

有机化学

Chinese Journal of Organic Chemistry

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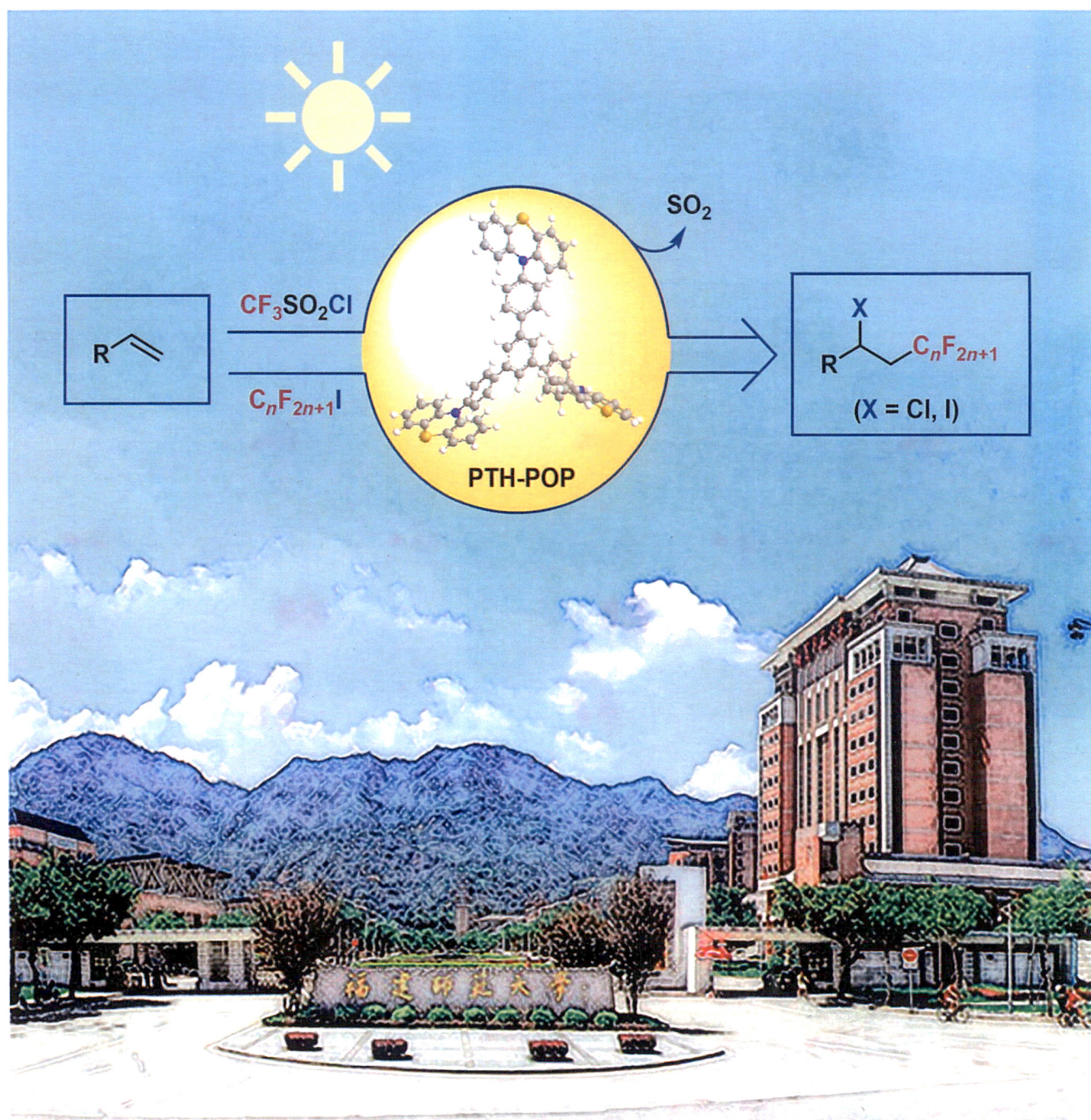


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中国女科学家专辑

Vol. 43 No. 3 March 2023



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中国科学院上海有机化学研究所 主办
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(YOUJI HUAXUE)

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* 通讯联系人.

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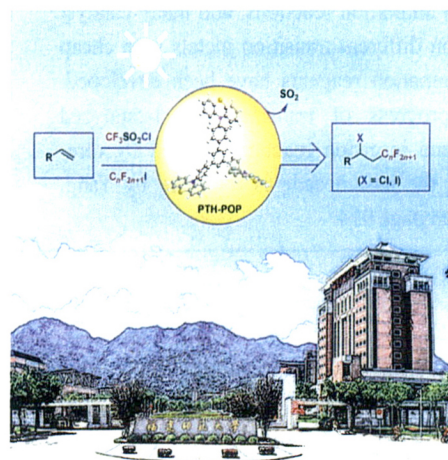
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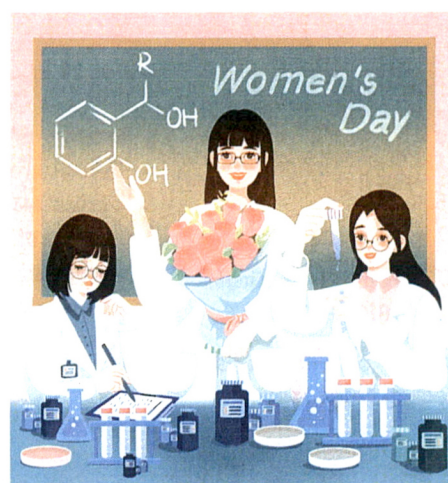
Cover Picture: Haloperfluoroalkylation of Unactivated Terminal Alkenes over Phenylphenothiazine-Based Porous Organic Polymers

Photocatalytic heterogeneous chlorotrifluoromethylation and iodoperfluoroalkylation of unactivated terminal alkenes achieved under the catalysis of PTH-POP (phenylphenothiazine-based porous organic polymer) are reported by Wang, Gao, Zhou and Zhang on page 1136. This method offers a transition-metal-free and recyclable platform to access valuable perfluoroalkylated compounds in a highly efficient fashion.



Inside Cover: Advances in Catalytic Asymmetric Reactions Involving *o*-Hydroxybenzyl Alcohols

The catalytic asymmetric reactions involving *o*-hydroxybenzyl alcohols, a kind of *o*-quinone methide precursors with unique advantages, are summarized by Wang, Yang, Zhang and Shi on page 974. This review will open a new window for the design of new kinds of *o*-hydroxybenzyl alcohols and their involved catalytic asymmetric reactions. Notably, this review is dedicated to the special issue “Women Scientists in China” to celebrate the International Women’s Day.



Inside Back Cover: Visible Light-Catalyzed Synthesis of Difluoroalkylated Polycyclic Indoles

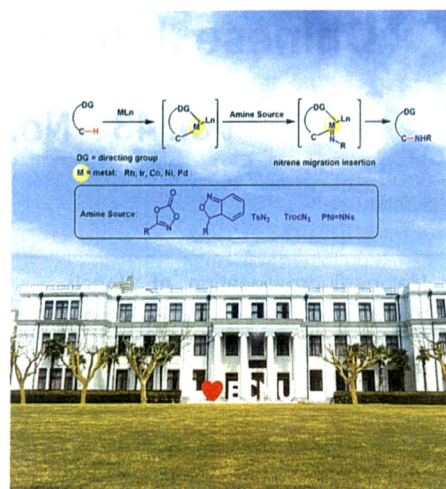
A light-promoted radical tandem cyclization reaction to synthesize difluoroalkylindoles was developed by Zhao, Wei, Ke, and Li on page 1102. By using difluorobromomethyl esters and 3-alkenyl indoles, various of fluorine-containing polycyclic indoles were generated in an easy-to-operate and mild in conditions with a wide range of substrate adaptability and good yields.



CONTENT

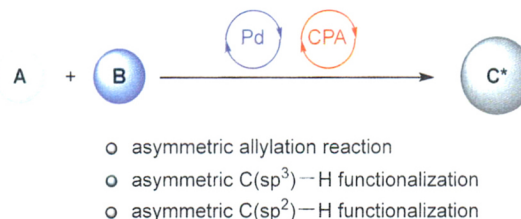
Back Cover: Recent Progress in Transition Metal Catalyzed C(sp³)—H Nitrene Insertion Reactions Assisted by Directing Groups

The reaction of transition metals catalyzed the activation of C(sp³)—H bonds to form carbon-nitrogen bonds has been a challenging and hot research area. Important progress has been made in directing group-assisted C(sp³)—H bond amination reactions, and many catalyst systems based on different transition metals with cheap and efficient amination reagents have been developed. The research progress of transition metal-catalyzed C(sp³)—H nitrene insertion reaction assisted by directing groups in the past decade is reviewed by Yang, Liu, and Wang on page 914



REVIEWS

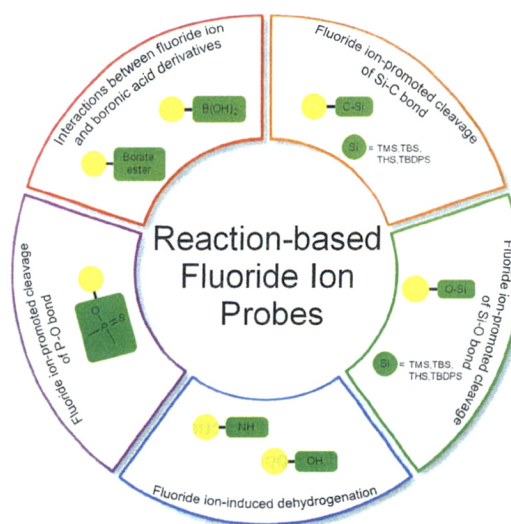
Recent Advances of Efficient Synthesis of Chiral Molecules Promoted by Pd/Chiral Phosphoric Acid Synergistic Catalysis



A variety of asymmetric catalytic reactions have been efficiently realized by the synergistic catalysis system of transition metal palladium catalytic system and chiral phosphoric acids with high chemo-, regio-, and stereoselectivity in recent years. The recent progress of asymmetric allylation reaction, C(sp³)—H functionalization, C(sp²)—H functionalization and other reactions promoted by this synergistic catalysis system is summarized.

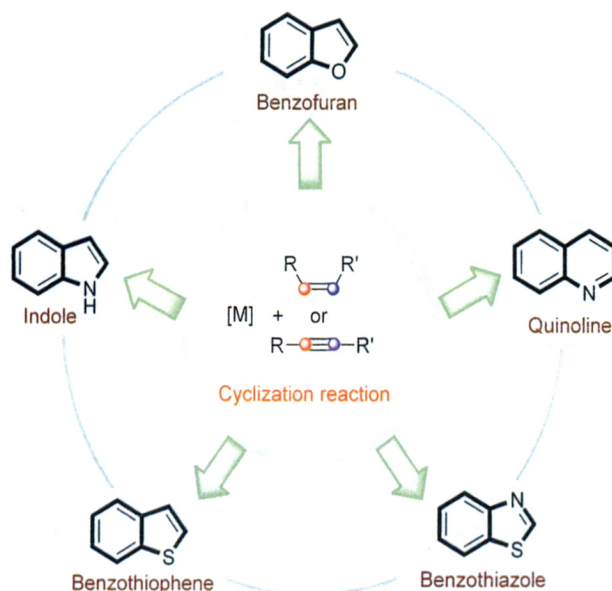
Xiang, Xun; He, Zhaolin*; Dong, Xiuqin*
Chin. J. Org. Chem. **2023**, 43(3), 791

Research Progress of Reaction-Based Probes for Detecting Fluoride Ion



The developments on reaction-based probes for detecting fluoride ion are summarized, which include five different types: interactions between fluoride ion and boronic acid derivatives, fluoride ion-promoted cleavage of Si—C bond, fluoride ion-promoted cleavage of Si—O bond, fluoride ion-induced dehydrogenation, and fluoride ion-promoted cleavage of P—O bond.

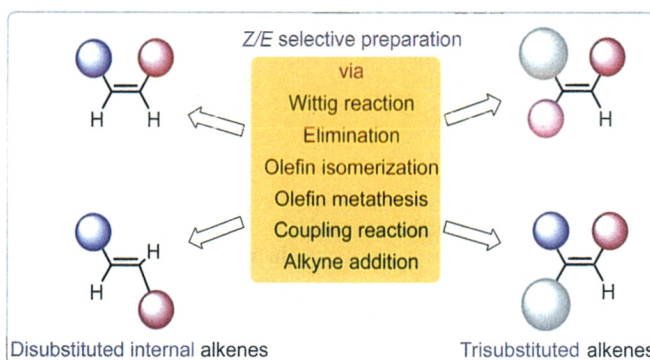
Qu, Yanjie; Li, Yajun; Bao, Hongli*
Chin. J. Org. Chem. **2023**, 43(3), 809

Recent Advances in the Synthesis of
Fused Heterocyclic Compounds and
Their Antitumor Activities

The recent progress on the reaction development of transition metal-catalyzed cyclizations involving unsaturated hydrocarbons for the synthesis of fused heterocyclic compounds including benzofurans, indoles, quinolines in the last five years has been summarized, as well as their applications in the field of medicinal chemistry with antitumor activities.

Duan, Kanghui; Tang, Junlong; Wu, Wan-qing*

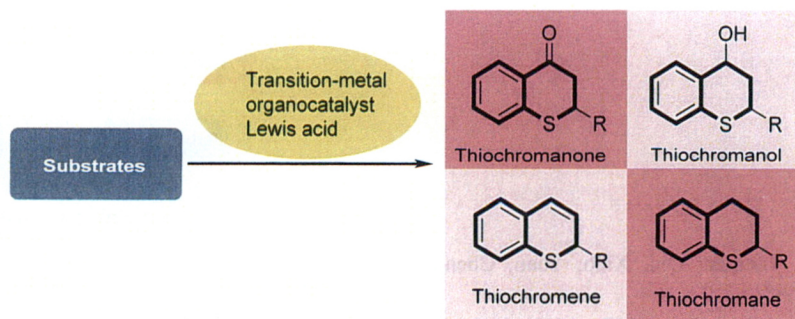
Chin. J. Org. Chem. **2023**, 43(3), 826

Z : E Selective Preparation of Disubstituted
Internal Alkenes and Trisubstituted
Alkenes

The selective synthetic methods of Z : E configurations of disubstituted inner alkenes and trisubstituted alkenes are reviewed, including the Wittig reaction, substituted alkane elimination reaction, olefin isomerization reaction, olefin metathesis, olefin coupling reaction, and alkyne addition reaction. The catalyst types and controlling factors of Z : E selectivity in these synthetic examples are described in detail.

Guo, Ping; Zhou, Yong; Zhao, Jie*

Chin. J. Org. Chem. **2023**, 43(3), 855

Research Progress on Synthesis of Thio-
flavonoids

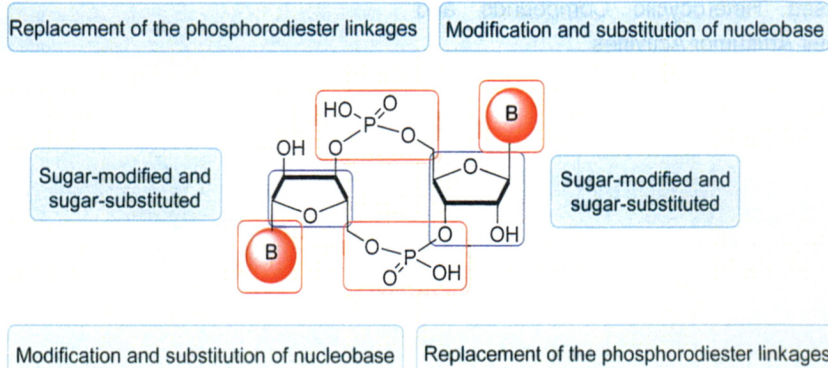
The synthetic approaches of thioflavonoids and key steps of reaction mechanisms according to the classification of thioflavonoids are summarized, and the development prospect of this research field is prospected.

Meng, Ling; Wang, Jun*

Chin. J. Org. Chem. **2023**, 43(3), 873

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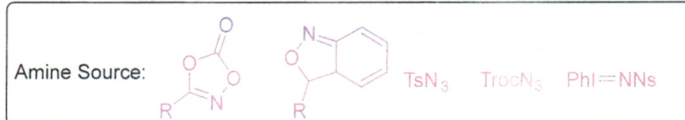
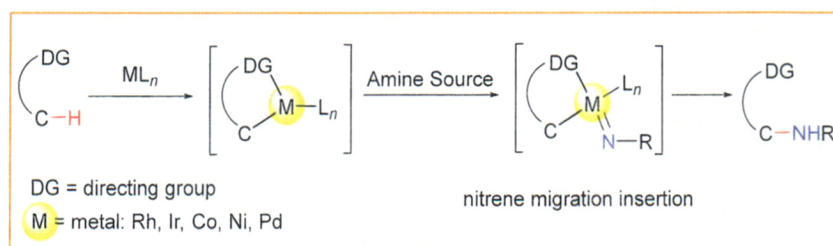
Progress on the Synthesis and Activity of Cyclic Dinucleotides as Stimulator of Interferon Gene (STING) Agonists



The important progress in the synthesis and activity of cyclic dinucleotides as stimulator of interferon Gene (STING) agonists is reviewed. The main types of cyclic dinucleotides modification, and their synthetic strategies are mainly discussed.

Wang, Tianyang; Li, Yan-Mei*
Chin. J. Org. Chem. **2023**, 43(3), 892

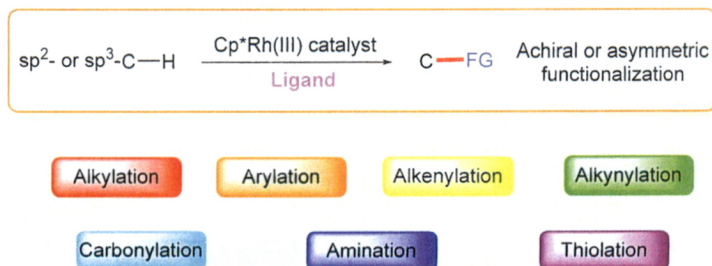
Recent Progress in Transition Metal Catalyzed C(sp³)—H Nitrene Insertion Reactions Assisted by Directing Groups



In recent years, important progress has been made in inner sphere C(sp³)—H bond amination reactions, and many catalyst systems based on different transition metals with cheap and efficient amination reagents have been developed. Herein, the research progress of C(sp³)—H nitrene migration insertion reaction assisted by directing groups in the past decade is reviewed.

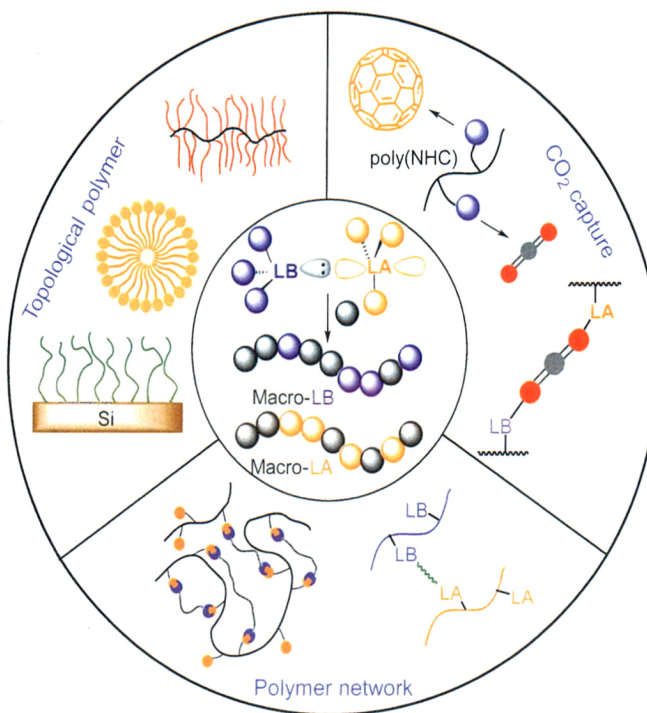
Yang, Xing; Liu, Xu; Wang, Lijia*
Chin. J. Org. Chem. **2023**, 43(3), 914

Application of Ligands in Cp*Rh(III)-catalyzed C—H Bond Functionalization Reaction



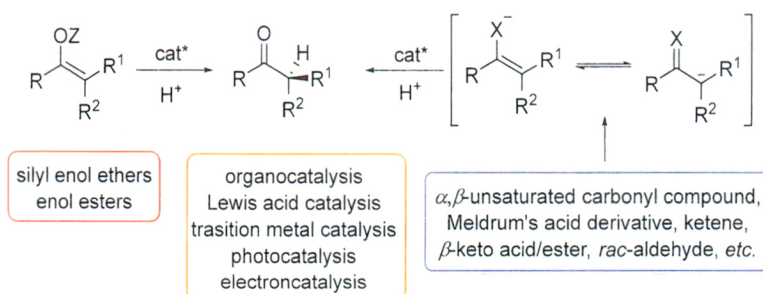
Pan, Yannian; Qin, Xiao; Yuan, Chengkai; Lu, Yi*
Chin. J. Org. Chem. **2023**, 43(3), 924

The related works of Cp*Rh(III) catalyzed C—H bond functionalization are systematically summarized, including both symmetric and asymmetric C—H activation, the role of ligands in the Cp*Rh(III) catalytic system is discussed, and some reaction mechanisms are briefly described.

Research Progress of Lewis Acid and
Base Pairs Applied in Materials Chemi-
stry

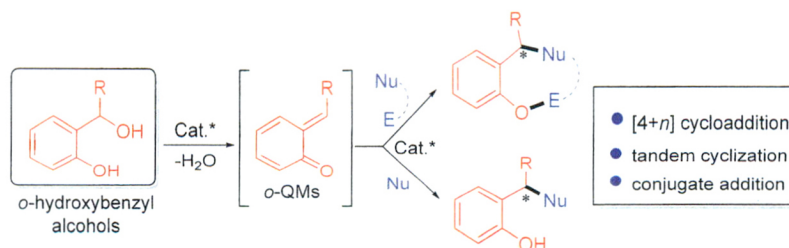
The application of Lewis Pairs (LPs) and Lewis pair polymerization (LPP) as a platform for developing new materials has attracted increasing interest. The diversity and versatility of LP and LPP in material chemistry applications are described. The progress of construction of supramolecular polymer networks, CO₂ capture and release, and the synthesis of novel topological polymers using LPs and LPPs highlighted.

Xiao, Lijuan; Zhang, Yanping; Hong, Miao*
Chin. J. Org. Chem. **2023**, 43(3), 949

Recent Advances on Catalytic Enanti-
oselective Protonation for Construction of
 α -Tertiary Carbonyl Compounds

The progress on enantioselective protonation for construction of α -tertiary carbonyl compound since 2019 is reviewed. The substrate category, catalytic system, reaction type and catalytic strategy are mainly discussed. Finally, the future development is also prospected.

Cao, Weidi; Liu, Xiaohua*
Chin. J. Org. Chem. **2023**, 43(3), 961

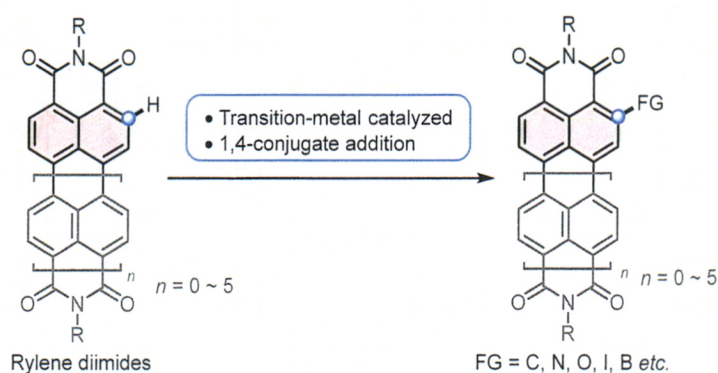
Advances in Catalytic Asymmetric Reac-
tions Involving *o*-Hydroxybenzyl Alcohols

The catalytic asymmetric reactions involving *o*-hydroxybenzyl alcohols have become efficient strategies for the synthesis of chiral oxygen-containing heterocycles and arylmethane derivatives. The catalytic asymmetric reactions involving *o*-hydroxybenzyl alcohols are summarized, which will open a new window for the design of new type of *o*-hydroxybenzyl alcohols and their involved catalytic asymmetric reactions.

Wang, Haiqing; Yang, Shuang; Zhang, Yu-
chen*, Shi, Feng*
Chin. J. Org. Chem. **2023**, 43(3), 974

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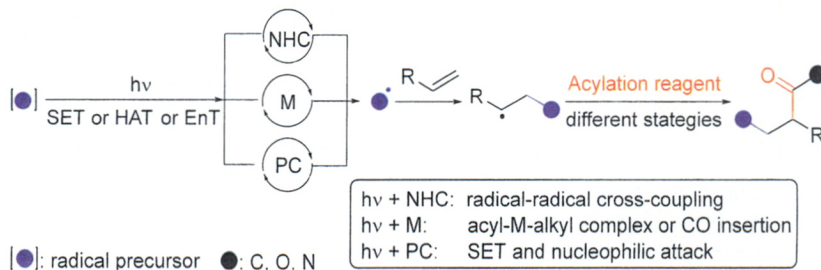
Research Progress in *Ortho*-C—H Bond Functionalization of Rylene Diimides



Precise modifications of rylene diimides (RDI) skeletons on the *ortho* positions can not only regulate molecular energy levels, but also facilitate controllable assembly between π -molecules, which is an effective means to create new π -molecular materials. The methods of *ortho*-C—H bond functionalization of RDIs such as perylene diimides and naphthalene diimides, and the influence of *ortho*-modification on the photoelectronic properties and assembly of RDIs derivatives are summarized.

Wu, Kongchuan; Lu, Kaihong; Lin, Jianbin*;
Zhang, Huijun*
Chin. J. Org. Chem. **2023**, 43(3), 1000

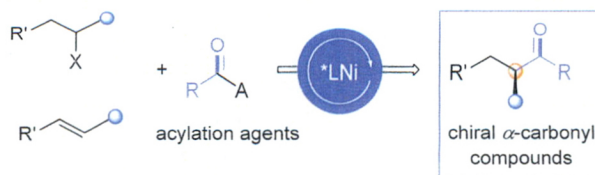
α -Acylation of Olefins via Photocatalysis



Rapid growth of photocatalysis in organic transformation has introduced new methodologies to undergo the α -acylation of olefins with broad substrate scope. The research progress and prospect for the future development in this active research field is highlighted.

Hou, Hongyu; Cheng, Yuanyuan; Chen, Bin;
Tung, Chenho; Wu, Lizhu*
Chin. J. Org. Chem. **2023**, 43(3), 1012

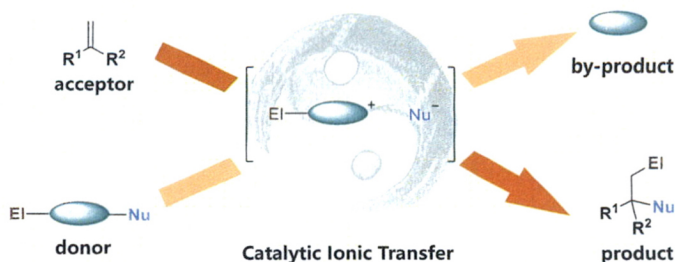
Recent Advances in Nickel Catalyzed Asymmetric Acylation Reactions



Zhang, Yanyan; Zhang, Zhuzhu; Zhu, Sheng-qing*;
Chu, Lingling*
Chin. J. Org. Chem. **2023**, 43(3), 1023

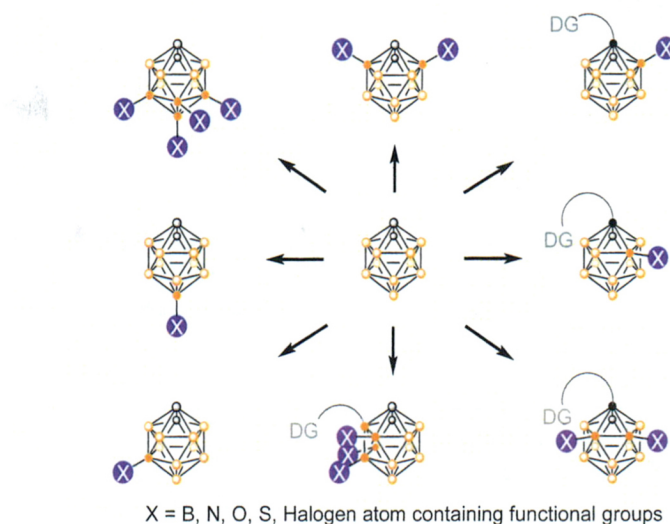
The latest progress of nickel-catalyzed asymmetric acylation reactions is summarized, including nickel-catalyzed asymmetric alkyl-acyl cross-coupling reactions, asymmetric hydroacylation of alkenes and asymmetric acyl-functionalization alkenes.

Recent Advances in Ionic Transfer Reactions



Li, Luomo; Yang, Xiaohui*
Chin. J. Org. Chem. **2023**, 43(3), 1036

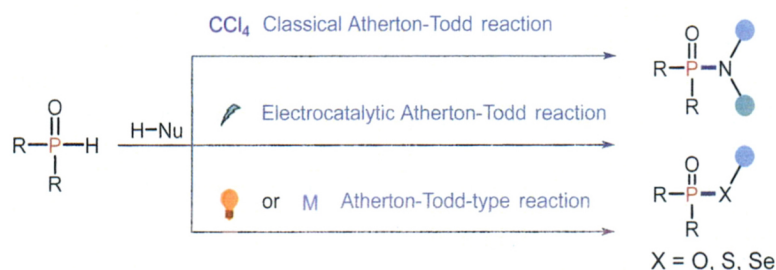
The recent progress of ionic transfer reactions and related mechanisms are summarized. Furthermore, the future developments of ionic transfer reactions are prospected.

Recent Advances in Transition Metal-Catalyzed B—H Bond Activation for Synthesis of *o*-Carborane Derivatives with B—Heteroatom Bond

The current state of functionalization of *o*-carboranes to form B—B, B—N, B—O, B—S, and B—halogen bonds using transition metal-catalyzed B—H activation strategy is summarized. Some reaction mechanisms are highlighted, and the future challenges and focus of the carborane B—heteroatom bond construction are discussed.

Jia, Hairui; Qiu, Zaozao*
Chin. J. Org. Chem. **2023**, 43(3), 1045

Recent Advances of the Atherton-Todd Reaction

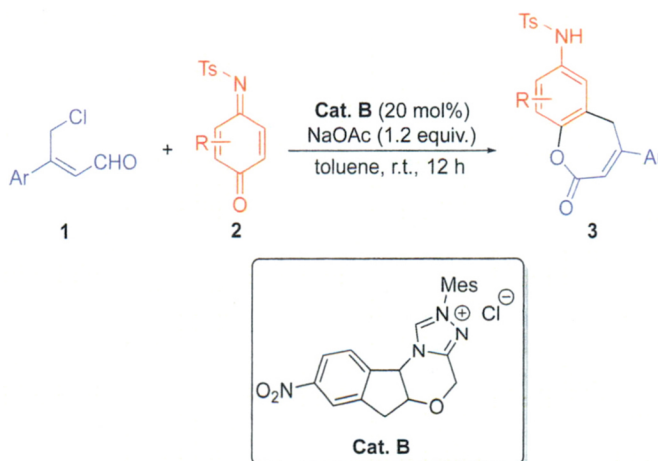


The research progress of the Atherton-Todd reaction and its application in organic synthesis in recent decades are summarized, and a brief outlook on the current research challenges is put forward, hoping to provide reference and thinking for the further development of the Atherton-Todd reaction.

Fang, Siqiang; Liu, Zanjiao; Wang, Tianli*
Chin. J. Org. Chem. **2023**, 43(3), 1069

ARTICLES

N-Heterocyclic Carbene (NHC)-Catalyzed [4 + 3] Cycloaddition to Synthesize 4-Aminobenzoheptenolactons

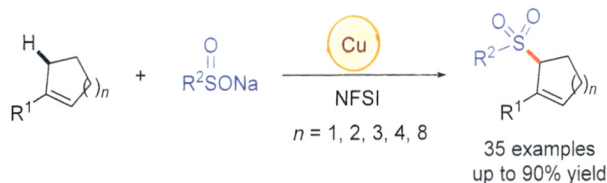


Dai, Chunbo; Xia, Siqi; Chen, Xiaoyu; Yang, Limin*
Chin. J. Org. Chem. **2023**, 43(3), 1084

A highly efficient N-heterocyclic carbene (NHC) catalyzed formal [3+4] cycloaddition reaction of γ -chloroaldehyde with iminoquinones has been developed, producing 4-aminobenzoheptenolactone derivatives in good yields (up to 74% yield). Based on computational investigation, the role of NHC on site selectivity is discussed.

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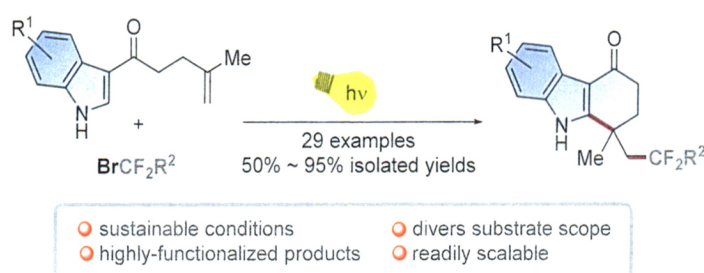
Copper-Catalyzed Allylic C(sp³)—H Sulfonylation of Cyclic Olefins



A highly efficient copper-catalyzed direct sulfonylation of allylic C(sp³)—H bond was developed using simple cyclic olefins and sodium sulfite as starting materials. A series of allylic sulfone derivatives were synthesized in moderate to good yields under mild conditions. The mechanism study shows that the reaction might involve radical intermediates.

Liu, Chunyang; Li, Yan*; Zhang, Qian*
Chin. J. Org. Chem. **2023**, 43(3), 1091

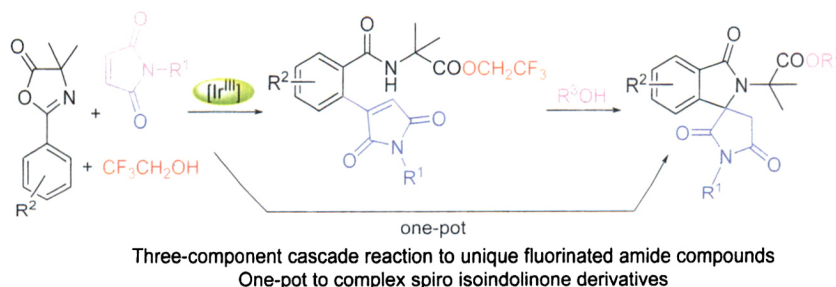
Visible Light-Catalyzed Synthesis of Difluoroalkylated Polycyclic Indoles



A one-step radical tandem cyclization reaction to synthesize difluoroalkylindoles with quaternary carbon centers by using difluorobromoesters as the fluorine source and 3-alkenyl indoles as the substrates under visible light-catalyzed conditions was developed. The method is easy-to-operate and mild in conditions, with a wide range of substrate adaptability and good yields, providing a green and efficient synthetic route for fluorine-containing polycyclic indoles.

Zhao, Jinxiao; Wei, Tonghui; Ke, Sen; Li, Yi*
Chin. J. Org. Chem. **2023**, 43(3), 1102

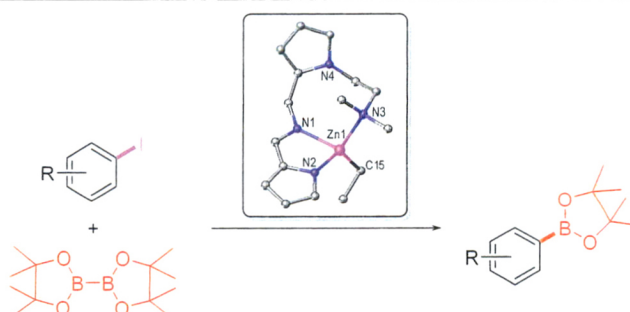
Ir(III)-Catalyzed Novel Three-Component Cascade Trifluoroethoxylation and One-Pot Method to Construct Complex Amide Compounds



Ir(III)-catalyzed three-component cascade reaction to construct unique trifluoroethoxylation amide compounds has been developed, meanwhile the fluorinated compounds could continue to react with alcohols to prepare complex spiro isoindolinone derivatives in one-pot. The highly efficient approaches produce various amide compounds by condition-controlled.

Zeng, Chengfu; He, Yuan; Li, Qing*; Dong, Lin*
Chin. J. Org. Chem. **2023**, 43(3), 1115

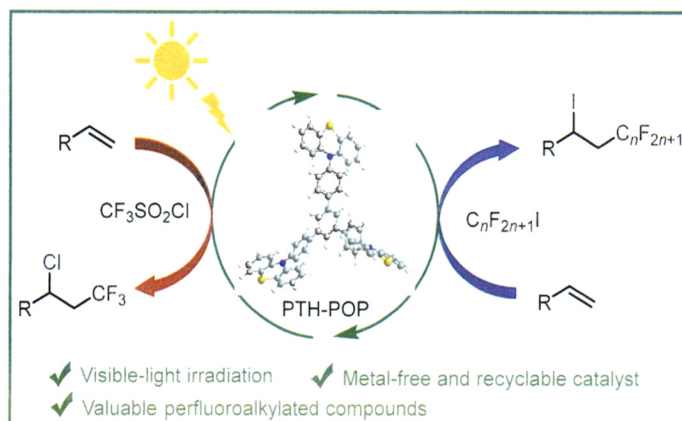
Synthesis and Characterization of Zinc, Lithium and Magnesium Complexes Containing Pyrrolyl Ligands, and Utilization as Catalysts in Borylation of Aryl Iodides and Hydroboration of Aldehydes and Ketones



Dang, Yan; Jia, Chaohong; Wang, Yalan; Wang, Li; Li, Yafei; Li, Yahong*
Chin. J. Org. Chem. **2023**, 43(3), 1124

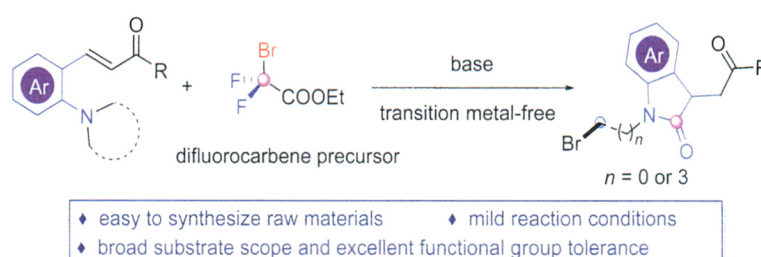
Two zinc complexes supported by pyrrolyl ligands were synthesized and characterized. They were both catalytically active toward the borylation of aryl iodides. The reaction features mild conditions, broad substrate scope and high functional group compatibility.

Haloperfluoroalkylation of Unactivated Terminal Alkenes over Phenylphenothiazine-Based Porous Organic Polymers



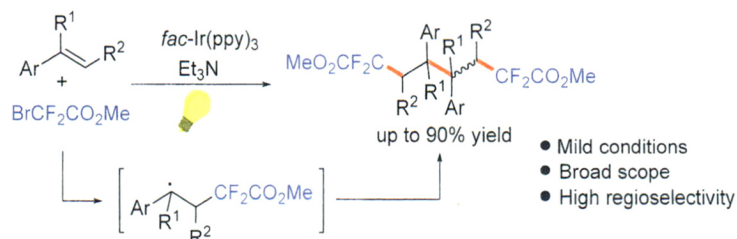
Wang, Rui; Gao, Lang; Zhou, Cen; Zhang, Xiao*
Chin. J. Org. Chem. **2023**, 43(3), 1136

Photocatalytic heterogeneous chlorotrifluoromethylation and iodoperfluoroalkylation of unactivated terminal alkenes have been achieved in a transition-metal-free and recyclable fashion under the catalysis of phenylphenothiazine-based porous organic polymer (PTH-POP).

Difluorocarbene-Enabled Synthesis of 3-Substituted-2-oxindoles from α -Vinylanilines

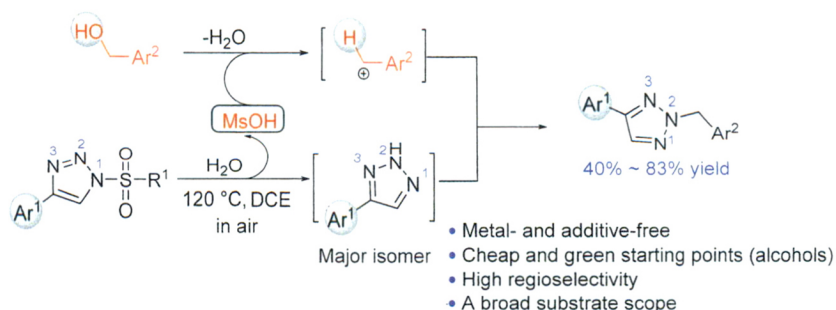
Huang, Hua; Li, Xin; Su, Jianke; Song, Qiu-ling*
Chin. J. Org. Chem. **2023**, 43(3), 1146

The synthesis of 3-substituted-2-oxindoles derivatives is further simplified and structures of these compounds are enriched, which is a great complement to the construction of 3-substituted-2-oxindoles derivatives.

Photocatalyzed 2 : 2 Coupling of Styrene and $\text{BrCF}_2\text{CO}_2\text{Me}$: A Facile Synthesis of Bis-difluoroacetylated Hexestrol Derivatives

Chen, Shenhao; Zou, Song; Xi, Chanjuan*
Chin. J. Org. Chem. **2023**, 43(3), 1157

Photocatalyzed functionalized difluoroacetylation of alkenes with $\text{XCF}_2\text{CO}_2\text{Me}$ has been developed via *in situ* generated $\beta\text{-CF}_2\text{CO}_2\text{Me}$ substituted radical, which affords difluoroacetylated hexestrol derivatives with high regioselectivity under mild conditions.

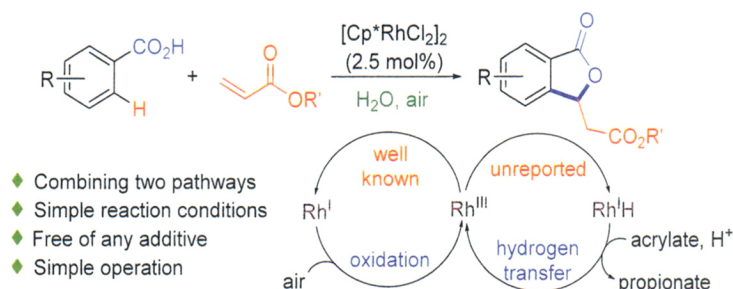
High Regioselective Synthesis of N^2 -Substituted-1,2,3-triazole via N -Sulfonyl-1,2,3-triazole Coupling with Alcohol Catalyzed by *in-situ* Generated Sulfonic Acid

Ji, Jian; Liu, Jinhua; Guan, Cong; Chen, Xuwen; Zhao, Yun; Liu, Shunying*
Chin. J. Org. Chem. **2023**, 43(3), 1168

Using easily accessible and environmentally friendly starting materials, a wide range of N^2 -substituted 1,2,3-triazoles were prepared with high regioselectivity.

CONTENT

Green Method for Constructing Phthalides via Oxidative Coupling of Aromatic Acids and Acrylates in Neat Water and Air

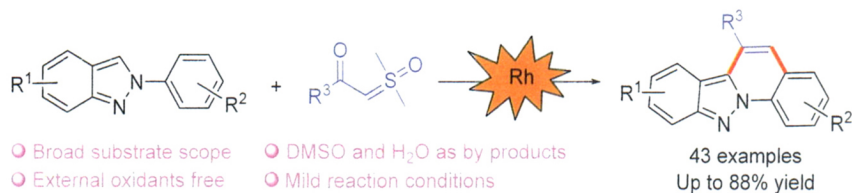


Wei, Wenting; Li, Zhuangzhuang; Li, Wand; Li, Jiaqi; Shi, Xianying*

Chin. J. Org. Chem. **2023**, 43(3), 1177

A water-promoted and rhodium-catalyzed [3+2] oxidative coupling of aromatic acids and acrylates has been developed in air and neat water free of any additives, which provides an environmentally benign approach for constructing phthalide motifs. Two pathways are involved to regenerate the active Rh species.

Rhodium-Catalyzed Tandem Acylmethylation/Annulation Reactions of 2-Aryl-2H-indazoles with Sulfoxonium Ylides: Easy Access to 6-Arylindazolo[2,3-*a*]quinolines



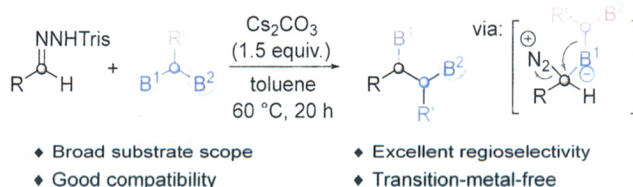
Tang, Zhen; Pi, Chao*; Wu, Yangjie; Cui, Xiuling*

Chin. J. Org. Chem. **2023**, 43(3), 1187

An efficient synthesis of 6-arylindazolo[2,3-*a*]quinolines starting from 2-aryl-2H-indazoles with sulfoxonium ylides via rhodium(III)-catalyzed C—H activation and cyclization reaction has been described. This transformation features high efficiency, tolerance of various functional groups, avoiding external oxidant and only dimethyl sulfoxide (DMSO) and H₂O as by-products. In addition, the scale-up reaction demonstrated the practicability of this protocol in industry.

HIGHLIGHTS

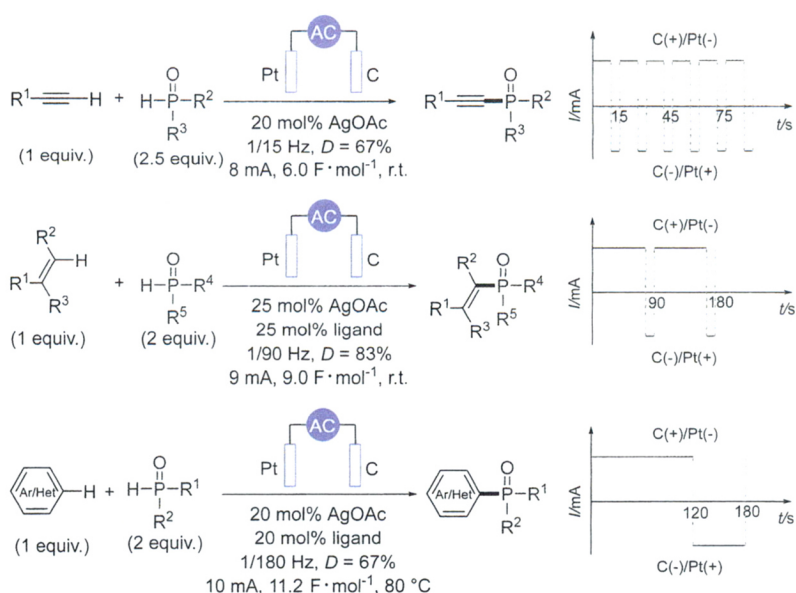
Selective Formal Carbene Insertion into C—B Bonds of Diboronates



Li, Xin; Song, Qiuling*

Chin. J. Org. Chem. **2023**, 43(3), 1197

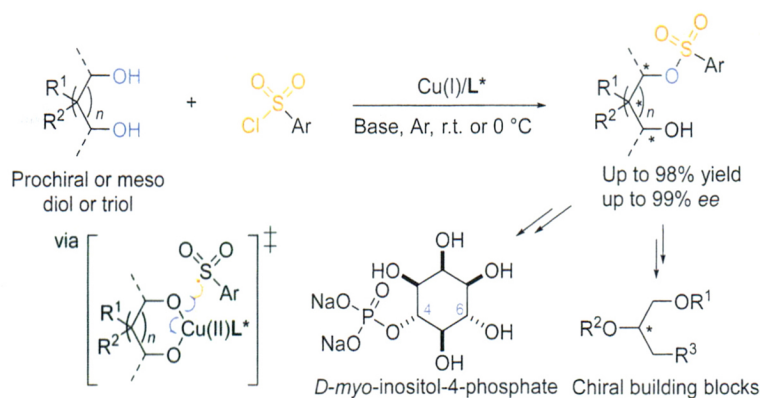
Alternating Current Promoted Silver Catalysis for C—H Phosphorylation



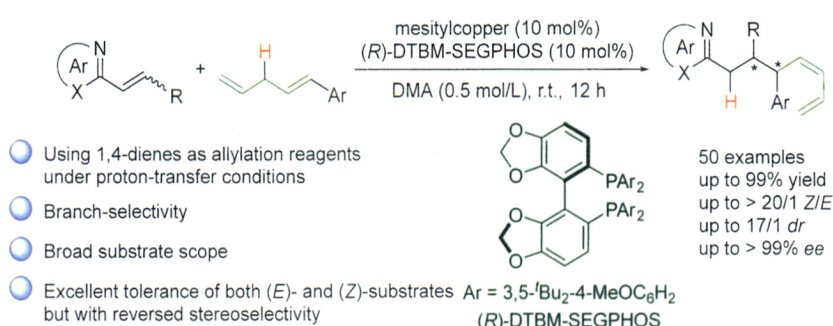
Chen, Na; Xu, Haichao*

Chin. J. Org. Chem. **2023**, 43(3), 1199

Copper-Catalyzed Enantioselective Radical Heteroatomic S—O Cross-Coupling

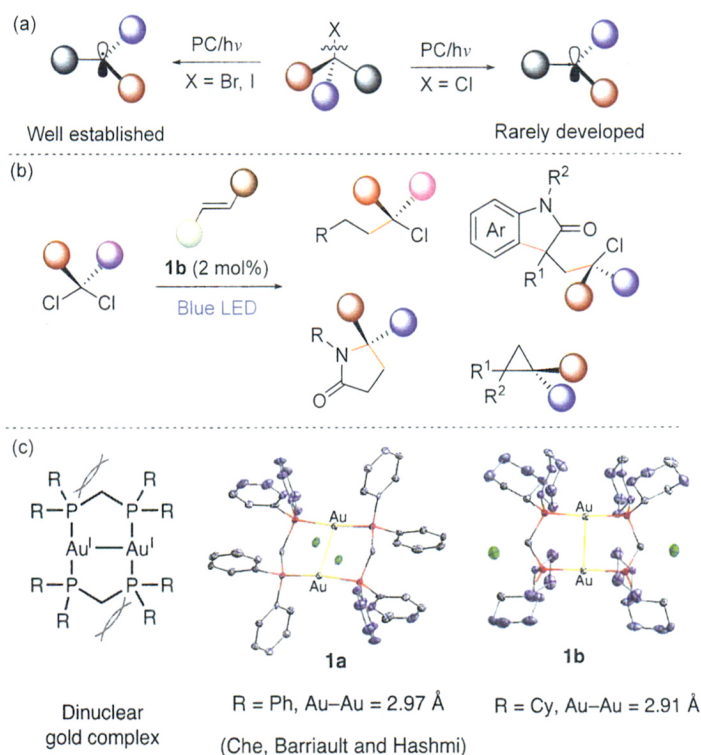


Han, Yuxuan; Cui, Xiuling*

Chin. J. Org. Chem. **2023**, 43(3), 1201Copper(I)-Catalyzed Asymmetric Conjugate Addition of 1,4-Dienes to β -Substituted Alkenyl Azaarenes

- Using 1,4-dienes as allylation reagents under proton-transfer conditions
- Branch-selectivity
- Broad substrate scope
- Excellent tolerance of both (*E*)- and (*Z*)-substrates but with reversed stereoselectivity

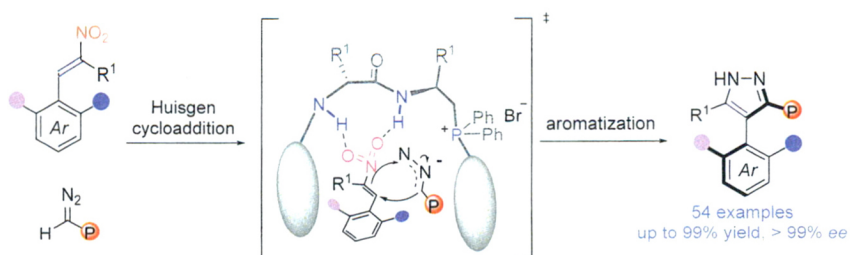
Yin, Yanli; Jiang, Zhiyong*

Chin. J. Org. Chem. **2023**, 43(3), 1203Photoinduced Gold-catalyzed Divergent Dechloroalkylation of *gem*-Dichloroalkanes

Lü, Peizhuo; Liu, Yuanhong*

Chin. J. Org. Chem. **2023**, 43(3), 1206

Asymmetric Construction of Axially Chiral Arylpyrazole-Based Phosphorus Frameworks by Dipeptide-Phosphonium Salt Catalysis



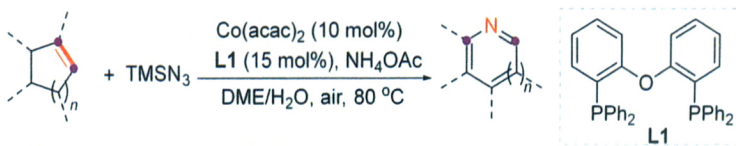
Zhu, Ziqi; Shi, Feng*

Chin. J. Org. Chem. **2023**, 43(3), 1208

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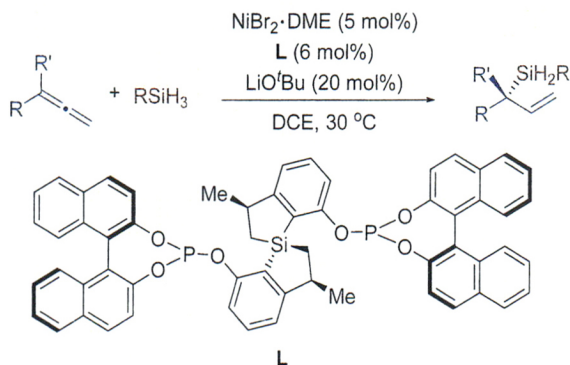
Cobalt-Catalyzed Nitrogen Atom Insertion and Ring Expansion of Cycloalkenes

Zhu, Baoying; Qu, Lingbo*; Tang, Conghui*
Chin. J. Org. Chem. **2023**, 43(3), 1211



Nickel-Catalyzed Enantioselective Hydrosilylation of 1,1-Disubstituted Allenes

Chen, Shaowei; Shen, Xiao*
Chin. J. Org. Chem. **2023**, 43(3), 1213



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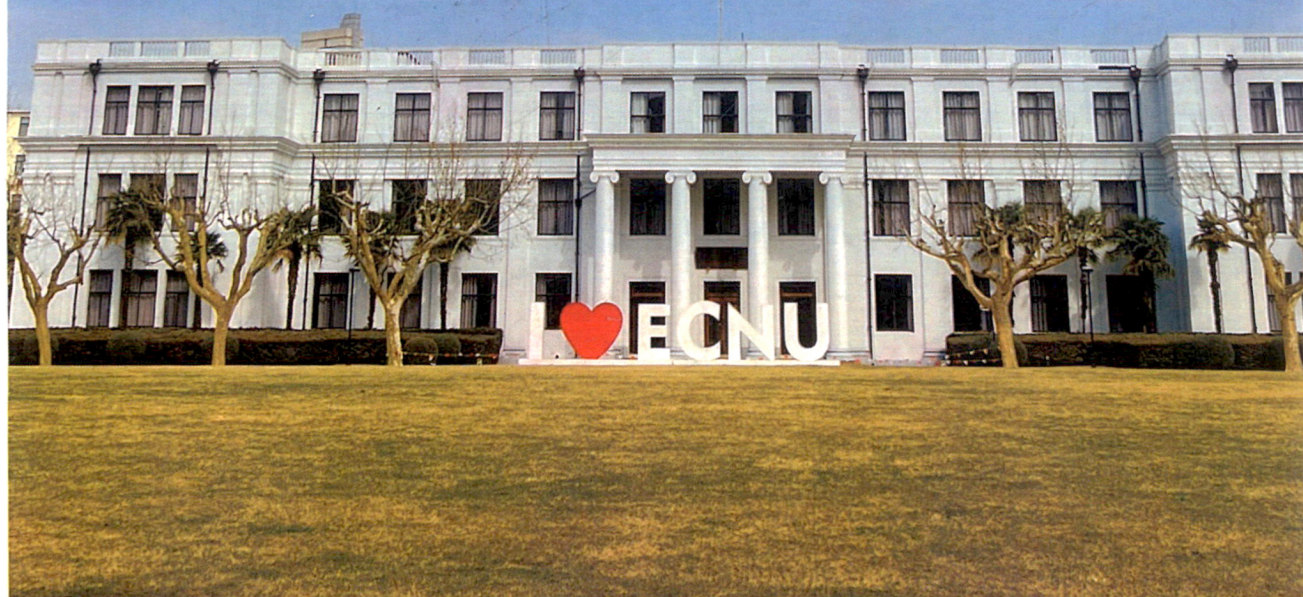
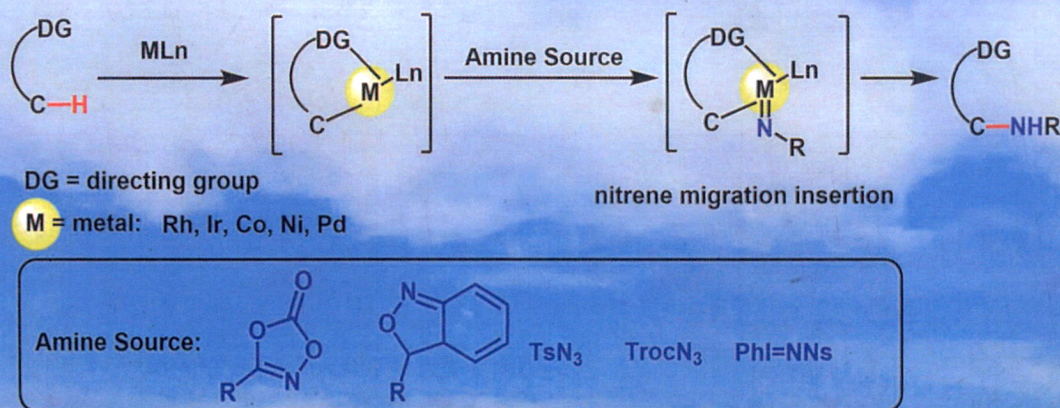
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