

第十九届全国金属有机化学学术讨论会
The 19th National Conference on Organometallic Chemistry of China

程序册及会议指南

主办单位：中国化学会

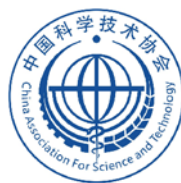
承办单位：浙江大学化学系、浙江省化学会

中国科学院上海有机化学研究所金属有机化学国家重点实验室

资助单位：



国家自然科学基金委员会



浙江省科学技术协会

2016年10月28-31日

浙江·杭州

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学术委员会

召集人：麻生明

委员（按姓氏笔画顺序排列）：

丁奎岭	王绍武	王彦广	冯小明	朱成建	江焕峰	沈之荃
肖文精	宋礼成	张俊良	吴养洁	李悦生	沈 琪	陆熙炎
周永贵	周其林	周锡庚	洪茂椿	施章杰	涂永强	唐 勇
夏海平	席振峰	黄汉民	游书力	谢作伟	雷爱文	戴立信

组织委员会

主 席：王彦广

秘书长：吕 萍

副秘书长：马 成 史炳锋

成员：

林旭锋	潘远江	傅春玲	张玉红	黄志真	陈万芝	陆 展
丁寒锋	李 昊	崔孙良	Simon Duttwyler	刘占祥	吴金龙	
雷 鸣	洪 鑫					

会 务 须 知

欢迎各位嘉宾来到美丽的西子湖畔，参加第十九届全国金属有机化学学术讨论会！

一、会议报到

时间：10月28日（10:00-20:00）

地点：为方便与会代表，本次会议设立四个报到地点，请各位代表选择相应的报到点，办理报到手续并领取会议资料：

- 1) **紫金港国际饭店：**会前已注册缴费且已在后台登记酒店为紫金港国际饭店、紫金港大酒店、威斯希顿大酒店和杭州亿泊城市艺术酒店的参会人员；
- 2) **杭州百瑞国际大酒店：**会前已注册缴费且已在后台登记酒店为杭州百瑞国际大酒店和山水宾馆的参会人员；
- 3) **唐人儒亿大酒店：**会前已注册缴费且已在后台登记酒店为唐人儒亿大酒店的参会人员；
- 4) **浙江大学紫金港校区体育馆：**除以上人员外的参会代表。

注：

延迟报到：对于本地会议代表及错过28日报到的会议代表，大会将在29日上午（8:00-11:30）在浙江大学紫金港校区体育馆一楼设报到点予以办理。

二、会议时间

- 10月29日上午 08:00-12:00 大会开幕式及大会报告
- 10月29日下午 14:00-18:00 大会报告及分会场报告
- 10月30日全天 08:00-18:00 分会场报告
- 10月31日上午 08:00-12:00 分会场报告
- 10月31日下午 14:00-18:00 大会报告、获奖报告及闭幕式

三、会场设置

- 1、开幕式、大会报告、获奖报告及闭幕式：紫金港校区体育馆
- 2、分会场：紫金港校区体育馆和蒙民伟楼 225 会场

四、会议用餐

- 1、早餐由各住宿宾馆提供
- 2、午餐及晚餐

1) 10月28日晚餐(17:30-19:00)，地点如下：

- 杭州百瑞国际大酒店：已注册且预订酒店为杭州百瑞国际大酒店和山水宾馆的参会人员；
- 唐人儒亿酒店：已注册且预订酒店为唐人儒亿酒店的参会人员；
- 威斯希顿大酒店：已注册且预订酒店为威斯希顿大酒店和杭州亿泊城市艺术酒店的参会人员；
- 紫金港国际饭店：已注册且预订酒店为紫金港国际饭店、紫金港大酒店和现场注册参会人员。

2) 会议期间（10月29-31日）

凭代表证就餐，地点：紫金港校区食堂二楼东西两区

- 就餐时间：中餐 12:30-13:30，晚餐 18:00-19:00

3) 清真或素食：请报到时告知会务组

五、墙报张贴

1) 墙报提供的展板规格：110cm*80cm(高*宽)；

2) 请各位参会代表严格按照会议日程安排中的张贴日期和编号进行张贴，现场工作人员将予以协助；

3) 展示结束后，请参会代表及时取下自己的展示材料。

六、医疗服务

会议配备了专业的医疗服务人员和常用药品，如有需要请联系：潘医生 13588082967。

七、交通安排

会议期间，杭州百瑞国际大酒店、山水宾馆和紫金港校区体育馆往返车辆，具体时间安排如下（其他酒店参会者自行安排）：

发 车 地 点 \ 日 期	10月29日	10月30日	10月31日
百瑞国际大酒店	7:15	7:15	7:15
山水宾馆	7:15	7:15	7:15
体育馆西门（藕舫北路西侧）	19:20； 19:40	19:20； 19:40	19:20； 19:40

若您错过以上班车时间，会务组推荐路线如下：

百瑞国际大酒店/山水宾馆出发，步行 850 米至翠苑一区站乘坐 10 路车至浙大紫金港校区站下车，全程 40 分钟，打车约 18 元。

浙大紫金港校区出发，步行 460 米至浙大紫金港校区站乘坐 10 路车至翠苑一区站下车，步行 850 米至酒店，全程 40 分钟，打车约 18 元。

八、 其它服务

需要其他会务服务的帮助请与会议工作人员联系，请注意会务组在酒店及会场贴出的通告或告示。

九、 会务组分工及联系方式

总负责：吕 萍：13777847196

史炳锋：18858108479

马 成：13957122980

住 宿：吕 萍：13777847196（总负责）

史炳锋：18858108479（紫金港国际饭店）

雷 鸣：13857190559（紫金港大酒店）

丁寒锋：18268080200（威斯希顿酒店）

崔孙良：18368109368（唐人儒亿酒店）

李 昊：13732268721（杭州百瑞国际大酒店）

洪 鑫：13735445027（山水宾馆）

餐 饮：郝 毅：13858198785

会 场：陆 展：18758292707（体育馆）

丁寒锋：18268080200（体育馆）

李 昊：13732268721（蒙民伟楼 225 室）

洪 鑫：13735445027（蒙民伟楼 225 室）

交 通：林旭锋：13185001399

布展、墙报：陈万芝：13819197926

赞助商：史炳锋：18858108479

医 疗：潘医生：13588082967

十、 校内示意图



十一、 温馨提示

为了确保您和他人会议期间的健康、安全与环保，请您注意以下有关事项：

- 1、为保障会议的顺利进行，请会议代表遵守大会作息时间和各项安排，凭代表证参加大会各项活动。
- 2、会议期间，请将手机关闭或置于震动状态，以便会议顺利进行。
- 3、请不要携带易燃、易爆化学物品及充压容器进入酒店及会场。
- 4、进入会场前，请首先熟悉会场的安全出口。
- 5、一旦发生紧急情况，请听从工作人员指挥，快步、有序的撤离现场。
- 6、如遇下雨，地面湿滑时，请注意防滑。

- 7、注意饮食安全，如有不适，请及时与我们会务组联系。
- 8、请勿在会场内及其他禁烟场所吸烟。
- 9、个人所带文件和贵重物品请妥善保管，外出时注意安全，离会前请将房卡交酒店服务台（31日退房可延迟到当天下午2：00前）。

日 程 简 表

日期	时间	内容	地点
10月28日 (星期五)	10:00-20:00	会议代表报到	紫金港校区体育馆和各指定酒店
	13:00-19:00	墙报张贴	紫金港校区体育馆二楼
	17:30-19:00	自助晚餐	各指定酒店
10月29日 (星期六)	08:00-08:30	开幕式	紫金港校区体育馆
	08:30-09:30	大会报告	
	09:30-10:00	茶 歇	
	10:00-12:00	大会报告	紫金港校区体育馆
	12:00-14:00	午餐	紫金港校区食堂二楼
	14:00-15:00	大会报告	紫金港校区体育馆
	15:00-15:10	金属有机终身成就奖 颁奖仪式	
	15:10-16:05	获奖报告	
	16:05-16:25	茶 歇	
	16:10-18:10	分会场报告	紫金港校区体育馆、蒙民伟楼 225 室
	18:10-19:00	晚餐	紫金港校区食堂二楼
10月30日 (星期日)	08:00-10:10	分会场报告	紫金港校区体育馆、蒙民伟楼 225 室
	10:10-10:25	茶 歇	
	10:25-12:10	分会场报告	紫金港校区体育馆、蒙民伟楼 225 室
	12:10-14:00	午餐	紫金港校区食堂二楼
	14:00-16:10	分会场报告	紫金港校区体育馆、蒙民伟楼 225 室
	16:10-16:25	茶 歇	
	16:25-18:10	分会场报告	紫金港校区体育馆、蒙民伟楼 225 室
18:10-19:00	晚餐	紫金港校区食堂二楼	
10月31日 (星期一)	08:00-10:10	分会场报告	紫金港校区体育馆、蒙民伟楼 225 室
	10:10-10:25	茶 歇	
	10:25-12:10	分会场报告	紫金港校区体育馆、蒙民伟楼 225 室
	12:10-14:00	午餐	紫金港校区食堂二楼
	14:00-15:00	大会报告	紫金港校区体育馆
	15:00-15:20	茶 歇	
	15:20-15:35	金属有机化学奖颁奖	紫金港校区体育馆
	15:35-16:55	获奖报告	
	16:55-17:40	获奖墙报颁奖及闭幕式	
	17:40-19:00	晚餐	紫金港校区食堂二楼
19:00~	离 会		

会议日程

10月28日（星期五）

紫金港校区体育馆和各指定酒店

10:00-20:00	报 到	紫金港校区体育馆和各指定酒店
13:00-19:00	墙报张贴	紫金港校区体育馆二楼
17:30-19:00	晚 餐	

10月29日（星期六）

时间	内容	主持人
会场：紫金港体育馆		
08:00-08:30	开幕式	王彦广 (浙江大学)
08:30-09:30	大会报告一 (PL1): 麻生明 (浙江大学/中科院上海有机所) Two stones for one bird	席振峰 (北京大学)
09:30-10:00	茶 歇	
10:00-11:00	大会报告二 (PL2): 冯小明 (四川大学) Recent Progress in the Asymmetric Synthesis of Biologically Active Molecules Catalyzed by Chiral N,N' -Dioxide-Metal Complexes	周其林 (南开大学)
11:00-12:00	大会报告三 (PL3): 王剑波 (北京大学) 卡宾偶联反应研究的新进展	
12:00-14:00	午 餐	
14:00-15:00	大会报告四 (PL4): 周其林 (南开大学) Privileged Chiral Spiro Catalysts	冯小明 (四川大学)
15:00-15:10	金属有机终身成就奖颁奖仪式 (颁奖嘉宾: 周其林)	
15:10-16:05	金属有机终身成就奖报告: 支志明 (香港大学)	
16:05-16:25	茶 歇	
会场一：紫金港体育馆		
16:25-17:05	邀请报告 1 (IL1): 焦宁 (北京大学) From Simple Hydrocarbons to N-Containing Compounds through Nitrogenation Strategy	谢作伟 (香港中文大学)
17:05-17:30	口头报告 1 (OL1): 陆良秋 (华中师范大学) 过渡金属催化的偶极环加成反应研究	
17:30-18:10	邀请报告 2 (IL2): 史炳锋 (浙江大学) 天然产物全合成导向的惰性 sp^3 碳氢键活化: 新试剂、新反应及机理研究	谢建华 (南开大学)

会场二：蒙民伟楼		
16:25-17:05	邀请报告 3 (IL3): 李兴伟 (中科院大连化物所) Substrate Activation Strategies in High-Valent Metal-Catalyzed C-H Functionalization of Arenes	雷爱文 (武汉大学)
17:05-17:30	口头报告 2 (OL2): 全杨健 (香港中文大学) Transition Metal Catalyzed Regioselective Cage B-H Activation and Functionalization of <i>o</i> -Carboranes	
17:30-18:10	邀请报告 4 (IL4): 吴劼 (复旦大学) 基于二氧化硫插入的若干转化	杨尚东 (兰州大学)
18:10-19:00	晚 餐	
10 月 30 日 (星期日)		
会场一：紫金港体育馆		
08:00-08:40	邀请报告 5 (IL5): 范仁华 (复旦大学) 利用“去芳构化”策略和过渡金属催化的串联反应合成[<i>cd</i>]-并环吡啶	施章杰 (北京大学)
08:40-09:05	口头报告 3 (OL3): 鲍红丽 (中科院福建物构所) Applications of Peroxides as Alkylating Reagents in Cross Coupling Reactions	
09:05-09:45	邀请报告 6 (IL6): 叶龙武 (厦门大学) 炔烃转化的区域选择性控制与杂环结构多样性合成	朱强 (中国科学院 广州生物医药 与健康研究院)
09:45-10:10	口头报告 4 (OL4): 李世军 (杭州师范大学) 利用金属配位作用组装、调控与超分子手性催化应用	
10:10-10:25	茶 歇	
10:25-11:05	邀请报告 7 (IL7): 王绍武 (安徽师范大学) 稀土金属胺基化物及烃基化物与亚胺官能化吡啶的反应性研究	陆展 (浙江大学)
11:05-11:30	口头报告 5 (OL5): 唐山 (武汉大学) Multimetallc Catalyzed Oxidative Radical Alkynylation	
11:30-12:10	邀请报告 8 (IL8): 赵亮 (清华大学) 有机金属簇的可控合成与反应研究	莫凡洋 (北京大学)
会场二：蒙民伟楼		
08:00-08:40	邀请报告 9 (IL9): 祝诗发 (华南理工大学) 基于氧鎓历程的过渡金属催化体系	王春江 (武汉大学)
08:40-09:05	口头报告 6 (OL6): 丛欢 (中科院北京理化所) Nickel-Mediated Carbon-Carbon Coupling Reactions	
09:05-09:45	邀请报告 10 (IL10): 王从洋 (中科院化学研究所) C-H Bond Activation <i>via</i> Manganese Catalysis	邓亮 (中科院上海 有机所)
09:45-10:10	口头报告 7 (OL7): 张文珍 (大连理工大学) Synthesis of α -Arylglycines from Aromatic Imines and Carbon Dioxide <i>via</i> Umpolung Carboxylation	

10:10-10:25	茶 歇	
10:25-11:05	邀请报告 11 (IL11): 朱成建 (南京大学) Transition Metal Catalyzed C-H Bond Functionalization and Access to Heterocycles and Fluorinated Compounds	林旭锋 (浙江大学)
11:05-11:30	口头报告 8 (OL8): 宋秋玲 (华侨大学) New Reactivity and Applications of Diboron Reagents	
11:30-12:10	邀请报告 12 (IL12): 蓝宇 (重庆大学) 基于电子兼容性的分步自由基-自由基偶联模型	张书宇 (上海交通大学)
12:10-14:00	午 餐	
会场一：紫金港体育馆		
14:00-14:40	邀请报告 13 (IL13): 苏伟平 (中科院福建物构所) Cu-催化的酮脱氢成烯串连反应及其机理研究	施 敏 (中科院上海 有机所)
14:40-15:05	口头报告 9 (OL9): 时磊 (中科院大连化学物理所) 不对称氢化合成手性四氢异喹啉	
15:05-15:45	邀请报告 14 (IL14): 栾新军 (西北大学) 过渡金属催化碳氢键活化/去芳构化的协同螺环化反应研究	刘元红 (中科院上海 有机所)
15:45-16:10	口头报告 10 (OL10): 洪鑫 (浙江大学) Computational Studies on Mechanism and Origins of Selectivity in Ni-mediated C-O and C-N Activations	
16:10-16:25	茶 歇	
16:25-17:05	邀请报告 15 (IL15): 黄正 (中科院上海有机所) 金属有机催化的烷烃官能团反应	侯雪龙 (中科院上海 有机所)
17:05-17:30	口头报告 11 (OL11): 刘路 (华东师范大学) 高化学选择性和区域选择性的苯酚碳氢键官能化	
17:30-18:10	邀请报告 16 (IL16): 黄汉民 (中国科学技术大学) 过渡金属催化的 C-N 键活化	李纲 (中科院福建 物构所)
会场二：蒙民伟楼		
14:00-14:40	邀请报告 17 (IL17): Jianrong (Steve) Zhou (新加坡南洋理工) Classical and Weak Hydrogen Bonding in Asymmetric Palladium Catalysis	周永贵 (中科院大连 化物所)
14:40-15:20	邀请报告 18 (IL18): 张前 (东北师范大学) N-Fluorobenzenesulfonimide: An Efficient Radical Aminating Reagent	
15:20-15:45	口头报告 12 (OL12): 余达刚 (四川大学) 二氧化碳在杂环合成中的应用	王佰全 (南开大学)
15:45-16:10	口头报告 13 (OL13): 周永波 (湖南大学) 铜催化 P-H/C-H 键选择性转化反应	
16:10-16:25	茶 歇	

16:25-17:05	邀请报告 19 (IL19): 廖建 (中科院成都生物研究所) Chiral Sulfoxides in Transition Metal Catalyzed Asymmetric Reactions	梅天胜 (中科院上海有机所)
17:05-17:30	口头报告 14 (OL14): 崔秀灵 (郑州大学) Synthesis of Planar Chiral Ferrocenes <i>via</i> Palladium-Catalyzed C-H Bond Activation	丁寒锋 (浙江大学)
17:30-17:55	口头报告 15 (OL15): 刘强 (清华大学) Cobalt-Catalyzed Chemodivergent Transfer Hydrogenation of Nitriles	
18:10-19:00	晚 餐	
10 月 31 日 (星期一)		
会场一: 紫金港体育馆		
08:00-08:40	邀请报告 20 (IL20): 胡文浩 (华东师范大学) 多组分反应及其结构多样性化合物高效构建	游书力 (中科院上海有机所)
08:40-09:05	口头报告 16 (OL16): 燕红 (南京大学) Inert B-H Activation by Metal-Metal Cooperativity	
09:05-09:45	邀请报告 21 (IL21): 汤平平 (南开大学) 对具有生物活性天然产物的全合成及方法学研究	周锡庚 (复旦大学)
09:45-10:10	口头报告 17 (OL17): 李洪基 (淮北师范大学) Constructing New Chemical Bonds <i>via</i> Transition Metal Catalyzed C-H Activation and Functionalization	
10:10-10:25	茶 歇	
10:25-11:05	邀请报告 22 (IL22): 李金恒 (南昌航空大学) Transition Metal Catalyzed Cycloaddition Reactions with Alkynes	张俊良 (华东师范大学)
11:05-11:30	口头报告 18 (OL18): 张振华 (中国农业大学) Pd-Catalyzed Coupling Reaction of Azide with σ -donor / π -acceptor	
11:30-12:10	邀请报告 23 (IL23): 刘国生 (中科院上海有机所) Difunctionalization of Alkenes: New Concept and Strategy	江焕峰 (华南理工大学)
会场二: 蒙民伟楼		
08:00-08:40	邀请报告 24 (IL24): 肖文精 (华中师范大学) Visible-Light Photocatalysis in Heterocycle Synthesis and Functionalization	张玉红 (浙江大学)
08:40-09:05	口头报告 19 (OL19): 柳凌艳 (南开大学) Hydroamination Cyclization-Povarov Cascade Reactions of Homopropargylic Amine with Electron-Rich Olefins	
09:05-09:30	口头报告 20 (OL20): 钟羽武 (中科院化学研究所) Design of Redox-Responsive Organometallic Molecular Materials Based on Ru-C Bond	
09:30-09:55	口头报告 21 (OL21): 朱军 (厦门大学) Aromaticity in Organometallics: The Magic of Transition Metals	

09:55-10:10	茶 歇	
10:10-10:50	邀请报告 25 (IL25): 游劲松 (四川大学) Construction of Organic Optoelectronic Molecules Based on Highly Efficient and Selective C-H Bond Transformations	陈万芝 (浙江大学)
10:50-11:15	口头报告 22 (OL22): 谢湖均 (浙江工商大学) 钯催化有机反应机理的理论研究	
11:15-11:40	口头报告 23 (OL23): 刘心元 (南方科技大学) Dual-Catalytic Asymmetric Radical Functionalization of Alkenes	马成 (浙江大学)
11:40-12:05	口头报告 24 (OL24): 莫冬亮 (广西师范大学) Copper-Promoted Direct <i>N/O</i> -Alkenylation of N-O Bonds and Their Applications	
12:05-14:00	午 餐	
会场: 紫金港体育馆		
14:00-15:00	大会报告五 (PL5): 吴骊珠 (中科院理化技术研究所) Artificial Photosynthetic Systems for Chemical Transformation	唐 勇 (中科院上海 有机所)
15:00-15:20	茶 歇	
15:20-15:35	金属有机化学奖颁奖仪式 (颁奖嘉宾: 麻生明)	戴立信 (中科院上海 有机所)
15:35-16:15	获奖报告一 夏海平 (厦门大学)	麻生明 (中科院上海 有机所)
16:15-16:55	获奖报告二 Jin-Quan Yu (The Scripps Research Institute)	
16:55-17:40	获奖墙报颁奖仪式和闭幕式	王彦广 (浙江大学)
17:40-19:00	晚 餐	

大会报告

PL1

Two Stones for One Bird*

Shengming Ma (麻生明)

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, Shanghai 200032, P. R. China

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Different from alkenes and alkynes, allenes are a class of unique compounds with a synthetically attractive axial chirality. However, their chemistry had been largely underdeveloped due to the prediction of instability based on their structure for quite some time. However, nowadays allenes have been demonstrated as an important class of very useful starting materials with a very decent level of stability in organic chemistry. In this lecture, some efficient syntheses of 1,3-disubstituted allenes from two readily available chemicals, i.e., terminal alkynes and aldehydes have been developed. The aerobic oxidation of alcohols to aldehydes, ketones, and carboxylic acids has been developed for such a purpose. With these "two stones" in hand, the efficiency for allene synthesis has been greatly upgraded to an unprecedented level-the optically active naturally allenes may now be prepared very easily-in just a few easy steps.

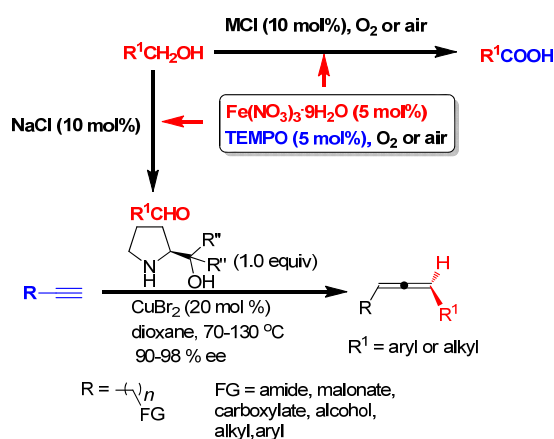


Figure 1.

References:

- [1] X. Huang, T. Cao, Y. Han, X. Jiang, W. Lin, J. Zhang and S. Ma* *Chem. Commun.*, **2015**, 51, 6956.
- [2] X. Tang, X. Huang, T. Cao, Y. Han, X. Jiang, W. Lin, Y. Tang, J. Zhang, Q. Yu, C. Fu and S. Ma* *Org. Chem. Front.*, **2015**, 2, 688.
- [3] X. Huang, C. Xue, C. Fu and S. Ma* *Org. Chem. Front.*, **2015**, 2, 1040.
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- [6] X. Jiang and S. Ma* *J. Am. Chem. Soc.* **2016**, 138, 8344.

*The NSFC (21232006) and National Basic Research Program (2015CB856600) for financial support.



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12. 1990-06. 1992: Research Associate, SIOC
06. 1992-09. 1992 Research Associate Professor of Chemistry, SIOC
09. 1992-09. 1993 Post-doctoral fellow, Laboratory of Inorganic Chemistry, ETH
(Supervisor: Prof. **Venanzi**)
10. 1993-03. 1997 Post-doctoral fellow, Department of Chemistry, Purdue University
(Supervisor: Prof. **Negishi**)
03. 1997-09. 1997 Research Associate Professor of Chemistry, SIOC
09. 1997-02. 2003 Research Professor of Chemistry at SIOC and Director of SKLOMC
02. 2003-09. 2007 Jointly appointed by SIOC and Zhejiang University:
Research Professor of Chemistry at SIOC,
Director of SKLOMC, and Cheung Kong
Scholars Program Professor at Zhejiang University
10. 2007-8.2014 Professor at SIOC, Chinese Academy of Sciences, Zhejiang University, and
East China Normal University
09.2014-present Professor at SIOC, Chinese Academy of Sciences, Zhejiang University, and
Fudan University

Research Interests

Methodologies, Target Synthesis

Awards

Mr. and Mrs. Sun Chan Memorial Award in Organic Chemistry (2004); First-Class Award for Progress in Science and Technology of Shanghai (2004); OMCOS 13 Award (2005); Second-Class National Natural Science Awards (2006); First-Class Natural Science Award of Shanghai (2010)

Representative Publications

1. S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701
2. S. Ma, *Acc. Chem. Res.* **2009**, *42*, 1679.
3. J. Ye, S. Ma, *Acc. Chem. Res.* **2014**, *47*, 989.
4. S. Wu, X. Huang, W. Wu, P. Li, C. Fu, S. Ma, *Nature Commun.* **2015**, *6*, 7946.
5. J. Dai, M. Wang, G. Chai, C. Fu, S. Ma, *J. Am. Chem. Soc.* , **2016**, *138*, 2532.
6. W. Yuan, L. Song, S. Ma, *Angew. Chem. Int. Ed.* **2016**, *55*, 3140.
7. X. Huang, S. Wu, W. Wu, P. Li, C. Fu, S. Ma, *Nature Commun.* **2016**, *in the press.*

Recent Progress in the Asymmetric Synthesis of Biologically Active Molecules Catalyzed by Chiral *N,N'*-Dioxide–Metal Complexes*

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The use of asymmetric catalysis is a powerful, economically feasible tool for the preparation of optically active organic compounds on both laboratory and industrial scales. In recent years, our group successfully created a kind of new chiral ligand, named *N,N'*-dioxide amides, and used them as privileged ligand-metal complexes in asymmetric reactions.¹ I will describe asymmetric synthesis of chiral compounds by chiral *N,N'*-dioxide–metal complexes. Representative examples are listed in the figure.

For examples, NITD609 which a potent novel antimalarial lead that it ideally meets the criterial of a new antimalarial drug, was synthesized through asymmetric aza-Diels–Alder reaction.^{2a} Paroxetine as one of the antidepressant drugs was realized through a catalytic asymmetric Michael reaction.^{2b} An enantioselective sulfa-Michael-cyclization reaction provide a facile approach to antidepressant drug *R*-(-)-thiazesim. The arylation process of oxindoles was conducted to get oxindole derivative which is used as an antiproliferative agent for the treatment of cancer.^{2c} In addition, asymmetric vinylogous Mukaiyama aldol reaction gave enantiomerically enriched 5-hydroxydec-2-enoate, which can be easily converted into (*R*)- δ -decalactone, and (*4R, 6R, 10R, 12R*)-verbalactone.^{2d}

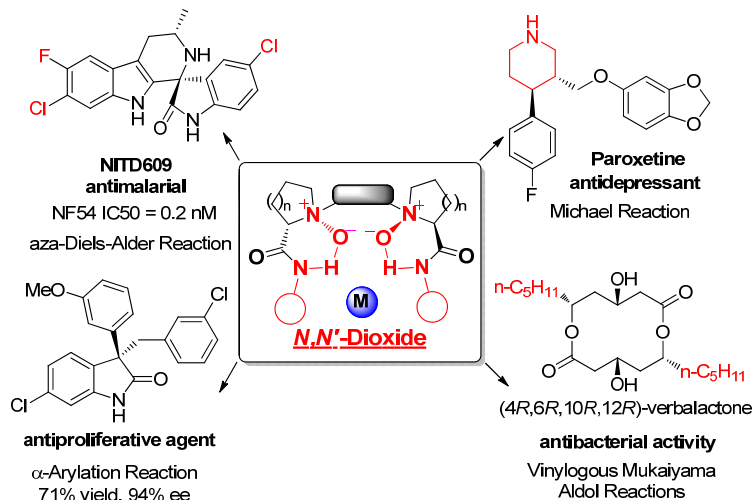


Figure 1. Asymmetric Synthesis of biologically active compounds

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- [1] X. H. Liu, L. L. Lin, X. M. Feng, *Org. Chem. Front.*, **2014**, *1*, 298.
 [2] (a) H. F. Zheng, X. H. Liu, C. R. Xu, Y. Xia, L. L. Lin, X. M. Feng, *Angew. Chem. Int. Ed.* **2015**, *54*, 10958. (b) Y. Zhang, Y. T. Liao, X. H. Liu, Q. Yao, Y. H. Zhou, L. L. Lin, X. M. Feng, *Chem. Eur. J.* **2016**, DOI: 10.1002/chem.201603056. (c) J. Guo, S. X. Dong, Y. L. Zhang, Y. L. Kuang, X. H. Liu, L. L. Lin, X. M. Feng, *Angew. Chem. Int. Ed.* **2013**, *52*, 10245. (d) K. Fu, J. F. Zheng, L. L. Lin, X. M. Feng, *Chem. Commun.* **2015**, *51*, 3106.

* The National Natural Science Foundation of China (Nos. 21432006, 21290182, and 21321061) for financial support.



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- 2000- Professor, Sichuan University
- 1998-1999 Postdoctoral Fellow, Colorado State University, US (with Prof. Yian Shi)
- 1997-2000 Professor, Chengdu Institute of Organic Chemistry, CAS
- 1996 Ph.D., Institute of Chemistry, CAS (supervisor: Prof. Zhitang Huang & Yao-Zhong Jiang)
- 1991-1993 Assistant to Associate Professor, Southwest Normal University
- 1988 M.Sc., Dept. of Chemistry, Lanzhou University (supervisor: Prof. Ziyi Zhang)
- 1985 B.Sc., Dept. of Chemistry, Lanzhou University

Research Interests

Design and synthesis of chiral organocatalysts and ligand-metal complex catalysts, asymmetric catalytic reaction, the synthesis of bioactive compounds

Awards

- 2002, the National Science Fund for Distinguished Young Scholars (China)
- 2005, the Special Professor of the Chang Jiang Scholars by the Ministry of Education of China
- 2011, SciFinder Award for Creative Work in Synthetic Organic Chemistry, CCS
- 2012, the State Natural Science Award, P.R. China (Second class, China)
- 2013, a Chinese Academy of Sciences Academician

Representative Publications

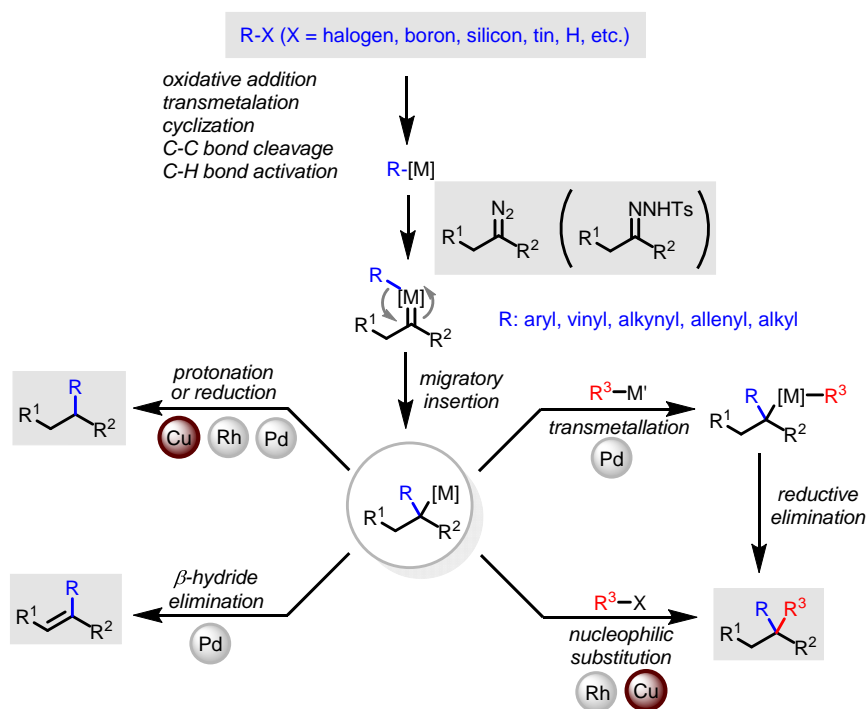
- [1] Xia, Y.; Lin, L. L.; Chang, F. Z.; Liao, Y. T.; Liu, X. H.; Feng, X. M. Asymmetric Ring Opening/Cyclization/Retro-Mannich Reaction of Cyclopropyl Ketones with Aryl 1,2-Diamines for the Synthesis of Benzimidazole Derivatives, *Angew. Chem. Int. Ed.* **2016**, *55*, 12544.
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- [3] Li, J.; Lin, L. L.; Hu, W. B.; Lian, X. J.; Wang, G.; Liu, X. H.; Feng, X. M. Bimetallic Gold(I)/Chiral *N,N'*-Dioxide Nickel(II) Asymmetric Relay Catalysis: Chemo- and Enantioselective Synthesis of Spiroketal and Spiroaminals, *Angew. Chem. Int. Ed.* **2016**, *55*, 6075.
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- [5] Li, W.; Tan, F.; Wang, G.; Tang, Y.; Liu, X. H.; Lin, L. L.; Feng, X. M. Catalytic Asymmetric Intramolecular Homologation of Ketones with α -Diazoesters: Synthesis of Cyclic α -Aryl/Alkyl β -Ketoesters, *Angew. Chem. Int. Ed.* **2015**, *54*, 1608.
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卡宾偶联反应研究的新进展*

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在过去的十多年里, 重氮化合物 (或者其前体 *N*-对甲苯磺酰脲) 逐渐成为过渡金属催化交叉偶联反应中的一类亲核性偶联组分。和经典的金属催化的卡宾反应相比, 这些反应代表了卡宾反应的一种新的类型; 而其作为一种新型的偶联反应也逐渐成为构建 C-C 单键和 C=C 双键的独特手段。这类反应的过程可以用以下的图式简单概括。首先, 可以通过各种过渡金属催化的经典过程 (例如, 氧化加成、转金属、环金属化、C-C 键断裂, C-H 键活化等) 来产生有机金属物种 R-[M], 然后其与体系中的重氮化合物作用生成金属卡宾中间体, 接着发生快速的迁移插入反应生成新的有机金属物种。这个新的金属有机物种可以进一步发生一系列后续转化 (包括 β -氢消除、转金属 / 还原消除、质子化等) 生成最终的产物, 并再生催化物种。这类反应被证明具有普遍性: 各种过渡金属, 包括 Pd、Cu、Rh、Ni、Co 和 Ir 均可以催化相似 / 相关的过程; 这类偶联反应的卡宾前体也被拓展到非重氮化合物; 基于卡宾迁移插入的各种类型串联反应也得到实现等。本次报告将阐述基本原理以及该领域研究的最新进展。



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* 国家自然科学基金委基金 (No. 21332002) 资助项目

** 通讯联系人: E-mail: wangjb@pku.edu.cn; <http://www.chem.pku.edu.cn/physicalorganic/home.htm>



王剑波

北京大学化学与分子工程学院教授，现任生物有机与分子工程教育部重点实验室主任。1983 年南京理工大学本科毕业，1984 年国家教委公派留日学习，1990 年于北海道大学获工学博士学位。1990-1995 年分别在瑞士日内瓦大学和美国威斯康星大学(麦迪逊)做博士后。1995 年底回国到北京大学化学与分子工程学院任教。1997 年获教育部优秀青年教师基金，2000 年获教育部跨世纪人才基金，2002 年获国家杰出青年基金，2005 年被聘为教育部长江特聘教授，2006 年获得“中国礼来科学贡献奖”，2007 年获宝钢优秀教师奖，2008 年获得“中国化学会-巴斯夫青年知识创新奖”，2013 年获国务院特殊津贴，2015 年获高等学校科学研究优秀成果一等奖。主要研究方向为金属卡宾经由的催化反应，独立工作以后在国内外主要学术刊物发表论文 240 余篇。

研究方向

1. 过渡金属催化的卡宾转移反应、卡宾偶联反应等；
2. 重氮化合物以及重氮盐类化合物的反应、含硼有机化合物的合成及反应等；
3. 有机化学中的基本官能团转化反应、自由基反应等。

代表性论文

- [1] Zhikun Zhang, Weizhi Yu, Chenggui Wu, Chengpeng Wang, Yan Zhang, Jianbo Wang, Reaction of Diazo Compounds with Difluorocarbene: An Efficient Approach toward 1,1-Difluoroolefins, *Angew. Chem. Int. Ed.* 2016, 55, 273-277.
- [2] Fei Ye, Shuanglin Qu, Lei Zhou, Cheng Peng, Chengpeng Wang, Jiajia Cheng, Mohammad Lokman Hossain, Yizhou Liu, Yan Zhang, Zhi-Xiang Wang, and Jianbo Wang, Pd-Catalyzed C-H Functionalization of Acyldiazomethane and Tandem Cross-Coupling Reactions, *J. Am. Chem. Soc.* 2015, 137, 4435-4444.
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- [6] Qing Xiao, Yan Zhang, Jianbo Wang, Diazo Compounds and *N*-Tosylhydrazones: Novel Cross-Coupling Partners in Transition-Metal-Catalyzed Reactions, *Acc. Chem. Res.* 2013, 46, 236-247.

PL4

Privileged Chiral Spiro Catalysts

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Chiral catalysts play a crucial role in the catalytic asymmetric synthesis. In last few decades many chiral catalysts have been developed. However, most of the reported chiral catalysts showed high activity and enantioselectivity for only limited reactions, sometime for only limited substrates. Very few chiral catalysts provided satisfied activity and enantioselectivity for a wide range of asymmetric reactions. Recently, we developed a type of chiral catalysts containing chiral spirobiindane ligands. The chiral spiro catalysts exhibited excellent activity and enantioselectivity for wide range of reactions such as asymmetric hydrogenation, carbon-carbon bond and carbon-heteroatom bond-forming reactions. This lecture will present the syntheses of chiral spiro ligands and catalysts, and their applications in asymmetric hydrogenations of olefins, ketones, and unsaturated acids, and asymmetric heteroatom-hydrogen bond insertion reactions.

References

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- [3] X.-H. Yang, J.-H. Xie, W.-P. Liu, Q.-L. Zhou, *Angew. Chem. Int. Ed.* **2013**, 52, 7833-7836.
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- [5] J.-H. Xie, X.-Y. Liu, J.-B. Xie, L.-X. Wang, Q.-L. Zhou, *Angew. Chem. Int. Ed.* **2011**, 50, 7329-7332.
- [6] S.-F. Zhu, Y. Cai, H.-X. Mao, J.-H. Xie, Q.-L. Zhou, *Nature Chemistry* **2010**, 2, 546-551.



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Professor

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Career

1999-present	Professor, Nankai University
1996-1999	Associate professor, East China University of Science and Technology
1988-1996	Postdoc, ECUST, MPI-Polymer, Basel University, Trinity University
1982-1987	PhD, Shanghai Institute of Organic Chemistry, CAS
1978-1982	BS, Lanzhou University

Research Interests

Organic chemistry, Organometallics, Asymmetric catalysis

Awards

1997	Award for Outstanding Young Scientists (National Natural Science Foundation of China)
1999	Cheung Kong Scholar (Ministry of Education of China)
2006	Yao-Zeng Huang Prize of Organometallics (Chinese Chemical Society)
2007	JSPS Fellowship Award (Japan Society for the Promotion of Science)
2008	PKU-Lilly Lectureship (Beijing University and Eli Lilly Co.)
2009	Academician of Chinese Academy of Sciences
2012	Prize of Chiral Chemistry (Chinese Chemical Society)
2013	Fellow of Royal Society of Chemistry
2014	Novartis Lecturer (the Scripps Research Institute)

Artificial Photosynthetic Systems for Chemical Transformation*

Li-Zhu Wu (吴骊珠)**

Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry & University of Chinese Academy of Sciences, Chinese Academy of Sciences Beijing 100190, P. R. China

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Fascinated by the ability of natural photosynthetic systems to convert solar energy into chemical energy, the scientific community long ago recognized the potential of light-driven reactions (photochemistry) as a powerful approach to chemical synthesis. From the high energy intermediate generated by photoinduced excitation of organic molecules, unique reaction manifolds can be accessed that are generally unavailable to conventional thermal pathways. Thus photochemical reactions considerably enrich the synthetic repertoire of modern organic chemists. Our group has long engaged in the photochemistry research related to the photoinduced energy transfer, electron transfer and chemical transformation (Figure 1). In this presentation, we will compile the following four stories to illustrate a few approaches that may be useful in the design of artificial photosynthetic systems for chemical transformation.

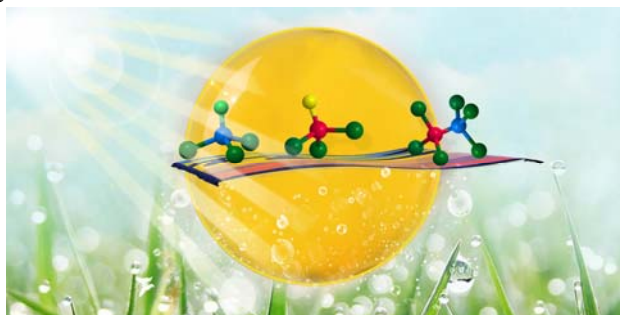


Figure 1. Artificial photosynthetic systems for chemical transformation

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1999.8-present	Professor, Technical Institute of Physics and Chemistry, CAS
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Research Interests

Our primary interests focus on photochemical conversion, including artificial photosynthesis, visible light-catalysis for efficient and large-scale organic synthesis, photo-induced electron transfer, energy transfer and chemical reaction in supramolecular systems.

Awards

National Nature Science Fund for Distinguished Young Scholar (2001); National candidates for the "New Century Talents Project" (2004); A 2nd prize of National Natural Science Award as second principal investigator (2005); "Hundred Talents Program" of the Chinese Academy of Sciences (2006); The 10th China Youth Science and Technology Award (2007); The 3th Ten Outstanding Women, CAS (2009); The 7th China Young Women Scientists (2010); Zhu Li Yuehua Prize of Excellent Teachers, CAS (2011); The Prize of 10th Physical Organic Chemistry (2013); the Chinese Chemical Society-Evonik Chemical Innovation Award (2016).

Representative Publications

- [1] Z.-J. Li, X.-B. Fan, X.-B. Li, J.-X. Li, C. Ye, J.-J. Wang, S. Yu, C.-Bo Li, Y.-J. Gao, Q.-Y. Meng, C.-H. Tung, L.-Z. Wu *J. Am. Chem. Soc.* **2014**, *136* (23), 8261.
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邀请报告

IL1

From Simple Hydrocarbons to N-containing Compounds through Nitrogenation Strategy

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Oxygen- or nitrogen-containing compounds are widely present in both natural products and synthetic compounds, for example, they show up within functional materials, top-selling drugs, as well as bioactive molecules. Thus, organic chemists have paid considerable attention in developing novel methodologies for their preparation. To synthesize these compounds in a green and sustainable way, researchers have focused on the direct functionalization of hydrocarbons via C–H and/or C–C bond cleavage. Although significant progress have made in the direct functionalization of simple hydrocarbons, direct incorporation of O- or N-atoms into the simple substrates via C–H and/or C–C bond cleavage remains challenging due to the inert chemical bonds and the unstable character of some N-sources under oxidative conditions. By using molecular oxygen¹ as oxygen source as well as azides as nitrogen source, we recently developed some C-H/C-C bond oxygenation and nitrogenation reactions for the synthesis O- and/or N-containing compounds.² In this presentation, our recent progress on the direct nitrogenation of simple hydrocarbons will be introduced.

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1999.9-2004.7	PhD Chemistry, Shanghai Institute of Organic Chemistry, CAS
1995.9-1999.7	BS Chemistry, Shandong University

Research Interests

Jiao's research interests are focused on: 1) To develop green and efficient synthetic methodologies through Single Electron Transfer (SET) process; 2) Aerobic oxidation, Oxygenation, Nitrogenation, Halogenation reactions; 3) The activation of inert chemical bonds and small molecules.

Awards

The National Science Fund for Distinguished Young Scholars (2013); Yangtze river scholars Distinguished Professor (2015); The Chinese Homogenous Catalysis Young Chemist Award (2013)

Representative Publications

1. Teng Wang, and **Ning Jiao***, Direct Approaches to Nitriles via Highly Efficient Nitrogenation Strategy through C–H or C–C Bond Cleavage, *Acc. Chem. Res.* **2014**, *47*, 1137-1145.
2. Yu-Feng Liang and **Ning Jiao***, Transition-Metal Free Highly Efficient C-H Hydroxylation of Carbonyls with Molecular Oxygen Under Mild Conditions, *Angew. Chem. Int. Ed.* **2014**, *53*, 548-552.
3. Teng Wang and **Ning Jiao***, TEMPO-catalyzed Aerobic Oxygenation and Nitrogenation of Olefins via C=C Double Bond Cleavage, *J. Am. Chem. Soc.* **2013**, *135*, 11692-11695.
4. Conghui Tang and **Ning Jiao***, Copper-catalyzed C-H Azidation of Anilines under Mild Conditions, *J. Am. Chem. Soc.* **2012**, *134*, 18924-18927.
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6. Wang Zhou, Liangren Zhang, and **Ning Jiao***, Direct Transformation of Methyl Aromatics to Aryl Nitriles at Room Temperature. *Angew. Chem. Int. Ed.* **2009**, *48*, 7094-7097.
7. Yu-Feng Liang, † Xinyao Li, † (†These two authors contributed equally to this work), Xiaoyang Wang, Miancheng Zou, Conghui Tang, Yujie Liang, Song Song, **Ning Jiao***, Conversion of Simple Cyclohexanones into Catechols, *J. Am. Chem. Soc.* **2016**, *138(37)*, 12271-12277.
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II.2

天然产物全合成导向的惰性 sp^3 碳氢键活化: 新试剂、新反应及机理研究*

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近年来, 过渡金属催化的惰性碳氢键活化备受关注, 由于直接以碳氢键为合成子, 无需进行预官能团化, 因此, 相对于传统合成方法, 将有望减少合成步骤, 提升合成效率, 从而能够实现天然产物的“理想合成”。¹ 另外, 发展温和条件下, 官能团容忍性高的碳氢键活化方法, 也能够为复杂天然产物及药物分子的后期衍生化提供新的思路与途径。近年来, 我们课题组致力于采用双齿导向策略, 实现惰性 sp^3 碳氢键的高效、选择性官能团化。² 在此基础上, 我们利用多重调控性的导向基策略, 发展了一类具有偕二甲基效应的 PIP-NH₂ 导向基试剂, 从简单原料出发, 高效构建了在天然产物和药物分子中广泛存在的骨架, 并应用于天然产物和药物分子的全合成及后期衍生化。³ 我们课题组也成功实现了 PIP-NH₂ 试剂在廉价金属 (如铜、钴、镍等) 催化的惰性碳氢键活化的应用, 构建碳碳键和碳杂原子键 (Figure 1)。⁴

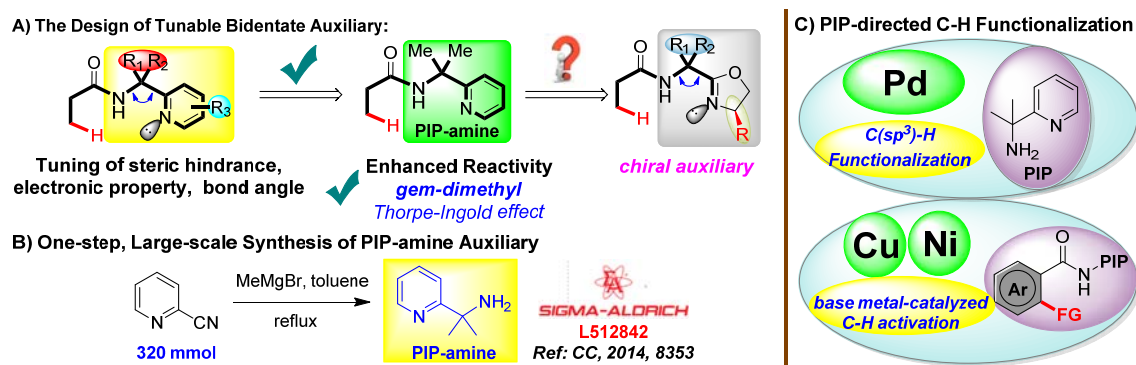


Figure 1. PIP 导向基试剂的设计、合成及应用

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* 国家自然科学基金 (21572201, 21422206, 21272206, 21002087) ; 浙江大学和科技部 973 项目 (2015CB856600) 资助项目.

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浙江大学化学系教授，博士生导师，独立课题组组长，有机与药物化学研究所所长。2001年本科毕业于南开大学化学系；2006年毕业于中科院上海有机所，获理学博士学位；2006-2007年在美国加州大学圣迭戈分校进行博士后研究；2007-2010年在美国 The Scripps Research Institute 作博士后研究。2010年5月加入浙江大学化学系。曾获国家自然科学基金优秀青年项目资助（2014），Thieme Chemistry Journal Award（2015），Distinguished Lectureship Award from Chemical Society of Japan（2015），钱江人才（2013），Gordon Research Conference 主席奖（2008），明治乳业生命科学奖（2006），罗氏创新化学奖（2006）等奖励。以独立通讯作者在 *Angew. Chem. Int. Ed.*, *J. Am. Chem. Soc.*, *Chem. Sci.* 等发表科研论文五十余篇。目前主要研究领域为过渡金属催化的合成方法及其在天然产物全合成中的应用研究。

研究方向

1. 过渡金属催化的惰性 sp^3 碳氢键选择性官能团化及其在天然产物全合成及复杂分子后期衍生化的合成应用
2. 原子经济性合成方法及其在天然产物全合成及复杂分子后期衍生化的应用；
3. 寡糖合成方法学及其在具有重要生物活性的糖化合物合成中的应用

代表性论文

- [1] Zhang, Q.; Chen, K.; Rao, W.; Zhang, Y.; Chen, F.-J.; Shi, B.-F. Stereoselective Synthesis of Chiral α -Amino- β -Lactams via Pd(II)-Catalyzed Sequential Monoarylation/Amidation of $C(sp^3)$ -H Bonds, *Angew. Chem. Int. Ed.* **2013**, *52*, 13588.
- [2] Zhang, Q.; Yin, X.-S.; Chen, K.; Zhang, S.-Q.; Shi, B.-F. Stereoselective Synthesis of Chiral β -Fluoro α -Amino Acids via Pd(II)-Catalyzed Fluorination of Unactivated Methylene $C(sp^3)$ -H Bonds: Scope and Mechanistic Studies, *J. Am. Chem. Soc.* **2015**, *137*, 8219.
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IL3

Substrate Activation Strategies in High-Valent Metal-Catalyzed C-H Functionalization of Arenes*

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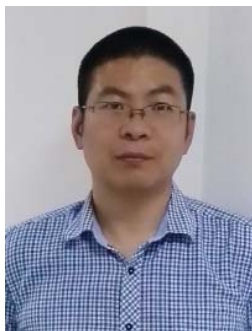
C-H bond activation has been established as an increasingly important strategy in the synthesis of complex structures owing to high step-economy and high efficiency. In recent years, high-valent transition metal catalysts such as Rh(III), Ir(III), Co(III) and Ru(II) have been extensively employed in functionalization of a diverse array of sp^2 and sp^3 C-H bonds. Such rich chemistry is ascribable to the high polarity/reactivity and unique properties of the corresponding M(II/III)-C bonds that can effectively interact with both polar and non-polar coupling partners under oxidative or redox-neutral conditions.¹ The efficient cooperation between the metal catalyst, the directing group, and the coupling partner will be discussed in the context of substrate activation. In particular, activation of the arene substrate allows weakly electrophilic² directing groups or oxidizing groups to function beyond their simple role of chelation assistance (directing effect). On the other hand, activation of the coupling partner has been realized using umpolung,³ strained rings/reactive rings,^{4,5} and rearomatization, which allowed diversified C-C, C-N, and C-S functionalization, especially under rather mild conditions.

Keywords: C-H activation, rhodium, umpolung, heterofunctionalization

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Research Interests

Metal-catalyzed activation of inert bonds, synthetic organometallic chemistry, mechanistic organometallic chemistry, homogeneous catalysis

Awards

National Science Fund for Distinguished Young Scholars (2015)

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Representative Publications

1. "Rh(III)-Catalyzed C-C and C-O Coupling of Quinoline *N*-Oxides with Alkynes: Combination of C-H Activation with O-Atom Transfer" Xueyun Zhang, Zisong Qi, Xingwei Li*, *Angew. Chem. Int. Ed.* **2014**, *53*, 10794-10798.
2. "Substrate Activation Strategies in Rhodium-Catalyzed Selective Functionalization of Arenes" Guoyong Song and Xingwei Li* *Acc. Chem. Res.* **2015**, *48*, 1007-1020.
3. "Anthranil: an Aminating Reagent for Both *sp*³ and *sp*² C-H Bonds Leading to Bifunctionality under Rhodium(III) Catalysis" Songjie Yu, Guodong Tang, Yingzi Li, Xukai Zhou, Yu Lan*, Xingwei Li*, *Angew. Chem. Int. Ed.* **2016**, *55*, 8696-8700.
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5. "Ru(II)-Catalyzed C-H Activation of Imidamides and Divergent Couplings with Diazo Compounds: Substrate-Controlled Synthesis of Indoles and 3*H*-Indoles" Yunyun Li, Zisong Qi, He Wang, Xifa Yang, Xingwei Li*, *Angew. Chem. Int. Ed.* **2016**, *55*, 11877-11881.
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8. "Mild Acylation of both C(*sp*³)-H and C(*sp*²)-H Bonds under Redox-Neutral Rh(III) Catalysis" Songjie Yu, Yingzi Li, Lingheng Kong, Xukai Zhou, Guodong Tang, Yu Lan*, Xingwei Li*, accepted by *ACS Catal.*

基于二氧化硫插入的若干转化*

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二氧化硫是大气主要的污染物之一, 其危害主要是通过酸雨的形式对自然界进行破坏。同时考虑到含有磺酰片段的化合物在医药以及化工生产中都有广泛的应用,¹将二氧化硫应用到有机合成中构建含磺酰片段的化合物符合现代化学高效、绿色、可持续发展的重要发展趋势。在工业生产中, 二氧化硫的廉价副产品--亚硫酸盐主要应用在工业漂白以及食品加工中, 这类化合物和有机碱的二氧化硫络合物一样在受热或者酸性条件下很容易释放出二氧化硫, 因此这类便宜易得、容易操作、简单稳定的化合物是很方便的二氧化硫替代品。

我们小组利用工业上便宜易得、简单稳定、操作方便的亚硫酸盐及有机碱的二氧化硫络合物作为二氧化硫来源, 实现了几类过渡金属催化及无催化条件下的二氧化硫插入反应, 发展了构建磺酰类化合物的新途径 (图 1)。²

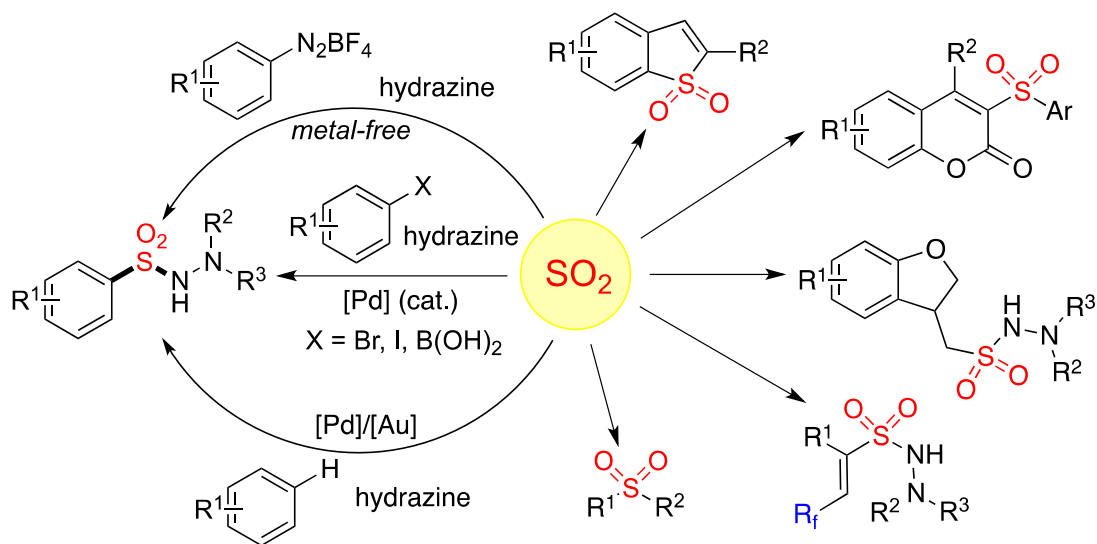


图 1. 基于二氧化硫插入的若干转化

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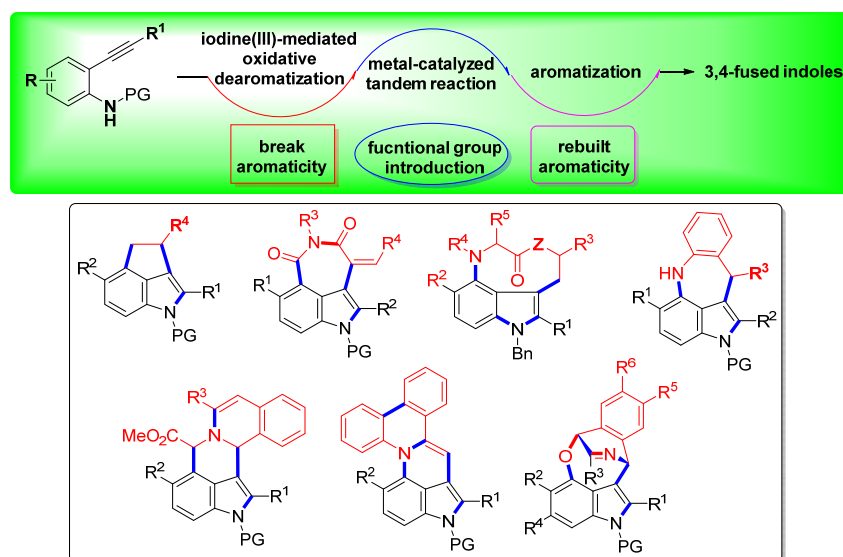
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利用“去芳构化”策略和过渡金属催化的串联反应合成[cd]-并环吡啶*

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芳香化合物的“去芳构化”(dearomatization)是指在一定条件下,通过对芳环的 π 电子共轭体系进行破坏,进而对其进行衍生化的过程。随着有机合成化学的发展,近年来“去芳构化”反应吸引了越来越多有机化学家的关注。通过“去芳构化”反应,芳香化合物可以作为有效的“合成子”用于有机合成中。将“去芳构化”反应串联反应巧妙结合,可以从简单的芳香化合物出发高效高选择性地合成一些复杂甚至具有多维结构的分子。另一方面,在吡啶家族中,[cd]-并环吡啶占有重要的位置,在Beilstein/Crossfire检索中有超过百种天然产物含有[cd]-并环吡啶结构单元,而这些化合物都表现出很好的生物活性。因此[cd]-并环吡啶类化合物的高效高选择性合成对相关新药的研发和已有药物合成工艺的改进具有重要意义。在我们的工作中,设计将邻-炔基苯胺的“去芳构化”和过渡金属催化的串联反应相结合,发展了一些高效构建[cd]-并环吡啶的新方法。



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研究方向

芳香化合物的去芳构化策略在复杂芳香化合物合成中的运用；
有机高碘化合物的新反应及其在合成中的应用

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炔烃转化的区域选择性控制与杂环结构多样性合成*

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过渡金属催化的选择性调控一直以来是有机合成的一大研究热点。通过简单的选择性调控, 不仅可以发现新的化学和过程, 而且可实现结构多样性合成, 从而为一些重要的功能分子如药物分子、有机材料等的合成提供简洁和高效的方法。近年来, 我们课题组致力于采用环张力策略和电性导向基策略, 实现了系列基于炔烃转化的区域选择性控制, 从而为一些重要杂环骨架的结构多样性合成提供了新的思路与途径。利用环张力策略, 发展了一系列金催化的基于手性高炔丙胺环异构化引发的新型串联反应, 实现了一系列具有光学活性的五员含氮杂环的多样性合成。¹ 在此基础上, 利用电性导向基策略, 发展了系列过渡金属催化的基于炔酰胺氧化、胺化、环异构化等反应引发的新型串联反应, 为系列有用杂环骨架的多样性合成提供了全新的方法 (Figure 1)。²

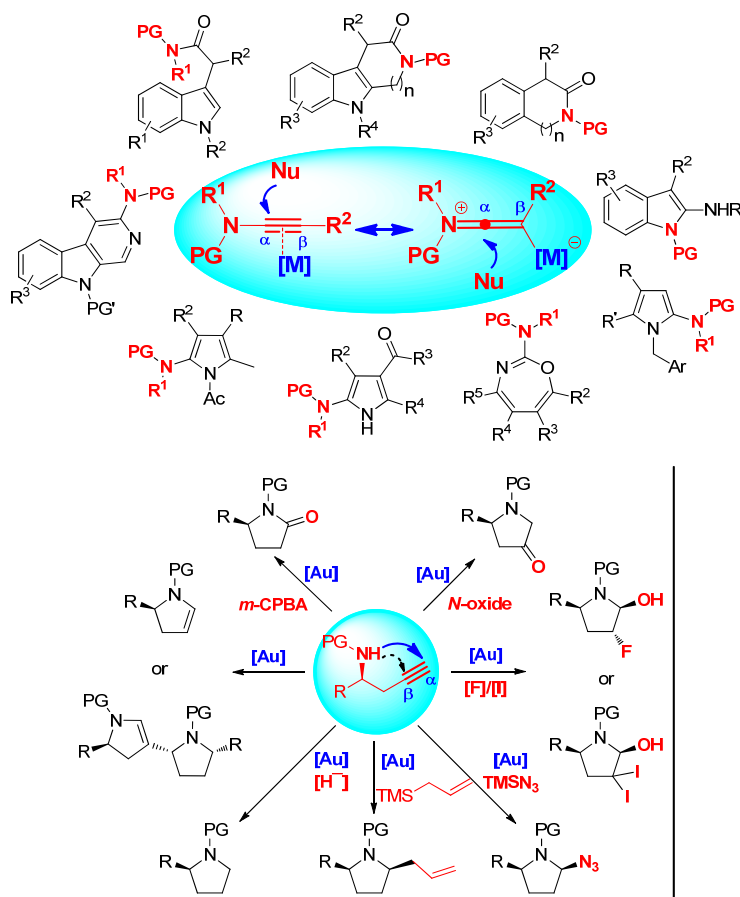


Figure 1. 过渡金属催化的基于高炔丙胺和炔酰胺的杂环结构多样性合成

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研究方向

1. 有机合成方法学：过渡金属催化的选择性控制
2. 有机合成方法学：过渡金属催化的多样性合成
3. 功能分子全合成：天然产物、生物活性分子及药物分子的合成

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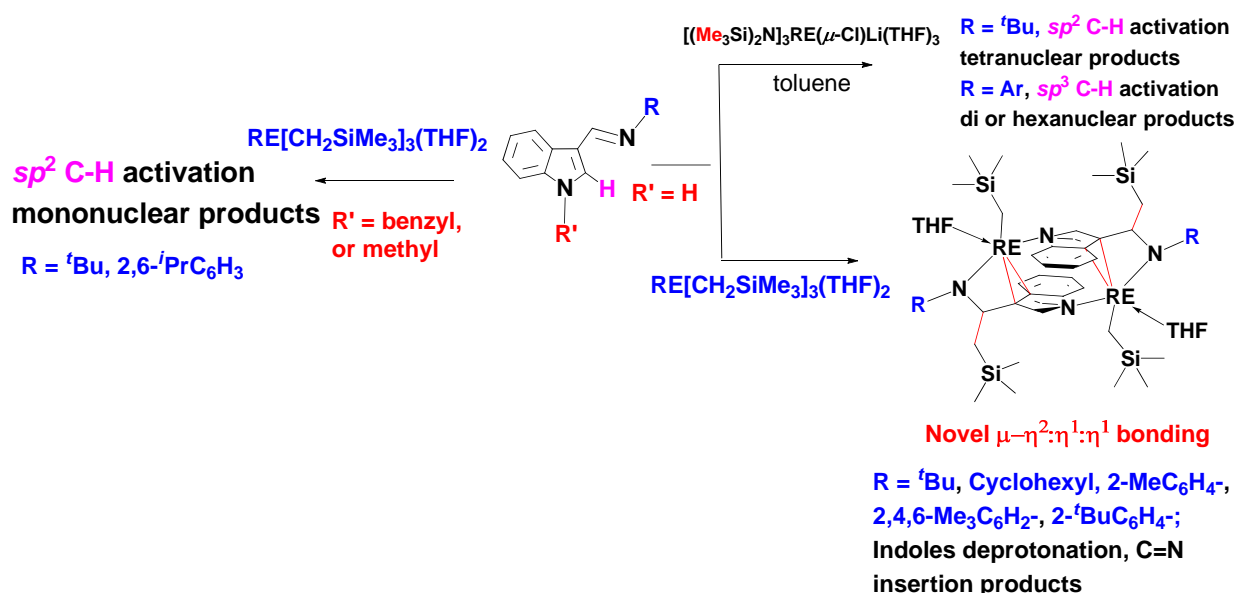
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稀土金属胺基化物及烃基化物与亚胺官能化吲哚的反应性研究*

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吲哚是一类重要的富电子杂环化合物, 官能化吲哚作为配体在后过渡金属中得到很好的研究, 并发现了一些新颖的吲哚与金属中心成键形式。最近我们系统地研究了稀土金属胺基化物 $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ 及稀土金属烃基化物 $\text{RE}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ 与不同亚胺官能化吲哚的反应 (Scheme-1), 发现取代基效应对反应形式、吲哚与金属中心的成键有重要影响, 同时发展了几类高活性的异戊二烯 1,4-顺式聚合催化剂¹⁻⁵。本次会议我们将报告这些结果。



Scheme-1

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* 国家自然科学基金基金 (Nos. 21432001, 21372010), 国家重点基础研究发展计划 (2012CB821600) 资助项目

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研究兴趣

- 新颖稀土金属有机配合物合成、成键与性能
- 非贵金属配合物及催化反应

近期主要论文

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有机金属簇的可控合成与反应研究*

赵亮**

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近些年来, 以两个或多个金属离子团聚为特征的金屬簇化合物被广泛应用于有机反应催化中, 表现出极高的催化效率和基于簇结构调控的良好反应选择性[1]。为了深入认识和理解金属簇催化有机反应的机理, 人们迫切需要厘清含有碳-金属键的有机金属簇的结构与反应性质。然而, 由于碳自身杂化形式以及与金属作用的多样性、碳-金属键的高反应活性, 使得合成获得稳定且具有明确结构的有机金属簇成为一项极具挑战性的课题。自 2010 年起, 我们开始尝试利用大环分子作为模板进行有机金属簇的可控合成。氮杂杯吡啶大环分子不仅可以通过其大环尺寸有效控制金属簇的核数, 也可以保持簇结构的高度稳定、实现有机金属簇的高效合成[2]。研究表明, 多齿柔性大环分子与金属离子结合过程中存在配位协同效应, 该效应促进了大环-金属簇化合物的最终形成[3]。我们进一步利用有机多负离子作为内模板, 实现了有机金属簇的构型控制, 获得了一系列手性金属簇[4]。以稳定的金属簇化合物为基础, 我们通过有机反应转化, 利用金属簇对于有机活性中间体的稳定作用获得了一系列具有结构多样性的新型有机金属簇化合物[5]。本研究为有机金属簇的理性设计合成提供了新的方法, 同时也为理解金属簇催化有机反应的过程和机理提供了基础。

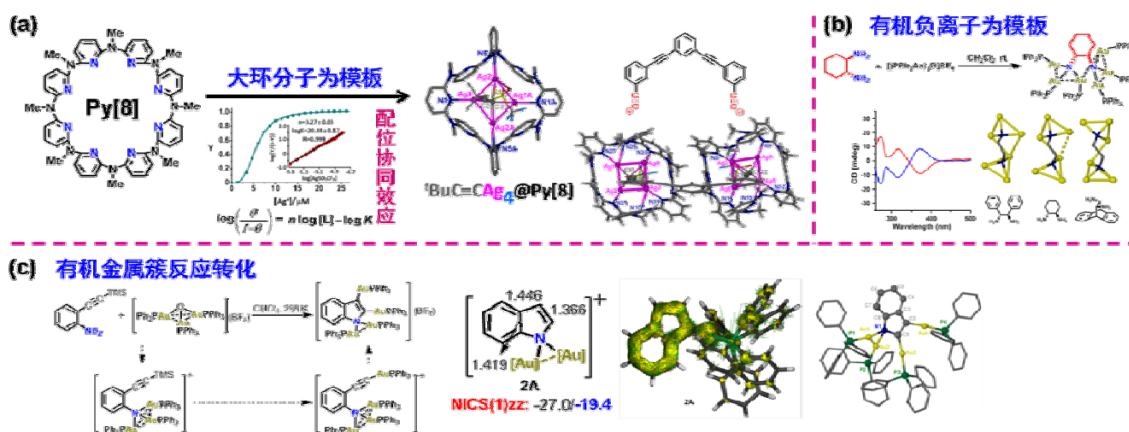


Figure 1. 模板法可控合成有机金属簇及金属簇的反应转化

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清华大学化学系副教授，博士生导师。2002年本科毕业于北京大学化学与分子工程学院。2002-2003年于北京大学分子动态与稳态国家重点实验室担任助研。2003年8月起于香港中文大学化学系麦松威院士指导下攻读博士学位，2007年8月毕业。2007年9月至2009年9月在美国犹他大学化学系 Peter J. Stang 教授课题组开展博士后研究工作。2009年11月加入清华大学化学系，任副教授，博士生导师；2016年7月起任特别研究员。曾获中国化学会青年化学奖（2013年），入选教育部“新世纪优秀人才支持计划”（2012年）、北京市“青年英才计划”（2013年）以及清华大学“基础研究青年人才支持计划”（2013年）。2015年获国家自然科学基金委“优秀青年基金”资助。目前科研工作主要将超分子化学与金属有机化学研究方法相结合，开展有机金属簇合物的可控合成与反应研究。

研究方向

- [1] 多齿大环分子的设计合成以及大环分子为模板的有机金属簇可控合成与反应研究；
- [2] 手性金属簇的设计合成以及手性金属簇催化剂的催化化学研究；
- [3] 大环-金属簇化合物的超分子自组装。

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- [1] J. Yuan, T. Sun, X. He, K. An, J. Zhu*, **L. Zhao***, “Synthesis of Tetra- and Octa-aurated Heteroaryl Complexes Toward Probing the Most Aromatic Indolium”, *Nat. Commun.* **2016**, *7*, 11489, DOI: 10.1038/ncomms11489.
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基于氧鎓历程的过渡金属催化体系*

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针对非质子型氧鎓离子产生困难, 反应类型单一, 应用较局限等缺点, 我们课题组近年围绕过渡金属催化基于氧鎓历程的串联反应开展了较系统的工作, 以反应过程中产生的各种活性中间体的高效选择性捕捉为切入点, 在环加成反应、卡宾转移反应等方面进行了较深入的研究。^[1]

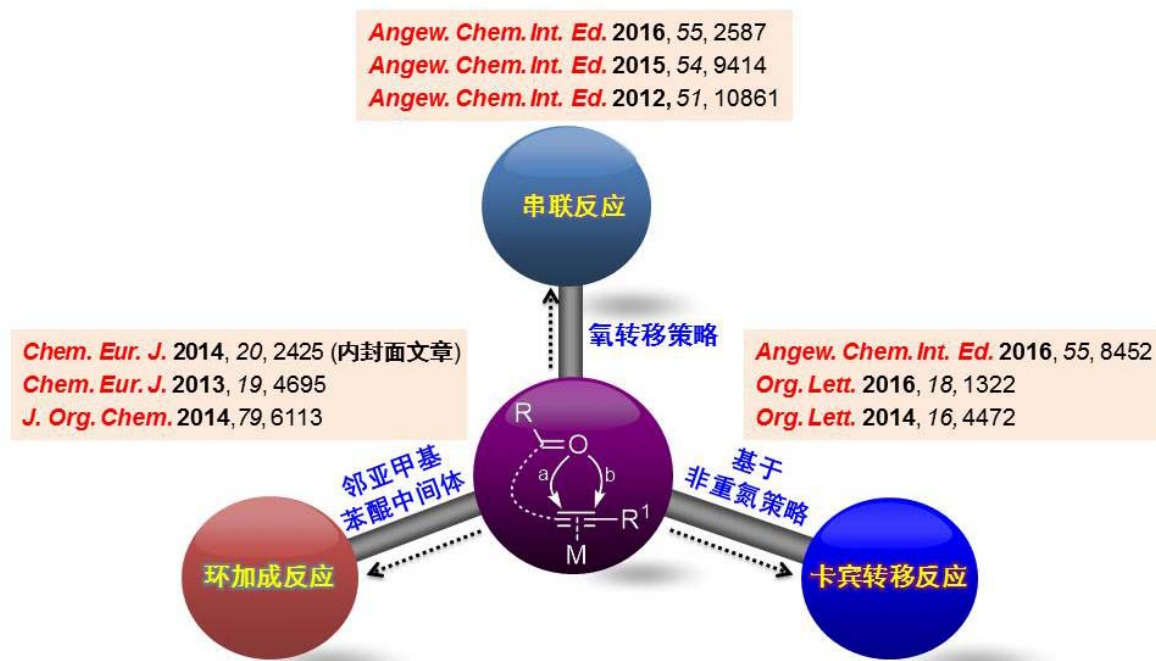


Figure 1. 基于氧鎓历程的过渡金属催化体系

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研究方向

- [1] 基于鎓化学的过渡金属催化体系；
- [2] 基于非重氮策略的卡宾化学；
- [3] 高活性反应中间体的产生及捕捉；

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IL10

C–H Bond Activation *via* Manganese Catalysis*

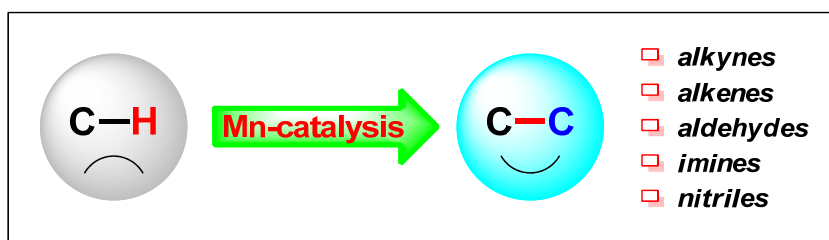
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The noble transition-metal (i.e., Pd, Ru, Rh, and Ir) catalysts play a dominant role in the stage of inert C–H bond functionalization. Given the rarity of these transition metals, the development of novel, efficient, and more economic catalysts is highly desirable. In this context, manganese might be a promising candidate for new catalyst hunting. Manganese is the twelfth most abundant element in the earth's crust, the richness of which ranks the third after iron and titanium among all transition metals. Our efforts are mainly dedicated to the development of catalytic transformations of C–H bonds promoted by manganese.¹

Despite that stoichiometric cyclometalation reactions of $\text{MnR}(\text{CO})_5$ ($\text{R} = \text{CH}_3, \text{Bn}, \text{etc.}$) have been well documented,² significant challenges still remain to achieve an efficient catalytic turnover and further develop new types of C–H transformations beyond the stoichiometric ones. Recently, we have achieved a series of manganese-catalyzed aromatic C–H transformations by using new strategies.³



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07/2005 - 06/2007	Postdoctoral Fellow, Peking University
09/2000 - 06/2005	Ph.D., Peking University
09/1996 - 06/2000	B.S., Nanjing University

Research Interests

Wang's research interests are to build up new organometallic catalytic systems in order to harness the cutting-edge challenging transformations. Currently, the work is focused on the development of catalytic processes promoted by manganese-group metals, which lie on the interface of the early and late transition metals in the periodic table.

Awards

2015	Thieme Chemistry Journal Award, Germany
2015	Asian Core Program Lectureship Award (Japan)
2015	Asian Core Program Lectureship Award (Singapore)
2013	The National Science Fund for Excellent Young Scholars, China
2011	Alexander von Humboldt Equipment Subsidy, Germany
2010	Outstanding Young Talent from Abroad Program, ICCAS
2008	Alexander von Humboldt Research Fellowship, Germany
2006	First Class Grant of China Postdoctoral Science Foundation, China
2005	Outstanding Graduate, Peking University, China

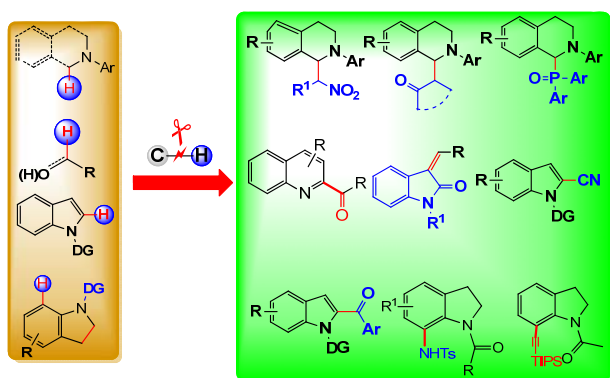
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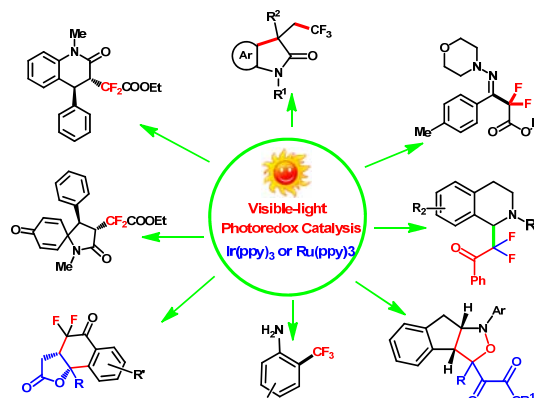
Transition Metal Catalyzed C-H Bond Functionalization and Access to Heterocycles and Fluorinated Compounds*

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The C-H functionalization is a perennial topic of interest for organic chemists, it is a great challenging task to accomplish highly selective C-H bond functionalization under mild conditions. In the past a few years, the directed alkylation, cyanation, oxidation, amination, acylation and phosphonation of C-H bond were realized in our laboratory, with transition metal (Au, Re, Rh, Cu etc.) catalysis or metal-free conditions. With those transformation methods, different kind of heterocyclic compounds were effectively constructed as shown in Scheme 1.¹



Scheme 1



Scheme 2

Owing to its significant advances in energy-saving and environmentally benign features, visible-light photoredox catalysis has witnessed rapid development and attracted considerable attention in both academia and industry. The incorporation of a fluorinated group into organic molecules is particularly intriguing because of its significant applications in the life sciences. Recently, our group achieved visible-light-induced trifluoromethylation and difluoroalkylation with different kind of fluoro reagents, several kinds of fluorinated compounds were synthesized efficiently (Scheme 2).²

* 国家自然科学基金 (21474048, 21372114) 资助项目

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2000 - 2003 南京大学化学化工学院副教授
2003 - 至今 南京大学化学化工学院教授

代表性论文

1. J. Cheng, P. Xu, Wei. Li, Yi. Cheng, C. Zhu, The Functionalization of a Cascade of C(sp²)-H/C(sp³)-H Bonds: Synthesis of Fused Dihydropyrazoles via Visible-light Photoredox Catalysis, *Chem. Comm.* **2016**, 52, 11901-11904.
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基于电子兼容性的分步自由基-自由基偶联模型*

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过渡金属催化的自由基-自由基偶联反应为碳-碳、碳-杂键的构建提供了新颖的方法。其背后的反应机理及选择性来源值得我们深入研究。由于自由基与过渡金属间的相互作用会改变自由基的稳定性和反应活性, 以往提出的稳态自由基效应可能不适用于过渡金属参与的自由基-自由基偶联反应。基于不同自由基物种亲电性、亲核性的不同, 我们提出了一种分步自由基-自由基偶联模型, 即过渡金属先后稳定两种不同种类自由基, 通过双电子转移过程得到偶联产物。更重要的是, 我们发现交叉偶联选择性最终是由自由基的电子兼容性控制的。以过渡金属催化的 C-N 自由基-自由基偶联为例, 理论计算表明 N 自由基具有较强的亲电性而 C 自由基具有较强的亲核性。因此, 富电子的低价态金属会首先与亲电的 N 自由基结合, 生成缺电子的高价态金属中间体。随后该亲电中间体更倾向与亲核的 C 自由基结合, 形成 Cu-C 键。由于 N 自由基的亲电性与 C 自由基的亲核性相匹配, C-N 偶联产物很容易通过双电子转移过程生成。另一方面, 因为该亲电中间体的电子兼容性与 N 自由基的亲电性相冲突, 该亲电中间体与 N 自由基的结合及 N-N 自由基自偶联过程在能量上都是不利的。因此, 反应体系中不会发生 N 自由基与 N 自由基的偶联反应。我们希望通过分步自由基-自由基偶联模型为自由基-自由基偶联反应的设计提供理论指导。

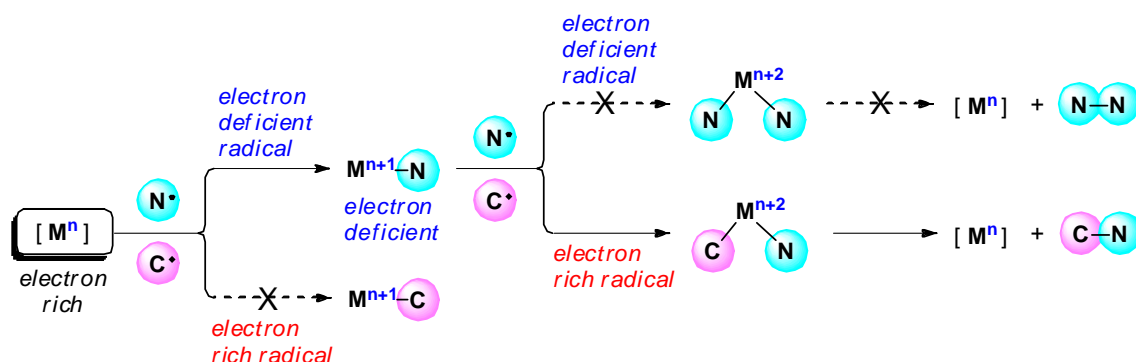


Figure-1. 基于电子兼容性的分步自由基-自由基偶联模型.

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蓝宇，男，1981年出生。重庆大学化学化工学院特聘研究员，博士生导师。2008年毕业于北京大学化学与分子工程学院并获有机化学博士学位，师从中国科学院院士吴云东教授；2009-2012年在 University of California, Los Angeles 从事博士后研究工作，导师为著名理论有机化学家 K. N. Houk 教授。2012年加入重庆大学化学化工学院开始独立科学研究工作，研究方向为计算化学、金属有机化学，主要研究内容包括：1) 通过理论计算研究有机化学反应机理相关问题；2) 通过全反应路径上的形变-结合能模型解释有机反应活性差别及选择性来源。2012年独立工作以来以通讯作者身份发表科研论文 *J. Am. Chem. Soc.* 三篇、*Angew. Chem. Int. Ed.* 四篇、*Nature Comm.* 二篇、*Chem. Sci.* 一篇、*ACS Catal.* 二篇、《中国科学：化学》(约稿) 一篇以及其他期刊论文共计 42 篇，并于 2015 年获得“中国化学会物理有机化学新人奖”。

研究方向

- [1] 使用全反应路径形变结合能分析模型研究双分子反应相对速率相关问题；
- [2] 通过理论计算研究过渡金属催化偶联反应机理；
- [3] 自由基-自由基偶联反应新模式的建立和发展；
- [4] 基于理论计算的新型大位阻配体设计和合成。

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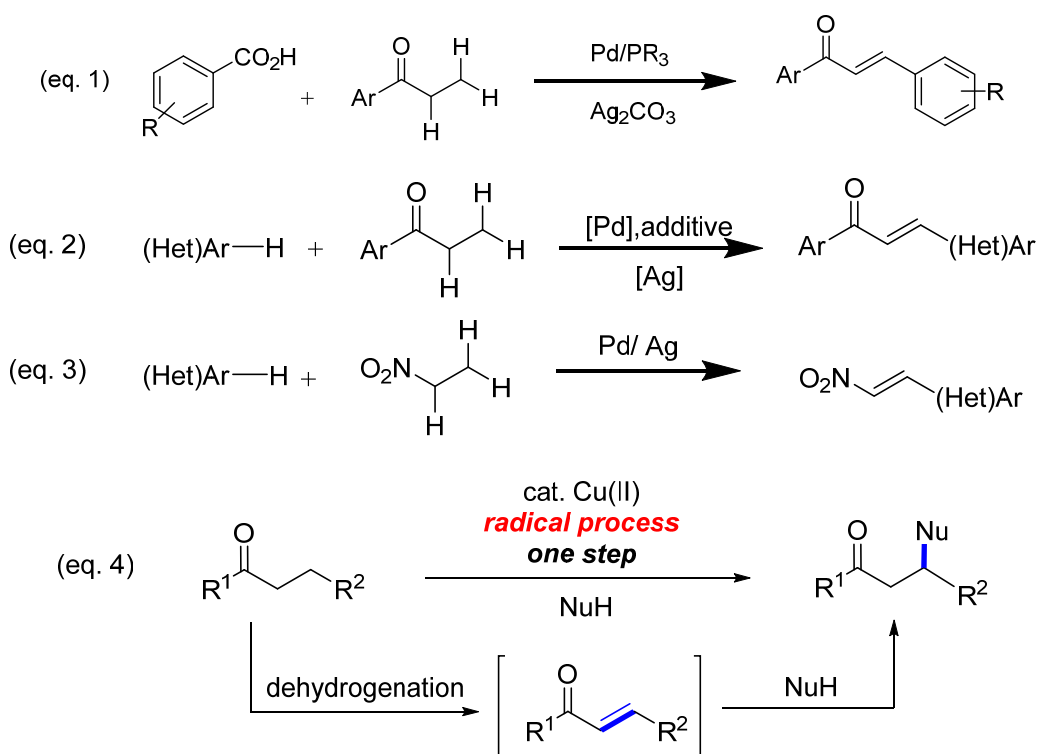
IL13

Cu-催化的酮脱氢成烯串连反应及其机理研究

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α , β -不饱和酮的传统合成方法要求从饱和的酮经历多步的过程如卤化/脱卤化氢来制备。最近, Pd 催化饱和酮氧化性脱氢提供一条直接的 α , β -不饱和酮合成路径, 但是这条路径仅限于环酮或 β -芳基取代的酮。我们课题组在最近的研究中, 发现具有酸性 α -H 的饱和起始物在反应中经历脱氢成烯炔中间体进而偶合形成目标产物的反应 (eq.1-3)。¹⁻⁴ 在此基础上, 我们发展出通过脱氢成烯进而偶合的 C-H 键官能团化反应路径。我们系统的研究建立了 Cu/TEMPO 催化的饱和酮的 β -位 C-H 胺基化、烷基化反应。⁵ 机理研究证实了 Cu/TEMPO 催化的反应发生涉及饱和酮脱氢原位形成 α , β -不饱和酮继而 Michael 加成。我们也对 Cu/TEMPO 催化的饱和酮催化的饱和酮脱氢成烯的过程进行详细的机理研究, 发现了饱和酮脱氢成烯涉及 Cu (II) 氧化酮形成 α -酮自由基, 进而 α -酮自由基被 TEMPO 俘获形成 TEMPO-酮加合物, 最后消除 TEMPOH 产生烯炔。这一机理发现可能开拓一条新的 C-H 官能团化反应的新路径。在这次会议上, 我们将报告 Cu/TEMPO 催化酮脱氢成烯的机理研究以及相关的 C-H 交叉偶联反应。



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苏伟平

苏伟平,研究员,博士生导师,中科院海西研究院福建物构所副所长,结构化学国家重点实验室副主任。1999年毕业于中科院福建物构所,获得博士学位,期间获中科院院长奖学金优秀奖。2000年、2001年分别获中科院自然科学二等奖(排名第四)、一等奖(排名第五),2002年获国家自然科学基金二等奖(排名第五)。2000-2005年在美国哈佛大学、新泽西州立大学和依阿华州立大学从事博士后研究。2006年应聘中科院“百人计划”回所开展独立研究工作,2007年获中科院“百人计划”择优资助,2011年终期评估优秀。2009年获得国家杰出青年基金并在终期考核中取得优秀。2012年获国务院特殊津贴。曾先后获得2012年度中科院优秀研究生指导教师奖、2014年度中科院朱李月华优秀教师奖。目前承担国家自然科学基金重点项目(2项)、海峡联合基金,中科院先导专项B类项目、前沿科学重点项目。

研究方向

1. 金属配合物结构构筑及其催化性能研究;
2. 原子经济性反应导向的金属促进的惰性化学键活化研究

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IL14

过渡金属催化碳氢键活化/去芳构化的协同螺环化反应研究*

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近年来, 过渡金属催化芳香化合物的直接官能团化获得了广泛关注, 并取得了许多令人瞩目的成绩。借助过渡金属催化, 合成化学家们可以实现惰性碳氢键的直接激活及转化, 克服了传统化学中需对碳氢键进行预官能团化的限制;¹ 同时能有选择性地来打破稳定芳香环的芳香性, 促使分子从平面向三维结构转变。² 过去几年间, 我们课题组从提高合成效率和原子经济性的角度出发, 通过使用过渡金属催化, 将惰性碳氢键官能团化与芳环去芳构化有机地融合在一起, 实现了芳香化合物碳氢键的激活与芳香性的同步破除, 发展了一类简捷、高效、经济的新颖合成方法, 快速构建了一系列全新的三维立体螺环骨架 (Figure 1)。³ 这一类方法的建立与发展实现了多个传统化学不能或者极难完成的化学转换, 一定程度上丰富了芳香化合物直接官能团化的工具箱。

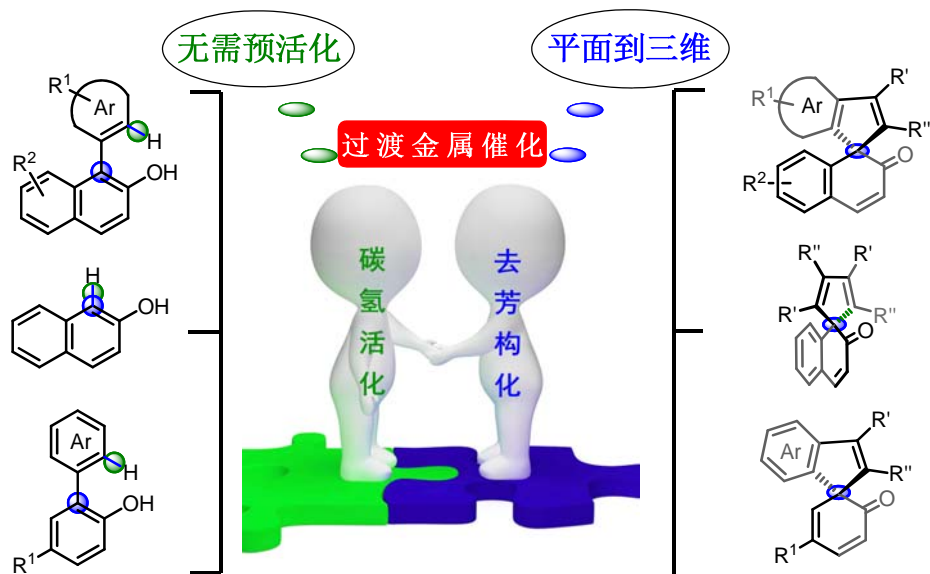


Figure 1. 碳氢键活化/去芳构化协同反应策略

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研究方向

过渡金属催化惰性碳氢键活化/去芳构化的协同反应研究。
轴手性向中心手性转变的动态动力学不对称转化研究。

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金属有机催化的烷烃官能团反应*

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烷烃是化石资源的重要组成体, 是量大价廉的基础化工原料。烷烃由高键能、非极性 C-C 单键和 Csp³-H 键组成, 是最惰性的有机分子之一, 其在合成化学中的应用价值较低。发展催化体系将简单易得的烷烃直接转化为高价值化学品并实现高的选择性控制具有重要的科学意义和应用价值。¹ 我们发展了一类新型的 PSCOP 螯钳型铱金属有机配合物, 其在烷烃脱氢反应中表现出非常高的催化活性, 但是在直链烷烃脱氢过程中, 由于催化剂具有烯烃异构活性, 在反应后期阶段不可避免地生成内烯烃混合物作为主要产物。² 最近, 我们课题组利用双金属催化一锅两步法进行烷烃末端高区域选择性硅基化, 实现烷烃至直链烷基硅的高效催化转化 (Figure 1)。催化体系包括 PSCOP 螯钳型铱金属有机络合物作为烷烃脱氢催化剂, 将烷烃脱氢生成内烯烃混合物, 吡啶二亚胺铁络合物作为串联烯烃异构和端烯烃反马氏硅氢化催化剂。³ 采用类似策略, 我们同时实现了烷烃末端高区域选择性硼化生成烷基硼酸酯化合物的反应。

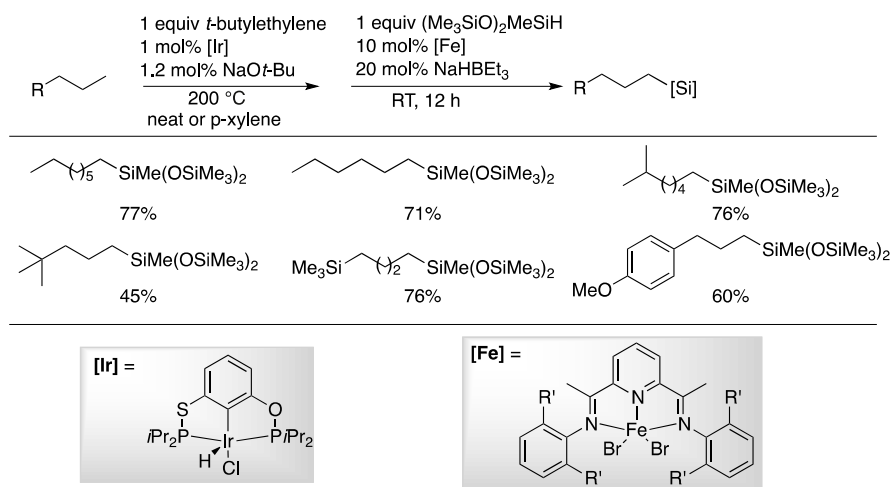


Figure 1. [Ir]/[Fe]双催化体系催化烷烃末端高区域选择性硅化反应

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* 国家自然科学基金委优秀青年基金 (21422209) 和重点项目(21432011)、科技部国家重点基础研究计划 (2015CB856600)、上海市科委基础研究领域项目 (13JC1406900)、国家青年千人计划项目、中国科学院及金属有机化学国家重点实验室的资助。

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黄正

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Thieme Chemistry Journal Awardees（2015），Shanghai Rising Star Program, Shanghai（2013）等奖励。以独立通讯作者在 *Nat. Chem.*, *Sci. Adv.*, *J. Am. Chem. Soc.*, *Angew. Chem. Int. Ed.* 等发表科研论文二十余篇。目前主要研究领域为能源化学、绿色化学及烯烃聚合研究。

研究方向：

烷烃官能团化、烯烃聚合、廉价金属催化方法学、机理研究

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过渡金属催化的 C-N 键活化*

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过渡金属催化的 C-C 及 C-N 成键交叉偶联反应已逐渐发展成为有机合成化学的重要手段, 是均相催化的重要研究内容之一, 如何通过简单的方法制备金属有机活性中间体是建立高效催化反应的关键因素之一。由于经典偶联反应的底物所包含的离去基团经常为卤素、磺酸基、金属盐等, 故而该类反应都具有一个有待提高的问题: 反应最后都不可避免的会产生我们所不期望得到的当量副产物。如果能发展一些新的方法或策略将 C-N 键切断, 制备得到相应的活性 C-M 键的同时也能将切断的 N-基团利用起来, 将会为解决上述问题提供一些新的可能途径。基于此, 我们利用 C-N 键活化的策略, 制备了一些新的金属有机活性中间体, 并发展了相应的 C-C 和 C-N 成键反应, 研究了反应机理积累了一些新的认识。

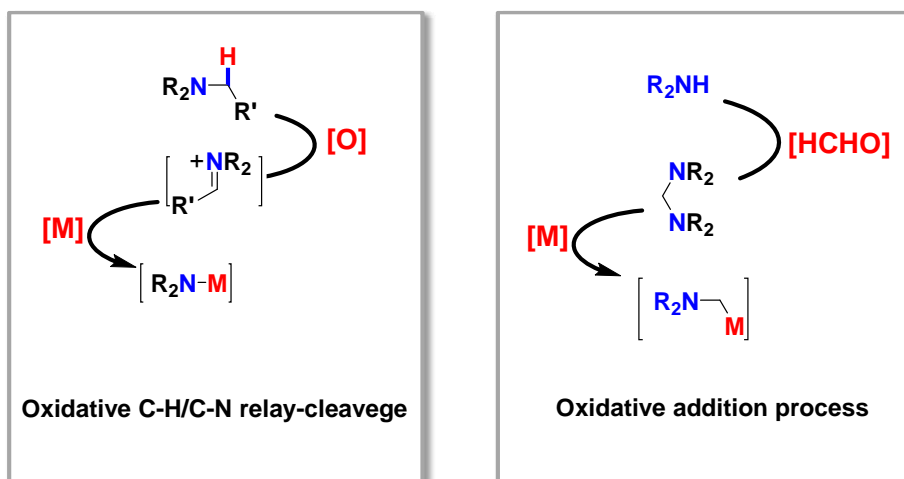


Figure 1. 制备金属活性中间体的 C-N 键活化方法

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研究方向

过渡金属催化的惰性键活化及其反应；
基于资源小分子活化的均相催化反应及机理研究；
不对称催化

代表性论文

- [1] Yang Liu, Yinjun Xie, Hongli Wang, and **Hanmin Huang***, Enantioselective Aminomethylation of Conjugated Dienes with Aminals Enabled by Chiral Palladium Complex-Catalyzed C-N Bond Activation, *J. Am. Chem. Soc.* **2016**, *138*, 4314-4317.
- [2] Quanjun Wang, Yijin Su, Lixin Li, and **Hanmin Huang***, Transition-Metal-Catalysed C-N Bond Activation, *Chem. Soc. Rev.* **2016**, *45*, 1257-1272.
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IL17

Classical and Weak Hydrogen Bonding in Asymmetric Palladium Catalysis*

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Our group in recent years exploited classical hydrogen bonding in asymmetric and regioselective Heck-type reactions. We used trialkylammonium cations in glycol to promote ionization of neutral arylpalladium halides, so as to access critical cationic species under mild conditions. This strategy has thus allowed us to achieve new catalytic processes using aryl halides directly, including a) regioselective Heck reaction of aliphatic olefins ; b) asymmetric intermolecular Heck reaction of aryl halides ; c) asymmetric cyclization to form indanones.^[1]

In our recent exploration of asymmetric palladium catalysis, we have detected rare examples of weak, attractive CH•••O interaction as key stereocontrolling element in elementary carbon-carbon bond forming processes, with the aid of high-level DFT calculations. The interaction is one type of weak hydrogen bonding by definition and it contributes about half to a few kcalmol⁻¹ to stabilization of major transition states leading to major enantiomers. Examples of this kind from our laboratory include a) enantioselective arylation of lactones, b) arylation of ketones, c) and intramolecular reductive Heck reaction.^[2] Furthermore, we observed similar roles played by the weak CH•••O interaction in inducing enantioselectivity in other metal-catalyzed processes, such as d) copper-catalyzed conjugate addition of enones using organoboroxines^[3] and e) nickel-catalyzed transfer hydrogenation of hydrazones.^[4] In all of the examples above, conventional steric repulsion or close contact was *not* involved.

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Research Interests

Transition metal catalysis and asymmetric synthesis

Awards

Thieme Chemistry Journal Award (2012)

GSK-EDB Green and Sustainable Manufacturing Award (2013)

Representative Publications

- [1] Nickel-Catalyzed Enantioselective Reductive Amination of Ketones with Both Arylamines and Benzhydrazide
Peng Yang, Li Hui Lim, Pratanphorn Chuanprasit, Hajime Hirao, Jianrong (Steve) Zhou *Angew. Chem. Int. Ed.* **2016**, 55, 12083.
- [2] Asymmetric Conjugate Addition of Organoboron Reagents to Common Enones Using Copper Catalysts.
Chunlin Wu, Guizhou Yue, Christian Duc-Trieu Nielson, Kai Xu, Hajime Hirao, Jianrong (Steve) Zhou *J. Am. Chem. Soc.* **2016**, 138, 742.
- [3] Palladium-Catalyzed Heteroarylation and Concomitant *ortho*-Alkylation of Aryl Iodides. Chuanhu Lei, Xiaojia Jin, Jianrong (Steve) Zhou *Angew. Chem. Int. Ed.* **2015**, 54, 13397
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IL18

N-Fluorobenzenesulfonimide: An Efficient Radical Aminating Reagent*

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The construction of C–N bond is of great importance because of the interesting and diverse biological activities of nitrogen-containing compounds. *N*-Fluorobenzenesulfonimide (NFSI) is widely used as fluoronium cation (“F⁺”) to undergo electrophilic fluorinating reaction.¹ In addition, due to the relatively small N–F bond dissociation energy (63.1 kcal/mol in acetonitrile), NFSI could also be used as a radical fluorine source to perform fluorination reactions.² Recently, NFSI^{3a} was successfully used as a nitrogen-centered radical reagent by our group for the first time.^{3b} As a result, highly regio-selective aminocyanation and diamination of styrene derivatives were realized.^{3b} In addition, aminooxygenation^{3c} and aminofluorination^{3d,e} and oxidative-amination^{3e} reactions of C–C double bonds; aminoarylation^{3f} and aminative multifunctionalization reaction^{3g} of C–C triple bonds were also developed. Details of these novel radical amination reactions will be presented at the symposium.



Figure 1.

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Research Interests

New method for the construction of nitrogen-containing heterocycle

New method for the construction of C–N bond

Representative Publications

- [1] Xiong, T.; Zhang, Q. New Amination Strategies Based on Nitrogen-centered Radical Chemistry, *Chem. Soc. Rev.* **2016**, 45, 3069.
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Chiral Sulfoxides in Transition Metal Catalyzed Asymmetric Reactions*

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Development of new chiral ligand is one of the most interesting topics in asymmetric catalysis. To date, various chiral ligands such as phosphine, nitrogen, olefine ligands have been well developed in asymmetric catalysis. However, till to the end of last century, the use of chiral sulfoxides as ligands in asymmetric catalysis has remained relatively unexplored.^[1] During the past decade, our research interest was focusing on the design of chiral sulfoxide ligands (Sulfoxide-Phosphines, Sulfoxide-Olefines and Bissulfoxides) based on *tert*-butylsulfinyl moiety and these ligands demonstrate excellent performances in transition-metal-catalyzed asymmetric reactions.^[2-4]

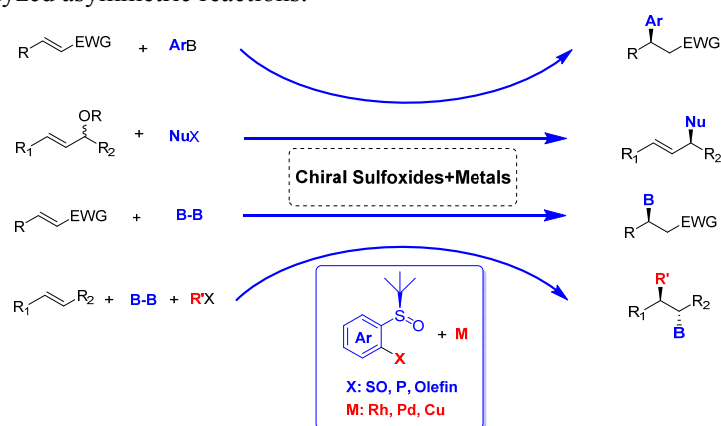
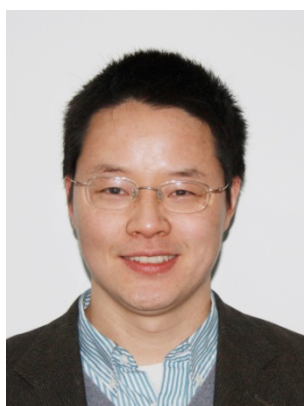


Figure 1. Chiral sulfoxide ligands and asymmetric catalysis

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Research Interests

Chiral Sulfoxide Ligands and Transition Metal Catalyzed Asymmetric Reactions.

Representative Publications

- [1] Tao Jia, Peng Cao, Bing Wang, Yazhou Lou, Xuemei Yin, Min Wang, Jian Liao* "A Cu/Pd Cooperative Catalysis for Enantioselective Allylboration of Alkenes" *J. Am. Chem. Soc.* **2015**, *137*, 13760.
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多组分反应及其结构多样性化合物高效构建*

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近年来, 多组分反应因其原子经济性和步骤经济性等特点成为现代有机化学的热点领域。相对于传统合成方法, 多组分反应可以一步形成多个化学键, 从而实现结构多样性化合物的高效合成, 属于“理想合成”反应的范畴。^[1] 近年来, 我们课题组致力于基于活泼中间体捕捉的多组分反应研究, 发现并发展了基于活泼羟基叶立德、铵基叶立德中间体和离子对中间体的系列新型多组分反应。^[2] 在反应的研究过程中, 我们采用双金属及有机小分子与金属协同催化策略, 实现了反应的高化学选择性、高立体选择性(包括非对映选择性和对映选择性)的“精确控制”, 阐明了相应的反应机理, 揭示了系列活泼中间体独特的化学性质, 为大量含羟基、氨基、杂环等多官能团的具有结构多样性和复杂性的化合物的高效构建提供了系列新方法 (Figure 1)。^[3]

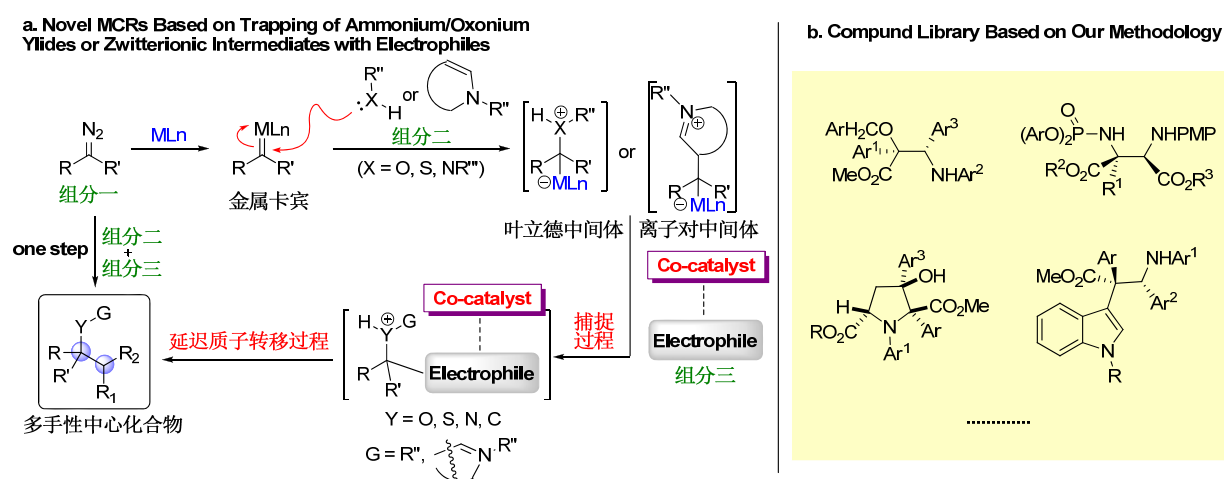


Figure 1. 基于亲电试剂捕捉活泼羟基/铵基叶立德和离子对中间体的多组分反应及其应用

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研究方向

- [1] 多组分新反应及其在生理活性化合物高效合成中的应用
- [2] 新型小分子药物研发
- [3] 非专利药的制药工艺研究

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- [1] D. Zhang, J. Zhou, F. Xia, Z. H. Kang, W. H. Hu*, Bond cleavage, fragment modification and reassembly in enantioselective three-component reactions, *Nature Commun.* **2015**, *6*, 5801.
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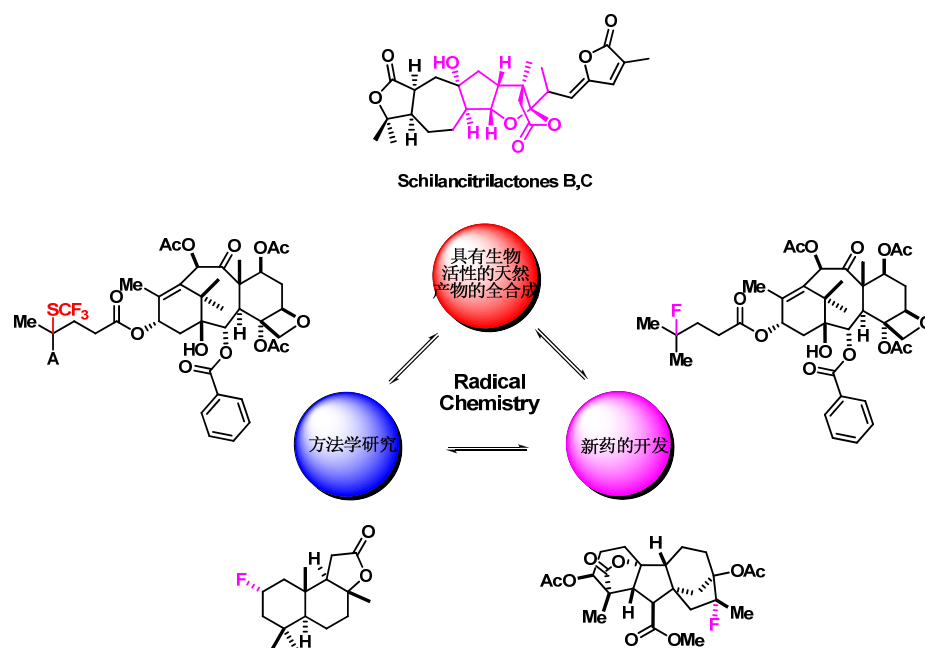
对具有生物活性天然产物的全合成及方法学研究*

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天然产物是寻找生物活性物质和实用药物的源泉。我们课题组自成立以来, 一直致力于以新药开发为导向的天然产物全合成: 高效简洁的合成具有重要生物活性的天然产物, 以及发展高效的方法学来实现其衍生物的合成, 寻找先导化合物, 为新药的开发做出自己的贡献。

在过去的几年时间中, 我们课题组开展了五味子降三萜类天然产物 Schilancitrilactones B, C 的全合成研究, 通过利用分子内自由基环化反应等关键化学反应, 实现了该类分子的首次全合成;¹ 此外, 鉴于含氟化合物其独特的性质, 被广泛使用于医药, 农药, 材料科学以及用于正电子发射计算机断层显像中的显像剂。近期我们利用自由基的反应机理, 首次实现了银催化的苄位 C-H 键的两次氟化反应来制备芳基二氟甲基化合物。在此基础上, 进一步发展了非活化 C(sp³)-H 的氟化反应以及非活化 C(sp³)-H 的硫三氟甲基化反应, 该方法可以有效地对复杂活性分子如紫杉醇, 赤霉素衍生物直接实现特定惰性 C-H 键的氟化反应。²



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* 国家自然科学基金 (21402098, 21421062, 21522205) .

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研究方向

- [1] 对具有生物活性的天然产物的全合成以及化学生物学研究。
- [2] 金属催化的合成方法学以及氟化学研究。
- [3] 寡糖的合成方法学研究以及对具有重要生物活性的寡糖以及糖缀合物的合成。

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Transition Metal Catalyzed Cycloaddition Reactions with Alkynes*

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Cycloaddition reactions are particularly fascinating for straightforward building diverse cycles, which are unique structural motifs presented in many biologically active natural products, and pharmaceuticals. However, methods for the cycloaddition, especially hetero-annulation, with alkynes, are less abundant and remain limited to the substrate scope with regard to both the *n*-atom units and the alkynes. In recent years, we have developed some new cycloaddition strategies for the transformation of alkynes leading to various valuable heterocycles (Figure 1).

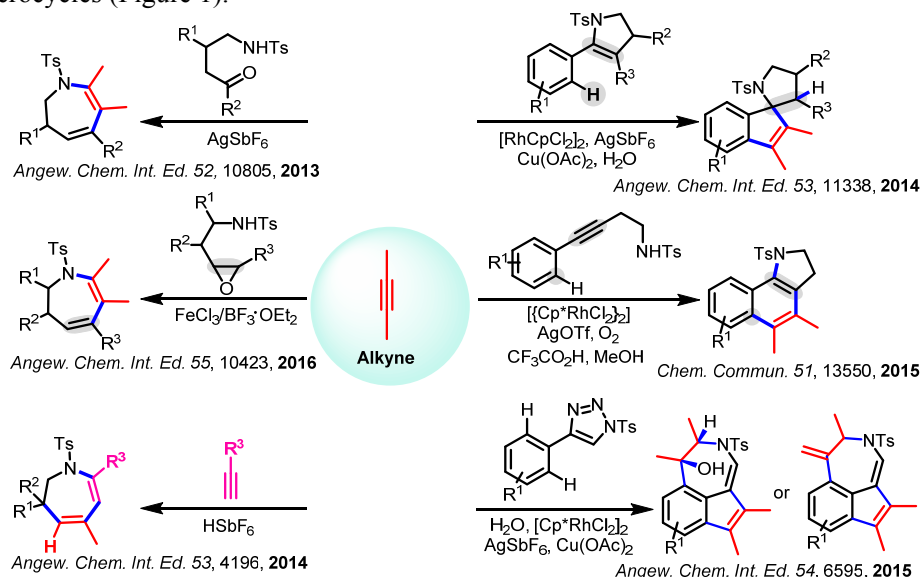


Figure 1. Hetero-Annulation with Alkynes

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1990 - 1994: B.S., Hunan Normal University

Research Interests

Oxidative Radical Methodologies, Cross-Coupling Reactions, and New Cycloaddition Strategies for the Construction of Large-Membered rings

Representative Publications

- [1] C. Hu, R.-J. Song, M. Hu, Y. Yang, J.-H. Li, S. Luo, [5+2] Cycloaddition of 2-(2-Aminoethyl)oxiranes with Alkynes via Epoxide Ring-Opening: A Facile Access to Azepines, *Angew. Chem. Int. Ed.* **55**, 10423, **2016**.
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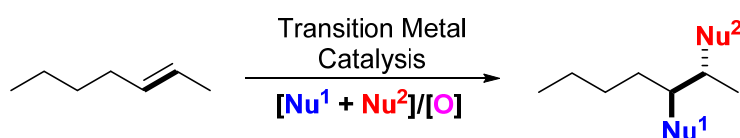
Difunctionalization of Alkenes: New Concept and Strategy*

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Difunctionalization alkenes presents one of the most efficient methods to synthesize various vicinal carbon-carbon and carbon-heteroatom bonds in a single step from simple precursors, which significantly enhanced the molecular complex with excellent step-economical strategy. Among them, transition metal catalysis have proven to be powerful tools. In the last several years, our efforts were focused on difunctionalization of C=C bonds utilizing transition metal catalyst, ranged from intramolecular to intermolecular reactions. We have developed two strategies for these transformation: (1) employing high-valent palladium catalysis, a various intramolecular difunctionalization of alkenes have been developed, such as aminofluorination, aminochlorination, aminohydroxylation as well as aryltrifluoromethylation, etc. Those methods presented the most efficient way to synthesize various heterocycles;^[1-2] (2) developing a new strategy by combination of radical chemistry and organometallic chemistry, a various of copper-catalyzed difunctionalization of alkenes have been discovered, such as azido-, cyano-, thio- and aryltrifluoromethylations. In these reaction, the selectivity of radical chemistry can be controlled by metal complex by tuning ligand.^[3]



From intramolecular to intermolecular reaction

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Research Interests

Organic/Organometallic Chemistry. Catalysis.

The research in Liu's group focused on the organometallic chemistry directed in organic synthesis and catalysis, specially in the field of difunctionalization of alkenes, which includes fluorination and related transformation, green oxidation, and others.

Representative Publications

- [1] Zhang, W.; Wang, F.; McCann, S. D.; Wang, D.; Chen, P.; Stahl, S. S.; Liu, G. Enantioselective cyanation of benzylic C-H bonds via copper-catalyzed radical relay, *Science* **2016**, *353*, 1014.
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IL24

Visible-Light Photocatalysis in Heterocycle Synthesis and Functionalization*

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Visible-light photocatalysis has recently received increasing attention from chemists because of its wide application in organic synthesis and its significance for sustainable chemistry. This catalytic strategy enables the generation of various reactive species, frequently without stoichiometric activation reagents under mild reaction conditions. Manipulation of these reactive intermediates can result in numerous synthetically useful bond formations in a controllable manner. Recently, we have successfully achieved some useful transformations of readily available starting materials under the irradiation of visible light in the presence of photocatalysts. These methods can be used in the synthesis of many useful heterocyclic motifs, which are widely presented in nature products and pharmaceutical agents.

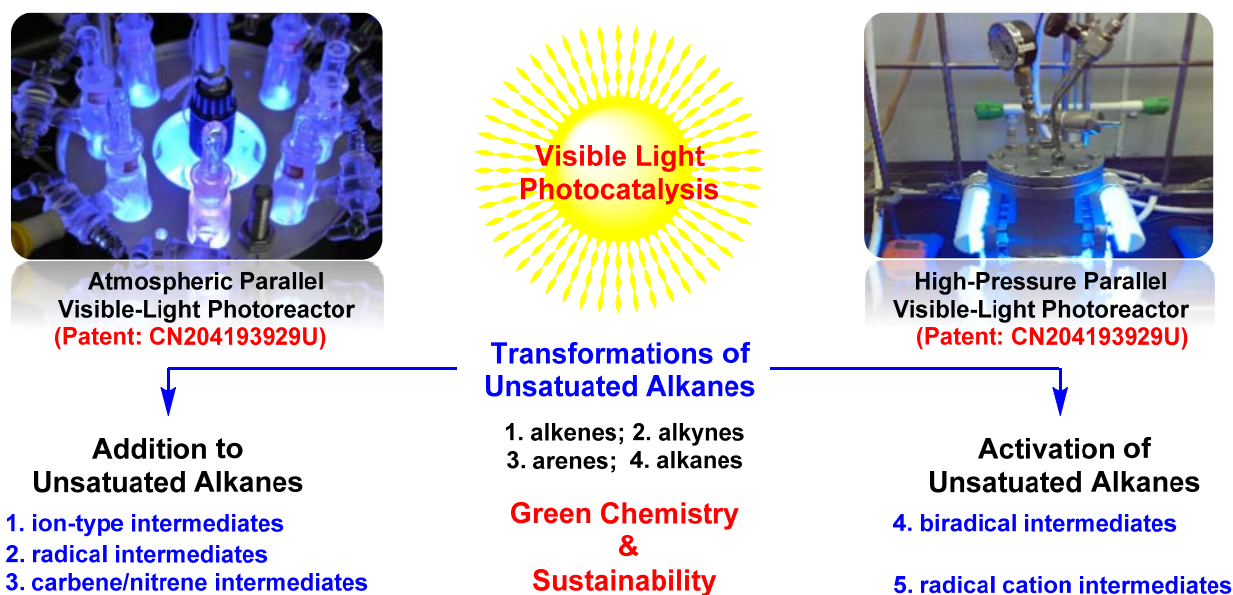


Figure 1. An overview of our research on visible light photocatalysis

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Research Interests

Visible-Light Promoted Photoredox Transformations and Their Synthetic Applications; Chemical Development of New Reactions Involving Sulfur Ylides and New Reagents for the Construction of Carbo- and Heterocyclic Compounds; Asymmetric Catalysis

Awards

Asian Core Program Lectureship Award, Singapore (2014); The 7th WuXi PharmaTech Life Chemistry Research Award (2013); The First Prize of Natural Science, Hubei Province (2013)

Representative Publications

- [1] Wang, Q.; Li, T.-R.; Lu, L.-Q.; Li, M.-M.; Zhang, K.; Xiao, W.-J. Catalytic Asymmetric [4 + 1] Annulation of Sulfur Ylides with Copper–Allenylidene Intermediates, *J. Am. Chem. Soc.* **2016**, *138*, 8360.
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IL25

Construction of Organic Optoelectronic Molecules Based on Highly Efficient and Selective C–H Bond Transformations*

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The design and synthesis of π -conjugated organic molecules are one of the most important research contents of organic chemistry and are also a source of innovation for molecular materials and devices. The development of straightforward accesses to organic functional materials through C–H activation is a revolutionary trend in organic synthesis. Our research aims to offer the chemical basis for the construction of organic photoelectric molecules through the development of highly efficient and selective transformations of C–H bonds. In recent years, we have successfully developed a number of synthetically challenging π -conjugated structures, especially the frameworks that are difficult to access by common synthetic disconnections without C–H activation tactics. Furthermore, we have also explored their applications in organic photoelectric materials such as organic photovoltaic, electroluminescence, field effect transistor, biosensing and piezochromism. The highly efficient routes to diverse organic photoelectric molecules developed by us have well exemplified the great charm of C–H activation and would finally boost the development of the organic optoelectronic materials.

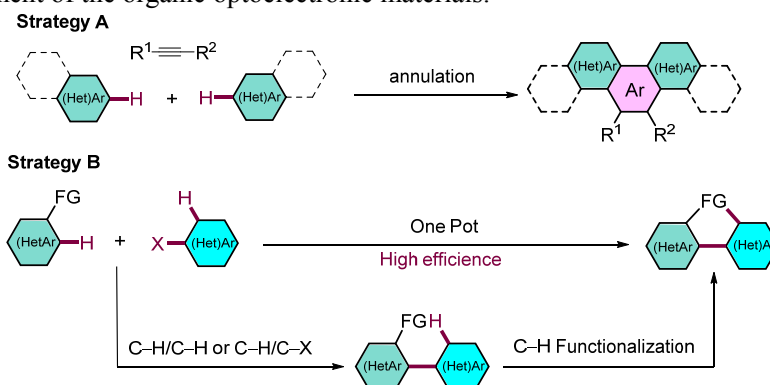


Figure 1. Strategy for the construction of π -conjugated organic molecules

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Research Interests

His research interests focus on developing new concepts and strategies to synthesize π -conjugated frameworks, especially via the transition metal catalyzed C–H functionalization of (hetero)arenes, and exploring their applications in the construction of organic optoelectronic materials.

Awards

The national ten thousand talents plan (2016); Principal scientist for 863 Program (2013); National Science Foundation for Distinguished Young Scholars (2010).

Representative Publications

- [1] Cheng, Y.; Li, G.; Liu, Y.; Shi, Y.; Gao, G.;* Wu, D.; Lan, J.; You, J.* Unparalleled Ease of Access to a Library of Biheteroaryl Fluorophores via Oxidative Cross-Coupling Reactions: Discovery of Photostable NIR Probe for Mitochondria, *J. Am. Chem. Soc.* **2016**, *138*, 4730.
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口头报告

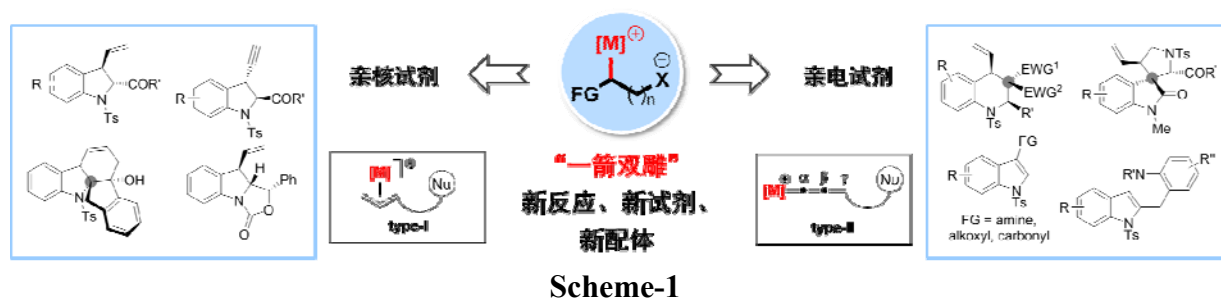
OL1

过渡金属催化的偶极环加成反应研究*

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杂环化合物种类繁多、结构多样并具有独特的化学、物理性质, 在药物化学、材料科学、生命科学等诸多领域具有十分重要的用途。因此, 杂环化合物的选择性合成是现代合成化学的一个重要研究内容。我们针对杂环合成中的效率和选择性控制等问题, 通过设计新反应、新试剂和新催化体系, 发展了一系列过渡金属催化的不对称偶极环加成反应, 实现了若干重要杂环骨架的选择性构建。主要包括: 1) 通过设计新反应与新试剂, 实现了过渡金属(Pd, Fe, Cu)稳定的偶极合成子与硫叶立德、苯胺等亲核试剂的环加成反应, 合成了高度官能化的手性吲哚啉、螺环吲哚啉和吲哚等多类含氮杂环化合物; 2) 通过发展新型的P, S手性配体, 实现了过渡金属Pd稳定的偶极合成子与三取代缺电子烯烃等亲电试剂的不对称环加成反应, 高效、高选择性地合成了含有三个连续立体中心(包含一个季碳中心)的手性四氢喹啉和螺环氧化吲哚。



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OL2

Transition Metal Catalyzed Regioselective Cage B-H Activation and Functionalization of *o*-Carboranes*

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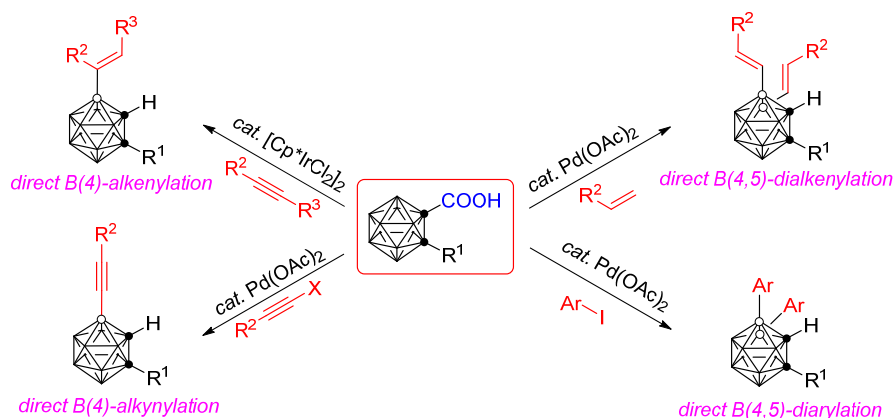
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Carboranes are a class of polyhedral boron hydride clusters in which one or more of the BH vertices are replaced by CH units, which can be viewed as three-dimensional relatives of benzene. They are finding many applications in medicine, supramolecular design, coordination/organometallic chemistry and very recent optoelectronic functional materials. The special 3D structure of *o*-carboranes make their derivatization difficult especially at cage boron positions, majorly owing to the selectivity issue resulting from total ten B-H bonds in four different electronic environments. Thus, we are interested in developing new methodologies for the functionalization of *o*-carboranes via direct and selective cage B-H activation.

With the help of a traceless directing group –COOH, transition metal catalyzed cage B(4)-alkenylation,^[1a] B(4,5)-dialkenylation,^[1b] B(4,5)-diarylation^[1c] and B(4)-alkynylation^[1d] of *o*-carboranes have been achieved. The directing group not only plays a key role in regioselectivity and mono-/di-selectivity of the reactions, but also is removable after the reaction. The resultant new cage B-substituted *o*-carborane derivatives may find some applications in materials.



Scheme 1. Transition metal catalyzed direct and selective cage B(4,5)-H activation of *o*-carboranes

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** 通讯联系人

OL3

Applications of Peroxides as Alkylating Reagents in Cross Coupling Reactions*

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Peresters and diacyl peroxides are cheap chemicals commonly used in industry and academia as oxidants or radical initiators. Nevertheless, the utilization of peroxides as alkylating reagents was underexplored and there were very few documented examples so far to our knowledge.

Here we would like to report applications of peresters and diacyl peroxides as alkylating reagents in cross coupling reactions, including Heck-type reaction, Sonogashira reaction and other reactions.¹

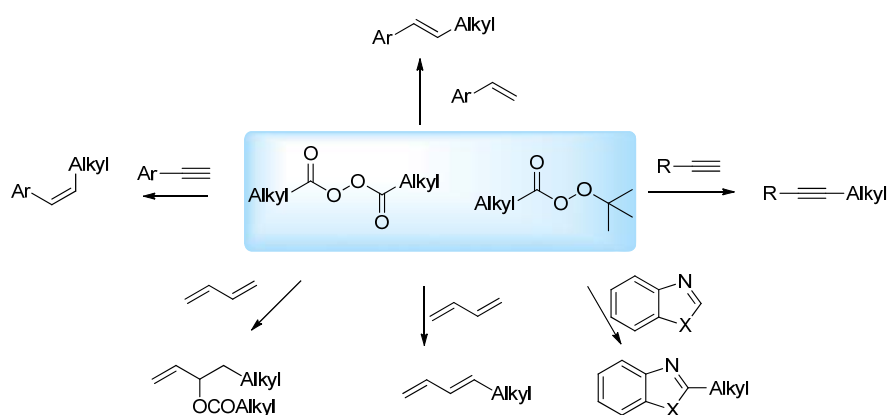


Figure 1. Applications of peroxides as alkylating reagents in cross coupling reactions

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* 国家自然科学基金 (21402200, 21502191, 21672213) 资助, 中国科学院战略性先导科技专项 (B 类) 资助 (Grant No. XDB20000000)

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OL4

利用金属配位作用组装、调控与超分子手性催化应用*

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金属配位键是一种键能大但又具有动态特性的特殊非共价作用, 通过金属配位作用进行组装与调控已得到广泛应用。我们利用铂配位驱动自组装与冠醚主客体化学相结合的正交策略制备了多组分索烃、分子项链和可逆交联的聚轮烷等机械互锁结构^[1]; 采用金属配位的模板导向法, 通过烯烃复分解反应合成了具有复杂拓扑结构和纳米尺度的柔性链连接的笼状双卟啉和环状三卟啉、六卟啉结构^[2]; 以手性 BINOL 二羧酸衍生物为组装单元, 通过配位自组装构筑了一系列 2D 和 3D 离散型手性组装体^[3]; 设计合成了一种新型的冠醚衍生的超分子手性配体, 利用配体上含吡啶基冠醚与具有不同离子半径的碱金属离子或铵盐的主客体作用调控该手性双膦配体, 并成功地应用于 Rh 催化不对称氢化还原 α -脱氢氨基酸酯和 α -芳基烯胺及 Ir 催化不对称氢化喹啉和喹啉啉, 发现碱金属离子或铵盐的加入可明显提高催化活性和 *ee* 值^[4]。

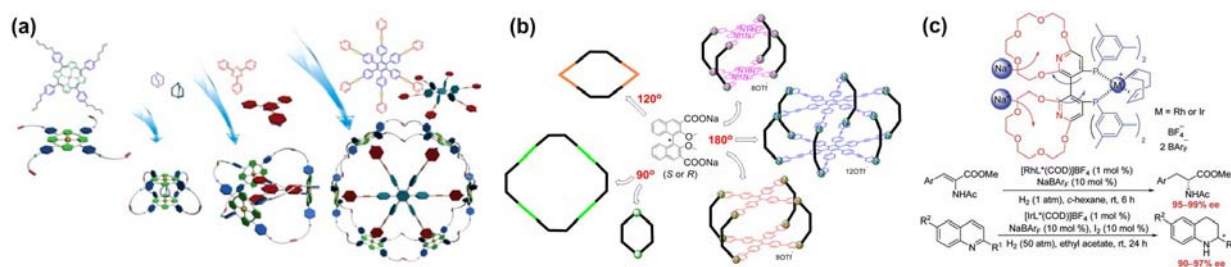


Figure-1 (a) Template-directed synthesis of porphyrin cages and nanorings, (b) controlled self-assembly of 2D and 3D chiral self-assemblies, and (c) supramolecular chiral catalysts and their applications.

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*国家自然科学基金(91127010, 21172049, 21032003, and 21572042)、教育部创新团队 (IRT 1231)、教育部留学回国人员启动基金、浙江省自然科学基金 (LZ13B030001 和 LZ16B020002)、浙江省公益性研究计划 (2015C31141)和杭州市高层次留学回国人员 (团队) 在杭创业创新资助项目

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OL5

Multimetallic Catalyzed Oxidative Radical Alkynylation*

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Radical involved cross-coupling has recently emerged as a powerful tool for the construction of C-C bonds.^[1] However, the developed radical involved C-C bond formation reactions largely rely on the radical addition to unsaturated bonds. It is difficult to achieve selective radical C(sp³)-C(sp) cross-coupling with terminal alkynes.

Here we would like to report a series of radical C(sp³)-C(sp) cross-coupling with terminal alkynes by utilizing a multimetallic oxidative radical alkynylation reaction strategy.^[1] Unactivated alkyl radical, benzyl radical, tetrahydrofuran methyl radical, methyl radical and α -cyano alkyl radical are all able to couple with terminal alkynes by judicious selection of the catalyst combination. This work offers an efficient alternative process for achieving direct alkynylation of terminal alkynes besides traditional Sonogashira coupling.

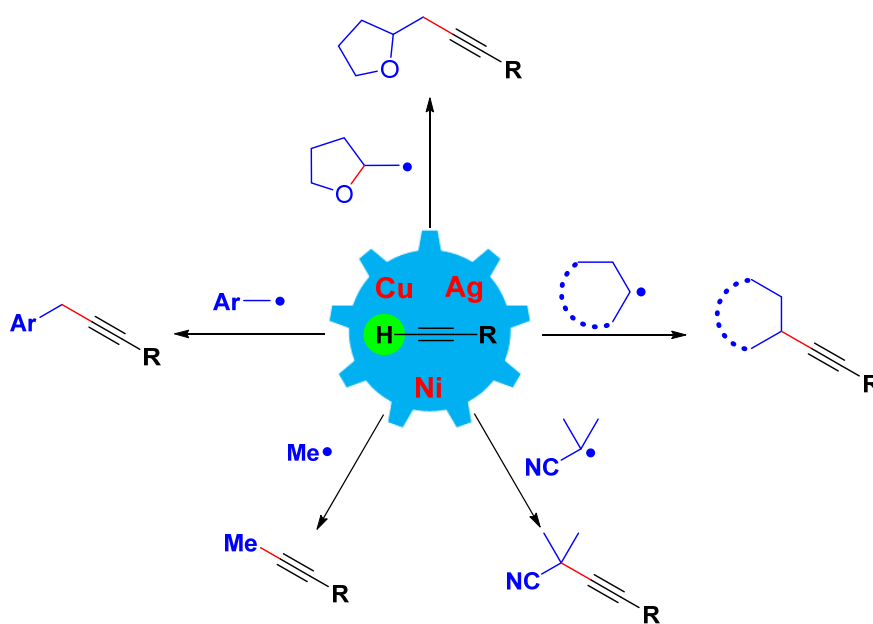


Figure 1. Oxidative Radical C(sp³)-C(sp) cross-coupling with terminal alkynes.

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* 国家自然科学基金 (21390400, 21520102003, 21272180, 21302148) 资助项目

**通讯联系人

OL6

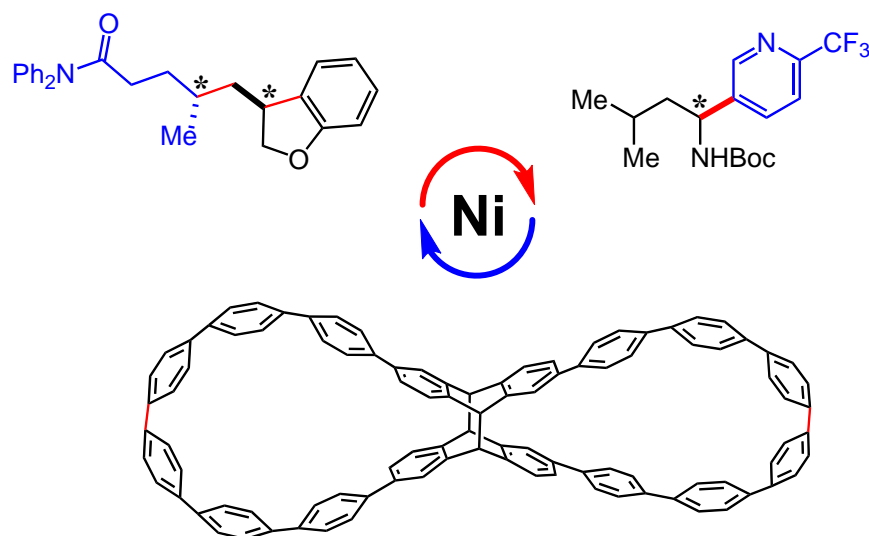
Nickel-Mediated Carbon–Carbon Coupling Reactions*

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Nickel-mediated carbon–carbon coupling reactions represent an important strategy to efficiently construct complex molecules. The first part entails the research completed during my postdoctoral training in Professor Gregory Fu’s laboratory at MIT and Caltech. We have developed two distinct variations of nickel-catalyzed asymmetric cross-couplings, namely the tandem cyclization-coupling of nucleophiles bearing a pendent olefin^[1] and the decarboxylative coupling of amino acids^[2]. The second part focuses on the synthesis of highly strained carbon nanomaterials, an ongoing project in my independent research group at Chinese Academy of Sciences. The key synthetic designs feature rigid anthracene photodimer synthon, late-stage ring expansion through cycloreversion, and high-yielding macrocycle formation via nickel-facilitated Yamamoto coupling^[3].



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OL7

Synthesis of α -Arylglycines from Aromatic Imines and Carbon Dioxide via Umpolung Carboxylation

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As a class of non-proteinogenic α -amino acids, α -arylglycine is a key structural unit presented in a vast array of important biologically active compounds.^[1] Synthesis of α -amino acids using carbon dioxide (CO_2) as a carboxyl source represents a highly attractive route since CO_2 is an abundant, non-toxic and renewable C1 feedstock.^[2] Herein we describe a straightforward and transition-metal-free approach for the efficient synthesis of α -arylglycine derivatives from aromatic imines and CO_2 via umpolung carboxylation reaction. Various substituted diphenylmethanimines underwent the carboxylation smoothly with CO_2 in the presence of potassium *tert*-butoxide and 18-crown-6 to give the corresponding carboxylated products in good to high yields. Besides the enhancement of solubility of potassium *tert*-butoxide in THF, 18-crown-6 also plays key roles in suppressing reverse protonation or 1,3-proton shift isomerization as well as stabilizing the carboxylated intermediate.

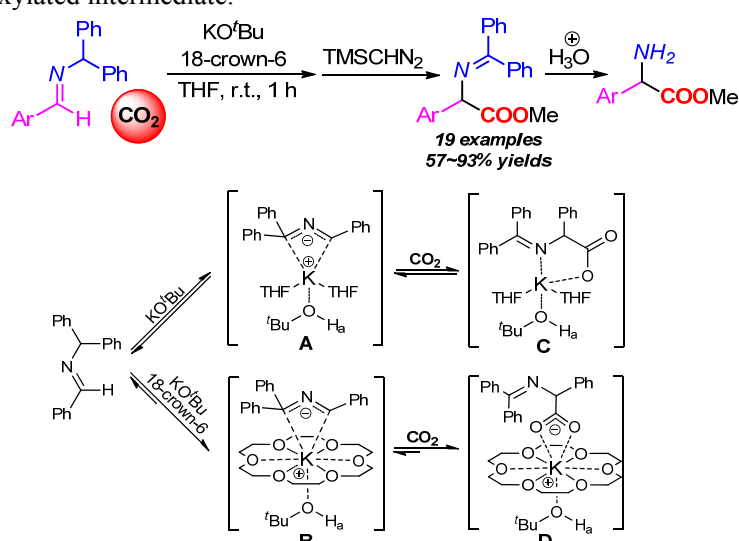


Figure 1. KO^tBu/18-crown-6 mediated carboxylation of imines with carbon dioxide

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OL8

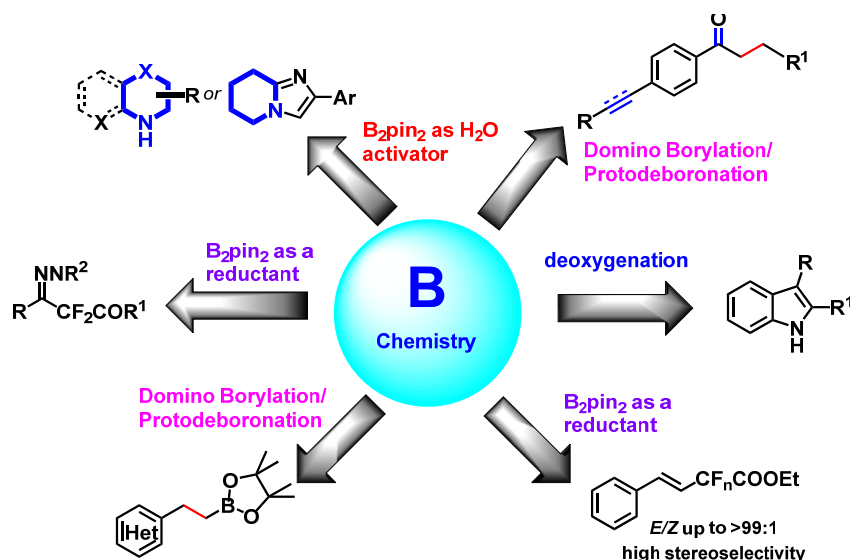
New Reactivity and Applications of Diboron Reagents in Organic Synthesis*

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Diboron compounds, especially (pinacol)diboron, are very important borylating reagents, which are widely employed in organic synthesis for the preparation of a myriad of organoboron compounds, since organoboronates are prevalent building blocks in organic synthesis and pharmaceutical industries. Numerous transition-metal catalyzed cross-coupling with organoboron as coupling partners have been developed and in a word, boron chemistry is one of the long-lasting themes in organic chemistry since its birth. Despite these advancements, surprisingly and interestingly, reductive property of diboron compounds and protodeboration reaction are underdeveloped and very few attentions have been focused on these topics. In this presentation, several useful and efficient methods have been developed based on the reductive property of diboron compounds as well as Domino-Borylation-Protodeboration (DBP reaction) strategy and thus a new role of diboron compounds is established in organic synthesis.



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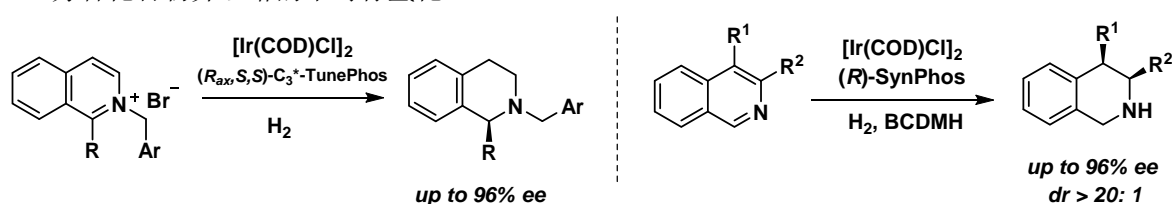
不对称氢化合成手性四氢异喹啉*

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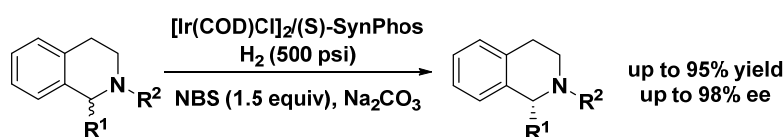
手性四氢异喹啉是很多天然生物碱和药物分子中的重要结构单元, 该类化合物具有广谱生物活性, 诸如抗癌、抗菌、抗疟等, 发展手性四氢异喹啉化合物的有效合成方法是具有挑战性和实用意义的课题^[1]。本课题组基于铱催化不对称氢化方法, 探索了几种有效的策略以实现手性四氢异喹啉的有效合成。

一、芳香化合物异喹啉的不对称氢化^[2]。



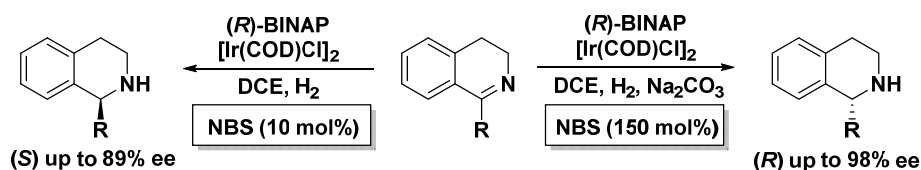
Scheme-1 异喹啉的不对称氢化

二、催化去外消旋化。采用氧化还原去外消旋化反应, 直接由外消旋化合物得到手性四氢异喹啉化合物^[3]。



Scheme-2 催化去外消旋化

三、仅通过调变反应中的非手性因素, 采用单一构型手性催化剂即可得到两种相反构型的手性四氢异喹啉化合物, 实现了双向对映选择性氢化^[4]。



Scheme-3 双向对映选择性氢化

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- [4] Unpublished results.

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OL10

Computational Studies on Mechanism and Origins of Selectivity in Ni-mediated C-O and C-N Activations*

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Computation has joined all aspects of chemistry today, and the collaboration between experiment and computation is one of the key driving forces that push the frontiers of science. In this talk, I will first discuss the mechanism and origins of the ligand-controlled selectivity in Ni-catalyzed C-O activations of aryl esters^[1]. The intrinsic differences between monodentate and bidentate phosphine ligands in Ni-mediated C-O activations will be elucidated through distortion-interaction model^[2]. Based on the mechanistic understandings of Ni-mediated C-O activations with phosphine ligands, the joint force of computation and experiment that leads to [Ni(NHC)]-catalyzed controlled transformation between ester and amide will be mentioned^[3].

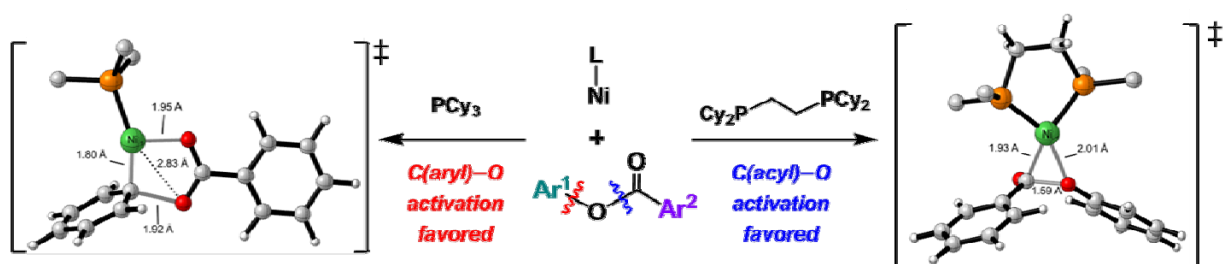


Figure 1. Ligand-controlled chemoselectivity in Ni-mediated C-O activations of aryl esters with phosphine ligands.

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** 通讯联系人

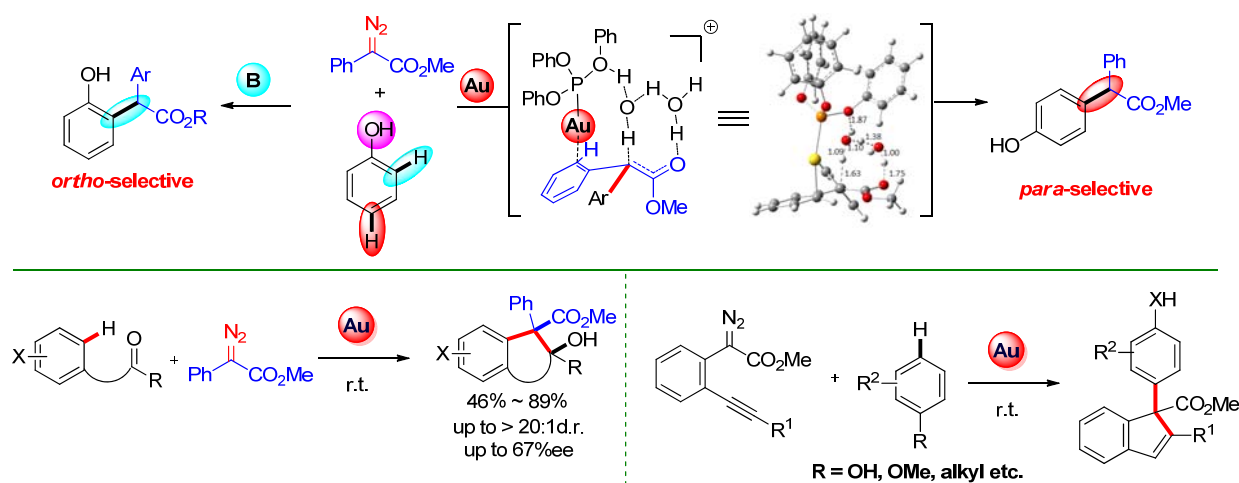
OL11

高化学选择性和区域选择性的苯酚碳氢键官能化*

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In last few years, gold revealed more and more unique properties in carbene chemistry.^[1] Last year, we disclosed that the gold carbenes have an unprecedented chemo- and site-selectivity and ligand effect toward the functionalization of C-H bond of phenol.^[2] In order to further understand the origin of this unique transformation, we report a comprehensively combined theoretical and experimental study on the mechanism of the insertion of gold carbenes into the C-H and O-H bonds in phenol.^[3] Moreover, this methodology is useful in organic synthesis, late-stage modification of natural products and design of domino reactions.^[4,5] Recently, we also realized the *ortho*-selective C-H functionalization of phenols.^[6]



Scheme-1

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* 国家自然科学基金 (No.21572065), 上海市浦江人才计划 (No. 14PJ1403100) 资助项目

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二氧化碳在杂环合成中的应用*

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温室气体分子二氧化碳 (CO₂) 是廉价易得且可再生的碳一 (C1) 资源，利用其制备重要的杂环分子具有重要的学术价值和社会意义。¹ 由于 CO₂ 在热力学和动力学方面具有较高的稳定性，反应活性较低，CO₂ 活化具有巨大的挑战。该领域虽然已有一定的进展，但反应体系和底物范围都有较大的局限性。我们课题组针对氧化羰基化反应中存在的问题 (需要使用剧毒的 CO 和氧化剂)，利用无毒的 CO₂ 代替 CO 制备重要的喹啉酮类² 和香豆素类化合物³ (式 1)，无需使用过渡金属催化剂或者氧化剂，不仅变废为宝，降低成本，还提高了反应的实用性。此外，我们利用 CO₂ 参与三组分反应，在铜催化条件下实现了烯丙胺的氧三氟甲基化反应，避免了胺基三氟甲基化这种背景反应，高效高选择性地合成具有重要生理活性的含氟噁啉酮类化合物⁴ (式 2)，为其活性检测和药物开发提供高效便捷的合成方法学，具有重要的学术意义和应用前景。

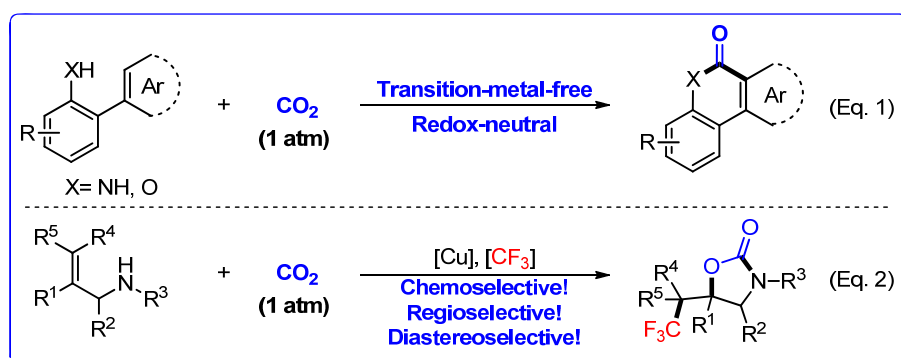


Figure-1 Heterocycles formation via CO₂ utilization

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铜催化 P-H/C-H 键选择性转化反应*

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铜低毒、廉价、易得, 在催化反应中官能团适应性广, 因铜盐具有适度的配位能力、氧化能力, 在催化反应中应用广泛, 特别是在选择性 E-H 键转化反应中应用广泛。

近期, 本课题组研究了铜催化 P-H/C-H 键选择性转化反应, 如: 末端炔烃高选择性不对称交叉偶反应合成不对称 1,3-二炔、末端炔烃的选择性氢化反应、P-N/P-C/P-P 键形成反应, C-N 三键断裂转移 N 原子的反应。这些反应可构建农药、医药及功能材料分子的重要结构骨架。

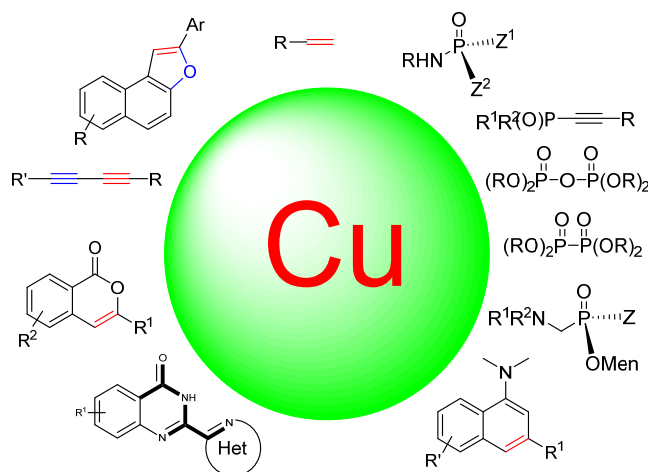


Figure-1. Copper catalyzed selective transformation of P-H/C-H bonds

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OL14

Synthesis of Planar Chiral Ferrocenes via Palladium-Catalyzed C-H Bond Activation*

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Planar chiral ferrocenes have received great attention in view of their increasing importance in the fields of asymmetric catalysis, enantioselective synthesis, and materials science.^[1] They have been widely used as privileged scaffolds for the synthesis of efficient ligands and catalysts. A widely used method is diastereoselective directed ortho-metalation reactions of ferrocenes with central chirality. Enantioselective directed ortho-metalation reactions have also been disclosed to introduce planar chirality into non-chiral ferrocenes. Both of these methods need stoichiometric chiral auxiliaries or chiral ligands to control the selectivity, and organolithium reagents are required as a strong base in these reactions.

Here we had developed efficient routes towards synthesis of planar chiral ferrocenes through a palladium-catalyzed C-H bond activation of N,N-dimethylaminomethylferrocene with alkyne, alkene, and diketone.^[2] All of the reactions are essentially the desymmetrization of cyclopentadiene rings in ferrocene by enantioselective C-H activation. Palladium-catalyzed enantioselective C-H activation has emerged as a simple, convenient, and efficient tool to synthesize planar chiral ferrocenes.

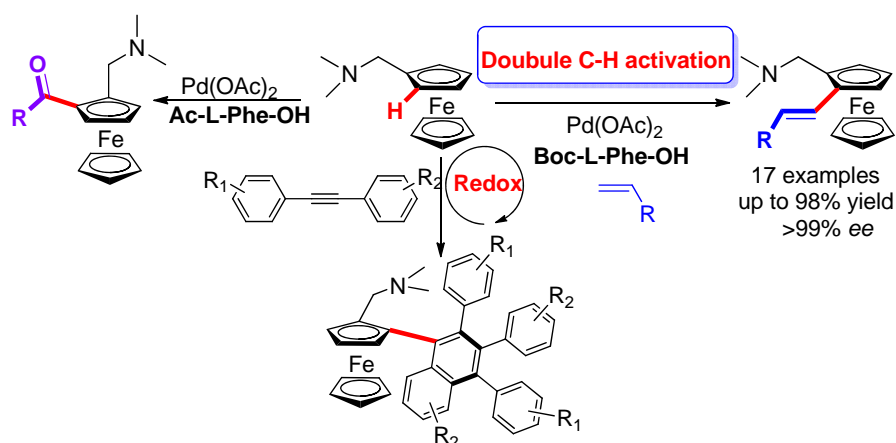


Figure 1. Synthetic strategy to Planar chiral ferrocenes

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Cobalt-Catalyzed Chemodivergent Transfer Hydrogenation of Nitriles*

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The catalytic reduction of nitriles represents an efficient and green one-step synthesis of valuable amine products.^[1] However, there is a crucial selectivity problem for this reaction due to the formation of mixtures of primary amines, secondary amines, imines^[2] and even tertiary amines. Within these possibilities, the selective synthesis of a certain amine product constitutes a particular challenge, especially for secondary and tertiary amines.

On the other hand, Nitriles are conventionally reduced using stoichiometric amounts of sensitive metal hydrides, which suffers from waste production and low functional group tolerance. Clearly, the catalytic hydrogenation of nitriles is a more sustainable synthetic route.

In line of our interests in the development of novel cobalt catalysts for transfer hydrogenation reactions,^[3] herein we describe the first cobalt catalyzed transfer hydrogenation of nitriles for a chemodivergent synthesis of primary and secondary amines.^[4] The selectivity control was achieved by using different solvents and cobalt catalysts. Moreover, a reductive amination of nitriles has been also realized in the presence of various amine substrates to produce unsymmetric secondary and tertiary amines (Figure 1).

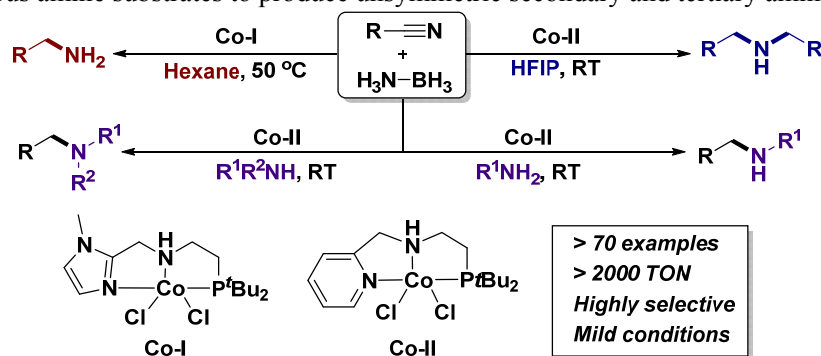


Figure 1: Cobalt-catalyzed Transfer Hydrogenation and Reductive Amination of Nitriles

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* 中组部第十一批“千人计划”青年人才项目

**通讯联系人

OL16

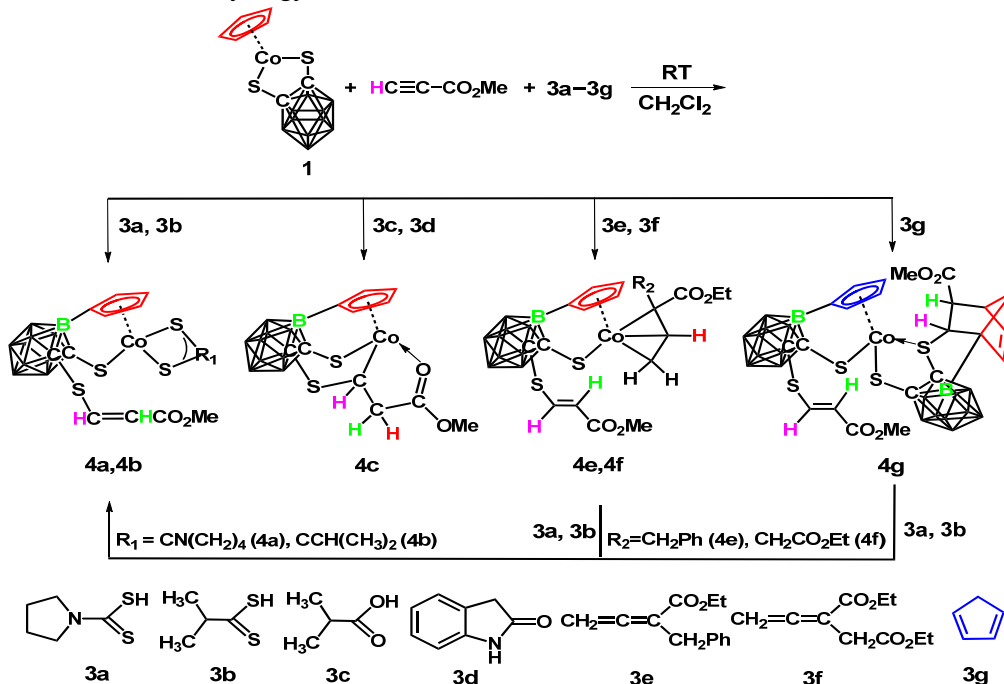
Inert B–H Activation by Metal–Metal Cooperativity*

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Our group has focused on a single metal induced cage B–H functionalization of carborane.^[1] In this strategy, the B–H bond of carborane at sites close to metal atom can be activated accompanied by a formation of M–B bond. In many cases, M–B bonds are stable enough and prevent further chemical transformations, which is different from traditional M–C bond. The narrow scopes of substrates and difficult further chemical transformations of intermediates containing a M–B bond constitute major problems in a single-metal system. Therefore, we propose to use metal–metal cooperativity which may lower energy barrier for the redox pathway of B–H activation and B–X bond formation. Here we report B–Cl bond formation using bimetallic system and provide mechanistic evidence for B–H activation through metal–metal redox synergy.^[2]



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** 通讯联系人

OL17

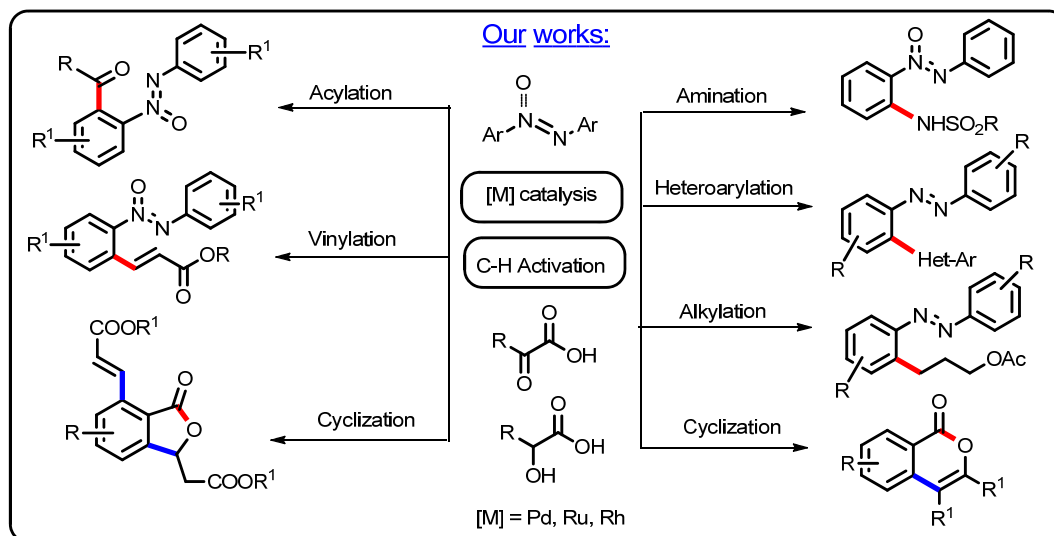
Constructing New Chemical Bonds via Transition Metal Catalyzed C–H Activation and Functionalization*

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Organic reactions that involve transition metal-catalyzed direct functionalization of non-activated C(sp²)-H bonds represent one of the attractive transformations, which offer significant advantages over the common couplings in terms of atom- and step-economy.^[1] Following the understanding of mechanistic aspects of C–H activation by transition metal catalysis, great efforts in our laboratory focused on the development of new protocols for the synthesis of potentially useful organic molecules (Following Scheme).^[2] Early in 2013, we found “N=N” serving as a very good directing group can well coordinate with transition metals, such as Pd, Ru and Rh, to form active species for versatile couplings. These examples of *ortho* C–H functionalization of azobenzenes mainly include acylation, vinylation, alkylation, heteroarylation and amination, which provide new approaches for the synthesis of complex azo molecules. Based on the C–H activation, a new decarboxylative strategy was successfully used for the Ru-catalyzed cyclization of α -keto acids with unsaturated alkenes or alkynes, in which high regioselectivity and good group tolerance was observed.



Scheme 1

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** 通讯联系人

OL18

Pd-Catalyzed Coupling Reaction of Azide with σ -donor / π -acceptor*

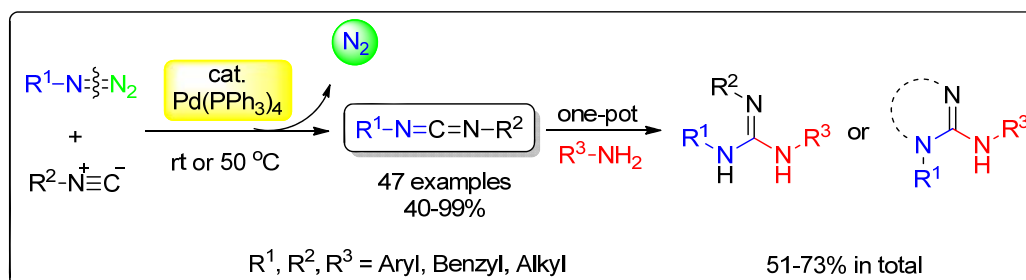
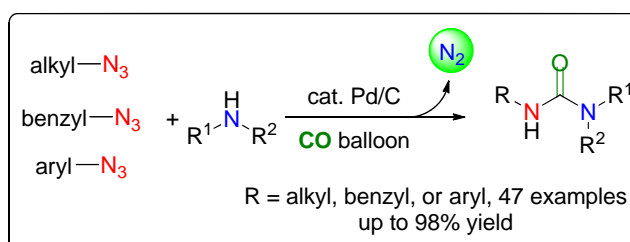
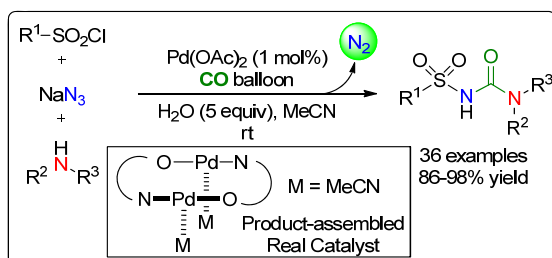
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Transition-metal-catalyzed selective C–N bond formation of azides *via* a highly reactive metal–nitrene intermediate has attracted great attention recently due to its apparent synthetic value for assembling diverse N-containing functional molecules. Conventional transformations involve C–H amination and aziridination, which are usually catalyzed by Rh, Ru, Fe, Ir, etc.

Here we would like to report a Pd-catalyzed coupling reaction between azide and σ -donor / π -acceptor ligand, CO and isocyanide, to construct active isocyanate / carbodiimide intermediate. In Pd(II) catalyzed carbonylation of sulfonylazides, which provides a new approach to sulfonylureas, the generation of a bridged bimetallic palladium species derived from the product sulfonylurea is disclosed as the crucial step for the catalytic cycle.^[1] For aliphatic and aromatic azides, simple Pd/C could catalyze the cross-carbonylation of azides with amines to give unsymmetric ureas.^[2] In addition, Pd-catalyzed efficient cross-coupling of azides with isocyanides is also developed, providing a general synthetic route to unsymmetric carbodiimides. A tandem amine insertion cascade to obtain unsymmetric trisubstituted guanidines has been achieved in a one-pot fashion.^[3]



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** 通讯联系人

OL19

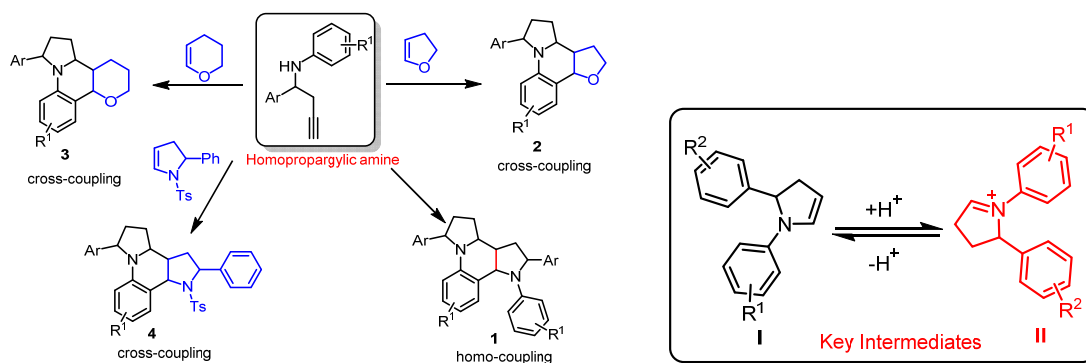
Hydroamination cyclization-Povarov cascade reactions of homopropargylic amine with electron-rich olefins*

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Hydroamination of alkynes through an intra- or intermolecule is an array of important reactions for the construction of natural products and pharmaceuticals. The noble metal gold^[1,2] or Pt complexes display unique behavior towards unactivated alkynes. Our group has recently developed a novel cascade cyclization reaction of homopropargylic amines catalyzed by copper (Scheme 1). This reaction leads to the formation of a tetracyclic framework **1**^[3]. And Intermediate **I** can only act as a **2C** synthon to react with additional simple imines (acting as **4C** synthon) via a Povarov reaction to form a series of hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline derivatives in good to high yields^[4]. Intriguingly by this, we herein developed a novel cascade reaction of homopropargylic amine with electron-rich olefins, such as 2,3-dihydrofuran, 3,4-2*H*-dihydropyran, *N*-Ts cycloenamine to give the fused heterocycles **2-4** in moderate to high yields, respectively. Notably, a key intermediate was involved, the intermediate **II** formed through an isomerization of intermediate **I**. And the inhibition of a competitive self-dimerization of homopropargylic amines remains a great challenge.



Scheme 1. Divergent cascade reactions of homopropargylic amines with electron-rich olefins

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OL20

Design of Redox-Responsive Organometallic Molecular Materials Based on Ru-C Bond*

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Stimuli-responsive compounds are important functional materials that are useful in a wide range of applications including chemical sensing, molecular machines, optoelectronic devices, energy conversion and storage, drug delivery, and medical diagnosis and treatment. Redox-responsive compounds are a special type of responsive materials, which display reversible changes among different redox states in response to electrochemical potential or chemical oxidants or reductants. They are characterized by easy operation, high sensitivity, and good reversibility, etc.

Polypyridine transition-metal complexes are important functional materials that have been widely used in various optoelectronic applications. However, normal polypyridine complexes have rather high oxidation potentials, which make them disadvantageous as redox-responsive materials. Here we would like to report an efficient molecular design strategy based on Ru-C bond, which has been used to prepare a series of redox-responsive organometallic materials with one, two, three, or four redox-active sites (Figure 1)^[1]. The applications of these materials in near-infrared electrochromism, molecular logic gates, and molecular electronics will be discussed^[2].

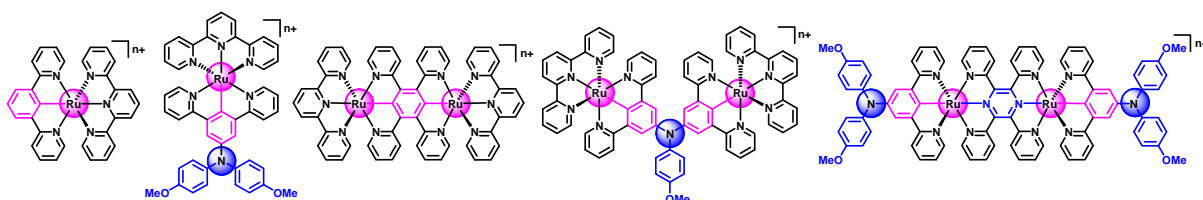


Figure 1. Redox-responsive cyclometalated ruthenium complexes with multiple redox-active sites

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** 通讯联系人

OL21

Aromaticity in Organometallics: The Magic of Transition Metals*

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Aromaticity, one of the most fundamental concepts in chemistry, has attracted considerable attention from both theoreticians and experimentalists. However, besides metallabenzenes, other transition metal-involved aromatics are less developed. Here, we report the magic rule of transition metals in several metallaaromatics by density functional theory calculations. Specifically, Craig-type Möbius aromaticity was first determined in osmapentalynes. The incorporation of the osmium centre not only reduces the ring strain of the parent pentalene, but also converts its Hückel anti-aromaticity into Craig-type Möbius aromaticity in the metallapentalynes.^[1] Secondly, the transition metal fragments also make both 16 and 18e osmapentalenes Möbius aromatic, indicating that the aromaticity in osmapentalene is rooted in osmapentalenes.^[2] Thirdly, the transition metal could “kill two birds with one stone” in stabilization of two classical antiaromatic frameworks, cyclobutadiene and pentalene.^[3] Fourthly, an introduction of a transition metal leads to σ -aromaticity first dominating in an unsaturated ring.^[4] Last but not least, the incorporation of the transition metal substituents can not only convert non-aromaticity in the parent indolium into aromaticity, but also outperform the traditional main group elements.^[5] All these findings show a magic power of transition metals originating from participation of more electrons from *d* orbitals in aromaticity rather than one electron for the carbon atom, opening an avenue to the design of novel metalla-aromatics.

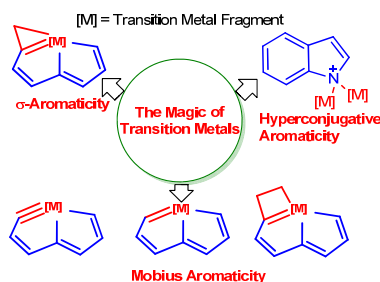


Figure 1. Schematic illustration of the magic role of transition metals in unconventional aromaticity

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**通讯联系人

钯催化有机反应机理的理论研究 *

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由于在有机合成和材料设计等领域的大规模应用, 钯催化的反应已经引起了科学家们广泛的兴趣。最近几年, 我们研究小组在金属有机领域, 尤其是钯催化有机反应的机理方面做了一系列工作, 主要包括钯和镍催化联烯的氢硅化反应机理和区域选择性, 钯和镍催化酸酐和炔烃的环加成反应机理和反应选择性, 钯催化氯甲基萘和吗啉的脱芳香化反应机理, 钯催化 2-炔基卤代苯和炔丙基醇的双环化反应机理, 钯催化分子内芳香羧酸和芳基卤脱酸的反应机理以及底物相关的决速步骤研究, 钯催化分子内硅基 C(sp³)-H 键的芳基化反应机理, 钯催化分子内脱酸氮丙环化反应机理, 以及中性 Pd(IV)配合物的还原消除反应机理, 并在中国科学撰写钯催化 C-C 键形成机理的理论计算综述一篇。

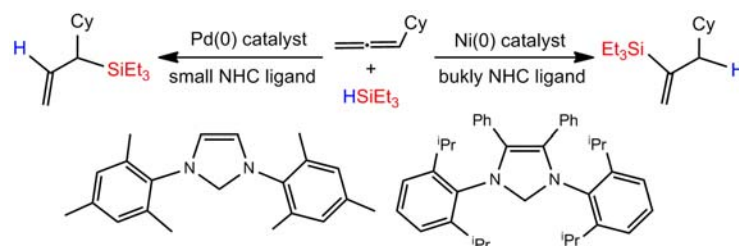


Figure 1 The hydrosilylation of allene via Pd and Ni catalysts with small and bulky NHC ligands.

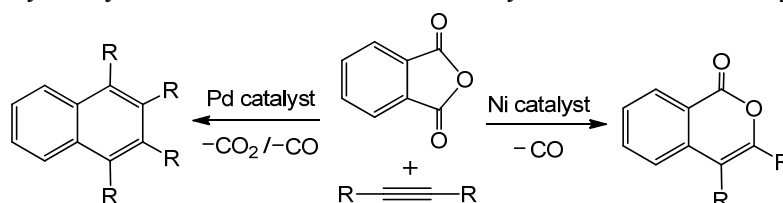


Figure 2. Mechanisms and reactivity differences for cycloaddition of anhydride to alkyne catalyzed by palladium and nickel catalysts

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Dual-Catalytic Asymmetric Radical Functionalization of Alkenes*

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Unactivated alkenes represent excellent building blocks for chemical synthesis, thus providing an exceptional opportunity for the construction of complex molecules. The selective addition of both carbon- and heteroatom-centered radicals to unactivated alkenes represents an exceptionally efficient way for the direct functionalization of such alkenes.^[1] Although great endeavors have been devoted to various racemic versions of radical functionalization of alkenes, the development of catalytic asymmetric methods has proven a formidable challenge largely due to the intrinsic reactivity of the involved odd-electron species.^[2] To address this challenge and as part of our continued interest in the area of radical chemistry^[3] and asymmetric catalysis,^[4] we have successfully developed some dual-catalytic asymmetric strategies for both asymmetric radical 1,2-difunctionalization of alkenes and novel enantioselective remote C-H/C bond functionalization triggered by radical addition of alkenes/alkynes (Figure 1).

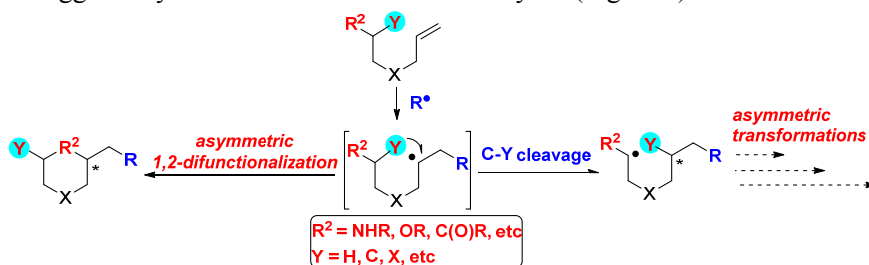


Figure 1. Our strategy

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OL24

Copper-promoted Direct *N*-/*O*-alkenylation of N-O Bonds and Their Applications*

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N-O bond compounds such as *O*-aryloxime or *O*-alkenyloxime ethers, nitrones and *N*-oxides, are important functional groups in various natural products, pharmaceuticals, and molecular drug design. Due to the N-O bond always acts as ambident nucleophiles (*O*- or *N*- nucleophile), the construction of N-O bond compounds by arylation or alkenylation was attracted much attention. These compounds have been successfully applied in to 1,3-rearrangement, 3,3-rearrangement, 2,3-rearrangement, C-H activation, radical trapping reaction or relative transformations.^[1]

Metal-free strategy to construct N-O bond compounds by direct *N*- or *O*-arylation with diaryliodonium salts was developed in our group in recent years.^[2] Here we would like to present a copper-promoted alkenylation of N-O bonds with alkenyl boronic acids. We found that direct *N*- or *O*-alkenylation of N-O bonds could be controlled by copper catalysts under mild conditions. DFT calculations revealed that the direct *N*-alkenylation was favourable from reductive elimination of Cu(III) species. *N*-Oxides, *N*-alkenyl nitrones, and α -amino ketones could be easily obtained in this strategy.

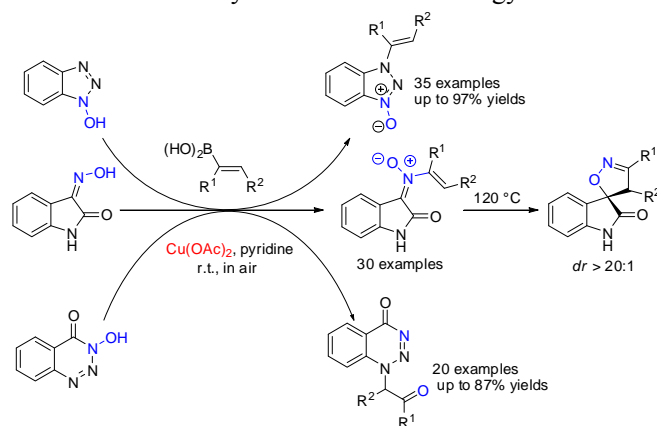


Figure 1. Copper-promoted *N*- or *O*-alkenylation of N-O bonds

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P96	Copper-Catalyzed Intermolecular Trifluoromethylthiocyanation of Alkenes: Convenient Access to CF ₃ -Containing Alkyl Thiocyanates	梁兆利, 王飞, 陈品红, 刘国生**	中国科学院上海有机化学研究所
P97	Palladium-Catalyzed Intramolecular Aminotrifluoromethoxylation of Alkenes	陈朝煌, 陈品红, 刘国生**	中国科学院上海有机化学研究所
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P113	Potassium Complexes Supported by Monoanionic Tetradentate Amino-Phenolates Ligands: Synthesis, Structure and Catalysis in ROP of rac-Lactide	姚晨晖, 马海燕**	华东理工大学化学系
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P117	苯并唑膦镁化合物的合成与性质研究	翁潇潇, 宋东东, 刘永祥, 皮承富**	杭州师范大学钱江学院
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P127	Syntheses and Electrochemistry of Thioamide-based Complexes	吴志丹, 石尧成**	扬州大学化学与化学工程学院
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P169	Redox-Neutral Palladium-Catalyzed C-H Functionalization to Form Isoindolinones with Carboxylic Acids or Anhydrides as Readily Available Starting Materials	梁洪文, 魏晔**	第三军医大学
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P173	Artificial Photosynthetic Systems for Chemical Transformation	吴骊珠**	中国科学院理化技术研究所
P174	Visible Light Initiated Synthesis of Substituted Pyrroles and Pyrazoles at Ambient Conditions	雷涛, 范秀为, 周超, 黄程, 佟振合, 吴骊珠**	中国科学院理化技术研究所

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P176	碘催化杂环氮氧化物 C-H 键的直接烯基化反应	张振豪, 崔秀灵**, 吴养洁**	郑州大学化学与分子工程学院
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