Category

Synthesis of Materials and Unnatural Products

Key words

helical structures

[2+2+2] cycloaddition

alkynes

enantioselectivity

rhodium

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Enantioselective Synthesis of [9]- and [11]Helicene-Like Molecules: Double Intramolecular [2+2+2] Cycloaddition
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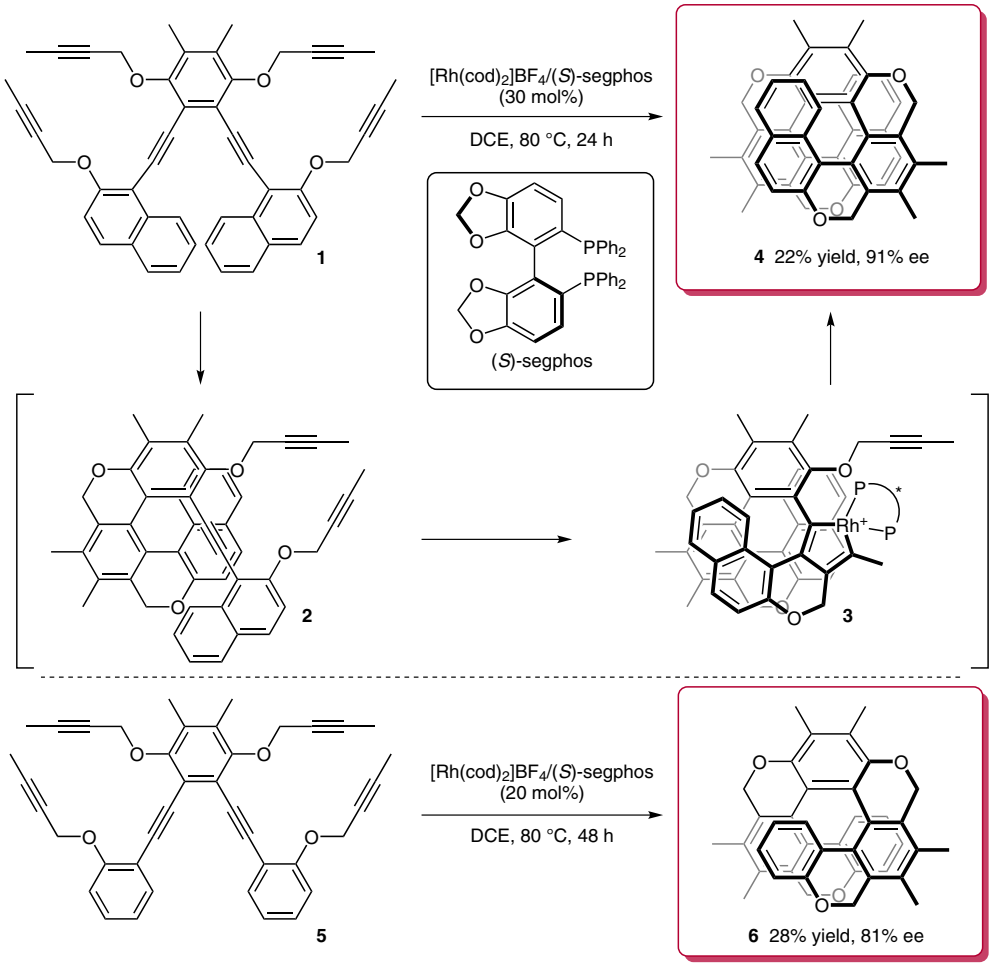
[2+2+2] to Twist: Synthesis of [9]- and [11]Helicene-Like Molecules



Significance: Higher order helicene-like molecules are difficult to synthesize enantioselectively due to steric constraints. The authors report the enantioselective synthesis of [9]- and [11]helicene-like molecules **4** and **6** via double intramolecular [2+2+2] cycloaddition of hexaynes, catalyzed by a cationic rhodium/chiral bis(phosphine) complex. Notably, molecules **4** and **6** both contain completely ortho-fused ring systems.

Comment: The authors report that the second cycloaddition is difficult to achieve because it proceeds through the highly sterically encumbered intermediate **3**. The diastereoselective synthesis of an [11]helicene-like molecule was reported previously (P. Sehnal et al. *Proc. Natl. Acad. Sci.* **2009**, *106*, 13169), but the reported molecule contained three para-fused rings.

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