Enantioselective Cycloaddition of Cyclopropylcarboxamides to Alkynes

Selected examples:

\[
\text{Ni}(\text{cod})_2 \quad \text{AlMe}_3 \quad \text{P ligand} \quad \text{mesitylene, 130 °C}
\]

Transformation:

\[
\text{aq HCl} \quad \text{EtOH, reflux} \quad \text{EtOAc} \quad \text{MeCN–H}_2\text{O} \quad \text{r.t.}
\]

Plausible mechanism:

Significance: Transition-metal-catalyzed cycloaddition of cyclopropanes to π-unsaturated compounds is a useful method for the formation of cyclic compounds that has been studied over recent decades. However, the reaction with cyclopropylcarboxamides remains challenging due to their relatively low reactivity. The authors have developed a Ni–Al bimetallic system that facilitates the cycloaddition reaction of cyclopropylcarboxamides to alkynes.

Comment: Whereas a nonenantioselective reaction was achieved by using Ph$_3$P(O)H as a bifunctional ligand, a TADDOL-derived chiral ligand realized highly enantioselective cycloaddition reactions.