Development of New Higher-Order Carbocyclization Reactions: Emulating Terpene Biosynthesis

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Transition metal-catalyzed higher-order carbocyclization reactions provide powerful methods for the stereoselective construction of complex polycyclic systems that are generally not accessible via classical pericyclic reactions.[1] We have demonstrated the merit of the rhodium-catalyzed \([m+n+n]\) carbocyclization reactions of carbon and heteroatom tethered 1,6-enynes with carbon monoxide, alkynes and dienes. More recently we have explored the development of a stereoselective rhodium-catalyzed \([3+2+2]\) carbocyclization of 1,6-alkenyldienecyclopropanes with activated alkynes for the construction of \(\text{cis}\)-fused bicycloheptadienes,\[2\] which prompted the isolation of the key metallacycle intermediate\[3\] and the expansion of the scope of \(\pi\)-fragments to carbon monoxide and allenes.\[4,5\] The seminar will outline some of these developments and their application to challenging bioactive natural products.

References