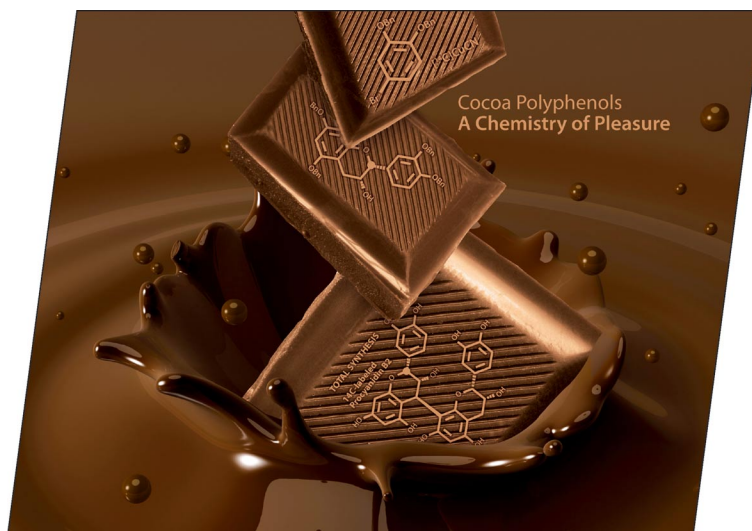


A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## COVER PICTURE

The cover picture shows the key steps of the first asymmetric total synthesis of procyanidin B2, one of the major dietary polyphenols present in cocoa and chocolate. During the last decades, the health benefits of foods consumed for pure pleasure have received much recognition. Many biological studies have evidenced the beneficial health effects of procyanidins. However, the absorption and metabolism of procyanidins is still not fully understood, and some aspects are still controversial. In order to strengthen this knowledge, the first total synthesis of procyanidin B2 was developed and applied to the preparation of a regioselectively radiolabeled analogue incorporating a  $^{14}\text{C}$  label at the 2-position of the upper C-ring moiety. This enantioselective synthesis was achieved in 14 “hot” steps, involving as key steps the Sharpless dihydroxylation of an elaborated alkene, a stereoselective intramolecular cyclization and the condensation of two (–)-epicatechin units. The radiolabelled procyanidin B2 obtained through this reaction pathway will be used in bioavailability studies. Details are discussed in the article by D. Barron et al. on p. 6069ff. The authors acknowledge Tonic Life Communications for the design of the cover page and the European Union 6th Framework project “FLAVO” for partial support of this research work.



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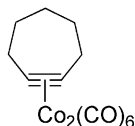
## MICROREVIEW

### Alkyne–Metal Complexes

J. R. Green\* ..... 6053–6062

(Cycloheptyne)dicobalt Complexes in Organic Synthesis

**Keywords:** Alkynes / Cobalt / Synthetic methods / Medium-ring compounds / Strained molecules



The dimetallic cobalt complexes of cycloheptynes are thermally stable compounds capable of isolation by conventional organic techniques and of long-term storage. Recent progress on the chemistry of these complexes has afforded a number of methods for the preparation of this ring system, elucidated the reactions that can be performed on the intact system, and revealed a series of methods for the decomplexation to give stable organic compounds. This review details these developments, along with the use of these complexes as intermediates in organic synthesis.

## SHORT COMMUNICATION

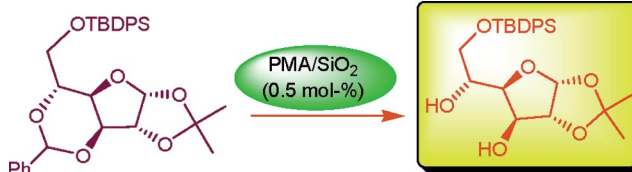
### Chemoselective Deprotection

P. S. Kumar, G. D. K. Kumar,  
S. Baskaran\* ..... 6063–6067



Truly Catalytic and Chemoselective Cleavage of Benzylidene Acetal with Phosphomolybdic Acid Supported on Silica Gel

**Keywords:** Chemoselectivity / Heterogeneous catalysis / Protecting groups / Supported catalysts



Phosphomolybdic acid supported on silica gel provides a truly catalytic method for the chemoselective cleavage of benzylidene

acetals having sensitive functional groups under mild conditions.

## FULL PAPERS

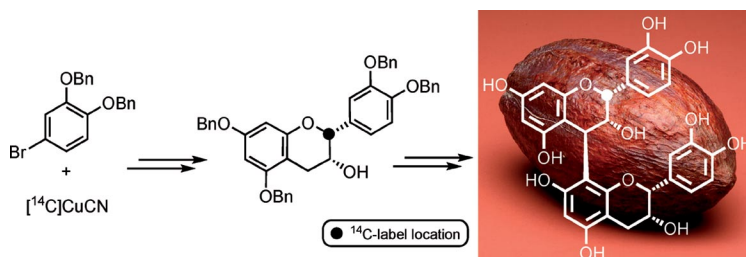
### Radiolabeled Polyphenols

F. Viton, C. Landreau, D. Rustidge,  
F. Robert, G. Williamson,  
D. Barron\* ..... 6069–6078



First Total Synthesis of  $^{14}\text{C}$ -Labeled Procyanidin B2 – A Milestone Toward Understanding Cocoa Polyphenol Metabolism

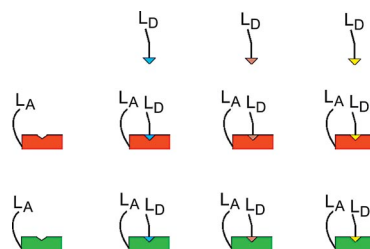
**Keywords:** Natural products / Polyphenols / Radiochemistry / Total synthesis



Health benefits of foods consumed for pure pleasure received much recognition in the recent years. Cocoa and dark chocolate are particularly rich in procyanidins. We developed the first asymmetric total synthesis of

procyanidin B2 and applied it to the preparation of a regioselectively radiolabeled  $^{14}\text{C}$ -analogue, which will be used to strengthen our knowledge on the metabolism of procyanidins.

This article describes the formation of a 450-membered (chiral) bidentate phosphorus ligand library for application in homogeneous asymmetric catalysis. The ligands are formed by noncovalent interactions, namely nitrogen–porphyrinato–zinc(II). Examples of their application in catalysis are given.



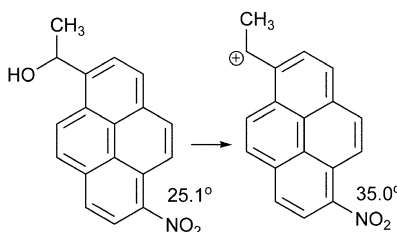
**P. E. Goudriaan, X.-B. Jang, M. Kuil, R. Lemmens, P. W. N. M. Van Leeuwen, J. N. H. Reek\*** ..... 6079–6092

Synthesis of Building Blocks for the Development of the SUPRAPHos Ligand Library and Examples of Their Application in Catalysis

**Keywords:** Bidentate ligands / Supramolecular chemistry / Ligand libraries / Phosphorus / Asymmetric catalysis

### Substituent Effects on PAHs

Stable-ion NMR spectroscopic and GIAO-DFT studies are reported for a series of  $\alpha$ -pyrenylcarboxonium ions and  $\alpha$ -pyrenyl carbocations.  $\text{NO}_2$  buttressing increases in the benzylic carbocations in order to decrease charge–charge repulsion.



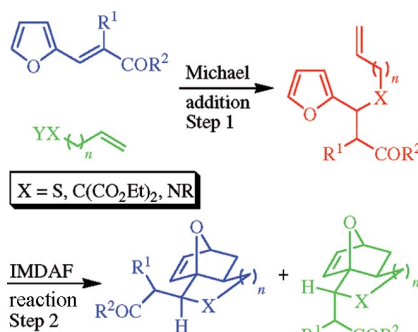
**K. K. Laali\*, M. A. Arrica, T. Okazaki, S. D. Bunge** ..... 6093–6105

Synthesis and Stable-Ion Studies of Regioisomeric Acetylnitropyrenes and Nitropyrenyl Carbinols and GIAO-DFT Study of Nitro Substituent Effects on  $\alpha$ -Pyrenyl Carbocations

**Keywords:** Substituent effects / Arenes / Fused-ring systems / Carbocations / Density functional calculations

### Intramolecular Diels–Alder Reactions

Michael adducts arising from the addition of nucleophiles possessing an unsaturated tether to  $\beta$ -furyl  $\alpha,\beta$ -unsaturated carbonyl compounds undergo a stereoselective intramolecular Diels–Alder reaction to afford five- and six-membered rings *exo*-fused to an oxanorbornene framework. The results are supported by quantum chemical calculations, NMR studies and X-ray crystallography.

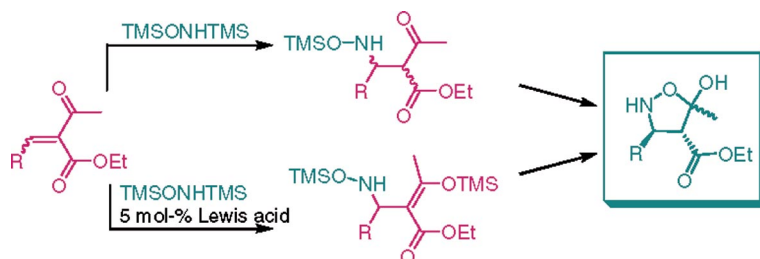


**M. Dadwal, M. K. Kesharwani, V. Danayak, B. Ganguly,\* S. M. Mobin, R. Muruganatham, I. N. N. Namboothiri\*** ..... 6106–6118

Synthetic and Theoretical Investigations on the Construction of Oxanorbornenes by a Michael Addition and Intramolecular Diels–Alder Furan Reaction

**Keywords:** Diels–Alder reaction / Michael addition / Oxanorbornene / B3LYP / Ab initio calculations

### Aza-Michael Additions



New 5-hydroxyisoxazolidine-4-carboxylates have been synthesized by 1,4-addition of *N,O*-bis(trimethylsilyl)hydroxylamine to alkylideneacetoacetates. Complete agree-

ment was observed between the detailed computational investigation performed on this reaction and the experimental evidence.

**F. Benfatti, A. Bottoni, G. Cardillo,\* L. Gentilucci, M. Monari, E. Mosconi, M. Stenta,\* A. Tolomelli** ..... 6119–6127

Synthesis of Ethyl 5-Hydroxyisoxazolidine-4-carboxylates via Michael Addition/Intramolecular Hemiketalisation

**Keywords:** Michael addition / Alkylideneacetoacetates / N,O-Heterocycles / Hemiketalisation / Computer chemistry / Reaction mechanism

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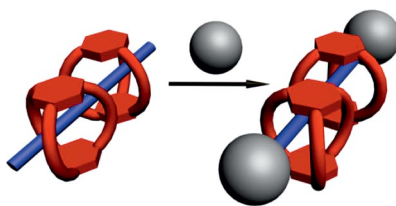
## Crown Ether Rotaxanes

S. Li, M. Liu, J. Zhang, B. Zheng, X. Wen,  
N. Li, F. Huang\* ..... 6128–6133



Preparation of Bis(*m*-phenylene)-32-crown-10-Based Cryptand/Bisparaquat [3]Rotaxanes with High Efficiency

**Keywords:** Rotaxanes / Cryptands / Crown compounds / Cooperative effects



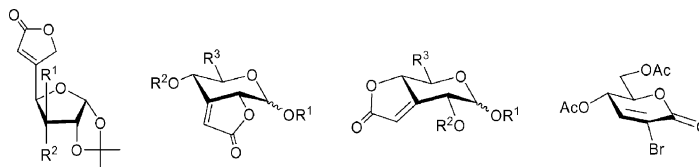
Two [3]rotaxanes were synthesized from two bis(*m*-phenylene)-32-crown-10-based cryptands and a bisparaquat derivative. As a result of strong association and positive cooperative complexation between the cryptands and the bisparaquat derivative, high yields and high selectivities were achieved.

## Sugar-Based Butenolides

N. M. Xavier, S. Silva, P. J. A. Madeira,  
M. H. Florêncio, F. V. M. Silva, J. Justino,  
J. Thiem, A. P. Rauter\* ..... 6134–6143

Synthesis and Biological Evaluation of Sugars Containing  $\alpha,\beta$ -Unsaturated  $\gamma$ -Lactones

**Keywords:** Wittig reaction / Lactones / Carbohydrates



The stereocontrolled synthesis of sugar-containing butenolides was achieved by Wittig reaction of 3-/5-keto sugars and intramolecular transesterification. The anti-

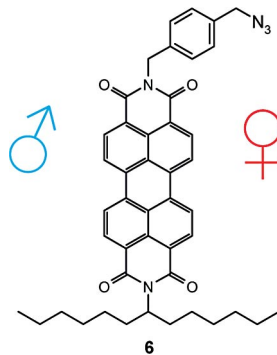
microbial activities of the products and that of a known pyranoid  $\alpha,\beta$ -unsaturated  $\delta$ -lactone were studied.

## Fluorescence Labelling

H. Langhals,\* A. Obermeier .... 6144–6151

A Click Reaction for Fluorescent Labelling: Application of the 1,3-Dipolar Cycloaddition Reaction

**Keywords:** Dyes / Fluorescence spectroscopy / Hormones / Photochemistry / Receptors



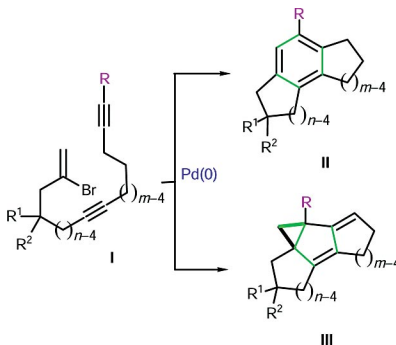
The perylene-tetracarboxdiimide unit was linked under mild conditions to a pharmacologically active compound by the copper-catalyzed cycloaddition of the azide group to form highly fluorescent derivatives. Applications such as for the detection of endocrine disruptors are discussed.

## Cascade Cyclizations

W. M. Tokan, F. E. Meyer, S. Schweizer,  
P. J. Parsons, A. de Meijere\* .... 6152–6167

Palladium-Catalyzed Oligocyclizations of 2-Bromoalk-1-ene-(*n*+1),(*m*+*n*+1)-diynes – Influence of Tether Lengths and Substituents on the Outcome of the Reaction (Part I)

**Keywords:** Cascade cyclizations / Palladium catalysis / Carbopalladiations / Carbooligocycles / Cyclopropanes




Palladium-catalyzed oligocyclizations of 2-bromoalk-1-ene-(*n*+1),(*m*+*n*+1)-diynes (**I**) under Heck reaction conditions can lead to products of type **II** or **III**, depending on the lengths of the tethers linking the multiple bonds, and the nature of the substituent R at the acetylene terminus.





Imidazole promotes the diastereoselective construction of multiply substituted cyclohexanes.


X.-G. Liu, M. Shi\* ..... 6168–6174

Imidazole-Mediated Cascade [2 + 2 + 2] Annulation Reactions: A Highly Diastereoselective Synthetic Protocol for the Construction of Multiply Substituted Cyclohexanes 

**Keywords:** Imidazole / (Arylmethylidene)-malononitriles / Nitroalkenes / Multiply substituted cyclohexanes / One-pot three-component reactions

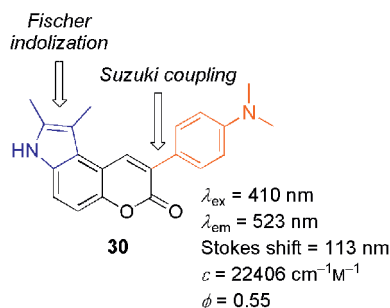
### Small-Molecule Fluorescent Dyes

L. Chen, T.-S. Hu,  
Z.-J. Yao\* ..... 6175–6182

Development of New Pyrrolocoumarin Derivatives with Satisfactory Fluorescent Properties and Notably Large Stokes Shifts 

**Keywords:** Fluorescence / Pyrrolocoumarin / Stokes shift / Fischer indolization / FRET (Fluorescence Resonance Energy Transfer) / Biological imaging

In this study, we designed and synthesized a number of fluorescent molecules on the basis of two novel pyrrolocoumarin skeletons. The examination and further optimization of the fluorescent properties afforded three new pyrrolocoumarin dyes with notably large Stokes shifts and satisfactory fluorescent properties. Among these, **30** showed potential applicability in biological FRET devices.

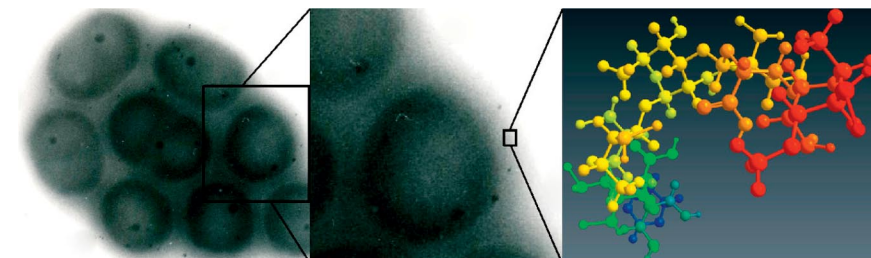


### Capsular Polysaccharides

A. Hanuszkiewicz, Z. Kaczyński,  
B. Lindner, T. Goldmann, E. Vollmer,  
J. Debarry, H. Heine,  
O. Holst\* ..... 6183–6188

Structural Analysis of the Capsular Polysaccharide from *Acinetobacter lwoffii* F78

**Keywords:** Carbohydrates / NMR spectroscopy / Mass spectrometry / Structure elucidation




The structure of the capsular polysaccharide of *Acinetobacter lwoffii* F78 was elucidated, and its nonendotoxic origin was proved. One repeating unit consisted of a trisaccharide backbone  $[\rightarrow 3)\text{-}\alpha\text{-L-FucNAc-}$

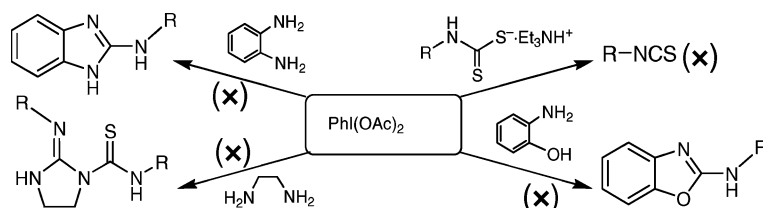
$(1\rightarrow 3)\text{-}\beta\text{-D-QuiN4N-(1}\rightarrow 4)\text{-}\beta\text{-L-GlcN3NA-(1}\rightarrow ]$ , where the amino groups of QuiN4N were substituted by AlaNAc or 3-HBA and the amino groups of GlcN3NA were substituted by 3-HBA and an acetyl group.

### Desulfurization by Iodine(III)

H. Ghosh, R. Yella, J. Nath,  
B. K. Patel\* ..... 6189–6196

Desulfurization Mediated by Hypervalent Iodine(III): A Novel Strategy for the Construction of Heterocycles 

**Keywords:** Iodine / Desulfurization / Oxidation / Isothiocyanates / Heterocycles / Hypervalent compounds



Several synthetically useful organic transformations have been carried out by using the hypervalent iodine reagent, diacetoxyiodobenzene (DIB). These transformations

rely on the desulfurization ability of DIB. The use of DIB makes these reactions simpler and more efficient, giving high yields of the desired products in one pot.

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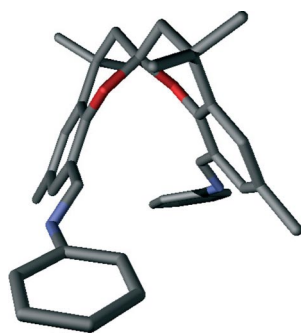
## Chiral Spiro Amines

X. Sala, E. J. García Suárez, Z. Freixa,\*  
J. Benet-Buchholz,  
P. W. N. M. van Leeuwen ..... 6197–6205



Modular Spiro Bidentate Nitrogen Ligands – Synthesis, Resolution and Application in Asymmetric Catalysis

**Keywords:** Diamines / Spiro compounds / Chiral ligands / Kinetic resolution / Asymmetric catalysis



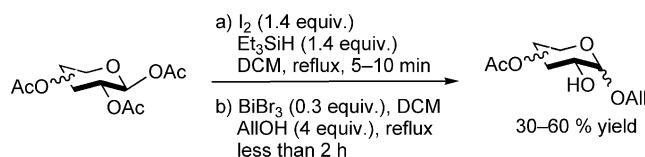
A family of new modular, chiral, spiro, bidentate, nitrogen-donor ligands containing the large spirobi(chroman) backbone SPAN has been prepared and isolated in enantiopure form. Some preliminary results related to the Pd-catalyzed oxidative kinetic resolution of 1-phenylethanol with these ligands are reported.

## Activated Glycosides

A. Pastore, M. Adinolfi,  
A. Iadonisi ..... 6206–6212

BiBr<sub>3</sub>-Promoted Activation of Peracetylated Glycosyl Iodides: Straightforward Access to Synthetically Useful 2-*O*-Deprotected Allyl Glycosides

**Keywords:** Protecting groups / Carbohydrates / Regioselectivity / Glycosylation



Substoichiometric amounts of BiBr<sub>3</sub> are able to promote anomeric activation of acetylated glycosyl iodides. This reactivity can

be exploited for straightforward access to useful building blocks such as allyl glycosides unprotected at the O-2 position.

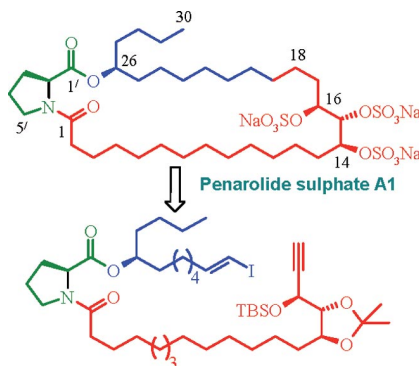
## Asymmetric Total Synthesis

D. K. Mohapatra,\* D. Bhattasali,  
M. K. Gurjar, M. I. Khan,  
K. S. Shashidhara ..... 6213–6224



First Asymmetric Total Synthesis of Penarolide Sulfate A<sub>1</sub>

**Keywords:** Macrocycles / Asymmetric synthesis / C–C coupling / Dihydroxylation / Epoxidation / Total synthesis / Regioselectivity



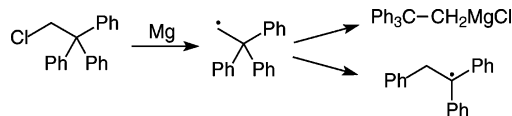
The first asymmetric total synthesis of the potent  $\alpha$ -glucosidase inhibitor penarolide sulfate A<sub>1</sub> is documented. The salient feature of our synthetic protocol is the intramolecular Sonogashira cross-coupling reaction for the construction of the key 30-membered macrocyclic ring of the natural product.

## Grignard Reagent

F. Bickelhaupt, M. Newcomb,  
C. B. DeZutter,  
H. J. R. de Boer\* ..... 6225–6231

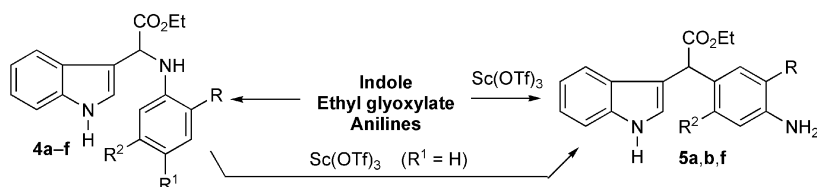
The Grignard Reagent Formation Reaction of 2-Chloro-1,1,1-triphenylethane Revisited

**Keywords:** Grignard reagent formation reaction / 2-Chloro-1,1,1-triphenylethane / Magnesium / Radicals / Carbanions



Reaction of 2-chloro-1,1,1-triphenylethane (**1**) with magnesium in THF produced a dark-red solution. After deuteryolysis with D<sub>2</sub>O, 1,1,1-triphenylethane (**2**; 16%), 2-D-1,1,1-triphenylethane (**3**; 52%) and 1,1,2-triphenylethane (**4**; 26%) were isolated. The

rate constant for phenyl migration in the 2,2,2-triphenylethyl radical at 20 °C is  $4.0 \times 10^5 \text{ s}^{-1}$ . The diffusion model for Grignard formation reactions of Garst et al. is in line with the product distribution.



News from the past: Reactions between indole, glyoxylate and anilines, the old Passerini reaction, give product **4**. When the reactions are catalysed by 5 mol-% scandium triflate, however, or when isolated **4**

is treated under the same conditions, rearrangements involving the arylamino groups of compounds **4** take place, and compounds **5** are obtained.

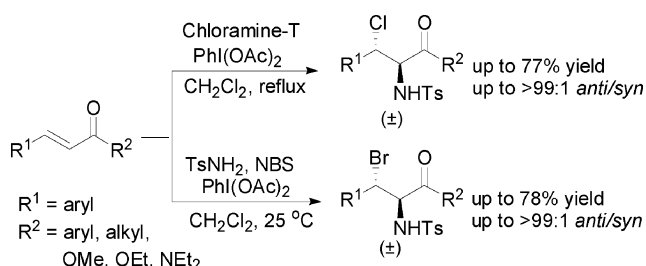
G. Desimoni,\* G. Faita, M. Mella,  
M. Toscanini, M. Boiocchi .... 6232–6238

News from the 80-Year-Old Passerini Variant of the Friedel–Crafts Alkylation of Indole



**Keywords:** Friedel–Crafts alkylation / Multi-component reactions / Indole / Scandium catalysis / Rearrangements

## Aminohalogenation



The aminochlorination and -bromination of electron-deficient olefins in dichloromethane, mediated by hypervalent iodine compounds and utilizing Chloramine-T tri-

hydrate and a combination of TsNH<sub>2</sub> and NBS as the nitrogen and bromine source, respectively, is reported.

X.-L. Wu, G.-W. Wang\* ..... 6239–6246

Aminohalogenation of Electron-Deficient Olefins Promoted by Hypervalent Iodine Compounds

**Keywords:** Aminohalogenation / Hypervalent compounds / Alkenes / Iodine

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*The editorial staff and the publishers thank all readers, authors, referees, and advertisers for their interest and support over the past year and wish them all a happy new year.*

\* Author to whom correspondence should be addressed.

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

If not otherwise indicated in the article, papers in issue 35 were published online on November 21, 2008