CJC | Chinese Journal of Chemistry
中国化学 - An International Journal

Pages 781–1032 | Number 4 | Volume 39 | April 2021

Chemistry Authors Up Close

Concise Total Syntheses of Bioactive Alkaloids Enabled by Development or Application of Cascade Reactions: A Personnel Adventure

Xingang Xie* and Xuegong She*

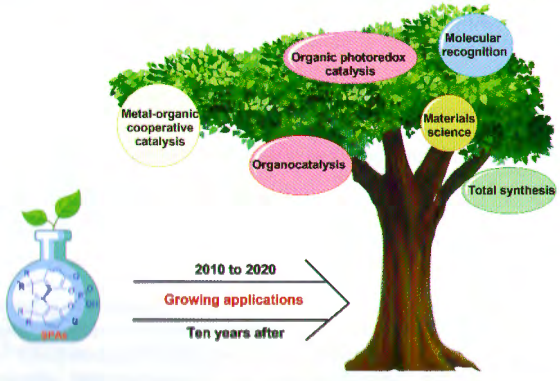
Chin. J. Chem. **2021**, *39*, 795—801. **DOI: 10.1002/cjoc.202000522**

The significance of cascade reaction developments and applications in concise syntheses of bioactive alkaloids was highlighted based on our own recent adventure in this research field.

Chiral Spirocyclic Phosphoric Acids and Their Growing Applications

Xufeng Lin,* Lei Wang, Zhao Han, and Zhouli Chen

Chin. J. Chem. **2021**, *39*, 802—824. **DOI: 10.1002/cjoc.202000446**

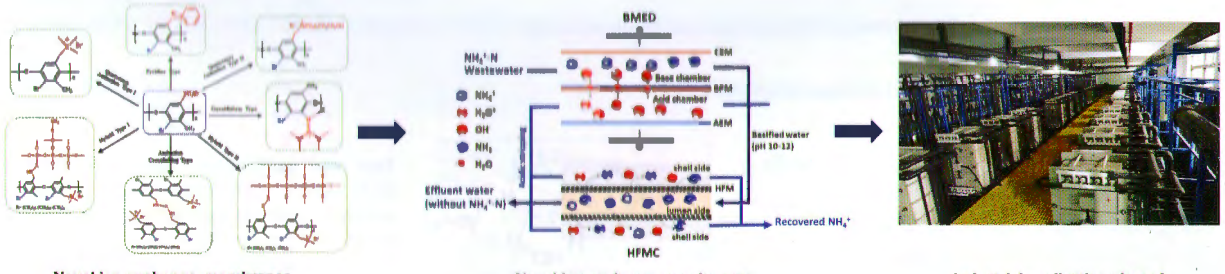


Chiral spirocyclic phosphoric acids are versatile catalysts capable of promoting a wide range of organocatalytic reactions, and also illustrate broad applications in metal-organic cooperative catalysis, organic photoredox catalysis, total synthesis, materials science and molecular recognition.

Ion Exchange Membrane "ABC" – A Key Material for Upgrading Process Industries

Yaoming Wang, Zhengjin Yang, Liang Wu, Liang Ge, and Tongwen Xu*

Chin. J. Chem. **2021**, *39*, 825—837. **DOI: 10.1002/cjoc.202000473**

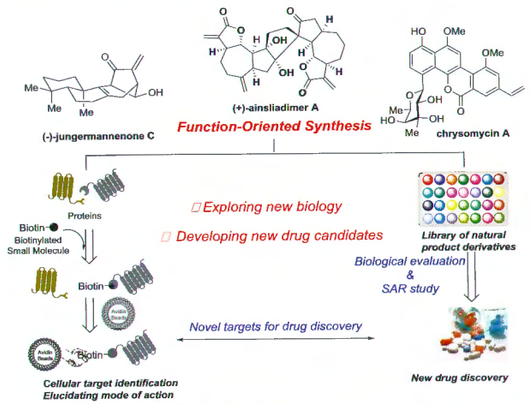


Novel ion exchange membranes design and fabrication

Novel ion exchange membranes processes

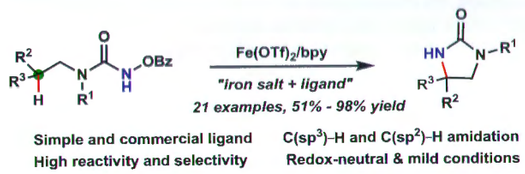
Industrial applications based on ion exchange membranes

Ion exchange membrane "ABC" plays a crucial role in transforming and upgrading traditional chemical manufacturing procedures and boosting a multitude of new applications.

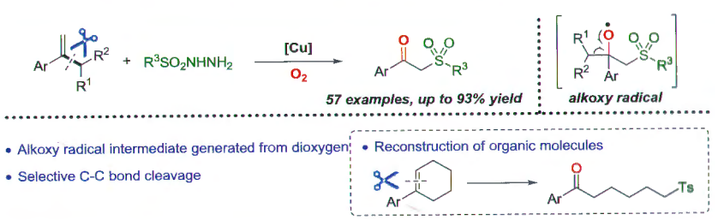


Our research programs focus on the interface between chemistry and biology. In this account, we describe several research accomplishments from our laboratory, merging the function-oriented natural product synthesis, the mechanism driven biological elucidation of the bioactive natural products and the subsequent drug discovery endeavours.

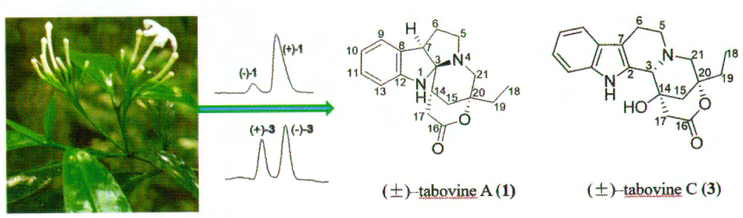
Concise Reports



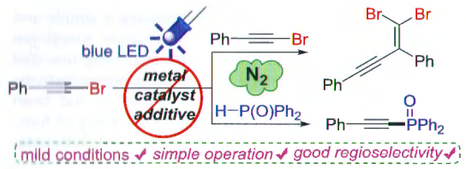
A redox-neutral Fe/bpy-catalyzed intramolecular C—H amidation of *N*-benzoyloxyureas under external oxidant-free conditions is reported. An array of cyclic ureas were synthesized *via* C—H bond nitrene insertion in moderate to excellent yields.



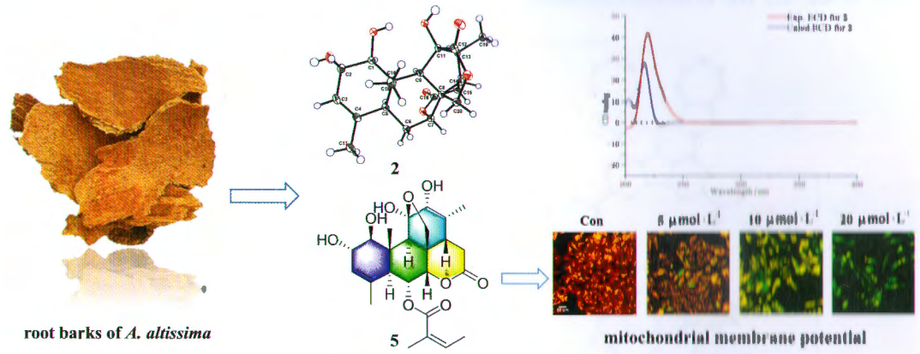
Herein, we report alkoxy radical, which was generated from alkyl radical and dioxygen, mediated selective cleavage of unstrained carbon-carbon bond for the oxysulfonylation of 1,1-disubstituted alkenes, providing facile access to a variety of valuable β-keto sulfones. Importantly, the strategy was successfully applied for constructing uneasily obtained architecturally intriguing molecules.



Two new pairs of monoterpenoid indole alkaloids (MIAs) enantiomers were isolated from stems of *Tabernaemontana bovina* Lour. (Apocynaceae). It is the first time to report co-occurring enantiomers of MIAs. Additionally, the explanation concerning biogenesis of MIAs was provided. The findings would open a new window, where we could disclose more diverse MIAs.

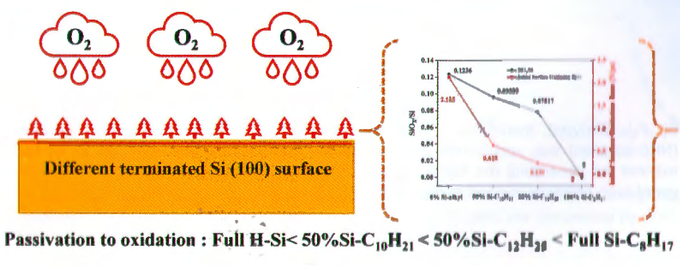


Visible-light-promoted synthesis of 1,1-dibromo-1-en-3-ynes and alkynylphosphine oxides *via* controllable formation of C—C and C—P bonds under photocatalyst-free conditions is developed.

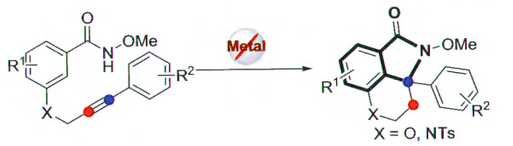


Five new quassinoids, chouchunlactone A—E (**1**—**5**), and two known ones were identified from the root barks of *A. altissima* Swingle. Biologically, compound **5** showed potencies equivalent to sorafenib against HepG2 cells.

The reaction of 2-alkynylanisoles/sulfides with $SOCl_2$ and DMSO was conducted to conveniently furnish the biologically interesting 3-(methylthio)- benzo[*b*]furans/thiophenes *via* intramolecular cyclization. DMSO acts as a solvent as well as a sulfur source and can also be replaced with DMSO-d_6, enabling the incorporation of the SCD_3 moiety of DMSO-d_6 to the 3-position of the heterocyclic frameworks.

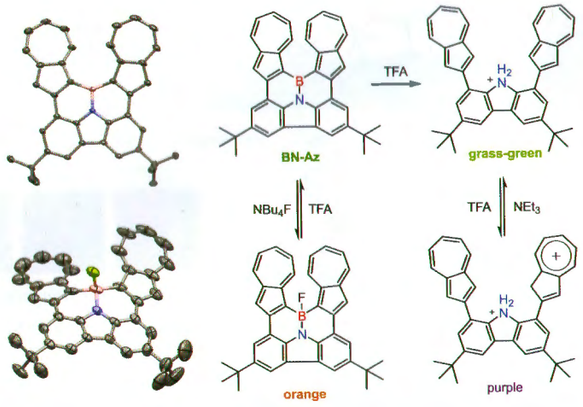


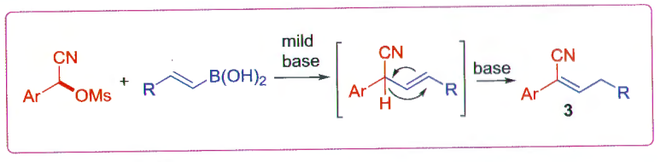
Herein, the oxidation of the full H-terminated Si surface and the chemical passivated silicon (100) surfaces at 300 K has been studied by ReaxFF molecular dynamic simulation. The results suggest that with the increase of alkyl chain length and the coverage of Si surface, the oxidized Si atoms and the initial oxidation rate also decrease.

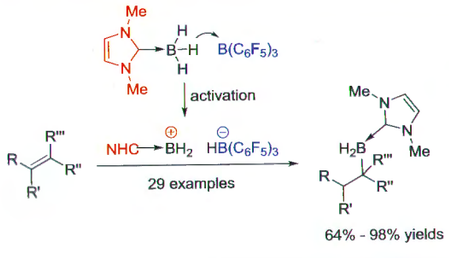


- metal-free catalysis
- 100% atomic economy
- gram-scale synthesis
- construction of quarternary carbon
- broad substrate scope
- DFT calculations

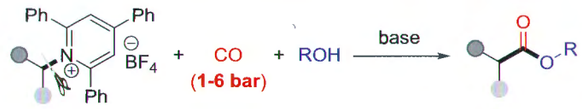
Through the intramolecular cyclization of *N*-methoxybenzamides, a simple and efficient method for constructing valuable isoindolinones under metal-free conditions was developed. The reaction was featured by employing low-cost catalyst, simple operation, 100% atomic economy and excellent regioselectivity. Moreover, a detailed computational study on the reaction system has been performed to clarify the mechanism. This protocol tolerated a variety of functional groups and provided a metal-free protocol for the synthesis of chromane- or tetrahydroquinoline-fused isoindolinones in good yields.





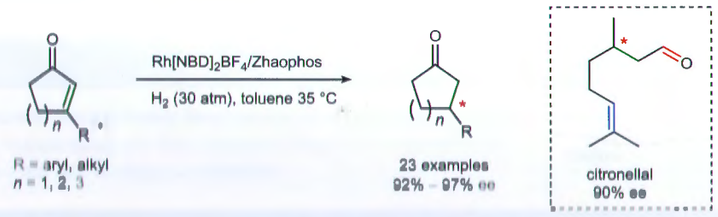


B(C_6F_5)$_3$-catalyzed hydroboration of alkenes with *N*-heterocyclic carbene boranes (NHC-boranes) was successfully realized by the activation of NHC-boranes in an FLP manner for generating the highly reactive zwitterion species to furnish the desired organoboron products in good to high yields.

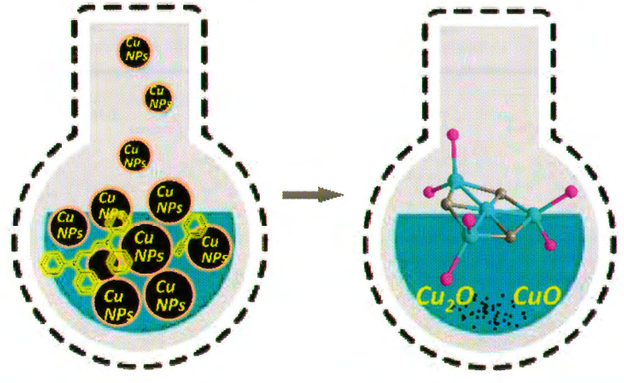


- ✓ Low CO pressure
- ✓ Transition-metal-free
- ✓ Phenols and alcohols as coupling partner
- ✓ Good functional group tolerance

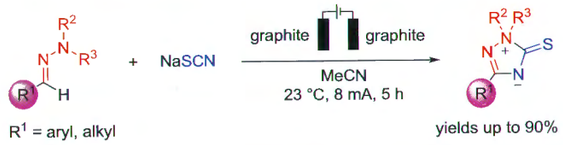
Transition-metal-free radical carbonylation of activated alkylamines with phenols and alcohols has been successful developed. This radical carbonylative strategy can be carried out under low CO pressure (1—6 bar). Esters with various functional groups were obtained in moderate to good yields.



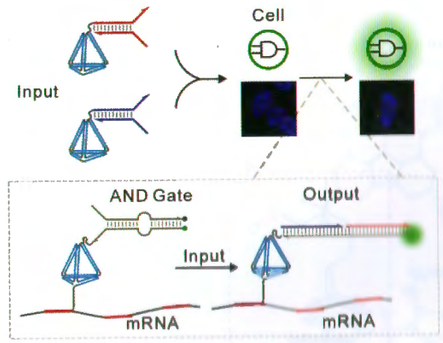
The enantioselective hydrogenation of cyclic enones has been a historical problem for homogeneous catalysis. We herein report an efficient method to reduce cyclic enones with molecular hydrogen. Catalyzed by a rhodium/Zhaophos complex, variety of enones with five-, six- or seven-member ring were hydrogenated with high enantioselectivity (92%—99% ee). Excellent chemo- and enantioselectivity demonstrated this method was successfully applied in the enantioselective hydrogenation of citral to produce enantio-enriched citronellal.



A top-down approach has been developed to synthesize three novel alkynyl and phosphine protected Cu clusters from Cu nanoparticles. A peculiar centered triangle Cu_4 and a Cu_6 uniform triangular prism clusters are discovered by simply using different bidentate phosphine ligands.

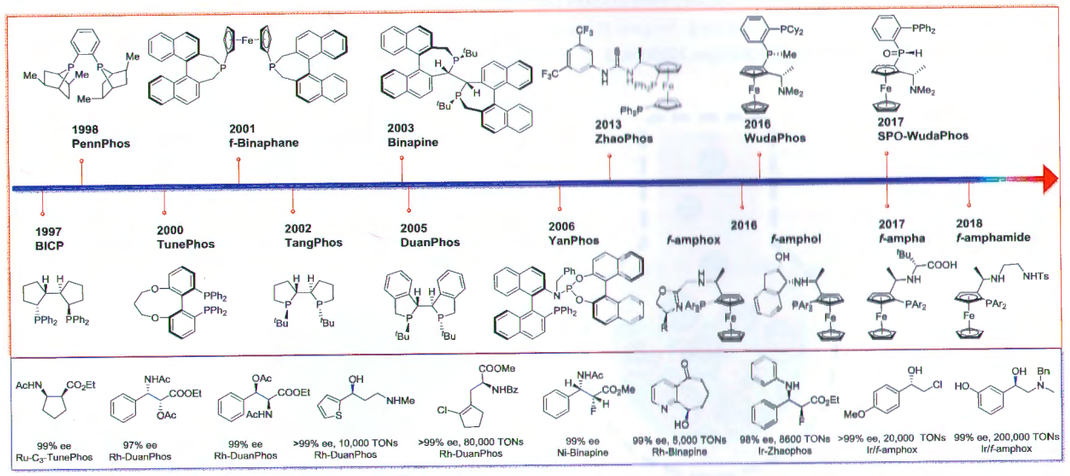


In this protocol, functionalized triazolium inner salts are achieved through the electrochemical thiocyanation and cyclization of aldehyde hydrazone derivative with ample scope and diverse functional group tolerance, under mild, catalyst- and external oxidant-free conditions.

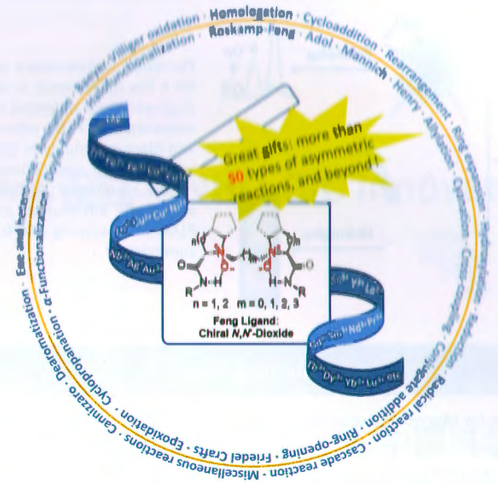


In this work, we reported framework nucleic acid-based circuits enabling intracellular logic computation for mRNA imaging.

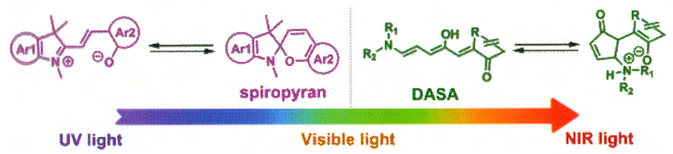
Cornerstones in Chemistry



Chiral phosphorus ligands have played a crucial role for the recent advances in asymmetric catalysis. This review summarizes chiral phosphorus ligands developed from the Laboratory of Professor Xumu Zhang in the latest 25 years. A number of iconic phosphorus ligands including bisphosphorus ligands with rigid chiral backbone such as BICP, PennPhos, TunePhos, and *f*-Binaphane, *P*-chiral bisphosphorus ligands TangPhos, Binapine, and DuanPhos, phosphine-phosphoramidte ligand YanPhos, noncovalent interaction-assisted ferrocenyl phosphorus ligand ZhaoPhos and WudaPhos, and tridentate ferrocenyl phosphorus ligands *f*-amphox are introduced, and their applications in asymmetric hydrogenation are emphasized.

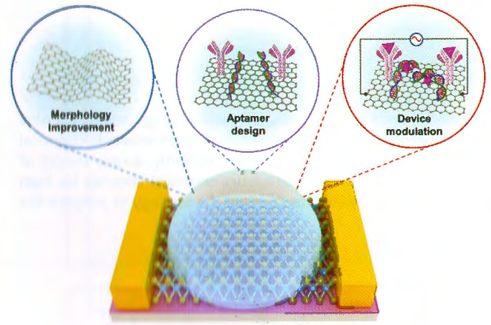


Recent Advances

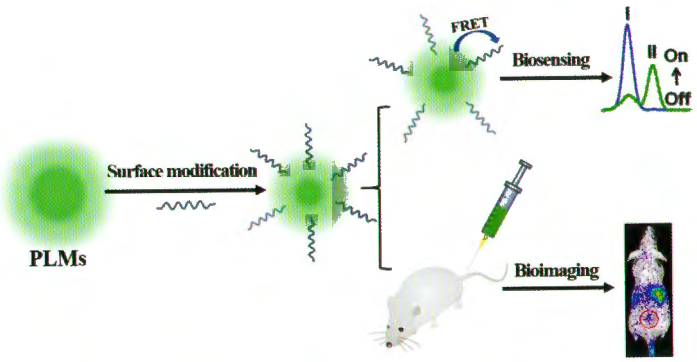


Donor-acceptor Stenhouse adducts (DASAs) as a species of novel photochromic molecules, show visible/near-infrared (NIR) light induced *linear*- to-*cyclic* isomerization and heat induced *cyclic*-to-*linear* isomerization. Spiropyrans (SPs) show similar molecular properties and comparable photoswitching with DASAs. UV light triggers *closed*-to-*open* (also known as *spirocyclic* (*SC*)-to-*merocyanine* (*MC*)) isomerization of SPs, while the reversed *open*-to-*closed* isomerization occurs under visible light or heat. The well-studied SPs have important reference values to the comprehensive developments of DASAs.

Critical Review

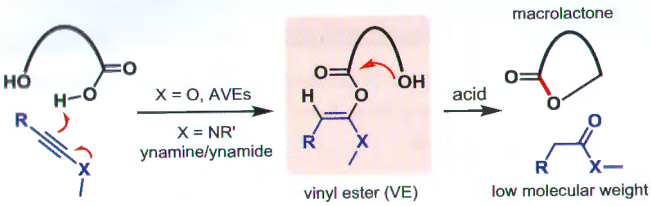


The performance of field effective transistor (FET) biosensors is limited to the charge screening in the solution, and previous reviews have not systematically elucidate this mechanism. In this review, we first expound the generation mechanism of this charge screening, then highlight recent advances to overcome this debye screening, including morphology improvements, aptamer design and device modulation. Finally, the challenges and perspectives involving overcoming charge screening are discussed. This review is beneficial to the development of label free, real-time and ultra-sensitivity FET biosensors.

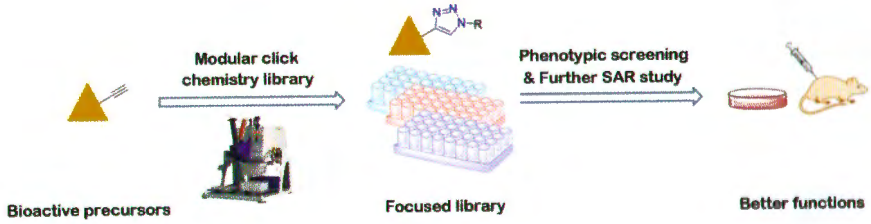


Persistent luminescence materials (PLMs) can remain luminescent for a few milliseconds to days without constant excitation and have displayed great potential in biosensing and bioimaging applications. However, bare PLMs often suffer from the poor stability, selectivity, and biocompatibility in biological system and *in vivo*, which greatly impedes their applications in biomedicine and bioanalysis. In this review, commonly used strategies for surface modification of PLMs are briefly introduced, and the applications of surface modified PLMs in biosensing and bioimaging as well as their challenges are summarized.

Emerging Topic



The renaissance of two half-century-old acyl donors, derived from AVEs and ynamines or ynamides, reminds us that the reactivities of specific functional groups are still waiting to be explored. The macrocyclization *via* the vinyl ester intermediates is mild, racemization-free, and an ease of work-up due to readily depletion of ester or amide derived from the coupling reagent. This novel approach is complementary to other macrolactonization methods and thus are of great expectation to future application.



High throughput screening towards chemical libraries is the primary way to discover lead compounds in developing innovative drugs, especially new molecular entities. Accordingly, the preparation of chemical libraries is the key step for drug development. Now, conventional small molecule chemical libraries and DNA-encoded chemical libraries are the main models of chemical libraries for high-throughput screening. Recently, a new model of chemical library, called modular click chemistry library, was proposed, which gives us an alternative choice to construct chemical libraries for high throughput screening and exhibits broad prospects to accelerate drug development. Herein, this article mainly focuses on the strategy to prepare the modular click chemistry library.