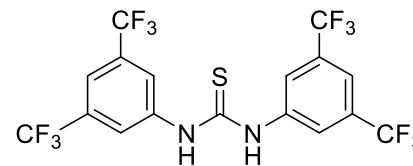


Thiourea Catalysis – Past, Present and Future?

Seminar talk presented by
Friedemann Dreßler

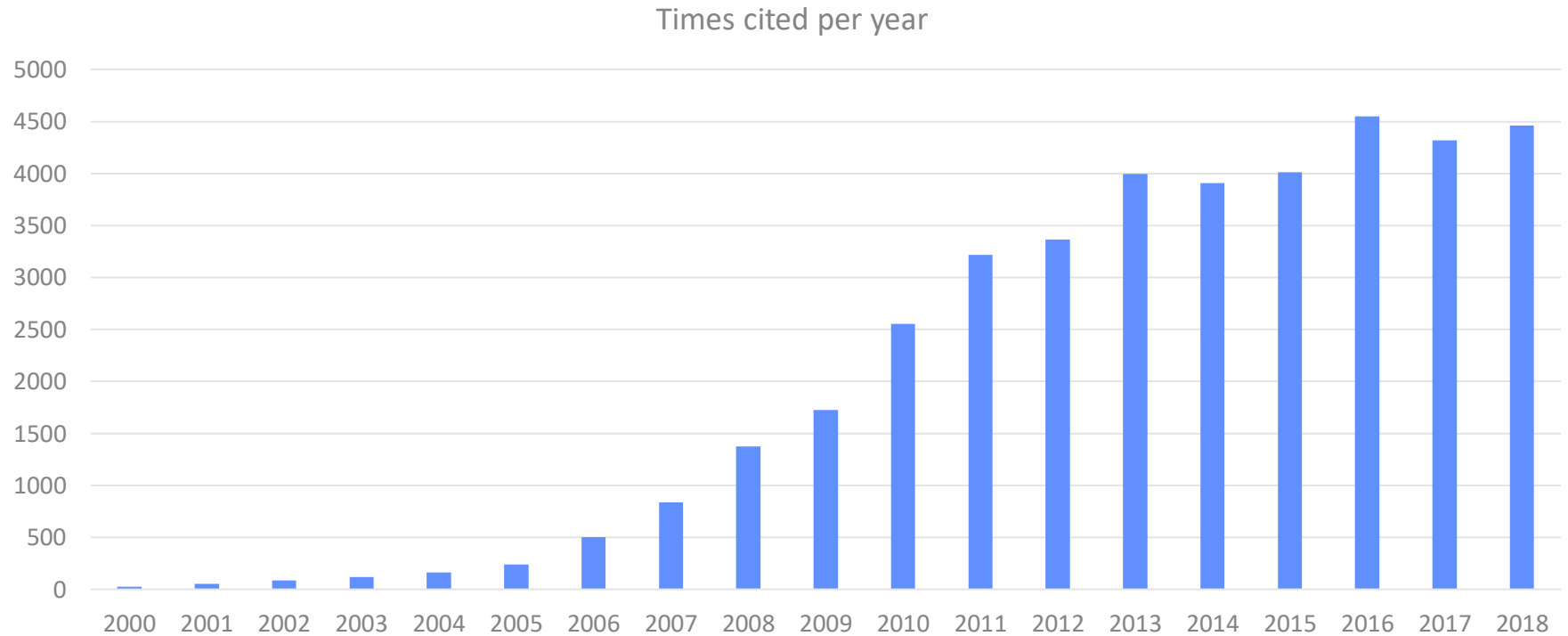
July 26th, 2019

*Institute of Organic Chemistry
Justus-Liebig University Giessen*



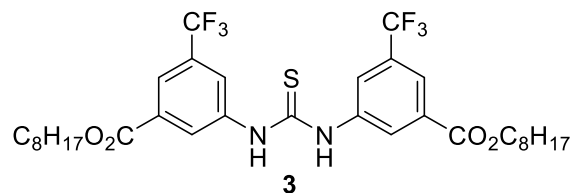
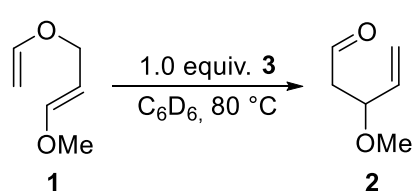


“Thiourea Catalysis” in Web of Science



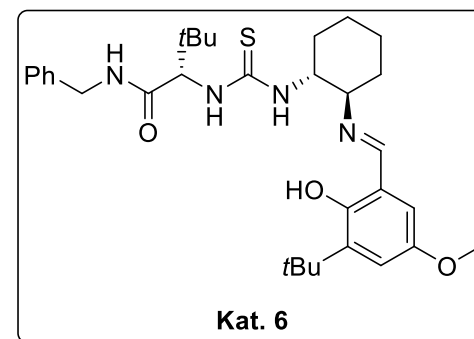
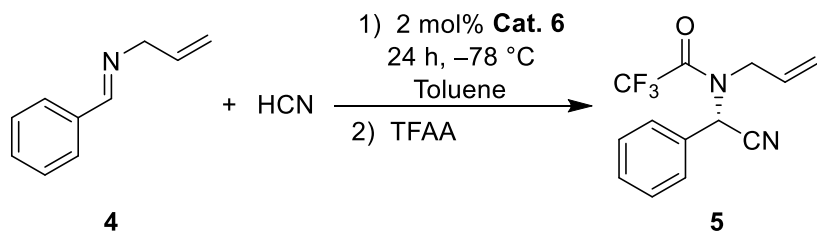


- 1995: Curran tested first Thiourea in „catalysis“



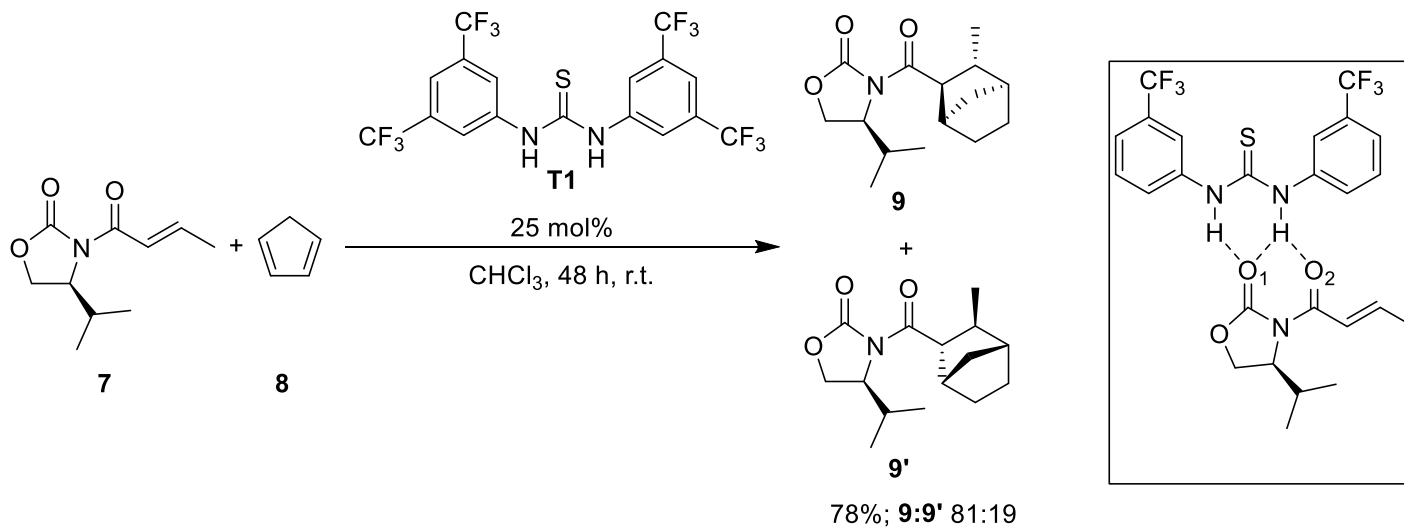
→ decompose of “catalyst”

- 1998: First effective Thiourea catalyst by Jacobsen
 - Asymmetric Strecker reaction
 - More than 170 catalyst were tested

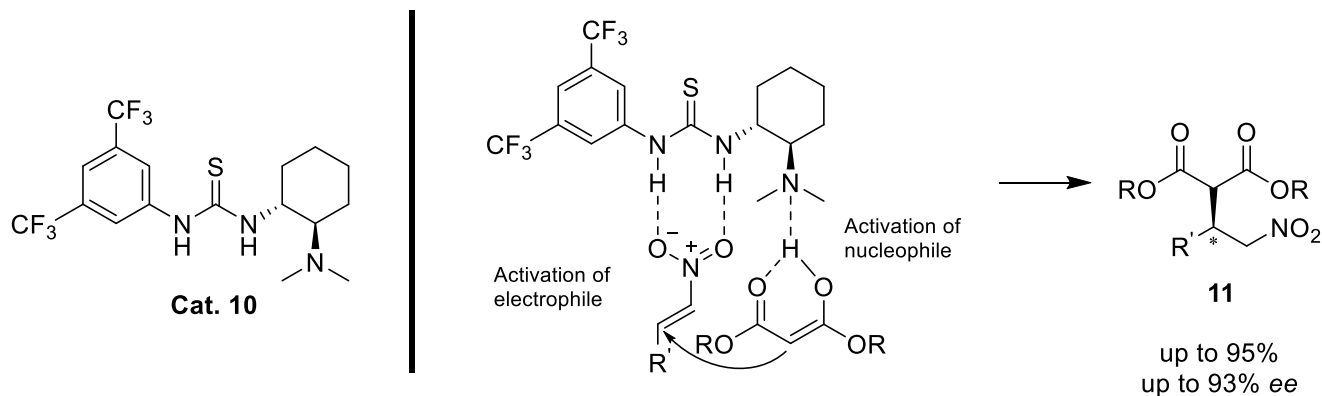


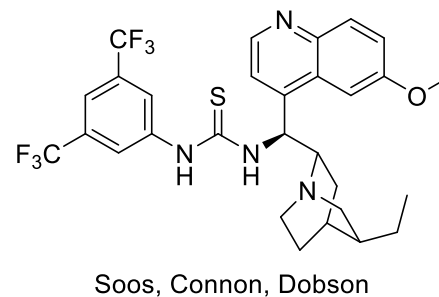
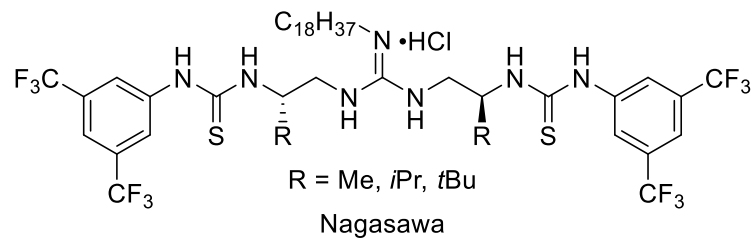
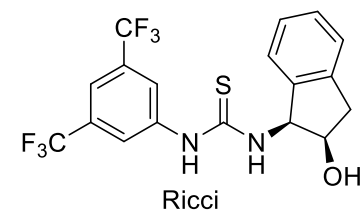
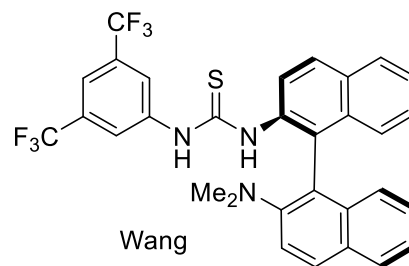
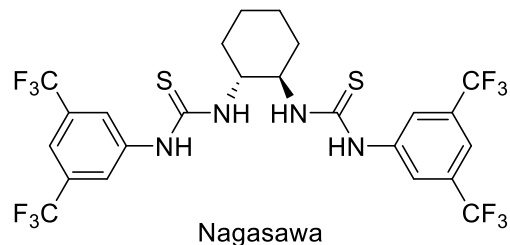


- 2002: First effective use of the Thiourea motif by Schreiner



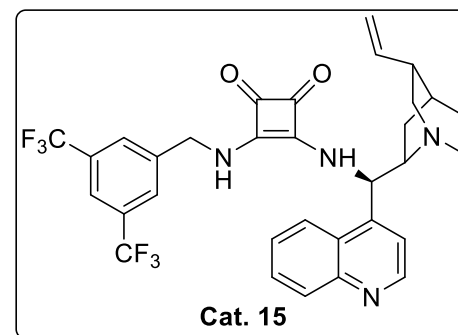
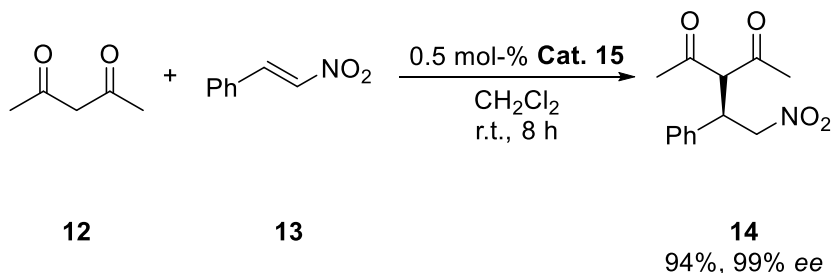
- 2003: First asymmetric Thiourea by Takemoto





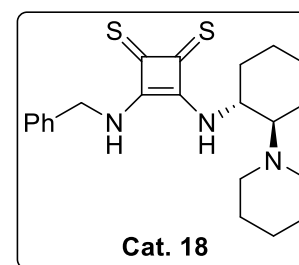
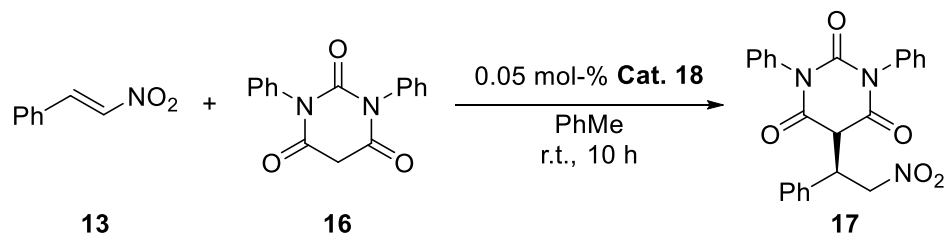


- 2008: First Squaramide catalyst



- Lower catalyst loading

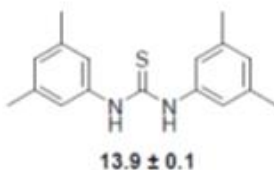
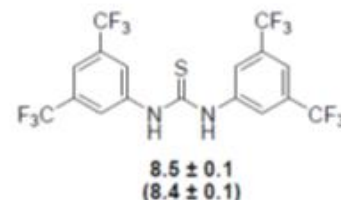
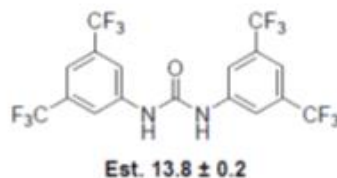
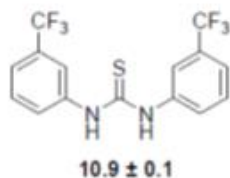
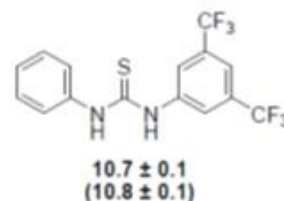
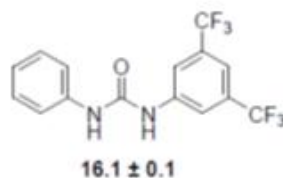
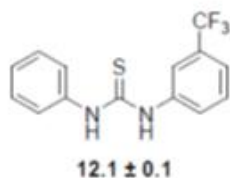
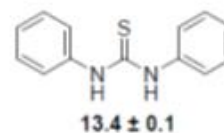
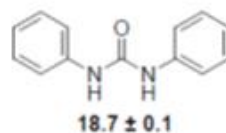
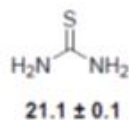
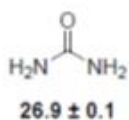
- 2017: Thiosquaramide catalyst



- Higher activity and solubility



The effect of CF₃ groups



S → O : ~ 5.5

Aryl : ~ 4

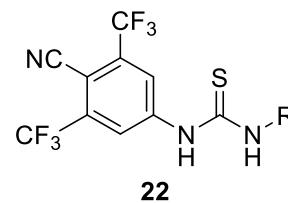
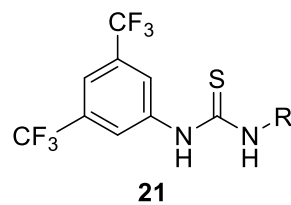
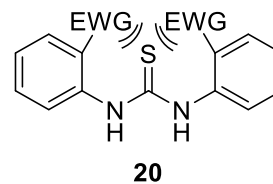
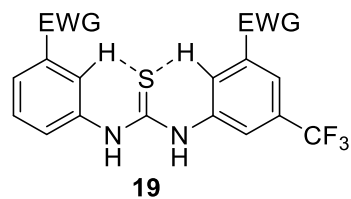
H → CF₃ : ~ 1.3

F. G. Bordwell *Acc.Chem.Res.* 1988, 21, 456.

X. Li, H. Deng, S. Luo, J.-P. Cheng *Eur.J.Org.Chem.* 2008, 4350.

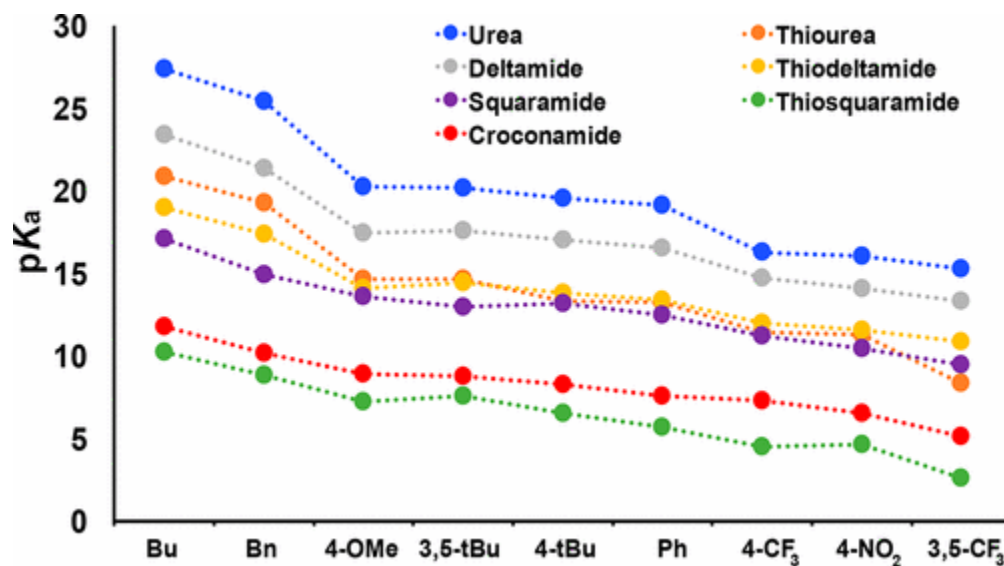
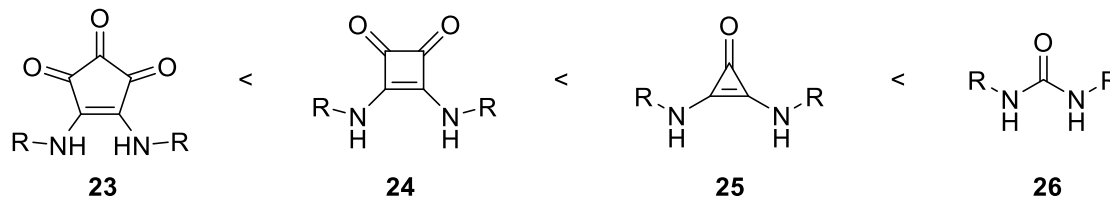
G. Jakab, C. Tancon, Z. Zhang, K. M. Lippert, P. R. Schreiner *Org.Lett.* 2012, 14, 1724.

→ Activity depend on pKa





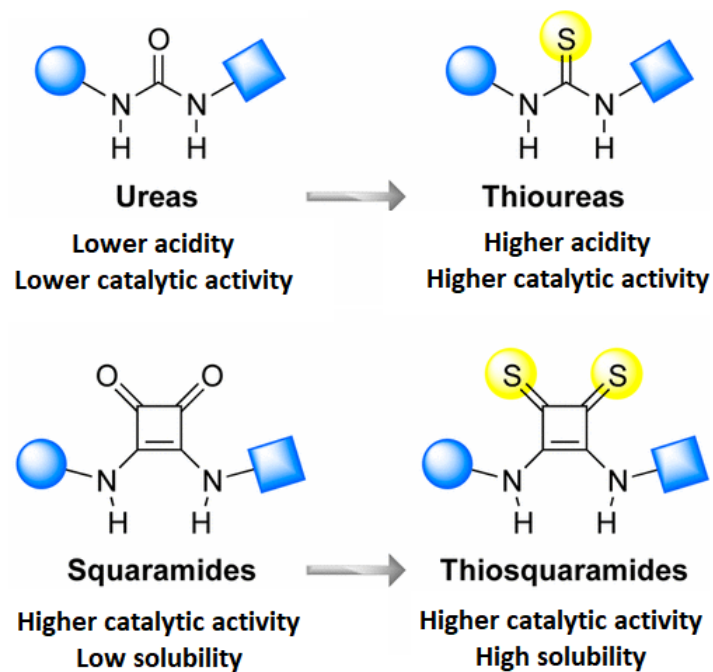
- 2018: Synthesis of Deltamides and Croconamides:
 - Dual H-Bond donors and anion recognition



G3(MP2)-RAD(+) (DMSO)

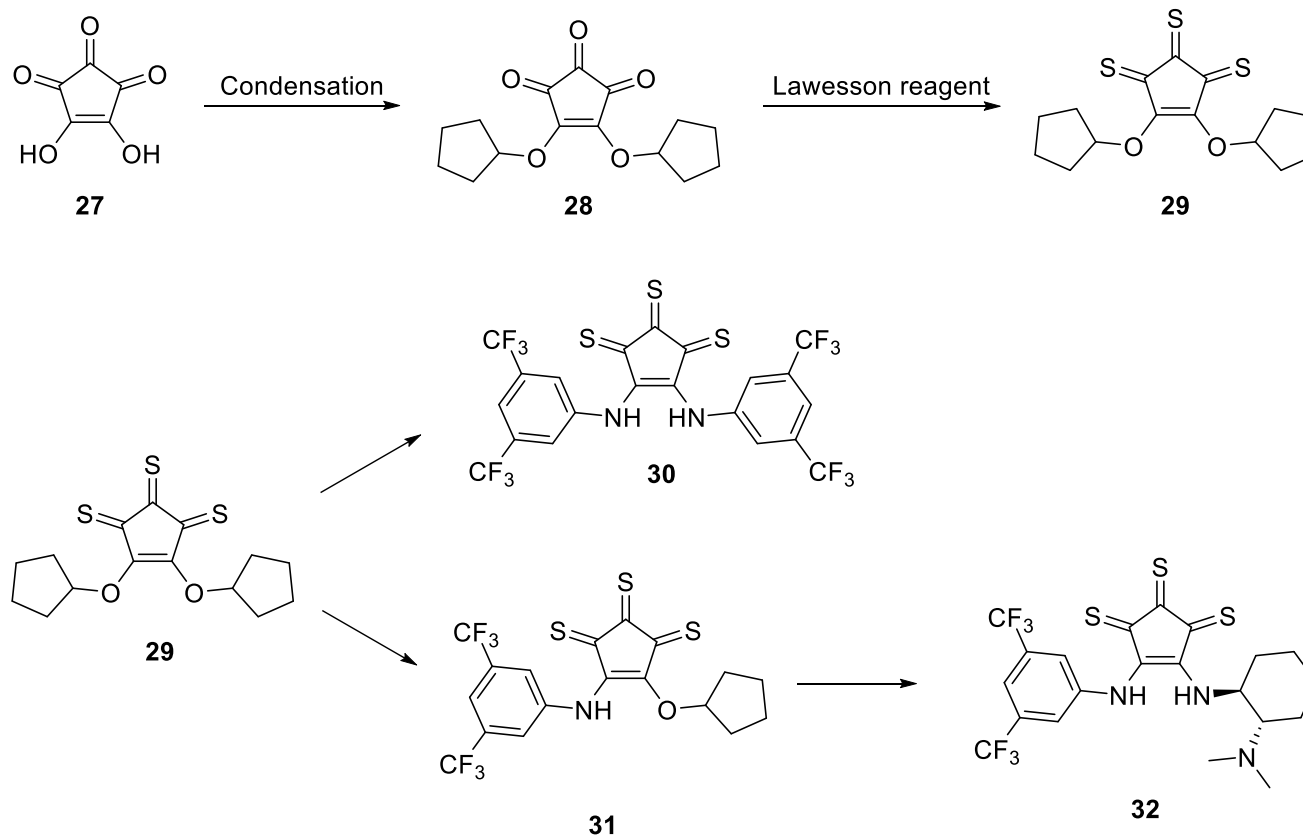


- Synthesis of Thiocroconamides and Thiodeltamides
- Comparison of all catalyst class





- Base on the Thiosquaramide synthesis



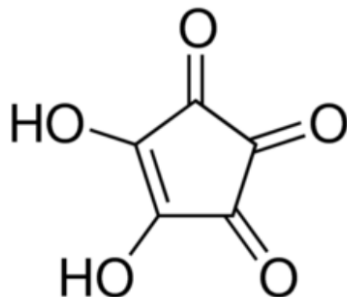


Croconic acid

98%

Synonym: 4,5-Dihydroxy-4-cyclopentene-1,2,3-trione

CAS Number 488-86-8 | Empirical Formula (Hill Notation) C₅H₂O₅ | Molecular Weight 142.07 | Beilstein Registry Number 2043130 | MDL number MFCD00181389 | PubChem Substance ID 24864397



[Sicherheitsdatenblätter \(SDS\)](#) [FTIR \(PDF\)](#)

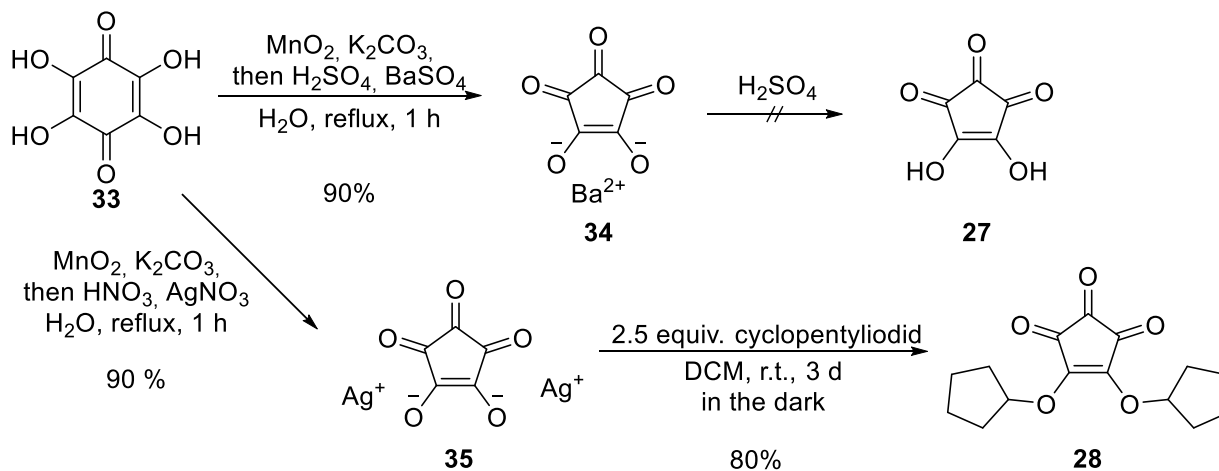
[Similar Products](#)

SKU-Packungsgröße	Verfügbarkeit	Preis (EUR)	Anzahl
391700-500MG	Nur noch 1 verfügbar. Mehr ist unterwegs. - ab	385.00	0

[Bulk oder Grossmengen-Bestellungen?](#)

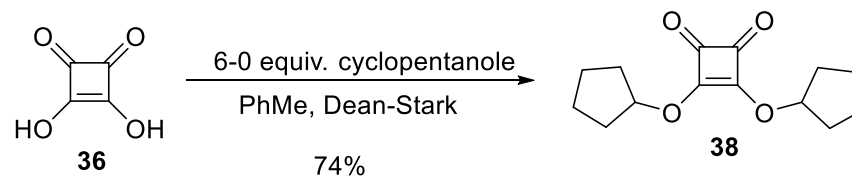
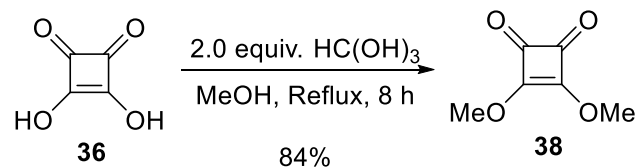
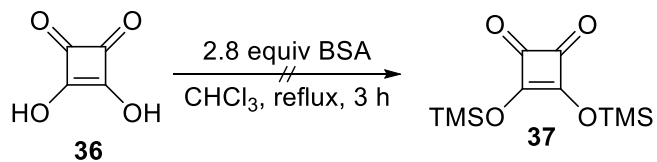
[zum Warenkorb hinzufügen](#)

Product Recommendations





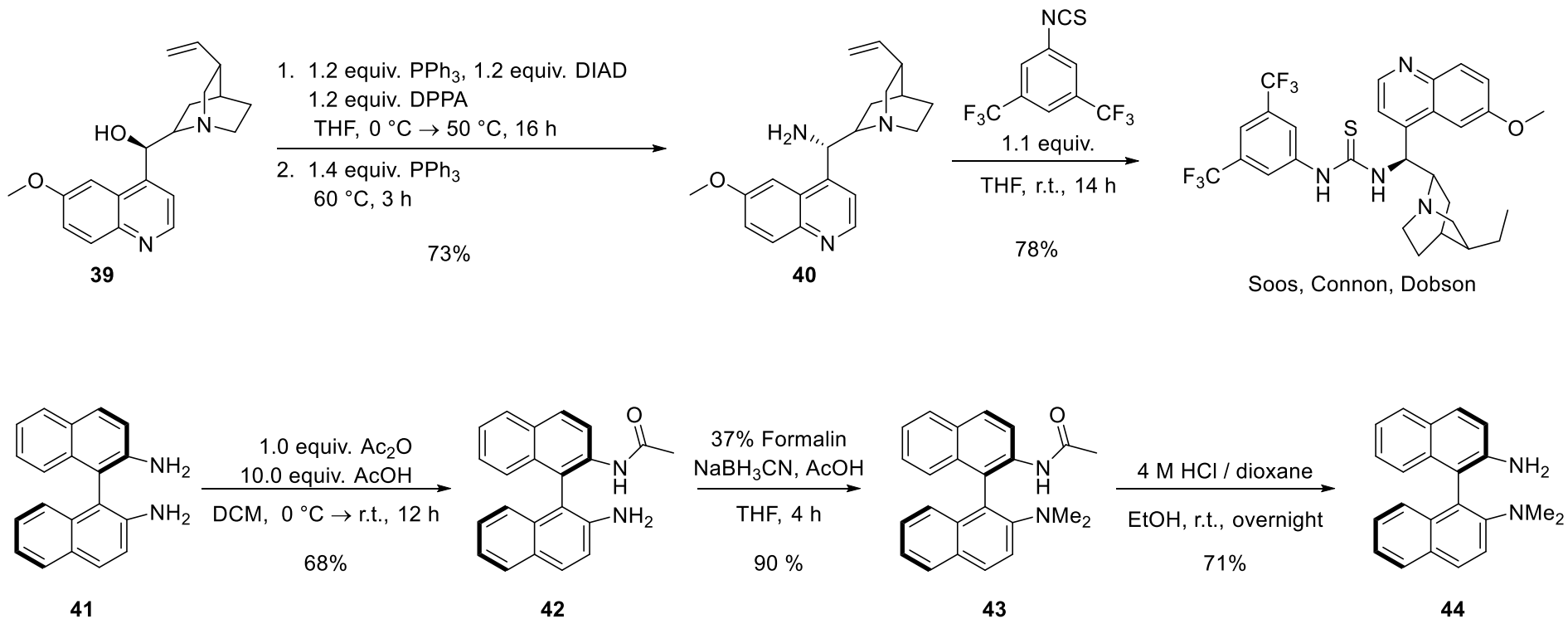
- General synthesis route to Deltic acid *via* Squaric acid



- Photolysis of Squaricesters \rightarrow Loss of CO

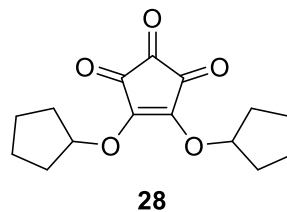


• Synthesis of chiral amines

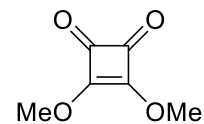




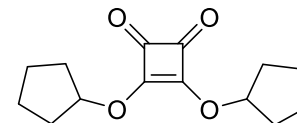
- Synthesis of different Croconic ester and Squaric ester



28

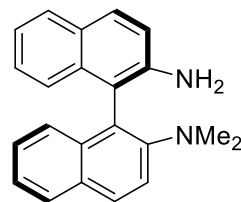


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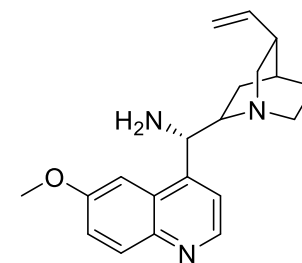


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- Synthesis of chiral amines



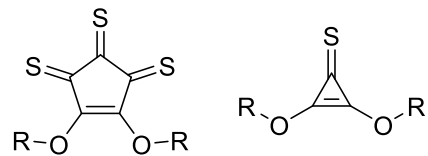
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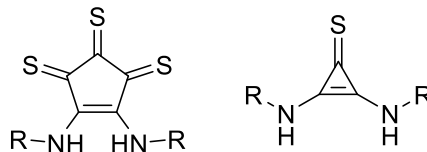
40



- Thionation of Croconicester and Delticester

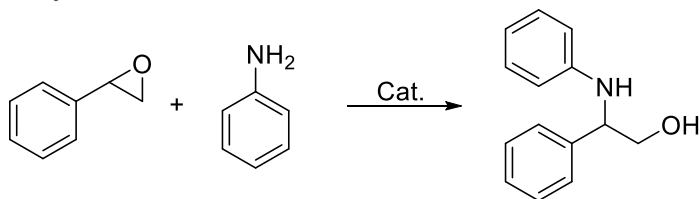


- Aminolysis to catalyst



- Determine pKa values

- Comparison of catalyst activity





- Prof. Peter R. Schreiner
- Analytical department
- Labs B204 and B205
- Bastian Bernhardt

- PRS-Group

