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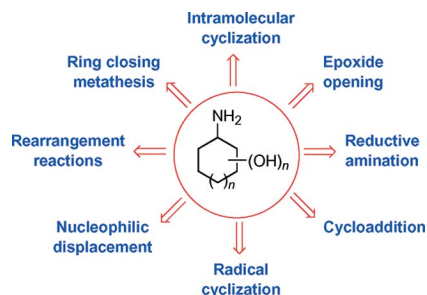
MICROREVIEW

Aminocyclitols

A. Delgado 3893–3906

Recent Advances in the Chemistry of Aminocyclitols

Keywords: Aminocyclitols / Cyclitols / Natural products / Synthetic methodology / Stereocontrol / Disatereoselectivity / Functional group interconversion



An update of the most relevant literature methods for the synthesis of aminocyclitols is presented. The material is organized according to the methodologies used for the construction of the aminocyclitol framework.

SHORT COMMUNICATIONS

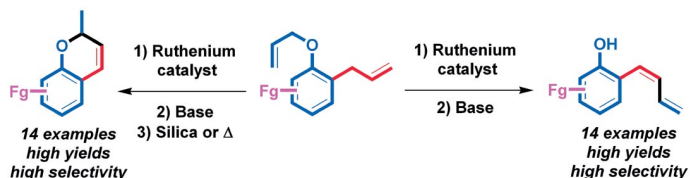
Multi-Catalysis Reactions

D. B. Ramachary,* V. V. Narayana,
K. Ramakumar 3907–3911



A New One-Pot Synthetic Approach to the Highly Functionalized (*Z*)-2-(Buta-1,3-dienyl)phenols and 2-Methyl-2*H*-chromenes: Use of Amine, Ruthenium and Base-Catalysis

Keywords: Heterocycles / Phenols / Multi-catalysis reactions / Ring closing metathesis



A novel and practical one-pot multi-catalysis process for the synthesis of highly substituted benzo[*b*]oxepines **5**, (*Z*)-2-(buta-1,3-dienyl)phenols **6** and 2-methyl-2*H*-chromenes **7** from simple starting materials

is described. (*Z*)-2-(Buta-1,3-dienyl)phenols **6** are obtained via base-induced ring opening of highly functionalized benzo[*b*]oxepines **5**.

Organic White Pigments

H. Langhals,* U. Ritter 3912–3915

γ -(Hydroxyalkyl)naphthalene-tetracarbox-diimides: Organic White Pigments

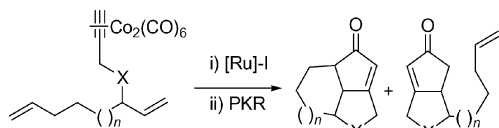
Keywords: Pigments / Naphthalene / Heterocycles / Aromatic compounds / Sun protection



(Hydroxyalkyl)naphthalene-tetracarboxdiimides – white pigment powders with strong opacifying properties – were prepared in three steps. Applications are discussed.

FULL PAPERS

RCM/Pauson–Khand Reactions



The combination of RCM followed by an intramolecular Pauson–Khand reaction gives direct entry to tricyclic compounds. The procedure has been studied for dienes containing heteroatoms and allows

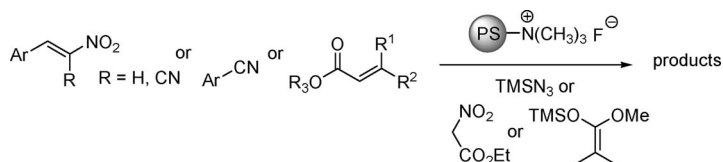
the building of [6,5,5] and [7,5,5] tricyclic systems. The feasibility of the process depends strongly on the nature of the substrate.

**M. Rosillo, E. Arnáiz, D. Abdi,
J. Blanco-Urgoiti, G. Domínguez,
J. Pérez-Castells*** 3917–3927

Combination of RCM and the Pauson–Khand Reaction: One-Step Synthesis of Tricyclic Structures

Keywords: Pauson–Khand reaction / Metathesis / Cyclization / One-pot reaction / Tricyclic compounds

Solid Catalysts



Amberlite IRA900F (Amb-F) is an efficient metal-free catalyst for activation of Si–N and Si–O bonds and a mild base in

a variety of organic transformations under solvent-free conditions.

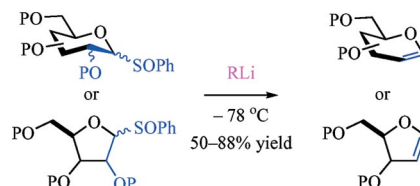
**F. Fringuelli,* D. Lanari, F. Pizzo,
L. Vaccaro*** 3928–3932

Amberlite IRA900F as a Solid Fluoride Source for a Variety of Organic Transformations under Solvent-Free Conditions

Keywords: Supported catalysts / Green chemistry / Nitro compounds

Glycols from Sulfoxides

Pyranoid and furanoid glycols can be conveniently prepared from glycosyl sulfoxides by treatment with organolithium reagents at low temperature.



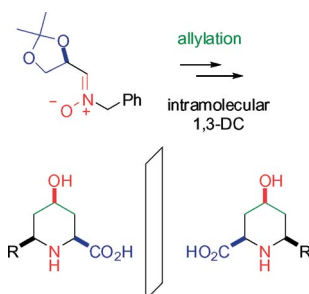
**A. M. Gómez,* M. Casillas, A. Barrio,
A. Gawel, J. C. López*** 3933–3942

Synthesis of Pyranoid and Furanoid Glycols from Glycosyl Sulfoxides by Treatment with Organolithium Reagents

Keywords: Glycosyl sulfoxides / Organolithium reagents / Pyranoid glycols / Furanoid glycols / Sulfoxide ligand exchange

Nitrone Chemistry

By using a D-glyceraldehyde-derived nitrone as the only chiral source the enantio-divergent synthesis of all-*cis* 6-substituted 4-hydroxypipelicolic acid derivatives has been achieved by sequential allylation and intramolecular cycloaddition of nitrones. The cycloaddition takes place by a hitherto unknown 2-aza-Cope rearrangement, as demonstrated by the observed cycloadducts.



**P. Merino,* V. Mannucci,
T. Tejero** 3943–3959

Exploring Nitrone Chemistry: Towards the Enantiodivergent Synthesis of 6-Substituted 4-Hydroxypipelicolic Acid Derivatives

Keywords: Pipelicolic acids / Piperidines / Nitrones / Nucleophilic Addition / Cycloaddition / Cope rearrangement / Allylation

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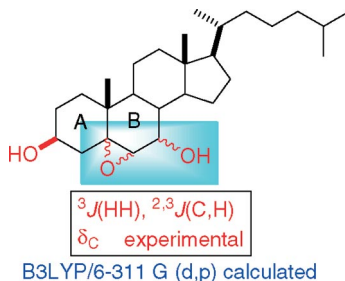
J-Based Analysis and DFT–NMR

J. J. Poza, C. Jiménez,*
J. Rodríguez* 3960–3969



J-Based Analysis and DFT–NMR Assignments of Natural Complex Molecules: Application to 3 β ,7-Dihydroxy-5,6-epoxy-cholestanes

Keywords: Steroids / NMR spectroscopy / Density functional calculations / J-Based analysis



An exhaustive QM-J-based analysis has been used to replicate the experimental H–H and C–H coupling constants and ^{13}C NMR chemical shifts. Also, the B3LYP GIAO methodology with the 6-311-G(d,p) basis set shows that data obtained from rings A and B are sufficient to calculate the correct stereochemistry of the 5,6-epoxy and 7-hydroxy groups.

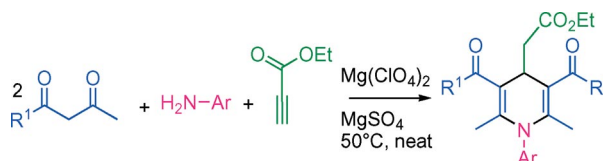
1,4-Dihydropyridine Synthesis

G. Bartoli, M. Bosco, P. Galzerano,
R. Giri, A. Mazzanti, P. Melchiorre,
L. Sambri* 3970–3975



Multicomponent Domino Reaction Promoted by $\text{Mg}(\text{ClO}_4)_2$: Highly Efficient Access to Functionalized 1,4-Dihydropyridines

Keywords: Multicomponent reactions / Magnesium perchlorate / Nitrogen heterocycles / Solvent-free conditions / Atropisomers



Substituted 1,4-dihydropyridines are easily obtained by a multicomponent one-pot and solvent-free condensation between aromatic amines, β -keto derivatives and ethyl propiolate mediated by $\text{Mg}(\text{ClO}_4)_2$. Con-

formational isomers generated from the use of *ortho*- or *meta*-substituted arylamines have been submitted to an NMR study to calculate the energy barriers involved in their interconversion.

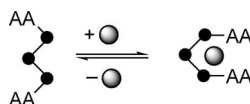
Reversible Folding Inducers

R. Annunziata,* M. Benaglia, A. Puglisi,
L. Raimondi, F. Cozzi* 3976–3983



Synthesis of Some 2,2':6',2''-Terpyridines Disubstituted in Positions 6 and 6'' with Head-to-Tail Oriented Amino Acids and Dipeptides: A Simple Entry to a Reversible Inducer of Folding in Amino Acid Sequences

Keywords: Conformational analysis / Terpyridines / Folding / Amino acids / Peptides



Fold and unfold: A terpyridine scaffold has been developed as a reversible inducer of folding of amino acids or dipeptide sequences by metal complexation/decomplexation or by protonation/deprotonation.

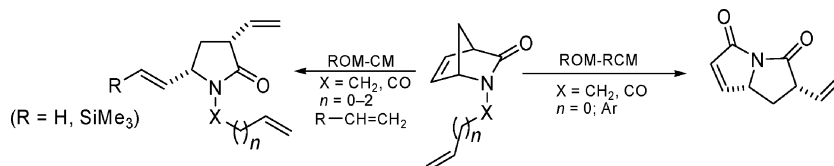
Metathesis Reactions

A. Aljarilla, J. Plumet* 3984–3990



Tuning the Chemoselectivity of the Metathesis Reactions of *N*-Substituted 2-Azabicyclo[2.2.1]hept-5-en-3-one

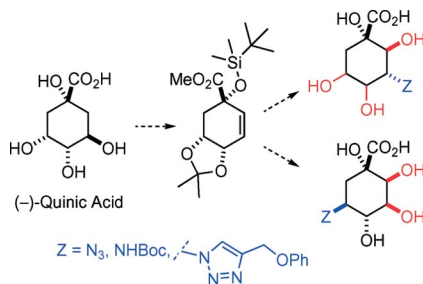
Keywords: Metathesis / Pyrrolidinone / Pyrrolizidinone / Hoveyda–Grubbs catalyst / Aza compounds / Bicyclic compounds



The chemoselectivity of the metathesis reactions of *N*-substituted 3-oxo-2-azanobornene derivatives may be tuned by using

the second-generation Hoveyda–Grubbs catalyst.

The synthesis of polyhydroxylated γ -azido and γ -amino acids from (–)-quinic acid is described. The reactivity of highly functionalized azides **2** and **4a** with alkynes by click chemistry has been explored and is demonstrated in the cases of triazoles **5** and **6**.

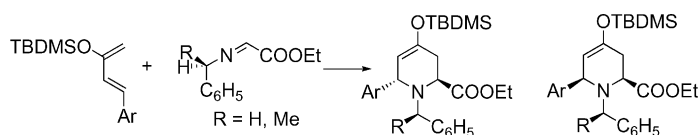


V. F. V. Prazeres, L. Castedo,
C. González-Bello* 3991–4003

Stereoselective Synthesis of Novel Cyclic γ -Amino Acids and Triazole Derivatives

Keywords: Cyclic γ -amino acids / Regioselectivity / Click chemistry / (–)-Quinic acid

Imino Cycloaddition



The diastereoselectivity of the process depends on the aryl group

New 6-aryl-4-oxopipercolic acid derivatives have been prepared by imino-Diels–Alder reactions. The effect on the reactivity and diastereoselectivity produced by the aro-

matic ring has been studied. Solid-supported imines yielded the *N*-deprotected cycloadducts by direct cleavage from the resin with no diastereoselectivity.

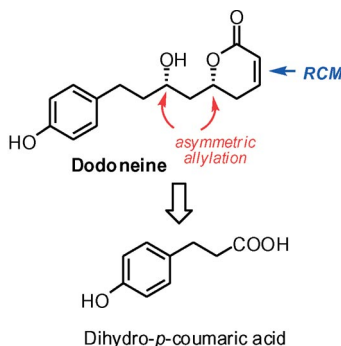
E. Caballero,* J. Figueroa, P. Puebla,
R. Peláez, F. Tomé,
M. Medarde 4004–4014

Imino-Diels–Alder Reactions of 1-Aryl-3-(trialkylsiloxy)-1,3-butadienes in Solution and the Solid Phase

Keywords: 1-Aryl-3-siloxy-1,3-butadienes / Ptercolic acid / Diastereoselectivity / Solid-phase synthesis / Diels–Alder reactions

Natural Product Synthesis

The first total synthesis of the naturally occurring dihydropyranone dodoneine is reported. Asymmetric allylation reactions were used for the stereoselective generation of the two stereogenic centers. The pyranone ring was created by ring-closing metathesis.

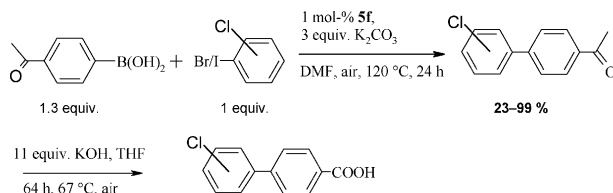


P. Álvarez-Becedo, E. Falomir,* J. Murga,
M. Carda, J. A. Marco* 4015–4018

Stereoselective Synthesis of the Naturally Occurring 2-Pyranone Dodoneine

Keywords: Dodoneine / Oxygen heterocycles / Dihydropyranones / Allylation / Asymmetric synthesis / Ring-closing metathesis

Suzuki Reaction Promotion



Several novel diimines (Salen-type ligands **2**) and their reduced diamine counterparts **3** form Pd complexes **4** and **5**. Employment

of the isolated complexes **4e** and **5f** yield polychlorinated biphenyls (PCBs) according to the Suzuki cross-coupling protocol.

T. Kymälä, N. Kuuloja, Y. Xu,
K. Rissanen, R. Franzén* 4019–4024

Synthesis of Chlorinated Biphenyls by Suzuki Cross-Coupling Using Diamine or Diimine-Palladium Complexes

Keywords: Diimine ligands / Diamine ligands / Palladium complexes / Suzuki cross-coupling / Biaryl compounds / Polychlorinated biphenyls (PCBs) / Biphenylcarboxylic acids (BCAs) / Suzuki reaction

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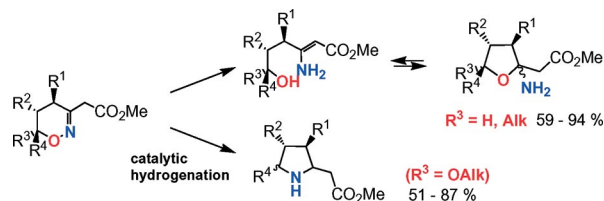
Transformation of Oxazines

A. Yu. Sukhorukov, A. V. Lesiv,
O. L. Eliseev, Yu. A. Khomutova,
S. L. Ioffe,* A. O. Borissova ... 4025–4034



Catalytic Hydrogenation of 5,6-Dihydro-4*H*-1,2-oxazines Bearing a Functionalized Methylene Group at C-3

Keywords: Oxazines / Reduction / Furan-
amines / Imines / Amino acids



Readily available methyl 2-(5,6-dihydro-4*H*-1,2-oxazin-3-yl)acetates **6** under catalytic hydrogenation conditions undergo selective N–O bond cleavage to give dynamic mixtures of enamines **7** and tetra-

hydro-2-furanamines **7'** or substituted pyrrolidines **13**. The products **7** ⇌ **7'** can be further transformed into dihydrofuran derivatives and 1,4-amino alcohols.

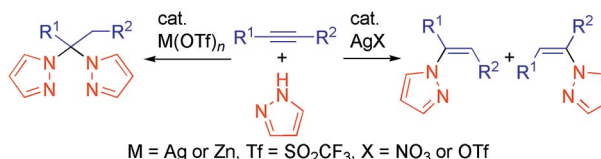
Addition Reactions

T. Tsuchimoto,* K. Aoki, T. Wagatsuma,
Y. Suzuki 4035–4040



Lewis Acid Catalyzed Addition of Pyrazoles to Alkynes: Selective Synthesis of Double and Single Addition Products

Keywords: Addition reactions / Alkynes / Nitrogen heterocycles / Regioselectivity / Synthetic methods



The addition of pyrazoles to alkynes with broad substrate scope was realized for the first time in the presence of a Lewis acid catalyst. The notable feature of this meth-

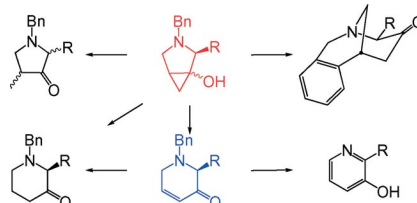
odology is that the appropriate selection of the Lewis acid catalyst allows us to change the reaction course between the double and single addition.

Enantioselective Synthesis

M. Jida, J. Ollivier* 4041–4049

Convergent and Selective Synthesis of Pyrrolidinones, Piperidinones, Dihydropyridinones and Pyridinols from a Common Intermediate – Potential Precursors of Bioactive Products

Keywords: Asymmetric synthesis / Fused-ring systems / Nitrogen heterocycles / Radical reactions / Titanium



Azabicyclo[3.1.0]hexan-1-ols undergo either base-catalyzed rearrangement to give racemic pyrrolidinones and piperidinones or oxidation to furnish chiral dihydropyridinones or chiral tricyclopiperidinones, whereas the palladium-mediated hydrogenation of the intermediate dihydropyridinones led to chiral piperidinones and pyridinols.

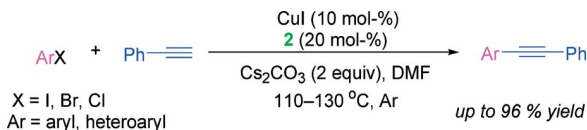
Copper-Catalyzed Alkynylation

M. Wu, J. Mao,* J. Guo,
S. Ji 4050–4054



The Use of a Bifunctional Copper Catalyst in the Cross-Coupling Reactions of Aryl and Heteroaryl Halides with Terminal Alkynes

Keywords: Alkynes / Halides / Copper / Bifunctional catalysts



Copper-catalyzed cross-coupling reactions of aryl and heteroaryl halides with terminal alkynes were carried out in DMF at 110–130 °C to provide the corresponding coupling products in satisfactory-to-good yields

by using inexpensive 8-hydroxyquinoline (**2**) as the ligand. The bifunctional copper catalyst was successfully used in this alkynylation reaction for the first time.

* Author to whom correspondence should be addressed.

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