Long Helicenes by Alkyne Cycloisomerization

Significance: Helicenes have many possible applications in the areas of materials science, asymmetric catalysis, and molecular recognition; however, long helicenes represent challenging synthetic targets. Reported here is a synthetic route to undecacyclic helicenes utilizing a cobalt-catalyzed intramolecular [2+2+2] alkyne cycloisomerization. This key step forms six new rings of the helicene backbone in a single transformation.

Comment: Cobalt catalysts performed better than nickel catalysts for the cycloisomerization reaction with CpCo(CO)$_2$Ph$_3$P giving higher yields than CpCo(C$_2$H$_4$)$_2$ or Ni(cod)$_2$. A slightly modified version of hexyne 4 underwent diastereoselective cyclization to afford a 10:90 ratio of products similar to 5 in 26% yield. Racemic helicene 7 was purified by chiral HPLC and the racemization barrier at 230 °C was found to be 37.5 kcal/mol.

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