

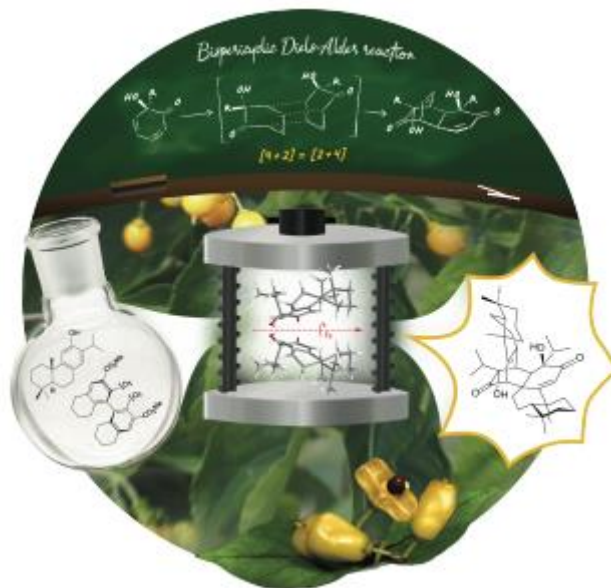
FROM FUNDAMENTAL BISPERICYCLISM TO PRACTICAL SYNTHESIS OF THE BISDITERPENOID (+)-MAYTENONE AND MORE...



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Many natural products of plant or microbial origins are derived from enzymatic dearomative oxygenation of 2-alkylphenolic precursors into 6-alkyl-6-hydroxycyclohexa-2,4-dienones.¹ These so-called *ortho*-quinols can cyclodimerize via a remarkably selective bispericyclic Diels–Alder reaction. Whether or not the intervention of catalytic or dirigent proteins is involved during this final step of the biosynthesis of these natural products, this cyclodimerization of *ortho*-quinols can be chemically reproduced in the laboratory with the same strict level of site-specific regioselectivity and stereoselectivity. This unique yet unified process, which finds its rationale in the inherent chemical reactivity of those *ortho*-quinols, will be illustrated by an efficient and bioinspired first chemical preparation of one of the most synthetically challenging examples of such natural cyclodimers, the bisditerpenoid (+)-maytenone. This synthesis was achieved *via* a chiral iodane-mediated dearomative hydroxylation of (+)-ferruginol and a high pressure-promoted Diels–Alder reaction.²



References

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- ² Peixoto, P. A.; El Assal, M.; Chataigner, I.; Castet, F.; Cornu, A.; Coffinier, R.; Bosset, C.; Deffieux, D.; Pouységu, L.; Quideau, S. Bispericyclic Diels–Alder Dimerization of *ortho*-Quinols in Natural Product (Bio)Synthesis – Bioinspired Chemical 6-Step Synthesis of (+)-Maytenone. *Angew. Chem. Int. Ed.* **2021**, 60, 14967-14974 (**Very Important Paper**) – DOI: <https://doi.org/10.1002/anie.202103410>.