

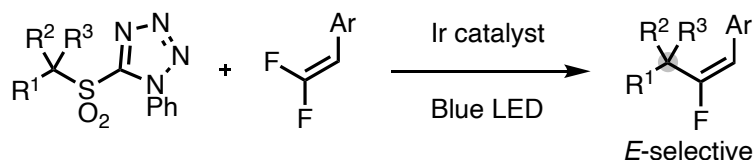
## Desulfonylative Coupling with *gem*-Difluoroalkenes by Visible-light Photoredox Catalysis

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A visible-light photoredox catalysis has emerged as a versatile toolkit to generate reactive radical species through a single-electron transfer (SET) process.<sup>1</sup> Various organo- and transition-metal photoredox catalysts bearing different redox potentials have been developed so far, enabling the catalytic generation of radical species from redox-active compounds through SET-induced fragmentation process. In recent years, the rational design of substituents in sulfonyl group has been demonstrated to allow direct generation of radicals from sulfones.<sup>2</sup> Such designed sulfones would be useful reagents, however, substrates are limited to reactive sulfones having relatively high reduction potential by introducing electron-withdrawing groups at  $\alpha$  position.

Recently, our group has established a new method for the generation of tertiary carbon radicals through single electron reduction of alkylsulfones promoted by Zn and 1,10-phenanthroline (phen) as a new reducing agent.<sup>3</sup> The use of tetrazolyl group in sulfonyl group was found to be critically important, and control experiments and theoretical calculation suggested the generation of phen radical anion as a single electron reductant. The resulting radicals could be employed in Giese reaction with various electron-deficient olefins to prepare a variety of quaternary products, but several olefins including fluorinated alkenes were not tolerated probably due to competitive reduction of olefins. Herein, we describe the reductive desulfonylative coupling of tertiary alkylsulfones with *gem*-difluoroalkenes catalyzed by visible-light Ir photoredox catalyst. Interestingly, our method could selectively afford sterically hindered *E*-fluoroalkenes in good yields, which are difficult to synthesize by previous methods. The origin of high *E* stereoselectivity of products was investigated by mechanistic studies.



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