README file

Dataset Title: **A New Class of Bidentate Nitrogen Ligands for Suzuki–Miyaura Cross-Coupling of Aryl Iodides and Bromides in Green Solvents**

Dataset Authors: **Tommaso Fantoni,[a] Silvia Rizzo,[a] Esaïe Reusser,[b] Alessandra Tolomelli,[a] Martin Albrecht,[b]* Walter Cabri[a]***

Affiliations: [a]Tolomelli-Cabri Lab, Center for Chemical Catalysis, Department of Chemistry "Giacomo Ciamician", University of Bologna, via Gobetti, 85-40129 Bologna, Italy;
[b]Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, Bern 3012, Switzerland.

Dataset contact person: **Tommaso Fantoni**, Department of Chemistry "Giacomo Ciamician", University of Bologna, Via P. Gobetti 85, 40129 Bologna, Italy, tommaso.fantoni3@unibo.it

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Dataset contents

The dataset consists of:

- 1 compressed folder named **1H13C-NMR_Dataset.zip** containing 19 subfolders named

  3aa, 3ad, 3ae, 3af, 3d, 3e, 3f, 3i, 3j, 3m, 3n, 3o, 3p, 3r, 3s, 3t, 3v, 3w, 3z

  each subfolder contains ^{1}H, ^{13}C-NMR spectra files in. fid format.

- 1 folder in .pdf format named **1H13C-NMR_Scheme_1-2.pdf**

- 1 readme file in .pdf format named **1H13C-NMR_Readme.pdf**

Dataset documentation

Abstract

Inexpensive nitrogen-based bidentate pyridinium amidate ligands with simple Pd(II) salts generate in situ Pd(0) catalysts that efficiently promote Suzuki–Miyaura cross-coupling of aryl iodides and bromides. Operating at very low palladium loadings (0.1–0.005 mol%) with TONs up to 17800, the reactions give high yields (51–96%) using K_2CO_3 in a green hydroxyethyl pyrrolidone/water (6:4) solvent mixture. The protocol minimizes metal residues, allows >90% palladium recovery and reduces PMI from 30 to 8. DFT studies indicate transmetalation as the rate-determining step.

Content of the files

The attached dataset includes the NMR spectra of the Suzuki-Miyaura products presented in Scheme 1 and Scheme 2, as shown in the '1H13C-NMR_Scheme_1-2,' file included in the document

Methodologies

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400-MR (400 MHz) (equipped with autoswitchable PFG probe) and Bruker Advance Neo 600 MHz (equipped with CryoProbe Prodigy Broadband 5mm) spectrometers. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t =triplet, q = quartet, spt = septet, m = multiplet, bs = broad signal. Coupling constants J are given in Hz. All ^{1}H and ^{13}C chemical shifts are calibrated to residual protic-solvents.

General Protocol

Preparation of precatalyst/ligand stock 5mM solution: to a flame-dried Schlenk tube equipped with stirring bar, degassed HEP/H_2O 6:4 (5.0 mL) was added under N_2 atmosphere, followed by $PdCl_2(MeCN)_2$ (25 µmol, 6.5 mg) and the selected ligand (37.5 µmol). The solution was stirred for 5 minutes.

Suzuki-Miyaura coupling: to a flame-dried Schlenk tube equipped with stirring bar, degassed HEP/H_2O 6:4 was added under N2 atmosphere, followed by precatalyst/ligand stock solution and K_2CO_3 (0.75 mmol, 104 mg, 1.5 equiv.). The mixture was stirred for 30 minutes at room temperature, then aryl halide (0.5 mmol, 1.0 equiv.) and boronic acid (0.55 mmol, 1.1 equiv.) were added. The mixture was then stirred at the selected temperature and the conversion was monitored via HPLC.

After completion, the mixture was extracted with iPrOAc (1 mL x3) and the collected organic phases were dried over Na_2SO_4 and subsequently filtered and dried by rotary evaporation. No further purification was required.

References

Tommaso Fantoni, Silvia Rizzo, Esaïe Reusser, Alessandra Tolomelli, Martin Albrecht,* Walter Cabri*, Eco-Friendly Catalyst Development: Bidentate Nitrogen Ligands in the Suzuki-Miyaura Reaction of Aryl Iodides and Bromides in Green Solvents. *ACS Sustain. Chem. Eng.,* 2025, Accepted.