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IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (13) 1341–1456 (2006)



Cover

See Ingrid Castro-Rodríguez and Karsten Meyer, page 1353 Alkane coordination, CO/CO₂ activation, and nitrogen-atom transfer using uranium complexes. Cover artwork by Ryan Holland. Background photo released by USGS from the Galileo Orbiter. Image reproduced by permission of Ingrid Castro-Rodríguez and Karsten Meyer from *Chem. Commun.*, 2006, 1353.



Inside cover

See Ashwini Nangia *et al.*, page 1369 Isonicotinamide *N*-oxide helical architecture and a barbiturate pyridine *N*-oxide cocrystal bridge crystal engineering principles to pharmaceutical development in heterosynthon chemistry. Image reproduced by permission of L. Sreenivas Reddy, N. Jagadeesh Babu and Ashwini Nangia from *Chem. Commun.*, 2006, 1369.

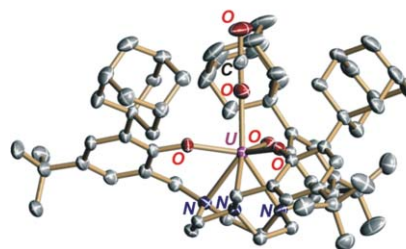
FEATURE ARTICLE

1353

Small molecule activation at uranium coordination complexes: control of reactivity *via* molecular architecture

Ingrid Castro-Rodríguez and Karsten Meyer*

We review the exciting chemistry of trivalent uranium ions coordinated to classic Werner-type ligand environments.



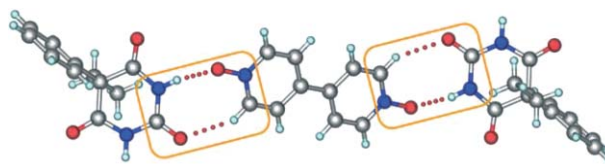
COMMUNICATIONS

1369

Carboxamide–pyridine *N*-oxide heterosynthon for crystal engineering and pharmaceutical cocrystals

L. Sreenivas Reddy, N. Jagadeesh Babu and Ashwini Nangia*

The two-point carboxamide–pyridine *N*-oxide heterosynthon, highlighted in the cocrystal of phenobarbital and 4,4'-bipyridine *N,N'*-dioxide, is strong and robust enough (11–12 kcal mol⁻¹) to control self-assembly in a variety of multi-functional and multi-component systems.



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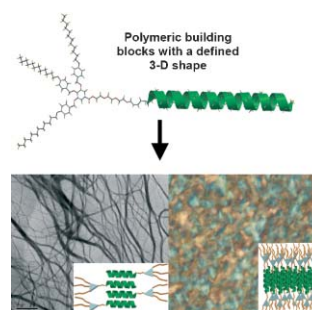
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Self-assembly of dendron-helical polypeptide copolymers: organogels and lyotropic liquid crystals

Kyoung Taek Kim, Chiyoung Park, Chulhee Kim, Mitchell A. Winnik* and Ian Manners*

New macromolecular self-assembling building blocks, dendron-helical polypeptide copolymers, have been synthesized. These materials possess a well-defined 3-D shape and self-assemble in solution to form nanoribbon and lyotropic liquid crystalline phases.

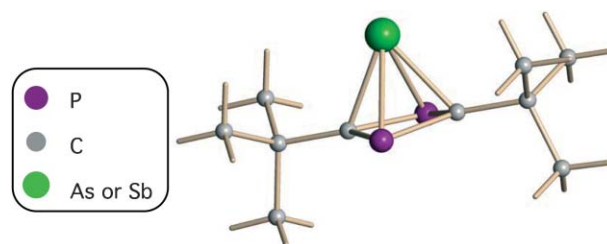


1375

Cationic phosphorus–carbon–pnictogen cages isolobal to $[C_5R_5]^+$

Cheryl Fish, Michael Green,* John C. Jeffery, Richard J. Kilby, Jason M. Lynam,* John E. McGrady,* Dimitrios A. Pantazis, Christopher A. Russell* and Charlotte E. Willans

The first examples of mixed P–C–As and P–C–Sb cationic clusters are seen in the *nido*- $[C_2Bu_2P_2E]^+$ (E = As, Sb)—X-ray crystallography, NMR and computational methods have been used to probe the behaviour of the complexes which are isolobal to the cyclopentadienyl cation.

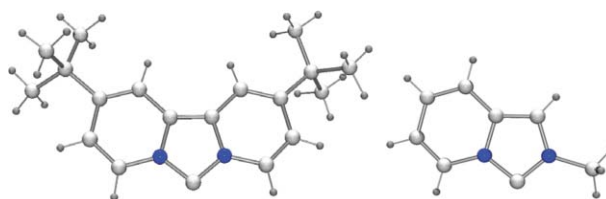


1378

X-ray crystal structures of 10 π - and 14 π -electron pyrido-annulated *N*-heterocyclic carbenes

Michael Nonnenmacher, Doris Kunz,* Frank Rominger and Thomas Oeser

The X-ray crystal structures of the *N*-heterocyclic carbenes (NHCs) with annulated pyridine rings that are reported here show the smallest N–C–N angles found in NHCs so far, which is congruent with a high-field shift of the carbene signals in ^{13}C NMR spectra.

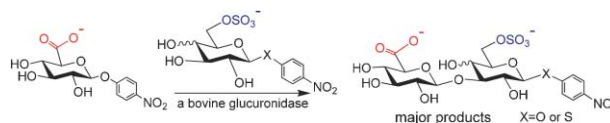


1381

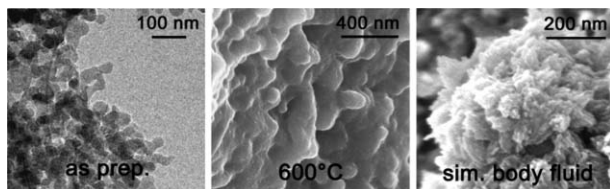
A bovine glucuronidase for assembly of β -D-glucuronyl-(1–3)-6-*O*-sulfo- β -D-gluco- and galacto-pyranosyl linkages

Hiroataka Uzawa,* Takehiro Nagatsuka, Hideo Hiramatsu and Yoshihiro Nishida

With 4-nitrophenyl β -D-glucuronide (D-GlcA-*O*-*p*NP) as the glycosyl donor, when *p*NP 6-*O*-sulfo- β -D-gluco- and D-galacto-pyranosides were used as the acceptors, a bovine enzyme was found to construct β -D-GlcA-(1–3)-linkages with the 6-*O*-sulfo-sugars in both a site- and β -selective way.



1384

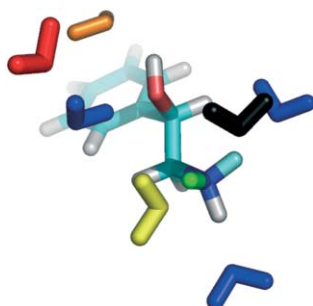


Glass and bioglass nanopowders by flame synthesis

Tobias J. Brunner, Robert N. Grass and Wendelin J. Stark*

The preparation of amorphous nanopowders by flame synthesis opens access to common soda-lime glass or complex metal-doped glasses and bioglasses in the range of 20–80 nm and offers a continuous, scalable route to materials of complex composition.

1387

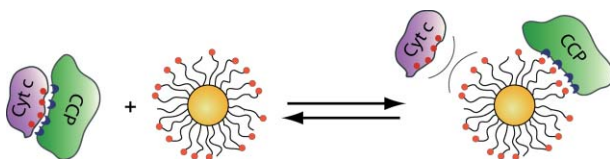


A solvent induced mechanism for conformational change

Christopher M. Baker and Guy H. Grant*

Molecular dynamics simulations are used to determine a mechanism for rotation of the amino groups in two neurotransmitter analogues, providing an insight into the molecular basis of solvent induced conformational change.

1390

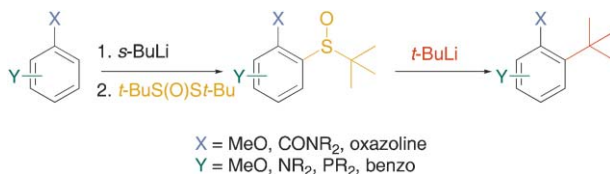


Disruption of protein–protein interactions using nanoparticles: inhibition of cytochrome c peroxidase

Halil Bayraktar, Partha S. Ghosh, Vincent M. Rotello* and Michael J. Knapp*

Functionalized gold nanoparticles bind selectively to cytochrome c or cytochrome c peroxidase and inhibit enzyme turnover.

1393



Contra-Friedel–Crafts *tert*-butylation of substituted aromatic rings *via* directed metallation and sulfinylation

Jonathan Clayden,* Christopher C. Stimson and Martine Keenan

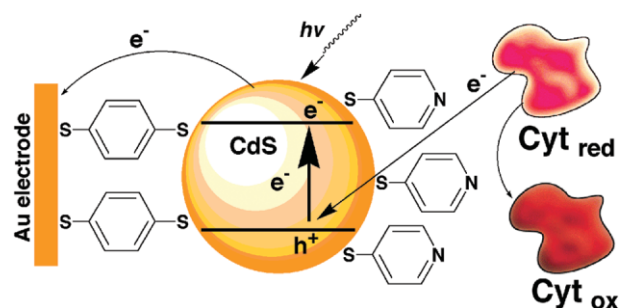
tert-Butylation *ortho* even to an electron-withdrawing group is now possible thanks to a two-step procedure involving directed metallation to introduce a *tert*-butylsulfinyl group followed by an unusual nucleophilic aromatic substitution reaction.

1395

Controlling the direction of photocurrents by means of CdS nanoparticles and cytochrome *c*-mediated biocatalytic cascades

Eugenii Katz, Maya Zayats, Itamar Willner* and Fred Lisdat

The direction of the photocurrents generated by a CdS monolayer associated with a Au electrode is controlled by the oxidation state of cytochrome *c* and the photocurrents are amplified by a biocatalytic cascade mediated by cytochrome *c*.

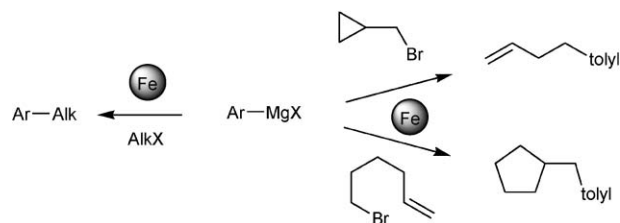


1398

Iron nanoparticles in the coupling of alkyl halides with aryl Grignard reagents

Robin B. Bedford,* Michael Betham, Duncan W. Bruce, Sean A. Davis, Robert M. Frost and Michael Hird

Iron nanoparticles, either formed *in situ* stabilised by 1,6-bis(diphenylphosphino)hexane or polyethylene glycol (PEG), or preformed stabilised by PEG, are a unique class of catalysts for Grignard cross-coupling and tandem cyclisation/cross-coupling reactions.

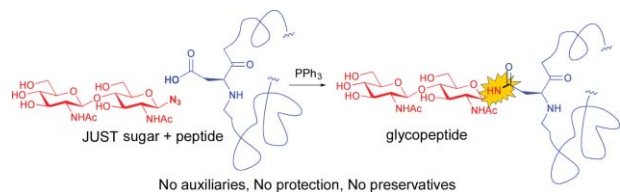


1401

Direct deprotected glycosyl–asparagine ligation

Katie J. Doores, Yusuke Mimura, Raymond A. Dwek, Pauline M. Rudd, Tim Elliott and Benjamin G. Davis*

A simple and efficient synthesis of *N*-linked glycoamino acids and glycopeptides from deprotected sugars using the Staudinger reaction.

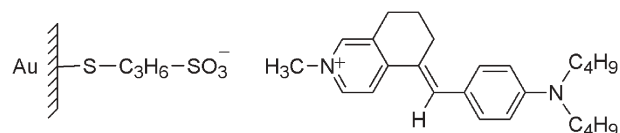


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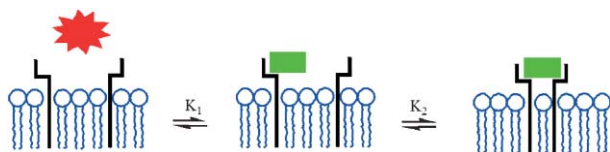
Controlled alignment of molecular diodes *via* ionic assembly of cationic donor–(π -bridge)–acceptor molecules on anionic surfaces

Geoffrey J. Ashwell* and Anna Chwialkowska

A novel method of alignment of cationic donor–bridge–acceptor molecules relies upon self-ordering on an anionically coated substrate and has resulted in the highest rectification ratio reported to date.



1407

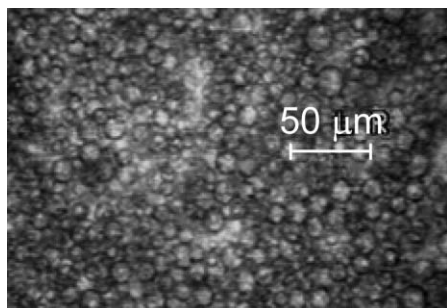


Dynamic molecular recognition on the surface of vesicle membranes

Hua Jiang and Bradley D. Smith*

The ability of a vesicle-bound receptor to associate with a water-soluble ligand increases with membrane loading level and the presence of membrane additives with cationic $N\text{-CH}_3$ groups.

1410

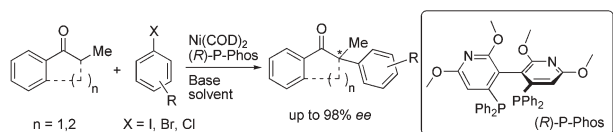


Stabilization of carbon dioxide-in-water emulsions by proteins

Brent S. Murray,* Eric Dickinson, Daniel A. Clarke and Christopher M. Rayner

Stable CO_2 -in-water emulsions are formed with β -lactoglobulin by fairly mild agitation at 40–100 bar pressure.

1413

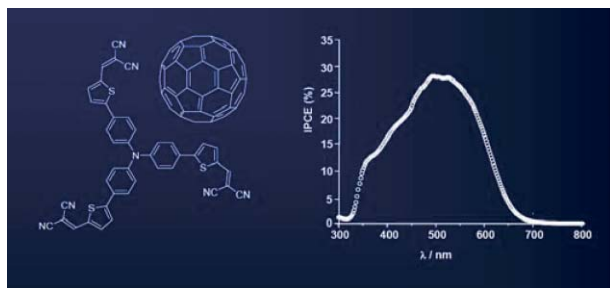


Nickel-catalyzed asymmetric α -arylation of ketone enolates

Guoshu Chen, Fuk Yee Kwong,* Hoi On Chan, Wing-Yiu Yu and Albert S. C. Chan*

Highly enantioselective α -arylations of five-, six- and seven-membered cyclic ketones with aryl halides were accomplished in the presence of a chiral Ni-P-Phos complex.

1416



A star-shaped triphenylamine π -conjugated system with internal charge-transfer as donor material for hetero-junction solar cells

Antonio Cravino, Sophie Roquet, Philippe Leriche, Olivier Alévêque, Pierre Frère and Jean Roncali*

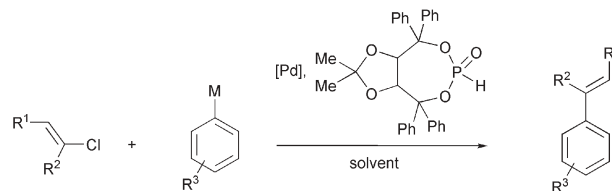
The introduction of dicyanovinyl groups on a triphenylamine-based conjugated system induces an intramolecular charge-transfer which enhances the spectral response and open-circuit voltage of the resulting hetero-junction solar cells.

1419

Cross-coupling reactions of aryl and vinyl chlorides catalyzed by a palladium complex derived from an air-stable *H*-phosphonate

Lutz Ackermann,* Christian J. Gschrei,
Andreas Althammer and Melanie Riederer

A palladium complex derived from air-stable TADDOLP(O)H efficiently catalyzes cross-coupling reactions between various organometallic species and aryl as well as vinyl chlorides.

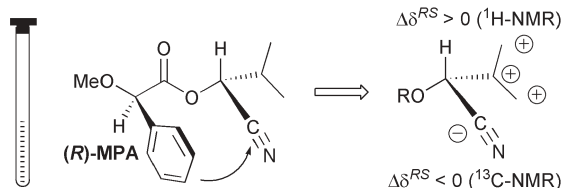


1422

The assignment of absolute configuration of cyanohydrins by NMR

Iria Louzao, José Manuel Seco, Emilio Quiñoá and
Ricardo Rigüera*

A general NMR spectroscopy protocol for determination of absolute configuration of cyanohydrins is described.

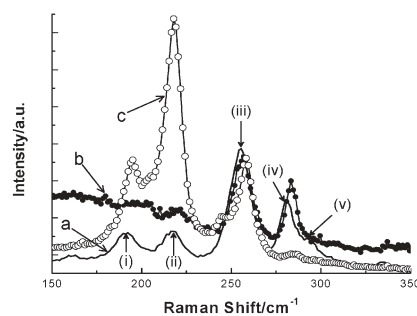


1425

Diameter-selective dispersion of single-walled carbon nanotubes using a water-soluble, biocompatible polymer

Hui Yang,* Shiunchin C. Wang, Philippe Mercier and
Daniel L. Akins*

A new strategy for the diameter-selective dispersion of single walled carbon nanotubes with an aqueous solution of chitosan has been developed.

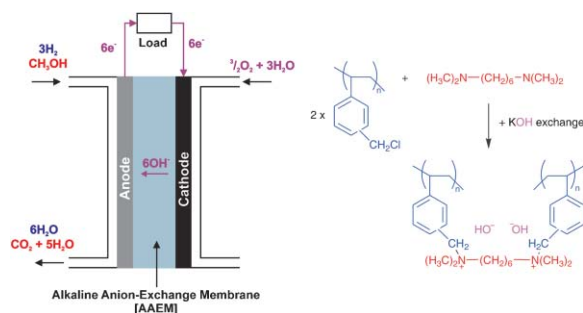


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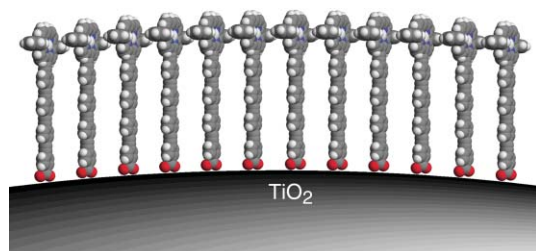
An alkaline polymer electrochemical interface: a breakthrough in application of alkaline anion-exchange membranes in fuel cells

John R. Varcoe,* Robert C. T. Slade and
Eric Lam How Yee

A novel alkaline interfacial polymer material has been developed for use in the preparation of metal-cation-free alkaline membrane electrode assemblies for all-solid-state alkaline fuel cells with long-term performance stability.



1430

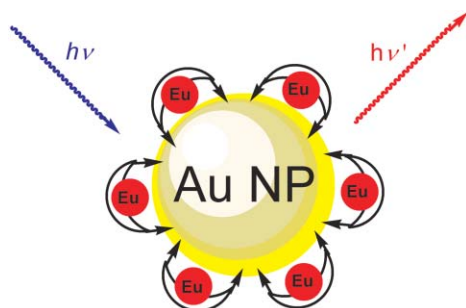


Evidence for the assembly of carboxyphenylethynyl zinc porphyrins on nanocrystalline TiO₂ surfaces

Chen-Fu Lo, Liyang Luo, Eric Wei-Guang Diao,*
I-Jy Chang and Ching-Yao Lin*

UV-visible absorption and AFM studies suggest that carboxyphenylethynyl zinc porphyrins are assembled on surfaces of nanocrystalline TiO₂ films in an H-aggregation fashion.

1433

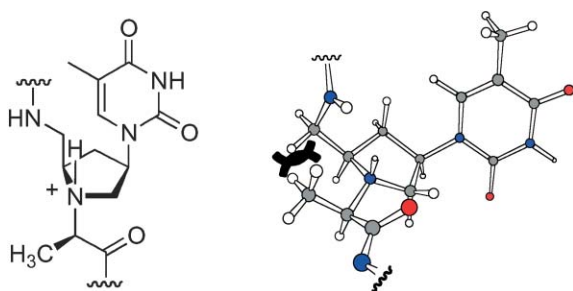


Luminescent nanobeads: attachment of surface reactive Eu(III) complexes to gold nanoparticles

David J. Lewis, Thomas M. Day, Julie V. MacPherson and
Zoe Pikramenou*

Gold nanoparticles were used as a scaffold to assemble multiple tailor-made europium(III) complexes yielding water-soluble gold nanoparticles that display red, Eu^{III}, luminescence.

1436

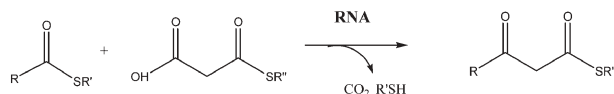


Stereospecific backbone methylation of pyrrolidine–amide oligonucleotide mimics (POM)

Anila I. Khan, T. H. Samuel Tan and Jason Micklefield*

The judicious, stereospecific introduction of backbone substituents can be used to modulate and fine tune the physicochemical properties of POM, without disrupting essential DNA and RNA recognition, for nucleic acid targeting, analysis or diagnosis.

1439



Decarboxylative Claisen condensation catalyzed by *in vitro* selected ribozymes

Youngha Ryu, Kil-Joong Kim, Charles A. Roessner and
A. Ian Scott*

Encapsulating the “RNA world”: The *in vitro* selection of RNAs catalyzing the decarboxylative Claisen condensation provides evidence that the “RNA world” could have synthesized the lipids necessary to make membranes for the primitive cell.

1442

Bromiodinanes with an I(III)–Br bond: preparation, X-ray crystallography and reactivity as electrophilic brominating agents

D. Christopher Braddock,* Gemma Cansell, Stephen A. Hermitage and Andrew J. P. White

Bromiodinanes are conveniently prepared in one step by the action of NBS on iodobenzene carbinols. The bromiodinanes act as electrophilic brominating agents, as exemplified by bromolactonisation and aromatic electrophilic substitution.

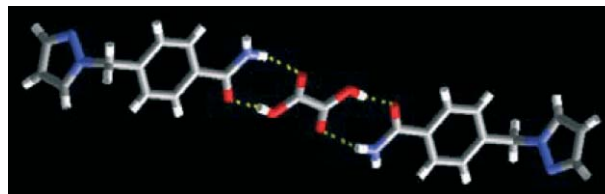


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Balancing supramolecular reagents for reliable formation of co-crystals

Christer B. Aakeröy,* John Desper and Benjamin M. T. Scott

The rational hydrogen bond-directed assembly of binary co-crystals with predictable primary hydrogen bond interactions, based upon an asymmetric ditopic supramolecular reagent and carboxylic acid, is presented.

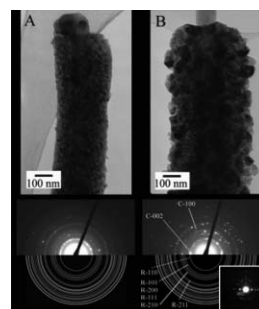


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Pure rutile nanotubes

Dominik Eder,* Ian A. Kinloch and Alan H. Windle

Pure rutile nanotubes have been produced by using a sacrificial carbon nanotube template. The carbon nanotube prevents the collapse of the inner pore of the titania's structure during the phase transformation from anatase to rutile.

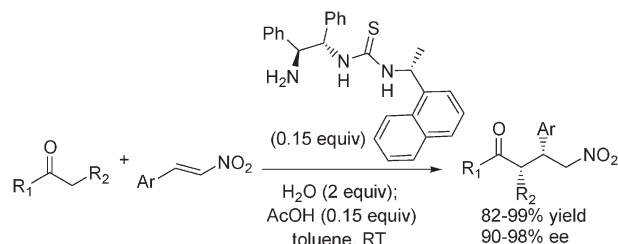


1451

Highly enantioselective addition of ketones to nitroolefins catalyzed by new thiourea–amine bifunctional organocatalysts

Svetlana B. Tsogoeva* and Shengwei Wei

A new and effective organocatalytic system: a primary amine derived chiral thiourea catalyst and AcOH–H₂O additive, which converts different ketones to γ -nitroketones in high yields and enantioselectivities has been described.




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