

Strategies and Tactics in Organic Synthesis: Chapter 10. Stereoselective Addition of Halogen to Conjugated Enynes and Its Application in the Total Synthesis of (-)-Kumausallene

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Addition of halogen and nucleophiles to conjugated 1,3-enynes in a 1,4-fashion produces a chiral allene and a stereogenic center. The diastereo- and enantioselectivity of this process are discussed in detail. The 1,4bromoetherification of 1,3-enynes can be applied to the synthesis of various bromoallene-containing natural products. Our diastereo- and enantioselective total synthesis of kumausallene is described in this chapter. The synthesis features a cascade reaction involving palladium-catalyzed desymmetrization and a DMFmediated diastereoselective 1,4-bromoetherification reaction.



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