

## ***Supporting Information***

# **Critical role of oxygen in silver-catalyzed Glaser-Hay coupling on Ag(100) in vacuum and in solution on Ag particles**

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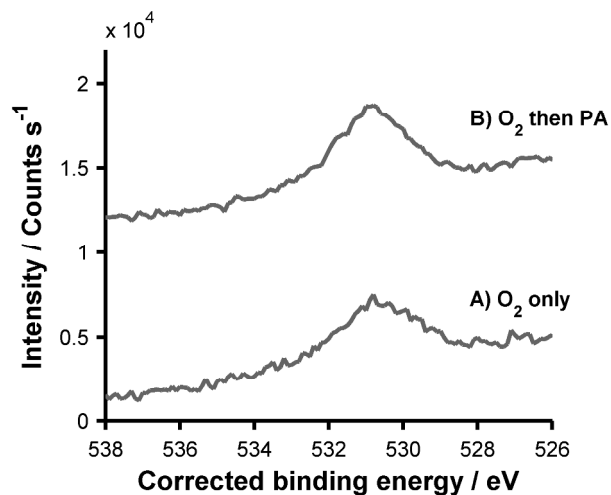
The ESI document includes:

Figure S1: Additional Laboratory O 1s XP Spectra

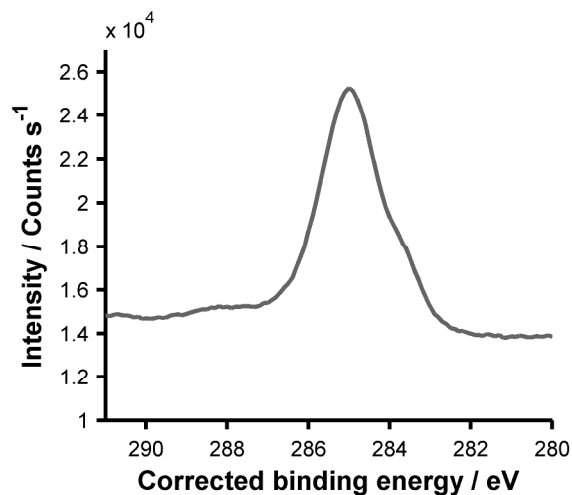
Figure S2: Additional Laboratory C 1s XP Spectrum

Figure S3: Additional selectivity data for phenylacetylene coupling reactions with and without oxygen.

Figure S4: Identification of  $\beta$ -phenylproiolophenone by GCMS of reaction product.

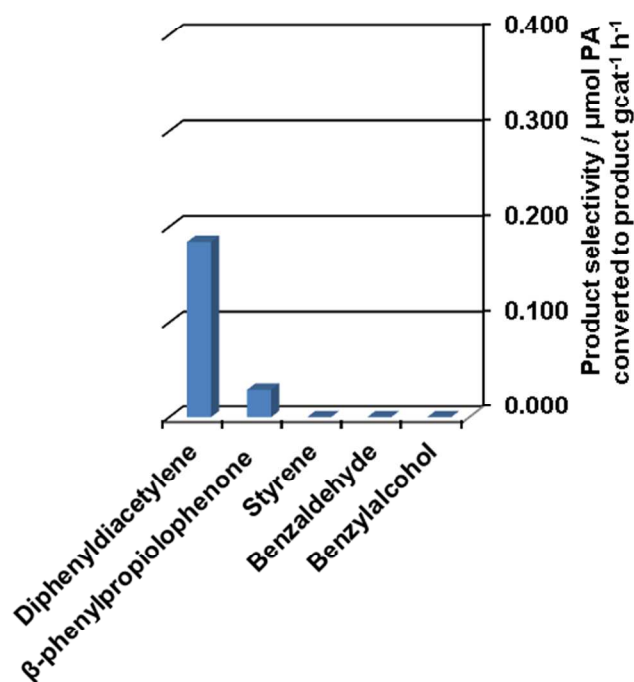


**Figure S1.** Laboratory XP spectra acquired at room temperature after dosing: A) 4500 L O<sub>2</sub>; B) 180,000 L O<sub>2</sub> followed by 120 L phenyl acetylene. Dosing was carried out at room temperature and the energy scale is referenced to the Ag 3d<sub>5/2</sub> peak at 368.3 eV. No significant differences between the two spectra are discernible.

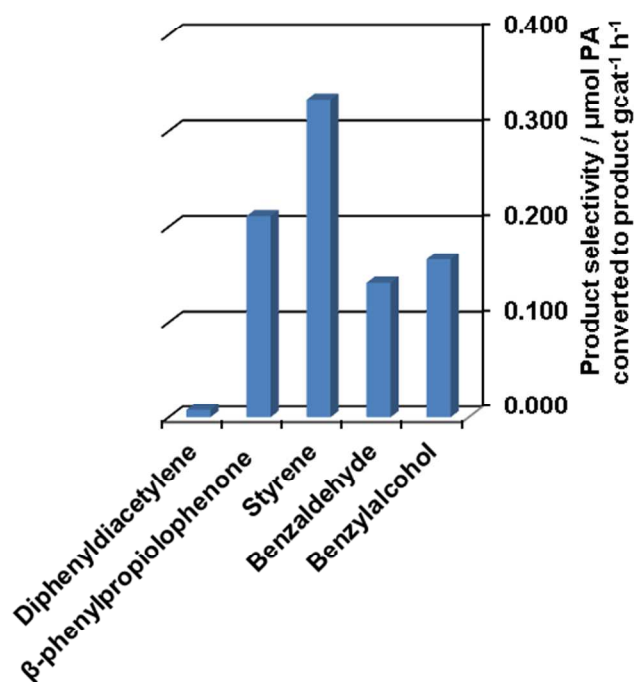


**Figure S2.** Laboratory XP spectra acquired at room temperature after dosing 180,000 L O<sub>2</sub> followed by 120 L phenyl acetylene. Dosing was carried out at room temperature and the energy scale is referenced to the Ag 3d<sub>5/2</sub> peak at 368.3 eV. A clear low binding energy shoulder is (given the lower resolving power of the laboratory instrument) very consistent with the synchrotron data reported in the manuscript.

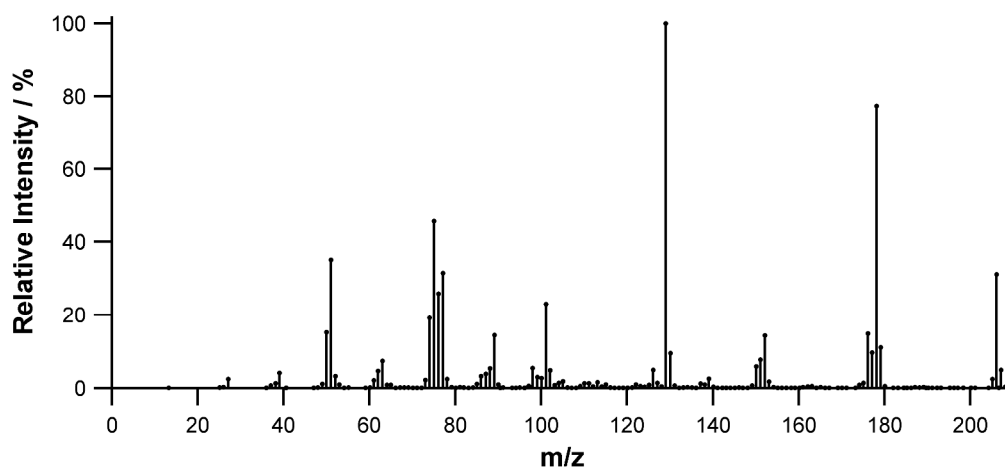
a) Nonane solvent



b) α,α,α-trifluorotoluene solvent



**Figure S3.** Product selectivity distribution for reaction of phenylacetylene (0.4 mmol) in 6 mL of solvent at 90 °C over 54 hours in the presence of oxygen in (a) nonane solvent and (b) the  $\alpha,\alpha,\alpha$ -trifluorotoluene (a high oxygen solubility solvent). Notably in nonane the desired product DPDA is produced selectively, while in  $\alpha,\alpha,\alpha$ -trifluorotoluene rapid formation of undesired products, but little DPDA, occurs. Selectivity data is given for the production of all detected products in  $\mu\text{mol PA}$  consumed per h per g of catalyst. Flame ionization detector sensitivities were calibrated by injection of known concentrations of decane with a known amount of a commercial sample of the analyte, for benzyl alcohol and  $\beta$ -phenylpropiolophenone peak identification was carried out by GCMS (Thermo scientific Trace 1300 GC fitted with an ISQ LT quadrupolar mass spectrometer, column: Thermo TG-SGC, 15m) and flame ionization detector sensitivities were estimated using the effective carbon number approach outlined in Scanlon and Willis.<sup>1</sup>



**Figure S4.** EI MS of  $\beta$ -phenylpropiolophenone side product by GCMS of reaction product mixture as used to identify unknown peak in routine GC measurements:  $m/z$  206 ( $M^+$ , 31%), 178 (77), 152 (14), 129 (100) (lit.,<sup>2</sup> (EI)  $m/z$  206 ( $M^+$ )).

#### REFERENCES:

- (1) Scanlon, J. T.; Willis, D. E. *J. Chromatogr. Sci.* **1985**, *23*, 333-340.
- (2) Atobe, S; Masuno, H; Sonoda, M; Suzuki, Y; Shinohara, H; Shibata, S; Ogawa, A. *Tetrahedron Lett.* **2012**, *53*, 1764-1767.