



José Joaquín Barluenga Mur was born in **Tardienta** 07/27/1940

1963 BS from the University of Zaragoza
 1963 - 1966 PhD with Prof. Vicente Gomez Aranda (Zaragoza)
 1967 - 1970 Postdoc with Prof. Heinz Hoberg at Max-Planck-Institute für Kohlenforschung an der Ruhr (Germany)
 1970 - 1972 Scientific collaborator CSIC (Zaragoza)
 1972 - 1975 Associate professor (Zaragoza)
 1975 - 2010 Professor at the University of Oviedo. 1993 - Director of the University Institute for Organometallic Chemistry "Enrique Moles" (Oviedo)
 2011 - today Emeritus Professor (Oviedo)

Numbers

632 Publications (SciFinder)
 35 Reviews

Research interests

1963 - 1966 PhD in organomercury chemistry
 1967 - 1970 Postdoc in organoaluminium chemistry
 1970 - 1984 Addition of nitrogen nucleophiles to alkenes and alkynes (thallium, mercury)
 1978 - 1988 Substituted organolithium compounds
 1979 - 1992 Azabutadiene cycloadditions
 1984 - 2008 Bis(pyridine)iodonium tetrafluoroborate $[IPy_2]BF_4$
 1994 - 2010 Fischer carbene complexes. Recently unstabilized carbenes.
 1995 - 2007 Organozirconium chemistry
 2005 - 2011 Late transition metal catalysis (palladium, gold, platinum, silver, nickel...)
 2009 - 2011 Metal-free reductive coupling



The Barluenga group outside the Faculty of Chemistry in 2004.



Awards

12 major awards
 1989 Alexander von-Humboldt Foundation
 1999 1st Gold Medal from the Spanish Royal Society of Chemistry
 2005 Rey Jaime I Research Award
 2009 Silver Medal of the Principality of Asturias
 2 Doctor Honoris Causa (Alcala de Henares and La Rioja)

The Group

4 Full professors (Fañanás, Aznar, Tomás and González)
 11 Professors
 ~ 19 Graduate students
 ~ 2 Visiting students
 ~ 2 Postdocs

Angewandte profile: *Angew. Chem. Int. Ed.* **2010**, 49, 6250.

"Where there's a will there's a way"

"Draw it!! kid..."

"The straws don't let you see the forest!!!"

"You must always try to undertake your daily work with passion, dedication and cope with standards of intellectual innovation and significance"

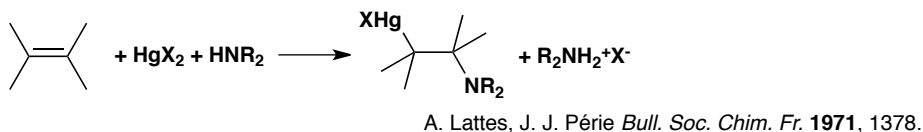
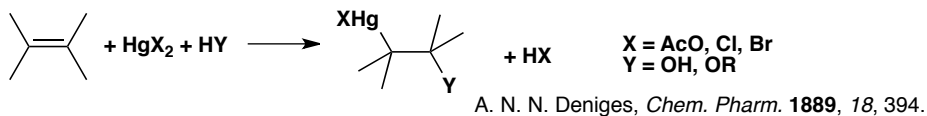
"If you continue to repeat experiments you're going to graduate in 10 years"

"For that trip no need to bring that saddlebag..."

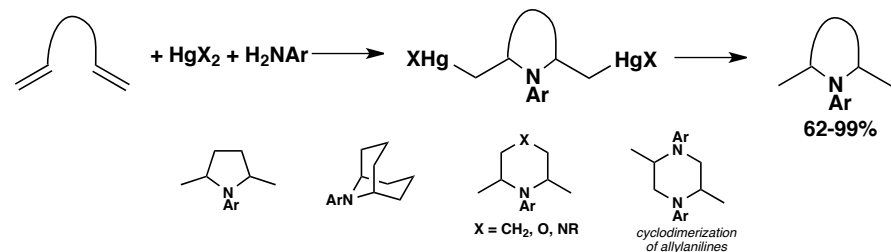
"Is that the way you want to be scientists?!?"

Mercury and thallium: Amination reactions.

Background - Seminal Publications

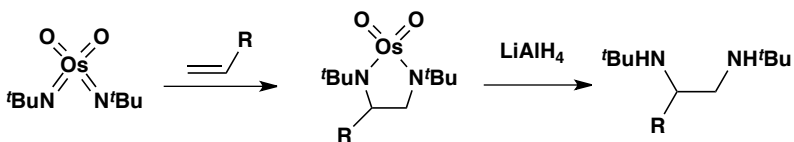
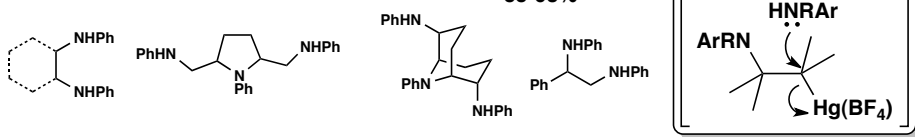
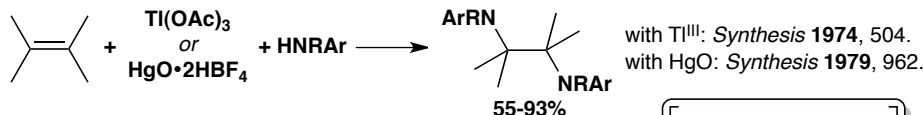


Aminomercuration of dienes



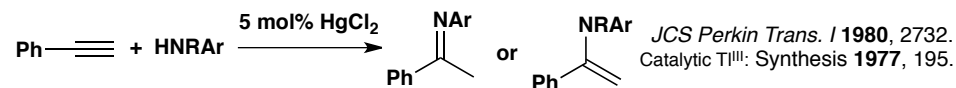
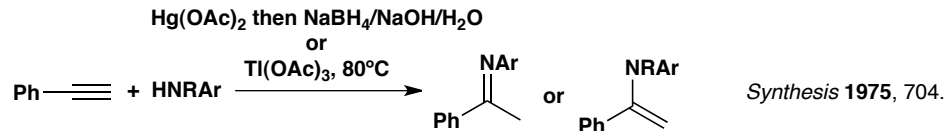
Anales RSEFQ **1972**, *68*, 221; *Tetrahedron Lett.* **1972**, 3621; *Synthesis* **1978**, 911; *Synthesis* **1979**, 896; *J. Heterocyclic Chem.* **1979**, *16*, 1017; *J. Heterocyclic Chem.* **1980**, *17*, 917.

Diamination of alkenes

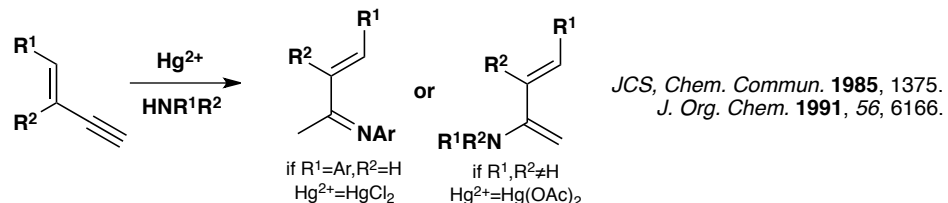
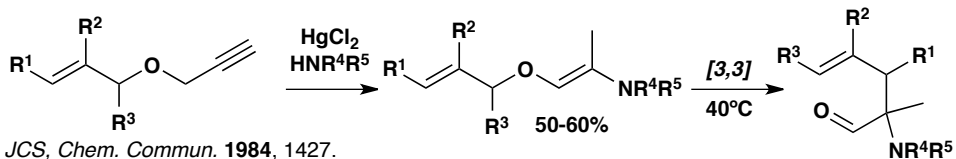


B. Sharpless et al. *J. Am. Chem. Soc.* **1977**, *99*, 3420. ---> only cited aminopalladation by J.E.-Backvall :)

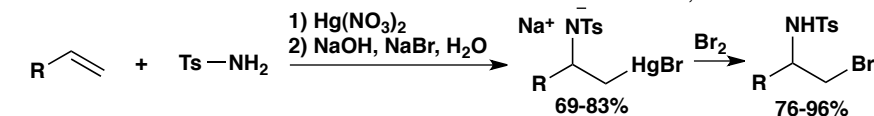
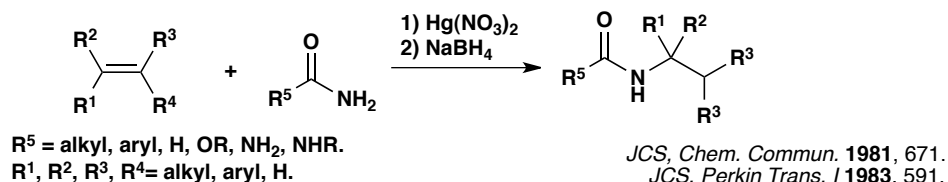
Addition of anilines across alkynes



Conjugated and deconjugated enynes

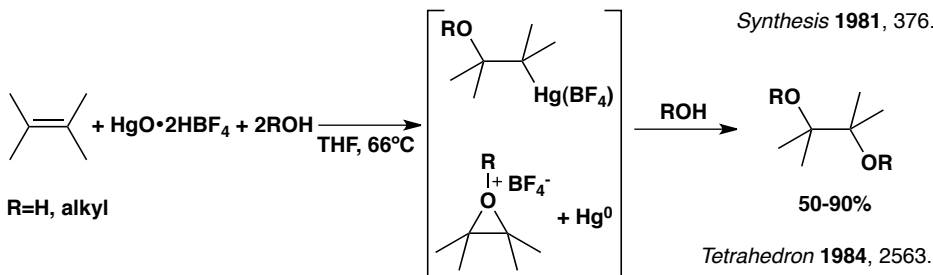
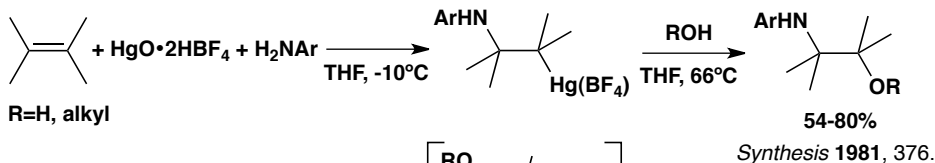
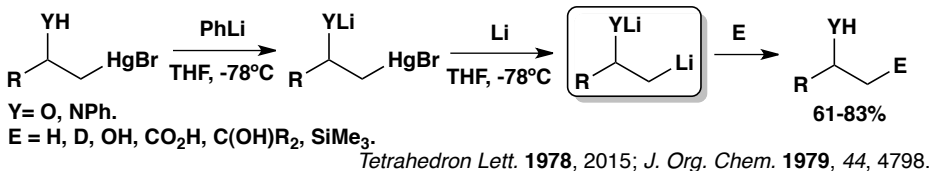
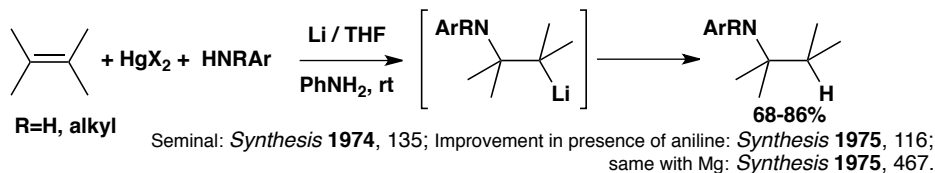
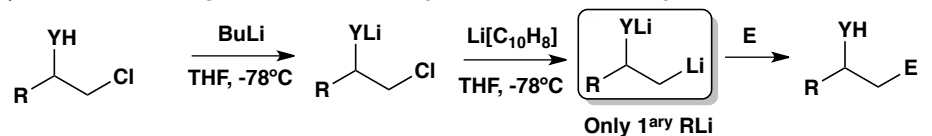


Hydro(sulf)amidation of alkenes



NaBH_4 quench: *JCS, Chem. Commun.* **1981**, 1178.
 Br_2 quench: *JCS, Perkin Trans. I* **1984**, 721.

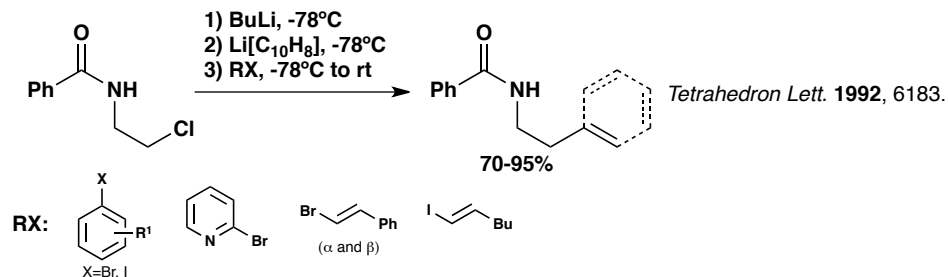
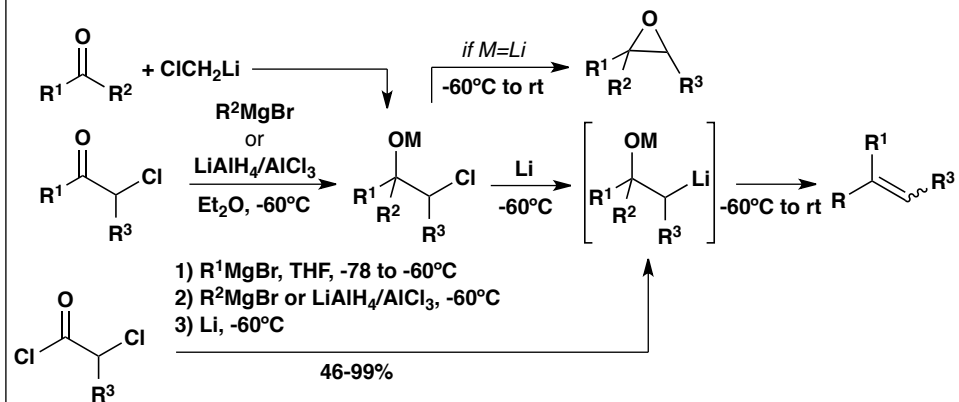
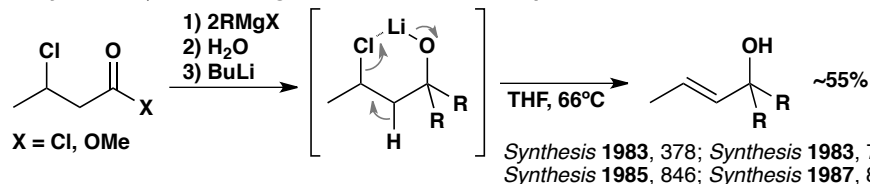
Oxygenated nucleophiles

Mercury - Lithium exchange: An entry to β -functionalized organolithiums β -Functionalized organolithiums from alkyl chlorides. Lithium naphthalenide.

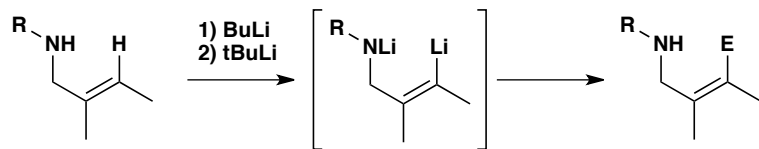
Y=O, NPh, N(CO)Ph.

E=H, D, OH, CO₂H, C(OH)R₂, SiMe₃, C(NHR¹)R₂, SMe.with Na and K: *J. Org. Chem.* 1981, 46, 1281;imines, sulphides and alkyl halides: *J. Org. Chem.* 1982, 47, 1560;Li[C₁₀H₈] (-100°C β -elimination): *JCS, Chem. Commun.* 1982, 1153; *JCS Perkin Trans. I* 1983, 3019.

Lithiation and direct coupling with aryl and vinyl bromides: The differential reactivity of dianionic intermediates.

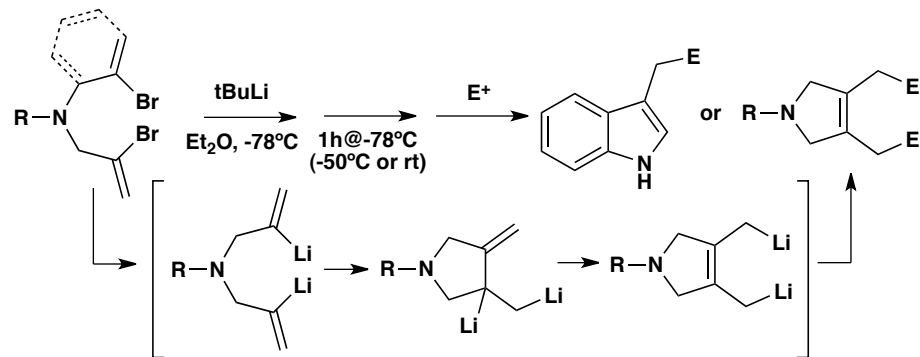
 β -Elimination of β -functionalized organolithium compounds: Synthesis of olefins.Seminal work on β -oxide elimination: J. J. Eisch *et al.* *J. Am. Chem. Soc.* 1976, 98, 4646;From chloroketones: *J. Org. Chem.* 1981, 46, 2721;From chloroacyl chlorides: *J. Org. Chem.* 1983, 48, 609; *J. Org. Chem.* 1983, 48, 3116;(Chloromethyl)lithium: *JCS, Chem. Commun.* 1988, 536; *JCS, Perkin Trans. I* 1990, 417;*JCS, Perkin Trans. I* 1989, 77; *J. Org. Chem.* 1999, 2843;*J. Org. Chem.* 1997, 5974; *Synthesis* 1988, 234. γ,δ,ϵ -functionalized organolithium compounds. δ,ϵ -functionalized compounds behave normally but the γ ones undergo a different elimination process...

Lithiation of allylamines

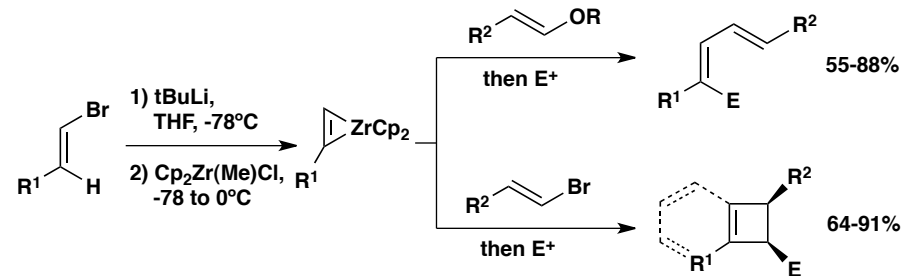


JCS, Chem. Commun. **1988**, 1135; *Tetrahedron Lett.* **1988**, 4859; *Tetrahedron Lett.* **1992**, 7573; *J. Org. Chem.* **1994**, 59, 602; *J. Org. Chem.* **1994**, 59, 1586.

Carbolithiation of lithiated double bonds.

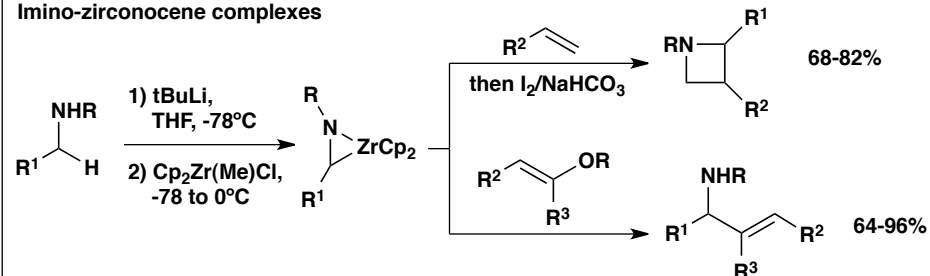


J. Am. Chem. Soc. **1998**, 120, 4865; *Chem. Eur. J.* **2001**, 7, 2896; *Eur. J. Org. Chem.* **2003**, 771.



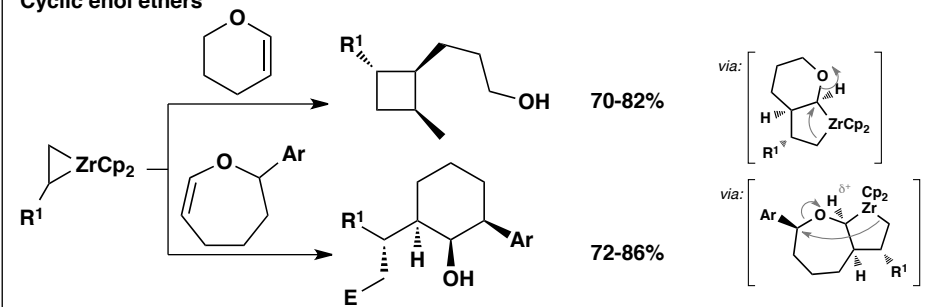
Z. Naturforsch B, **1995**, 50, 312; *Chem. Commun.* **1995**, 1009; *Chem. Eur. J.* **1997**, 3, 1324; *Chem. Eur. J.* **2004**, 10, 101; *Synlett* **2005**, 2513; *Org. Lett.* **2008**, 10, 4469.

Imino-zirconocene complexes



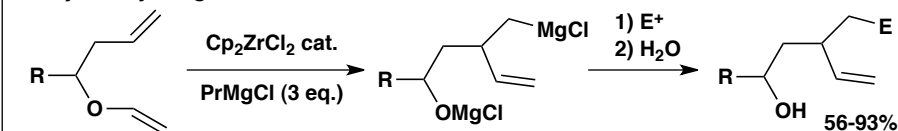
JCS, Chem. Commun. **1994**, 989; *J. Org. Chem.* **1997**, 62, 5953; *Chem. Eur. J.* **2004**, 10, 109.

Cyclic enol ethers

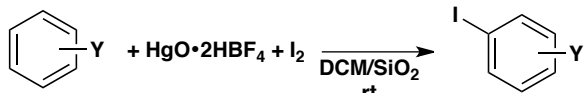


Angew. Chem. Int. Ed. **2004**, 43, 3932; *Angew. Chem. Int. Ed.* **2007**, 46, 2607.

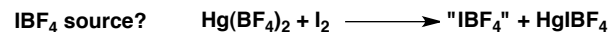
Catalytic vinyl-magnesation of unactivated olefins.



Angew. Chem. Int. Ed. **2006**, 45, 6362; *Org. Lett.* **2007**, 9, 3081.

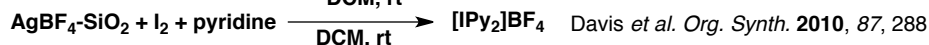
The serendipitous birth of $[\text{IPy}_2]\text{BF}_4$ - Barluenga's reagent

Y=H; 54%
Y=tBu; 78%
Y=OMe; 87%
Y=CO₂H; 35%
Y=NO₂; 12%



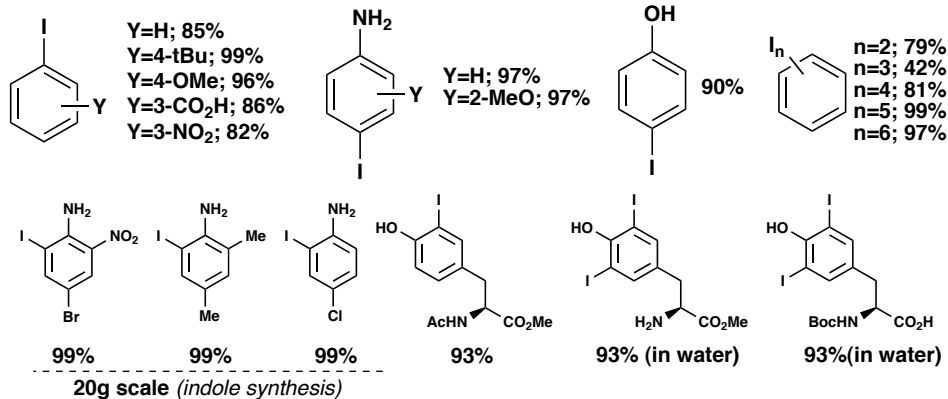
JCS, Perkin Trans. I 1984, 2623.

Pyridine as stabilizer of iodonium...



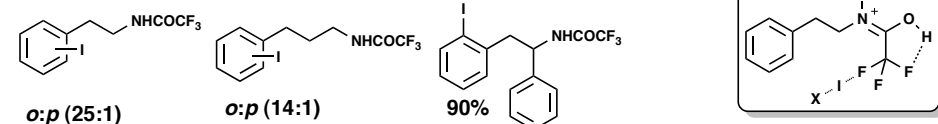
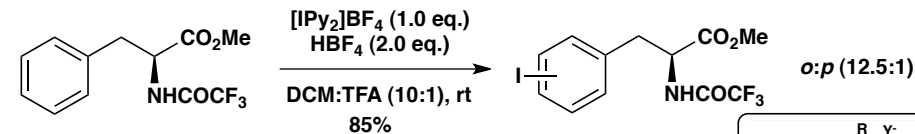
Electrophilic iodination of activated and unactivated arenes

For activated arenes, the reagent is reactive enough. For non-activated ones, 1-2 eq. HBF₄ or TfOH is needed.

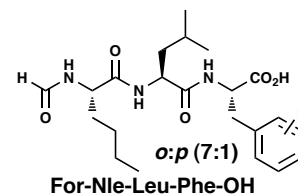
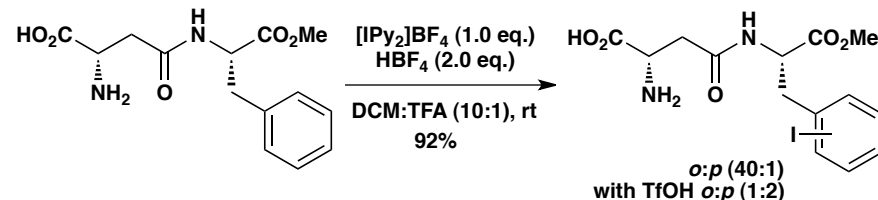


JCS, Chem. Commun. 1992, 1016; J. Org. Chem. 1993, 58, 2058; Tetrahedron Lett. 1993, 34, 3893; J. Org. Chem. 1996, 61, 5804; JCS, Chem. Commun. 1996, 1505; Chem. Commun. 2000, 1307.

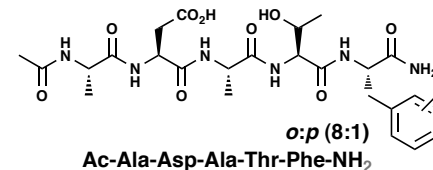
Directed aromatic iodination...Does it remind you of something?



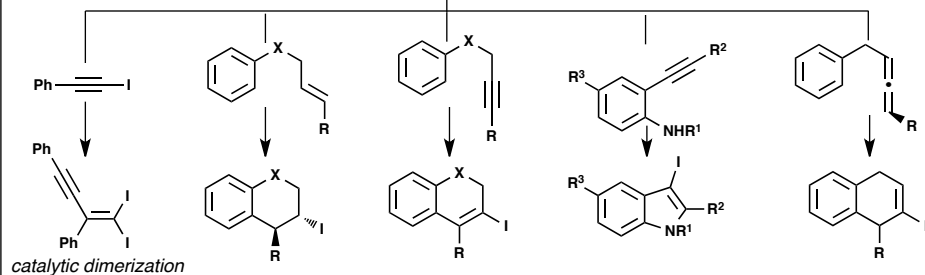
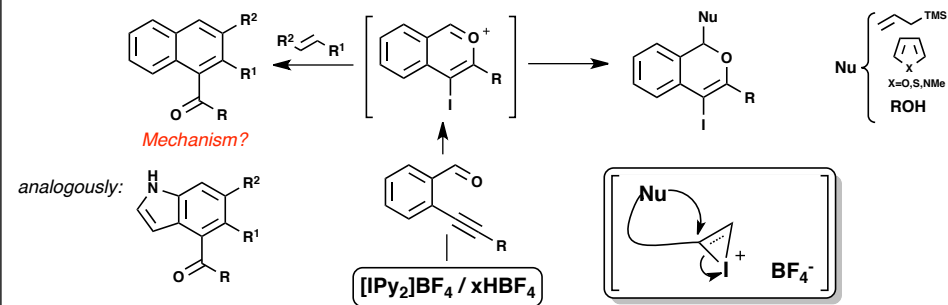
Direct iodination of Phe residues in peptides - Iodine radiolabelling in proteins.



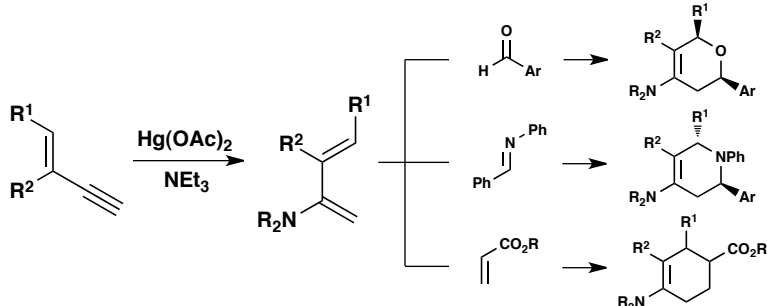
Angew. Chem. Int. Ed. 2004, 43, 325. Peptides in solid phase: Tetrahedron Lett. 1999, 7279.



Iodonium as C-C (or C-X) bond forming promoter

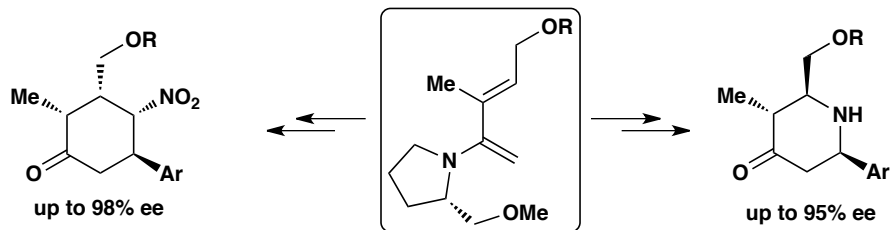


Mining the gold of enyne hydroamination... 2-amino-1,3-butadienes



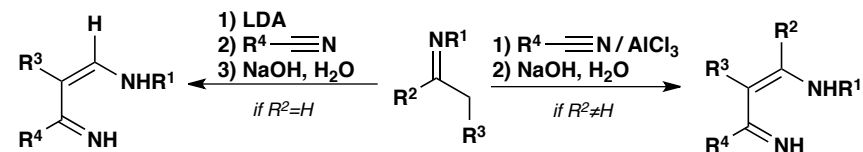
Chiral 2-amino-1,3-butadienes

Highlight: K. Krohn, *Angew. Chem. Int. Ed.* **1993**, *32*, 1582



JCS, Chem. Commun. **1988**, 1247; *J. Org. Chem.* **1991**, *56*, 6166; *J. Am. Chem. Soc.* **1993**, *115*, 4403; *J. Org. Chem.* **1993**, *58*, 3391; *Chem. Eur. J.* **1996**, *2*, 805; *J. Org. Chem.* **1997**, *62*, 6746; *J. Org. Chem.* **1998**, *63*, 3918; *J. Org. Chem.* **1999**, *64*, 3736.

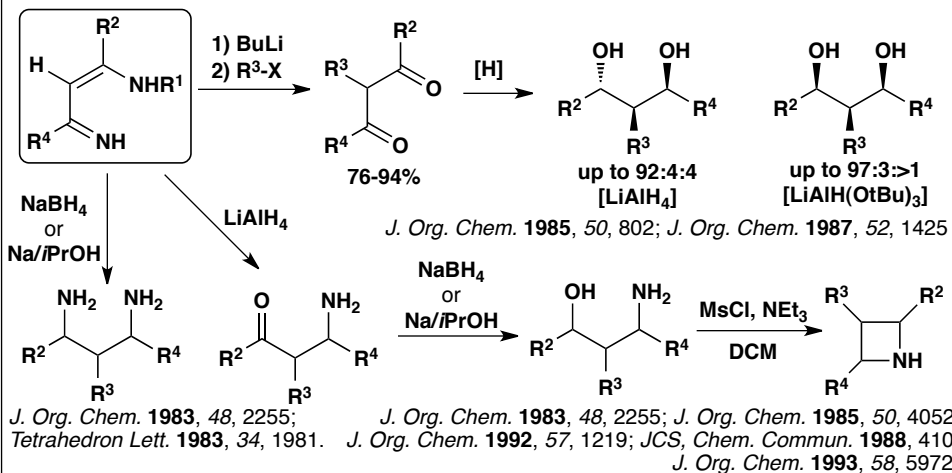
4-amino-1-aza-1,3-butadienes - Synthesis.



G. Wittig et al. *Liebigs Ann. Chem.* **1973**, 1075.

Synthesis **1970**, 142

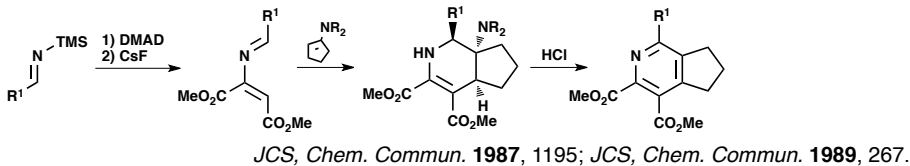
4-amino-1-aza-1,3-butadienes - Basic reactivity.



J. Org. Chem. **1985**, *50*, 802; *J. Org. Chem.* **1987**, *52*, 1425

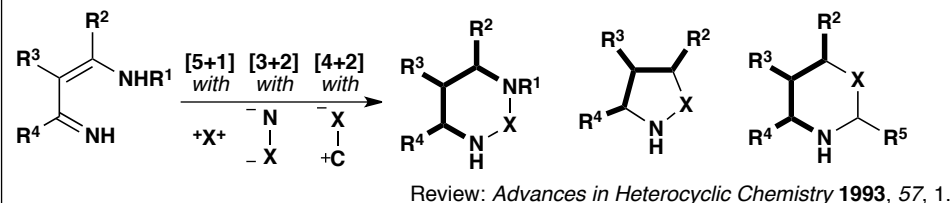
J. Org. Chem. **1983**, *48*, 2255; *J. Org. Chem.* **1985**, *50*, 4052; *Tetrahedron Lett.* **1983**, *34*, 1981. *J. Org. Chem.* **1992**, *57*, 1219; *JCS, Chem. Commun.* **1988**, 410; *J. Org. Chem.* **1993**, *58*, 5972.

2-aza-1,3-butadienes - Normal and inverse demand [4+2] cycloadditions.



JCS, Chem. Commun. **1987**, 1195; *JCS, Chem. Commun.* **1989**, 267.

4-amino-1-aza-1,3-butadienes - cycloaddition en route to heterocycles.



Review: *Advances in Heterocyclic Chemistry* **1993**, *57*, 1.

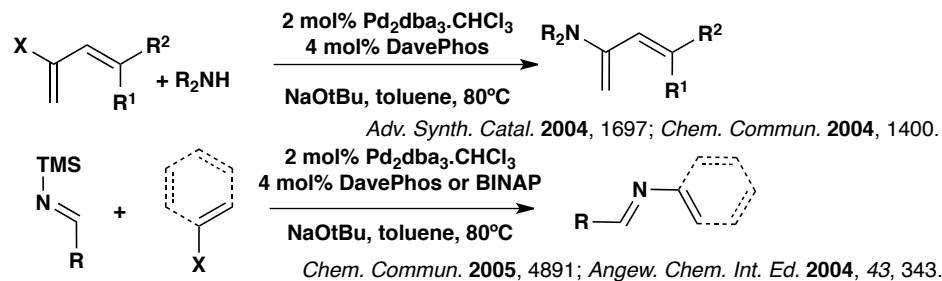
[5+1] - Dihydropyrimidines: *Synthesis* **1974**, 720; *Synthesis* **1979**, 346; *Synthesis* **1989**, 230; *Synlett* **1992**, 563; *JCS, Chem. Commun.* **1988**, 410. Pyrimidones: *JCS, Chem. Commun.* **1979**, 675; *J. Org. Chem.* **1980**, *45*, 2592. Thiadiazines: *JCS, Chem. Commun.* **1979**, 675; *JCS, Perkin Trans I* **1981**, 1891. Diazaphosphorines: *Synthesis* **1983**, 370; *Synthesis* **1985**, 309. Diazasilines: *Angew. Chem. Int. Ed.* **1986**, *25*, 181. Diazagermines: *Organometallics* **1992**, *11*, 2348.

[3+2] - Pyrazoles: *JCS, Chem. Commun.* **1979**, 891; *JCS, Perkin Trans I*, **1981**, 1891. Isoxazoles: *J. Org. Chem.* **1983**, *48*, 1379. Pyrroles: *J. Org. Chem.* **1982**, *47*, 1696.

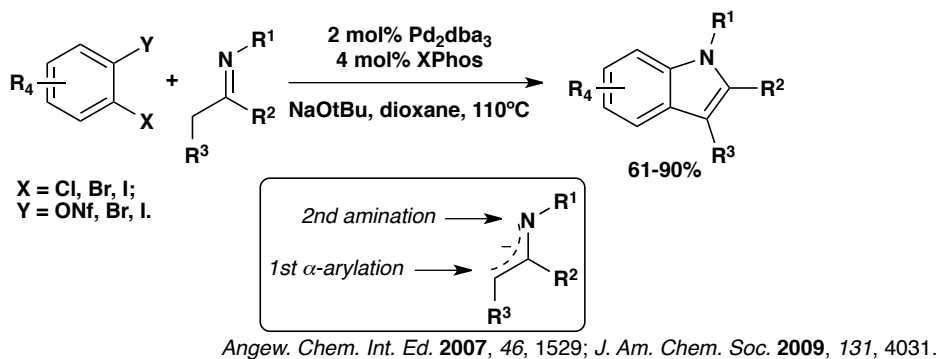
[4+2] - Pyrimidines: *Synthesis* **1970**, 363. Pyridines: *Synthesis* **1975**, 191.

Chem. Ber. **1985**, *36*, 52; *JCS, Chem. Commun.* **1986**, 1179; *JCS, Perkin Trans. I*, **1988**, 1739; *Tetrahedron Lett.* **1989**, *30*, 2685.

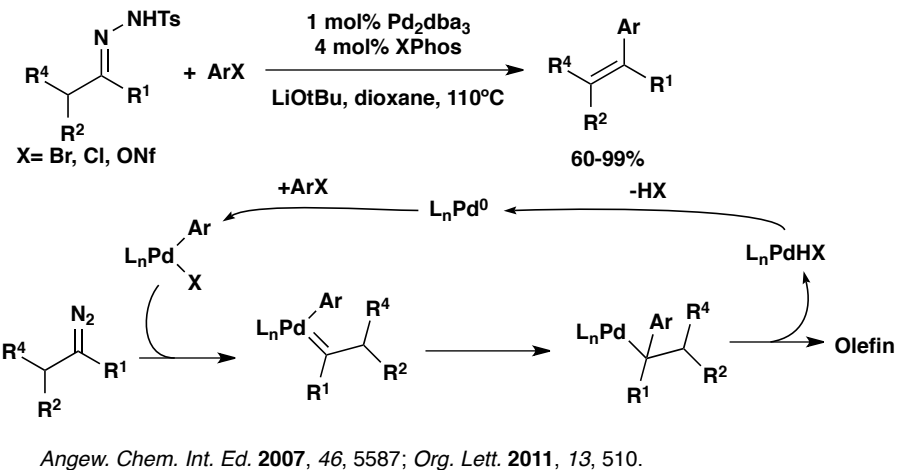
Palladium catalysis - new entry to amino and azadienes?



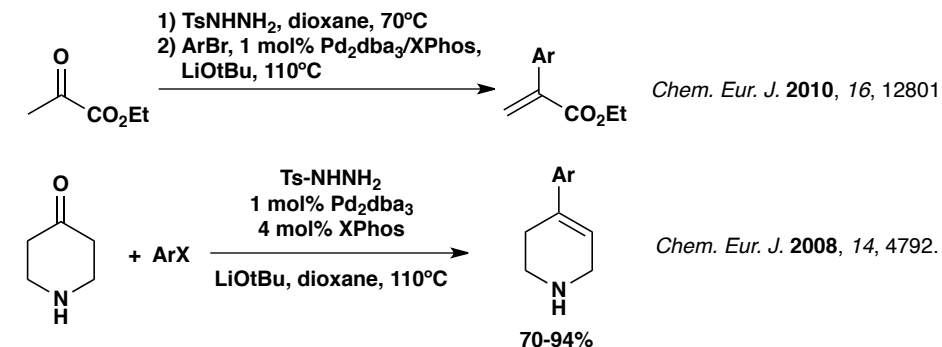
A general approach to the indole ring...



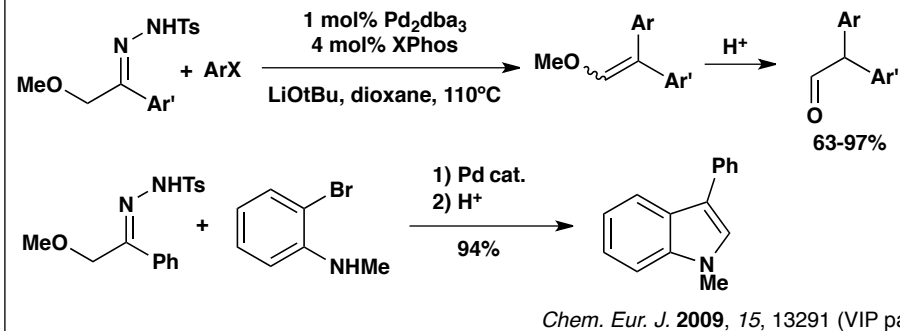
Tosylhydrazones... Efforts in fundamental research finds a neat reward!!



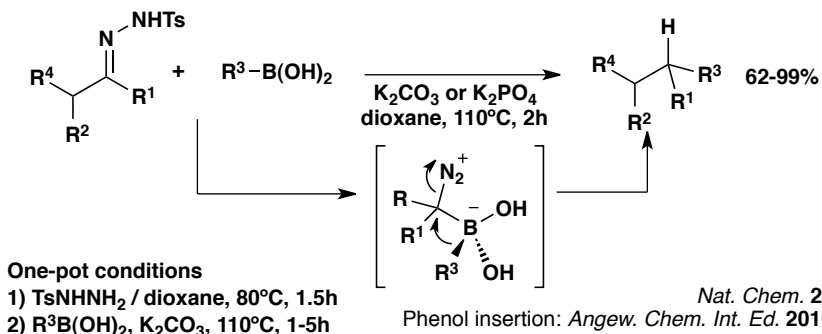
Application of the olefination reaction to cases of special interest...

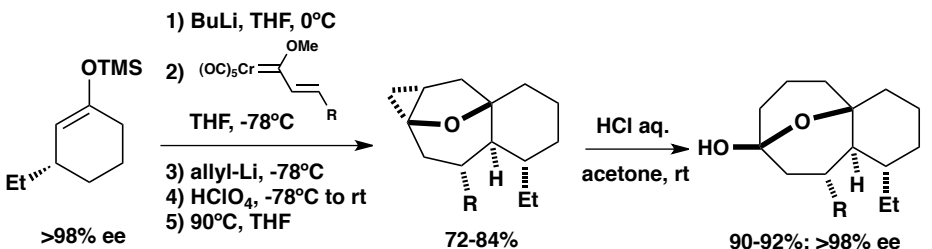


Maria Escribano's work...

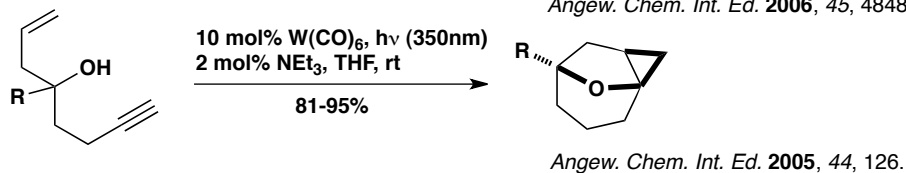


Metal-free reductive coupling of tosylhydrazones and boronic acids...

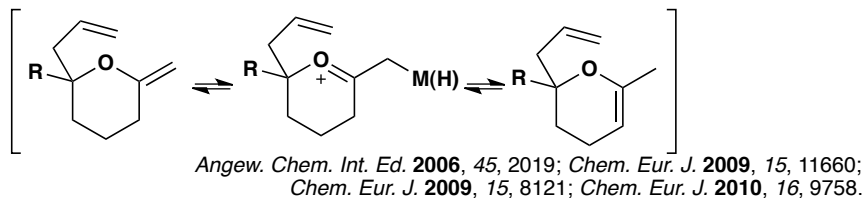
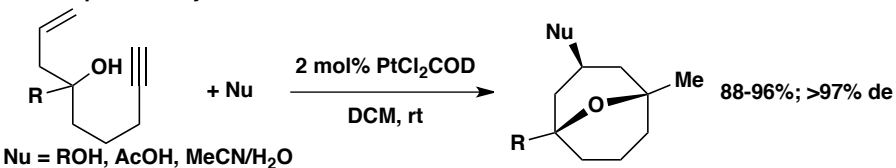


From Fischer carbene complexes to π -electrophilic catalysis

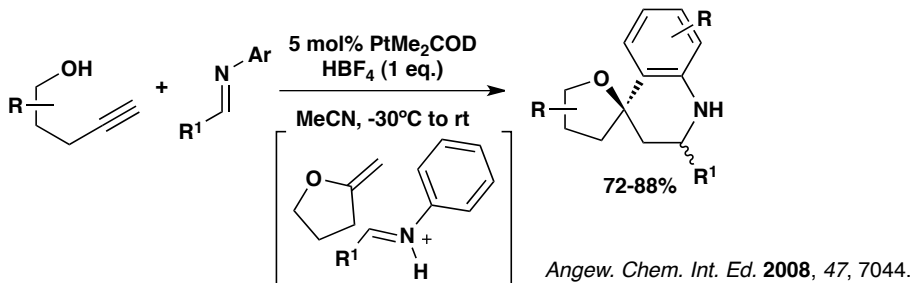
HCl aq.
acetone, rt
90-92%; >98% ee
J. Am. Chem. Soc. **2002**, *124*, 9056.
Angew. Chem. Int. Ed. **2006**, *45*, 4848.



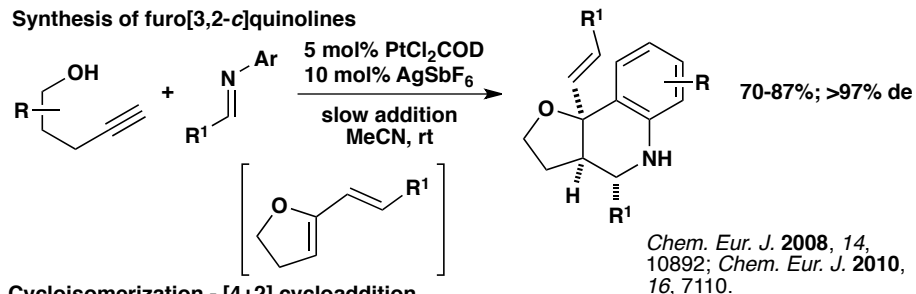
Development of cycloisomerization-Prins cascade...



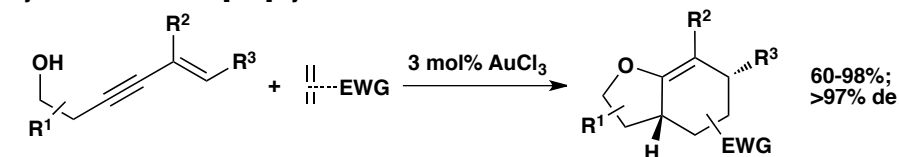
The pursuit of the catalytic generation of exocyclic enol ethers. Proof-of-concept: Povarov.



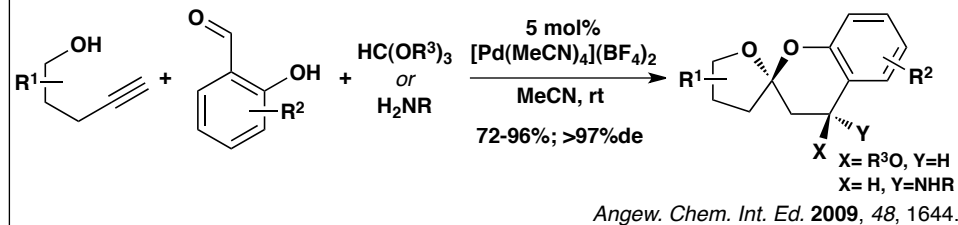
Synthesis of furo[3,2-c]quinolines



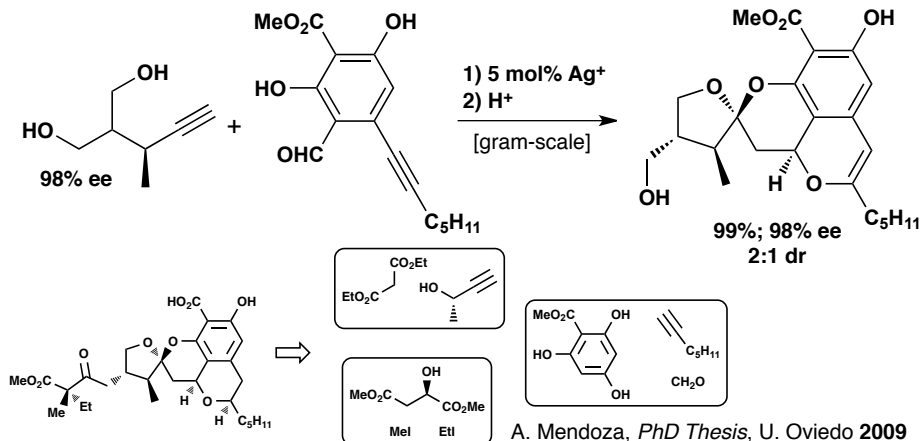
Cycloisomerization - [4+2] cycloaddition



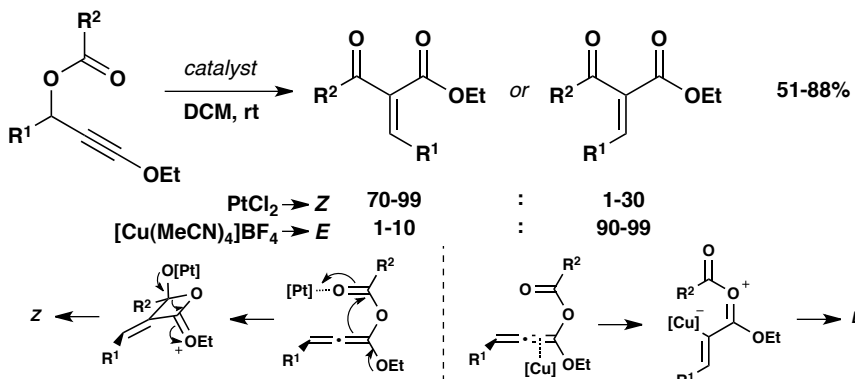
Synthesis of chroman-spiroketal



Gram-scale total synthesis of (-)-berkelic acid

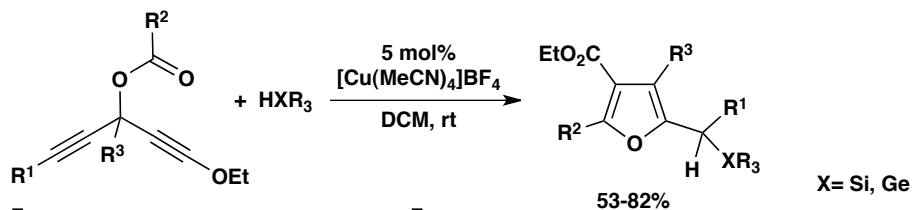


Activated propargylic esters: A new scaffold with new interesting reactivity to explore.



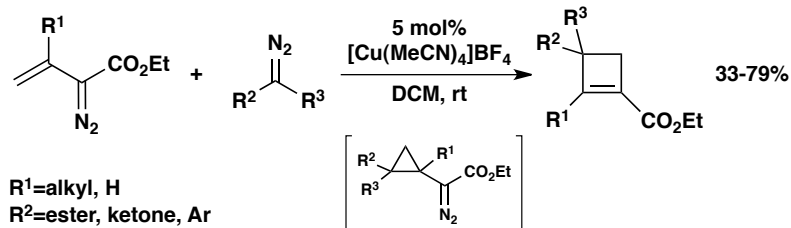
J. Am. Chem. Soc. 2007, 129, 7772.

New rearrangement to (2-furyl)carbenes. Hydrosilylation and hydrogermanation.



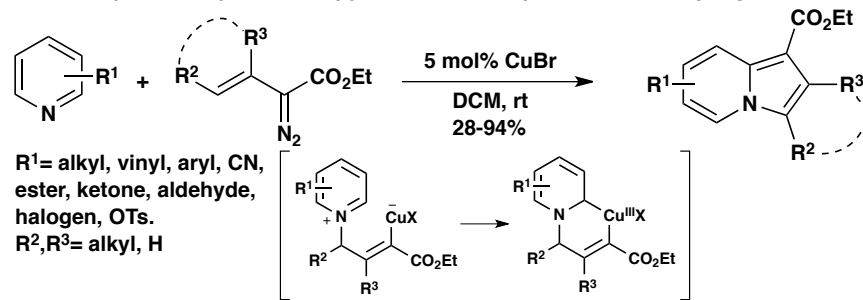
J. Am. Chem. Soc. 2008, 130, 13528.

Diazo-heterocoupling



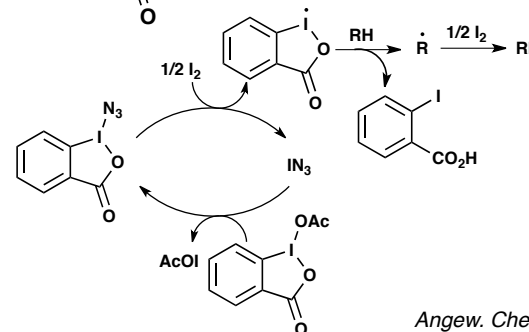
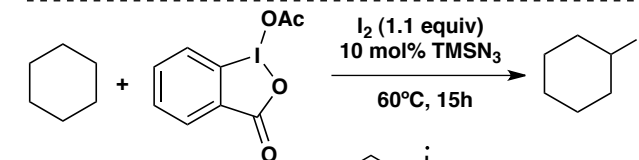
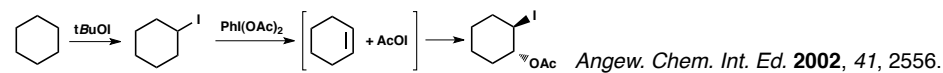
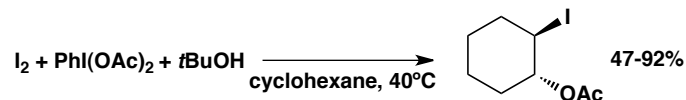
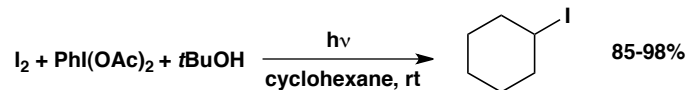
Angew. Chem. Int. Ed. 2009, 48, 7569.

Indolizine synthesis by means of pyridine/diazocompound cross-coupling.



J. Am. Chem. Soc. 2010, 132, 13200.

Some radical iodine reactions you could be interested in...



Angew. Chem. Int. Ed. 2005, 44, 5851.