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Extending the Substrate Scope in the Hydrogenation of Unfunctionalized Tetrasubstituted Olefins with Ir-P Stereogenic Aminophosphine−Oxazoline Catalysts

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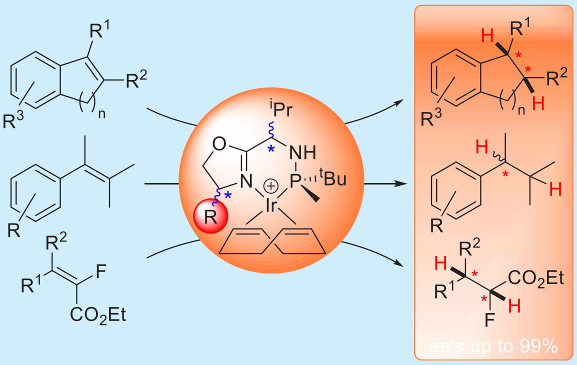
Supporting Information

ABSTRACT: Air-stable and readily available Ir-catalyst precursors modified with MaxPHOX-type ligands have been successfully applied in the challenging asymmetric hydrogenation of tetrasubstituted olefins under mild reaction conditions. Gratifyingly, these catalyst precursors are able to efficiently hydrogenate not only a range of indene derivatives (ee's up to 96%) but also 1,2-dihydronapthalene derivatives and acyclic olefins (ee's up to 99%), which both constitute the most challenging substrates for this transformation.



Asymmetric hydrogenation (AH) is one of the most common, reliable, and environmentally friendly industrial processes for the preparation of chiral compounds, such as drugs and crop-protecting chemicals.[1] Its strategic relevance has spurred research in both academia and industry over the last decades. Nowadays, an important number of Rh, Ru, and Ir catalysts exist for the AH of a broad range of substrates.[2] However, for some substrates such as tetrasubstituted olefins, attaining high activity and enantioselectivity is still a challenge. Their reduction would open up opportunities to simultaneously generate two vicinal tertiary stereocenters, which are present in many natural and high-valued products.[3] Achieving high enantiocontrol is even more difficult if the olefin lacks a coordinative group that can assist in the transfer of the chiral information from the catalyst to the product.[2] The AH of tetrasubstituted unfunctionalized olefins is therefore underdeveloped compared to the AH of olefins that contain a coordinative functional group.[3] To date, high catalytic performance has been reported in very few publications and with a limited substrate scope. In addition, for each type of olefin a different ligand family was required. In 1999 Buchwald's group reported the first successful AH of tetrasubstituted unfunctionalized olefins.[4] A series of indenes were hydrogenated using the zirconozene catalyst **1** (Figure 1) with moderate-to-high enantioselectivities (ee's in the range 52−99%).[5] They found that enantioselectivity was negatively affected by substituents other than a methyl in the benzylic position of the substrate. In addition to the low substrate scope, the high catalyst loading (8 mol %), the high H_2 pressure (typically >110 bar) required, and the low stability of

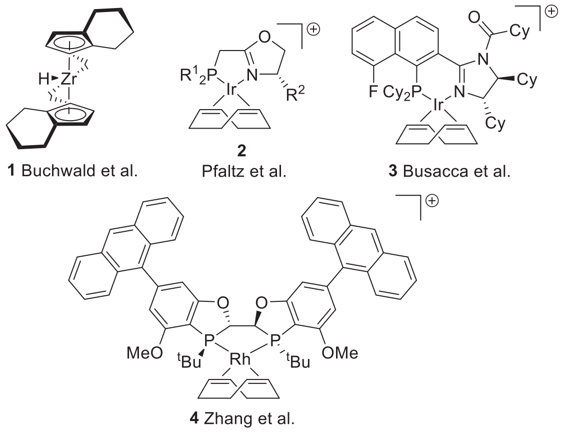


Figure 1. Representative catalysts for the AH of unfunctionalized tetrasubstituted olefins.

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