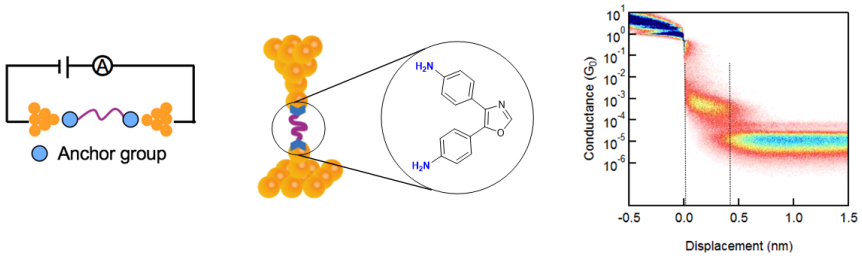
Conductance and Geometry of Oxazole-linked Single-molecule Junctions

Hao Yu, Kenneth Schwieter, Songsong Li, Charles Schroeder, and Jeffery S. Moore

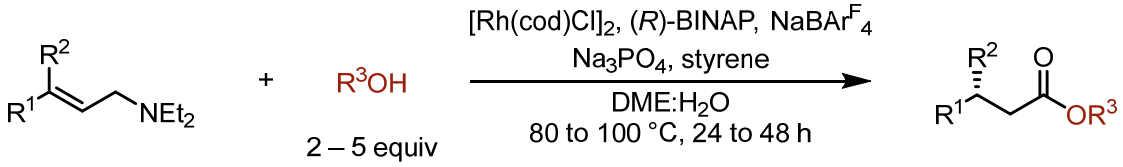
A single-molecule junction is generated using anchor groups to link the molecular bridge to the electrode. The structure–property relationship of the anchor and the molecular bridge profoundly affect the conductance properties and functions of the single-molecule device. However, few studies discuss the electron transfer mechanism when a potential anchor group is incorporated in the molecular bridge. Here, we report a new anchor group, oxazole, and the conducting pathway when oxazole is inserted into a phenyl molecular bridge. A series of oxazole-terminated and oxazole-containing molecules are efficiently synthesized by Van Leusen reaction. Detailed conductance data measured by scanning tunneling microscopy-break junction (STM-BJ) demonstrate that the major conducting pathway is along the bridge backbone. We anticipate this work will help us gain a better understanding of how nanoscale organic molecules work as conducting wires.



Rhodium-catalyzed Asymmetric Synthesis of Chiral, β-branched Esters from Allylic Amines

Summer D. Laffoon, Zhao Wu, and Kami L. Hull

Allylic amines are readily converted to chiral, β-branched esters under rhodium catalysis in the presence of alcohol nucleophiles. 3,3-dialkyl-, 3,3-diaryl-, and 3-alkyl-3-aryl-substituted allylic amines are cleanly converted to product with excellent enantioselectivities in all cases. A Rh-BINAP complex mediates a 1,3-hydride shift to form an optically pure enamine which serves as an excellent intermediate for further functionalization. In the presence of H_2O and alcohol nucleophiles, the enamine is hydrolyzed to form a hemiacetal which is then oxidized to form the final ester product. Several alcohol nucleophiles have been demonstrated including 1° and 2° alcohols. Many catalytic esterification strategies that have been developed thus far rely on solvent quantities of nucleophile. Furthermore, previous methods for setting the β-stereocenter are sensitive to steric perturbations of the substituents at β-position. We disclose a method that does not require solvent quantities of nucleophile thereby enabling fine coupling of chemicals. Additionally, we demonstrate an excellent scope of substitution patterns at the β-position.



21