# Electronically flexible pyridylidene amide ligands for palladium-catalyzed α-arylation of ketones

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Electronically flexible ligands such as pyridylideneamides (PYAs, Fig. 1A) can vary their degree of donor ability and may stabilize several intermediates of a catalytic cycle.[1] This ligand flexibility is a highly desirable feature in catalytic processes, especially when different oxidation states are involved.[2] In their zwitterionic form, these ligands exhibit strongly donating properties that facilitate oxidative additions on the coordinated metal center. Furthermore, their ease of production, low-cost synthesis and high tunability make them efficient alternatives to carbenes and phosphines. Surprisingly, the potential of such donor-flexible PYA ligands has been poorly investigated in palladium-catalyzed cross-coupling processes. Here we introduce different bidentate pyridyl-PYA ligands coordinated to palladium(II), which afford highly active and robust ketone α-arylation catalysts with unprecedented turnover numbers (TONs) for N-based ligands in this transformation (Fig. 1B).[3] Moreover, we will discuss mechanistic details that emerged from using these well-defined precatalysts.

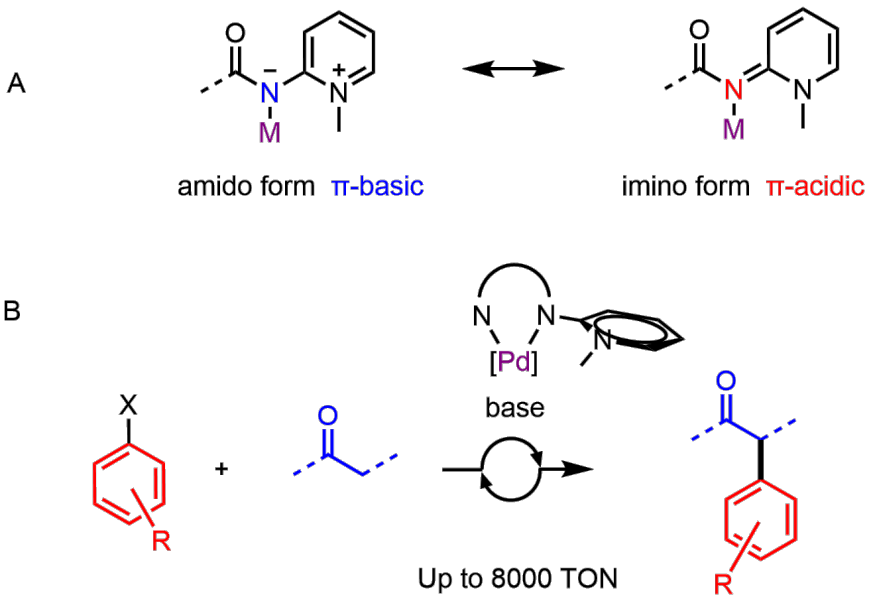



Figure 1. A: Resonance forms of the PYA ligand. B: Schematic representation of a palladium complex containing a pyridyl-pyridylidene amide ligand that is active in the α-arylation of ketones.

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[3] P. Novák, R. Martin, *Curr. Org. Chem.*, **2011**, 15, 3233-3262.