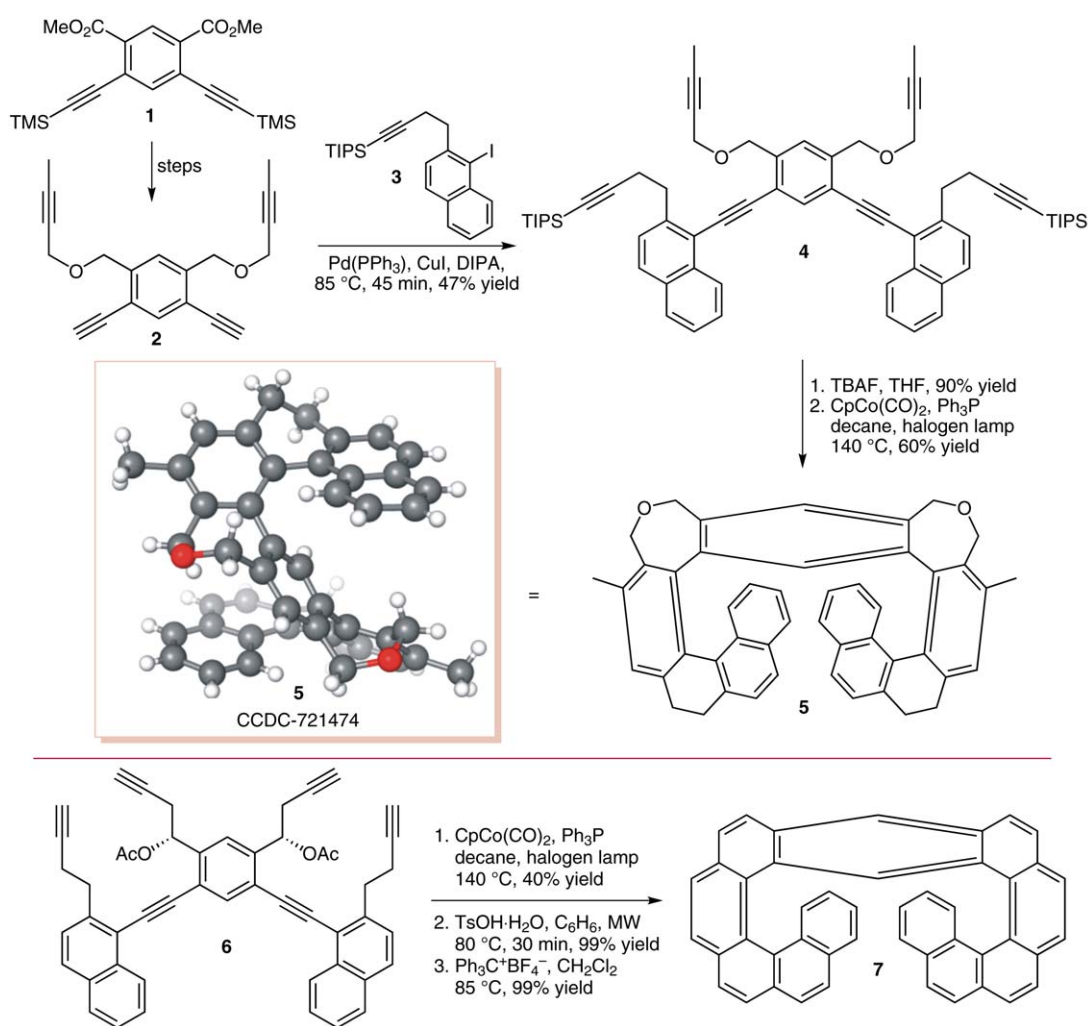


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An Organometallic Route to Long Helicenes

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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.

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Comment: Cobalt catalysts performed better than nickel catalysts for the cycloisomerization reaction with CpCo(CO)₂/Ph₃P giving higher yields than CpCo(C₂H₄)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.

Category

Synthesis of
Materials and
Unnatural Products

Key words

helicenes

alkyne
cycloisomerization

cobalt

SYNFACT
of the month