

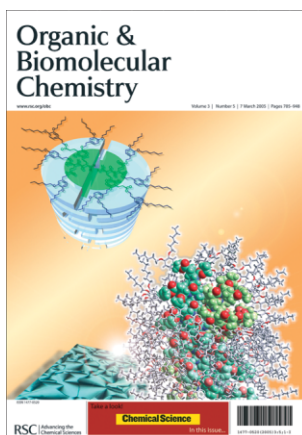
In this issue...

Asymmetric organocatalysis

An Emerging area presenting a brief overview of this rapidly developing field. See List and Seayad page 719.



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



Cover

See Masayuki Nishii, Toru Matsuoka, Yuko Kamikawa and Takashi Kato, pp. 875–880
Columnar association of peptide derivatives consisting of an oligo(glutamic acid) with lipophilic chains on the polarizing optical photomicrograph of the columnar liquid-crystalline material.

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CHEMICAL SCIENCE

C17

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Chemical Science

March 2005/Volume 2/Issue 3

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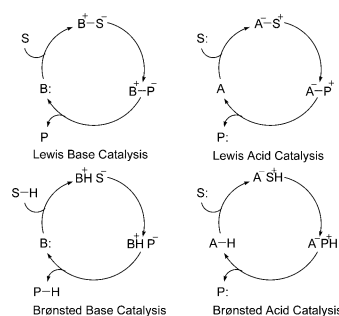
EMERGING AREA

719

Asymmetric organocatalysis

Jayasree Seayad and Benjamin List*

The rapidly developing area of organocatalysis is briefly reviewed on the basis of a mechanistic classification in which organocatalysts are categorized as Lewis base, Lewis acid, Brønsted base, or Brønsted acid.



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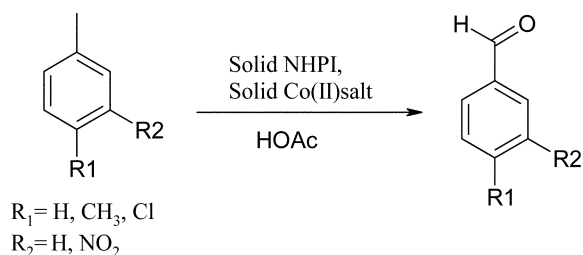
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725

The selective aerobic oxidation of methylaromatics to benzaldehydes using a unique combination of two heterogeneous catalysts

Fatemeh Rajabi, James H Clark,* Babak Karimi* and Duncan J Macquarrie*

The use of a novel supported NHPI promoter in combination with a known supported Co(II) catalyst enables higher reactivity and unusual selectivity, through the surprising use of acetic acid as the reaction medium.

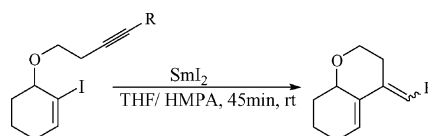


727

Cyclization of samarium diiodide-generated vinyl radicals in 6-(π -*exo*)-*exo*-dig mode

Zhuang-Ping Zhan* and Kai Lang

Radical cyclization of vinyl iodides in 6-(π -*exo*)-*exo*-dig mode were effected by SmI_2 to give *exo*-cyclic dienes fused to six-membered rings.

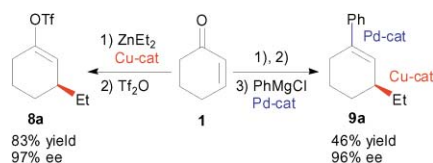


729

Tandem one pot asymmetric conjugate addition–vinyl triflate formation–cross coupling methodology

Rosa M. Suárez, Diego Peña,* Adriaan J. Minnaard and Ben L. Feringa*

Optically active vinyl triflates are obtained and employed in a series of one pot metal-catalyzed tandem asymmetric transformations.

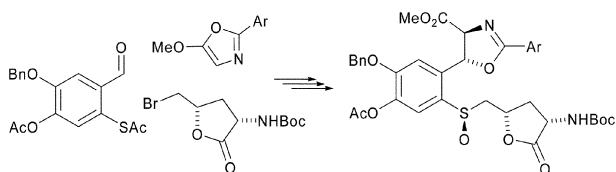


732

Synthesis of the β -hydroxydopa– γ -hydroxy– δ -sulfinylnorvaline component of ustiloxins A and B

Luke Hunter, Malcolm D. McLeod and Craig A. Hutton*

The dopa–sulfinylnorvaline component of ustiloxins A and B has been prepared using a salen–Al-catalysed aldol reaction to prepare the functionalised dopa residue, followed by incorporation of the norvaline group and asymmetric oxidation at sulfur.



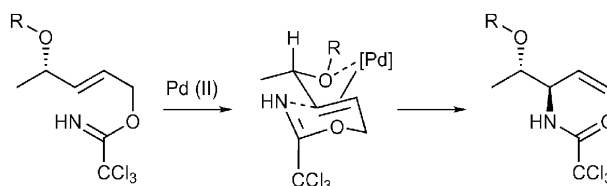
735



A highly stereoselective ether directed palladium catalysed aza-Claisen rearrangement

Andrew G. Jamieson and Andrew Sutherland*

A highly stereoselective rearrangement of allylic trichloroacetimidates to allylic trichloroamides has been achieved using adjacent ether groups to direct facial coordination of the palladium(II) catalyst.



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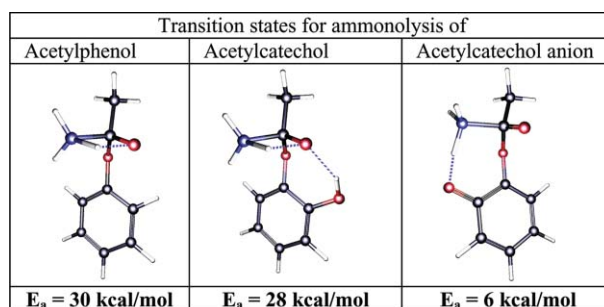
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737

Theoretical study of the *o*-OH participation in catechol ester ammonolysis

Miroslav A. Rangelov, Georgi N. Vayssilov, Vihra M. Yomtova and Dimitar D. Petkov*

The ammonolysis of ionised acetylcatechol was found to proceed orders of magnitude faster than that of acetylphenol or non-ionised acetylcatechol due to intramolecular catalysis by *o*-oxyanion.

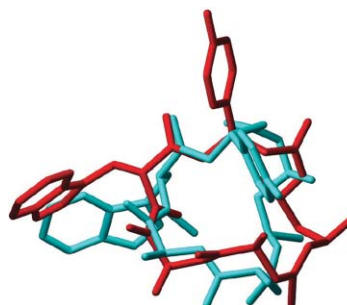


745

Conformational studies of free and Li^+ complexed jaspalinolide, a cyclic depsipeptide from the Fijian marine sponge *Jaspis splendens*

Jioji N. Tabudravu, Linda A. Morris, Bruce F. Milne and Marcel Jaspars*

Conformations of the cyclic depsipeptide jaspalinolide were determined in the presence and absence of lithium by NOE restrained MD calculations.

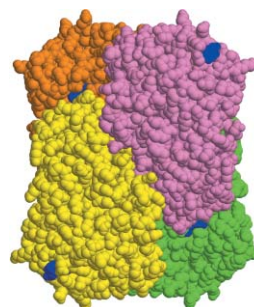


750

TBADH activity in water-miscible organic solvents: correlations between enzyme performance, enantioselectivity and protein structure through spectroscopic studies

Linus Olofsson,* Ian A. Nicholls and Susanne Wikman*

The activity and structure of TBADH in water-miscible organic solvents was investigated. The tetrameric form is not critical for catalysis.

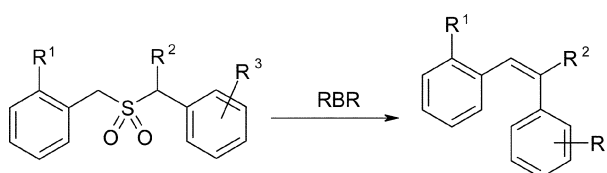


756

Unexpected *Z*-stereoselectivity in the Ramberg–Bäcklund reaction of diarylsulfones leading to *cis*-stilbenes: the effect of aryl substituents and application in the synthesis of the integrastatin nucleus

Jonathan S. Foot, Gerard M. P. Giblin, A. C. Whitwood and R. J. K. Taylor*

Unprecedented amounts of the *cis*-isomers of stilbene systems are formed *via* the Meyers variant of the Ramberg–Bäcklund reaction.



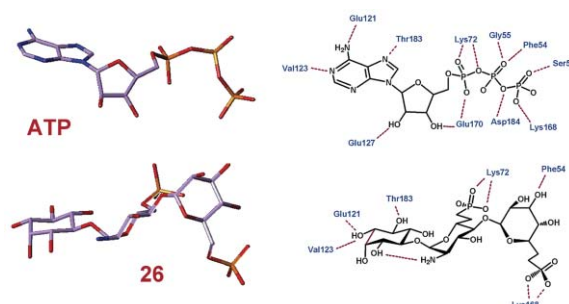
11 examples, up to 95% *cis*-stereoselectivity

764

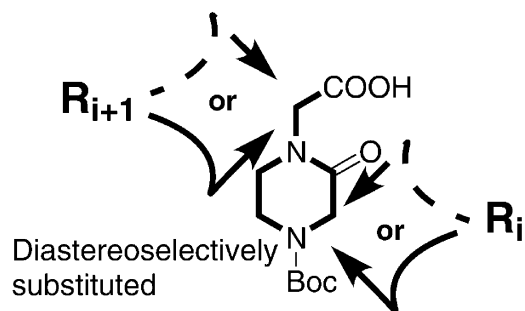
Design and synthesis of inositolphosphoglycan putative insulin mediators

Javier López-Prados, Félix Cuevas, Niels-Christian Reichardt, José-Luis de Paz, Ezequiel Q. Morales and Manuel Martín-Lomas*

Inositolphosphoglycans fitting into the ATP binding site of PKA have been designed and effectively synthesised as putative insulin mediators.



787

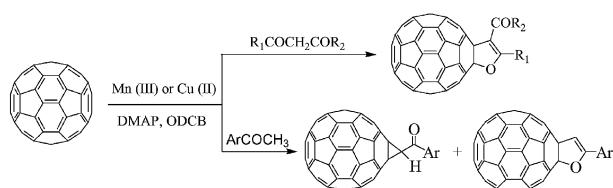


Simple, versatile and highly diastereoselective synthesis of 1,3,4-trisubstituted-2-oxopiperazine-containing peptidomimetic precursors

Nicolas Franceschini, Pascal Sonnet and Dominique Guillaume*

The diastereoselective synthesis of each 1,3,4-trisubstituted-2-oxopiperazine isomer is reported.

794

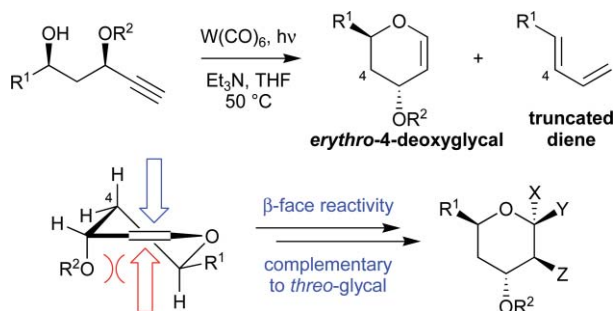


Cu(II) acetate- and Mn(III) acetate-mediated radical reactions of [60]fullerene with ketonic compounds

Guan-Wu Wang* and Fa-Bao Li

The reaction of [60]fullerene with β -keto esters or 1,3-diketones in the presence of Cu(II) acetate or Mn(III) acetate afforded only dihydrofuran-fused C_{60} derivatives. However, aromatic methyl ketones gave both methanofullerenes and dihydrofuran-fused C_{60} derivatives.

798

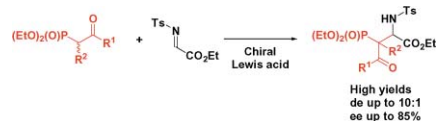


Enantioselective synthesis of *erythro*-4-deoxyglycals as scaffolds for target- and diversity-oriented synthesis: new insights into glycal reactivity

Sirkka B. Moilanen and Derek S. Tan*

An enantioselective synthesis and stereoselective transformations of *erythro*-4-deoxyglycals have been developed, highlighting the striking reactivity differences that can arise from seemingly subtle structural variations.

804

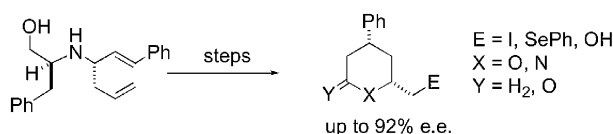


Catalytic asymmetric addition of β -keto phosphonates to an activated imine—formation of optically active functionalized phosphonate α -amino acid derivatives

Anne Kjærsgaard and Karl Anker Jørgensen*

A detailed study of the addition of an activated imine to β -keto phosphonates in the presence of Lewis acid complexes has been performed. High yields, moderate diastereoselectivity and good enantioselectivity are obtained.

809



Applications of the amino-Cope rearrangement: synthesis of tetrahydropyran, δ -lactone and piperidine targets

Steven M. Allin,* Munira Essat, Catarina Horro Pita, Robert D. Baird, Vickie McKee, Mark Elsegood, Mark Edgar, David M. Andrews, Pritom Shah and Ian Aspinall

The asymmetric amino-Cope rearrangement has been applied as a key synthetic step to access enantiomerically enriched heterocycles.

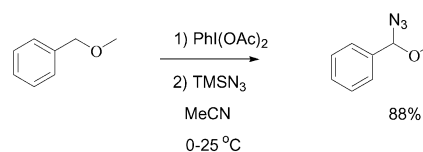
816



Radical substitution with azide: $\text{TMSN}_3\text{-PhI(OAc)}_2$ as a substitute of IN_3

Christian Marcus Pedersen, Lavinia Georgeta Marinescu and Mikael Bols*

TMSN_3 and PhI(OAc)_2 were found to promote fast, high yield azide substitutions of ethers, aldehydes and benzal acetals.

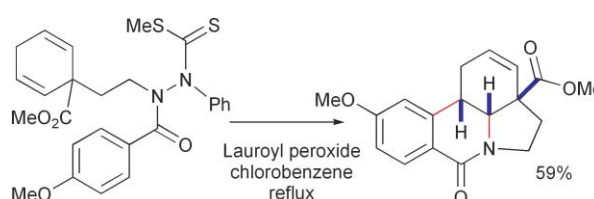


823

Model studies toward the synthesis of kirkin

Gillian L. Barclay, Béatrice Quiclet-Sire, Graciela Sanchez-Jimenez and Samir Z. Zard*

In model studies towards the synthesis of kirkin, the carbon skeleton was constructed using a radical cascade reaction. Two different approaches towards the synthesis have been examined as well as the regioselectivity of the radical cyclisation.

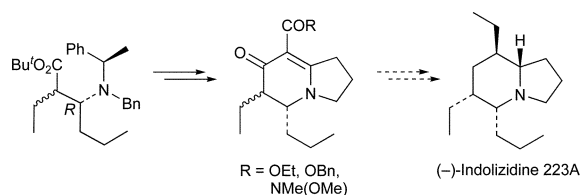


836

Studies towards the enantioselective synthesis of 5,6,8-trisubstituted amphibian indolizidine alkaloids via enamionone intermediates

Joseph P. Michael,* Charles B. de Koning and Christiaan W. van der Westhuyzen

Approaches to the synthesis of indolizidine 223A and related alkaloids via chiral 5,6,8-trisubstituted 2,3,5,6-tetrahydroindolizin-7(1H)-ones are described.

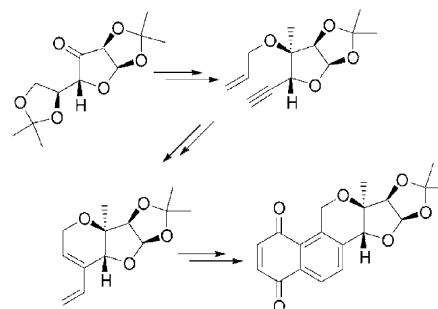


848

Design and synthesis of novel sugar-oxasteroid-quinone hybrids

Krishna P. Kaliappan* and Velayutham Ravikumar

A new class of sugar-oxasteroid-quinone hybrid molecules has been designed and synthesized involving an efficient enyne metathesis/Diels-Alder reaction strategy.

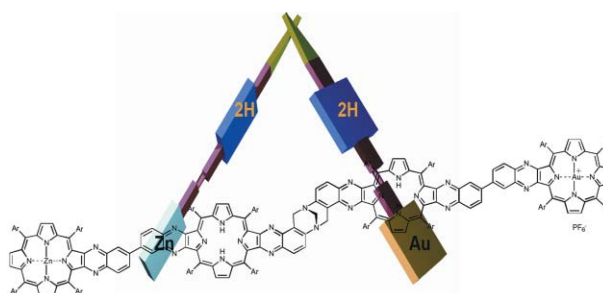


852

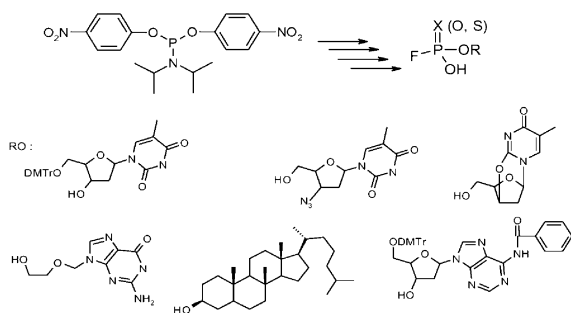
Chemical models for aspects of the photosynthetic reaction centre: synthesis and photophysical properties of tris- and tetrakis-porphyrins that resemble the arrangement of chromophores in the natural system

Maxwell J. Crossley,* Paul J. Santic, James A. Hutchison and Kenneth P. Ghiggino*

A tris-porphyrin and a tetrakis-porphyrin, designed to resemble aspects of natural photosynthetic reaction centres, have been synthesised and have long-lived photo-induced charge shift states.



866

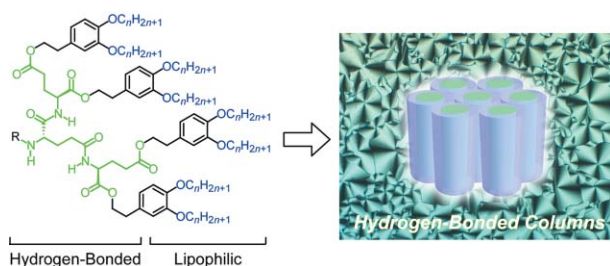


Synthesis of phosphorofluoridates and phosphorofluoridothioates *via* the phosphoramidite approach

Wojciech Dabkowski* and Izabela Tworowska

We present a very efficient synthetic procedure leading to the phosphorofluoridates RO-P(O)(OH)F or phosphorofluoridothioates RO-P(S)(OH)F, which is based on the intermediary of fluorophosphoramidites.

875



Thermotropic liquid-crystalline peptide derivatives: oligo(glutamic acid)s forming hydrogen-bonded columns

Masayuki Nishii, Toru Matsuoka, Yuko Kamikawa and Takashi Kato*

Amino acid derivatives consisting of hydrogen-bonded oligo(glutamic acid) moieties and lipophilic alkyl chains show enantiotropic thermotropic columnar phases.

881

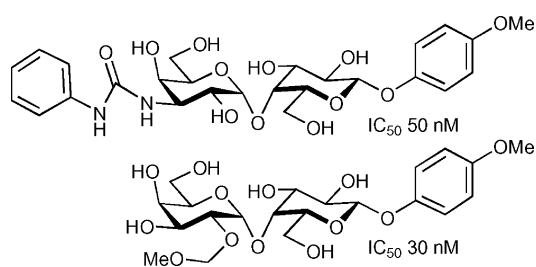


Mechanisms of photoinduced electron transfer reactions of lappaconitine with aromatic amino acids. Time-resolved CIDNP study

Nikolai E. Polyakov,* Vladimir K. Khan, Marc B. Taraban, Tatyana V. Leshina, Olga A. Luzina, Nariman F. Salakhutdinov and Genrikh A. Tolstikov

The photoinitiated single electron transfer step between lappaconitine and an amino acid might also serve as a model of drug-receptor interactions.

886



Structure-activity relationships of galabioside derivatives as inhibitors of *E. coli* and *S. suis* adhesins: nanomolar inhibitors of *S. suis* adhesins

Jörgen Ohlsson, Andreas Larsson, Sauli Haataja, Jenny Alajääski, Peter Stenlund, Jerome S. Pinkner, Scott J. Hultgren, Jukka Finne,* Jan Kihlberg* and Ulf J. Nilsson*

Aromatic galabiosides modified with urea groups at C3' or acetals at O2' are high-affinity adhesion inhibitors of the respiratory pathogen *Streptococcus suis* type P_N.

901



Neutral cumulene oxide CCCCCO is accessible by one-electron oxidation of $[\text{CCCCO}]^{\bullet-}$ in the gas phase

Mark Fitzgerald, Andrew M. McAnoy, John H. Bowie,* Detlef Schröder and Helmut Schwarz

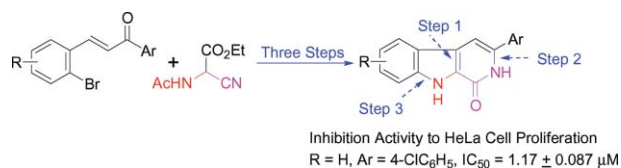
Neutral CCCCCO is accessible by one-electron oxidation of $[\text{CCCCO}]^{\bullet-}$. Some CCCCCO neutrals are stable for the microsecond-duration NR experiment, others are energised, decomposing to CCC and CO.

911

3-Aryl β -carbolin-1-ones as a new class of potent inhibitors of tumor cell proliferation: synthesis and biological evaluation

Shaoyong Wang, Yanmei Dong, Xinyan Wang, Xiaoyi Hu, Jun O Liu and Yuefei Hu*

Novel synthesis of 3-aryl β -carbolin-1-ones from non-indole starting materials has been developed. The target compounds were found to possess significant activity against tumor cell proliferation.

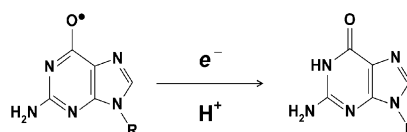


917

Involvement of proton transfer in the reductive repair of DNA guanyl radicals by aniline derivatives

Anne Ly, Nancy Q. Tran, Kathrina Sullivan, Simona L. Bandong and Jamie R. Milligan*

Anilines are able to repair oxidative DNA damage by returning the missing electron.

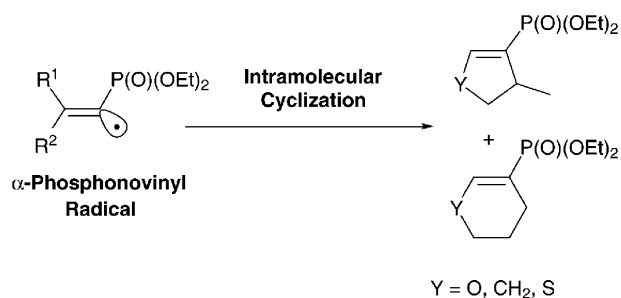


924

Generation of α -phosphonovinyl radicals and development of a new route to highly functionalized vinylphosphonates and vinylphosphonate-incorporated carbocyclic or heterocyclic compounds *via* a radical trapping sequence

Takafumi Ageno, Tatsuo Okauchi, Toru Minami* and Masaru Ishida*

The first direct generation of synthetically useful α -phosphonovinyl radicals was achieved by treatment of α -phosphonovinyl halides with a tributyltin radical.

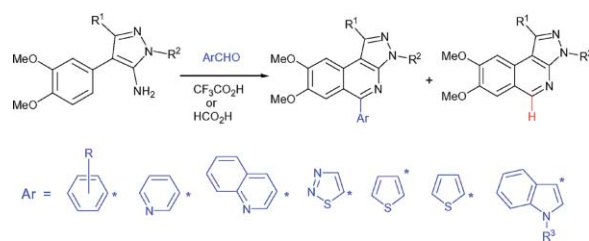


932

A versatile synthesis of pyrazolo[3,4-*c*]isoquinoline derivatives by reaction of 4-aryl-5-aminopyrazoles with aryl/heteroaryl aldehydes: the effect of the heterocycle on the reaction pathways

S. L. Bogza,* K. I. Kobrakov, A. A. Malienko, I. F. Perepichka,* S. Yu. Sujkov, M. R. Bryce,* S. B. Lyubchik, A. S. Batsanov and N. M. Bogdan

In the cyclization of 4-(3,4-dimethoxyphenyl)-5-aminopyrazoles into 5-heteroarylpyrazolo[3,4-*c*]isoquinolines loss of the heterocyclic fragment is observed for some 5-membered heterocyclic aldehydes.

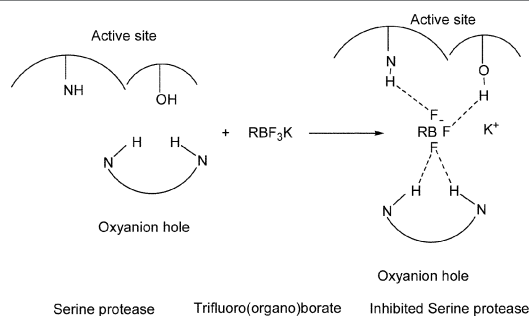


941

Noncovalent inhibition of the serine proteases, α -chymotrypsin and trypsin by trifluoro(organo)borates

Reem Smoum, Abraham Rubinstein* and Morris Srebnik*

Trifluoro(organo)borates inhibit serine proteases reversibly and competitively through the formation of noncovalent interactions with these enzymes.



- Ageno, Takafumi, 924
 Alajääski, Jenny, 886
 Allin, Steven M., 809
 Andrews, David M., 809
 Aspinall, Ian, 809
 Baird, Robert D., 809
 Bandong, Simona L., 917
 Barclay, Gillian L., 823
 Batsanov, Andrei S., 932
 Bogdan, Natalya M., 932
 Bogza, Sergei L., 932
 Bols, Mikael, 816
 Bowie, John H., 901
 Bryce, Martin R., 932
 Clark, James H., 725
 Crossley, Maxwell J., 852
 Cuevas, Félix, 764
 Dabkowski, Wojciech, 866
 de Koning, Charles B., 836
 de Paz, José-Luis, 764
 Dong, Yanmei, 911
 Edgar, Mark, 809
 Elsegood, Mark, 809
 Essat, Munira, 809
 Feringa, Ben L., 729
 Finne, Jukka, 886
 Fitzgerald, Mark, 901
 Foot, Jonathan S., 756
 Franceschini, Nicolas, 787
 Ghiggino, Kenneth P., 852
 Giblin, Gerard M. P., 756
 Guillaume, Dominique, 787
 Haataja, Sauli, 886
 Hu, Xiaoyi, 911
 Hu, Yuefei, 911
 Hultgren, Scott J., 886
 Hunter, Luke, 732
 Hutchison, James A., 852
 Hutton, Craig A., 732
 Ishida, Masaru, 924
 Jamieson, Andrew G., 735
 Jaspars, Marcel, 745
 Jørgensen, Karl Anker, 804
 Kaliappan, Krishna P., 848
 Kamikawa, Yuko, 875
 Karimi, Babak, 725
 Kato, Takashi, 875
 Khan, Vladimir K., 881
 Kihlberg, Jan, 886
 Kjærsgaard, Anne, 804
 Kobrakov, Konstantin I., 932
 Lang, Kai, 727
 Larsson, Andreas, 886
 Leshina, Tatyana V., 881
 Li, Fa-Bao, 794
 List, Benjamin, 719
 Liu, Jun O, 911
 López-Prados, Javier, 764
 Luzina, Olga A., 881
 Ly, Anne, 917
 Lyubchik, Svetlana B., 932
 Macquarrie, Duncan J, 725
 Malienko, Anna A., 932
 Marinescu, Lavinia Georgeta, 816
 Martín-Lomas, Manuel, 764
 Matsuoka, Toru, 875
 McAnoy, Andrew M., 901
 McKee, Vickie, 809
 McLeod, Malcolm D., 732
 Michael, Joseph P., 836
 Milligan, Jamie R., 917
 Milne, Bruce F., 745
 Minami, Toru, 924
 Minnaard, Adriaan J., 729
 Moilanen, Sirkka B., 798
 Morales, Ezequiel Q., 764
 Morris, Linda A., 745
 Nicholls, Ian A., 750
 Nilsson, Ulf J., 886
 Nishii, Masayuki, 875
 Ohlsson, Jörgen, 886
 Okauchi, Tatsuo, 924
 Olofsson, Linus, 750
 Pedersen, Christian Marcus, 816
 Peña, Diego, 729
 Perepichka, Igor F., 932
 Petkov, Dimiter D., 737
 Pinkner, Jerome S., 886
 Pita, Catarina Horro, 809
 Polyakov, Nikolai E., 881
 Quiclet-Sire, Béatrice, 823
 Rajabi, Fatemeh, 725
 Rangelov, Miroslav A., 737
 Ravikumar, Velayutham, 848
 Reichardt, Niels-Christian, 764
 Rubinstein, Abraham, 941
 Salakhutdinov, Nariman F., 881
 Sanchez-Jimenez, Graciela, 823
 Schröder, Detlef, 901
 Schwarz, Helmut, 901
 Seayad, Jayasree, 719
 Shah, Pritom, 809
 Sentic, Paul J., 852
 Smoum, Reem, 941
 Sonnet, Pascal, 787
 Srebnik, Morris, 941
 Stenlund, Peter, 886
 Suárez, Rosa M., 729
 Sujkov, Sergei Yu., 932
 Sullivan, Kathrina, 917
 Sutherland, Andrew, 735
 Tabudravu, Jioji N., 745
 Tan, Derek S., 798
 Taraban, Marc B., 881
 Taylor, R. J. K., 756
 Tolstikov, Genrikh A., 881
 Tran, Nancy Q., 917
 Tworowska, Izabela, 866
 van der Westhuyzen, Christiaan W., 836
 Vayssilov, Georgi N., 737
 Wang, Guan-Wu, 794
 Wang, Shaozhong, 911
 Wang, Xinyan, 911
 Whitwood, A. C., 756
 Wikman, Susanne, 750
 Yomtova, Vihra M., 737
 Zard, Samir Z., 823
 Zhan, Zhuang-Ping, 727

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