

**The Fast Formation of a Highly Active Homogeneous Catalytic System
upon the Soft Leaching of Pd Species from a Heterogeneous Pd/C
Precursor**

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XPS measurements

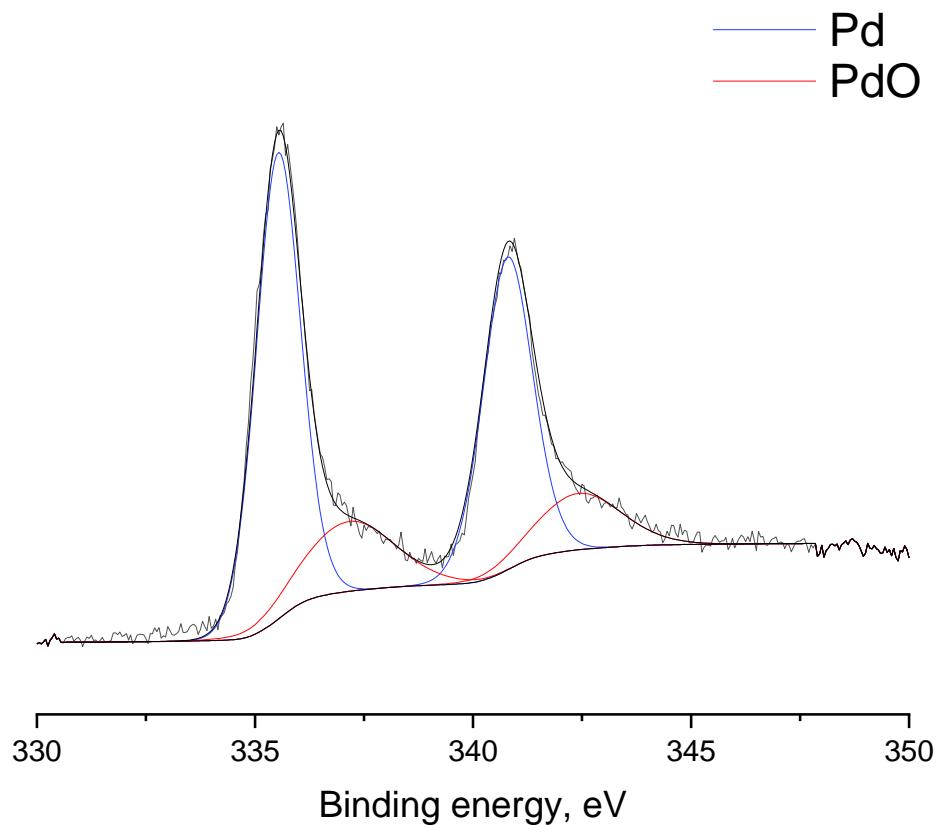


Figure S1. XPS spectrum of palladium.

Sample: 1 wt.% Pd/graphite. Pd was deposited from Pd_2dba_3 in CHCl_3 .

State of palladium	Ratio, mol.%
Pd(0)	76.3
PdO	23.7

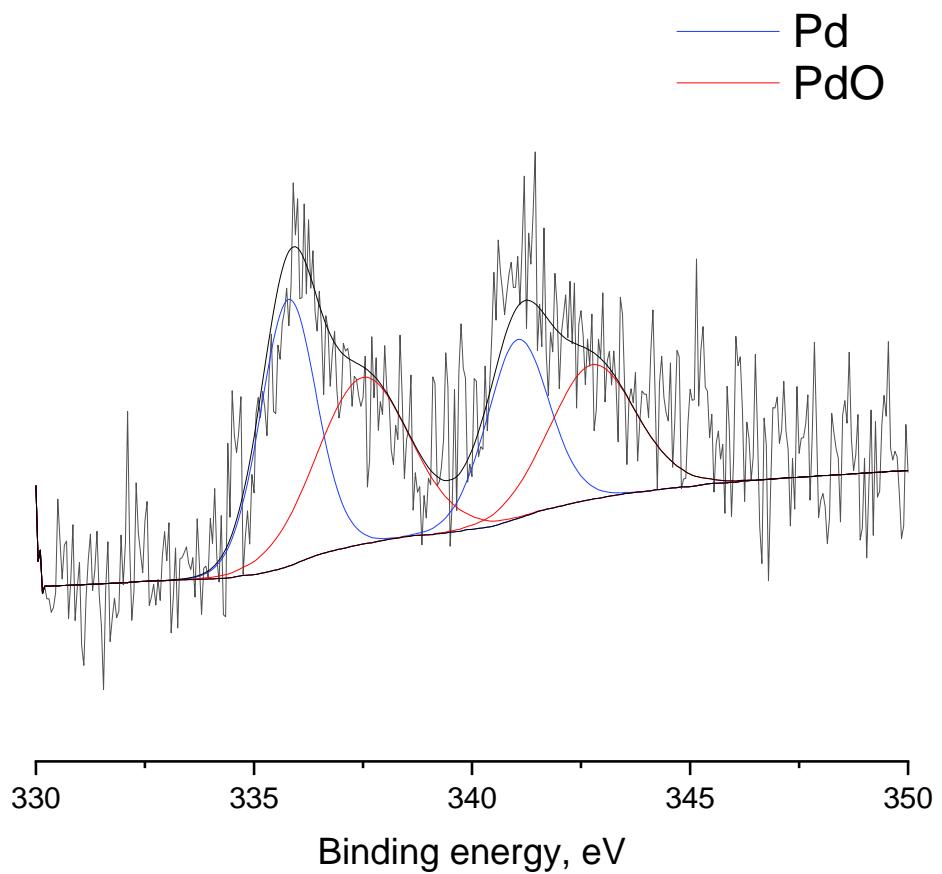


Figure S2. XPS spectrum of palladium.

Sample: 1 wt.% Pd/MWCNTs. Pd was deposited from Pd_2dba_3 in CHCl_3 .

State of palladium	Ratio, mol.%
Pd(0)	49.0
PdO	51.0

ESI-MS study

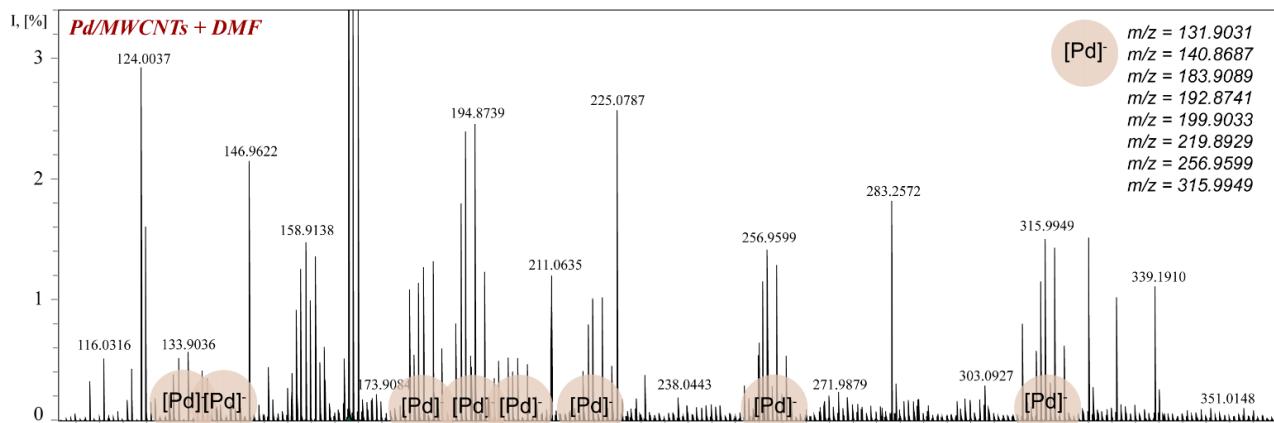


Figure S3. Full ESI-MS spectra in negative ion mode: ions formed in 1 wt.% Pd/MWCNTs suspension in DMF.

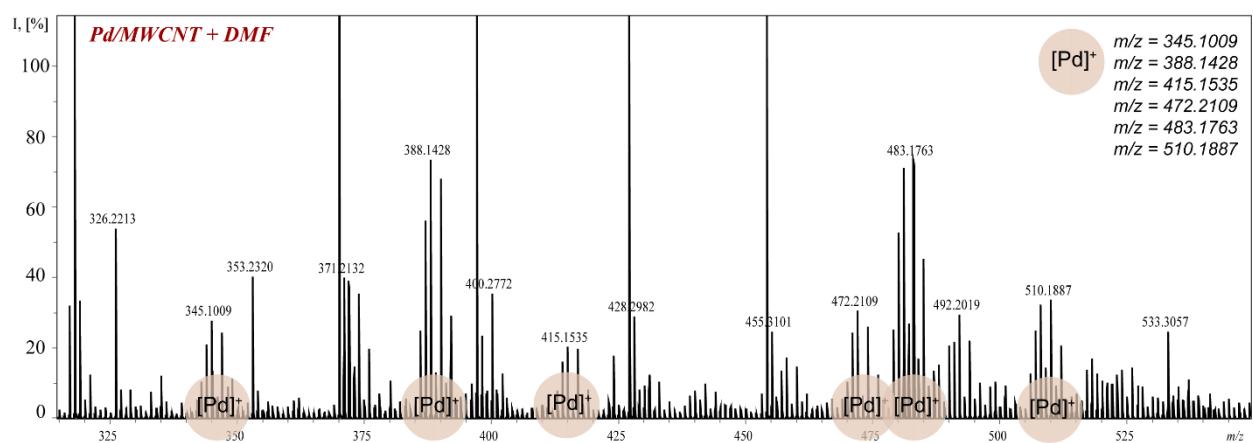


Figure S4. Full ESI-MS spectra in positive ion mode: ions formed in 1 wt.% Pd/MWCNTs suspension in DMF.

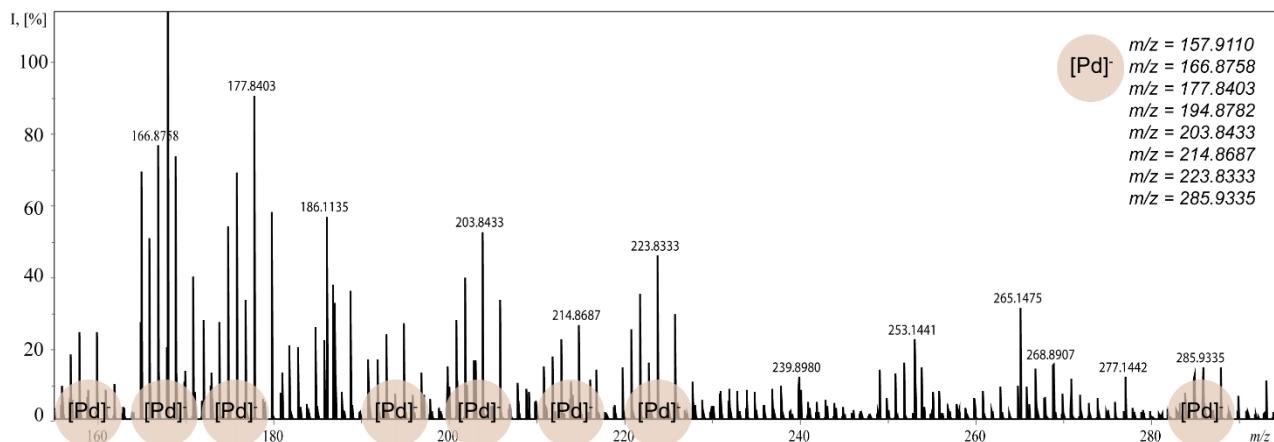


Figure S5. Full ESI-MS spectra in negative ion mode: ions formed in 1 wt.% Pd/graphite suspension in DMF.

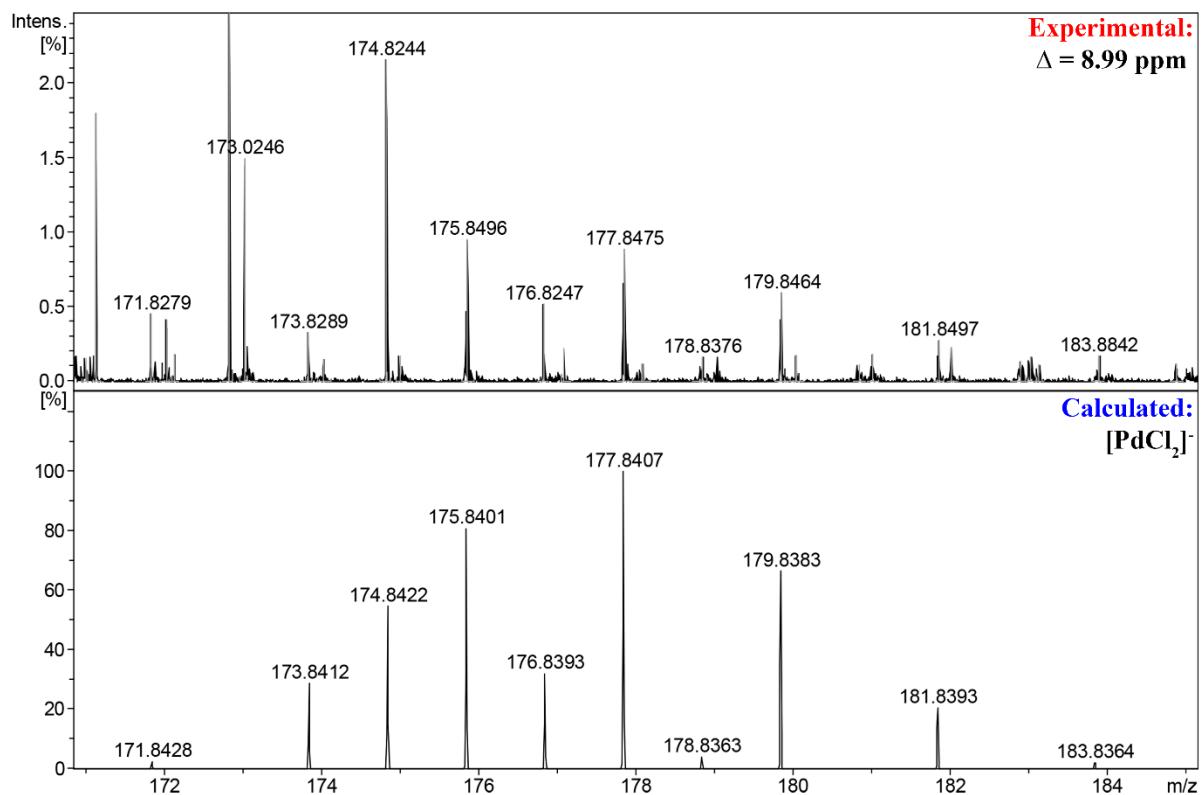


Figure S6. ESI-MS spectra in negative ion mode: ions formed in Pd/graphite rod (1 h of heating). Experimental (top) and calculated (bottom) spectra of $[\text{PdCl}_2]^-$.

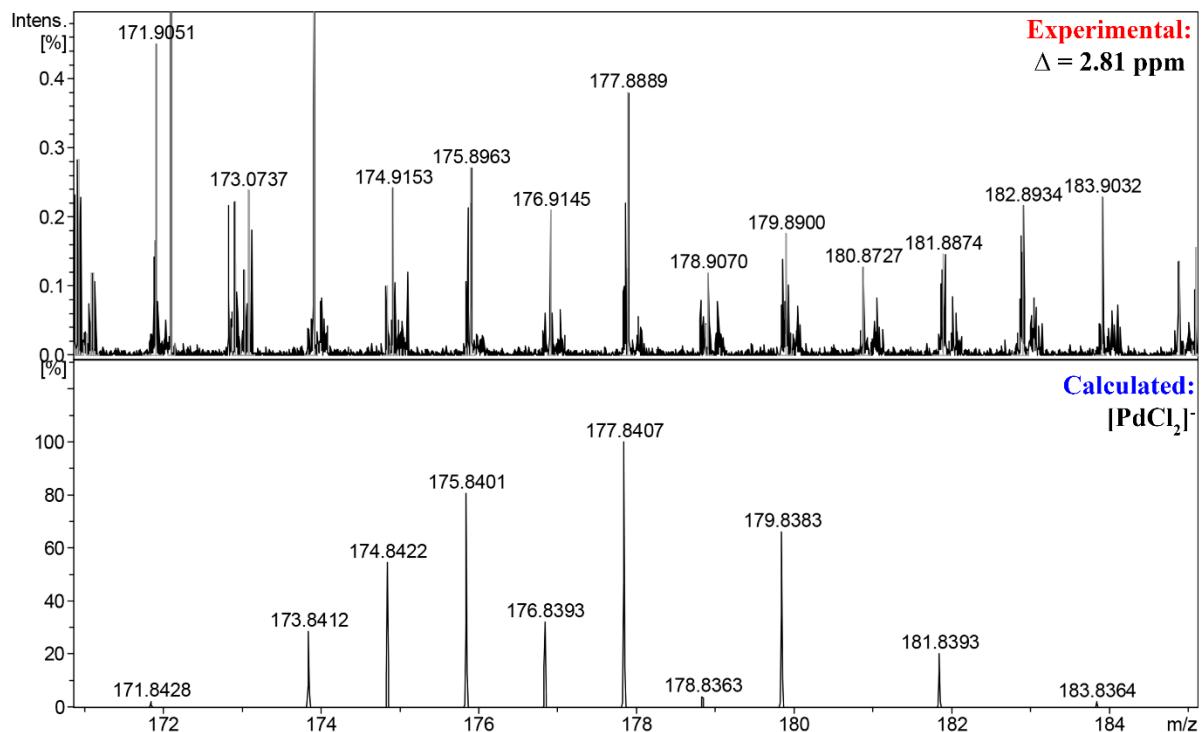


Figure S7. ESI-MS spectra in negative ion mode: ions formed in Pd/graphite rod (2 h of heating). Experimental (top) and calculated (bottom) spectra of $[\text{PdCl}_2]^-$.

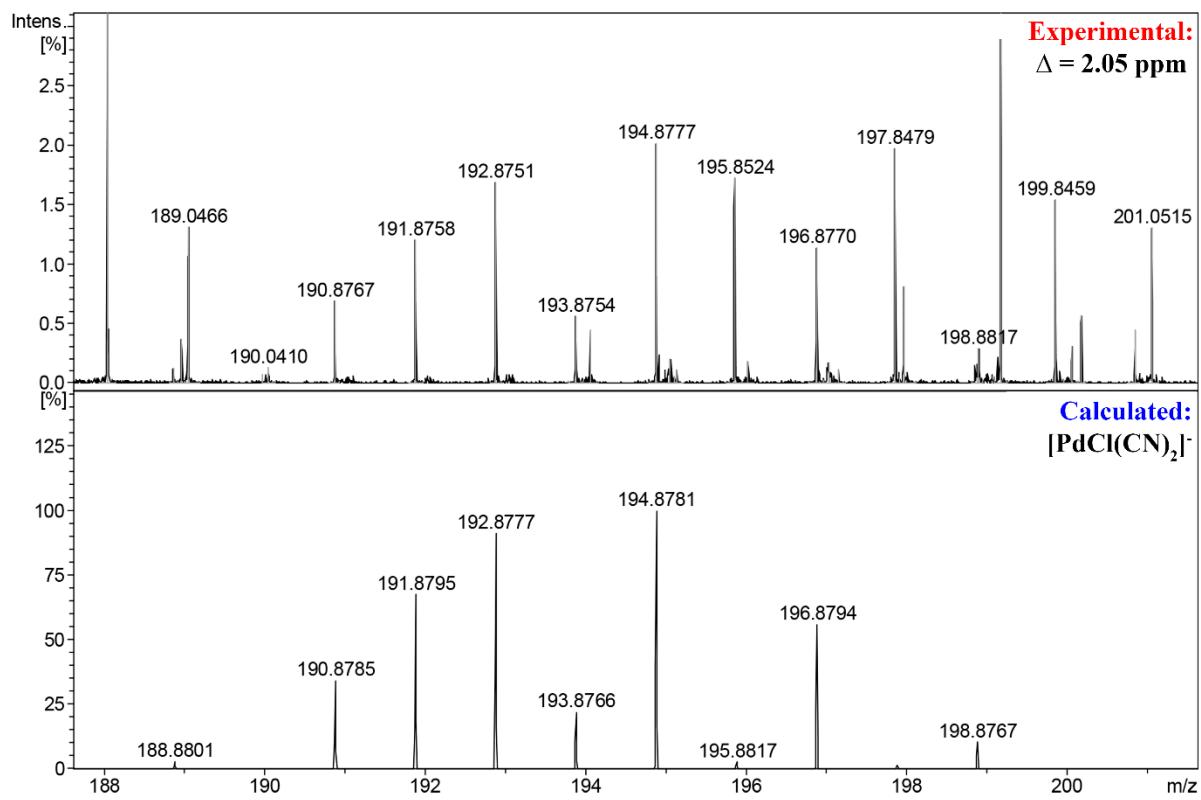


Figure S8. ESI-MS spectra in negative ion mode: ions formed in Pd/graphite rod (1 h of heating). Experimental (top) and calculated (bottom) spectra of $[\text{PdCl}(\text{CN})_2]^-$.

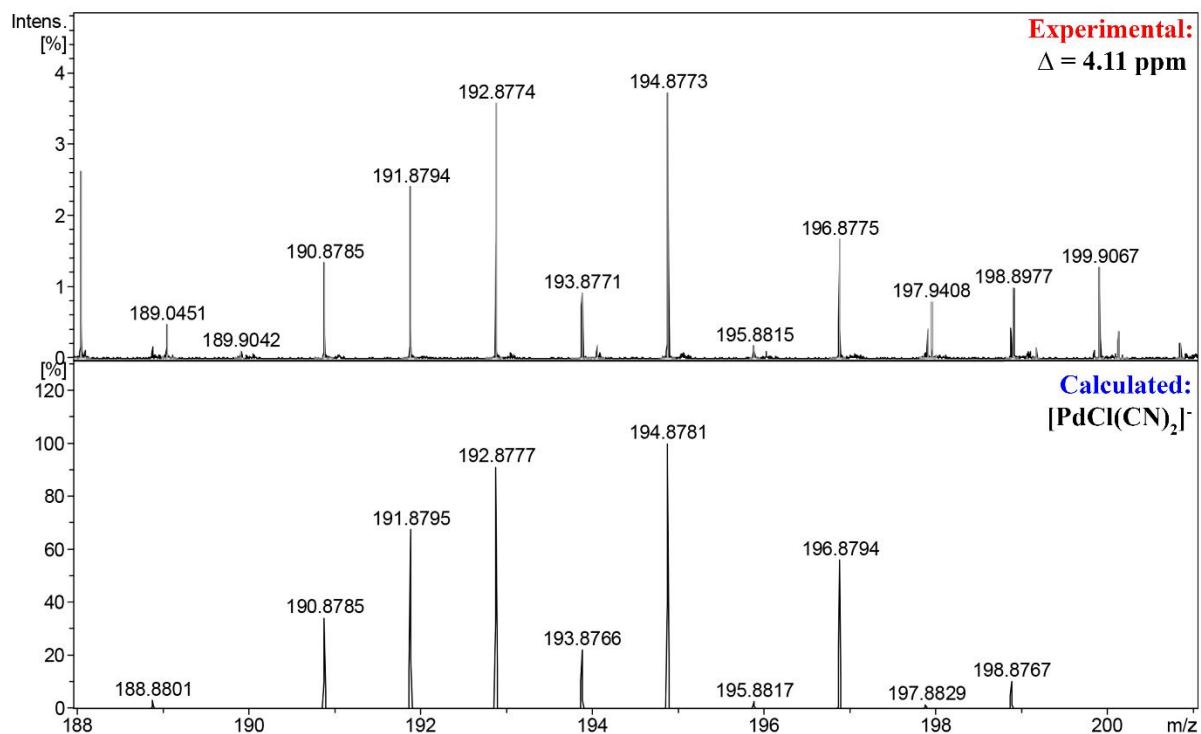


Figure S9. ESI-MS spectra in negative ion mode: ions formed in Pd/graphite rod (2 h of heating). Experimental (top) and calculated (bottom) spectra of $[\text{PdCl}(\text{CN})_2]^-$.

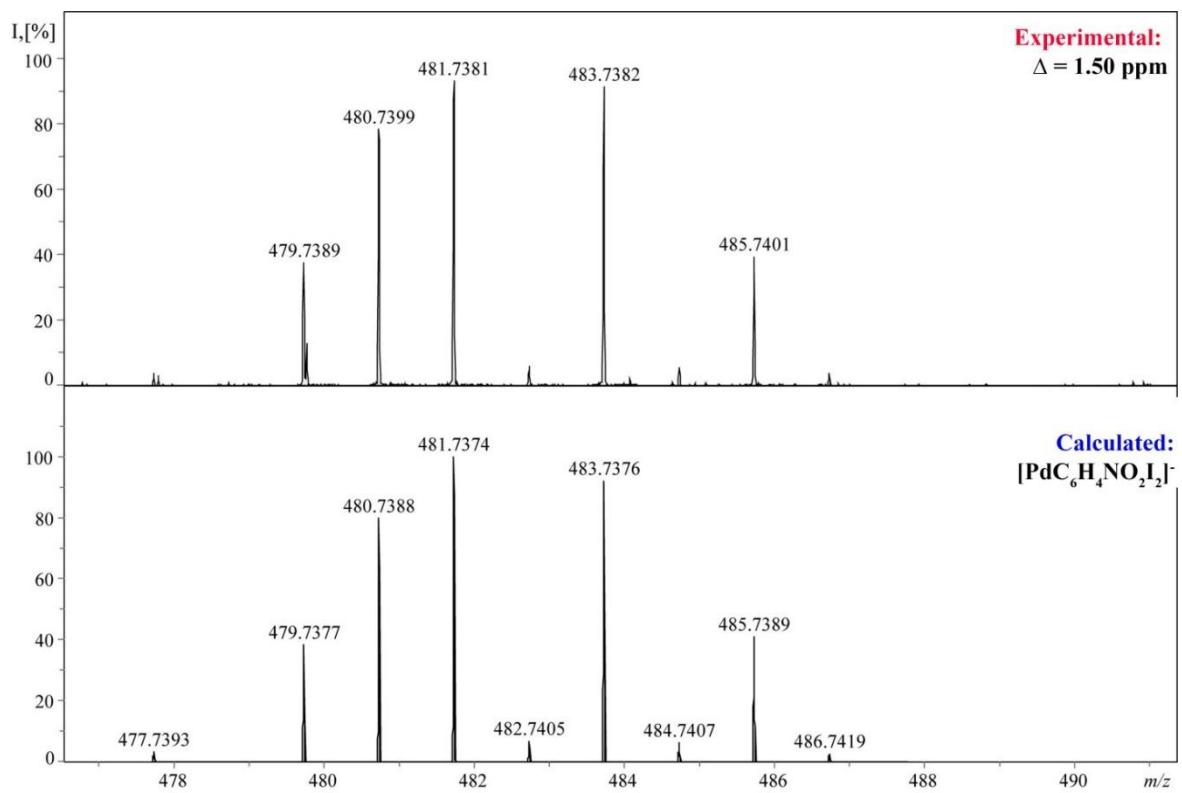


Figure S10. ESI-MS spectra in negative ion mode: $[\text{Pd}(\text{C}_6\text{H}_4\text{NO}_2)\text{I}_2]^-$ found in reaction mixture in the Mizoroki-Heck reaction with leached palladium species to DMF.

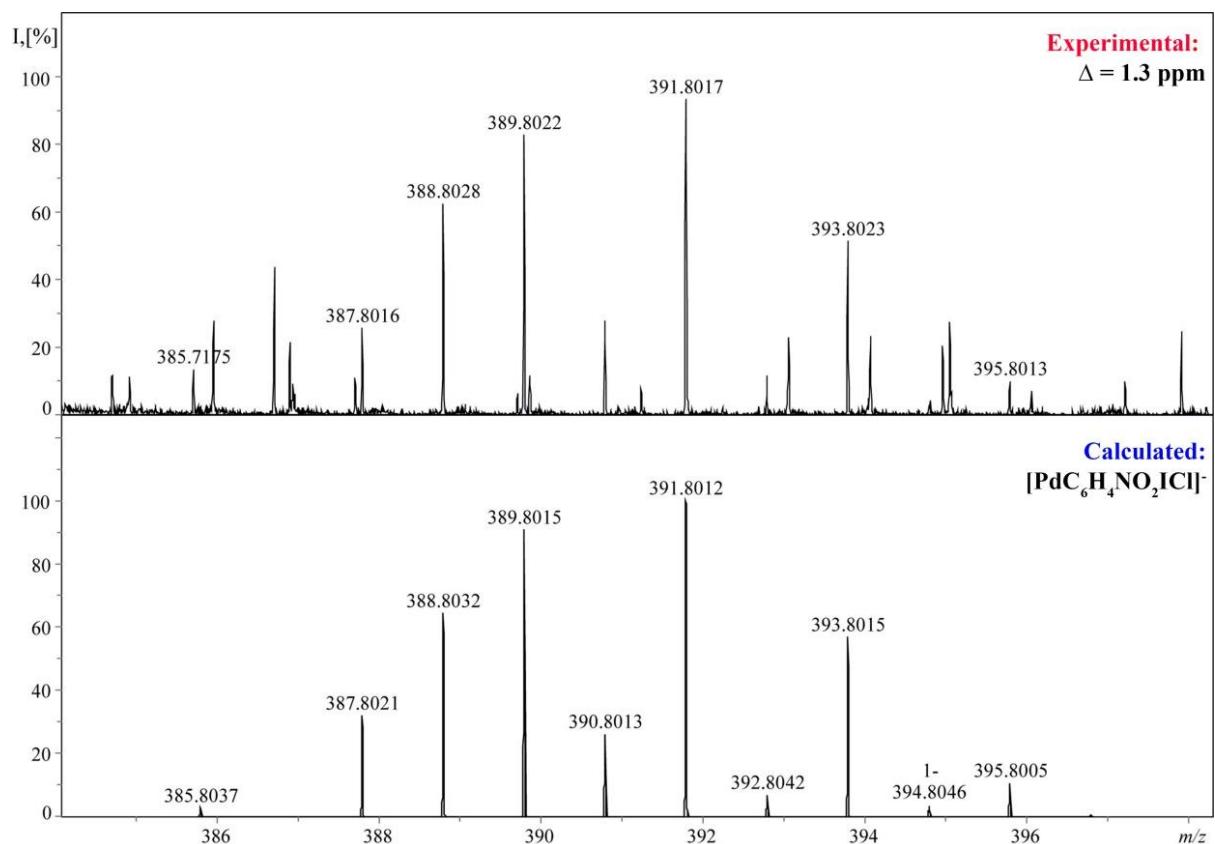


Figure S11. ESI-MS spectra in negative ion mode: $[\text{Pd}(\text{C}_6\text{H}_4\text{NO}_2)\text{Cl}]^-$ found in Mizoroki-Heck reaction with leached palladium species to DMF.

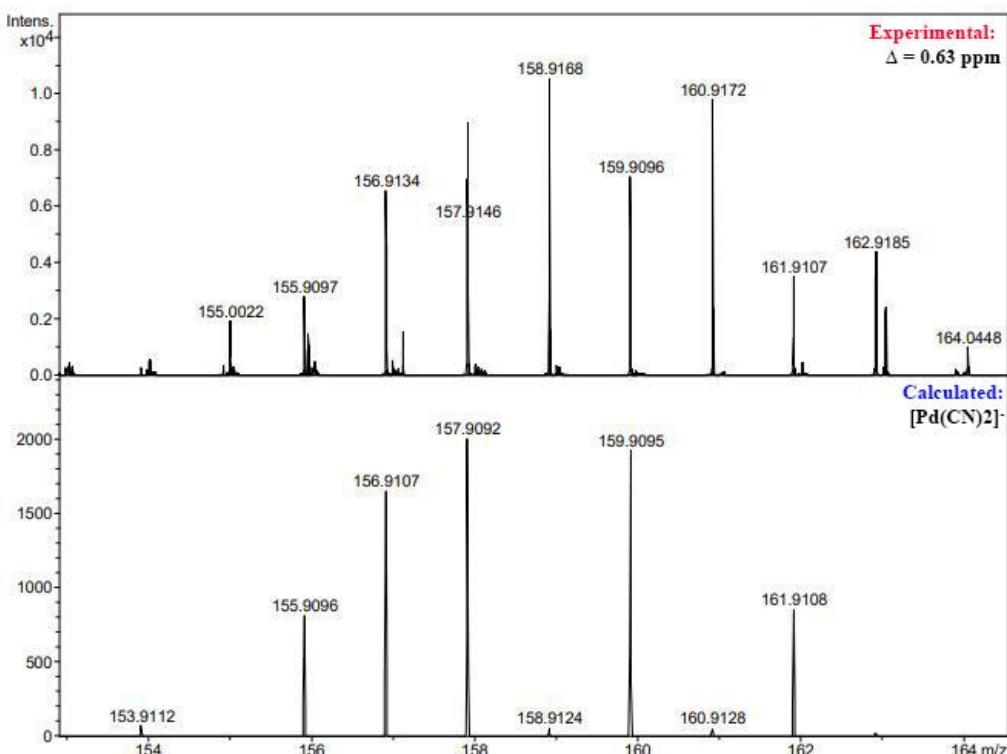


Figure S12. ESI-MS spectra in negative ion mode: Experimental (top) and calculated (bottom) spectra of $[\text{Pd}(\text{CN})_2]^-$.

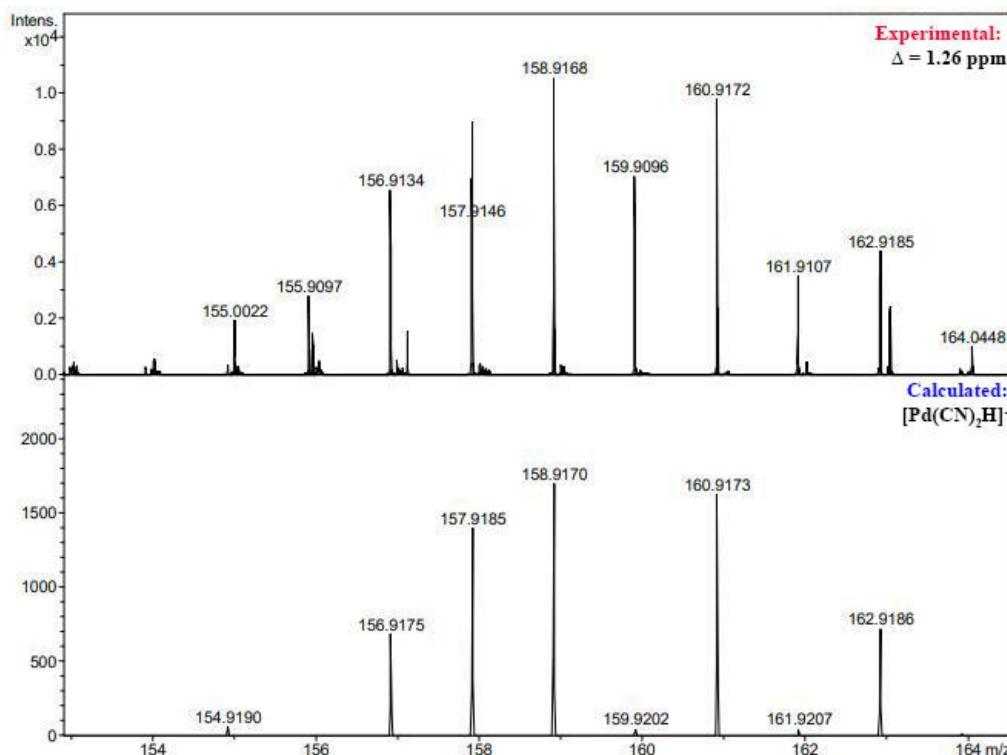


Figure S13. ESI-MS spectra in negative ion mode: Experimental (top) and calculated (bottom) spectra of $[\text{Pd}(\text{CN})_2\text{H}]^-$.

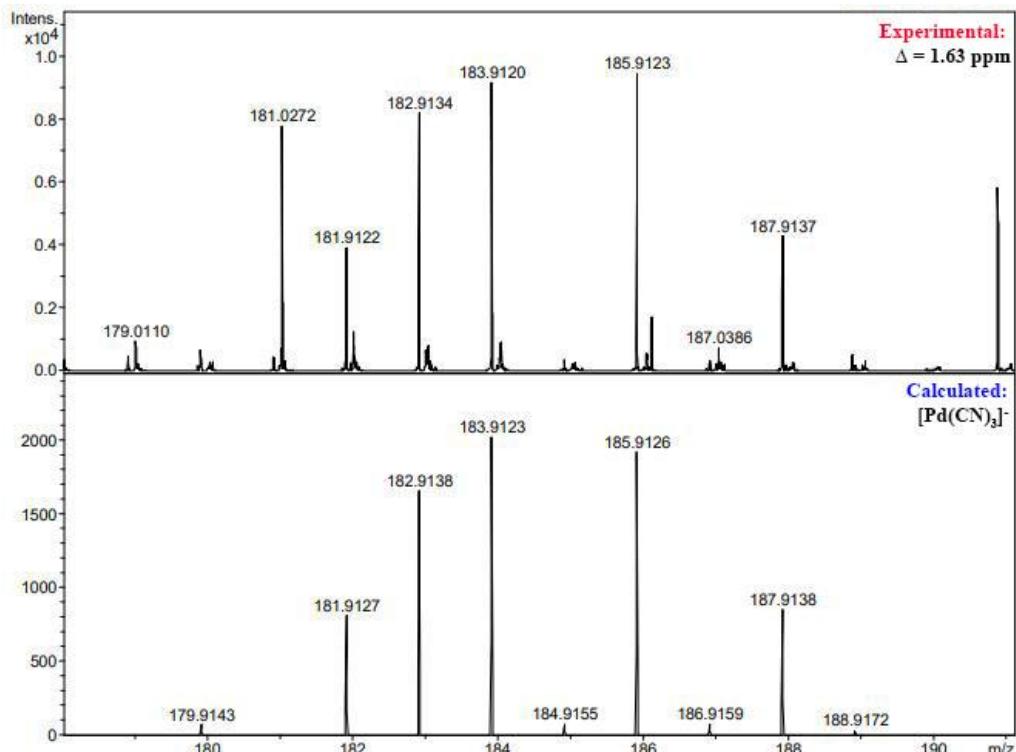


Figure S14. ESI-MS spectra in negative ion mode: Experimental (top) and calculated (bottom) spectra of $[\text{Pd}(\text{CN})_3]^-$.

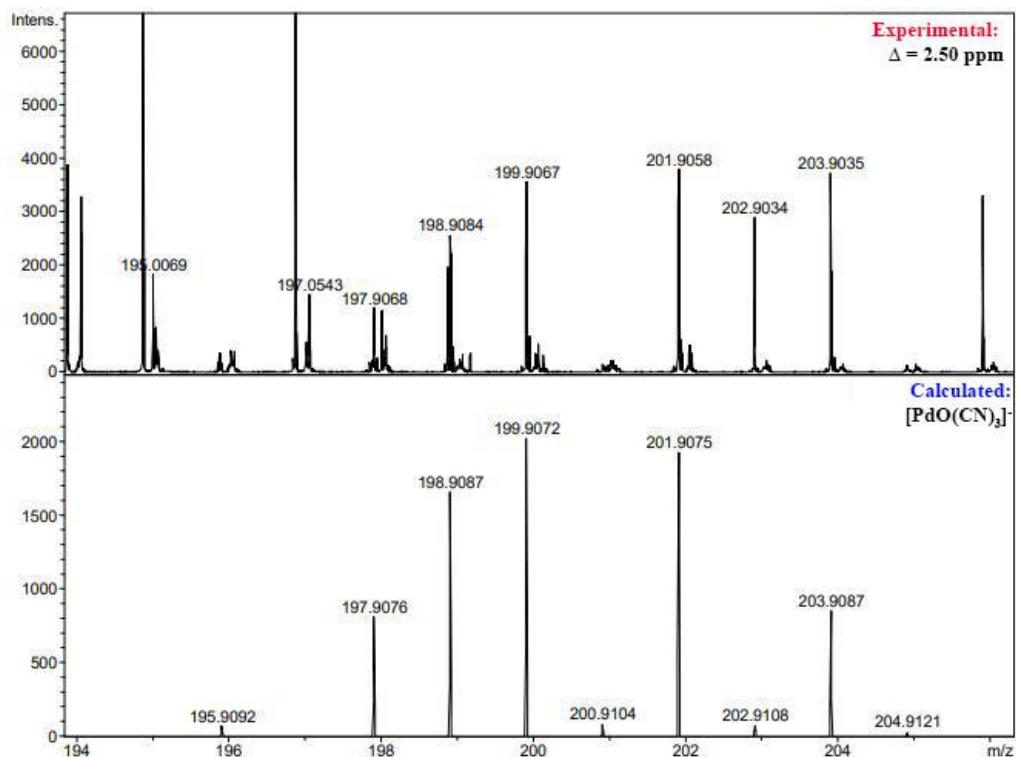


Figure S15. ESI-MS spectra in negative ion mode: Experimental (top) and calculated (bottom) spectra of $[\text{PdO}(\text{CN})_3]^-$.

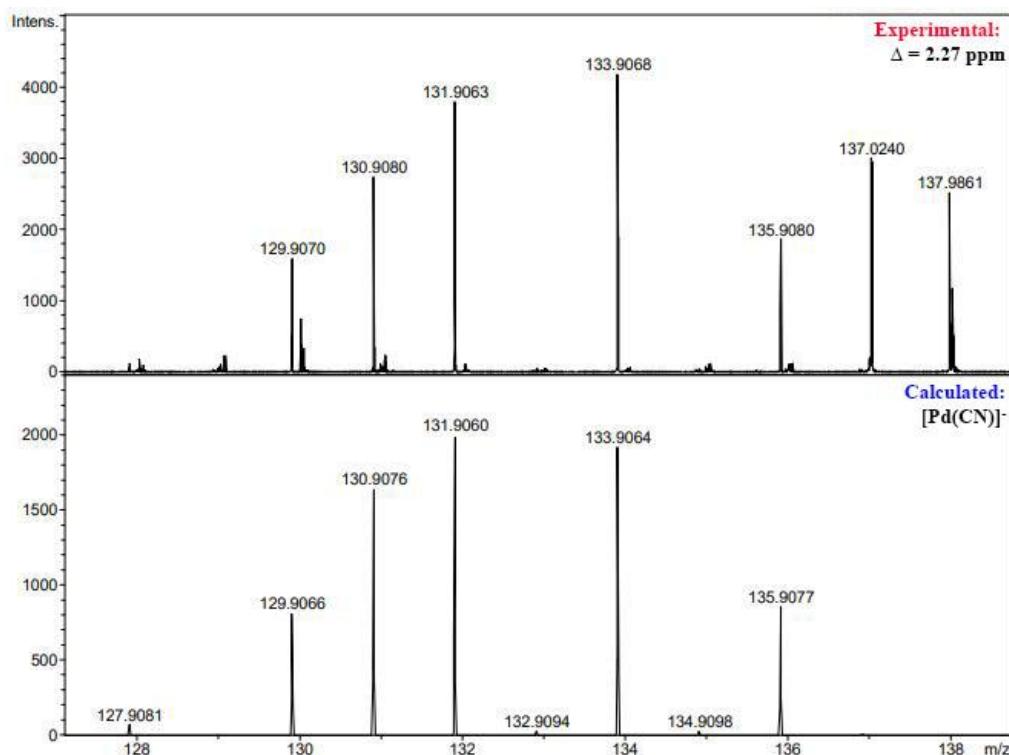


Figure S16. ESI-MS spectra in negative ion mode: Experimental (top) and calculated (bottom) of $[\text{Pd}(\text{CN})]^-$.

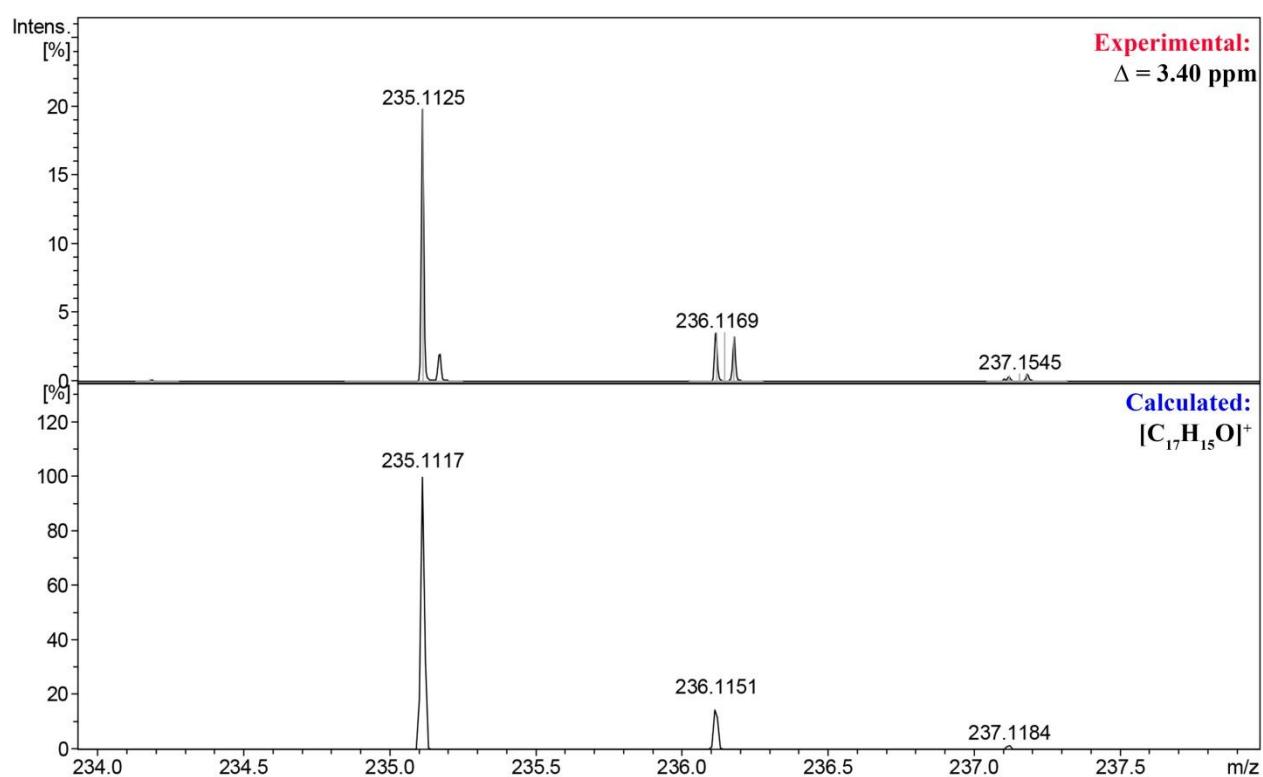


Figure S17. ESI-MS spectra in positive ion mode: Experimental (top) and calculated (bottom) of dibenzylideneacetone found in mixture Pd/MWCNT in DMF.