

Organic & Biomolecular Chemistry

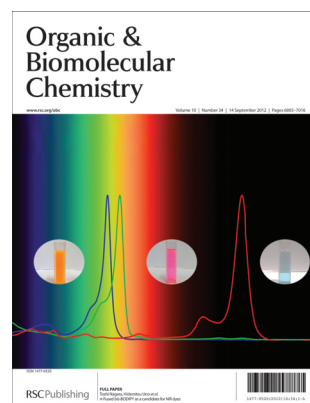
An international journal of synthetic, physical and biomolecular organic chemistry

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ISSN 1477-0520 CODEN OBCRAK 10(34) 6805–7016 (2012)



Cover

See Toshi Nagata, Hidemitsu Uno *et al.*, pp. 6840–6849.

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Inside cover

See Xin-Dong Jiang, Weili Zhao *et al.*, pp. 6861–6865.

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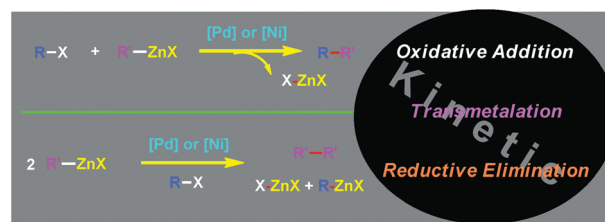
PERSPECTIVE

6817

Insights into the elementary steps in Negishi coupling through kinetic investigations

Liqun Jin and Aiwen Lei*

Kinetic studies: an important and efficient approach to reveal the mechanism of Negishi coupling.



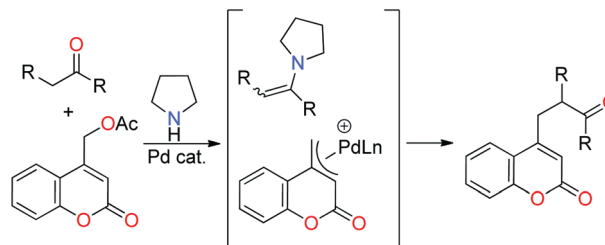
COMMUNICATIONS

6826

Palladium-catalyzed, pyrrolidine-mediated arylmethylation of ketones and aldehydes with coumarinyl(methyl) acetates

Kalicharan Cattopadhyay, Antonio Recio III and Jon A. Tunge*

We report the palladium-catalyzed, pyrrolidine-mediated α -benzylation of enamines which couples medicinally relevant coumarin moieties with aldehydes and ketones.



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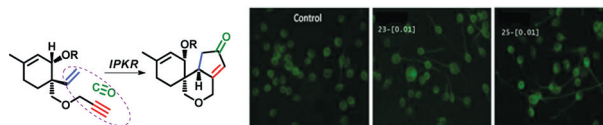
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COMMUNICATIONS

6830

Diverted organic synthesis (DOS): accessing a new, natural product inspired, neurotrophically active scaffold through an intramolecular Pauson–Khand reactionGoverdhan Mehta,* Ramesh Samineni, Pabbaraja Srihari,*
R. Gajendra Reddy and Sumana Chakravarty

Inspired by the natural product paecilomycine A and its impressive neurotrophic activity, we have designed a new 2-oxa-spiro[5.5]-undecane based scaffold, and evaluated several compounds based on this new ring system for their neurotrophic activity.

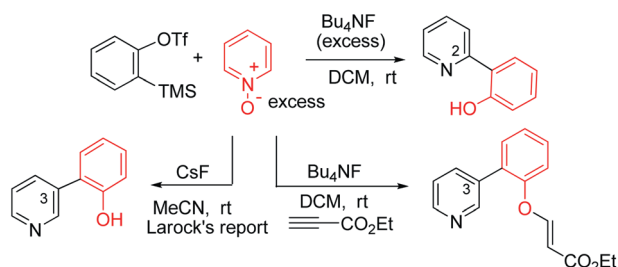


6834

Regioselective synthesis of 2-(2-hydroxyaryl)pyridines from the reactions of benzynes with pyridine *N*-oxides

Balagopal S. Shaibu, Rahul Kisan Kawade and Rai-Shung Liu*

By modifying the conditions from those in Larock's reported synthesis of 3-(2-hydroxyaryl)pyridines from benzynes, and pyridine *N*-oxides, we altered the regioselectivity of the reaction toward an efficient synthesis of 2-substituted pyridines; we conducted appropriate control experiments that enable a full understanding of the mechanism.

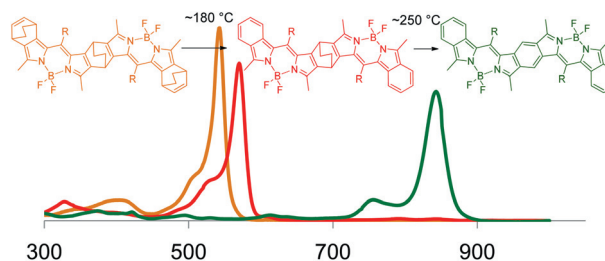


PAPERS

6840

 π -Fused bis-BODIPY as a candidate for NIR dyesMitsunori Nakamura, Hiroyuki Tahara, Kohtaro Takahashi,
Toshi Nagata,* Hiroki Uoyama, Daiki Kuzuhara, Shigeki Mori,
Tetsuo Okujima, Hiroko Yamada and Hidemitsu Uno*

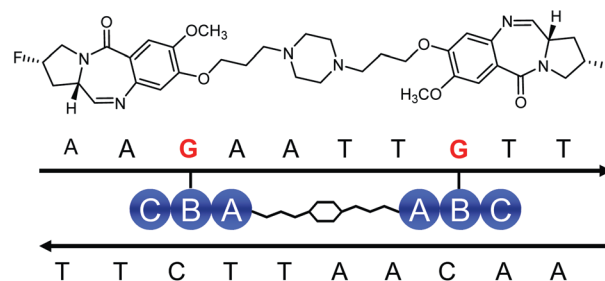
anti-Bis-benzoBODIPY prepared by a retro-Diels–Alder reaction of the corresponding BCOD-fused bis-BODIPY is revealed to have absorption and emission maxima exceeding 840 nm and to keep good transparency in the visible region.



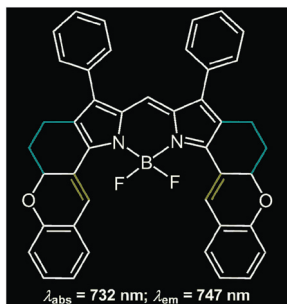
6850

Inter- and intrastrand DNA crosslinks by 2-fluoro-substituted pyrrolobenzodiazepine dimers: stability, stereochemistry and drug orientationJenny Seifert, Soheil Pezeshki, Ahmed Kamal and
Klaus Weisz*

2-Fluoro-substituted pyrrolobenzodiazepine dimers form inter- and intrastrand DNA bis-adducts, whose stereochemistry and orientation may be directly deduced from chemical shift changes of specific drug protons.



6861

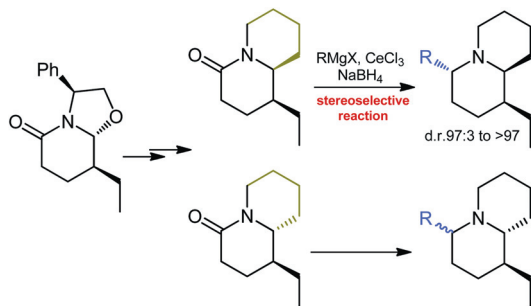


A NIR BODIPY dye bearing 3,4,4a-trihydroxanthene moieties

Xin-Dong Jiang,* Ruina Gao, Yi Yue, Guo-Tao Sun and Weili Zhao*

A novel 3,4,4a-trihydroxanthene-fused pyrrole was synthesized by the reaction of 2,3,4,4a-tetrahydro-1H-xanthen-1-one with 3-phenyl-2H-azirine in the presence of LDA. Using this pyrrole a NIR BODIPY that is stable, non-cytotoxic, and suited to labeling living cells for imaging assay in the NIR region was prepared.

6866

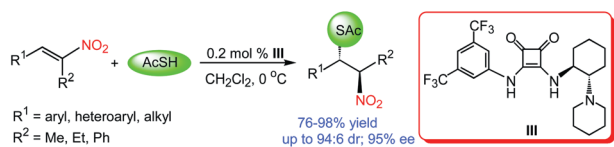


Enantioselective, protecting group-free synthesis of 1S-ethyl-4-substituted quinolizidines

Mercedes Amat,* Vladislav Semak, Carmen Escolano,* Elies Molins and Joan Bosch

A straightforward protecting group-free enantioselective synthesis of 1S-ethyl-4-substituted quinolizidines is reported. Theoretical studies were performed to justify the stereochemical outcome in the addition of Grignard reagents to 1-ethyl-4-oxo-quinolizidine derivatives.

6876



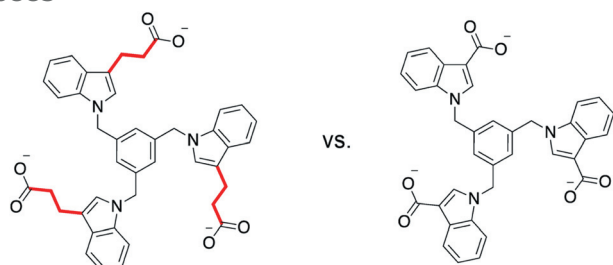
R¹ = aryl, heteroaryl, alkyl
R² = Me, Et, Ph

Squaramide-catalysed enantio- and diastereoselective sulfa-Michael addition of thioacetic acid to α,β -disubstituted nitroalkenes

Wen Yang and Da-Ming Du*

A highly enantio- and diastereoselective sulfa-Michael addition of thioacetic acid to α,β -disubstituted nitroalkenes catalysed by a chiral squaramide organocatalyst (0.2 mol%) afforded β -nitro sulfides in excellent yields with good diastereoselectivities and high enantioselectivities (up to 94 : 6 dr, 95% ee). This catalytic reaction can be performed on a 10 gram scale.

6885



Binding trimethyllysine and other cationic guests in water with a series of indole-derived hosts: large differences in affinity from subtle changes in structure

Amanda L. Whiting and Fraser Hof*

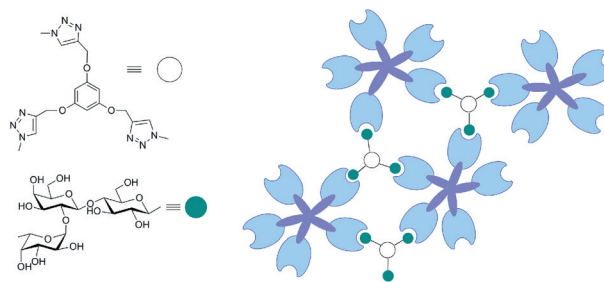
Not so innocent: seemingly minimal changes to pendent solubilizing groups were found to have a significant impact on binding quaternary ammonium cations in water.

6893

Bi- to tetravalent glycoclusters: synthesis, structure–activity profiles as lectin inhibitors and impact of combining both valency and headgroup tailoring on selectivity

Guan-Nan Wang, Sabine André, Hans-Joachim Gabius and Paul V. Murphy*

The emerging functional versatility of cellular glycans makes research on the design of synthetic inhibitors of receptor(lectin)-carbohydrate interactions a timely topic.

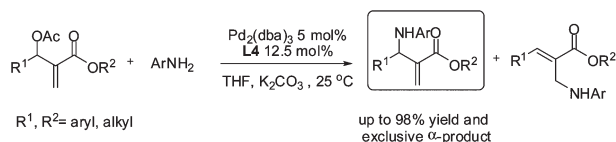


6908

Palladium-catalyzed α -regioselective allylic amination of Morita–Baylis–Hillman acetates with simple aromatic amines

Yan Wang, Li Liu,* Dong Wang and Yong-Jun Chen

An efficient allylic amination of Morita–Baylis–Hillman acetates with simple aromatic amines provided good yields with excellent α -regioselectivity (up to exclusive α -product) under the catalysis of $\text{Pd}_2(\text{dba})_3$ /ferrocene-type diphosphine ligand.

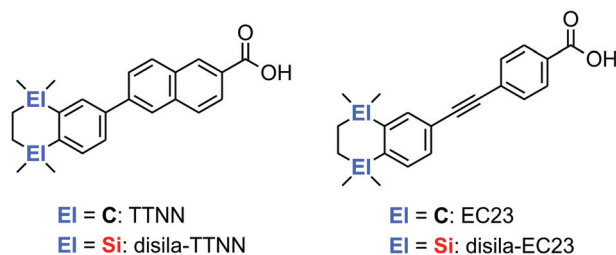


6914

Disila-analogues of the synthetic retinoids EC23 and TTNN: synthesis, structure and biological evaluation

Josef B. G. Gluyas, Christian Burschka, Steffen Dörrich, Judith Vallet, Hinrich Gronemeyer and Reinhold Tacke*

C/Si switch: Two-fold sila-substitution (*C/Si* exchange) in the synthetic retinoids EC23 and TTNN leads to disila-EC23 and disila-TTNN. The chemistry and biology (RAR α,β,γ activation) of these *C/Si* pairs and related compounds are reported.

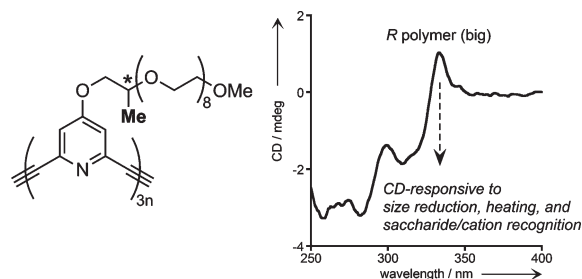


6930

Formation of higher-order structures of chiral poly(ethynylpyridine)s depending on size, temperature, and saccharide recognition

Hajime Abe,* Kotaro Okada, Hiroki Makida and Masahiko Inouye*

Chiral helical *meta*-ethynylpyridine polymers were developed, which are CD-responsive to size, temperature, and recognition of saccharide and metal cations.



New process for crystal data files

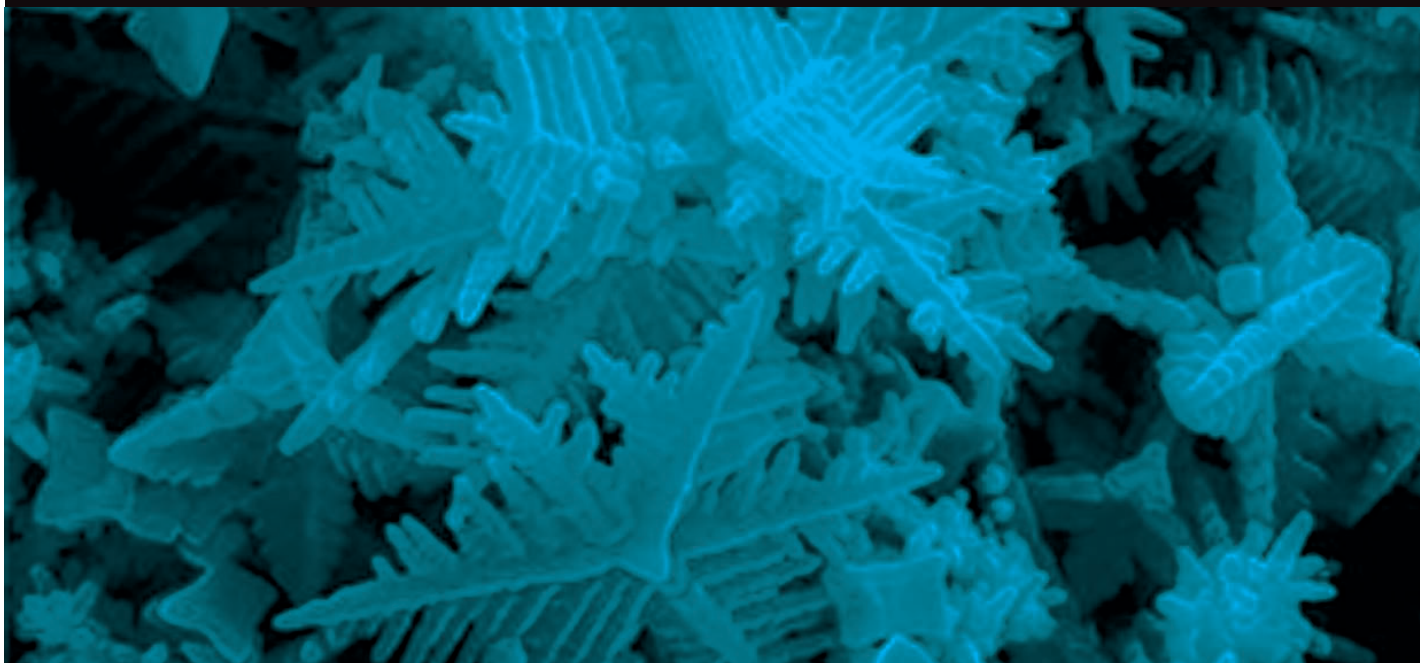


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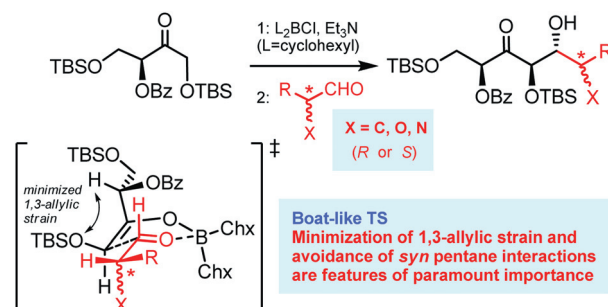
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6937

Double diastereoselection in *anti* aldol reactions mediated by dicyclohexylchloroborane between an L-erythrose derivative and chiral aldehydes

Santiago Díaz-Oltra, Purificación Ruiz, Eva Falomir, Juan Murga, Miguel Carda* and J. Alberto Marco*

Anti boron aldol reactions of an L-erythrose derivative with α -chiral aldehydes are examined. Boat-like transition states with minimized 1,3-allylic strain and avoidance of *syn* pentane interactions are proposed.

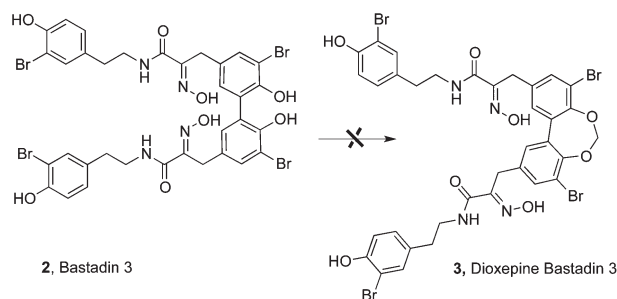


6945

First total synthesis of dioxepine bastadin 3

Santiago Pérez-Rodríguez, Raquel Pereira-Cameselle and Ángel R. de Lera*

Dioxepine bastadin 3 has been synthesized by a route that constructs the dibenzo-1,3-dioxepine ring early in the synthesis after the unsuccessful attempts to derive this compound from the putative biogenetic precursor bastadin 3.

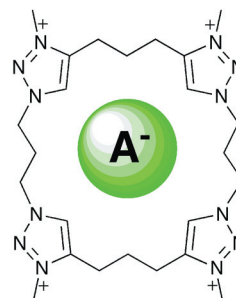


6951

Anion binding in aqueous media by a tetra-triazolium macrocycle

Nicholas G. White, Silvia Carvalho, Vítor Félix and Paul D. Beer*

A tetra-triazolium macrocycle is prepared and shown to bind strongly the larger halides, bromide and iodide, and sulfate anions in aqueous solvent media through charge-assisted C–H...anion hydrogen bonds.

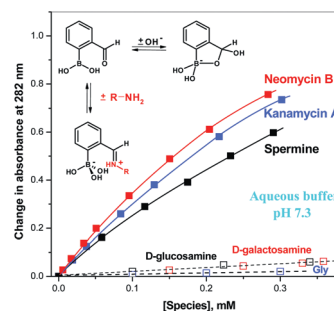


6960

Schiff base formation and recognition of amino sugars, aminoglycosides and biological polyamines by 2-formyl phenylboronic acid in aqueous solution

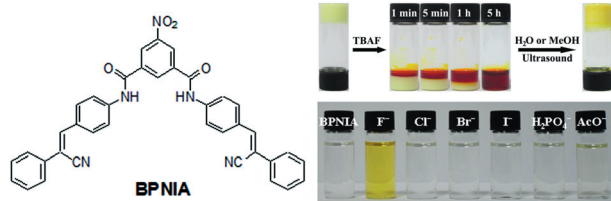
Nini J. Gutiérrez-Moreno, Felipe Medrano and Anatoly K. Yatsimirsky*

2-Formyl phenylboronic acid undergoes cyclization to an anionic benzoboroxole in basic aqueous solutions and forms zwitterionic Schiff bases containing protonated imine nitrogen with amines, including amino sugars, which are particularly stable with aminoglycosides and biological polyamines.



PAPERS

6973

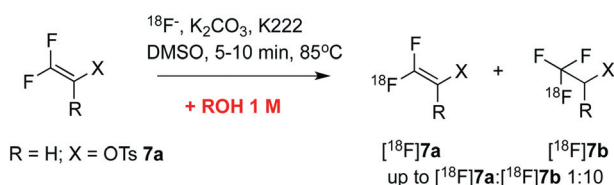


Fluoride-responsive gelator and colorimetric sensor based on simple and easy-to-prepare cyano-substituted amide

Yuping Zhang and Shimei Jiang*

BPNIA could allow a two channel fluoride response by proton controlled reversible sol–gel transition and color changes.

6980

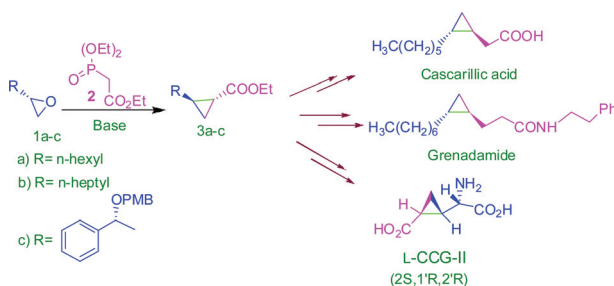


Direct, nucleophilic radiosynthesis of $[^{18}\text{F}]$ trifluoroalkyl tosylates: improved labelling procedures

Patrick J. Riss,* Valentina Ferrari, Laurent Brichard, Paul Burke, Robert Smith and Franklin I. Aigbirhio

An improved, efficient procedure for nucleophilic addition of $[^{18}\text{F}]\text{HF}$ is described.

6987

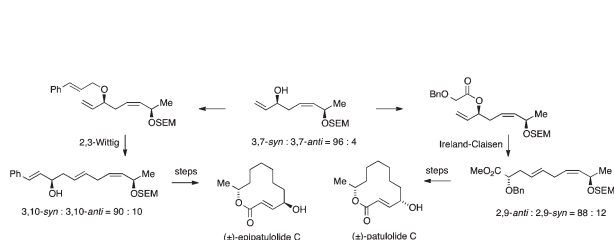


Enantio- and diastereocontrolled conversion of chiral epoxides to *trans*-cyclopropane carboxylates: application to the synthesis of cascarillic acid, grenadamide and L-(–)-CCG-II

Pradeep Kumar,* Abhishek Dubey and Anand Harbindu

A very concise and practical synthesis of cascarillic acid, grenadamide and L-CCG-II, a cyclopropane containing natural products is accomplished employing Wadsworth-Emmons cyclopropanation reaction as key step.

6995



An approach to aliphatic 1,8-stereocontrol: diastereoselective syntheses of (±)-patulolide C and (±)-epipatulolide C

E. Kate Hoegenauer and Eric J. Thomas*

Aliphatic compounds with *syn*- and *anti*-1,8-related stereogenic centres were prepared stereoselectively using Ireland–Claisen and 2,3-Wittig rearrangements of products that had been prepared with 1,5-stereocontrol using an allylstannane, and were taken through to complete diastereoselective syntheses of (±)-patulolide C and (±)-epipatulolide C.

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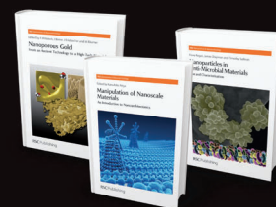
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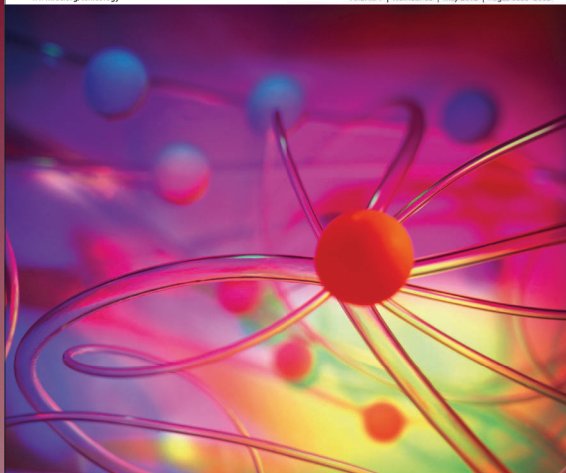
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