



Entry	Iodide: R ¹	Thiol: R ²	Reaction time (h)	Yield (%)
1	H	C ₆ H ₄ OMe- <i>p</i>	9.5	99
2	H	C ₆ H ₄ NO ₂ - <i>p</i>	15	88
3	H	C ₆ H ₄ Br- <i>o</i>	9	90
4	H	(CH ₂) ₅ CH ₃	7	91
5	H	Ph	5	71
6	<i>p</i> -MeO	Ph	5	14
7	<i>p</i> -O ₂ N	Ph	5	83

Recent Advances In Copper Catalyzed C S Cross Coupling

Gary A. Molander



Recent Advances In Copper Catalyzed C S Cross Coupling:

Copper-Mediated Cross-Coupling Reactions Gwilherm Evano, Nicolas Blanchard, 2013-11-11 Providing comprehensive insight into the use of copper in cross coupling reactions Copper Mediated Cross Coupling Reactions provides a complete up to date collection of the available reactions and catalytic systems for the formation of carbon heteroatom and carbon carbon bonds This essential reference covers a broad scope of copper mediated reactions their variations key advances improvements and an array of academic and industrial applications that have revolutionized the field of organic synthesis The text also discusses the mechanism of these transformations the use of copper as cost efficient alternative to palladium as well as recently developed methods for conducting copper mediated reactions with supported catalysts **New Trends in Cross-Coupling** Thomas Colacot, 2014-10-13 Palladium catalysed cross coupling reactions constitute a powerful class of chemical methods for the creation of carbon carbon and carbon heteroatom bonds used in organic synthesis famously recognized by the 2010 Nobel Prize awarded to Richard F Heck Ei ichi Negishi and Akira Suzuki for palladium catalysed cross couplings in organic synthesis These methods have become ubiquitous in academic and industrial settings alike as applications span from industrial production of pharmaceuticals agrochemicals polymers and dyes to the synthesis of complex natural products New Trends in Cross Coupling provides the reader with the history and basic concepts of cross coupling up to the state of the art in modern coupling reactions from both technology and applied perspectives A wide breadth of topics including selecting prominent ligand types advances in Pd phosphine precatalysts and Pd N heterocyclic carbene complexes new reactions such as carboiodination implementation of new technologies such as continuous flow and advanced metal detection methods greener approaches to cross coupling as well as large scale applications in the syntheses of pharmaceutical materials are covered Edited by Thomas J Colacot an Industrial expert on cross coupling the book contains contributions from academic and industrial world leaders in the field as well as a Forewords from Professor Barry M Trost Gregory C Fu and 2010 Nobel Laureate in Chemistry Professor Ei ichi Negishi New Trends in Cross Coupling serves as a reference guide for both undergraduate and graduate students as well as those who are experts in the area this compilation a Must for anyone interested in learning and using newer trends in cross coupling Ei ichi Negishi 2010 Nobel Laureate in Chemistry I am very pleased to see such a book concerning cross coupling reactions published Professor Akira Suzuki 2010 Nobel Laureate in Chemistry this book is invaluable to anyone involved in synthesis of organic compounds for any purpose Professor Barry Trost Stanford University *Recent Advances in Nanoparticle Catalysis* Piet W.N.M. van Leeuwen, Carmen Claver, 2020-07-01 This book provides an overview of the latest developments in the field of nanoparticle catalysis It not only discusses established topics in detail but also explores several emerging topics Catalysis with nanoparticles is expanding exponentially and is attracting significant interest due to the many exciting findings being reported Mastering the synthesis characterization stabilization and use of these catalysts offers numerous possibilities that far exceed those of classic

heterogeneous and homogeneous catalysis

Synthesis of Bioactive Scaffolds Rakesh Kumar Sharma, Bubun Banerjee, 2022-08-22 Carbon-carbon and carbon-heteroatom bond-forming reactions are the backbone of synthetic organic chemistry. Scientists are constantly developing and improving these techniques in order to maximize the diversity of synthetically available molecules. These techniques must be developed in a sustainable manner in order to limit their environmental impact. This book highlights green bond-forming reactions for bioactive scaffolds.

Strategic Applications of Named Reactions in Organic Synthesis Laszlo Kurti, Barbara Czako, 2005-04-29 Kurti and Czako have produced an indispensable tool for specialists and non-specialists in organic chemistry. This innovative reference work includes 250 organic reactions and their strategic use in the synthesis of complex natural and unnatural products. Reactions are thoroughly discussed in a convenient two-page layout using full color. Its comprehensive coverage, superb organization, quality of presentation, and wealth of references make this a necessity for every organic chemist. The first reference work on named reactions to present colored schemes for easier understanding. 250 frequently used named reactions are presented in a convenient two-page layout with numerous examples. An opening list of abbreviations includes both structures and chemical names. Contains more than 10 000 references grouped by seminal papers, reviews, modifications, and theoretical works. Appendices list reactions in order of discovery, group by contemporary usage, and provide additional study tools. Extensive index quickly locates information using words found in text and drawings.

Advances in Organic Synthesis Atta-ur-Rahman, 2018-10-18 *Advances in Organic Synthesis* is a book series devoted to the latest advances in synthetic approaches towards challenging structures. The series presents comprehensive reviews written by eminent authorities on different synthetic approaches to selected target molecules and new methods developed to achieve specific synthetic transformations or optimal product yields. *Advances in Organic Synthesis* is essential for all organic chemists in academia and the industry who wish to keep abreast of rapid and important developments in the field. This volume presents the following reviews: o Recent Progress on Asymmetric Synthesis of Chiral Flavanones, Chromanones, and Chromenes; o Supramolecular Chemistry of Modified Amino Acids and Short Peptides; o The Use of Nanocatalysts in the Synthesis of Heterocycles; A Contemporary Approach; o Synthesis and Applications of 1,2,3-Triazoles; o Ring C-H Functionalization of Aromatic N-Oxides.

Enabling Tools and Techniques for Organic Synthesis Stephen G. Newman, 2023-08-08 **ENABLING TOOLS AND TECHNIQUES FOR ORGANIC SYNTHESIS** Provides the practical knowledge of how new technologies impact organic synthesis, enabling the reader to understand literature, evaluate different techniques, and solve synthetic challenges. In recent years, new technologies have impacted organic chemistry to the point that they are no longer the sole domain of dedicated specialists. Computational chemistry, for example, can now be used by organic chemists to help predict outcomes, understand selectivity, and decipher mechanisms. To be prepared to solve various synthetic problems, it is increasingly important for chemists to familiarize themselves with a range of current and emerging tools and techniques. *Enabling Tools and Techniques*

for Organic Synthesis A Practical Guide to Experimentation Automation and Computation provides a broad overview of contemporary research and new technologies applied to organic synthesis Detailed chapters written by a team of experts from academia and industry describe different state of the art techniques such as computer assisted retrosynthesis spectroscopy prediction with computational chemistry high throughput experimentation for reaction screening and optimization using Design of Experiments DoE Emphasizing real world practicality the book includes chapters on programming for synthetic chemists machine learning ML in chemical synthesis concepts and applications of computational chemistry and more Highlights the most recent methods in organic synthesis and describes how to employ these techniques in a reader s own research Familiarizes readers with the application of computational chemistry and automation technology in organic synthesis Introduces synthetic chemists to electrochemistry photochemistry and flow chemistry Helps readers comprehend the literature assess the strengths and limitations of each technique and apply those tools to solve synthetic challenges Provides case studies and guided examples with graphical illustrations in each chapter Enabling Tools and Techniques for Organic Synthesis A Practical Guide to Experimentation Automation and Computation is an invaluable reference for scientists needing an up to date introduction to new tools graduate students wanting to expand their organic chemistry skills and instructors teaching courses in advanced techniques for organic synthesis **Metals and Non-metals**

Navjeet Kaur,2020-01-28 Design of new processes that avoid the use of toxic reagents has been the focus of intense research of late Catalysis by metals and non metals offers diverse opportunities for the development of new organic reactions with promising range of selectivities chemoselectivity regioselectivity diastereoselectivity and enantioselectivity Furthermore these transformations frequently occur under mild conditions tolerate a broad array of functional groups and proceed with high stereoselectivity The area of catalysis is sometimes referred to as a foundational pillar of green chemistry Catalytic reactions often reduce energy requirements and decrease separations because of increased selectivity they are also capable of permitting the use of renewable feedstocks of less toxic reagents or minimizing the quantities of reagents needed New catalytic organic synthesis methodologies have thus offered several possibilities for considerable improvement in the eco compatibility of fine chemical production Hence these catalytic methodologies have emerged as powerful tools for the efficient and chemoselective synthesis of heterocyclic molecules Key Features Presents the synthesis of different five membered heterocycles Contains the most up to date information in this fast moving field Covers novel catalytic approaches used in the study and application of catalysts in synthetic organic reactions Presents new methodologies for the synthesis of heterocycles Copper Catalysis in Organic Synthesis Gopinathan Anilkumar,Salim Saranya,2020-12-07 The most current information on growing field of copper catalysis Copper Catalysis in Organic Synthesis contains an up to date overview of the most important reactions in the presence of copper catalysts The contributors noted experts on the topic provide an introduction to the field of copper catalysis reviewing its development scope and limitations as well as providing descriptions

of various homo and cross coupling reactions In addition information is presented on copper catalyzed C H activation amination carbonylation trifluoromethylation cyanation and click reactions Comprehensive in scope the book also describes microwave assisted and multi component transformations as well as copper catalyzed reactions in green solvents and continuous flow reactors The authors highlight the application of copper catalysis in asymmetric synthesis and total synthesis of natural products and heterocycles as well as nanocatalysis This important book Examines copper and its use in organic synthesis as a more cost effective and sustainable for researchers in academia and industry Offers the first up to date book to explore copper as a first line catalyst for many organic reactions Presents the most significant developments in the area including cross coupling reactions C H activation asymmetric synthesis and total synthesis of natural products and heterocycles Contains over 20 contributions from leaders in the field Written for catalytic chemists organic chemists natural products chemists pharmaceutical chemists and chemists in industry Copper Catalysis in Organic Synthesis offers a book on the growing field of copper catalysis covering cross coupling reactions C H activation and applications in the total synthesis of natural products

Copper-catalyzed Benzylic C-h Cross Couplings Sijie Chen, 2021 Cross coupling methods are among the most synthetically useful and widely applied reaction classes in constructing architecturally complex molecules Among these reactions methods that employ sp² hybridized coupling partners have found broad applications in organic syntheses and streamlined the preparation of pharmaceutically relevant compounds Despite such advances the prevalence of sp² hybridized coupling partners has resulted in a massive collection of planar compounds which could contribute to undesirable physicochemical properties for drug discovery The past decade has witnessed an increasing demand of more topologically diverse libraries for drug discovery Recent development of C sp³ H functionalization has created opportunities for organic chemists to enrich molecular libraries and incorporate three dimensionality construction This thesis discloses our recent development of Cu catalyzed cross couplings of benzylic C sp³ H bonds and diverse nucleophilic reagents enabled by a redox buffering strategy and application of these methods in medicinal chemistry research Chapter 2 discussed our recent development of a copper catalyzed benzylic C H cross coupling with alcohols and the identification of the redox buffering strategy Recent radical relay cyanation and arylation of benzylic C sp³ H bonds precedents prompted us to develop a etherification method However direct application of standard cyanation or arylation conditions failed to afford productive catalysis Mechanistic interrogation revealed that cyanides and arylboronic acids can induce reduction of CuII to CuI the catalytically reactive form whereas nucleophiles like alcohols do not reduce CuII under the same conditions We identified dialkylphosphite as a sacrificial reductant or a redox buffer that allows continuously generation of CuI species in a controlled manner which enabled effective etherification of the diverse hetero benzylic C H substrates Evaluation of the alcohol scope as well as the cross coupling reactivity validated the utility of this method for library synthesis Chapter 3 disclosed our development of a N site selective copper catalyzed benzylic C H cross couplings with azoles We demonstrated that good

coupling reactivity can be achieved with the redox buffering strategy and modification of the reaction conditions allowed N site selective coupling with azoles This reactivity proved effective with diverse N H heterocycles and cross coupling of an array of benzylic C H substrate and azoles was also successful which should find broad application in pharmaceutical research Chapter 4 detailed our recent investigation into the 3D diversity introduced by benzylic C H cross coupling methods A cheminformatic approach was taken to virtually enumerate a collection of ethers and ureas with benzylic C H etherification and isocyanation amine coupling sequence Analyses of these products proved benzylic cross couplings reliable methods to deliver 3D structures in comparison to existing bioactive molecules and selected C sp² derived coupling products Examination of the physicochemical properties of these benzylic coupling products found them highly relevant to a drug like chemical space We successfully synthesized and isolated representative drug like 3D benzylic ethers and ureas and validated the utility of this cheminformatic guided approach Further intake of this approach should transform how future synthetic methodologies are developed Chapter 5 covered our recent development of a site selective benzylic C H azidation method Employment of the copper radical relay catalysis enabled highly benzylic selective C H azidation of a diverse collection hetero benzylic C H substrates Experimental and density functional theory identified a radical polar crossover pathway for the reaction of a benzyl radical and a CuII azide complex Conversions of benzyl azide products to various functional groups benchmarked the broad utility of this method for target compound synthesis and medicinal chemistry Collectively Cu catalyzed cross couplings of benzylic C sp³ H bonds contributed to a growing library of medicinally relevant compounds and represented a unique opportunity to explore chemical space for drug discovery Analyses of the physicochemical and topological properties of these benzylic derivatives revealed their drug likeness as well as outstanding three dimensional features comparing to existing bioactive molecules Broad applications of these benzylic coupling methods guided by cheminformatics should complement the existing synthetic tools and allow medicinal chemists to assemble compound libraries with higher diversity and complexity

Copper-catalyzed Benzylic C-h Cross Couplings Sijie Chen, 2021 Cross coupling methods are among the most synthetically useful and widely applied reaction classes in constructing architecturally complex molecules Among these reactions methods that employ sp² hybridized coupling partners have found broad applications in organic syntheses and streamlined the preparation of pharmaceutically relevant compounds Despite such advances the prevalence of sp² hybridized coupling partners has resulted in a massive collection of planar compounds which could contribute to undesirable physicochemical properties for drug discovery The past decade has witnessed an increasing demand of more topologically diverse libraries for drug discovery Recent development of C sp³ H functionalization has created opportunities for organic chemists to enrich molecular libraries and incorporate three dimensionality construction This thesis discloses our recent development of Cu catalyzed cross couplings of benzylic C sp³ H bonds and diverse nucleophilic reagents enabled by a redox buffering strategy and application of these methods in medicinal chemistry

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SYNTHESIS OF NATURAL PRODUCTS Kocvosky,1986-09 **C-C Cross Couplings with 3d Base Metal Catalysts**

Xiao-Feng Wu,2023-06-13 This volume presents recent progress on 3d base metal catalyzed C C cross coupling reactions The contributions provide detailed discussions on the use of cheap metal catalysts such as Cr Mn Fe Co Ni Cu and Zn to construct Csp² Csp² Csp² Csp³ and Csp³ Csp³ bonds with a variety of substrates These non noble metal catalyst have many advantages such as being inexpensive having low toxicity and are environmentally benign Therefore the use of cheap metal catalysts in organic synthesis has gained much attention in efforts to develop more sustainable synthetic green chemistry Each chapter is written by international experts in the field and is a great resource for students researchers and chemists working in industry to gain an overview on the latest developments *New Pd and Cu-based Catalysts for Carbon-heteroatom Bond Formation* Nootaree Niljianskul,2015 The research presented in this dissertation is aimed at the development of novel methodologies for carbon heteroatom cross coupling reactions catalyzed by late transition metals Both palladium and copper are central to the field of transition metal catalysis and are integral to the catalyst systems developed as part of our continual advancement in cross coupling reactions The first part of this thesis focuses on the use of palladium catalysts to form carbon sulfur bonds directed towards aryl sulfonamide synthesis The second part of the thesis describes the recent development in the copper hydride mediated formation of carbon nitrogen bonds via hydroamination of olefins Part I Chapter 1 Palladium Catalyzed Chlorosulfonylation of Arylboronic Acids Using a biaryl phosphine ligand platform the first palladium catalyzed cross coupling reaction of phenyl chlorosulfate with arylboronic acids was achieved In this context the arylsulfonyl chloride products serve as useful precursors to a variety of sulfonyl functional groups such as aryl sulfonamides aryl sulfones and arenesulfonate esters In particular this method allows for the preparation of a number of arylsulfonyl chlorides that are not accessible via electrophilic aromatic substitution pathways and under mild reaction conditions Additionally this methodology points to an unprecedented selectivity for the phenylchlorosulfate electrophiles used in the cross coupling reactions Part II Chapter 2 Enantio and Regioselective Copper Catalyzed Hydroamination of Styrenes and the Extension of the Methodology towards Anti Markovnikov Hydroamination of Terminal Aliphatic Alkenes The development of a copper mediated strategy towards the hydroamination of styrene derivatives is reported In this system the reaction proceeds regioselectively and enantioselectively to generate alpha branched amines The system can transform a wide variety of substituted styrenes including trans cis and beta disubstituted styrenes In addition our extension to copper catalyzed hydroamination reactions of unactivated aliphatic olefins is reported Using terminal aliphatic alkenes the copper catalyzed hydroamination reactions proceed with anti Markovnikov regioselectivity Preliminary results point to the application of this methodology towards beta chiral amine synthesis via the hydroamination of 1,1 disubstituted alkenes Chapter 3 alpha Aminosilane Synthesis via Copper Catalyzed Hydroamination of Vinylsilanes The copper catalyzed hydroamination of vinylsilanes is described This regioselective reaction generates a chiral aminosilanes in high yields and enantioselectivities

The method is compatible with differentially substituted vinylsilanes and allows access to many valuable chiral organosilicon compounds Chapter 4 Synthesis of gamma Chiral Amines via Copper Catalyzed Hydroamination of 3 3 Disubstituted Allylic Alcohols and 3 3 Disubstituted Allylic Benzoates An investigation into the copper catalyzed hydroamination of allylic alcohols and allylic benzoates is reported The reaction proceeds via a beta alkoxy elimination setting a stereogenic center at the 3 position to generate gamma chiral amine products The reaction is more efficient using allylic benzoates This method is completely regioselective and is applicable to aliphatic allylic benzoates as well as aromatic allylic benzoates Additionally we demonstrated that this strategy is applicable towards an allylic epoxide substrate to generate delta chiral amine

Cross-coupling Reactions Joffrey Vrijdag, 2020 Cross Coupling Reactions An Overview opens with an overview of the fundamentals and applications of the young and fast developing area of transition metal catalyzed mediated oxidative dehydrogenative C H C H coupling reactions between two hetero arenes Continuing the authors highlight the recent advances regarding the ligand supported transition metal catalyzed domino cascade or one pot syntheses of various heterocycles involving cross coupling reactions The recent advances in Cu catalyzed tandem reactions for heterocycle synthesis are also addressed Cu metal chemistry has garnered attention as a potential alternative to precious transition metals being cheaper more sustainable and more easily available A comprehensive account of research on green chemical routes is provided involving various palladium metal based catalysts utilized in facilitating cross coupling reaction in aqueous media Reported decarboxylative cross coupling reactions are discussed along with suitable examples focusing on their mechanism of action **Catalyst Components for Coupling Reactions** Gary A. Molander, 2008-09-02 The long awaited Handbook for all synthetic chemists working on coupling reactions compiling all major catalyst components in use in the area Consists of a compilation of articles taken from the EROS database with the inclusion of about 20 newly commissioned catalysts pre catalysts ligands that have made an impact in this area of synthetic organic chemistry Includes catalyst systems used in Heck Kumada Tamao Corriu Suzuki Miyaura Hiyama Hatanaka Negishi Migita Kosugi Stille Buchwald Hartwig and Tsuji Trost coupling reactions *Copper in N-Heterocyclic Chemistry* Ananya Srivastava, 2020-11-13 Copper in N Heterocyclic Chemistry provides an overview of copper catalyzed synthesis and functionalization of N heterocyclic compounds covering all recent developments in a way that is ideal for researchers and students working in the area of synthetic organic chemistry and medicinal chemistry The book explores N heterocyclic compounds as unique structural units in the development of natural products and pharmaceuticals along with the remarkable progress made in the area of high atom economic strategies and more recently copper catalyzed C H activation and its applications in organic synthesis Readers will find troubleshooting protocols as well as the advantages and limitations of each method discussed As copper catalysts show versatile chemical reactivity in many aspects including their oxidation states 0 3 are accessible and their ability to facilitate bond formations due to their ability to serve as Lewis acids oxidizing agents and catalysts this book is an

ideal resource on the topics explored Discusses novel synthetic methods developed over the past decade for copper catalyzed synthesis of N heterocyclic compounds Covers the most recent methodologies adapted in synthetic chemistry for applications in natural products and pharmaceuticals Includes troubleshooting protocols as well as the advantages and limitations of each method discussed in detail **Chemtracts** ,2003 **Chemical and Engineering News** ,1995

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