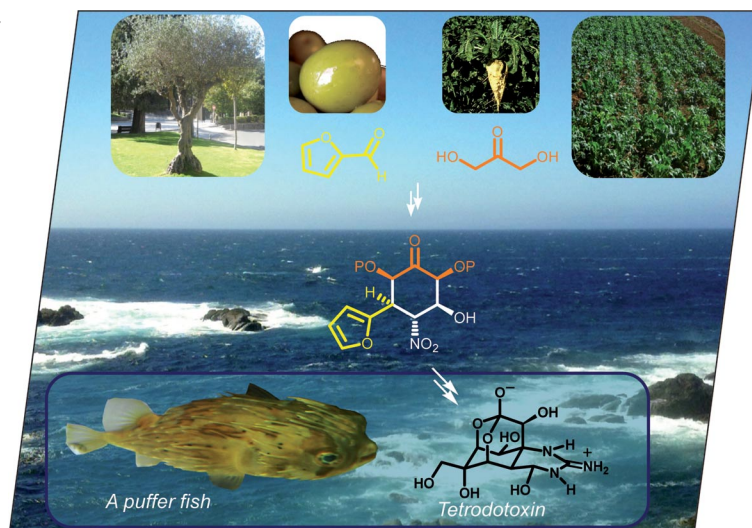


**EurJOC** is a journal of ChemPubSoc Europe, a union of 16 European chemical societies formed for the purpose of publishing high-quality science. All owners merged their national journals to form two leading chemistry journals, the *European Journal of Organic Chemistry* and the *European Journal of Inorganic Chemistry*.

Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem*.

## COVER PICTURE

The cover picture shows furfural and dihydroxyacetone, which are two compounds that can be obtained from plant sources, for example, from olive stones and sugar beets, respectively. These compounds can be used as building blocks for a convergent, cascade annulation based synthetic approach to the sodium channel blocker tetrodotoxin isolated from puffer fish. Details are discussed in the article by F. Cagide-Fagín and R. Alonso on p. 6741ff.



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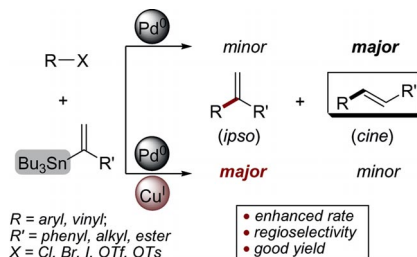
## MICROREVIEW

### cine Substitution

Y. Peng, W.-D. Z. Li\* ..... 6703–6718

*cine* Substitution and the Cu Effect in Stille Cross-Coupling Reactions: Mechanistic Perspectives and Synthetic Utility

**Keywords:** Natural products / Cross-coupling / *cine* Substitution / Copper / Stille reaction



*cine* Substitution resulting from slow transmetallation is an “abnormal” phenomenon in classic Stille cross-couplings of sterically hindered vinyltins. Two mechanistic explanations are critically evaluated. As a method of countering *cine* substitution, co-catalysis by  $\text{Cu}^{\text{I}}$  can accelerate transmetallation remarkably and on occasion restore the *ipso* selectivity.

## SHORT COMMUNICATIONS

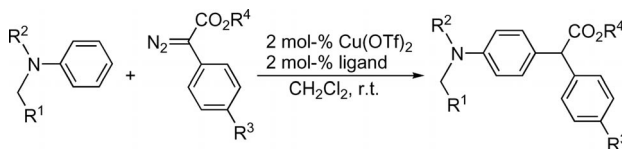
### Aromatic Substitution

E. Tayama,\* T. Yanaki, H. Iwamoto,  
E. Hasegawa ..... 6719–6721



Copper(II) Triflate Catalyzed Intermolecular Aromatic Substitution of *N,N*-Disubstituted Anilines with Diazo Esters

**Keywords:** Aromatic substitution / Substituent effects / Synthetic methods / Arenes / Diazo compounds



The intermolecular aromatic substitution of *N,N*-disubstituted anilines with diazo esters is shown to proceed under mild conditions in the presence of a catalytic

amount of copper(II) triflate/ligand complex (up to 89% yield). The scope and limitations regarding substrates, diazoesters, and ligands in this reaction are described.

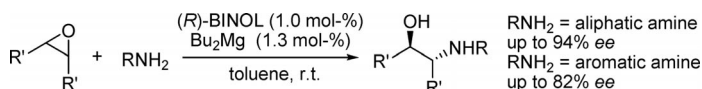
### Enantioselective Catalysis of Epoxides

H. Bao, J. Wu, H. Li, Z. Wang, T. You,  
K. Ding\* ..... 6722–6726



Enantioselective Ring Opening Reaction of *meso*-Epoxides with Aromatic and Aliphatic Amines Catalyzed by Magnesium Complexes of BINOL Derivatives

**Keywords:** Asymmetric catalysis / Epoxides / Amino alcohols / Amines / Magnesium



Cheap and easily available chiral BINOLate/ $\text{Bu}_2\text{Mg}$  complexes have been demonstrated to be efficient catalysts in the enantioselective ring opening aminolysis of *meso*-epoxides with both aromatic and

aliphatic amines as nucleophiles. The corresponding  $\beta$ -amino alcohols were obtained in good yields with moderate to high *ee* values.

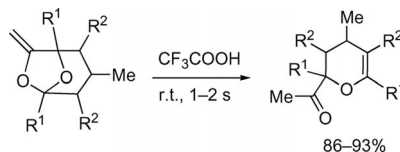
### Synthetic Methods

E. Y. Schmidt, B. A. Trofimov,\*  
N. V. Zorina, A. I. Mikhaleva,  
I. A. Ushakov, E. V. Skital'tseva,  
O. N. Kazheva, G. G. Alexandrov,  
O. A. Dyachenko ..... 6727–6730

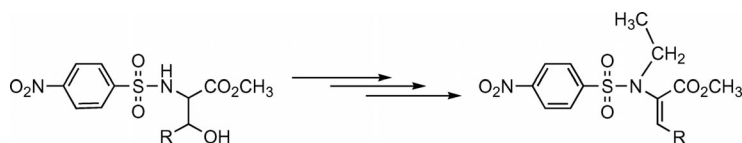


Synthesis of Functionalized 3,4-Dihydropyrans via Rearrangement of the Products of a One-Pot Diastereoselective Assembly of Ketones and Acetylene

**Keywords:** Heterocycles / Oxygen heterocycles / Synthetic methods / Dihydropyran synthesis



The products of the one-pot assembly of ketones and acetylene, 7-methylene-6,8-dioxabicyclo[3.2.1]octanes, congeners of an insect pheromone frontalin, undergo an acid-catalyzed rearrangement to diastereomerically pure 2-acetyl-3,4-dihydropyrans in excellent yields. The synthesis is realizable in a one-pot manner procedure directly from ketones and acetylene.



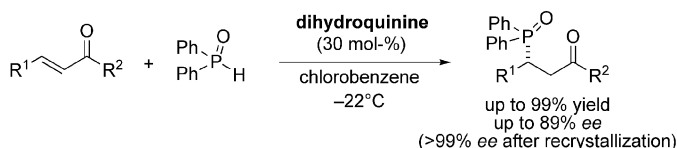
Two routes for the synthesis of *N*-ethyl-*N*-(4-nitrophenylsulfonyl)- $\alpha,\beta$ -dehydroamino acid derivatives from serine, threonine and phenylserine derivatives are presented. In both a sequential alkylation/dehydration

procedure is carried out, but in alternative sequence. This methodology allowed the synthesis for the first time of new non-natural amino acids, which incorporate both the *N*-ethyl and  $\alpha,\beta$ -dehydro moieties.

**L. S. Monteiro,\* J. Kołomańska,  
A. C. Suarez ..... 6731–6735**

Synthesis of Novel Nonproteinogenic Amino Acids: *N*-Ethyl- $\alpha,\beta$ -dehydroamino Acid Methyl Esters

**Keywords:** Amino acids / Elimination /  $\alpha,\beta$ -Dehydroamino acids / Alkylation / *N*-Ethyl- $\alpha,\beta$ -dehydroamino acids



The first enantioselective conjugate addition of commercially available diphenylphosphane oxide to *trans*-chalcones has been conveniently developed by using

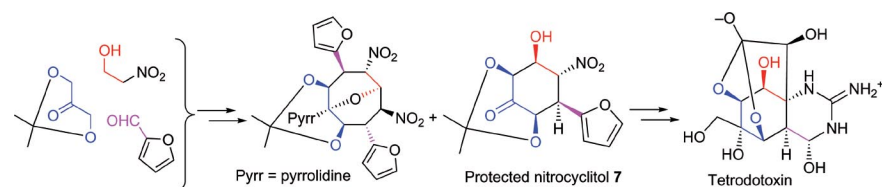
dihydroquinine as the catalyst. The adducts were isolated in high yield and up to 89% *ee*.

**A. Russo, A. Lattanzi\* ..... 6736–6739**

Asymmetric Organocatalytic Conjugate Addition of Diarylphosphane Oxides to Chalcones

**Keywords:** Michael addition / Alkaloids / Organocatalysis / Phosphorus / Enones

## FULL PAPERS



A batch preparation (11 g) of the protected nitrocyclitol **7** and its capability to sustain a convergent formal synthesis of ( $\pm$ )-tetrodotoxin in only 26 steps illustrate the practicability of the formal [3+3] annulation of

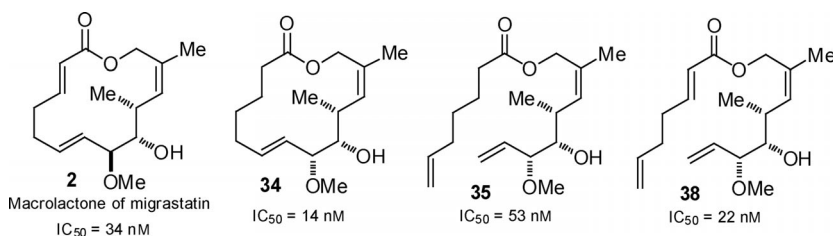
$\beta$ -heteroaryl- $\alpha$ -nitro- $\alpha,\beta$ -enals as well as its versatility for the synthesis of natural products containing highly oxygenated cyclohexanes.

**F. Cagide-Fagín, R. Alonso\* ... 6741–6747**

A Cascade Annulation Based Convergent Approach to Racemic Tetrodotoxin

**Keywords:** Natural products / Annulation / Cyclitols /  $\beta$ -(Hetero)aryl- $\alpha$ -nitro- $\alpha,\beta$ -enals / 2,2-Dimethyl-1,3-dioxan-5-one

## Natural Product Synthesis



The synthesis of macrolactones **2** and **34** as well as esters **35** and **38** proceeds in good overall yields. Macrolactone **34** and ester **38** are amongst the most active compounds

of the migrastatin family prepared so far and show good promise as anticancer compounds.

**L. C. Dias,\* F. G. Finelli, L. S. Conejero,  
R. Krogh, A. D. Andricopulo ... 6748–6759**

Synthesis of the Macrolactone of Migrastatin and Analogues with Potent Cell-Migration Inhibitory Activity

**Keywords:** Total synthesis / Natural products / Lactones / Antitumor agents / Inhibition

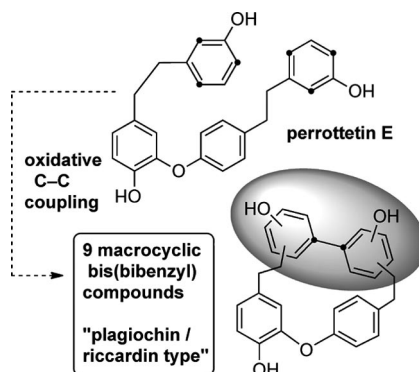
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## Natural Product Synthesis

A. Speicher,\* M. Groh, M. Hennrich,  
A.-M. Huynh ..... 6760–6778

Syntheses of Macroyclic Bis(bibenzyl)  
Compounds Derived from Perrottetin E

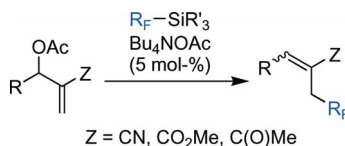
**Keywords:** Total synthesis / Natural products / Macrocycles / Bryophyte constituents



Nine isomeric macrocyclic bis(bibenzyl) compounds of the plagiochin/riccardin type, some of which have been found in liverworts, derive biochemically from perrottetin E. Growing interest due to recent reports on new isolated compounds and their remarkable biological activities prompted us to synthesize these bryophyte constituents. We report a flexible general approach to the total set of nine bis(bibenzyl) compounds.

## Fluorinated Compounds

A. A. Zemtsov, V. V. Levin, A. D. Dilman,\*  
M. I. Struchkova, P. A. Belyakov,  
V. A. Tartakovsky, J. Hu ..... 6779–6785



Reactions of Baylis–Hillman adducts with fluorinated silanes triggered by catalytic amounts of Bu<sub>4</sub>NOAc are described.

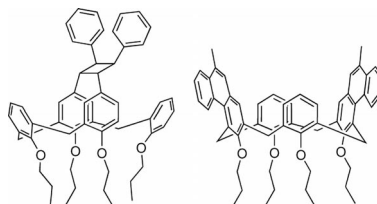


Reaction of Baylis–Hillman Adducts with  
Fluorinated Silanes

**Keywords:** Fluorine / Silanes / Michael addition / Baylis–Hillman adducts / Chemo-selectivity

## Calixarenes

W. Hüggenberg, A. Seper, I. M. Oppel,  
G. Dyker\* ..... 6786–6797



Multifold Photocyclization Reactions of  
Styrylcalix[4]arenes

**Keywords:** Photochemistry / Calixarenes / Fused-ring systems / Cycloaddition / Annulation

Oxidative cyclization to phenanthrenes and the transannular [2+2] cycloaddition reaction are observed as competing processes during the photolysis of distyryl- and tetra-styryl-substituted calix[4]arenes.

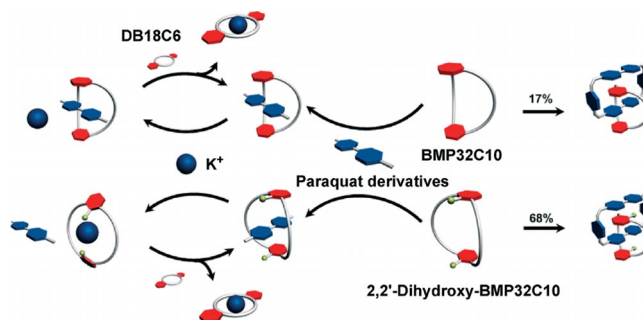
## Host-Guest Chemistry

M. Zhang, Y. Luo, B. Zheng, X. Yan,  
F. R. Fronczek, F. Huang\* ..... 6798–6803



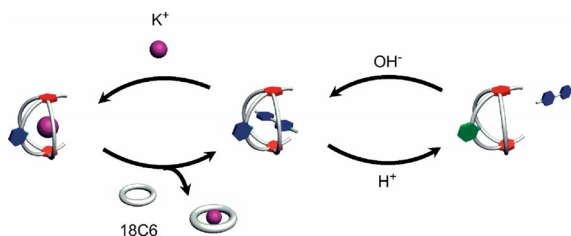
Improved Pseudorotaxane and Catenane  
Formation from a Derivative of Bis(*m*-  
phenylene)-32-crown-10

**Keywords:** Catenanes / Host-guest systems / Crown compounds / Pseudorotaxanes / Complexation geometry



A bis(*m*-phenylene)-32-crown-10 derivative formed pseudorotaxanes and not the previously reported “taco complexes” with paraquat derivatives both in solution and in the solid state, as seen in the efficient for-

mation of a [2]catenane and its crystal structure with a paraquat derivative. Another unique feature was that its binding to paraquat derivatives could be switched off and back on.



A novel bis(1,2,3-phenylene) cryptand has been synthesized and used to prepare 1:1 complexes with paraquat and diquat, with association constants of  $2.2 \times 10^3 \text{ M}^{-1}$  and  $3.7 \times 10^3 \text{ M}^{-1}$  ( $\text{CHCl}_3/\text{CH}_3\text{CN}$  1:1). In the

solid state the cryptand forms a taco complex with paraquat, never found before in cryptand/paraquat complexes. Binding to paraquat and diquat can be controlled by addition or removal of  $\text{K}^+$  or acid.

M. Zhang, B. Zheng, B. Xia, K. Zhu,  
C. Wu, F. Huang\* ..... 6804–6809

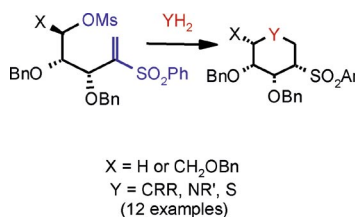
Synthesis of a Bis(1,2,3-phenylene) Cryptand and Its Dual-Response Binding to Paraquat and Diquat



**Keywords:** Cryptands / Crown compounds / Host-guest systems / Taco complexes / Controllable assembly

## Carbocycles and Heterocycles

In a diversity-oriented and metal-free approach, acyclic vinyl sulfones with a leaving group at the  $\delta$  position reacted with externally delivered C, N, and S nucleophiles to afford six-membered carbo- and heterocycles diastereoselectively. Isolation of intermediates showed these are examples of a Michael– $\text{S}_{\text{N}}2$  sequence and not an  $\text{S}_{\text{N}}2$ –Michael sequence, as is more prevalent in this class of reactions.

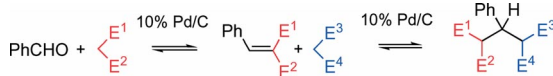


A. K. Atta, T. Pathak\* ..... 6810–6819

A Tandem Michael– $\text{S}_{\text{N}}2$ -Mediated General Route to Six-Membered Heterocycles and Carbocycles



**Keywords:** Carbocycles / Heterocycles / Sulfones / Desulfonation / Michael addition / Nucleophilic substitution



Palladium on carbon (10% Pd catalyzes the (retro-)Michael addition of activated methylene compounds **2a–d** to mono- and

doubly activated styrenes. The scope and limitations of the reaction are described. A mechanism is proposed.

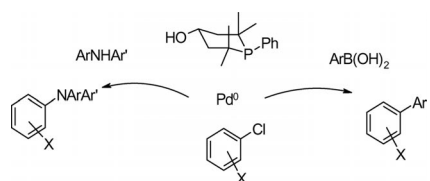
## Palladium-Catalyzed Michael Addition

N. I. Nikishkin, J. Huskens,  
W. Verboom\* ..... 6820–6823

Study on the Pd/C-Catalyzed (Retro-) Michael Addition Reaction of Activated Methylene Compounds to Electron-Poor Styrenes

**Keywords:** Michael addition / Palladium / C-H activation

A two-step entry to a chemically robust, hindered P,O-type phosphorinane-based ligand and its application toward Pd-mediated cross-coupling reactions of unactivated aryl chlorides is presented.



## Unactivated Arylhalide Cross-Coupling

E. Ullah, J. McNulty,\* V. Larichev,  
A. J. Robertson ..... 6824–6830

*P*-Phenyl-2,2,6,6-tetramethylphosphorinane-4-ol: An Air-Stable P,O-Type Ligand for Palladium-Mediated Cross-Coupling Reactions

**Keywords:** Phosphane ligands / Palladium / Organopalladium chemistry / Amination



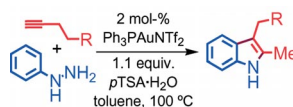
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## Tandem Reactions

N. T. Patil,\* A. Konala ..... 6831–6839



Mechanistic Dichotomy with Alkynes in the Formal Hydrohydrazination/Fischer Indolization Tandem Reaction Catalyzed by a  $\text{Ph}_3\text{PAuNTf}_2/p\text{TSA}$  Binary System



A method for the synthesis of 2,3-disubstituted indoles from alkynes and arylhydrazines is reported that utilizes a  $\text{Ph}_3\text{PAuNTf}_2/p\text{TSA}\cdot\text{H}_2\text{O}$  binary catalytic system. Mechanistic aspects including an alkyne-dependent dichotomy is also discussed.

Alkyne	Intermediate	Key mechanism
$\text{R} = (\text{CH}_2)_2\text{OH}$	cyclic enol ether	hydroalkoxylation
$\text{R} = \text{CH}_2\text{COOH}$	cyclic enol lactone	hydrocarboxylation
$\text{R} = \text{Ph}$	4-phenylbutan-2-one	alkyne hydration

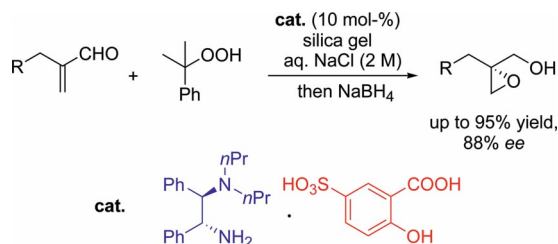
**Keywords:** Alkynes / Gold / Cyclization / Hydroamination / Nitrogen heterocycles

## Asymmetric Catalysis

J. Li, N. Fu, L. Zhang, P. Zhou, S. Luo,\*  
J.-P. Cheng ..... 6840–6849



Chiral Primary Amine Catalyzed Asymmetric Epoxidation of  $\alpha$ -Substituted Acroleins



**Keywords:** Asymmetric catalysis / Epoxidation / Amines / Chirality

A primary-tertiary diamine Brønsted acid conjugate, combined with 5-sulfosalicylic acid (5-SSA), was found to be an efficient catalyst for the asymmetric epoxidation of  $\alpha$ -substituted acroleins.

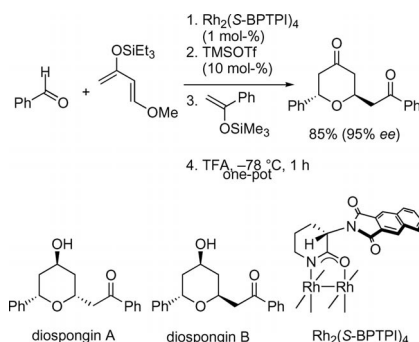
$p\text{TSA}\cdot\text{H}_2\text{O}$  binary catalytic system. Mechanistic aspects including an alkyne-dependent dichotomy is also discussed.

## Natural Products

M. Anada, T. Washio, Y. Watanabe,  
K. Takeda, S. Hashimoto\* ..... 6850–6854



A Short, Catalytic, Asymmetric Synthesis of Diospongins A and B by a One-Pot, Sequential Hetero-Diels–Alder/Mukaiyama–Michael Reaction Process



**Keywords:** Asymmetric catalysis / Rhodium / Natural products / Oxygen heterocycles

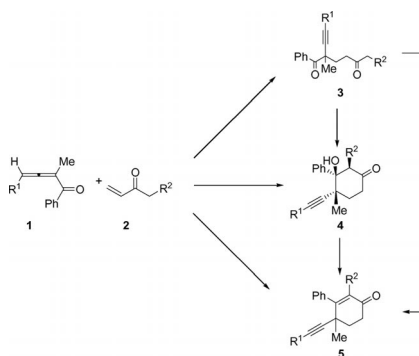
A short, catalytic, asymmetric synthesis of diospongins A and B has been achieved by using a one-pot, sequential  $[\text{Rh}_2(\text{S-BPTPI})_4]$ -catalyzed enantioselective hetero-Diels–Alder reaction combined with a TMSOTf-catalyzed Mukaiyama–Michael reaction.

## Tandem Reaction

D. Malhotra, L.-P. Liu,\*  
G. B. Hammond\* ..... 6855–6862



Tandem Michael Addition/Aldol Reaction of Allenic Ketones with Alkyl Vinyl Ketones: Versatile Synthesis of 2-Alkynyl 1,5-Diketones, 4-Alkynyl-3-hydroxycyclohexanones and 4-Alkynylcyclohexenones



**Keywords:** Michael addition / Aldol reactions / Allenic ketones / Vinyl ketones / Alkynes

Further investigations on the chemistry of alkynolenolate were performed and a tandem Michael addition/aldol reaction of allenic ketones with vinyl ketones was developed. Various products were obtained from the same starting materials under different conditions and only one diastereoisomer of hydroxycyclohexanone was isolated.

\* 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 34 were published online on November 22, 2010