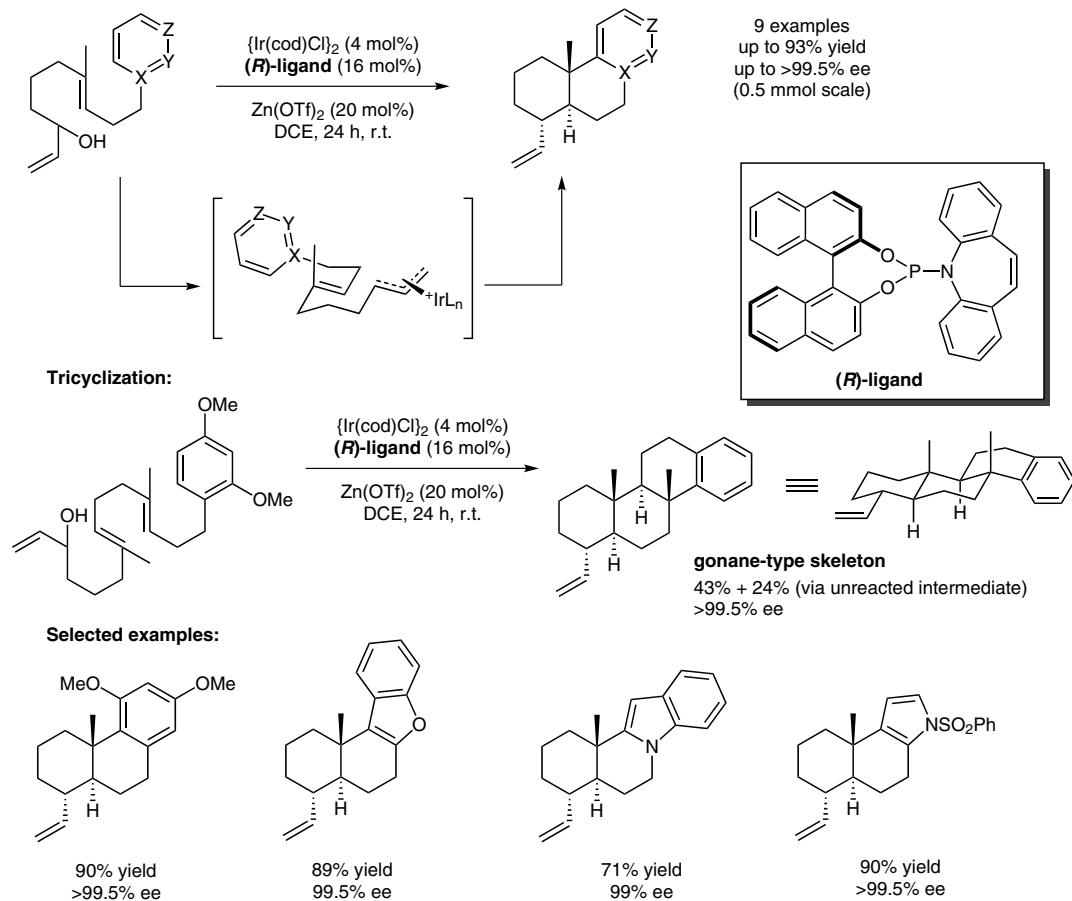


## Mimicking Nature: Enantioselective Cationic Polyene Cyclization



**Significance:** The biogenic isoprene rule, established in 1955 by Ruzicka, Eschenmoser, and Stork (*Helv. Chim. Acta* 1955, 38, 1890; *J. Am. Chem. Soc.* 1955, 77, 5068), stimulated biomimetic studies for the construction of polycyclic frameworks, like the steroid skeleton. Approaches based on Brønsted/Lewis acid catalysis (Yamamoto, Loh, Corey), organocatalysis (Ishihara, MacMillan, Jacobsen), and transition-metal catalysis (Takeuchi, Helmchen, Hartwig) are reported.

**Comment:** The authors report the development of a highly enantioselective polycyclization method using the combination of Lewis acid activation with iridium-catalyzed allylic substitution. This strategy relies on direct use of branched, racemic allylic alcohols and furnishes a diverse and unique set of carbo- and heteropolycyclic ring systems in good yield and  $\geq 99\%$  ee.