北京大学
PEKING UNIVERSITY

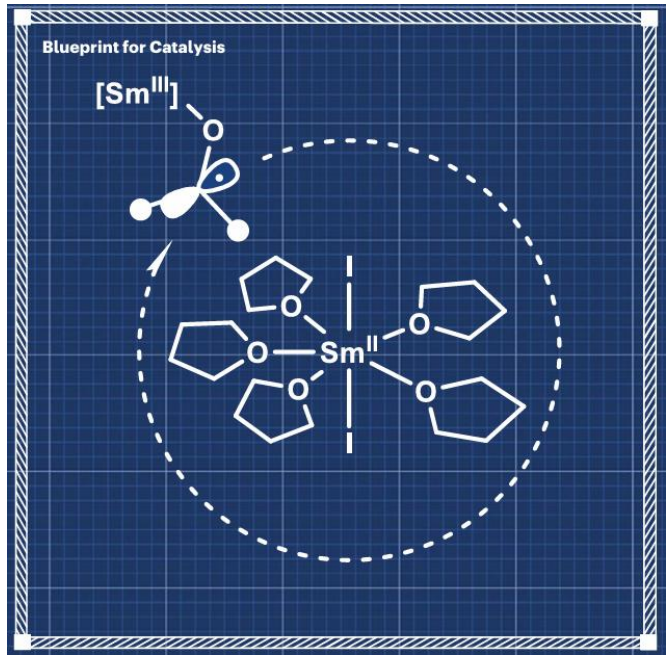
An Brief Introduction of SmI_2 in Total Synthesis

Contents come from :

Catalysis **2023**, *13*, 24;

RSC Adv. **2022**, *12*, 9944–9994;

Chem. Rev. **2014**, *114*, 5959-6039 and ...



***Supervisor*: Prof. Jia Yanxing**

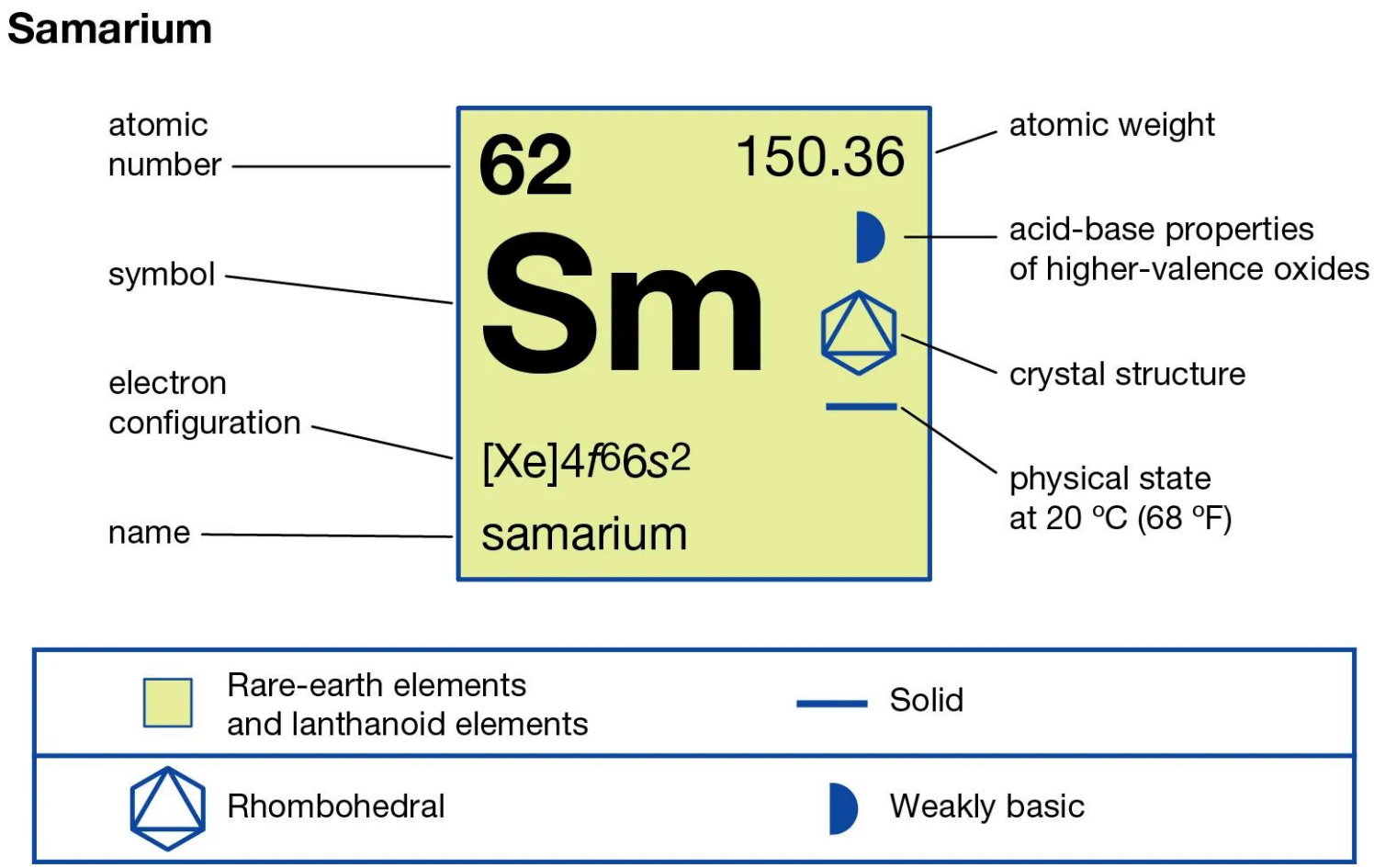
***Reporter*: Cheng Yifu**

***Date*: 2026/04/09**

Content

Content

What is Samarium(II) Diiodide?

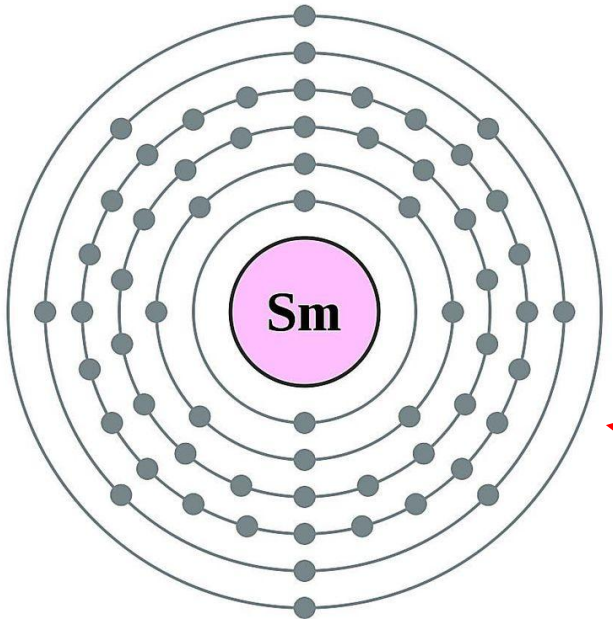


Samarium, represented by the chemical symbol Sm, is a bright, fairly **hard lanthanide element** belonging to the family of **rare earth metals**. In 1879, French chemist Paul Émile Lecoq de Boisbaudran **first isolated** and identified samarium. Subsequently, samarium has gradually been used in the manufacture of **mobile phones**, **MRI machines**, and other applications.

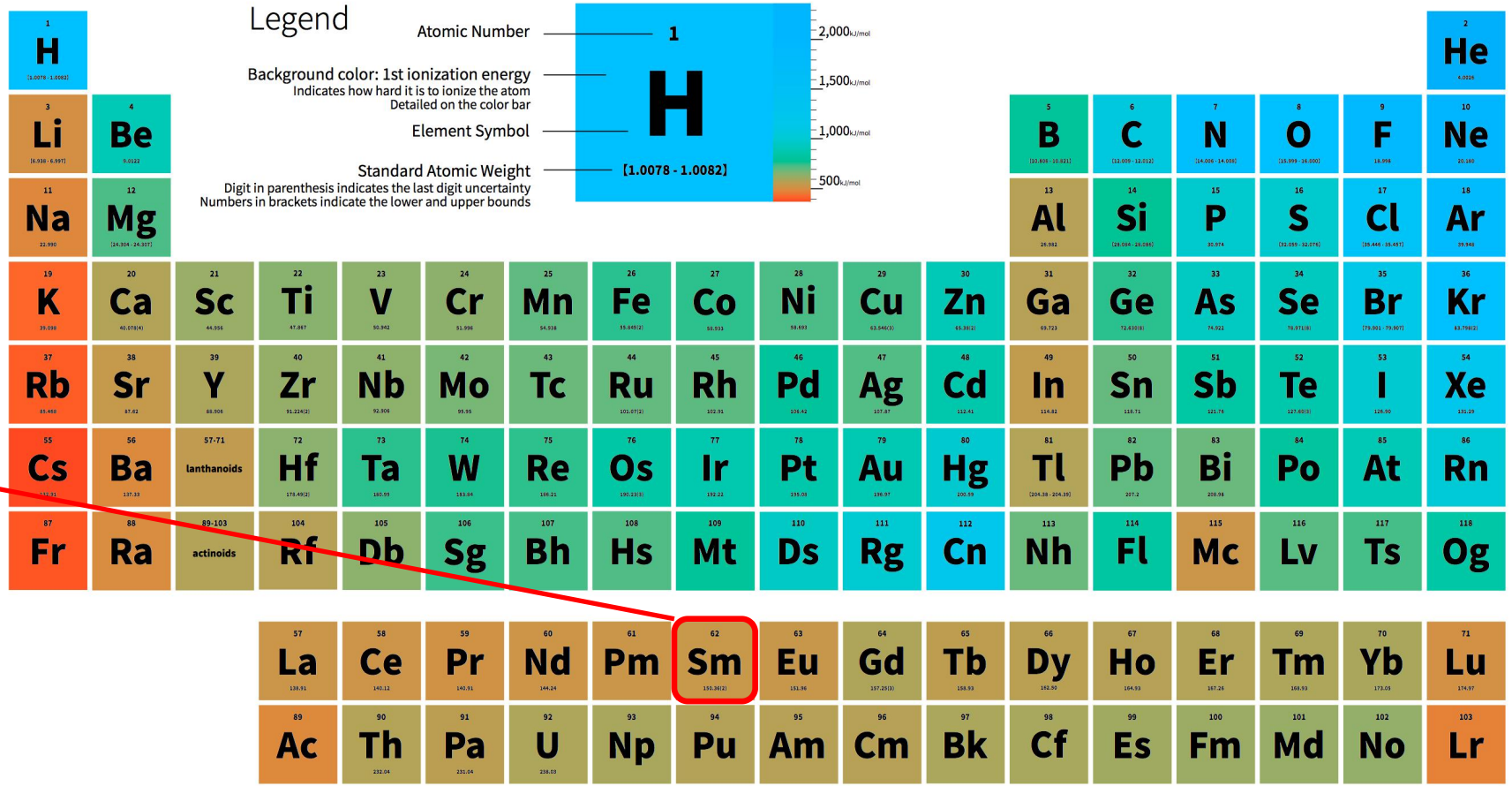
https://www.chemistrylearner.com/samarium.html

What is Samarium(II) Diiodide?

62: Samarium **2,8,18,24,8,2**



Periodic Table



https://www.britannica.com/science/lanthanide

What is Samarium(II) Diiodide?

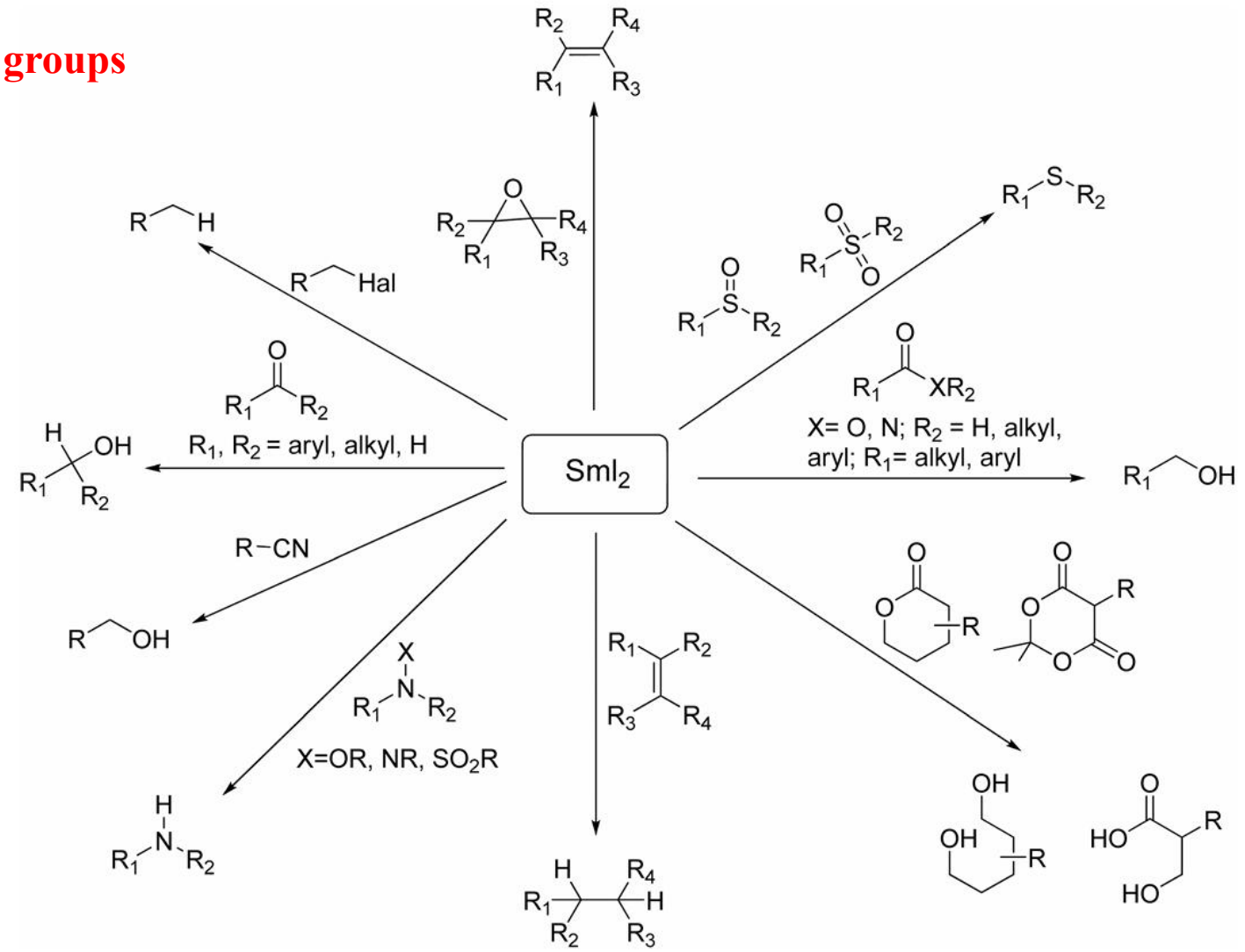
原子序数	符号	原子价电子层结构	氧化态		
			RE^{2+}	RE^{3+}	RE^{4+}
21	Sc	$3d^14s^2$	—	[Ar]	—
39	Y	$4d^15s^2$	—	[Kr]	—
57	La	$5d^16s^2$	—	[Xe]	—
58	Ce	$4f^15d^16s^2$	$4f^2$	$4f^1$	[Xe]
59	Pr	$4f^36s^2$	—	$4f^2$	$4f^1$
60	Nd	$4f^46s^2$	$4f^4$	$4f^3$	$4f^2$
61	Pm	$4f^56s^2$	—	$4f^4$	—
62	Sm	$4f^66s^2$	$4f^6$	$4f^5$	—
63	Eu	$4f^76s^2$	$4f^7$	$4f^6$	—
64	Gd	$4f^15d^16s^2$	—	$4f^7$	—
65	Tb	$4f^96s^2$	—	$4f^8$	$4f^7$
66	Dy	$4f^{10}6s^2$	—	$4f^9$	$4f^8$
67	Ho	$4f^{11}6s^2$	—	$4f^{10}$	—
68	Er	$4f^{12}6s^2$	—	$4f^{11}$	—
69	Tm	$4f^{13}6s^2$	$4f^{13}$	$4f^{12}$	—
70	Yb	$4f^{14}6s^2$	$4f^{14}$	$4f^{13}$	—
71	Lu	$4f^{14}5d^16s^2$	—	$4f^{14}$	—

https://www.britannica.com/science/lanthanide

Content

SmI_2-mediated functional group reduction

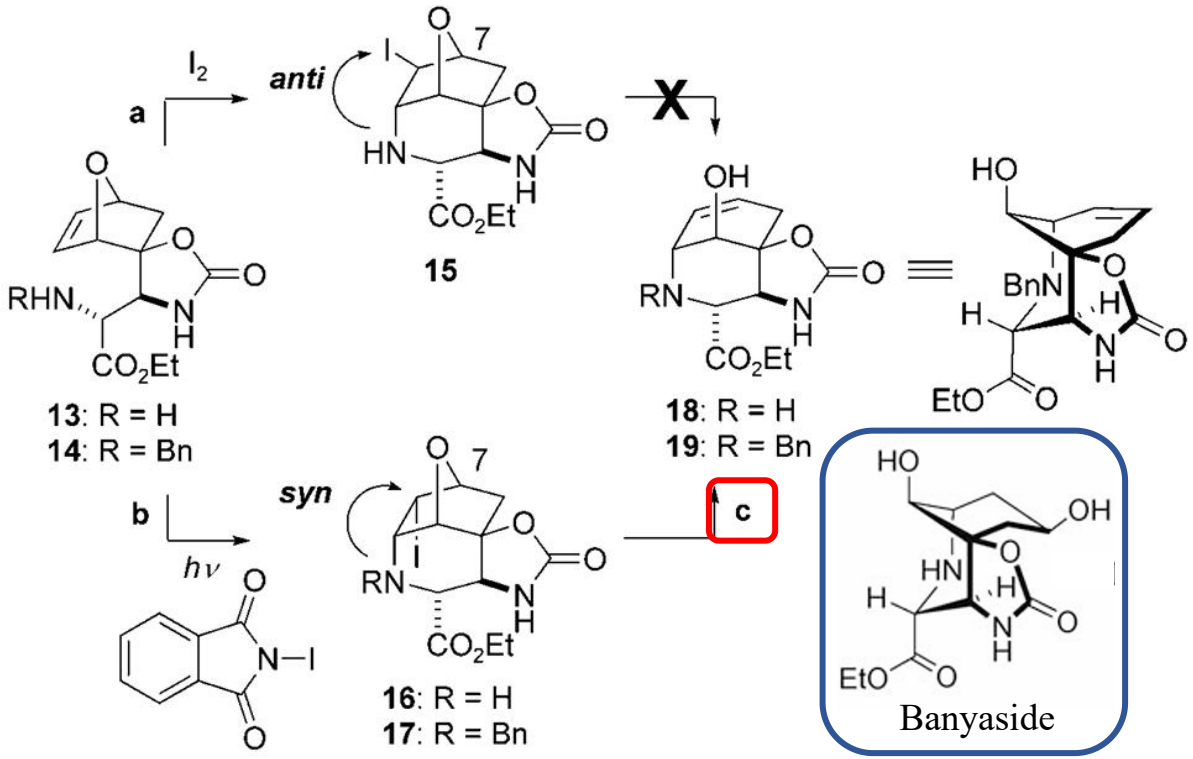
Reduction of functional groups



1. Majid. M. Heravi, *RSC Adv.,* **2022***, 12,* 9944–9994; **2.** David J. Procter, *Chem. Soc. Rev.*, **2013**, *42*, 9155--9183

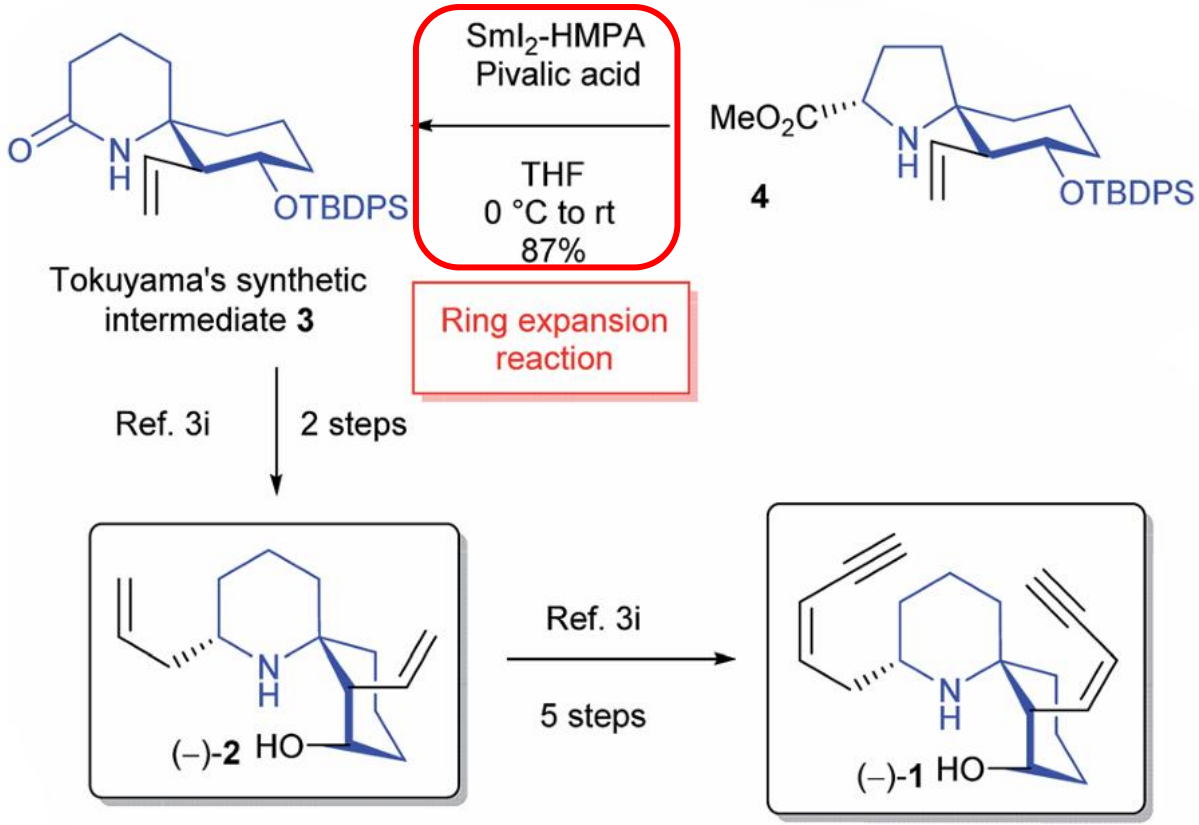
SmI_2-mediated functional group reduction

Carreira's work



Scheme 5. a) I_2, $NaHCO_3$, THF, H_2O, 23 °C, 73 % (**13**→**15**); b) *N*-iodophthalimide, *hν*, CH_2Cl_2, 89 % (**14**→**17**), 63 % (**13**→**16**); c) 4.0 equiv SmI_2, THF, 0→23 °C, 82 % (**17**→**19**), 62 % (**16**→**18**).

Morimoto's work



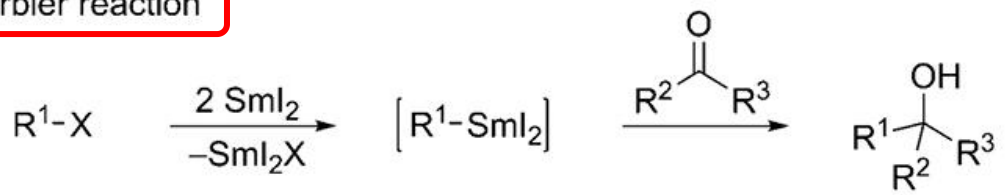
1. E. M. Carreira, *Angew. Chem., Int. Ed.*, **2008**, *47*, 8852.; **2.** Morimoto, Y., *RSC Adv.*, **2018**, *8*, 11296–11303

Content

SmI_2-mediated reductive C–C bond formation

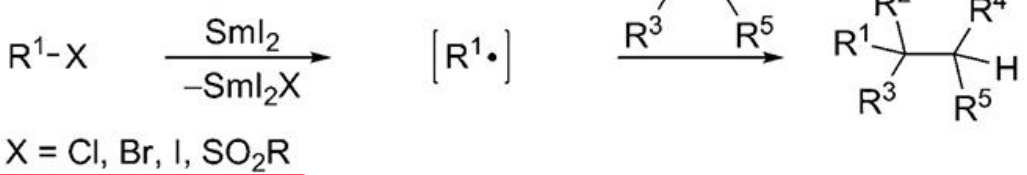
Formation of C-C bond

a) Barbier reaction



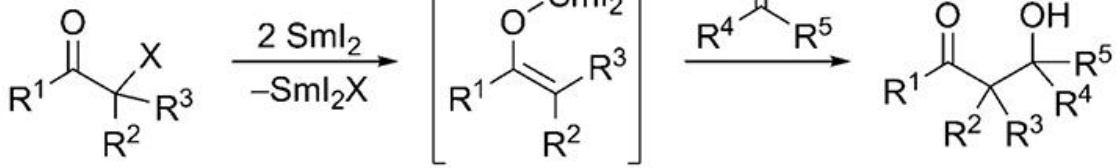
X = Cl, Br, I, SO_2R

b) Radical–alkene/alkyne reaction



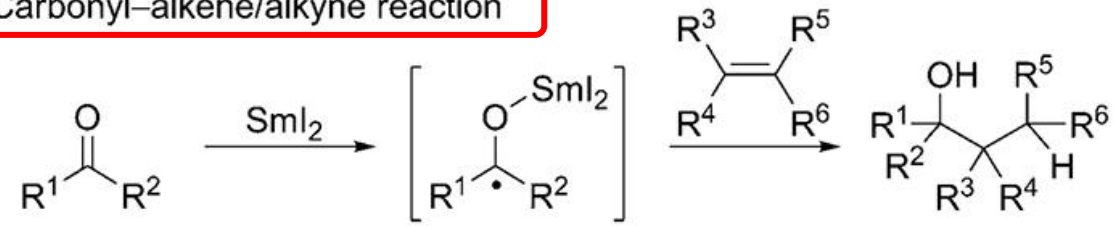
X = Cl, Br, I, SO_2R

c) Reformatsky reaction

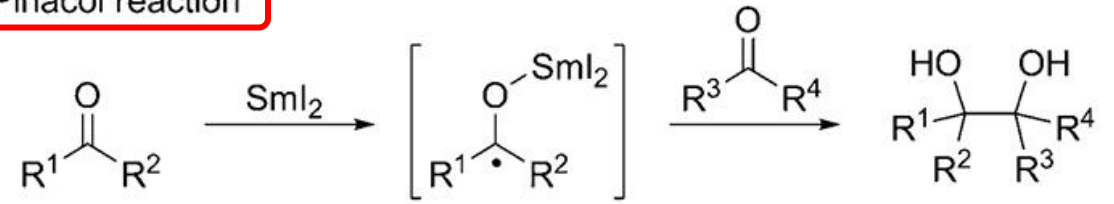


X = Cl, Br, I, SO_2R, NR_2, OR, SR

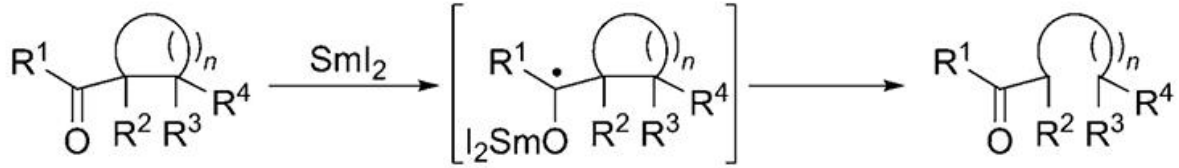
d) Carbonyl–alkene/alkyne reaction



e) Pinacol reaction

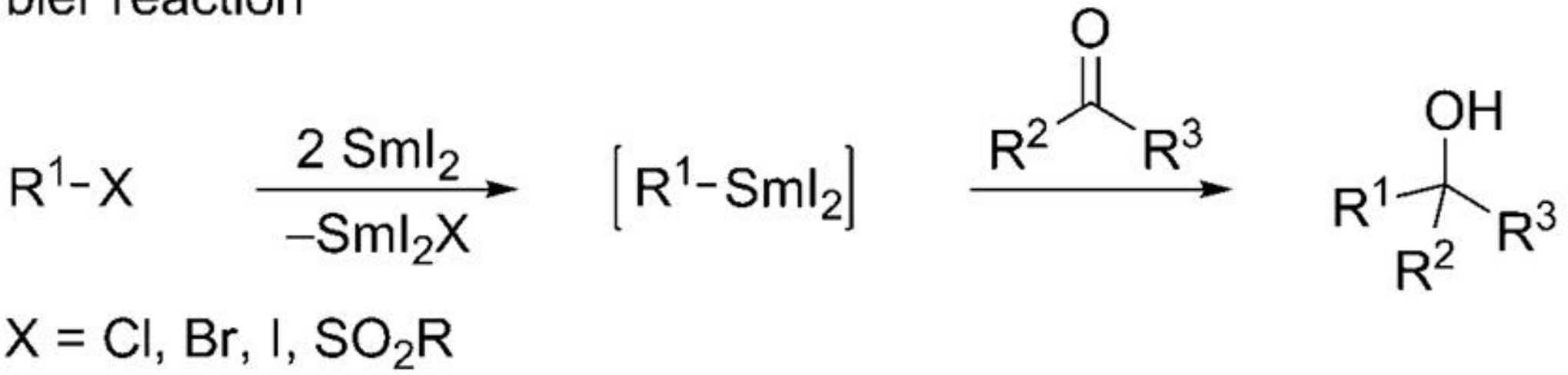


f) Fragmentation reaction



Barbier Reaction

a) Barbier reaction

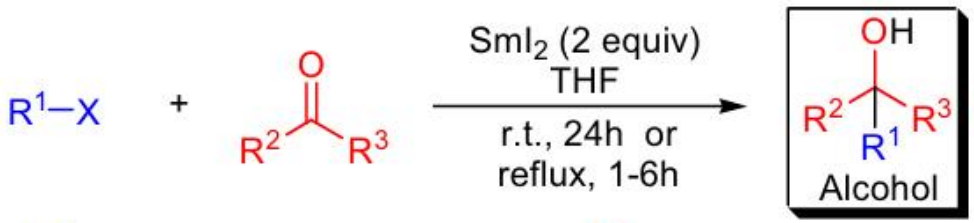


X = Cl, Br, I, SO_2R

First used in organic chemistry

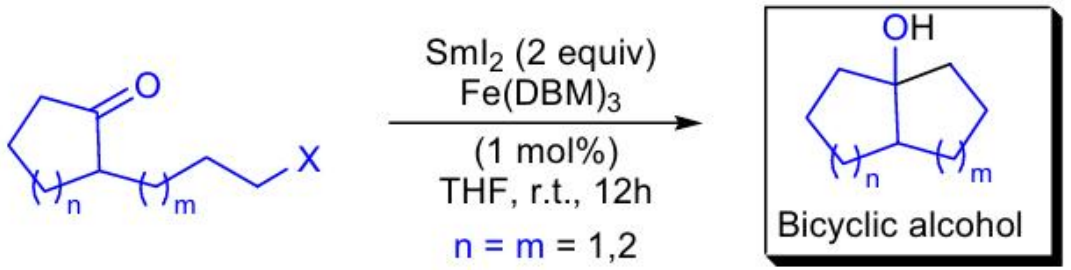
Kagan-Molander Coupling

Intermolecular reaction (Kagan 1980)



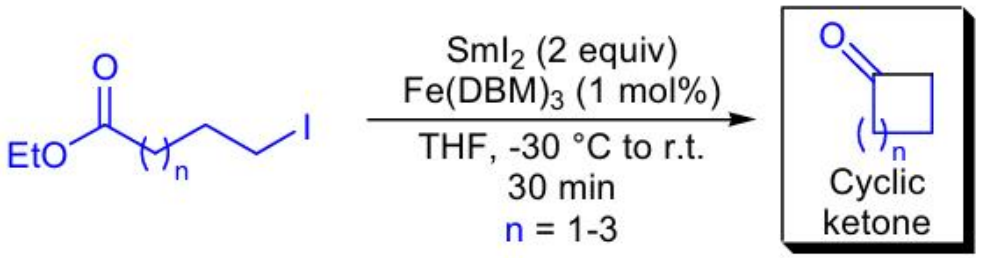
R^1 = alkyl, allyl, benzyl, propargyl; R^2 = H, alkyl, aryl;
R^3 = alkyl aryl; X=Br, I, OTs

Intramolecular reaction (Molander 1984)

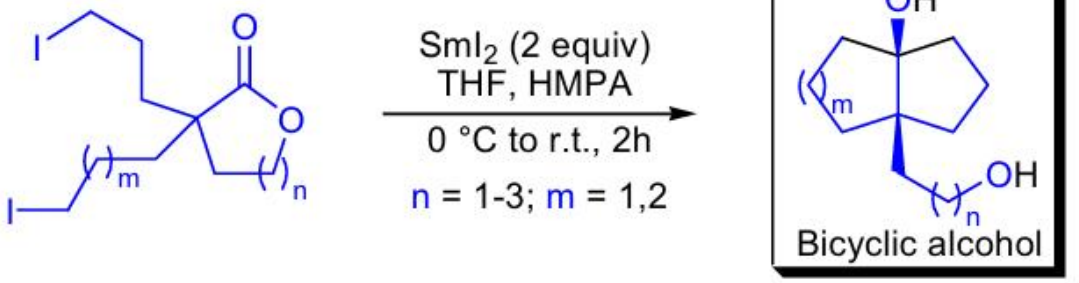


H.B.Kagan

Nucleophilic acyl substitution (Molander 1993):



Tandem reactions (Molander 1995):

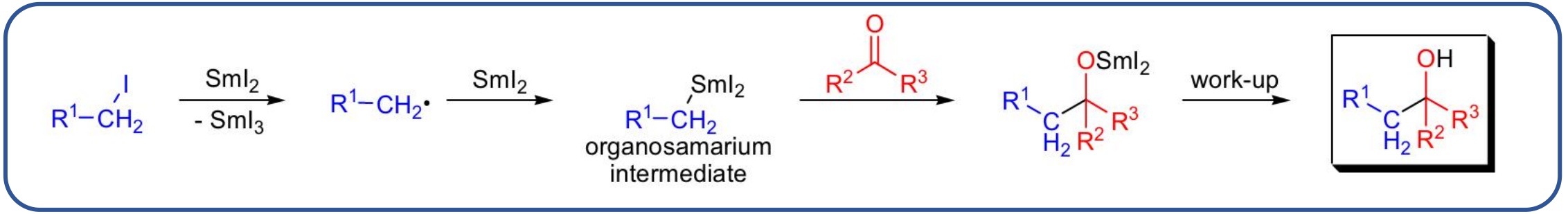


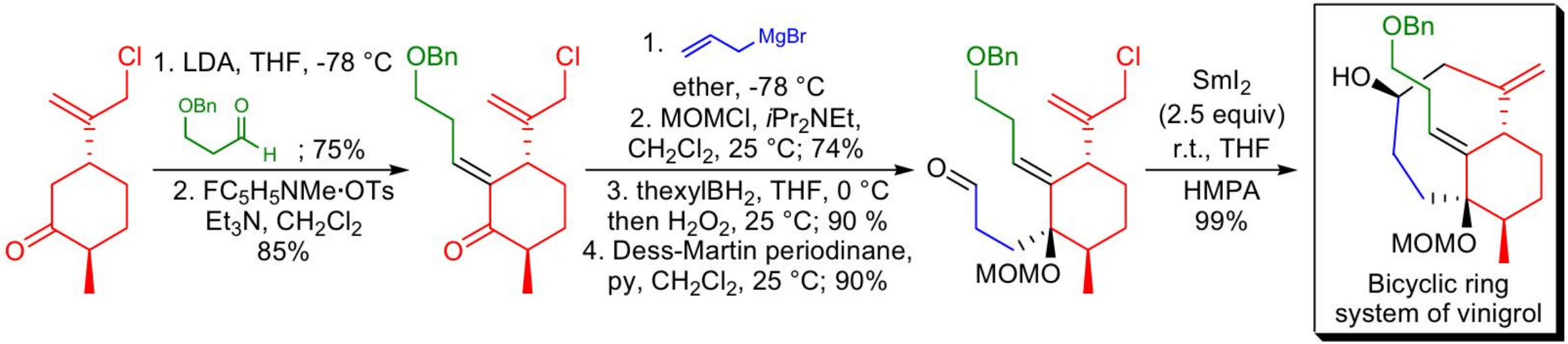
G.A.Molander

1. H. B. Kagan, *J. Am. Chem. Soc*. **1980**, *102*, 2693–2698; **2.** G. A. Molander, *Tetrahedron Lett*. **1984**, *25*, 3281-3284

First used in organic chemistry

Kagan-Molander Coupling

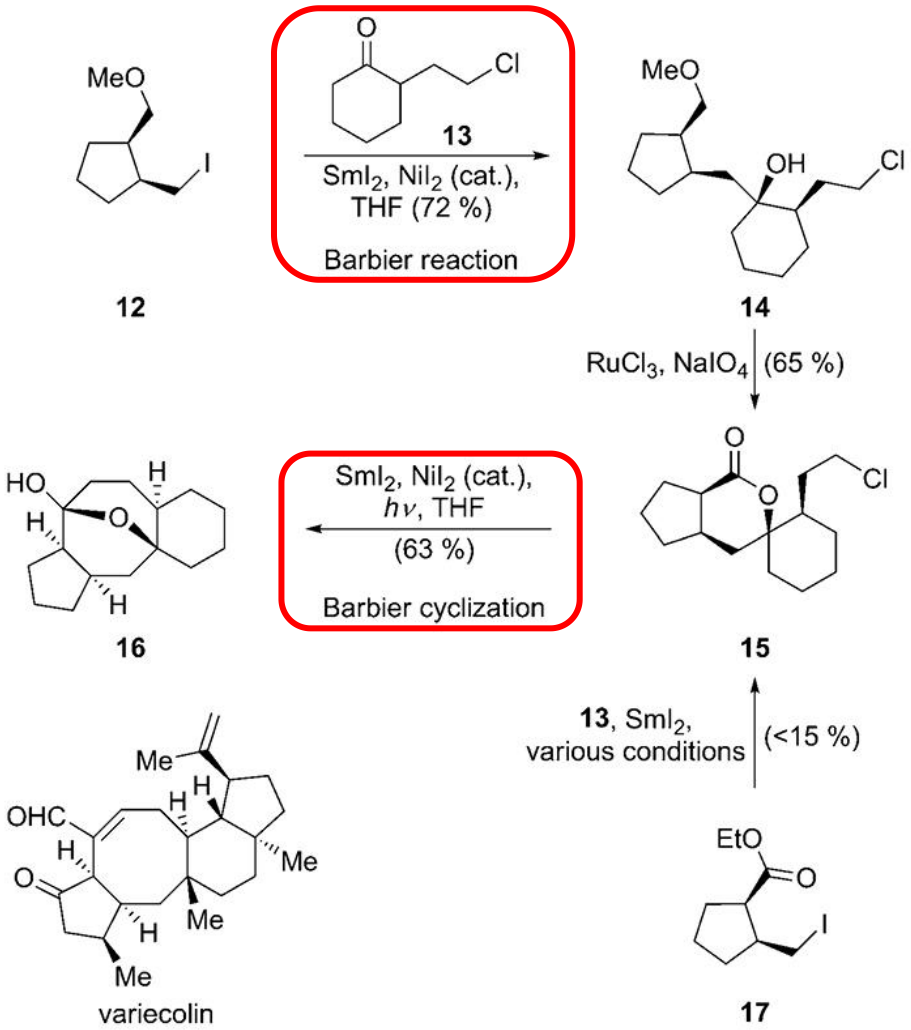




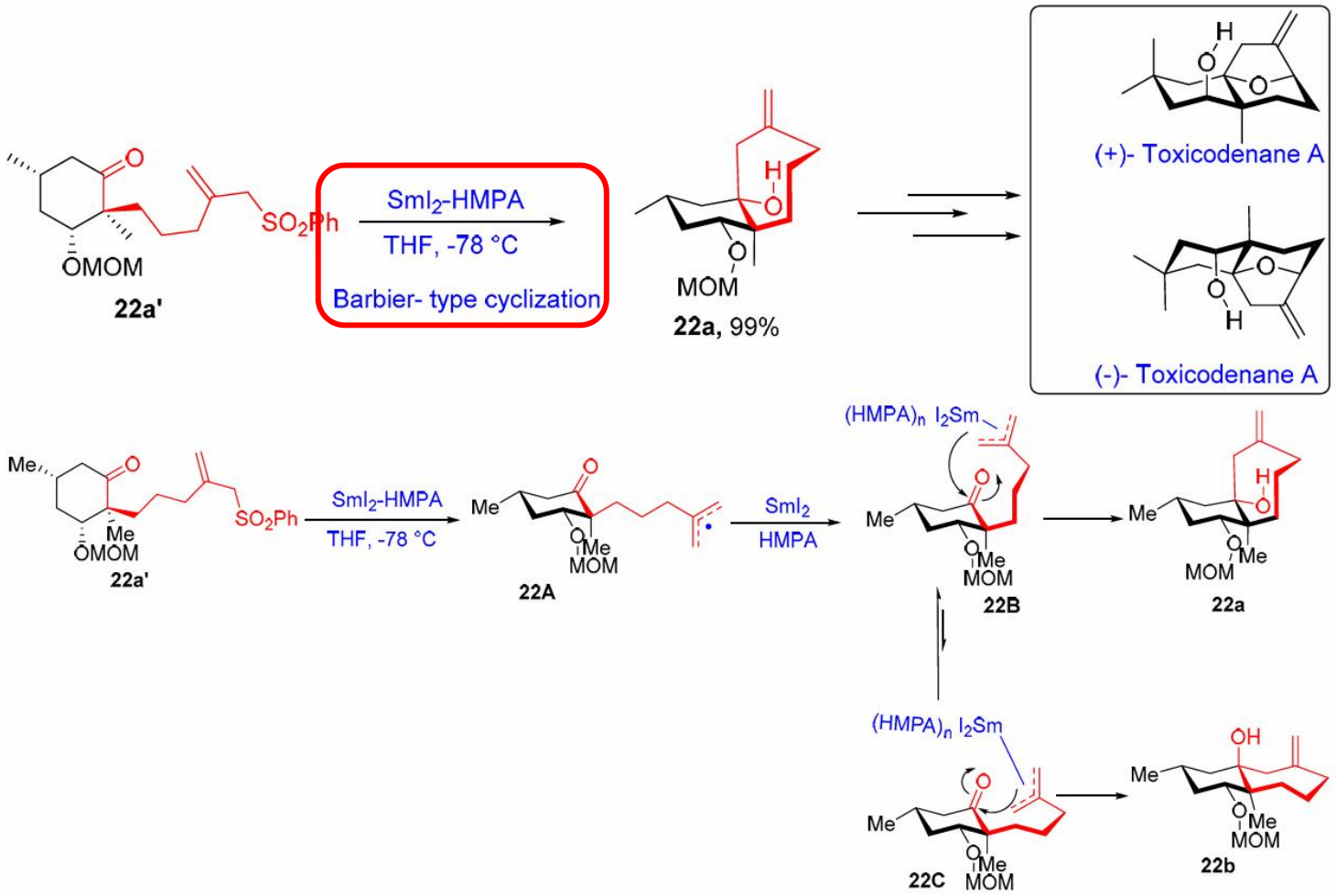
Matsuda, F., *Tetrahedron* **1999**, *55*, 14369-14380

Barbier Reaction

Molander's work



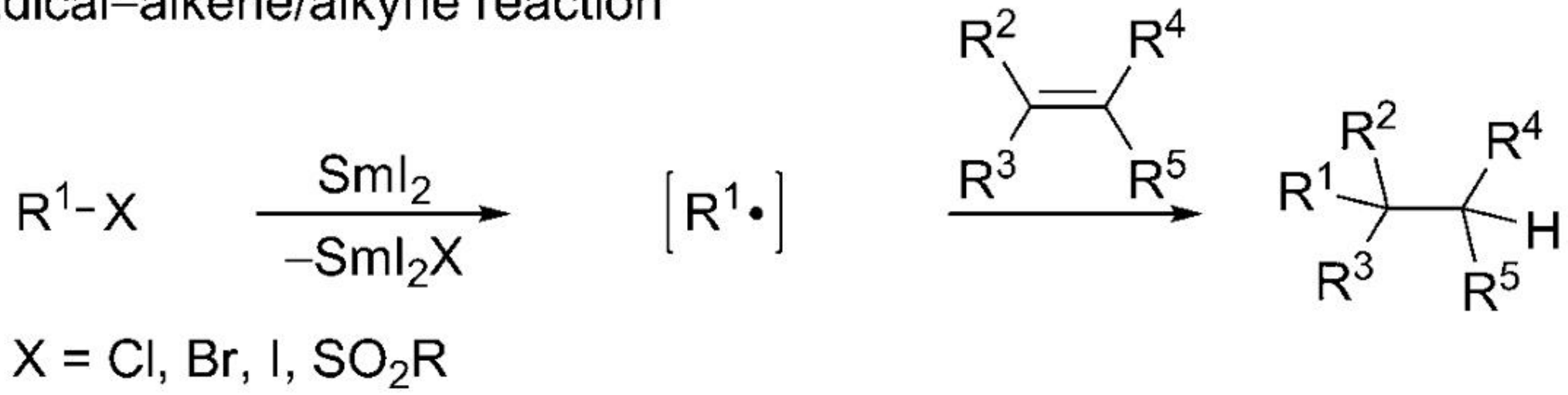
Morimoto's work



1. G. A. Molander, *Org. Lett.* **2001**, *3*, 2257-2260; **2.** Morimoto, Y., *Org. Lett.* **2022**, *24*, 531–535

Radical–Alkene/Alkyne Reaction

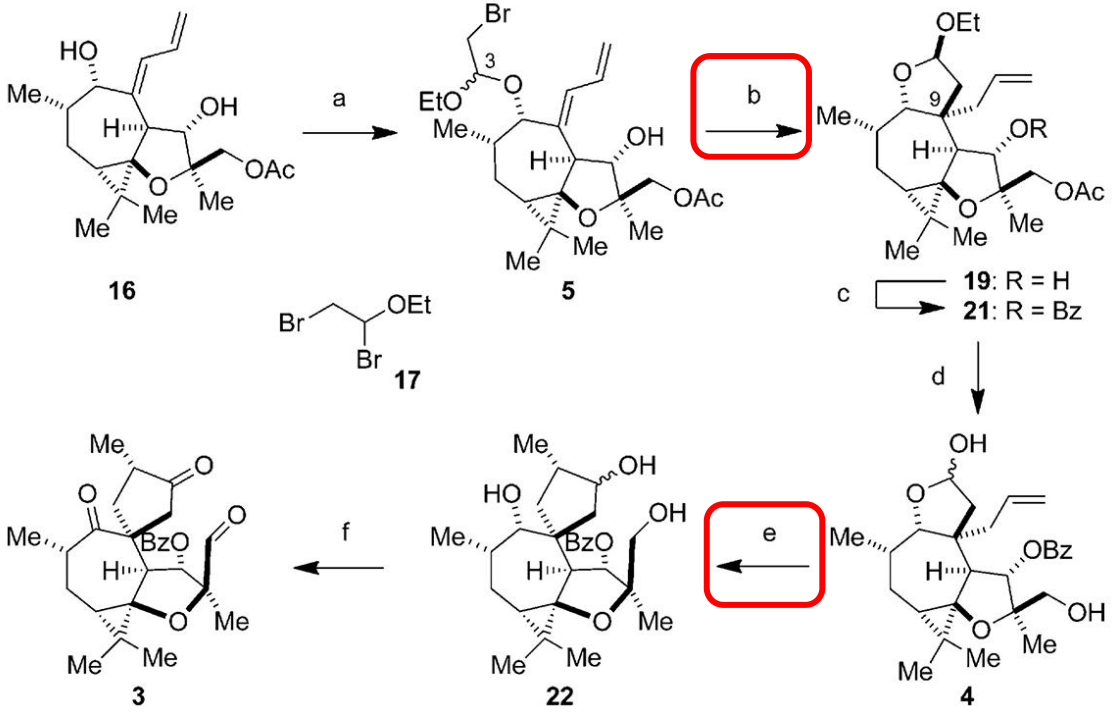
b) Radical–alkene/alkyne reaction



X = Cl, Br, I, SO_2R

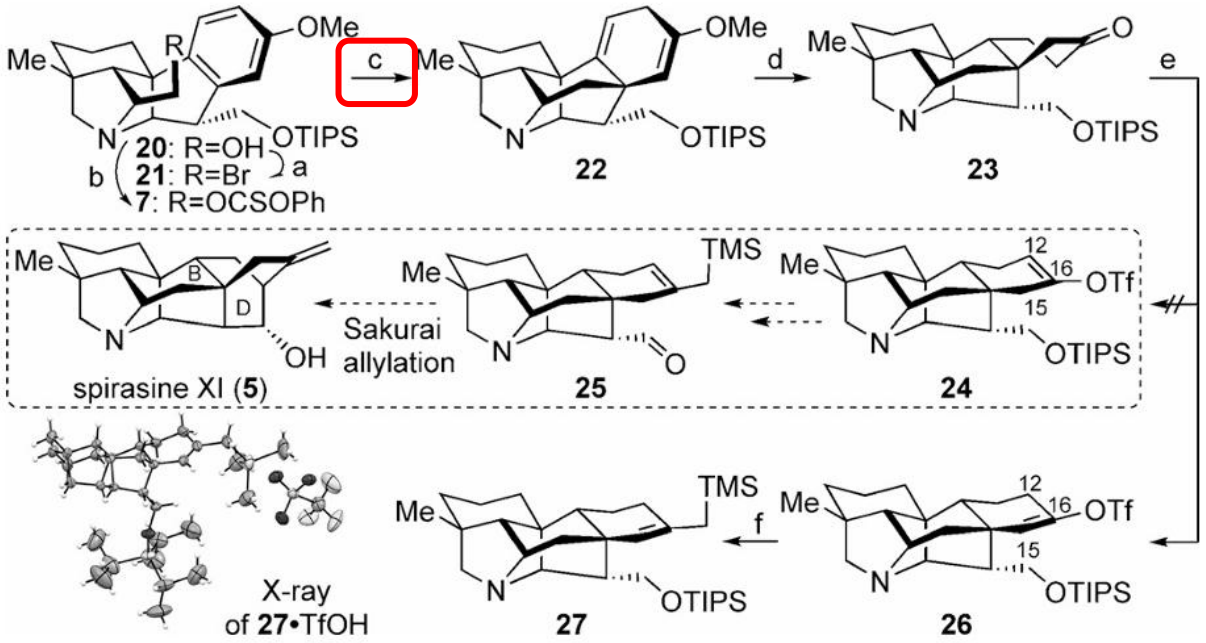
Radical–Alkene/Alkyne Reaction

Ding's work



conditions: a) **17** (2.0 equiv), $PhNMe_2$ (3.0 equiv), CH_2Cl_2, 25 °C, 2 h, 95%, 1.5:1 d.r. at C3; b) SmI_2 (0.1 M in THF, 2.0 equiv), HMPA (8.0 equiv), *t*BuOH (1.2 equiv), THF, 25 °C, 45 min, **19** (50%), **20** (35%); c) Bz_2O (1.2 equiv), Et_3N (2.0 equiv), 4-DMAP (0.2 equiv), CH_2Cl_2, 25 °C, 30 min, 95%; d) *p*-TsOH (1.0 equiv), acetone/H_2O (4:1), 60 °C, 6 h, 86%, 4:1 d.r. at C3; e) SmI_2 (0.1 M in THF, 2.0 equiv), HMPA (4.0 equiv), THF, 50 °C, 6 h, 90%, 5:1 d.r. at C3; f) Dess–

Zhang's work

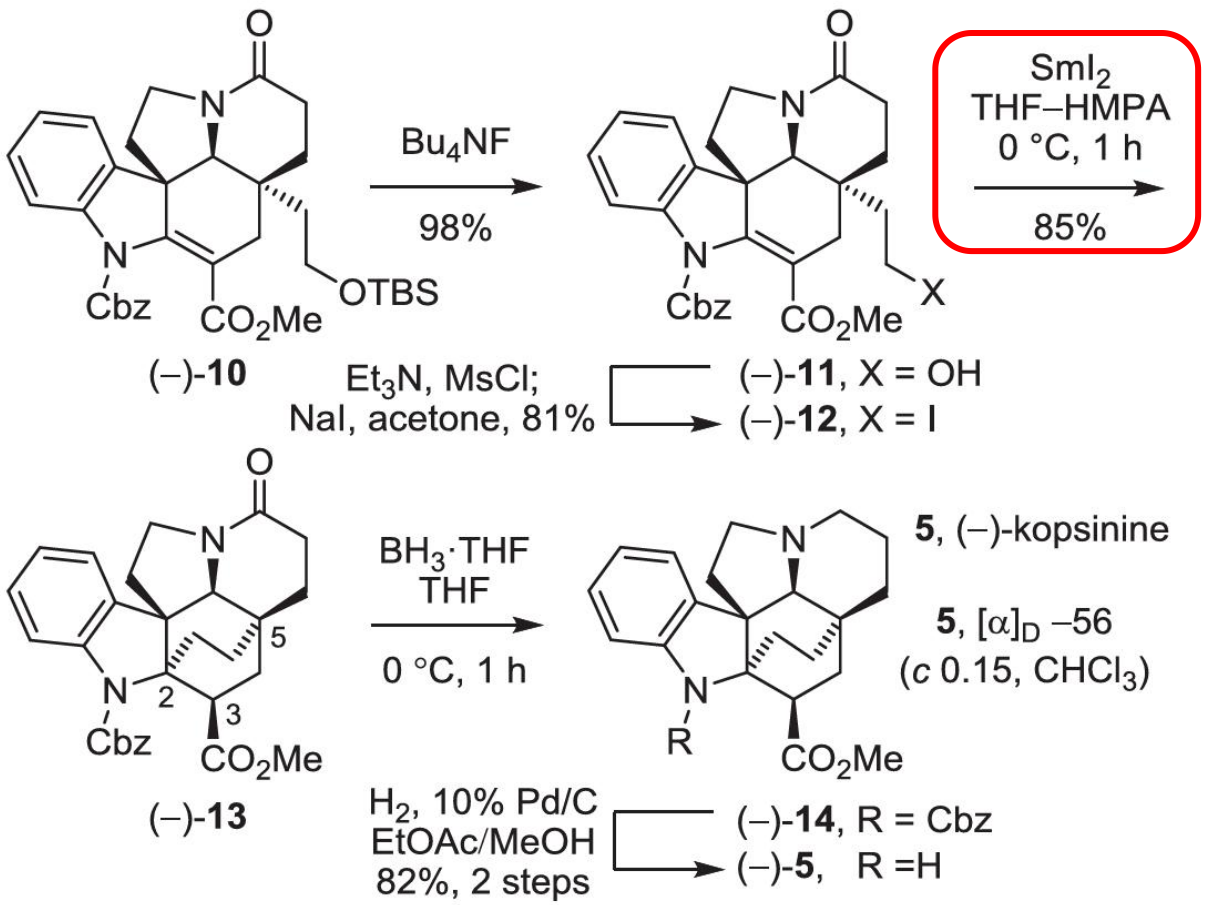


Scheme 4. Study toward the construction of the B and D rings. Reagents and conditions: a) MsCl, pyridine, CH_2Cl_2, room temperature; then LiBr, CH_3CN, reflux, 30%; b) PhOCSCl, DMAP, CH_2Cl_2, −40 °C, 87%; c) SmI_2, *t*BuOH, HMPA, THF, 0 °C, 67% from **21**, 61% from **7**; d) *p*-TsOH, H_2O, THF, room temperature; then Pd/C, H_2 (1 atm), MeOH, 66%; e) $PhNTf_2$, LiHMDS, THF, −78 °C, 70% for **26**; f) $TMSCH_2MgCl$, $Pd(PPh_3)_4$, THF, room temperature, 83%.

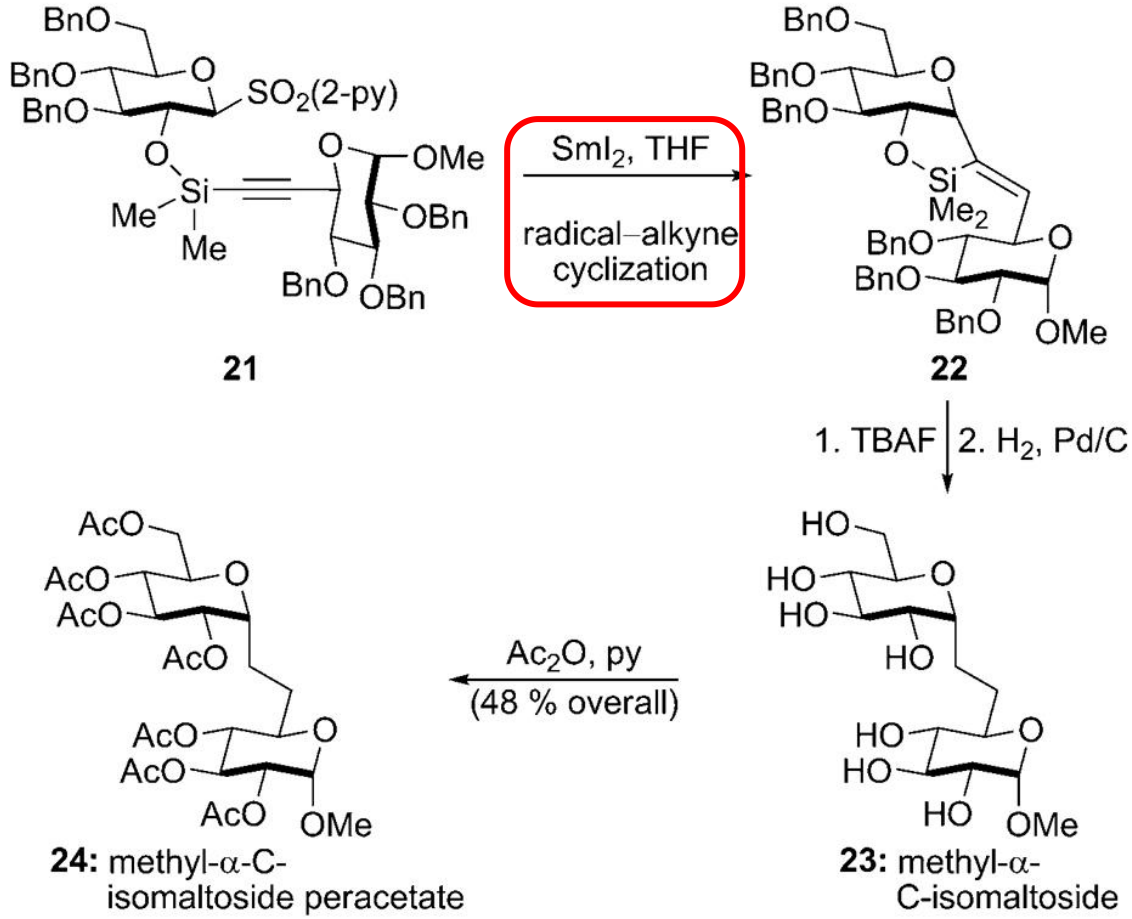
1. Ding, H., *Angew. Chem. Int. Ed.* **2015**, *54*, 6905–6908; **2.** Zhang, M., *Angew. Chem. Int. Ed.* **2018**, *57*, 937–941

Radical–Alkene/Alkyne Reaction

Boger's work



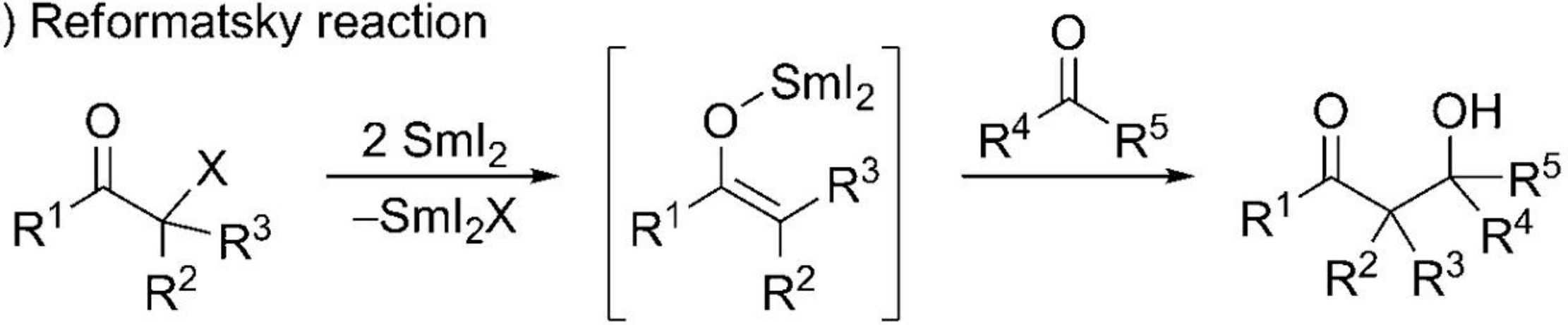
Beau's work



1. D. L. Boger, *Tetrahedron,* **2015**, *71,* 3741–3746. ; **2.** J. M. Beau, *Angew. Chem. Int. Ed.* **1994**, *33,* 1383–1386.

Reformatsky and Aldol-Type Reactions

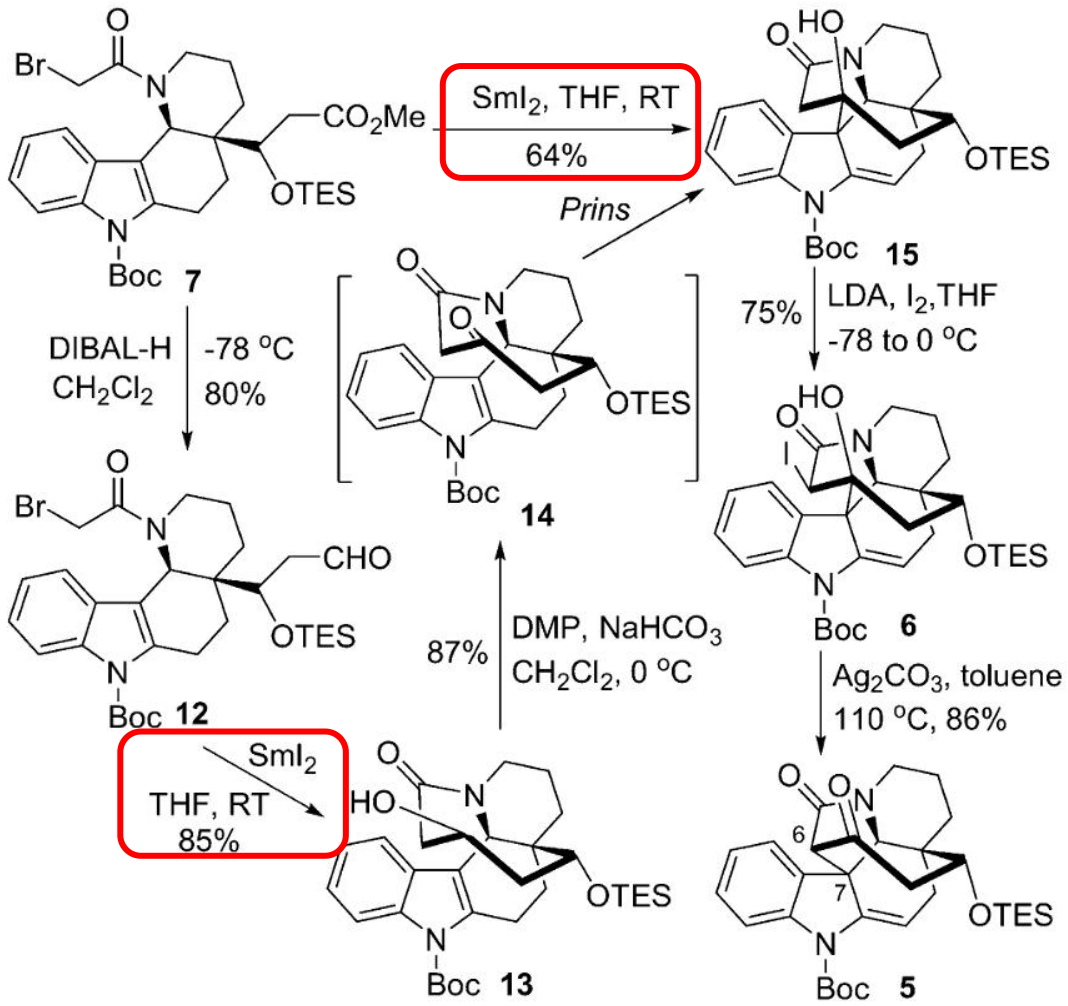
c) Reformatsky reaction



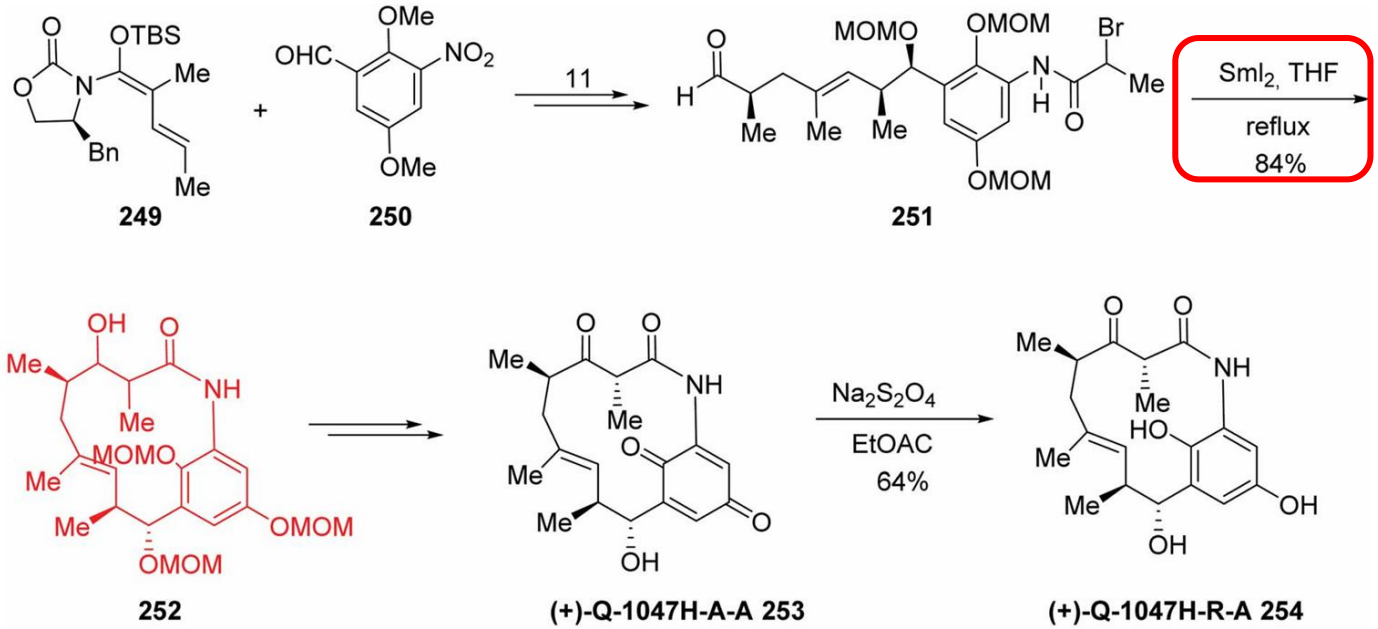
X = Cl, Br, I, SO_2R, NR_2, OR, SR

Reformatsky and Aldol-Type Reactions

Ma's work



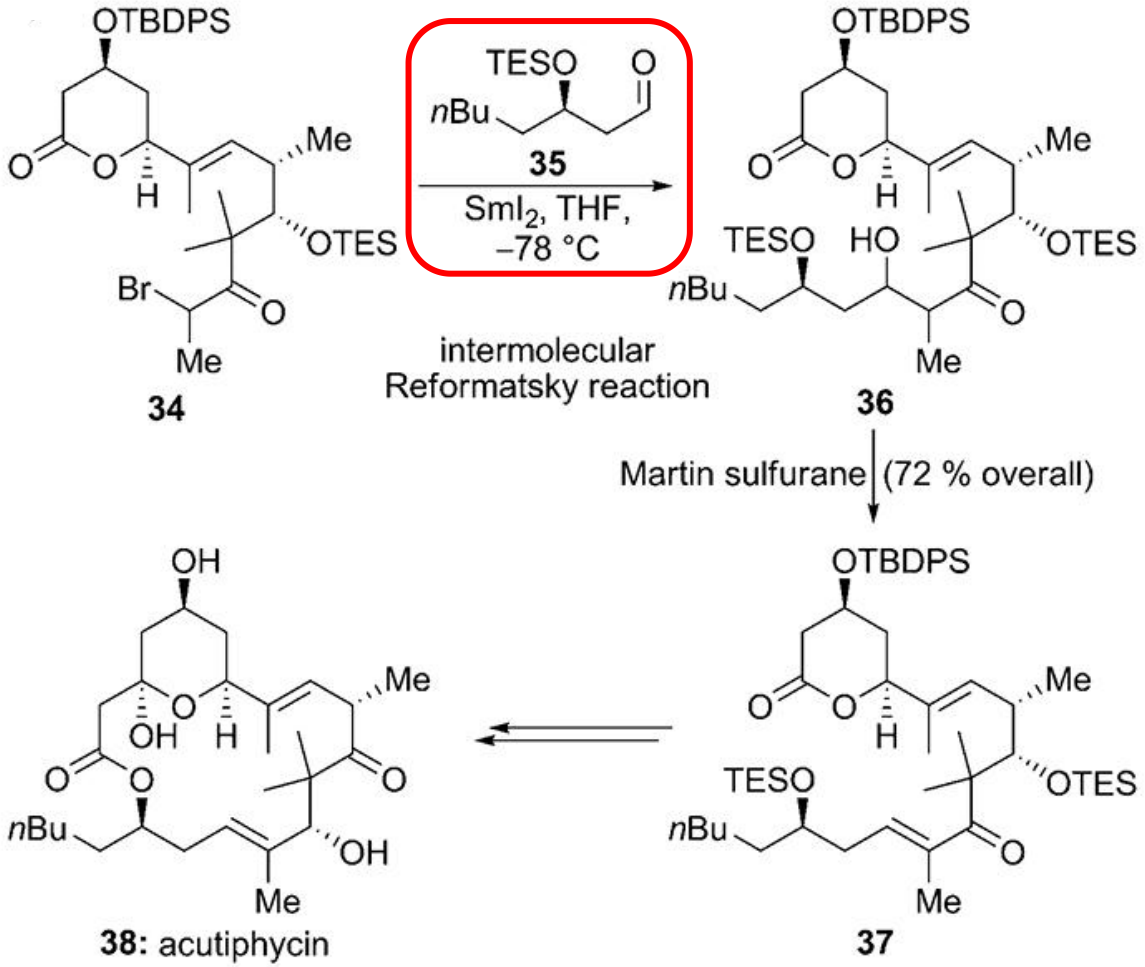
Yang's work



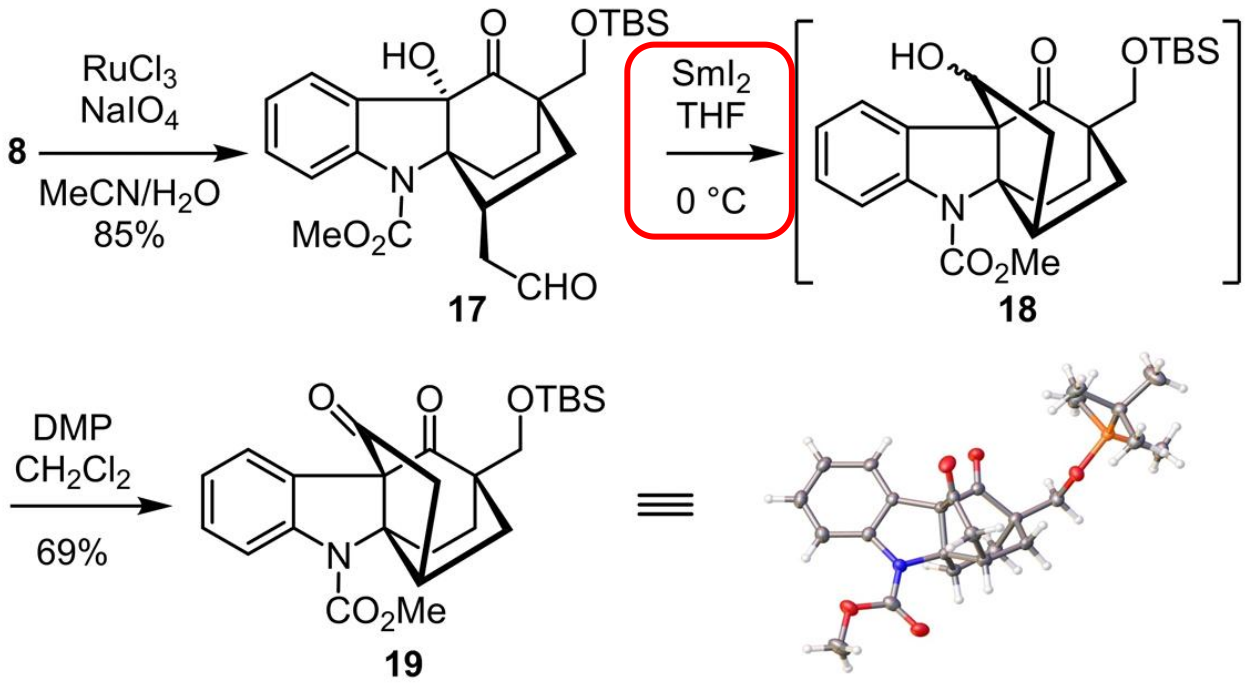
1. Ma, D., *Angew. Chem. Int. Ed.* **2020**, *59,* 22039–22042; **2.** Yang. Z., *Org. Lett.,* **2013**, *15(4),* 812-815

Reformatsky and Aldol-Type Reactions

Jamison's work



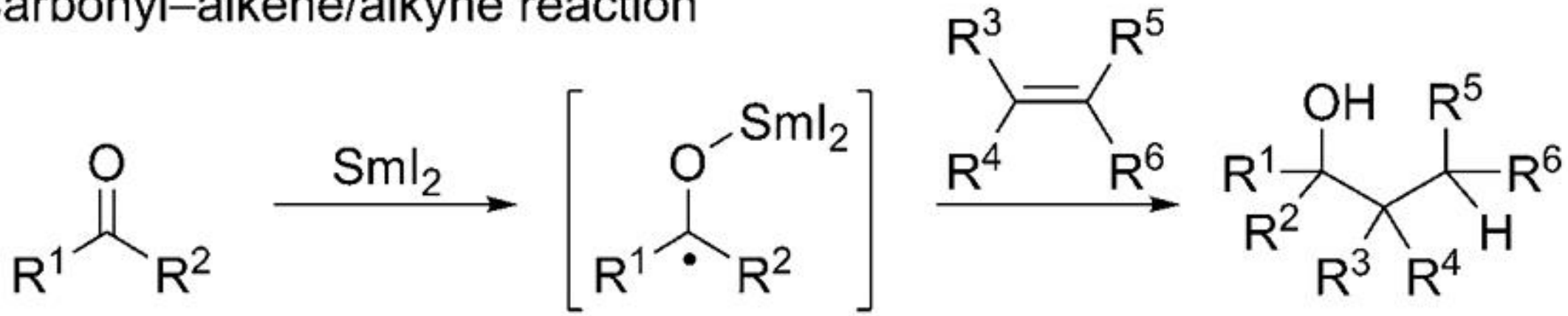
Jia's work



1. T. F. Jamison, *J. Am. Chem. Soc*. **2006**, *128*, 15106–15107; **2.** Jia, Y., *Angew. Chem. Int. Ed.* **2022**, *61*, e202201712

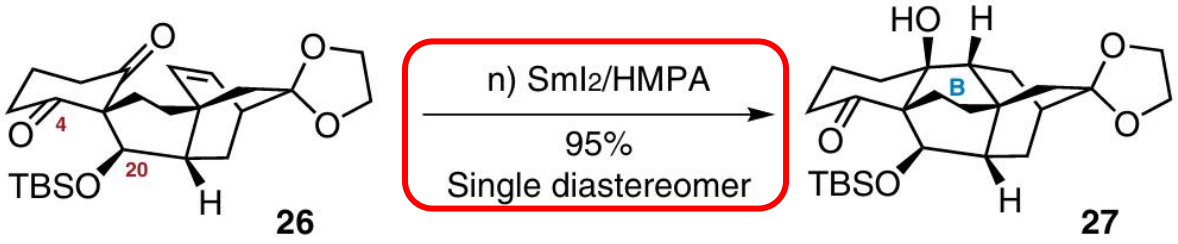
Carbonyl–Alkene/Alkyne and Related Reactions

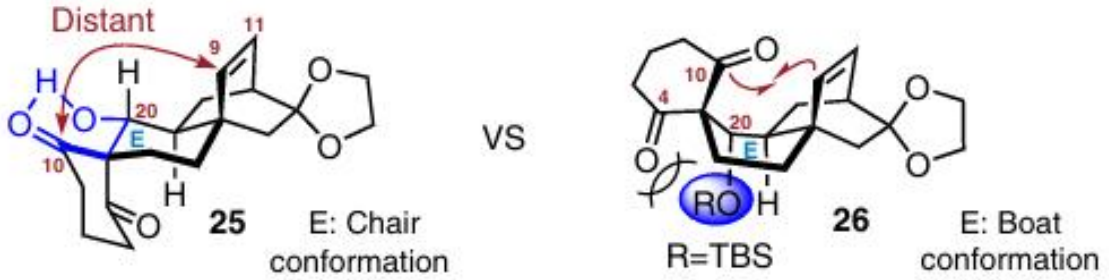
d) Carbonyl–alkene/alkyne reaction

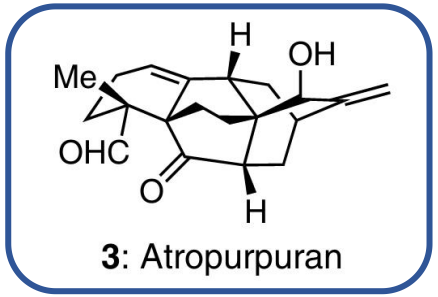


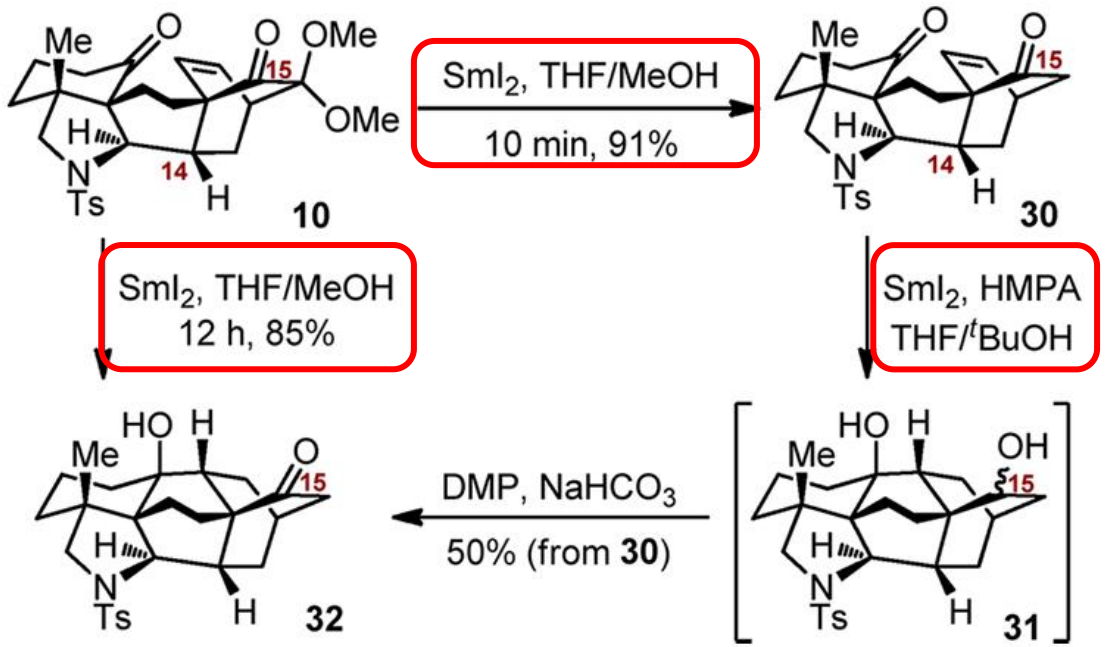
Carbonyl–Alkene/Alkyne and Related Reactions

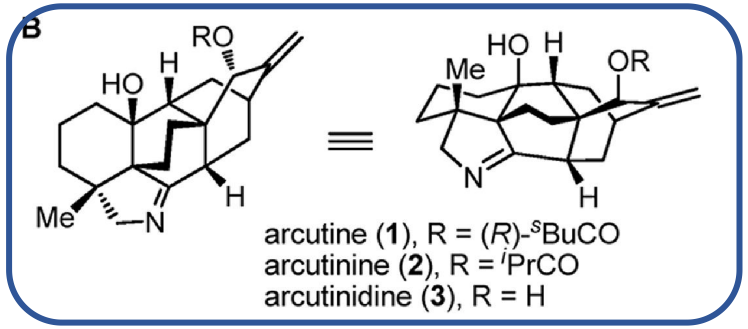
Qin's work







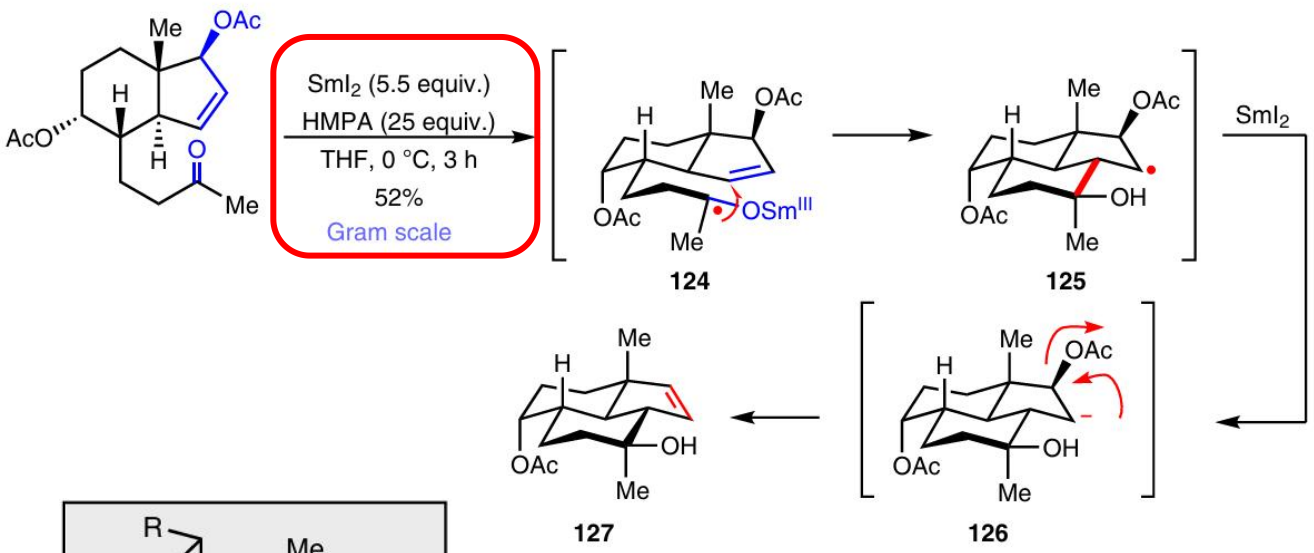


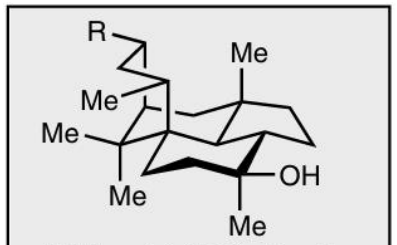


1. Qin, Y., *Nat. Commun*. **2016**, *7*, 12183; **2.** Qin, Y., *J. Am. Chem. Soc*. **2019**, *141*, 9712–9718

Carbonyl–Alkene/Alkyne and Related Reactions

Gui's work

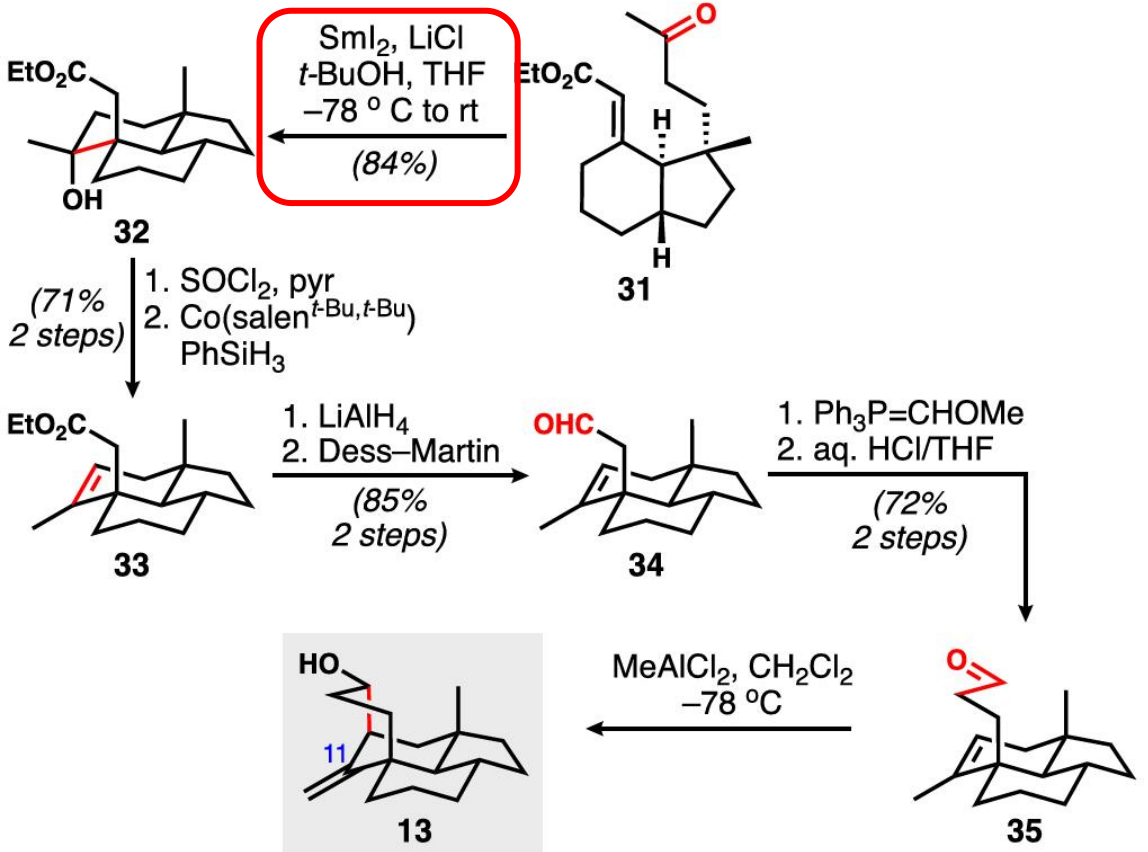




Wickerol A (**128**): R = H

Wickerol B (**129**): R = OH

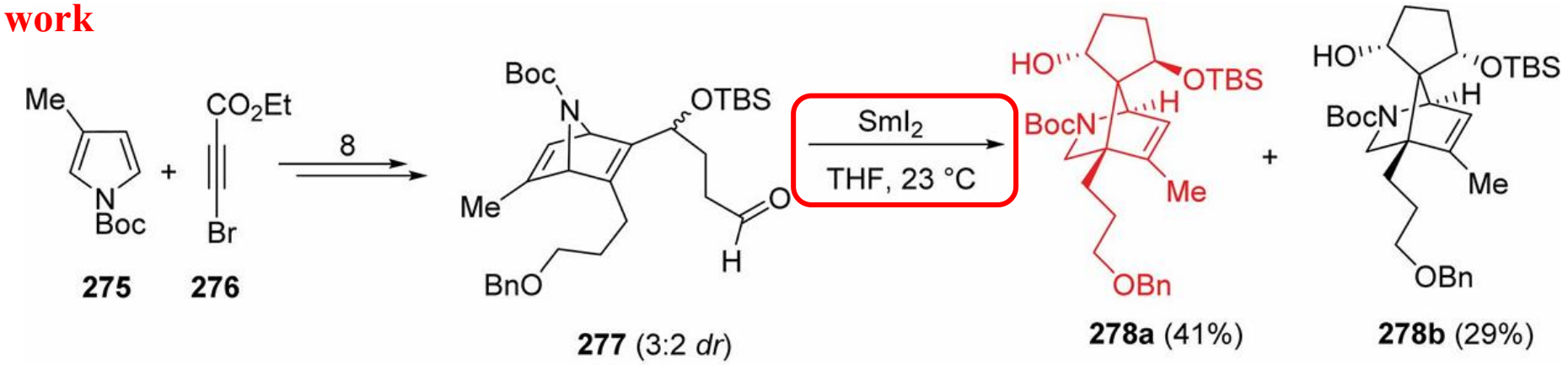
Vanderwal's work

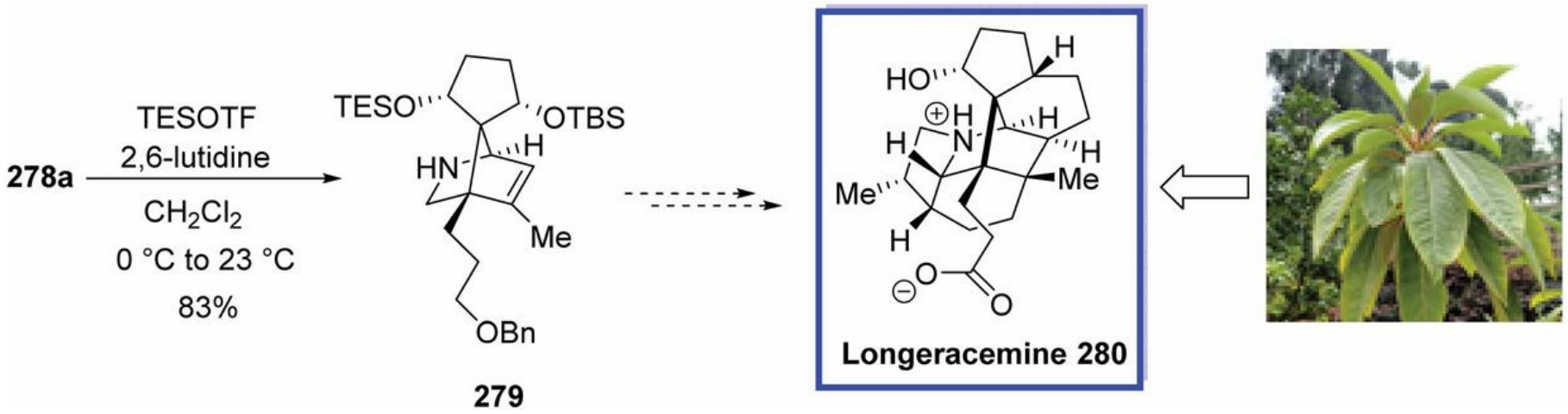


1. Gui, J., *J. Am. Chem. Soc*. **2020**, *142*, 4690–4695 ; **2.** C. D. Vanderwal, *J. Am. Chem. Soc*. **2023**, *145*, 6486–6497

Carbonyl–Alkene/Alkyne and Related Reactions

Wood's work

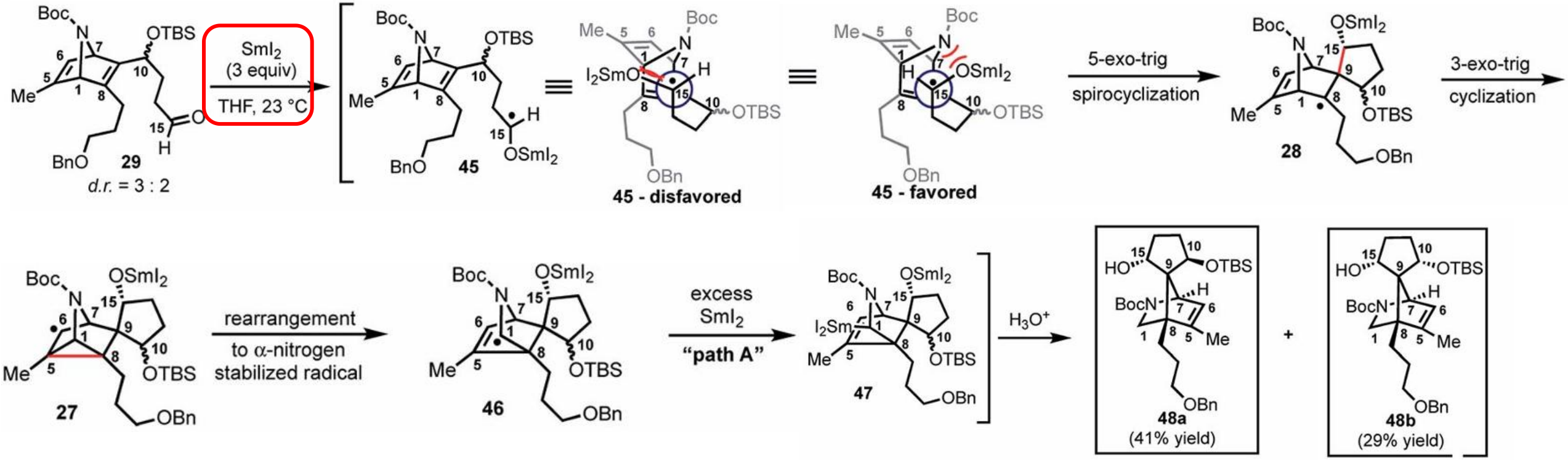




J. L. Wood, *Chem. Sci.*, **2020**, *11*, 9488–9493

Carbonyl–Alkene/Alkyne and Related Reactions

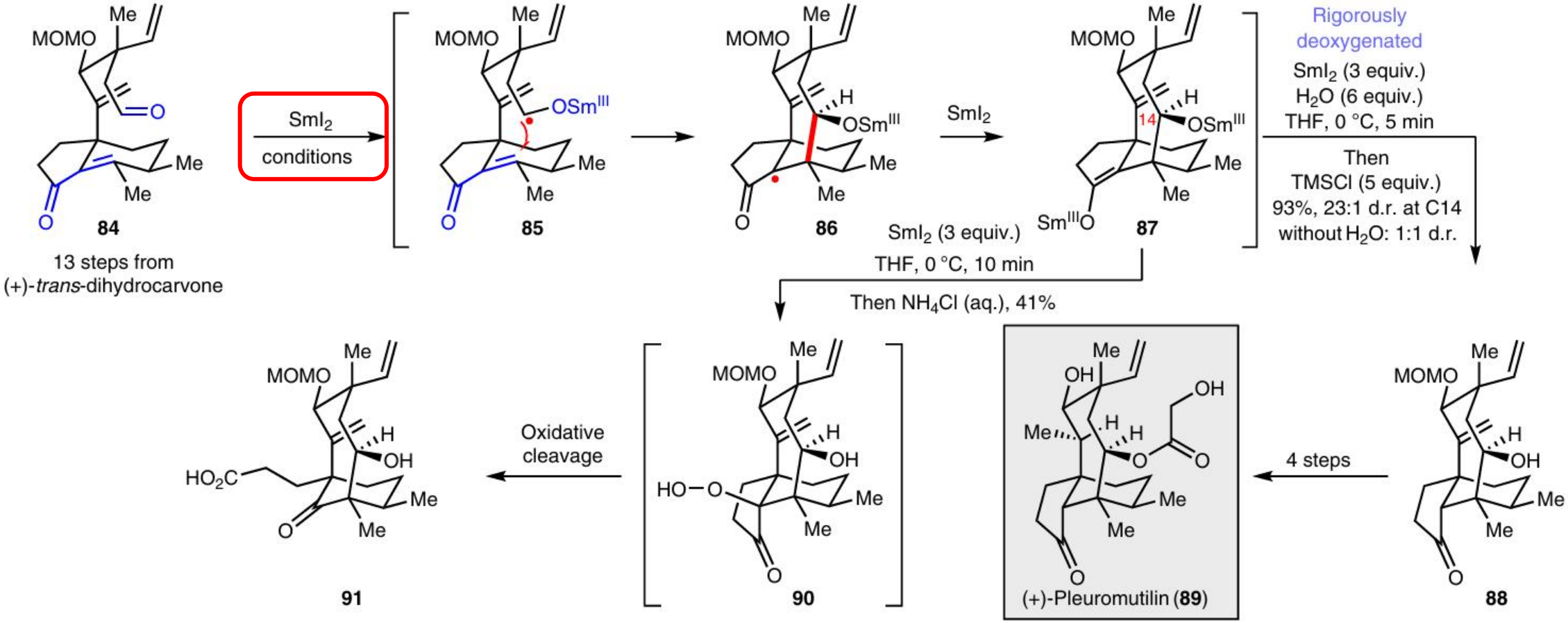
Wood's work



J. L. Wood, *Chem. Sci.*, **2020**, *11*, 9488–9493

Carbonyl–Alkene/Alkyne and Related Reactions

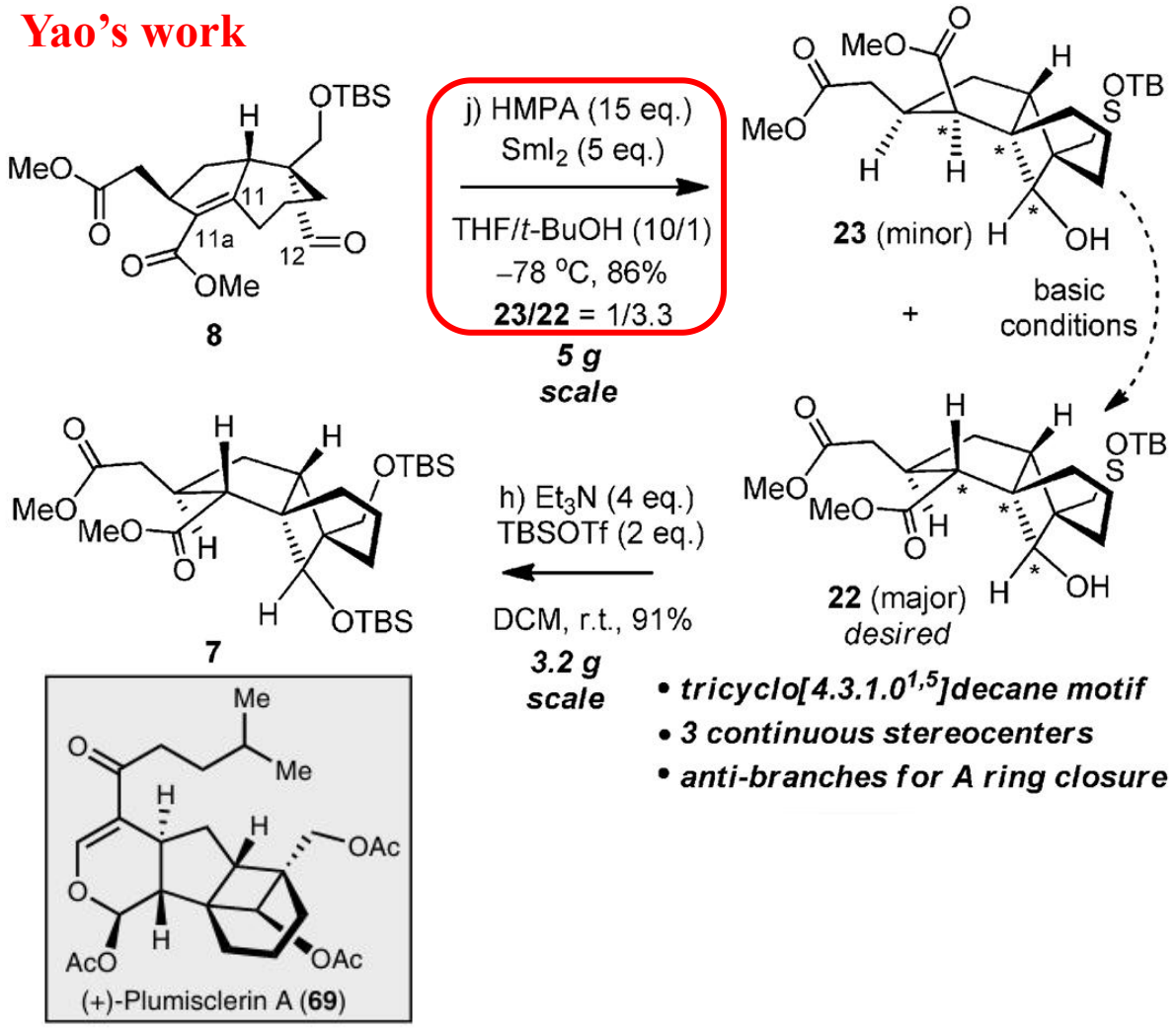
Reisman's work



S. E. Reisman, *J. Am. Chem. Soc*. **2018**, *140*, 1267–1270 ;

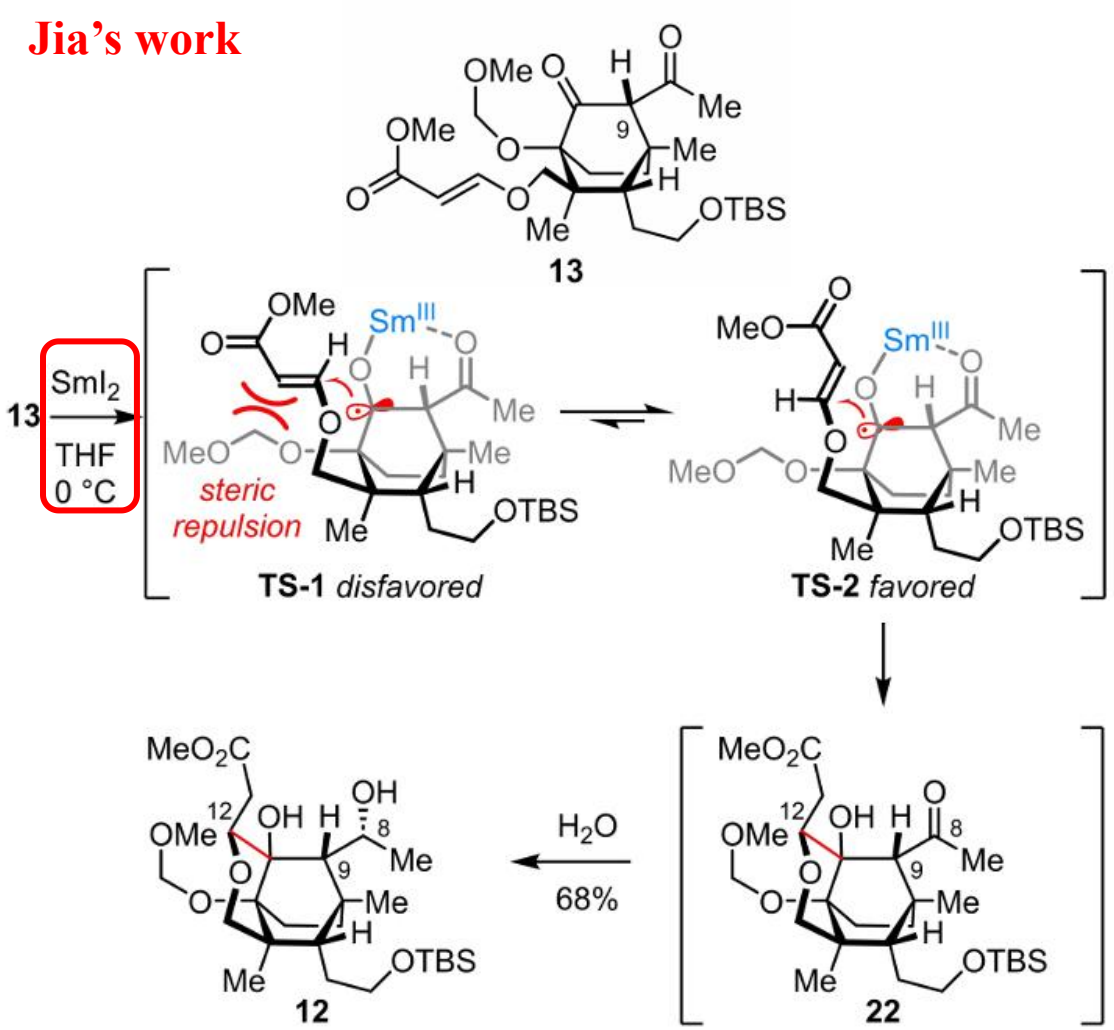
Carbonyl–Alkene/Alkyne and Related Reactions

Yao's work



- *tricyclo[4.3.1.0^{1,5}]decane motif*
- *3 continuous stereocenters*
- *anti-branches for A ring closure*

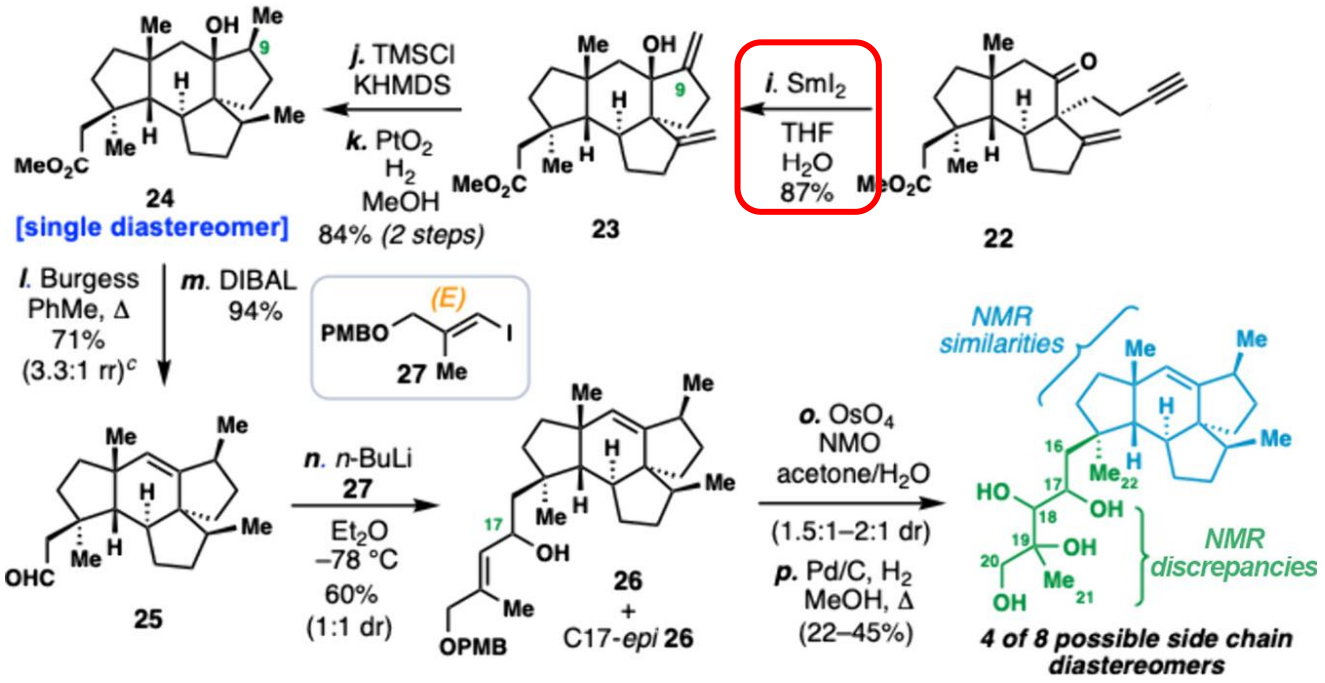
Jia's work



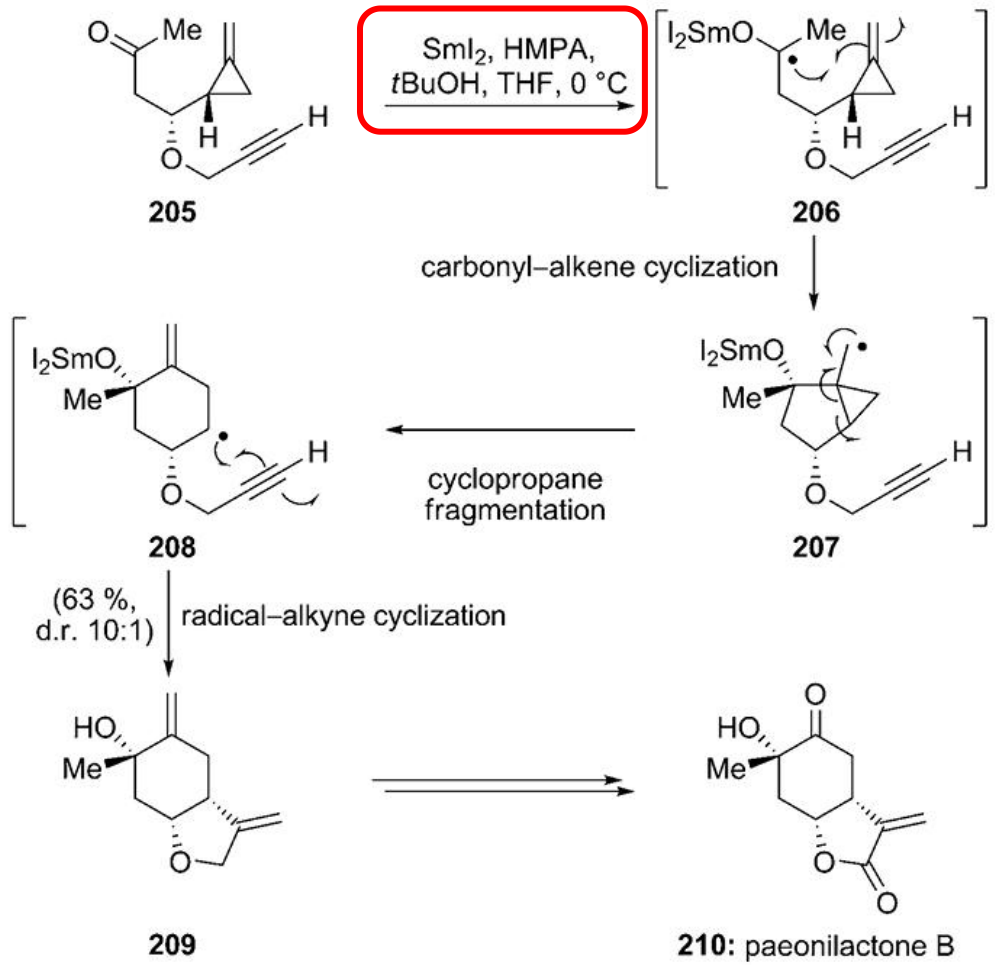
1. Yao, Z., *Angew. Chem. Int. Ed.* **2018**, *57, 13313*–13318; **2.** Jia, Y., *Angew. Chem. Int. Ed.* **2024**, *63,* e202319127

Carbonyl–Alkene/Alkyne and Related Reactions

Maimone's work



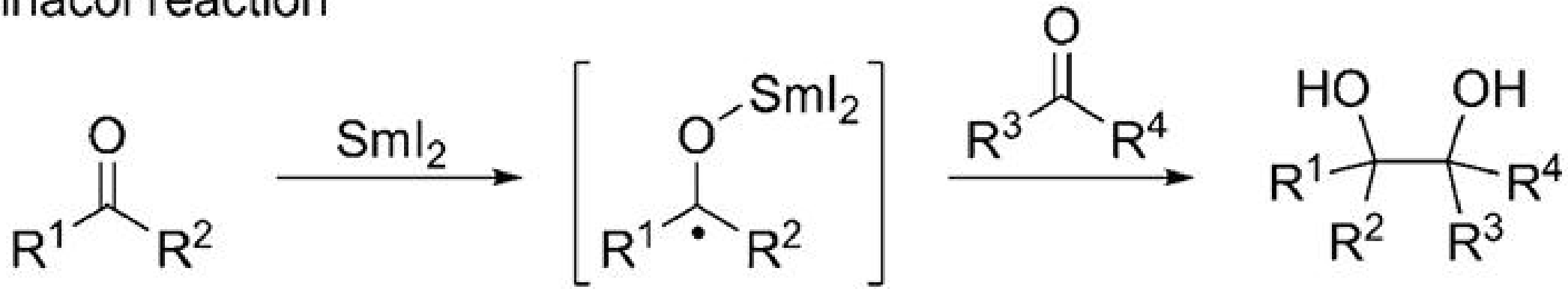
Kilburn's work



1. T. J. Maimone, *J. Am. Chem. Soc.* **Articles ASAP**; **2.** J. D. Kilburn, *Chem. Commun.* **1998**, 1875–1876.

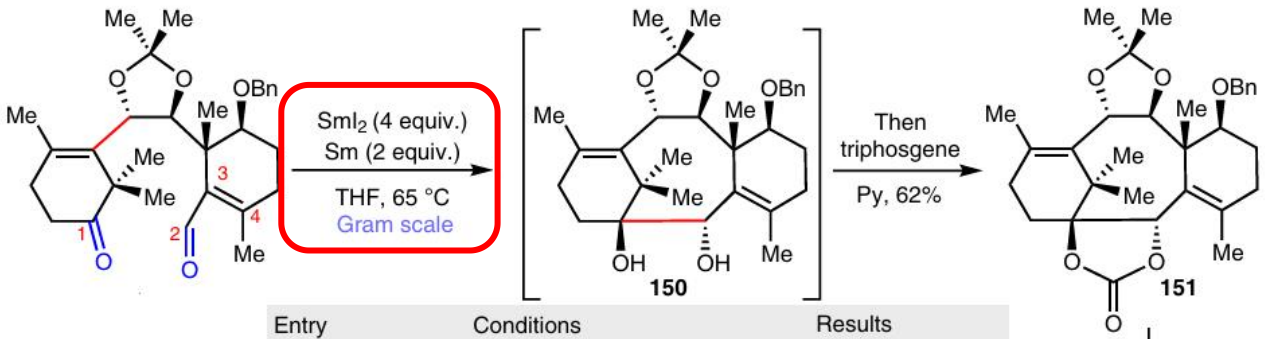
Pinacol-Type Reaction

e) Pinacol reaction



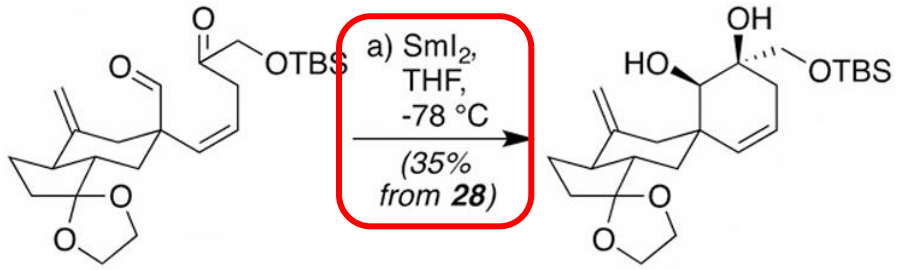
Pinacol-Type Reaction

Li's work

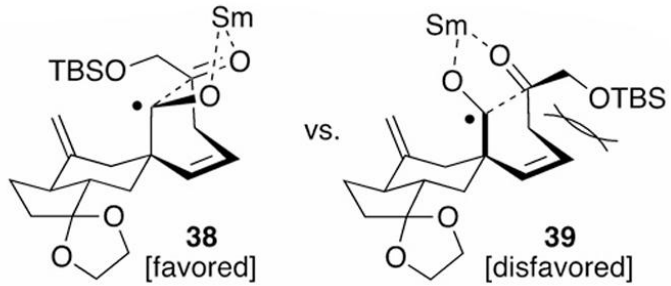


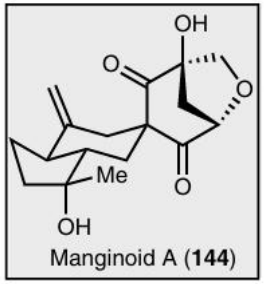
Entry	Conditions	Results
1	$TiCl_4$/Zn/pyridine	48% **151** (not scalable)
2	Cp_2TiCl_2/Zn	No reaction
3	$VCl_3(THF)_3$/Zn	No reaction
4	SmI_2	38% **152**
5	SmI_2/HMPA	38% **153**
6	SmI_2/^{t}BuOH	48% **152**

Synder's work



Entry	Additive	Temp. (°C)	Yield
1	none	23	~10%
2	LiCl/LiBr	23	~10%
3	HMPA	23	decomp.
4	MeOH/*t*-BuOH	23	decomp.
5	none	-78	35%

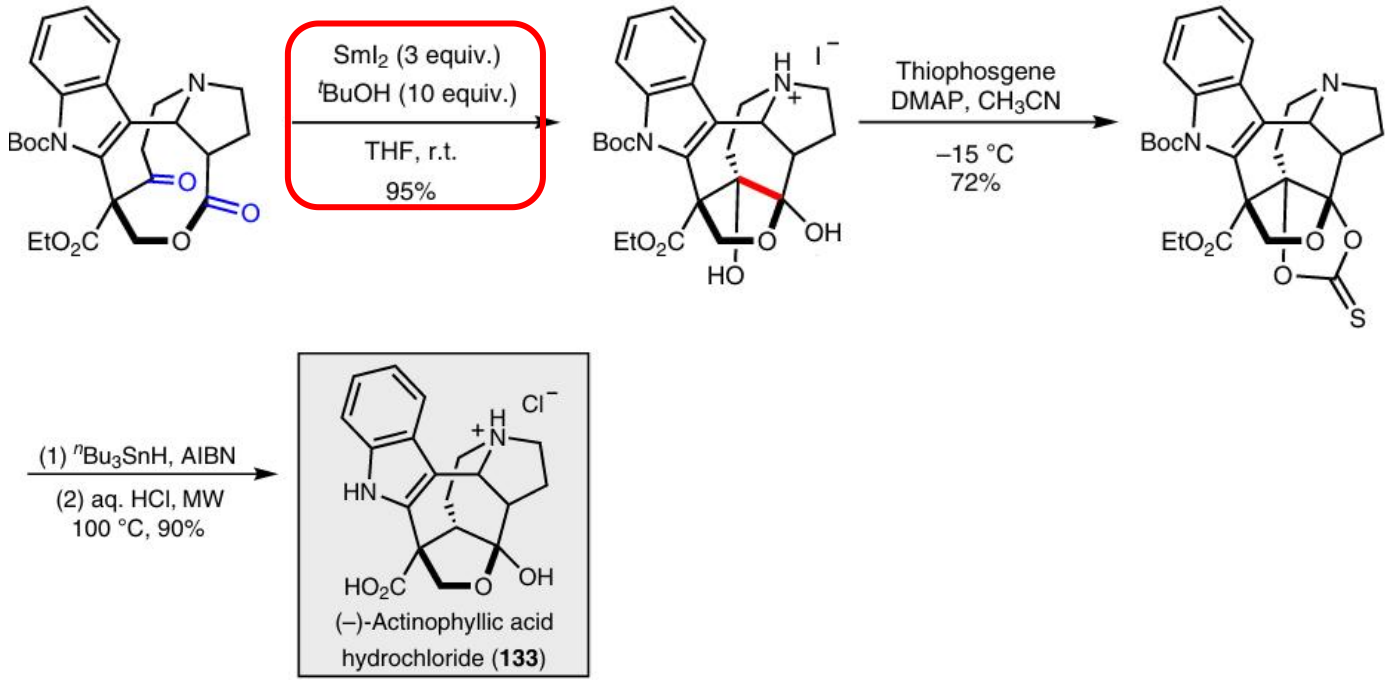




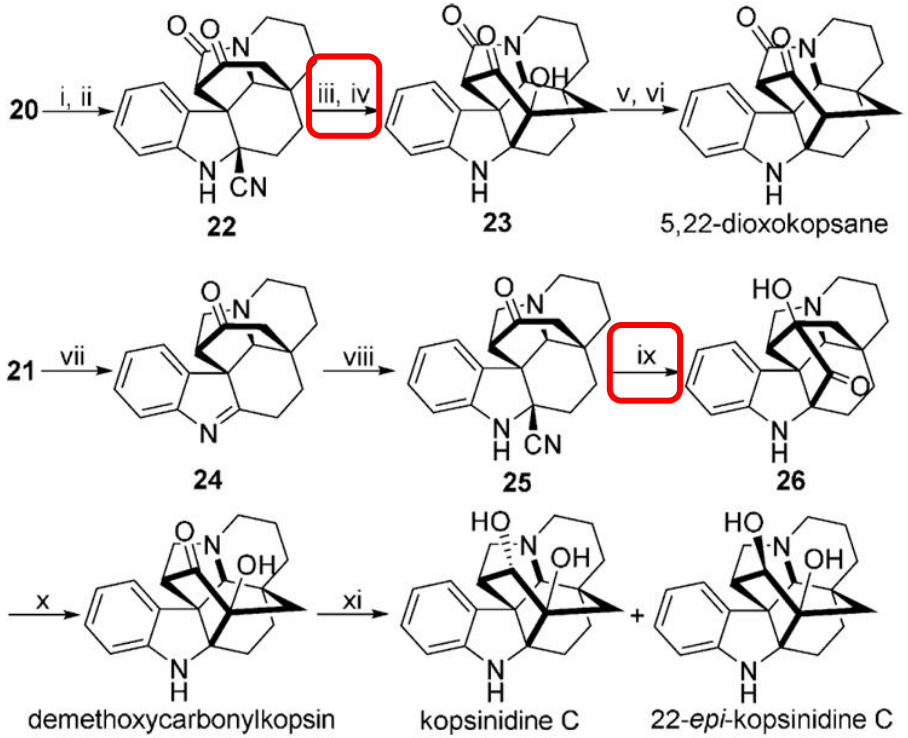
1. Li, C., *J. Am. Chem. Soc*. **2021**, *143*, 17862–17870; **2.** S. A. Synder. *Angew. Chem. Int. Ed.* **2021**, *60,* 11127–11132

Pinacol-Type Reaction

Kwon's work



Ma's work

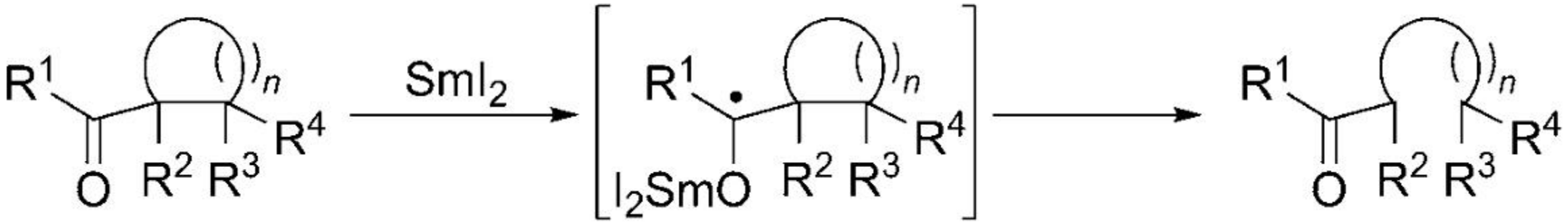


Scheme 3. Reagents and conditions: i) TFA, CH_2Cl_2, 0 °C, 92%; ii) TMSCN, THF, MeOH, 60 °C, 92%; iii) SmI_2, THF, 79%; iv) NaOH, THF, 89%; v) $ClCOCO_2Me$, DMAP, CH_2Cl_2, 85%; vi) *n*-Bu_3SnH, AIBN, toluene, reflux, 44% (with recovery of **23** in 31% yield); vii) BH_3·THF, THF, reflux; then TFA, CH_2Cl_2, 0 °C, 80%; viii) TMSCN, THF, MeOH, 60 °C, 91%; ix) SmI_2, THF, 75%; x) NaOH, dioxane, 80%; xi) $LiAlH_4$, THF, 0 °C, kopsinidine C (40%), 22-*epi*-kopsinidine C (30%).

1. O. Kwon, *J. Am. Chem. Soc*. **2016**, *138*, 3298–3301; **2.** Ma, D., *Angew. Chem. Int. Ed.* **2018**, *57, 10207*–10211

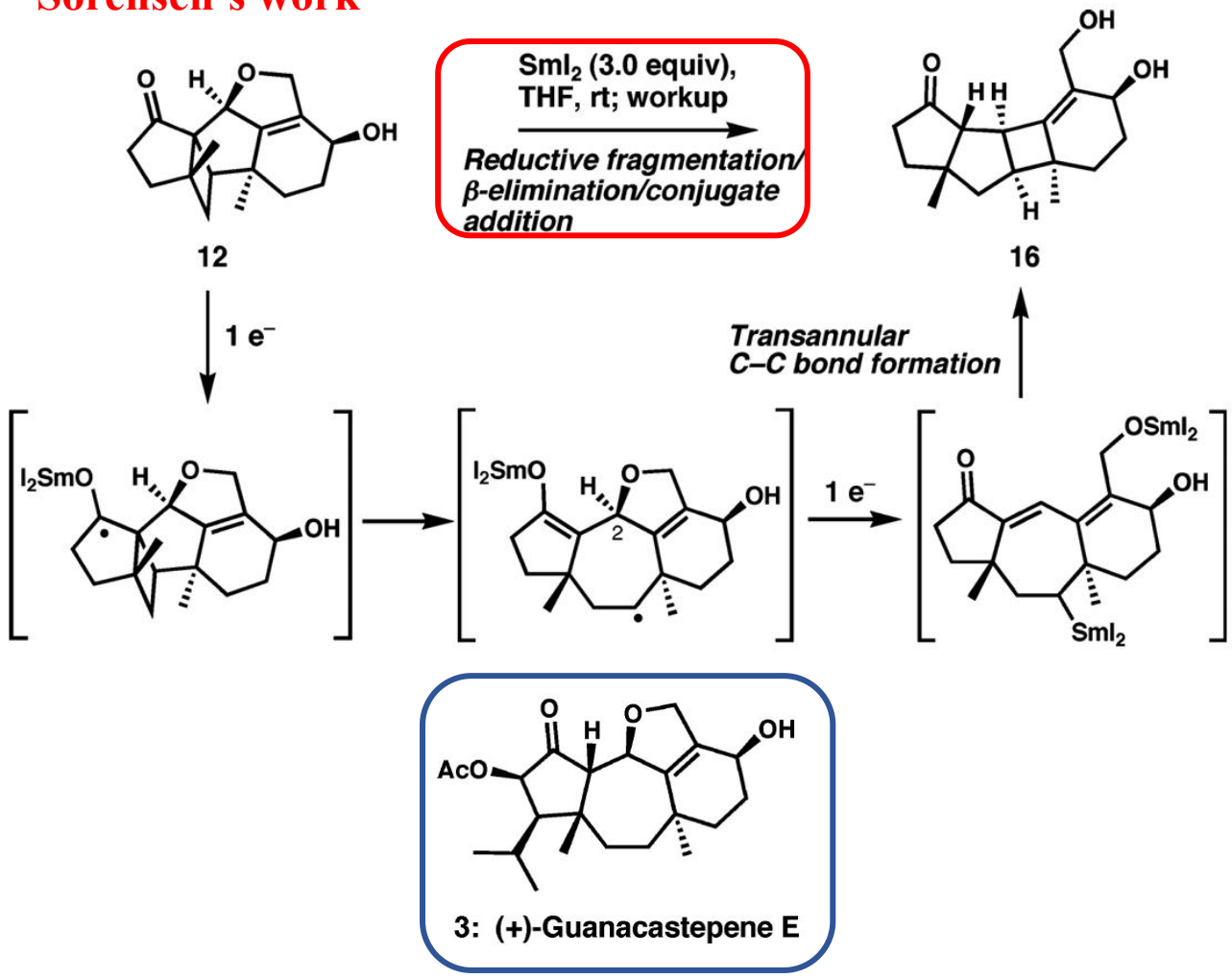
Fragmentation Reaction

f) Fragmentation reaction

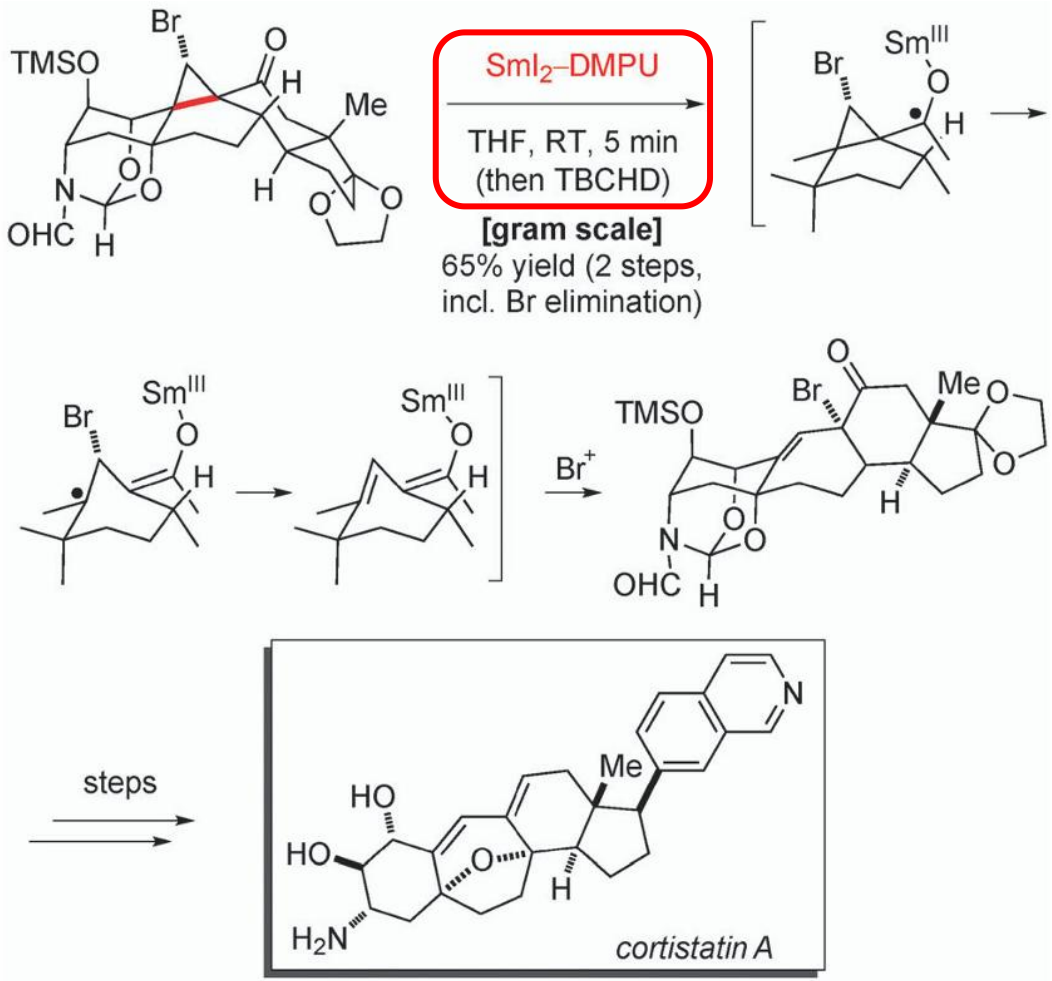


Fragmentation Reaction

Sorensen's work



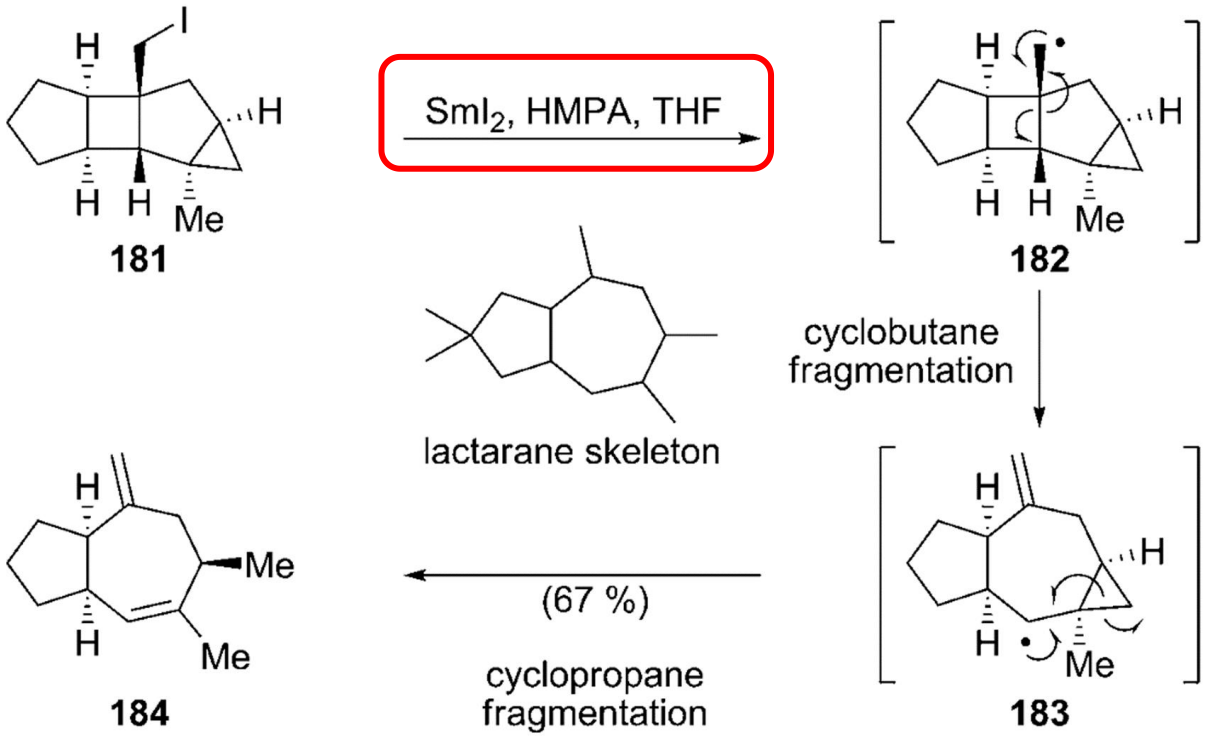
Baran's work



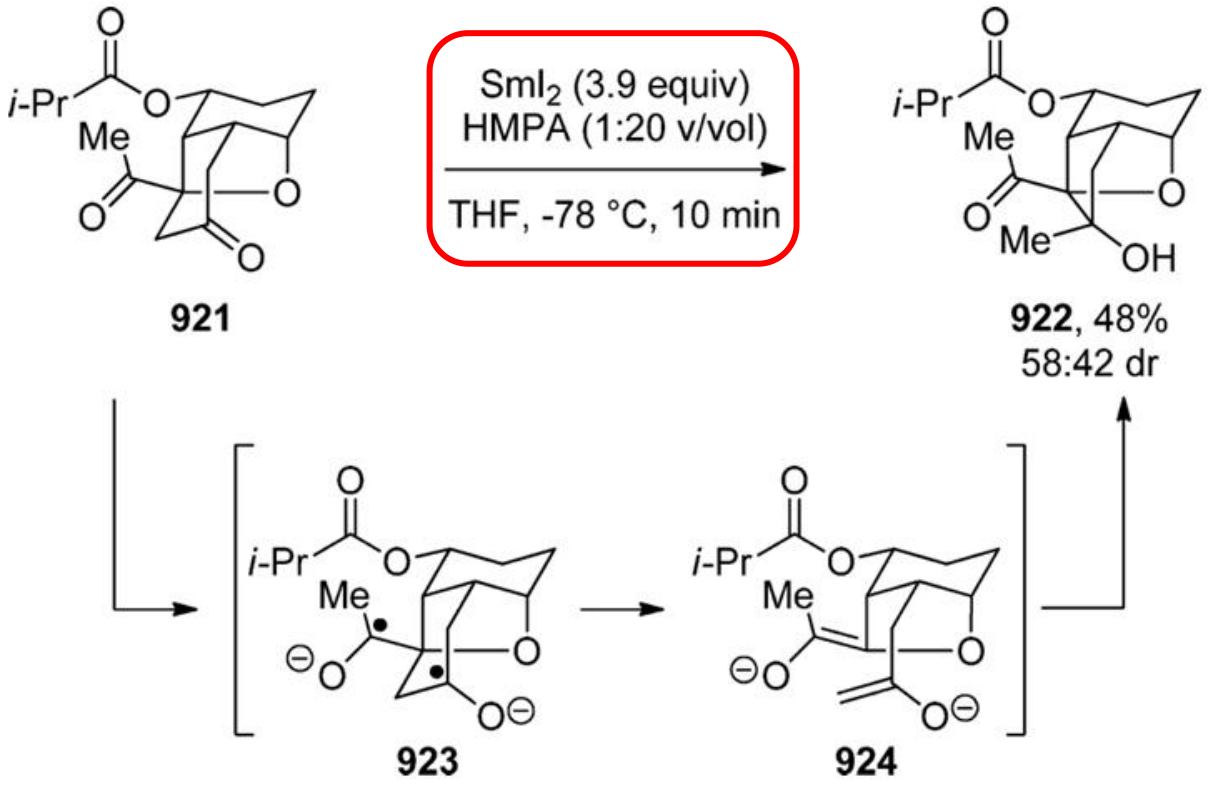
1. E. J. Sorensen, *J. Am. Chem. Soc.*, **2011**, *133*, 8014; **2.** P. S. Baran, *J. Am. Chem. Soc.*, **2011**, *133*, 8014

Fragmentation Reaction

Lange's work



Schwartz's work



1. G. L. Lange, *Tetrahedron Lett.* **2007**, *48*, 1963-1965; **2.** A. Schwartz, *Monatsh. Chem.* **2001**, *132*, 855-858.

Thanks for your attention