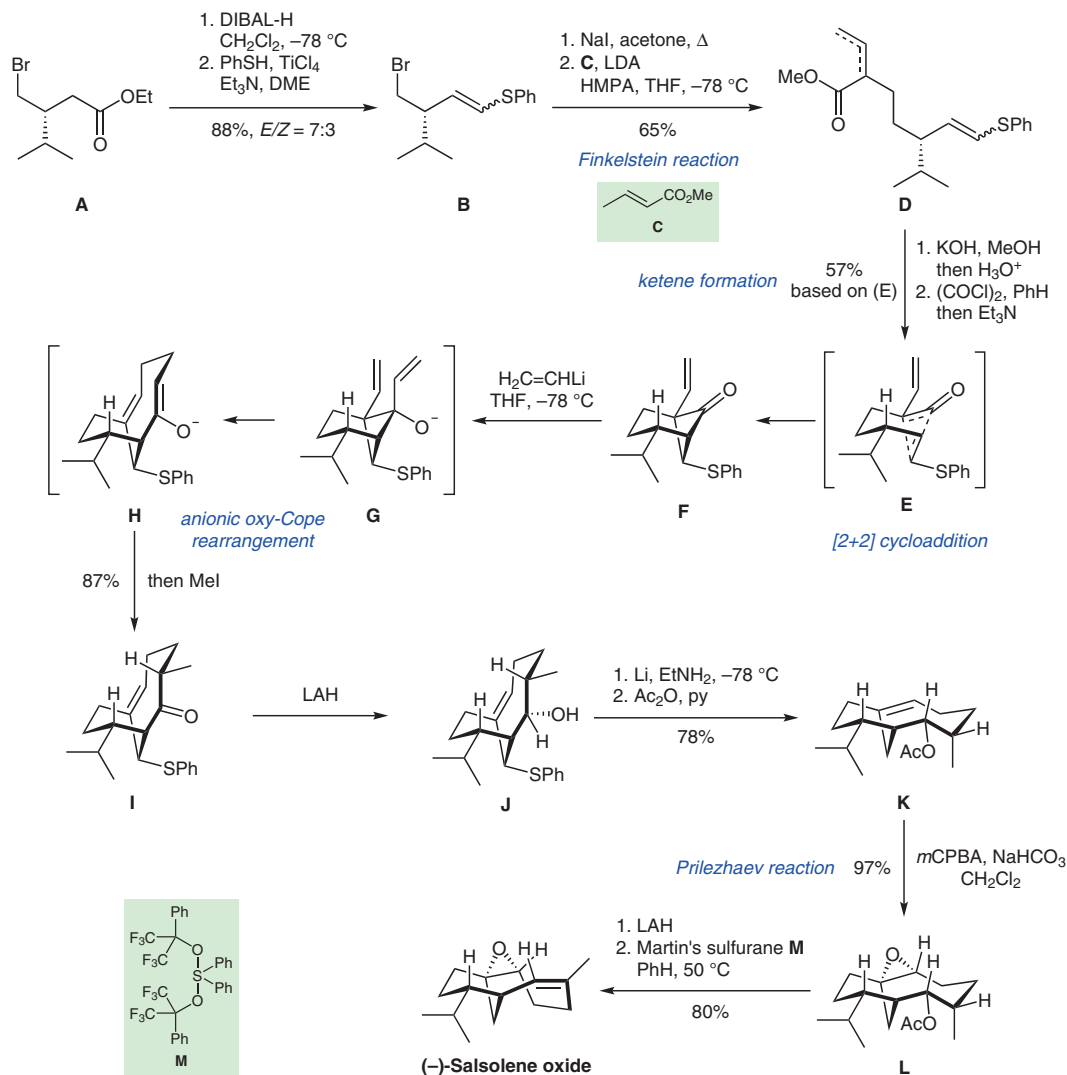


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Bridgehead Oxiranyl Sesquiterpenoids. Asymmetric Total Synthesis of (-)-Salsolene Oxide
J. Am. Chem. Soc. **1997**, *119*, 2767–2768, DOI: 10.1021/ja964221.

Total Synthesis of (-)-Salsolene Oxide



Significance: In 1997, Paquette and co-workers demonstrated a [2+2] cycloaddition in a complex setting. The phenyl thioether plays a crucial role in controlling reactivity and stereoselectivity of the [2+2] cycloaddition. Blocking of the *endo* face during vinyl lithium addition enables an anionic oxy-Cope rearrangement. Moreover, the bridge-head olefin is isomerized to the desired geometry during reductive cleavage.

Comment: The synthesis exploits a ketene–olefin [2+2] cycloaddition to yield a bicyclo[3.1.1]heptane skeleton. A stereoselective addition of vinyl lithium to ketone F triggers an anionic oxy-Cope rearrangement furnishing eight-membered ring enolate H which was smoothly trapped with methyl iodide. Late-stage Prilezhaev reaction installs the bridge head epoxide. Final deprotection and elimination yields (-)-salsolene oxide in a total of 13 steps.

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