

## Solvent-Controlled Selective Synthesis of 1,4-Benzodithiins and 1,4-Benzodithiafulvenes *via* Cyclization and Ring Contraction

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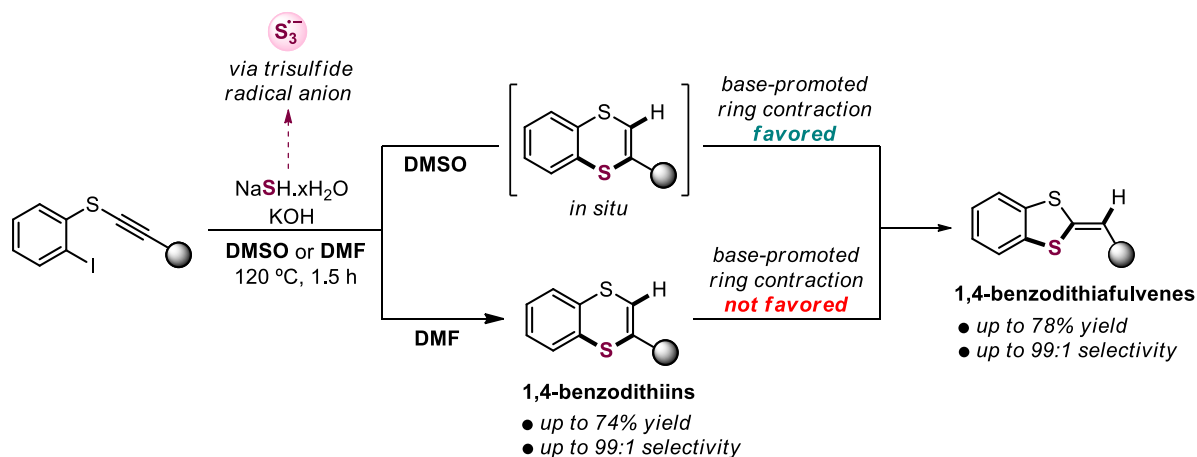
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### ABSTRACT

1,4-Dithiins are a class of non-aromatic, sulfur-rich heterocycles with promising applications in materials sciences due to their non-planar structure and reversible one- and two-electron oxidations.<sup>1</sup> In contrast, dithiafulvene (DTF) derivatives exhibit remarkable electron-donating properties and have been used as valuable molecular building blocks for the preparation of  $\pi$ -extended tetrathiafulvalene vinylogues (TTFV).<sup>2</sup> In this study, we present a solvent-controlled selective synthesis of 1,4-benzodithiins and 1,4-benzodithiafulvenes through the addition of NaHS to 2-iodoaryl thioalkynes in DMF and DMSO, respectively. These reactions rapidly form a 6-membered ring (1,4-benzodithiin) in both solvents. However, in DMSO, a base-promoted ring contraction occurs, leading to the highly selective formation of a 5-membered ring (1,4-benzodithiafulvene). The reaction scope is currently under investigation, and so far, more than 15 examples of these 6- and 5-membered heterocycles have been selectively obtained with yields of up to 78% and selectivity ratios of up to 99:1.



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