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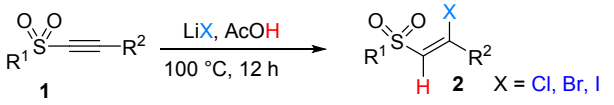

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ABSTRACT

We have developed an efficient synthesis of β-halo *Z*-sulfonyl alkenes *via* hydrohalogenations of readily available sulfonyl alkynes. The high hydrogen bonding acidity of linear acetic acid network or aggregate may play a vital role in activation of sulfonyl alkyne substrates. Our condition offers high stereoselectivity, good chemical yields, and high functional group tolerance.

Alkenyl halides are important targets in medicine, agrochemicals and advanced materials.[1] Moreover, alkenyl halides are also important synthetic building blocks which have been used extensively in cross-coupling chemistry[2] such as Suzuki couplings[3], Sonogashira couplings,[4] Stille couplings[5], and Buchwald-Hartwig aminations.[6] More specifically, halogenated sulfonyl alkenes are especially versatile synthons for synthesis of highly functionalized alkenes due to presence of two synthetic handles.[7]

As a result, the efficient synthesis of halogenated sulfonyl alkenes has attracted much attention. For example, iron catalyzed reactions of sulfonyl chlorides with alkynes has been reported for the preparation of chlorinated sulfonyl alkenes (Scheme 1a).[7a] Alternatively, halogenated sulfonyl alkenes could be prepared by iron[7b] (Scheme 1b) catalyzed or copper[8] (Scheme 1c) catalyzed halosulfonylation of terminal alkynes using sulfonylhydrazides. Other common methods are transition metal (such as Co, Ni, Cu) catalyzed[9] or uncatalyzed[10] sulfonylation of alkynes using sodium sulfinates and various halide sources (Scheme 1d). β-Halo sulfonyl alkenes could also be prepared from a multicomponent reaction with insertion of sulfur dioxide (Scheme 1e).[11] Halogenated sulfonyl alkenes also could be prepared indirectly from oxidation of haloalkenyl sulfides.[12] Despite these important progresses, there are still challenges for synthesis of halogenated sulfonyl alkenes: 1) most of the above methods work only for aromatic substrates; 2) complex conditions were used; 3) *E*-isomers were obtained in most cases.[10f-i]