

## Supporting information

### Phosphine free SBA-15-EDTA-Pd highly active recyclable catalyst: Synthesis Characterization and application for Suzuki and Sonogashira reaction

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#### *Suzuki reaction (NMR RESULTS)*

##### **(2a) biphenyl**

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.34-7.62 (m, 10H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 127.20 (s, 5C), 128.79 (s, 5C).

##### **(2b) 4-nitro 1,1' biphenyl**

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.40-7.44 (m, 3H), 7.54-7.59 (m, 2H), 7.65-7.69 (m, 2H), 8.21-8.26 (d, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 123.09 (s, 2C), 126.37 (s, 2C), 126.78 (s, 2C), 127.89 (s, 1C) 128.13 (s, 2C),  
137.77 (s, 2C), 146.62 (s, 2C).

##### **(2c) 4-methyl 1, 1' biphenyl**

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.32 (s, 3H), 7.16-7.53 (m, 9H)

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 21.14 (s, 1C), 127.02 (s, 5C), 128.75 (s, 2C), 129.52 (s, 2C), 137.06 (s, 1C)  
138.39 (s, 1C), 141.19 (s, 1C).

##### **(2d) 4-methoxy 1, 1' biphenyl**

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 3.83 (s, 3H), 6.96-6.99 (d, 2H), 7.29-7.32 (m, 1H), 7.37-7.41 (m, 2H), 7.50-  
7.57 (m, 4H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>):** 55.38 (s, 1C), 114.26 (s, 2C), 126.71 (s, 1C) 126.78 (s, 2C), 128.20 (s, 2C), 128.77 (s, 2C), 133.83 (s, 1C), 140.88 (s, 1C), 159.21 (s, 1C).

### **2.3.2. Sonogashira reaction (NMR RESULTS)**

#### **(3a) 1, 2-diphenylethyne**

**<sup>1</sup>H NMR (CDCl<sub>3</sub>):** 6.93-7.79 (m, 10H)

**<sup>13</sup>C NMR (CDCl<sub>3</sub>):** 125-136 (m, 12C), 77.25 (d, 2C).

#### **(3b) 1-nitro-4-(phenylethynyl) benzene**

**<sup>1</sup>H NMR (CDCl<sub>3</sub>):** 7.07-8.31 (m, 9H)

**<sup>13</sup>C NMR (CDCl<sub>3</sub>):** 68.17 (s, 2C), 122.53 (s, 1C), 123.68 (s, 1C), 127.22 (s, 1C), 128.03 (s, 2C), 120.72 (s, 1C), 129.83 (s, 2C), 130.90 (s, 1C), 131.72 (s, 1C), 132.50 (s, 1C), 142.36 (s, 1C).

#### **(3c) 1-methyl-4-(phenylethynyl) benzene**

**<sup>1</sup>H NMR (CDCl<sub>3</sub>):** 4.0 (3H), 7.32-8.7 (9H)

**<sup>13</sup>C NMR (CDCl<sub>3</sub>):** 28.24 (s,1C), 97.95 (s,1C), 80.95(s,1C), 120.76(s, 1C), 121.10 (s,1C), 123.47( s,1C), 124.11 (s,1C), 127.38 (s,1C), 131.14 (s,1C), 132.89 (s,1C), 134.83 (s,1C), 139.89 (s,1C), 140.94 (s,1C), 154.20 (s,1C), 154.95 (s,1C).

## Experimental Section

Tetraethylorthosilicate (TEOS), pluronic 123(P123, Average Mol Wt = 5800), 3-aminopropyl trimethoxysilane (3-APTMS), dimethoxydimethylsilane ((MeO)<sub>2</sub>Me<sub>2</sub>Si), Palladium chloride, N,N-Ethylene diammine tetra acetic acid (EDTA), boronic acid, phenyl acetylene and aryl halide purchased from Aldrich. All solvents used in these experiments were obtained from Merck (India) and dried before use according to standard methods.

Powder X-ray diffractograms (XRD) of the materials were recorded using a PANalytical X'pert Pro dual goniometer diffractometer. The radiation used was Cu K $\alpha$  (1.5418 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg-Brentano geometry (0.5 to 5°; 0.2°/min). N<sub>2</sub> adsorption–desorption isotherms, pore size distributions as well as the textural properties of the hybrid materials were determined by using a Micromeritics ASAP 2020 instrument and Autosorb 1C Quantachrome USA. Pore size distribution curves were obtained via the NLDFIT model assuming cylindrical pore geometry and the micropore volume calculated via t-plot analyses as a function of relative pressure using the Broekhoff de Boer model for thickness curve measured between 3.5-5.0 Å. A JEOL JEM-3010 and Tecnai (Model F30) both operating at 300KV were used for HRTEM samples observation. Chemical analysis was carried out in a Lab Tam 8440 Plasma lab sequential mode ICP-OES Spectrometer and a Spectro Arcos ICP-OES instrument. The scanning electron micrographs of the samples were obtained in dual beam scanning electron microscope (FEI company, model Quanta 200 3D) operating at 30 kV. The samples were loaded on stubs and sputtered with thin gold film to prevent surface charging and also to protect from thermal damage due to electron beam. <sup>1</sup>H NMR spectra were recorded on Bruker AC-200 instruments using deuteriated solvent. Chemical shifts are reported in ppm. Liquid <sup>13</sup>C NMR spectra were recorded on Bruker AC-200 instruments operating at 50 MHz. <sup>13</sup>C NMR chemical shifts are reported in ppm relative to the central line of CDCl<sub>3</sub> (d 77.0). Solid-state <sup>13</sup>C CP MAS NMR and <sup>29</sup>Si MAS NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer with a resonance frequency of 75.5 MHz and 59.6 MHz for <sup>13</sup>C and <sup>29</sup>Si, and the chemical shifts were referenced to glycine and TMS respectively. Infrared spectra were recorded using a Perkin Elmer, Spectrum one FTIR spectrophotometer. The liquid samples or dilute solution of the solid samples in THF were spread over KBr plates, and their spectra were recorded. Thermal analysis (TG-DTA) of the samples was conducted using a Pyris Diamond TGA analyzer with a heating rate of 100°C min<sup>-1</sup> under air atmosphere. XPS of Palladium core

levels was studied using an ambient pressure photoelectron spectrometer and more details of the instrument are available in reference 1.

Surface modification of SBA-15 was achieved by a post synthesis grafting method (scheme 1A). One gram of SBA-15 was suspended in a 100 ml of dry toluene and refluxed with 2.5 mmol of 3-aminopropyltrimethoxysilane (3-APTMS) for 8 h under N<sub>2</sub> atmosphere. The material was filtered after cooling to ambient temperature, washed with dry toluene and dichloromethane, respectively. Soxhlet extraction was carried out for 24 h in dichloromethane (DCM) to remove occluded organosilane. The sample was dried in vacuum for 10 h. The obtained material is designated as NH<sub>2</sub>-SBA-15. The free -OH groups present in NH<sub>2</sub>-SBA-15 were protected (scheme 1B) by adding 1.5 mmol of dimethoxydimethylsilane [(MeO)<sub>2</sub>Me<sub>2</sub>Si] to a stirred suspension of 1 g of NH<sub>2</sub>-SBA-15 in dry toluene (50 ml), followed by stirring of 12 h at reflux temperature under inert atmosphere [40,41]. Obtained material was filtered, washed with toluene and soxhlet extracted with DCM for 24 h. The obtained material was named as -OH protected NH<sub>2</sub>-SBA-15.

## Reference

- [1] K. Roy, C. P. Vinod and C. S. Gopinath, J. Phys. Chem. C, 2013, 117, 4717-4726.

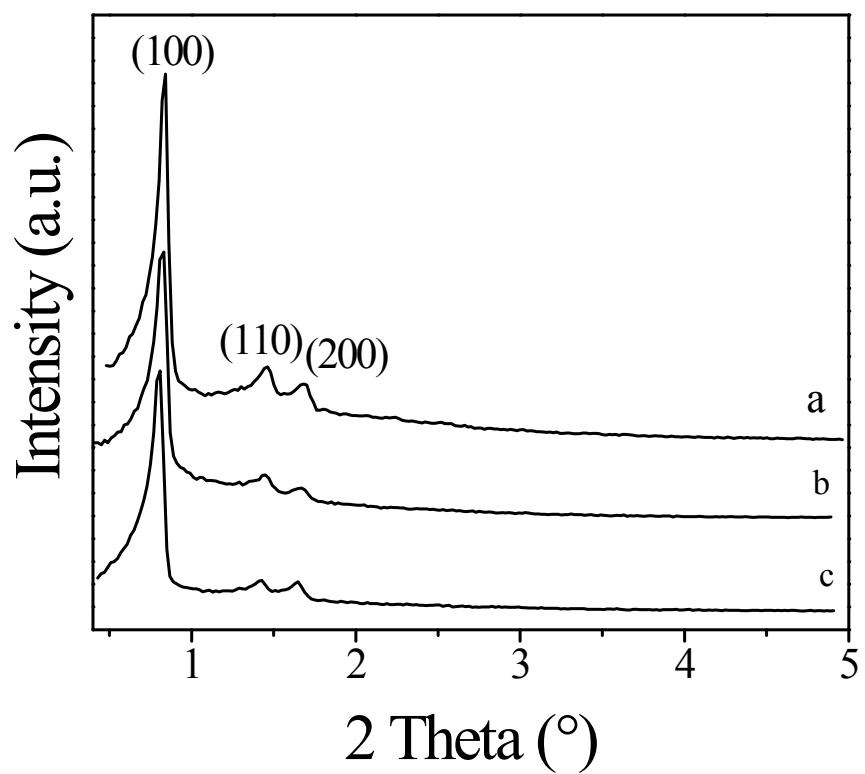


Figure S1. XRD pattern of (a) SBA-15-EDTA-Pd(7), (b) SBA-15-EDTA-Pd(11), (c) SBA-15-EDTA-Pd(15)

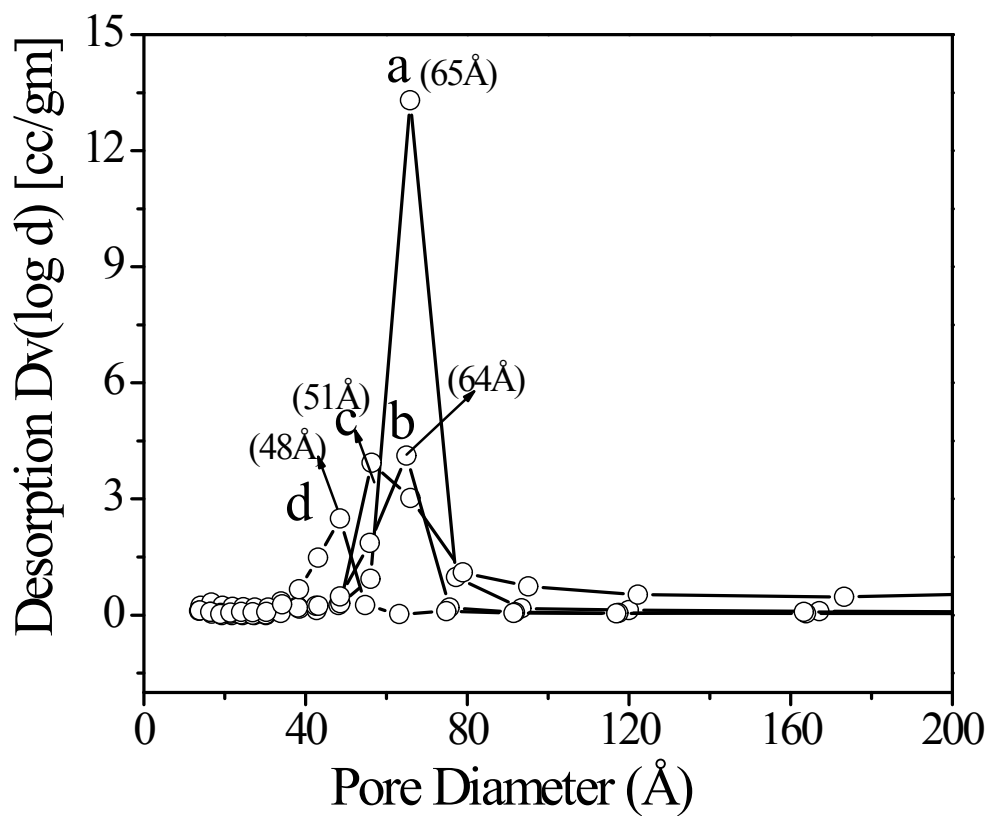


Figure S2 . Pore size distribution of (a) calcined SBA-15, (b) SBA-15-EDTA-Pd (7), (c) SBA-15-EDTA-Pd(11), (d) SBA-15-EDTA-Pd(15).

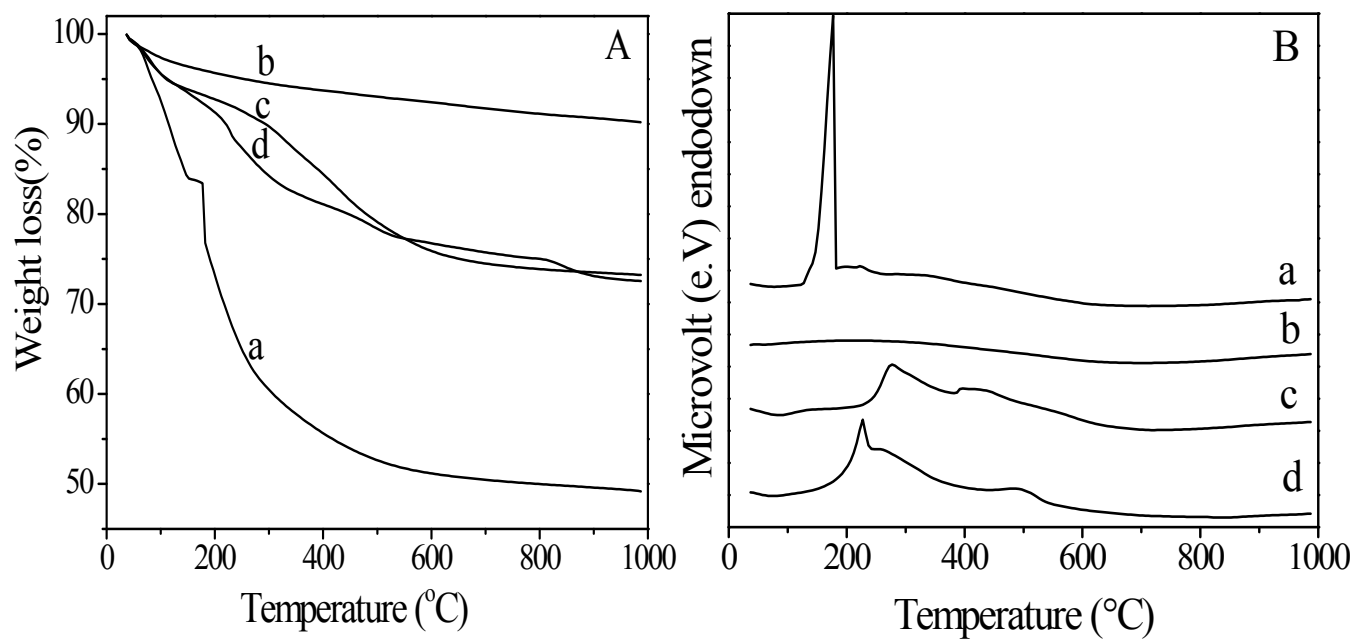


Figure S3 (A) TGA, 6(B) DTA pattern of (a) as-synthesized SBA-15, (b) calcined SBA-15, (c)-OH protected NH<sub>2</sub>-SBA-15, (d) SBA-15-EDTA-Pd(11).

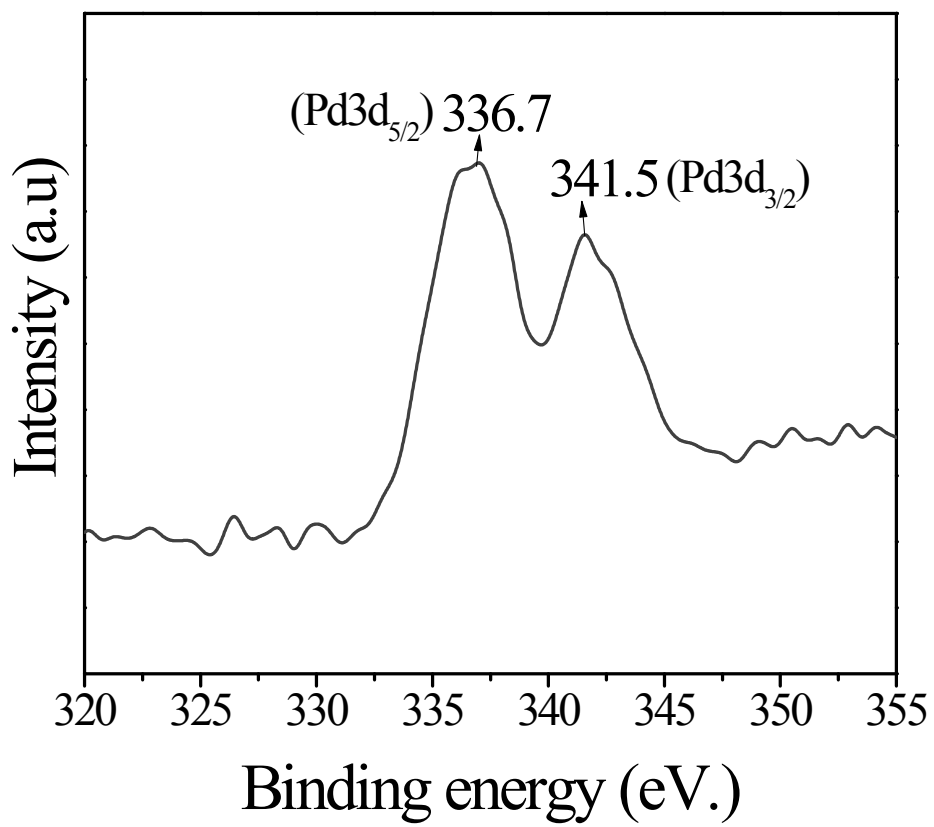


Figure S4. X-ray photoelectron spectroscopy (XPS) of SBA-15-EDTA-Pd (11).



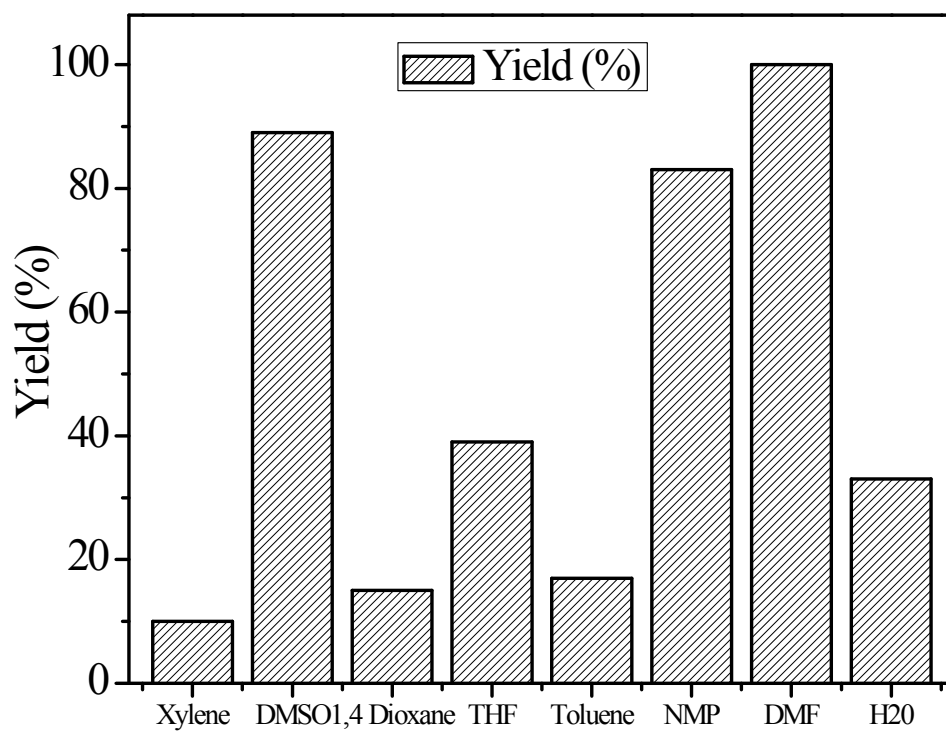


Figure S5. Solvent optimization for Suzuki coupling reaction

Reaction Time : 5 h except H<sub>2</sub>O (12 h)

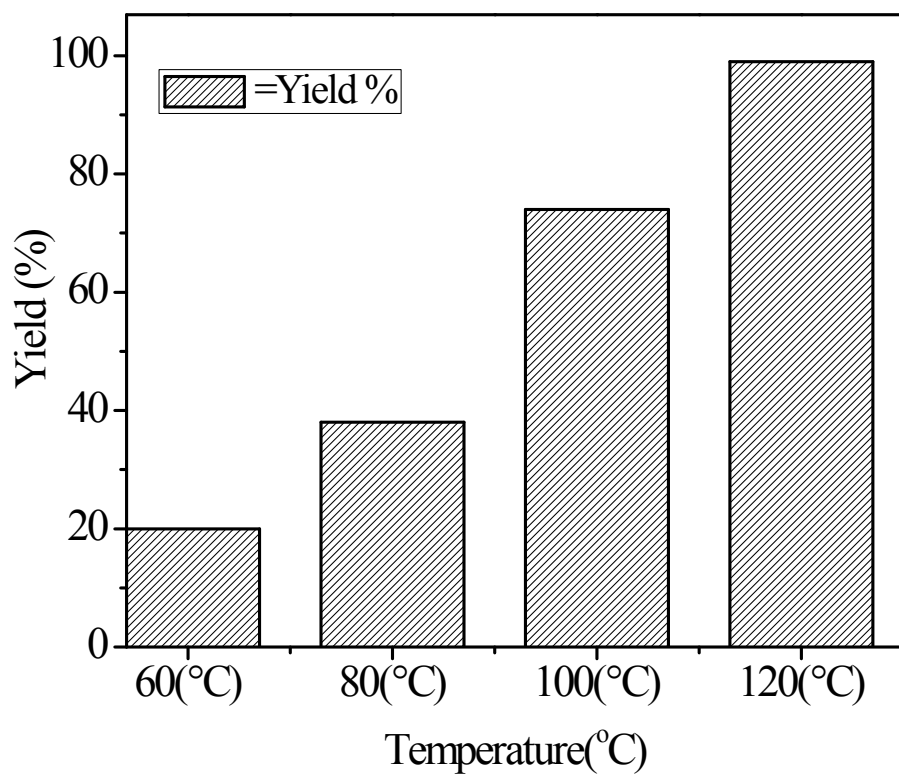


Figure S6. Temperature optimization for the Suzuki coupling reaction

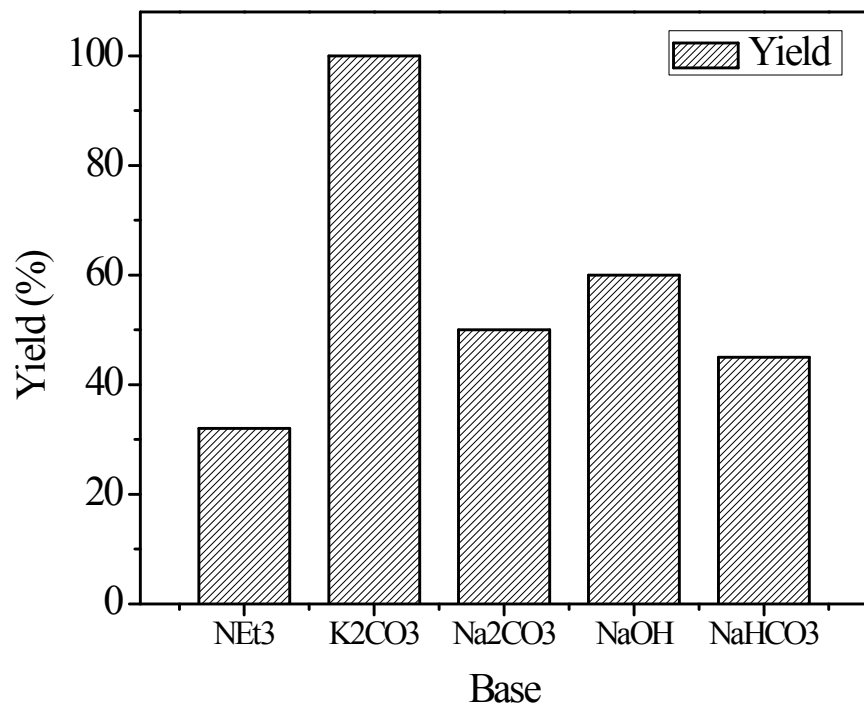


Figure S7 Base optimization for the Suzuki coupling reaction

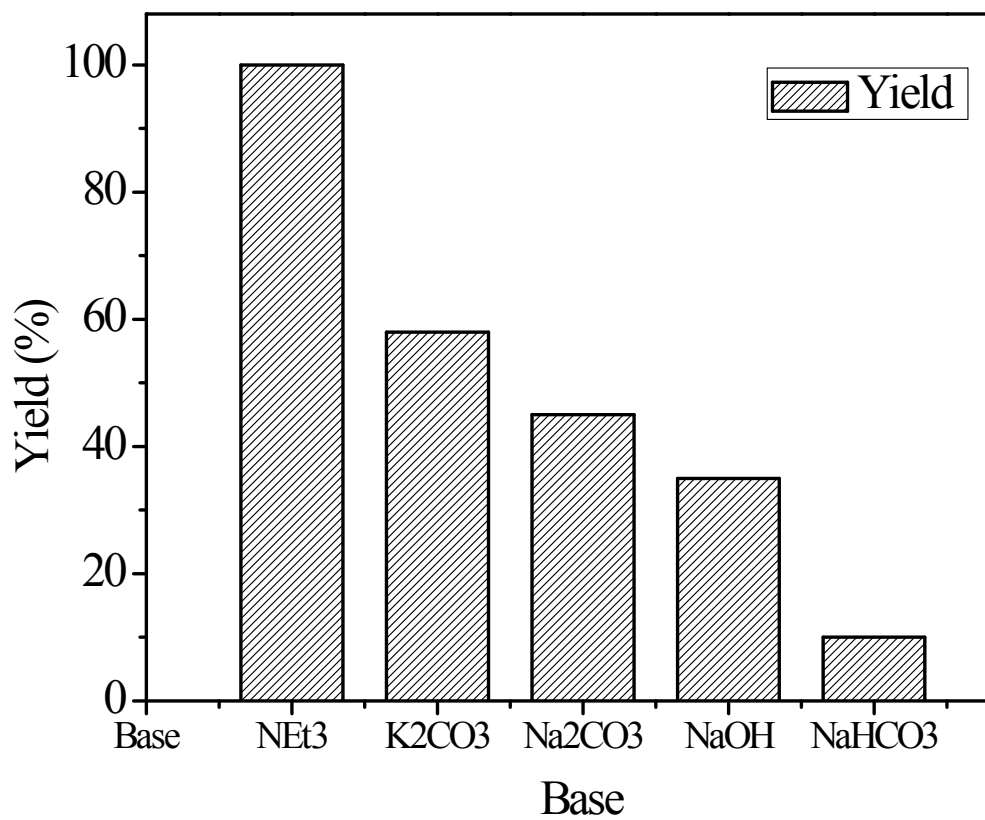


Figure S8 Base optimization for the Sonogashira reaction