

有机化学

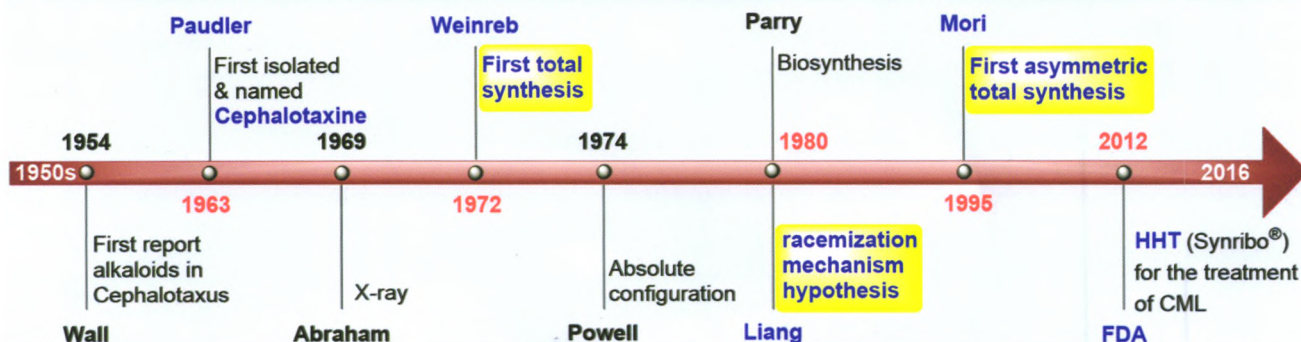
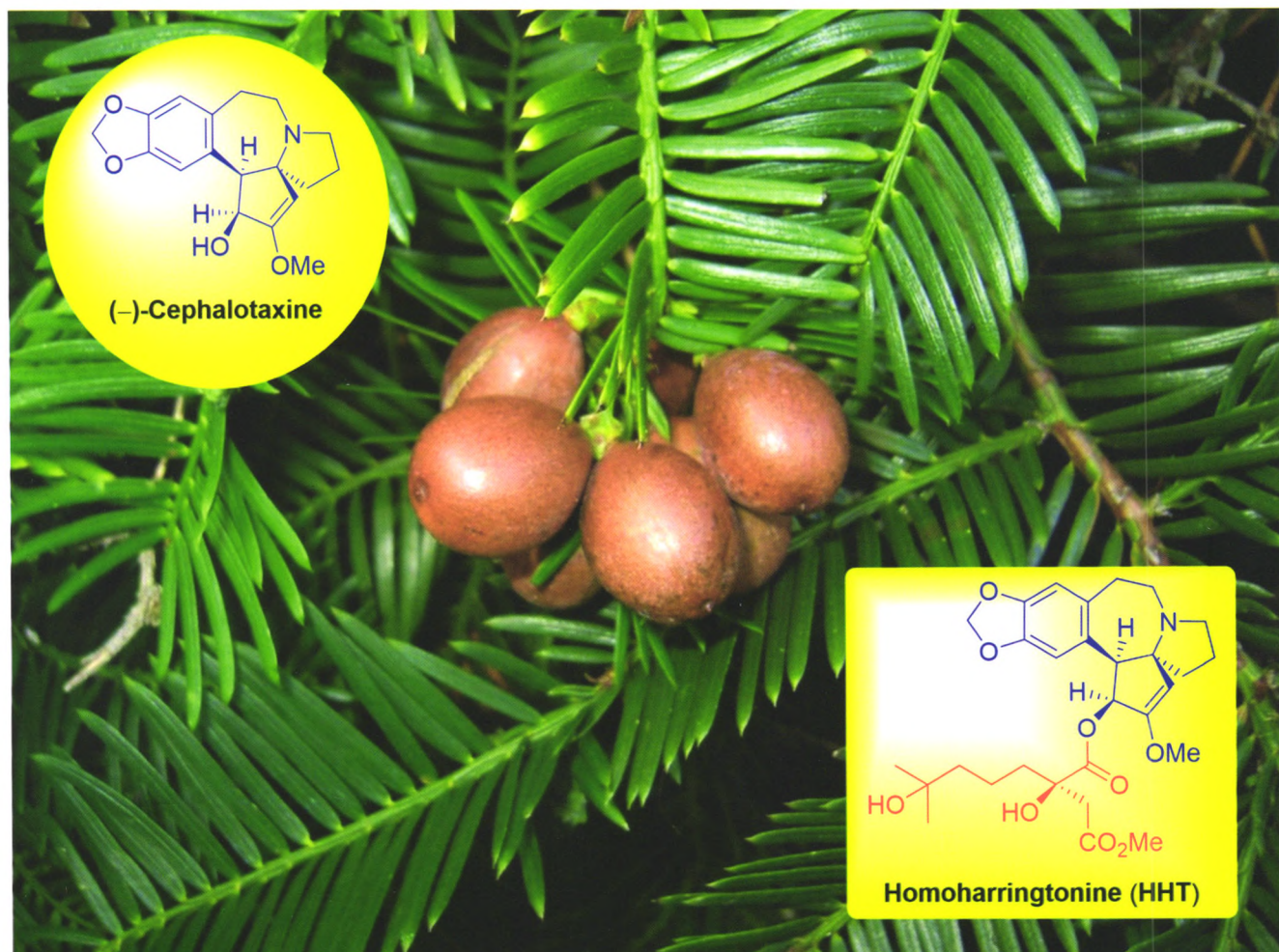
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Youji Huaxue

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(YOUJI HUAXUE)

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* 通讯联系人.

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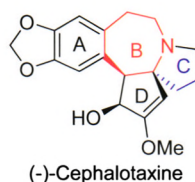
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On the Cover

The recent progresses in the asymmetric total synthesis of (–)-cephalotaxine are reviewed by Chen and Li on page 1885, with different synthetic strategies towards azatri-cyclic ring construction being delineated. Cephalotaxine is the parent structure of a series of natural *Cephalotaxus* alkaloids. Despite the inactivity of cephalotaxine itself, homoharringtonine as one of its natural esters alkaloids has been approved by the Food and Drug Administration (FDA) for treatment of chronic myeloid leukemia since 2012.

REVIEWS

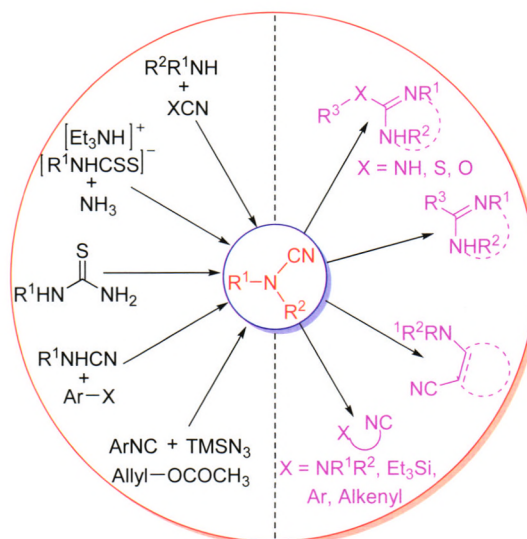
Asymmetric Total Synthesis of (–)-Cephalotaxine



Chen, Yang; Li, Wei-Dong Z.*
Chin. J. Org. Chem. **2017**, 37(8), 1885

Cephalotaxine is the parent structure of an anticancer drug homoharringtonine. The strategic approaches toward the asymmetric total synthesis of (–)-cephalotaxine are summarized.

Progress on the Synthesis and Applications of Cyanamides



Li, Jihui*; Li, Zhengzhang; Zhang, Yucang;
 Xu, Wenrong; Xu, Shuying
Chin. J. Org. Chem. **2017**, 37(8), 1903

Cyanamides are an important class of fine chemicals containing amino and cyano functionalities, which have been widely used for the synthesis of pharmaceuticals, agricultural chemicals, health products and materials, and attracted considerable attention from both organic synthetic chemists and medicinal chemists. Great advances in the synthesis and transformations of cyanamides were made, a diversity of synthetic methods and transformations of cyanamides were developed in the past two decades. In this paper, various synthetic methods and reactions of cyanamides are introduced comprehensively, their characteristics, rules, advantages and disadvantages are also summarized and discussed for the development of new synthetic methods and reactions of cyanamides.

CONTENT

Progress in C—N Bonds Formation Using *t*-BuONO

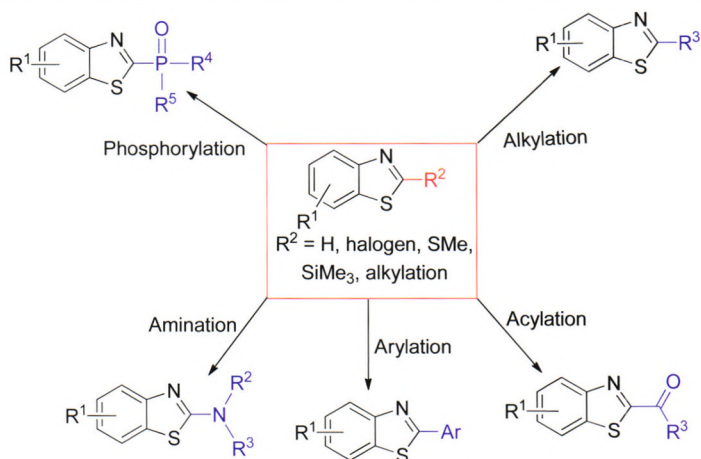
Wei, Wenting*; Zhu, Wenming; Wu, Yi; Huang, Yiling; Liang, Hongze
Chin. J. Org. Chem. **2017**, 37(8), 1916



The formation of C—N bonds by nitration is a powerful strategy for organic synthesis. Recently, the remarkable progress has been made in synthesis of nitrogen compounds using *tert*-butyl nitrite as nitration reagent. The present protocol, with a mild reaction condition and an excellent region selectivity, provides a green and efficient approach to construct C—N bonds. This review will summarize the recent development in this area on the basis of different substrates systems.

Progress in 2-Position Functionalized Synthesis of 2-Substitutedbenzothiazoles

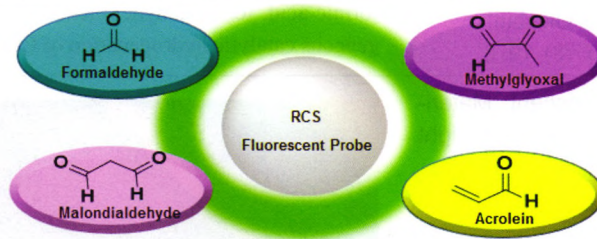
Dai, Xiaoqiang; Zhu, Yabo; Wang, Zhouyang; Weng, Jianquan*
Chin. J. Org. Chem. **2017**, 37(8), 1924



2-Substitutedbenzothiazoles were widely used in chemical, pharmaceutical and agricultural fields, and the synthesis of them has attracted more and more attentions. In this paper, the synthesis of 2-substitutedbenzothiazoles by 2-position functionalized method is summarized and their future outlook is also discussed.

Recent Progress in Fluorescent Probe for the Detection of Reactive Carbonyl Species

Chen, Yi; Hu, Aohan; Yang, Lingyi; Li, Zaoying; Yan, Kun*
Chin. J. Org. Chem. **2017**, 37(8), 1939

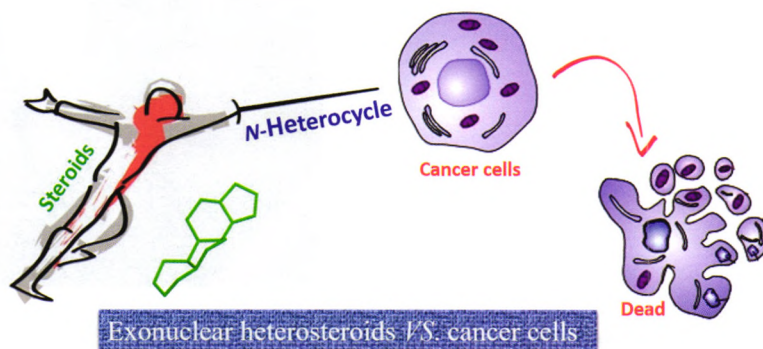


A general overview of the reaction-based fluorescent in the selected recent research is provided involving the design, recognition mechanism and application

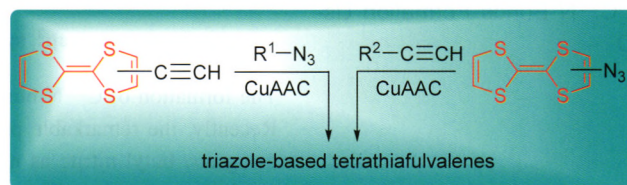
of fluorescent probes for detecting reactive carbonyl species of formaldehyde, methylglyoxal, malondialdehyde, acrolein and so on.

Recent Advances on the Synthesis and Antitumor Evaluation of Exonuclear Heterosteroids

Yu, Bin; Cai, Zuyun; Wang, Shuai; Liu, Hongmin*
Chin. J. Org. Chem. **2017**, 37(8), 1952

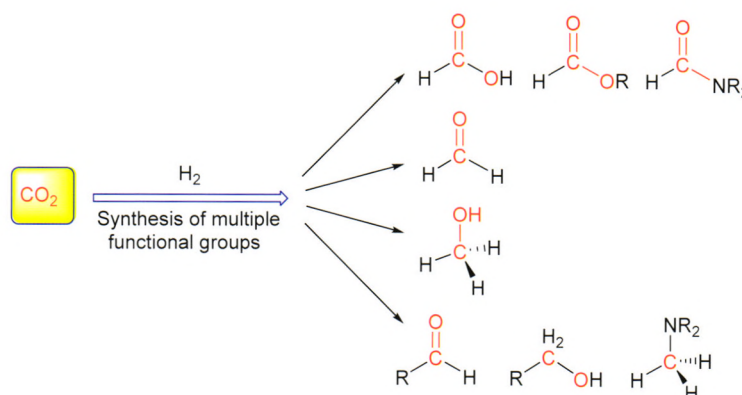


The synthesis and antitumor evaluation of exonuclear heterosteroids are highly pursued in last decades, several compounds such as abiraterone and galeterone are presently used in clinic for cancer therapy. More exonuclear heterosteroids will be synthesized and evaluated for their anticancer efficacy.

Progress on Synthesis and Application of
Triazole-Based Tetrathiafulvalene Derivatives

Zhao, Bangtun*; Tao, Jingjing; Chen, Xiaoji;
Zhu, Weimin*
Chin. J. Org. Chem. **2017**, 37(8), 1964

The evolution of the clicked tetrathiafulvalenes for molecular recognition, molecular assembly along with photoelectric and photovoltaic functional materials is reviewed.

Progress in Homogeneous Catalytic Hydrogenation of CO₂

The application of carbon dioxide (CO₂) as a resource for chemical synthesis has attracted chemists' attention along with the rising of sustainable development strategies and concerning about global warming. Herein the recent progress in the homogeneous hydrogenated CO₂ catalyzed by organometallic complexes is reviewed, which included homogeneous catalysts types, structures, activity and selectivity for the production of formic acid, formaldehyde, methanol and as C₁ synthons, and the mechanism of homogeneous catalytic hydrogenation of CO₂.

Li, Yong; Wang, Zheng; Liu, Qingbin*
Chin. J. Org. Chem. **2017**, 37(8), 1978

New Member of Luminescent Materials—Status and Future of White Light Emitting Gel



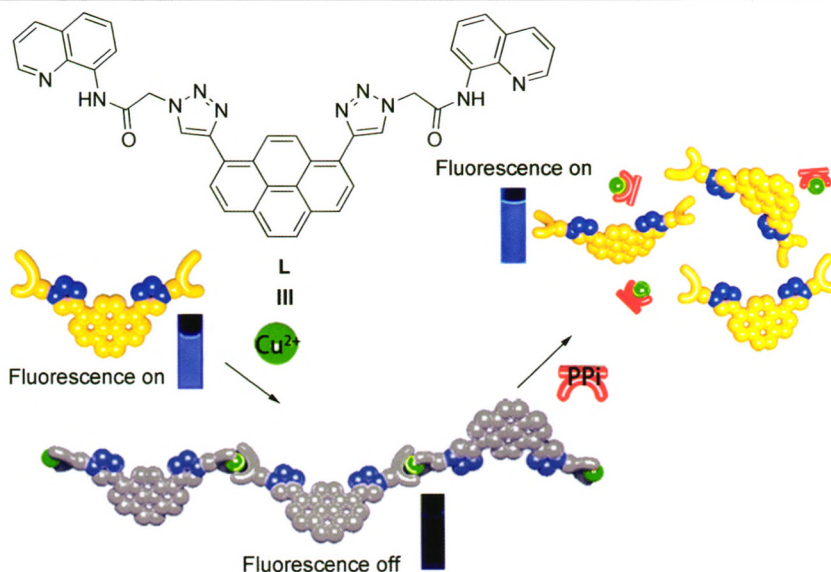
Yang, Hewei; Zhang, Yuzhe; Li, Yanjie;
Wang, Jingxiang; Li, Xiaomeng; Song, Jian;
Zhang, Bao*; Feng, Yaqing*
Chin. J. Org. Chem. **2017**, 37(8), 1991

The recent progress in the mechanism, structure, properties and applications of white light emitting gels is reviewed. The effects of the energy transfer on the luminescence properties of chromophore in the gels are mainly discussed. Finally, the potential application and current deficiency of them are also prospected.

CONTENT

ARTICLES

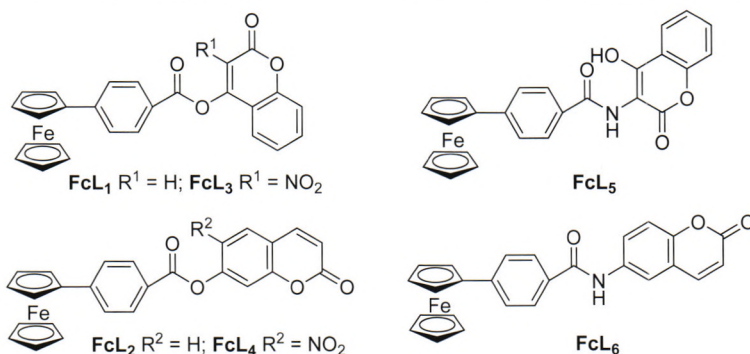
A Novel 1,8-Disubstituted Pyrene-Based Fluorescent Probe for Subsequent Detection of Cu^{2+} and Pyrophosphate



Zhong, Keli; Guo, Baofeng; Sun, Xiaohan; Zhou, Xue; Zhang, Qiang; Tang, Lijun*; Zhang, Xingrong*
Chin. J. Org. Chem. **2017**, 37(8), 2002

A novel 1,8-disubstituted pyrene fluorescence probe **L** was synthesized and used for relay recognition of Cu^{2+} and pyrophosphate (PPi) in THF/H₂O ($V:V=1:1$, HEPES $10\text{ mmol}\cdot\text{L}^{-1}$, pH=7.4) with good selectivity and sensitivity, fast response.

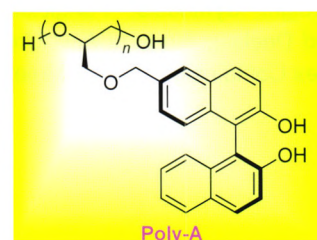
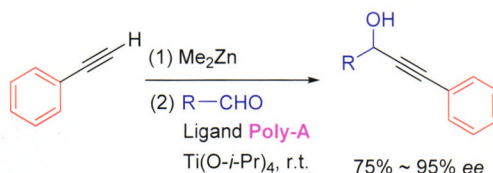
Synthesis and Properties of 4-Ferrocenyl-carboxybenzene-coumarin Derivatives



Li, Biao; Liu, Qiuxia; Zhou, Yuanqing; Jia, Zhaodong; Zhu, Manyu; Xu, Yan*; Song, Maoping
Chin. J. Org. Chem. **2017**, 37(8), 2008

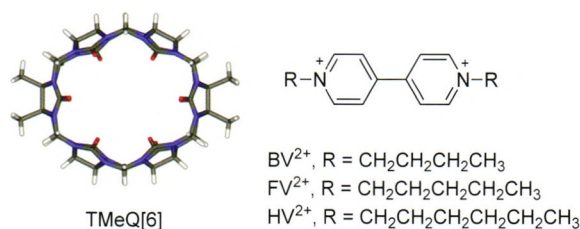
Six novel ferrocenyl-carboxybenzene-coumarin derivatives **FcL₁~FcL₆** were designed, synthesized, and evaluated for antibacterial and anticancer activities. The structures of compounds were characterized by IR, ¹H NMR, ¹³C NMR and elemental analysis. All the six compounds showed good inhibition against *Curvularia lunata* and *Fusarium graminearum*. **FcL₁** and **FcL₂** exhibited significant anticancer activities and selectivities against *Esophageal carcinoma* cell (IC_{50} value=2.10 and 1.25 $\mu\text{mol/L}$, respectively).

Synthesis of Two 1,1'-Bi-2-naphthol-Based Chiral Polyethers for the Enantioselective Addition of Phenylacetylene to Aldehydes



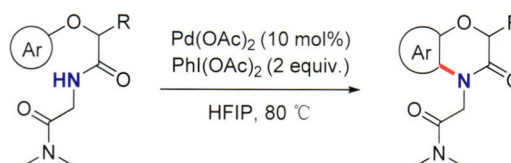
Yu, Zengda; Liu, Feng; Zhang, Lingjun*; Yang, Nianfa*
Chin. J. Org. Chem. **2017**, 37(8), 2015

Two polyethers derived from 1,1'-bi-2-naphthol were synthesized and its asymmetric induction in the addition of phenylacetylene to aldehydes was studied. The addition products have good enantioselectivity with up to 95% enantiomeric excess (*ee*). Furthermore, the polyether could be conveniently recovered and reused at least 6 times without loss of catalytic ability.

Supramolecular Self-Assembly between
Tetramethyl Cucurbit[6]uril and Alkyl
Viologens

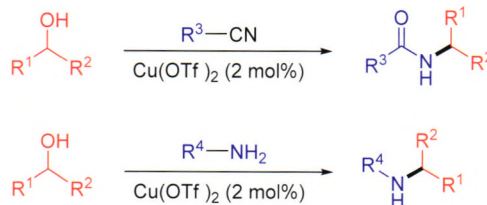
Three symmetric viologen derivatives bearing aliphatic substituents of variable length were employed as guests, and the supramolecular self-assembly between tetramethyl cucurbit[6]uril (TMeQ[6]) and these viologen derivatives guests has been studied by 1H NMR spectroscopy, electronic absorption spectroscopy, isothermal titration calorimetry, mass spectrometry and X-ray diffraction methods in details.

Bai, Dong; Wang, Xin; Gao, Zhongzheng; Qiu, Shengchao; Tao, Zhu; Zhang, Jianxin*; Xiao, Xin*
Chin. J. Org. Chem. **2017**, 37(8), 2022

Facile Synthesis of Benzoxazinone Derivatives via Palladium Catalyzed Intra-
molecular Amination

Benzoxazinone and its derivatives are well-known as a broad-spectrum of physiological activities compounds. Herein a novel approach is reported for the synthesis of benzoxazine derivatives via a *N,O*-bidentate directing assisted Pd-catalyzed intramolecular amination reactions. Various benzoxazinone derivatives are obtained in moderate to good yields. The directing group can be removed under mild condition, highlighting potential synthetic utility of this method.

Zhou, Panpan; Guan, Mingyu; Zhang, Jingyu*; Xu, Fan*; Zhao, Yingsheng*
Chin. J. Org. Chem. **2017**, 37(8), 2028

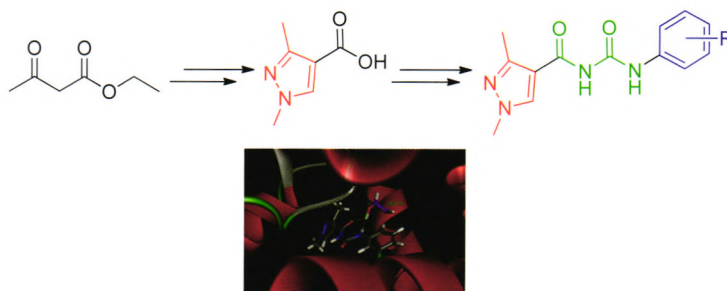
Synthesis of Alkylated Amides and
Amines by $Cu(OTf)_2$ -Catalyzed *N*-Alkyl-
ation of Nitriles and Amines with Alcohols

30 examples, up to 92% yield

$R^1 = \text{aryl}; R^2 = \text{aryl, alkyl, H}; R^3 = \text{aryl, alkyl}; R^4 = \text{aryl}$

Ma, Xiantao; Li, Bo; Xiao, Yinglin; Yu, Xiaochun*; Su, Chenliang*; Xu, Qing*
Chin. J. Org. Chem. **2017**, 37(8), 2034

A low loading $Cu(OTf)_2$ -catalyzed Ritter reaction of nitriles with secondary alcohols and some primary alcohols has been developed for the synthesis of the useful alkyl amides. The same method can also be extended to the dehydrative *N*-alkylation of anilines with secondary alcohols to obtain the *N*-alkylated anilines.

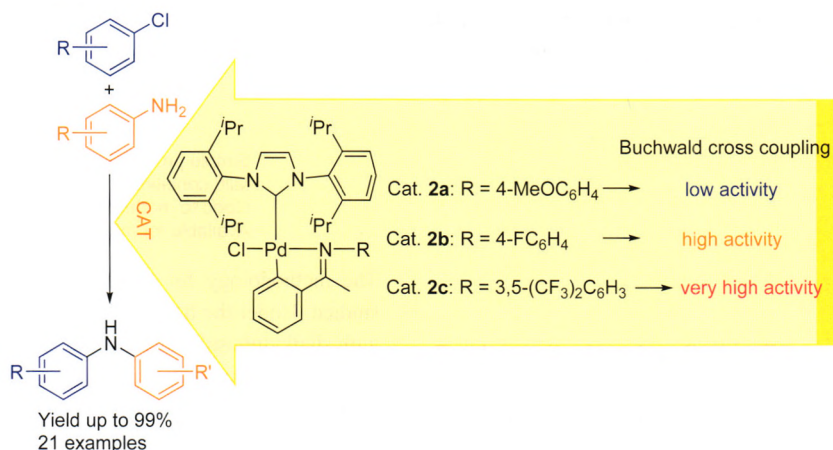
Design, Synthesis, Fungicidal Activity
and Docking Study of Acyl Urea Deriva-
tives Containing Pyrazole Moiety

Sun, Nabo; Shen, Zhonghua; Zhai, Zhiwen; Wu, Hongke; Weng, Jianquan; Tan, Chengxia; Liu, Xinghai*
Chin. J. Org. Chem. **2017**, 37(8), 2044

A series of novel pyrazole acylurea derivatives were synthesized. The target compounds were evaluated for their fungicidal activities, and the results indicated that some of the title compounds displayed good fungicidal activities. The structure activity relationship was studied using Docking method.

CONTENT

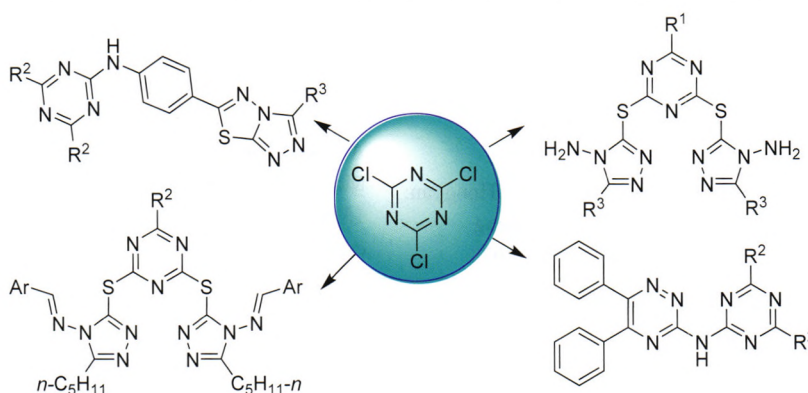
Novel Pd-*N*-Heterocyclic Carbene Complexes: Design, Synthesis and Application in Buchwald-Hartwig Cross Coupling Reaction



Wang, Fan; Hu, Yucai; Shen, An*; Cao, Yucai*
Chin. J. Org. Chem. **2017**, 37(8), 2050

N-Heterocyclic carbene palladium complexes with different imine ligands have been developed and applied in Buchwald-Hartwig cross coupling reaction. Performance of catalysts is determined by the structure of imine ligands.

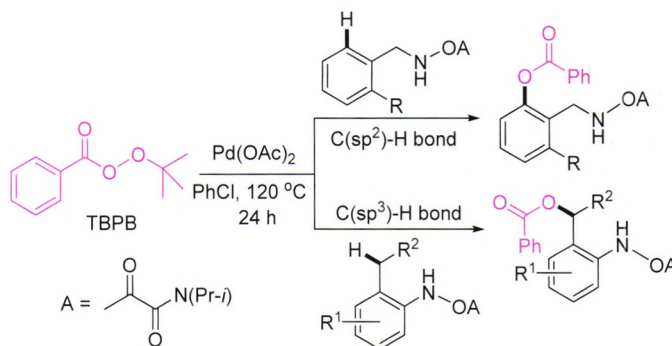
Synthesis and Bioactivities of Multiheterocyclic Molecules Based on *s*-Triazine



Liu, Yaning; Sun, Xiaona; Gao, Ran; Li, Chuanyin; Wang, Jing; Li, Yizheng; Zhang, Chenglu*
Chin. J. Org. Chem. **2017**, 37(8), 2057

Twenty-one novel target molecules were first designed and synthesized by combination of 1,2,4-triazole, triazolo[3,4-*b*]thiadiazole and 1,2,4-triazine unit with *s*-triazine respectively. The structures of the target molecules were characterized by IR, ¹H NMR and HRMS. The inhibitory activities of the 21 target molecules against Cdc25B were evaluated.

Palladium-Catalyzed Direct Acyloxylation of C(sp²)—H and C(sp³)—H Bonds under the Assistance of Oxalyl Amide

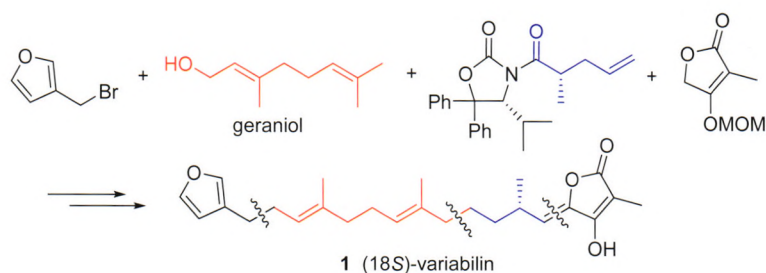


Zheng, Yongxiang; Han, Jian; Huang, Zhibin; Shi, Daqing*; Zhao, Yingsheng*
Chin. J. Org. Chem. **2017**, 37(8), 2066

A practical palladium-catalyzed direct acyloxylation of C(sp²)—H and C(sp³)—H bonds under the assistance of oxalyl amide with *tert*-butyl peroxybenzoate (TBPB) as oxidant was developed. Selective acyloxylation of C(sp²)—H bond for oxalyl amide protected benzyl amine using TBPB or carboxylic acids as acyloxylation reagent was achieved. For oxalyl amide protected 2-alkylanilines, the selective acyloxylation of benzylic C(sp³)—H bond was also achieved. This protocol provided an efficient and practical method for the synthesis of aryl esters.

CONTENT

Total Synthesis of Marine Furanosester- terpene Natural Product, (18S)-Variabilin

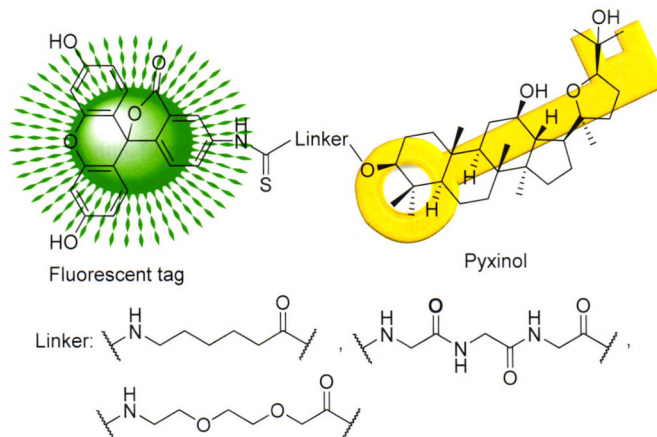


Xiong, Weiyan; Zhao, Yingchun; Xu, Liang*; Ji, Hong*
Chin. J. Org. Chem. **2017**, 37(8), 2101

Starting from geraniol and the key chiral segment prepared via Evans' asymmetric alkylation protocol, (18*S*)-variabilin has been totally synthesized in the longest linear 13 steps involving Julia-Lythgoe coupling reaction and aldol-type condensation.

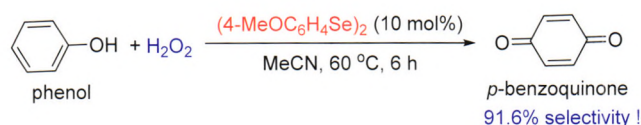
NOTES

Novel Fluorescent Pyxinol-Based Probes: Design, Synthesis and Biological Evaluation



Yang, Gangqiang*; Yang, Yanting; Yang, Qing; Li, Yang; Jiang, Yongtao; Fu, Fenghua; Wang, Hongbo*
Chin. J. Org. Chem. **2017**, 37(8), 2109

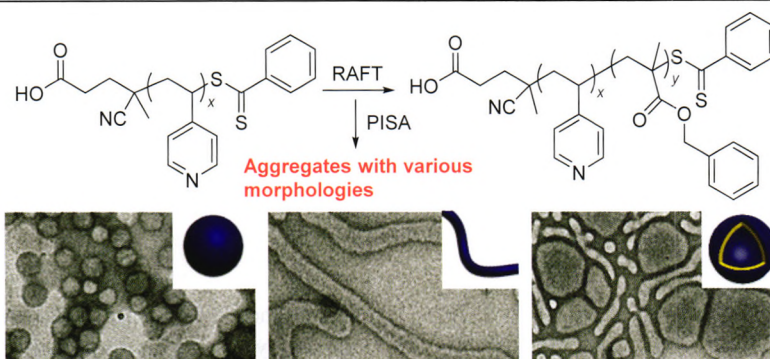
The synthesized fluorescent probe with hydrophilic flexible polyethylene glycol linker retained the protective activity of pyxinol against myocardial ischemia-reperfusion injury.

Investigation on Preparation of *p*-Benzoquinone through the Organoselenium-Catalyzed Selective Oxidation of Phenol

Wang, Fang; Xu, Lin; Sun, Cheng; Xu, Qing;
Huang, Jiejun; Yu, Lei*
Chin. J. Org. Chem. **2017**, 37(8), 2115

By using organoselenium catalyst, the green oxidation of phenol to produce *p*-benzoquinone was achieved. The reaction was metal-free, waste-free and was performed under mild conditions, producing *p*-benzoquinone in the excellent 91.6% selectivity.

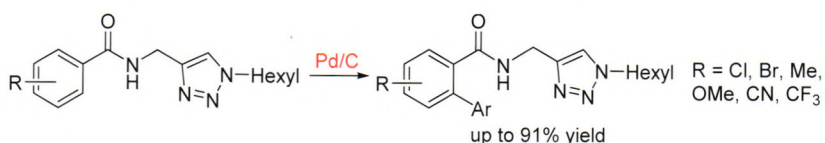
Polymerization-Induced Self-Assembly of P4VP-*b*-PBzMA Copolymer in Ethanol



Chen, Lingzhi; Tian, Chen; Yao, Yuan;
Lin, Shaoliang*
Chin. J. Org. Chem. **2017**, 37(8), 2119

Aggregates with various morphologies were obtained during polymerization-induced self-assembly process of P4VP-*b*-PBzMA copolymer in ethanol.

Pd/C-Catalyzed C—H Arylation with Click-Triazoles as Removable Directing Group

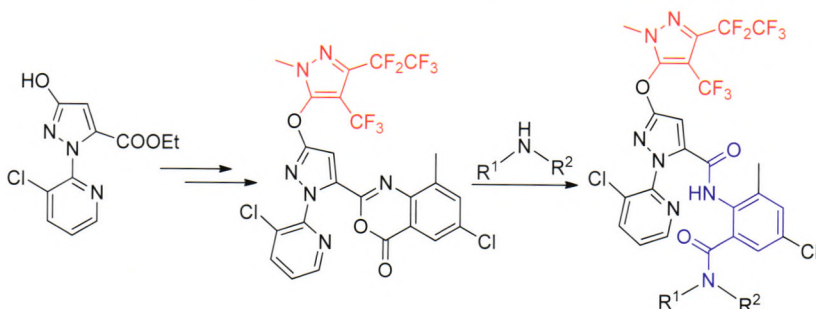


Xie, Xiaoqiang; Xing, Yunzhe; Zhang, Guofu*; Ding, Chengrong*

Chin. J. Org. Chem. **2017**, 37(8), 2124

A novel protocol for Pd/C catalyzed C(sp²)—H arylation of benzamides with good functional group compatibility under silver-free conditions by using click-triazoles as a removable directing group has been first developed.

Synthesis and Insecticidal Activity of Novel Anthranilic Diamides Containing Polyfluoroalkyl Pyrazole Moiety

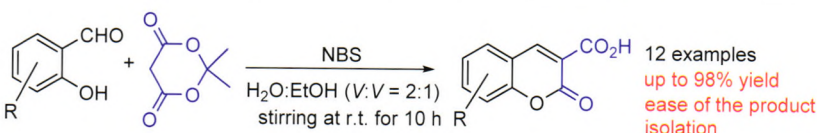


Shi, Jianjun; Ren, Guihua; Wu, Ningjie; Liu, Xinghai; Xu, Tianming; Tan, Chengxia*

Chin. J. Org. Chem. **2017**, 37(8), 2131

A series of novel anthranilic diamides containing polyfluoroalkyl pyrazole were synthesized. The bioassay results indicated that some of the title compounds exhibited moderate to excellent insecticidal activities against *Mythimna separata* Walker, *Prodenia litura* Fabricius and *Plutella xylostella* Linnaeus.

N-Bromosuccinimide Mediated the Reaction of 2-Hydroxyaryl Aldehydes with Meldrum's Acid for Synthesis of Coumarin-3-carboxylic Acids

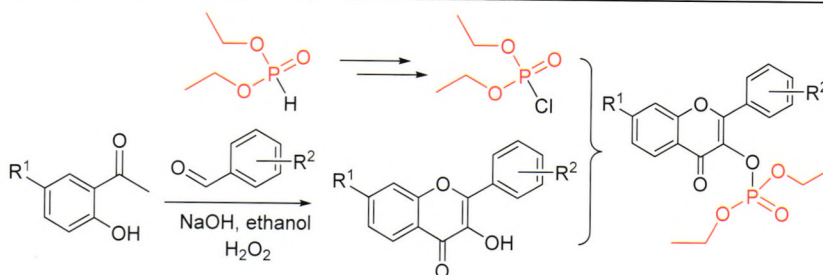


Ruan, Hongli; Zhang, Jingyuan; Sun, Sai; Yang, Ying; Zhu, Xiaolei; Lü, Chengwei*

Chin. J. Org. Chem. **2017**, 37(8), 2139

A *N*-bromosuccinimide (NBS) promoted, convenient and efficient procedure for the synthesis of coumarin-3-carboxylic acids via the condensation of 2-hydroxyarylaldehydes with Meldrum's acid has been developed at room temperature.

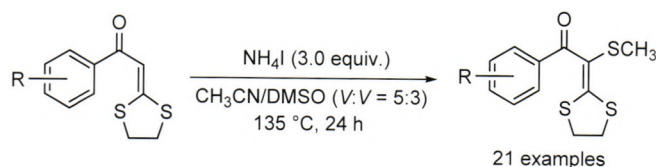
Synthesis and Antibacterial Activity of Novel Phosphonate Derivatives Containing Flavonoids



Huang, Minguo; Ruan, Xianghui; Zhang, Juping; Li, Qin; Wang, Yihui; Chen, Lijuan; Zhang, Cheng; Li, Pu; Xue, Wei*

Chin. J. Org. Chem. **2017**, 37(8), 2145

By introducing flavonoids group into H-phosphonate, 14 novel phosphonate derivatives containing flavonoids unit were designed and synthesized, and their antibacterial activities were evaluated via turbidimeter test *in vitro*.

Metal-Free Thiomethylation of α -Oxo-ketene Dithioacetals

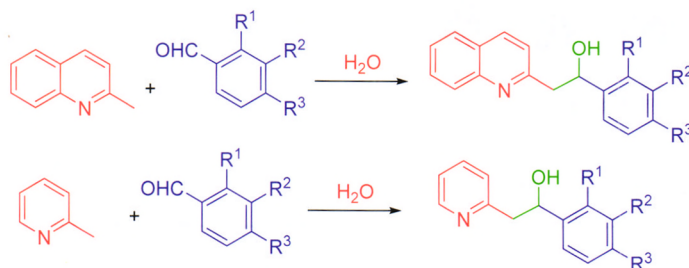
Zhang, Haifeng; Bao, Hanyang; Xu, Zheng; Liu, Yunkui*

Chin. J. Org. Chem. **2017**, 37(8), 2153

With dimethyl sulfoxide as a source of thiomethyl group and NH₄I as a promotor, the thiomethylation of α -oxo-ketene dithioacetals has been achieved to afford thiomethylated α -oxo-ketene dithioacetals in moderate to good yields. The optimized reaction conditions were established through systematic investigations of solvents, temperature, time, promoters and their dosages in the reaction.

CONTENT

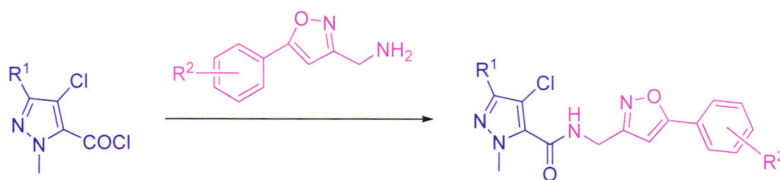
Reaction of 2-Methylquinoline and 2-Methylpyridine with Aromatic Aldehydes in High Temperature Water



Xiao, Shangyou*; Bi, Jingfu; Mu, Xiaojing; Zhou, Zhao; Xu, Guang
Chin. J. Org. Chem. **2017**, 37(8), 2159

Alkyl aza-arene derivatives were synthesized in high-temperature water without catalyst. The results indicate that it is an efficient way to synthesize 2-methylquinoline derivatives and 2-methylpyridine derivatives from 2-methylquinoline and 2-methylpyridine with various aromatic aldehydes by C—H bond activation. This process is clean and easy to operate.

Synthesis and Biological Activities of Novel Pyrazole Amide Derivatives Containing Substituted Isoxazole Group



Dai, Hong; Yao, Wei; Ye, Linyu; Fang, Yuan; Shi, Yujun*; Song, Chan; Li, Chunjian; Shi, Jian*
Chin. J. Org. Chem. **2017**, 37(8), 2165

A series of novel pyrazole amides bearing substituted isoxazole group were synthesized, and their bioactivities were evaluated.

HIGHLIGHTS

Chin. J. Org. Chem. **2017**, 37(8), 2172

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