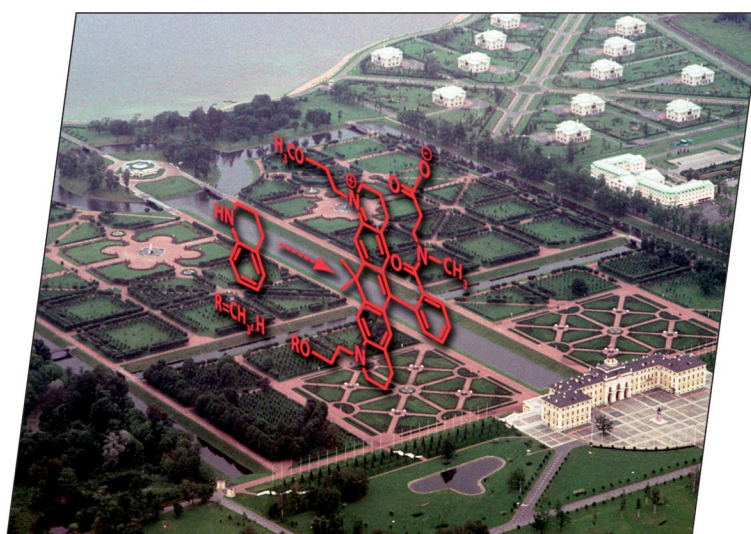


EurJOC is co-owned by 11 societies of ChemPubSoc Europe, a union of European chemical societies for the purpose of publishing high-quality science. All owners merged their national journals to form two leading chemistry journals, the *European Journal of Organic Chemistry* and the *European Journal of Inorganic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem*.

## COVER PICTURE

The cover picture shows a unique bird's eye view of the regular park in Strelna – one of the most desolate, yet stunning historical suburbs of St. Petersburg (Russia). Famous European architects of the 18th century, such as C.-B. Rastrelli, A. Le Blanc, G.-B. Chiprianni, P. Michetti, and L. Ruska, participated in the construction of “the Russian Versailles” – this is what the Russian Tsar Peter the Great planned this country residence to be. The northern façade of the Konstantinovsky Palace looks at the hazy and rainy Gulf of Finland. The regular cyclic pattern of the park lanes and shipping canals is reminiscent of the polycyclic structure of carbopyrnone dyes decorated with hydrophilic groups. These fluorescent markers are described in the article by V. N. Belov, S. W. Hell et al. on p. 3593ff. The authors report a detailed and strategically sound synthesis of the carbopyrnone scaffold with great potential for dye design. Important photophysical properties and some nanoscopic applications of the new red emitting dyes are also described, and interesting future applications (e.g. as caged carbopyrnone) are mentioned. Photo: V. N. Belov; the artwork of Mr. H. Sebesse (Max Planck Institute for Biophysical Chemistry, Göttingen, Germany) is acknowledged.



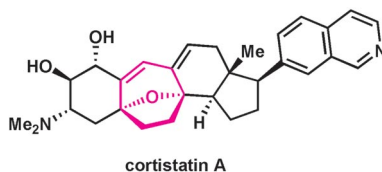
## MICROREVIEW

### Natural Products

A. R. Hardin Narayan, E. M. Simmons,  
R. Sarpong\* ..... 3553–3567

Synthetic Strategies Directed Towards the  
Cortistatin Family of Natural Products

**Keywords:** Natural products / Total syn-  
thesis / Steroidal alkaloids / Cortistatins /  
Ring expansion / Pericyclic reactions



The cortistatin family of natural products have captured the attention both of synthetic chemists and of workers interested in understanding and exploiting their potent anti-angiogenic activity. Many synthetic strategies have been devised to build the rearranged steroidal cortistatin core, which has in turn enabled studies probing the origins and mechanism of these compounds' biological activity.

## SHORT COMMUNICATIONS

### Reaction Monitoring

E. Heller,\* J. Klöckner,  
W. Lautenschläger,  
U. Holzgrabe\* ..... 3569–3573



Online Monitoring of Microwave-En-  
hanced Reactions by UV/Vis Spectroscopy

**Keywords:** Online monitoring / Microwave  
chemistry / UV/Vis spectroscopy / Sensors



Fast microwave-enhanced reactions were monitored online by UV/Vis spectroscopy with a sensor in solution. This method is superior to slower methods (e.g. NMR, HPLC, TLC), because it is much faster and can also be performed in concentrated solutions.

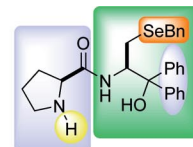
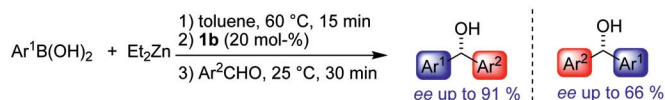
### Asymmetric Catalysis

R. S. Schwab, L. C. Soares, L. Dornelles,  
O. E. D. Rodrigues,\* M. W. Paixão,  
M. Godoi, A. L. Braga\* ..... 3574–3578



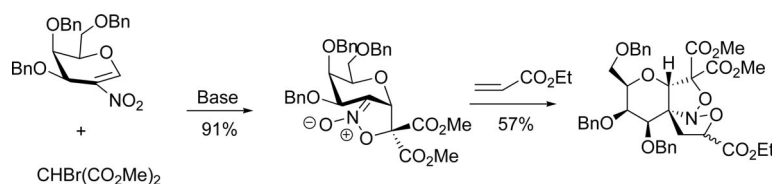
Chiral Chalcogen Peptides as Ligands for  
the Catalytic Enantioselective Aryl Trans-  
fer Reaction to Aldehydes

**Keywords:** Asymmetric synthesis / Chalco-  
gen peptides / Arylboronic acids / Diaryl-  
methanols / Organozinc reagents / Sele-  
nium



A new class of chiral chalcogen peptide based ligands was prepared and applied in the zinc-catalyzed addition of arylboronic acids to aldehydes. The chiral diaryl-

methanol products were obtained in excel-  
lent yields and with a high level of enantio-  
selectivity up to 91% *ee*.



Condensation of bromomalonate esters with 2-nitroglycals afforded isoxazoline *N*-oxides in moderate to high yields and with high facial selectivity. Further treatment of

the resulting isoxazoline *N*-oxides with dipolarophiles led to the corresponding nitroso acetals.

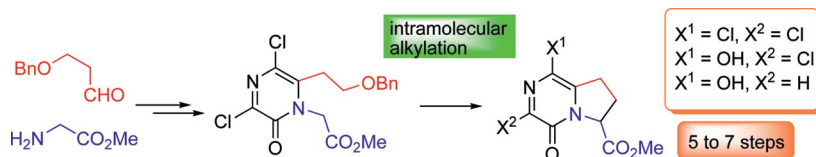
**Q. Zhang, J. Sun,\* F. Zhang,  
B. Yu\*** ..... 3579–3582

Synthesis of Sugar-Fused Isoxazoline *N*-Oxides from 2-Nitroglycals



**Keywords:** Synthetic methods / 2-Nitroglycal / Isoxazoline *N*-oxide / 1,3-Dipolar cycloaddition

## Fused Pyrazinones



Important pharmaceutical intermediates for the synthesis of constrained fused pyrazinones were efficiently prepared by

construction of a five-membered ring by intramolecular alkylation.

**V. Gembus,\* S. Janvier, J.-P. Lecouvé,  
P. Gloanec, F. Marsais,  
V. Levacher\*** ..... 3583–3586

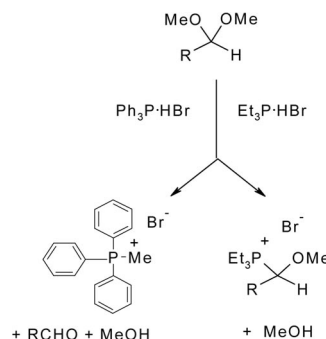
Novel Approach for the Synthesis of Five-Membered-Ring-Fused Pyrazinones



**Keywords:** Alkylation / Heterocycles / Peptidomimetics / Pyrazinones / Serine protease inhibitor

## α-Functionalized P-Ylides

***P*-methylate or not *P*-methylate?** The discovery of dichotomous reactivity in the reaction of trialkyl- vs. triphenylphosphane HBr salts with acetals allows entry to functionalized α-methoxy phosphonium salts and a novel process for tertiary phosphane methylation. The new protocol opens a general entry to the synthesis of vinyl ethers and differentially substituted 1,3-dienes.



**P. Das, J. McNulty\*** ..... 3587–3591

Dichotomous Reactivity in the Reaction of Triethyl- and Triphenylphosphane HBr Salts with Dimethyl Acetals: A Novel Entry to α-Alkoxy-Functionalized Ylides and General Synthesis of Vinyl Ethers and Alkoxy Dienes

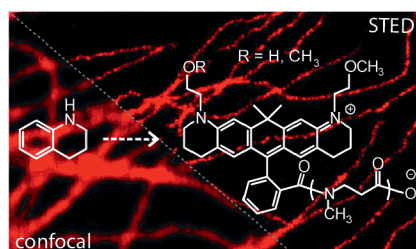


**Keywords:** Alkenes / Wittig reactions / Enol ethers / Acetals

## FULL PAPERS

## Fluorescent Dyes

A general route leading to fluorescent carbopyronines with variable functional groups is presented. The dyes absorb at 640 nm and emit at 660 nm, with a low intersystem crossing rate and possess excellent cellular imaging properties. Stimulated emission depletion provides nanoscopic images.



**K. Kolmakov, V. N. Belov,\* C. A. Wurm,  
B. Harke, M. Leutenegger, C. Eggeling,  
S. W. Hell\*** ..... 3593–3610

A Versatile Route to Red-Emitting Carbopyronine Dyes for Optical Microscopy and Nanoscopy



**Keywords:** Fluorescence / Chromophores / Carbocycles / Fluorescent probes / Fluorescence spectroscopy

# CONTENTS

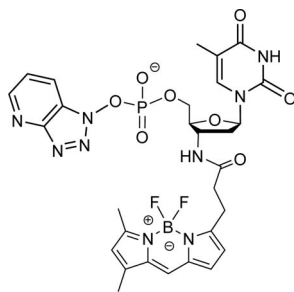
## Labeled Nucleotides

K. Gießler, H. Griesser, D. Göhringer,  
T. Sabirov, C. Richert\* ..... 3611–3620



Synthesis of 3'-BODIPY-Labeled Active Esters of Nucleotides and a Chemical Primer Extension Assay on Beads

**Keywords:** DNA / Oligonucleotides / Templated synthesis / Fluorescence



A synthesis of 3'-BODIPY-labeled active esters of nucleoside-5'-monophosphates was developed, and their template-directed incorporation was demonstrated in chemical primer extension assays performed on beads.

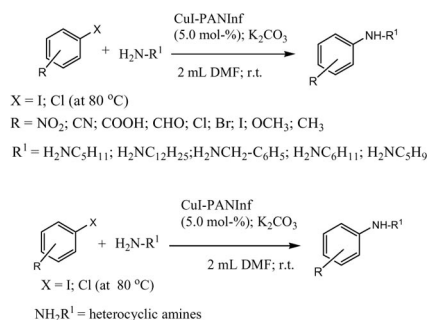
## Supported Catalysts

R. Arundhathi, D. C. Kumar,  
B. Sreedhar\* ..... 3621–3630



C–N Bond Formation Catalysed by CuI Bonded to Polyaniline Nanofiber

**Keywords:** Supported catalysts / Catalyst recycling / Copper / Aryl halides / Amines / Nitrogen heterocycles



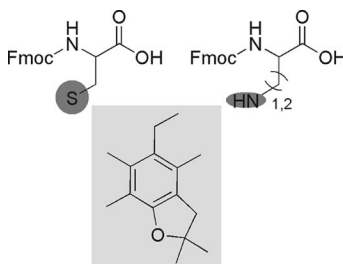
Polyaniline nanofiber as a macroligand for the supported cuprous iodide catalyst (CuI-PANInf) has been developed for the coupling of aryl halides with aliphatic, aromatic, and N(H)-heterocyclic amines under ambient conditions. This simple and efficient method is highly versatile, convenient and also the catalyst can be used for several cycles with good-to-excellent yields.

## Cys/Asn/Gln Side-Chain Protection

O. Garcia, J. M. Bofill, E. Nicolas,\*  
F. Albericio\* ..... 3631–3640

2,2,4,6,7-Pentamethyl-2,3-dihydrobenzofuran-5-methyl (Pbfm) as an Alternative to the Trityl Group for the Side-Chain Protection of Cysteine and Asparagine/Glutamine

**Keywords:** Amino acids / Peptides / Protecting groups / Amides / Solid-phase synthesis / Thiols



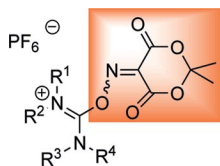
The benzyl derivative of the Pbf group has been proposed for the protection of the side chains of Cys/Asn/Gln. In the three cases, the new protecting group (Pbfm) can easily be removed during the cleavage and global deprotection step. Furthermore, when Cys is protected with the Pbfm group, it can be removed by oxidative treatment, thereby directly rendering the disulfide bridge on the solid phase.

## Peptide Coupling Reagents

A. El-Faham,\* R. Subirós-Funosas,  
F. Albericio\* ..... 3641–3649

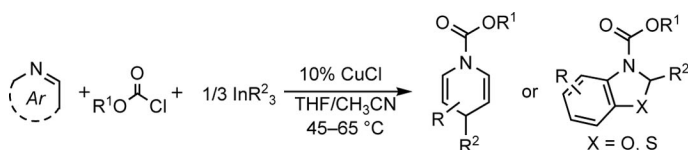
A Novel Family of Onium Salts Based Upon Isonitroso Meldrum's Acid Proves Useful as Peptide Coupling Reagents

**Keywords:** Solid-phase synthesis / Peptides / Amides / Coupling reagents / Chirality



A new family of uronium salts (HTMU, HMMU, and HDmPyMU) has been successfully synthesized from the sodium salt of isonitroso Meldrum's acid (HONM). The dimethylmorpholino analogue HMMU especially shows promising results in reducing racemization and enhancing coupling extension with poor nucleophiles.





A copper-catalyzed, multicomponent method to directly derivatize pyridine and other nitrogen-containing heterocycles (e.g. benzoxazoles, benzothiazoles, phthalazines) is described. This provides a mild and

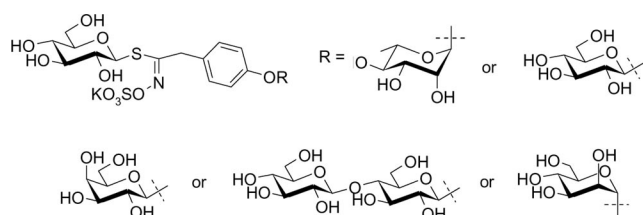
one-step approach to couple heterocycles with organoindium reagents without initial pre-derivatization of the ring or the use of strong nucleophiles.

**R. E. Beveridge, D. A. Black,  
B. A. Arndtsen\*** ..... 3650–3656

Copper-Catalyzed Multicomponent Coupling of Organoindium Reagents with Nitrogen-Containing Aromatic Heterocycles

**Keywords:** Nitrogen heterocycles / Organoindium reagents / Copper / Multicomponent reactions / Pyridinium salts

## Carbohydrate Chemistry



The synthesis of the major glucosinolate of *Moringa oleifera* and of other non-natural *O*-glycosylated derivatives of glucosinolate is reported. The synthetic sequence applied, which involves the conversion of carbo-

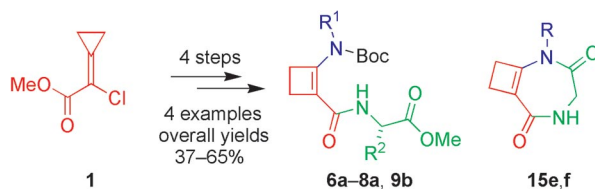
hydrate-based nitrostyrenes into the key thiohydroximates, appears to be sufficiently versatile to synthesize a range of glucosinolates bearing a glycosylated phenolic function.

**D. Gueyraud,\* R. Iori, A. Tatibouët,  
P. Rollin** ..... 3657–3664

Glucosinolate Chemistry: Synthesis of *O*-Glycosylated Derivatives of Glucosinolate

**Keywords:** Natural products / Carbohydrates / Glycosides / Hydroximates

## Non-Natural $\beta$ -Amino Acids



Methyl 2-chloro-2-cyclopropylideneacetate (**1**) is easily converted, in four steps each, into acyclic (**6**, **8**, **9**) as well as cyclic dipep-

tides **15** containing a cyclobutene-derived dehydro- $\beta$ -amino acid.

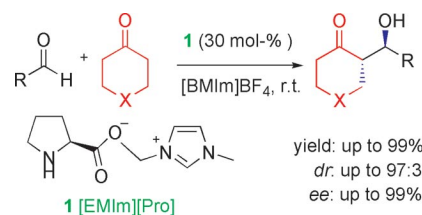
**A. de Meijere,\* M. Limbach, A. Janssen,  
A. Lygin, V. S. Korotkov** ..... 3665–3671

Versatile Access to 2-Aminocyclobutene-1-carboxylic Acid Derivatives and Their Incorporation into Small Peptides

**Keywords:** Cyclopropanes / Amino acids / Cyclobutenes / Peptidomimetics / Molecular diversity

## Asymmetric Catalysis

The first chiral anion modified ionic liquid catalyzed direct asymmetric aldol reaction has been developed. Moderate to good isolated yields, high *anti*-diastereoselectivities, and excellent enantioselectivities were afforded. The reaction was also carried out in an ionic liquid, and the system could be reused four times.



**Y. Qian, X. Zheng,  
Y. Wang\*** ..... 3672–3677

A Green and Efficient Asymmetric Aldol Reaction Catalyzed by a Chiral Anion Modified Ionic Liquid

**Keywords:** Asymmetric synthesis / Ionic liquids / Organocatalysis / Aldol reactions / Chirality

# CONTENTS

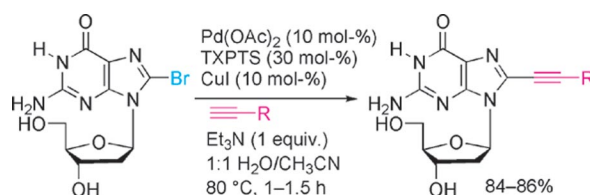
## Alkynylated Nucleosides

J. H. Cho, C. D. Prickett,  
K. H. Shaughnessy\* ..... 3678–3683



Efficient Sonogashira Coupling of Unprotected Halonucleosides in Aqueous Solvents Using Water-Soluble Palladium Catalysts

**Keywords:** Nucleosides / Cross-coupling / Palladium / Nitrogen heterocycles



The combination of  $\text{Pd}(\text{OAc})_2$ ,  $\text{CuI}$ , and TXPTS [trisodium tri(2,4-dimethyl-5-sulfonatophenyl)phosphane] provided a highly active catalyst for the alkylation of 8-bromopurines and 5-iodouridine in

$\text{H}_2\text{O}/\text{CH}_3\text{CN}$  in yields ranging from 42 to 98%. This methodology represents the first example of alkylation of unprotected 8-bromoguanosine in an aqueous solvent system.

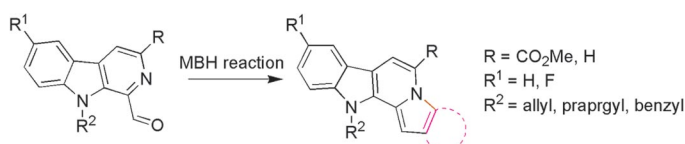
## Heterocyclic Chemistry

V. Singh, S. Hutait,  
S. Batra\* ..... 3684–3691



Advancing the Morita–Baylis–Hillman Chemistry of 1-Formyl- $\beta$ -carboline for the Synthesis of Indolizino-indole Derivatives

**Keywords:** Nitrogen heterocycles / Alkaloids / Morita–Baylis–Hillman reaction / Harmicine / Homofascaplysin



The utility of the Morita–Baylis–Hillman reaction of *N*-substituted 1-formyl- $\beta$ -carboline for the synthesis of indolizino-

indole derivatives mimicking harmicine and homofascaplysin frameworks is described.

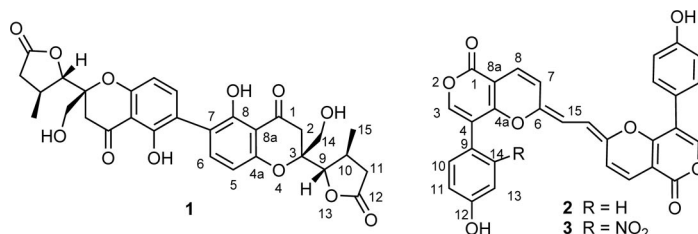
## Marine Fungi Metabolites

J. Yang, F. Xu, C. Huang, J. Li, Z. She,  
Z. Pei, Y. Lin\* ..... 3692–3695



Metabolites from the Mangrove Endophytic Fungus *Phomopsis* sp. (#zsu-H76)

**Keywords:** Natural products / Structure elucidation / Lactones / Biological activity



From the mangrove endophytic fungus *Phomopsis* sp. (#zsu-H76), three new dimers were isolated. Their structures were elucidated by spectroscopic analysis. Pri-

mary bioassays showed that **1** accelerated the growth of subintestinal vessel plexus (SIV) branch markedly, whereas **3** showed inhibition of SIV.

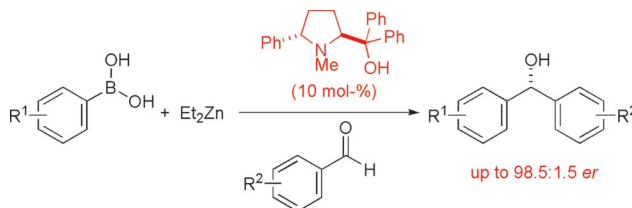
## Asymmetric Arylation of Aldehydes

A. V. Moro, E. R. T. Tiekink,  
J. Zukerman-Schpector, D. S. Lüdtkke,\*  
C. R. D. Correia\* ..... 3696–3703



Chiral Triphenylprolinol Ligands for the Efficient Catalytic Asymmetric Arylation of Aldehydes

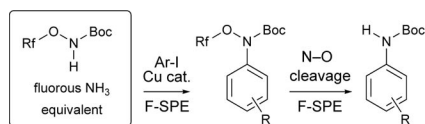
**Keywords:** Asymmetric synthesis / Amino alcohols / Heck reaction / Chirality / Aldehydes



The synthesis of several, easily recyclable, new chiral amino alcohols by Heck arylation of an endocyclic enecarbamate is described. These compounds were used as

chiral ligands for the catalytic asymmetric arylation of aldehydes. Chiral, nonracemic diarylmethanols were obtained in high yields and enantioselectivities

An ammonia equivalent for the amination of aryl iodides using a Cu catalyst is described. Purification of the products is greatly simplified through the use of a fluorous tag attached to a N–O linker. The linker is subsequently cleaved off under mild conditions. Sixteen different anilines were obtained in high yields and purities.

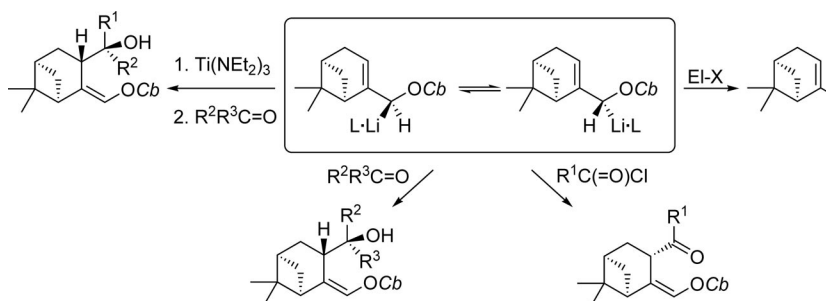


S. D. Nielsen, G. Smith, M. Begtrup,  
J. L. Kristensen\* ..... 3704–3710

Amination of Aryl Iodides Using a Fluorous-Tagged Ammonia Equivalent 

**Keywords:** Amination / Ammonia equivalent / Fluorous synthesis / N–O linker

## Chiral Homoenoate Reagents



Enantiopure myrtenyl *N,N*-diisopropylcarbamate is lithiated in the presence of achiral or chiral diamines. Analysis of the stereochemistry of the substitution products and of the homoallylic alcohols ob-

tained after reaction with carbonyl compounds (with or without transmetalation to titanium) allows conclusions regarding the dynamic diastereomeric resolution of the reaction to be drawn.

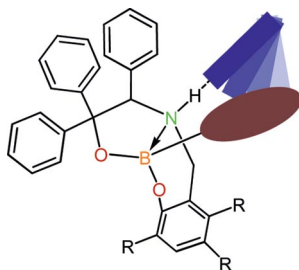
T. Hémerly, J. Becker, R. Fröhlich,  
D. Hoppe\* ..... 3711–3720

(–)-Myrtenyl *N,N*-Diisopropylcarbamate: Stereochemistry of Lithiation and Electrophilic Substitution Directed by Dynamic Kinetic Diastereoisomer Resolution

**Keywords:** Enantioselectivity / Diastereoselectivity / Lithiation / Aldol reactions / Kinetic resolution / Lithium/titanium exchange

## Liquid Crystals

Induced helicity results upon doping nematic mesophases with novel boronate–amine complexes that feature configurationally stable stereogenic boron and nitrogen centers.  $\pi$ -Stacking and hydrogen bonding, as indicated by NMR spectroscopy, offer a rationale for the efficient twisting of the nematic compounds and the sign of the induced helix.



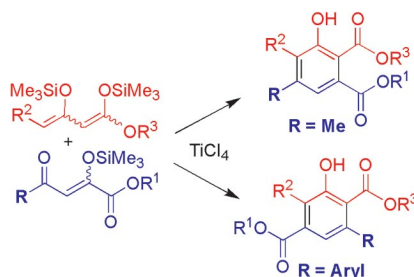
S. Schlecht, W. Frank,  
M. Braun\* ..... 3721–3731

Chelated Boronate–Imine and Boronate–Amine Complexes as Chiral Dopants for Nematic Liquid Crystals

**Keywords:** Chirality / Crystal structures / NMR spectroscopy / Optical properties / Supramolecular chemistry

## [3+3] Cyclocondensations

[3+3] Cyclocondensations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with ester-substituted 3-ethoxy- and 3-silyloxy-2-en-1-ones provide a regioselective approach to 3-hydroxyphthalates and 2-hydroxyterephthalates.



M. Shkoor, O. Fatunsin, A. Riahi,  
M. Lubbe, S. Reim, M. Sher, A. Villinger,  
C. Fischer, P. Langer\* ..... 3732–3742

Competing Regiodirecting Effects of Ester and Aryl Groups in [3+3] Cyclocondensations of 1,3-Bis(trimethylsilyloxy)-1,3-butadienes: Regioselective Synthesis of 3-Hydroxyphthalates and 2-Hydroxyterephthalates

**Keywords:** Arenes / Cyclization / Regioselectivity / Silicon / Enols

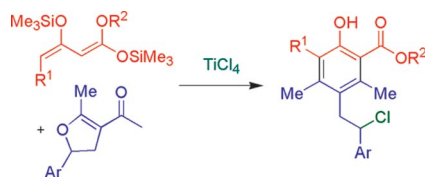
# CONTENTS

## [3+3] Cyclocondensation Reactions

M. Lau, M. Sher, A. Villinger, C. Fischer,  
P. Langer\* ..... 3743–3753

Domino [3+3] Annulation/Ring-Cleavage Reactions of 1,3-Bis(trimethylsilyloxy)-1,3-butadienes with 5-Aryl- and 5-Vinyl-3-acyl-4,5-dihydrofurans: Efficient Synthesis of 5-(4-Chlorobut-2-en-1-yl)- and 5-(2-Aryl-2-chloroethyl)salicylates

**Keywords:** Arenes / Regioselectivity / Annulation / Ring cleavage / Silyl enol ethers



The domino “[3+3] cyclization–ring-opening” reactions of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-acetyl-5-vinyl- and 3-acetyl-5-aryl-4,5-dihydrofurans give 5-(4-halobut-2-en-1-yl)- and 5-(2-aryl-2-chloroethyl)salicylates, respectively.

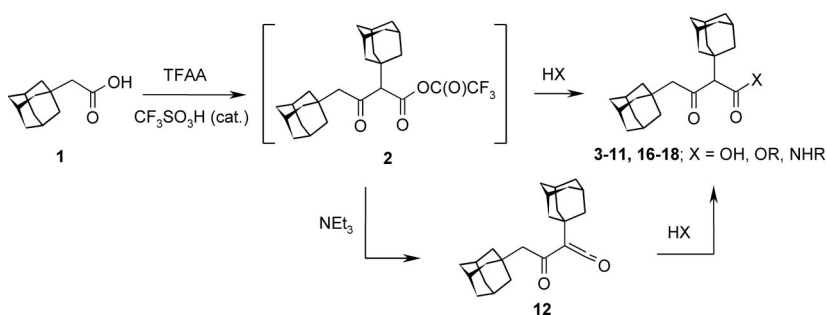
## β-Keto Acid Chemistry

V. Kovalev,\* E. Shokova, A. Shmailov,  
I. Vatsouro, V. Tafeenko ..... 3754–3761



Self-Acylation of 1-Adamantylacetic Acid in Trifluoroacetic Anhydride Medium: A Route to 2,4-Bis(1-adamantyl)acetoacetic Acid and Its Derivatives

**Keywords:** Acylation / Aldol reactions / Carboxylic acids / Perfluorinated solvents / Synthetic methods



2,4-Bis(1-adamantyl)acetoacetic acid, its ester and amide derivatives, and the stable 1-adamantyl-1-(1-adamantylacetyl)ketene were obtained through self-acylation of

1-adamantylacetic acid (**1**) in trifluoroacetic anhydride/ $\text{CF}_3\text{SO}_3\text{H}$  following treatment of mixed anhydride **2** with different nucleophilic reagents.

\* Author to whom correspondence should be addressed.

Supporting information on the WWW (see article for access details).