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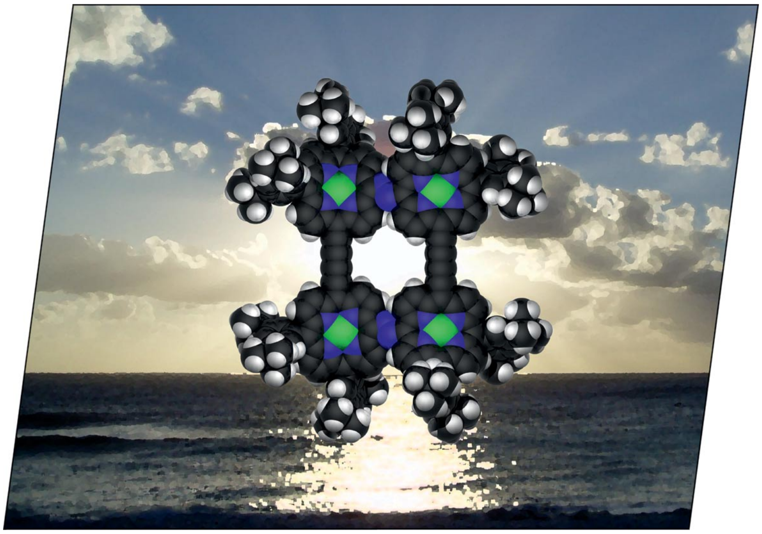
COVER PICTURE

The cover picture shows the tetranickel complex of a rectangular porphyrin array with novel connectivity. Conjugating azo and butadiyne bridges link the opposite sides of the rectangle, and the absorption spectrum demonstrates strong electronic communication between the chromophores. The synthesis and characterisation of this tetramer are described in the article by D. P. Arnold et al. on p. 4381 ff. The molecule is set against a background of a sunset on the Great Barrier Reef, emphasising the role of porphyrinoid pigments in solar energy capture.



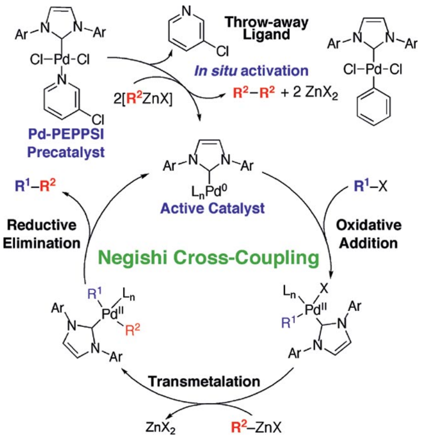
MICROREVIEW

Negishi Cross-Coupling

C. Valente, M. E. Belowich, N. Hadei, M. G. Organ* **4343–4354**

Pd-PEPPSI Complexes and the Negishi Reaction

Keywords: Palladium / Carbene ligands / Zinc / Cross-coupling



The application of Pd-PEPPSI complexes in the Negishi cross-coupling reaction is reviewed. Mechanistic considerations are presented, as is a brief summary of synthetic routes to organozinc halide reagents. A comparison between Pd-PEPPSI-IPr and the IPent analogue is made, with the latter being well-suited for sterically hindered and heterocyclic substrates.

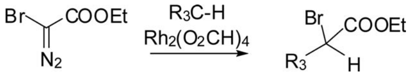
SHORT COMMUNICATIONS

C–H Insertion Reactions

H. T. Bonge, T. Hansen* **4355–4359**

Computational Study of C–H Insertion Reactions with Ethyl Bromodiazoacetate

Keywords: Computational chemistry / Insertion / Reaction mechanisms / Carbenoids / Rhodium



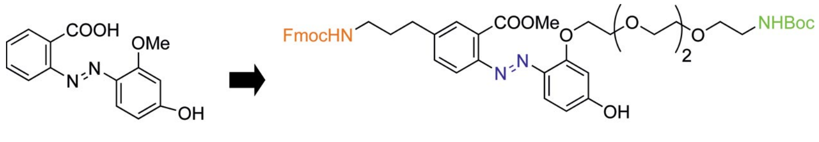
A computational study of the reaction mechanism for intermolecular C–H insertion reactions with ethyl bromodiazoacetate is presented.

Extra-Mild Cleavable Linkers

G. Leriche, G. Budin, L. Brino, A. Wagner* **4360–4364**

Optimization of the Azobenzene Scaffold for Reductive Cleavage by Dithionite; Development of an Azobenzene Cleavable Linker for Proteomic Applications

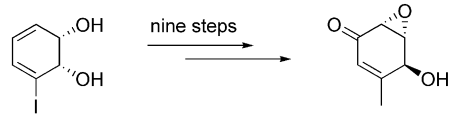
Keywords: Affinity purification / Azo compounds / Proteomics / Cleavable linkers / Reduction



Orthogonally diprotected HAZA cleavable linker

Structural optimization of the azobenzene scaffold for dithionite reductive cleavage led to the development of an efficient azo–arene cleavable linker. This highly reactive compound was designed to be orthogonally diprotected and easily derivatized by alkyne and biotin. This water-soluble linker showed a half-life of < 1 s in biological media and is ready to be used for proteomic applications.

Natural Product Synthesis



2 (X = I)

isoepiepoformin (**1**)

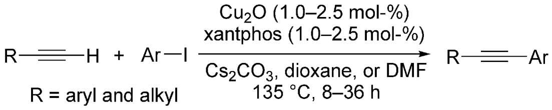
The enantiomerically pure *cis*-1,2-dihydrocatechol **2** (X = I), which is obtained by enzymatic dihydroxylation of iodobenzene, has been converted over nine steps into the epoxyquinol natural product isoepiepoformin (**1**).

L. V. White, C. E. Dietinger, D. M. Pinkerton, A. C. Willis, M. G. Banwell* **4365–4367**

An Enantioselective Synthesis of the Epoxyquinol (+)-Isoepiepoformin

Keywords: C–C coupling / *cis*-1,2-Dihydrocatechol / Enones / (+)-Isoepiepoformin / Total synthesis / Natural products

Cross-Coupling



A copper-catalyzed cross-coupling reaction of alkynes with aryl iodides is described. The system tolerates a broad range of functional groups and enables the use of sterically demanding substrates with only 1.0–2.5 mol-% of Cu_2O and 1.0–2.5 mol-% of xantphos as the catalyst.

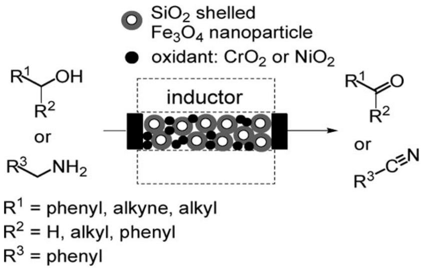
C.-H. Lin, Y.-J. Wang, C.-F. Lee* **4368–4371**

Efficient Copper-Catalyzed Cross-Coupling Reaction of Alkynes with Aryl Iodides

Keywords: Cross-coupling / Copper / Alkynes / Phosphane ligands

Microreactors

Cooperation of two metal oxides inside a microreactor results in a flow device that promotes facile oxidations under inductive heating conditions.

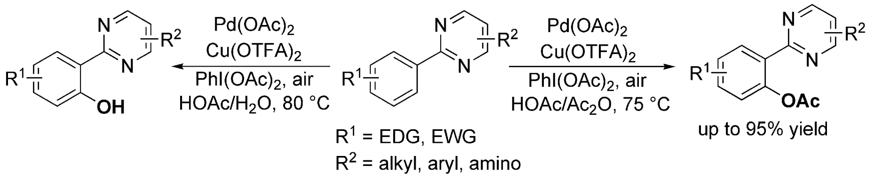


J. Wegner, S. Ceylan, C. Friese, A. Kirschning* **4372–4375**

Inductively Heated Oxides Inside Microreactors – Facile Oxidations under Flow Conditions

Keywords: Inductive heating / Microreactors / Oxidation / Metal oxides

C–H Acetoxylation



Pyrimidines and their derivatives are very important motifs in materials and medicinal chemistry. In this paper, a palladium-catalyzed *ortho* C–H bond acetoxylation of arylpyrimidines was developed regioselectively under mild conditions.

X. Zheng, B. Song, B. Xu* **4376–4380**

Palladium-Catalyzed Regioselective C–H Bond *ortho*-Acetoxylation of Arylpyrimidines

Keywords: Nitrogen heterocycles / C–H activation / Palladium / Regioselectivity

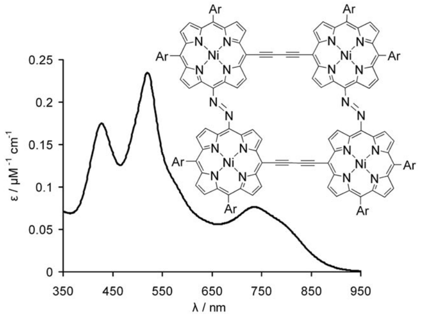
FULL PAPERS

Azo/Butadiyne Porphyrin Tetramer

B. Bašić, J. C. McMurtrie, D. P. Arnold* **4381–4392**

A Cyclic Porphyrin Tetramer Linked by Azo and Butadiyne Bridges

Keywords: Porphyrinoids / Porphyrins / Azo compounds



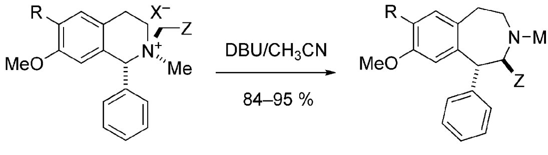
A porphyrin tetramer in which the porphyrin units are linked alternately by azo and butadiyne bridges has been prepared. The electronic absorption spectrum implies strong electronic interaction between the porphyrin units.

1*H*-3-Benzazepines

M. Valpuesta,* M. Ariza, A. Díaz,* R. Suau **4393–4401**

Diastereoselective Synthesis of 1,2-Disubstituted 2,3,4,5-Tetrahydro-1*H*-3-benzazepines by Means of the Stevens Rearrangement

Keywords: Benzazepines / Rearrangement / Diastereoselectivity / Ylides / Isoquinolines



5a–g: R = OMe
10: R = Cl

1a–g: R = OMe
11: R = Cl

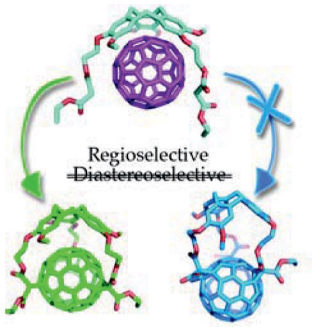
The synthesis of 1,2-disubstituted 2,3,4,5-tetrahydro-1*H*-3-benzazepines has been conveniently developed by making use of the diastereoselective Stevens rearrangement. The application of this methodology has provided a fair number of novel analogue compounds of SCH 23390. The adequate choice of the isoquinolinium salt allowed us to control the Stevens rearrangement to obtain exclusively the 1*H*-3-benzazepines (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).

Fullerene Chirality

A. Kraszewska, P. Rivera-Fuentes, G. Rapenne, J. Crassous, A. G. Petrovic, J. L. Alonso-Gómez, E. Huerta, F. Diederich, C. Thilgen* **4402–4411**

Regioselectivity in Tether-Directed Remote Functionalization – The Addition of a Cyclotriveratrylene-Based Trimalonate to C_{60} Revisited

Keywords: Chirality / Circular dichroism / Fullerenes / Structure elucidation / Template synthesis



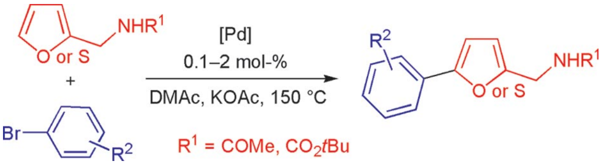
Triple Bingel addition of enantiomerically pure cyclotriveratrylene-tethered trimalonates to C_{60} was reinvestigated with regard to the regio- and diastereoselectivity. Electronic and vibrational circular dichroism studies showed that the addition proceeds regioselectively, yielding *trans*-3,*trans*-3,*trans*-3 tris-adducts, contrary to earlier reports.

Pd-Catalysed Direct Arylation

J. Roger, H. Doucet* **4412–4425**

Palladium-Catalysed Direct 5-Arylation of Furfurylamine or 2-(Aminoalkyl)thiophene Derivatives

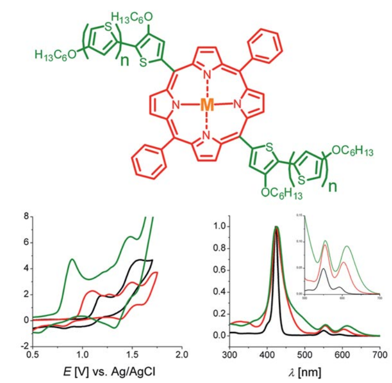
Keywords: Arylation / Heterocycles / Homogeneous catalysis / C-H activation / Palladium



The palladium-catalysed direct arylation of furan or thiophene derivatives bearing CH_2NHR substituents (with R = COMe or CO_2tBu) at the C2 position with aryl bromides was studied. A low loading of a phosphane-free catalyst was found to give regioselectively the 5-arylated compounds.

Thiophene–Porphyrin Hybrids

A series of linearly and laterally linked porphyrin–thiophene hybrids was synthesised and analysed with respect to their UV/Vis absorption and cyclic voltammetry behaviour. The results proved that linear hybrids must be considered as independent redox units that are competing for the 1st oxidation. It was found that Co^{II} took an exceptional role.



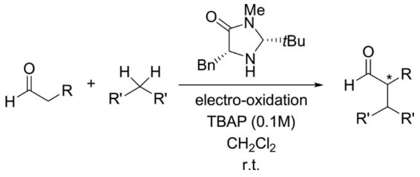
M. J. Zöllner, E. Becker, U. Jahn,
W. Kowalsky,
H.-H. Johannes* 4426–4435

New Versatile Strategy towards Zinc(II)-, Copper(II)- and Cobalt(II)-Metallated Thiophene/Porphyrin-Hybrids

Keywords: Porphyrinoids / Ligand design / Hybrid monomers / UV/Vis spectroscopy / Cyclic voltammetry

Electro-Organocatalysis

By using electrochemical techniques (electrolysis and cyclic voltammetry), the scope of the asymmetric organocatalyzed reaction can be expanded to the α-alkylation of aldehydes without chemical oxidants (tetrabutylammonium perchlorate, TBAP). The optimization and scope of this reaction along with DFT calculations and control experiments to understand the mechanism have been demonstrated.

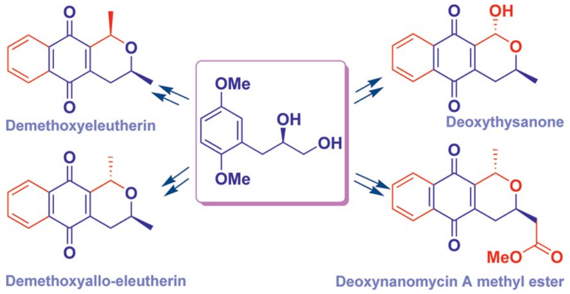


X.-H. Ho, S.-i. Mho, H. Kang,
H.-Y. Jang* 4436–4441

Electro-Organocatalysis: Enantioselective α-Alkylation of Aldehydes

Keywords: Organocatalysis / Electrochemistry / Enantioselectivity / Alkylation / Radicals

Deoxypyranonapthoquinones



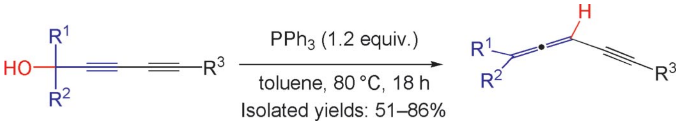
Enantioselective synthesis of deoxy analogues of pyranonaphthoquinone antibiotics was achieved from the common intermediate (*R*)-3-(2,5-dimethoxyphenyl)-propane-1,2-diol. The key step involved highly diastereoselective intra- and intermolecular oxa-Pictet–Spengler cyclization for rapid access to the pyran skeleton.

R. T. Sawant, S. G. Jadhav,
S. B. Waghmode* 4442–4449

Intra- and Intermolecular Oxa-Pictet–Spengler Cyclization Strategy for the Enantioselective Synthesis of Deoxy Analogues of (+)-Nanomycin A Methyl Ester, (+)-Eleutherin, (+)-Allo-Eleutherin, and (+)-Thysanone

Keywords: Quinones / Antibiotics / Organocatalysis / Cyclization / Enantioselectivity

Allenynylation Reaction



Trisubstituted allenynes were conveniently synthesized in moderate to good yields under mild reaction conditions through phosphane-mediated deoxygenation of 2,4-pentadiyn-1-ol derivatives.

H. Jiang,* W. Wang, B. Yin,
W. Liu 4450–4453

Facile Synthesis of Trisubstituted Allenynes by Phosphane-Mediated Deoxygenation of 2,4-Pentadiyn-1-ol

Keywords: Allenes / Phosphanes / Deoxygenation / Alkynes / Synthetic methods

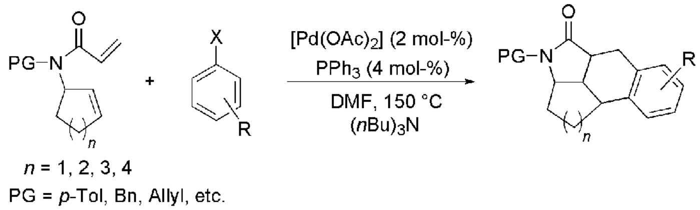
CONTENTS

Domino Reaction

Y. Hu,* D. Ren, L. Zhang, X. Lin,
J. Wan 4454–4459

Palladium-Catalyzed C–C Coupling/C–H Activation: Formation of Isoindolinone-Fused Heterocyclic Compounds

Keywords: Cyclization / Domino reactions / Fused-ring systems / Palladium / Isomerization



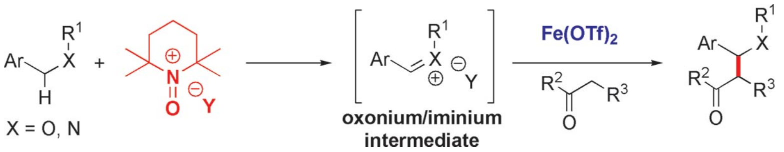
Reactions of different unactivated cycloalkenes with different substituted aryl halides in the presence of Pd(OAc)$_2$ allowed different kinds of heterocyclic derivatives to be prepared through highly regioselective C–C coupling and C–H functionalization. In particular, the C–H functionalization and allyl isomerization could occur simultaneously with an allyl protecting group.

Dehydrogenative Cross-Coupling

H. Richter,
O. García Mancheño* 4460–4467

Dehydrogenative Functionalization of C(sp^3)–H Bonds Adjacent to a Heteroatom Mediated by Oxoammonium Salts

Keywords: C–H activation / Cross-coupling / Dehydrogenation / Iron



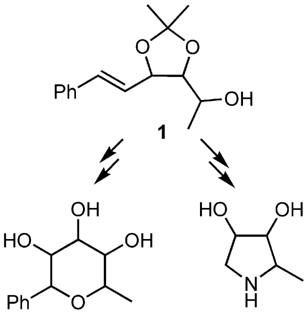
The dehydrogenative cross-coupling reactions of C(sp^3)–H bonds α to a heteroatom with enolizable nucleophiles by using easy-to-handle and nontoxic TEMPO salts is presented. These soft oxidants in combination with a Fe catalyst were efficiently employed to selectively generate the desired C–C coupling products under mild reaction conditions.

Lipase-Mediated Kinetic Resolution

D. Acetti, E. Brenna,*
F. G. Gatti 4468–4475

Oxygenated Stereotriads with Definite Absolute Configuration by Lipase-Mediated Kinetic Resolution: De Novo Synthesis of Imino Sugars and 6-Deoxy-*C*-glycosides

Keywords: Iminosugars / Enzymes / Kinetic resolution / Chirality / C-glycosides



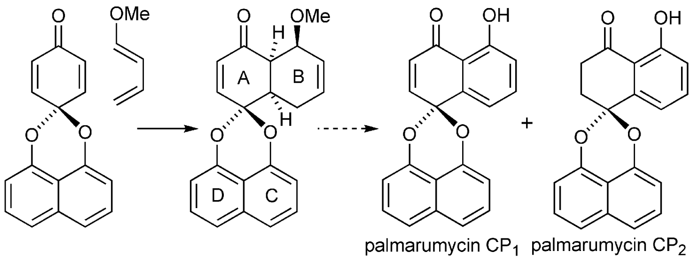
Oxygenated stereotriads in a definite configurational arrangement were prepared by lipase-mediated kinetic resolution of substrates **1**. They were then embedded into biologically relevant structures, such as hydroxylated pyrrolidines and C-phenyl glycosides

Natural Product Synthesis

K. Krohn,* S. Wang, I. Ahmed, S. Altun,
A. Aslan, U. Flörke, I. Kock,
S. Schlummer 4476–4481

Flexible Route to Palmarumycin CP$_1$ and CP$_2$ and CJ-12.371 Methyl Ether

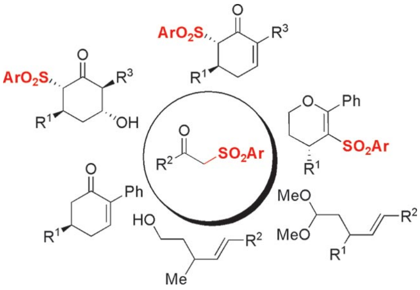
Keywords: Total synthesis / Cycloaddition / Spiro compounds / Oxidation / Dehydrogenation



The total synthesis of palmarumycin CP$_1$ (**4**) and CP$_2$ (**5**) and racemic CJ-12.371 methyl ether (**17**) is described using the Diels–Alder reaction of benzoquinone 1,8-dihydroxynaphthalene acetal (**10**) with 1-methoxy-1,3-butadiene under neat reaction conditions. The transformation of **15** into targets **4**, **5**, and **17** involved dehydrogenation, methyl ether cleavage, reduction, and oxidation.

Organocatalysis

We have studied the influence of different reaction conditions on the conjugated addition of β-keto sulfones to α,β-unsaturated aldehydes catalyzed by silyl prolinol ethers. Small changes in the starting material and/or in the experimental protocol are able to produce significant variations in the structures of the final products.

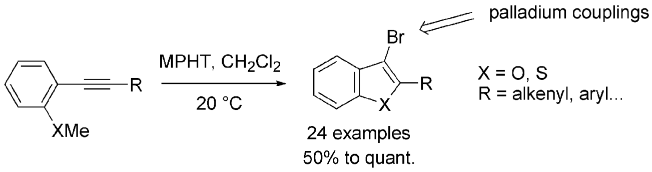


J. Alemán,* V. Marcos, L. Marzo, J. L. García Ruano* 4482–4491

Influence of the Reaction Conditions on the Evolution of the Michael Addition of β-Keto Sulfones to α,β-Unsaturated Aldehydes 💻

Keywords: Organocatalysis / Michael addition / Aldehydes / Keto sulfones

Cyclization Reactions



The cyclization of *ortho*-substituted arylalkynes in the presence of *N*-methylpyrrolidin-2-one hydrotribromide, a soft and easy-to-handle electrophilic brominating reagent, afforded 2-substituted 3-bromobenzofurans and -benzothiophenes. Subsequent Pd-catalyzed functionalization reactions afforded 2,3-disubstituted benzofurans and benzothiophenes of biological interest.

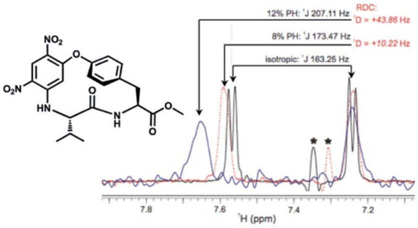
M. Jacubert, A. Tikad, O. Provot, A. Hamze, J.-D. Brion, M. Alami* 4492–4500

MPHT-Promoted Bromocyclization of *ortho*-Substituted Arylalkynes: Application to the Synthesis of 2-Substituted 3-Bromobenzofurans and -Benzo[*b*]thiophenes

Keywords: Enynes / Alkynes / Oxygen heterocycles / Sulfur heterocycles / Cyclization

Constrained Peptide Conformation

The structure of a cyclic peptide was determined with great precision by using residual dipolar couplings (RDCs) in a polymer containing the sample to partially align the molecules.



C. J. Arnusch, J. H. Ippel, H. Kooijman, A. L. Spek, R. M. J. Liskamp, J. Kemmink,* R. J. Pieters* 4501–4507

Direct Structural Comparison of a Rigid Cyclic Peptidic Scaffold Using Crystallography and NMR in Strained PH Polymer Gels 💻

Keywords: NMR spectroscopy / Structure elucidation / Peptides / Amino acids

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* Author to whom correspondence should be addressed.

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