

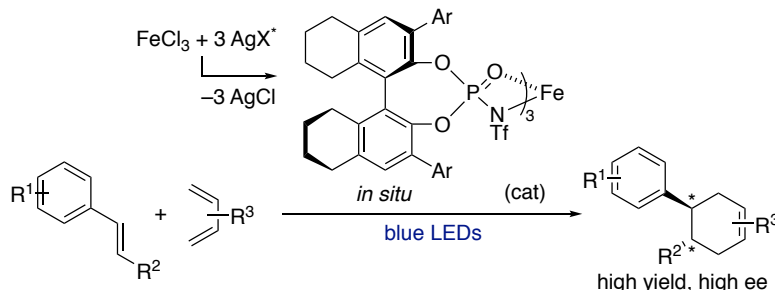
光照射下で進行するエナンチオ選択的ラジカルカチオン[4+2]環化付加反応に有効なキラル鉄(III)塩の開発

(名大院工) ○加藤 春奈・片桐 佳・大村 修平・堀部 貴大・石原 一彰
 Development of Chiral Iron(III) Salts for Enantioselective Radical Cation [4+2] Cycloaddition Accelerated by Photoirradiation (*Graduate School of Engineering, Nagoya University*)
 ○Haruna Kato, Kei Katagiri, Shuhei Ohmura, Takahiro Horibe, Kazuaki Ishihara

Radical cation [4+2] cycloaddition has received increased attention since it constructs various six-membered rings that cannot be easily accessed by thermal [4+2] cycloaddition.¹ Such a great advantage is attributed to the one-electron oxidation of an electron-rich alkene for generating a radical cation intermediate, which smoothly reacts with an electron-rich diene. Moreover, the resulting [4+2] cycloadducts serve as key intermediates for the synthesis of bioactive natural products.² However, enantioselective variants of this type of reaction have been still challenging because those require precise control for labile radical cation intermediates stereoselectively. Here, we developed a chiral iron(III) salt as a catalytic initiator for enantioselective radical cation [4+2] cycloaddition of anetholes. Photoirradiation dramatically accelerated the reaction, affording the desired cycloadducts in high yield with high enantioselectivity by using catalytic amounts of chiral iron(III) salts which could be prepared *in situ* from iron(III) chlorides and chiral silver *N*-triflyl phosphoramides.

Keywords: Radical Cation; [4+2] Cycloaddition; Chiral Iron(III) Salt; Chiral Counter Anion; Photoirradiation

電子豊富なアルケンの一電子酸化を鍵とするラジカルカチオン[4+2]環化付加反応が近年注目を集めている¹。熱的[4+2]環化付加反応とは異なる基質適用条件および位置選択性を有する高い有用性から、生物活性天然物の合成への応用が期待されている²。しかし、不安定なラジカルカチオンを精密かつ立体化学的に制御するのが難しいことから、エナンチオ選択的手法の開発は大きく遅れている。今回、我々はキラル鉄(III)塩を触媒的開始剤に用いるアネオール類のエナンチオ選択的ラジカルカチオン[4+2]環化付加反応を検討した。青色LED照射下、塩化鉄(III)とキラル*N*-トリフルルホスホロアミド銀から系中で調製可能なキラル鉄(III)塩を用いることで、[4+2]環化付加体を高収率および高エナンチオ選択的に得ることに成功した。



1) T. Horibe, K. Ishihara *Chem. Lett.* **2020**, 49, 107. 2) S. Lin, M. A. Ischay, C. G. Fry, T. P. Yoon *J. Am. Chem. Soc.* **2011**, 133, 19350.