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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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