

Ketene chemistry and the application in synthesis

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Nov 14, 2013

Ketene chemistry

Content

- A brief history of ketene
- Type of ketenes
- Ketene preparation
- Ketenes in synthesis

Reviews about ketenes:

T. T. Tidwell, *Ketenes*, 2nd ed., Wiley Interscience, Hoboken, NJ, **2006**.

T. T. Tidwell, *Eur. J. Org. Chem.* **2006**, 563-576.

T. T. Tidwell, *Angew. Chem. Int. Ed.* **2005**, 44, 5778-5785.

A brief history of ketene

The first reported ketene: Diphenylketene



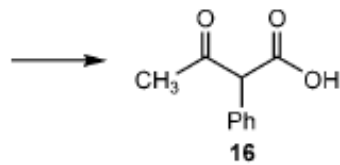
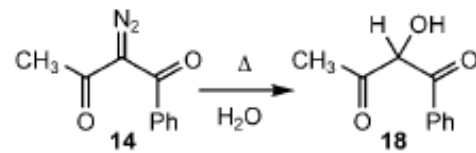
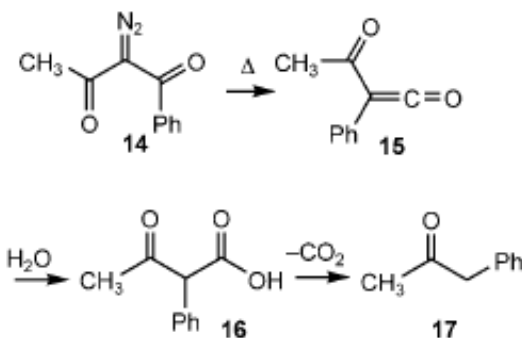
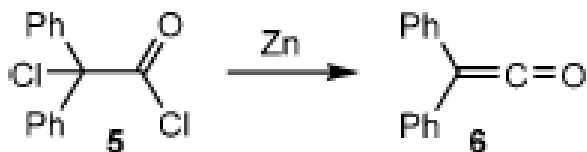
Figure 2. Hermann Staudinger (1881–1965).



Figure 3. Ludwig Wolff (1857–1919).



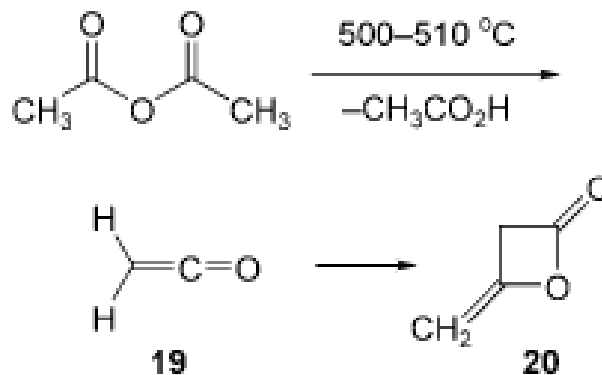
Wedekind



Ketene and its Dimer:



Figure 4. N. T. M. Wilsmore (1868–1940).

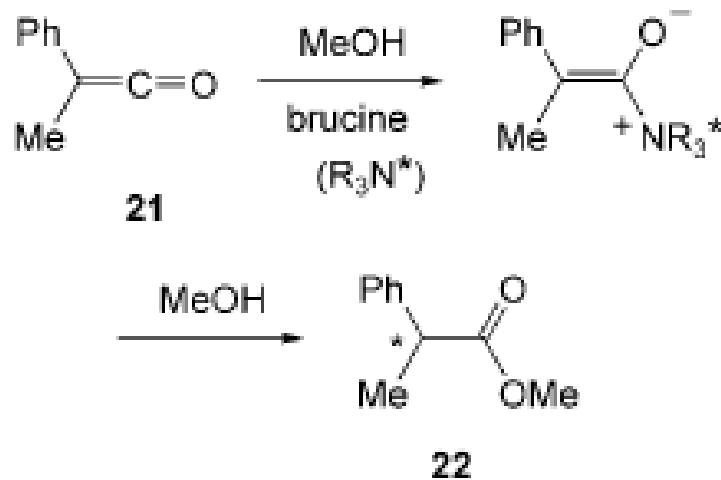


N.T.M. Wilsmore, *J. Chem. Soc.* **1907**, 91, 1938

Asymmetric reactions of ketene:



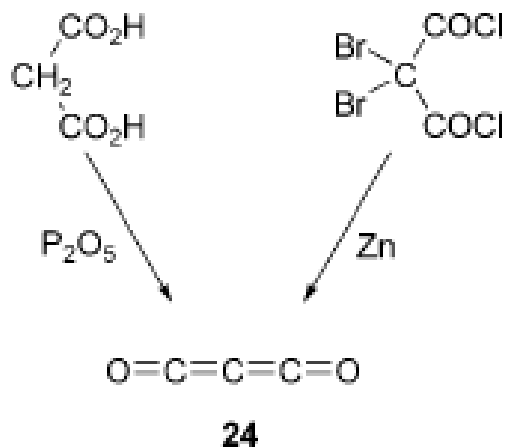
Figure 7. Horst Pracejus (1927–1987).



H. Pracejus, *Justus liebig's Ann. Chem.* **1969**, 722, 1-11

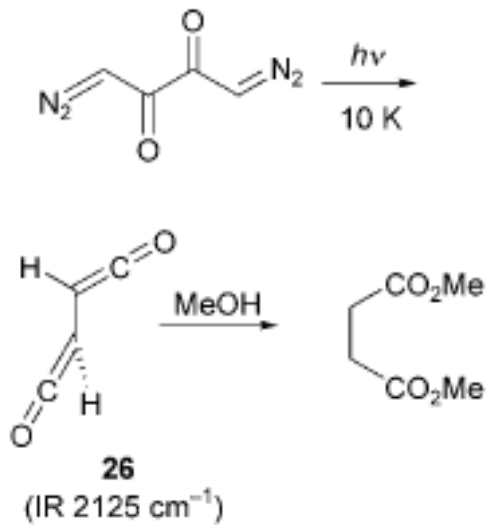
Bisketenes

First prepared bisketenes by Wolf in 1906



O. Diels, B. Wolf, *Ber. Dtsch. Chem. Ges.* **1906**, 39, 689-697

First observed bisketenes in 1982



G. Maier, H. P. Reisenauer, T. Sayrac, *Chem. Ber.* **1982**, 115, 2192

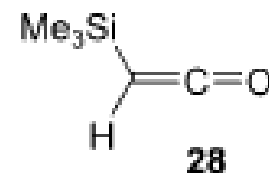
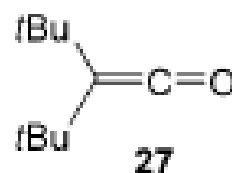
Substituent effects of ketene



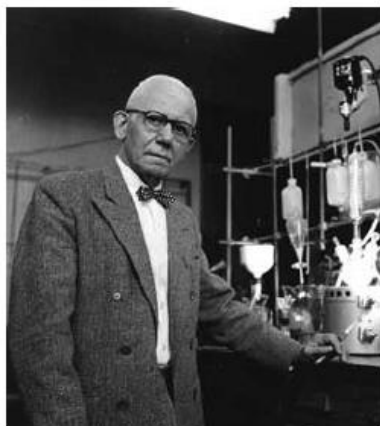
Melvin Newman



Shchukovskaya



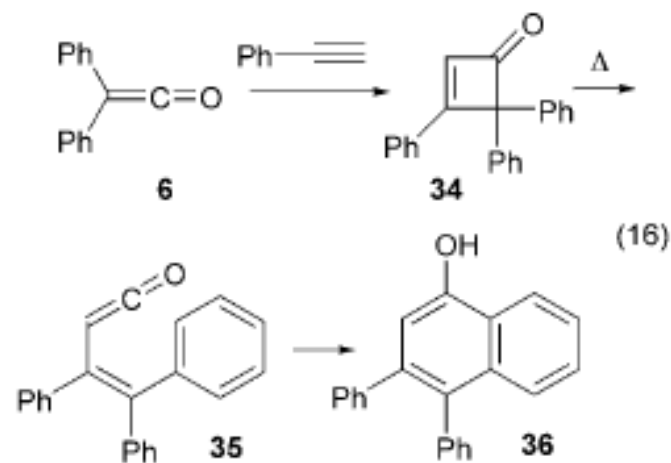
Cycloadditions of ketenes



Lee Irvin Smith



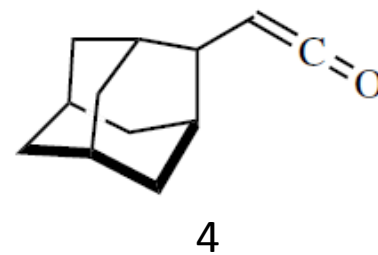
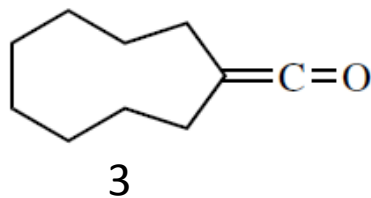
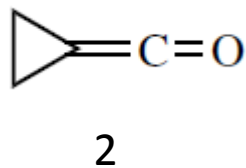
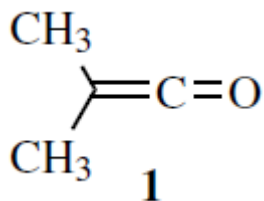
Derek H.R. Barton



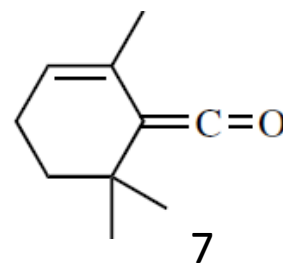
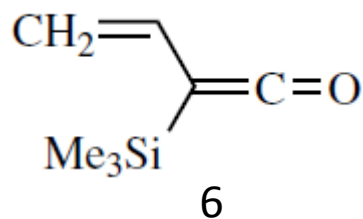
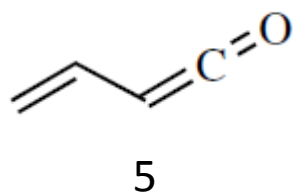
Type of ketenes

Carbon-substituted ketenes

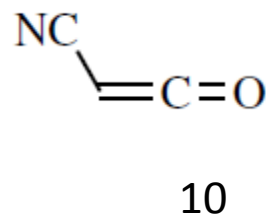
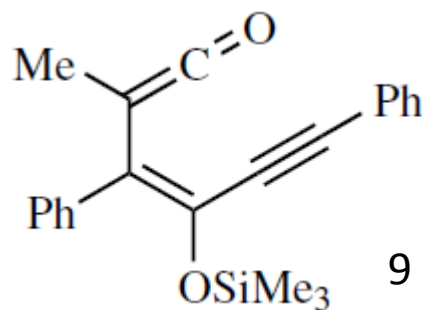
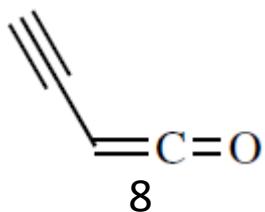
- Alkylketenes



- Alkenylketenes

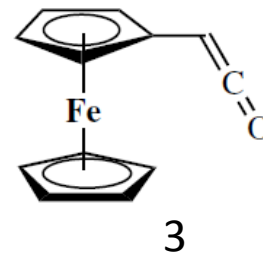
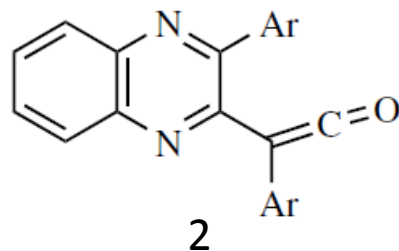
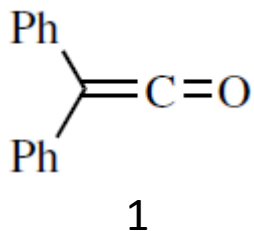


- alkynylketenes and cyanoketenes

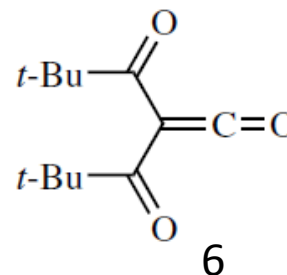
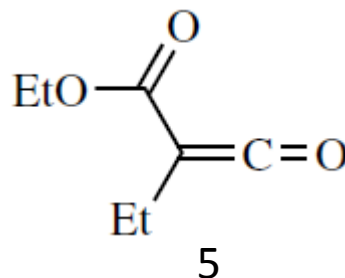
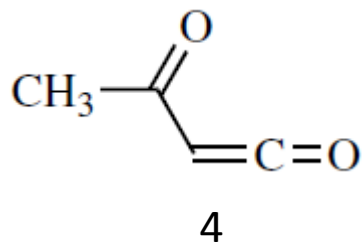


Type of ketenes

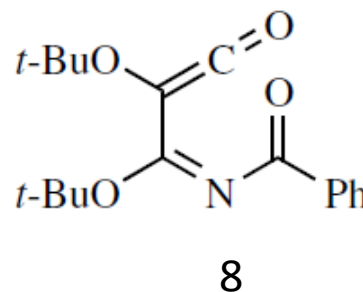
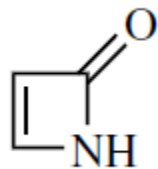
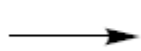
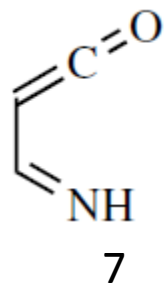
- Arylketenes



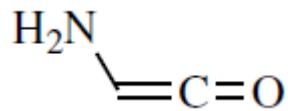
- Acylketenes



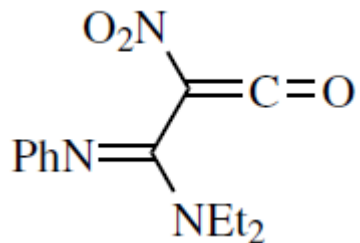
- Imidoalkenes



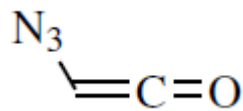
Nitrogen-substituted ketenes



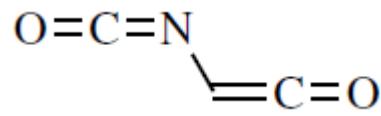
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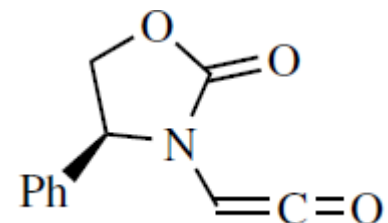
Nitroketene



Azidoketene

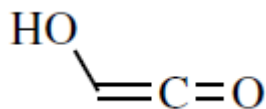


Isocyanatoketene

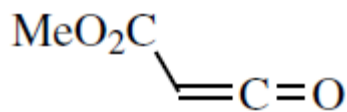


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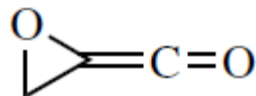
Oxygen-substituted ketenes



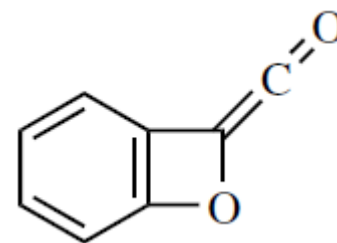
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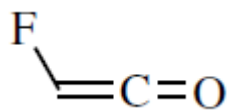


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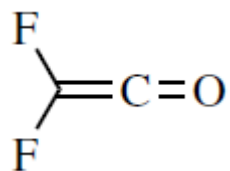


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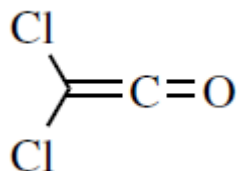
Halogen-substituted ketenes



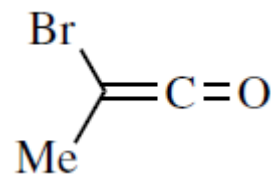
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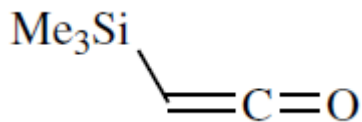


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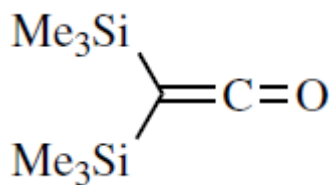


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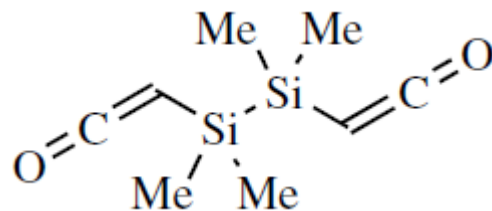
Silyl-ketenes



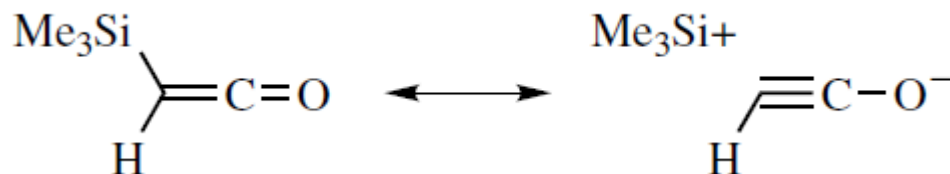
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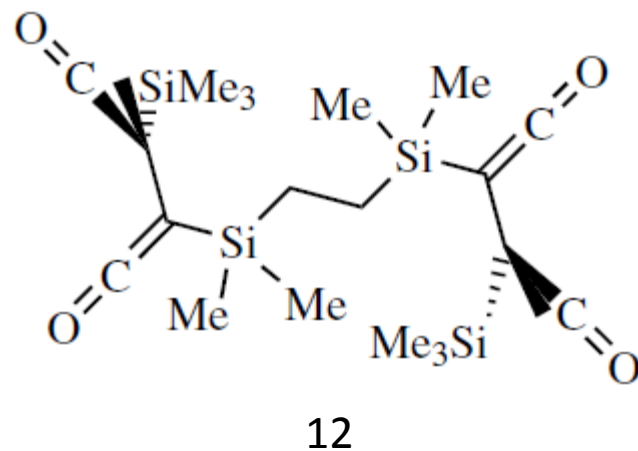
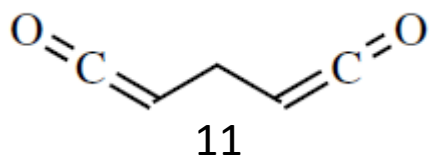
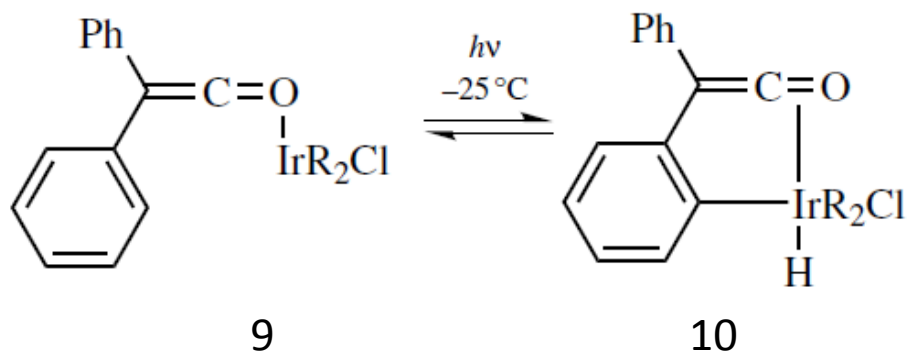
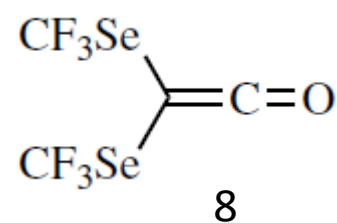
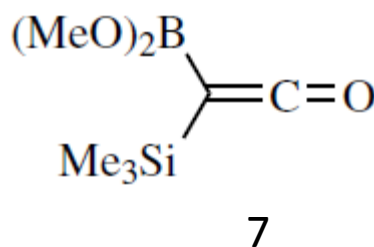
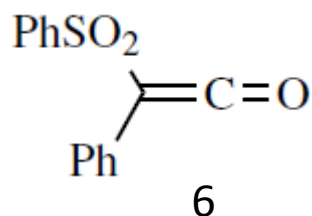
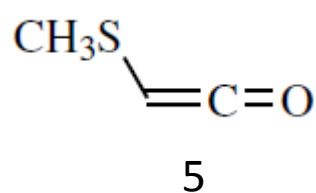
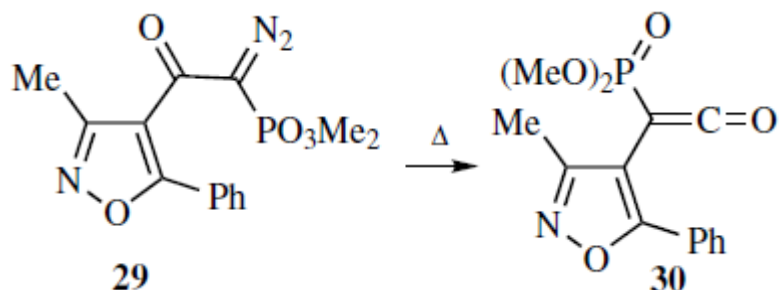
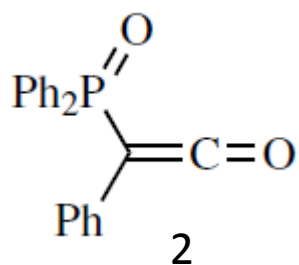
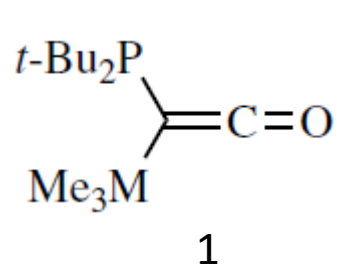
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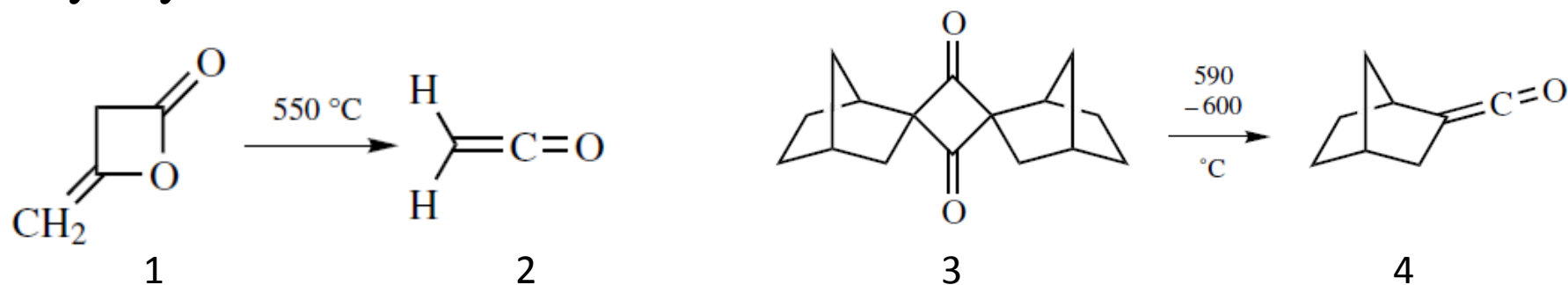
Phosphorous, sulfur, metal-substituted and bis ketenes



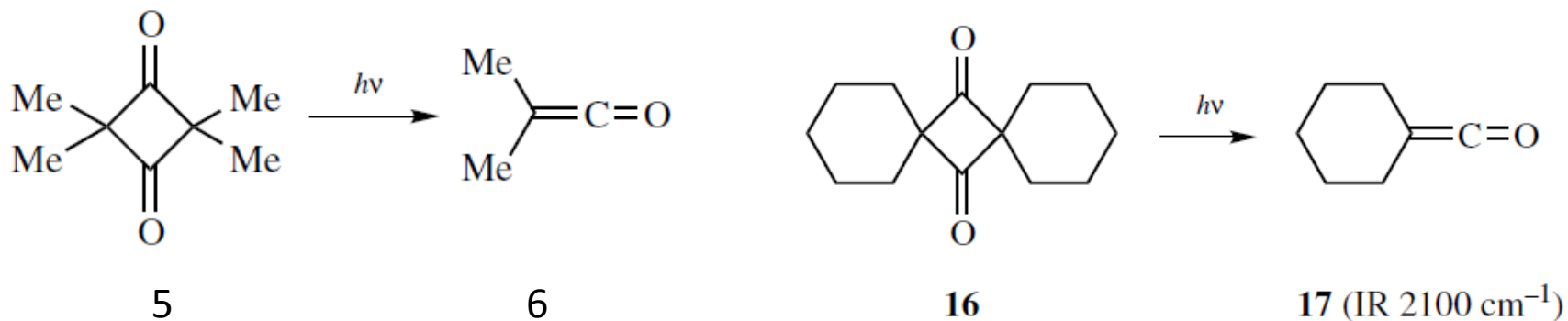
Ketene preparation

Ketenes from ketene dimers

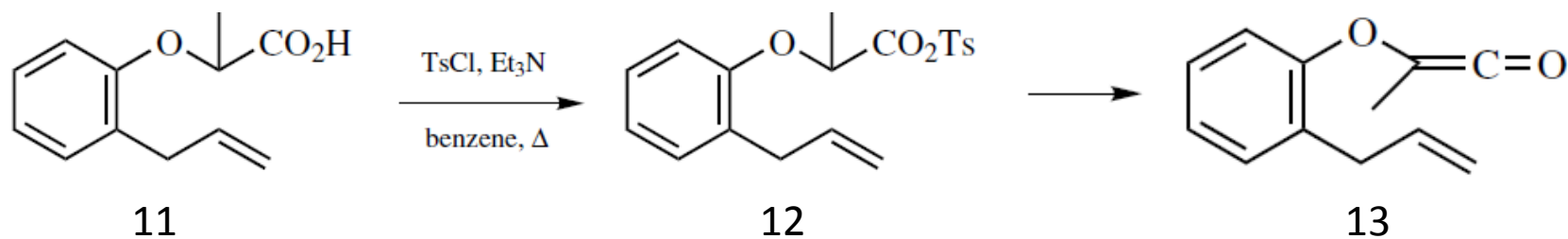
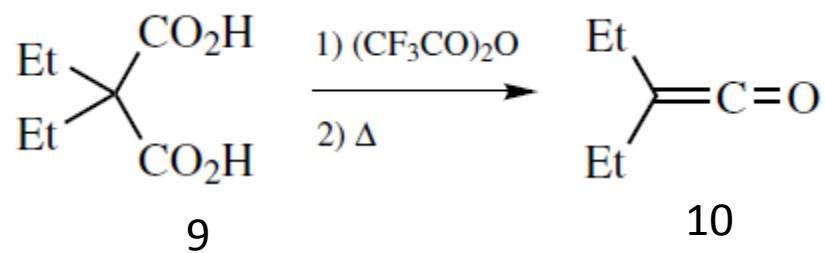
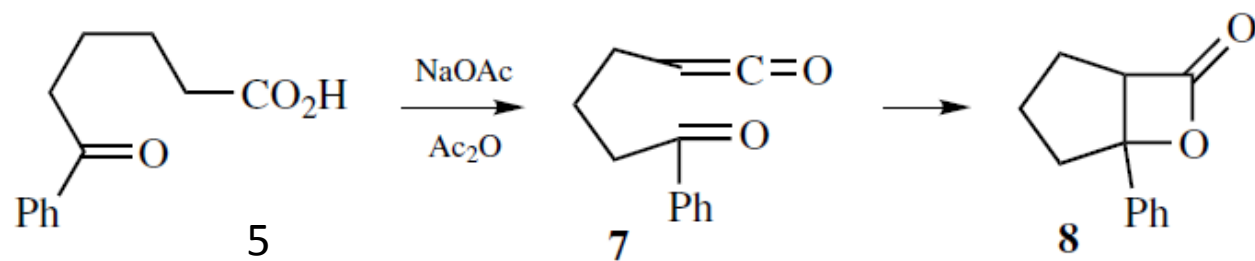
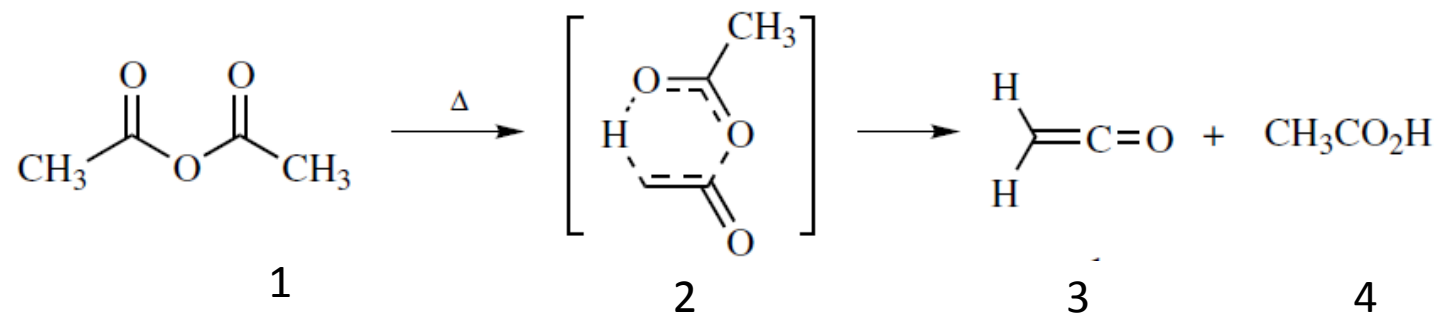
•Pyrolysis of ketene dimer



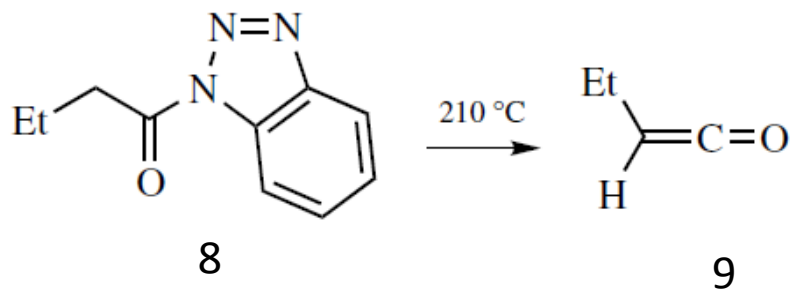
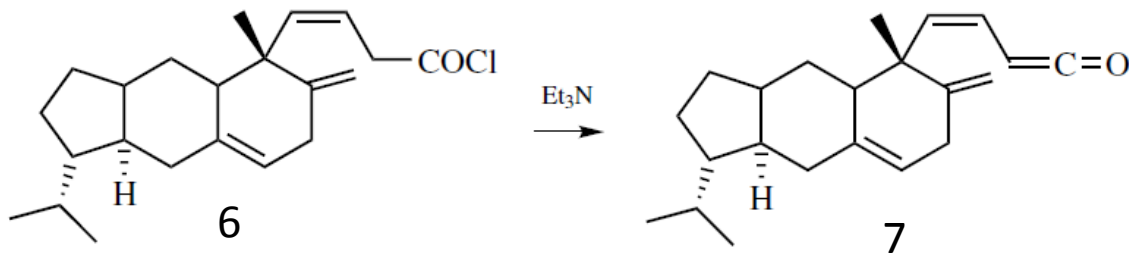
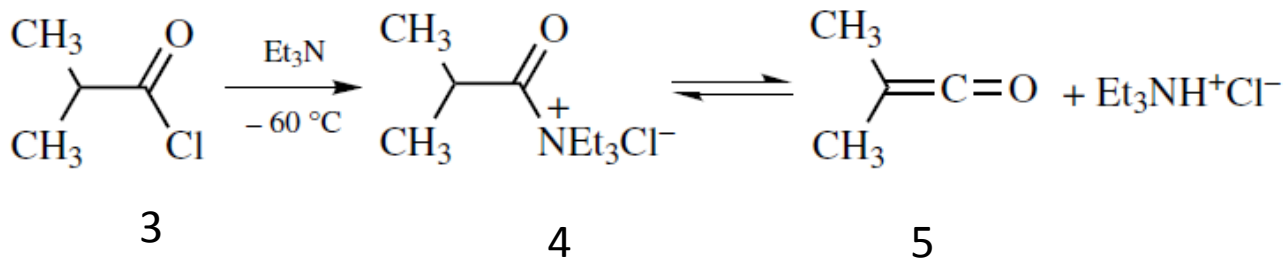
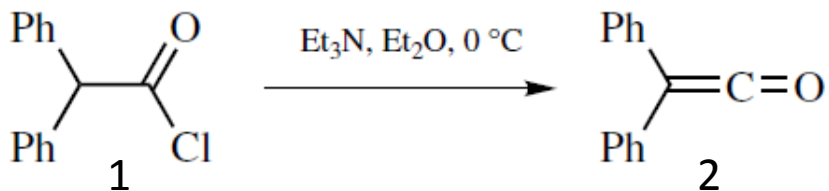
•Photolysis of ketene dimer



Ketene from carboxylic anhydrides

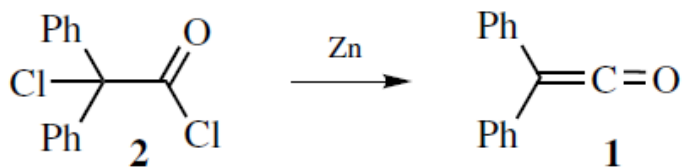


Ketenes from acyl halides and activated acids

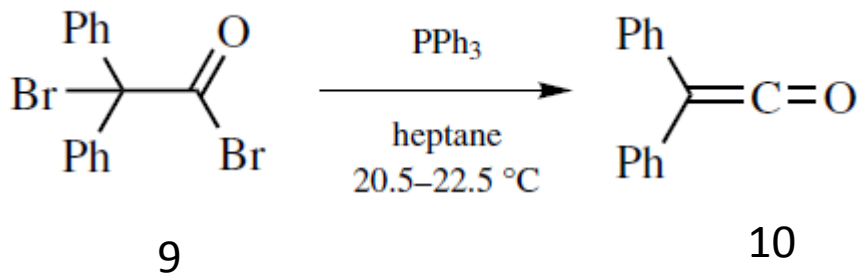
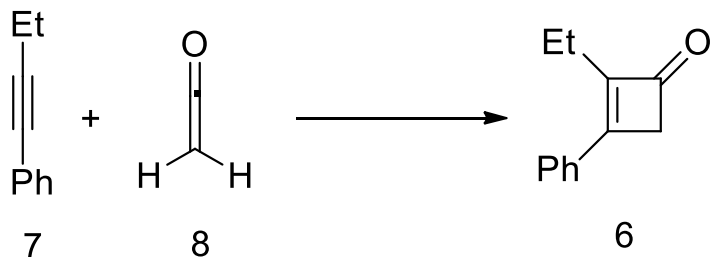
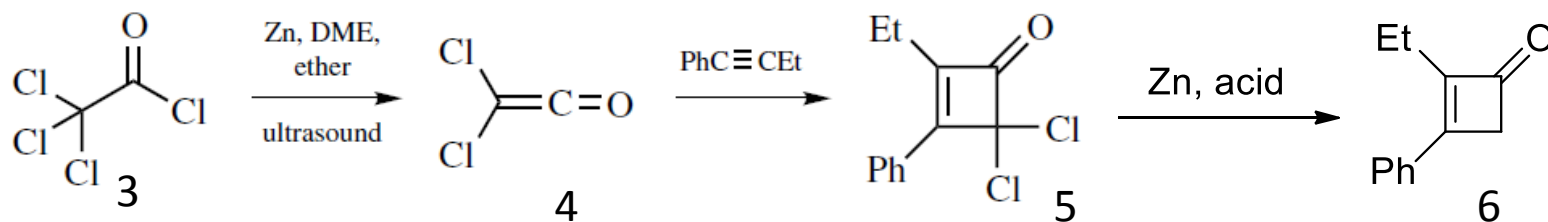


Ketenes by dehalogenation of α -Halo carboxylic acid derivatives

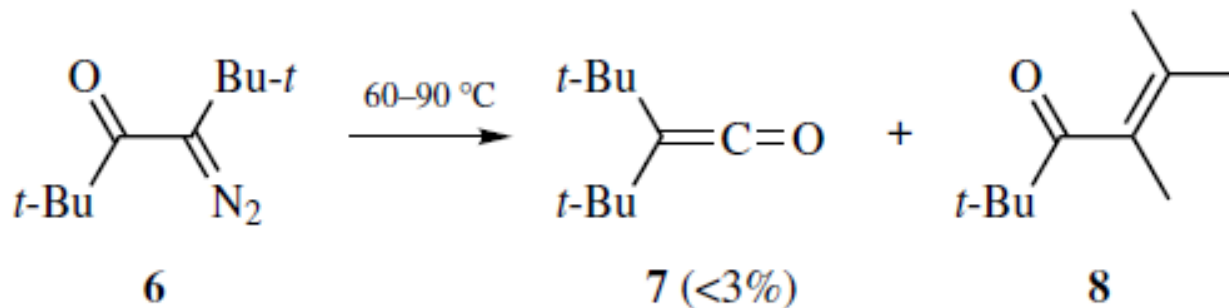
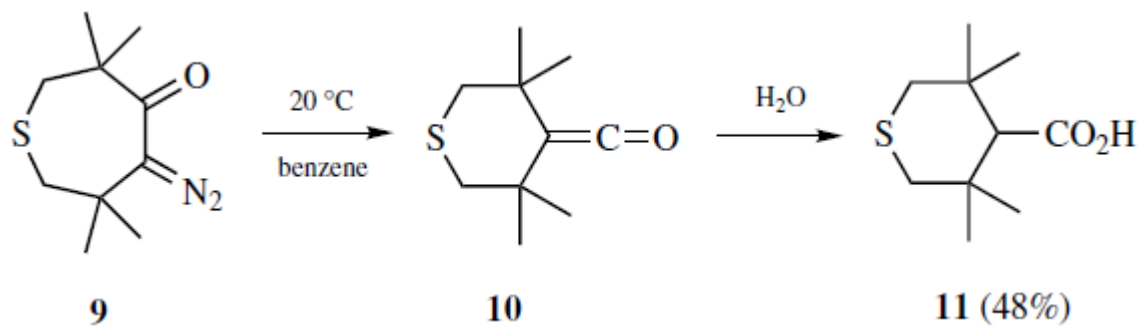
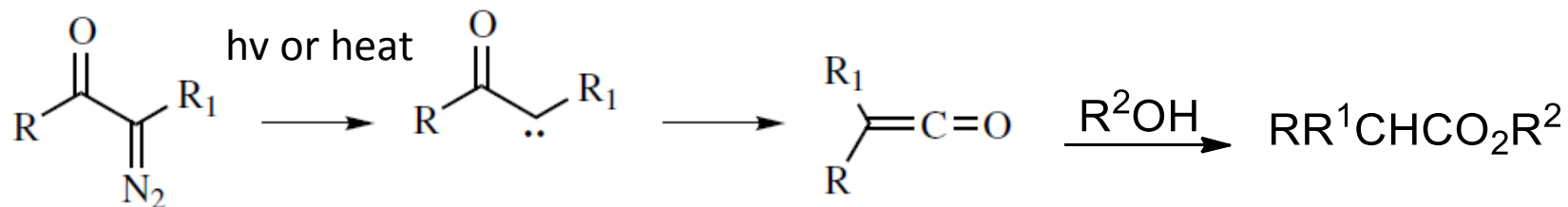
The first prepared ketene



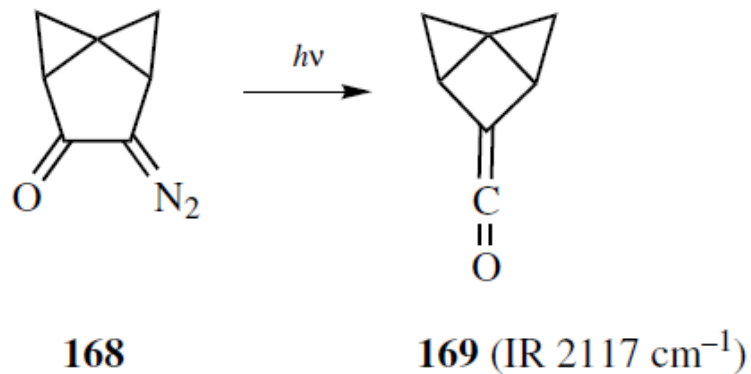
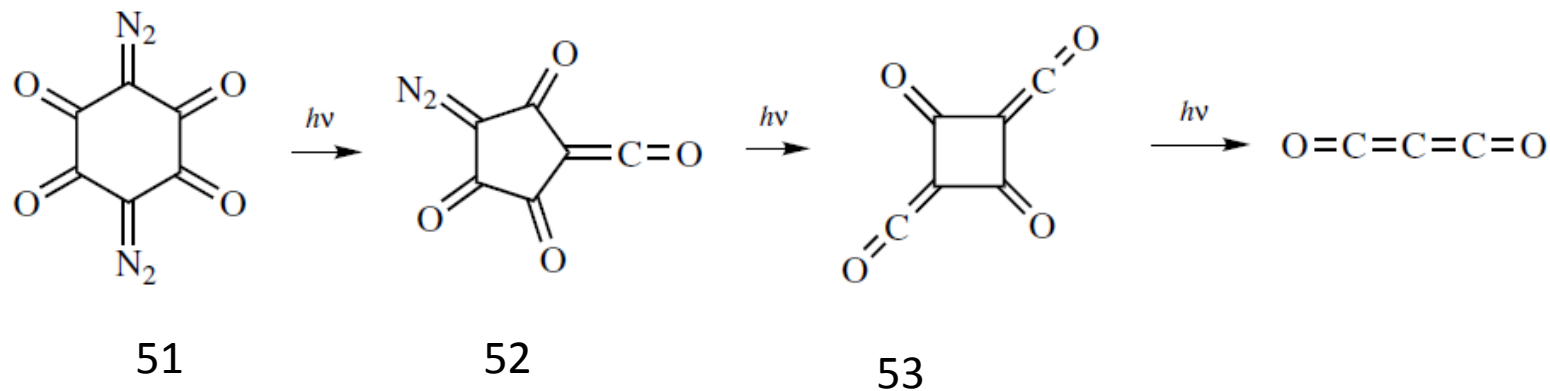
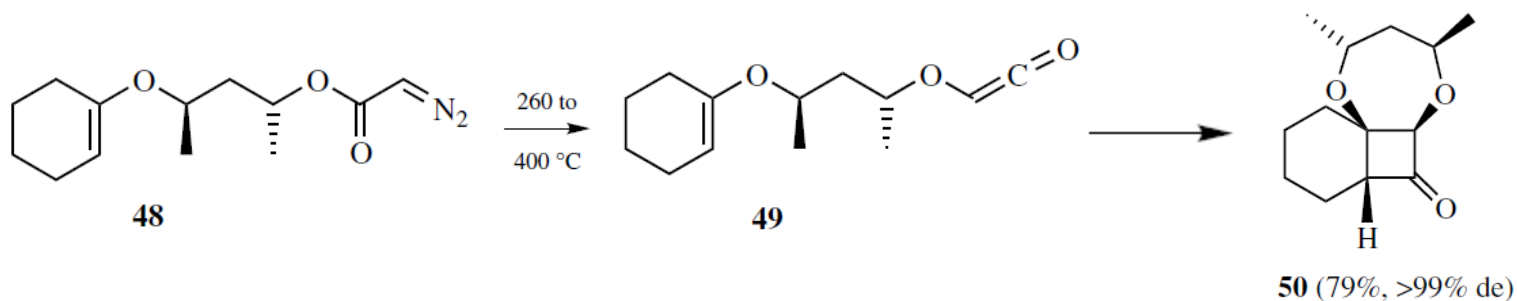
The most common used ketene-dichloroketene



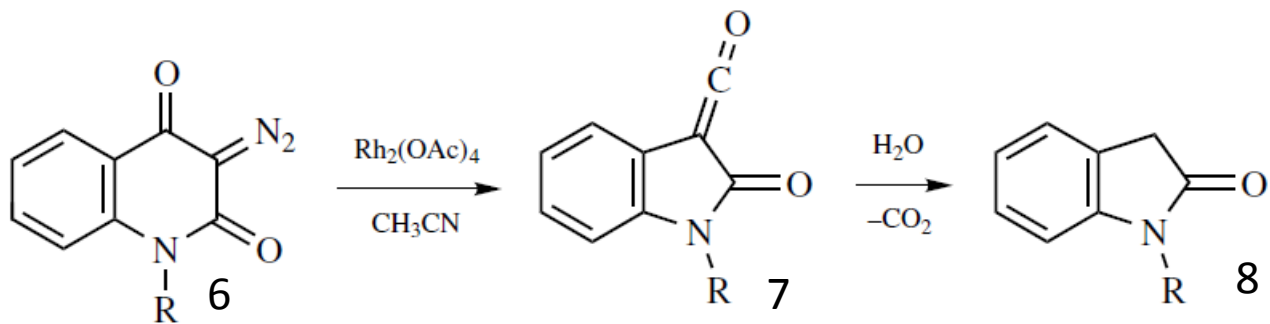
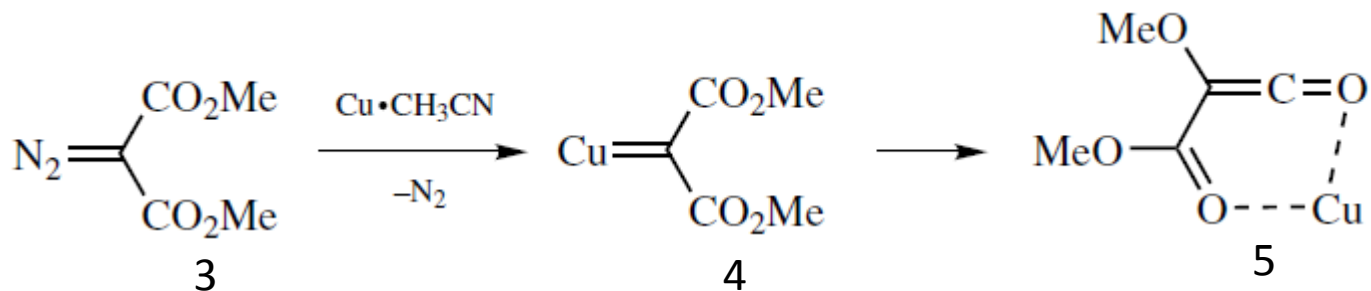
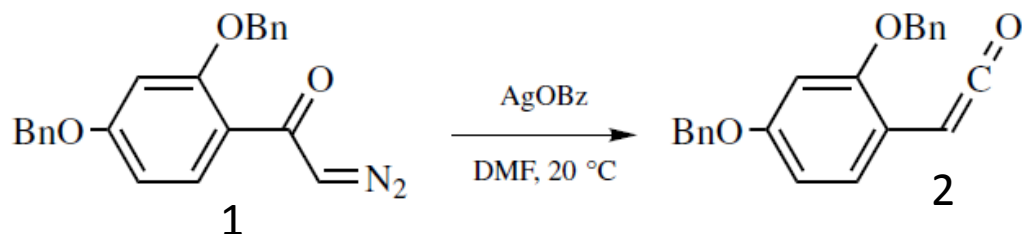
Ketenes from diazo ketones (Wolff rearrangements)



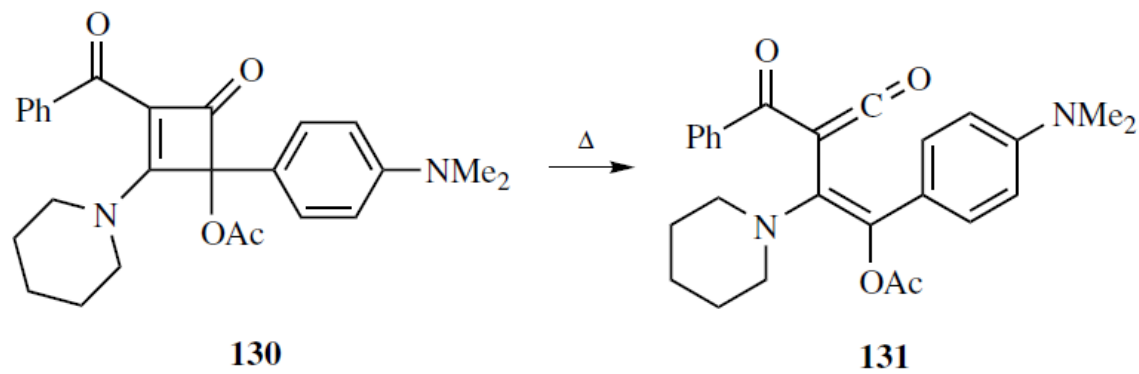
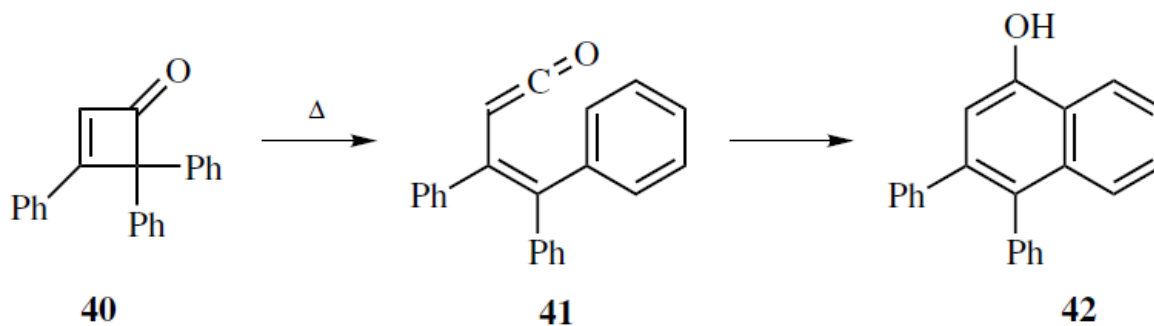
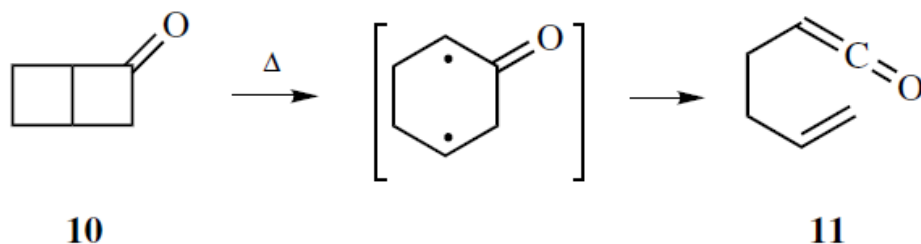
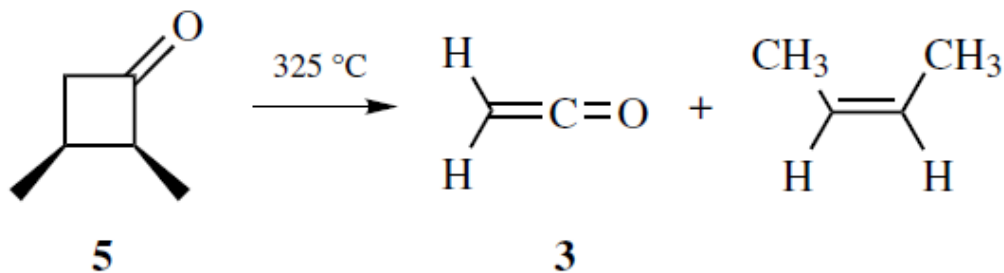
Wolff rearrangements in synthesis



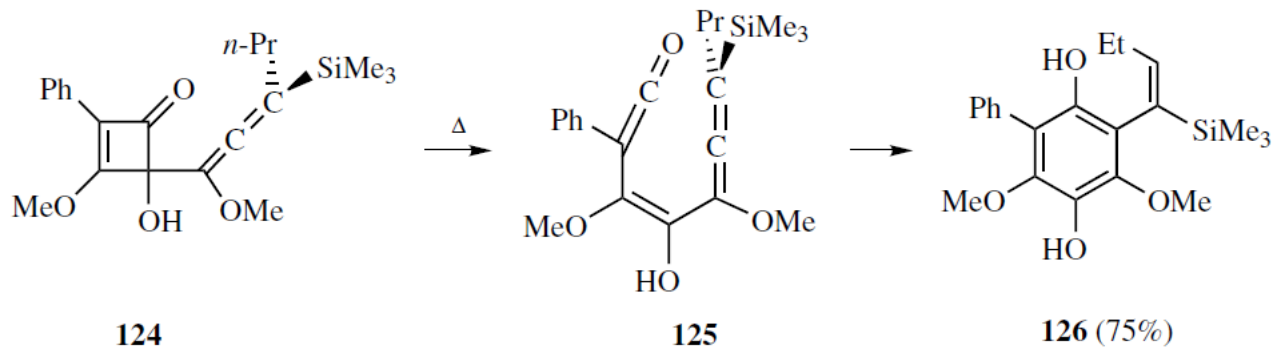
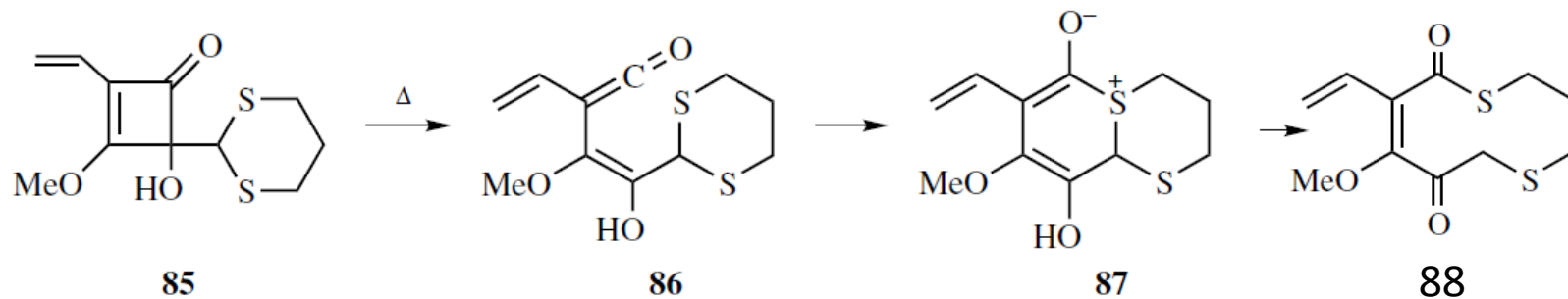
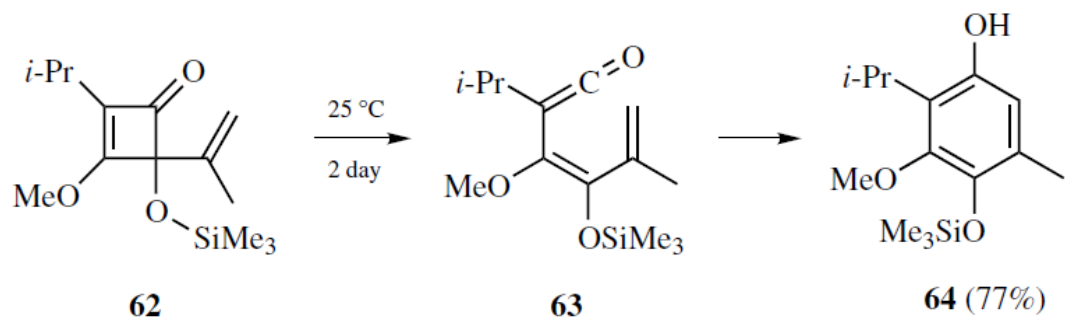
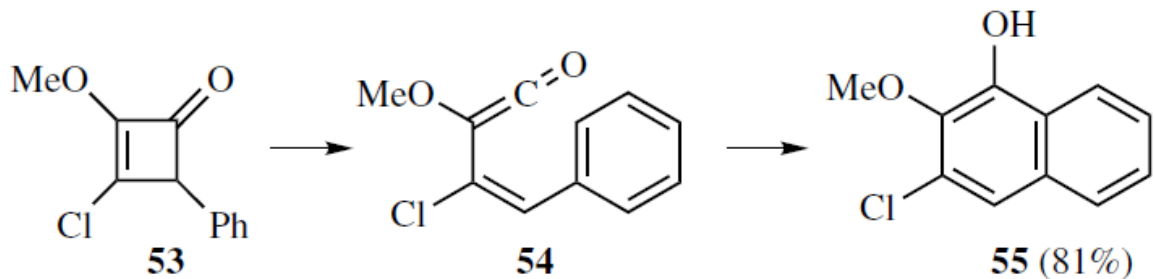
Catalyzed Wolff rearrangements



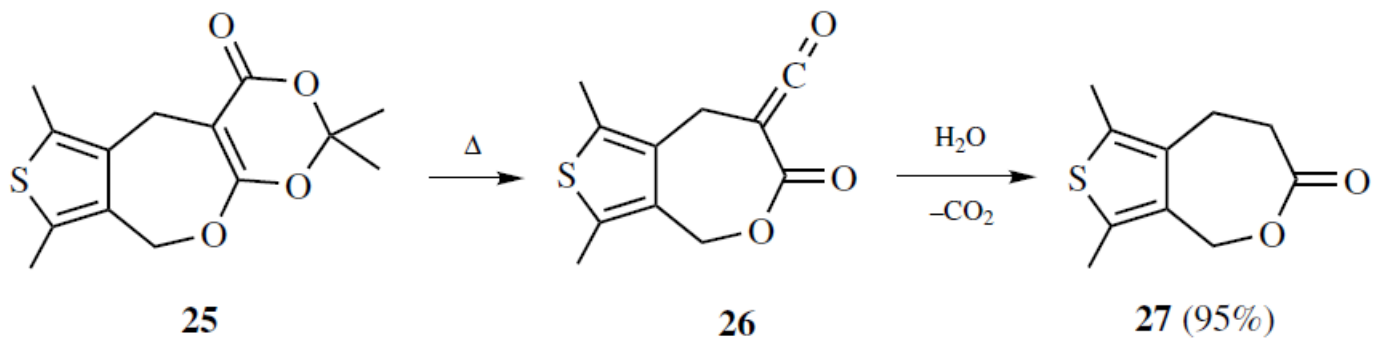
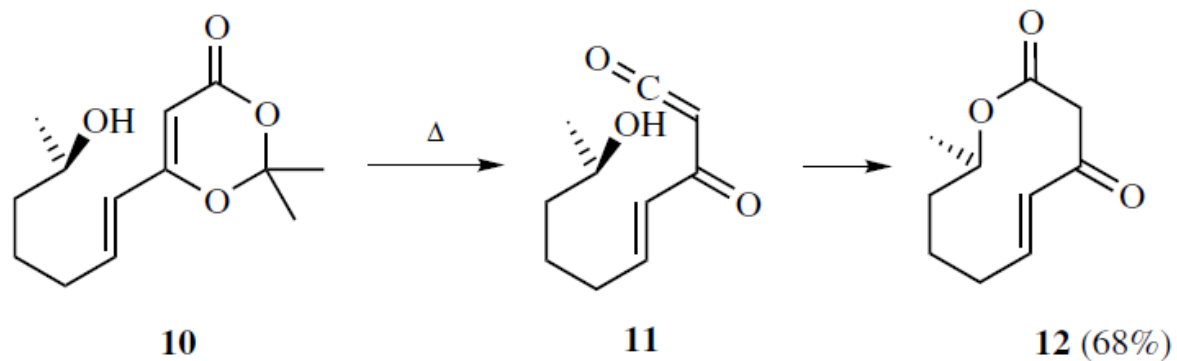
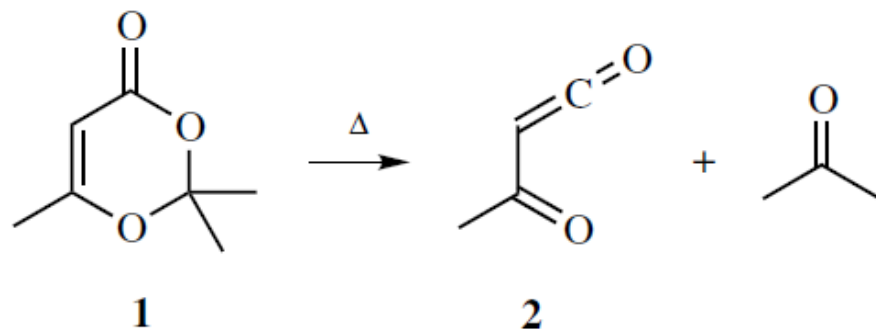
Ketene from cyclobutanone and cyclobutenone



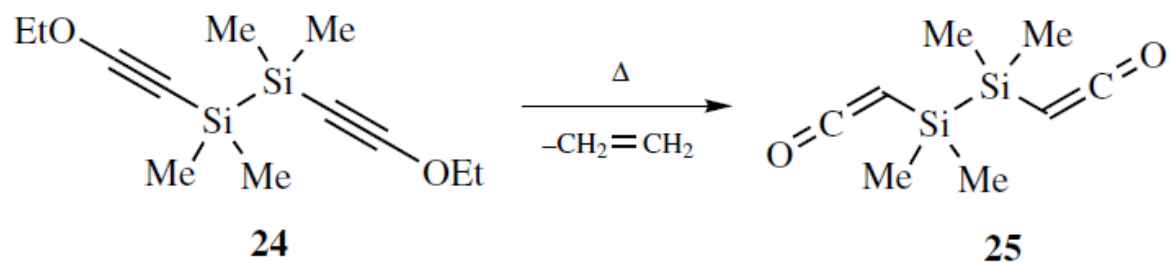
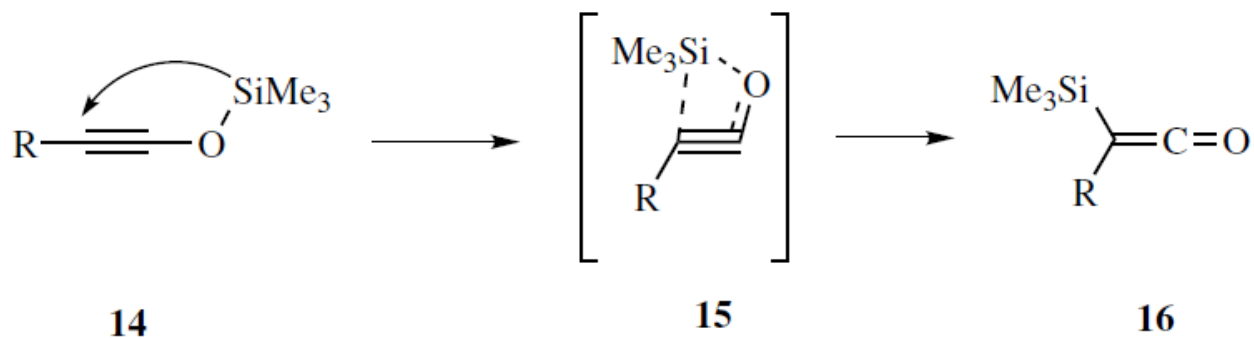
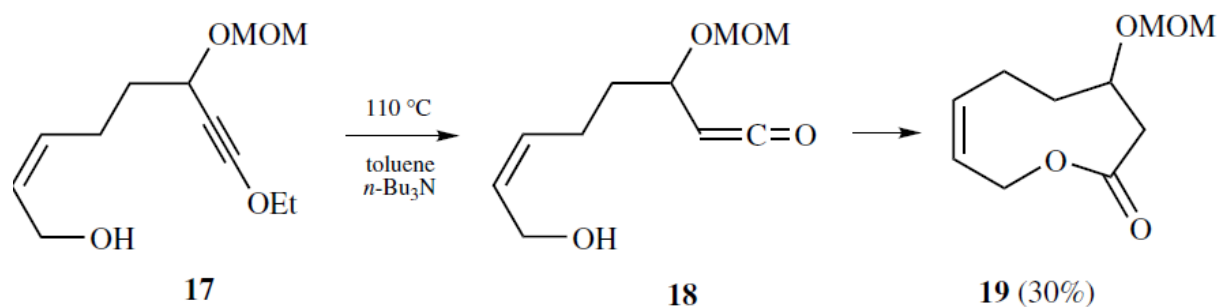
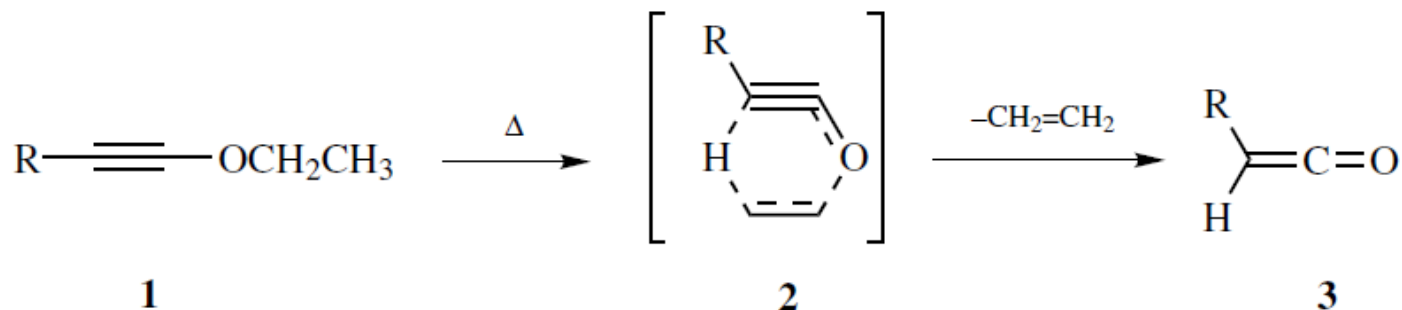
Ketene from cyclobutanone and cyclobutenone



Ketenes from dioxinones

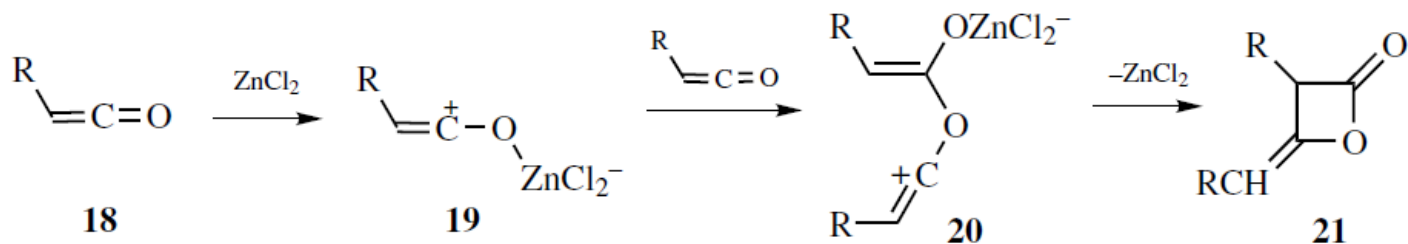
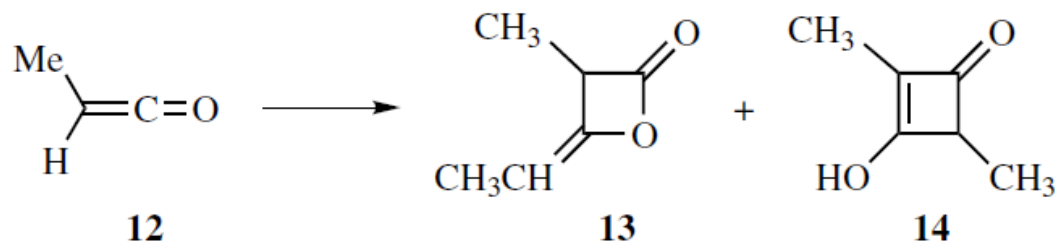
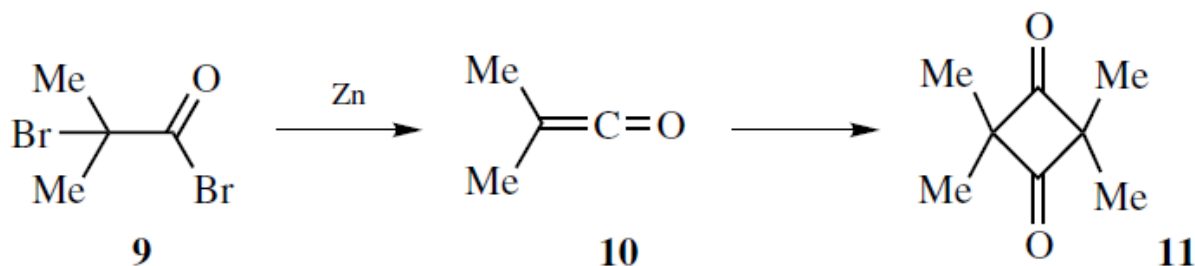
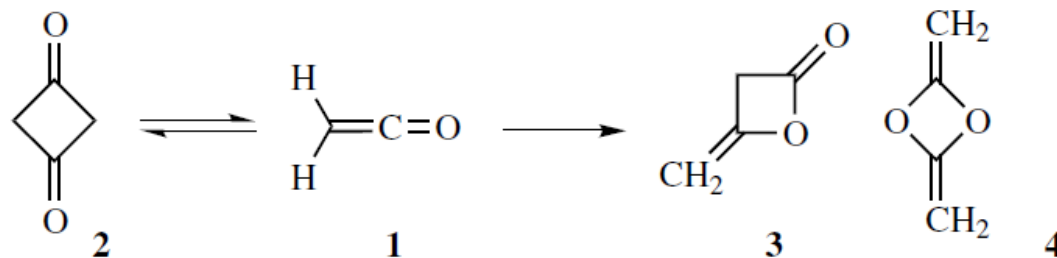


Ketene by thermolysis of Alkynyl ethers



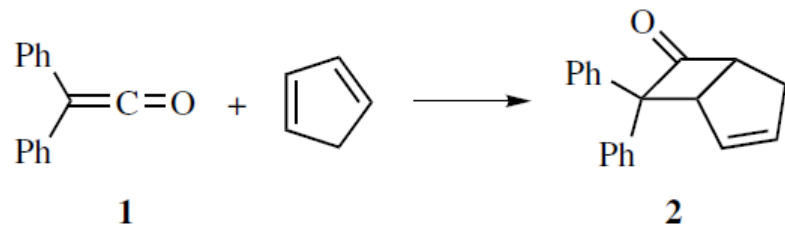
[2+2] cycloaddition of ketenes

Regio-selectivity of [2+2]

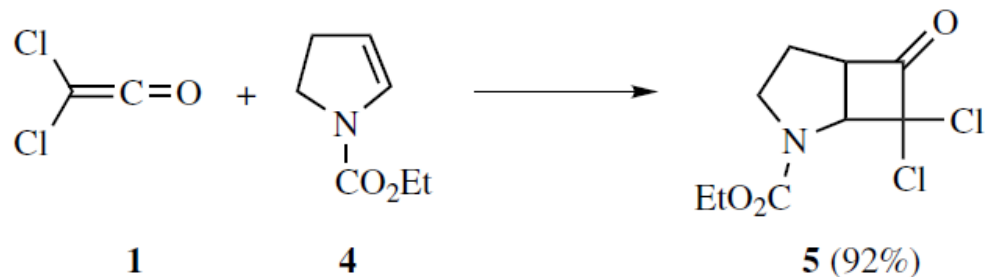


[2+2] cycloaddition of ketenes

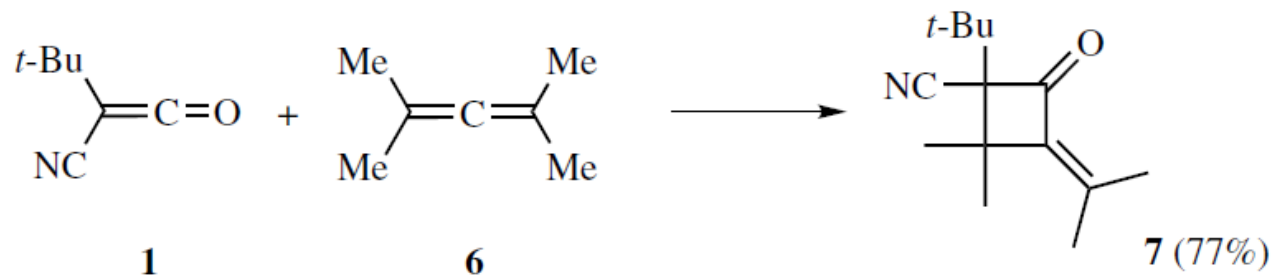
Cycloaddition ketenes with Alkenes



Cycloaddition ketenes with nucleophilic alkenes

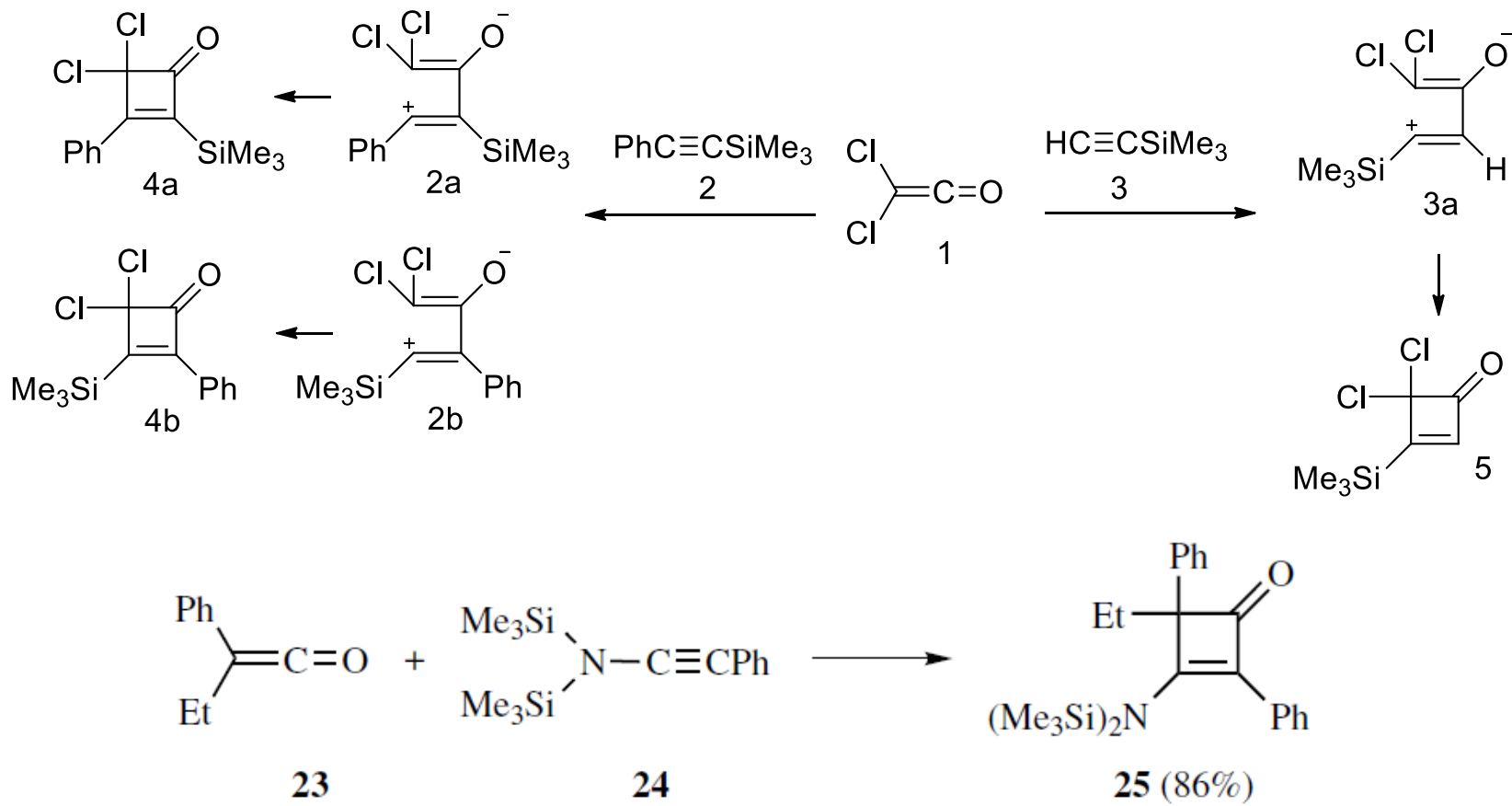


Cycloaddition ketenes with Allenes



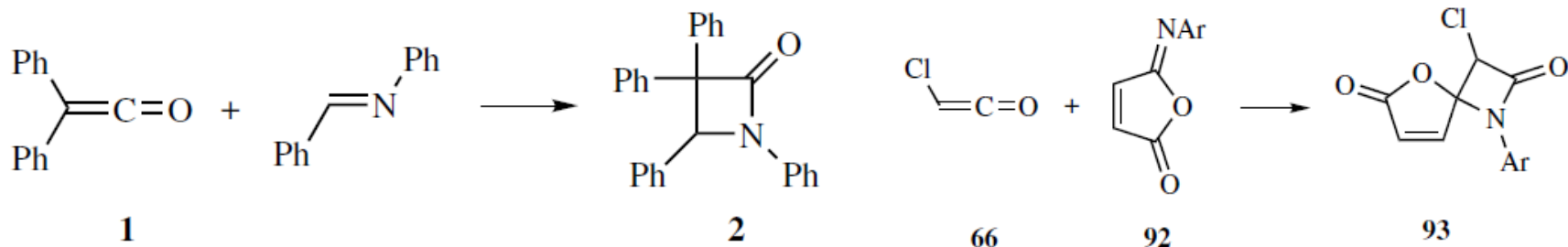
[2+2] cycloaddition of ketenes

Cycloaddition ketenes with alkynes

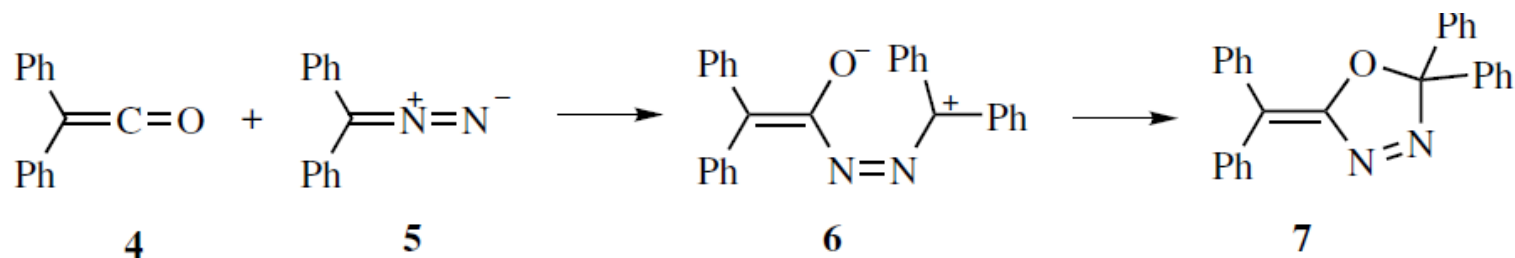


Reactions of ketenes

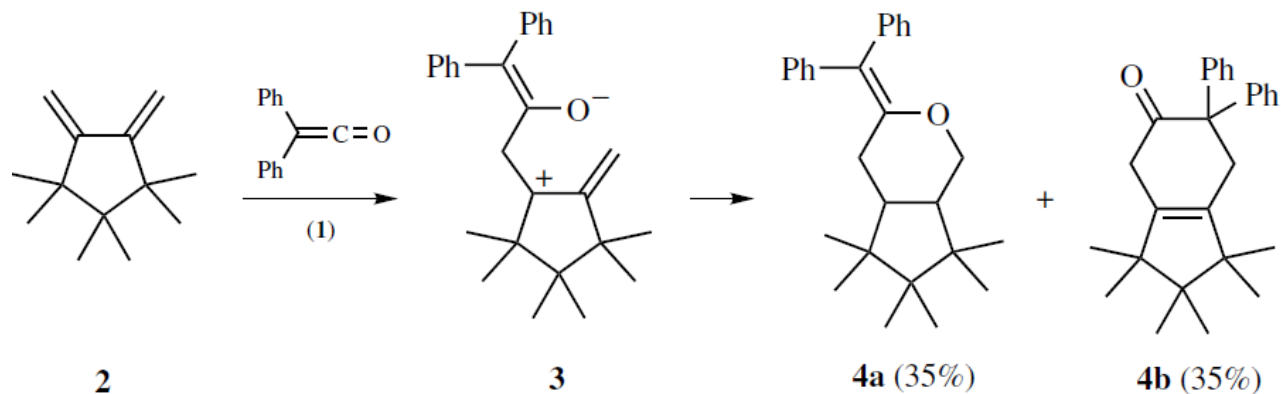
Cycloaddition ketenes with imines form β -lactam



[3+2] Cycloaddition of ketenes

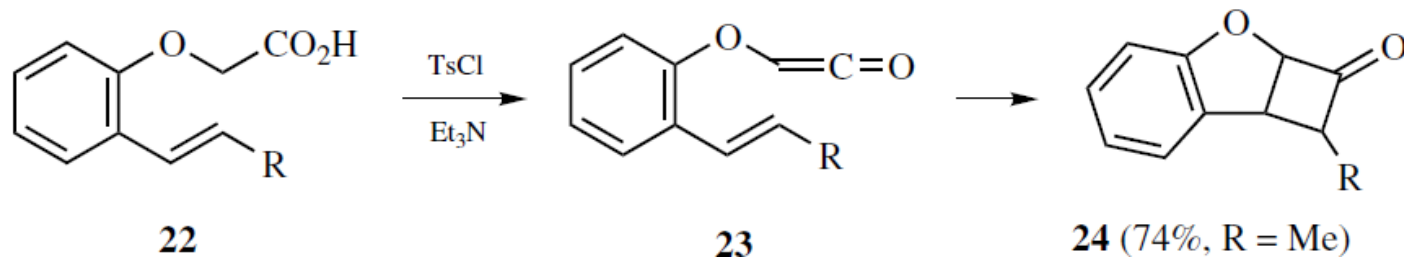


[4+2] Cycloaddition of ketenes

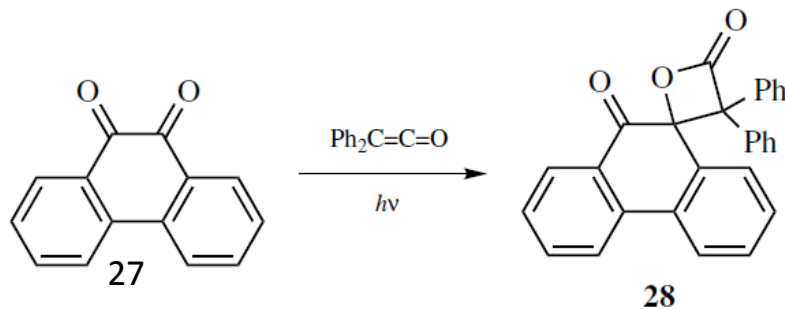


Reactions of ketenes

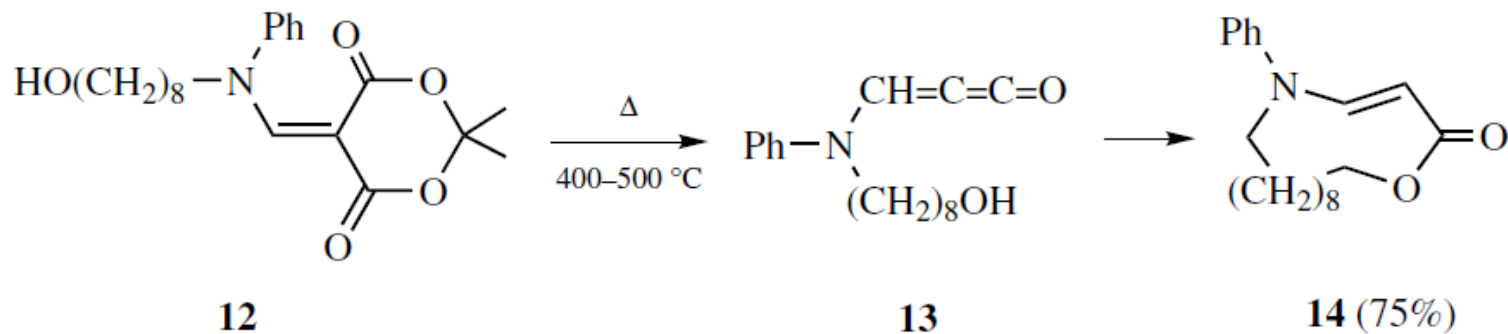
Intramolecular cycloaddition of ketenes



cycloaddition of ketenes with carbonyl groups

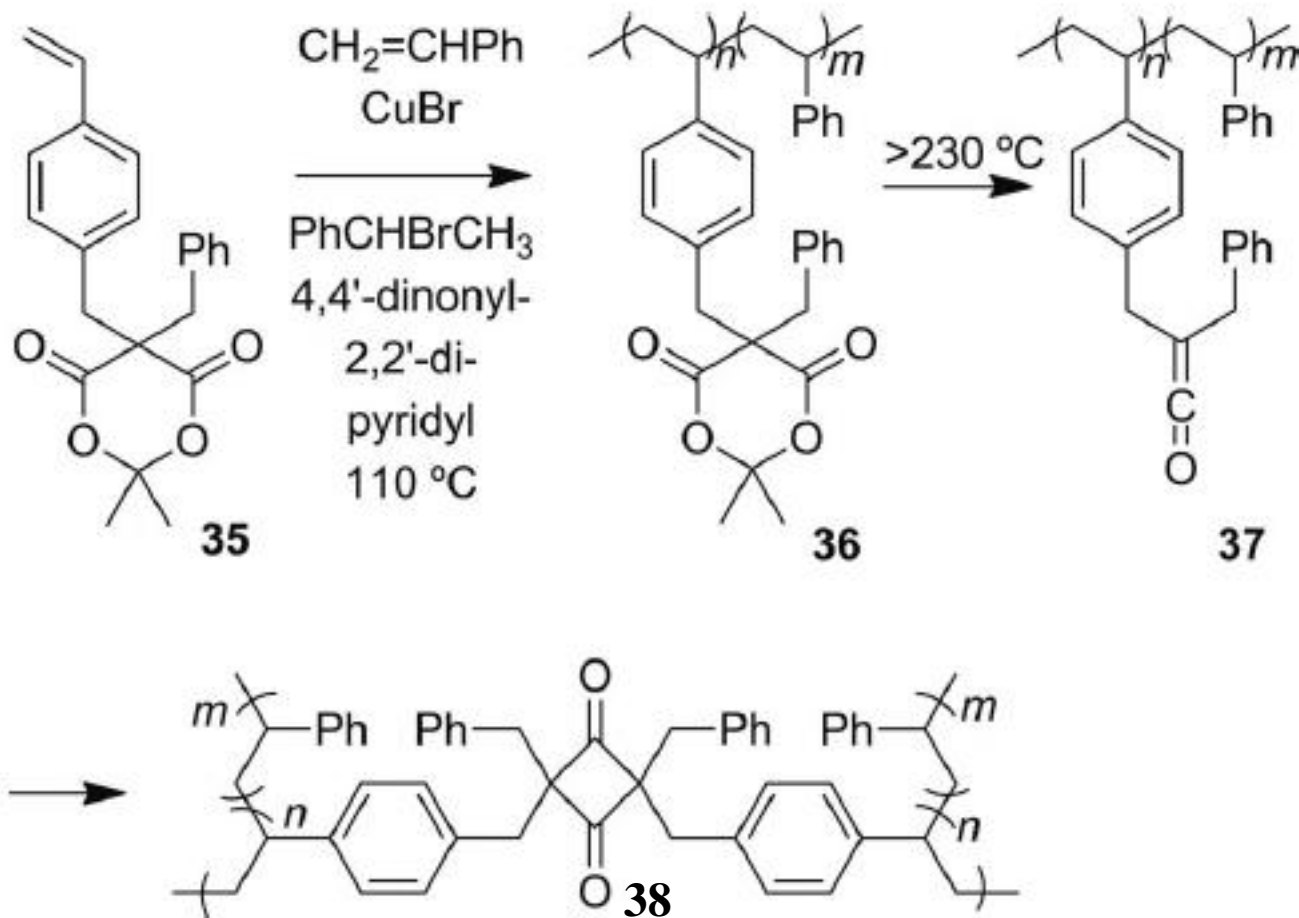


Nucleophilic addition to ketenes

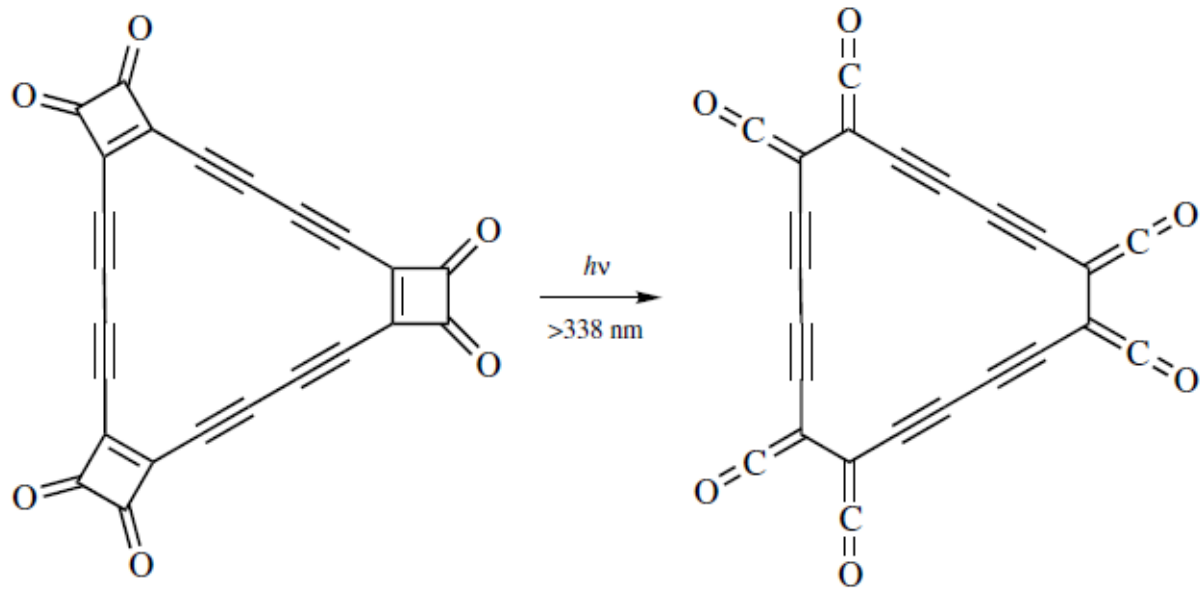


Ketenes in synthesis

Ketenes in polymer chemistry

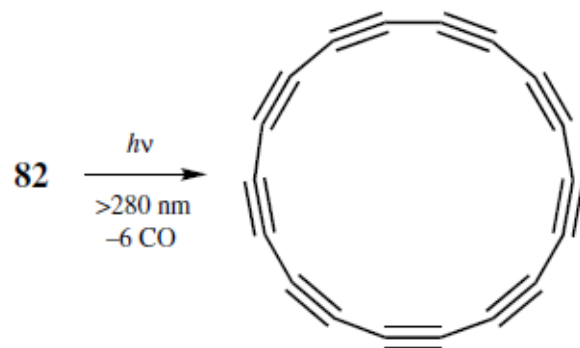


Ketenes in polymer chemistry



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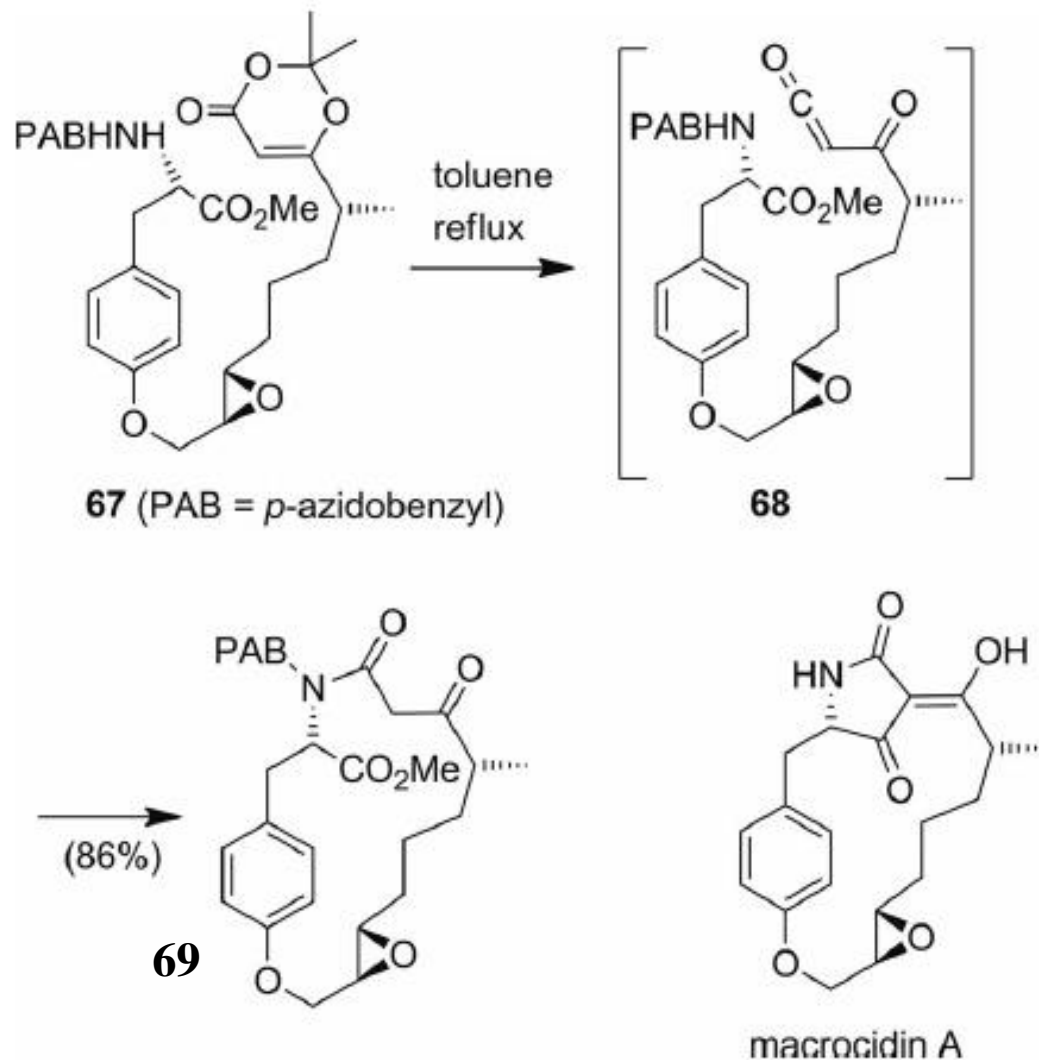
82



83

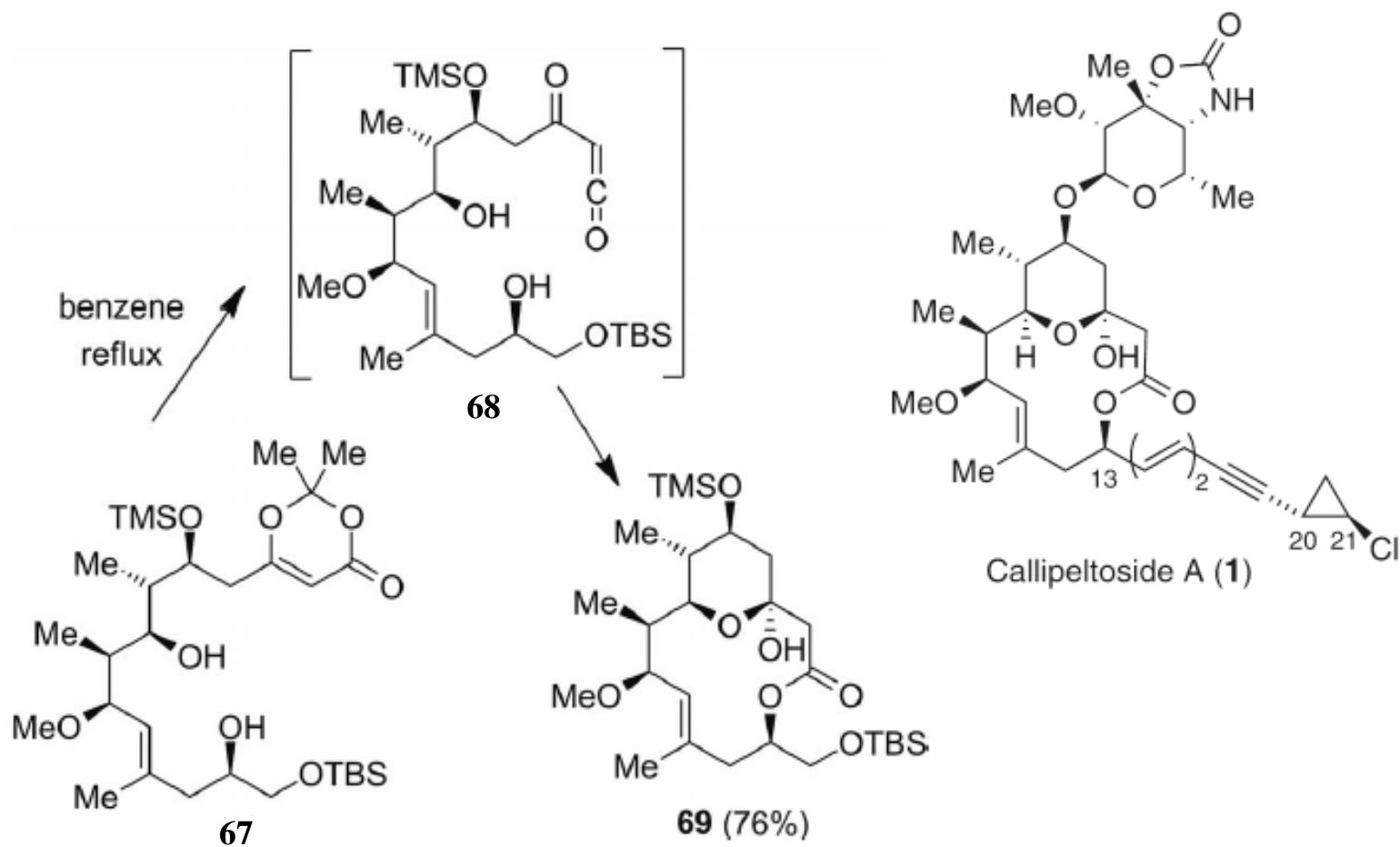
Ketenes in synthesis

Total synthesis of macrocycin A



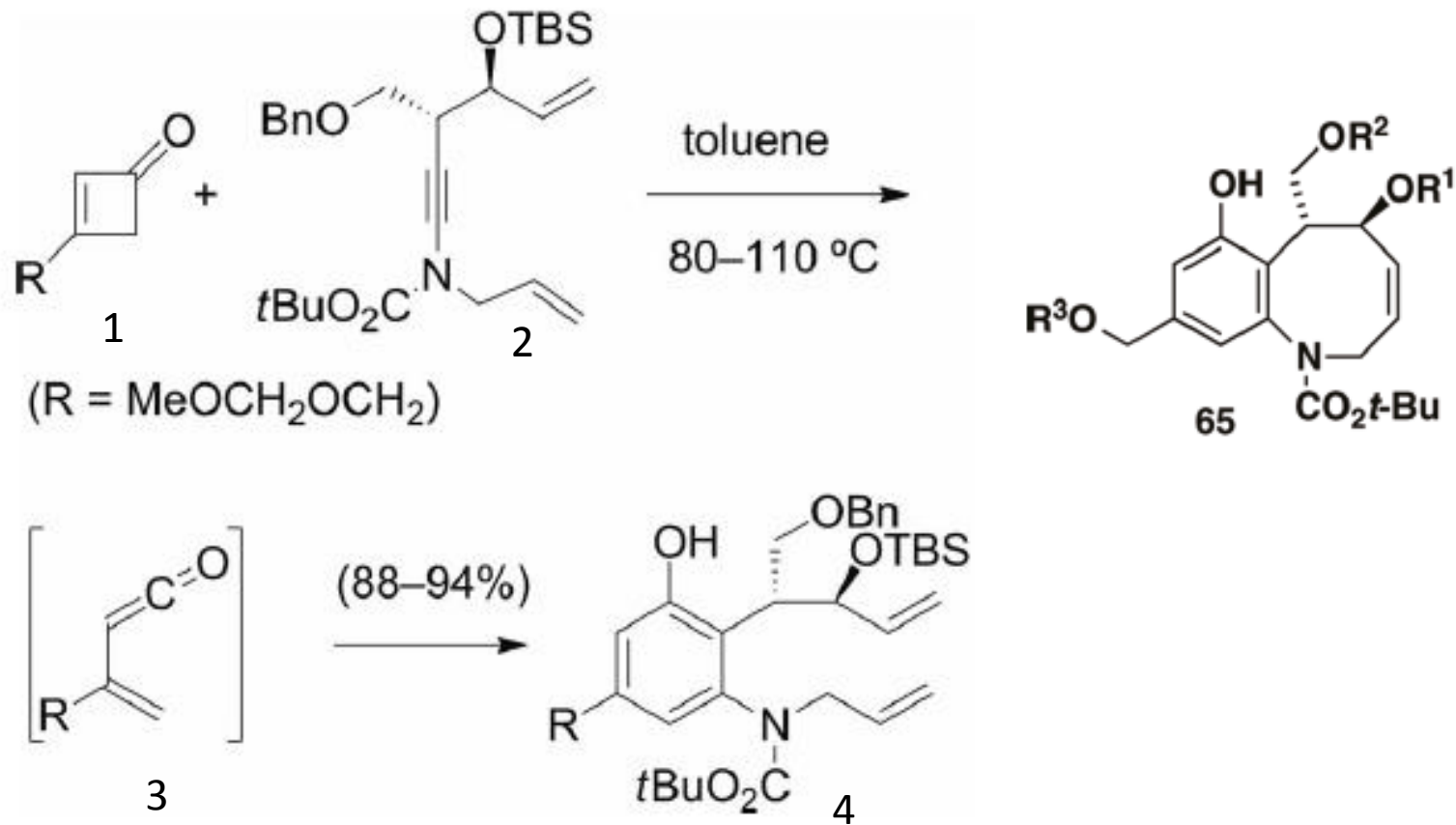
Ketenes in synthesis

Total synthesis of (-)-callipeltoside A



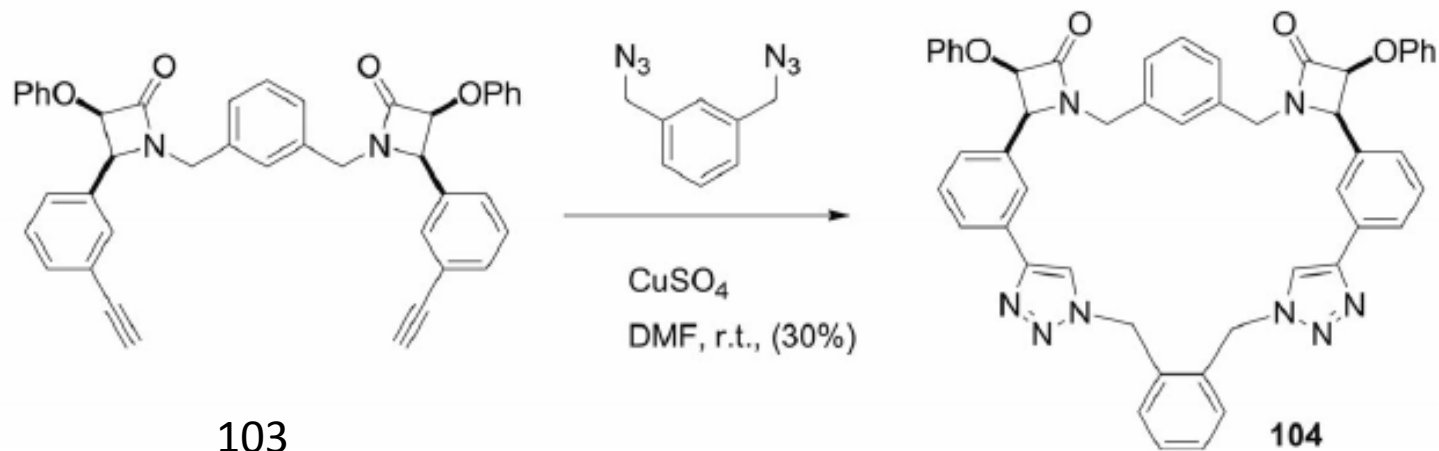
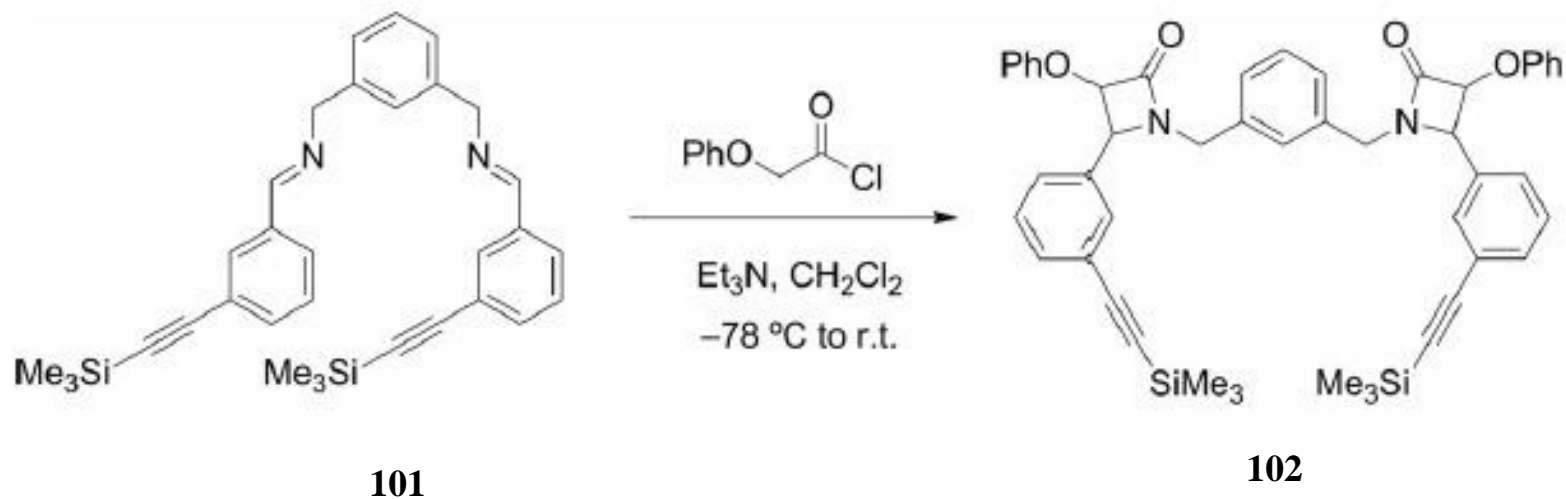
Ketenes in synthesis

Synthesis antitumor agent (+)-FR900482



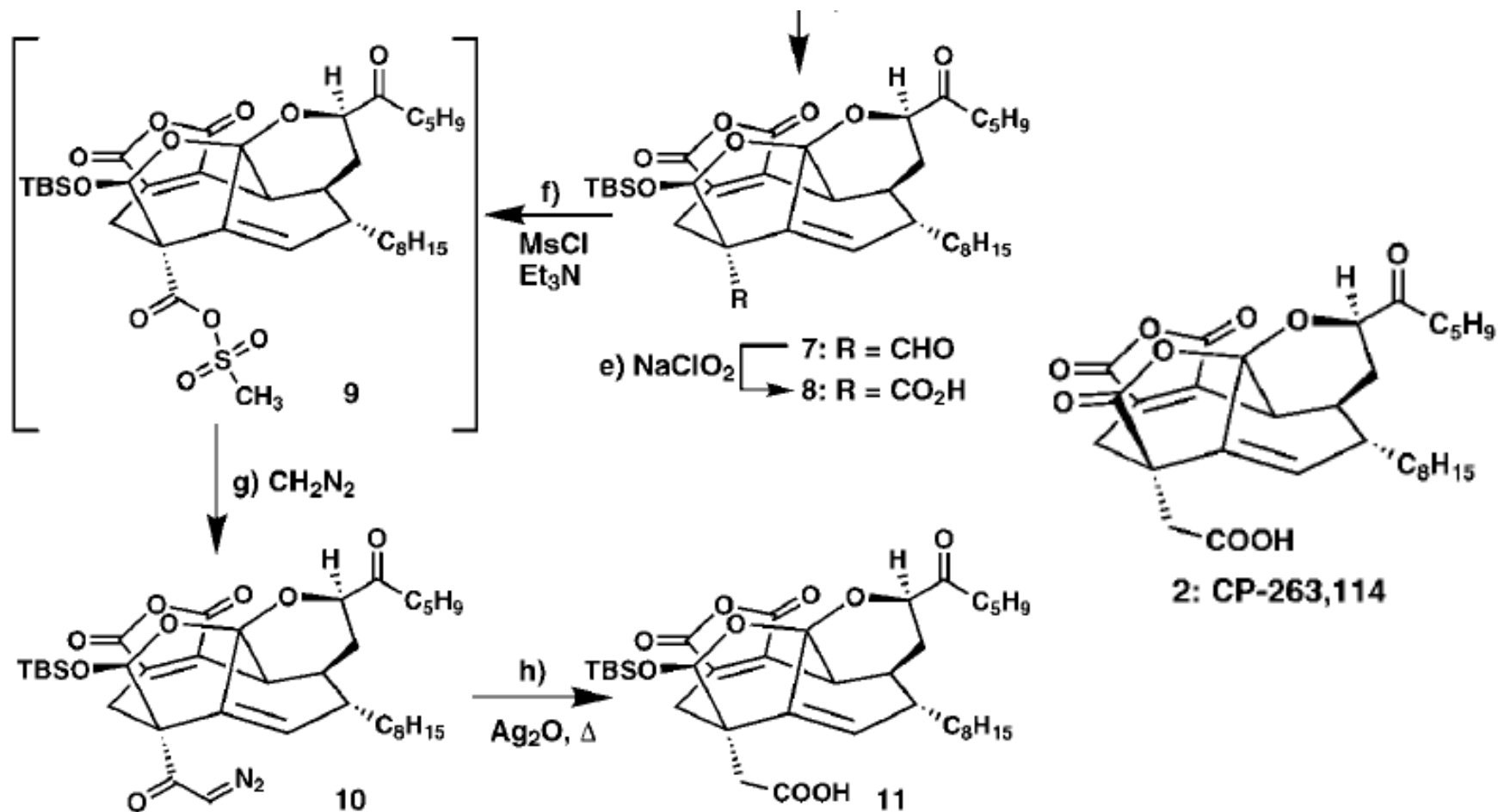
Ketenes in synthesis

Bis (β -lactam) preparation



Ketenes in synthesis

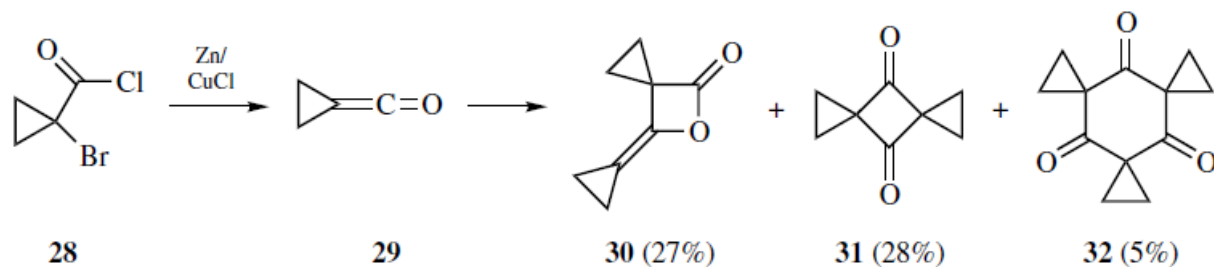
Synthesis CP-263



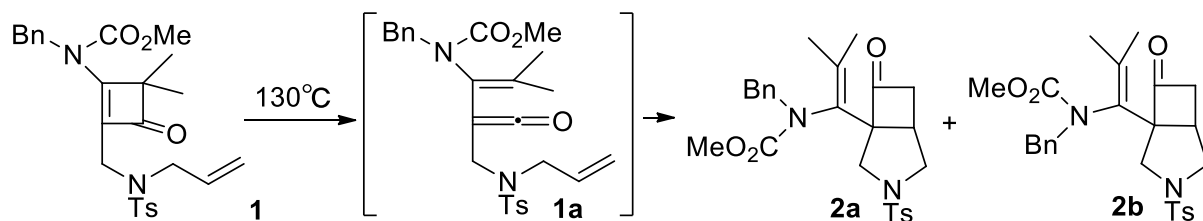
Thanks!
Congratulations to Huang and Zhe!



Question 1



Question 2



Question 3

