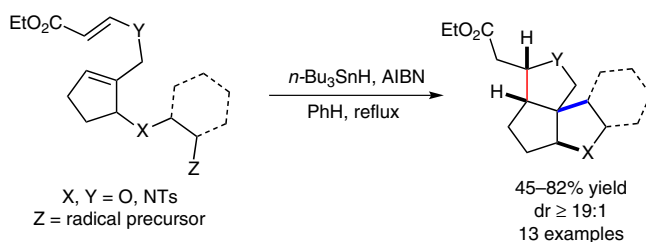
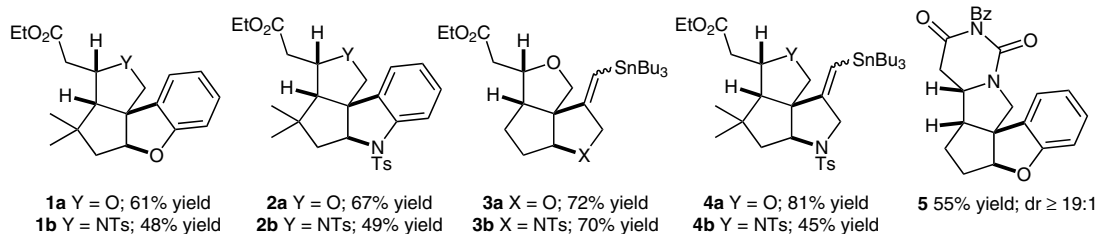


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Stereoselective Synthesis of Oxa- and Aza-Angular Triquinanes Using Tandem Radical Cyclization to Vinyllogous Carbonates and Carbamates  
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## Synthesis of Heterocyclic Triquinanes via Sequential Radical Cyclizations



### Representative examples:



**Significance:** Tandem radical cyclizations are a powerful synthetic strategy to form polycyclic motifs from acyclic precursors (D. P. Curran *Synlett* **1991**, 63). Numerous synthetic strategies have been applied to the synthesis of all-carbon triquinane frameworks as they are related to various terpene natural product skeletons (G. Mehta, A. Srikrishna *Chem. Rev.* **1997**, *3*, 671; V. Singh, B. Thomas *Tetrahedron* **1998**, *54*, 3647). Highlighted in this report is the synthesis of angular O- and N-triquinanes. The proposed mechanism describes radical initiation using standard conditions from either an aryl iodide or terminal alkyne, followed by successive 5-exo-trig cyclizations. The high level of diastereoselectivity observed in the cyclization is attributed to developing steric interactions observed in the transition state of the second cyclization event. The method affords complex products with a predictable outcome and a high level of stereochemical fidelity in an efficient manner.

**Comment:** The cyclization precursors are generated using a three-to-four step sequence using standard synthetic transformations in moderate to high yield. The method described is not limited to aryl substitution (**1**, **2**) as exposure of terminal alkyne precursors to the reaction conditions affords vinyl stannane products (**3**, **4**). Proto-destannylation of the aforementioned intermediates using either SiO<sub>2</sub> or TsOH provides the terminal olefin products. The vinyl stannanes are valuable precursors for further functionalization using transition-metal-mediated processes, which was not described. The major drawback to the methodology, due to inherent toxicity issues, is the use of stoichiometric quantities of tin.

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