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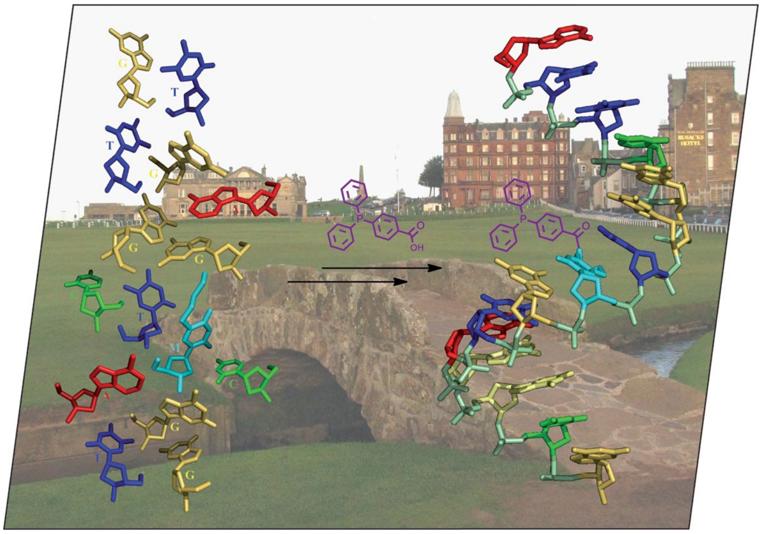
COVER PICTURE

The cover picture shows the formation of a 15-base-long DNA strand from individual nucleosides. The light-blue nucleoside has been modified so that it can form an amide bond with a phosphanylcarboxylic acid, once the strand has been prepared. In this way, artificial “metallo-DNAzymes” can be developed by complex formation of transition metals with phosphane-modified oligonucleotides, bridging the cap between homogeneous and biocatalysis. This is symbolised in the background by the famous Swilcan Bridge at the 18th hole of the Old Course of St Andrews, Scotland. Details are discussed in the article by P. C. J. Kamer et al. on p. 3229 ff.



CONTENTS

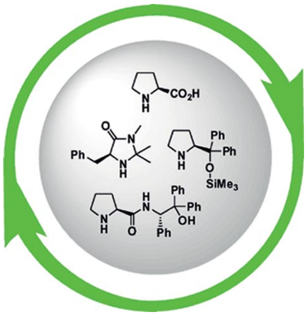
MICROREVIEW

Polymer-Supported Organocatalysts

T. E. Kristensen,
T. Hansen* 3179–3204

Polymer-Supported Chiral Organocatalysts: Synthetic Strategies for the Road Towards Affordable Polymeric Immobilization

Keywords: Organocatalysis / Immobilization / Asymmetric catalysis / Asymmetric synthesis / Biomimetic synthesis



The preparation and utilization of enamine and iminium organocatalysts have seen a tremendous growth during the last decade. In this microreview, we highlight the polymer-supported versions of these catalysts, with a special focus on the synthetic strategies that have been undertaken to prepare them and analyze these strategies in a historical context.

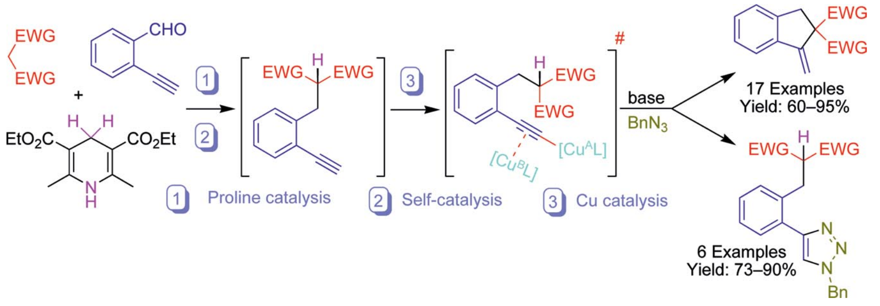
SHORT COMMUNICATIONS

Multicatalysis Cascade Reactions

D. B. Ramachary,* R. Mondal,
C. Venkaiah 3205–3210

Rapid Synthesis of Functionalized Indenes, Triazoles, and Glucocorticoid Receptor Modulators by Sequential Multicatalysis Cascade Reactions

Keywords: Amino acids / Carbocycles / Heterocycles / Organocatalysis / Domino reactions



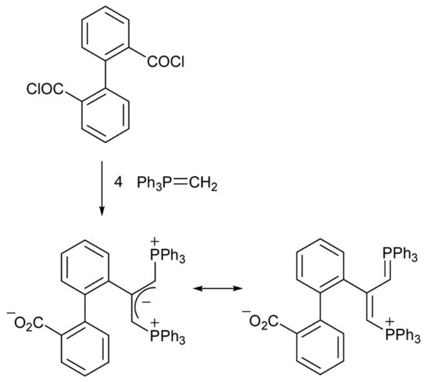
Common catalyst for dual activation: A general process for the synthesis of highly substituted indenes, 1,2,3-triazoles, and glucocorticoid receptor modulators was achieved for the first time. In this communication, a single copper catalyst is for the first time employed for two different reactions.

Stable Phosphonium Ylides

R. A. Aitken,* L. P. Cleghorn,
R. M. Leitch, L. C. Morrill,
A. M. Z. Slawin 3211–3214

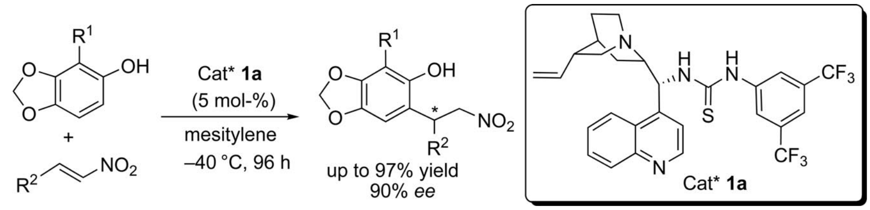
Unexpected Rearrangement Leading to Formation of a 1,3-Bis(triphenylphosphonio)prop-1-en-3-idyl Carboxylate

Keywords: Rearrangement / Phosphorus / Ylides



Unexpected access to a zwitterionic compound containing the rare 1,3-bis(triphenylphosphonio)allyl anion function is achieved in a simple one-step reaction between biphenyl-2,2′-dicarbonyl dichloride and methylenetriphenylphosphorane.

Bifunctional Organocatalysts



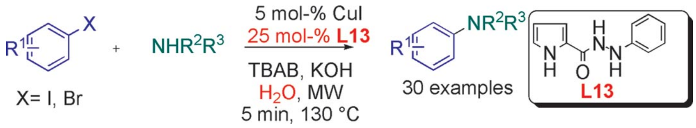
Enantioselective Friedel–Crafts alkylation of sesamol and its 2-substituted derivatives with a wide variety of aromatic nitro olefins promoted by chiral thiourea–tertiary amine catalyst **1a** proceeded in mesitylene at −40 °C to give the corresponding products in good yields (up to 97%) and good enantioselectivities (up to 90%*ee*).

H. Zhang, Y.-H. Liao, W.-C. Yuan, X.-M. Zhang* **3215–3218**

Organocatalytic Enantioselective Friedel–Crafts Alkylation of Sesamol with Nitro Olefins

Keywords: Alkenes / Organocatalysis / Alkylation / Enantioselectivity

Aqueous Chemistry



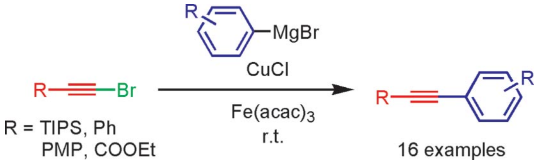
A highly efficient and environmentally friendly CuI/*N′*-phenyl-1*H*-pyrrole-2-carbohydrazide (**L13**) system was developed for the C–N coupling of aryl halides with amines in pure water under microwave irradiation or conventional heating.

J. Xie, X. Zhu, M. Huang, F. Meng, W. Chen, Y. Wan* **3219–3223**

Pyrrole-2-carbohydrazides as Ligands for Cu-Catalyzed Amination of Aryl Halides with Amines in Pure Water

Keywords: Pyrrole-2-carbohydrazides / Copper / Amination / Microwave chemistry / Water chemistry

Homogeneous Catalysis



The cross-coupling reaction between 6 different alkynyl bromides and Grignard-derived organocuprates catalyzed by Fe(acac)$_3$ is reported. A series of alkynylarenes was successfully synthetized. The use of organocopper instead of simple Grignard reagents represents the key factor, which leads the reactions to completition. The present methodology was finally applied in the stereoselective synthesis of combretastatins.

D. Castagnolo, M. Botta* **3224–3228**

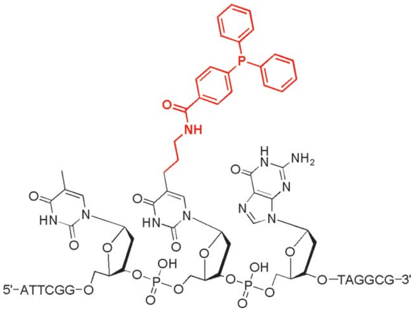
Iron-Catalyzed Cross-Coupling between 1-Bromoalkynes and Grignard-Derived Organocuprate Reagents

Keywords: Alkynes / Cross-coupling / Iron / Grignard reagents / Homogeneous catalysis

FULL PAPERS

Phosphane-Based DNAzymes

Diphenylphosphanyl units have been attached to (oligo)nucleotides by amide bond formation in water/DMF. X-ray structures of two phosphane-modified mononucleosides have been determined. This method enables modification of DNA strands with transition metal-phosphane complexes.



M. Nuzzolo, A. Grabulosa, A. M. Z. Slawin, N. J. Meeuwenoord, G. A. van der Marel, P. C. J. Kamer* **3229–3236**

Functionalization of Mono- and Oligonucleotides with Phosphane Ligands by Amide Bond Formation

Keywords: Nucleosides / Oligonucleotides / DNA / Phosphanes / Palladium

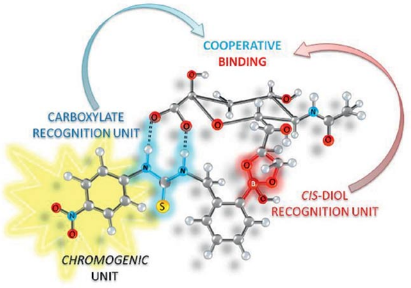
CONTENTS

Sialic Acid Recognition

M. Regueiro-Figueroa, K. Djanashvili, D. Esteban-Gómez, A. de Blas, C. Platas-Iglesias,* T. Rodríguez-Blas* 3237–3248

Towards Selective Recognition of Sialic Acid Through Simultaneous Binding to Its *cis*-Diol and Carboxylate Functions

Keywords: Carbohydrates / Supramolecular chemistry / Sialic acids / Hydrogen bonds / Molecular recognition



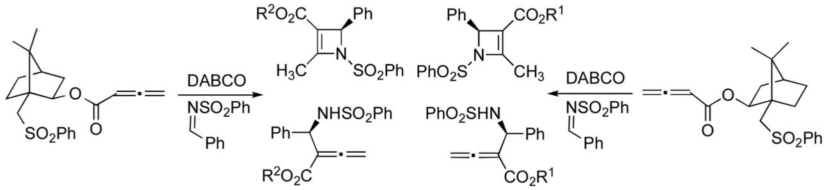
Receptors containing phenylboronic acid and urea or thiourea units recognize sialic acids through a cooperative two-site binding mode based on 1) ester formation through interaction at the phenylboronic acid function of the receptor and 2) hydrogen-bond interaction between the thiourea moiety and the carboxylate group of the saccharide.

Chiral α-Allenylamines and 2-Azetines

B. S. Santos, A. L. Cardoso, A. Matos Beja, M. Ramos Silva, J. A. Paixão, F. Palacios, T. M. V. D. Pinho e Melo* 3249–3256

Diastereoselective Aza-Baylis–Hillman Reactions: Synthesis of Chiral α-Allenylamines and 2-Azetines from Allenic Esters

Keywords: Allenes / Nitrogen heterocycles / Chiral auxiliaries / Diastereoselectivity



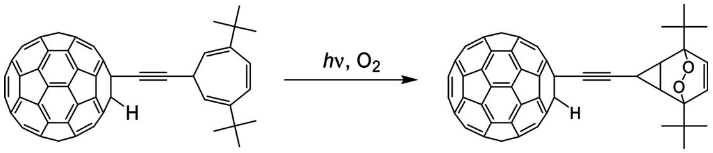
A DABCO-catalysed reaction of 2,3-allenoates, bearing a chiral auxiliary on the ester moiety, with *N*-arylidenebenzenesulfonamide provides the first examples of optically active α-allenylamines and 2-azetines.

Fullerene Photochemistry

M. Hanamura, J. Kamada, A. Amano, K. Takeuchi, T. Okazaki, K. Hirai, T. Kitagawa* 3257–3264

Self-Sensitized Photooxygenation of a C_{60}–Cycloheptatriene Dyad to Form Norcaradiene-Derived Endoperoxides

Keywords: Photooxidation / Fullerenes / Peroxides / Sensitizers / Valence isomerization



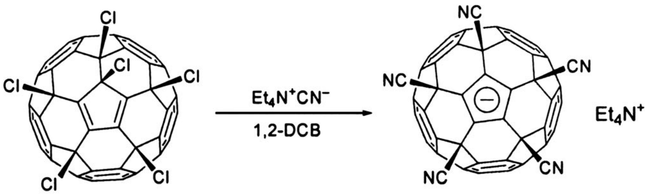
A dyad of [60]fullerene, an excellent photosensitizer, and a cycloheptatrienyl group, a good singlet-oxygen acceptor, has been synthesized. Its chemoselective, self-sensitized photooxygenation to norcaradiene-derived endoperoxides is presented.

Stable Fullerene Anions

P. A. Troshin,* E. A. Khakina, A. S. Peregudov, D. V. Konarev, I. V. Soulimenkov, S. M. Peregudova, R. N. Lyubovskaya 3265–3268

$[C_{60}(CN)_5]^-$: A Remarkably Stable [60]Fullerene Anion

Keywords: Fullerenes / Nucleophilic substitution / Anions / Ionic complexes / Magnetic properties

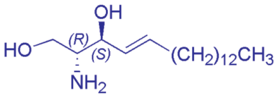


$C_{60}Cl_6$ 1

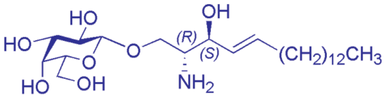
Treatment of $C_{60}Cl_6$ with organic cyanide yielded the first air-stable salt with the fullerene anion $[C_{60}(CN)_5]^-$. This salt showed unprecedented robustness with respect to oxidation, hydrolysis, protonation by organic and inorganic acids, and reactions with electrophiles.

Glycosphingolipids

The accumulation of psychosine (galactosyl sphingosine) has been associated with the pathogenesis of Krabbe disease; however, the exact mechanism of its cytotoxicity remains unclear. Herein, we describe the synthesis of the unnatural enantiomer of erythro-sphingosine, psychosine, and related derivatives thereof that would allow for the mechanistic elucidation of the toxicity of psychosine.



***ent*-Sphingosine**



***ent*-Psychosine**

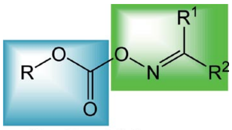
A. R. Parameswar, J. A. Hawkins, L. K. Mydock, M. S. Sands, A. V. Demchenko* 3269–3274

Concise Synthesis of the Unnatural Sphingosine and Psychosine Enantiomer

Keywords: Carbohydrates / Enantioselectivity / Glycosylation / Sphingolipids

Peptide Protecting Groups

Fmoc- and Alloc-oxime-based carbonate-type reagents were successfully synthesized from the corresponding chloroformates. The performance of these compounds in the α-amino protection of glycine proceeded with very low dipeptide formation, in the absence of other byproducts, and in a safe manner. The cyanopyridine analogue afforded the best results in terms of purity and prevention of dimerization.



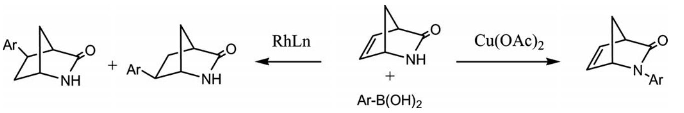
R = Fm, Allyl

S. N. Khattab, R. Subirós-Funosas, A. El-Faham,* F. Albericio* ... 3275–3280

Oxime Carbonates: Novel Reagents for the Introduction of Fmoc and Alloc Protecting Groups, Free of Side Reactions

Keywords: Amino acids / Protecting groups / Peptides / Oximes

Cross-Coupling



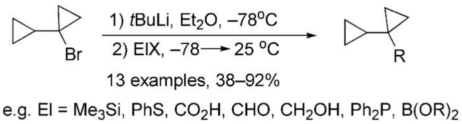
Copper- and rhodium-catalyzed reactions between 2-azabicyclo[2.2.1]hept-5-en-3-ones (**1**) and arylboronic acids were successfully effected under microwave irradiation conditions, leading to *N*-aryl and *C*-aryl derivatives of **1**, respectively.

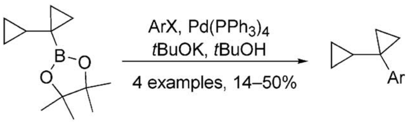
T. Abe, H. Takeda, Y. Takahashi, Y. Miwa, K. Yamada, M. Ishikura* 3281–3294

Metal-Catalyzed Reactions between 2-Azabicyclo[2.2.1]hept-5-en-3-ones and Arylboronic Acids

Keywords: 2-Azabicyclo[2.2.1]hept-5-en-3-one / Arylboronic acids / Rhodium / Copper / Cross-coupling / Catalytic arylation

1-Cyclopropylcyclopropanes





1-Bromo-1-cyclopropylcyclopropane undergoes bromine/lithium exchange upon treatment with *tert*-butyllithium at −78 °C, and the resulting 1-lithio derivative can be trapped with various electrophiles. A (1-cyclopropylcyclopropyl)boronate, prepared along this route, undergoes Suzuki coupling with aryl halides to furnish (1-cyclopropylcyclopropyl)arenes.

A. de Meijere,* A. F. Khlebnikov, H. W. Sünnemann, D. Frank, K. Rauch, D. S. Yufit 3295–3301

Convenient Access to Various 1-Cyclopropylcyclopropane Derivatives

Keywords: Cyclopropanes / Organolithium compounds / Electrophilic substitution / Cross coupling / Cycloaddition / Small ring systems

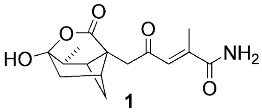
CONTENTS

Fungal Metabolites

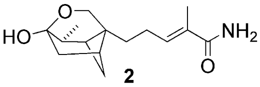
L. Liu, H. Gao, X. Chen, X. Cai, L. Yang, L. Guo, X. Yao, Y. Che* .... 3302−3306

Brasilamides A−D: Sesquiterpenoids from the Plant Endophytic Fungus *Paraconiothyrium brasiliense*

Keywords: Antiviral agents / Biological activity / Structure elucidation / Natural products / Configuration determination



1



2

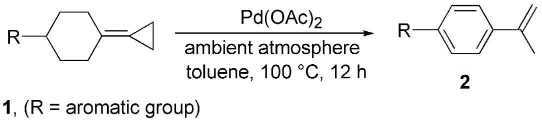
Paraconiothyrium brasiliense produced four new tricyclic sesquiterpenoids named brasilamides A−D (**1**−**4**); compounds **1** and **2** possess an unprecedented 4-oxatricyclo[3.3.1.0^{2,7}]nonane skeleton. Compounds **2**−**4** showed modest inhibitory effects on HIV-1 replication in C8166 cells.

Biaryl Synthesis

M. Jiang, Y. Wei, M. Shi* ..... 3307−3311

Palladium Acetate Catalyzed Oxidative Aromatization of Methylenecyclopropanes

Keywords: Small ring systems / Palladium / Biaryls / Dehydrogenation / Rearrangement



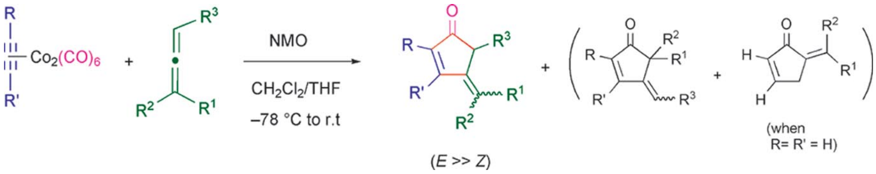
Isopropenylbiaryl derivatives were produced in moderate to good yields at high temperature from the reaction of methylenecyclopropanes (MCPs) in the presence of Pd(OAc)$_2$ in air by tandem intramolecular C−H and C−C bond activation and aromatization through dehydrogenated rearrangement of the MCPs. A plausible mechanism has been proposed on the basis of deuterium labeling and control experiments.

Allene Cycloaddition

F. Antras, S. Laurent, M. Ahmar, H. Chermette, B. Cazes* ...... 3312−3336

Pauson−Khand Reaction of Allenic Hydrocarbons: Synthesis of 4-Alkylidenecyclopentenones

Keywords: Allenes / Cycloaddition / Enones / Configuration determination / Density functional calculations



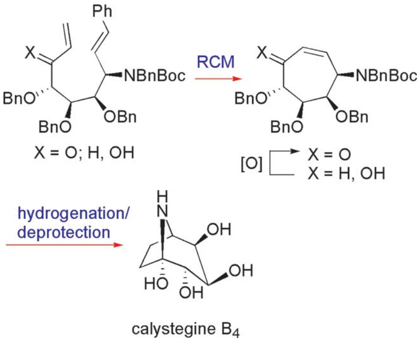
The Pauson−Khand reaction of allenic hydrocarbons gives the title product as the major cycloadduct. The regio and stereoselectivities depend on the substituents on both the alkyne and the allene. Results and DFT calculations show that both pseudo-equatorial and pseudo-axial modes of coordination of the allene to the cobalt nucleus of the alkyne−dicobalt complex may be involved.

Nortropane from an RCM Reaction

P. Moosophon, M. C. Baird, S. Kanokmedhakul, S. G. Pyne* .... 3337−3344

Total Synthesis of Calystegine B$_4$

Keywords: Mannich reaction / Metathesis / Natural products / Total synthesis



The total synthesis of calystegine B$_4$ was achieved in 10 steps from (−)-D-lyxose. The key steps included a Petasis−borono-Mannich reaction and a ring-closing metathesis reaction.

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* Author to whom correspondence should be addressed.

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