

In this issue...

New reactivity pattern for vinyl bromides

In a new one-pot transformation, *in situ*-generated enamines are trapped with vinyl halides to give a new C–C bond. See Willis *et al.*, pp. 3094–3095.



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Cover

See Nigel A. Jones, Sergey A. Nepogodiev and Robert A. Field, pp. 3201–3206.

The figure shows the fast and flexible synthetic route to the branched tetrasaccharide structures present in many saponins, including the tomato glycoalkaloid α -tomatine.

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COMMUNICATIONS

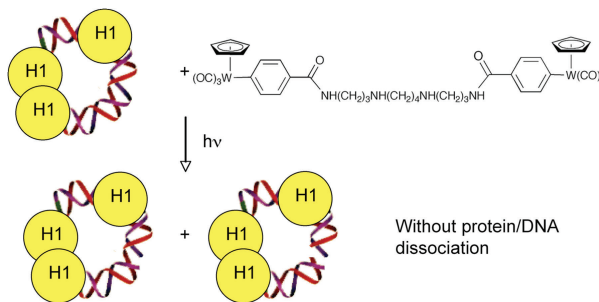
3091



Selective targeting of DNA for cleavage within DNA–histone assemblies by a spermine–[CpW(CO)₃Ph]₂ conjugate

Thomas A. Shell and Debra L. Mohler*

Upon photolysis, a spermine–[CpW(CO)₃Ph]₂ conjugate cleaves DNA in DNA–histone assemblies, causing protein–DNA dissociation.



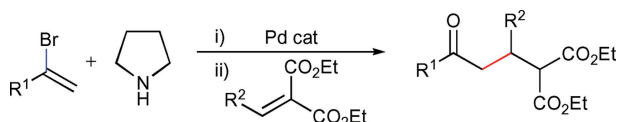
3094



A new reactivity pattern for vinyl bromides: *cis*-substitution *via* palladium catalysed C–N coupling/Michael addition reactions

Michael C. Willis,* Jay Chauhan and William G. Whittingham

Palladium catalysed enamine formation followed by Michael addition allows vinyl bromides to be substituted *cis* to the original C–Br bond.



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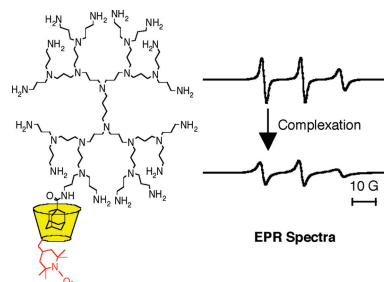
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3096

Spin-labelled cyclodextrins as hosts for large supramolecular assemblies

Gabriela Ionita and Victor Chechik*

EPR spectroscopy was used to study formation of inclusion complexes of monofunctionalised spin-labelled β -cyclodextrins; this method is very sensitive to the interactions of cyclodextrins with large guest molecules.

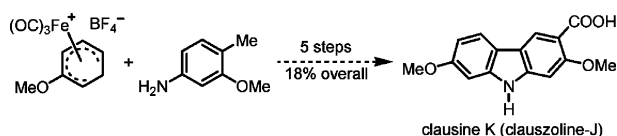


3099

First total synthesis of the biologically active 2,7-dioxygenated tricyclic carbazole alkaloids 7-methoxy-*O*-methylmukonal, clausine H (clauszoline-C), clausine K (clauszoline-J) and clausine O

Olga Kataeva, Micha P. Krahl and Hans-Joachim Knölker*

Using the iron-mediated arylamine cyclization as the key step we have achieved a short and highly efficient access to the biologically active 2,7-dioxygenated tricyclic carbazole alkaloids 7-methoxy-*O*-methylmukonal, clausine H (clauszoline-C), clausine K (clauszoline-J) and clausine O.

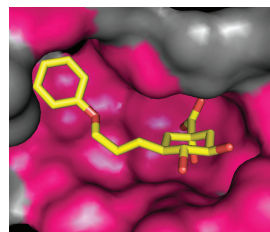


3102

Rational design of new bifunctional inhibitors of type II dehydroquinase

Miguel D. Toscano, Kirsty A. Stewart, John R. Coggins, Adrian J. Laphorn and Chris Abell*

New selective inhibitors of type II dehydroquinase were rationally designed to explore extra binding interactions, resulting in increased potency.



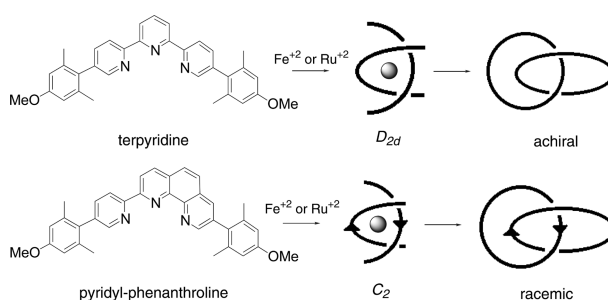
ARTICLES

3105

Synthesis of achiral and racemic catenanes based on terpyridine and a directionalized terpyridine mimic, pyridyl-phenanthroline

Jon C. Loren, Peter Gantzel, Anthony Linden and Jay S. Siegel*

Structurally similar terpyridine and pyridyl-phenanthroline give rise to achiral and chiral metal complexes, respectively, from which catenanes are formed that retain their stereochemistry even after demetallation.

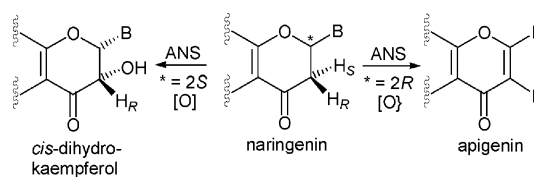


3117

Structural and mechanistic studies on anthocyanidin synthase catalysed oxidation of flavanone substrates: the effect of C-2 stereochemistry on product selectivity and mechanism

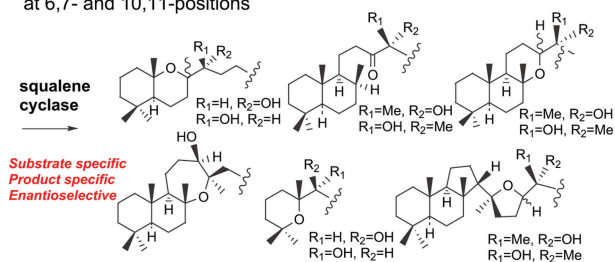
Richard W. D. Welford, Ian J. Clifton, Jonathan J. Turnbull, Stuart C. Wilson and Christopher J. Schofield*

Anthocyanidin synthase (ANS) catalyses hydroxylation and desaturation of flavanone substrates with the product selectivity being dependent on the C-2 stereochemistry of the starting material. The results indicate that dependent on substrate, ANS can catalyse desaturation *via* two mechanisms, one of which likely proceeds *via* a gem-diol intermediate.



3127

Threo- and *erythro*-diols of squalene at 6,7- and 10,11-positions

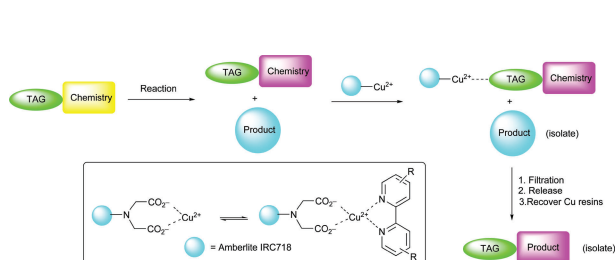


Enzymatic cyclizations of squalene analogs with *threo*- and *erythro*-diols at the 6,7- or 10,11-positions by recombinant squalene cyclase. Trapping of carbocation intermediates and mechanistic insights into the product and substrate specificities

Takamasa Abe and Tsutomu Hoshino*

Stable tertiary cations were trapped using squalene diols.

3140

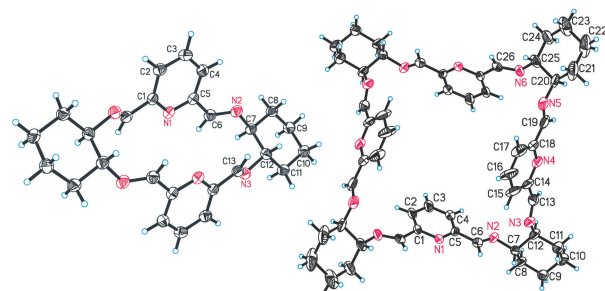


A phase-switch purification approach for the expedient removal of tagged reagents and scavengers following their application in organic synthesis

Jason Siu, Ian R. Baxendale, Russell A. Lewthwaite and Steven V. Ley*

A series of tagged reagents and scavengers have been prepared which aid in post reaction purification. This approach is based on a phase switching methodology using a metal chelating bipyridine tag.

3161

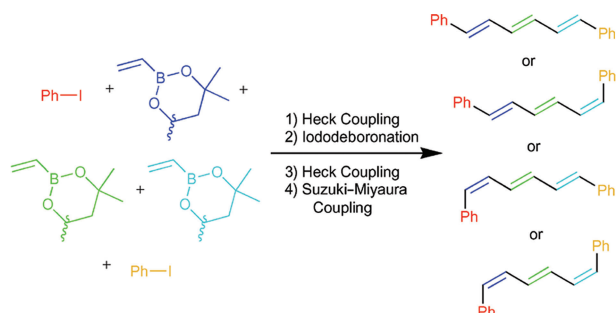


New 2+2, 3+3 and 4+4 macrocycles derived from 1,2-diaminocyclohexane and 2,6-diformylpyridine

Janusz Gregoliński, Jerzy Lisowski* and Tadeusz Lis

Two new Schiff base macrocycles – a 4+4 condensation product and a meso-type 2+2 condensation product – were obtained in a reaction of *trans*-1,2-diaminocyclohexane and 2,6-diformylpyridine.

3167

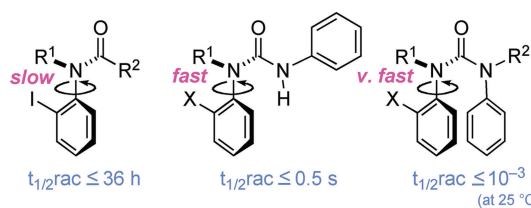


A stereoselective synthesis of 1,6-diphenyl-1,3,5-hexatrienes utilising 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane as a two-carbon alkenyl building block

Andrew P. Lightfoot, Steven J. R. Twiddle and Andrew Whiting*

Various stereoisomers of 1,6-diphenyl-1,3,5-hexatriene can be readily accessed using only iodobenzene and a hindered boronate ester using a series of palladium-catalysed reactions and iododeboronations.

3173



Slow interconversion of enantiomeric conformers or atropisomers of anilide and urea derivatives of 2-substituted anilines

Thomas Adler, Josep Bonjoch, Jonathan Clayden,* Mercè Font-Bardía, Mark Pickworth, Xavier Solans, Daniel Solé and Lluís Vallverdú

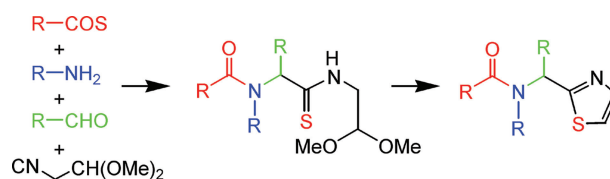
Ortho substituted anilides and ureas show rotational restriction: we report barriers to interconversion of their enantiomeric conformers. Rotation is sometimes slow enough for even mono-*ortho*substituted anilides to exhibit atropisomerism.

3184

A straightforward approach towards thiazoles and endothiopeptides *via* Ugi reaction

Uli Kazmaier* and Stefanie Ackermann

Endothiopeptides can easily be obtained *via* Ugi reaction and can directly be converted into thiazoles under microwave irradiation.

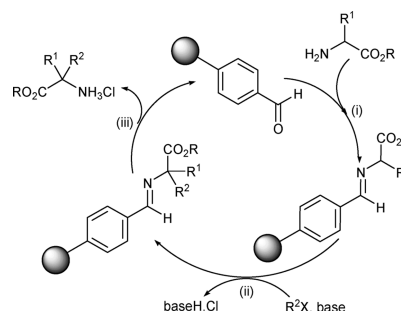


3188

Wang-aldehyde resin as a recyclable support for the synthesis of α,α -disubstituted amino acid derivatives

Meritxell Guinó and King Kuok (Mimi) Hii*

Merrifield resin was functionalised with hydroxybenzaldehyde under microwave irradiation and used as a means for immobilisation and activation of α -amino acid esters for alkylation reactions; α,α -disubstituted and cyclic amino acid esters were prepared in high yields.

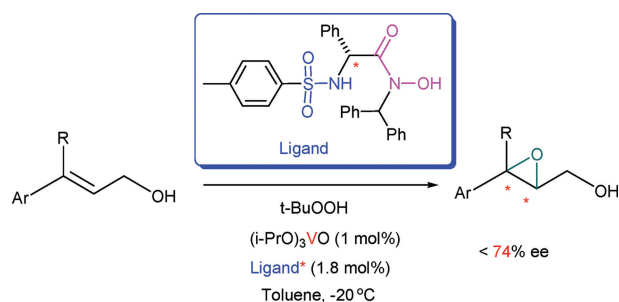


3194

Amino acid-derived hydroxamic acids as chiral ligands in the vanadium catalysed epoxidation

Andrei V. Malkov,* Zainaba Bourhani and Pavel Kočovský

New sulfonamide-derived hydroxamic acids showed high reactivity at subzero temperatures and moderate to good enantioselectivity in the V-catalysed asymmetric epoxidation.

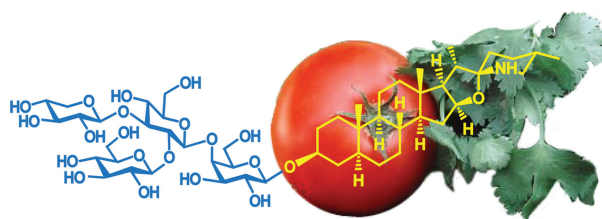


3201

Efficient synthesis of methyl lycotetraoside, the tetrasaccharide constituent of the tomato defence glycoalkaloid α -tomatine

Nigel A. Jones, Sergey A. Nepogodiev* and Robert A. Field*

The branched tetrasaccharide present as a glycone of plant saponins of the *Solanaceae* family has been synthesised in the form of methyl glycoside in eight steps in 19% overall yield.

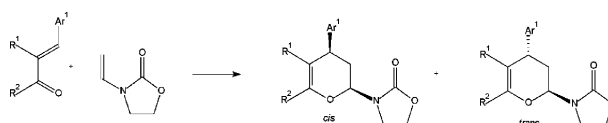


3207

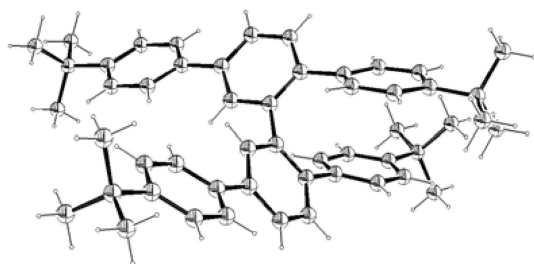
Synthesis of 3,4-dihydro-2*H*-pyrans by hetero-Diels–Alder reactions of functionalized α,β -unsaturated carbonyl compounds with *N*-vinyl-2-oxazolidinone

Aleksandra Pałasz*

The hetero-Diels–Alder reactions of selected 4-aryl-1-oxa-1,3-butadienes with *N*-vinyl-2-oxazolidinone have been shown to proceed regio- and diastereoselectively leading to functionalized 3,4-dihydro-2*H*-pyrans.



3213

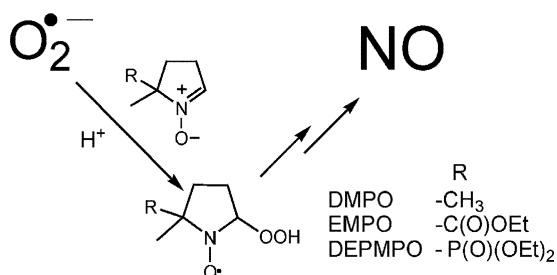


Synthesis and spectroscopy of an oligophenyl based cruciform with remarkable π - π assisted folding

Benjamin S. Nehls, Frank Galbrecht, Askin Bilge, David J. Brauer, Christian W. Lehmann, Ullrich Scherf* and Tony Farrell*

A prototype of a new family of oligophenyls with a propensity towards foldamer formation regardless of the medium was prepared and characterised.

3220

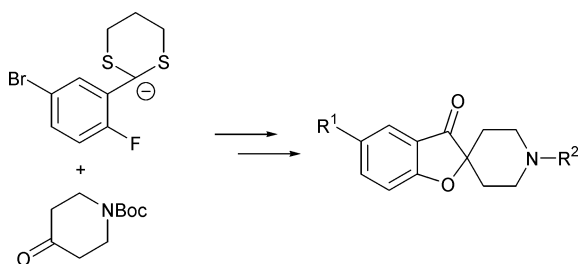


Nitric oxide release from the unimolecular decomposition of the superoxide radical anion adduct of cyclic nitrones in aqueous medium

Edward J. Locigno, Jay L. Zweier* and Frederick A. Villamena*

Unimolecular decomposition of the superoxide radical anion adduct of cyclic nitron leads to the formation of nitric oxide.

3228

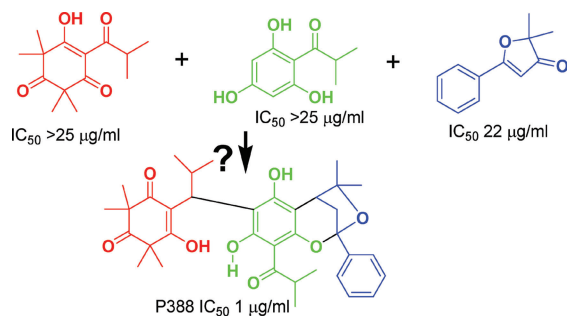


Synthesis and derivatisation of a novel spiro[1-benzofuran-2,4'-piperidin]-3-one scaffold

Rowan A. Wilson, Lai Chan, Robin Wood and Richard C. D. Brown*

The synthesis and elaboration of a scaffold containing the "privileged" spiro-piperidine substructure is reported.

3236

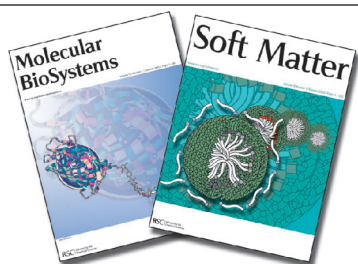


A cytotoxic triketone-phloroglucinol-bullatenone hybrid from *Lophomyrtus bullata*

Lesley Larsen, Michael H. Benn, Masood Parvez and Nigel B. Perry*

A complex new hybrid natural product, bullataketal, is over twenty times more cytotoxic than the component building blocks.

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- Abe, Takamasa, 3127
 Abell, Chris, 3102
 Ackermann, Stefanie, 3184
 Adler, Thomas, 3173
 Baxendale, Ian R., 3140
 Benn, Michael H., 3236
 Bilge, Askin, 3213
 Bonjoch, Josep, 3173
 Bourhani, Zainaba, 3194
 Brauer, David J., 3213
 Brown, Richard C. D., 3228
 Chan, Lai, 3228
 Chauhan, Jay, 3094
 Chechik, Victor, 3096
 Clayden, Jonathan, 3173
 Clifton, Ian J., 3117
 Coggins, John R., 3102
 Farrell, Tony, 3213
 Field, Robert A., 3201
 Font-Bardía, Mercè, 3173
 Galbrecht, Frank, 3213
 Gantzel, Peter, 3105
 Gregoliński, Janusz, 3161
 Guinó, Meritxell, 3188
 Hii, King Kuok (Mimi), 3188
 Hoshino, Tsutomu, 3127
 Ionita, Gabriela, 3096
 Jones, Nigel A., 3201
 Kataeva, Olga, 3099
 Kazmaier, Uli, 3184
 Knölker, Hans-Joachim, 3099
 Kočovský, Pavel, 3194
 Krahl, Micha P., 3099
 Laphorn, Adrian J., 3102
 Larsen, Lesley, 3236
 Lehmann, Christian W., 3213
 Lewthwaite, Russell A., 3140
 Ley, Steven V., 3140
 Lightfoot, Andrew P., 3167
 Linden, Anthony, 3105
 Lis, Tadeusz, 3161
 Lisowski, Jerzy, 3161
 Locigno, Edward J., 3220
 Loren, Jon C., 3105
 Malkov, Andrei V., 3194
 Mohler, Debra L., 3091
 Nehls, Benjamin S., 3213
 Nepogodiev, Sergey A., 3201
 Pałasz, Aleksandra, 3207
 Parvez, Masood, 3236
 Perry, Nigel B., 3236
 Pickworth, Mark, 3173
 Scherf, Ullrich, 3213
 Schofield, Christopher J., 3117
 Shell, Thomas A., 3091
 Siegel, Jay S., 3105
 Siu, Jason, 3140
 Solans, Xavier, 3173
 Solé, Daniel, 3173
 Stewart, Kirsty A., 3102
 Toscano, Miguel D., 3102
 Turnbull, Jonathan J., 3117
 Twiddle, Steven J. R., 3167
 Vallverdú, Lluís, 3173
 Villamena, Frederick A., 3220
 Welford, Richard W. D., 3117
 Whiting, Andrew, 3167
 Whittingham, William G., 3094
 Willis, Michael C., 3094
 Wilson, Rowan A., 3228
 Wilson, Stuart C., 3117
 Wood, Robin, 3228
 Zweier, Jay L., 3220

FORTHCOMING ARTICLES

Heterocyclic ring scaffolds as small-molecule cholesterol absorption inhibitors

Tobias Ritter, Lisbet Kværnø, Moritz Werder, Helmut Hauser and Erick M. Carreira (DOI: 10.1039/b510100j)

Highly-functionalised difluorinated cyclohexane polyols *via* the Diels–Alder reaction: regiochemical control *via* the phenylsulfonyl group

Patrick J. Crowley, John Fawcett, Gerry A. Griffith, Andrew C. Moralee, Jonathan M. Percy and Vittoria Salafia (DOI: 10.1039/b507131c)

Synthesis of (6*R*)- and (6*S*)-5,10-dideazatetrahydrofolate oligo- γ -glutamates: kinetics of multiple glutamate ligations catalyzed by folypoly- γ -glutamate synthetase

John W. Tomsho, John J. McGuire and James K. Coward (DOI: 10.1039/b505907k)

The unprecedented reaction of dimethylsulfonium methylide with Michael acceptors: synthesis of 1-substituted vinyl silanes and styrenes

Sonali M. Date, Rekha Singh and Sunil K. Ghosh (DOI: 10.1039/b509102k)

Non-metal catalysed intramolecular alkyne cyclotrimerization reactions promoted by focussed microwave heating in batch and flow modes

Steen Saaby, Ian R. Baxendale and Steven V. Ley (DOI: 10.1039/b509540a)

An *ortho*-palladated dimethylbenzylamine complex as a highly efficient turnover catalyst for the decomposition of P=S insecticides. Mechanistic studies of the methanolysis of some P=S containing phosphorothioate triesters

Zhong-Lin Lu, Alexei A. Neverov and R. Stan Brown (DOI: 10.1039/b508917d)

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