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 Radical Alkyne *peri*-Annulation Reactions for the Synthesis of Functionalized Phenalenes, Benzanthenes, and Olympicene
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Category

Synthesis of
Materials and
Unnatural Products

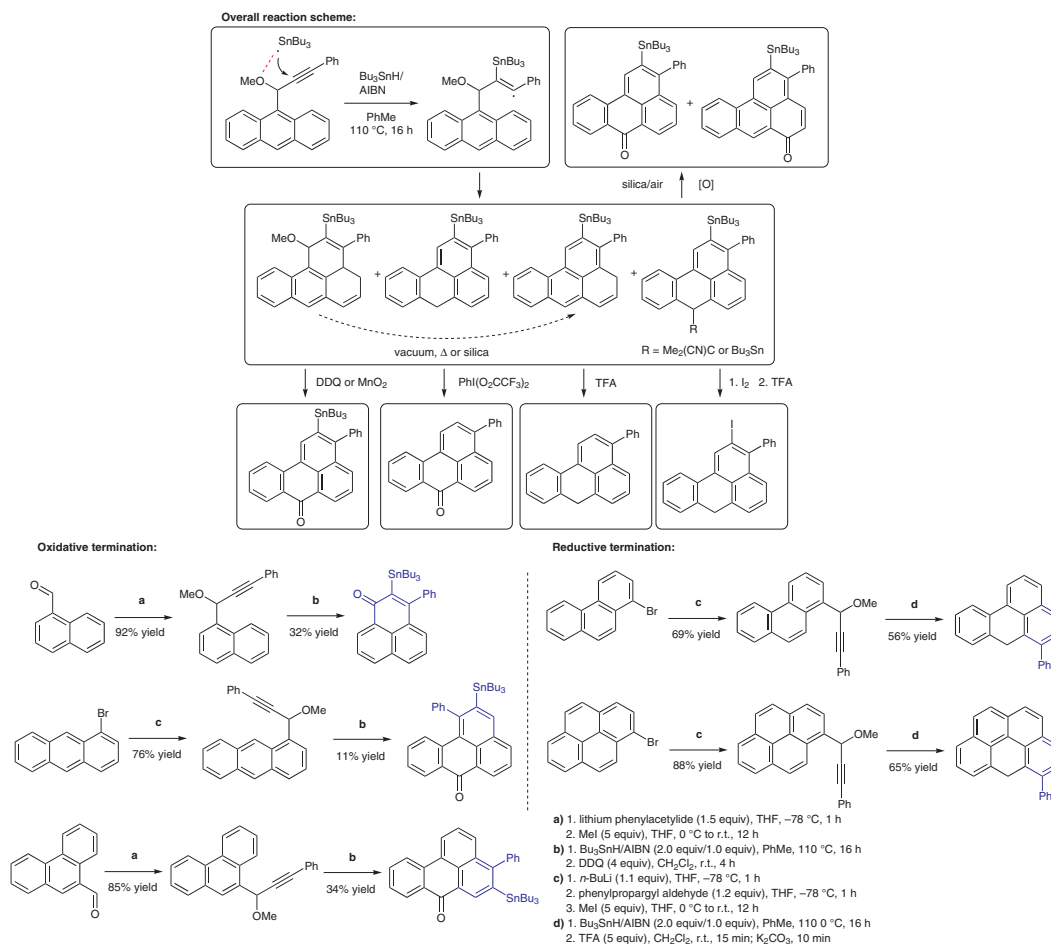
Key words

peri-annulation

L-region
benzoannulation

oxidative/reductive
termination

peri-Annulation for Polyaromatic Hydrocarbons



Significance: Benzoannulation on an aromatic system has mostly been achieved on arm-chair edges, so-called bay and K-regions. L-Region annulation is scarce because of the rigidity of the product, which requires higher activation energy, even though it might look thermodynamically favorable owing to lower loss of aromatic stabilizations. Here, the authors demonstrated L-region *peri*-annulation using radical alkynes. Depending on the workup conditions (either oxidative or reductive), functionalized phenalenes, benzanthenes, and olympicene were obtained.

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Comment: The optimized conditions involve two equivalents Bu_3SnH and one equivalent AIBN under toluene. The annulated product, formed via a radical intermediate, was labile, slowly oxidizing. The oxidation could be accelerated upon treatment with MnO_2 or DDQ. The intermediates also could be reduced with TFA to the benzoanthracene structures. Iodination or destannylation offered diversity of structures for further functionalization through Stille or Suzuki coupling. DFT simulations provided rationales for the most stable structures among many possibilities.