

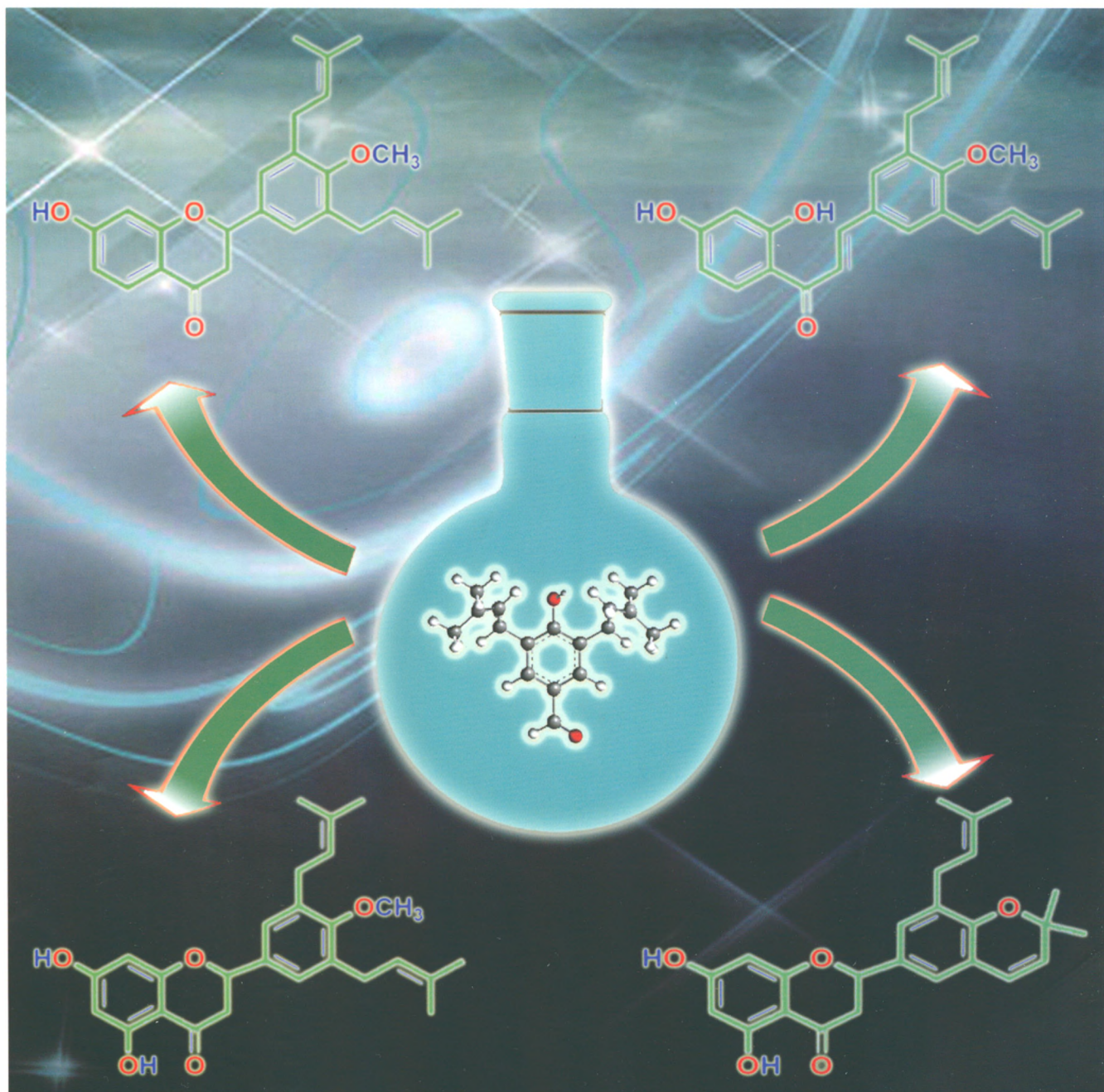
有机化学

Youji Huaxue

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* 通讯联系人。

研究简报

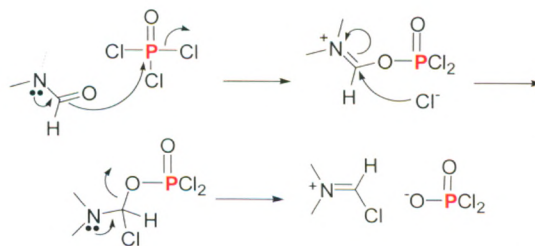
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Application of Vilsmeier Reagents in Cyclization in Recent Years

Qian, Xiaoqing; Zhou, Heng; Zhan, Xiaoping; Liu, Zenglu; Mao, Zhenmin*
Chin. J. Org. Chem. **2012**, 32(12), 2223

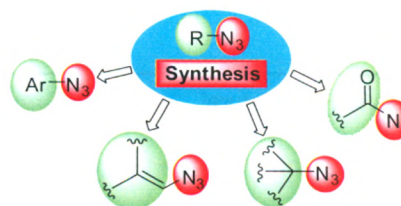


The Vilsmeier-Hack reaction provides a facile entry into large numbers of aromatic and heteroaromatic systems. Vilsmeier reagents generated from amides and halides have been found to be very important in organic synthesis.

Acylation, chlorination, chloroformylation, aromatization, rearrangement, dehydration and cyclization are the most reactions of Vilsmeier reagents. The application of Vilsmeier reagents in cyclization is introduced.

Advances in the Synthesis of Organic Azides

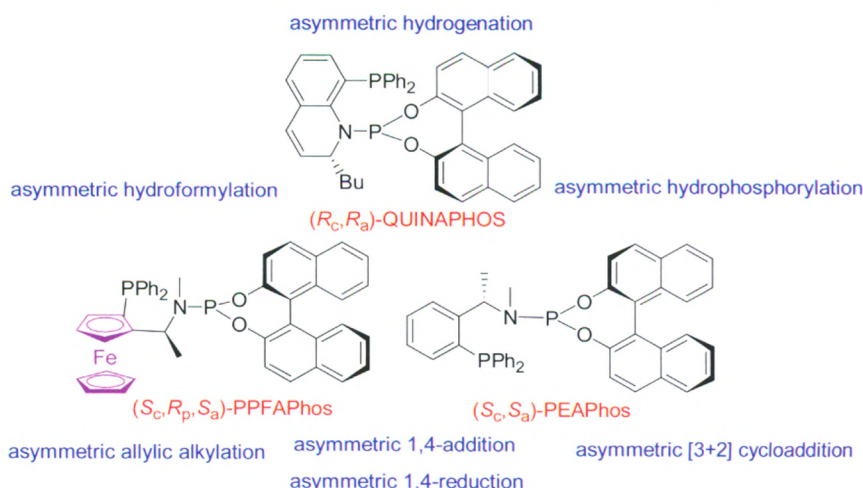
Jiang, Yubo*; Kuang, Chunxiang*; Han, Chunmei; Wang, Hong; Liang, Xueqiu
Chin. J. Org. Chem. **2012**, 32(12), 2231



The recent advances in the synthesis of organic azides is mainly reviewed, based on the categories of these compounds including alkyl azides, alkenyl azides, aryl azides, and acyl azides. Mechanism of some reactions is also discussed.

Progress on Unsymmetrical Hybrid Chiral Phosphine-phosphoramidite Ligands and Their Application in Asymmetric Catalytic Reactions

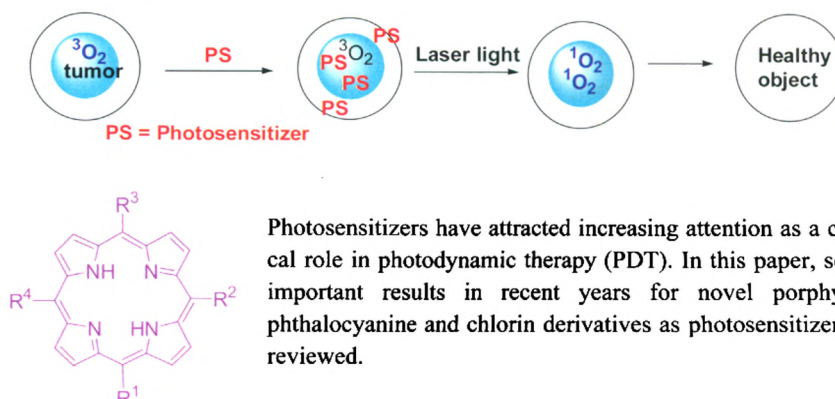
Hou, Chuanjin*; Liu, Xiaoning; Xia, Ying; Hu, Xiangping*
Chin. J. Org. Chem. **2012**, 32(12), 2239



The progress on unsymmetrical hybrid chiral phosphine-phosphoramidite ligands and their application in asymmetric catalytic reactions is reviewed, including hydrogenation, hydroformylation, allylic alkylation, hydrophosphorylation, [3 + 2] cycloaddition, 1,4-addition and 1,4-reduction.

Research Advances of Porphyrin Photosensitizers in Photodynamic Therapy

Wang, Lingyun*; Cao, Derong
Chin. J. Org. Chem. **2012**, 32(12), 2248



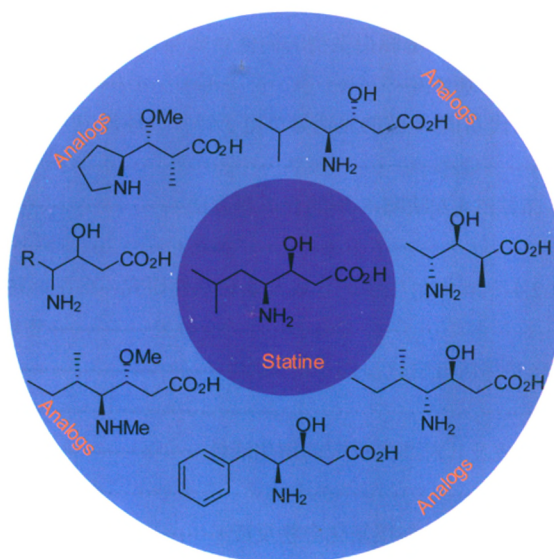
Photosensitizers have attracted increasing attention as a critical role in photodynamic therapy (PDT). In this paper, some important results in recent years for novel porphyrin, phthalocyanine and chlorin derivatives as photosensitizer are reviewed.

On the Cover

The total synthesis of prenylated flavonoids, (±)-abyssinone-VI-4-*O*-methyl ether, (±)-abyssinone-IV-4'-*O*-methyl ether, (±)-abyssinone-V-4'-*O*-methyl ether and (±)-sigmoidin E has been described by Zuo *et al.* on page 2276. The key intermediate 4-hydroxy-3,5-di-(3-methylbut-2-enyl)benzaldehyde (**6**) was synthesized that features regioselective prenylation of 4-hydroxybenzaldehyde and crystallizing with petroleum ether from the reaction mixture by freeze-out effect.

REVIEWS

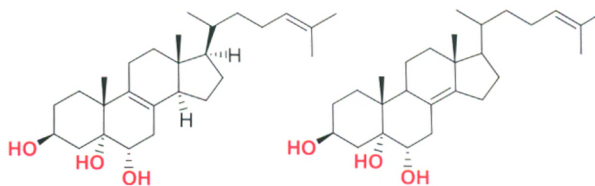
Progress in the Asymmetric Synthesis of Statine and Its Analogs



Zhang, Wei
Chin. J. Org. Chem. **2012**, 32(12), 2203

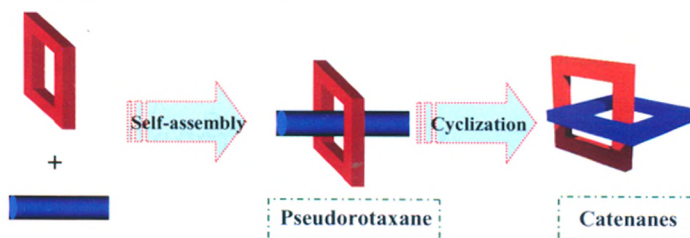
Statine and its analogs are special kind of β -hydroxy- γ -amino acids, which are usually core segments in many bioactive compounds. In this paper, several synthetic strategies are summarized.

Polyhydroxysterols with Bioactivities from Marine Organisms



Lin, Qifu; Cui, Jianguo*; Gan, Chunfang;
Liu, Liang; Yao, Qiucui; Huang, Yanmin*
Chin. J. Org. Chem. **2012**, 32(12), 2214

Polyhydroxysterols are a kind of natural compounds with significant physiological activities, widely exist in marine organisms. Recent researches on polyhydroxysterols with bioactivities isolated from marine organisms are reviewed according to the number of hydroxyl group on sterols.



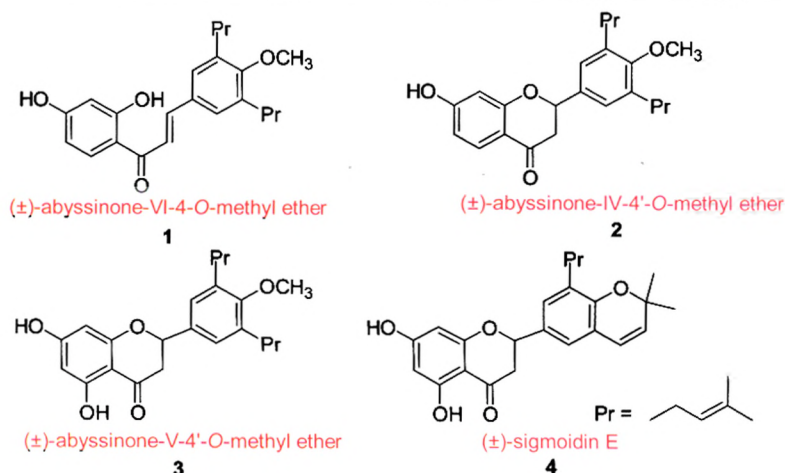
Shen, Jianfeng; Yu, Xuetao; Ye, Yuyuan;
Chen, Renér*; Jiang, Huajiang; Zhou, Qi-
zhong*

Chin. J. Org. Chem. **2012**, 32(12), 2265

Template-directed protocols have facilitated the efficient preparations of various kinds of catenanes. Thereinto, as the first macrocyclic host, crown ether derivatives have been widely used to prepare catenanes. Therefore, the development of supramolecular catenane chemistry based on crown ether derivatives is systematically addressed.

ARTICLES

Study on Total Synthesis of Four Natural Prenylated Flavonoids

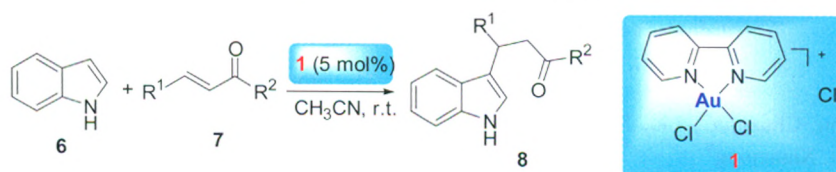


A facile approach for the total synthesis of prenylated flavonoids, (±)-abyssinone-VI-4-O-methyl ether (1), (±)-abyssinone-IV-4'-O-methyl ether (2), (±)-abyssinone-V-4'-O-methyl ether (3) and (±)-sigmodin *E* (4), has been described. The key intermediate 4-hydroxy-3,5-di-(3-methylbut-2-enyl)benzaldehyde (6) was synthesized that features regioselective prenylation of 4-hydroxybenzaldehyde and crystallizing with petroleum ether from the reaction mixture by freeze-out effect.

Zuo, Wubiao; Yang, Jinhui*; Li, Hongjun;
Guo, Dongdong; Luo, Junshan; Huang,
Wenqian

Chin. J. Org. Chem. **2012**, 32(12), 2276

Highly Efficient Michael-Type Friedel-Crafts Reactions Catalyzed by Gold-bipyridine Complexes

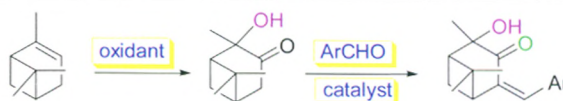


Zhang, Yan*; Zhu, Chengjian

Chin. J. Org. Chem. **2012**, 32(12), 2283

A novel highly efficient gold-bipyridine catalyst system has been tested for Michael-type Friedel-Crafts reactions.

Synthesis and Ultraviolet Absorption Characteristics of 4-Arylidene-2-hydroxy-3-pinanes

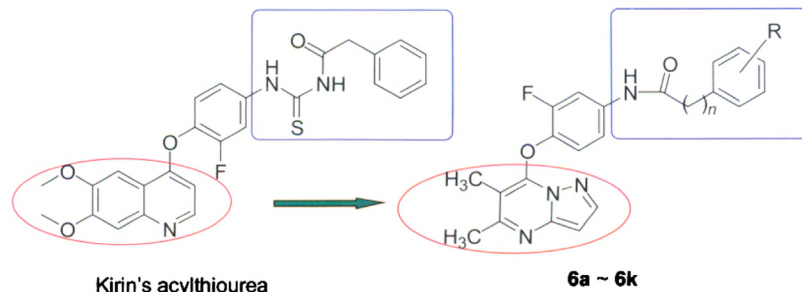


Wei, Baisong; Xu, Xu; Yang, Yiqin; Cao,
Xiaoqin; Wang, Shifa*

Chin. J. Org. Chem. **2012**, 32(12), 2287

A new series of 4-arylidene-2-hydroxy-3-pinanes were synthesized from (–)-α-pinene. (+)-2-Hydroxy-3-pinone was obtained from (–)-α-pinene by selective oxidation with potassium permanganate, and it was reacted with aromatic aldehydes including benzaldehyde, *p*-methylbenzaldehyde, *p*-methoxybenzaldehyde, *p*-hydroxybenzaldehyde, *p*-chlorobenzaldehyde, *p*-nitrobenzaldehyde, and furfural catalyzed with alkali catalysts to get optical activity 4-arylidene-2-hydroxy-3-pinanes.

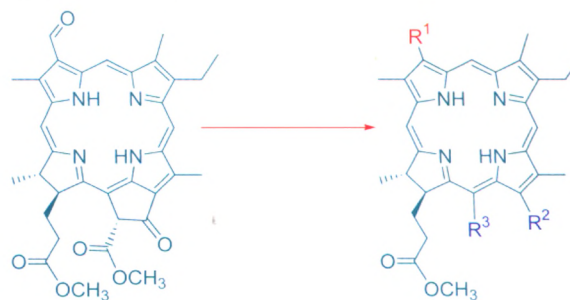
Synthesis and Bioactivity of Pyrazolo-[1,5-a]pyrimidine Derivatives as Novel c-Met Inhibitors



Ni, Chunyan; Zhang, Yuting; Zhao, Yu*; Zhu, Li
Chin. J. Org. Chem. **2012**, 32(12), 2294

A series of pyrazolo[1,5-a]pyrimidines were synthesized. Their antitumor activities were evaluated by MTT and ELISA assay.

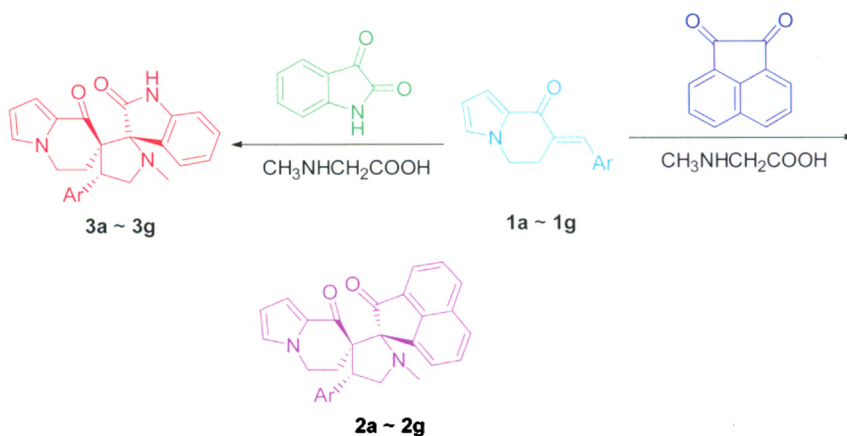
Chemical Modification of Methyl Pyropheophorbide-d and Synthesis of Chlorophyllous Chlorin Derivatives



Wang, Zhen; Yang, Ze; Liu, Yang; Xu, Xisen; Qi, Caixia; Wang, Jinjun*
Chin. J. Org. Chem. **2012**, 32(12), 2300

Methyl pyropheophorbide-d was used as starting material and its formyl and carbonyl group on E-ring were modified to build different chemical structures at 3-position and exocyclic E-ring. A series of chlorins with basic skeleton of chlorophyll were synthesized, and the relations between the molecular structures and their UV-Vis spectra were discussed. The possible mechanisms about corresponding reactions were tentatively proposed.

Synthesis of Novel Spiro Indolizidine Derivatives via 1,3-Dipolar Cycloaddition of Azomethine Ylide

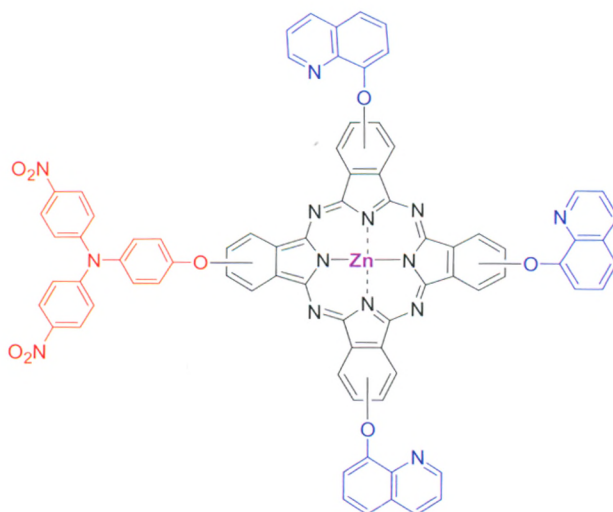


a Ar = C₆H₅, b Ar = 4-ClC₆H₄, c Ar = 2,4-Cl₂C₆H₃, d Ar = 4-FC₆H₄,
 e Ar = 4-CH₃SC₆H₄, f Ar = 4-CH₃C₆H₄, g Ar = 3,4,5-(CH₃O)₃C₆H₂

Li, Xiaofang; Yi, Rongqiong; Liu, Bin; Li, Zhikui; Yu, Xianrong; Yi, Pinggui*
Chin. J. Org. Chem. **2012**, 32(12), 2309

The 1,3-dipolar cycloaddition of azomethine ylide generated *in situ* from acenaphthenequinone (isatin) and sarcosine to 7-arylmethylidene-6,7-dihydroindolizine-8(5H)-ones afforded novel 4'-aryl-1'-methyl-5'',6''-dihydro-2H,8''H-dispiro[acenaphthylene-1,2'-pyrrolidine-3',7''-indolizine]-2,8''-diones and 4'-aryl-1'-methyl-5'',6''-dihydro-8''H-dispiro[indole-3,2'-pyrrolidine-3',7''-indolizine]-2,8''(1H)-diones in moderate yields. The structures of the products were characterized thoroughly by NMR, IR, MS, elemental analysis together with X-ray crystallographic analysis.

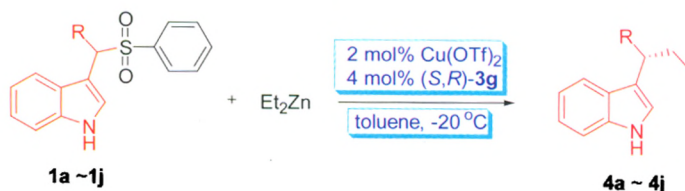
Synthesis and Study of Properties for Asymmetric Triphenylamine-Zinc Phthalocyanine



Mao, Lijun; Tan, Qinglong; Xin, Guanqiong;
Han, Mingliang; Zhang, Xuejun*
Chin. J. Org. Chem. **2012**, 32(12), 2315

It is the structure of triphenylamine-quinoline-zinc phthalocyanine based sensitizer for dye-sensitized solar cells. The properties of the two sensitizers-triphenylamine and phthalocyanine are combined.

Enantioselective Conjugate Addition of Diethylzinc to Vinylogous Imines Gener- ated *in situ* from Sulfonyl Indoles

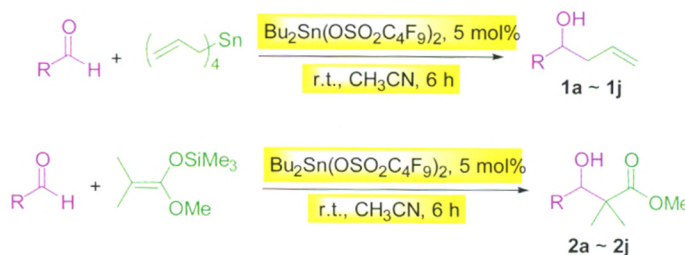


Ni, Chengyan; Li, Wenke; He, Long*; Liu
Quanzhong*; Kang Tairan
Chin. J. Org. Chem. **2012**, 32(12), 2322

Enantioselective conjugate addition of diethyl zinc to vinylogous imines generated *in situ* from sulfonyl indoles was developed. Various sulfonyl indoles reacted with diethyl zinc in the presence of chiral phosphoramidites in combination with copper triflate affording the corresponding indole substituted alkanes in up to 99% yield with moderate to good enantioselectivity (up to 80% *ee*).

NOTES

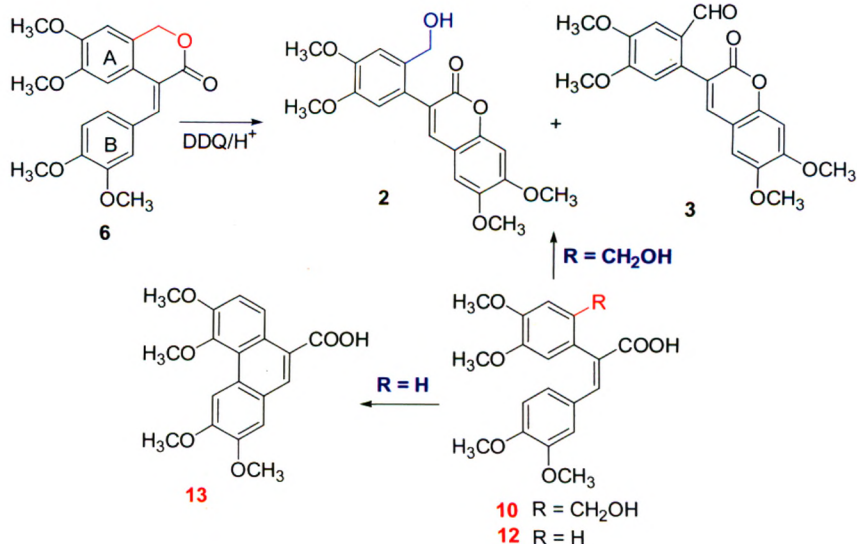
Bis(perfluorobutyl)sulfonate Bisbutyltin Catalyzed Allylation and Mukaiyama- aldol Reaction of Aldehyde



Liu, Yi; Wang, Xie; Chen, Jinyang; Li,
Ningbo; Xu, Xinhua*
Chin. J. Org. Chem. **2012**, 32(12), 2328

Bis(perfluorobutyl)sulfonate bisbutyltin complex was successfully synthesized by treating $C_4F_9SO_3Ag$ with Bu_2SnCl_2 in acetone at room temperature. When the complex was exposed to air two days, 1H NMR spectra showed that its structure had no change. TG-DSC showed that the complex was stable below 220 °C. The complex had a good solubility in polar solvents, such as ethyl acetate, acetone, acetonitrile, THF, ethyl ether. But it was poor soluble in hexane, CH_2Cl_2 , toluene at room temperature. In the presence of 1.0 and 5.0 mol% of bis(perfluorobutyl)sulfonate bisbutyltin respectively, allylation of aldehyde and Mukaiyama aldol reaction could efficiently occur in CH_3CN at room temperature and give high yield of the corresponding products.

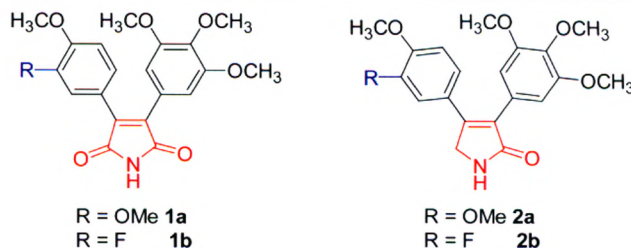
Intramolecular Oxidative Coupling Reaction of 4-Phenylmethylene-3-isochromanones with 2,3-Dichloro-5,6-dicyanobenzquinone as an Oxidant



Isochromen-3-one (6), oxidized by DDQ/CH₃SO₃H in CH₂Cl₂, gave no polymethoxy-substituted phenanthrene derivative but unexpected coumarins 2 and 3. Further experiments showed that the steric hindrance of a ring of 6 resulted in coumarin not phenanthrene derivative, supported by comparative experiments of 10 and 12. The possible mechanism of 2 via radical cation and 3 through oxidation of precursor of 2 was proposed based on the result of experiments.

Ji, Derong; Su, Lidan; Zhang, Chenggang*
Chin. J. Org. Chem. **2012**, 32(12), 2334

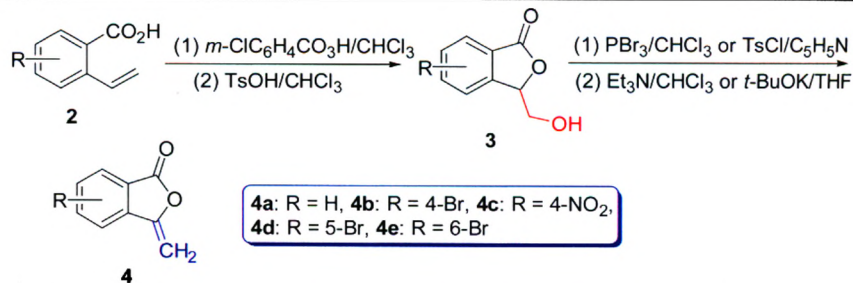
Synthesis and *in vitro* Antitumor Activities of 3,4-Diaryl Substituted Pyrrolones Derivatives



The structures of these new compounds were confirmed by ¹H NMR, ¹³C NMR, ESI-MS and elemental analysis. The *in vitro* antitumor activities of CA-4 analogues against HL-60, SMMC-7721 and A549 human gastric cancer cell lines were tested using colorimetric MTT assay. The preliminary result indicates that 3-(3-fluoro-4-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)pyrrole-2,5-dione (1b) shows significant antitumor activity (0.03~0.05 μmol•L⁻¹), which is closely to the natural CA-4.

Wei, Li; Yang, Xiaoli; Yuan, Jiwen; Hu, Hongwen; Lu, Guoyuan*
Chin. J. Org. Chem. **2012**, 32(12), 2339

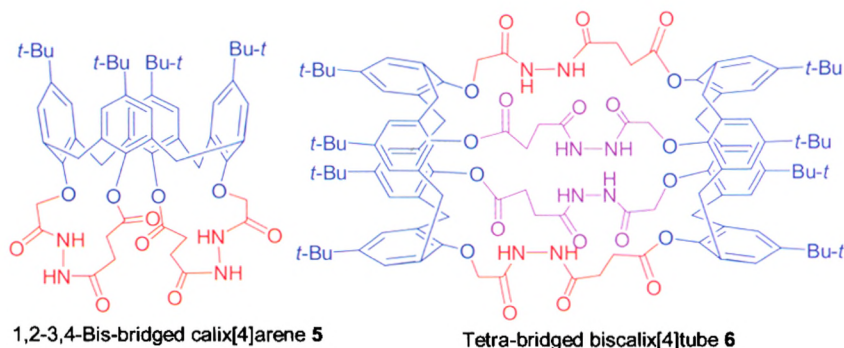
Synthesis of 3-Methyleneisobenzofuran-1(3H)-one and Their Derivatives



Starting from 2-vinylbenzoic acid methyl ester and derivatives, 3-hydroxymethylisobenzofuran-1(3H)-one and derivatives were prepared through hydrolysis of esters, followed by epoxidation with *m*-chloroperoxybenzoic acid, cyclization reaction catalyzed by *p*-toluenesulfonic acid; then nucleophilic substitution with phosphorus tribromide or tosyl chloride and elimination reaction, 3-methyleneisobenzofuran-1(3H)-one and their derivatives were synthesized. The yield of tosyl chloride method was higher than phosphorus tribromide method in the nucleophilic substitution and elimination reaction.

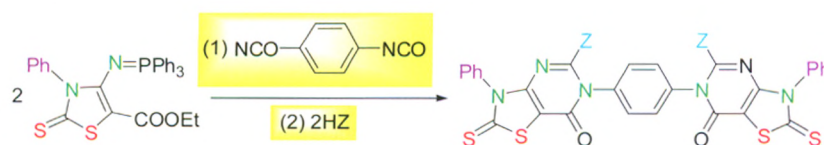
Zhang, Jizhen*; Wu, Jian; Wang, Yazhen; Zhao, Dejian; Jia, Hongbin
Chin. J. Org. Chem. **2012**, 32(12), 2344

Convenient Synthesis of Novel Tetra-bridged Biscalix[4]tube and 1,2-3,4-Bis-bridged Calix[4]arene



Zhang, Yingme; Yang, Fafu*; Bai, Xiaoyan;
Liu, Zhiqiang; Guo, Hongyu
Chin. J. Org. Chem. **2012**, 32(12), 2350

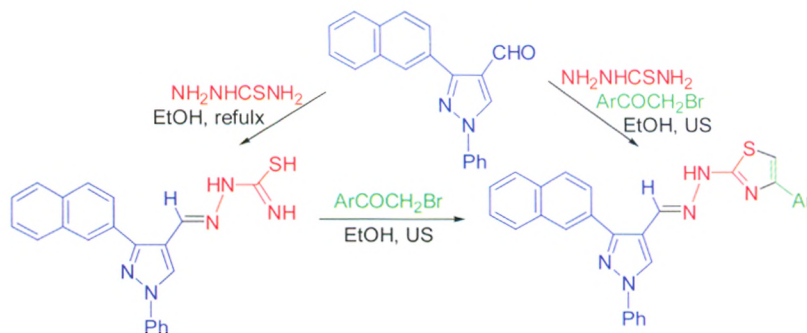
Novel tetra-bridged calix[4]tube and 1,2-3,4-bis-bridged calix[4]arenes were conveniently synthesized.

Synthesis of Benzene-Bridged Bis(thiazolo[4,5-*d*]pyrimidin-7(6*H*)-one) Derivatives

Fang, Zhengdong*; Yuan, Yi; Ye, Hualing
Chin. J. Org. Chem. **2012**, 32(12), 2354

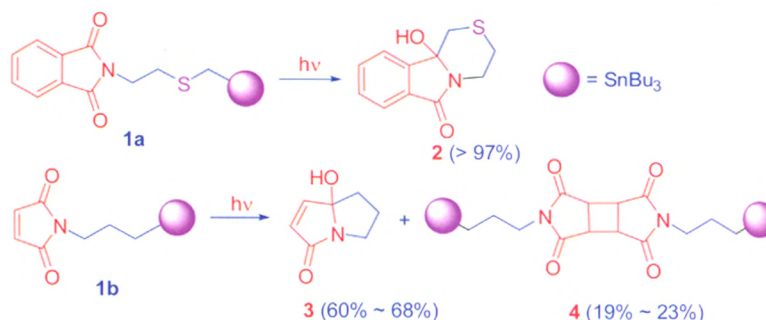
Bis-aza-Wittig reactions of ethyl 4-((triphenylphosphanylidene)amino)-2,3-dihydro-3-phenyl-2-thioxothiazole-5-carboxylate with aromatic diisocyanate and nucleophilic reagents produced novel benzene-bridged bis(thiazolo[4,5-*d*]pyrimidin-7(6*H*)-one) derivatives in the presence of EtONa in 56%~92% yields.

Convenient Synthesis and Characterization of Hydrazone Derivatives of 3-(2-Naphthyl)-1-phenyl-pyrazole-4-carbaldehyde



Ablajan, Keyume*; Wang, Liju
Chin. J. Org. Chem. **2012**, 32(12), 2358

A series of 1-(3- β -naphthyl-1-phenylpyrazole-4-methylene)-2-(4-arylthiazol-2-yl)hydrazones were synthesized via two different methods including multi step reactions and one-pot synthetic route. The products were obtained in good yield under ultrasonic irradiation condition rather than heating.

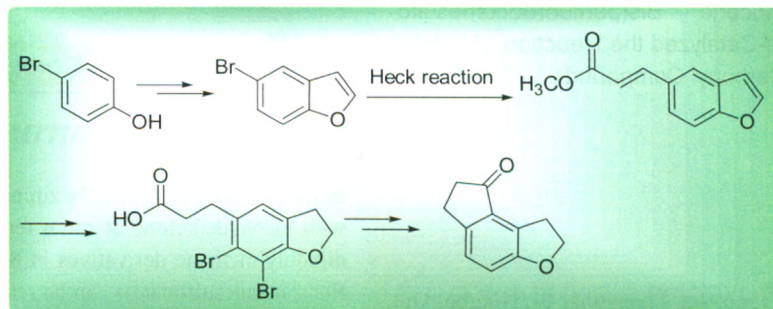
Photoinduced Single Electron Transfer Cyclization Reactions of *N*-(Trimethylstannyl terminated substituent group)-imide

Jin, Yingxue; Wang, Xin; Qu, Fengyu; Tan, Guanghui; Yue, Qunfeng*
Chin. J. Org. Chem. **2012**, 32(12), 2363

Two novel intramolecularly electronical donor-acceptor systems, *N*-[2-(2-tributylstannylmethylsulfonyl)ethyl]phthalimide (**1a**) and *N*-(3-tributylstannylpropyl)maleimide (**1b**), were synthesized, and their photoinduced single electron transfer (SET) reactions in MeOH, CH₃CN-30% H₂O and pure CH₃CN were carried out, respectively.

An Improved Synthesis of 1,2,6,7-Tetrahydro-8*H*-indeno[5,4-*b*]furan-8-one

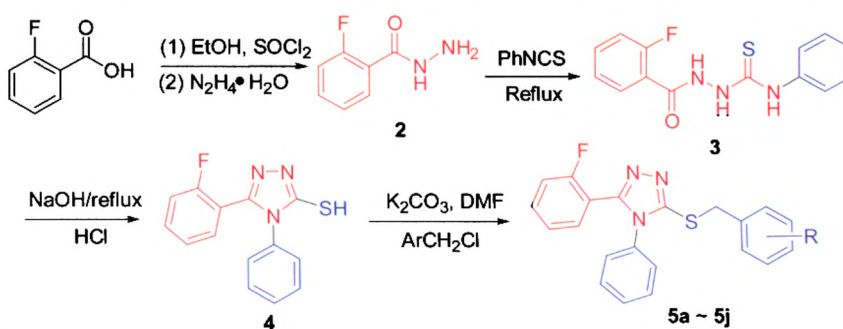
Huang, Zhixiong; Wu, Chenglong; Shang, Zhipei; Deng, Yong*
Chin. J. Org. Chem. **2012**, 32(12), 2368



A novel synthesis of 1,2,6,7-tetrahydro-8*H*-indeno[5,4-*b*]furan-8-one, a key intermediate for preparation of ramelteon has been achieved in seven steps from *p*-bromophenol. The key step of the synthesis is an efficient condensation of 5-bromobenzofuran with methyl acrylate via Heck coupling reaction.

Synthesis and Fungicidal Activity of 1,2,4-Triazole Derivatives Containing 2-Fluorophenyl Moiety

Tong, Jianying; Shi, Yanxia; Liu, Xinghai*; Sun, Nabo; Li, Baoju*
Chin. J. Org. Chem. **2012**, 32(12), 2373



A series of novel 1,2,4-triazole derivatives were synthesized. The target compounds were evaluated for their fungicidal activities *in vivo*, and the results indicated that some of the title compounds displayed excellent fungicidal activities.

Application of Microwave Technique into Etherification of 10-Hydroxycamptothecin

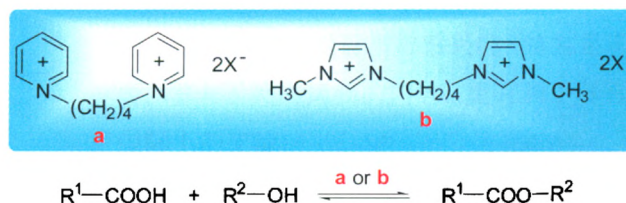
Meng, Guangrong; Li, Jiajun; Zhang, Qian; Ma, Hongmei*
Chin. J. Org. Chem. **2012**, 32(12), 2378



Microwave technique was applied in the etherification of 10-hydroxycamptothecin with the improved yield of 50%~83%. This reaction condition could be used for reference in other relative reactions of camptothecins.

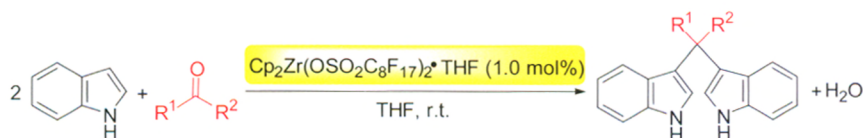
Synthesis of Binuclear Ionic Liquids and Their Catalytic Activity for Esterification

Zhao, Dishun*; Liu, Mengshuai; Ge, Jing-jing; Zhang, Juan; Ren, Peibing
Chin. J. Org. Chem. **2012**, 32(12), 2382



A series of dicationic ionic liquids were synthesized and characterized. Key physico-chemical properties were determined. The synthesized dicationic salt tested for the esterification of monocarboxylic acids and dicarboxylic acids with different alcohols. The esterification was carried out under mild reaction conditions and without any additional organic solvent. The produced esters were easily recovered due to immiscibility with the ionic liquid as green reaction medium. The ionic liquid was recycled and reused. Thus, the reported dicationic ionic liquid was a promising catalyst for esterification reaction.

Zirconocene Bis(perfluorooctanesulfonate)s-Catalyzed the Reaction of Indoles and Carbonyl Compounds



In the presence of 1.0 mol% zirconocene bis(perfluorooctanesulfonate)s, indoles reacted with aldehyde/ketone at room temperature in tetrahydrofuran for 10~25 min to give diindolylmethane derivatives in 86%~96% yields. The catalyst zirconocene bis-(perfluorooctanesulfonate)s can be reused 6 times, and the conversion rate is still as high as 90%. This reaction does not require strict anhydrous conditions. This procedure provides a new and efficient way for preparing diindolylmethane derivatives.

Yi, Weiguo; Jia, Zhenyong; Li, Ningbo; Qui, Renhua; Chen, Jinyang; Xu, Xinhua*
Chin. J. Org. Chem. **2012**, 32(12), 2390

HIGHLIGHTS

Chin. J. Org. Chem. **2012**, 32(12), 2394