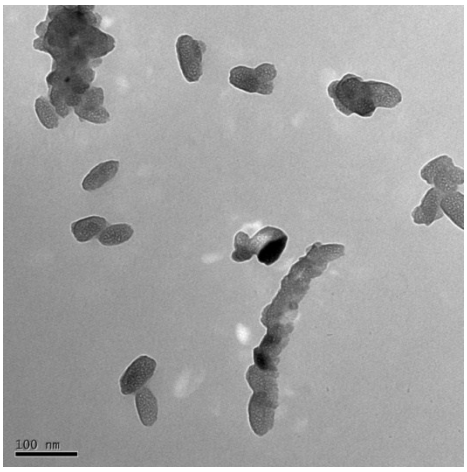
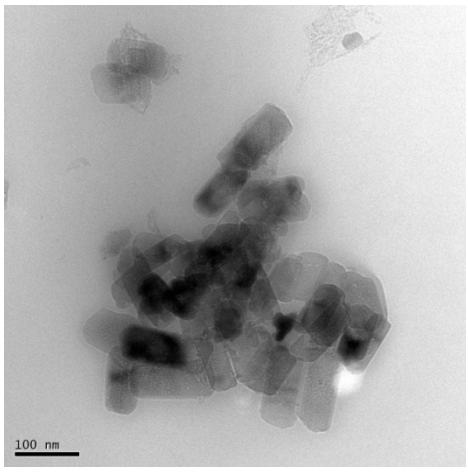


Figure S23. EDX pattern of the prismatic $Pd_{17}Se_{15}$ nanoparticles.



(a)



(b)

Figure S24. TEM Images of (a) $Pd_{16}S_7$ NPs (Scale Bar 100 nm). (b) $Pd_{17}Se_{15}$ NPs (Scale Bar 100 nm) after 4 Run Cycle .

Proposed mechanism for Suzuki-Miyaura coupling

The mechanism for Suzuki–Miyaura coupling reaction, where $Pd_{16}S_7$ and $Pd_{17}Se_{15}$ NPs are catalytic species is shown in Fig. S25. It based on earlier proposed pathway.[2]

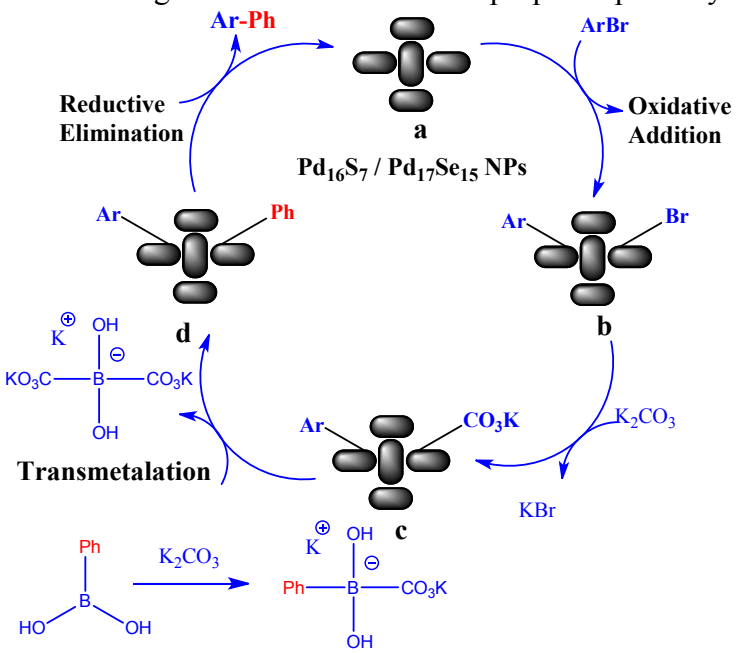


Figure S25. Mechanism for Suzuki–Miyaura coupling reactions.

Proposed Mechanism for C–O coupling

The mechanism for C–O coupling reaction catalyzed with $Pd_{16}S_7$ / $Pd_{17}Se_{15}$ NPs is proposed on the basis of earlier reports[3] and is shown in Fig. S26. It is based on Pd(0).

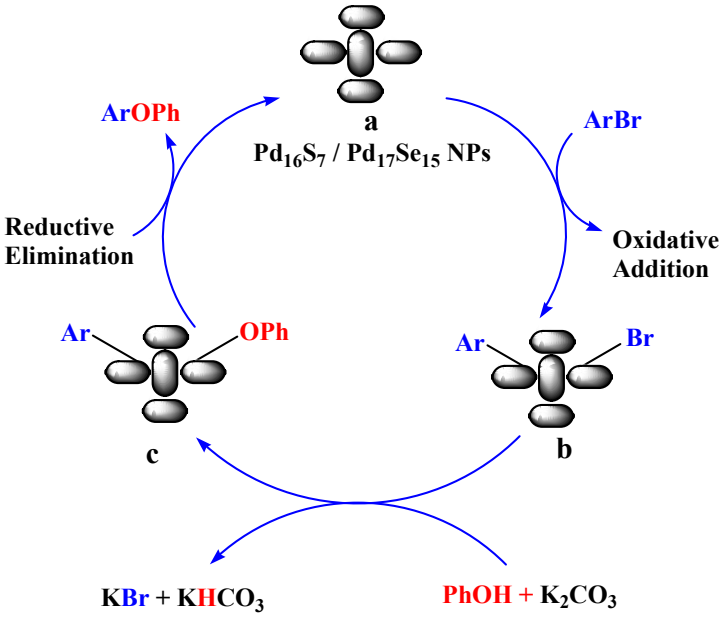
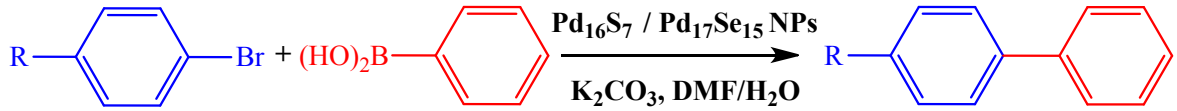


Figure S26. Mechanism for C–O coupling reactions.

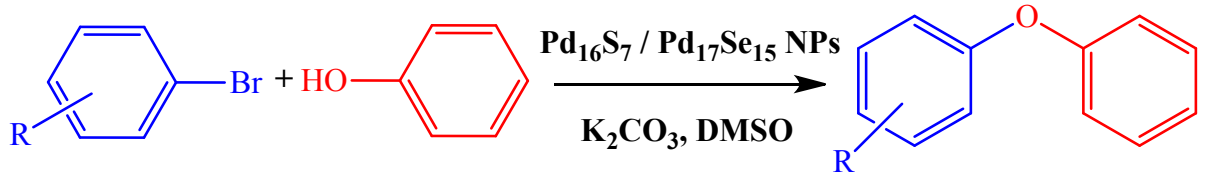
Table S6. Optimization of conditions for Suzuki–Miyaura cross coupling reaction catalyzed with $Pd_{16}S_7$ / $Pd_{17}Se_{15}$ NPs[a]



S. No.	Catalyst[a]	Solvent	Base	Time (h)	Conversion (%)
1.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF (4 mL)	K_2CO_3	12	81/75
2.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF (4 mL)	Cs_2CO_3	12	55/58
3.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	Toluene (4 mL)	CH_3ONa	12	44/45
4.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	EtOH (4 mL)	K_2CO_3	12	38/40
5.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	H_2O (4 mL)	K_2CO_3	12	12/< 10
6.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF:H_2O (3:1 mL)	Cs_2CO_3	12	68/70
7.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF:H_2O (3:1 mL)	K_2CO_3	12	100/100
8.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF:H_2O (3:1 mL)	K_2CO_3	6	100/100
9.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF:H_2O (3:1 mL)	K_2CO_3	3	90/96
10.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF:H_2O (3:1 mL)	K_2CO_3	1	61/68
11.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$*	DMF:H_2O (3:1 mL)	K_2CO_3	1	65/72
12.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	EtOH:H_2O (3:1 mL)	K_2CO_3	12	42/50

[a]Reaction conditions: 4-bromobenzaldehyde (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), $Pd_{16}S_7$ / $Pd_{17}Se_{15}$ nanoparticles: 0.5 mol % of Pd, temp. 100 °C. Conversion: ^{1}H NMR based. *$Pd_{16}S_7$ / $Pd_{17}Se_{15}$ NPs equivalent to 1.0 mol % of Pd.

Table S7. Optimization of Conditions for C–O Coupling Reaction Catalyzed with $Pd_{16}S_7$ / $Pd_{17}Se_{15}$ NPs[a]



S. No.	Catalyst[a]	Solvent	Base	Time (h)	Conversion (%)
1.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF (4 mL)	K_2CO_3	12	42/45
2.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF(4 mL)	Cs_2CO_3	12	24/30
3.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMF (4 mL)	NaO^{t}Bu	12	19/25
4.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMSO (4 mL)	K_2CO_3	12	85/88
5.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMSO (4 mL)	Cs_2CO_3	12	59/65
6.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMSO (4 mL)	K_2CO_3	6	82/85
7.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMSO (4 mL)	K_2CO_3	3	80/85
8.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	DMSO (4 mL)	K_2CO_3	1	55/58
9.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	ETOH (4 mL)	K_2CO_3	12	29/35
10.	$Pd_{16}S_7$/ $Pd_{17}Se_{15}$	ETOH (4 mL)	Cs_2CO_3	12	22/30

[a]Reaction conditions: 4-bromobenzaldehyde (1.0 mmol), phenol (1.1 mmol), base (2.0 mmol), $Pd_{16}S_7$/$Pd_{17}Se_{15}$ NPs: 0.5 mol % of Pd, temp. 100 °C. Conversion: ^{1}H NMR based.

Table S8. Optimization of base, solvent and time for Suzuki–Miyaura coupling reaction catalyzed with **C1**/**C2**.

S. No.	Catalyst[a]	Solvent	Base	Time (h)	Conversion (%)
1.	C1/C2	DMF (4 mL)	K_2CO_3	12	79/72
2.	C1/C2	DMF (4 mL)	Cs_2CO_3	12	61/58
3.	C1/C2	Toluene (4 mL)	CH_3ONa	12	48/46
4.	C1/C2	EtOH (4 mL)	K_2CO_3	12	35/37
5.	C1/C2	H_2O (4 mL)	K_2CO_3	12	28/21
6.	C1/C2	EtOH : H_2O (3 : 1 mL)	K_2CO_3	12	45/39
7.	C1/C2	DMF : H_2O (3 : 1 mL)	Cs_2CO_3	12	73/72
8.	C1/C2	DMF : H_2O (3 : 1 mL)	K_2CO_3	12	100/100
9.	C1/C2	DMF : H_2O (3 : 1 mL)	K_2CO_3	3	100/100
10.	C1/C2	DMF : H_2O (3 : 1 mL)	K_2CO_3	2	100/97

[a]Reaction conditions: 4-bromobenzaldehyde (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), **C1** / **C2** (0.01 mol %), temp. 100 °C, Conversion: ^{1}H NMR based.

Table S9. Optimization of base, solvent and time for C–O coupling reaction catalyzed with **C1**/**C2**.

S. No.	Catalyst[a]	Solvent	Base	Time (h)	Conversion (%)
1.	C1/C2	DMF (4 mL)	K_2CO_3	12	44/39
2.	C1/C2	DMF(4 mL)	Cs_2CO_3	12	32/21
3.	C1/C2	DMF (4 mL)	NaO^tBu	12	24/19
4.	C1/C2	DMSO (4 mL)	K_2CO_3	12	98/79
5.	C1/C2	DMSO (4 mL)	Cs_2CO_3	12	62/55
6.	C1/C2	DMSO (4 mL)	K_2CO_3	6	95/75
7.	C1/C2	DMSO (4 mL)	K_2CO_3	3	95/72
8.	C1/C2	DMSO (4 mL)	K_2CO_3	1	80/59
9.	C1/C2	ETOH (4 mL)	K_2CO_3	12	31/26
10.	C1/C2	ETOH (4 mL)	Cs_2CO_3	12	29/28

[a]Reaction conditions: 4-bromobenzaldehyde (1.0 mmol), phenol (1.1 mmol), base (2.0 mmol), **C1** 0.1 mol %, temp. 100 °C. Conversion: ^{1}H NMR based.

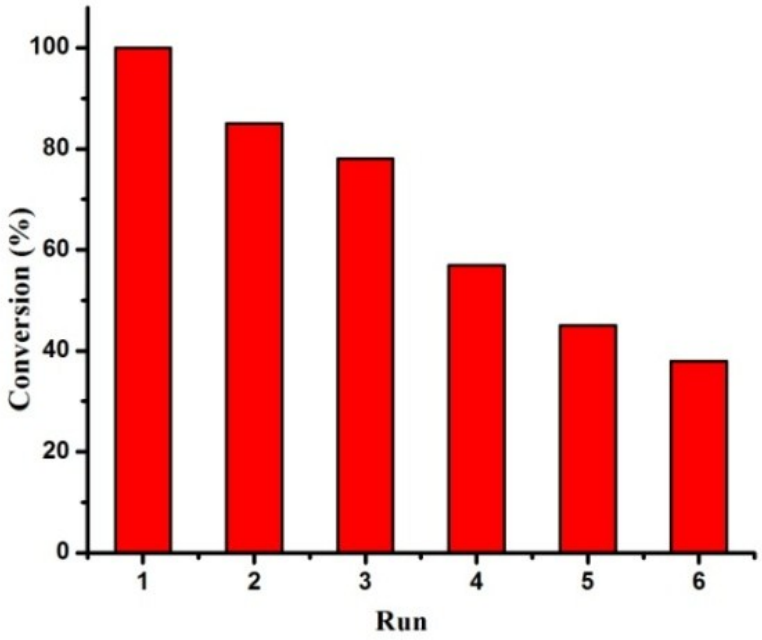


Figure S27. 'Catalyst Alive' Test for SMC of 4-Bromobenzaldehyde, Catalyst 0.001 mol%.

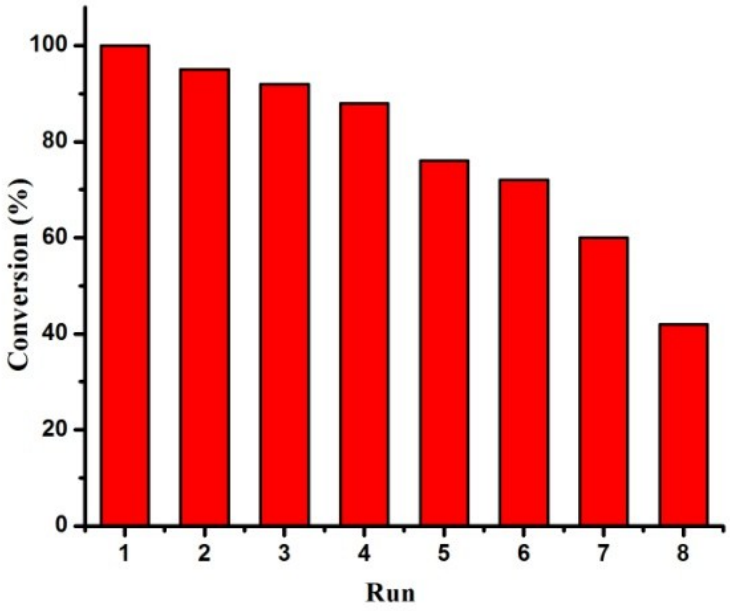


Figure S28. 'Catalyst Alive' Test for C−O Coupling of 1-Bromo-4-nitrobenzene, Catalyst 0.1 mol%.

C−C couplin reaction:[4,5]

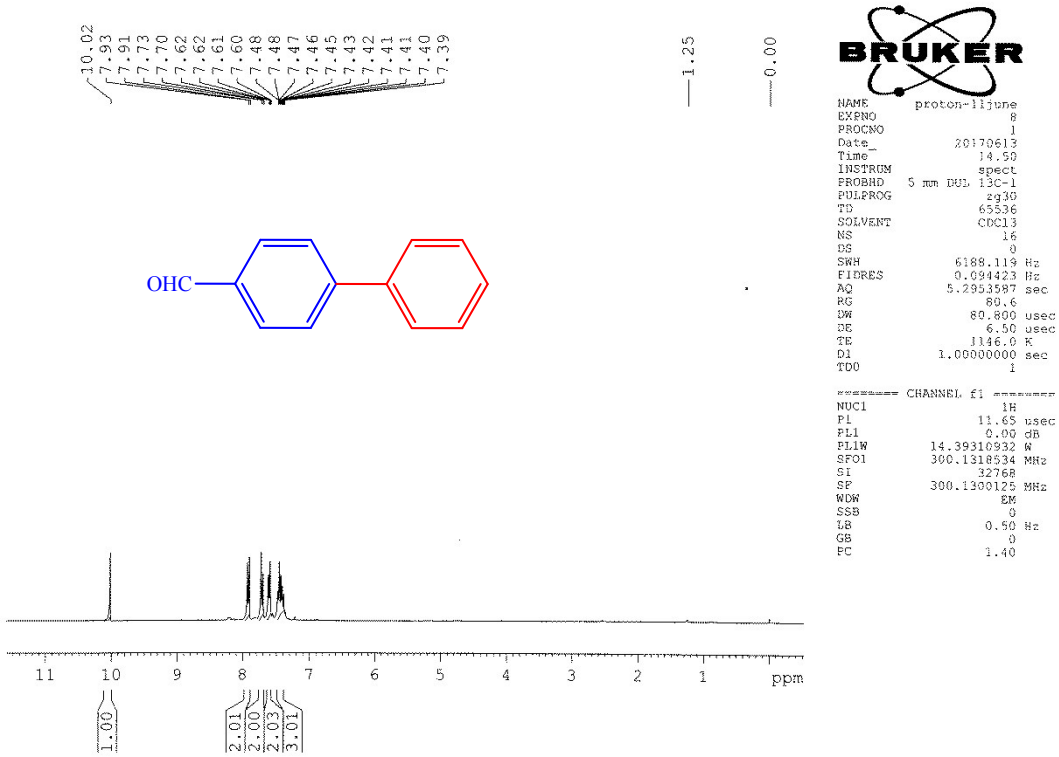


Figure S29. ^{1}H NMR of 4−Phenylbenzaldehyde

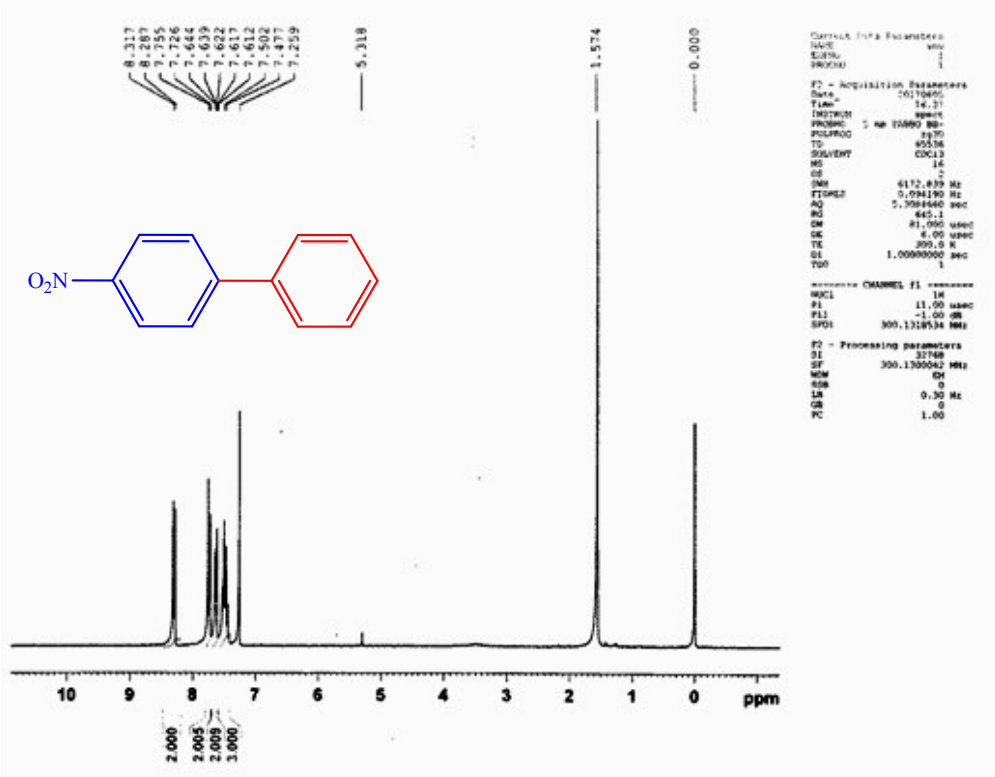


Figure S30. ^{1}H NMR of 4−Nitrobiphenyl

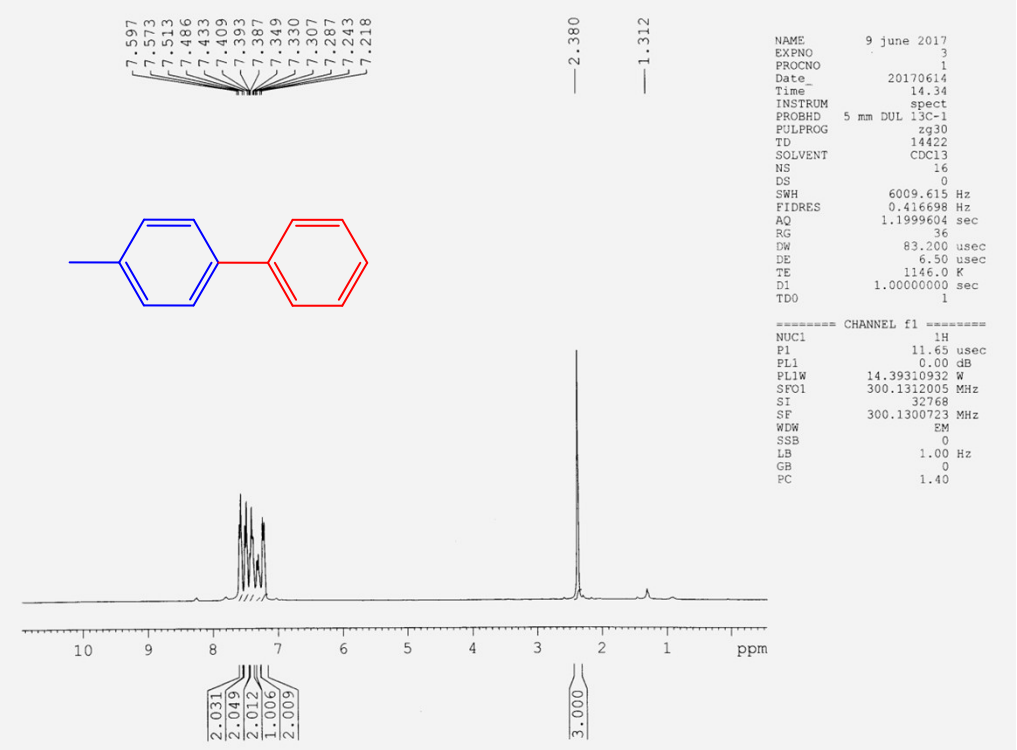


Figure S31. ^{1}H NMR of 4−Methylbiphenyl

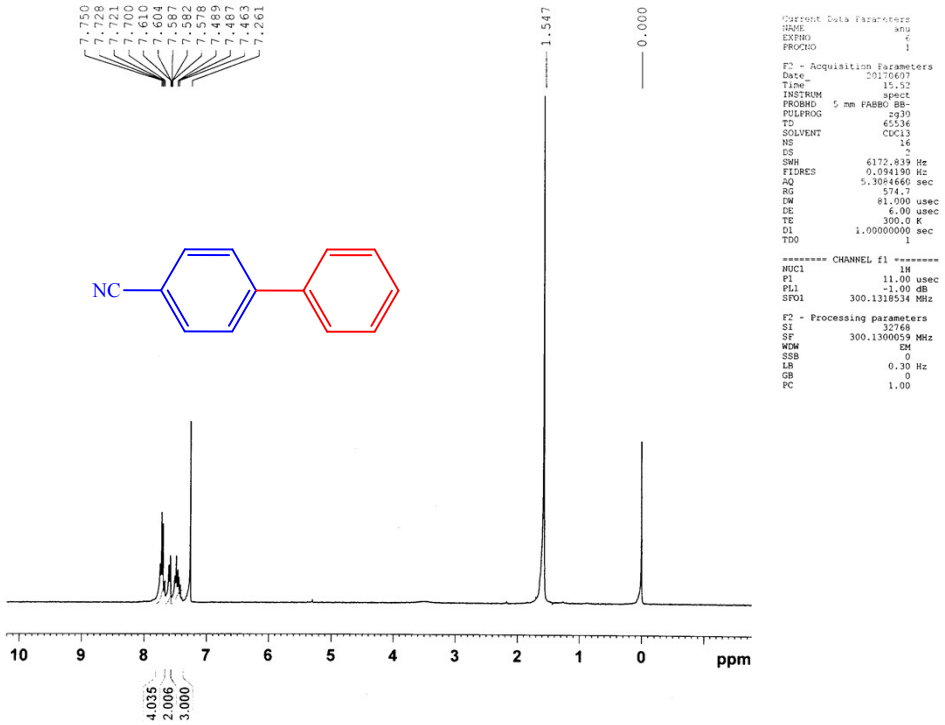


Figure S32. ^{1}H NMR of 4−Phenylbenzonitrile

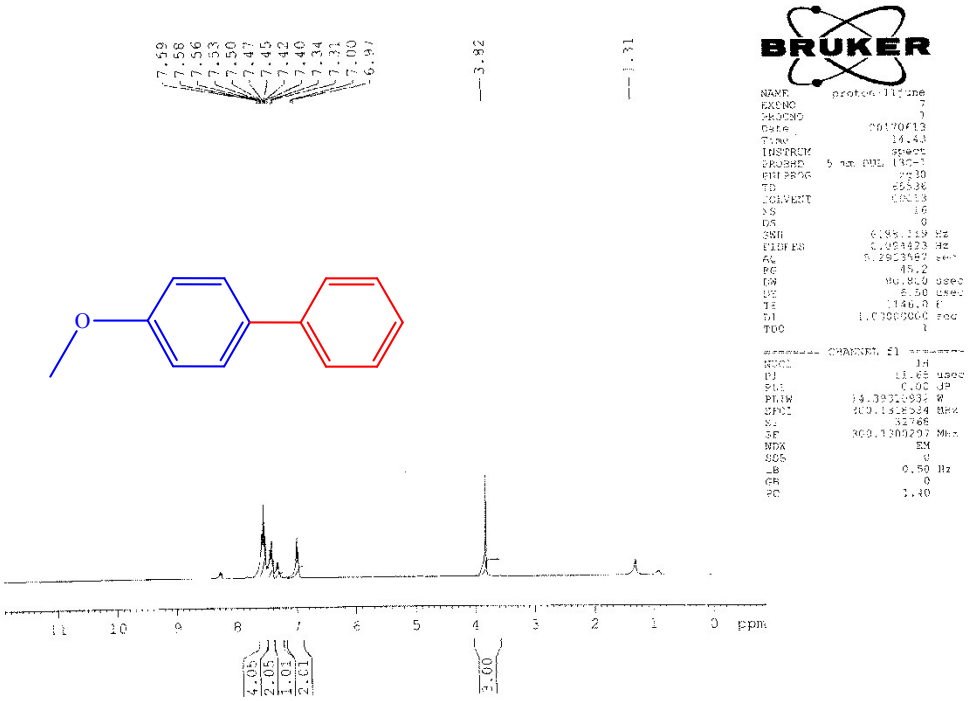


Figure S33. ^{1}H NMR of 4−Methoxybiphenyl

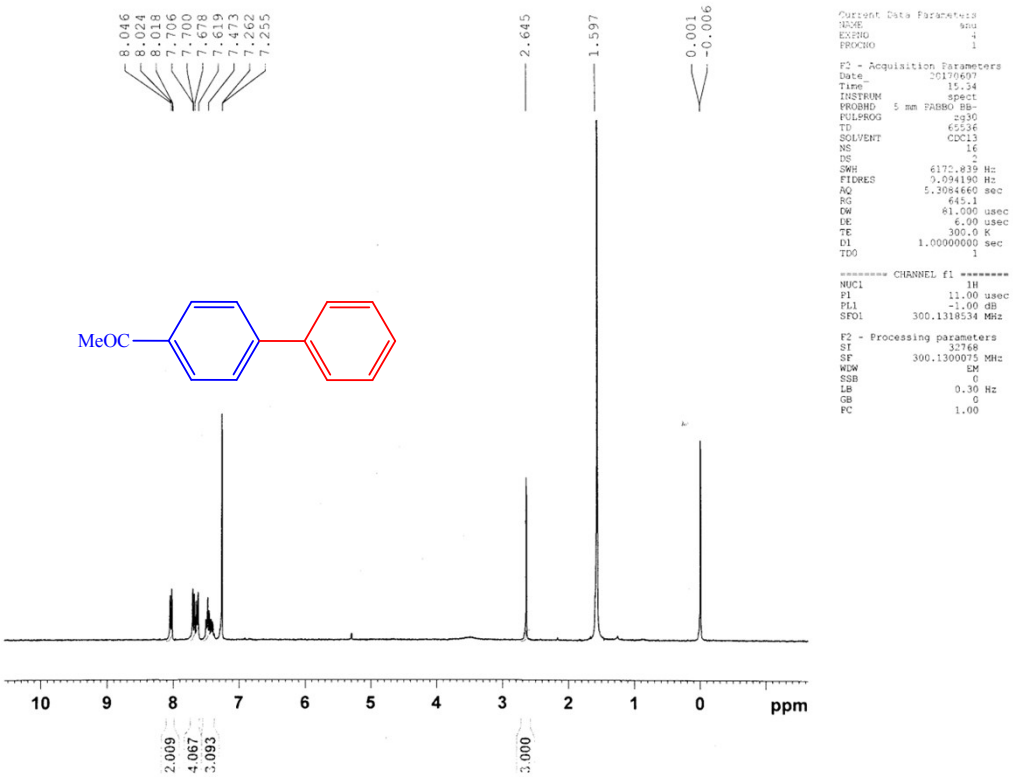


Figure S34. ^{1}H NMR of 4−Acetylbiphenyl

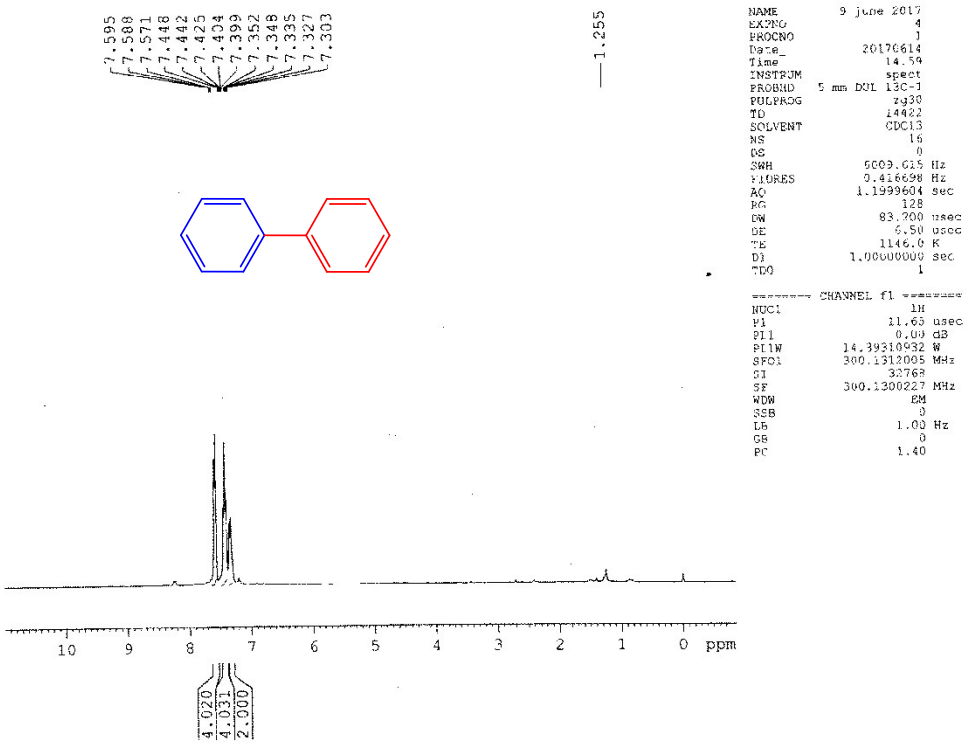


Figure S35. ^{1}H NMR of Biphenyl

C−O coupling reaction:[6,7]

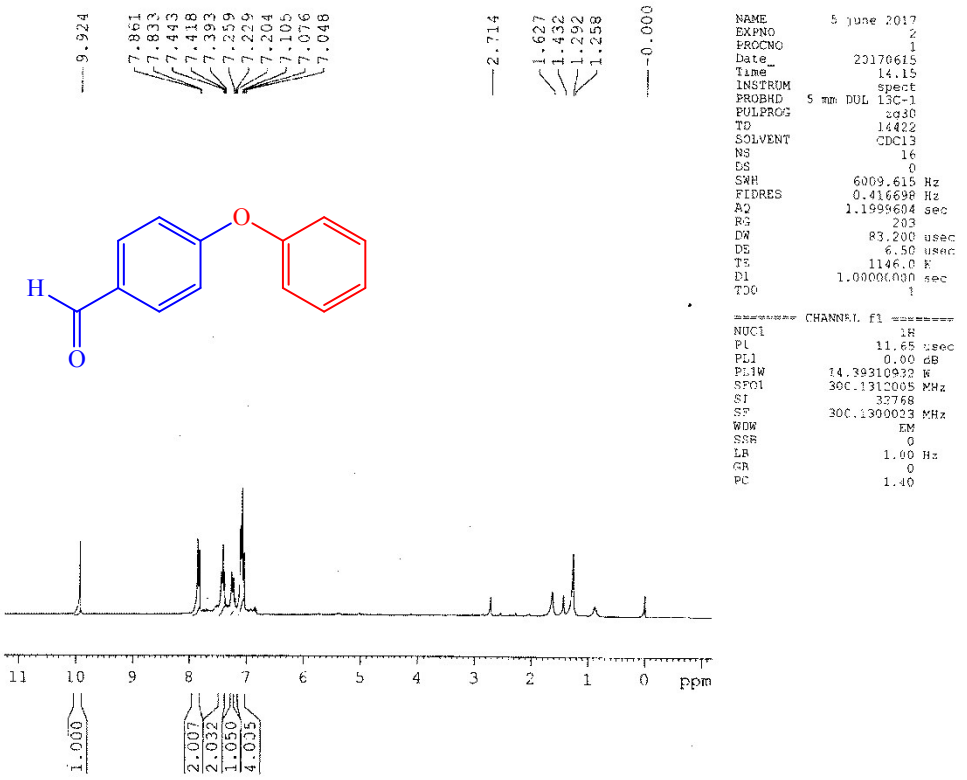


Figure S36. ^{1}H NMR of 4−phenoxybenzaldehyde

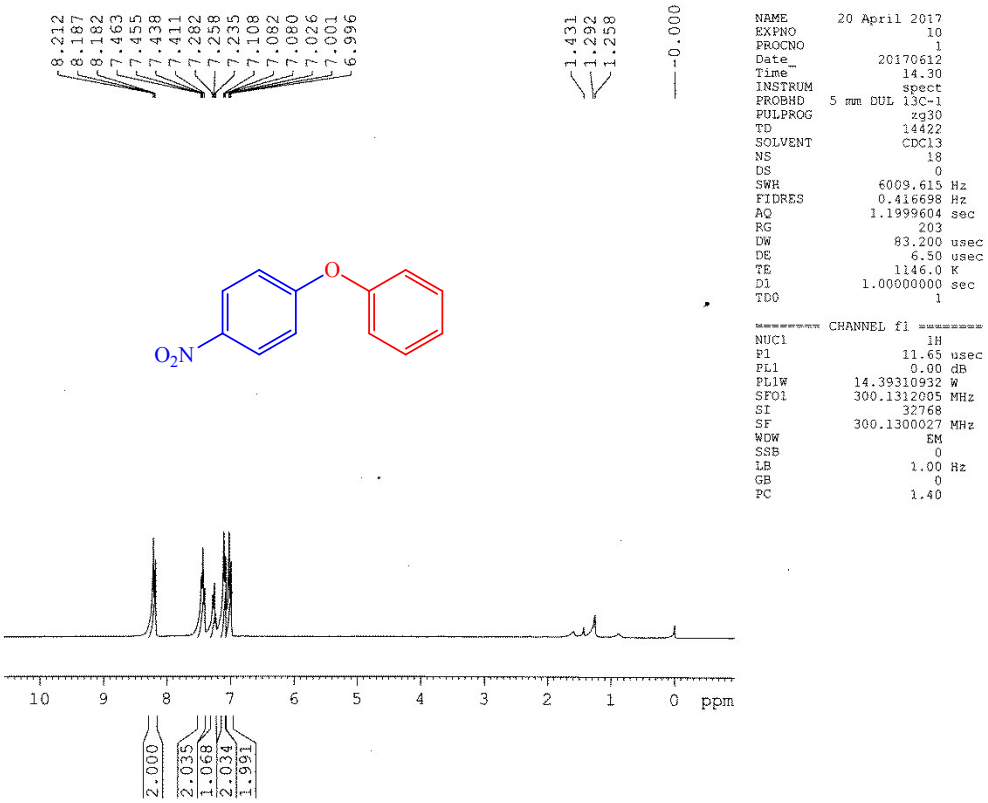


Figure S37. ^{1}H NMR of 1−Nitro-4-phenoxybenzene

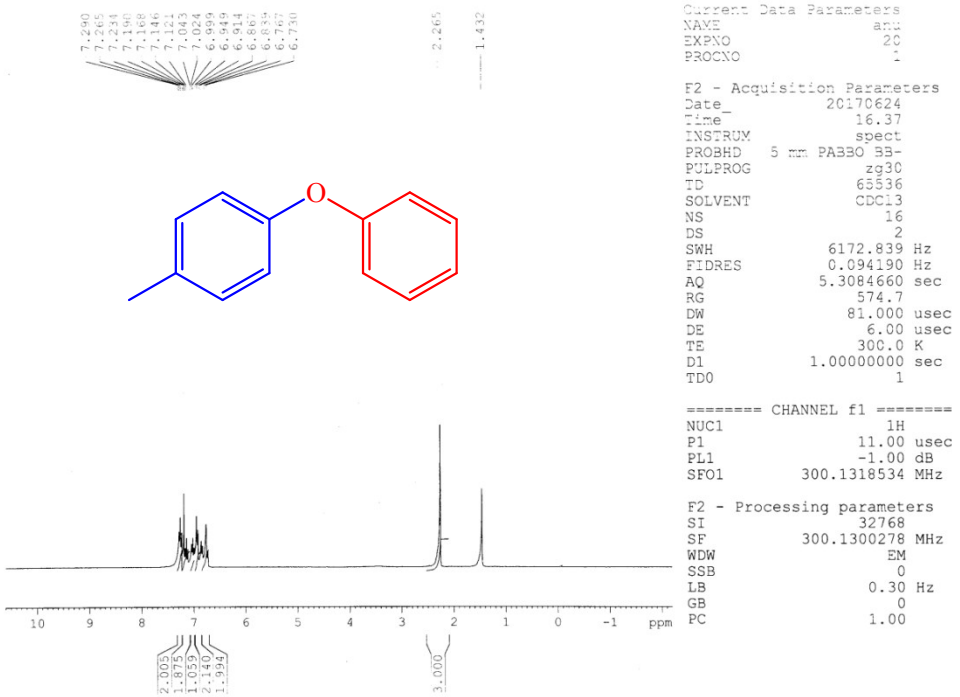


Figure S38. ^{1}H NMR of 1−Methyl-4-phenoxybenzene

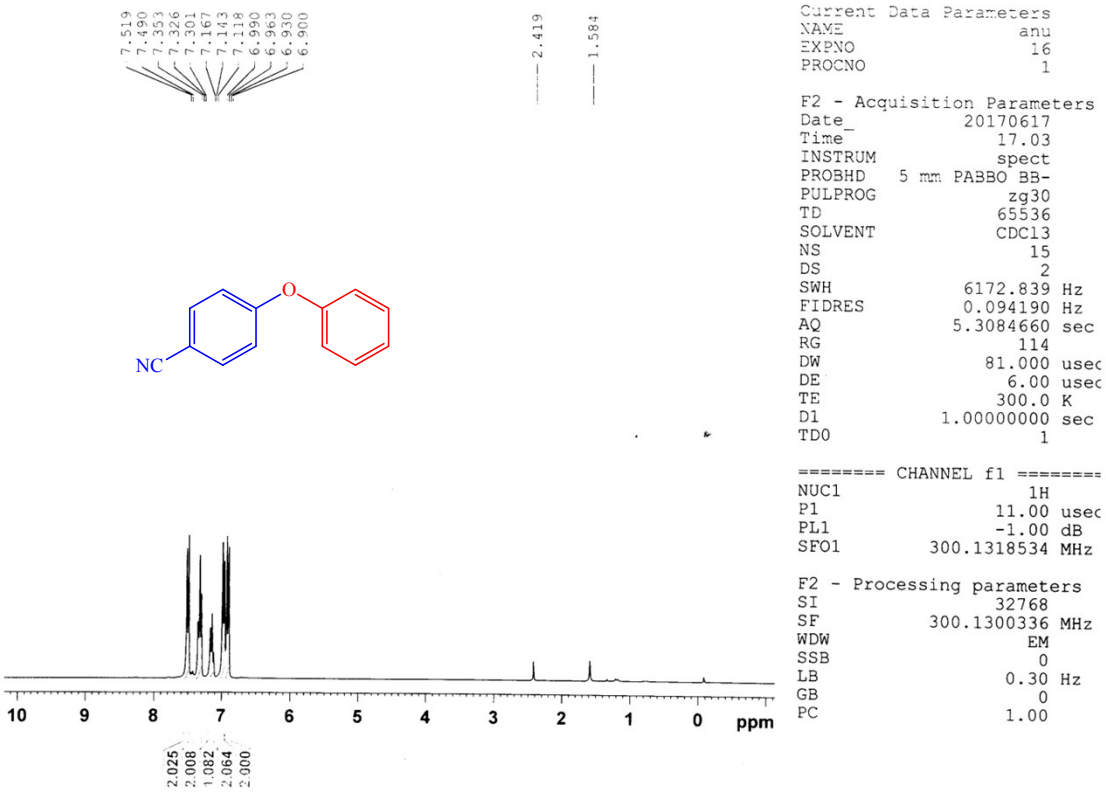


Figure S39. ^{1}H NMR of 4−phenoxybenzonitrile

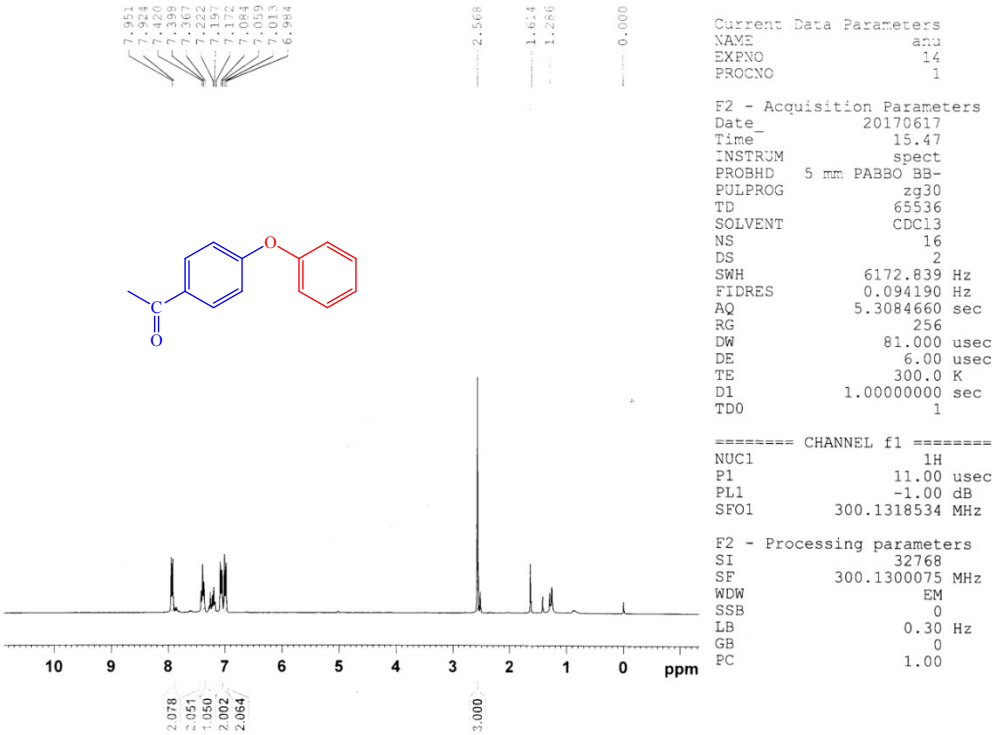


Figure S40. ^{1}H NMR of 1− (4-phenoxyphenyl)ethanone

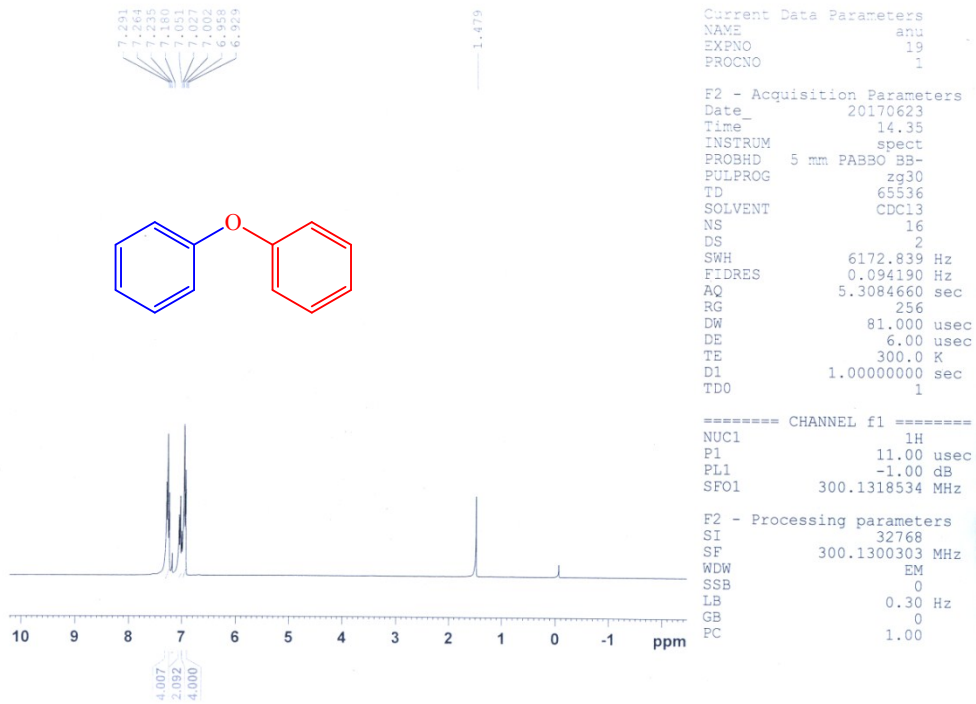


Figure S41. ^{1}H NMR of Diphenyl ether

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