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Total Synthesis of (±)-Stemodinone via an Efficient Ring-Exchange Strategy

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A total synthesis of (±)-Stemodinone, a tetracyclic stemodane diterpene, from the known tricyclic methyl olefin 11 is described. The key steps involve an efficient ring-exchange reaction and palladium(0)-catalyzed lactone migration. The ring-exchange strategy for controlling the stereochemistry was based on an initial Diels-Alder reaction to form a new ring followed by cleavage of the original ring. Cleavage of the original ring of the Diels-Alder adduct 9 was achieved by an initial regio- and chemoselective Baeyer-Villiger oxidation followed by the Pd(0)-catalyzed lactone_migration reaction reported by us.