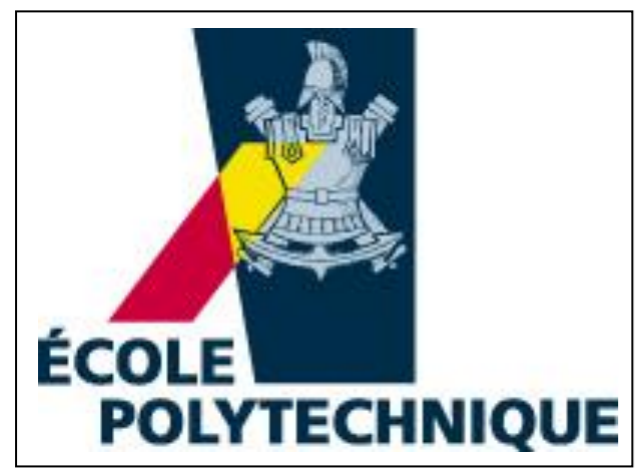


FROM A REMARKABLE MANIFESTATION OF POLAR EFFECTS IN A RADICAL FRAGMENTATION TO THE SYNTHESIS OF HIGHLY FUNCTIONALIZED KETONES



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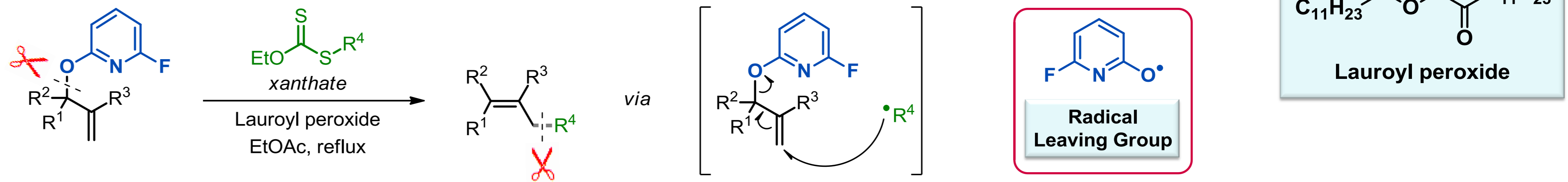
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Precedent Work: Radical Allylation of Simple Allylic Alcohols

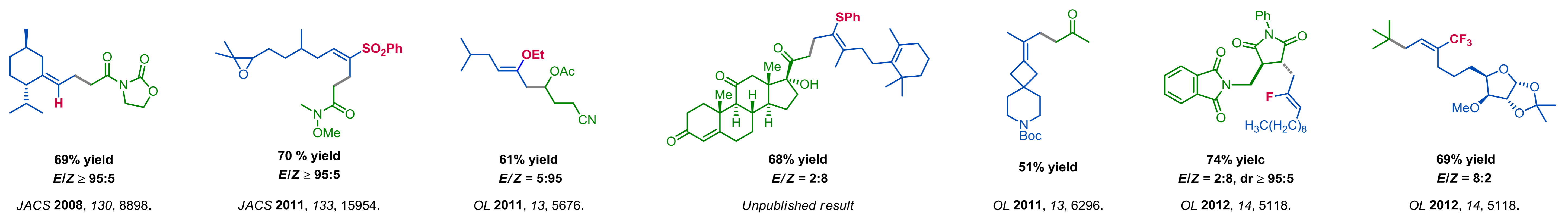
□ Process featuring:

- The **formation** of a C–C σ -bond and a C=C π -bond
- The **homolytic cleavage** of the usually strong C–O bond

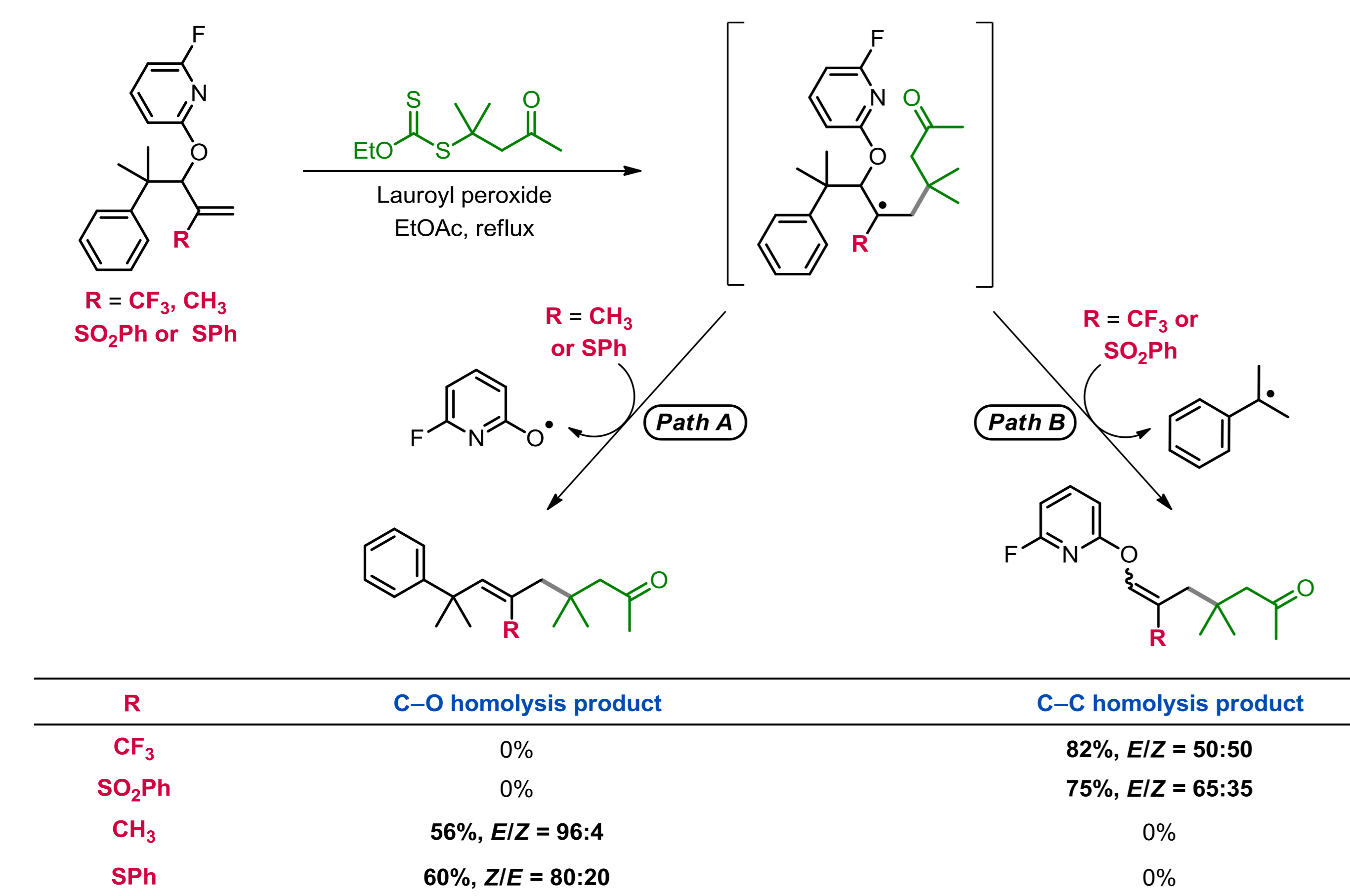


Scope of the Radical Allylation of Xanthates: Selected Examples

- Method applied to the synthesis of (*E*)-vinylsulfones, stereodefined alkenes, enol ethers and thioethers, alkylidene cyclubutanes, fluoro- and trifluoromethyl-olefins
- **Exceptional functional group tolerance** and **operational simplicity**
- **Over 100 functionalized olefins** prepared using this method to date!

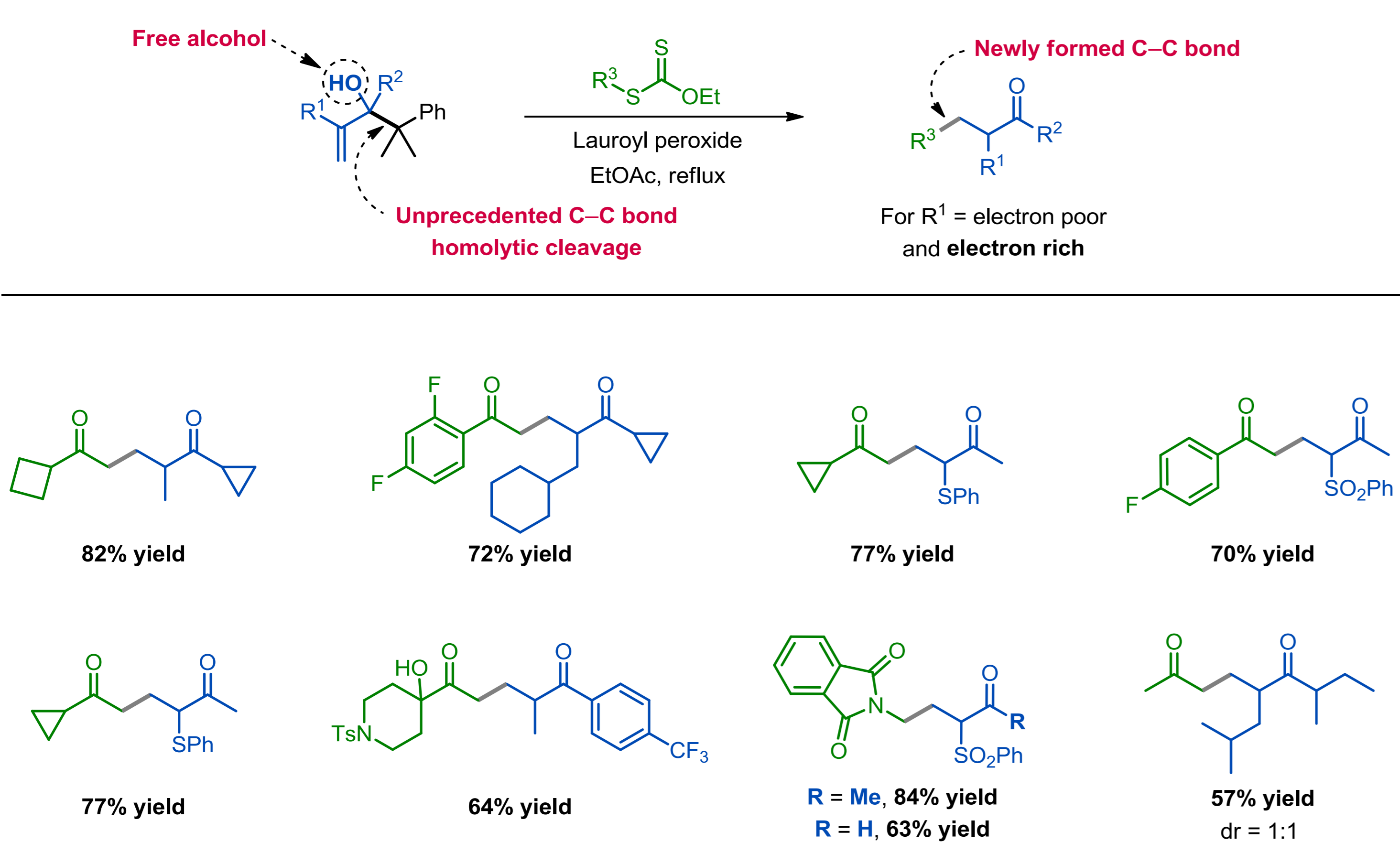


Discovery of a New Mode of Fragmentation: C–O versus C–C Cleavage



- Polar R groups trigger a rare C–C bond fragmentation
- Identification of the cumyl radical as a **new radical leaving group**

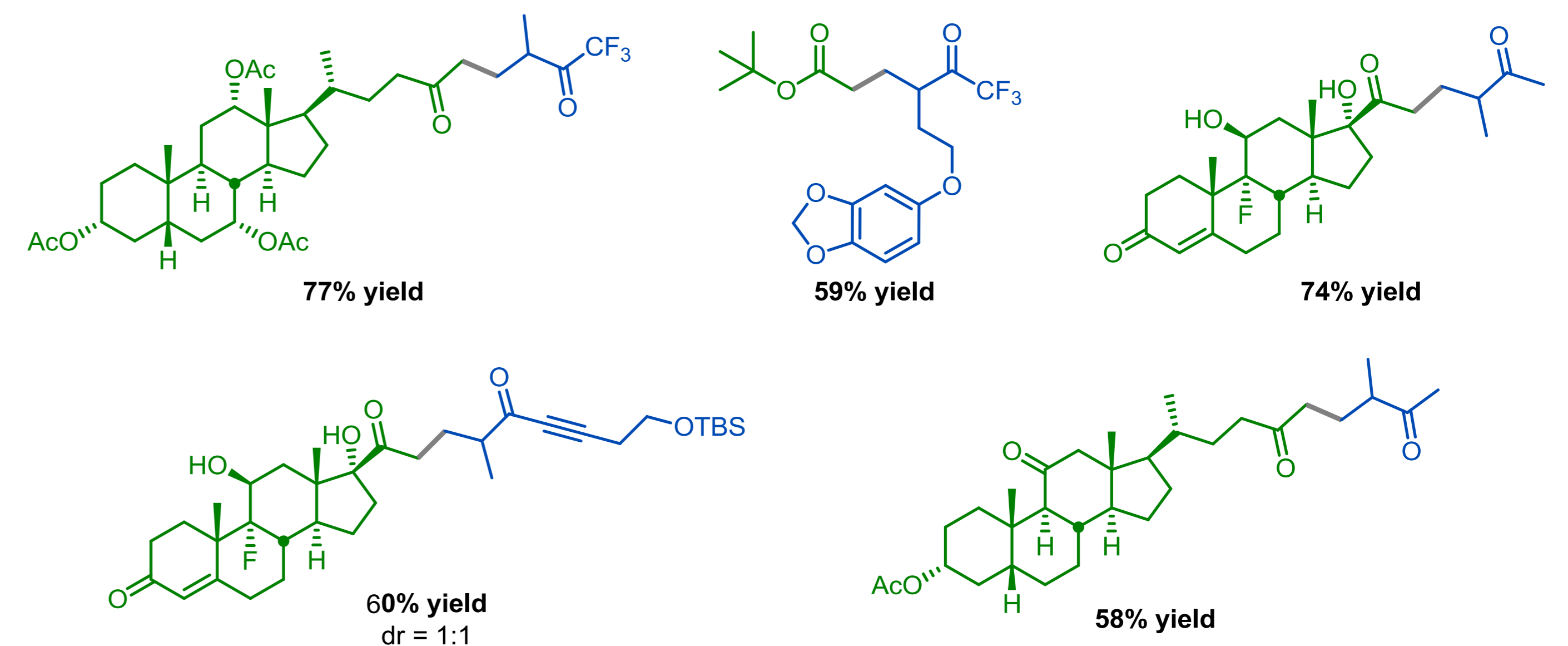
New Radical Allylation for the Synthesis of 1,5-Diketones



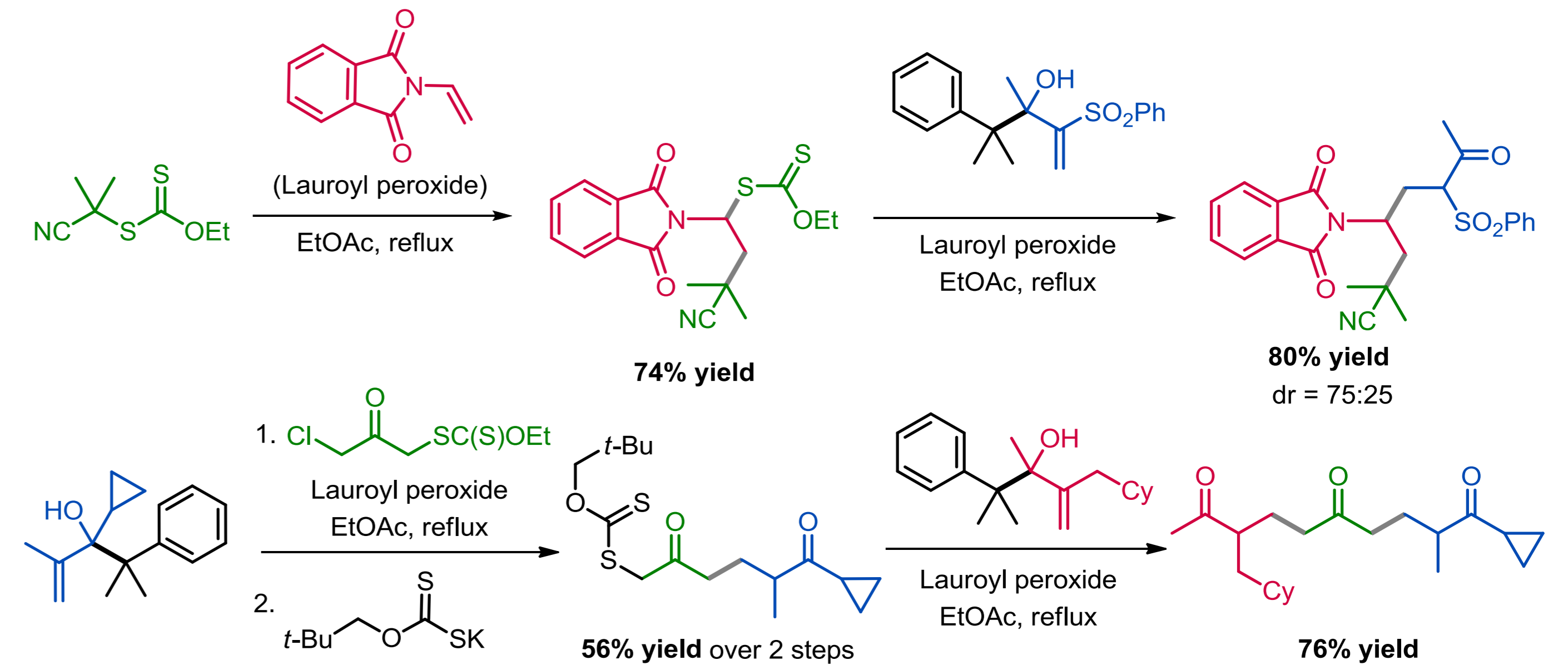
Debien, L.; Zard, S. Z. *J. Am. Chem. Soc.* **2013**, *135*, 3808.

Preparation of Complex Structures

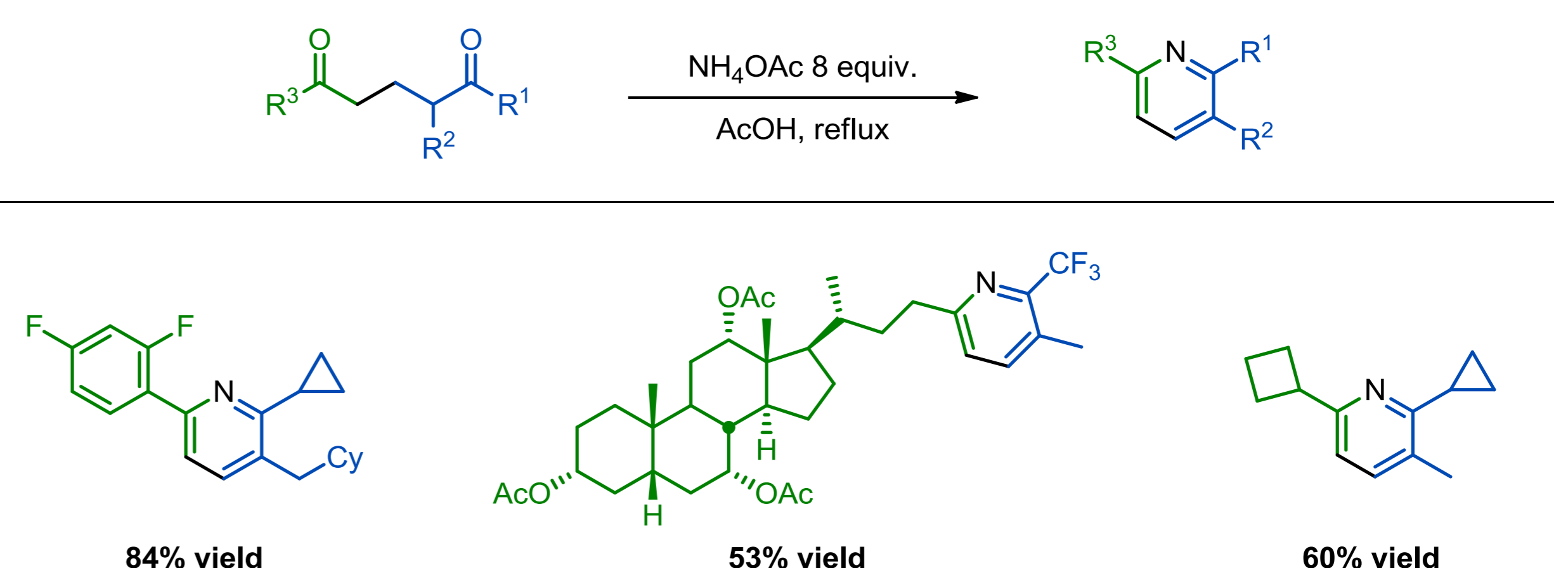
- Further demonstration of the process tolerance



- Sequential radical reactions: assembly of a polysubstituted ketones



Application to the Synthesis of Pyridines



Acknowledgements

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- Zard group
- Funding and organizing agencies

