In contrast to the rich (4+3) cycloaddition chemistry of furans [1], only one instance of an intermolecular (4+3) cycloaddition of a thiophene has appeared with an unreported yield [2]. This paucity of examples is reflective of the high aromaticity of thiophenes that make them generally incompetent as dienes for cycloadditions.

We have been working on (4+3) cycloadditions of epoxy enolsilanes with various dienes [3]. Herein, we report the first series of effective (4+3) cycloadditions of thiophenes which occurred in the intramolecular context. Thiophenes tethered to epoxy or aziridinyl enolsilanes underwent (4+3) cycloadditions under silyl triflate catalysis, to afford *endo* and *exo* cycloadducts in overall yields up to 83%, and with diastereomeric ratio of up to 8:1 (Eq. 1). Subsequent derivatizations of the cycloadducts afforded functionalized desulfurized dienes in moderate to high yields (Scheme 1). This strategy allows us to further utilize this (4+3) cycloaddition for organic synthesis applications.

![Reaction Scheme](image)

**Scheme 1:** Conditions: a. TBSCI, imidazole, DMF, 95%; b. mCPBA, 88%; c. LiHAH, THF; d. heat, 49% over 2 steps.

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