

## MECHANISTIC INVESTIGATION OF AN OXIME ETHER ELECTROCYCLIZATION

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A range of functionalized heteroaromatic boronic acid derivatives is readily accessed by a diboration/ $6\pi$ electrocyclization sequence [1]. This study revealed the surprising observation that there is a direct relationship between oxime ether stereochemistry and reactivity towards electrocyclization. Specifically, *E*-oxime ethers are found to be significantly more reactive than their *Z*-counterparts.

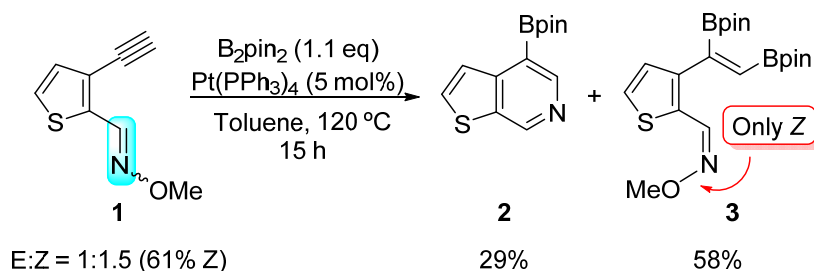


Figure 1. Synthesis of borylated thienopyridines.

In contrast, the configuration at the azatriene alkene terminus has little impact on reaction rates. Computational analysis offers a rationale for this observation; a  $N_{\text{lone pair}} \rightarrow C=C \pi^*$  orbital interaction lowers the energy of the transition state in the electrocyclization of *E*-oxime ethers. The aromaticity of the transition state of the reaction was also studied, calculating the NICS index and performing AICD calculations [2], which lead to the classification of this reaction as pseudopericyclic.

[1] Mora-Radó, H.; Sotorríos, L.; Ball-Jones M. P.; Bialy, L.; Czechtizky, W.; Méndez, M.; Gómez-Bengoa, E.; Harrity, J. P. A. *Chem. Eur. J.* **2018**, *24*, 9530–9534.

[2] Geuenich, D.; Hess, K.; Köhler, F.; Herges, R.; *Chem. Rev.*, **2005**, *105* (10), 3758–3772