

α,β -ungesättigte Acylammoniumsalze in der Katalyse

08.09.17

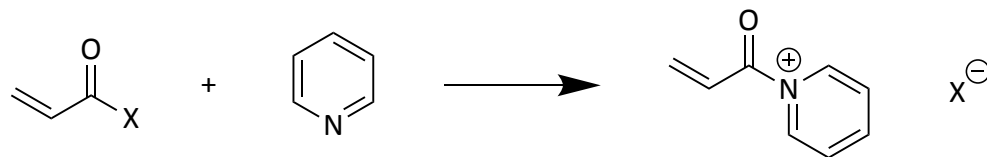
Felix Keul

Spezialisierungsvortrag

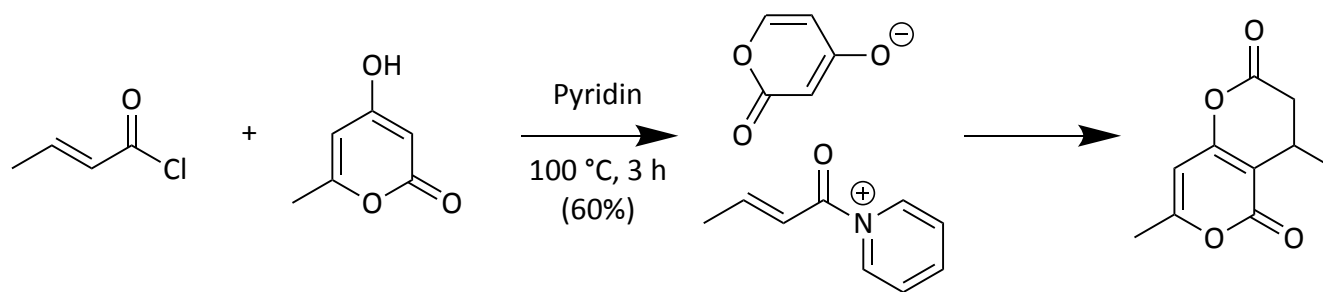
Institut für Organische Chemie

Justus-Liebig-Universität

35392 Gießen

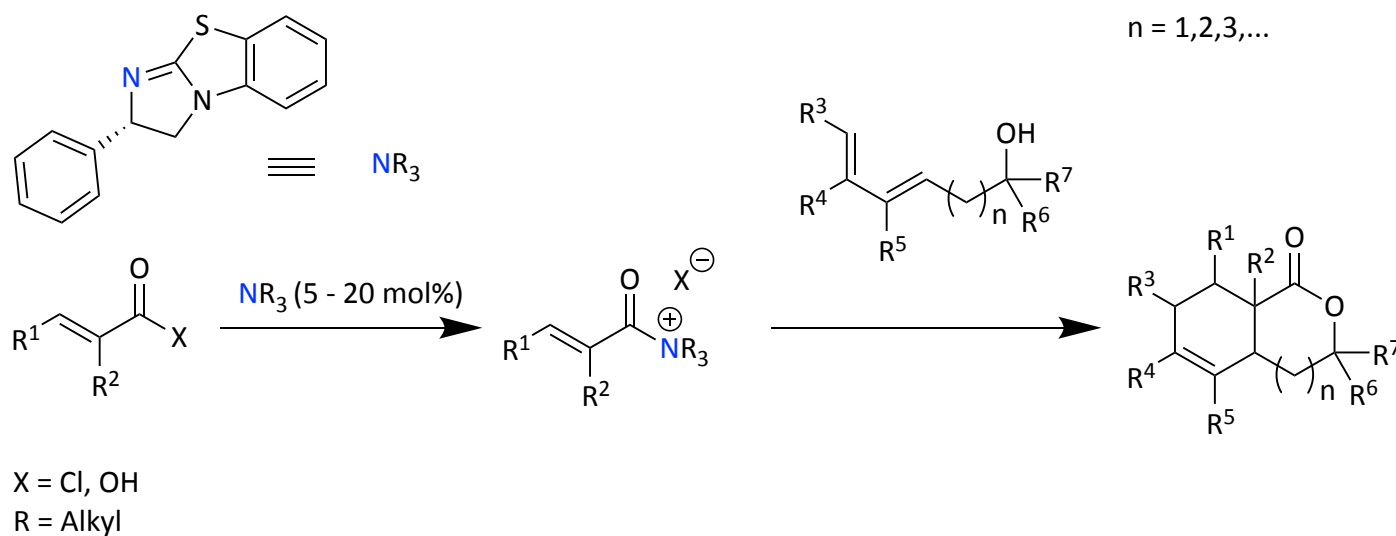


X = Cl, Anhydrid





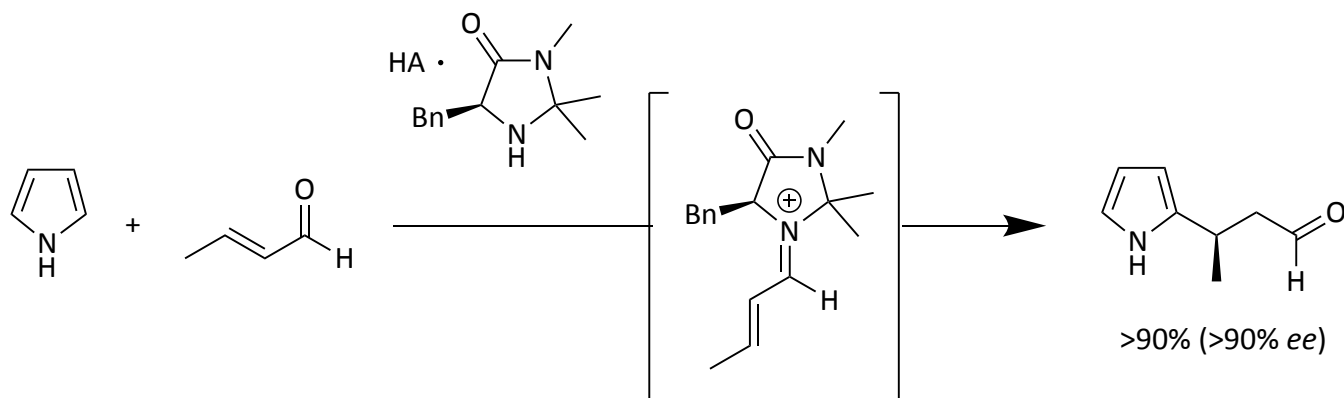
Romo *et al.* entwickelten die erste enantioselective Diels-Alder-Reaktion mit Acylammoniumsalzen







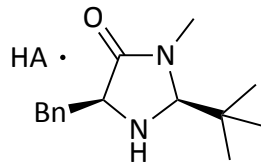
- Seit dem 19. Jahrhundert bekannt
- Hauptsächlich basierend auf Metallen und Lewis-Säuren
- MacMillan *et al.* entwickelten die erste organokatalytische Variante



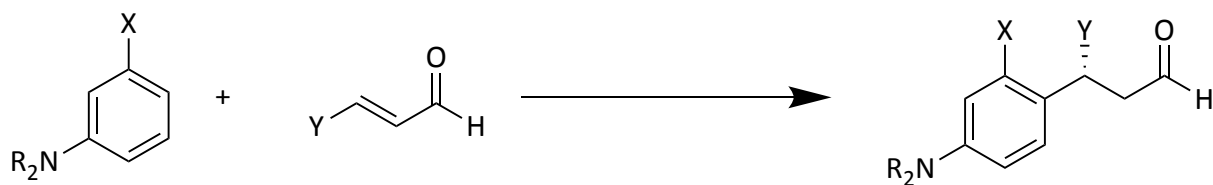
HA = NCCH₂CO₂H, Cl₂CHCO₂H, Cl₃CO₂H, TFA



- MacMillan



- Erweiterung auf Indole als Nukleophil
- Erweiterung auf elektronenreiche Benzole

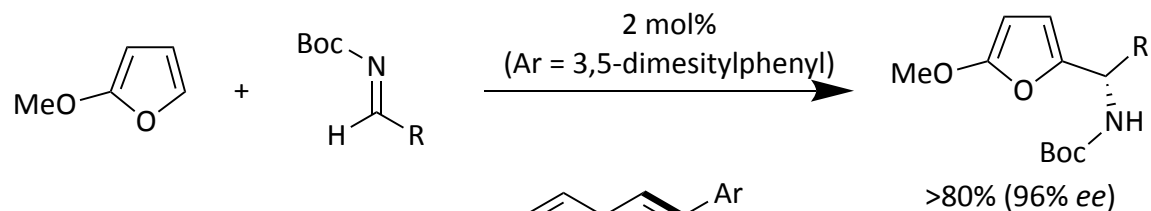


R = Dimethyl, Cyclopentenyl
 X = H, OMe
 Y = Me, Et, Ph, CO₂Me, CH₂OBz
 HA = TFA

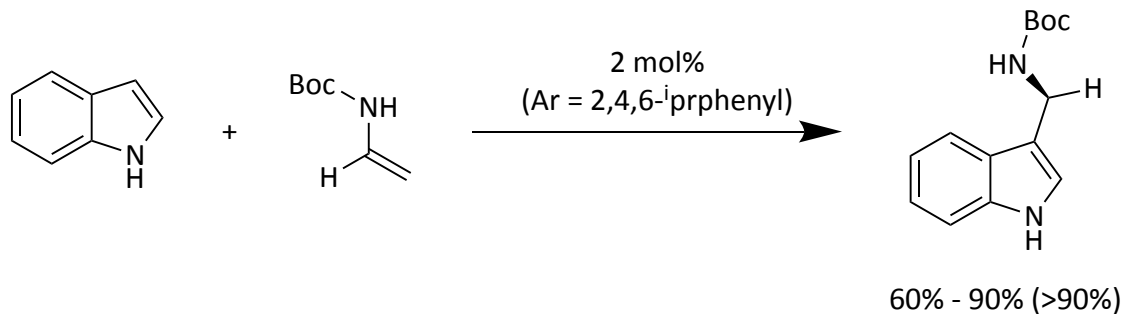
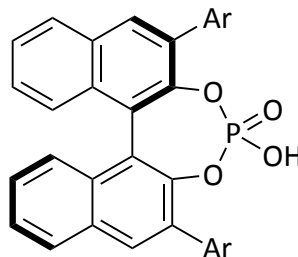
70-90% (90% ee)



- Terada *et al.*

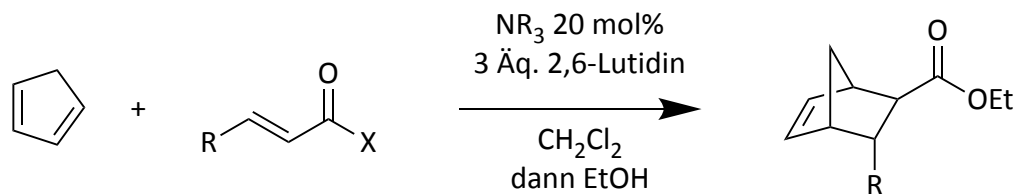


R = Naphtyl, Ph, Br-Ph, Cl-Ph,
 Me-Ph, MeO-Ph





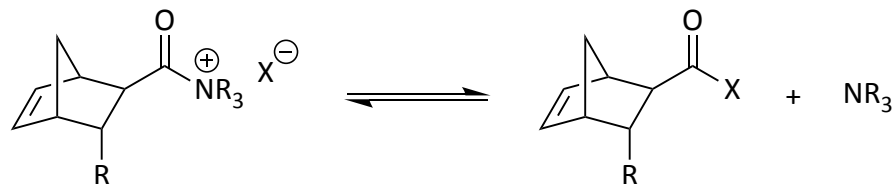
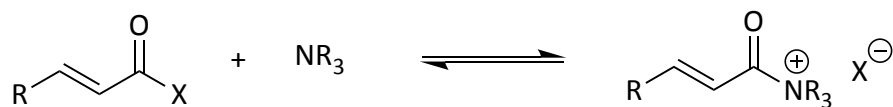
- Grundstein für Multikatalyse



R = Me, CO₂Et

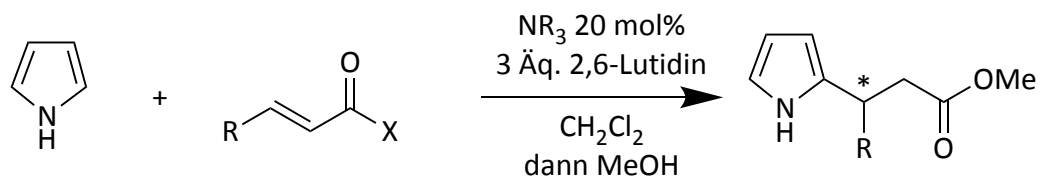
X = Cl, Anhydrid

NR₃ = 1-Methylimidazol, DMAP

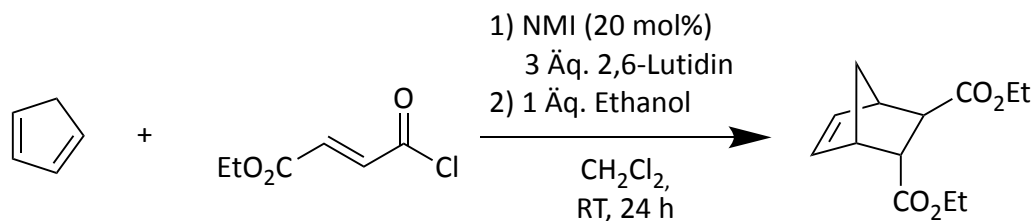
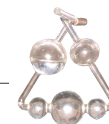




- Friedel-Crafts-Reaktion



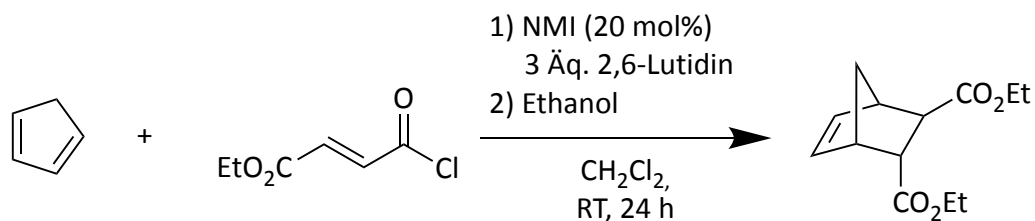
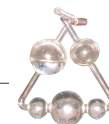
R = Me, CO₂Et
 X = Cl, Anhydrid



NMI = 1-Methylimidazol

- Variation der Substratkonzentration

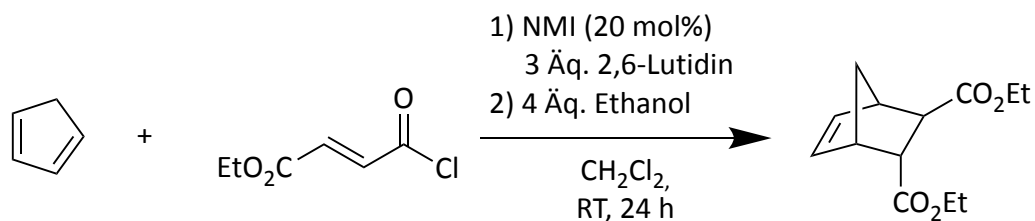
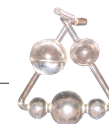
Konzentration	pur	0,2 $\frac{\text{mmol}}{\text{mL}}$	0,1 $\frac{\text{mmol}}{\text{mL}}$	0,01 $\frac{\text{mmol}}{\text{mL}}$
Umsatz [%]	-	22%	26%	-
Blindproben [%]	-	10%	-	-



NMI = 1-Methylimidazol

- Variation der Äquivalente an Ethanol

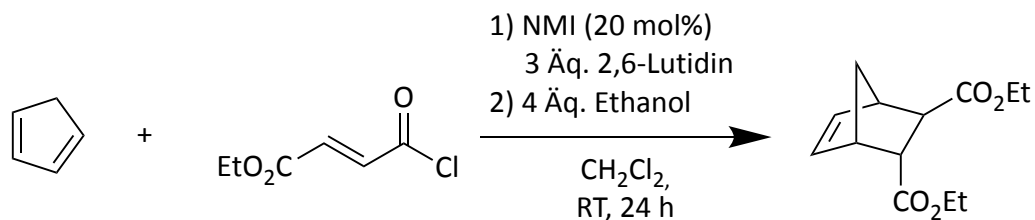
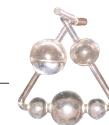
Äquivalente	1	1,5	2	4	10
Umsatz [%]	26	18	23	37	37



NMI = 1-Methylimidazol

- Variation der Reaktionszeit der Veresterung

Reaktionszeit [h]	5	24
Umsatz [%]	27	22



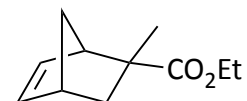
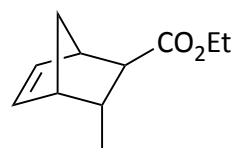
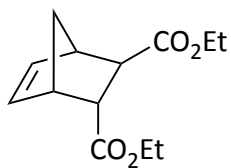
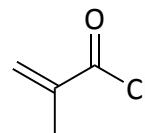
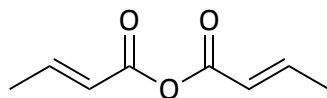
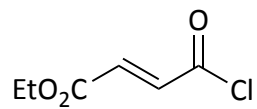
NMI = 1-Methylimidazol

- Variation der Art der Zugabe an Ethanol

Zugabeart	Blindprobe	direkt	0,8 Äq. pro Stunde
Umsatz [%]	48	78	28

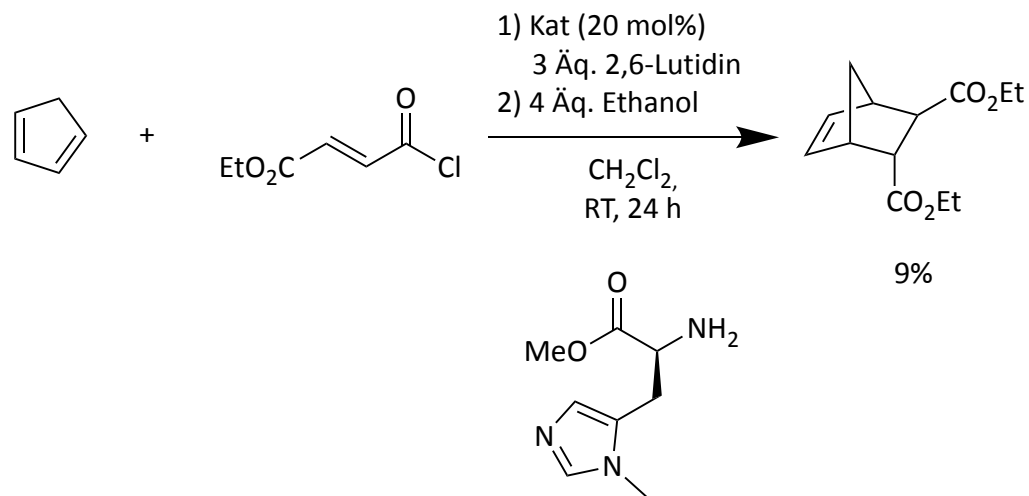


- Variation des Dienophils



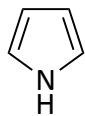
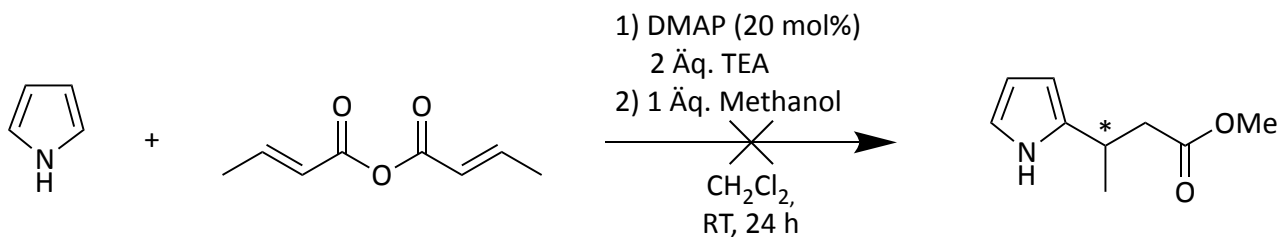


- π -Methylhistidin als Katalysator

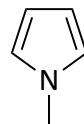




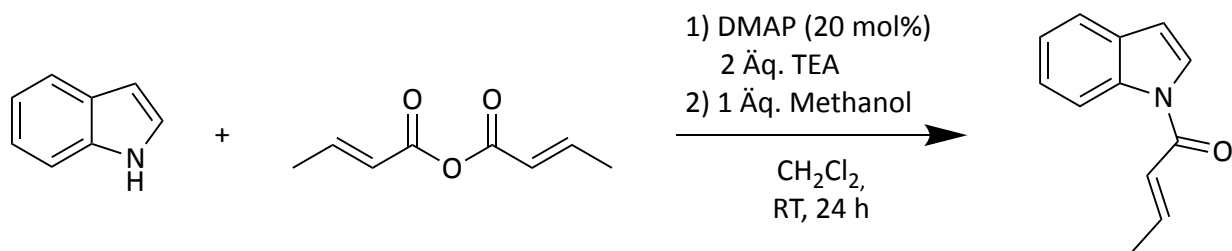
- Pyrrol als erstes Substrat
- Verwendung von *N*-Methylpyrrol als Substrat



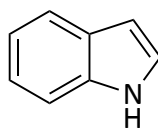
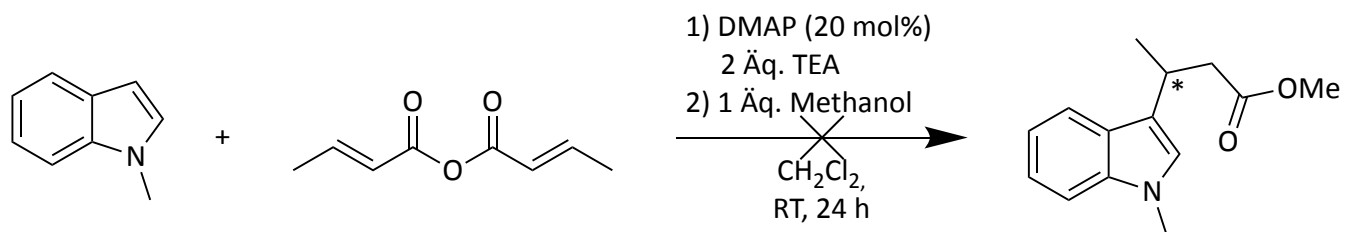
$N = 4,63$



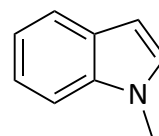
$N = 5,85$



Spuren



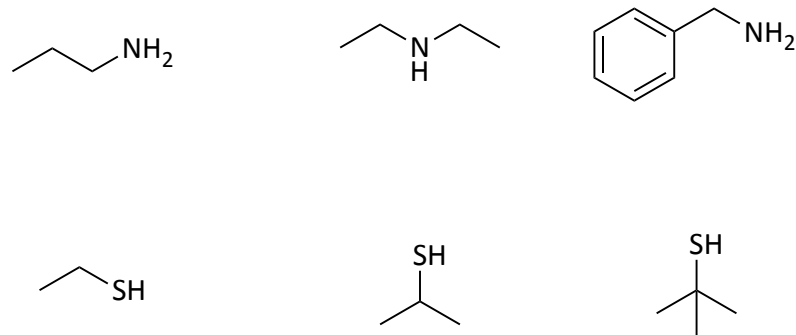
$N = 5,55$



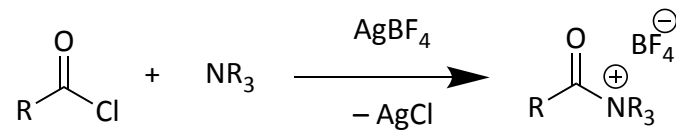
$N = 5,75$



- Verwendung von weiteren Nukleophilen



- Isolierung/Synthese des Acylammoniumsalzes

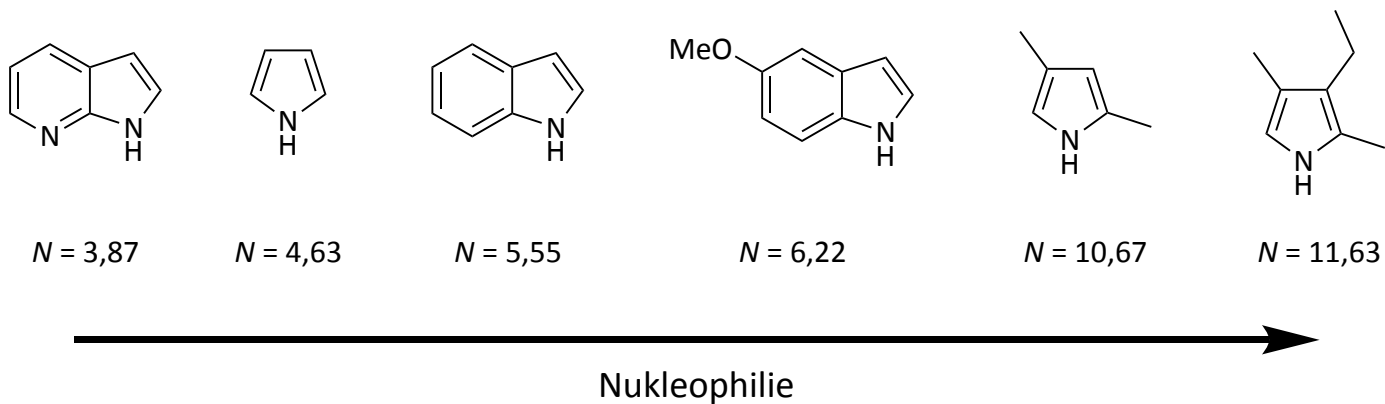


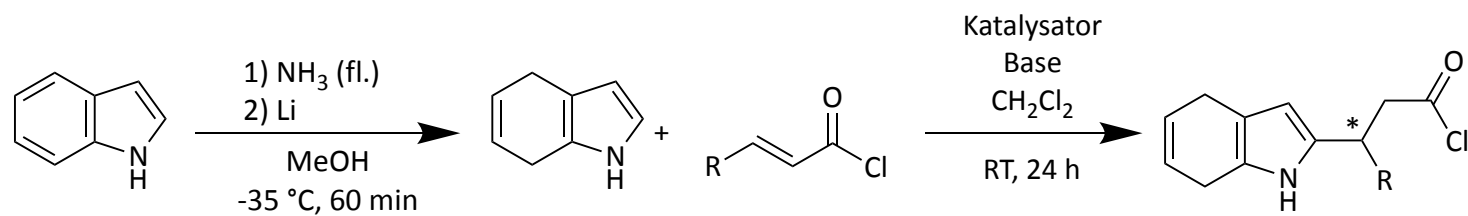
R = Alkyl, Aryl

NR₃ = Pyridin, DMAP, TEA, TMA

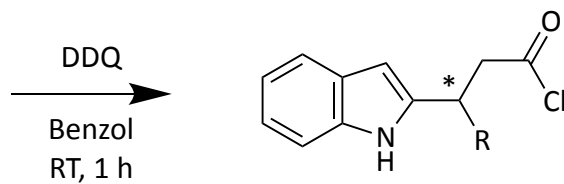


- Testen von weiteren Substraten





$\text{R} = \text{Me}, \text{CO}_2\text{Et}$



DDQ = 2,3-Dichlor-5,6-dicyano-1,4-benzochinon

Ich danke

Prof. Dr. Peter R. Schreiner

Christian Eschmann

Dr. Raffael Wende, Dominik Niedek, Jan-Philipp Berndt, Alexander Seitz, Jan Schümann, Frederik Erb



Vielen Dank für Ihre
Aufmerksamkeit!

