

A Divergent Stereocontrolled Synthesis of the Enantiopure Tetracyclic Cores of Asparagamine A and Stemofoline via an Intramolecular 2-Propylidene-1,3-(bis)silane Bicyclization

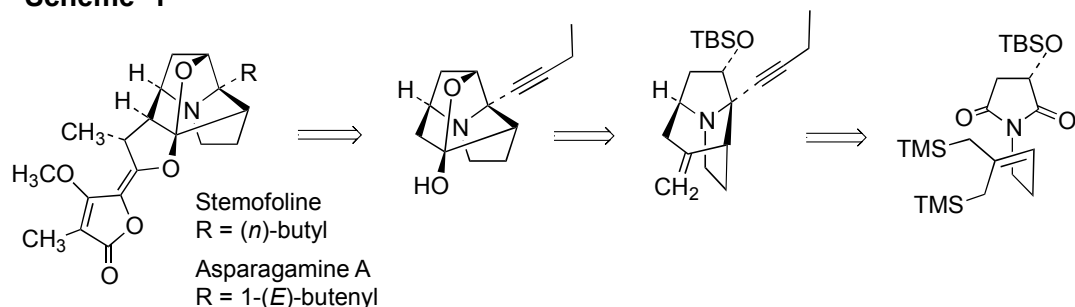
Thomas Livinghouse, Bryon Anderson, Bryce Sundahl

Montana State University, Bozeman, MT, USA

A concise and highly diastereoselective synthesis of the polyfused tetracyclic cores of the *Stemoa* alkaloids asparagamine A and stemofoline that relies on a 2-propylidene-1,3-(bis)silane bicyclization onto an enantiodefined pyrrolidine 2,5-di(cation) equivalent derived from L-malic acid will be described. A crucial feature of this divergent synthetic approach involves the solvolysis of a transient and highly labile tertiary-propargylic lactamol trifluoroacetate in the strongly ionizing medium 5M LiClO₄/Et₂O. The acyliminium ion generated in this manner undergoes stereospecific interception by the aforementioned (bis)silane nucleophile (Scheme 1).

The second topic of this discussion will be concerned with highly diastereoselective metalloamination/cyclizations of zinc(II) hydrazides derived from the reaction of diethylzinc and N,N-dimethylhydrazinoalkenes. The resulting organozinc intermediates have been found to undergo facile allylation and acylation, in-situ, to provide the corresponding functionalized piperidines and pyrrolidines respectively (Scheme 2).

Scheme 1



Scheme 2

