

What is going on in 1975

- Bill Gates and Paul Allen founded Microsoft (April 4th).
- Highest-grossing film was Jaws.
- Minimum Wage was 2.10 dollars per hour.
- Price of a gallon of gas was 57 cents.
- Price of a movie ticket was 2 dollars.



Vladimir Prelog

Nobel Prizes in 1975

Chemistry – Vladimir Prelog (for work on the stereochemistry of organic molecules and reactions); John Cornforth (for research into stereochemistry of enzyme-catalyzed reactions)

Physics – Aage Bohr; Ben Mottelson; James Rainwater (for the discovery of the connection between collective motion and particle motion in atomic nuclei and the development of the theory of the structure of the atomic nucleus based on this connection)

Physiology or Medicine – David Baltimore; Renato Dulbecco; Howard Martin Temin (for their discoveries concerning the interaction between tumour viruses and the genetic material of the cell)

JACS Statistics 1975

Total papers: 1498

Top publishing authors:

1. George A. Olah (17)
2. Leo A. Paquette (16)
3. Michael J. S. Dewar (15)
4. Herbert C. Brown (14)

Top cited papers:

1. **General Definition of Ring Puckering Coordinates**
Pople, J. A. *et. al.*, 6, 1354. (5200 citations)
2. **Characterization of Molecular Branching**
Radic, M. 23, 6609. (2395 citations)
3. **Ground-states of Molecules. MINDO/3 An Improved Version of the MINDO Semiempirical SCF-MO Method**
Dewar, M. J. S. *et. al.*, 6, 1285. (1561 citations)

What is going to be covered?

1. Pericyclic Chemistry
2. Heterocyclic Chemistry
3. 1,4-diketone Synthesis
4. Selected Total Synthesis (Prostaglandin)
5. Selected Total Synthesis (Methymycin)
6. Selected Total Synthesis (Longifolene)
7. Selected Total Synthesis (Spirovetivane)
8. Alkyne-Related Synthesis
9. Organometallic Chemistry

What is more? (won't be covered)**1. Porphyrins**

Picket fence porphyrins. Synthetic models for oxygen binding hemoproteins

Collman, J. P. *et. al.*, 6, 1427

Luminescence Studies on Several Tetraarylporphyrins and Their Zinc Derivatives

Longo, F. R. *et. al.*, 18, 5111

2. Hydroboration

Catecholborane as a new hydroboration reagent for alkenes and alkynes

Brown, H. C. *et. al.*, 18, 5249

3. Organometallic

Novel $[\sigma+\pi]$ Reactions of Hexaorganodisilanes with Acetylenes Catalyzed by Palladium Complexes

Sakurai, H. *et. al.*, 4, 931

Conversion of Ketones to Enones by Selenoxide Syn Elimination

Reich, I. L. *et. al.*, 19, 5434

4. Sugar Chemistry

Halide Ion Catalyzed Glycosidation Reactions. Syntheses of alpha-Linked Disaccharides

Lemieux, R. U. *et. al.*, 14, 4056

5. Pericyclic Chemistry

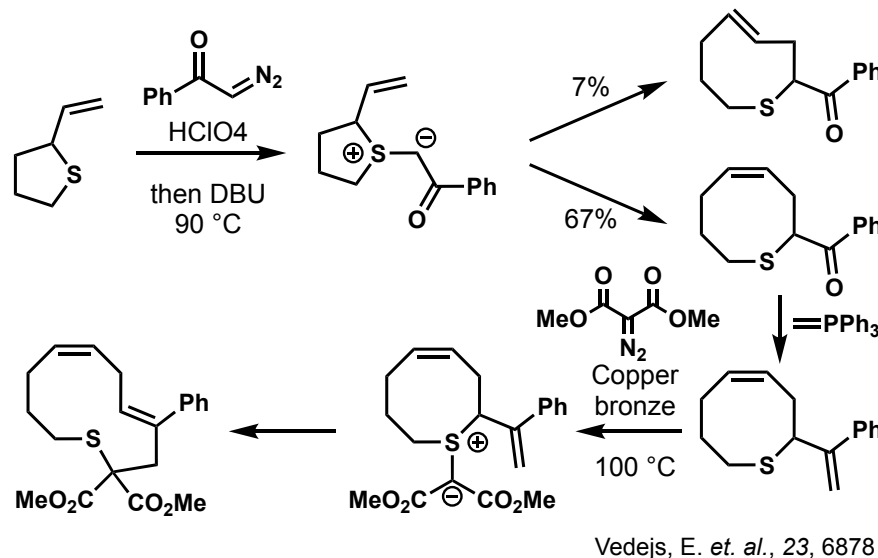
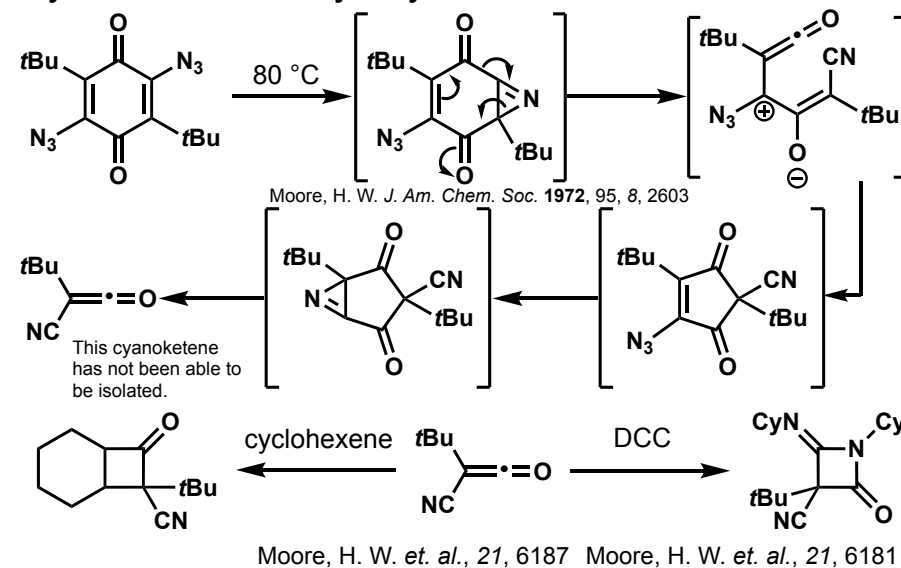
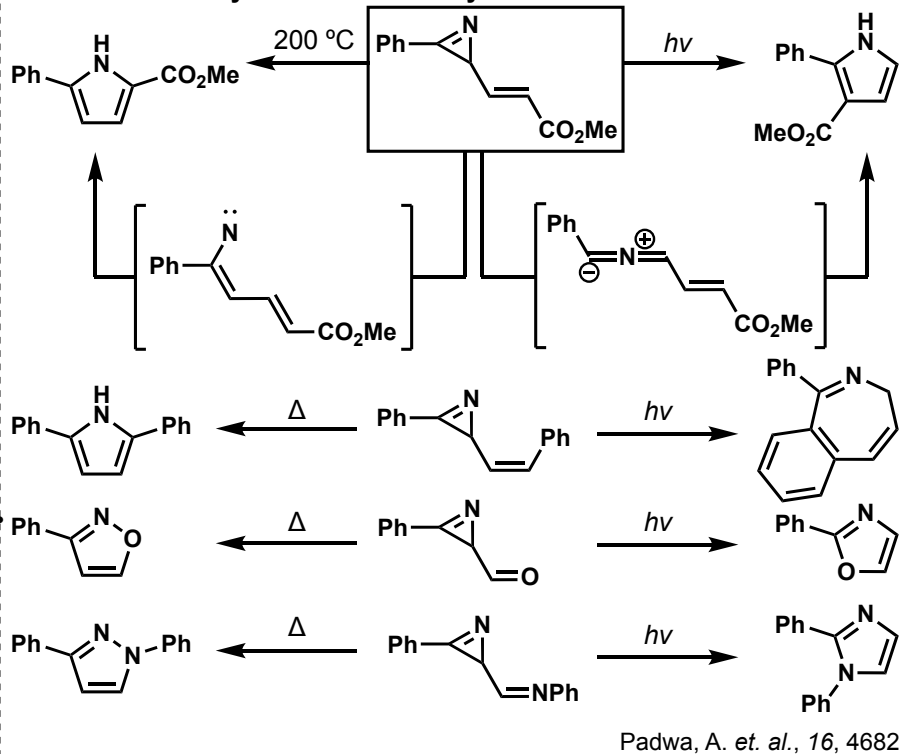
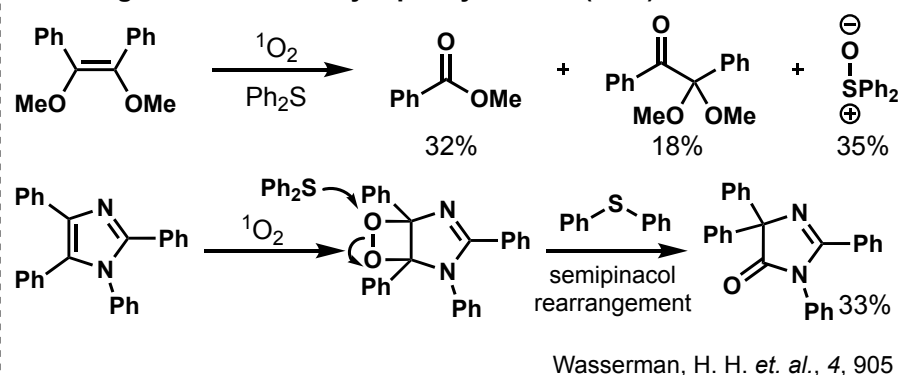
[3,3]Sigmatropic Rearrangements of 1,5-diene alkoxides. Powerful accelerating effects of the alkoxide substituent

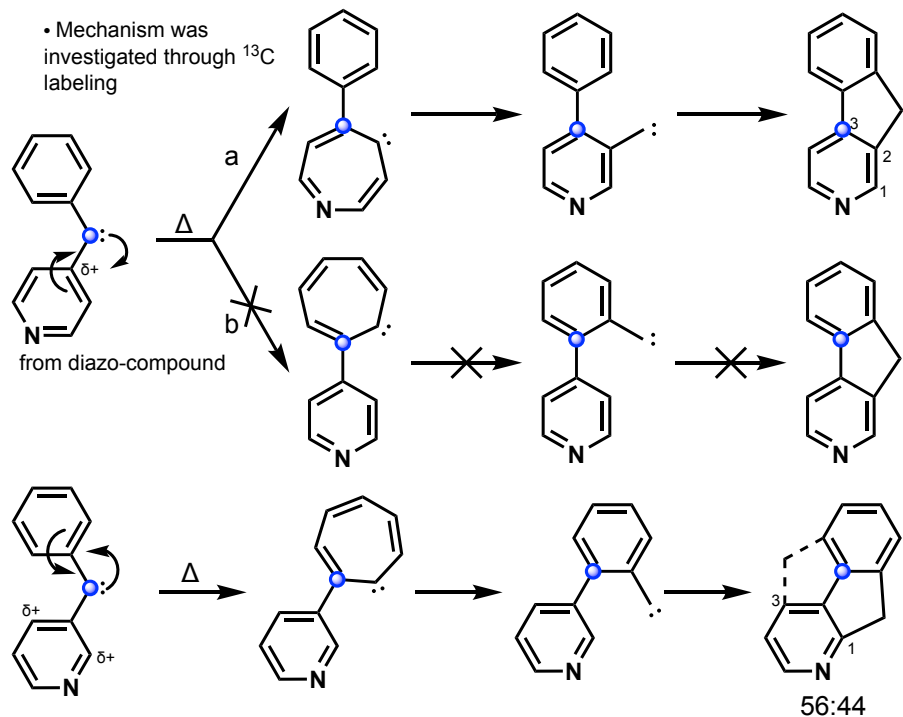
Evans, D. A. *et. al.*, 16, 4765

6. Total Synthesis

Preparation of an Optically Active Prostaglandin Intermediate via Asymmetric Induction

Corey, E. J. *et. al.*, 23, 6908

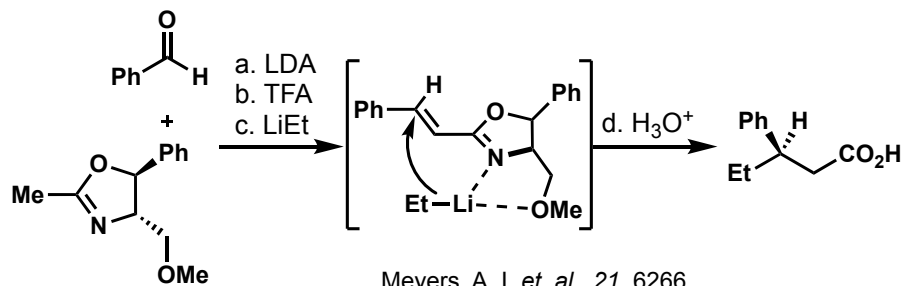
Pericyclic Chemistry**- Macrocycle synthesis through 2,3-Sigmatropic Rearrangement****- Synthesis and Chemistry of Cyanoketenes****Heterocyclic Chemistry****- Intramolecular cycloaddition of vinyl azirine****- Cleavage of dioxetanes by diphenyl sulfide (DPS)**

- Synergic nucleophilic and electrophilic properties of carbenes

Why opposite selectivities?

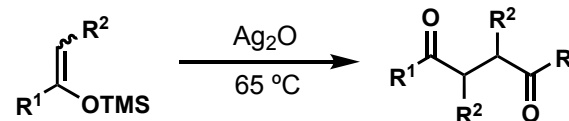
- Regioselectivities of carbene ring expansion can be predicted from a consideration of formal σ -LUMO and p-HOMO interactions.

Wentrup, C. *et. al.*, 26, 7467

- Asymmetric Synthesis of 3-substituted alkanolic acids

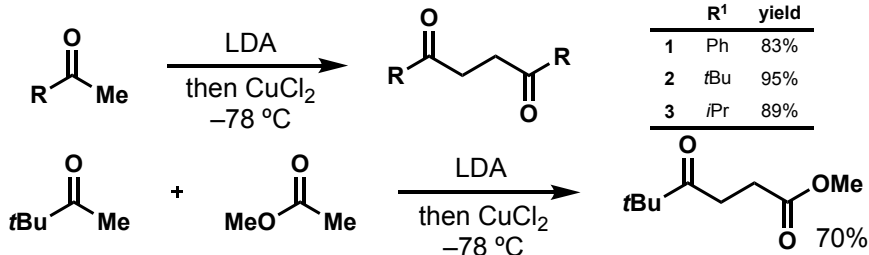
Meyers, A. I. *et. al.*, 21, 6266

Meyers, A. I. *J. Heterocyclic Chem.* 1981, 35, 991

1,4-diketone Synthesis**- Silyl enol ether with Ag_2O** 

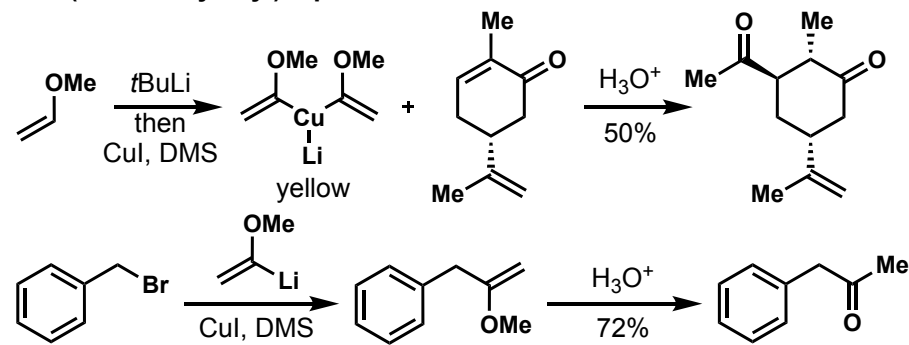
	R^1	R^2	yield
1	Ph	H	73%
2	Et	H	76%
3	Me	Me	38%

Saegusa, T. *et. al.*, 3, 649

- Ketone enolate with CuCl_2 

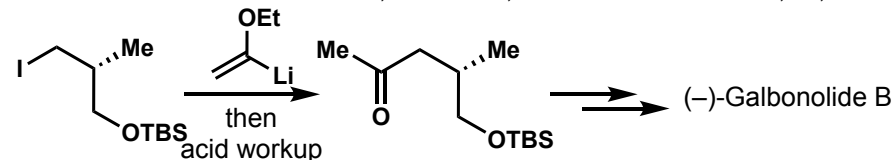
	R^1	yield
1	Ph	83%
2	<i>t</i> Bu	95%
3	<i>i</i> Pr	89%

Saegusa, T. *et. al.*, 10, 2912

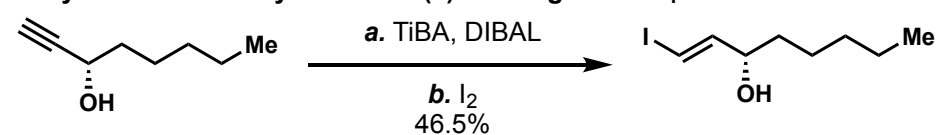
- Li di(α -methoxyvinyl)cuprate

Heathcock, C. H. *et. al.*, 13, 3822

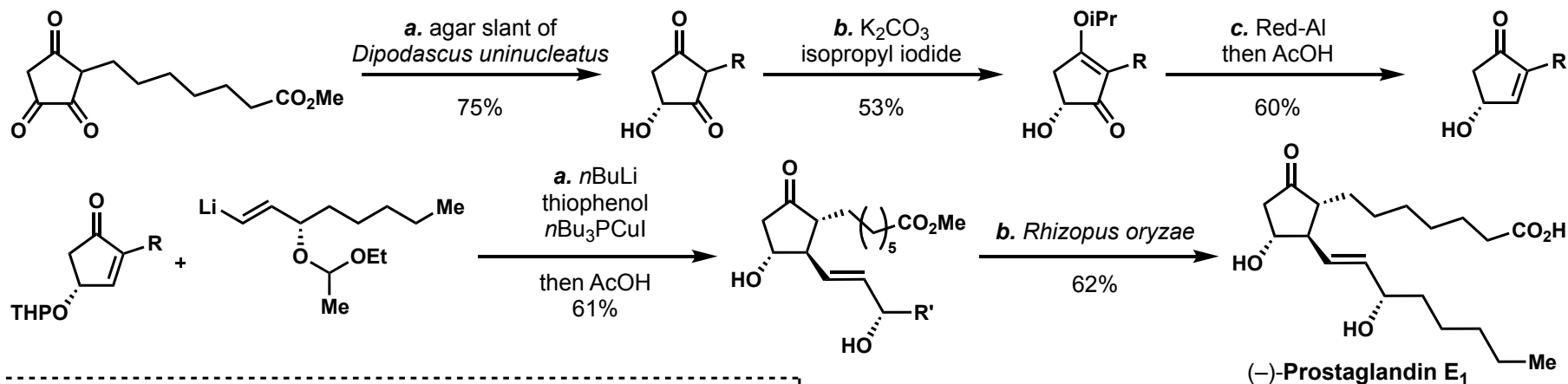
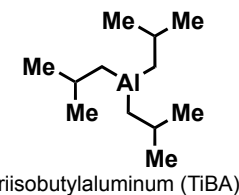
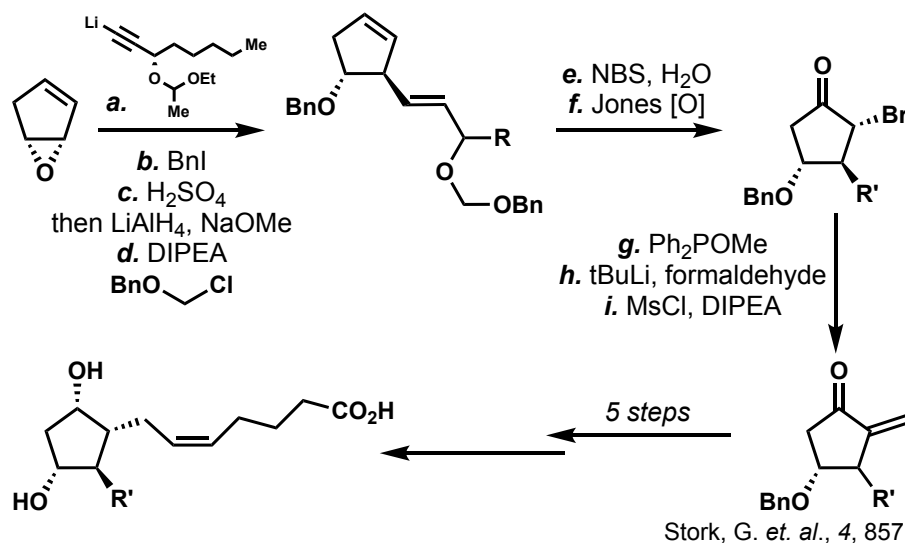
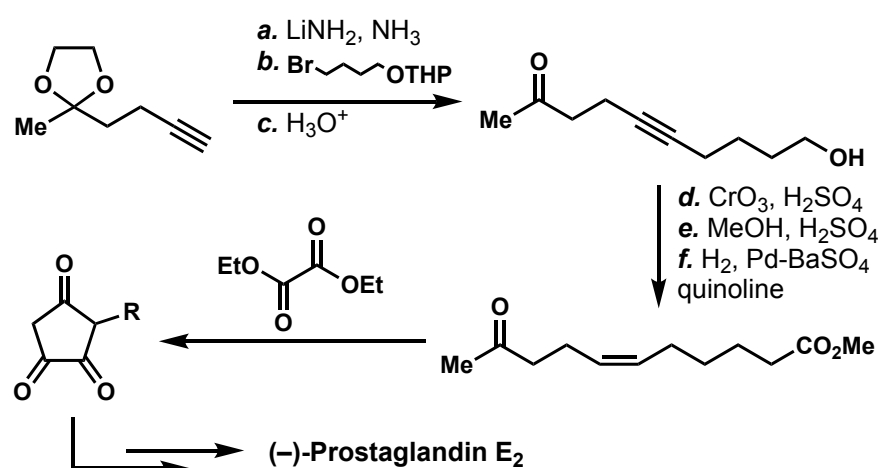
Baldwin, J. E. *et. al.*, *J. Am. Chem. Soc.* 1974, 96, 7125



Bruno, T. *J. Am. Chem. Soc.* 1996, 118, 30, 7094

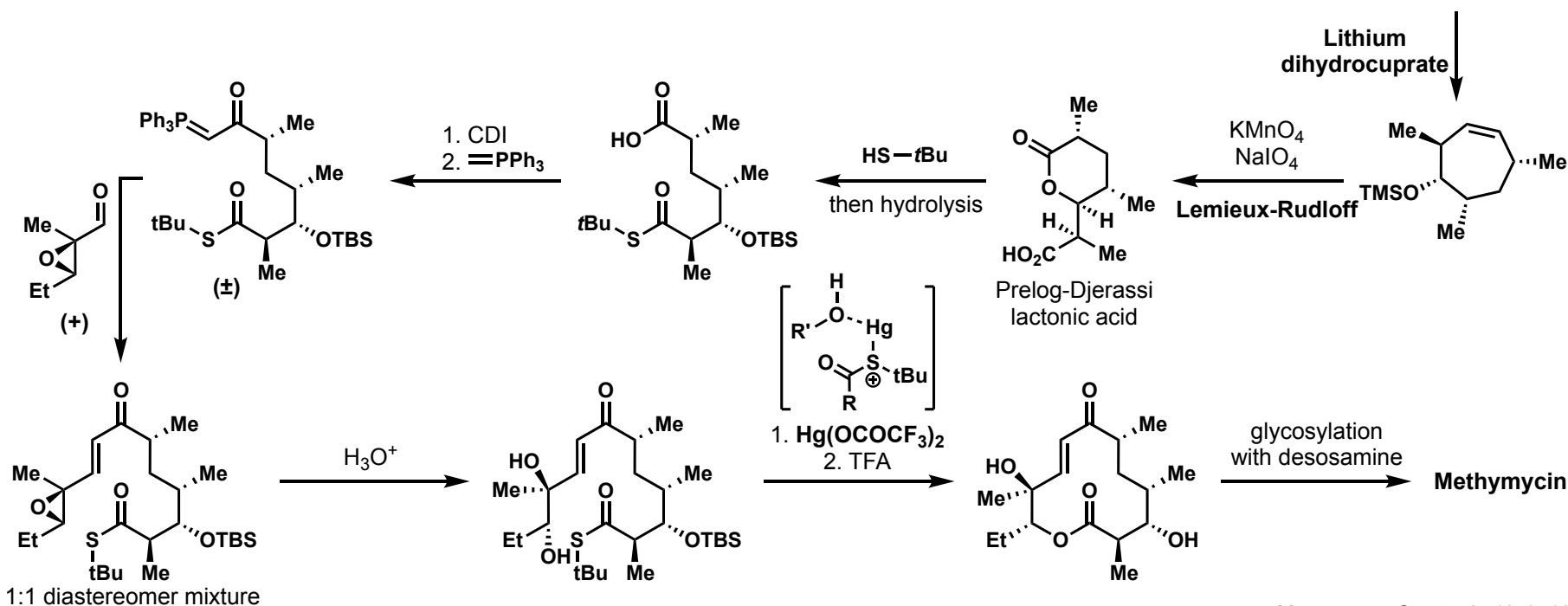
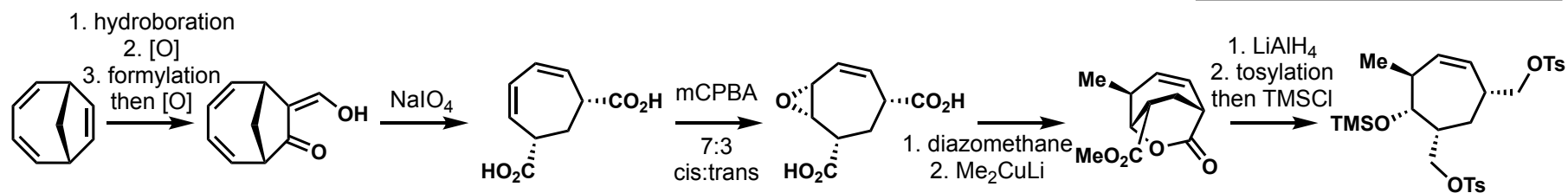
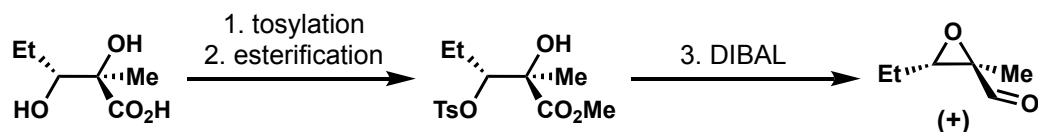
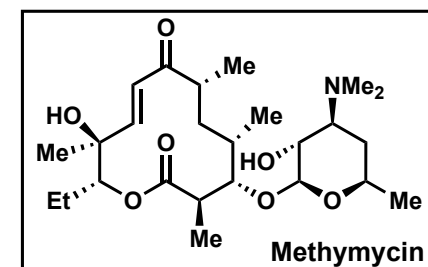
Selected Total Synthesis**- Asymmetric Total Synthesis of (-)-Prostaglandin E₁**

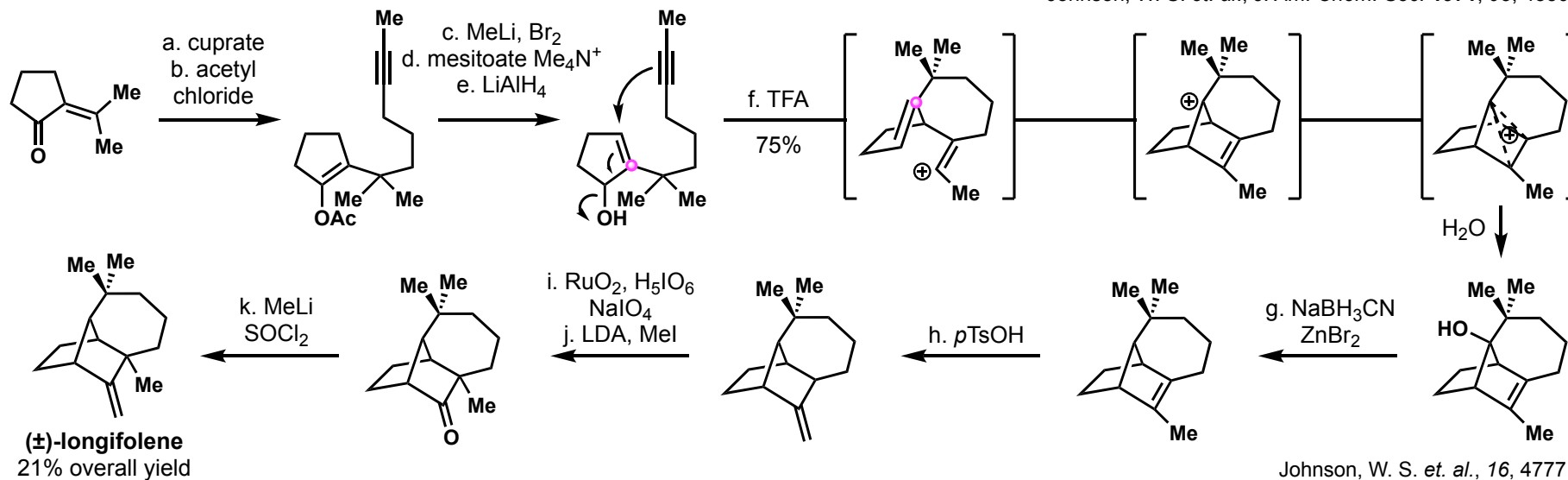
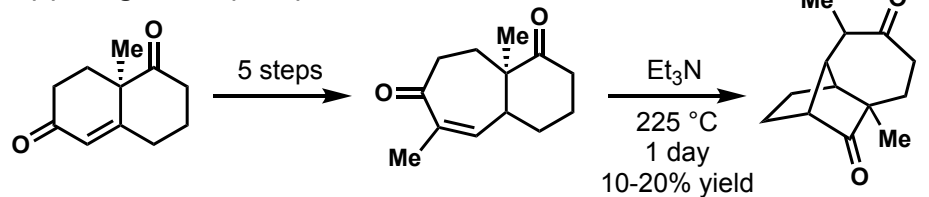
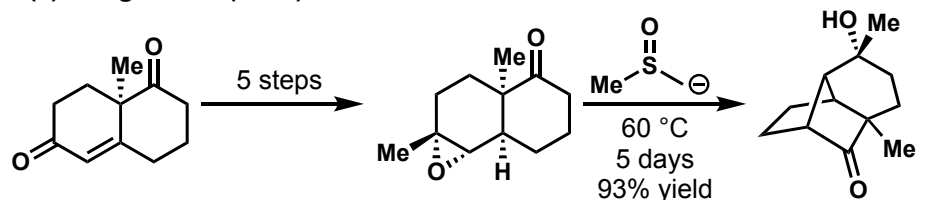
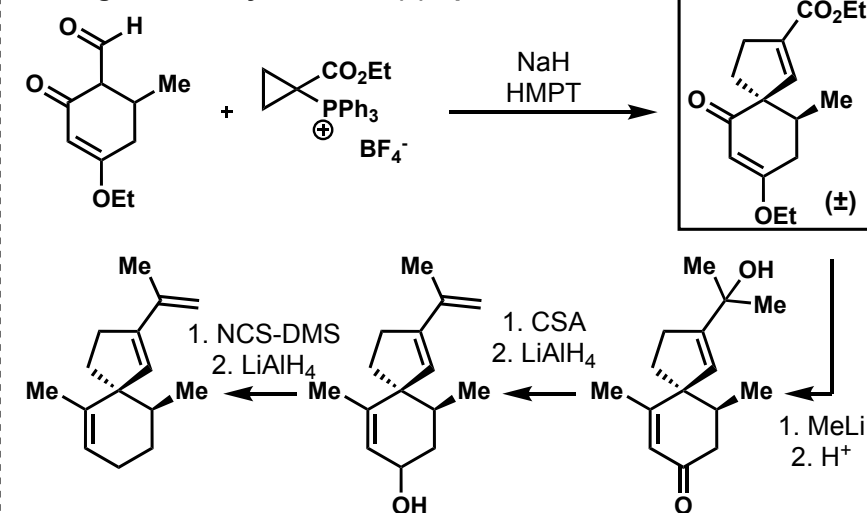
- Utilization of enzymes to introduce chirality into a synthetic prochiral substrate
- The rest of the stereochemistry centers are built around the first chiral center

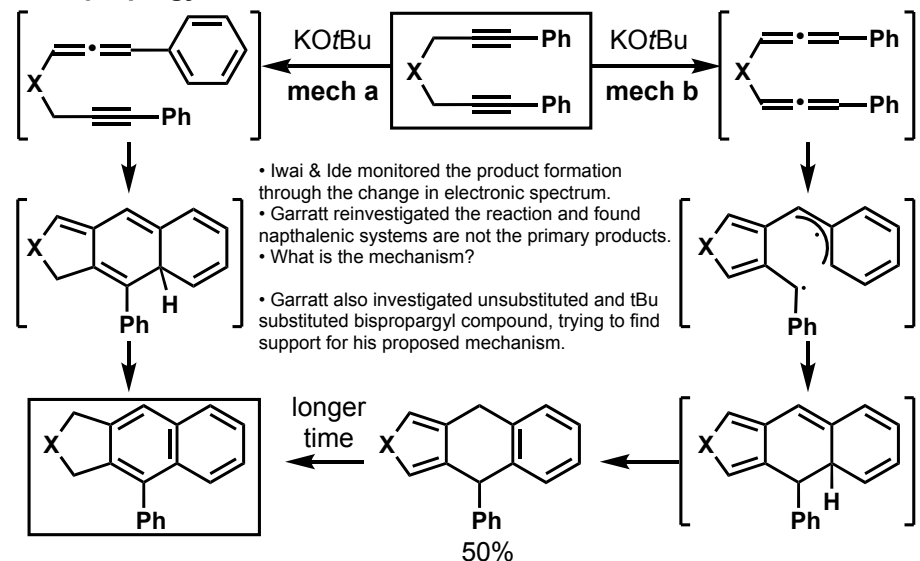
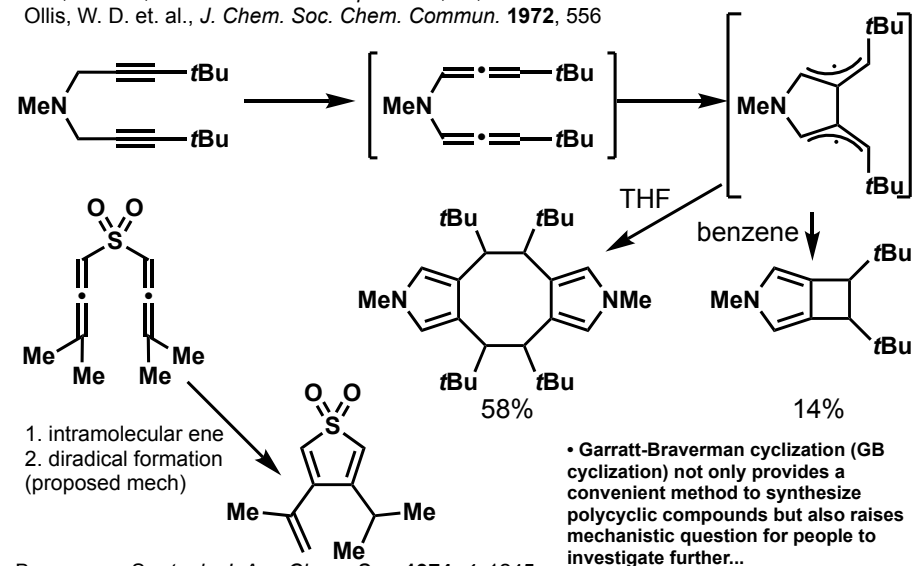
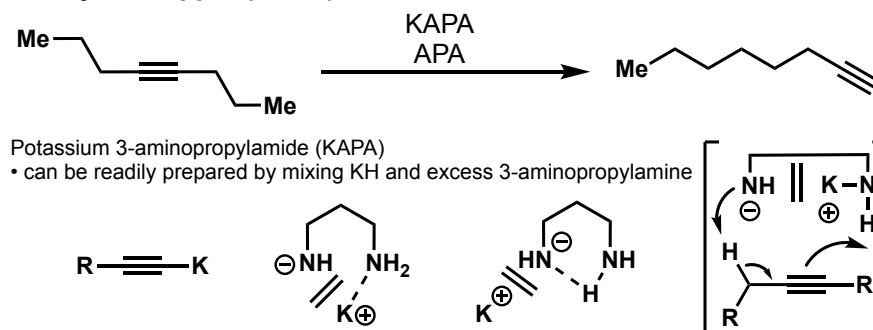
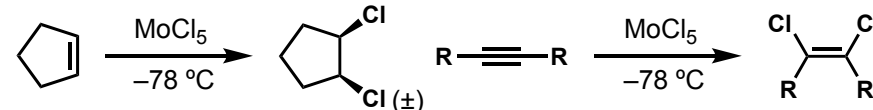
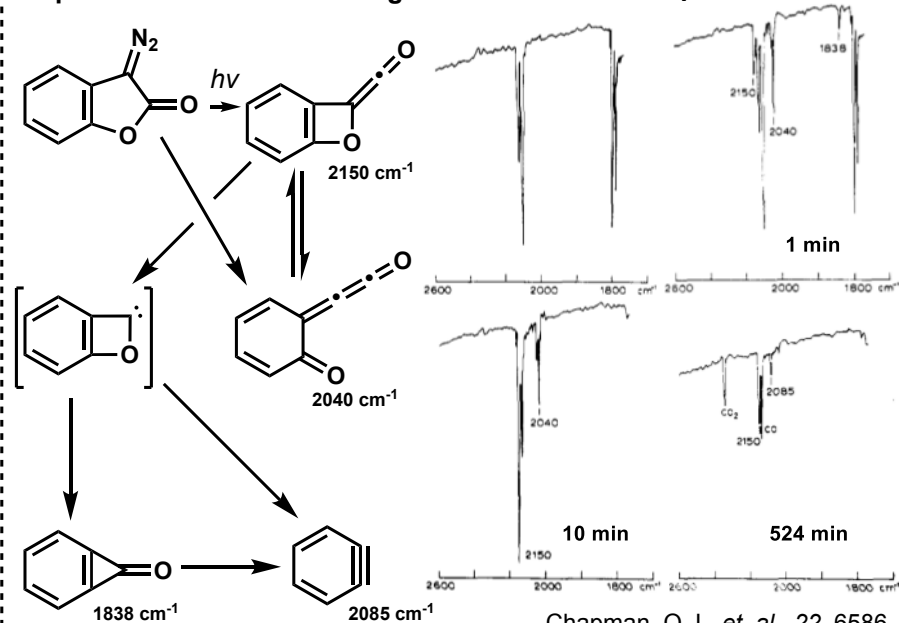
**- Total Synthesis of (±)-Prostaglandin F_{2α}****- (-)-Prostaglandin E₂**

- Total synthesis of Methymycin

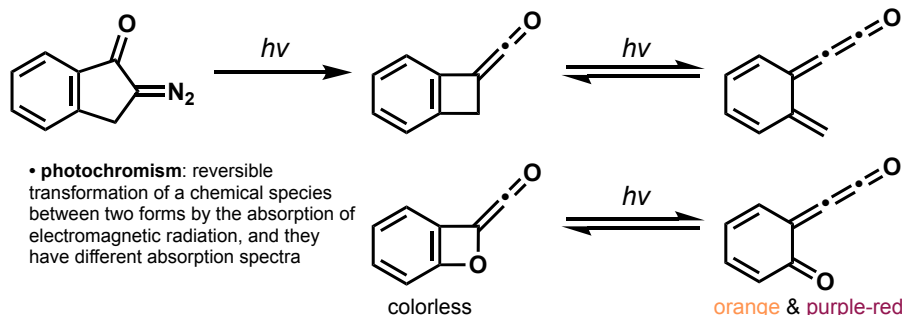
Natural product: Djerassi, C. *et al.*, *J. Am. Chem. Soc.* **1956**, *78*, 6390
 Prelog, V. *et al.*, *Helv. Chim. Acta.* **1956**, *39*, 1785
 Rickards, R. W. *et al.*, *Tetrahedron Lett.* **1970**, 1025



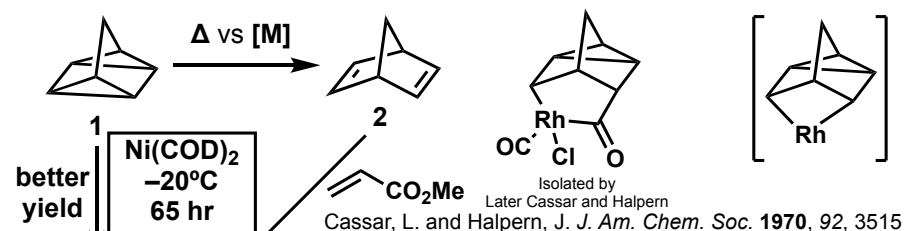
- Total synthesis of (\pm)-LongifoleneJohnson, W. S. *et al.*, *J. Am. Chem. Soc.* **1972**, 94, 8604
Johnson, W. S. *et al.*, *J. Am. Chem. Soc.* **1971**, 93, 4330- (\pm)-Longifolene (1964)- (\pm)-Longifolene (1972)- Divergent Total Synthesis of (\pm)-Spirovetivanes

Alkyne-Related ChemistryGarratt, P. J. *et. al.*, 11, 3255**- Bispropargyl X = S/O/N**Iwai, I. *et. al.*, *Chem. Pharm. Bull. Jpn.* **1964**, 12, 1094
Ollis, W. D. *et. al.*, *J. Chem. Soc. Chem. Commun.* **1972**, 556Braverman, S. *et. al.*, *J. Am. Chem. Soc.* **1974**, 4, 1245**- Acetylene Zipper (KAPA)**Brown, C. A. *et. al.*, 4, 891**- Chlorination with MoCl₅**Sanfilippo, J. *et. al.*, 6, 1599**- A photochemical method to generate strained multiple bond**Chapman, O. L. *et. al.*, 22, 6586

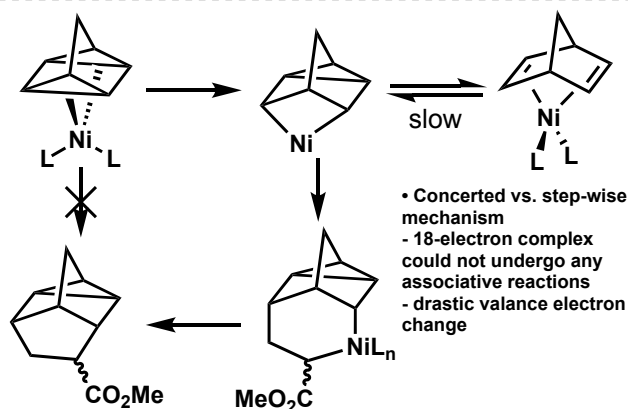
- A photochemical method to generate strained multiple bond (conti.)

Organometallic Chemistry

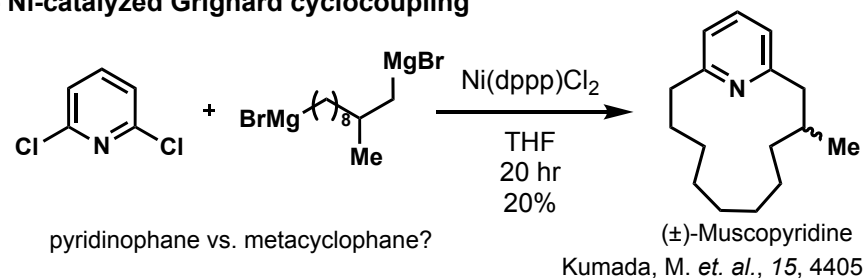
- Ni(0)-catalyzed cycloaddition between quadricyclane and EW-olefin



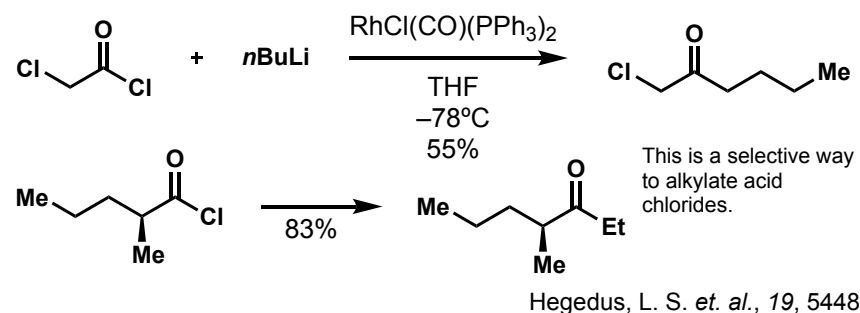
Comparison of the reactivities of 1 and 2 in the presence of Ni(0) catalysts is understood via separate and competitive reactions. 1 is more facile to proceed to product with 22% yield while 2 only gives ~1% yield of product due to 2's strong coordination tendency with Ni(0).

Proposed MechanismNoyori, R. *et. al.*, 4, 812

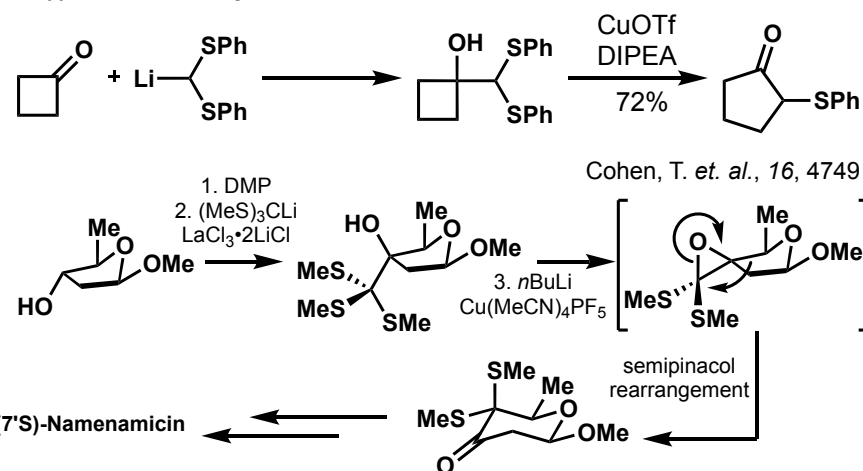
- Ni-catalyzed Grignard cyclocoupling



- Alkylation of Acid Chlorides by Alkylrhodium(I) Complexes



- Cu(I) induced thiophenoxide removal

Nicolaou, K. C. *et. al.*, *J. Am. Chem. Soc.* 2018, 140, 8091