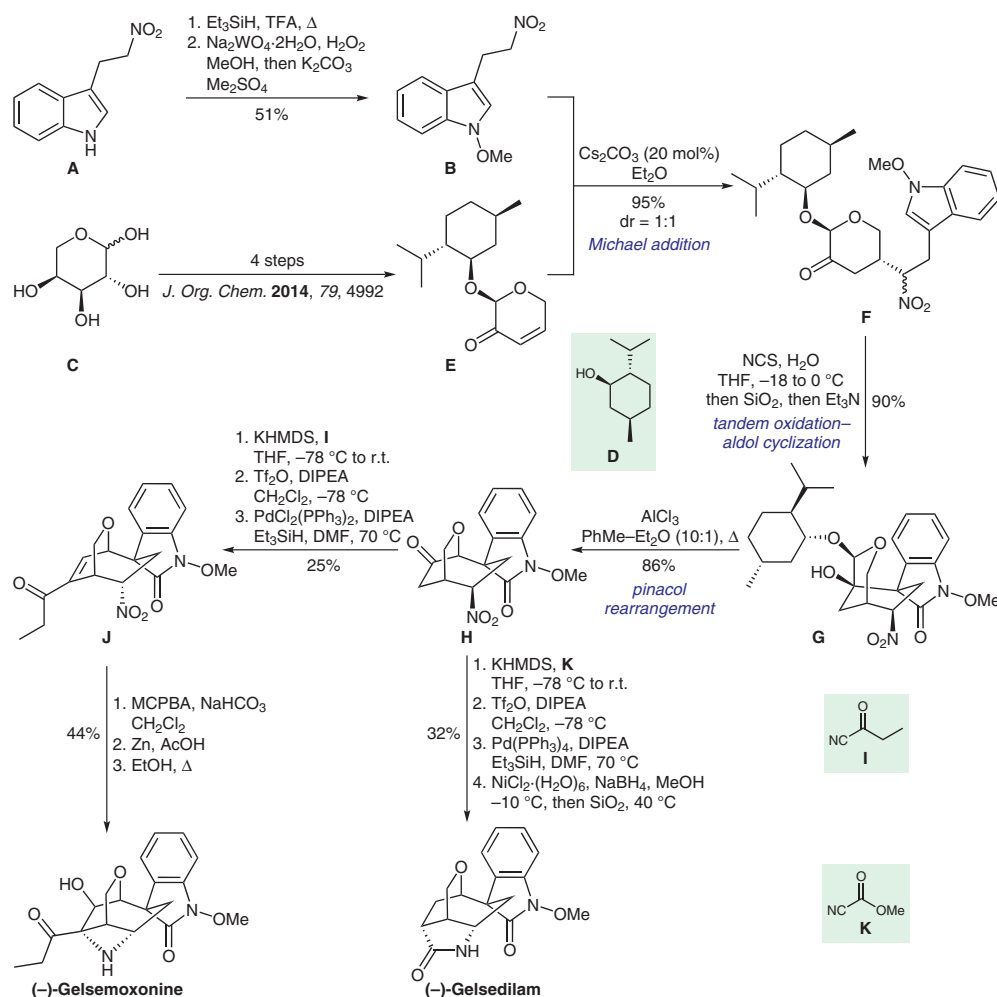


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Divergent Entry to Gelsedine-Type Alkaloids: Total Syntheses of (–)-Gelsedilam, (–)-Gelsenicine, (–)-Gelsedine, and (–)-Gelsemoxonine

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Divergent Route to Gelsedine-Type Alkaloids



Significance: Gelsedine-type natural products have attracted considerable interest from the synthetic community owing to their interesting biological properties and complex architectures. Ma and co-workers have developed and executed an elegant synthetic route culminating in the preparation of four such alkaloids relying on an asymmetric Michael addition, tandem oxidation-aldol cyclization, and a pinacol rearrangement.

Comment: Indole derivative **B** and enone **E** underwent conjugate addition to furnish **F**. Oxidation and aldol cyclization resulted in the formation of key structure **G** in a single pot. Cationic rearrangement of **G** provided the oxabicyclo[3.2.2]nonane skeleton present in all targets. (–)-Gelsedilam was synthesized from **H** in four steps. (–)-Gelsemoxonine, (–)-gelsenicine, and (–)-gelsedine were accessed via ethyl ketone **J**.

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