C–C Coupling

The development of metal-catalyzed cross-coupling reactions over the past 30 years has revolutionized the way carbon-carbon bonds between sp and sp² carbon atoms are formed. These methods have profoundly changed the protocols for the construction of natural products, building blocks for supramolecular chemistry and self-assembly, organic materials and polymers, and lead compounds in medicinal chemistry from simpler entities. The 2010 Nobel prize in chemistry for E. Negishi, R. Heck, and A. Suzuki underlines the importance of direct bond formation between carbon atoms.

Read the laureates' lectures:


Find all articles on C–C coupling in Wiley Online Library...

Recent Articles

- **Synthesis of Iron Oxide Palladium Nanoparticles and Their Catalytic Applications for Direct Coupling of Acyl Chlorides with Alkynes**
  - Creating new bonds: A new, magnetic, silica-based palladium nanocatalyst has been synthesized and applied for the first time in the direct coupling of acyl chlorides with terminal alkynes to prepare a variety of ynones under copper-free, phosphine-free, and aerobic conditions at room temperature without relying on additives or inert conditions.

- **Nitroxyl-Radical-Catalyzed Oxidative Coupling of Amides with Silylated Nucleophiles through N-Halogenation**
  - A halo to make them shine: A high-yielding nitroxyl-radical-catalyzed oxidative coupling reaction between amines protected with an electron-withdrawing group and silylated nucleophiles proceeded through the activation of N-halogenated amides by the nitroxyl-radical catalyst to give imines. The N-halogenated amide intermediates were generated in situ from amides by treatment with a halogenation reagent (see scheme).

- **Sequential Functionalization of Alkynes and Alkenes Catalyzed by Gold(I) and Palladium(II) N-Heterocyclic Carbene Complexes**
  - Golden combination: The iodination of terminal alkynes using N-iodosuccinimide in the presence of a AuI-NHC (NHC=N-heterocyclic carbene) catalyst was achieved in good to excellent yields under mild reaction conditions. The resulting 1-idoalkynes were used as organic building blocks for the synthesis of trisubstituted (2)-fluoroalkenes in two sequential
The selective AuI-catalyzed hydrofluorination to yield (Z)-2-fluoro-1-iodoalkenes, followed by a Suzuki–Miyaura cross-coupling with aryl boronic acids catalyzed by a PdII-NHC complex.

Alberto Gómez-Herrera, Fady Nahra, Marcel Brill, Steven P. Nolan, Catherine S. J. Cazin
ChemCatChem, September 26, 2016, DOI: 10.1002/cctc.201600868. Read article

Generation of an 4-Isoxazolyl Anion Species: Facile Access to Multifunctionalized Isoxazoles

Taking position: Preparation of a 4-isoxazolyl anion species from 4-iodoisoxazole using iPrMgCl⋅LiCl enabled introduction of a wide variety of functional groups into the 4-position of the isoxazole ring in good to excellent yields. This approach provides various isoxazolyl metal species which can be used for multifunctionalization of isoxazoles. The step-by-step synthesis of 3,4,5-trisubstituted isoxazoles was achieved by using the this 4-isoxazolyl anion method.

Taiki Morita, Shinichiro Fuse, Hiroyuki Nakamura

Surface-Functionalized Electrospun Titania Nanofibers for the Scavenging and Recycling of Precious Metal Ions

Must have the precious: Precious metals are widely used as catalysts in industry. It is of critical importance to keep the precious metal ions leached from catalysts at a level below one part per million (ppm) in final products and to recycle the expensive metals. Precious metal ions were scavenged by surface-functionalized electrospun TiO₂ nanofibers and further recycled for use as catalysts. This system can be potentially applied in pharmaceutical industry.

Yunqian Dai, Eric Formo, Haoxuan Li, Jiajia Xue, Younan Xia
ChemSusChem, September 23, 2016, DOI: 10.1002/cssc.201600787. Read article

Palladium(II)@Zirconium-Based Mixed-Linker Metal–Organic Frameworks as Highly Efficient and Recyclable Catalysts for Suzuki and Heck Cross-Coupling Reactions

In the mix: It is possible to control the density of the introduced active centers by adjusting the feed ratio of the linkers that contain functional groups during the synthesis of metal–organic frameworks. The prepared heterogeneous Pd catalysts are very efficient for Suzuki and Heck cross-coupling reactions with a very low Pd loading and could be recycled in at least 10 cycles.

Rong Sun, Bing Liu, Bo-Geng Li, Suyun Jie
ChemCatChem, September 22, 2016, DOI: 10.1002/cctc.201600774. Read article

[[Pd(µ-OH)Cl(IPr)]2] - a highly efficient precatalyst of Suzuki - Miyaura coupling, able to act also under base-free conditions

Sylwia Ostrowska, Jan Lorkowski, Maciej Kubicki, Cezary Pietraszuk
ChemCatChem, September 10, 2016, DOI: 10.1002/cctc.201600998. Read article

Phosphine-Catalyzed Direct δ-Carbon Addition of Alkynes to Electron-Deficient Carbonyl-Group-Containing Compounds: Preparation of Conjugated Dienes

All about the δ Carbon: The unexplored δ-carbon of alkynes could be activated as a nucleophilic reaction site and trapped by electron-deficient carbonyl-group-containing compounds upon phosphine catalysis, providing diverse δ-addition and isomerization products in moderate to excellent yields.

Yao-Liang Sun, Xiao-Nan Zhang, Yin Wei, Min Shi
ChemCatChem, September 01, 2016, DOI: 10.1002/cctc.201600811. Read article
Metal-Promoted Coupling Reactions Implying Ligand-Based Redox Changes

Ligand, camera, action! The advent of innovative (catalytic) pathways relying on ligand-based redox events is reviewed in the context of coupling reactions. This cooperative approach between ligand and metal can offer attractive alternatives to the classic two-electron catalytic cycles and foster new reactivities.


Synthesis and Optical Properties of meso-CF₃-BODIPY with Acylethynyl Substituents in the 3-Position of the Indacene Core

Mechanoactivated BODIPY synthesis: BODIPY chromophores, combining a meso-CF₃ group and acylethynyl substituents in one molecule, were synthesized for the first time. The key step is the solid-phase mechanoactivated ethynylation of meso-CF₃-dipyrromethanes by acylbromoacetylenes in Al₂O₃ or K₂CO₃ media.


Silver-Catalyzed Cross-Dehydrogenative Coupling (CDC) Strategy for the Construction of Dialkyl/Dibenzyldibenzo[b,f][1,4]thia-/oxazepin-11-yl Phosphonates

Silver surfer: Medicinally important dialkyl/diaryl dibenzo[b,f][1,4]thia-/oxazepin-11-yl phosphonates were synthesized by the atom-economical cross-dehydrogenative coupling of dibenzothia-/oxazepines and dialkyl/diaryl phosphites.


Palladium-Catalyzed Suzuki–Miyaura Coupling Reactions of Boronic Acid Derivatives with Aryl Chlorides

Improved coupling reactions: A series of new biphenyl N,P-monophosphine ligands L have been developed by introduction of two methoxy groups to the biphenyl backbone. The ligands were found to be much more effective than their counterpart Buchwald ligands in Suzuki–Miyaura coupling reactions of sterically hindered and electron-rich aryl chlorides with aryl boronic acids. A variety of tri-ortho-substituted or tetra-ortho-substituted biaryl or hetero-biaryl were conveniently prepared in up to 99 % yield by using L₁-[Pd₂(dba)₃] (dba=dibenzylideneacetone) as the catalyst.


Structure-Defined 3D Nanocomposite Polymer Networks: Versatile Heterogeneous Catalytic Platforms in Organic Synthesis

Structure-defined 3D catalytic nanocomposite polymer networks were synthesized based on monodisperse polyvinylpyrrolidone (PVP)-stabilized Pd colloidal nanohybrids encapsulated within 1,2-bis-(2-iodoethoxy)ethane (BIEE)-
crosslinked poly(2-dimethylamino)ethyl methacrylate homopolymer networks. These materials were evaluated as heterogeneous catalytic supports in Heck, Suzuki-Miyaura and Sonogashira coupling reactions.


The Hiyama Cross-Coupling Reaction: New Discoveries

In this account recent developments in the Hiyama cross-coupling reaction from 2010 up today are presented. The most important methodology involves formation of biaryl systems by using aryl bromides or iodides and aryl trialkoxy silanes: other variants are far less studied.


Nickel-Catalyzed Borylation of Aryl and Benzyl 2-Pyridyl Ethers: A Method for Converting a Robust ortho-Directing Group


Iron-Catalyzed Cross-Coupling of 1-Alkynylcyclopropyl Tosylates and Related Substrates


Self-Assembled Multilayer-Stabilized Nickel Nanoparticle Catalyst for Ligand-Free Cross-Coupling Reactions: in situ Metal Nanoparticle and Nanospace Simultaneous Organization


Catalytic Efficiency of Primary β-Amino Alcohols and Their Derivatives in Organocatalysis

This review demonstrates the catalytic efficiency of primary β-amino alcohols and their derivatives in organocatalysis. These simple amino alcohols are inexpensive alternatives to other primary amino organocatalysts, being easy to synthesize and air-stable and offering the potential for introduction of different functional groups and alteration of steric sites.


Discogens Possessing Aryl Side Groups Synthesized by Suzuki Coupling of Triphenylene Triflates and Their Self-Organization Behavior
Versatile Suzuki cross-coupling reactions between arylboronic acids and triphenylenyl triflates generate a rich diversity of attractive functional discogens.

[Full Paper]
Ke-Qing Zhao, Yue Gao, Wen-Hao Yu, Ping Hu, Bi-Qin Wang, Benoît Heinrich, Bertrand Donnio

**Water-Soluble C-Scorpionate Complexes – Catalytic and Biological Applications**

Water-soluble carbon homoscorpionates and their coordination chemistry are reviewed. Moreover, the application of the resulting water-soluble tris(pyrazol-1-yl)methane metal complexes as catalysts for C–C bond formation and oxidative functionalization as well as their use as antiproliferative and antimicrobial agents are addressed.

[Microreview]
Luísa M. D. R. S. Martins, Armando J. L. Pombeiro

**Multicomponent Cascade Synthesis of Biaryl-Based Chalcones in Pure Water and in an Aqueous Micellar Environment**

The multicomponent cascade synthesis of biaryl-based chalcones was carried out in pure water and in an aqueous micellar system. The first step of the protocol was a simple Pd-catalysed, ligand-free, and aerobic Suzuki–Miyaura reaction in aqueous medium. The resulting intermediates then underwent an in-situ aldol condensation reaction to give biaryl(hetero)chalcones in good to excellent yields.

[Full Paper]
Nicola Armenise, Danilo Malferrari, Sara Ricciardulli, Paola Galletti, Emilio Tagliavini

**Allylic C–H Activation of Olefins by a TpMe2IrIII Compound**

The IrIII complex \([\text{TpMe}_2\text{Ir(C}_6\text{H}_5)_2(N_2)]\) reacts with different olefins to yield organometallic compounds that derive from allylic C–H activations in processes that also generate organic coupling products that involve the vinylic positions of the olefin.

[Full Paper]
Crispín Cristóbal, Laura L. Santos, Rubén Gutiérrez-González, Eleuterio Alvarez, Margarita Paneque, Manuel L. Poveda

**Triphenylphosphine-Mediated Deoxygenative Reduction of CF3SO2Na and Its Application for Trifluoromethylthiolation of Aryl Iodides**

Efficient synthesis! A low cost method for the generation of CuSCF3 by a triphenylphosphine-mediated deoxygenative reduction of Langlois’ reagent (CF3SO2Na) has been developed (see scheme). This method can be applied for the convenient synthesis of a wide array of ligated and air-stable CuSCF3 complexes. Additionally, the CuSCF3 complexes generated in situ by this protocol were found to trifluoromethylthiolate (hetero)aryl iodides with high efficiency.

Stairway to heaven? In a convergent synthesis of racemic 5-amino[6]hexahelicene (see figure), cross-coupling reactions assemble a pentacyclic framework, with a metal-catalyzed ring closure as the final step. The enantiomers are separated by means of chromatography and the absolute configurations assigned by comparison of the CD spectra with hexahelicene. Furthermore, scanning tunneling microscopy (STM) on Au(111) was performed under ultrahigh vacuum.

Near-IR BODIPY Dyes à la Carte—Programmed Orthogonal Functionalization of Rationally Designed Building Blocks

Versatile functionalization of the BODIPY core: The borondipyrrmethene (BODIPY) system has been derivatized in a versatile manner through a strategy based on orthogonal reactivity (see figure). This has allowed access to some red/NIR-emitting dyes with superior properties to current commercial laser dyes.

Direct Carboxylation of Aryl Tosylates by CO\textsubscript{2} Catalyzed by In situ-Generated Ni\textsuperscript{0}

Direct carboxylation of aryl tosylates by CO\textsubscript{2} is rendered possible by a Ni\textsuperscript{0} catalyst, generated in situ by reduction of [NiBr\textsubscript{2}(bipy)] with manganese metal. This approach, which requires neither a glove-box nor the preparation of a sensitive organometallic derivative, is applicable to a wide range of aromatic phenols, bearing either electron-donating or withdrawing substituents.