

**M.Sc. Semester-IV**  
**Core Course-9 (CC-9)**  
**Synthetic Organic Chemistry**



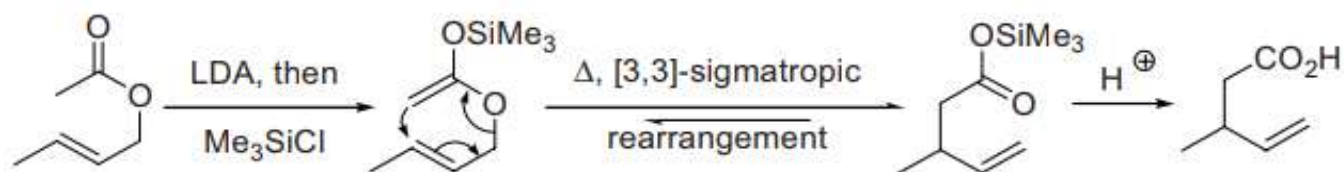
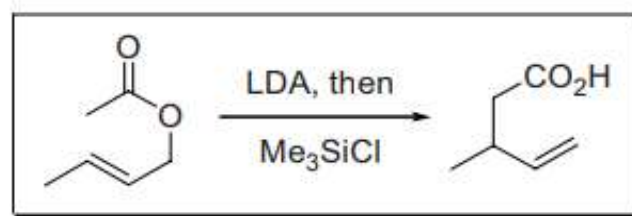
**II. Pericyclic Reactions**  
**6. Ireland-Claisen Rearrangement**



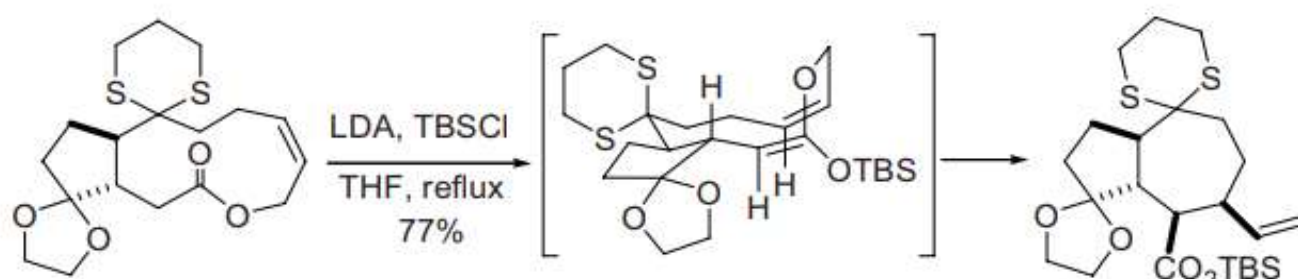
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## Ireland–Claisen (silyl ketene acetal) rearrangement

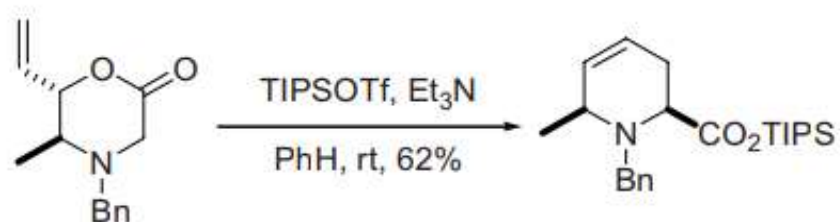
Rearrangement of allyl trimethylsilyl ketene acetal, prepared by reaction of allylic ester enolates with trimethylsilyl chloride, to yield  $\gamma,\delta$ -unsaturated carboxylic acids. The Ireland–Claisen rearrangement seems to be advantageous to the other variants of the Claisen rearrangement in terms of *E/Z* geometry control and mild conditions.

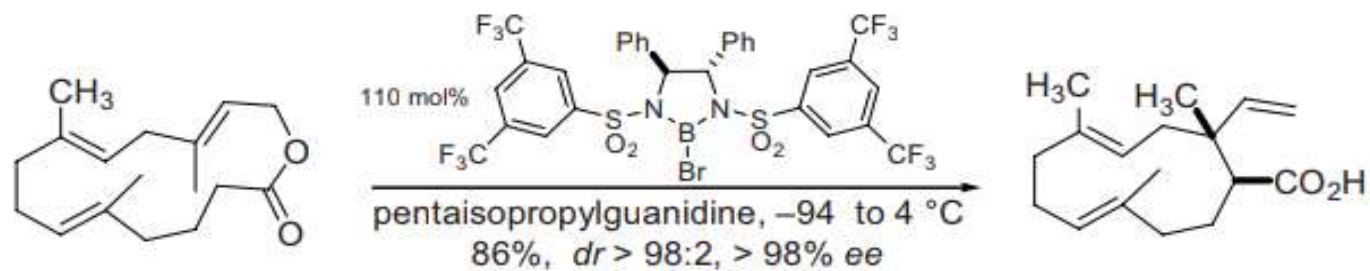
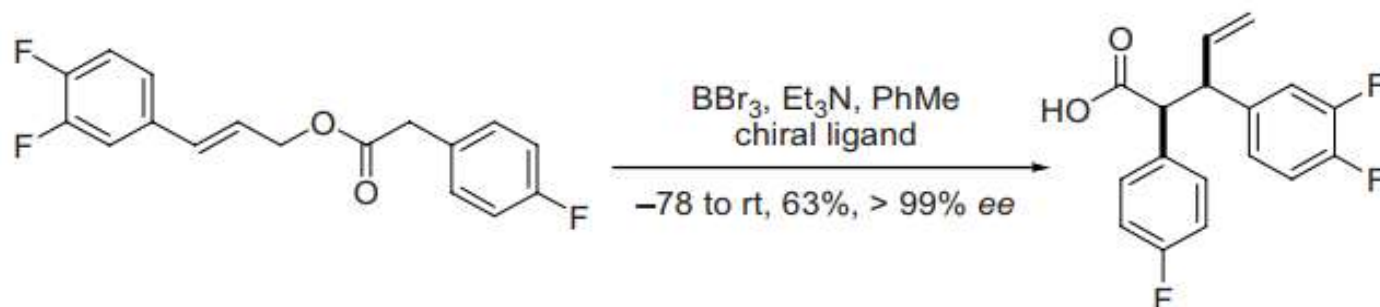
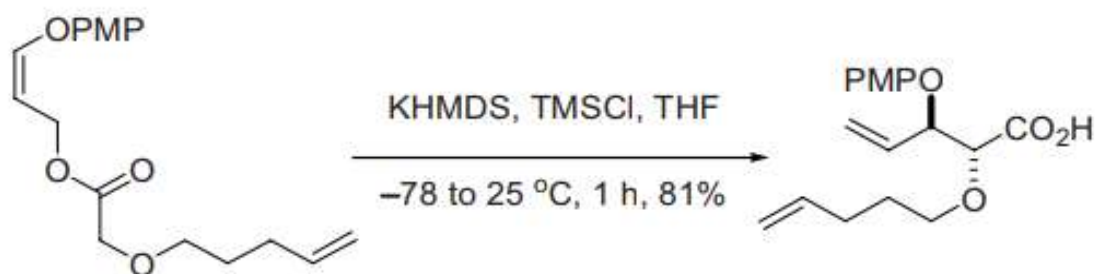


### Example 1<sup>2</sup>



### Example 2<sup>3</sup>



Example 3, Enantioselective ester enolate-Claisen Rearrangement<sup>6</sup>Example 4, A modified Ireland–Claisen rearrangement<sup>8</sup>Example 5<sup>9</sup>

## References

1. Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897–5898. Also *J. Am. Chem. Soc.* **1976**, *98*, 2868–2877. Robert E. Ireland obtained his Ph.D. from William S. Johnson before becoming a professor at the University of Virginia and later at the California Institute of Technology. He is now retired.
2. Begley, M. J.; Cameron, A. G.; Knight, D. W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1933–1938.
3. Angle, S. R.; Breitenbucher, J. G. *Tetrahedron Lett.* **1993**, *34*, 3985–3988.
4. Pereira, S.; Srebnik, M. *Aldrichimica Acta* **1993**, *26*, 17–29. (Review).
5. Ganem, B. *Angew. Chem., Int. Ed.* **1996**, *35*, 936–945. (Review).
6. Corey, E.; Kania, R. S. *J. Am. Chem. Soc.* **1996**, *118*, 1229–1230.
7. Chai, Y.; Hong, S.-p.; Lindsay, H. A.; McFarland, C.; McIntosh, M. C. *Tetrahedron* **2002**, *58*, 2905–2928. (Review).
8. Churcher, I.; Williams, S.; Kerrad, S.; Harrison, T.; Castro, J. L.; Shearman, M. S.; Lewis, H. D.; Clarke, E. E.; Wrigley, J. D. J.; Beher, D.; Tang, Y. S.; Liu, W. *J. Med. Chem.* **2003**, *46*, 2275–2278.
9. Fujiwara, K.; Goto, A.; Sato, D.; Kawai, H.; Suzuki, T. *Tetrahedron Lett.* **2005**, *46*, 3465–3468.
10. Williams, D. R.; Nag, P. P. *Claisen and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Corey, E. J., Eds.; Wiley & Sons: Hoboken, NJ, **2009**, pp 45–51. (Review).

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