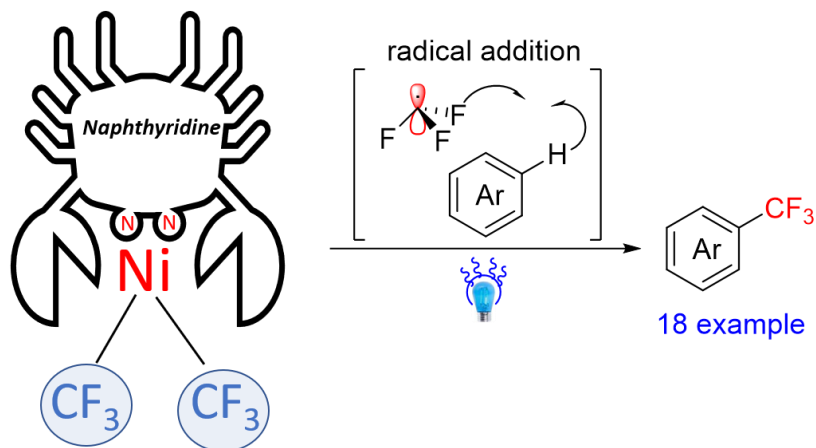


High valent nickel-catalyzed trifluoromethylation of arenes and heteroarenes induced by light irradiation

(¹Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University) ○Shubham Deolka,¹, Govindarajan Ramadoss¹, Eugene Khaskin,¹ Julia R. Khusnutdinova*¹.

Keywords: Nickel; Naphthyridine; Trifluoromethylation; Blue Light.

Trifluoromethylation¹ of C-H bonds is an industrially important reaction for the synthesis of pharmaceutical compounds, with a functional group that can significantly change the pharmacokinetics of a known drug. While many protocols are known for metal-catalyzed trifluoromethylation of C-H bonds in arenes and heteroarenes, it would be practically advantageous to develop photoinduced trifluoromethylation as a way to control the reactivity. Although photoredox catalysis has been reported in radical trifluoromethylation, the typical protocols utilize precious metal catalysts based on Ru or Ir, and no examples are known for photoinduced reactivity that would involve only inexpensive base metal complexes.



In the currently presented work, we developed² a family versatile Ni catalysts supported by N-donor naphthyridine based chelating ligands that efficiently catalyzes C-H bond trifluoromethylation of arenes and heteroarenes in the presence of visible light using two alternative protocols including Langlois or Umemoto reagents.

Interestingly, we were able to obtain stable and robust Ni(III) complexes simply by aerobic oxidation of Ni(II) precursors. EPR studies reveal that such Ni(III) trifluoromethyl complexes undergo light-induced Ni-CF₃ bond homolysis. We further developed it into catalytic protocols for C-H bond trifluoromethylation in the presence of blue LED irradiation. A number of electron-rich simple arenes or heterocycles (pyrroles, indoles) could be trifluoromethylated under these conditions.

Preliminary mechanistic studies suggest a radical mechanism via NiII/NiIII couple. This reactivity is an important example of the merge of Ni and photoredox catalysis into one system that utilizes only simple N-donor ligands and nickel as an inexpensive first row transition metal.

References:

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