Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting information

"Dba-free" palladium intermediates in the Heck-Matsuda reaction

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A. General experimental conditions

1. Wacker Type Reduction of Palladium (II) to Palladium (0)

An ependorff flask was charged with $Pd(OAc)_2$ (0.80 mg, 3.56 μmol), MeCN (1 mL), 2,3-dihydrofuran (0.27 μL, 3.56 μmol), and the resulting mixture was homogenized with a vortex stirrer. Next, a aliquot of the reaction (10μL) was diluted with MeCN (1 mL) in an ependorff flask and analysed by ESI-(+)-MS/MS.

2. The Heck-Matsuda using $Pd(OAc)_2$ as palladium source

An ependorff flask was charged with $Pd(OAc)_2$ (0.80 mg, 3.56 μmol), MeCN (1 mL), 2,3-dihydrofuran (0.27 μL, 3.56 μmol), and the resulting mixture was homogenized with a vortex stirrer. After 5 minutes, 0.4 mg of 4-$MeOPhN_2BF_4$ (1.78 μmol) were added to the reaction mixture. A aliquot of this reaction (10μL) was diluted with MeCN (1 mL) in an ependorff flask and the solution was analysed by ESI-(+)-MS/MS. Next, another portion of 4-$MeOPhN_2BF_4$ (0.4 mg, 1.78 μmol) was added to the reaction mixture. Again, an aliquot of this reaction (10μL) was diluted with MeCN (1 mL) in an ependorff flask and this solution was analysed once again by ESI-(+)-MS/MS.

ESI-MS and ESI-MS/MS.

All reagents were used without purification. ESI mass and tandem mass spectra in the positive-ion mode were acquired using a Micromass (Manchester, UK) QTof instrument of ESI-QTof configuration with 5.000 mass resolution and 50 ppm mass accuracy in the TOF mass analyzer. The following typical operating conditions were used: 3 kV capillary voltage, 8 V cone voltage, and desolvation gas temperature of 100 °C. Tandem ESI-MS/MS were collected after 4-32 eV collision-induced dissociation (CID) of mass-selected ions with argon. Mass-selection was performed by Q1 using a unitary *m/z* window, and collisions were performed in the rf-only hexapole collision cell, followed by mass analysis of product ions by the high-resolution orthogonal reflectron TOF analyzer.

B. Characterization Data for the Intermediates

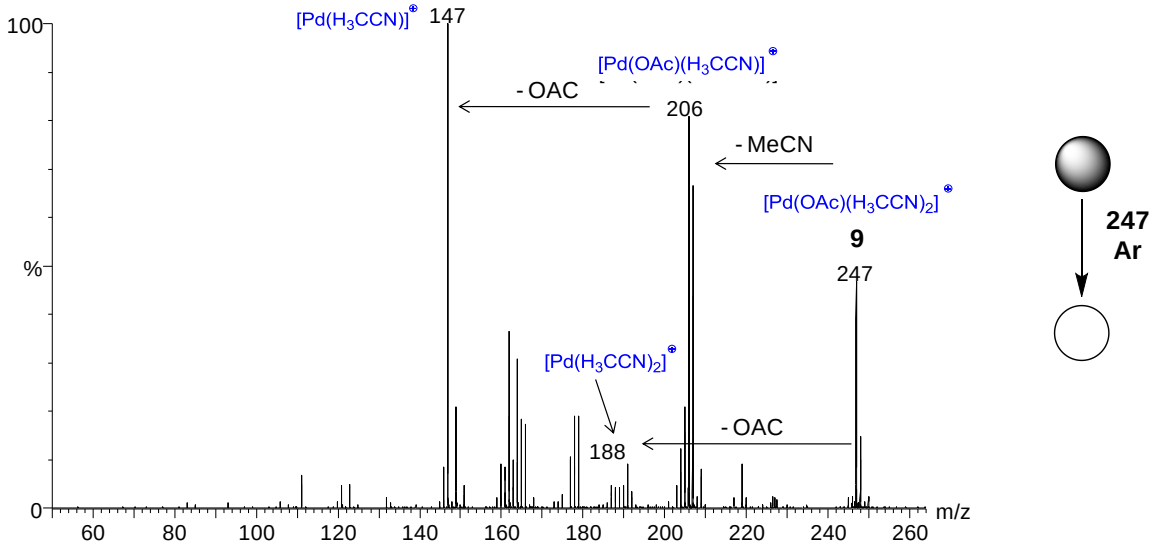

Figure S1. ESI-MS/MS of the ion of *m/z* 247 (**9**) obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 5 minutes).

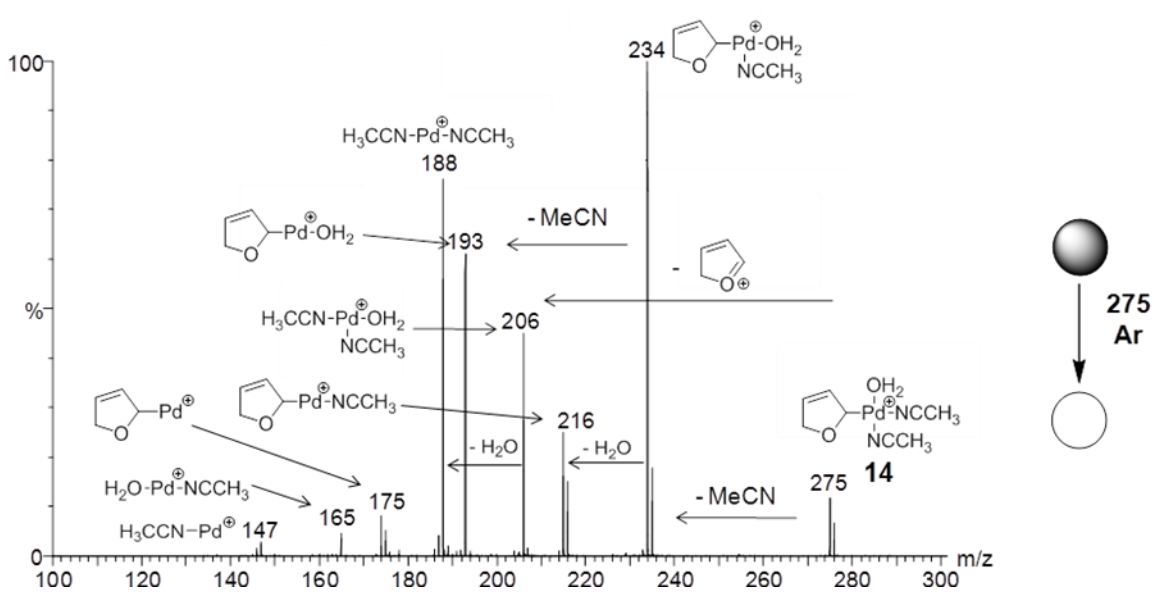

Figure S2. ESI-MS/MS of the ion of *m/z* 275 (**14**) obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 5 minutes).

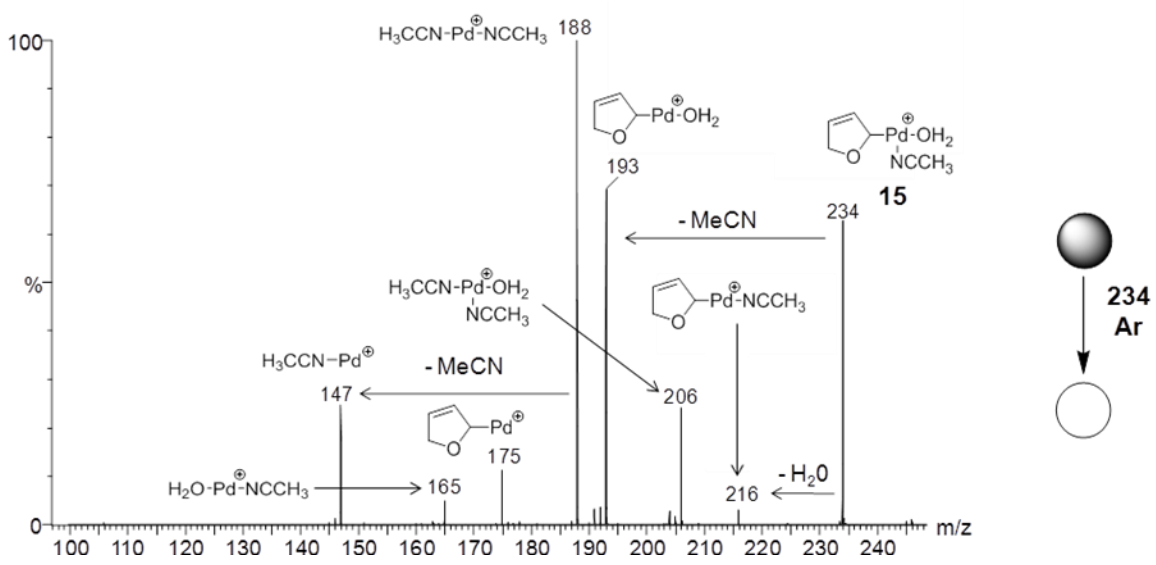

Figure S3. ESI-MS/MS of the ion of *m/z* 234 (**15**) obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 5 minutes).

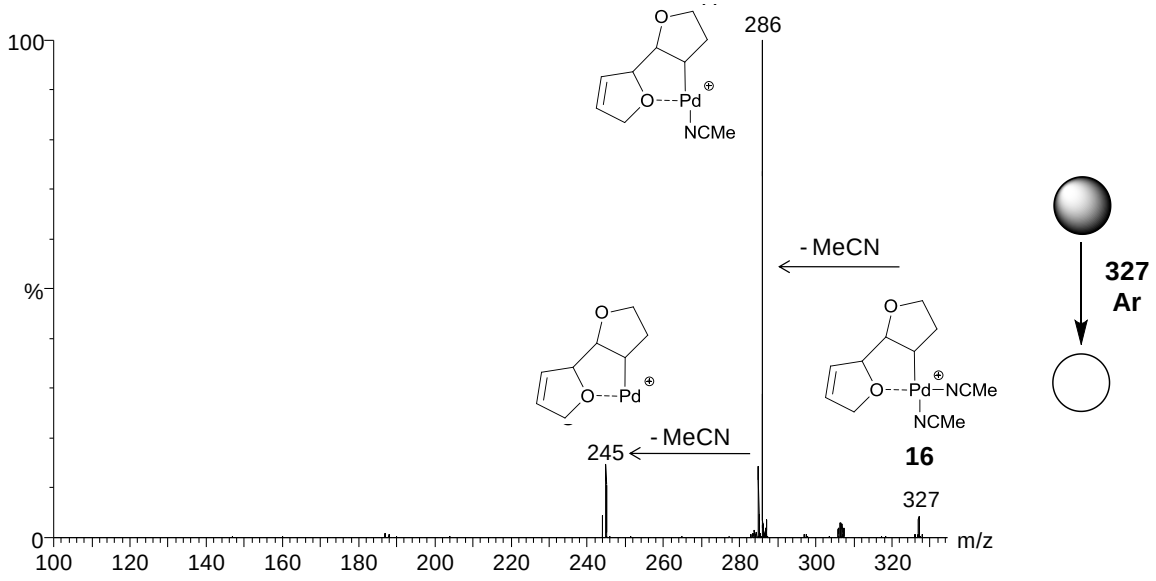

Figure S4. ESI-MS/MS of the ion of *m/z* 327 (**16**) obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 5 minutes).

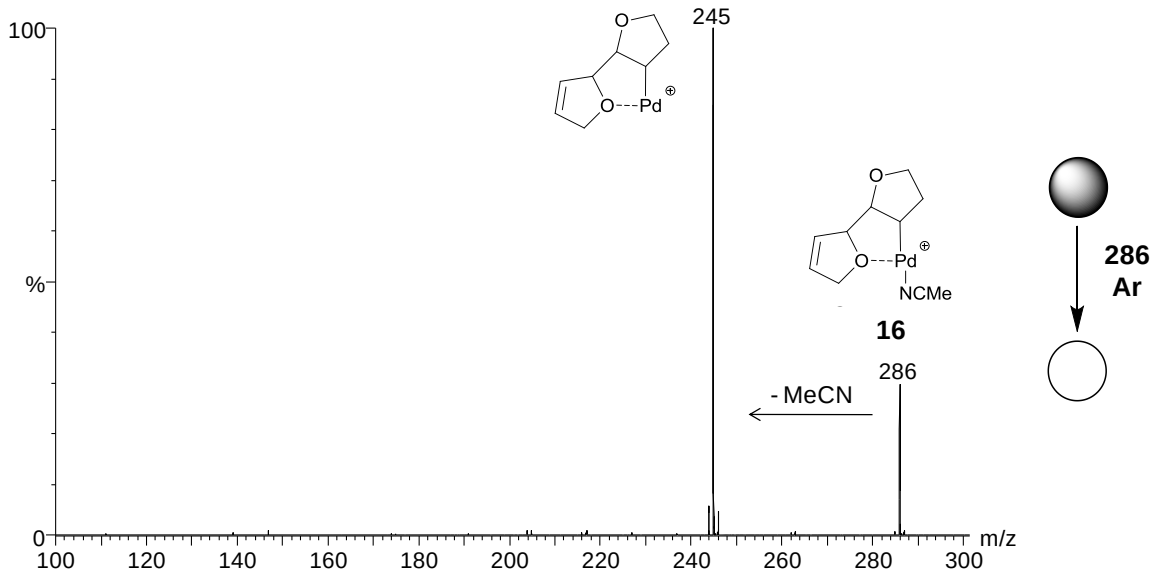

Figure S5. ESI-MS/MS of the ion of *m/z* 286 (**17**) obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 5 minutes).

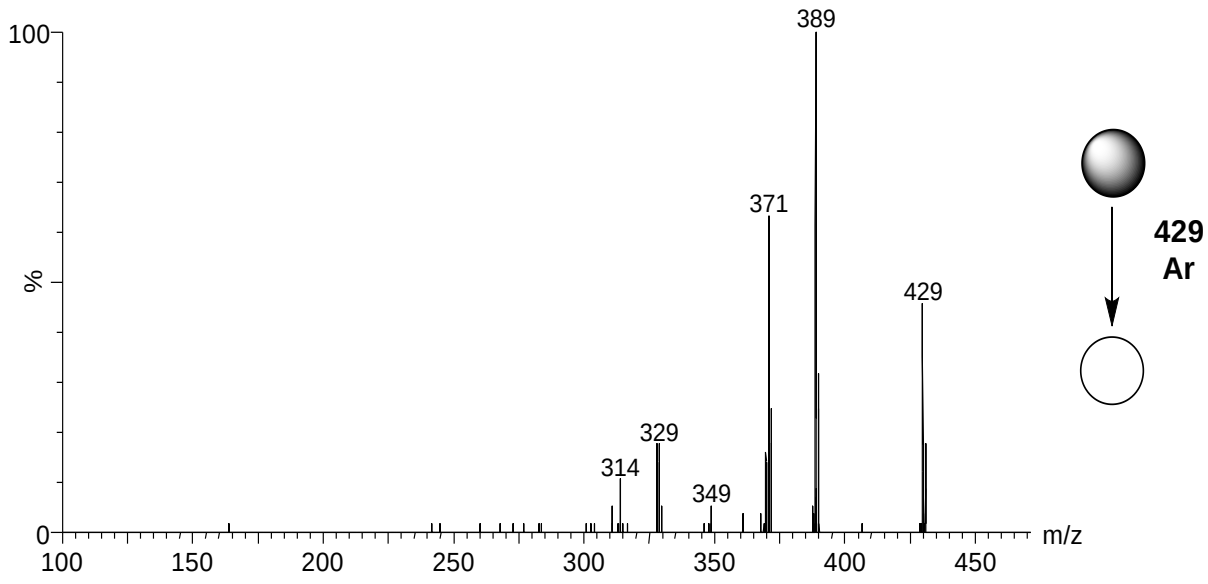

Figure S6. ESI-MS/MS of the ion of *m/z* 429 obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 30 minutes).

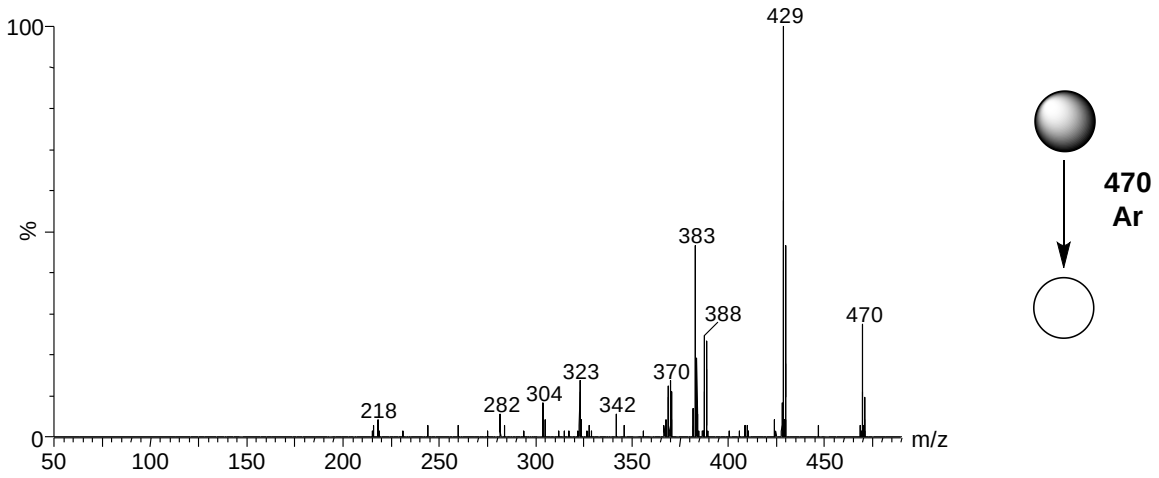

Figure S7. ESI-MS/MS of the ion of *m/z* 470 obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 30 minutes).

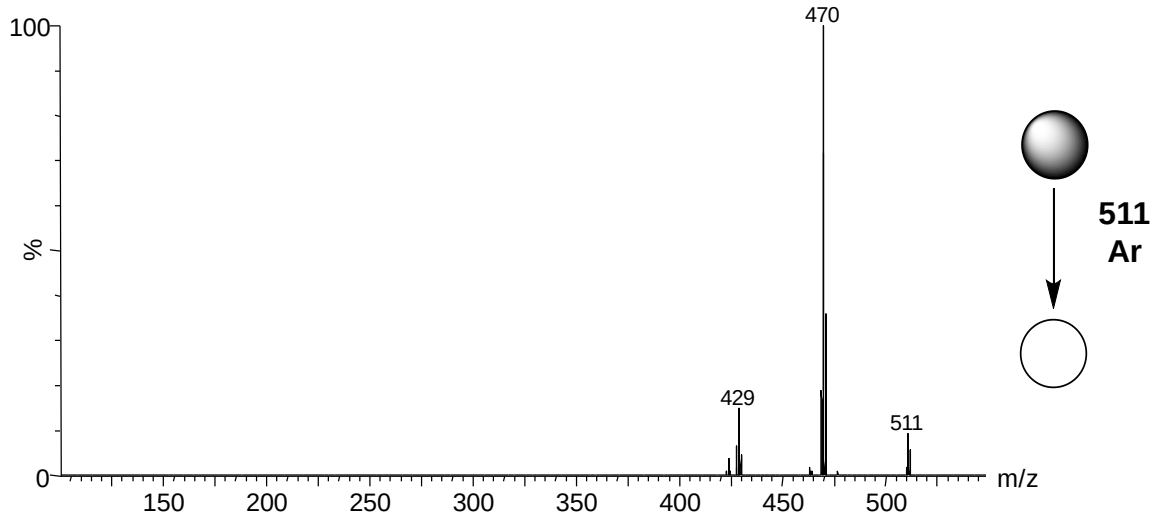

Figure S8. ESI-MS/MS of the ion of *m/z* 511 obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 30 minutes).

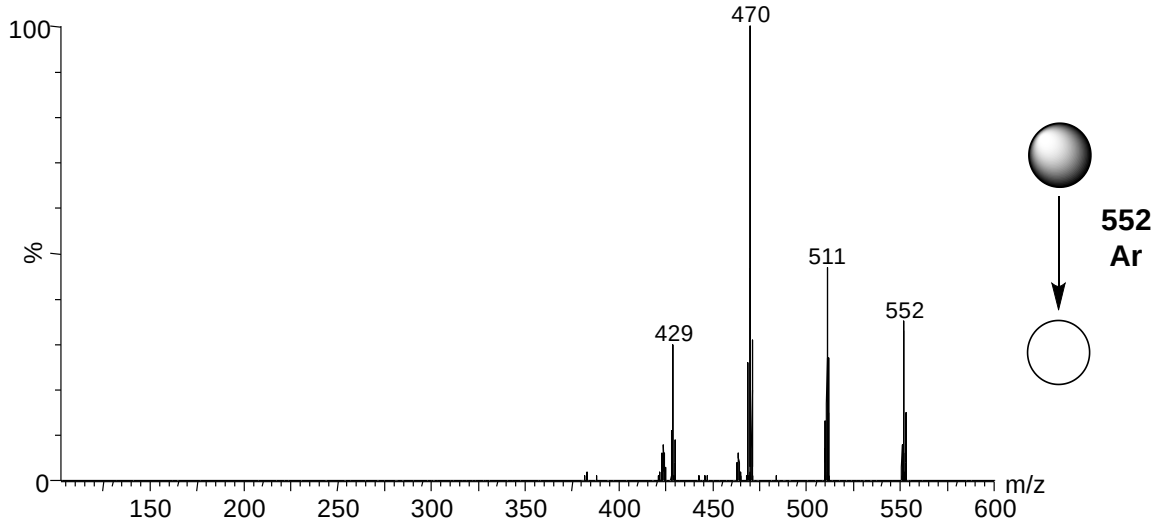

Figure S9. ESI-MS/MS of the ion of *m/z* 552 obtained in the reaction of stoichiometric $Pd(OAc)_2$ and DHF in MeCN (t = 30 minutes).

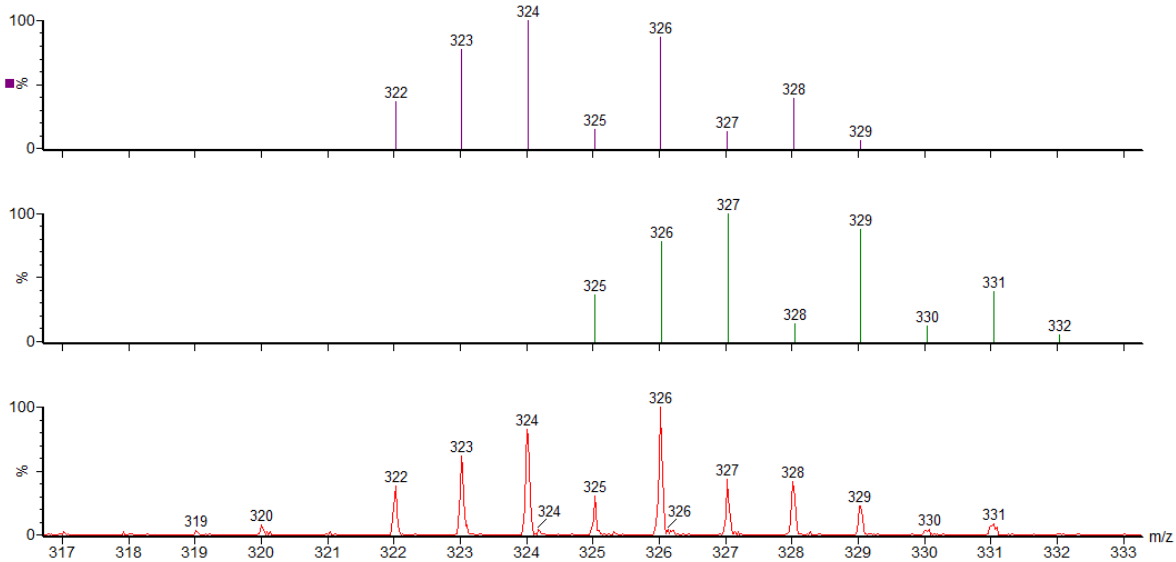

Figure S10. Cluster containing Palladium species (**16**) and (**19**) detected after addition of arenediazonium salt and corresponding isotopological distribution to these species proposed by MassLynx V 4.0 SP4 .

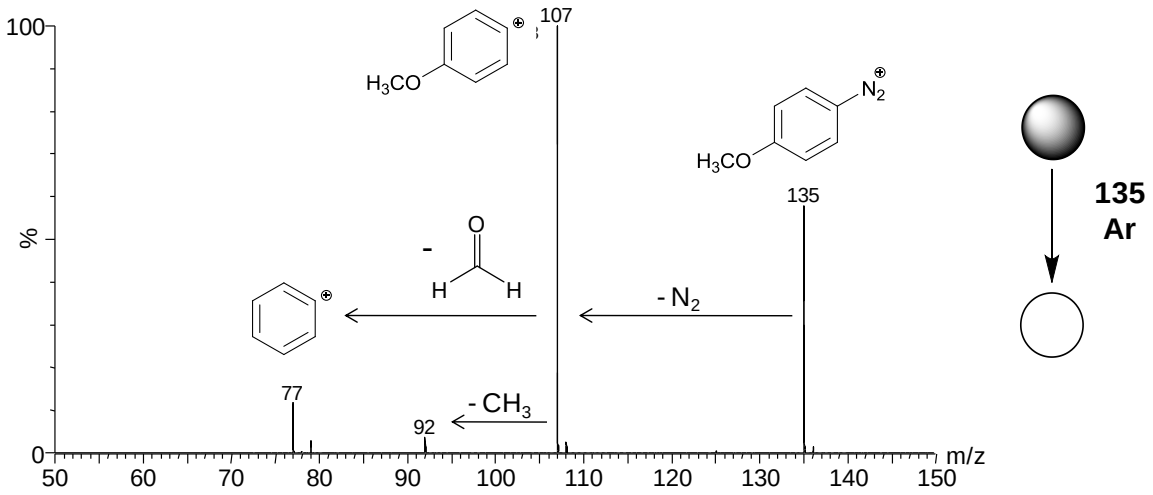

Figure S11. ESI-MS/MS of the ion of *m/z* 135 obtained after addition of arenediazonium salt.

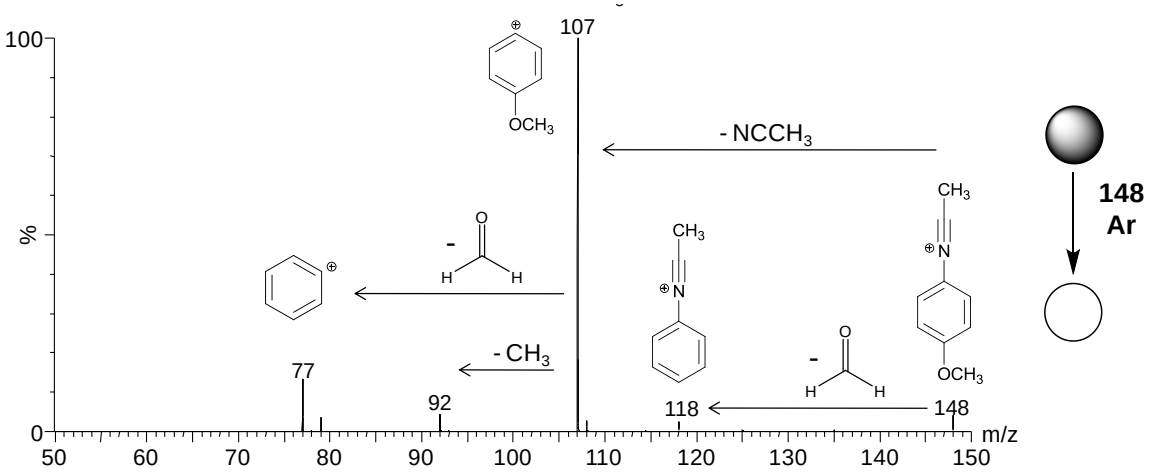

Figure S12. ESI-MS/MS of the ion of *m/z* 148 (**18**) obtained after addition of arenediazonium salt.

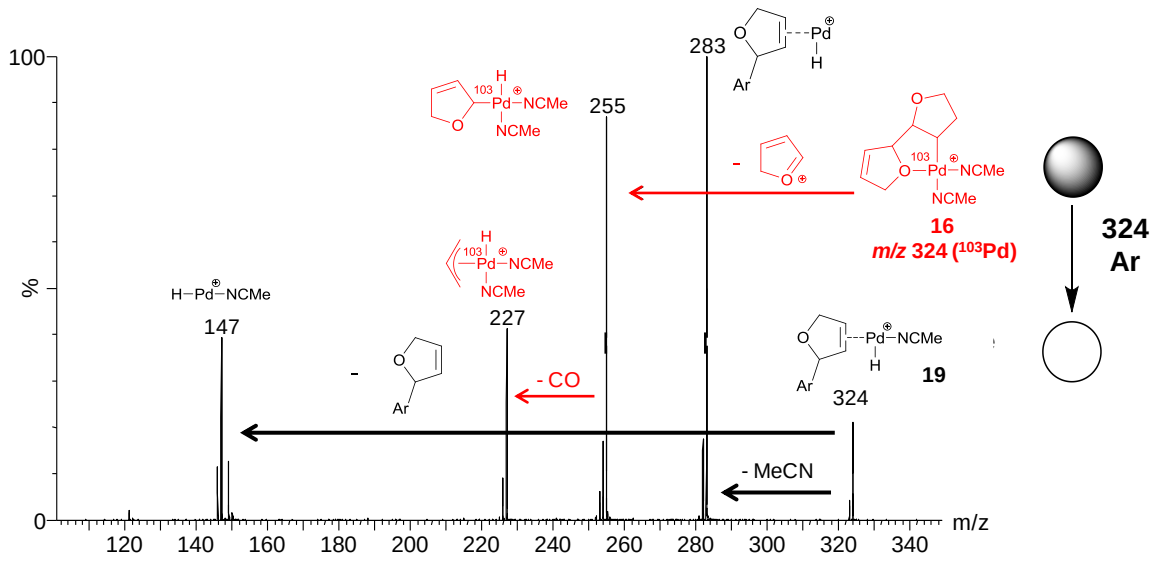

Figure S13. ESI-MS/MS of the ion of *m/z* 324 (**19**) obtained after addition of arenediazonium salt.

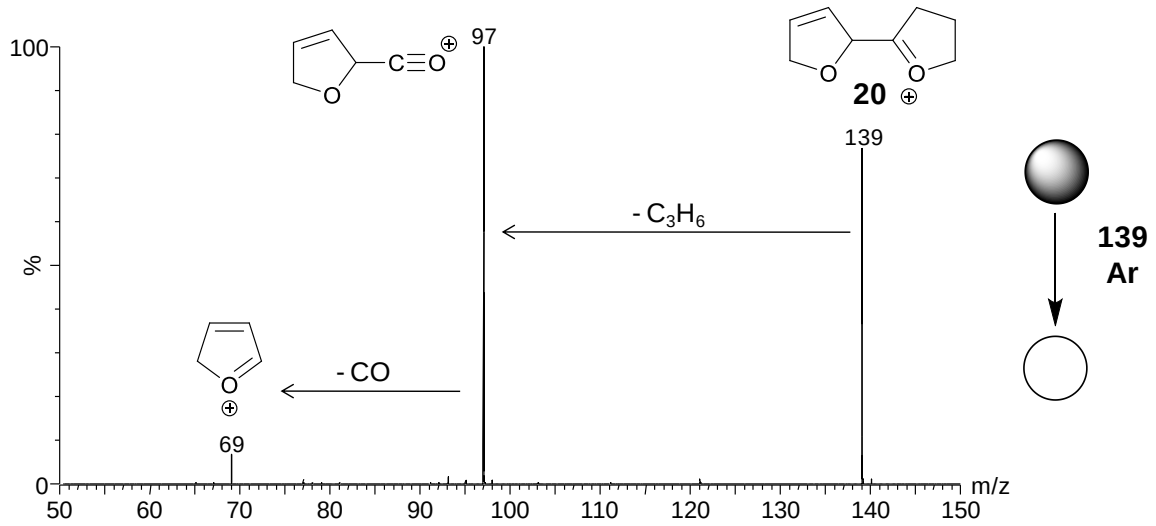

Figure S14. ESI-MS/MS of the ion of *m/z* 139 (**20**) obtained after addition of arenediazonium salt.

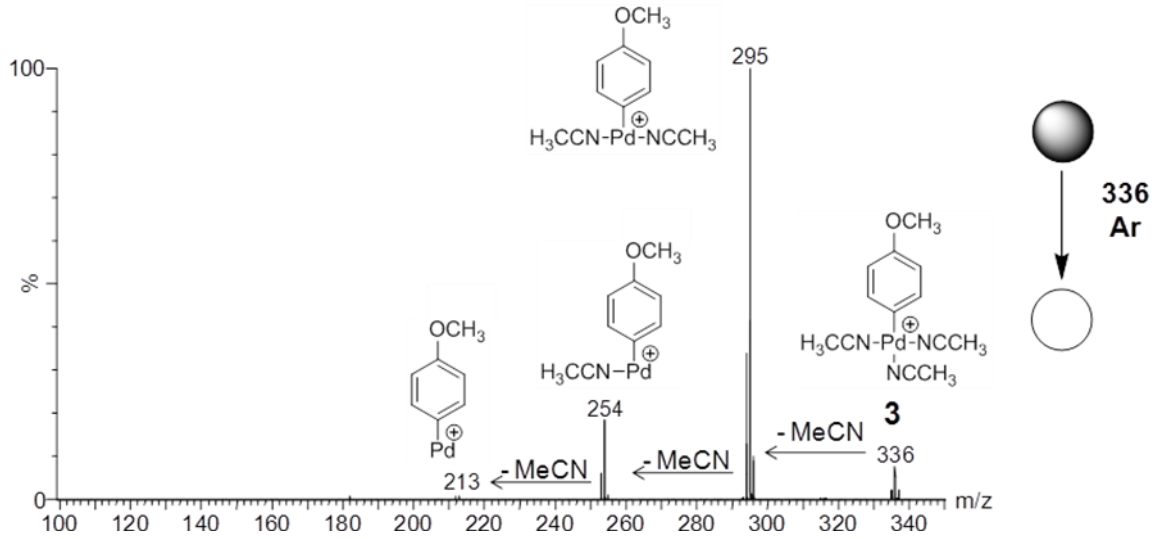

Figure S15. ESI-MS/MS of the ion of *m/z* 336 (**3**) obtained after addition of arenediazonium salt.

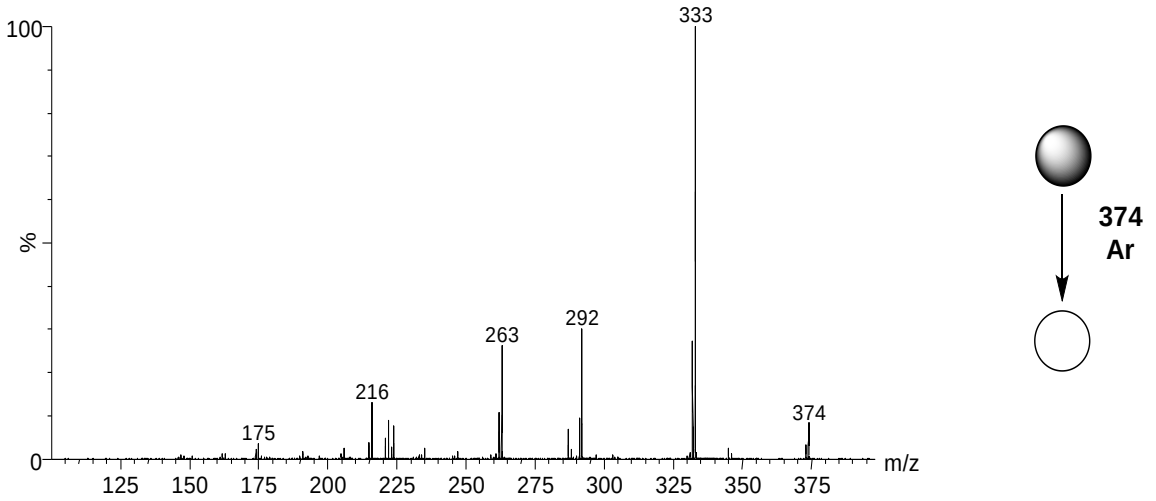

Figure S16. ESI-MS/MS of the ion of *m/z* 374 obtained after addition of arenediazonium salt.

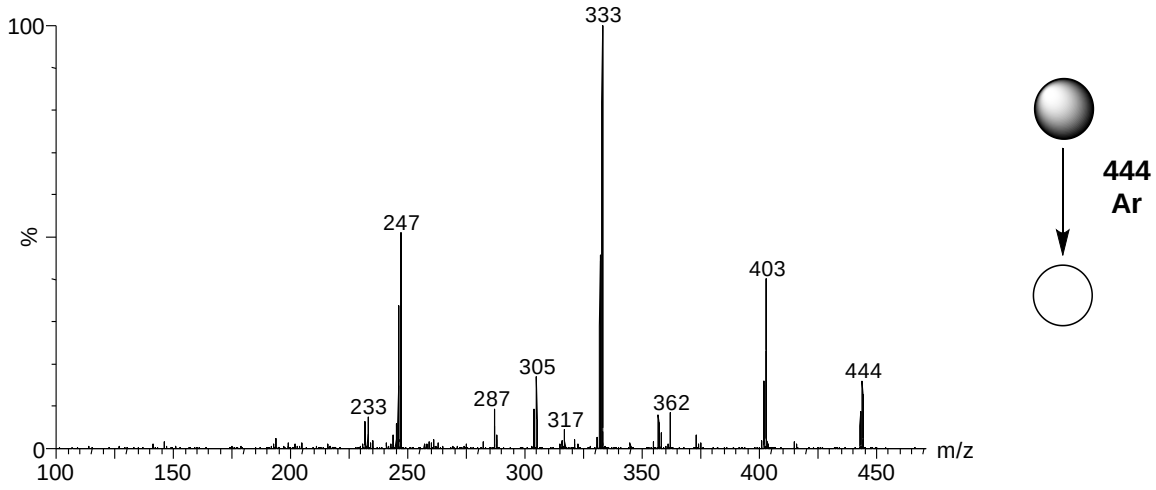

Figure S17. ESI-MS/MS of the ion of *m/z* 444 obtained after addition of arenediazonium salt.