Chiral oxorhenium complexes for the observation of parity violation in chiral molecules

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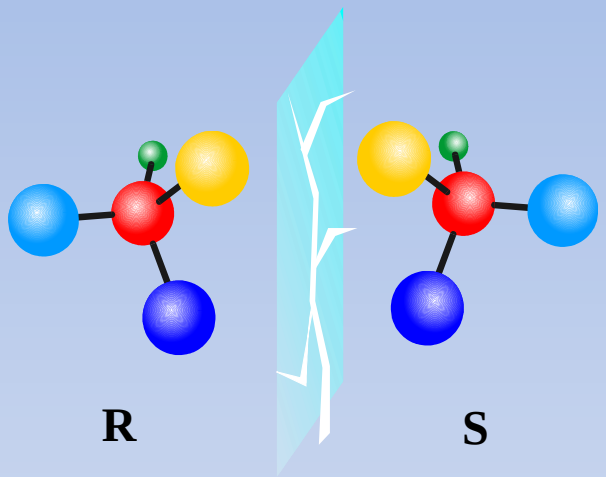
Parity violation (PV) in molecules: Fundamental effect

The broken mirror



ΔE_{PV}

ΔE_{PV} c.a. 10^{-17}kT

Fundamental effect

Comes from the weak nuclear interaction

(one of the four fundamental forces: electromagnetic, gravitational, weak and strong nuclear forces)

Electroweak theory predicts a small energy difference (ΔE_{pv}) between pairs of enantiomers, and thus a breakdown of mirror-image symmetry.

As a Chemist: Ideal Candidate:

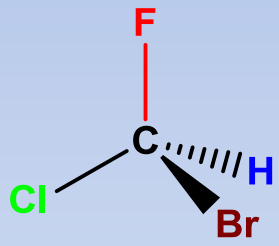
- **Chiral-heavy-Transition metal (PV proportional to Z^n).**
- **M-L IR stretching frequency lies in the CO_2 frequency range (850-1120 cm^{-1}).**
- **Available in large enantiomeric excess , or ideally, in enantiopure form.**
- **Not too bulky (Very simple chiral molecule).**
- **Preferably sublimate without decomposition.**
- **Gram scale synthesis.**

Theoretical Relativistic calculations of PV effects

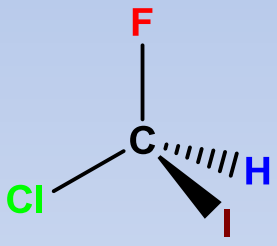
Pr Schwerdtfeger, Aukland

T. Saue, R. Bast, Université de Strasbourg

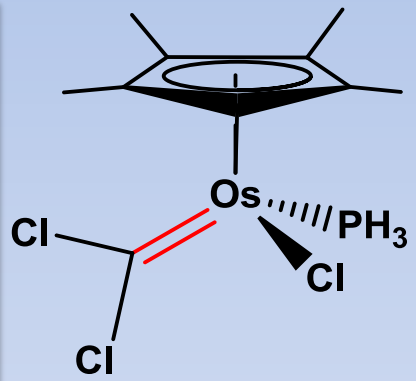
mHz → **Hz**



$\Delta\nu_{PNC}$ = 1.7 mHz
For C-F stretching

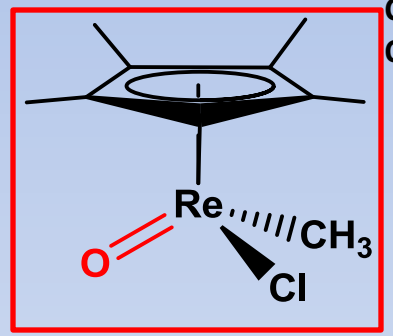


$\Delta\nu_{PNC}$ = 24 mHz
For C-F stretching



$\Delta\nu_{PNC}$ =1.30 Hz
For Os=C stretching
at 901 cm^{-1}

Chiral
OxoRhenium



$\Delta\nu_{PNC}$ =1.09 Hz
For Re=O stretching
at 989 cm^{-1}

$E_{PV} \alpha Z^2 Z'^3$

Z,Z': atomic numbers

P. Schwerdtfeger, T. Saue, J. N. P. van Stralen and L. Visscher, *Phys. Rev. A,* **2005**, 71, 012103

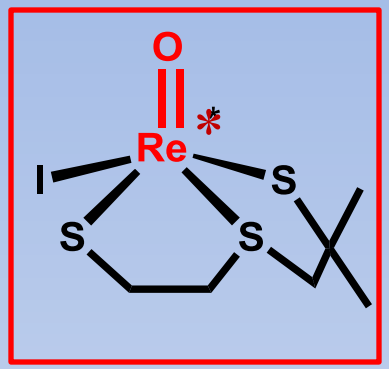
Schwerdtfeger, Bast, *JACS,* **2004**, 126, 1652

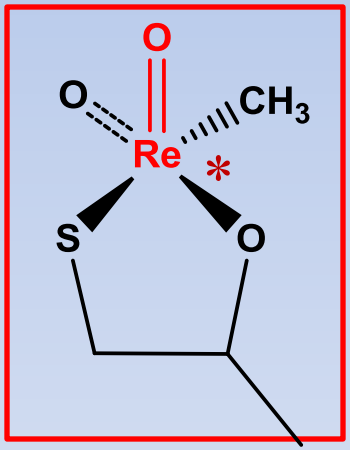
Outline:

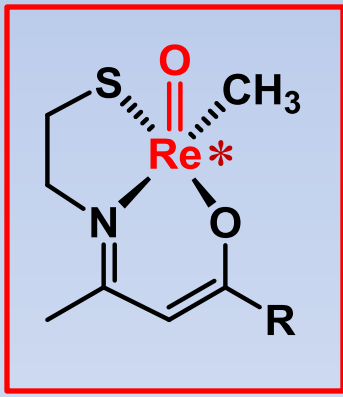
1. *Bibliography*

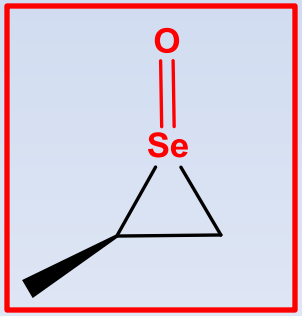
2. *Synthesis of novel chiral OxoRhenium Complexes derived from MTO.*

3. *Perspectives*

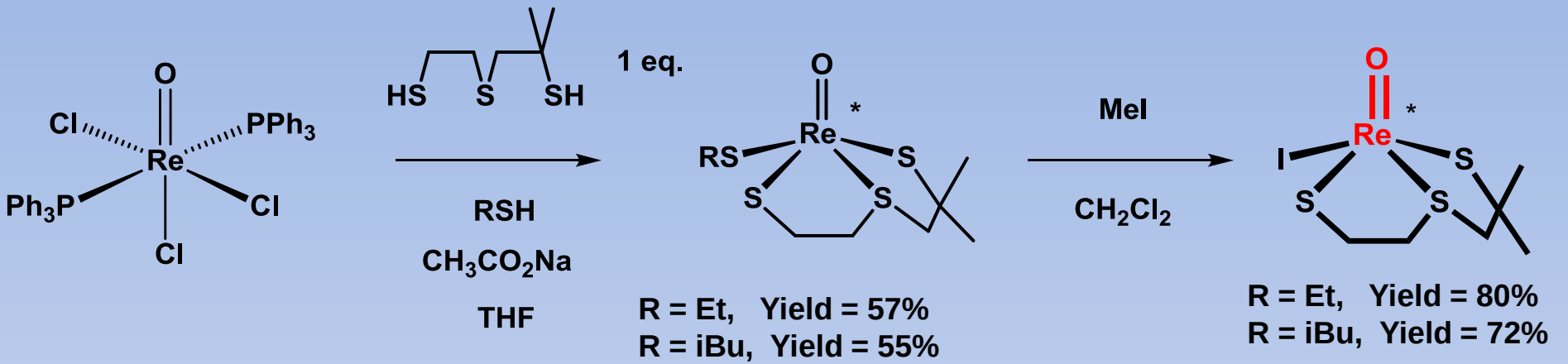


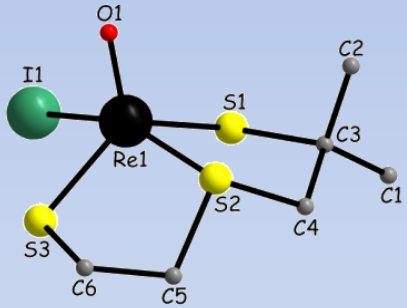






Chiral OxoRhenium complexes bearing sulfur





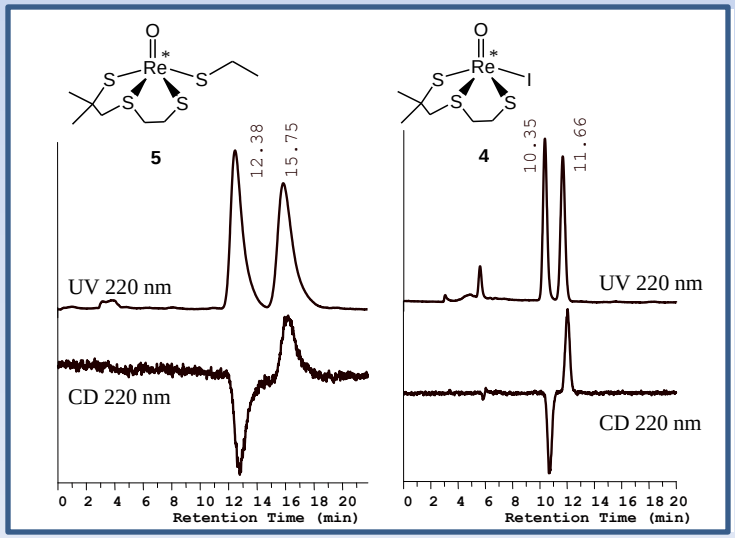
Enantiomers separated by

HPLC over a chiral stationary phase

Chiralpak AS-H
Hexane/ethanol (1/1) – 1 ml/min
Detection : UV and CD at 220 nm

Pr Roussel et Dr Vanthuyne,

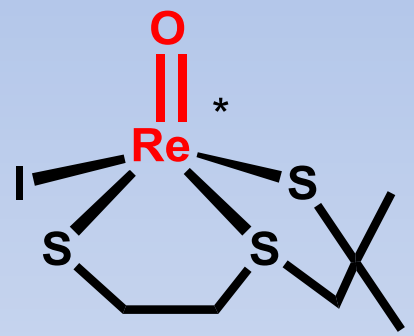
Chirotechnologies, UMR 6180, Marseille



Chem. Commun., 2009, 4841-4843
Phys. Chem. Chem. Phys., 2010, 12, 1-12

Chiral-heavy-Transition metal → Chiral OxoRhenium Complexes

3+1 sulfurated oxorhenium complexes



Intense vibrational band around 1000 cm^{-1}

Efficient sysnthesis (racemic and enantiopure)

Calculated High parity violation effects (0.1-1 Hz)

But:

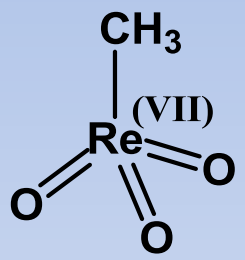
Decomposition in the sublimation conditions

Decomposition in the molecular beam

Thérèse HUET (Lille)
Pierre ASSELIN, Pascale SOULARD, (Paris)

Chiral-heavy-Transition metal → **Chiral OxoRhenium Complexes**

Methyltrioxorhenium (MTO)



MTO is commercially available : 5 G / 500 euros (Alfa Aesar)

Intense vibration Band around 1000 cm^{-1}

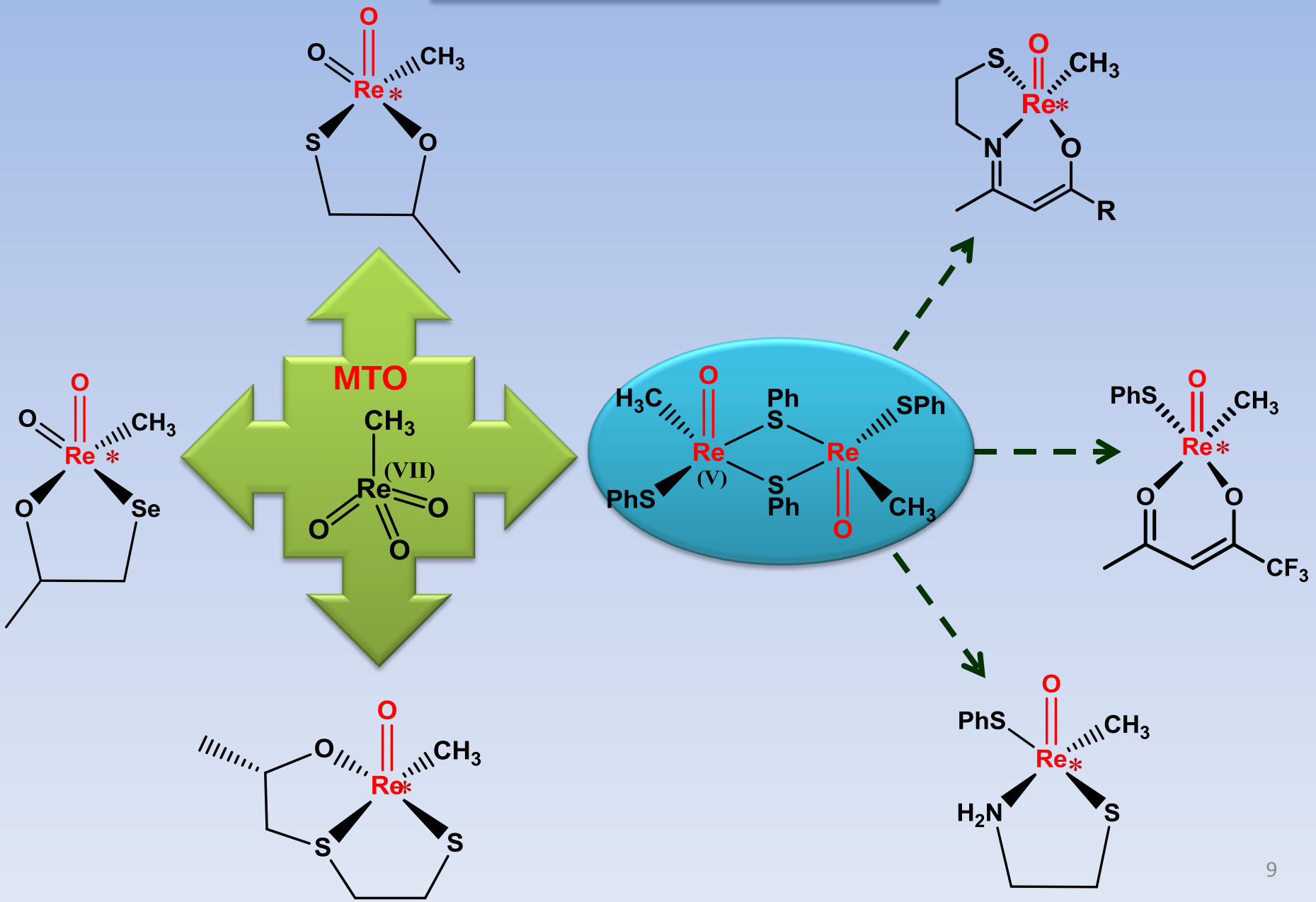
Easy sublimation

Spectroscopy of a molecular beam*

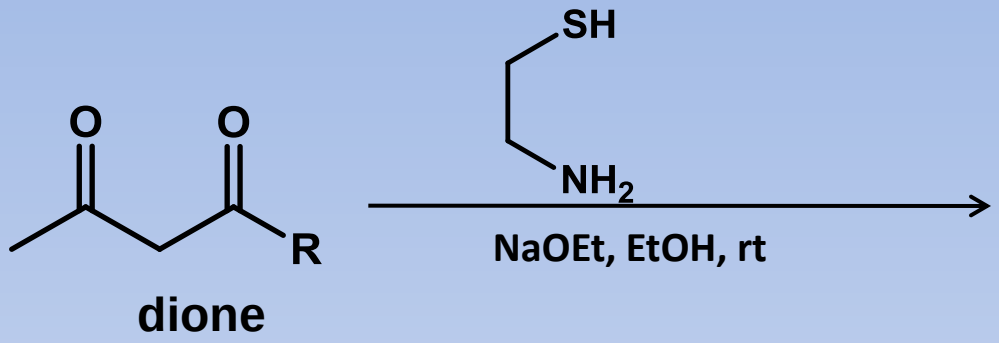
Synthesis of chiral derivatives

* C. Stoeffler, B. Darquié, A. Shelkovnikov, C. Daussy, A. Amy-Klein, C. Chardonnet, L. Guy, J. Crassous, T. R. Huet, P. Soulard, P. Asselin, *Phys. Chem. Chem. Phys*. **2011**, *13*, 854-863.

New oxorhenium complexes derived from MTO



New oxorhenium complexes derived from MTO



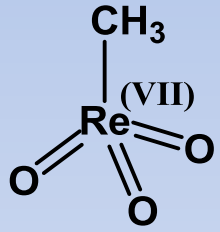
R = CH_3 : Yield = 73 %

R = CF_3 : Yield = 82 %

Sublimation ✓ (100° C)

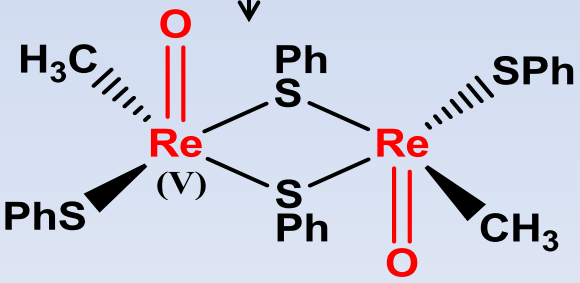
Stability ✓

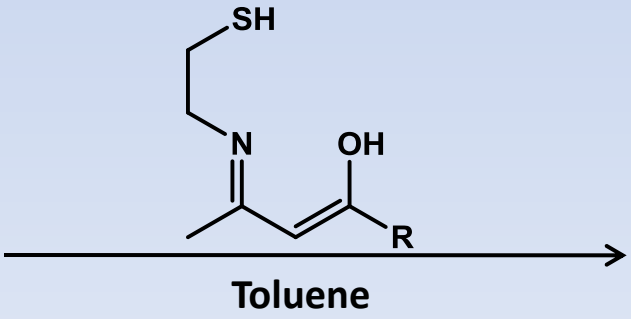
Rhenium : stereogenic ✓

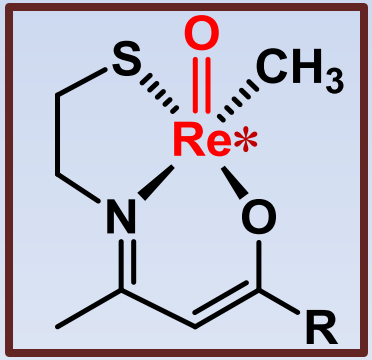


PhSH
Toluene
60%

MTO ✗

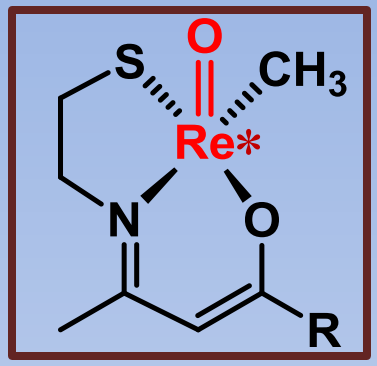






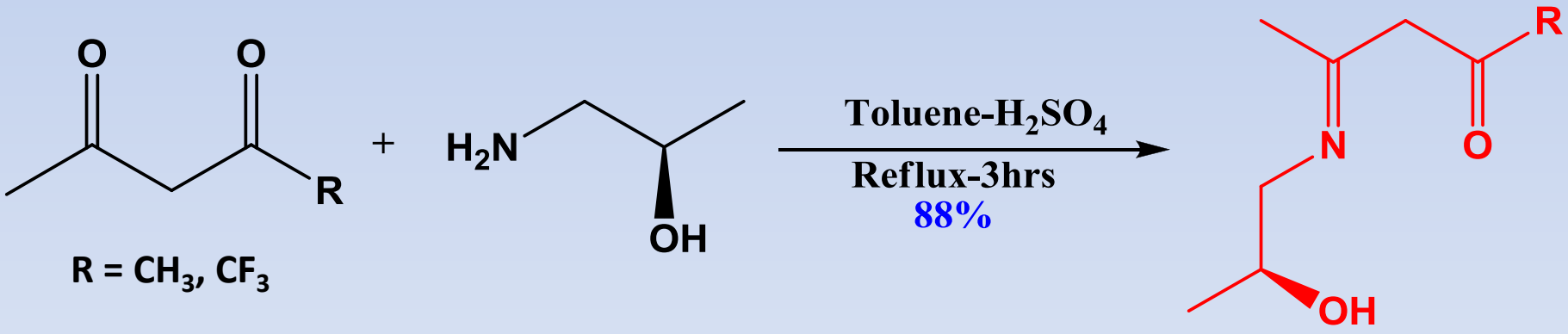
R = CH_3, CF_3

Organometallics, **1991**, 10, 316

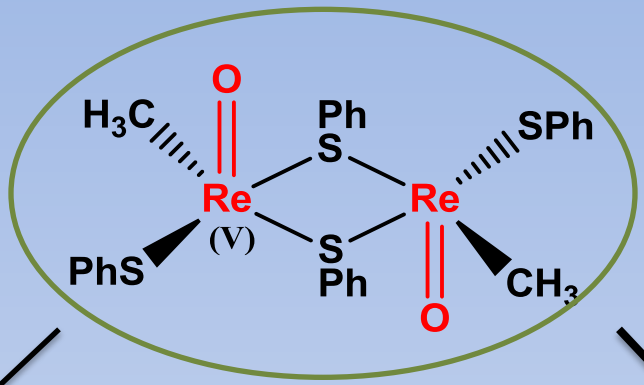


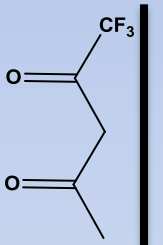
Competitive compound, but unfortunately not stable in the column

Synthesis of enantiopure-containing acac ligands.

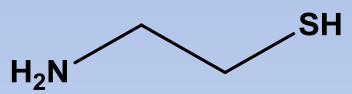


New oxorhenium complexes derived from MTO

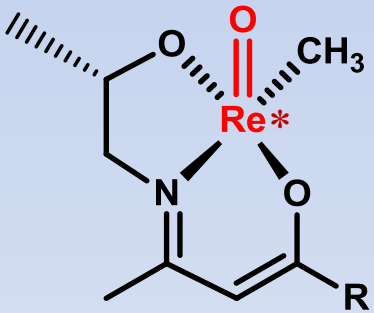


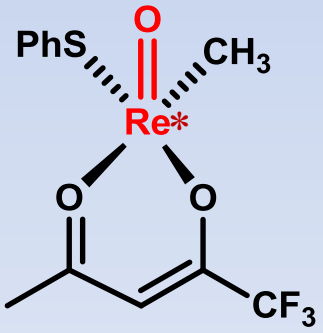


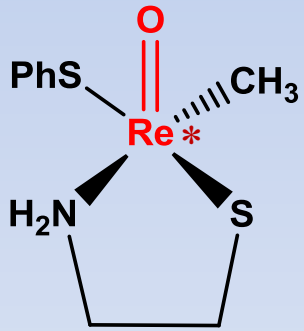
Toluene



Ethanol - KOH



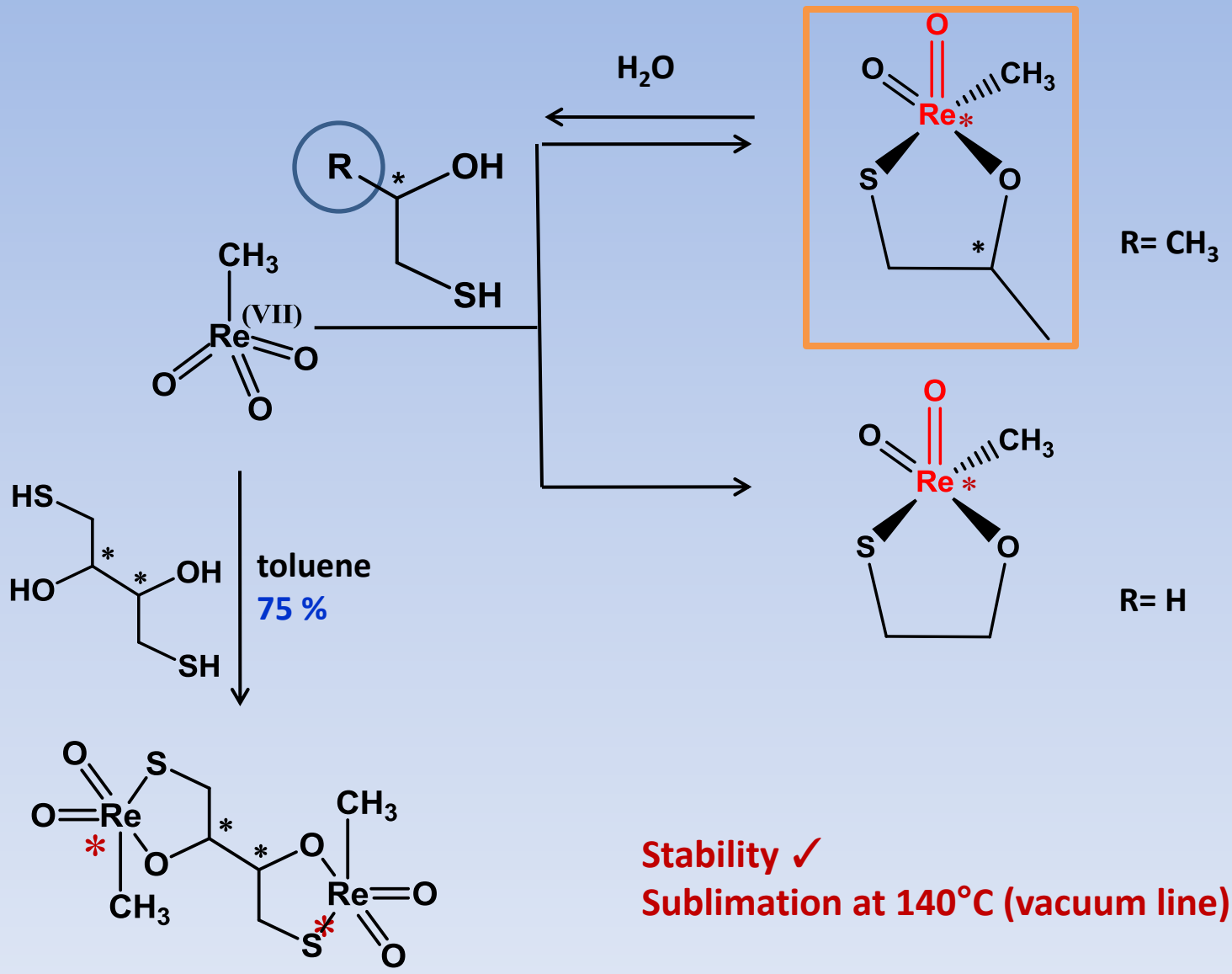




Sublimation at T > 130° C

NO Sublimation

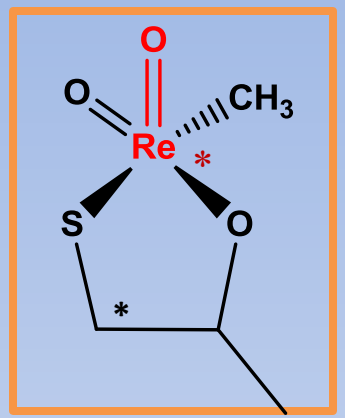
New oxorhenium complexes derived from MTO



Stability ✓
Sublimation at 140°C (vacuum line)

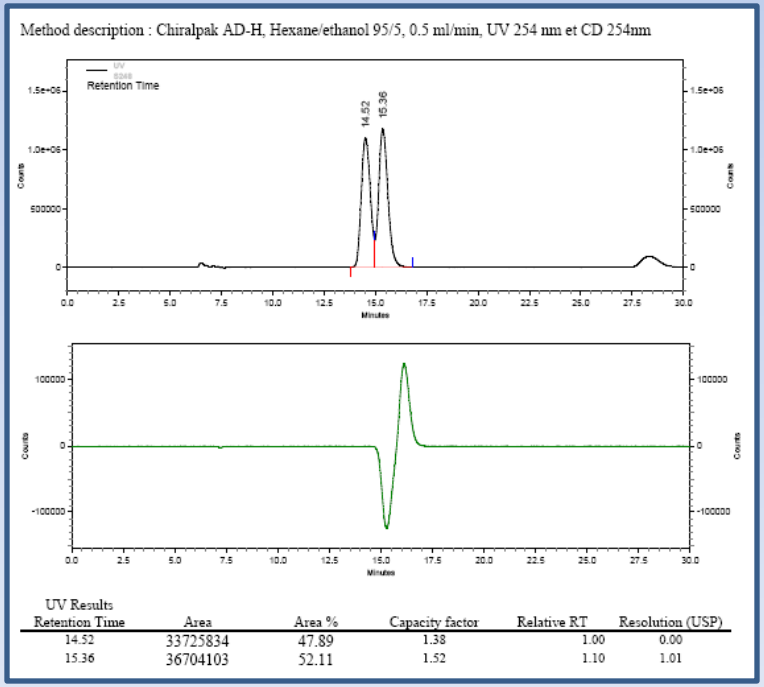
Inorg. Chem. **2002**, *41*, 4727

New oxorhenium complexes derived from MTO



- Sublimation possible around 60°C (vacuum line)
- Reasonable stability

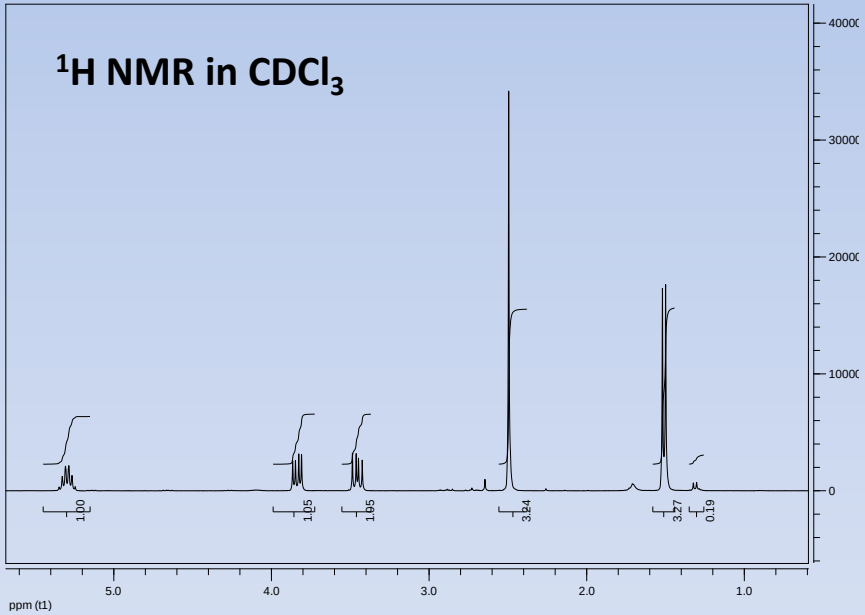
Chiral HPLC : two enantiomers



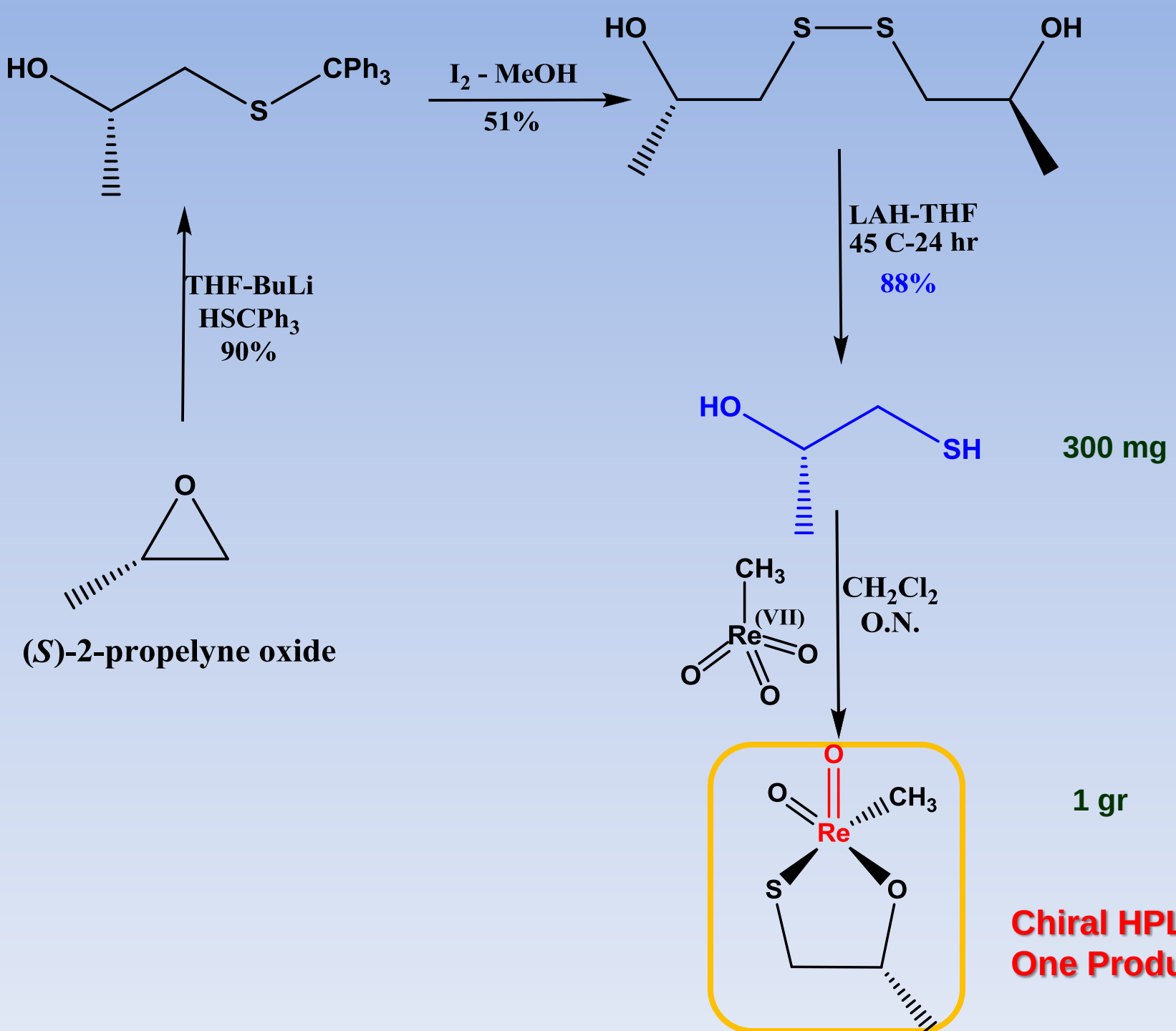
UV Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
14.52	33725834	47.89	1.38	1.00	0.00
15.36	36704103	52.11	1.52	1.10	1.01

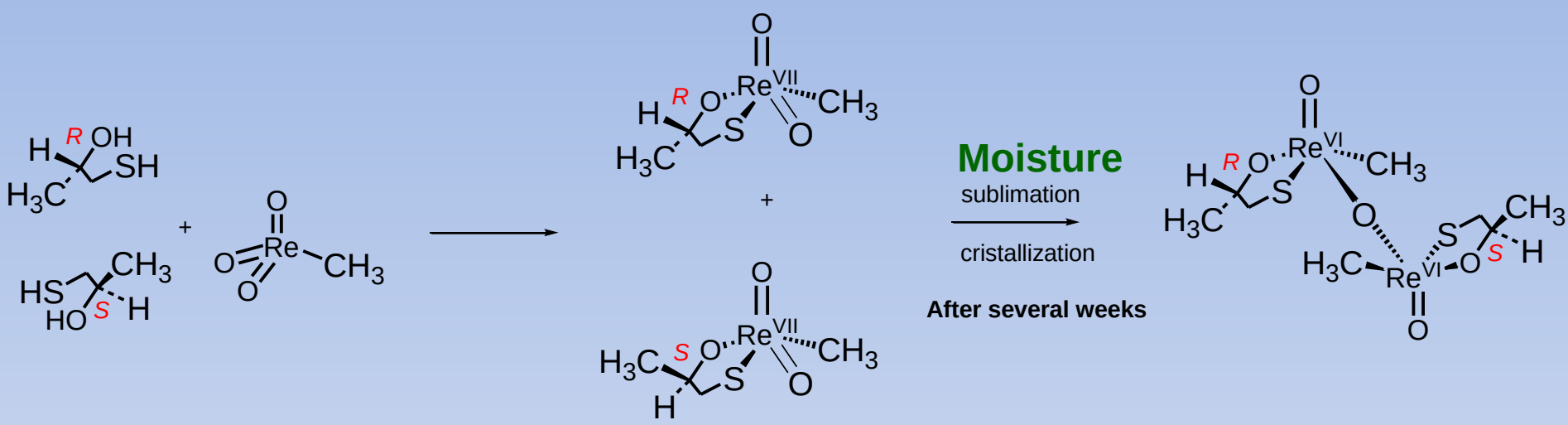
^{1}H NMR in $CDCl_3$



Prepare the enantiopure ligands ?

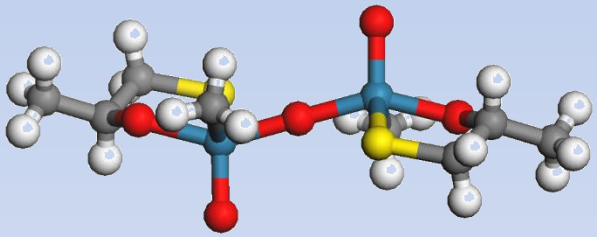

HO
CPh3
S
I2 - MeOH
51%
HO
S
S
OH
LAH-THF
45 C-24 hr
88%
THF-BuLi
HSCPh3
90%
HO
SH
300 mg
O
(S)-2-propelyne oxide
CH3
(VII)
Re
O
O
O
CH2Cl2
O.N.
O
O
CH3
Re
S
O
1 gr
Chiral HPLC
One Product

Dimer formation in the presence of moisture

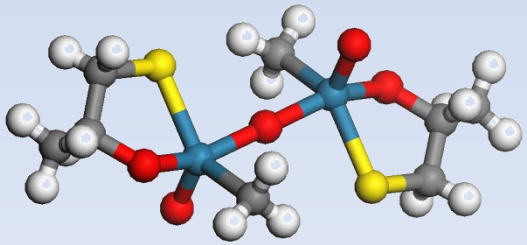


The stereochemistry of the ligand is transferred to the rhenium atom!

This is confirmed with the pure enantiomers …

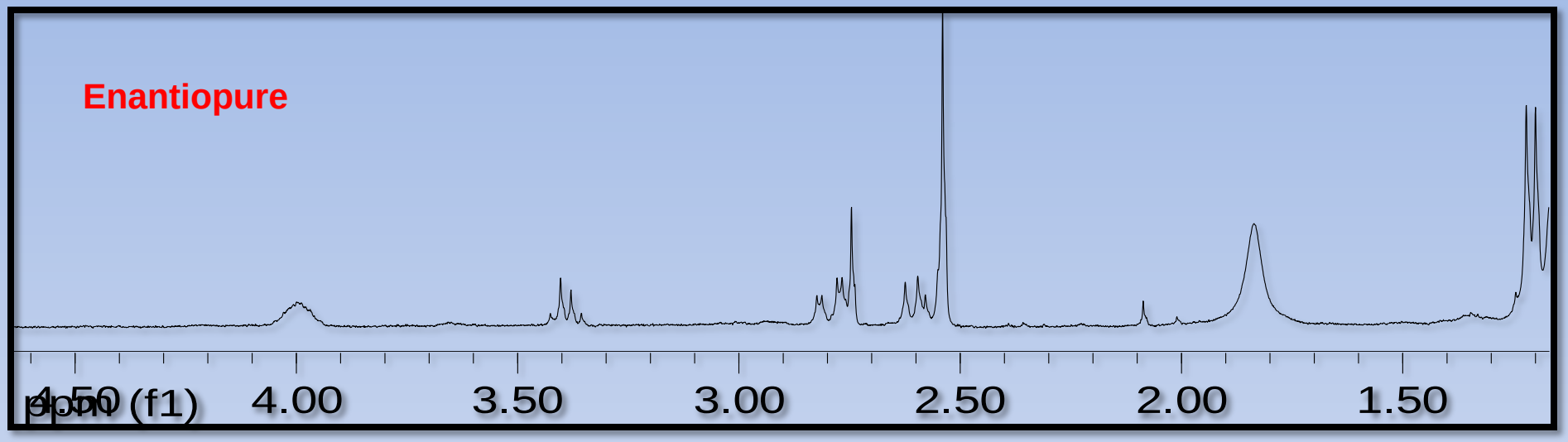


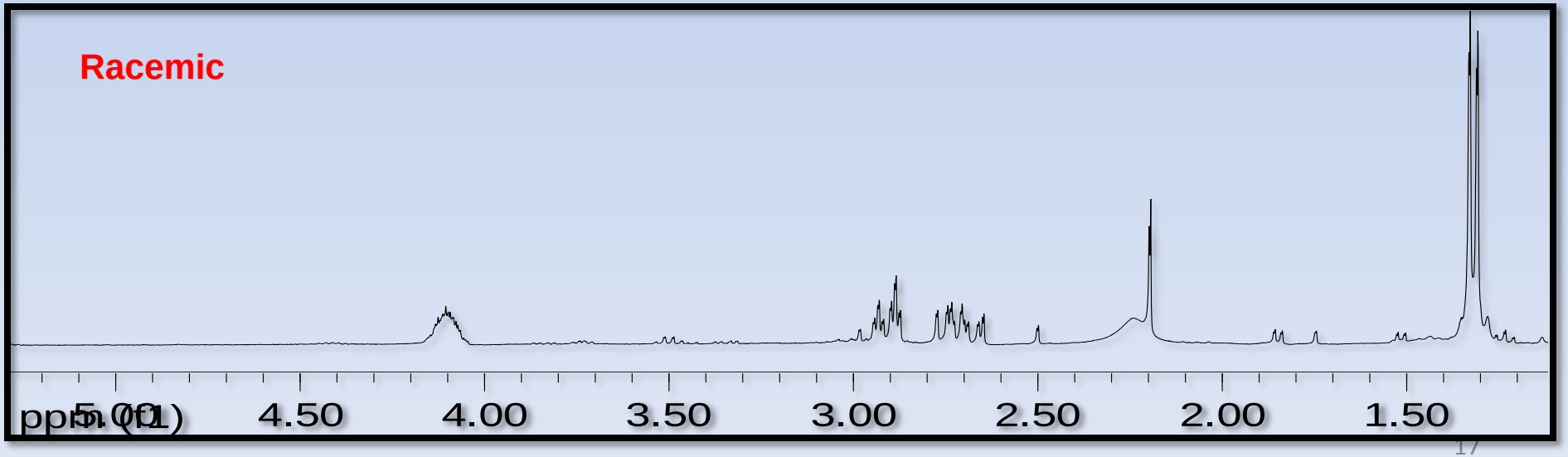
X-ray structure

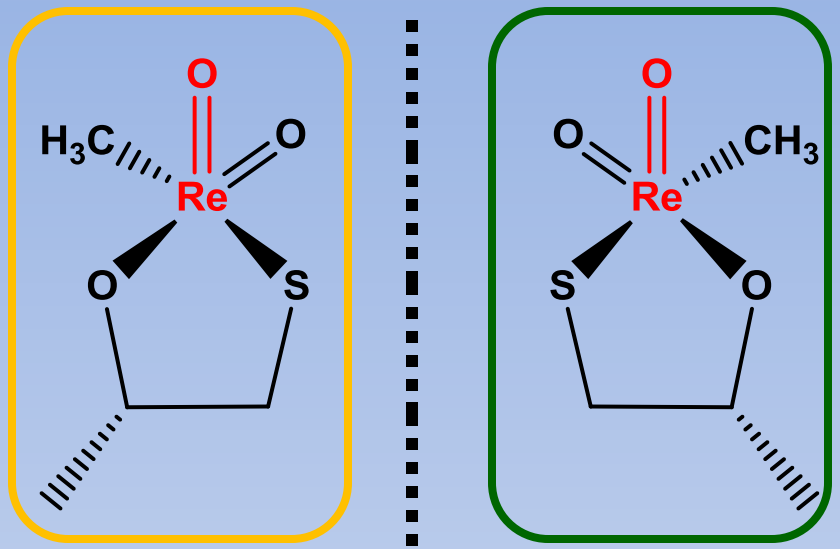


16

Racemic Dimer NMR V/S Enantiopure Dimer NMR

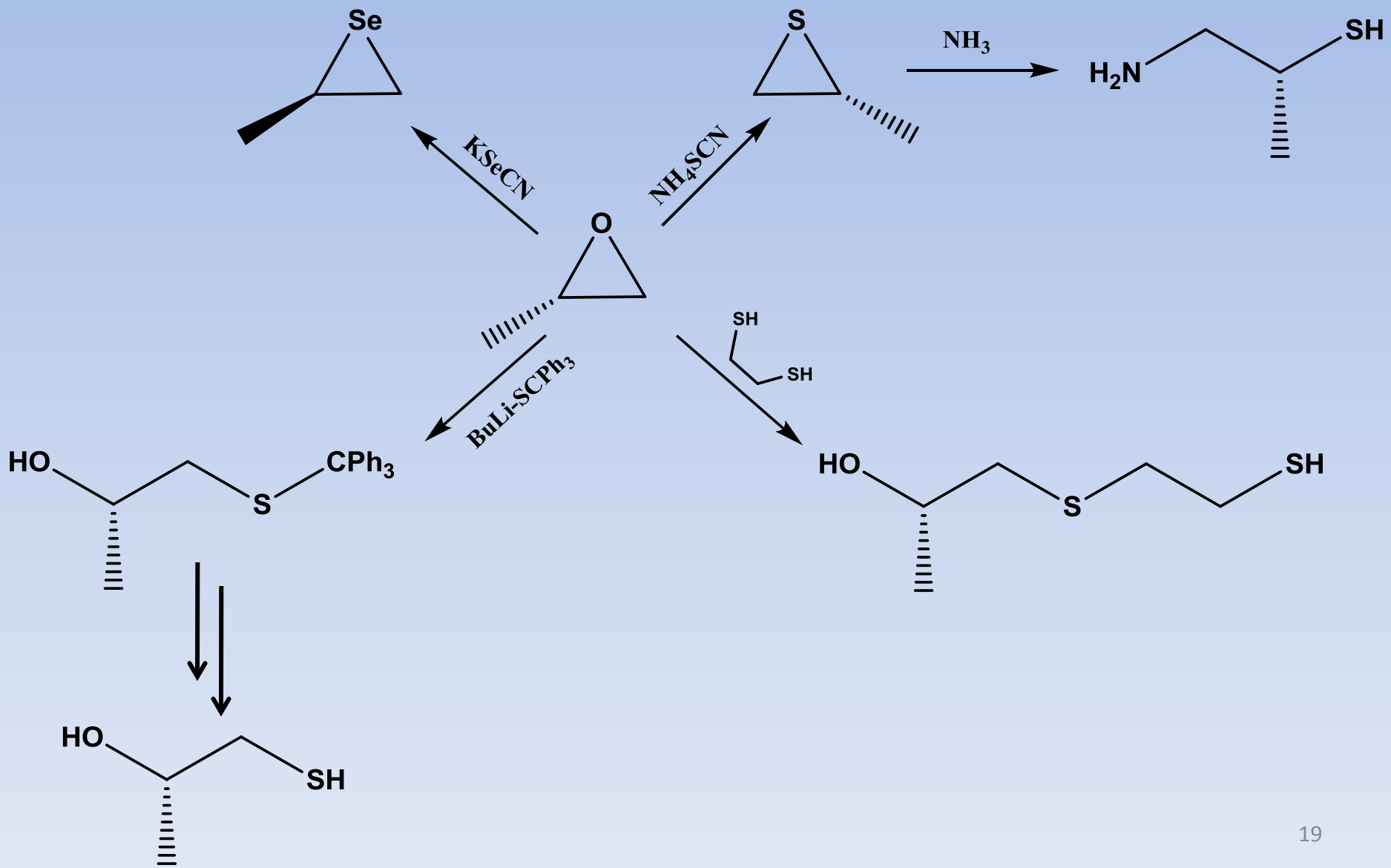




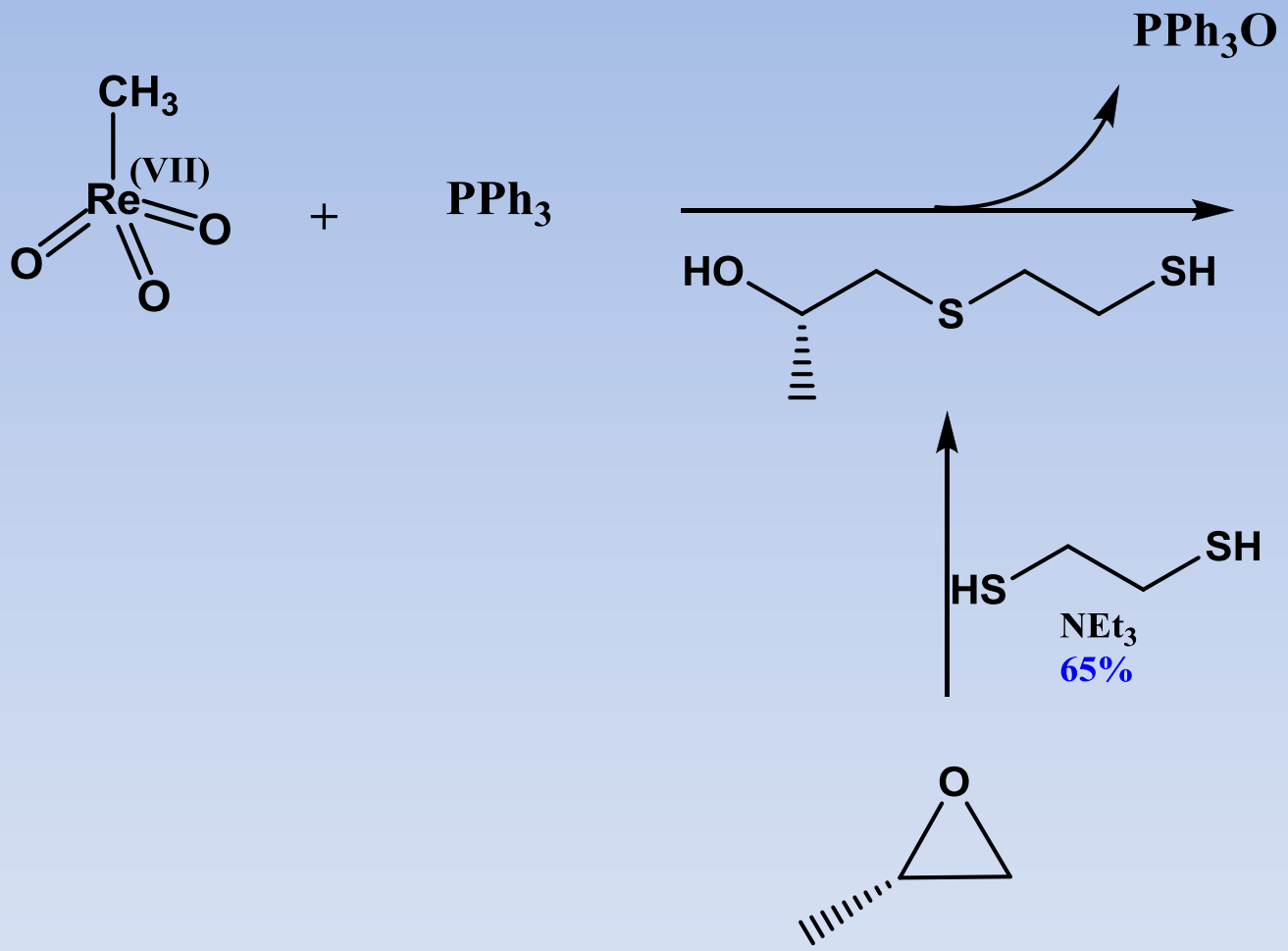


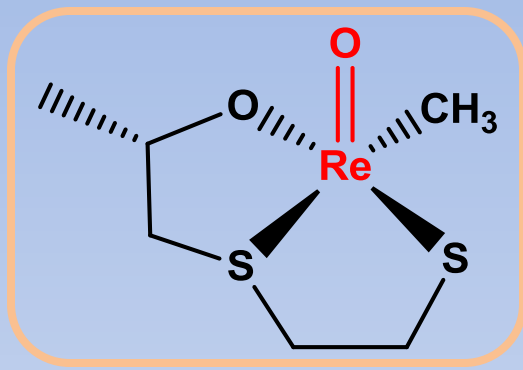
- **Enantiopure oxorhenium complexes**
- **Easy sublimation**
- **Intense vibration Band around 1000 cm^{-1}**
- **Calculated ΔE_{PV}?**
- **Spectroscopy of a molecular beam?**

Propylene oxide: synthetic route for the preparation of *enantiopure ligands*



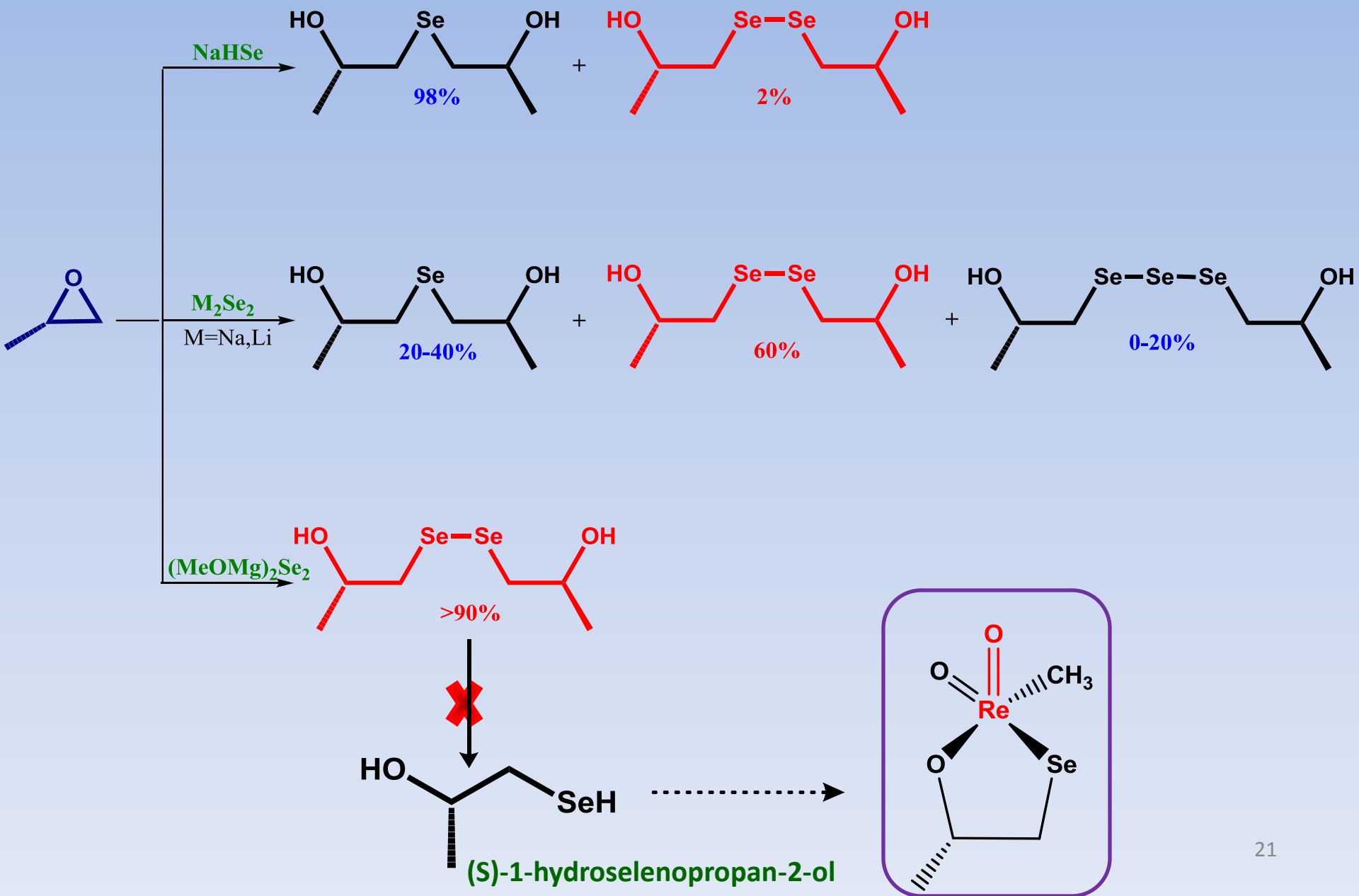
New oxorhenium complexes derived from MTO



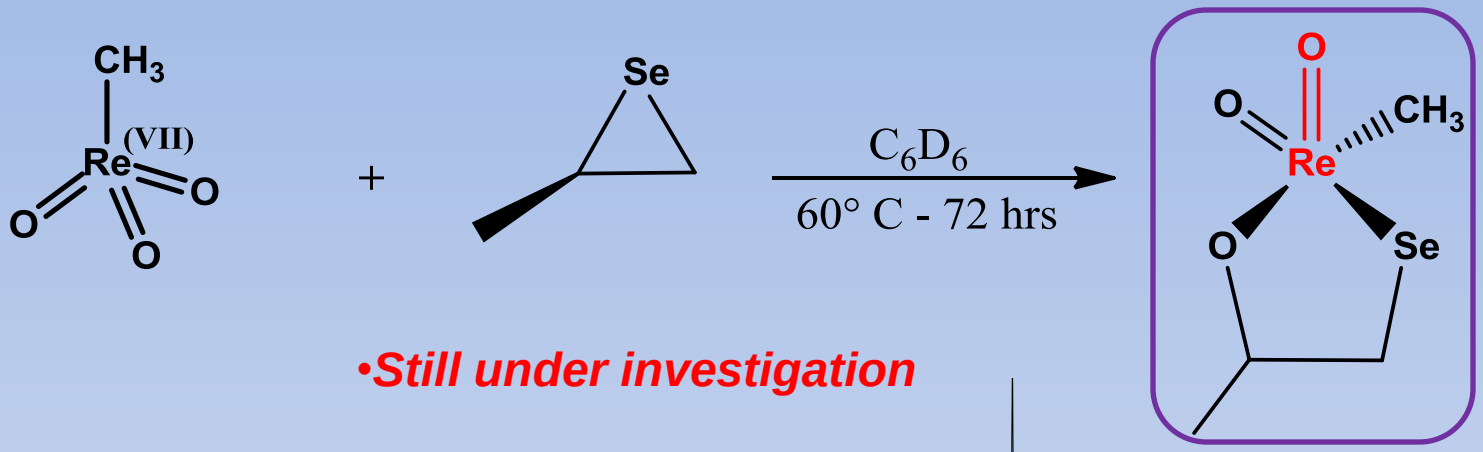


Problems in Stability

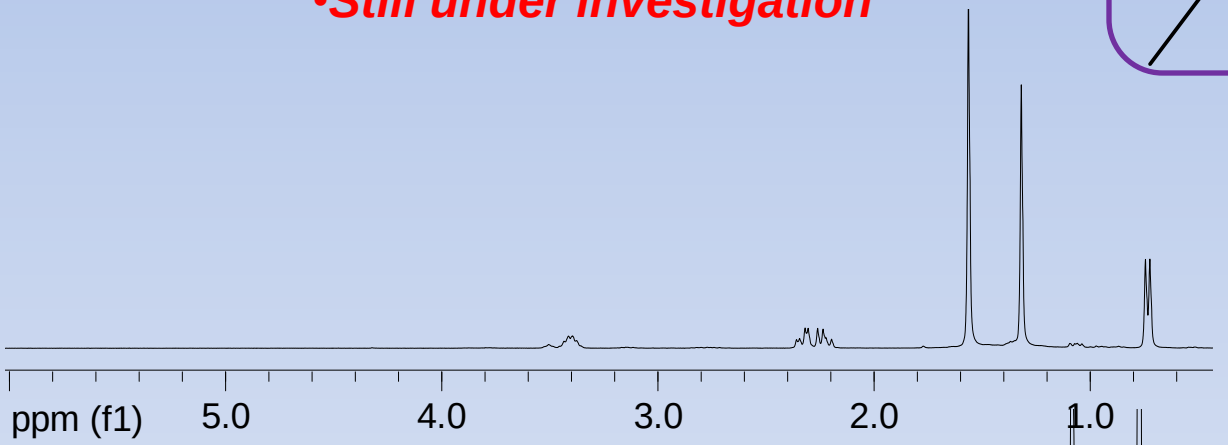
Preparation of *Selenium-Containing Ligands*

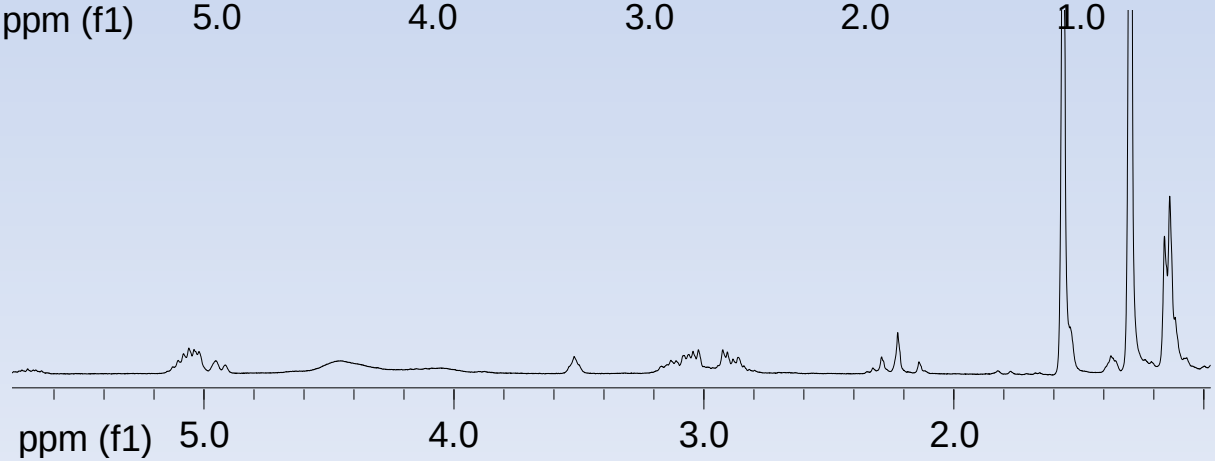


Preparation of *Selenium-Containing Ligands*

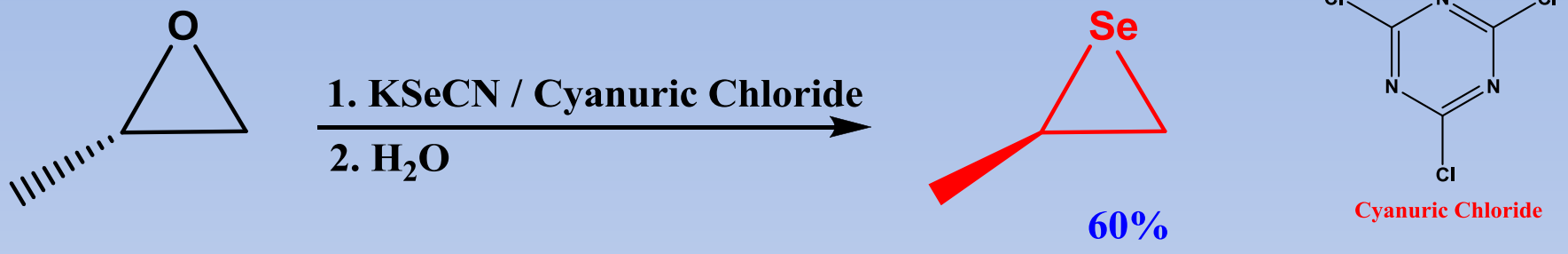


- ***Still under investigation***

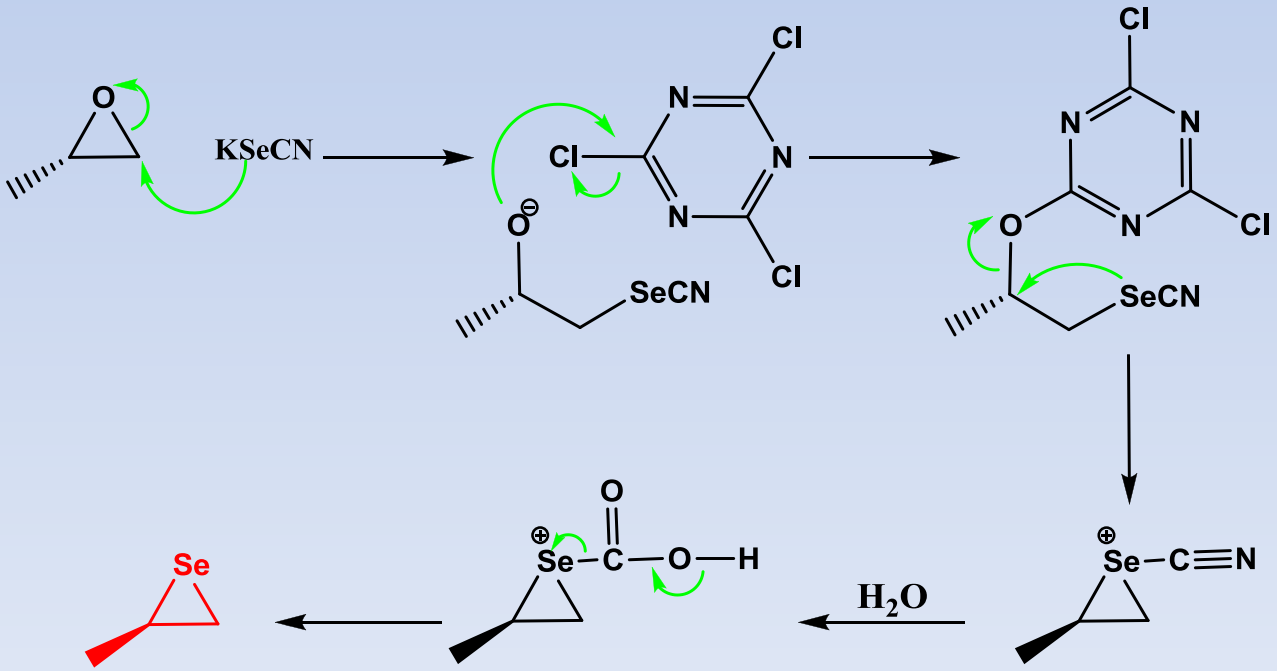




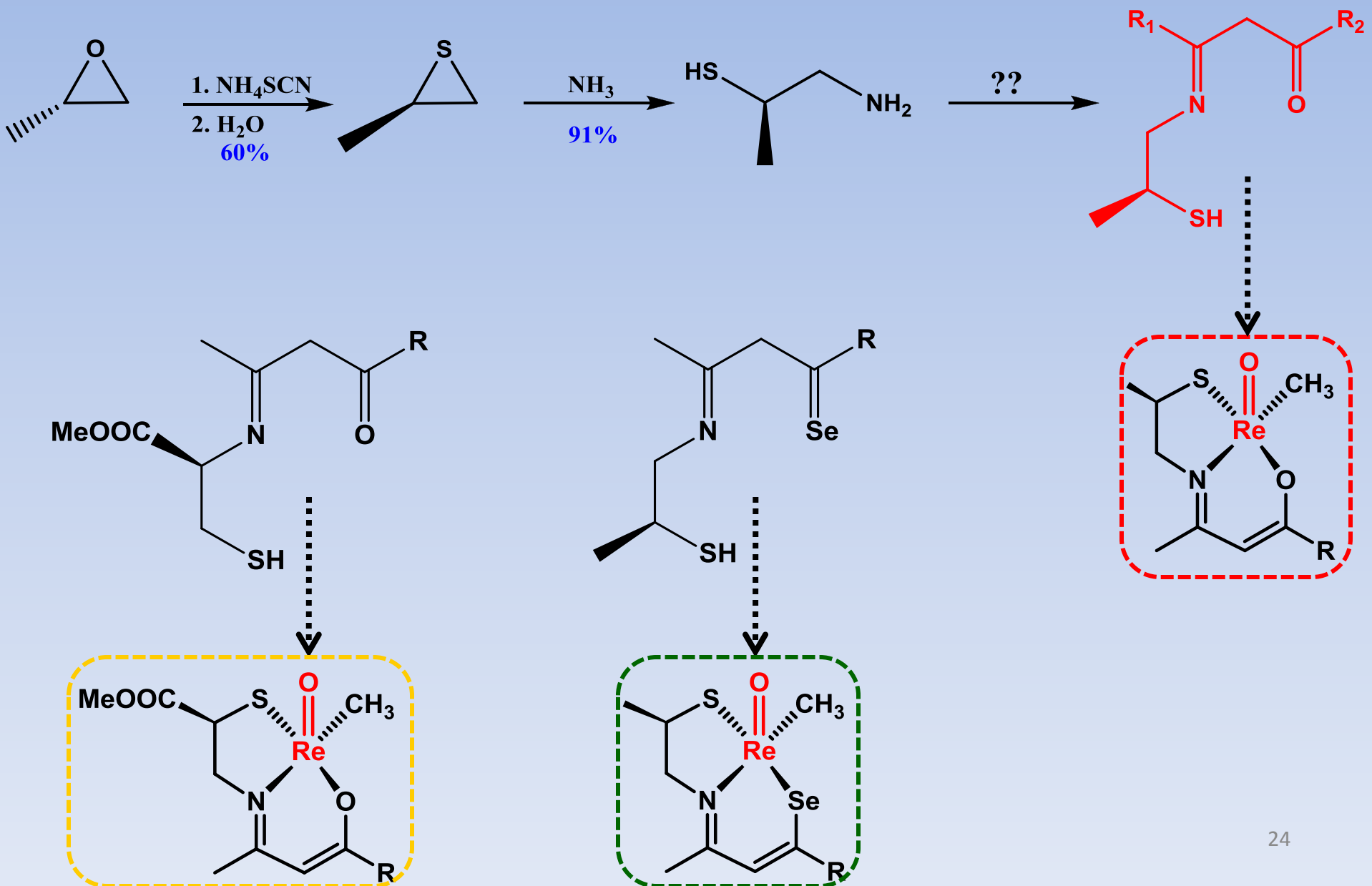
Synthesis of *Selenirane*



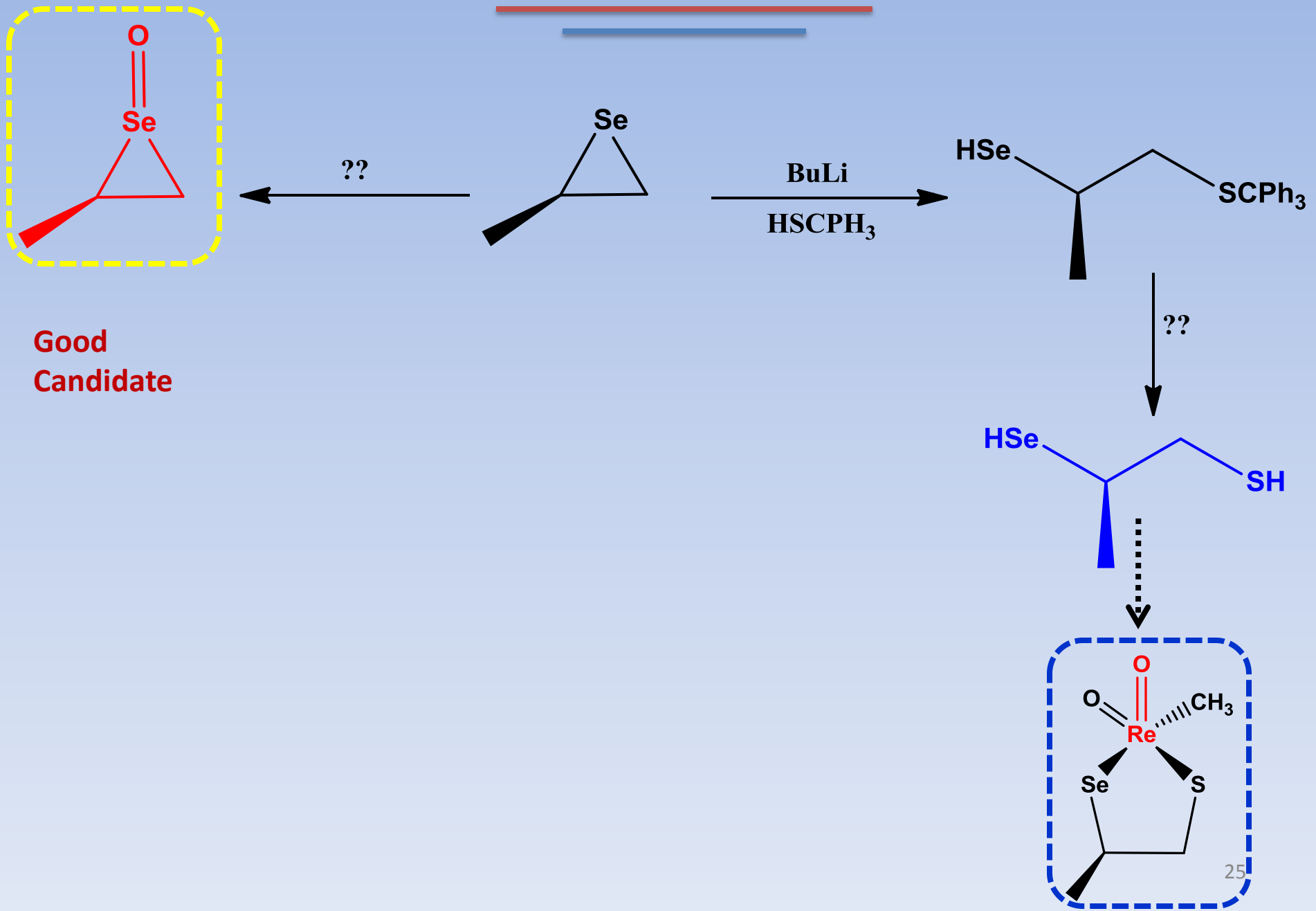
Proposed Mechanism



Perspectives



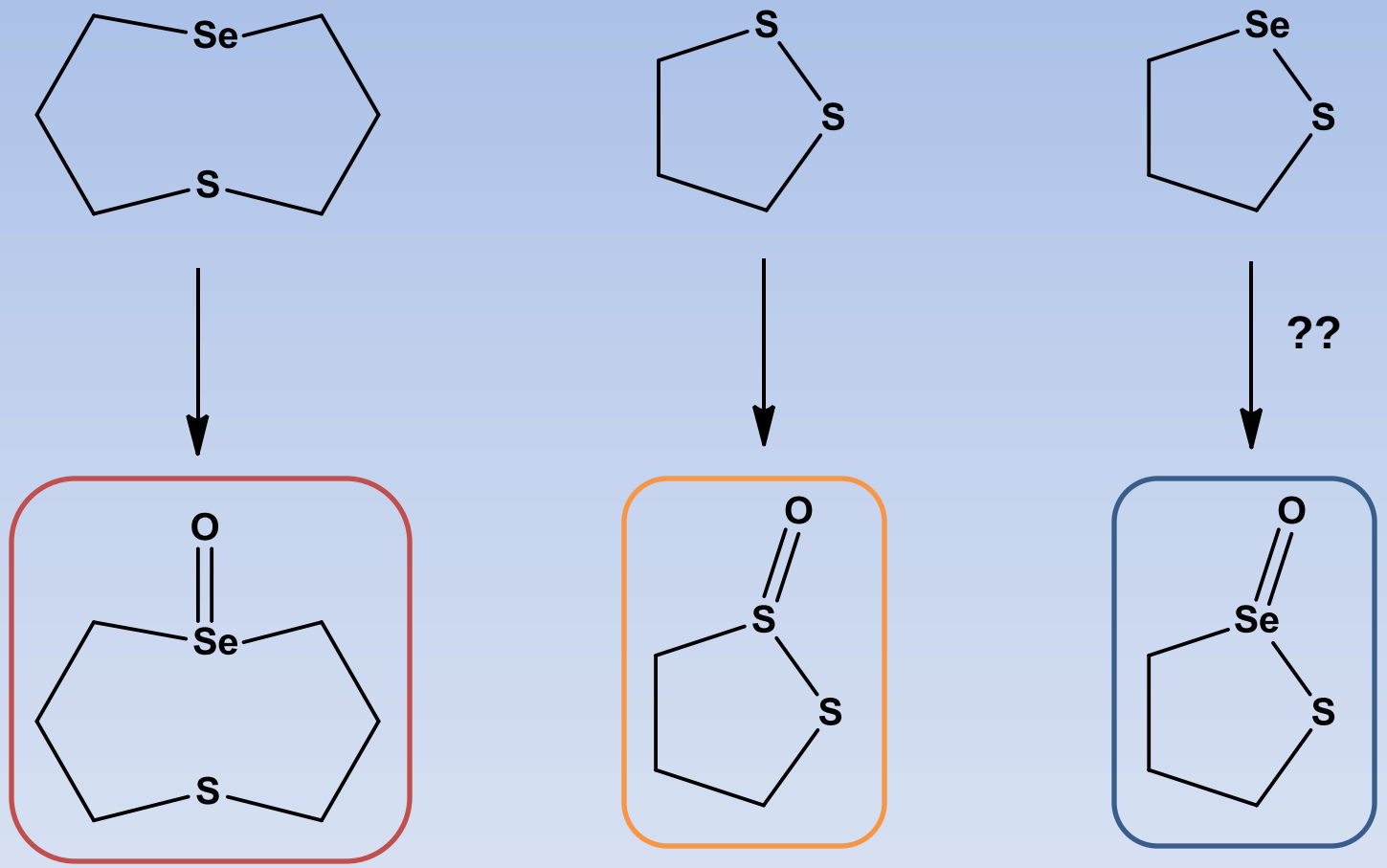
Perspectives



Good Candidate

Perspectives

- ***New good Canditates ??***



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Thanks for your attention