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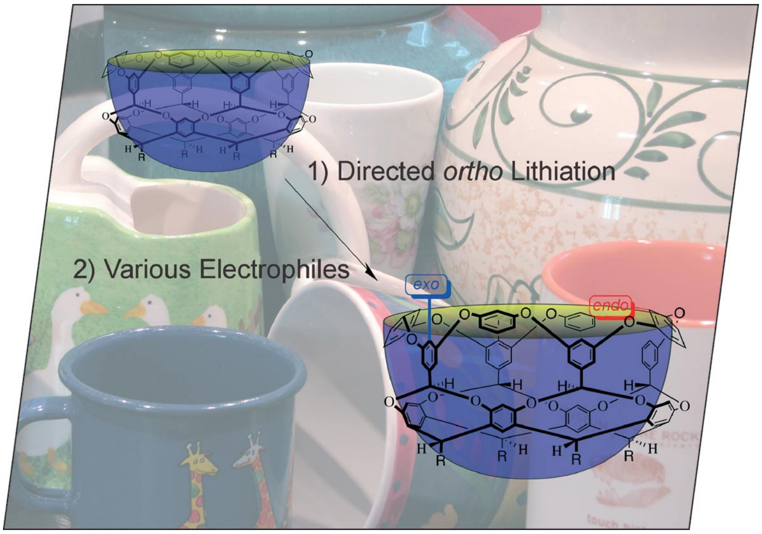
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows a collection of china, pewter cups, mugs, and jugs. For these and other macroscale objects, it is easier to decorate their exterior rather than their interior surface. Not surprisingly, the same asymmetry is seen at the molecular scale; it is generally easier to decorate/functionalize a convex than a concave surface. One approach to *endo* functionalization of deep-cavity cavitands is directed *ortho* metalation (D*o*M). In the paper by K. Srinivasan et al., on p. 3265 ff, it is shown that various electrophiles quench the lithiates formed according to D*o*M protocols. Reaction control leads to between one and five functional groups being introduced at the *endo* and *exo* positions of these hosts.



CONTENTS

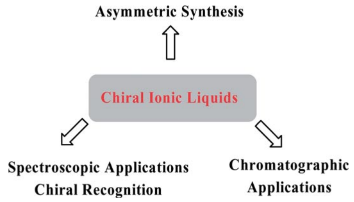
MICROREVIEW

Chiral Ionic Liquids

K. Bica, P. Gaertner* .... 3235−3250

Applications of Chiral Ionic Liquids

Keywords: Ionic liquids / Asymmetric synthesis / Immobilization / Chiral resolution / Analytical methods



This review deals with the application of CILs as solvents, catalysts or ligands in asymmetric synthesis. Chiral recognition abilities in spectroscopic techniques such as NMR, NIR or fluorescence spectroscopy are discussed as well as the application of CILs for separation in chromatography.

SHORT COMMUNICATIONS

Glycosylation

L. O. Kononov,* N. N. Malysheva,
E. G. Kononova,
A. V. Orlova .... 3251−3255

Intermolecular Hydrogen-Bonding Pattern of a Glycosyl Donor: The Key to Understanding the Outcome of Sialylation

Keywords: Amides / Glycosylation / Hydrogen bonds / Reactivity / Sialic acids

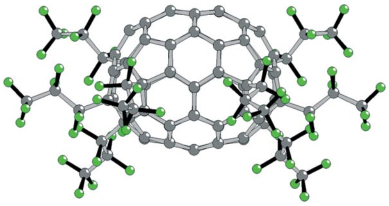
Which one of the two glycosyl donors shown in this picture is more reactive? Conflicting opinions are known. Our approach, which relies on supramolecular aggregation in solutions, can provide a clue to the reasons for the inconsistencies in the literature data on the relative reactivity of sialyl donors.

Perfluoroalkylated Fullerenes

T. Mutig, E. Kemnitz,*
S. I. Troyanov* .... 3256−3259

Synthesis and Structural Characterization of Four Isomers of $C_{70}(n\text{-}C_3F_7)_8$

Keywords: Fullerenes / Fluorine / Liquid chromatography / Structure elucidation



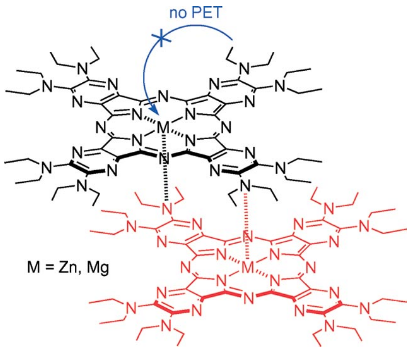
The first four isomers of $C_{70}(n\text{-}C_3F_7)_8$ synthesized by the ampoule reaction of C_{70} with $n\text{-}C_3F_7I$, isolated by HPLC, and characterized by X-ray crystallography possess unprecedented addition patterns among $C_{70}X_8$ compounds.

Phthalocyanine Dimers

V. Novakova, P. Zimcik,* K. Kopecky,
M. Miletin, J. Kuneš,
K. Lang .... 3260−3263

Self-Assembled Azaphthalocyanine Dimers with Higher Fluorescence and Singlet Oxygen Quantum Yields than the Corresponding Monomers

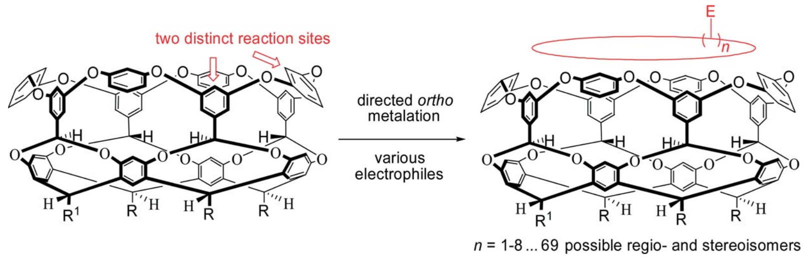
Keywords: Aggregation / Electron transfer / Fluorescence / Phthalocyanines / Singlet oxygen



Azaphthalocyanine self-assembled J-dimers are formed in noncoordinating solvents. The addition of pyridine leads to monomerization and quenching of fluorescence and singlet oxygen formation as a result of intramolecular photoinduced electron transfer (PET). PET is inhibited in dimers; therefore, dimers have higher fluorescence and singlet oxygen quantum yields than the corresponding monomers.

FULL PAPERS

Cavitands



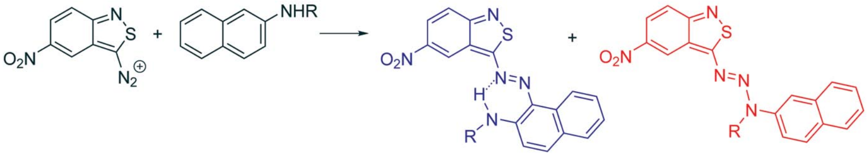
The *endo*- and *exo*-rim positions of deep-cavity cavitand **1** were functionalized by directed *ortho* metalation procedures to give a range of cavitands with ester, phenol, and thioether functionality.

K. Srinivasan, Z. R. Laughrey,
B. C. Gibb* **3265–3271**

Broad Functionalization of Deep-Cavity Cavitands by Directed *ortho* Metalation

Keywords: Cavitands / Lithiation / Receptors / Supramolecular chemistry

Azo Coupling



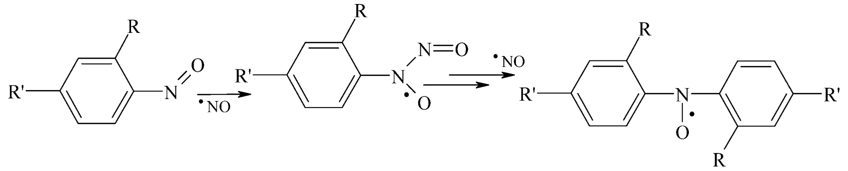
Triazenes derived from 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium and primary or secondary aromatic amines are protonated in acid media at the heterocyclic nitrogen atom, which explains their high stability. Stable triazenes are formed by the reaction of this diazonium cation and 2-alkylaminonaphthalenes.

J. Přikryl, V. Macháček,* P. Jansa,
M. Svobodová, A. Růžička, P. Nachtigall,
M. Černý **3272–3278**

Stable Triazenes Derived from 2-Alkylaminonaphthalenes and 5-Nitrobenzo[*c*]-1,2-thiazole-3-diazonium Hydrogensulfate

Keywords: Azo compounds / Diazoniums / Triazenes / Density functional calculations / Amines

Nitrosoarenes and Nitrogen Oxides



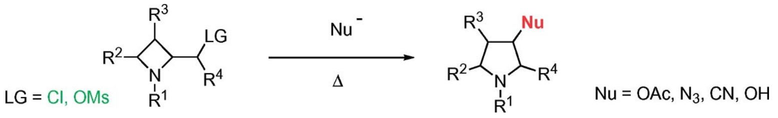
Nitrosoarenes react with nitric oxide in aprotic media and in an ESR cavity to afford the corresponding diarylnitroxides through the intermediate formation of *N*-nitrosoarylnitroxides. Diarylnitroxides are also obtained from nitrosoarenes when treated with small amounts of nitrogen dioxide. The mechanism of this reaction is proposed and discussed.

P. Astolfi, P. Carloni, E. Damiani,
L. Greci,* M. Marini, C. Rizzoli,
P. Stipa **3279–3285**

Reactions of Nitrosoarenes with Nitrogen Monoxide (Nitric Oxide) and Nitrogen Dioxide: Formation of Diarylnitroxides

Keywords: Nitrosoarenes / Nitrogen oxides / Diazonium salts / Diarylnitroxides

Stereospecific Ring Expansion



Azetidines undergo stereospecific ring expansion to produce stereodefined pyrrolidines bearing a functional group at C-3 (N_3, OAc, OH, CN, Cl, or OMS). The scope and mechanism of this rearrangement was investigated, and it involves the formation of an intermediate bicyclic aziridinium ion, which is opened regioselectively at the bridgehead carbon atom.

F. Durrat, M. V. Sanchez, F. Couty,*
G. Evano, J. Marrot **3286–3297**

Ring Expansion of 2-(α-Hydroxyalkyl)-azetidines: A Synthetic Route to Functionalized Pyrrolidines

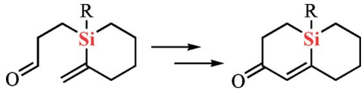
Keywords: Nitrogen heterocycles / Rearrangement / Ring expansions

Organosilicon Compounds

S. Díez-González, R. Paugam,
L. Blanco* **3298–3307**

Synthesis of 1-Silabicyclo[4.4.0]dec-5-en-4-ones: A Model of the A and B Rings of 10-Silatestosterone

Keywords: Silicon / Synthesis design / Ene reaction / Diastereoselectivity / Fused-ring systems



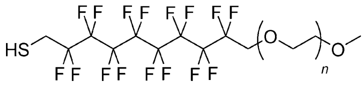
Bicyclic compounds with a silicon atom at the ring junction have been prepared in a few steps from commercially available chlorosilanes. The bicyclic core was constructed by a diastereoselective ene reaction.

Fluorinated Thiols

C. Gentilini, M. Boccalon,
L. Pasquato* **3308–3313**

Straightforward Synthesis of Fluorinated Amphiphilic Thiols

Keywords: Synthesis design / Sulfur / Thiols / Amphiphiles / Fluorine



n = 3, 4, 6, and 12–13

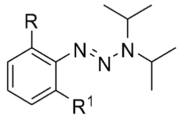
C8-perfluoroalkyl thiols bearing a polyoxyethylene chain of variable length were prepared in good yields following a straightforward synthetic strategy. These thiols are soluble in organic solvents of different polarities from chloroform to methanol. The thiol with a PEG550 chain shows very good solubility in water.

Triazene Chemistry

R. Reingruber, S. Vanderheiden,
A. Wagner, M. Nieger, T. Muller,
M. Es-Sayed, S. Bräse* **3314–3327**

1-Aryl-3,3-diisopropyltriazenes: An Easily Accessible and Particularly Stable Class of Triazenes Towards Strong Basic and Lewis Acid Conditions

Keywords: Triazenes / Synthetic intermediates / Heterocycles / Cyclopropanation / Reductive amination



R = nitrile, imine, ketone

R^1 = H or CF_3

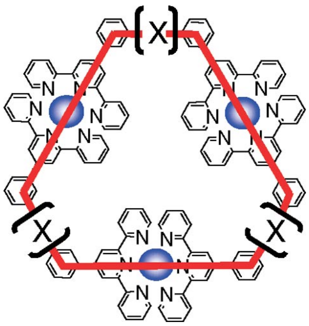
1-(2-Substituted phenyl)-3,3-diisopropyltriazenes are versatile and valuable synthetic intermediates because they are capable to stand strong bases. Beside they tolerate, in contrast to most triazenes, metal/acid reductive conditions and even the presence of strong Lewis acids like $AlMe_3$.

Self-Assembly

S. Li, C. N. Moorefield, P. Wang,
C. D. Shreiner,
G. R. Newkome* **3328–3334**

Self-Assembly of Shape-Persistent Hexagonal Macrocycles with Trimeric Bis(terpyridine)–Fe^{II} Connectivity

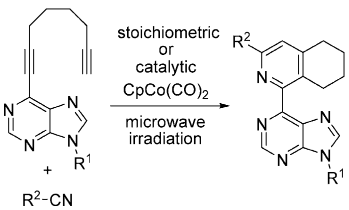
Keywords: Bis(terpyridine)s / Iron complexes / Hexamers / Macrocyclization / Pd-coupling



The construction of a series of bis(terpyridine) building blocks has resulted in the formation of a family of trimetallic hexamers using Fe^{II} for terpyridine connectivity. The synthesis involved Suzuki and Sonogashira couplings as key transformations. The metallomacrocycles were fully characterized by standard methods; their UV spectroscopic and electrochemical properties are also reported.

Cyclotrimerization

A novel, efficient, and atom-economic methodology for the preparation of a large series of diversely substituted (pyridin-2-yl)purines has been developed based on the microwave-enhanced cyclotrimerization of 6-(diynyl)purines with nitriles in the presence of a stoichiometric or catalytic amount of [CpCo(CO)$_2$].

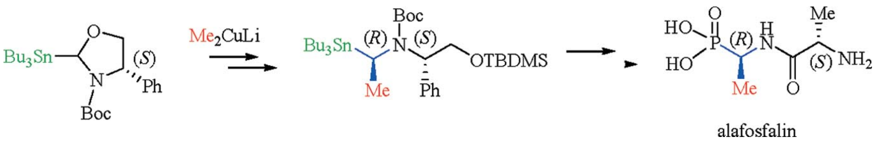


**P. Turek, M. Hocek,* R. Pohl,
B. Klepetářová, M. Kotora*** ... **3335–3343**

Cobalt-Induced Synthesis of 6-(Pyridin-2-yl)-purines by Microwave-Enhanced [2+2+2] Cyclotrimerization

Keywords: Cyclotrimerization / Cobalt / Pyridines / Purines / Microwave reactions

Aminoorganostannanes



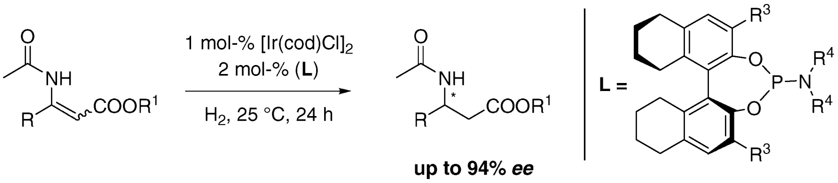
Enantioenriched tributylstannylated α-amino alcohols were synthesised by an improved procedure based on ring opening of 2-tributylstannyloxazolidines. Corresponding α-amino organolithiums were generated from *O*-silylated tributylstannylated α-amino alcohols and trapped with retention of configuration. Thereby, this methodology was used to synthesise alafosfalin.

**V. Coeffard, I. Beaudet,
M. Evain, E. Le Grognec,*
J.-P. Quintard*** **3344–3351**

Preparation and Transmetallation of Enantioenriched α-Aminoorganostannanes Derived from *N*-Boc Phenylglycinol: Application to the Synthesis of Alafosfalin

Keywords: Asymmetric synthesis / Amino acids / Lithium / Tin / Transmetallation

Iridium-Catalyzed Hydrogenation



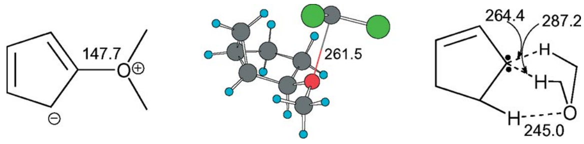
The iridium-catalyzed asymmetric hydrogenation of various β-dehydroamino acids is presented. For transferring chirality easily accessible monodentate octahydrobinaphthol-based phosphoramidite ligands have been used. Good to excellent enantioselectivities and yields were obtained for the first time in the presence of monodentate ligands.

**S. Enthaler, G. Erre, K. Junge,
K. Schröder, D. Addis, D. Michalik,
M. Hapke, D. Redkin,
M. Beller*** **3352–3362**

Iridium-Catalyzed Hydrogenation of β-Dehydroamino Acid Derivatives Using Monodentate Phosphoramidites

Keywords: Asymmetric catalysis / Homogeneous catalysis / Hydrogenation / P ligands / Amino acids / Iridium

Carbenes



The influence of ethers upon carbenes has been investigated. Ylide formation is only obtained with reactive electrophilic carbenes like cyclopentadienylidene, whereas more nucleophilic carbenes like cyclopent-2-enylidene associate by interactions of the lone pair of the carbon atom and the lone pairs of the oxygen atom with C–H bonds. Between the stabilized electrophilic dichlorocarbene and the oxygen lone pair only weak complexes are formed.

**J.-L. Mieusset,
U. H. Brinker*** **3363–3368**

Reactions of Carbenes with Ethers: The Role of Noncovalent Interactions

Keywords: Carbenes / Ethers / Density functional calculations / Reactive intermediates / C–H activation

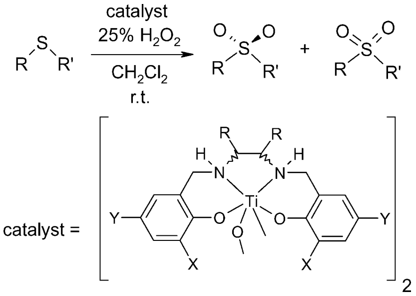
CONTENTS

Asymmetric Catalysis

K. P. Bryliakov,*
E. P. Talsi 3369–3376

Titanium-Salan-Catalyzed Asymmetric Oxidation of Sulfides and Kinetic Resolution of Sulfoxides with H_2O_2 as the Oxidant

Keywords: Asymmetric catalysis / Kinetic resolution / Hydrogen peroxide / Sulfoxides / Titanium / Oxidation



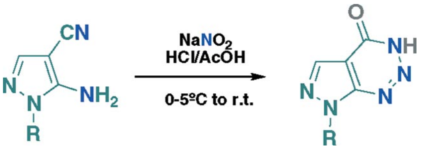
Catalytic oxidation of alkyl aryl sulfides to sulfoxides by H_2O_2 catalyzed by Ti-salan complexes is reported. The high *ee* values observed (up to 97%) are due to tandem asymmetric oxidation/kinetic resolution processes.

Pyrazolotriazines

E. L. Moyano,* J. P. Colomer,
G. I. Yranzo* 3377–3381

New Application of Heterocyclic Diazonium Salts: Synthesis of New Pyrazolo[3,4-*d*][1,2,3]triazin-4-ones

Keywords: Diazonium ions / Pyrazolotriazines / Aminopyrazoles / Nitrogen heterocycles



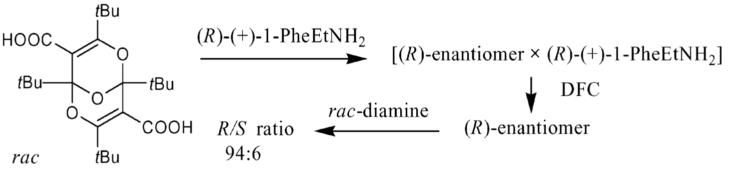
The diazotization reaction of 5-amino-4-carbonitriles is a very good methodology to prepare pyrazolo[3,4-*d*][1,2,3]triazin-4-ones in one step. In this work we report the synthesis of new pyrazolotriazinones, and we also describe how the reaction conditions affect the formation of the products in the diazotization of 5-amino-1-phenyl-1*H*-pyrazole-4-carbonitrile.

Enantiopure (*R*)-Dicarboxylic Acid

J. Kremsner, B. C. Wallfisch, F. Belaj,
G. Uray, C. O. Kappe, C. Wentrup,
G. Kollenz* 3382–3388

Tetra-*tert*-butyltrioxabicyclo[3.3.1]nonadienedicarboxylic Acid: Optical Resolution, Absolute Configuration and Application in Chiral Discrimination

Keywords: Carboxylic acids / Chiral resolution / Configuration determination / Chiral auxiliaries



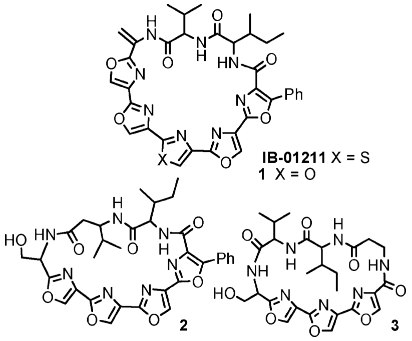
rac-Tetra-*tert*-butyltrioxabicyclo[3.3.1]-nonadienedicarboxylic acid was successfully resolved by formation of diastereomeric salts, the release of the pure enantiomers was achieved by DF chromatography. The absolute configuration of the (*R*)-enantiomer was determined by X-ray crystallography, it can serve as chiral auxiliary for resolving *rac*-diamines.

Natural Product Derivatives

D. Hernández, E. Riego, F. Albericio,*
M. Álvarez* 3389–3396

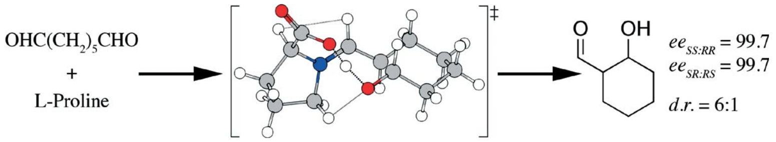
Synthesis of Natural Product Derivatives Containing 2,4-Concatenated Oxazoles

Keywords: Concatenated oxazoles / Peptides / Nitrogen heterocycles / Macrocyclization



The synthesis of several oxazole-containing derivatives of IB-01211 is described. Studies on the macrocyclization reactions of peptides containing three, four, and five 2,4-concatenated azoles were performed.

Intramolecular Aldol Reaction



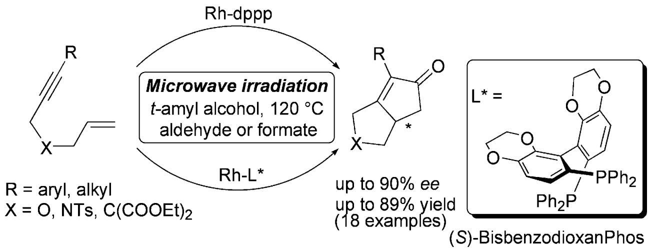
TSs associated with the C–C bond-formation step in proline-catalyzed intramolecular aldol reactions of 1,7-dialdehydes are studied using DFT methods. Two reactive channels, corresponding to the anhydrous system or to the explicit inclusion of water are analysed. Theoretical data allows the rationalization of the experimental results and validates the proposed mechanism.

F. J. S. Duarte, E. J. Cabrita, G. Frenking, A. G. Santos* **3397–3402**

Mechanistic Study of Intramolecular Aldol Reactions of Dialdehydes 💻

Keywords: Asymmetric catalysis / Aldol reactions / Transition states / Density functional calculations

Catalytic Microwave Reactions



Microwave-assisted Rh–diphosphane-complex-catalyzed dual catalysis is reported. This cooperative process provides [2+2+1] cycloadducts by sequential decarbonylation of aldehyde or formate and carbonylation of enynes within a short period of time. In the presence of the chiral Rh complex, the cyclopentenone products were achieved with *ee* values up to 90%.

H. W. Lee, L. N. Lee, A. S. C. Chan, F. Y. Kwong* **3403–3406**

Microwave-Assisted Rhodium-Complex-Catalyzed Cascade Decarbonylation and Asymmetric Pauson–Khand-Type Cyclizations 💻

Keywords: Microwave / Rhodium / Asymmetric catalysis / Cyclization

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* Author to whom correspondence should be addressed.

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