

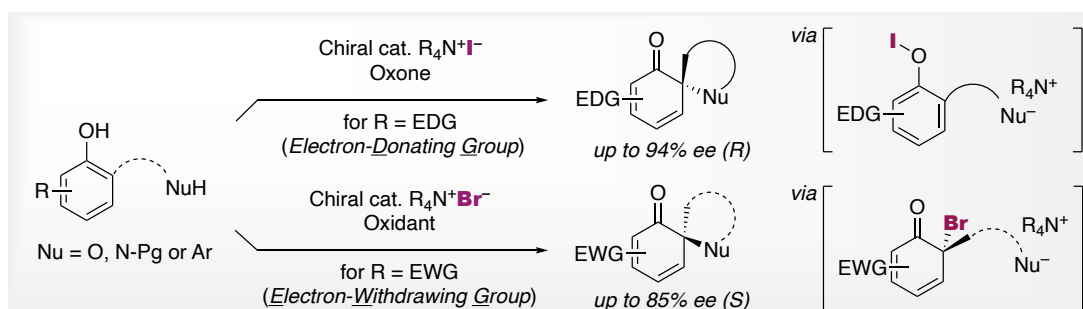
## Oxidative Dearomative Coupling Reaction of Arenols Using Hypohalite Catalysis

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Enantioselective oxidative dearomatization of arenols is an important tool for the synthesis of several biologically important compounds. Many elegant strategies have been developed using transition metal or hypervalent iodine catalysts or reagents.<sup>1</sup> In this regard, we have developed chiral quaternary ammonium hypoiodite-catalyzed enantioselective oxidative dearomatization of 1-naphthols.<sup>2</sup> However, long times (~3 days) were required to complete the reactions, even for these highly reactive substrates. Notably, no reaction took place for the oxidation of phenols.

Here, we developed a high-performance ammonium hypohalite catalysis for the enantioselective oxidative dearomatization reactions. Hypohalite catalytic active species could be generated *in situ* from the corresponding chiral quaternary ammonium halides with environmentally benign oxidants such as oxone or potassium bromate. Only inorganic wastes were generated from the oxidant used. By using hypoiodite catalysis, the oxidation of a wide range of naphthols and electron-rich phenols could proceed under mild conditions to afford the corresponding spirolactones with high enantioselectivity.<sup>3,4</sup> On the other hand, by using hypobromite catalysis, oxidative dearomatization of electron-deficient phenols, which were hardly reactive using the hypoiodite catalysis, readily proceeded to give the corresponding inter- and intramolecular dearomative C–O, C–N and C–C coupling adducts. We also achieved the first enantioselective hypobromite catalysis for oxidative dearomative coupling reactions. Notably, control experiments revealed that the reaction mechanism of hypobromite catalysis might be different from that of hypoiodite catalysis.



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