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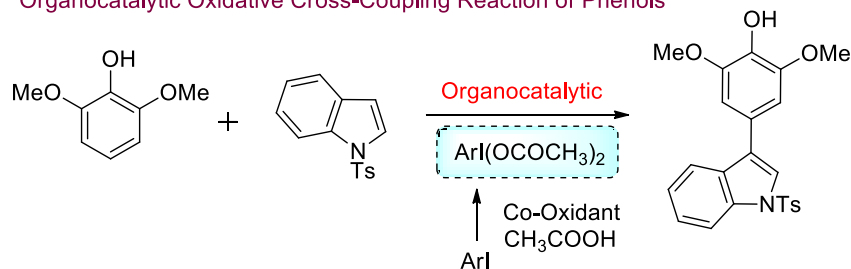
Organo-Iodine(III)-Catalyzed Oxidative Phenol–Arene and Phenol–Phenol Cross-Coupling Reaction

Koji Morimoto, Kazuma Sakamoto, Takao Ohshika, Toshifumi Dohi, Yasuyuki Kita

Angew. Chem. Int. Ed. **2016**, *55*, 3652–3656.

DOI: 10.1002/anie.201511007

Organocatalytic Oxidative Cross-Coupling Reaction of Phenols



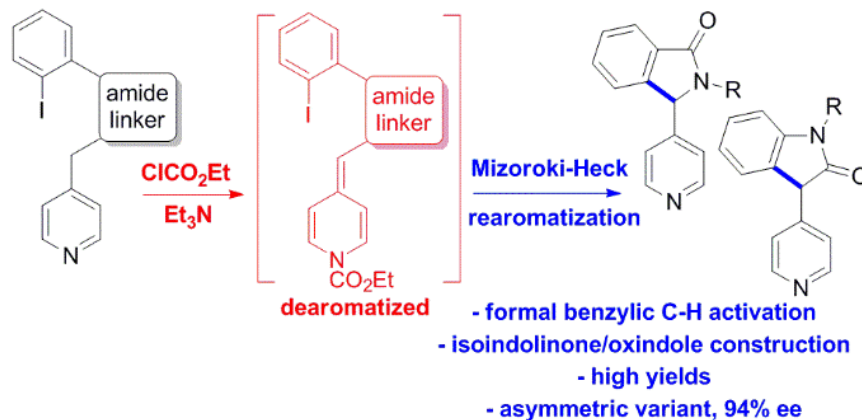
Abstract: The direct oxidative coupling reaction has been an attractive tool for environmentally benign chemistry. Reported herein is that the hypervalent iodine catalyzed oxidative metal-free cross-coupling reaction of phenols can be achieved using Oxone as a terminal oxidant in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). This method features a high efficiency and regioselectivity, as well as functional-group tolerance under very mild reaction conditions without using metal catalysts.

Dearomatized Alkylidene Dihydropyridines as Substrates for Mizoroki-Heck Cyclizations

Madhur S. Joshi and F. Christopher Pigge

ACS Catal. **2016**, *6*, 4465–4469.

DOI: 10.1021/acscatal.6b01151



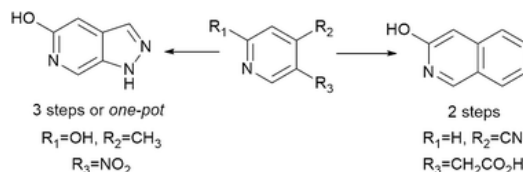
Abstract: 4-Substituted pyridines linked to iodoarene groups with alkyl amide tethers can be converted to the corresponding alkylidene dihydropyridines by treatment with ethyl chloroformate and Et_3N . Subsequent exposure to Pd-catalyzed Mizoroki–Heck reaction conditions results in efficient intramolecular cyclization at the exocyclic alkene to afford isindolinone and oxindole derivatives. Asymmetric construction of 3,3-disubstituted oxindoles and isindolinones has also been achieved. This work demonstrates the ability to utilize reactive pyridine anhydrobases in metal-catalyzed transformations and provides the basis for design of new approaches to important heterocyclic ring systems.

Synthesis of Two ‘Heteroaromatic Rings of the Future’ for Applications in Medicinal Chemistry

P. E. Silva Júnior, L. C. D. Rezende, Julia Possamai Gimenes, Vinícius Gonçalves Maltarollo, James Dale, G. H. G. Trossini, F. S. Emery, A. Ganesan

RSC Adv. **2016**, 6 22777–22780.

DOI: 10.1039/c6ra01099g



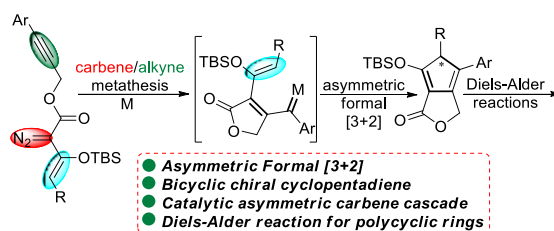
Abstract: In a computational study, the 1*H*-pyrazolo[3,4-*c*]pyridin-5-ol and 2,6-naphthyridin-3-ol heterocycles were identified as unknown heteroaromatic ring systems of potential value for medicinal chemistry. Here we report robust and concise synthetic protocols that provide access to these two scaffolds on a multigram scale.

Enantioselective Carbene Cascade: An Effective Approach to Cyclopentadienes and Applications in Diels–Alder Reactions

Xiangbo Wang, Yunfei Zhou, Lihua Qiu, Ruwei Yao, Yang Zheng, Cheng Zhang, Xiaoguang Bao, Xinfang Xu

Adv. Synth. Catal. **2016**, 358, 1571–1576.

DOI: 10.1002/adsc.201501106



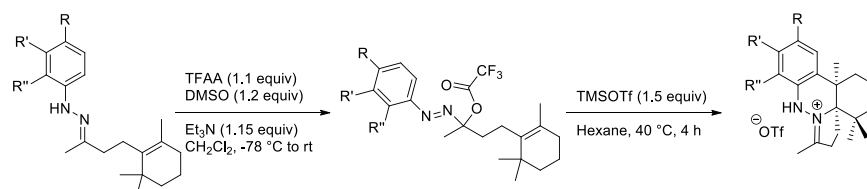
Abstract: An asymmetric carbene cascade reaction, which proceeds through carbene/alkyne metathesis and formal (3+2) cycloaddition and converts alkynyl-tethered enol diazoacetates to chiral bicyclic cyclopentadienes, is presented; and no catalytic asymmetric version of these carbene cascade transformations has been disclosed so far. The proton signals of the cyclopropane intermediates are observed in the mechanism study, which clearly demonstrate the reaction pathways. In addition, these products are intercepted *via* Diels–Alder reactions to provide bridged polycyclic structures in high yields and enantioselectivities.

Intramolecular (4+2) cycloaddition of aryl-1-aza-2-azoniaallene salts: a practical approach to highly sterically-congested polycyclic protonated azomethine imines

Ram C. Dhakal and Matthias Brewer

Tetrahedron **2016**, 72, 3718–3728.

DOI: 10.1016/j.tet.2016.03.037



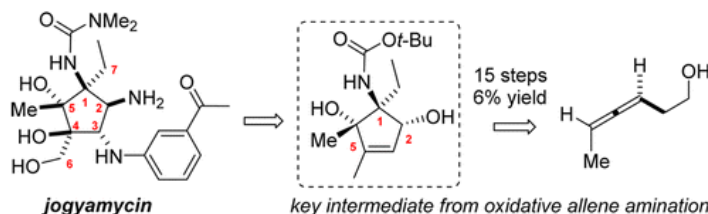
Abstract: We report an improved two-step reaction sequence that gives tricyclic protonated azomethine imine products containing a 1,2,3,4-tetrahydrocinoline scaffold in high yield. This sequence involves the oxidation of aryl hydrazones with TFAA-activated DMSO to give the corresponding α -trifluoroacetoxyazo products, which react readily with TMSOTf to give 1-aza-2-azoniaallene salt intermediates that undergo intramolecular (4+2) cycloadditions with pendant alkenes. This reaction sequence is more general, more practical and more environmentally friendly than our initially reported method. The cycloaddition provides exceptionally sterically-hindered products in high yield.

Diastereoselective Synthesis of the Aminocyclitol Core of Jogyamycin via an Allene Aziridination Strategy

Nels C. Gerstner, Christopher S. Adams, R. David Grigg, Maik Tretbar, Jaren W. Rigoli, and Jennifer M. Shomaker

Org. Lett. **2016**, *18*, 284–287.

DOI: 10.1021/acs.orglett.5b03453



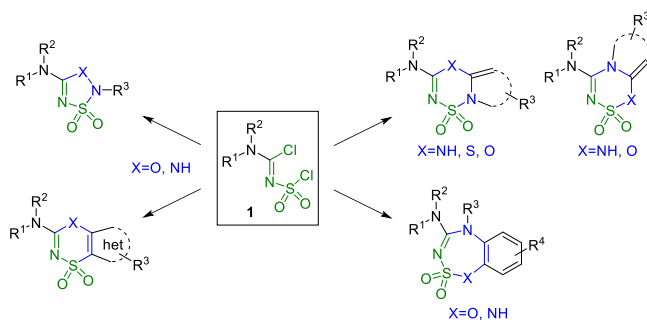
Abstract: Oxidative allene amination provides rapid access to densely functionalized amine-containing stereotriads through highly reactive bicyclic methyleneaziridine intermediates. This strategy has been demonstrated as a viable approach for the construction of the densely functionalized aminocyclitol core of jogyamycin, a natural product with potent antiprotozoal activity. Importantly, the flexibility of oxidative allene amination will enable the syntheses of modified aminocyclitol analogues of the jogyamycin core.

New Heteroatom-Rich Ring Systems from *N,N*-Dialkyl-*N'*-chlorosulfonyl Chloroformamidines

Craig L. Francis

Arkivoc **2016**, *i*, 212–275.

DOI: <http://dx.doi.org/10.3998/ark.5550190.p009.629>



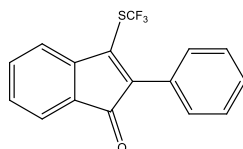
Abstract: *N,N*-Dialkyl-*N'*-chlorosulfonyl chloroformamidines constitute a class of readily available and very versatile bis-electrophiles. This Account describes the application of these unusual $\delta^+C=N-S^{\delta+}$ building blocks for construction of a cornucopia of previously unknown or uncommon heterocyclic ring systems. Regioselectivity encountered during heterocycle formation and some properties and chemistry of the newly-formed ring systems are also discussed.

A Facile Trifluoromethylthiolation of 3-Chloro-1H-inden-1-ones Employing $AgSCF_3$ and KI

Biao Dong, Xiaofei Zhang, Ruiling Liu, and Chunhao Yang

Arkivoc **2016**, *iv*, 296–305.

DOI: <http://dx.doi.org/10.3998/ark.5550190.p009.606>

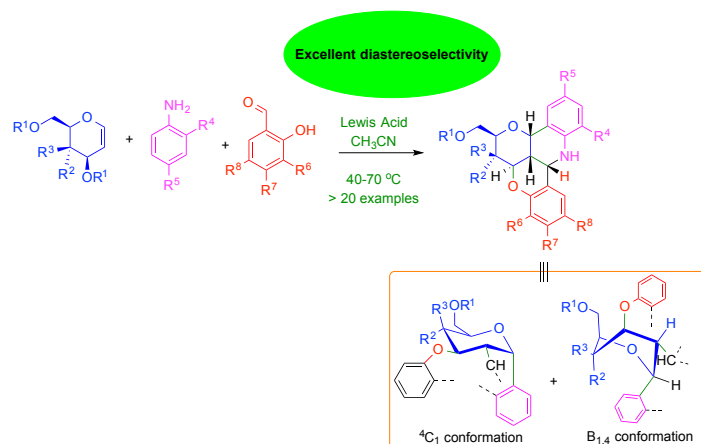


Abstract: An efficient method for trifluoromethylthiolation of functionalized 3-chloro-1H-inden-1-ones was described. Within this method, $AgSCF_3$ was employed as a nucleophilic reagent and KI was functionalized as an activator. This reaction provided the trifluoromethylthiolated indenones with excellent yields under moderate conditions.

A Convenient Domino Ferrier Rearrangement-Intramolecular Cyclization for the Synthesis of Novel Benzopyran-fused Pyranoquinolines

Paseka T. Moshapo, Mokela Sokamisa, Edwin M. Mmutlane, Richard M. Mampa, Henok H. Kinfe
Org. Biomol. Chem. **2016**, *14*, 5627–5638.

DOI: 10.1039/C5OB02536B



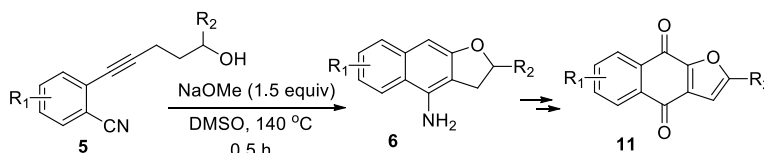
Abstract: The Ferrier rearrangement and the Povarov reaction have proven indispensable tools in carbohydrate chemistry and the synthesis of *N*-heterocycles, respectively. We hereby report a one-pot cyclization sequence involving the Ferrier and Povarov-like reactions in the synthesis of novel pentacyclic *N*-heterocycles: benzopyran-fused pyranoquinolines. The reaction entails three component condensation of a glycal with a variety of anilines and 2-hydroxybenzaldehydes under Lewis acid catalysis to yield the title compounds in 4–24 hours of reaction time, in moderate to high yields and excellent diastereoselectivity. Of the Lewis acid catalysts deployed [Sc(OTf)₃, Al(OTf)₃, Cu(OTf)₃, CuOTf, I₂, InCl₃, and La(OTf)₃] in various solvents (acetonitrile, THF, dichloromethane, 1,2-dichloroethane and diethyl ether) at room and elevated temperatures, Sc(OTf)₃ (10 mol%) in acetonitrile at 70 °C gave the best results, with excellent diastereoselectivity. CAN-mediated oxidative ring opening of the pentacyclic *N*-heterocycle gave the corresponding enantiomerically pure chromenoquinoline bearing a pendant sugar moiety.

Base-Mediated Cyclization Reaction of 2-(5-Hydroxy-1-pentynyl)benzonitriles to 4-Amino-2,3-dihydronaphtho[2,3-*b*]furanes and Synthesis of Furanonaphthoquinones

Chih-Jyun Tsai, Chin-Chau Chen, Chih-Wei Tsai and Ming-Jung Wu

J. Org. Chem. **2016**, *81*, 3882–3889.

DOI: 10.1021/acs.joc.5b02514



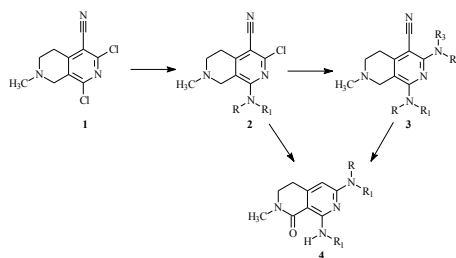
Abstract: An efficient transformation of 2-(5-hydroxy-1-pentynyl)benzonitriles **5** to furanonaphthoquinones **11** is presented. Treatment of **5** with 1.5 equiv of NaOMe in DMSO at 140 °C for 0.5 h gave **6** in good yields. Conversion of **6** to **11** was carried out by oxidation of **6** with Fremy's salt and KH₂PO₄ in acetone and water, followed by dehydrogenation using palladium on charcoal in diphenylether at reflux temperature.

The Azide/Tetrazole Equilibrium: An Investigation in the Series of Furo- and Thieno[2,3-*e*]tetrazolo[3,2-*d*]pyrimidine Derivatives

Samvel N. Sirakanyan, Domenico Spinelli, Athina Geronikaki, Viktor G. Kartsev, Henrik A. Panosyan, Armen G. Ayvazyan, Rafael A. Tamazyan, Vincenzo Frenna and Anush A. Hovakimyan

Tetrahedron **2016**, *72*, 1919–1927.

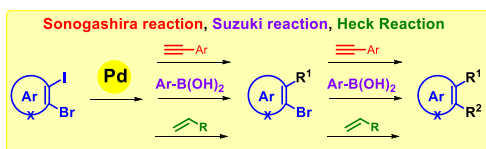
DOI: <http://dx.doi.org/10.1016/j.tet.2016.02.048>



Abstract: Starting from 7(8)-chlorofuro(thieno)[3,2-*d*]pyrimidines **1**, the corresponding 7(8)-hydrazinofuro(thieno)[3,2-*d*]pyrimidines **2** were obtained by reaction with hydrazine. By treatment with nitrous acid, compounds **2** gave fused furo- and thieno[2,3-*e*]tetrazolo[1,5-*c*]pyrimidines **3T** and **4T** in excellent yields, which in solution exist in equilibrium with 7(8)-azidofuro(thieno)[3,2-*d*]pyrimidines **3A** and **4A**. Compounds **3T/3A** and **4T/4A** represent useful substrates for investigating the azide/tetrazole equilibrium: it has been examined as a function of solvent, temperature, and their structure. We have observed that, in solution, in both **3** and **4** the equilibrium was strongly affected by the solvent used. In contrast, X-ray analysis has shown that both thieno[2,3-*e*]tetrazolo[1,5-*c*]pyrimidines and furo[2,3-*e*]tetrazolo[1,5-*c*]pyrimidines in solid state exist only in the tetrazole tautomeric form. For this reason the equilibrium constants and the relevant thermodynamic parameters have been calculated in different solvents: finally excellent logarithmic plots of ΔG° values versus dielectric constants have been observed (slopes $10.00 \div 10.57$; correlation coefficients $0.9962 \div 0.9999$) for a series (seven examples) of furo compounds **3**.

Pd-Catalyzed One-Pot Sequential Unsymmetrical Cross-Coupling Reactions of Aryl/Heteroaryl 1,2-Dihalides

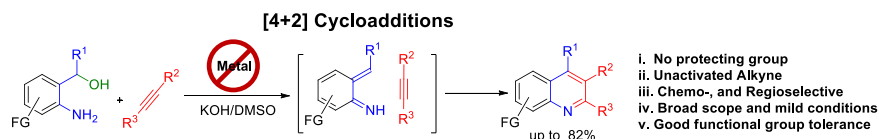
Abhinandan K. Danodia, Rakesh K. Saunthwal, Monika Patel, Rakesh K. Tiwari and Akhilesh K. Verma
Org. Biomol. Chem. **2016**, *14*, 6487–6496. DOI: 10.1039/C6OB01049K



Abstract: Efficient, step-economic, Pd(II)-catalyzed one-pot sequential Sonogashira/Sonogashira, Sonogashira/Suzuki, Sonogashira/Heck, Suzuki/Sonogashira, Suzuki/Suzuki, Suzuki/Heck, Heck/Sonogashira, Heck/Suzuki and Heck/Heck cross coupling reactions of sterically hindered aryl/heteroaryl 1,2-dihalides have been developed. The present methodology allows the conversion of easily available aryl/heteroaryl 1,2-dihalides into synthetically useful unsymmetrically substituted arenes/heteroarenes in good to excellent yields under mild reaction conditions. This methodology is a powerful tool for building a versatile substrate which can be utilized for the synthesis of various organic scaffolds.

Metal- and Protection-Free [4+2] Cycloadditions of Alkynes with Azadienes: Assembly of Functionalized Quinolines

Rakesh K. Saunthwal, Monika Patel and Akhilesh K. Verma
Org. Lett. **2016**, *18*, 2200–2203. DOI: 10.1021/acs.orglett.6b00817



Abstract: A base promoted, protection-free and regioselective synthesis of highly functionalized quinolines via [4+2] cycloaddition of azadienes (generated *in situ* from *o*-amino benzyl alcohol) with internal alkynes has been discovered. The reaction tolerates a wide variety of functional groups which has been successfully extended with diynes, (2-amino pyridin-3-yl)methanol, and 1,4-bis(phenylethynyl)benzene to afford (*Z*)-phenyl-2-styryl quinolines, phenylnaphthyridine and alkyne substituted quinolines respectively. The proposed mechanism and significant role of the solvent were well supported by isolating the azadiene intermediate and deuterium labelling studies.