Convenient and Efficient Suzuki-Miyaura Cross-Coupling Reaction Catalyzed by a Palladium/Diazabutadiene System

Gabriela A. Grasa, Anna C. Hillier and Steven P. Nolan

Department of Chemistry, University of New Orleans
New Orleans, Louisiana 70148

Supporting Information

Mailing Address: Department of Chemistry, University of New Orleans
New Orleans, LA, 70148
Telephone: SPN (504) 280-6445
FAX: (504) 280-6860
Email: snolan@uno.edu

General Information

- All aryl halides (Aldrich), TBAF (1.0 M in THF, Aldrich) were used as received. 1,4-Dioxane (anhydrous, Aldrich) was distilled under argon from sodium benzophenone ketyl. Cesium carbonate, potassium carbonate, sodium hydroxide, cesium fluoride, potassium fluoride, sodium methoxide, potassium methoxide, potassium *tert* butoxide, barrium hydroxide, calcium hydroxide, 2,2'-bipyridyl, and 1,10-phenantroline (Aldrich) were stored in desiccators over anhydrous calcium carbonate. Palladium acetate was purchased from Strem Chemical Company. Flash chromatography was performed on silica gel 60 (230-400 mesh) (Natland International corporation).
- Diazabutadiene ligands **1** (N, N'-Dicyclhexyl-1,4-diazabutadiene), **2** (N, N'-Diadamantanyl-1,4-diazabutadiene), **3** (N, N'-Bis(2,6-diisopropylphenyl)-1,4-diazabutadiene), **4** (N, N'-Bis(2,4,6-trimethylphenyl)-1,4-diazabutadiene), **5** (N, N'-Bis(2,4,6-trimethylphenyl)-1,4-diaza-1,3-dimethyl-butadiene), **6** (N, N'-1,2-acenaphthylidene-bis-[2,4,6-trimethyl]-benzenamine), **7** (N, N'-Bis(2,6-dimethylphenyl)-1,4-diazabutadiene) were synthesized according to the literature methods: Kliegman, J. M.; Barnes, R. K. *Tetrahedron*, **1970**, *26*, 2555-2560, Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, A.; Hugh, A.; Goerlich, J. R.; William, J. *Tetrahedron*, **1999**, *55*, 14523-14534, tomDieck, H.; Renk, I. W.; Franz, K. D. *J. Organomet. Chem.*,**1975**, *94*, 417-424, van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Neth. Recl. Trav. Chim. Pays-Bas*, **1994**, *113*, 88-98.
- ^{1}H NMR and spectra were recorded on a Varian-300 or Varian-400 MHz spectrometer at ambient temperature in $CDCl_3$ (Cambridge Isotope Laboratories, Inc.).
- All reactions were carried out under an atmosphere of argon in Schlenk tubes with magnetic stirring, unless otherwise indicated.
- The identity of every product was confirmed by comparison with literature spectroscopic data: 4-methylbiphenyl,[1] 4-acetylbiphenyl,[2] 2,4,6-trimethylbiphenyl,[3] 4-methoxibiphenyl,[i] 2-cyanobiphenyl,[4] 2,4'-dimethylbiphenyl,[5] 4-chlorobiphenyl,[6] 4,4'-dimethylbiphenyl,[7] 3-cyano-4'-methylbiphenyl,[8] 3-methoxy-4'-methylbiphenyl.[9]

$Pd(OAc)_2$/DAB-R Cross-Coupling Reactions of Aryl Halides with Phenylboronic Acid. *General procedure*: Under an atmosphere of argon 1,4-dioxane (3 mL), aryl halide (1 mmol), Cs_2CO_3 (2.0 mmol) and arylboronic acid (1.5 mmol) were added in turn to a Schlenk tube charged with $Pd(OAc)_2$, DAB-R, and a magnetic stirring bar. The vial was placed in a 80^0 C oil bath and stirred. The reaction was monitorred by GC. In some cases the yields were determined by GC (HP Model 6890 using HP-5 column) using 2,2'-bipyridyl as internal standard. The mixture was then allowed to cool at room temperature. The mixture was purified either directly by flash chromatography, or filtered through a pad of celite, concentrated, and then purified by flash chromatography (ethyl acetate/hexane, 1: 10 per volume).

---

[1] Rao, M. S. C.; Rao, G. S. K. *Synthesis* **1987**,231.
[2] Barba, I.; Chinchilla, R.; Gomez, C. *Tetrahedron* **1990**, *46*, 7813.
[3] Anderson, J. C.; Namli, H.;Roberts, C. A. *Tetrahedron,* **1997,** *53*, 15123.
[4] Lipshutz, B. H.; Sclafani, J. A.; Blomgren, P. A. *Tetrahedron* , **2000**, *56*, 2139-2144.
[5] Kosugi, M.; Shikawa, T.; Nogami, T.; Migito, T., *Nippon Kagakau Kaishi* **1985**, 520.
[6] Klement, I.; Rottlander, M.; Tucker, C. E.; Majid, T. N. *Tetrahedron* **1996**, *53*, 7201-7200.
[7] Uozumi, Y.; Danjo, H.; Hayashi, T. *J. Org. Chem*. **1999**, *64*, 3384-3388.
[8] Kageyama, H.; Miyazaki, T.; Kimura, Y. *Synlett* **1994**, *5*, 371-372.
[9] Hatanake, Y.; Goda, K.; Okahara, Y. *Tetrahedron*, **1994**, *59*, 8301.