Significance: The communesin alkaloids feature a fused heptacyclic ring system containing two adjacent quaternary carbons. Movassaghi and co-workers describe an enantioselective synthesis of (-)-communesin F, a member of this intriguingly complex natural product family. Highlights include the biomimetic heterodimerization of A and B, and aminal exchange from H to J.

Comment: Building blocks A and B were unified through displacement at the sulfamate, followed by oxidation to diazene F. The diazene was irradiated to give G as a single diastereomer under extrusion of nitrogen. After deprotection of the Boc groups, the aminal exchange was induced by t-BuOLi. The natural product was then obtained after deprotection.