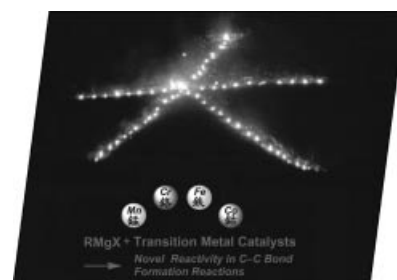


## COVER PICTURE

The cover picture shows a concept that the combination of a Grignard reagent (RMgX) with various transition metal catalysts opens up an opportunity to explore new reactions for carbon–carbon bond formation. Grignard reagents are the most classical organometallics and useful compounds in organic synthesis. The addition of transition metal salts to this classic reagent gives novel reaction patterns such as carbometallation, rearrangement, electron transfer, cross-coupling, and so forth. Manganese-, chromium-, iron-, and cobalt-catalyzed carbon–carbon bond formation reactions with Grignard reagents are discussed in the Microreview by H. Shinokubo and K. Oshima on p. 2081 ff.



## MICROREVIEWS

### Contents

### 2081 H. Shinokubo,\* K. Oshima\*

Transition Metal-Catalyzed Carbon–Carbon  
 Bond Formation with Grignard Reagents –  
 Novel Reactions with a Classic Reagent

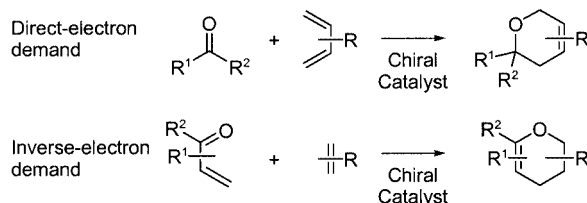
**Keywords:** Chromium / Cobalt / Grignard reagent /  
 Iron / Manganese

RMgX  $\longrightarrow$  C–C Bond Formation  
*Mn, Cr, Fe, Co catalysts*

2093 K. A. Jørgensen

Hetero-Diels–Alder Reactions of Ketones — A Challenge for Chemists

**Keywords:** Asymmetric catalysis / Cycloaddition / Ketones / Alkenes / Synthesis design

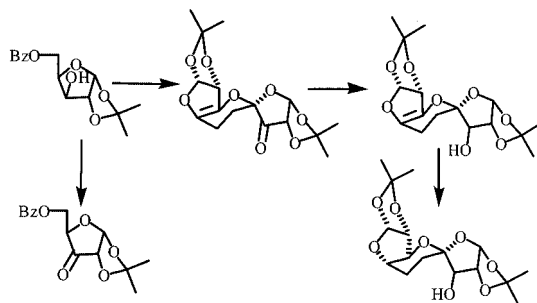


## SHORT COMMUNICATION

2103 H.-M. Liu,\* D.-P. Zou, F. Zhang,  
W.-G. Zhu, T. Peng

Stereoselective Synthesis of New Higher Carbon Sugars from D-Xylose

**Keywords:** Carbohydrates / Cycloaddition / Hetero-Diels–Alder reaction / Higher carbon sugars

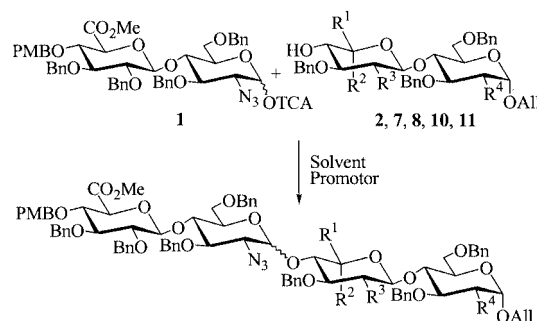


## FULL PAPERS

2107 R. Lucas, D. Hamza, A. Lubineau,  
D. Bonnaffé\*

Synthesis of Glycosaminoglycan Oligosaccharides — An Unexpected Inhibitory Effect of a Remote *N*-Acetyl Group upon Trichloroacetimidate-Mediated Couplings

**Keywords:** Oligosaccharides / Combinatorial chemistry / Glycosylation

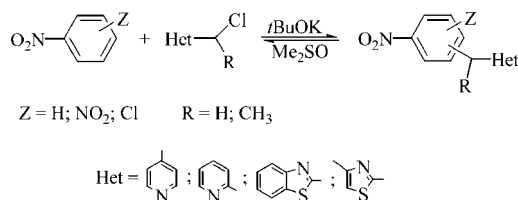


$R^4 = \text{NHAc}$ : no tetrasaccharide isolated.  
 $R^4 = \text{N}_3$ : depending on the solvent and the promoter, the tetrasaccharides were isolated in yields up to 90%, with  $\alpha/\beta$  diastereoselectivities up to 92:8.

2118 S. Florio,\* P. Lorusso, R. Luisi, C. Granito,  
L. Ronzini, L. Troisi\*

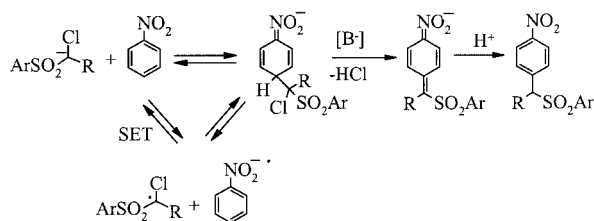
Vicarious Nucleophilic Substitution of (Chloroalkyl)heterocycles with Nitroarenes

**Keywords:** Heterocycles / Vicarious nucleophilic substitution / Arenes / Regioselective synthesis



2125 M. Małosza,\* A. Kwast

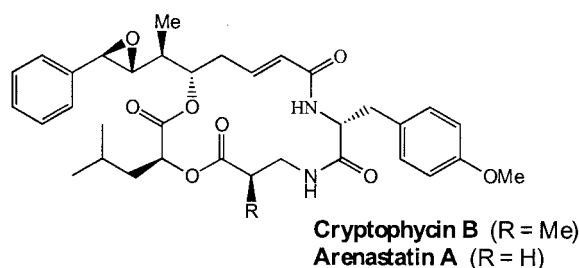
Direct Nucleophilic Addition versus a Single-Electron Transfer Pathway of  $\sigma^H$  Adduct Formation in Vicarious Nucleophilic Substitution of Hydrogen



**Keywords:** Carbanions / Nucleophilic addition / Nucleophilic substitution / Electron transfer

2131 A. K. Ghosh,\* A. Bischoff

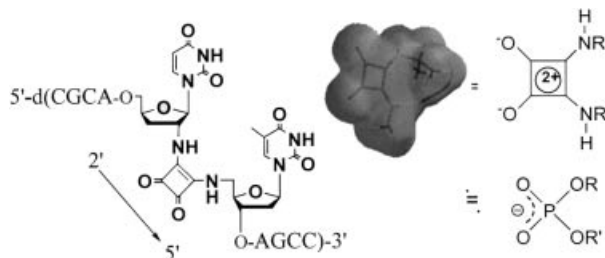
Asymmetric Syntheses of Potent Antitumor Macrolides Cryptophycin B and Arenastatin A



**Keywords:** Natural products / Cryptophycins / Arenastatin A / Asymmetric synthesis / Aldols

2142 K. Sato, R. Tawarada, K. Seio, M. Sekine\*

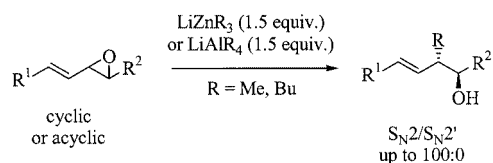
Synthesis and Structural Properties of New Oligodeoxynucleotide Analogues Containing a 2',5'-Internucleotidic Squaryldiamide Linkage Capable of Formation of a Watson–Crick Base Pair with Adenine and a Wobble Base Pair with Guanine at the 3'-Downstream Junction Site



**Keywords:** Hybridization / Hydrogen bonds / Phosphate mimic / Squaric acid / Watson–Crick base pair / Wobble base pair

2151 O. Equey, E. Vrancken, A. Alexakis\*

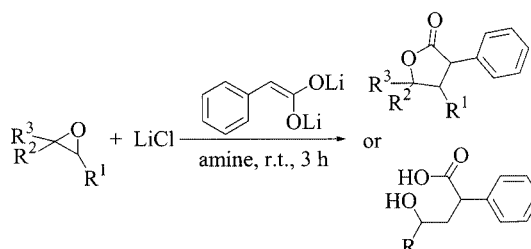
Regioselective  $S_N2$  Opening of Vinylic Epoxides with Trialkylzincates and Trialkylaluminates



**Keywords:** Aluminum / Nucleophilic substitution / Regioselectivity / Vinylic epoxides / Zinc

2160 S. Gil, M. Torres, N. Ortúzar, R. Wincewicz, M. Parra\*

Efficient Addition of Acid Enediolates to Epoxides

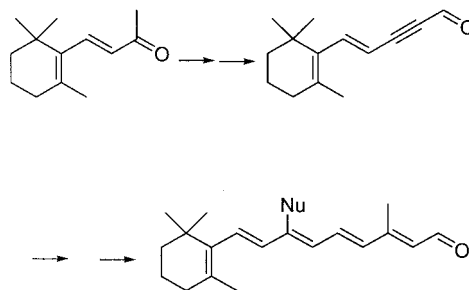


**Keywords:** Lactones / Lithium chloride / Nucleophilic addition / Regioselectivity / Diastereoselectivity

**2166** Y. Wang, W. S. Woo, I. van der Hoef,  
J. Lugtenburg\*

9-Demethyl-9-haloretinals by Wadsworth–Emmons Coupling – Easy Preparation of Pure (*all-E*), (*9Z*) and (*11Z*) Isomers

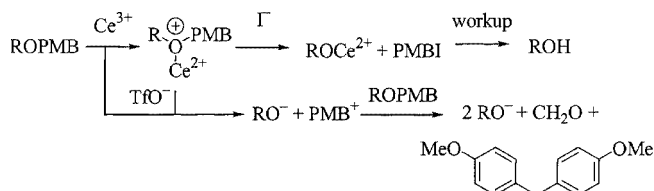
**Keywords:** Diphenyl phosphonate reagents / Visual analogues / Stereo isomeric synthesis / Synthetic methods / Isomers



**2176** G. Bartoli, R. Dalpozzo, A. De Nino,\*  
L. Maiuolo, M. Nardi, A. Procopio,  
A. Tagarelli

Cerium(III) Triflate versus Cerium(III) Chloride: Anion Dependence of Lewis Acid Behavior in the Deprotection of PMB Ethers

**Keywords:** Cerium / Triflate / *p*-Methoxybenzyl ethers / Deprotection / Lewis acids

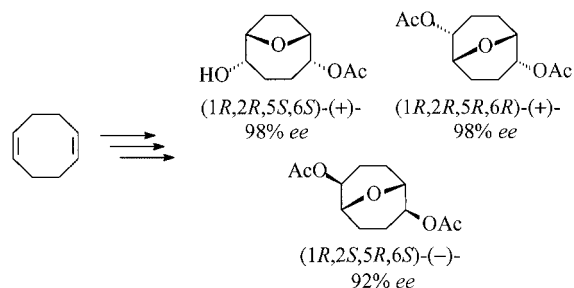


**2181** K. Hegemann, R. Fröhlich, G. Haufe\*



Synthesis of Enantiopure 9-Oxabicyclononane-diol Derivatives by Lipase-Catalyzed Transformations and Determination of Their Absolute Configuration

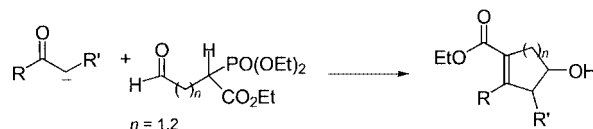
**Keywords:** Alcohols / Chiral resolution / Diols / Enantioselectivity / Lipases / Polycycles



**2193** G. A. Kraus,\* P. K. Choudhury

Phosphonate Aldehyde Annulation – A One-Pot Synthesis of Hydroxycycloalkenoic Esters – Application to Analogs of Glycinoeclepin A

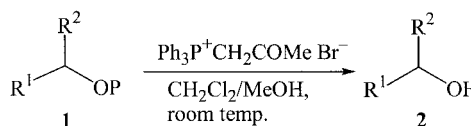
**Keywords:** Anions / Annulation / Synthetic methods



**2198** A. T. Khan,\* S. Ghosh, L. H. Choudhury

A Simple and Useful Synthetic Protocol for Selective Deprotection of *tert*-Butyldimethylsilyl (TBS) Ethers

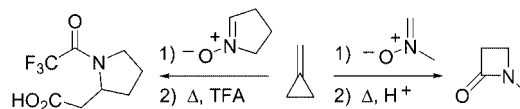
**Keywords:** Deprotection / Ethers / Protecting groups / Synthesis design



**2205** F. M. Cordero,\* M. Salvati, F. Pisaneschi,  
A. Brandi\*

Novel Prospects of the Acidic Thermal Rearrangement of Spiro[cyclopropane-1,5'-isoxazolines] to  $\beta$ -Lactams

**Keywords:**  $\beta$ -Lactams /  $\beta$ -Homoproline / Cycloaddition / Small ring systems / Spiro compounds

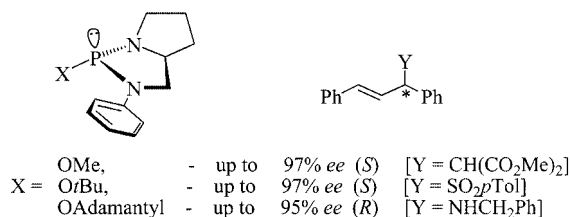


**2214** V. N. Tsarev,\* S. E. Lyubimov,  
A. A. Shiryaev, S. V. Zheglov,  
O. G. Bondarev, V. A. Davankov,  
A. A. Kabro, S. K. Moiseev,  
V. N. Kalinin, K. N. Gavrilov



*P*-Chiral Monodentate Diamidophosphites – New and Efficient Ligands for Palladium-Catalysed Asymmetric Allylic Substitution

**Keywords:** Allylic substitution / Asymmetric catalysis / P ligands / Palladium / Rhodium

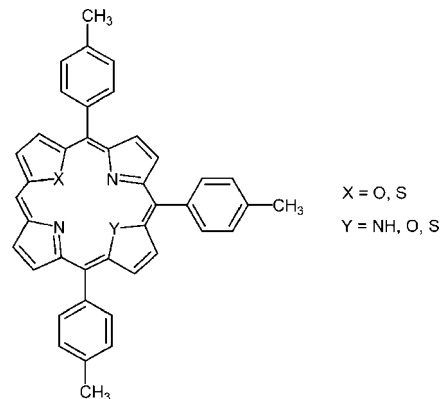


**2223** S. Punidha, N. Agarwal, R. Burai,  
M. Ravikanth\*



Synthesis of  $N_3S$ ,  $N_3O$ ,  $N_2S_2$ ,  $N_2O_2$ ,  $N_2SO$  and  $N_2OS$  Porphyrins with One *meso*-Unsubstituted Carbon

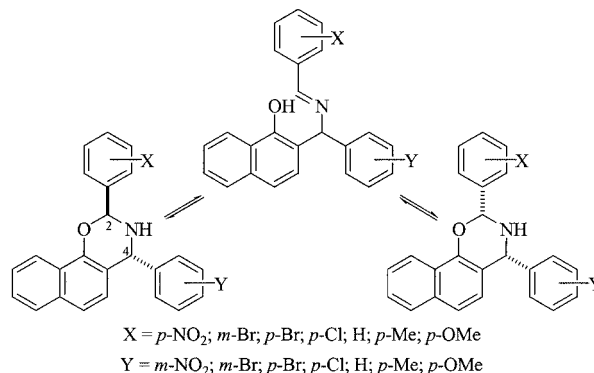
**Keywords:** Porphyrins / Heck reaction / Synthetic methods / Thiophenes / Furan diols



**2231** I. Szatmári, T. A. Martinek, L. Lázár,  
F. Fülöp\*

Synthesis of 2,4-Diaryl-3,4-dihydro-2*H*-naphth-[2,1-*e*][1,3]oxazines and Study of the Effects of the Substituents on Their Ring-Chain Tautomerism

**Keywords:** Amino alcohols / Mannich bases / Heterocycles / Tautomerism / Substituent effects

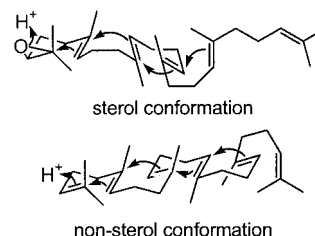


2239 B. A. Hess, Jr.



Formation of the B Ring in Steroids and Hopanoids from Squalene

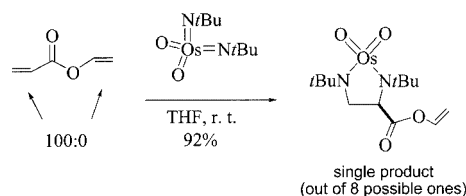
**Keywords:** Density functional calculations / Steroids / Conformational analysis / Terpenoids / Reaction mechanisms



2243 K. Muñiz

Electronic Effects in Olefin Oxidation by Imido-osmium(VIII) Compounds

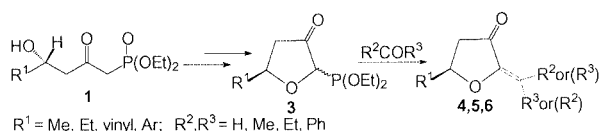
**Keywords:** Osmium / Oxidations / Imido compounds / Diamination / Heterocycles



2253 C. Xu, Y. Zhang, C. Yuan\*

A New and Convenient Route to Optically Active 2-Phosphoryl-3-oxo-5-alkyl/-aryltetrahydrofurans and Their Reactions

**Keywords:** Tetrahydrofurans / Horner–Wadsworth–Emmons reactions / Rhodium catalyst / O–H Insertion reaction

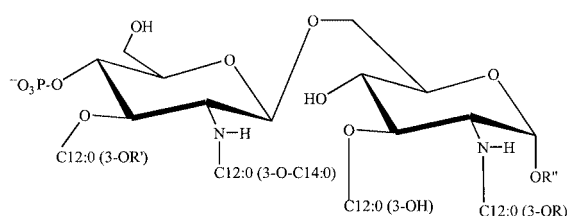


2263 A. Silipo, L. Sturiale, D. Garozzo,  
C. de Castro, R. Lanzetta, M. Parrilli,  
W. D. Grant, A. Molinaro

Structure Elucidation of the Highly Heterogeneous Lipid A from the Lipopolysaccharide of the Gram-Negative Extremophile Bacterium *Halomonas Magadiensis* Strain 21 M1

**Keywords:** *Halomonas magadiensis* / Extremophilic bacteria / Lipid A / NMR spectroscopy / Mass spectrometry

|     | 1a                           | 1b                           | 2a                           | 2b                           | 3                            | 4a                           | 4b                           | 5a                           | 5b    | 6                            | 7                            | 8a                           | 8b |
|-----|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|-------|------------------------------|------------------------------|------------------------------|----|
| R   | C10:0                        | C10:0                        | H                            | H                            | C10:0                        | H                            | H                            | C10:0                        | C10:0 | H                            | H                            | H                            | H  |
| R'  | C16:0                        | C18:1                        | C16:0                        | C18:1                        | H                            | C16:0                        | C18:1                        | H                            | H     | H                            | H                            | H                            | H  |
| R'' | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | H     | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | PO <sub>3</sub> <sup>−</sup> | H  |



2272 A. C. Benniston,\* A. Harriman,  
D. J. Lawrie, S. A. Rostron

A Closely-Coupled Pyrene Dimer Having Unusually Intense Fluorescence

**Keywords:** Fluorescence / Sensors / Pyrene / Charge transfer / Glaser coupling

