

Stereoselective construction of functionalized allenes and subsequent diversification

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The use of organocatalysts with substrates containing organometallic auxiliaries is an area virtually unexplored. In this presentation, we report our development of chiral ammonium catalyzed isomerization of manganese-complexed alkyne substrates to afford non-racemic allene products. We have previously demonstrated that methylcyclopentadienyl manganese dicarbonyl (MMD) can be complexed to alkynes followed by isomerization to give uniquely stable η^2 -complexed MMD-allenyl aldehydes. Normally, conjugated alkynyl aldehydes do not isomerize to their thermodynamically less stable allene isomers. However, with the MMD auxiliary in place to promote allene formation, we discovered that asymmetric isomerization is possible with a variety of ammonium phase transfer catalysts (PTCs) in a biphasic reaction system. To highlight the utility of these allenes in complex synthesis, the current method was also used to prepare a nitrile-substituted allenol in a fully stereoselective manner. This allenol was then converted to Hagen's gland lactone in its most succinct total synthesis to date. In addition to this total synthesis, a few useful allene transformations recently developed in our group will also be presented.

