

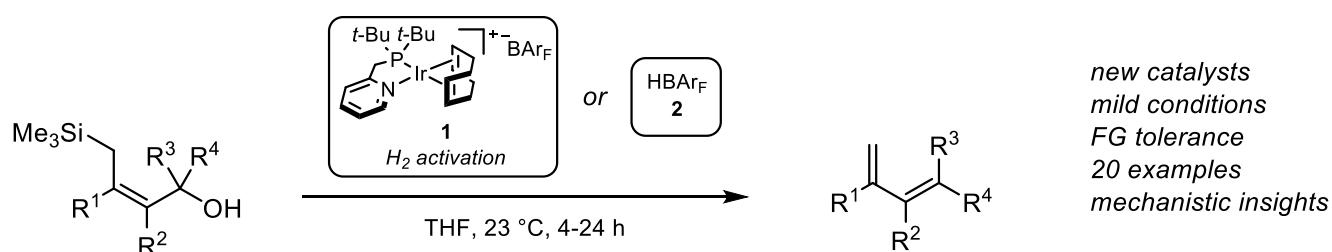
## Exploring Site Selectivity of Iridium Hydride Insertion into Allylic Alcohols: Serendipitous Discovery and Comparative Study of Two Catalysts for the Vinylogous Peterson Elimination

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The 1,2-migratory insertion of an olefin into a transition metal hydride is a fundamental elementary step in organometallic chemistry that constitutes the basis of a plethora of catalytic processes.<sup>[1]</sup> In recent years, our group has pursued the development of iridium complexes of general formula [(P,N)Ir(cod)]BAR<sub>F</sub> for the enantio- and diastereoselective isomerization of primary allylic alcohols to aldehydes.<sup>[2]</sup> Productive isomerization proceeds via an intermolecular hydride-type mechanism involving insertion of the in situ generated [Ir–H] intermediate across the C=C bond of the allylic alcohol, followed by β-hydride elimination and tautomerization to deliver the carbonyl compound.<sup>[2a]</sup>

Herein we describe how attempts to control site-selectivity of [Ir–H] insertion by introduction of a silyl substituent in the vicinity of the C=C bond of the allylic alcohol led to the serendipitous discovery of two novel and complementary catalytic systems for the vinylogous Peterson elimination: (i) an [Ir–H] catalyst generated upon activation of **1** by molecular hydrogen and (ii) an unusually mild Brønsted acid catalyst (HBA<sub>R<sub>F</sub></sub> (**2**)).<sup>[3]</sup> Preliminary studies revealed two distinct mechanistic pathways are operating. Optimization of this rather underdeveloped reaction was pursued to afford a variety of 1,3-dienes in excellent yields. Remarkably, the mild reaction conditions under which **1** and **2** operate are compatible with sensitive functional groups that would not be tolerated by more conventional acidic or basic reagents.<sup>[4]</sup>



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- [4] H. Li, D. Fiorito, C. Mazet, *submitted*.