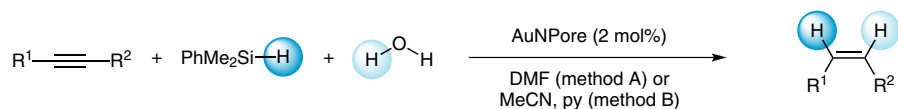


M. YAN, T. JIN,* Y. ISHIKAWA, T. MINATO, T. FUJITA, L.-Y. CHEN, M. BAO, N. ASAO, M.-W. CHEN, Y. YAMAMOTO (TOHOKU UNIVERSITY, SENDAI, JAPAN AND DALIAN UNIVERSITY OF TECHNOLOGY, P. R OF CHINA)

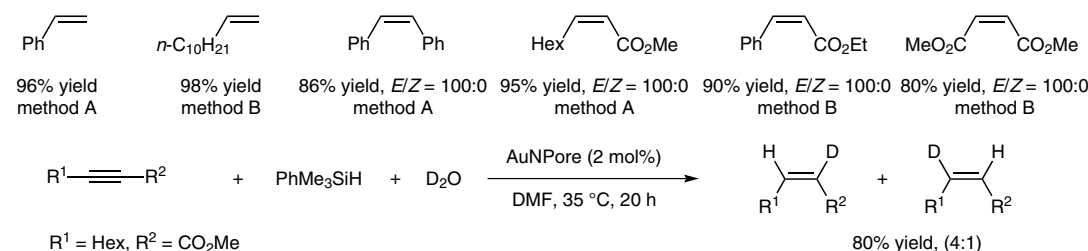
Nanoporous Gold Catalyst for Highly Selective Semihydrogenation of Alkynes: Remarkable Effect of Amine Additives

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

Nanoporous Gold Catalyst for the Selective Semihydrogenation of Alkynes



Selected examples:



Significance: A nanoporous gold catalyst (AuNPore), which was prepared by dealloying a homogeneous Au₃₀Ag₇₀ 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 PhMe₂SiH 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%), Au₃₀Ag₇₀ 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-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

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Category

Polymer-Supported Synthesis

Key words

nanoporous gold
semihydrogenation
alkynes
amines

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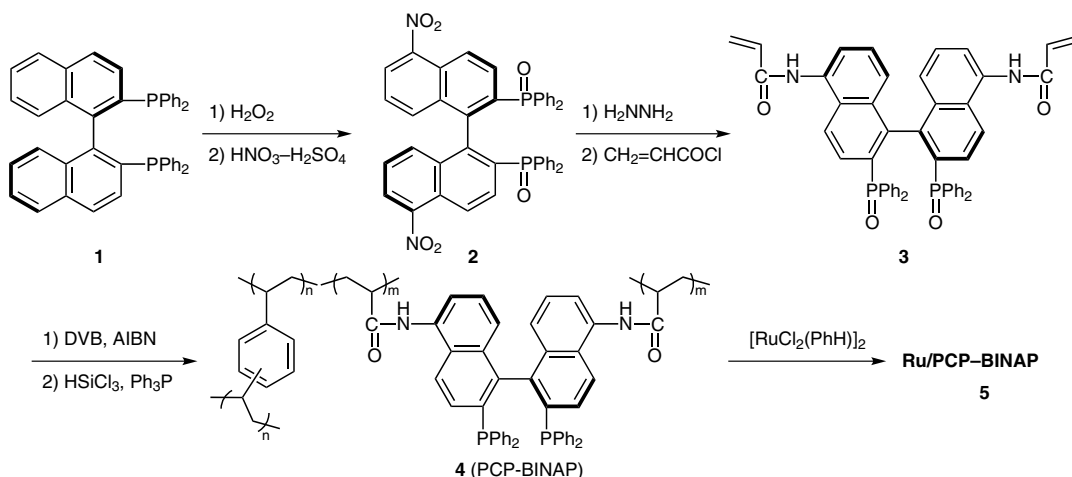
Q. SUN, X. MENG,* X. LIU, X. ZHANG, Y. YANG, Q. YANG,* F. S. XIAO* (ZHEJIANG UNIVERSITY, HANGZHOU, CHINA)

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

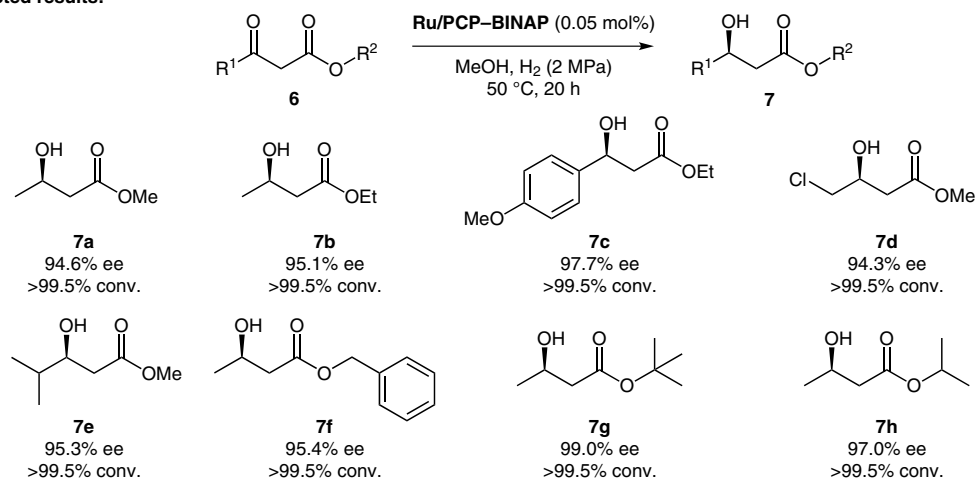
Chem. Commun. **2012**, 48, 10505–10507.

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 $[\text{RuCl}_2(\text{PhH})_2]$ 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.

SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Heeyoel Baek

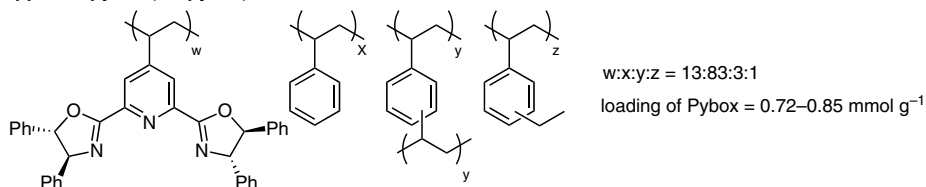
Synfacts 2013, 9(1), 0108 Published online: 17.12.2012

DOI: 10.1055/s-0032-1317918; Reg-No.: Y14712SF

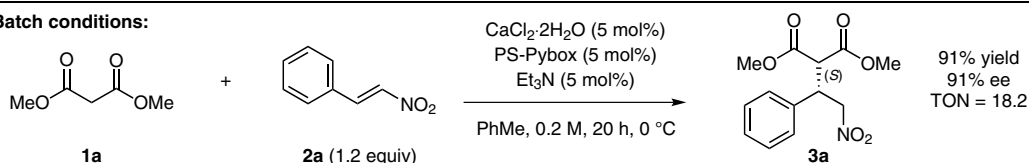
Comment: Ru/PCP–BINAP was readily recovered and reused six times without significant loss of its catalytic ability (1st reuse: >99.5% conversion, 94.3% ee, 6th reuse: >99.5% conversion, 95.3% ee).

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

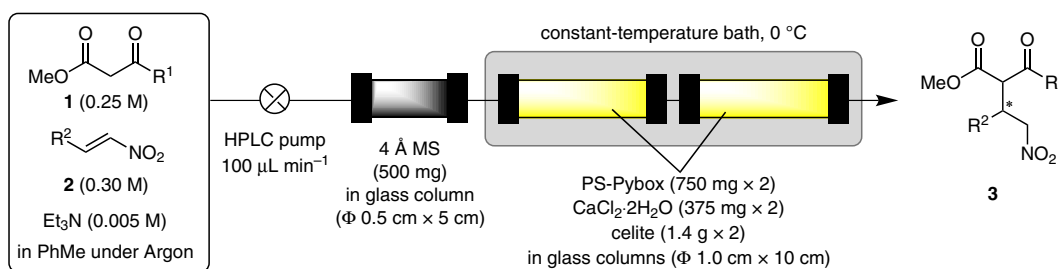
Polymer-supported pybox (PS-pybox)



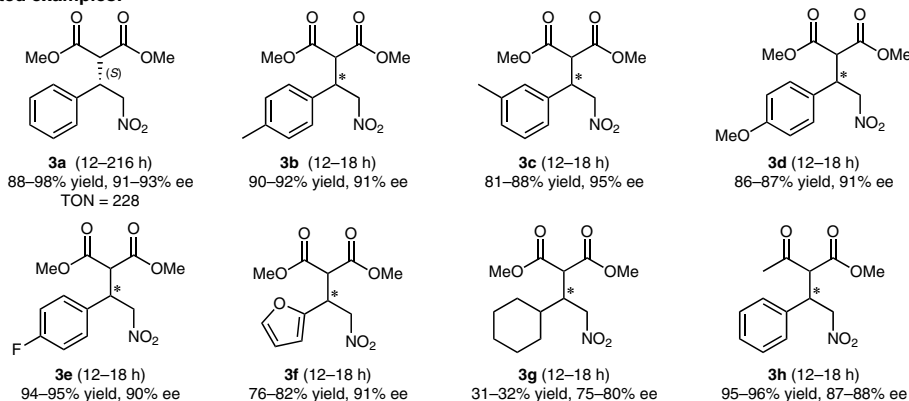
Batch conditions:



Flow conditions:



Selected examples:



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.

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

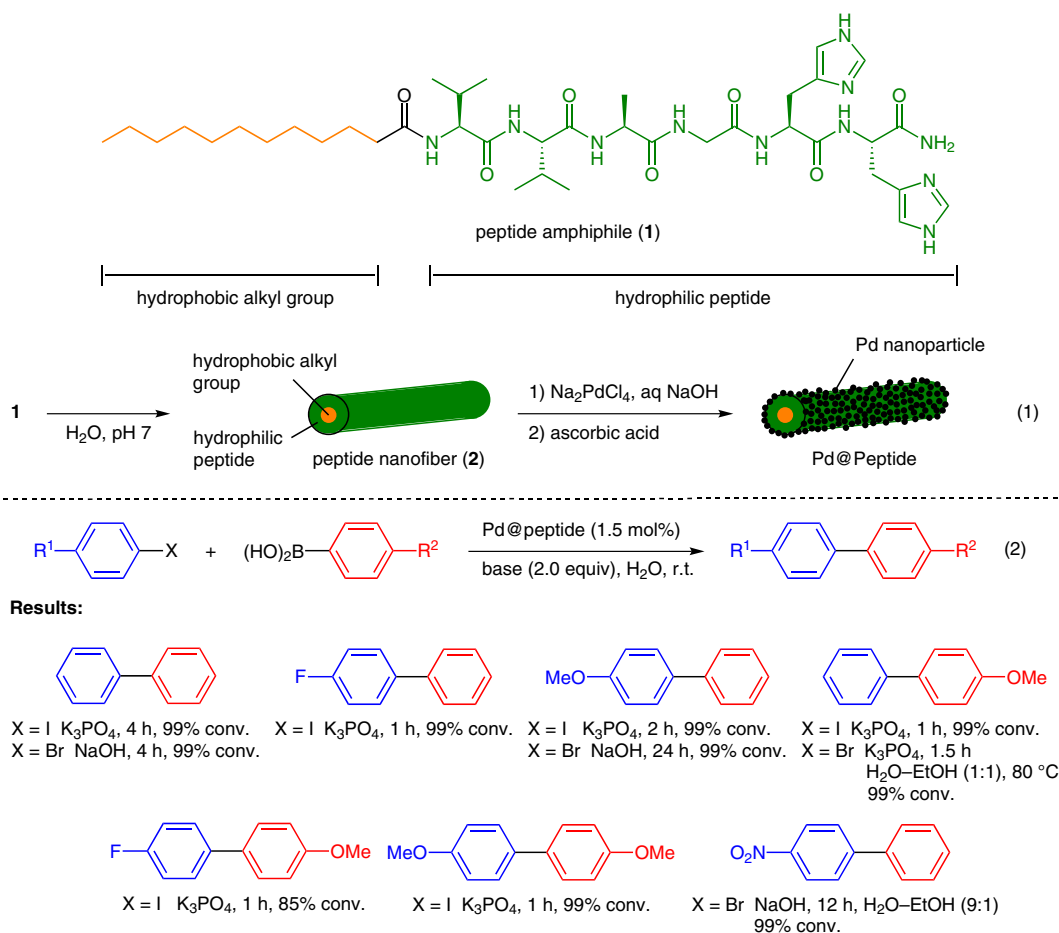
Comment: The flow system worked for 204 hours without significant loss of catalytic activity to give **3a** in 95.5% yield with 92.0% ee on average. The total amount of product was 291.4 mmol and the turn-over number (TON) reached 228.

M. A. KHALILY, O. USTAHUSEYIN, R. GARIFULLIN, R. GENÇ, M. O. GÜLER* (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-assembly 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).

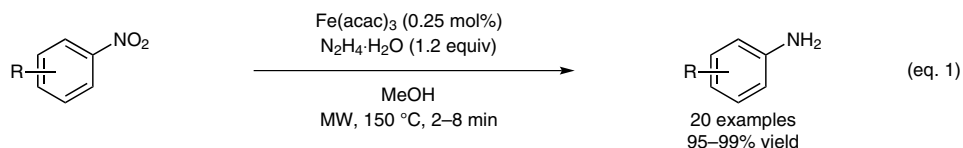
Comment: Pd@Peptide were characterized with TEM, SEM, XRD, and TGA. In the coupling reaction of bromobenzene and 4-methoxyphenylboronic acid, the catalyst was reused four times without significant loss of catalytic activity (1st reuse: 97% conversion, 2nd reuse: 97% conversion, 3rd reuse: 97% conversion,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

SYNFACTS Contributors: Yasuhiro Uozumi, Hiroaki Tsuji
Synfacts 2013, 9(1), 0110 Published online: 17.12.2012

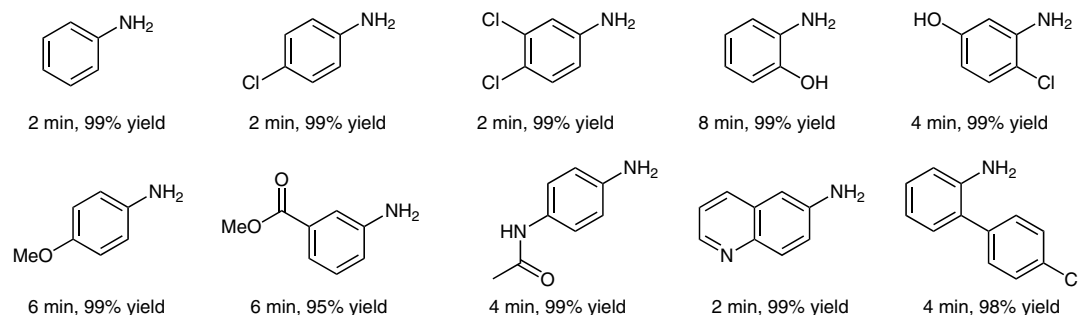
DOI: 10.1055/s-0032-1317909; **Reg-No.:** Y13712SF

Reduction of Nitroarenes Using In Situ Generated Iron Oxide Nanocrystals

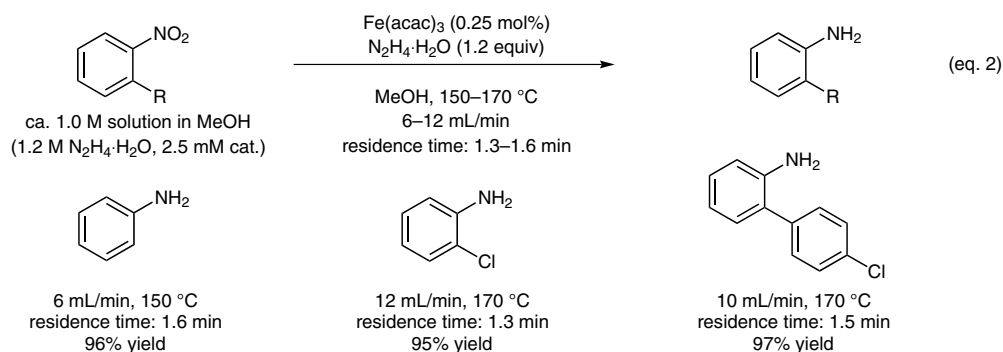
Reduction of nitroarenes using the batch system:



Selected examples:



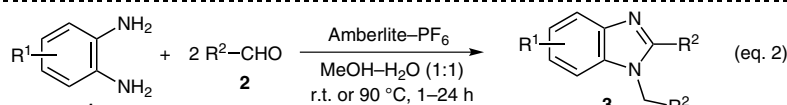
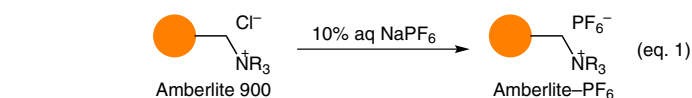
Continuous-flow reduction of nitroarenes:



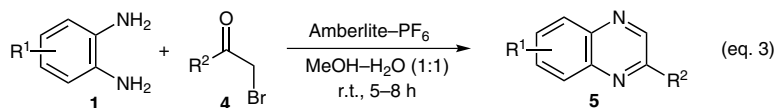
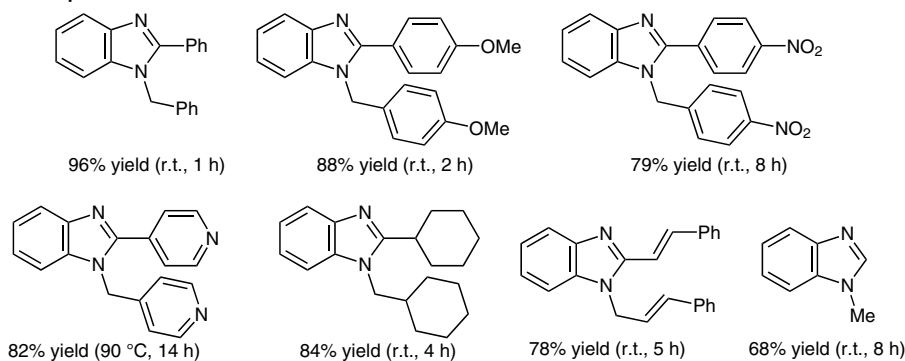
Significance: Iron oxide nanocrystals, generated in situ from Fe(acac)₃ and hydrazine hydrate, catalyzed the reduction of nitroarenes with hydrazine hydrate under microwave conditions to give the corresponding anilines in 95–99% yield (20 examples, eq. 1). In the reduction of nitrobenzene to aniline 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.

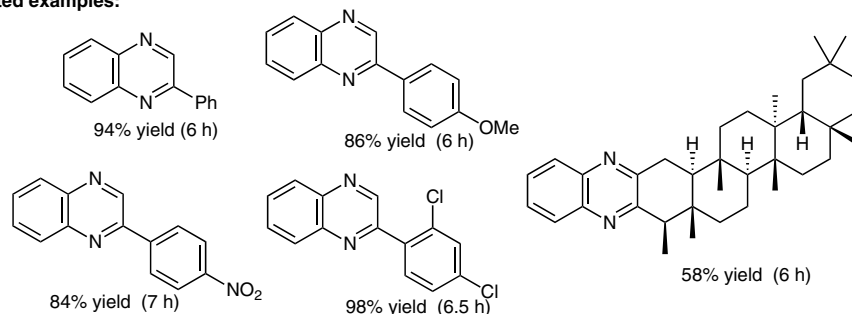
Annulation Reactions Catalyzed by Amberlite-Bound Hexafluorophosphate



Selected examples:



Selected examples:



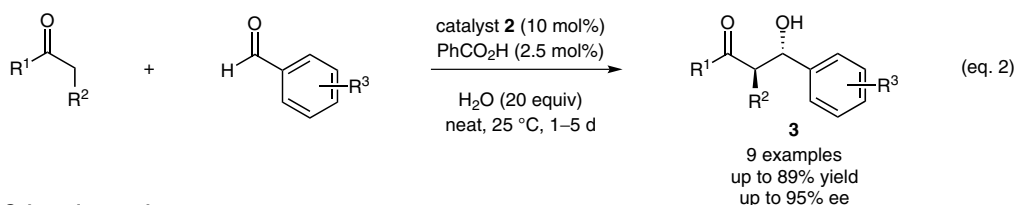
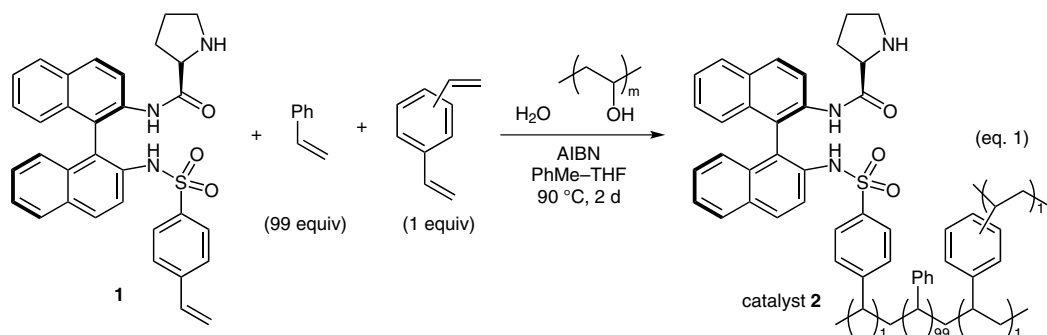
Significance: Amberlite resin-bound hexafluorophosphate (Amberlite-PF₆) was prepared by treatment of Amberlite 900 with aqueous NaPF₆ (eq. 1). In the presence of Amberlite-PF₆, the annulation of phenylenediamines **1** with aldehydes **2** took place to give the corresponding benzimidazoles **3** (25 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-PF₆ to give the corresponding quinoxalines **5** via an aromatization step.

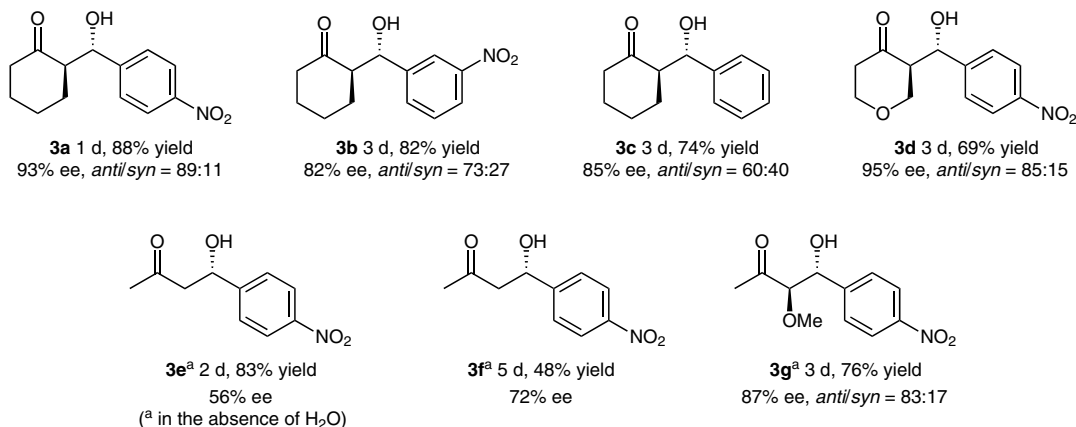
SYNFACTS Contributors: Yasuhiro Uozumi, Makoto Nagaosa
Synfacts 2013, 9(1), 0113 Published online: 17.12.2012
DOI: 10.1055/s-0032-1317917; Reg-No.: Y14612SF

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



Selected examples:



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

Asymmetric Miyaura–Michael Reaction with Polymeric Rh/Ag Catalysts

Category

Polymer-Supported Synthesis

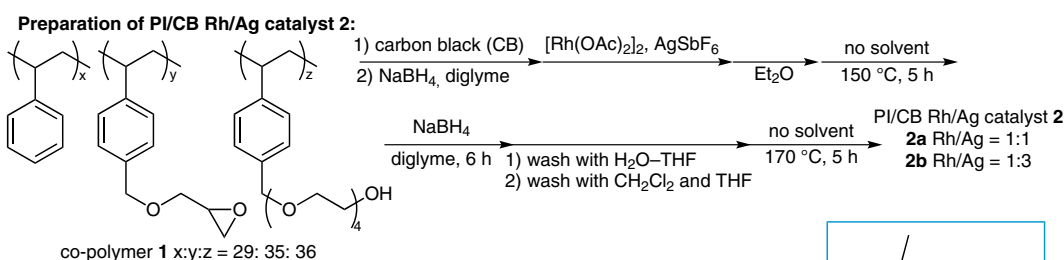
Key words

bimetallic nanoparticle catalysts

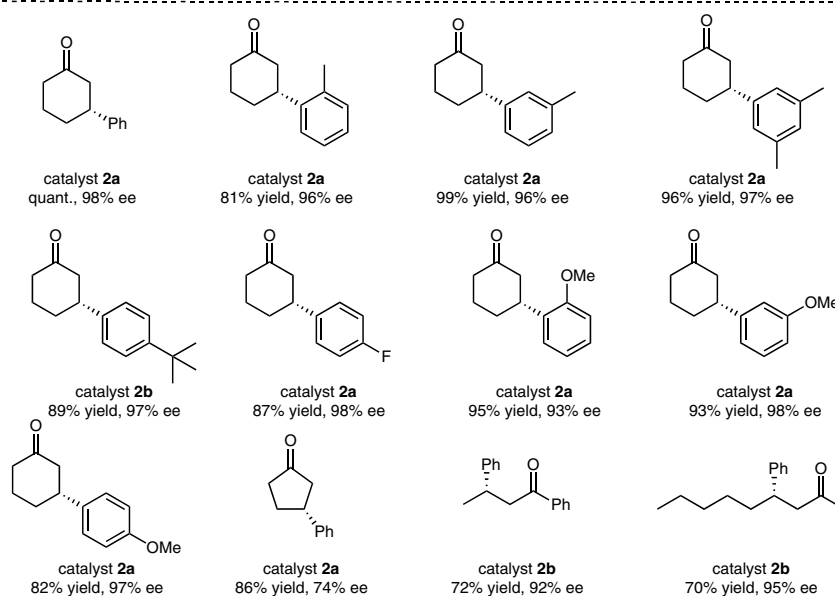
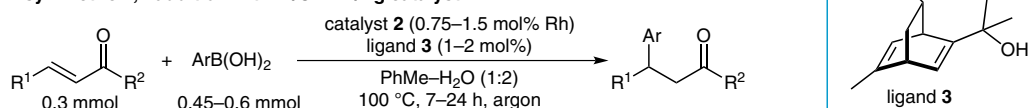
rhodium

silver

asymmetric 1,4-addition



Asymmetric 1,4-addition with PI/CB Rh/Ag catalyst 2:



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 AgSbF₆. 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 10th use, the recovered catalyst was heated at 170 °C to regain its catalytic activity (1st–8th use: >94% yield, 9th use: 67% yield, 10th use: 60% yield, 11th–14th use: >90% yield, with 98% ee in all cycles).

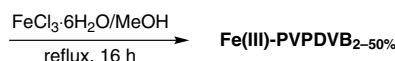
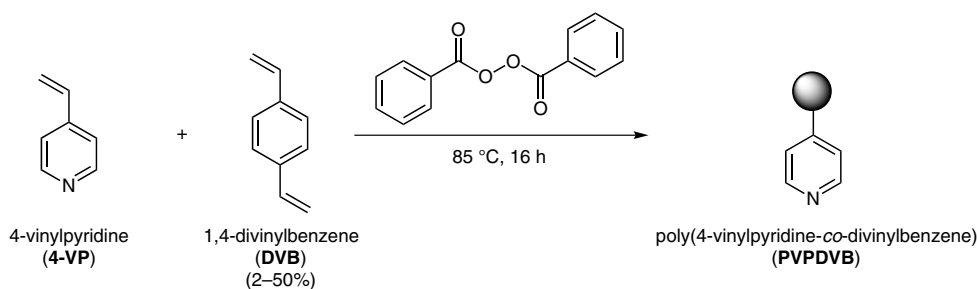
SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Yoshinari Yuyama
Synfacts 2013, 9(1), 0115 Published online: 17.12.2012
DOI: 10.1055/s-0032-1317915; Reg-No.: Y14312SF

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

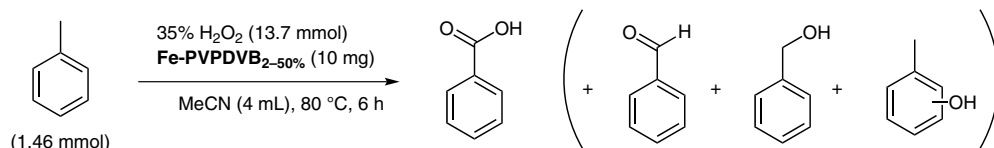
Poly(4-vinylpyridine-co-divinylbenzene) Supported Iron(III) Catalyst for Selective Oxidation of Toluene to Benzoic Acid with H_2O_2

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

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



Fe(III)-PVPDVB_{2%} 75% yield, 0.55 mmol/g Fe
Fe(III)-PVPDVB_{6%} 75% yield, 0.54 mmol/g Fe
Fe(III)-PVPDVB_{10%} 96% yield, 0.41 mmol/g Fe
Fe(III)-PVPDVB_{25%} 73% yield, 0.52 mmol/g Fe
Fe(III)-PVPDVB_{50%} 97% yield, 0.46 mmol/g Fe



Fe(III)-PVPDVB_{2%} 73.0% conv., 91.0% selectivity to benzoic acid
Fe(III)-PVPDVB_{6%} 78.8% conv., 90.2% selectivity to benzoic acid
Fe(III)-PVPDVB_{10%} 89.7% conv., 91.2% selectivity to benzoic acid
Fe(III)-PVPDVB_{25%} 77.0% conv., 89.3% selectivity to benzoic acid
Fe(III)-PVPDVB_{50%} 77.9% conv., 88.3% selectivity to benzoic acid

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, $\text{FeCl}_3 \cdot \text{H}_2\text{O}$, 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

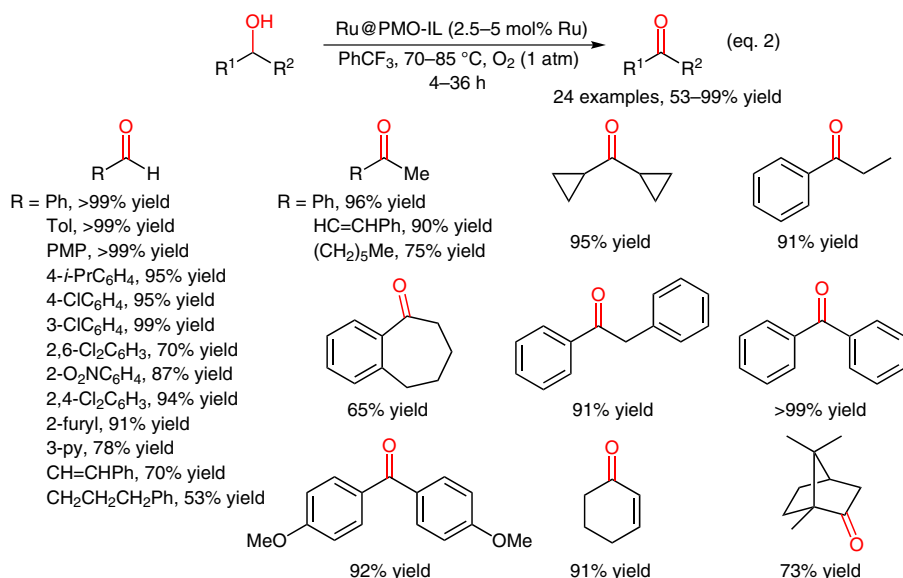
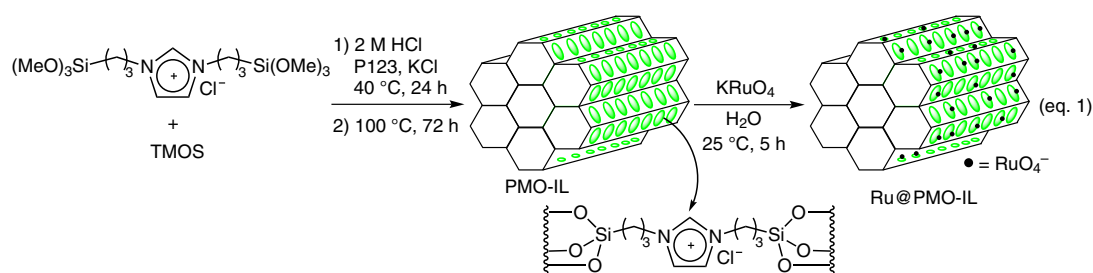
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B. KARIMI,* D. ELHAMIFAR, O. YARI, M. KHORASANI, H. VALI, J. H. CLARK, A. J. HUNT
(INSTITUTE FOR ADVANCED STUDIES IN BASIC SCIENCES, ZANJAN AND YASOUJ
UNIVERSITY, IRAN; MCGILL UNIVERSITY, MONTREAL, CANADA; UNIVERSITY OF YORK,
UK)

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



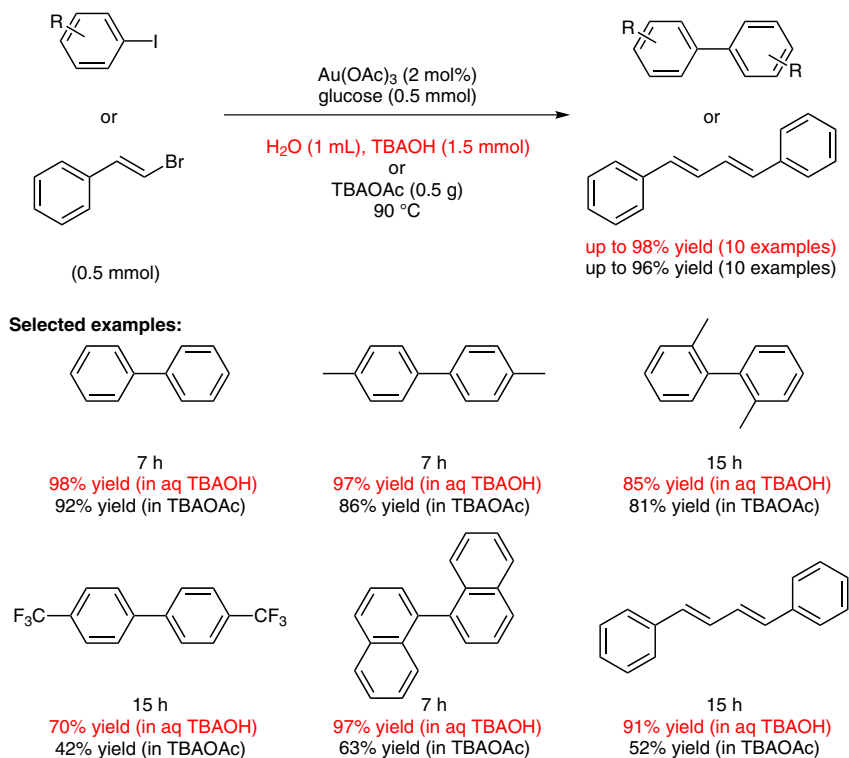
Significance: Perruthenate was supported on ionic-liquid-based periodic mesoporous organosilica (Ru@PMO-IL) via the reaction of 1,3-bis-(3-trimethoxysilylpropyl)imidazolium chloride with tetramethoxysilane, followed by treatment with KRuO_4 (eq. 1). Ru@PMO-IL catalyzed the oxidation of alcohols in trifluorotoluene 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%).

SYNFACTS Contributors: Yasuhiro Uozumi, Go Hamasaka
Synfacts 2013, 9(1), 0117 Published online: 17.12.2012
DOI: 10.1055/s-0032-1317907; Reg-No.: Y13512SF

A. MONOPOLI,* P. COTUGNO, G. PALAZZO, N. DITARANTO, B. MARIANO, N. CIOFFI, F. CIMINALE, A. NACCI* (UNIVERSITÀ DEGLI STUDI DI BARI 'ALDO MORO', ITALY)
Ullmann Homocoupling Catalysed by Gold Nanoparticles in Water and Ionic Liquid
Adv. Synth. Catal. **2012**, 354, 2777–2788.

Ullmann Homocoupling in Water or Molten TBAOAc with Gold Nanoparticles



Significance: Gold nanoparticles, generated in situ from $\text{Au}(\text{OAc})_3$ 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 larger surfaces.

SYNFACTS Contributors: Yasuhiro Uozumi, Noboru Kobayashi
Synfacts 2013, 9(1), 0118 Published online: 17.12.2012
DOI: 10.1055/s-0032-1317910; **Reg-No.:** Y13812SF