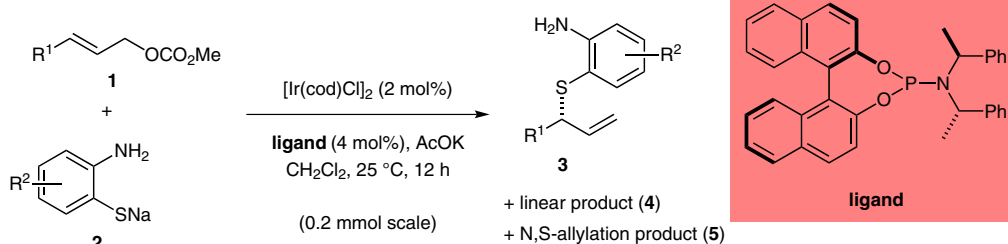


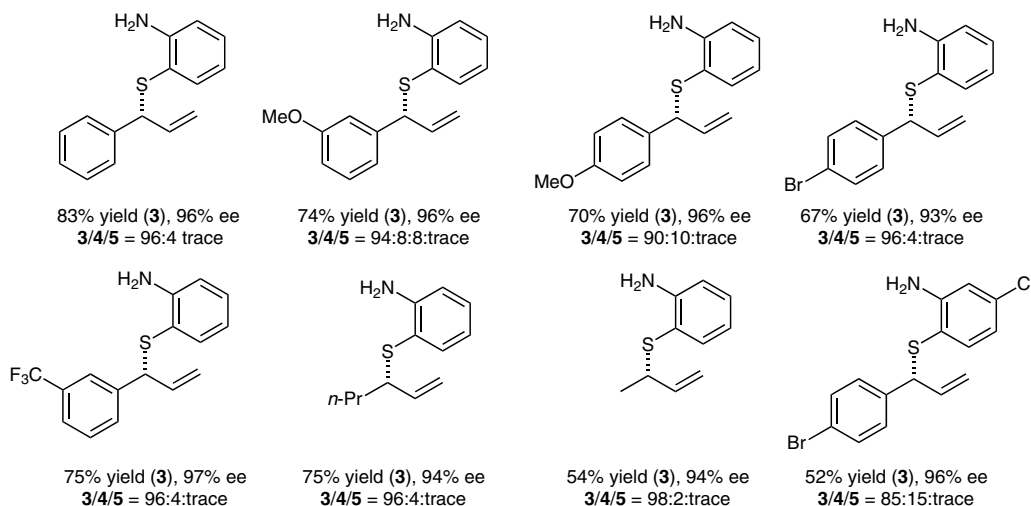
N. GAO, X.-W. GUO, S.-C. ZHENG, W.-K. YANG, X.-M. ZHAO* (TONGJI UNIVERSITY, SHANGHAI AND DALIAN UNIVERSITY OF TECHNOLOGY, P. R OF CHINA)
 Iridium-Catalyzed Enantioselective Allylation of Sodium 2-Aminobenzenethiolate: An Access to Chiral Benzo-Fused N,S-Heterocycles
Tetrahedron **2012**, *68*, 9413–9418.

Enantioselective Iridium(I)-Catalyzed Allylation of Sodium 2-Aminobenzenethiolates

Overall transformation:



Selected substrate scope:



Significance: Iridium-catalyzed enantioselective allylation has emerged as a powerful method to synthesize structurally diverse, chiral molecules. Despite much progress in the area of enantioselective carbon–sulfur bond formation using iridium, there have been no reports on the use of sodium 2-aminobenzenethiolate as a nucleophile in this class of reaction. Despite the potential of this substrate class to encounter detrimental ‘*ortho*-substituent effects’ on stereoselectivity, Zhao accomplishes selective and highly enantioselective S-allylation.

SYNFACTS Contributors: Mark Lautens, David A. Petrone
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Comment: The authors report an iridium-catalyzed asymmetric S-allylation reaction using chiral phosphoramidite ligands. The method is highly regio- and enantioselective for a variety of aryl- and alkyl-substituted allyl carbonates. Yields range from moderate to good with excellent enantiocontrol. In most cases, the authors are able to completely inhibit bisallylation and maintain high levels of branched-to-linear selectivity. The authors use the products to synthesize enantioenriched N,S-heterocycles via an N-allylation/ring-closing metathesis sequence.