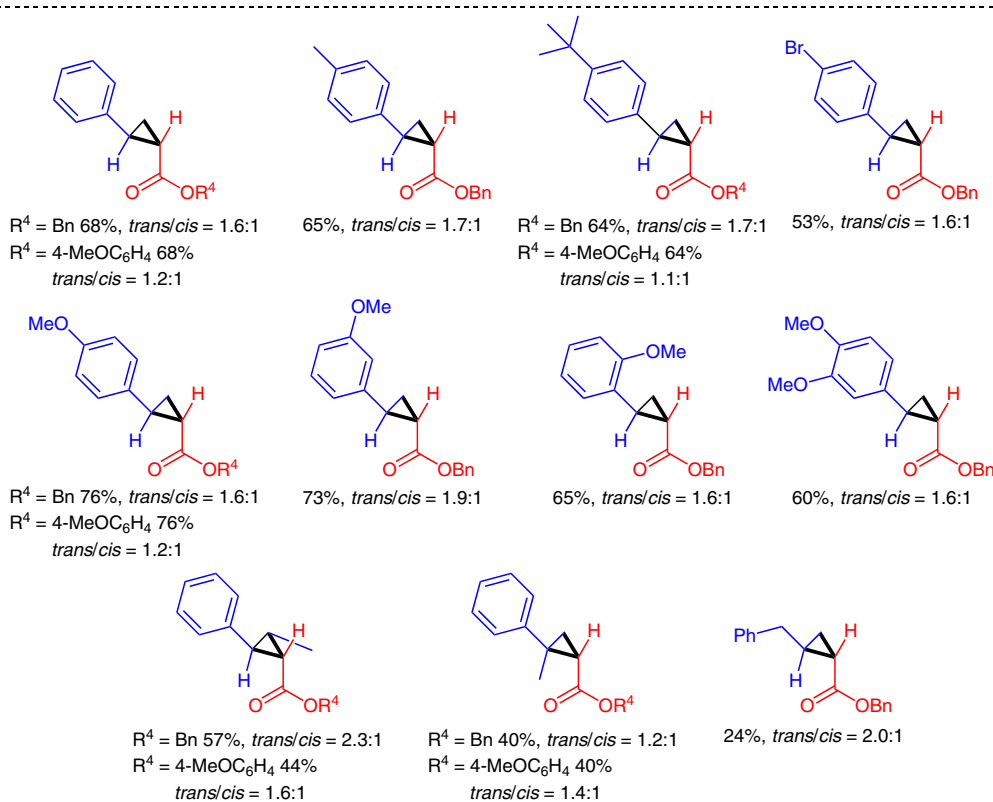
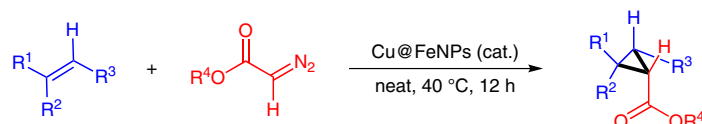


S. ISHIKAWA, R. HUDSON, M. MASNADI, M. BATEMAN, A. CASTONGUAY, N. BRAIDY, A. MOORES,\* C.-J. LI\* (MCGILL UNIVERSITY, MONTREAL AND UNIVERSITÉ DE SHERBROOKE, CANADA)

Cyclopropanation of Diazoesters with Styrene Derivatives Catalyzed by Magnetically Recoverable Copper-Plated Iron Nanoparticles

*Tetrahedron* **2014**, *70*, 8952–8958.

## Cyclopropanation of Alkenes with Diazoesters Using Cu@FeNPs



**Significance:** Copper-plated iron nanoparticles (Cu@FeNPs) catalyzed the cyclopropanation of alkenes with diazoesters to give the corresponding substituted cyclopropanes in up to 76% yield (16 examples). In the reaction of 4-vinylanisole with benzyl diazoacetate, the catalyst was recovered by magnetic separation and reused four times without significant loss of catalytic activity.

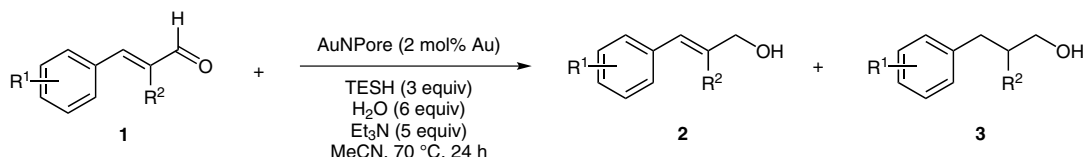
**Comment:** The authors reported previously the preparation of Cu@FeNPs and its application to the Huisgen reaction (*Green Chem.* **2012**, *14*, 622). ICP analysis revealed that 12 ppm of copper leached out from the fresh catalyst during the reaction. The leached copper species showed no catalytic activity.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Hiroaki Tsuji  
Synfacts 2015, 11(1), 0097 Published online: 15.12.2014  
DOI: 10.1055/s-0034-1379711; Reg-No.: Y14114SF

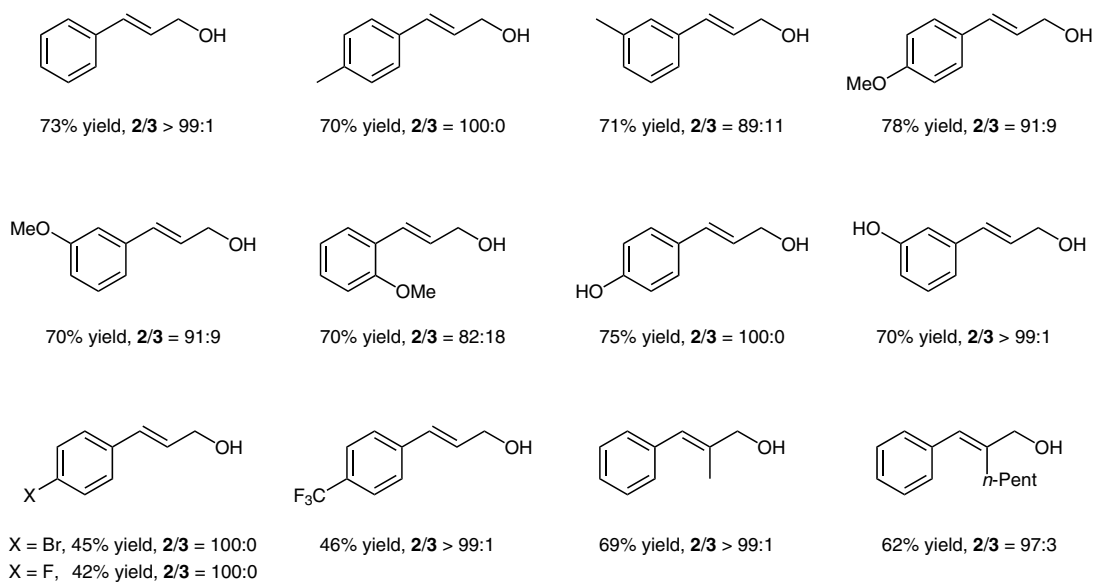
B. S. TAKALE, S. WANG, X. ZHANG, X. FENG, X. YU, T. JIN, M. BAO,\* Y. YAMAMOTO\*  
(DALIAN UNIVERSITY OF TECHNOLOGY, P. R. OF CHINA AND TOHOKU UNIVERSITY,  
SENDAI, JAPAN)

Chemoselective Reduction of  $\alpha,\beta$ -Unsaturated Aldehydes Using An Unsupported Nanoporous Gold Catalyst  
*Chem. Commun.* **2014**, 50, 14401–14404.

## Chemoselective Reduction of $\alpha,\beta$ -Unsaturated Aldehydes with AuNPore



### Results:



**Significance:** Nanoporous gold (AuNPore) catalyzed the 1,2-reduction of  $\alpha,\beta$ -unsaturated aldehydes **1** with triethylsilane. The reduction was carried out in the presence of water and triethylamine to give the corresponding allyl alcohols **2** in 42–78% yield with 82:18 to 100:0 (**2/3**) chemoselectivity.

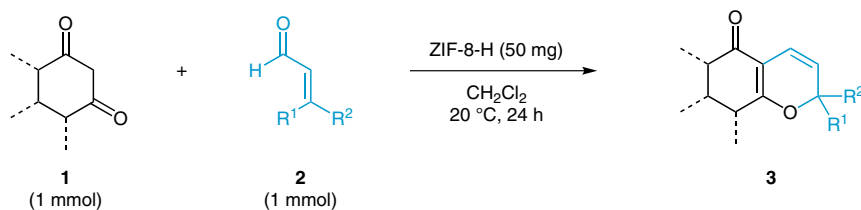
**Comment:** Previously, the authors reported the AuNPore-catalyzed chemoselective reduction of imines with dimethylphenylsilane (*Org. Lett.* **2014**, 16, 2558). In the reduction of cinnamyl aldehyde, the catalytic activity of AuNPore was superior to that of Au<sub>30</sub>Ag<sub>70</sub> alloy, homogeneous AuCl(Ph<sub>3</sub>P)/Bu<sub>3</sub>P, and AuCl/IPr·HCl. ICP-MS analysis showed that no gold content was leached from the catalyst during the reaction.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Fumie Sakurai  
Synfacts 2015, 11(1), 0098 Published online: 15.12.2014  
DOI: 10.1055/s-0034-1379712; Reg-No.: Y14214SF

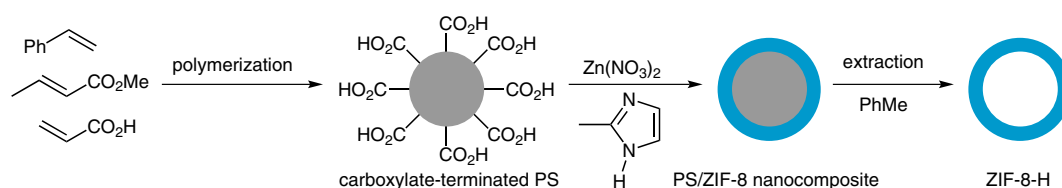
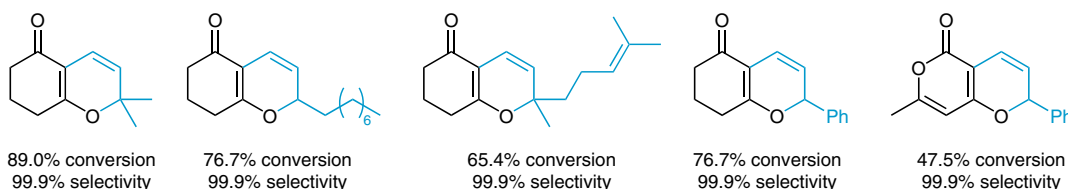
2015 © THIEME STUTTGART • NEW YORK

F. ZHANG, Y. WEI, X. WU, H. JIANG, W. WANG,\* H. LI\* (SHANGHAI NORMAL UNIVERSITY, P. R. OF CHINA AND UNIVERSITY OF NEW MEXICO, ALBUQUERQUE, USA)  
Hollow Zeolitic Imidazolate Framework Nanospheres as Highly Efficient Cooperative Catalysts for [3+3] Cycloaddition Reactions  
*J. Am. Chem. Soc.* **2014**, *136*, 13963–13966.

# A Zeolitic Imidazolate Framework Catalyst for [3+3] Cycloadditions



## Selected examples:



**Significance:** The authors developed a hollow-structured zeolitic imidazolate framework (ZIF-8-H) nanosphere as a catalyst for [3+3] cycloadditions. ZIF-8-H was prepared via complexation of carboxylic groups on the surface of nano-PS ( $\phi = 400$  nm) with zinc ions and 2-methylimidazole, followed by subsequent removal of the PS nanosphere by extraction with toluene. The reaction of 1,3-dicarbonyl compounds **1** with  $\alpha,\beta$ -unsaturated aldehydes **2** proceeded in the presence of ZIF-8-H to give the pyranal heterocycles **3** with up to 89.0% conversion and 99.9% selectivity.

**Comment:** The reaction of 1,3-hexanedione and 3-methyl-2-butenal proceeded in the presence of ZIF-8-H with 89.0% conversion, whereas the use of bulk ZIF-8 showed lower catalytic efficiency (73.2% conversion). Toluene vapor adsorption isotherm showed that ZIF-8-H absorbed toluene to a cage-filling level with a high adsorption amount (6.34 mmol/g). Based on this observation, the authors discussed that the limiting aperture size of ZIF-8-H exceeded the kinetic diameter of toluene (0.61 nm), which is much larger than the reported window size of ZIF-8 (0.34 nm).

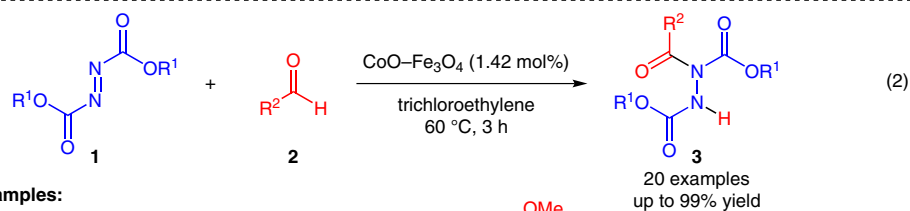
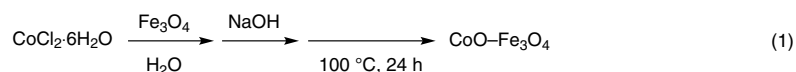
**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Takuma Sato  
Synfacts 2015, 11(1), 0099 Published online: 15.12.2014  
DOI: 10.1055/s-0034-1379726; Reg-No.: Y15314SF

J. M. PÉREZ, D. J. RAMÓN\* (UNIVERSIDAD DE ALICANTE, SPAIN)

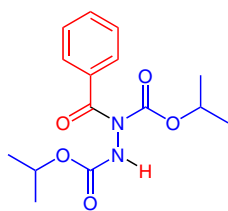
Cobalt-Impregnated Magnetite as General Heterogeneous Catalyst for the Hydroacylation Reaction of Azodicarboxylates

*Adv. Synth. Catal.* **2014**, *356*, 3039–3047.

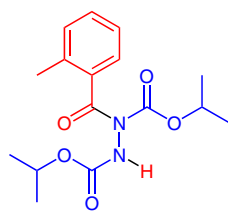
## Hydroacylation of Azodicarboxylates with Aldehydes Using $\text{CoO-Fe}_3\text{O}_4$



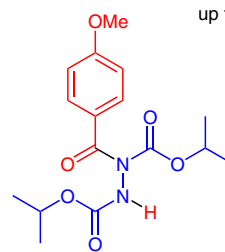
## Selected examples:



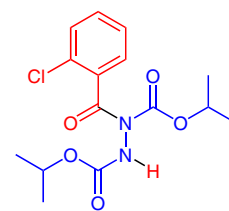
3a 89% yield



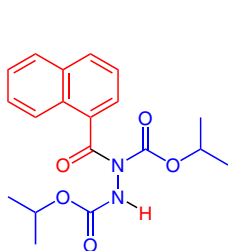
3b 86% yield



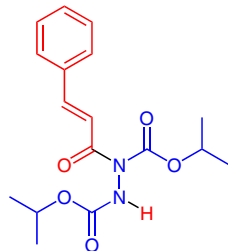
3c 67% yield



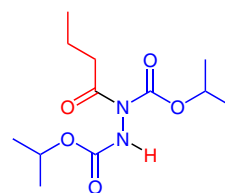
3d 95% yield



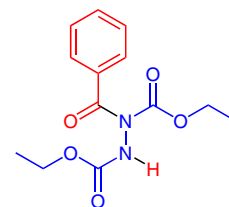
3e 87% yield



3f 74% yield



3g 99% yield



3h 99% yield

**Significance:** Magnetite-supported cobalt oxide ( $\text{CoO-Fe}_3\text{O}_4$ ) was prepared by mixing  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}_3\text{O}_4$  in water followed by treatment with NaOH (eq. 1).  $\text{CoO-Fe}_3\text{O}_4$  catalyzed the hydroacylation of azodicarboxylates **1** with aldehydes **2** in trichloroethylene to afford the hydroacylated products **3** in up to 99% yield (eq. 2).

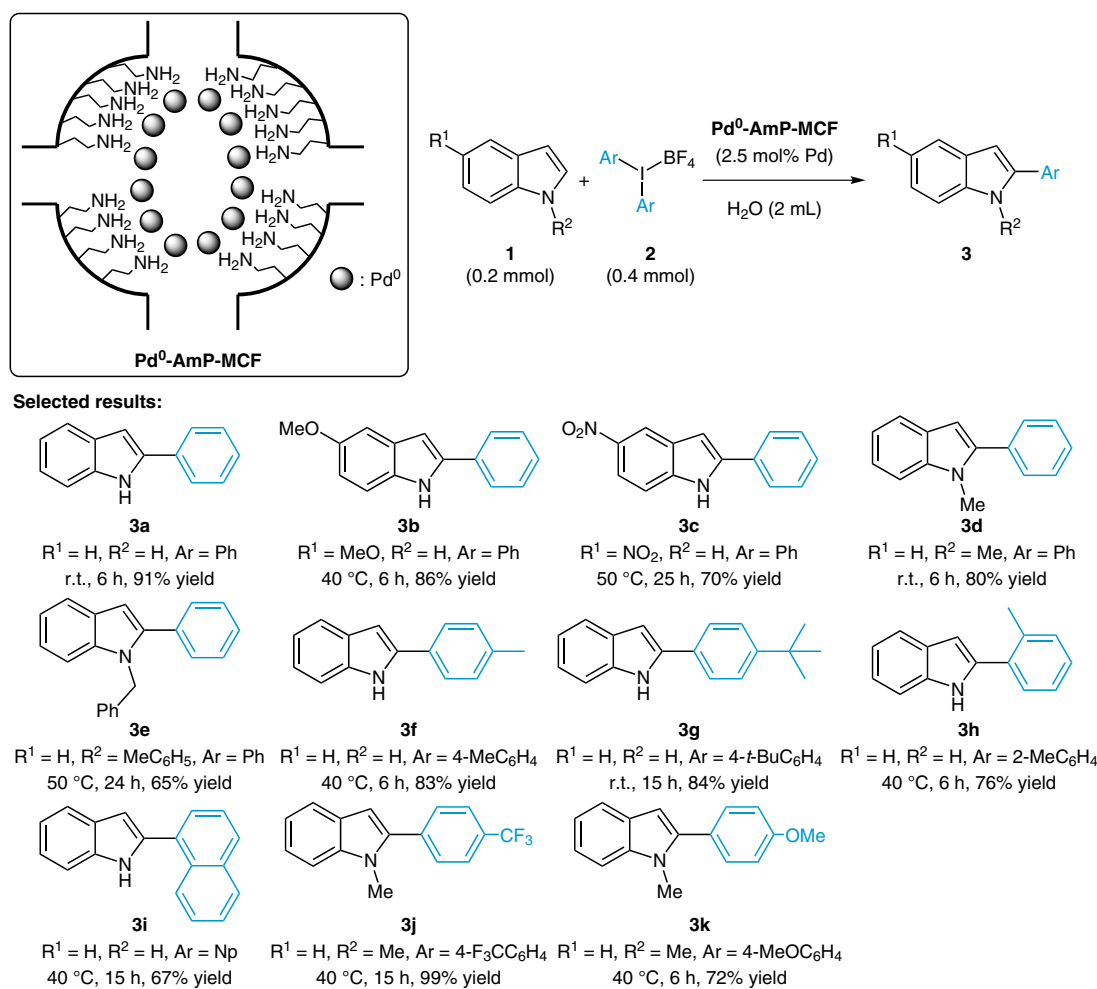
**Comment:** In the formation of **3a**, the catalyst was recovered by magnetic separation and reused nine times with slight loss of its catalytic activity. The catalytic activity of  $\text{CoO-Fe}_3\text{O}_4$  was superior to that of the other metal oxides supported on  $\text{Fe}_3\text{O}_4$  ( $\text{NiO-Fe}_3\text{O}_4$ ,  $\text{CuO-Fe}_3\text{O}_4$ ,  $\text{Ru}_2\text{O}_3\text{-Fe}_3\text{O}_4$ ,  $\text{Rh}_2\text{O}_3\text{-Fe}_3\text{O}_4$ ,  $\text{PdO-Fe}_3\text{O}_4$ ,  $\text{Ag}_2\text{O/Ag-Fe}_3\text{O}_4$ ,  $\text{WO}_x\text{-Fe}_3\text{O}_4$ ,  $\text{OsO-Fe}_3\text{O}_4$ ,  $\text{PtO/PtO}_2\text{-Fe}_3\text{O}_4$ ,  $\text{Au}_2\text{O}_3\text{/Au-Fe}_3\text{O}_4$ ,  $\text{NiO/Cu-Fe}_3\text{O}_4$ ,  $\text{PdO/Cu-Fe}_3\text{O}_4$ ) and unsupported CoO.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Noboru Kobayashi  
Synfacts 2015, 11(1), 0100 Published online: 15.12.2014

**DOI:** 10.1055/s-0034-1379716; **Reg-No.:** Y14614SF

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# A Heterogeneous Palladium Catalyst for C2-Selective Arylation of Indoles



**Significance:** Pd<sup>0</sup>-AmP-MCF constitutes of silica-based mesocellular foam (MCF) functionalized with aminopropylsilane (for the preparation, see: M. Shakeri et al. *Chem. Eur. J.* **2011**, *17*, 13269). Pd<sup>0</sup>-AmP-MCF (palladium particles  $\phi$ : 2–3 nm) catalyzed the C2-selective arylation of indoles **1** and substituted diaryliodonium tetrafluoroborates **2** to give the corresponding indole derivatives in 65–99% yield (15 examples).

**Comment:** The reactions of an electron-rich indole (**3b**), an N-methylated indole (**3d**), *para*-alkyl-substituted salts (**3f,g**), or an electron-deficient CF<sub>3</sub>-substituted salt (**3j**) afforded high yields, whereas an N-benzylated indole (**3e**) or a naphthyl salt (**3i**) resulted in lower yield. ICP-OES analysis showed 0.6 ppm of palladium leaching from the reaction mixture (**3a**).

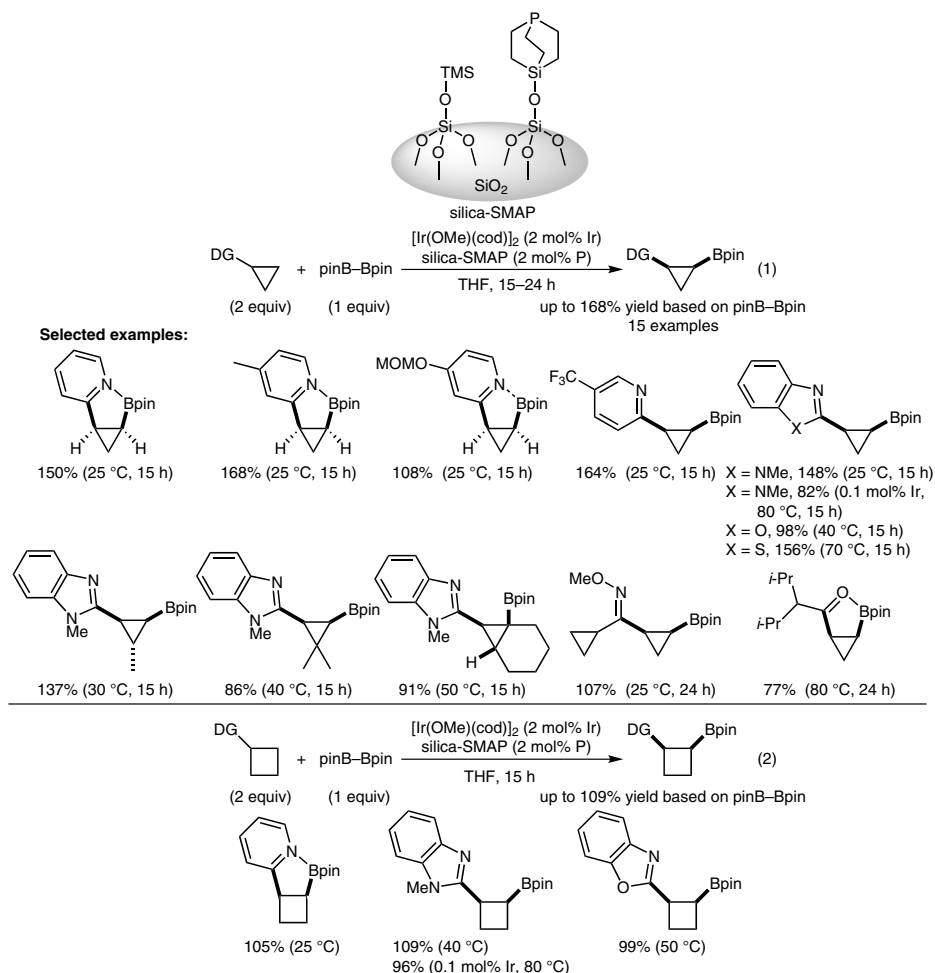
**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Rikako Ishii  
Synfacts 2015, 11(1), 0101 Published online: 15.12.2014  
DOI: 10.1055/s-0034-1379722; Reg-No.: Y14914SF

R. MURAKAMI, K. TSUNODA, T. IWAI, M. SAWAMURA\* (HOKKAIDO UNIVERSITY, SAPPORO, JAPAN)

Stereoselective C–H Borylations of Cyclopropanes and Cyclobutanes with Silica-Supported Monophosphane–Ir Catalysts

*Chem. Eur. J.* **2014**, *20*, 13127–13131.

## C–H Borylation of Cyclopropanes and Cyclobutanes with Silica-SMAP–Iridium



**Significance:** The heteroatom-directed C–H borylation of cyclopropanes and cyclobutanes with bis(pinacolato)diboron was carried out in the presence of  $[\text{Ir}(\text{OMe})(\text{cod})_2]_2$  and silica-SMAP to give the corresponding borylated products in up to 168% yield based on bis(pinacolato)diboron (eqs. 1 and 2).

**Comment:** In the reaction of 2-cyclopropylpyridine with bis(pinacolato)diboron, the catalytic activity of the silica-SMAP–iridium system was superior to that of the other ligand–iridium systems (for example, 0% yield for Ph-SMAP–Ir,  $\text{Me}_3\text{P}$ –Ir,  $t\text{-Bu}_3\text{P}$ –Ir,  $\text{Ph}_3\text{P}$ –Ir, XPhos–Ir, dtbpy–Ir, and 2,9- $\text{Me}_2\text{Phen}$ –Ir).

**SYNFACTS Contributors:** Yasuhiro Uozumi, Go Hamasaka  
Synfacts 2015, 11(1), 0102 Published online: 15.12.2014  
DOI: 10.1055/s-0034-1379710; Reg-No.: Y14014SF

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S.-W. CHEN, Z.-C. ZHANG, M. MA, C.-M. ZHONG,\* S.-G. LEE\* (NORTHWEST A&F UNIVERSITY, YANGLING, P. R. OF CHINA AND EWHA WOMANS UNIVERSITY, SEOUL, REPUBLIC OF KOREA)

Supported Ruthenium–Carbene Catalyst on Ionic Magnetic Nanoparticles for Olefin Metathesis  
*Org. Lett.* **2014**, *16*, 4969–4971.

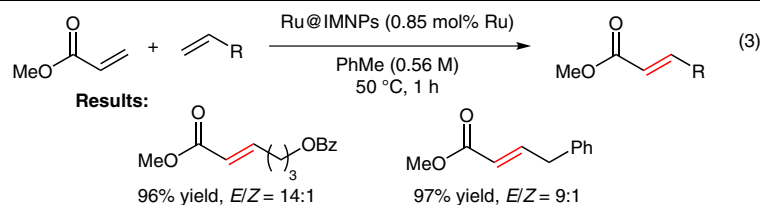
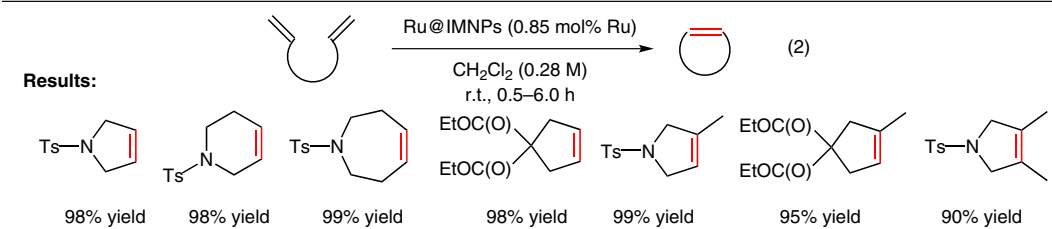
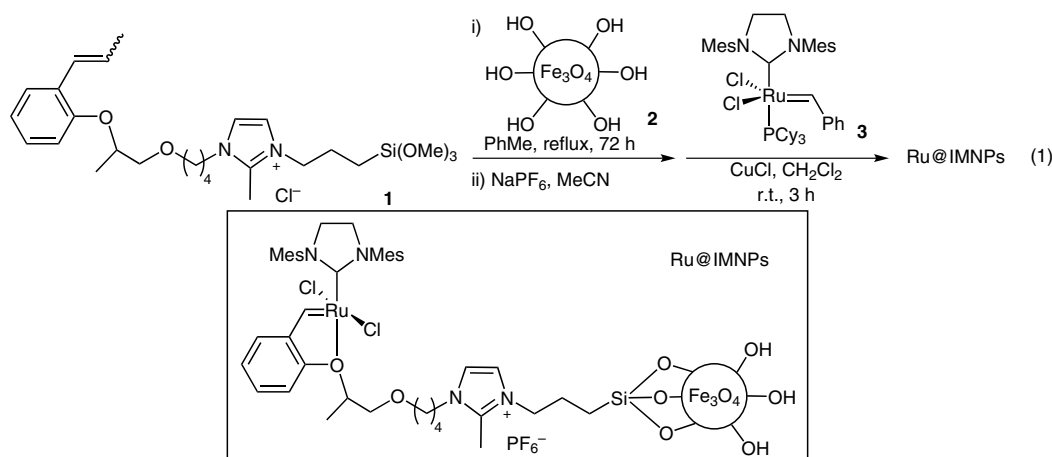
# Olefin Metathesis with Ruthenium–Carbene Supported on Iron Oxide

Category

Polymer-Supported Synthesis

Key words

carbenes  
 iron oxide  
 olefin metathesis  
 ruthenium



**Significance:** The Grubbs–Hoveyda ruthenium–carbene complex supported on ionic magnetic nanoparticles (Ru@IMNPs) was prepared by immobilization of imidazolium chloride **1** onto Fe<sub>3</sub>O<sub>4</sub> **2**, anion exchange with NaPF<sub>6</sub>, and metathesis with ruthenium complex **3** (eq. 1). Ru@IMNPs catalyzed the ring-closing metathesis of dienes to give the corresponding cyclic olefins in 90–99% yield (eq. 2). The cross-metathesis of methyl acrylate with olefins using Ru@IMNPs also proceeded with high *E*-selectivity (eq. 3).

**Comment:** In the ring-closing metathesis of *N,N*-diallyl tosylamide, the catalyst was recovered magnetically and reused five times without significant loss of catalytic activity (6<sup>th</sup> run: 96% conversion), although ICP-MS analysis showed significant leaching of the ruthenium species into the product (a loss of 54% of the ruthenium content of the fresh catalyst) during the initial three runs of the recycling experiment.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Takao Osako  
 Synfacts 2015, 11(1), 0103 Published online: 15.12.2014

**DOI:** 10.1055/s-0034-1379713; **Reg-No.:** Y14314SF

triazoles

hydroamination

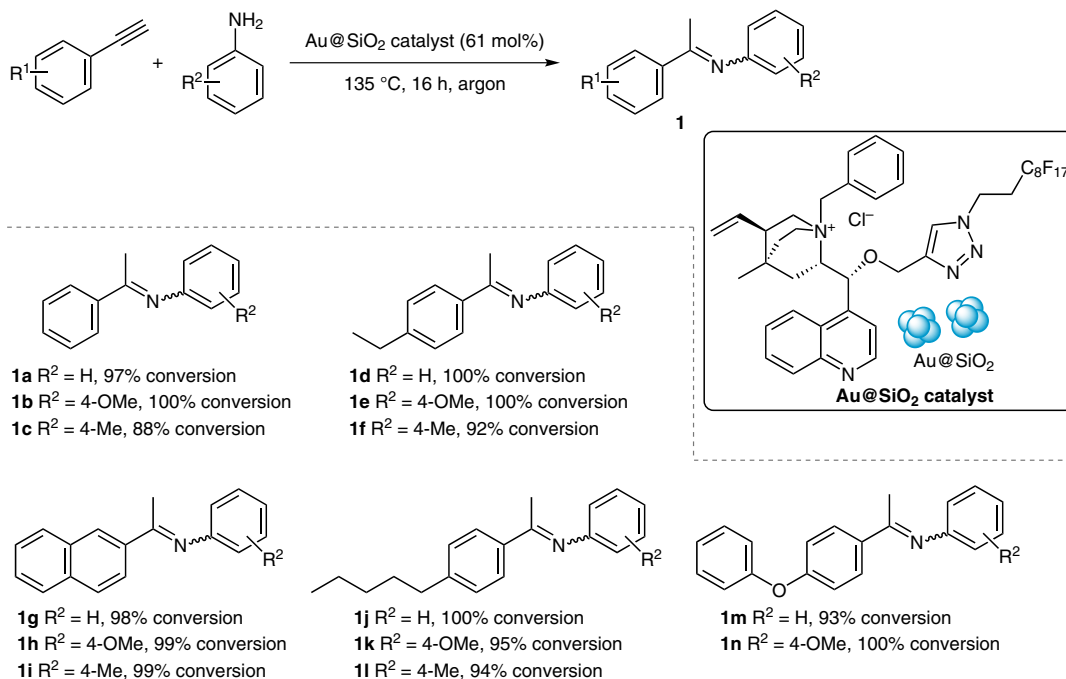
gold nanoparticles

heterogeneous  
catalysis

V. A. SOLOVYEVA, K. B. VU, Z. MERICAN, R. SOUGRAT, V. O. RODIONOV\* (KING ABDULLAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, THUWAL, KINGDOM OF SAUDI ARABIA)

One-Pot Synthesis of Au@SiO<sub>2</sub> Catalysts: A Click Chemistry Approach  
*ACS Comb. Sci.* **2014**, *16*, 513–517.

## Hydroamination of Alkynes Using Amphiphiles-Based Au@SiO<sub>2</sub>



**Significance:** The porous Au@SiO<sub>2</sub> catalyst was prepared from a gold precursor and a TEOS solution in the presence of cinchonidine-based triazole amphiphiles. The hydroamination of alkynes was carried out with Au@SiO<sub>2</sub> to give the corresponding imine products **1a–n** in up to 99% conversion.

**Comment:** The turnover number of Au@SiO<sub>2</sub> was 1604 for the formation of **1b**. The catalyst was characterized by cryo-TEM, XPS, UV/Vis, zeta potential, and ICP-OES analyses.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Heeyoel Baek  
Synfacts 2015, 11(1), 0104 Published online: 15.12.2014  
**DOI:** 10.1055/s-0034-1379718; **Reg-No.:** Y14814SF

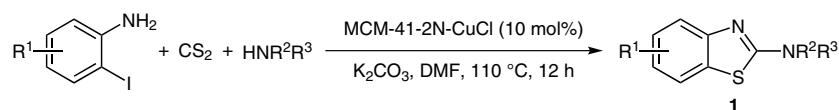
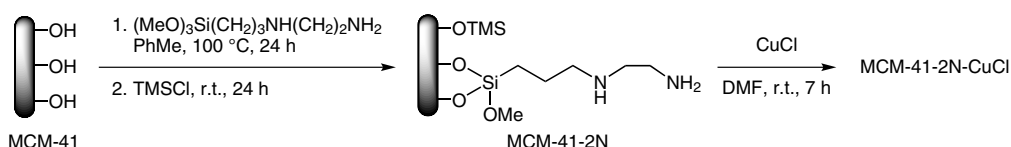
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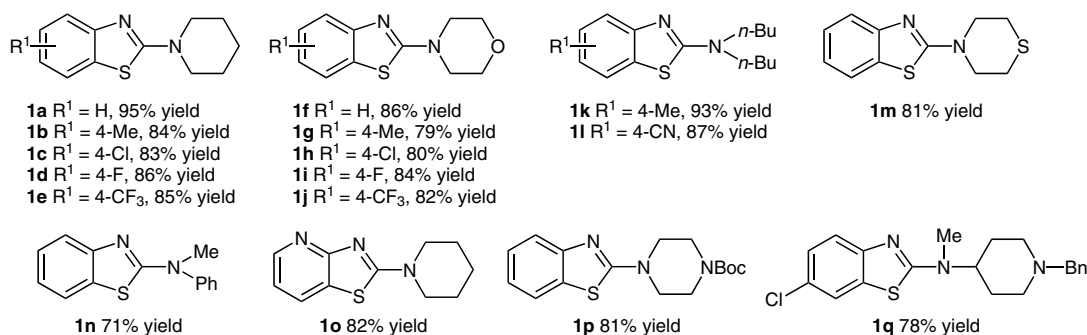
H. ZHAO, W. HE, R. YAO, M. CAI\* (JIANGXI NORMAL UNIVERSITY, NANCHANG AND GUANGDONG PHARMACEUTICAL UNIVERSITY, GUANGZHOU, P. R. OF CHINA)  
Heterogeneous Copper-Catalyzed Cascade Three-Component Reaction of Amines, Carbon Disulfide and 2-Iodoanilines Leading to 2-Aminobenzothiazoles  
*Adv. Synth. Catal.* **2014**, *356*, 3092–3098.

# Preparation of 2-Aminobenzothiazoles with an MCM-41-Cu Catalyst

## Preparation of the MCM-41-supported copper complex catalyst:



## Selected results:



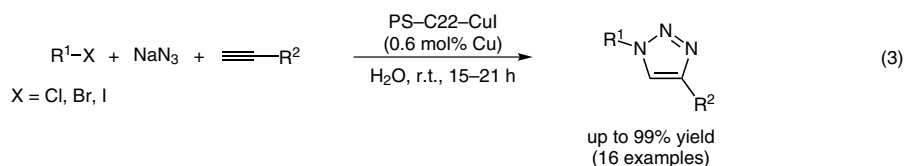
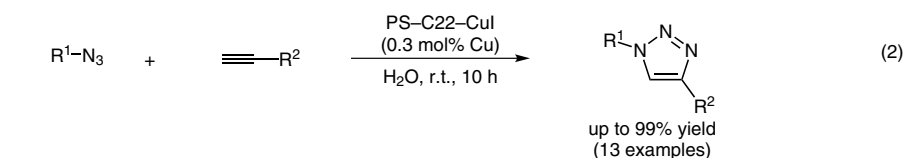
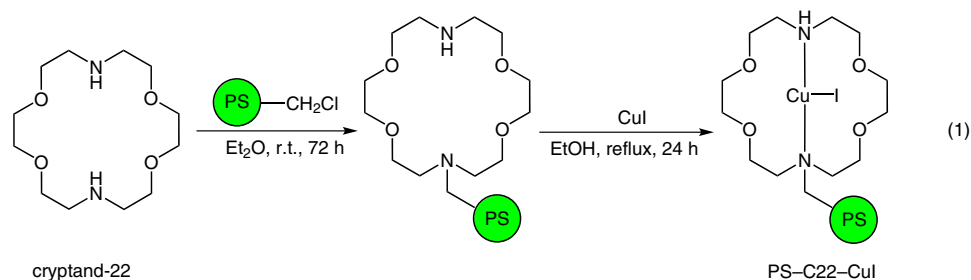
**Significance:** The mesoporous catalyst MCM-41-2N-CuCl was prepared by immobilization of a 3-(2-aminoethylamino)propyl moiety on MCM-41 with CuCl. The reaction of 2-iodoanilines, carbon disulfide (CS<sub>2</sub>) and amines with 10 mol% of MCM-41-2N-CuCl gave the corresponding 2-aminobenzothiazoles **1a–q** in up to 95% yield.

**Comment:** The MCM-41-2N-CuCl catalyst was recovered by filtration and reused nine times to give **1a** (5<sup>th</sup> reuse: 94% yield, 9<sup>th</sup> reuse: 93% yield). ICP-AES analysis revealed that no copper species leached into the reaction mixture.

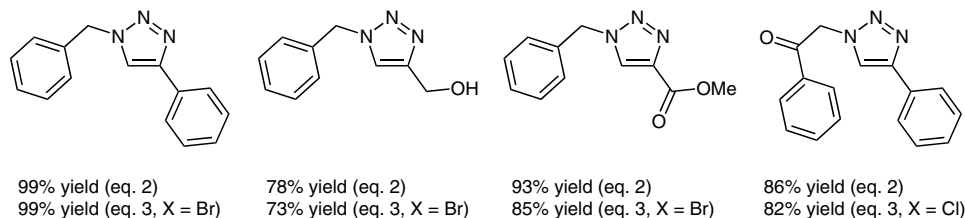
**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Heeyoel Baek  
*Synfacts* 2015, 11(1), 0105 Published online: 15.12.2014  
**DOI:** 10.1055/s-0034-1379717; **Reg-No.:** Y14714SF

B. MOVASSAGH,\* N. REZAEI (K. N. TOOSI UNIVERSITY OF TECHNOLOGY, TEHRAN, IRAN)  
Polystyrene Resin-Supported CuI–Cryptand-22 Complex: A Highly Efficient and Reusable Catalyst for Three-Component Synthesis of 1,4-Disubstituted 1,2,3-Triazoles Under Aerobic Conditions in Water  
*Tetrahedron* 2014, 70, 8885–8892.

## Click Reaction Using Polymer-Supported CuI–Cryptand-22



### Selected examples:

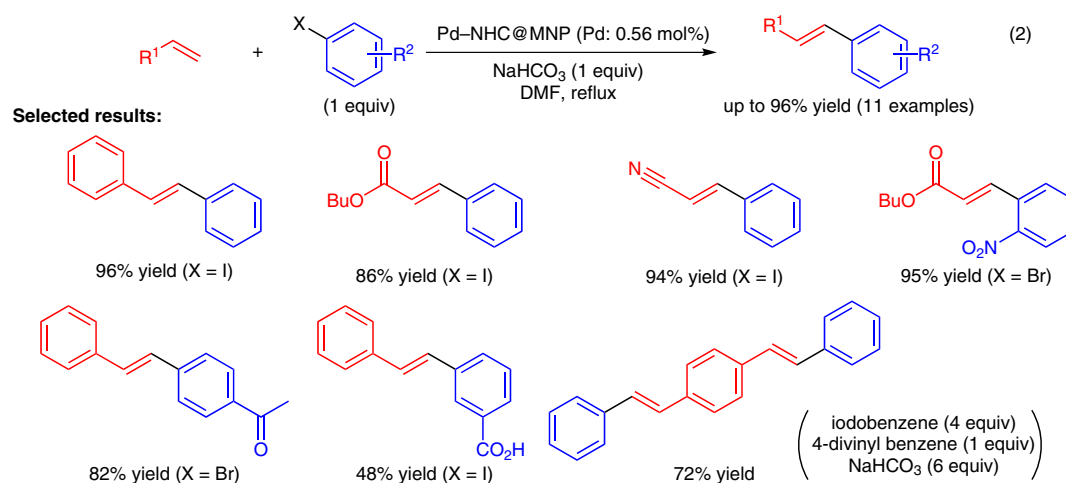
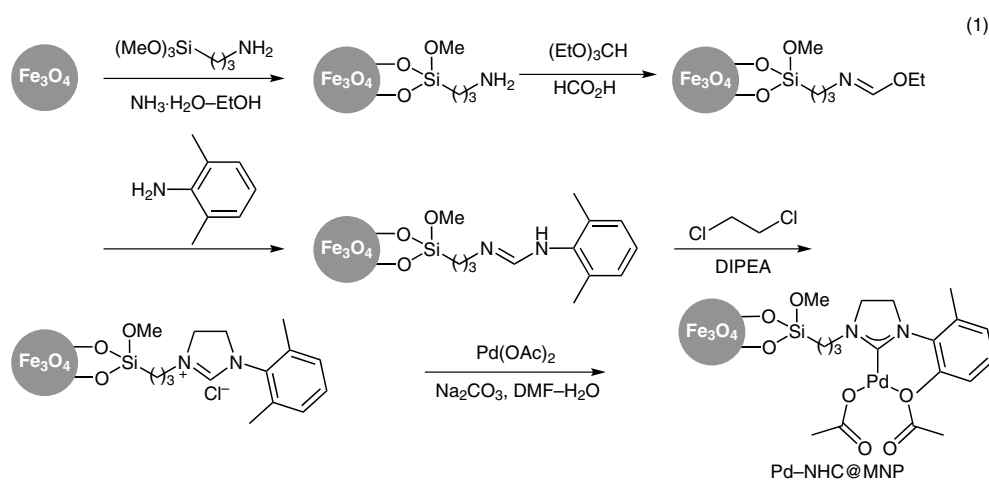


**Significance:** A polystyrene resin supported CuI–cryptand-22 complex (PS–C22–CuI) was prepared by mixing chloromethylated polystyrene with cryptand-22 in diethyl ether, followed by the complexation with CuI in ethanol (eq. 1). PS–C22–CuI catalyzed the click reaction of azides with terminal alkynes (eq. 2, method A) or the one-pot three-component reaction from alkyl halides, sodium azide, and terminal alkynes (eq. 3, method B) to give the corresponding 1,2,3-triazoles in up to 99% yield.

**Comment:** The PS–C22–CuI complex was characterized by FT-IR, EDX, SEM, XPS, and TG-DTA analysis. In both methods A and B for synthesizing 1-benzyl-4-phenyl-1H-1,2,3-triazole, the catalyst was recovered by filtration and reused three times.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Shiguang Pan  
 Synfacts 2015, 11(1), 0106 Published online: 15.12.2014  
 DOI: 10.1055/s-0034-1379715; Reg-No.: Y14514SF

## The Mizoroki–Heck Reaction Using a Palladium–NHC Complex Supported on MNP



**Significance:** A palladium–NHC complex was immobilized on magnetic nanoparticles (Pd–NHC@MNP) according to the sequences shown above. Pd–NHC@MNP catalyzed the Mizoroki–Heck reaction of terminal alkenes with aryl halides to afford the corresponding internal alkenes in up to 96% yield (eq. 2).

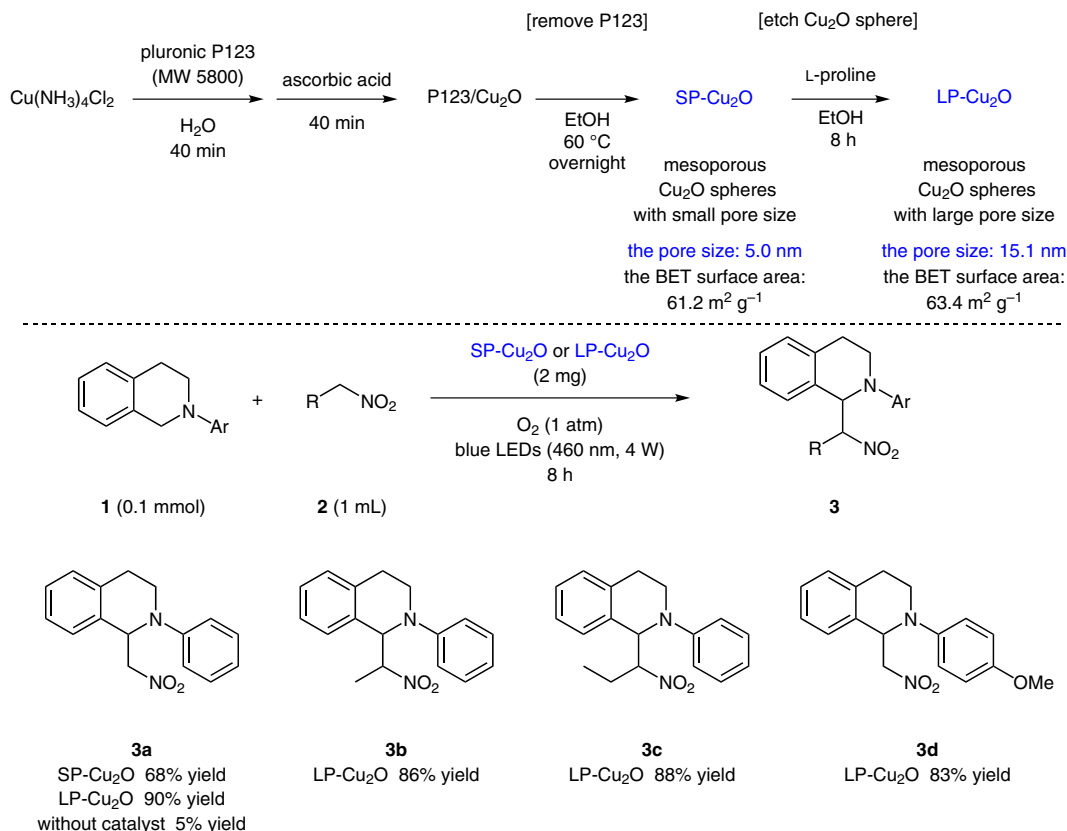
**Comment:** The characterization of Pd–NHC@MNP was performed by TEM, EDX, IR, TGA, DSC, <sup>1</sup>H NMR spectroscopy, and ETAAS analyses. In the Mizoroki–Heck reaction of butyl acrylate with iodobenzene, the catalyst was recovered magnetically and reused four times without loss of its catalytic activity (1<sup>st</sup> run: 85% yield, 3<sup>rd</sup> run: 87% yield, 5<sup>th</sup> run: 85% yield).

J. WANG, J. MA, X. LI, Y. LI, G. ZHANG, F. ZHANG, X. FAN\* (TIANJIN UNIVERSITY, P. R. OF CHINA)

Cu<sub>2</sub>O Mesoporous Spheres with a High Internal Diffusion Capacity and Improved Catalytic Ability for the aza-Henry Reaction Driven by Visible Light

*Chem. Commun.* **2014**, 50, 14237–14240.

## Visible-Light-Promoted aza-Henry Reaction Using Mesoporous Cu<sub>2</sub>O



**Significance:** Mesoporous copper(I) oxide spheres with different pore sizes (5 nm for SP-Cu<sub>2</sub>O and 15 nm for LP-Cu<sub>2</sub>O) were prepared and applied to the visible-light-promoted aza-Henry reaction. The reaction of *N*-aryl tetrahydroisoquinolines **1** with nitroalkanes **2** was carried out in the presence of LP-Cu<sub>2</sub>O and molecular oxygen under the irradiation of blue LEDs to afford the corresponding coupling products **3** in 83–90% yield. The reaction without catalyst gave **3a** in only 5% yield under otherwise similar conditions.

**Comment:** The catalysts were characterized by SEM, TEM, XRD, and N<sub>2</sub> adsorption–desorption analyses. For the formation of **3a**, LP-Cu<sub>2</sub>O was recovered by centrifugation and reused four times without significant loss of catalytic activity. SEM observation of LP-Cu<sub>2</sub>O after the fifth run showed no change of its morphology. The preparation of mesoporous Cu<sub>2</sub>O spheres with small pore size was previously reported by Shang, Zhang and Guo (*J. Mater. Chem.* **2012**, 22, 856).

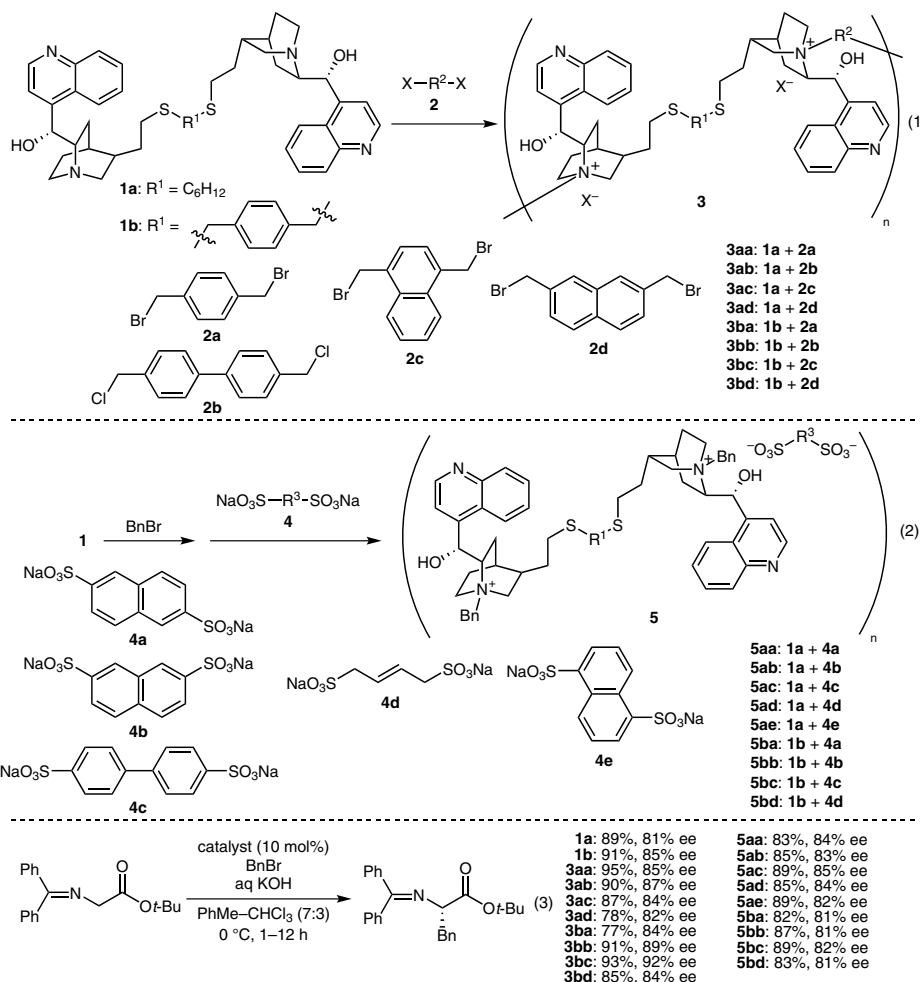
**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Aya Ohno

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# Asymmetric $\alpha$ -Benzylation with Cinchonidinium Salt Based Polymers



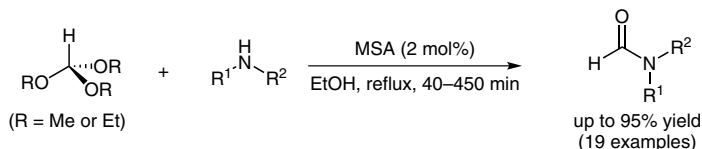
**Significance:** Chiral polymers **3** and **5** were prepared from cinchonidine dimers **1** (eqs. 1 and 2). All polymers showed high catalytic performance in the asymmetric  $\alpha$ -benzylation of *N*-diphenylmethylene glycine *tert*-butyl ester with benzyl bromide (eq. 3, 77–95% yield, 81–92% ee).

**Comment:** The polymer catalysts were recovered by filtration and reused without loss of catalytic performance. The reaction also took place at –40 °C to give the product with improved ee (with **3bc**: 24 h, 83% yield, 95% ee). The catalytic activity and the stereoselectivity observed with the polymeric catalysts **3** and **5** were comparable to those obtained with the homogeneous catalysts **1**.

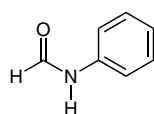
B. KARAMI,\* M. FARAH, F. PAM (YASOUJ UNIVERSITY, IRAN)

A Green Protocol for the N-Formylation of Amines Using Molybdate Sulfuric Acid as a Reusable Solid Catalyst  
*Tetrahedron Lett.* **2014**, *55*, 6292–6296.

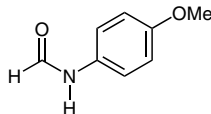
## N-Formylation of Amines Using Molybdate Sulfuric Acid



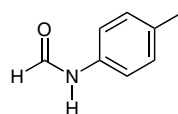
### Selected examples:



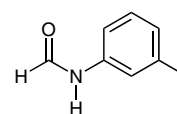
90% yield (R = Et)  
85% yield (R = Me)



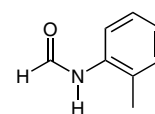
95% yield (R = Et)



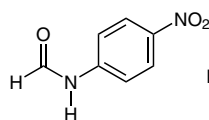
95% yield (R = Et)  
90% yield (R = Me)



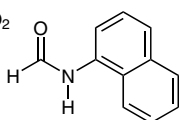
92% yield (R = Et)



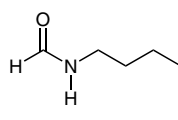
90% yield (R = Et)



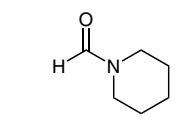
67% yield (R = Et)  
70% yield (R = Me)



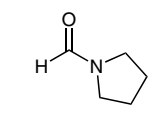
87% yield (R = Et)



80% yield (R = Et)  
80% yield (R = Me)



65% yield (R = Et)



73% yield (R = Et)

**Significance:** Molybdate sulfuric acid (MSA) catalyzed the N-formylation of amines with orthoformates to give the corresponding formamide derivatives in up to 95% yield (19 examples). In the N-formylation of aniline with triethyl orthoformate, the catalyst was recovered by filtration and reused three times with a slight loss of catalytic activity (1<sup>st</sup> reuse: 87% yield, 3<sup>rd</sup> reuse: 80% yield).

**Comment:** The catalytic activity of MSA was superior to that of the other catalysts (ZnO, ZrOCl<sub>2</sub>, MgBr<sub>2</sub>, ZnCl<sub>2</sub>, and H<sub>2</sub>SO<sub>4</sub>). The authors have reported previously the preparation of molybdate sulfuric acid and its application to the synthesis of phenazines and quinoxalines (*Polycycl. Aromat. Compd.* **2011**, *31*, 97).