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An international journal of synthetic, physical and biomolecular organic chemistry

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Cover

See Lucio Pellacani *et al.*,
pp. 524–528.

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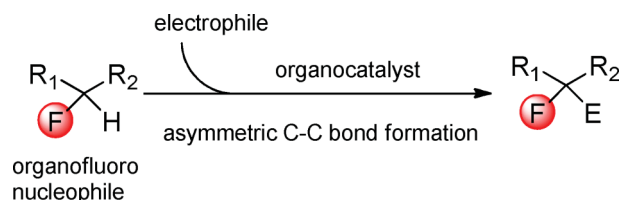
PERSPECTIVE

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Enantioselective organocatalytic fluorination using organofluoro nucleophiles

Yujun Zhao, Yuanhang Pan, Sui-Boon Derek Sim and Choon-Hong Tan*

While methods of electrophilic fluorination have been extensively developed to stereoselectively install fluorine atoms onto molecules, nucleophilic fluorination is a much less explored approach. In this review, recent advances in the application of organofluoro nucleophiles in organocatalysis are summarised.



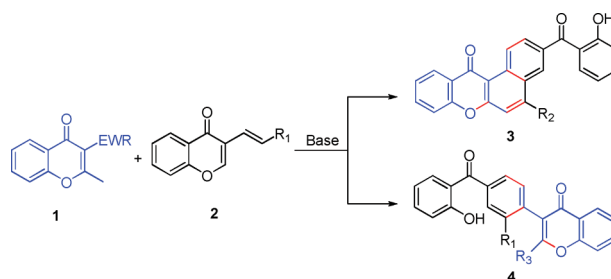
COMMUNICATIONS

486

Domino reactions of 2-methyl chromones containing an electron withdrawing group with chromone-fused dienes

Jian Gong, Fuchun Xie, Wenming Ren, Hong Chen and Youhong Hu*

These mild tandem reactions provide efficient access to functionalized benzo[*a*]xanthenes and novel chromone derivatives.



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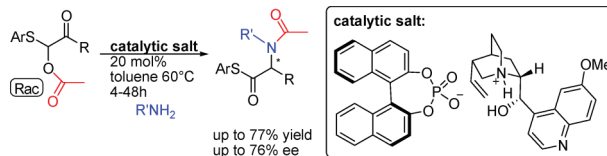
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Organocatalytic asymmetric tandem condensation–intramolecular rearrangement–protonation: an approach to optically active α -amino thioester derivatives

Francesca Capitta, Angelo Frongia,* Pier Paolo Piras, Patrizia Pitzanti and Francesco Secci

A conceptually novel chiral Brønsted base/Brønsted acid catalytic method for the enantioselective synthesis of α -amino thioesters through a tandem condensation–intramolecular rearrangement–protonation has been developed which provides a number of important synthetic building blocks in good yield and with moderate to good enantioselectivities.

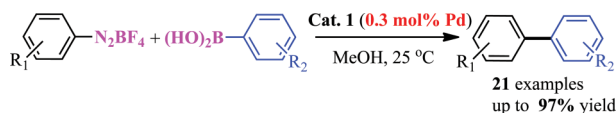


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Suzuki–Miyaura cross-couplings of arenediazonium tetrafluoroborate salts with arylboronic acids catalyzed by aluminium hydroxide-supported palladium nanoparticles

Xing Li,* Xu-Ying Yan, Hong-Hong Chang,* Li-Chao Wang, Yan Zhang, Wen-Wen Chen, Yan-Wei Li and Wen-Long Wei

Suzuki–Miyaura cross-couplings of arenediazonium salts with arylboronic acids catalyzed by highly active aluminium hydroxide-supported palladium nanoparticles catalyst have been investigated for the first time.

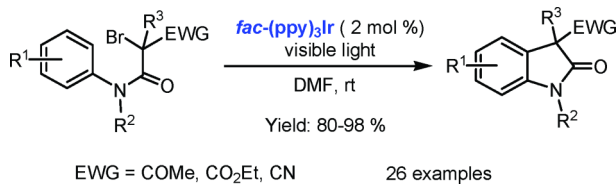


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Synthesis of oxindoles *via* visible light photoredox catalysis

Xuhui Ju, Yan Liang, Pingjing Jia, Weifei Li and Wei Yu*

fac-Ir(ppy)₃-catalyzed cyclisation of 2-EWG-substituted 2-bromoanilides under visible light irradiation constitutes an efficient synthesis of the 3,3-disubstituted oxindoles.

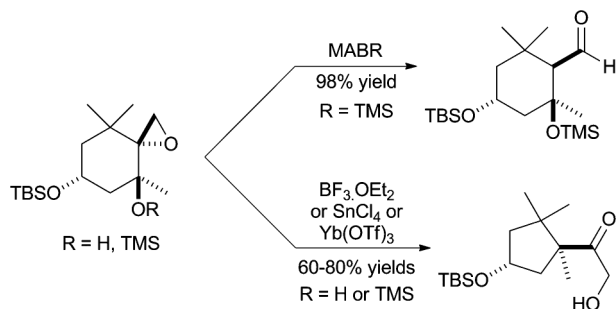


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Tandem Payne/Meinwald *versus* Meinwald rearrangements on the α -hydroxy- or α -silyloxy-spiro epoxide skeleton

Jane Totobenazara, Heloua Haroun, Julien Rémond, Karim Adil, Fabrice Dénès, Jacques Lebreton, Catherine Gaulon-Nourry* and Pascal Gosselin*

Original new α -silyloxy-spiro epoxides rearrange according to either a Payne/Meinwald (*e.g.*, with SnCl₄) or a Meinwald (with MABR) rearrangement.

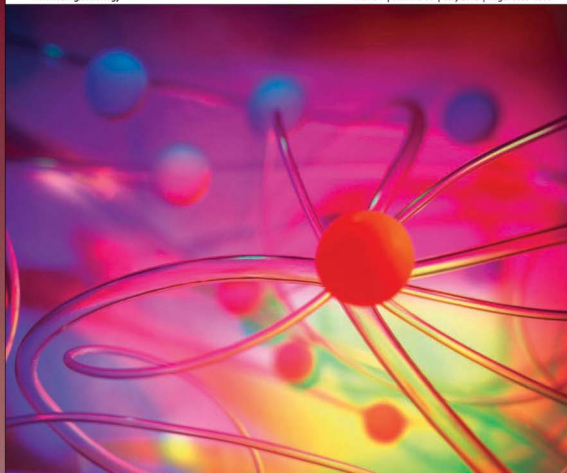


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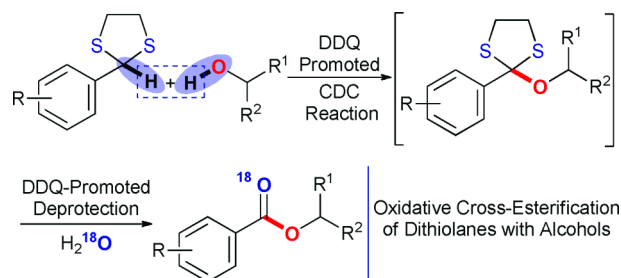
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Oxidative cross-esterification of dithiolanes with alcohols through a cross-dehydrogenative coupling (CDC)/deprotection sequence

Liang Fu, Chang-Jiang Yao, Ning-Jie Chang, Jia-Rong Chen, Liang-Qiu Lu* and Wen-Jing Xiao*

An unprecedented oxidative cross-esterification in an equimolar mixture of dithiolanes, alcohols and water through a CDC/deprotection sequence has been developed. The reaction itself features simple experimental procedures under mild conditions and offers a new strategic protocol for the efficient synthesis of structurally diverse esters.

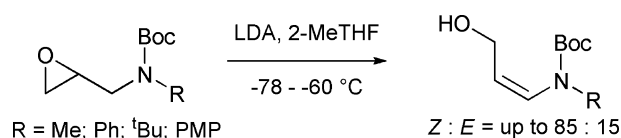


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E- and *Z*-Stereoselectivity in the preparation of enamides from glycidyl sulfonamides and carbamates

Jack A. Brown, Vijay Chudasama, Melvyn E. Giles, Duncan M. Gill,* Philip S. Keegan, William J. Kerr, Rachel H. Munday, Karen Griffin and Andrew Watts

Treatment of glycidyl sulfonamides with LDA delivers the anticipated enesulfonamide with good *E*-isomer selectivity, whereas the corresponding carbamates exhibit selectivity for the *Z*-enecarbamate. An E1cB elimination mechanism *via* substrate–base chelate complex is advanced as rationalisation of the *Z*-selective outcomes.

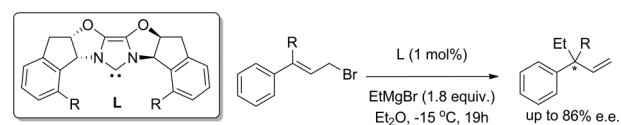


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The design and synthesis of novel IBiox N-heterocyclic carbene ligands derived from substituted amino-indanols

Jean-Noël Levy, Christopher M. Latham, Loïc Roisin, Nadine Kandziora, Paolo Di Fruscia, Andrew J. P. White, Simon Woodward and Matthew J. Fuchter*

A synthetic route towards novel IBiox N-heterocyclic carbene (NHC) ligands has been developed. The ligands have restricted flexibility and high steric demand, and preliminary studies show they give high levels of asymmetric induction in the copper-free allylic alkylation of cinnamyl bromide.

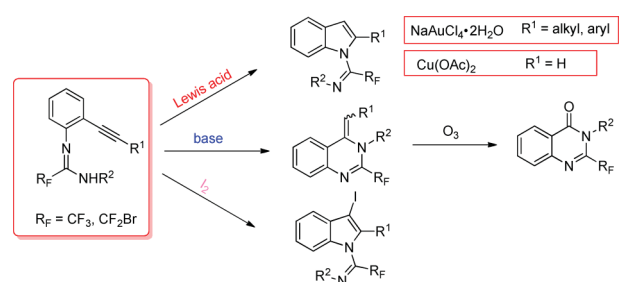


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A detailed study of the intramolecular hydroamination of *N*-(*ortho*-alkynyl)aryl-*N'*-substituted trifluoroacetamidines and bromodifluoroacetamidines

Jiangtao Zhu, Haibo Xie, Zixian Chen, Shan Li and Yongming Wu*

The intramolecular hydroamination of fluorinated (*ortho*-alkynylaryl)amidines under Lewis acid, base and iodine occurred in different ways, constructing different fluorinated azaheterocycles.



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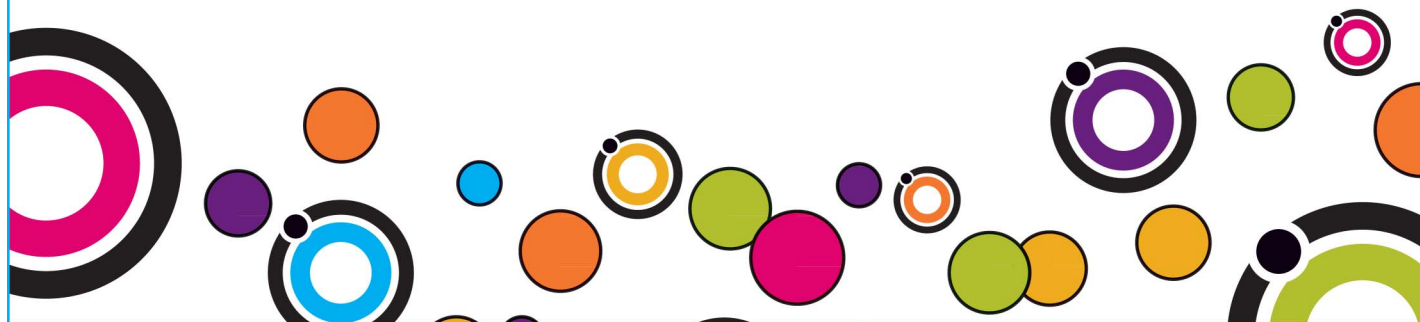


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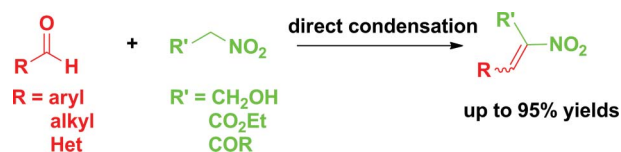


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Domino reactions for the synthesis of various α -substituted nitro alkenes

Stefania Fioravanti,* Lucio Pellacani* and Maria Cecilia Vergari

Conjugated nitro alkenes were synthesised from nitro derivatives and aldehydes, the *E/Z* ratio depending on groups present in both reagents.

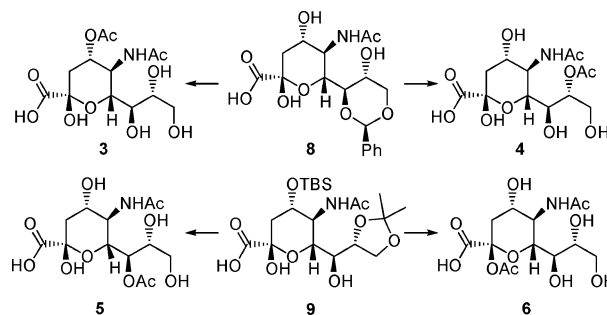


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Synthesis of the complete series of mono acetates of *N*-acetyl-D-neuraminic acid

Paul A. Clarke,* Nimesh Mistry and Gavin H. Thomas

The short syntheses of each of the mono-acetates of *N*-acetyl-D-neuraminic acid are reported. Neu4,5Ac₂ and Neu5,8Ac₂ were synthesised from a common precursor in 2 and 4 steps respectively, while Neu2,4Ac₂ and Neu5,7Ac₂ were synthesised in 3 and 4 steps respectively from another common precursor. Both precursors could be easily prepared from Neu5Ac. No scrambling of the anomeric stereochemistry was detected throughout the course of these syntheses.

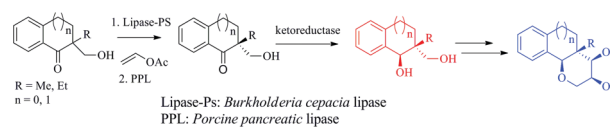


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Enantiomeric scaffolding of α -tetralone and related scaffolds by EKR (Enzymatic Kinetic Resolution) and stereoselective ketoreduction with ketoreductases

Rajib Bhuniya and Samik Nanda*

Stereochemically pure novel tricyclic compounds have been synthesized by two consecutive biocatalytic processes.

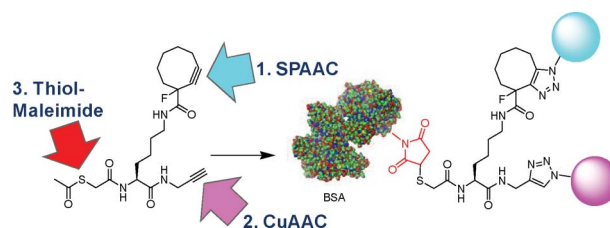


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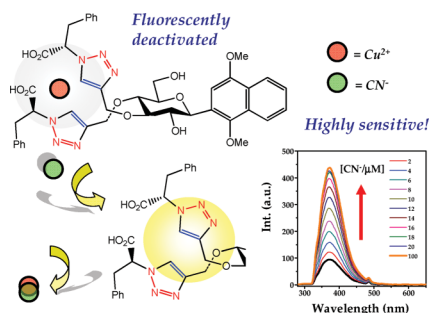
Click-enabled heterotrifunctional template for sequential bioconjugations

David M. Beal,* Victoria E. Albrow, George Burslem, Louisa Hitchen, Carla Fernandes, Cris Laphorn, Lee R. Roberts, Matthew D. Selby and Lyn H. Jones

A heterotrifunctional template was developed that utilizes thiol-maleimide and click chemistries (both copper-free and copper-mediated) to effect sequential biomolecule conjugations in a one-pot process.



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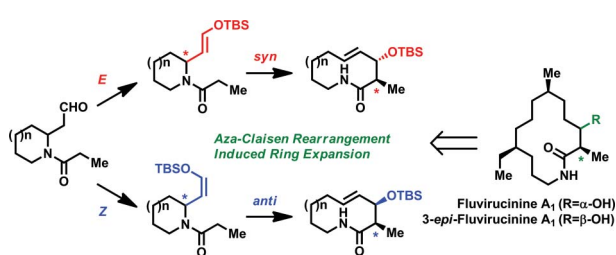


Discovery of a sensitive Cu(II)-cyanide “off–on” sensor based on new C-glycosyl triazolyl bis-amino acid scaffold

Yan-Hui Tang, Yi Qu, Zhuo Song, Xiao-Peng He,*
Juan Xie, Jianli Hua* and Guo-Rong Chen*

A unique triazolyl peptidomimetic–Cu(II) complex is developed as a satisfactorily sensitive “off–on” fluorescent chemosensor for cyanide.

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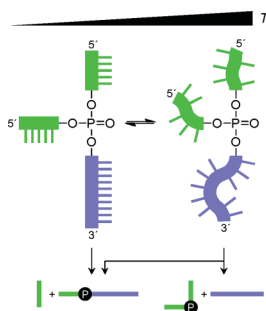


A stereo-controlled access to functionalized macrolactams via an aza-Claisen rearrangement

Young-Ger Suh,* Yong-Sil Lee, Seok-Ho Kim,
Jae-Kyung Jung, Hwayoung Yun, Jaebong Jang,
Nam-Jung Kim and Jong-Wha Jung*

A novel and stereo-controlled method that offers an attractive alternative to the intramolecular amide–aldol reaction for the elaboration of β-alkoxy-α-substituted motifs has been developed.

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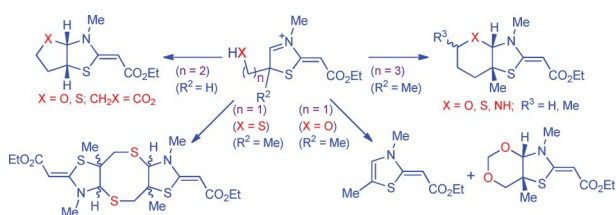


Impact of steric constraints on the product distribution of phosphate-branched oligonucleotide models of the large ribozymes

Tuomas Lönnberg* and Kirsi-Maria Kero

Product distribution of the hydrolysis of phosphate-branched oligonucleotides is temperature-dependent, suggesting a major role for steric constraints in catalysis by the large ribozymes.

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Synthesis of thiazolidine-fused heterocycles via exo-mode cyclizations of vinylogous N-acyliminium ions

Milovan Stojanović, Rade Marković, Erich Kleinpeter and
Marija Baranac-Stojanović*

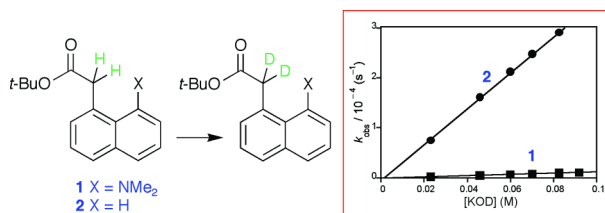
Syntheses of thiazolidine-fused heterocycles via exo-mode cyclizations of vinylogous N-acyliminium ions incorporating heteroatom-based nucleophiles have been examined and discussed. The reaction outcome and stereochemistry are rationalized using quantum chemical calculations.

590

peri-Dimethylamino substituent effects on proton transfer at carbon in α -naphthylacetate esters: a model for mandelate racemase

Richard J. Delley, Subhajit Bandyopadhyay, Mark A. Fox, Constanze Schliehe, David R. W. Hodgson, Florian Hollfelder,* Anthony J. Kirby* and AnnMarie C. O'Donoghue*

A 29-fold lower second order rate constant for DO⁻-catalyzed H/D-exchange was observed for ester **1** versus **2**, and intramolecular catalysis was not detected within **2**.

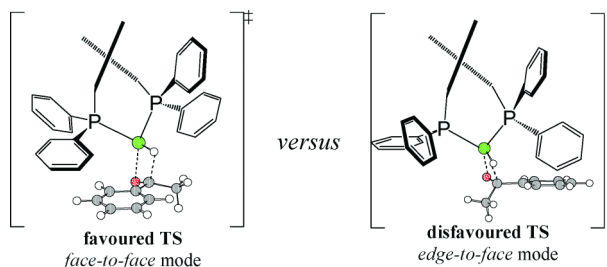


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Origins of enantioselectivity in the chiral diphosphine-ligated CuH-catalyzed asymmetric hydrosilylation of ketones

Wei Zhang, Weiyi Li and Song Qin*

TSs in the face-to-face mode, suffering less steric hindrance, are more stable than those in the edge-to-face mode.

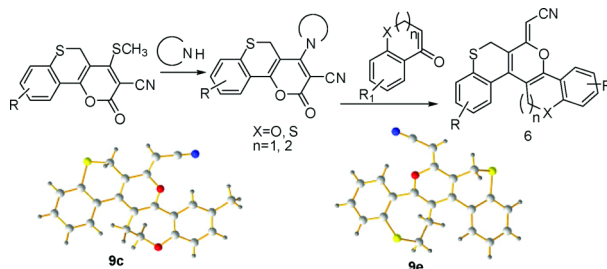


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Non-catalytic approach to the synthesis of partially reduced 'S' shaped dioxathia- and oxadithiahelicenes through base induced inter- and intramolecular C–C bond formation

Hardesh K. Maurya, Vishnu K. Tandon,* Brijesh Kumar, Abhinav Kumar, Volker Huch and Vishnu Ji Ram*

An efficient route for the construction of helical S shaped dioxathia- and oxadithiahelicenes with oxygen and sulfur atoms located in the middle of the outer helix is developed.

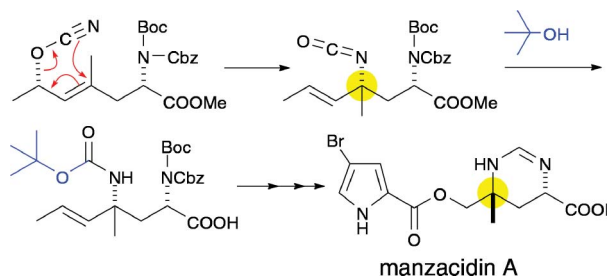


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Synthesis of manzacidin A and C: efficient construction of quaternary carbon stereocenters bearing nitrogen substituents

Yoshiyasu Ichikawa,* Ken Okumura, Yasunori Matsuda, Tomoyuki Hasegawa, Mitsuhiro Nakamura, Aya Fujimoto, Toshiya Masuda, Keiji Nakano and Hiyoshizo Kotsuki

An efficient method for stereoselective construction of asymmetric quaternary carbon stereocenters, bearing nitrogen in the form of Boc-protected allyl amines, has been developed and used in the synthesis of manzacidin A and C.



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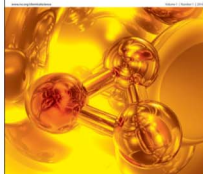
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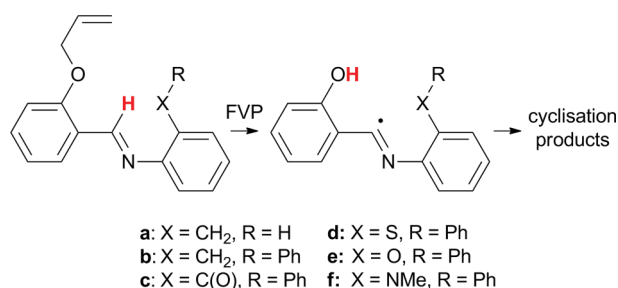
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Gas-phase generation and cyclisation reactions of imidoyl radicals

Rino Leardini, Hamish McNab, Daniele Nanni,*
Anton G. Tenan and Andrew Thomson

Some 1,2-diaryl-imidoyl radicals, generated in the gas-phase by H-transfer to phenoxyls, reacted by intramolecular translocation/cyclisation sequences to give a variety of heterocyclic products.

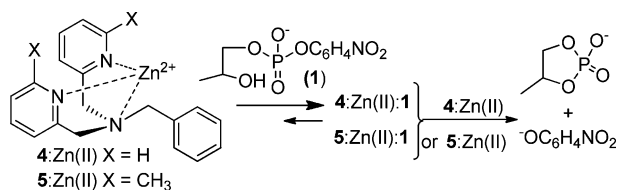


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Solvent induced cooperativity of Zn(II) complexes cleaving a phosphate diester RNA analog in methanol

Mark F. Mohamed, Irma Sánchez-Lombardo,
Alexei A. Neverov and R. Stan Brown*

Mononuclear 4:Zn(II) and 5:Zn(II) promote transesterification of HPNPP in methanol forming L:Zn(II):1, followed by cooperative interaction with a second L:Zn(II).

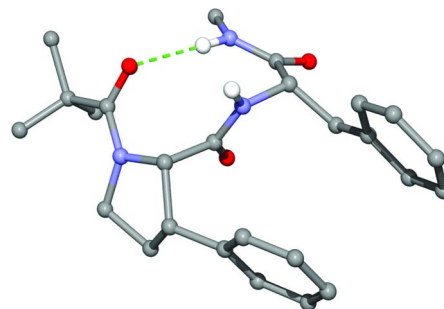


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β-Phenylproline: the high β-turn forming propensity of proline combined with an aromatic side chain

Paola Fatás, Ana I. Jiménez,* M. Isabel Calaza and
Carlos Cativiela*

The β-phenyl group attached to proline does not disrupt the β-turn propensity of the natural amino acid.

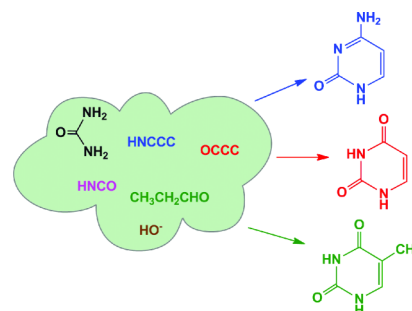


652

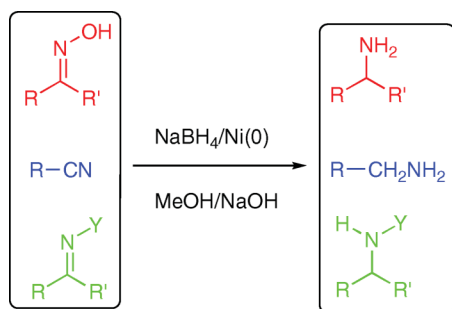
Can cytosine, thymine and uracil be formed in interstellar regions? A theoretical study

Tianfang Wang and John H. Bowie*

Theoretical calculations indicate that cytosine, uracil and thymine can be synthesised from specific interstellar molecules.



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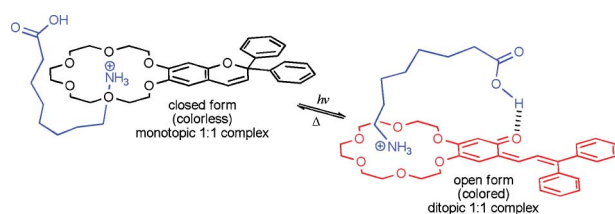


Enhanced reduction of C–N multiple bonds using sodium borohydride and an amorphous nickel catalyst

Shouxin Liu,* Yihua Yang, Xiaoli Zhen, Junzhang Li, Huimin He, Juan Feng and Andrew Whiting*

An amorphous nickel powder (Ni^0) catalyst enhances NaBH_4 reduction C–N multiple bonds, including oximes, imines, hydrazones and nitriles to produce the amines in good to excellent yields.

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Mono- and ditopic models of binding of a photochromic chromene annelated with an 18-crown-6 ether with protonated amino acids

Sergey Paramonov,* Yury Fedorov, Vladimir Lokshin, Elena Tulyakova, Gaston Vermeersch, Stéphanie Delbaere and Olga Fedorova

The initial and photoinduced forms of a chromene annelated with an 18-crown-6 ether form different complexes with protonated amino acids.