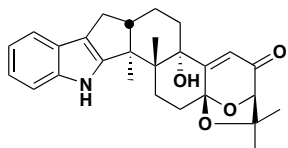
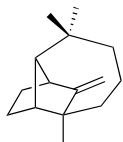


Wednesday, January 14, 2004

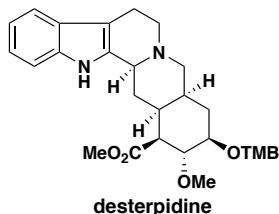
Syntheses discussed:



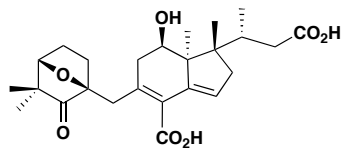
(+)-Paspalinine



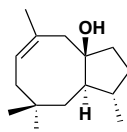
(+)-longifolene



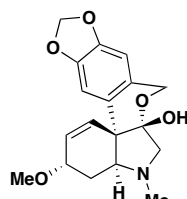
desterpidine



glycinoclepin



(±)-dactylof



tazettine

Partial list of transforms discussed:

Gassman indole synthesis

Moffatt Oxidation

RhCl₃ olefin isomerization (Grieco)

Wenkert Cyclization

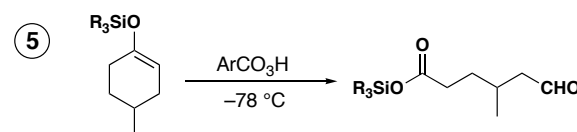
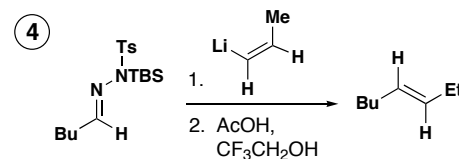
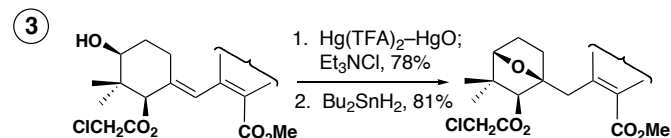
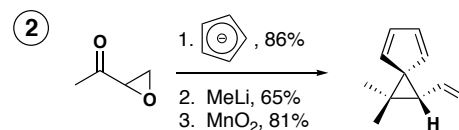
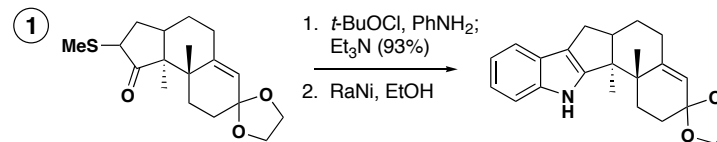
Saegusa-Ito oxidation

Luche Reduction

Myers Olefin Synthesis

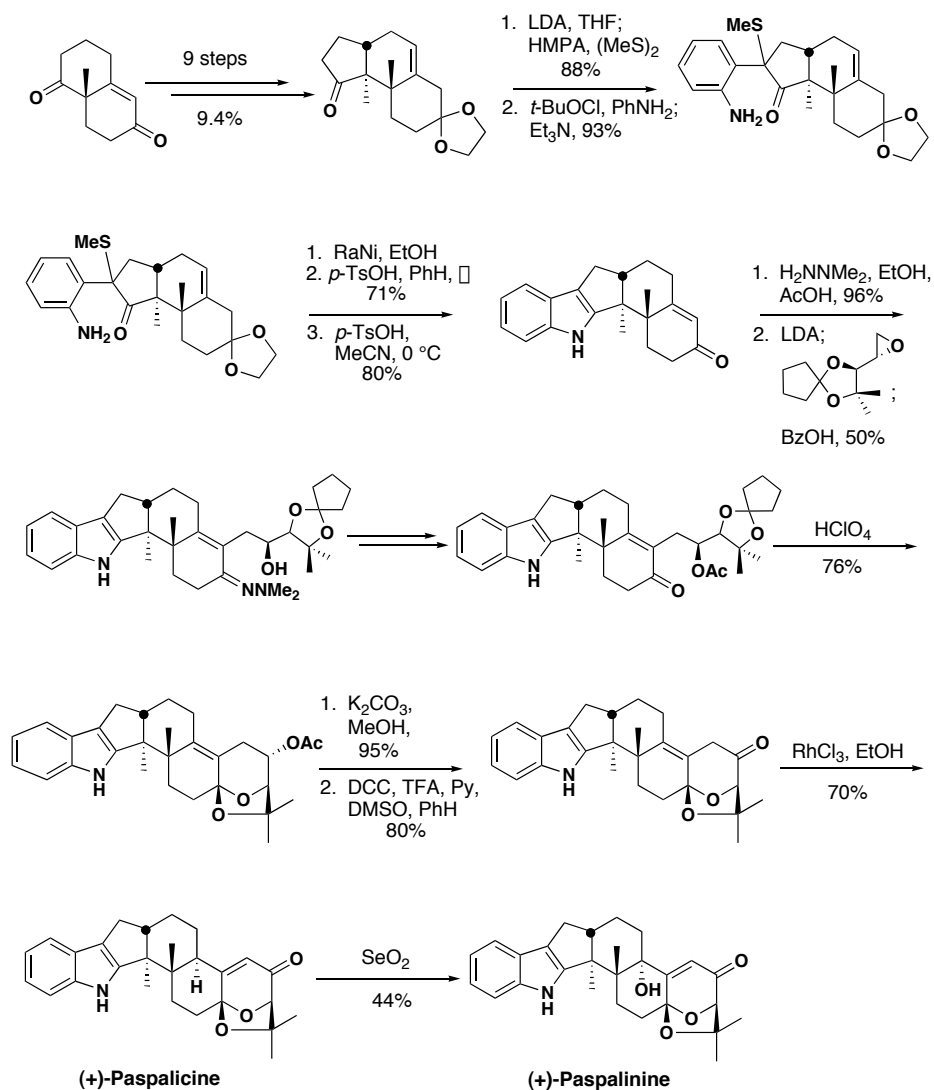
Sharpless Allylic Amination

Problems of the day:



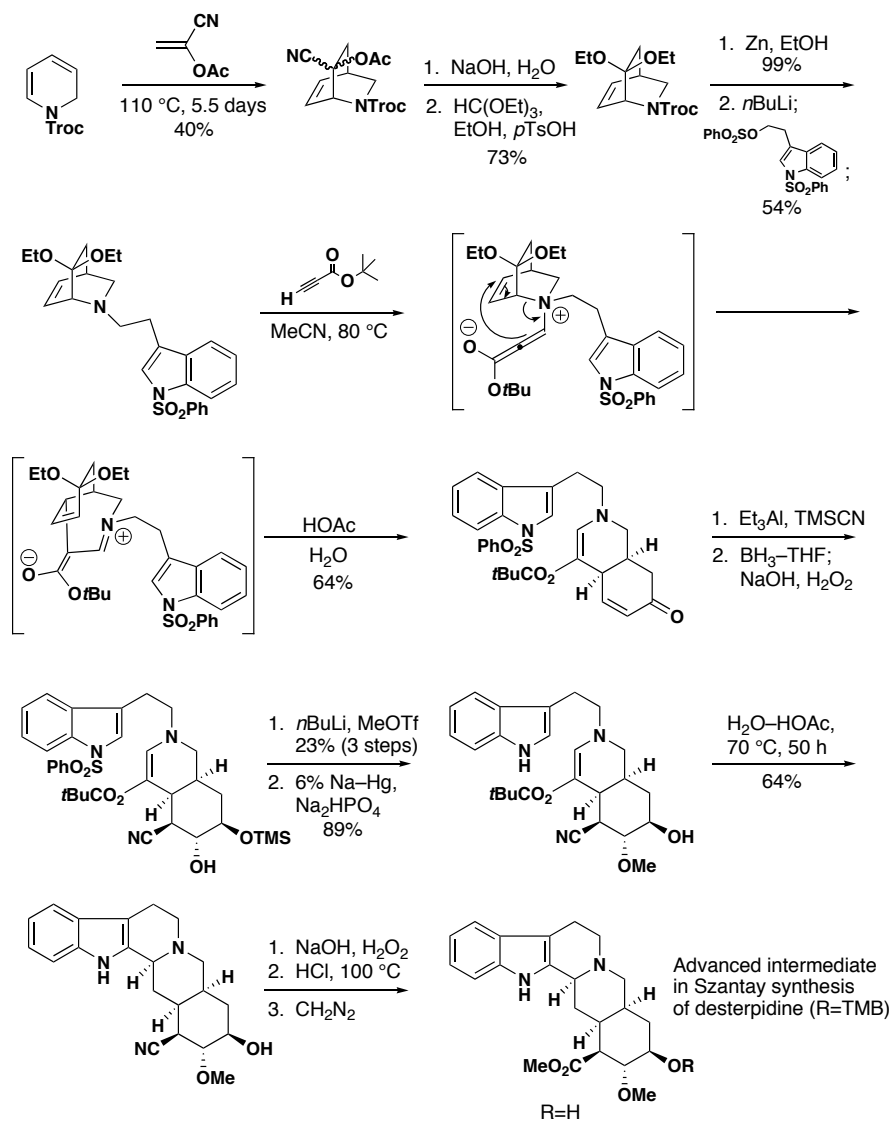
Total syntheses of (+)-paspalicine and (+)-paspalinine

Amos B. Smith III, Toshiaki Sunazuka, Tamara L. Leenay, Jill Kingery-Wood;
J. Am. Chem. Soc. **1990**, *112*, 8197-8198.

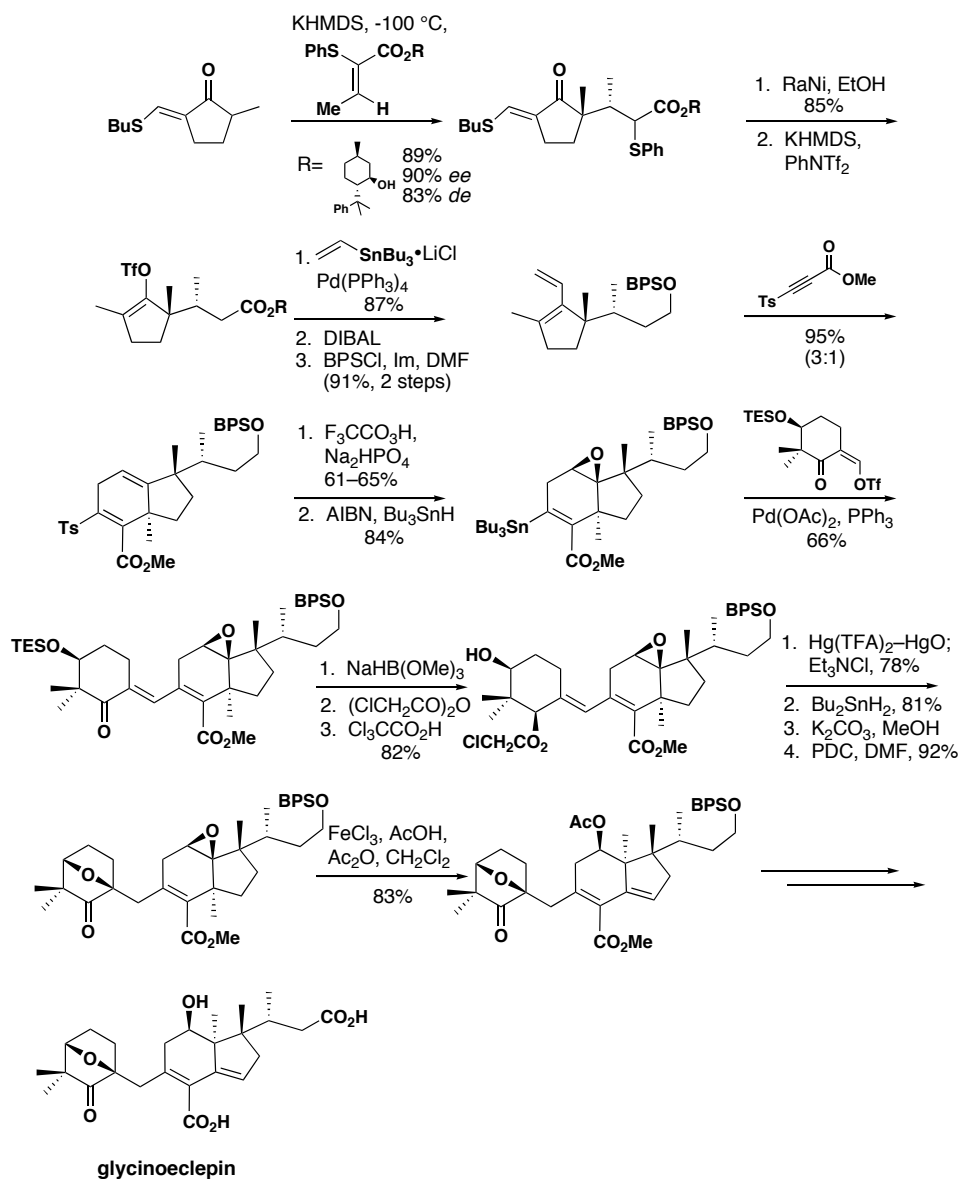


Formal total synthesis of deserpidine . . .

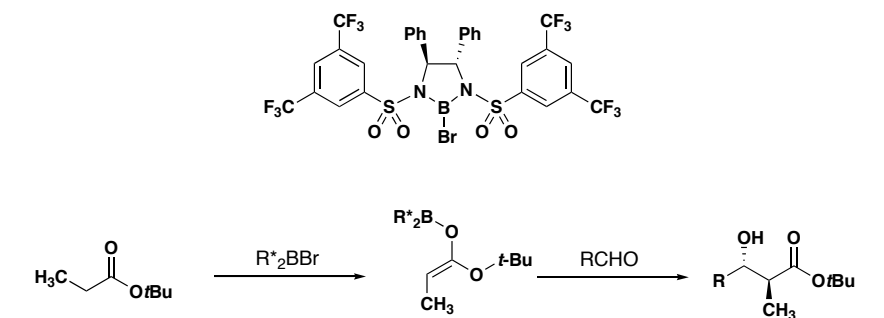
Ellen W. Baxter, David Labaree, Herman L. Ammon, Patrick S. Mariano;
J. Am. Chem. Soc. **1990**, *112*, 7682-7692.



Total synthesis of glycinoeclepin A, E. J. Corey, Ioannis N. Houpis;
J. Am. Chem. Soc. **1990** *112*, 8997-8998.

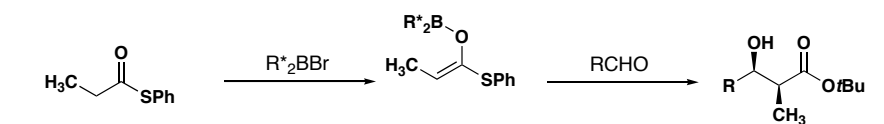


Versatile Catalyst for the Highly Enantioselective Synthesis of Either Anti or Syn Ester Aldols, E. J. Corey, Sung Soo Kim; *J. Am. Chem. Soc.* **1990** *112*, 4976-4977.



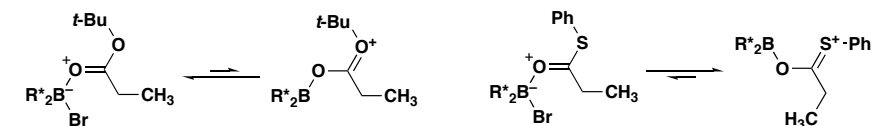
Reaction of Aldehydes with Propionate Esters Promoted by Bromoborane Catalyst and Triethylamine To Form Anti Aldols

R	propionate ester	solvent	% yield	anti:syn	% ee
C_6H_5	<i>t</i> -Bu	1:2 toluene-hexane	93	98:2	94
C_6H_5	<i>t</i> -Bu	CH_2Cl_2	90	96:4	89
$(E)\text{-C}_6\text{H}_5\text{CH=CH}$	<i>t</i> -Bu	1:2 toluene-hexane	81	99:1	98
$(E)\text{-C}_6\text{H}_5\text{CH=CH}$	<i>t</i> -Bu	CH_2Cl_2	91	96:4	97
cyclohexyl	<i>t</i> -Bu	1:2 toluene-hexane	82	94:6	75
cyclohexyl	(+)-menthyl	1:2 toluene-hexane	91	99:1	87
cyclohexyl	(+)-menthyl	CH_2Cl_2	86	98:2	94
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$	(+)-menthyl	1:2 toluene-hexane	83	99:1	95
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$	(+)-menthyl	CH_2Cl_2	80	97:3	96



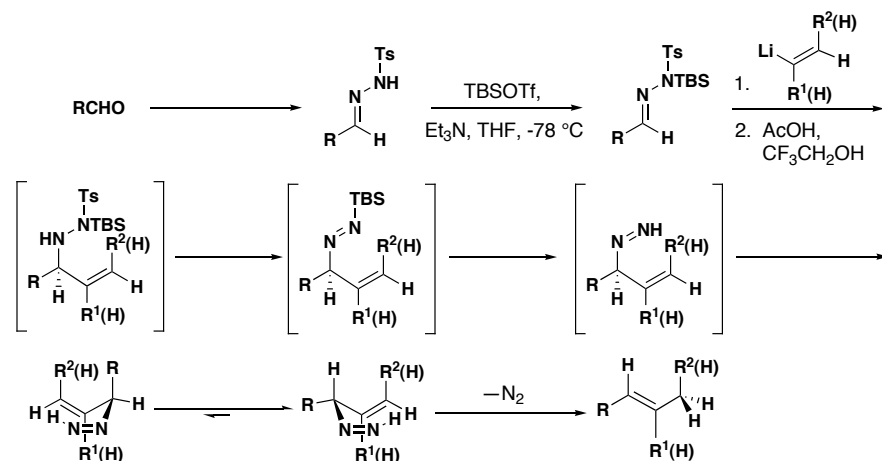
Reaction of Aldehydes with Thio Esters Promoted by Bromoborane Catalyst and DPEA To Form Syn Aldols

R	thioester	solvent	% yield	anti:syn	% ee
C_6H_5	Ph	CH_2Cl_2	93	1:99	97
C_6H_{11}	Ph	CH_2Cl_2	86	1:98	91



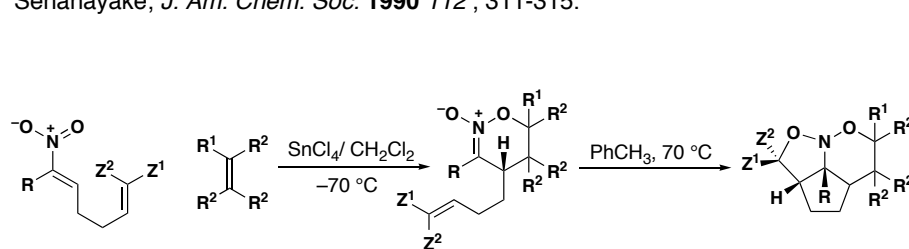
Differences in enolate geometry rationalized by competing rates of assisted bromide dissociation and deprotonation

Stereoselective Synthesis of Olefins from Silylated Sulfonylhydrazones,
Andrew G. Myers and Paivi J. Kukkola; *J. Am. Chem. Soc.* **1990** *112*, 8208-8210.



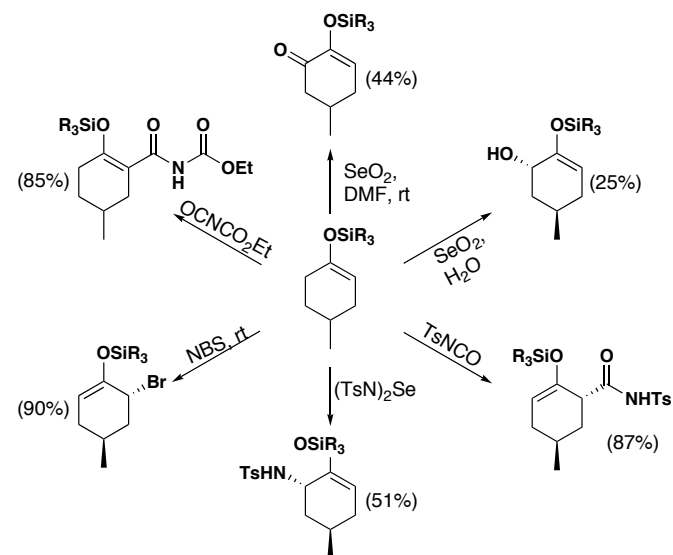
aldehyde	organolithium reagent	%yield (stereoselectivity)
		77 (>20:1)
		90 (2:1)
-		83 (>20:1)
		86 (>20:1)
-		79 (1:1)
-		81 (>20:1)

Tandem [4 + 2]/[3 + 2] Cycloadditions: Facile and Stereoselective Construction of Polycyclic Frameworks, Scott E. Denmark, Young-Choon Moon, C. B. W. Senanayake; *J. Am. Chem. Soc.* **1990** *112*, 311-315.



R	Z ¹	Z ²	R ¹	R ²	t ₁ , h	t ₂ , h	ds	yield, %
H	CO ₂ Me	H	Me	Me	7	0	>100:1	68
Me	CO ₂ Me	H	Me	Me	7	0	>100:1	72
H	H	CO ₂ Me	Me	Me	8	2.5	6:1:1:8	76
Me	H	CO ₂ Me	Me	Me	8	3	20:1	78
Me	CO ₂ Me	H	<i>n</i> -OBu	H	1	0	>100:1	80

New Trialkylsilyl Enol Ether Chemistry. Regiospecific and Stereospecific Sequential Electrophilic Addition, Philip Magnus and Benjamin Murgage; *J. Am. Chem. Soc.* **1990** *112*, 462-464.



Total syntheses of (+)-paspalinine and (+)-paspalinine, Amos B. Smith III, Toshiaki Sunazuka, Tamara L. Leenay, Jill Kingery-Wood; 8197-8198.

Total syntheses of (-)-histrionicotoxin and (-)-histrionicotoxin 235A, Gilbert Stork, Kang Zhao; 5875-5876.

General approach to the synthesis of macroline-related alkaloids. Stereospecific total synthesis of (-)-alstonerine, L. H. Zhang, J. M. Cook; 4088-4090.

Facile reduction of ethyl thiol esters to aldehydes: application to a total synthesis of (+)-neothramycin A methyl ether, Tohru Fukuyama, Shao Cheng Lin, Leping Li; 7050-7051.

Direct total synthesis of (+)-longifolene via an intramolecular Diels-Alder strategy, Lei Bo, Alex G. Fallis; 4609-4610.

Total synthesis of (+)-saframycin A, Tohru Fukuyama, Lihu Yang, Karen L. Ajeck, Richard A. Sachleben; 3712-3713.

Total synthesis of ionophores. 6. Asymmetric induction in the permanganate-promoted oxidative cyclization of 1,5-dienes, David M. Walba, Claire A. Przybyla, Christopher B. Walker Jr.; 5624-5625.

Total synthesis of glycinoeclepin A, E. J. Corey, Ioannis N. Houpis; 8997-8998.

Total synthesis of (+)-latrunculin A, James D. White, Motoji Kawasaki; 4991-4993.

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Enantioselective total synthesis of neoxazolomycin, Andrew S. Kende, Kuniaki Kawamura, Robert J. DeVita; 4070-4072.

The total synthesis of dl-indolizomycin, Guncheol Kim, Margaret Y. Chu-Moyer, Samuel J. Danishefsky; 2003-2005.

Stereocontrolled total synthesis of (-)-anisatin: a neurotoxic sesquiterpenoid possessing a novel spiro. beta.-lactone, Haruki Niwa, Masanori Nisiwaki, Itaru Tsukada, Takeshi Ishigaki, Shigeki Ito, Kazumasa Wakamatsu, Tatsuya Mori, Megumi Ikagawa, Kiyoyuki Yamada; 9001-9003.

Total synthesis of calicheamicinone: a solution to the problem of the elusive urethane, Maria Paz Cabal, Robert S. Coleman, Samuel J. Danishefsky; 3253-3255.

Total synthesis of (+)-breynolide, David R. Williams, Paul A. Jass, H. L. Allan Tse, Ricky D. Gaston; 4552-4554.

Asymmetric tandem Claisen-ene strategy for steroid total synthesis: an efficient access to (+)-9(11)-dehydroestrone methyl ether, Koichi Mikami, Kazuhiko Takahashi, Takeshi Nakai; 4035-4037.

A total synthesis of racemic paulownin using a type II photocyclization reaction, George A. Kraus, Li Chen; 3464-3466.

Total synthesis of (+)-verrucosidin, Konghyun Whang, R. J. Cooke, Gurol Okay, Jin K. Cha; 8985-8987.

Enantioselective total synthesis of a protosterol, 3.beta.,20-dihydroxyprotost-24-ene, E. J. Corey, Scott C. Virgil; 6429-6431.

Total synthesis of (+)-dactylole and related studies, Ken S. Feldman, Ming Jung Wu, David P. Rotella; 8490-8496.

Construction of quaternary carbon centers by palladium-catalyzed intramolecular alkene insertions. Total synthesis of the Amaryllidaceae alkaloids (+)-tazettine and (+)-6a-epipretazettine, Matthew M. Abelman, Larry E. Overman, Vinh D. Tran; 6959-6964.

The total synthesis of (+)-epi-jatrophone and (+)-jatrophone using palladium-catalyzed carbonylative coupling of vinyl triflates with vinyl stannanes as the macrocycle-forming step, Albert C. Gyorkos, John K. Stille, Louis S. Hegeudus; 8465-8472.

Stereoselective total syntheses of the antitumor antibiotics (+)-actinobolin and (-)-bactobolin from a common bridged lactone intermediate, Ravi S. Garigipati, David M. Tschaen, Steven M. Weinreb; 3475-3482.

Total synthesis of (+)-isobolophytolide and (+)-crassin by titanium-induced carbonyl coupling, John E. McMurry, Russell G. Dushin; 6942-6949.

The total syntheses of dl-zygosporin E and dl-C18-desmethylcytochalasin D, Edwin Vedejs, S. J. Wittenberger; 4357-4364.

Total syntheses of (+)- and (-)-didemnonenes A and B. Anti selectivity in the intramolecular carbomercuration reaction, Craig J. Forsyth, Jon Clardy; 3497-3505.

Asymmetric total synthesis of atisine via intramolecular double Michael reaction, Masataka Ihara, Makoto Suzuki, Keiichiro Fukumoto, Chizuko Kabuto; 1164-1171.

Sequential radical cyclization approach to propellane triquinanes. Total synthesis of (+)-modhephene, Craig P. Jasperse, Dennis P. Curran; 5601-5609.

Formal total synthesis of deserpidine demonstrating a versatile amino-Claisen rearrangement/ Wenkert cyclization strategy for the preparation of functionalized yohimbane ring systems, Ellen W. Baxter, David Labaree, Herman L. Ammon, Patrick S. Mariano; J. Am. Chem. Soc.; 7682-7692.

Total synthesis of both (+)-compactin and (+)-mevinolin. A general strategy based on the use of a special titanium reagent for dicarbonyl coupling, Derrick L. J. Clive, K. S. Keshava Murthy, Andrew G. H. Wee, J. Siva Prasad, Gil V. J. Da Silva, Marek Majewski, Paul C. Anderson, Claire F. Evans, Richard D. Haugen, et al.; 3018-3028.

Asymmetric, stereocontrolled total synthesis of (-)-brevianamide B, Robert M. Williams, Tomasz Glinka, Ewa Kwast, Hazel Coffman, James K. Stille; 808-821.

Total syntheses of (-)-nocardicins A-G: a biogenetic approach, Gino M. Salituro, Craig A. Townsend; 760-770.

Asymmetric total synthesis of dibenzocyclooctadiene lignans (-)-schizandrin and (-)-isoschizandrin. Structure revision of (+)-isoschizandrin, Alan M. Warshawsky, A. I. Meyers; 8090-8099.

Studies on Gelsemium alkaloids. Total synthesis of (+)-koumine, (+)-taberpsychine, and (+)-koumidine, Philip Magnus, Benjamin Mugrage, Mark R. DeLuca, Gary A. Cain; 5220-5230.

Synthetic aspects of an asymmetric nitrogen-insertion process: preparation of chiral, non-racemic caprolactams and valerolactams. Total synthesis of (-)-alloyohimbane, Jeffrey Aube, Yuguang Wang, Marlys Hammond, Mehmet Tanol, Fusao Takusagawa, David Vander Velde; 4879-4891.

Total synthesis and structural investigations of didemnins A, B, and C, Wen Ren Li, William R. Ewing, Bruce D. Harris, Madeleine M. Joulie; 7659-7672.

The total synthesis of (+)-ionomycin, Stephen Hanessian, Nigel G. Cooke, Brad DeHoff, Yoji Sakito; 5276-5290.

Chemistry of tricarbonyl hemiketals and application of Evans technology to the total synthesis of the immunosuppressant (-)-FK-506, Todd K. Jones, Robert A. Reamer, Richard Desmond, Sander G. Mills; 2998-3017.

Total synthesis of FK506 and an FKBP probe reagent, [C(8),C(9)-13C2]-FK506, Masashi Nakatsuka, John A. Ragan, Tarek Sammakia, David B. Smith, David E. Uehling, Stuart L. Schreiber; 5583-5601.

Total synthesis of the polyether antibiotic ionomycin, David A. Evans, Robert L. Dow, Thomas L. Shih, James M. Takacs, Robert Zahler; 5290-5313.

Total synthesis of the macrolide antibiotic cytovaricin, David A. Evans, Stephen W. Kaldor, Todd K. Jones, Jon Clardy, Thomas J. Stout; 7001-7031.

Synthesis of (+)-marasmic acid via 1-oxaspirohexane rearrangement, Yoshito Tobe, Dai Yamashita, Tohru Takahashi, Masashi Inata, Junichi Sato, Kiyomi Kakiuchi, Kazuya Kobiro, Yoshinobu Odaira; 775 - 779.

Enantiocontrolled synthesis of quaternary carbon centers via anionic oxy-Cope rearrangement: an efficient synthesis of (+)-dihydromayurone, Eun Lee, In Jae Shin, Tae Seong Kim; 260 - 264.

Template-directed synthesis of (+)-allosamizoline and its 3,4-epimers, Barry M. Trost, David L. Van Vranken; 1261 - 1263.

Synthesis of the Antitumor Bisindole Alkaloid Vinblastine: Diastereoselectivity and Solvent Effect on the Stereochemistry of the Crucial C-15—C-18' Bond, Philip Magnus, Andrew Stamford, Mark Ladlow; 260 - 264.