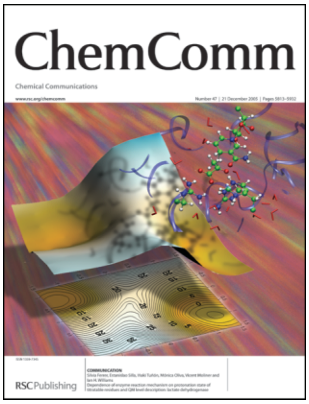
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (47) 5813–5932 (2005)

Cover
See Michael L. Neidig and Edward I. Solomon, page 5843. Spectroscopic methodologies developed for non-heme iron enzymes allow elucidation of the geometric and electronic structures of their active sites and provide molecular level insight into the mechanisms of catalysis and differences in reactivity. Image reproduced by permission of Edward I. Solomon *et al.*, from *Chem. Commun.*, 2005, 5843.



Inside cover
See Silvia Ferrer, Estanislao Silla, Iñaki Tuñón, Mónica Oliva, Vicent Moliner and Ian H. Williams, page 5873. Transition state structure of the chemical reaction mechanism of L-lactate dehydrogenase (LDH) obtained by means of hybrid QM/MM methods with an appropriate re-calculation of the pK_a values of the residues in the enzyme environment. The full LDH tetramer solvated by water molecules (22139 atoms) has been used as a molecular model. Image reproduced by permission of Vicent Moliner *et al.*, from *Chem. Commun.*, 2005, 5873.

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T45

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Chemical Technology

December 2005/Volume 2/Issue 12

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40TH ANNIVERSARY ARTICLES

5825

Self-assembly and generation of complexity

Mir Wais Hosseini

Supramolecular synthesis, by combining molecules through non-covalent interactions, makes it possible to build up extremely sophisticated supramolecular assemblies in the solid state and offers endless architectural possibilities.

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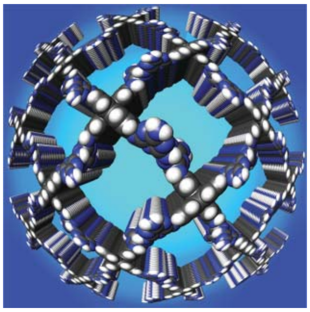
40TH ANNIVERSARY ARTICLES

5830

Engineering crystals by the strategy of molecular tectonics

James D. Wuest

Detailed structures of molecular crystals cannot yet be predicted with consistent accuracy, but the strategy of molecular tectonics offers crystal engineers a powerful tool for designing molecules that are predisposed to form crystals with particular structural features and properties.



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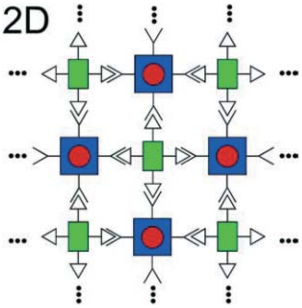
Design of crystalline molecular networks with charge-assisted hydrogen bonds

Michael D. Ward

Empirical guidelines for steering molecular assembly into prescribed crystal architectures *via* hydrogen bonding continue to emerge, with recent developments demonstrating that charge-assisted hydrogen bonds introduce both strength and compliance that can facilitate solid state design.



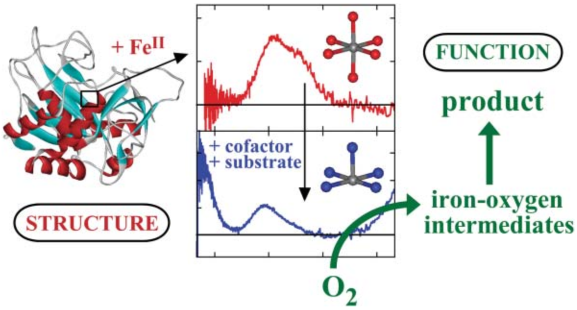
FEATURE ARTICLE

5843

Structure–function correlations in oxygen activating non-heme iron enzymes

Michael L. Neidig and Edward I. Solomon*

Structure–function correlations in O_2 activating mononuclear non-heme iron enzymes derived from a spectroscopic methodology developed for Fe^{II} active sites are presented, including mechanisms of O_2 activation and contributions to differences in reactivity.



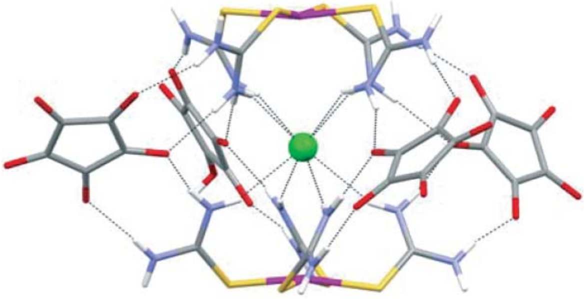
COMMUNICATIONS

5864

Solvent-induced supramolecular isomerism in $[Pt(S{=}C(NH_2)_2)_4]^{2+}$ croconate salts

Philip A. Gale,* Mark E. Light and Roberto Quesada

Platinum tetrakis(thiourea) croconate salts form a variety of network type structures dependent on the presence of solvent and other species.



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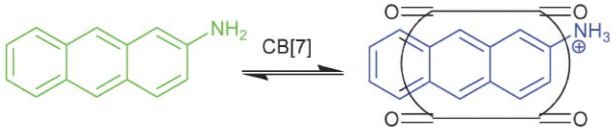
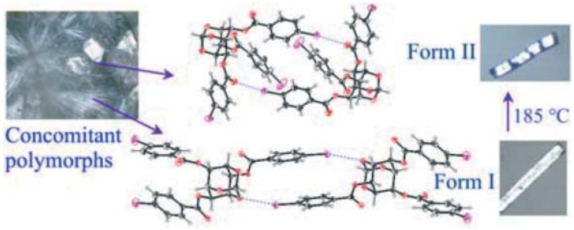


A green to blue fluorescence switch of protonated 2-aminoanthracene upon inclusion in cucurbit[7]uril

Ruibing Wang, Lina Yuan and Donal H. Macartney*

The inclusion of protonated 2-aminoanthracene in the cavity of cucurbit[7]uril results in a significant decrease in the acidity of the excited state, and a switch from green to blue fluorescence emission in acidic aqueous solution.

5870

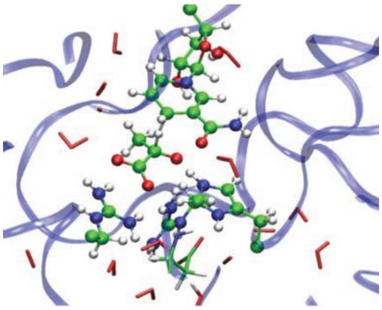


Concomitant dimorphs of tri-*O*-[*p*-halobenzoyl]-*myo*-inositol 1,3,5-orthoformates with different halogen bonding contacts: first order crystal-to-crystal thermal phase transition of kinetic form to the thermodynamic form

Rajesh G. Gonnade, Mohan M. Bhadbhade,*
Mysore S. Shashidhar* and Aditya K. Sanki

The kinetic polymorph with C–Br···O–C contacts undergoes crystal-to-crystal thermal transition to the thermodynamic form with C–Br···O=C contacts.

5873

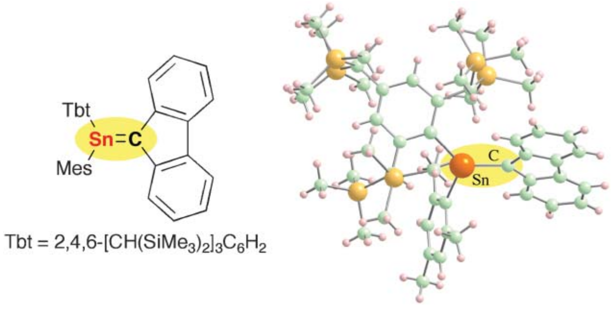


Dependence of enzyme reaction mechanism on protonation state of titratable residues and QM level description: lactate dehydrogenase

Silvia Ferrer, Estanislao Silla, Iñaki Tuñón,*
Mónica Oliva, Vicent Moliner* and Ian H. Williams

The dependence of the chemical reaction mechanism of L-lactate dehydrogenase (LDH) on the protonation state of titratable residues and on the level of the quantum mechanical (QM) description has been studied by means of hybrid QM/MM methods using the LDH tetramer solvated by water molecules.

5876



Synthesis and properties of a stable 6-stannapentafulvene

Yoshiyuki Mizuhata, Nobuhiro Takeda,
Takahiro Sasamori and Norihiro Tokitoh*

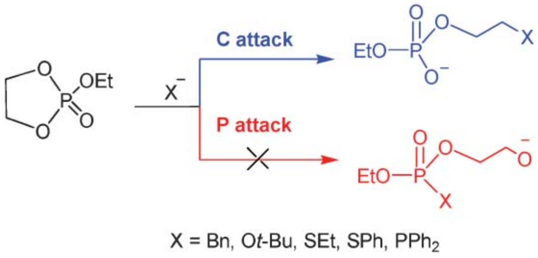
The first donor-free 6-stannapentafulvene stable at ambient temperature was synthesized and isolated, exhibiting the shortest tin–carbon bond length among those previously reported.

5879

Selective site controlled nucleophilic attacks in 5-membered ring phosphate esters: unusual C–O *vs.* common P–O bond cleavage

Nissan Ashkenazi,* Sanjio S. Zade, Yoffi Segall, Yishai Karton and Michael Bendikov*

Clean endocyclic C–O bond cleavage has been achieved in the reactions of 5-membered phosphate triesters with various nucleophiles. This new reactivity will be important for organic transformations in biological systems.

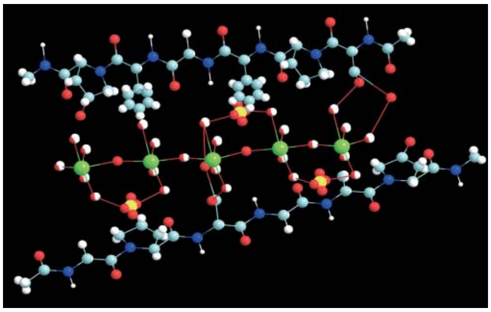


5882

Collagen fiber immobilized Fe(III): a novel catalyst for photo-assisted degradation of dyes

Rui Tang, Xue-Pin Liao, Xin Liu and Bi Shi*

A novel catalyst for the Fenton reaction was prepared by immobilizing Fe(III) onto collagen fiber and its high activity as a catalyst for degradation of dyes under irradiation of UVC was proved.

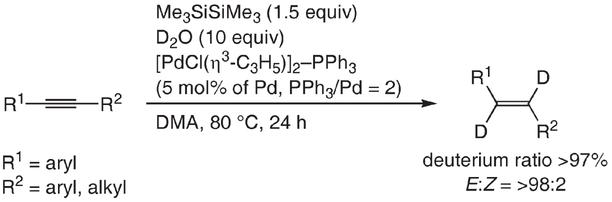


5885

Reduction of alkynes into 1,2-dideuterioalkenes with hexamethyldisilane and deuterium oxide in the presence of a palladium catalyst

Eiji Shirakawa,* Hidehito Otsuka and Tamio Hayashi*

(*E*)-1,2-Dideuterioalkenes are obtained by deuterium transfer reaction from deuterium oxide, the most inexpensive deuterium source, to alkynes using a palladium–triphenylphosphine catalyst and hexamethyldisilane as a reductant, where high deuterium ratios (>97%) are compatible with high stereoselectivities (>98%).

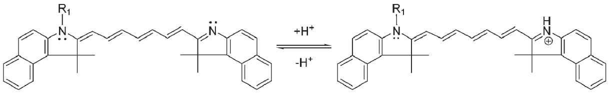


5887

Design, synthesis and evaluation of near-infrared fluorescent pH indicators in a physiologically relevant range

Zongren Zhang and Samuel Achilefu*

Removal of one hydroxylsulfonylbutyl arm from indocyanine green dye afforded a near infrared fluorescent pH-sensitive dye. With a pK_a of 7.23, this molecular probe is useful for measuring pH-dependent biological processes.



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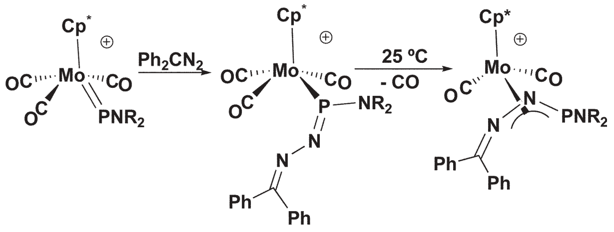
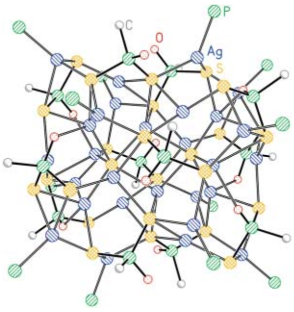


Reactivity patterns of thermally stable, terminal, electrophilic phosphinidene complexes towards diazoalkanes: oxidation at the phosphorus centre and formation of P-bound η^1-phosphaazine, η^1-phosphaalkene and η^3-diazaphosphaallene complexes

Todd W. Graham, Konstantin A. Udachin and Arthur J. Carty*

Cationic, η^1-PNR$_2$–Cr, Mo, W or Fe complexes react with the diazoalkanes to form η^1-phosphaazine, η^1-phosphaalkene or η^3-diazaphosphaallene complexes.

5893

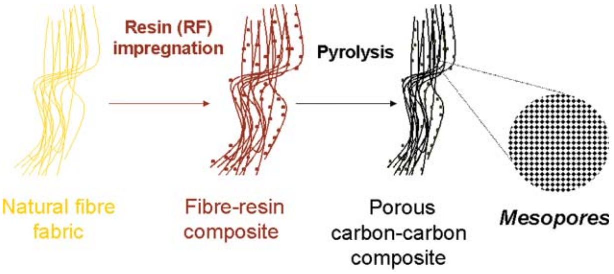


Reactions of P/S-containing proligands with coinage metal salts: a new route to polynuclear complexes with unusual structural types

Weifeng Shi, Reinhart Ahlrichs, Christopher E. Anson, Alexander Rothenberger,* Claudia Schrodt and Maryam Shafaei-Fallah

The thiophilicity of coinage metals and the oxophilicity of phosphorus can drive the assembly of clusters and novel complexes containing P/S ligands.

5896

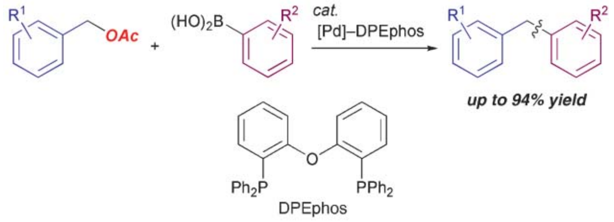


Porous carbon–carbon composite replicated from a natural fibre

Mariano M. Bruno, N. Gustavo Cotella, Maria C. Miras and Cesar A. Barbero*

Carbon–carbon composites can be produced by pyrolysis of natural fibre materials impregnated with resorcinol–formaldehyde resins. The materials develop significant mesoporosity without using template agents or special drying of the polymer gels.

5899



Cross-coupling of benzylic acetates with arylboronic acids: one-pot transformation of benzylic alcohols to diarylmethanes

Ryoichi Kuwano* and Masashi Yokogi

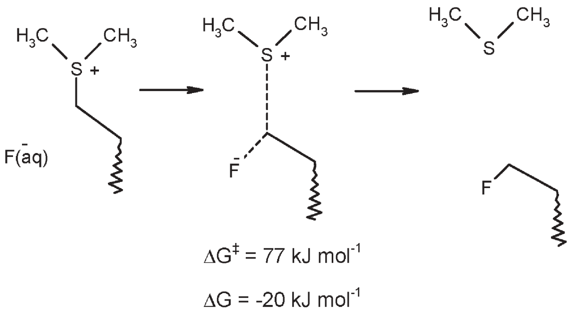
Benzylic acetates reacted with arylboronic acids by means of a DPEphos–palladium catalyst. This is the first reaction involving the cleavage of a benzylic C–O bond of benzyl acetate by a transition metal complex.

5902

The solvated fluoride anion can be a good nucleophile

Mark A. Vincent and Ian H. Hillier*

Computations show how the solvated fluoride ion can be a good nucleophile in spite of its high solvation energy.

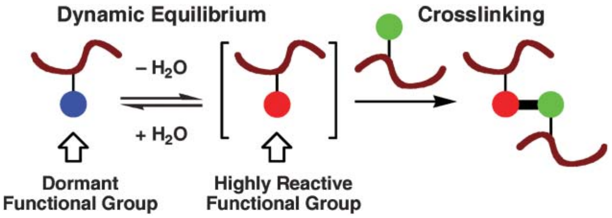


5904

Latent reactive groups unveiled through equilibrium dynamics and exemplified in crosslinking during film formation from aqueous polymer colloids

David J. Berrisford,* Peter A. Lovell,* Nadia R. Suliman and Andrew Whiting*

We introduce the concept of using equilibrium dynamics to provide for both protection and unveiling of latent functional groups at appropriate times in aqueous polymer colloid coatings designed for crosslinking only during film formation.

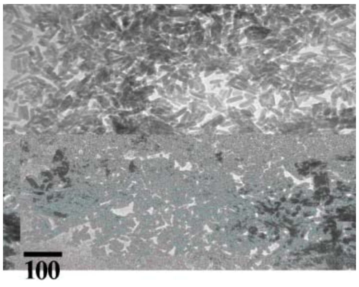


5907

Rod-like Cu/La/O nanoparticles as a catalyst for phenol hydroxylation

Linfeng Gou and Catherine J. Murphy*

Amorphous nanorods containing La, Cu and O are surprisingly good catalysts for phenol hydroxylation.

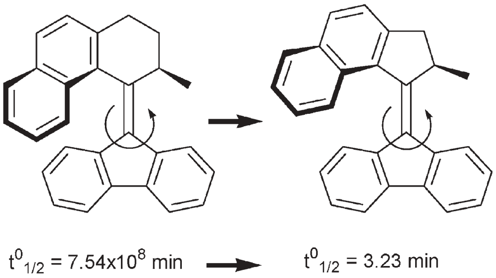


5910

Controlling the speed of rotation in molecular motors. Dramatic acceleration of the rotary motion by structural modification

Javier Vicario, Auke Meetsma and Ben L. Feringa*

Simply replacing a 6-membered by a 5-membered ring in a light driven unidirectional molecular motor enhances the speed by a factor of 10^8.



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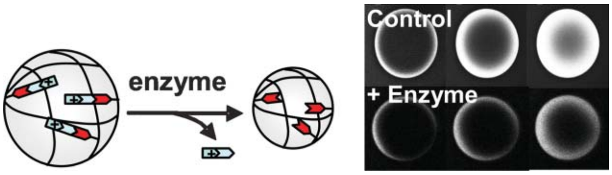
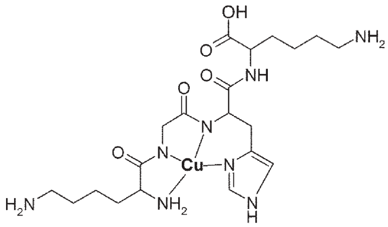


Enzyme responsive polymer hydrogel beads

Paul D. Thornton, Gail McConnell and Rein V. Ulijn*

We report on a new class of enzyme responsive polymer hydrogels, the molecular accessibility of which can be changed selectively by enzymes present in a sample fluid.

5916

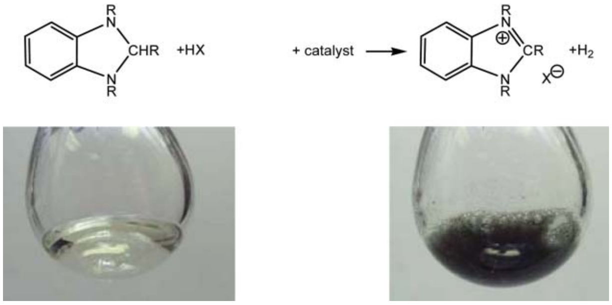


Inactivation of human angiotensin converting enzyme by copper peptide complexes containing ATCUN motifs

Nikhil H. Gokhale and J. A. Cowan*

The copper complex $[\mathrm{Cu(KGHK)}]^+$ demonstrates catalytic inactivation of angiotensin converting enzyme at sub-saturating concentrations, under oxidative conditions, with an observed rate constant $k \sim 2.9 \times 10^{-2}\ \mathrm{min}^{-1}$.

5919



Hydrogen evolution from organic "hydrides"

Daniel E. Schwarz, Thomas M. Cameron, P. Jeffrey Hay, Brian L. Scott, William Tumas and David L. Thorn*

Benzimidazolines (dihydrobenzimidazoles) are shown for the first time to eliminate hydrogen (H_2) by catalyzed reaction with protic compounds.

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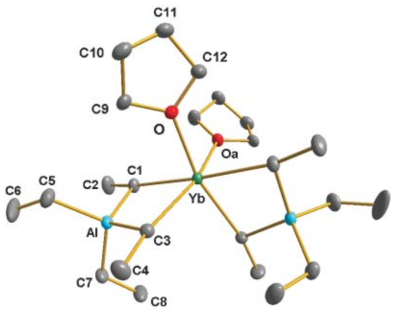


$[\mathrm{Ln^{II}Al^{III}}_2(\mathrm{alkyl})_8]_x$: donor addition instead of donor-induced cleavage

Marcus G. Schrems, H. Martin Dietrich, Karl W. Törnroos and Reiner Anwander*

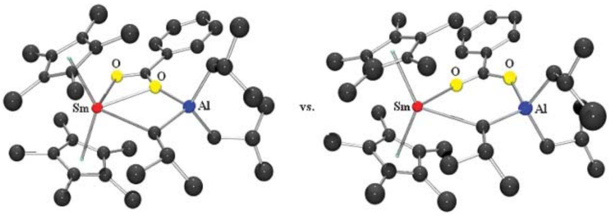
Peralkylated $\mathrm{Ln^{II}}$–$\mathrm{Al^{III}}$ heterobimetallic complexes form stable Lewis base adducts with THF, pyridine and 1,10-phenanthroline. The absence of any donor(Do)-induced $\mathrm{AlR_3(Do)}$ separation reflects a higher degree of covalent bonding in $\mathrm{Ln^{II}}$ *versus* $\mathrm{Ln^{III}}$ tetraalkylaluminate complexes.

5925

Samarium *versus* aluminium Lewis acidity in a mixed alkyl carboxylate complex related to alkylaluminium activation in diene polymerization catalysis

William J. Evans,* Timothy M. Champagne and Joseph W. Ziller

A mixed metal carboxylate complex $[(C_5Me_5)_2Sm(\mu\text{-}O_2CPh)(\mu\text{-}{}^iBu)Al({}^iBu)_2]$ that crystallizes with two different binding modes is reported that shows the delicate balance in the Lewis acidities of aluminium *versus* samarium.



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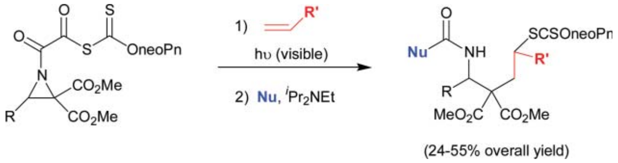
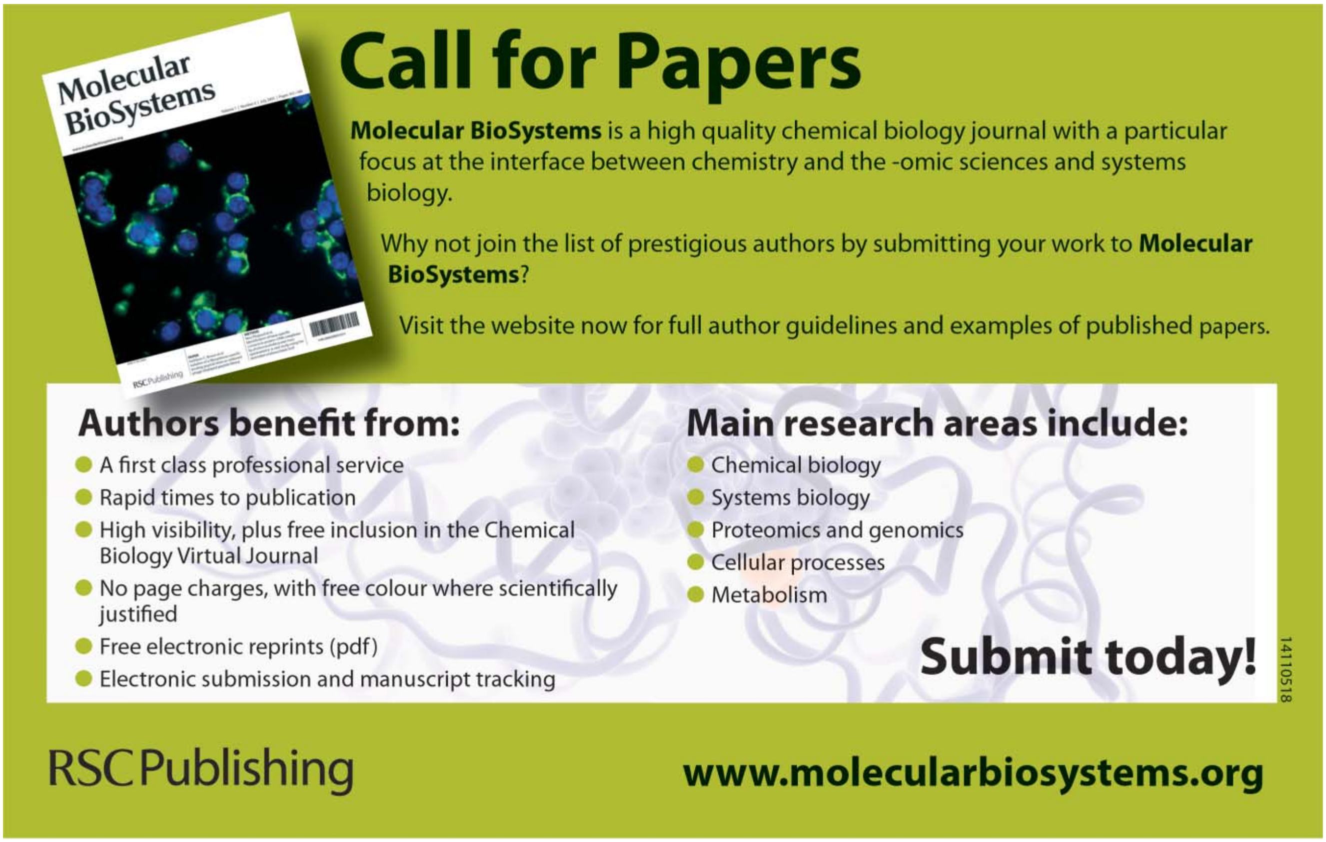
Generation and ring opening of aziridine *N*-carbonyl radicals

Markus R. Heinrich, Inés Pérez-Martín and Samir Z. Zard*

Aziridine *N*-carbonyl radicals, generated by irradiating the corresponding *S*-oxalyl xanthates, undergo ring opening to give 2-isocyanato radicals, which can be trapped by an external olefin.





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