

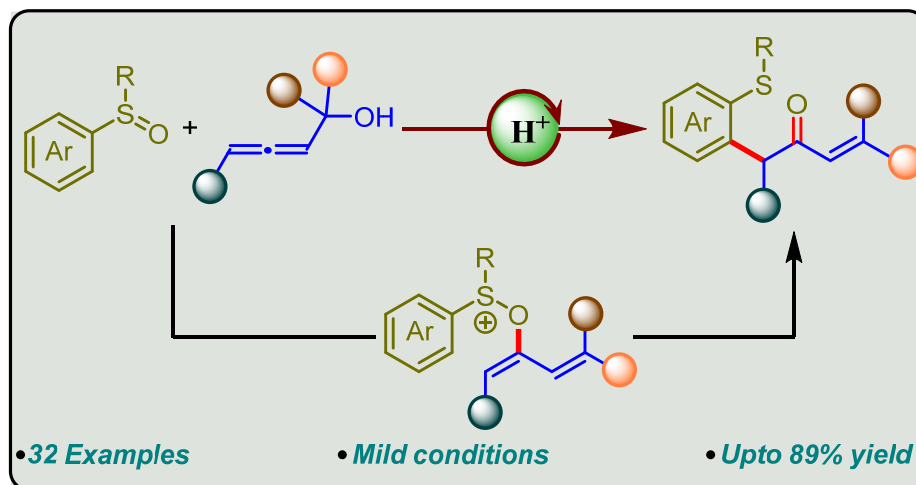
BRØNSTED ACID CATALYZED C-H FUNCTIONALIZATION OF ARYL SULFOXIDES VIA A CHARGE ACCELERATED [3,3]-SIGMATROPIC REARRANGEMENT OF BUTADIENYL SULFONIUM CATION INTERMEDIATES

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Sigmatropic rearrangements play a pivotal role in constructing molecular intricacy in organic synthesis. Interrupted Pummerer reaction allows the C-H functionalization of arenes through electrophilic activation of sulfoxides, coupling with suitable partners and subsequent thia-Claisen rearrangement.¹ Maulide reported a more elegant and atom economic Brønsted acid catalyzed oxy-arylation of ynamides.²

Herein we describe a highly efficient and metal-free approach for redox-neutral arylation of allenyl alcohols to gain access to benzylic enones. Reaction proceeds *via* activation of the allenyl alcohols by acid catalyst, trapping of resulting electrophile by sulfoxide and subsequent 3,3-sigmatropic rearrangement. The generation of water molecule as the sole by-product makes this protocol a highly atom economical and environmentally benign. For the first time, allenes have been engaged in sulfonium ion mediated thia-Claisen rearrangement. Furthermore, the versatility of the developed protocol was demonstrated by carrying out sequential bis-functionalizations and gram scale synthesis.



[1] (a) Yanagi, T.; Otsuka, S.; Kasuga, Y.; Fujimoto, K.; Murakami, K.; Nogi, K.; Yorimitsu, H.; Osuka, A. *J. Am. Chem. Soc.* 2016, *138*, 14582. (b) Eberhart, A. J.; Procter, D. J. *Angew. Chem. Int. Ed.* 2013, *52*, 4008.

[2] Peng, B.; Huang, X.; Xie, L.-G.; Maulide, N. *Angew. Chem. Int. Ed.* 2014, *53*, 8718.