

TRANSACTIONS OF
K.C. WONG EDUCATION FOUNDATION
SUPPORTED LECTURES

王宽诚教育基金会

学术讲座汇编

主 编 周哲玮

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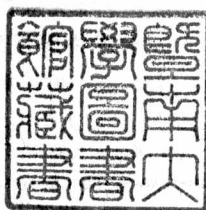
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王宽诚教育基金会

学 术 讲 座 汇 编

(第 33 集)

主编 周哲玮



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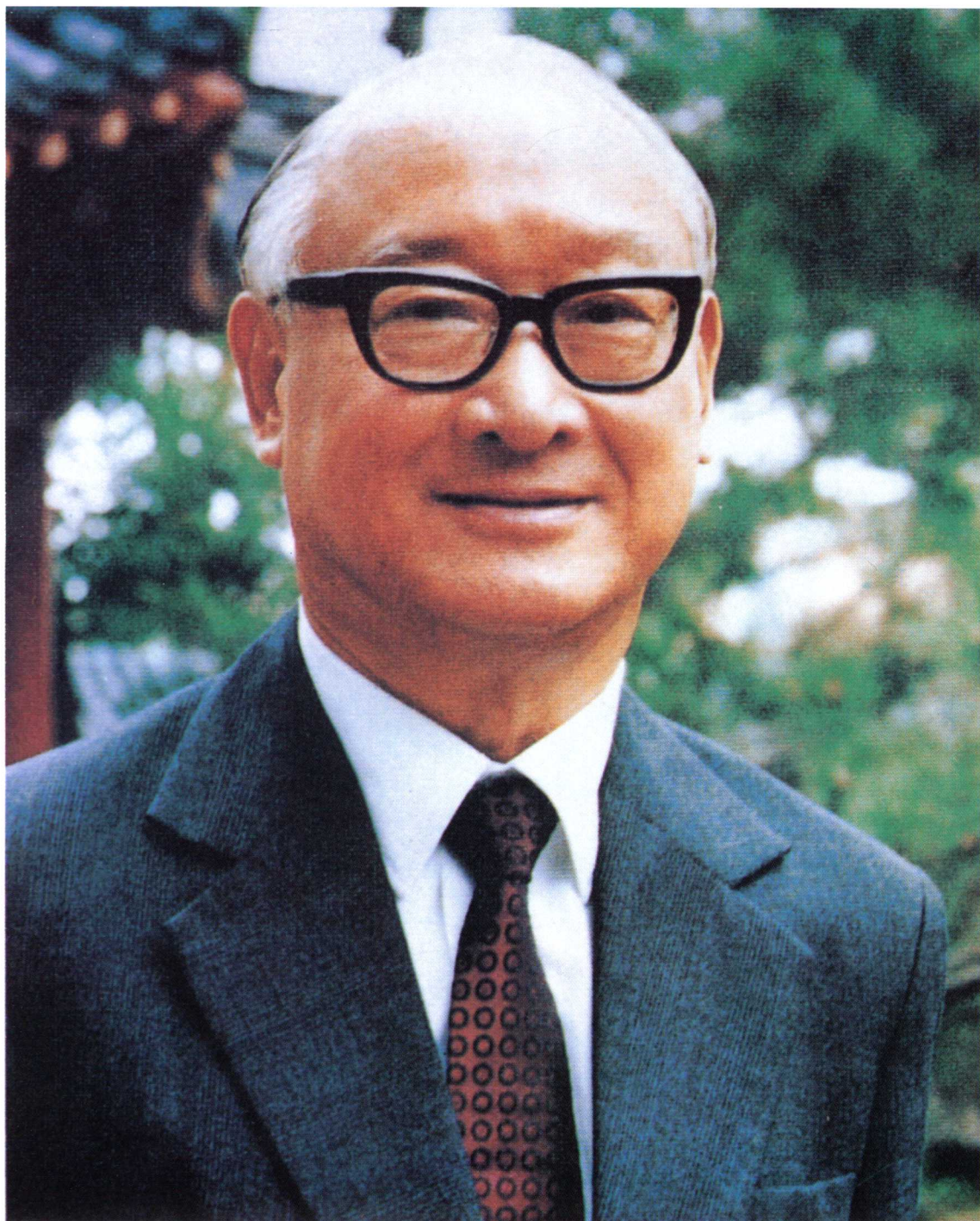
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王寬誠先生

K.C.WONG(1907-1986)

惠 存

王宽诚教育基金会敬赠

2011 年 12 月

谨以此书纪念本会创建人、故董事会主席王宽诚先生

王宽诚教育基金会

**DEDICATED TO THE MEMORY OF MR. K. C. WONG,
FOUNDER OF THE FOUNDATION AND THE LATE
CHAIRMAN OF THE BOARD OF DIRECTORS**

K. C. WONG EDUCATION FOUNDATION

王宽诚教育基金会简介

王宽诚先生(1907—1986)为香港著名爱国人士,热心祖国教育事业,生前为故乡宁波的教育事业做出积极贡献。1985年独立捐巨资创建王宽诚教育基金会,其宗旨在于为国家培养高级技术人才,为祖国四个现代化效力。

王宽诚先生在世时聘请海内外著名学者担任基金会考选委员会和学务委员会委员,共商大计,确定采用“送出去”和“请进来”的方针,为国家培养各科专门人才,提高内地和港澳高等院校的教学水平,资助学术界人士互访以促进中外文化交流。在此方针指导下,1985、1986两年,基金会在国家教委支持下,选派学生85名前往英、美、加拿大、德国、瑞士和澳大利亚各国攻读博士学位,并计划资助内地学者赴港澳讲学,资助港澳学者到内地讲学,资助美国学者来国内讲学。正当基金会事业初具规模、蓬勃发展之时,王宽诚先生一病不起,于1986年年底逝世。这是基金会的重大损失,共事同仁,无不深切怀念,不胜惋惜。

1987年起,王宽诚教育基金会继承王宽诚先生为国家培养高级技术人才的遗愿,继续对中国内地、台湾及港澳学者出国攻读博士学位、博士后研究及学术交流提供资助。委请国家教育部、中国科学院和上海大学校长钱伟长教授等逐年安排资助学术交流的项目。相继与(英国)皇家学会、法国科研中心、德国学术交流中心、法国高等科学研究院等著名欧洲学术机构合作,设立“王宽诚(英国)皇家学会奖学金”、“王宽诚法国科研中心奖学金”、“王宽诚德国学术交流中心奖学金”、“王宽诚法国高等科学研究院奖学金”,资助具有副教授或同等职称以上的中国内地学者前往英国、法国、德国等地的高等学府及科研机构进行为期2至12个月之博士后研究。

王宽诚教育基金会过去和现在的工作态度一贯以王宽诚先生倡导的“公正”二字为守则,谅今后基金会亦将秉此行事,奉行不辍,借此王宽诚教育基金会《学术讲座汇编》出版之际,特简明介绍如上。王宽诚教育基金会日常工作繁忙,基金会各位董事均不辞劳累,做出积极贡献。

前 言

王宽诚教育基金会是由已故全国政协常委、香港著名工商企业家王宽诚先生(1907—1986)出于爱国热忱,出资一亿美元于1985年在香港注册登记创立的。

1987年,基金会开设“学术讲座”项目,此项目由当时的全国政协委员、历任第六、七、八、九届全国政协副主席、著名科学家、中国科学院院士、上海大学校长、王宽诚教育基金会贷款留学生考选委员会主任委员兼学务委员会主任委员钱伟长教授主持。由钱伟长教授亲自起草设立“学术讲座”的规定,资助内地学者前往香港、澳门讲学,资助美国学者来中国讲学,资助港澳学者前来内地讲学,用以促进中外学术交流,提高内地及港澳高等院校的教学质量。

本汇编收集的文章,均系各地学者在“学术讲座”活动中的讲稿,文章内容有科学技术,有历史文化,有经济专论,有文学,有宗教和中国古籍研究等。本汇编涉及的学术领域颇为广泛,而每篇文章都有一定的深度和广度,分期分册以《王宽诚教育基金会学术讲座汇编》的名义出版,并无偿分送国内外部分高等院校、科研机构 and 图书馆,以广流传。

王宽诚教育基金会除资助“学术讲座”学者进行学术交流之外,还资助由国内有关高等院校推荐的学者前往欧、美、亚、澳等参加国际学术会议,出访的学者均向所出席的会议提交论文,这些论文亦颇有水平,本汇编亦将其收入,以供参考。

王宽诚教育基金会学务委员会

凡 例

（一）编排次序

本书所收集的王宽诚教育基金会学术讲座的讲稿及由王宽诚教育基金会资助学者赴欧、美、亚、澳等参加国际学术会议的论文均按照文稿日期先后或文稿内容编排刊列,不分类别。

（二）分期分册出版并作简明介绍

因文稿较多,为求便于携带,有利阅读与检索,故分期分册出版,每册约 150 页至 220 页不等。为便于读者查考,每篇学术讲座的讲稿均注明作者姓名、学位、职务、讲学日期、地点、访问院校名称。内地及港、澳学者到欧、美、澳及亚洲的国家和地区参加国际学术会议的论文均注明学者姓名、参加会议的名称、时间、地点和推荐的单位。上述两类文章均注明由王宽诚教育基金会资助字样。

（三）文字种类

本书为学术性文章汇编,均以学术讲座学者之讲稿原稿或参加国际学术会议者向会议提交的论文原稿文字为准,原讲稿或论文是中文的,即以中文刊出,原讲稿或论文是外文的,仍以外文刊出。

目 录 CONTENTS

Gold Catalyzed Organic Transformation Reactions	CHE Chi-ming (1)
Openness: Freedom and Control	SIU Kin Wai Michael (31)
City Planning for the New Age	SIU Kin Wai Michael (44)
Public Sphere and the Third Realm	SIU Kin Wai Michael (58)
Reception: A Theoretical Review	SIU Kin Wai Michael (64)
Main Factors Affecting Soil-Water Characteristic Curve	SUN De-an, LI Jie (72)
Molecular Dynamics Study on Different Melting Behaviours of Cu_N ($N=51-53$) Clusters	ZHANG Lin, SUN Hai-xia (79)
Finite Element Simulation of Mix Driven by Electroosmotic Flow in Microchannels	LIU Ying, GE Zhong-nian (90)
Review and Verification of Chinese Code for Seismic Design from Damage of Buildings During Wenchuan Earthquake	LI Ying-min, LIU Li-ping, JI Shu-yan, HAN Jun, TIAN Qi-xiang (98)
Improved Design for Digital Audio Effect of Flanging	CHEN Jian-ping, JI Xiao-dong, GU Xiang, ZHOU Jin-jie (110)
Multiple Classifier Combination for Target Identification from High Resolution Remote Sensing Image	DU Pei-jun, SUN Hao, ZHANG Wei (116)
Numerical Analysis on the Radiant Characteristics of Three-dimensional Random Rough Surfaces	FENG Yan-hui, LIU Wei, ZHANG Xin-xin (127)
战后日本发展模式——经济发展中的政府作用	王新生 (139)
战后东亚地区政治发展——另一种类型的政治现代化	王新生 (148)
发达城市的城乡收入差距实证研究——基于 Panel Data 模型的应用	郑方贤 (159)
Investigation of Different Casing Treatments for Flow Control in a Centrifugal Compressor with Splitter Blade	LIU Bo, WANG Qing-wei, CHEN Yun-yong (168)
Model-based Thermal Analysis of Piezoelectric Transducers	FU Bo, HEMSEL Tobias (179)
Kinetics Study on the Gasification of the Poor Quality Coal	LI Xiao-hong, CHANG Li-ping, LÜ Yong-kang, LI Fan (189)
Synthesis, Characterization and Properties of $(\text{ppy})_2\text{Ir}(\text{acylamido})$: Application of Acylamide as Ligand in Phosphorescence Materials	YANG Wei, DING Yu-qiang (197)
编后记	(211)

Gold Catalyzed Organic Transformation Reactions

CHE Chi-ming *

(Department of Chemistry, The University of Hong Kong, Hong Kong, P. R. China)

Abstract: Transition metal-catalyzed organic transformations have led to many useful tools for organic synthesis over the past several decades. Gold is the latest metal to enter the arena of transition metal catalysis. Gold catalysis has developed impressively over the past decade, and has already provided valuable contributions to organic synthesis. The unique properties of gold complexes, including high carbophilicity, insensitivity towards air/moisture conditions and high reactivity under mild conditions, render them to be powerful catalysts for unprecedented organic transformations. In particular, gold-catalyzed tandem C—C bond formations have been receiving a growing interest due to the intriguing selectivity and high atom economy. Recently, we have developed a variety of simple and highly efficient methods for the synthesis of structurally diverse organic compounds of increased complexity, where several C—C bonds can be formed in a one-pot reaction from simple starting materials catalyzed by gold complexes. We believe that these works help in the fundamental study of gold chemistry, and provide new and efficient synthetic methods for organic synthesis. On the other hand, despite the success of gold catalysts, surprisingly few enantioselective gold (I)-catalyzed reactions have been reported. This is possibly due to the linear coordination geometry of gold(I) complex, which alleviates the steric interactions between the chiral inducer and the reactive functional group of the substrate. To circumvent this problem, we recently reported the latest development within enantioselective gold catalysis, namely the use of cooperative catalysis composed of an achiral gold complex and a chiral organic molecule for gold(I)-catalyzed asymmetric organic reaction. This work would serve as a complementary approach to the conventional chiral gold(I)-catalyzed asymmetric organic synthesis. In this seminar, the gold(I)-catalyzed tandem

* 支志明, 中国科学院院士, 香港大学化学系。由王宽诚教育基金会资助, 于 2009 年 9 月赴清华大学、中国科学院理化技术研究所及中国科学院化学研究所讲学, 此为其讲学内容。

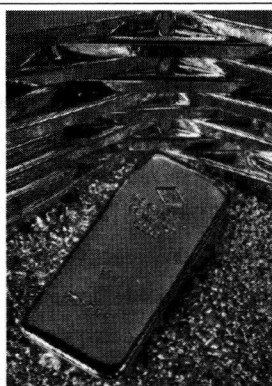
reactions with excellent enantio-, regio- and chemoselectivities will be presented. We will also disclose our unpublished results on enantioselective intermolecular hydroarylation of allenes with indoles catalyzed by chiral binuclear gold(I) complex.

Key words: gold chemistry, gold catalysis, organic transformations, tandem C—C bond formations, chiral binuclear gold(I) complex, enantioselective, regioselective, chemoselective, hydroarylation, allenes, indoles

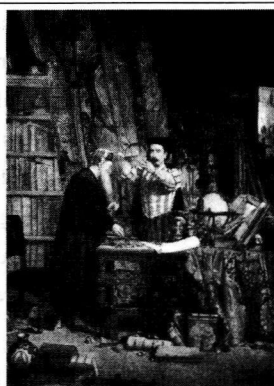
本讲座内容以 PPT 格式演示。

Outline

- Introduction
- Gold-catalyzed nucleophilic addition to alkenes
- Gold-catalyzed nucleophilic addition to alkynes and related tandem reactions
- Gold-catalyzed nucleophilic addition to allenes
- Summary



Gold is one of earliest known metals long before copper, iron, zinc and lead. It stands for wealthy.



The best-known goals of the alchemists were the transmutation of common metals to gold. The practical aspect of alchemy generated the basics of modern chemistry.

Periodic Table of the Elements

■ hydrogen

■ alkali metals

■ alkali earth metals

■ transition metals

■ poor metals

□ nonmetals

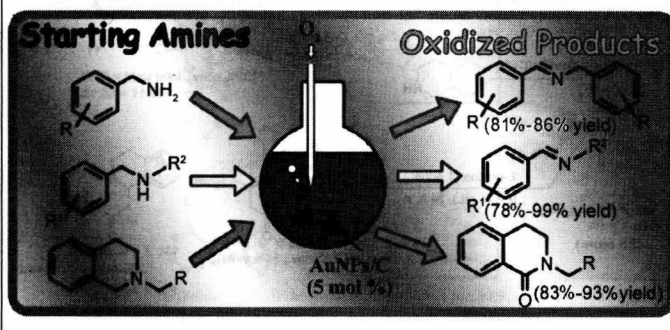
■ noble gases

■ rare earth metals

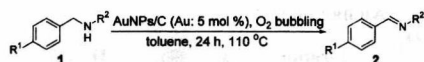
H ¹																	B ⁵	C ⁶	N ⁷	O ⁸	F ⁹
Li ³	Be ⁴															Ne ¹⁰					
Na ¹¹	Mg ¹²															Ar ¹⁸					
K ¹⁹	Ca ²⁰	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰					As ³³	Se ³⁴	Br ³⁵			
Rb ³⁷	Sr ³⁸	Y ³⁹	Zr ⁴⁰	Nb ⁴¹	Mo ⁴²	Tc ⁴³	Ru ⁴⁴	Rh ⁴⁵	Pd ⁴⁶	Ag ⁴⁷	Cd ⁴⁸					Sb ⁵¹	Te ⁵²	I ⁵³			
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf ⁷²	Ta ⁷³	W ⁷⁴	Re ⁷⁵	Os ⁷⁶	Ir ⁷⁷	Pt ⁷⁸	Au ⁷⁹	Hg ⁸⁰					Po ⁸⁴	At ⁸⁵				
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹	Unq ¹⁰⁴	Unh ¹⁰⁵	Unl ¹⁰⁶	Unl ¹⁰⁷	Unl ¹⁰⁸	Unl ¹⁰⁹	Unl ¹¹⁰												

Ce ⁵⁸	Pr ⁵⁹	Nd ⁶⁰	Pm ⁶¹	Sm ⁶²	Eu ⁶³	Gd ⁶⁴	Tb ⁶⁵	Dy ⁶⁶	Ho ⁶⁷	Er ⁶⁸	Tm ⁶⁹	Yb ⁷⁰	Lu ⁷¹
Th ⁹⁰	Pa ⁹¹	U ⁹²	Np ⁹³	Pu ⁹⁴	Am ⁹⁵	Cm ⁹⁶	Bk ⁹⁷	Cf ⁹⁸	Es ⁹⁹	Fm ¹⁰⁰	Md ¹⁰¹	No ¹⁰²	Lr ¹⁰³

Aerobic Oxidation of Benzylic Amines by “AuNPs/C + O₂” Protocol



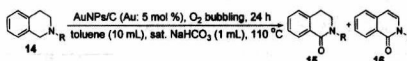
Aerobic Oxidation of Benzylic Amines by “AuNPs/C + O₂” Protocol



Entry	Substrate	R ¹	R ²	Product	Conv. / % ^[b]	Yield / % ^[b]
1	1b	OMe	Ph	2b	100	95
2	1b	OMe	Ph	2b	100 ^[d]	97
3	1b	OMe	Ph	2b	81 ^[d]	95
4	1c	Me	Ph	2c	100	97
5	1d	<i>n</i> Bu	Ph	2d	100	98
6	1e	H	Ph	2e	100	96
7	1f	Cl	Ph	2f	94	99
8	1g	Br	Ph	2g	88	99
9	1h	NMe ₂	Ph	2h	100	95
10	1i	OMe	4-MeOC ₆ H ₄	2i	100	95
11	1j	H	(CH ₂) ₃ CH ₃	2j+2a	100	93 (79:14)
12	1k	H	(CH ₂) ₃ Ph	2k+2a	100	88 (78:10)
13	1l	H	(CH ₂) ₃ CN	2l	100	88
14	1m	H	Cy	2m+2a	100	81 (58:23)
15	1n	NO ₂	Cy	2n+2a	71	93 (48:45)
16	1o	OMe	Cy	2o	100	86

[a] Reaction conditions: amines (0.4 mmol), AuNPs/C (Au: 5 mol %), toluene (8 mL), O₂ bubbling, 110 °C, 24 h; unless otherwise stated. [b] Conversion and yield were determined by ¹H-NMR using Ph₃C=CH₂ as the internal standard. [c] Yield was calculated based on substrate conversion. The ratio of products is shown in parentheses. [d] AuNPs/C (Au: 1 mol %), 17 h. [e] AuNPs/C (Au: 0.5 mol %), 17 h.

Aerobic Oxidation of Benzylic Amines by "AuNPs/C + O₂" Protocol

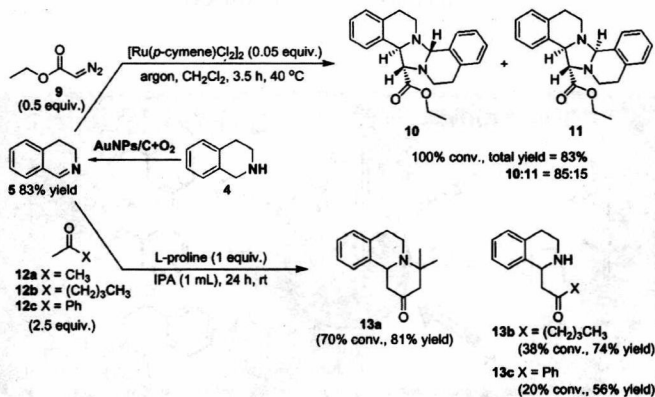


Entry	Substrate	R	Products	Conv., % ^[b]	Yield, % ^[c]
1	14a	Me	15a+16a	100	93(32:61) ^[d]
2	14a	Me	16a	27	90 ^[d]
3	14a	Me	15a+16a	100	95 (90:5) ^[d]
4	14b	Et	15b+16b	100	91 (79-12) ^[d]
5	14a	Me	15a+16a	100	96 (92:4)
6	14b	Et	15b+16b	100	99 (93:6)
7	14c	nPr	15c+16c	100	90 (85:5)
8	14d	nBu	15d+16d	100	90 (83:7)
9	14e	Octyl	15e+16e	100	94 (88:6)
10	14f	Bn	15f+16f	100	97 (93:4)

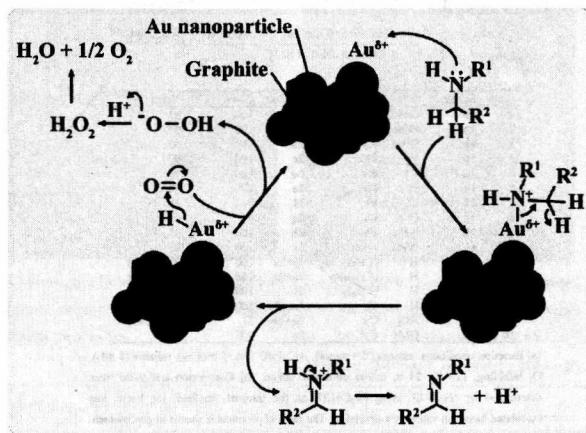
[a] Reaction conditions: amine (0.4 mmol), AuNPs/C (Au: 5 mol %), toluene (10 mL), saturated NaHCO₃ aqueous solution (1 mL), O₂ bubbling, 110 °C, 24 h; unless otherwise stated. [b] Conversion and yield were determined by ¹H-NMR using Ph₃C-CH₃ as the internal standard. [c] Yield was calculated based on substrate conversion. The ratio of products is shown in parentheses. [d] Without addition of saturated NaHCO₃ aqueous solution. [e] Only anhydrous toluene (10 mL) was used as solvent without addition of saturated NaHCO₃ aqueous solution. [f] H₂O (1 mL) was used instead of saturated NaHCO₃ aqueous solution.

High Selectivity of Amide Products!!!

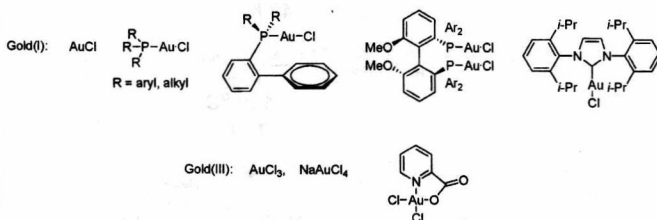
Applications of "AuNPs/C + O₂" Protocol Imines are versatile building blocks for organic synthesis.



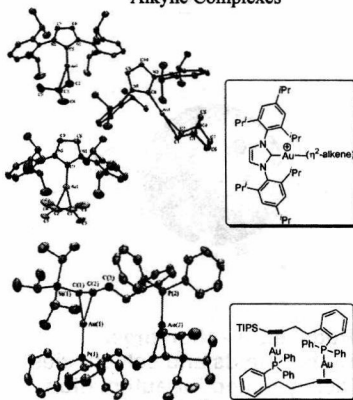
Mechanism of AuNPs/C-Catalyzed Amine Oxidation



Commonly Used Gold Catalyst

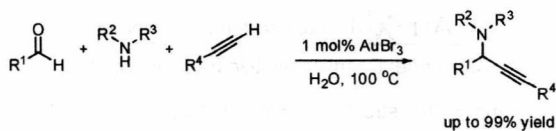


X-ray Crystal Structures of Gold(I) π -alkene and Alkyne Complexes

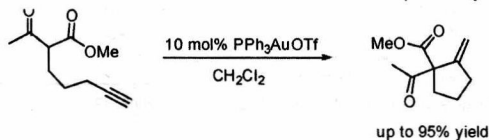


Brown, T. J.; Dickens, M. G.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2009**, *131*: 6350–6351.
Shapiro, N. D.; Toste, F. D. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*: 2779–2782.

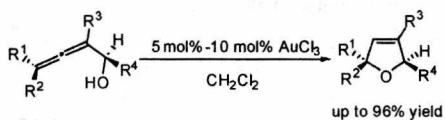
Gold Catalysis: C–H and Multiple Bond Activation



up to 99% yield



up to 95% yield



up to 96% yield

Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*: 395–403.

