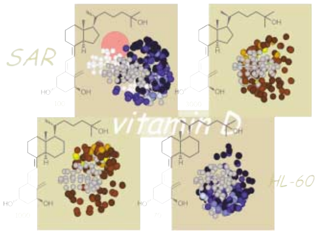
ISSN 1477-0520 OBCRAK(2) 215–440(2003)

Organic & Biomolecular Chemistry

FORMERLY PERKIN TRANSACTIONS 1 AND 2

Incorporating Acta Chemica Scandinavica



Cover
See P. J. De Clercq *et al.* page 257
Structure–activity relationship (SAR) studies of analogs of the calcium regulating hormone 1α,25-dihydroxyvitamin D_3 (top left) reveal a remarkable connection between the preferred orientation of the side chain, as determined by conformational analysis, and their biological activities, illustrated here by the effect on the cell differentiation of human leukemia cancer cells (HL-60). Higher occupation by the oxygen atom of the terminal hydroxy group of the side chain (colored spheres) of the region in space represented by the red sphere results in increased activity, as shown by the analog in which the stereochemistry at C-20 in the side chain is reversed (top right). In accordance with this observation, replacement of the hydrindane CD-ring part of the natural hormone by a *trans*-decalin system leads to the inverse situation, *i.e.* the analog with the natural configuration at C-20 (bottom left) shows higher activity than its 20-epimer (bottom right). The activites are given as relative values, the reference value of the natural hormone being defined as 100.

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contents

PERSPECTIVE

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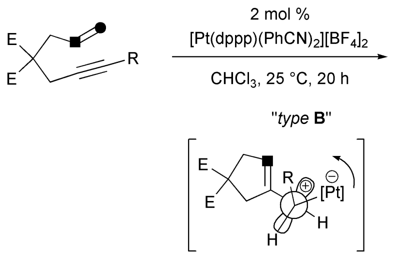


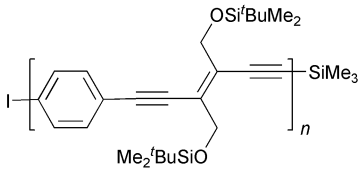
Mechanistic aspects of transition metal catalysed 1,6-diene and 1,6-enyne cycloisomerisation reactions

Guy C. Lloyd-Jones

Isotopic, kinetic, spectroscopic, structural and computational investigations into the mechanisms by which transition metals effect the title reaction are reviewed.

COMMUNICATIONS

237 239



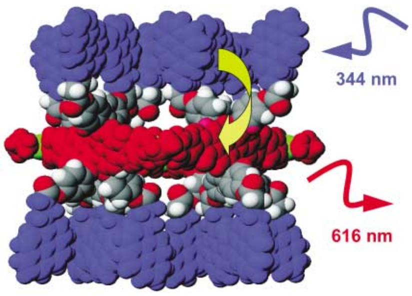
1 $n = 1$
2 $n = 2$
3 $n = 3$
4 $n = 4$

Acetylenic scaffolding on solid support: poly(triacetylene)-derived oligomers by Sonogashira and Cadiot–Chodkiewicz-type cross-coupling reactions

Nils F. Utesch and François Diederich

The first synthesis of oligo(phenylene triacetylene)s **1**–**4**, members of a new family of linearly π-conjugated oligomers with an all-carbon backbone, was carried out by repetitive Sonogashira cross-coupling on polymeric support and shown to exhibit dramatically enhanced fluorescence quantum yields compared with the corresponding oligo(triacetylene)s.

240 243

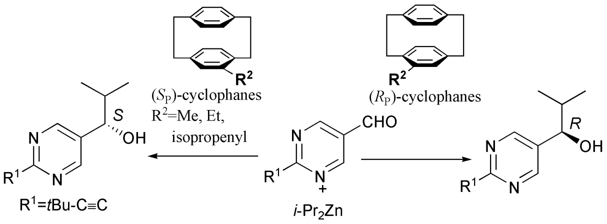


Energy transfer in multichromophoric self-assembled molecular squares

Frank Würthner and Armin Sautter

Metal-ion directed self-assembly of pyrene-substituted perylene bisimide dyes afforded well-defined multichromophoric squares that exhibit energy transfer from the pyrene to the perylene manifold.

244 246

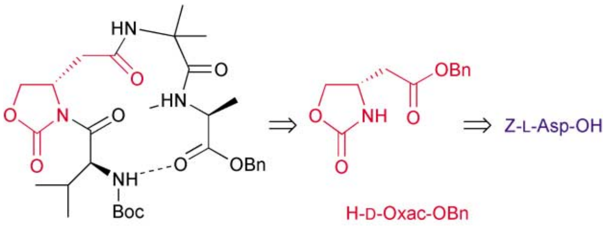


Asymmetric autocatalysis induced by chiral hydrocarbon [2.2]paracyclophanes

Itaru Sato, Atsushi Ohno, Yohei Aoyama, Toshinari Kasahara and Kenso Soai

Hydrocarbon mono-substituted [2.2]paracyclophanes have been successfully used as chiral initiators in asymmetric autocatalysis. Highly enantiomerically enriched 5-pyrimidyl alkanol was obtained from the reaction.

247 250

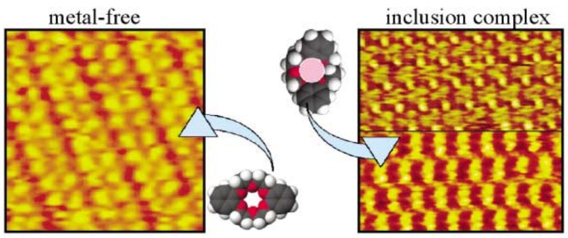


Introduction of 4(*S*)-oxazolidineacetic acid, 2-oxo (D-Oxac) motif in a polypeptide chain: synthesis and conformational analysis

Gianluigi Luppi, Marzia Villa and Claudia Tomasini

A convenient and straightforward method for the synthesis of 4(*S*)-oxazolidineacetic acid, 2-oxo benzyl ester (D-Oxac-OBn) from commercially available Z-L-Asp-OH. This molecule is a promising scaffold for the design and synthesis of libraries of short oligomers with a well-defined secondary structure.

251 253

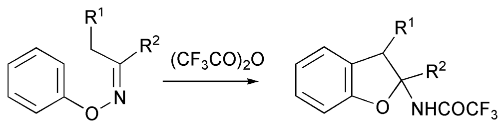


2D-supramolecular arrangements of dibenzo-18-crown-6-ether and its inclusion complex with potassium ion by potential controlled adsorption

Akihiro Ohira, Masayo Sakata, Chuichi Hirayama and Masashi Kunitake

In-situ visualization of the inclusion complex at high-resolution, has allowed us to distinguish the host part from a guest part, leading to an enhanced understanding of host–guest chemistry at the submolecular scale.

254 256

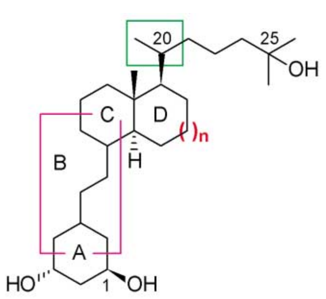


Efficient [3,3]-sigmatropic rearrangement accelerated by a trifluoroacetyl group: synthesis of benzofurans under mild conditions

Okiko Miyata, Norihiko Takeda, Yoshiaki Morikami and Takeaki Naito

The [3,3]-sigmatropic rearrangement took place smoothly during the course of trifluoroacetylation of *O*-phenyloxime at below room temperature to give the dihydrobenzofuran or benzofuran as a result of concomitant cyclization.

257 267



Synthesis, biological activity, and conformational analysis of CD-ring modified *trans*-decalin 1α,25-dihydroxyvitamin D analogs

Yong-Jun Chen, Ling-Jie Gao, Ibrahim Murad, Annemieke Verstuyf, Lieve Verlinden, Christel Verboven, Roger Bouillon, Davide Viterbo, Marco Milanesio, Dirk Van Haver, Maurits Vandewalle and Pierre J. De Clercq

trans-Decalin ($n = 1$) analogs of 1α,25-dihydroxyvitamin D_3 show surprising biological activities when compared with the corresponding natural ($n = 0$) derivatives, following modifications of the stereochemistry at C-20 and of the seco-B-ring.

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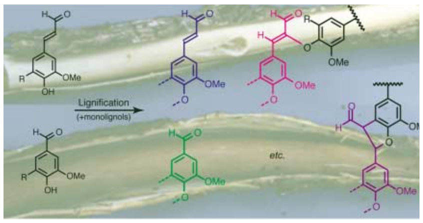
268 281



NMR analysis of lignins in CAD-deficient plants. Part 1. Incorporation of hydroxycinnamaldehydes and hydroxybenzaldehydes into lignins

Hoon Kim, John Ralph, Fachuang Lu, Sally A. Ralph, Alain-M. Boudet, John J. MacKay, Ronald R. Sederoff, Takashi Ito, Shingo Kawai, Hideo Ohashi and Takayoshi Higuchi

Modes of incorporation of hydroxycinnamaldehydes and hydroxybenzaldehydes into lignins, by radical coupling mechanisms, are elucidated by model studies and NMR.

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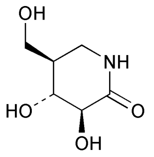
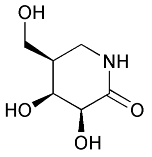
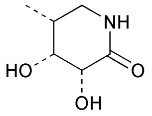
282 287



9
K_i 9 μM
(β-mannosidase)



10
K_i 67 nM
(β-galactosidase)



11
K_i 18 μM
(α-fucosidase)

Isofagomine lactams, synthesis and enzyme inhibition

Vinni H. Lillelund, Huizhen Liu, Xifu Liang, Helmer Søhoel and Mikael Bols

The synthesis of the novel isofagomine lactams **9**–**11** is reported and their inhibition of glycosidases investigated.

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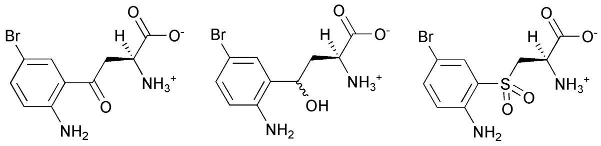
288 295



Differential effects of bromination on substrates and inhibitors of kynureninase from *Pseudomonas fluorescens*

Christian Heiss, Jay Anderson and Robert S. Phillips

Bromine substitution has unexpected effects on properties of substrates and inhibitors of kyureninase.

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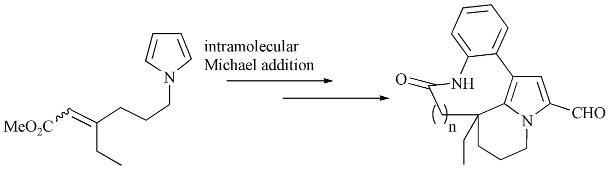
296 305



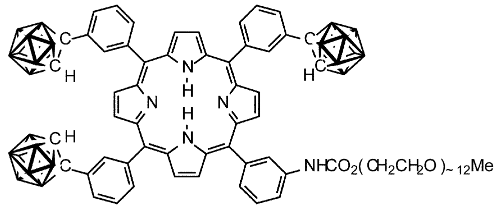
(±)-B-norrhazinal (n=1)
(±)-rhazinal (n=2)

Total synthesis of (±)-rhazinal, an alkaloidal spindle toxin from *Kopsia teoi*

Martin G. Banwell, Alison J. Edwards, Katrina A. Jolliffe, Jason A. Smith, Ernest Hamel and Pascal Verdier-Pinard

Total synthesis of (±)-rhazinal, an alkaloidal spindle toxin from *Kopsia teoi*.

306 317



Synthesis of *meso*-substituted porphyrins carrying carboranes and oligo(ethylene glycol) units for potential applications in boron neutron capture therapy

Christophe Frixa, Mary F. Mahon, Andrew S. Thompson and Michael D. Threadgill

Condensations of carboranylbenzaldehydes with 3-nitrophenyldipyrromethane give separable mixtures of porphyrins; these provide functionalised carborane–porphyrin constructs with applications in BNCT.

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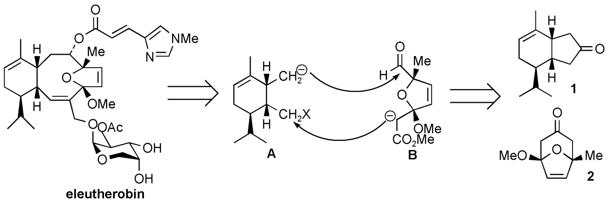
318 327



A convergent approach to the marine natural product eleutherobin: synthesis of key intermediates and attempts to produce the basic skeleton

Gaia Scalabrino, Xiao-Wen Sun, John Mann and Anne Baron

We describe the synthesis of key intermediates and attempts to produce the basic skeleton of eleutherobin.

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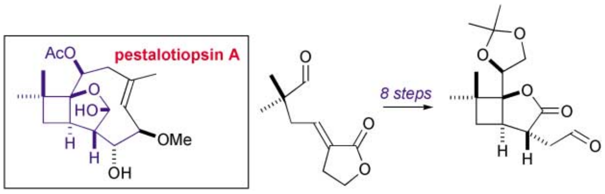
328 337



The first synthetic studies on pestalotiopsin A. A stereocontrolled approach to the functionalised bicyclic core

Derek Johnston, Emmanuel Couché, David J. Edmonds, Kenneth W. Muir and David J. Procter

A Sm(II) 4-*exo-trig* cyclisation and an alkylytterbium addition/trans-lactonisation form the basis of an approach to the core of pestalotiopsin A.

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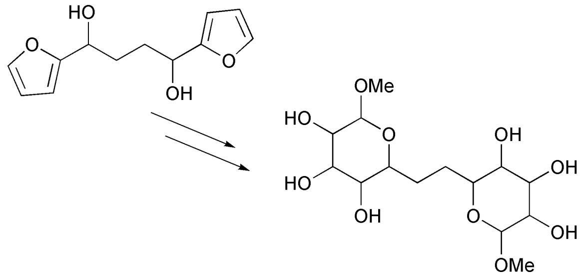
338 349



A stereodivergent, two-directional synthesis of stereoisomeric *C*-linked disaccharide mimetics

Michael Harding, Robert Hodgson, Tahir Majid, Kenneth J. McDowall and Adam Nelson

The polyols, synthesised using dipyranones as templates, represent a new and interesting class of *C*-linked disaccharide analogues with promising biological activity.

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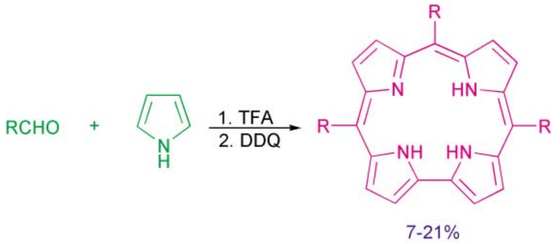
350 357



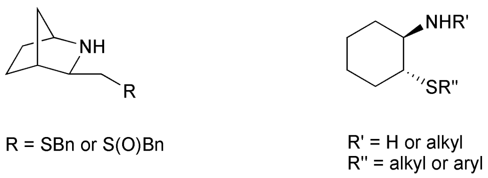
Refined methods for the synthesis of meso-substituted A_3- and *trans*-A_2B-corroles

Daniel T. Gryko and Beata Koszarna

Detailed optimization led to a comprehensive and efficient method for the one-pot synthesis of A_3-corroles, superior to other procedures.

358 366

Synthesis and evaluation of *N*,*S*-compounds as chiral ligands for transfer hydrogenation of acetophenone



Jenny K. Ekegren, Peter Roth, Klas Källström, Tibor Tarnai and Pher G. Andersson

Evaluation of ligands in the transfer hydrogenation of acetophenone utilising $[Ir(COD)Cl]_2$ as metal precursor afforded up to 80% ee and 98% conversion in 0.5 h

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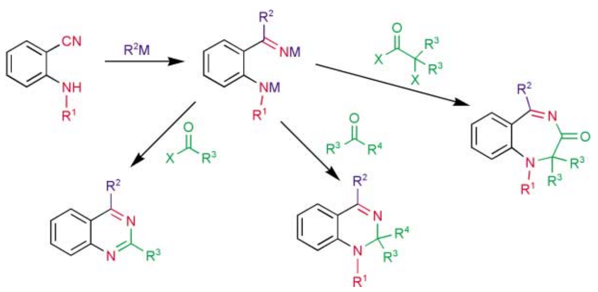
367 372

Ring forming reactions of imines of 2-aminobenzaldehyde and related compounds



Per Wiklund and Jan Bergman

Quinazolines and 1,4-benzodiazepine-3-ones were obtained after addition of organometallic reagents to 2-aminobenzonitriles, followed by quenching with suitable electrophiles (acyl halides, aldehydes or ketones).

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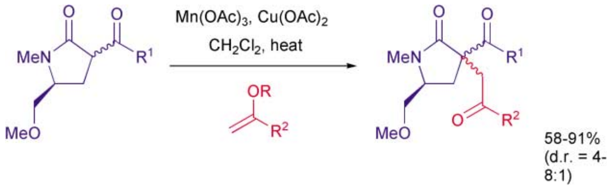
373 380

Manganese(III) acetate-mediated alkylation of β-keto esters and β-keto amides: an enantio- and diastereo-selective approach to substituted pyrrolidinones



Gregory Bar, Andrew F. Parsons and C. Barry Thomas

An attractive alternative to classical base-mediated alkylation of β-keto esters and amides; this synthetic approach could find application in the alkylation of base-sensitive pyrrolidinone substrates.

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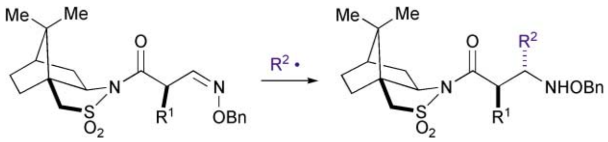
381 390

Radical addition to oxime ethers for asymmetric synthesis of β-amino acid derivatives



Hideto Miyabe, Kayoko Fujii and Takeaki Naito

Radical addition to chiral oxime ethers provides a synthetic method for the preparation of α,β-dialkyl-β-amino acid derivatives with excellent diastereoselectivity.

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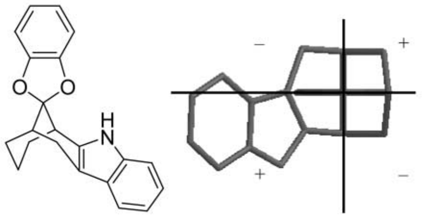
391 394

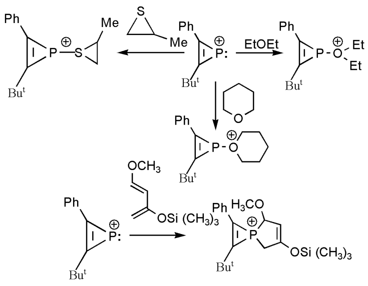
Synthesis, chiroptical properties and absolute configuration of spiro[1,3-benzodioxole-methanocyclooct[*b*]indole]



Eugenius Butkus, Julė Malinauskienė and Sigitas Stončius

Semiempirical rules should be applied cautiously in the determination of the absolute configuration of structures containing several chromophores.

395 400



Gas phase chemistry of the 2-*tert*-butyl-3-phenylphosphirenylium cation: novel onium ions by nucleophilic attack at phosphorus and *de novo* *P*-spiro bicyclic phosphonium ions *via* $[4 + 2^+]$ cycloaddition with dienes

Adão A. Sabino, Marcos N. Eberlin, Luis Alberto B. Moraes and Kenneth K. Laali

The present study constitutes the first successful attempt to unravel the chemistry of 2-*tert*-butyl-3-phenylphosphirenylium ion, a unique 2π-Hückel phosphirenylium ion for which no direct solution chemical reactivity data are as yet available.

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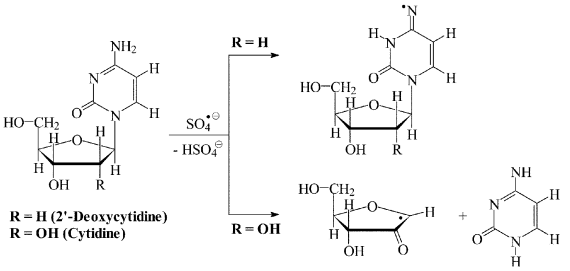
401 408



The reactions of cytidine and 2′-deoxycytidine with $SO_4^{\bullet-}$ revisited. Pulse radiolysis and product studies

Charuvila T. Aravindakumar, Man Nien Schuchmann, Balijepalli S. M. Rao, Justus von Sonntag and Clemens von Sonntag

2′-Deoxycytidine reacts with $SO_4^{\bullet-}$ to a base radical while cytidine gives rise to a sugar radical without involving radical cations.

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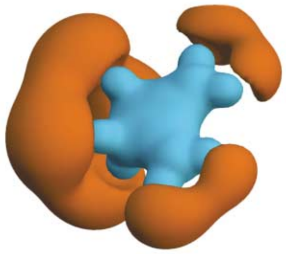
409 414



Experimental charge density of octafluoro-1,2-dimethylenecyclobutane: atomic volumes and charges in a perfluorinated hydrocarbon

Dieter Lentz, Mona Patzschke, Ansgar Bach, Stephan Scheins and Peter Luger

Atomic properties of fluorine bonds to sp^2 and sp^3 carbon atoms in a perfluorinated hydrocarbon were studied by X-ray crystallography and DFT and their transferability demonstrated.

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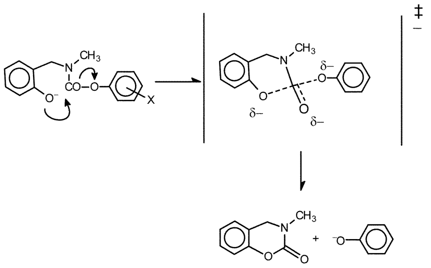
415 421



The base-catalysed cyclisation of phenyl *N*-(2-hydroxybenzyl)-*N*-methylcarbamates is concerted

Vojeslav Štěrba, Oldřich Hrabík, Jaromír Kaválek, Jaromír Mindl and Andrew Williams

Cross-interaction substituent effects support a concerted displacement mechanism at a carbonyl centre under certain conditions of nucleophile, leaving group and acyl function.

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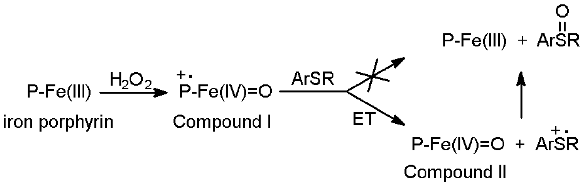
422 426



Mechanism of the oxidation of aromatic sulfides catalysed by a water soluble iron porphyrin

Enrico Baciocchi, Maria Francesca Gerini, Osvaldo Lanzalunga, Andrea Lapi and Maria Grazia Lo Piparo

Evidence is presented suggesting an electron transfer mechanism for aromatic sulfide sulfoxidation catalysed by a water soluble iron porphyrin.

ARTICLES

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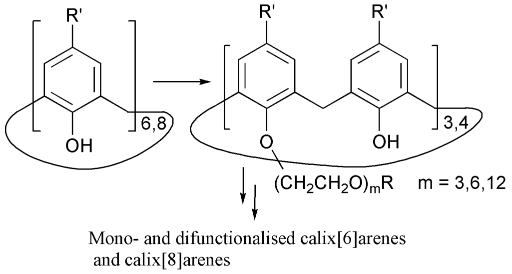
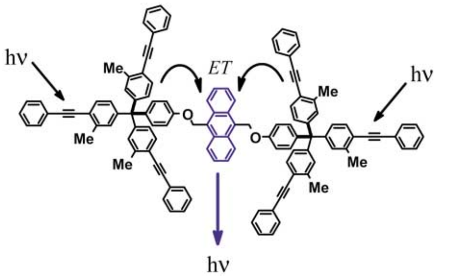


The selective functionalisation and difunctionalisation of *p*-substituted calix[6]arene and calix[8]arenes using hydrophilic moieties

Gwénaëlle Hervé, Dirk Uwe Hahn, Anne-Cécile Hervé, Kerry J. Goodworth, Alison M. Hill and Helen C. Hailes

Methodologies to access symmetrical partially functionalised and fully functionalised water soluble large ringed calixarenes in good yield are described.

436 440



A tetraphenylmethane based dendritic tolan–anthracene dyad: synthesis and energy transfer properties

Saumitra Sengupta and Pradipta Purkayastha

In order to synthesize a peripherally rigid dendritic donor–acceptor dyad for energy transfer studies, a tritolan dendron based on a tetraphenylmethane scaffold was prepared from New Fuchsin.

CONFERENCE DIARY

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Dates, venues and contact details of forthcoming events.

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