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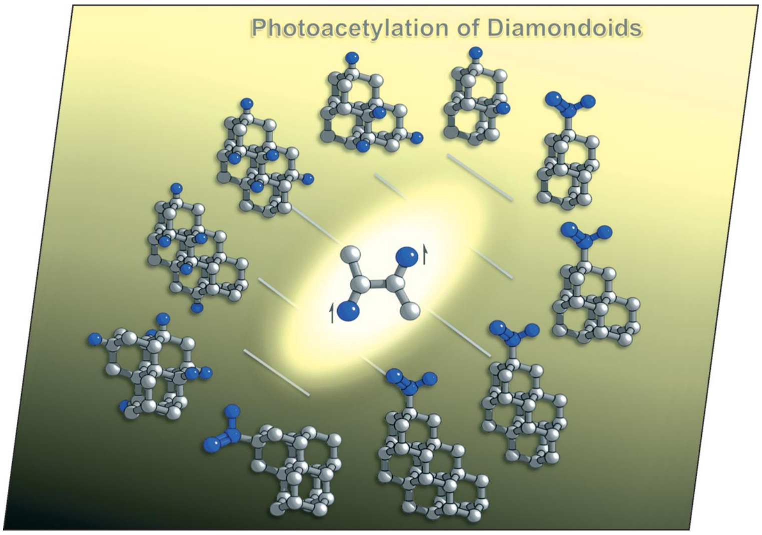
ChemPubSoc Europe

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 photochemical generation of triplet diacetyl (butadione, center) and its highly selective C−H bond-activation reactions in the functionalizations of tertiary C−H bonds. Despite several similarly reactive tertiary C−H bonds and a multitude of secondary C−H bonds with similar or even smaller bond dissociation energies (blue hydrogen atoms on structures on the left), this reagent shows remarkable selectivity for the apical positions of diamondoids owing to its high sensitivity to steric hindrance. This gives the respective apical acetyl diamondoids (blue groups on the right) in high yields. Deuterium kinetic isotope effects and accompanying computational studies shed light on the rate-determining C−H bond-activation step. Details are discussed in the article by A. A. Fokin, P. R. Schreiner et al. on p. 5153ff.



CONTENTS

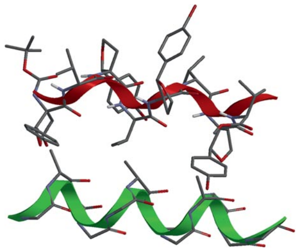
MICROREVIEWS

Peptidomimetics

A. Grauer, B. König* 5099–5111

Peptidomimetics – A Versatile Route to Biologically Active Compounds

Keywords: Peptidomimetics / Biological activity / Amino acids / Peptides



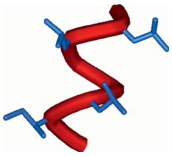
Peptidomimetics are of importance for the development of new biologically active compounds. A brief survey of the different approaches leading to this class of compounds is given and illustrated with selected examples of their applications.

Peptide Design

V. Haridas* 5112–5128

From Peptides to Non-Peptide Alpha-Helix Inducers and Mimetics

Keywords: Helical structures / Alpha-helix / Peptidomimetics / Secondary structure / Peptides / Amino acids



Alpha helix is the most abundant secondary structure motif in proteins. It is involved in many protein–protein interactions of vital biological significance. The design and synthesis of artificial helical structures are prominent research area in chemical biology.

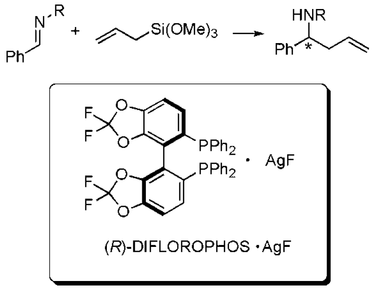
SHORT COMMUNICATIONS

Asymmetric Synthesis

M. Naodovic, M. Wadamoto,
H. Yamamoto* 5129–5131

Enantioselective Ag-Catalyzed Allylation of Aldimines

Keywords: Aldimines / Silver / Allylsilane / Asymmetric synthesis



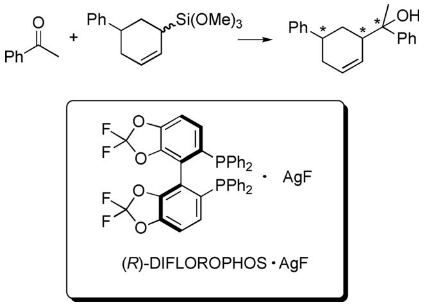
Highly enantioselective synthesis of homoallylamines using allyltrimethoxysilane in the presence of Ag^I catalyst is achieved. The methodology can be efficiently applied to crotylation of imines which proceeds in a distereoselective fashion.

Asymmetric Synthesis

M. Wadamoto, M. Naodovic,
H. Yamamoto* 5132–5133

Stereochemical Studies of Ag-Catalyzed Hosomi–Sakurai Reaction Using Chiral Silanes

Keywords: Ketones / Silver / Asymmetric synthesis / Allylation / Chiral allylsilanes



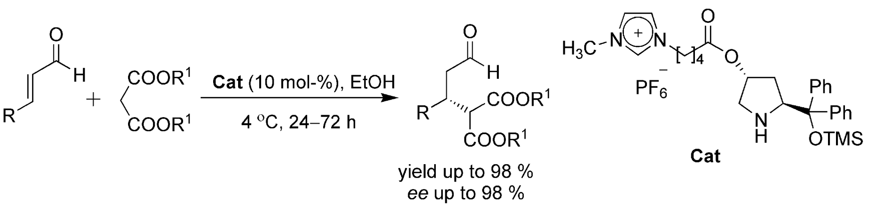
A robust asymmetric Hosomi–Sakurai reaction using various allyltrimethoxysilanes and chiral silver catalyst has been developed. Stereochemical studies indicate that the formation of a single allylsilver intermediate which undergoes addition the ketone. Regio- and stereochemical outcome of the reaction depends on the stability and/or reactivity of the intermediate.

Organocatalysis

O. V. Maltsev, A. S. Kucherenko, S. G. Zlotin* 5134–5137

O-TMS-α,α-diphenyl-(*S*)-prolinol Modified with an Ionic Liquid Moiety: A Recoverable Organocatalyst for the Asymmetric Michael Reaction between α,β-Enals and Dialkyl Malonates

Keywords: Organocatalysis / Michael addition / Ionic liquids / Supported catalysts / Sustainable chemistry



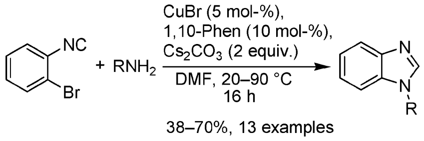
The first representative of *O*-TMS-α,α-diphenyl-(*S*)-prolinol derivatives bearing ionic liquid fragments was synthesized. It was proven to be an efficient recoverable catalyst for Michael reaction between dialkyl malonates and α,β-enals, affording the respective adducts in high yields (up to 98%) and with high enantioselectivities (up to 98%*ee*).

Catalysis

A. V. Lygin, A. de Meijere* ... 5138–5141

Synthesis of 1-Substituted Benzimidazoles from *o*-Bromophenyl Isocyanide and Amines

Keywords: Isocyanides / Copper / Homogeneous catalysis / Benzimidazoles / Cyclization



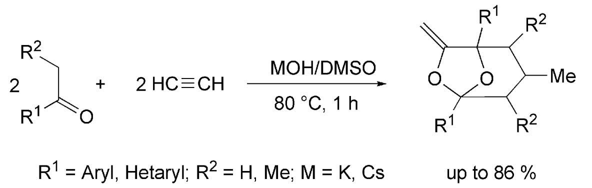
A novel synthesis of 1-substituted benzimidazoles by a Cu^I-catalyzed reaction of *o*-bromophenyl isocyanide with primary amines is reported.

Synthetic Methods

B. A. Trofimov,* E. Yu. Schmidt,
I. A. Ushakov, A. I. Mikhaleva,
N. V. Zorina, N. I. Protsuk,
E. Yu. Senotrusova, E. V. Skital'tseva,
O. N. Kazheva, G. G. Alexandrov,
O. A. Dyachenko 5142–5145

One-Pot Assembly of 7-Methylene-6,8-dioxabicyclo[3.2.1]octanes, Congeners of Frontalin, from Ketones and Acetylene

Keywords: Ketones / Alkynes / Oxygen heterocycles / Pheromones / Superbasic systems



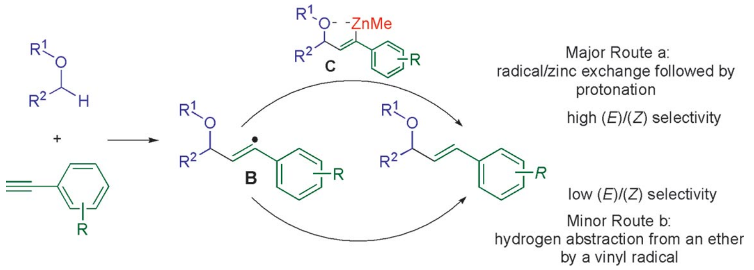
When two molecules of a ketone and two molecules of acetylene interact in MOH/DMSO systems, only one reaction path is pursued, resulting in the assembly of 7-methylene-6,8-dioxabicyclo[3.2.1]octanes, which are important analogs of insect pheromones. This unprecedented reaction can provide important naturally occurring compounds, powerful building blocks, and precursors of advanced materials.

Radical Reactions

Z. Chen,* Y.-X. Zhang, Y. An,
X.-L. Song, Y.-H. Wang, L.-L. Zhu,
L. Guo* 5146–5152

Radical Addition of Ethers to Terminal Alkynes with High *E*-Selectivity

Keywords: Radicals / Radical reactions / Hydrogen abstraction / Vinylzinc



Direct radical addition of ethers to terminal alkynes were investigated by using Me_2Zn/O_2 as radical initiator to afford 2-vinyl ether derivatives with high *E*-selectivity. Reversed *E*/*Z* selectivity is obtained by using Et_3B/O_2. Two competitive pathways are proposed for the formation of vinyl radical **B**.

CONTENTS

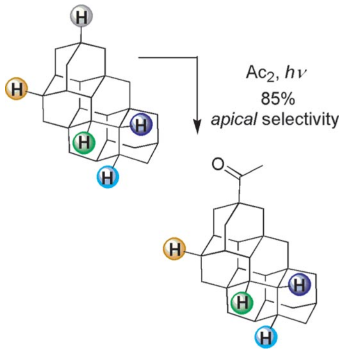
FULL PAPERS

Nanodiamonds

A. A. Fokin,* P. A. Gunchenko, A. A. Novikovsky, T. E. Shubina, B. V. Chernyaev, J. E. P. Dahl, R. M. K. Carlson, A. G. Yurchenko, P. R. Schreiner* **5153–5161**

Photoacetylation of Diamondoids: Selectivities and Mechanism

Keywords: C–H activation / Hydrocarbons / Isotope effects / Nanostructures



Despite many nonequivalent C–H bonds present in the structures of hydrogen-terminated nanodiamonds (diamondoids), photoacetylation with diacetyl gives apical derivatives almost exclusively as a result of the higher polarizabilities of the structures in the apical molecular direction.

Lipids

S. M. Polyakova, V. N. Belov,* S. F. Yan, C. Eggeling, C. Ringemann, G. Schwarzmann, A. de Meijere, S. W. Hell* **5162–5177**

New GM1 Ganglioside Derivatives for Selective Single and Double Labelling of the Natural Glycosphingolipid Skeleton

Keywords: Lipids / Carbohydrates / Glycosphingolipids / Gangliosides / Fluorescence / Fatty acids / Rhodamines

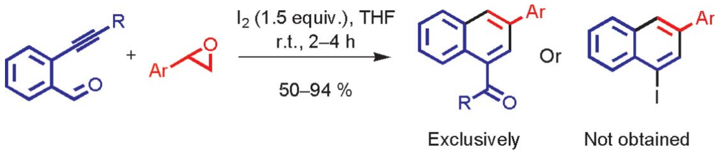
New derivatives of ganglioside GM1 containing α-amino-, ω-amino- and ω-mercaptostearic acid residues are useful precursors for the introduction of various labels into different parts of the glycosphingolipid molecule without changing its natural skeleton.

Benzannulation

N. T. Patil,* A. Konala, V. Singh, V. V. N. Reddy **5178–5184**

Highly Selective Electrophile-Induced Cascade Reactions between *o*-Alkynylbenzaldehydes and Styrene Oxides Leading to the Formation of 1-Naphthyl Ketones

Keywords: Alkynes / Enols / Cycloaddition / Domino reactions / Ketones



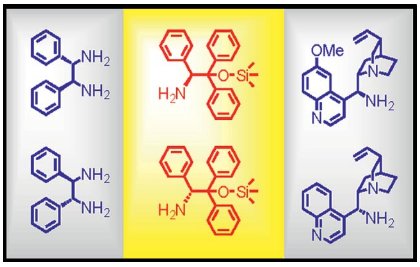
The synthesis of 1-naphthyl ketones was achieved through the reaction of *o*-alkynylbenzaldehyde with styrene oxides in the presence of molecular iodine. The reaction was found to very selective, and of two possible products, only one was formed.

Primary Amine Organocatalysis

T. E. Kristensen, K. Vestli, F. K. Hansen, T. Hansen* **5185–5191**

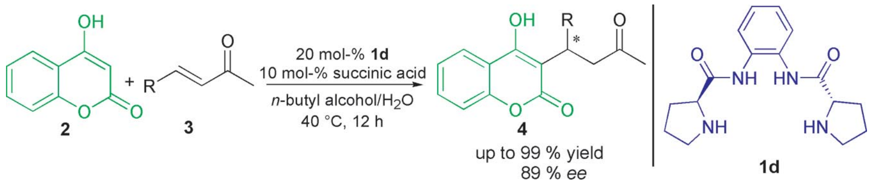
New Phenylglycine-Derived Primary Amine Organocatalysts for the Preparation of Optically Active Warfarin

Keywords: Amines / Amino alcohols / Asymmetric synthesis / Michael addition / Organocatalysis



Whereas chiral diamines and Cinchona-derived primary amines have been the traditional organocatalysts for the preparation of warfarin, we want to introduce a new, fully synthetic phenylglycine derivative, equally available in both enantiomeric forms. This organocatalyst may be perceived as a type of primary amine analogue of the Jørgensen/Hayashi diarylprolinol.

Asymmetric Michael Addition



C_2-symmetric secondary amine amide catalysts were developed for the asymmetric Michael addition of 4-hydroxycoumarin to α,β-unsaturated ketones. Biologically and pharmaceutically active compounds were obtained in excellent yields (up to 99%) with high enantioselectivities (up to 89%*ee*) under mild conditions. In addition, enantiopure product could be obtained by a single recrystallization.

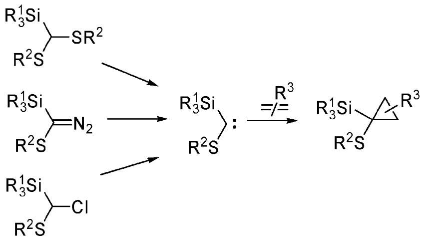
Z. Dong, L. Wang, X. Chen, X. Liu, L. Lin, X. Feng* **5192–5197**

Organocatalytic Enantioselective Michael Addition of 4-Hydroxycoumarin to α,β-Unsaturated Ketones: A Simple Synthesis of Warfarin

Keywords: Organocatalysis / Biological activity / Michael addition / Ketones / Enantioselectivity

Carbenes

Does silicon and sulfur substitution lead to a stable carbene? Not really, but the title carbenes can be conveniently generated by α-elimination or diazo decomposition and used in stereospecific [2+1] cycloaddition chemistry.

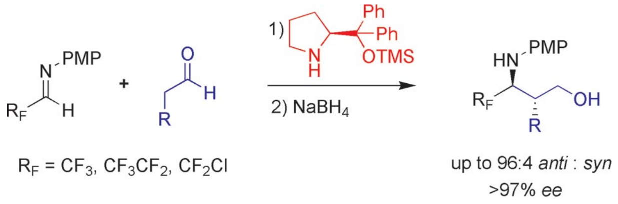


T. Wagner, J. Lange, D. Grote, W. Sander, E. Schaumann,* G. Adiwidjaja, A. Adam, J. Kopf **5198–5207**

Organylthio(silyl)carbenes

Keywords: Carbenes / Carbanions / Diazo compounds / Cycloaddition / Sulfur heterocycles

Organocatalysis



The access to *anti*-β-alkyl-γ-fluoroalkyl-γ-amino alcohols is described via a highly diastereo- and enantioselective Mannich addition of aldehydes to fluorinated imines by using commercially available α,α-diphenylprolinol TMS ether as an organocatalyst.

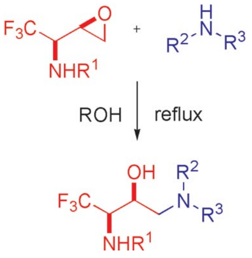
S. Fustero,* F. Mojarrad, M. D. P. Carrión, J. F. Sanz-Cervera, J. L. Aceña **5208–5214**

Organocatalytic *anti*-Selective Mannich Reactions with Fluorinated Aldimines: Synthesis of *anti*-γ-Fluoroalkyl-γ-amino Alcohols

Keywords: Organocatalysis / Enantioselectivity / Mannich reaction / Fluorinated imines / Amino alcohols

Protease Inhibitor Synthesis

A very easy access to new trifluoromethylated hydroxyethylamine (Tf-HEA) derivatives by epoxide ring opening using amines is described. The reaction can be carried out in protic solvents, without the use of any catalyst or any other additive. Total regioselectivity is observed, and the stereochemistry of the compounds is preserved.



C. Philippe, T. Milcent, T. Nguyen Thi Ngoc, B. Crousse,* D. Bonnet-Delpon **5215–5223**

Synthesis of New Trifluoromethylated Hydroxyethylamine-Based Scaffolds

Keywords: Protease / Hydroxyethylamine / Fluorine / Epoxides / Amino acids / Peptidomimetics

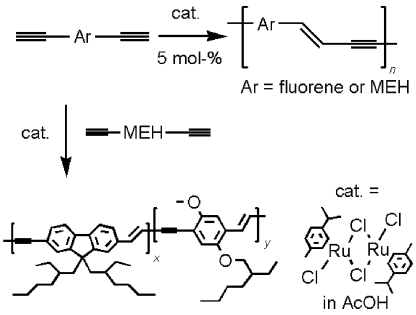
CONTENTS

Conjugated Polymers

C. Pasquini, I. Fratoddi, M. Bassetti* **5224–5231**

Homo- and Copolymerization of Aromatic Diynes by Ruthenium/Acid-Promoted (RAP) Catalysis

Keywords: Polymerization / Homogeneous catalysis / Ruthenium / C–C coupling / Enynes



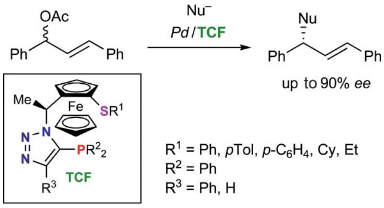
Conjugated polymers with alternating fluorene-enyne and/or MEH-enyne [MEH = 1-(2′-ethylhexyloxy)-4-methoxybenzene] segments are obtained under mild reaction conditions by catalysis of the [{RuCl(μ-Cl)(*p*-cymene)}$_2$/AcOH system. The first example of a random copolymer derived by the polyaddition process of terminal diynes exhibits intramolecular resonance energy transfer processes between the fluorene and the MEH subunits.

ThioClickFerrophos P,S Ligands

M. Kato, T. Nakamura, K. Ogata, S.-i. Fukuzawa* **5232–5238**

Synthesis of Novel Ferrocenyl-Based P,S Ligands (ThioClickFerrophos) and Their Use in Pd-Catalyzed Asymmetric Allylic Substitutions

Keywords: Metallocenes / Asymmetric catalysis / Allylic compounds / Palladium / P,S ligands / Allylic substitution



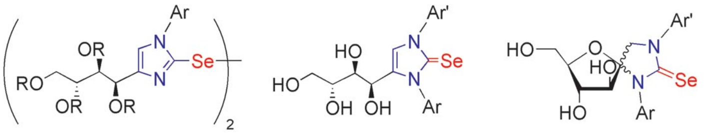
Pd complexes of novel ferrocenyl P,S ligands with triazole backbones (ThioClickFerrophos) were effectively employed with good enantioselectivities in asymmetric allylic alkylation, etherification, and amination of (±)-1,3-diphenylprop-2-enyl acetate.

Selenonucleosides

S. Maza, Ó. López, S. Martos, I. Maya, J. G. Fernández-Bolaños* **5239–5246**

Synthesis of the First Selenium-Containing Acyclic Nucleosides and Anomeric Spironucleosides from Carbohydrate Precursors

Keywords: Selenium / Carbohydrates / Spiro compounds / Nucleosides / Heterocycles



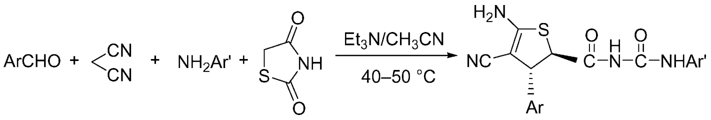
Treatment of aryl isoselenocyanates with glucosamine followed by acetylation allows the synthesis of (polyhydroxyalkylimidazol-2-yl)diselenides, a new type of acyclic C-selenonucleosides. Imidazoline-2-selones and spiranic imidazole-*C*-selenonucleosides are obtained from *N*-arylfructosamines via *N*,*N*′-disubstituted 4-hydroxy-4-polyhydroxyalkyl-imidazolidine-2-selones.

Multicomponent Domino Reactions

J. Sun, E.-Y. Xia, L.-L. Zhang, C.-G. Yan* **5247–5254**

Triethylamine-Catalyzed Domino Reactions of 1,3-Thiazolidinedione: A Facile Access to Functionalized Dihydrothiophenes

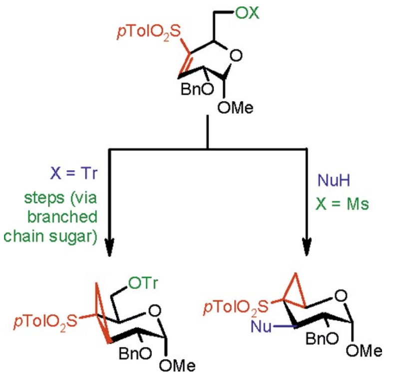
Keywords: Domino reactions / Multicomponent reactions / Cyclization / Heterocycles / Amines



Aromatic amines have successfully been used as substrates in the domino ring-opening/recyclization reactions of 1,3-thiazolidinedione, malononitrile, and aromatic aldehydes to give polysubstituted dihydrothiophenes in high yields. The dihydrothiophene derivatives were converted efficiently into the corresponding thiophenes by oxidation with DDQ.

Cyclopropanated Pyranosides

A new strategy for the synthesis of C3–C4 and C4–C5 cyclopropanated pyranosides starting from closely related vinyl sulfone modified carbohydrates was described. This nonmetal-based efficient strategy affords three distinct classes of hitherto unknown cyclopropanated pyranosides.



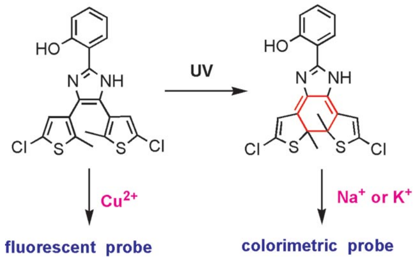
R. Bhattacharya, D. Dey, T. Pathak* **5255–5260**

Vinyl Sulfone Modified Hex-3-enopyranosides: Novel Routes to C3–C4 and C4–C5 Cyclopropanated Pyranosides 💻

Keywords: Small-ring systems / Cyclization / Carbohydrates / Michael addition / Vinyl sulfone

Bifunctional Sensors

A bifunctional metal detection system with independent signal outputs and regulable detection limits was developed by using a photochromic diarylethene with an imidazole unit as the ligand. The sensor can be used for the detection of Cu^{2+} by fluorescence recognition and for the detection of Na^+ or K^+ by colorimetric recognition.



H.-h. Liu, Y. Chen* **5261–5265**

A Bifunctional Metal Probe with Independent Signal Outputs and Regulable Detection Limits

Keywords: Sensors / Fluorescence / Photochromism / Cations

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* Author to whom correspondence should be addressed.

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