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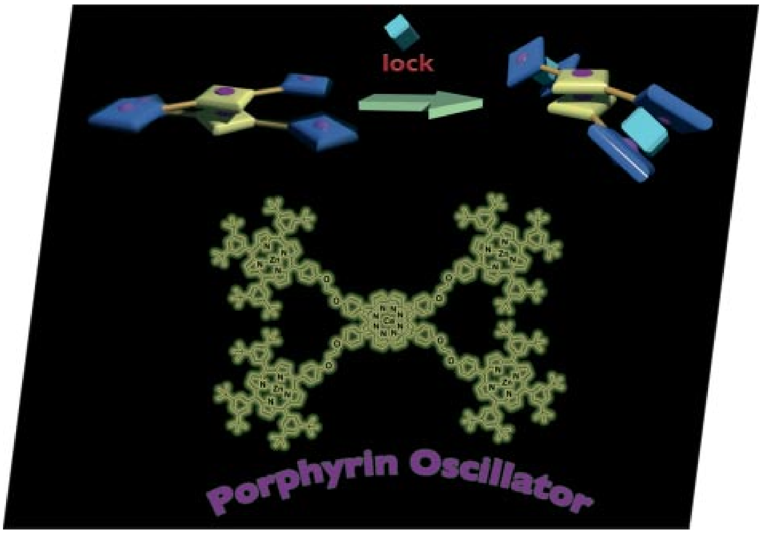
## COVER PICTURE

**The cover picture shows** a porphyrin oscillator that comprises a cerium(IV) bis(porphyrinate) bearing four peripheral zinc(II) porphyrinates. The cooperative binding of guest molecules (shown as “lock”) slows down the rotational oscillation frequency of the porphyrin oscillator in solution, which is evaluated by VT NMR spectroscopy. Details are discussed in the Short Communication by M. Takeuchi, S. Shinkai et al. on p. 1883 ff.



# CONTENTS

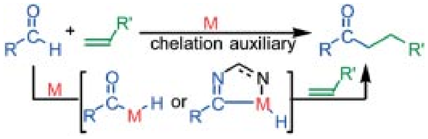
## MICROREVIEW

### C–H Activation

**C.-H. Jun,* E.-A. Jo,**
**J.-W. Park ............................ 1869–1881**

Intermolecular Hydroacylation by Transition-Metal Complexes

**Keywords:** Acylation / Ketones / C–H activation / Homogeneous catalysis / Transition metals



Various transition-metal-catalyzed intermolecular hydroacylation reactions have been developed with aldehydes bearing a coordinating heteroatom or chelation-auxiliary in order to avoid decarbonylation. Hydroacylation or its variations can also be applied to the synthesis of cycloalkanones and an α,β-unsaturated ketone or to the carbon–carbon triple bond cleavage of an alkyne.

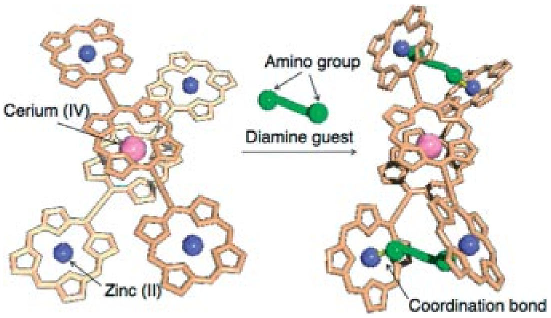
## SHORT COMMUNICATIONS

### Molecular Machinery

**M. Ikeda, Y. Kubo, K. Yamashita, T. Ikeda,**
**M. Takeuchi,* S. Shinkai* ..... 1883–1886**

Dynamic Rotational Oscillation of Cerium(IV) Bis(porphyrinate) and Its Control by Diamine Guest Binding with Positive Homotropic Allosterism

**Keywords:** Molecular recognition / Supramolecular chemistry / Porphyrinoids / Host–guest systems



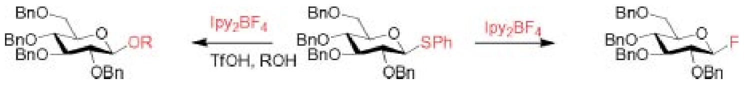
We report the synthesis of a new porphyrin oscillator composed of cerium(IV) bis(porphyrinate) bearing four peripheral zinc(II) porphyrinates by a convergent synthetic method. The influence of diamine guest binding on the rotational oscillation frequency of the porphyrin oscillator was evaluated in solution by variable temperature NMR spectroscopy.

### Glycosylation Reactions

**K.-T. Huang,**
**N. Winssinger* ..................... 1887–1890**

IPy$_2$BF$_4$-Mediated Glycosylation and Glycosyl Fluoride Formation

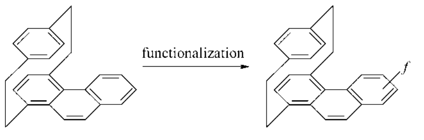
**Keywords:** Carbohydrates / Glycosylation / Thioglycosides / Iodine



A facile method to convert thioglycosides to glycosyl fluorides with Ipy$_2$BF$_4$ (py = pyridine) is presented. Alternatively, activation of thioglycosides with Ipy$_2$BF$_4$ in the presence of acids and glycosyl acceptors led to glycosylation reactions. Perbenzylated (armed) glycosyl donors yielded predominantly the β-anomeric product. This methodology is compatible with one-pot sequential glycosylation.

## Paracyclophanes

Two protocols leading to functionalized phenanthrenophanes are described, one subjecting the complete hydrocarbon to aromatic substitution, the other using functionalized precursors and photocyclising them to the desired phenanthrenophanes.



*f* (= functional groups): Br, $COCH_3$, CHO, $CH_2OH$, $CH_3$, OH etc.

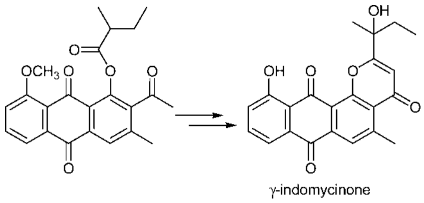
**H. Hopf,* J. Hucker, L. Ernst** ................................ **1891–1904**

On the Functionalization of [2.2](1,4)-Phenanthrenoparacyclophane

**Keywords:** Cyclophanes / Photocyclization / Stilbenes / *o*-Quinones / Heterophanes

## Total Synthesis of γ-Indomycinone

The total synthesis of racemic γ-indomycinone (*rac*-**3**) was achieved by Baker–Venkataraman rearrangement of ester **11** to the diketone **12**, acid-catalyzed cyclization to the anthrapyranone **13**, followed by methyl ether cleavage and acetylation to **16**, selective bromination of the branched side chain with $S_N1$-type hydroxy substitution to **23** and transesterification to *rac*-**3**.

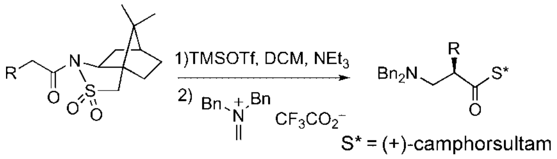


**K. Krohn,* H. T. Tran-Thien, J. Vitz, A. Vidal** ................................ **1905–1911**

Total Synthesis of *rac*-γ-Indomycinone by Baker–Venkataraman Rearrangement

**Keywords:** Total synthesis / Anthrapyranone antibiotics / γ-Indomycinone / Baker–Venkataraman rearrangement / Radical bromination

## Synthesis of β²-Amino Acids



S* = (+)-camphorsultam

β-Amino acids are useful tools in the design of peptidomimetics, and the development of new methods for their syntheses, particularly the synthesis of β²-amino acids, remains an important challenge. A new scalable route is reported based on the aminomethylation of silyl ketene N,O-acetals by Mannich-type iminium electrophiles.

**R. Moumné, B. Denise, K. Guitot, H. Rudler, S. Lavielle, P. Karoyan*** ........................... **1912–1920**

New Scalable Asymmetric Aminomethylation Reaction for the Synthesis of β²-Amino Acids

**Keywords:** β²-Amino acids / Aminomethylation / Silyl ketene acetals / Mannich-type iminium electrophiles / Scalable synthesis

## Regioselective Phenol Bromination

The use of THF as solvent instead of DMF in NBS-mediated bromination reactions offers a convenient and regioselective access at low temperatures to activated bromophenols, their ethers, and Boc derivatives.

**D. Pla, F. Albericio,* M. Álvarez*** .......................... **1921–1924**

Regioselective Monobromination of Free and Protected Phenols

**Keywords:** *N*-Bromosuccinimide / Aromatic substitution / Phenols / Alkoxybenzenes / Bromobenzene / Regioselectivity

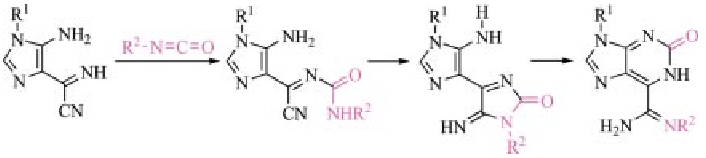
# CONTENTS

## Purine Chemistry

**A. M. Dias, I. Cabral, A. S. Vila-Chã,**
**D. S. Costa, M. F. Proença* ... 1925−1934**

The Synthesis of 6-Amidino-2-oxopurine Revisited: New Evidence for the Reaction Mechanism

**Keywords:** Nitrogen heterocycles / Amidinopurines / Isocyanates / Rearrangement / 4,4′-Biimidazoles



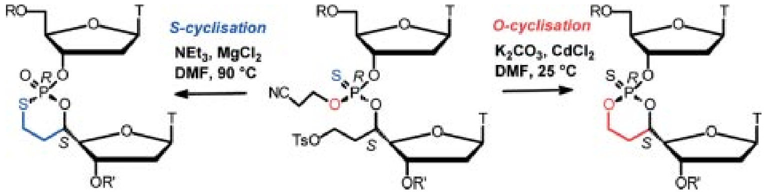
Reactions between substituted imidazoles and acyl or tosyl isocyanates proceed efficiently to afford 6-amidinopurines through 4,4′-biimidazole intermediates.

## Constrained Nucleotides

**I. Le Clézio, A. Vigroux,**
**J.-M. Escudier* .................... 1935−1941**

Diastereoselective and Regioselective Synthesis of Conformationally Restricted Thio-dioxa- and Oxo-oxathiaphosphorinane Dinucleotides Featuring Noncanonical α/β Torsion Angle Combinations (α,β-CNAs)

**Keywords:** Constrained molecules / Nucleic acids / Phosphorothioate / Cyclisation / Regioselectivity



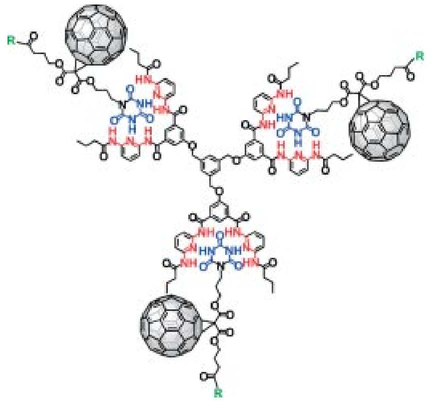
Control of the regioselective cyclisation of a stereodefined 5′-C-tosyloxy phosphorothioate dinucleotide unit provided conformationally restricted dinucleotides of either thio-dioxa- or oxo-oxathiaphosphorinane types. Structural analysis showed the α and β torsional angles to be constrained to noncanonical values {*gauche*(+), *trans*} or {*anticlinal*(−), *trans*}.

## Dendrimers

**K. Hager, U. Hartnagel,**
**A. Hirsch* ............................ 1942−1956**

Supramolecular Dendrimers Self-Assembled from Dendritic Fullerene Ligands and a Homotritopic Hamilton Receptor

**Keywords:** Cooperativity / Dendrimers / Depsipeptides / Fullerenes / Hydrogen bonding / Self-assembly



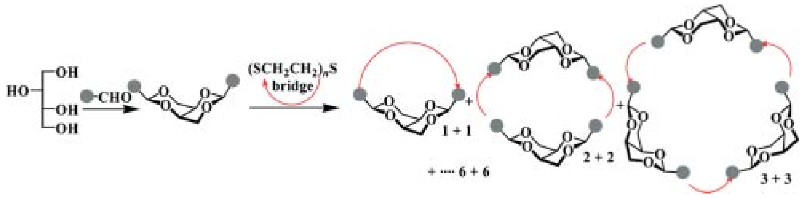
The self-assembly of a homotritopic Hamilton receptor with dendritic fullerene ligands leads to the highly cooperative formation of supramolecular dendrimers.

## Polythiacrown Macrocycles

**S. Abramson, D. Berkovich-Berger,**
**S. Dagan, I. Goldberg, L. Golender,**
**M. Grabarnik, N. G. Lemcoff,***
**S. Weinman, B. Fuchs* .......... 1957−1975**

Polythiacrown Macro- and Gigantocycles with Chiral Diacetal Cores

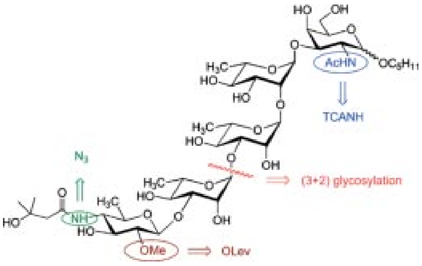
**Keywords:** Macrocycles / Crown compounds / S ligands / Chiral diacetals / Tetraoxadecalins



Polythiacrown macro- and gigantocyclic systems, having one to six chiral *cis*-tetraoxadecalin cores bridged by variable ($n$ = 1−4) poly(ethylene thioglycol) spacers, have been prepared and studied by NMR, MS, X-ray and computation.

## Carbohydrate Synthesis

The first total synthesis of the pentasaccharide attached to BclA spore surface protein of *Bacillus anthracis* is reported. Key to differentiating the two amino groups is the one-pot conversion of an *N*-trichloroacetyl into an *N*-acetyl group and simultaneous reduction of the azide to a free amine by excess tributyltin hydride under radical-forming conditions.



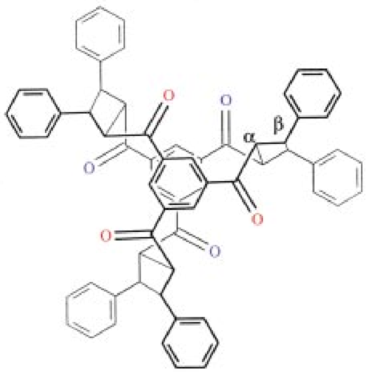
**D. B. Werz, A. Adibekian, P. H. Seeberger*** .................. **1976–1982**

Synthesis of a Spore Surface Pentasaccharide of *Bacillus anthracis*

**Keywords:** Anthrose / *Bacillus anthracis* / Carbohydrates / Oligosaccharides / Total synthesis

## Cyclodimerization

[4.4.4](1,3,5)Cyclophane **8** is obtained by *anti*-head-to-head [2π+2π] photocycloaddition reactions of all-*cisoid*-(*E*,*E*,*E*)-1,3,5-tricinnamoylbenzene (**7**). The opposite orientation of the enone units leads only to a single reaction of this type. Irradiation of the crystals effects single *syn*-head-to-tail processes, even when the distance between the reacting olefinic double bonds amounts to 5.07 Å.

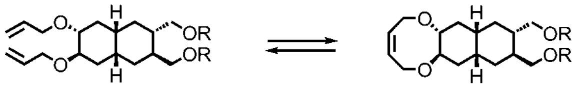


**E. Karpuk, D. Schollmeyer, H. Meier*** ............................ **1983–1990**

Photochemical Generation of Cyclophanes from 1,3,5-Trisubstituted Benzenes with Chalcone Chromophores

**Keywords:** Cycloaddition / Cyclophanes / Diastereoselectivity / Photochemistry / Regioselectivity

## Switching by Olefin Metathesis



A ring-closing olefin metathesis (RCM) to an eight-membered ring is suitable to induce a conformational switch of a tetrasubstituted *cis*-decalin.

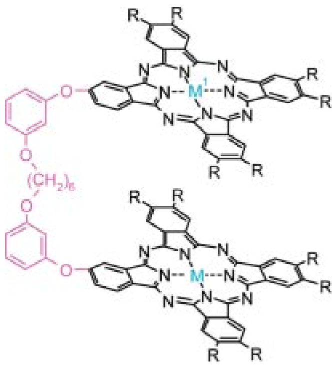
**M.-E. J. Garcia, U. Fröhlich, U. Koert*** ............................. **1991–1999**

Olefin Metathesis: A Reversible Stimulus for a Conformational Switch

**Keywords:** *cis*-Decalin / Molecular switch / Ring-closing olefin metathesis / Conformational design

## Phthalocyanine Chemistry

Novel unsymmetrically substituted phthalocyanines possessing free phenolic OH groups have been synthesized by standard methodologies, and dimeric mononuclear and heteronuclear phthalocyanines have been prepared by single-step and two-step alkylations of the OH groups in the corresponding precursors with 1,6-dibromohexane. The spectroscopic properties of the products have been studied.



**A. Lyubimtsev, S. Vagin, S. Syrbu, M. Hanack*** .......................... **2000–2005**

Synthesis of Novel Covalently Linked Dimeric Phthalocyanines

**Keywords:** Statistical condensation / Phthalonitriles / Phthalocyanines / Alkylation / Metal complexes

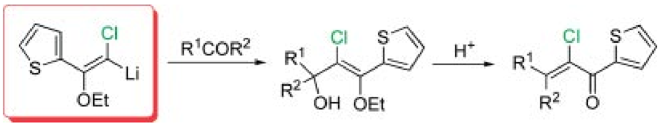
# CONTENTS

## 1,3-Bis(hetaryl)-2-chloropropen-1-ones

**A. Itoh, M. Sakai,**
**M. Yoshimatsu* ..................... 2006–2014**

A Convenient Preparative Method for New 1,3-Bis(hetaryl)-2-chloropropen-1-ones Using β-Alkoxy-β-chloroalkenyllithium Compounds

**Keywords:** 1-Aryl-2-chloro-1-ethoxyethene / 1,3-Biarylpropen-1-one / Alkenyllithium / Suzuki coupling



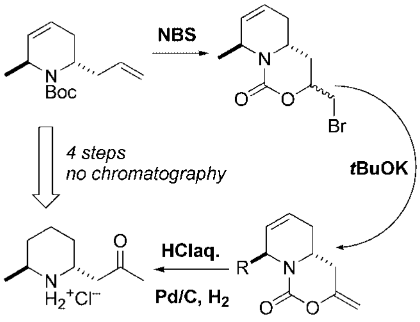
1,3-Bisaryl and 1,3-bis(hetaryl)propen-1-ones and the corresponding acetals were successfully synthesized by a stepwise process using β-alkoxyalkenyllithium compounds.

## Piperidine Alkaloids

**N. Yu. Kuznetsov, V. N. Khrustalev,**
**I. A. Godovikov,**
**Yu. N. Bubnov* ....................... 2015–2021**

Preparation of α-Acetonylpiperidines from α-Allylated Heterocycles by a Bromocyclocarbamation Reaction

**Keywords:** Alkaloids / Allylic compounds / Boranes / Nitrogen heterocycles / Halocyclocarbamation



**(±)-6-Epipinidinone**

2,6-Disubstituted (alkyl)(allyl)- and diallylpiperidines containing C=C bonds in different environments can be selectively transformed into α-acetonylpiperidines, including the alkaloid (±)-6-epipinidinone.