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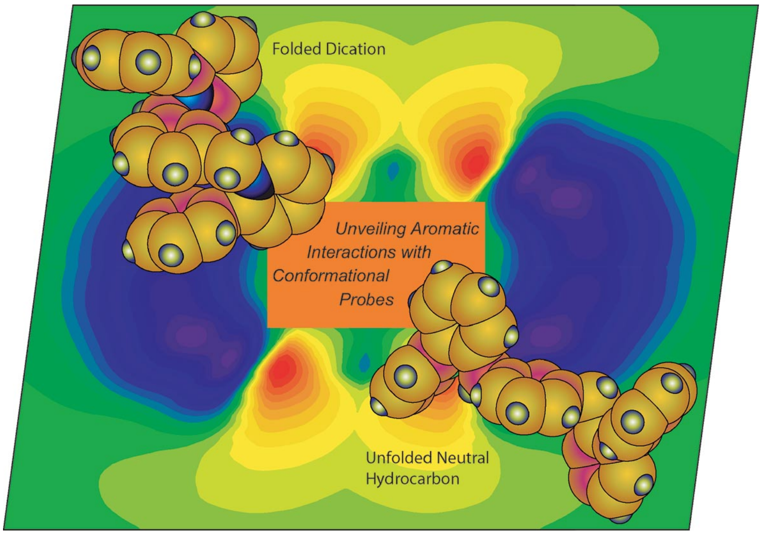
**A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.**

# COVER PICTURE

**The cover picture shows** isostructural, conformationally assayable molecules capable of associating aromatic moieties. The molecule that tends to fold is dicationic; the molecule that tends to unfold is a neutral hydrocarbon. This simple result deepens the conversation regarding dispersion in the context of π-stacking as a viable component in the control of conformation. Details are discussed in the article by A. Cammers et. al. on p. 5511ff.



# CONTENTS

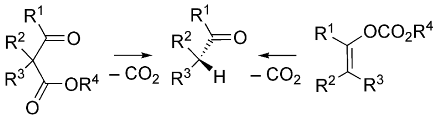
## MICROREVIEW

### Enantioselective Protonation

**J. Blanchet, J. Baudoux, M. Amere, M.-C. Lasne, J. Rouden* ....... 5493–5506**

Asymmetric Malonic and Acetoacetic Acid Syntheses – A Century of Enantioselective Decarboxylative Protonations

**Keywords:** Enantioselective protonation / Decarboxylation / Organocatalysis / Palladium / Enzymes



| Catalyst | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| Enzyme | OH | H, Ar, $NH_2$ | H, F, Me | H |
| Chiral base | OR | R, Ar, NHCOR | | H |
| Pd complex | R, Ar | R, Ar, F, Bn | | allyl, Bn |

The enantioselective decarboxylative protonation (EDP) of malonic or acetoacetic acid derivatives is a synthetic methodology by which the chirality of the product is generated during the enolate protonation step. This review focuses on the enantioselective decarboxylative protonation for the stereocontrol of C–H bond formation.

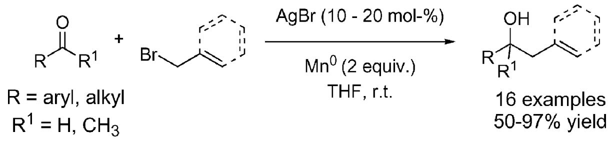
## SHORT COMMUNICATION

### Barbier-Type Alkylation

**N. T. Barczak, E. R. Jarvo* ... 5507–5510**

Silver-Catalyzed, Manganese-Mediated Allylation and Benzylation Reactions of Aldehydes and Ketones

**Keywords:** Allylation reaction / Barbier reaction / Silver / Manganese / Radical trap



Barbier-type alkylation reactions are catalyzed by a silver salt, AgBr, and mediated by standard, unactivated manganese powder. Allylation and benzylation reactions of aldehydes and ketones can be performed under these conditions. Preliminary mechanistic experiments are consistent with discrete organometallic complexes, not radical intermediates, taking part in the key C–C bond forming event.

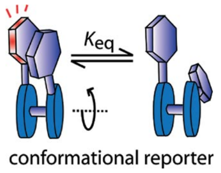
## FULL PAPERS

### Organic Solution State Conformation

**P. P. Poudel, J. Chen, A. Cammers* ......................... 5511–5517**

Intramolecular π-Stacking in Isostructural Conformational Probes Depends Strongly on Charge Separation, a Proton NMR Study

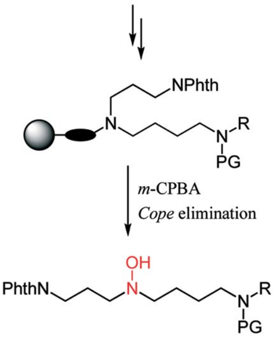
**Keywords:** π-Stacking / Solution state / Crystalline state / Conformation / NMR anisotropy



The solution-state conformation of a neutral analogue of a previously reported cationic π-stacking template is investigated to probe the effect of charge on conformation and to investigate the conformational control imparted by intramolecular aromatic association.

## Polyamine Chemistry

We present a general approach for the synthesis of *N*-hydroxylated polyamine derivatives on solid support. Protected polyamine frameworks, potential starting units for the synthesis of polyamine alkaloids, were convergently prepared "from the centre". The *N*-hydroxy groups were introduced during the cleavage of the products from the resins.

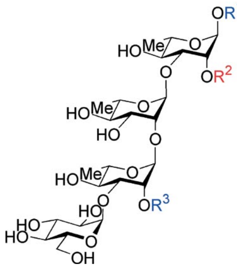


**M. Méret, S. Bienz*** .............. **5518–5525**

### Efficient and Flexible Solid-Phase Synthesis of *N*-Hydroxypolyamine Derivatives

**Keywords:** Polyamine / Hydroxylamine / Solid-phase synthesis / Elimination / Toxin

## Bacterial Oligosaccharides



| $R^1$ | $R^2$ | $R^3$ |
|---|---|---|
| Pr | Ac | H |
| Pr | H | H |
| Pr | Ac | βDGlc*p*NAc-(1 → |
| Pr | H | βDGlc*p*NAc-(1 → |
| → 3)-βDGlc*p*NAc-(1 → Pr | Ac | H |
| → 3)-βDGlc*p*NAc-(1 → Pr | H | H |

The convergent synthesis of a fully protected **(E)AB$_{\mathbf{Ac}}$C** tetrasaccharide and its efficient conversion into two tetra- and four pentasaccharides, representative of fragments of *Shigella flexneri* 3a and/or X O-antigens, synthesized as their propyl glycosides, is described.

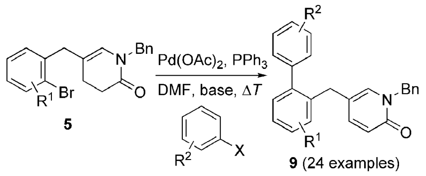
**J. Boutet, L. A. Mulard*** ....... **5526–5542**

### Synthesis of Two Tetra- and Four Pentasaccharide Fragments of *Shigella flexneri* Serotypes 3a and X O-Antigens from a Common Tetrasaccharide Intermediate

**Keywords:** Carbohydrates / Glycosylation / Antigens / Solvent effects / Protecting groups

## Biaryl Formation

Aryl bromides **5** react in the presence of a palladium catalyst and base with aryl halides to form unsymmetrical biaryl compounds **9**. In the course of the coupling reaction, the heterocycle is oxidized to the pyridinone.

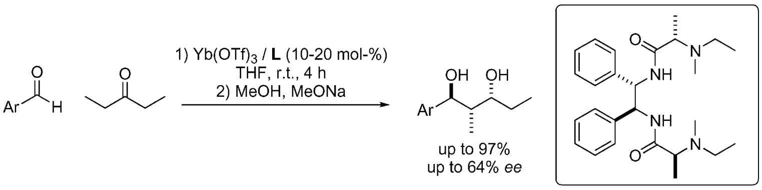


**G. Satyanarayana,**
**M. E. Maier*** ........................ **5543–5552**

### Unsymmetrical Biaryls by Palladium-Catalyzed Coupling of Aryl Halides with Internal Reduction

**Keywords:** Palladacycles / Biaryls / Cross-coupling / Domino reactions / Pyridinones

## Direct Asymmetric Aldol Reaction



A tandem asymmetric aldol reaction has been realized with chiral Yb complexes containing amino-acid-equipped chiral ligands. 1,3-*anti*-Diols with three stereogenic centers have been isolated as a result of the condensation of aliphatic ketones with aromatic aldehydes with up to 64% *ee*. Additional detailed investigations of the catalyst structure and the nature of the binding of both class of ligands has also been performed.

**M. Stodulski, J. Jaźwiński,**
**J. Mlynarski*** ........................ **5553–5562**

### Synthesis of Yb Complexes with Amino-Acid-Armed Ligands for Direct Asymmetric Tandem Aldol Reduction Reactions

**Keywords:** Aldol reactions / Chiral ligands / Asymmetric catalysis / Yterbium / Amino acids

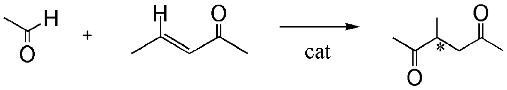
# CONTENTS

## Asymmetric Umpolung Catalysis

**K. J. Hawkes, B. F. Yates* ..... 5563–5570**

The Mechanism of the Stetter Reaction – A DFT Study

**Keywords:** Asymmetric catalysis / Umpolung / Carbenes / Reaction mechanisms / Density functional calculations



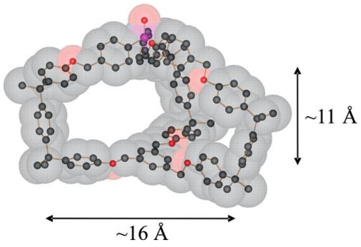
Density functional calculations on the mechanism and intermediates for a model asymmetric Stetter reaction are presented. C–C Coupling of the Breslow intermediate and the Michael acceptor is found to be rate determining, while the reaction stereoselectivity is linked to the relative stability of Breslow intermediate isomers.

## Homeomorphic Isomerisation

**F. Däbritz, A. Jäger,**
**I. Bauer* ............................... 5571–5576**

Synthesis, Derivatisation and Structural Characterisation of a New Macrobicyclic Phosphane Oxide Cryptand

**Keywords:** Macrobicycles / Cryptands / Homeomorphic isomers / Phosphanes / Phosphane oxides



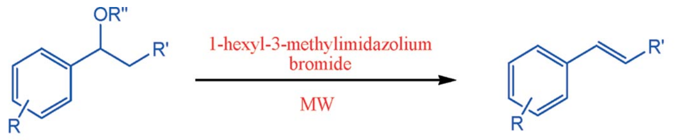
A tripod-coupling strategy led to a new phosphane oxide cage compound in high yield. The X-ray crystal structure shows a very large cavity and an *out*-positioned P=O moiety in the solid state. Surprisingly, the molecule appears to be flexible enough to undergo homeomorphic isomerisation in solution.

## Ionic-Liquid-Catalyzed Dehydration

**R. Kumar, A. Sharma, N. Sharma,**
**V. Kumar, A. K. Sinha* .......... 5577–5582**

Neutral Ionic Liquid [hmim]Br as a Green Reagent and Solvent for the Mild and Efficient Dehydration of Benzyl Alcohols into (*E*)-Arylalkenes Under Microwave Irradiation

**Keywords:** Ionic liquids / Dehydration / Benzyl alcohol / Microwave-assisted reaction / Alkenes



R = H, $OCH_3$, OH, $NO_2$, $C_6H_5$ etc. R' = H, $CH_3$, $C_2H_5$, $C_3H_7$ etc. R" = H, Ac, $COC_6H_5$

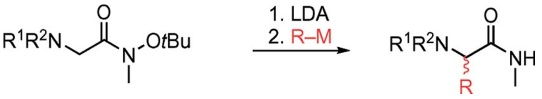
A mild and efficient, ionic-liquid-assisted, green protocol for the dehydration of benzyl alcohols and their acetylated/benzoylated derivatives to the corresponding (*E*)-arylalkenes under microwave irradiation has been developed. A wide range of olefins can be obtained without using harsh and expensive Brønsted/Lewis acids.

## Amino Acid Synthesis

**S. Hirner, D. K. Kirchner,**
**P. Somfai* ............................ 5583–5589**

Synthesis of α-Amino Acids by Umpolung of Weinreb Amide Enolates

**Keywords:** Amino acids / Umpolung / Arylglycines / Grignard reaction / Weinreb amides

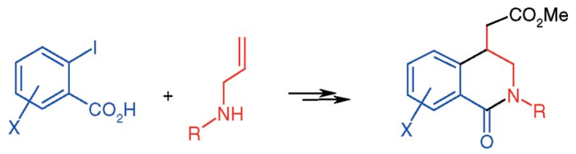


An efficient and diastereoselective synthesis of α-amino acids from readily available starting materials has been developed.

## Pd-Catalyzed Carbonylative Cyclization

**G. A. Ardizzoia, E. M. Beccalli, E. Borsini, S. Brenna, G. Broggini,* M. Rigamonti** ........................ **5590−5596**

Palladium-Catalyzed Cyclization/Carbonylation as a Direct Route to 4-[(Methoxycarbonyl)methyl]-3,4-dihydroisoquinolinones



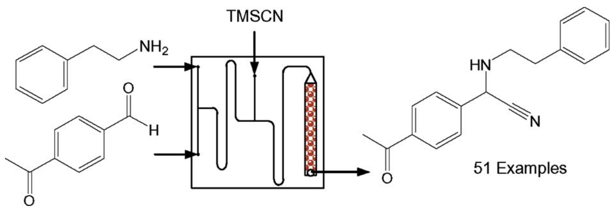
4-[(Methoxycarbonyl)methyl]-3,4-dihydroisoquinolin-1-ones have been efficiently prepared from *N*-allylamides of 2-iodobenzoic acids under 100 atm of carbon monoxide. Pyridine ring formation occurs through an intramolecular Pd-catalyzed carbon−carbon bond formation, followed by an alkoxycarbonylation process, which gives rise to the desired products and Pd$^0$-species.

**Keywords:** Carbonylations / Cyclizations / Palladium / Nitrogen heterocycles

## Micro-Reaction Technology

**C. Wiles,* P. Watts** ............... **5597−5613**

Evaluation of the Heterogeneously Catalyzed Strecker Reaction Conducted Under Continuous Flow



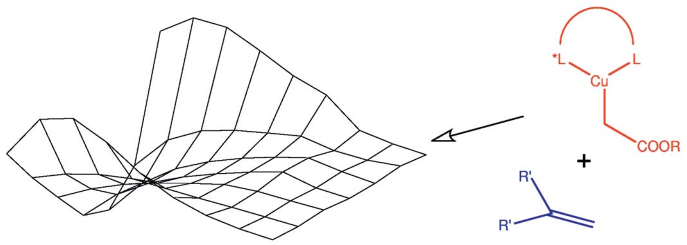
Using an integrated micro reactor capable of performing solution-phase and polymer-assisted steps in series, a solid-supported Lewis acid catalyst (polymer-supported scandium triflate) is evaluated and optimized for the high throughput synthesis of fifty one α-aminonitriles, in all cases demonstrating excellent yields (> 99.6%) and purities.

**Keywords:** Micro reactor / Strecker reaction / α-Aminonitriles / Heterogeneous catalysis / Solid-supported Lewis acid

## Homogeneous Catalysis

**G. Drudis-Solé, F. Maseras,* A. Lledós, A. Vallribera, M. Moreno-Mañas** ................ **5614−5621**

DFT/MM Study on Copper-Catalyzed Cyclopropanation − Enantioselectivity with No Enthalpy Barrier



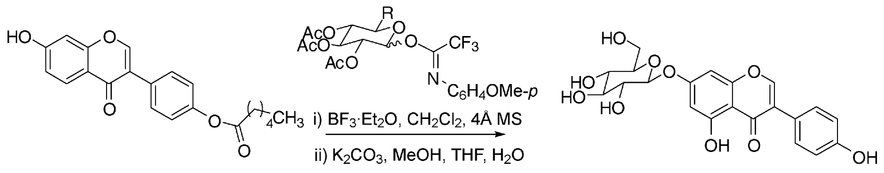
No barrier, no problem. The absence of an enthalpy barrier is only a minor obstacle for the computational analysis of the origin of enantioselectivity in the cyclopalladation of olefins by copper carbene complexes.

**Keywords:** Density functional calculations / Enantioselectivity / Cyclopropanation / Copper / Carbene ligands

## Isoflavone Phytoestrogens

**N. Al-Maharik, N. P. Botting*** ........................ **5622−5629**

An Efficient Method for the Glycosylation of Isoflavones



A new efficient, high-yielding glycosylation procedure is described for isoflavones, which employs 2,2,2-trifluoro-*N*-(*p*-methoxyphenyl)acetamidates as the glycosyl donors. This methodology was used to prepare isoflavone 7-*O*-glycosides and 7-*O*-glucuronides.

**Keywords:** Isoflavones / Phytoestrogens / Glucuronides / Glycosylation / Genistein

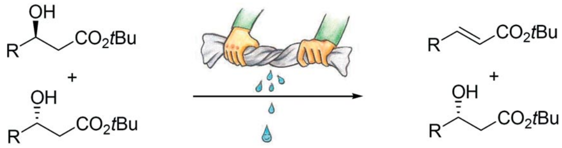
# CONTENTS

## Asymmetric Dehydration

**M. H. Lee, E. T. Choi, D. Kim, Y. M. Lee, Y. S. Park* ............................ 5630–5637**

Kinetic Resolution of β-Alkenyl-, β-Alkynyl- and β-Flavenyl-Substituted β-Hydroxy Esters in Asymmetric Dehydration

**Keywords:** Kinetic resolution / Asymmetric catalysis / Dehydration / Chiral ligands / Flavonoids



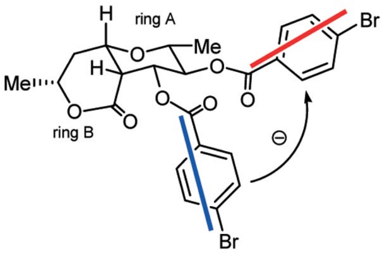
The catalytic asymmetric dehydration of β-hydroxy *tert*-butyl esters by kinetic resolution has been explored. In the presence of a prolinol chiral ligand and $BrZnCH_2$-$CO_2tBu$ highly enantio-enriched β-hydroxy esters were formed with selectivity factors up to 59.

## Natural Products

**K. Krohn,* M. H. Sohrab, T. van Ree, S. Draeger, B. Schulz, S. Antus, T. Kurtán ............................... 5638–5646**

Dinemasones A, B and C – New Bioactive Metabolites from the Endophytic Fungus *Dinemasporium strigosum*

**Keywords:** Endophytic fungi / *Dinemasporium strigosum* / Dinemasones A, B and C / Absolute configuration / Exciton chirality method / Octant rule



(2*R*,3*R*,4*R*,4a*R*,7*R*,8a*S*)-**2c**

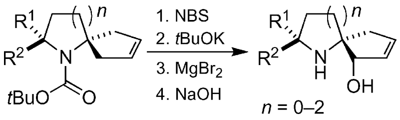
Three new metabolites, dinemasones A, B and C (**1a**, **2a**, **3a**) were identified from the endophytic fungus *Dinemasporium strigosum*. The compounds have the 1,7-dioxaspiro[5.5]undecane and hexahydropyrano-[4,3-*b*]pyran-5(7*H*)-one skeletons. Their absolute configurations were established by both their carbonyl n–π* CD transition and the exciton chirality method of their dibenzoates.

## Cephalotaxine Synthesis

**N. Yu. Kuznetsov, G. D. Kolomnikova, V. N. Khrustalev, D. G. Golovanov, Yu. N. Bubnov* ...................... 5647–5655**

The Combination of Diallylboration and Ring-Closing Metathesis in the Synthesis of Spiro-β-Amino Alcohols and (±)-Cephalotaxine

**Keywords:** Allylboration / Metathesis / Spiro compounds / Cephalotaxine / Allylic compounds / Rearrangement / Amino alcohols



A general method for the synthesis of diastereomerically pure spiro-β-amino alcohols is presented. These types of compounds are used in the preparation of a number of natural products such as cephalotaxine and halichlorine.

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* Author to whom correspondence should be addressed.

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