# CONTENTS

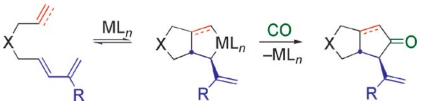
## MICROREVIEW

### Cycloaddition Reactions

**M. P. Croatt, P. A. Wender* .......... 19−32**

The Diene Effect: The Design, Development, and Mechanistic Investigation of Metal-Catalyzed Diene-yne, Diene-ene, and Diene-allene [2+2+1] Cycloaddition Reactions

**Keywords:** Cycloaddition / Pauson−Khand reaction / Rhodium / Heterogeneous catalysis / Allenes



This review covers the design and development aspects of the recently reported [2+2+1] reactions of dienes tethered to alkynes, alkenes, and allenes. The dienes in these reactions were found to behave very differently than other π-systems and accelerated or enabled the respective [2+2+1] reactions. Additionally, mechanistic insights into these reactions and a synthetic application of the diene-ene [2+2+1] reaction are presented.

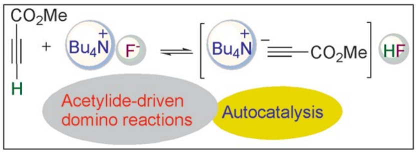
## SHORT COMMUNICATIONS

### Domino Synthesis

**D. Tejedor,* S. López-Tosco,**
**G. Méndez-Abt,**
**F. García-Tellado* .......................... 33−37**

Fluoride-Triggered Domino Reactions Involving Ammonium Acetylides and Carbonyl Compounds

**Keywords:** Autocatalysis / Fluorides / Multicomponent reactions / Domino reactions / Alkynes



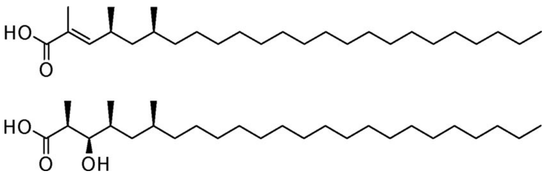
Fluoride anions were found to trigger domino reactions capable of generating structurally diverse products from methyl propiolate and carbonyl derivatives. These processes construct different molecular architectures through three different autocatalytic reaction networks. Reactions are both bench-friendly and bench-economical: they are performed at room temperature, under an aerobic atmosphere, and by using non-dried solvents.

### Natural Product Synthesis

**B. ter Horst, J. van Wermeskerken,**
**B. L. Feringa,* A. J. Minnaard* ..... 38−41**

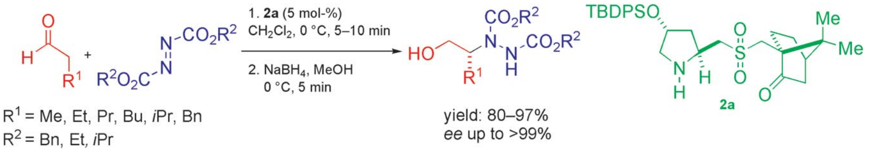
Catalytic Asymmetric Synthesis of Mycolipenic and Mycolipanolic Acid

**Keywords:** Mycolipenic acid / Mycolipanolic acid / Asymmetric synthesis / *Mycobacterium tuberculosis*



The first enantioselective total synthesis of mycolipenic acid and related mycolipanolic acid is described. The acids are prepared by an iterative enantioselective 1,4-addition protocol. The unsaturated system in mycolipenic acid and the propionate moiety in mycolipanolic acid are prepared by stereoselective Wittig olefination and stereoselective Evans aldol reaction, respectively.

### Organocatalysis



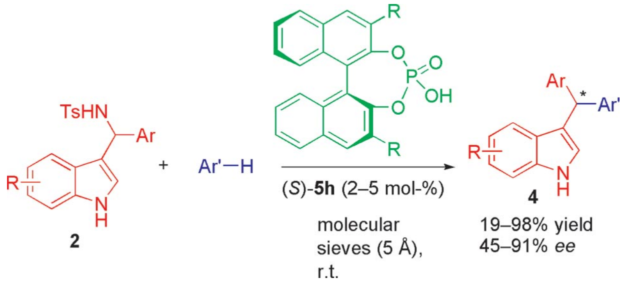
Remarkable reaction rate and excellent enantioselective direct α-amination of aldehydes with various azodicarboxylates was catalyzed by pyrrolidinylcamphor organocatalyst **2a** (5 mol-%) to provide the desired aminated products with excellent chemical yield and enantioselectivity (up to >99% *ee*) at 0 °C in $CH_2Cl_2$.

**P.-M. Liu, C. Chang, R. J. Reddy, Y.-F. Ting, H.-H. Kuan, K. Chen*** ...................................... **42–46**

Remarkable Reaction Rate and Excellent Enantioselective Direct α-Amination of Aldehydes with Azodicarboxylates Catalyzed by Pyrrolidinylcamphor-Derived Organocatalysts

**Keywords:** Amination / Asymmetric catalysis / Organocatalysis / Nitrogen heterocycles

### Friedel–Crafts Alkylations



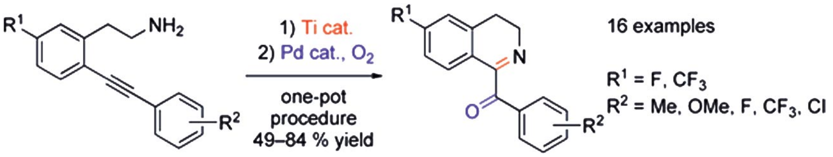
Enantioselective synthesis of unsymmetrical triarylmethanes has been realized by a chiral Brønsted acid catalyzed Friedel–Crafts alkylation of electron-rich arenes with (3-indolyl)methanamines. With 5 mol-% of a newly developed chiral phosphoric acid, the enantioenriched unsymmetrical triarylmethanes were obtained in excellent yields with up to 91% *ee*.

**F.-L. Sun, X.-J. Zheng, Q. Gu, Q.-L. He, S.-L. You*** ...................................... **47–50**

Enantioselective Synthesis of Unsymmetrical Triarylmethanes by Chiral Brønsted Acids

**Keywords:** Chiral Brønsted acids / Enantioselectivity / Friedel–Crafts reaction / Indole / Organocatalysis

### Fluorinated Heterocycles



Potentially antitumor-active fluorinated 1-benzoyl-3,4-dihydroisoquinolines can easily be synthesized by a new one-pot procedure from fluorinated [2-(*o*-alkynylphenyl)ethyl]amines in high yields. The main reaction steps are an initial Ti-catalyzed intramolecular alkyne hydroamination and a subsequent Pd-catalyzed oxidation.

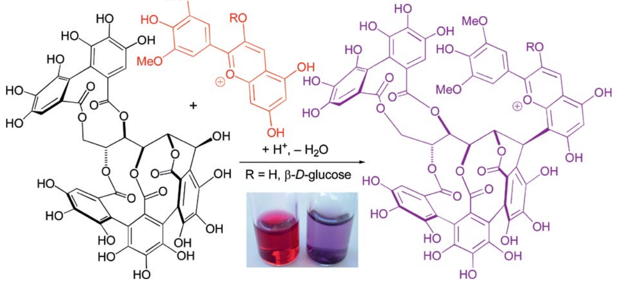
**R. Severin, J. Reimer, S. Doye*** ...................................... **51–54**

One-Pot Synthesis of Fluorinated 1-Benzoyl-3,4-dihydroisoquinolines from [2-(*o*-Alkynylphenyl)ethyl]amines by a Hydroamination/Oxidation Sequence

**Keywords:** Antitumor agents / Nitrogen heterocycles / Hydroamination / Palladium / Oxidation / Titanium

## FULL PAPERS

### Grape Pigments



Purple-colored anthocyano-ellagitannins, derived from the oak ellagitannin vescalagin and the red-colored grape pigments oenin and malvidin, are likely to play a role in the modulation of wine color during aging in oak barrels.

**S. Chassaing, D. Lefeuvre, R. Jacquet, M. Jourdes, L. Ducasse, S. Galland, A. Grelard, C. Saucier, P.-L. Teissedre, O. Dangles,* S. Quideau*** ............ **55–63**

Physicochemical Studies of New Anthocyano-Ellagitannin Hybrid Pigments: About the Origin of the Influence of Oak *C*-Glycosidic Ellagitannins on Wine Color

**Keywords:** Natural products / Dyes/Pigments / Anthocyanins / Polyphenols / Ellagitannins

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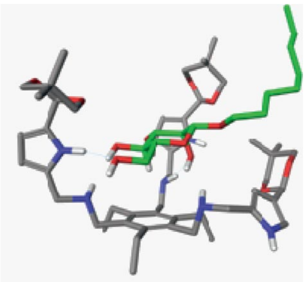
## Carbohydrate Recognition

**A. Ardá, C. Venturi, C. Nativi, O. Francesconi, F. J. Cañada, J. Jiménez-Barbero,* S. Roelens*** .................................... **64–71**

Selective Recognition of β-Mannosides by Synthetic Tripodal Receptors: A 3D View of the Recognition Mode by NMR

**Keywords:** Molecular recognition / Carbohydrates / Conformation analysis / NMR spectroscopy / Receptors



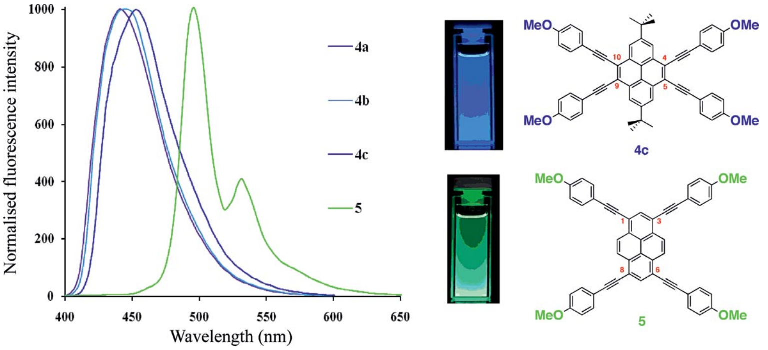
A 3D model of the complex of a synthetic tripodal receptor with octyl β-D-mannoside based on molecular mechanics calculations and NMR experimental data is proposed. The structure explains the observed selectivity for β-mannosyl in terms of hydrogen bonding, intermolecular van der Waals interactions and conformational bias

## Blue OLED Material

**J. Hu, M. Era, M. R. J. Elsegood, T. Yamato*** .................................... **72–79**

Synthesis and Photophysical Properties of Pyrene-Based Light-Emitting Monomers: Highly Pure-Blue-Fluorescent, Cruciform-Shaped Architectures

**Keywords:** Fluorescence / Conjugation / Photochemistry / Organic light-emitting diodes



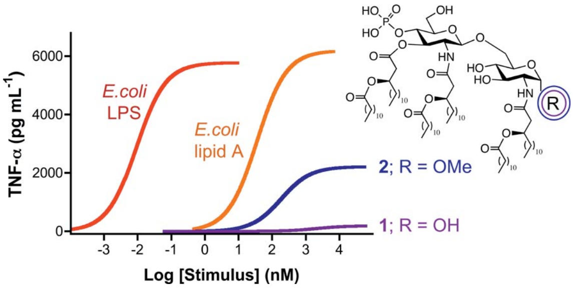
Cruciform-shaped, conjugated monomers based on pyrene were successfully synthesised by a Sonogashira coupling reaction. Both single-crystal X-ray analysis and photophysical studies strongly indicate their promising use as blue-emitting materials in organic light-emitting diodes (OLEDs).

## Synthetic Monophosphoryl Lipid A

**K. K. Maiti, M. DeCastro, A.-B. M. Abdel-Aal El-Sayed, M. I. Foote, M. A. Wolfert, G.-J. Boons*** ......... **80–91**

Chemical Synthesis and Proinflammatory Responses of Monophosphoryl Lipid A Adjuvant Candidates

**Keywords:** Carbohydrates / Lipids / Lipopolysaccharides / Immunochemistry / Cytokines / Protecting groups / Adjuvant / Tumor necrosis factor / Inflammation



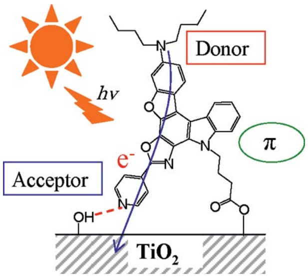
A methylated monophosphoryl lipid A derivative exhibits reduced potency and efficacy for cytokine production making it an attractive candidate for adjuvant development.

## Dye-Sensitized Solar Cells

**Y. Ooyama, S. Inoue, R. Asada, G. Ito, K. Kushimoto, K. Komaguchi, I. Imae, Y. Harima*** ................................. **92–100**

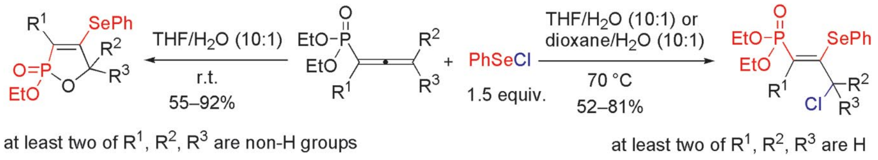
Dye-Sensitized Solar Cells Based on a Novel Fluorescent Dye with a Pyridine Ring and a Pyridinium Dye with the Pyridinium Ring Forming Strong Interactions with Nanocrystalline $TiO_2$ Films

**Keywords:** Solar cells / Titanium / Sensitizers / Dyes/pigments / Fluorescence



As a new-type donor–acceptor π-conjugated (D–π–A) dye capable of forming a strong interaction between the electron-acceptor moiety of the sensitizer and a $TiO_2$ surface, the fluorescent dye **OH11**, with a pyridine ring as the electron-accepting group, has been designed and synthesized as a photosensitizer for use in dye-sensitized solar cells (DSSCs).

## Electrophilic Reactions



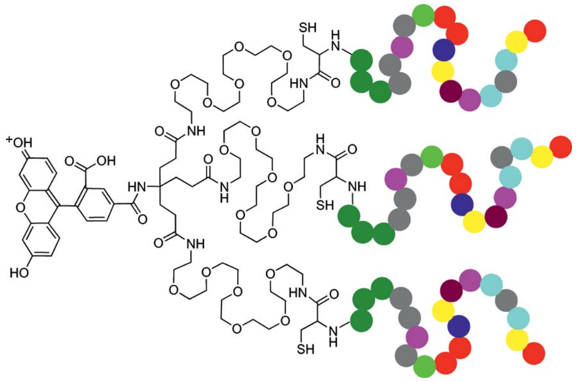
The reactions of monosubstituted 1,2-alkadienylphosphonates with PhSeCl in THF or dioxane/H$_2$O (10:1) afforded [(*Z*)-3-chloro-2-(phenylselanyl)-1-alkenyl]phosphonates with a very high (*Z*) stereoselectivity, whereas the same reaction with di- and trisubstituted allenylphosphonates afforded 2-ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-oxides exclusively.

**G. He, Y. Yu, C. Fu,* S. Ma* ... 101–110**

Highly Selective Synthesis of [(*Z*)-3-Chloro-2-(phenylselanyl)-1-alkenyl]phosphonates and 2-Ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxides by Electrophilic Reaction of 1,2-Alkadienylphosphonates with PhSeCl

**Keywords:** Allenes / Phosphorus / Selenium / Electrophilic addition / Cyclization

## Multifunctional Peptide Dendrimers



An efficient, modular and broadly applicable strategy is presented for the synthesis of multivalent and multifunctional peptide dendrimers. The scope of the method is demonstrated by introduction of a variety of popular targeting peptides at the periphery and other biologically relevant groups at the focal point of AB$_n$-type ($n$ = 2−5) dendrons.

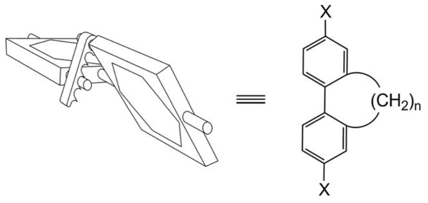
**E. H. M. Lempens, B. A. Helms, A. R. Bayles, M. Merkx, E. W. Meijer* ............................ 111–119**

A Versatile, Modular Platform for Multivalent Peptide Ligands Based on a Dendritic Wedge

**Keywords:** Dendrimers / Peptides / Multivalency / Modular approach / Native chemical ligation / Orthogonal functionalization

## Molecular Electronics

The synthesis of a series of modular biphenyl building blocks with restricted torsion angles is described. Short alkyl bridges dictate the conformation and provide rigid rod-type structures with well-defined backbone conjugation.



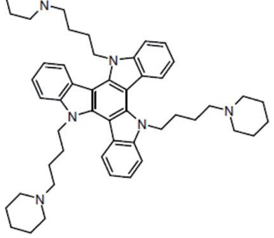
**D. Vonlanthen, J. Rotzler, M. Neuburger, M. Mayor* ................................ 120–133**

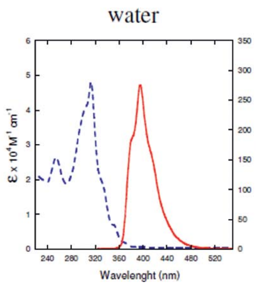
Synthesis of Rotationally Restricted and Modular Biphenyl Building Blocks

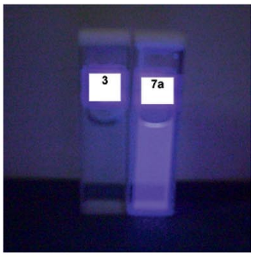
**Keywords:** Molecular electronics / Conjugation / X-ray diffraction / Biphenyls / UV/Vis spectroscopy

## Hydrosoluble Triazatruxenes

**AZATRUX (7a)**







In this paper, we compare different synthetic routes for the preparation of hydrophilic triazatruxene derivatives and show that they are fluorescent both in organic solvents and in water.

**M. Franceschin,* L. Ginnari-Satriani, A. Alvino, G. Ortaggi, A. Bianco ................................. 134–141**

Study of a Convenient Method for the Preparation of Hydrosoluble Fluorescent Triazatruxene Derivatives

**Keywords:** Fused-ring systems / Nitrogen heterocycles / Hydrosolubility / Cyclotrimerization / Fluorescence spectroscopy

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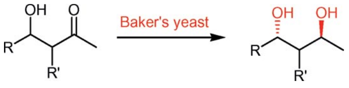
## Baker's Yeast Stereoselectivity

**D. Acetti, E. Brenna,* C. Fuganti,**
**F. G. Gatti, S. Serra** ................. **142–151**

Baker's Yeast Reduction of β-Hydroxy Ketones

**Keywords:** Enzymes / Baker's yeast / Reduction / Asymmetric synthesis / 1,3-Diols / Ketones



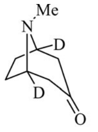
Stereoselective reduction of hydroxy ketones by baker's yeast was exploited for concomitant control of the configurations of 1,3-diol triads.

## Labelled Tropane Alkaloids

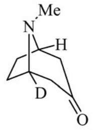
**A. Fournial, T. Ranaivondrambola,**
**M. Mathé-Allainmat, R. J. Robins,**
**J. Lebreton*** ............................... **152–156**

A Short and Efficient Synthesis of Bridgehead Mono- and Dideuteriated Tropinones

**Keywords:** Alkaloids / Tropane / Deuterium / Isotopic labeling



**[1,5-$^2H_2$]tropinone**



**[1-$^2$H]tropinone**

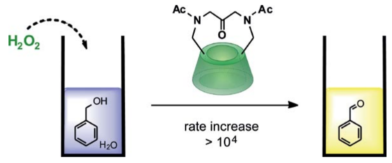
An efficient synthesis of 1,5-dideuterio- and racemic 1-deuteriotropinone is described in which high levels of deuterium are incorporated from the corresponding di- and mono-labelled 2,5-dibutoxytetrahydrofuran, respectively, at either one or both of the bridgehead carbons C-1 and C-5.

## Artificial Enzymes

**L. G. Marinescu,* E. G. Doyagüez,**
**M. Petrillo, A. Fernández-Mayoralas,**
**M. Bols** .................................... **157–167**

Amino–Acetone-Bridged Cyclodextrins – Artificial Alcohol Oxidases

**Keywords:** Amines / Enzyme catalysis / Alcohols / Oxidation / Cyclodextrins



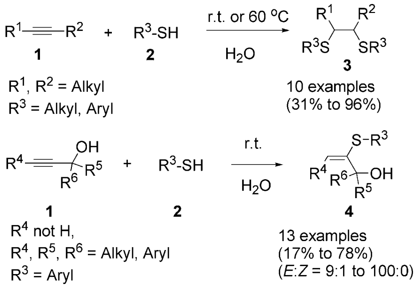
Three amino–acetone-bridged cyclodextrins have been synthesized and kinetic studies revealed very good substrate-selective enzymatic catalysis for the oxidation of benzyl alcohols with a rate increase of up to 18500 under neutral conditions at room temperature using hydrogen peroxide as co-oxidant. They also exhibit stereoselectivity in the oxidation of different enantiomers.

## Green Chemistry

**Z. Jin, B. Xu,**
**G. B. Hammond*** ...................... **168–173**

Green Synthesis of Vicinal Dithioethers and Alkenyl Thioethers from the Reaction of Alkynes and Thiols in Water

**Keywords:** Radicals / Green chemistry / Alkynes / Thiols / Hydrothiolation



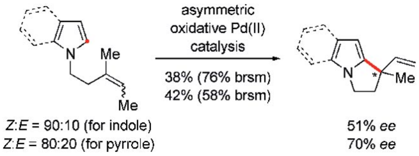
Alkynes reacted with thiols in water to give vicinal dithioethers, and non-terminal propargyl alcohols reacted with phenyl thiols to produce a highly regio and stereoselective monohydrothiolation product, (*E*)-alkenyl thioether.

## Asymmetric Catalysis

**J. A. Schiffner, T. H. Wöste,**
**M. Oestreich*** ........................... **174–182**

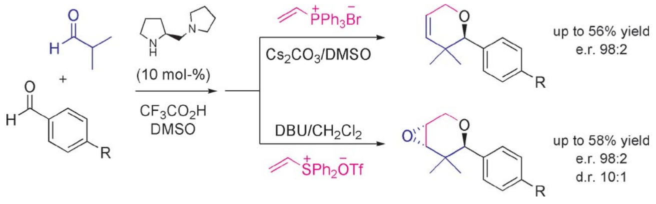
Enantioselective Fujiwara–Moritani Indole and Pyrrole Annulations Catalyzed by Chiral Palladium(II)–NicOx Complexes

**Keywords:** Asymmetric catalysis / C–H activation / Fujiwara–Moritani reaction / Heck reaction / Palladium



The long known Fujiwara–Moritani arylation of alkenes, an oxidative palladium(II) catalysis, is finally accomplished in an asymmetric sense. C–H bond activation at indoles and pyrroles followed by conventional Heck-type C–C bond formation allows for enantioselective construction of a congested quaternary carbon atom.

## Asymmetric Tandem Process



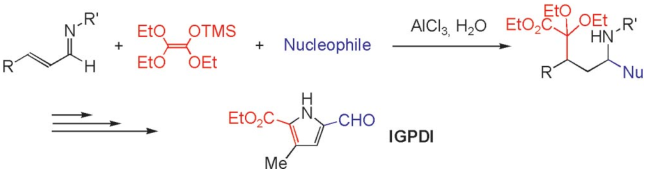
An efficient and convenient two-step synthesis of enantiomerically enriched dihydropyran and epoxytetrahydropyran derivatives is described. The key step involves a tandem conjugative addition-intramolecular cyclisation/epoxidation process from easily available enantiomerically pure β-hydroxy aldehydes.

**S. Catalán-Muñoz, C. A. Müller, S. V. Ley*** ................................ **183–190**

### An Asymmetric Tandem Conjugative Addition-Intramolecular Cyclisation Process to Provide Functionalised 3,6-Dihydropyrans and 4,5-Epoxytetrahydropyrans 💻

**Keywords:** Epoxidation / Organocatalysis / Aldol reactions / Wittig reactions

## Multisubstituted Pyrroles



The double nucleophilic addition reactions of dialkoxy ketene silyl acetals proceeded with α,β-unsaturated imines to give 1,4- and 1,2-double addition products, and their subsequent transformations afforded multisubstituted pyrroles in good yields.

**A. Takahashi, S. Kawai, I. Hachiya, M. Shimizu*** ............................. **191–200**

### A New Method for the Synthesis of Multisubstituted Pyrroles of Biological Interest by Double Nucleophilic Addition to α,β-Unsaturated Imines 💻

**Keywords:** Nucleophilic addition / Nitrogen heterocycles / Synthetic methods

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* Author to whom correspondence should be addressed.

💻 Supporting information on the WWW (see article for access details).