Organic Letters 2004

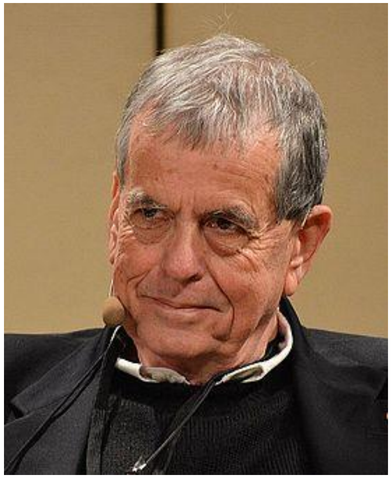
Gaich-Group Seminar

Konstantin Samarin

21.05.2015

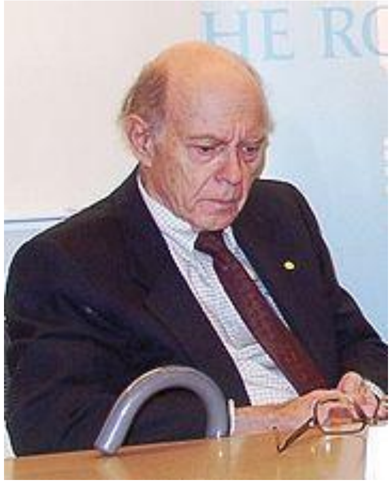
The Nobel Prize in Chemistry 2004

Discovery of ubiquitin-mediated protein degradation.



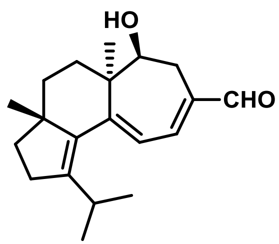
Aaron Ciechanover

Avram Hershko

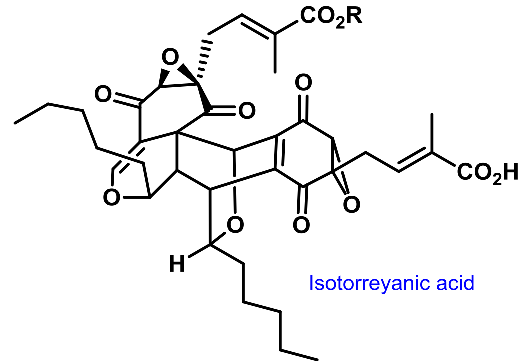


Irwin Rose

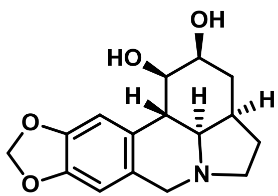
Total synthesis



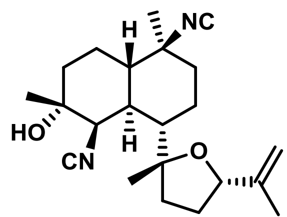
(+)-allocyanthin B_2



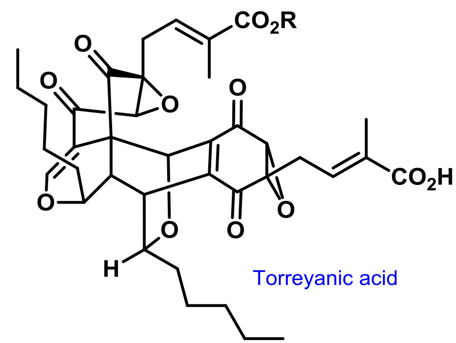
Isotorreyanic acid



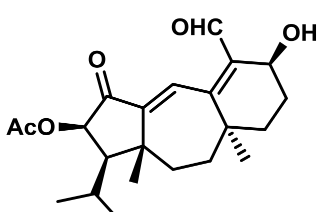
epi-zephyranthine



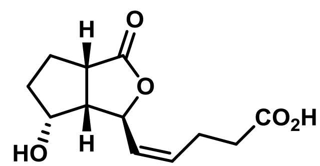
kalihinol C



Torreyanic acid

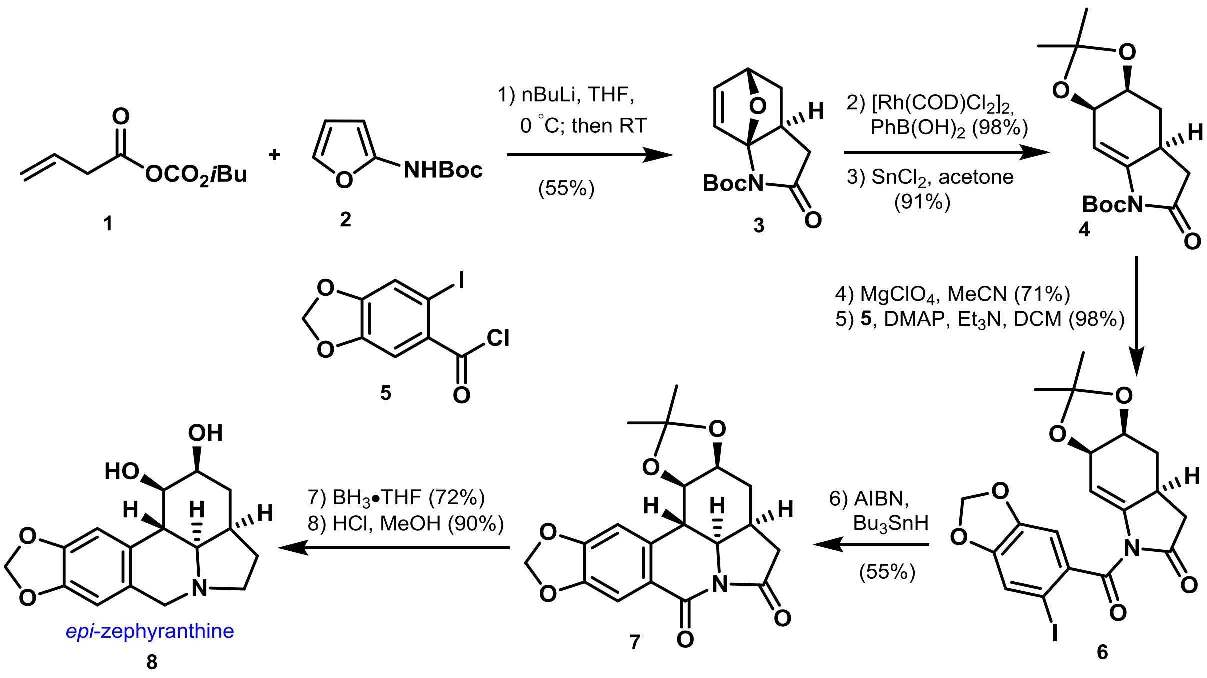


Guanacastepene



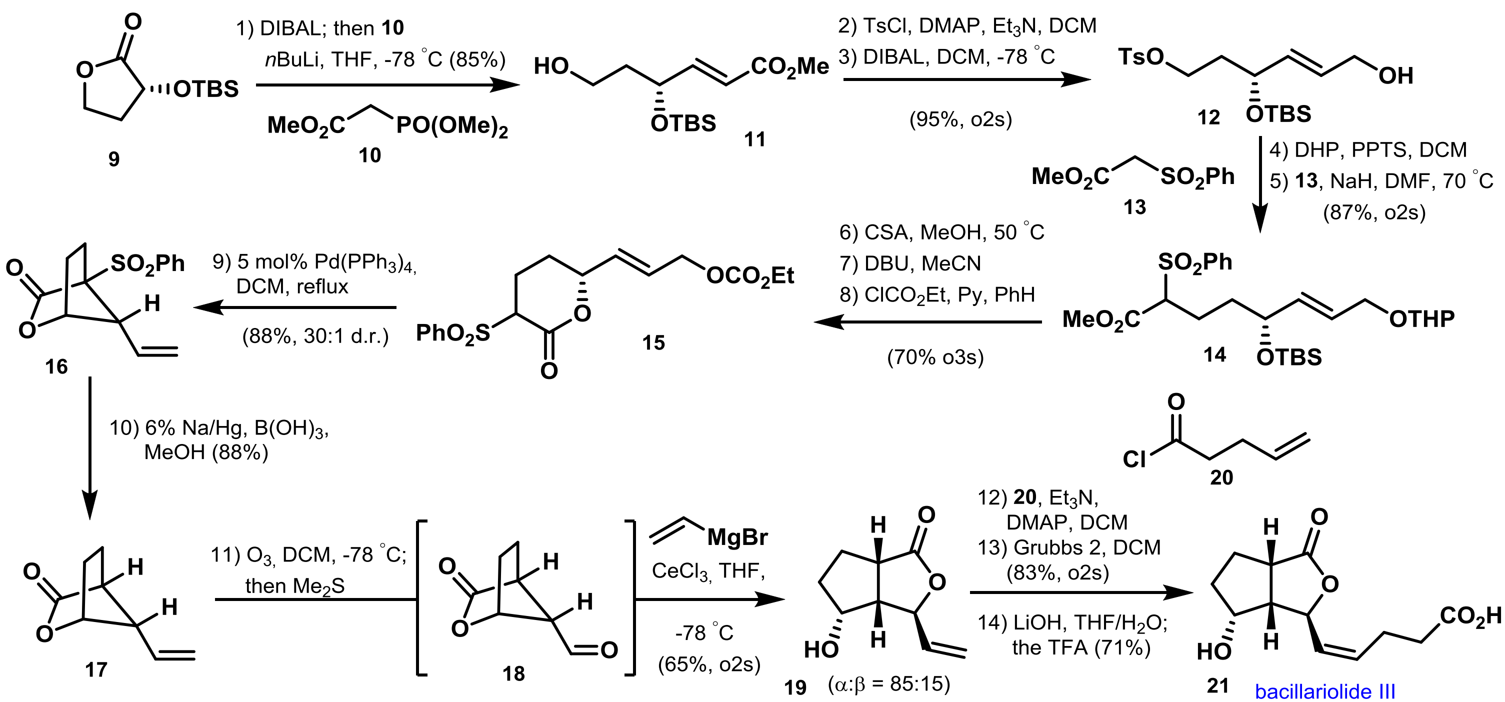
bacillariolide III

epi-Zephyranthine

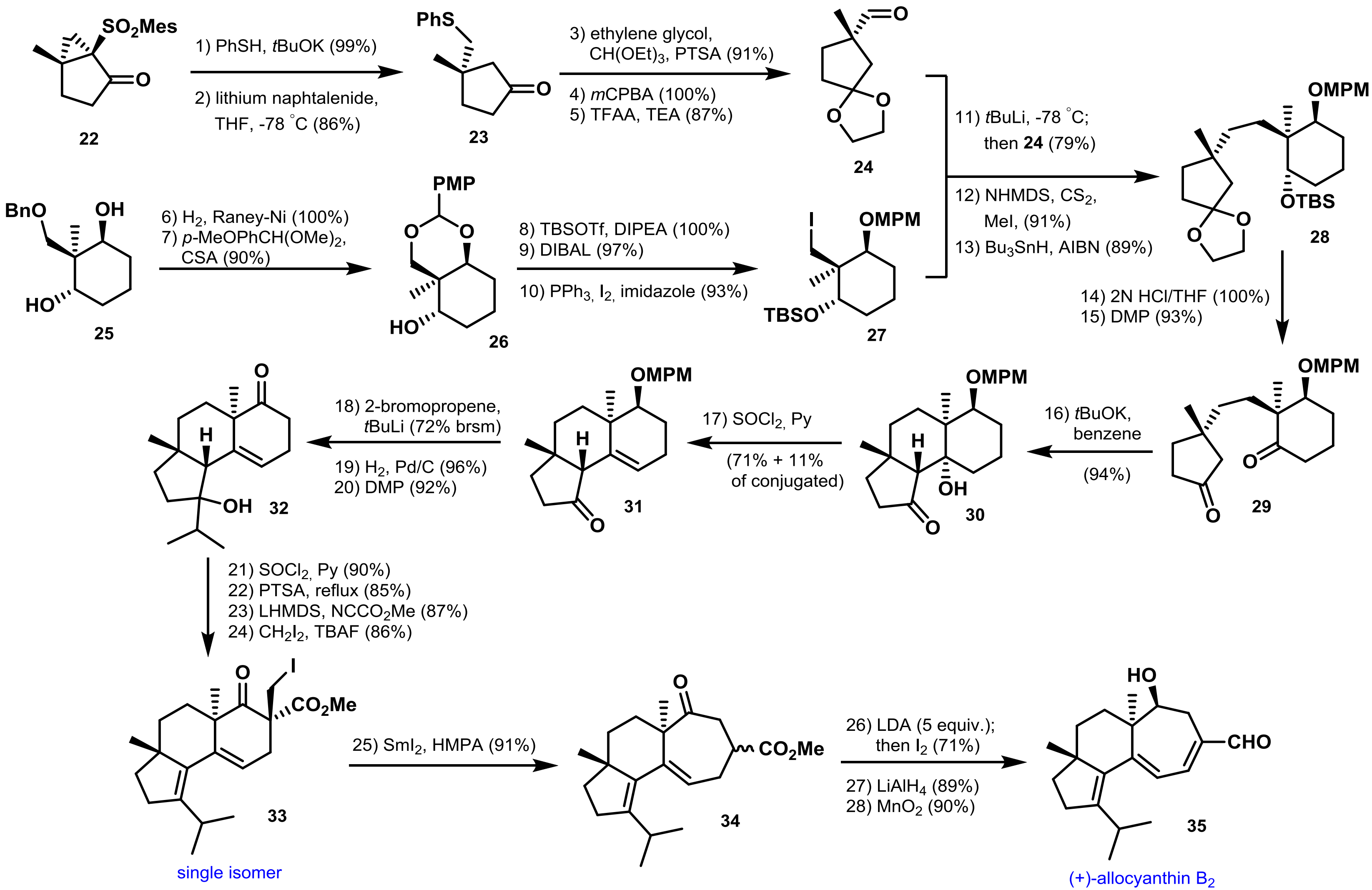


Wang Q., Padwa A. *Org. Lett*. **2004**, *6*, 2189 – 2192.

Bacillariolide III

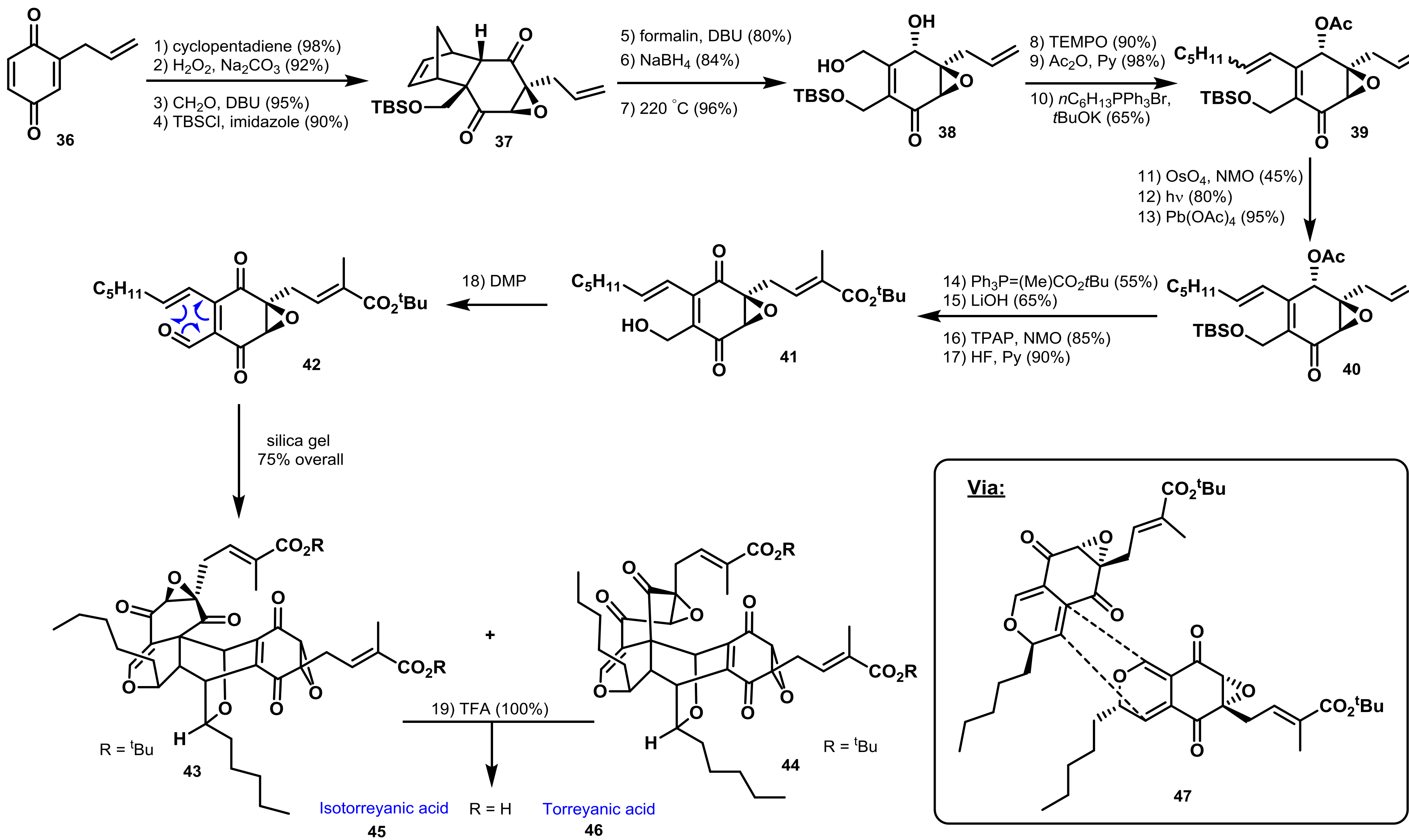


(+)-Allocyanthin B2



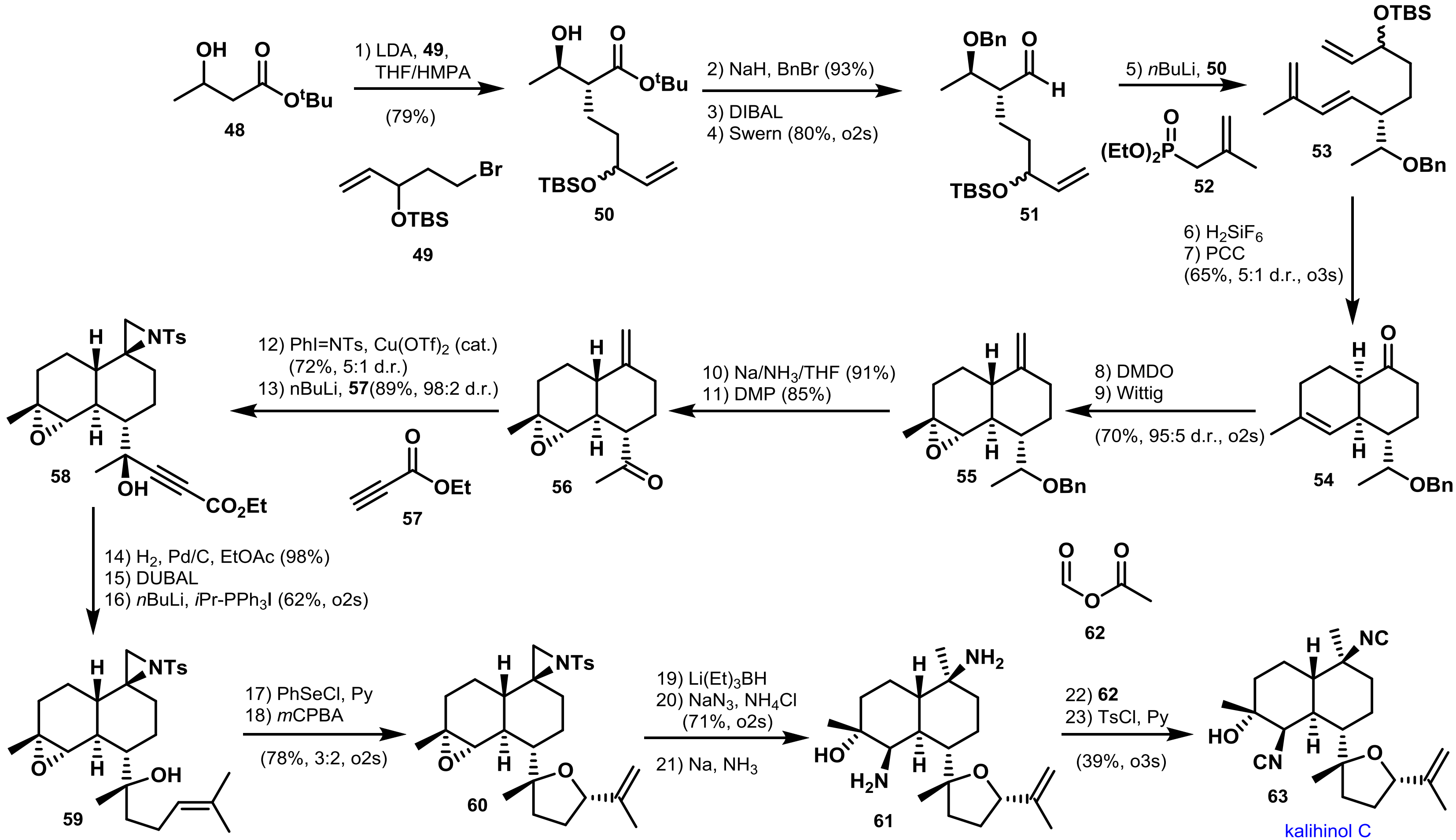
Takano M., Umino A., Nakada M. *Org. Lett.* **2004**, *26*, 4897 – 4900.

Torreyanic and Isotorreyanic acid



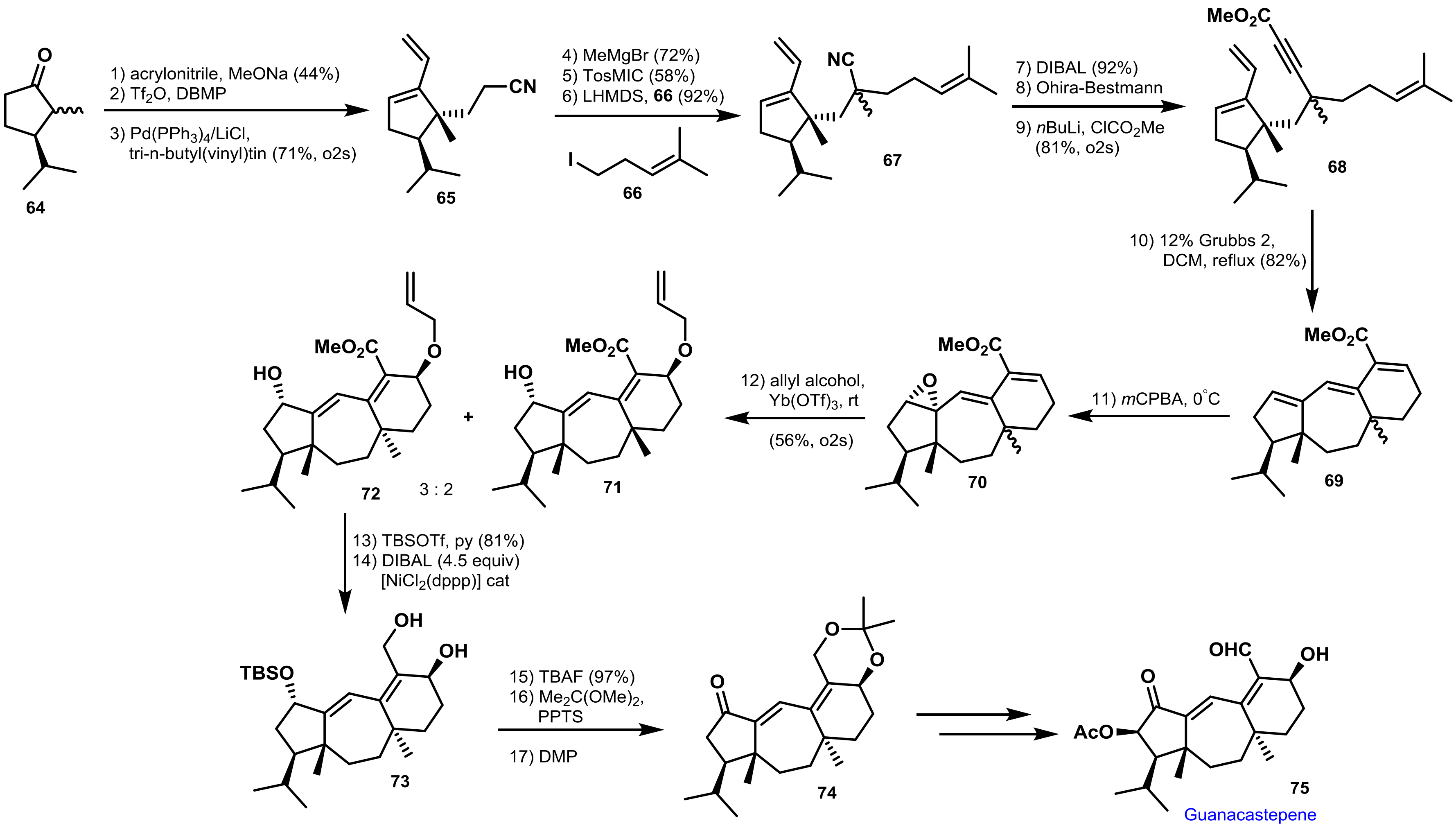
Metha G., Pan S. C. *Org. Lett*. **2004**, *22*, 3985 – 3988.

Kalihinol C



White R.D., Keaney G.F., Slown C.D., Wood J.L. *Org. Lett*. **2004**, *7*, 1123 – 1126.

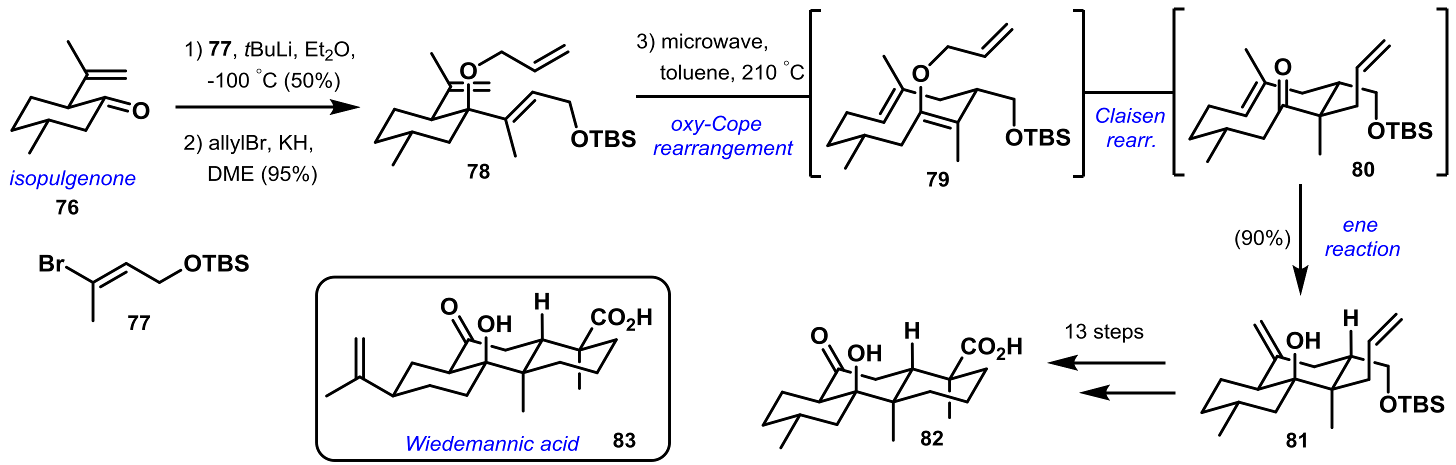
(±)-Guanacastepene A



Boyer F.-D., Hanna I., Ricard L. *Org. Lett.* **2004**, *6*, 1817 – 1820.

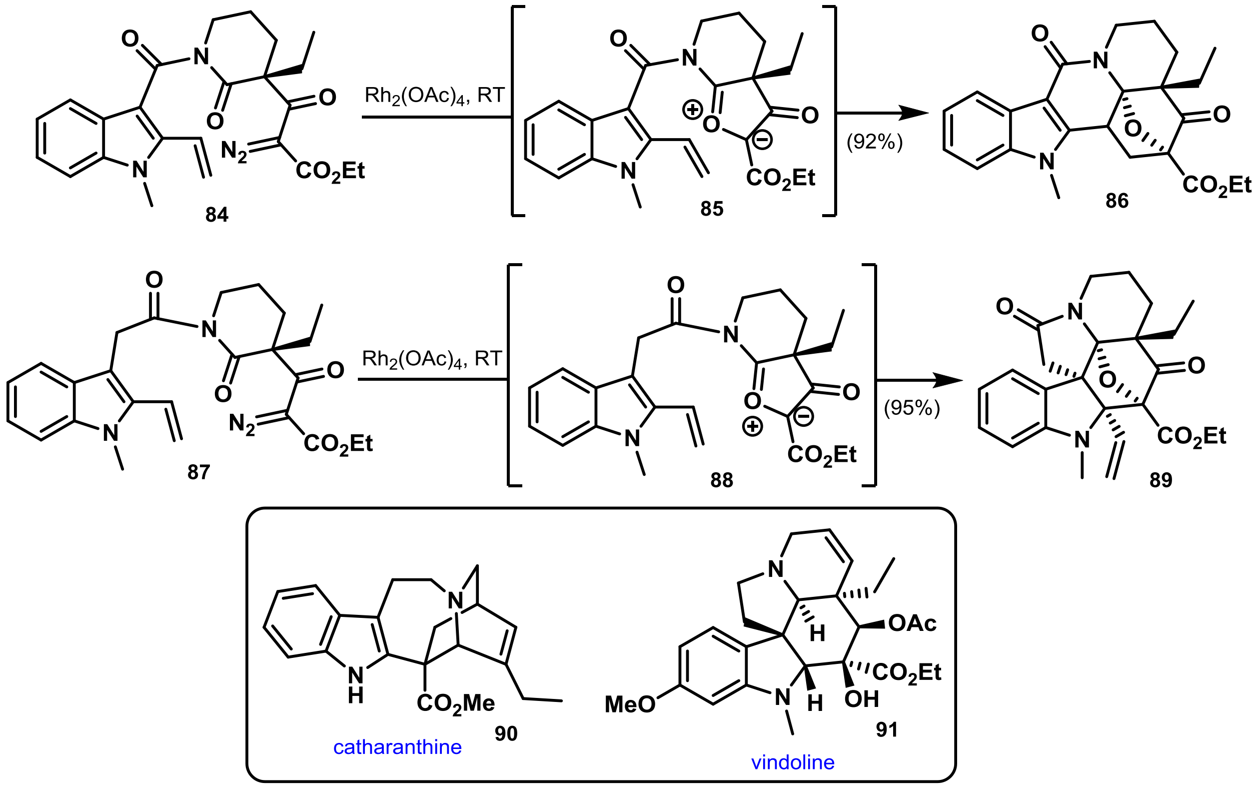
Interesting Approaches

Wiedemannic acid



Sauer E. L. O., Barriault L. *Org. Lett.* **2004**, *6*, 3329 – 3332.

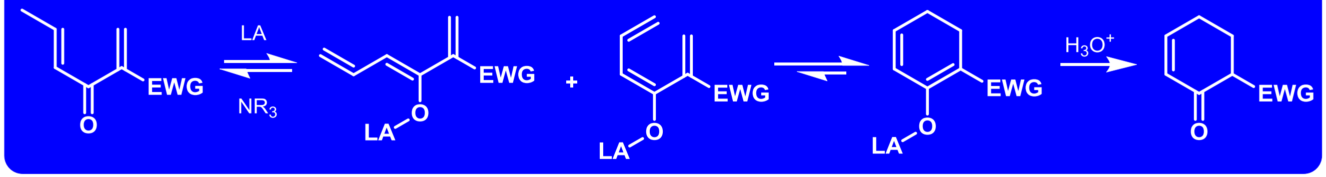
Indole alkaloids



Methodology

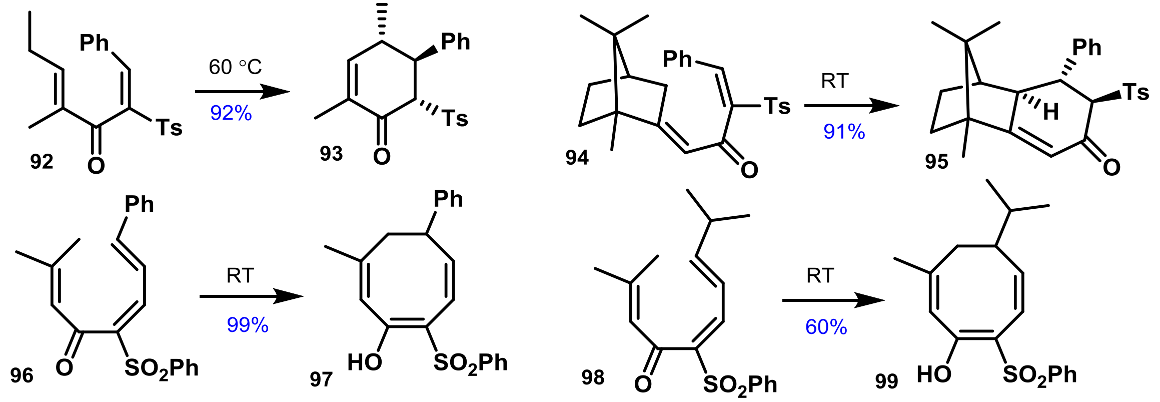
Cyclizations of Divinyl Ketones to Cyclohexenones

Mechanism:



Scope

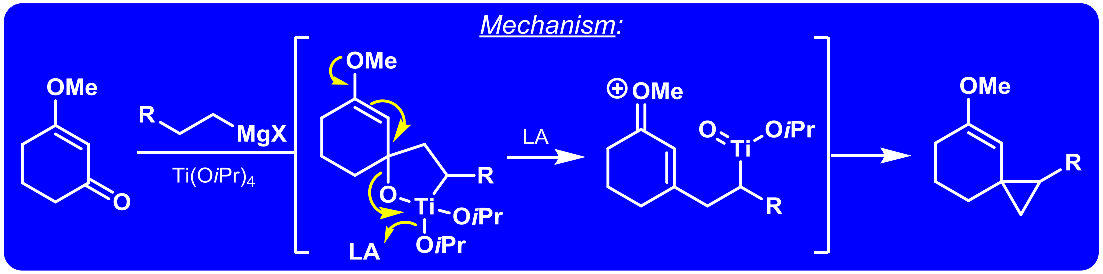
Conditions: MAD (2 equiv.), Et_3N (1.1 equiv.), toluene



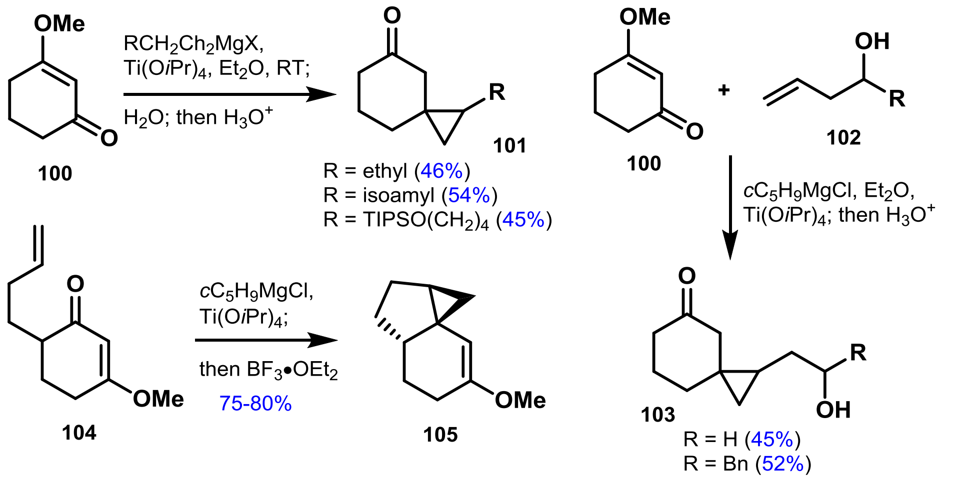
Key features:

- ***divinyl ketones ("Nazarov" substrates)***
- ***strong electron withdrawing groups*** => - ***disrotatory 6π-electrocyclization***
- ***sterically demanding Lewis acid***

Cyclopropanation of Vinylogous Esters



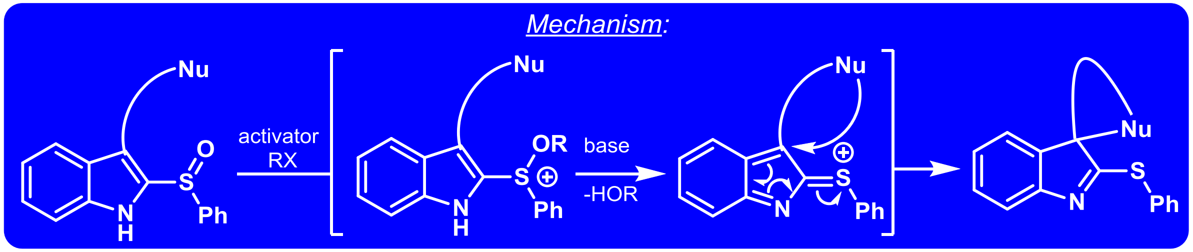
Scope



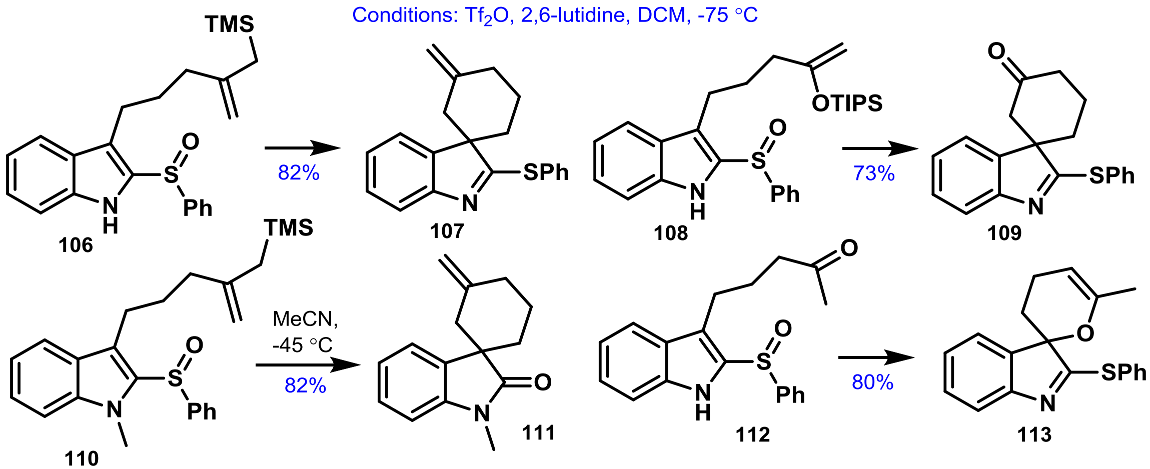
Key features:
- ***Cyclopropanation of vinylogous esters utilizing Kulinkovich conditions***
- ***non Lewis basic solvents secure cyclopropane formation***
- ***inter- and intramolecular cyclopropanation are possible***

Masalov N., Feng W., Cha J.K. *Org. Lett.* **2004**, *6*, 2365 – 2368.

Oxidative Cyclization of Indole Derivatives



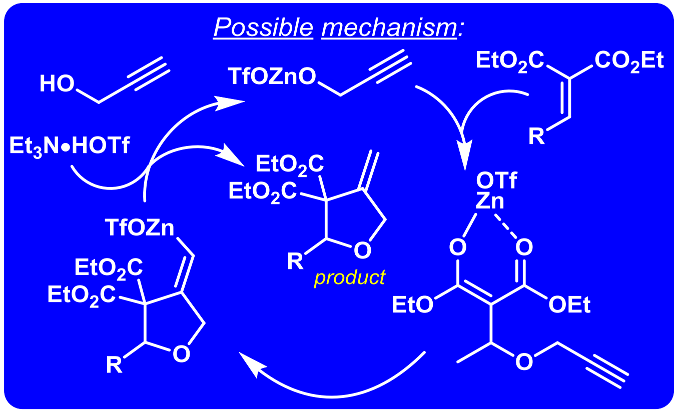
Scope



Key features:
- Pummerer-like cyclization
- feasable route to spirooxindoles

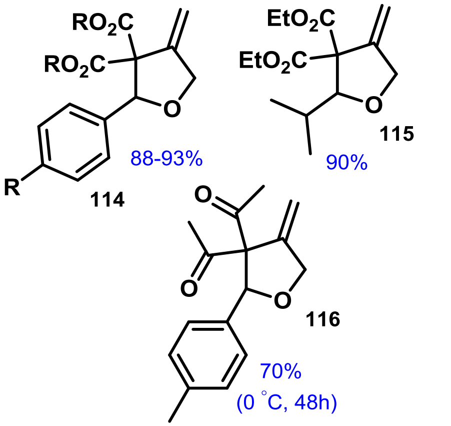
Feldman K.S., Vidulova D.B. *Org. Lett.* **2004**, *6*, 1869 – 1871.

One-Pot Synthesis of Methylenetetrahydrofurans



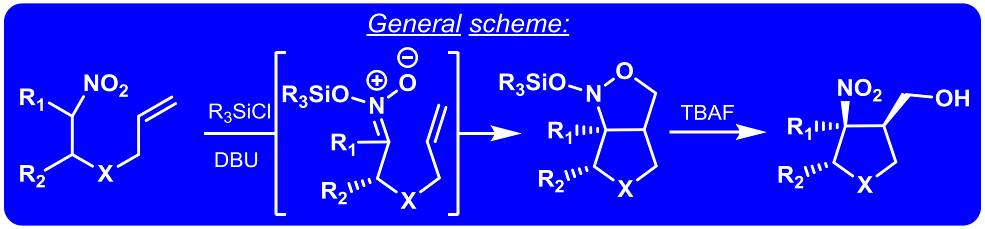
Scope

Conditions: 10 mol% $Zn(OTf)_2$, 10 mol% Et_3N, RT, 12h, neat

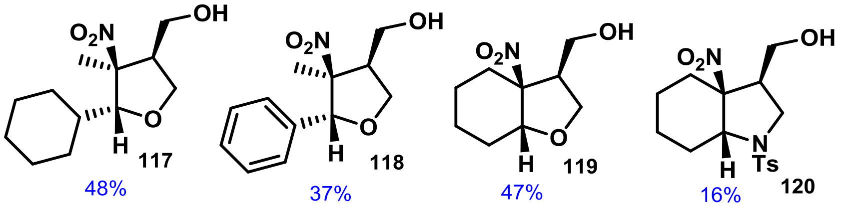


Key features:
- strong Michael acceptors
- Zn(II)/Amine-Catalyzed Coupling

In Situ Oxidative Ring Cleavage of Isoxazolidines



Scope



Key features:
- unactivated olefin
- silyl nitronate
- 1,3-dipolar cycloaddition

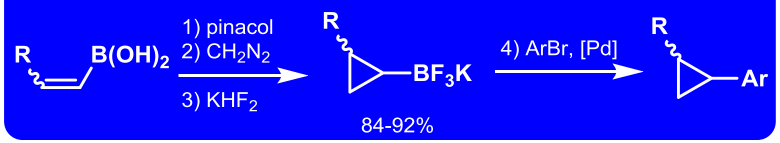
=>

- some isoxazilidines are isolable
- 3-hydroxy tetrahydro-furanes(-pyrollidines)

Roger O.-Y., Durand A.-C., Rodriquez J., Dulcere J.-P. *Org. Lett.* **2004**, *6*, 2027 – 2029.

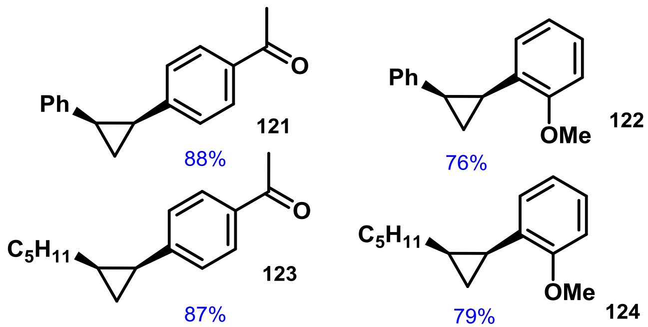
Cross-Coupling of Cyclopropyl Trifluoroborates

General scheme:



Scope

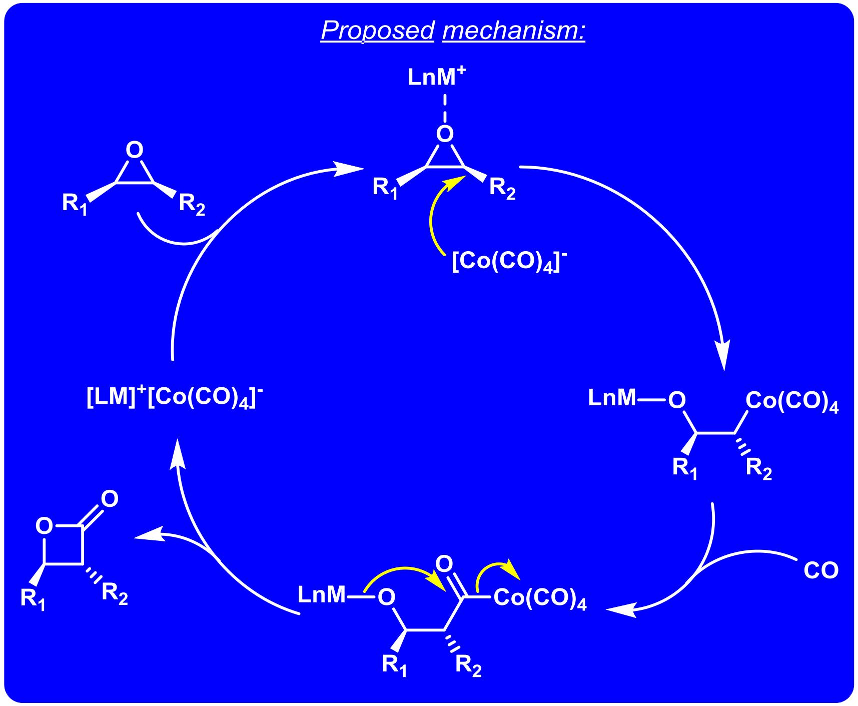
Conditions: $Pd(PPh_3)_4$, toluene-H_2O, K_3PO_4•$3H_2O$, reflux

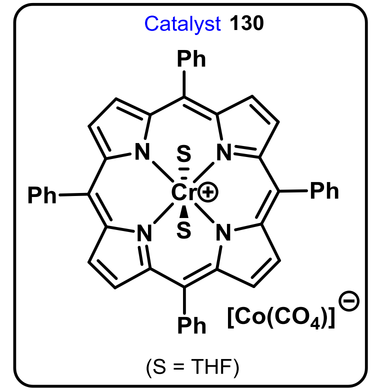


Key features:
- readily avalaible cyclopropyl trifluoroborates
- Suzuki-Miyaura cross-coupling
- retention of configuration by coupling

Fang G.-H.m Yan Z.-J., Deng M.-Z. *Org. Lett*. **2004**, *6*, 357 – 360.

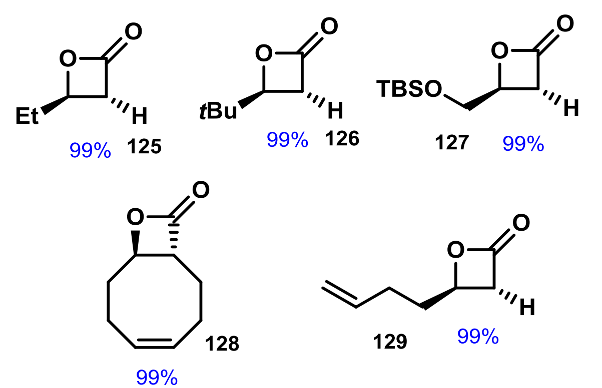
Catalytic carbonylation of epoxides





Scope

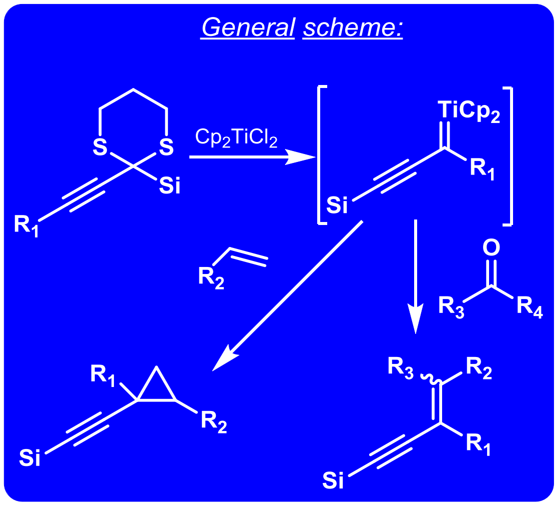
Conditions: catalyst (0.3-0.5 mol %), CO(900 psi), neat, 60 °C, 6h



> ***Key features:***
> ***- effective elongation of terminal epoxides***
> ***- high regio- and sterioselectivity***

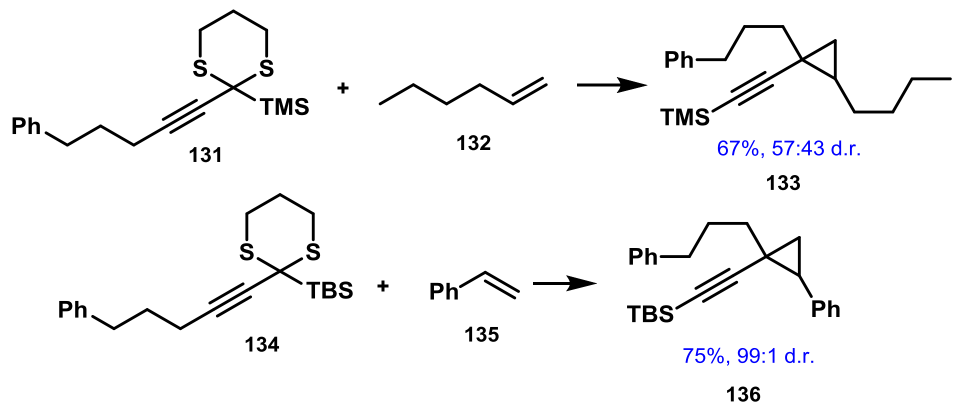
Schmidt J.A.R., Mahadevan V., Getzler Y.D.Y.L., Coates G.W. *Org. Lett*. **2004**, *6*, 373 – 376.

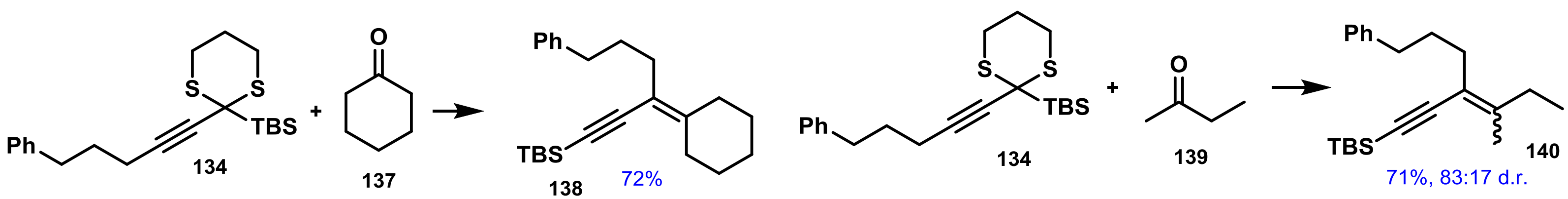
Cp2Ti[P(OEt)3]2-promoted cyclopropanation/olefination



Scope

Conditions: Cp_2TiCl_2, Mg, MS 4 A, $P(OEt)_3$, RT

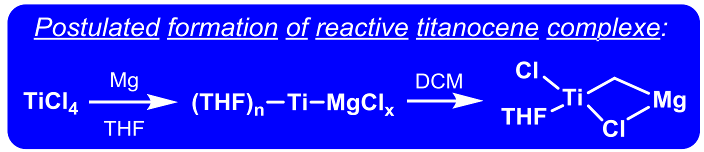




Key features:
- trialkylsilyl-1,3-dithianes as substrate
- via titanium α-(silylethynyl)-carbene complexes

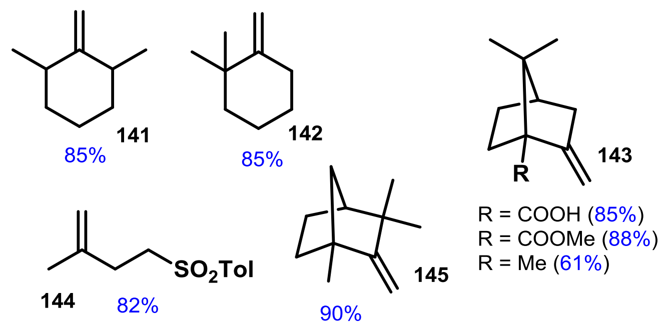
Takeda T., Kuroi S., Ozaki M., Tsubouchi A. *Org. Lett.* **2004**, *6*, 3207 – 3210.

Dichloromethane Activation. Methylenation of Ketones



Scope

Conditions: $TiCl_4$ (2 equiv.), Mg (8 equiv.), DCM/THF, 0 °C



Key features:

- easy procedure/common reagents

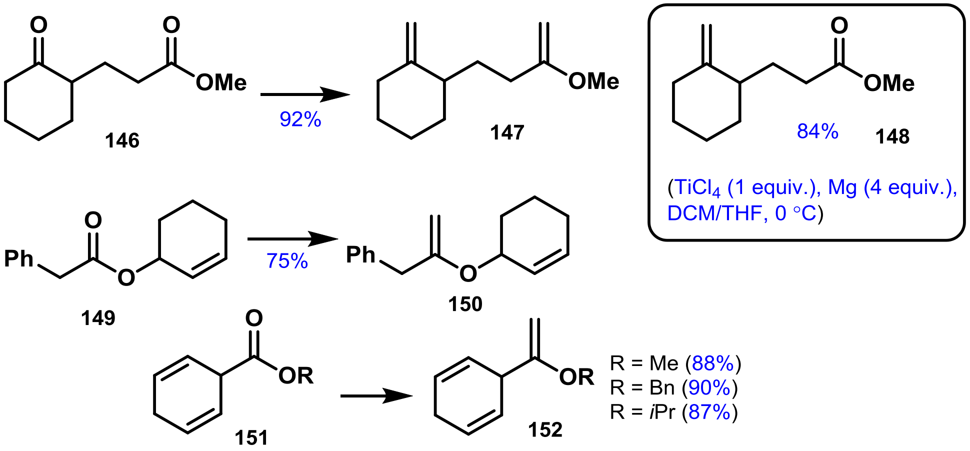
- enolizable and sterically hindered substrates underwent facile methylenation

Yan T.-H., Tsai C.-C., Chien C.-C., Cho C.-C. Huang P.-C. *Org. Lett.* **2004**, *6*, 4961 – 4963.

Dichloromethane Activation. Methylenation of Esters

Scope

Conditions: $TiCl_4$ (2 equiv.), Mg (8 equiv.), DCM/THF, 25 °C



Key features:
- ***fine tuning of reaction conditions enable differentiation between keto and ester functionalities***
- ***stericaly demanding ester do not undergo methylenation***

Yan T.-H., Chien C.-C.,Tsai C.-C., Lin K.-W., Wu Y.-H. *Org. Lett.* **2004**, *6*, 4965 – 4967.

Questions