Electronic Supplementary Information (ESI)

Rapid and selective extraction of Pd(II) ions using the SCS type pincer ligand 1,3-bis(dimethylthiocarbamoyloxy)benzene, and its Pd(II) extraction mechanism

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Supporting figures

Supporting Tables

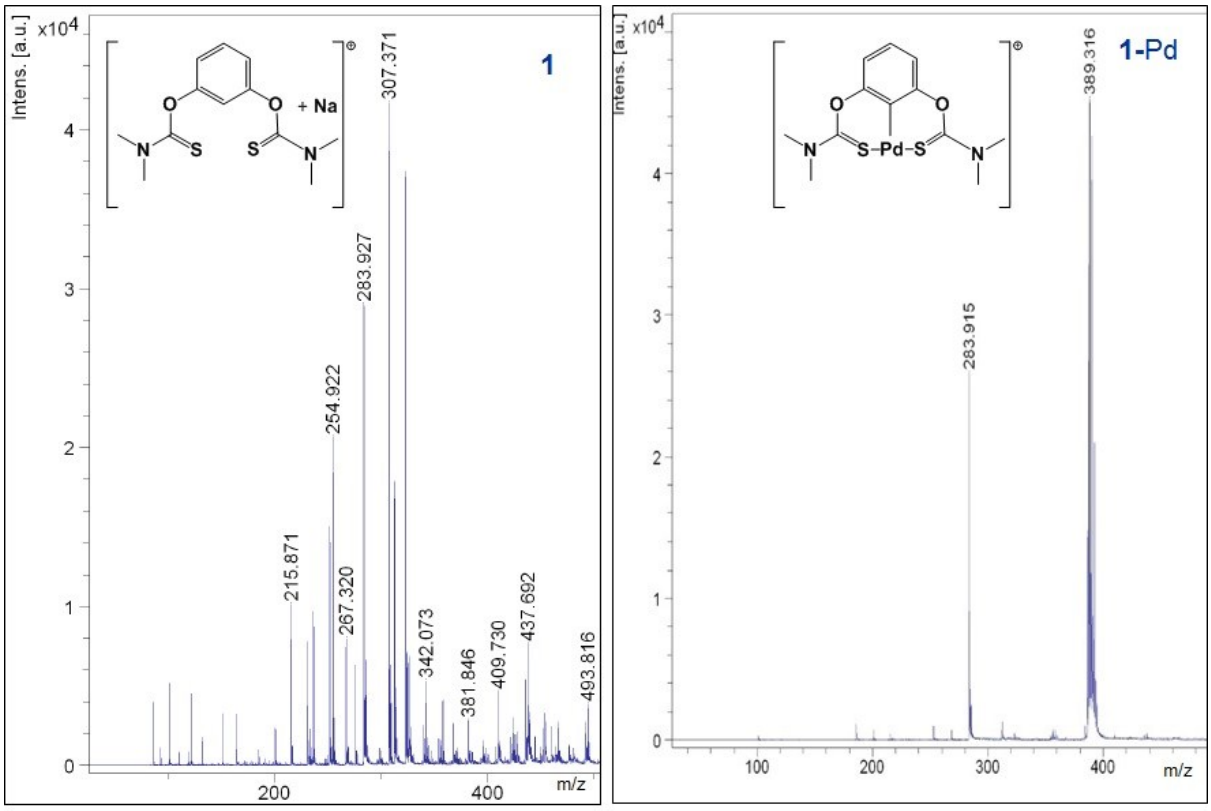


Fig. S1 MALDI-TOF MS spectra of **1** and **1**-Pd complex.

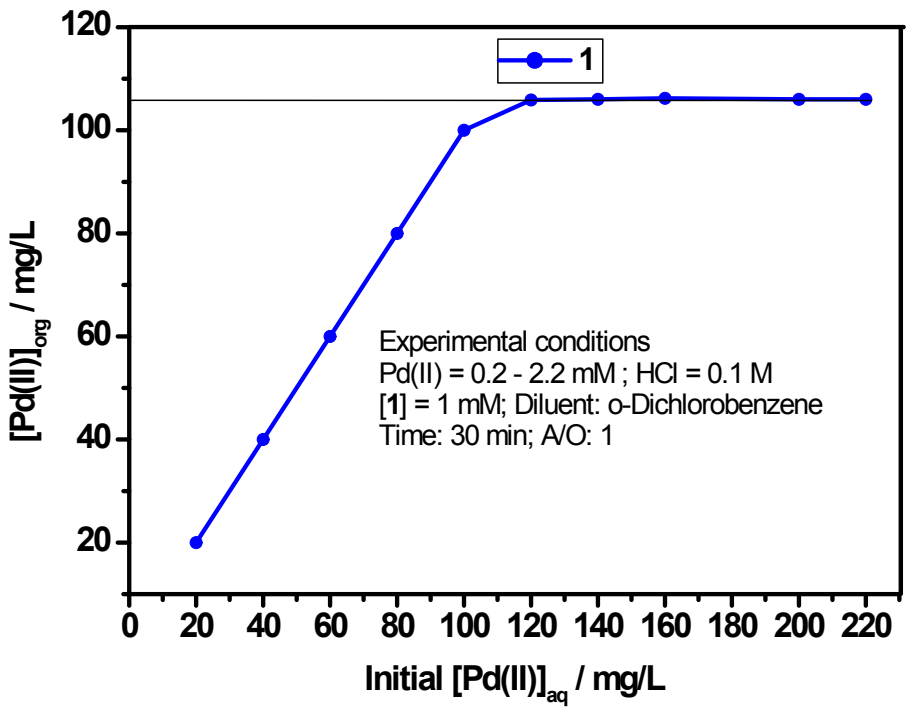


Fig. S2 Pd(II) loading capacity of **1**.

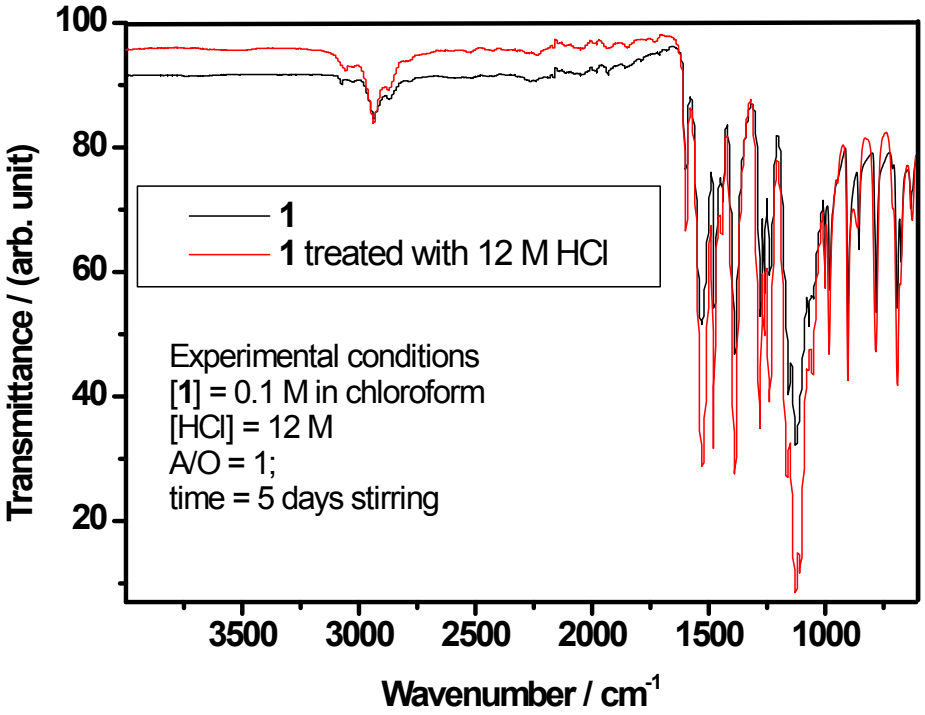


Fig. S3 FT-IR spectra of **1** and HCl (12 M) treated **1**.

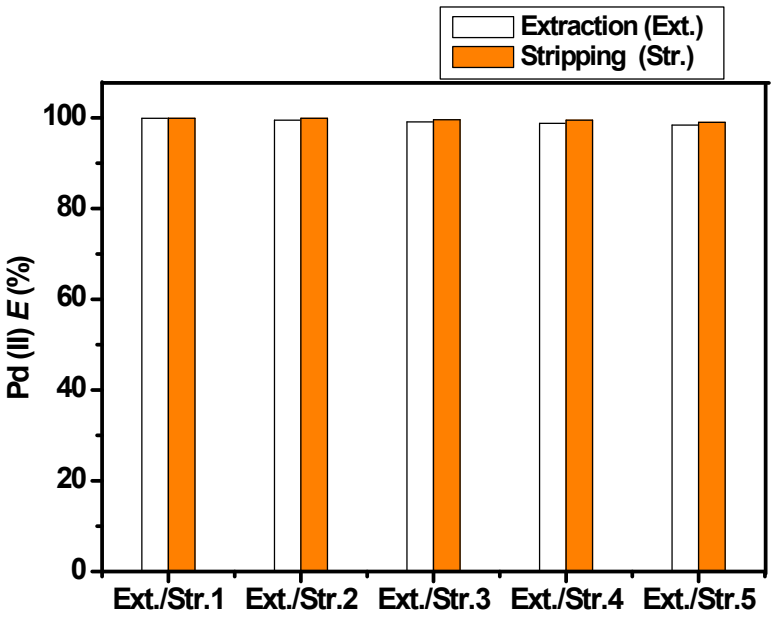


Fig. S4 Extraction and stripping cycle of **1** from automotive catalyst solution.

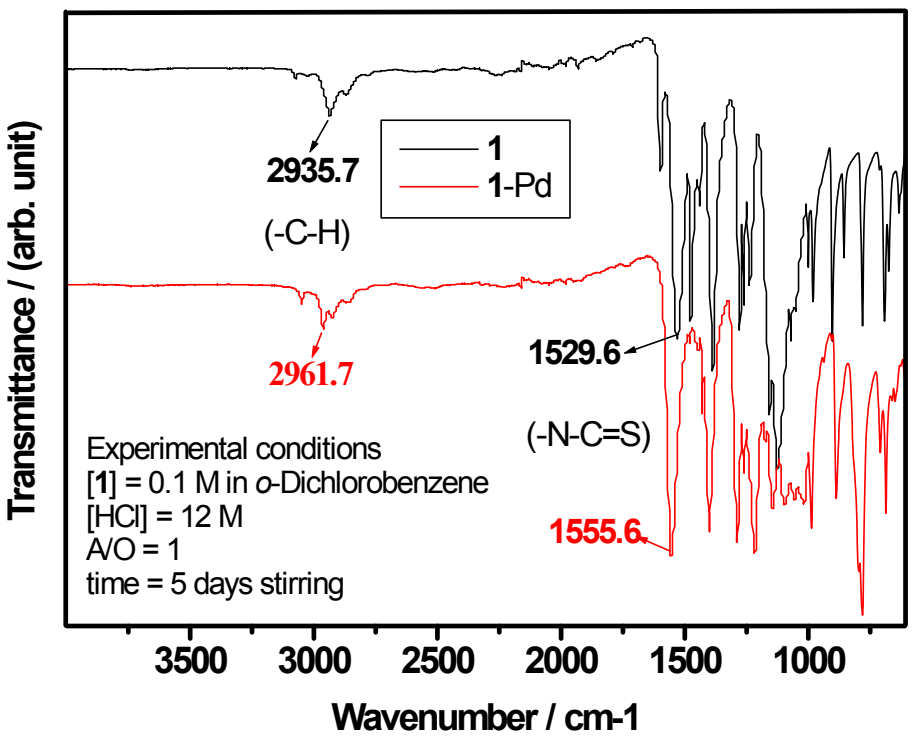


Fig. S5 FT-IR spectra of **1** and **1**-Pd complex.

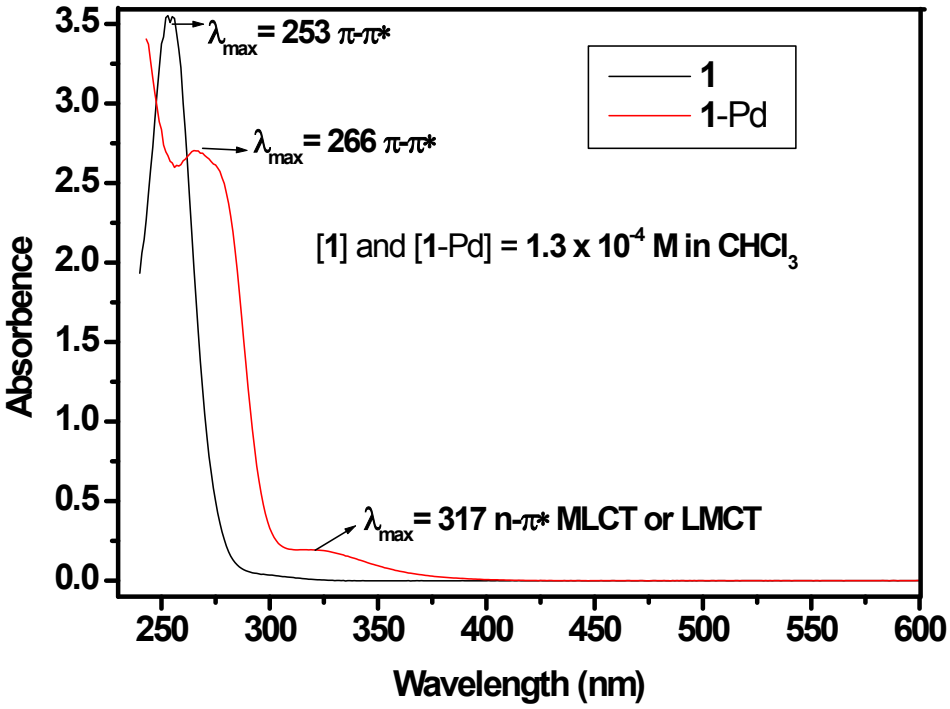


Fig. S6 UV-vis spectra of **1** and **1**-Pd complex.

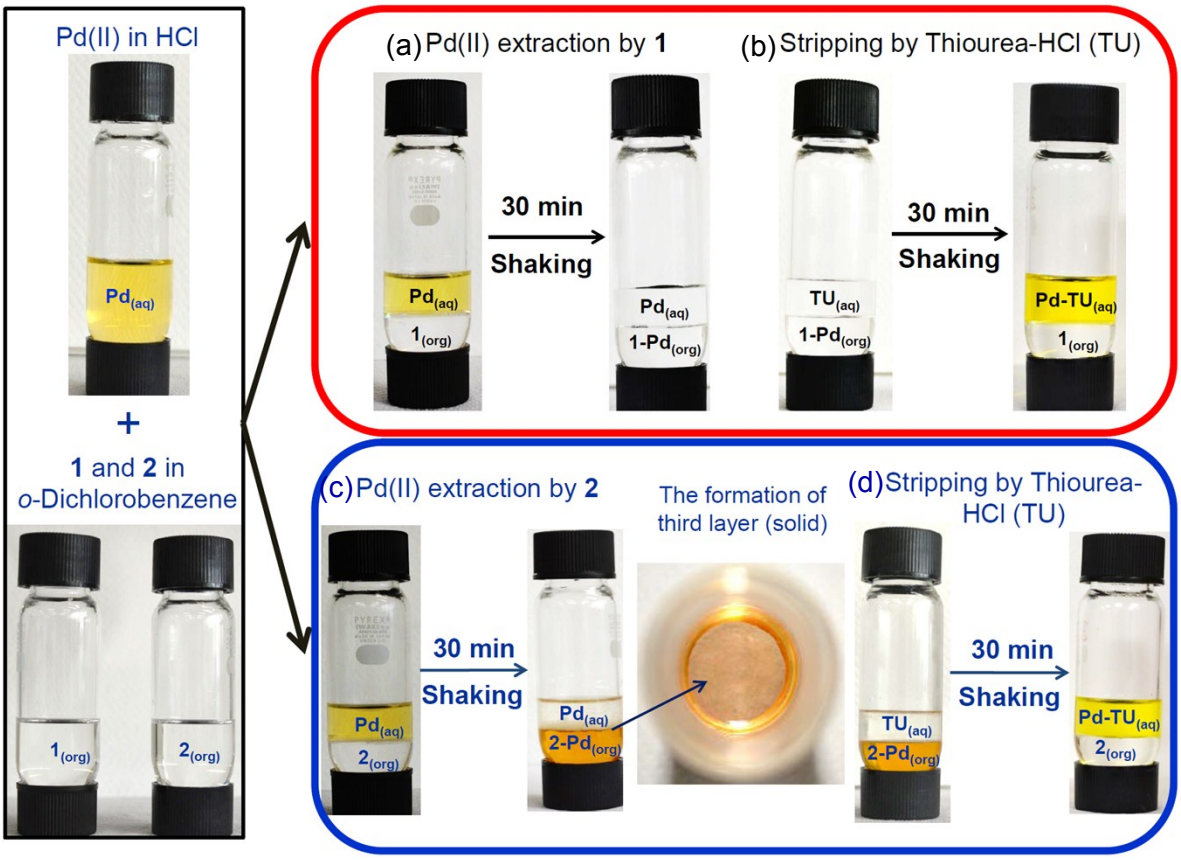


Fig. S7 Color changes during extraction and striping of extractants **1** and **2**. (a) Pd(II) extraction by **1**; (b) stripping of Pd(II) from $\mathbf{1}_{(org)}$ using 0.1 M thiourea/1.0 M HCl and (c) Pd(II) extraction by **2**; (d) stripping of Pd(II) from $\mathbf{2}_{(org)}$ using 0.1 M thiourea/1.0 M HCl).

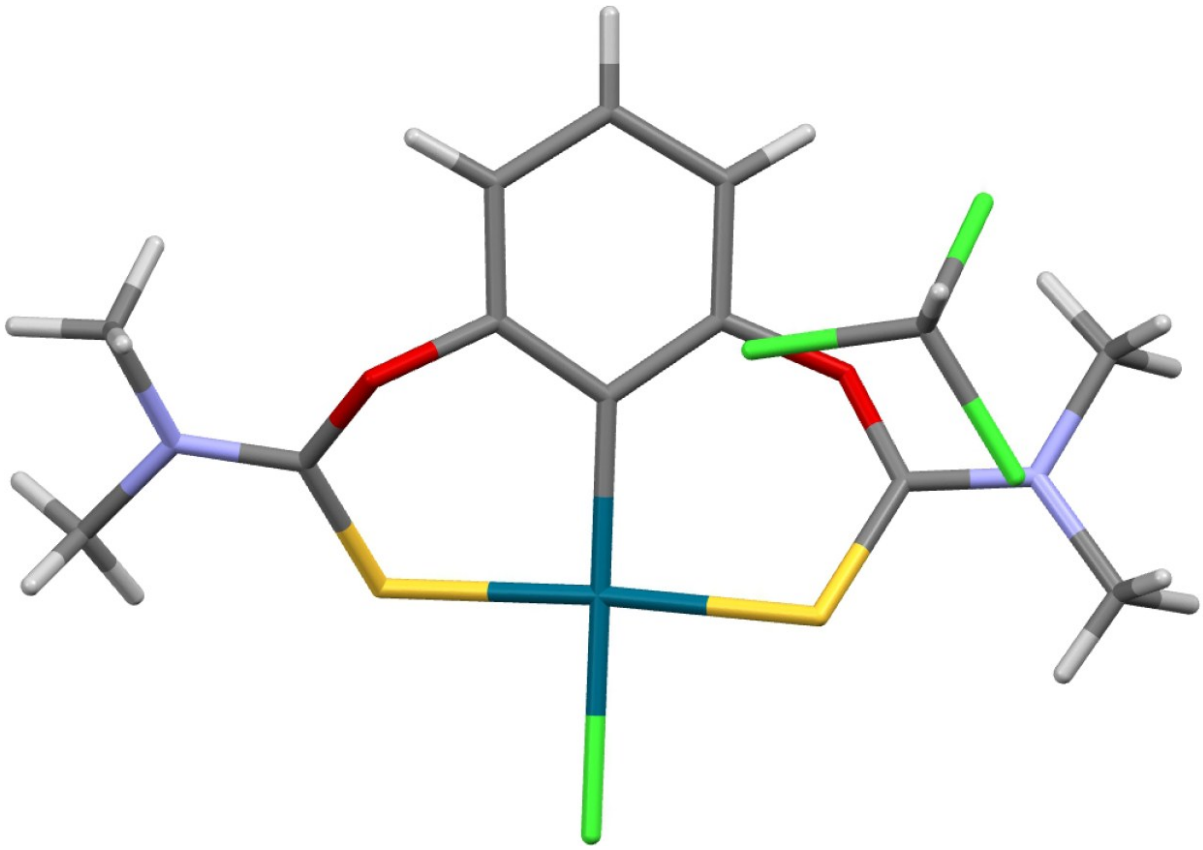
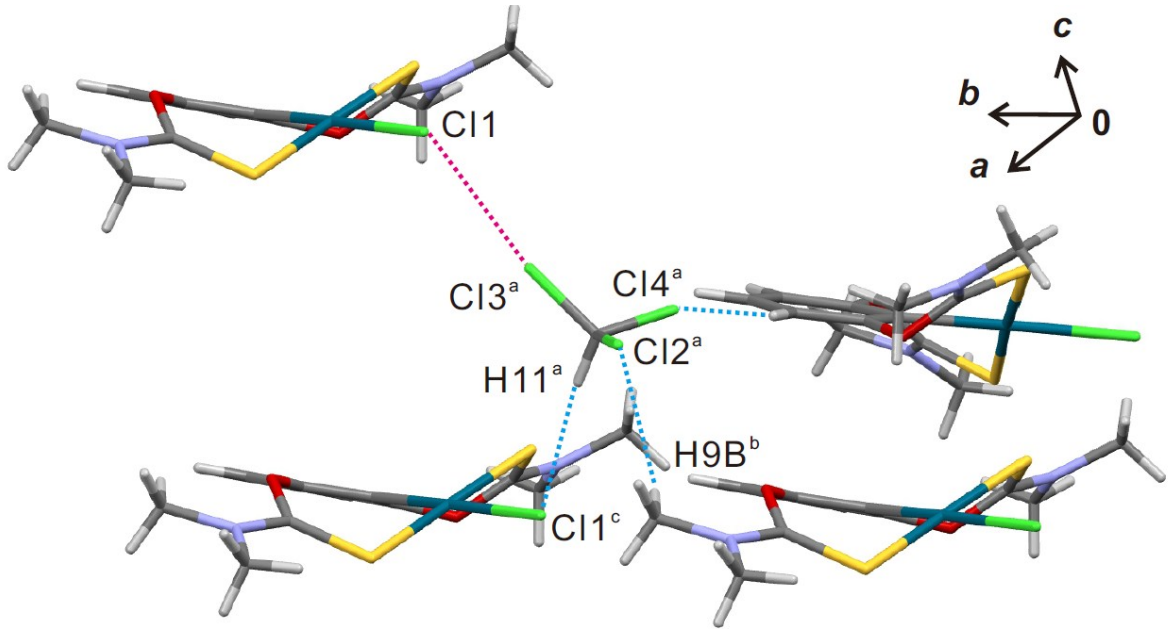


Fig. S8 Crystal structure of **1**-Pd(Cl)·$CHCl_3$.



Description: one $CHCl_3$ molecule acts as a joint to connect four Pincer-Pd ligands by Cl···Cl halogen-halogen interaction and halogen-H interactions. These Cl1-Cl3[a], H11[a]-Cl1[b], Cl2[a]-H9B[c], and Cl4[a]-H3[d] distances are 3.309(1), 2.589, 2.908, and 2.812 Å (Symmetry operation: [a]; -1+x, y, -1+z, [b]; x, y, -1+z, [c]; -1+x, y, -2+z, [d]; -1+x, 1/2-y, -3/2+z).

Fig. S9 Cl···Cl (halogen-halogen) interaction and (Cl) halogen-H interactions of **1**-Pd(Cl)·$CHCl_3$.

Table S1 ^{13}C NMR spectra of **1** and **1**-Pd complex.

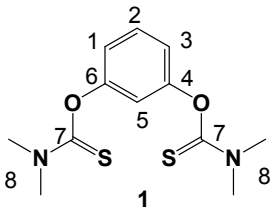
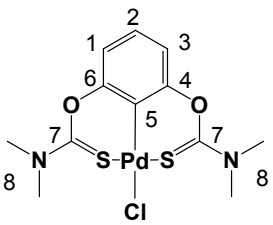
Structure	**C**-8	**C**-2	**C**-1,3	**C**-5	**C**-4,6	**C**-7
 **1**	43.2, 38.8	118.0	120.4	129.0	154.2	187.4
 **1**-Pd	43.6, 39.7	115.7	117.7	125.7	153.8	180.8

Table S2 Bond distances (Å) for **1**-Pd(Cl)

S. No	Bonds		Distance (Å)
1	Pd(1)	Cl(1)	2.3948(8)
2	Pd(1)	C(5)	1.988(3)
3	Pd(1)	S(1)	2.297(1)
4	Pd(1)	S(2)	2.284(1)
5	S(1)	C(16)	1.702(4)
6	C(16)	N(1)	1.312(5)
7	N(1)	C(8)	1.465(6)
8	N(1)	C(7)	1.481(5)
9	C(16)	O(1)	1.336(5)
10	O(1)	C(4)	1.428(4)
11	C(4)	C(5)	1.387(5)
12	C(5)	C(6)	1.386(5)
13	C(6)	O(2)	1.422(4)
14	O(2)	C(15)	1.329(5)
15	C(15)	S(2)	1.694(4)
16	C(15)	N(2)	1.322(5)
17	N(2)	C(9)	1.476(5)
18	N(2)	C(10)	1.464(5)
19	C(6)	C(1)	1.386(5)
20	C(1)	C(2)	1.390(6)
21	C(2)	C(3)	1.385(5)
22	C(3)	C4	1.378(5)
23	S(1)	S(2)	4.579(1)

Table S3 Bond angles (°) for **1**-Pd(Cl)

S. No	Atom 1	Atom 2	Atom 3	Angle (°)
1	Cl(1)	Pd(1)	S(1)	88.23(3)
2	Cl(1)	Pd(1)	S(2)	88.25(3)
3	Cl(1)	Pd(1)	C(5)	179.1(1)
4	S(1)	Pd(1)	S(2)	176.42(4)
5	S(1)	Pd(1)	C(5)	91.9(1)
6	S(2)	Pd(1)	C(5)	91.7(1)
7	Pd(1)	S(1)	C(16)	106.7(1)
8	Pd(1)	S(2)	C(15)	107.3(1)
9	C(4)	O(1)	C(16)	121.5(3)
10	C(6)	O(2)	C(15)	124.6(3)
11	C(7)	N(1)	C(8)	116.3(3)
12	C(7)	N(1)	C(16)	122.2(4)
13	C(8)	N(1)	C(16)	121.5(4)
14	C(9)	N(2)	C(10)	115.4(3)
15	C(9)	N(2)	C(15)	122.4(4)
16	C(10)	N(2)	C(15)	122.1(4)
17	C(2)	C(1)	C(6)	118.8(4)
20	C(1)	C(2)	C(3)	118.8(4)
23	C(2)	C(3)	C(4)	119.0(4)
26	O(1)	C(4)	C(3)	111.8(3)
27	O(1)	C(4)	C(5)	122.8(4)
28	C(3)	C(4)	C(5)	125.4(4)
29	Pd(1)	C(5)	C(4)	123.0(3)
30	Pd(1)	C(5)	C(6)	124.3(3)
31	C(4)	C(5)	C(6)	112.7(4)
32	O(2)	C(6)	C(1)	111.0(3)
33	O(2)	C(6)	C(5)	123.7(3)
34	C(1)	C(6)	C(5)	125.1(4)
59	S(2)	C(15)	O(2)	124.7(3)
60	S(2)	C(15)	N(2)	122.4(3)
61	O(2)	C(15)	N(2)	112.9(3)
62	S(1)	C(16)	O(1)	122.9(3)
63	S(1)	C(16)	N(1)	123.5(3)
64	O(1)	C(16)	N(1)	113.4(4)