ISSN 1477-0520 OBCRAK(21) 3625–3866(2003)

Indexed in Medline from issue 1

Organic & Biomolecular Chemistry

FORMERLY PERKIN TRANSACTIONS 1 AND 2

Incorporating Acta Chemica Scandinavica

Cover
See Jeremy Knowles, page 3625.
The cover shows the brand-new Chemistry Research Laboratory (silver-topped building, top-centre) situated directly across South Parks Road from the Dyson Perrins Laboratory ('the DP') which has been the centre of organic chemistry in Oxford, from 1916 until now. Also shown is a small selection of molecules historically associated with the DP's four Waynflete Professors. Cover photograph courtesy of Karl Harrison, University of Oxford.

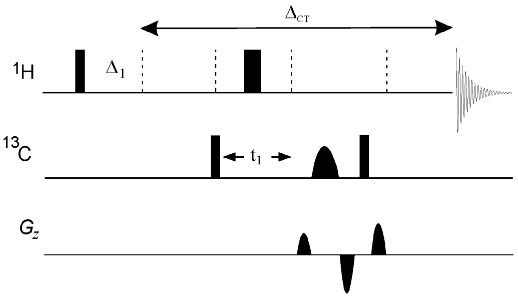
Chemical biology articles published in this journal also appear in the *Chemical Biology Virtual Journal*: **www.rsc.org/chembiol**

contents

COMMENT

COMMUNICATIONS

3632 3634

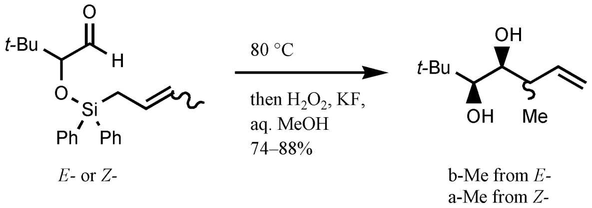


Enhanced ^{13}C resolution in semi-selective HMBC: a band-selective, constant-time HMBC for complex organic structure elucidation by NMR

Tim D. W. Claridge and Ignacio Pérez-Victoria

A high-resolution ^1H–^{13}C HMBC technique is described for the structure elucidation of complex organic molecules with crowded ^{13}C NMR spectra.

3635 3638

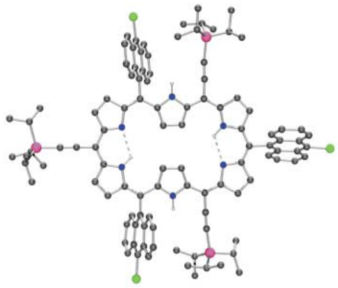


Stereospecificity in the silicon tethered α-(methyl)allylation of aldehydes

Jeremy Robertson, Michael J. Hall and Stuart P. Green

Routes are described for the synthesis and stereospecific cyclisation under neutral conditions of *E*- and *Z*-2-(crotylsilyl)oxyaldehydes.

3639 3641

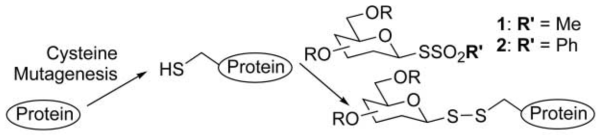


Synthesis and crystal structure of a *meso*-trialkynyl-[28]hexaphyrin

Alexander Krivokapic and Harry L. Anderson

Boron trifluoride-catalysed condensation of a *meso*-anthryl dipyrromethane and triisopropylsilylpropynal gives a [28]hexaphyrin as the main product in 37% yield.

3642 3644

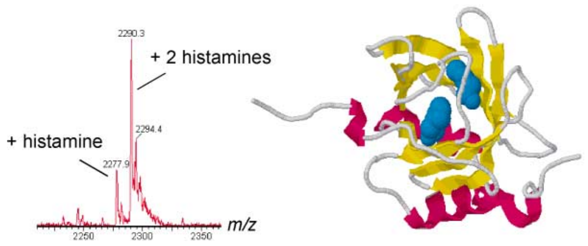


Glycosyl phenylthiosulfonates (Glyco-PTS): novel reagents for glycoprotein synthesis

David P. Gamblin, Philippe Garnier, Sarah J. Ward, Neil J. Oldham, Antony J. Fairbanks and Benjamin G. Davis

The glyco-PTS reagents described are more stable, more efficient, easier and cheaper to prepare than earlier thiol glycosylating reagents and, with a phenyl group in the aglycone, allow *in situ* UV monitoring of glycosylation.

3645 3646



Non-denaturing electrospray ionisation-mass spectrometry reveals ligand selectivity in histamine-binding protein RaHBP2

Neil J. Oldham, Olga Lissina, Miles A. Nunn and Guido C. Paesen

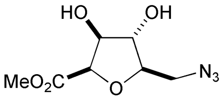
The amine-binding protein RaHBP2 binds two molecules of histamine in preference to tyramine, dopamine, tryptamine and serotonin.

ARTICLES

3647 3655

Bend ribbon-forming tetrahydrofuran amino acids

Martin D. Smith, Timothy D. W. Claridge,
Mark S. P. Sansom and George W. J. Fleet



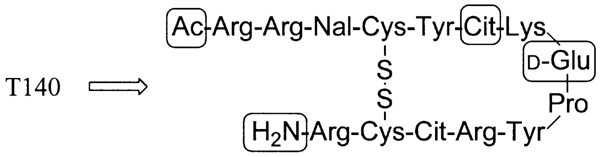
1

Oligomeric chains of THF amino acid derivatives such as **1** adopt a bend-ribbon secondary structure stabilised by (i, $i-2$) hydrogen bonds.

3656 3662

Synthesis of potent CXCR4 inhibitors possessing low cytotoxicity and improved biostability based on T140 derivatives

Hirokazu Tamamura, Kenichi Hiramatsu, Shuichi Kusano,
Shigemi Terakubo, Naoki Yamamoto, John O. Trent,
Zixuan Wang, Stephen C. Peiper, Hideki Nakashima,
Akira Otaka and Nobutaka Fujii



Ac-TE14011

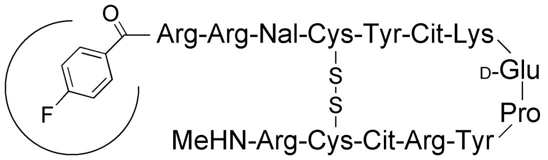
Nal = L-3-(2-naphthyl)alanine
Cit = L-citrulline

CXCR4 inhibitors which possess high selectivity indexes have been developed.

3663 3669

Enhancement of the T140-based pharmacophores leads to the development of more potent and bio-stable CXCR4 antagonists

Hirokazu Tamamura, Kenichi Hiramatsu, Makiko Mizumoto,
Satoshi Ueda, Shuichi Kusano, Shigemi Terakubo,
Miki Akamatsu, Naoki Yamamoto, John O. Trent,
Zixuan Wang, Stephen C. Peiper, Hideki Nakashima,
Akira Otaka and Nobutaka Fujii



New
Pharmacophore

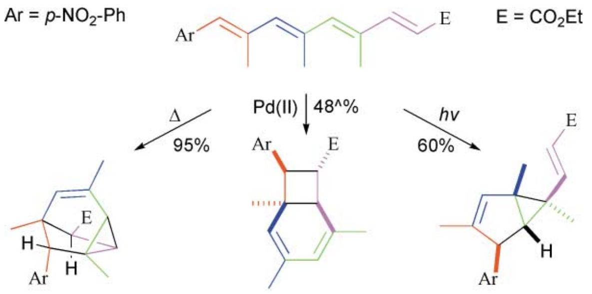
4F-benzoyl-TE14011-Me

The enhancement of the T140-based pharmacophores led to development of a novel CXCR4 antagonist, 4F-benzoyl-TE14011-Me.

3670 3684

Biomimetic studies on polyenes

John E. Moses, Jack E. Baldwin, Sébastien Brückner,
Serena J. Eade and Robert M. Adlington

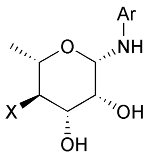


Several classes of complex polypropionate derived core structures were prepared from simple strained polyene precursors by varying the reaction conditions.

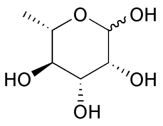
3685 3691

An approach to the generation of simple analogues of the antitumour agent spicamycin

Stéphane Mons and George W. J. Fleet



1 X = OH
2 X = CH$_3$(CH$_2$)$_{10}$CONH



3

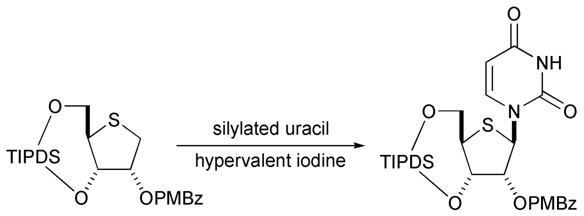
We report a new route to the preparation of rhamnospicamycin analogues **1** and **2** from rhamnose **3** which is much faster than previous procedures and likely broader in scope.

3692–3697

A novel method for the synthesis of 4′-thiopyrimidine nucleosides using hypervalent iodine compounds

Naozumi Nishizono, Ryosuke Baba, Chika Nakamura, Kazuaki Oda and Minoru Machida

4′-Thiopyrimidine nucleosides were synthesized by the coupling reaction of cyclic sulfides with a silylated nucleobase using PhI=O.



3698–3707

Asymmetric synthesis of (1*R*,2*S*,3*R*)-3-methylcispentacin and (1*S*,2*S*,3*R*)-3-methyltranspentacin by kinetic resolution of *tert*-butyl (±)-3-methylcyclopentene-1-carboxylate

Mark E. Bunnage, Ann M. Chippindale, Stephen G. Davies, Richard M. Parkin, Andrew D. Smith and Jonathan M. Withey

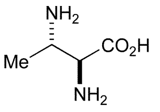
Kinetic resolution of *tert*-butyl (±)-3-methylcyclopentene-1-carboxylate with lithium (*S*)-*N*-benzyl-*N*-α-methylbenzylamide proceeds to give, at 51% conversion, *tert*-butyl (1*R*,2*S*,3*R*,α*S*)-3-methyl-2-*N*-benzyl-*N*-α-methylbenzylaminocyclopentane-1-carboxylate consistent with $E > 130$, and in 39% yield and 99 ± 0.5% de after isolation.

3708–3715

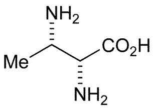
Asymmetric synthesis of *anti*-(2*S*,3*S*)- and *syn*-(2*R*,3*S*)-diaminobutanoic acid

Mark E. Bunnage, Anthony J. Burke, Stephen G. Davies, Nicholas L. Millican, Rebecca L. Nicholson, Paul M. Roberts and Andrew D. Smith

A general asymmetric synthesis of 2,3-diamino acids is described, with application to the synthesis of *anti*-(2*S*,3*S*)- and *syn*-(2*R*,3*S*)-diaminobutanoic acid (98% de and 98% ee).



anti-(2*S*,3*S*)
98% d.e.,
98% e.e.



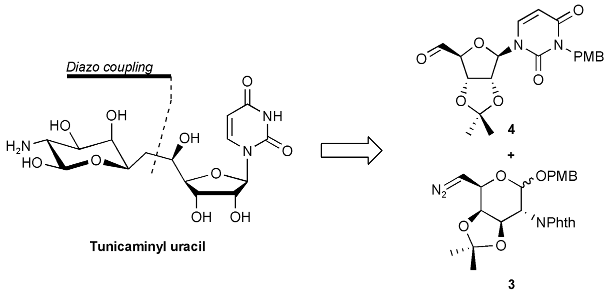
syn-(2*R*,3*S*)
98% d.e.,
98% e.e.

3716–3725

Synthetic studies towards the tunicamycins and analogues based on diazo chemistry. Total synthesis of tunicaminyl uracil

Francisco Sarabia, Laura Martín-Ortiz and F. Jorge López-Herrera

The syntheses of tunicaminyl uracil and related compounds were achieved based on the coupling of aldehydo-sugars with different non-stabilized diazo compounds derived from 2-amino-2-deoxy-D-galactopyranose and uridine derivatives.

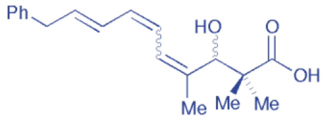


3726–3737

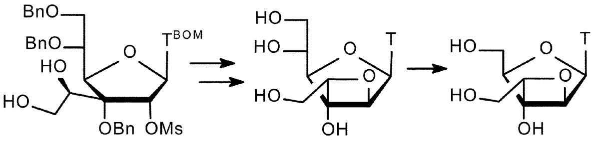
A multicomponent coupling strategy suitable for the synthesis of the triene component of the oxazolomycin antibiotics

Paul G. Bulger, Mark G. Moloney and Paul C. Trippier

Direct access to the triene fragment of oxazolomycin using an efficient multicomponent coupling sequence is reported.



3738 3748

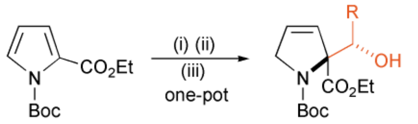


Synthesis of hydroxymethyl branched [3.2.0]bicyclic nucleosides using a regioselective oxetane ring-formation

Nanna K. Christensen, Ann Katrine L. Andersen,
Trine R. Schultz and Poul Nielsen

Two [3.2.0]bicyclic nucleosides with one or two hydroxymethyl substituents have been efficiently synthesized from a stereoselective dihydroxylation and a regioselective oxetane ring-formation.

3749 3757



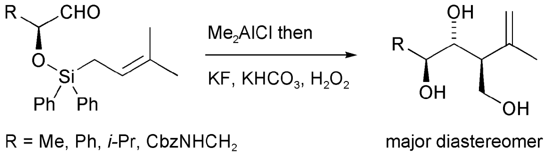
(i) LiDBB, BMEA, THF, –78°C, then $Br(CH_2)_2Br$;
(ii) $MgBr_2•OEt_2$; (iii) RCHO then NH_4Cl.

Scope of the reductive aldol reaction: application to aromatic carbocycles and heterocycles

Timothy J. Donohoe, David House and K. W. Ace

The reductive aldol reaction has been developed into a highly diastereoselective process which is compatible with a range of aldehydes.

3758 3767

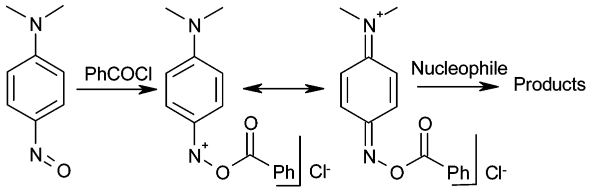


Ene cyclisations of α-(prenyl)dialkylsilyloxy aldehydes: formation and oxidative cleavage of oxasilacyclohexanols

Jeremy Robertson, Michael J. Hall, Petra M. Stafford and Stuart P. Green

Silicon-tethered ene cyclisation provides a route to functionalised alkenyl triols with moderate to good stereoselectivity.

3768 3771

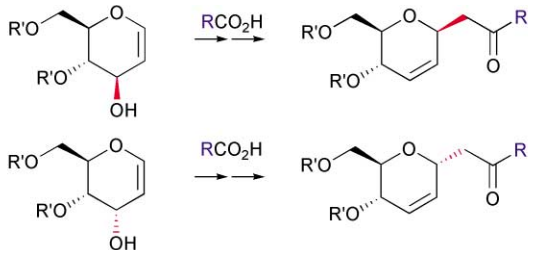


Nitrenium ions. Reactions of *N*,*N*-dimethyl-*p*-benzoyloxy-aniline-iminium chloride with indoles and indolizines. X-ray structure of unexpected [2-chloro-4-(4-dimethylaminophenyl-*ONN*-azoxy)phenyl]dimethylamine (azoxy derivative)

Lucedio Greci, Riccardo Castagna, Patricia Carloni, Pierluigi Stipa, Corrado Rizzoli, Lara Righi and Paolo Sgarabotto

The reactions between the nitrenium ion deriving from *N*,*N*-dimethyl-*p*-nitrosoaniline and benzoyl chloride, with different nucleophiles (indoles, indolizines) are reported.

3772 3786

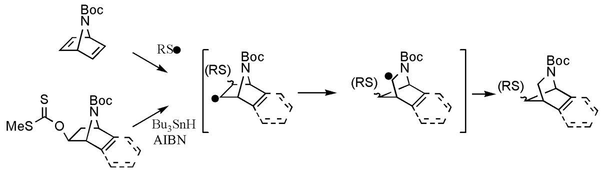


Stereoselective synthesis of *C*-glycosides from carboxylic acids: the tandem Tebbe–Claisen approach

H. Yasmin Godage, David J. Chambers, Graham R. Evans and Antony J. Fairbanks

A wide variety of *C*-glycosides may be accessed in a completely stereoselective fashion by esterification of glycals with carboxylic acids and subsequent Tebbe methylenation and Claisen rearrangement.

3787 3798

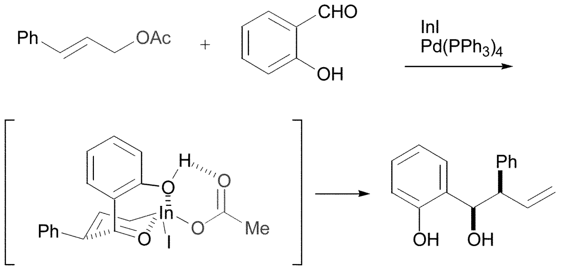


Development of two processes for the synthesis of bridged azabicyclic systems: intermolecular radical addition–homoallylic rearrangements leading to 2-azanorborn-5-enes and neophyl-type radical rearrangements to 2-azabenzonorbornanes

David M. Hodgson, Magnus W. P. Bebbington and Paul Willis

Two synthetically useful radical rearrangement processes have been established, leading to azabicycles that are not readily accessible by other means.

3799 3803

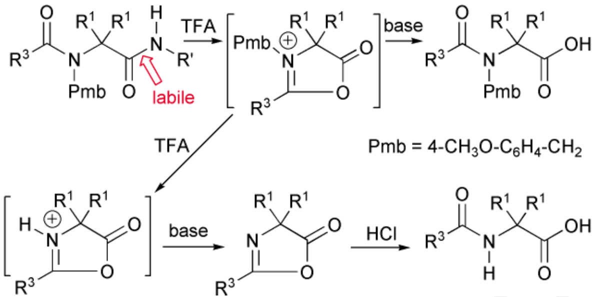


Control of diastereoselectivity in the crotylation and cinnamylation of aldehydes by the selection of ligands on allylic indium reagents

Tsunehisa Hirashita, Toshiya Kamei, Makoto Satake, Tomoaki Horie, Hidetaka Shimizu and Shuki Araki

Diastereoselectivity of the indium-mediated allylation of aldehydes can be controlled not only by the α-oxygenated substitution in aldehydes, but also by a proper choice of the ligands on allylindium reagents.

3804 3810

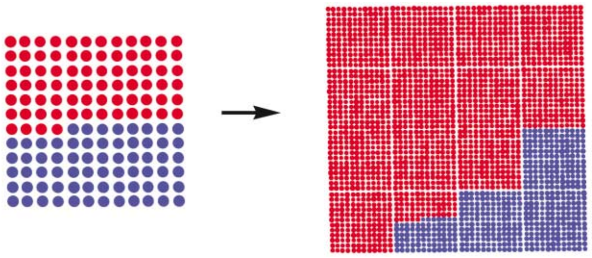


Synthesis of *N*-acyl-*N*,α,α-trialkyl and *N*-acyl-α,α-dialkyl glycines by selective cleavage of Ugi–Passerini adducts. Qualitative assessment of the effect of substituents on the path and yield of reaction

Wei-Qun Jiang, Susana P. G. Costa and Hernâni L. S. Maia

Different cleavage paths and yields according to the size and nature of the substituents and the concentration of acid.

3811 3819

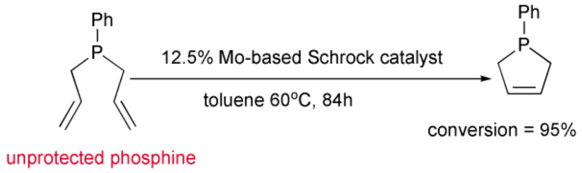


Reflections on spontaneous asymmetric synthesis by amplifying autocatalysis

Ilya D. Gridnev, Joerg M. Serafimov, Harry Quiney and John M. Brown

Spontaneous asymmetric synthesis has been observed in a variety of experiments involving autocatalytic Zn alkylation.

3820 3825

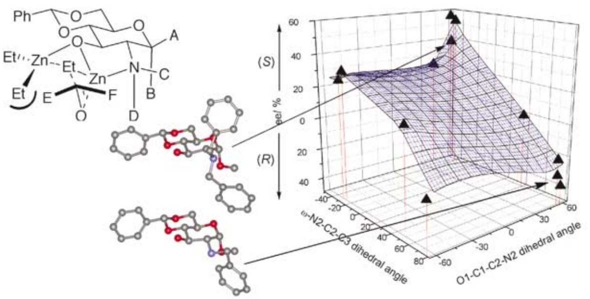


Synthesis of unprotected and borane-protected cyclic phosphines using Ru– and Mo– based olefin metathesis catalysts

Catherine A. Slinn, Alison J. Redgrave, S. Lucy Hind, Chris Edlin, Steven P. Nolan and Veronique Gouverneur

The compatibility of the Mo-based Schrock catalyst with various borane-protected phosphines and one unprotected phosphine has been demonstrated.

3826 3838

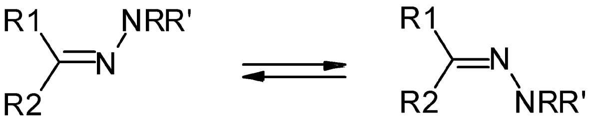


Precise structure activity relationships in asymmetric catalysis using carbohydrate scaffolds to allow ready fine tuning: dialkylzinc–aldehyde additions

Daniel P. G. Emmerson, Renaud Villard, Claudia Mugnaini, Andrei Batsanov, Judith A. K. Howard, William P. Hems, Robert P. Tooze and Benjamin G. Davis

A 24 member array of hexosamine sugars has allowed the first factorial analysis of ligand design.

3839 3844

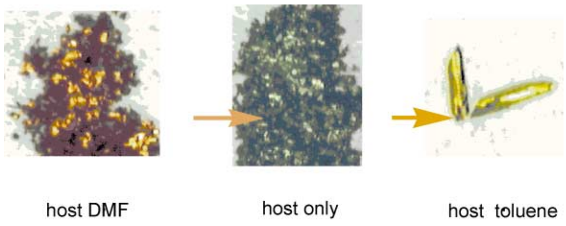


Investigation of the configuration of alkyl phenyl ketone phenylhydrazones from *ab initio* ^{1}H NMR chemical shifts

Mahmoud Trabelsi, Mansour Salem and Benoît Champagne

Using *ab initio* calculations the experimental ^{1}H NMR spectra of the *E* and *Z* isomers of alkyl phenyl ketone phenylhydrazones R1–C(Ph)=N–NH–Ph (R1 = Me, Et, iPr, and tBu) have been re-interpreted.

3845 3850

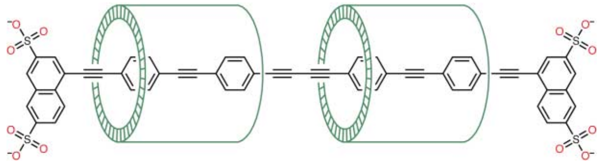


Formation of gold-like metal-lustrous inclusion crystals from 1-phenyl-2,5-bis[5-(tricyanoethenyl)-2-thienyl]pyrrole host and an electron-donating aromatic guest

Katsuyuki Ogura, Rui Zhao, Takashi Mizuoka, Motohiro Akazome and Shoji Matsumoto

All the inclusion compounds containing toluene, *p*-xylene, anisole, dimethoxybenzenes and indene have a common stoichiometric ratio (host–guest) of 2 : 1 and a similar layer structure in their crystals.

3851 3856

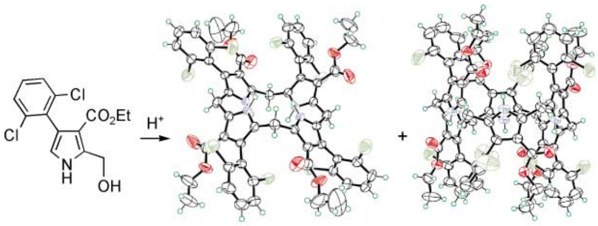


Hindered fluorescence quenching in an insulated molecular wire

Peter N. Taylor, Andrew J. Hagan and Harry L. Anderson

The presence of two threaded cyclophane macrocycles on a conjugated dumbbell inhibits electron-transfer from the excited state of the dumbbell π-system.

3857 3865



Oligocyclization of 2-(hydroxymethyl)pyrroles with electron-withdrawing groups at β-positions: formation and structural elucidation of porphyrinogens and hexaphyrinogens

Hidemitsu Uno, Kentarou Inoue, Takashi Inoue and Noboru Ono

The acidic treatment of ethyl 2-(hydroxymethyl)pyrrole-3-carboxylates with bulky aryl groups gave type I isomers of porphyrinogens and hexaphyrinogens.

CONFERENCE DIARY

xi Dates, venues and contact details of forthcoming events.

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