Enantioselective Radical Cation [2+2] Cycloaddition Initiated by Chiral Iron(III) Salts and Mechanistic Insight into the Effect of Photoirradiation

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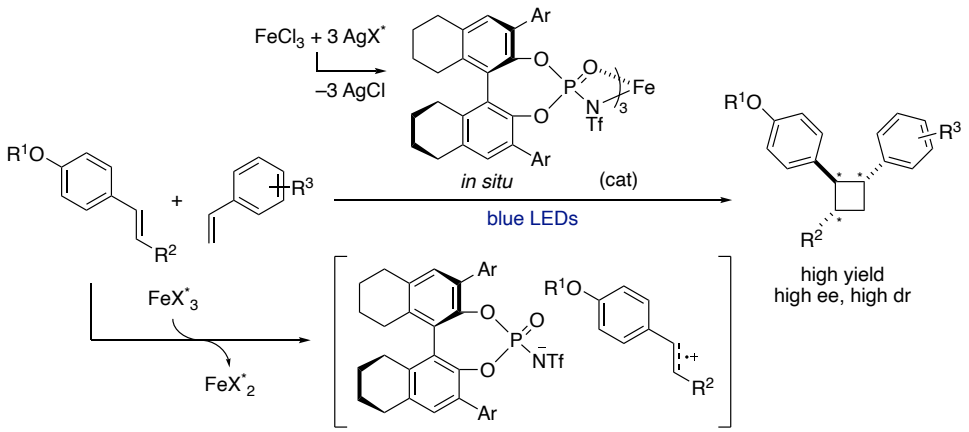
Radical cation [2+2] cycloaddition of anetholes with styrenes is of interest because it is one of the most straightforward methods to synthesize 1,2-diarylcyclobutanes, which are present in various natural products and pharmaceuticals. Generally, the reaction commences with the oxidation of an anethole derivative to provide an anethole radical cation intermediate. To generate such a reactive intermediate, great progress has been made on the development of several initiators over the past few decades. However, enantioselective variants of this type of reaction have been still challenging because those require precisely stereoselective control for labile radical cation intermediates.[1]

We previously developed radical cation [2+2] cycloadditions initiated by iron(III) salts as effective one-electron oxidants.[2] Here, we developed a chiral iron(III) salt, which could be prepared *in situ* from an iron(III) chloride and chiral silver *N*-triflyl phosphoramides, for enantioselective radical cation [2+2] cycloaddition. Several anetholes could be oxidized, and the resulting radical cation intermediates bearing chiral *N*-triflyl phosphoramide reacted with styrenes affording the [2+2] cycloadducts stereoselectively. Intriguingly, irradiation with blue LEDs dramatically improved the yield. As a result, the products were obtained in high yield with high enantioselectivity and diastereoselectivity. To elucidate the effect of photoirradiation, several control experiments and spectroscopy analyses were conducted.



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