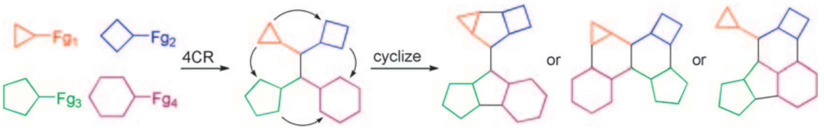
CONCEPTS

Heterocyclic Compounds

J. D. Sunderhaus,
*S. F. Martin** .... 1300 – 1308

Applications of Multicomponent Reactions to the Synthesis of Diverse Heterocyclic Scaffolds



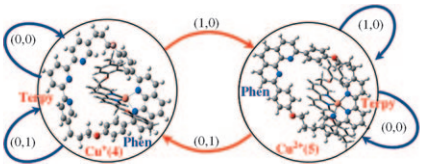
So much from so little! The sequencing of multicomponent reactions (MCRs) with subsequent cyclization reactions is a powerful method for generating diverse collections of functionalized heterocyclic scaffolds (see scheme).

COMMUNICATIONS

Copper Rotaxanes

G. Periyasamy, J.-P. Collin,
J.-P. Sauvage, R. D. Levine,
*F. Remacle** .... 1310 – 1313

Electrochemically Driven Sequential Machines: An Implementation of Copper Rotaxanes

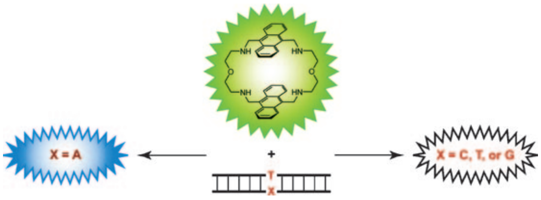


It's logical, captain! The operation of a set–reset logic machine based on the electrochemical switching of the redox states in a Cu rotaxane followed by ligand reorganization (Cu^+(4) four-coordinate copper complex to Cu^{2+}(5) five-coordinate copper complex; see scheme) is demonstrated.

DNA Recognition

A. Granzhan,
*M.-P. Teulade-Fichou** ...... 1314 – 1318

A Fluorescent Bisanthracene Macrocycle Discriminates between Matched and Mismatch-Containing DNA

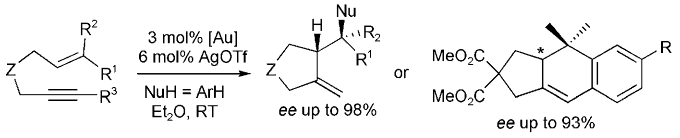


Mix and measure: A fluorescent bisanthracene macrocycle binds to fully matched and thymine-mismatched (TX) DNA duplexes by different binding modes, which may be differentiated spectroscopically. This behavior allows an easy fluorimetric or "naked-eye" discrimination between matched (X = A) and mismatch-containing (X = C, T, or G) oligonucleotides.

Asymmetric Catalysis

C.-M. Chao, M. R. Vitale, P. Y. Toullec,
*J.-P. Genêt, V. Michelet** .... 1319 – 1323

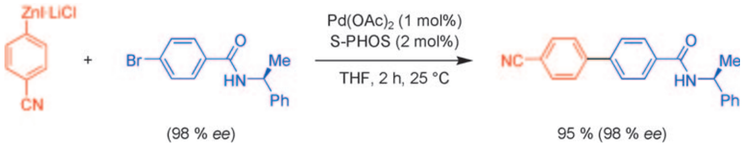
Asymmetric Gold-Catalyzed Hydroarylation/Cyclization Reactions



[Au] = (*R*)-4-MeO-3,5-(*t*Bu)$_2$MeOBIPHEP(AuCl)$_2$
Z = O, C(CO$_2$Me)$_2$, C(CO$_2$*i*Pr)$_2$, C(SO$_2$Ph)$_2$

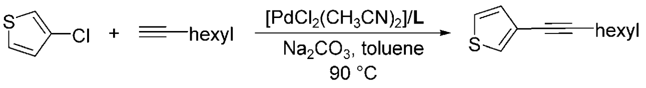
Gold efficiency: An efficient Au^I catalytic system is described for the enantioselective hydroarylation/cyclization reaction of 1,6-enynes (see scheme). Use of the (*R*)-4-MeO-3,5-(*t*Bu)$_2$-MeOBIPHEP–gold complex led to clean rearrangements implying the formal addition of a carbon nucleophile (1,3,5-trimethoxybenzene, 1,3-dimethoxybenzene, pyrrole, 1,3,5-trimethoxy-2-bromobenzene and indole derivatives) to an alkene followed by a cyclization process.

Cross-Coupling



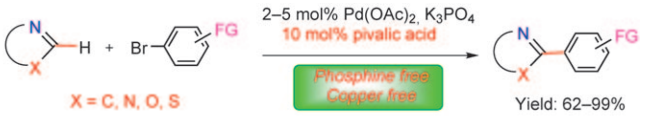
Mild mannered: Unprotected amides and sulfonamides containing aryl bromides and iodides undergo, in the presence of S-PHOS, smooth Negishi cross-couplings with various zinc organometallic reagents, allowing the preparation of pharmaceutically relevant molecules (see scheme; S-PHOS = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl).

C–C Coupling



Well matched: Novel palladium/heteroaryl-phosphines are introduced for Sonogashira reactions of aryl and heteroaryl chlorides including challenging substrates (see scheme). The desired coupling reactions proceed smoothly and tolerate various functional groups.

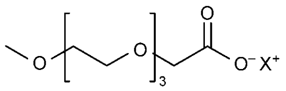
Palladium Catalysis



Ligand-free C-arylation: A general palladium-catalyzed C-arylation of N-heterocycles with aryl bromides has been performed without the presence of phosphines, the aid of CuI, or other metal additives by using pivalic acid as a cocatalyst (see scheme).

Ionic Liquids

On the way to greener ILs: The combination of a short oligoether carboxylate (CH$_3$O-(CH$_2$CH$_2$O)$_3$-CH$_2$COO$^-$) with small alkali metal cations leads to the formation of a new class of ionic liquids that exhibit high thermal and electrochemical stability as well as low cytotoxicity.

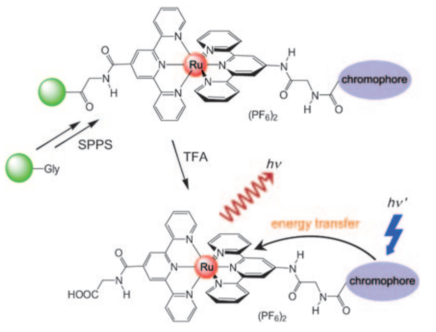


X = Li, Na, K

FULL PAPERS

Solid-Phase Synthesis

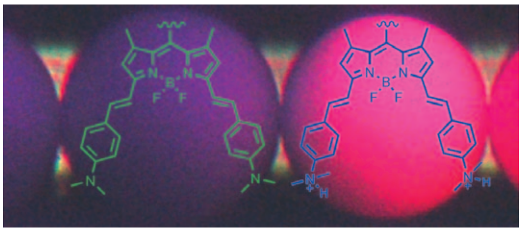
It works for metals too! Solid-phase peptide synthesis procedures were employed for the selective stepwise assembly of bis(terpyridine)ruthenium(II) chromophores and organic antennas to yield peptidic dyads. Electrochemistry, absorption spectroscopy and DFT calculations suggest electronically isolated chromophores in the ground state, while energy-transfer processes from the organic dye to the ruthenium complex occur in the excited dyads (see scheme).



Gas Sensors

R. Ziessel, G. Ulrich, A. Harriman, M. A. H. Alamiry, B. Stewart, P. Retailleau* .... 1359 – 1369

Solid-State Gas Sensors Developed from Functional Difluoroboradiazaindacene Dyes

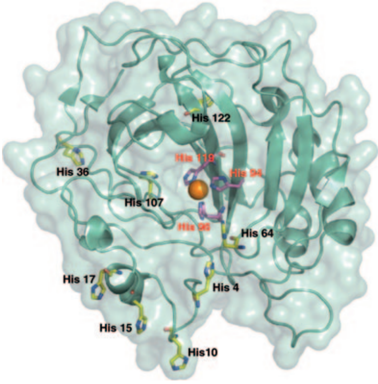


All change please! Highly porous, spherical beads have been coated with near-IR absorbing difluoroboradiazaindacene dyes that possess tertiary amine fragments. When suspended in a gas flow spiced with trace amounts of acid or phosgene, the beads change color from green to blue and there is the concomitant appearance of bright red fluorescence. These processes are reversed on addition of ammonia or an organic amine.

Enzyme Catalysis

*Q. Jing, K. Okrasa, R. J. Kazlauskas** .... 1370 – 1376

Stereoselective Hydrogenation of Olefins Using Rhodium-Substituted Carbonic Anhydrase—A New Reductase

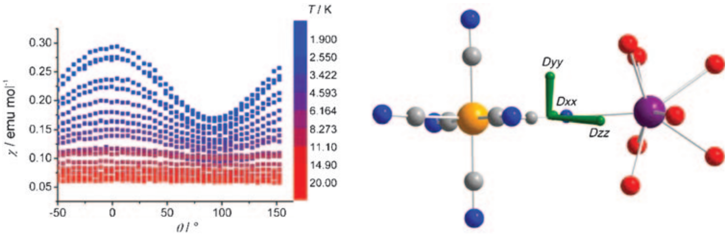


Protein as ligand: Replacing the active-site zinc in carbonic anhydrase (CA) by rhodium formed a new reductase for cofactor-free hydrogenation of olefins with hydrogen (see figure). Unlike free rhodium, this rhodium–protein hybrid, [Rh]-CA, was stereoselective (≈20:1) for *cis*-stilbene over *trans*-stilbene.

Magnetic Properties

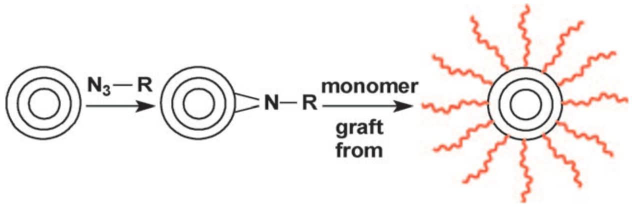
L. Sorace, C. Sangregorio, A. Figuerola, C. Benelli, D. Gatteschi* .... 1377 – 1388

Magnetic Interactions and Magnetic Anisotropy in Exchange Coupled 4f–3d Systems: A Case Study of a Heterodinuclear Ce^{3+}–Fe^{3+} Cyanide-Bridged Complex



Antisymmetry matters: A single-crystal magnetic and EPR study of a series of homologous Ln–M (Ln = La^{III}, Ce^{III}; M = Fe^{III}, Co^{III}) complexes necessitated the introduction of isotropic, anisotropic and antisymmetric exchange terms to rationalise the observed behaviour (see figure). We propose this as a case study that may improve our understanding of the anisotropic magnetic properties of exchange coupled pairs containing orbitally non-degenerate ions.

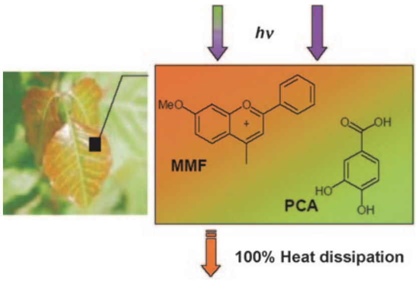
Nanomaterials



Onions that don't make you cry: Multilayer fullerenes (carbon nano-onions, CNOs) are functionalized by direct [2+1] cycloaddition of nitrenes and subsequent use of the "grafting from" strategy of in situ ring-opening polymerization and atom transfer radical polymerization (see scheme). This comprehensive investigation of the chemistry of CNOs could lead to the fabrication of novel CNO-based nanomaterials and nanodevices.

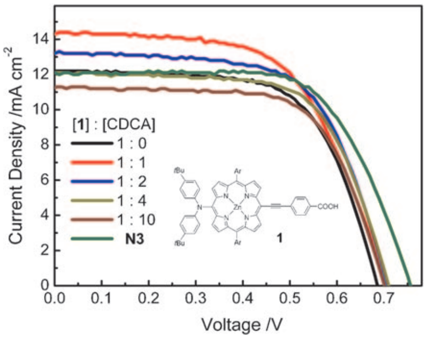
Photochemistry

Shedding light on anthocyanins: Light absorbed by a model anthocyanin–copigment complex dissipates into heat on a sub-picosecond timescale by internal conversion to the ground state (see graphic; MMF: 7-methoxy-4-methylflavylium, PCA: protocatechuic acid).



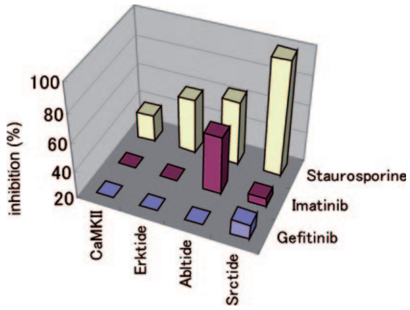
Solar Cells

Colorful character: A diarylamino-substituted porphyrin (**1**) exhibits an overall efficiency of power conversion of 6.0%. From a comparison of cell performance using the same TiO_2 films, the green dye **1** (see figure) outperforms the best reported porphyrin sensitizer and gives a performance comparable to that of an **N3**-based dye-sensitized solar cell.



Kinase Inhibitors

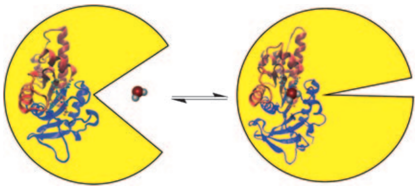
A game of chemical tag: A MALDI-TOF mass-spectrometry-based quantitative characterization of human protein kinases is now possible by using novel synthetic peptides bearing both N-terminal stable isotope tags and C-terminal mass-spectrometry-sensitive enhancement reagents. This method allows rapid and precise kinetic analysis (see picture) of recombinant c-Abl kinases in vitro and direct monitoring of cellular kinase activity by using mouse B16 melanoma cells and human cancer K652 cells.



Enzyme Catalysis

A. Jiménez, P. Clapés,
*R. Crehuet** .... 1422 – 1428

Protein Flexibility and Metal Coordination Changes in DHAP-Dependent Aldolases

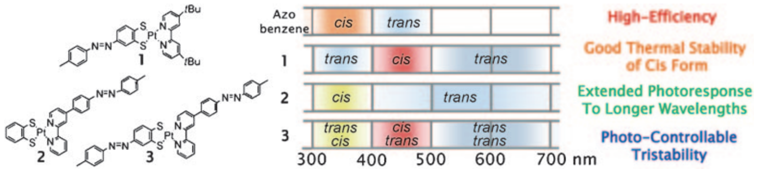


Reshaping active sites: Although crystallographic diffraction produces static structures, protein motion can be extracted by combining different experimental and computational techniques. The structure of two related aldolases shows that domain motions alter the coordination of the metal in the active site, which results in different catalytic power for the different conformations (see figure).

Photochemistry

R. Sakamoto, S. Kume, M. Sugimoto,
*H. Nishihara** .... 1429 – 1439

trans–cis Photoisomerization of Azobenzene-Conjugated Dithiolato-Bipyridine Platinum(II) Complexes: Extension of Photoresponse to Longer Wavelengths and Photocontrollable Tristability



Look into the light: Azobenzene-conjugated dithiolato-bipyridine platinum(II) complexes **1**–**3** show photoresponses at long wavelengths, high photoisomerization quantum yields, and thermal stability of the *cis* forms (see picture). In addition, complex **3** exhibits photocontrollable tristability in a single molecule, and can be interconverted by irradiation at 365, 405, and 578 nm.

Magnetic Resonance Imaging

E. Terreno, D. Delli Castelli,
E. Violante, H. M. H. F. Sanders,
N. A. J. M. Sommerdijk,
*S. Aime** .... 1440 – 1448

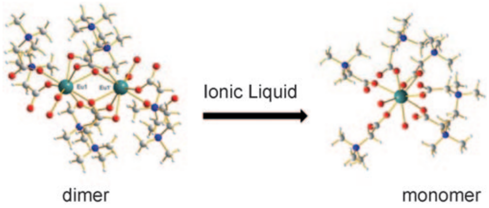
Osmotically Shrunken LIPOCEST Agents: An Innovative Class of Magnetic Resonance Imaging Contrast Media Based on Chemical Exchange Saturation Transfer

Honey, I Shrunk the Liposomes! Osmotically shrunken liposomes loaded with paramagnetic lanthanide(III) complexes (see figure) acting as shift reagents towards water protons represent an innovative class of highly sensitive agents for magnetic resonance imaging (MRI) applications. Their contrast is generated by a chemical exchange saturation transfer (CEST) mechanism.

Ionic Liquids

P. Nockemann, B. Thijs, K. Lunstroot,*
T. N. Parac-Vogt, C. Görller-Walrand,
K. Binnemans, K. Van Hecke,
L. Van Meervelt, S. Nikitenko,
J. Daniels, C. Hennig,
*R. Van Deun** .... 1449 – 1461

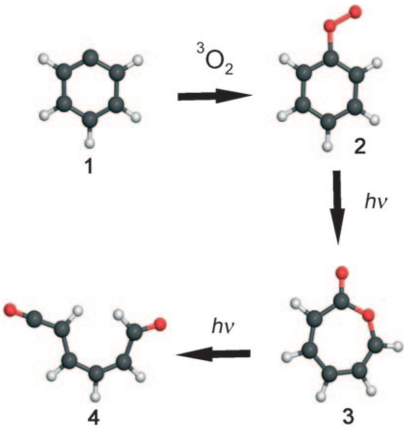
Speciation of Rare-Earth Metal Complexes in Ionic Liquids: A Multiple-Technique Approach



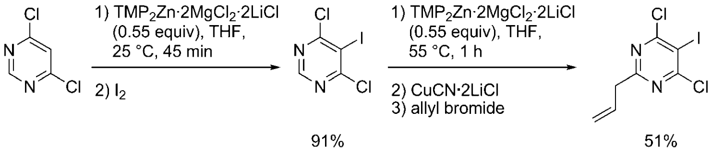
Rare-earth metal speciation in the ionic liquids betainium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (see figure) was investigated by a multiple-technique approach by using luminescence spectroscopy, ^{1}H, ^{13}C, and ^{89}Y NMR spectroscopy and the synchrotron techniques EXAFS (extended X-ray absorption fine structure) and HEXS (high-energy X-ray scattering).

Radicals

Radical changes: The phenylperoxy radical **2** can be synthesized by the reaction of the phenyl radical **1** with $^3O_2$. Irradiation of **2** with visible light produces the 2-oxepinoxy radical **3** in a clean reaction. Subsequent irradiation results in ring-opening and formation of several conformers of ketoketene **4**. The radicals **2**, **3**, and **4** play an important role in the combustion of aromatic hydrocarbons.



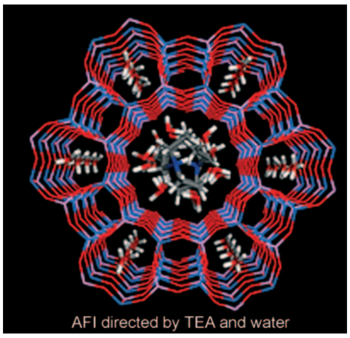
Heterocyclic Chemistry



Fully functional! The pyrimidine ring is fully functionalized at the C5 and C2 positions under mild conditions by successive regio- and chemoselective zincation with $TMP_2Zn·2MgCl_2·2LiCl$ (TMP = 2,2,6,6-tetramethylpiperidyl) as the metalation agent (see scheme).

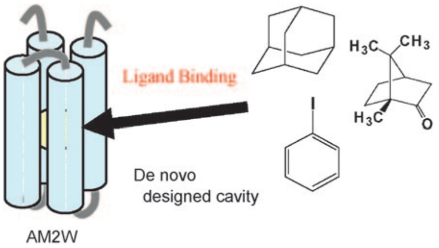
Aluminophosphates

Competitive molecules: A combination of experimental techniques and computational simulations of the AFI-type structure synthesised with different organic molecules has revealed the structure direction of microporous aluminophosphates (see picture). Water molecules play an important role during the crystallisation of these networks, by competing with organic structure-directing agents to be occluded within the AFI structure. TEA: triethylamine.



Protein Design

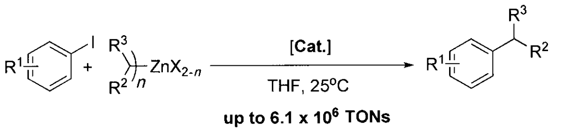
Plugging the hole: A de novo protein (AM2W in the schematic repersentation), which is a tetrameric coiled-coil protein with a designed hydrophobic cavity, exhibited affinity for size-complementary ligands. Ligand binding induced an increase in protein-structure stability, probably due to plugging of the cavity.

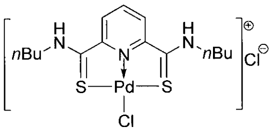


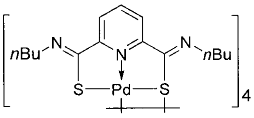
Cross-Coupling

H. Wang, J. Liu, Y. Deng, T. Min, G. Yu, X. Wu, Z. Yang, A. Lei** .... 1499 – 1507

Pincer Thioamide and Pincer Thioimide Palladium Complexes Catalyze Highly Efficient Negishi Coupling of Primary and Secondary Alkyl Zinc Reagents at Room Temperature




1

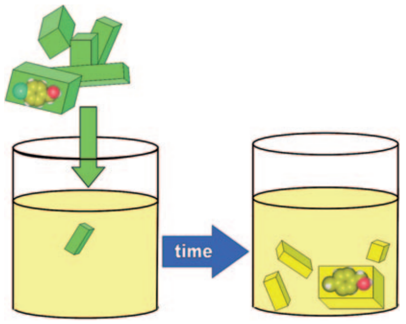

2

TONs of potential: Turnover numbers up to 6.1×10^6 were obtained in Negishi coupling of aryl iodides with primary and secondary alkyl zinc reagents promoted by pincer thioamide Pd complex **1** or pincer thioimide Pd complex **2** under mild conditions (see scheme). Alkyl zinc reagents with β-H atoms are also tolerated. The different reactivity of monoalkyl zinc and dialkyl zinc reagents was rationalized by a preliminary kinetic investigation.

Crystal Engineering

D. Braga, F. Grepioni, L. Maini,* M. Polito, K. Rubini, M. R. Chierotti, R. Gobetto** .... 1508 – 1515

Hetero-Seeding and Solid Mixture to Obtain New Crystalline Forms

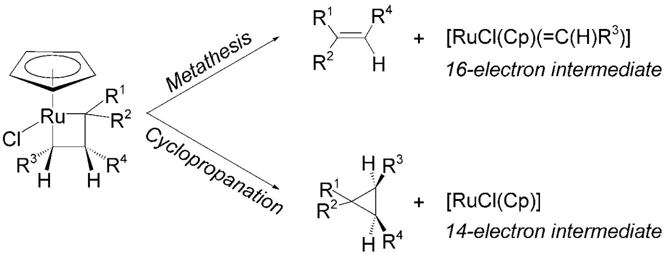


Tailoring crystal structures: *Para*-methyl benzyl alcohol (*p*-MeBA) and *para*-chloro benzyl alcohol (*p*-ClBA) are quasi-isostructural and share the same hydrogen bond patterns, but their crystals are not isomorphous. Formation of a new polymorph of *p*-MeBA was induced by hetero-seeding with powdered *p*-ClBA (see figure).

Organometallics

M. Basato, C. Tubaro, A. Biffis, M. Bonato, G. Buscemi, F. Lighezzolo, P. Lunardi, C. Vianini, F. Benetollo, A. Del Zotto* .... 1516 – 1526

Reactions of Diazo Compounds with Alkenes Catalysed by [RuCl(cod)(Cp)]: Effect of the Substituents in the Formation of Cyclopropanation or Metathesis Products



Cyclopropanation versus metathesis: The reaction of diazo compounds with alkenes affords metathesis or cyclopropanation products depending on the steric and electronic properties of the substituents in the ruthenacyclobutane intermediate (see scheme; Cp = cyclopentadienyl).

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* Author to whom correspondence should be addressed

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

VIP Full Papers labeled with this symbol have been judged by two referees as being “very important papers”.

A video clip is available as Supporting Information on the WWW (see article for access details).

SERVICE

CORRIGENDUM

X. Jiang, C. Fu, S. Ma 9656–9664

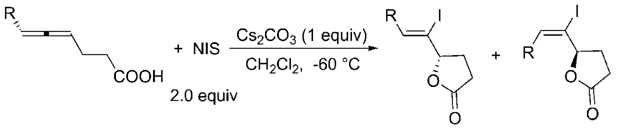
Highly Stereoselective Iodolactonization of 4,5-Allenoic Acids—An Efficient Synthesis of 5-(1′-Iodo-1′(Z)-alkenyl)-4,5,dihydro-2(3*H*)-furanones

Chem. Eur. J., **2008**, *14*

DOI: 10.1002/chem.200801363

Some mistakes have been noted in the paper by S. Ma, C. Fu, and X. Jiang, as detailed below; the authors apologize for these errors.

1) On page 9658, the last equation in Scheme 2 should be as follows:



2) Also on page 9658, the sentence “In this way, (*S*)-(+)-(*Z*)-**2b** and (*R*)-(+)-(*Z*)-**2a** were prepared in >98 % *ee* and with 96:4 *Z*/*E* selectivity (Scheme 4)” at the top of the right-hand column should be read as: “In this way, (*S*)-(+)-(*Z*)-**2b** and (*S*)-(+)-(*Z*)-**2a** were prepared in >98 % *ee* and with 96:4 *Z*/*E* selectivity (Scheme 4)”.

3) The legend of Scheme 4 should be read as: “Scheme 4. Kinetic resolution of *Z*/*S* and *E*/*R* mixtures of **2a** and **2b**.”

4) On page 9663, the heading “Typical procedure for the preparation of optically active 5-(1′-iodo-1′-alkenyl)-4,5-dihydro-2(3*H*)-furanones (*R*)-**2a** and (*R*)-**2b**” should be read as: “Typical procedure for the preparation of optically active 5-(1′-iodo-1′-alkenyl)-4,5-dihydro-2(3*H*)-furanones (*S*)-**2a** and (*S*)-**2b**”

5) Also on page 9663, the heading “Typical procedure for the kinetic resolution of (*R*)-(*Z*)- and (*S*)-(*E*)-isomers of optically active products **2a** and **2b**” should be read as: “Typical procedure for the kinetic resolution of (*S*)-(*Z*)- and (*R*)-(*E*)-isomers of optically active products **2a** and **2b**”.