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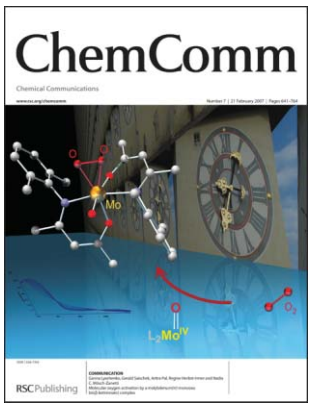
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (7) 641–764 (2007)

Cover
See D. Venkataraman *et al.*, page 692. The illustration shows the packing of naphthyl ether and naphthalimide moieties into segregated stacks due to mutually phobic side-chain interactions. Image reproduced by permission of Travis L. Benanti, Pranorm Saejueng and D. Venkataraman, from *Chem. Commun.*, 2007, 692.



Inside cover
See Nadia C. Mösch-Zanetti *et al.*, page 701. Molecular oxygen is activated by a molybdenum(IV) compound. The kinetics of its formation was monitored by UV/VIS spectrometry, while the Uhrturm of Graz measured the time. Image reproduced by permission of Ganna Lyashenko, Gerald Saischek, Aritra Pal, Regine Herbst-Irmer and Nadia C. Mösch-Zanetti, from *Chem. Commun.*, 2007, 701.

CHEMICAL SCIENCE

C9

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

Chemical Science

February 2007/Volume 4/Issue 2

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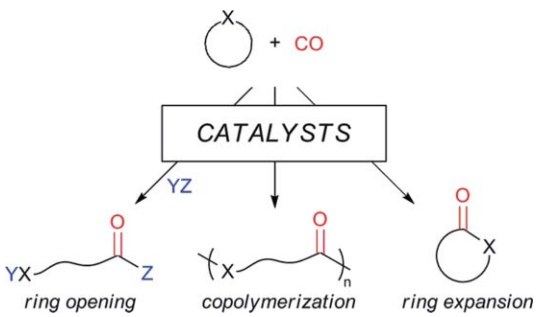
FEATURE ARTICLES

657

Carbonylation of heterocycles by homogeneous catalysts

Tamara L. Church, Yutan D. Y. L. Getzler, Christopher M. Byrne and Geoffrey W. Coates*

This article summarizes the recent developments (particularly the uses of homogeneous organometallic catalysts) in ring-opening carbonylations, ring-opening carbonylative polymerizations and ring-expansion carbonylations of heterocycles, particularly epoxides, aziridines, lactones and oxazolines.



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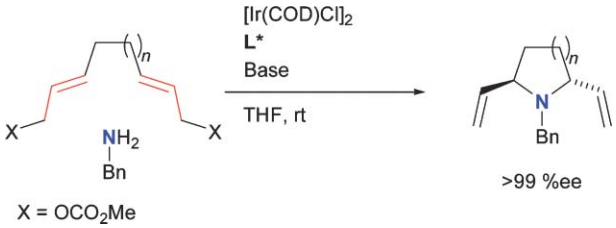
FEATURE ARTICLES

675

Iridium-catalysed asymmetric allylic substitutions

Günter Helmchen,* Axel Dahnz, Pierre Dübon, Mathias Schelwies and Robert Weihofen

Ir-catalysed allylic substitutions can be carried out with a variety of C-, N- and O-nucleophiles to give branched substitution products with high degrees of regio- and enantioselectivity.



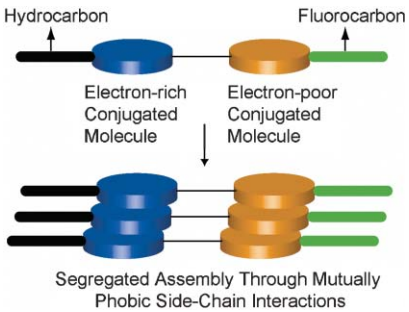
COMMUNICATIONS

692

Segregated assemblies in bridged electron-rich and electron-poor π-conjugated moieties

Travis L. Benanti, Pranorm Saejueng and D. Venkataraman*

We report a general strategy for the spontaneous segregation of electron-rich and electron-poor π-conjugated molecules using mutually phobic aliphatic fluorocarbon–hydrocarbon interactions.

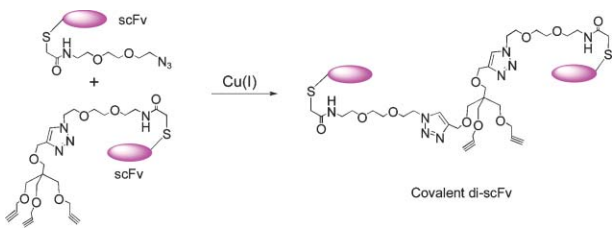


695

Construction of di-scFv through a trivalent alkyne–azide 1,3-dipolar cycloaddition

Arutselvan Natarajan, Wenjun Du, Cheng-Yi Xiong, Gerald L. DeNardo, Sally J. DeNardo* and Jacquelyn Gervay-Hague*

Site specific ligation of scFv was achieved using 1,3-dipolar cycloaddition. Incorporation of a trialkyne linker was critical for efficient conjugation.

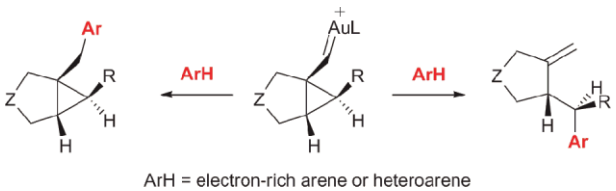


698

Gold(I)-catalysed arylation of 1,6-enynes: different site reactivity of cyclopropyl gold carbenes

Catelijne H. M. Amijs, Catalina Ferrer and Antonio M. Echavarren*

Gold(I)-catalysed addition of electron-rich arenes and heteroarenes to 1,6-enynes gives two different types of products by reaction of the intermediate cyclopropyl gold carbenes at the cyclopropane or at the carbene.

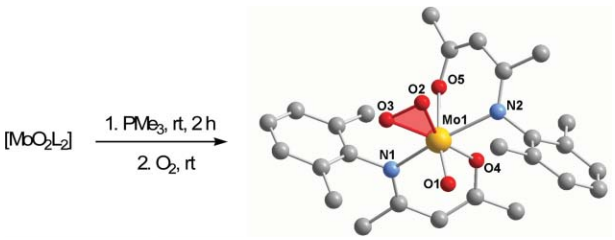


701

Molecular oxygen activation by a molybdenum(IV) monooxo bis(β-ketiminato) complex

Ganna Lyashenko, Gerald Saischek, Aritra Pal, Regine Herbst-Irmer and Nadia C. Mösch-Zanetti*

Molybdenum(IV) monooxo compound that contains bis(β-ketiminato) ligands formed by oxygen atom transfer activates molecular oxygen forming a molybdenum(VI) monooxo peroxo complex. This represents a new entry into molybdenum peroxo derivatives.

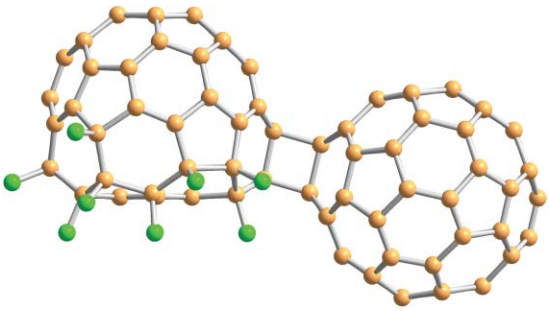


704

The former "$C_{60}F_{16}$" is actually a double-caged adduct: $(C_{60}F_{16})(C_{60})$

Alexey A. Goryunkov, Ilya N. Ioffe, Pavel A. Khavrel, Stanislav M. Avdoshenko, Vitaly Yu. Markov, Z. Mazej, Lev N. Sidorov and Sergey I. Troyanov*

X-ray diffraction study of the substance originally believed to be $C_{60}F_{16}$ reveals a double-caged structure, $(C_{60}F_{16})(C_{60})$, a finding supported by MALDI mass spectra and theoretical calculations.

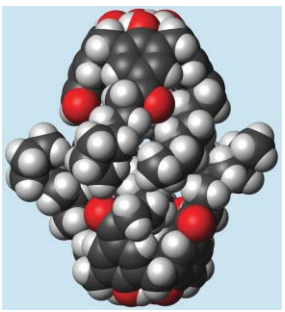


707

A molecular turnstile in *para*-octanoyl calix[4]arene nanocapsules

Gennady S. Ananchenko,* Konstantin A. Udachin, Michaela Pojarova, Said Jebors, Anthony W. Coleman and John A. Ripmeester

The thermal treatment of different inclusion complexes of *para*-octanoyl calix[4]arene leads to the formation of a guest-free van der Waals nanocapsular framework possessing a remarkable stability caused by the high mobility of alkanoyl arms.

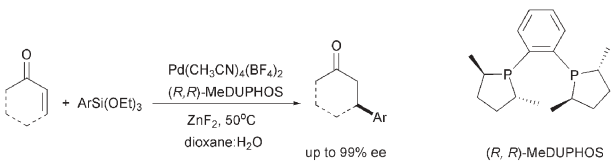


710

Enantioselective palladium-catalysed conjugate addition of arylsiloxanes

Francesca Gini, Bart Hessen, Ben L. Feringa and Adriaan J. Minnaard*

The complex formed from $Pd(CH_3CN)_4(BF_4)_2$ and (*R*,*R*)-MeDUPHOS is a highly enantioselective catalyst for the asymmetric conjugate addition of aryltriethylsiloxanes to a variety of unsaturated ketones, lactones and lactams.

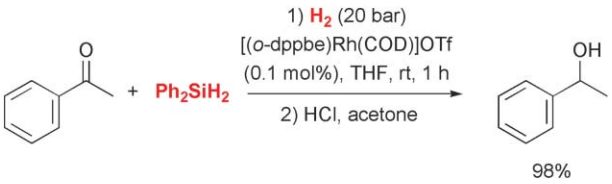


713

From inconsistent results to high speed hydrosilylation

Virginie Comte,* Cédric Balan, Pierre Le Gendre* and Claude Moïse

The hydrosilylation of various ketones in the presence of cationic rhodium catalysts containing diphosphine ligands proceeds much faster under dihydrogen pressure than under an inert atmosphere.

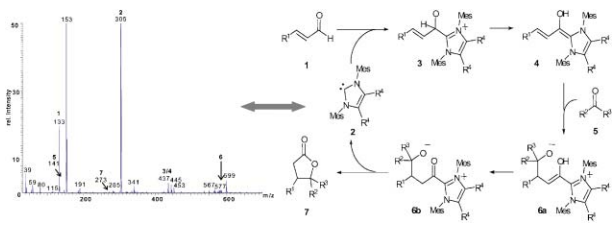


716

Investigating organocatalytic reactions: mass spectrometric studies of a conjugate *umpolung* reaction

Wolfgang Schrader,* Peni Purwa Handayani, Christian Burstein and Frank Glorius

An organocatalyzed conjugate *umpolung* reaction has been studied in detail using electrospray mass spectrometry, which allows support of the catalytic cycle by intercepting intermediates.

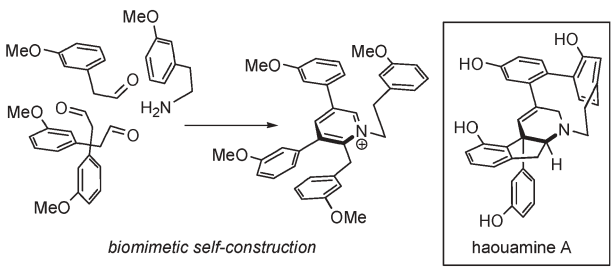


719

Biogenetic hypothesis and first steps towards a biomimetic synthesis of haouamines

Edmond Gravel, Erwan Poupon* and Reynald Hocquemiller

Following a plausible biogenetic pathway, advanced intermediates for the total synthesis of haouamines have been prepared. This is the first biomimetic approach reported for this class of complex alkaloids.

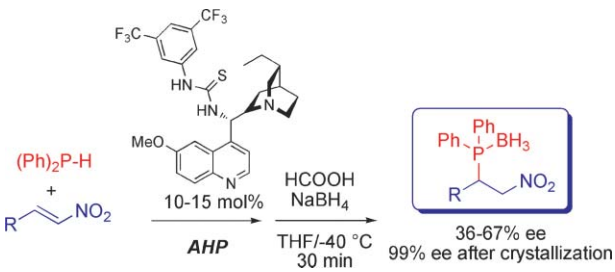


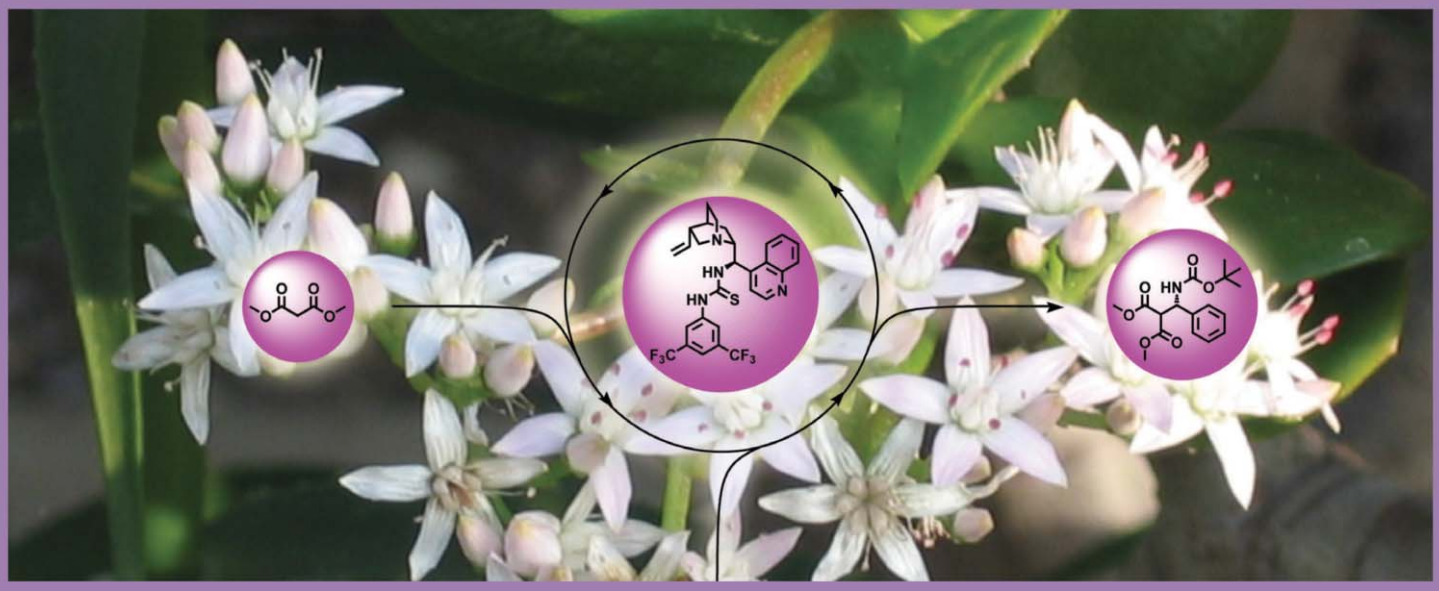
722

Organocatalytic asymmetric hydrophosphination of nitroalkenes

Giuseppe Bartoli, Marcella Bosco, Armando Carlone, Manuela Locatelli, Andrea Mazzanti, Letizia Sambri and Paolo Melchiorre*

The first direct asymmetric hydrophosphination (AHP) of nitroalkenes, catalyzed by a bifunctional *Cinchona* alkaloid derivative, has been accomplished.





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US Associate Editor for organic chemistry

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Happy to receive papers on important developments in organic chemistry, Professor Evans can be contacted via **chemcomm@indiana.edu**

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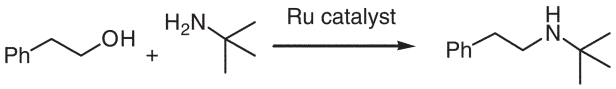
725

Ruthenium catalysed *N*-alkylation of amines with alcohols

Malai Haniti S. A. Hamid and Jonathan M. J. Williams*

Borrowing hydrogen in the *N*-alkylation of amines has been achieved using a ruthenium based catalyst.

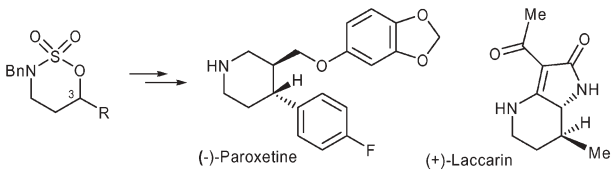


728

Stereospecific construction of substituted piperidines. Synthesis of (−)-paroxetine and (+)-laccarin

John F. Bower, Thomas Riis-Johannessen, Peter Szeto, Andrew J. Whitehead and Timothy Gallagher*

Short and efficient enantioselective syntheses of (−)-paroxetine and (+)-laccarin are described based on the highly stereospecific cleavage of C(3)-substituted 1,3-cyclic sulfamidates.



731

Silver-catalyzed [2,3]-rearrangement of halonium ylides derived from allyl and propargyl halides and alkyl diazoacetates

Pasupathy Krishnamoorthy, R. Greg Browning, Shreeyukta Singh, Rasapalli Sivappa, Carl J. Lovely* and H. V. Rasika Dias*

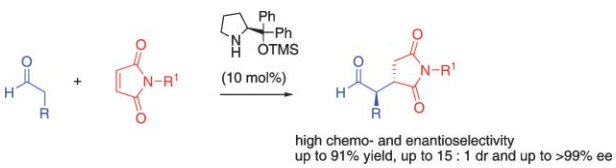
A silver(I) complex derived from a polyfluorinated tris(pyrazolyl)borate effectively catalyzes carbene transfer to allylic and propargylic halides, leading to the formation of α-haloacetate derivatives.

734

Organocatalytic enantioselective conjugate addition of aldehydes to maleimides

Gui-Ling Zhao, Yongmei Xu, Henrik Sundén, Lars Eriksson, Mahmoud Sayah and Armando Córdova*

The first highly enantioselective organocatalytic conjugate addition of unmodified aldehydes to maleimides is presented. The novel reaction gives access to α-substituted succinimides with up to 15 : 1 dr and generally 97 → 99% ee.



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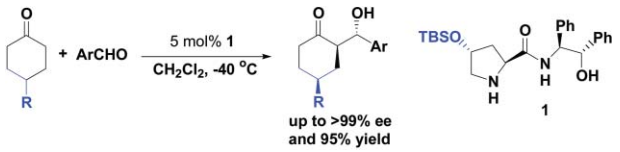
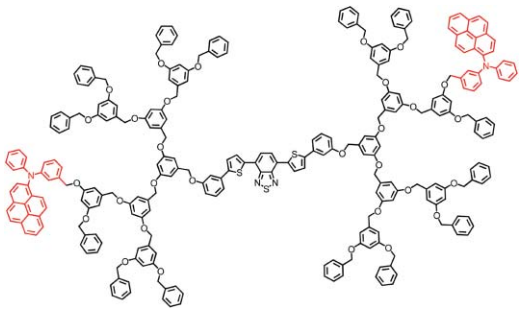


Enantioselective desymmetrization of prochiral cyclohexanone derivatives *via* the organocatalytic direct aldol reaction

Jun Jiang, Long He, Shi-Wei Luo, Lin-Feng Cun and Liu-Zhu Gong*

Asymmetric desymmetrization of 4-substituted cyclohexanones using proline amide-catalyzed direct aldol reaction afforded β-hydroxyketones with three stereogenic centers in high enantioselectivities of up to >99% ee.

739

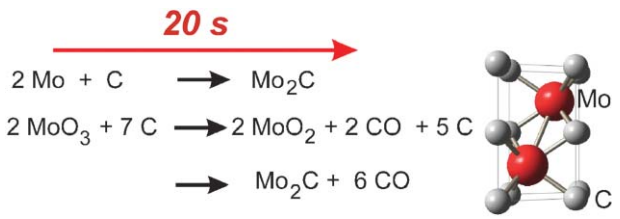


Probing the periphery of dendrimers by heterogeneous electron transfer

K. Krishnamoorthy, Raghunath Reddy Dasari, Arpornrat Nantalaksakul and S. Thayumanavan*

Generation-dependence in the accessibility to the peripheral electroactive functionalities in dendrimers has been studied by comparing two different classes of dendrimers with linear molecules.

742

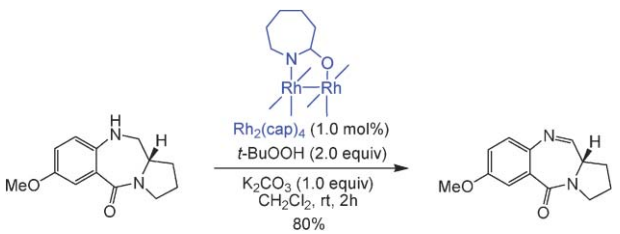


Ultra-rapid processing of refractory carbides; 20 s synthesis of molybdenum carbide, Mo_2C

Simon R. Vallance, Sam Kingman* and Duncan H. Gregory*

Ultra-rapid microwave reactions yield refractory carbides such as superconducting Mo_2C in 20 s; dielectric properties of the components mediate the reaction process.

745



Oxidation of secondary amines catalyzed by dirhodium caprolactamate

Hojae Choi and Michael P. Doyle*

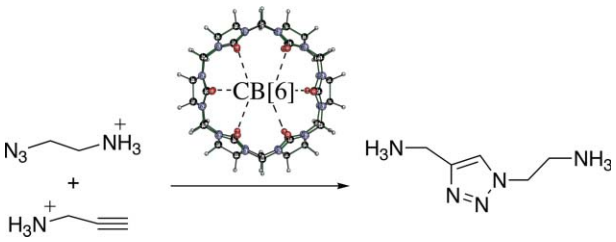
Secondary amines are converted to their corresponding imines with high chemo- and regioselectivity in oxidation reactions of *tert*-butyl hydroperoxide catalyzed by dirhodium caprolactamate [$Rh_2(cap)_4$].

748

A theoretical analysis of a classic example of supramolecular catalysis

Peter Carlqvist and Feliu Maseras*

Computational chemistry is applied to the study of the 1,3-dipolar cycloaddition between an azide and an alkyne inside the macrocycle cucurbit[6]uril.

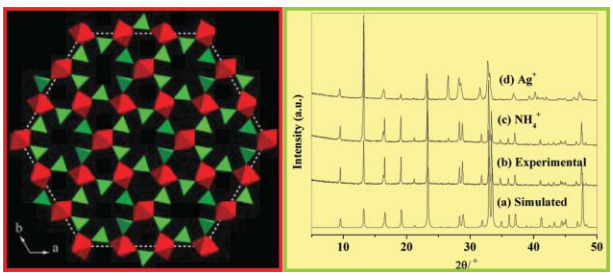


751

A (4,2)-connected niobium phosphate $Na_{13}Nb_3P_6O_{28}F_2$ with a unique 6.12-net layer: Synthesis, structure and ion exchange properties

Guang-Zhen Liu, Shou-Tian Zheng and Guo-Yu Yang*

A two-step hydrothermal process was employed to make a very open (4,2)-connected layered niobium phosphate, $Na_{13}Nb_3P_6O_{28}F_2$. The sheet consists of alternating 4-connected niobium octahedra and 2-connected phosphorus tetrahedra, forming a unique 6.12-net that has never previously been found in metal phosphates.

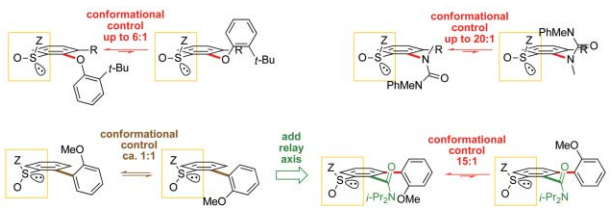


754

Achieving conformational control over C–C, C–N and C–O bonds in biaryls, *N*,*N*′-diarylureas and diaryl ethers: advantages of a relay axis

Mark S. Betson, Ann Bracegirdle, Jonathan Clayden,* Madeleine Helliwell, Andrew Lund, Mark Pickworth, Timothy J. Snape and Christopher P. Worrall

A sulfoxide substituent can control the orientation of a C–C, C–N or C–O bond.

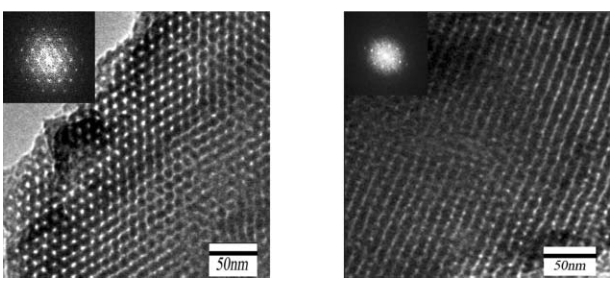


757

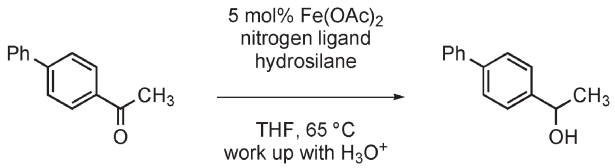
Facile synthesis of ordered mesoporous carbons from F108/resorcinol–formaldehyde composites obtained in basic media

Changyi Liu, Lixia Li, Huaihe Song* and Xiaohong Chen

Highly ordered mesoporous carbon with cubic *Im*3*m* symmetry has been synthesized successfully *via* a direct carbonization of self-assembled F108 ($EO_{132}PO_{50}EO_{132}$) and resorcinol–formaldehyde composites obtained in a basic medium of nonaqueous solution.



760



An iron-catalysed hydrosilylation of ketones

Hisao Nishiyama* and Akihiro Furuta

The combination of $Fe(OAc)_2$ and multi-nitrogen-based ligands can efficiently catalyse hydrosilylation of ketones to give the corresponding alcohols in high yields including asymmetric catalysis.

AUTHOR INDEX

Amijs, Catelijne H. M., 698
Ananchenko, Gennady S., 707
Avdoshenko, Stanislav M., 704
Balan, Cédric, 713
Bartoli, Giuseppe, 722
Benanti, Travis L., 692
Betson, Mark S., 754
Bosco, Marcella, 722
Bower, John F., 728
Bracegirdle, Ann, 754
Browning, R. Greg, 731
Burstein, Christian, 716
Byrne, Christopher M., 657
Carlone, Armando, 722
Carlqvist, Peter, 748
Chen, Xiaohong, 757
Choi, Hojae, 745
Church, Tamara L., 657
Clayden, Jonathan, 754
Coates, Geoffrey W., 657
Coleman, Anthony W., 707
Comte, Virginie, 713
Córdova, Armando, 734
Cun, Lin-Feng, 736
Dahnz, Axel, 675
Dasari, Raghunath Reddy, 739
DeNardo, Gerald L., 695
DeNardo, Sally J., 695
Dias, H. V. Rasika, 731
Doyle, Michael P., 745
Du, Wenjun, 695
Dübon, Pierre, 675
Echavarren, Antonio M., 698
Eriksson, Lars, 734
Feringa, Ben L., 710
Ferrer, Catalina, 698
Furuta, Akihiro, 760
Gallagher, Timothy, 728
Gervay-Hague, Jacquelyn, 695
Getzler, Yutan D. Y. L., 657
Gini, Francesca, 710
Glorius, Frank, 716
Gong, Liu-Zhu, 736
Goryunkov, Alexey A., 704
Gravel, Edmond, 719
Gregory, Duncan H., 742
Hamid, Malai Haniti S. A., 725
Handayani, Peni Purwa, 716
He, Long, 736
Helliwell, Madeleine, 754
Helmchen, Günter, 675
Herbst-Irmer, Regine, 701
Hessen, Bart, 710
Hocquemiller, Reynald, 719
Ioffe, Ilya N., 704
Jebors, Said, 707
Jiang, Jun, 736
Khavrel, Pavel A., 704
Kingman, Sam, 742
Krishnamoorthy, K., 739
Krishnamoorthy, Pasupathy, 731
Le Gendre, Pierre, 713
Li, Lixia, 757
Liu, Changyi, 757
Liu, Guang-Zhen, 751
Locatelli, Manuela, 722
Lovely, Carl J., 731
Lund, Andrew, 754
Luo, Shi-Wei, 736
Lyashenko, Ganna, 701
Markov, Vitaly Yu., 704
Maseras, Feliu, 748
Mazej, Z., 704
Mazzanti, Andrea, 722
Melchiorre, Paolo, 722
Minnaard, Adriaan J., 710
Moïse, Claude, 713
Mösch-Zanetti, Nadia C., 701
Nantalaksakul, Arpornrat, 739
Natarajan, Arutselvan, 695
Nishiyama, Hisao, 760
Pal, Aritra, 701
Pickworth, Mark, 754
Pojarova, Michaela, 707
Poupon, Erwan, 719
Riis-Johannessen, Thomas, 728
Ripmeester, John A., 707
Saejueng, Pranorm, 692
Saischek, Gerald, 701
Sambri, Letizia, 722
Sayah, Mahmoud, 734
Schelwies, Mathias, 675
Schrader, Wolfgang, 716
Sidorov, Lev N., 704
Singh, Shreeyukta, 731
Sivappa, Rasapalli, 731
Snape, Timothy J., 754
Song, Huaihe, 757
Sundén, Henrik, 734
Szeto, Peter, 728
Thayumanavan, S., 739
Troyanov, Sergey I., 704
Udachin, Konstantin A., 707
Vallance, Simon R., 742
Venkataraman, D., 692
Weihofen, Robert, 675
Whitehead, Andrew J., 728
Williams, Jonathan M. J., 725
Worrall, Christopher P., 754
Xiong, Cheng-Yi, 695
Xu, Yongmei, 734
Yang, Guo-Yu, 751
Zhao, Gui-Ling, 734
Zheng, Shou-Tian, 751

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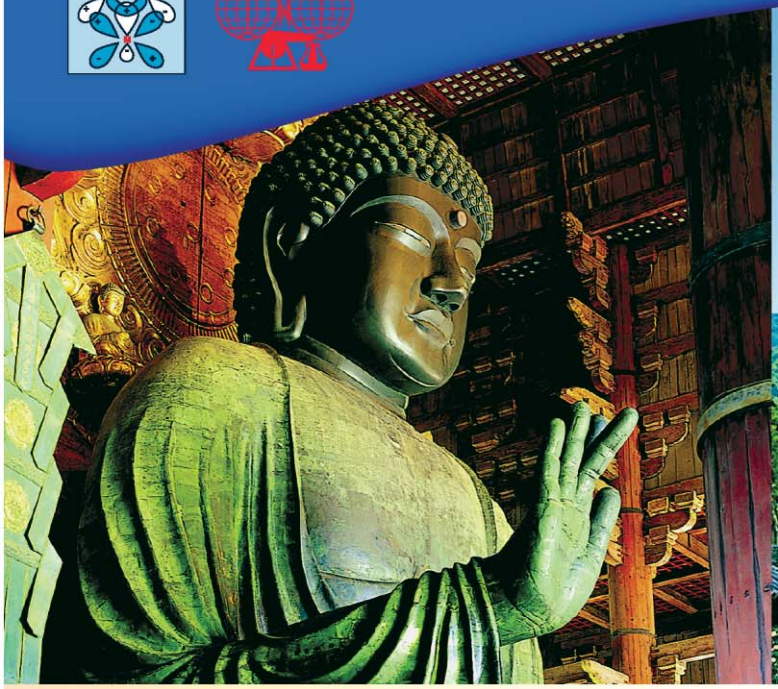

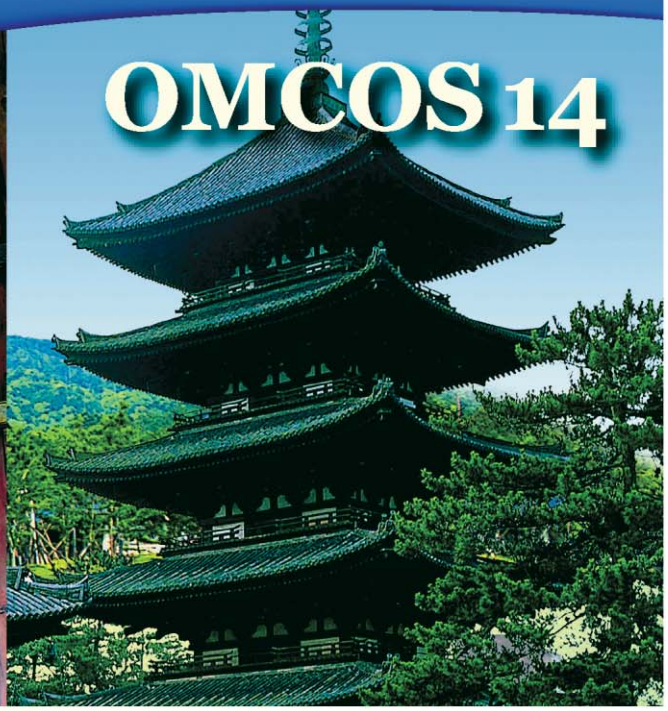

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