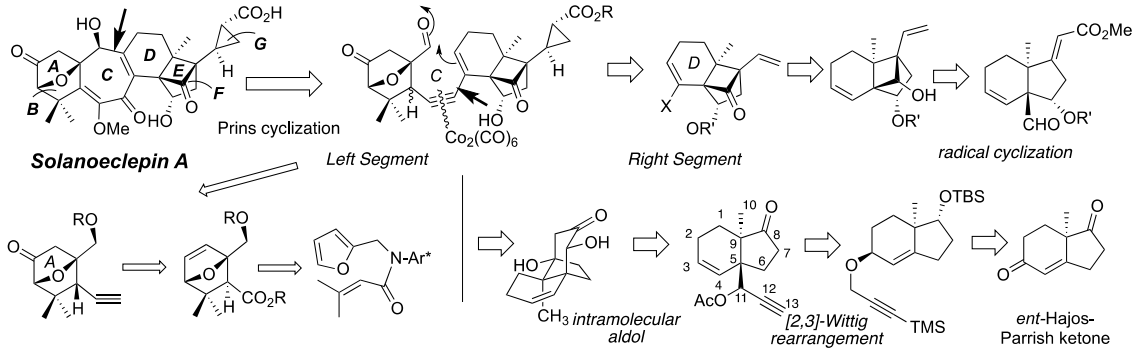
Stereochemical Control in Natural Product Synthesis:
---Solanoeclepin A and Wittig Rearrangements---

Minoru Isobe

Dept. Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, minoru@mail.nsysu.edu.tw

We have been studying stereochemical control for natural product synthesis such as solanoeclepin A (**1**), for which we have recently achieved the partial syntheses aiming at the cyclobutane-ring formation via the following retrosynthetic route from ent-*Hajos-Parrish ketone* via [2,3]-Wittig rearrangement, and radical cyclization through aldehyde-enone. The Left Segment was recently synthesized via intramolecular Diels-Alder cycloaddition. After coupling with a C-ring model, the *Prins-carbonyl-ene* cyclization with the acetylene dicobalt complex gave the seven membered product using a Lewis acid catalyst. The resulting stereochemistry of the *sec*-hydroxyl group can be beta-selective but the double bond control has to be waited for improvement. During the synthesis, we have explored a synthesis of trans-C/D ring system, which was generally very difficult to obtain. The key reaction is [2,3]-Wittig rearrangement, which has been known since long time ago. Recently the rearrangement on allyl-propargyl ether on dihydropyrane ring was studied to find unique mechanism, which will be also discussed as the general methodology for the synthesis of other natural products.



Retrosynthesis of Solanoeclepin A

Reference: (i) Isobe, M.; Chiang, C. T.; Tsao, K. W.; Cheng, C. Y.; Brüning, R., *Eur J. Org. Chem.* **2012**, *11*, 2109-2113. (ii) Tsao, K. W.; Cheng, C. Y.; Isobe, M. *Org. Lett.* **2012**, *14*, 5274-5277. (iii) Huang, K. H.; Isobe, M. *Eur. J. Org. Chem.* **2014**, *22*, 4733-4740. (iv) Chou, C. M.; Tung, Y. W.; Isobe, M. *BioOrg. Med. Chem.* **2014**, *22*, 4177-4188. (v) Chuang, H. Y.; Isobe, M. *Org. Lett.* **2014**, *16*, 4166-4169.

Minoru Isobe 磯部　稔 b. 1944 in Nagoya, Japan. PhD Nagoya U. 1973, Postdoc Columbia U. 1973-75, Assoc. Prof. Nagoya U. 1975-1991, Prof. Nagoya U. 1991-2008. Prof. Emeritus Nagoya U., Nat'l Tsing Hua U. (Taiwan) 2008-2014, Nat'l Sun Yat-Sen U. 2014-present. Natural products chemistry (Bioluminescence, Insect Diapause, Ultra micro analysis, Protein phosphatase inhibition, Total synthesis, Stereochemical control methods). IUPAC Org. Div. President 2004-07. Medal with Purple Ribbon 紫綬褒章 2008, Princess Chulabhorn Gold Medal 2011, NTHU President Award 2014.