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SYNFACTS Highlights in Chemical Synthesis

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Category

Synthesis of Heterocycles

Key words

cobalt catalysis

isoxazoles

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***2H*-azirines**

chiral auxiliary

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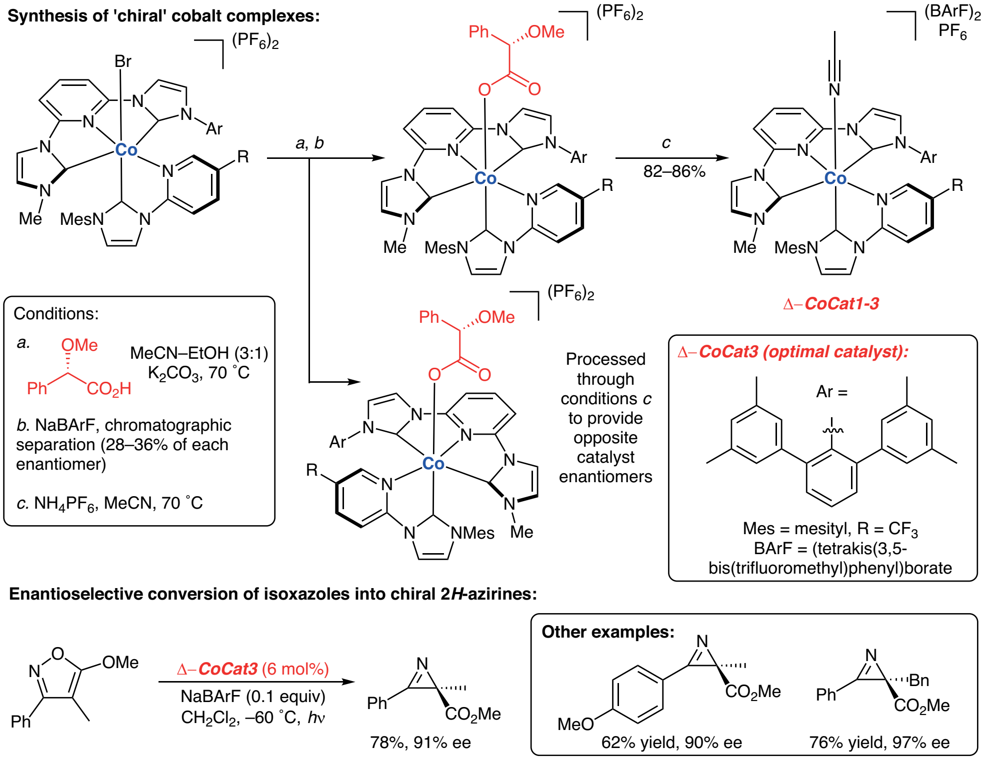
Cobalt Catalyst with Exclusive Metal-Centered Chirality for Asymmetric Photocatalysis
Nat. Commun. **2025**, *16*, 6635, DOI: 10.1038/s41467-025-61727-9

'Chiral at Metal' Complex Mediates Asymmetric Formation of 2*H*-Azirines



Significance: Cobalt represents an attractive alternative to precious metals for the development of new catalytic reactions based on its abundant nature as well as the ability to access a range of oxidation states. Asymmetric homogeneous catalysis typically involves the utilization of chiral ligands such as diphosphines, N-heterocyclic carbenes to set the chiral environment around the metal. The current report describes the design and utilization of a series of cobalt complexes that comprise only achiral ligands though can mediate the enantioselective conversion of isoxazoles to 2*H*-azirines under photocatalyzed conditions owing to the stereogenic metal center.

Comment: The racemic complexes were synthesized through standard coordination chemistry starting from $CoBr_2$ with subsequent reaction with the tridentate and bidentate ligands. Resolution was achieved through chromatographic separation of the diastereomers derived from the reaction with (*S*)-methoxyphenylacetic acid. The final complexes were formed after reaction with acetonitrile and proved to be thermally stable though could be activated upon exposure to light through dissociation of the MeCN ligand revealing the reactive stereogenic Co(II) center. Key to the success of the enantioselective formation of the desired 2*H*-azirines was judicious selection of sterically bulky substituents on the pincer ligand, and mechanistic studies highlighted the importance of the BARF additive in promoting the photodissociation to form the active catalyst.

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