

Supporting Information for
A *p*-phosphinophenolate ligand for the palladium-catalysed arylation of alkenes

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General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen or an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian Gemini 2000 (^1H , 300 MHz) spectrometer using tetramethylsilane (^1H) as an internal standard. Analytical gas chromatography was performed on a Shimadzu model GC-18A instrument equipped with a capillary column of CP-SIL 5 CB (100% dimethyl polysiloxane, 30 m x 0.25 mm x 0.25 μm) using helium as carrier gas. Flame ionization detection was used. The column oven temperature was held at 50 $^\circ\text{C}$ for 2 min and then increased at 10 $^\circ\text{C}/\text{min}$ to 280 $^\circ\text{C}$, where it was held constant for 15 min. Toluene was distilled from sodium/benzophenone ketyl. Anhydrous DMA was purchased from Kanto Chemicals. 4-(Diphenylphosphino)phenol (***p*-PO**),¹ 2-(diphenylphosphino)phenol (***o*-PO**),² 3-(diphenylphosphino)phenol (***m*-PO**),³ 4-(diphenylphosphino)anisole (***p*-POMe**)¹ and tris(4-dimethylaminophenyl)phosphine (**5**)⁴ were prepared according to literature procedures.

Palladium-*p*-PO⁻-catalysed arylation of alkenes. A General Procedure. To a solution of tetrabutylammonium bromide (2.6 mg, 8.1 μmol), 4-(diphenylphosphino)phenol (2.2–8.8 mg, 7.9–32 μmol) and $\text{Pd}(\text{OAc})_2$ (0.90 mg, 4.0 μmol) in toluene (1.0 mL) were added an aqueous solution (1.0 mL) of NaOH (19 mg, 0.48 mmol), an aryl bromide (0.40 mmol) and an alkene (0.44 mmol), and the resulting mixture was stirred at 100 $^\circ\text{C}$. After the time specified in Table 2, the mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by silica gel chromatography gave the corresponding product. Yields are listed in Table 2. GC analysis in Table 1 was performed using *p*-dimethoxybenzene as an internal standard (retention time for **3a**: 16.3 min; **4a**: 13.9 min). The reaction shown in Scheme 1 was performed in a similar manner but with NaOAc instead of NaOH as a base in DMA instead of toluene– H_2O . All the products, which are listed below, are the compounds already reported in literature.

(*E*)-4-(Trifluoromethyl)stilbene (**3a**).⁵

α -[4-(Trifluoromethyl)phenyl]styrene (**4a**).⁶

(*E*)-4-Methylstilbene.⁷
(*E*)-4-Methoxystilbene.⁸
(*E*)-4-Acetylstilbene.⁹
(*E*)-3-Acetylstilbene.¹⁰
(*E*)-4-Methyl-4'-methoxystilbene.¹¹
(*E*)-4-Methyl-4'-(trifluoromethyl)stilbene.⁷
Butyl cinnamate.¹²

References

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