

Organic & Biomolecular Chemistry

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COMMUNICATION

Christian Hertweck *et al.*

Divergolide congeners illuminate alternative reaction channels for ansamycin diversification

Organic & Biomolecular Chemistry

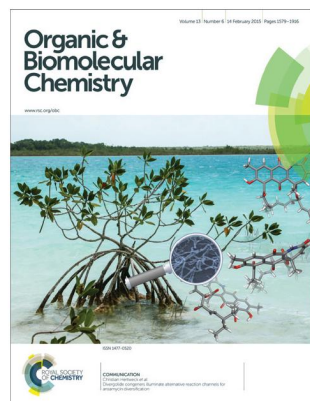
An international journal of synthetic, physical and biomolecular organic chemistry

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IN THIS ISSUE

ISSN 1477-0520 CODEN OBCRAK 13(6) 1579–1916 (2015)

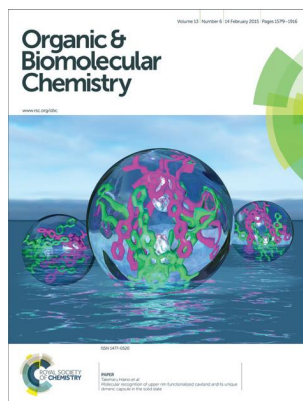


Cover

See Christian Hertweck *et al.*, pp. 1618–1623.

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Inside cover

See Takeharu Haino *et al.*, pp. 1647–1653.

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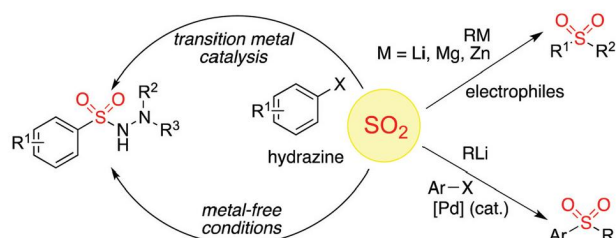
REVIEWS

1592

Fixation of sulfur dioxide into small molecules

Gang Liu,* Congbin Fan and Jie Wu*

Recent advances in the insertion of sulfur dioxide under transition metal catalysis or metal-free conditions *via* a radical process are presented.

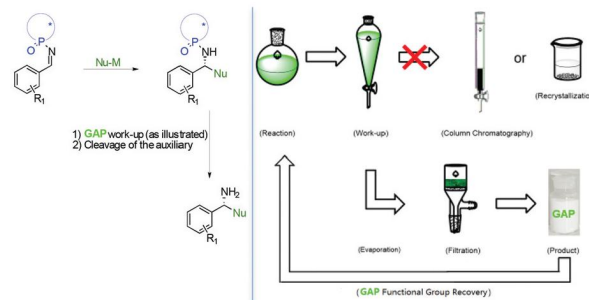


1600

N-Phosphonyl/phosphinyl imines and group-assisted purification (GAP) chemistry/technology

Guanghui An, Cole Seifert and Guigen Li*

Group-assisted purification (GAP) chemistry, which can provide various chiral amines and other functionalities without the use of column chromatography or recrystallization; products are consistently obtained with excellent stereocontrol.



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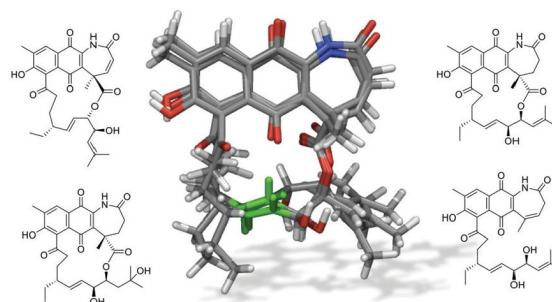
COMMUNICATIONS

1618

Divergolide congeners illuminate alternative reaction channels for ansamycin diversification

Ling Ding, Jakob Franke and Christian Hertweck*

Isolation and structure elucidation of six new divergolides reveal unusual ansamycin diversification reactions including formation of the unusual isobutenyl side chain from a branched polyketide synthase extender unit, azepinone ring closure, macrolide ring contraction and formation of a seco variant by a neighboring group-assisted decarboxylation.

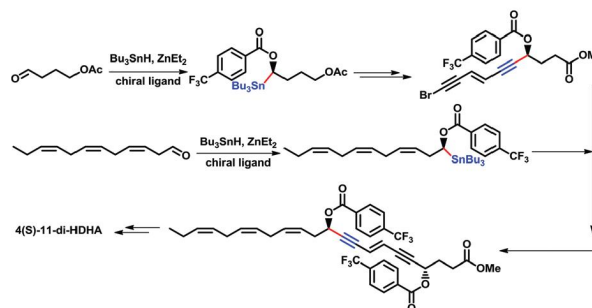


1624

Studies towards asymmetric synthesis of 4(S)-11-dihydrodocosahexaenoic acid (diHDHA) featuring cross-coupling of chiral stannane under mild conditions

Rui Wang* and John R. Falck

An efficient and asymmetric synthesis approach towards the biologically interesting molecule 4(S)-11-dihydrodocosahexaenoic acid (diHDHA) was developed. This protocol mainly relied on our mild cross-coupling and asymmetric stannylation.

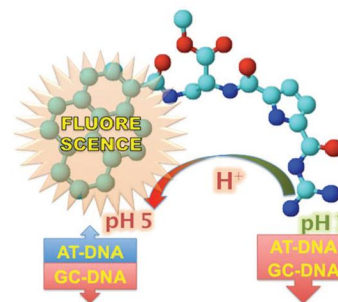


1629

A short, rigid linker between pyrene and guanidiniocarbonyl-pyrrole induced a new set of spectroscopic responses to the ds-DNA secondary structure

Marijana Radić Stojković, Patrycysz Piotrowski, Carsten Schmuck* and Ivo Piantanida*

A DNA-targeting dye exhibited pH-dependent selectivity toward AT-DNA (pH 7) or GC-DNA (pH 5), accompanied by fluorimetric (pH 5) and ICD (pH 7) recognition.

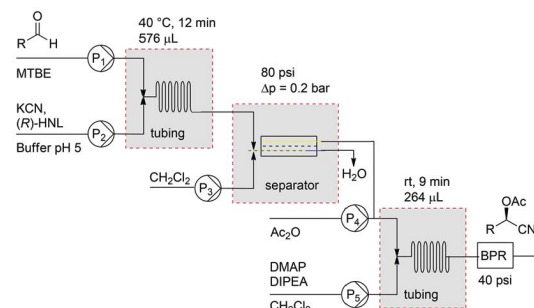


1634

Chemoenzymatic flow cascade for the synthesis of protected mandelonitrile derivatives

Mariëlle M. E. Delville, Kaspar Koch, Jan C. M. van Hest and Floris P. J. T. Rutjes*

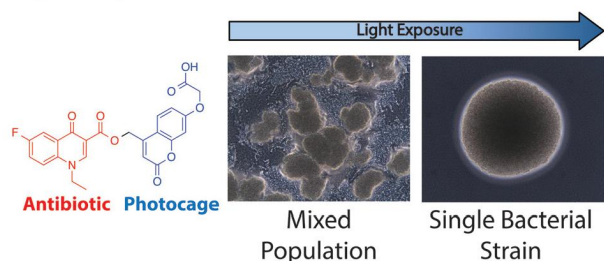
Integrated two-step chemoenzymatic continuous flow process for the synthesis of protected cyanohydrins from aldehydes.



COMMUNICATIONS

1639

Light-exposure time controls bacterial selection

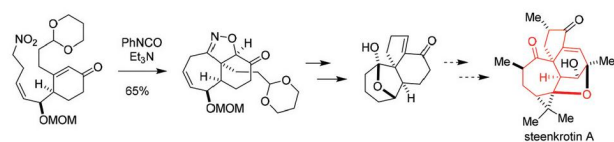


Bacterial patterning controlled by light exposure

Willem A. Velema, Jan Pieter van der Berg, Wiktor Szymanski, Arnold J. M. Driessen and Ben L. Feringa*

Patterning of multiple bacterial strains in one system is achieved by employing a single photo-activated antibiotic.

1643



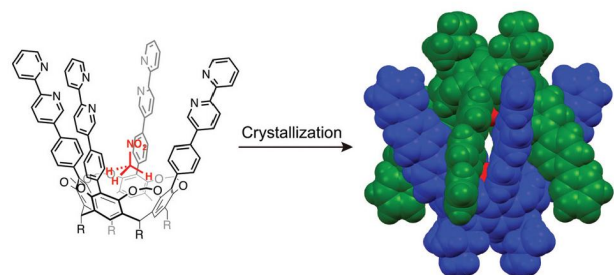
Construction of the tricyclic core of steenkrotin-type diterpenoids via intramolecular [3 + 2] cycloaddition

Jun Xuan, Saiyong Pan, Yuanbao Zhang, Bin Ye and Hanfeng Ding*

A concise and diastereoselective route to the [5–6–7] tricyclic skeleton of steenkrotins was developed based on an intramolecular [3 + 2] cycloaddition.

PAPERS

1647

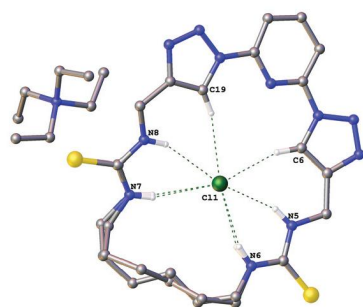


Molecular recognition of upper rim functionalized cavitaand and its unique dimeric capsule in the solid state

Mutsumi Kobayashi, Mei Takatsuka, Ryo Sekiya and Takeharu Haino*

Calix[4]resorcinarene-based cavitaand recognized the methyl group of the guests to form 1 : 1 host–guest complexes. In the solid state, the cavitaand formed a dimeric capsule in which two molecules of nitromethane were entrapped by weak noncovalent interactions.

1654



Anion binding and transport properties of cyclic 2,6-bis(1,2,3-triazol-1-yl)pyridines

Tamara Merckx, Cally J. E. Haynes, Louise E. Karagiannidis, Harriet J. Clarke, Katie Holder, Alexandra Kelly, Graham J. Tizzard, Simon J. Coles, Peter Verwilst, Philip A. Gale* and Wim Dehaen*

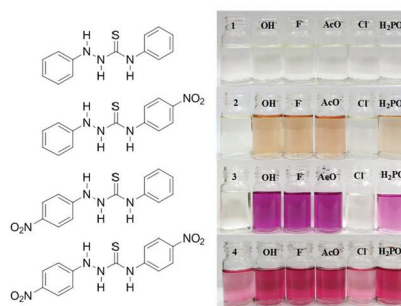
The anion binding and membrane transport properties of a series of cyclic 2,6-bis-(1,2,3-triazolyl)-pyridine receptors with thiourea functionalities are reported.

1662

UV-visible and ^1H – ^{15}N NMR spectroscopic studies of colorimetric thiosemicarbazide anion sensors

Kristina N. Farrugia, Damjan Makuc, Agnieszka Podborska, Konrad Szacitowski, Janez Plavec and David C. Magri*

Four model thiosemicarbazide anion chemosensors containing three N–H bonds, substituted with phenyl and/or 4-nitrophenyl units, were synthesised and studied for their anion binding abilities with hydroxide, fluoride, acetate, dihydrogen phosphate and chloride.

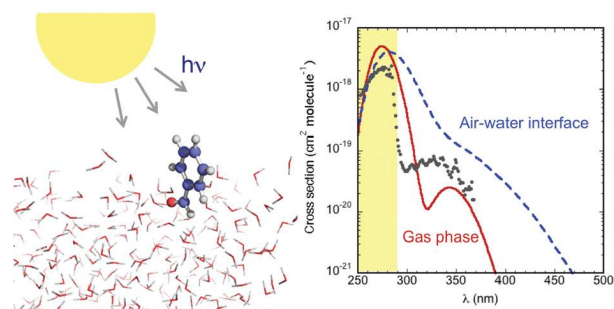


1673

Reactivity of aldehydes at the air–water interface. Insights from molecular dynamics simulations and *ab initio* calculations

Marilia T. C. Martins-Costa, Francisco F. García-Prieto and Manuel F. Ruiz-López*

Computer simulations show that solvation effects at the air–water interface significantly influence the chemistry of aldehydes, enhancing for instance the benzaldehyde photolysis rate constant by one order of magnitude.

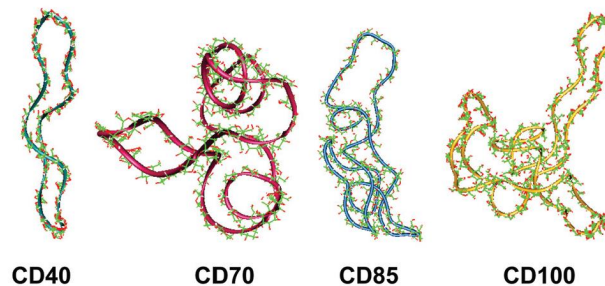


1680

Computational study on the intramolecular self-organization of the macrorings of some 'giant' cyclodextrins (CD_n, n = 40, 70, 85, 100)

Petko M. Ivanov,* Emanouil J. Atanassov and Carlos Jaime

A limited number of modes determine the overall deformations of the macrorings, which may have more than one cavity. Accordingly, they have the potential to accommodate more than one substrate molecule.

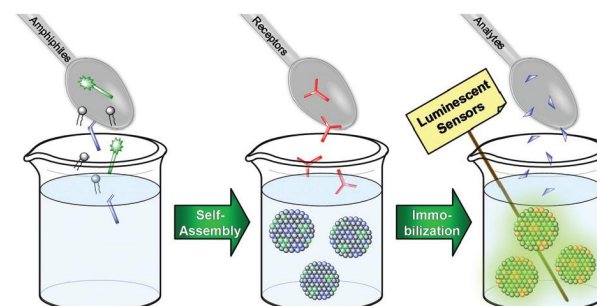


1690

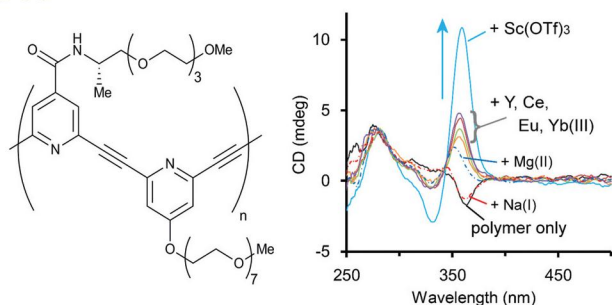
Preparation of luminescent chemosensors by post-functionalization of vesicle surfaces

Andreas Müller and Burkhard König*

A variety of luminescent chemosensors is obtained by post-functionalization of self-assembled phospholipid vesicles with receptor units ranging from metal complexes to aptamers.



1700

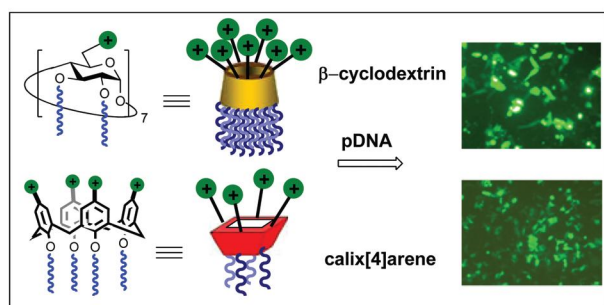


Highly efficient stabilisation of *meta*-ethynylpyridine polymers with amide side chains in water by coordination of rare-earth metals

Hiroki Makida, Hajime Abe* and Masahiko Inouye*

An amphiphilic *meta*-ethynylpyridine polymer with chiral amide side chains coordinated with rare-earth metal salts, especially strongly with Sc(III), to stabilise its helical structure with CD enhancement.

1708

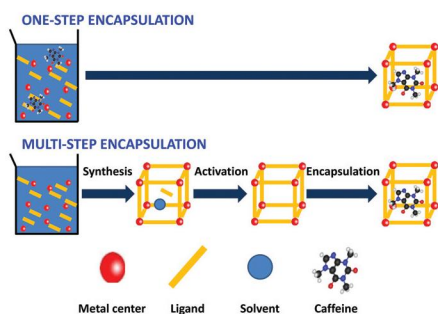


Cyclodextrin- and calixarene-based polycationic amphiphiles as gene delivery systems: a structure–activity relationship study

Laura Gallego-Yerga, Michela Lomazzi, Valentina Franceschi, Francesco Sansone,* Carmen Ortiz Mellet,* Gaetano Donofrio,* Alessandro Casnati and José M. García Fernández*

Multi-head/multi-tail facial amphiphiles built on cyclodextrin (CD) and calixarene (CA) scaffolds are paradigmatic examples of monodisperse gene delivery systems.

1724

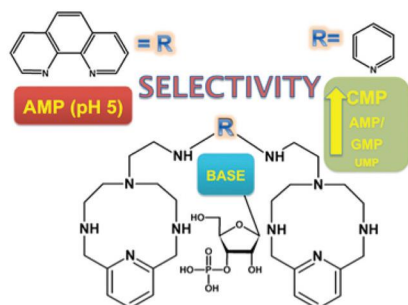


Using Hansen solubility parameters to study the encapsulation of caffeine in MOFs

Lorena Pasetta, Grégory Potier, Steven Abbott and Joaquín Coronas*

In this work the application of Hansen solubility parameters in the study of caffeine encapsulation in metal organic frameworks (MOFs) has been initiated.

1732



Aryl-bis-(scorpiand)-aza receptors differentiate between nucleotide monophosphates by a combination of aromatic, hydrogen bond and electrostatic interactions

Jorge González-García, Sanja Tomić, Alberto Lopera, Lluís Guijarro, Ivo Piantanida* and Enrique García-España*

Bis-scorpiaids bind nucleotides in water with 10–100 μM affinity, with selectivity: at pH 7 pyridine-scorpiaid toward CMP; at pH 5 phenanthroline-scorpiaid toward AMP.

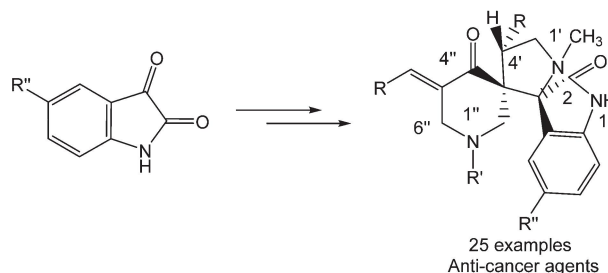
PAPERS

1741

Synthesis, and QSAR analysis of anti-oncological active spiro-alkaloids

Adel S. Girgis, Siva S. Panda, I. S. Ahmed Farag, A. M. El-Shabiny, A. M. Moustafa, Nasser S. M. Ismail, Girinath G. Pillai, Chandramukhi S. Panda, C. Dennis Hall* and Alan R. Katritzky

QSAR study describes the anti-neoplastic spiro-alkaloids with relevant molecular descriptors using CODESSA III software.

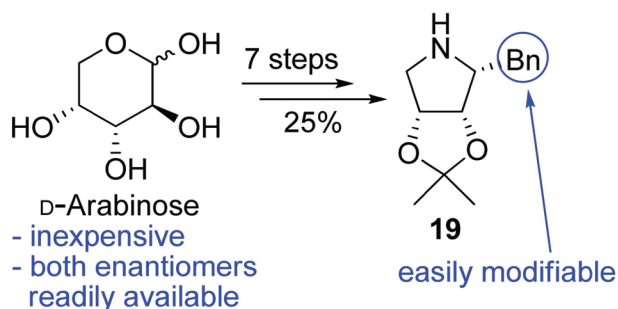


1754

Syntheses of arabinose-derived pyrrolidine catalysts and their applications in intramolecular Diels–Alder reactions

Tony K. M. Shing,* Kwun W. Wu, Ho T. Wu and Qicai Xiao

Six hydroxylated pyrrolidine catalysts were synthesized from D-arabinose and applied to asymmetric intramolecular Diels–Alder reactions with concomitant desymmetrization.

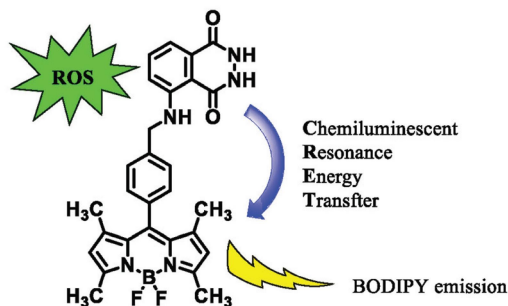


1763

A BODIPY-luminol chemiluminescent resonance energy-transfer (CRET) cassette for imaging of cellular superoxide

S. Bag, J.-C. Tseng* and J. Rochford*

Chemiluminescent resonance energy transfer is investigated for a BODIPY-luminol dyad demonstrating *in cellulo* biochemiluminescence with reactive oxygen species in activated splenocytes.

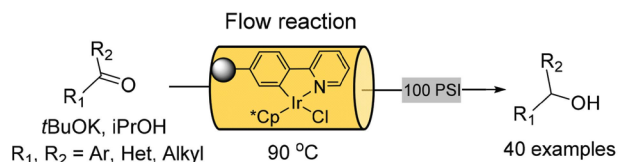


1768

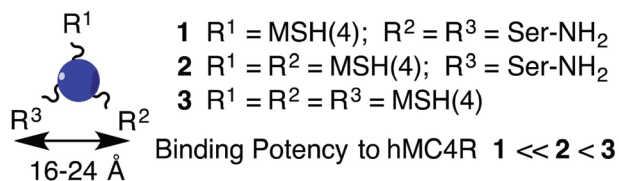
A monolith immobilised iridium Cp* catalyst for hydrogen transfer reactions under flow conditions

Maria Victoria Rojo,* Lucie Guetzoyan and Ian R. Baxendale

An immobilised iridium hydrogen transfer catalyst has been developed for use in flow based processing by incorporation of a ligand into a porous polymeric monolithic flow reactor.



1778

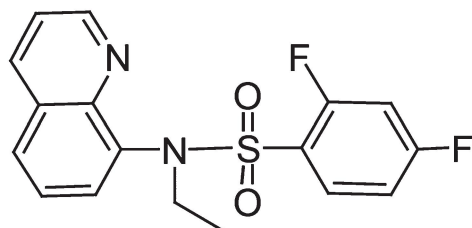


Trigonal scaffolds for multivalent targeting of melanocortin receptors

N. G. R. Dayan Elshan, Thanuja Jayasundera, Bobbi L. Anglin, Craig S. Weber, Ronald M. Lynch and Eugene A. Mash*

Short, efficient syntheses of multivalent molecules targeted to the human melanocortin 4 receptor based on phloroglucinol, tripropargylamine, and 1,4,7-triazacyclononane are described.

1792



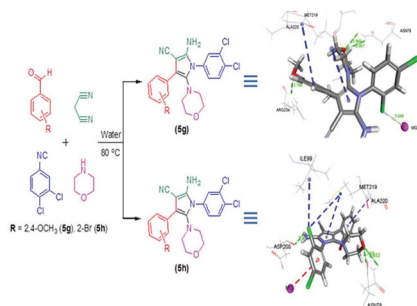
$\text{IC}_{50} = 0.28 \mu\text{M}$, $\text{CC}_{50} > 50 \mu\text{M}$

Identification of benzenesulfonamide quinoline derivatives as potent HIV-1 replication inhibitors targeting Rev protein

Fudi Zhong, Guannan Geng, Bing Chen, Ting Pan, Qianwen Li, Hui Zhang* and Chuan Bai*

A benzenesulfonamide quinoline compound with potent anti-HIV-1 replication activity and low toxicity by targeting HIV-1 Rev protein was identified with high-throughput screening and SAR studies.

1800

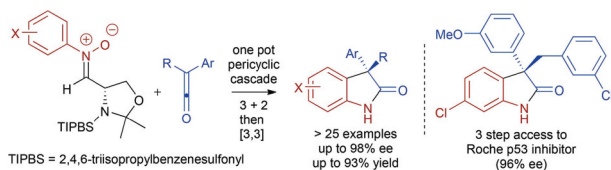


Multicomponent one-pot synthesis of highly-functionalized pyrrole-3-carbonitriles in aqueous medium and their computational study

Ramakanth Pagadala, Devendar Reddy Kommidi, Shrivankumar Kankala, Suresh Maddila, Parvesh Singh, Brenda Moodley, N. A. Koobanally and Sreekantha B. Jonnalagadda*

A one-pot protocol involving four-components in water is developed to synthesize functionalized pyrroles.

1807



An asymmetric pericyclic cascade approach to 3-alkyl-3-aryloxindoles: generality, applications and mechanistic investigations

E. Richmond, K. B. Ling, N. Duguet, L. B. Manton, N. Çelebi-Ölçüm, Y.-H. Lam, S. Alsancak, A. M. Z. Slawin, K. N. Houk* and A. D. Smith*

The reaction of L-serine derived N-arylnitronones with alkylarylketenes generates 3-alkyl-3-aryloxindoles in good yields and excellent enantioselectivities.

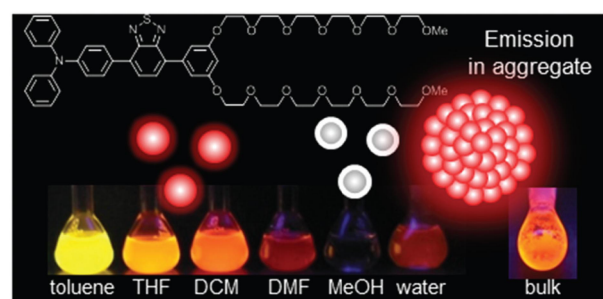
PAPERS

1818

Amphiphilic benzothiadiazole–triphenylamine-based aggregates that emit red light in water

Tsutomu Ishi-i,* Ikumi Kitahara, Shimpei Yamada, Yusuke Sanada, Kazuo Sakurai, Asami Tanaka, Naoya Hasebe, Toshitada Yoshihara and Seiji Tobita*

An amphiphilic donor–acceptor dye can provide red light emission in water in an aggregate state.

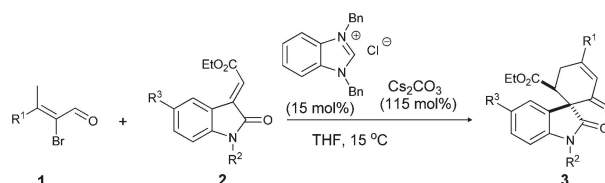


1829

N-heterocyclic carbene-catalyzed [4 + 2] cyclization of 2-bromo-2-enal with 3-alkylenyloxindoles: efficient assembly of spirocarbocyclic oxindole

Yuanwei Xie, Yonglei Que, Tuanjie Li, Ling Zhu, Chenxia Yu and Changsheng Yao*

A NHC-catalyzed [4 + 2] cyclization of 2-bromo-2-enal bearing γ -H with 3-alkylenyloxindoles under mild reaction conditions gives spirocarbocyclic oxindoles containing one quaternary carbon with high diastereoselectivities.

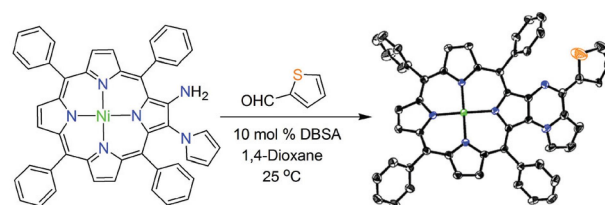


1836

Ambient temperature synthesis of β,β' -fused nickel(II) pyrrolo[1,2-a]pyrazinoporphyryns via a DBSA-catalyzed Pictet–Spengler approach

Dileep Kumar Singh and Mahendra Nath*

Synthesis of novel β,β' -fused nickel(II) pyrrolo[1,2-a]-pyrazinoporphyryns is accomplished for the first time at ambient temperature *via* a DBSA-catalyzed Pictet–Spengler approach.

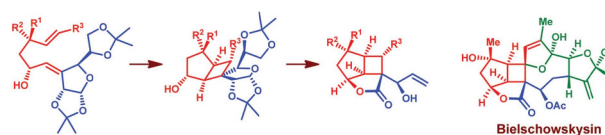


1846

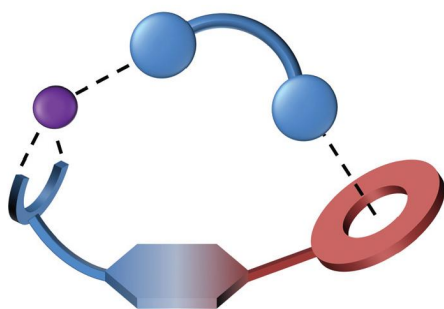
Studies towards the synthesis of bielschowskysin. Construction of the highly functionalized bicyclo[3.2.0]heptane segment

Anupam Jana, Sujit Mondal and Subrata Ghosh*

A stereocontrolled approach for the construction of a highly functionalized bicyclo[3.2.0]heptane derivative embodying the bridged lactone present in the diterpene bielschowskysin is reported.



1860

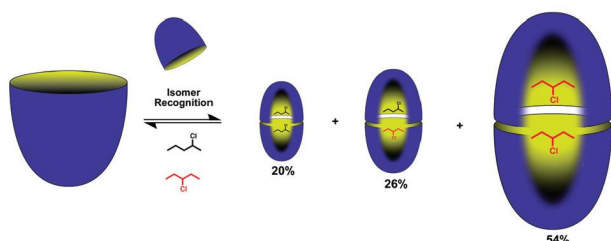


Phosphate binding by a novel Zn(II) complex featuring a *trans*-1,2-diaminocyclohexane ligand. Effective anion recognition in water

Oscar Francesconi, Matteo Gentili, Francesco Bartoli, Andrea Bencini,* Luca Conti, Claudia Giorgi and Stefano Roelens*

Excellent affinities and selectivities toward triphosphates are achieved through an adaptive ditopic receptor featuring a metal ion and a macrocyclic polyammonium cation binding sites, concertedly bridging phosphate anions.

1869

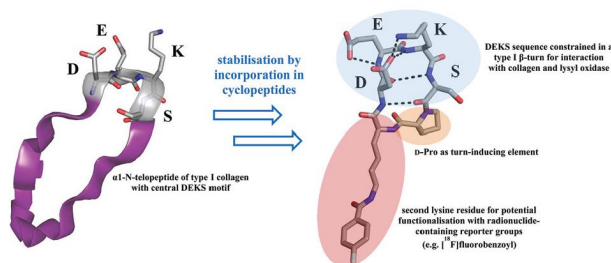


Differentiation of small alkane and alkyl halide constitutional isomers *via* encapsulation

Matthew R. Sullivan and Bruce C. Gibb*

Previously we have demonstrated that host **1** is capable of hydrocarbon gas separation by selective sequestration of butane from a mixture with propane in the headspace above a solution of the host (C. L. D. Gibb, B. C. Gibb, *J. Am. Chem. Soc.*, 2006, **128**, 16498–16499).

1878

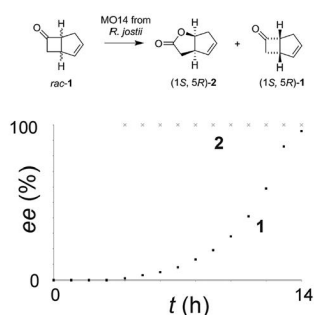


Cyclopeptides containing the DEKS motif as conformationally restricted collagen telopeptide analogues: synthesis and conformational analysis

Robert Wodtke, Gloria Ruiz-Gómez, Manuela Kuchar, M. Teresa Pisabarro, Pavlina Novotná, Marie Urbanová, Jörg Steinbach, Jens Pietzsch and Reik Löser*

The conformational stabilisation of the DEKS motif at the α 1(I) collagen *N*-telopeptide within a cyclic hexapeptide together with its conformational analysis is described. This sequence is critical for lysyl oxidase-mediated collagen crosslinking, a process which is deregulated during tumour progression.

1897



E. coli cells expressing the Baeyer–Villiger monooxygenase 'MO14' (*ro03437*) from *Rhodococcus jostii* RHA1 catalyse the gram-scale resolution of a bicyclic ketone in a fermentor

Benjamin D. Summers, Muhiadin Omar, Thomas O. Ronson, Jared Cartwright, Michael Lloyd and Gideon Grogan*

(1*S*,5*R*)-2-Oxalactone of >99% ee and (1*S*,5*R*)-ketone of 96% ee are produced after approximately 14 h at a temperature of 16 °C.

1904

Studies on the diastereoselective oxidation of 1-thio- β -D-glucopyranosides: synthesis of the usually less favoured R_S sulfoxide as a single diastereoisomer

Juan Francisco Moya-López, Eleonora Elhalem, Rocío Recio, Eleuterio Álvarez, Inmaculada Fernández* and Nouredine Khier*

The *exo*-anomeric effect paves the way for the synthesis of the usually less favored R_S - β -sulfinyl glycoside as a single diastereoisomer.

