## **Supporting Information**

# Aza-Wacker-Type Reaction between Electron-Deficient Olefins and N-Alkylsulfonamides

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#### **Table of Contents**

Interaction between palladium and 1i	1
Interaction between palladium acetate and MeSO <sub>3</sub> H	4
Interaction between palladium acetate and 2a	7
Copies of Compounds' NMR spectra and ORTEPs	9

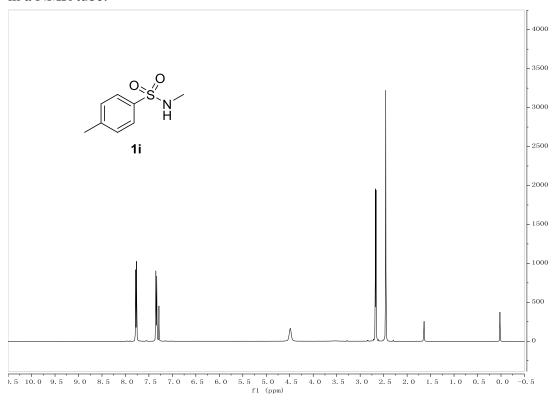
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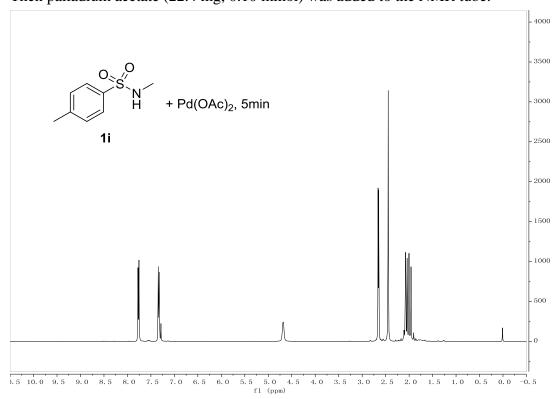
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# Procedure and <sup>1</sup>H NMR spectra for reveal the interaction between palladium with 1i:

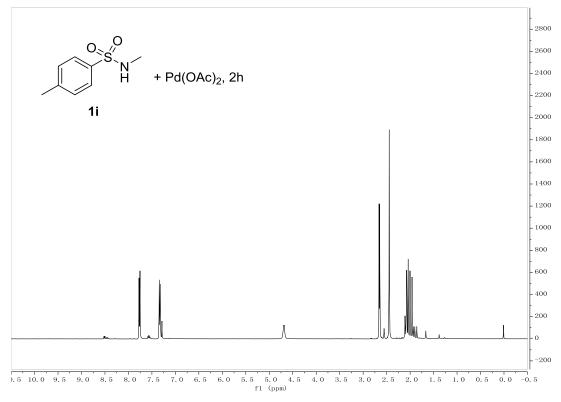
N,4-dimethylbenzenesulfonamide (19 mg, 0.10 mmol) was added to 0.60 mL CDCl<sub>3</sub> in a NMR tube:



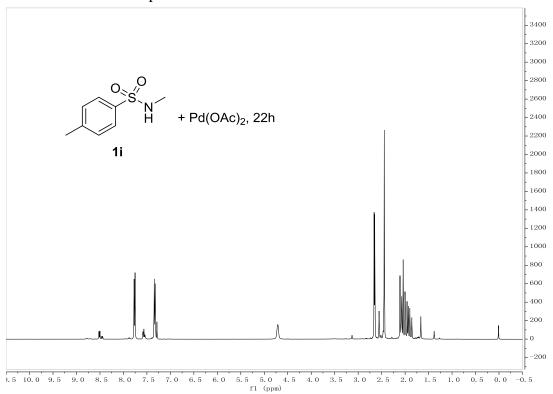
Then palladium acetate (22.4 mg, 0.10 mmol) was added to the NMR tube:



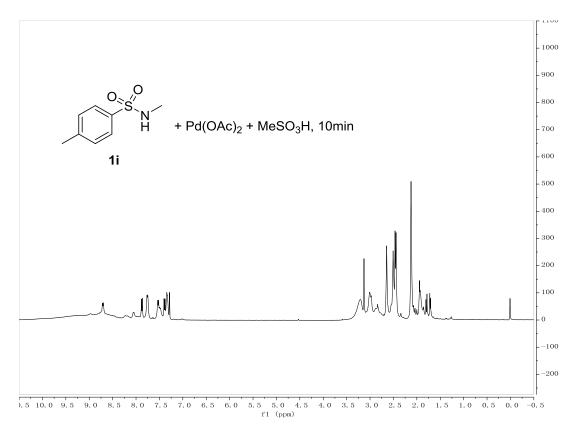
After 2h at room temperature:



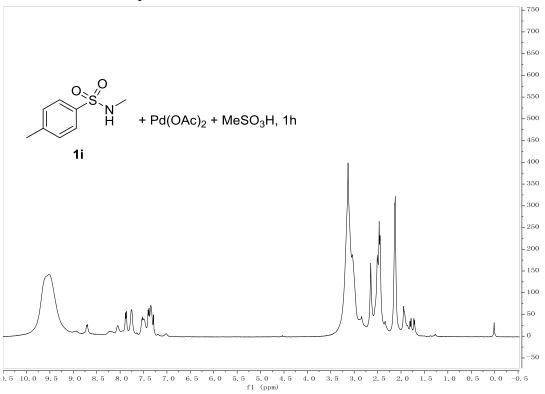
After 22h at room temperature:



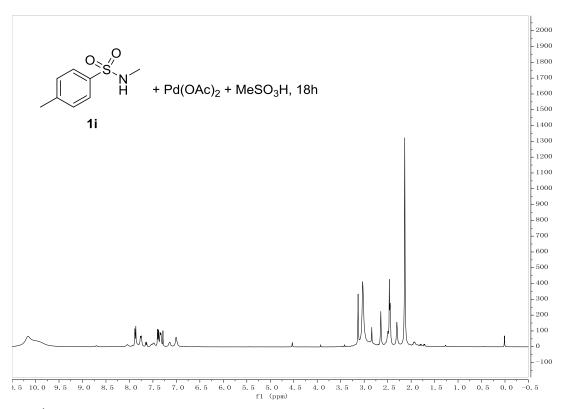
Then methanesulfonic acid (13  $\mu$ L, 0.20 mmol) was added to the NMR tube, after 10min:



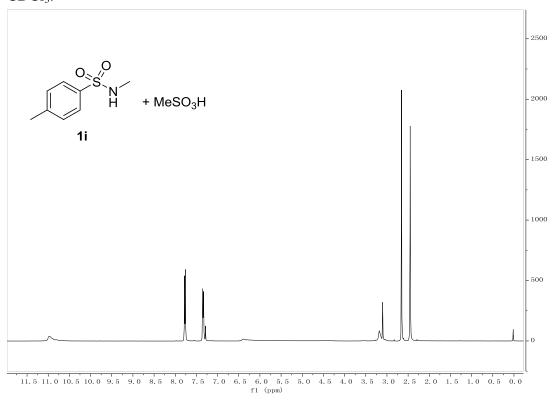
### After 1h at room temperature:



After 18h at room temperature:

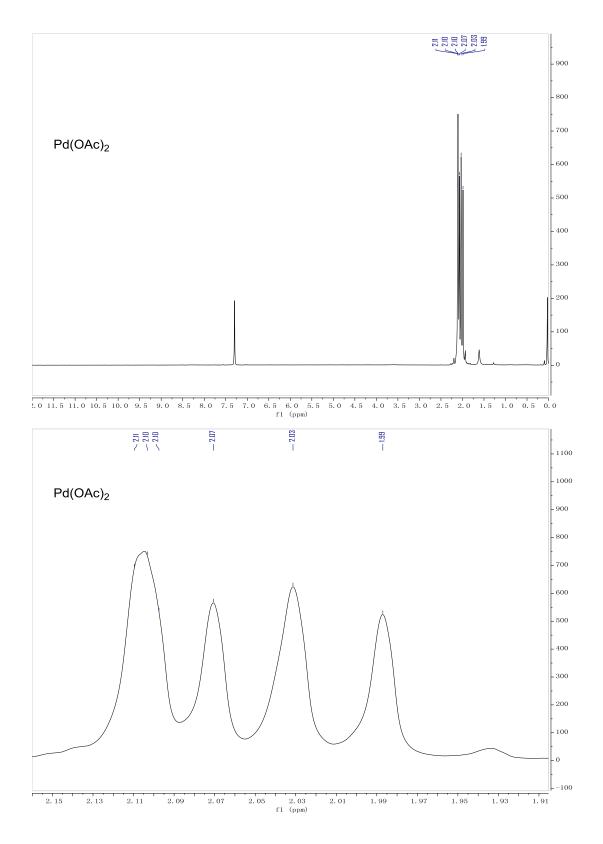


The <sup>1</sup>H NMR spectra of **1i** (0.10 mmol) with MeSO<sub>3</sub>H (0.20 mmol) in 0.60 mL CDCl<sub>3</sub>:

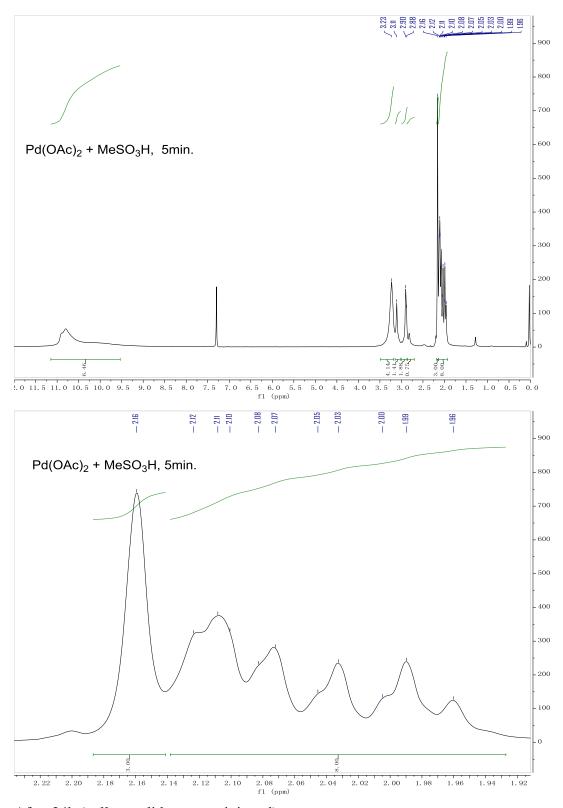


Procedure and <sup>1</sup>H NMR spectra for reveal the interaction between palladium acetate and MeSO<sub>3</sub>H:

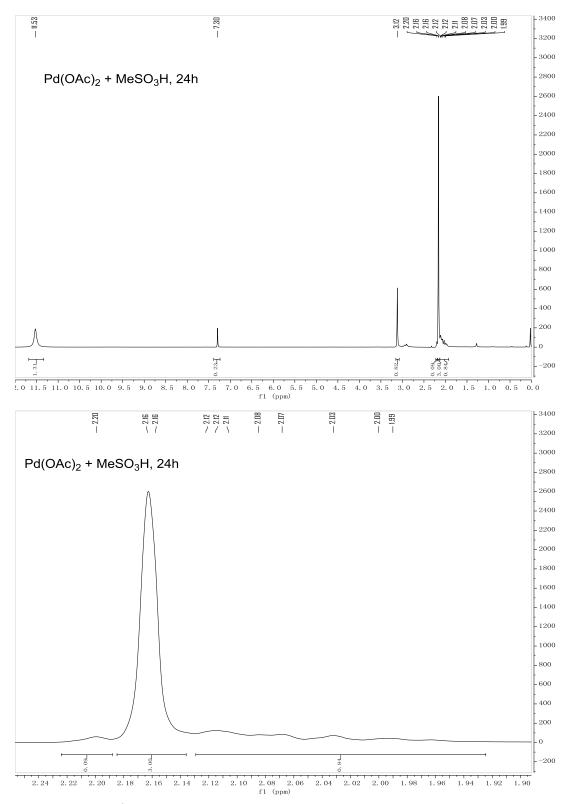
Palladium acetate (11.2 mg, 0.050 mmol) was added to 0.60 mL CDCl $_3$  in a NMR tube:



Then 0.10 mmol MeSO<sub>3</sub>H was added, after 5mins:

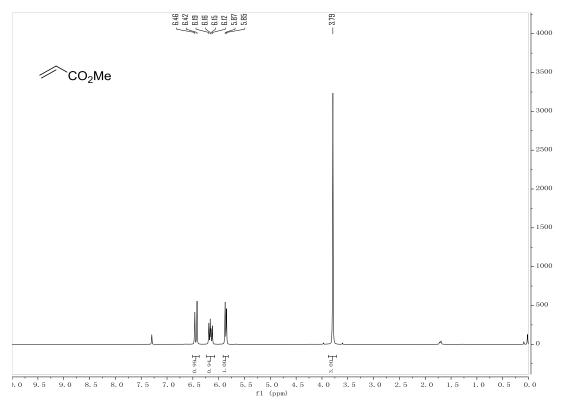


After 24h (yellow solid was precipitated):

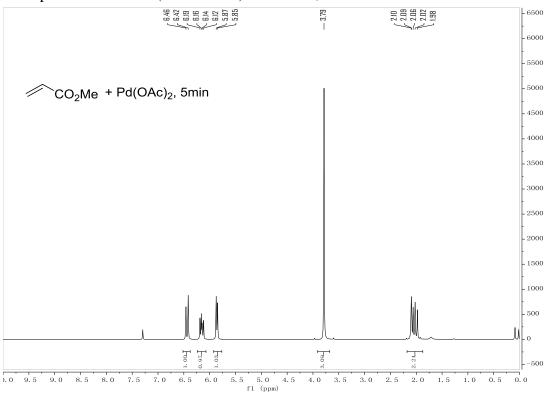


Procedure and <sup>1</sup>H NMR spectra for reveal the interaction between palladium acetate and methyl acrylate (2a):

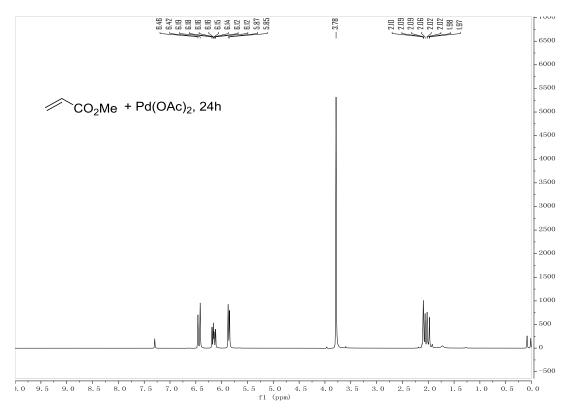
Methyl acrylate (0.10 mmol) was added to 0.60 mL CDCl<sub>3</sub> in a NMR tube:



Then palladium acetate (0.050 mmol) was added, after 5min:



After 24h:



### Copies of Compounds' NMR spectra and ORTEP:

