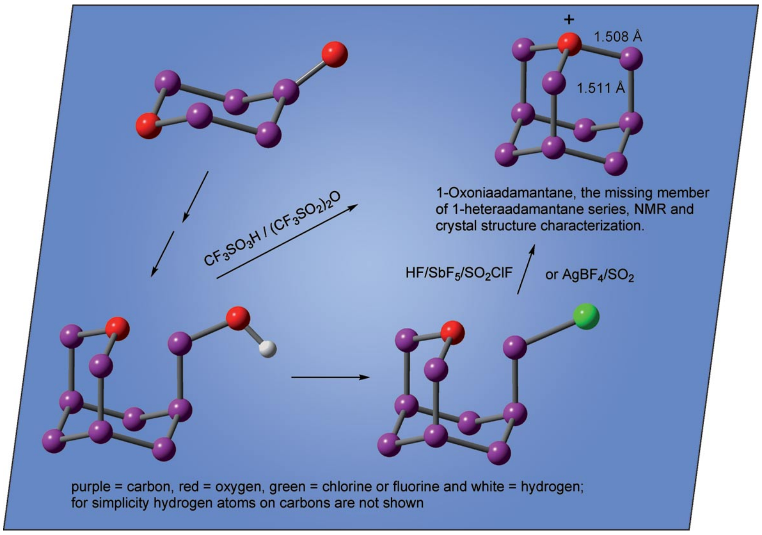
HUNGARY
ITALY
GERMANY
GREECE
BELGIUM
FRANCE
SWEDEN
CZECH REPUBLIC
AUSTRIA
PORTUGAL
SPAIN
NETHERLANDS

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 the preparation of 1-oxonia-adamantane by several different pathways under superacidic conditions. The structure of the intriguing bridgehead oxonium ion was characterized by NMR spectroscopy, DFT calculations and X-ray crystallography as a $CB_{11}C_{16}H_6$ counteranion salt. The cation is a missing member of the diamondoid 1-heteroadamantane series. Details are discussed in the Short Communication by G. K. S. Prakash, G. A. Olah et al. on p. 4555ff.



CONTENTS

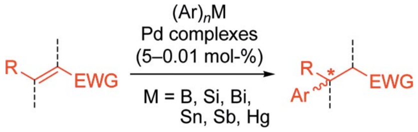
MICROREVIEW

Asymmetric Catalysis

A. Gutnov* **4547–4554**

Palladium-Catalyzed Asymmetric Conjugate Addition of Aryl–Metal Species

Keywords: Michael additions / Asymmetric catalysis / Palladium / Arylboronic acids / Enones



The use of Pd complexes as catalysts for asymmetric conjugate additions of organometallics to activated Michael acceptors is reviewed. It may be viewed as an important complement to the traditional Cu- and Rh-catalyzed reactions for the construction of homochiral aryl-containing molecular frameworks, offering high enantioselectivities, lower catalyst loadings, and mild reaction conditions.

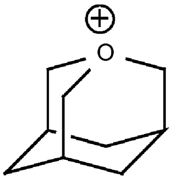
SHORT COMMUNICATIONS

Cage Oxonium Ions

M. Etzkorn, R. Aniszfeld, T. Li, H. Buchholz, G. Rasul, G. K. S. Prakash*, G. A. Olah* **4555–4558**

1-Oxoniaadamantane

Keywords: Tertiary cage oxonium ions / 1-Oxoniaadamantane / Bridgehead oxonium ions / Heteroadamantanes



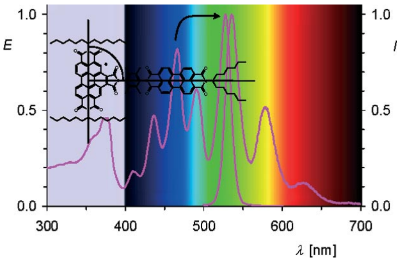
The unusual tertiary cage oxonium ion, 1-oxoniaadamantane, was prepared from suitable bicyclic precursors. The compound was characterized by NMR spectroscopy and X-ray crystallographic structure determination. Calculations compare the data with those for the parent adamantane, 1-oxonia-, and 1-thiaadamantanes.

FRET and Orthogonality

H. Langhals,* S. Poxleitner, O. Krotz, T. Pust, A. Walter **4559–4562**

FRET in Orthogonally Arranged Chromophores

Keywords: FRET (Fluorescence Resonance Energy Transfer) / Fluorescence spectroscopy / Nitrogen heterocycles / Arenes / Photophysics



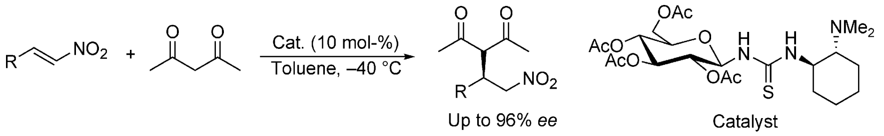
Perylene and benzoperylene carboxylic imides were arranged to form a bichromophoric dye with orthogonal electronic transition moments. However, quantitative Förster-type energy transfer (FRET) proceeds in spite of this orthogonality.

Asymmetric Michael Addition

P. Gao, C. Wang, Y. Wu, Z. Zhou,* C. Tang **4563–4566**

Sugar-Derived Bifunctional Thiourea Organocatalyzed Asymmetric Michael Addition of Acetylacetone to Nitroolefins

Keywords: Thiourea / Michael addition / Ketones / Nitroalkenes / Enantioselectivity



An efficient bifunctional thiourea organocatalyzed asymmetric Michael addition of acetylacetone to nitroolefins was developed affording the corresponding enantiomerically enriched nitro ketone derivatives with good to excellent chemical yields (up to >99%) and enantioselectivities (up to 96%).

Electrooxidative Homocouplings

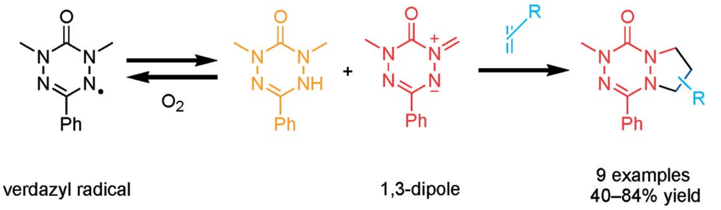
Electron uptake and it goes... A new anaerobic electrooxidative homocoupling of aryl−boron derivatives was developed in the presence of catalytic amounts of both $Pd(OAc)_2$ and *p*-benzoquinone, which serves as a redox mediator. The homocoupling can be performed in water and avoids the use of stoichiometric chemical oxidants.

C. Amatore,* C. Cammoun, A. Jutand* .... **4567−4570**

$Pd(OAc)_2$/*p*-Benzoquinone-Catalyzed Anaerobic Electrooxidative Homocoupling of Arylboronic Acids, Arylboronates and Aryltrifluoroborates in DMF and/or Water

Keywords: Palladium / Homocoupling / Boron / Borates / Electrooxidation

Synthetic Methods



The 1,5-dimethyl-3-phenyl-6-oxoverdazyl radical reacts with itself in the presence of oxygen to form an azomethine imine which undergoes a 1,3-dipolar cycloaddition with various dipolarophiles to form a series of dihydrotetrazinone heterocyclic structures.

A. Yang, T. Kasahara, E. K. Y. Chen, G. K. Hamer, M. K. Georges* .... **4571−4574**

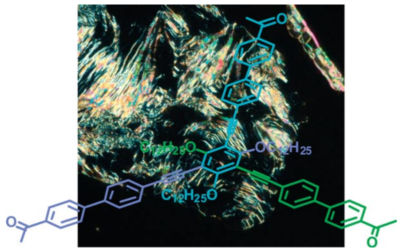
1,3-Dipolar Cycloaddition Reactions Initiated with the 1,5-Dimethyl-3-phenyl-6-oxoverdazyl Radical

Keywords: Verdazyl radicals / 1,3-Dipolar cycloaddition / Azomethine imine / Dihydrotetrazinone

FULL PAPERS

Disc−Rod Mesogens

Biphenylylacetylene-based mesogens are prepared by Sonogashira coupling and their mesomorphic properties are related to the structural (linear vs. trigonal) and electronic features of the target compounds. While the C_3-symmetric tris(alkynyl) compound is non-mesogenic, the linear biphenylylacetylene forms a smectic liquid-crystal phase.



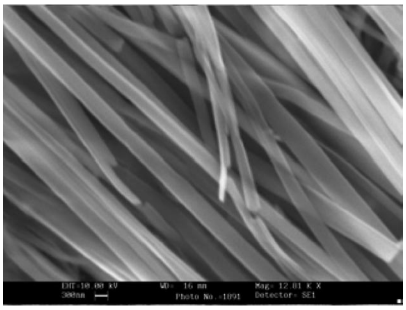
G. Hennrich,* P. D. Ortiz, E. Cavero, R. E. Hanes, J. L. Serrano .... **4575−4579**

Biphenyl-Based Disc- vs. Rod-Shaped Phenylacetylenes: Mesomorphism and Electronic Properties

Keywords: Liquid crystals / Structure-activity relationships / Alkynes / Cross-coupling / Biphenyls

Biomimetic Gels

Using the silk peptidic sequence Gly−Ala−Gly−Ala as a core, self-assembling tetrapeptides were constructed, and their aggregation process was been controlled by modulation of the length of the alkyl terminal groups.



S. Iqbal, J. F. Miravet,* B. Escuder* .... **4580−4590**

Biomimetic Self-Assembly of Tetrapeptides into Fibrillar Networks and Organogels

Keywords: Self-assembly / Gels / Peptides / Silk / Fibers / Protein folding

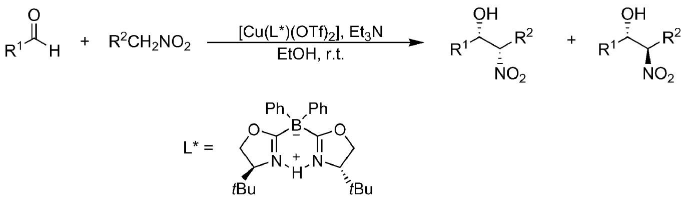
CONTENTS

Asymmetric Catalysis

A. Toussaint, A. Pfaltz* 4591–4597

Asymmetric Henry Reactions Catalyzed by Metal Complexes of Chiral Boron-Bridged Bisoxazoline (borabox) Ligands

Keywords: Henry reaction / Asymmetric catalysis / Borabox ligands / Copper complexes / Nitropropane



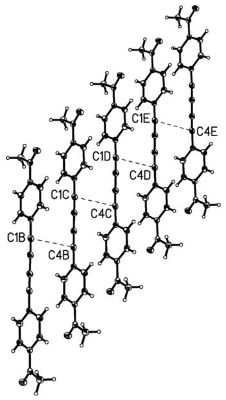
Readily available boron-bridged bisoxazolines induce high enantio- and diastereoselectivities in copper-catalyzed nitroaldol (Henry) reactions.

Polyynes

K. Osowska, T. Lis,
S. Szafert* 4598–4606

Protection/Deprotection-Free Syntheses and Structural Analysis of (Keto-aryl)-diynes

Keywords: Polyynes / Homocoupling / Dimerization / Halogenation / Alkynes



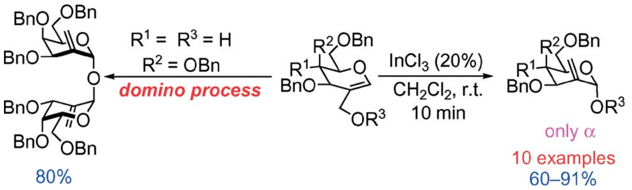
New two- and three-step synthetic routes for the synthesis of (keto-aryl)diacetylenes have been developed. Neither include protection/deprotection of the carbonyl substituent. All compounds were characterized and their crystal structures (including packing motifs) analyzed in detail.

InCl$_3$-Catalyzed [1,3]-Migrations

P. Nagaraj, N. G. Ramesh* 4607–4614

InCl$_3$-Catalyzed Rapid 1,3-Alkoxy Migration in Glycal Ethers: Stereoselective Synthesis of Unsaturated α-*O*-Glycosides and an α,α-(1→1)-Linked Disaccharide

Keywords: Carbohydrates / Glycosylation / Lewis acids / Glycosides / Disaccharides



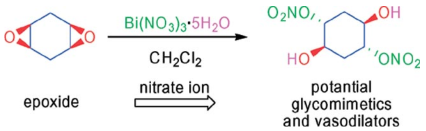
InCl$_3$ rapidly facilitates [1,3]-alkoxy migrations of allylic ethers of glycals, resulting in stereoselective formation of α-*O*-unsaturated glycosides. Quite surprisingly, under identical conditions, 2-*C*-hydroxymethyl galactal (an allylic alcohol) is transformed into an α,α-(1→1)-linked disaccharide derivative by a domino process.

Cyclitol Organonitrates

H. Cavdar, N. Saracoglu* 4615–4621

Synthesis of New β-Hydroxy Nitrate Esters as Potential Glycomimetics or Vasodilators

Keywords: Cyclitols / Epoxidation / Nucleophilic addition / Ring expansion / Lewis acids

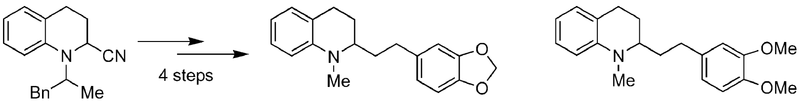


New β-hydroxy nitrates have been synthesized by the ring-opening reaction of epoxides with Bi(NO$_3$)$_3$·5H$_2$O used both as a catalyst and reagent. The synthesized molecules are both potential cyclitol mimics and vasodilators due to the presence of the hydroxy groups and nitrate esters.

Tetrahydroquinoline Alkaloids

S. Shahane, F. Louafi, J. Moreau,
J.-P. Hurvois,* J.-L. Renaud,
P. van de Weghe, T. Roisnel ... 4622–4631

Synthesis of Alkaloids of *Galipea officinalis* by Alkylation of an α-Amino Nitrile



(±)-Galipinine (±)-Cuspareine

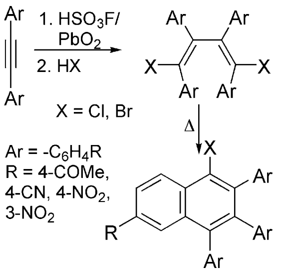
Four *G. officinalis* tetrahydroquinoline alkaloids were synthesised by alkylation of an α-aminonitrile prepared by controlled potential electrolysis. New C–C bonds were formed by reversal of the C=N bond's polarity, giving bifunctional α-amino nitriles. $NaBH_4$-mediated reduction proceeded stereoselectively, yielding 2-alkyl-tetrahydroquinolines that were readily converted into the title compounds.

Keywords: Alkaloids / Alkylation / Tetrahydroquinolines / α-Amino nitriles / Umpolung

Cyclization of Diarylacetylenes

A. V. Vasilyev,* A. O. Shchukin,
S. Walspurger, J. Sommer* ... 4632–4639

Protonation of Diarylacetylenes in Superacid HSO_3F and Their Oxidation in the HSO_3F/PbO_2 System: One-Pot Synthesis of Polysubstituted Naphthalenes



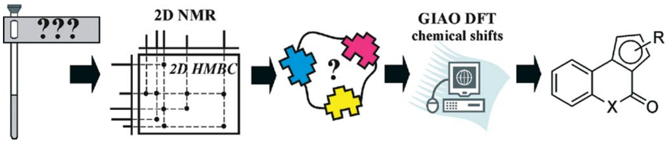
In HSO_3F, diarylacetylenes bearing electron-withdrawing groups form stable ions, protonated at these groups. Oxidation of the diarylacetylenes in HSO_3F/PbO_2 and quenching with HCl (or HBr) results in the formation of (*E*,*E*)-1,4-dichloro(or dibromo)-1,2,3,4-tetraarylbuta-1,3-dienes, which spontaneously undergo electrocyclic transformation into substituted naphthalenes.

Keywords: Alkynes / Protonation / Oxidation / Radical ions / Electrocyclic reactions

GIAO Structure Elucidation

S. Latypov,* A. Balandina,
M. Boccalini, A. Matteucci, K. Usachev,
S. Chimichi* 4640–4646

Structure Determination of Regioisomeric Fused Heterocycles by the Combined Use of 2D NMR Experiments and GIAO DFT ^{13}C Chemical Shifts



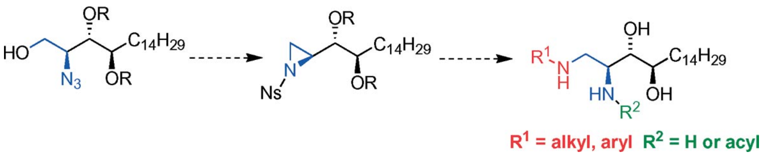
A combination of NMR experiments (2D HMBC) and theory (DFT GIAO) is a reliable and convenient way for the structure elucidation of regioisomeric heterocyclic systems.

Keywords: NMR spectroscopy / Structure elucidation / Density functional calculations / Oxazoloquinolinones / Oxazolocoumarins / Heterocycles

Sphingolipid Analogues

Y. Harrak, A. Llebaria,
A. Delgado* 4647–4654

A Practical Access to 1,2-Diaminophytosphingolipids



A practical approach to the synthesis of phytosphingolipids containing the 1,2-diamino framework is described. The method is based on the regioselective ring-opening of *N*-nosylaziridines with primary or secondary amines, acylation and subsequent deprotection steps.

Keywords: Small ring systems / Sphingolipids / Aziridines / Sulfonamides / Heterocycles

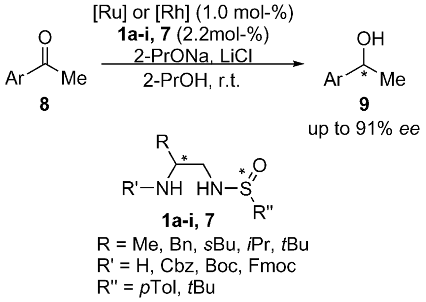
CONTENTS

Enantioselective Transfer Hydrogenation

L. Zani, L. Eriksson, H. Adolfsson* **4655–4664**

Synthesis of Novel Amino-Acid-Derived Sulfinamides and Their Evaluation as Ligands for the Enantioselective Transfer Hydrogenation of Ketones

Keywords: Amino acids / Sulfinamides / N-Ligands / Homogeneous catalysis / Transfer hydrogenation



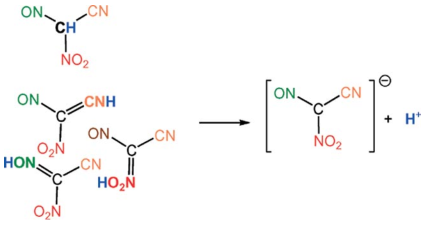
A series of novel chiral mono-sulfinyl diamines were prepared using a straightforward procedure starting from simple amino acids. Rhodium and ruthenium catalysts based on these mono-sulfinyl diamines were employed in the enantioselective transfer hydrogenation of alkyl-aryl ketones generating the corresponding chiral alcohols with up to 91% *ee*.

Gas-Phase Acidities

H. Brand, J. F. Liebman, A. Schulz* **4665–4675**

Cyano-, Nitro- and Nitrosomethane Derivatives: Structures and Gas-Phase Acidities

Keywords: Methanides / Pseudohalides / Resonance / Acidity / Protonation



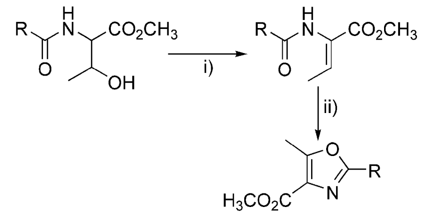
The structures and intrinsic gas-phase acidities of CN-, NO_2- and NO-substituted methanes have been studied by using the B3LYP/aug-cc-pvTZ method of theory. For the NO-substituted methanes, the oxime species (*aci* form) represents the most stable isomer, whereas for the cyano- and nitromethane derivatives the C–H bonded isomer was found to be the more stable species.

Oxazoles from β-Hydroxyamino Acids

P. M. T. Ferreira,* L. S. Monteiro,* G. Pereira **4676–4683**

Synthesis of Substituted Oxazoles from *N*-Acyl-β-hydroxyamino Acid Derivatives

Keywords: Amino acids / Dehydroamino acids / Iodine / Cyclization / Oxygen heterocycles / Nitrogen heterocycles



i) 1. Boc_2O (1 equiv.), DMAP in dry ACN; 2. TMG
ii) 1. I_2, K_2CO_3 in THF at 80 °C; 2. DBU at 80°C

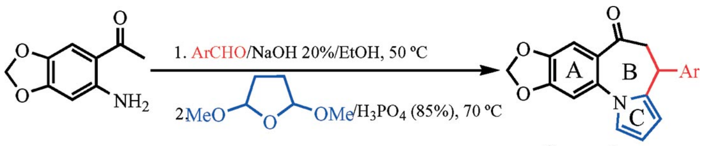
Several 2-substituted methyl 5-methyloxazole-4-carboxylates were prepared from *N*-acyldehydroaminobutyric acid derivatives by treatment with I_2 and then DBU. Under the same conditions, *N*-acyldehydrophenylalanine and alanine derivatives gave low or zero yields of oxazoles. However, when DBU was omitted, the major products obtained were the corresponding β-iodo- or β,β-diiododehydroamino acids.

Heterocyclic Chemistry

R. Abonia,* P. Cuervo, B. Insuasty, J. Quiroga, M. Nogueras, J. Cobo **4684–4689**

A Simple Two-Step Sequence for the Synthesis of Novel 4-Aryl-4,5-dihydro-6*H*-[1,3]dioxolo[4,5-*h*]pyrrolo[1,2-*a*][1]benzazepin-6-ones from 6-Amino-3,4-methylenedioxyacetophenone

Keywords: Phosphoric acid / Michael addition / Chalcones / Cyclization / Heterocycles



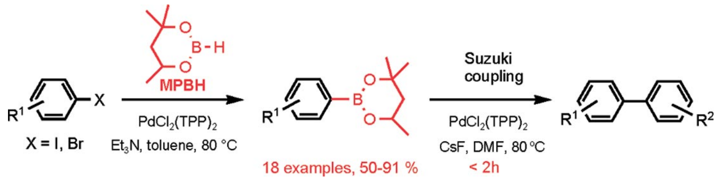
8 examples

We have implemented an efficient and selective procedure for the synthesis of novel 6*H*-[1,3]dioxolobenzo[4,5-*h*]pyrrolo[1,2-*a*][1]benzazepin-6-one derivatives in high yields from a short two-step sequence promoted by commercial phosphoric acid.

Borylation Reagents

N. PraveenGanesh,
P. Y. Chavant* **4690–4696**

Improved Preparation of 4,6,6-Trimethyl-1,3,2-dioxaborinane and Its Use in a Simple [PdCl$_2$(TPP)$_2$]-Catalyzed Borylation of Aryl Bromides and Iodides



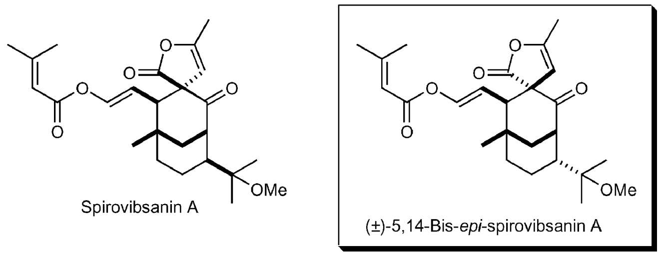
Easily prepared from hexylene glycol, 4,6,6-trimethyl-1,3,2-dioxaborinane (MethylPentaneDiolBorane, MPBH) is an excellent reagent for the [PdCl$_2$(PPh$_3$)$_2$]-catalyzed formylation of aryl bromides and iodides. The arylboronic esters are stable and readily undergo Suzuki coupling reactions. MPBH is thus an excellent alternative to pinacolborane.

Keywords: Borylation / Cross-coupling / Palladium / Pinacolborane / Biaryls

Vibsanin-Type Diterpene Total Synthesis

M. J. Gallen,
C. M. Williams* **4697–4705**

Towards the Total Synthesis of Spirovibsanin A: Total Synthesis of (±)-5,14-Bis-*epi*-spirovibsanin A



Synthesis of (±)-5,14-bis-*epi*-spirovibsanin A allowed direct stereochemical comparison to spirovibsanin A.

Keywords: Spirovibsanin A / (±)-5,14-Bis-*epi*-spirovibsanin A / Spirolactone / Diterpene / Natural product

---

* Author to whom correspondence should be addressed.

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