

## Supporting Information

### **Comparative study of aryl halides in Pd-mediated reactions: key factors beyond the oxidative addition step**

Alexey S. Galushko, Darya O. Prima, Julia V. Burykina, Valentine P. Ananikov\*

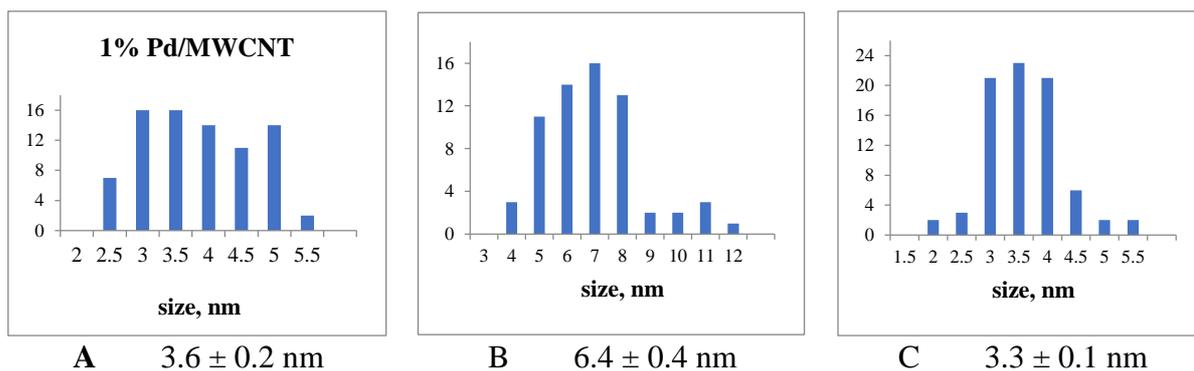
*Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prospekt 47,  
Moscow, 119991, Russia*

E-mail: val@ioc.ac.ru; <http://AnanikovLab.ru>

## Contents

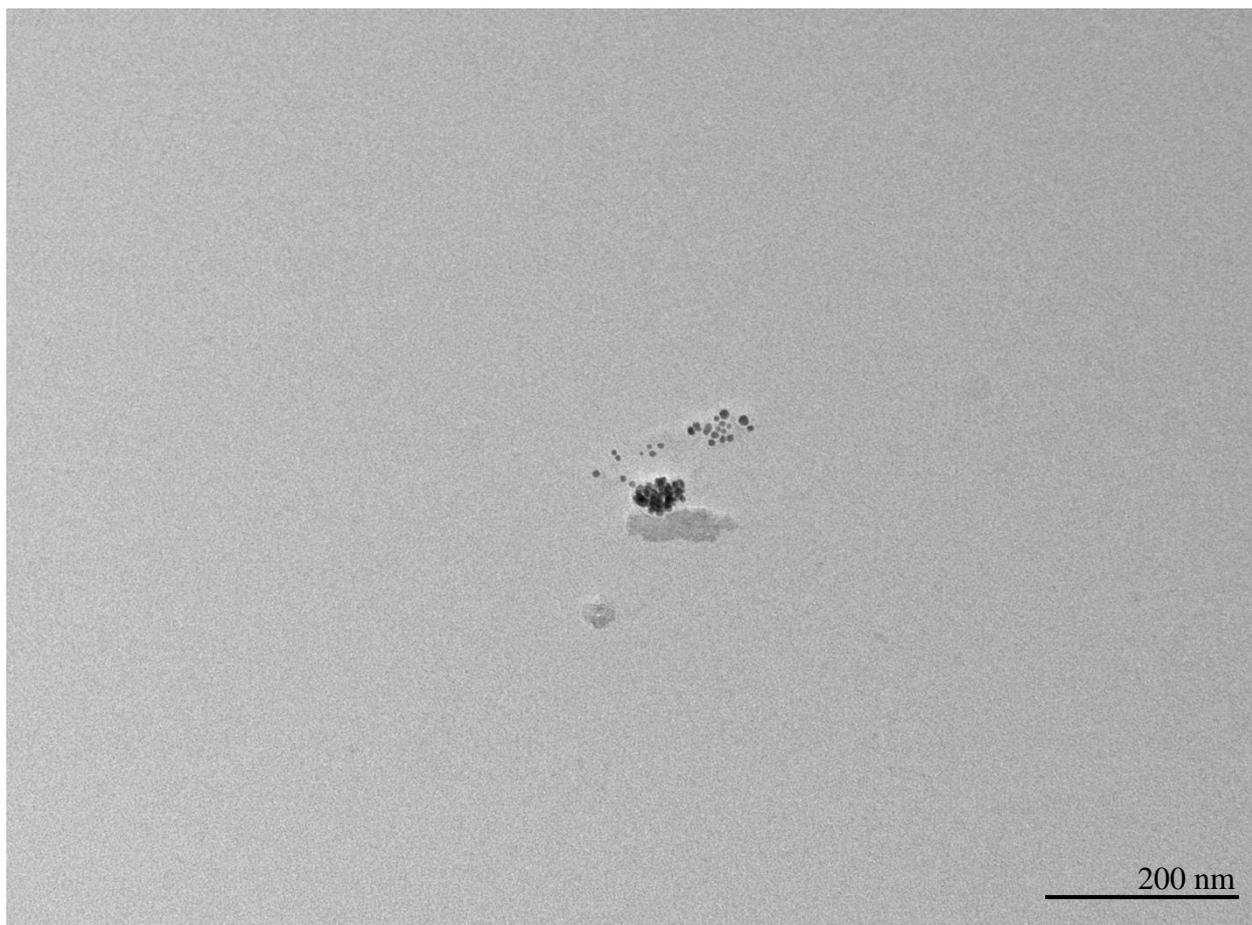
Size distribution of palladium nanoparticles before and after Heck reaction.....	3
Palladium nanoparticles found in the Heck reaction mixture .....	4
Overview of the «nanofishing» approach.....	8
ESI-MS spectrum .....	11
Nanofishing procedure for Heck reaction at 140 °C .....	12

## Size distribution of palladium nanoparticles before and after Heck reaction

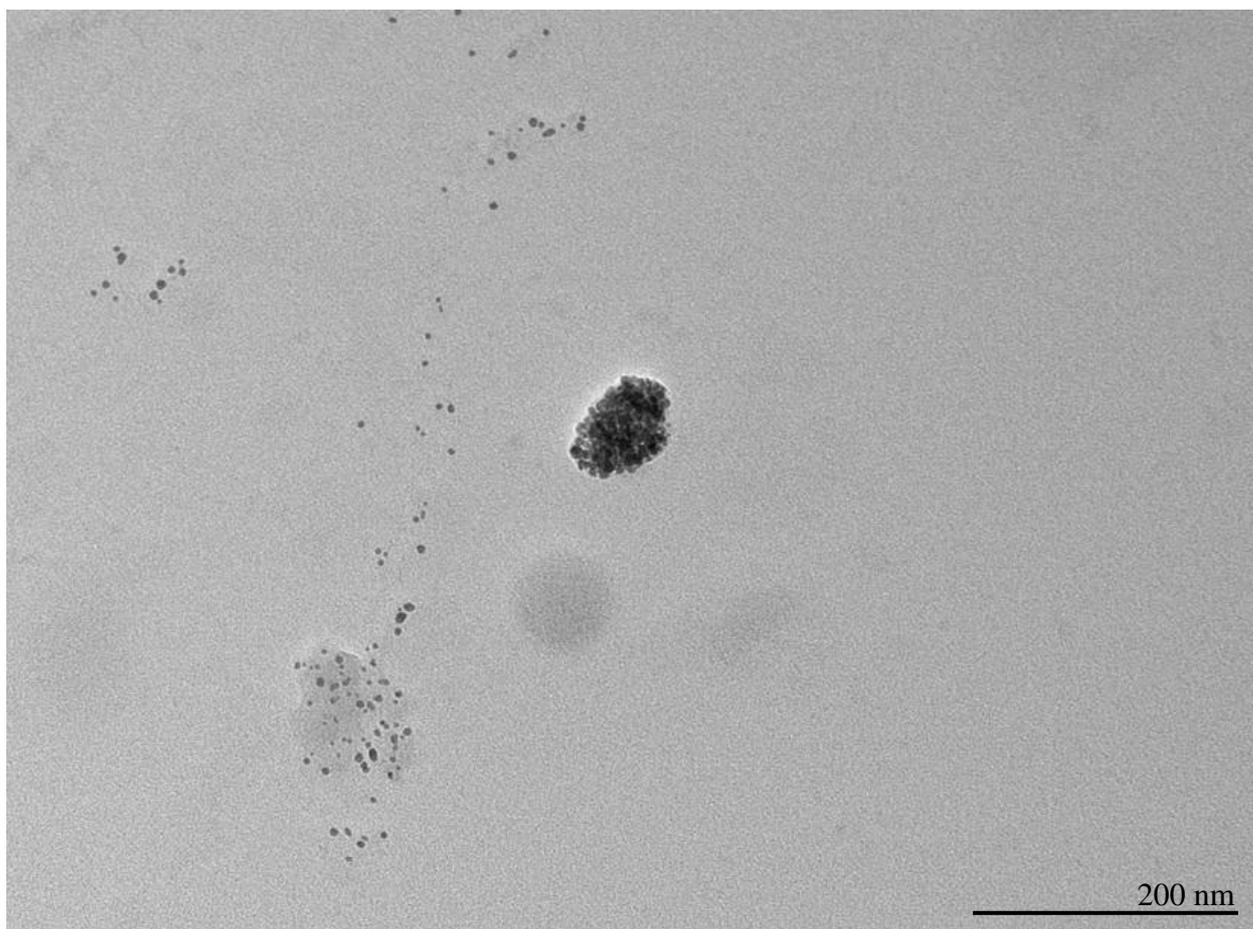


**Figure S1.** Size distribution of palladium nanoparticles in the initial catalyst (**A**); after Heck reaction with *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>Br remaining on the Pd/MWCNT (**B**); after Heck reaction with *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>Cl remaining on the Pd/MWCNT (**C**).

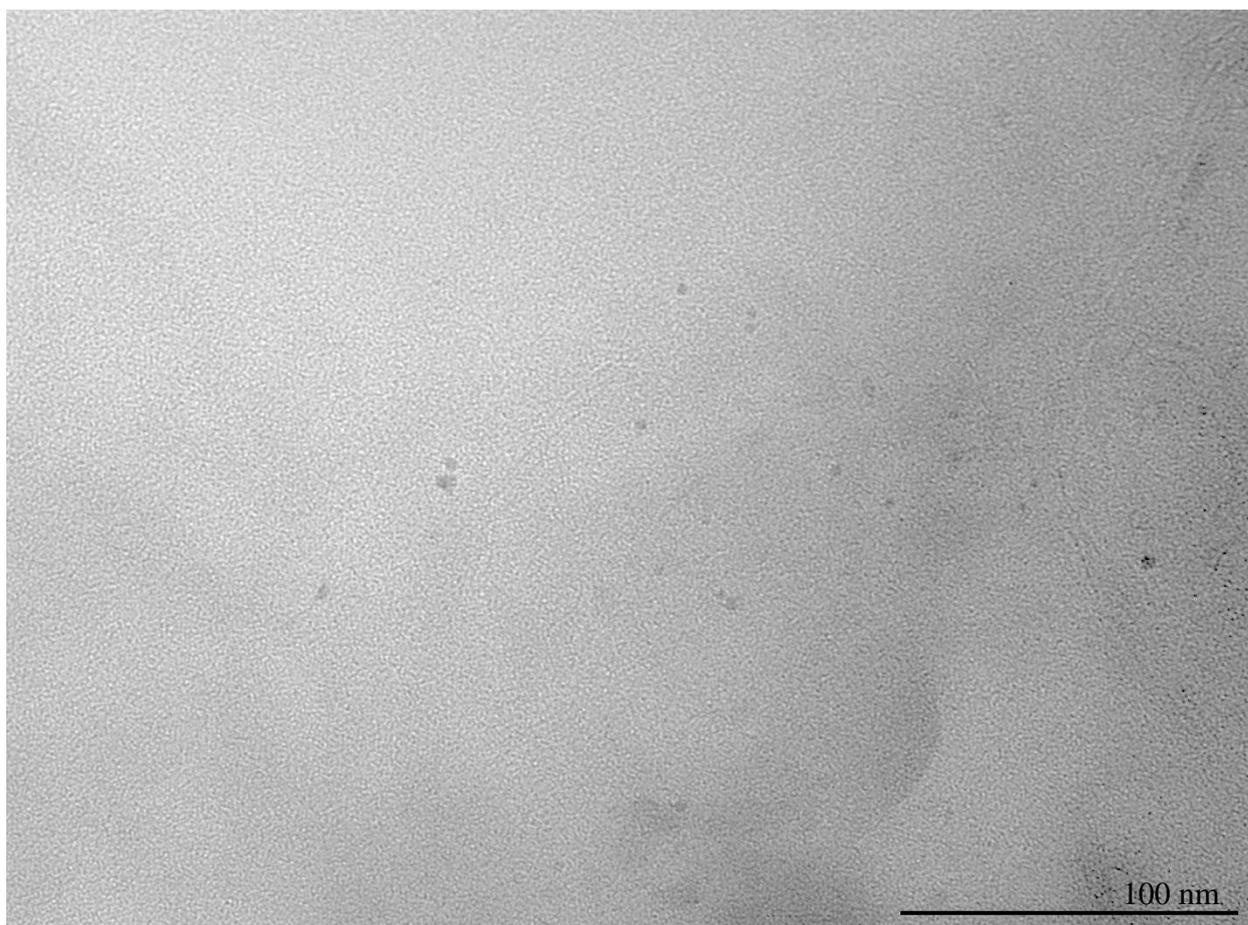
## Palladium nanoparticles found in the Heck reaction mixture



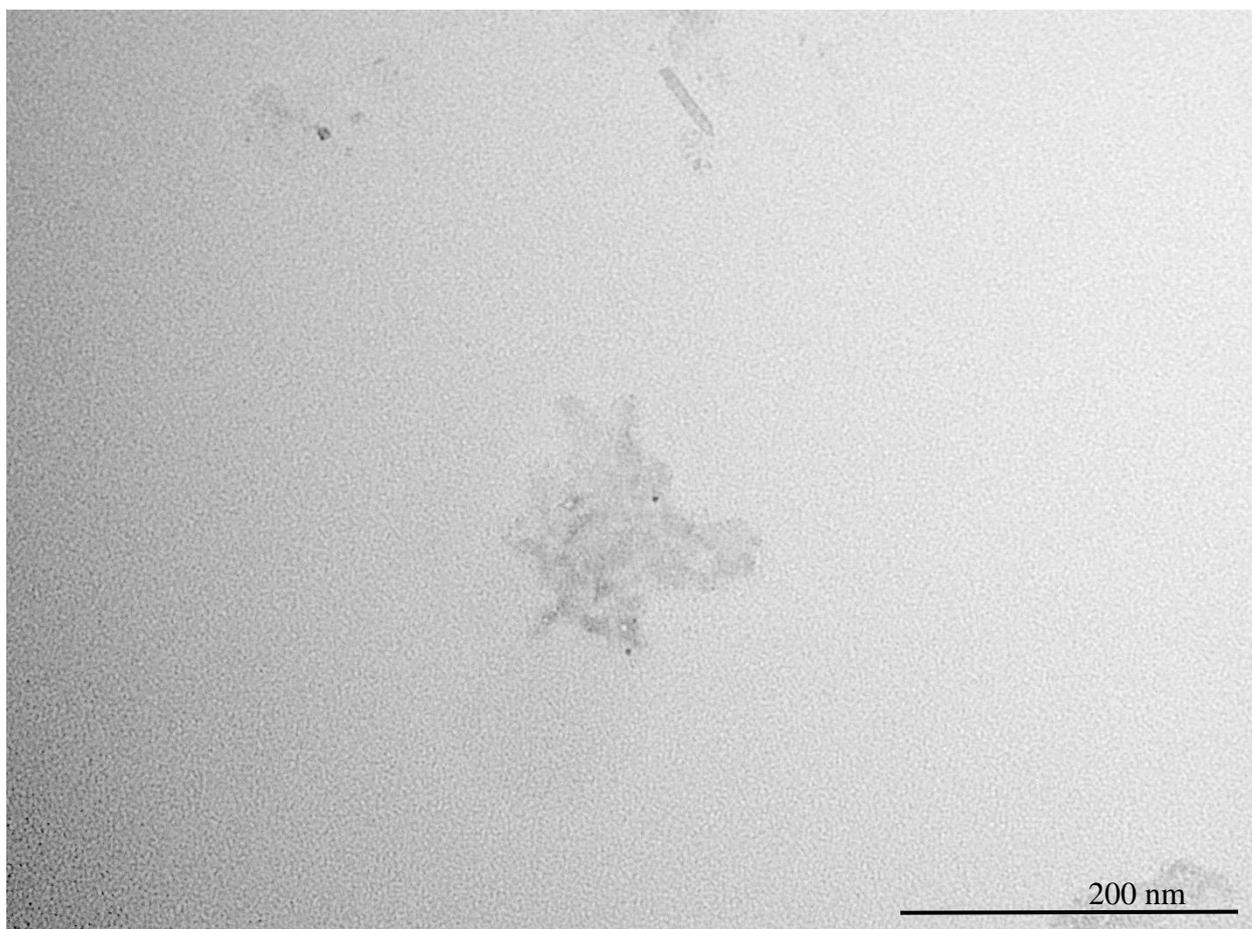
**Figure S2.** TEM image of palladium nanoparticles captured with “nanofishing” procedure after 1 h of Heck reaction involving PhBr and Pd/MWCNT.



**Figure S3.** TEM image of palladium nanoparticles captured with “nanofishing” procedure after 1 h of Heck reaction involving PhBr and Pd/MWCNT.

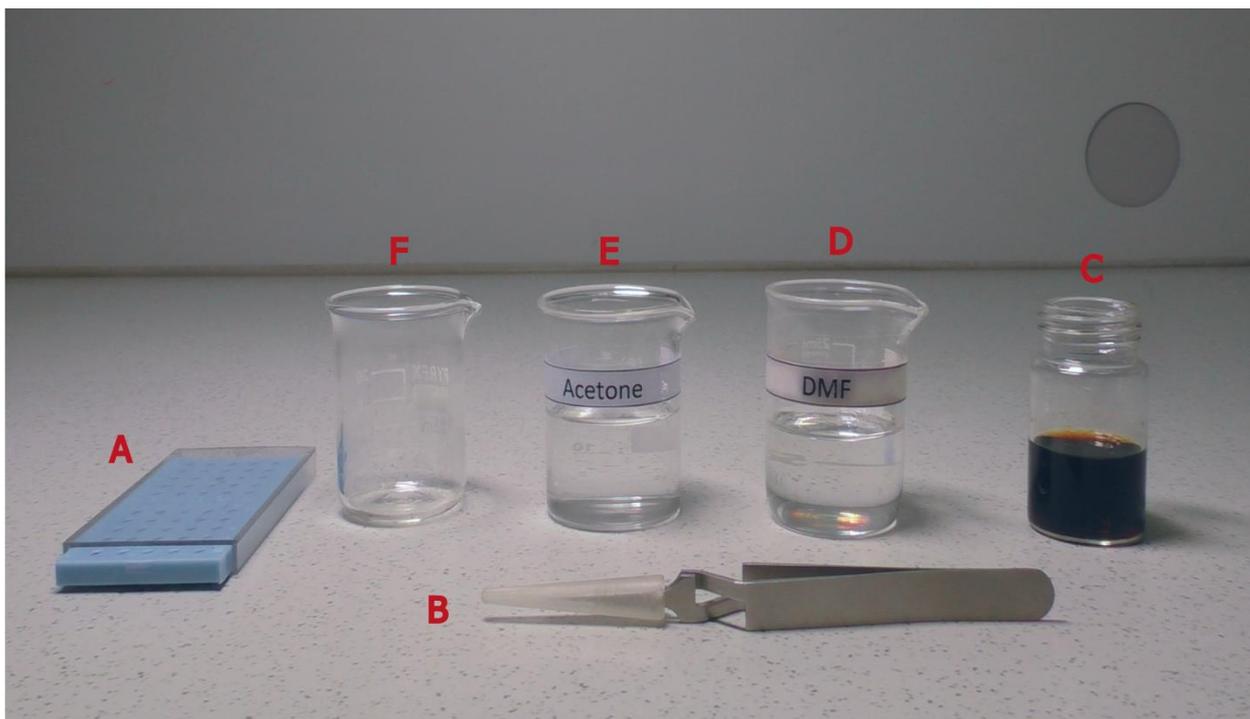


**Figure S4.** TEM image of palladium nanoparticles captured with “nanofishing” procedure after 1 h of Heck reaction involving PhBr and Pd/MWCNT.



**Figure S5.** TEM image of palladium nanoparticles captured with “nanofishing” procedure after 1 h of Heck reaction involving PhBr and Pd/MWCNT.

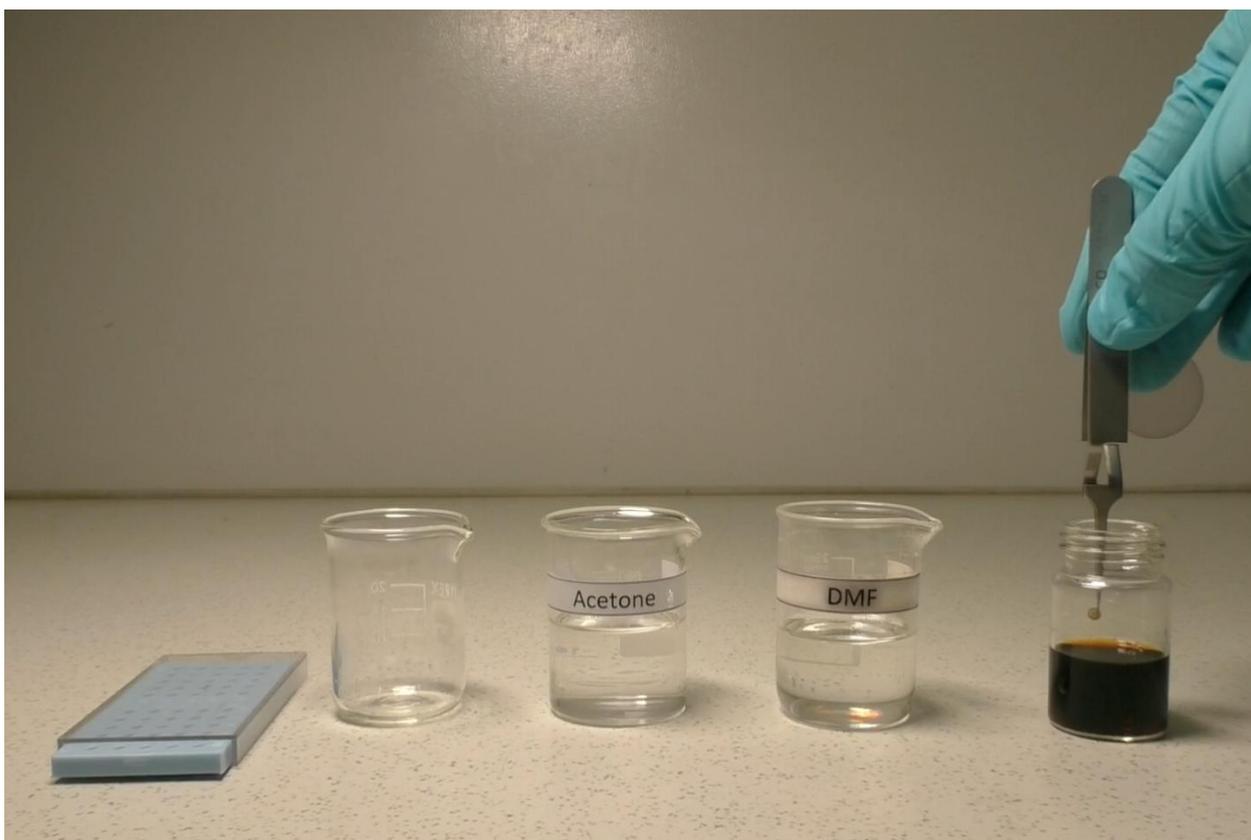
## Overview of the «nanofishing» approach



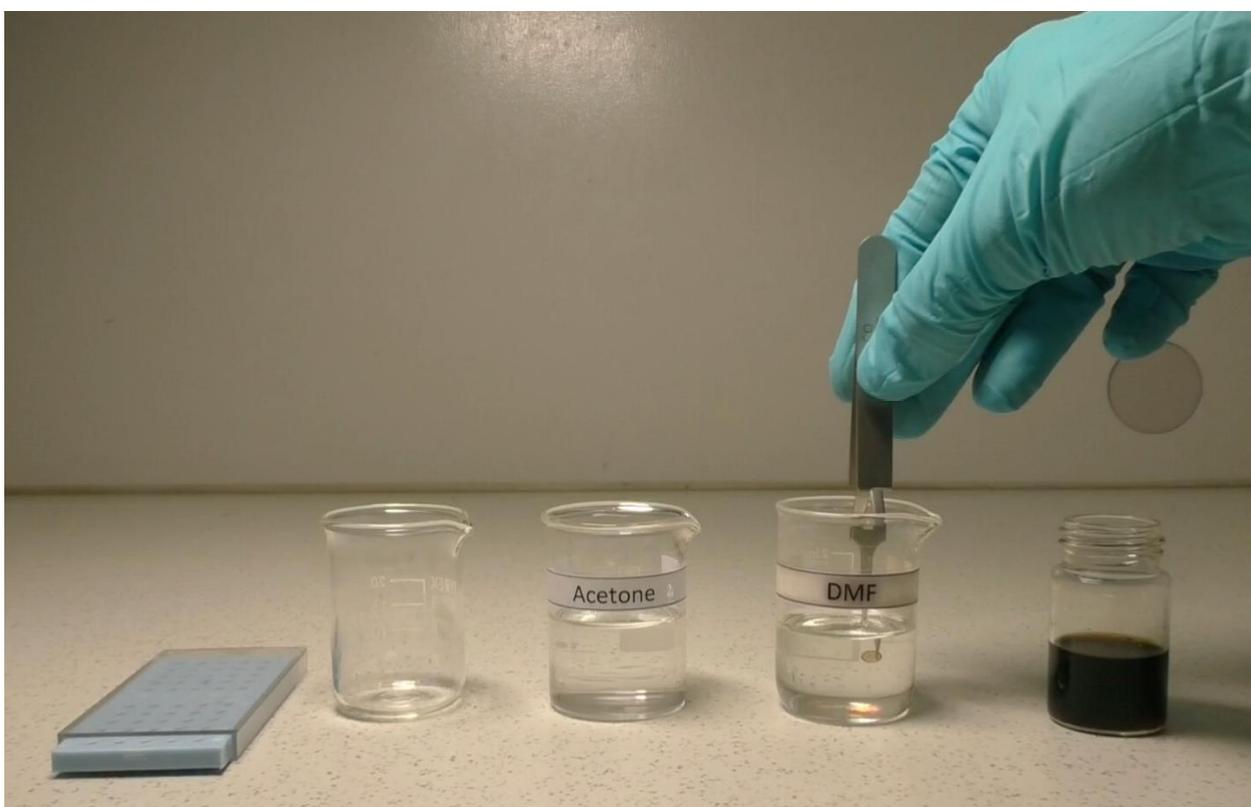
**Figure S6.** (A) Cassette for the storage of copper grids for TEM; (B) Reverse tweezers; (C) Studied solution containing nanoparticles; (D) reaction solvent for washing the grid; (E) volatile solvent (acetone) for washing grid after the reaction solvent; (F) Holder for drying in air.



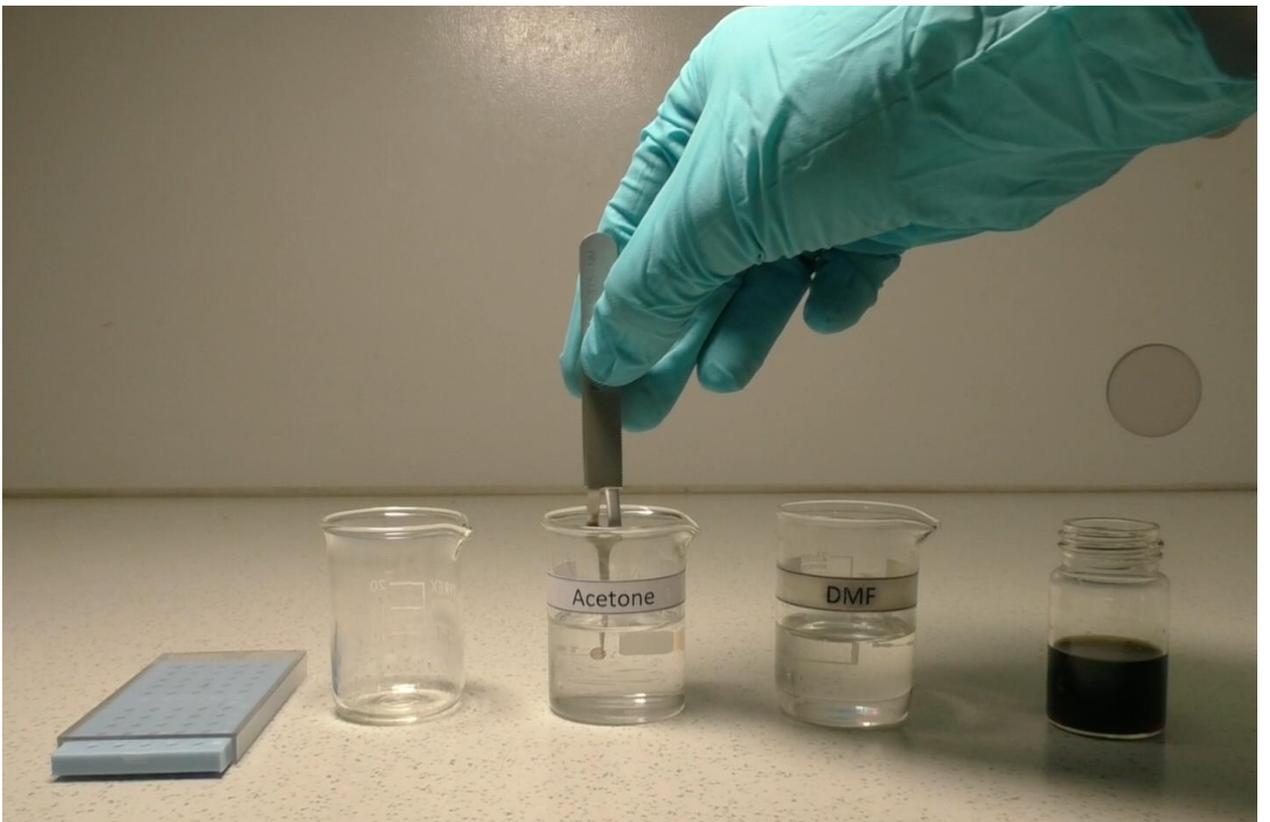
**Figure S7.** Pick the grid with reverse tweezers.



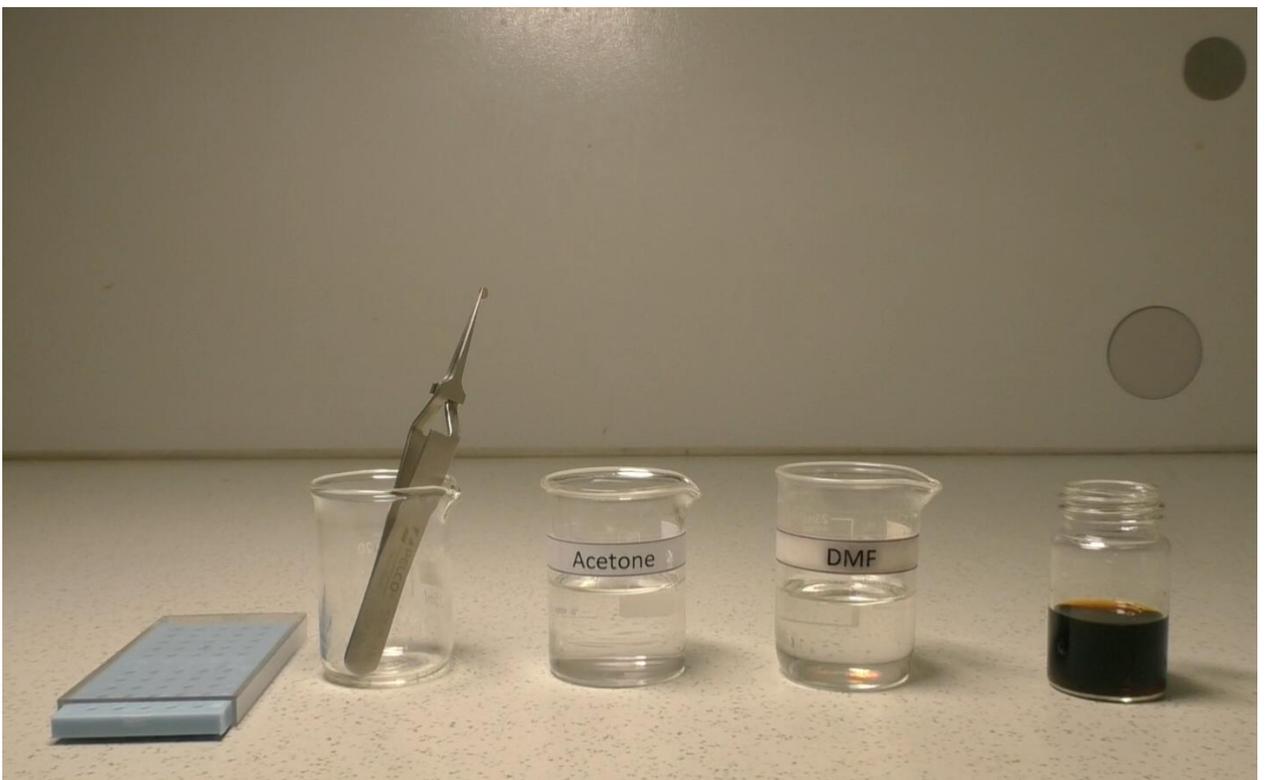
**Figure S8.** Place the grid into the reaction mixture for a few seconds.



**Figure S9.** Wash the grid with the reaction solvent (DMF in this case).

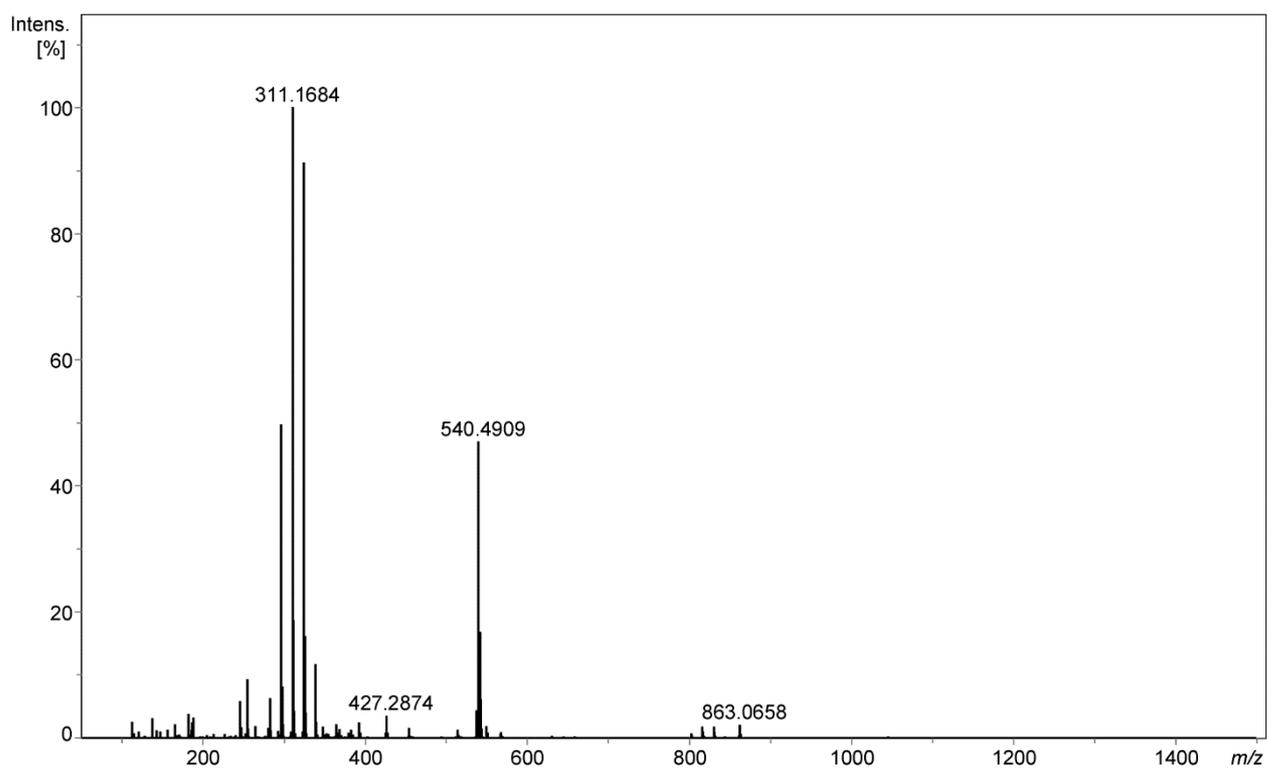


**Figure S10.** Wash the grid with a volatile solvent (acetone).



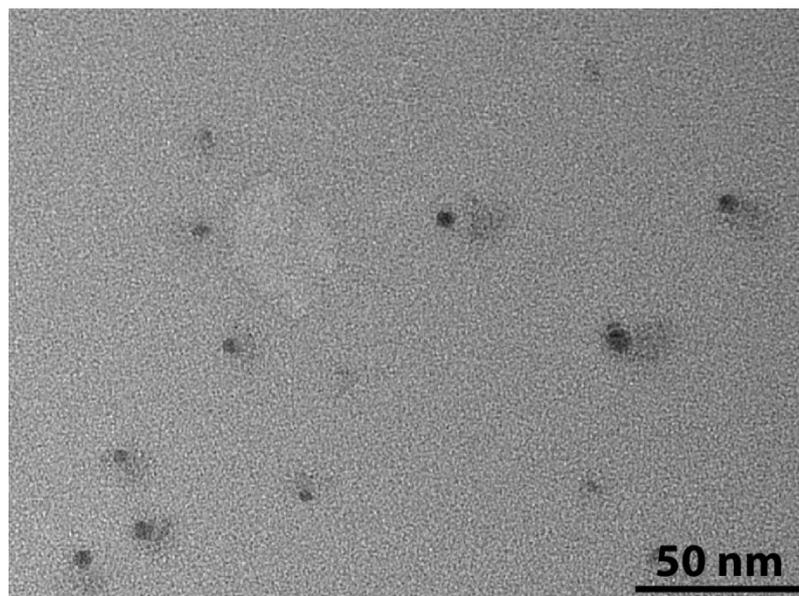
**Figure S11.** Dry the grid in air at room temperature and analyze by TEM.

## ESI-MS spectrum



**Figure S12.** Experimental ESI(-)MS spectrum of the reaction mixture *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-Cl and styrene with Pd/MWCNT in DMF solution. No corresponding palladium complexes were observed in the ArCl/[Pd]/styrene system.

**Nanofishing procedure for Heck reaction at 140 °C**



**Figure S13.** TEM study of palladium nanoparticles obtained at 1 h from the reaction mixture of the Heck reaction with ArBr at 140 °C.