Reakcje Diesla-Aldera i inne reakcje cykloaddycji

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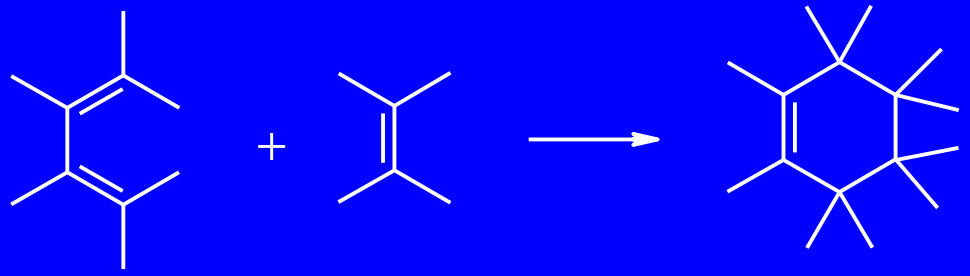
Reakcje cykloaddycji

$S^1 + S^2 + \ldots S^n$ S

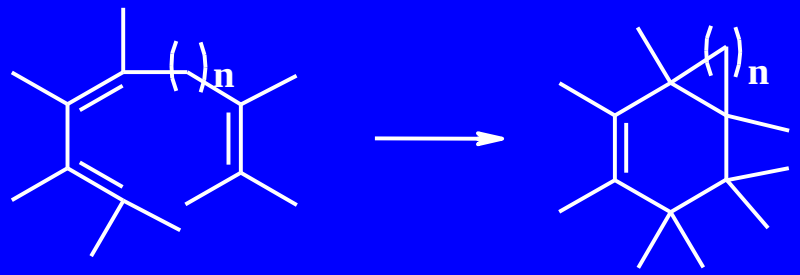
Produkt cykliczny

Reakcje Dielsa-Aldera

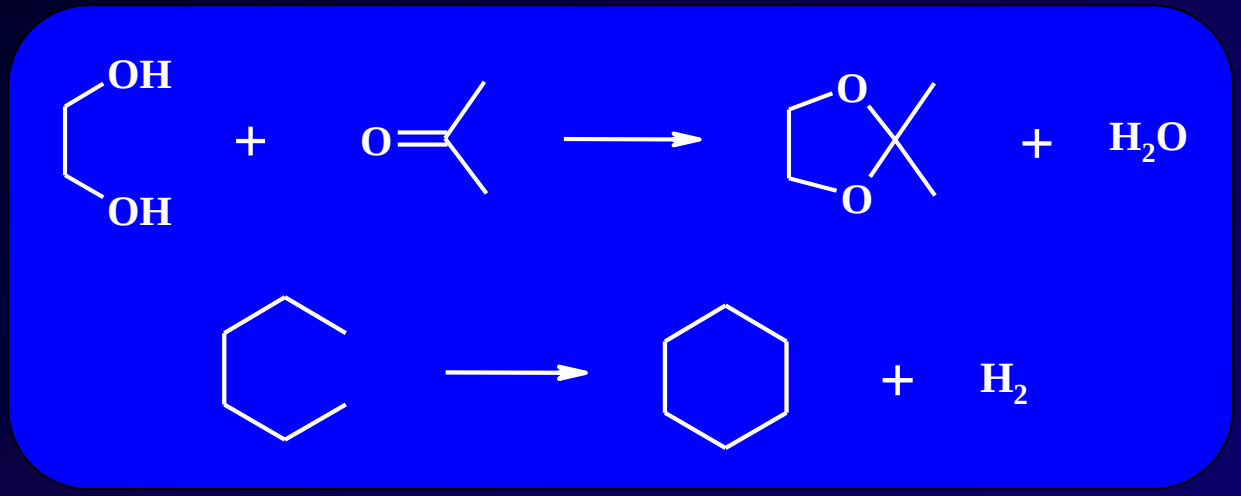
Intermolecular

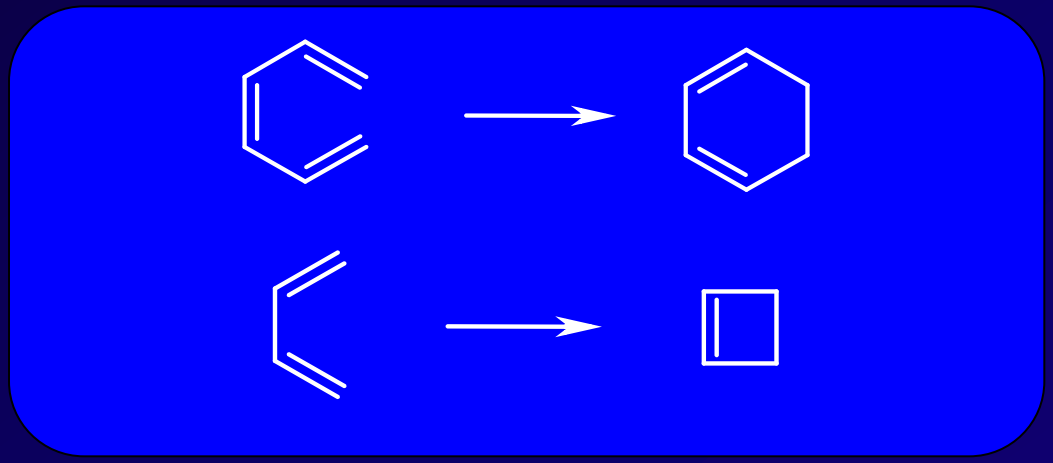


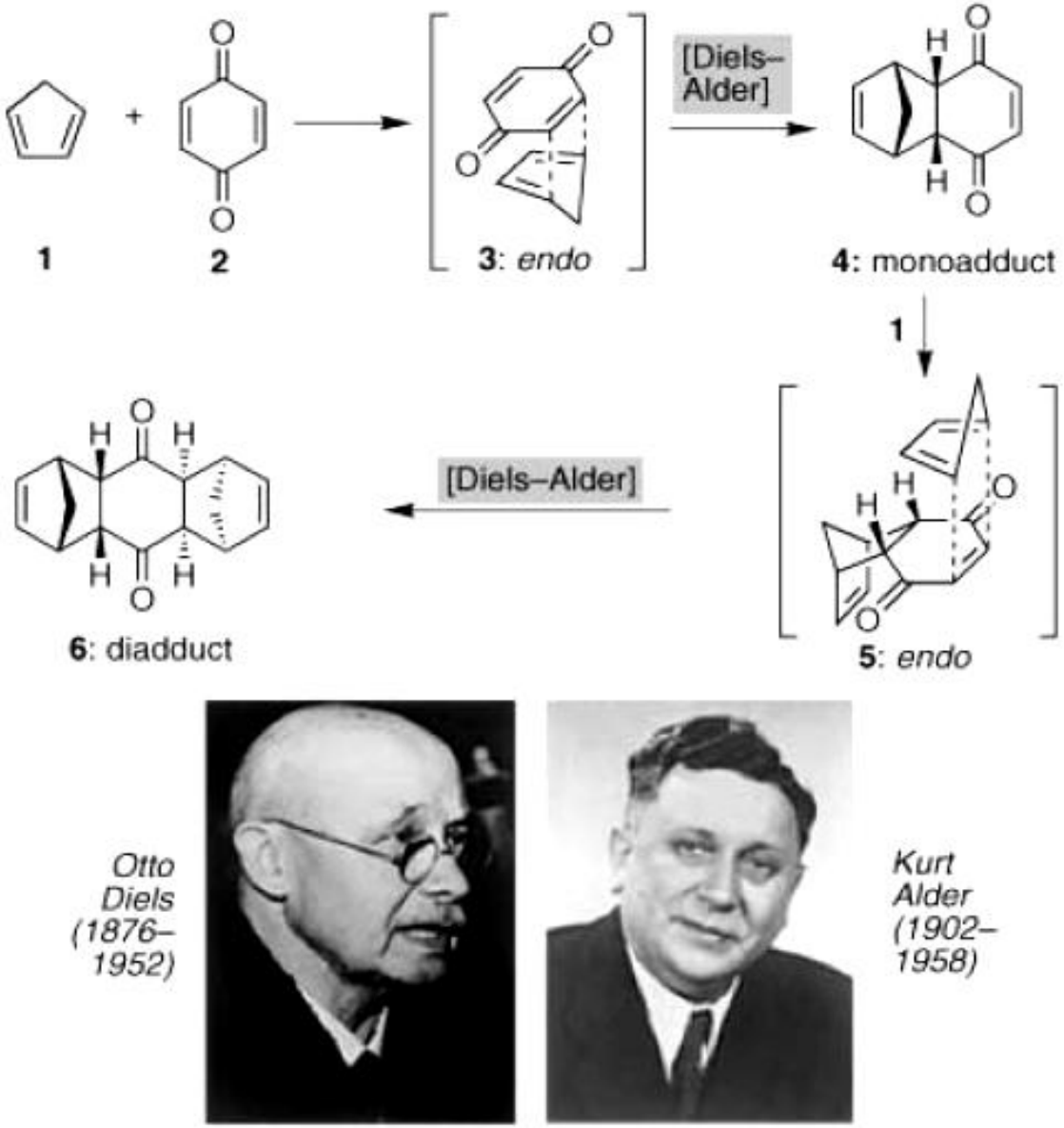
Intramolecular



Cykloaddycja, cyklokondensacja, reakcje elektrocykliczne



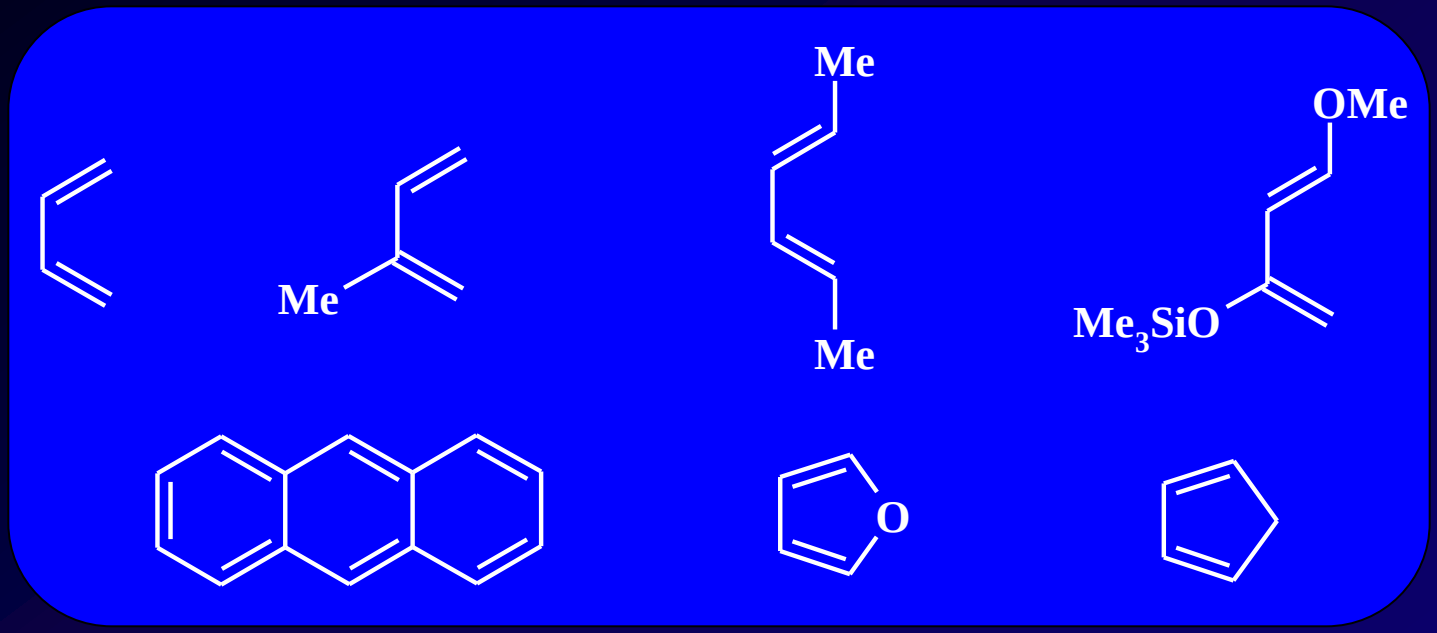


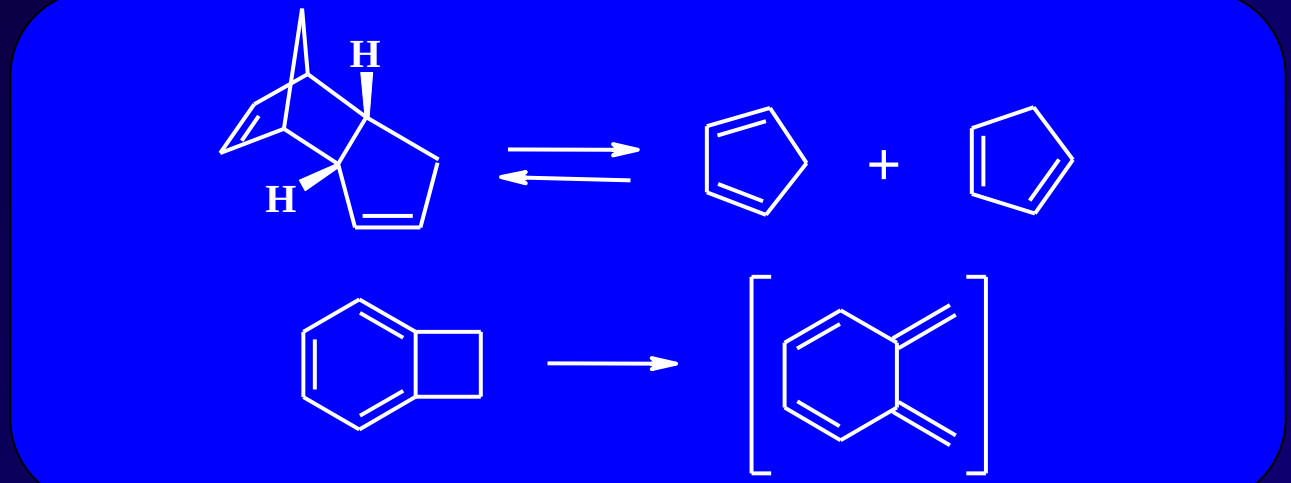


Scheme 1. The discovery of the Diels–Alder reaction in 1928, a reaction for which the namesakes would receive the Nobel Prize in Chemistry in 1950: Diels the professor, Alder the student.[5]

Reakcje Dielsa-Aldera

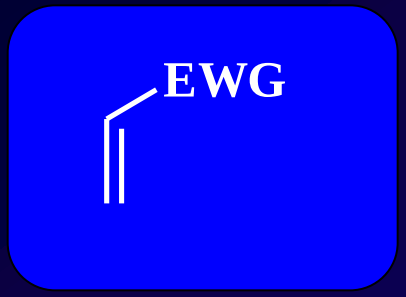
Dieny





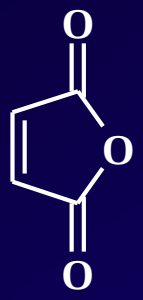
Reakcje Dielsa-Aldera

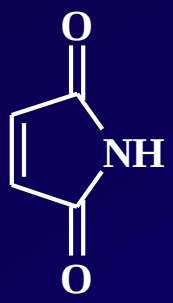
Dienofile

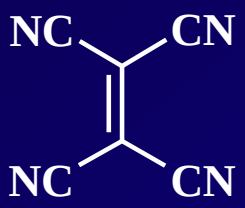


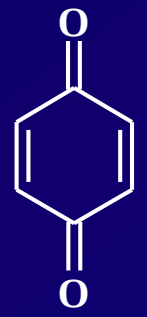
CHO, COOR, CN

NO_2, Aryl, COR

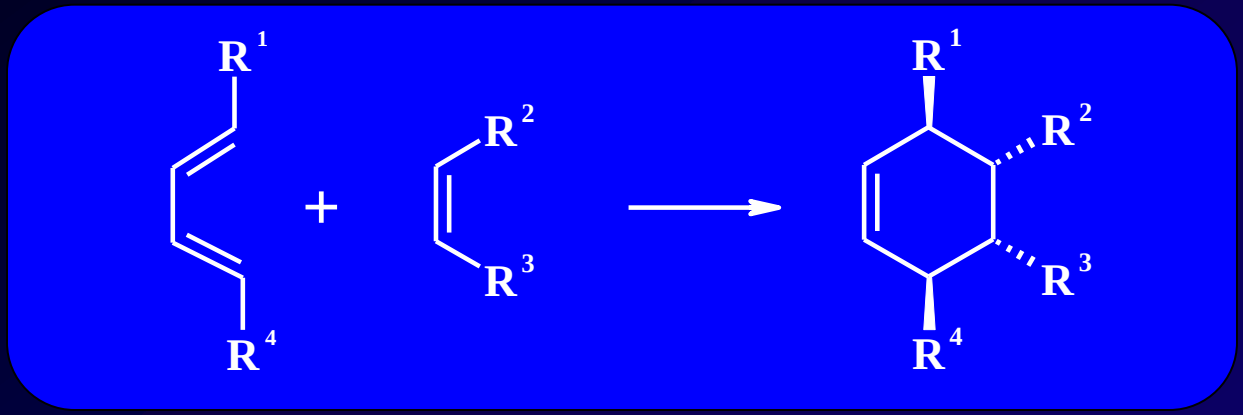




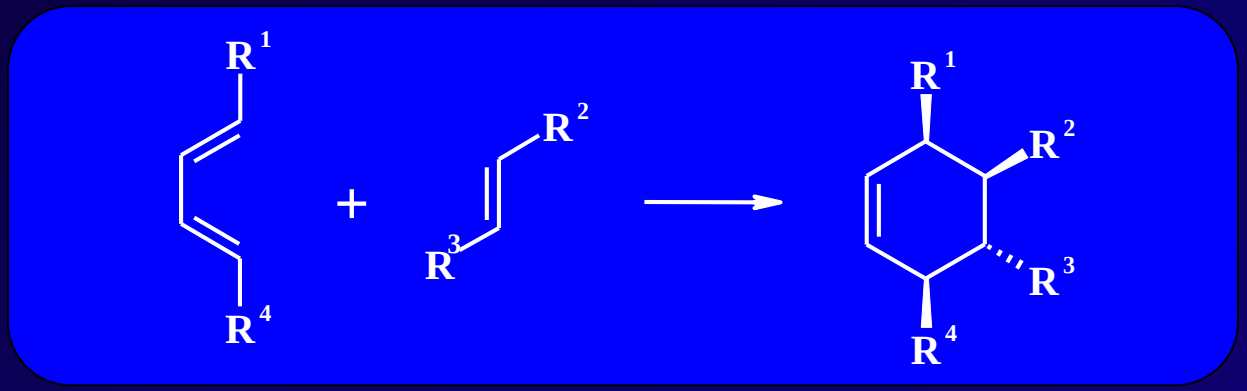




Cykloaddycja [4 + 2]
Stereoselektywność



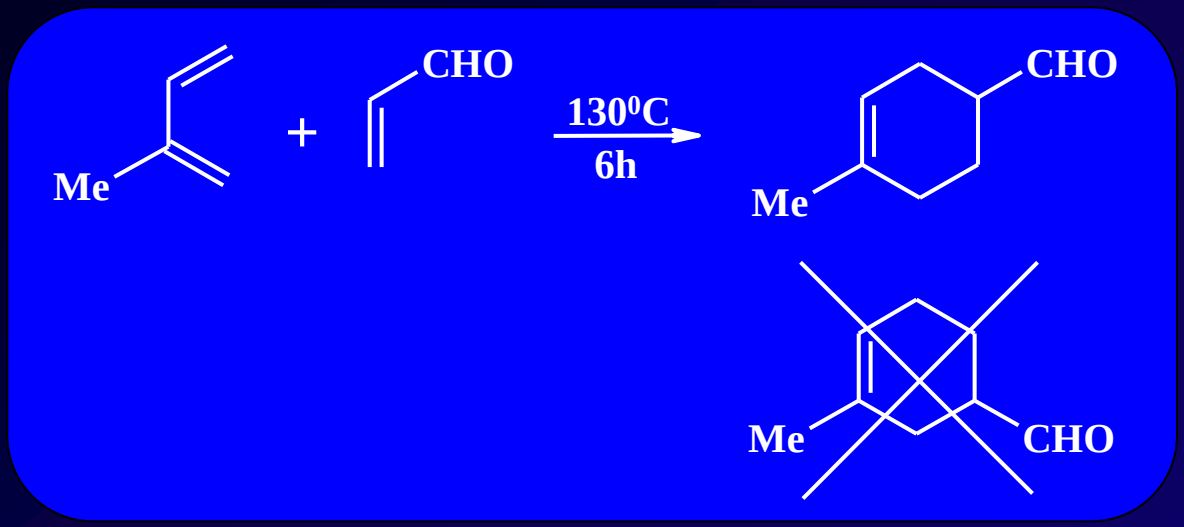
R^1/R^4 i R^2/R^3 syn; R^1/R^2 i R^3/R^4 anti

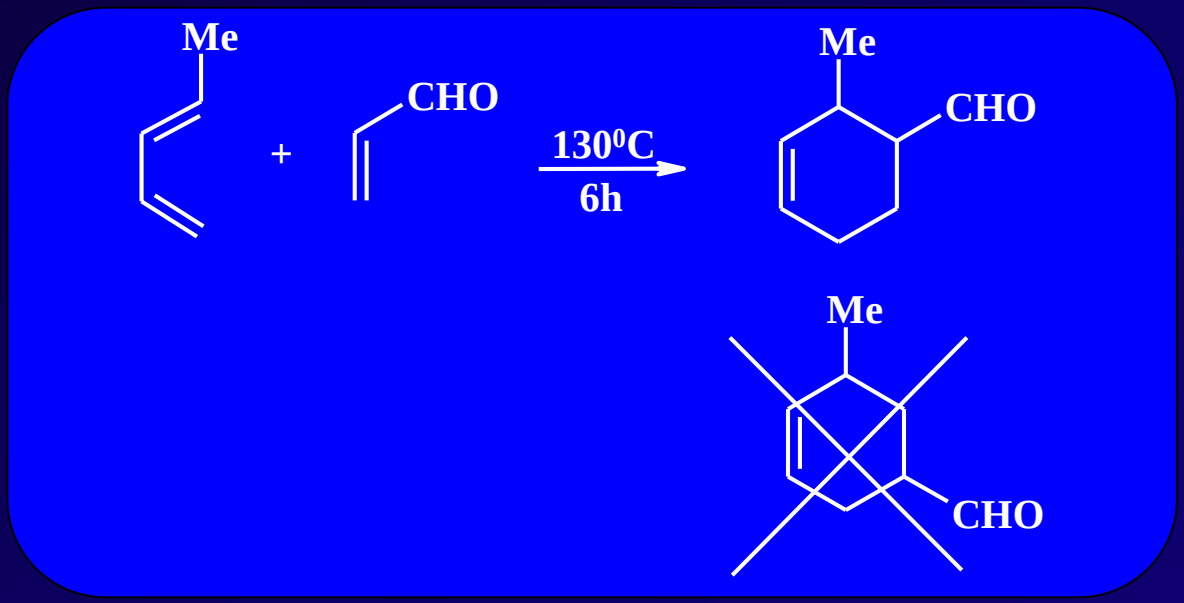


R^1/R^4 i R^1/R^2 syn; R^2/R^3 i R^3/R^4 anti

Reakcja Dielsa-Aldera

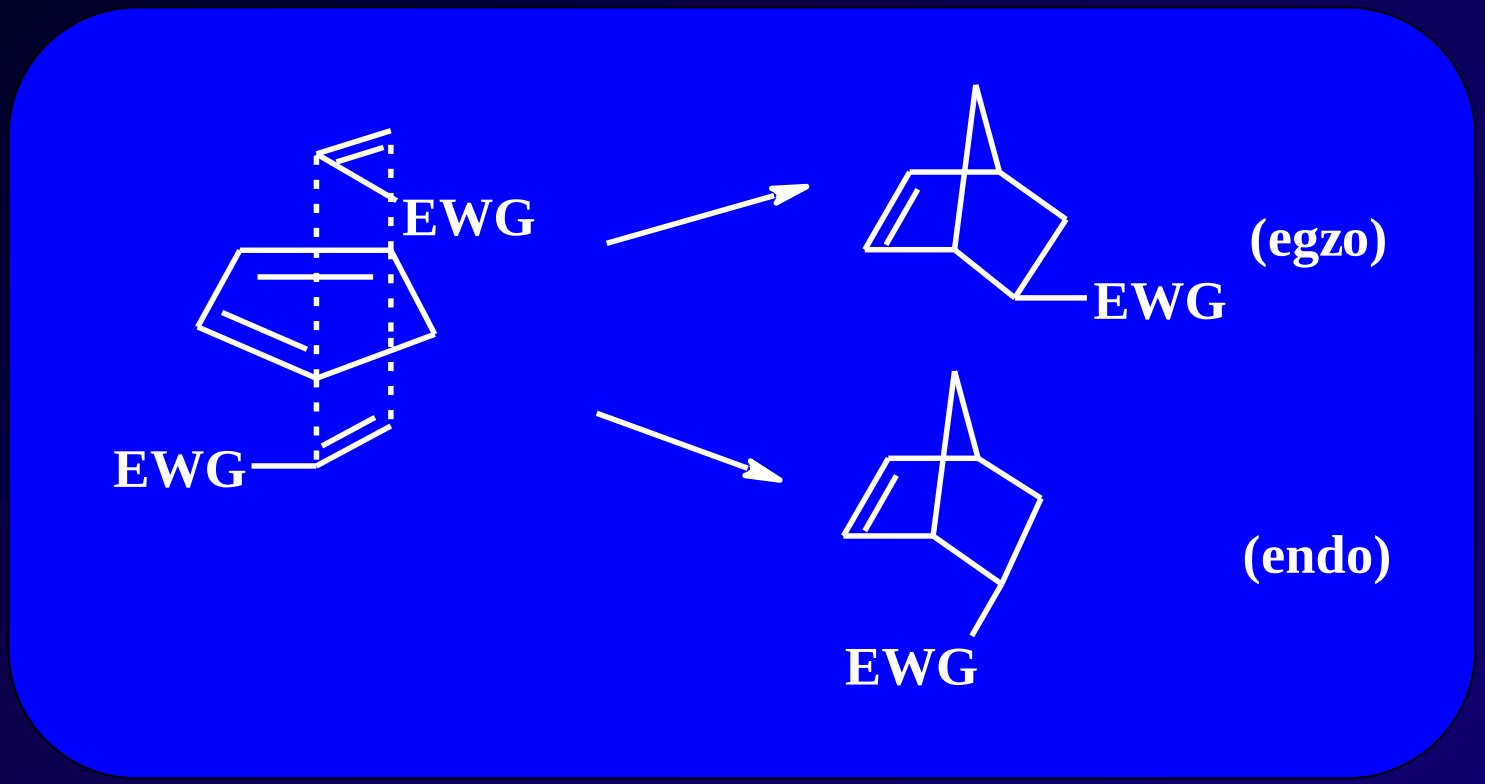
Regioselektywność





Reakcja Dielsa-Aldera

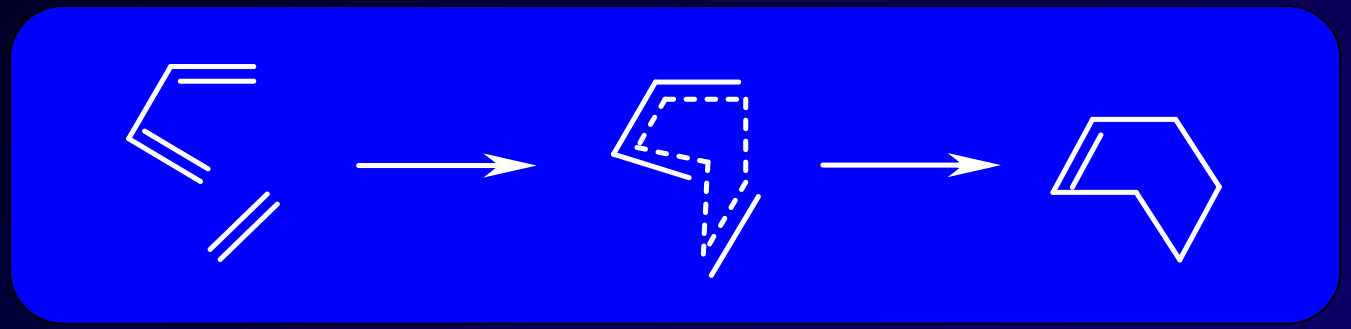
Addukty endo- i egzo-

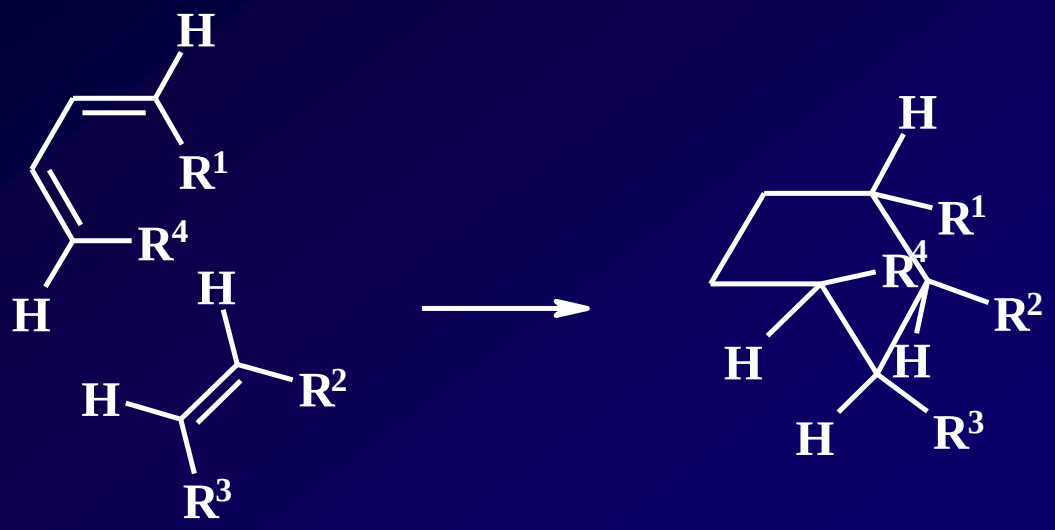


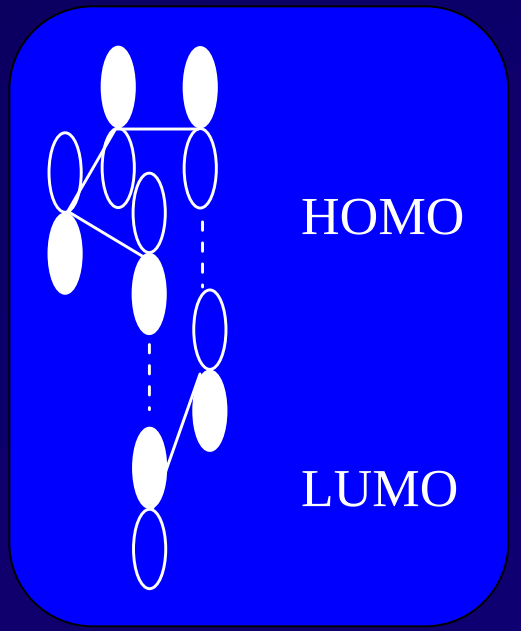
EWG = CHO, NO_2, COOH, …

Reakcja Dielsa-Aldera

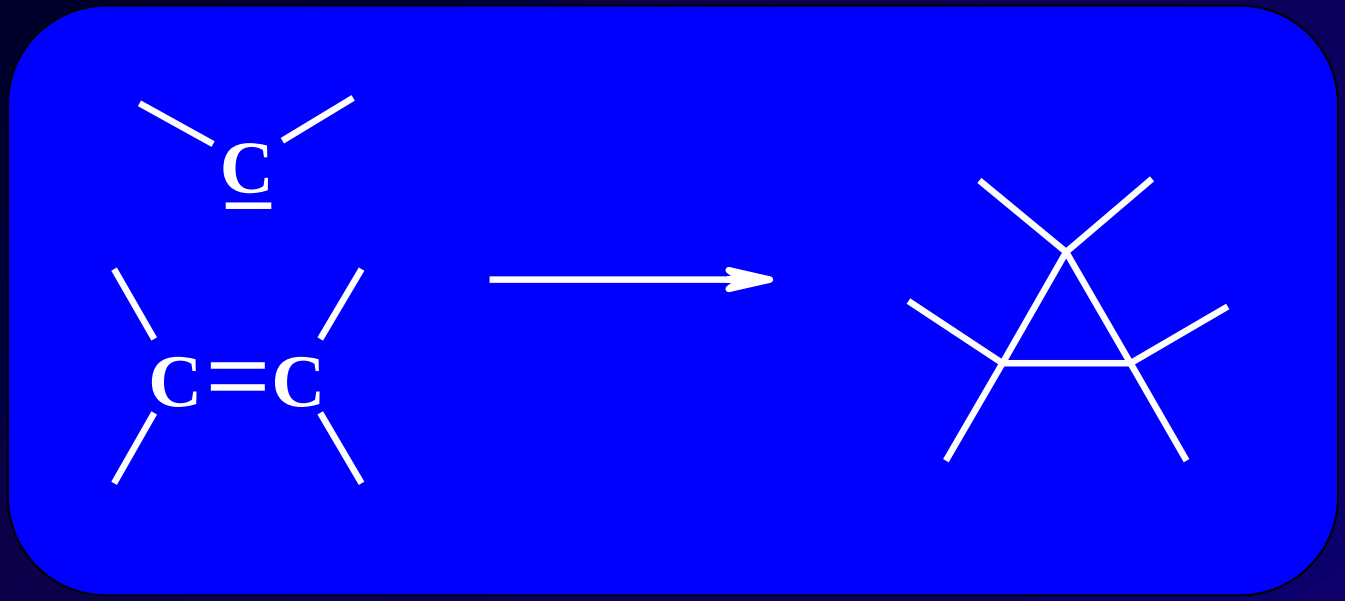
Mechanizm





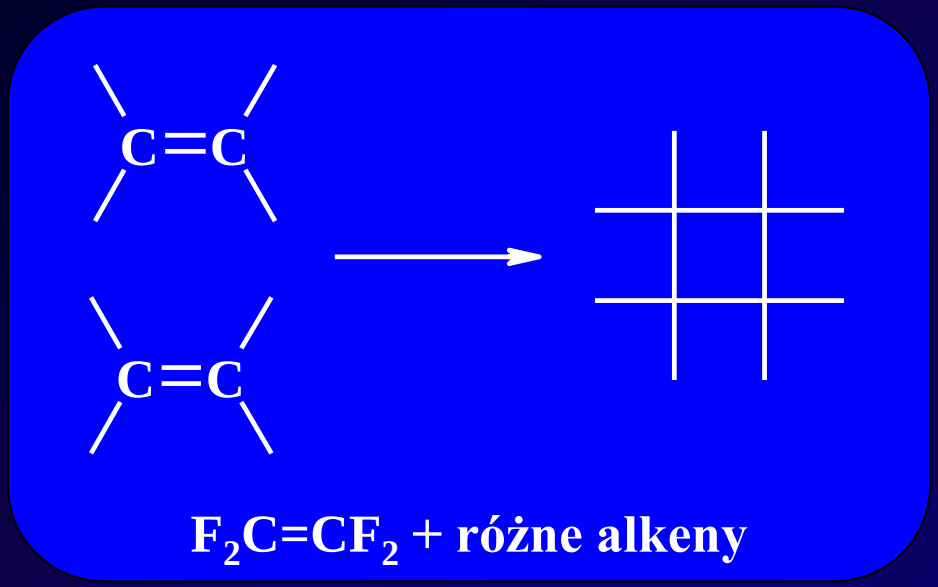


Cykloaddycja [2 + 1]

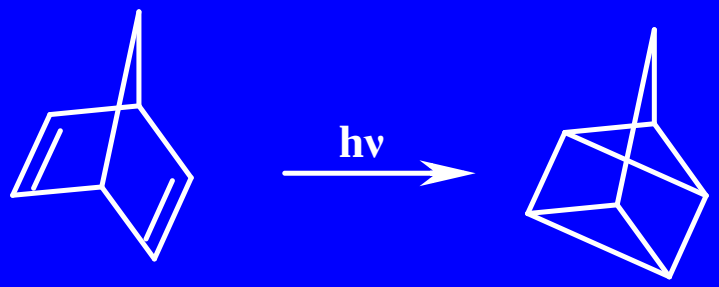


CH_2 CCl_2 $C(CN)_2$ PhCH

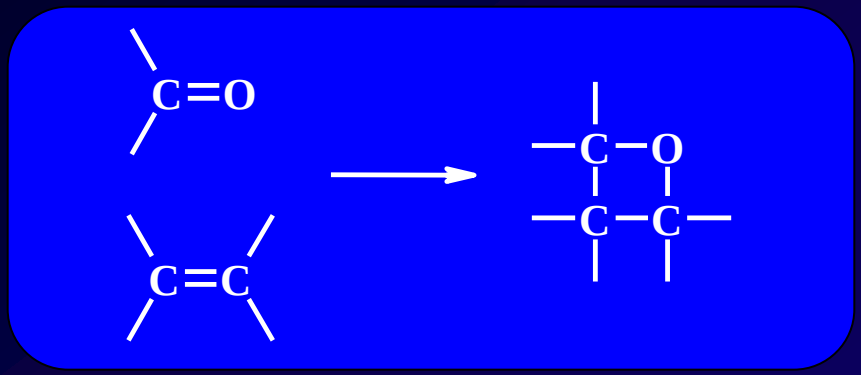
Cykloaddycja [2 + 2]

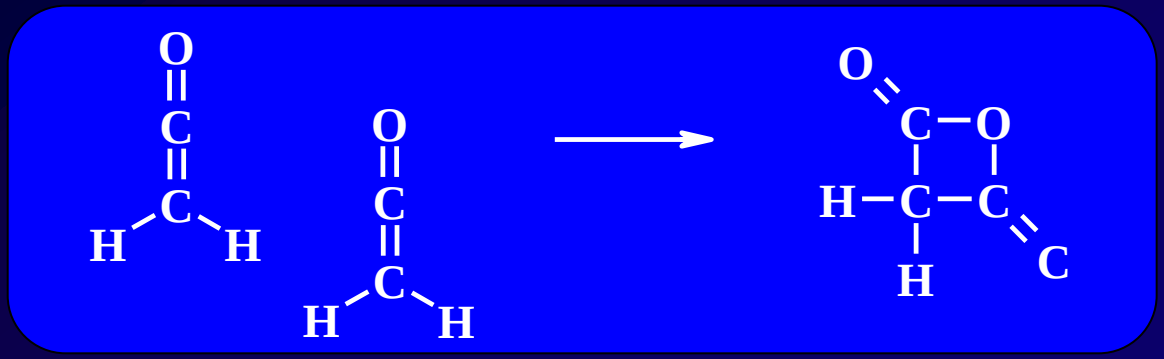


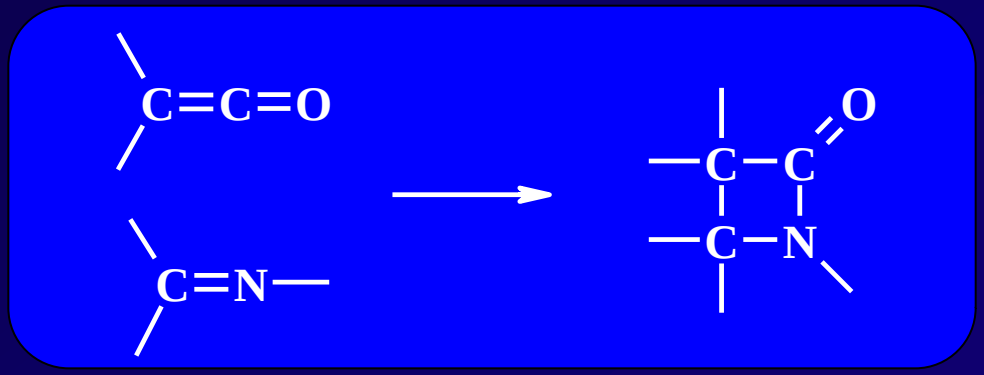
$F_2C{=}CF_2$ + różne alkeny



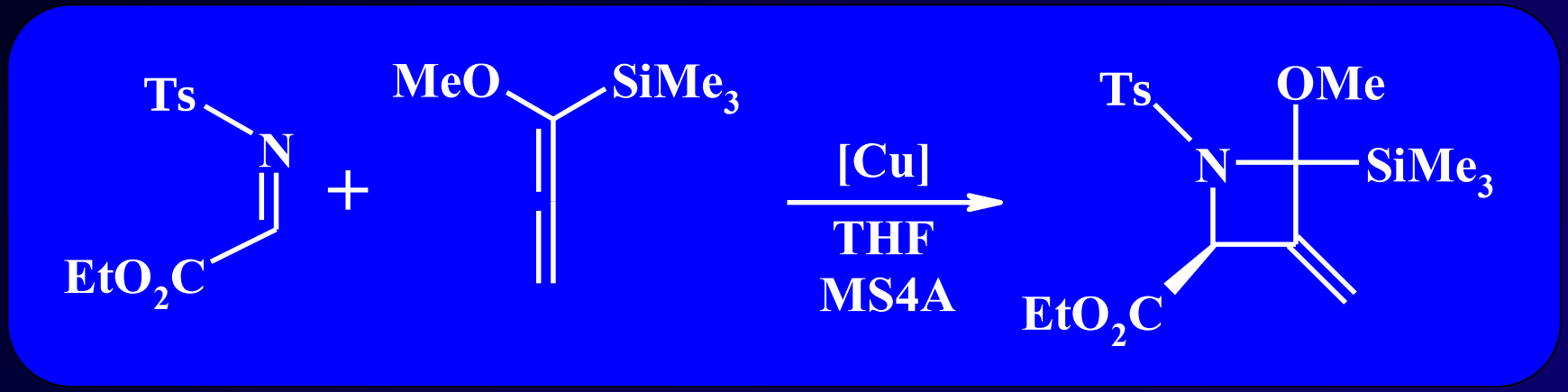
Cykloaddycja [2 + 2]
Heterocykloaddycja







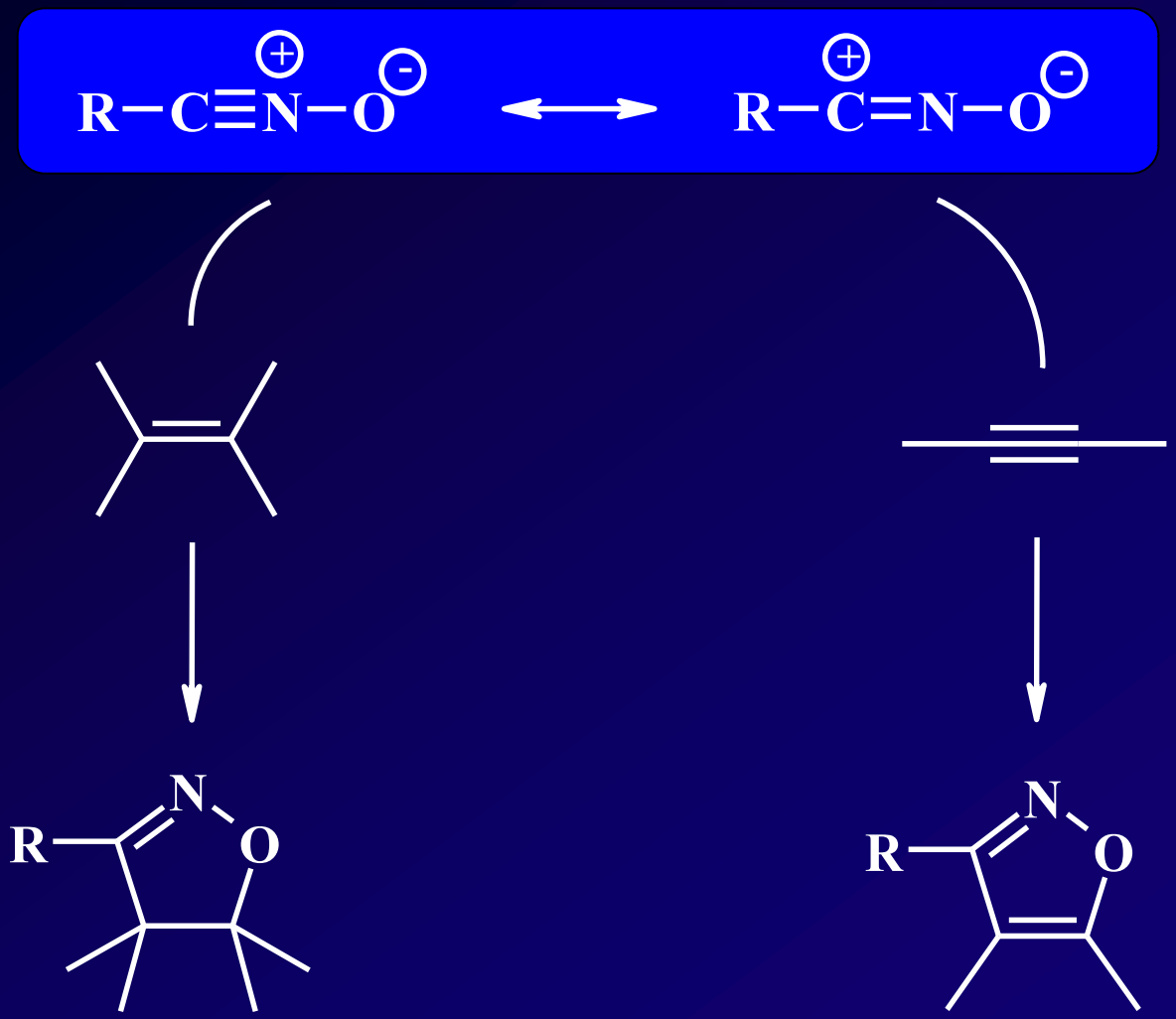
Asymetryczna cykloaddycja [2 + 2]



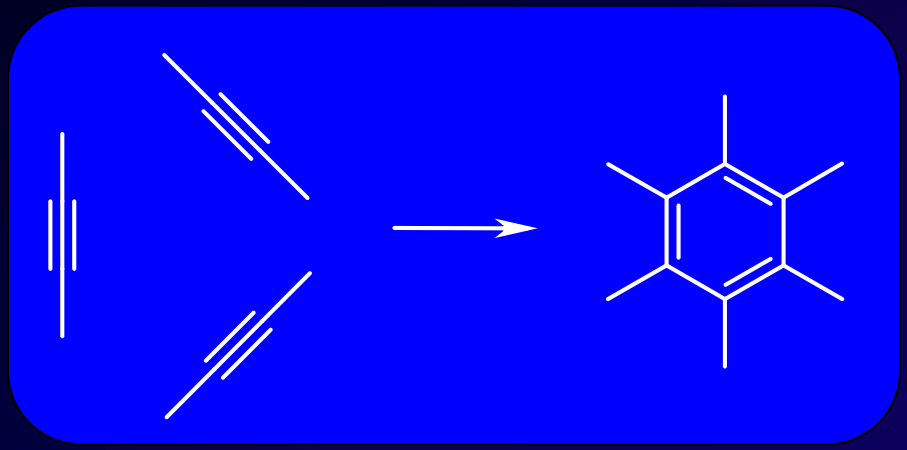
The Enantioselective cycloaddition of allenylsilanes with a imino ester

Cykloaddycja [3 + 2]

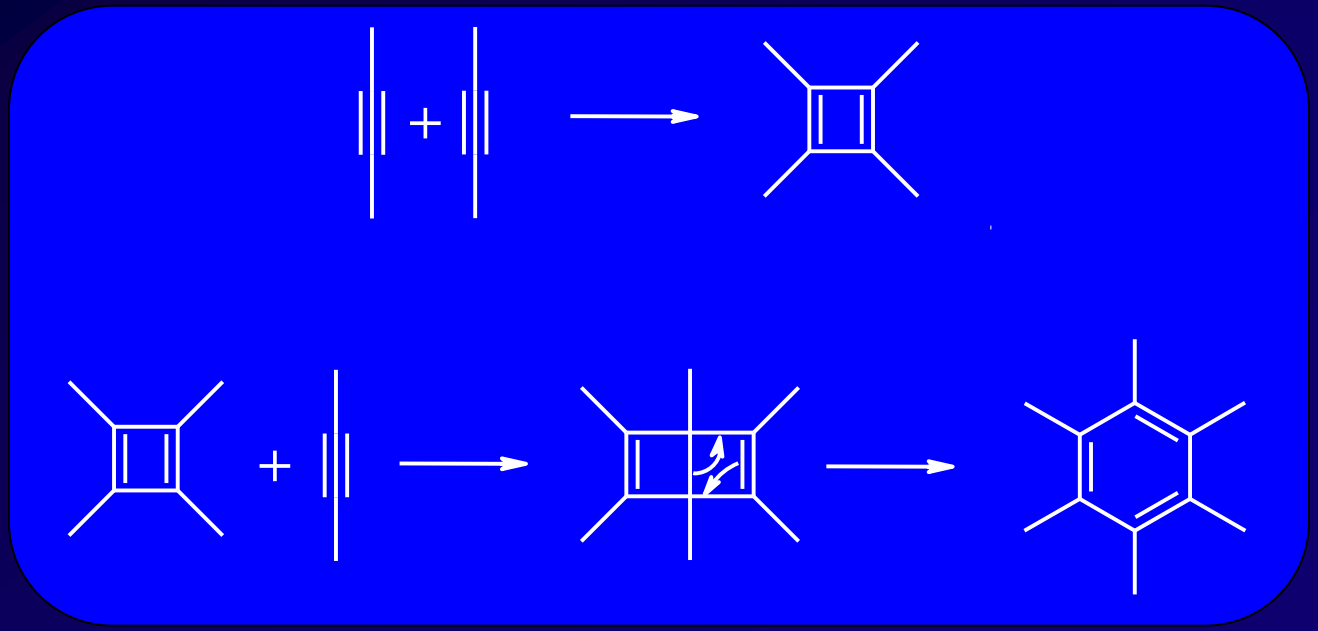
Cykloaddycja dipolarna tlenków nitryli do alkenów lub alkinów



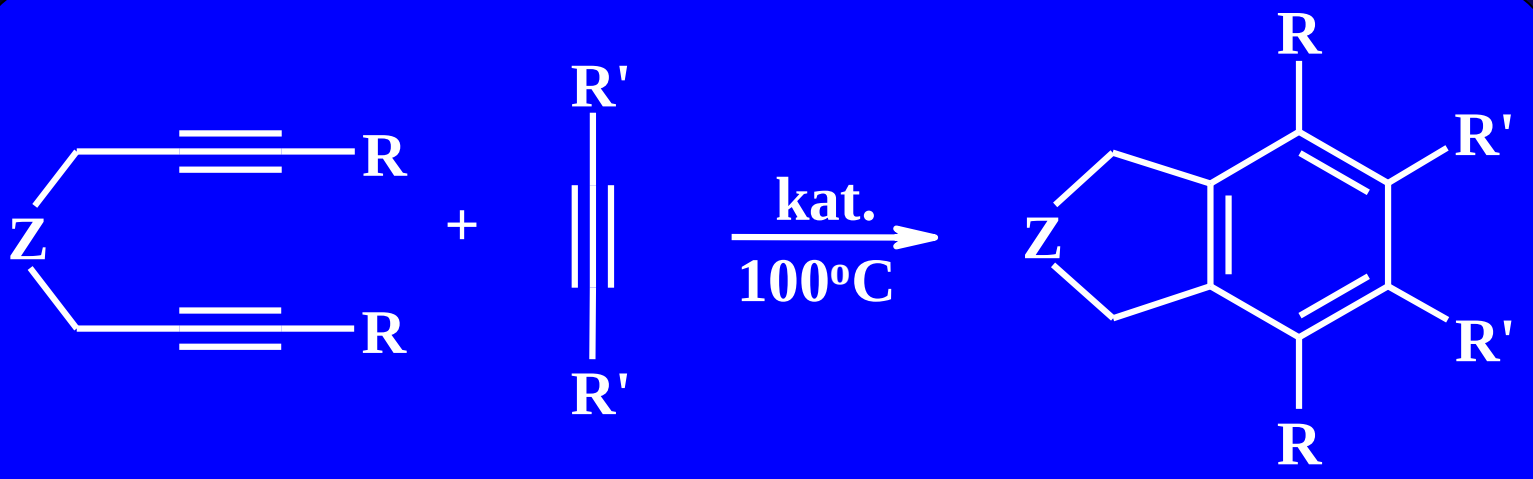
Cykloaddycja [2 + 2 + 2]



Cykloaddycja [2 + 2] i [2 + 2]



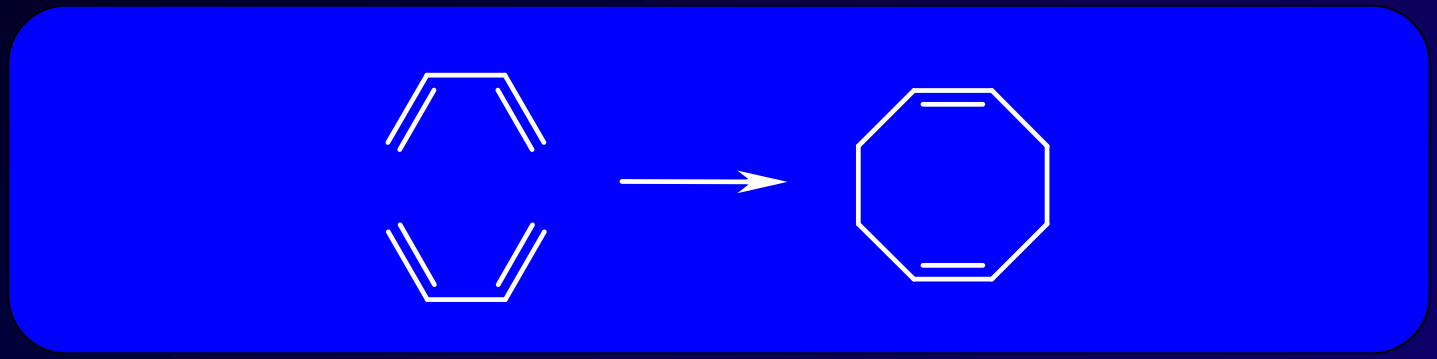
Cykloaddycja [2 + 2 + 2]

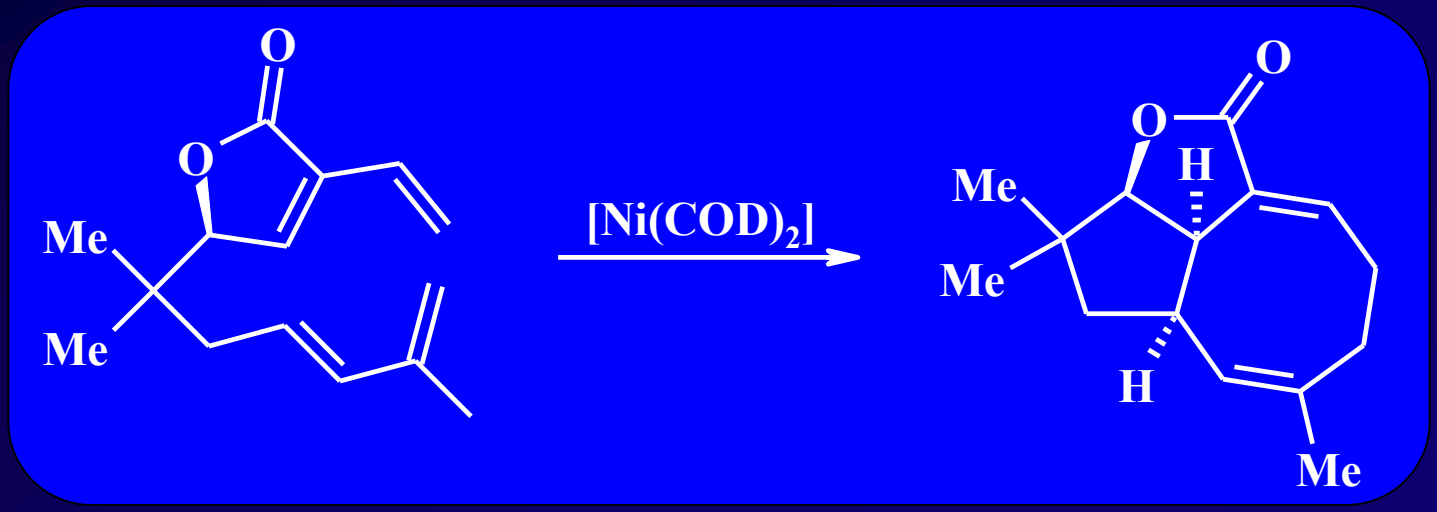


10% $[IrCl(COD)]_2$ + 20% MeDuPhOS

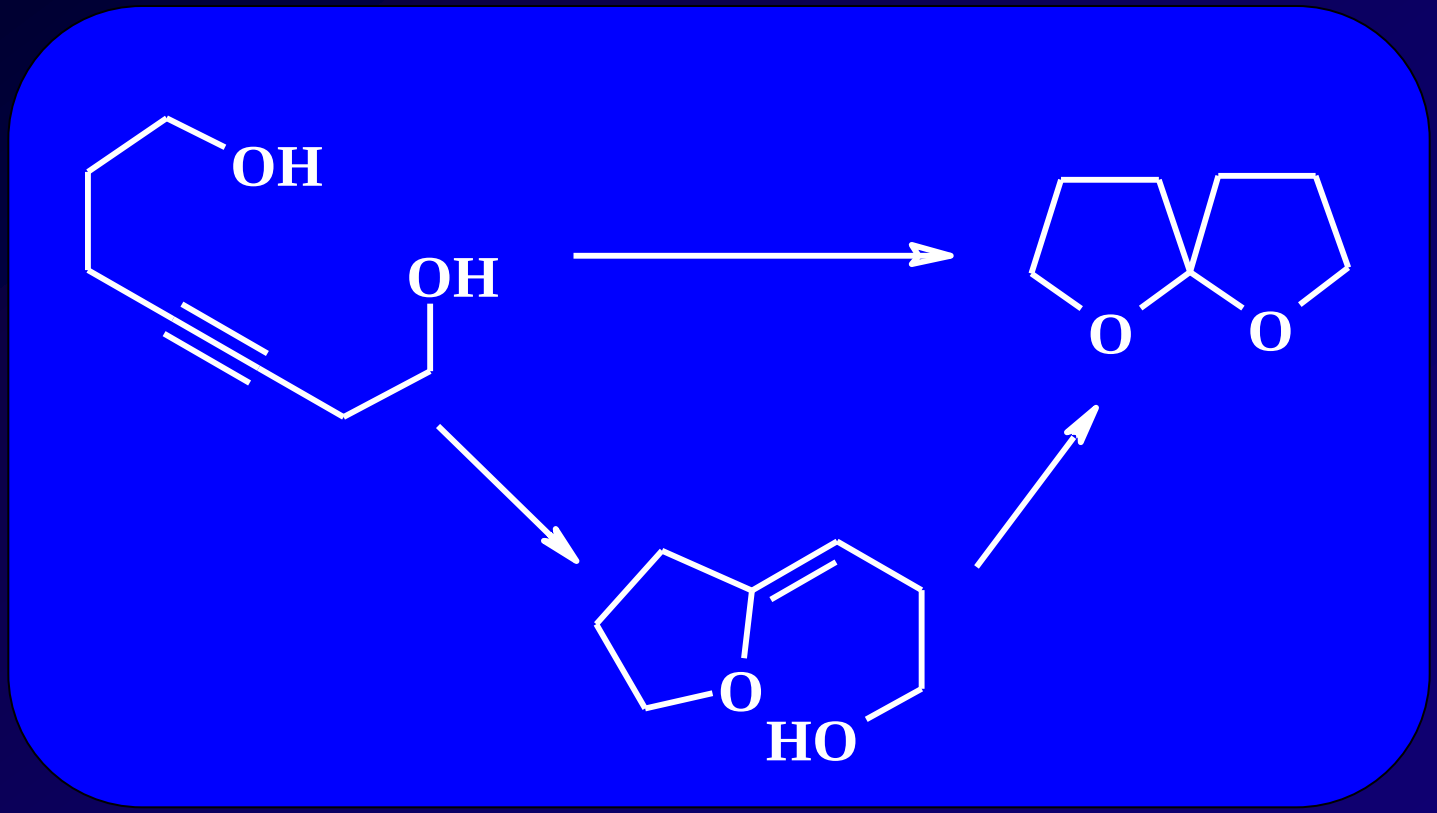
Z = CH_2, O, ...

Cykloaddycja [4 + 4]



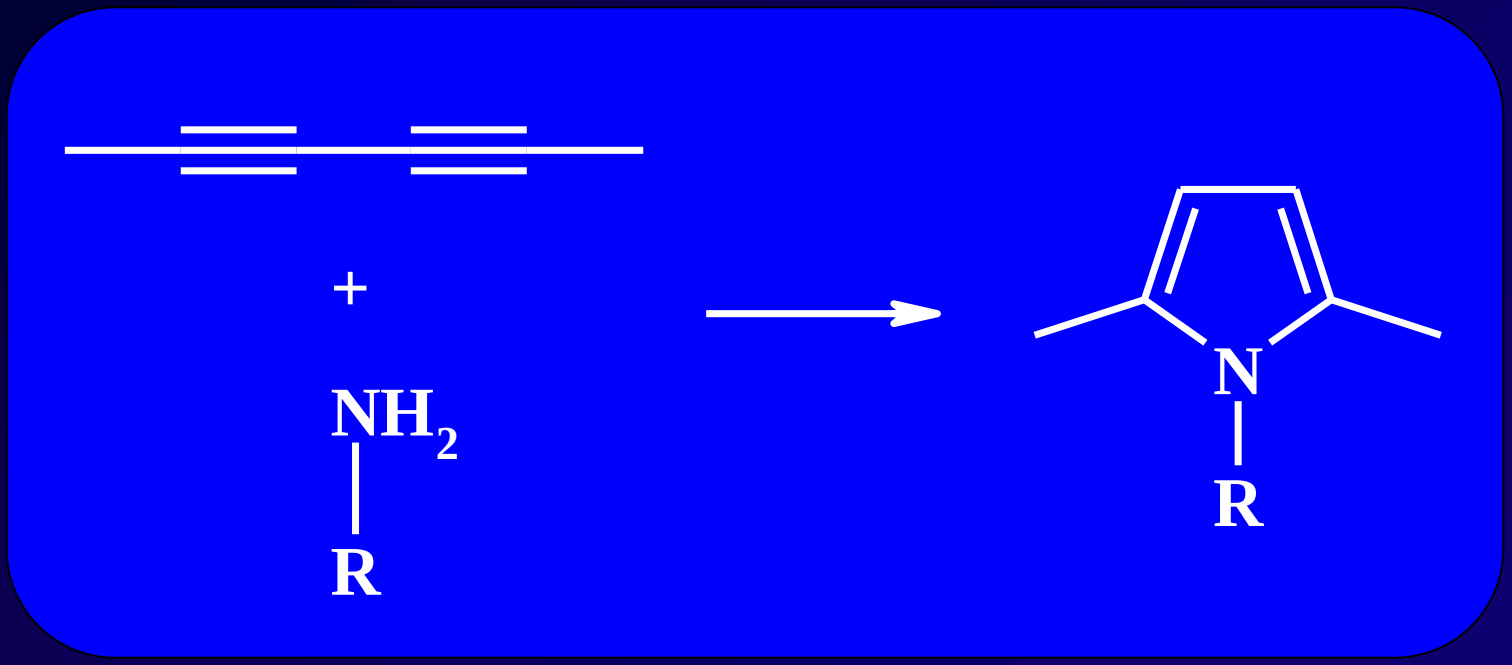


Cykloaddycja wiązań H-heteroatom do wiązań wielokrotnych węgiel- węgiel

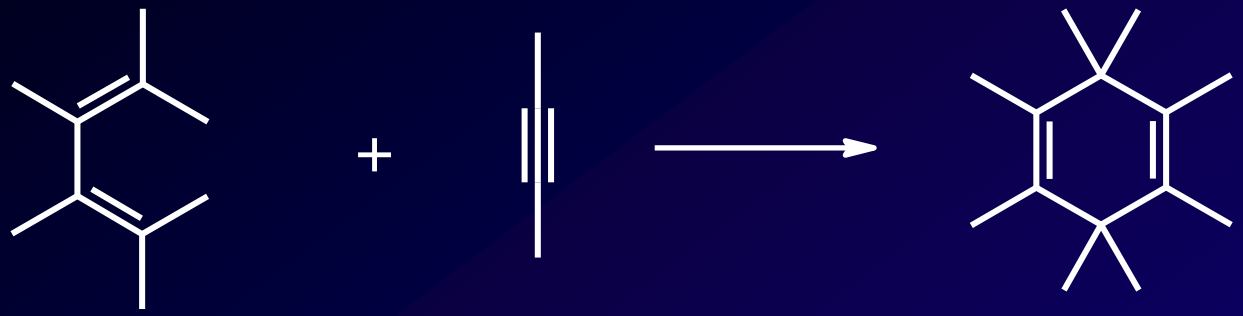


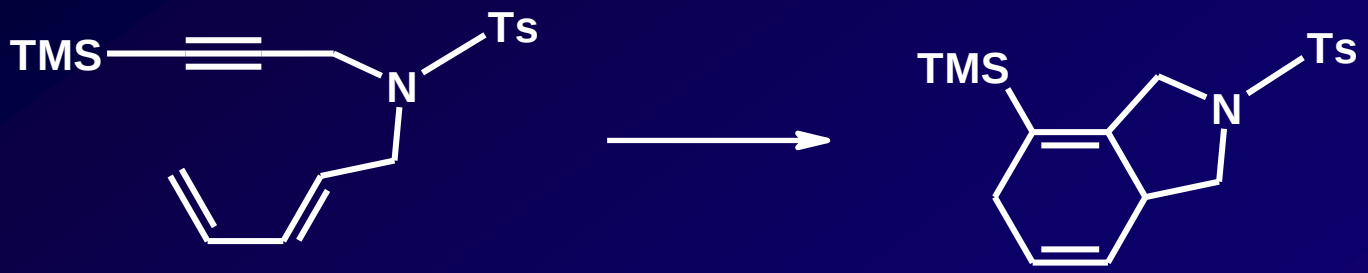
Cykloaddycja wiązań H-heteroatom do wiązań wielokrotnych węgiel- węgiel

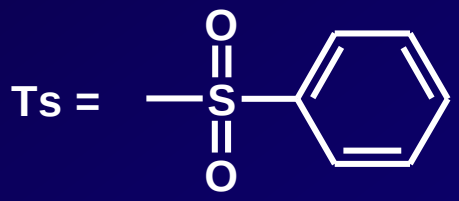
HN- do



Cykloaddycja [4+2] do alkinów



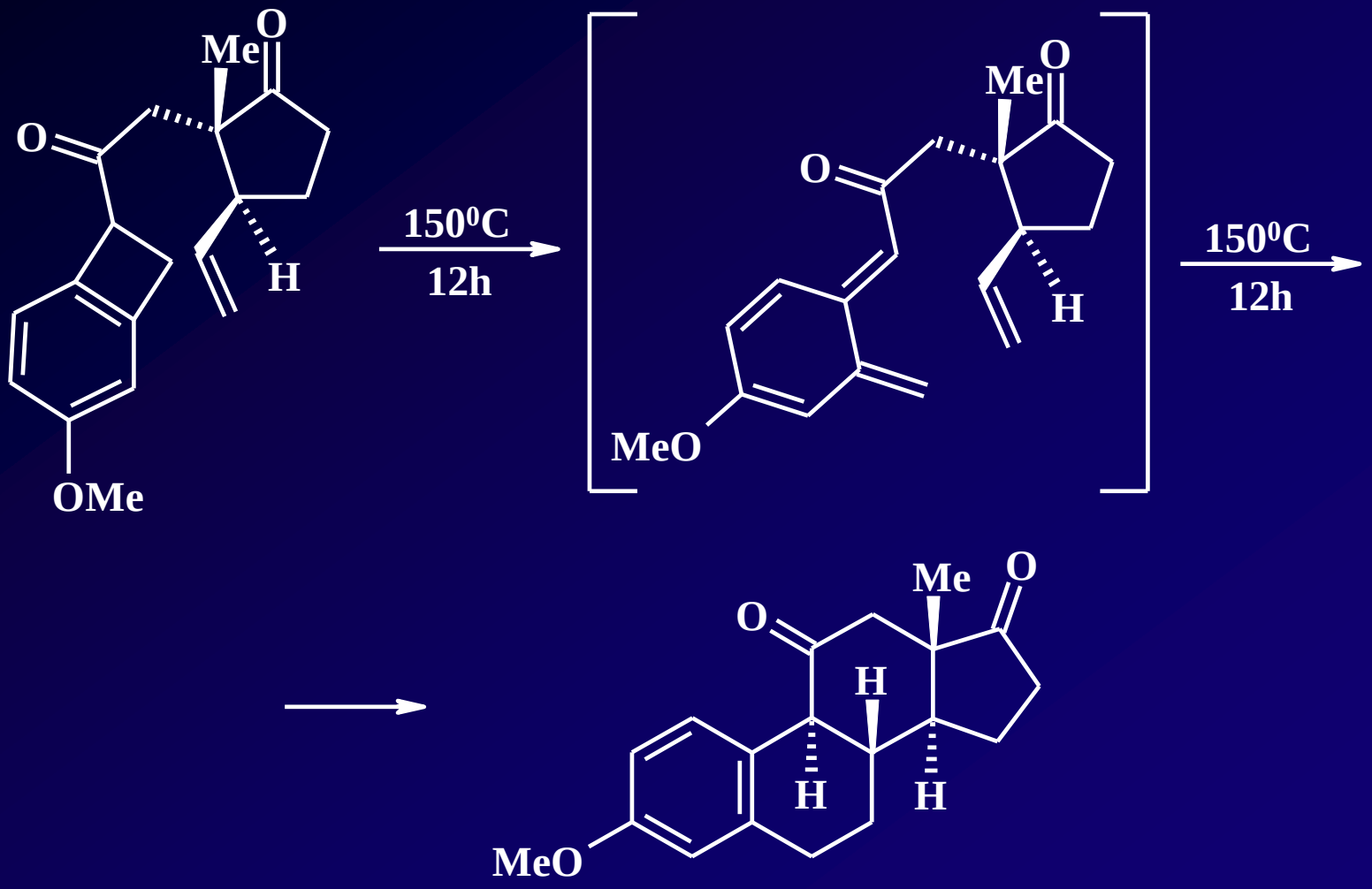




TMS = Me_3Si-

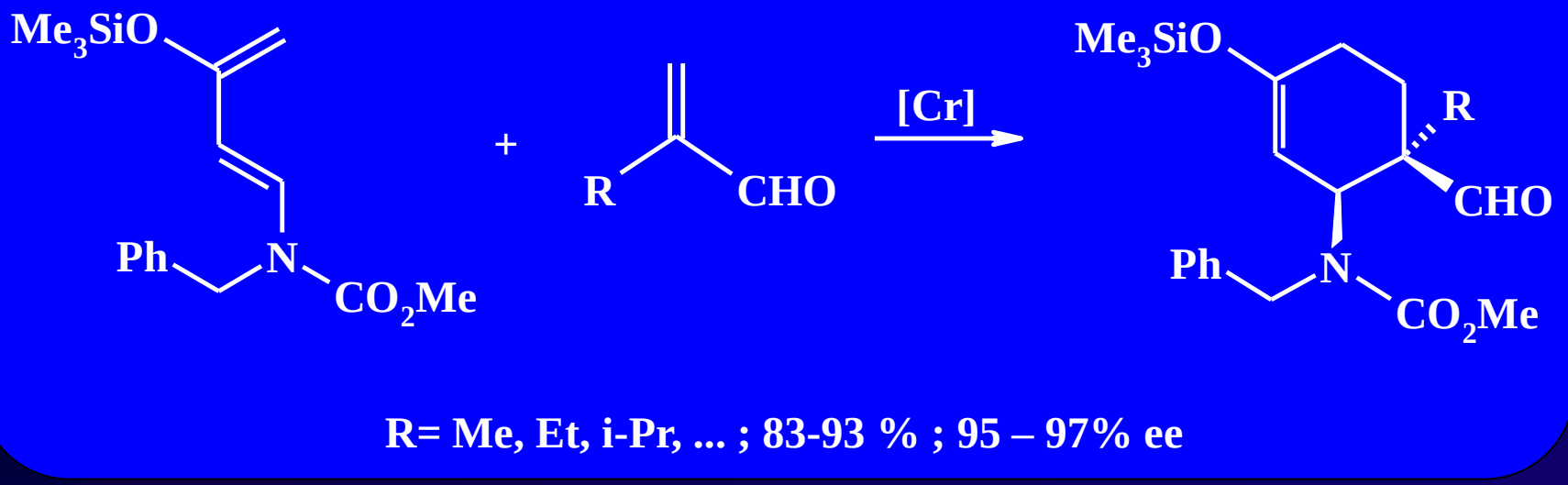
Stereoselektywne reakcje Dielsa-Aldera

Tandem: termiczne otwarcie pierścienia cyklobutenu (generowanie dienu)- następcza cykloaddycja [4+2]

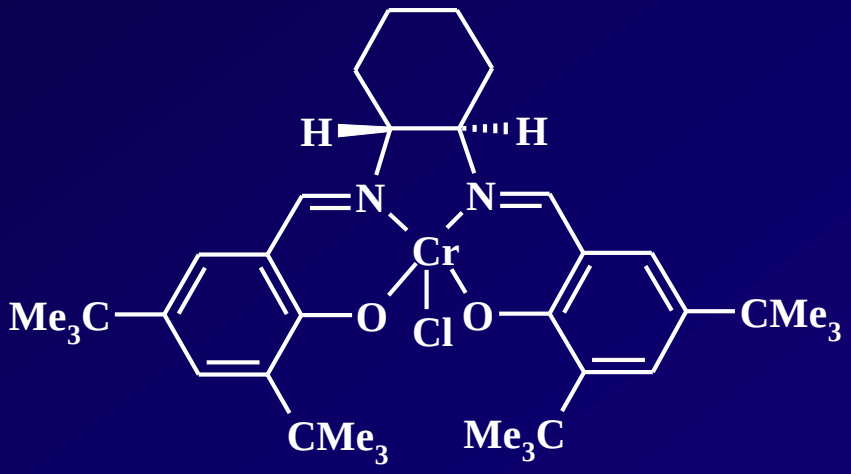


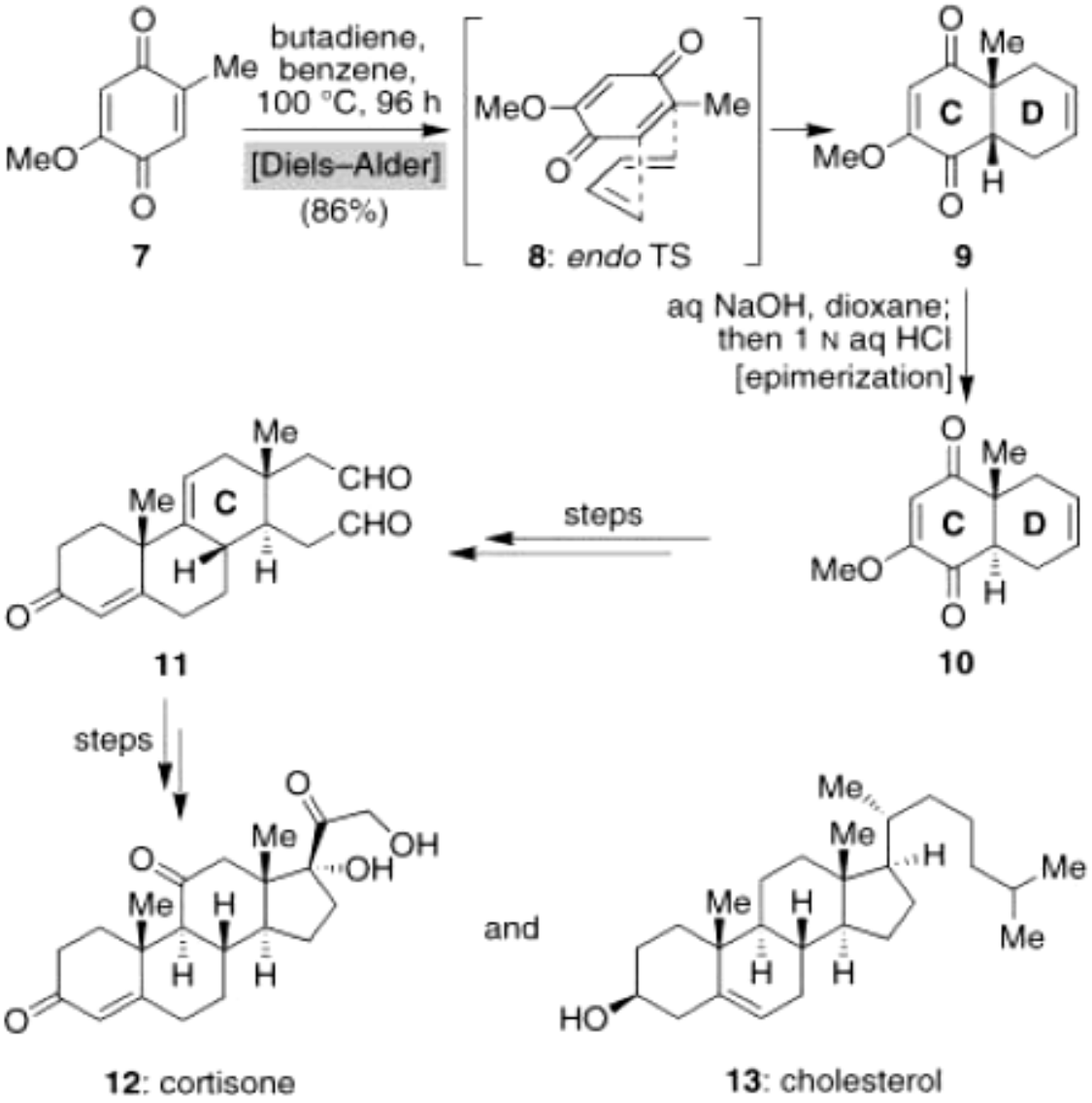
Asymetryczna reakcja Dielsa-Aldera

Chiralny katalizator

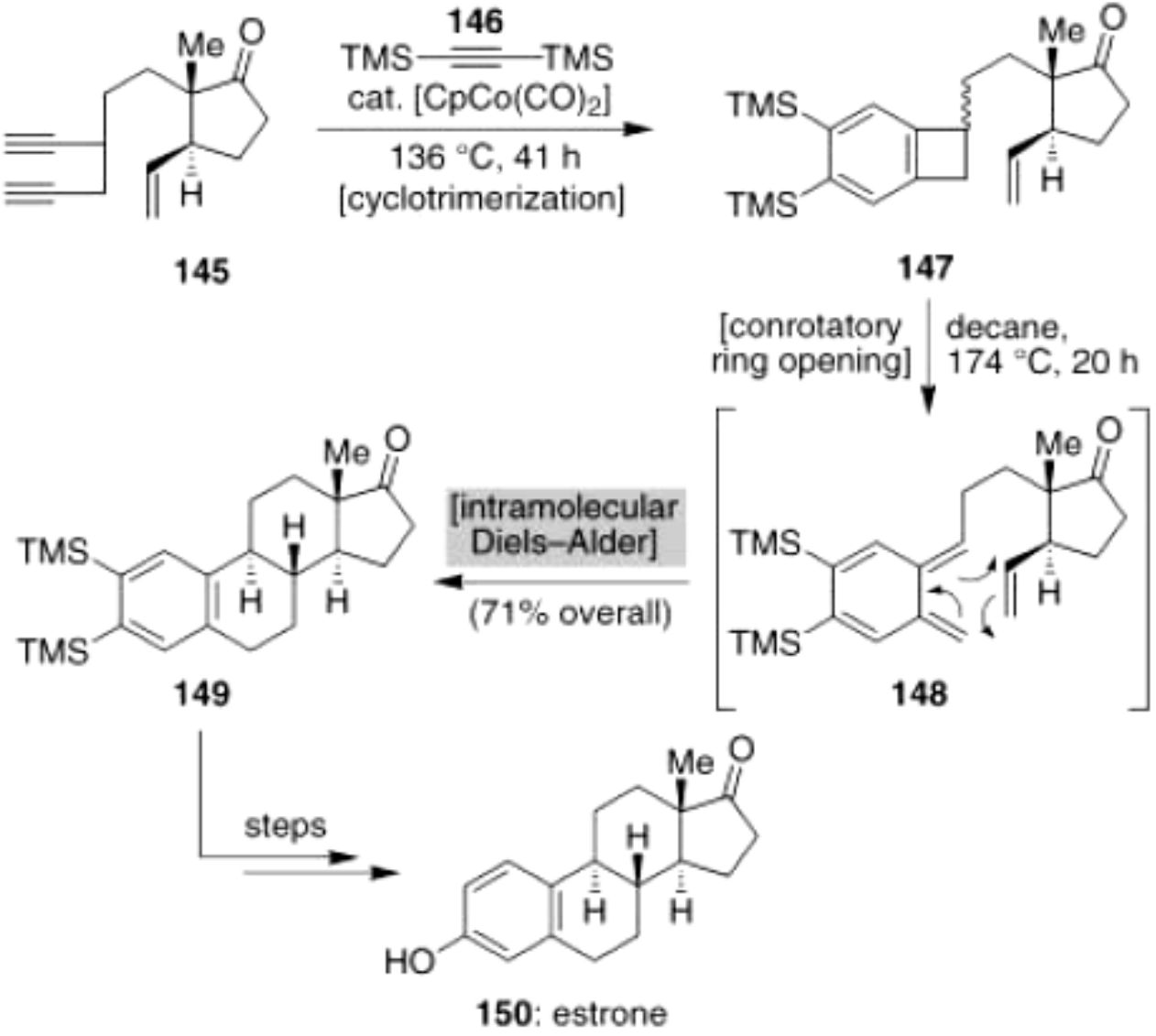


R= Me, Et, i-Pr, ... ; 83-93 % ; 95 – 97% ee

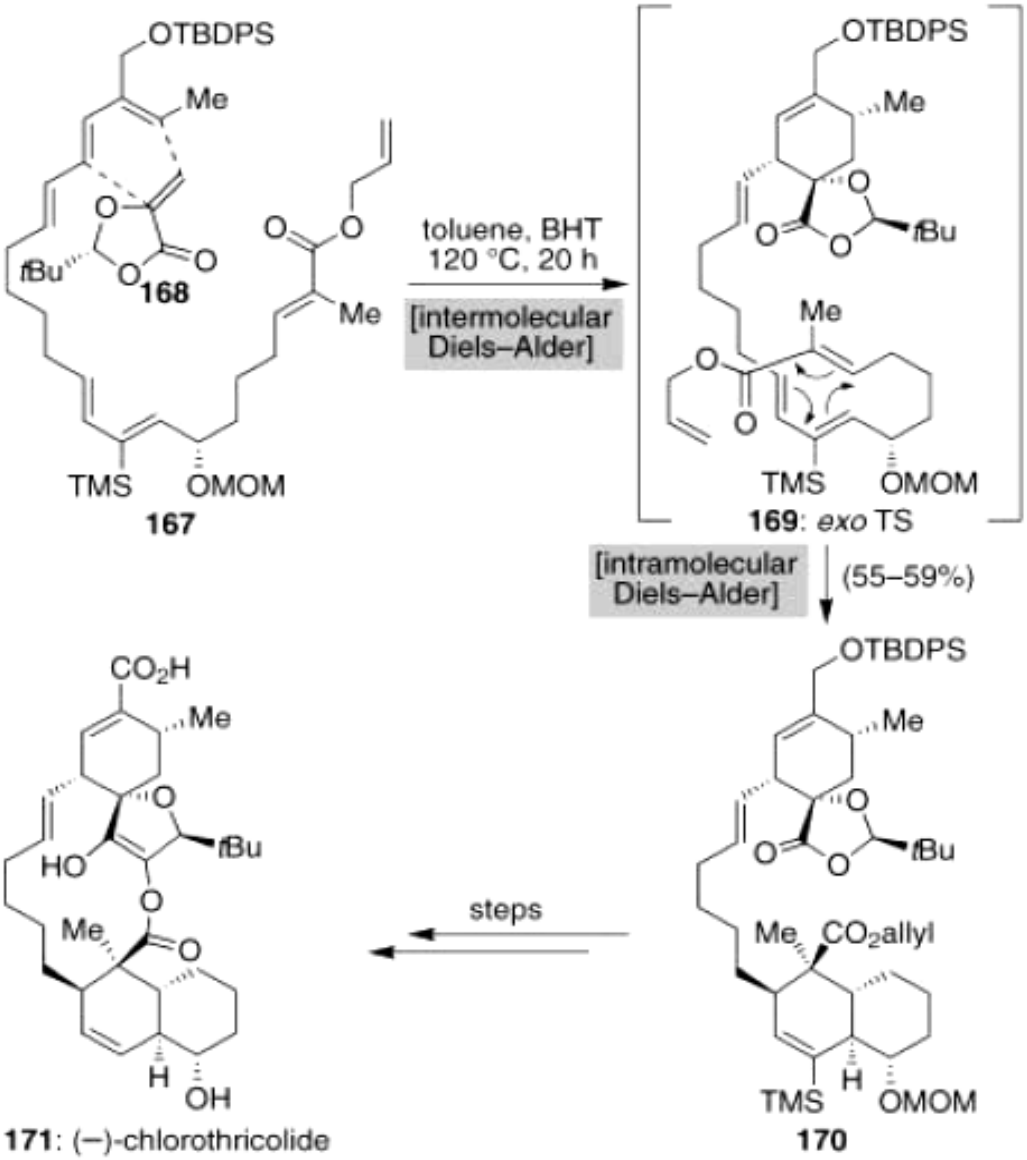




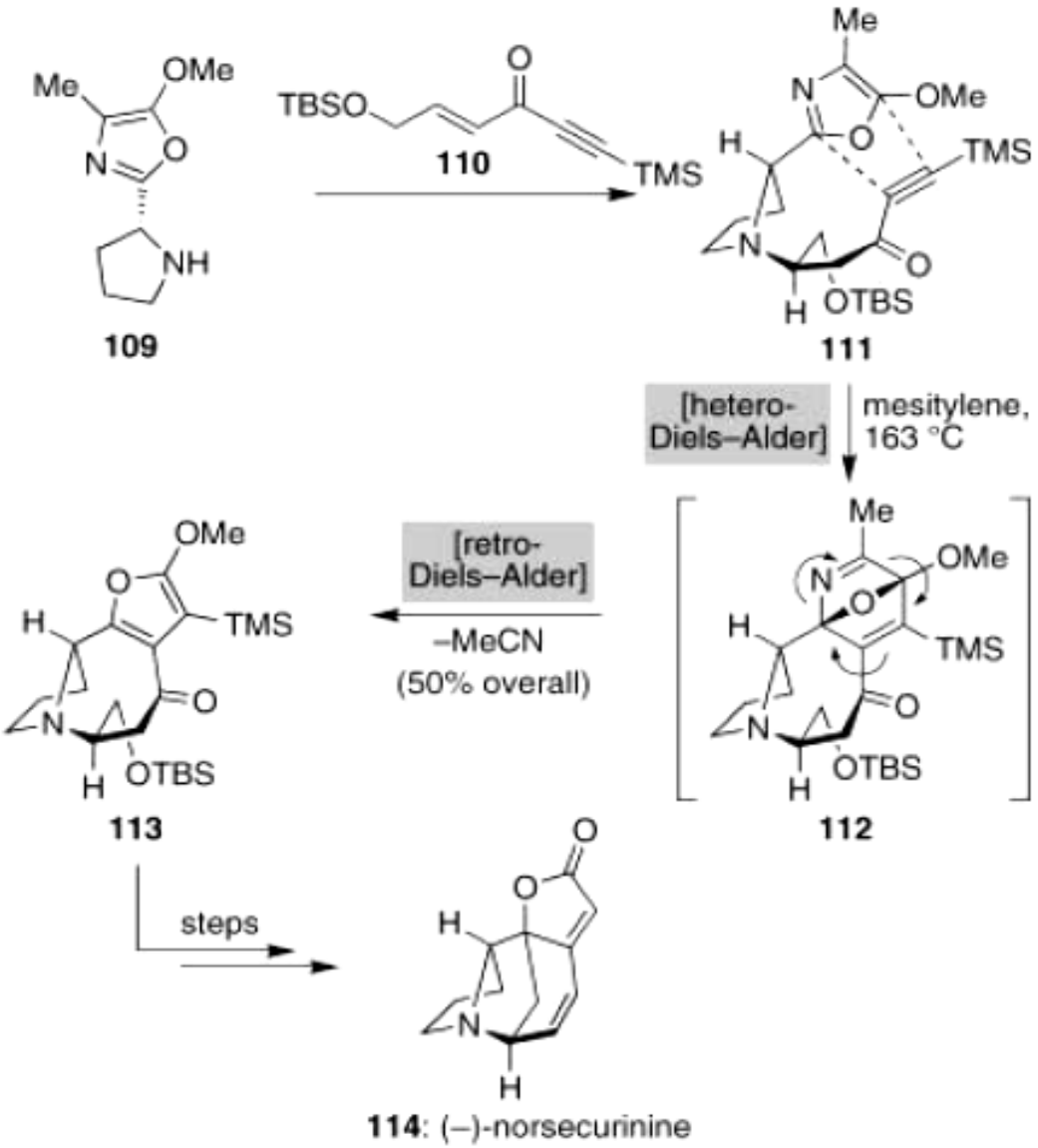
Scheme 2. The pioneering adoption of a quinone-based Diels–Alder reaction by Woodward et al. in 1952 as the key step in the total synthesis of the steroid hormones cortisone (**12**) and cholesterol (**13**).[11]



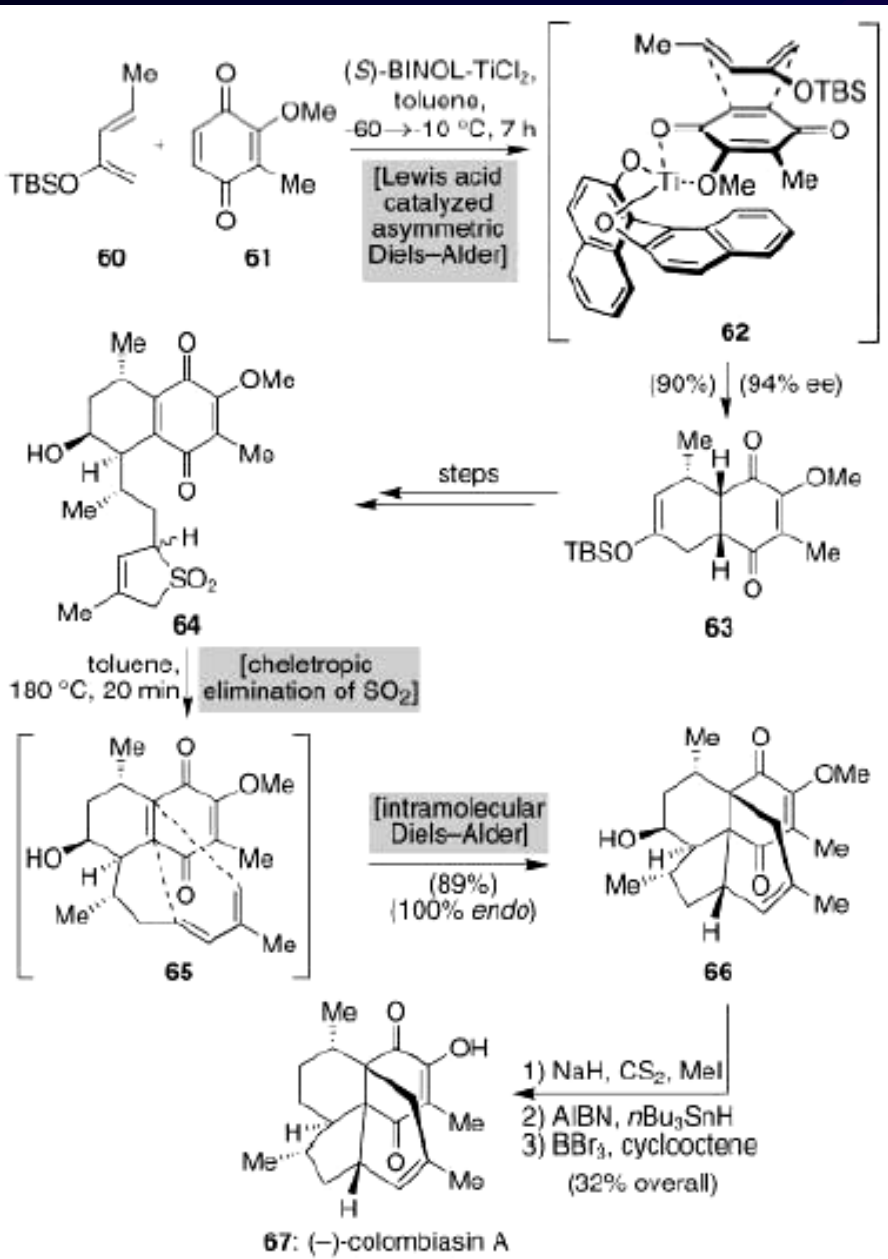
Scheme 22. The brilliant total synthesis of estrone (**150**) by a tandem ring opening/Diels–Alder sequence based on cobalt cyclotrimerization of acetylenic substrates by Vollhardt and co-workers (1979).[74]



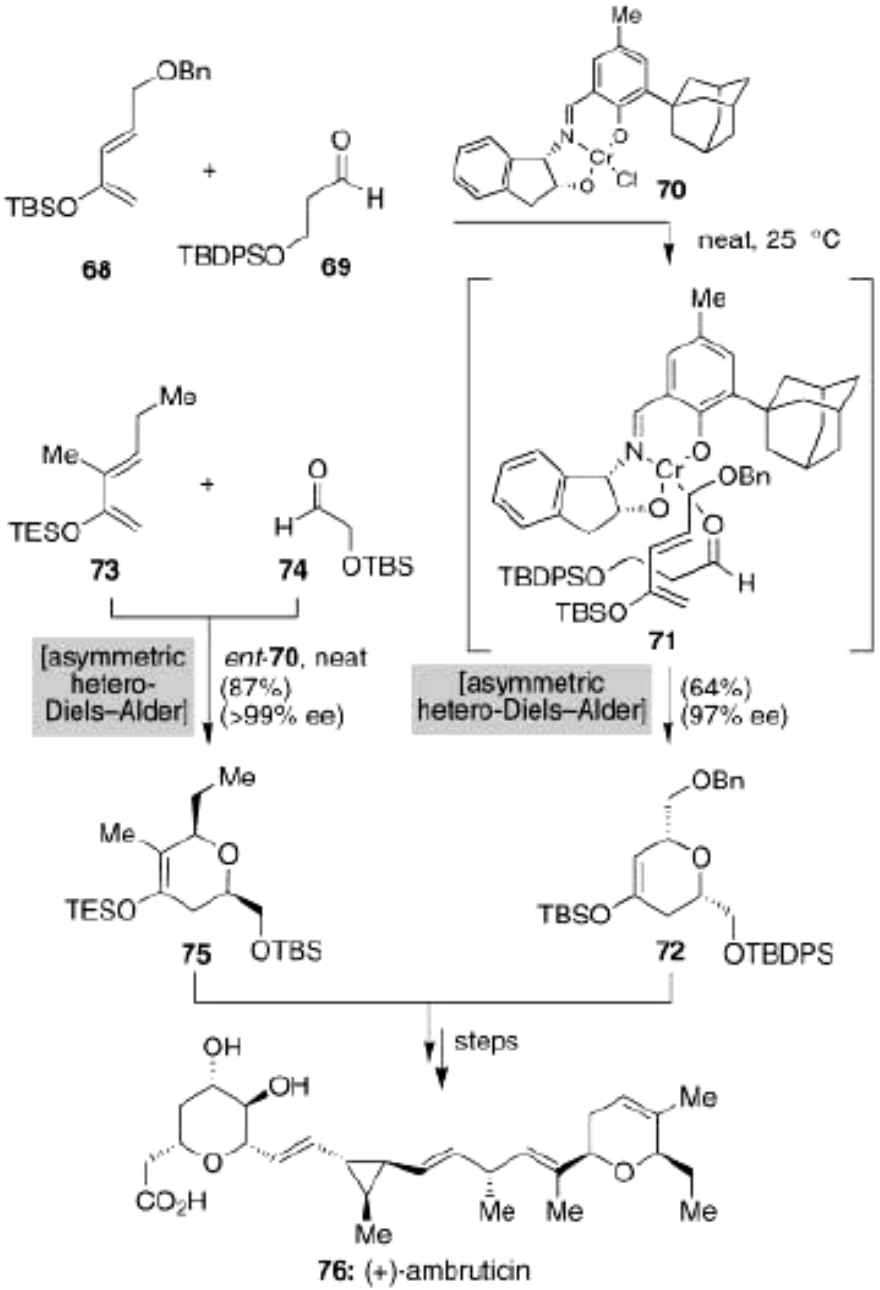
Scheme 26. Beautiful enantioselective total synthesis by Roush and Sciotti of (−)-chlorothricolide (**171**) featuring a tandem inter-/intramolecular Diels–Alder cascade. Note that these processes could certainly occur in the reverse order from that shown here (1994).[90]



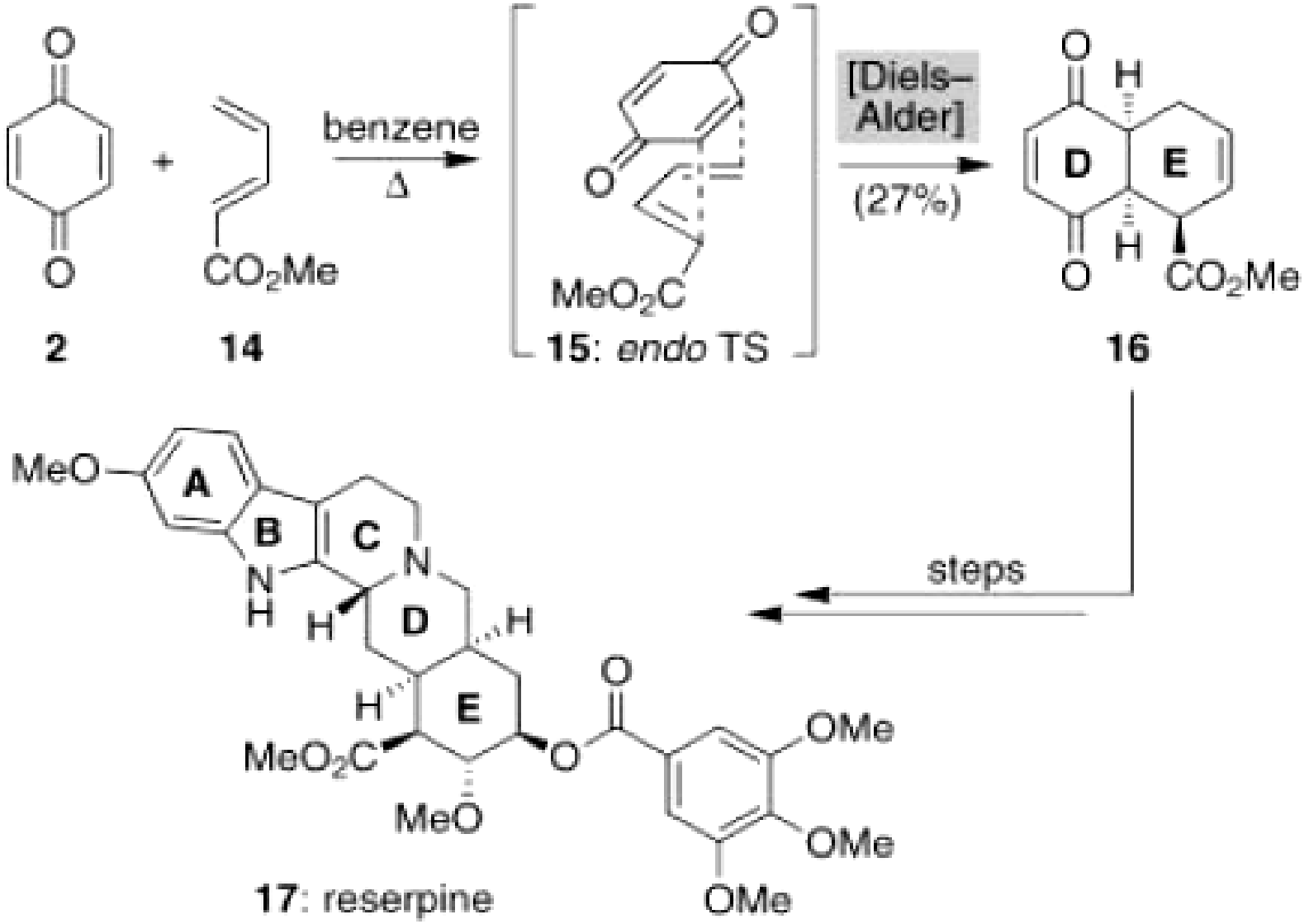
Scheme 16. The elegant use of a hetero-Diels–Alder/retro-Diels–Alder cascade sequence by Jacobi and co-workers to fashion the molecular framework of (–)-norsecurinine (**114**; 1989).[60]



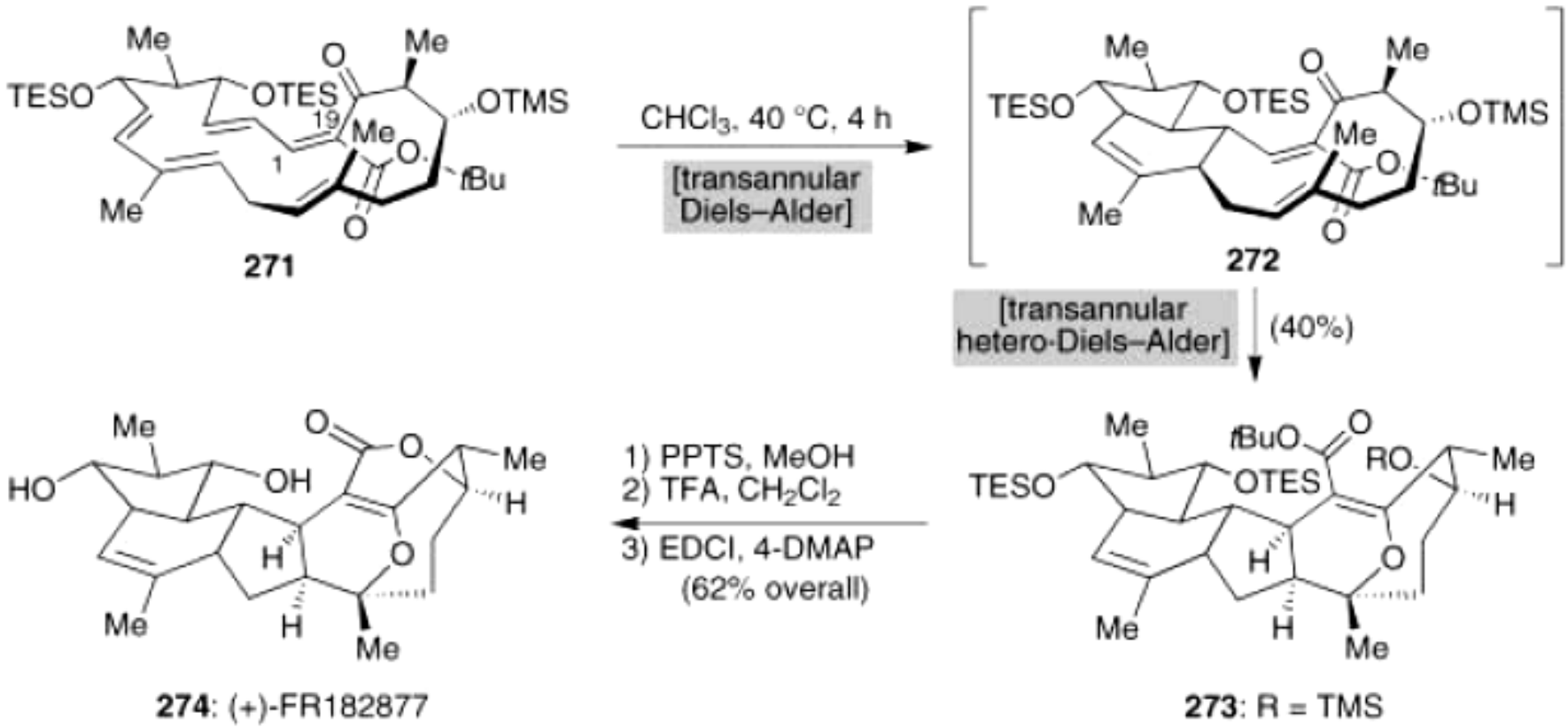
Scheme 9. Reiterative quinone-based Diels–Alder reactions incorporating the use of a sulfone-masked diene in the asymmetric total synthesis of (−)-colombiasin A (67; Nicolaou et al., 2001).[36]



Scheme 10. Use of a novel chromium-catalyzed hetero-Diels–Alder reaction by Jacobsen and co-workers to fashion the two terminal pyran systems in an asymmetric total synthesis of (+)-ambruticin (76; 2001).[37]



Scheme 3. Application of the Diels–Alder reaction in the total synthesis of reserpine (**17**) by Woodward et al. in 1956.[13]



Scheme 40. The beautiful total synthesis of (+)-FR182877 (**274**) by Sorensen and co-workers featuring a novel double transannular Diels–Alder cascade to fashion the molecule's polycyclic scaffold (2002).[133]