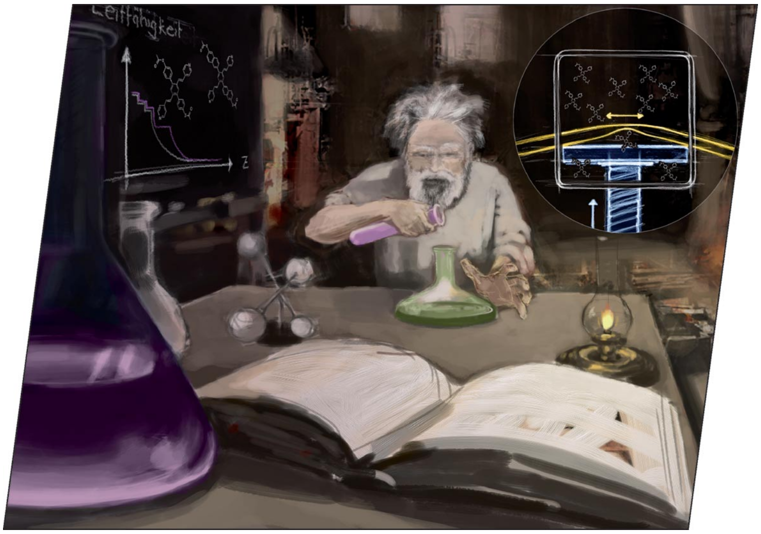
COVER PICTURE

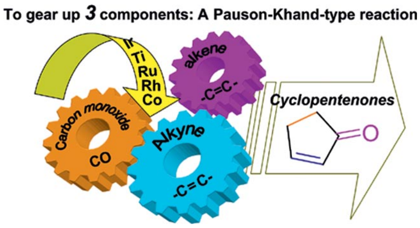
The cover picture shows the fertile combination of synthetic chemistry and experimental physics, both permanently making central contributions to hot scientific topics in spite of being classical scientific disciplines with long-standing traditions. The displayed scientist struggles with the synthesis of cruciform structures (displayed on the black board) for single-molecule-transport investigations in a mechanically controlled break junction setup (sketched in the inset at the upper right corner). More information on the design and synthesis of the cruciform structures, such as their immobilization experiments, is found in the article by M. Calame, M. Mayor et al. on p. 833ff. Serafin Pazdera is greatly akknowledged for the cover artwork.



MICROREVIEW

Pauson–Khand Reactions

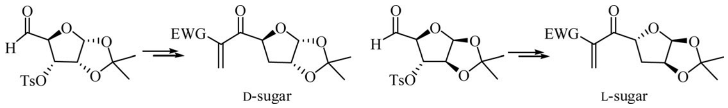
Keywords: Catalyst design / Cycloaddition / Carbon monoxide / Pauson–Khand reactions / Alkenes / Alkynes



Catalytic gearing up of alkene, alkyne and carbon monoxide: Pauson–Khand-type cyclizations.

SHORT COMMUNICATIONS

3-Deoxy Sugars



An innovative synthetic protocol is reported for the ready access to 3-deoxy sugars in both D and L forms as exclusive products (des >95%) in high yields through a stereodefined Lewis acid catalyzed reaction sequence of the sugar-derived Baylis−Hillman adducts.

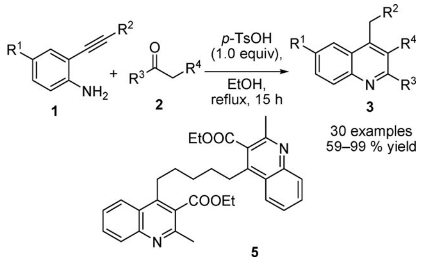
P. Radha Krishna,* A. Manjuvani, M. Narsingam, G. Raju .... **813−817**

Stereodefined Access to 3-Deoxy Sugars Through a Tandem Baylis−Hillman and Lewis Acid Catalyzed Reaction Sequence

Keywords: Carbohydrates / Deoxy sugars / Sugar-derived aldehydes

Quinoline Synthesis

A variety of 4-alkylquinolines were synthesized in good to excellent yields by reaction of readily available 2-alkynylanilines with activated ketones promoted by *p*-toluenesulfonic acid. Quinoline dimers can also be prepared with alkyl or aryl linkers at C-4.

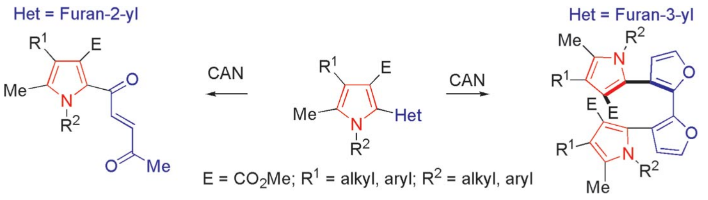


C. Peng, Y. Wang, L. Liu, H. Wang, J. Zhao, Q. Zhu* .... **818−822**

p-Toluenesulfonic Acid Promoted Annulation of 2-Alkynylanilines with Activated Ketones: Efficient Synthesis of 4-Alkyl-2,3-Disubstituted Quinolines

Keywords: Nitrogen heterocycles / Annulation / Friedländer reaction / Dimerization / Ketones

Heterocycles



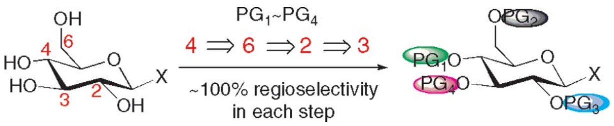
Although one might think that the 4-methoxyphenyl (PMP) group is probably prone to a removal under oxidative cleavage conditions, the cerium(IV)-mediated single-electron oxidations of PMP-substituted or -unsubstituted 2-(furan-2-yl)pyrroles and 2-(furan-3-yl)pyrroles provided a pyrrole-based 1,4-dicarbonyl compound and 3,3′-bis(pyrrol-2-yl)-2,2′-bifurans, respectively.

B. Alcaide,* P. Almendros,* R. Carrascosa, M. R. Torres .... **823−826**

Synthesis of a New Class of C_2-Symmetrical Biheteroaryls by Ammonium Cerium(IV) Nitrate Mediated Dimerization of 2-(Furan-3-yl)pyrroles

Keywords: Allenes / Cerium / Chemoselectivity / Dimerization / Heterocycles

Regioselective Protection



An acyl group was introduced at C(4)-OH of the glycopyranosides by organocatalysis with >99% regioselectivity. TBDPS, Boc, and BOM groups were sequentially introduced into the 4-*O*-acylglycopyranoside at C(6)-OH, C(2)-OH, and C(3)-OH, respectively, with ca. 100% regioselectivity in each step. Thus, a perfectly regioselective and sequential method for the preparation of orthogonally protected glycopyranosides has been developed.

W. Muramatsu, K. Mishiro, Y. Ueda, T. Furuta, T. Kawabata* .... **827−831**

Perfectly Regioselective and Sequential Protection of Glucopyranosides

Keywords: Regioselectivity / Protecting groups / Organocatalysis / Carbohydrates / Sequential protection

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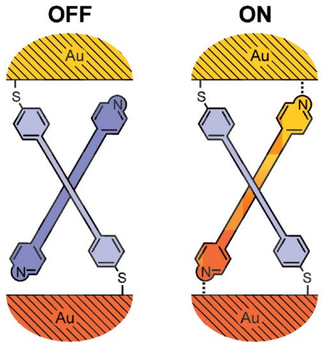
FULL PAPERS

Molecular Electronics

S. Grunder, R. Huber, S. Wu,
C. Schönenberger, M. Calame,*
M. Mayor* .... 833−845

Oligoaryl Cruciform Structures as Model Compounds for Coordination-Induced Single-Molecule Switches

Keywords: Molecular electronics / Conducting materials / Arenes / Cross-coupling / Rearrangement



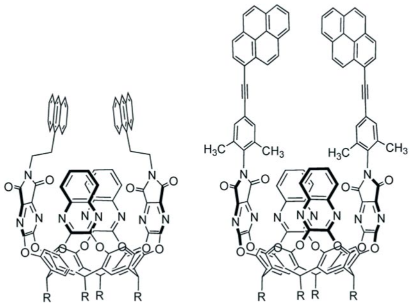
Two novel cruciform structures based on a crossed oligoaryl/oligo(phenylene-vinylene) system are synthesized and investigated as model compounds for a coordination-induced switching mechanism. The target structures are successfully integrated in a "wet" mechanically controllable break junction.

Molecular Switches

L. D. Shirtcliff,* H. Xu,
F. Diederich* .... 846−855

Complexation and Dynamic Switching Properties of Fluorophore-Appended Resorcin[4]arene Cavitands

Keywords: Host−guest systems / Cavitands / Excimer formation / Solvent effects / Fluorescence / Conformation analysis



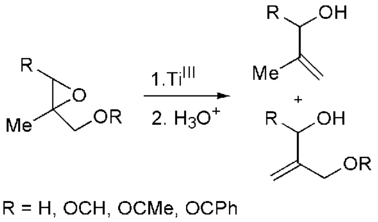
Dipyrene- and dianthracene-appended resorcin[4]arene cavitands undergo acid- or temperature-induced *vase−kite* switching and form remarkably stable complexes with suitably sized cycloalkanes. ^{1}H NMR spectroscopic investigations of intramolecular π−π stacking and fluorescence studies of excimer formation reveal a surprising conformational flexibility, which was further supported by molecular dynamics simulations.

Radical Elimination Reactions

A. Fernández-Mateos,* S. E. Madrazo,
P. H. Teijón, R. R. González ..... 856−861

Titanocene-Promoted Eliminations on Epoxy Alcohols and Epoxy Esters

Keywords: Radical reactions / Titanium / Elimination / Epoxides / Alcohols / Oxygen heterocycles



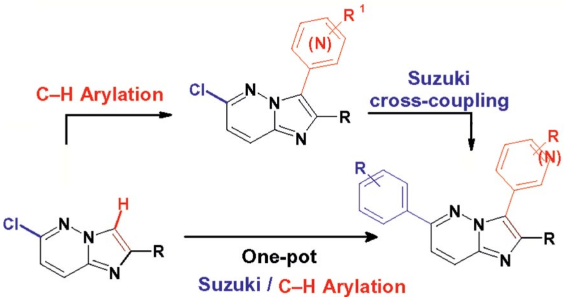
The scope and kinetics of the titanocene-induced selective elimination of hydrogen, hydroxy, formyloxyl, acetoxyl, and benzoyloxyl groups from substituted epoxides has been studied.

Arylated Imidazo[1,2-*b*]pyridazines

A. El Akkaoui, S. Berteina-Raboin,*
A. Mouaddib, G. Guillaumet ..... 862−871

Direct Arylation of Imidazo[1,2-*b*]pyridazines: Microwave-Assisted One-Pot Suzuki Coupling/Pd-Catalysed Arylation

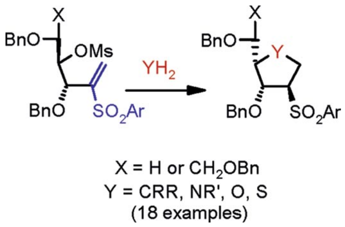
Keywords: Imidazo[1,2-*b*]pyridazines / C−H arylation / Microwaves / Multicomponent reactions / Cross-coupling / C−C coupling



Direct intermolecular C−H arylation of 6-chloroimidazo[1,2-*b*]pyridazine in its 3-position was achieved, and various 3-(hetero)arylimidazo[1,2-*b*]pyridazines were synthesized in good yields. This methodology was applied to the synthesis of 3,6-di- and 2,3,6-trisubstituted imidazo[1,2-*b*]pyridazines by a microwave-assisted, one-pot, two-step Suzuki cross-coupling/Pd-catalysed arylation process.

Carbocycles and Heterocycles

Pentosyl and hexosyl acyclic vinyl sulfones having a suitably positioned leaving group reacted with externally delivered carbon, nitrogen, oxygen, and sulfur nucleophiles to afford a series of five-membered carbocycles and heterocycles in a diastereoselective fashion. This diversity-oriented synthetic method generates a wide range of chirally pure cyclic compounds without using any metal catalyst.



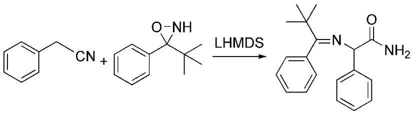
A. K. Atta, T. Pathak* .... 872−881

A General and Diastereoselective Route to Five-Membered Carbocycles and Heterocycles from Acyclic Vinyl Sulfone-Modified Carbohydrates

Keywords: Acyclic vinyl sulfones / Carbohydrates / Carbocycles / Heterocycles / Desulfonylation

Electrophilic Amination

A number of stable new *N*-H oxaziridines have been designed and prepared, and their reactivity as electrophilic sources of nitrogen investigated.



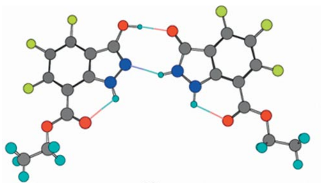
S. Blanc, C. A. C. Bordogna, B. R. Buckley, M. R. J. Elsegood, P. C. B. Page* .... 882−889

New Stable *N*-H Oxaziridines − Synthesis and Reactivity

Keywords: Oxaziridine / Amination / Nitrogen / Small ring systems

Fluorinated Indazoles

A series of new fluoroindazol-3-ols have been prepared from perfluorinated benzene dicarboxylic acids and fully studied by NMR (^{1}H, ^{13}C, ^{19}F, ^{15}N), affording data relating to the tautomeric forms in solution and in the solid state. An interesting solid-state structure containing both major tautomers − indazol-3-ol and indazolin-3-one − linked by hydrogen bonds is postulated for compound **12**.



12

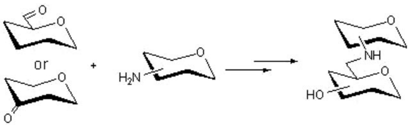
C. Pérez Medina,* C. López,* R. M. Claramunt, J. Elguero ..... 890−899

Trifluoro-3-hydroxy-1*H*-indazolecarboxylic Acids and Esters from Perfluorinated Benzenedicarboxylic Acids

Keywords: Nitrogen heterocycles / Indazoles / Tautomerism / Fluorine

Bridged Oligosaccharide Mimetics

Fast and facile approaches employing iodoxybenzoic acid (IBX) or Dess−Martin oxidation led to saccharide carbonyl structures which were *N*-linked to give the title compounds by subsequent reductive amination.



J. Neumann, J. Thiem* .... 900−908

Synthesis of Amino-Bridged Oligosaccharide Mimetics

Keywords: Carbohydrate mimetics / Reductive amination / Oxidation / Oligosaccharides / Bridging ligands / Natural killer cell

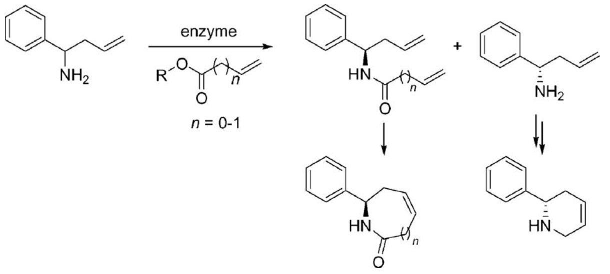
CONTENTS

Chemoenzymatic Synthesis

A. Hietanen, T. Saloranta, S. Rosenberg, E. Laitinen, R. Leino,* L. T. Kanerva* 909–919

Synthesis of Enantiopure Benzyl Homoallylamines by Indium-Mediated Barbier-Type Allylation Combined with Enzymatic Kinetic Resolution: Towards the Chemoenzymatic Synthesis of N-Containing Heterocycles

Keywords: Amines / Allylation / Enzyme catalysis / Kinetic resolution / Ring-closing metathesis



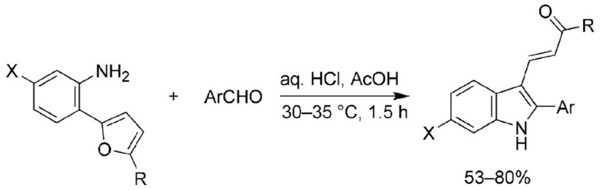
A series of enantiopure homoallylic amines were synthesized by Barbier-type allylation of *N*,*N*-dimethylsulfamoyl-protected aldimines followed by lipase-catalyzed enzymatic kinetic resolution. When an acyl donor with a terminal double bond was applied, both the enantiopure amine and the resolution product could be derivatized into N-containing heterocycles by ring-closing metathesis.

New Indole Synthesis

A. V. Butin,* M. G. Uchuskin, A. S. Pilipenko, F. A. Tsiunchik, D. A. Cheshkov, I. V. Trushkov 920–926

Furan Ring-Opening/Indole Ring-Closure: Pictet–Spengler-Like Reaction of 2-(*o*-Aminophenyl)furans with Aldehydes

Keywords: Aldehydes / Cyclization / Pictet–Spengler reaction / Synthetic methods / Heterocycles



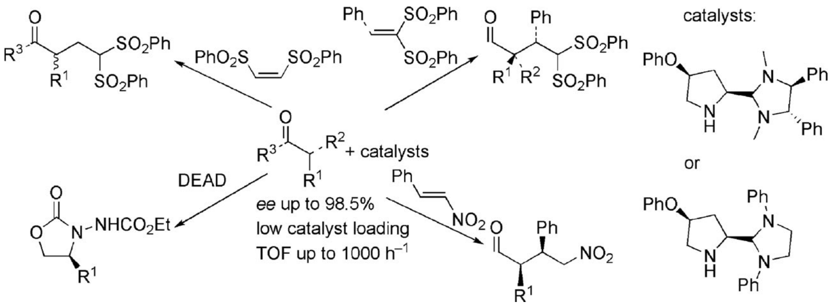
The indole unit has been synthesized by acid-induced C2–C3 bond formation. Under very mild conditions 2-(2-furyl)anilines react with (hetero)aromatic aldehydes to form 2-arylindoles bearing a 2-acylvinyl moiety at the 3-position that is suitable for further modification. This method also allows the synthesis of 2,3,6-trisubstituted indoles, which cannot be efficiently obtained by other methods.

Organocatalysis

A. Quintard, S. Belot, E. Marchal, A. Alexakis* 927–936

Aminal–Pyrrolidine Organocatalysts – Highly Efficient and Modular Catalysts for α-Functionalization of Carbonyl Compounds

Keywords: Asymmetric catalysis / Organocatalysis / Michael addition / Enamine / Pyrrolidine



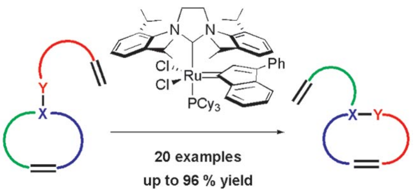
By changing the substituents of the pyrrolidine ring, two new highly complementary catalysts have been discovered. Even with low catalyst loadings, excellent enantioselectivities [enantiomeric excesses (*ee*s) up to 98.5%] could be reached in the α-functionalization of a wide range of linear/branched aldehydes and ketones at TOFs up to 1000 h^{-1}.

Olefin Metathesis

H. Clavier,* J. Broggi, S. P. Nolan* 937–943

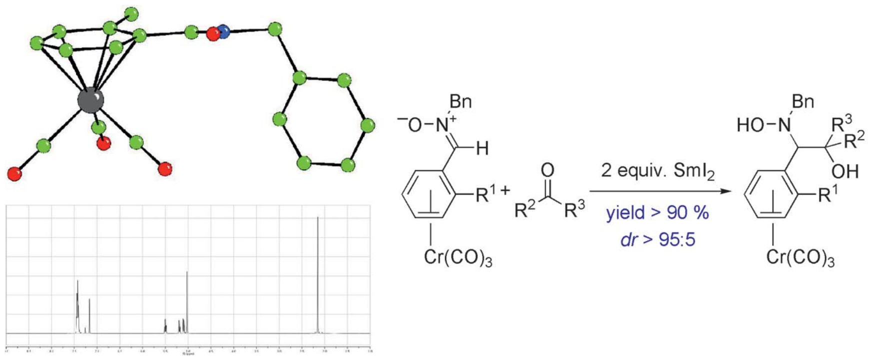
Ring-Rearrangement Metathesis (RRM) Mediated by Ruthenium-Indenylidene Complexes

Keywords: Metathesis / Ruthenium / Nitrogen heterocycles / Carbene ligands / Phosphanes / Rearrangement



Ruthenium-indenylidene complexes bearing N-heterocyclic carbenes and phosphanes have been investigated and found to promote efficiently the ring rearrangement of several cyclic compounds by alkene metathesis.

$Cr(CO)_3$-Complexed Aromatic Nitrones



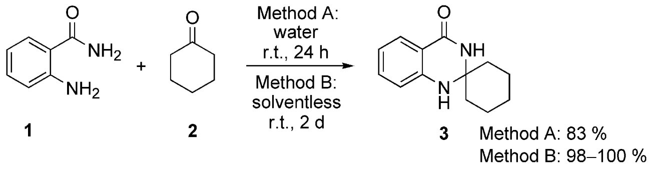
$Cr(CO)_3$-complexed aromatic nitrones were synthesized and characterized in solution and as solids. The reactivities of the planar-chiral complexes in SmI_2-induced pinacol-type reactions were studied. Reductive cross-coupling of *ortho*-substituted nitrones with carbonyl compounds proved to be highly chemo- and diastereoselective and afforded enantioenriched β-amino alcohol precursors in good yields.

M. Chavarot-Kerlidou,* M. Rivard,
B. Chamiot, F. Hahn, F. Rose-Munch,*
E. Rose, S. Py, P. Herson 944–958

Synthesis and Structural Characterization of Planar Chiral $Cr(CO)_3$-Complexed Aromatic Nitrones – Valuable Substrates for Asymmetric SmI_2-Induced Coupling Reactions

Keywords: Nitrones / Arene ligands / Chromium / Planar chirality / Samarium / Cross-coupling / Amino alcohols

Spirocyclization



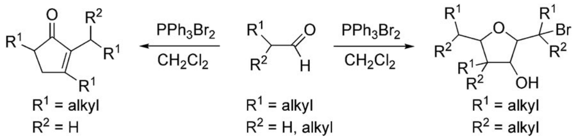
Spirocyclization of anthranilamide (**1**) with cyclohexanone (**2**) under either aqueous or solventless conditions led to spiroquinazolinone **3**. To investigate the limit of the green methodologies, α- and β-amino(cyclo)alkyl carboxamides and ketones were reacted together to give 1,4-diazaspiro[4.5]decan-2-one and 2,2′-disubstituted quinazolinones.

F. Miklós, F. Fülöp* 959–965

“Dry” and “Wet” Green Synthesis of 2,2′-Disubstituted Quinazolinones

Keywords: Water chemistry / Spiro compounds / Nitrogen heterocycles / Green chemistry / Sustainable chemistry

Cyclotrimerization of Aldehydes



Cyclotrimerization of α-monosubstituted (R^1 = alkyl, R^2 = H) or α-disubstituted (R^1,R^2 = alkyl) aldehydes with dibromotriphenylphosphorane (PPh_3Br_2) yields cyclopentenones or tetra-substituted tetrahydrofurans, respectively.

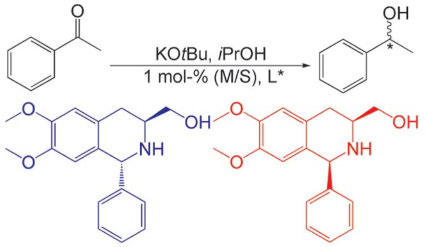
M.-P. Heck,* C. Matt, A. Wagner,
L. Toupet, C. Mioskowski 966–971

New Cyclotrimerization of Aldehydes to Cyclopentenone or Tetrahydrofuran Induced by Dibromotriphenylphosphorane

Keywords: Aldehydes / Aldol reactions / Cyclotrimerization / Phosphorus

Tetrahydroisoquinoline Ligands

The synthesis of new chiral tetrahydroisoquinoline (TIQ) ligands for asymmetric transfer hydrogenation reactions is reported. The ligands were complexed with Ru, Rh and Ir and tested in the hydrogenation reaction of alkyl aryl ketones. The best ligand gave an enantioselectivity of 99 %.



S. K. Chakka, P. G. Andersson,
G. E. M. Maguire, H. G. Kruger,*
T. Govender* 972–980

Synthesis and Screening of C^1-Substituted Tetrahydroisoquinoline Derivatives for Asymmetric Transfer Hydrogenation Reactions

Keywords: Tetrahydroisoquinoline / Amino alcohols / Ruthenium / Hydrogenation / Asymmetric catalysis

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* Author to whom correspondence should be addressed.

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

XXIVth European Colloquium on Heterocyclic Chemistry

Plenary Lectures

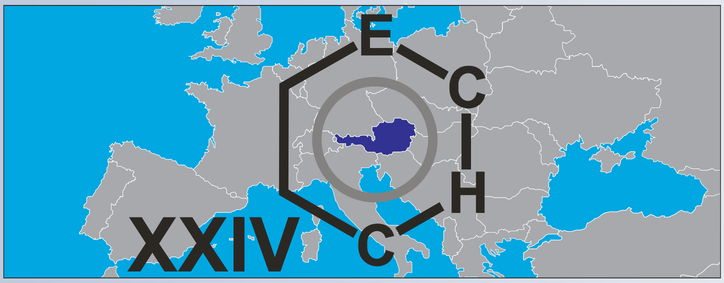
Janine Cossy	(FRA)
Alois Fürstner	(GER)
Frank Glorius	(GER)
David W. Knight	(UK)
Paul Kosma	(AUT)
Lechoslaw Latos-Grażyński	(PL)
Enrico Marcantoni	(ITA)
Carmen Najera	(ESP)
Mogens Nielsen Bronsted	(DK)
Jay Siegel	(CH)
Tomas Torres	(ESP)
Rodney Townsend	(GB)
Kristina Wähälä	(FIN)

August 23 - 27, 2010
Vienna / Austria

The meeting will focus on the following topics

- Novel Methods in Heterocyclic Synthesis
- Heterocycles in Medicinal Chemistry
- Heterocyclic Agrochemicals
- Heterocyclic Materials
- Heterocycles in Sustainable Chemistry

The meeting in the Heart of Europe



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Johannes Fröhlich, Chairman of the XXIVth ECHC
Institute of Applied Synthetic Chemistry, Vienna University of Technology
Getreidemarkt 9/163-OC, A-1060 Vienna (Austria/EU)
Tel.: +43 1 58801 16301 Fax: +43 1 58801 16399

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