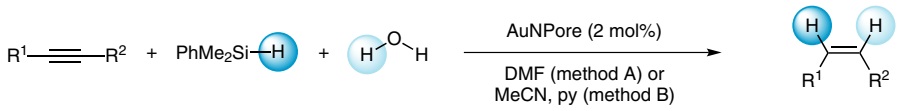
M. YAN, T. JIN,* Y. ISHIKAWA, T. MINATO, T. FUJITA, L.-Y. CHEN, M. BAO, N. ASAO, M.-W. CHEN, Y. YAMAMOTO (TOHOKU UNIVERSITY, SENDAI, JAPAN AND DALIAN UNIVERSITY OF TECHNOLOGY, P. R OF CHINA)

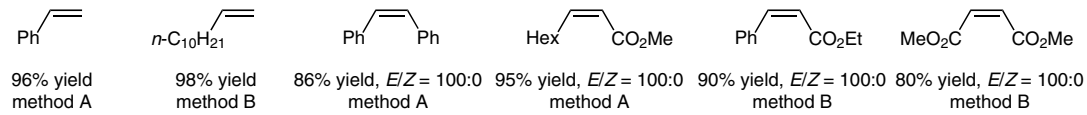
Nanoporous Gold Catalyst for Highly Selective Semihydrogenation of Alkynes: Remarkable Effect of Amine Additives

*J. Am. Chem. Soc.* **2012**, *134*, 17536–17542.

# Nanoporous Gold Catalyst for the Selective Semihydrogenation of Alkynes




**Selected examples:**




96% yield
method A

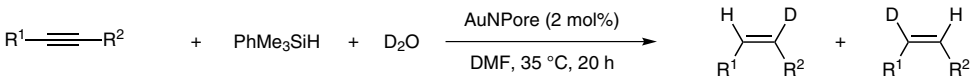
98% yield
method B

86% yield, *E*/*Z* = 100:0
method A

95% yield, *E*/*Z* = 100:0
method A

90% yield, *E*/*Z* = 100:0
method B

80% yield, *E*/*Z* = 100:0
method B




$R^1$ = Hex, $R^2$ = $CO_2Me$

80% yield, (4:1)

**Significance:** A nanoporous gold catalyst (AuNPore), which was prepared by dealloying a homogeneous $Au_{30}Ag_{70}$ alloy in nitric acid (70 wt%), catalyzed the semihydrogenation of alkynes with organosilanes and water as the hydrogen source to afford the corresponding alkenes. The reaction of phenylacetylene with $PhMe_2SiH$ and water in DMF proceeded in the presence of 2 mol% of AuNPore to give styrene as the sole product (method A: 35 °C, 3 h, 96% yield). 1-Dodecyne underwent the semihydrogenation efficiently in acetonitrile with 50 mol% of pyridine (method B: 80 °C, 8 h, 98% yield).

**Comment:** The catalytic ability of various catalysts was examined for the semihydrogenation of phenylacetylene: AuNPore (96%), AuCl (18%), $Au_{30}Ag_{70}$ alloy (0%), PdNPore (54%), and Pd/C (20%). The authors proposed the reaction pathway including the generation of the $H^-$ on the AuNPore surface ($[AuNPore\text{-}H]^-$) and pyridinium cation ($[HPy]^+$) which subsequently react with the alkynes to form the corresponding *Z*-alkenes.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Takuma Sato
Synfacts 2013, 9(1), 0107 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317911; **Reg-No.:** Y13912SF





**Category**

**Polymer-Supported Synthesis**

**Key words**

nanoporous gold

semihydrogenation

alkynes

amines

**Category**

**Polymer-Supported Synthesis**

**Key words**

**BINAP**

**mesoporous catalysts**

**asymmetric hydrogenation**

**co-polymerization**

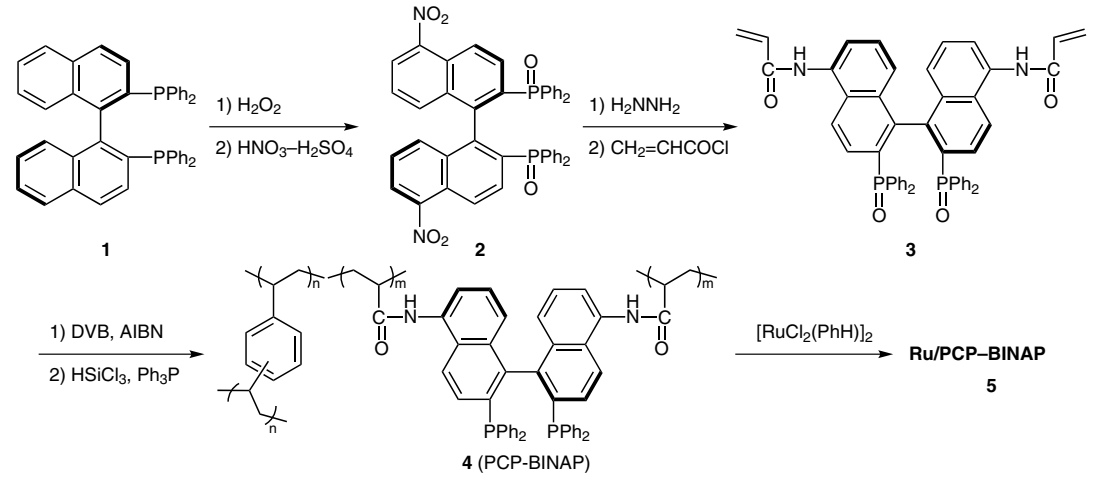
Q. SUN, X. MENG,* X. LIU, X. ZHANG, Y. YANG, Q. YANG,* F. S. XIAO* (ZHEJIANG UNIVERSITY, HANGZHOU, CHINA)

Mesoporous Cross-Linked Polymer Copolymerized with Chiral BINAP Ligand Coordinated to a Ruthenium Species as an Efficient Heterogeneous Catalyst for Asymmetric Hydrogenation

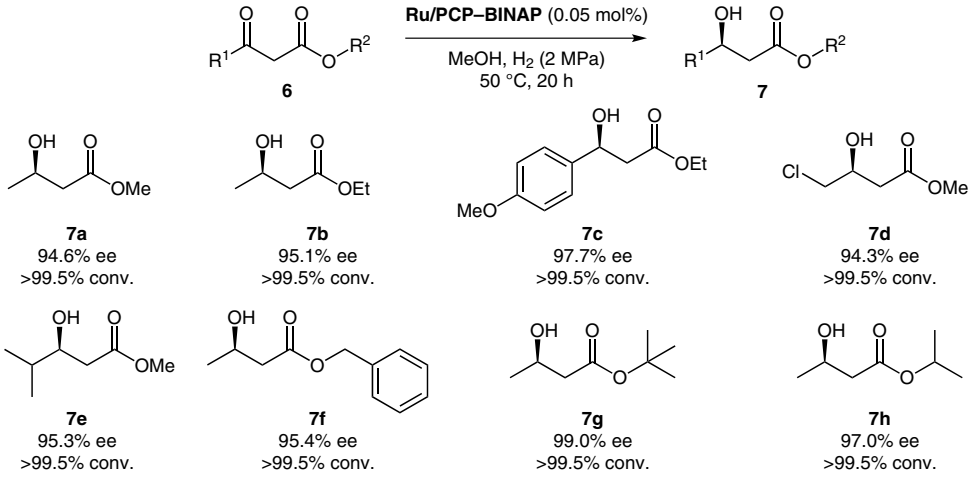
*Chem. Commun.* **2012**, *48*, 10505–10507.

# Asymmetric Hydrogenation Using Polymer-Supported BINAP

**Preparation of chiral Ru/PCP–BINAP 5:**




**Selected results:**




**Significance:** A polymeric BINAP–ruthenium complex (Ru/PCP-BINAP) was prepared by treatment of $[RuCl_2(PhH)]_2$ with the mesoporous cross-linked polymeric (*R*)-BINAP ligand **4**. Ru/PCP-BINAP catalyzed the asymmetric hydrogenation of β-keto esters under hydrogen (2 MPa) to give the corresponding β-hydroxy esters **7a–h** in >99.5% conversion with 94.3–99.0% ee.

**Comment:** Ru/PCP-BINAP was readily recovered and reused six times without significant loss of its catalytic ability (1st reuse: >99.5% conversion, 94.3% ee, 6th reuse: >99.5% conversion, 95.3% ee).

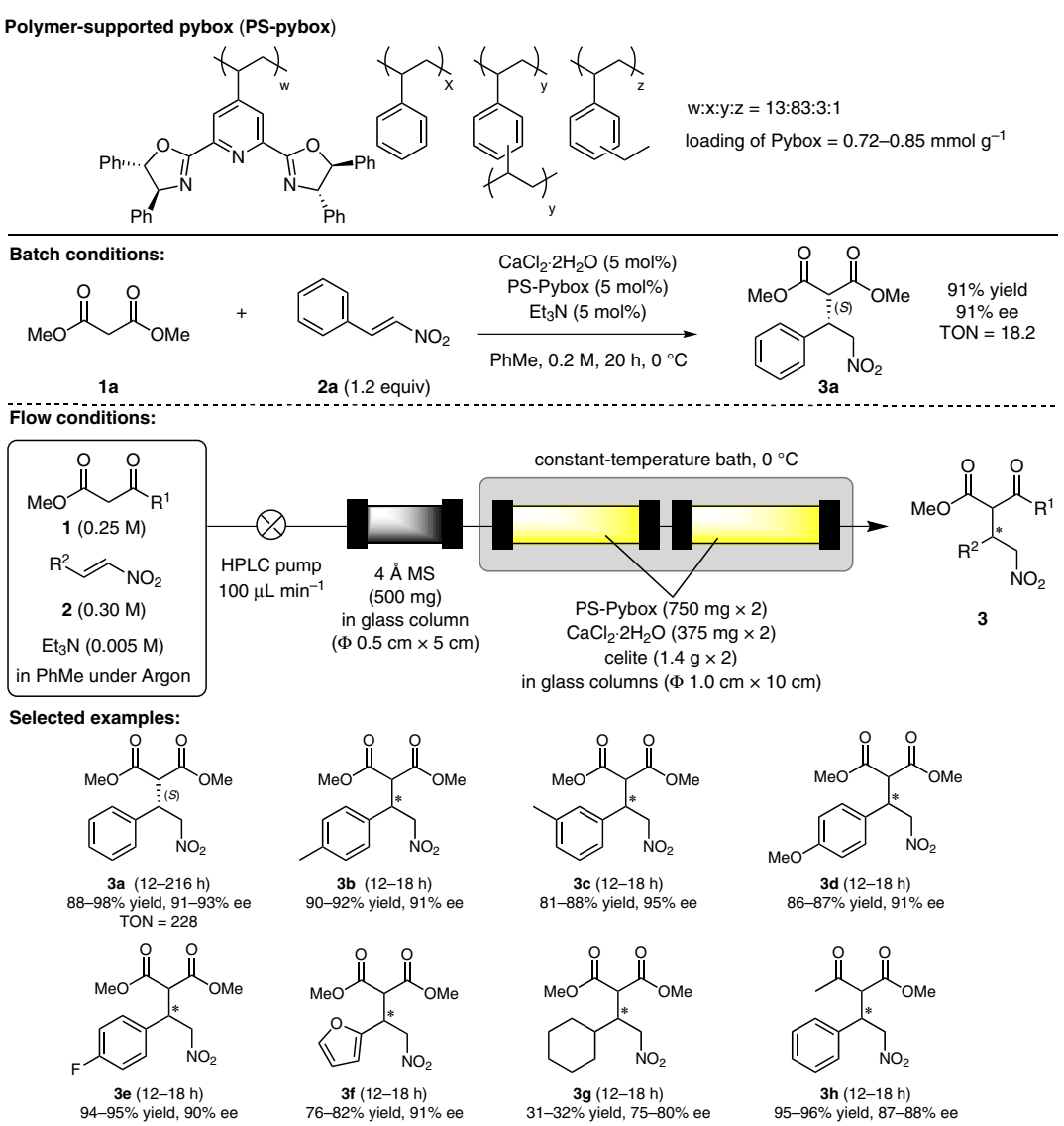
**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Heeyoel Baek
Synfacts 2013, 9(1), 0108 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317918; **Reg-No.:** Y14712SF

T. TSUBOGO, Y. YAMASHITA, S. KOBAYASHI* (THE UNIVERSITY OF TOKYO, JAPAN)

Toward Efficient Asymmetric Carbon–Carbon Bond Formation: Continuous Flow with Chiral Heterogeneous Catalysts

*Chem. Eur. J.* **2012**, *18*, 13624–13628.

# Asymmetric 1,4-Addition with a Chiral Calcium–Pybox Catalyst




**Significance:** A polymer-supported homochiral Pybox–calcium chloride complex catalyzed the asymmetric 1,4-addition of 1,3-dicarbonyl compounds **1** to nitroalkenes **2**, to afford the corresponding adducts **3** in up to 98% yield and 95% ee under batch or flow conditions.

**Comment:** The flow system worked for 204 hours without significant loss of catalytic activity to give **3a** in 95.5% yield with 92.0% ee on average. The total amount of product was 291.4 mmol and the turn-over number (TON) reached 228.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Aya Ohno
Synfacts 2013, 9(1), 0109 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317727; **Reg-No.:** Y14412SF



**Category**

**Polymer-Supported Synthesis**

**Key words**

**asymmetric catalysis**

**Michael addition**

**calcium**

**continuous-flow synthesis**

**Category**

**Polymer-Supported Synthesis**

**Key words**

**amphiphiles**

**nanofibers**

**palladium nanoparticles**

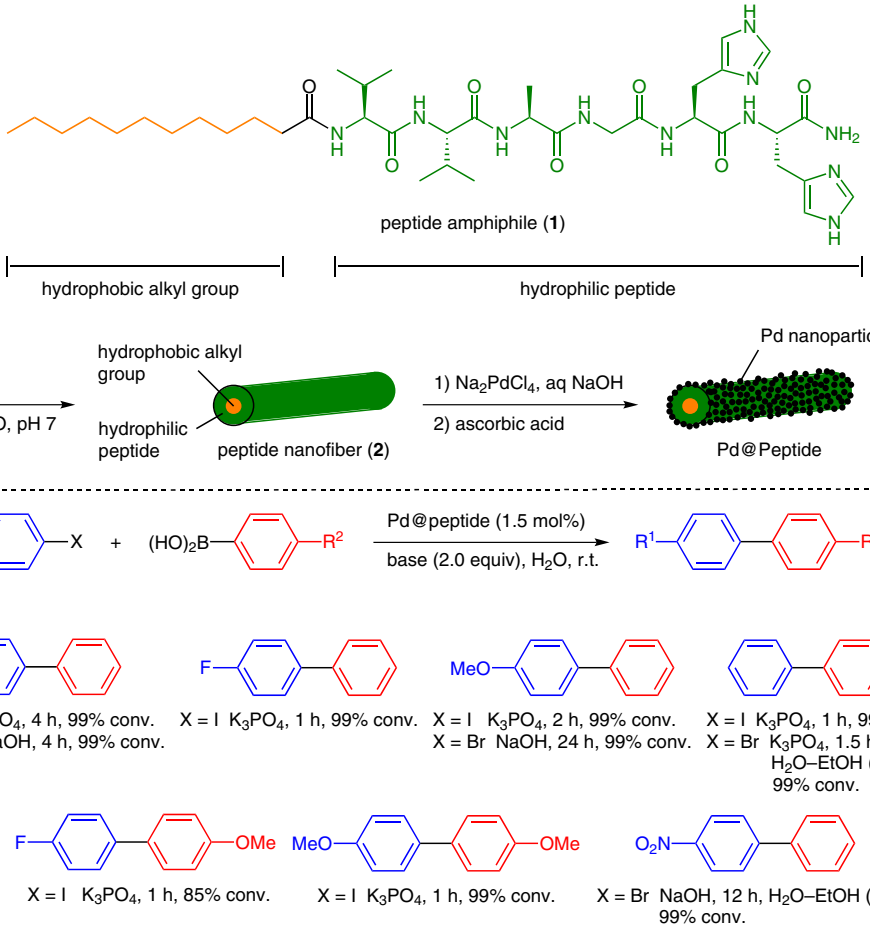
**Suzuki–Miyaura coupling**

M. A. KHALILY, O. USTAHUSEYIN, R. GARIFULLIN, R. GENC, M. O. GULER* (BILKENT UNIVERSITY, ANKARA, TURKEY)

A Supramolecular Peptide Nanofiber Templated Pd Nanocatalyst for Efficient Suzuki Coupling Reactions Under Aqueous Conditions

*Chem. Commun.* **2012**, *48*, 11358–11360.

# The Suzuki-Miyaura Coupling with Pd@Peptide




**Significance:** Palladium nanoparticles supported on peptide nanofiber (Pd@Peptide) were prepared by complexation of peptide nanofiber **2**, prepared via self-assembling of peptide amphiphile **1**, with $Na_2PdCl_4$ in aqueous NaOH followed by reduction with ascorbic acid (eq. 1). Pd@Peptide catalyzed the Suzuki–Miyaura coupling of aryl halides with arylboronic acids in water to give the corresponding biaryls in up to 99% conversion (10 examples, eq. 2)

**Comment:** Pd@Peptide were characterized with TEM, SEM, XRD, and TGA. In the coupling reaction of bromobenzene and 4-methoxyphenylboronic acid, the catalyst was reused four times without significant loss of catalytic activity (1st reuse: 97% conversion, 2nd reuse: 97% conversion, 3rd reuse: 97% conversion, 4th reuse: 95% conversion).

**SYNFACTS Contributors:** Yasuhiro Uozumi, Hiroaki Tsuji
Synfacts 2013, 9(1), 0110 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317909; **Reg-No.:** Y13712SF

D. CANTILLO, M. BAGHBANZADEH, C. O. KAPPE* (KARL-FRANZENS-UNIVERSITY, GRAZ, AUSTRIA)

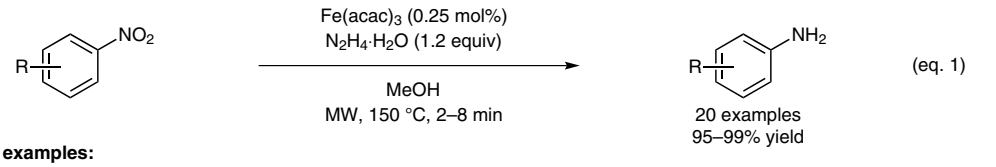
In Situ Generated Iron Oxide Nanocrystals as Efficient and Selective Catalysts for the Reduction of Nitroarenes Using a Continuous Flow Method
*Angew. Chem. Int. Ed.* **2012**, *51*, 10190–10193.

# Reduction of Nitroarenes Using In Situ Generated Iron Oxide Nanocrystals

**Category**
**Polymer-Supported Synthesis**

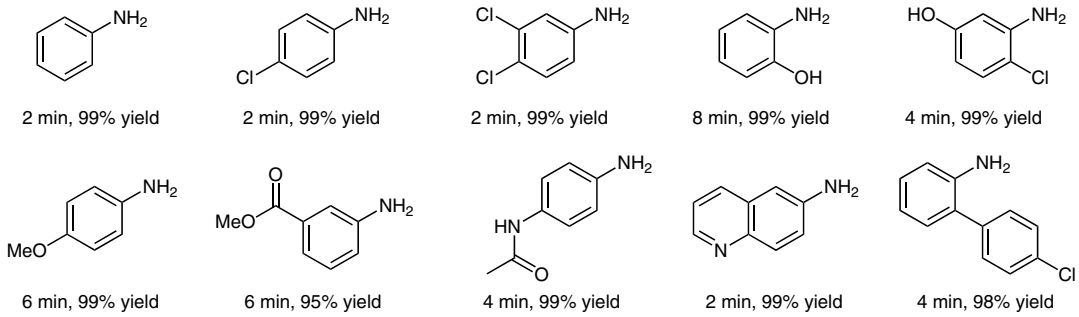
**Key words**
**iron**
**nanoparticles**
**nitroarenes**
**reduction**
**flow reaction**

**Reduction of nitroarenes using the batch system:**

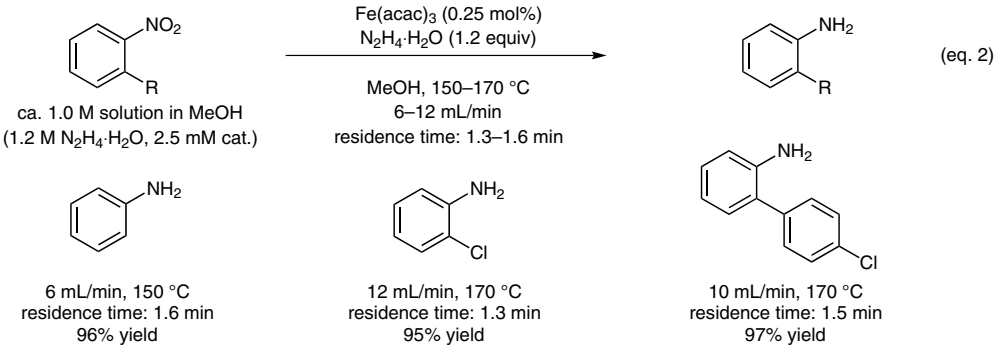



(eq. 1)

**Selected examples:**




**Continuous-flow reduction of nitroarenes:**




(eq. 2)

**Significance:** Iron oxide nanocrystals, generated in situ from $Fe(acac)_3$ and hydrazine hydrate, catalyzed the reduction of nitroarenes with hydrazine hydrate under microwave conditions to give the corresponding anilines in 95–99% yield (20 examples, eq. 1). In the reduction of nitrobenzene to aniline using the batch system, the catalyst was magnetically separated from the reaction mixture and reused seven times.

**Comment:** The reduction of nitroarenes was also performed using a continuous-flow system to afford the anilines in 95–97% yield (eq. 2). The in situ generated iron oxide nanoparticles were characterized by XRD and HRTEM analyses. ICP–MS showed 7.9% iron leaching from the catalyst during the reduction using the batch system.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Fumie Sakurai
Synfacts 2013, 9(1), 0111 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317912; **Reg-No.:** Y14012SF

**Category**

**Polymer-Supported Synthesis**

**Key words**

**gold nanoparticles**

**titanium dioxide**

**1,2-disilanes**

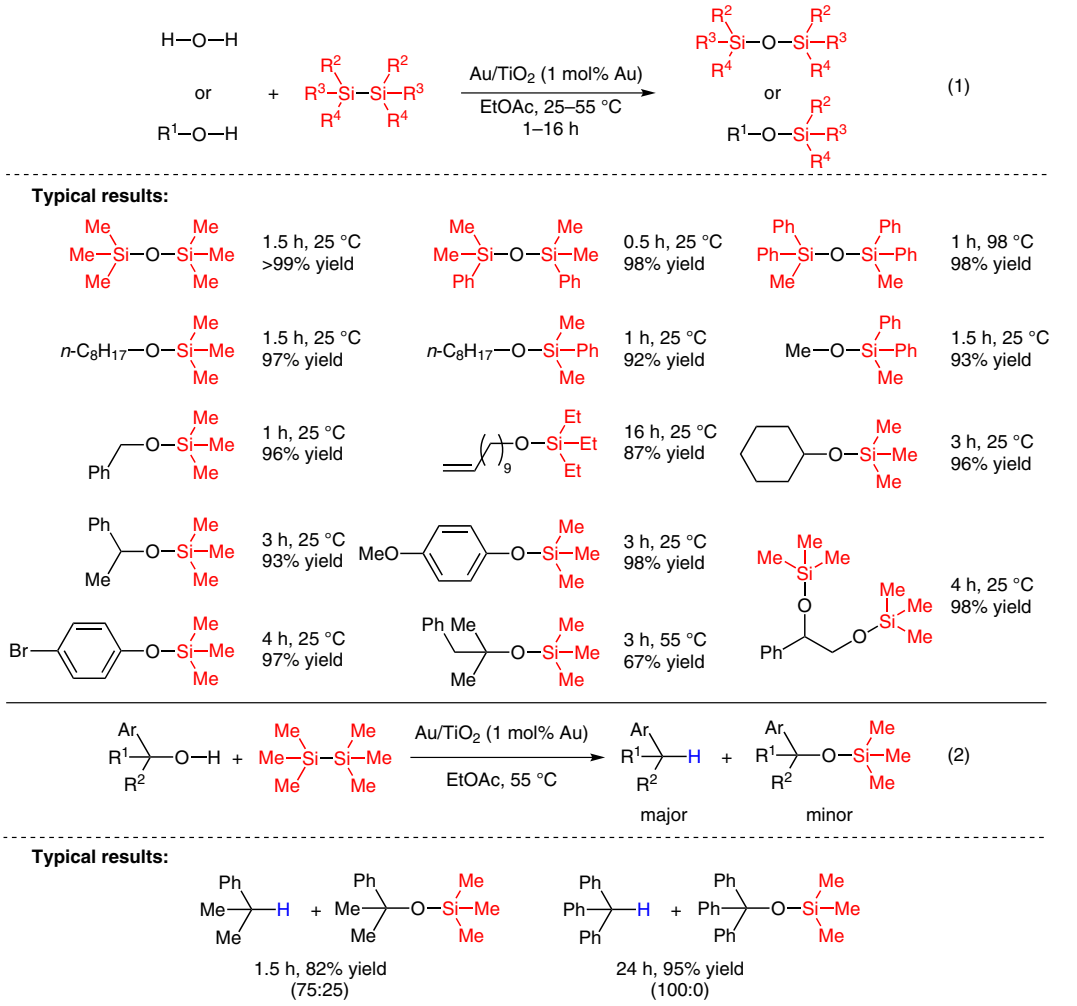
**alcohols**

C. GRYPARIS, M. STRATAKIS* (UNIVERSITY OF CRETE, IRAKLION, GREECE)

Gold Nanoparticles-Catalyzed Activation of 1,2-Disilanes: Hydrolysis, Silyl Protection of Alcohols and Reduction of *tert*-Benzylic Alcohols

*Chem. Commun.* **2012**, *48*, 10751–10753.

# Silylation of Alcohol Derivatives with 1,2-Disilanes Catalyzed by $Au/TiO_2$



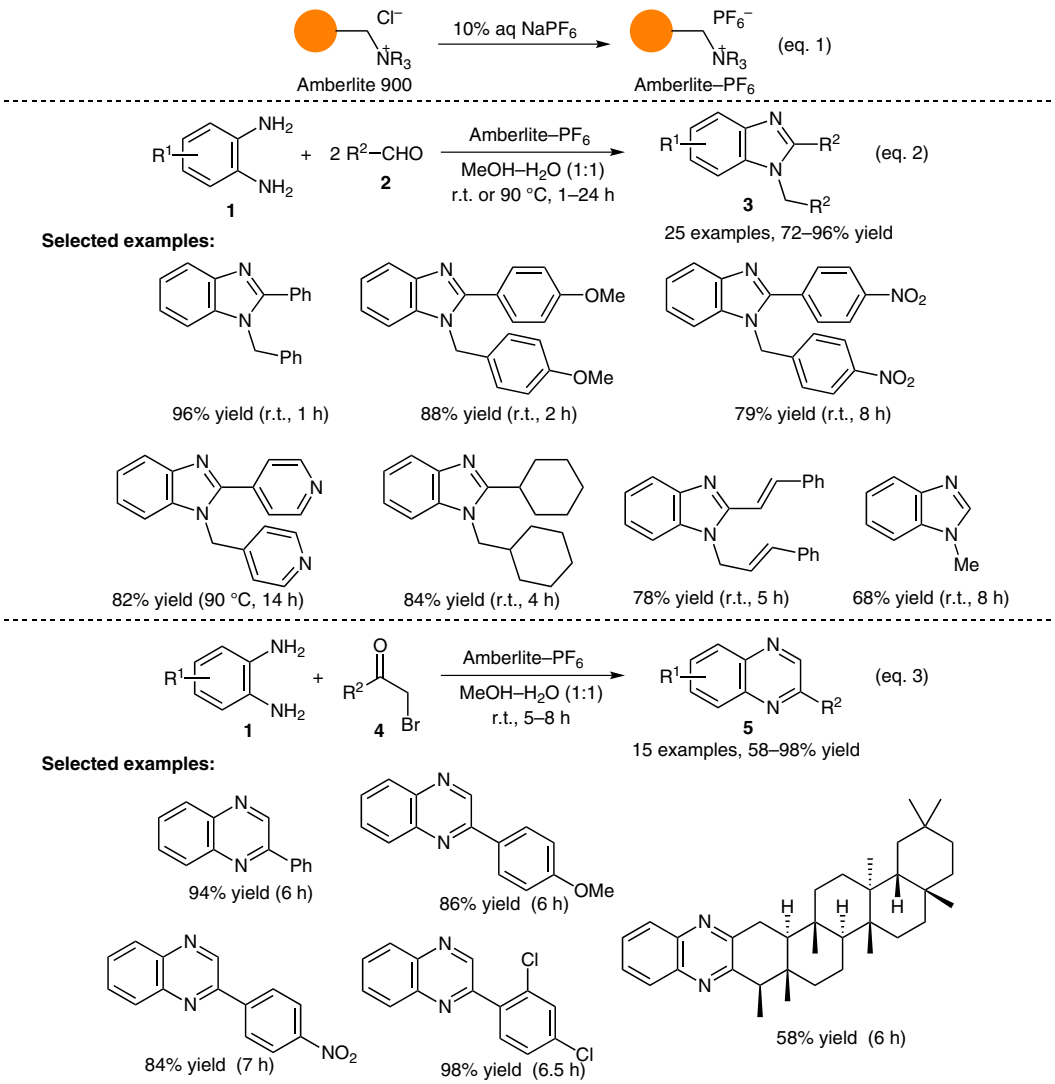

**Significance:** Gold nanoparticles supported on titanium dioxide ($Au/TiO_2$) catalyzed the silylation of water and primary, secondary, and tertiary aliphatic alcohols with 1,2-disilanes via Si–Si bond cleavage to give the corresponding silyl ethers in up to >99% yield (eq. 1). When tertiary benzylic alcohols were used for the reaction, the reduction proceeded to afford the corresponding alkanes as the major products (eq. 2).

**Comment:** The authors previously reported the oxidative cycloaddition of 1,1,3,3-tetramethyldisiloxane to alkynes catalyzed by $Au/TiO_2$ (*J. Am. Chem. Soc.* **2011**, *133*, 10426). The catalytic activity of $Au/TiO_2$ for the silylation of water was superior to that of gold nanoparticles supported on other supports such as aluminum oxide ($Al_2O_3$) and zinc oxide (ZnO).

**SYNFACTS Contributors:** Yasuhiro Uozumi, Takao Osako
Synfacts 2013, 9(1), 0112 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317908; **Reg-No.:** Y13612SF

P. GHOSH,* A. MANDAL (UNIVERSITY OF NORTH BENGAL, DARJEELING, INDIA)
Synthesis of Functionalized Benzimidazoles and Quinoxalines Catalyzed by Sodium Hexafluorophosphate Bound Amberlite Resin in Aqueous Medium
*Tetrahedron Lett.* **2012**, *53*, 6483–6488.

# Annulation Reactions Catalyzed by Amberlite-Bound Hexafluorophosphate




**Significance:** Amberlite resin-bound hexafluorophosphate (Amberlite-$PF_6$) was prepared by treatment of Amberlite 900 with aqueous $NaPF_6$ (eq. 1). In the presence of Amberlite-$PF_6$, the annulation of phenylenediamines **1** with aldehydes **2** took place to give the corresponding benzimidazoles **3** (25 examples, 72–96% yield).

**Comment:** The binding of hexafluorophosphate on Amberlite resin was confirmed by IR spectra (557 and 832 $cm^{-1}$), though other characterizations were not given. Phenylenediamines **1** also reacted with α-bromoketones **4** in the presence of Amberlite-$PF_6$ to give the corresponding quinoxalines **5** via an aromatization step.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Makoto Nagaosa
Synfacts 2013, 9(1), 0113 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317917; **Reg-No.:** Y14612SF



**Category**
**Polymer-Supported Synthesis**

**Key words**
**catalysis**
**Amberlite**
**diamines**
**benzimidazoles**
**quinoxalines**

**Category**

**Polymer-Supported Synthesis**

**Key words**

**aldol reaction**

**organocatalysis**

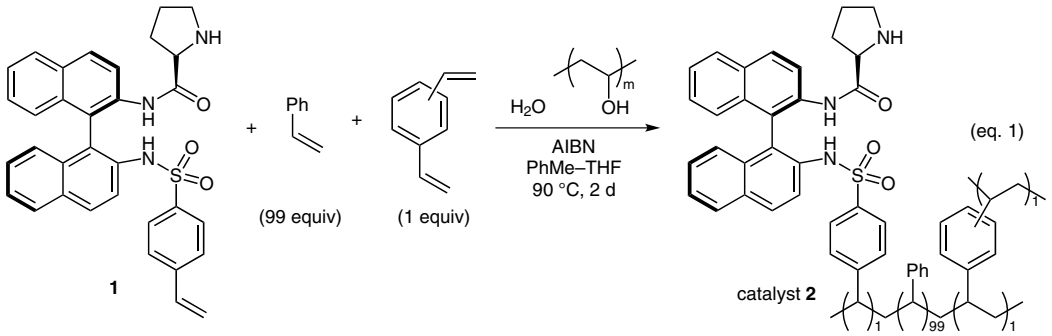
**solvent-free**

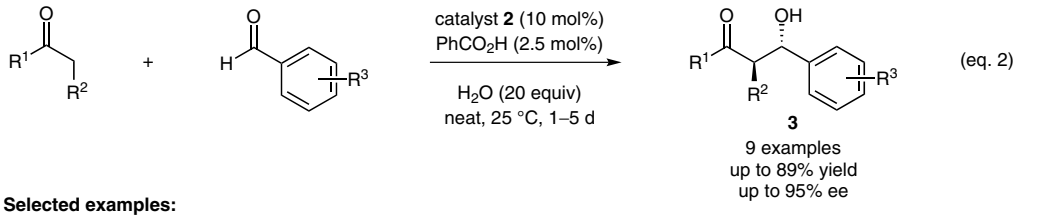
A. BAÑÓN-CABALLERO, G. GUILLENA,* C. NÁJERA* (UNIVERSIDAD DE ALICANTE, SPAIN)

Cross-Linked-Polymer-Supported *N*-{2′-[(Arylsulfonyl)amino][1,1′-binaphthalen]-2-yl}prolinamide as Organocatalyst for the Direct Aldol Intermolecular Reaction under Solvent-Free Conditions

*Helv. Chim. Acta* **2012**, *95*, 1831–1841.

# Asymmetric Aldol Reaction with BINAM-Sulfonyl Polymeric Organocatalyst

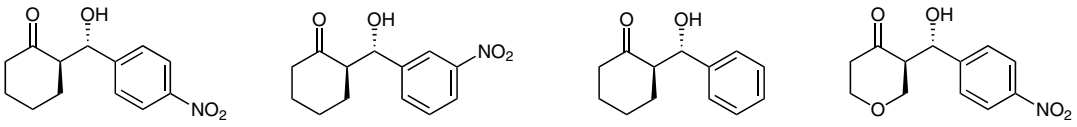



**3**

9 examples
up to 89% yield
up to 95% ee

**Selected examples:**

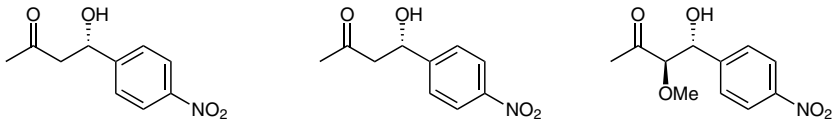



**3a** 1 d, 88% yield
93% ee, *anti*/*syn* = 89:11

**3b** 3 d, 82% yield
82% ee, *anti*/*syn* = 73:27

**3c** 3 d, 74% yield
85% ee, *anti*/*syn* = 60:40

**3d** 3 d, 69% yield
95% ee, *anti*/*syn* = 85:15




**3e**[a] 2 d, 83% yield
56% ee
([a] in the absence of $H_2O$)

**3f**[a] 5 d, 48% yield
72% ee

**3g**[a] 3 d, 76% yield
87% ee, *anti*/*syn* = 83:17

**Significance:** The BINAM-sulfonyl polymeric organocatalyst **2** was prepared by the AIBN-promoted copolymerization of BINAM-derived sulfonamide **1**, styrene, and divinylbenzene (eq. 1). Polymer **2** catalyzed the asymmetric aldol reaction of aliphatic ketones with aromatic aldehydes to give the corresponding aldol products **3** in up to 89% yield with up to 95% ee (9 examples, eq. 2).

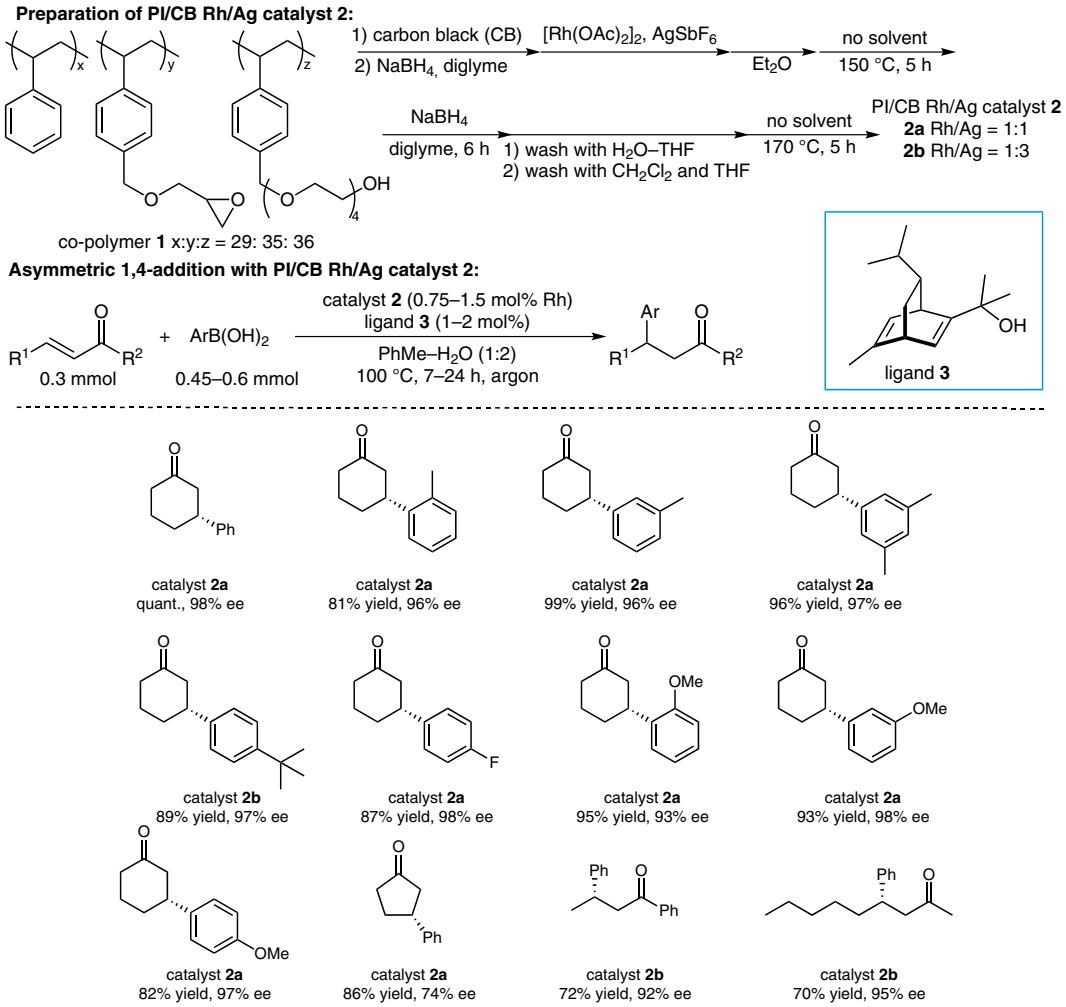
**Comment:** In the aldol reaction of cyclohexanone with 4-nitrobenzaldehyde, the catalyst was recovered by filtration and reused six times with a slight decrease in its catalytic activity (1st reuse: 90% yield, 90% ee, *anti*/*syn* = 87:13, 6th reuse: 77% yield, 92% ee, *anti*/*syn* = 86:16).

**SYNFACTS Contributors:** Yasuhiro Uozumi, Fumie Sakurai
Synfacts 2013, 9(1), 0114 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317913; **Reg-No.:** Y14112SF

T. YASUKAWA, H. MIYAMURA, S. KOBAYASHI* (THE UNIVERSITY OF TOKYO, JAPAN)

Polymer-Incarcerated Chiral Rh/Ag Nanoparticles for Asymmetric 1,4-Addition Reactions of Arylboronic Acids to Enones: Remarkable Effects of Bimetallic Structure on Activity and Metal Leaching
*J. Am. Chem. Soc.* **2012**, *134*, 16963–16966.

# Asymmetric Miyaura–Michael Reaction with Polymeric Rh/Ag Catalysts




**Significance:** Polystyrene-based polymer-incarcerated bimetallic rhodium nanoparticle catalysts PI/CB Rh/Ag **2a–b** were prepared from co-polymer **1**, carbon black (CB), $[Rh(OAc)_2]_2$, and $AgSbF_6$. Asymmetric 1,4-addition of arylboronic acids to enones was carried out with **2** and chiral ligand **3** to give the corresponding ketones in 70–99% yield with 74–98% ee without leaching of rhodium.

**Comment:** Catalyst **2a** was reused 13 times for the reaction of phenylboronic acid with 2-cyclohexenone. After the 10$^{th}$ use, the recovered catalyst was heated at 170 °C to regain its catalytic activity (1$^{st}$–8$^{th}$ use: >94% yield, 9$^{th}$ use: 67% yield, 10$^{th}$ use: 60% yield, 11$^{th}$–14$^{th}$ use: >90% yield, with 98% ee in all cycles).

**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Yoshinari Yuyama
Synfacts 2013, 9(1), 0115 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317915; **Reg-No.:** Y14312SF



**Category**
**Polymer-Supported Synthesis**

**Key words**
**bimetallic nanoparticle catalysts**
**rhodium**
**silver**
**asymmetric 1,4-addition**

**Category**

**Polymer-Supported Synthesis**

**Key words**

**catalysis**

**iron**

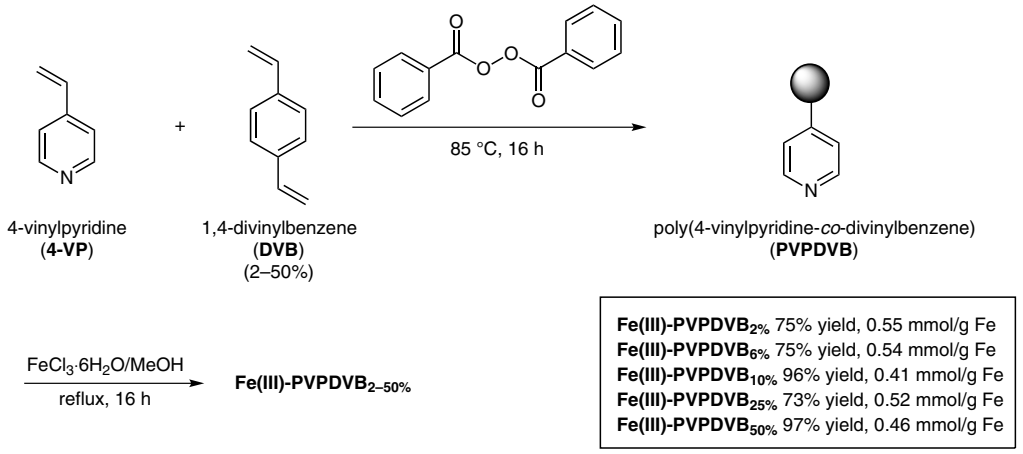
**oxidation**

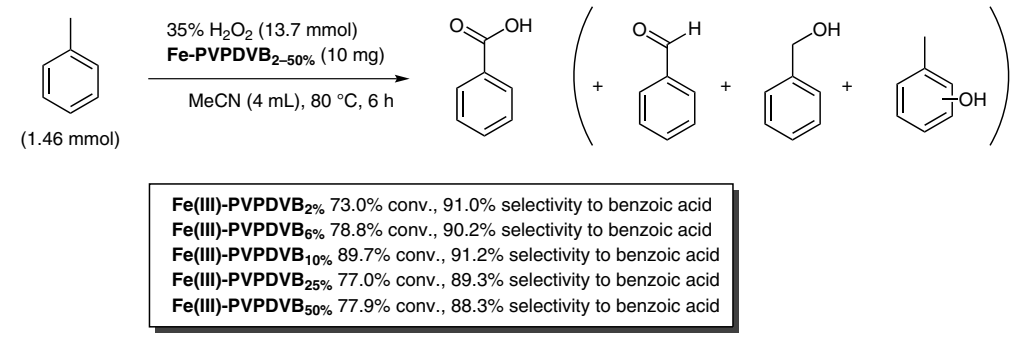
W. KARUEHANON, C. SIRATHANYAROTE, M. PATTARAWARAPAN* (CHIANG MAI UNIVERSITY, THAILAND)

Poly(4-vinylpyridine-*co*-divinylbenzene) Supported Iron(III) Catalyst for Selective Oxidation of Toluene to Benzoic Acid with $H_2O_2$

*Tetrahedron* **2012**, *68*, 9423–9428.

# Polymer-Supported Iron(III) Catalyst for the Selective Oxidation of Toluene




**Significance:** Poly(4-vinylpyridine-*co*-divinylbenzene)-supported iron(III) catalysts bearing different amounts (2–50%) of DVB cross-linker [Fe(III)-PVPDVB$_{2–50\%}$] were prepared and applied to the oxidation of toluene with hydrogen peroxide (73.0–89.7% conversion, 88.3–91.2% selectivity to benzoic acid). The polymer-supported catalyst containing 10% DVB [Fe(III)-PVPDVB$_{10\%}$] led to the selective oxidation of toluene to benzoic acid in 90% conversion with up to 96% selectivity under optimized conditions.

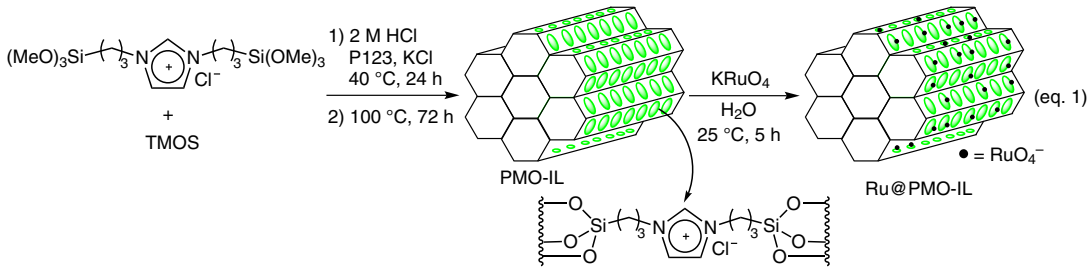
**Comment:** The catalytic activity of reused Fe(III)-PVPDVB$_{10\%}$ decreased due to leaching of iron ions from the polymer support. No oxidation of toluene occurred in the absence of the polymer-supported iron catalysts or in the presence of iron-free PVPDVB. The toluene oxidation with the homogeneous counterpart, $FeCl_3·H_2O$, resulted in lower substrate conversion (<58%), while the reaction selectivity was as high as with the polymeric catalyst (92%).

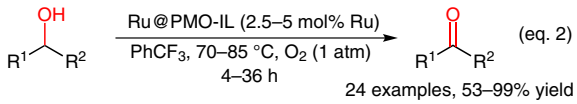
**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Maki Minakawa
Synfacts 2013, 9(1), 0116 Published online: 17.12.2012
**DOI:** 10.1055/s-0032-1317914; **Reg-No.:** Y14212SF

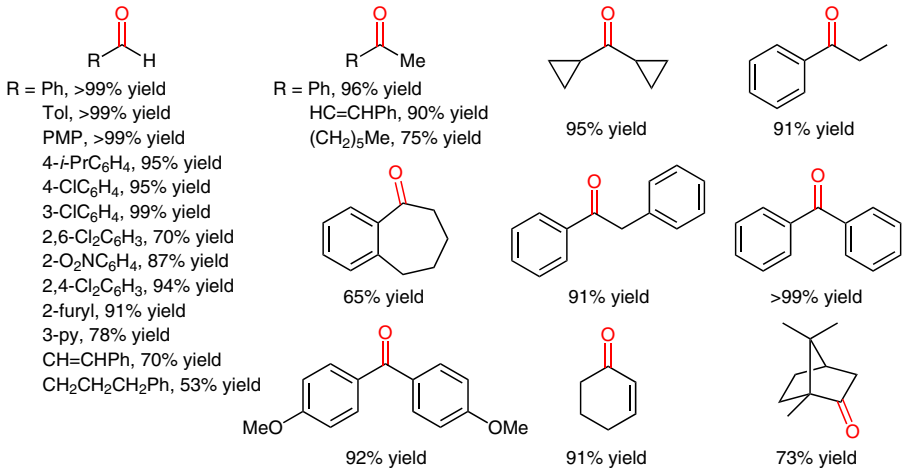
B. KARIMI,* D. ELHAMIFAR, O. YARI, M. KHORASANI, H. VALI, J. H. CLARK, A. J. HUNT
(INSTITUTE FOR ADVANCED STUDIES IN BASIC SCIENCES, ZANJAN AND YASOUJ UNIVERSITY, IRAN; MCGILL UNIVERSITY, MONTREAL, CANADA; UNIVERSITY OF YORK, UK)

Synthesis and Characterization of Alkyl-Imidazolium-Based Periodic Mesoporous Organosilicas: A Versatile Host for the Immobilization of Perruthenate ($RuO_4^-$) in the Aerobic Oxidation of Alcohols
*Chem. Eur. J.* **2012**, *18*, 13520–13530.

# Aerobic Oxidation of Alcohols with Ru@PMO-IL




**Significance:** Perruthenate was supported on ionic-liquid-based periodic mesoporous organosilica (Ru@PMO-IL) via the reaction of 1,3-bis-(3-trimethoxysilylpropyl)imidazolium chloride with tetramethoxysilane, followed by treatment with $KRuO_4$ (eq. 1). Ru@PMO-IL catalyzed the oxidation of alcohols in trifluorotoluene at 70–85 °C under 1 atm of oxygen to give the corresponding carbonyl compounds in up to >99% yield (24 examples, eq. 2).

**Comment:** The catalyst was recovered by centrifugation and subjected to recycling runs. ICP-AES analysis showed no significant ruthenium leaching (<1 ppm) under the reaction conditions. Nitrogen adsorption and TEM analyses of the recovered catalyst revealed no morphology change of the mesoporous structure. However, a slight loss of catalytic activity was observed during the recycling runs (for the oxidation of benzyl alcohol; 2nd reuse: 99%, 4th reuse: 89%, 5th reuse: 75%).

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**Category**

**Polymer-Supported Synthesis**

**Key words**

**gold nanoparticles**

**Ullmann homocoupling**

**aryl iodides**

**β-bromostyrene**

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Ullmann Homocoupling Catalysed by Gold Nanoparticles in Water and Ionic Liquid

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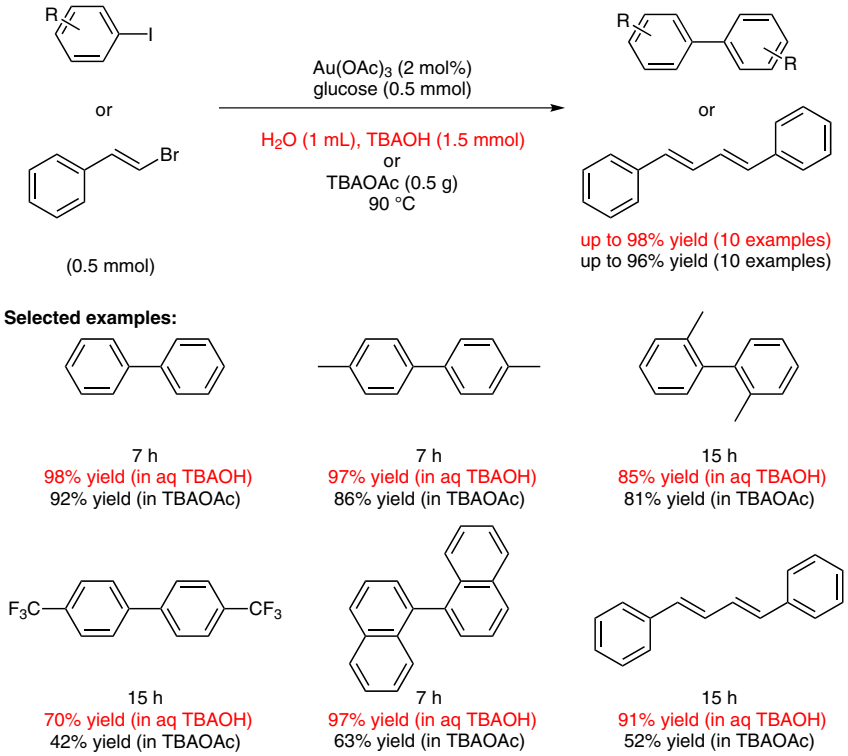
# Ullmann Homocoupling in Water or Molten TBAOAc with Gold Nanoparticles




**Significance:** Gold nanoparticles, generated in situ from $Au(OAc)_3$ and glucose, catalyzed the Ullmann homocoupling of aryl iodides or β-bromostyrene in aqueous tetrabutylammonium hydroxide (TBAOH) or in molten tetrabutylammonium acetate (TBAOAc) at 90 °C to afford the corresponding coupling products in up to 98% yield (10 examples) or in up to 96% yield (10 examples), respectively.

**Comment:** The gold nanoparticles were characterized with TEM, UV/Vis, DLS, and XPS. The particle size of the nanoparticles was about 1 nm in aqueous TBAOH and 20 nm in TBAOAc, respectively. The smaller nanoparticles showed higher catalytic activity because of their lager surfaces.

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