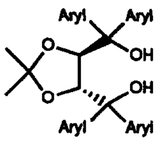
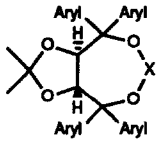
Tetrahedron, **1993**, *49*, 1711

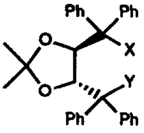
Derivatives of α,α,α',α'-Tetraaryl-2,2-dimethyl-1,3-dioxolan-4,5-dimethanol (TADDOL) Containing Nitrogen, Sulfur, and Phosphorus Atoms. New Ligands and Auxiliaries for Enantioselective Reactions.

Dieter Seebach, Michiya Hayakawa, Jun-ichi Sakaki, W. Bernd Schweizer
Laboratorium für Organische Chemie der Eidgenössischen Technishen Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland

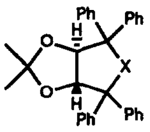
TADDOLs (1) were converted to the corresponding phosphites and phosphonites (2), cyclic sulfite (3), amino alcohols (4), diamine derivatives (5), thiocyanide (6), and cyclized compounds (7, 8).


1 (Aryl = Ph, 2-Naphth)


2, 3 (X = PR, SO)


4-6

4 (X = OH, Y=NR^{1}R^2)
5 (X = Y = NR^{1}R^2)
6 (X = Y = SCN)

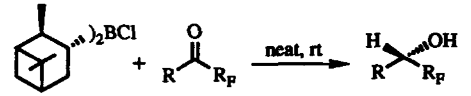

7, 8 (X = NH, S)

Tetrahedron, **1993**, *49*, 1725

CHIRAL SYNTHESIS *VIA* ORGANOBORANES. 38. SELECTIVE REDUCTIONS. 48. ASYMMETRIC REDUCTION OF TRIFLUOROMETHYL KETONES BY *B*-CHLORODIISOPINOCAMPHEYLBORANE IN HIGH ENANTIOMERIC PURITY

P. Veeraraghavan Ramachandran, Aleksandar V. Teodorovic', and Herbert C. Brown*
H. C. Brown and R. B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907

B-Chlorodiisopinocampheylborane (DIP-Chloride) reduces prochiral aryl and alkyl perfluoroalkyl ketones in very high ee. This reduction reveals an unexpected feature. The product alcohols have a configuration opposite to those obtained in the reduction of the corresponding hydrogen analogs. Consequently, the perfluoroalkyl group must control the stereochemistry of the reduction unlike the corresponding hydrocarbon groups.



(–)-DIP-Chloride, 1

78%-≥99% ee

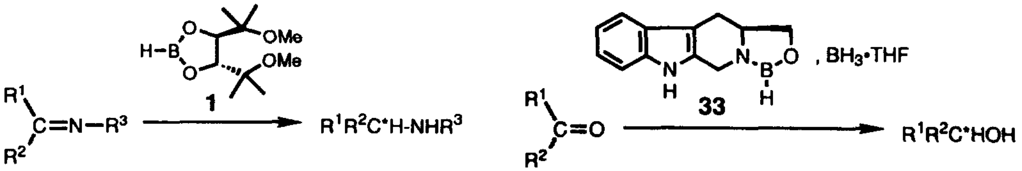
R = aryl or alkyl
$R_F = CF_3, C_2F_5, C_3F_7$

Tetrahedron, **1993**, *49*, 1739

ASYMMETRIC REDUCTIONS OF IMINES AND KETONES BY CHIRAL OXABOROLIDINES

Masako Nakagawa, Tomohiko Kawate, Taro Kakikawa, Hideki Yamada, Teruaki Matsui, and Tohru Hino
Faculty of Pharmaceutical Sciences, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba-shi, 263, Japan.

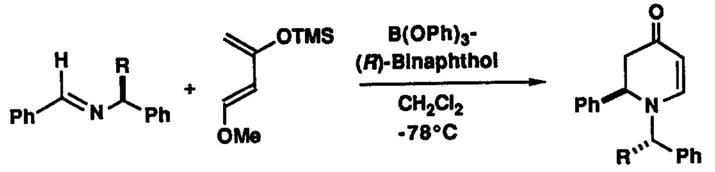
Asymmetric reduction of imines and ketones take place with moderate to high enantioselectivity by 1 and 33, respectively.



Tetrahedron, **1993**, *49*, 1749

Asymmetric Aza-Diels-Alder Reaction: Enantio- and Diastereoselective Reaction of Imine Mediated by Chiral Lewis Acid

Kouji Hattori and Hisashi Yamamoto*
Department of Applied Chemistry, Nagoya University, Chikusa, Nagoya 464-01, Japan

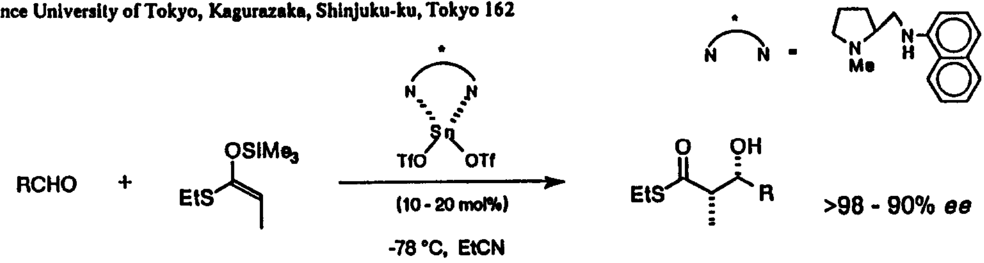


R=H
82% ee (75%)
R=Me
>98% de (61%)

Tetrahedron, **1993**, *49*, 1761

Catalytic Asymmetric Aldol-type Reaction Using a Chiral Tin(II) Lewis Acid

Shū KOBAYASHI, Hiromi UCHIRO, Isamu SHIINA, and Teruaki MUKAIYAMA
Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162



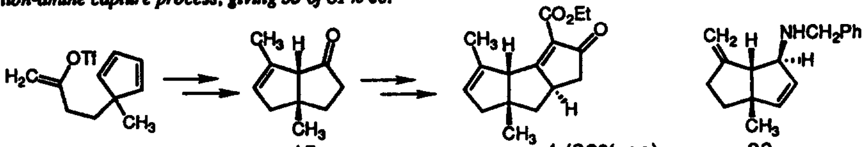
>98 - 90% *ee*

Tetrahedron, **1993**, *49*, 1773

Asymmetric Heck Reaction-Anion Capture Process. A Catalytic Asymmetric Synthesis of the Key Intermediates for the Capnellenols

Katsuji Kagechika,[a] Takashi Ohshima,[b] and Masakatsu Shibasaki[b]*
[a] Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan
[b] Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

A catalytic asymmetric synthesis of the key intermediates 4 and 15 for the capnellenols has been achieved through an asymmetric Heck reaction followed by the acetate anion capture process. The above reaction has been also applied to an asymmetric Heck reaction-amine capture process, giving 33 of 81% ee.

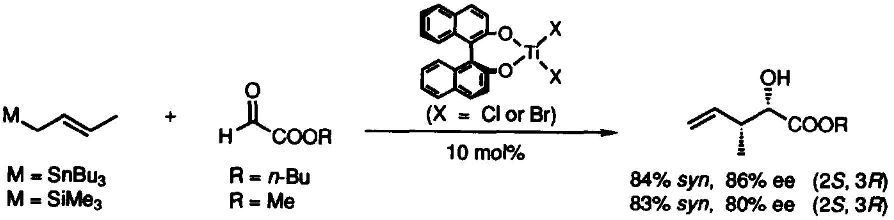


15
4 (80% ee)
33

Tetrahedron, **1993**, *49*, 1783

Enantio- and Diastereoselective Catalysis of Addition Reaction of Allylic Silanes and Stannanes to Glyoxylates by Binaphthol-derived Titanium Complex

Seiichi Aoki, Koichi Mikami*, Masahiro Terada, and Takeshi Nakai*
Department of Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

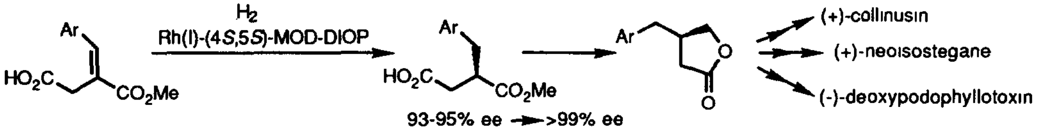


Tetrahedron, **1993**, *49*, 1793

EFFICIENT ASYMMETRIC SYNTHESES OF NATURALLY OCCURRING LIGNAN LACTONES USING CATALYTIC ASYMMETRIC HYDROGENATION AS A KEY REACTION

Toshiaki Morimoto, Mitsuo Chiba, and Kazuo Achiwa*
School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422, Japan

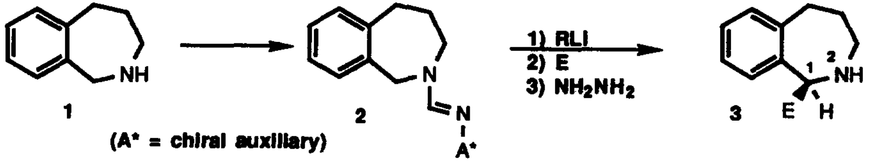
Asymmetric total syntheses of several naturally occurring lignan lactones were achieved *via* several steps from (*R*)-γ-butyrolactones obtained by using catalytic asymmetric hydrogenation as a key reaction.



Tetrahedron, **1993**, *49*, 1807

THE ASYMMETRIC SYNTHESIS OF 1-ALKYL-2,3,4,5-TETRAHYDROBENZAZEPINES AND BENZO[β]-1-AZABICYCLO[5,3,1]DECANES

A. I. Meyers* and Richard H. Hutchings
Department of Chemistry, Colorado State University, Fort Collins, CO 80523 USA

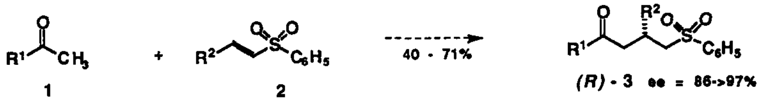


Tetrahedron, **1993**, *49*, 1821

ASYMMETRIC MICHAEL ADDITIONS VIA SAMP-/ RAMP - HYDRAZONES ENANTIOSELECTIVE SYNTHESIS OF 2-SUBSTITUTED 4-OXOSULFONES

Dieter Enders *, Kyriakos Papadopoulos and Eberhardt Herdtweck
Institut für Organische Chemie, RWTH Aachen, Professor-Pirlet-Str. 1, D-5100 Aachen, FRG

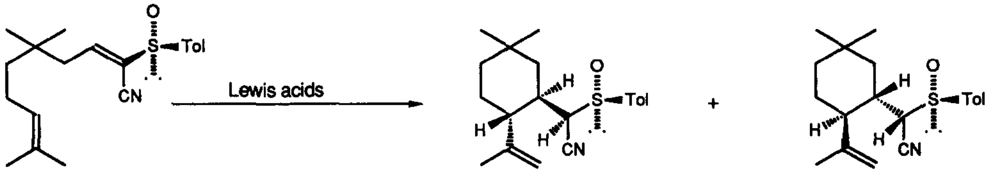
The enantioselective synthesis of 2-substituted 4-oxosulfones by asymmetric 1.4-addition of ketones to alkenyl sulfones is described



Tetrahedron, **1993**, *49*, 1831

THE LEWIS ACID-CATALYZED INTRAMOLECULAR ASYMMETRIC ENE REACTION USING A CHIRAL α-CYANOVINYLIC SULFOXIDE AS A ENOPHILE

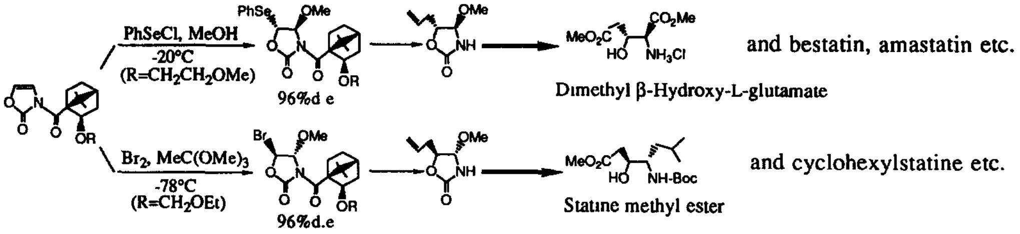
Kunio Hiroi* and Masayuki Umemura
Department of Synthetic Organic Chemistry, Tohoku College of Pharmacy, 4-4-1 Komatsushima, Aoba-ku, Sendai, Miyagi 981, Japan



Tetrahedron, **1993**, *49*, 1841

CHIRAL SYNTHONS FOR 2-AMINO ALCOHOLS. FACILE PREPARATION OF OPTICALLY ACTIVE AMINO HYDROXY ACIDS OF BIOLOGICAL INTEREST.

Tadao Ishizuka, Seigo Ishibuchi and Takehisa Kunieda*
Faculty of Pharmaceutical Sciences, Kumamoto University, Oe-honmachi, Kumamoto 862, Japan



Tetrahedron, **1993**, *49*, 1853

MATHEMATICAL TREATMENT OF KINETIC RESOLUTION OF CHIRALLY LABILE SUBSTRATES

Masato Kitamura, Makoto Tokunaga, and Ryoji Noyori
Department of Chemistry, Nagoya University, Chikusa, Nagoya 464-01, Japan

Quantitative analysis of the dynamic kinetic resolution having the simplest framework was done on the basis of mathematical treatment of the two rate equations. The selectivity profiles were graphically expressed with imaginary k_{inv}/k_R and k_R/k_S values.

$$\begin{tikzcd}
S_R \arrow[r, "k_R"] \arrow[d, shift right, "k_{inv}"'] & P_R \\
S_S \arrow[r, "k_S"] \arrow[u, shift right, "k_{inv}"'] & P_S
\end{tikzcd}$$

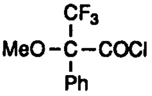
$$\begin{cases} -\dfrac{d[S_R]}{dt} = (k_R + k_{inv})[S_R] - k_{inv}[S_S] \\[2ex] -\dfrac{d[S_S]}{dt} = (k_S + k_{inv})[S_S] - k_{inv}[S_R] \end{cases}$$

Tetrahedron, **1993**, *49*, 1861

CHEMISTRY OF NOVEL COMPOUNDS WITH MULTIFUNCTIONAL CARBON STRUCTURE. 8 APPLICATION OF THE α-CYANO-α-FLUOROPHENYLACETIC ACID (CFPA) METHOD TO ENANTIOMERIC EXCESS DETERMINATION OF SOME HINDERED ALCOHOLS IN ASYMMETRIC AND NATURAL PRODUCT SYNTHESES

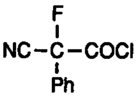
Yoshio Takeuchi,* Noriaki Itoh, Shun-ichi Kawahara and Toru Koizumi
Faculty of Pharmaceutical Sciences, Toyama Medical & Pharmaceutical University, Sugitani, Toyama 930-01, Japan

The much higher reactivity of CFPA chloride (**2b**) than the widely used MTPA chloride (**1b**) allows the CFPA method to induce potentially much less kinetic resolution during the course of condensation, even with hindered nucleophiles.



$$\mathrm{MeO{-}}\overset{\displaystyle CF_3}{\underset{\displaystyle Ph}{C}}\mathrm{{-}COCl}$$

1b (MTPA-Cl)



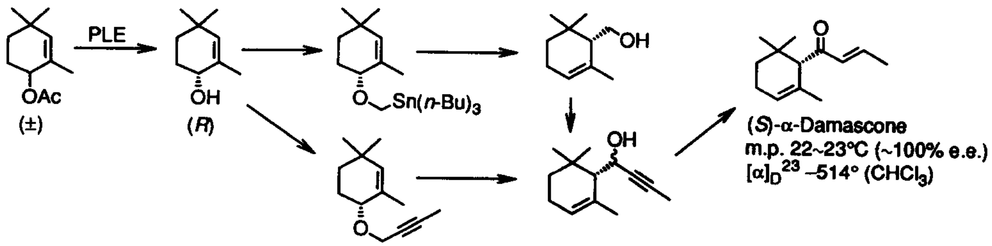
$$\mathrm{NC{-}}\overset{\displaystyle F}{\underset{\displaystyle Ph}{C}}\mathrm{{-}COCl}$$

2b (CFPA-Cl)

Tetrahedron, **1993**, *49*, 1871

SYNTHESIS OF (*S*)-α-DAMASCONE

Kenji Mori,* Masayasu Amaike and Masamichi Itou
Department of Agricultural Chemistry, The University of Tokyo,
Yayoi 1-1-1, Bunkyo-ku, Tokyo 113, Japan.



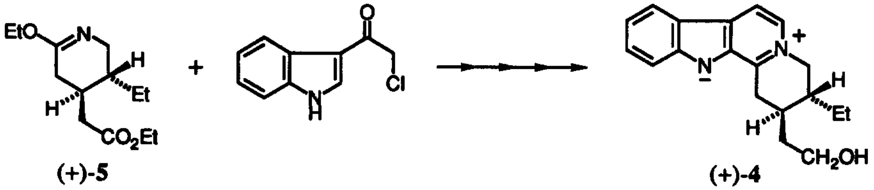
(*S*)-α-Damascone
m.p. 22~23°C (~100% e.e.)
$[\alpha]_D^{23}$ −514° ($CHCl_3$)

Tetrahedron, **1993**, *49*, 1879

QUINOLIZIDINES. XXXII. A CHIRAL SYNTHESIS OF 3,4,5,6-TETRADEHYDRO-17-HYDROXYCORYNANIUM, THE ZWITTERIONIC STRUCTURE ASSIGNED TO AN ALKALOID FROM *ASPIDOSPERMA MARCGRAVIANUM*

Tozo Fujii,* Masashi Ohba, and Takako Ohashi
Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan

The zwitterionic structure (+)-4 has been synthesized from the lactim ether (+)-5 and 3-chloroacetylindole through an 8-step route.

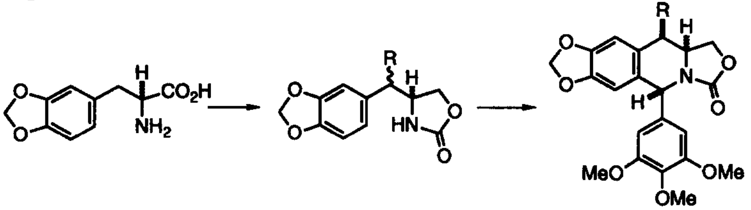


(+)-5 (+)-4

Tetrahedron, **1993**, *49*, 1891

DESIGN, SYNTHESIS, AND ANTITUMOR ACTIVITY-ABSOLUTE CONFIGURATION RELATIONSHIPS OF PODOPHYLLOTOXIN AZA-ANALOGUES

K. Tomioka,* Y. Kubota, and K. Koga*, Faculty of Pharmaceutical Sciences, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

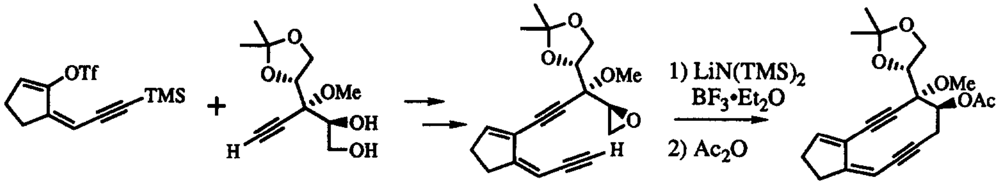


Tetrahedron, **1993**, *49*, 1901

SYNTHETIC STUDIES ON THE COMPOUNDS RELATED TO NEOCARZINOSTATIN CHROMOPHORE. 3.
NOVEL SYNTHESIS OF A CHIRAL CYCLIC DIENEDIYNE SYSTEM

Kazuhiko Nakatani, Katsuko Arai, and Shiro Terashima*
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan

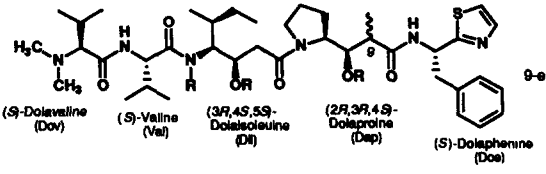
The chiral cyclic dienediynes were synthesized by employing a novel (Z)-dienediyne system construction - cyclization sequence.



Tetrahedron, **1993**, *49*, 1913

Stereoselective Synthesis of Dolastatin 10 and Its Congeners

Takayuki Shioiri,* Kyoko Hayashi, and Yasumasa Hamada*
Faculty of Pharmaceutical Sciences, Nagoya City University
Tanabe-dori, Mizuho-ku, Nagoya 467, JAPAN



dolastatin 10 (1) R=CH_3, C_9-β-CH_3
trisnordolastatin 10 (2) R=H, C_9-β-CH_3
9-epi-trisnordolastatin 10 (3) R=H, C_9-α-CH_3