Nickel Catalysed Electrosynthesis of [4]-Dendralenes

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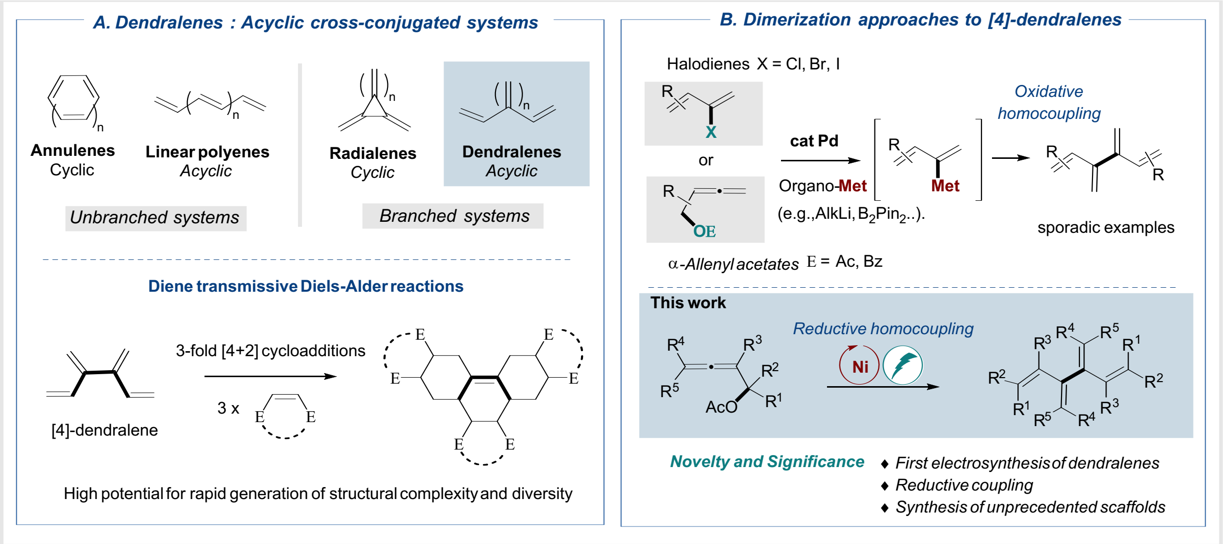
Dendralenes are a family of cross-conjugated polyenic systems with maximal branching that are gathering significant interest due to their potential to undergo sequential, diene-transmissive Diels-Alder reactions for rapid generation of structural complexity and diversity (Figure, part A).[1] They are also found as the core structures of several bioactive natural products. However, their access remains difficult and relies mainly on sequential cross-coupling strategies involving haloalkenes and metalloalkenes. In this area, only few syntheses of [4]-dendralenes have been reported so far, based essentially on palladium catalysis.[2]



Our group's recent interest in nickel catalyzed homocoupling reactions of unsaturated electrophiles,[3] as a means of accessing highly unsaturated sensitive compounds under mild conditions, led us to wonder whether a similar approach could be applied to the synthesis of [4]-dendralenes from α-allenyl electrophiles. Notably, only sporadic examples of these dendralenes have been produced so far through oxidative homocoupling of halodienes or α-allenyl acetates, and they were typically obtained as poorly functionalized unexpected products.[4] In this communication, we present a new access to highly substituted [4]-dendralenes based on a nickel catalyzed electrochemical reductive homocoupling process, in which electricity is used as a green reductive agent (Figure, part B).

References

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[4] Sherburn, M. S. et Al. *J. Am. Chem. Soc.* **2005**, 127, 35, *12188–12189 ; Tetrahedron* **2007**, 26, *10939-10948.*