Lukas Nattmann

Max Planck Institut für Kohlenforschung Part II
- Directors Cut -

Cornella Group Meeting
07.09.2018

Please note: The resarch of nearly 30 years from an institute of this size is overwhelming. Therefore I had to chose a subgroup of publications and decided to focus only on the directors´ work. Also, this seminar only features work published while the directors were already working at the Max Planck Institut. Therefore previous or later works are not included. Also, each of the directors actually deserves a separate group seminar for thier contributions to chemistry. Lastly, this is an organic chemist´s view on the published work and might, in terms of selection, differ strongly from an expert´s view on the respective fields. The seminar is inevitably not comprehensive.

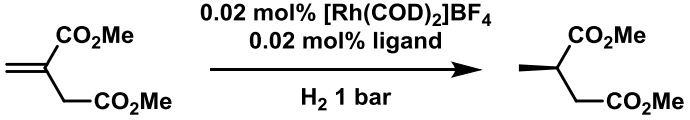
This Group seminar will feature (in the order of their starting dates as directos): **Manfred Reetz** (1991-2011), **Andreas Pfalz** (1995-1998), **Alois Fürstner** (1998 - today), **Ferdi Schüth** (1998 - today), **Walter Thiel** (1999-2018), **Benjamin List** (2005 - today), **Tobias Ritter** (2015 - today) and **Frank Neese** (2018 - today).

Manfred Reetz

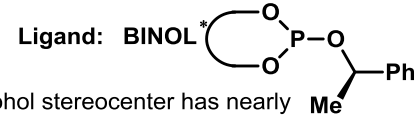
Director from 1991 (replaced Günther Wilke) until 2011
Established the concept of several directors
Main interests: Biocatalysis, directed evolution, Metal catalysis
Emeritus since 2011, but still active @University of Marburg

Prizes (selection):
Arthur C. Cope Award (2009)
Prelog Medal (2006)
Karl Ziegler Prize (2005)
Leibniz Prize (1989)
Otto-Bayer Prize (1986)

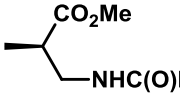
Asymmetric hydrogenation with a monophosphite ligand: ACIE, **2000,** 3889



99.4% ee

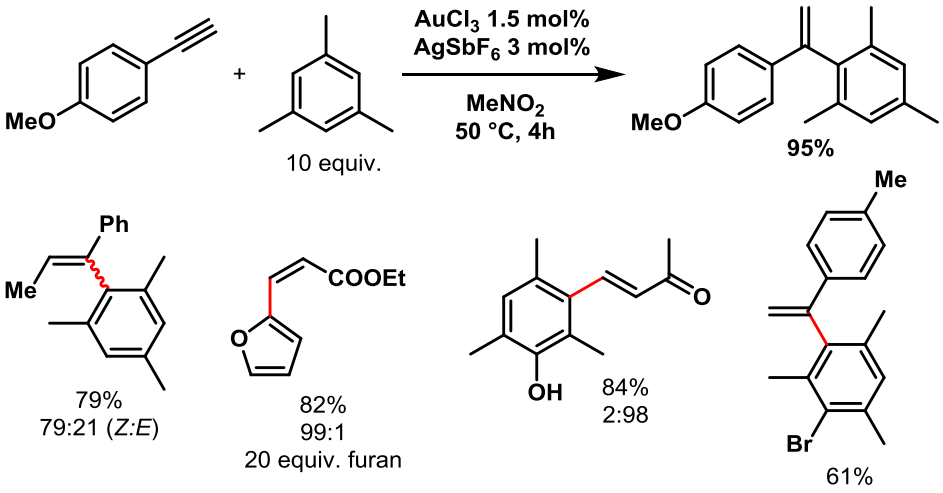


alcohol stereocenter has nearly no significance and be racemic

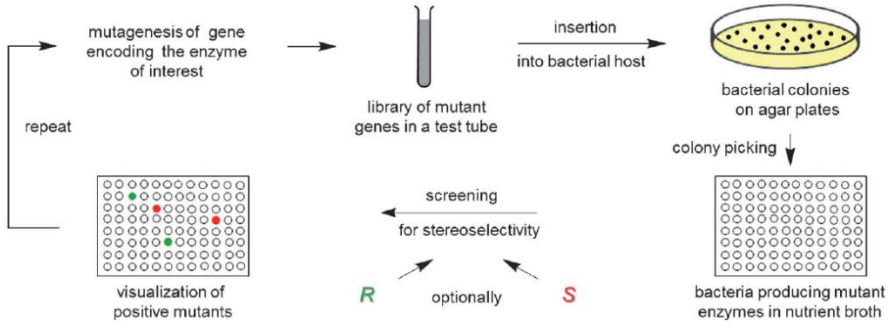


only other substrate: 95.5% ee

Gold catalyzed Hydroarylation: Eur. J. Org. Chem., **2003,** 3485



General Procedure for evolution in the lab:



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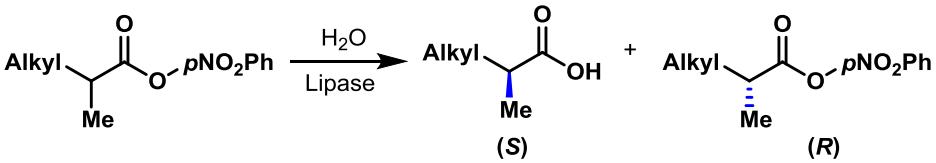
Evolution of an enantioselective Lipase: ACIE, **1997**, 2830

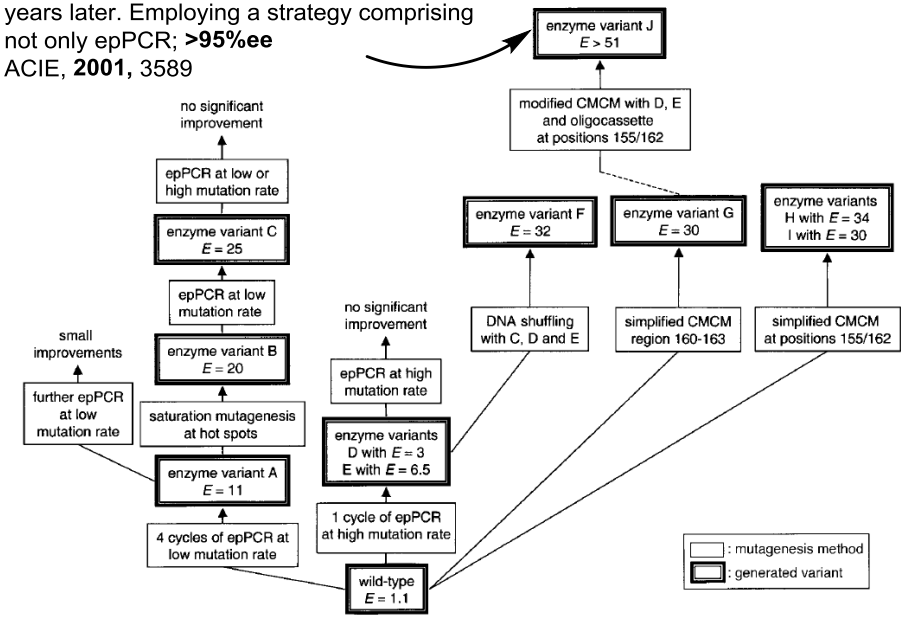


4 generations of epPCR: Isolation of the best mutant and subjecting this to another epPCR cycle: 2% ee → 31%ee → 57%ee → 75%ee → 81%ee

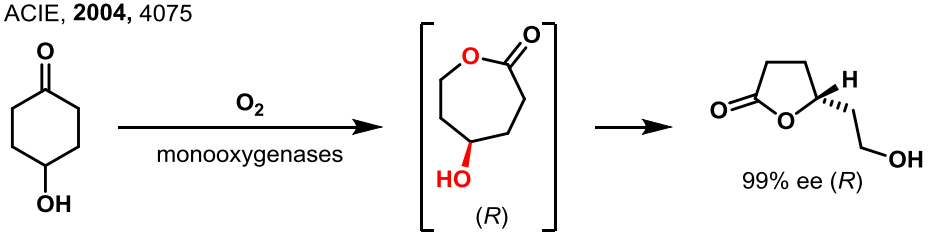
TERMS:
epPCR: error prone polymerase chain reaction **-** an amplification method for DNA that incorporates a certain percent of wrong bases
saturation mutagenisis: a generalized term pertaining to the substitution or insertion of codons encoding all possible 20 proteinogenic amino acids at any predetermined position of the enzyme
DNA-shuffling: two or more genes are fragmented and then reassembled

Advantage of directed evolution to produce potent enzymes for a specific reaction: the mechanism of the reaction or structure of the enzyme can be unknown

Improvements for the same reaction a few years later. Employing a strategy comprising not only epPCR; **>95%ee**
ACIE, **2001,** 3589



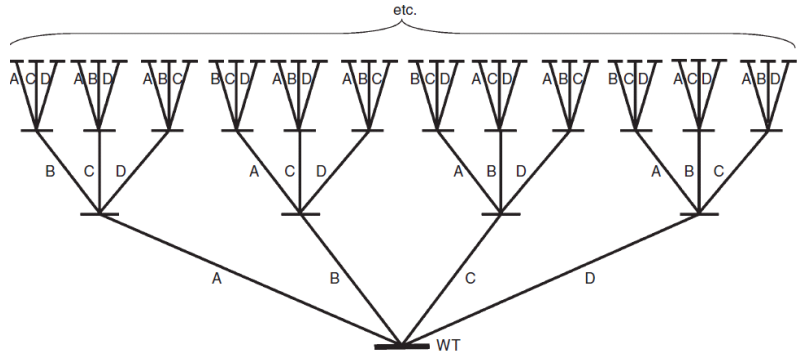
Employing epPCR for the evolution of an enantioselective monooxygenase:
ACIE, **2004,** 4075



Iterative saturation mutagenesis and CASTing: Quality not quantity:
JACS, **2010,** 9144

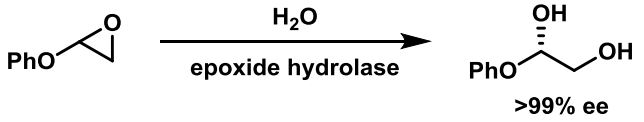
"[...] appropriate sites in the protein, comprising one or more amino acid positions, are first randomized with formation of focused libraries."

CASTing **(combinatorial active-site saturation test)**: "the catalytically active center is used as the reference point of the enzyme, around which the Cartesian space within a radius of approximately 10 Å is partitioned into defined regions(sites) to be randomized by saturation mutagenesis"
Nature Protocols, **2007,** 891



>99% ee was achieved for the above mentioned ester hydrolysis by using the ISM technique, requiring only 10,000 transformations (compared to >40,000 previously). JACS, **2010,** 9144

Employing ISM to evolve an epoxide hydrolase: ACIE, **2006,** 1236



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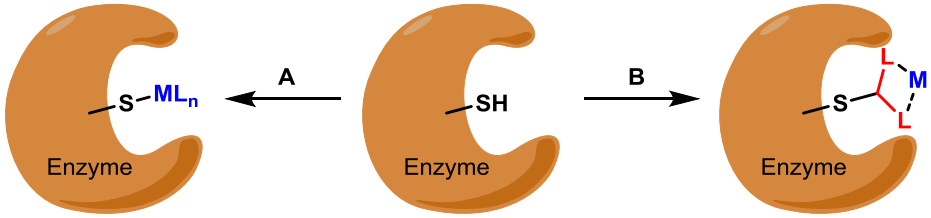
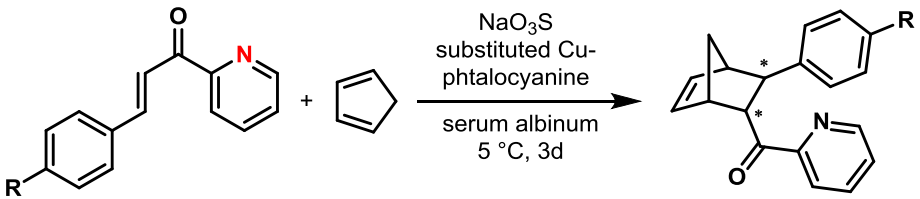
Hybrid catalysis: ACIE, **2006,** 2416

Concept: Using the chiral environment of an enzyme to induce enantioselectivity in metal catalysed transformations that are impossible with enzymes.



PNAS, **2004,** 5716



up to 98% ee

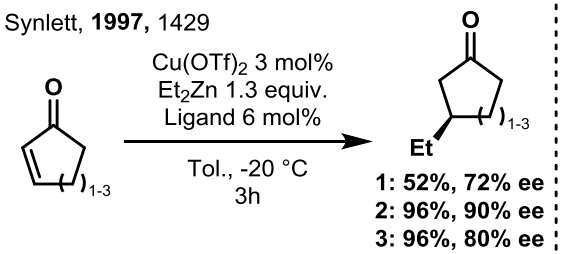
Serum Albinum = group of enzymes from blood plasma (commercially available) →Cu complex binds to a not specified region in the enzyme, which induces ee. **Experiments without enzyme are faster but racemic.** Substitution of pyridine for phenyl lowered the ee dramatically suggesting stabilization over the nitrogen.

Andreas Pfaltz

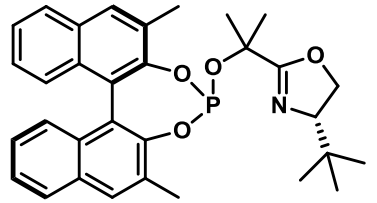
Director from 1995-1998
@ Univ. Basel since 1998
Main interests: Enantioselective Transformations,
Pioneer in PHOX (Phosphinoxazoline Ligand)

Prizes (selection):
Ryoji Noyori Prize (2008)
Prelog Medal (2003)

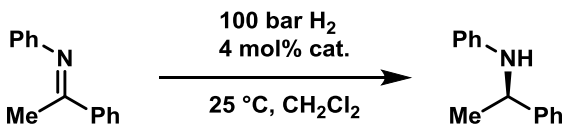
Synlett, **1997,** 1429



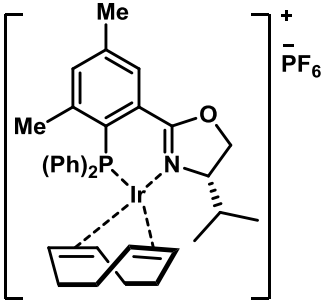
1: 52%, 72% ee
2: 96%, 90% ee
3: 96%, 80% ee



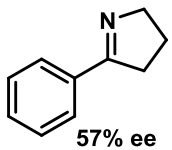
Asymmetric Hydrogenation of Imines: Chem. Eur. J., **1997,** 887



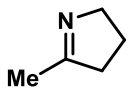
71% ee



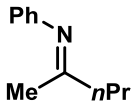
By lowering the concentration to 0.035 M, the catalyst loading to 0.1 mol% and the temperature to 5 °C, the ee could be raised to 89%.



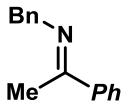
57% ee



N.R.



17% ee



76% ee

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Further reading: ACIE, **2014,** 8587

Editorial "What matters?" ACIE, **2014,** 8

"Those who think of organic and organometallic chemistry as mature fields underestimate the capability of fellow chemists to innovate." ACIE, **2014,** 858

Alois Fürstner

Director since 1998
Head of Organometallic Chemistry
Main interests: Total Synthesis, Metathesis, π-Acids, Metal Catalysis

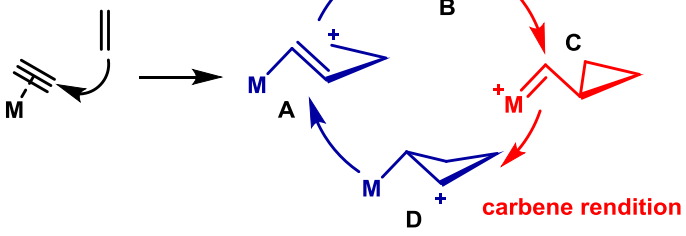
Editor of Angewandte Chemie and member on the advisory board of ChemCatChem, ChemMedChem, Advanced Synthesis & Catalysis and others

Prizes: (selection)
Karl Ziegler Prize (2013)
Prelog Medal (2011)
Otto-Bayer Prize (2006)
Mukayama award (2005)
Leibniz Prize (1999)

π-Acid Catalysis:

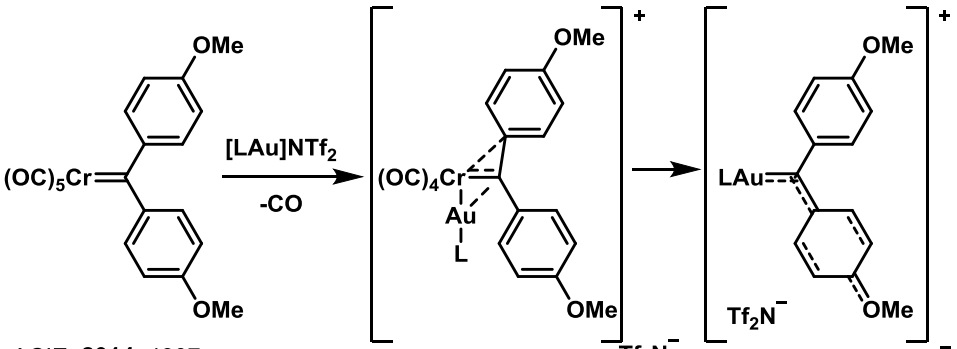
The ensemble of resonance extremes A–D collectively, provide an adequate description of the reactive intermediate

ACIE, **2005,** 2510



M = e.g. Au^I

Mechanistic investigations:

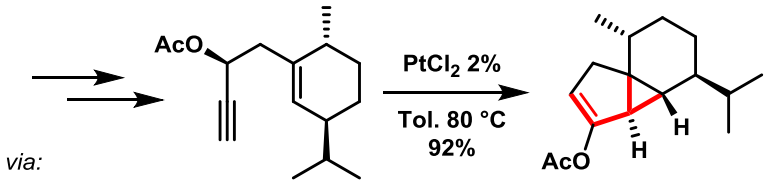


ACIE, **2014,** 4807

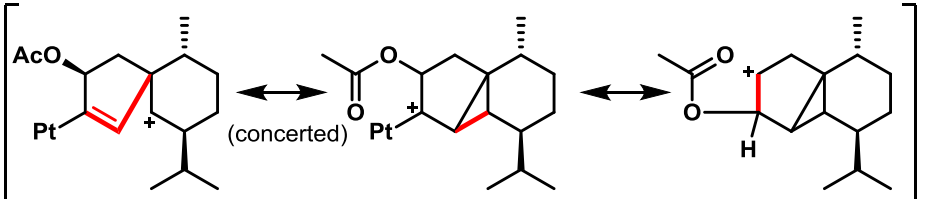
If OMe = H → stops at this intermediate

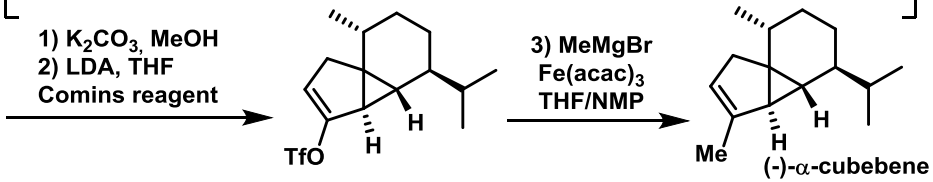
Even though still in mesomeric resonance, the Au-C bond has an bond order of close to one and the ligands carry most of the positive charge. Therefore these intermediates cannot be characterized as bearing a Au-C double bond, but rather they are gold-carbenoids or gold-stabilized cations.
Picture: above gold carbenoid with L = PCy_3 in CD_2Cl_2

Total synthesis example: (-)-α-cubebene (Chem. Eur. J., **2006**, 3006)



via:





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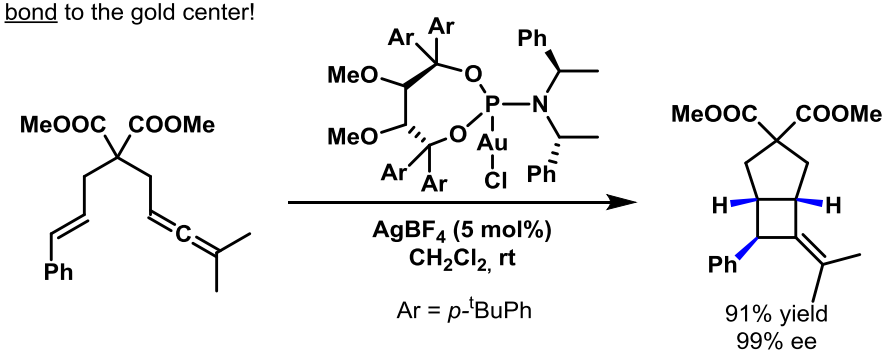
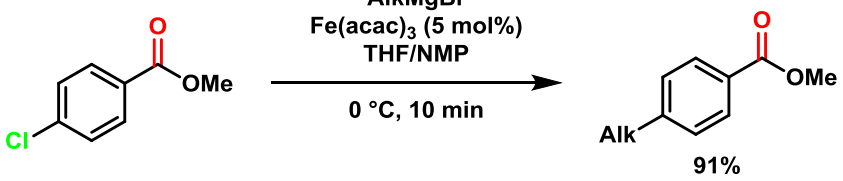
Development of an TADDOL derived ligand frameworks for enantioselective [2+2], [4+2], En-yne and hydroaminations (JACS, **2012,** 15331)
This is a significant achievement, since the Ligand can only coorinate over a single bond to the gold center!

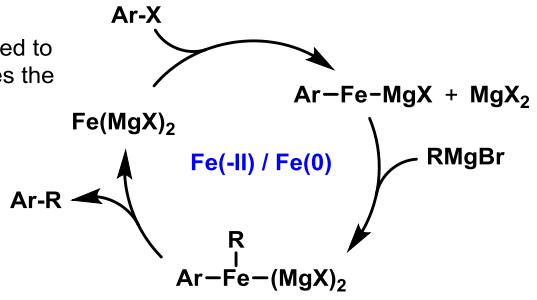


Breakthrough in Iron Catalysis: JACS, **2002,** 13856

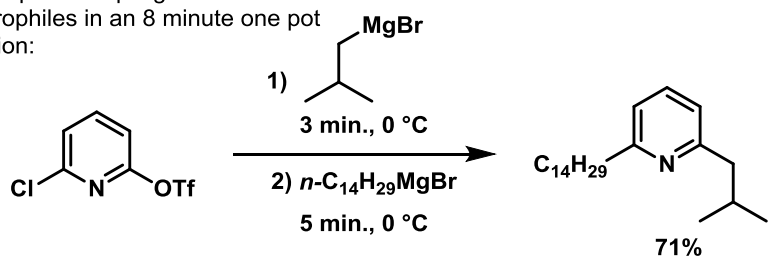


Chlorides are generally more reactive than bromides/ iodides, which lead to protodehalogenation and grignard homocoupling. The coupling was so fast, that nucleophilic attack on various electrophiles was outperformed and several **functional groups could be tolerated e.g. CN, COOMe, SO_2NR_2, SO_3R, SMe**

The active species was proposed to be $Fe(MgX)_2$ in which Fe carries the formal oxidation state of -II

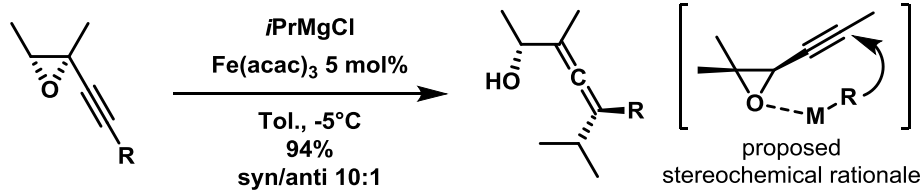


Subsequent coupling of different electrophiles in an 8 minute one pot reaction:

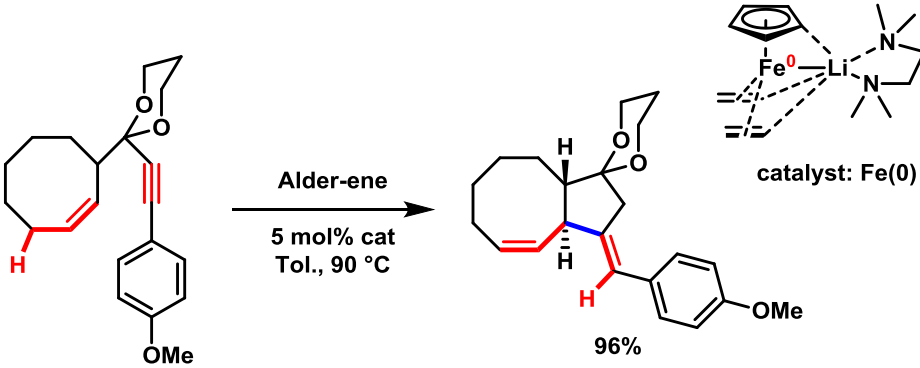


Aryl-aryl couplings as well as aryl electrophiles with alkyl halides can also successfully be achieved with iron catalysis. (Chem. Lett., **2006,** 624)
In an incredible follow up paper Fürstner corroborated the Fe(-II) species as being the most active. However, also higher valent species can be active. (JACS, **2008**, 8773)

Making use of the smooth reactiviy: ACIE, **2003,** 5355
Transfer of chirality & complementary to Cu chemistry (delivers anti prod. mostly)



Employing the investigated low valent iron catalysts for intramolecular Alder-ene, [4+2], [5+2], [2+2+2] reactions: JACS, **2008,** 1992



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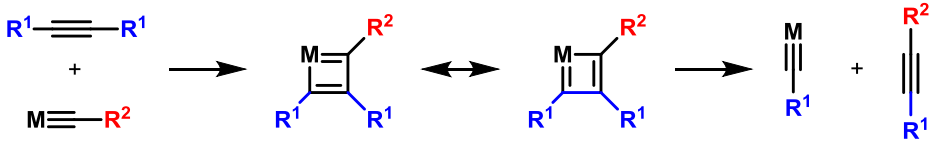
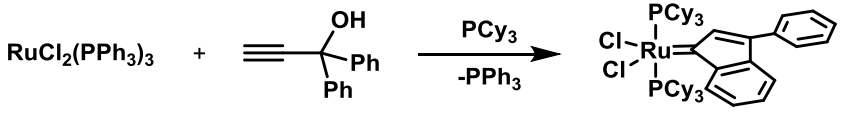
Contributions to Olefin and Alkyne Metathesis:

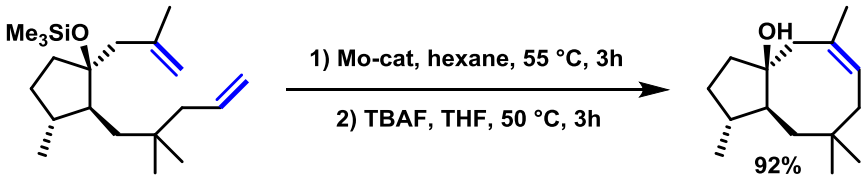
Alkyne metathesis can be easily performed with methyl end-capped alkynes. The reaction will then generate 2-butyne as byproduct which can be leveraged to drive the equilibrium to full conversion by applying vacuum or adding 5A molecular sieves.

General reaction mechanism for alkyne metathesis:



Fürstner contributed to olefin metathesis on various occasions, e.g. the industrial scale route to a ruthenium indenylidene catalyst (below, Chem. Eur. J. **2001,** 4811) and has also employed ring closing olefin metathesis (RCM) in several total synthesis.

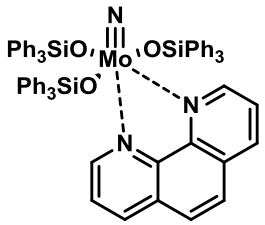




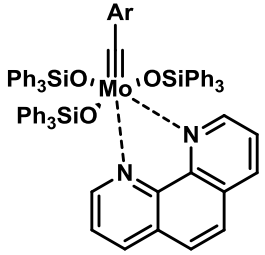
JOC, **1996,** 8746 — **92% Dactylol**

Despite his groundbreaking contributions to RCM, Fürstner might be even better known for alkyne metathesis.

Synthesis of the first highly reactive, functional group tolerant and bench stable RCAM catalyst. The reversible (with $MnCl_2$) phenantroline coordination makes the catalyst bench stable. JACS, **2010,** 11045

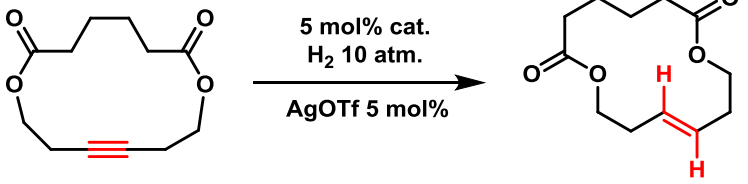


indefinitely bench stable Nitride / alkylidyne exchange at 80 °C



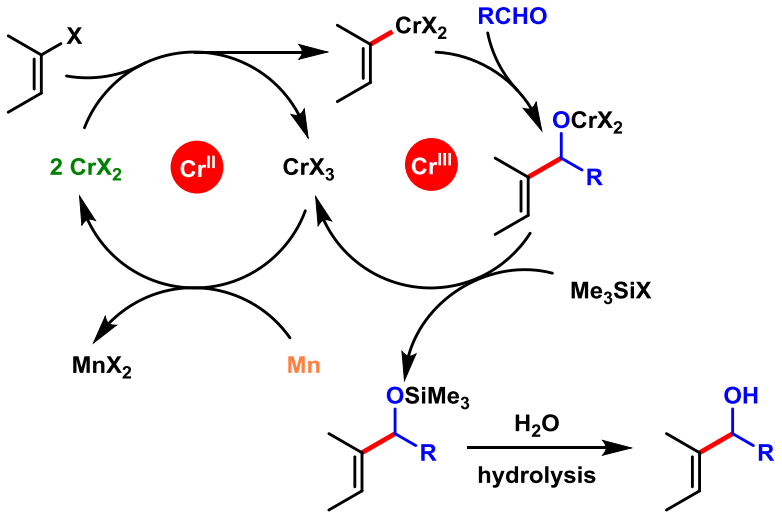
bench stable for hours

***Trans*-hydrogenation** as a way to postfunctionalize after alkyne metathesis: ACIE, **2013,** 355

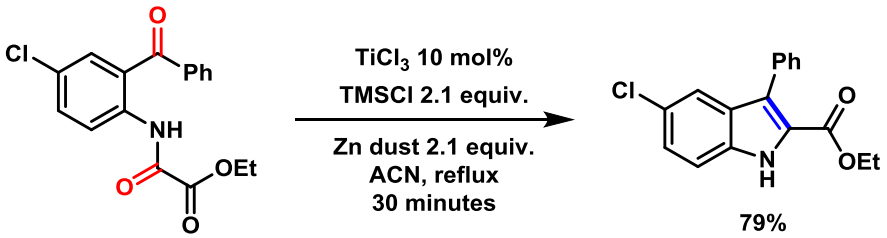


92:8 trans/cis
89 %

Nozaki-Hiyama-Kishi reaction catalytic in Cr (JACS, **1996,** 12349)



McMurry coupling catalytic in Ti: JACS, **1995,** 4468



79%

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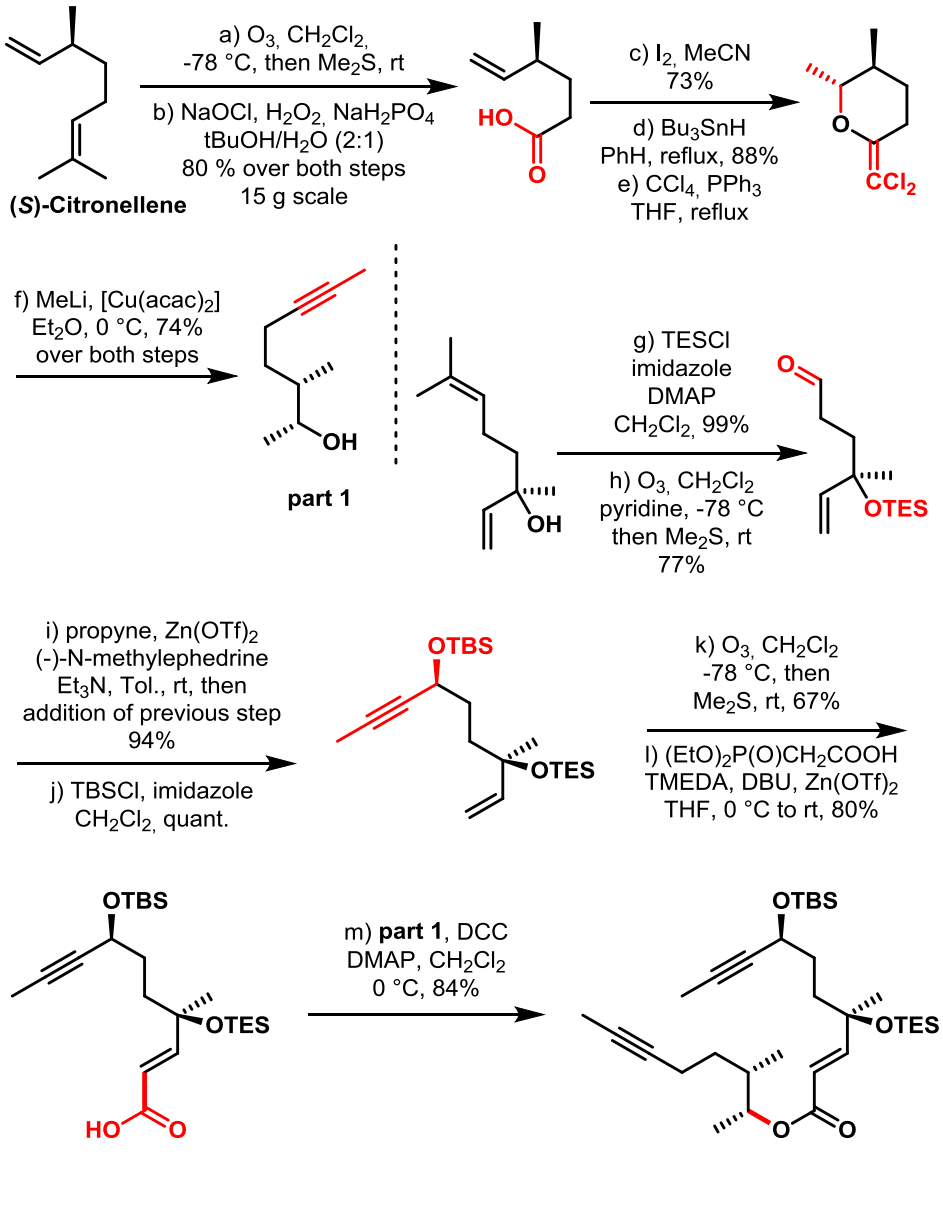
Total Synthesis of 5,6-dihydrocineromycin B: ACIE, **2015**, 6241



Comments on steps:

a) Ozonolysis of the higher substituted double bond
b) Pinnick oxidation
c) Iodolactonization
d) Protodehalogenation
e) Wittig reaction
f) reductive alkylation

g) Protection of alcohol
h) Ozonolysis of the higher substituted double bond
i) Carreira reaction
j) Protection of alcohol
k) Ozonolysis towards aldehyde
l) HWE reaction
m) Steglich esterfication
n) RCAM
o) deprotection of alcohols
p) trans hydrostannylation
q) Stille coupling

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(Franz) **Ferdi**(nand) **Schüth**

Director since 1998
Head of Heterogeneous Catalysis
Main interests: Hydrogen storage, mesoprous solids, biomass conversion, high throughput processes
Editor of Handbook of Heterogeneous Catalysis
Editor of Handbook of Porous Solids

Vice President of the Max Planck Society
Vice President of DECHEMA

Founder of the company "hte AG" (sold to BASF)

Prizes (selection):
Wilhelm Klemm Prize (2012)
ERC Advanced Grant (2009)
Leibniz Prize (2002)

Hydrogen storage:

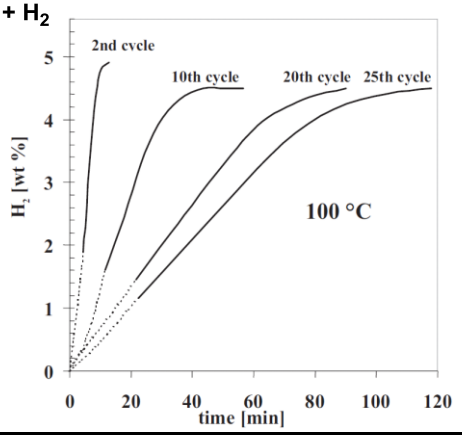
Goals: Chem. Comm., **2004,** 2249
1) Hydrogen storage of >5 wt%
2) "refueling" in <10 minutes

One option is the storage of H_2 in $NaAlH_4$: Adv. Mater. **2003,** 1012

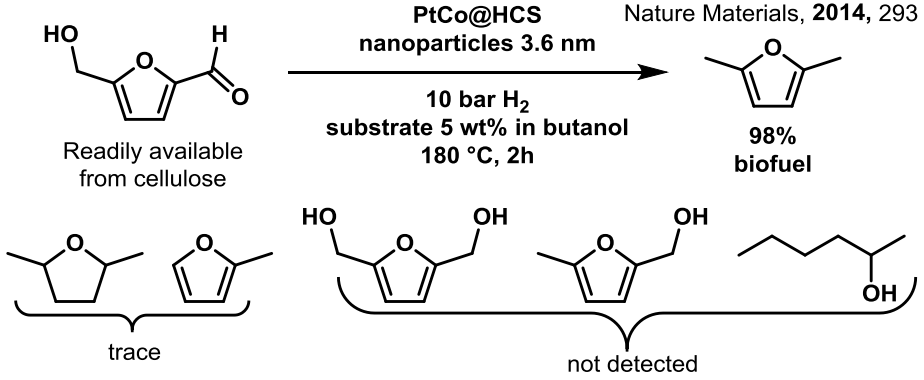
1) $NaAlH_4 \rightleftharpoons 1/3\ Na_3AlH_6 + 2/3\ Al + H_2$
<120 °C 3.7 wt.% H_2

2) $NaAlH_4 \rightleftharpoons NaH + Al + 3/2\ H_2$
>120 °C 5.5 wt.% H_2

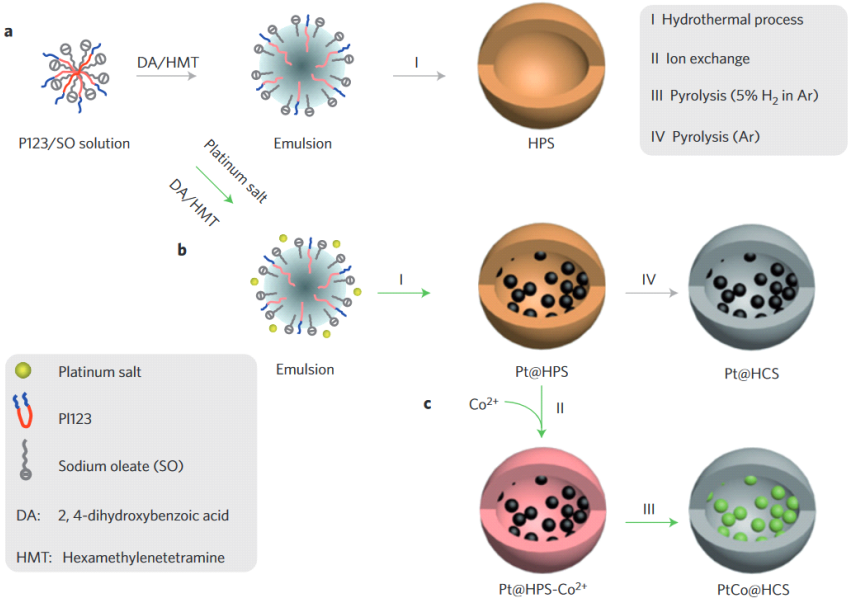
Doping the $NaAlH_4$ with Ti×0.5 THF increases its hydrogenation rate significantly by a factor of 40 and increases H_2 storage. However, the resulting species is still not perfect and shows decreased hydrogenation rate over time. However the system largely remains its storage capacity (Figure right)



Biomass conversion:



Process for the preparation of PtCo@HCS: HCS = hollow carbon spheres; HPS = hollow polymer spheres; P123 & SO (sodium oleate) = surfactants
1) P123 and SO together form micelles with controlled diameter and shell thickness
2) Acidic polymer precursors convert the mixed micells to uniform emulsions
3) Hydrothermal process activates the polymerization leading to HPS
4) Addition of noble metals automatically leads to absortion of these on the surface
5) Pyrolysis under air and under argon



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Methane oxidation to methanol: ACIE, **2009,** 6909

Challenges:

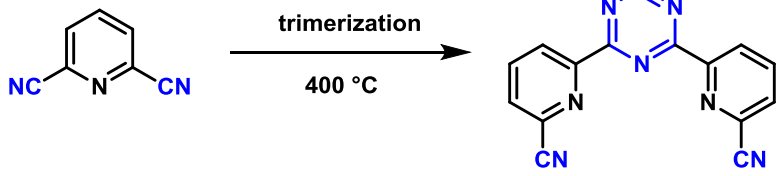
H_3C—H bond energy: 435 kJ/mol **Ease of overoxidation to CO_2**

1) $CH_4 + H_2SO_4 + SO_3 \rightarrow CH_3OSO_3H + H_2O + SO_2$

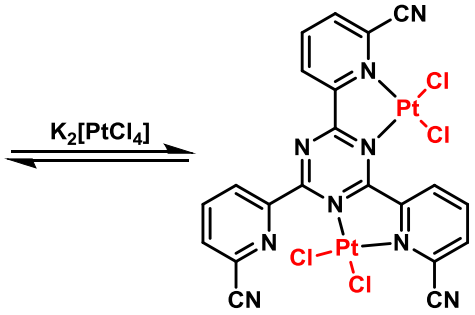
2) $CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4$

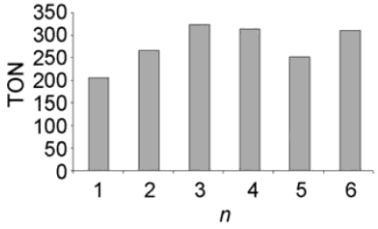
3) $SO_2 + 1/_2\ O_2 \rightarrow SO_3$

4) $\sum$ **$CH_4 + 1/_2\ O_2 \rightarrow CH_3OH$**



Further trimerizations of the trimer lead to CTF (covalent triazine framework)





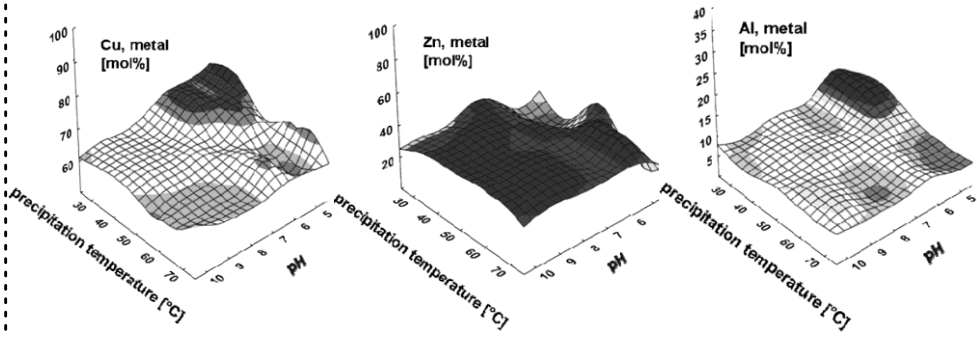
Reaction conditions:
15 mL H_2SO_4 (30% SO_3), 40 bar CH_4 pressure, 25 °C, 2.5h
Major side product: CO_2

Final methanol concentration after reaction: 1.5 - 1.8 mol/L

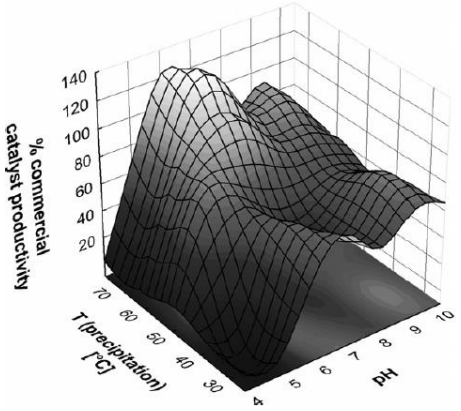
The TON (turnover numbers) are kept constant over several cycles indicating a stable and recycable catalyst. Imaging afterwards showed loss of Cl-ligands, suggesting they are not needed for the catalytic turnover.

Methanol production by reduction from syngas: J. Catal., **2008,** 334
Ternary catalysts of Cu / ZnO / Al_2O_3 were tested in methanol production from syngas (CO_2, CO, H_2)

The study precipitated the metal mixtures by addition of a Na_2CO_3 solution to a solution of the corresponding metal-nitrates. During this process, the **pH, temperature and aging** were controlled. Following the precipitation the hydroxy carbonate precursors were washed, dried, ground and calcinated at 300 °C under air to obtain the corresponding oxides.



The methanol synthesis activity was evaluated in a 49-channel parallel reactor under reaction conditions similar to those of the commercial methanol production route.



Influence of the catalyst preparation conditions (pH and precipitation temperature) on methanol productivity measured at 245 °C and 4.5 MPa. Productivity of the commercial catalyst under these conditions: 40 mol MeOH/(kg cat/h).

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Walter Thiel

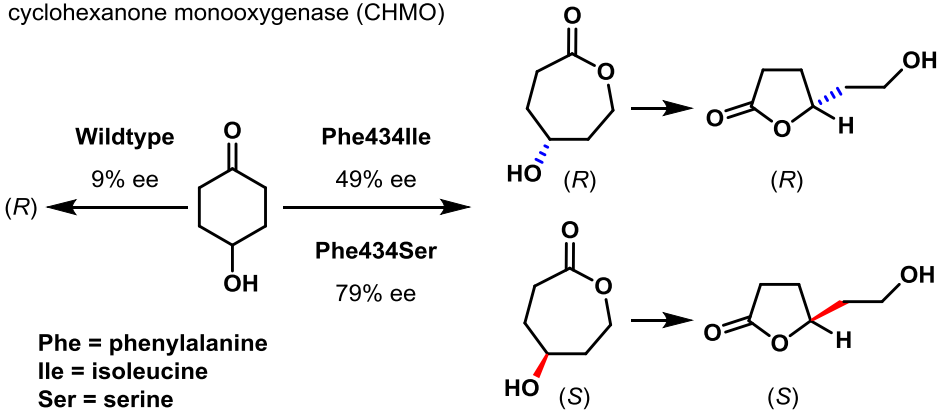
Director from 1999 until 2018
Head of Theoretical Chemistry
Main interests: DFT, Ab initio Methods, QM/MM, Semiempirical Methods

Former Editorial Advisor of: Journal of Computational Chemistry, ACS Catalysis, Acc. Chem. Res., WIRES

Prizes: (selection)
ERC Advanced Grant (2013)
Schrödinger Medal (2002)

Computations on Reetz´ enzymatic and enantioselective Baeyer Villiger Oxidation
J. Phys. Chem. B, **2013,** 4993

QM/MM (Quantum mechanical/molecular mechanical) study on mutation of Phe434 in cyclohexanone monooxygenase (CHMO)



Phe = phenylalanine
Ile = isoleucine
Ser = serine

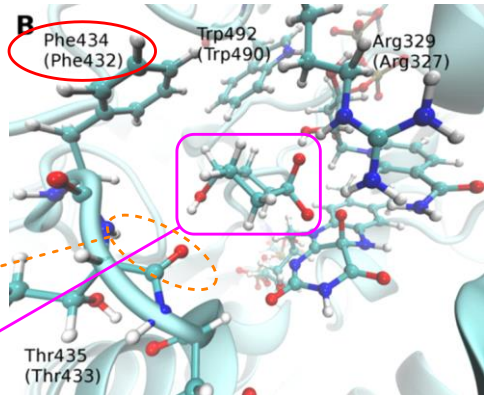
"The migration step is rate-limiting and stereoselective because of the requirement of antiperiplanarity for the migrating σ-bond so that a given orientation of a substituent at the cyclohexanone ring gives rise to a particular enantiomeric product."
→Therefore the **transition states for the migratory steps** were calculated and are depicted in the following:

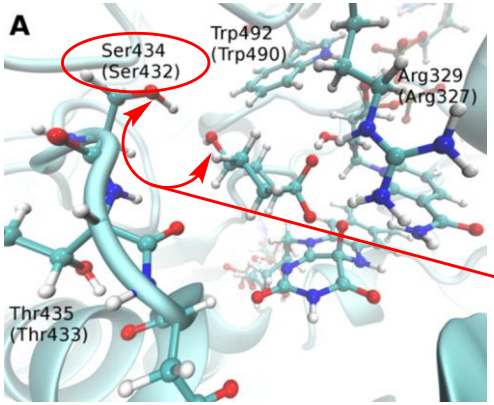
Wildtype: axial preferred, leading to (*R*)

"Taking into account the hydrophobic nature of the residues around the WT CHMO binding site, there are no obvious specific interactions between substrate and protein environment."

Threonine carbonyl function is the only available binding side for the hydroxy group

Substrate



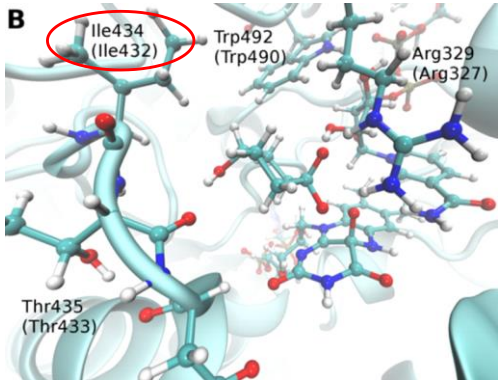


Ser: equatorial preferred, leading to (*S*)

Hydrogen bonding between Ser and substrate reverses the TS and leads to an equatorial -OH group. The serine can overwrite the threonine, because the distance is much shorter.

Ile: axial preferred, leading to (*R*)

The Ile side chain prohibits hydrogen bonding even better than the Ph group of Phe. The only available polar functional group is again the carbonyl moiety of Thr.



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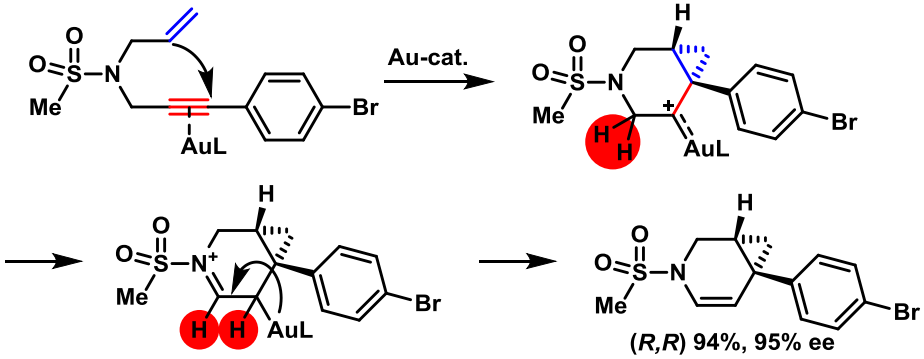
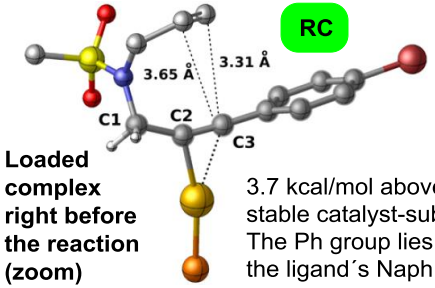
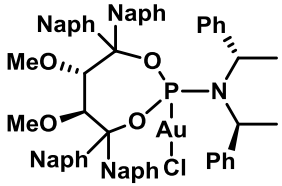
Computed insights on an enantioselective cycloisomerization: JACS, **2012,** 15331





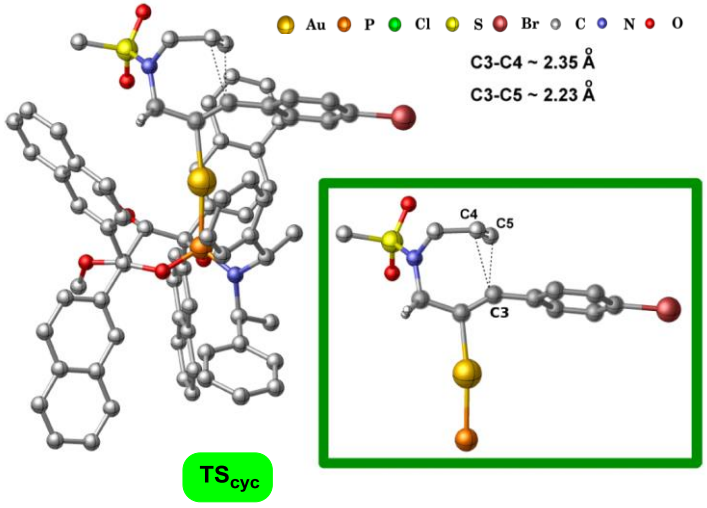
Loaded complex right before the reaction (zoom)

Au-cat.:



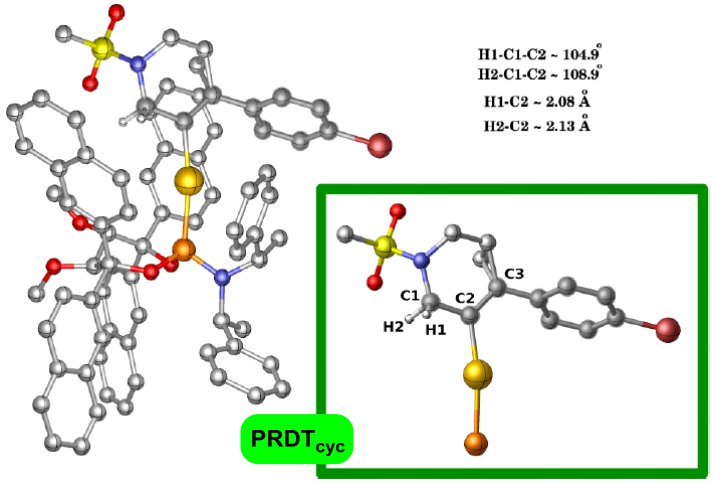
(*S,S,S,S*)

3.7 kcal/mol above the most stable catalyst-substrate adduct
The Ph group lies orthogonal to the ligand´s Naph. (not visible)

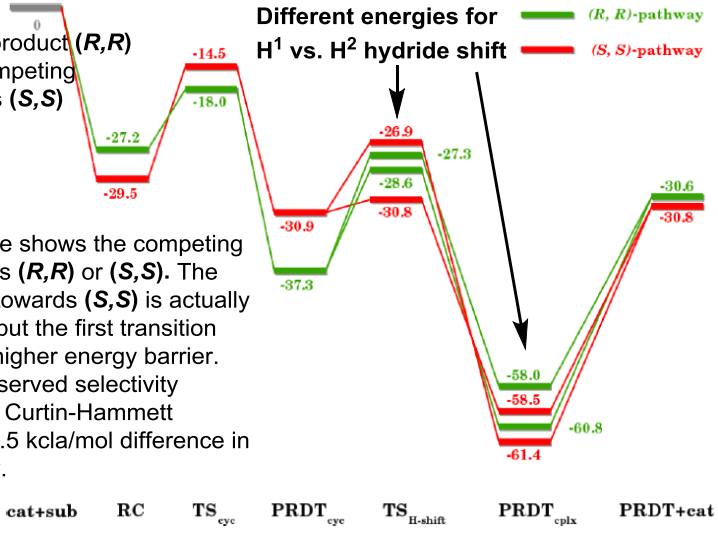


Rotation around the N-ally brings the DB closer to the benzylic position and leads to **TS_{cyc}**. The triple bond now deviates from linearity and shows an angle of 133°. A concerted cyclopropanation formes the carbenoid structure.

The two new bonds are formed almost simultaneously with distances of 2.23 & 2.35 A in TS_{cyc}. The rehybridization of the benzylic carbon atom forces the phenyl group to rotate. The backside is blocked with the Naph. group, therefore the phenyl group rotates to the front and the much smaller cyclopropane group forms on the backside. This process was calculated to be 9.2 kcal/mol.



Green profile = product **(*R,R*)**
Red profile = competing pathway towards **(*S,S*)**



The energy profile shows the competing pathways towards **(*R,R*)** or **(*S,S*)**. The loaded complex towards **(*S,S*)** is actually lower in energy, but the first transition state requires a higher energy barrier. Therefore the observed selectivity originates from a Curtin-Hammett scenario with a 3.5 kcla/mol difference in activation energy.

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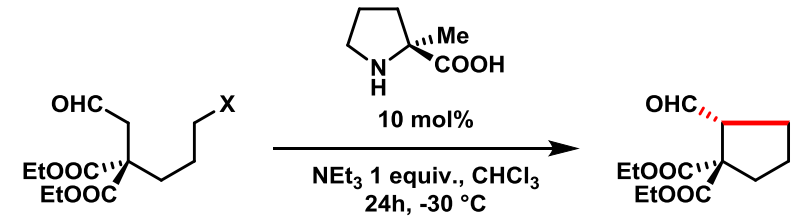
Ben(jamin) **List**
Director since 2005
Head of Homogeneous Catalysis
Main interests: Organocatalysis, ACDC, Lewis- & Brønsted Acid catalysis

Chief Editor of Synlett
Editorial Advisory Board of Nat. Comm. and Beilstein Journal of Organic Chem.

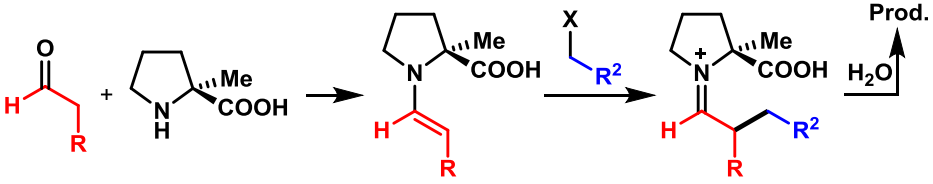
Prizes: (selection)
Leibniz Prize (2016)
Mukaiyama Award (2013)
Otto-Bayer Prize (2012)
ERC Advanced Grant (2011)

Asymmetric intramolecular Alkylation of Aldehydes: JACS, **2004**, 450

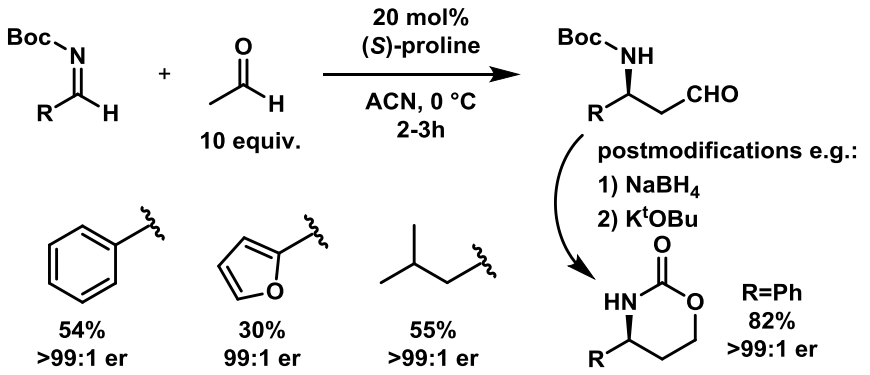


X = I 92%, 95% ee
X = Br 90%, 94% ee (15 mol% cat.)
X = OTs 20%, 91% ee (20 mol%, 48h)

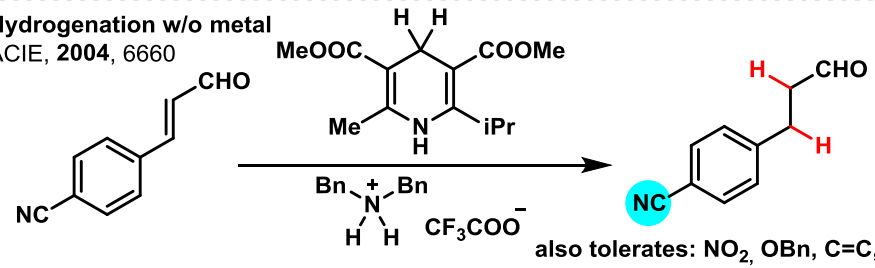
Via enamine catalysis:



Enantioselective Mannich Reactions with Acetaldehyde: Nature, **2008,** *452,* 453

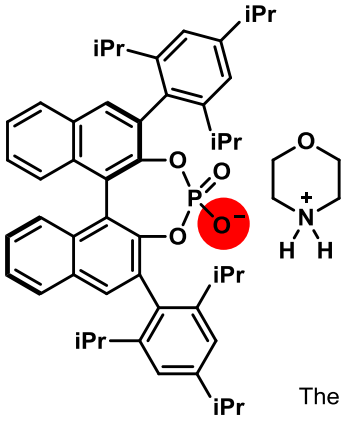


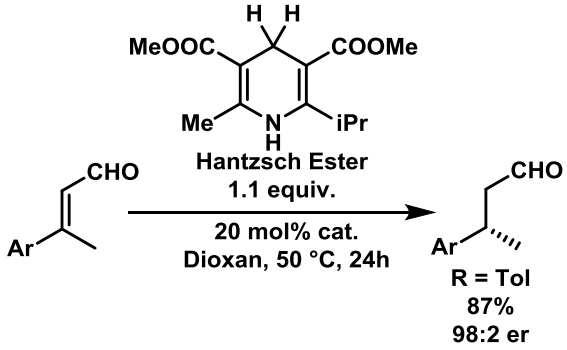
Hydrogenation w/o metal
ACIE, **2004**, 6660



also tolerates: NO_2, OBn, C=C, Ac

Same Hydrogenation, but enantioselective, & introduction of Asymmetric Counterion-Directed Catalysis (ACDC): ACIE, **2006**, 4193
Shows for the first time that enantioselectivity of cationic intermediates can be controlled by anionic counterions.





The reaction works similarily well with alphatic substrates.

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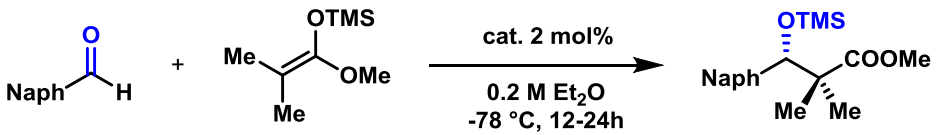
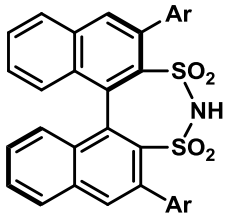
Disulfonimid catalysed Mukaiyama Aldol reaction: ACIE, 2009, 4363

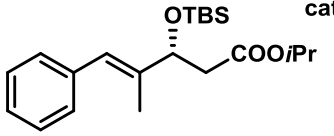


98% / 97:3 er



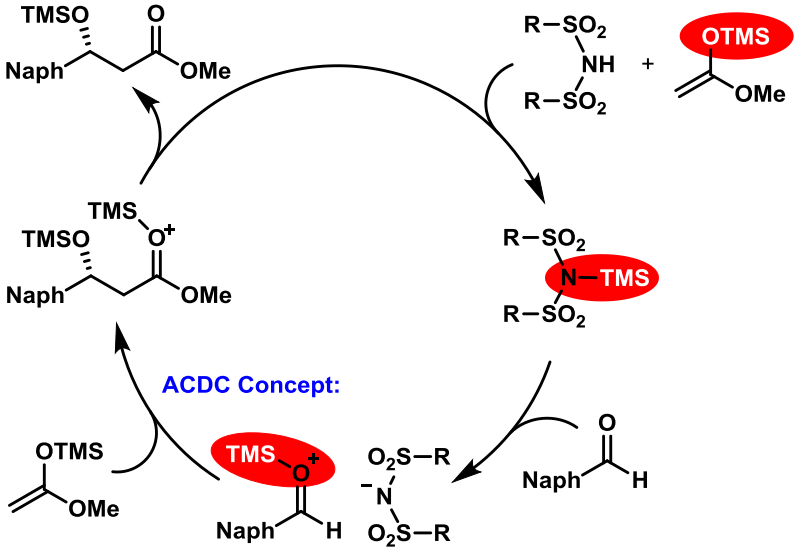
catalyst
Ar = 2,5 CF_3-Ph

The disulfonimid´s acid moiety is burried deeper in the catalyst´s backbone than for corresponding phosphates. The authors concluded that this might lead to an enhanced stereochemical communication between catalyst and substrate.
They also studied the minimum necessary cat. loading:

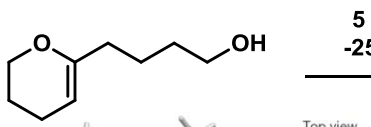


cat loading:	yield/ er
2%	95% / 93:7
0.1%	90% / 93:7
0.05%	90% / 93:7
0.01%	88% / 88:12

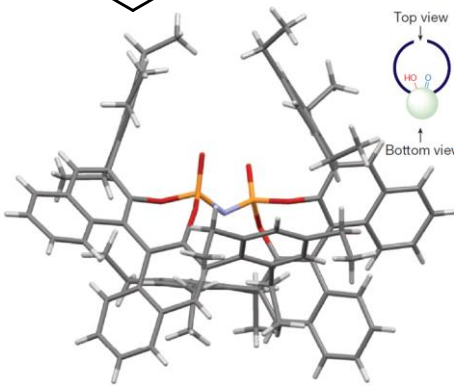
The catalytic cycle is believed to start with silylation of the lewis acid catalyst from the silylenolate, which subsequently transfers the silyl group onto the carbonyl oxygen of the aldehyde. This activated species can now be attacked by the silylenolate and form the product.

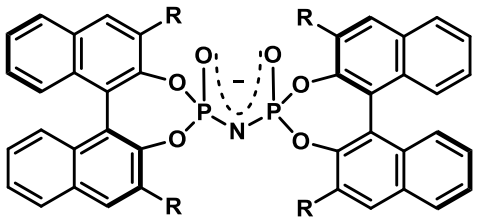


Enantioselective Spiroacetalization: Nature, **2012,**, *483,* 315



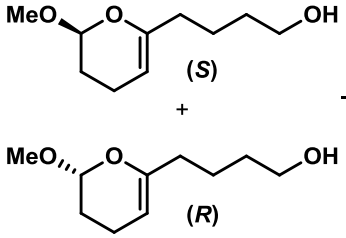
77%, er 98:2





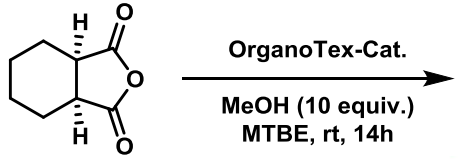
catalyst: R = 2,4,6 Et_3Ph

Useful as catalyst for kinetic resolution:



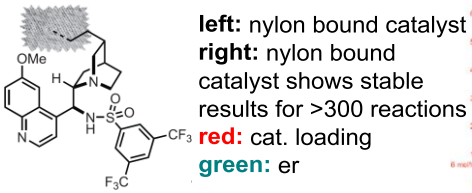
70%
97.5:2.5 er
>50:1 dr
thermodynamic product

+ 86% unreacted (*R*) 97:3 er

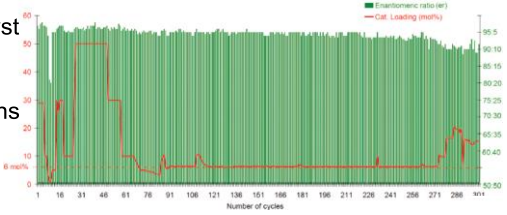


99%
96.5:3.5 er

Science, **2013,** *341,* 1225



left: nylon bound catalyst
right: nylon bound catalyst shows stable results for >300 reactions
red: cat. loading
green: er



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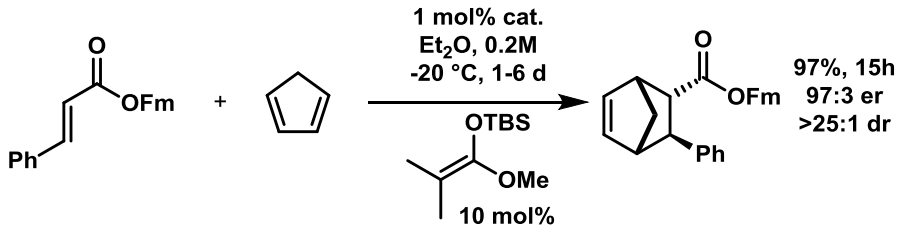
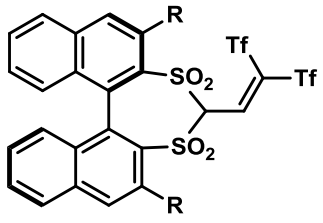
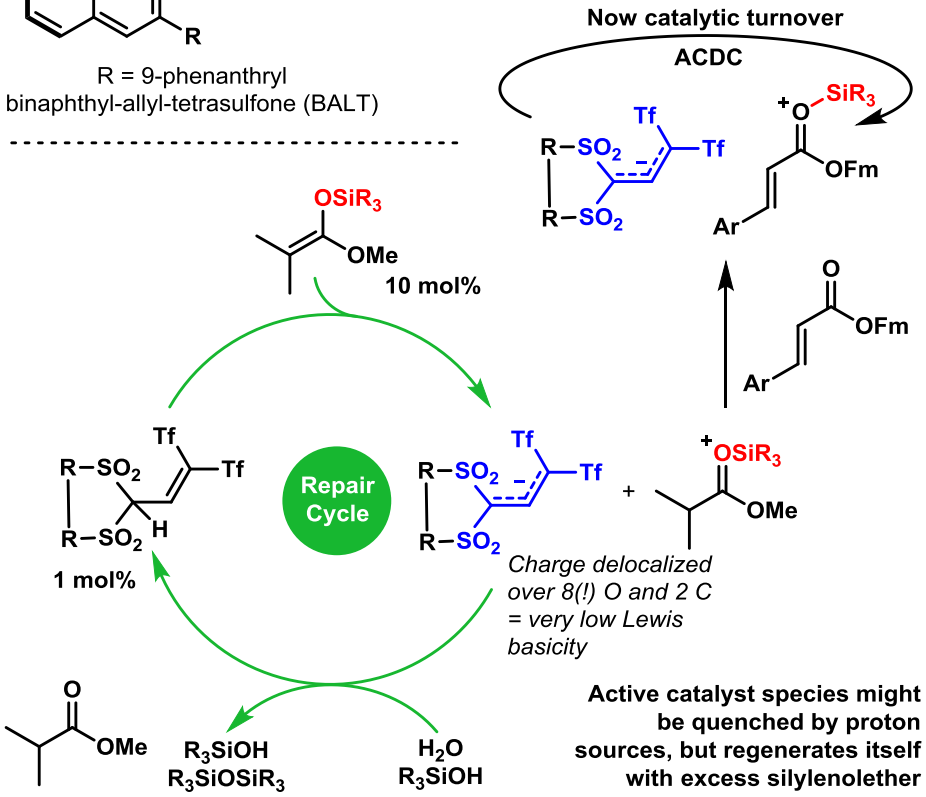
ACDC Diels-Alder reaction: Science, **2016,** *351,* 949



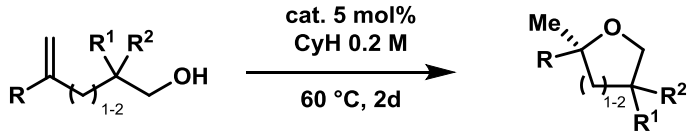


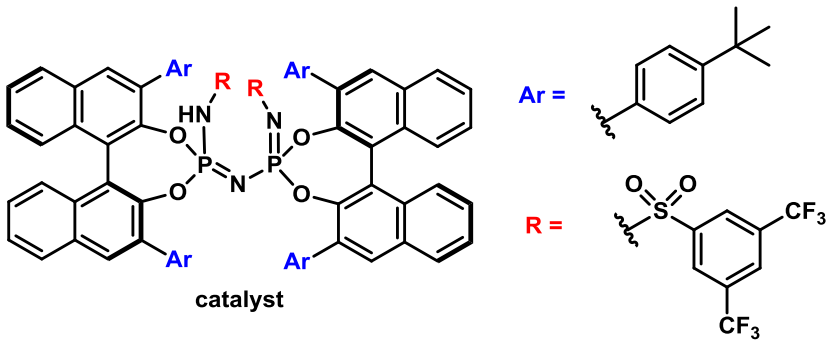
R = 9-phenanthryl
binaphthyl-allyl-tetrasulfone (BALT)

Substrate scope contains examples with heterocycles, as well as the phenyl group substituted on every position, including halides, without influence on yield, er or dr.

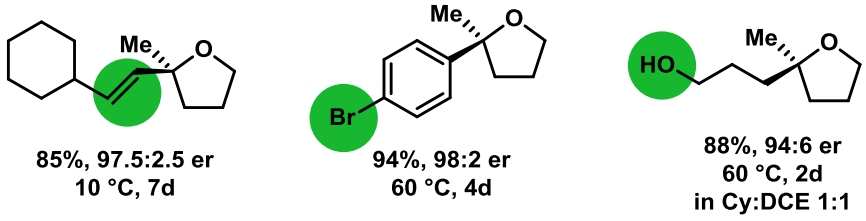


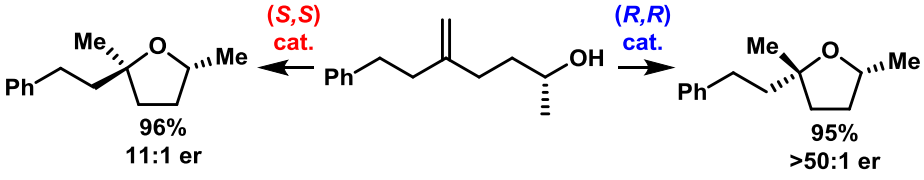
Activation of Olefins with Brønsted acids to form asymmetric cyclic ethers:
Science, **2018,** *359,* 1501

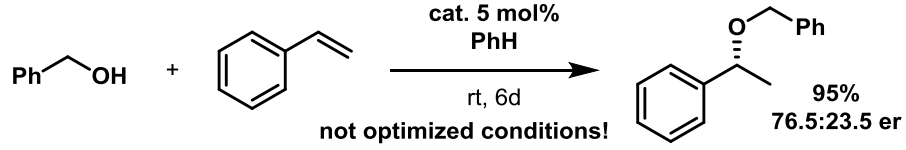




Scope examples:







Lukas Nattmann

Max Planck Institut für Kohlenforschung Part II
- Directors Cut -

Cornella Group Meeting
07.09.2018

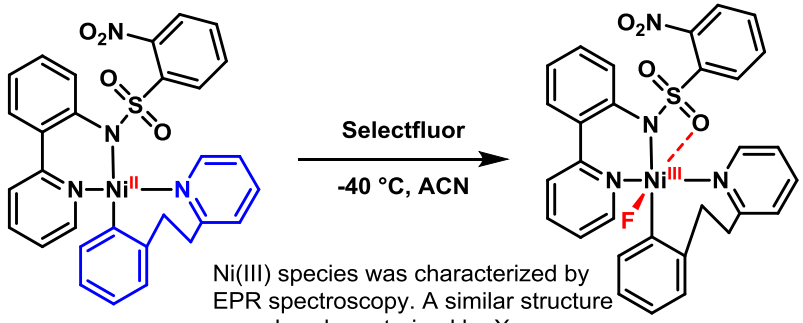
Tobias Ritter

Director since 2015
Head of Organic Synthesis
Main interests: Fluorination, Late Stage Functionalization, Organometal Chem.

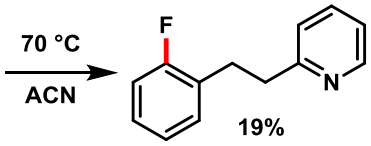
Associated with the Massachusetts General Hospital
Founder of the company "SciFoluor"

Prizes: (selection)
RSC Fluorine Chemistry Prize (2013)
BASF Catalysis Award (2011)
Bayer Early Excellence in Science Award (2009)

Investigations into C-F reductive elimination from Ni(III): ACIE, **2017,** 6966



Ni(III) species was characterized by EPR spectroscopy. A similar structure was also characterized by X-ray

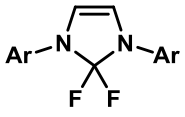


Reductive elimination was found to be faster from Ni(III) than from Pd(IV) and the barrier was calculated to be roughly 9 kcal/mol lower.
When the Ni complex was oxidized to Ni(IV), no reductive elimination occured.

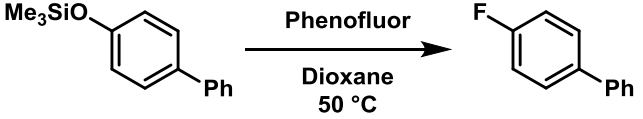
For facile reductive elimination, the ligand structure must stabilize a Ni(III) intermediate and allow geometry change to overlap the orbitals productively.

First proof of concerted nucleophilic aromatic substitutions with PhenoFluor:
Nature, **2016,** *534*, 369

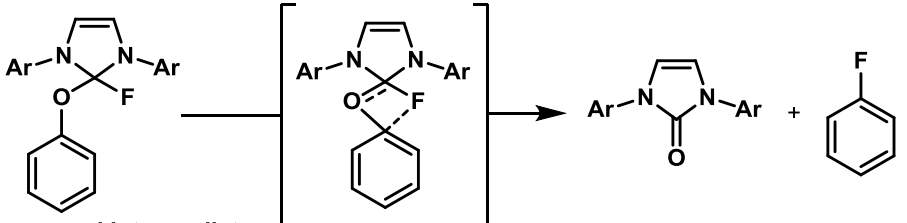
Concerted aromatic substitutions were generally deemed to be impossible, because the large lobe of the σ* orbital points into the ring.



Phenofluor

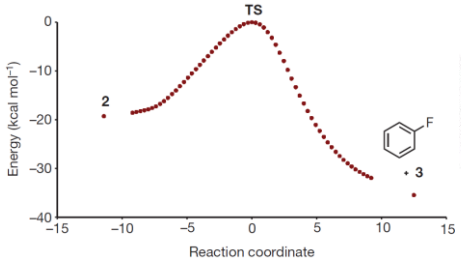


kinetic isotope effect $^{16}O/^{18}O$: 1.080 ± 0.021
→ primary isotope effect suggests C-O bond cleavage in the rate determining step.

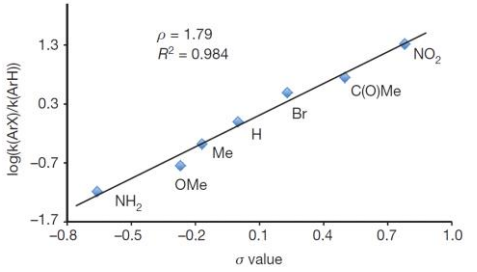


proposed intermediate (isolated)

ΔG = 21.8 kcal/mol

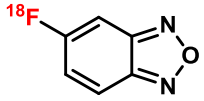


single transition state calc. by DFT
→ concerted mechanism



Hammett plot for deoxifluorination of *p*-substituted phenols shows linearity → no change in mechanism or rate determining step → concerted mechanism; standard ρ values for S_NAr: 3-8

Scope could be extended to ^{18}F



RCC = 98% (radiochemical conversion)
RCY = 27% (radiochemical yield)

Lukas Nattmann

Max Planck Institut für Kohlenforschung Part II
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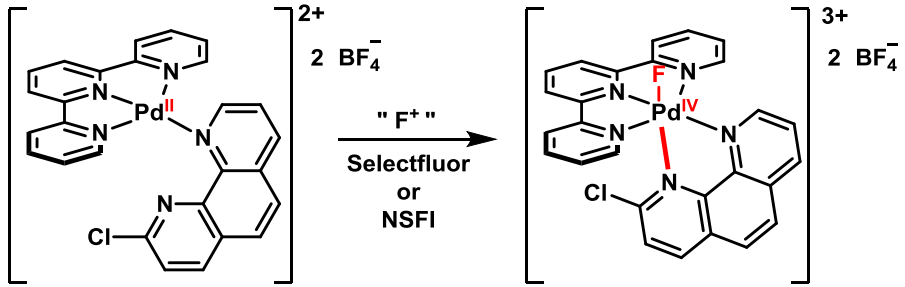
07.09.2018

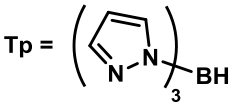
Electrophilic aromatic C-H Fluorination: Nature, **2018,** *554*, 511

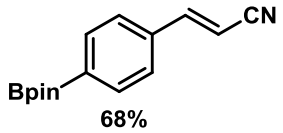


This reaction is an unusual C-H activation case where the metal is first oxidized to a high valent intermediate, which in turn oxidizes the substrate by ligand transfer.

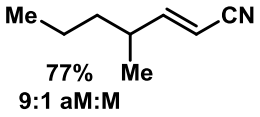
The TS is best described as **singlet diradical**, since the Pd and the aryl carbons both show a high spin-density.
This catalyst can fluorinate a broad variety of unactivated aryl substrates

Anti Markownikow Hydrocyanation of Alkynes:
JACS, **2017,** 7184

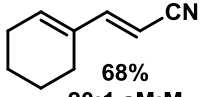




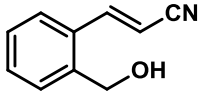
68%



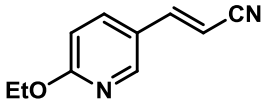
77%
9:1 aM:M



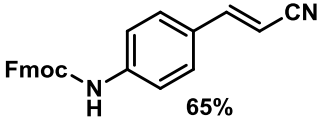
68%
20:1 aM:M



1 mmol, 71%



72%



65%

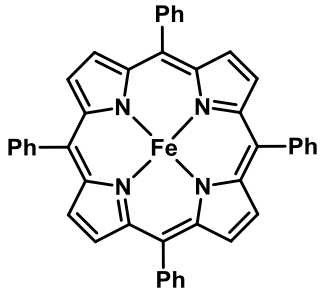
Frank Neese

Director since 2018
Head of Molecular Theory and Spectroscopy
Main interests: Quantum chemical method development, Computational Chemistry, Molecular Spectroscopy

Inventor of ORCA

Editorial Board of "Structure and Bonding" & "J. Biol. Inorg. Chem."
Associate Editor of PhysChemChemPhys and Inorg. Chem.

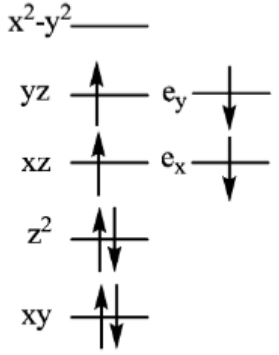
Prizes: (selection)
Leibniz Award (2010)
Klung-Wilhelmy-Weberbank Award (2008)



Inorg. Chem., **2018**, 2141

Iron-porphyrins are important catalysts for catalytic CO_2 reduction. However the localization of the charge (metal or ligand) for this 2 electron process has been a long lasting question.

With the help of marker bands in resonance Raman spectroscopy as well as caculations the charghe was localized on the ligand. The electronic ground state of the active catalyst was found to be an Fe(II) d^6 intermediate spin iron center antiferromagnetically coupled to a TPP diradical tetra-anion.



Schematic spin coupling formulations (overall spin S = 0); Iron 3d orbitals and ligand Gouterman orbitals e_x and e_y