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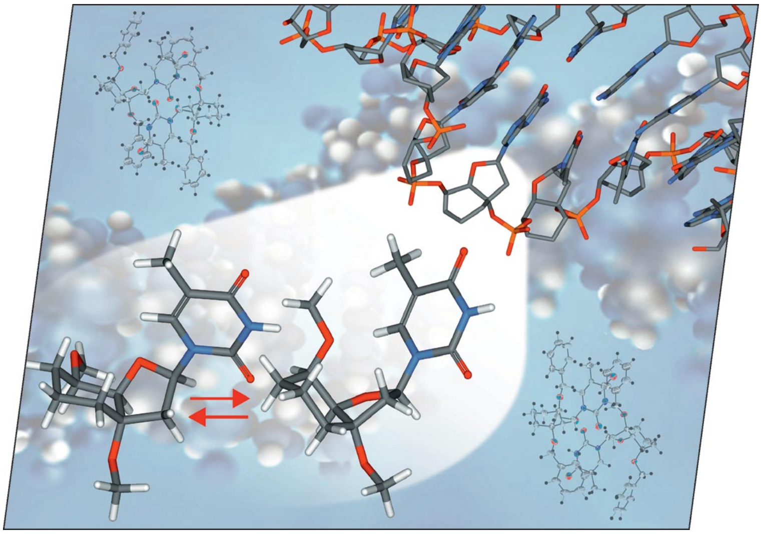
A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further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

COVER PICTURE

The cover picture shows two low-energy conformations of monomeric units of [4.3.0]bicyclo-DNA, a conformationally restricted DNA analogue. In an energy-minimized double helix containing a fully modified strand paired against its complementary DNA, the [4.3.0]bicyclo-DNA sugar arranges in such a way that O(5′) adopts a pseudoaxial orientation. In the article by A. Stauffiger and C. J. Leumann on p. 1153ff the synthesis of the modified DNA building block, the X-ray structure of the monomeric unit as well as thermal melting properties of oligonucleotides are discussed. The authors would like to thank Michael Eggli for his help in designing the cover picture.



CONTENTS

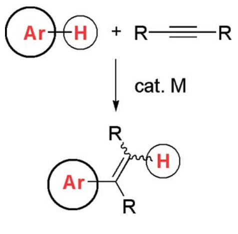
MICROREVIEW

Hydroarylation of Alkynes

T. Kitamura* **1111–1125**

Transition-Metal-Catalyzed Hydroarylation Reactions of Alkynes Through Direct Functionalization of C–H Bonds: A Convenient Tool for Organic Synthesis

Keywords: Hydroarylation / Alkynes / Transition metals / C–H Functionalization / Alkenylation / Synthetic methods



Hydroarylation of alkynes is an efficient and atom-economic process that directly introduces alkenyl moieties into aromatic substrates. This microreview focuses on hydroarylation catalyzed by transition metals through direct functionalization of C–H bonds, affording aromatic alkenes, diarylalkanes, heterocycles, carbocycles, and arylbutadienes.

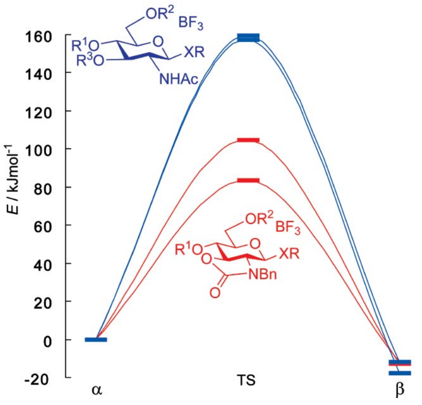
SHORT COMMUNICATIONS

endo-Cleavage of Pyranosides

H. Satoh,* J. Hutter, H. P. Lüthi, S. Manabe, K. Ishii, Y. Ito **1127–1131**

Low-Barrier Pathway for *endo*-Cleavage Induced Anomerization of Pyranosides with *N*-Benzyl-2,3-*trans*-oxazolidinone Groups

Keywords: Anomerization / Carbohydrates / Density functional calculations / Transition states / Protecting groups



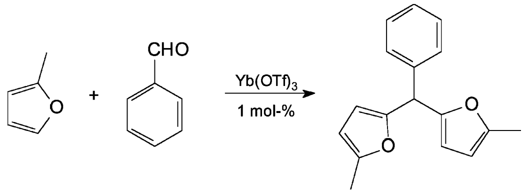
endo-Cleavage induced anomerization reactions were experimentally (by reduction reactions) and theoretically investigated. BLYP/6-31G(d,p) calculations showed that for pyranosides with 2,3-*trans*-oxazolidinones, BF_3 induces *endo*-cleavage followed by rotation of the C1–C2 bond to give the α form via lower-energy transition states.

Ytterbium Triflate Catalysis

S. Genovese,* F. Epifano, C. Pelucchini, M. Curini **1132–1135**

Preparation of Triaryl- and Triheteroarylmethanes under Ytterbium Triflate Catalysis and Solvent-Free Conditions

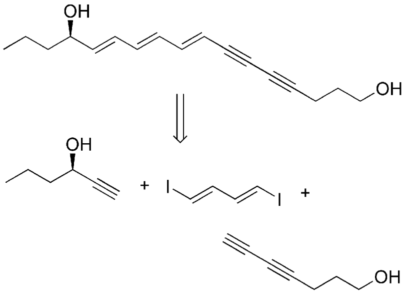
Keywords: Triarylmethanes / Triheteroarylmethanes / Ytterbium / Activated arenes / Condensation reactions



Ytterbium triflate was shown to be an effective catalyst in promoting the synthesis of triaryl- and triheteroarylmethanes from differently substituted aldehydes and 2-methylfuran or methoxybenzene, respectively.

Natural Product Synthesis

A concise synthesis of the natural polyenyne R-(−)-cicutoxin (**1**) is described. After several trials, the successful synthesis commenced with three key fragments, R-(−)-1-hexyn-3-ol (**8**), 1,4-diiodo-1,3-butadiene (**9**), and THP-protected 4,6-heptadiyn-1-ol (**6**). The triply convergent synthesis gave R-(−)-cicutoxin in 18% overall yield.

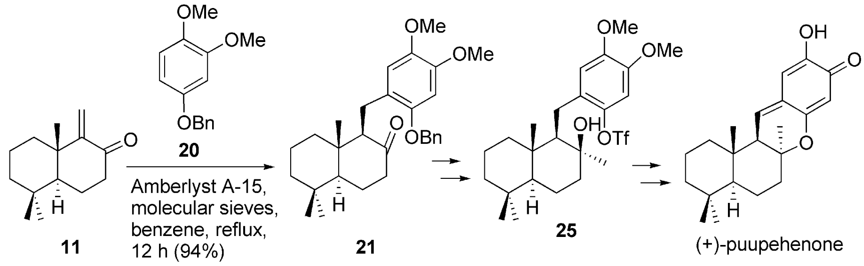


B. W. Gung*, A. O. Omollo ... 1136–1138

A Concise Synthesis of R-(−)-Cicutoxin, a Natural 17-Carbon Polyenyne

Keywords: Total synthesis / Biological activity / Natural products / Enynes / Conjugation

Marine Metabolites



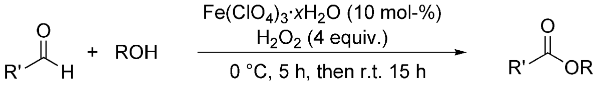
A new methodology for synthesizing bioactive merosesquiterpenes, such as the marine (+)-puupehenone and related metabolites, is reported. The sequence involves a cationic-resin-promoted Friedel–Crafts alkylation of an aryl ether with a norsesquiterpene α,β-enone and further C–O coupling catalyzed by palladium.

**E. Alvarez-Manzaneda,* R. Chahboun,
E. Cabrera, E. Alvarez, A. Haidour,
J. M. Ramos, R. Alvarez-Manzaneda,
R. Tapia, H. Es-Samti, A. Fernández,
I. Barranco 1139–1143**

A Convenient Enantiospecific Route towards Bioactive Merosesquiterpenes by Cationic-Resin-Promoted Friedel–Crafts Alkylation with α,β-Enones

Keywords: Terpenoids / Arenes / Aromatic substitution / Cyclization / Biological activity

Iron Catalysis



A highly efficient, mild, and simple protocol for the direct oxidative esterification of aromatic and aliphatic aldehydes with simple alcohols was accomplished by using a catalytic amount of $Fe(ClO_4)_3\cdot xH_2O$ with hydroperoxide as an oxidant.

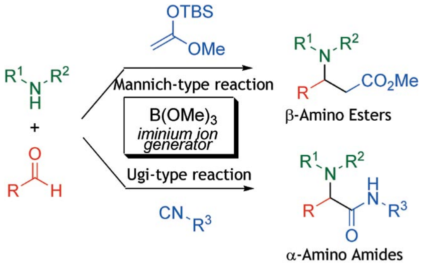
X.-F. Wu, C. Darcel* 1144–1147

Iron-Catalyzed One-Pot Oxidative Esterification of Aldehydes

Keywords: Iron / Esterification / Aldehydes / Homogeneous catalysis / Oxidation

Iminium Ion Generator

Trimethoxyborane serves as an inexpensive and virtually nonacidic iminium ion generator, allowing Mannich-type reaction of aldehydes, secondary amines, and ketene silyl acetals to afford β-amino esters. The reagent also allowed nonacidic Ugi-type three-component coupling of aldehydes, secondary amines, and isocyanides, which leads to the formation of α-amino acid derivatives.



**Y. Tanaka, K. Hidaka, T. Hasui,
M. Suginome* 1148–1151**

$B(OMe)_3$ as a Nonacidic Iminium Ion Generator in Mannich- and Ugi-Type Reactions

Keywords: Amination / Nucleophilic addition / Boron / Iminium ions / Amino acids

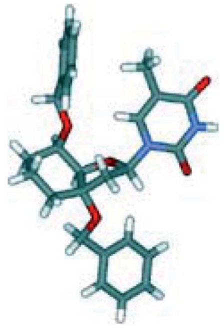
FULL PAPERS

Bicyclonucleosides

A. Stauffiger,
C. J. Leumann* 1153–1162

Screening the Structural Space of Bicyclo-DNA: Synthesis and Thermal Melting Properties of bc^{4,3}-DNA

Keywords: Oligonucleotides / Nucleosides / RNA recognition / DNA structures / Nucleosides



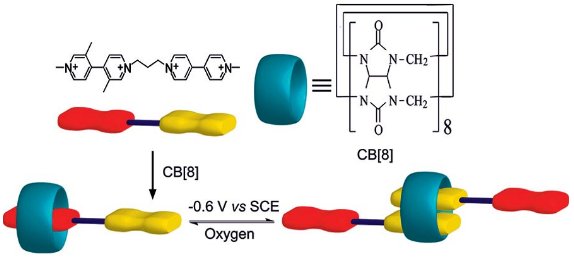
A novel member of the bicyclonucleoside family [4.3.0]bicyclothymidine was synthesized and incorporated into oligodeoxynucleotides. Their pairing properties to complementary DNA and RNA were investigated and found to be similar to that of the known [3.3.0]bicyclo-DNA.

Supramolecular Device

S. Andersson, D. Zou, R. Zhang, S. Sun,
B. Åkermark, L. Sun* 1163–1172

Selective Positioning of CB[8] on Two Linked Viologens and Electrochemically Driven Movement of the Host Molecule

Keywords: Cyclic voltammetry / Host-guest systems / Molecular devices / Inclusion compounds / Supramolecular chemistry



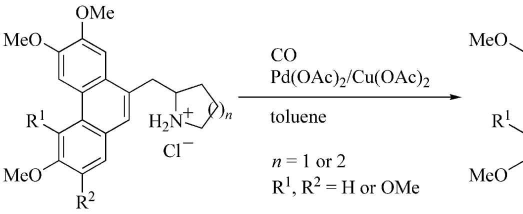
The host CB[8] was selectively positioned on the DMV moiety of a DMV-MV molecular dyad and subsequently moved to the MV moiety through an electrochemical reduction. The host was moved back to the DMV moiety by oxidation. The ability to reversible move the host from one guest to another contributes to the fundamental understanding required for the design of more advanced molecular devices.

Pd-Catalyzed Carbonylation

S. Yamashita, N. Kurono, H. Senboku,
M. Tokuda, K. Orito* 1173–1180

Synthesis of Phenanthro[9,10-*b*]indolizidin-9-ones, Phenanthro[9,10-*b*]quinolizidin-9-one, and Related Benzolactams by Pd(OAc)$_2$-Catalyzed Direct Aromatic Carbonylation

Keywords: Palladium / Carbonylation / Benzolactams / Nitrogen heterocycles



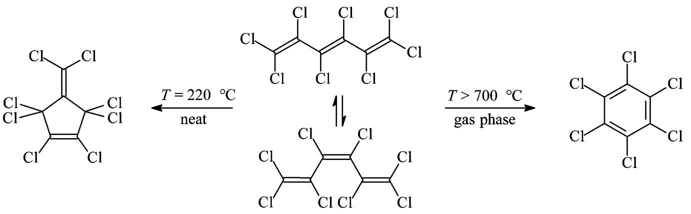
Phenanthro[9,10-*b*]indolizidin-9-ones, phenanthro[9,10-*b*]quinolizidin-9-one, and related benzolactams were obtained by phosphane-free Pd(OAc)$_2$-catalyzed direct aromatic carbonylation from the corresponding amines. This constitutes a formal synthesis of the representative phenanthroindolizidine and -quinolizidine alkaloids (±)-tylophorine, (±)-antofine, and (±)-cryptopleurine.

Thermal Rearrangements

H. Detert,* D. Lenoir,
H. Zipse* 1181–1190

Thermal Rearrangements of Perchlorohexatrienes–Structures and Experimental and Theoretical Evaluation of Pathways to Isomerization and Cyclization

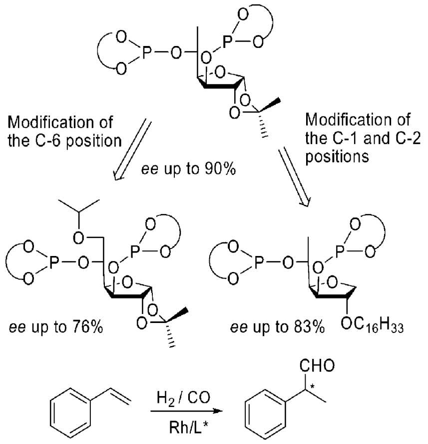
Keywords: Perchlorinated compounds / Isomerization / Cyclization / Pyrolysis / Aromaticity / Thermochemistry / Ab initio calculations



Ab initio calculations and pyrolysis experiments are combined to investigate the unique chemical behavior of perchloroalkenes. Thermolysis of perchlorohexatrienes in the condensed and in the gas phase result in *cis*/*trans* isomerisation followed by cyclization to cyclopentene or hexachlorobenzene.

Asymmetric Hydroformylation

New diphosphite ligands derived from 1,2:5,6-di-*O*-isopropylideneglucofuranose have been synthesized and successfully tested in the rhodium-catalyzed asymmetric hydroformylation of styrene. The modification of the carbohydrate backbone and diphosphite bridge affects the activity and selectivity of the reaction.

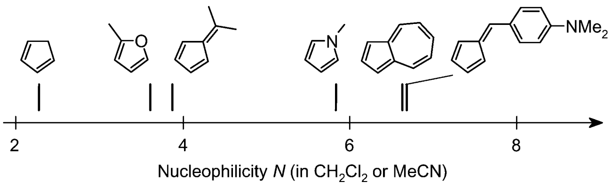


A. Gual, C. Godard, C. Claver,*
S. Castillón* **1191–1201**

C_1-Symmetric Diphosphite Ligands Derived from Carbohydrates: Influence of Structural Modifications on the Rhodium-Catalyzed Asymmetric Hydroformylation of Styrene

Keywords: Phosphorus / Carbohydrates / Asymmetric catalysis / Hydroformylation / Styrene

Reactivity



The kinetics of the reactions of benzhydrylium ions with azulene and a series of fulvenes were determined and analyzed according to the correlation $\log k(20\,°C) = s(N + E)$. The nucleophilicities (N) of the title compounds allowed for the comparison of their reactivities with those of other π-systems and will guide synthetic chemists to explore further electrophilic reaction partners.

M. Kędziorek, P. Mayer,
H. Mayr* **1202–1206**

Nucleophilic Reactivities of Azulene and Fulvenes

Keywords: Carbocations / Aromaticity / Kinetics / Linear free energy relationships / UV/Vis spectroscopy / Nucleophilic addition

Double H-Bond Activation

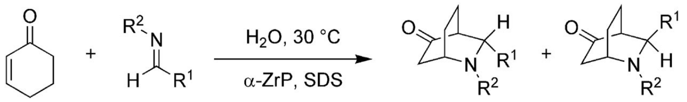
The bifurcated and cooperative complexation of carbonyls with double-site hydrogen-bond donors were computationally studied. A different activation pattern was found for reactions of distinct polarity, like the Diels–Alder and enamine-aldol reactions.

E. Gómez-Bengoa* **1207–1213**

DFT Studies on Double Hydrogen Bond Catalysis of Reactions of Distinct Polarity

Keywords: Density functional calculations / Hydrogen bonds / Cycloaddition / Aldol reactions

Brønsted Heterogeneous Catalysis



The direct aza-Diels–Alder reaction between 2-cyclohexen-1-one and benzaldimines in water has been efficaciously catalyzed by layered α-zirconium hydrogen phosphate (α-ZrP) in the presence of sodium dodecyl sulfate . The one-pot, three-component version of the reaction and the recycling of both the catalyst and the aqueous mother liquor in toto have also been investigated.

U. Costantino, F. Fringuelli, M. Orrù,
M. Nocchetti, O. Piermatti,*
F. Pizzo **1214–1220**

Direct Aza-Diels–Alder Reaction in Water Catalyzed by Layered α-Zirconium Hydrogen Phosphate and Sodium Dodecyl Sulfate

Keywords: Heterogeneous catalysis / Layered compounds / Green chemistry / Multicomponent reactions / Azo compounds

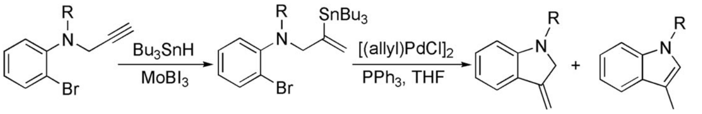
CONTENTS

Cross Couplings

H. Lin, U. Kazmaier* 1221–1227

Molybdenum-Catalyzed α-Hydrostannations of Propargylamines as the Key Step in the Synthesis of N-Heterocycles

Keywords: Hydrostannation / Indoles / Molybdenum / Nitrogen heterocycles / Stille couplings / Stannanes



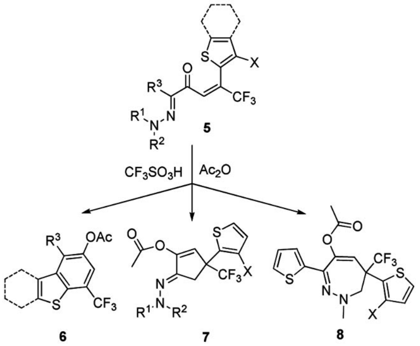
The Mo-catalyzed hydrostannation of propargylic amines and amides gave rise to functionalized vinylstannanes in good yield. Starting from halogenated aromatic amines, indoles and isoquinolines were accessible through intramolecular Stille couplings.

Superelectrophilic Cyclizations

N. Ghavtadze, R. Fröhlich,
E.-U. Würthwein* 1228–1240

Cyclization Reactions of 1-Amino-5-trifluoromethyl-5-thienyl-1-azapenta-1,4-dien-3-ones under Superelectrophilic Conditions: Synthesis of Novel Benzothiophenols, Cyclopentenols and Dihydrodiazepinols

Keywords: Aza compounds / Cyclization / Cations / Ab initio calculations / Heterocycles



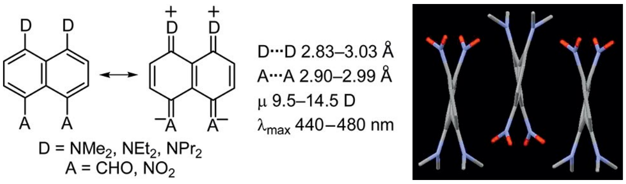
CF$_3$-substituted 1-amino-5-thienyl-1-aza-1,4-dien-3-ones **5** undergo three different cyclization reactions upon treatment with an excess of triflic acid, leading to novel five-, six- and seven-membered carbo- and heterocycles depending on the substitution pattern. The cyclization reactions are believed to proceed under superelectrophilic conditions involving mono- and dicationic intermediates.

Push–Pull Proton Sponges

V. A. Ozeryanskii,* A. F. Pozharskii,
A. K. Artaryan, N. V. Vistorobskii,
Z. A. Starikova 1241–1248

1,8-Bis(dialkylamino)-4,5-dinitronaphthalenes and 4,5-Bis(dimethylamino)naphthalene-1,8-dicarbaldehyde as "Push–Pull" Proton Sponges: When and Why Formyl Groups Become Stronger π-Electron Acceptors than Nitro Group

Keywords: Push–pull systems / Donor–acceptor systems / Proton sponges / *peri*-Interaction / Conjugation / Nitronaphthalenes



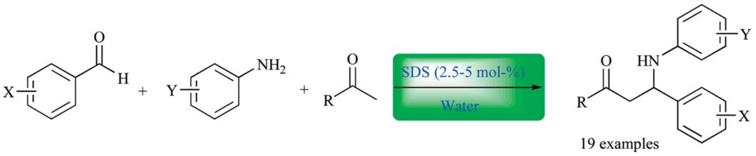
Experimental and theoretical studies of a series of 1,8-bis(dialkylamino)-4,5-dinitronaphthalenes and a *peri*-dialdehyde analogue have unexpectedly disclosed essentially higher π-acceptor ability of the CHO groups in the solid and gas phase compared to the NO$_2$ groups. In solution, the through-conjugation is almost equally effective for all molecules, with some predominance of the nitro compounds.

Click Mannich Reaction

A. A. Jafari,* F. Moradgholi,
F. Tamaddon 1249–1255

Pronounced Catalytic Effect of a Micellar Solution of Sodium Dodecylsulfate (SDS) Upon a Three-Component Reaction of Aldehydes, Amines, and Ketones Under Neutral Conditions

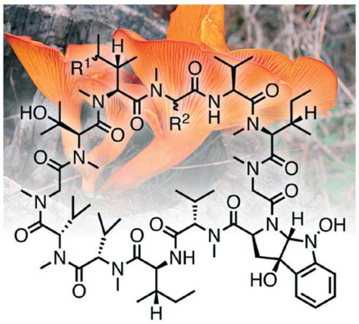
Keywords: Click chemistry / Green chemistry / Water / Micelles / Surfactants / Mannich bases / β-Amino ketones



A micellar solution of sodium dodecylsulfate (SDS) efficiently catalyzes a three-component Mannich reaction in neutral pure water at room temperature. The products precipitate in good to excellent yields. The salient features of this protocol include the use of water as a eivronmentally friendly solvent, low SDS loading, neutral conditions, high yields, excellent regio- and stereoselectivity, and clean reaction profiles.

Cyclopeptide Natural Products

Omphalotins E–I, modified cyclododecapeptides, were isolated from cultures of *Omphalotus olearius*. Four of the five omphalotins contained an unprecedented *N*-hydroxylated tryptophan derivative. All compounds exhibited strong and selective nematicidal activity against the plant pathogen *Meloidogyne incognita*, whereas no cytotoxic effects were found.

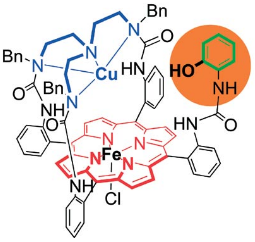


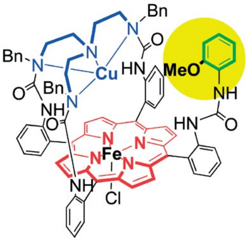
**J. C. Liermann, T. Opatz,*
H. Kolshorn, L. Antelo, C. Hof,
H. Anke** **1256–1262**

Omphalotins E–I, Five Oxidatively Modified Nematicidal Cyclopeptides from *Omphalotus olearius* 💻

Keywords: Natural products / NMR spectroscopy / Structure elucidation / Peptides

Biomimetic Dioxygen Reduction





Fe and Fe-Cu complexes of a super-structured porphyrin derivative have been studied for their ability to reduce dioxygen once adsorbed onto the surface of a rotating graphite electrode.

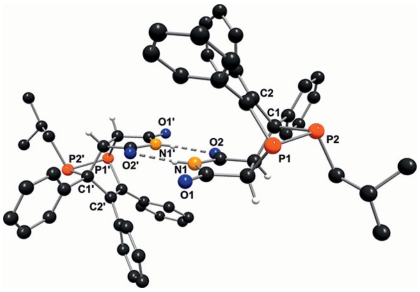
**G. Charalambidis,
K. Ladomenou, B. Boitrel,
A. G. Coutsolelos*** **1263–1268**

Synthesis and Studies of a Super-Structured Porphyrin Derivative – A Potential Building Block for C*c*O Mimic Models 💻

Keywords: Mimic models / Porphyrinoids / Enzyme models / Metalloenzymes / Oxidase / Dioxygen / Copper / Iron

Cycloaddition Reactions

1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes **1** can act both as dienes and as dienophiles in cycloaddition reactions, similar to 2*H*-phospholes. However, in contrast to 2*H*-phospholes, the cyclodimerization reactions of **1** occur only under harsh reaction conditions to give a [2+2] cycloaddition product.



**V. Miluykov,* I. Bezkishko,
A. Zagidullin, O. Sinyashin, P. Lönnecke,
E. Hey-Hawkins** **1269–1274**

Cycloaddition Reactions of 1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes 💻

Keywords: Cycloaddition / Phosphacyclopentadienes / Phosphorus heterocycles / Phosphorus

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* Author to whom correspondence should be addressed.

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