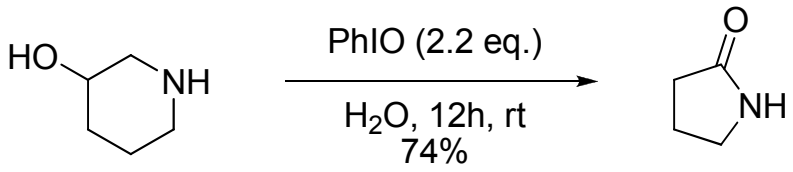
Hypervalent (III) iodine chemistry

Alcohol and phenol oxydation by Diacetyliodobenzene (DIB)



Ochiai, M. et al., *Chem. Pharm. Bull.* **2004**, 1143-1144

Summary

- Generalities
  - Brief history of hypervalent iodine
  - Structure and bonding
  - Classification
  - Most common reagents
  - Objectives
- Reactivity towards alcohols
- Reactivity towards phenols
- Reactivity towards phenol ethers
- Short glimpse at the rest of iodine chemistry

About Iodine

- **Organohypervalent iodine:**

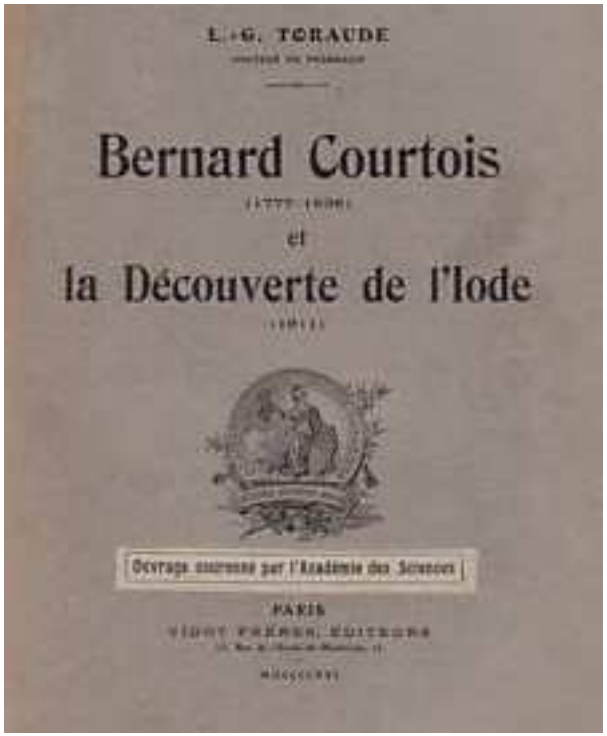
  - Varvoglis, A., *Synthesis* **1984,** 709-726
  - Stang, P. J. and Zhdankin, V. V., *Chem. Rev.* **1996**, 1123-1178
  - Stang, P. J. and Zhdankin, V. V., *Chem. Rev.* **2002**, 2523-2584
  - Stang, P. J. and Zhdankin, V. V., *Chem. Rev.* **2008,** 5299-5358
  - Moriarty, R. M., *J. Org. Chem.* **2005**, 2893-2903

- Key words about hypervalent iodine:

Oxydation, Umpolung

A brief history of (hypervalent) iodine

- **1811** iodine was first isolated by B. Courtois
- **1813** J. L. Gay Lussac names it iodine
- **1886** Willgerodt prepared the first polyvalent organic iodine $PhICl_2$
- **1914** Willgerodt publishes *Die Organischen Verbingungen mit Mehrwertigen Jod*
- **1980-1990** commercialisation of iodosylbenzene, Dess-Martin periodinane and [Bis(acetyloxy)iodo]benzene



Structure and bonding

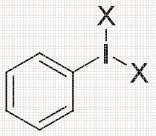
3 parts:

Iodine central atom

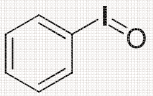
Carbon ligand

Apical ligands

Organohypervalent (III) Iodine families

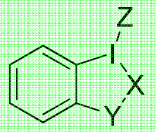


Willgerodt, C. et coll. 1886

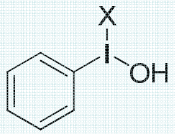


X = F, Cl, Br, N_3, OC(O)R, NR_2, $NC(O)CF_3$

Boeeseken et coll. 1932

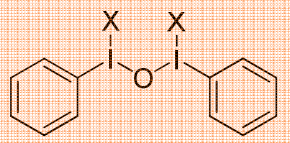


X= O, NH
Y= CO, SO_2, OP(O)(OH), CMe_2, P(O)Me, etc...
Z= Cl, OH, OAc

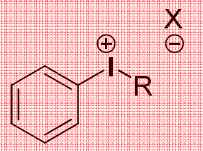


X = OSO_3R, $OP(O)(OR)_2$

Koser, G. F. Wettach, R. H. 1977

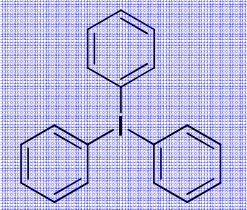


Godstein, H. Grampoloff, A. V. 1932

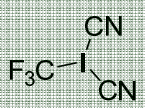


X= OTs, OTf, BF_4
R= CN, Ar, Alkyne, Alkene

Hartman, M. et coll. 1894



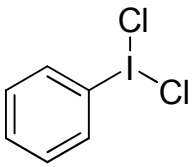
Wittig, R. et coll. 1949



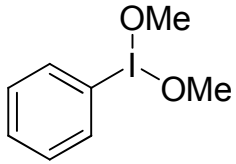
Tyrra, W. Naumann, D. 1989

Most common reagents

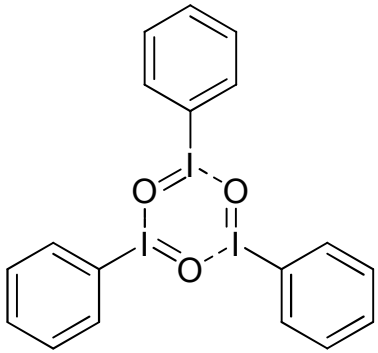
iodobenzene dichloride



Moriarty's reagent

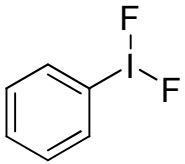


Iodosylbenzene

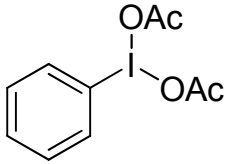


oligomer

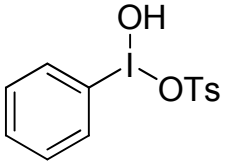
iodobenzene difluoride



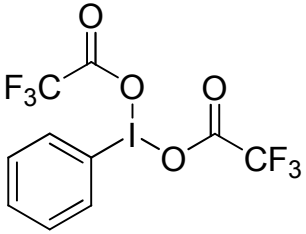
Diacetoxy Iodobenzene (DIB)



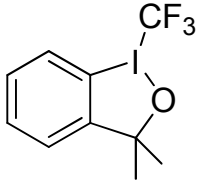
Koser's reagent



Ditrifluoroacetoxy Iodobenzene



Togni's reagent



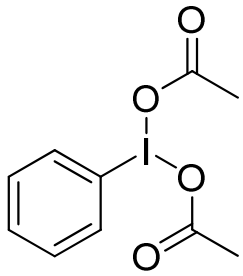
Why

Alcohol and phenol oxydation by Diacetyliodobenzene (DIB)

?

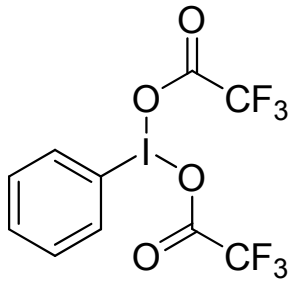
Diacyloxy iodobenzene

- **Diacetoxy iodobenzene (DIB):**
  - **Alternative names:** Iodobenzene diacetate, (Diacetoxyiodo)benzene, Iodosobenzene diacetate, PIA, PIDA
  - **CAS:** 3240-34-4
  - **Price:** Sigma-Aldrich 25 g / 63.90 €, Acros Organics 25 g / 62.20 €
  - **Melting point:** 161–165 °C
  - **Aspect:** white powder
  - **Risks:** Harmful, irritant



= $PhI(OAc)_2$

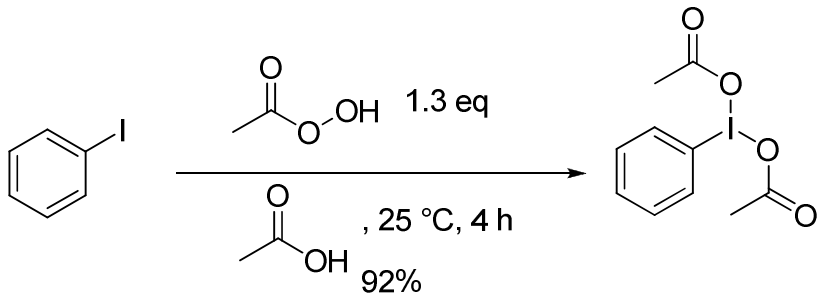
- **Bis(trifluoacetyloxy)iodobenzene (BTI):**
  - **CAS:** 2712-78-9
  - **Price:** Sigma-Aldrich 25 g / 135.00 €, Acros Organics 50 g / 131.50 €
  - **Melting point:** 121-125 °C
  - **Aspect:** white powder
  - **Risks:** Irritant



= $PhI(OCOCF_3)_2$

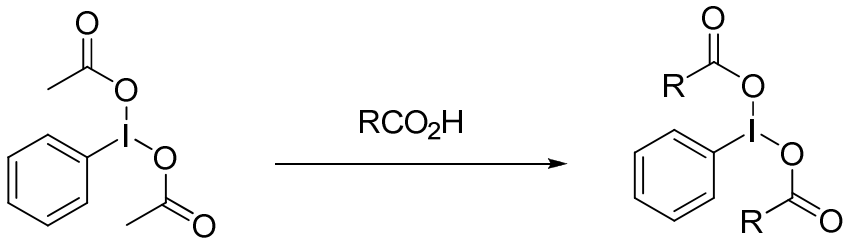
Diacyloxy iodoarenes

- **Preparation:**
  - Oxydation of iodoarenes in the presence of a carboxylic acid (1)



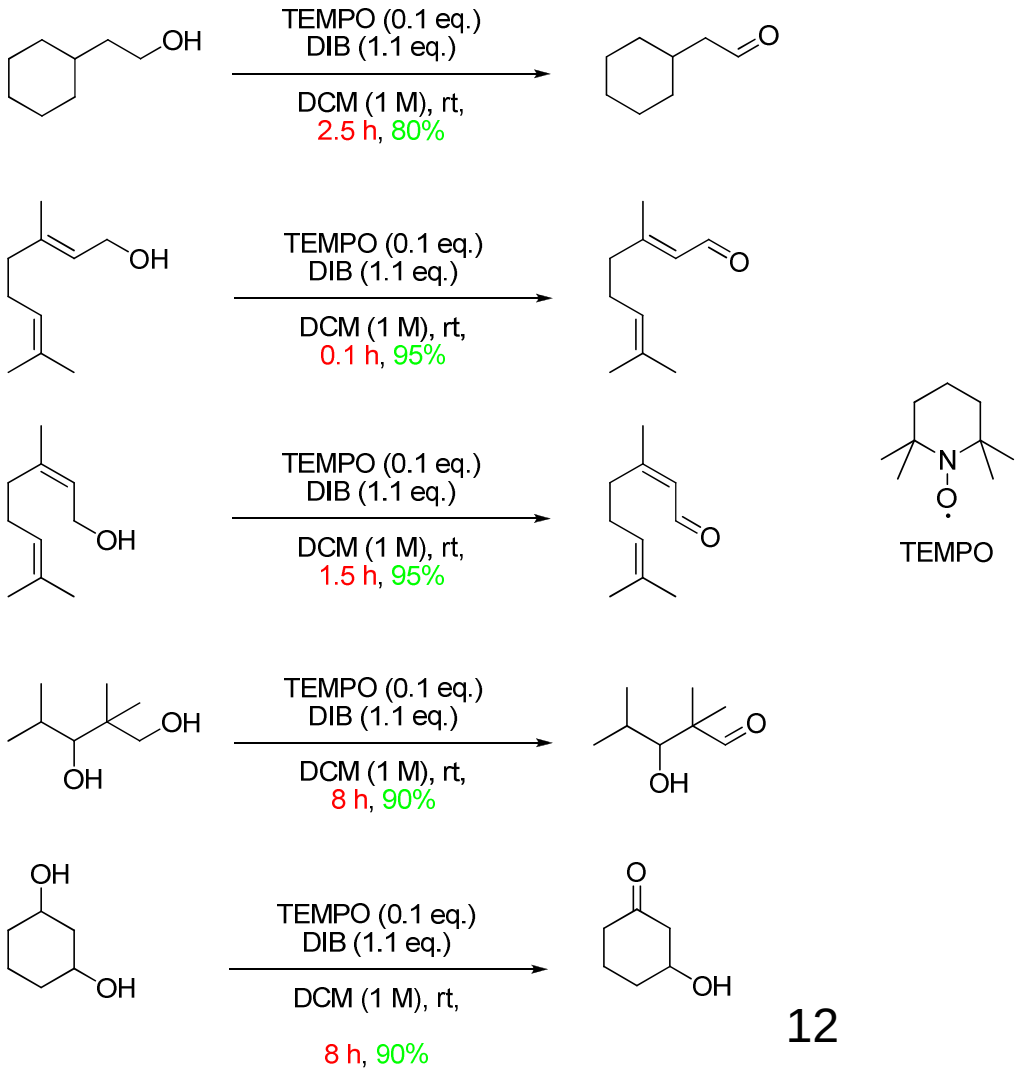
Koser G. F. et al., *Molecules*, 2005, 217-225

  - Ligand exchange of the readily available DIB (2)



Reactivity towards alcohols

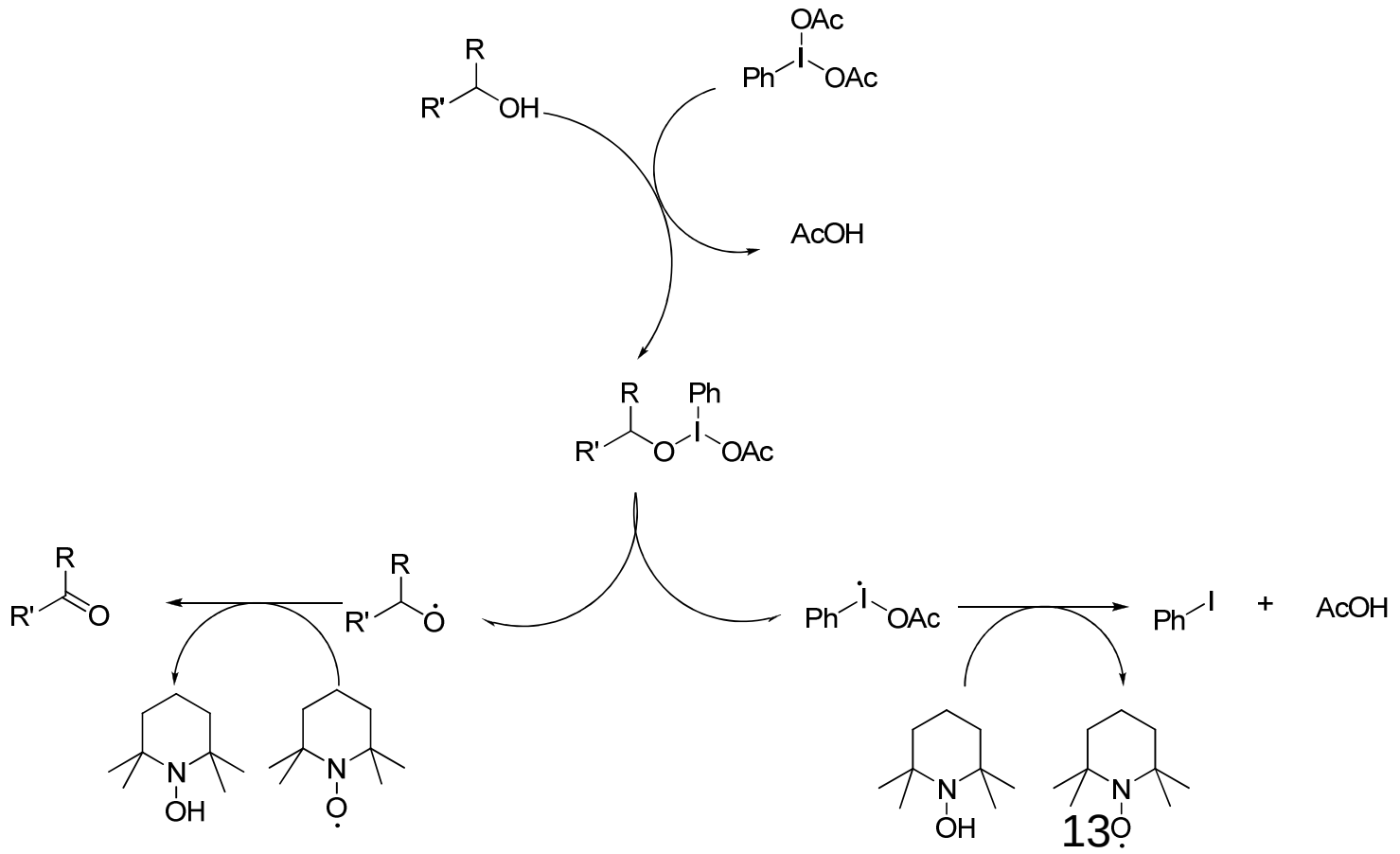
- Examples:



G. Piancatelli et al., *J. Org. Chem.,* 1997, 6974-6977

Reactivity towards alcohols

- Suggested mechanism:



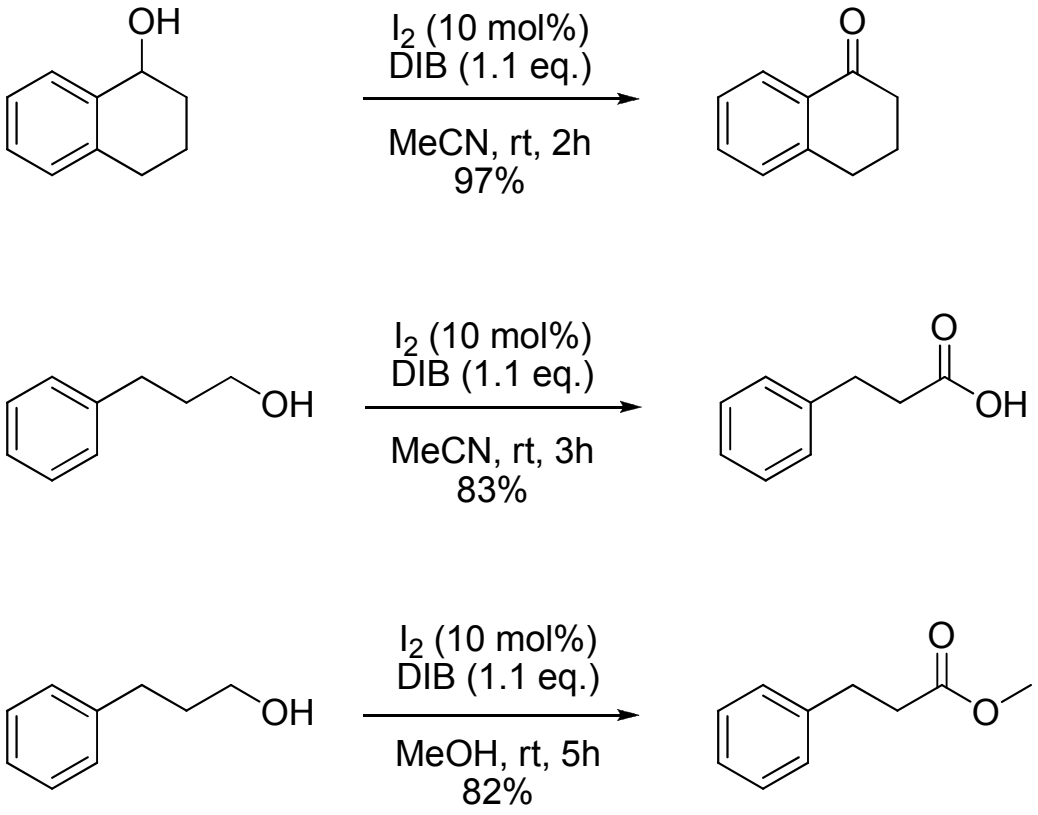
Reactivity towards alcohols

- Advantages:
  - Selective method
  - Very mild reagent
  - Easy purification

- Reaction scope:
  - Primary > secondary alcohol
  - No double bond isomerisation
  - Compatible with various oxydation-sensitive functionnalities

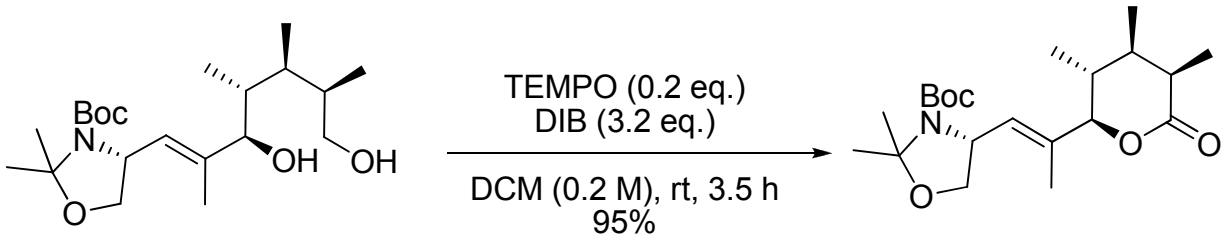
Reactivity towards alcohols

- Primary alcohols can also be converted to esters and lactones

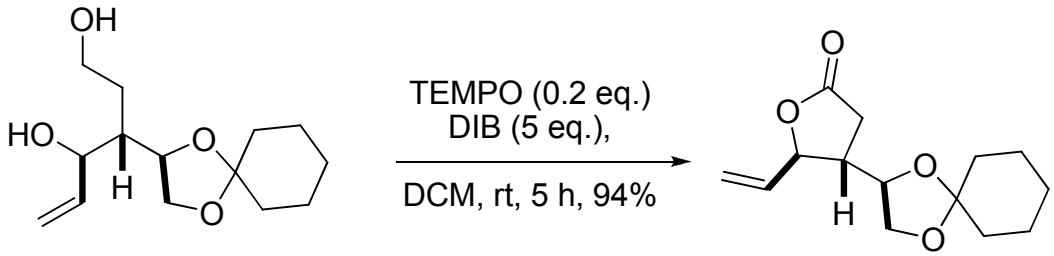


Karade, N. N., *Synlett* **2005**, 2039-2042

Reactivity towards alcohols



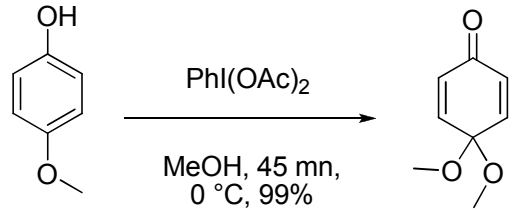
C. J. Forsyth et al., *Tetrahedron Lett.* 2003, 57-59



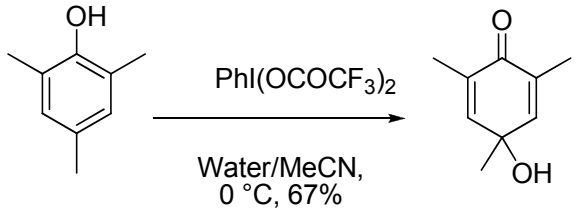
Hale, K. J., *Org. Lett.* **2007**, 1267-1270

Reactivity towards phenols

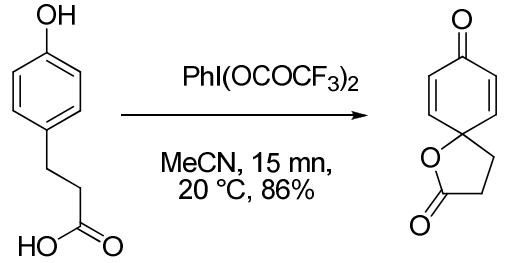
- Examples:



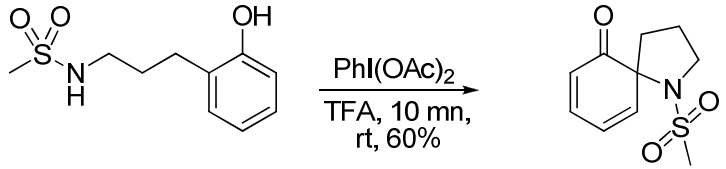
Pelter, A. et al., *J. Chem. Soc., Perkin Trans. 1* **1993**, 1891-1896



Taylor, R. J. K. et al., *J. Chem. Soc., Perkin Trans. 1* **1994**, 2047-2048

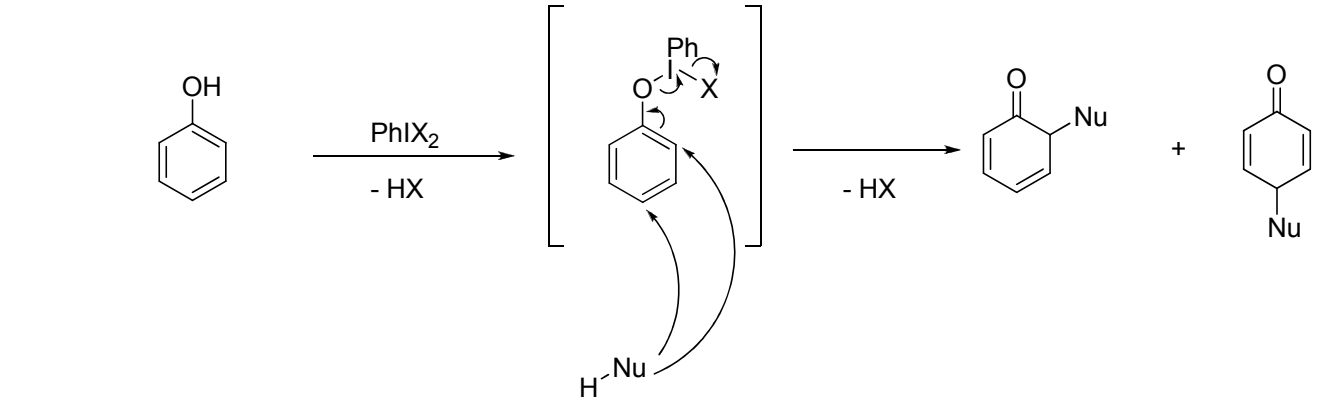


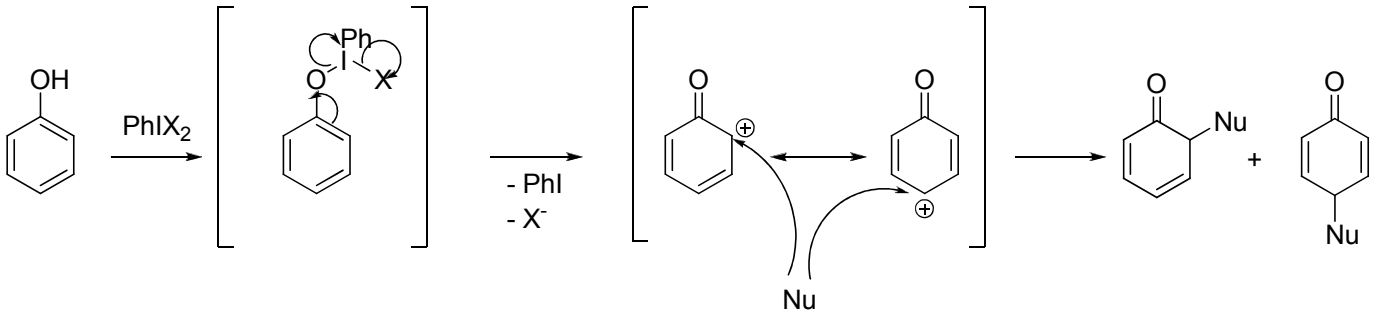
Tamura Y. et al., *J. Org. Chem.* **1987**, 3927-3930



Ciufolini, M. A. et al., *Chem. Eur. J.* **2010**, 13262-13270

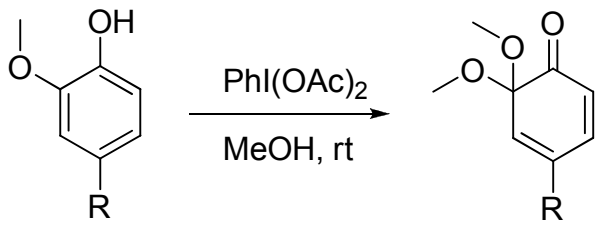
Reactivity towards phenols





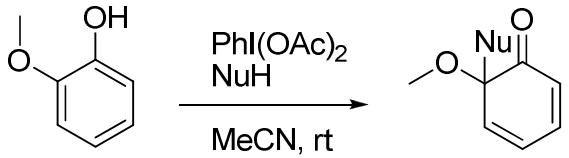
Reactivity towards phenols ortho-substitution

- Regioselectivity
  - Requires a group stabilizing Wheland's intermediate

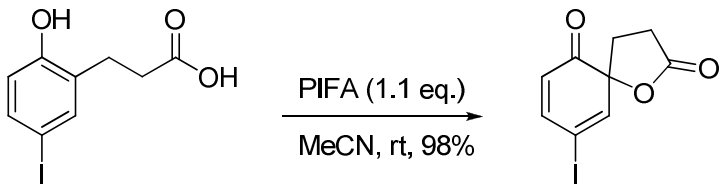


R = H, Alk, C(O)Alk, C(O)OAlk, Cl, Br, F, CN

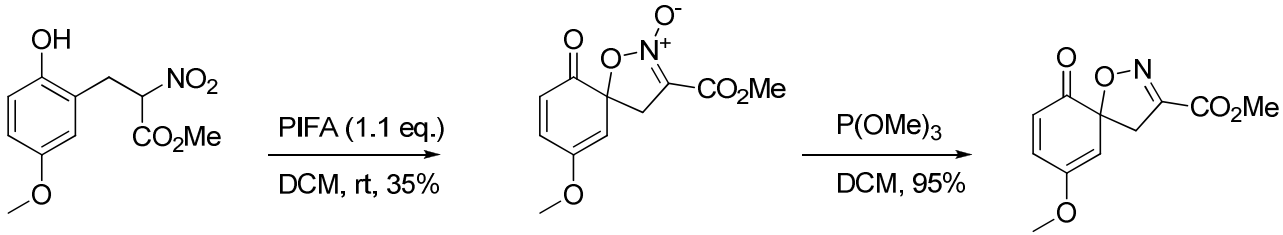
- Nucleophile:
  - Solvent
  - Organoiodine ligand
  - Intramolecular moiety
  - Nucleophile added to the reaction mixture



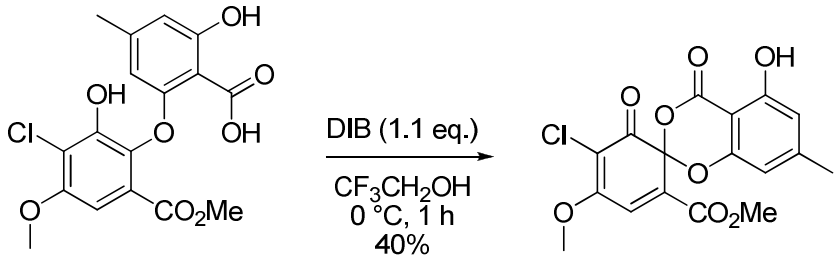
NuH = AcOH, F, Cl, OH, RO, RC(O)O, $F_3CC(O)OH$



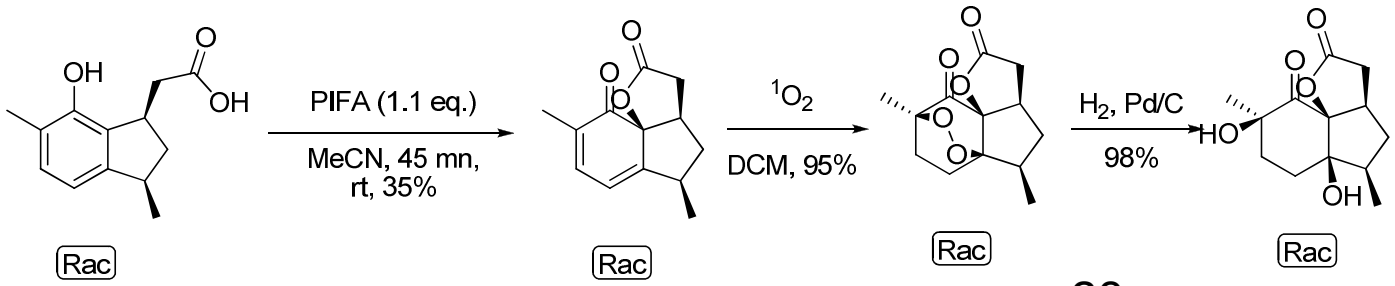
Wood, J. et al., *Org. Lett.* **2002**, 493-496



Pettus, T. R. R. et al., *Org. Lett.* **2007**, 3229-3232



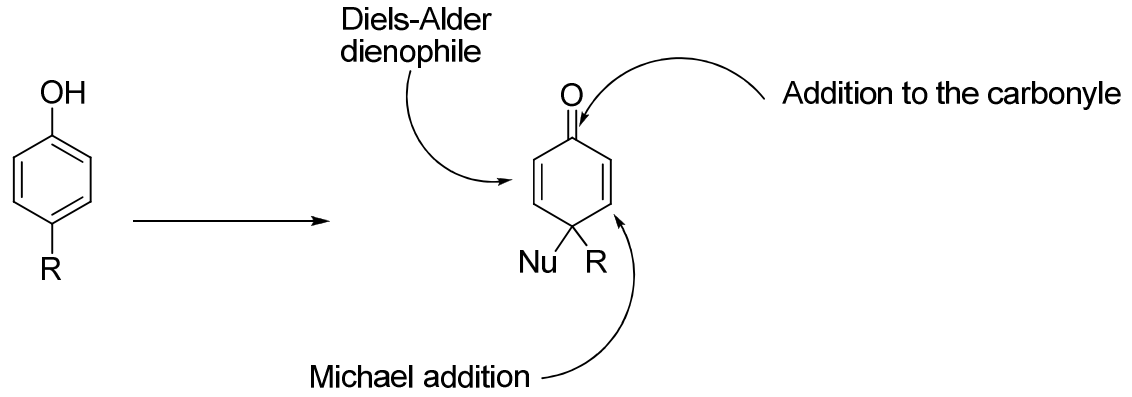
Snider, B. B. et al., *Org. Lett.* **2011**, 4224-4227



Wood, J. et al., *Tetrahedron* **2003**, 8855-8858

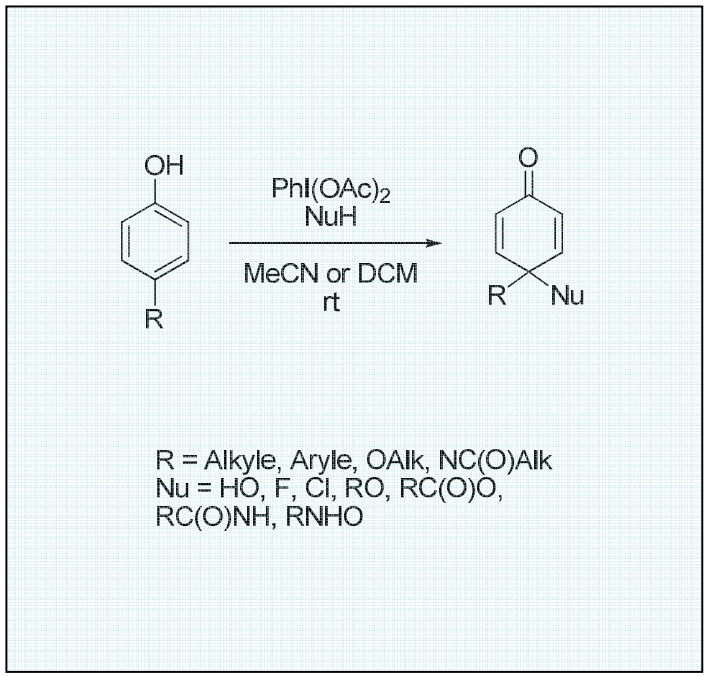
Reactivity towards phenols
para-substitution

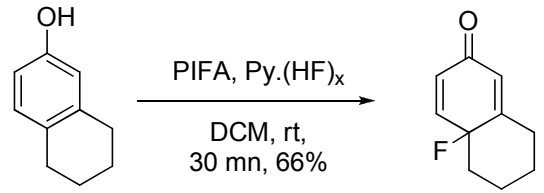
- Much more examples in the litterature:



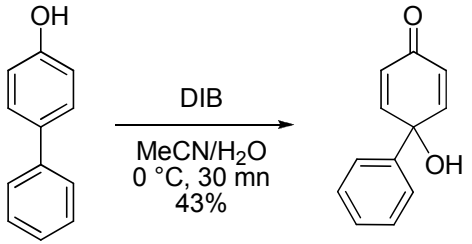
product is a prochiral highly functionnalizable molecule

Reactivity towards phenols
para-substitution

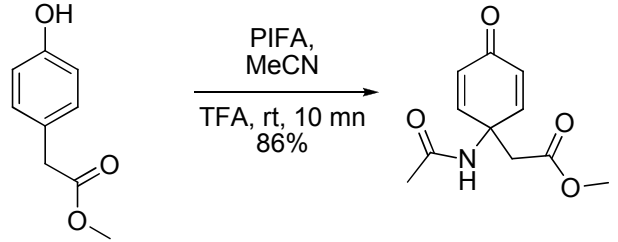




Jouannetaud, M.-P. et al., *Tetrahedron Lett.* **1994**, 2541-2544

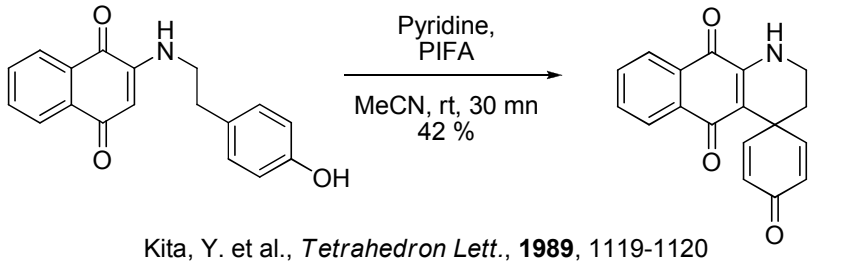


Glover, S. A. et al., *J. Am. Chem. Soc.* **2004**, 7748-7749

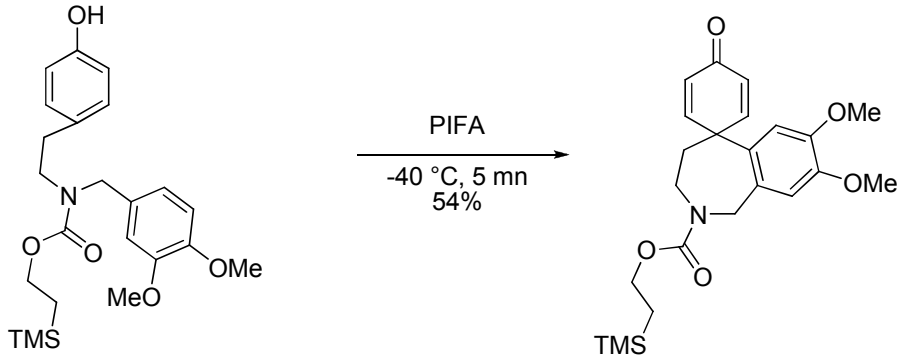


Ciufolini, M. A. et al., *J. Org. Chem.* **2008**, 4299-4301

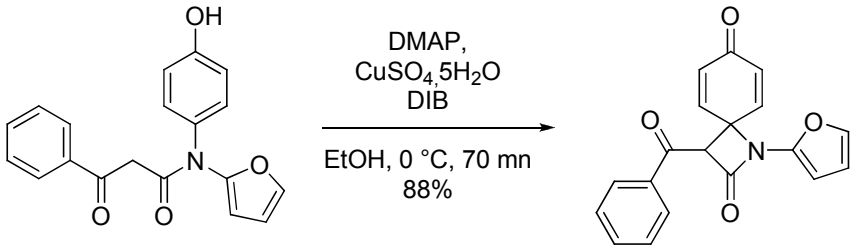
Reactivity towards phenols carbon-carbon bond formation



Kita, Y. et al., *Tetrahedron Lett.*, **1989**, 1119-1120



Kita, Y. et al., *J. Org. Chem.*, **1996**, 5857-5864



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Reactivity towards phenols carbon-carbon bond formation

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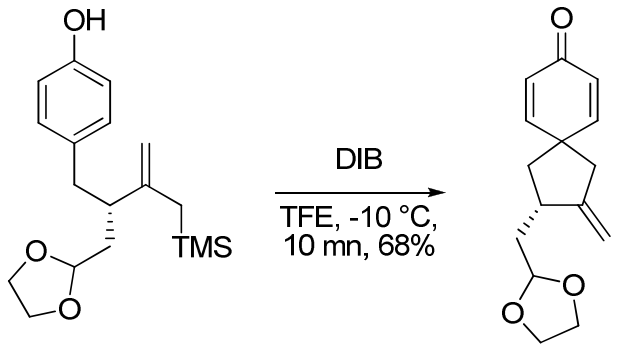
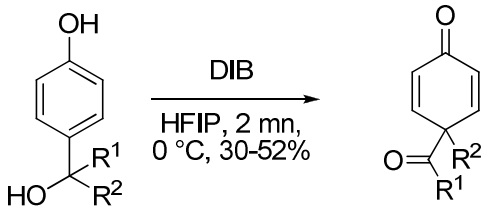


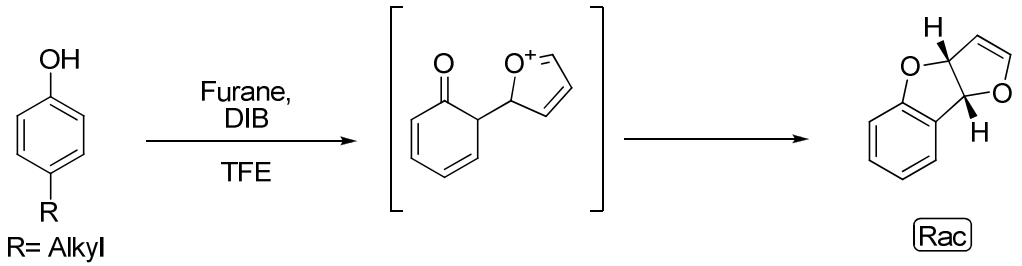
Nicolaou, K. C. et al., *Angew. Chem. Int. Ed.*, **2007**, 3942-3945

Reactivity towards phenols carbon-carbon bond formation



R^1= H, Me
R^2= Alkyle, Allyle, Vinyle, Aryle

Canesi, S. et al., *Org. Lett.* **2009**, 4756-4759



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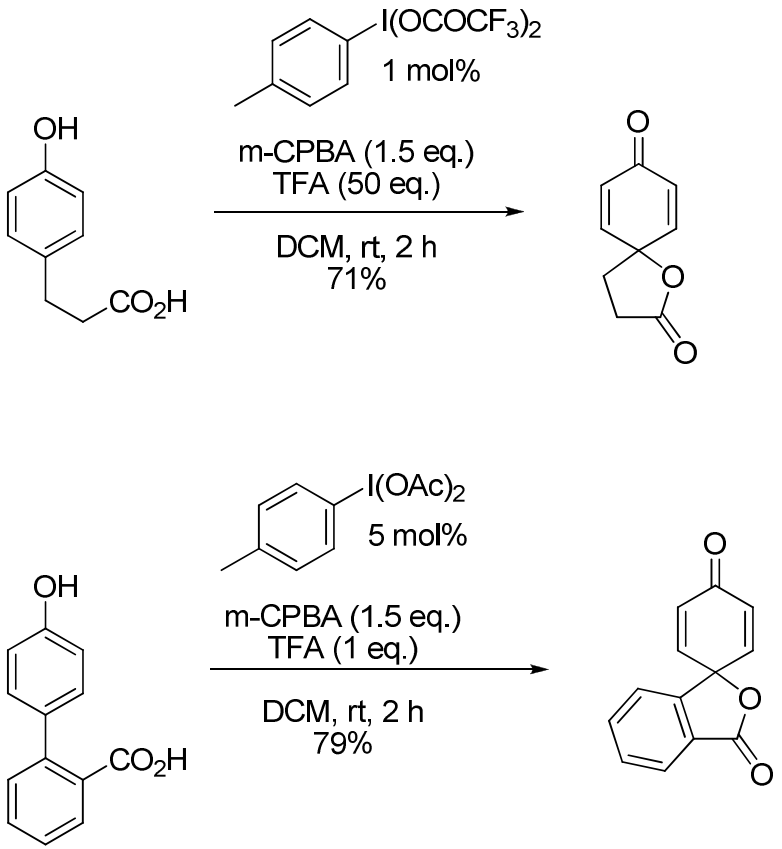
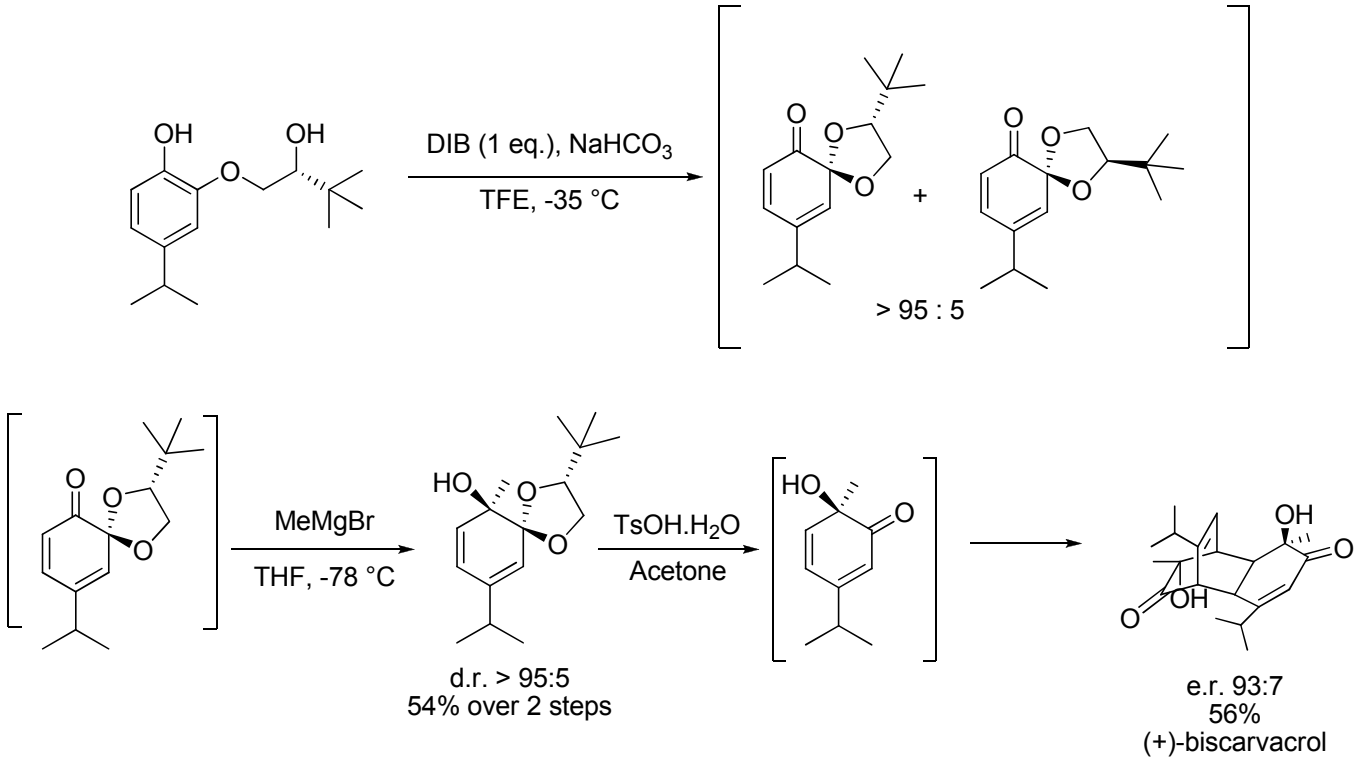
Reactivity towards phenols catalysis



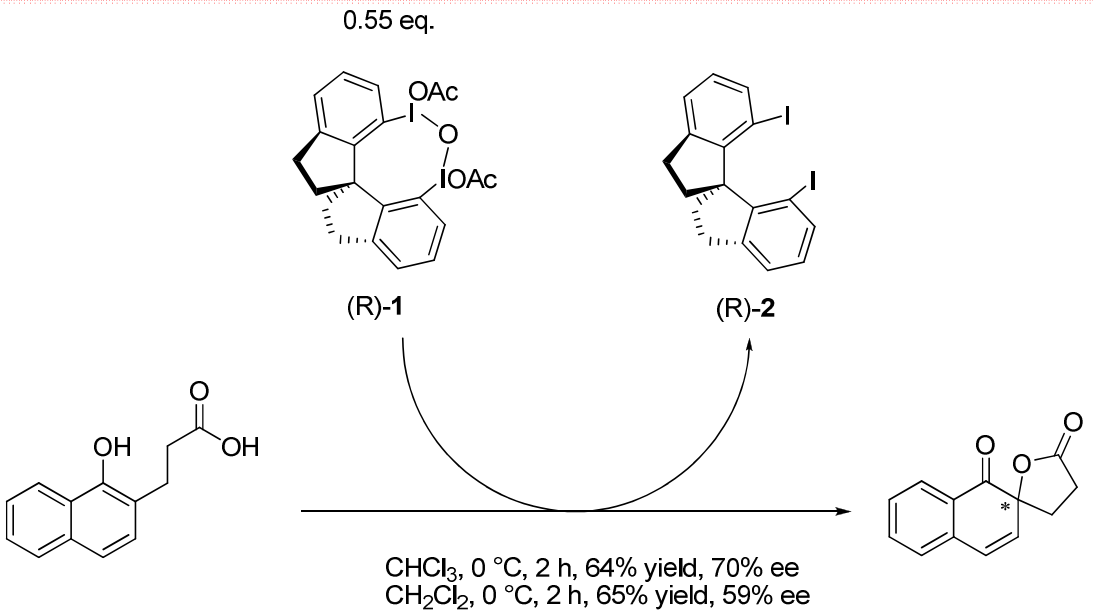
Kita, Y. et al., *Angew. Chem. Int. Ed.*, **2005**, 6193

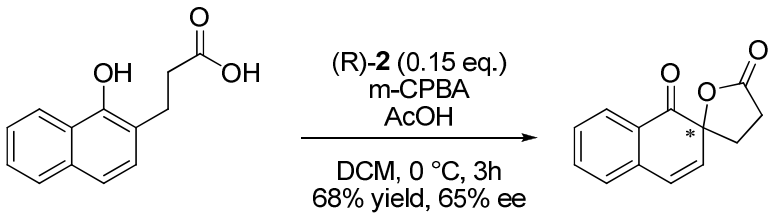
Reactivity towards phenols chirality



Quideau, S. et al., *Angew. Chem. Int. Ed.* **2008**, 3552-3555

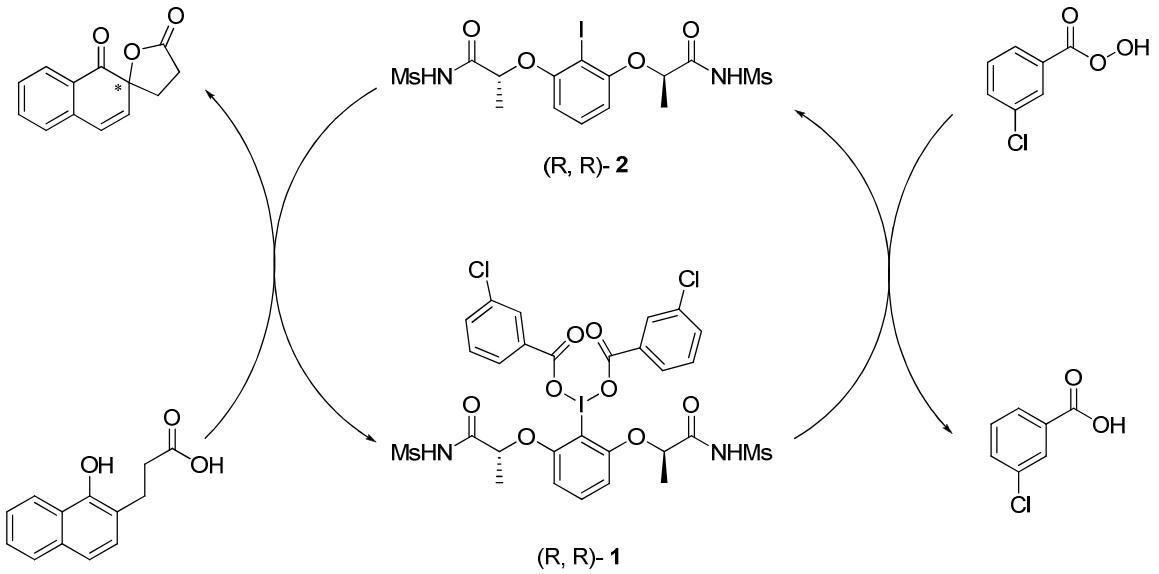
Reactivity towards phenols chirality

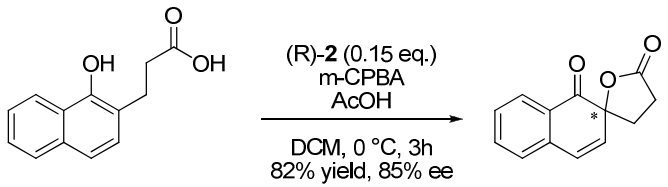




Kita, Y. et al., *Angew. Chem. Int. Ed.* **2008**, 3787-3790

Reactivity towards phenols chirality

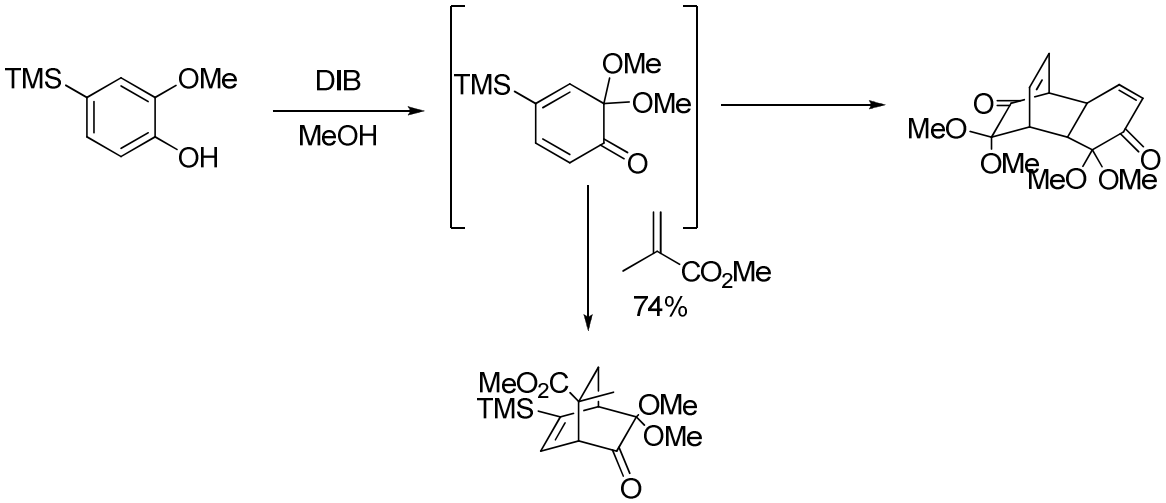




Ishihara, K. et al., *Angew. Chem. Int. Ed.* **2010**, 2175-2177

Reactivity towards phenols tandem oxydation/Diels-Alder reactions

- Shortcoming: some product dimerise by Diels-Alder reactions



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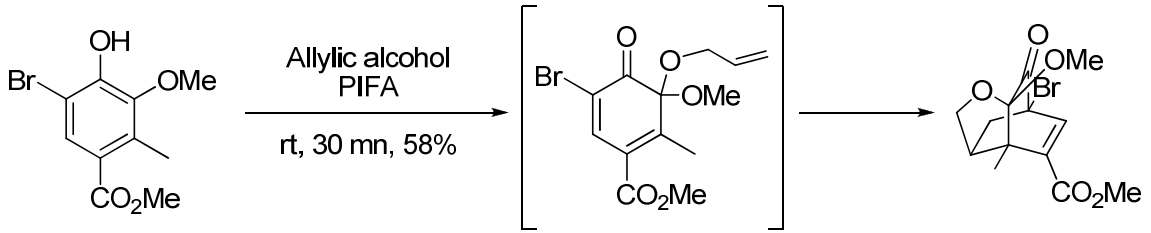
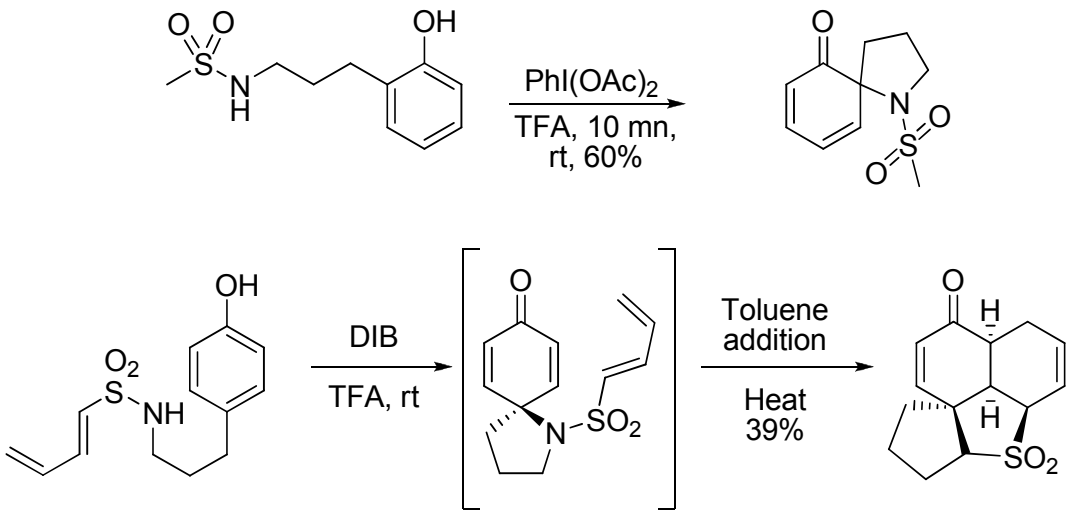


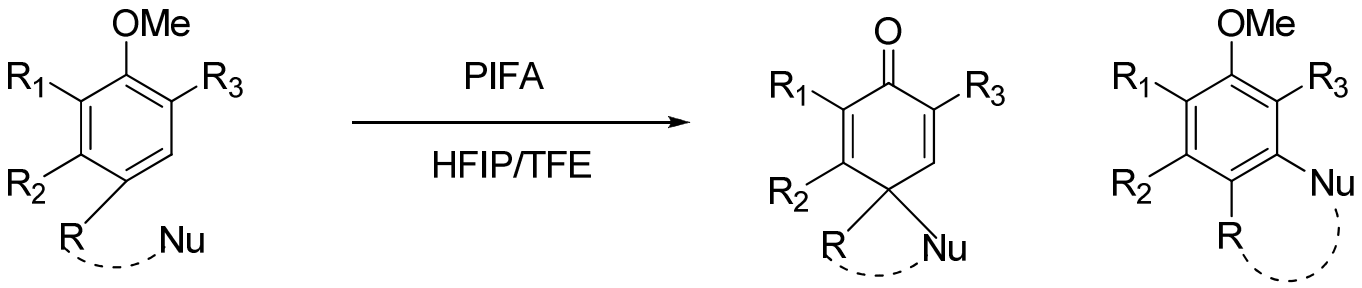
Danishefsky, S. J. et al., *Org. Lett.* **2006**, 5693-5695

Reactivity towards phenols tandem oxydation/Diels-Alder reactions



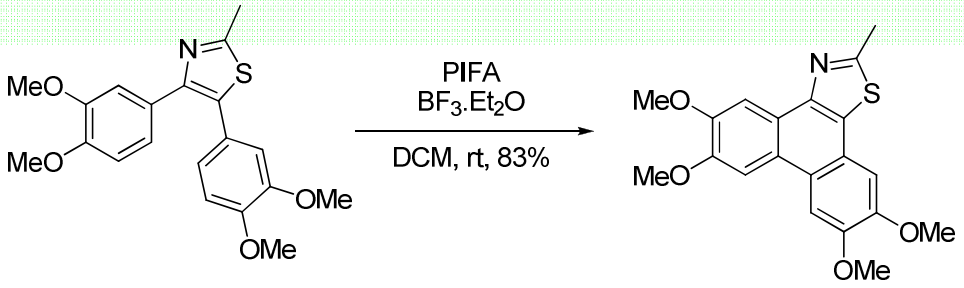
Ciufolini, M. A. et al., *Chem. Eur. J.* **2010**, 13262-13270

Reactivity towards phenol ethers

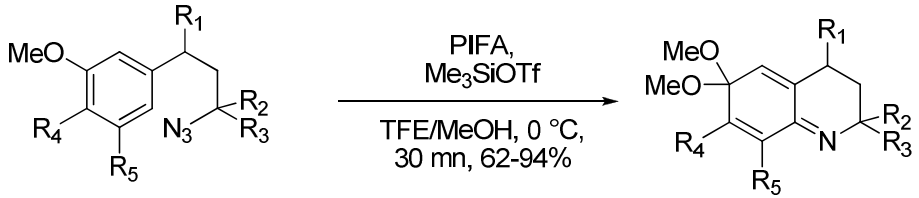


R = alkyl, alkoxy, halogen, etc…
Nu = external or internal nucleophilic group

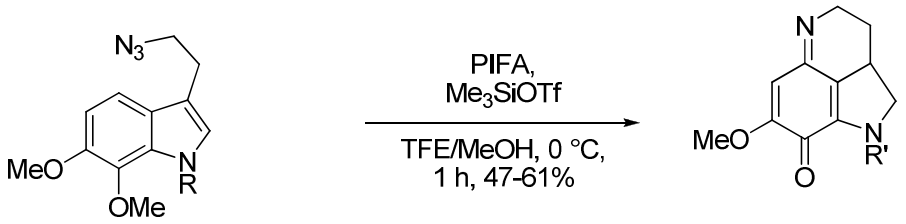
Reactivity towards phenol ethers



Dominguez, E., *Tetrahedron Lett*. **1999**, 3479



R_1, R_2, R_3 = H, Me
R_3, R_4 = H, OMe



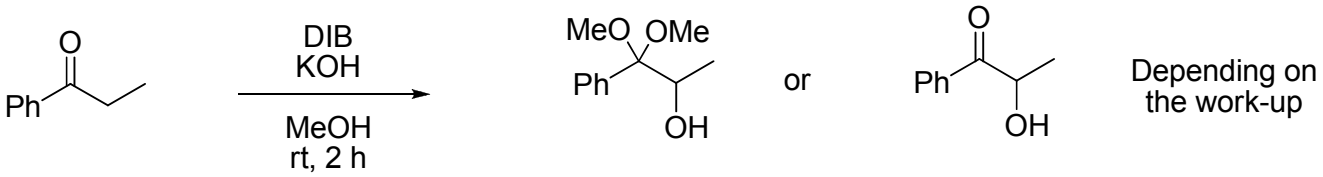
R= Ts, Cbz, Ac, Bz

R' = Ts, Cbz, H

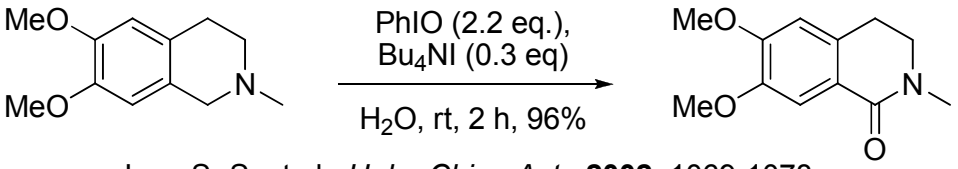
Kita, Y. et al., *J. Chem. Soc., Chem. Commun.*, **1999**, 143

A glimpse of iodine (III) chemistry

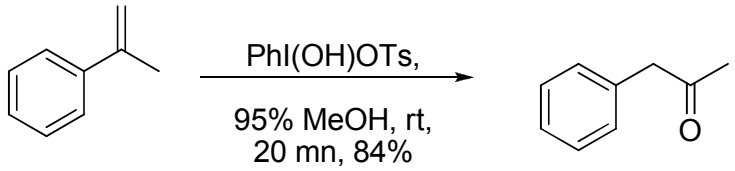
Moriarty oxydation



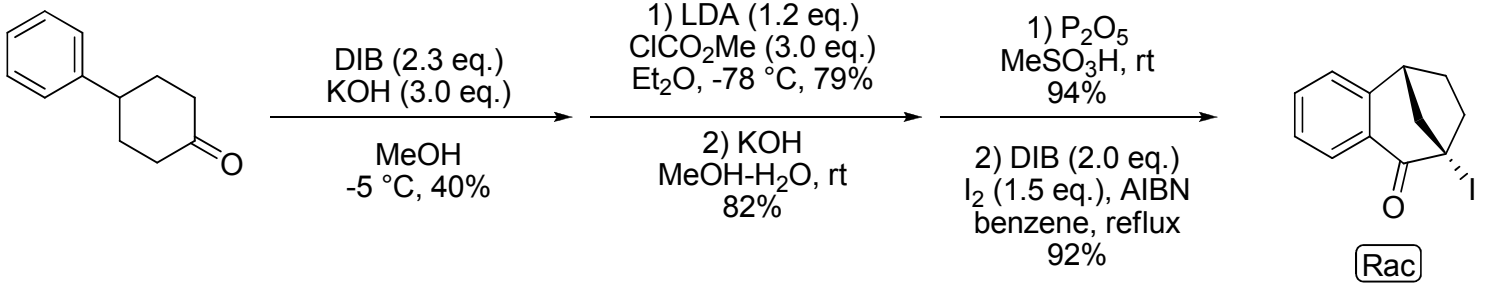
Frye, S. V. et al., *J. Am. Chem. Soc.*, **1992**, 1778-1784



Lee, S.-S. et al., *Helv. Chim. Acta* **2002**, 1069-1078



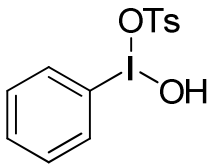
Koser, G. F. et al., *Tetrahedron Lett.* **2004**, 6159

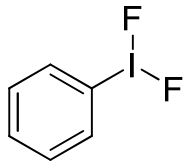


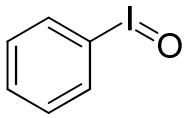
Moriarty, R. M. et al., *J. Med. Chem.*, **1998**, 468

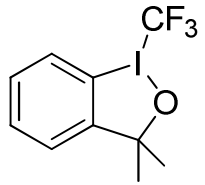
To go further…

- More to know:
  - Rest of DIB chemistry
  - Iodosylbenzene (PhIO)
  - Koser's reagent (PhI(OH)OTs)
  - Togni's Reagent

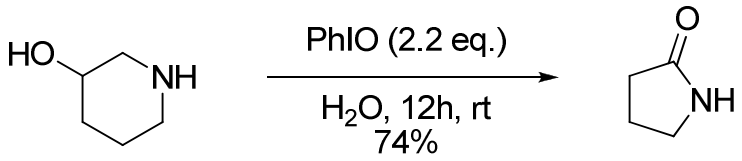








- Challenges:
  - Chirality
  - Mechanism understanding
  - More reactivity still to be discovered



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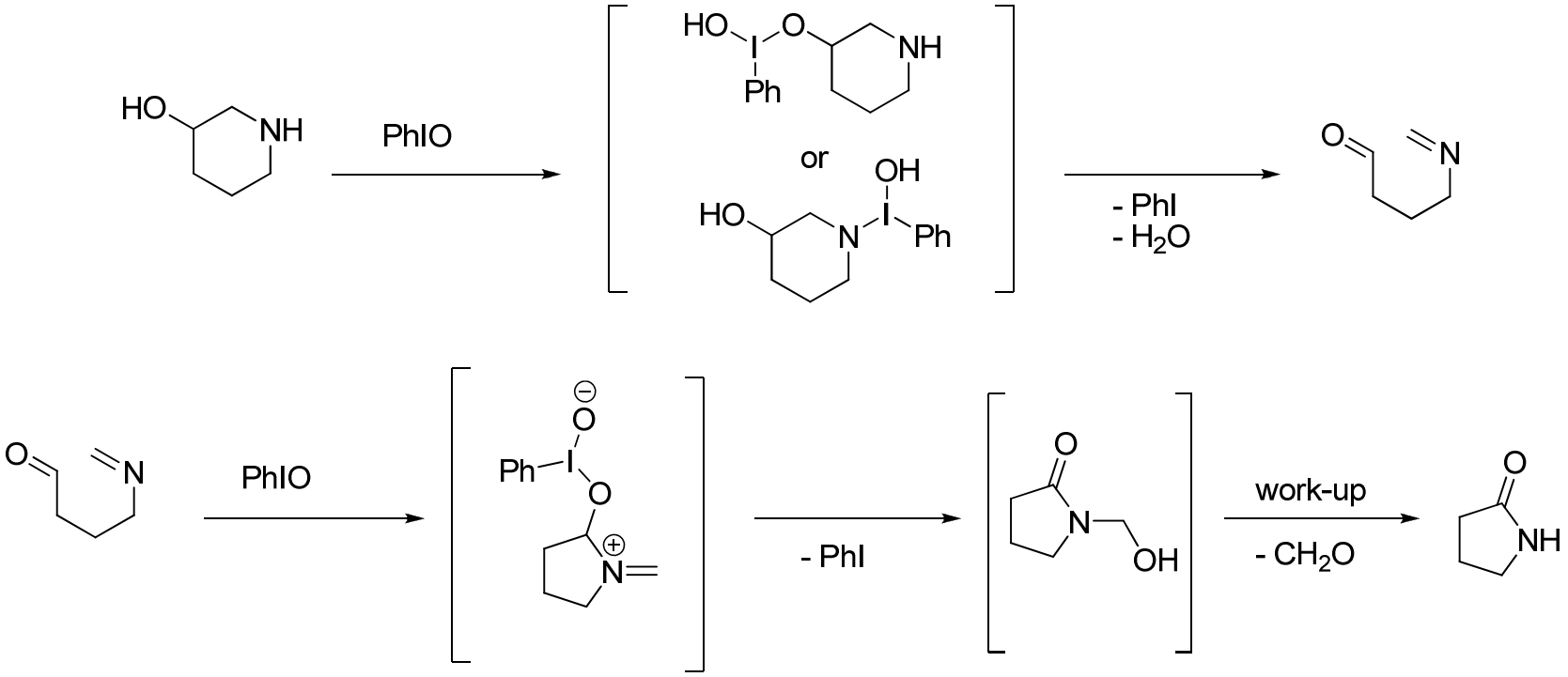

Thanks for your kind attention

Organohypervalent iodine:

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