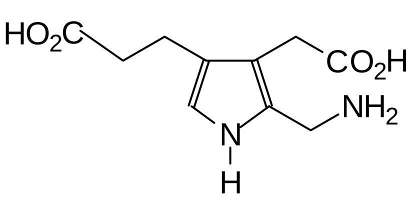
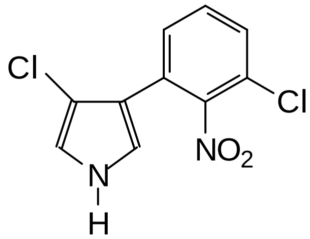
Chapter 6 Five-Membered Ring Systems

6.1 Pyrroles

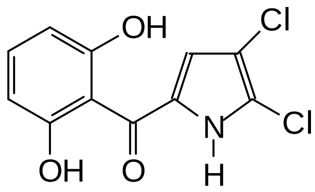
6.1.1 Introduction



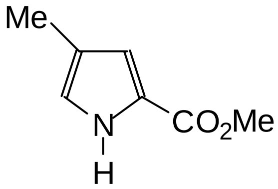
porphobilinogen

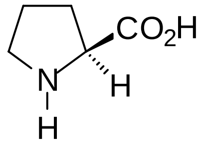


pyrrolnitrin

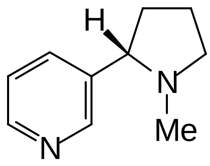


pyoluteorin



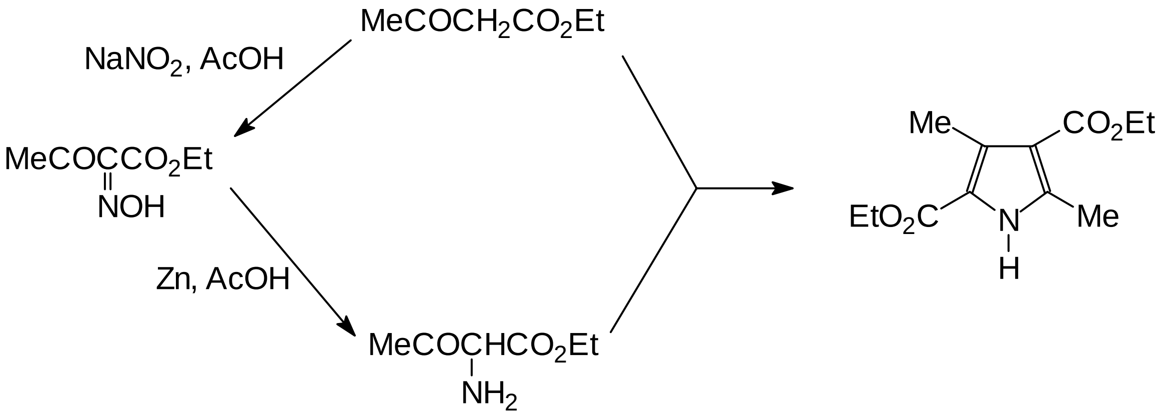


(*S*)-proline

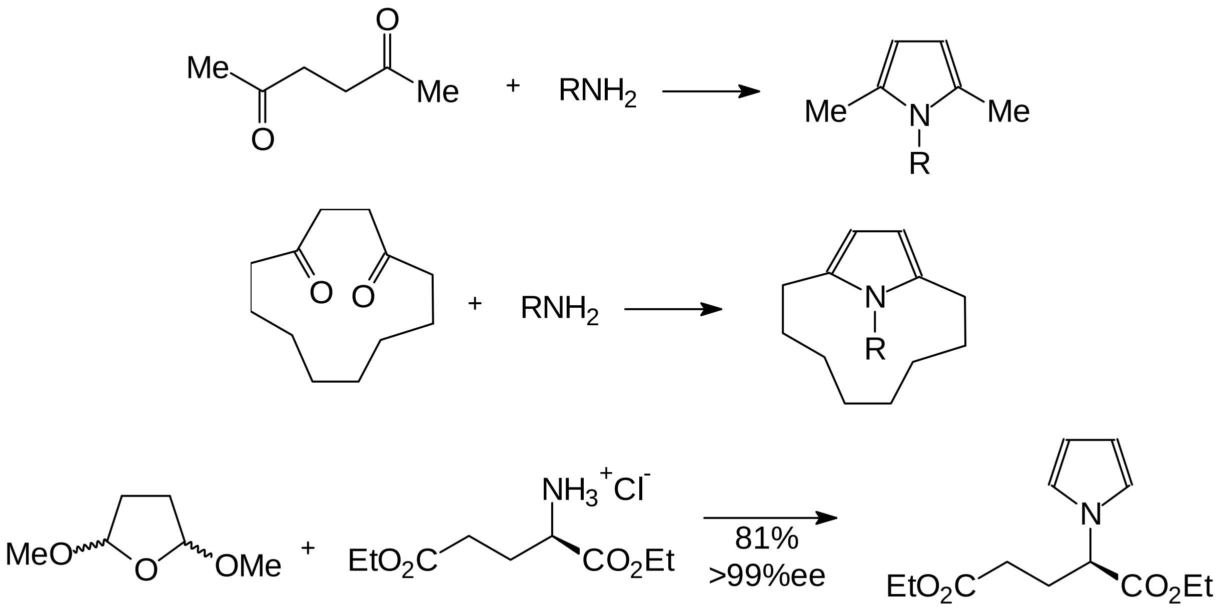


nicotine

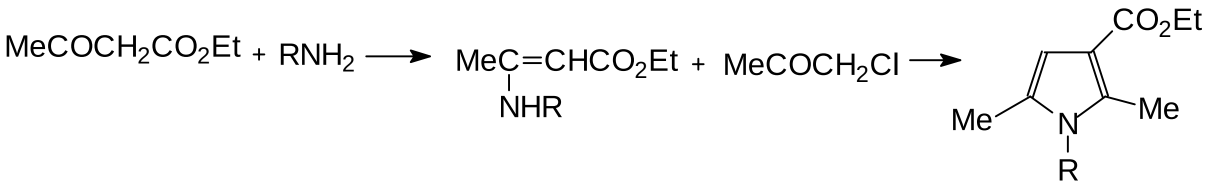
6.1.2 Ring Synthesis



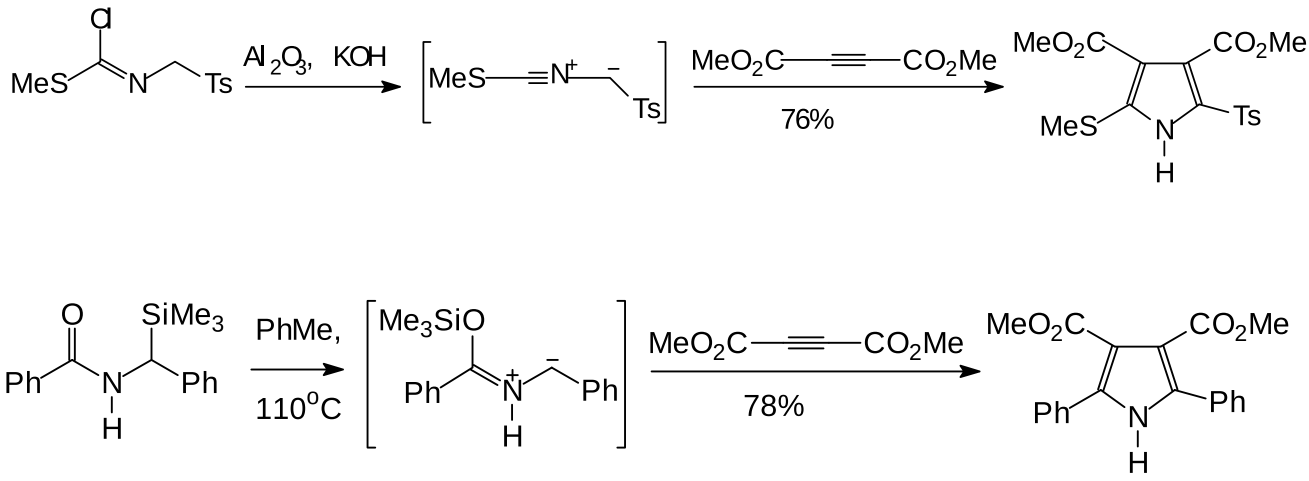
Knorr pyrrole synthesis



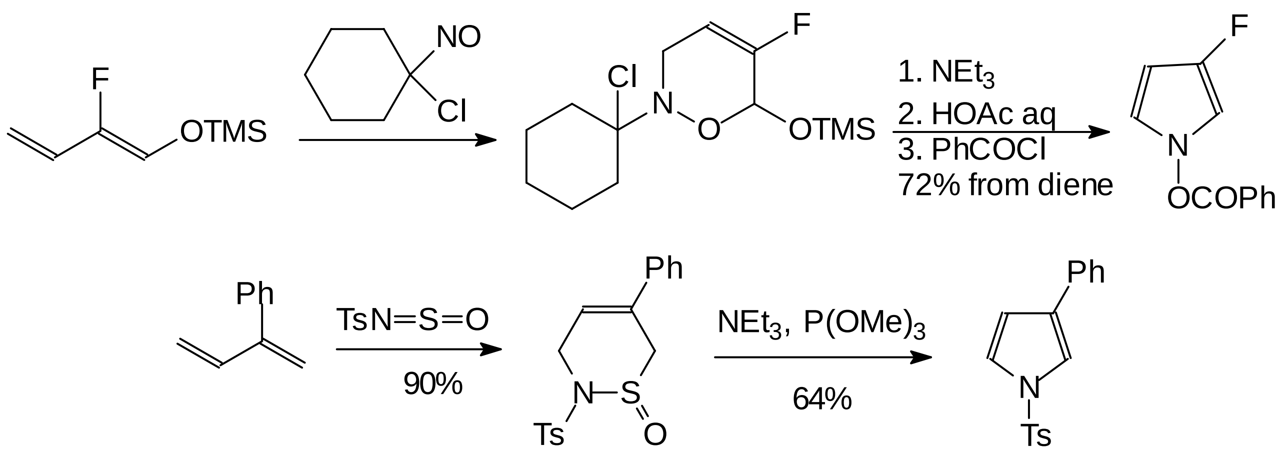
Paal-Knorr pyrrole synthesis



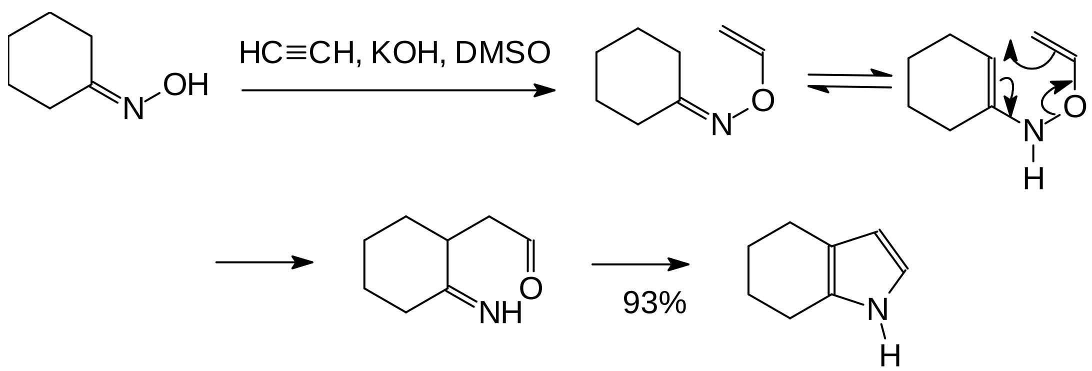
Hantzsch pyrrole synthesis



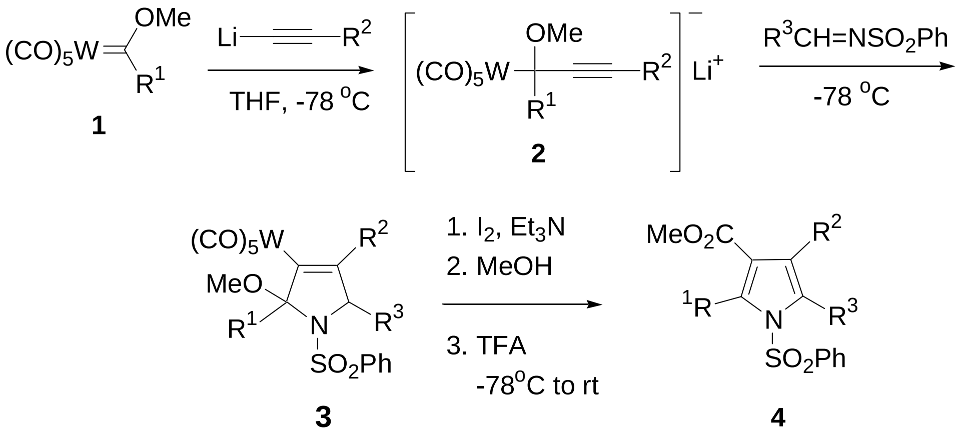
Pyrroles by 1,3-dipolar cycloaddition



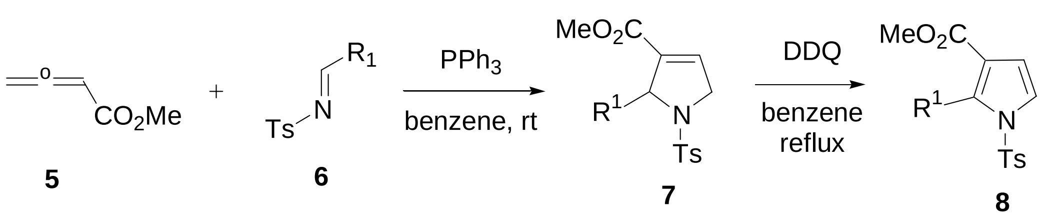
Pyrroles by Diels-Alder cycloaddition and ring contraction.

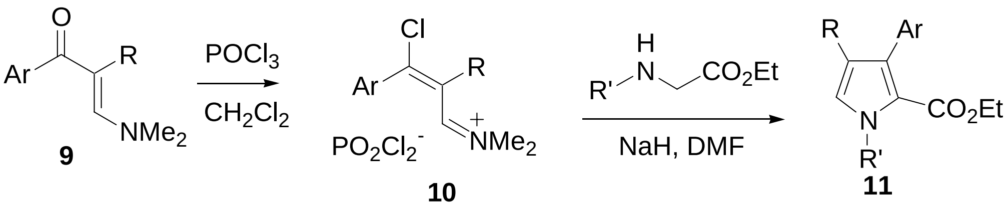


Synthesis of pyrroles from oximes and acetylene.

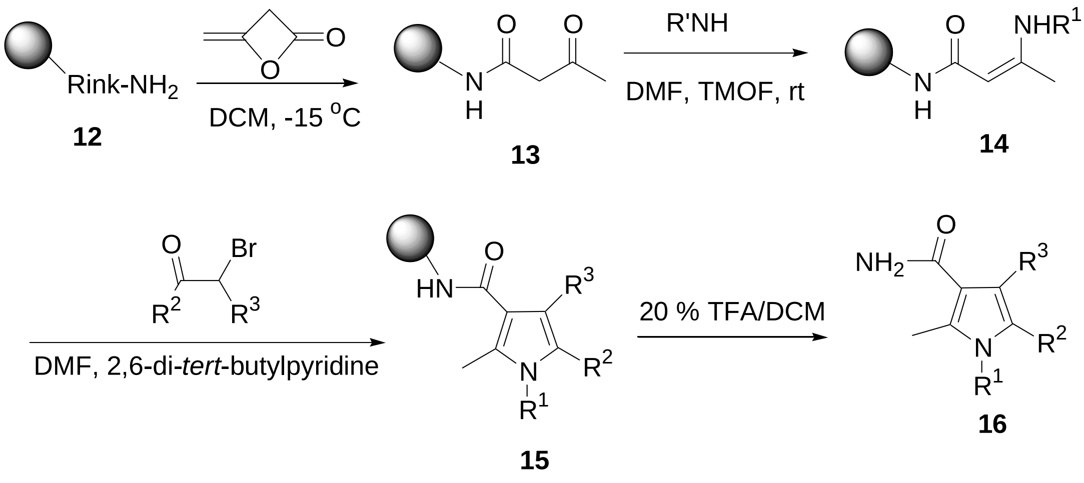


J. Org. Chem. **1998**, 3164.

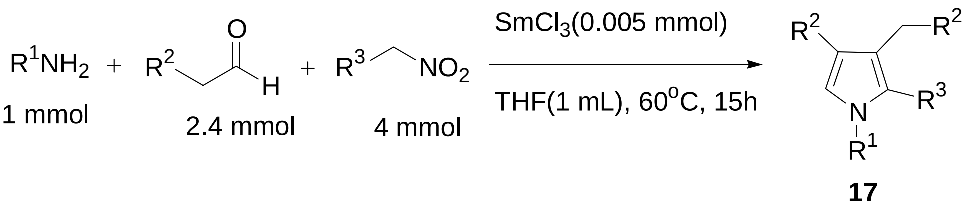




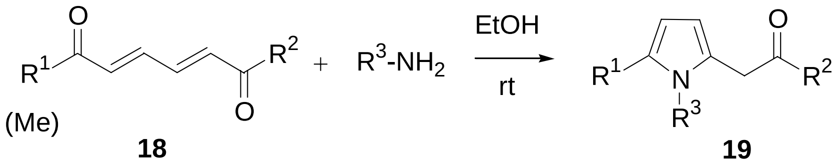
Tetrahedron Lett. **1997**, 3461. *J. Org. Chem*. **1998**, 5031. *Tetrahedron*, **1998**, 5075.



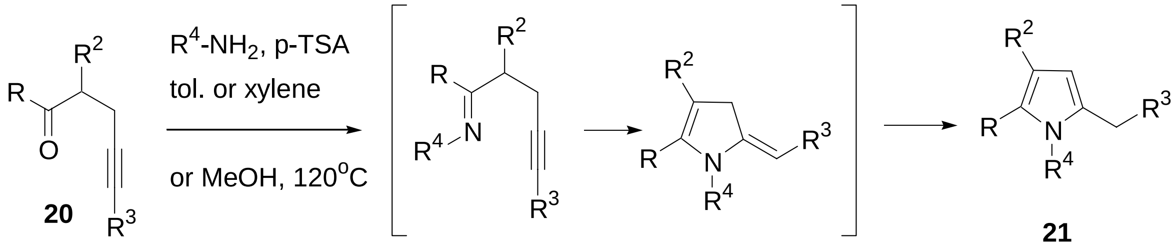
Tetradedron Lett. **1998**, 8263.



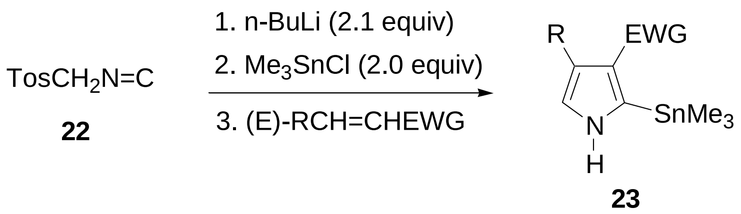
J. Org. Chem. **1998**, 6234.



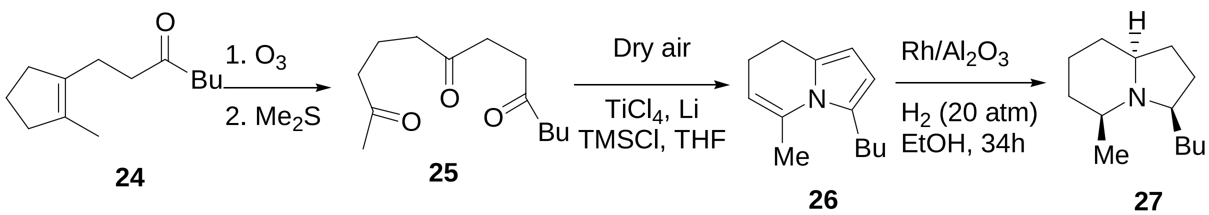
J. Org. Chem. **1998**, 9131.



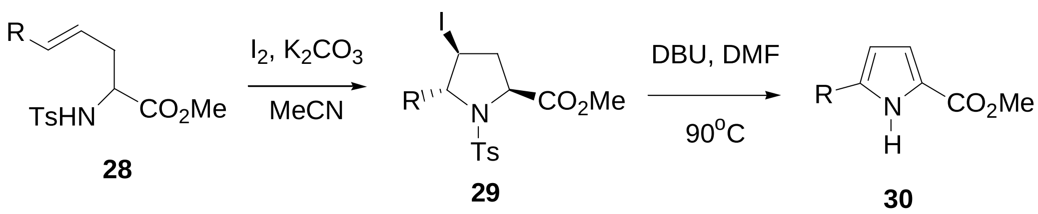
Tetrahedron, **1998**, 15253.



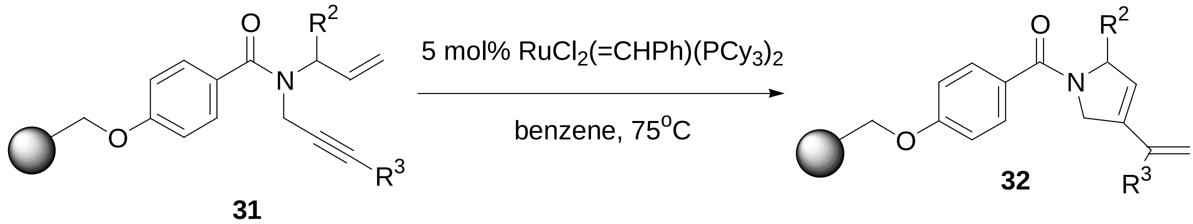
J. Org. Chem. **1998**, 5332.



Angew. Chem. Int. Ed. **1998**, 636.



Synlett, **1998**, 731.

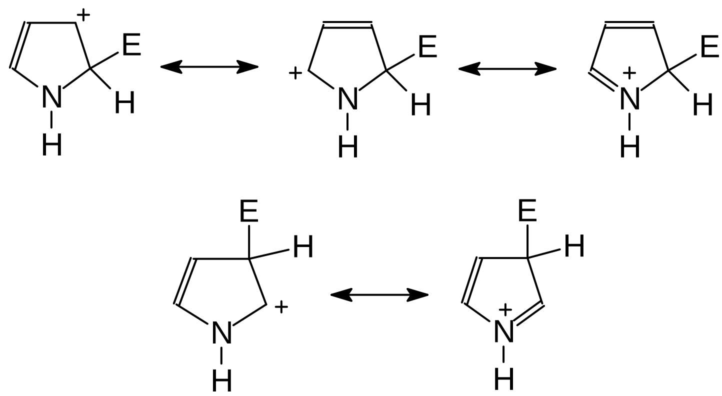


Tetrahedron Lett. **1998**, 6815.

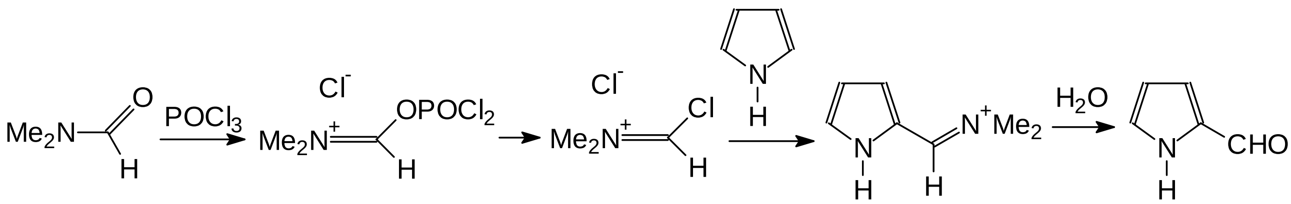
6.1.3 Acidity and metallation reactions

6.1.4 Substitution at nitrogen

6.1.5 Substitution at carbon



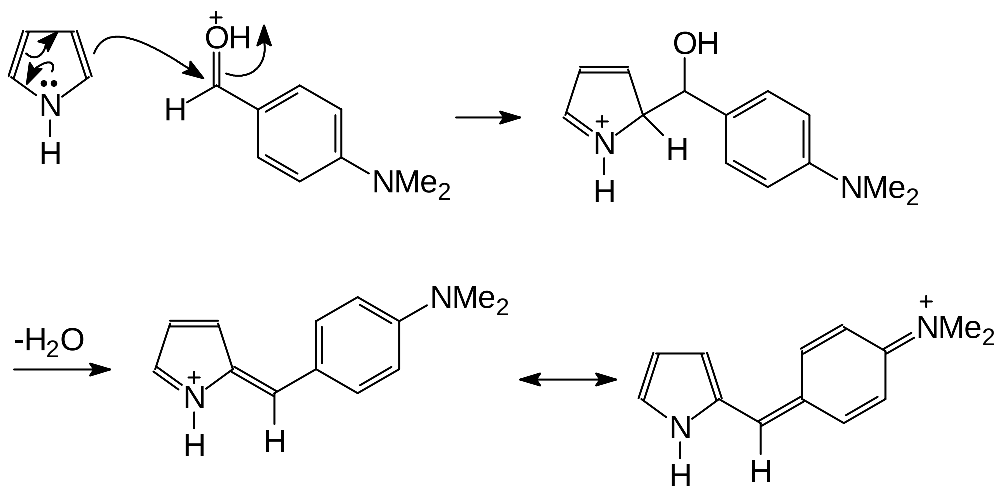
Intermediates in the electrophilic substitution of pyrrole



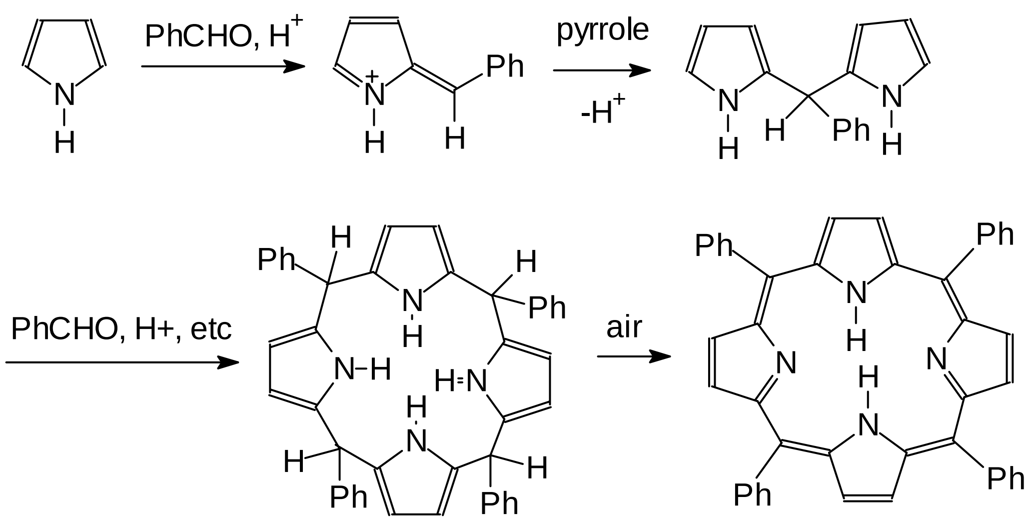
Vilsmeier-Haack reaction of pyrrole.

Table. Electrophilic substitution of pyrrole

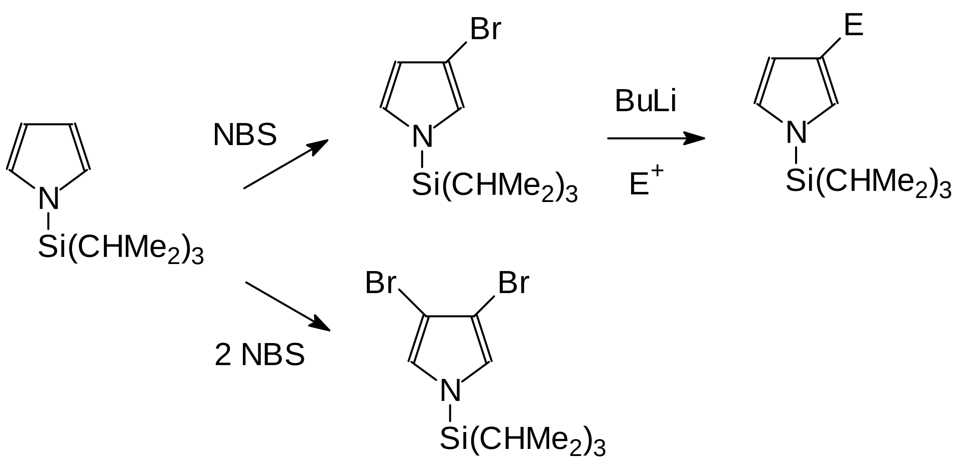
FG introduced	Reagents & condition	Product
NO_2	HNO_3, $(MeCO)_2O$, 20^oC	2- and 3- (14:1)
Cl	SO_2Cl_2, ether	2- and 2,5-
Br	NBS	2-
CHO	Me_2NCHO	2-
COMe	$MeC\equiv N^+Me$, BF_4^- then H_2O	2-
$COCH_2Cl$	Me_2NCOCH_2Cl, $POCl_3$	2-
CH_2CH_2COMe	H_2C=CHCOMe, BF_3	2- and 2,5-
CH_2NMe_2	CH_2O, Me_2NH, H^+	2-
SO_3H	SO_3-Py, 100^oC	2-
MeS	MeSCl, K_2CO_3	2- and 2,5-
N=NPh	$PhN_2^+Cl^-$	2-



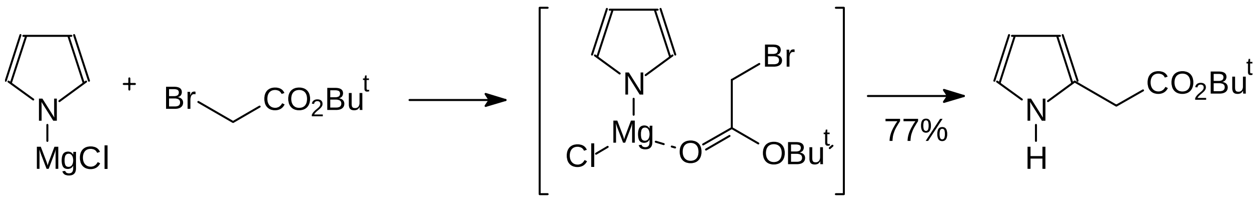
Ehrlich test for pyrroles



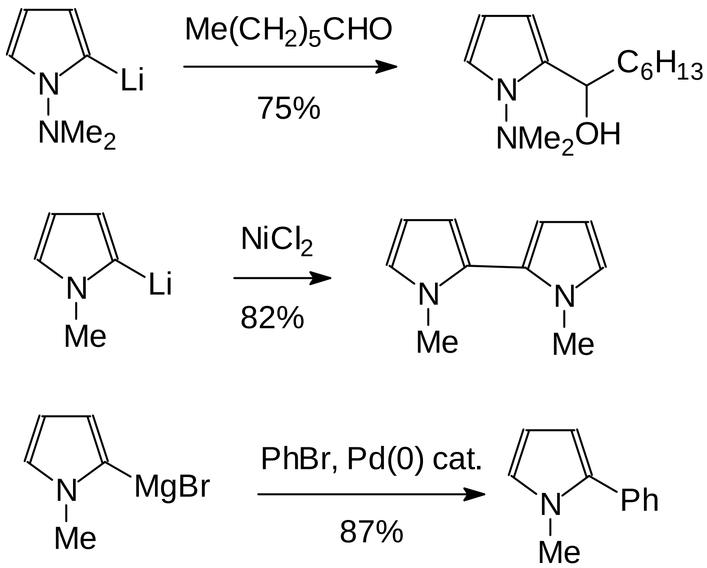
Tetraphenylporphyrin from pyrrole and benzaldehyde.



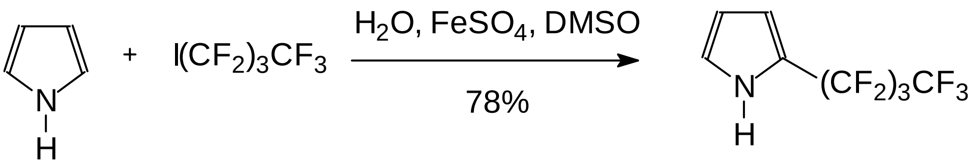
3-Substitution via 1-triisopropylsilylpyrrole.



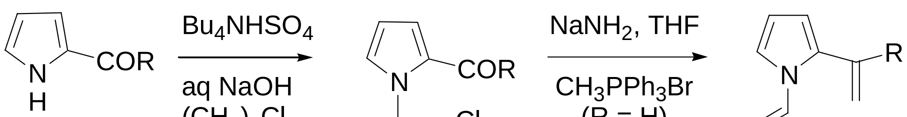
t-Butyl pyrrole-2-acetate from pyrrylmagnesium chloride



Substitution of 2-metallated pyrroles.

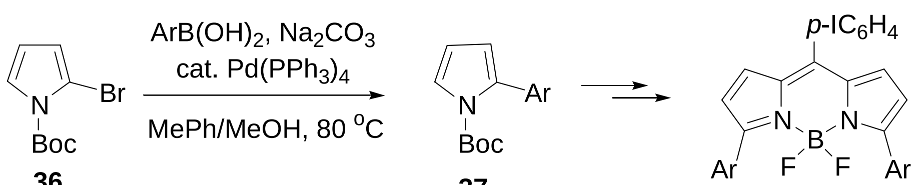


Free-radical substitution of pyrrole.



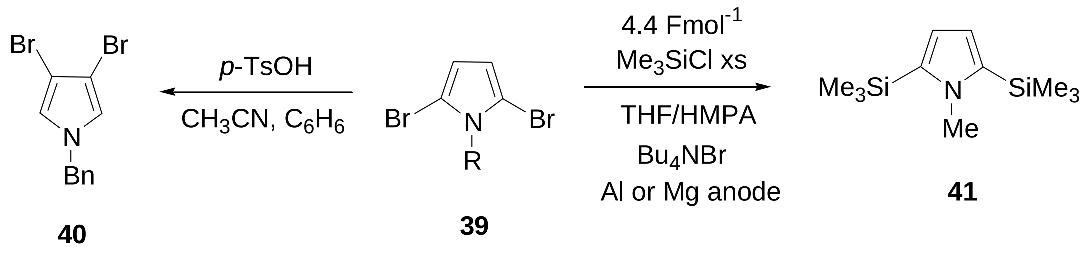
33 **34** **35**

J. Org. Chem. **1998**, 10022.

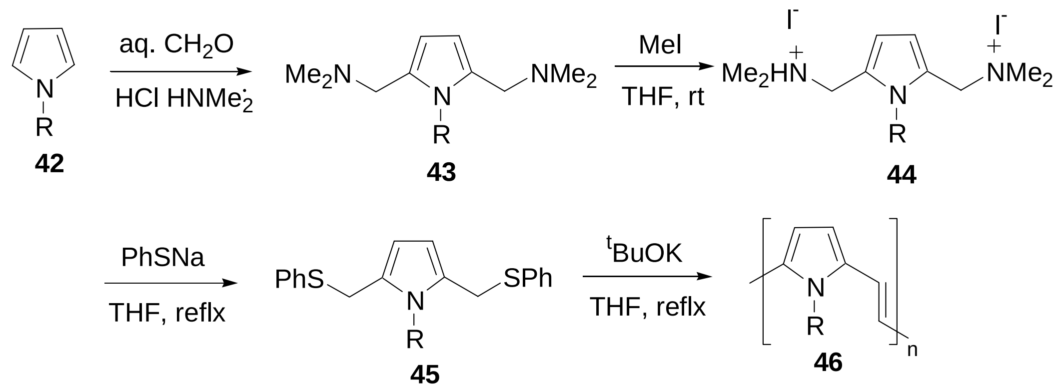


36 **37** **38**

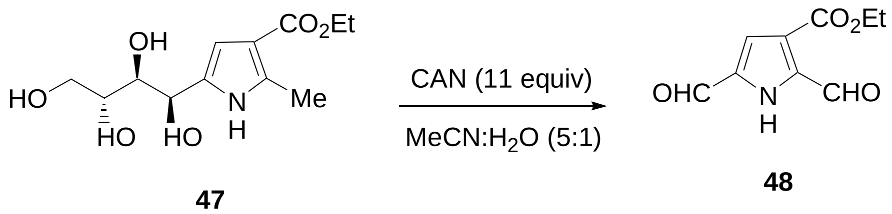
J. Heterocyclic Chem. **1998**, 1325.



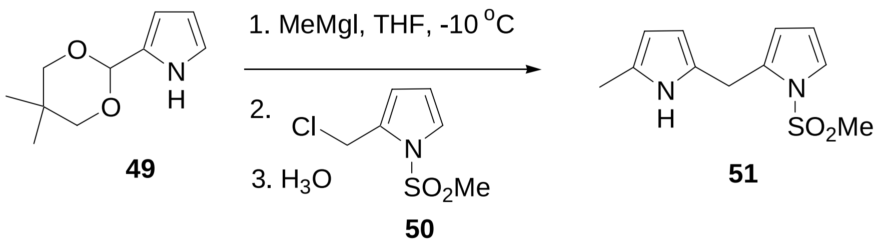
Syn. Commun. **1998**, 3403.



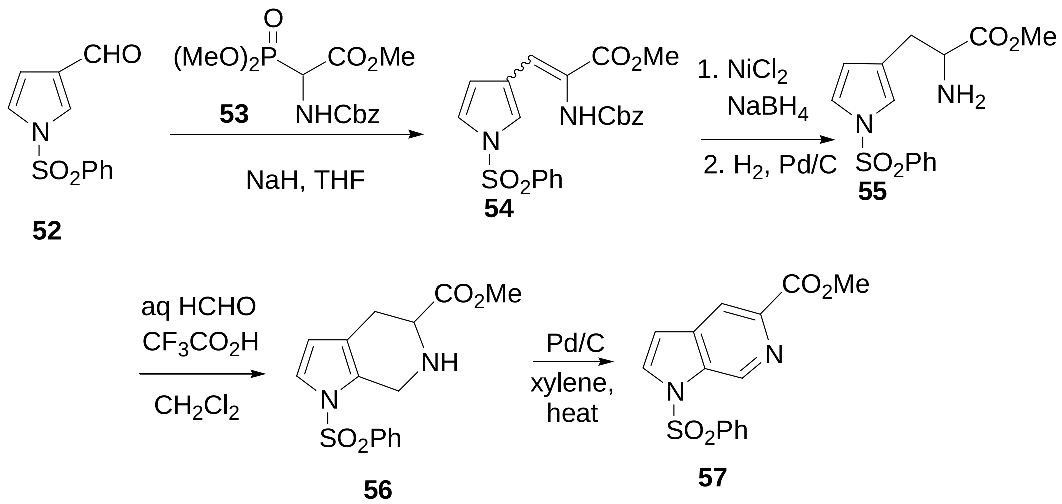
Chem. Commun. **1998,** 327.*Tetrahedron Lett*. **1998**, 1087.



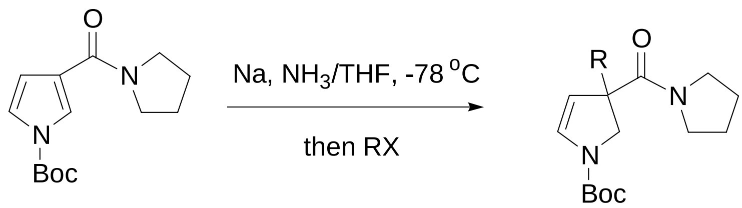
Tetrahedron Lett. **1998**, 9271.



J. Org. Chem. **1998**, 8163.



J. Org. Chem. **1998**, 2731.



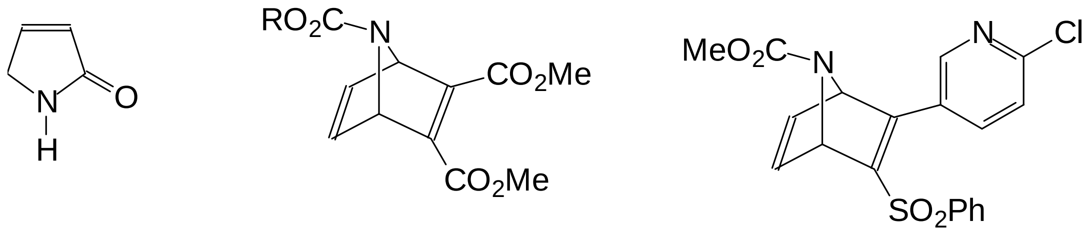
58 **59**

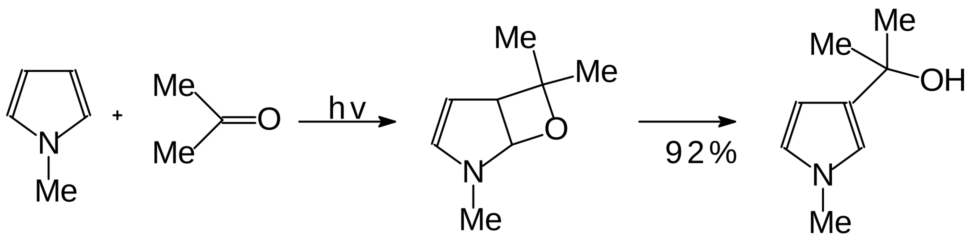
Tetrahedron Lett. **1998,** 3075.

60 **61**

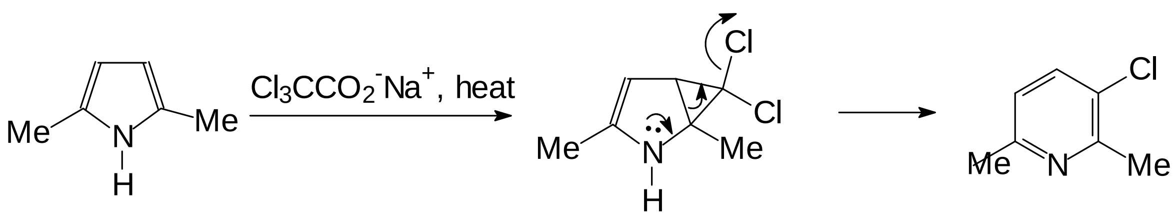
J. Org. Chem. **1998**, 9183.

6.1.6 Addition and cycloaddition reactions



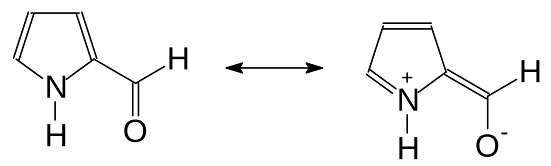


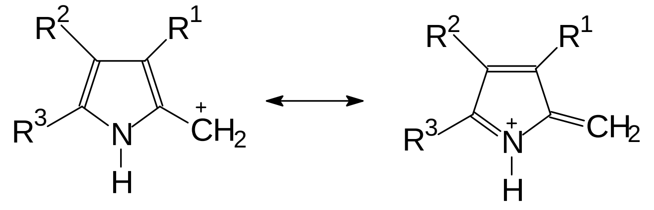
Photoaddition of acetone to 1-methylpyrrole

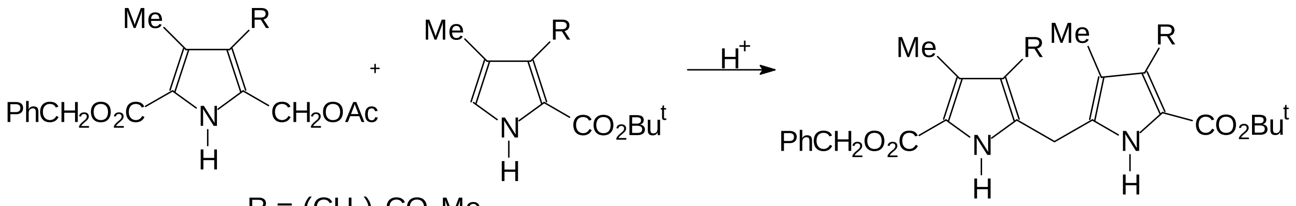


Reaction of 2,5-dimethylpyrrole with dichlorocarbene

6.1.7 Properties of substituted pyrroles

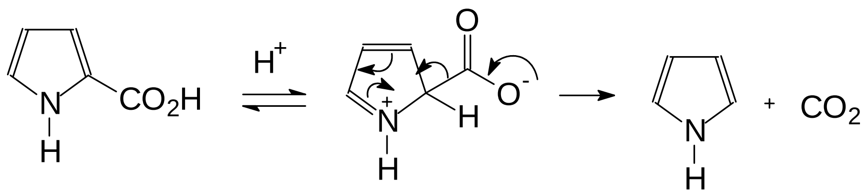




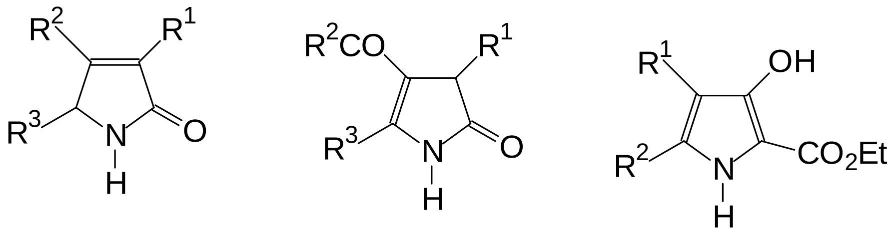


R = $(CH_2)_2CO_2Me$

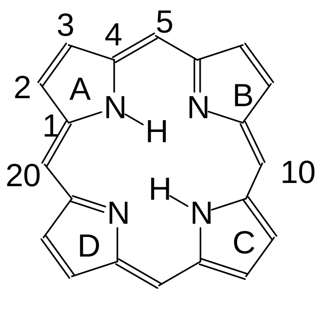
Coupling of pyrroles through an acetoxymethyl derivatives

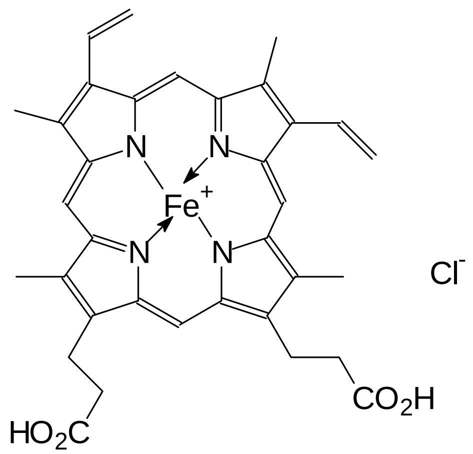


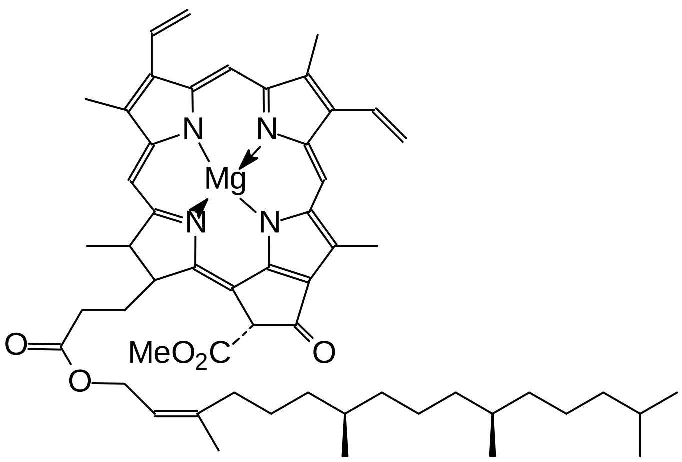
Decarboxylation of pyrrole-2-carboxylic acid

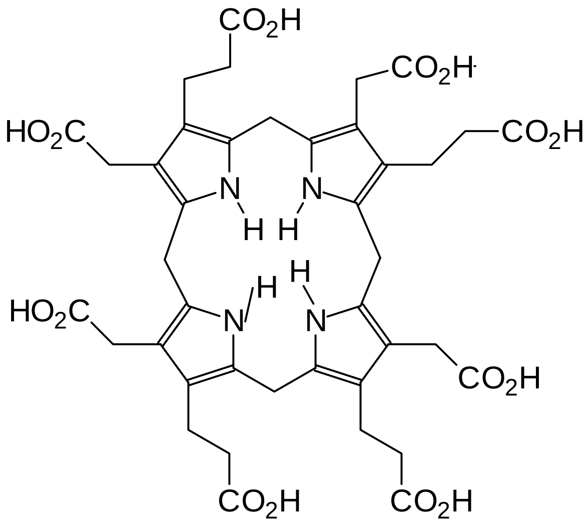


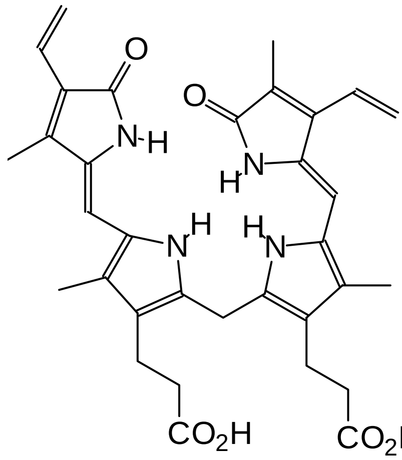
6.1.8 Porphyrins and related pyrrolic natural products

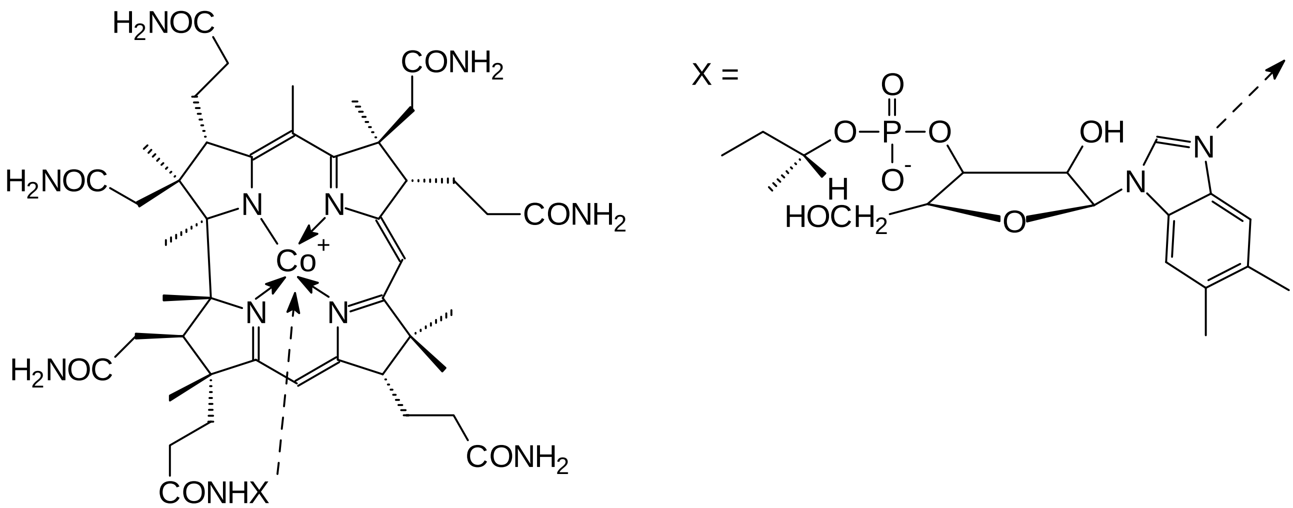






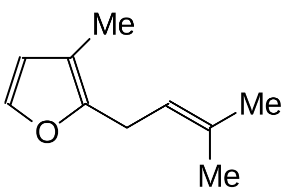


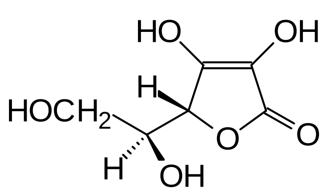


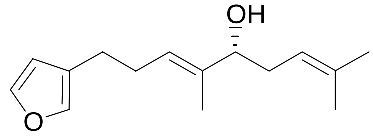


6.2 Furans

6.2.1 Introduction







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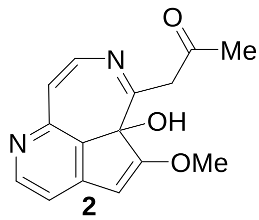

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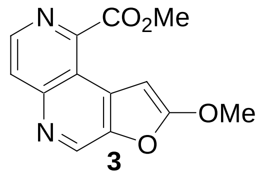

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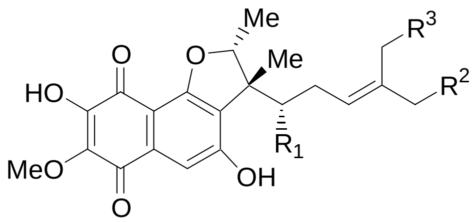
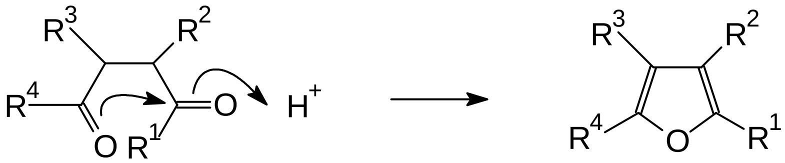
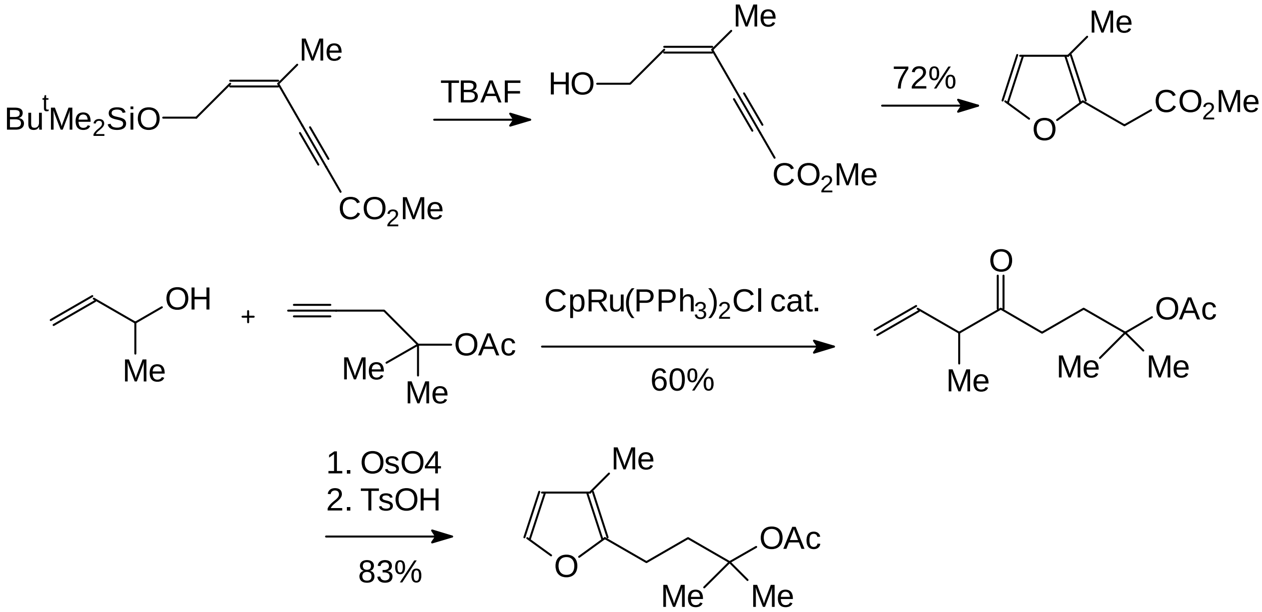


R_1, R_2, R_3= H, OH 4

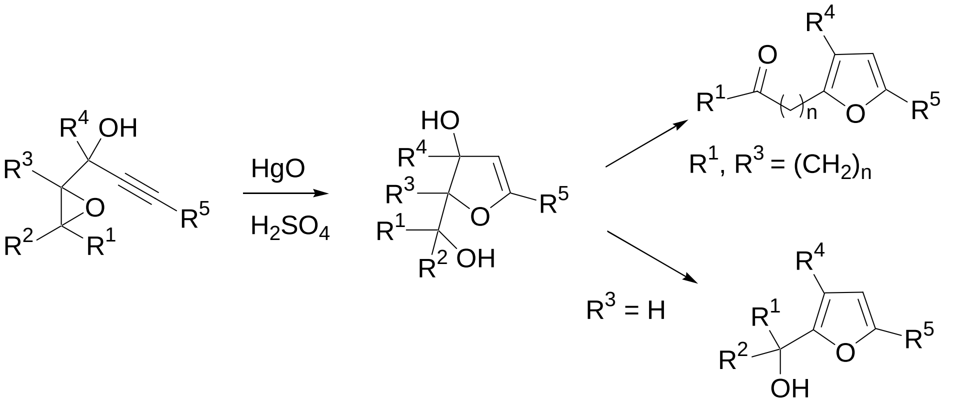
6.2.2 Ring synthesis



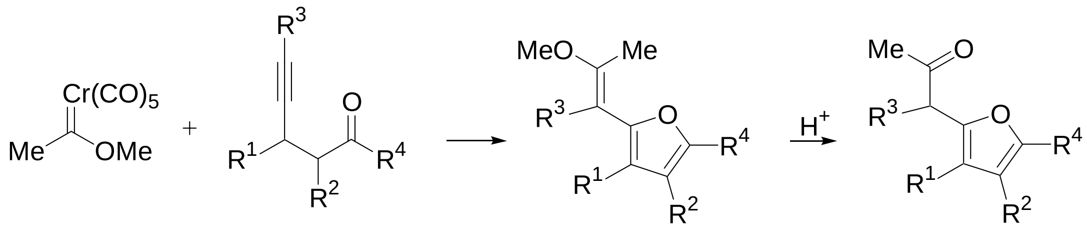
Paal-Knorr furan synthesis



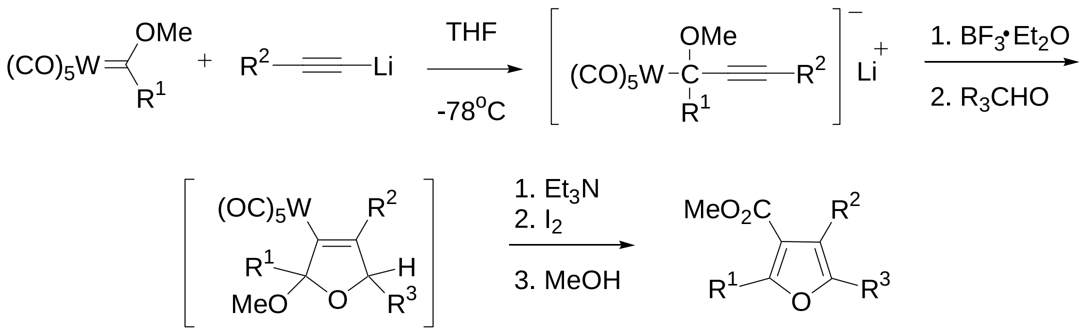
Two routes to 2,3-disubstituted furans.



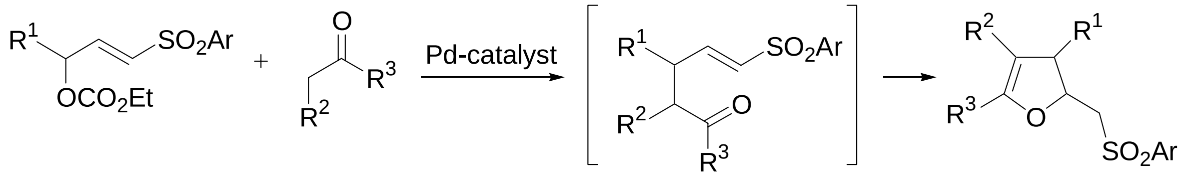
J. Org. Chem. **1998**, 9223.



J. Org. Chem. **1998**, 4564.



J. Org. Chem. **1998**, 3164.



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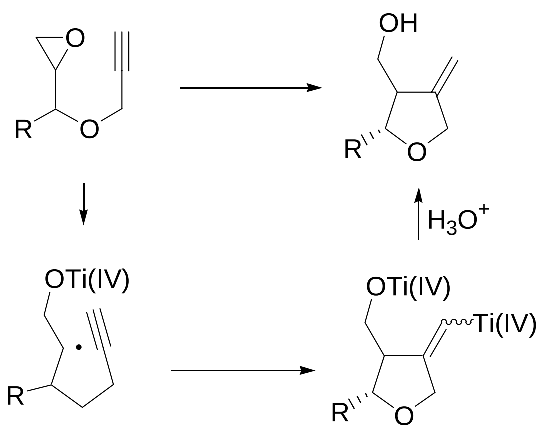
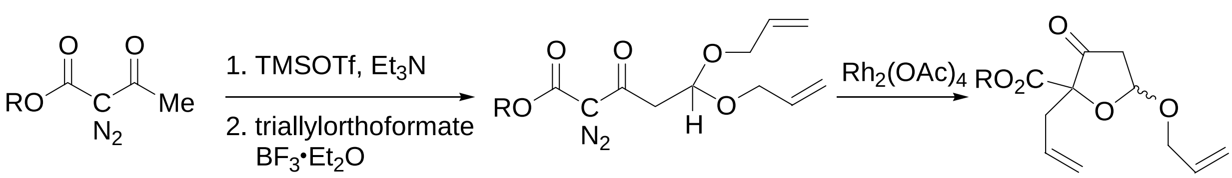
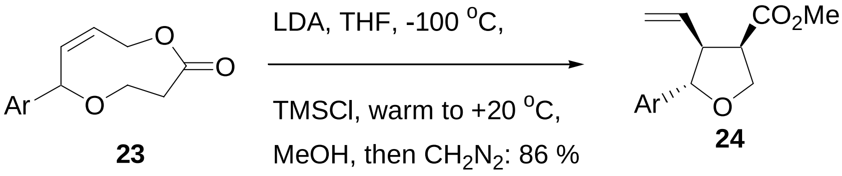


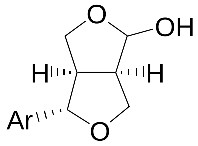
J. Org. Chem. **1998**, 2829.



Tetrahedron Lett. **1998**, 8813.



J. Chem. Soc. Perkin 1. **1998**, 1779.



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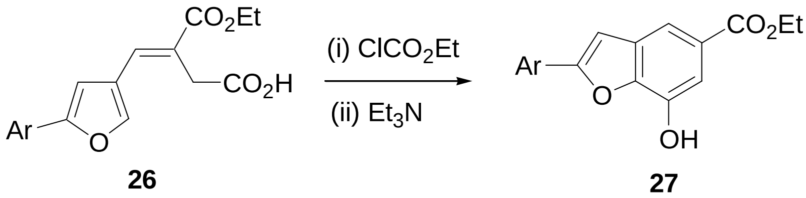
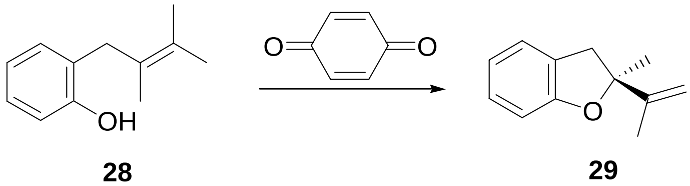
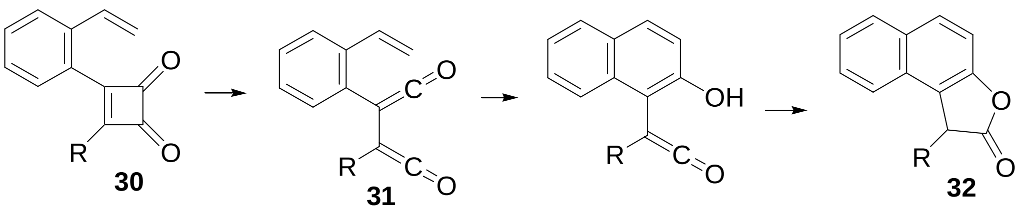


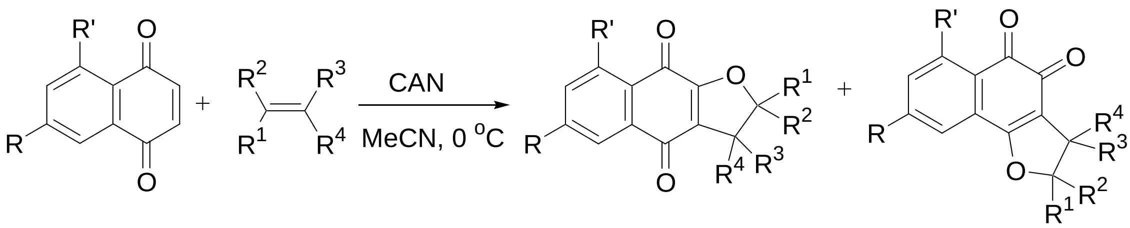
Tetrahedron Lett. **1998**, 5609.



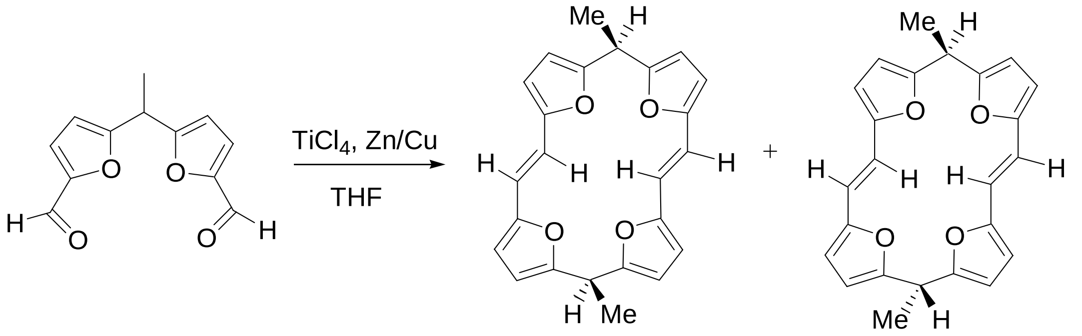
J. Org. Chem. **1998**, 5071.



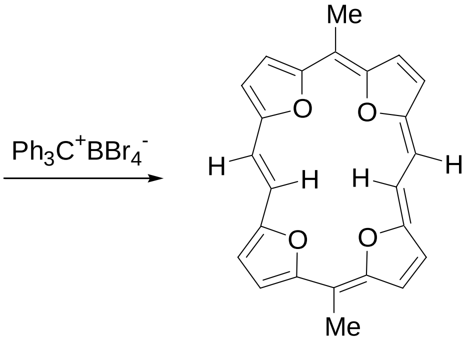
Tetrahedron lett. **1998**, 3643.



Bull. Chem. Soc. Jpn. **1998**, 1691.



(+ syn - (Z,Z) + anti - (Z,Z))



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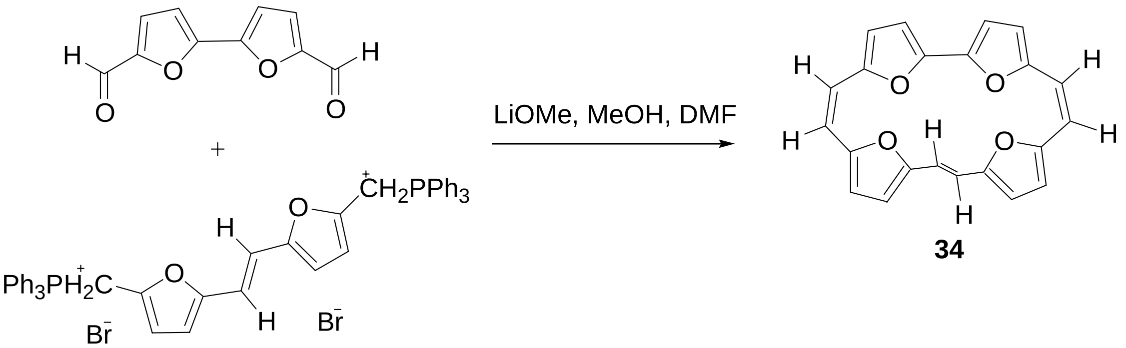
Helv. Chim. Acta. **1998**, 93. *Helv. Chim. Acta.* **1998**, 1077.



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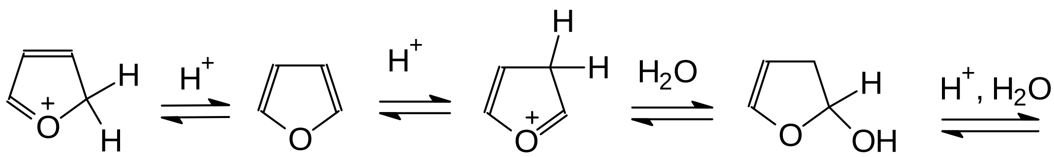
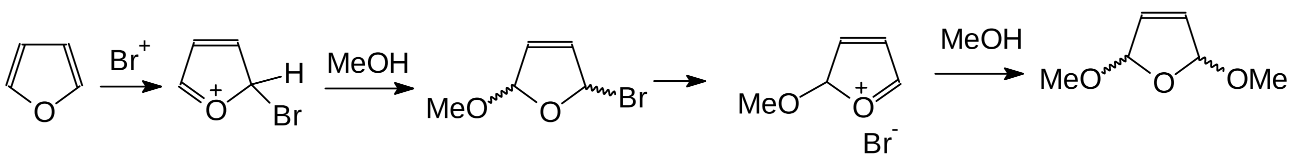
J. Org. Chem. **1998**, 5228.

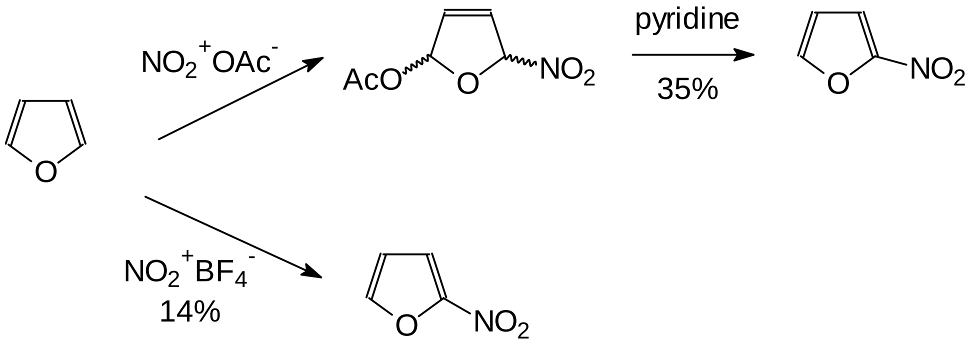
6.2.3 Reactions with electrophiles



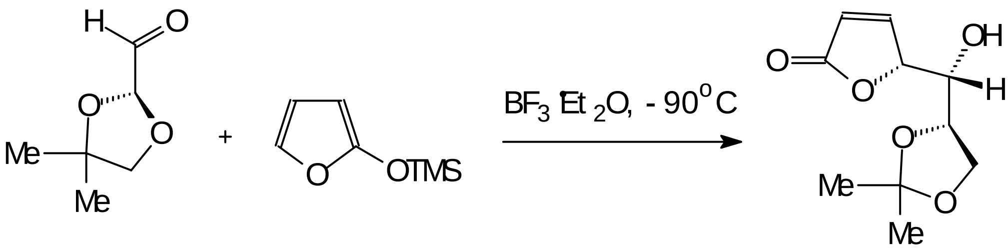
Protonation of furan



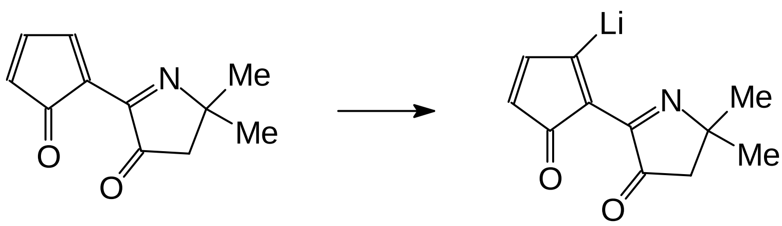
Bromination of furan in methanol



Nitration of furan

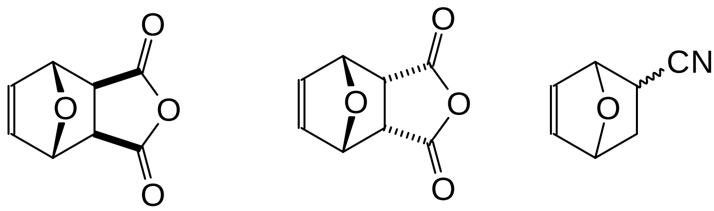


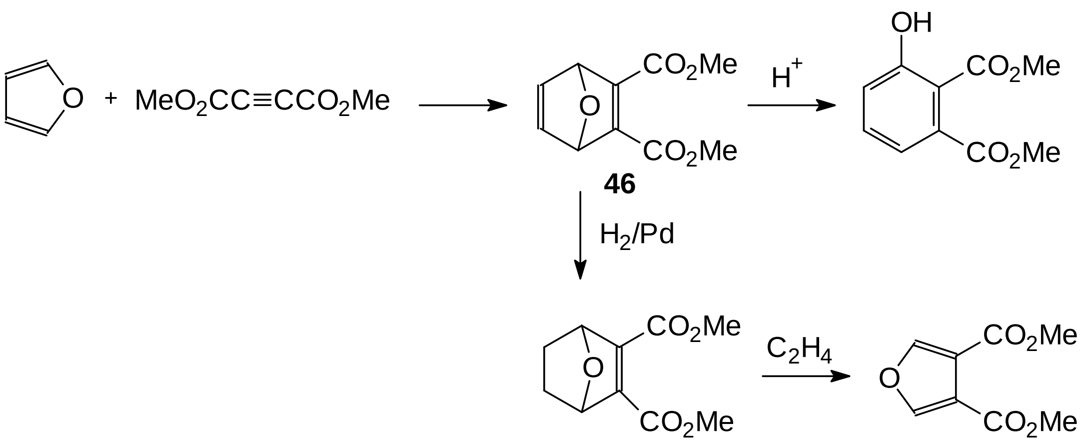
Reaction of 2-trimethylsilyloxyfuran with a chiral aldehyde



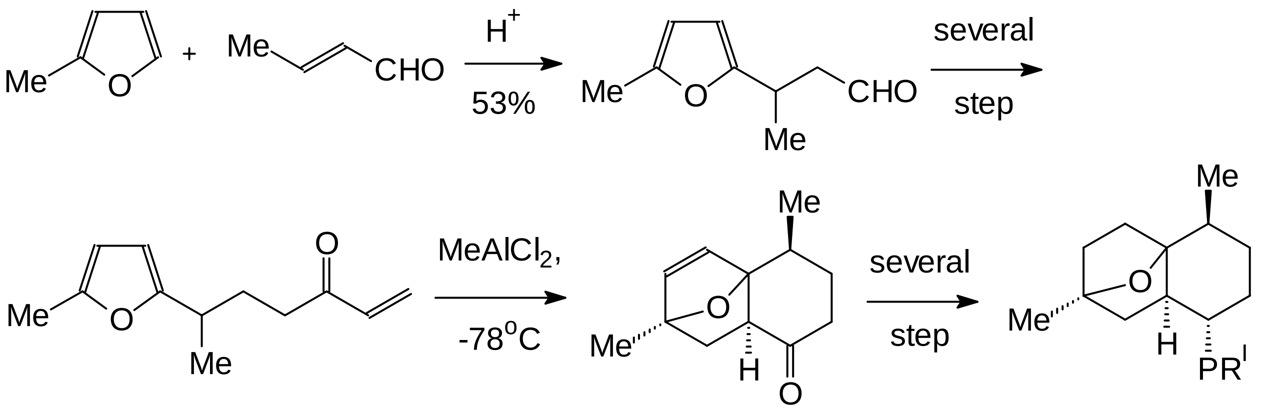
Directed lithiation.

6.2.4 Radical substitution and nucleophilic substitution

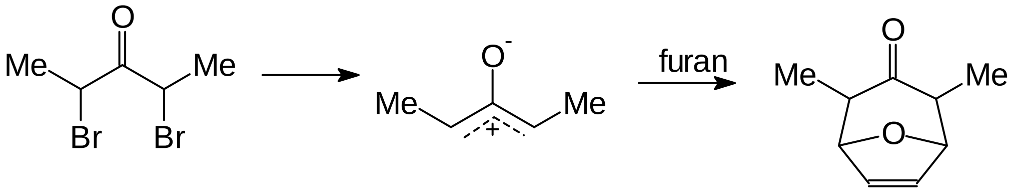




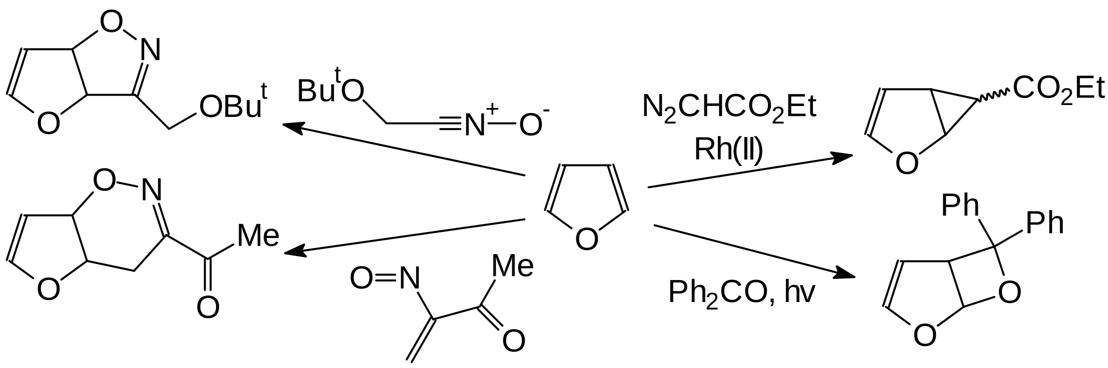
Formation and reaction of the **46**



Intrmolecular Diels-Alder reaction



Cycloaddition of furan to an oxallyl cation.



Cycloaddition reaction – furan acts as a 2π component.