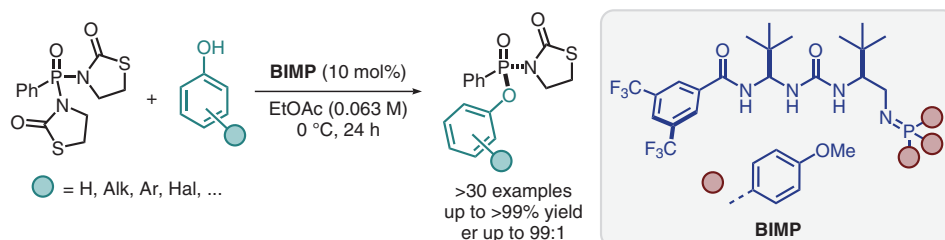
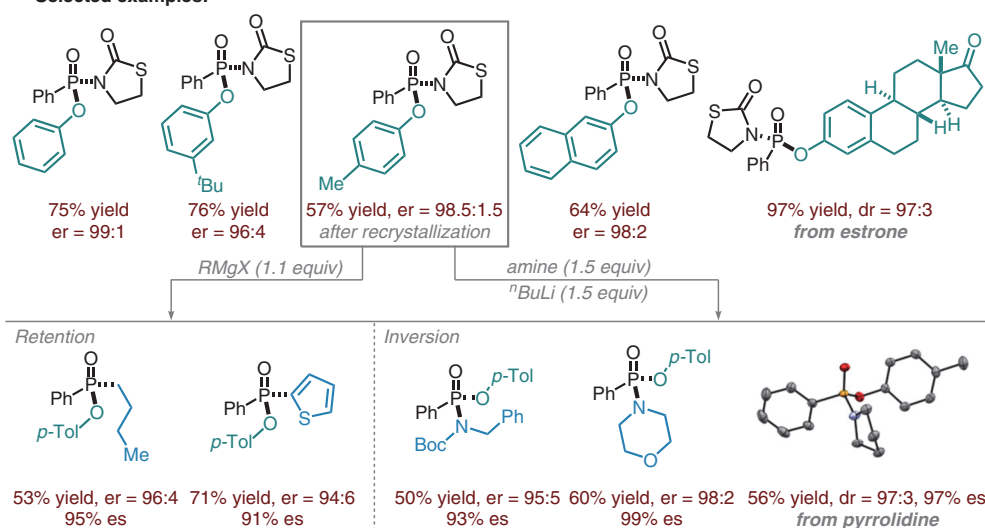


M. FORMICA, B. FERKO, T. MARSH, T. A. DAVIDSON, K. YAMAZAKI*, D. J. DIXON* (OKAYAMA UNIVERSITY, JAPAN AND UNIVERSITY OF OXFORD, UK)
 Second Generation Catalytic Enantioselective Nucleophilic Desymmetrization at P(V): Improved Generality, Efficiency and Modularity
Angew. Chem. Int. Ed. 2024, DOI: 10.1002/anie.202400673.

Organocatalytic Nucleophilic Desymmetrization of P(V) Precursors



Selected examples:



Significance: Dixon and co-workers report a 2nd-generation catalytic strategy for enantioselective nucleophilic desymmetrization at phosphorus(V) with a bifunctional iminophosphorane (BIMP) catalyst. This approach provides various chiral phosphorus compounds in good to high yields and enantioselectivities. Furthermore, DFT calculations provide insights into the mechanism, particularly the nature of enantioselectivity and the efficiency of the catalyst/leaving group combination.

Comment: The research focuses on nucleophilic substitution mechanisms: retention and inversion. Retention occurs when Grignard reagents maintain the stereochemistry at the phosphorus center, while thiols invert it. This distinction is crucial for synthesizing specific enantiomers and underpins a versatile method for creating enantioenriched phosphorus(V) compounds. Computational insights into reaction dynamics support the methodology, which potentially will have implications for organic synthesis and pharmaceutical development.

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Category

Organo- and Biocatalysis

Key words

phosphorus
 organocatalysis
 desymmetrization
 enantioselectivity
 bifunctional iminophosphorane
 pinacol borane

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