

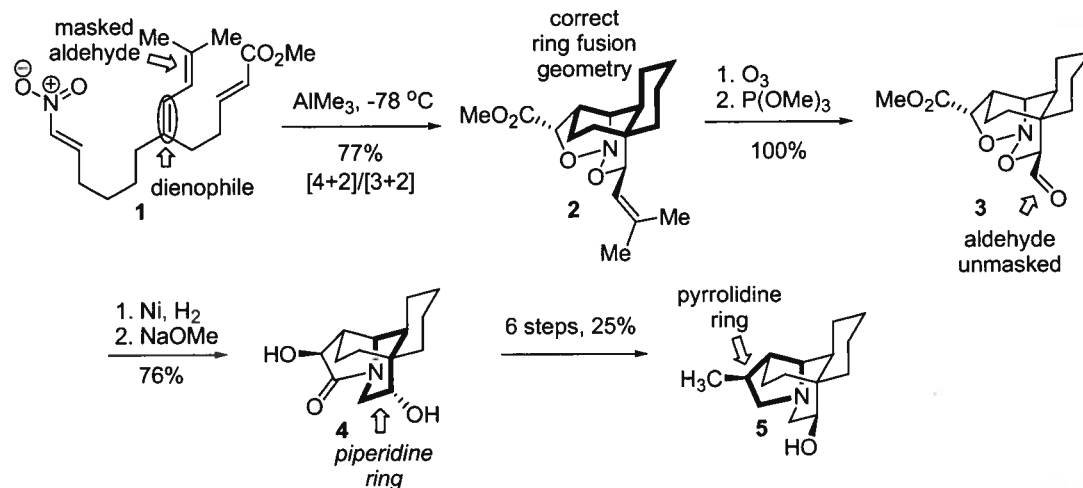
## Studies Toward the Total Synthesis of Daphnilactone B Using a Tandem Double Intramolecular [4+2]/[3+2] Cycloaddition of Nitroalkenes

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The core of daphnilactone B (8) can be constructed using a tandem double intramolecular [4+2]/[3+2] cycloaddition of nitroalkenes. In a model study, a 1,3-diene in 1 served as an electron-rich  $2\pi$ -component in the [4+2] cycloaddition with the nitroalkene to provide nitroso acetal 2 stereoselectively, after the spontaneous [3+2] step. Unmasking of the aldehyde in 3 through ozonolysis, followed by hydrogenolysis, allowed the construction of piperidine 4 via intramolecular reductive alkylation. Functional group manipulations provided 5 and completed the stereocontrolled construction of four of the rings in the core of the natural product.

A more functionalized nitroalkene 6 provided nitroso acetal 7 selectively and in high yield. This cycloadduct contains the vicinal quaternary stereogenic centers needed for the total synthesis of daphnilactone B.

### The model study:



### The total synthesis:

