

Dioxygen Controlled Chemodivergent Carbon-Carbon Bond Formation Reaction Using Redox Non-innocent Azo Aromatic Complexes of Cobalt

Dr. Kamal

Kamal@iitjammu.ac.in, Department of Chemistry, Indian Institute of Technology Jammu, Jagti-181221, India.

The replacement of a noble metal catalyst with an earth-abundant 3d-transition metal catalyst is an atom-economic and environmentally benign catalytic pathway for synthesizing new organic molecules. Various carbon-carbon and carbon-hetero atom bond forming reactions using alcohols as reactants with acceptorless dehydrogenative coupling (ADC)/borrowing hydrogen (BH) strategy have received tremendous research interest in recent times. Herein, employing redox non-innocent pincer like cobalt (II) complexes containing azo-benzimidazole ligand a switchable and chemodivergent catalytic cross-coupling of primary and secondary alcohols are reported. The complexes were fully characterized by various spectroscopic techniques as well as by X-ray crystallography. Taking the advantage of redox non-innocent behavior of azo-aromatic compound which is known to exist in one-electron reduced azo-anion radical and two-electron reduced hydrazido forms, first cross-coupling between two alcohols are scrutinized. Thus, the reactions are environmentally benign and atom efficient. It liberates water and hydrogen gas as the only by products. While the reaction in inert condition gives α -alkylated ketones, in presence of air as well as lower temperature and base loading selectively the reaction results in α,β -unsaturated compounds. Both the catalytic protocols have a very good functional group tolerance. Thus, a wide range of substrates have been found to be effective for the synthesis of α -alkylated ketones as well as α,β -unsaturated alkylated ketones via dehydrogenative cross-coupling reaction of alcohols. Several control experiments and kinetic studies were performed to elucidate the reaction pathways.

