

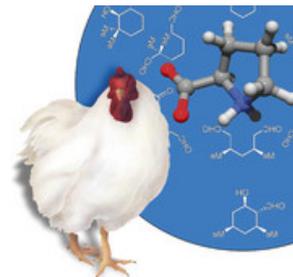
Hot Topics

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Organocatalysis

The term organocatalysis describes the acceleration of chemical reactions through the addition of a substoichiometric quantity of an organic compound. The interest in this field has increased spectacularly in the last few years as result of both the novelty of the concept and, more importantly, the fact that the efficiency and selectivity of many organocatalytic reactions meet the standards of established organic reactions. Organocatalytic reactions are becoming powerful tools in the construction of complex molecular skeletons.^[1,2]



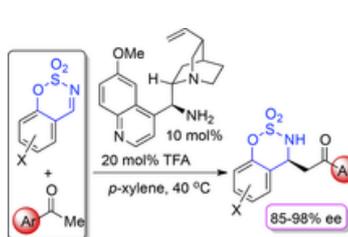
[1] P. I. Dalko, L. Moisan, *Angew. Chem.* **2001**, *113*, 3840; *Angew. Chem. Int. Ed.* **2001**, *40*, 3726
Angew. Chem. **2004**, *116*, 5248; *Angew. Chem. Int. Ed.* **2004**, *43*, 5138.

[2] Special issue of *Adv. Synth. Catal.* **2004**, *346*, Nr. 9-10.

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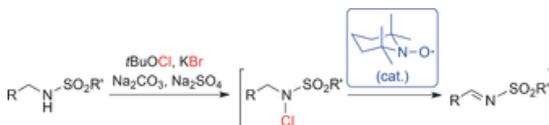
Asymmetric Mannich Reaction of Aryl Methyl Ketones with Cyclic Imines Benzo[e][1,2,3]oxathiazine 2,2-Dioxides Catalyzed by Cinchona Alkaloid-based Primary Amines



An asymmetric Mannich reaction of various aryl methyl ketones (acetophenone derivatives) with different substituted cyclic imine benzo[e][1,2,3]oxathiazine 2,2-dioxides has been developed using an alkaloid-derived primary amine as organocatalyst, providing benzo-fused cyclic sulfamidate *N*-heterocycles with 85-98 % *ee*.

[Full Paper]
Xiao-Yu Cui, Hui-Xin Duan, Yongna Zhang, You-Qing Wang
Chem. Asian J., September 30, 2016, DOI: 10.1002/asia.201601149. [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

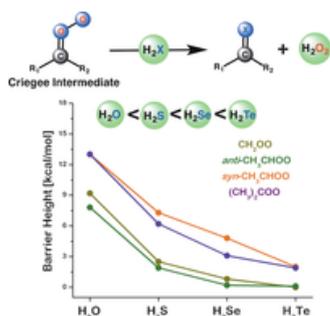
nitroxyl-radical catalyst to give imines. The *N*-halogenated amide intermediates were generated in situ from amides by treatment with a halogenation reagent (see scheme).

[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](#)

Heteroatom Tuning of Bimolecular Criegee Reactions and Its Implications

Gas-phase reactions: The calculated barriers for the bimolecular reactions of Criegee intermediates and H_2X inversely correlate with the bond strength of $X-H$ bond of H_2X or directly correlate with the first pK_a value of H_2X . Thus, it is not only the substitutions of Criegee intermediates but also the properties of the heteroatom in H_2X that play a crucial role in determining the reactivity.

[Communication]
Manoj Kumar, Joseph S. Francisco
Angew. Chem. Int. Ed., September 28, 2016, DOI: 10.1002/anie.201604848. [Read article](#)



Sequential NHC-Catalyzed Reaction of Enals and Cyclic Aryldiene-1,3-Diones: Synthesis of Tricyclic Chromenones and Related Compounds.

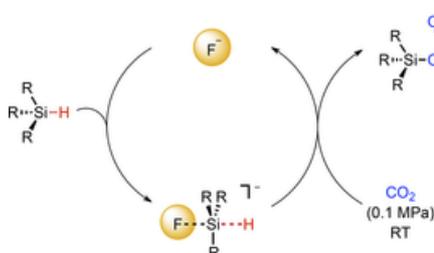
N-heterocyclic carbene (NHC) catalyzed synthesis of highly functionalized pyrano[3,2-c]chromene-2,5-dione derivatives, pyrano[3,2-c]quinoline-2,5(6H)-dione derivatives and pyrano[4,3-b]pyran-2,5-dione derivatives with potential biological activities is reported. The reaction occurs via a Knoevenagel condensation and NHC-catalyzed enolate addition in one pot.

[Communication]

Vijay Nair, JAGADEESH KRISHNAN, SNEHA MATHEW, ANJANA JAYAPRAKASH P, SASIDHAR B. S., MAYADEVI T. S., SURESH E.

Asian J. Org. Chem., September 27, 2016, DOI: 10.1002/ajoc.201600419. [Read article](#)

Carbon Dioxide Based N-Formylation of Amines Catalyzed by Fluoride and Hydroxide Anions



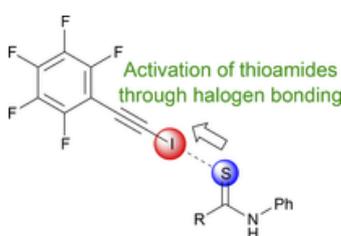
I've got anion you: A simple approach for the N-formylation of aliphatic and aromatic amines with CO₂ and hydrosilane reducing agents at room temperature and atmospheric pressure is described. Fluoride and hydroxide salts efficiently catalyze the reaction, principally through activation of the hydrosilanes. Using *n*-Bu₄NF as a simple ammonium salt catalyst, the N-formylated products are obtained in excellent yields with high selectivities.

[Communication]

Martin Hulla, Felix D. Bobbink, Shoubhik Das, Paul J. Dyson

ChemCatChem, September 26, 2016, DOI: 10.1002/cctc.201601027. [Read article](#)

Iodoalkyne-Based Catalyst-Mediated Activation of Thioamides through Halogen Bonding



Building relationships: An iodoalkyne bearing a pentafluorophenyl group was found to be effective in the catalytic activation of thioamides through halogen bonding. The thus activated thioamides reacted with 2-aminophenol to produce benzoxazoles in good yield. Mechanistic studies provided concrete evidence that this catalytic activation is based on halogen bonding.

[Communication]

Akinobu Matsuzawa, Shiho Takeuchi, Kazuyuki Sugita

Chem. Asian J., September 21, 2016, DOI: 10.1002/asia.201601130. [Read article](#)

Organocatalyzed Assembly of Chlorinated Quaternary Stereogenic Centers

The catalytic asymmetric construction of chiral quaternary stereocenters is always a continuous area of research in organic chemistry. In this sense, when a chlorine atom takes part in a quaternary stereocenter, the difficulty of its synthesis increases along with the significance of the resulting products. This is true, not only because of the intrinsic interest of such chlorinated molecules, but also because they are considered as highly valuable chiral building blocks in organic synthesis, as they can be easily converted to more complex molecules by a simple S_N2 displacement. Among the different strategies followed to create chlorinated quaternary stereogenic centers, organocatalysis has played a pivotal role during the last decade. In this review, a comprehensive analysis of such organocatalyzed transformations is presented.

[Focus Review]

Melania Gómez-Martínez, Diego A. Alonso, Isidro M. Pastor, Gabriela Guillena, Alejandro Baeza

Asian J. Org. Chem., September 20, 2016, DOI: 10.1002/ajoc.201600404. [Read article](#)

Insights into N-Heterocyclic Carbene-Catalyzed [4 + 2] Annulation Reaction of Enals with Nitroalkenes: Mechanisms, Origin of Chemo- and Stereoselectivity, and Role of Catalyst

In this paper, the density functional theory (DFT) has been employed to investigate the detailed mechanisms, origin of chemo- and stereoselectivity, and role of catalyst for the reaction of enals with nitroalkenes catalyzed by N-heterocyclic carbene (NHC). The calculated results disclose that the reaction contains seven steps, i.e., the nucleophilic attack on the α -unsaturated aldehyde by NHC, the [1, 2]-proton transfer for the formation of Breslow intermediate, the β -protonation for

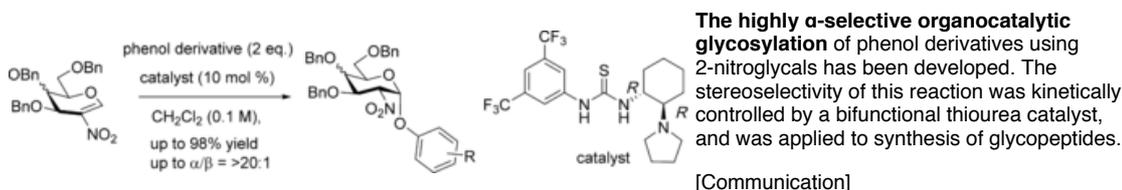
affording enolate intermediate, the nucleophilic addition on the Re/Si face of enolate by the nitroalkenes, the [1, 5] proton transfer, the ring-closure process, and the regeneration of NHC. The addition on the Re/Si face of enolate is identified to be the stereocontrolling step, in which the chiral centers including α -carbon of enals and β -carbon of nitroalkenes are formed. Moreover, the reaction pathway leading to the RR-configured product has the lowest Gibbs free energy barrier, which is in agreement with the experimental observation. Furthermore, the analyses of electrophilic and nucleophilic Parr functions and global reactivity indexes (GRIs) have been performed to explore the origin of chemoselectivity and the role of catalyst. This theoretical work would provide valuable insights for the rational design of more effective organocatalyst for this kind of reactions with high stereoselectivities.

[Full Paper]

Linjie Zheng, Donghui Wei, Yang Wang, Yan Qiao

Chem. Asian J., September 08, 2016, DOI: 10.1002/asia.201601022. [Read article](#)

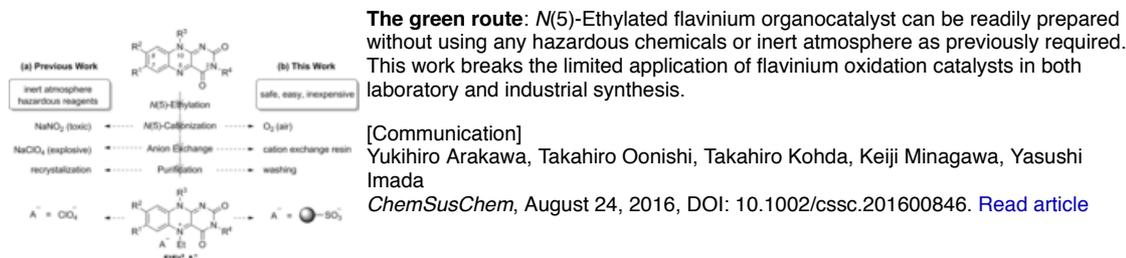
Kinetically Controlled α -Selective O-Glycosylation of Phenol Derivatives Using 2-Nitroglycals by a Bifunctional Chiral Thiourea Catalyst



Keisuke Yoshida, Yohei Kanoko, Kenichi Takao

Asian J. Org. Chem., August 25, 2016, DOI: 10.1002/ajoc.201600307. [Read article](#)

Facile Preparation of Flavinium Organocatalysts



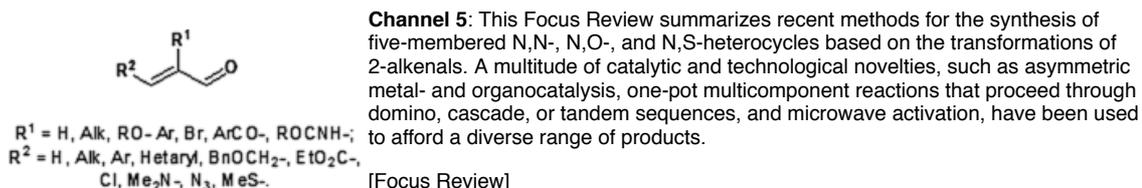
Promotion of Organic Reactions by Non-Benzenoid Carbocyclic Aromatic Ions

[Review]

Demelza J. M. Lyons, Reece D. Crocker, Marcus Blümel, Thanh Vinh Nguyen

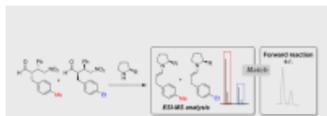
Angew. Chem. Int. Ed., August 10, 2016, DOI: 10.1002/anie.201605979. [Read article](#)

Synthesis of Diheteroatomic Five-Membered Heterocyclic Compounds from α,β -Unsaturated Aldehydes



Asian J. Org. Chem., August 01, 2016, DOI: 10.1002/ajoc.201600227. [Read article](#)

Mass Spectrometric Back Reaction Screening of Quasi-Enantiomeric Products as a Mechanistic Tool



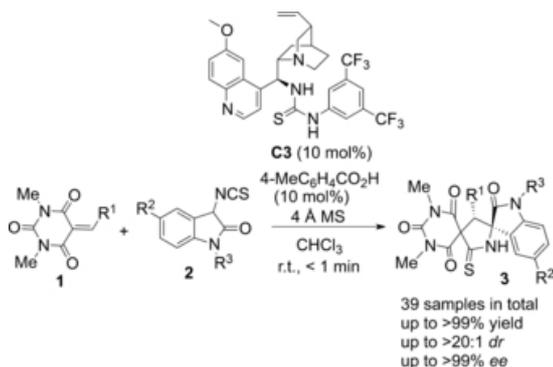
Observing back and forth: Mass spectrometric back reaction screening of quasi-enantiomeric products may serve as a valuable tool for examining the mechanism of an enantioselective catalytic process. By comparing the results from the forward and back reaction, direct evidence for the involvement of a catalytic intermediate in the enantioselective step can be obtained. The potential of this method is demonstrated for various organocatalytic asymmetric reactions.

[Personal Account]

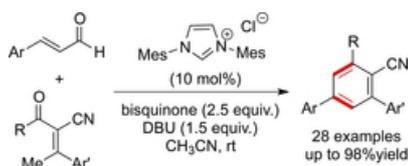
Patrick G. Isenegger, Andreas Pfaltz

The Chemical Record, July 15, 2016, DOI: 10.1002/tr.201600072. [Read article](#)

Organocatalytic [3+2] Cycloadditions of Barbiturate-Based Olefins with 3-Isothiocyanato Oxindoles: Highly Diastereoselective and Enantioselective Synthesis of Dispirobarbiturates



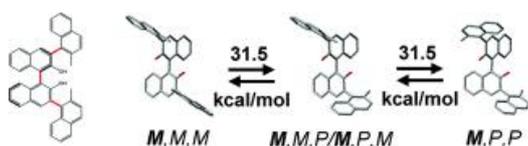
N-Heterocyclic Carbene-Catalyzed Synthesis of Multi-Substituted Benzenes from Enals and α -Cyano- β -methyleneones



[Communication]

Chun-Lin Zhang, Zhong-Hua Gao, Zhi-Qin Liang, Song Ye
Adv. Synth. Catal., June 20, 2016, DOI: 10.1002/adsc.201600531. [Read article.](#)

An Atropisomerically Enforced Phosphoric Acid for Organocatalytic Asymmetric Reactions

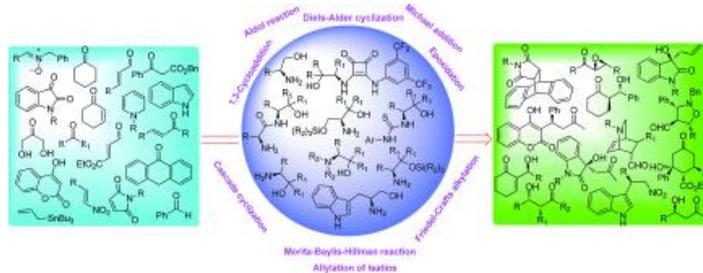


Three atropisomeric phosphoric acids for organocatalysis were obtained by a single Suzuki coupling reaction, and resolved by HPLC. All three catalysts could be used to promote organocatalytic reactions, rendering up to excellent enantioselectivity (98 % ee), confirming the potential of atropisomeric conformational control at the 3,3'-position of the BINOL core to influence catalyst performance.

[Full Paper]

Luca Bernardi, Giada Bolzoni, Mariafrancesca Fochi, Michele Mancinelli, Andrea Mazzanti
Eur. J. Org. Chem., May 2, 2016, DOI: 10.1002/ejoc.201600296. [Read article.](#)

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



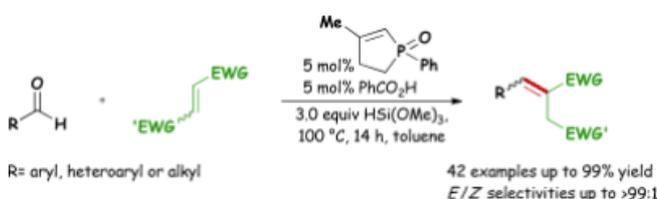
This review demonstrates the catalytic efficiency of primary β -amino alcohols and their derivatives in organocatalysis. These simple amino alcohols are inexpensive alternatives to other primary amino organocatalysts, being easy to synthesize and air-stable and offering the potential for introduction 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.](#)

Novel Base-Free Catalytic Wittig Reaction for the Synthesis of Highly Functionalized Alkenes



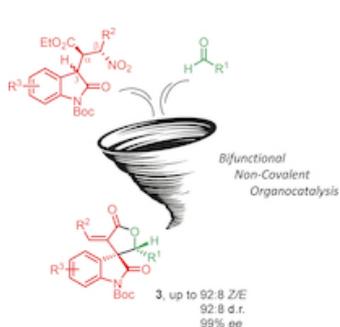
Drop the base: A novel catalytic system based on a readily available phosphine oxide precatalyst for base-free catalytic Wittig reactions has been developed (see scheme). Under the optimized reaction conditions, numerous functionalized alkenes were prepared in yields up to 99% and with good to excellent *E/Z* selectivities.

[Full Paper]

Marie-Luis Schirmer, Sven Adomeit, Anke Spannberg, Thomas Werner

Chem. Eur. J., January 13, 2016, DOI: 10.1002/chem.201503744. [Read article.](#)

The First Enantioselective Organocatalytic Synthesis of 3-Spiro- α -Alkylidene- γ -Butyrolactone Oxindoles

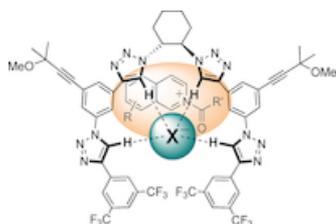


An innovative and flexible methodology catalyzed by bifunctional chiral thioureas was developed to react β -nitro oxindoles with aldehydes (see scheme). This approach allows the first enantioselective synthesis of 3-spiro- α -alkylidene- γ -butyrolactone oxindoles **3** with the aim of merging two potentially bioactive structural motifs: the spirooxindole and the α -alkylidene- γ -butyrolactone.

[Full Paper]

Lucia Cerisoli, Marco Lombardo, Claudio Trombini, Arianna Quintavalla
Chem. Eur. J., January 7, 2016, DOI: 10.1002/chem.201504157. [Read article.](#)

Chiral Triazoles in Anion-Binding Catalysis: New Entry to Enantioselective Reissert-Type Reactions

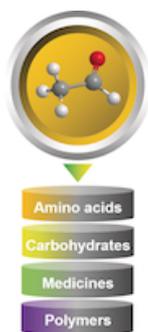


Against the elements: A family of chiral triazoles has been introduced as innovative C-H bond-based hydrogen donors for anion-binding catalysis. Contrary to the believed inefficiency of the low polarized C-H bonds for promoting organocatalysis, these structures proved to be competitive with respect to the more established N-H-type hydrogen donors in enantioselective Reissert-type reactions.

[Full Paper]

Mercedes Zurro, Sören Asmus, Julia Bamberger, Stephan Beckendorf, Olga García Mancheño
Chem. Eur. J., January 7, 2016, DOI: 10.1002/chem.201504094. [Read article.](#)

Acetaldehyde: A Small Organic Molecule with Big Impact on Organocatalytic Reactions

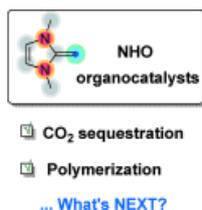


Utility of acetaldehyde: Acetaldehyde has recently received a great deal of attention as the simplest enolizable carbonyl compound because of its versatile applications in the synthesis of poly(vinyl alcohol), unnatural amino acids, and medicine (see graphic). This Minireview summarizes a methodologically diverse approach to the synthesis of target molecules by outlining a diverse array of reactions such as aldol, Mannich, Michael, and NHC-catalyzed reactions.

[Minireview]

Sun Min Kim, Young Sug Kim, Dong Wan Kim, Ramon Rios, Jung Woon Yang
Chem. Eur. J., December 15, 2015, DOI: 10.1002/chem.201503960. [Read article.](#)

The Resurgence of the Highly Ylidic N-Heterocyclic Olefins as a New Class of Organocatalysts

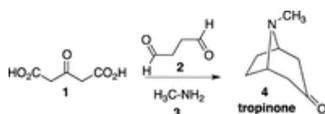


One carbon better: N-Heterocyclic olefins, the alkylidene derivatives of the prevalent N-heterocyclic carbenes, have recently emerged as efficient promoters for CO₂ fixation and polymerization reactions. Their extraordinarily strong Lewis/Bronsted basicity suggests great potential as a new class of organocatalysts for a broad range of reactions in synthetic chemistry.

[Concept]

Reece D. Crocker, Thanh V. Nguyen
Chem. Eur. J., November 26, 2015, DOI: 10.1002/chem.201503575. [Read article.](#)

Whither Organic Synthesis?



[Review]

Douglass F. Taber
Isr. J. Chem., April 15, 2015, DOI: 10.1002/ijch.201500006. [Read article](#)