README file

Dataset Title: **Dataset of "Mastering palladium catalyzed cross-coupling reactions: the Critical role of in situ pre-catalyst reduction design"**

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Dataset contents

The dataset consists of:

- 1 compressed folder named **31P-NMR Dataset.zip** containing 14 subfolders named

  31P-NMR_TableX_EntryY_RefDOI10.1039D4QO02335H

  (with **X** = **1**, **2**, **3**, **4**, **5**, **6**, or **7** and **Y** = **1**, **2**, **3**, **5**, **6**, **7**, **8**, **9**, **11**, **14**, or **15**)

  each subfolder contains ^{31}P-NMR spectra files in .fid format

- 1 readme file in .pdf format
  31P-NMR_README.pdf

Dataset documentation

Abstract

The dataset contains 31 P-NMR spectra as .fid files used to characterize palladium complexes formed during the in-situ generation of Pd(0) catalysts from Pd(II) precatalysts in cross-coupling reactions. The reduction process was examined via NMR to evaluate the influence of reagents, solvents, bases, ligands, and counterions. The spectra represent the optimal results obtained from the screening of each parameter.

Content of the files

The attached dataset includes the ^{31}P-NMR spectra referring to the best outcomes deriving from the screening of reaction parameters for Pd(II) to Pd(0) reduction in cross-coupling reaction, reported in the

tables 1 to 7 of the publication: **T. Fantoni, C. Palladino, R. Grigolato, B. Muzzi, L. Ferrazzano, A. Tolomelli and W. Cabri (2025) Mastering palladium-catalyzed cross-coupling reactions: the critical role of in situ pre-catalyst reduction design. Org. Chem. Front. DOI: https://doi.org/10.1039/D4QO02335H.** In particular:

- Folders labelled as "**Table1_Entry3**" and "**Table1_Entry7**" contains the the ^{31}P-NMR spectra associated to Pd(II)Cl_2(SPhos)$_2$ and Pd(0)SPhos catalysts, respectively.
- Folders labelled as "**Table2_Entry8**" and "**Table 2_Entry15**" contains the ^{31}P-NMR spectra associated to Pd(0)$(PPh_3)_2$ obtained through reduction via N-hydroxyethylpyrrolidone used as cosolvent of DMF.
- Folders labelled as "**Table3_Entry2**" and "**Table3_Entry11**" contains the ^{31}P-NMR spectra both associated to Pd(0)$DPPF_2$ catalyst, obtained via phosphine mediated reduction.
- Folders labelled as "**Table4_Entry3**" and "**Table4_Entry9**" contains the ^{31}P-NMR spectra both associated to Pd(0)DPPP catalyst, obtained via phosphine mediated reduction.
- Folders labelled as "**Table5_Entry5**" and "**Table5_Entry6**", contains the ^{31}P-NMR spectra both associated to Pd(0)Xantphos catalyst. The first obtained through reduction via phosphine, the latter obtained through reduction via N-hydroxyethylpyrrolidone used as cosolvent of DMF.
- Folders labelled as "**Table6_Entry6**" and "**Table6_Entry14**" contains the ^{31}P-NMR spectra both associated to Pd(0)SPhos catalyst, obtained through reduction via N-hydroxyethylpyrrolidone used as cosolvent of DMF.
- Folders labelled as "**Table7_Entry1**" and "**Table7_Entry6**" contains the ^{31}P-NMR spectra associated to Pd(0) catalysts, obtained through reduction of PdCl2 and SPhos or RuPhos, as Buchwald's ligands respectively.

Methodologies

^{31}P-NMR spectra were recorded on Varian 400-MR (400 MHz) (equipped with autoswitchable PFG probe) and Bruker Avance Neo 600 MHz (equipped with CryoProbe Prodigy Broadband 5mm) spectrometers. The used software for acquisition were OpenVnmrJ and TopSpin. The file can be opened via the abovementioned softwares or via MestreNova or SpinWorks, or any other software for NMR data reeleaboration. All ^{31}P chemical shifts are referenced to external 85% phosphoric acid (δ = 0 ppm). The acquisition was conducted at room temperature, with standard phosphorus parameters. The samples for the analysis were prepared dissolving 0.013 mmol of starting Pd(II) complex, 1 or 2 eq of ligand in 600 µl of DMF or DMF/HEP=4:2 (for specific sample conditions refer to DOI: 10.1039/D4QO02335H). Due to the absence of deuterated solvents in the samples prepared as in the description, external locking of 31P default parameters was performed using a sample of pure DMF-δ_7.

Detailed synthetic procedures for catalysts generation were reported in the manuscript this dataset refers to (see "References" section).

References

T. Fantoni, C. Palladino, R. Grigolato, B. Muzzi, L. Ferrazzano, A. Tolomelli and W. Cabri **(**2025) Mastering palladium-catalyzed cross-coupling reactions: the critical role of in situ pre-catalyst reduction design. Org. Chem. Front. DOI https://doi.org/10.1039/D4QO02335H.