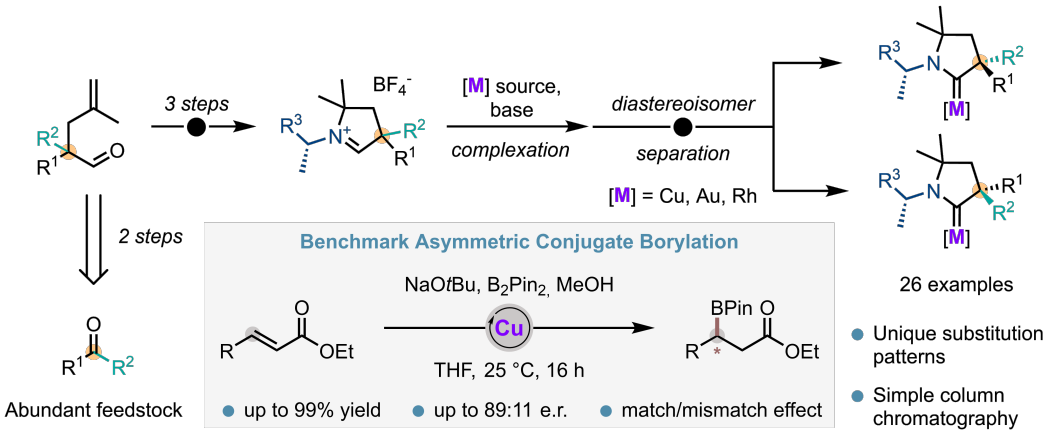
Streamlined Synthesis and Catalytic Performance of Chiral Cyclic (Alkyl)(Amino)Carbene Transition Metal Complexes Bearing α-Quaternary Stereogenic Centers

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Despite recent advances in the field of chiral Cyclic (Alkyl)(Amino)Carbenes (CAACs), achieving chirality in α-position to the carbene center remains remarkably challenging. CAAC complexes displaying such attributes involved in asymmetric transformations are yet limited to few examples[1,2]. Most efforts were currently targeted at asymmetric ruthenium catalysis (AROCM, ARM, ACM) with optically pure complexes obtained after chiral resolution on preparative HPLC[3]. Herein we describe a complementary approach to access highly modular carbene precursors featuring chiral α-quaternary centers. Chiral amines and readily prepared preallylated racemic aldehydes were merged to prepare diastereoisomeric carbene precursor salts. The two corresponding metal complexes can be obtained separately following the purification step, after complexation with a variety of transition metals (Cu, Au, Rh). A library comprising more than 20 complexes was prepared, showcasing unprecedented α-substitution patterns. The copper complexes unique steric and electronic environments were investigated in benchmark Asymmetric Conjugate Borylation (ACB) reaction, providing excellent yields and high enantioselectivities.



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