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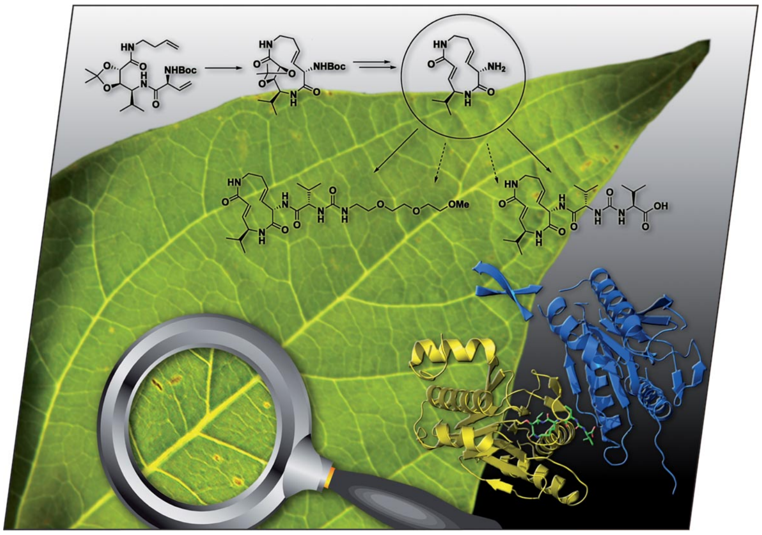
## COVER PICTURE

**The cover picture shows** the key steps of a convergent and versatile synthesis of Syringolin A (SylA) and other syrbactins. SylA is a small-molecule virulence factor produced by some plant pathogenic *Pseudomonas syringae* pv. *syringae* strains during infection. It leads to irreversible inhibition of the plant's 20S proteasome (lower right corner depicts the binding mode of SylA to one of the active-site centres of the proteasome), resulting in the so-called brown-spot disease. The synthetic preparation of SylA and its analogues opens up further possibilities for biological investigation into the mode of action of SylA in plant–pathogen interactions. Details are discussed in the article by M. Kaiser et al. on p. 3991ff.



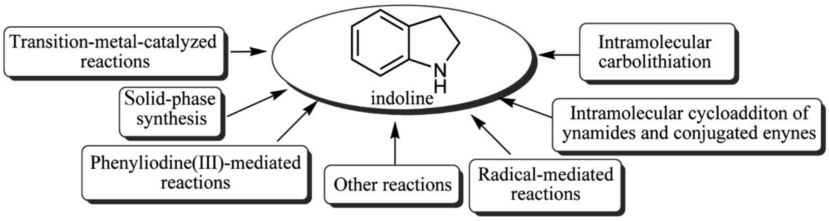
## MICROREVIEW

### Indoline Scaffold

**G. Zhao, L. Xiang* ................ 3975–3984**

Diverse Strategies for the Synthesis of the Indoline Scaffold

**Keywords:** Nitrogen heterocycles / Fused-ring systems / Synthetic methods / Natural products



This microreview describes the recent advances in the strategies for the synthesis of the indoline scaffold, including Cu- and Pd-catalyzed reactions, radical-mediated reactions, and intramolecular carbolithiation reactions. Solid-phase synthesis, as well as other reaction types for the synthesis of indoline derivatives is explored.

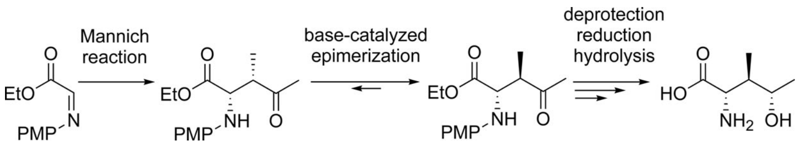
## SHORT COMMUNICATION

### Dynamic Resolution

**S. De Lamo Marin, C. Catala,**
**S. R. Kumar, A. Valleix, A. Wagner,***
**C. Mioskowski ........................ 3985–3989**

A Practical and Efficient Total Synthesis of Potent Insulinotropic (2*S*,3*R*,4*S*)-4-Hydroxyisoleucine through a Chiral *N*-Protected γ-Keto-α-aminoester

**Keywords:** Amino acids / Organocatalysis / Asymmetric synthesis / Chiral resolution / Total synthesis



We present herein a straightforward strategy to obtain (2*S*,3*R*,4*S*)-4-OH-iLeu in >99%*de* and >99%*ee* in a 22% overall yield. The strategy relies on two key reactions: Mannich-type condensation followed by base-promoted epimerization/crystallization to introduce the two contiguous stereogenic centers. The reaction sequence is simple and straightforward.

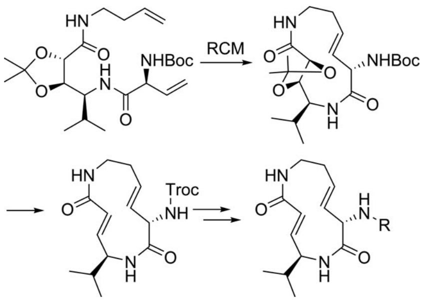
## FULL PAPERS

### Natural Products

**J. Clerc, B. Schellenberg, M. Groll,**
**A. S. Bachmann, R. Huber, R. Dudler,**
**M. Kaiser* .............................. 3991–4003**

Convergent Synthesis and Biological Evaluation of Syringolin A and Derivatives as Eukaryotic 20S Proteasome Inhibitors

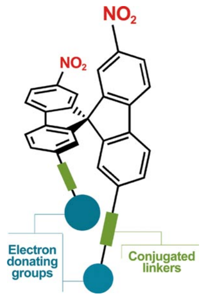
**Keywords:** Synthetic methods / Natural products / Biological activity / Metathesis / Inhibitors



A convergent synthesis to SylA and derivatives was developed and employed for the synthesis of a small collection of SylA analogues. The critical key step is ring-closing metathesis of a preorganized precursor, yielding a fully functionalized SylA macrocycle for further decoration with various side chains. The biological activities of these compounds were tested.

### Nonlinear Optical Spiro Compounds

A new class of push−pull chromophores with disubstituted amines and nitro groups connected to a spirobifluorene core has been synthesized. The first and second hyperpolarizability ($\beta$ and $\gamma$) of these compounds have been investigated through a joint experimental and theoretical approach and compared to those of reference fluorenes.

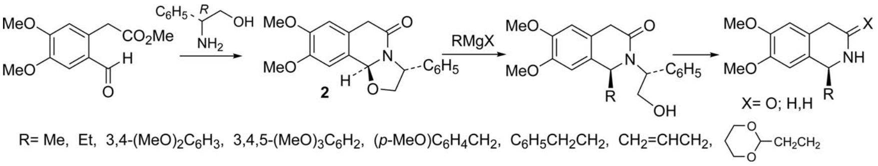


**F. Rizzo, M. Cavazzini, S. Righetto, F. De Angelis, S. Fantacci, S. Quici* .............................. 4004−4016**

A Joint Experimental and Theoretical Investigation on Nonlinear Optical (NLO) Properties of a New Class of Push−Pull Spirobifluorene Compounds

**Keywords:** Spiro compounds / Nonlinear optics / Ab initio calculations / Push−pull molecules

### Tetrahydroisoquinolines



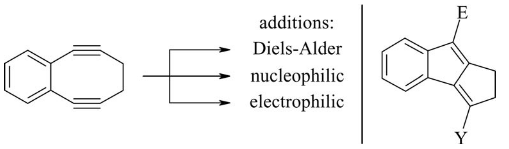
Tricyclic (*R*)-phenylglycinol-derived lactam **2** has proven to be a versatile scaffold that provides general access to enantiopure 1-substituted tetrahydroisoquinoline derivatives as well as more complex alkaloids, for example, (−)-crispine A, bearing the tetrahydroisoquinoline moiety.

**M. Amat,* V. Elias, N. Llor, F. Subrizi, E. Molins, J. Bosch ............... 4017−4026**

A General Methodology for the Enantioselective Synthesis of 1-Substituted Tetrahydroisoquinoline Alkaloids

**Keywords:** Alkaloids / Heterocycles / Lactams / Asymmetric synthesis / Total synthesis

### Strained Triple Bonds



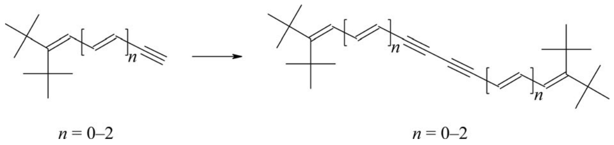
3,4-Benzocycloocten-1,5-diyne is a highly reactive hydrocarbon that readily undergoes different types of addition reactions. Electrophilic additions cause ring contractions to dihydropentalene derivatives.

**C. Werner, H. Hopf,* J. Grunenberg, P. G. Jones ............................ 4027−4034**

The Chemical Behavior of 3,4-Benzocycloocten-1,5-diyne

**Keywords:** Alkynes / Strained molecules / Ring contraction / Transannular interactions

### Carbon-Rich Compounds



Sterically shielded and therefore stable oligoenynes were readily prepared from acetylenic building blocks and characterized by spectroscopic and X-ray diffraction data.

**P. Kiliçkiran, H. Hopf,* I. Dix, P. G. Jones ............................ 4035−4045**

Preparation of Highly Hindered Polyenynes

**Keywords:** Alkynes / Polyene/polyyne hybrid compounds / Carbon-rich compounds / Thiophenes

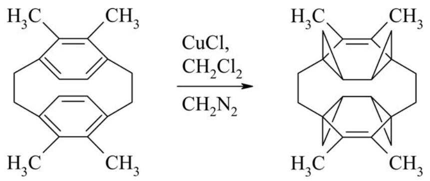
# CONTENTS

## Stable Homobenzene Synthesis

**D. Wullbrandt, H. Hopf,***
**P. G. Jones** ............................. **4046–4048**

Preparation and Structure Determination of a Stable *cis*-Bis-σ-homobenzene Derivative

**Keywords:** Cyclophanes / Cyclopropanation / Homobenzenes



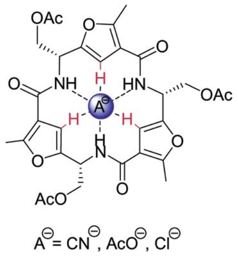
By cyclopropanation of a [2.2]paracyclophane a stable *cis*-bis-σ-homobenzene derivative was prepared. The X-ray structure of this hydrocarbon is the first for this class of compounds.

## Cyclopeptidic Anion Receptors

**L. Molina, E. Moreno-Clavijo,**
**A. J. Moreno-Vargas,* A. T. Carmona,**
**I. Robina*** .............................. **4049–4055**

Synthesis of a $C_3$-Symmetric Furyl-Cyclopeptide Platform with Anion Recognition Properties

**Keywords:** Heterocycles / Cyclopeptides / Peptidomimetics / Anion receptors / Host-guest systems



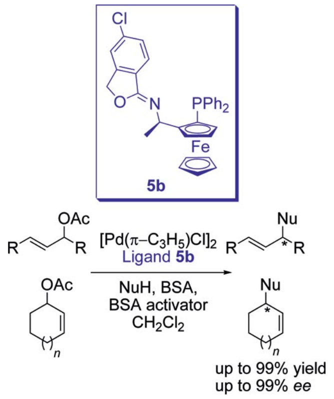
The synthesis and structural analysis of a new furyl-cyclopeptide is reported. This compound shows interesting anion-recognition properties towards cyanide, acetate and chloride based on the enhanced formation of unusual hydrogen bonds between the aromatic CH and the guest anion.

## Mixed Imidate–Phosphane Ligands

**T. Noël, K. Bert, E. Van der Eycken,**
**J. Van der Eycken*** ................. **4056–4061**

Imidate–Phosphanes as Highly Versatile N,P Ligands and Their Application in Palladium-Catalyzed Asymmetric Allylic Alkylation Reactions

**Keywords:** Asymmetric catalysis / N,P ligands / Palladium / Allylic alkylation / Imidate ligands



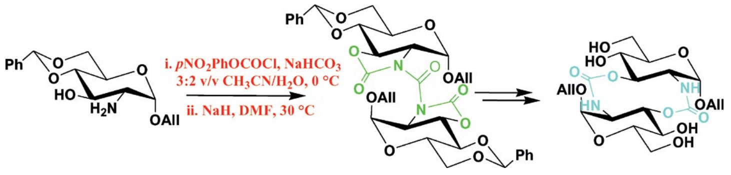
Chiral imidates were developed as a new class of N,P ligands and are easily obtained in one step. Excellent performance of the catalyst system was observed with various carbon nucleophiles in the $Pd^0$-catalyzed asymmetric allylic alkylation.

## Carbohydrate Mimics

**L. Cirillo, A. Silipo, E. Bedini,***
**M. Parrilli** ............................. **4062–4074**

A Urea-Linked Glucosamine Dimer as a Building Block for the Synthesis of Linear and Cyclic Neosaccharides

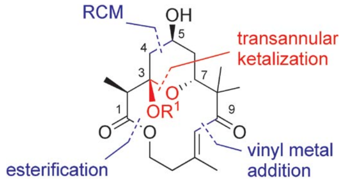
**Keywords:** Carbohydrates / Glycoconjugates / Macrocycles / Oligosaccharides / Reaction mechanisms



A novel urea-linked glucosamine dimer was obtained through a modification of the standard oxazolidinone closure reaction on a 2,3-amino alcohol monomer. Its 3D structure as well as the mechanism for its formation was studied in detail. Chemoselective reactions on its oxazolidinone–urea–oxazolidinone moiety allowed access to linear and cyclic neosaccharides.

## Natural Product Synthesis

The macrocyclic core of marine natural macrolides of the auriside type product is accessible by two approaches based on the ring-closing metathesis reaction (Yamaguchi macrocyclization). The convergent stereocontrolled synthesis of a truncated auriside analogue was accomplished.

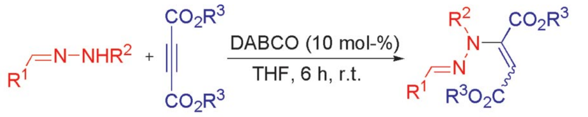


**E. Bourcet, F. Fache,**
**O. Piva* ................................ 4075–4087**

Stereocontrolled Synthesis of the Highly Functionalized Core Structure of Aurisides by Ring-Closing Metathesis

**Keywords:** Natural products / Synthetic methods / Ring closing metathesis / Aurisides / Macrolides

## Activated Alkynes



$R^1$ = aromatic group, aliphatic group, ester group or trifluoromethyl group
$R^2$ = Ts group or Bz group
$R^3$ = Methyl or Ethyl

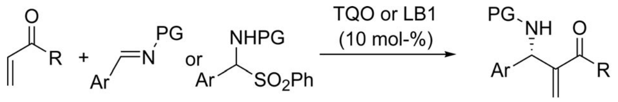
DABCO (10 mol-%) can promote aza-Michael addition reactions of a series of hydrazones with activated alkynes to give the corresponding adducts in moderate to good yields.

**Z.-L. Yuan, Y. Wei,**
**M. Shi* ................................ 4088–4097**

Aza-Michael Addition Reactions of Hydrazones with Activated Alkynes Catalyzed by Nitrogen-Containing Organic Bases

**Keywords:** Organocatalysis / Michael addition / Hydrazones / Alkynes

## Aza-MBH Reactions of *N*-Boc Imines



PG = Boc, Bz, $CO_2Et$

up to 94% *ee*

DABCO-catalyzed aza-MBH reactions of *N*-Boc imines with MVK and its asymmetric version have been thoroughly investigated in this paper. A facile and direct route was identified that allows highly enantioselective aza-MBH adducts to be obtained from the reaction of *N*-protected α-amidoalkyl phenyl sulfones with alkyl vinyl ketones catalyzed by chiral phosphane catalyst LB1.

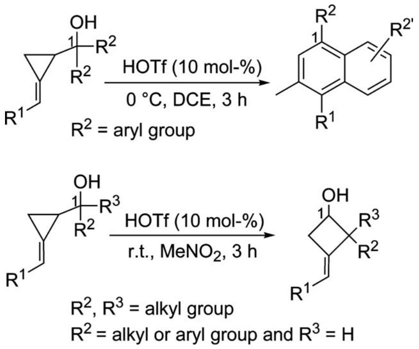
**X.-Y. Guan, Y. Wei,***
**M. Shi* ................................ 4098–4105**

Asymmetric Aza-Morita–Baylis–Hillman Reactions of Alkyl Vinyl Ketones with *N*-Protected Imines or In Situ Generated *N*-Protected Imines

**Keywords:** Nucleophilic addition / Enantioselectivity / Sulfur / Phosphanes / Lewis bases / Asymmetric synthesis

## Cyclopropane Ring Manipulation

In the presence of TfOH, methylenecyclopropane diaryl alcohols **1** or dialkyl-, monoalkyl- as well as monoaryl alcohols **3** underwent a ring-opening/ring-enlargement process in dichloroethane or nitromethane to afford the corresponding naphthalene or cyclobutanol derivatives in moderate to good yields, respectively.



**X.-Y. Tang, M. Shi* .............. 4106–4110**

HOTf-Catalyzed Rearrangement of Methylenecyclopropane Aryl and Alkyl Alcohols

**Keywords:** Small ring systems / Alcohols / Ring expansion / Aromaticity

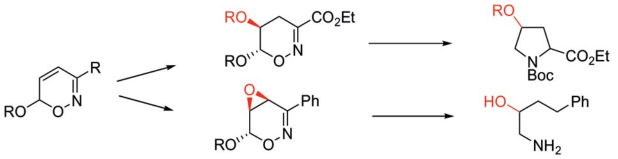
# CONTENTS

## Heterocyclic Chemistry

**R. Zimmer, M. Buchholz, M. Collas,**
**J. Angermann, K. Homann,**
**H.-U. Reissig* ......................... 4111–4121**

1,2-Oxazines as Building Blocks for Stereoselective Synthesis: Preparation of Oxygen-Substituted 1,2-Oxazines, either by Alcohol Addition or by Epoxidation, and Subsequent Hydrogenation Leading to 1,2-Amino Alcohols and Pyrrolidines

**Keywords:** N,O Heterocycles / Epoxidation / Hydrogenation / Amino alcohols / 1,2-Oxazines / Proline esters



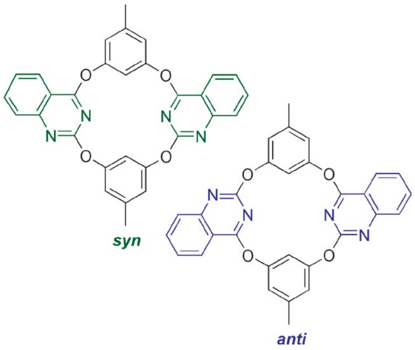
Oxygen-substituted 1,2-oxazines were prepared from 6*H*-1,2-oxazines. 1,4-Additions of alcohols provided 5-alkoxy-substituted derivatives. Use of hydroperoxides furnished epoxides. Reduction of these substituted 1,2-oxazines gave hydroxyproline derivatives or 1,2-amino alcohols.

## Oxacalixarenes

**W. Van Rossom, L. Kishore, K. Robeyns,**
**L. Van Meervelt, W. Dehaen,***
**W. Maes ................................ 4122–4129**

Synthetic Exploration of Oxacalix[2]arene[2]quinazolines

**Keywords:** Calixarenes / Nitrogen heterocycles / Aromatic substitution / Regioselectivity / Conformation analysis



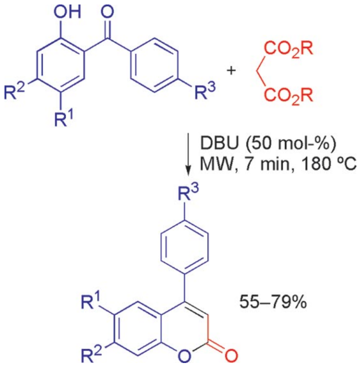
Oxacalix[2]arene[2]quinazolines were synthesized by efficient $S_NAr$ cyclocondensation protocols. Due to the asymmetry of the dichloroquinazoline precursors, two regioisomers (*syn*/*anti*) were obtained and their relative ratio could be varied. These O-bridged macrocycles provide novel prospects for supramolecular recognition.

## Neoflavonoids

**J. Crecente-Campo,**
**M. P. Vázquez-Tato,***
**J. A. Seijas* ........................... 4130–4135**

Microwave-Promoted, One-Pot, Solvent-Free Synthesis of 4-Arylcoumarins from 2-Hydroxybenzophenones

**Keywords:** Microwave chemistry / Natural products / Neoflavonoids / Lactones / Synthetic methods



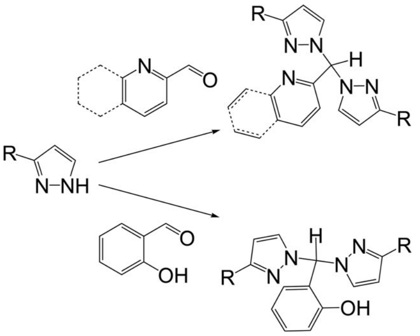
A highly efficient, microwave-assisted, solvent-free synthesis of neoflavonoids was developed. The procedure consists of one-pot Knoevenagel condensation, lactonization, and decarboxylation. The use of microwaves considerably reduced the reaction times, and the yields were significantly increased in comparison to those observed under classic heating conditions.

## Peterson Rearrangement

**A. Hoffmann, U. Flörke, M. Schürmann,**
**S. Herres-Pawlis* .................. 4136–4144**

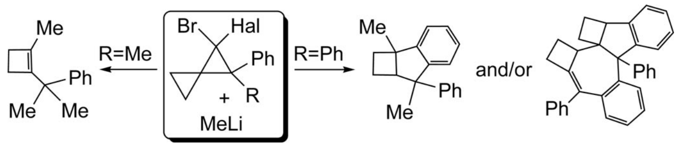
Novel Synthetic Strategy towards the Efficient Synthesis of Substituted Bis(pyrazolyl)(2-pyridyl)methane Ligands

**Keywords:** N ligands / Ligand design / Heteroscorpionate ligands / Structure elucidation



An efficient method for a general synthesis of substituted bis(pyrazolyl)methanes is reported. This method makes use of $SOCl_2$ instead of $COCl_2$ and allows the combination of various substituted pyrazoles with different aldehydes in order to built up a library of new bis(pyrazolyl)methanes.

## Carbenoid Rearrangement



An unusual cationic carbenoid rearrangement followed by electrophilic substitution in the phenyl ring was observed in the reaction of 2-phenyl-substituted *gem*-dihalogenospiropentanes with methyllithium.

**K. N. Sedenkova, E. B. Averina,***
**Yu. K. Grishin, V. B. Rybakov,**
**T. S. Kuznetzova,**
**N. S. Zefirov** .......................... **4145−4150**

Cationic Carbenoid Rearrangement of 2-Phenyl Substituted *gem*-Dihalogenospiropentanes

**Keywords:** Carbenoids / Carbocations / Rearrangement / Spiro compounds

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* Author to whom correspondence should be addressed.

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