

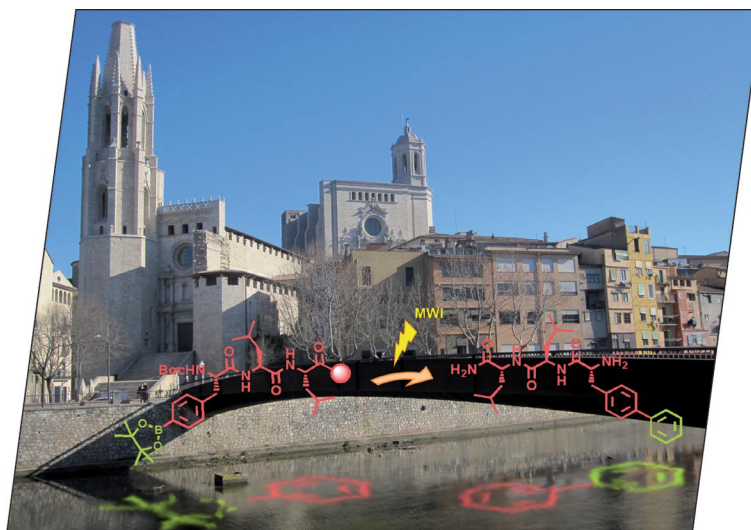


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COVER PICTURE

The cover picture shows the skyline of the old part of Girona in northeast Catalonia, Spain. In the foreground is one of the many bridges that span the river Onyar from the new part of the town to the Jewish quarter. This bridge, named the Pont de Sant Feliu, is the usual starting point for visiting this quarter. It offers a nice view of the narrow colourful houses that back onto the river and allows an impressive view of the Cathedral and the Sant Feliu church. Built in different styles (11th–17th century AD), the Cathedral preserves a Gothic nave with the widest arched span in the world. In this picture, the Pont de Sant Feliu serves as a means to depict the synthesis of a 4-arylphenylalanine tripeptide from a resin-bound phenylalanine boronate. Details can be found in the article by L. Feliu et al. on p. 1461ff, and results on the formation of the boronate through a solid-phase Miyaura borylation are also discussed.



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CONFERENCE REPORT

N. Martín* 1407–1410

Jean-Pierre Sauvage: The Lord of the Rings



An overview of the *Chimie Supramoléculaire Journées Scientifiques en l'honneur de Jean-Pierre Sauvage*, organized by the Institut de Science et d'Ingénierie Supramolé-

culaires (ISIS) at the University of Strasbourg, held on November 26 and 27, 2009 in Strasbourg is presented.

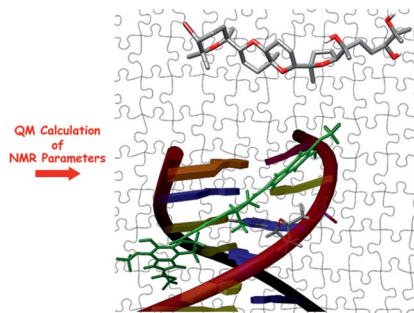
MICROREVIEW

QM Calculation of NMR Parameters

S. Di Micco, M. G. Chini, R. Riccio, G. Bifulco* 1411–1434

Quantum Mechanical Calculation of NMR Parameters in the Stereostructural Determination of Natural Products

Keywords: Natural products / NMR spectroscopy / Stereochemistry / Quantum chemistry / Drug-Macromolecule interactions



The present microreview highlights the recent goals reached by the application of quantum mechanical calculation of NMR properties for structural studies of natural products. It is also shown how this method can lead the total synthesis of complex natural compounds and its potential application in ligand–macromolecule interaction studies.

SHORT COMMUNICATIONS

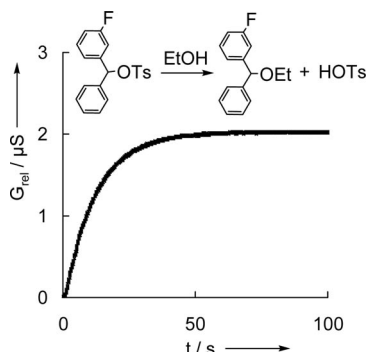
Nucleofugality Scales

C. Nolte, H. Mayr* 1435–1439



Kinetics of the Solvolyses of Fluoro-Substituted Benzhydryl Derivatives: Reference Electrofuges for the Development of a Comprehensive Nucleofugality Scale

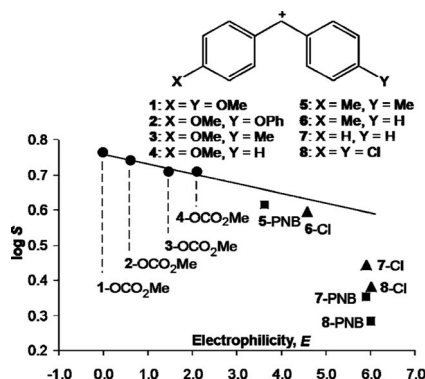
Keywords: Carbocations / Kinetics / Nucleophilic substitution / Linear free relationships / Solvent effects



Solvolysis rate constants of *m*-fluoro-substituted benzhydryl derivatives with good leaving groups have been determined in different solvents. The rate constants were subjected to a least-squares fit to the correlation $\log k_s = s_f(N_f + E_f)$ for determining the electrofugality parameters E_f of destabilized benzhydrylium ions.

Selectivity of Benzhydrylium Ions

The selectivities ($S = k_E/k_W$) of stabilized benzhydrylium ions in the series of aqueous ethanols depend on solvent polarity because of different microsolvation of the transition states for hydrolysis and ethanolysis, respectively. The selectivities of ions 1–4 are higher than those for less stable cations 5–8 and do not depend on the leaving group, indicating that in given conditions free ions are formed.

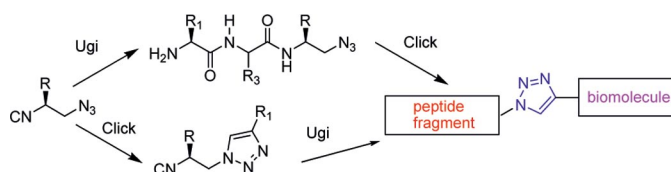


B. Denegri, M. Matic,
O. Kronja* 1440–1444

Selectivity of Stabilized Benzhydrylium Ions

Keywords: Kinetics / Solvolysis / Microsolvation / Stabilized benzhydrylium ions

Isocyanoazides



Efficient synthesis of chiral scaffolds combining isocyanide and azide groups permits the efficient construction of both amino

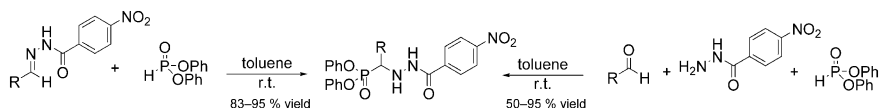
(hydroxy) acids and triazole derivatives and the preparation of hybrid peptide molecules by Ugi/click or click/Ugi strategies.

V. G. Nenajdenko,* A. V. Gulevich,
N. V. Sokolova, A. V. Mironov,
E. S. Balenkova 1445–1449

Chiral Isocyanoazides: Efficient Bifunctional Reagents for Bioconjugation

Keywords: Isocyanides / Azides / Multicomponent reactions / Click chemistry / Bioconjugation

Hydrophosphonylation



The uncatalyzed preparation of α -hydrazido phosphonate derivatives was achieved by playing with the pK_a s of different dialkyl/diphenyl phosphites. The syn-

thesis was conducted under mild and efficient conditions and, under an atom-economy point of view, for a variety of aliphatic aldehydes.

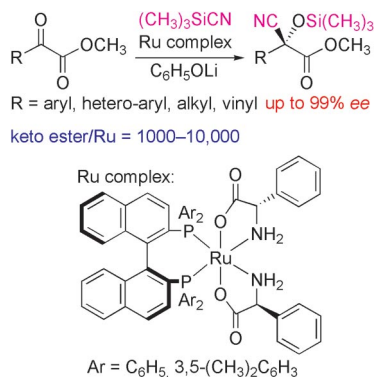
R. P. Herrera,* D. Roca-López,
G. Navarro-Moros 1450–1454

Uncatalyzed Three-Component Synthesis of α -Hydrazido Phosphonates

Keywords: Multicomponent reactions / Phosphonates / Hydrazones / Nucleophilic addition

Asymmetric Cyanosilylation

Asymmetric cyanosilylation of α -keto esters with the catalyst system consisting of $[\text{Ru}(\text{phgly})_2(\text{binap})]$ and $\text{C}_6\text{H}_5\text{OLi}$ affords the silylated cyanohydrins in high enantioselectivity (up to 99% *ee*). This catalyst is sufficiently active to complete the reaction with a substrate-to-catalyst molar ratio of 10,000 at -50°C . A plausible reaction pathway is also proposed.



N. Kurono, M. Uemura,
T. Ohkuma* 1455–1459

Asymmetric Cyanosilylation of α -Keto Esters Catalyzed by the $[\text{Ru}(\text{phgly})_2(\text{binap})]$ – $\text{C}_6\text{H}_5\text{OLi}$ System

Keywords: Asymmetric catalysis / Lithium / Ruthenium / Cyanosilylation

FULL PAPERS

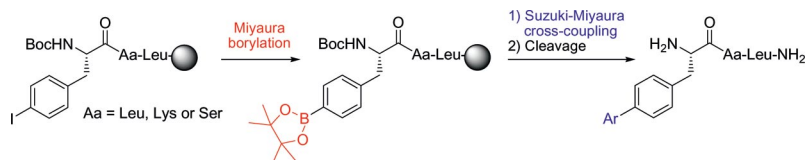
Peptide Solid-Phase Borylation

A. Afonso, C. Rosés, M. Planas,
L. Feliu* 1461–1468



Biaryl Peptides from 4-Iodophenylalanine by Solid-Phase Borylation and Suzuki–Miyaura Cross-Coupling

Keywords: Borylation / Biaryl peptides / Microwave chemistry / Cross-coupling / Solid-phase synthesis



A convenient strategy for the modification of phenylalanine peptides through solid-phase borylation and subsequent cross-coupling was developed. This methodology yielded resin-bound phenylalanine bor-

onates in good purities. Moreover, the cross-coupling between a polymer-bound phenylalanine boronate with different aryl halides led to a set of 4-arylphenylalanine tripeptides.

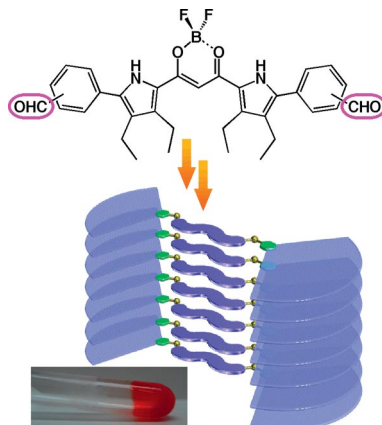
Supramolecular Chemistry

H. Maeda,* R. Fujii,
Y. Haketa 1469–1482



Supramolecular Assemblies Derived from Formyl-Substituted π -Conjugated Acyclic Anion Receptors

Keywords: Anions / Boron / Formyl units / Pyrrole derivatives / Receptors / Supramolecular chemistry



The synthesis and properties of formyl-substituted dipyrrolyl diketone–BF₂ complexes (anion receptors) and their extended derivatives are reported. The extended derivatives, which are prepared by formation of Schiff bases and subsequent reduction, behave as building subunits to provide anion-responsive gel-like materials.

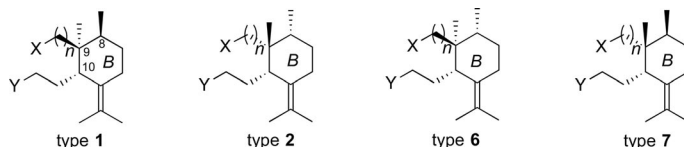
A-*seco* Terpenes

A. Corbu, J. M. Castro, M. Aquino,
Z. Gandara, P. Retailleau,
S. Arseniyadis* 1483–1493



Synthetic Studies Directed Towards Various Homologues of Natural Sesquiterpene-Coumarin Ethers: The Domino Approach

Keywords: Configuration determination / Terpenoids / Galbanic acid analogues / Secodriol analogues



Because six-membered rings can adopt various conformations, care should be taken when relying on NMR spectroscopic data even in apparently simple molecular contexts. Structural studies based on NMR

and corroborated by X-ray crystallography directed towards the development of a diagnostic tool for assigning the B-ring stereochemistries of various natural and unnatural A-*seco* terpenes are described.

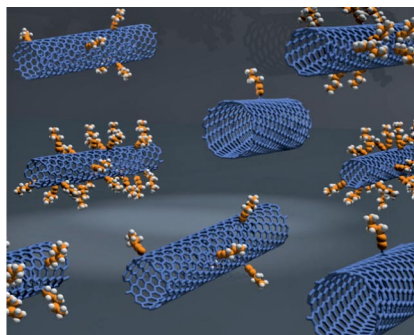
Functionalization of SWCNTs

B. Gebhardt, R. Graupner, F. Hauke,
A. Hirsch* 1494–1501



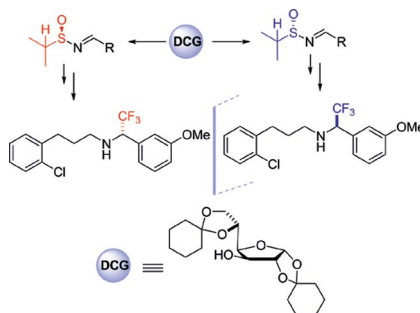
A Novel Diameter-Selective Functionalization of SWCNTs with Lithium Alkynyl-ides

Keywords: Nanotubes / Carbon / Alkynes / Raman spectroscopy / Nucleophilic addition



Single-walled carbon nanotubes (SWCNTs) have been functionalized with different terminal lithium acetylides in a nucleophilic addition sequence to yield soluble SWCNT derivatives that have been characterized by TGA/MS, Raman, UV/Vis/NIR and fluorescence spectroscopy. Based on a detailed radial breathing-mode analysis, size-selective sidewall functionalization of small-diameter tubes is revealed.

The first synthesis of both enantiomers of trifluoromethylated analogues of the calcimimetic NPS R-569 is reported. The method is based on the enantiodivergent synthesis of both enantiomers of *N*-(isopropylsulfinyl)imines using the “DAG methodology” and on a highly diastereoselective addition of Ruppert–Prakash’s reagent to these *N*-(isopropylsulfinyl)imines.

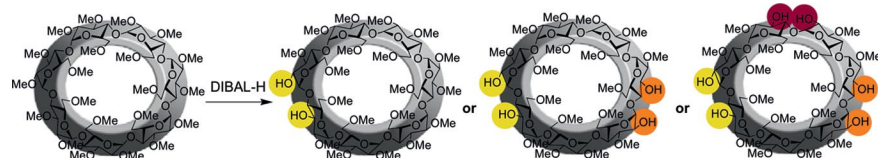


I. Fernández,* V. Valdivia, A. Alcudia,
A. Chelouan, N. Khiar* 1502–1509

Enantiodivergent Approach to Trifluoromethylated Amines: A Concise Route to Both Enantiomeric Analogues of Calcimimetic NPS R-568

Keywords: Amines / Diastereoselectivity / Enantioselectivity / Sulfinylimines / Sulfinamides

Modified Cyclodextrins



Diisobutylaluminium hydride regioselectively delivers a diol, a tetrol or an hexol from permethylated β -cyclodextrin. The

mechanism for this remarkable reaction is proposed in this paper.

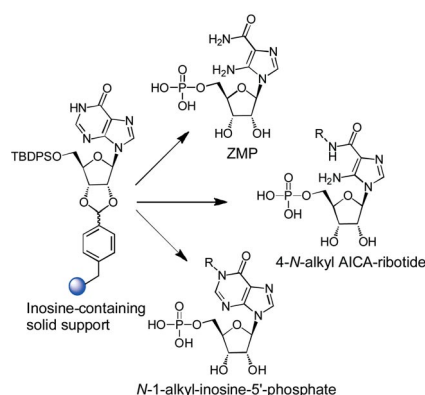
S. Xiao, M. Yang, P. Sinaï, Y. Blériot,
M. Sollogoub,* Y. Zhang* 1510–1516

Diisobutylaluminium Hydride (DIBAL-H) Promoted Secondary Rim Regioselective Demethylations of Permethylated β -Cyclodextrin: A Mechanistic Proposal

Keywords: Cyclodextrins / Dealkylation / Reaction mechanisms / Regioselectivity / Protecting groups

Nucleotide Analogues

5-Amino-1-(β -D-ribofuranosyl)imidazole-4-carboxamide-5'-monophosphate (ZMP), as well as collections of its 4-*N*-alkyl derivatives and *N*-1-alkylinosine-5'-phosphates, have been synthesised in high yields by a solid-phase strategy using a 5'-protected inosine connected to the solid support through the 2',3'-positions.



G. Oliviero, S. D'Errico, N. Borbone,
J. Amato, V. Piccialli, G. Piccialli,*
L. Mayol 1517–1524

Facile Solid-Phase Synthesis of AICAR 5'-Monophosphate (ZMP) and Its 4-*N*-Alkyl Derivatives

Keywords: ZMP / Nucleotides / Solid-phase synthesis / Phosphorylation

Multicomponent Heterocyclization



Novel multicomponent reactions based on primary 1,2- and 1,3-diamines, carbonyl compounds, and isocyanides have been developed as a general strategy for the synthesis of unique amino derivatives of

various privileged azaheterocycle structures, including pyrazines, 1,4-diazepines, quinoxalines, and their fused and spirocyclic analogues.

V. Kysil,* A. Khvat, S. Tsurulnikov,
S. Tkachenko, C. Williams, M. Churakova,
A. Ivachtchenko 1525–1543

General Multicomponent Strategy for the Synthesis of 2-Amino-1,4-diazaheterocycles: Scope, Limitations, and Utility

Keywords: Multicomponent reactions / Molecular diversity / Heterocycles / Lewis acids / Cyclization

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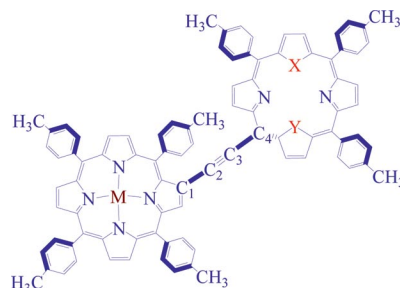
β ,*meso*-Porphyrin Dyads

M. Yedukondalu, D. K. Maity,*
M. Ravikanth* 1544–1561



β ,*meso*-Acetylenyl-Bridged, Asymmetrical, Porphyrin Dyads – Synthesis, Spectral, Electrochemical and Computational Studies

Keywords: Molecular devices / FRET / Density functional calculations / Porphyrin dyads / Heteroporphyrins / Acetylenyl bridge



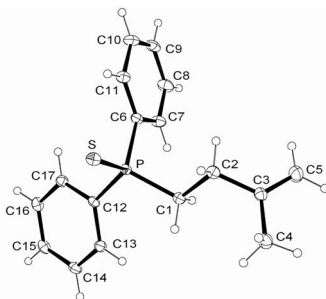
β ,*meso*-Acetylenyl-bridged, asymmetrical, porphyrin dyads containing two different types of subunits were synthesized, and the electronic interactions between the two subunits were investigated by spectral, electrochemical and computational studies.

Synthetic Methods

A. Perrier, V. Comte, C. Moïse,
P. Richard, P. Le Gendre* 1562–1568

*n*BuLi-Mediated Hydrophosphination: A Simple Route to Valuable Organophosphorus Compounds

Keywords: Alkenes / Alkynes / Hydrophosphination / Ligand design / Phosphorus



A variety of alkenylphosphanes have been synthesized by *n*BuLi-mediated hydrophosphination of conjugated dienes, trienes and alkynes.

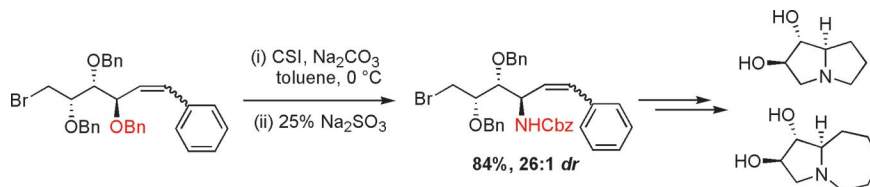
Synthesis of Lentiginosine Analogues

I. S. Kim, Q. R. Li, G. R. Dong,
Y. C. Kim, Y. J. Hong, M. Lee, K.-W. Chi,
J. S. Oh, Y. H. Jung* 1569–1573



A Facile Synthesis of Lentiginosine Analogues Based on a Highly Regio- and Diastereoselective Allylic Amination Using Chlorosulfonyl Isocyanate

Keywords: Azasugars / Synthetic methods / Inhibitors / Amination / Alkaloids



The total synthesis of the lentiginosine analogues pyrrolizidine alkaloid **2** and pyrrolazepine alkaloid **3** starting from readily available D-lyxose has been achieved by the regio- and diastereoselective allylic amination

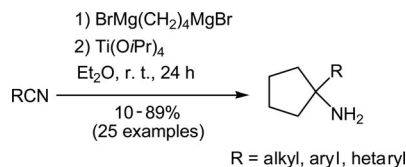
of the *anti*-3,4-tribenzyl ether using chlorosulfonyl isocyanate (CSI), intra- or intermolecular olefin metathesis, and Appel cyclization.

Cyclopentylamines

O. A. Tomashenko, A. E. Rudenko,
V. V. Sokolov,* A. A. Tomashevskiy,
A. de Meijere* 1574–1578

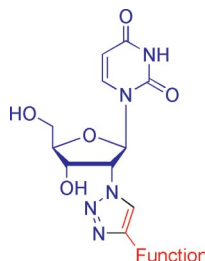
1-Substituted Cyclopentylamines from Nitriles- and Tetramethylenebismagnesium Dibromide in the Presence of Ti(O*i*Pr)₄

Keywords: Amines / Nitriles / Nucleophilic addition / Grignard reagents



Various 1-substituted cyclopentylamines are conveniently obtained from nitriles and tetramethylenebismagnesium dibromide in the presence of Ti(O*i*Pr)₄.

New uridines were synthesized by Cu-catalyzed cycloaddition of 2'-azido-2'-deoxyuridine with alkynes, wherein a biochemically interesting function (lipid, fluorescent label, amino acid, glucose, or biotin) was tethered to the uridine through a 1,2,3-triazole ring. The anchoring of the cholesterol-functionalized uridines in the phospholipid membrane was studied by NMR spectroscopy.

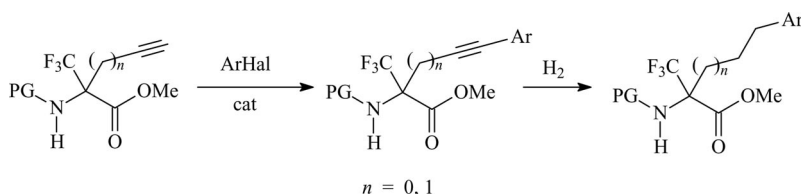


O. Kaczmarek, H. A. Scheidt, A. Bunge,
D. Föse, S. Karsten, A. Arbuzova,
D. Huster, J. Liebscher* 1579–1586

2'-Linking of Lipids and Other Functions to Uridine through 1,2,3-Triazoles and Membrane Anchoring of the Amphiphilic Products

Keywords: Cycloaddition / Nucleosides / Lipids / Membranes / NMR spectroscopy / Azides

Trifluoroalanine Derivatives



α -CF₃- α -amino acid derivatives bearing an arylalkynyl moiety at the α -carbon atom can be prepared by an efficient method based on palladium-catalyzed cross-coupling of the corresponding α -propargyl

(ethynyl) α -amino esters with aryl halides to afford amino acid derivatives with an internal triple bond that is suitable for further modifications.

G. T. Shchetnikov, M. A. Zotova,
C. Bruneau, P. H. Dixneuf,
S. N. Osipov* 1587–1592

Synthesis of α -Alkynyl- β,β,β -trifluoroalanine Derivatives by Sonogashira Cross-Coupling Reaction

Keywords: Amino acids / Alkynes / Cross-coupling / Peptidomimetics / Hydrogenation

CORRECTION

Keywords: Asymmetric catalysis / Alkylation / Palladium / P ligands / Fukui function / Kinetics

A Comparison of (*R,R*)-Me-DUPHOS and (*R,R*)-DUPHOS-*i*Pr Ligands in the Pd⁰-Catalysed Asymmetric Allylic Alkylation Reaction: Stereochemical and Kinetic Considerations

V. R. Marinho, J. P. P. Ramalho,
A. I. Rodrigues, A. J. Burke* 1593

* Author to whom correspondence should be addressed.

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

If not otherwise indicated in the article, papers in issue 7 were published online on February 16, 2010