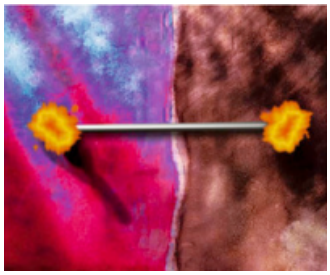
Hot Topics

WILEY-VCH

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 sp^2 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 betweeen carbon atoms.

Read the laureates' lectures:

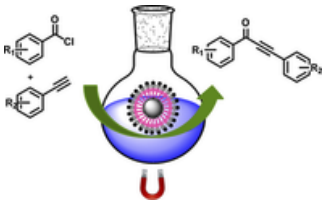
- *Ei-ichi Negishi**
  Magical Power of Transition Metals: Past, Present, and Future (Nobel Lecture)
  Angew. Chem. **2011**, *123*, 6870–6897; *Angew. Chem. Int. Ed.* **2011**, *50*, 6738–6764
- *Akira Suzuki**
  Cross-Coupling Reactions Of Organoboranes: An Easy Way To Construct C–C Bonds (Nobel Lecture)
  Angew. Chem. **2011**, *123*, 6854–6869; *Angew. Chem. Int. Ed.* **2011**, *50*, 6722–6737

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

Recent Articles

RSS feed

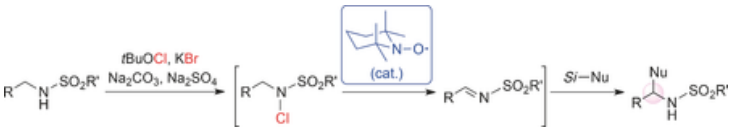
Synthesis of Iron Oxide Palladium Nanoparticles and Their Catalytic Applications for Direct Coupling of Acyl Chlorides with Alkynes



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.

[Full Paper]
Rakesh K. Sharma, Manavi Yadav, Rashmi Gaur, Radhika Gupta, Alok Adholeya, Manoj B. Gawande
ChemPlusChem, September 30, 2016, DOI: 10.1002/cplu.201600321. Read article

Nitroxyl-Radical-Catalyzed Oxidative Coupling of Amides with Silylated Nucleophiles through N-Halogenation

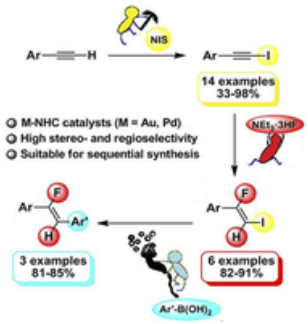


A halo to make them shine: A high-yielding nitroxyl-radical-catalyzed oxidative coupling reaction between amines protected with an electron-withdrawing group and silylated nucleophiles proceeded through the activation of N-halogenated amides by the nitroxyl-radical catalyst to give imines. The N-halogenated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

[Communication]
Katsuhiko Moriyama, Masako Kuramochi, Kozo Fujii, Tsuyoshi Morita, Hideo Togo
Angew. Chem. Int. Ed., September 29, 2016, DOI: 10.1002/anie.201607223. Read article

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 Au^{I}-NHC (NHC=N-heterocyclic carbene) catalyst was achieved in good to excellent yields under mild reaction conditions. The resulting 1-iodoalkynes were used as organic building blocks for the synthesis of trisubstituted (*Z*)-fluoroalkenes in two sequential



steps: The selective Au^{I}-catalyzed hydrofluorination to yield (*Z*)-2-fluoro-1-iodoalkenes, followed by a Suzuki–Miyaura cross-coupling with aryl boronic acids catalyzed by a Pd^{II}-NHC complex.

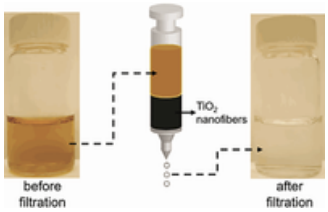
[Full Paper]
Alberto Gómez-Herrera, Fady Nahra, Marcel Brill, Steven P. Nolan, Catherine S. J. Cazin
ChemCatChem, September 26, 2016, DOI: 10.1002/cctc.201600868. Read article

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 *i*PrMgCl·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.

[Communication]
Taiki Morita, Shinichiro Fuse, Hiroyuki Nakamura
Angew. Chem. Int. Ed., September 26, 2016, DOI: 10.1002/anie.201608039. Read article

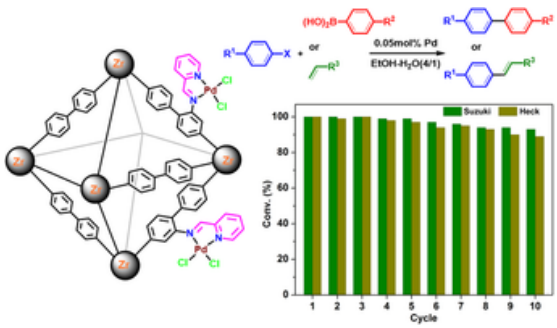
Surface-Functionalized Electrospun Titania Nanofibers for the Scavenging and Recycling of Precious Metal Ions



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 TiO_2 nanofibers and further recycled for use as catalysts. This system can be potentially applied in pharmaceutical industry.

[Communication]
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.

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

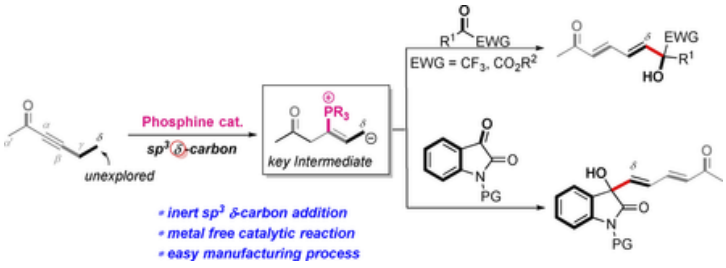
[{Pd(μ-OH)Cl(IPr)}2] - a highly efficient precatalyst of Suzuki - Miyaura coupling, able to act also under base-free conditions

[Communication]
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 Alkynones to Electron-Deficient Carbonyl-Group-Containing Compounds: Preparation of Conjugated Dienes

All about the δ Carbon: The unexplored δ-carbon of alkynones 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.

[Full Paper]
Yao-Liang Sun, Xiao-Nan Zhang, Yin Wei, Min Shi
ChemCatChem, September 01, 2016, DOI: 10.1002/cctc.201600811. Read article

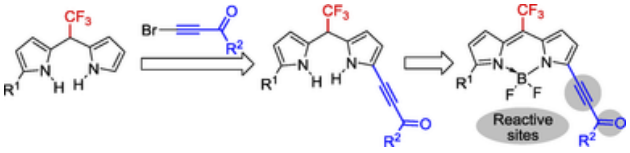


Metal-Promoted Coupling Reactions Implying Ligand-Based Redox Changes

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.

[Minireview]
Jérémy Jacquet, Marine Desage-El Murr, Louis Fensterbank
ChemCatChem, September 01, 2016, DOI: 10.1002/cctc.201600616. Read article

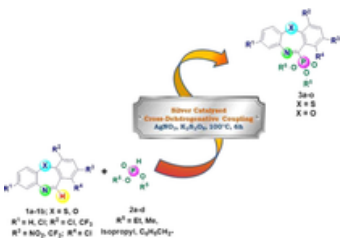
Synthesis and Optical Properties of *meso*-CF_3-BODIPY with Acylethynyl Substituents in the 3-Position of the Indacene Core



Mechanoactivated BODIPY synthesis: BODIPY chromophores, combining a *meso*-CF_3 group and acylethynyl substituents in one molecule, were synthesized for the first time. The key step is the solid-phase mechanoactivated ethynylation of *meso*-CF_3-dipyrromethanes by acylbromoacetylenes in Al_2O_3 or K_2CO_3 media.

[Full Paper]
Denis N. Tomilin, Konstantin B. Petrushenko, Lyubov N. Sobenina, Maxim D. Gotsko, Igor A. Ushakov, Anna D. Skitnevskaya, Alexander B. Trofimov, Boris A.Trofimov
Asian J. Org. Chem., August 30, 2016, DOI: 10.1002/ajoc.201600303. Read article

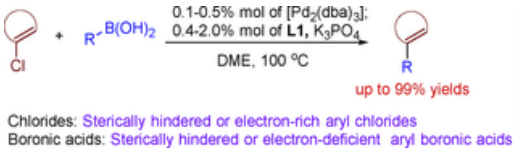
Silver-Catalyzed Cross-Dehydrogenative Coupling (CDC) Strategy for the Construction of Dialkyl/Dibenzyl Dibenzo[*b,f*][1,4]thia-/oxazepin-11-yl Phosphonates

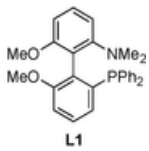


Silver surfer: Medicinally important dialkyl/diaryl dibenzo[*b,f*][1,4]thiazepin-11-yl phosphonates were synthesized by the atom-economical cross-dehydrogenative coupling of dibenzothia-/oxazepines and dialkyl/diaryl phosphites.

[Full Paper]
Debasmita Saha, Tanpreet Kaur, Anuj Sharma
Asian J. Org. Chem., August 24, 2016, DOI: 10.1002/ajoc.201600283. Read article

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



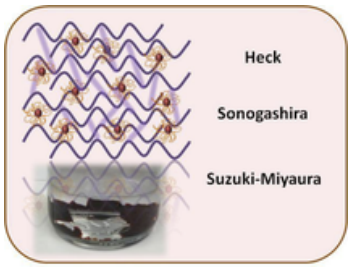


Improved coupling reactions: A series of new biphenyl N,P-monophosphine ligands **L** have been developed by introduction of two methoxy groups to the biphenyl backbone. The ligands were found to be much more effective than their counterpart Buchwald ligands in Suzuki–Miyaura coupling reactions of sterically hindered and electron-rich aryl chlorides with aryl boronic acids. A variety of tri-*ortho*-substituted or tetra-*ortho*-substituted biaryls or hetero-biaryls were conveniently prepared in up to 99% yield by using **L1**-[$Pd_2(dba)_3$] (dba=dibenzylideneacetone) as the catalyst.

[Full Paper]
Zihong Zhou, Yaqi Zhang, Wang Xia, Huixuan Chen, Hao Liang, Xuefeng He, Sifan Yu, Rihui Cao, Liqin Qiu
Asian J. Org. Chem., August 16, 2016, DOI: 10.1002/ajoc.201600319. Read article

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

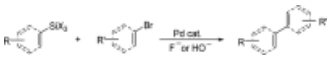
Structure-defined 3D catalytic nanocomposite polymer networks were synthesized based on monodisperse polyvinylpyrrolidone (PVP)-stabilized Pd colloidal nanohybrids encapsulated within 1,2-bis-(2-iodoethoxy)ethane (BIEE)-



crosslinked poly(2-dimethylamino)ethyl methacrylate homopolymer networks. These materials were evaluated as heterogeneous catalytic supports in Heck, Suzuki-Miyaura and Sonogashira coupling reactions.

[Full Paper]
Andreas S. Kalogirou, Mariliz Achilleos, Constantina Procopiou, Eugenia Vasile, Panayiotis A. Koutentis, Theodora Krasia-Christoforou
ChemistrySelect, July 18, 2016, DOI: 10.1002/slct.201600318. Read article

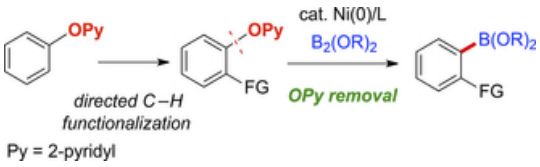
The Hiyama Cross-Coupling Reaction: New Discoveries



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.

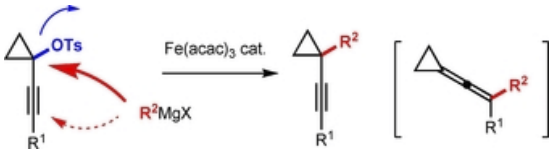
[Personal Account]
Francisco Foubelo, Carmen Nájera, Miguel Yus
The Chemical Record, July 14, 2016, DOI: 10.1002/tcr.201600063. Read article

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



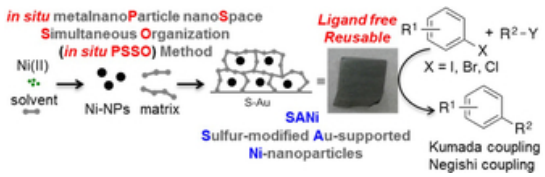
[Communication]
Mamoru Tobisu, Jiangning Zhao, Hirotaka Kinuta, Takayuki Furukawa, Takuya Igarashi, Naoto Chatani
Adv. Synth. Catal., June 2, 2016, DOI: 10.1002/adsc.201600336. Read article.

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



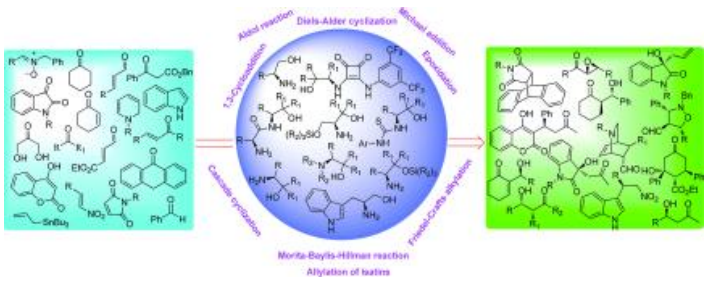
[Communication]
Daniel J. Tindall, Helga Krause, Alois Fürstner
Adv. Synth. Catal., May 25, 2016, DOI: 10.1002/adsc.201600357. Read article.

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



[Full Paper]
Naoyuki Hoshiya, Katsumasa Fujiki, Takahisa Taniguchi, Tetsuo Honma, Yusuke Tamenori, Mincen Xiao, Nozomi Saito, Mami Yokoyama, Akira Ishii, Hiromichi Fujioka, Satoshi Shuto, Yoshihiro Sato, Mitsuhiro Arisawa
Adv. Synth. Catal., April 27, 2016, DOI: 10.1002/adsc.201600024. Read article.

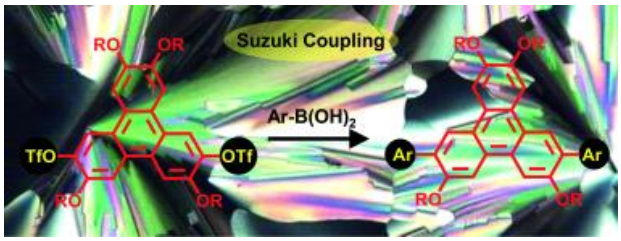
Catalytic Efficiency of Primary β-Amino Alcohols and Their Derivatives in Organocatalysis



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.

[Microreview]
Ummareddy Venkata Subba Reddy, Madhu Chennapuram, Chigusa Seki, Eunsang Kwon, Yuko Okuyama, Hiroto Nakano
Eur. J. Org. Chem., April 26, 2016, DOI: 10.1002/ejoc.201600164. Read article.

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.

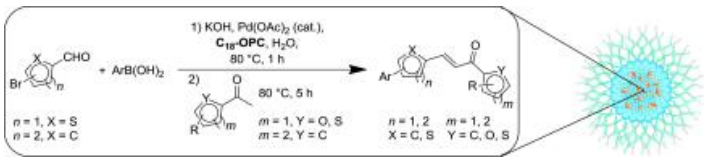
[Full Paper]
Ke-Qing Zhao, Yue Gao, Wen-Hao Yu, Ping Hu, Bi-Qin Wang, Benoît Heinrich, Bertrand Donnio
Eur. J. Org. Chem., April 13, 2016, DOI: 10.1002/ejoc.201600270. Read article.

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
Eur. J. Inorg. Chem., March 31, 2016, DOI: 10.1002/ejic.201600053. Read article.

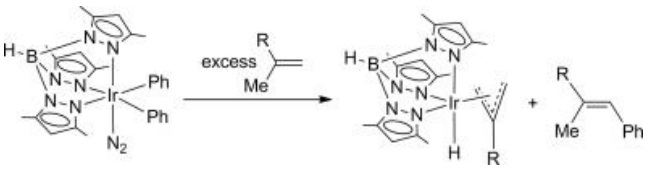
Multicomponent Cascade Synthesis of Biaryl-Based Chalcones in Pure Water and in an Aqueous Micellar Environment



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
Eur. J. Org. Chem., March 2, 2016, DOI: 10.1002/ejoc.201600095. Read article.

Allylic C–H Activation of Olefins by a $Tp^{Me2}Ir^{III}$ Compound



The Ir^{III} complex $[Tp^{Me2}Ir(C_6H_5)_2(N_2)]$ [Tp^{Me2} = hydridotris(3,5-dimethylpyrazolyl)borate] 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.

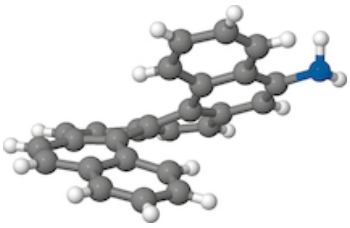
[Full Paper]
Crispín Cristóbal, Laura L. Santos, Rubén Gutiérrez-González, Eleuterio Alvarez, Margarita Paneque, Manuel L. Poveda
Eur. J. Inorg. Chem., January 19, 2016, DOI: 10.1002/ejic.201501253. Read article.

Triphenylphosphine-Mediated Deoxygenative Reduction of CF_3SO_2Na and Its Application for Trifluoromethylthiolation of Aryl Iodides

Efficient synthesis! A low cost method for the generation of $CuSCF_3$ by a triphenylphospine-mediated deoxygenative reduction of Langlois' reagent (CF_3SO_2Na) has been developed (see scheme). This method can be applied for the convenient synthesis of a wide array of ligated and air-stable $CuSCF_3$ complexes. Additionally, the $CuSCF_3$ complexes generated in situ by this protocol were found to trifluoromethylthiolate (hetero)aryl iodides with high efficiency.

[Communication]
Yi Yang, Long Xu, Siqi Yu, Xiaoqiang Liu, Yu Zhang, David A. Vicic
Chem. Eur. J., December 21, 2015, DOI: 10.1002/chem.201504790. Read article.

Synthesis, Properties, and Two-Dimensional Adsorption Characteristics of 5-Amino[6]hexahelicene



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.

[Full Paper]
Maarten W. van der Meijden, Edith Gelens, Natalia Murillo Quirós, Javier D. Fuhr, J. Esteban Gayone, Hugo Ascolani, Klaus Wurst, Magalí Lingenfelder, Richard M. Kellogg
Chem. Eur. J., December 14, 2015, DOI: 10.1002/chem.201502798. Read article.

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

Versatile functionalization of the BODIPY core: The borondipyrromethene (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.

[Full Paper]
Cesar F. A. Gómez-Durán, Ixone Esnal, Ismael Valois-Escamilla, Arlette Urías-Benavides, Jorge Bañuelos, Iñigo López Arbeloa, Inmaculada García-Moreno, Eduardo Peña-Cabrera
Chem. Eur. J., November 26, 2015, DOI: 10.1002/chem.201503090. Read article.

Direct Carboxylation of Aryl Tosylates by CO_2 Catalyzed by In situ-Generated Ni^0

Direct carboxylation of aryl tosylates by CO_2 is rendered possible by a Ni^0 catalyst, generated in situ by reduction of [$NiBr_2$(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.

[Full Paper]
Fatima Rebih, Manuel Andreini, Aurélien Moncomble, Anne Harrison-Marchand, Jacques Maddaluno, Muriel Durandetti
Chem. Eur. J., October 30, 2015, DOI: 10.1002/chem.201503926. Read article.