

The ISHC Bulletin

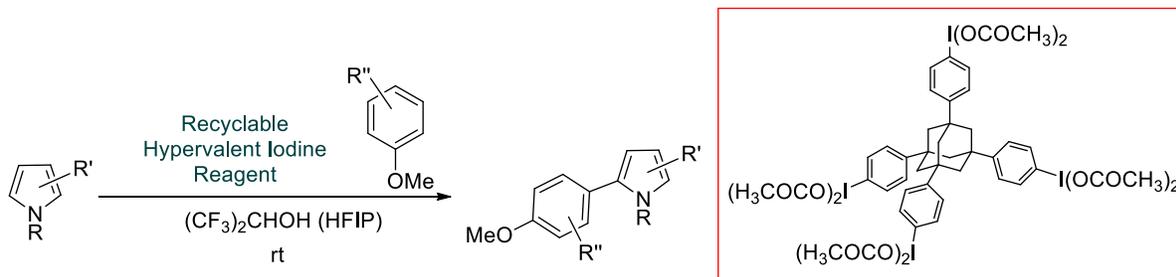
Recent Publications of ISHC Members

Issue 29; March 2019

Metal-Free Oxidative Cross-Coupling of Pyrroles with Electron-Rich Arenes using Recyclable Hypervalent Iodine(III) Reagent

Koji Morimoto, Tohru Kamitanaka, Toshifumi Dohi, and Yasuyuki Kita* (kita@ph.ritsumei.ac.jp)
Heterocycles **2018**, *97*, 632–645.

DOI: 10.3987/COM-18-S(T)52



Recyclable Hypervalent Iodine Reagent

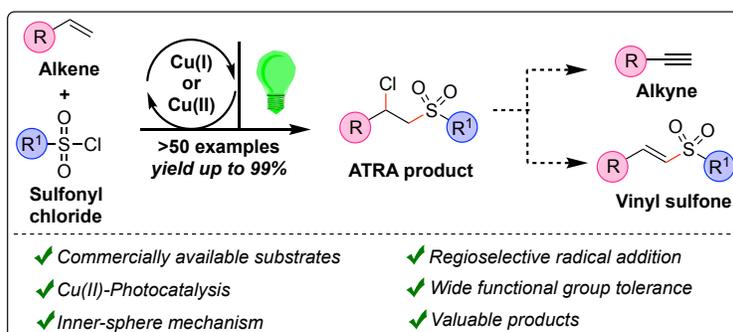
Abstract: The facile and clean oxidative cross-coupling reaction of pyrroles has been developed using the recyclable hypervalent iodine(III) reagents having an adamantane core. The recyclable iodine(III) reagent could be recovered from the reaction mixtures as the corresponding reduced forms, *i.e.*, the tetraiodide **2**, by a simple solid-liquid separation. By re-oxidizing the recovered **2** to the initial reagent **1a** using *m*-chloroperbenzoic acid (*m*CPBA), the reagent **1a** can be reused.

Visible-Light-Mediated Regioselective Chlorosulfonylation of Alkenes and Alkynes: Introducing the Cu(II) Complex [Cu(dap)Cl₂] to Photochemical ATRA Reactions

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ACS Catal. **2019**, *9*, 1103–1109.

DOI: 10.1021/acscatal.8b04188



Abstract: A visible-light-mediated photocatalyzed protocol utilizing copper–phenanthroline-based catalysts has been developed that can convert a large number of olefins into their chlorosulfonylated products. Besides the Cu(I) complex [Cu(dap)₂]Cl, now well-established in photo-ATRA processes, the corresponding Cu(II) complex [Cu(dap)Cl₂] proved to be often even more efficient in the title reaction, being advantageous from an economic point of view but also opening up new avenues for photoredox catalysis. Moreover, the copper complexes outperformed commonly used ruthenium, iridium, or organic dye based photocatalysts, owing to their ability to stabilize or interact with transient radicals by inner sphere mechanisms. The use of stoichiometric Na₂CO₃ in combination with the copper photocatalysts was found to be essential to convert unactivated olefins to the desired products, in contrast to activated olefins for which no additive was required. As suggested by appropriate control experiments, the role of Na₂CO₃ is attributed to prevention of poisoning of the catalyst.

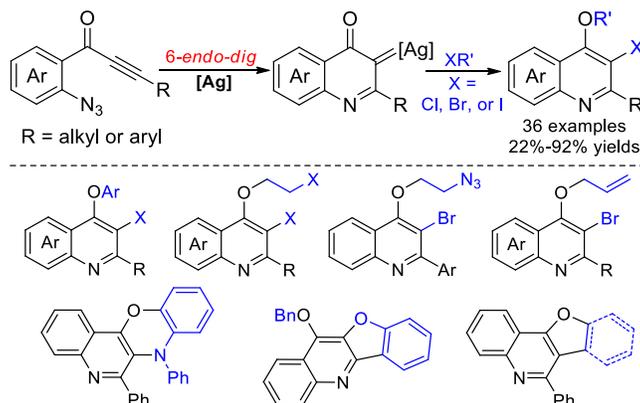
Silver-Catalyzed Carbocyclization of Azide-Tethered Alkynes: Expeditious Synthesis of Polysubstituted Quinolines

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Adv. Synth. Catal. **2019**, *361*, 826–831.

DOI: 10.1002/adsc.201801425



Abstract: A silver-catalyzed carbocyclization of azide-tethered alkynes has been developed for the synthesis of polysubstituted quinolines in good to high yields. Mechanistic studies indicate that this reaction is initiated by a silver-catalyzed 6-*endo-dig* azide-yne cyclization, followed by a formal R–X (X = Cl, Br, or I) insertion with external halide through a ylide intermediate. The salient features of this reaction include readily available materials, inexpensive silver-catalyst mild reaction conditions, good functional group tolerance, and ease in further transformations.

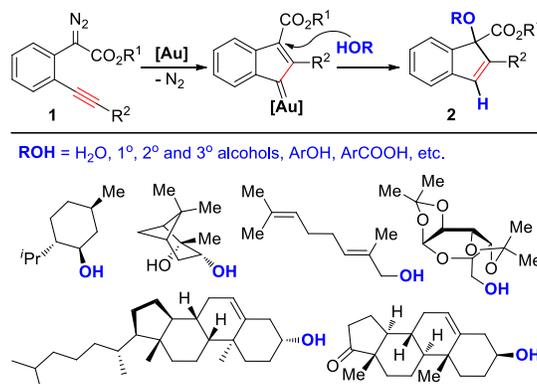
Selective Vinylogous Reactivity of Carbene Intermediate in Gold-Catalyzed Alkyne Carbocyclization: Synthesis of Indenols

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ACS Catal. **2019**, *9*, 2440–2447.

DOI: 10.1021/acscatal.8b04144



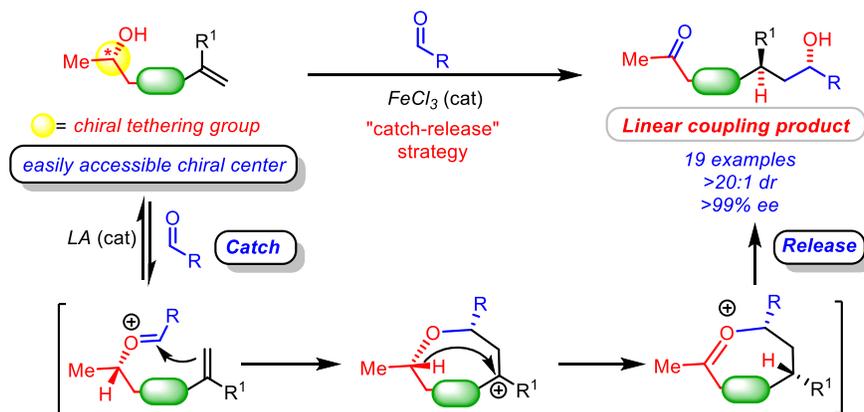
Abstract: A gold-catalyzed carbocyclization of alkynes with a pendant diazo group that is completed by reaction with a protic nucleophile for the synthesis of indenol derivatives with a tertiary center is described. Mechanistic studies and DFT calculations indicate that the transformation is initiated by a gold-promoted 5-*endo-dig* carbocyclization to form the key intermediate vinyl gold-carbene, which is intercepted by an unprecedented vinylogous addition and followed by external protic nucleophile assisted protodeauration. Furthermore, in this catalytic alkyne transformation, various nucleophiles, including water, commercially available 1°, 2° and 3° alcohols, menthol, D-galactose, cholesterol, steroid, etc., all perform well under these mild conditions to produce the corresponding indenol derivatives in high yields with structural diversity.

Enantioselective Redox-Neutral Coupling of Aldehydes and Alkenes by an Iron-Catalyzed “Catch–Release” Tethering Approach

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J. Am. Chem. Soc. **2019**, *141*, 143–147.

DOI: 10.1021/jacs.8b12242



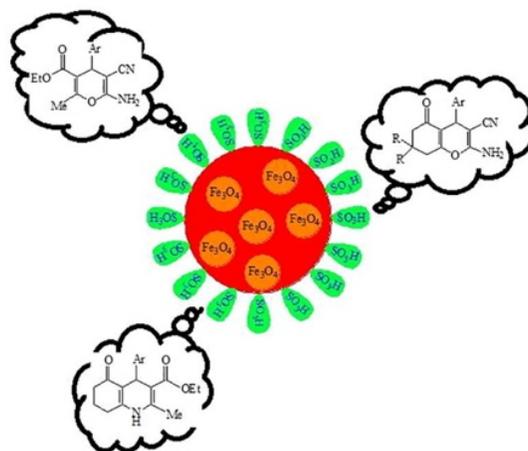
Abstract: The reductive coupling of aldehydes and alkenes is an emerging technology that holds the potential to reinvent carbonyl addition chemistry. However, existing enantioselective methods are limited to form “branched” products. Herein, we present a directed enantio- and diastereoselective alkylation of aldehydes with simple olefins to selectively yield linear coupling products. This is achieved by redox-neutral remote functionalization, whereby a tethering “catch–release” strategy decisively solves the key problems of reactivity and selectivity.

SO₃H-Dendrimer Functionalized Magnetic Nanoparticles (Fe₃O₄@D–NH–(CH₂)₄–SO₃H): Synthesis, Characterization and its Application as a Novel and Heterogeneous Catalyst for the One-Pot Synthesis of Polyfunctionalized Pyrans and Polyhydroquinolines

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Polyhedron **2019**, *162*, 129–141.

DOI: 10.1016/j.poly.2019.01.055



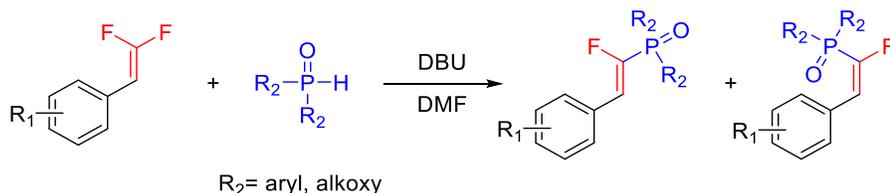
Abstract: In this study, novel SO₃H-dendrimer functionalized magnetic nanoparticles (Fe₃O₄@D–NH–(CH₂)₄–SO₃H) were prepared and characterized by using FT-IR, X-ray diffraction patterns, scanning electron microscopy, transmission electron microscopy, thermogravimetry analysis, and energy-dispersive X-ray spectroscopy. The synthesized nanosized catalyst was successfully applied to the synthesis of highly substituted pyrans and polyhydroquinolines via a straightforward one-pot multicomponent condensation reaction. The key advantages are the short reaction time, high yields, simple workup, and purification of products by simple recrystallization from ethanol.

Metal-Free Access to (*E/Z*)- α -Fluorovinyl Phosphorus Compounds from *gem*-Difluorostyrenes

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Eur. J. Org. Chem. **2019**, 5, 1170–1177.

DOI: 10.1002/ejoc.201801602



- Metal-free
- Excellent yields
- Room temperature
- Short reaction time
- 21 examples
- up to 96% overall yield
- easily separated *Z*- and *E*-type isomers

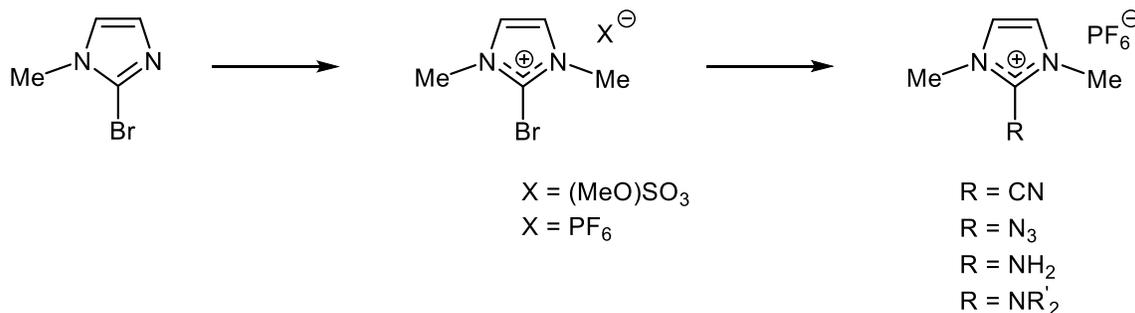
Abstract: A facile and efficient method for the synthesis of (*E/Z*)- α -fluorovinyl phosphorus compounds from *gem*-difluorostyrenes with diphenylphosphine oxide/dialkyl phosphate and DBU at room temperature was developed. A series of 1-fluorovinyl phosphine oxides/phosphonates were obtained with moderate to excellent yields in these reactions. Additionally, most isomers (*E/Z* type) of the target compounds could be easily separated and purified by column chromatography.

2-Functionalized Derivatives of 2-Bromo-1,3-Dimethylimidazole

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Hubert Huppertz, and Herwig Schottenberger (sven.nerdinger@sandoz.com)

Heterocycles **2018**, 97, 1116–1127.

DOI: 10.3987/COM-18-S(T)94



Abstract: Attempts at direct bromination of 1,3-dimethylimidazolium salts with bromine were futile. A tribromide or a carbene-lithium-THF adduct were received instead. The quaternary 2-bromo compound was obtained by methylation of 2-bromo-1-methylimidazole and subsequent ion metathesis, which was converted to the corresponding 2-cyano and 2-azido derivatives. Typical reactions of the latter include a dipolar cycloaddition and the Staudinger reaction. Crystal structures of eight compounds have been determined by single-crystal X-ray diffraction.

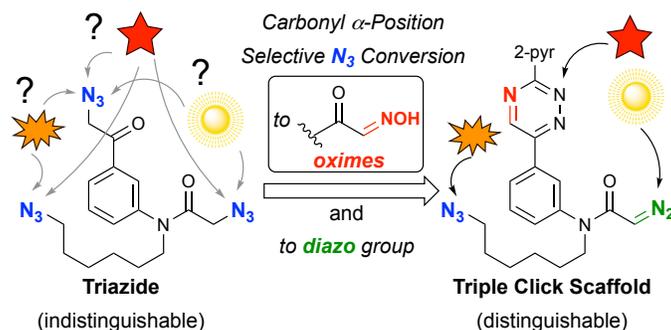
Site-Selective Conversion of Azido Groups at Carbonyl α -Positions into Oxime Groups Leading Triazide to a Triple Click Conjugation Scaffold

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Chem. Commun. **2019**, 55, 1891–1894.

DOI: 10.1039/C8CC09415B



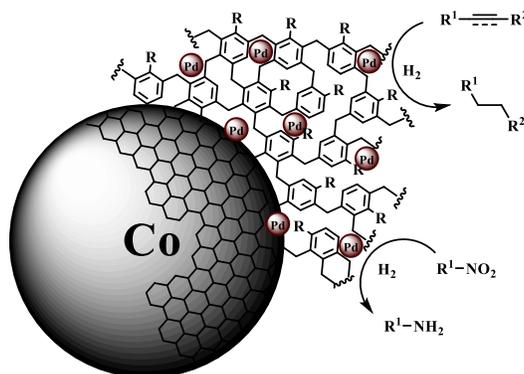
Abstract: This paper reports the selective conversion of alkyl azido groups at the carbonyl α -position into oximes through β -elimination of dinitrogen, followed by transoximation. With this method and diazo conversion, a triazide molecule was transformed into a triple click conjugation scaffold allowing one-pot four-component coupling.

Recyclable Magnetic Microporous Organic Polymer (MOP) Encapsulated with Palladium Nanoparticles and Co/C Nanobeads for Hydrogenation Reactions

Lisa Stadler, Maryann Homafar, Andreas Hartl, Sharif Najafshirtari, Massimo Colombo, Radek Zboril, Petr Martin, Manoj B. Gawande, Jian Zhi, and Oliver Reiser* (oliver.reiser@chemie.uni-regensburg.de)

ACS Sustainable Chem. Eng. **2019**, 7, 2388–2399.

DOI: 10.1021/acscuschemeng.8b05222



Abstract: Highly active and magnetically retrievable palladium nanocatalysts embedded in MOPs grown on Co/C nanoparticles for hydrogenation of alkenes, alkynes, and nitroarenes are reported.