**Metals in Synthesis** 

## **Key words**

**Curtius rearrangement N-formylanilines** oxalic acid palladium catalysis



N. POOTHERI, S. LEE\* (CHONNAM NATIONAL UNIVERSITY, GWANGIU, REPUBLIC OF KOREA) Palladium-Catalyzed One-Pot Synthesis of N-Formylaniline Derivatives Using Oxalic Acid as a Dual Carbon Monoxide and Hydrogen

Org. Lett. 2024, 26, 9407-9412, DOI: 10.1021/acs.orglett.4c03714

## Palladium-Catalyzed Formamidation of Aryl Halides Using Sodium Azide and Oxalic Acid

Proposed mechanism: 
$$[Pd^0] CO + CO_2 + H_2O \xrightarrow{\Delta} H \xrightarrow{O} H$$

$$2CO_2 \xrightarrow{H_2} Ar \xrightarrow{N_2} N_2$$

$$Pd^{11} Ar \xrightarrow{N_3} [Pd^{11}] Ar$$

$$Nal NaN_3$$
Selected examples: 
$$H \xrightarrow{N_3} H \xrightarrow{N_4} H \xrightarrow{N_4}$$

Significance: Lee and Pootheri report a palladium-catalyzed protocol for the direct synthesis of N-formylanilines from aryl halides. While sodium azide is used as the nitrogen donor, oxalic acid serves as both the carbon monoxide and hydrogen source. Aryl iodides generally lead to higher yields than the corresponding bromides.

**Comment:** The catalytic cycle initially furnishes the acyl azide, which then undergoes a Curtius rearrangement to the aryl isocyanate. The latter is reduced by hydrogen originating from oxalic acid. This reaction is not facilitated by the palladium catalyst as verified by performing the reaction in a two-chamber reactor with separated oxalic acid.

SYNFACTS Contributors: Martin Oestreich<sup>®</sup>, Hendrik F. T. Klare<sup>®</sup>, Emilio Acuña Bolomey<sup>®</sup> Synfacts 2025; 21(01), 32 Published online: 20.12.2024