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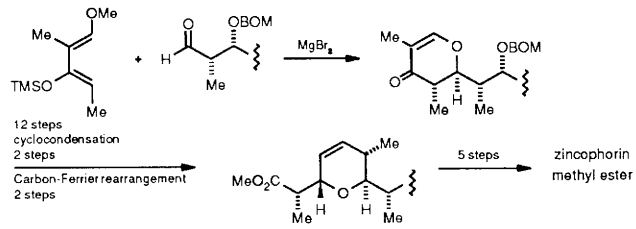
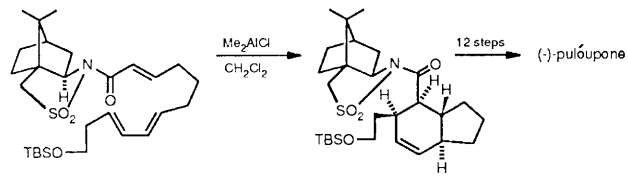
Asymmetric Diels-Alder Reaction

The Diels-Alder reaction represents one of the most effective methods of creating four contiguous and potentially chiral centers with largely predictable regio- and stereoselectivity. This outstanding feature has allowed it to become a pivotal point in numerous synthetic studies. The development of an asymmetric version of this reaction was fueled by the advent of new ideas in asymmetric synthesis about 25 years ago[1,2] and this area of research continues to blossom with vigor. The study of the asymmetric Diels-Alder reaction has focused on the design of chiral dienophiles, dienes and Lewis acid catalysts, and great strides have been made in each of these areas. The following examples illustrate a few of the recent synthetic accomplishments.

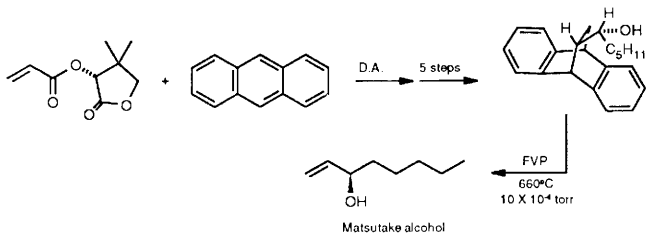
An elegant combination of diene-aldehyde cyclocondensations and the carbon analog of the Ferrier rearrangement provided a cornerstone for the successful construction of the zinc-sequestering polyether antibiotic zincophorin by the Danishefsky group.[3]



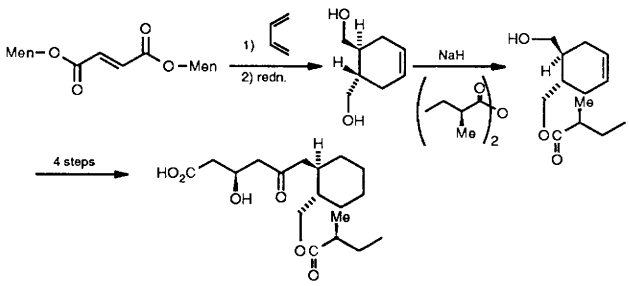
An excellent application of the intramolecular asymmetric Diels-Alder reaction came from across the Atlantic in the form of the synthesis of (-)-pulóupone by the Oppolzer group. D-2,10-Camphorsultam served as a chiral director in the key step.[4]



The Helmchen group, on the other hand, used an interesting combination of the asymmetric Diels-Alder/retro Diels-Alder reactions to prepare the Matsutake alcohol. (*R*)-Pantolactone-derived acrylate and anthracene served as the key-step reactants.[5]



Chiral acrylates, crotonates, fumarates and related amides have been extensively studied as dienophiles in the asymmetric Diels-Alder reaction.[1] One of the recent applications includes the synthesis of a monocyclic analog of compactin by the Heathcock group.[6] Optically active 4-cyclohexen-1,2-dimethanol derived from dimenthyl fumarate served as a key intermediate in this transformation.



The wide variety of chiral auxiliaries designed thus far and the continued research in asymmetric Diels-Alder reactions reaffirms the importance of this versatile transformation.

Aldrich offers some of the reagents used in the above transformations as well as many chiral auxiliaries from which chiral acrylates, fumarates and chiral dienes are derived.[1c]

29,835-2	**D-2,10-Camphorsultam,** 98%	**250mg $11.05; 1g $28.90**
30,580-4	**L-(+)-2,10-Camphorsultam,** 98%	**250mg $14.10; 1g $32.90**
34,901-1	**(*S*)-(+)-3-Crotonoyl-4-isopropyl-2-oxazolidinone,** 98%	**1g $32.00**
29,765-8	**(-)-10-Dicyclohexylsulfamoyl-D-isoborneol,** 98%	**1g $16.40**
30,579-0	**(+)-10-Dicyclohexylsulfamoyl-L-isoborneol,** 98%	**1g $17.60**
34,891-0	**(-)-Dimenthyl fumarate,** 97%	**1g $10.00; 5g $30.00**
30,114-0	**(*R*)-(-)-Hexahydromandelic acid,** 98%	**1g $16.20**
30,115-9	**(*S*)-(+)-Hexahydromandelic acid,** 98%	**1g $16.20**
24,896-7	**(*R*)-(-)-α-Methoxyphenylacetic acid,** 99%	**1g $27.80**
24,898-3	**(*S*)-(+)-α-Methoxyphenylacetic acid,** 99%	**1g $27.80**
A8,340-7	**(*S*)-(-)-2-Methyl-1-butanol,** 99%	**1g $6.05; 10g $23.35**
34,856-2	**(*S*)-(+)-2-Methylbutyric anhydride,** 97%	**1g $15.00**
14,799-0	**(*R*)-(-)-2-Octanol,** 99%	**1g $18.30; 5g $53.10; 10g $99.40**
23,781-7	**(*R*)-(-)-Pantolactone,** 99%	**5g $7.10; 25g $20.20**
32,948-7	**(-)-8-Phenylmenthol,** 98%	**250mg $16.80; 1g $57.20**

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