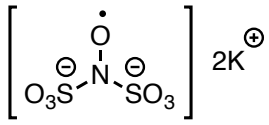
Asymmetric Radical Reactions

Literature Review

MARIE WONG | 12 JULY 2019

Introduction

- Frémy's salt (1845)
  - First man-made persistent radical



- Moses Gomberg – triphenylmethyl radical (1900)
  - "The experimental evidence presented above forces me to the conclusion that we have to deal here with a free radical."

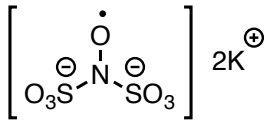
AN INSTANCE OF TRIVALENT CARBON: TRIPHENYL-METHYL.

By M. Gomberg.

Compt. Rend., **1845**, *21*, 218; *J. Am. Chem. Soc.*, **1990**, *22*, 757.

Introduction

- Frémy's salt (1845)
  - First man-made persistent radical



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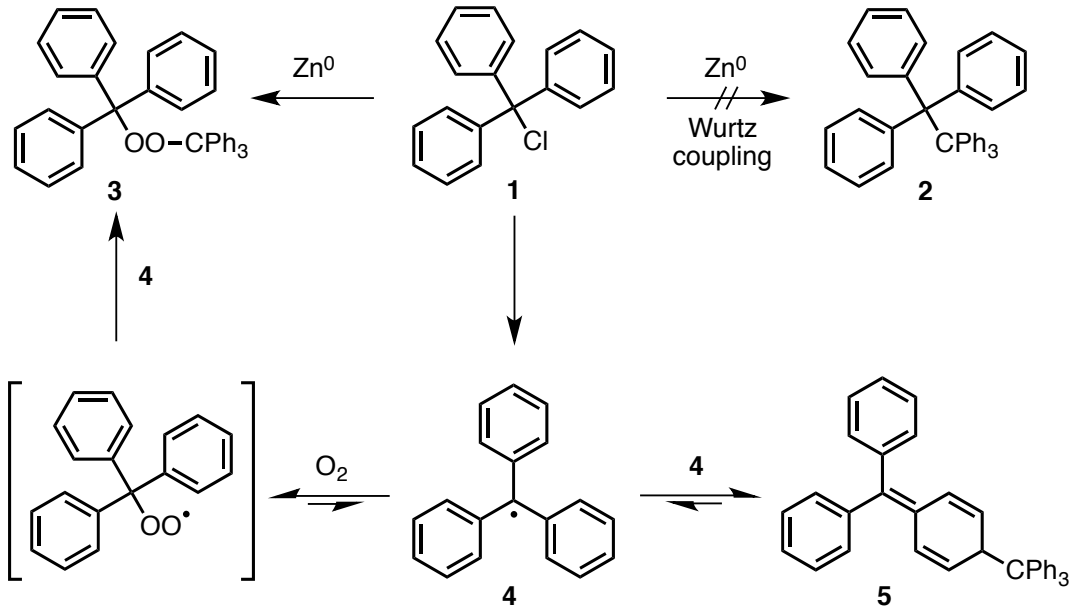
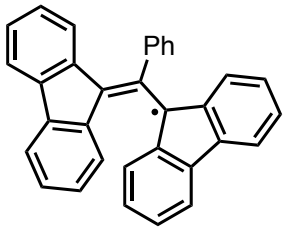


"This work will be continued and I wish to reserve the field for myself."

Compt. Rend., **1845**, *21*, 218; *J. Am. Chem. Soc.*, **1990**, *22*, 757.

Introduction

- C. F. Koelsch (1932)
  - EPR (1957)



- Sir Christopher Ingold (1993)
  - "Homolysis, even between consenting adults, is grounds for instant dismissal from this Department"

- Morris Kharasch
  - Barton, D. H. R. Private communication.
  - "…became so frustrated with his manuscripts being rejected by the reviewers of his day that he used his influence to convince the ACS board to launch *The Journal of Organic Chemistry*."
  - "Being on the Board of Editors made it easier for him to identify reviewers with the correct expertise."

J. Am. Chem. Soc., **1957**, *79*, 4439; *Bull. Hist. Chem.*, **1996**, *91*, 1; *Org. Lett.*, **2017**, *19*, 1257.

Introduction

"Radical chemistry has always taken a backseat to ionic chemistry."

low selectivity • scarce • exotic • messy • unpredictable
unpromising • mysterious • chemical curiosity • impatient
invisible • unselective • chaotic • uncontrollable
mysteriously baffling • suspicious • unwieldiness

"…radicals still occasionally conjure up visions of runaway reactions, of messy black tars, and of intractable mixtures."

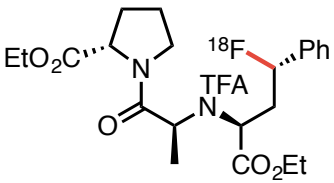
beautiful • predictability • reactivity • selectivity • generality
variability • functional group tolerance • pH neutral • elaborate
efficient • molecular complexity • green chemistry

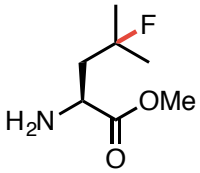
"I didn't think that radical chemistry could be so mild and selective."

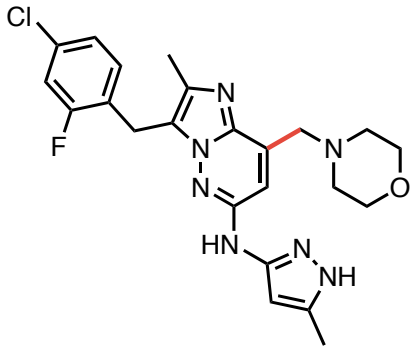
J. Am. Chem. Soc., **2016**, *138*, 12692; *Org. Lett.*, **2017**, *19*, 1257; *Topics in Current Chemistry: Radicals in Synthesis I*, **2006**.

Introduction

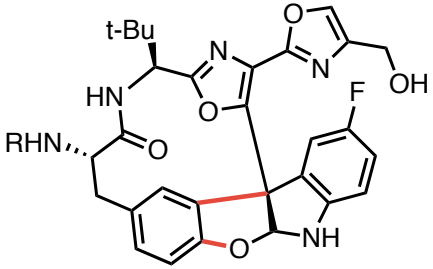
- Practical reactions and unique reactivities



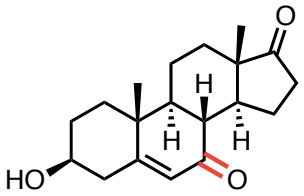




process scale

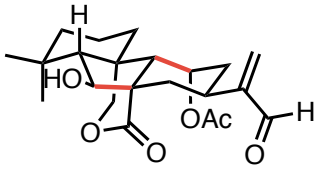


60g scale

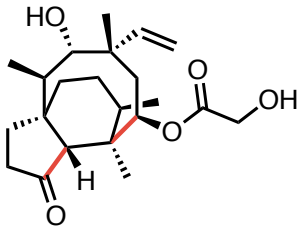


100 g scale

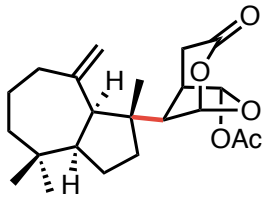
- Natural product synthesis



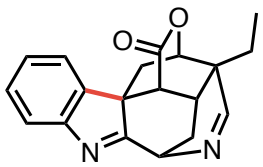
(–)-maoecrystal Z



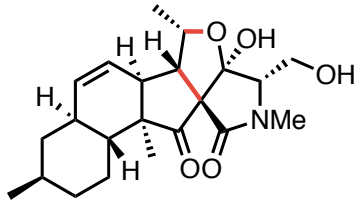
(+)-pleuromutilin



(–)-aplyviolene

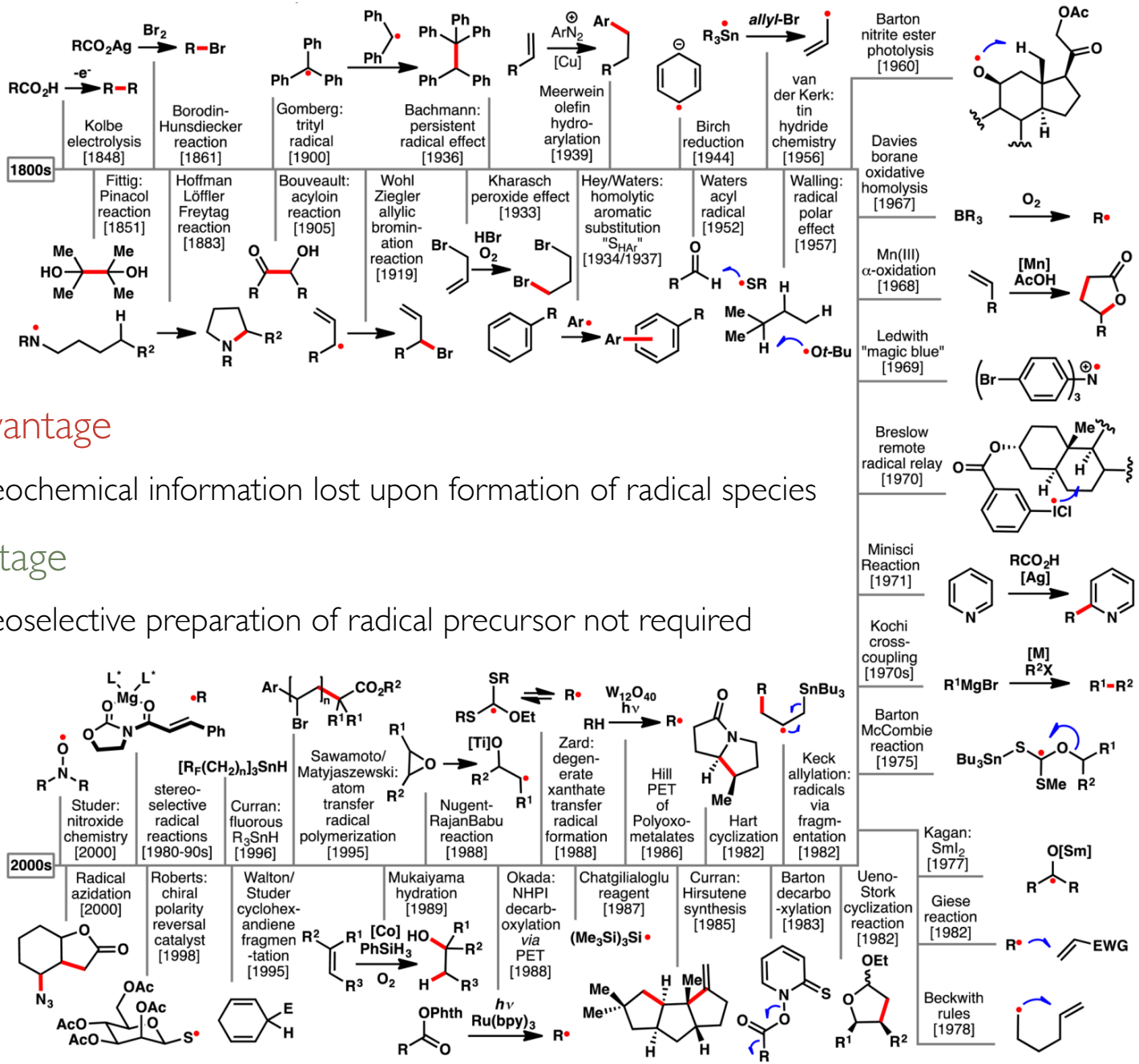


(+)-scholarisine A



(+)-fusarisetin A

J. Am. Chem. Soc., **2016**, *138*, 12692.



- Disadvantage
  - Stereochemical information lost upon formation of radical species
- Advantage
  - Stereoselective preparation of radical precursor not required

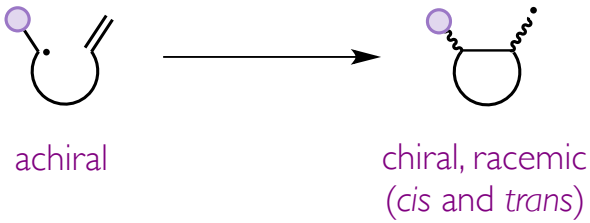
Contents

- Diastereoselective reactions
  - Substrate control
    - Intramolecular reactions
    - Intermolecular reactions
  - Reagent control
  - Chiral auxiliaries

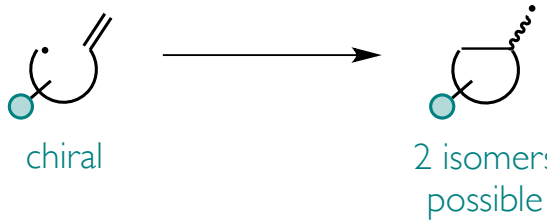
- Enantioselective reactions
  - Substrate control
    - Intramolecular reactions
    - Intermolecular reactions
  - Reagent control

Diastereoselective reactions

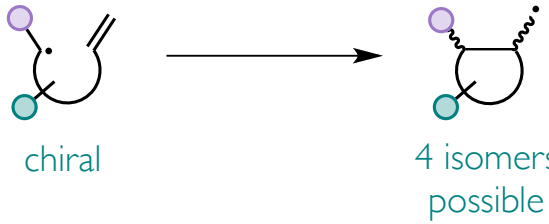
- Substrate control – Intramolecular reactions
  - Achiral radicals with a prostereogenic radical or acceptor



  - Chiral radicals
    - Prostereogenic acceptor



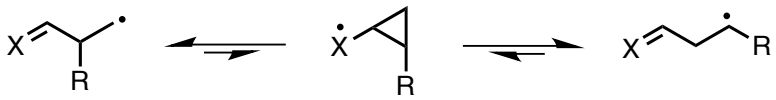
    - Prostereogenic radical and acceptor



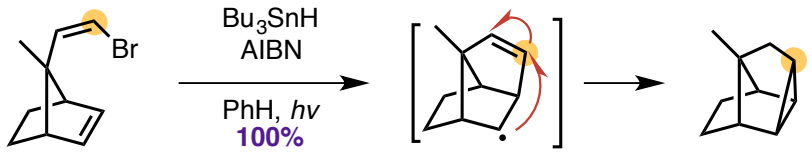
Stereochemistry of Radical Reactions, **1995**.

Diastereoselective reactions

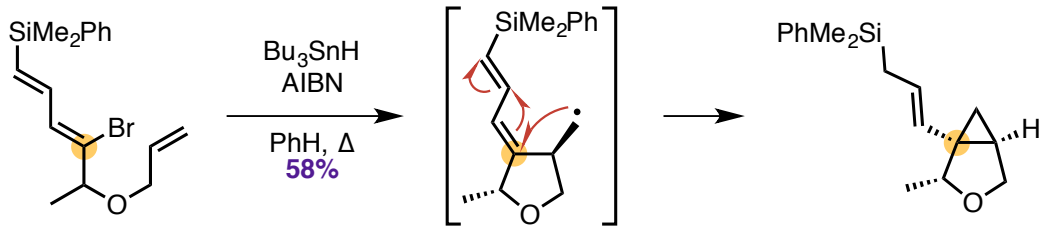
- Face selective radical cyclization to multiple bonds
  - 3-membered rings



  - Ring strain into precursor



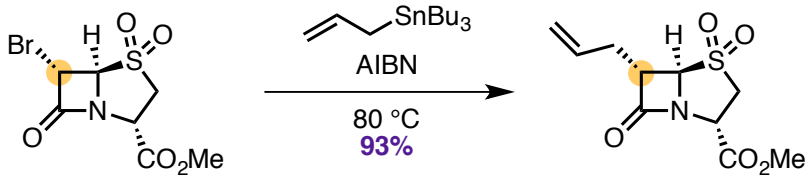
  - Substitution to stabilize product
    - Radical cyclization forms ring fusion bond – predominantly *cis*

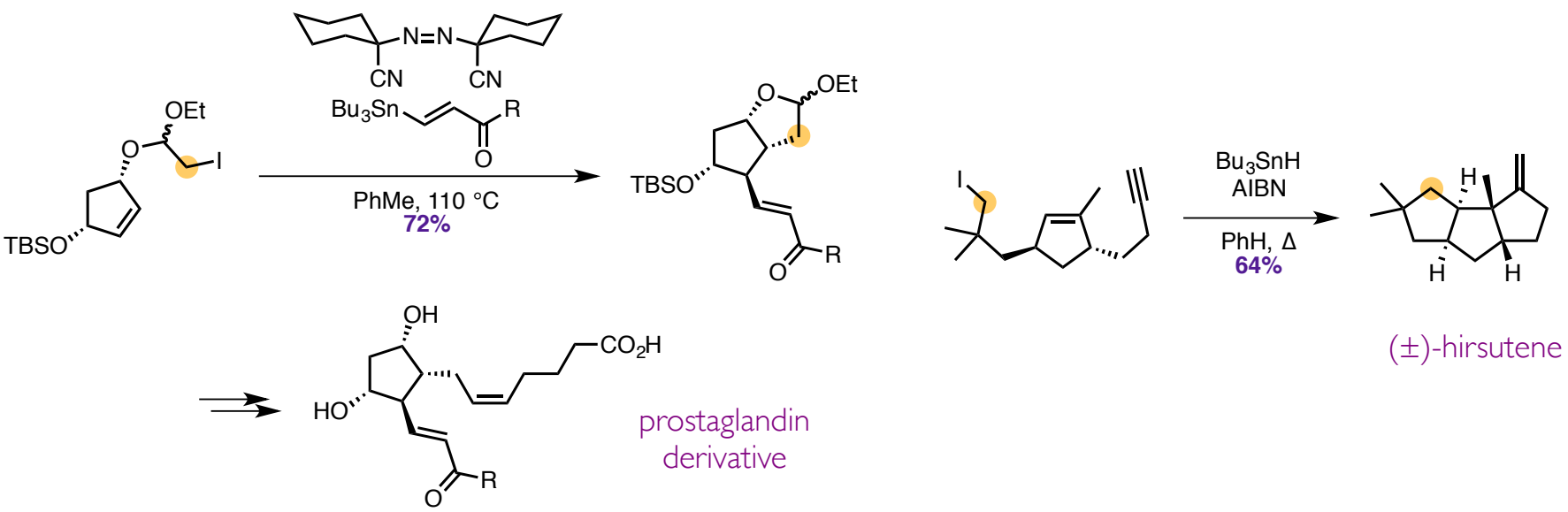


Stereochemistry of Radical Reactions, **1995**; *Tetrahedron Lett.*, **1993**, *34*, 2091; *J. Org. Chem.*, **1993**, *58*, 5574.

DIASTEREOSELECTIVE REACTIONS

- Face selective radical cyclization to multiple bonds
  - 4- and 5-membered rings
    - Pre-existing ring stereocenter

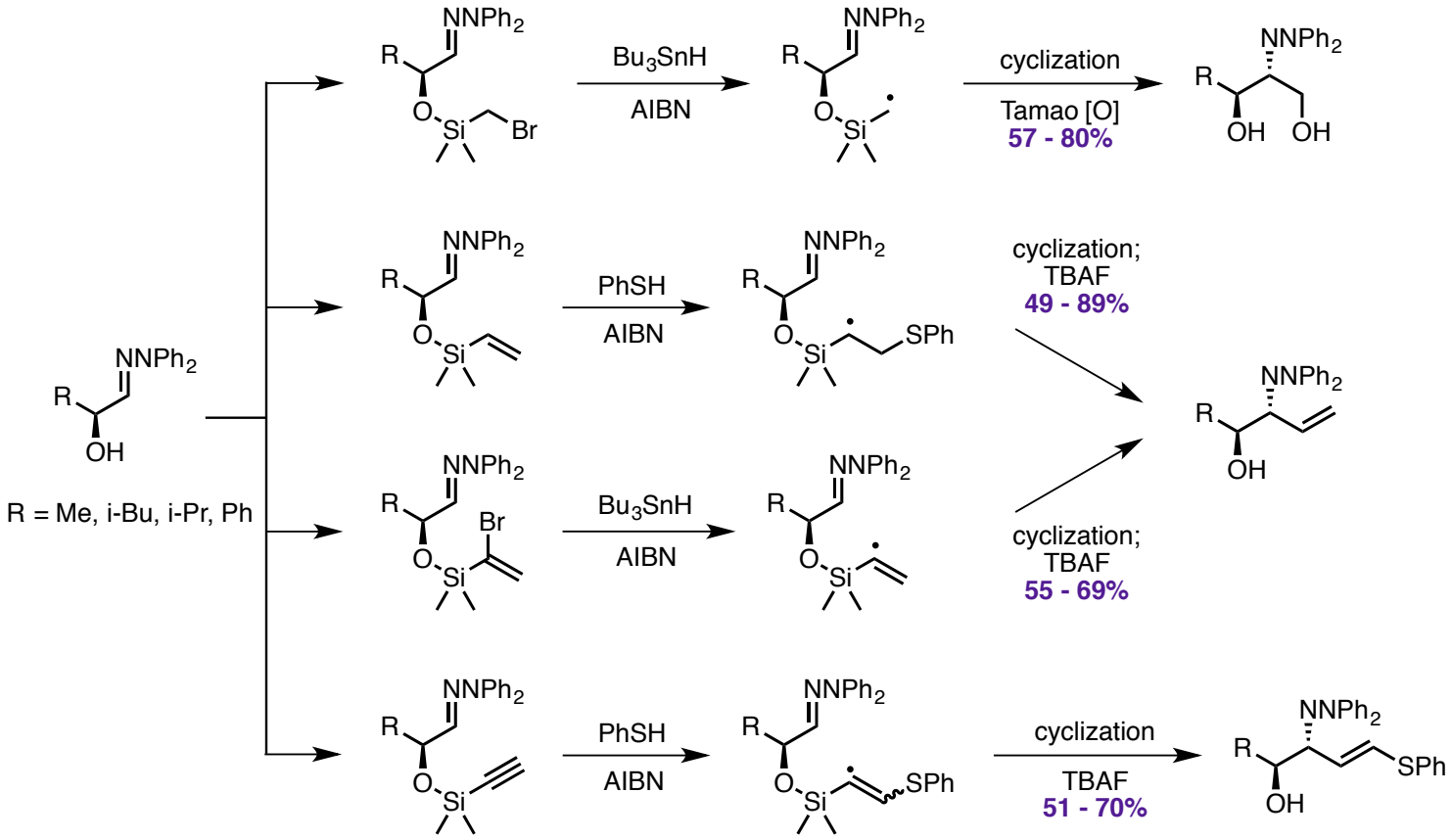




Stereochemistry of Radical Reactions, **1995**; *Tetrahedron*, **1989**, *45*, 941; *J. Org. Chem.*, **1987**, *52*, 2958; *J. Am. Chem. Soc.*, **1985**, *107*, 1448.

Diastereoselective reactions

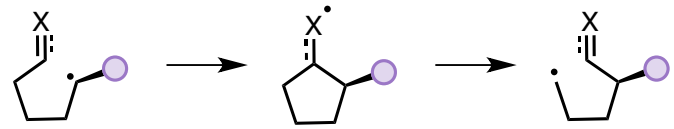
- Face selective radical cyclization to multiple bonds
  - Silicon tethered radical addition

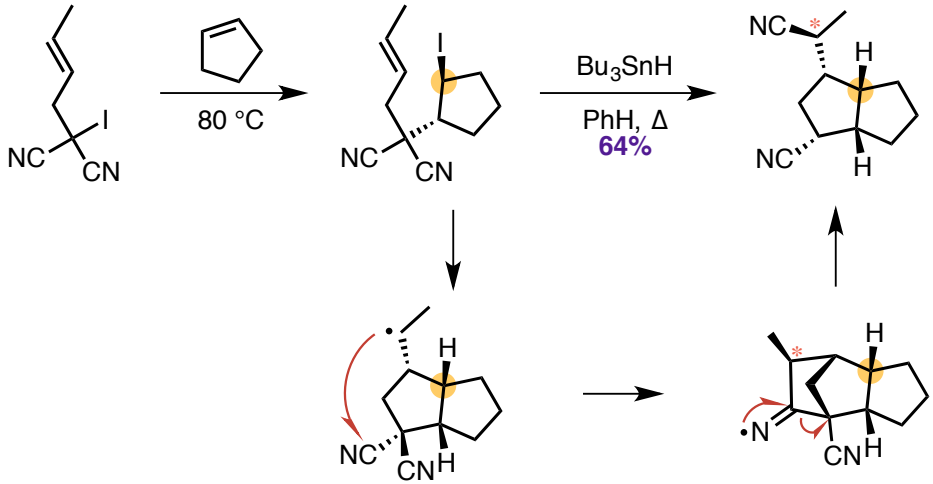


Topics in Current Chemistry: Radicals in Synthesis III, **2012**; *Org. Lett.*, **1999**, *1*, 1499; *Org. Lett.*, **2000**, *2*, 4237; *J. Org. Chem.*, **2004**, *69*, 863; *Tetrahedron*, **2003**, *63*, 3964; *Tetrahedron: Asymmetry*, **2003**, *14*, 2853.

Diastereoselective reactions

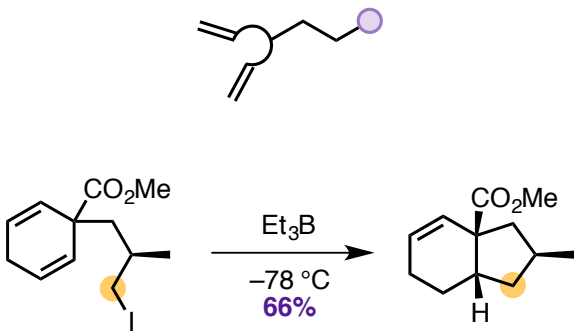
- Cyclization-fragmentation
  - Use of stereoselective cyclization to indirectly control acyclic stereochemistry



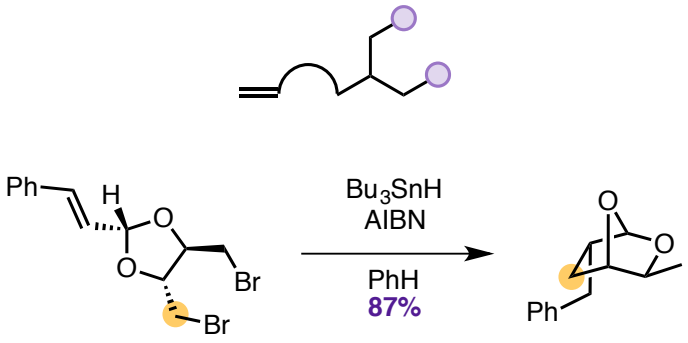


Diastereoselective reactions

- Group selective cyclizations
  - One radical precursor and two diastereotopic radical acceptors



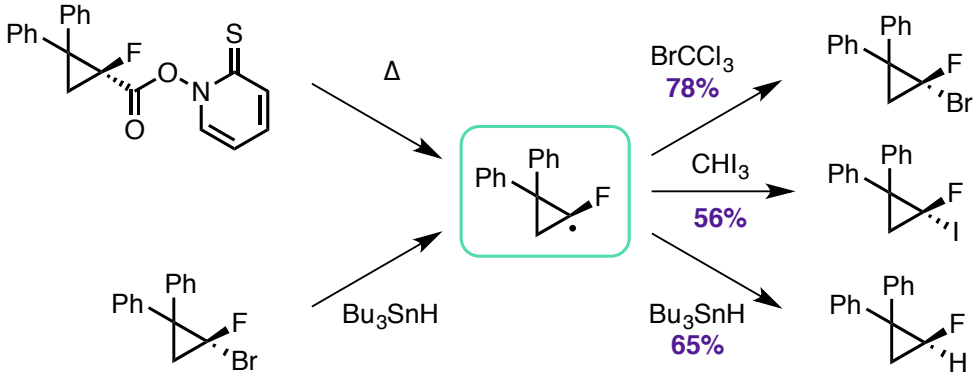
  - Two diastereotopic radical precursors and one acceptor



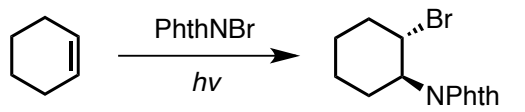
Stereochemistry of Radical Reactions, **1995**; *J. Am. Chem. Soc.*, **1994**, *116*, 8430; *Chem. Lett.*, **1991**, *20*, 203.

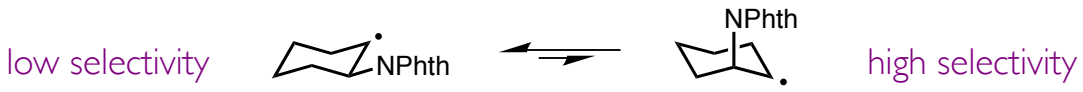
DIASTEREOSELECTIVE REACTIONS

- Substrate control – Intermolecular reactions
  - Cyclic radicals
    - Rate of inversion



    - Reactive conformer



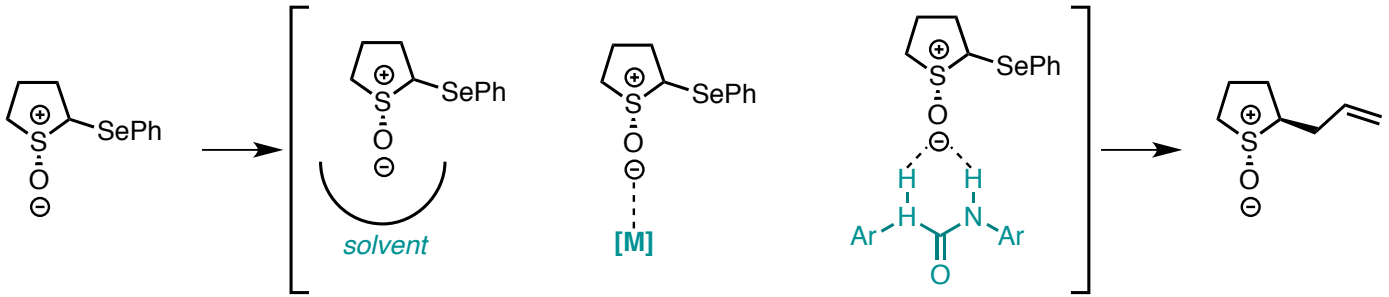


–78 °C	77:23 (*trans*:*cis*)	**20%**
0 °C	89:11	**26%**
40 °C	98:2	**29%**

Stereochemistry of Radical Reactions, **1995**; *J. Org. Chem.*, **1991**, *56*, 2193; *Radicals in Organic Synthesis*, **2001**; *J. Prakt. Chem.*, **1999**, *341*, 649.

DIASTEREOSELECTIVE REACTIONS

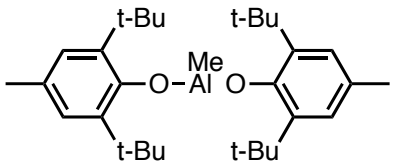
- Substrate control – Intermolecular reactions
  - Cyclic radicals
    - Additive effects



C_6H_6 **70:30** ***dr***
MeOH **83:17** ***dr***

w/o MABR **82:18** ***dr***
MABR (1.1 eq.) **98:2** ***dr***

w/o Urea **70:30** ***dr***
Urea **87:13** ***dr***

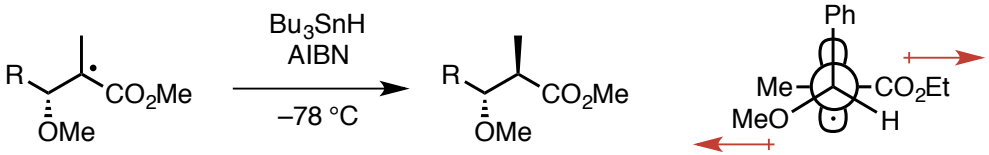


MABR

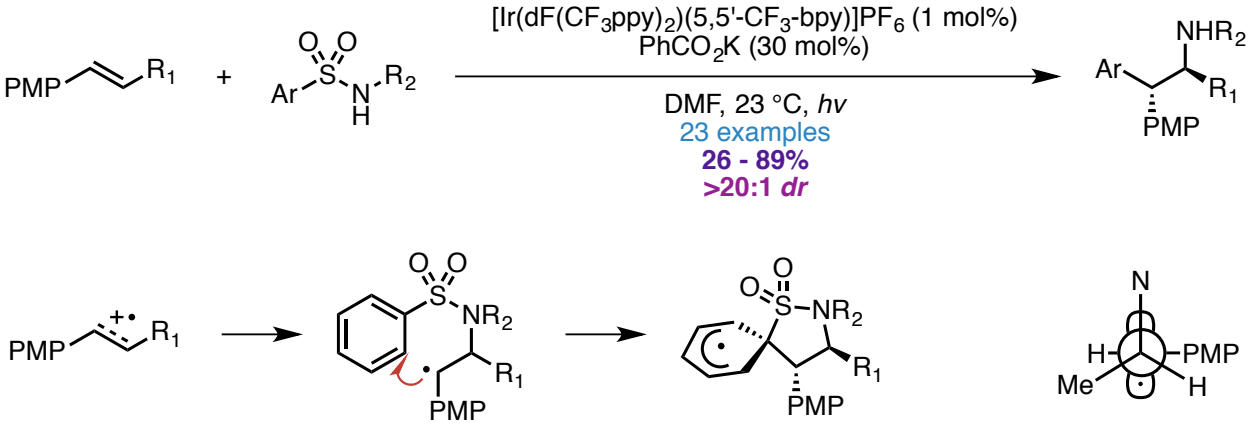
Stereochemistry of Radical Reactions, **1995**; *J. Org. Chem.*, **1994**, *59*, 3547; *J. Org. Chem.*, **1994**, *59*, 3259.

Diastereoselective reactions

- Substrate control – Intermolecular reactions
  - Acyclic radicals
    - Polar substituents



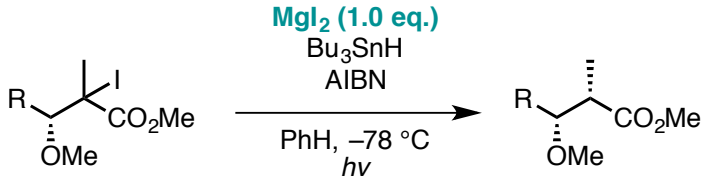
    - Sterics



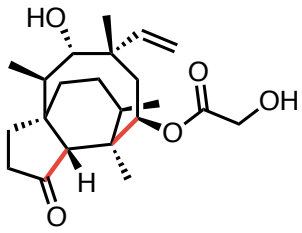
Stereochemistry of Radical Reactions, **1995**; *Tetrahedron Lett.*, **1990**, *31*, 2845; *J. Org. Chem.*, **1986**, *51*, 2024; *J. Am. Chem. Soc.*, **1991**, *113*, 9701; *Science*, **2018**, *361*, 369.

DIASTEREOSELECTIVE REACTIONS

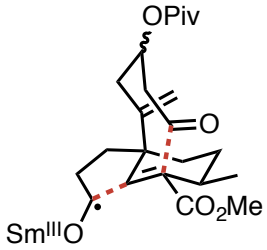
- Reagent control
  - Lewis acid additives



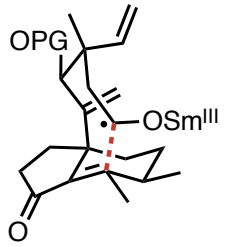
  - Electron transfer reactions



(+)-pleuromutilin



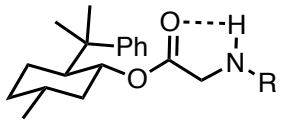
Angew. Chem. Int. Ed., **2009**, *48*, 9315
Chem. Eur. J., **2013**, *19*, 6718

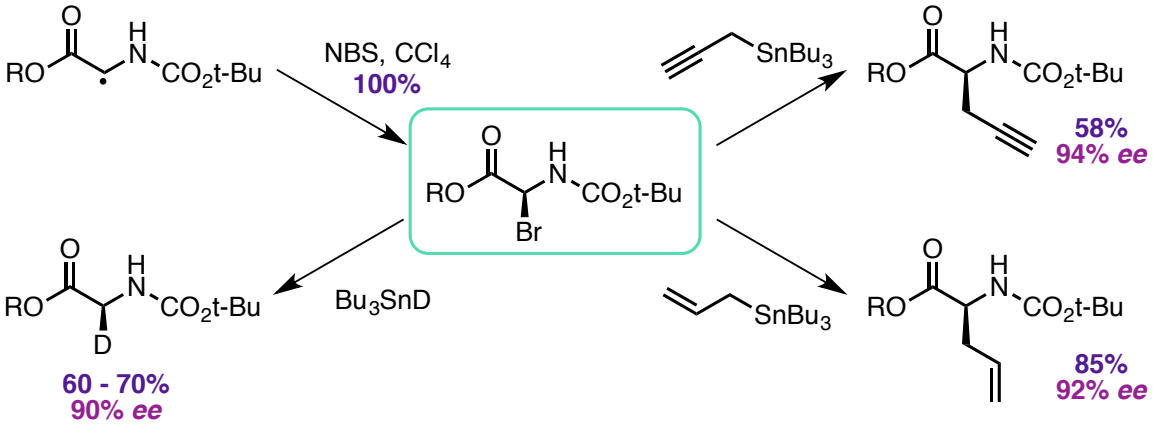


J. Am. Chem. Soc., **2018**, *140*, 1267

Diastereoselective reactions

- Chiral auxiliaries
  - Ester chiral auxiliaries



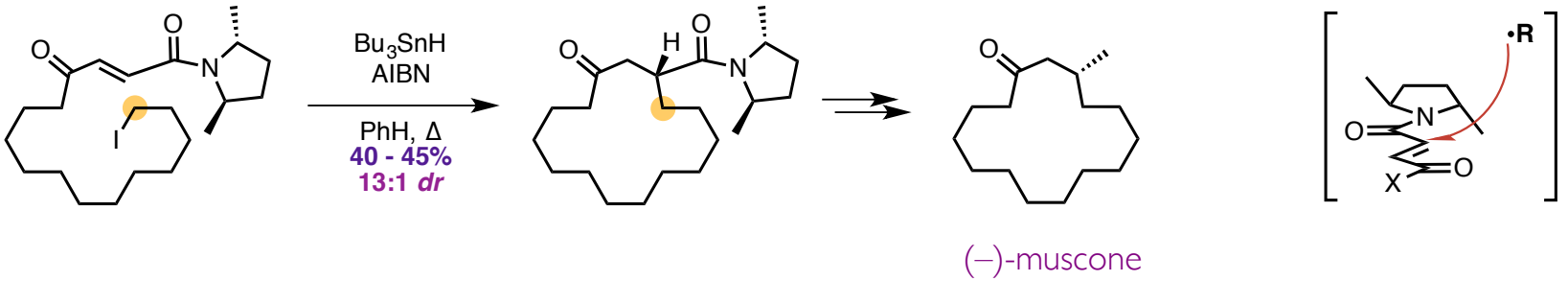


- Also used with Lewis acids: *J. Org. Chem.*, **2000**, *65*, 2208

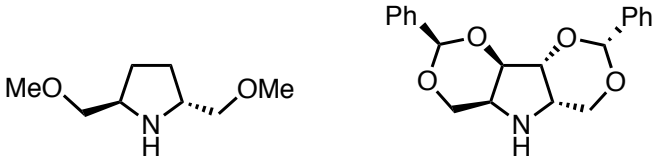
J. Chem. Soc. Chem. Commun., **1991**, 332; *J. Chem. Soc. Chem. Commun.*, **1991**, 722.

Diastereoselective reactions

- Chiral auxiliaries
  - C2 symmetry



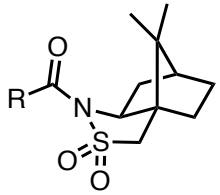
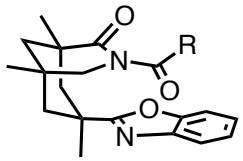
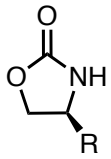
  - Disadvantages
    - Chiral auxiliary difficult to prepare
    - Difficult to hydrolyze, especially without racemization



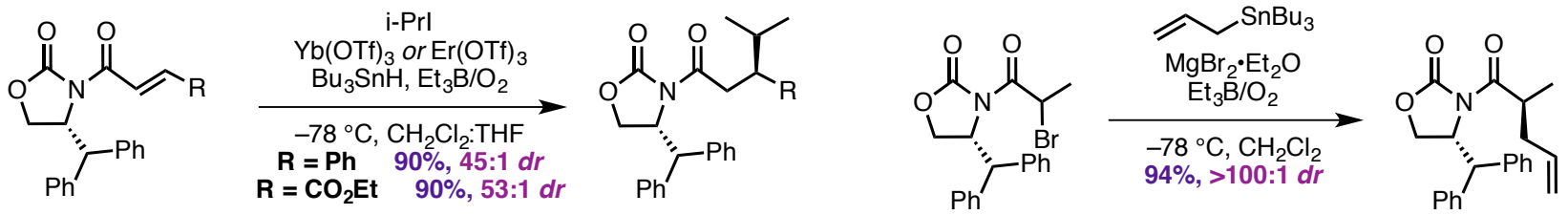
J. Am. Chem. Soc., **1989**, *111*, 8309; *J. Am. Chem. Soc.*, **1989**, *111*, 8311; *Helv. Chim. Acta.*, **1993**, *76*, 441.

Diastereoselective reactions

- Chiral auxiliaries
  - Steric conformational control

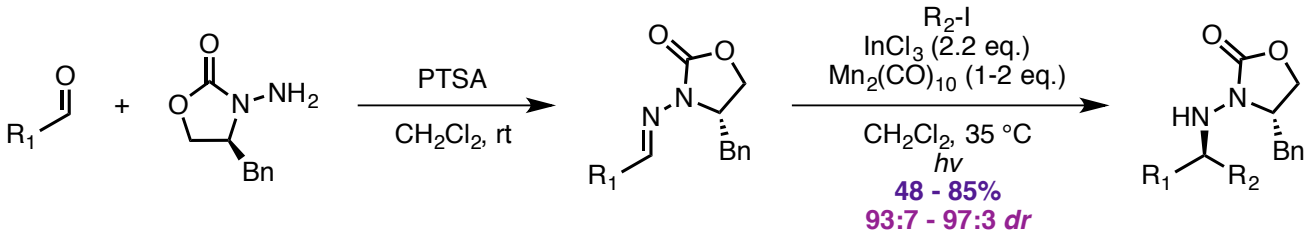
  - Oxazolidinone auxiliaries
    - Lewis acid catalysis
      - Similar reactions: *J. Org. Chem.*, **1996**, *61*, 6090; *J. Am. Chem. Soc.*, **1999**, *121*, 5155; *J. Am. Chem. Soc.*, **2002**, *124*, 2924.

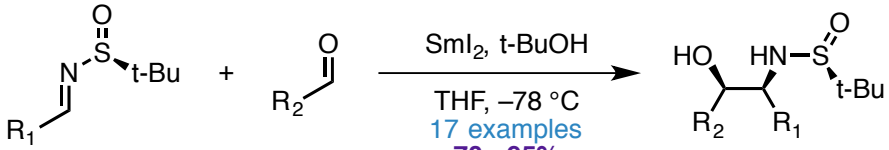


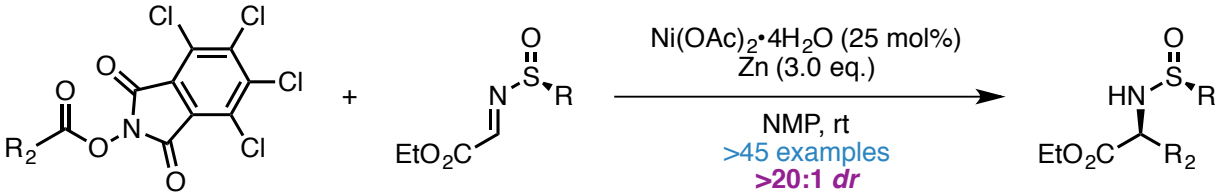
J. Am. Chem. Soc., **1995**, *117*, 10779; *J. Am. Chem. Soc.*, **1999**, *121*, 7517; *Angew. Chem. Int. Ed.*, **1996**, *35*, 190; *Angew. Chem. Int. Ed.*, **1998**, *37*, 2562.

DIASTEREOSELECTIVE REACTIONS

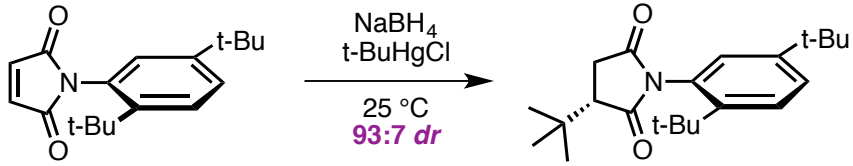
- Chiral auxiliaries
  - Imine addition







- Restricted rotation



J. Am. Chem. Soc., **2001**, *123*, 9922; *J. Am. Chem. Soc.*, **2005**, *127*, 11956; *Angew. Chem. Int. Ed.*, **2018**, *57*, 14560.

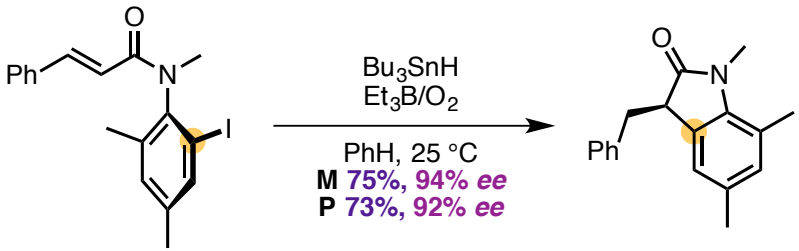
Contents

- Diastereoselective reactions
  - Substrate control
    - Intramolecular reactions
    - Intermolecular reactions
  - Reagent control
  - Chiral auxiliaries

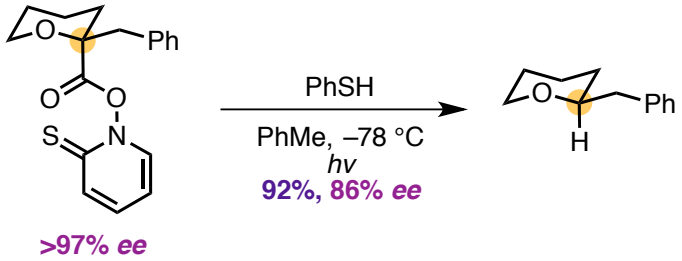
- Enantioselective reactions
  - Substrate control
    - Intramolecular reactions
    - Intermolecular reactions
  - Reagent control

Enantioselective reactions

- Substrate control – Intramolecular reactions
  - Restricted rotation
    - Axial chirality transferred into new stereocenter

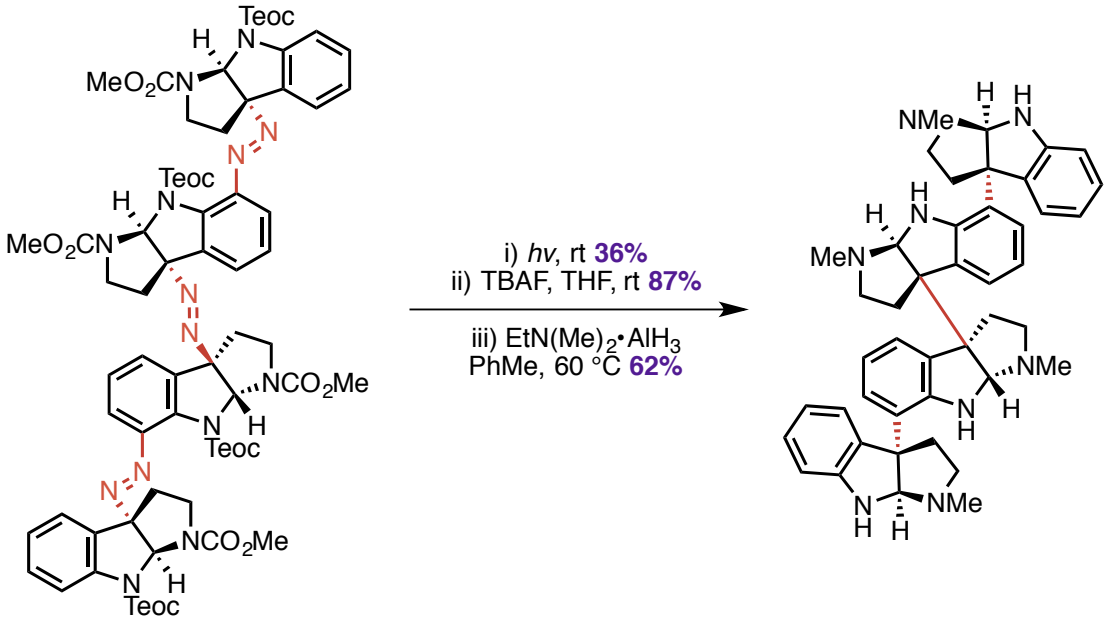


- Substrate control – Intermolecular reactions
  - Memory of chirality



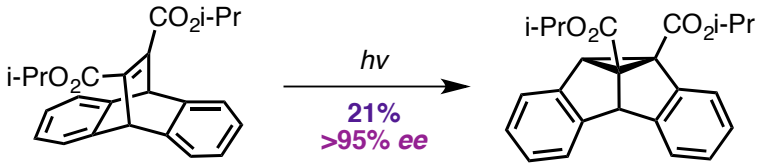
Enantioselective reactions

- Substrate control – Intermolecular reactions
  - Radical recombination

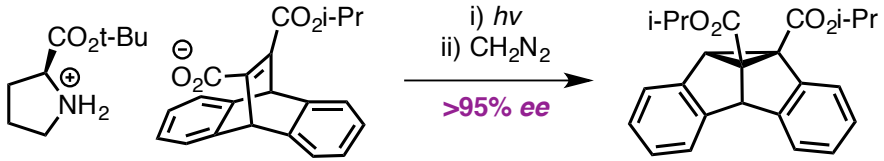


Enantioselective reactions

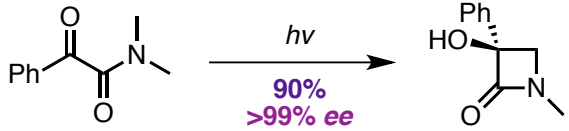
- Substrate control – Solid state
  - Photochemical processes – generation of biradicals and recombination
    - Chiral space group



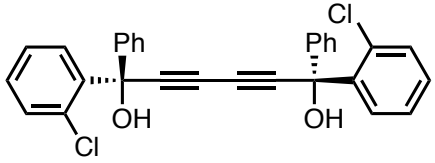
    - Ionic chiral auxiliaries



    - Host-guest complexes



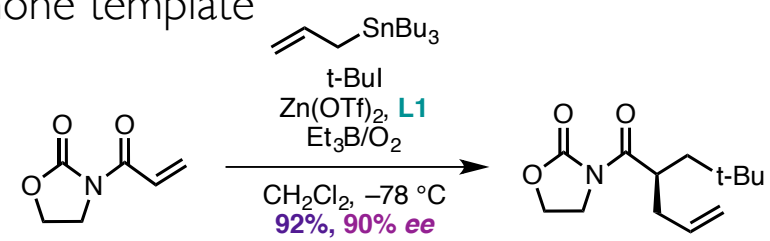
    - Zeolites with chiral inductor

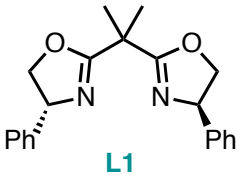


Chem. Rev., **2003**, *103*, 3263; *J. Am. Chem. Soc.*, **1989**, *111*, 4985; *Acc. Chem. Res.*, **1996**, *29*, 203; *J. Org. Chem.*, **1988**, *53*, *4391*.

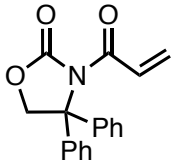
Enantioselective reactions

- Reagent control – Lewis Acids & chiral ligands
  - Oxazolidinone template

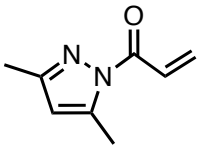




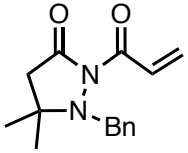
    - Similar reactions: *Tetrahedron Lett.*, **1997**, *38*, 2067; *J. Org. Chem..*, **1997**, *62*, 3800
  - Other templates



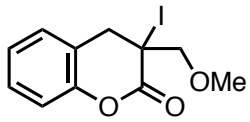
Org. Lett.., **2001**, *3*, 299



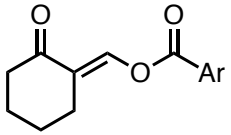
Tetrahedron Lett., **1997**, *38*, 5955



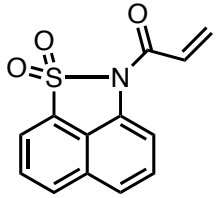
Synlett., **2004**, 2421



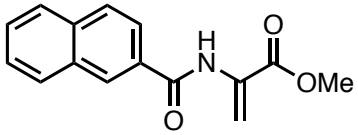
J. Chem. Soc. Chem. Commun., **1995**, 481



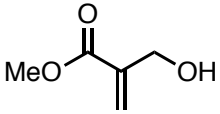
Angew. Chem. Int. Ed., **2007**, *46*, 9231



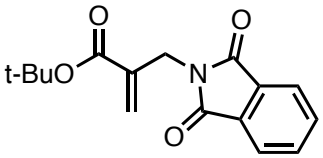
J. Am. Chem. Soc., **2002**, *124*, 984



Angew. Chem. Int. Ed., **2001**, *40*, 1293



Org. Lett.., **2005**, *7*, 1453

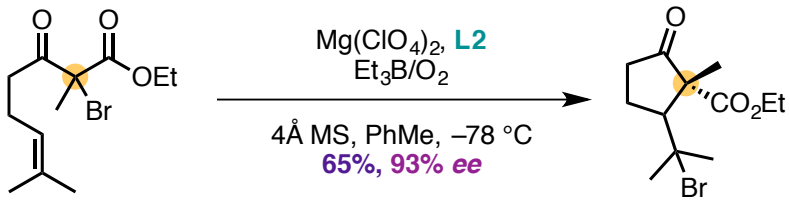


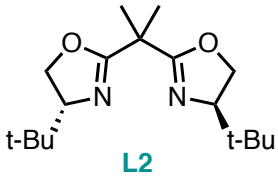
Angew. Chem. Int. Ed., **2004**, *43*, 1235

J. Am. Chem. Soc., **1995**, *117*, 11029.

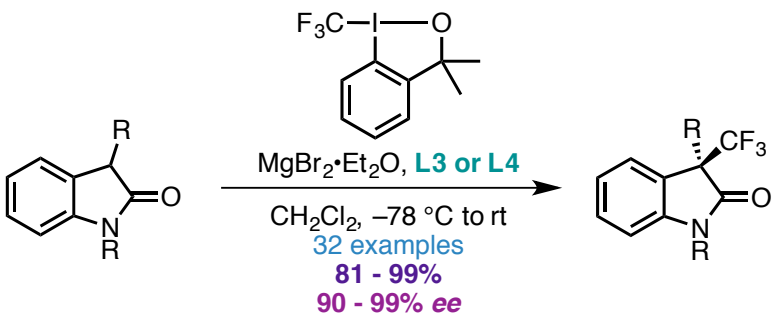
Enantioselective reactions

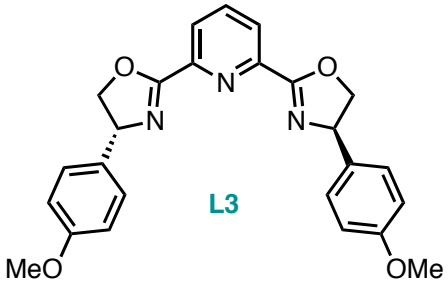
- Reagent control – Lewis Acids & chiral ligands
  - Atom transfer radical cyclization

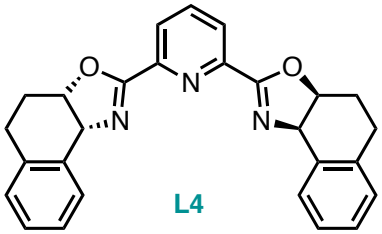




  - Trifluoromethylation



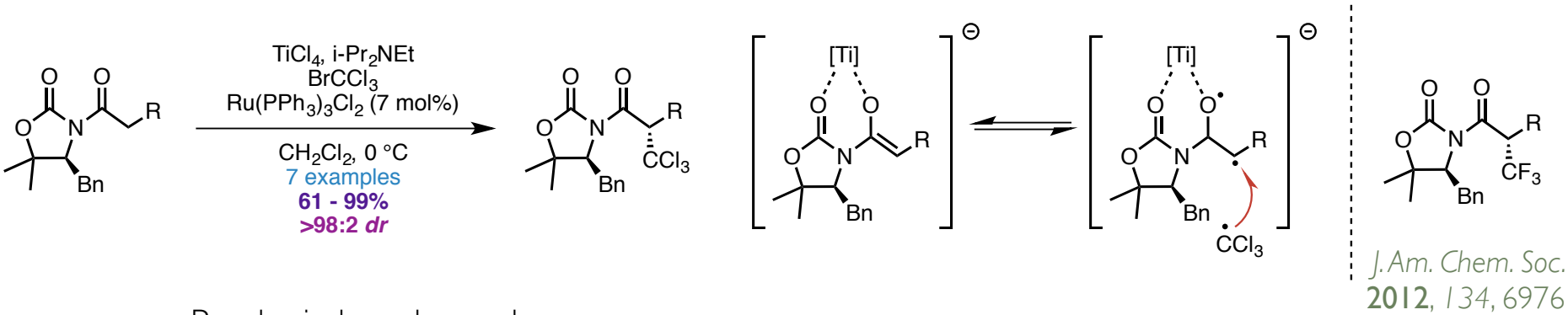




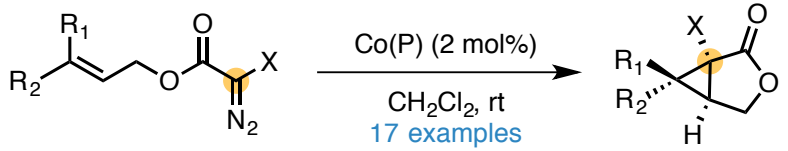
J. Am. Chem. Soc., **2001**, *123*, 8612; *Angew. Chem. Int. Ed.*, **2019**, *58*, 1447.

Enantioselective reactions

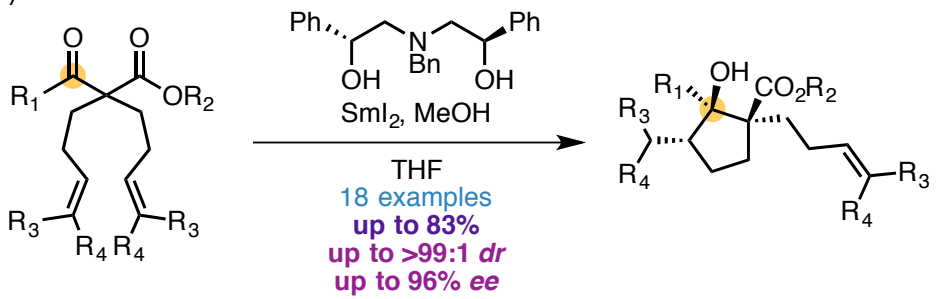
- Reagent control – Metal & chiral ligands
  - Electron transfer reactions
    - Valence tautomerism



    - Porphyrin-based complexes
      - Oxidations
      - Cyclopropanation



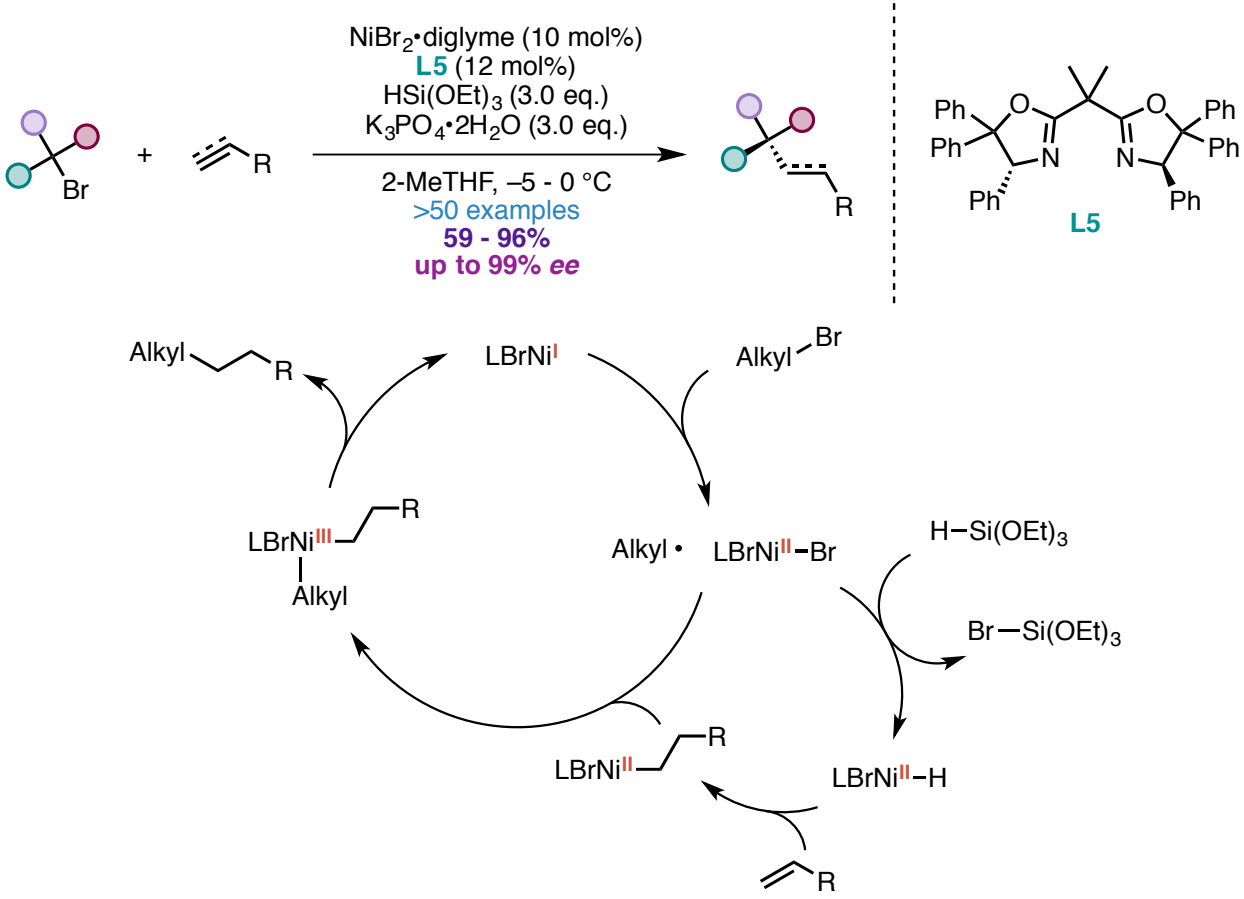
    - Ketyl radicals



J. Am. Chem. Soc., **2010**, *132*, 1482; *Angew. Chem. Int. Ed.*, **2011**, *50*, 7136; *J. Am. Chem. Soc.*, **2011**, *133*, 15292; *Nat. Chem.*, **2017**, *9*, 1198.

Enantioselective reactions

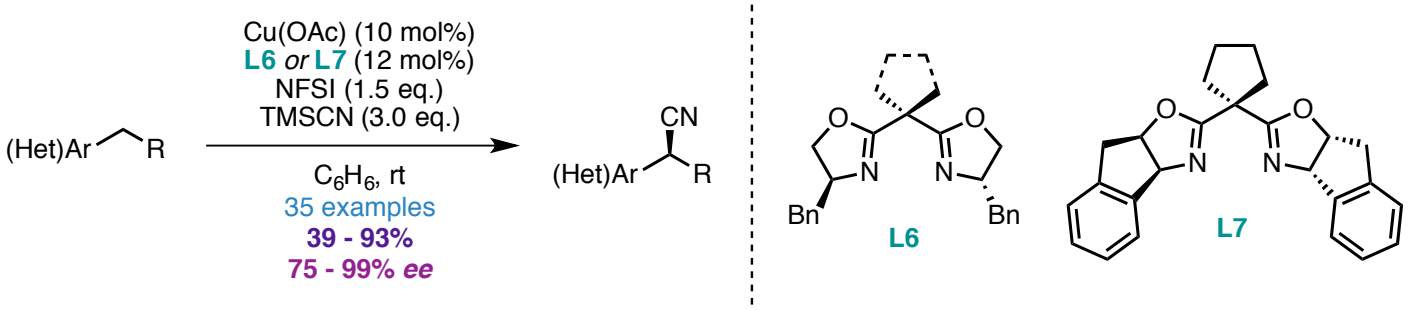
- Reagent control – Metal & chiral ligands
  - Cross coupling
    - Alkyl halides generally react with Ni(I) complexes through e^- transfer processes

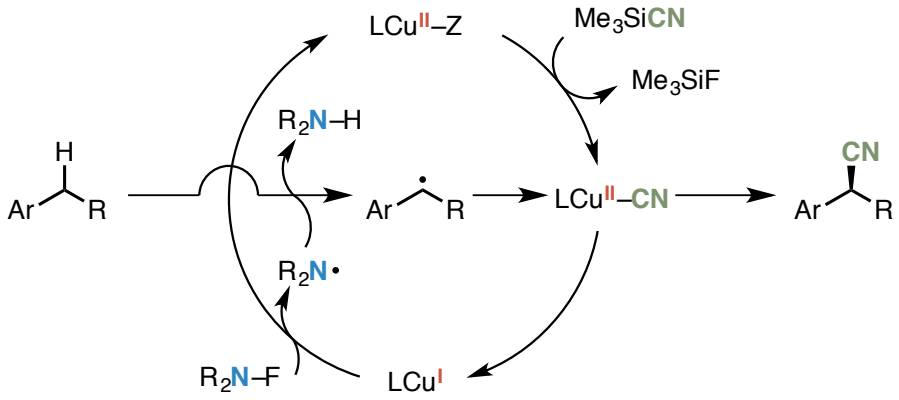


Nature, **2018**, *563*, 379.

Enantioselective reactions

- Reagent control – Metal & chiral ligands
  - Radical relay
    - Reactive radical abstracts H atom

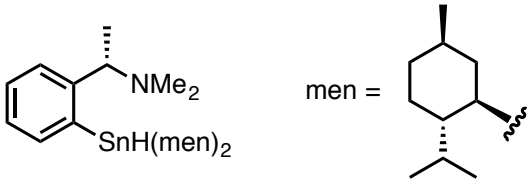




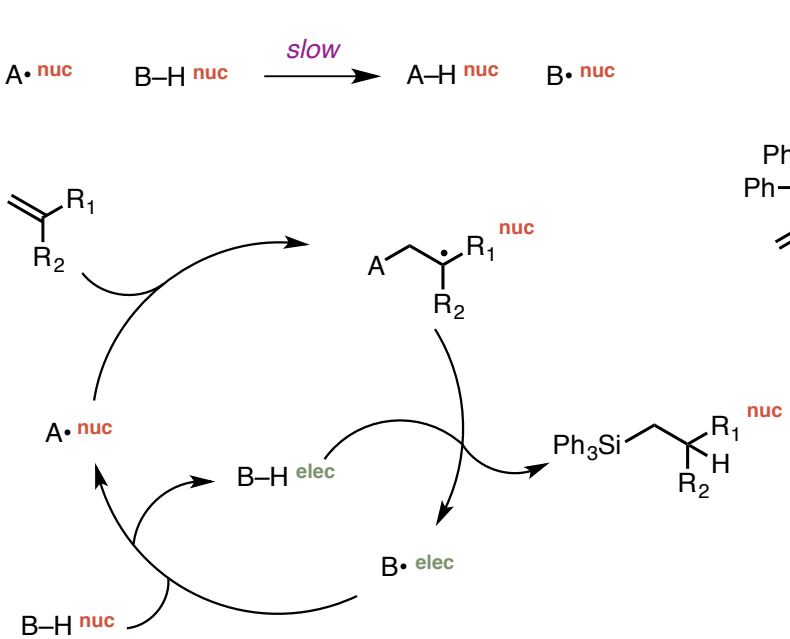
Science, **2016**, *353*, 1014.

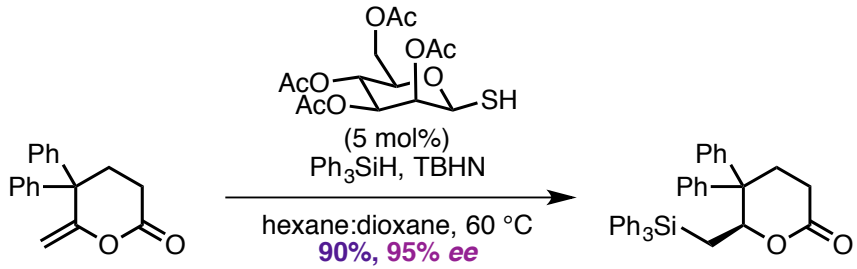
Enantioselective reactions

- Reagent control – Chiral reagents
  - Chiral tin reagent



  - Chiral thiols
    - Polarity reversal catalysis

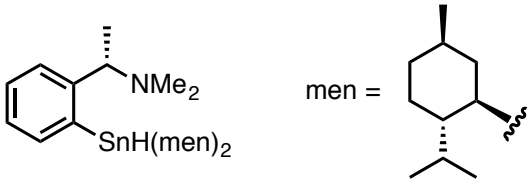




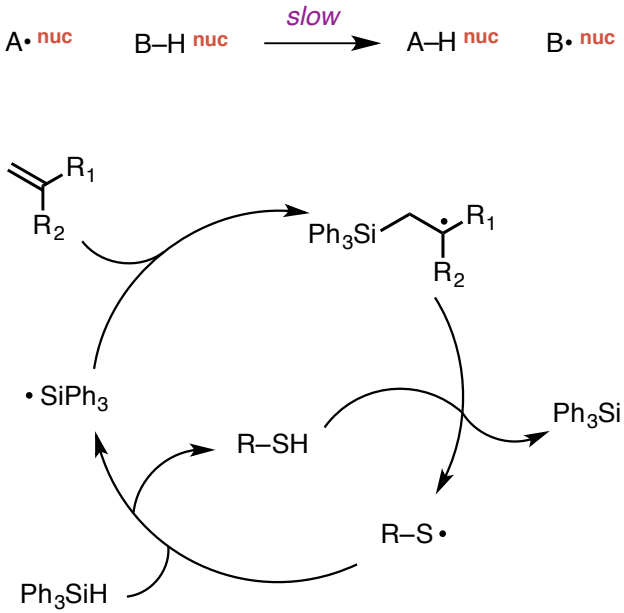
Chem. Commun., **1999**, 1665; *J. Chem. Soc., Perkin Trans.*, **2002**, 1376.

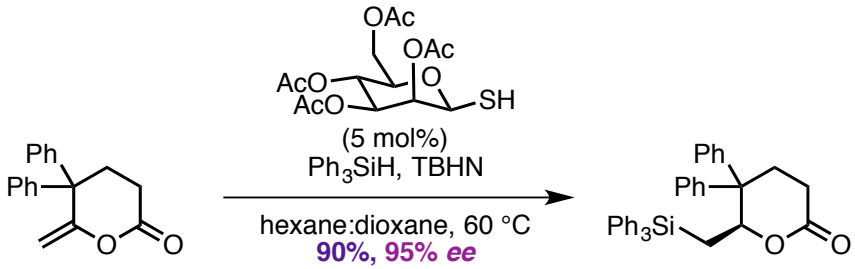
Enantioselective reactions

- Reagent control – Chiral reagents
  - Chiral tin reagent



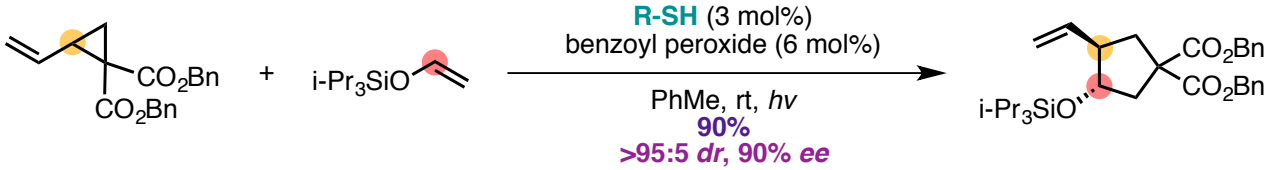
  - Chiral thiols
    - Polarity reversal catalysis

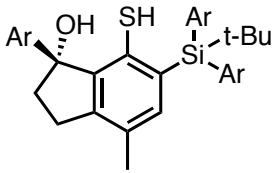


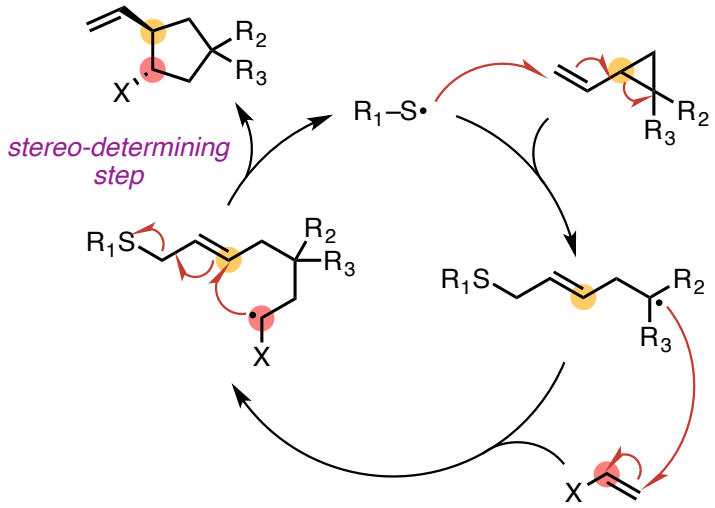


Enantioselective reactions

- Reagent control – Chiral reagents
  - Chiral thiols
    - Addition/elimination

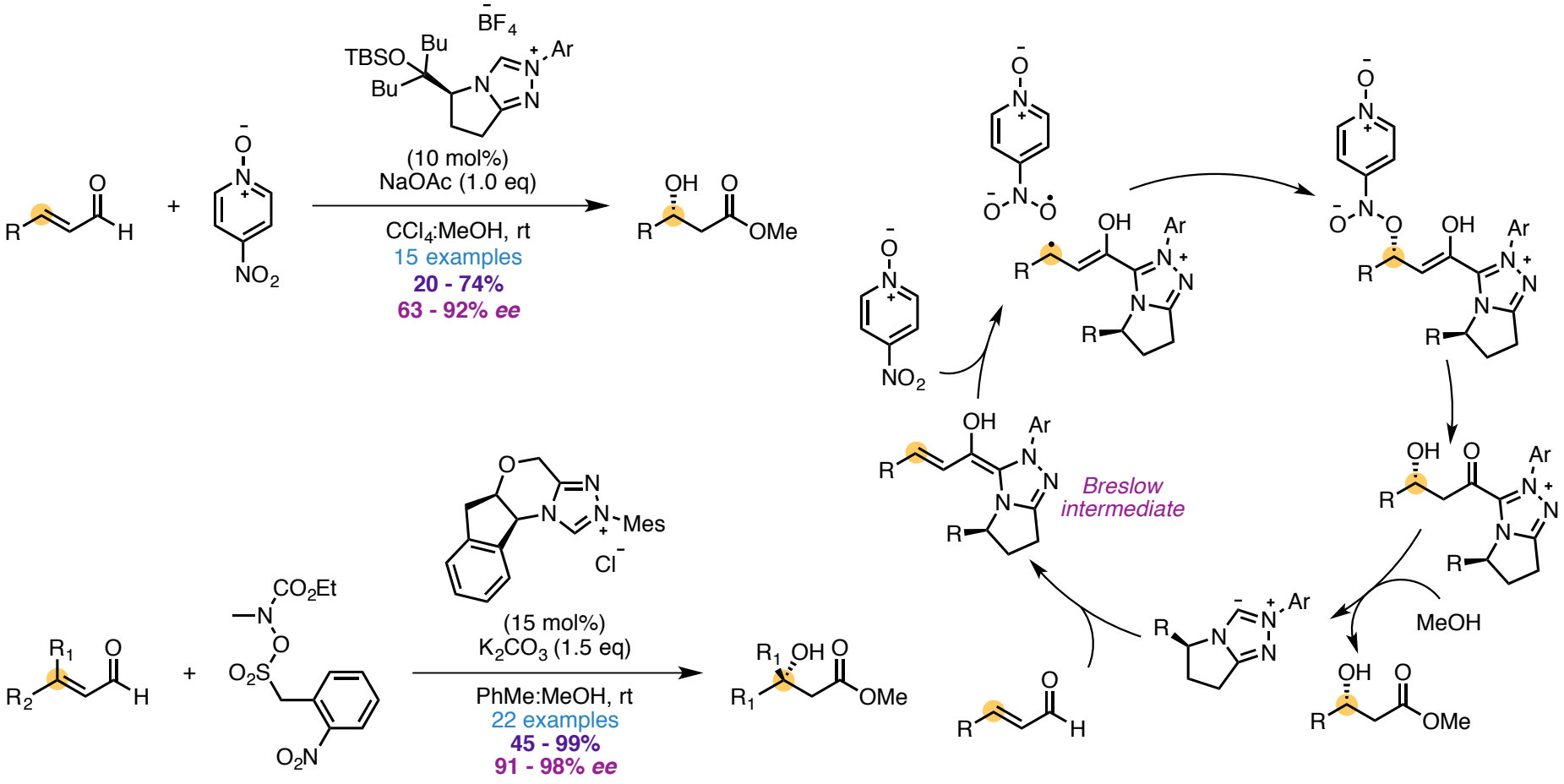






Enantioselective reactions

- Reagent control – NHC catalysis



Chirality control in Photochemical Reactions

- Giacomo Ciamician (1912)
  - Photochemistry of the future
  - "On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature."

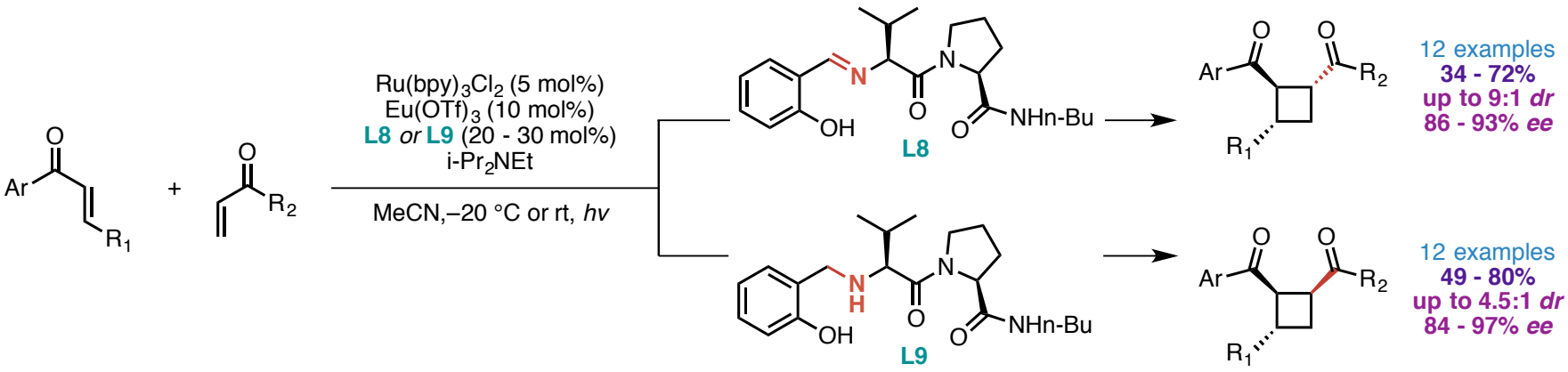
- "…until very recently the enantioselective catalysis of photochemical reactions has – somewhat figuratively speaking – been hidden in the dark."

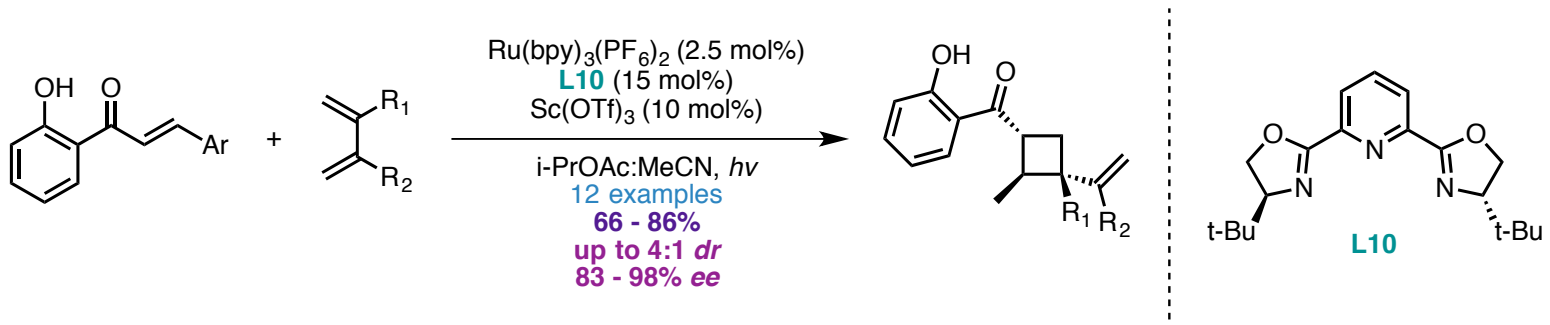
- Circularly polarized light
- Dual catalyst strategies

Science, **1912**, *36*, 385; *Angew. Chem. Int. Ed.*, **2015**, *54*, 3872; *Aust. J. Chem.*, **2008**, *61*, 557; *Chem. Rev.*, **2016**, *116*, 10035.

Enantioselective reactions

- Reagent control – Lewis acids
  - [2+2] photocycloadditions

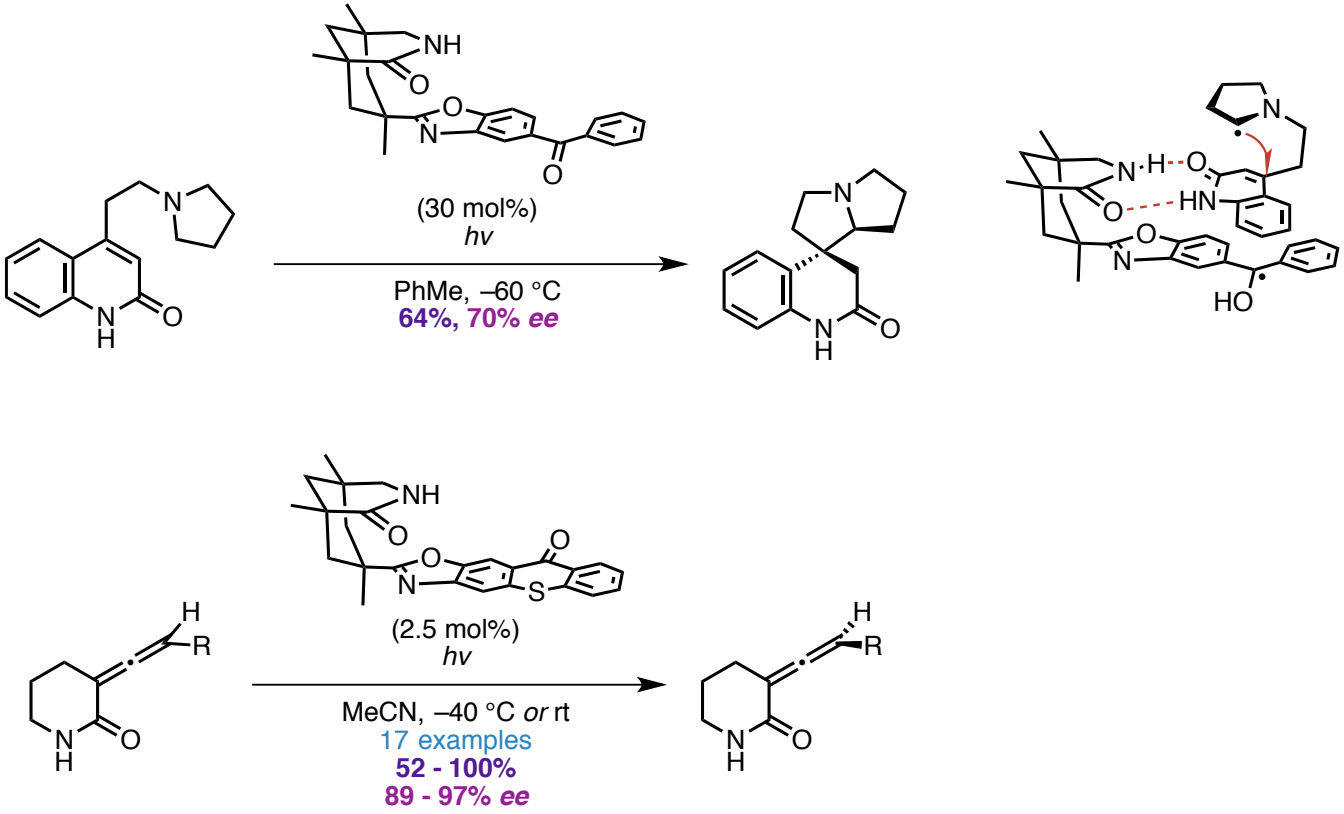




Science, **2014**, *344*, 392; *Science*, **2016**, *354*, 1391.

Enantioselective reactions

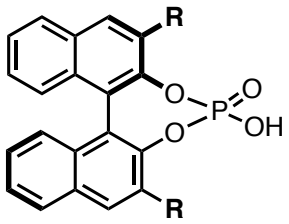
- Reagent control – H-bonding/ion pairing
  - Chiral sensitizers
    - Chiral iridium: *J. Am. Chem. Soc.*, **2017**, *139*, 17186.



Nature, **2005**, *436*, 1139; *Nature*, **2018**, *564*, 240.

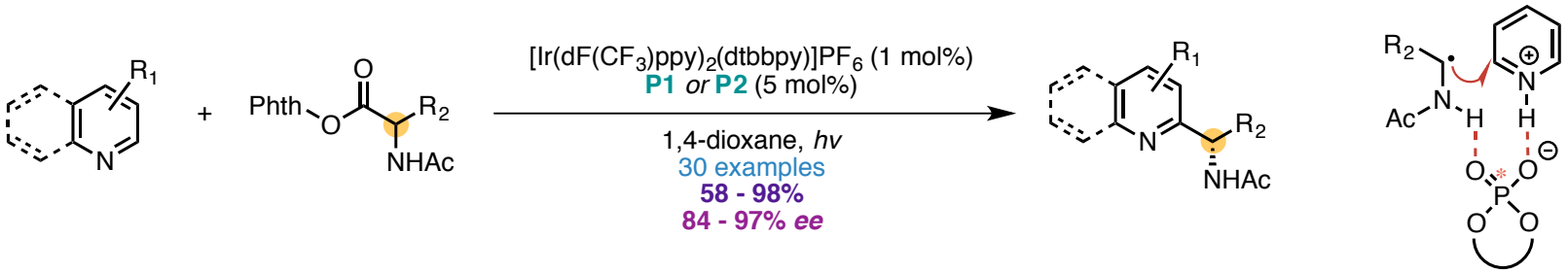
Enantioselective reactions

- Reagent control – H-bonding/ion pairing
  - Chiral phosphoric acids

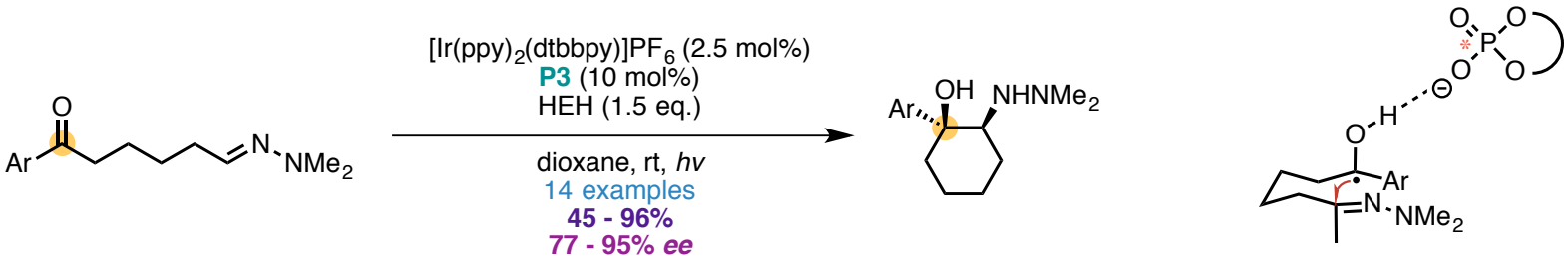


P1 **R** = 2,4,6-i-Pr-C_6H_2
P2 **R** = 2,4,6-Cy-C_6H_2
P3 **R** = $SiPh_3$

  - Minisci reaction



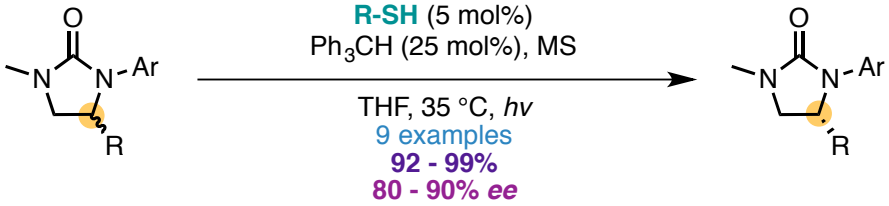
  - Proton coupled electron transfer

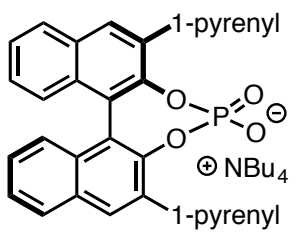


Science, **2018**, *360*, 419; *J. Am. Chem. Soc.*, **2013**, *135*, 17735.

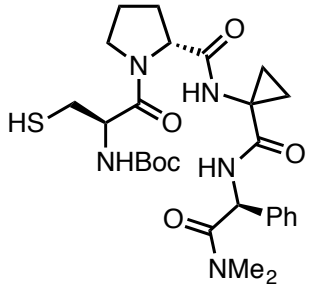
ENANTIOSELECTIVE REACTIONS

- Reagent control – H-bonding/ion pairing
  - Chiral phosphoric acid + chiral thiol



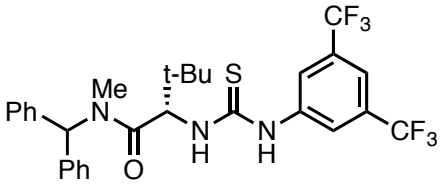


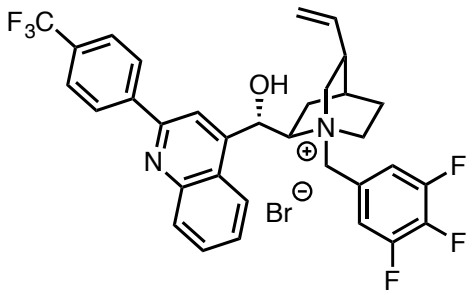
P4



  - Phase transfer catalysis

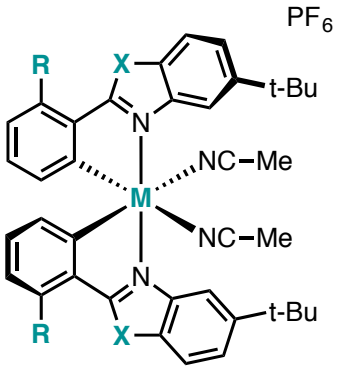
  - Chiral urea



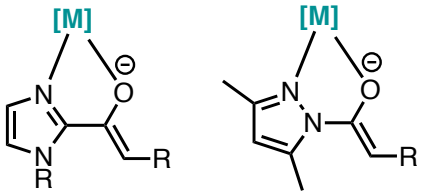


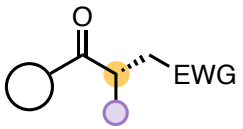
Enantioselective reactions

- Reagent control – Chiral photocatalysts

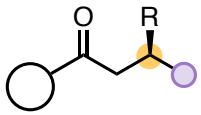


M = Ir, Rh
X = O, S
R = H, Ph

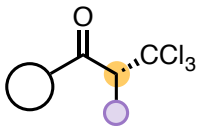




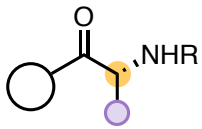
Nature **2014**, *515*, 100
JACS **2016**, *138*, 12636



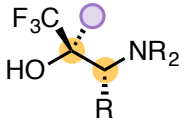
JACS **2016**, *138*, 6936



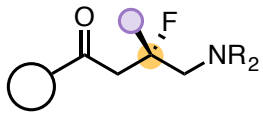
JACS **2015**, *137*, 9551



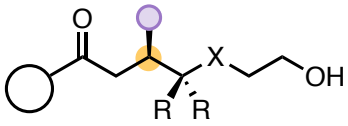
JACS **2016**, *138*, 12636



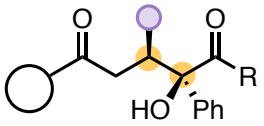
ACIE **2016**, *55*, 685



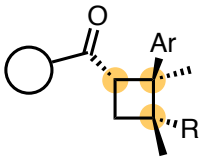
ACIE **2018**, *57*, 11193



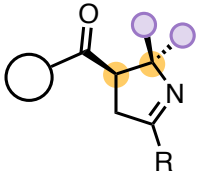
ACIE **2016**, *55*, 13495



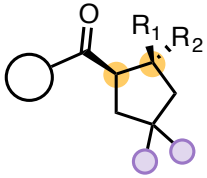
JACS **2017**, *139*, 17245



JACS **2017**, *139*, 9120



Nat Commun **2017**, *8*, 2245

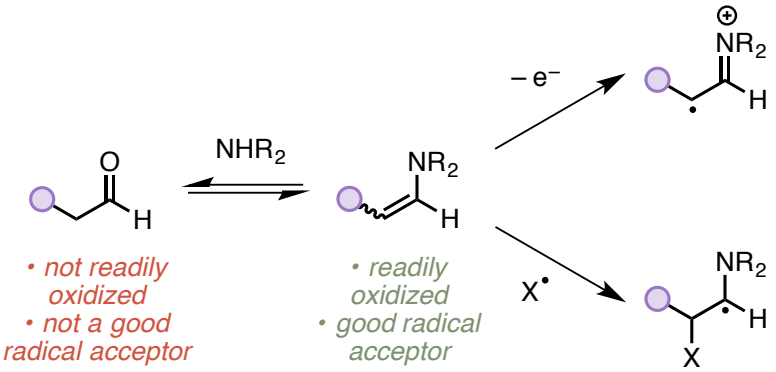


ACIE **2018**, *57*, 5454

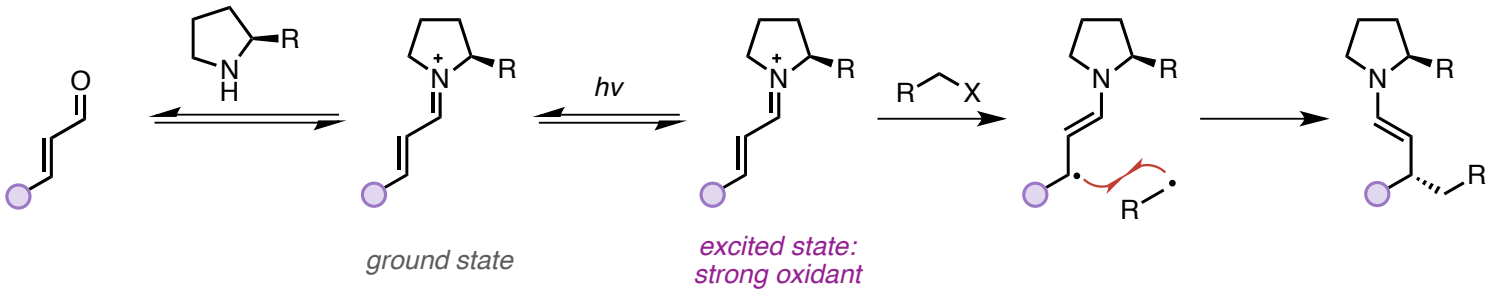
Nature, **2014**, *515*, 100.

Enantioselective reactions

- Reagent control – Enamine and iminium ion catalysis
  - Enamine catalysis

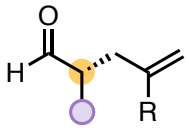


  - Iminium ion catalysis

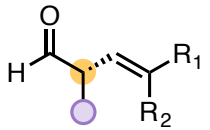


Enantioselective reactions

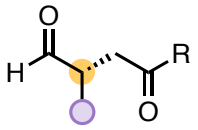
- Reagent control – Enamine catalysis



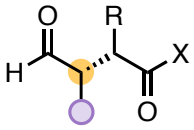
Science **2007,** *316*, 582



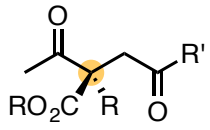
JACS **2008,** *130*, 398



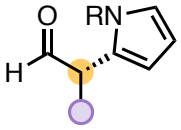
JACS **2007,** *129*, 7004



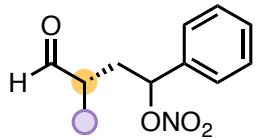
Science **2008,** *322*, 77



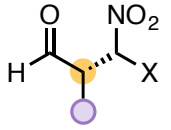
JACS **2014,** *136*, 14642



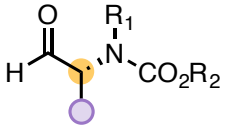
Science **2007,** *316*, 582



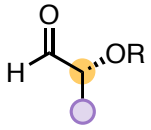
JACS **2008,** *130*, 16494



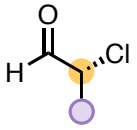
JACS **2009,** *131*, 11332



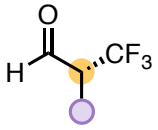
JACS **2013,** *135*, 11521



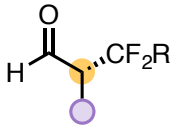
JACS **2007,** *129*, 4124
Chem Sci **2012,** *3*, 58



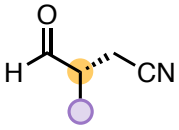
ACIE **2009,** *48*, 5121



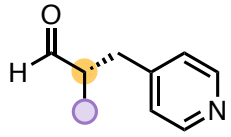
JACS **2009,** *131*, 10875
JACS **2010,** *132*, 4986



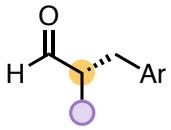
JACS **2009,** *131*, 10875



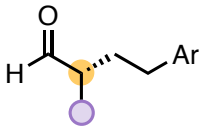
ACIE **2015,** *54*, 1



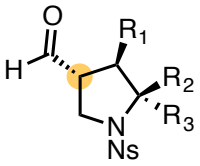
JACS **2018,** *140*, 3322



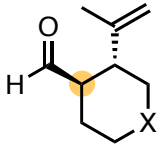
JACS **2010,** *132*, 13600



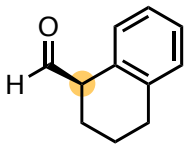
Nat Chem **2017,** *9*, 1073



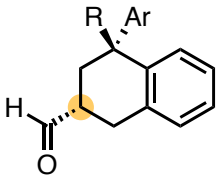
JACS **2012,** *134*, 11400



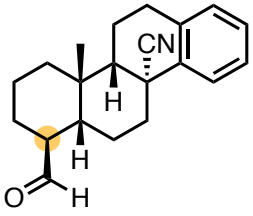
Chem Sci **2011,** *2*, 1470
JACS **2013,** *135*, 9358



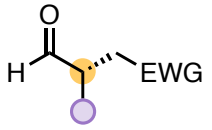
JACS **2009,** *131*, 11640



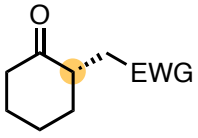
JACS **2010,** *132*, 10015



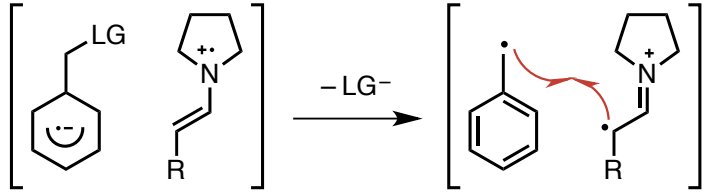
JACS **2010,** *132*, 5027



Nat Chem **2013,** *5*, 750
ACIE **2017,** *56*, 4447

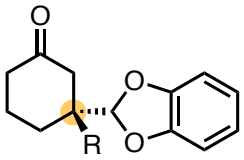


Chem Sci **2014,** *5*, 2438

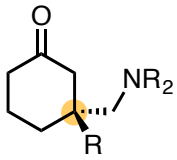


Enantioselective reactions

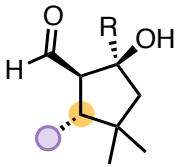
- Reagent control – Iminium ion catalysis



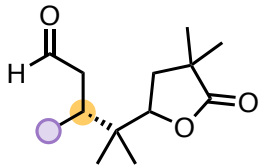
Nature **2016,** *532*, 218



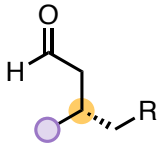
Nature **2016,** *532*, 218
Nat. Commun. **2018,** *9*, 3274



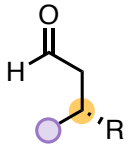
ACIE **2018,** *57*, 1068



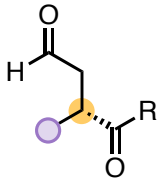
ACIE **2018,** *57*, 12819



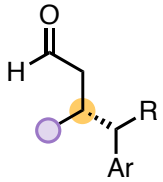
Nat. Chem. **2017,** *9*, 868



ACS Catal. **2018,** *8*, 1062



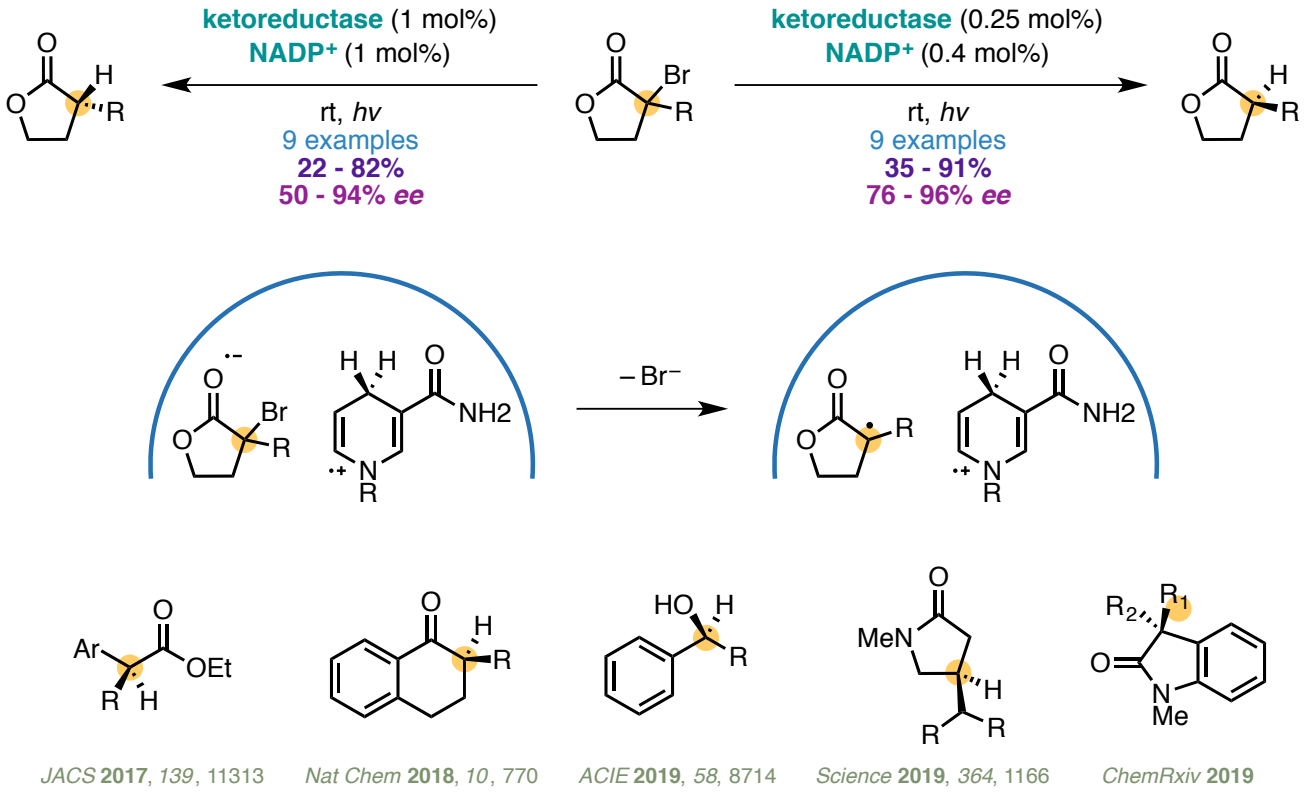
ACIE **2019,** *58*, 1213



JACS **2018,** *140*, 8439

Enantioselective reactions

- Reagent control – Redox active cofactors
  - Molecules that assist enzyme mediated catalysis
  - Enzymes with photoactive cofactors – adapted to generate radical intermediates



Conclusion

Reactions are ever so quizzical,

Some gentle some wild, some hysterical;

But the good ones I've seen

So seldom are clean,

And the clean ones so seldom are radical

References

General

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