Significance: Gelsemine-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. (−)-Gelsemoxonine was synthesized from H in four steps. (−)-Gelsemoxonine, (−)-gelsenicine, and (−)-gelsedine were accessed via ethyl ketone J.