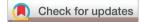
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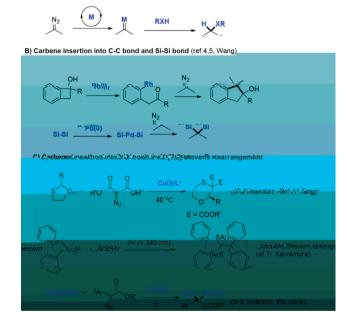
Copper-catalyzed carbene insertion into the sulfur-sulfur bond of benzenesulfonothioate†

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An unprecedented copper-catalyzed intermolecular sulfur-sulfur bond insertion between aryldiazo-acetates and benzenesulfonothioate has been successfully developed. Diverse α -disulfur functionalized esters were synthesized in good to excellent yields. The sulfur ylide formation and subsequent Stevens rearrangement are considered as the key steps for the discovered reaction.

A) Classic carbene insertion into X-H bond (well established)

f f tt t. , etc.) f t 1B).4 t. t (0)t 1B).⁵ t in situ, t. f t t 2,3 -1,2 - t f 1,2 - t



Scheme 1 Catalytic carbene insertion into σ bonds.

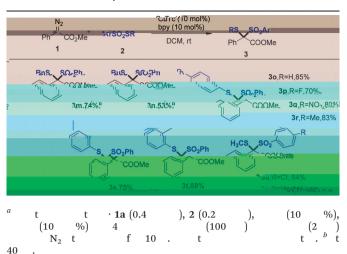
^{200,} t t t 1,2 - tvia 11 t 1,3t 1). f Nt.12 f t f f f via **6** 340

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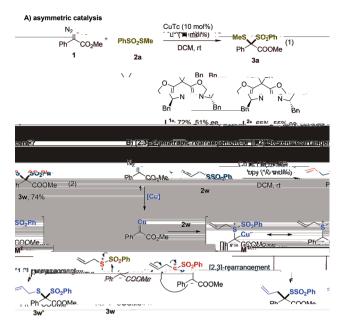
[†] t t f t () . · 10.103 / 01131

Table 3 Substrate scope of benzenesulfonothioate^a



3h 56% 36% t 3g t t tt 40 t t meta t (3i),orthott t f t t t t t, ff 66% 84% 31). (3k t t f t f t 2 t. 3). t (3a 3m-v). f t t, t , N 2, t (3o-t). t t paratt t f t (3u-v). f f t t t t t f t (f †). ft t f f 55% tt t t t 3) t t f t f t t t 2w 3, t t t $2\mathbf{w}$ t M^2 . f 1,2 t t t , f t t 3w. t 3w'. t t f t t

1,2 -



Scheme 3 Asymmetric reactions and proposed mechanism.

f 1,2 f t t t t t $t \quad t$ 2,3 t. ffi ()f t f f t t t f t t f t f t t

Conflicts of interest

f t t .

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Notes and references

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