

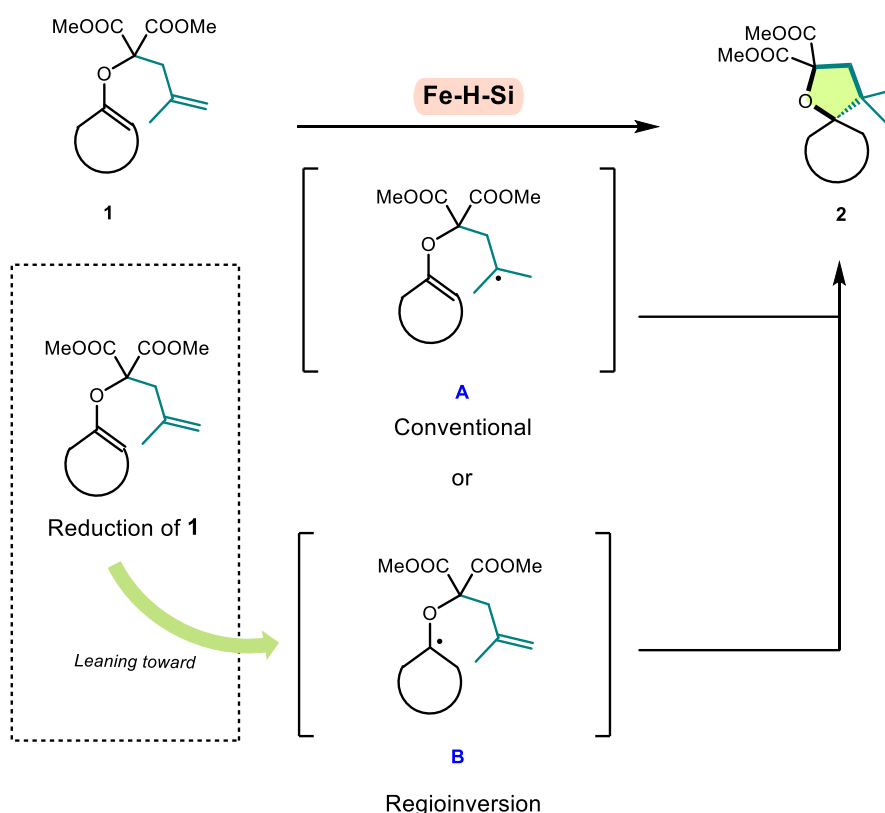
Iron-mediated Hydride Hydrogen Atom Transfer (Fe-HAT) for Oxa-spirocycle Formation from Olefins and Enol Ethers

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Spiro derivatives are increasingly utilized as scaffolds, gaining significant attention in medicinal chemistry.^[1] In this work, the direct construction of spiro oxa-compounds via Metal-Hydride Hydrogen Atom Transfer (MHAT) reactions is reported; a radical-based methodology using non-toxic Fe(acac)₃ and readily available silane at ambient atmosphere.^[2] Key malonate enol ether substrates are accessed in one step from cyclic ketones and diazo reagents, following an unusual carbonyl-ylide reactivity previously reported in our group.^[3] Despite simple concept and reaction conditions, the mechanistic understanding remains challenging. Conventionally, the initial step would be the radical formation from the donor olefin **1** to give the intermediate **A** by an in situ-generated Fe hydride,^{[3],[4]} followed by the intramolecular cyclization via 5-exo trig pathway to give spirocyclic product **2**. However, our observations point to a rapid reduction of enol moiety of **1** first. Further mechanistic investigation and reactivity scope will be on display during the poster presentation.



[1] K. Hiesinger, D. Dar'in, E. Proschak, M. Krasavin, *Journal of Medicinal Chemistry*, **2021**, *64*, 150-183.

[2] J. C. Lo, Y. Yabe, P. S. Baran, *JACS*, **2014**, *136*, 1304-1307.

[3] J. Viñas-Lóbez, G. Levitre, A. de Aguirre, C. Besnard, A.I. Poblador-Bahamonde, J. Lacour, *ACS Org. Inorg. Au*, **2021**, *1*, 11-17.

[4] K. Iwasaki, K. K. Wan, A. Oppedisano, S. W. M. Crossley, R. A. Shenvi, *JACS*, **2014**, *136*, 1300-1303.