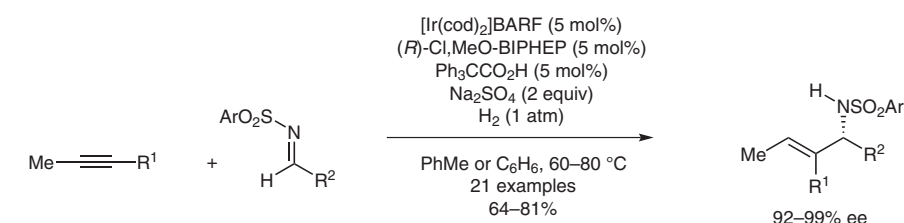
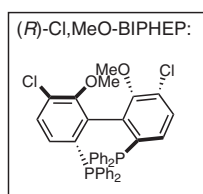


M.-Y. NGAI, A. BARCHUK, M. J. KRISCHE* (UNIVERSITY OF TEXAS AT AUSTIN, USA)
Enantioselective Iridium-Catalyzed Imine Vinylation: Optically Enriched Allylic Amines via Alkyne-Imine Reductive Coupling Mediated by Hydrogen
J. Am. Chem. Soc. **2007**, *129*, 12644-12645.

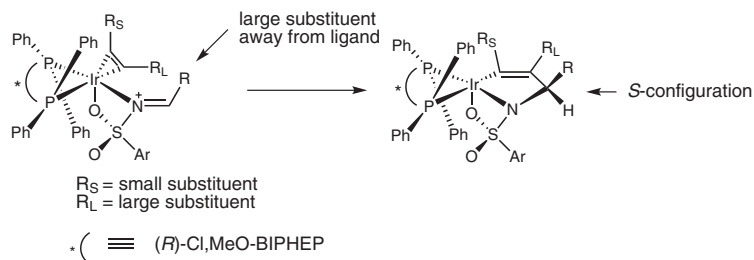
Iridium-Catalyzed Enantioselective Alkyne-Imine Reductive Coupling



R¹ = Me, *n*-Pr, *i*-Pr, CH₂CH₂OTBS
R² = Ph, 4-MeOPh, 3-MeOPh, 4-ClPh, 4-CO₂MePh,
2-Naph, HC=CHPh, 2-furyl, 2-thienyl, *c*-Hex,
c-Pent, *c*-Pr, Me, *n*-Bu, *i*-Pr, *i*-Bu
Ar = Bs, Ts



Proposed mechanism via:



Significance: This paper demonstrates the first catalytic enantioselective alkyne-imine reductive coupling which the authors use to devise a convenient route for synthesizing optically enriched allylic amines. An advantage of this approach is the absence of stoichiometric byproducts. The scope is very broad with excellent yields and enantioselectivities for a wide variety of alkynes and *N*-arylsulfonyl imines.

Comment: The reaction is both regioselective and enantioselective. The stereochemistry can be explained by the binding of the alkyne and imine to the catalyst (shown above) which results in insertion of the imine at its pro-*S* face. In the case of unsymmetrical alkynes, the regiochemistry can be explained by the Ir-catalyst binding to the alkyne in a manner where the large substituent points away from the bulky chiral ligand.

SYNFACTS Contributors: Mark Lautens, Praew Thansandote
Synfacts 2008, 2, 0159-0159 Published online: 23.01.2008
DOI: 10.1055/s-2007-992487; **Reg-No.:** L16407SF

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Category

Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

Key words

iridium

allylic amines

alkyne-imine
reductive coupling

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of the month

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