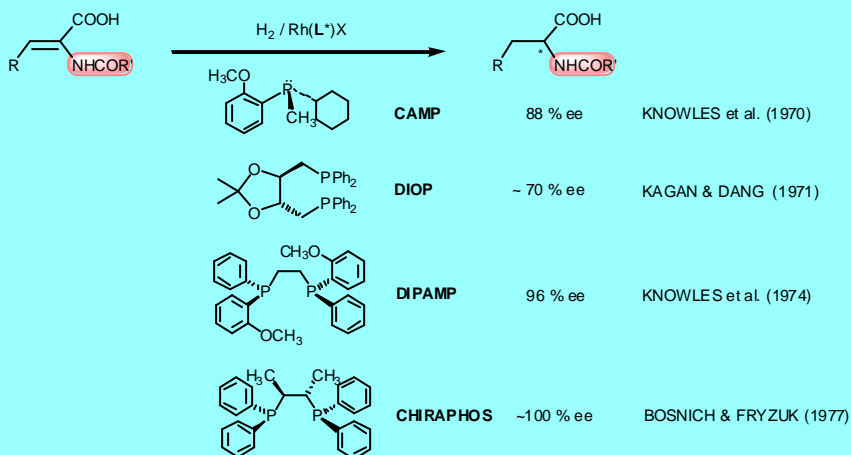
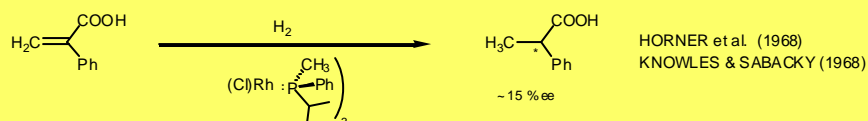


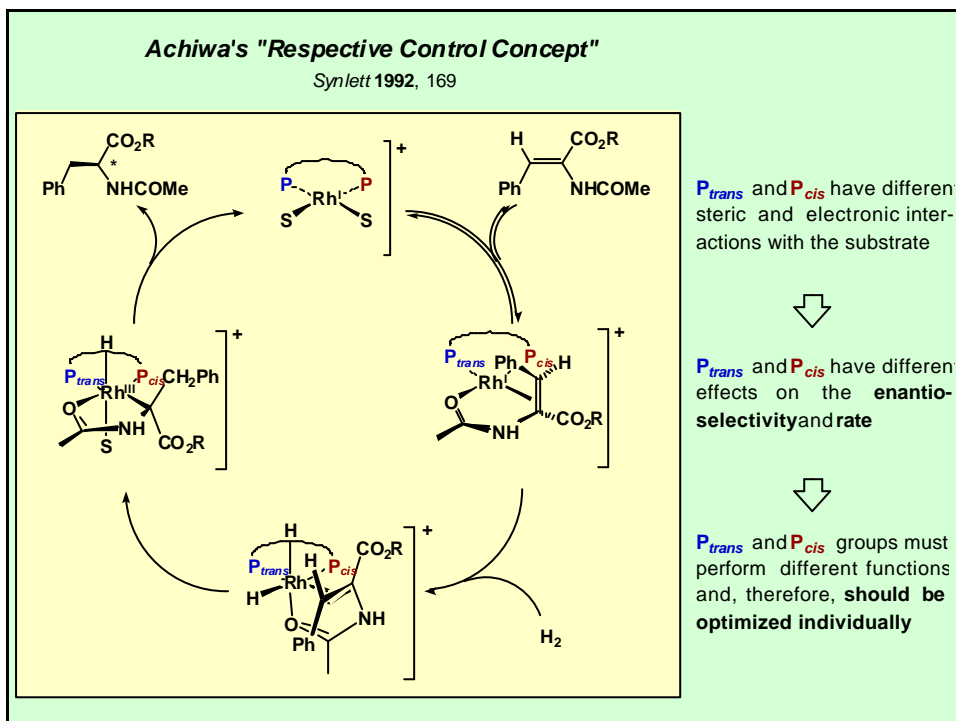
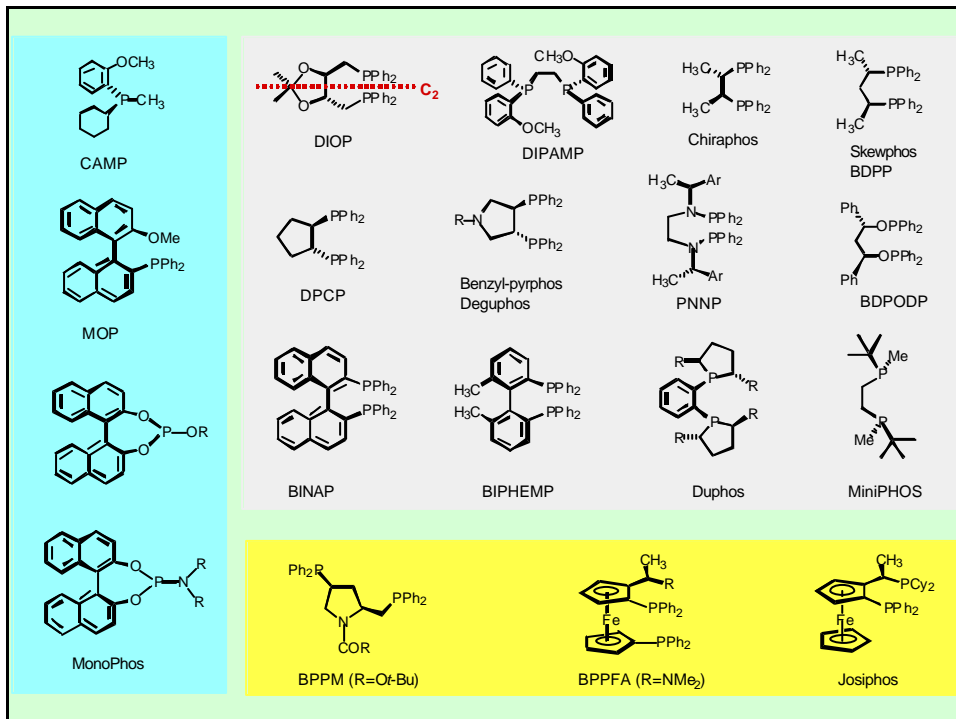
Iridium-Catalyzed Asymmetric Hydrogenation

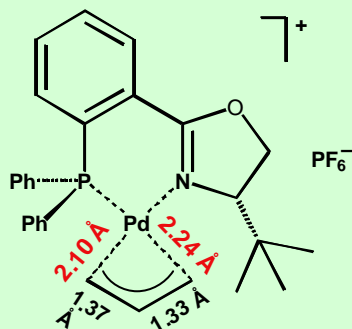
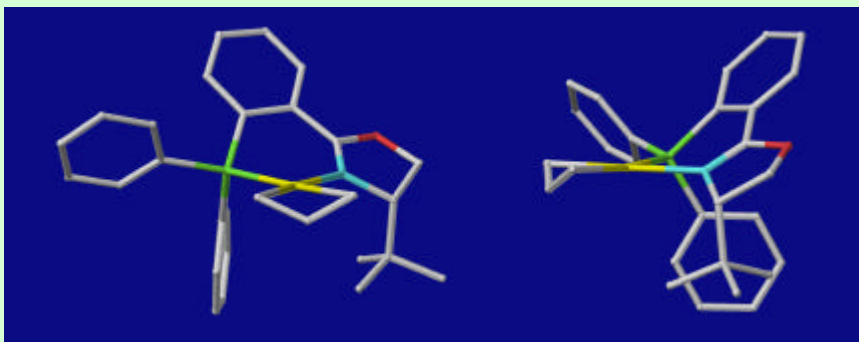
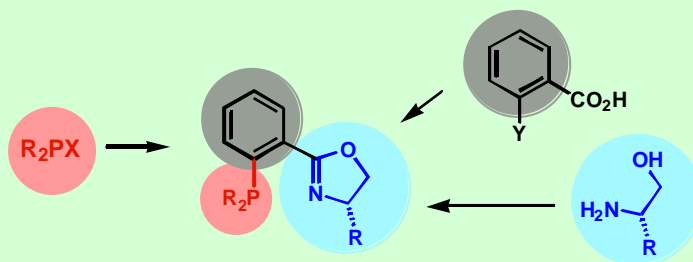
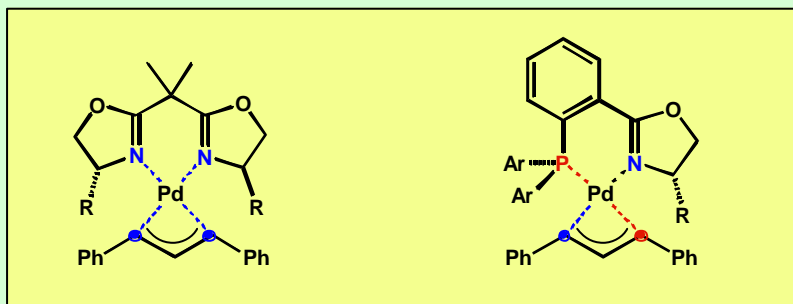
Andreas Pfaltz

Department of Chemistry, University of Basel
St. Johanns-Ring 19, CH-4056 Basel
Switzerland
E-mail: andreas.pfaltz@unibas.ch

ENANTIOSELECTIVE HYDROGENATION

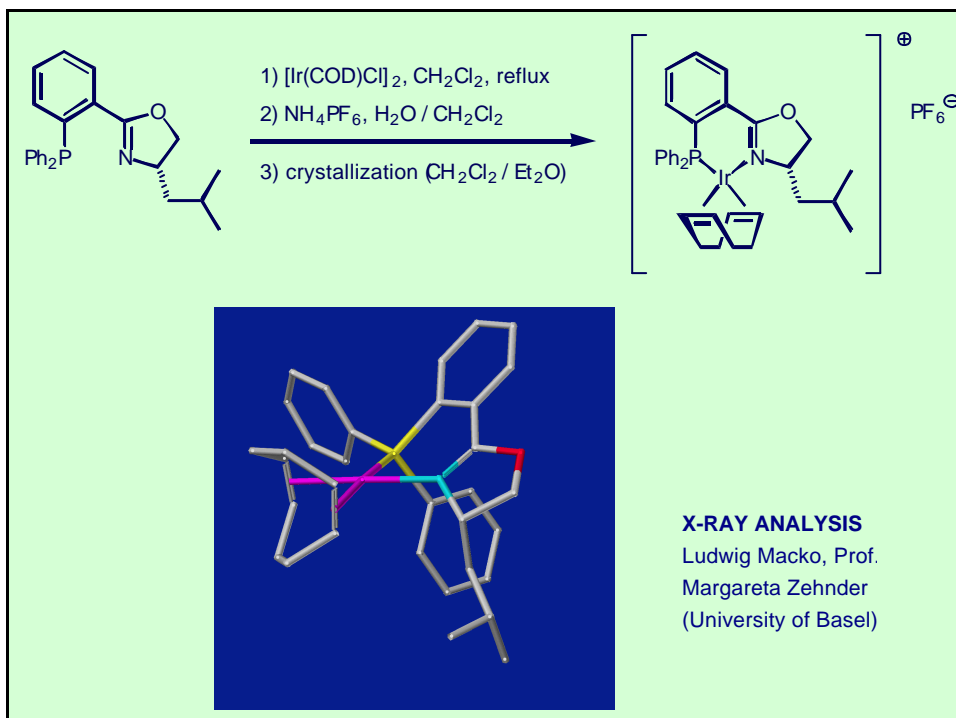
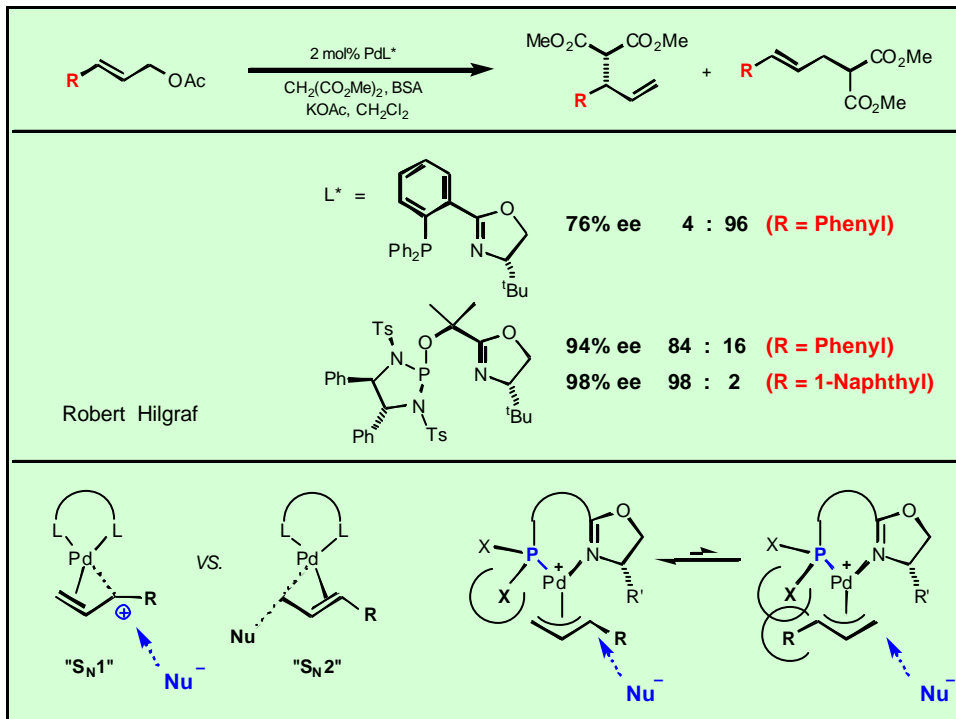


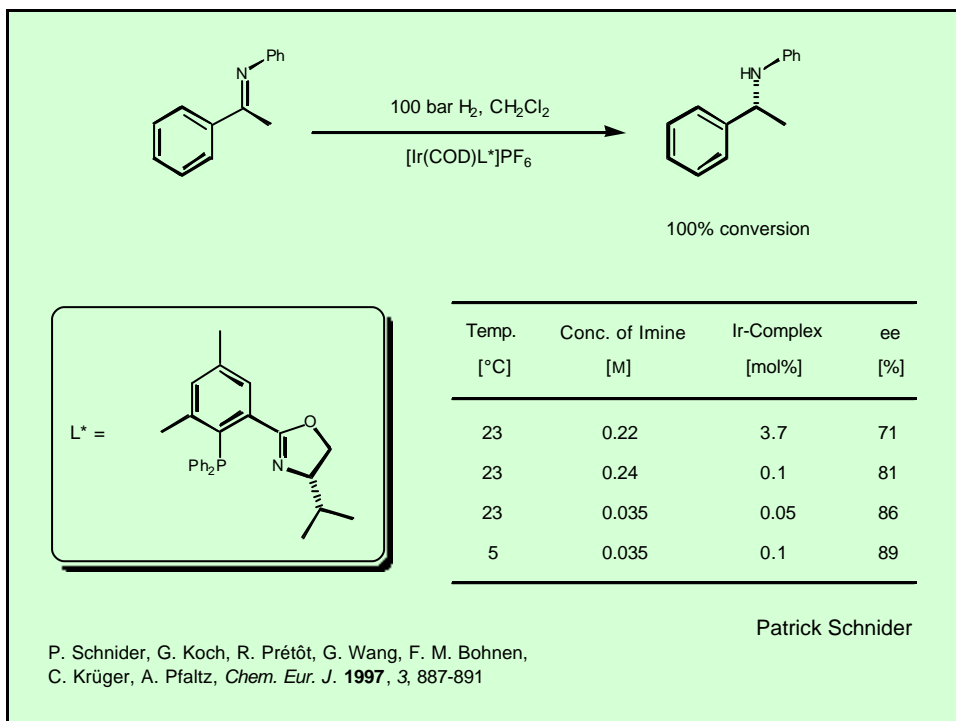
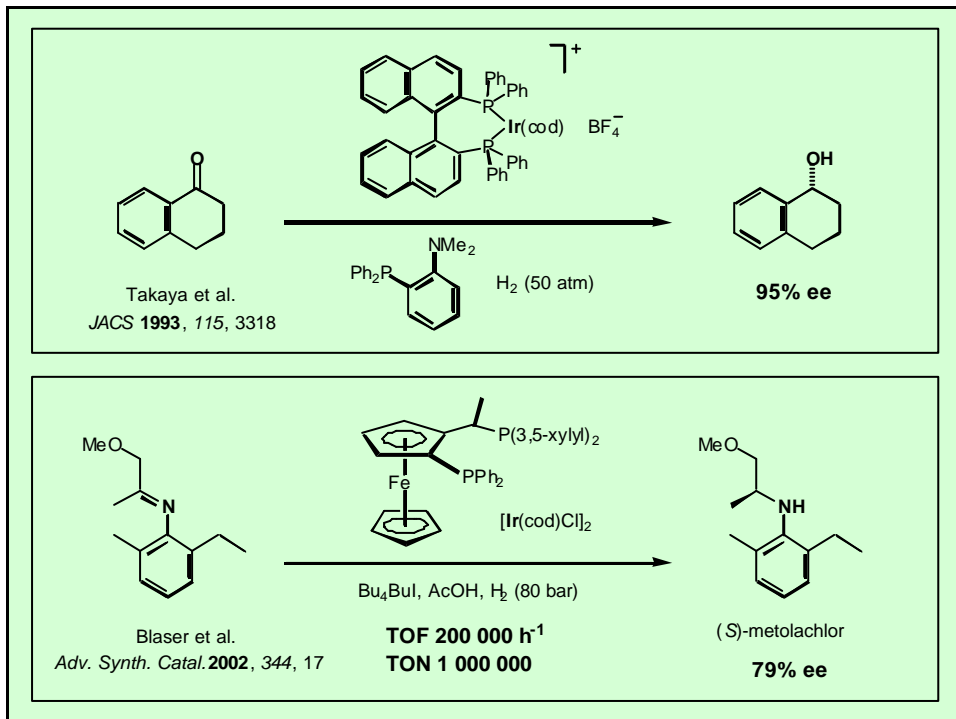




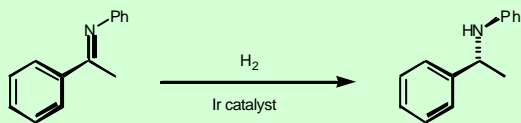
X-ray analysis:

M. Zehnder, M. Neuburger,
L. Macko
University of Basel



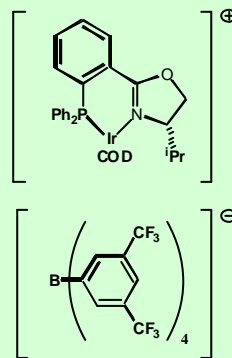
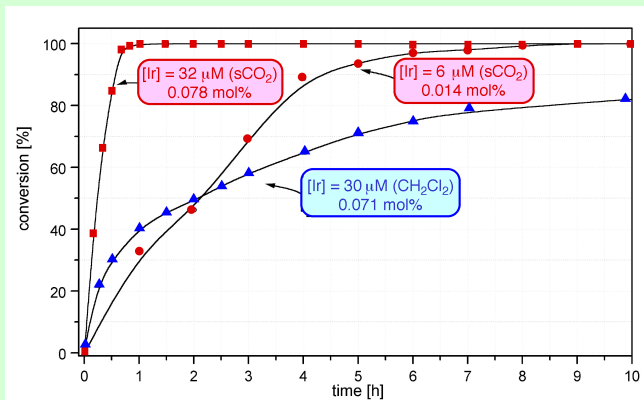


HYDROGENATION IN SUPERCRITICAL CO₂



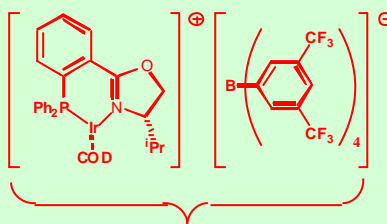
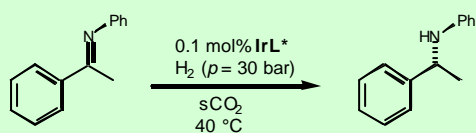
sCO₂
78-81% ee (40 °C)
TON 1000-7000
TOF 1200-2800 h⁻¹

CH₂Cl₂
86% ee (23 °C)
TON 500-1500
TOF 600-1200 h⁻¹

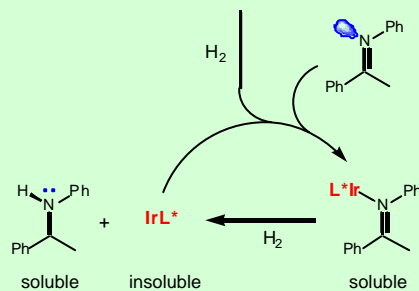


Sabine Kainz, Axel Brinkmann, Walter Leitner (Max-Planck-Institut für Kohlenforschung)

CATALYST RECYCLING IN SUPERCRITICAL CO₂



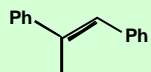
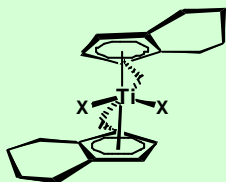
insoluble



Cycle	Time for full conv.	%ee
1	1 h	79
2	1 h	80
3	1 h	76
4	2 h	75
5	20 h	72
6	40 h	74
7	65 h	70

Unfunctionalized Olefins

Buchwald

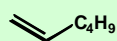
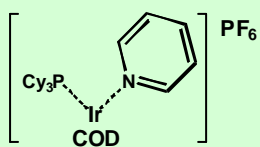


94% yield
99% ee

High yield and ee
5-8 mol% catalyst
low TOF (1-2 h⁻¹)

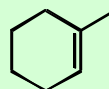
Broene & Buchwald, JACS
1993, 115, 12569

Crabtree



TOF (h⁻¹)

6400

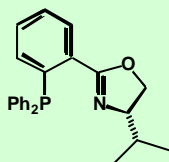
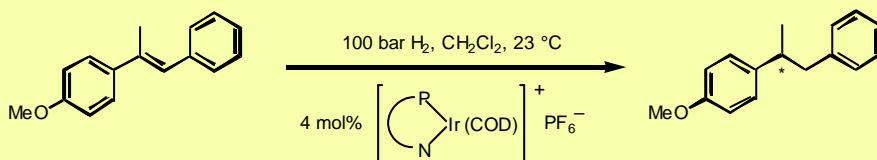


3800

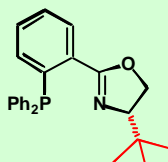


4000

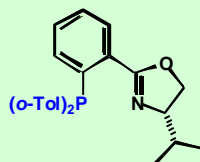
Ligand Variation



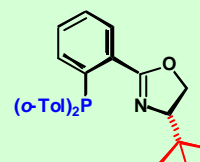
78% conv.
75% ee



98% conv.
90% ee



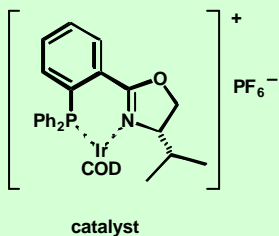
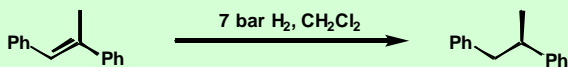
100% conv.
91% ee



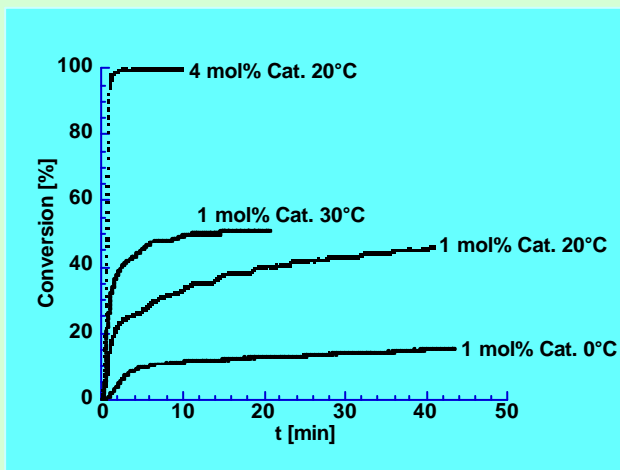
72% conv.
97% ee

PATRICK SCHNIDER, ANDREW LIGHTFOOT

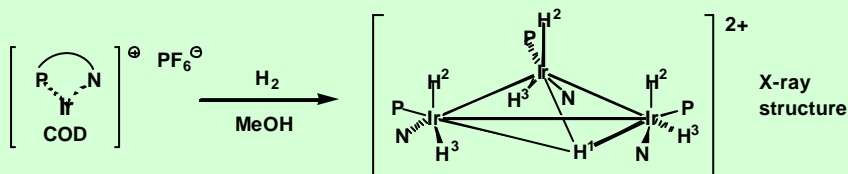
Kinetic Studies




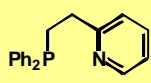
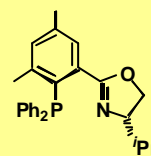
Prof. Donna G. Blackmond
Thorsten Rosner
(MPI für Kohlenforschung)



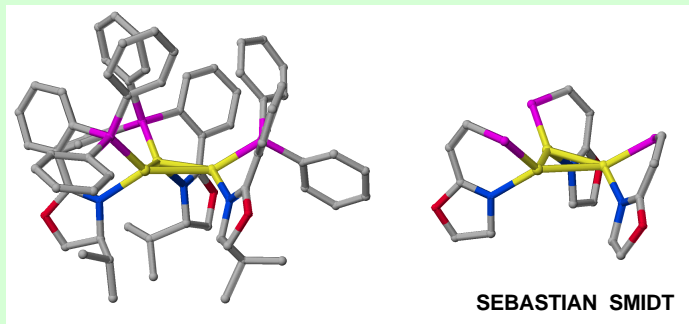
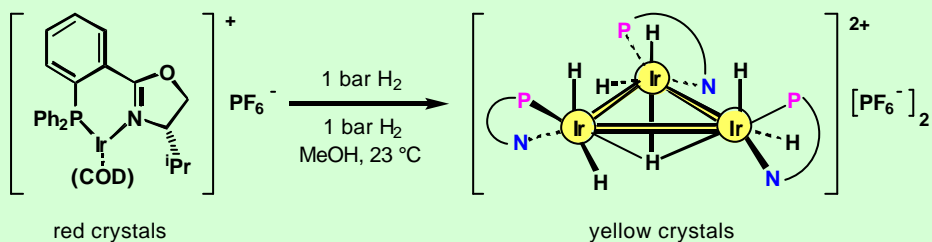
Hydride-Bridged Trimer



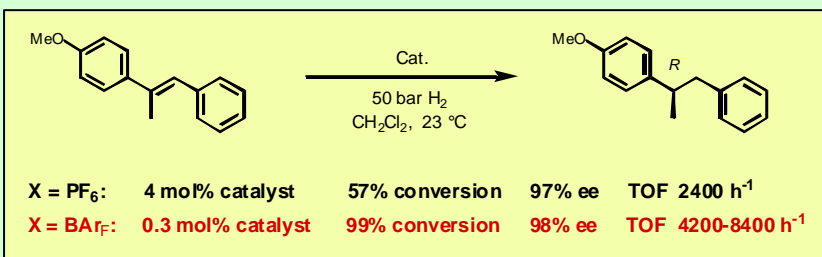
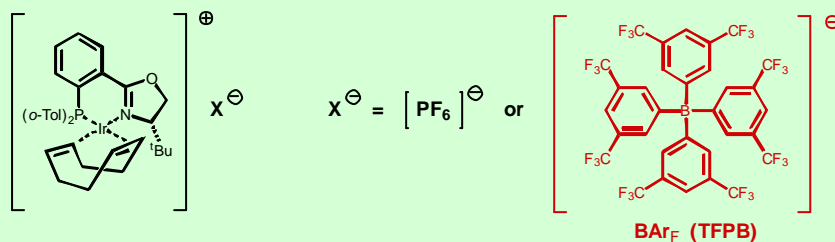
L. Pignolet et al.,
Inorg. Chem.
1988, 325

	¹ H-NMR
	<ul style="list-style-type: none"> - 2.0 (q, J_{PH, trans} = 47 Hz, 1 H; H¹) - 18.7 (d, J_{PH, cis} = 12 Hz, 3 H; H² or H³) - 22.5 (d, J_{PH, cis} = 26 Hz, 3 H; H³ or H²)
	<ul style="list-style-type: none"> - 8.0 (q, J_{PH} = 47 Hz, H¹) - 16.6 (br. s, 3H) - 20.5 (d, J_{PH} = 21 Hz, 3H)

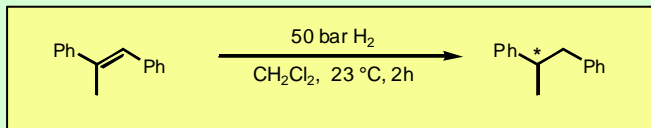
Preparation and X-ray analysis of the hydride-bridged trimer $[\{\text{Ir}(\text{PHOX})\text{H}\}_3] [\text{PF}_6]_2$



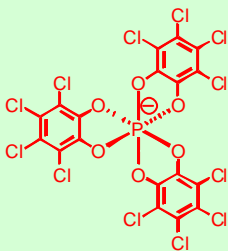
EFFECT OF THE COUNTER ION



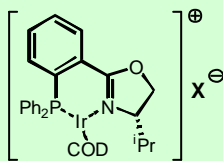
ANDREW LIGHTFOOT



D-TRISPHAT:

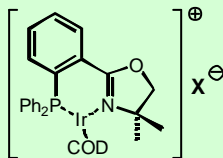


Jérôme Lacour
(University of Geneva)



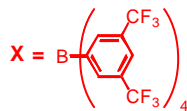
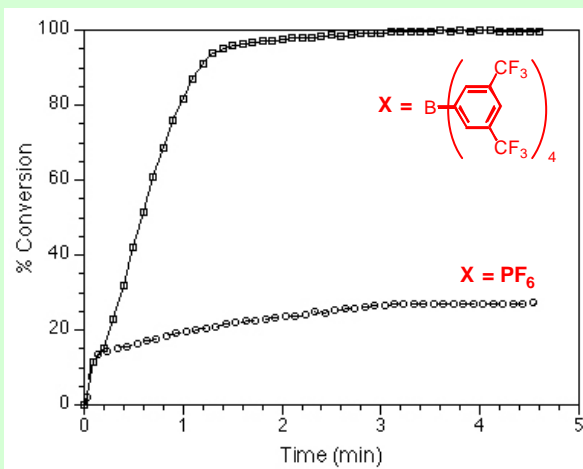
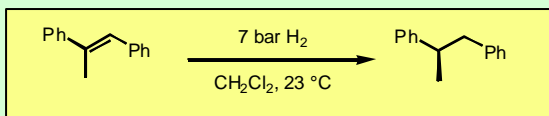
X = BARF: 70% ee
(1 mol% cat.) 100% conv.

X = D-TRISPHAT: 70% ee
(4 mol% cat.) 100% conv.

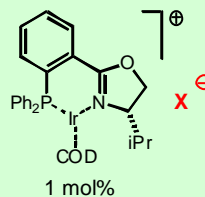


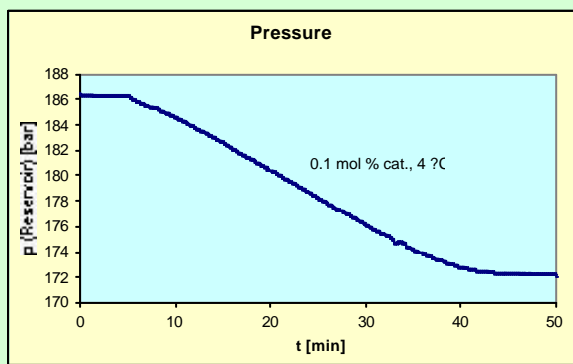
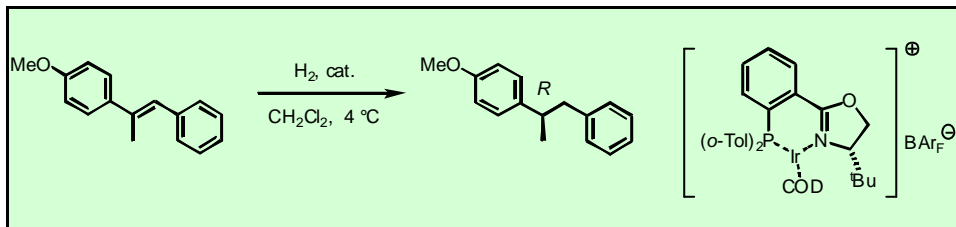
X = D-TRISPHAT: 0% ee
(4 mol% cat.) 100% conv.

X = D-TRISPHAT: 0% ee
(1 mol% cat.) 70% conv.



X = PF₆

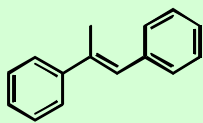




- ◆ 4 °C: up to 5000 TON
- ◆ 1st order in [H₂]
- ◆ 5-30 bar (97-98% ee)
- ◆ 0 order in [olefin] (at high conc. -0.2)
- ◆ 1st order in [cat] at low conc. 0.3 at high conc.
- ◆ 23 °C: rate diffusion-limited

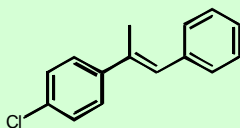
Nicole Zimmermann, Dr. Martin Studer (Solvi)

 0.1 mol% cat. 97% ee, >99% conv.	 0.5 mol% cat. 95% ee, 98% conv.	 0.3 mol% cat. 95% ee, 97% conv.
 0.3 mol% cat. 61% ee, >99% conv.	 0.5 mol% cat. 91% ee, >99% conv.	 X = B-C6H2(CF3)2
 4 mol% cat. 84% ee, 60% conv.	 1 mol% cat. 96% ee, 95% conv.	 X = PF₆



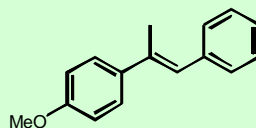
1 97 % ee

2 99 % ee



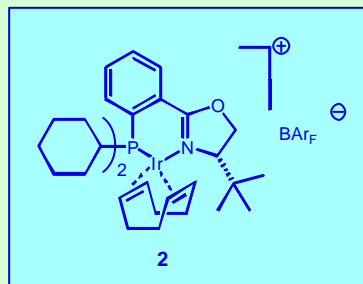
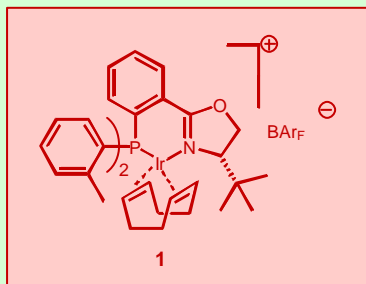
95 % ee

99 % ee



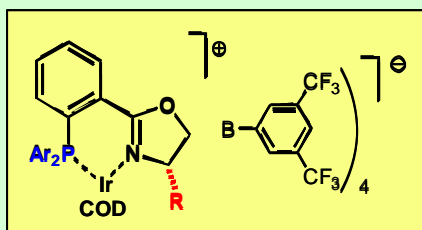
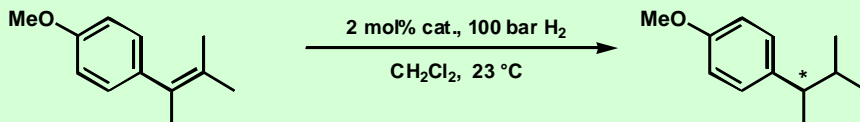
98 % ee

99 % ee



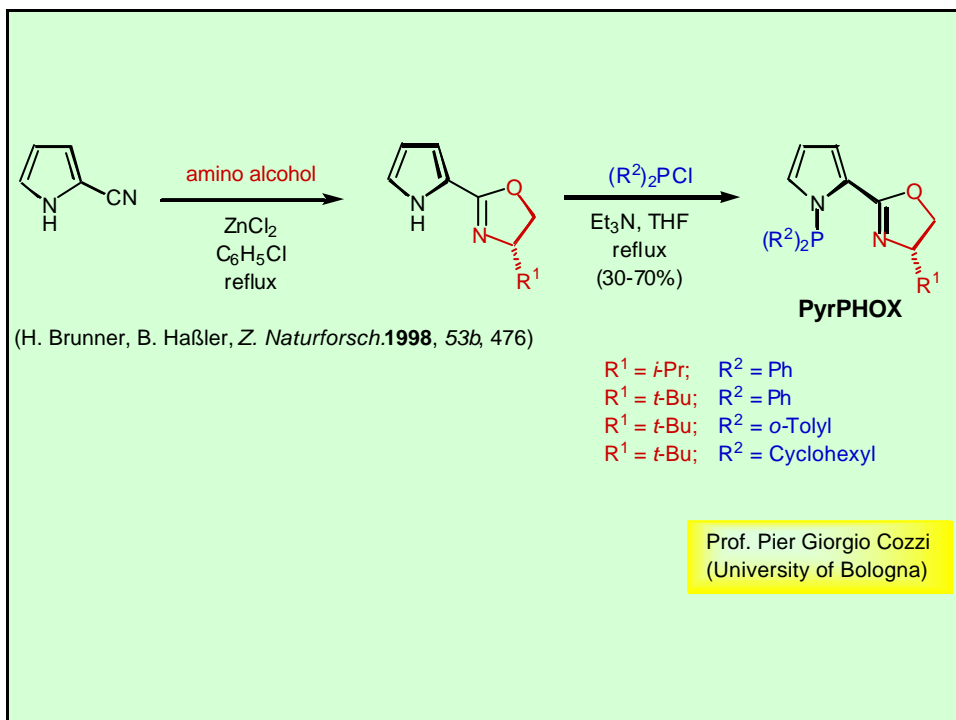
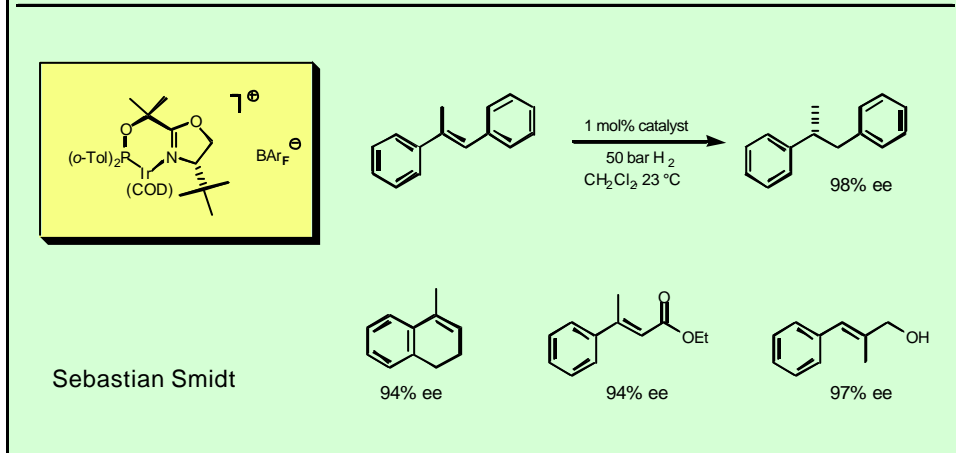
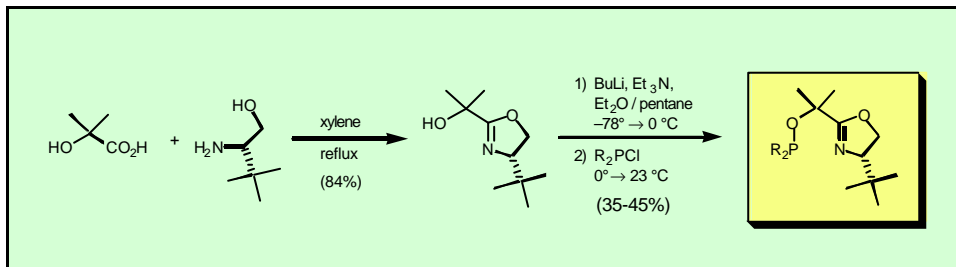
NICOLE ZIMMERMANN

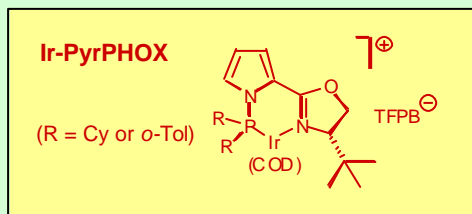
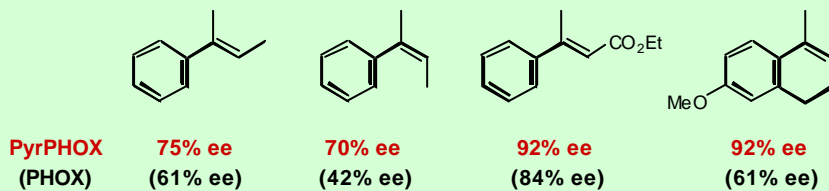
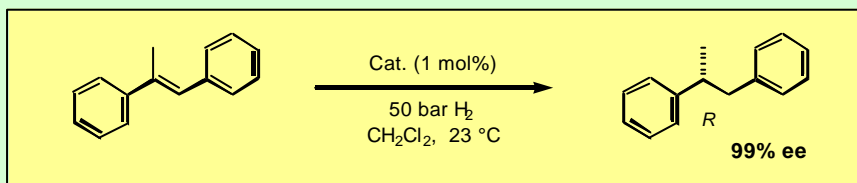
TETRASUBSTITUTED OLEFINS



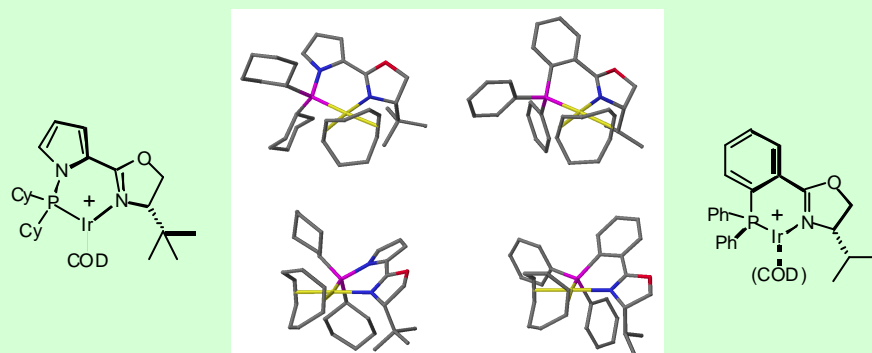
Ar	R	Conv.	ee
<i>o</i> -Tol	<i>t</i> Bu	37%	3% ee
<i>o</i> -Tol	<i>i</i> Pr	97%	8% ee
Ph	<i>t</i> Bu	23%	31% ee
Ph	<i>i</i> Pr	>99%	58% ee
Ph	CH ₂ <i>t</i> Bu	>99%	81% ee

ANDREW LIGHTFOOT



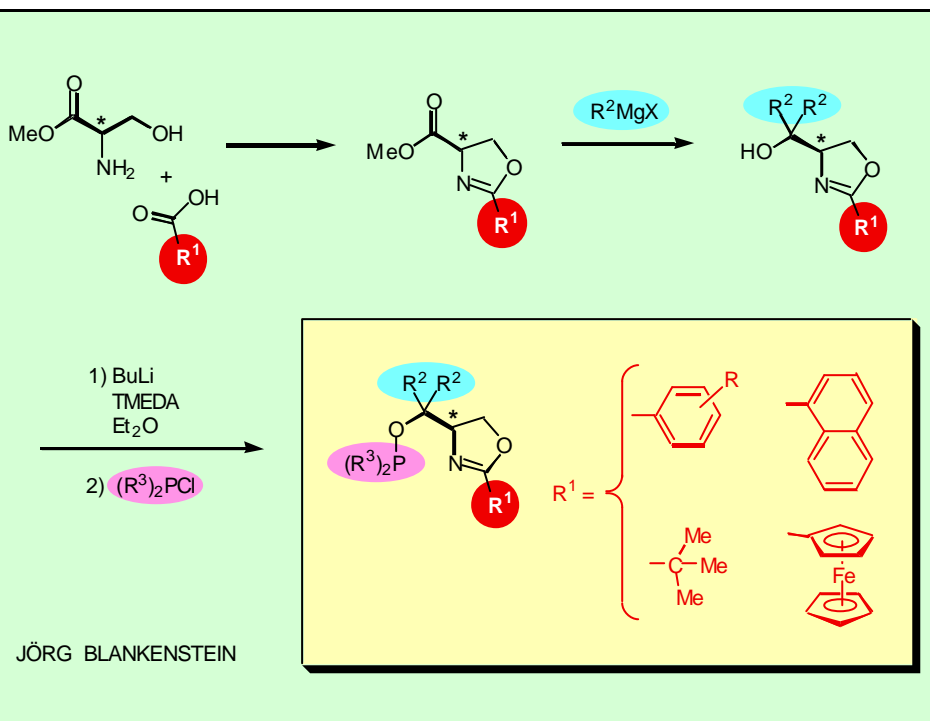
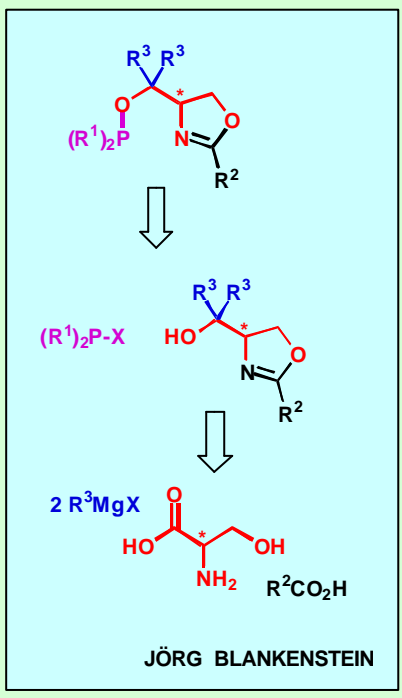
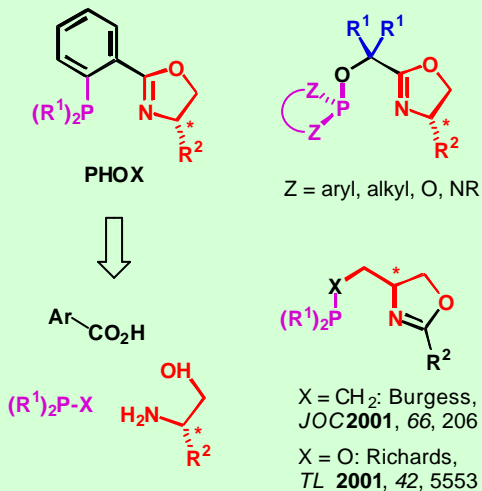


P. G. Cozzi
Nicole Zimmerman

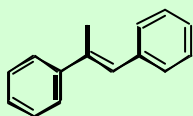


X-ray: Dr. Silvia Schaffner, Prof. Margarete
 Neuburger-Zehnder (University of Basel)

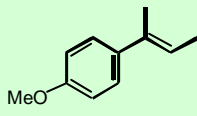
FURTHER VARIATION OF THE PHOSPHINOXAZOLINE STRUCTURE



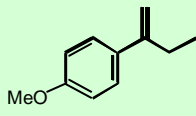
Iridium-Catalyzed Hydrogenation



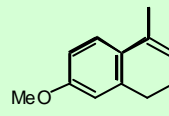
97% ee



96% ee



80-90% ee



82% ee

R¹ = Ph, ferrocenyl

R² = isopropyl

R¹ = 3,5-(^tBu)₂-Ph

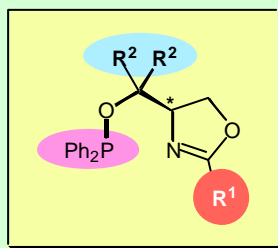
R² = benzyl

R¹ = ferrocenyl

R² = isobutyl

R¹ = ferrocenyl

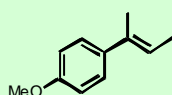
R² = benzyl



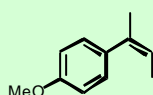
Conditions:

0.1-0.3 mol% [Ir(L*)(COD)]BARf
50 bar H₂, toluene or CH₂Cl₂, RT

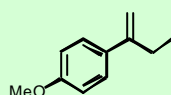
JÖRG BLANKENSTEIN



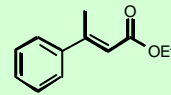
98% ee (*R*)



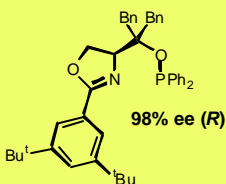
74% ee (*S*)



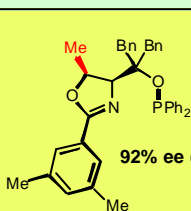
89% ee (*R*)



55% ee (*R*)

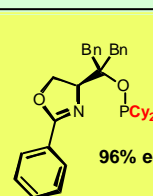


99.4% ee (*S*)



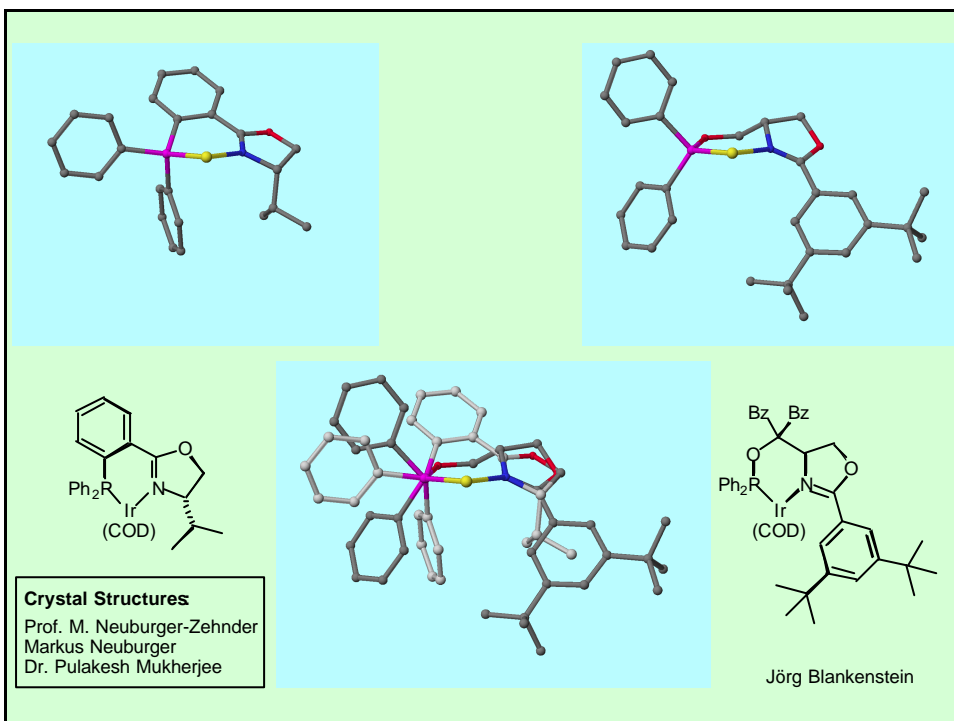
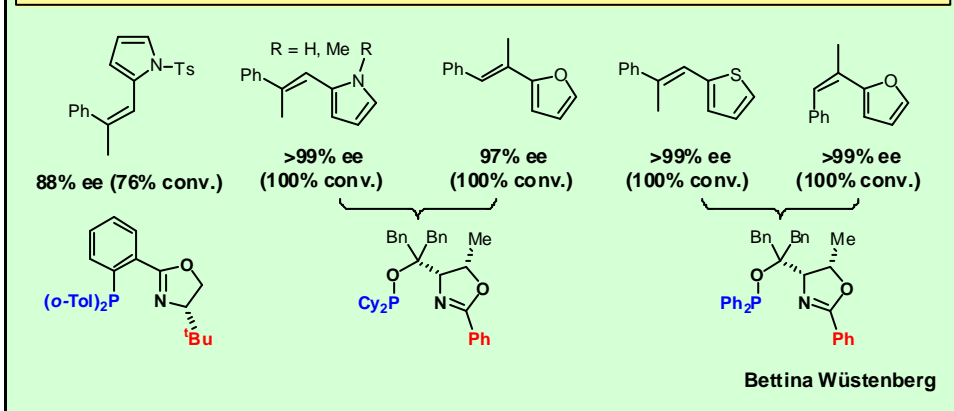
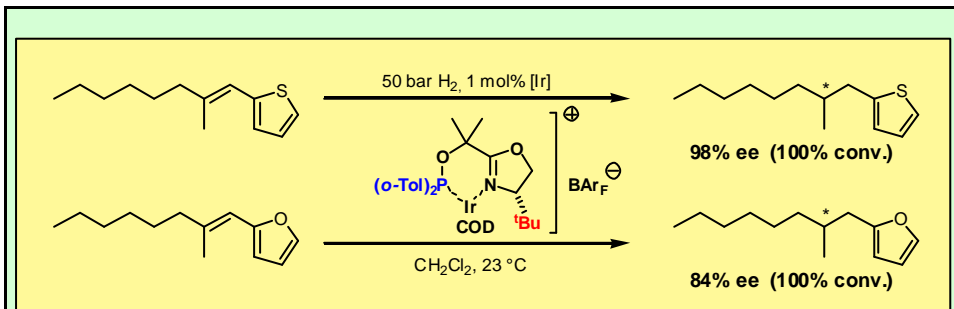
92% ee (*S*)

89% ee (*R*)

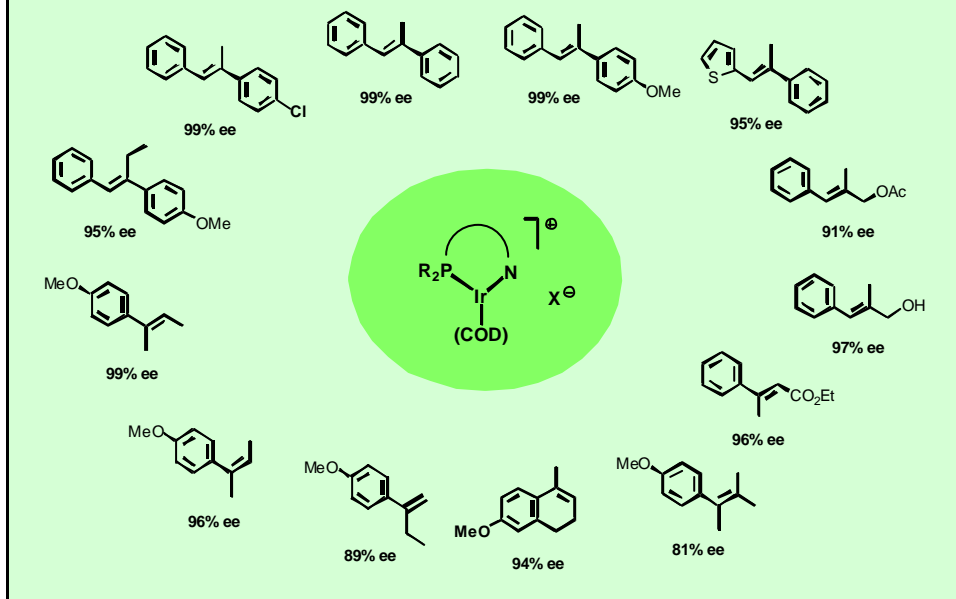


96% ee (*R*)

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IRIDIUM-CATALYZED HYDROGENATION OF C=C BONDS



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