

Iron-Catalyzed 1,4-Difunctionalization of 1,3-Enynes with Arylboronates and Unactivated Alkyl Electrophiles

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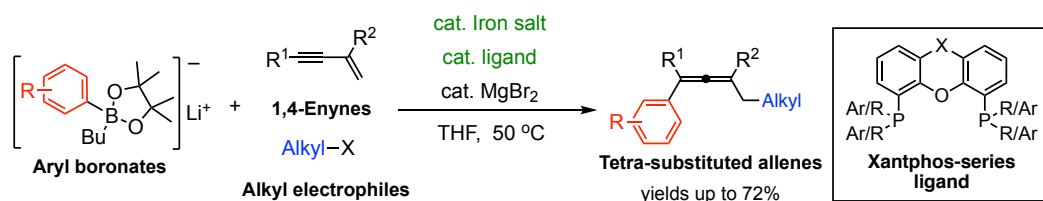
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Allene is one of the most versatile building blocks to construct complex molecular scaffolds in natural products and pharmaceuticals.¹ Hence, the stereoselective synthesis of allenes has attracted increasing attention in medical and material chemistry fields.² In recent years, transition metal-catalyzed 1,4-difunctionalizations of 1,3-enynes have been proved a powerful strategy for efficiently synthesizing the multi- or tetra-substituted allenes. Although the first-row transition metal catalysts significantly improved and complemented this reaction based on the single electron transfer process, there are still limited reports to date.³ Herein, we report the first iron-catalyzed radical 1,4-difunctionalizations of 1,3-enynes with aryl boronates and unactivated alkyl electrophiles which afford tetra-substituted allenes (Scheme 1).

The three-component coupling reaction of 1,3-enynes, aryl boronates, and alkyl electrophiles was carried out in the presence of a catalytic amounts of iron salts, bisphosphine ligands, and magnesium bromide, to give the corresponding tetra-substituted allenes in moderate to good yields. After the ligand screening, we confirmed that a family of bisphosphine ligands bearing xanthene-type backbones (Xantphos-series ligands) selectively afforded the corresponding allene products, avoiding the formation of a direct-coupling byproduct between aryl boronates and alkyl electrophiles. In this presentation, we will report the detailed ligand screening and scope studies and discuss the possible reaction mechanism.

Scheme 1



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