IRON-CATALYZED CYCLOPROPANATION OF 1,3-ENYNES UNDER THERMAL OR PHOTOCHEMICAL CONDITIONS

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Within the past years our group has been interested in exploring the catalytic activity of the electron-rich iron complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe])^[1]. We previously demonstrated that this nucleophilic complex was able to activate diazo compounds in various carbene-transfer reactions, specifically in the Doyle-Kirmse reaction and X-H insertion reactions (Fig. 1)^[2]. Based on these results, we hypothesized that TBA[Fe] could also catalyze the cyclopropanation of olefins using ethyldiazoacetate as carbene precursor.

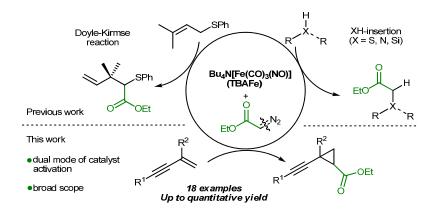


Figure 1: TBA[Fe]-catalyzed cyclopropanation of 1,3-enynes.

Herein, we report that TBA[Fe] successfully catalyzes the cyclopropanation of non-isomerizable as well as isomerizable 1,3-enynes into the corresponding propargyl cyclopropanes^[3]. The catalyst can be activated thermally or photochemically to give the desired cyclopropanes in good to excellent yields, under otherwise mild reaction conditions. Notably, this catalytic process is selective towards conjugated enynes, as alternative olefinic moieties remain unaffected. Moreover, no X-H insertion into electron-poor X-H is observed in the course of the reaction.

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^[2] a) M.S. Holzwarth, I. Alt, B. Plietker, *Angew. Chem. Int. Ed.* **2012**, *51*, 5351; b) A. Röske, I. Alt, B. Plietker, *ChemCatChem* **2019**, doi: 10.1002/cctc.201900459.

^[3] M.-I. Picher, B. Plietker, Manuscript in preparation.