

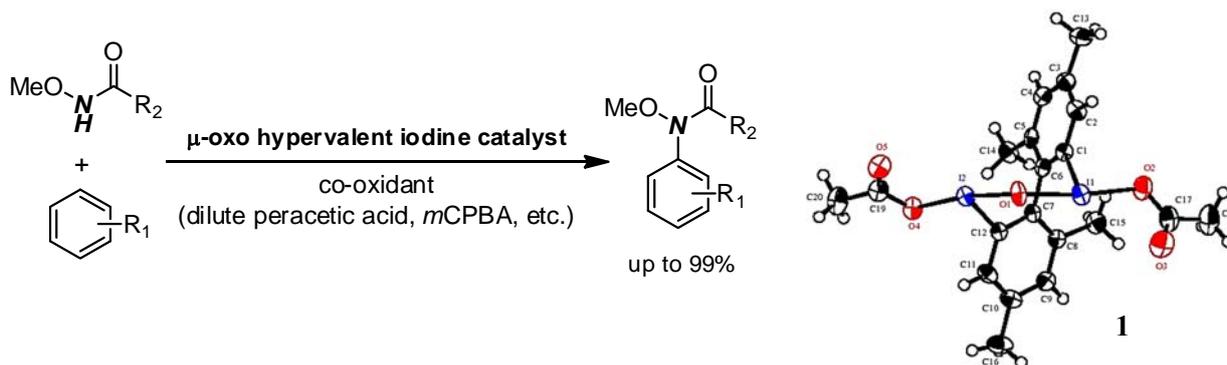
μ -Oxo Hypervalent Iodine Catalyst for Oxidative Coupling of N-H Substrates to Various Aromatics

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Oxidative coupling that can directly convert C-H group for chemical transformations is, in theory, an ideal strategy in organic synthesis to reduce the number of synthetic steps and byproduct generation. Hypervalent iodine reagent has become one of the promising tools in developing oxidative couplings due to its unique reactivities similar to metal oxidants.¹⁾ We have pioneered the metal-free oxidative coupling chemistry using hypervalent iodine reagent, *i.e.*, phenyliodine(III) diacetate (PIDA, $\text{PhI}(\text{OAc})_2$) and bis(trifluoroacetate) (PIFA).²⁾

Herein, we report our new developments of the oxidative couplings utilizing reactive μ -oxo hypervalent iodine reagent. The μ -oxo PIDA, $[\text{PhI}(\text{OAc})]_2\text{O}$, exhibits excellent reactivity over conventional reagent, PIDA, in many hypervalent iodine-mediated transformations, especially phenolic oxidations.³⁾ Catalytic utilization of μ -oxo PIDA is possible by its theoretical modification to a designer biaryl compound **1**, and various metal-free oxidative coupling reactions initiated by nitrogen atom activation of organic substrates, such as the oxidative dearomatization, spirolactamization of aryl-substituted amides and oxidative biaryl coupling of sulfonanilides with aromatic hydrocarbons, can smoothly proceed by using this catalyst.⁴⁾ The designer catalyst **1** developed in our laboratory is also superior in the oxidative amidations of aromatic rings in view of the catalytic activity (less than 2 mol% loading) and product yields.



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2. (a) Our recent account: T. Dohi and Y. Kita, *Curr. Org. Chem.* **2016**, *138*, 580. (b) Early study: *Angew. Chem. Int. Ed.* **2008**, *47*, 1301. (c) Recent study: *Adv. Synth. Catal.* **2017**, *359*, 2503.
3. T. Dohi, Y. Kita, et al. *Tetrahedron Lett.* **2011**, *52*, 2212.
4. (a) T. Dohi, Y. Kita, et al. *Chem. Commun.* **2010**, *46*, 7697. (b) *Angew. Chem. Int. Ed.* **2011**, *50*, 3784. (c) *J. Am. Chem. Soc.* **2013**, *135*, 4558. (d) Recent study: *J. Org. Chem.* **2017**, *82*, 11954 and references therein.