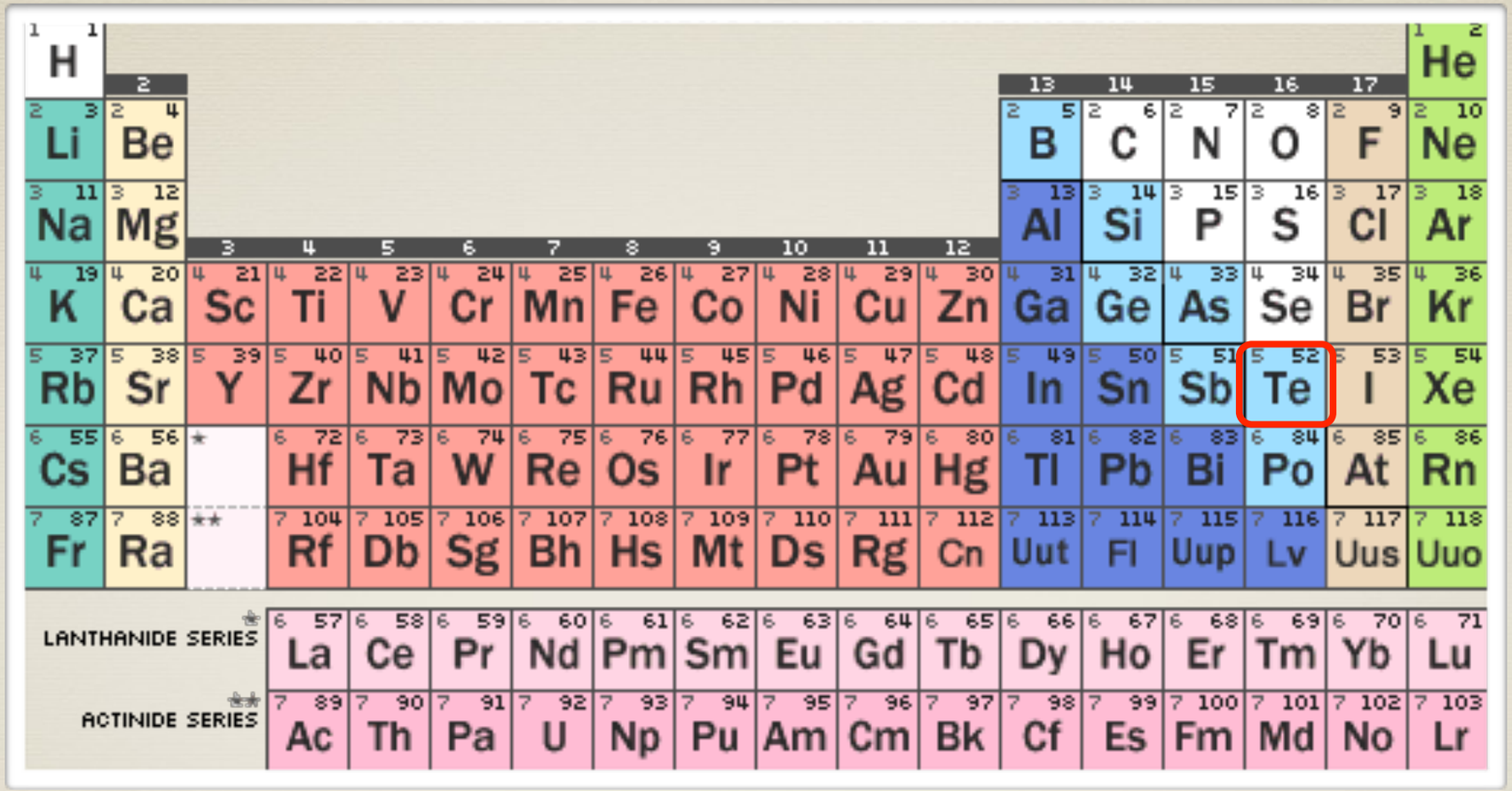
Tellurium (Te) in organic synthesis

Reporter: Lin Deng
Supervisor: Guangbin Dong
Date: Jan 28. 2014

Petragnani, N.; Stefani, H. A. *Tellurium in Organic Synthesis,* 2nd ed.; Academic Press: London, 2007.

Brief introduction to Tellurium (Te)



Some physical properties of the VIA family of elements

Element	Atomic number	Atomic mass	Electronic configuration	Pauling electronegativity	Ionization potential	Ionic radius	Atomic radius
O	8	15.99	$1s^2 2s^2 2p^4$	3.5	13.61	1.40	0.66
S	16	32.06	$2s^2 2p^6 3s^2 3p^4$	2.5	10.36	1.84	1.04
Se	34	78.96	$3s^2 3p^6 3d^{10} 4s^2 4p^4$	2.4	9.75	1.98	1.17
Te	52	127.6	$4s^2 4p^6 4d^{10} 5s^2 5p^4$	2.1	9.01	2.21	1.37

- 2.5 for carbon & large volume atom
- easily polarize Te-C bonds
- Highly reactive

Tellurium (Te) in organic synthesis

- **Several important types of reactions**
  - Reductions
  - Tellurium-Mediated Formation of anion species and their reactions with electrophiles
  - Organotellurium-based ring closure reactions

- **Remove the Tellurium**
  - With formation of new C-C bonds
  - With formation of other functionalities

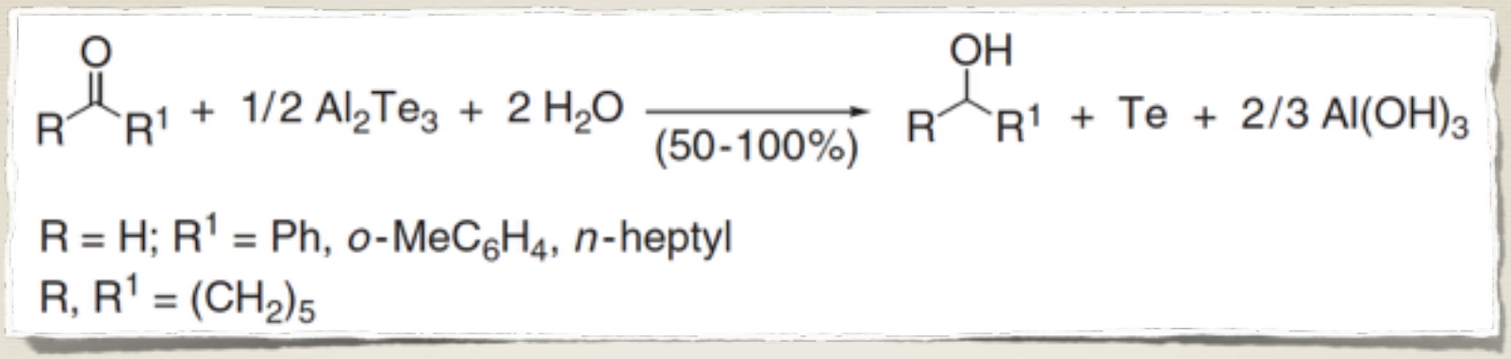
- **Application of Tellurium chemistry**
  - Vinylic tellurides
  - Free radical chemistry

Reductions

with deuterium, 100%PhCHDOD is observed

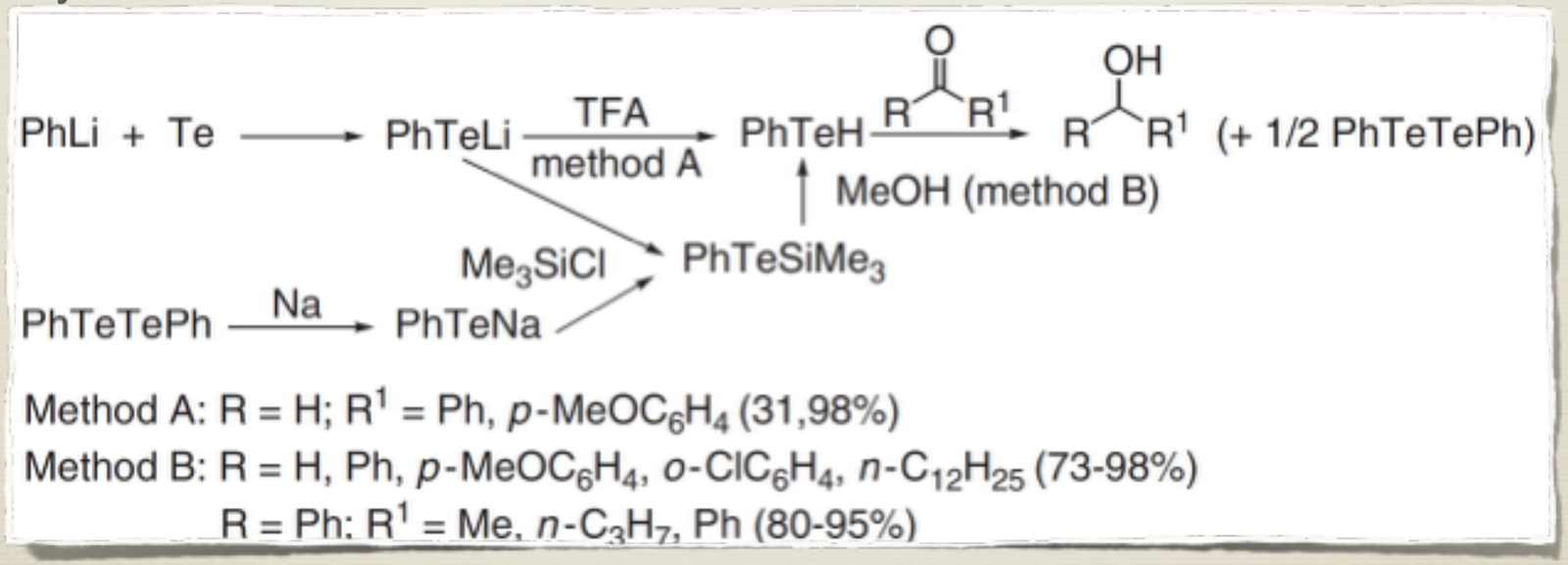
aliphatic ketones and esters are not applicable

- **Reduction of carbonyl compounds**
  - Using hydrogen telluride



Kambe, N.; Kondo, K.; Morita, S.; Murai, S.; Sonoda, N. *Angew. Chem.* **1980**, *92*, 1009.

  - Using phenyl telluride

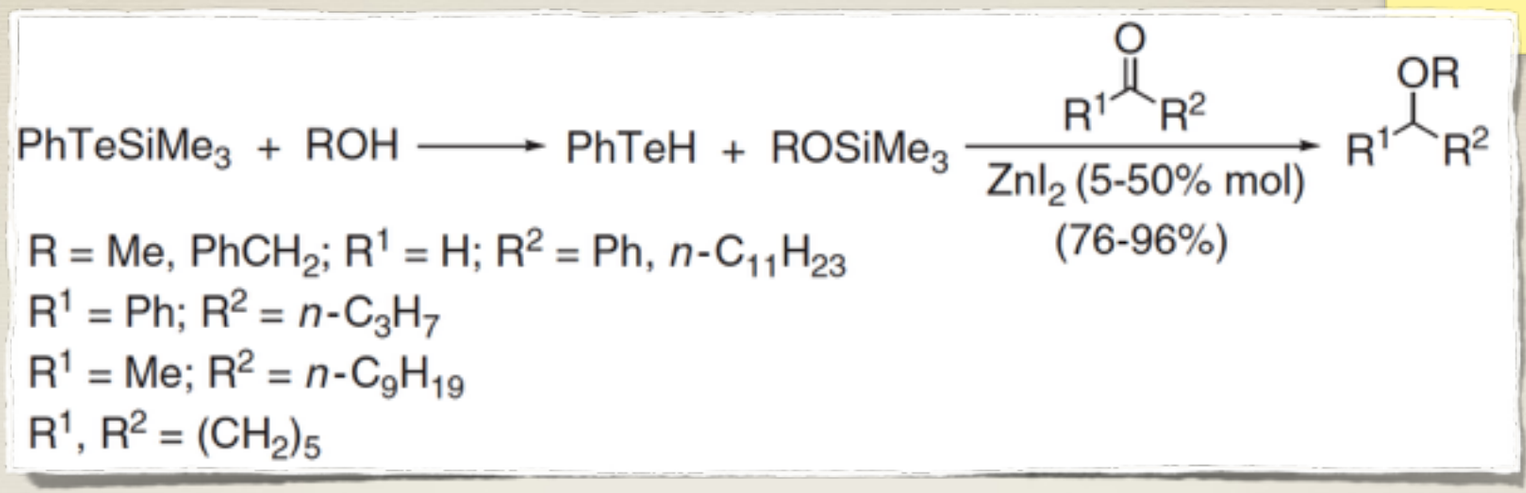


(1) Akiba, M.; Cava, M. P. *Synth. Commun.* **1984**, *12*, 1119. (2) Aso, Y.; Ogura, F. et al. *Nippon Kagaku Kashi* **1987,** 1490.

Aliphatic ketones and esters are not applicable

Reductions

- Using phenyl telluride



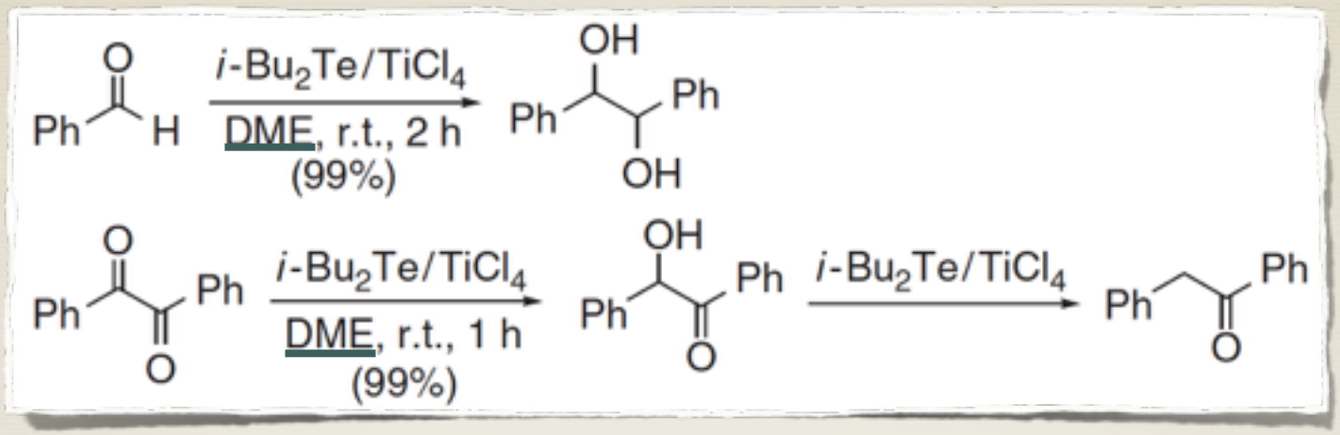
Q1: Why the reaction will give ether instead of alcohol as product in the presence of zinc iodide?

Nagakawa, K.; Osuka, M.; Sasaki, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1987**, 1331.

Reductions

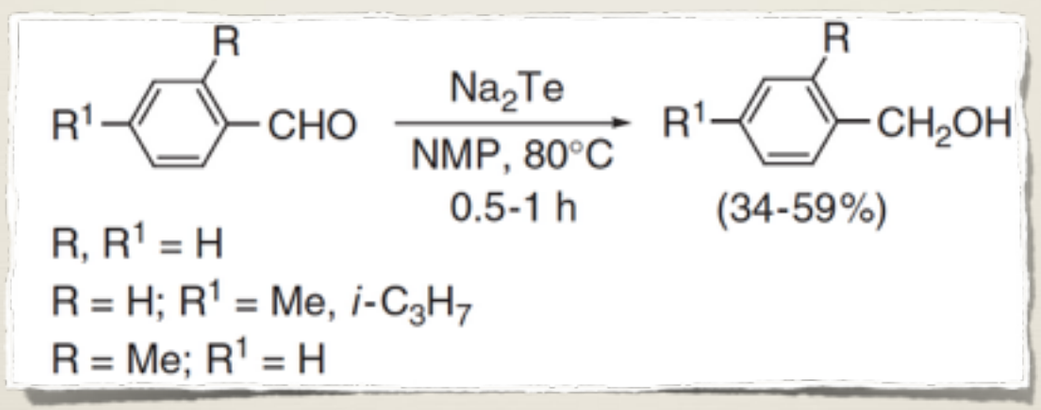
- Using other tellurides

DCM

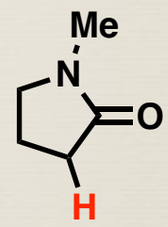


Ti (III) as reducing reagent; Coupling mechanism is unclear

Suzuki, S. H.; Manabe, H.; Enokiya, R.; Hanazaki, Y. *Chem. Lett.* **1986**, 1339.; Suzuki, H.; Hanazaki, Y. *Chem. Lett.* **1986,** 549.



Suzuki, H.; Nakamura, T. *J. Org. Chem.* **1993**, *58*, 241.



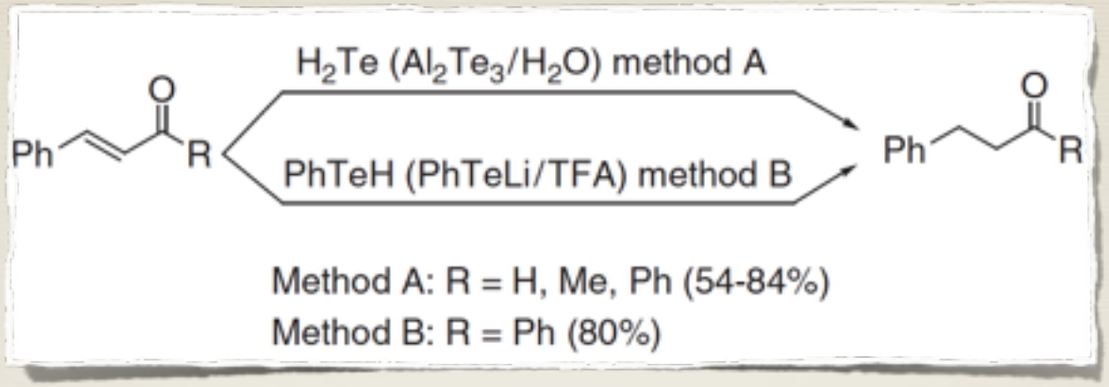
NMP

- Deuterium experiments
- Mechanism involves radical intermediate

generate Ti(III) to reduce the carbonyl group

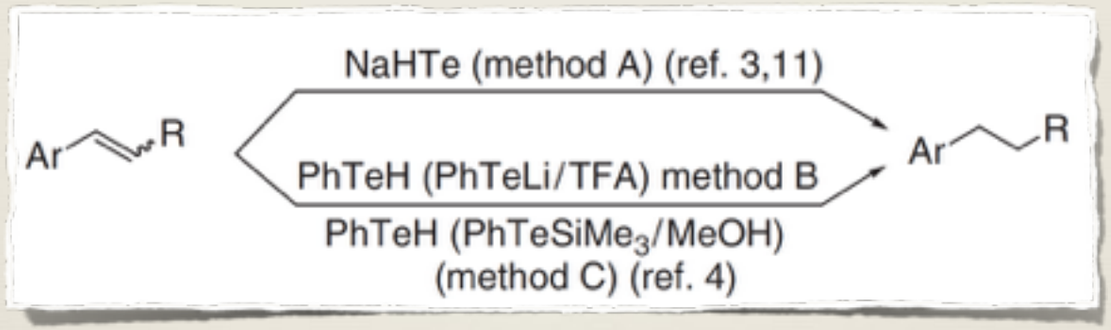
Reductions

- **Selective Reduction of α,β-unsaturated carbonyl compounds**

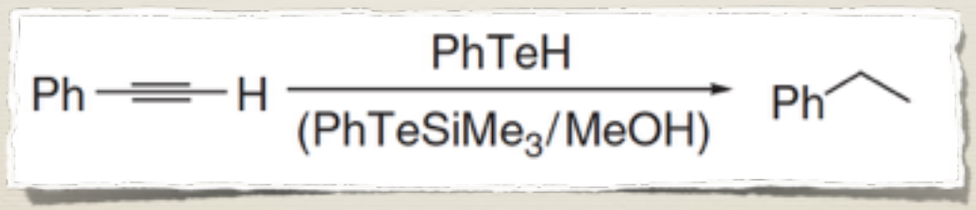


Kambe, N.; Kondo, K.; Morita, S.; Murai, S.; Sonoda, N. *Angew. Chem.* **1980**, *92*, 1009.; Akiba, M.; Cava, M. P. *Synth. Commun.* **1984**, *12*, 1119

- **Reduction of conjugated arylalkenes and arylalkynes**



- Works well with terminal alkenes

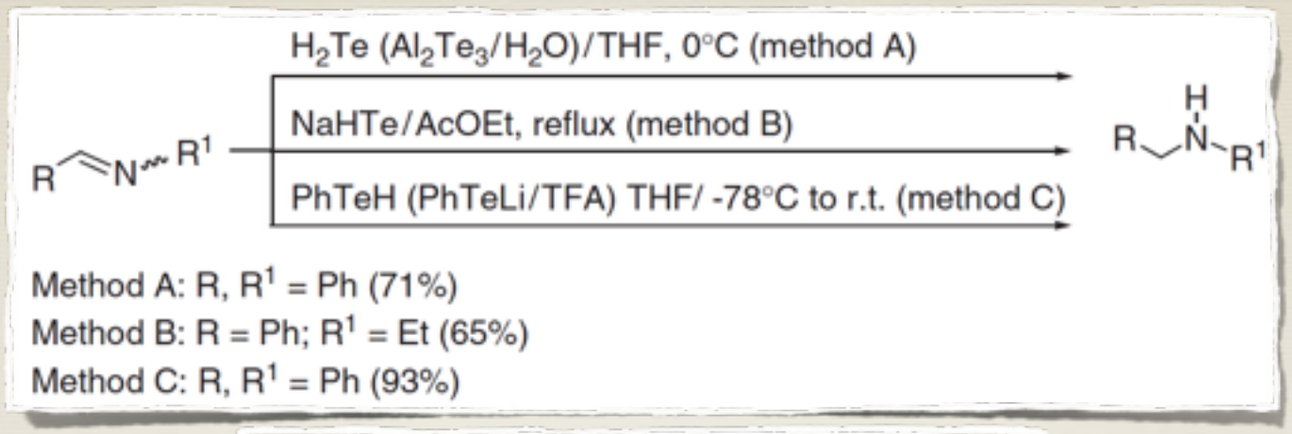


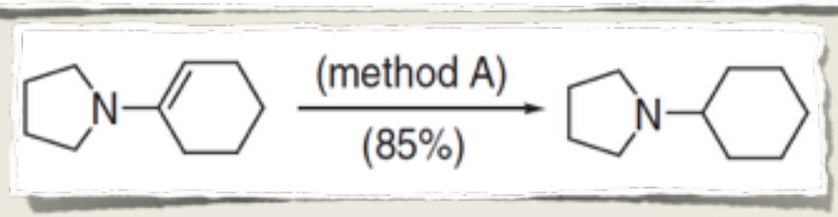
acceptable yield

(1) Akiba, M.; Cava, M. P. *Synth. Commun.* **1984**, *12*, 1119. (2) Aso, Y.; Ogura, F. et al. *Nippon Kagaku Kashi* **1987,** 1490.

Reductions

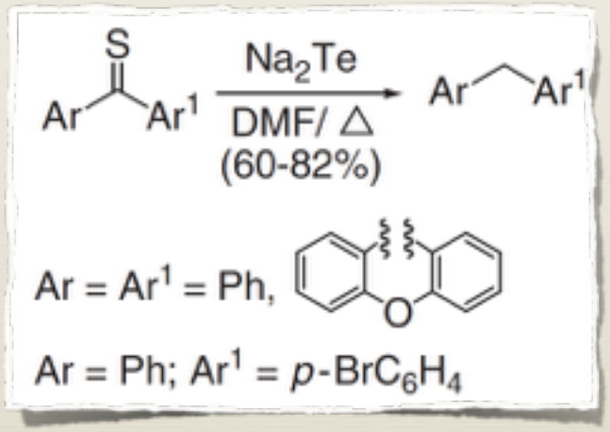
- **Reduction of imines and enamines**





Kambe, N.; Inagaki, T.; Miyoshi, N.; Ogawa, A.; Sonoda, N. *Chem. Lett.* **1987**, *7,* 1275.

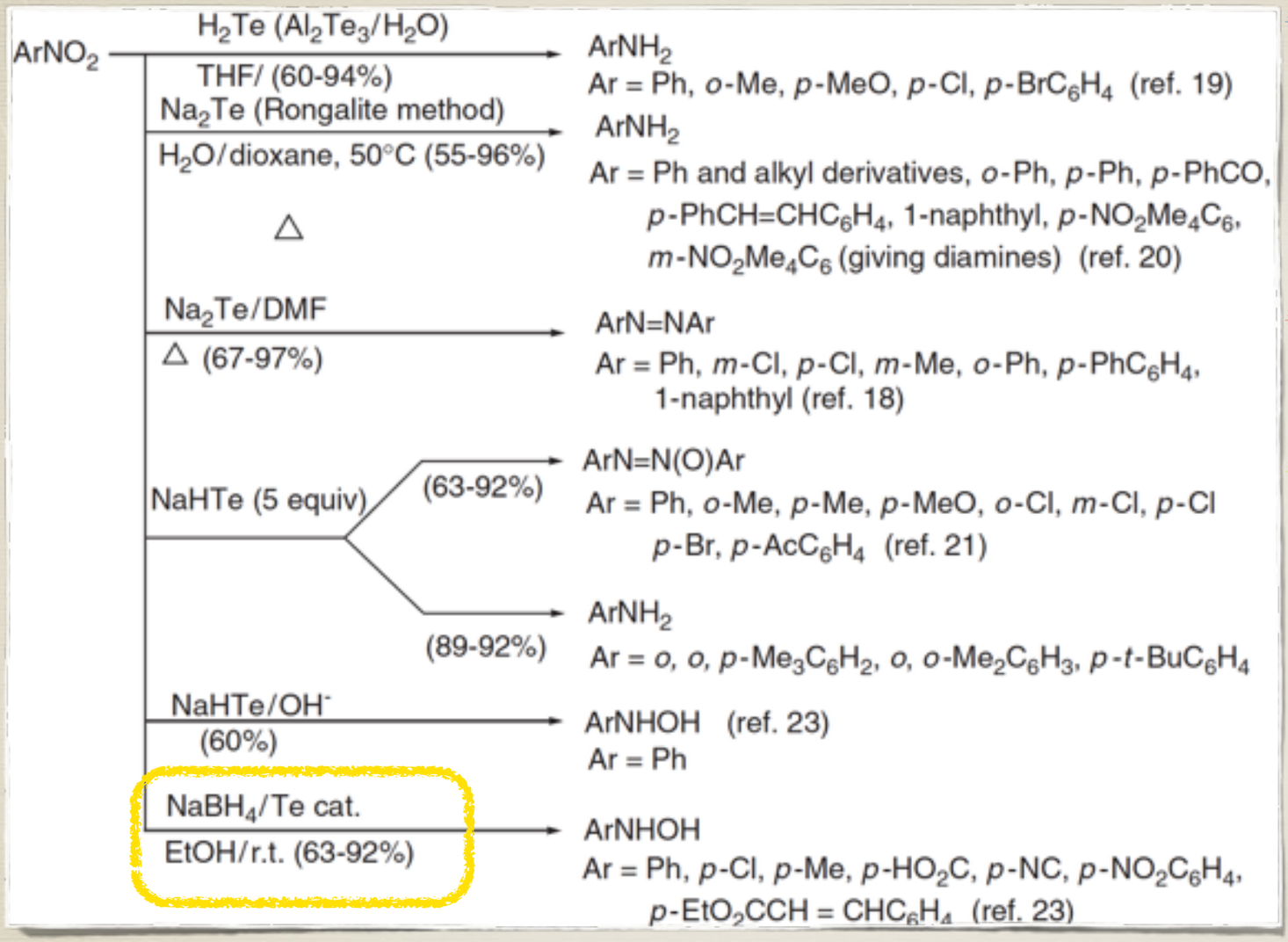
- **Reductive desulphuration and reduction of nitro groups**



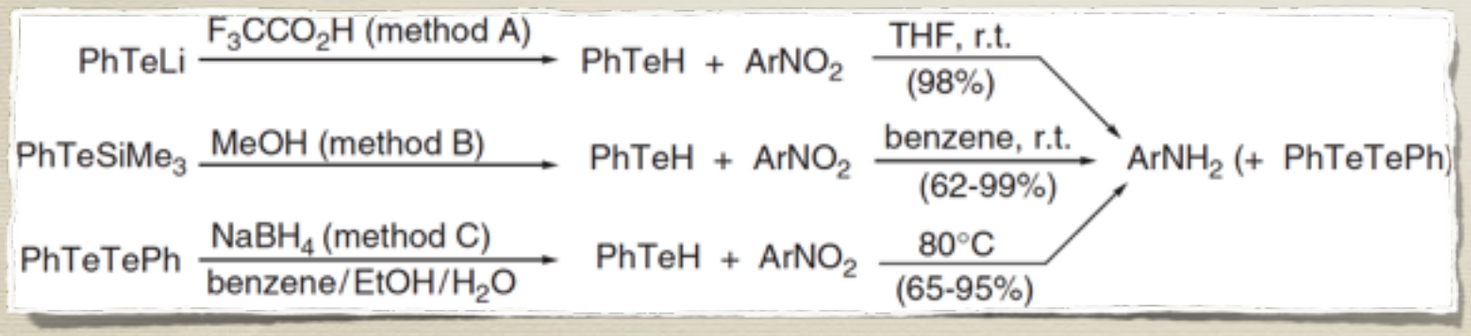
Suzuki, H.; Manabe, H.; Kawaguchi, T.; Inouye, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 771

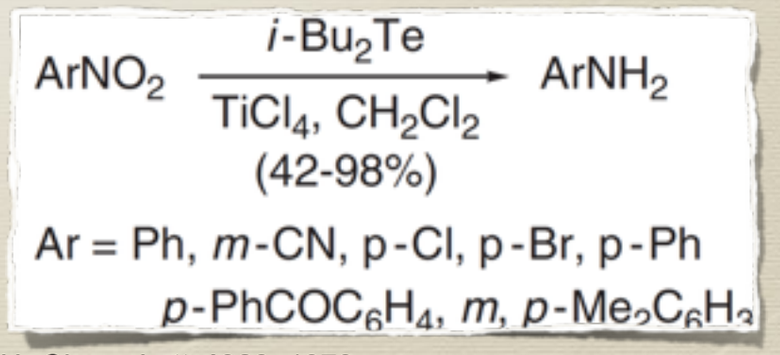
Reductions

- **Reductive desulphuration and reduction of nitro groups**



- Protic solvent — higher reducing ability
- Aprotic solvent — Azo compounds
- Steric hindered nitro compounds are easier to be reduced
- More practical condition



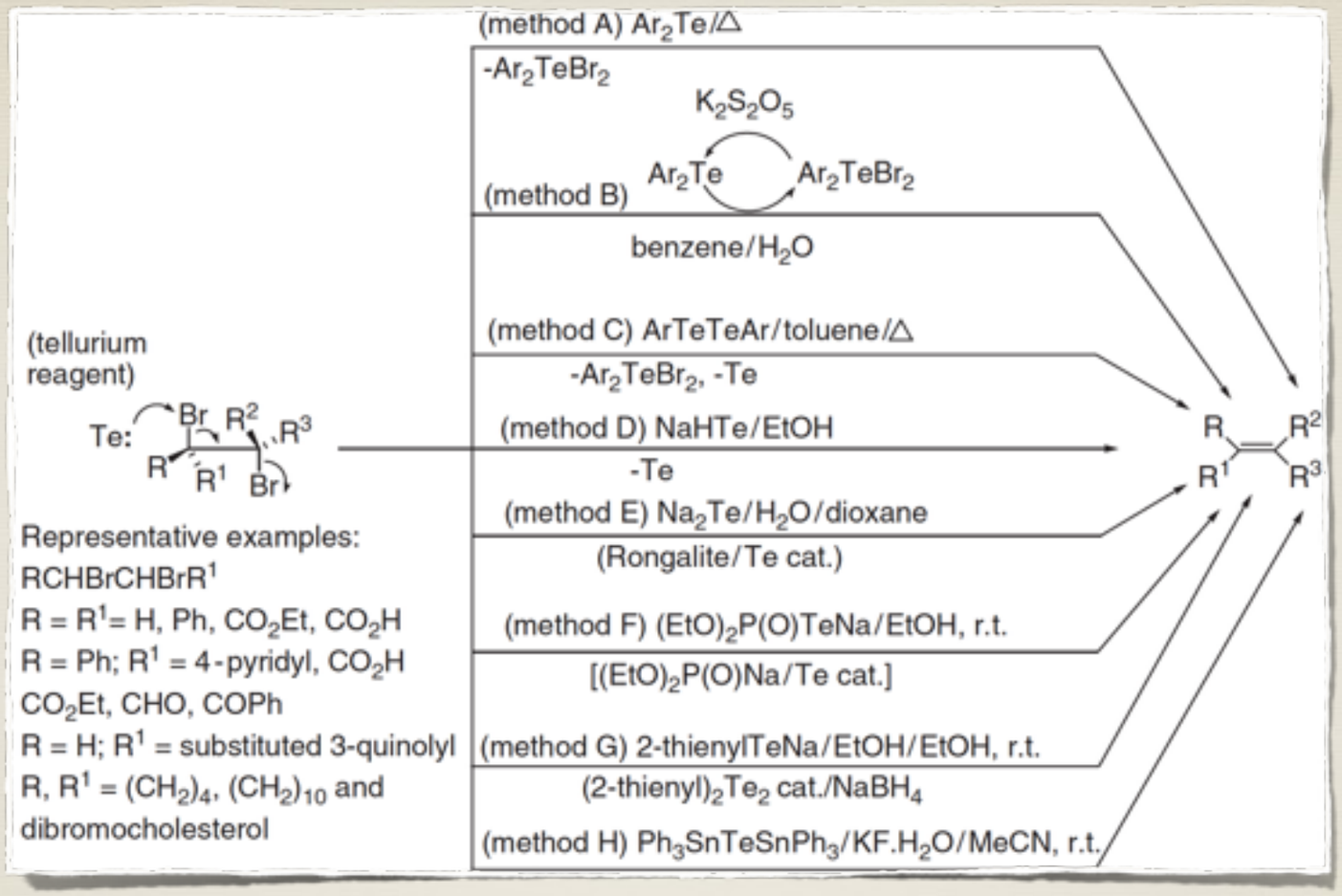


Suzuki, H.; Manabe, H.; Inouye, M. *Chem. Lett.* **1985**, 1671. Osuka, A.; Shimizu, H.; Suzuki, H. *Chem. Lett.* **1983**, 1373.

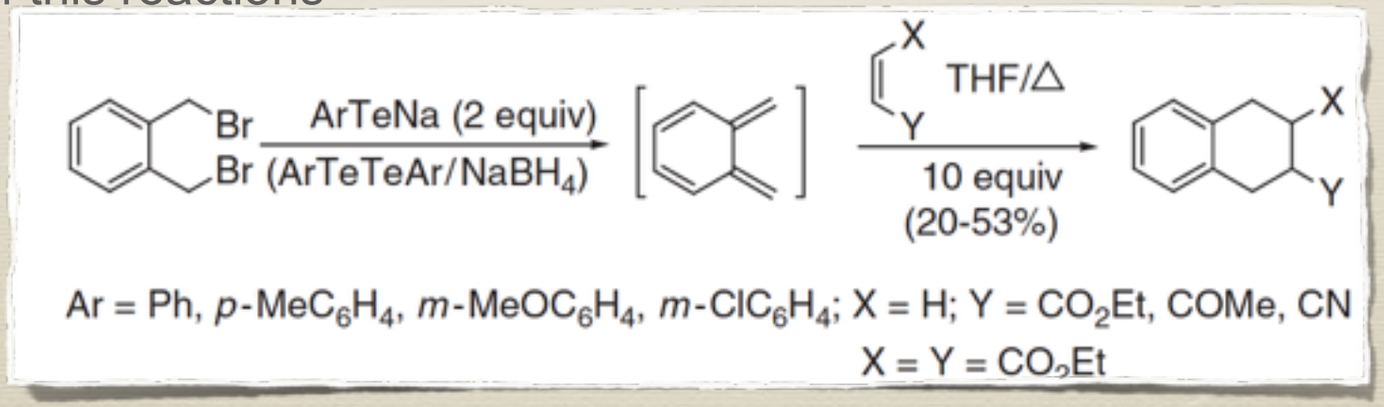
Akiba, M.; Cava, M. P. *Synth. Commun.* **1984**, *14*, 1119. Uchida, S.; Yanada; K.; Yamaguchi, H.; Meguri, H. *Chem. Lett.* **1986**, 1069.

Reductions

- **Debromination**



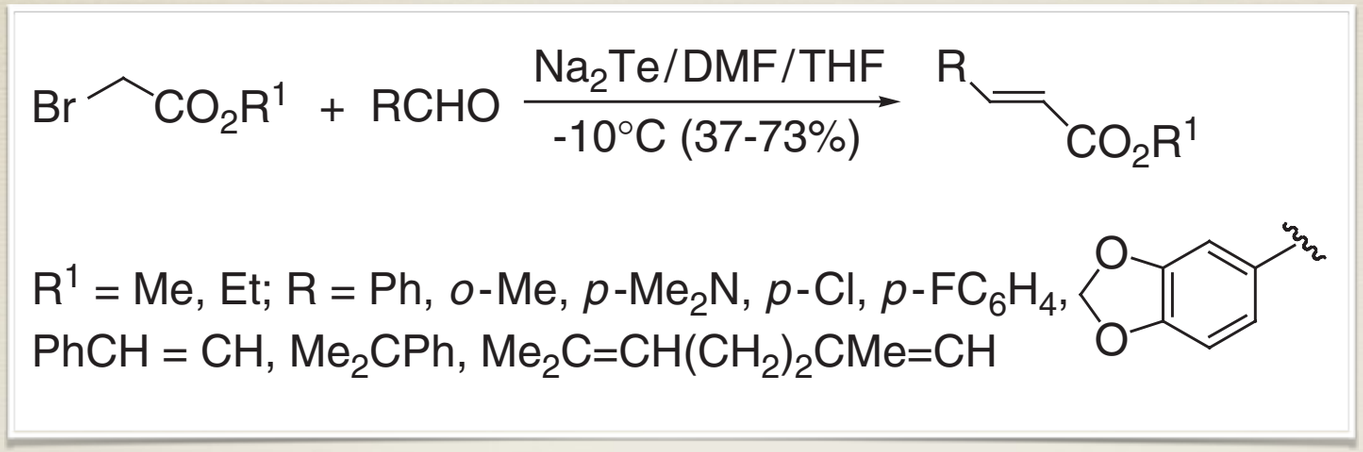
- Application of this reactions



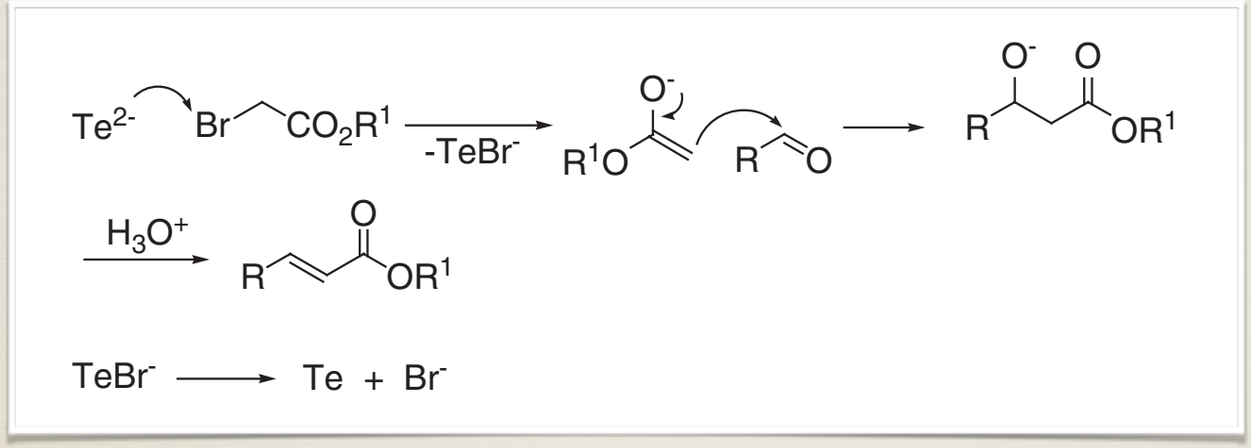
Kambe, N.; Tsukamoto, T.; Miyoshi, N.; Murai, S.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1986,** *59*, 3013.

Formation of anion species and their reactions with electrophiles

- **Reformatsky-type reactions**



In accordance with normal mechanism, Te(-2) as anion

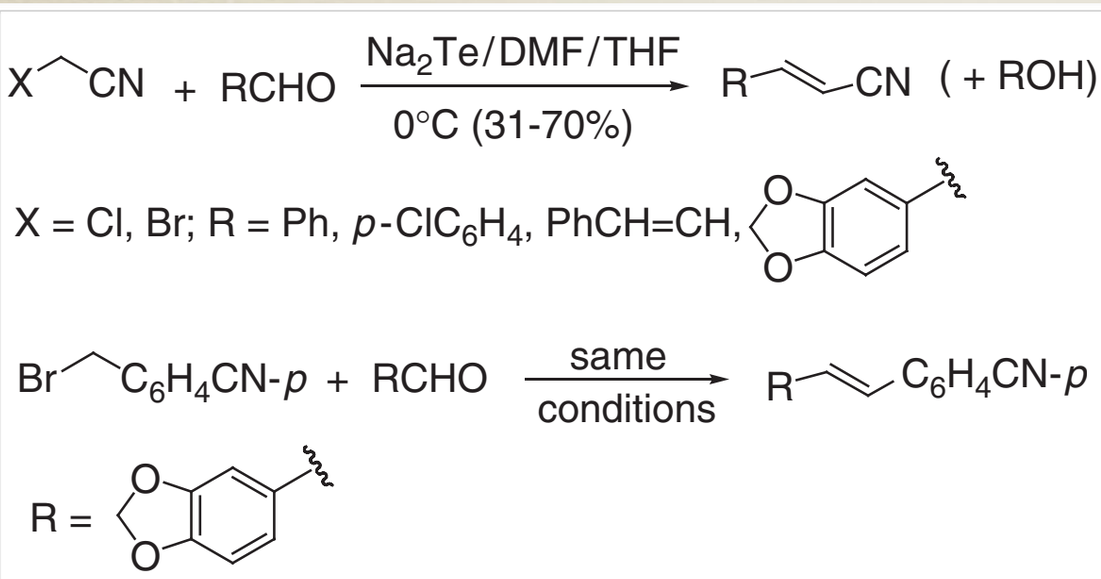


- E configuration of double bond;
- for α,β-unsaturated carbonyl, only 1,2-addition
- ketone is not applicable
- need large excess of bromoacetate and sodium telluride

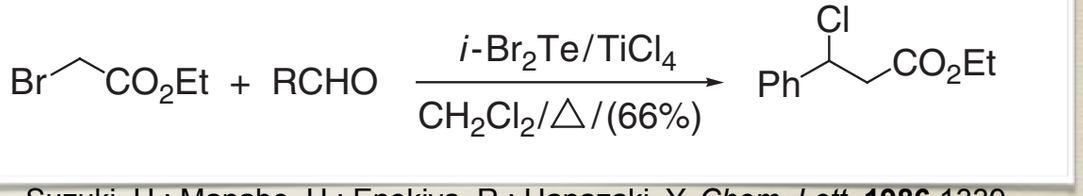
Suzuki, S.; Inouye, M. *Chem. Lett.* **1986**, 403.

Formation of anion species and their reactions with electrophiles

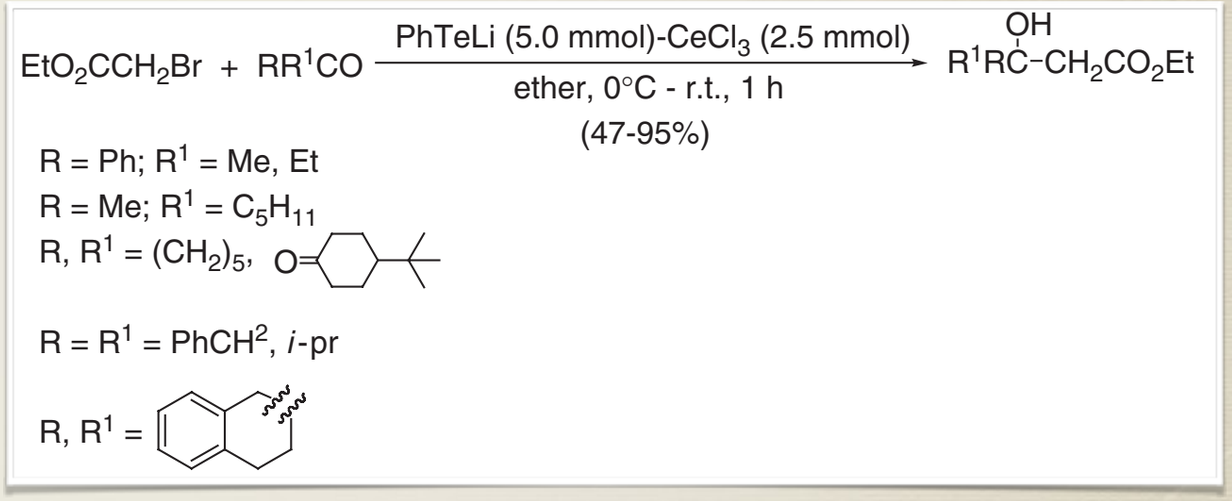
- **Reformatsky-type reactions**

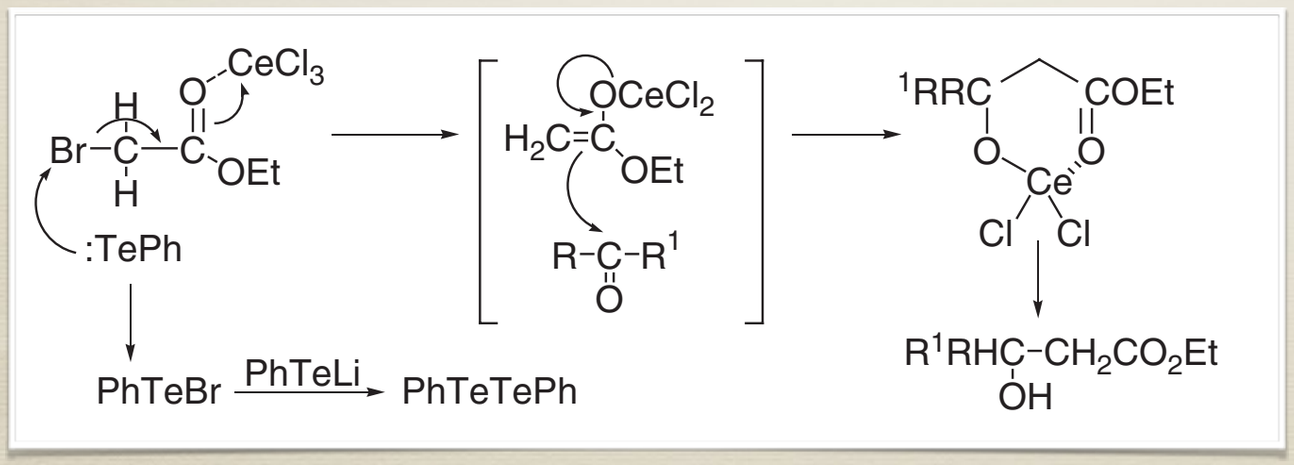


Suzuki, H.; Manabe, H.; Inouye, M. *Nippon Kagaku Kaishi* **1987**, 1485.



Suzuki, H.; Manabe, H.; Enokiya, R.; Hanazaki, Y. *Chem. Lett.* **1986**,1339.



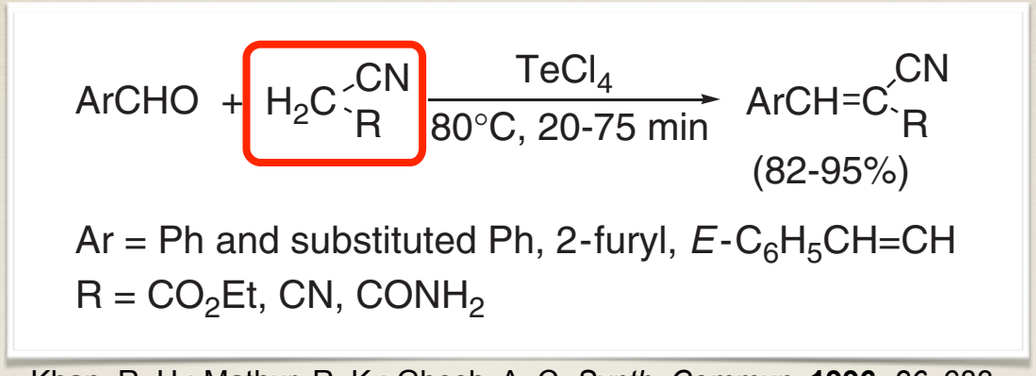


Fukuzawa, S. I.; Irai, K. *J. Chem. Soc. Perkin Trans. 1* **1993**, 1963.

- applicable to ketone
- Less eq. of bromoacetate and sodium telluride

Formation of anion species and their reactions with electrophiles

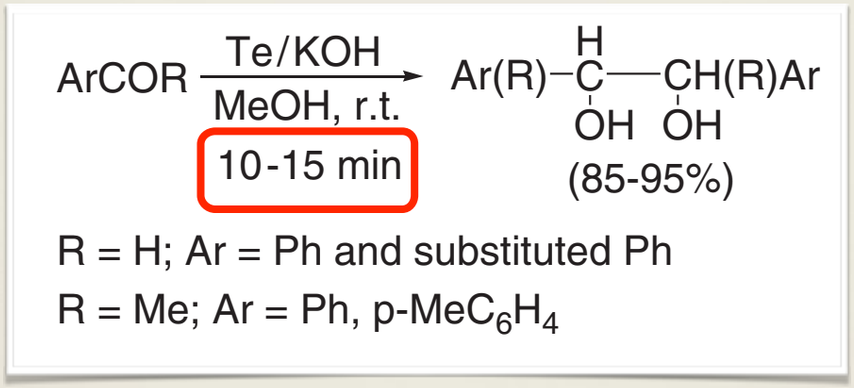
- **Knoevenagel-type reaction**



activated methylene is required

Khan, R. H.; Mathur, R. K.; Ghosh, A. C. *Synth. Commun.* **1996**, *26*, 683.

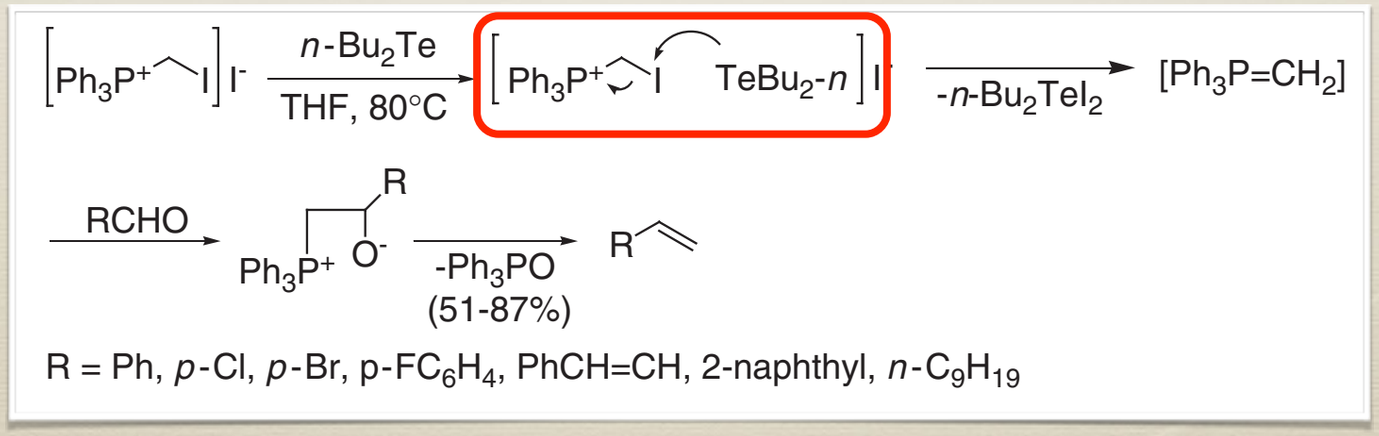
- **Pinacol reaction**



- very fast reaction

Khan, R. H.; Mathur, R. K.; Ghosh, A. C. *Synth. Commun.* **1997**, 27, 2193.

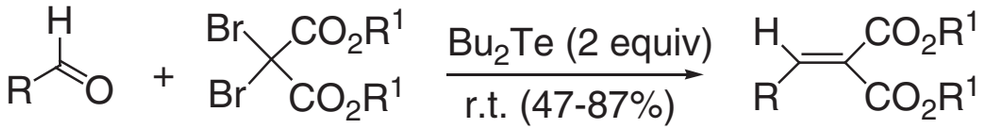
- **Wittig-type reaction**



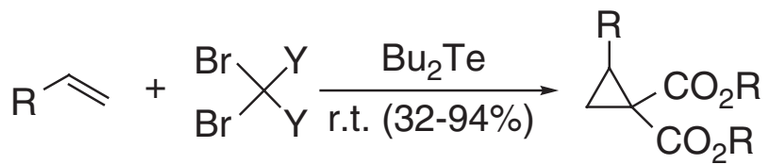
Li, S. W.; Huang, Y. Z.; Shi, L. L. *Chem. Ber.* **1990**, *123*, 1441.

Formation of anion species and their reactions with electrophiles

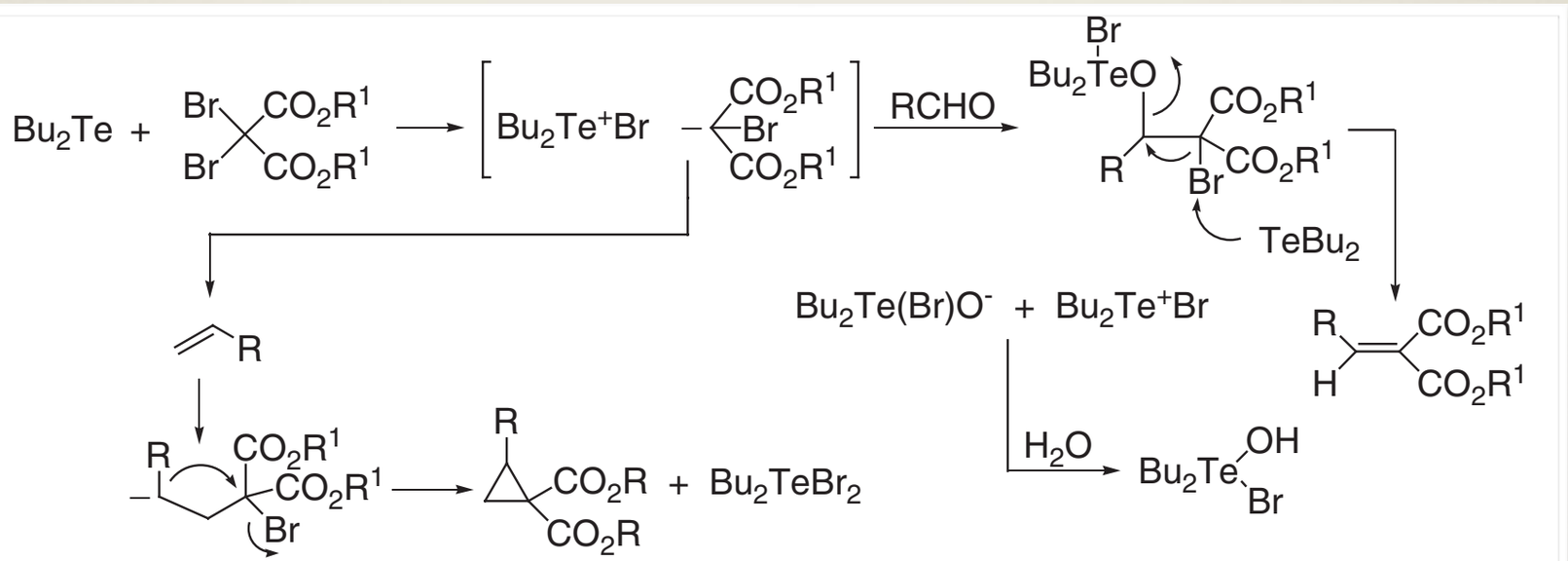
- **Alkylidenation of aldehydes and cyclopropanation of α,β -unsaturated carbonyl compounds with dibromomalonic esters**



R = Ph, *n*-hexyl, CH_2=CH, MeCH=CH, CH_2=CMe, *trans*-PhCH=CH
R^1 = Me, Et



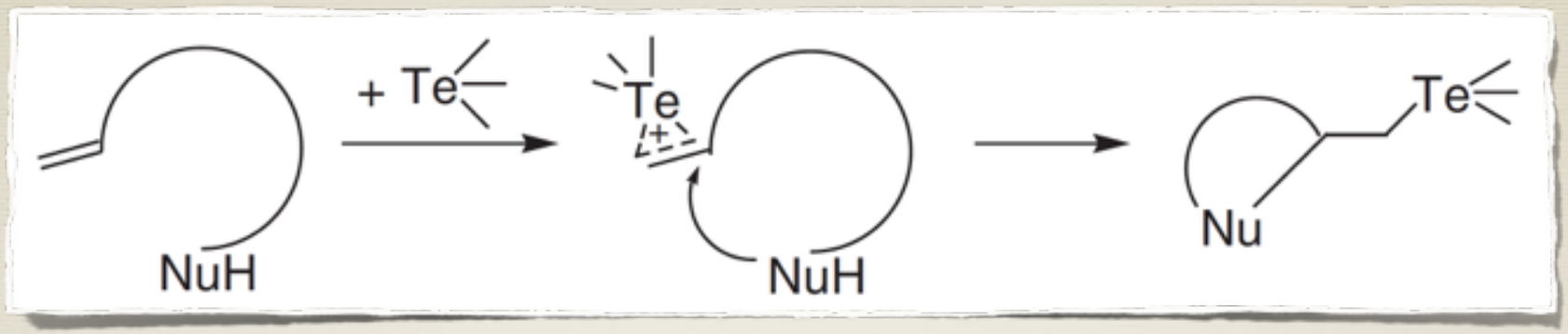
R = CO_2Me, CO_2Et, CO_2Bu, COMe, CN;
Y = CO_2Me, CO_2Et, CN



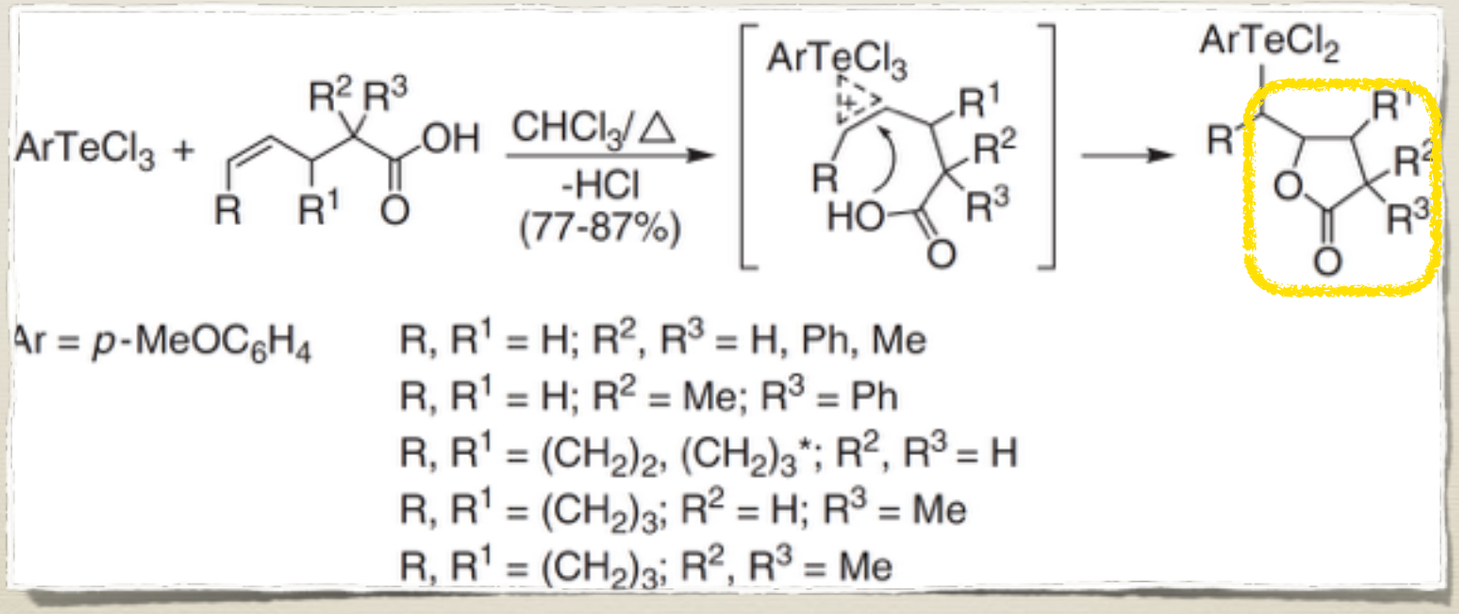
Matsuki, T.; Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2105.

Organotellurium-based ring closure reactions

- **General expression of ring closure reactions**



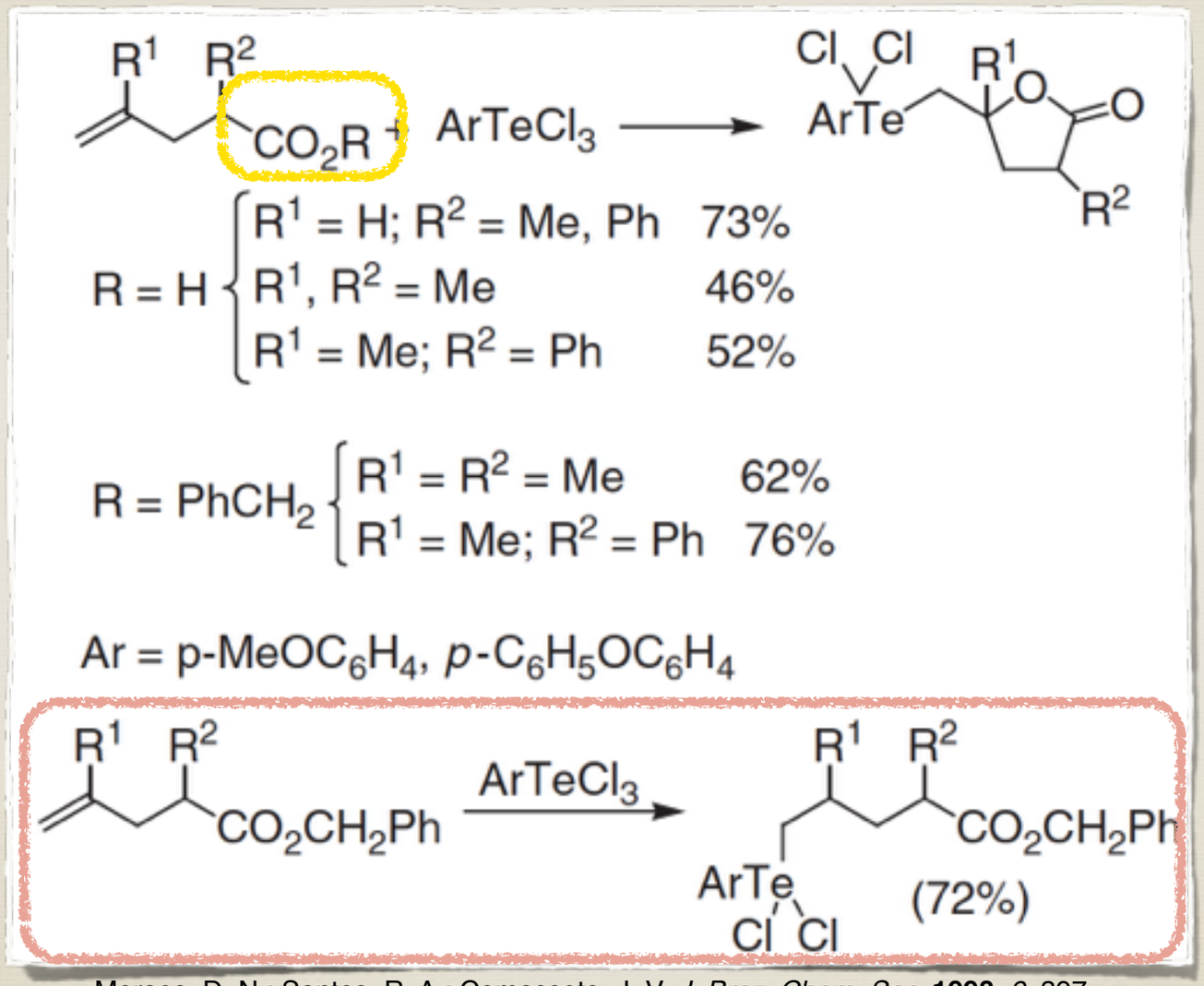
- **Tellurolactonization of unsaturated carboxylic acids**
  - With aryltellurium trichlorides



Moura Campos, M.; Petragnani, N. *Chem. Ber.* **1960**, *93*, 317. ; Comasseto, J. V.; Petragnani, N. *Synth. Commun.* **1983**, *13*, 889

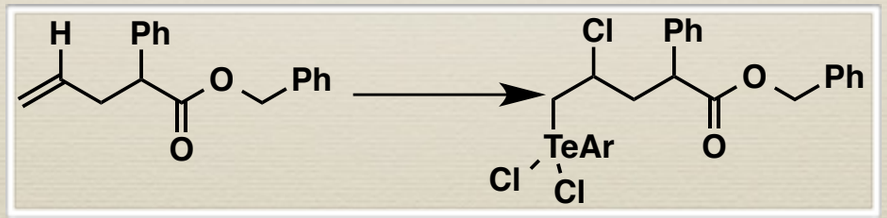
Organotellurium-based ring closure reactions

- **Tellurolactonization of unsaturated carboxylic acids**
  - With aryltellurium trichlorides



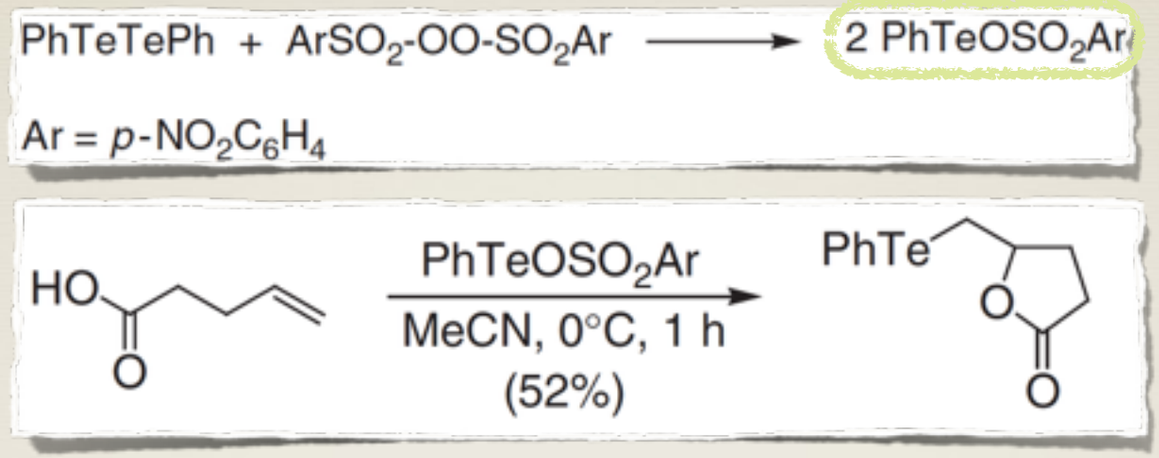
Without clear explanation

Moraes, D. N.; Santos, R. A.; Comasseto, J. V. *J. Braz. Chem. Soc.* **1998**, *9*, 397.



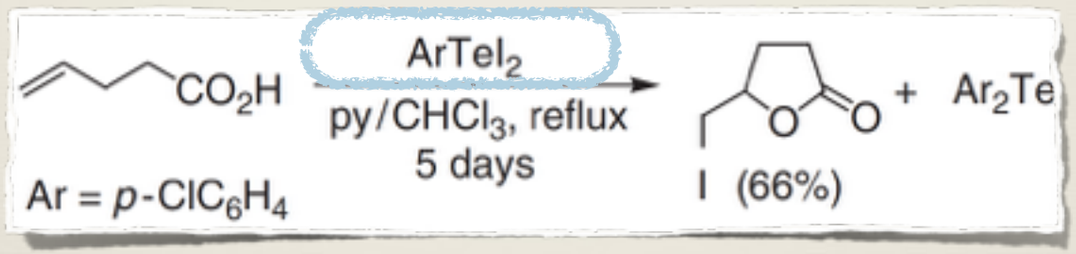
Organotellurium-based ring closure reactions

- **Tellurolactonization of unsaturated carboxylic acids**
  - With benzenetellurenyl nitrobenzenesulphonate



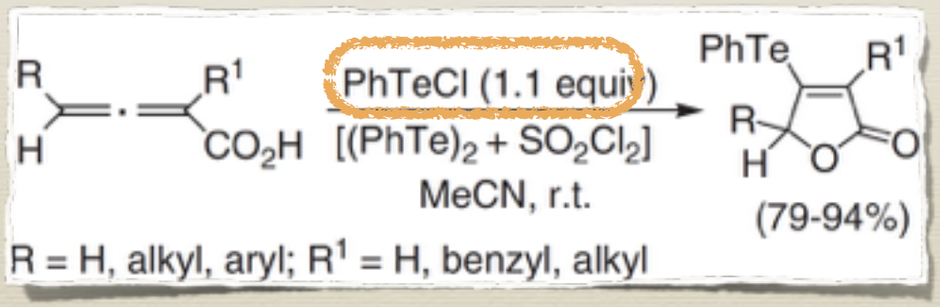
Yoshida, M.; Suzuki, T.; Kamigata, N. *J. Org. Chem.* **1992,** *57*, 383.

  - With diaryl tellurium dihalides



Leonard, K. A.; Zhou, F.; Detty, M. R. *Organometallics* **1996**, *15*, 4285.

  - With phenyltellurenyl chloride



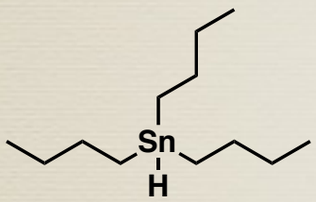
Xu, Q.; Huang, X.; Yuan, J. J. Org. Chem. 2005, *70*, 6948.

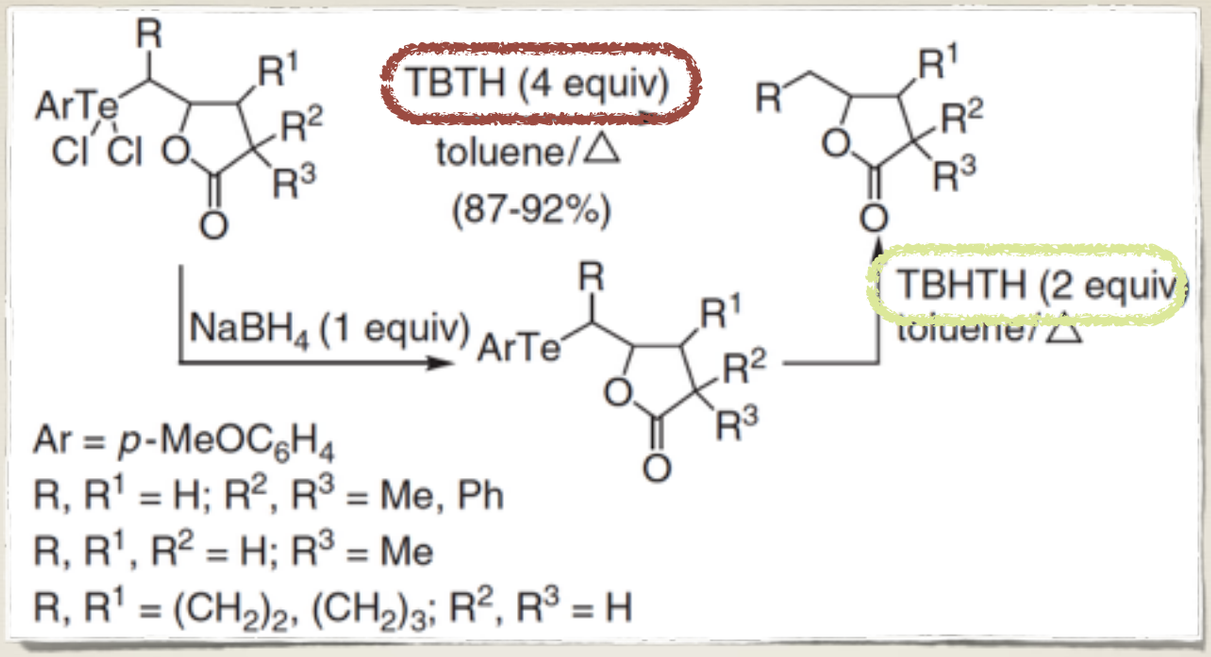
Organotellurium-based ring closure reactions

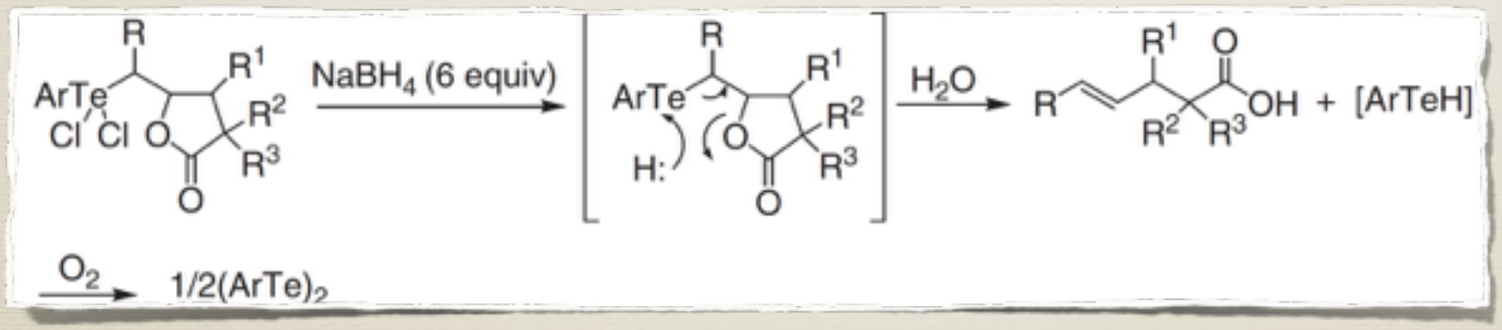
- Reductive detelluration of tellurolactones

constitutes
tributyltin hydride (TBTH)

TBTH: tributyltin hydride





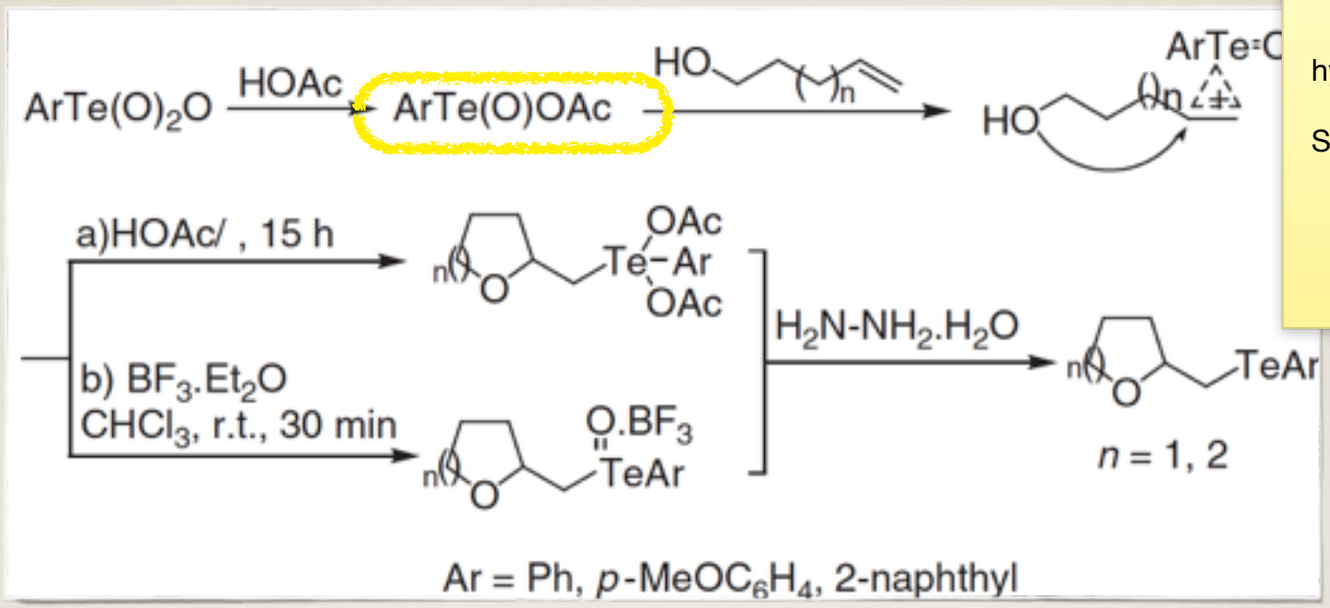


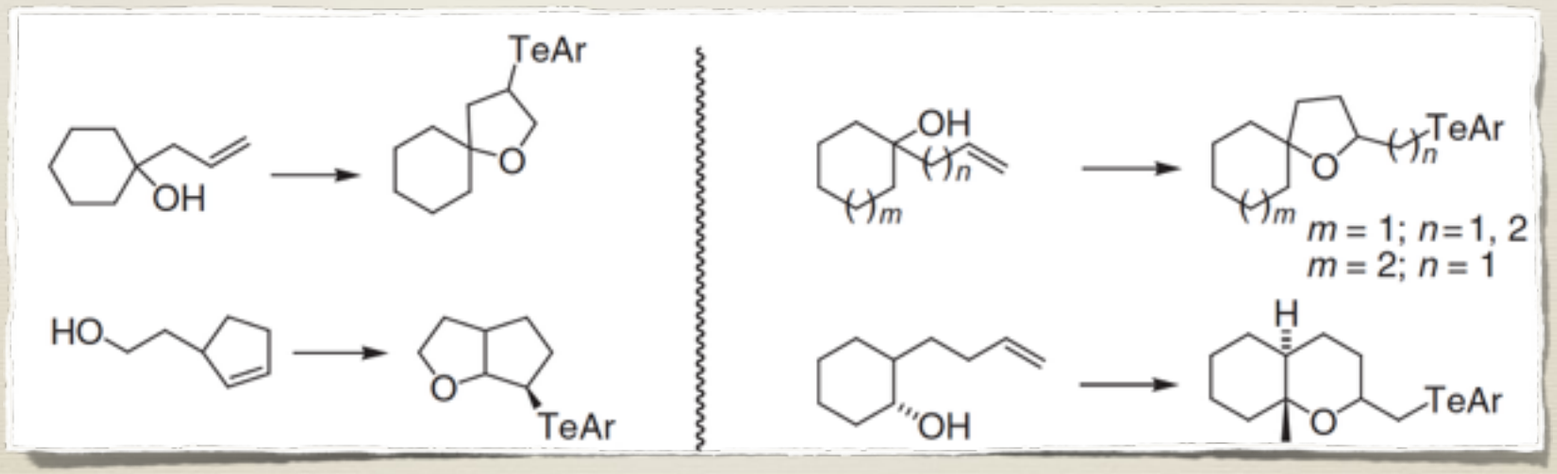
a formal protective method for γ,δ - unsaturated acids

Comasseto, J. V.; Ferraz, H. M. C.; Brandt, C. A.; Gaeta, K. K. *Tetrahedron Lett.* **1989**, *30*, 1209.;
Comasseto, J. V.; Petragnani, N. *Synth. Commun.* **1983**, *13*, 889.

Organotellurium-based ring closure reactions

- **Cyclotelluroetherification of unsaturated alcohols and allylphenols**
  - With aryltellurinyl acetates





hygroscopicity and intractable nature

Some structures are problematic

- Moderate yield.
- Small amount of 7-membered ring product

Hu, N. X.; Aso, Y.; Otsuba, T.; Ogura, F. *Tetrahedron Lett.* **1987**, *28*, 1281.; Hu, N. X.; Aso, Y.; Otsuba, T.; Ogura, F. *J. Org. Chem.* **1989**, *54,* 4391.; Hu, N. X.; Aso, Y.; Otsuba, T.; Ogura, F. *Phosphorus Sulfur* **1988**, *38*, 177.

In accordance with the Baldwin rules

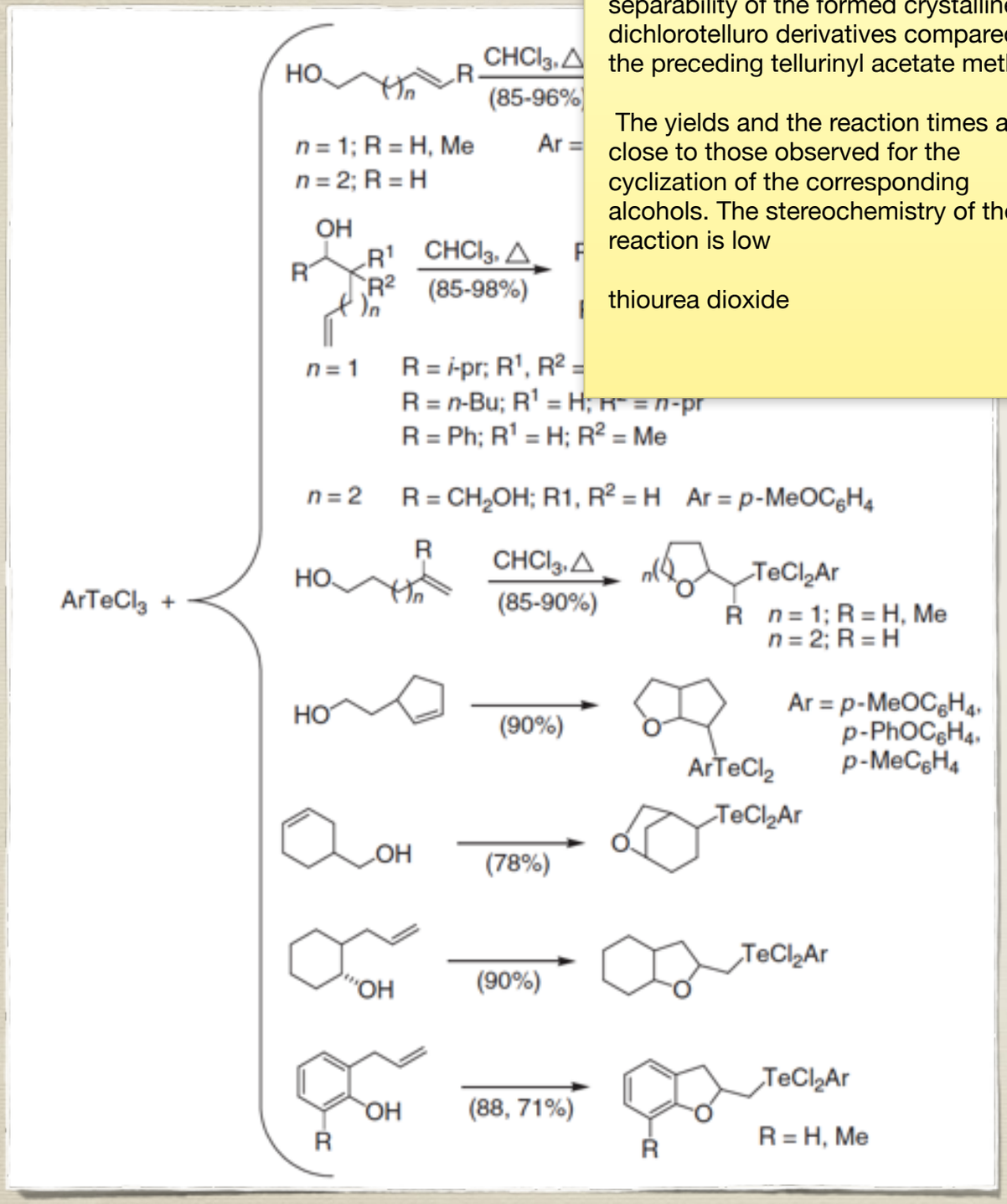
Organotellurium-based ring closure reactions

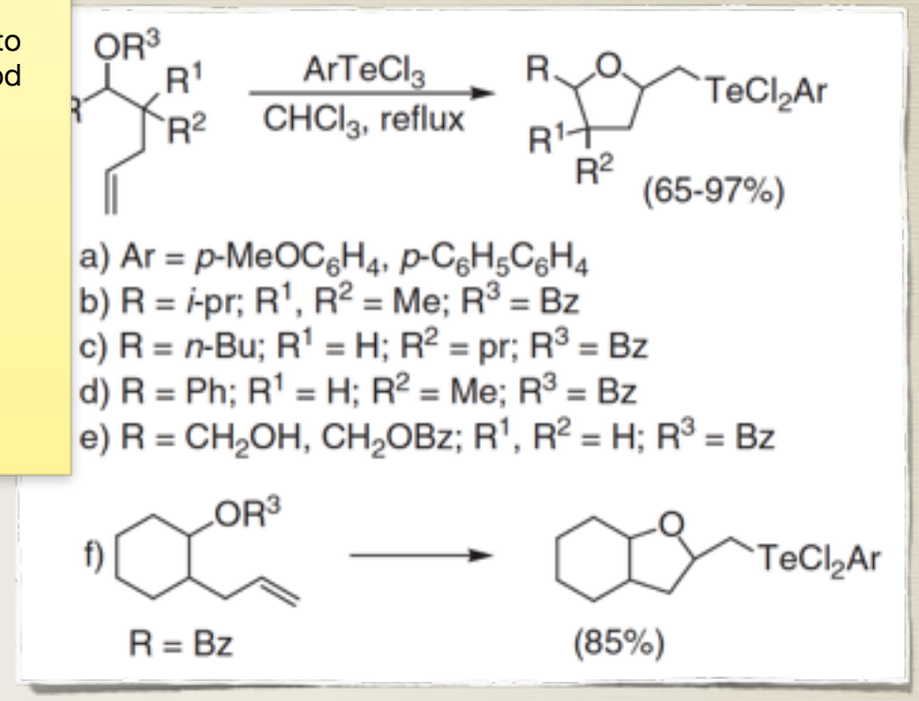
- With aryltellurium trichlori

the advantages of stability and easy separability of the formed crystalline dichlorotelluro derivatives compared to the preceding tellurinyl acetate method

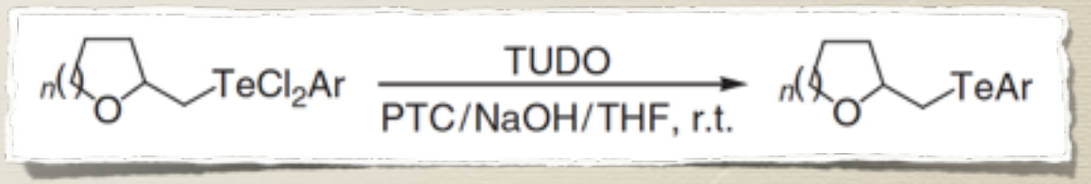
The yields and the reaction times are close to those observed for the cyclization of the corresponding alcohols. The stereochemistry of the reaction is low

thiourea dioxide

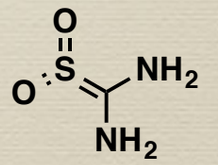




- Similar yield
- Less stereoselectivity



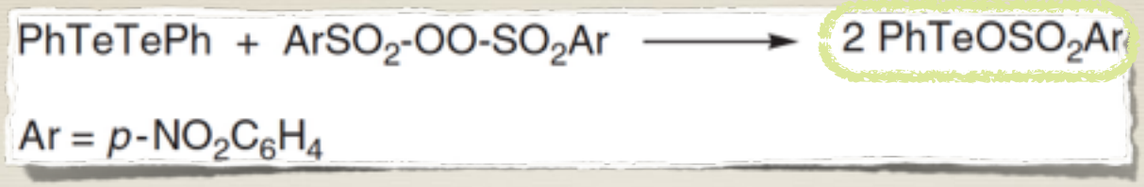
TUDO: thiourea dioxide

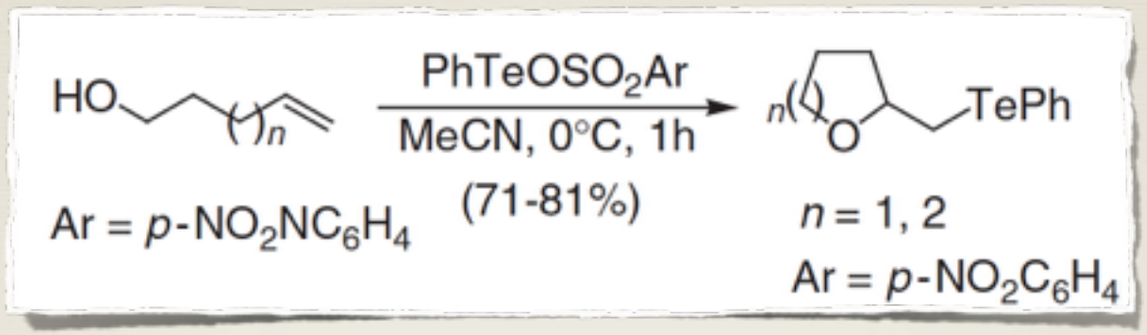


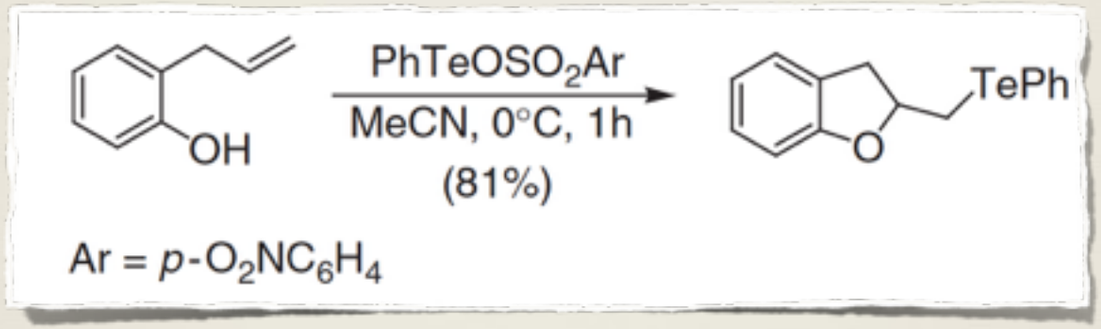
Comasseto, J. V.; Ferraz, H. M. C.; Petragnani, N.; Brandt, C. A. *Tetrahedron Lett.* **1987**, *28,* 5611.; Comasseto, J. V. Grazini, M. V. A. *Synth. Commun.* **1992**, *22*, 949.
Comasseto, J. V.; Ferraz, H. M. C.; Brandt, C. A.; Gaeta, K. K. *Tetrahedron Lett.* **1989**, *30*, 1209.

Organotellurium-based ring closure reactions

- With benzenetellurenyl nitrobenzenesulphonate





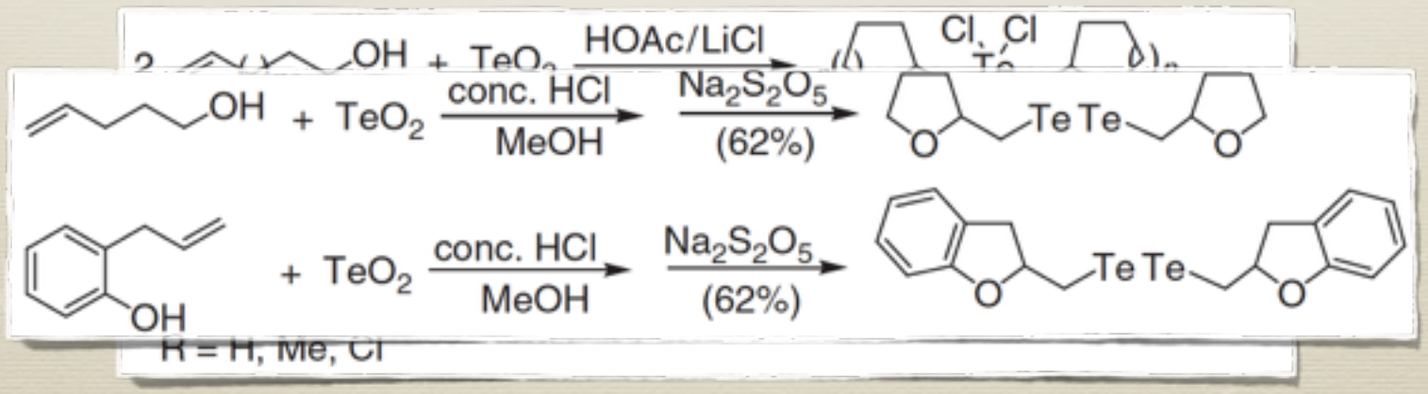


hygroscopicity and intractable nature

Some structures are problematic

Yoshida, M.; Suzuki, T.; Kamigata, N. *J. Org. Chem.* **1992,** *57*, 383.

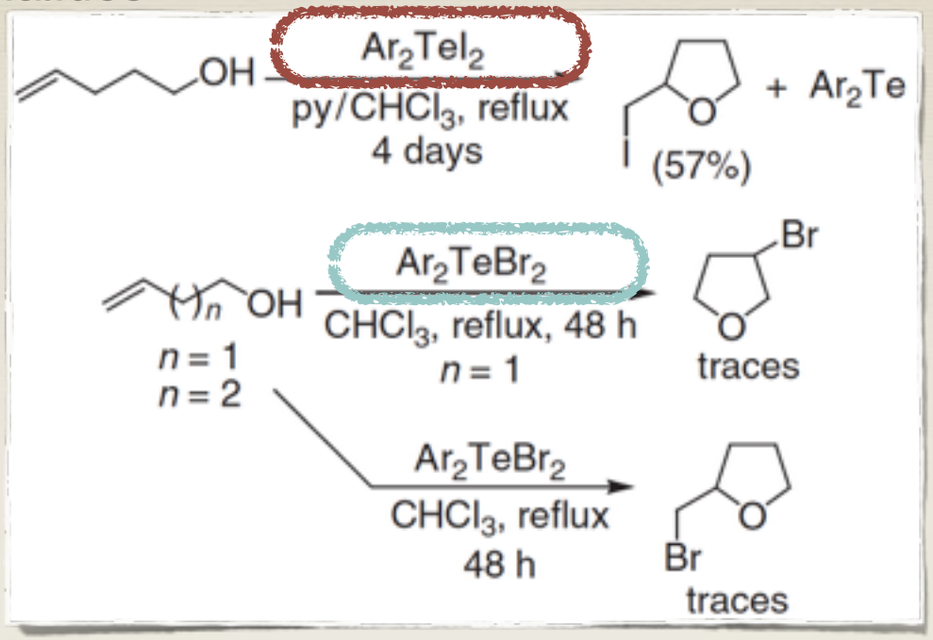
- With TeO_2/HOAc/LiCl or TeO_2/HCl



Bergman, J.; Engman, L. *J. Am. Chem. Soc.* **1981**, *103*, 5196.; Engman, L. *Organometallics* **1989**, *8*, 1997.

Organotellurium-based ring closure reactions

- With diaryl tellurium dihalides

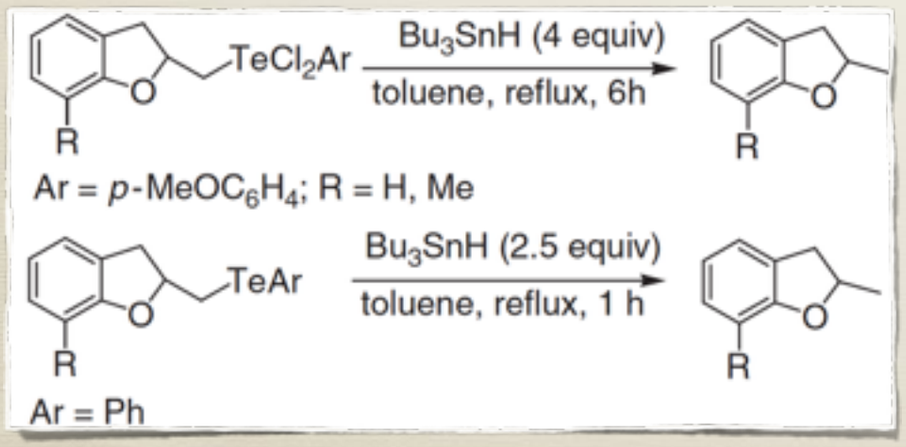


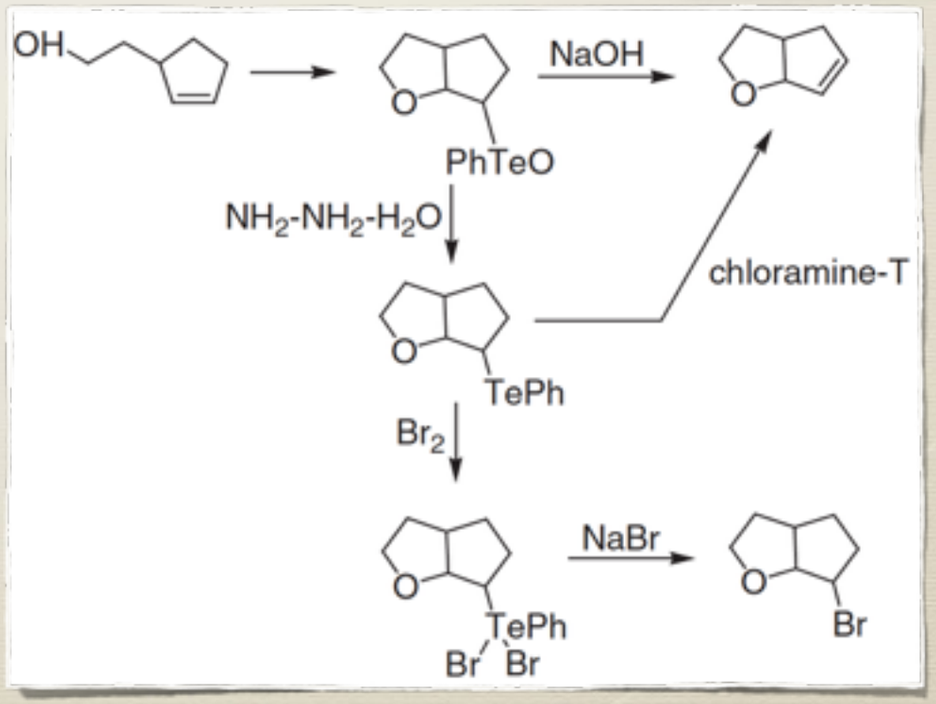
Leonard, K. A.; Zhou, F.; Detty, M. R. *Organometallics* **1996**, *15*, 4285.

hygroscopicity and intractable nature

Some structures are problematic

- Synthetic applications

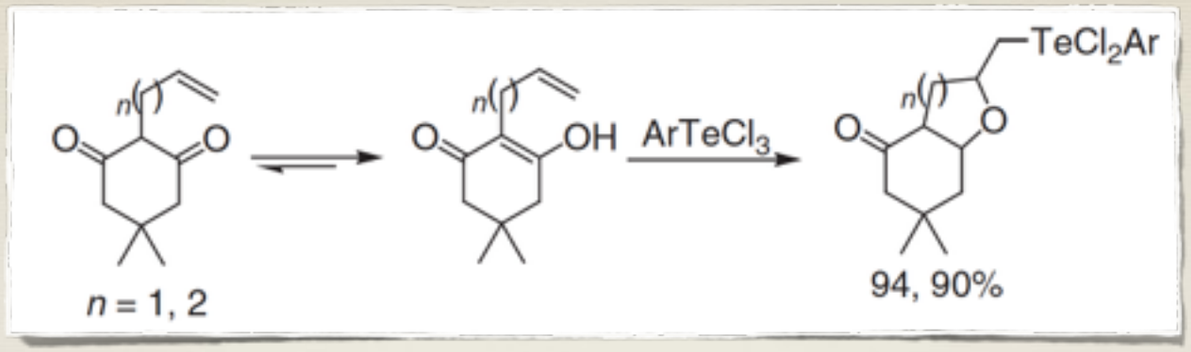




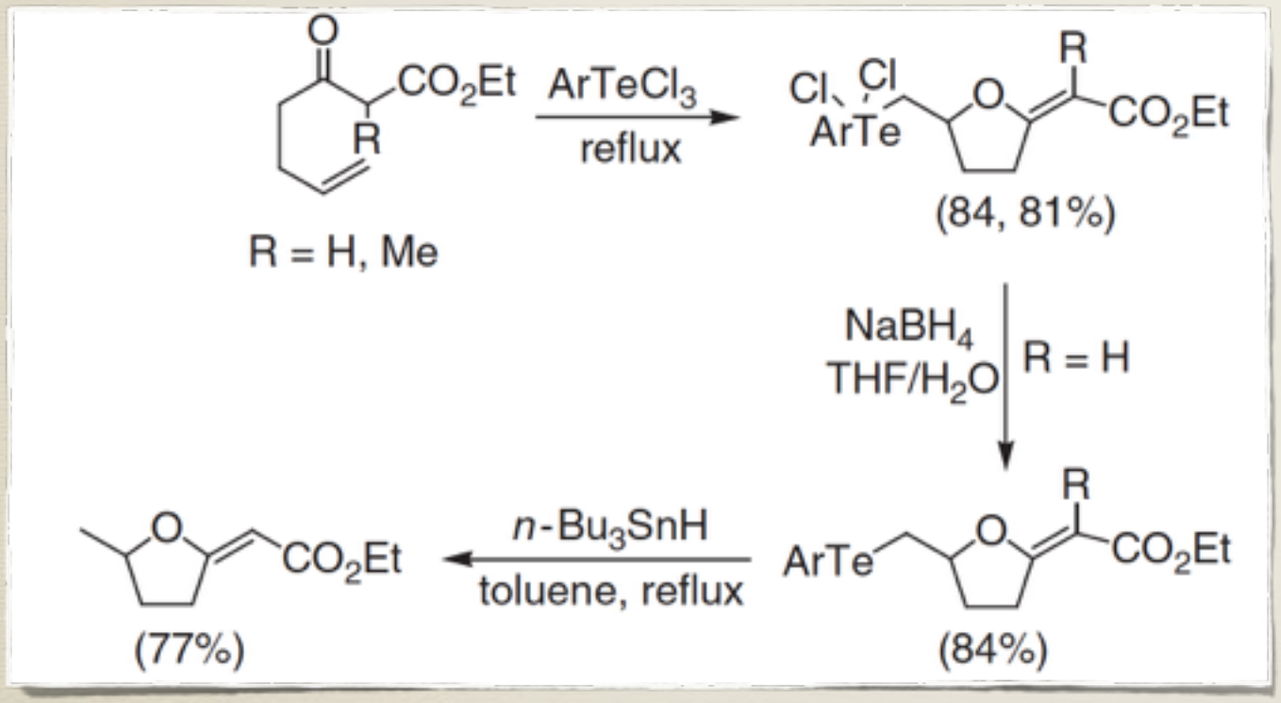
Comasseto, J. V.; Ferraz, H. M. C.; Brandt, C. A.; Gaeta, K. K. *Tetrahedron Lett.* **1989**, *30*, 1209.;Hu, N. X.; Aso, Y.; Otsuba, T.; Ogura, F. *J. Org. Chem.* **1989**, *54,* 4391

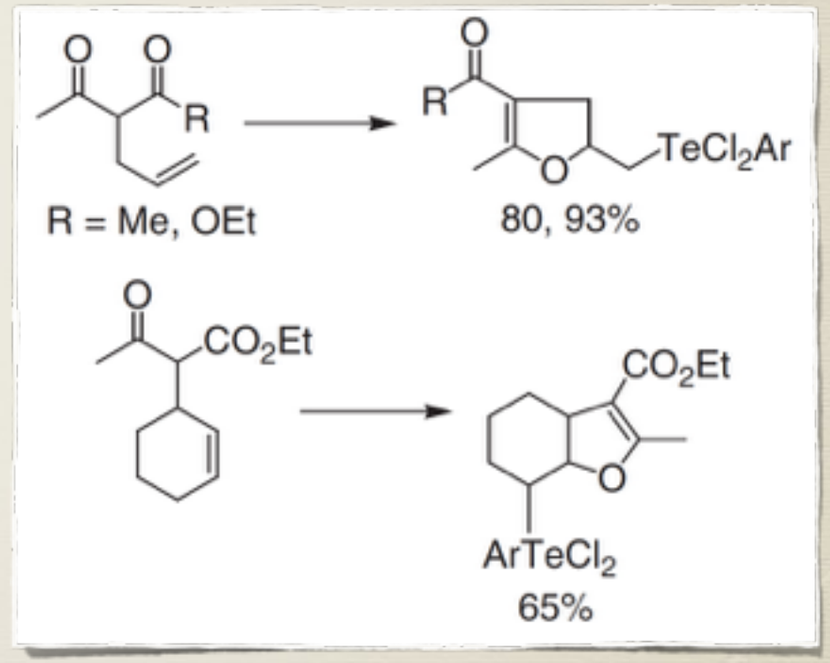
Organotellurium-based ring closure reactions

- **Tellurocyclofunctionalization of alkenyl-substituted β-dicarbonyl compounds**

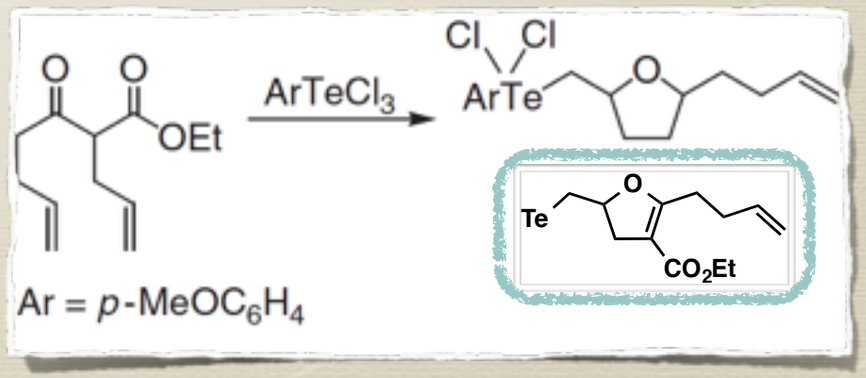


- exo-mode
- through enolate





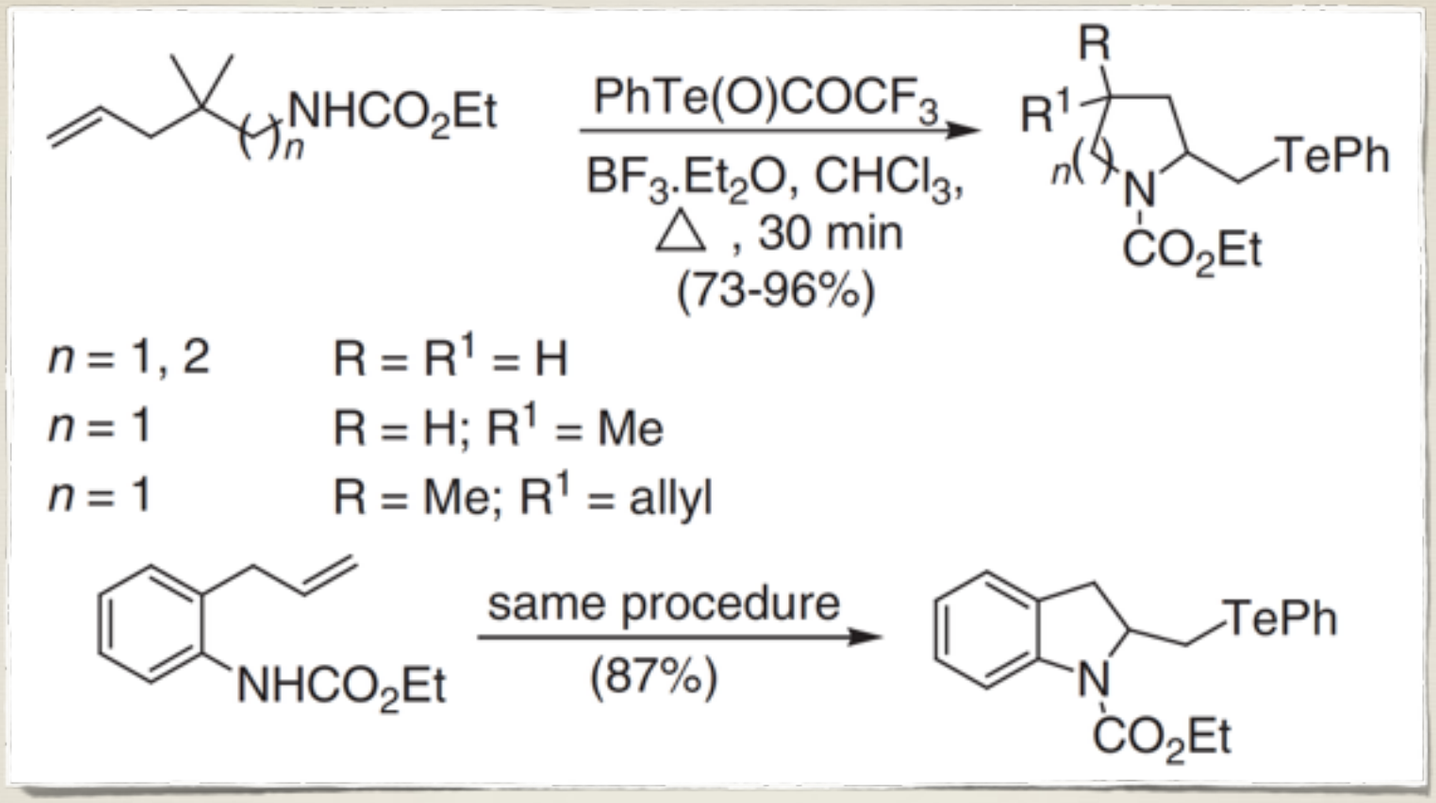
Compare with Se: Much higher yield and shorter reaction time



Ferraz, M. H. C.; Comasseto, J. V.; Borba, E. B. *Quim. Nova* **1992**, *15*, 298.; Ferraz, M. H. C.; Sano, M. K.; Scalfo, A. C. *Synlett* **1999**, *5*, 567.; Stefani, H. A.; Petragnani, N.; Brandt, C. A.; Rando, D. G.; Valduga, C. J. *Synth. Commun.* **1999**, *29*, 3517.

Organotellurium-based ring closure reactions

- **Tellurocyclization of olefinic carbamates**

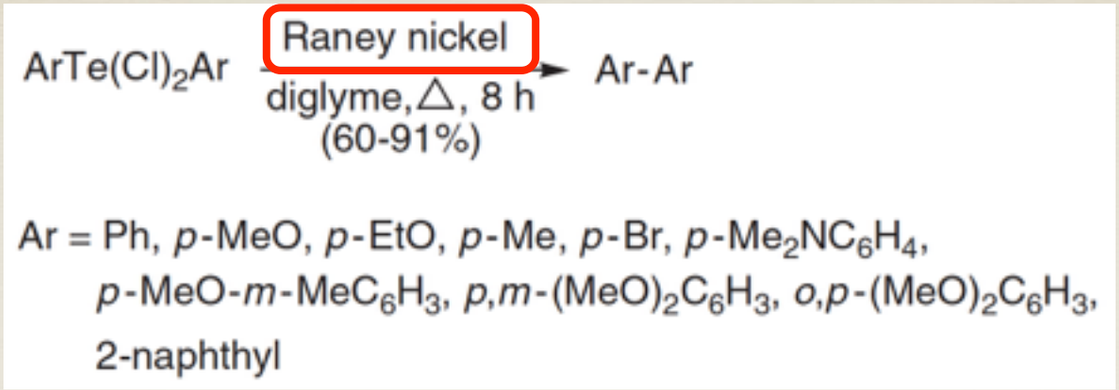


pyrrolidine and piperidine derivatives

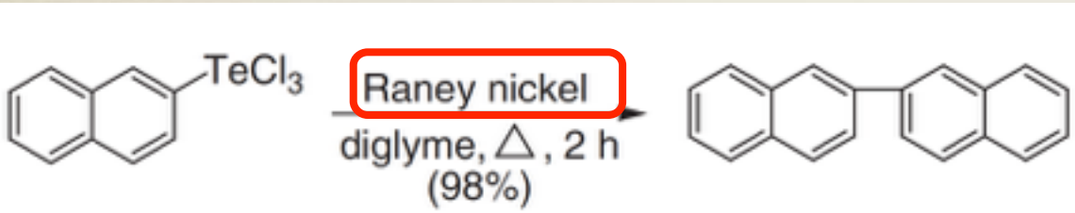
Hu, N. X.; Aso, Y.; Otsuba, T.; Ogura, F. *Chem. Lett.* **1987**, 1327.

Remove the Tellurium

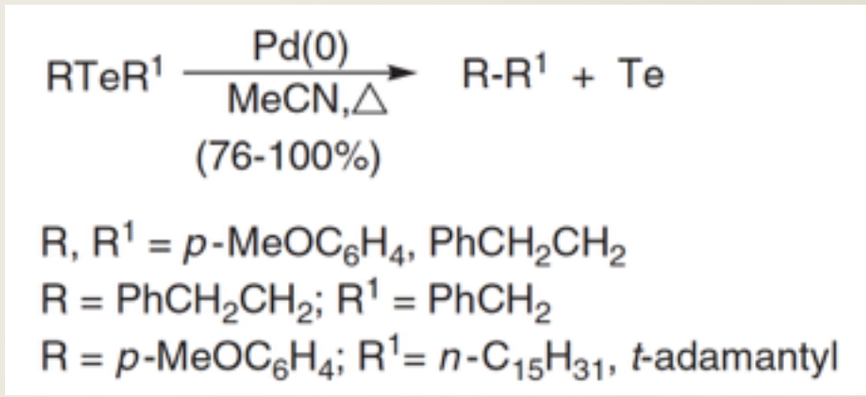
- **With formation of new C-C bonds**



Bergman, J. *Tetrahedron* **1972**, *28*, 3323. Bergman, *J. Org. Synth.* **1977**, *57*, 18.

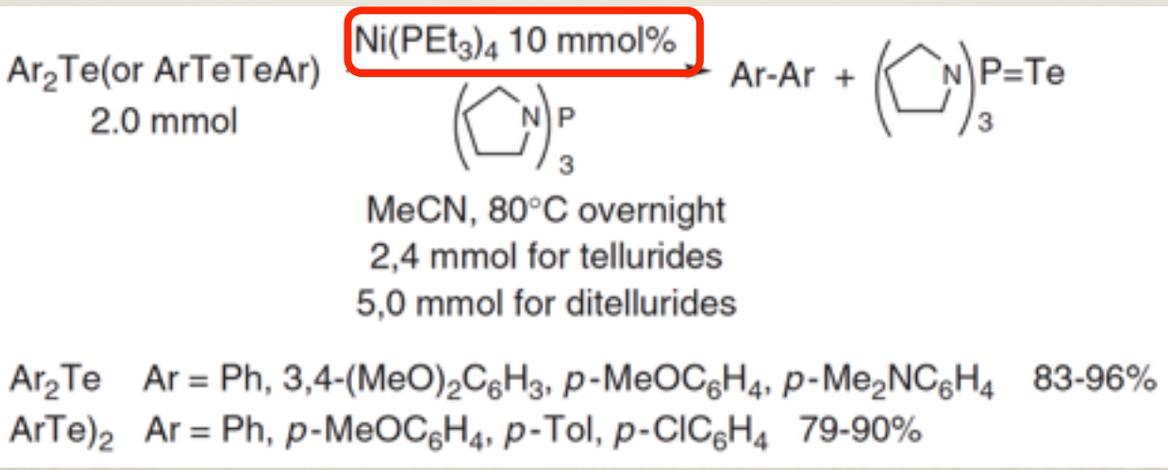


Bergman, J. *Tetrahedron* **1972**, *28*, 3323. Bergman, *J. Org. Synth.* **1977**, *57*, 18.



Bergman, J.; Engman, L. *Tetrahedron* **1980**, *36*, 1275.

1 eq. of metal



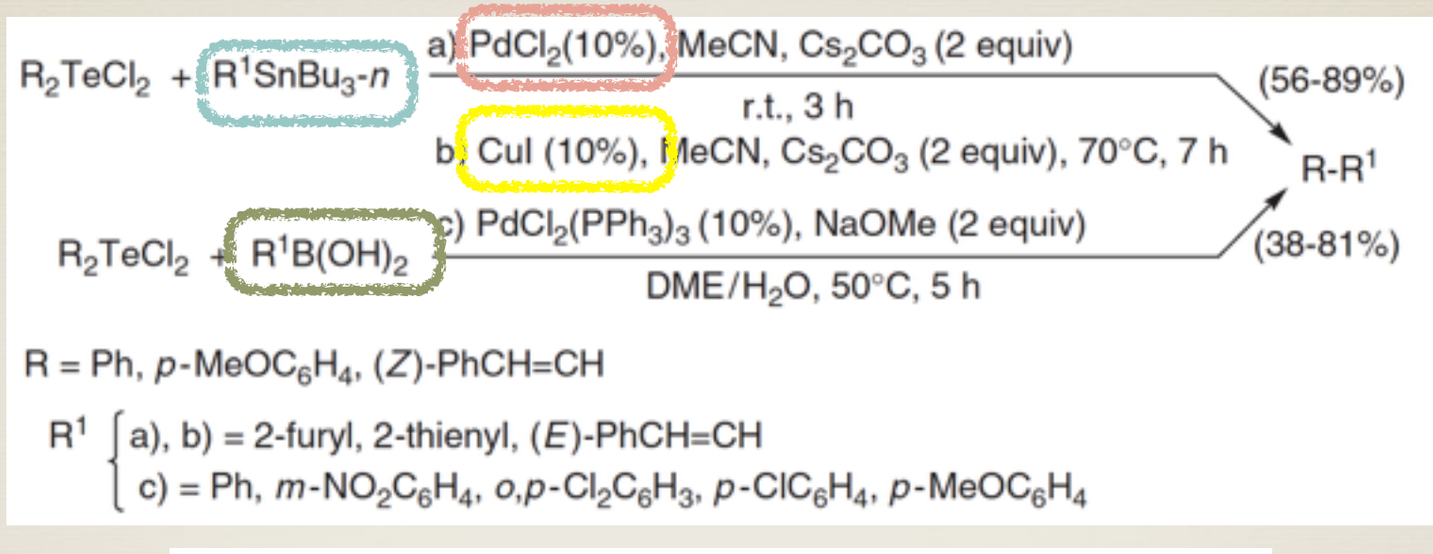
Han, L. B.; Tanaka, M. *Chem. Commun.* **1998**, *47*.

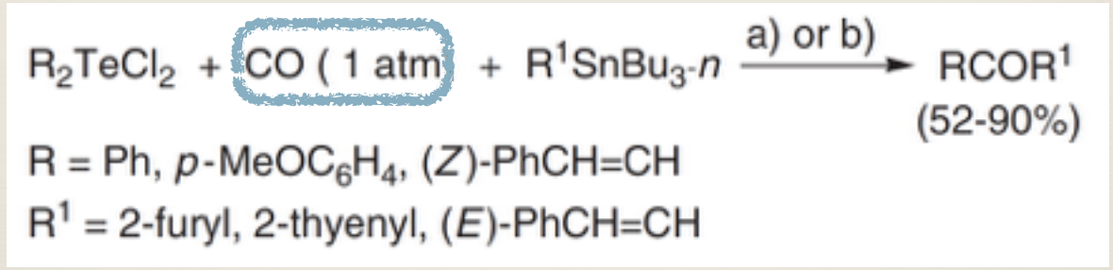
Catalytic amount

Remove the Tellurium

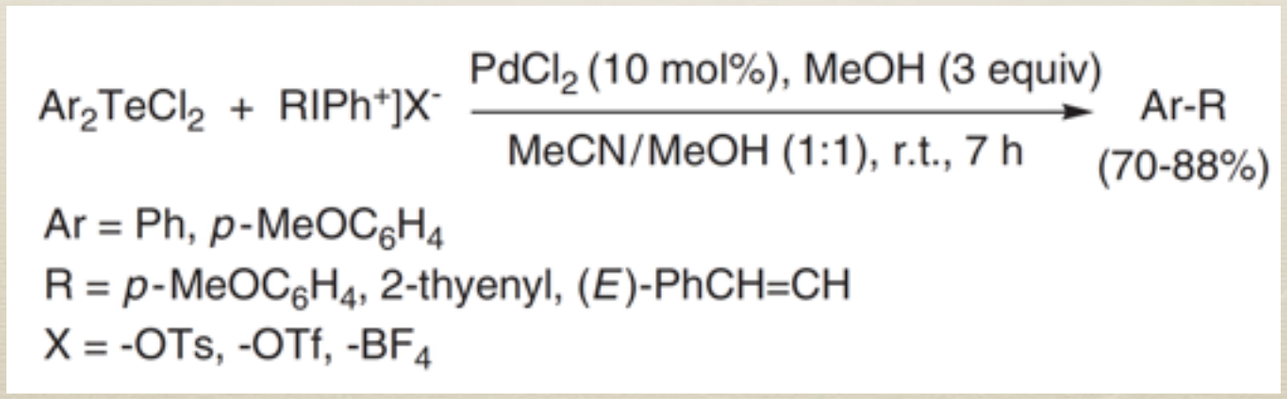
- **With formation of new C-C bonds**

Coupling methods will be further discussed in application part





Kang, S. K.; Lee, S. W.; Ryu, H. C. *Chem. Commun*. **1999**, 2117. Kang, S. K.; Hong, Y. T.; Kim, D. H.; Lee, S. W. *J. Chem. Res. (S)* **2001**, 283.

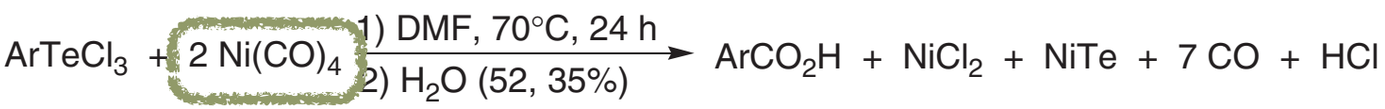


Utilizing hypervalent iodonium salts

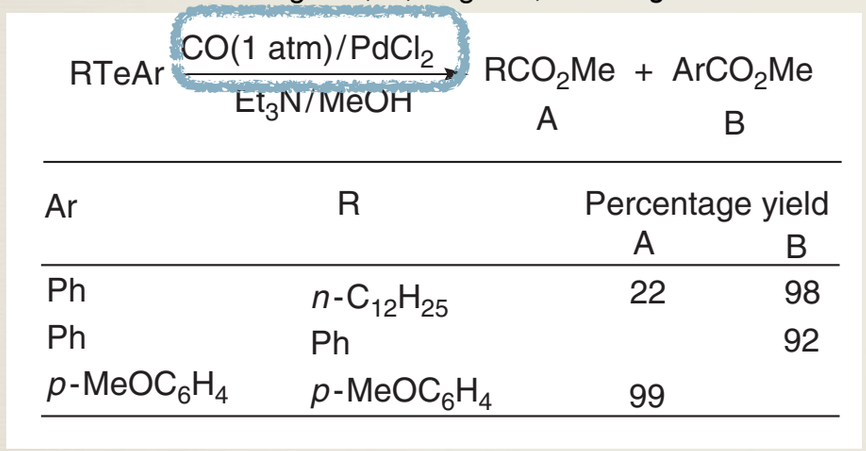
Kang, S. K.; Lee, S. W.; Kim, M. S.; Kwon, H. S. *Synth. Commun*. **2001**, *31*, 1721.

Remove the Tellurium

- **With formation of new C-C bonds**



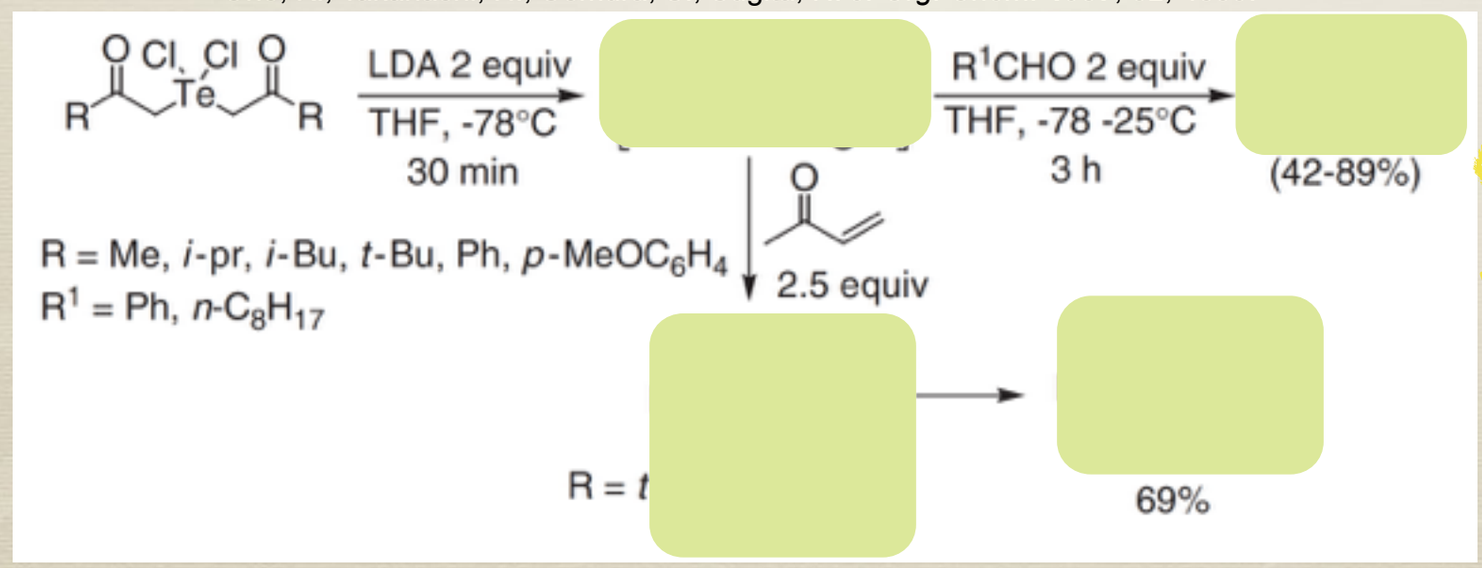
Bergman, J.; Engman, L. *J. Organomet. Chem.* **1979**, *175*, 233.



Ar	R	Percentage yield A	B
Ph	n-$C_{12}H_{25}$	22	98
Ph	Ph		92
p-$MeOC_6H_4$	p-$MeOC_6H_4$	99	

sulphur and selenium compounds give unsatisfactory results.

Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* **1987**, *52*, 4859.

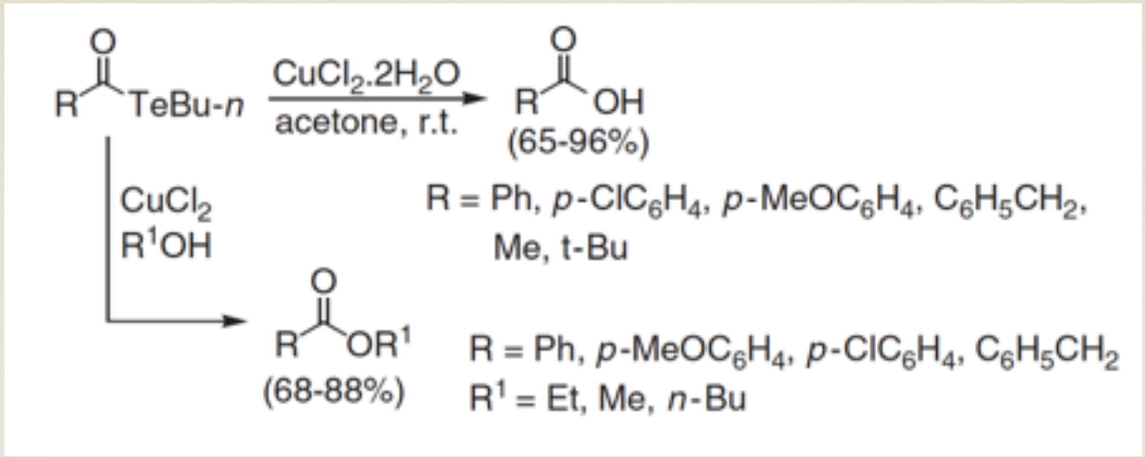


Q2: Intermediates and Products?

Han, L. B.; Kambe, N.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1993**, 561.

Remove the Tellurium

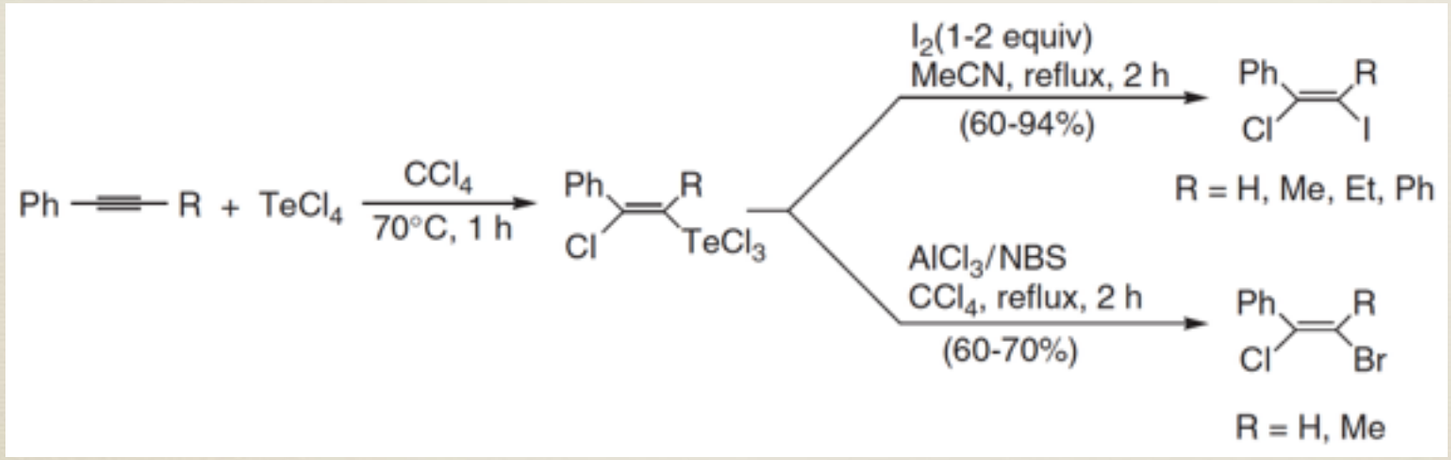
- **With formation of other functionalities**
  - By hydroxy group



Dabdoub, M. J.; Viana, L. H. *Synth. Commun*. **1992**, *22*, 1619.

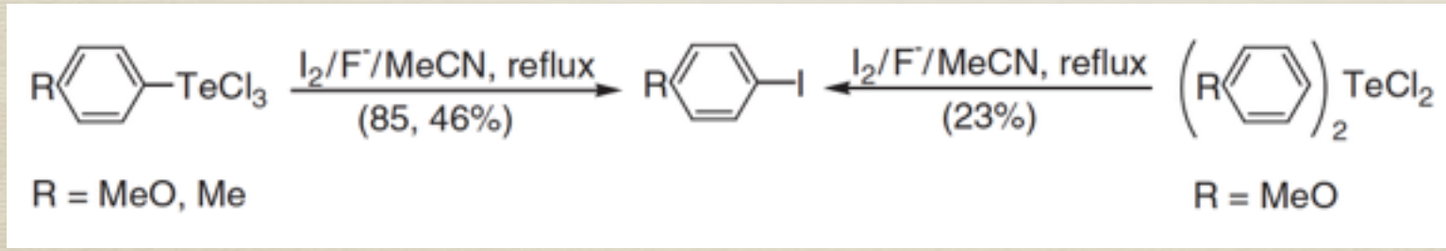
An electrophilic mechanism is plausible for these reactions, on the basis of the depend- ence on para-electron-releasing groups and the enhancement by F– ions (forming ArTeCl3F22– or

  - By halogens



Retention of stereochemistry

Uemura, S.; Miyoshi, H.; Okano, M. *Chem. Lett.* **1979**, 1357.

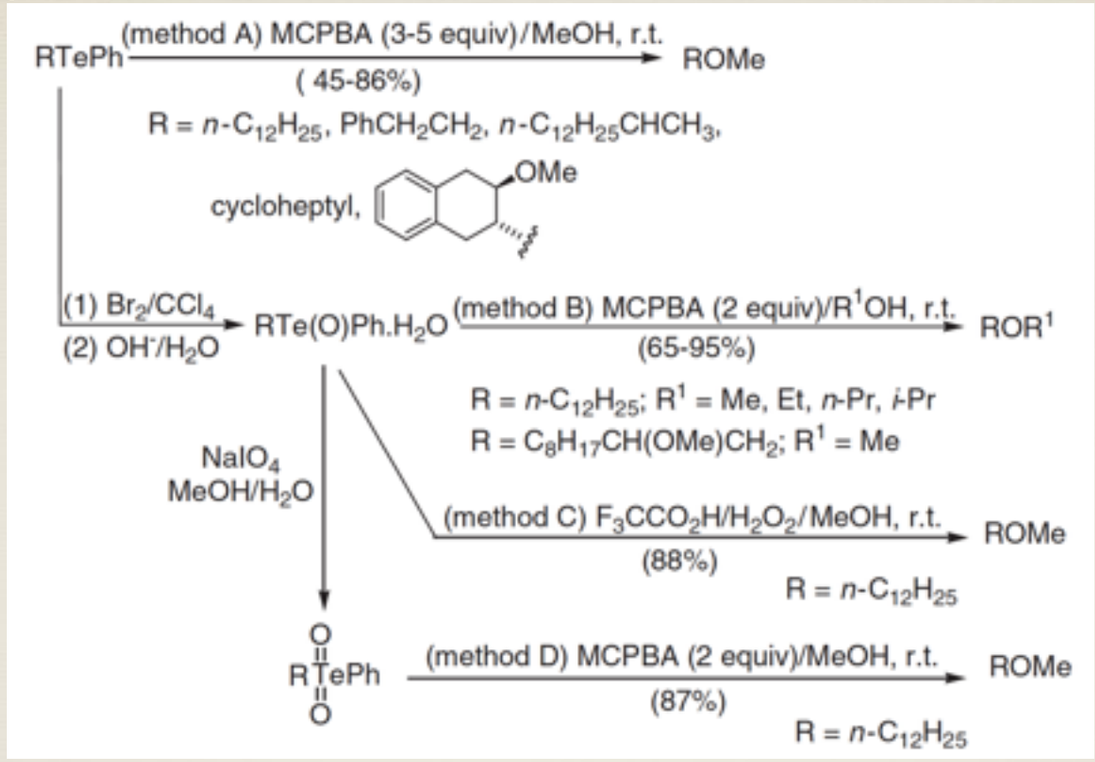


electrophilic mechanism is plausible

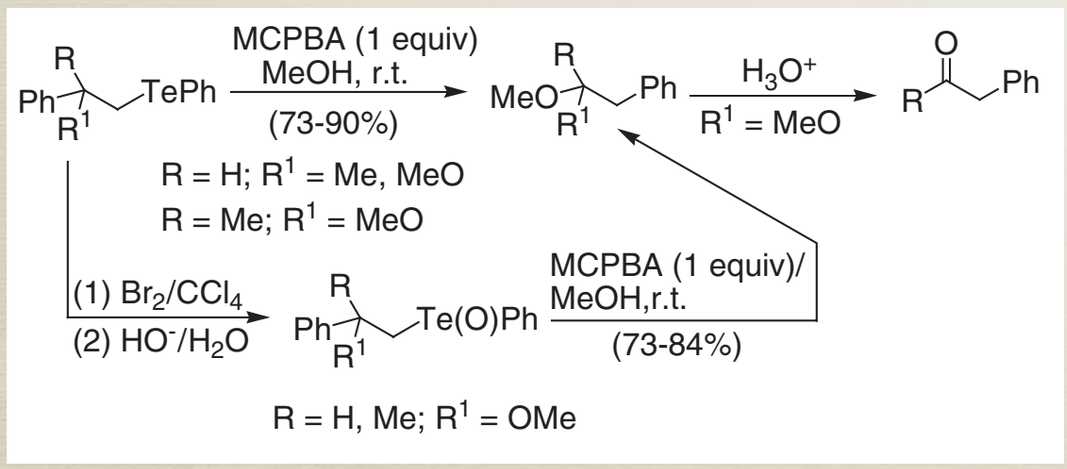
Hu, N. X.; Aso, Y.; Otsuba, T.; Ogura, F. *Chem. Lett*. **1987**, 1327.

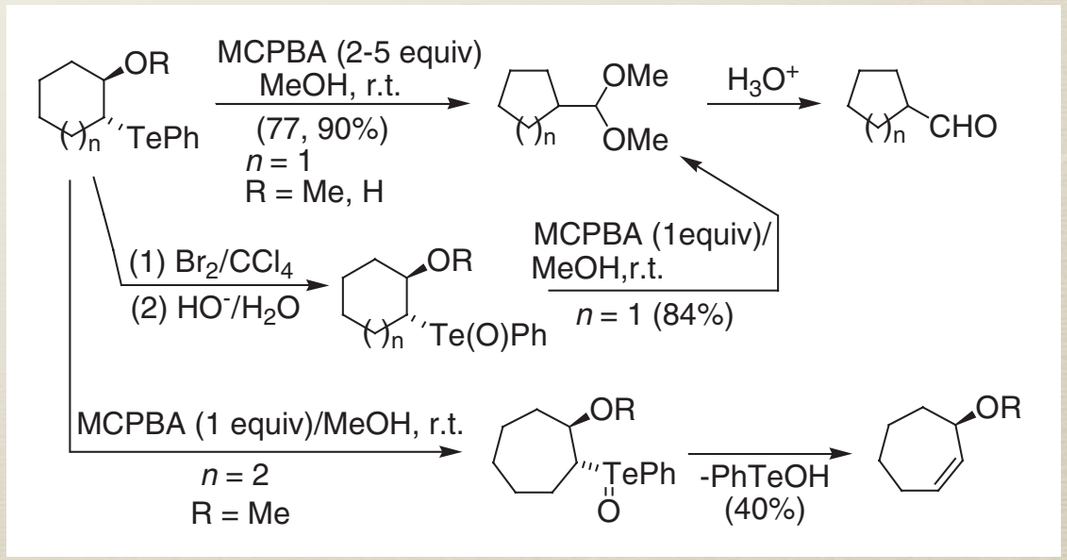
Remove the Tellurium

- **With formation of other functionalities**
  - By methoxy group



Rearrangement could happen



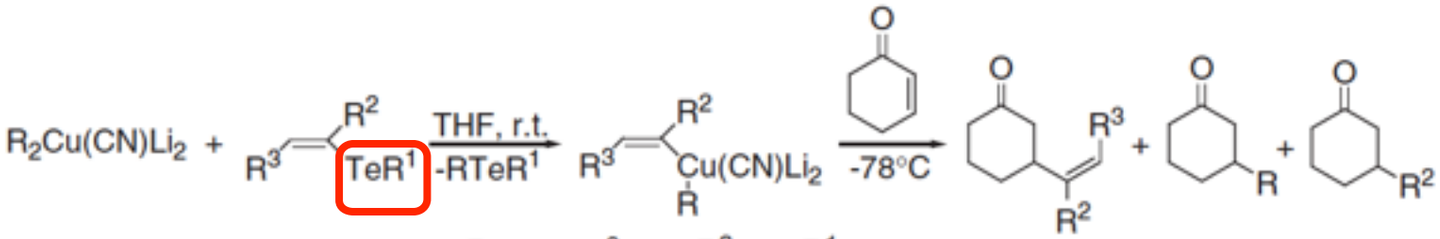


Uemura, S.; Fukuzawa, S. I. *Tetrahedron Lett.* **1983**, *24*, 4347. Uemura, S.; Fukuzawa, S. I. *J. Chem. Soc. Perkin Trans. 1* **1985**, 471.

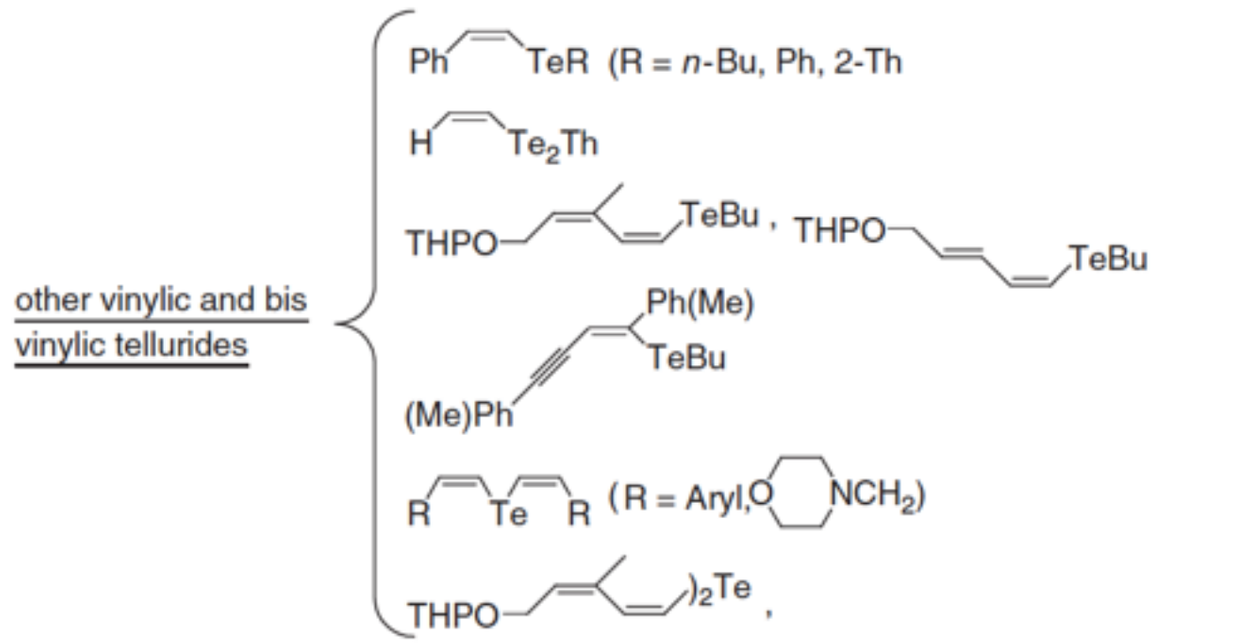
Detty, M. R. J. Org. Chem. **1980**, 45, 274

Vinylic tellurides

- **Vinylcuprates by copper–tellurium exchange**
  - **Conjugate addition of enones**



R	R^3	R^2	R^1			
Me	Ph	H	*n*-Bu	90%	trace	------
Me	H	Ph	*n*-Bu	88%	trace	------
n-Bu	H	H	Ph	55%	------	45%
n-Bu	Ph	H	*n*-Bu	75%	23%	------



higher order cyanocuprates: $Bu(2\text{-}Th)Cu(CN)Li_2$, $Me_2Cu(CN)Li_2$, $Bu(imid)Cu(CN)Li_2$

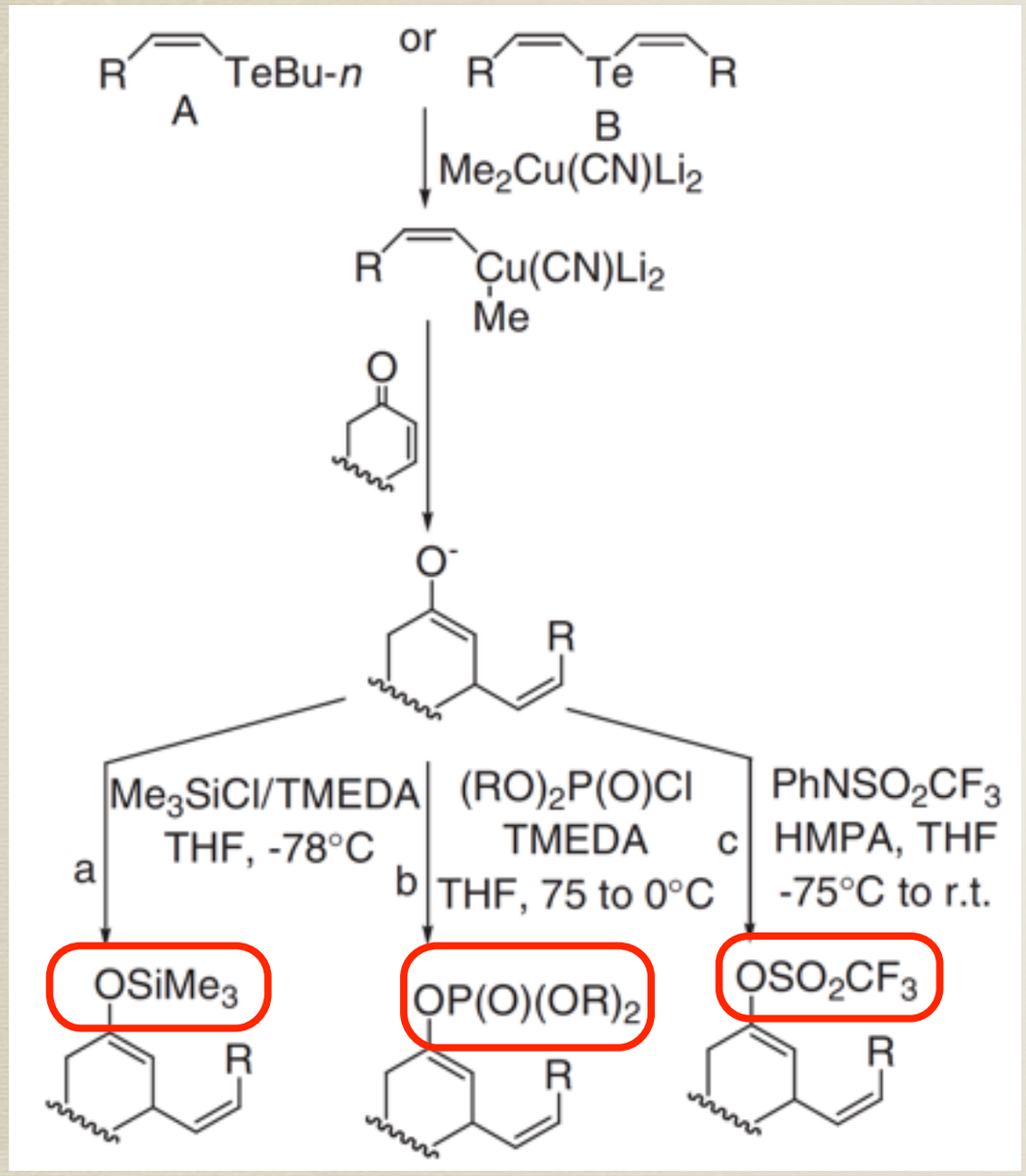
enones : MCK,

R1 and the vinyl group should be different in migrative property

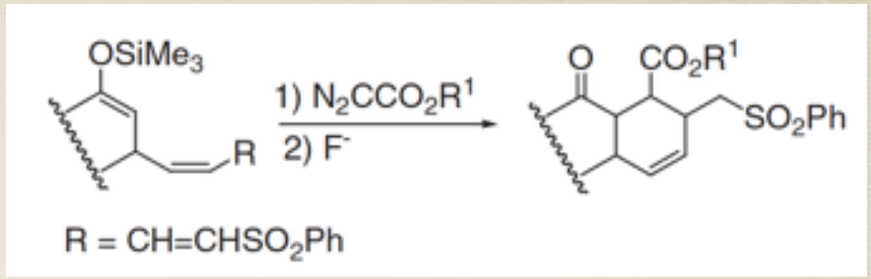
Comasseto, J. V.; Berriel, G. N. *Synth. Commun.* **1990**, *20*, 1681.; Tucci, F. C.; Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 5721.

Vinylic tellurides

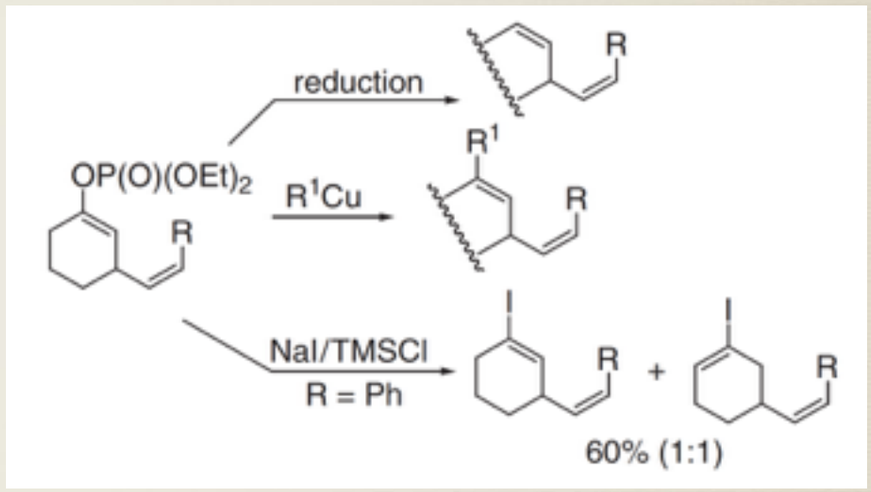
- Further functionalization



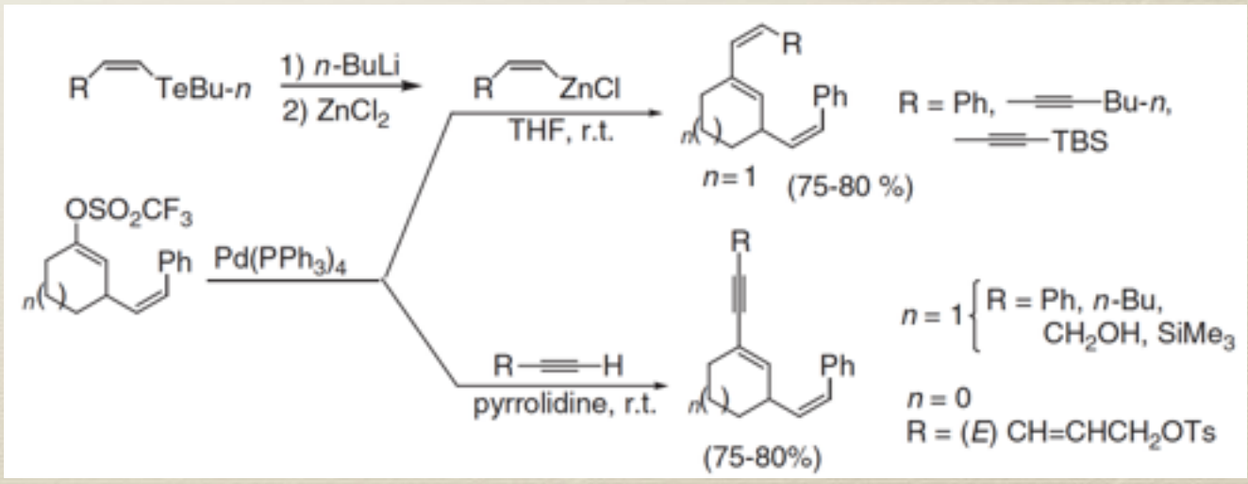
Moraes, D. N.; Barrientos-Astigarraga, R. E.; Castelani, P.; Comasseto, J. V. *Tetrahedron* **2000**, *56*, 3327.



Marino, J. P.; Simonelli, F.; Stengel, P. G.; Ferreira, J. T. B. *J. Braz. Chem. Soc.* **1998**, *9*, 345



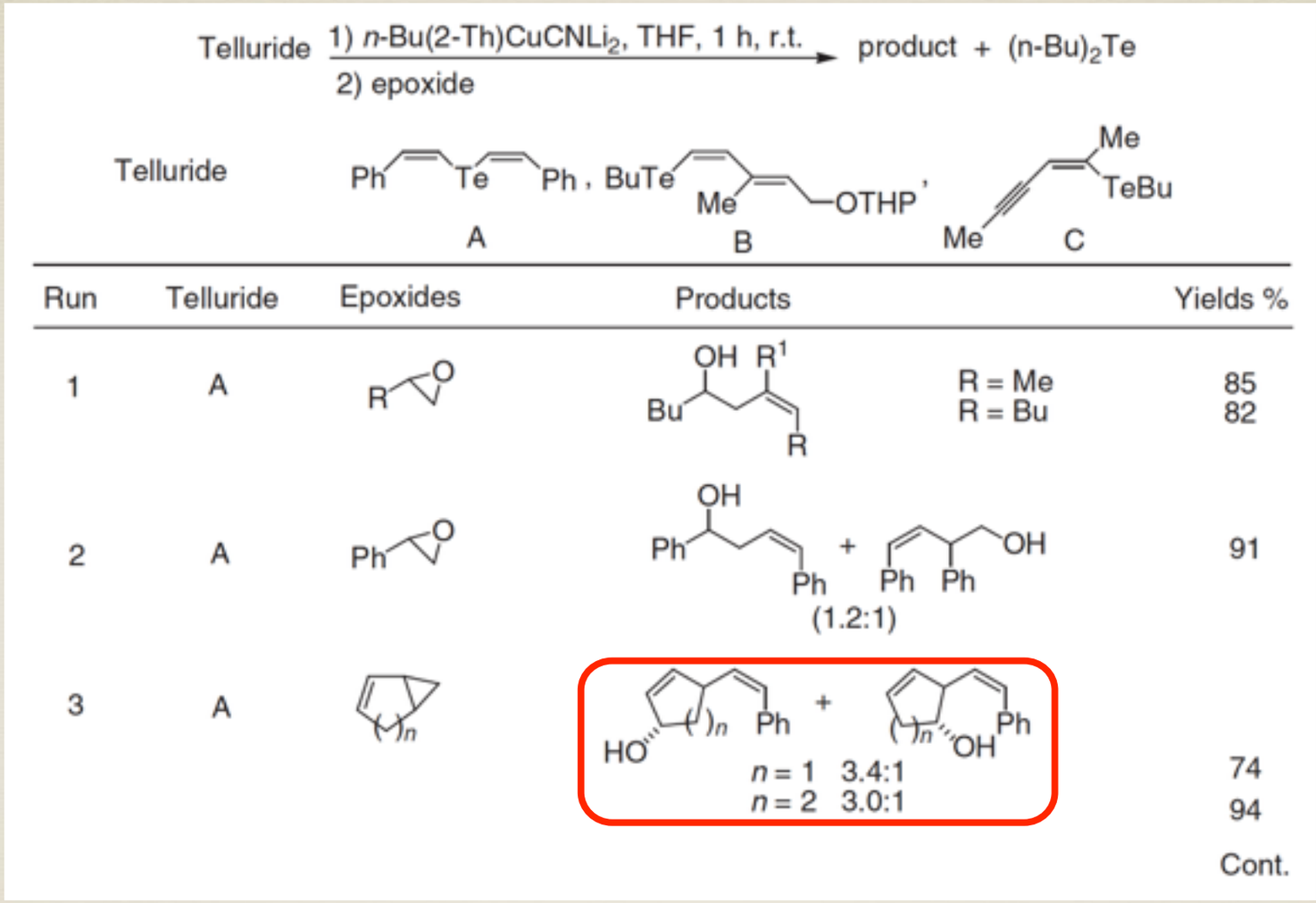
Moorhoff, C. M.; Schneider, D. F. *Tetrahedron* **1998**, *54*, 3279; Lee, K.; Wiemer, D. F. *Tetrahedron Lett.* **1993**, *34*, 2433.



Barrientos-Astigarraga, R. E.; Moraes, D. N.; Comasseto, J. V. *Tetrahedron Lett.* **1999**, *40*, 265.

Vinylic tellurides

- **Reaction with epoxides**



Run	Telluride	Epoxides	Products		Yields %
1	A	R, O	OH, R^1, Bu, R	R = Me R = Bu	85 82
2	A	Ph, O	OH, Ph, Ph + OH, Ph, Ph (1.2:1)		91
3	A	$(\ )_n$	HO, $(\ )_n$, Ph + $(\ )_n$, OH, Ph $n = 1$ 3.4:1 $n = 2$ 3.0:1		74 94

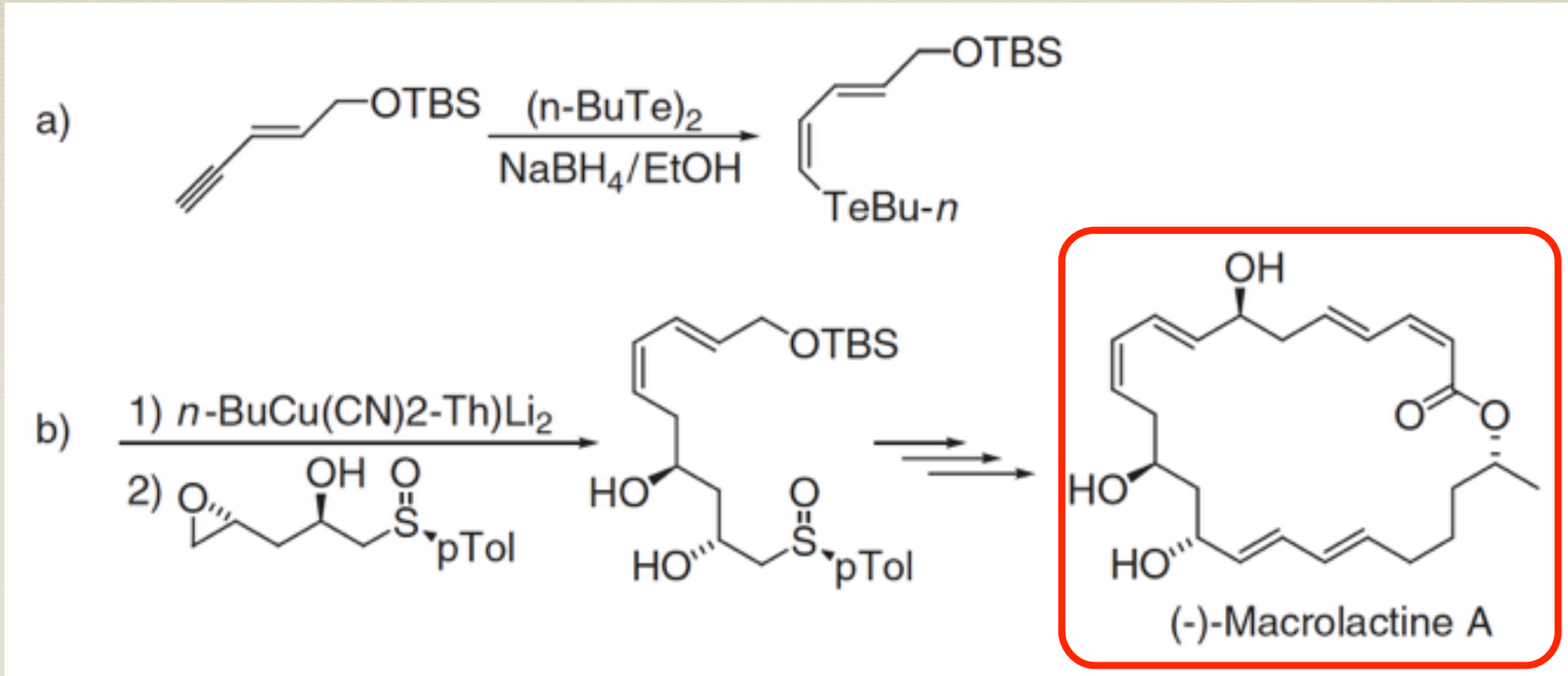
Cont.

Tucci, F. C.; Chieffi, A.; Comasseto, J. V.; Marino, J. P. *J. Org. Chem.* **1996**, *61*, 4975.

1,4- & 1,2- openning of epoxides

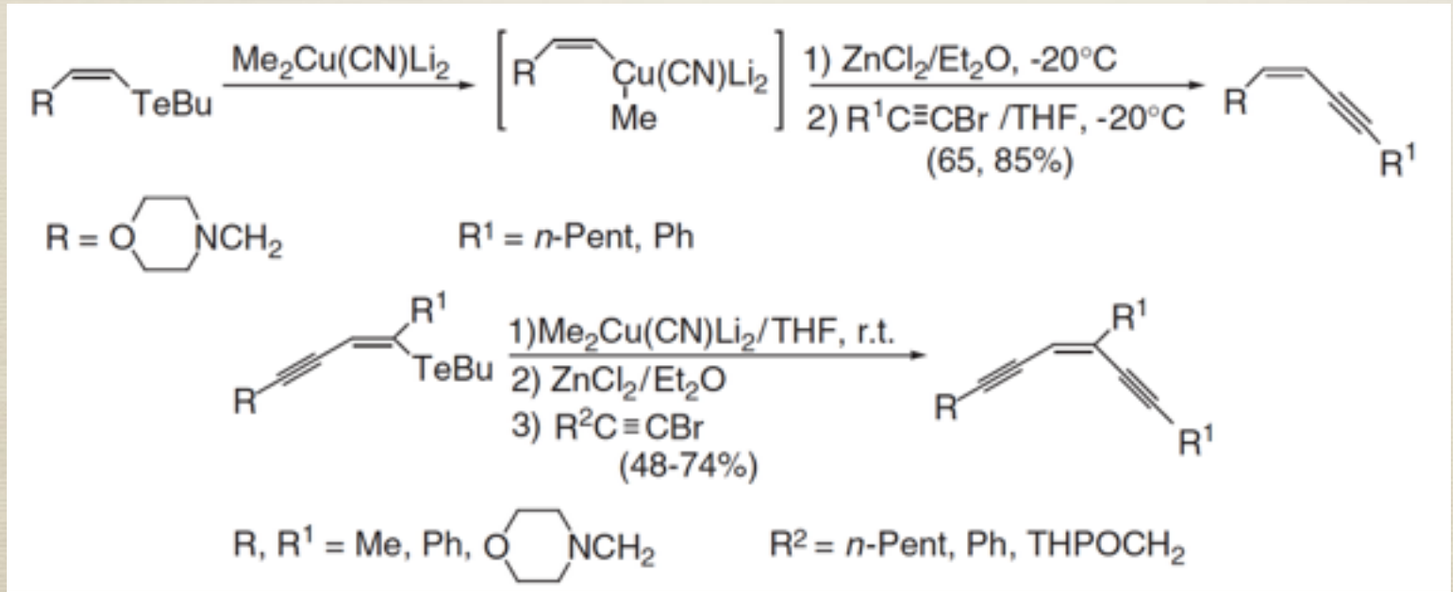
Vinylic tellurides

- Application in Total synthesis



Marino, J. P.; McClure, M. S.; Holub, D. P.; Comasseto, J. V.; Tucci, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 1664.

- **Reaction with bromoalkynes**

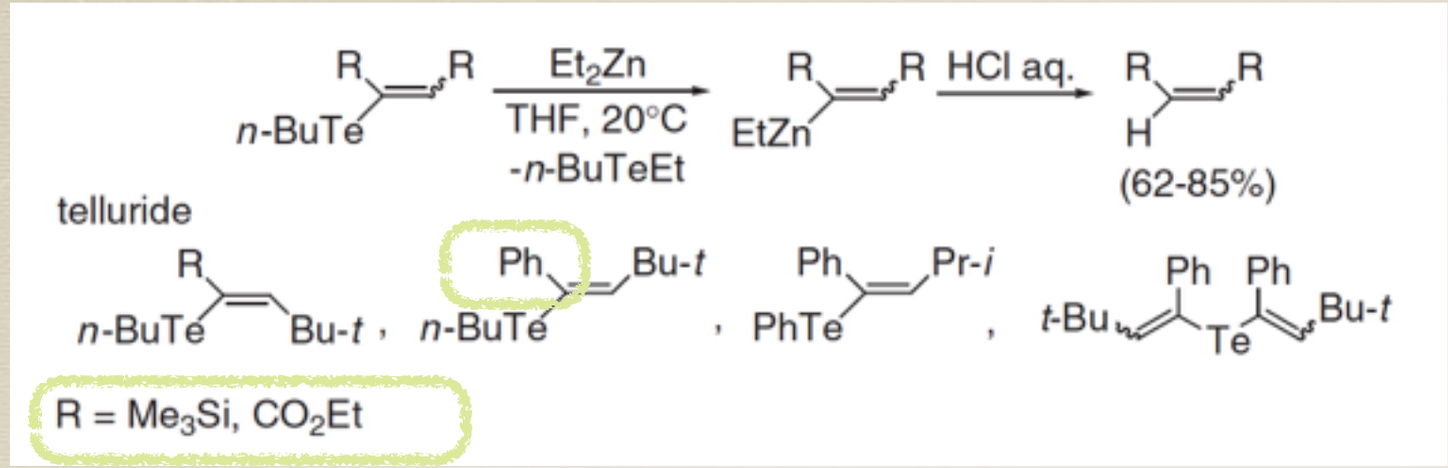


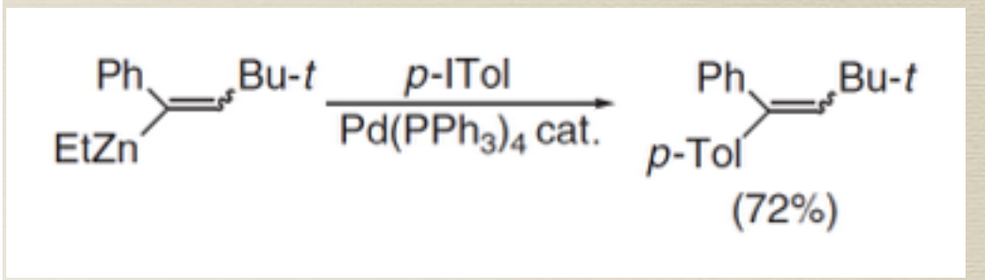
(Z)-enynes &
(Z)-enediynes

Araujo, M. A.; Comasseto, J. V. *Synlett* **1995**, 1145.

Vinylic tellurides

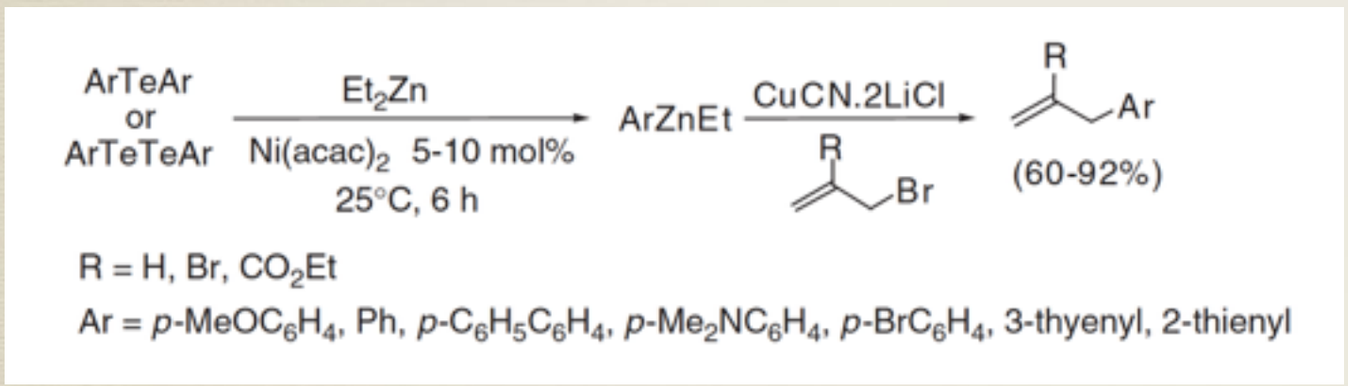
- **Exchange with Zinc and Aluminum**

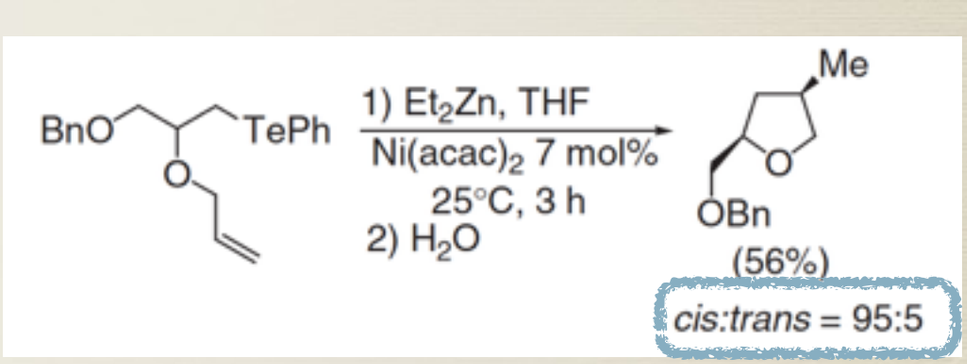




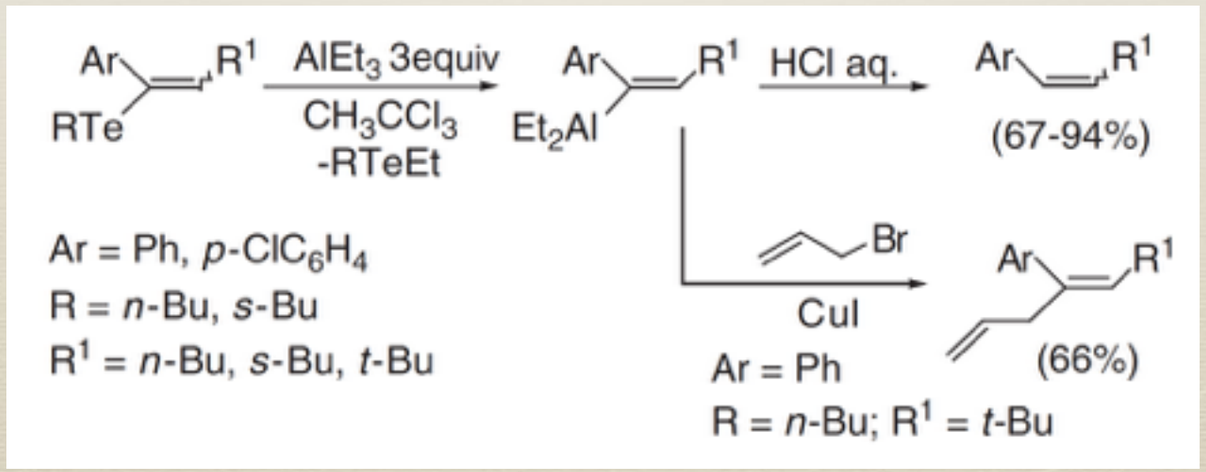
Stabilization from phenyl, ester or $SiMe_3$ is required

Terao, Y.; Kambe, N.; Sonoda, N. Tetrahedron Lett. 1996, 37, 4741. Dabdoub, M. J.; Dabdoub, V. M.; Marino, J. P. *Tetrahedron Lett.* **2000**, *41*, 433.





Stüdemann, T.; Gupta, V.; Engman, L.; Knochel, P. *Tetrahedron Lett.* **1997**, *38*, 1005.

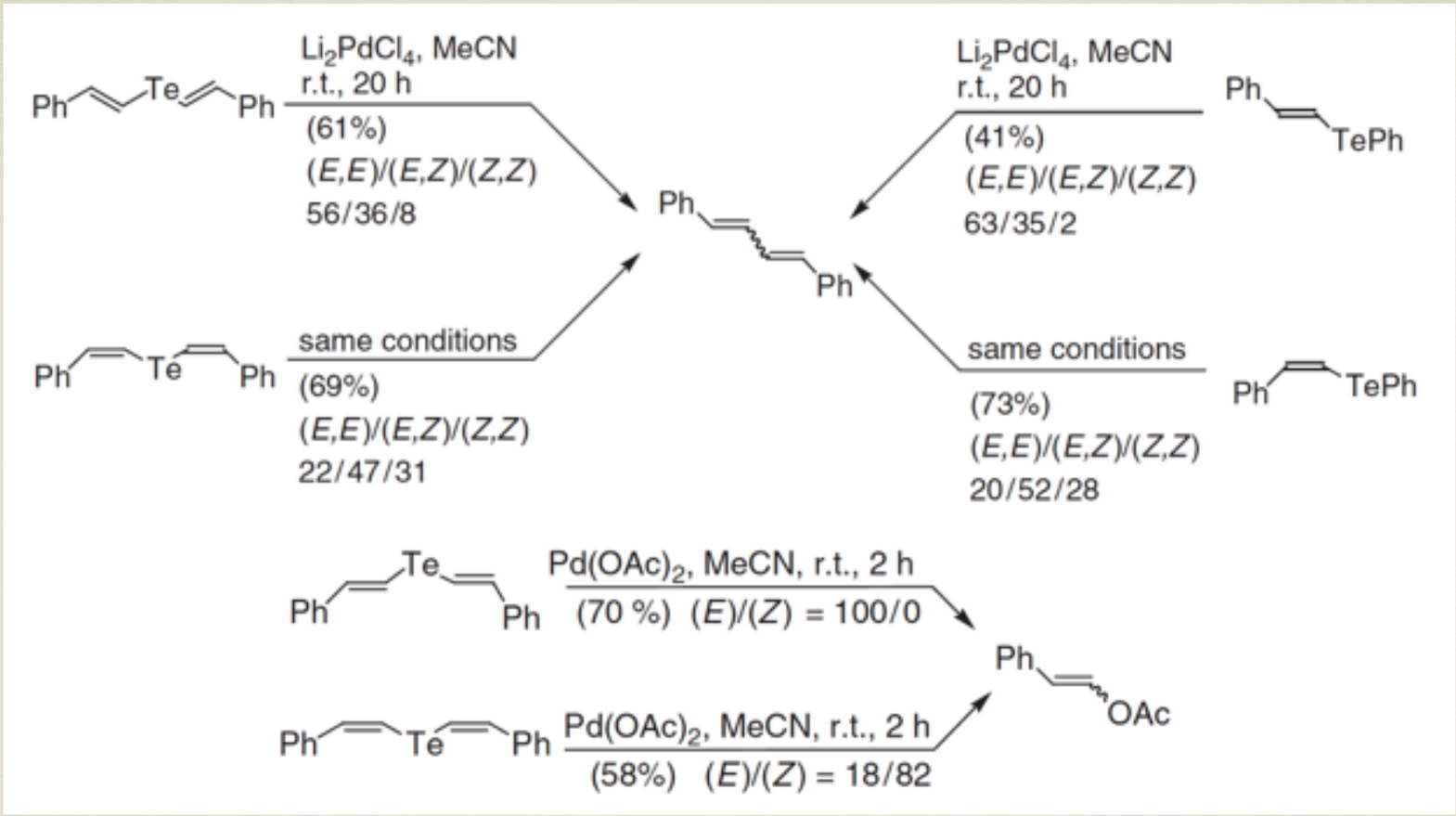


- trapping experiments shows no organometallic intermediates
- Radical intermediate?

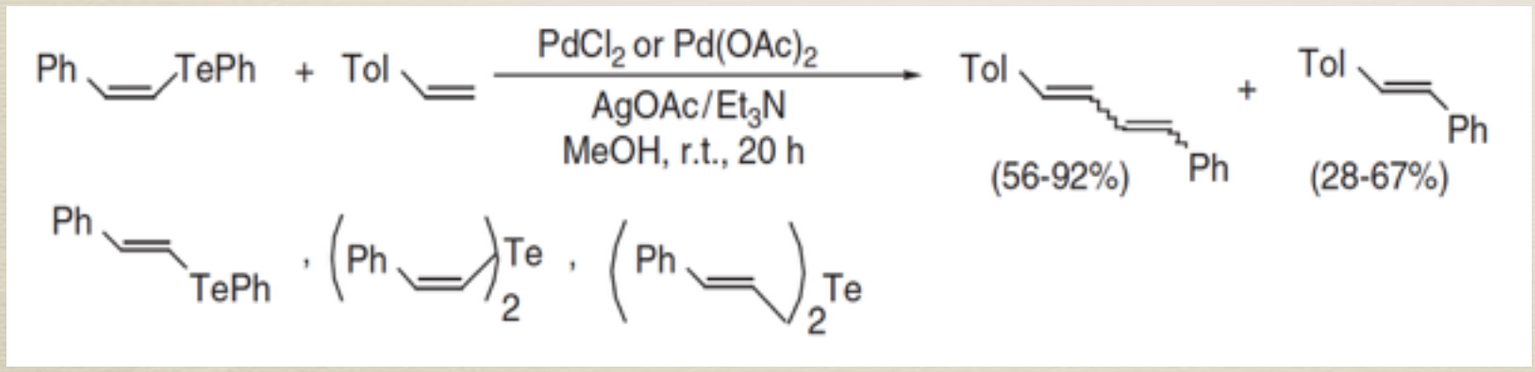
Terao, J.; Kambe, N.; Sonoda, N. *Synlett* **1996**, 779.

Vinylic tellurides

- **Coupling reactions**
  - Pd(II)-catalysed coupling of vinyl tellurides



Nishibayashi, Y.; Cho, C. S.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **1996**, *526*, 335.; Uemura, S.; Takahashi, H.; Ohe, K. *J. Organomet. Chem.* **1992**, *423*, 19.

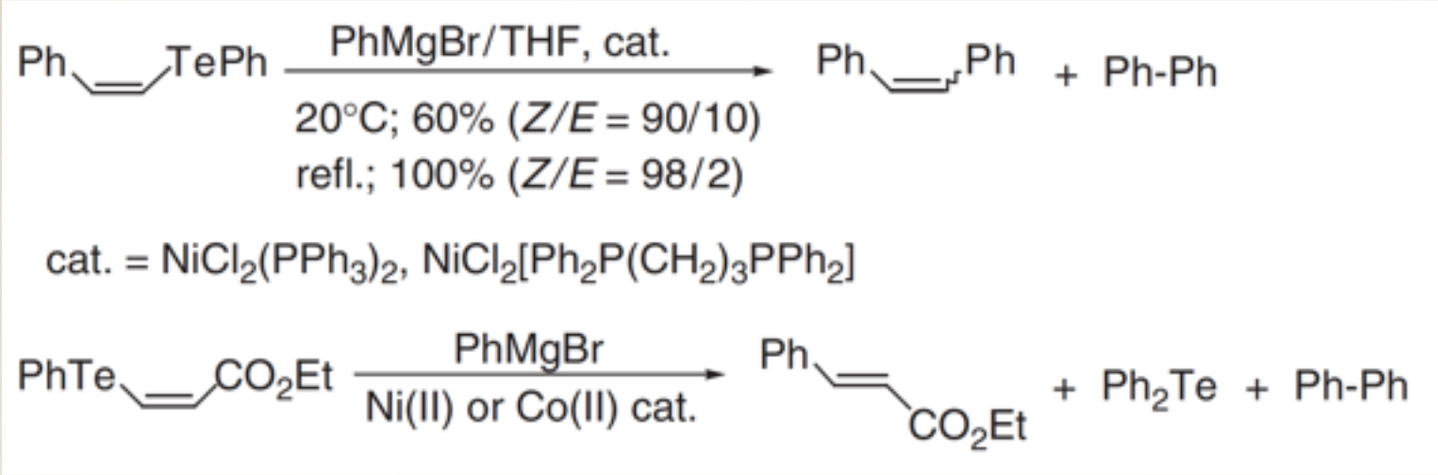


Retention of stereochemistry

Nishibayashi, Y.; Cho, C. S.; Uemura, S. *J. Organomet. Chem.* **1996**, *507*, 197.

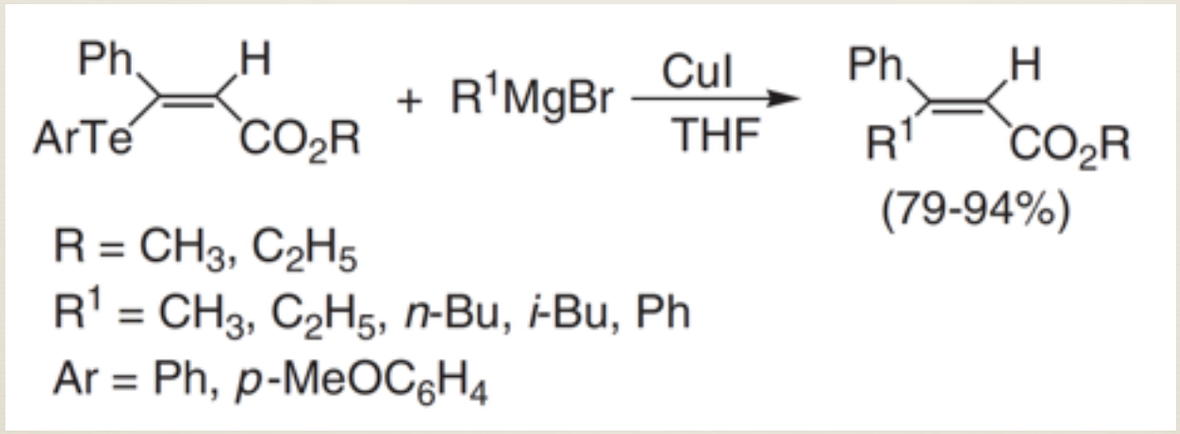
Vinylic tellurides

- Ni(II)- or Cu(I)-catalyzed cross-coupling with Grignard reagents



substrate control

Uemura, S.; Fukuzawa, S. I.; Patil, S. R. *J. Organomet. Chem.* **1983**, *243*, 9.

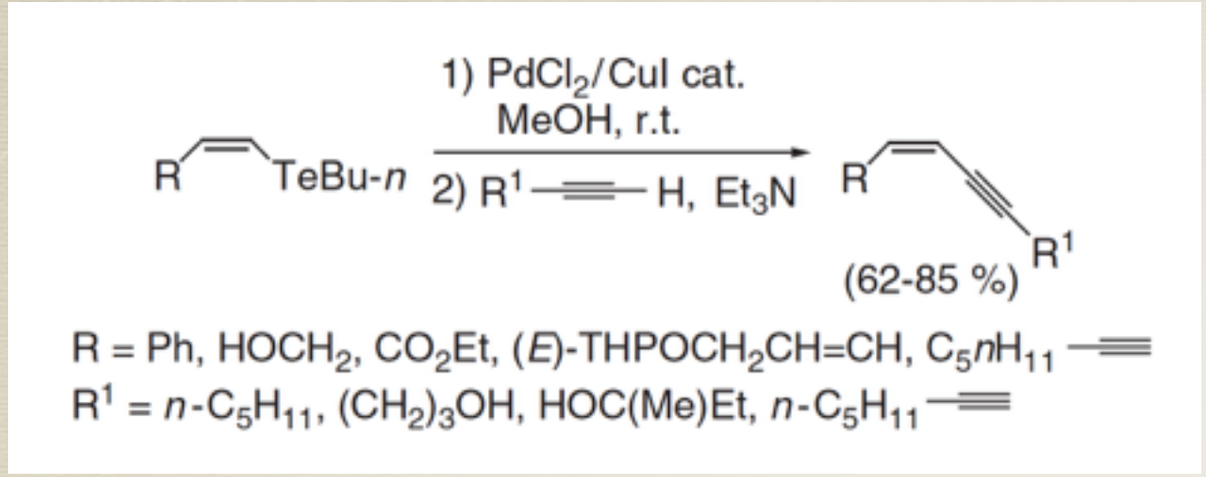


Double bond stereochemistry retention

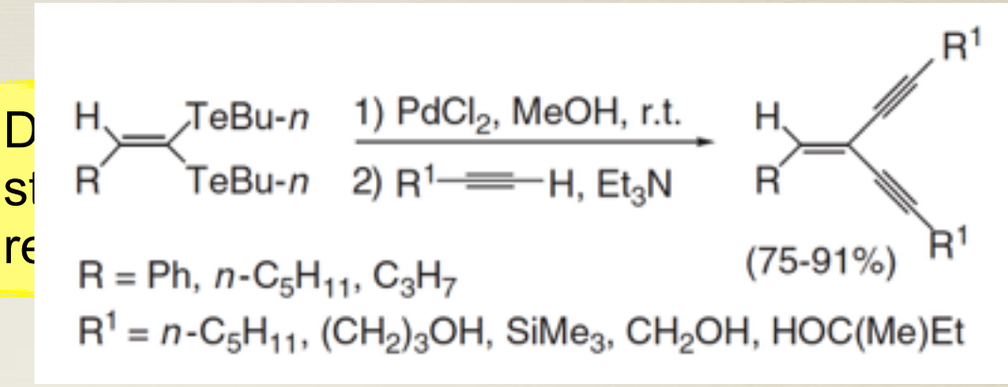
Huang, X.; Zhao, C. Q. *Synth. Commun.* **1997**, *27*, 237.

Vinylic tellurides

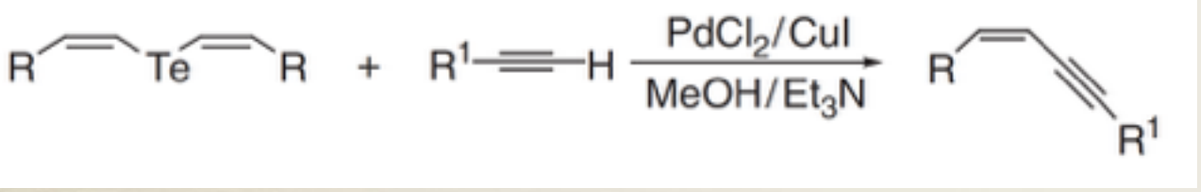
- Ni(II)- or Pd(II)-catalyzed Sonogashira-type cross-coupling



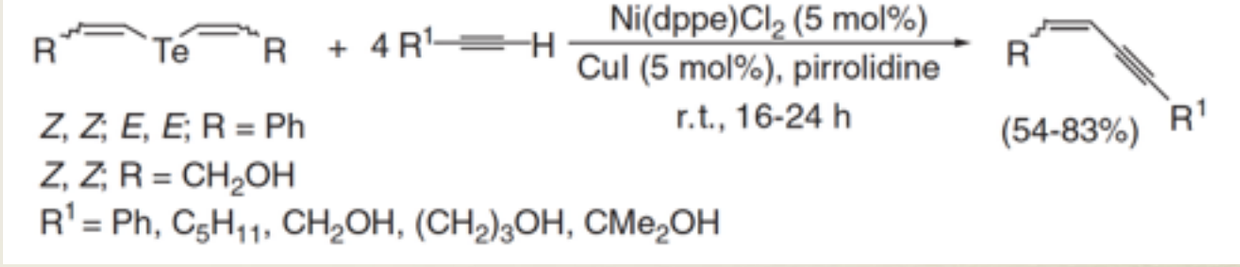
Zeni, G.; Comasseto, J. V. *Tetrahedron Lett.* **1999**, *40*, 4619.



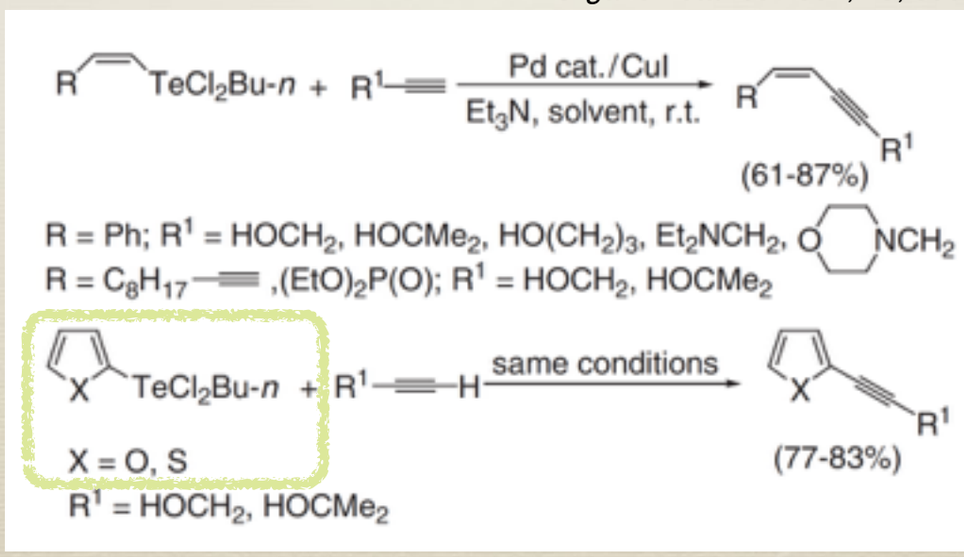
Zeni, G.; Perin, G.; Cella, R.; Jacob, R. G.; Braga, A. L.; Silveira, C. C. *Synlett* **2002**, *10*, 1.



Zeni, G.; Menezes, P. H.; Moro, A. V.; Braga, A. L.; Silveira, C. C. *Synlett* **2001**, *9*, 1473.



Silveira, C. C.; Braga, A. L.; Vieira, A. S.; Zeni, G. *J. Org. Chem.* **2003**, *68*, 662.
Raminelli, C.; Prechtl, M. M. G.; Santos, L. S.; Eberlin, M. N.; Comasseto, J. V. *Organometallics* **2004**, *23*, 3990.

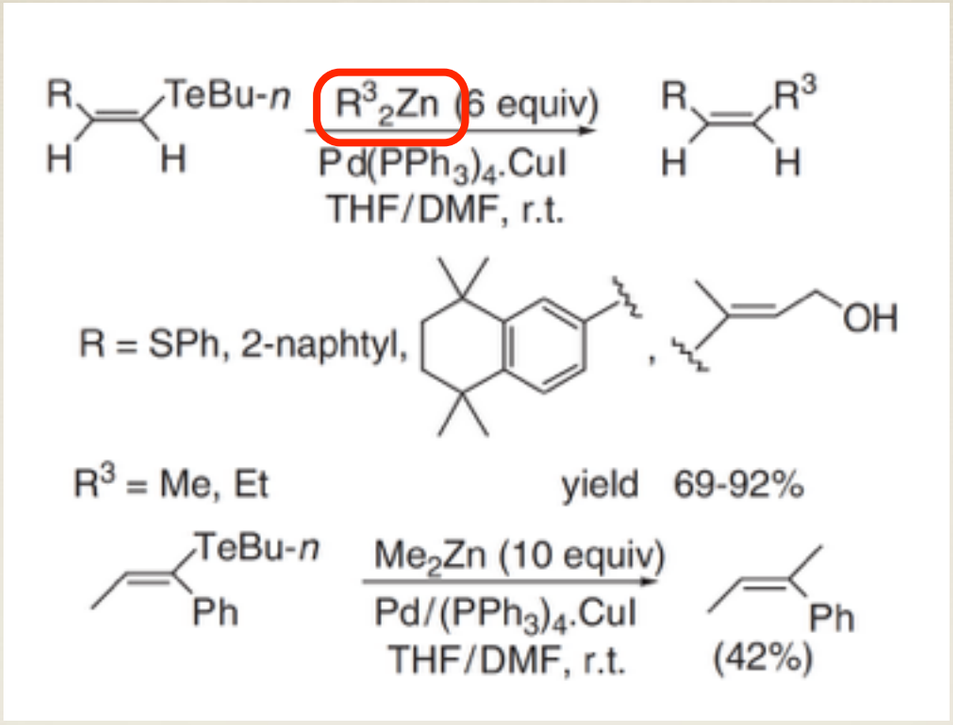


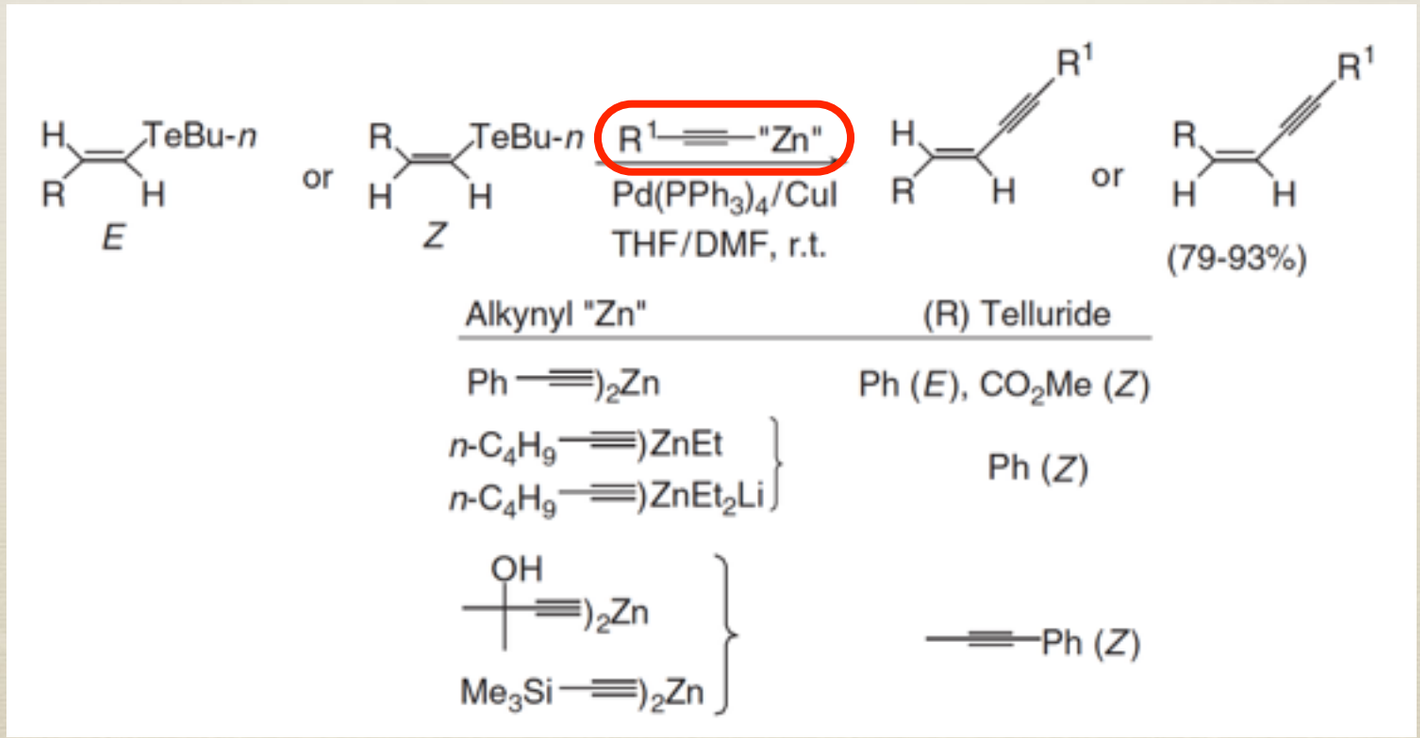
heteroaromatic tellurium dichlorides

Braga, A. L.; Lüdtke, D. S.; Vargas, F.; Donato, R. K.; Silveira, C. C.; Stefani, H. A., Zeni, G. *Tetrahedron Lett.* **2003**, *44*, 1779..

Vinylic tellurides

- Pd/Cu-catalysed cross-coupling with organyl zinc reagents

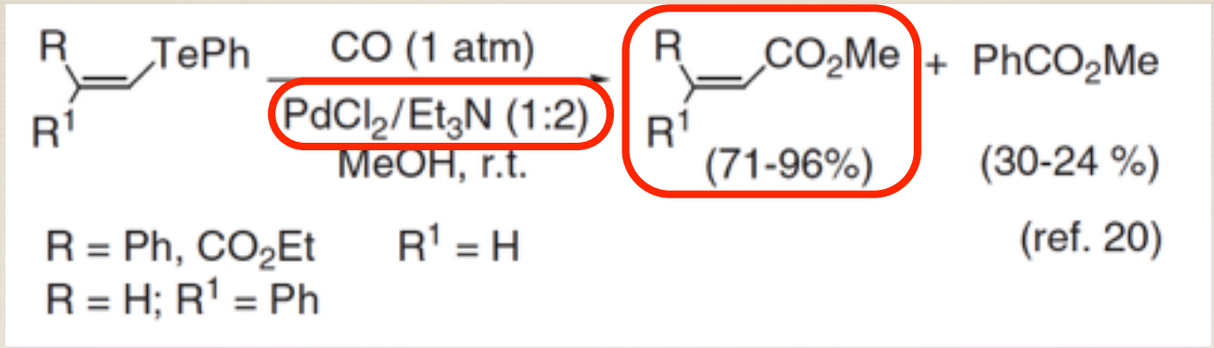




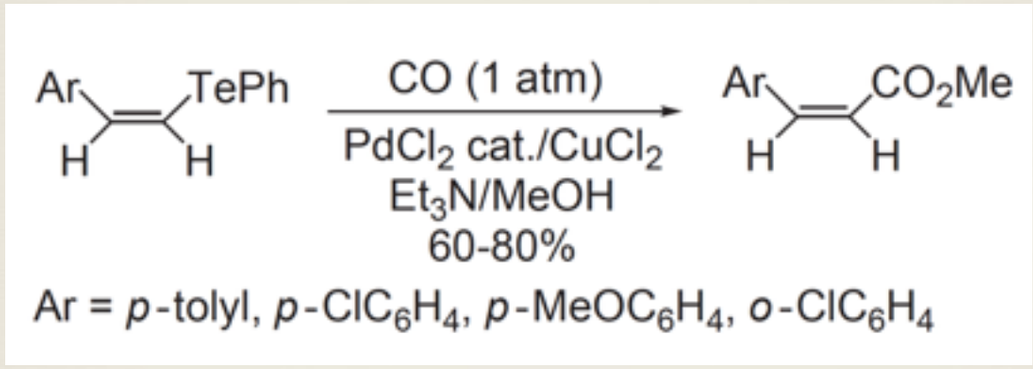
Dabdoub, M. J.; Dabdoub, V. M.; Marino, J. P. *Tetrahedron Lett.* **2000**, *41*, 433. Dabdoub, M. J.; Dabdoub, V. M.; Marino. J. P. *J. Org. Chem.* **2000**, *41*, 437.

Vinylic tellurides

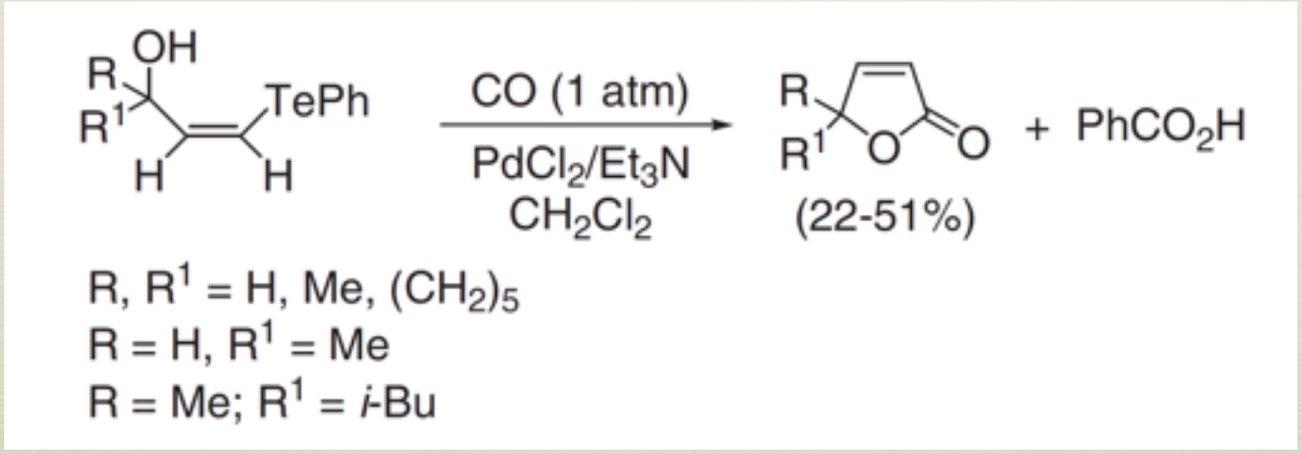
- **Palladium catalyzed detellurative carbonylation**



Double bond stereochemistry retention



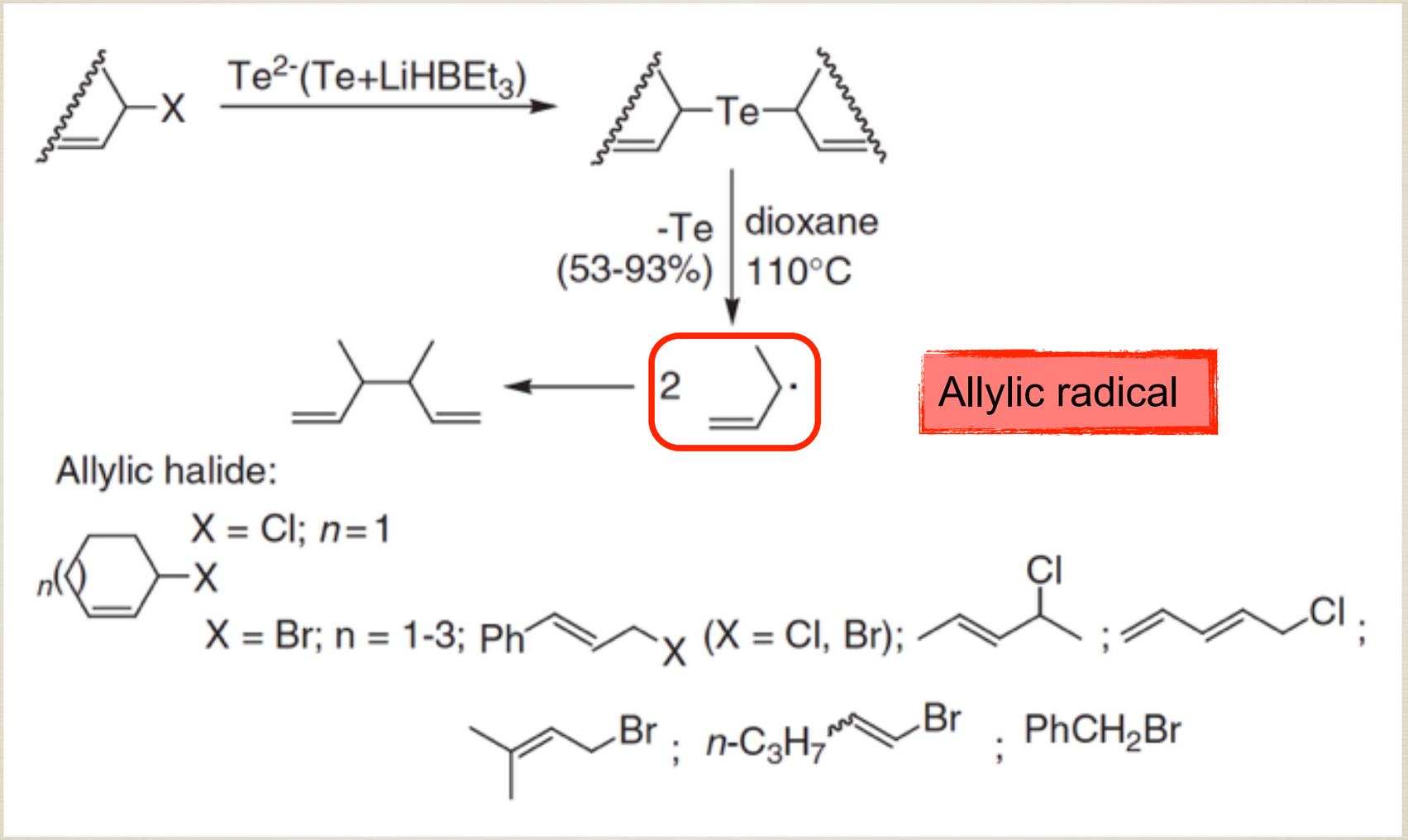
Oxidant can also be $CuCl_2$, $CuCl/O_2$, $FeCl_3$, Ce(IV) salts or benzoquinone; $CuCl_2$ is most efficient.



Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* **1987**, *52*, 4859.

Free Radical Chemistry

- **Telluride-ion-promoted coupling of allylic halides**

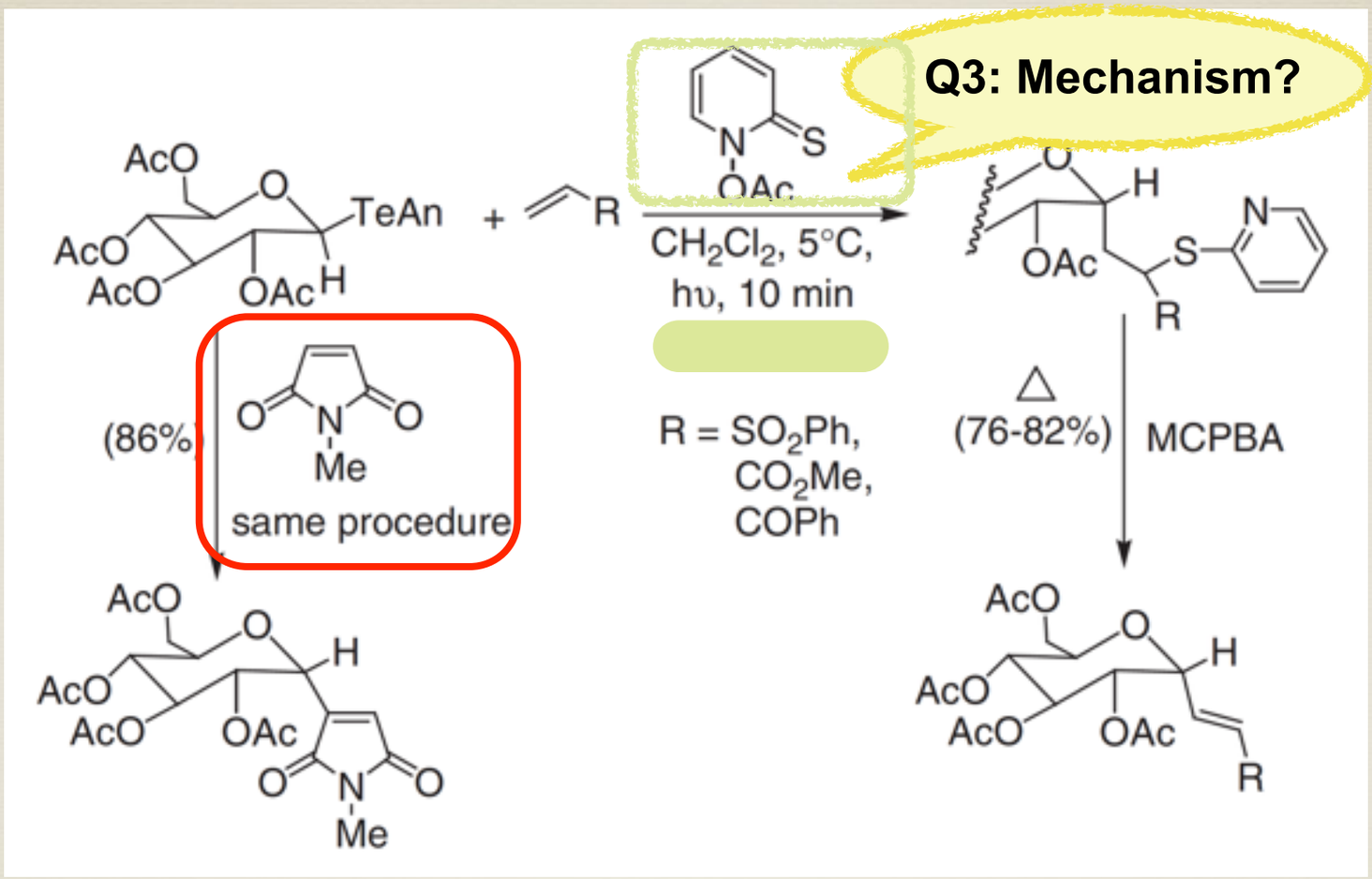


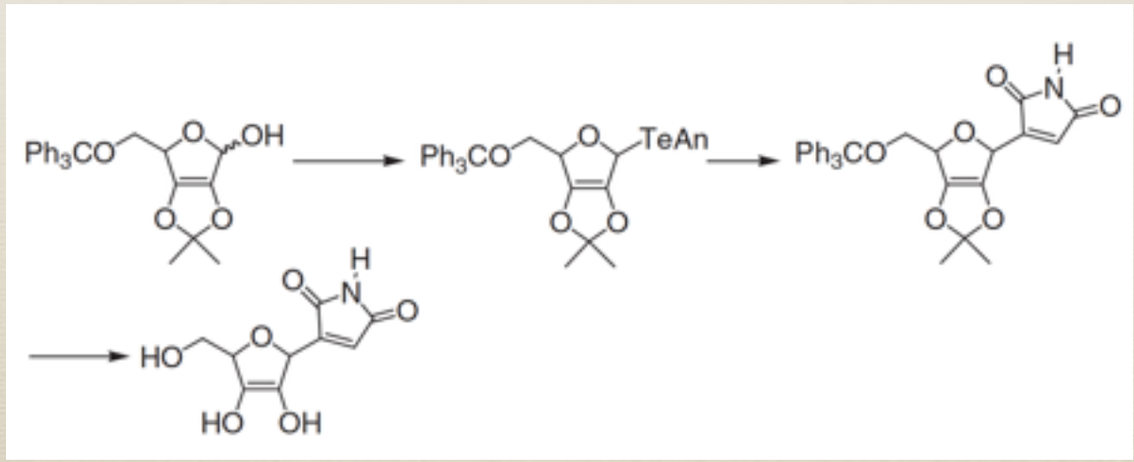
Clive, D. L. J.; Anderson, P. C.; Moss, N.; Singh, A. *J. Org. Chem.* **1982**, *47*, 1641.

Free Radical Chemistry

- **Organyl tellurides as exchangers of carbon radicals**

Initiator: N-acetoxy-2-thiopyridone



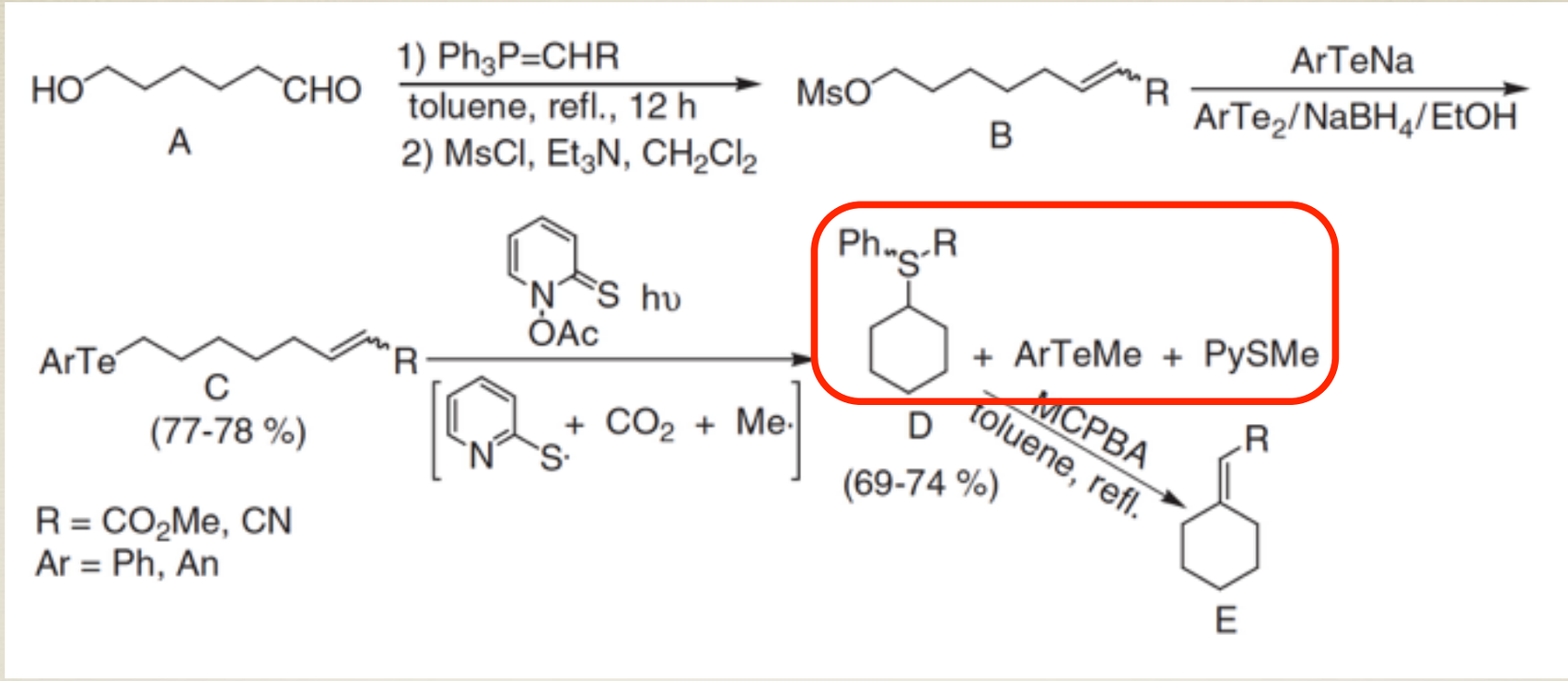


Synthesis of antibiotic showdomycin

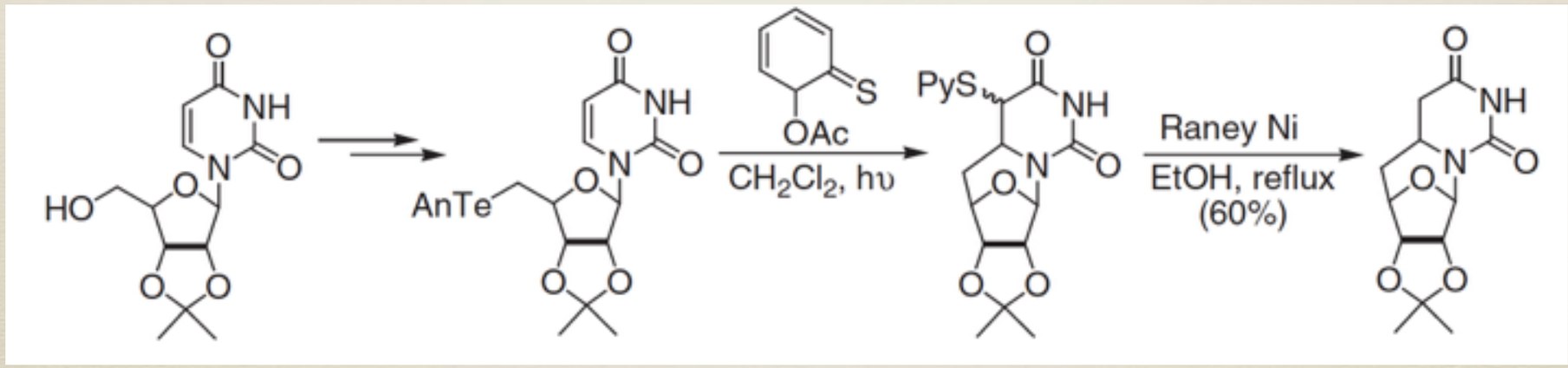
Barton, D. H. R.; Ramesh, M. *J. Am. Chem. Soc.* **1990**, *112*, 891.

Free Radical Chemistry

- Intramolecular radical cyclizations



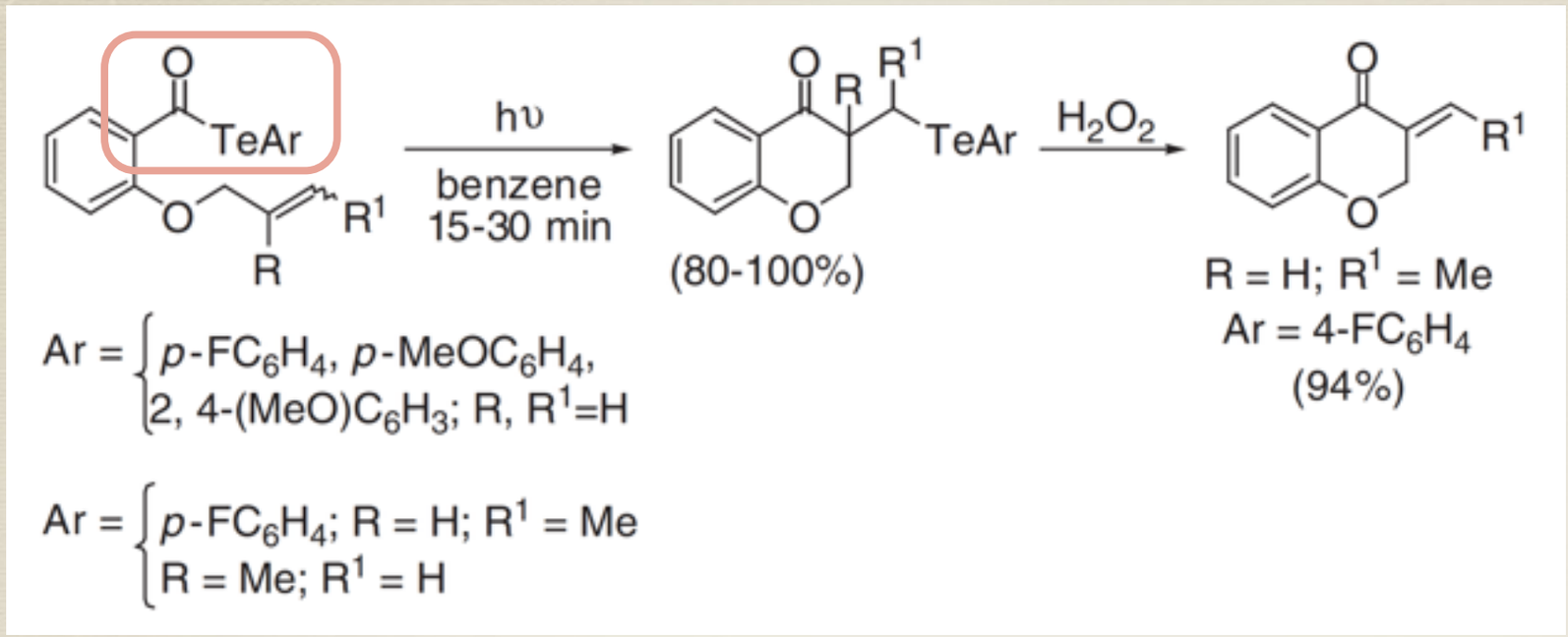
Barton, D. H. R.; Ramesh, M. *J. Am. Chem. Soc.* **1990**, *112*, 891.



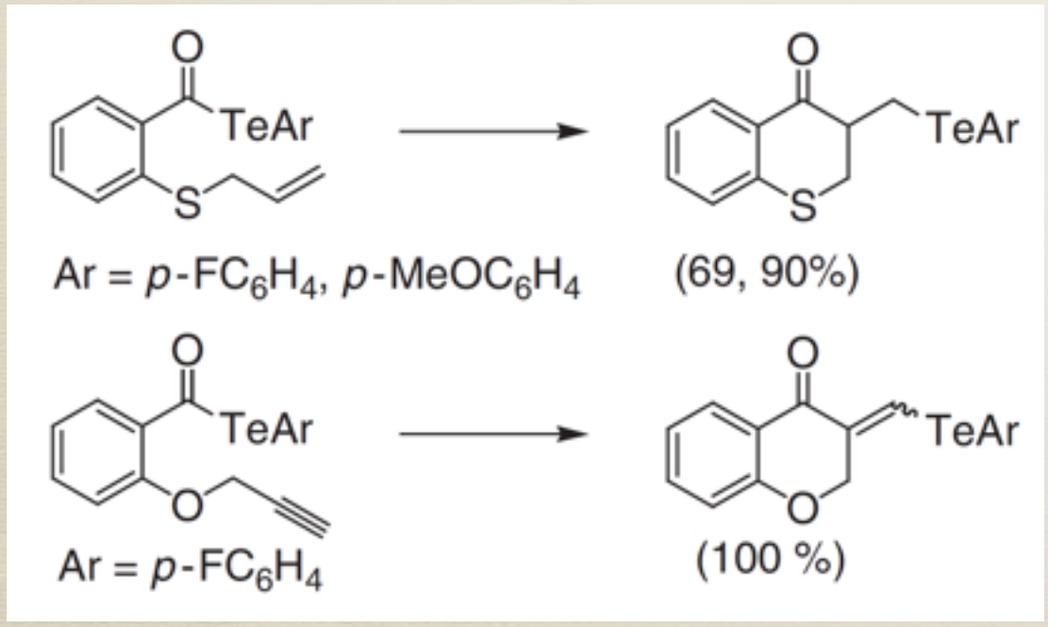
Barton, D. H. R.; Gero, S. D.; Sire, B. Q.; Samadi, M.; Vincent, C. *Tetrahedron* **1991**, *47*, 9383.

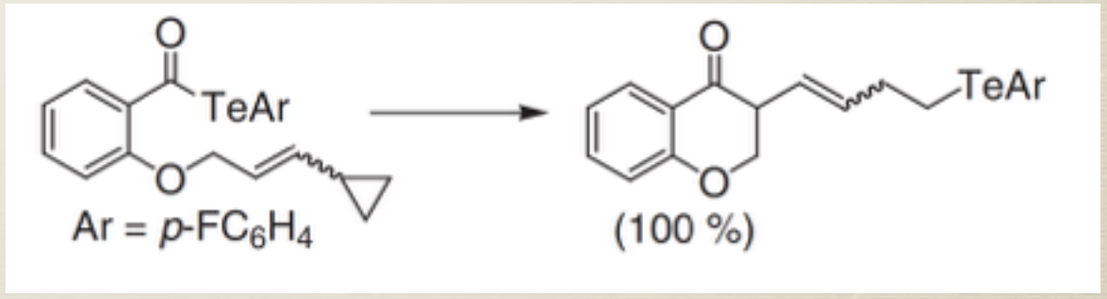
Free Radical Chemistry

- **Telluroesters as source of acyl radicals**



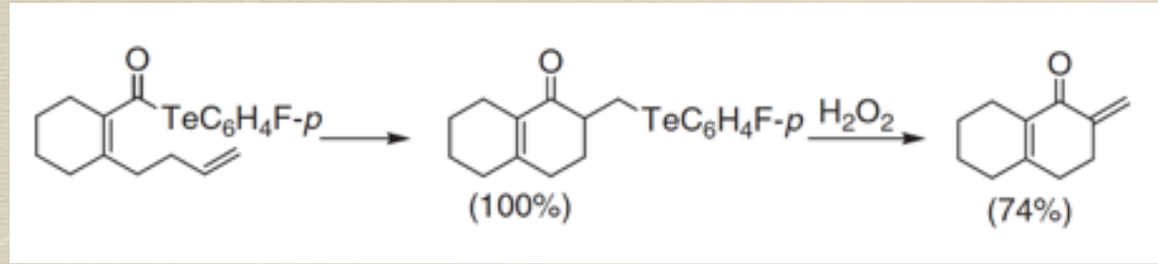
Telluroesters: excellent sources of acyl radicals [upon photolysis with a 250 W tungsten lamp, or thermal process (benzene at reflux) in the dark.]

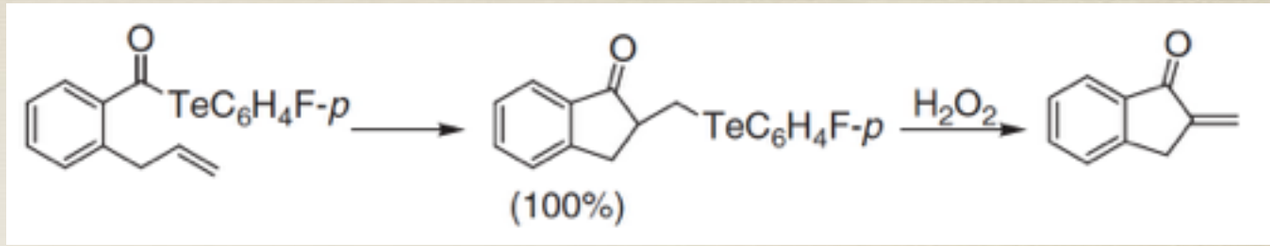


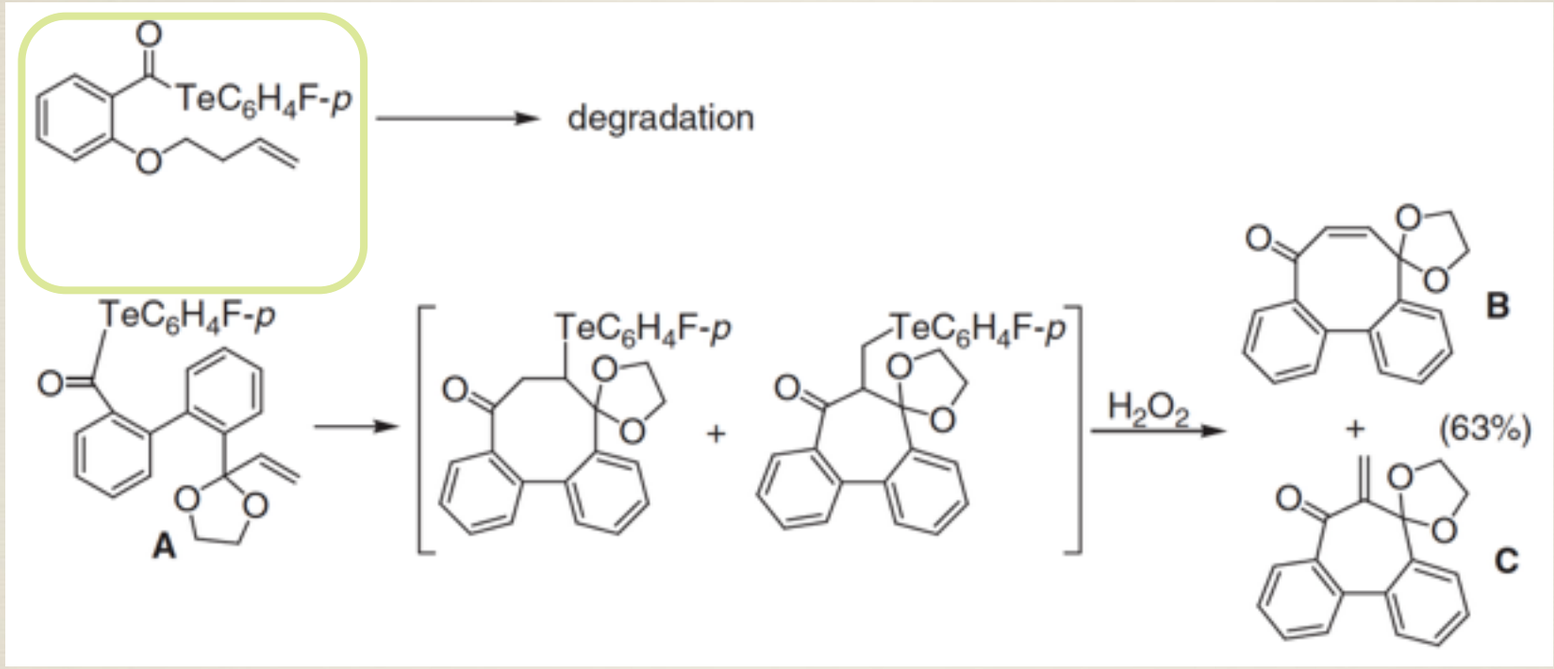


Crich, D.; Chen, C.; Hwang, J. T; Yuan, H.; Papadatos, A.; Walter, R. I. *J. Am. Chem. Soc.* **1994**, *116*, 8937.

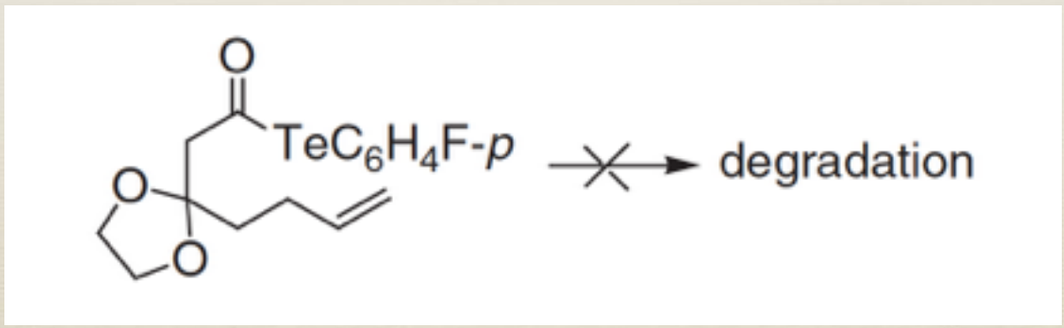
Free Radical Chemistry







Achieve 7,8-membered ring with strained substrate

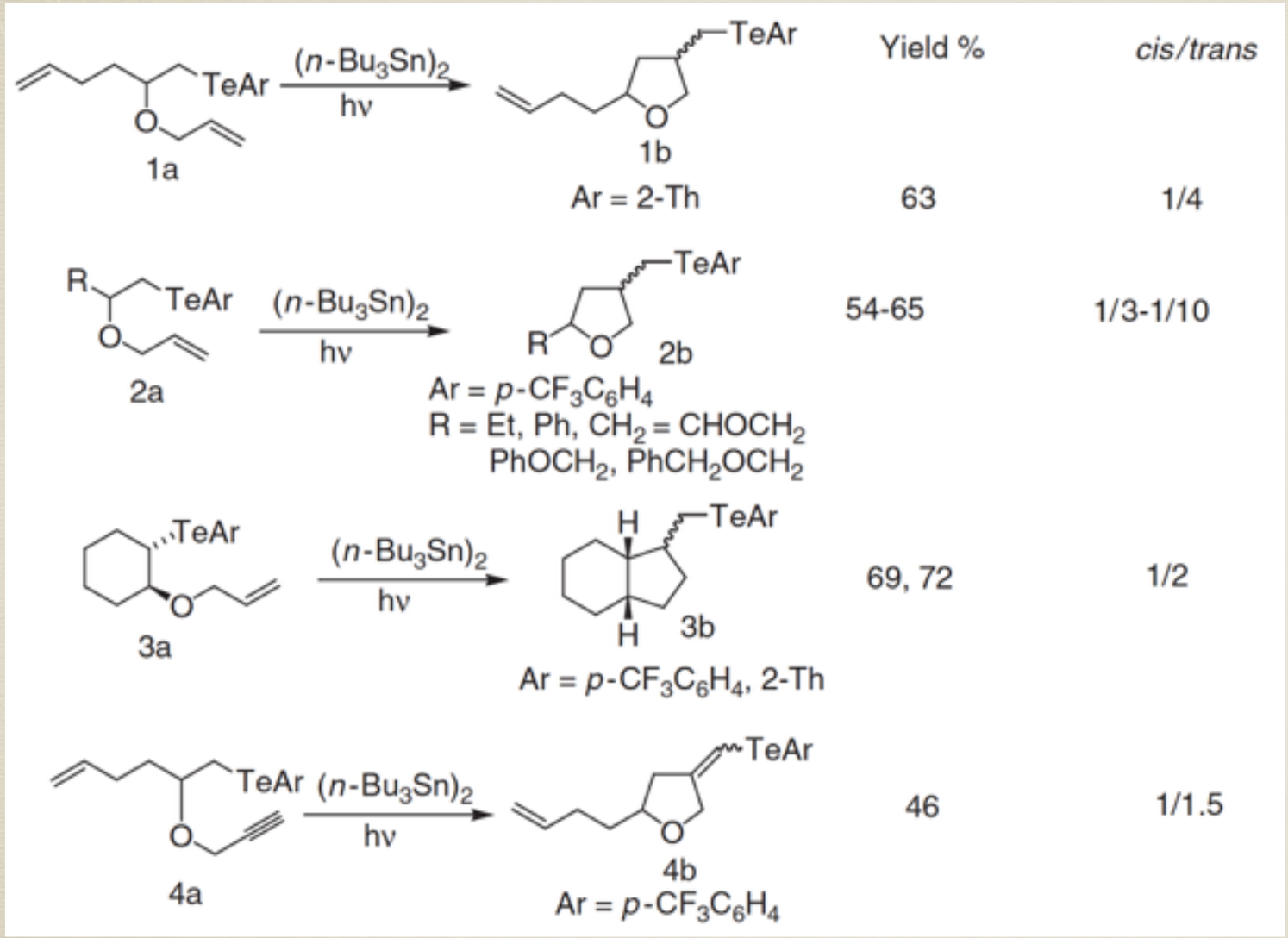


The importance of conjugated olefin or aromatic ring

Crich, D.; Chen, C.; Hwang, J. T; Yuan, H.; Papadatos, A.; Walter, R. I. *J. Am. Chem. Soc.* **1994**, *116*, 8937.

Free Radical Chemistry

- **2-Allyloxy alkyl tellurides as precursors of tetrahydrofuran derivatives**

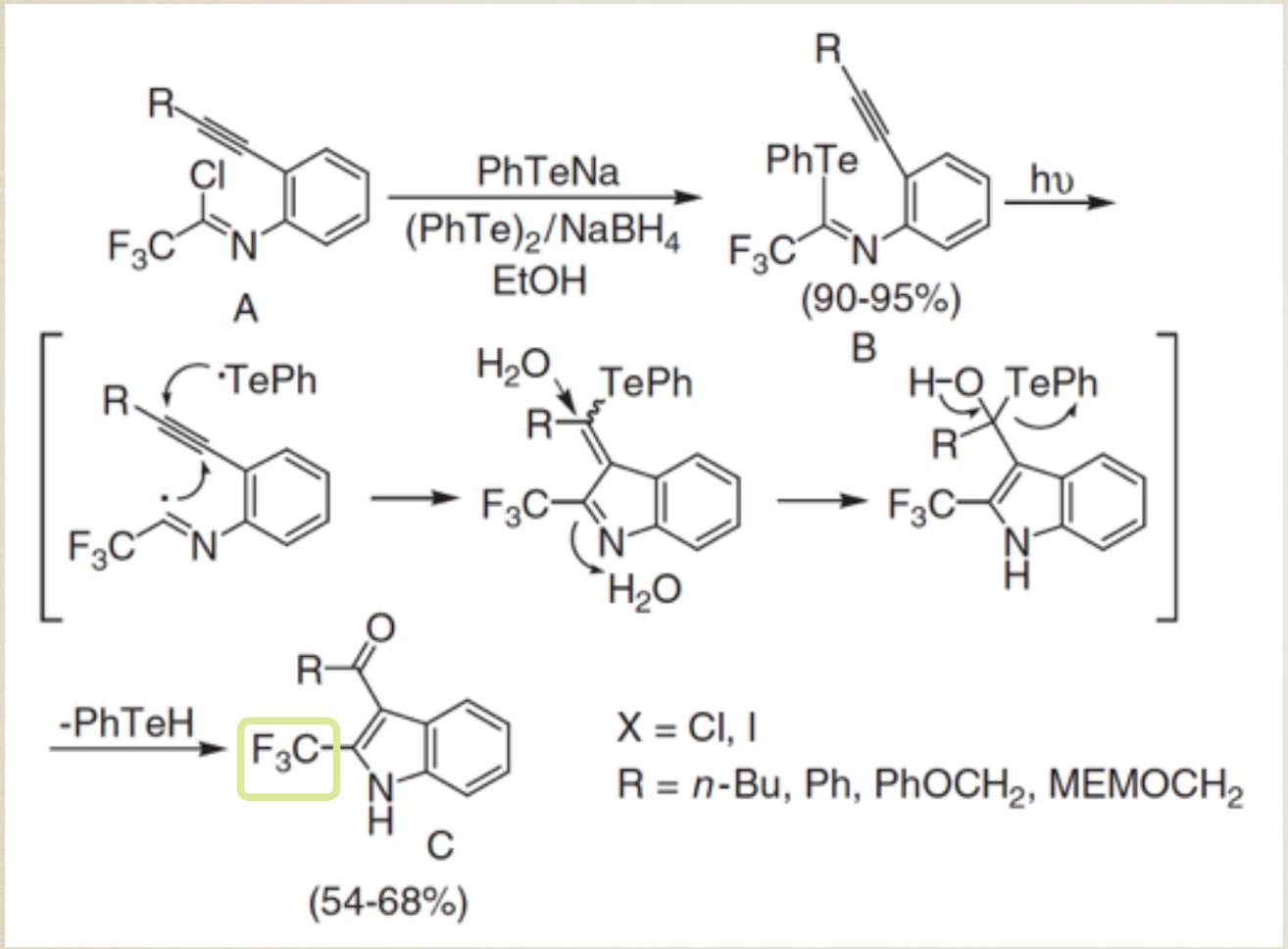


The control of DB configuration is not satisfying

Engman, L.; Gupta, V. *J. Chem. Soc. Chem. Commun.* **1995**, 2515. Engman, L.; Gupta, V. *J. Org. Chem.* **1997**, *62*, 157.

Free Radical Chemistry

- **Synthesis of indole derivatives via radical cyclization**

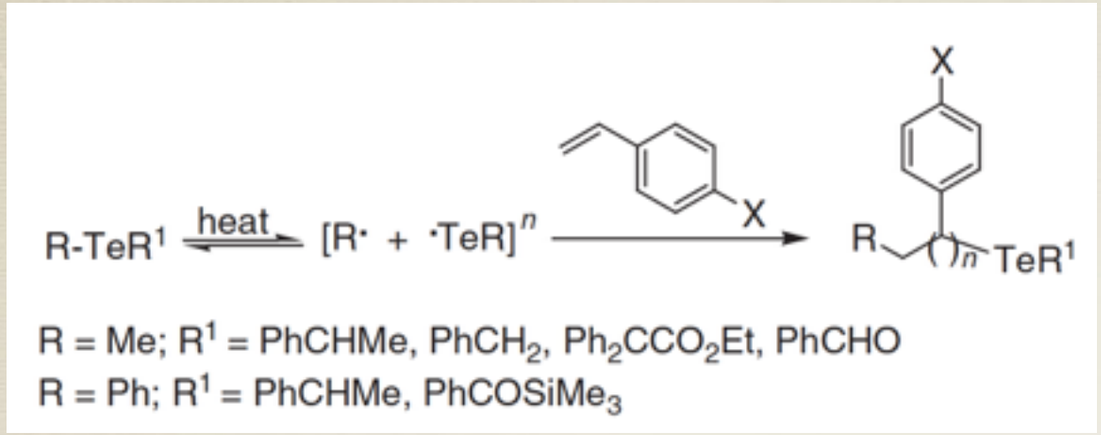


important target in medicinal and agricultural chemistry

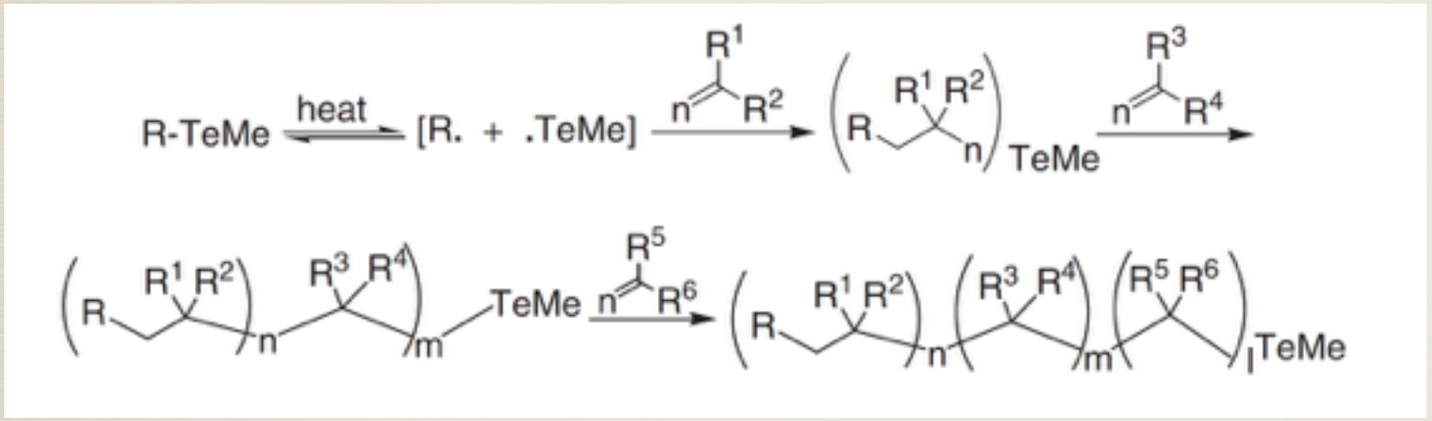
Ueda, Y.; Watanabe, H.; Uemura, J.; Uneyama, K. *Tetrahedron Lett.* **1993**, *34*, 7933.

Free Radical Chemistry

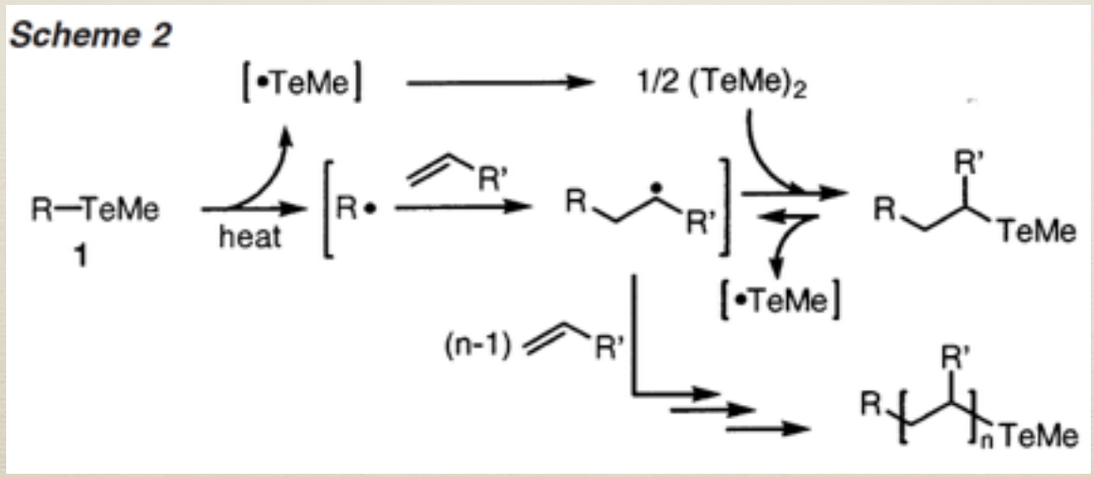
- **Organotellurium compounds as initiators for controlled living radical polymerization**



Advantages:
- Easy to synthesize a tailor-made initiator
- Easy to modify the polymer end-group



diblock and triblock copolymer synthesis



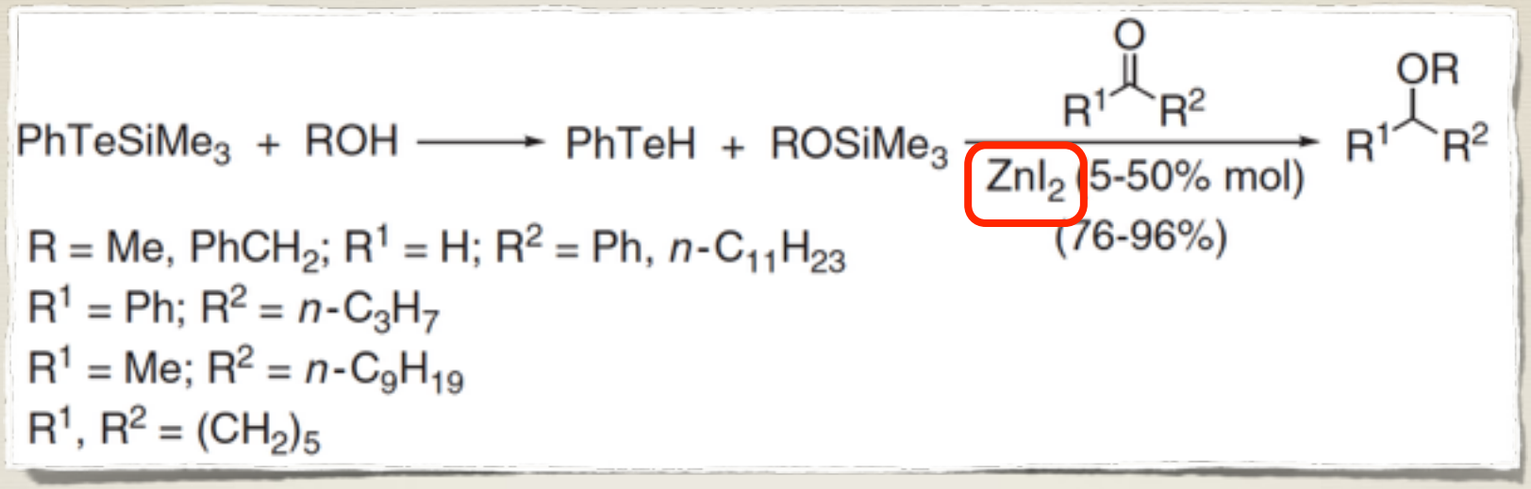
ditelluride-capping mechanism

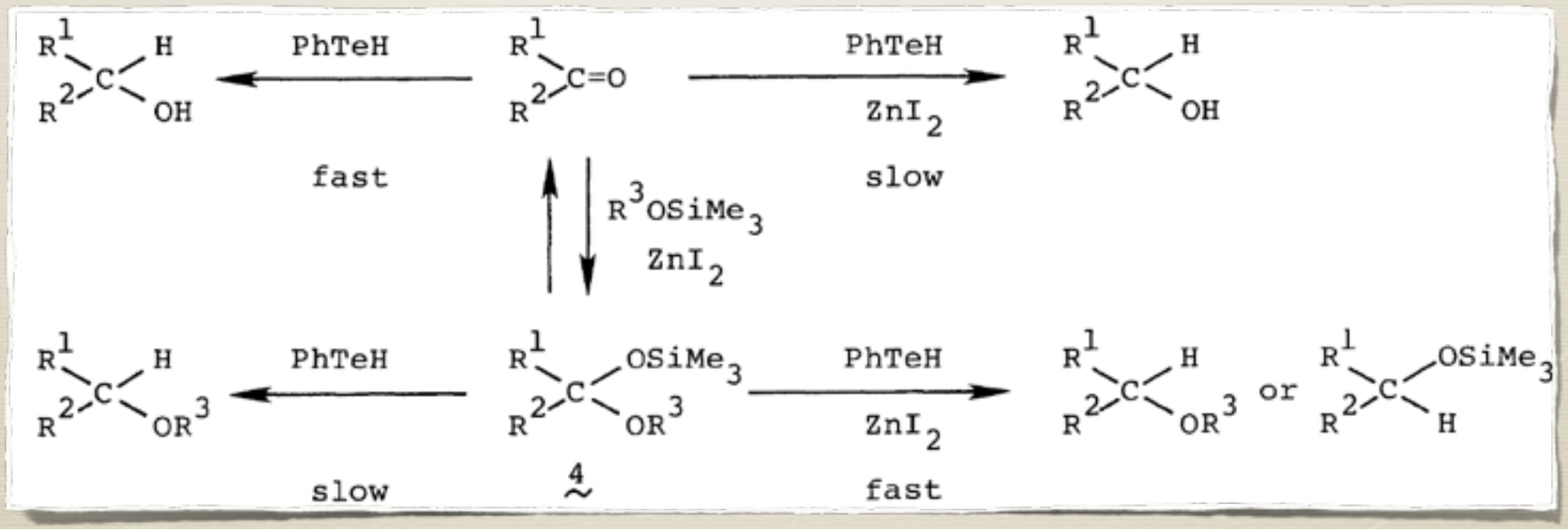
Yamago, S.; Lida, K.; Yoshida, J. I. *J. Am. Chem. Soc.* **2002**, *124*, 2874. Yamago, S.; Lida, K.; Yoshida, J. I. *J. Am. Chem. Soc.* **2002**, *124*, 13666.

Thanks for your attention!

Q1 answers

Q1: For the following reactions, please give an explanation to the observed result that ether instead of alcohol is the main product in the existence of zinc iodide.

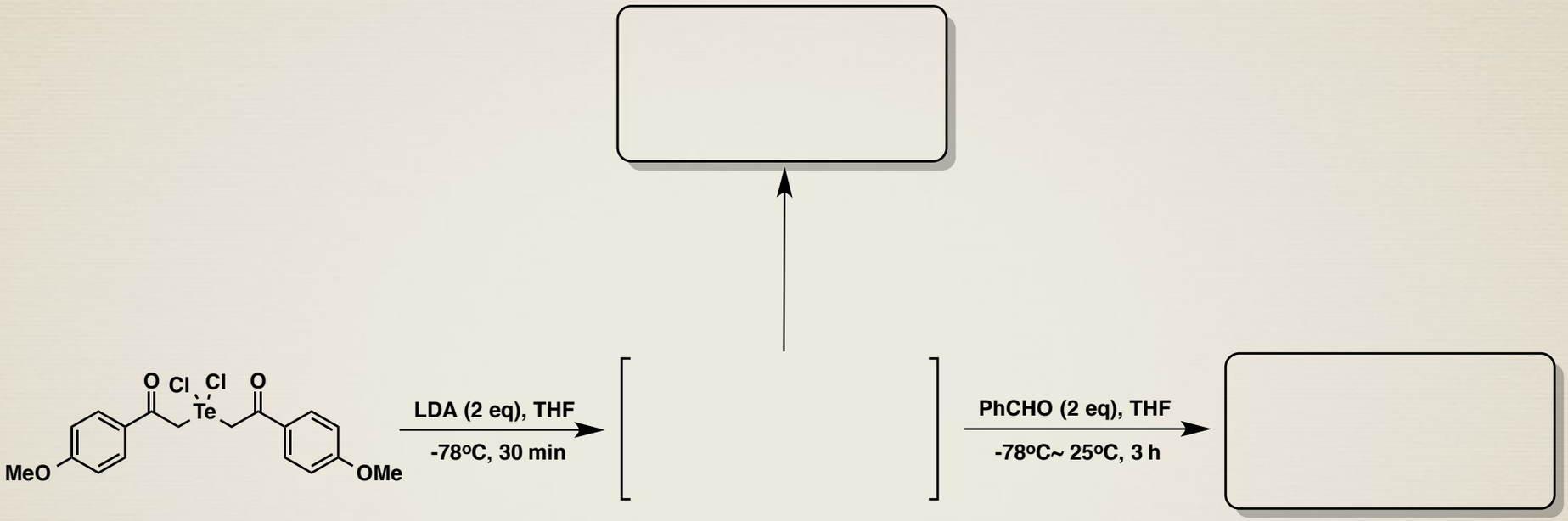


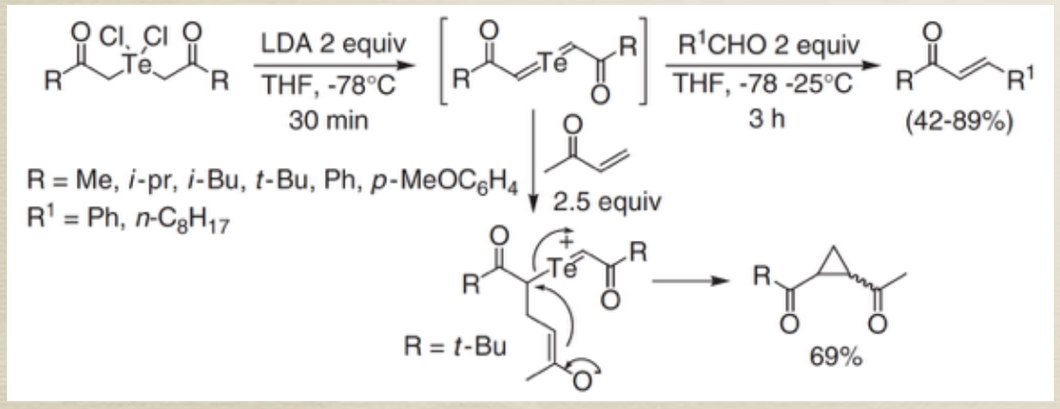


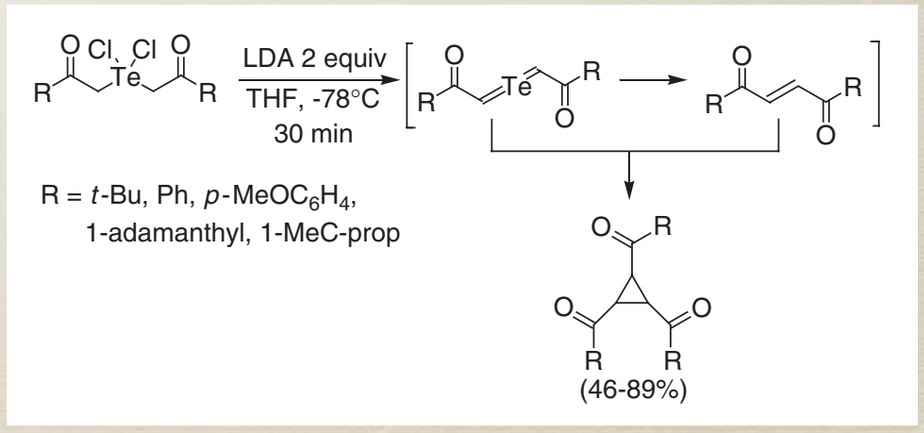
Nagakawa, K.; Osuka, M.; Sasaki, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1987**, 1331.

Q2 answers

Q2: From bis(oxoalkyl)tellurium dichlorides, we can synthesize enones and cyclopropanes. The mechanism involves the intermediacy of a bis-ylide which further reacts with aldehydes or enone. Please fill out the missing structures in **Graph.1**.



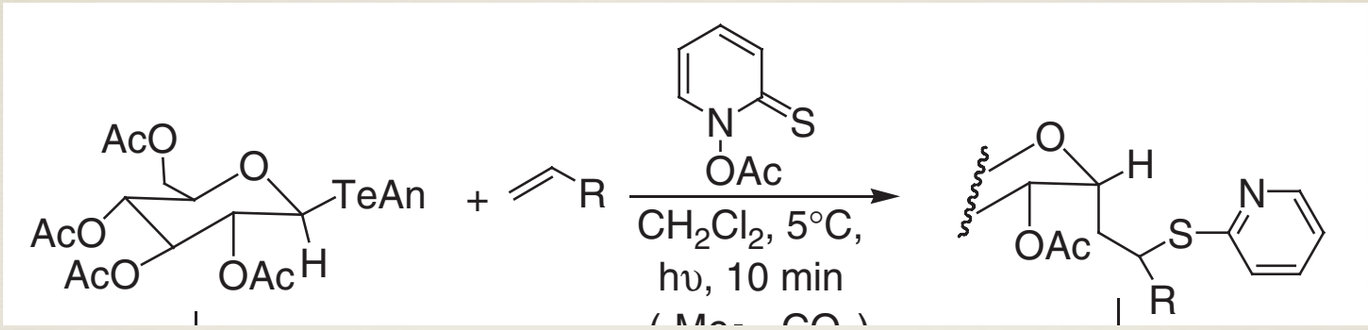


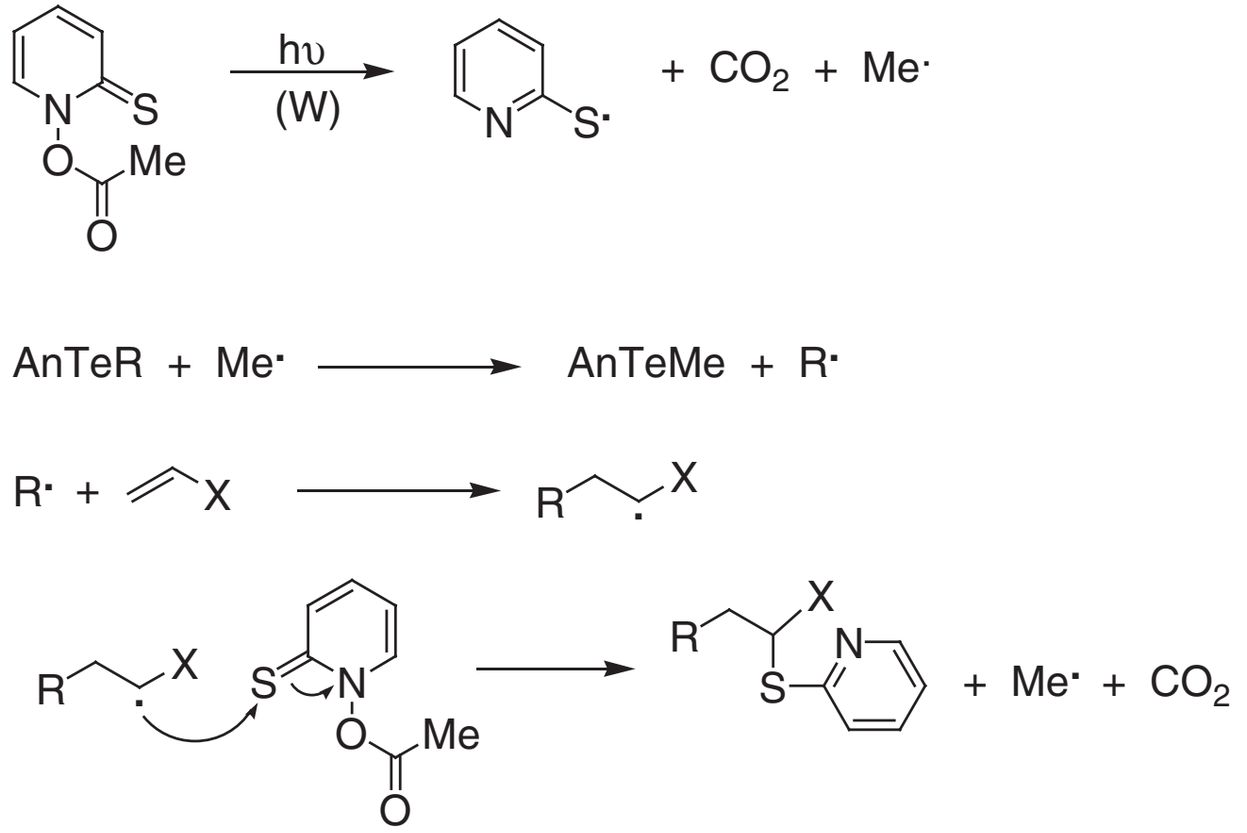


Han, L. B.; Kambe, N.; Ryu, I.; Sonoda, N. *Chem. Lett.* **1993**, 561.

Q3 answers

Q3: In the presentation, we have talked about the free radical chemistry of organyl tellurides. Reactions using N-acetoxy-2-thiopyridone as initiator have shown to be useful in the synthesis of antibiotics. Please draw the **mechanism** for the following reaction.





Barton, D. H. R.; Ramesh, M. *J. Am. Chem. Soc.* **1990**, *112*, 891.