

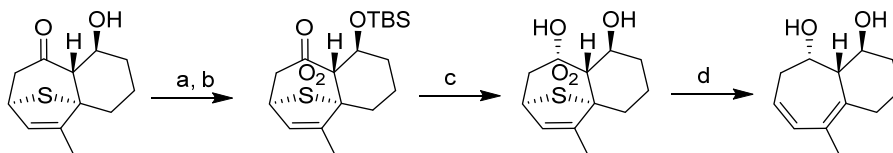
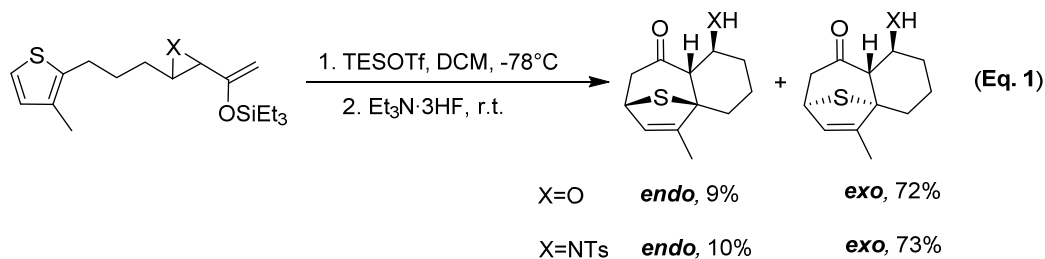
INTRAMOLECULAR (4+3) CYCLOADDITIONS OF THIOPHENES

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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.



Scheme 1: Conditions: a. TBSCl, imidazole, DMF, **95%**; b. mCPBA, **88%**; c. LiAlH₄, THF; d. heat, **49%** over 2 steps.

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[2] Pacheco, D.; Vargas, F.; Rivas, C. *Phosphorus and Sulfur*, **1985**, 25, 245-25.

[3] Chung, W. K.; Lam, S. K.; Lo, B.; Liu, L. L.; Wong, W. T.; Chiu, P. *J. Am. Chem. Soc.*, **2009**, 131, 4556-4557; Lam, S. K.; Lam, S.; Wong, W. T.; Chiu, P. *Chem. Commun.*, **2014**, 50, 1738-1741.