

## Unexpected activation of carbon-bromide bond promoted by palladium nanoparticles in Suzuki C-C couplings

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### Supplementary Information

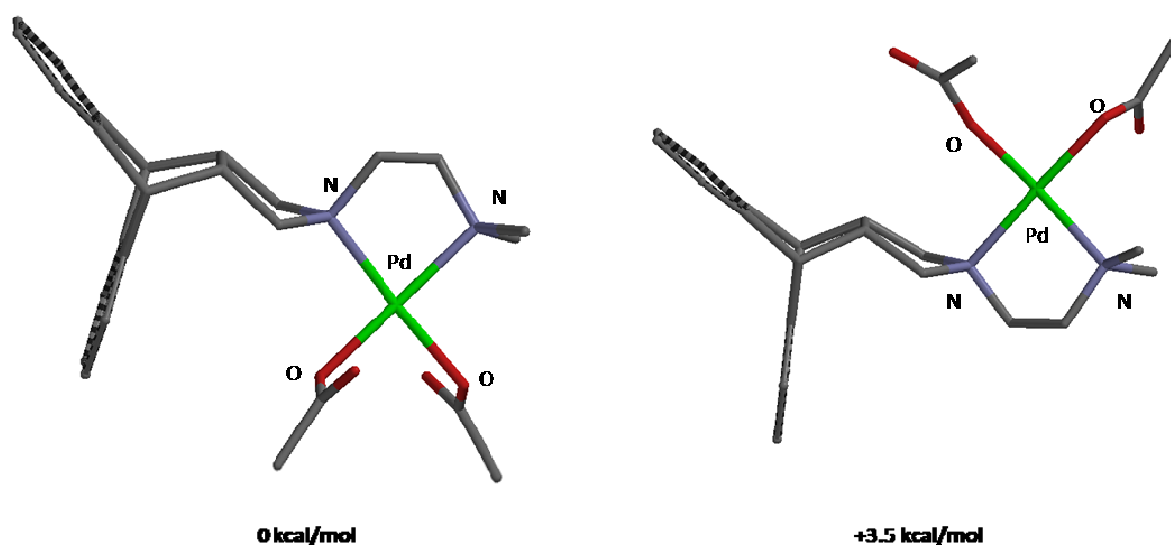
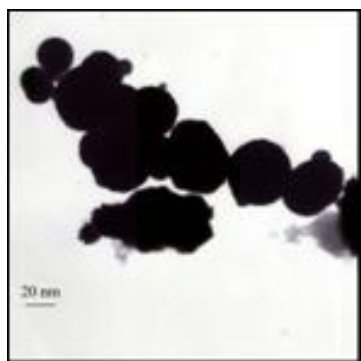
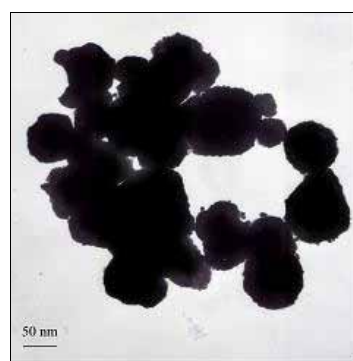


Fig. S1 Calculated structures (at DFT level) for both conformations of complex C6 with the data concerning the relative formation energy.

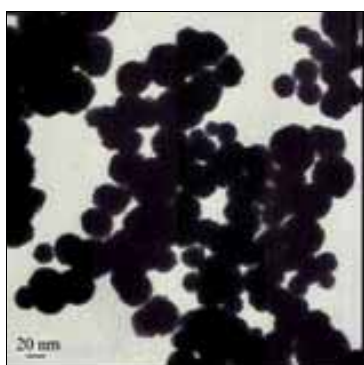
a)



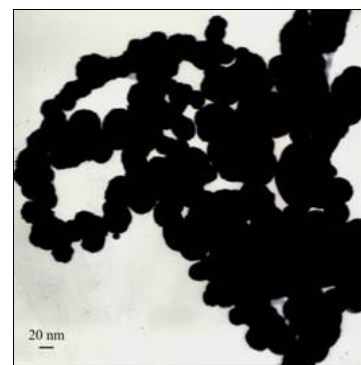
b)



c)



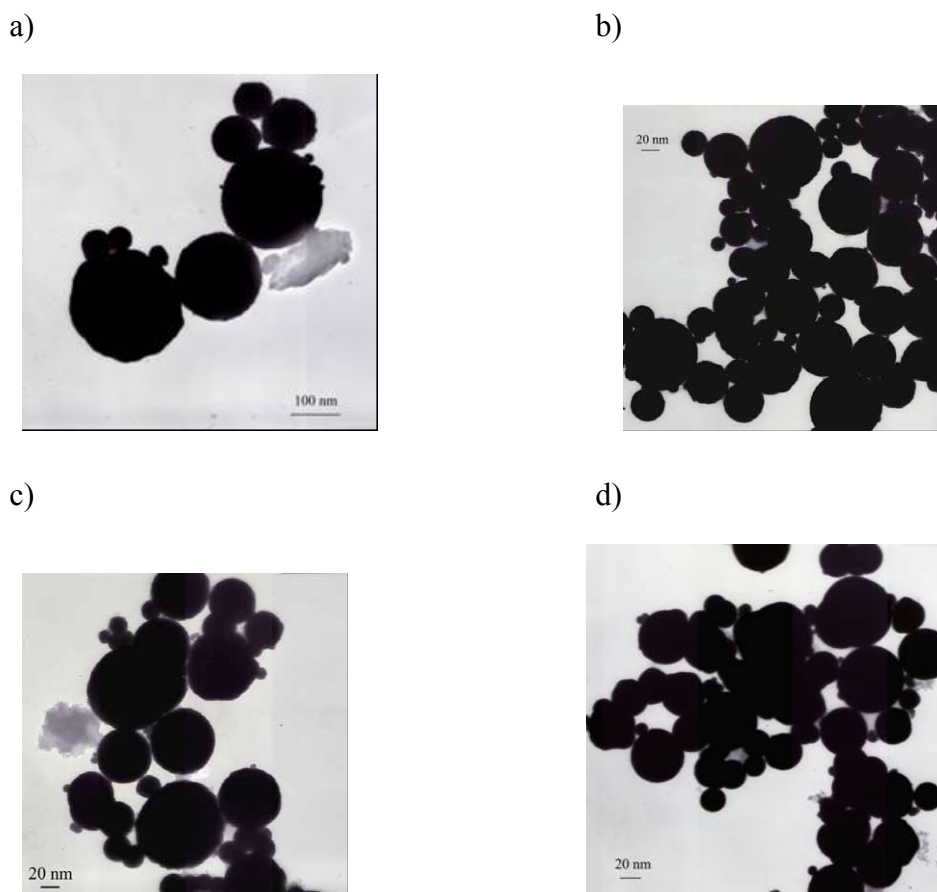
d)



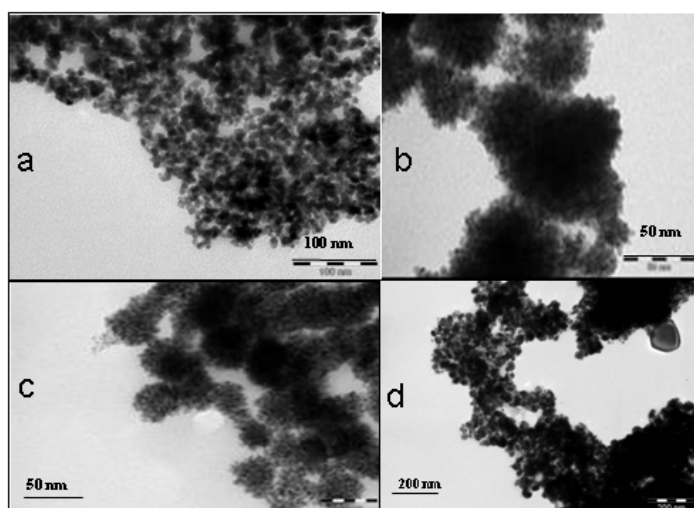
**Fig. S2** TEM micrographs of palladium particles from  $[\text{PdCl}_2(\text{cod})]$  and dispersed in THF: a) **Pd1a**; b) **Pd2a**; c) **Pd4a**; d) **Pd5a**.

PdNP	d (TEM) (nm)	IR (cm <sup>-1</sup> )	Free ligand IR (cm <sup>-1</sup> )
<b>Pd1a</b>	Agglomerates	2959 (C-H), 1702 (C=O), 1465 (C=C)	2958 (C-H), 1702 (C=O), 1465 (C=C)
<b>Pd2a</b>	Agglomerates	3431 (O-H), 2959 (C-H), 1767-1697 (C=O), 1461 (C=C)	3447 (O-H), 3026 (=C-H), 2961 (C-H), 1770 (C=O), 1702 (C=O), 1465-1458 (C=C)
<b>Pd4a</b>	Agglomerates	2929 (C-H), 1454 (C=C)	3062 (=C-H), 2927 (C-H), 1654-1457 (C=C)
<b>Pd5a</b>	Agglomerates	3306 (O-H), 2924-2854 (C-H), 1647-1458 (C=C)	3409 (O-H), 3064-3018 (=C-H), 2935-2788 (C-H), 1477-1456 (C=C)
<b>Pd1b</b>	Agglomerates	2958-2929 (C-H), 1701 (C=O), 1465 (C=C)	2958 (C-H), 1702 (C=O), 1465 (C=C)
<b>Pd2b</b>	Agglomerates	3439 (O-H), 2963 (C-H), 1770-1688 (C=O), 1458 (C=C)	3447 (O-H), 3026 (=C-H), 2961 (C-H), 1770 (C=O), 1702 (C=O), 1465-1458 (C=C)
<b>Pd4b</b>	Agglomerates	2922 (C-H), 1458 (C=C)	3062 (=C-H), 2927 (C-H), 1654-1457 (C=C)
<b>Pd5b</b>	Agglomerates	3310 (O-H), 2924-2854 (C-H), 1458 (C=C)	3409 (O-H), 3064-3018 (=C-H), 2935-2788 (C-H), 1477-1456 (C=C)
<b>Pd1c</b>	3.5 ± 1.8 (Pd <sub>1542</sub> )	2958 (C-H), 1701 (C=O), 1458 (C=C)	2958 (C-H), 1702 (C=O), 1465 (C=C)
<b>Pd2c</b>	1.9 ± 0.5 (Pd <sub>247</sub> )	3401 (O-H), 3064-3018 (=C-H), 2923-2848 (C-H), 1684 (C=O), 1458 (C=C)	3447 (O-H), 3026 (=C-H), 2961 (C-H), 1770 (C=O), 1702 (C=O), 1465-1458 (C=C)
<b>Pd3c</b>	Agglomerates	2954-2846 (C-H), 1695 (C=O), 1464 (C=C)	3072-3012 (=C-H), 2977-2815 (C-H), 1704 (C=O), 1479-1465 (C=C)
<b>Pd4c</b>	3.6 ± 1.2 (Pd <sub>1678</sub> )	2915-2841 (C-H), 1458 (C=C)	3062 (=C-H), 2927 (C-H), 1654-1457 (C=C)
<b>Pd5c</b>	2.4 ± 0.9 (Pd <sub>497</sub> )	3425 (O-H), 2959-2856 (C-H), 1638 (C=C)	3409 (O-H), 3064-3018 (=C-H), 2935-2788 (C-H), 1477-1456 (C=C)
<b>Pd6c</b>	2.0 ± 0.8 (Pd <sub>288</sub> )	2959-2863 (C-H), 1617-1457 (C=C)	3065-3017 (=C-H), 2935-2774 (C-H), 1466-1456 (C=C)
<b>Pd1d</b>	Agglomerates	2961-2853 (C-H), 1700 (C=O), 1650-1465 (C=C)	2958 (C-H), 1702 (C=O), 1465 (C=C)
<b>Pd2d</b>	1.41 ± 0.62 (Pd <sub>101</sub> )	3398 (O-H), 2963-2848 (C-H), 1767-1696 (C=O)	3447 (O-H), 3026 (=C-H), 2961 (C-H), 1770 (C=O), 1702 (C=O), 1465-1458 (C=C)
<b>Pd3d</b>	Agglomerates	2960-2852 (C-H), 1702 (C=O), 1458 (C=C)	3072-3012 (=C-H), 2977-2815 (C-H), 1704 (C=O), 1479-1465 (C=C)
<b>Pd4d</b>	Agglomerates	2922 (C-H), 1561 (C=C)	3062 (=C-H), 2927 (C-H), 1654-1457 (C=C)
<b>Pd5d</b>	1.93 ± 0.77 (Pd <sub>259</sub> )	3395 (O-H), 2959-2849 (C-H), 1561 (C=C)	3409 (O-H), 3064-3018 (=C-H), 2935-2788 (C-H), 1477-1456 (C=C)
<b>Pd6d</b>	Agglomerates	2959-2863 (C-H), 1457 (C=C)	3065-3017 (=C-H), 2935-2774 (C-H), 1466-1456 (C=C)

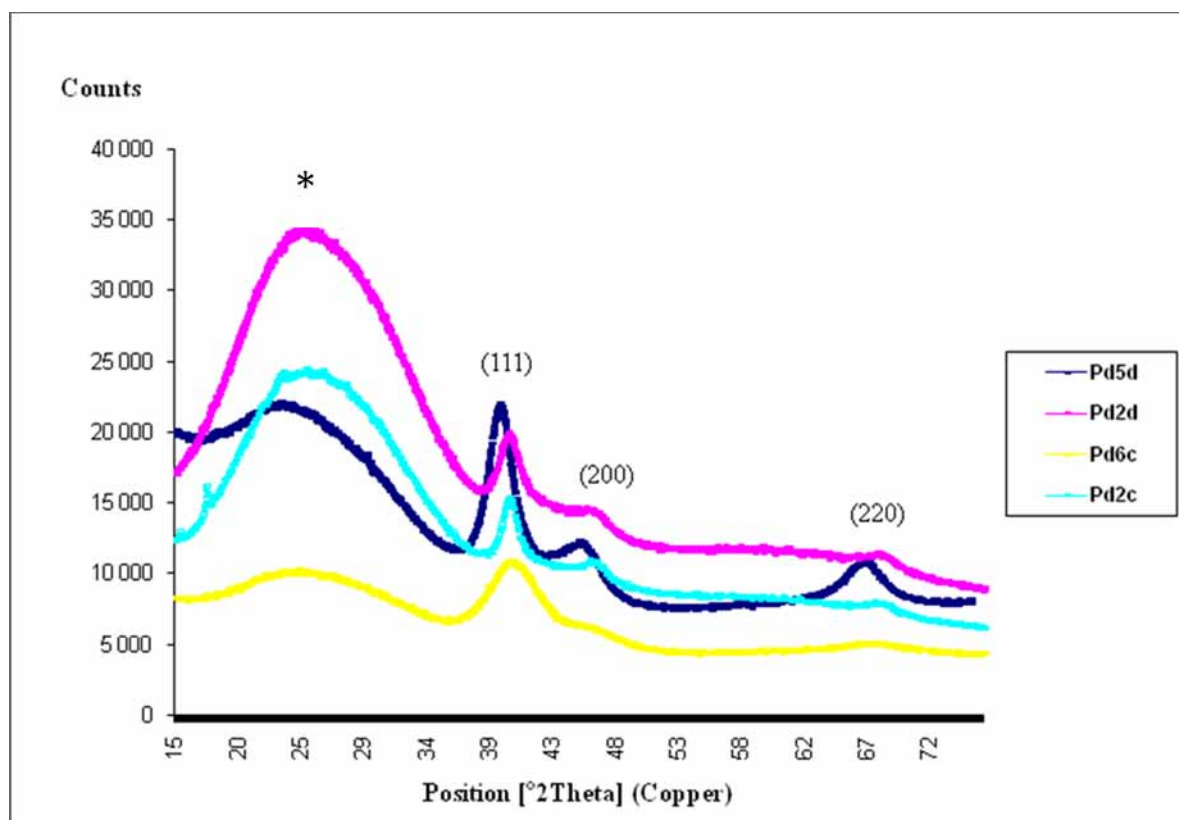
**Table S1** Diameter and IR data for PdNP, and IR data for ligands **1-6**



**Fig. S3** TEM micrographs of palladium particles from  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$  and dispersed in THF: a) **Pd1b**; b) **Pd2b**; c) **Pd4b**; d) **Pd5b**.



**Fig. S4** TEM micrographs of palladium particles from  $[\text{Pd}(\text{ma})(\text{nb})]$  and dispersed in THF: a) **Pd1d**; b) **Pd3d**; c) **Pd4d** and d) **Pd6d**.



**Fig. S5** X-ray powder diffraction (XRD) of **Pd2c**, **Pd6c**, **Pd2d** and **Pd5d**. \* denotes amorphous material due to the glass capillary. Below, peak list and stick pattern for Pd showing fcc crystal structure.

### Peak list

No.	h	k	l	d [Å]	2Theta [deg]	I [%]
1	1	1	1	2.30420	39.060	100.0
2	2	0	0	1.99550	45.414	44.2
3	2	2	0	1.41103	66.174	21.4
4	3	1	1	1.20333	79.605	21.2
5	2	2	2	1.15210	83.919	5.9

### Stick Pattern

