

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-alkenyldenecyclopropanes with activated alkynes for the construction of *cis*-fused bicycloheptadienes,^[2] which prompted the isolation of the key metallacycle intermediate^[3] and the expansion of the scope of \square -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

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