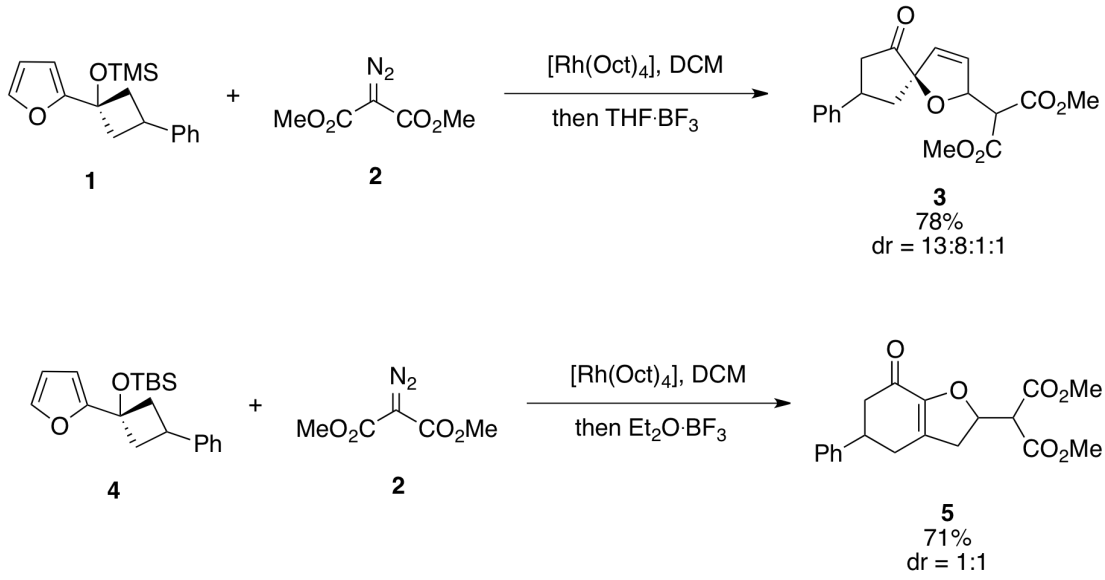
Submitted by (Nicolas Millius)

Direct Syntheses of Spiro- and Fused-Hydrofurans by a Tunable Tandem ??? Rearrangement/??? Addition Protocol

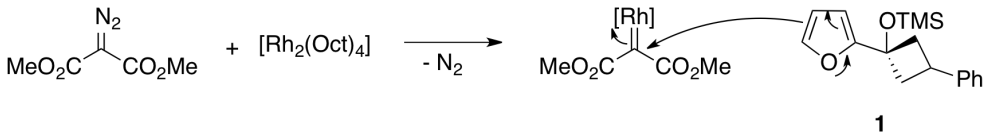
Problem:



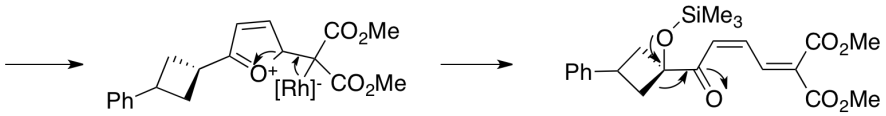
- Probose a mechanism for the formation of **3** and **5**.
- How is the starting material **1** and **4** prepared (2 steps).

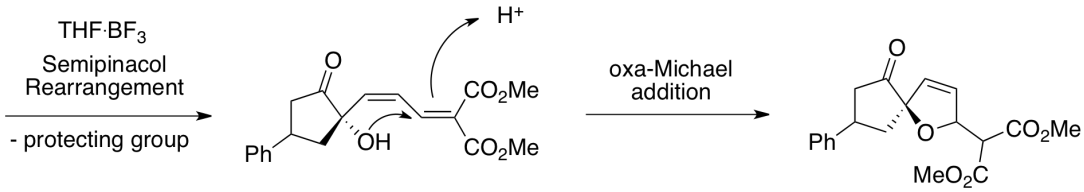
Solution:

Mechanism for the formation of Spiro-Hydrofuran:



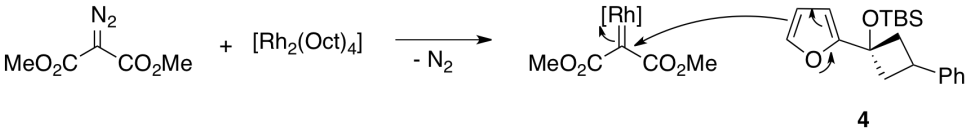
1



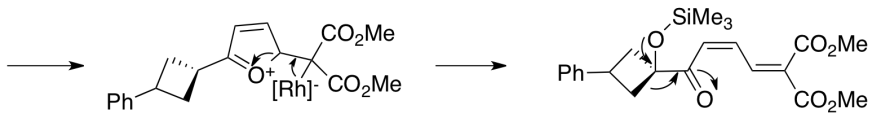


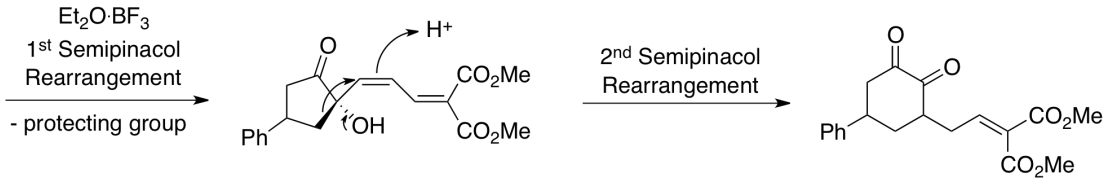
3

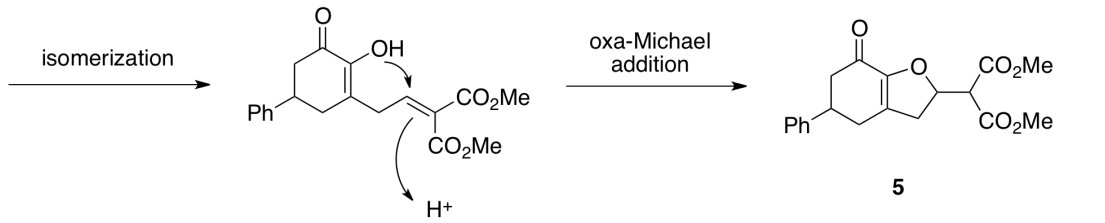
Mechanism for the formation of Fused-Hydrofuran:



4

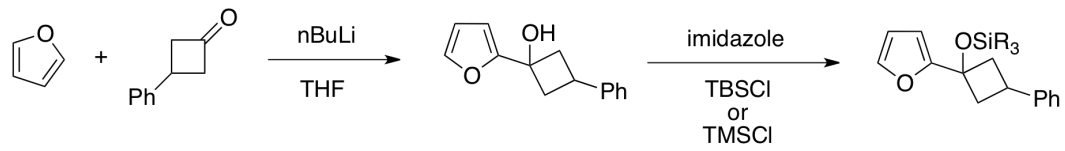






5

Synthesis of starting material:



Comments:
The formation of the spiro and fused products might be attributed to the stronger acidity of $Et_2O{\cdot}BF_3$ relative to that of $THF{\cdot}BF_3$, with former capable of inducing the second 1,2-migration and the subsequent oxa-Michael addition.

References:
B.-S. Li, W.-X. Liu, Q.-W. Zhang, S.-H. Wang, F.-M. Zhang, S.-Y. Zhang, Y.-Q. Tu, X.-P. Cao, *Chem. Eur. J.* **2013**, web-published 13.03.2013.

Keywords: Tandem Semipinacol rearrangement, Oxa-Michael addition