Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Palladium(II)-complexes of bi- and tri-dentate phosphines ligands: Precursor for palladium-phosphorous nanoparticles and activity towards Suzuki-Miyaura coupling

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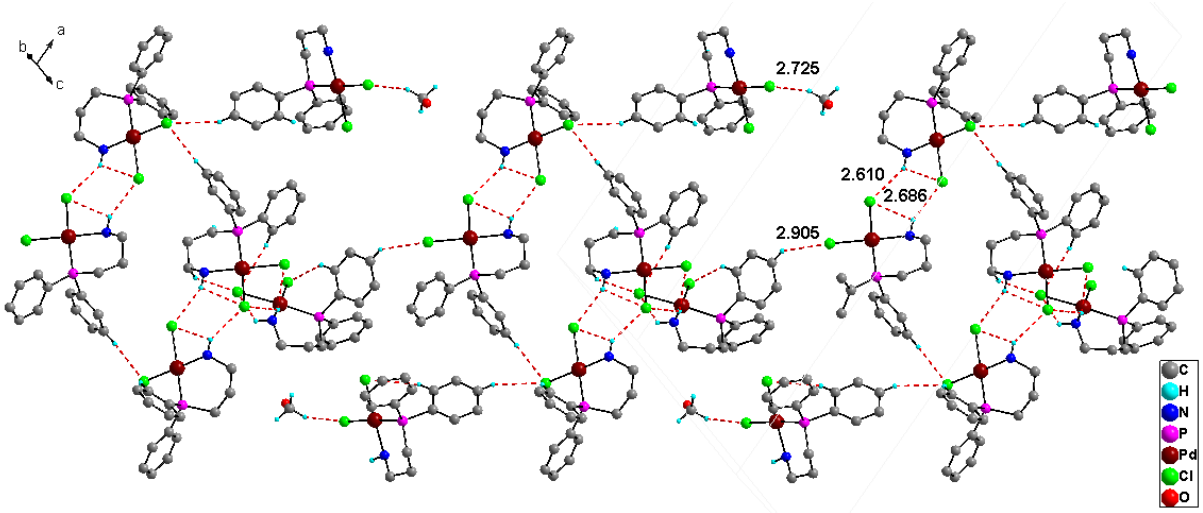


Fig. S1. Intra and intermolecular Cl···H and N–H···Cl interactions of complex **1.**

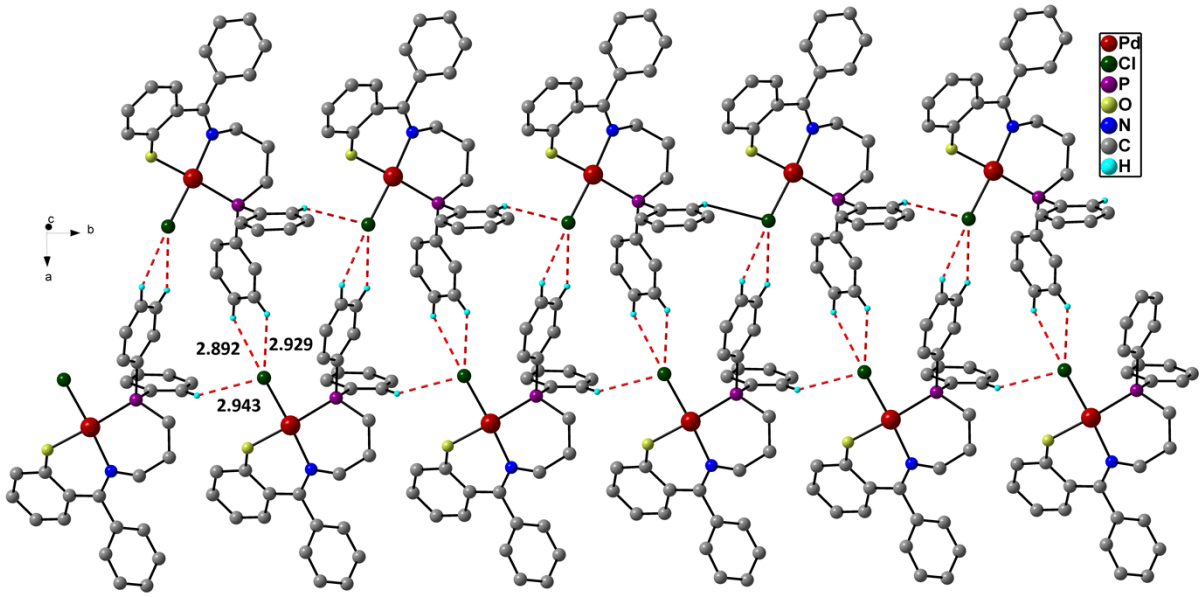


Fig. S2. Molecular packing of **2** showing Cl···H (aromatic) interaction.

Table S1. Crystal data and structure refinement parameters for **1** and **2**

	1	**2**
Empirical formula	C_{15} H_{17} Cl_2 N P Pd	$C_{28}H_{25}ClNOPPd$
Formula weight	419.57	564.31
Colour	Orange	Red
Crystal size, mm^3	0.343 × 0.290 × 0.225	0.370 × 0.312 × 0.295
Crystal system	Monoclinic	Monoclinic
Space group	*C 2/c*	*P 21/n*
Unit Cell dimension	*a* = 34.786(10) Å *b* = 12.983(4) Å *c* = 17.594(5) Å *α* = 90.00° *β* = 107.457(5)° *γ* = 90.00°	*a* = 12.606(3) Å *b* = 8.4228(19) Å *c* = 22.778(5) Å *α* = 90.00° *β* = 96.878(5)° *γ* = 90.00°
Volume [$Å^3$]	7580(4)	2401.0(9)
Z	16	4
ρ, (calc.) Mg/m^3	1.471	1.561
μ, mm^{-1}	1.336	0.973
F(000)	3344	1144
θ, range (°)	1.68 to 25.00	1.8 to 25.00
Index ranges	$-41 \le h \le 41$ $-15 \le k \le 15$ $-20 \le l \le 20$	$-13 \le h \le 14$ $-10 \le k \le 9$ $-27 \le l \le 25$
Reflections collected	34521	12118
Independent reflections($R_{int.}$)	6673 [R_{int} = 0.0744]	4206 [*R(int)* = 0.0707]
Completeness to max. θ, %	99.8	99.8
Data/restraints/ parameters	6673 / 0 / 361	4196 / 0 / 298
Goodness–of–fit on F^2	1.079	0.939

Final R indices [I >2σ(I)]	R_1 = 0.0589, wR_2 = 0.1226	R_1 = 0.0466 wR_2 = 0.0908
R indices (all data)	R_1 = 0.0785, wR_2 = 0.1313	R_1 = 0.0649, wR_2 = 0.0964
Largest diff. peak/hole [e.Å^{-3}]	1.01/−0.69	1.07/−0.85
CCDC No.	2225178	2225179

Table S2. Selected bond lengths (Å) and bond angles (°) of **1**

Bond Length (Å)			
Pd(2)-Pd(2)	2.2223(17)	C(10)-C(10)	1.380(9)
Pd(2)-Pd(2)	2.3923(17)	C(18)-C(18)	1.544(9)
Pd(2)-Pd(2)	2.2903(17)	C(25)-C(25)	1.385(9)
Pd(2)-Pd(2)	2.072(5)	C(25)-C(25)	1.383(9)
Pd(1)-Pd(1)	2.2250(16)	C(19)-C(19)	1.375(8)
Pd(1)-Pd(1)	2.294(2)	C(19)-C(19)	1.395(8)
Pd(1)-Pd(1)	2.3865(18)	C(23)-C(23)	1.383(9)
Pd(1)-Pd(1)	2.053(6)	C(23)-C(23)	1.369(10)
P(2)-P(2)	1.813(6)	C(14)-C(14)	1.386(10)
P(2)-P(2)	1.814(6)	C(14)-C(14)	1.357(12)
P(2)-P(2)	1.810(7)	C(12)-C(12)	1.333(12)
P(4)-P(4)	1.820(6)	C(12)-C(12)	1.395(10)
P(4)-P(4)	1.806(7)	C(16)-C(16)	1.498(9)
P(4)-P(4)	1.819(6)	C(26)-C(26)	1.380(10)
C(4)-C(4)	1.394(9)	C(1)-C(1)	1.496(10)
C(4)-C(4)	1.375(9)	C(9)-C(9)	1.384(10)
N(2)-N(2)	1.471(8)	C(7)-C(7)	1.353(11)
N(1)-N(1)	1.475(9)	C(22)-C(22)	1.372(10)
C(6)-C(6)	1.374(9)	C(30)-C(30)	1.391(9)
C(6)-C(6)	1.384(11)	C(29)-C(29)	1.360(11)
C(3)-C(3)	1.528(9)	C(28)-C(28)	1.374(12)
C(10)-C(10)	1.375(9)	C(21)-C(21)	1.397(10)
Bond Angle (°)			
P(2)-Pd(2)-Cl(3)	173.83(6)	C(15)-C(10)-C(11)	119.1(6)
P(2)-Pd(2)-Cl(4)	91.21(6)	C(11)-C(10)-P(4)	122.0(6)
Cl(4)-Pd(2)-Cl(3)	92.47(6)	C(17)-C(18)-P(2)	114.0(4)
N(2)-Pd(2)-P(2)	90.02(15)	C(26)-C(25)-P(2)	121.7(5)
N(2)-Pd(2)-Cl(3)	86.34(15)	C(30)-C(25)-P(2)	118.8(5)
N(2)-Pd(2)-Cl(4)	178.71(16)	C(30)-C(25)-C(26)	119.4(6)
P(4)-Pd(1)-Cl(1)	90.35(7)	C(6)-C(5)-C(4)	120.7(7)
P(4)-Pd(1)-Cl(2)	176.77(8)	C(24)-C(19)-P(2)	118.9(4)
Cl(1)-Pd(1)-Cl(2)	92.50(8)	C(24)-C(19)-C(20)	118.3(6)
N(1)-Pd(1)-P(4)	91.76(17)	C(20)-C(19)-P(2)	122.9(5)
N(1)-Pd(1)-Cl(1)	174.92(18)	C(22)-C(23)-C(24)	119.7(7)
N(1)-Pd(1)-Cl(2)	85.52(17)	C(19)-C(24)-C(23)	121.4(6)
C(18)-P(2)-Pd(2)	110.1(2)	C(13)-C(14)-C(15)	119.9(9)
C(18)-P(2)-C(25)	104.3(3)	C(13)-C(12)-C(11)	120.8(8)
C(25)-P(2)-Pd(2)	119.4(2)	N(2)-C(16)-C(17)	114.3(6)
C(19)-P(2)-Pd(2)	108.0(2)	C(27)-C(26)-C(25)	119.8(7)
C(19)-P(2)-C(18)	107.8(3)	C(16)-C(17)-C(18)	112.9(5)
C(19)-P(2)-C(25)	106.6(3)	N(1)-C(1)-C(2)	112.7(6)
C(4)-P(4)-Pd(1)	116.9(2)	C(4)-C(9)-C(8)	121.0(7)
C(3)-P(4)-Pd(1)	111.0(2)	C(8)-C(7)-C(6)	120.3(7)
C(3)-P(4)-C(4)	102.1(3)	C(23)-C(22)-C(21)	120.6(7)

C(3)-P(4)-C(10)	107.1(3)	C(25)-C(30)-C(29)	120.0(7)
C(10)-P(4)-Pd(1)	112.1(2)	C(10)-C(15)-C(14)	120.2(7)
C(10)-P(4)-C(4)	106.8(3)	C(7)-C(8)-C(9)	120.1(8)
C(5)-C(4)-P(4)	118.8(5)	C(12)-C(13)-C(14)	120.8(7)
C(9)-C(4)-P(4)	122.9(5)	C(28)-C(29)-C(30)	120.2(8)
C(9)-C(4)-C(5)	118.2(6)	C(29)-C(28)-C(27)	120.1(8)
C(16)-N(2)-Pd(2)	121.6(4)	C(1)-C(2)-C(3)	114.9(6)
C(1)-N(1)-Pd(1)	126.0(4)	C(22)-C(21)-C(20)	119.6(6)
C(5)-C(6)-C(7)	119.6(7)	C(28)-C(27)-C(26)	120.5(8)
C(2)-C(3)-P(4)	114.3(5)	C(10)-C(11)-C(12)	119.3(8)
C(15)-C(10)-P(4)	118.9(5)	C(19)-C(20)-C(21)	120.4(6)

Table S3. Selected bond lengths (Å) and bond angles (°) of **2**

Bond Length (Å)			
Pd(1)-Cl(1)	2.2791(13)	C(24)-C(25)	1.409(6)
Pd(1)-P(1)	2.2376(13)	C(17)-C(22)	1.389(6)
Pd(1)-O(1)	2.039(3)	C(17)-C(18)	1.385(6)
Pd(1)-N(1)	2.034(4)	C(25)-C(26)	1.369(6)
P(1)-C(13)	1.813(4)	C(28)-C(27)	1.371(6)
P(1)-C(12)	1.823(5)	C(22)-C(21)	1.382(7)
P(1)-C(6)	1.815(5)	C(26)-C(27)	1.384(7)
O(1)-C(24)	1.313(5)	C(6)-C(1)	1.377(6)
N(1)-C(16)	1.306(5)	C(6)-C(5)	1.392(6)
N(1)-C(15)	1.490(5)	C(4)-C(5)	1.380(7)
C(16)-C(23)	1.472(6)	C(4)-C(3)	1.372(7)
C(16)-C(17)	1.504(6)	C(1)-C(2)	1.384(7)
C(23)-C(24)	1.426(6)	C(8)-C(9)	1.366(8)
C(23)-C(28)	1.405(6)	C(18)-C(19)	1.358(7)
C(7)-C(12)	1.376(6)	C(9)-C(10)	1.358(7)
C(7)-C(8)	1.385(7)	C(10)-C(11)	1.391(6)
C(13)-C(14)	1.526(6)	C(19)-C(20)	1.381(8)
C(14)-C(15)	1.518(6)	C(20)-C(21)	1.361(8)
C(12)-C(11)	1.381(6)	C(3)-C(2)	1.363(7)
Bond Angles (°)			
P(1)-Pd(1)-Cl(1)	88.38(5)	C(23)-C(24)-O(1)	123.5(4)
O(1)-Pd(1)-Cl(1)	88.35(9)	C(25)-C(24)-O(1)	119.2(4)
O(1)-Pd(1)-P(1)	175.25(9)	C(25)-C(24)-C(23)	117.3(4)
N(1)-Pd(1)-Cl(1)	176.19(11)	C(14)-C(15)-N(1)	113.0(3)
N(1)-Pd(1)-P(1)	95.40(11)	C(22)-C(17)-C(16)	120.9(4)
N(1)-Pd(1)-O(1)	87.85(13)	C(18)-C(17)-C(16)	119.3(4)
C(13)-P(1)-Pd(1)	111.86(15)	C(18)-C(17)-C(22)	119.6(5)
C(12)-P(1)-Pd(1)	111.31(15)	C(26)-C(25)-C(24)	121.8(5)
C(12)-P(1)-C(13)	106.5(2)	C(27)-C(28)-C(23)	122.4(5)
C(6)-P(1)-Pd(1)	118.71(16)	C(21)-C(22)-C(17)	118.8(5)
C(6)-P(1)-C(13)	102.0(2)	C(27)-C(26)-C(25)	121.1(5)
C(6)-P(1)-C(12)	105.5(2)	C(1)-C(6)-P(1)	122.2(4)
C(24)-O(1)-Pd(1)	116.7(3)	C(5)-C(6)-P(1)	119.5(4)
C(16)-N(1)-Pd(1)	122.8(3)	C(5)-C(6)-C(1)	118.2(4)
C(15)-N(1)-Pd(1)	118.5(3)	C(3)-C(4)-C(5)	120.6(5)
C(15)-N(1)-C(16)	118.4(4)	C(26)-C(27)-C(28)	118.6(4)
C(23)-C(16)-N(1)	123.9(4)	C(2)-C(1)-C(6)	120.8(5)
C(17)-C(16)-N(1)	121.5(4)	C(4)-C(5)-C(6)	120.4(5)
C(17)-C(16)-C(23)	114.5(4)	C(9)-C(8)-C(7)	119.7(5)
C(24)-C(23)-C(16)	122.1(4)	C(19)-C(18)-C(17)	120.2(5)
C(28)-C(23)-C(16)	119.1(4)	C(10)-C(9)-C(8)	120.9(5)
C(28)-C(23)-C(24)	118.8(4)	C(11)-C(10)-C(9)	119.7(5)
C(8)-C(7)-C(12)	120.3(5)	C(20)-C(19)-C(18)	120.8(5)
C(14)-C(13)-P(1)	113.4(3)	C(21)-C(20)-C(19)	119.1(5)

C(15)-C(14)-C(13)	112.9(4)	C(10)-C(11)-C(12)	120.1(5)
C(7)-C(12)-P(1)	121.8(4)	C(2)-C(3)-C(4)	119.5(5)
C(11)-C(12)-P(1)	119.0(4)	C(20)-C(21)-C(22)	121.4(5)
C(11)-C(12)-C(7)	119.2(4)	C(3)-C(2)-C(1)	120.5(5)

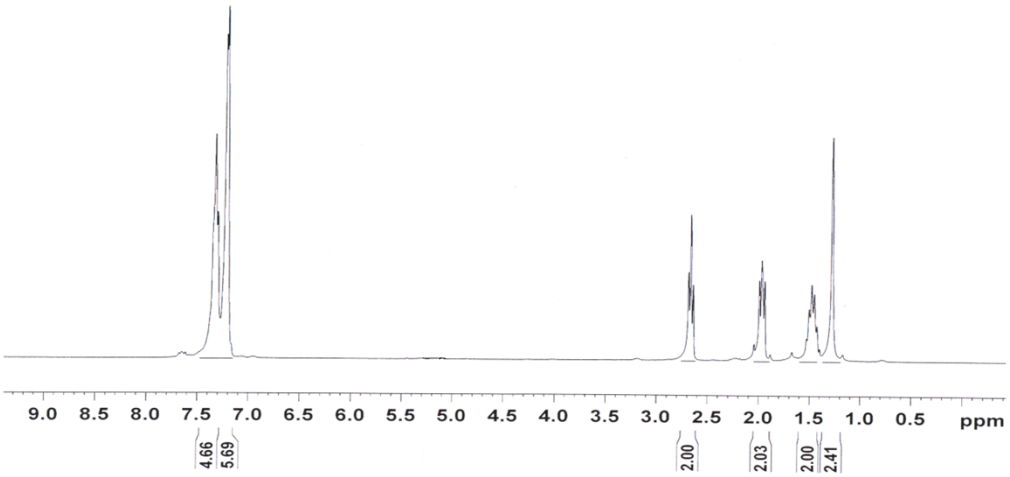


Fig. S3. ^{1}H NMR Spectra of ligand **L1**

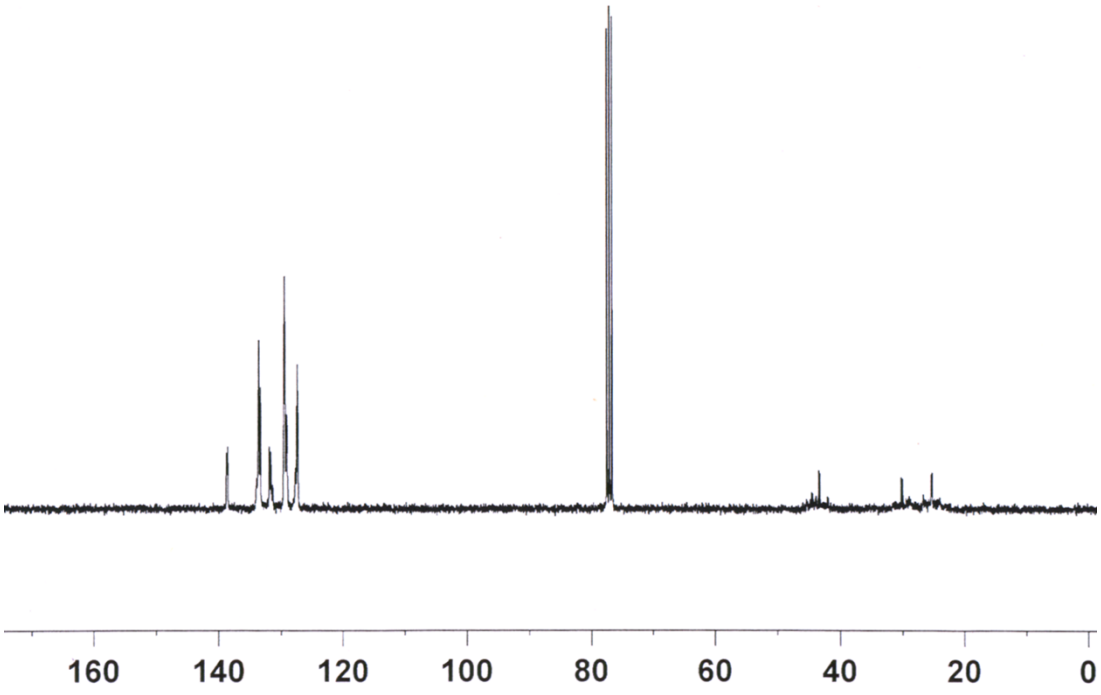


Fig. S4. ^{13}C{^{1}H} NMR Spectra of ligand **L1**

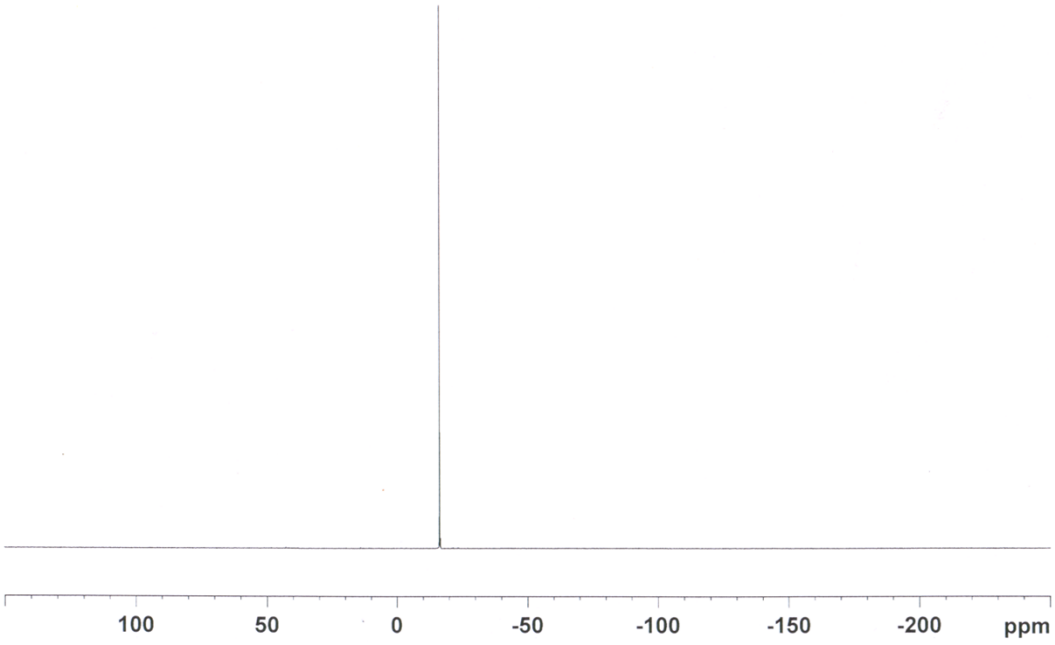


Fig. S5. $^{31}P\{^{1}H\}$ NMR Spectra of ligand **L1**

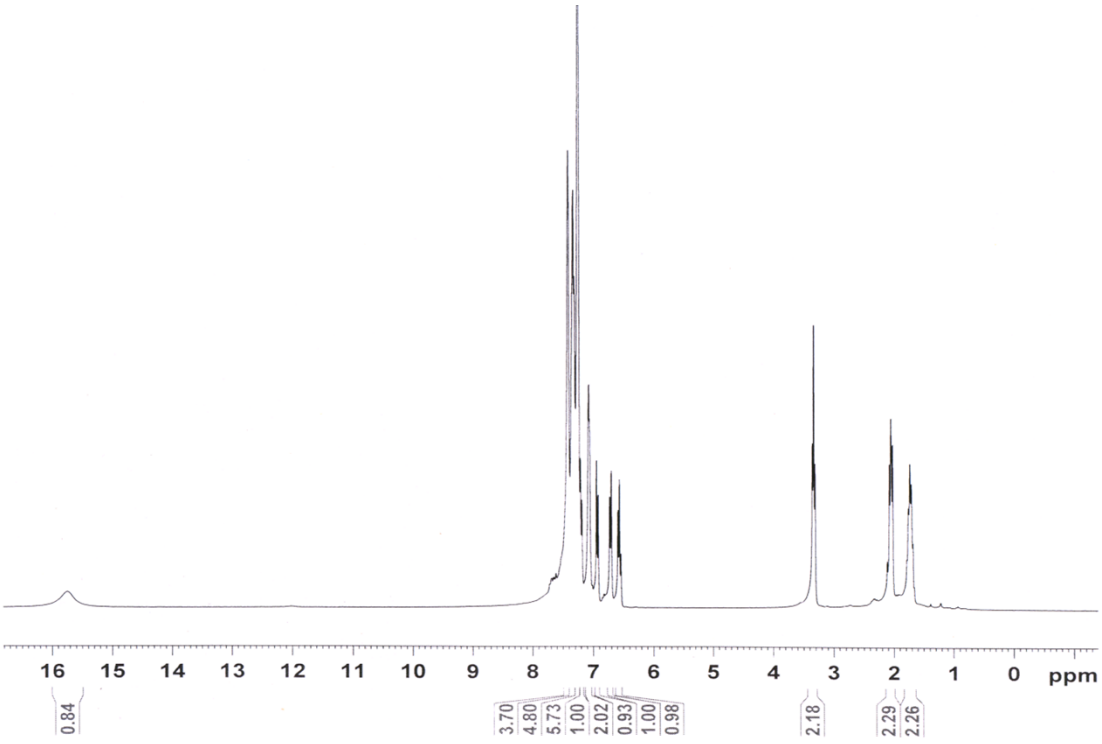


Fig. S6. ^{1}H NMR Spectra of ligand **L2**

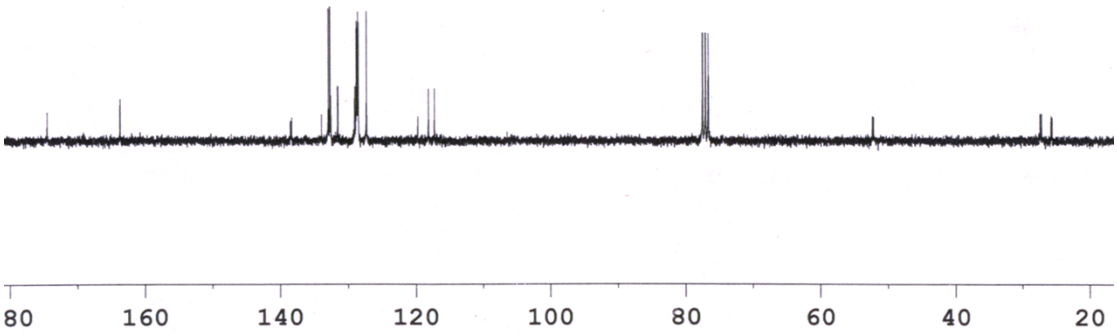


Fig. S7. $^{13}C\{^{1}H\}$ NMR Spectra of ligand **L2**

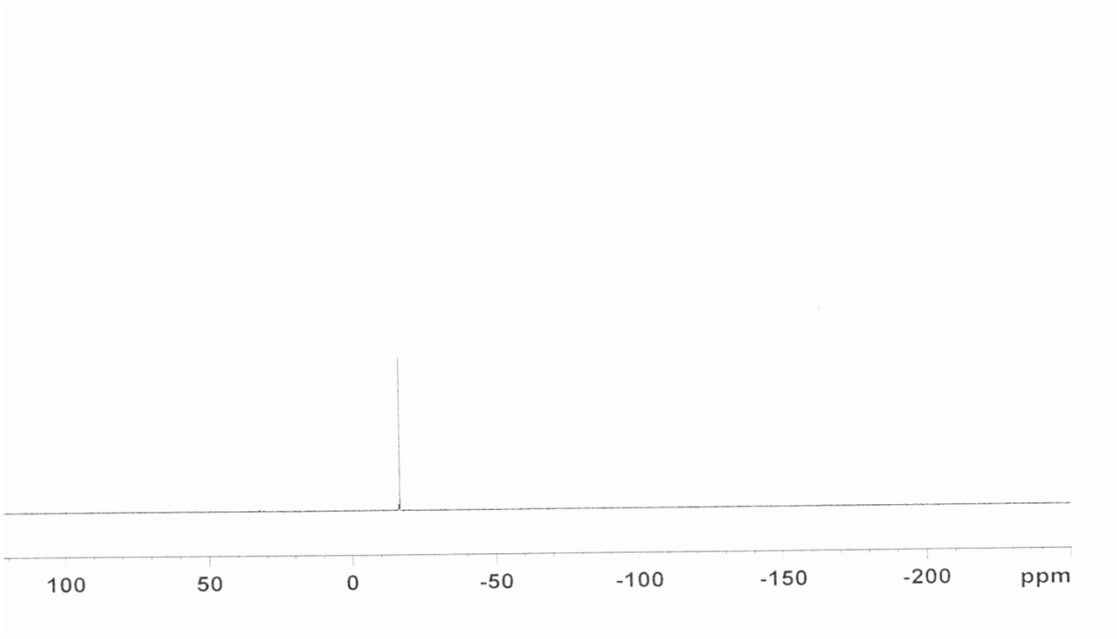


Fig. S8. $^{31}P\{^{1}H\}$ NMR Spectra of ligand **L2**

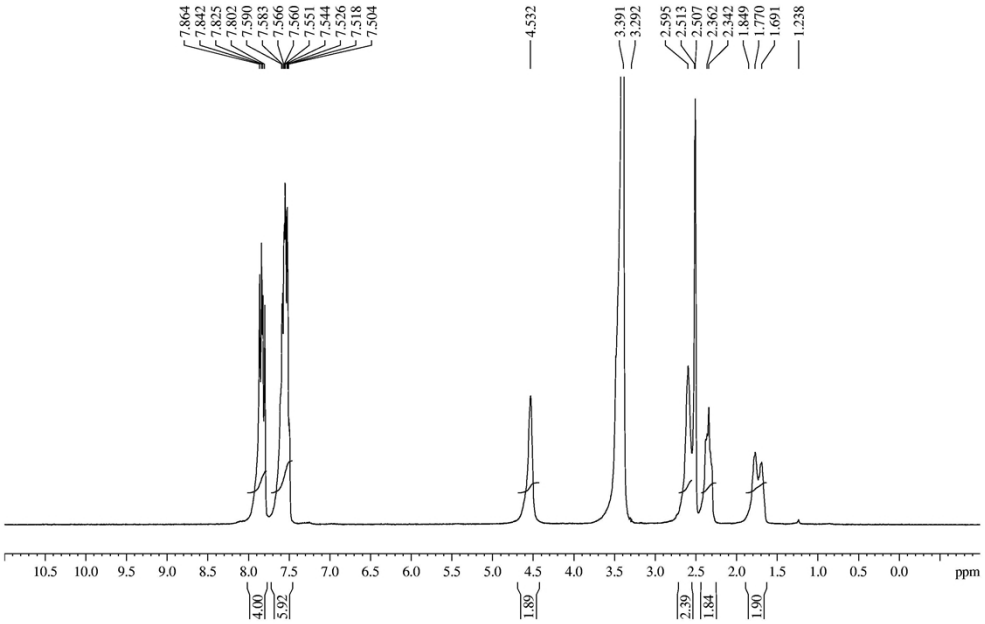


Fig. S9. ^{1}H NMR Spectra of complex **1**

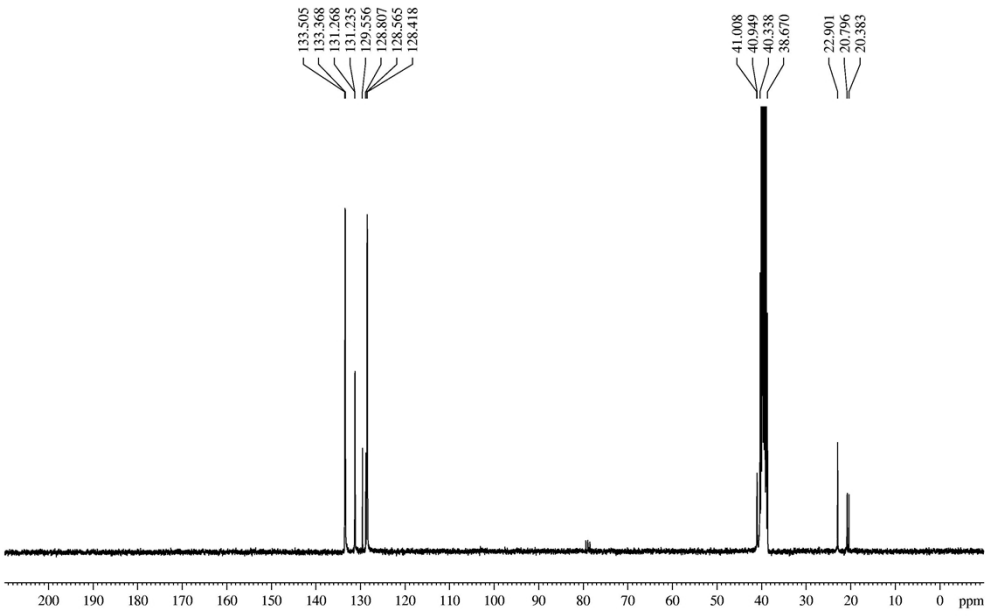


Fig. S10. $^{13}C\{^{1}H\}$ NMR Spectra of complex **1**

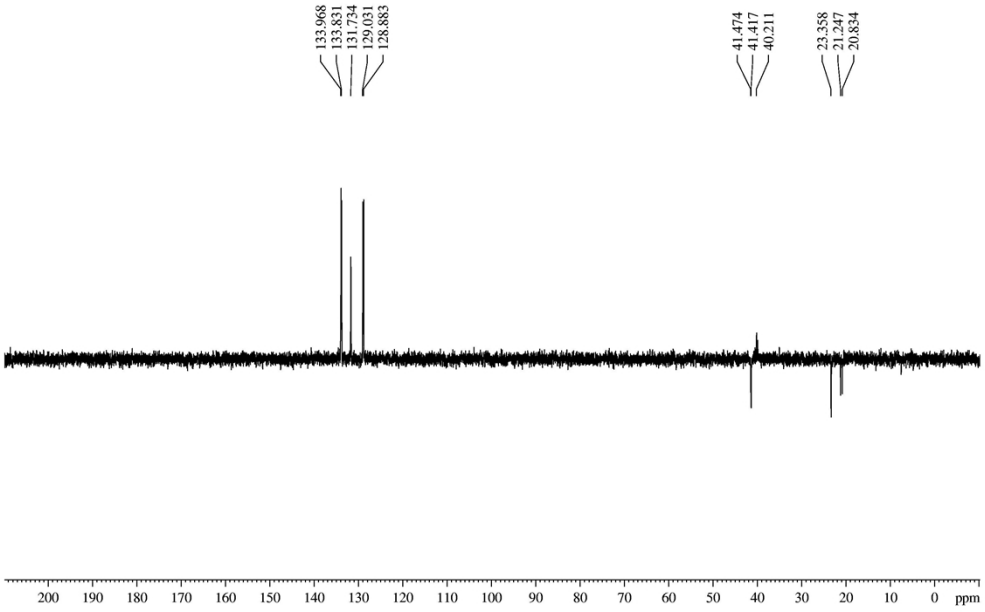


Fig. S11. DEPT-135 NMR Spectra of complex **1**

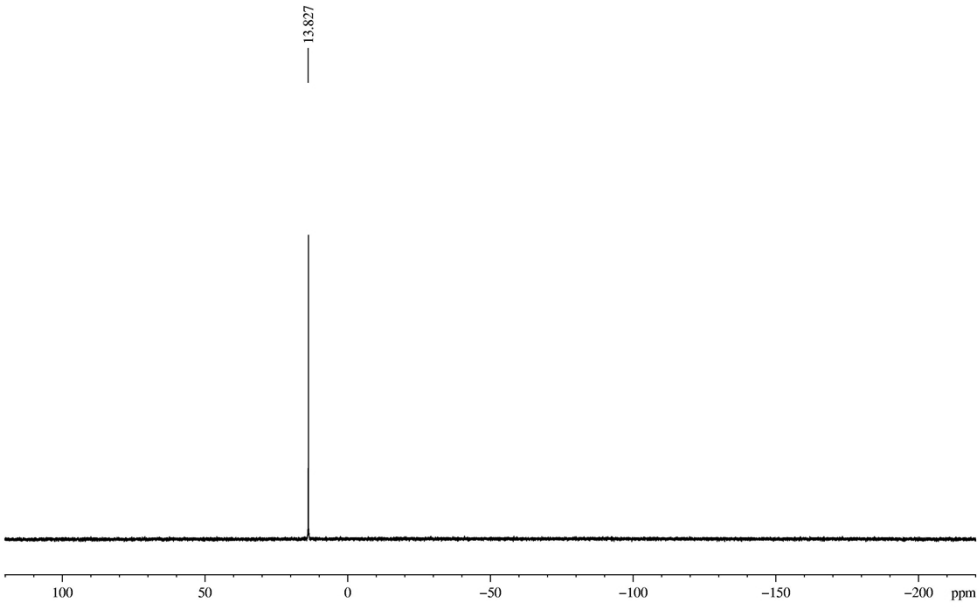


Fig. S12. $^{31}P\{^{1}H\}$ NMR Spectra of complex **1**

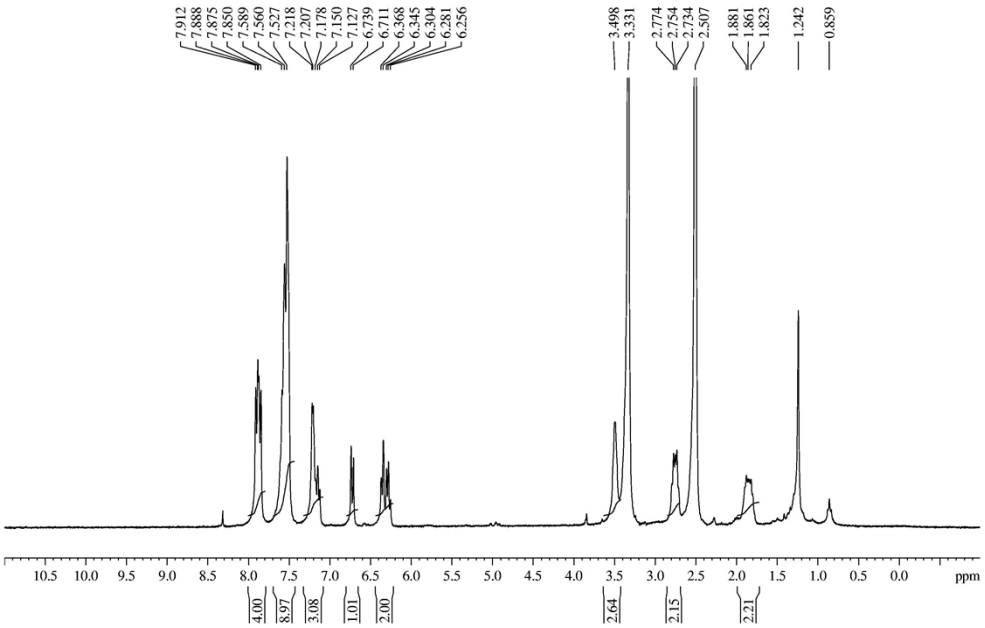


Fig. S13. ^{1}H NMR Spectra of complex **2**

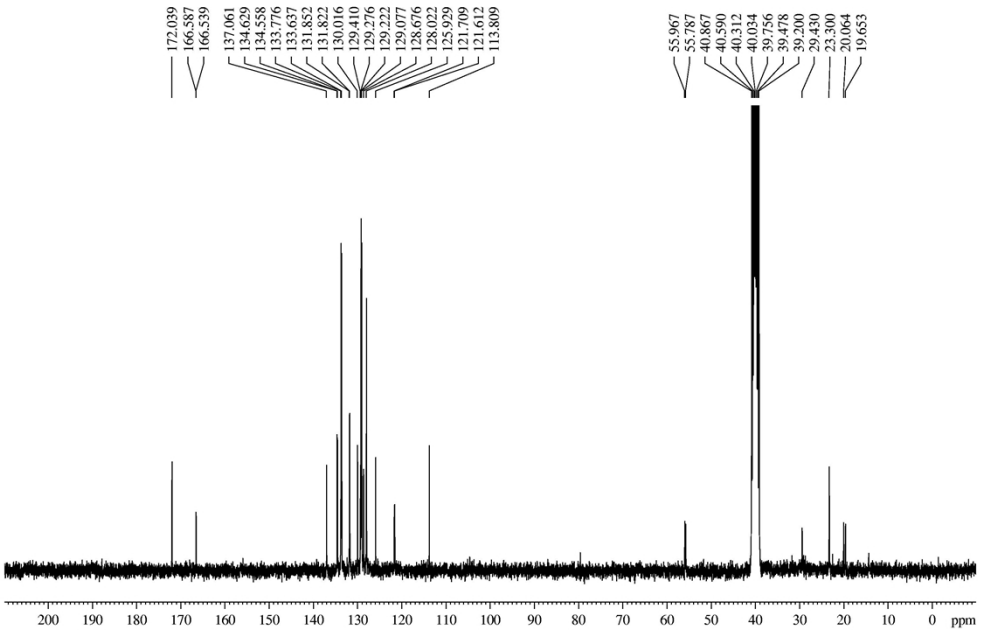


Fig. S14. $^{13}C\{^{1}H\}$ NMR Spectra of complex **2**

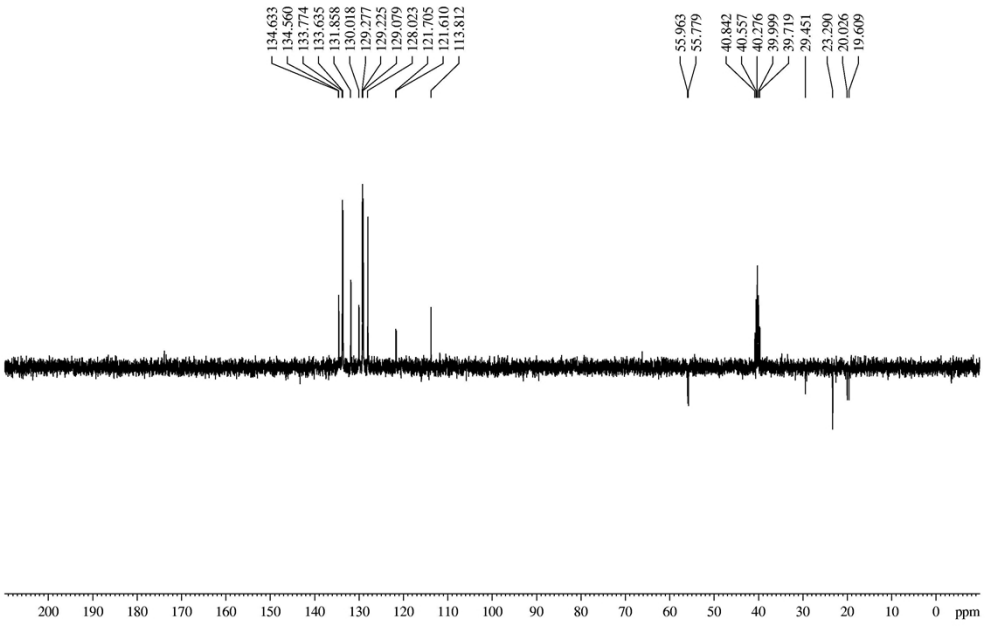


Fig. S15. DEPT-135 NMR Spectra of complex **2**

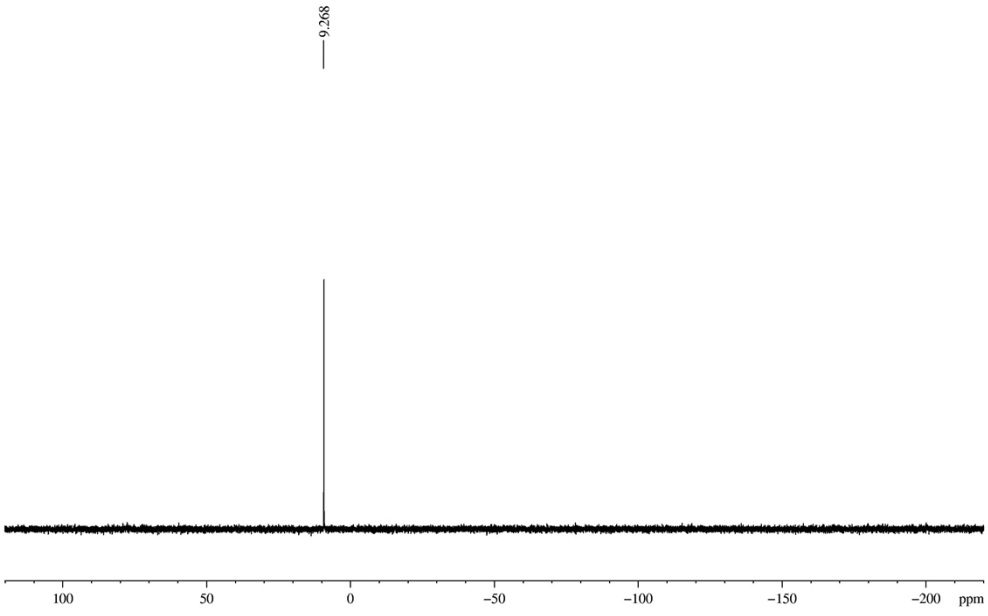


Fig. S16. $^{31}P\{^{1}H\}$ NMR Spectra of complex **2**

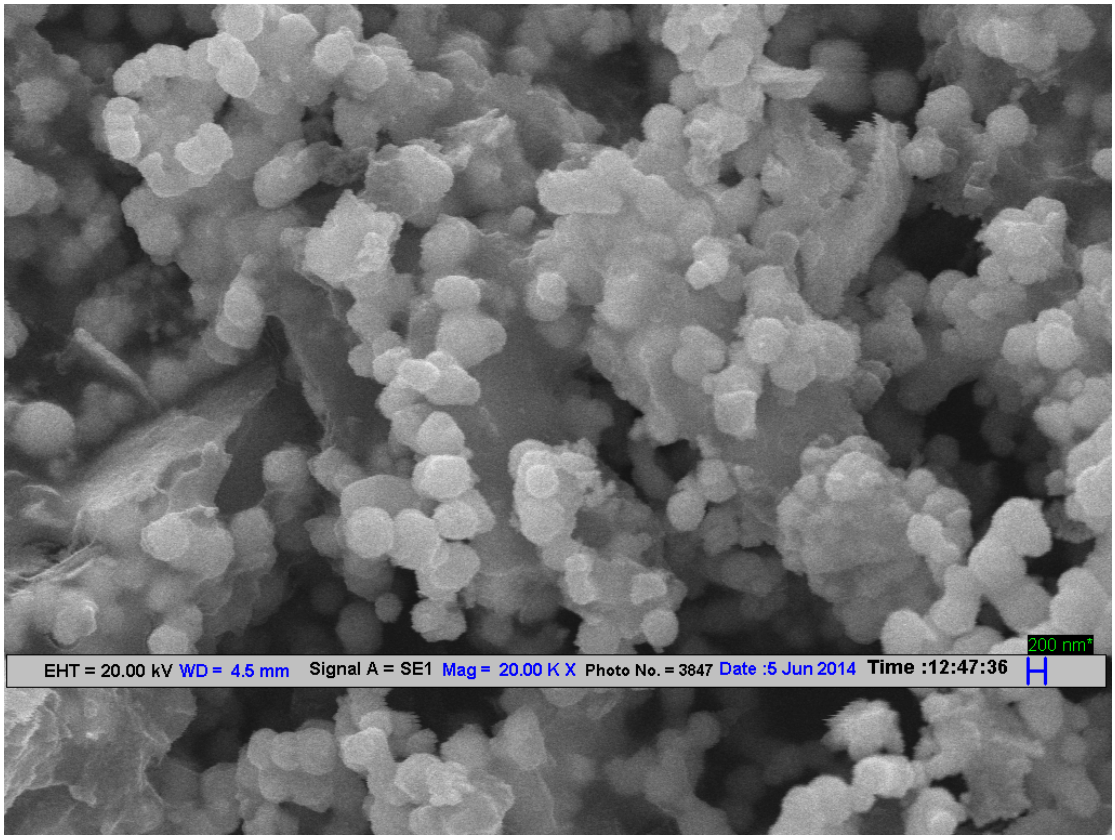


Figure S17. SEM image of Pd_7P_3 NPs obtained from complex **1**

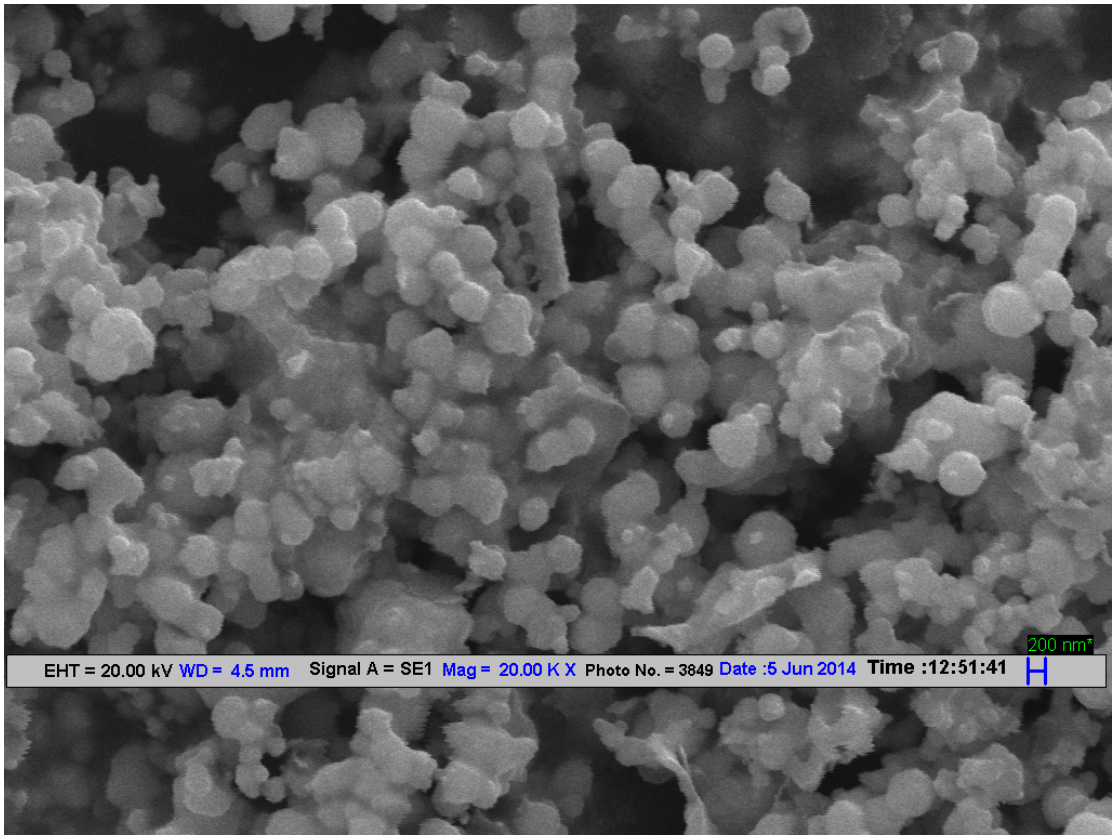
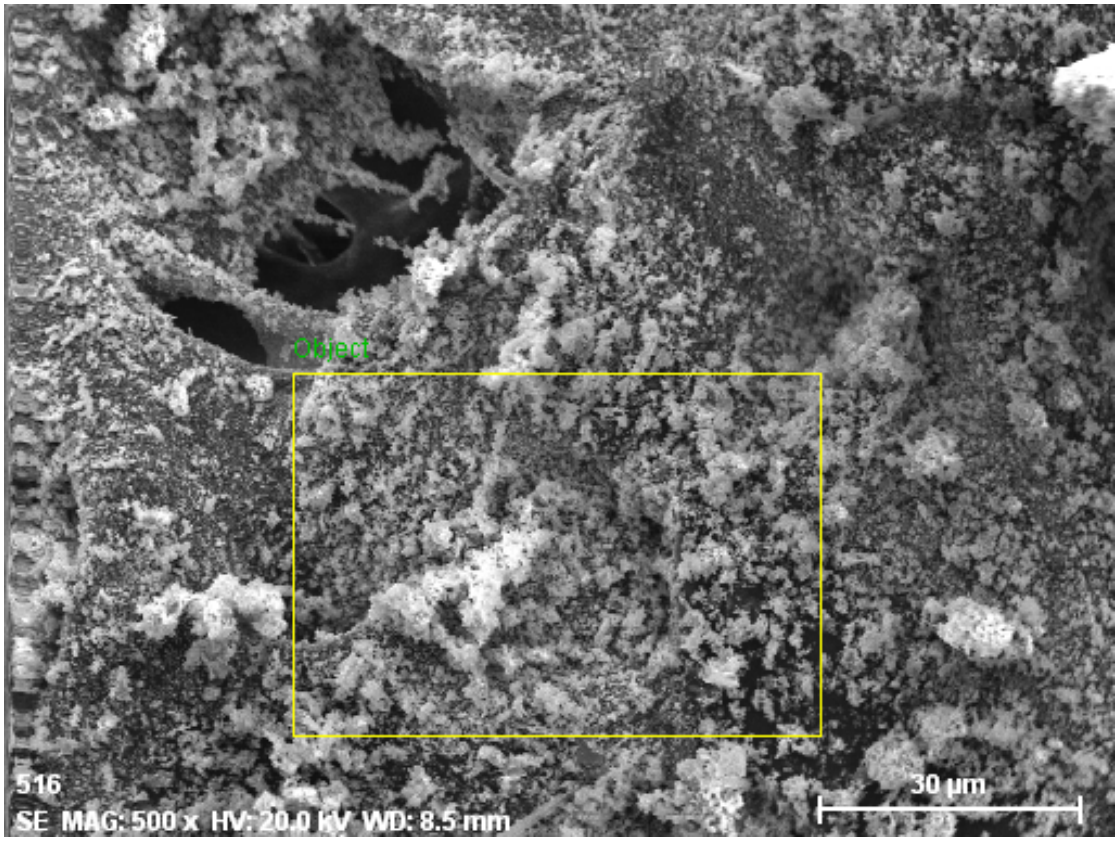


Fig. S18. SEM image of $Pd_3P_{0.8}$ NPs obtained from complex **2**



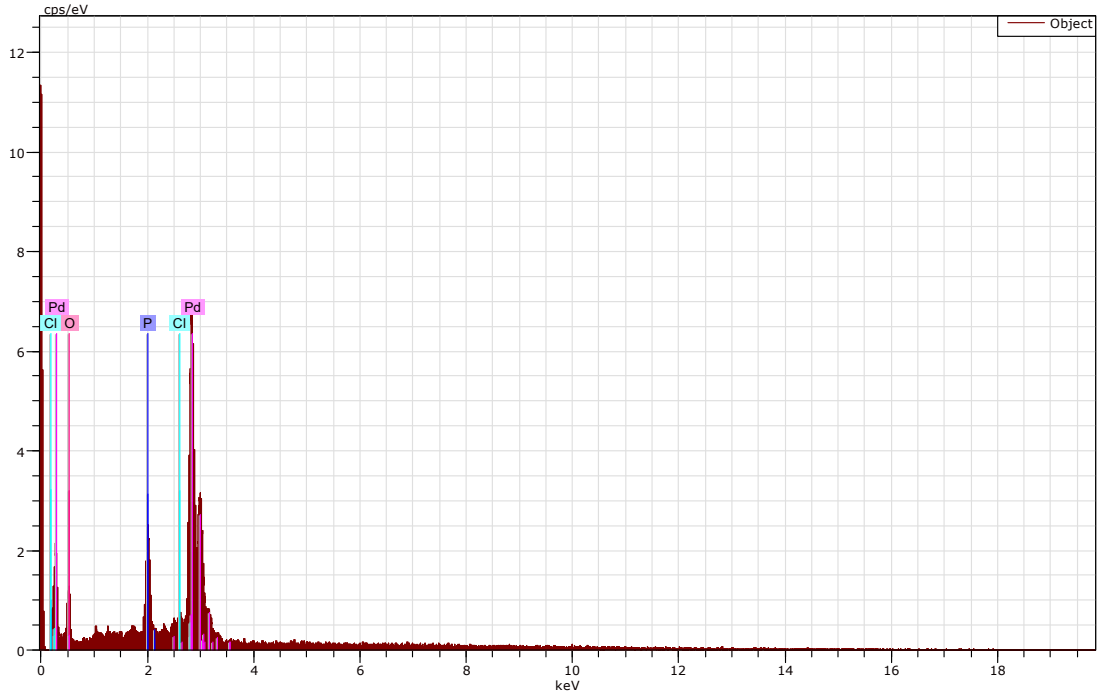
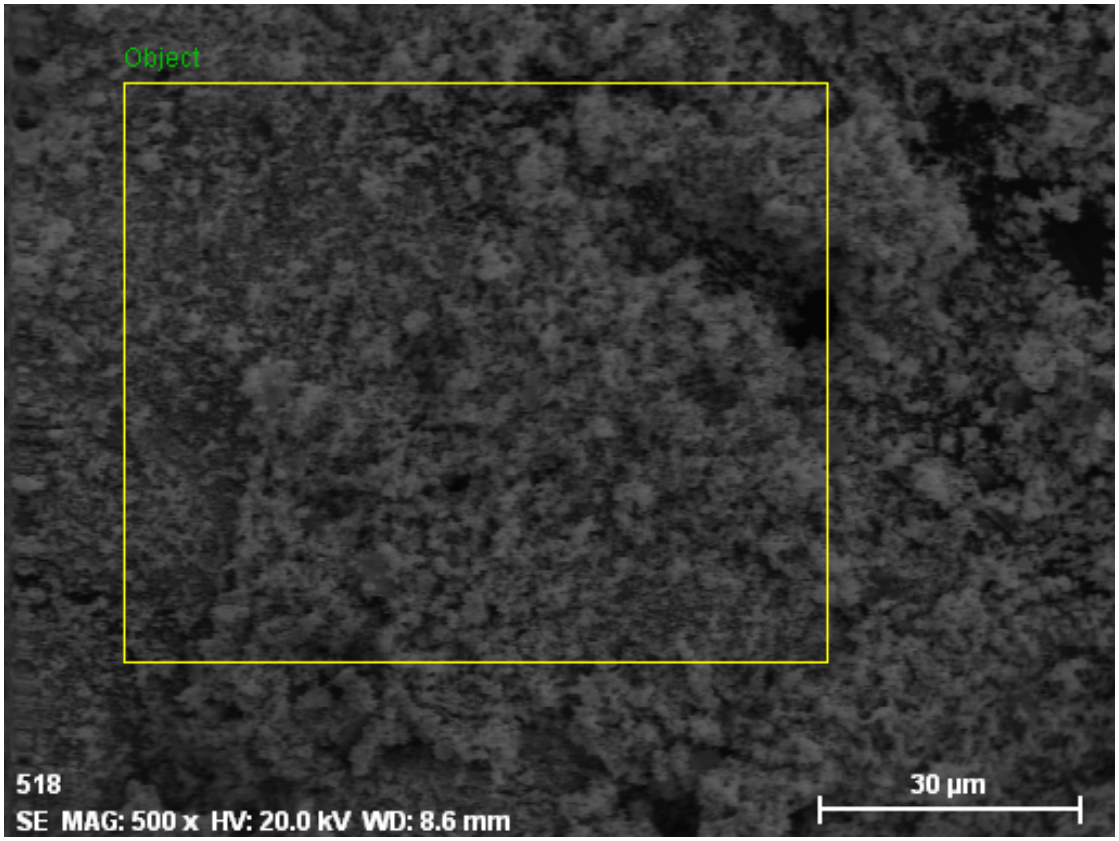


Fig. S19. SEM-EDX of Pd_7P_3 NPs obtained from complex **1**



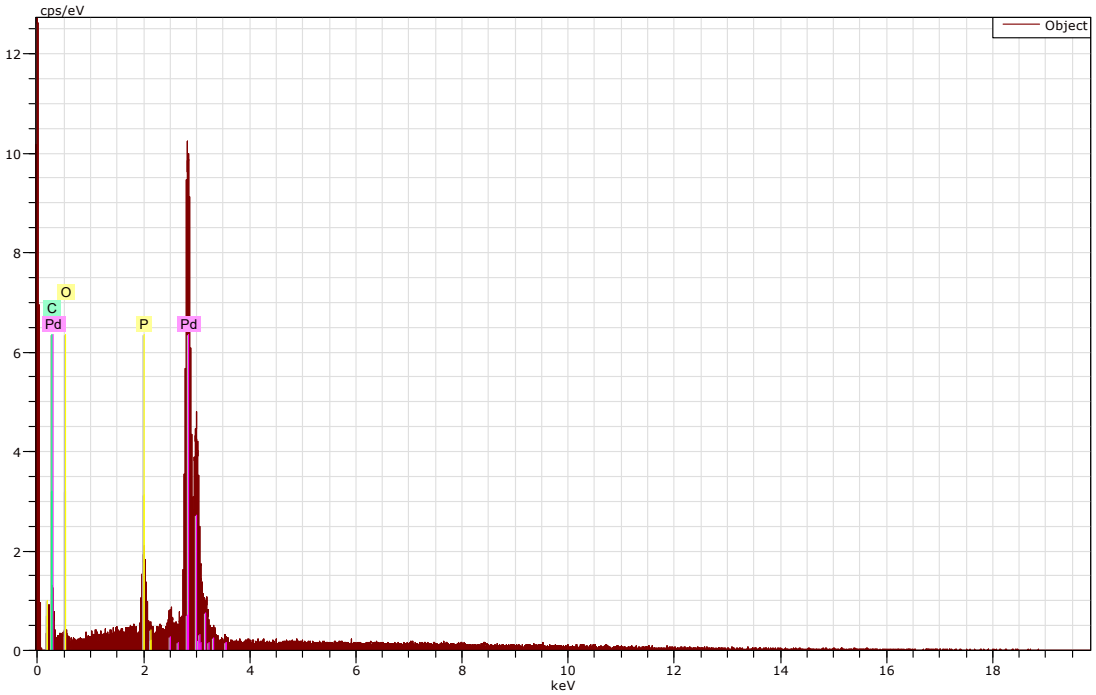


Fig. S20. SEM-EDX of $Pd_3P_{0.8}$ NPs obtained from complex **2**

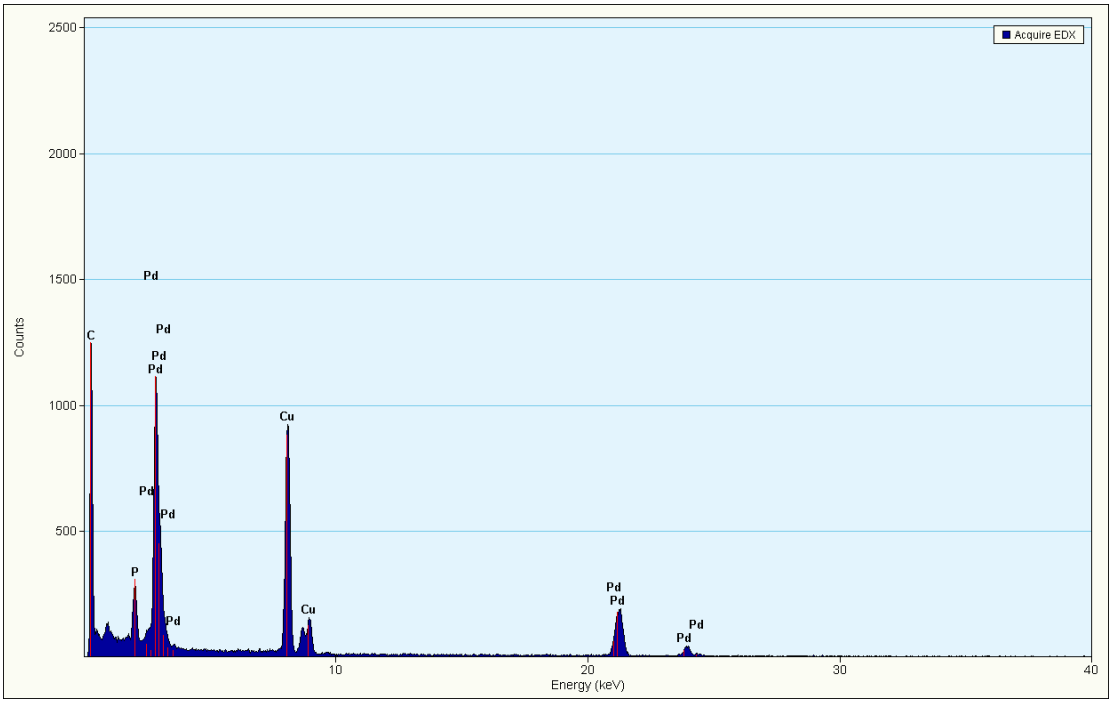


Fig. S21. TEM-EDX of Pd_7P_3 NPs obtained from complex **1**

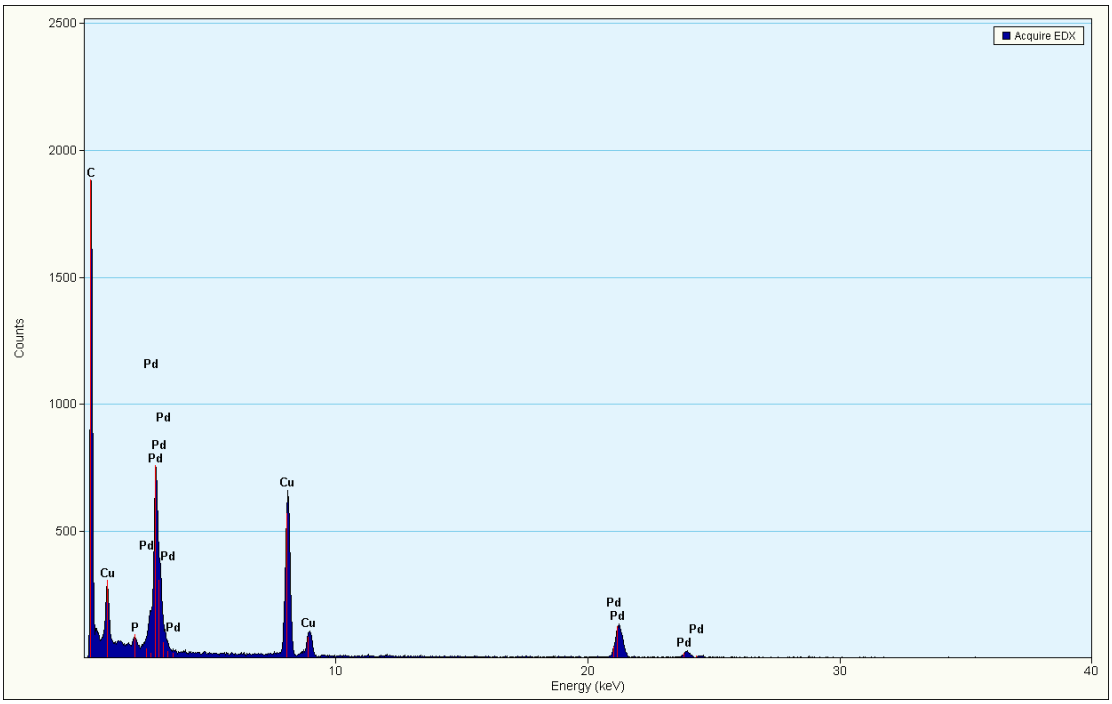


Fig. S22. TEM-EDX of $Pd_3P_{0.8}$ NPs obtained from complex **2**

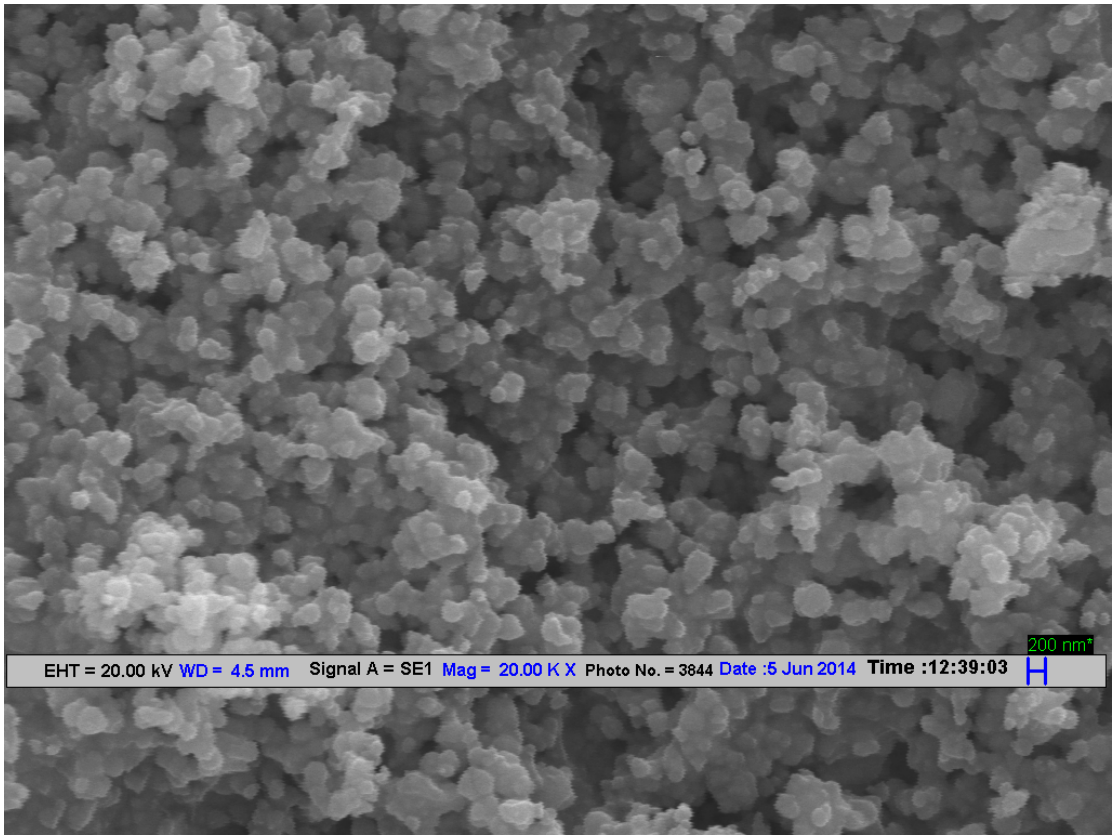


Fig. S23. SEM image of decomposition product of **1** obtained after Suzuki coupling reaction

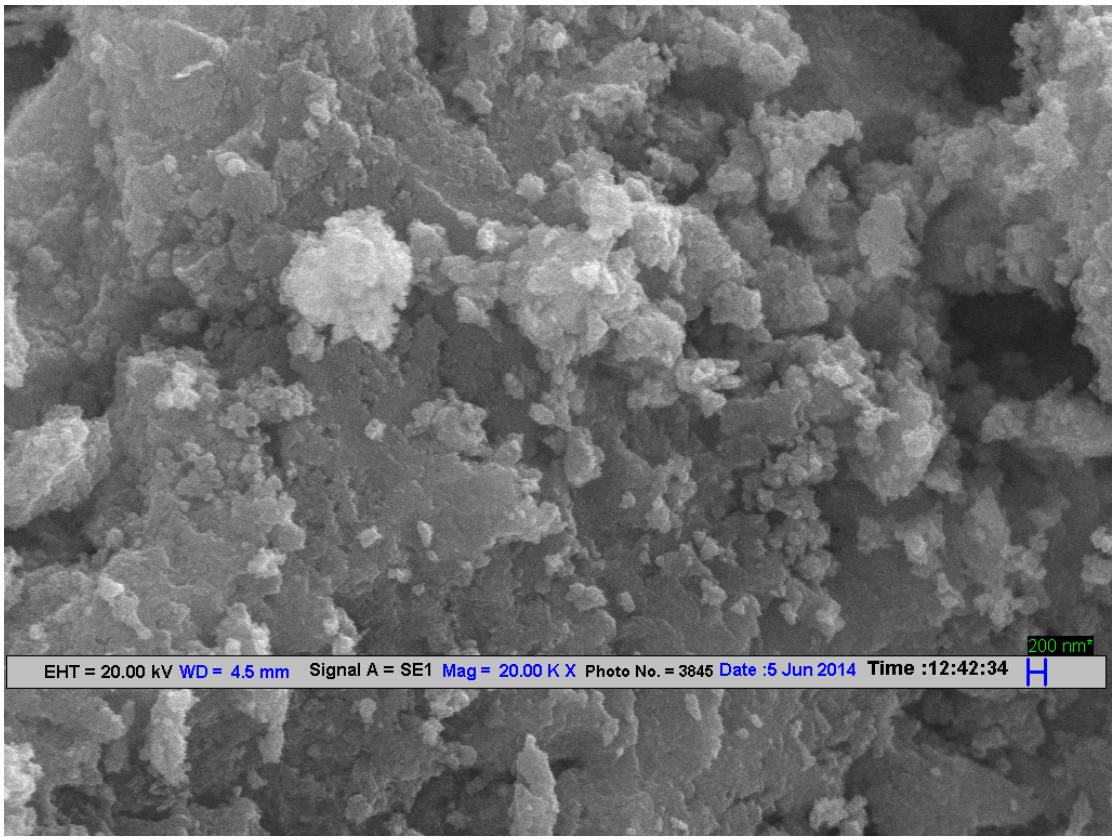
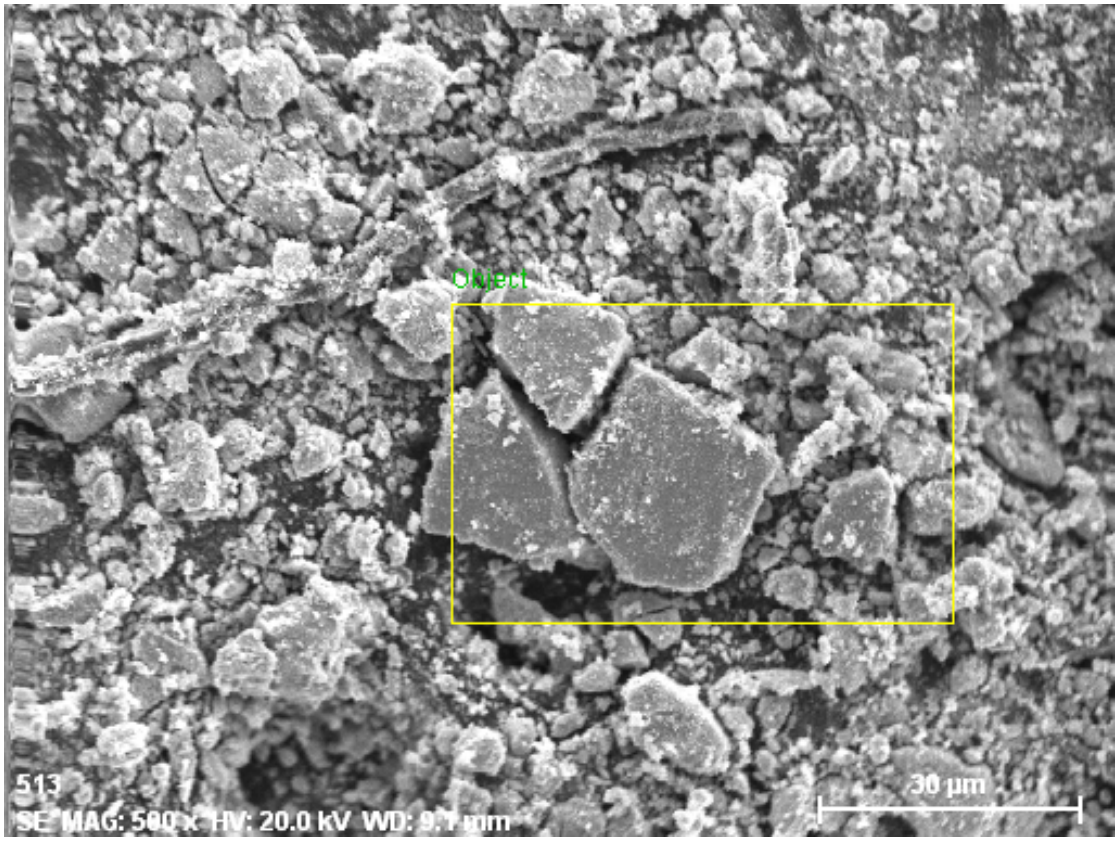


Fig. S24. SEM image of decomposition product of **2** obtained after Suzuki coupling reaction



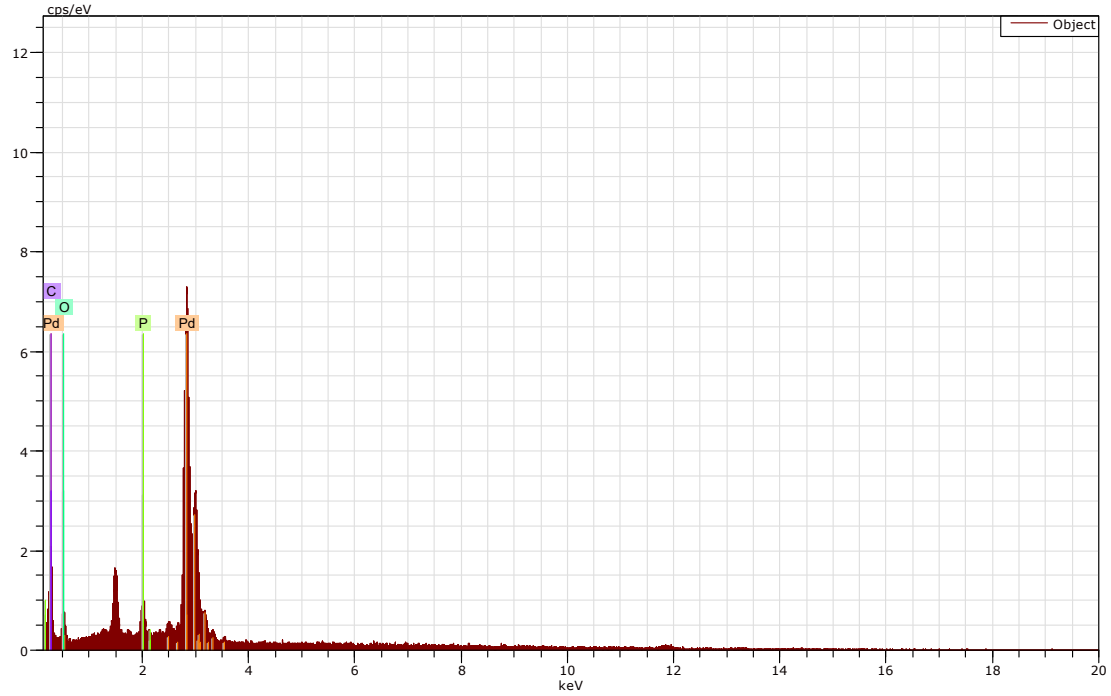
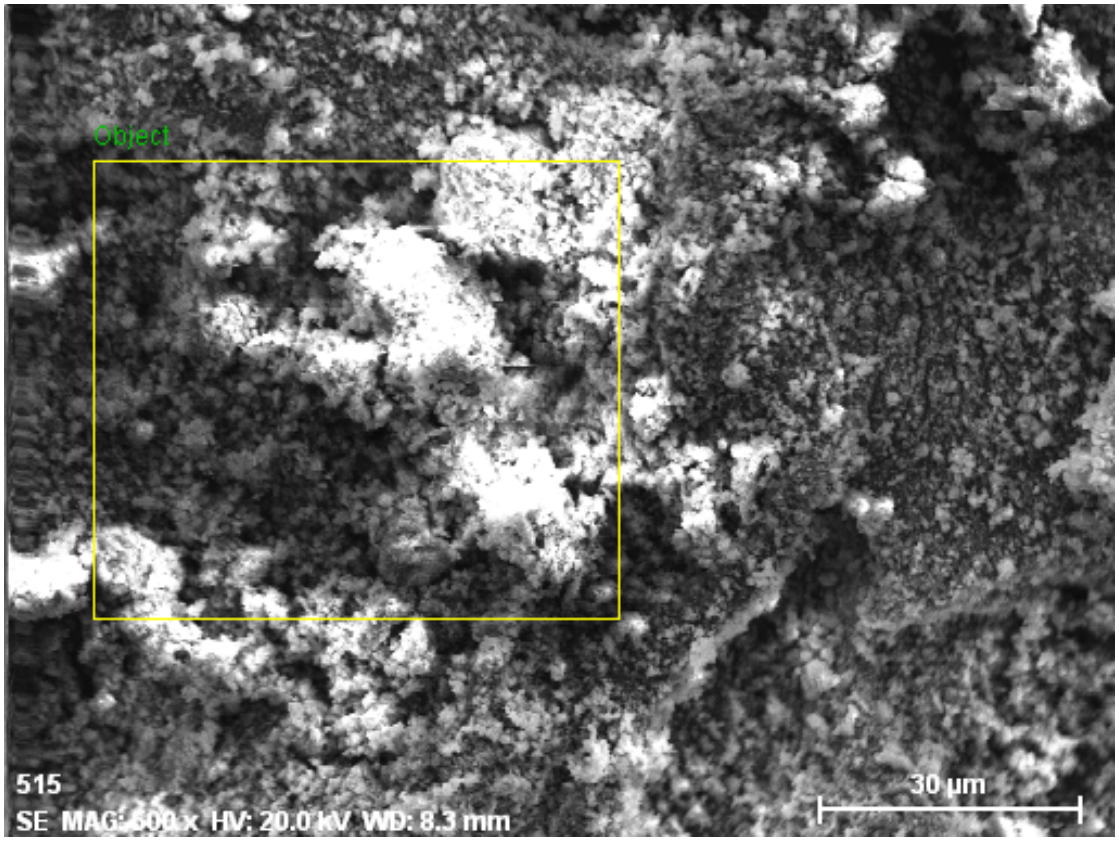


Fig. S25. SEM-EDX of decomposition product of **1** obtained after Suzuki coupling reaction



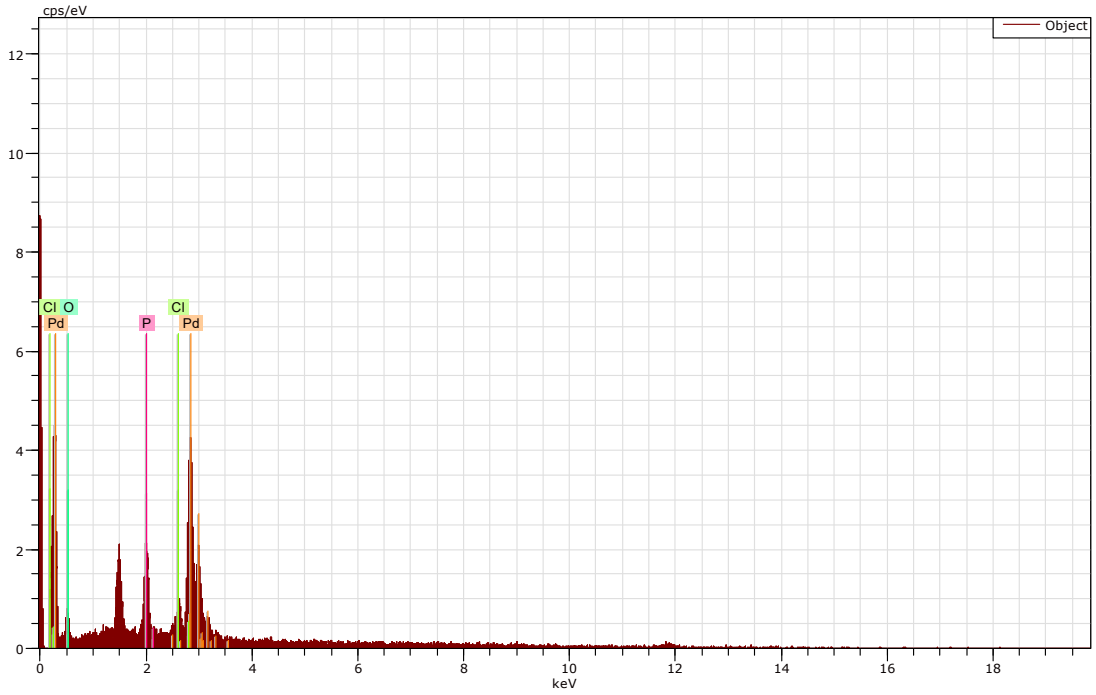


Fig. S26. SEM-EDX of decomposition product of **2** obtained after Suzuki coupling reaction

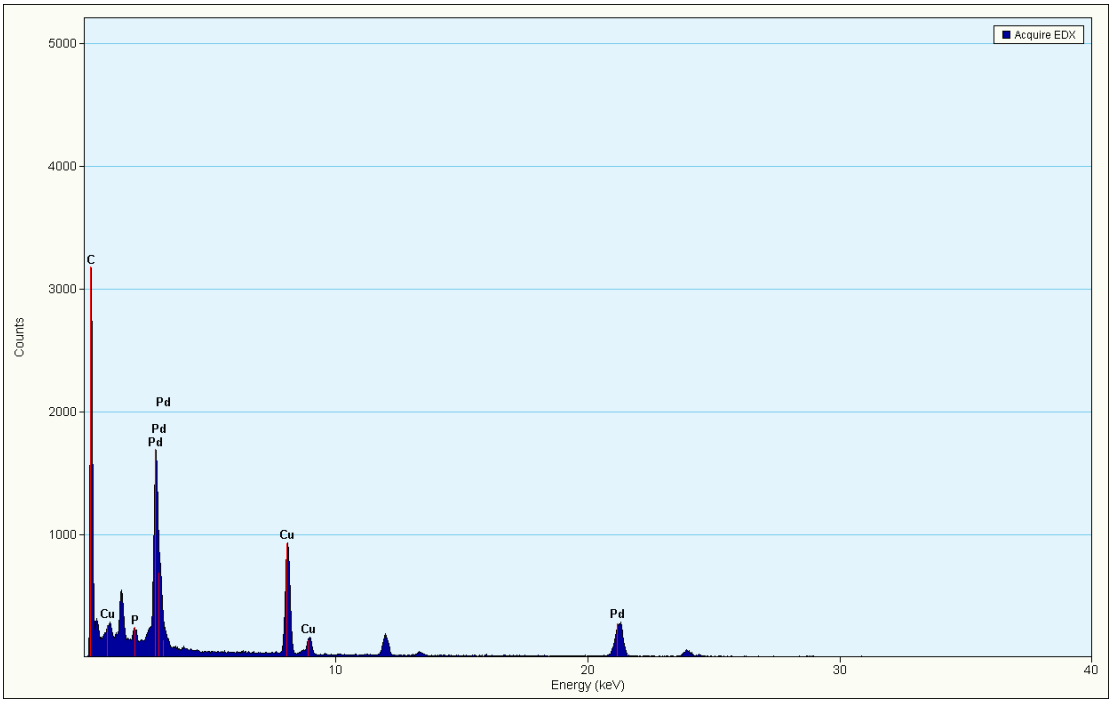


Fig. S27. TEM-EDX of decomposition product of **1** obtained after Suzuki coupling reaction

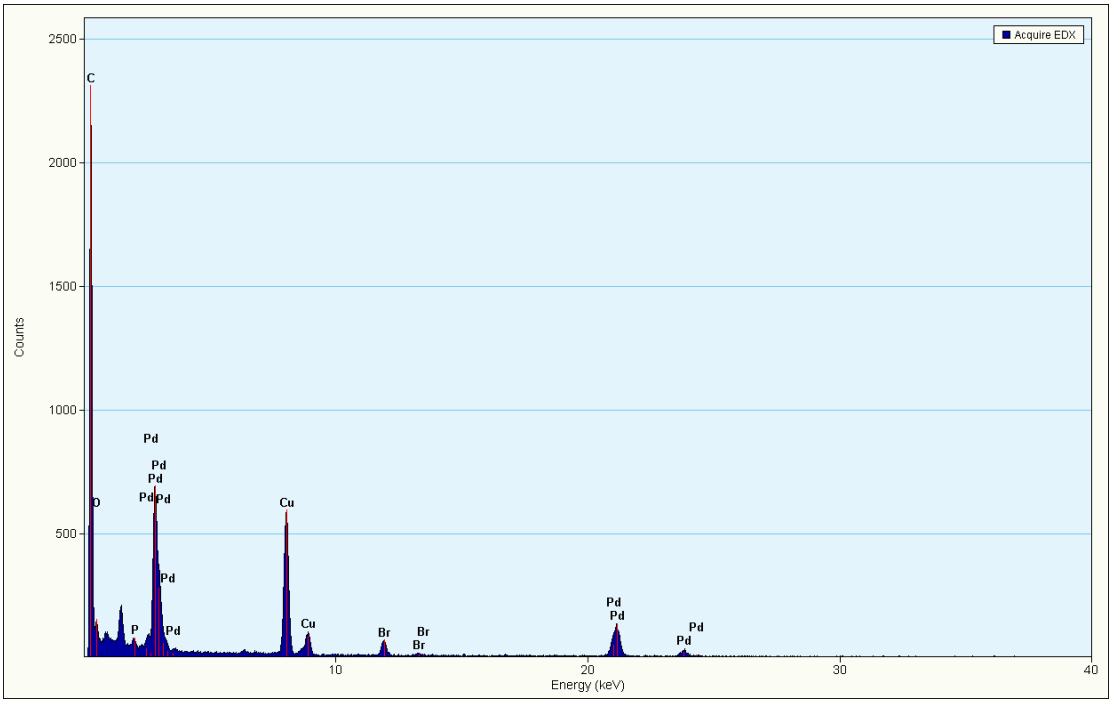


Fig. S28. TEM-EDX of decomposition product of **2** obtained after Suzuki coupling reaction