

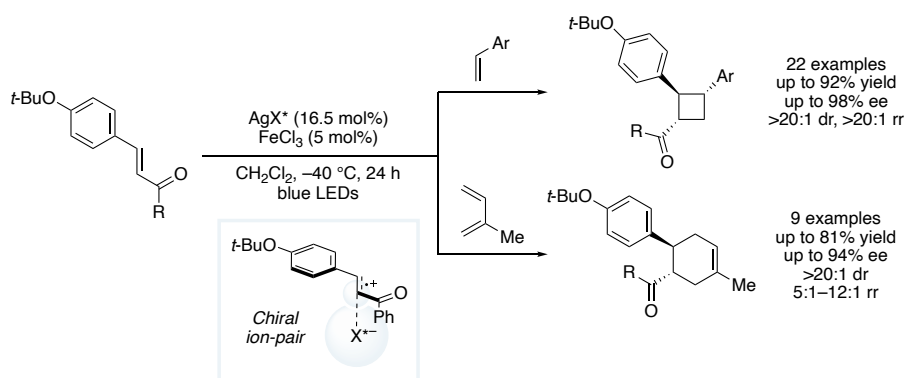
## Enantioselective Radical Cation [2+2] and [4+2] Cycloadditions Using Chiral Iron(III) Catalyst with Photoirradiation

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Radical cations are open-shell cationic species that are usually generated by the one-electron oxidation of neutral molecules. As their behavior is distinct from those of cations generated by two-electron processes (e.g., protonation, heterolysis, and coordination to Lewis acids), considerable effort has been directed toward using radical cations as alternative cationic intermediates for organic reactions. On the other hand, asymmetric catalysis to promote enantioselective radical cation reactions remains a major challenge in contemporary organic synthesis. However, over the last few years, Luo and Nicewicz have independently developed a novel class of chiral photoredox catalysts that provided the targeted products with modest enantioselectivity.<sup>1</sup> These pioneering studies have demonstrated the feasibility of controlling the reactivity of such labile species in order to accomplish highly enantioselective reactions.

We have already developed radical cation cycloadditions using iron(III) salts as effective and earth-abundant one-electron oxidants. According to our previous reports,<sup>2</sup> the X-ray crystallographic analysis of a radical cation generated by  $\text{FeCl}_3$  reveals a structure with a tight ion pair between the radical cation and  $\text{FeCl}_4^-$ . These findings inspired us to develop a chiral version of this iron(III) catalysis. Here, we report that an iron(III) salt containing a relatively weakly coordinating chiral anion is able to catalyze enantioselective radical cation [2+2] cycloadditions under irradiation with blue LEDs. To demonstrate the practical utility of this approach, we also explored enantioselective [4+2] cycloadditions to afford unusual regioisomers, highlighting the complementarity of our method to well-known Lewis-acid-mediated [4+2] cycloadditions.



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