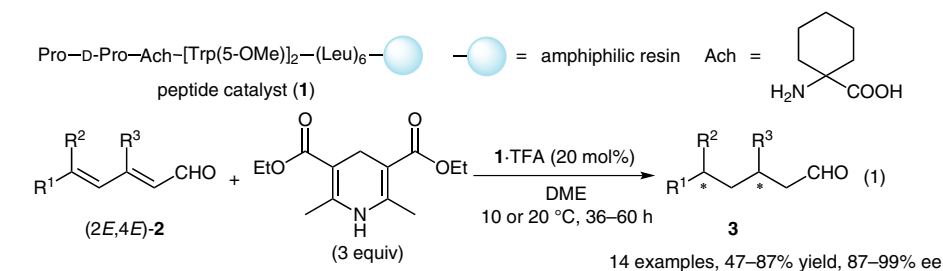
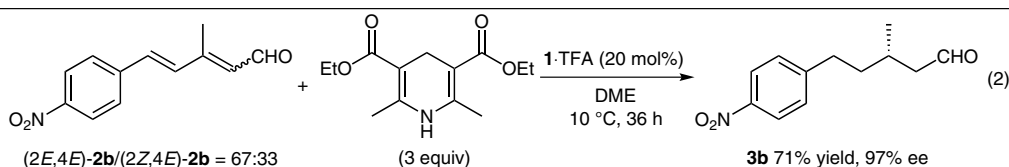
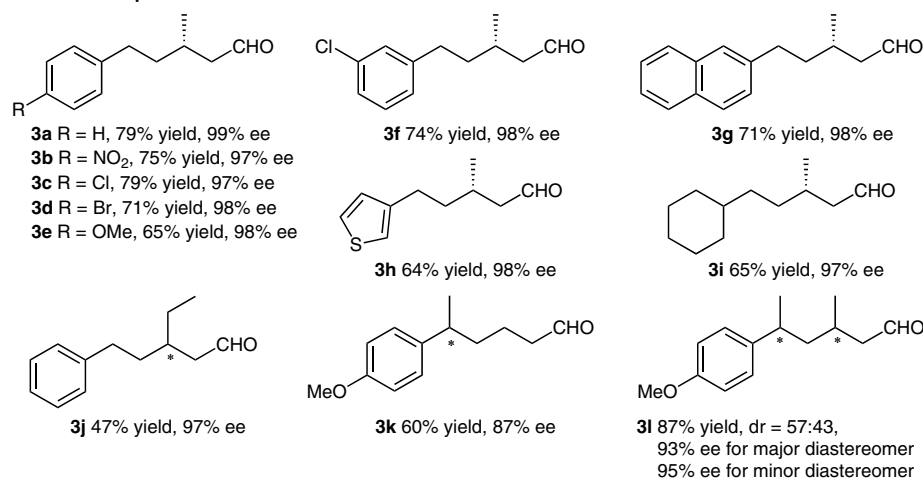


Regio- and Enantioselective Hydrogenation Using a Peptide Catalyst



Selected examples:



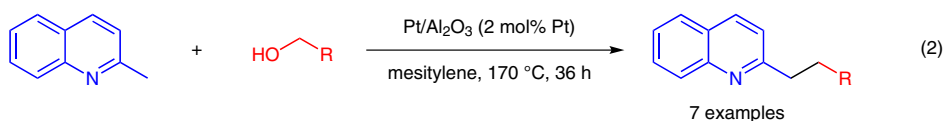
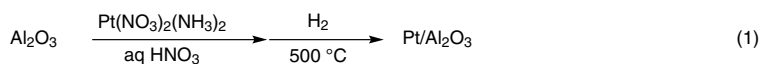
Significance: The amphiphilic resin-supported peptide **1** catalyzed the regio- and enantioselective transfer hydrogenation of (2*E*,4*E*)- $\alpha,\beta,\gamma,\delta$ -unsaturated aldehydes **2** with a Hantzsch ester to give the corresponding aldehydes **3** in 47–87% yield with 87–99% ee (14 examples, eq. 1).

Comment: In the hydrogenation of the mixture of (2*E*,4*E*)-**2b** and (2*Z*,4*E*)-**2b**, aldehyde **3b** was obtained in 71% yield with 97% ee (eq. 2). The authors have previously reported the asymmetric transfer hydrogenation of α,β -unsaturated aldehydes with a Hantzsch ester in the presence of resin-supported peptides (*Org. Lett.* **2008**, 10, 2035; *Tetrahedron: Asymmetry* **2009**, 20, 461).

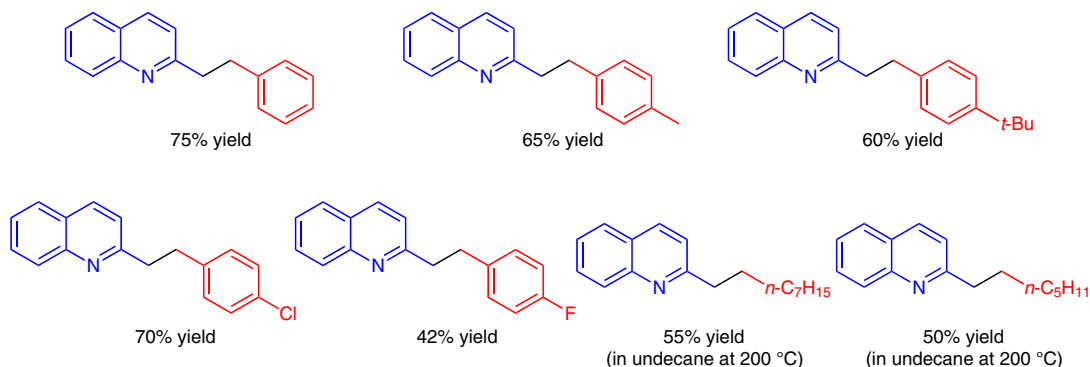
C. CHAUDHARI, S. M. A. H. SIDDIKI, K.-I. SHIMIZU* (HOKKAIDO UNIVERSITY, SAPPORO AND KYOTO UNIVERSITY, JAPAN)

Alkylation of 2-Methylquinoline with Alcohols under Additive-Free Conditions by Al_2O_3 -Supported Pt Catalyst
Tetrahedron Lett. **2013**, 54, 6490–6493.

Dehydrative Alkylation of 2-Methylquinoline with Alcohols Using $\text{Pt}/\text{Al}_2\text{O}_3$



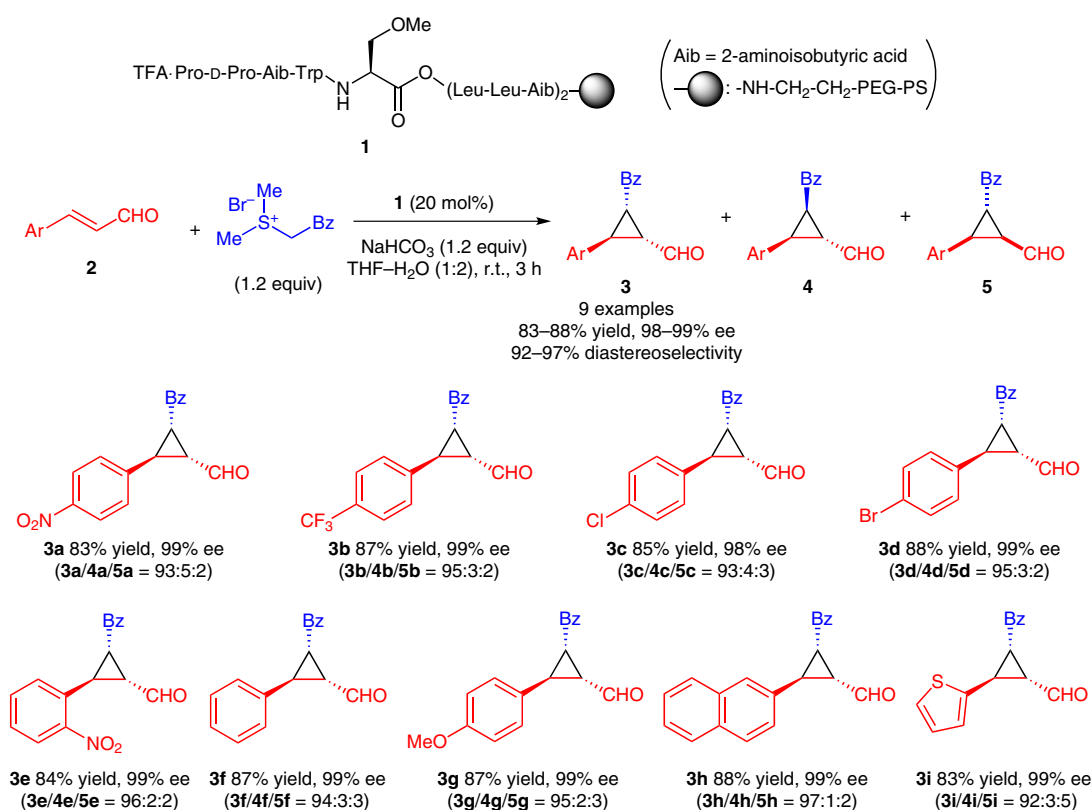
Results:



Significance: The Al_2O_3 -supported platinum nanoclusters ($\text{Pt}/\text{Al}_2\text{O}_3$) were prepared by mixing Al_2O_3 and an aqueous HNO_3 solution of $\text{Pt}(\text{NO}_3)_2(\text{NH}_3)_2$ followed by reduction with hydrogen (eq. 1). $\text{Pt}/\text{Al}_2\text{O}_3$ catalyzed the dehydrative alkylation of 2-methylquinoline with alcohols in mesitylene. The alkylation took place at the 2-methyl group to afford the corresponding alkylated products in up to 75% yield (7 examples). The catalyst was recovered by centrifugation, reactivated by reduction with hydrogen and reused four times with a slight decrease of its catalytic activity.

Comment: The $\text{Pt}/\text{Al}_2\text{O}_3$ nanoclusters were characterized by XANES, EXAFS and CO adsorption analyses. In the reaction of 2-methylquinoline with benzyl alcohol, the catalytic activity of $\text{Pt}/\text{Al}_2\text{O}_3$ was superior to that of the other Al_2O_3 -supported metal catalysts ($\text{Ir}/\text{Al}_2\text{O}_3$: 53% yield, $\text{Rh}/\text{Al}_2\text{O}_3$: 31% yield, $\text{Pd}/\text{Al}_2\text{O}_3$: 32% yield, $\text{Ag}/\text{Al}_2\text{O}_3$: 5% yield) and Pt nanoclusters supported on the other solid supports ($\text{Pt}/\text{Nb}_2\text{O}_5$: 20% yield, Pt/C : 7% yield, Pt/ZrO_2 : 1% yield). ICP-AES analysis showed no leaching of Pt from the catalyst during the reaction.

Cyclopropanation of α,β -Unsaturated Aldehydes with a Supported Peptide

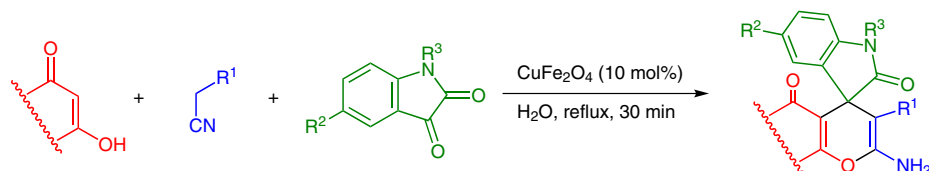


Significance: The amphiphilic resin-supported peptide **1** catalyzed the diastereo- and enantioselective cyclopropanation of aromatic α,β -unsaturated aldehydes **2** with dimethylphenacylsulfonium bromide in the presence of NaHCO_3 to give the corresponding cyclopropanes **3** in 83–88% yield with 98–99% ee and 92–97% diastereoselectivity (9 examples, eq. 1). In the formation of **3g**, the catalyst was recovered by filtration and reused five times without significant loss of its catalytic performance (1st reuse: 87% yield, 99% ee, 94% diastereoselectivity; 5th reuse: 83% yield, 99% ee, 95% diastereoselectivity).

Comment: The authors have previously reported the preparation of a series of amphiphilic resin-supported peptides and their application to asymmetric hydrogenation (*Org. Lett.* **2008**, *10*, 2035), asymmetric Friedel–Crafts-type alkylation (*Adv. Synth. Catal.* **2012**, *354*, 1280) and asymmetric Michael addition (*Angew. Chem. Int. Ed.* **2012**, *51*, 12786).

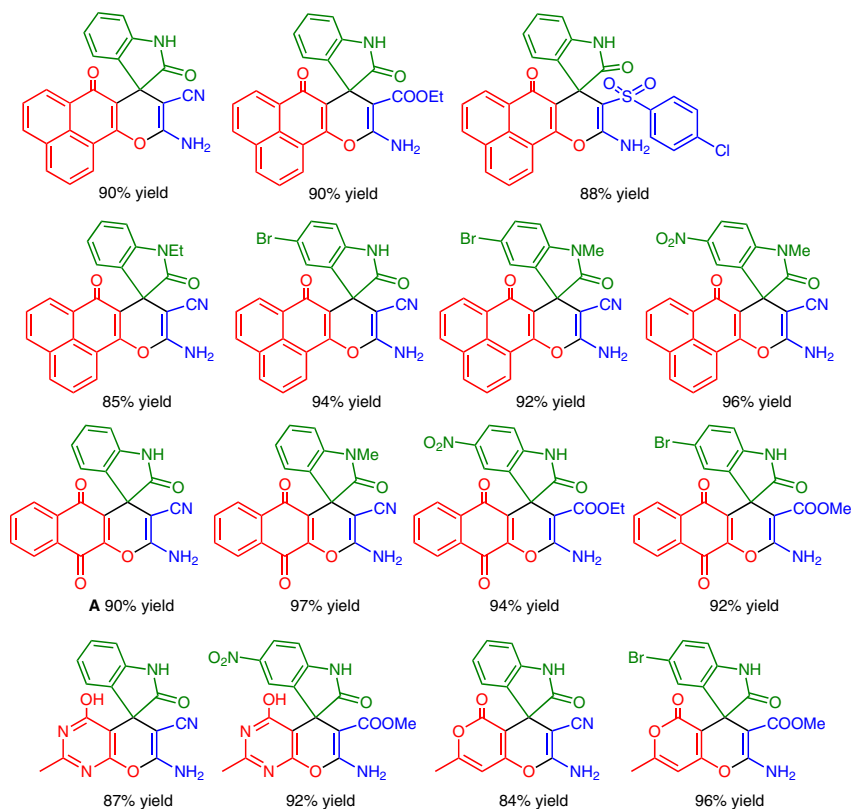
A. BAZGIR, G. HOSSEINI, R. GHahremanzadeh* (SHAHID BEHESHTI UNIVERSITY, TEHRAN AND AVICENNA RESEARCH INSTITUTE, TEHRAN, IRAN)
Copper Ferrite Nanoparticles: An Efficient and Reusable Nanocatalyst for a Green One-Pot, Three-Component Synthesis of Spirooxindoles in Water
ACS Comb. Sci. **2013**, *15*, 530–534.

Synthesis of Spirooxindoles Using CuFe_2O_4 Nanoparticles



Selected examples:

38 examples, 81–97% yield



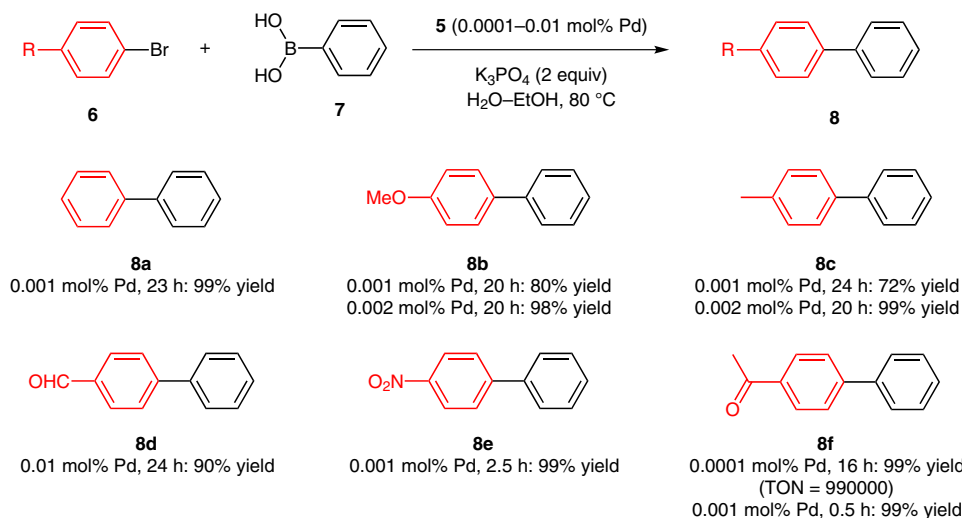
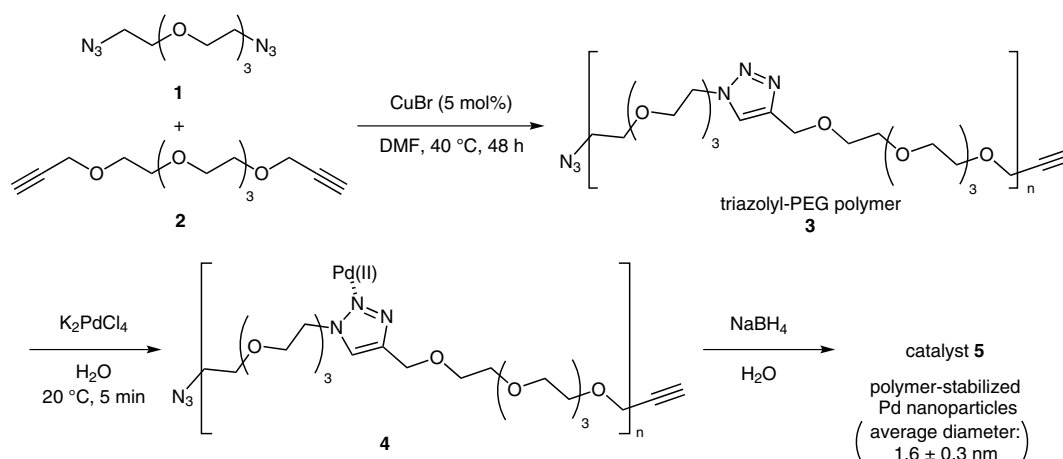
Significance: CuFe_2O_4 nanoparticles catalyzed the three-component coupling of cyclohexane-1,3-diones, activated acetonitriles and isatins to give the corresponding spirooxindoles (38 examples, 81–97% yield).

Comment: In the synthesis of product **A**, the catalyst was recovered magnetically and reused four times (1st reuse: 90% yield, 2nd reuse: 89% yield, 3rd reuse: 88% yield, 4th reuse: 80% yield).

SYNFACTS Contributors: Yasuhiro Uozumi, Makoto Nagaosa
Synfacts 2014, 10(1), 0100 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340397; Reg-No.: Y13813SF

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Suzuki–Miyaura Coupling Using Polymer-Stabilized Pd Nanoparticles



Significance: Triazolyl-PEG polymer-stabilized palladium nanoparticles (PdNPs) **5** were prepared and applied to the Suzuki–Miyaura coupling. The reaction of aryl bromides **6** and phenylboronic acid (**7**) took place with 0.0001–0.01 mol% Pd of catalyst **5** to give the corresponding products **8** in 90–99% yield. The turnover number (TON) reached up to 990000.

Comment: The Pd(II) catalyst **4** showed lower catalytic activity than the reduced catalyst **5** for the formation of **8f** with 0.001 mol% Pd. For a quantitative reaction of 4-bromoacetophenone and phenylboronic acid, 22 hours were needed with catalyst **4** instead of two hours with PdNP catalyst **5**. The average diameter of the Pd nanoparticles of **5** is 1.6 ± 0.3 nm.

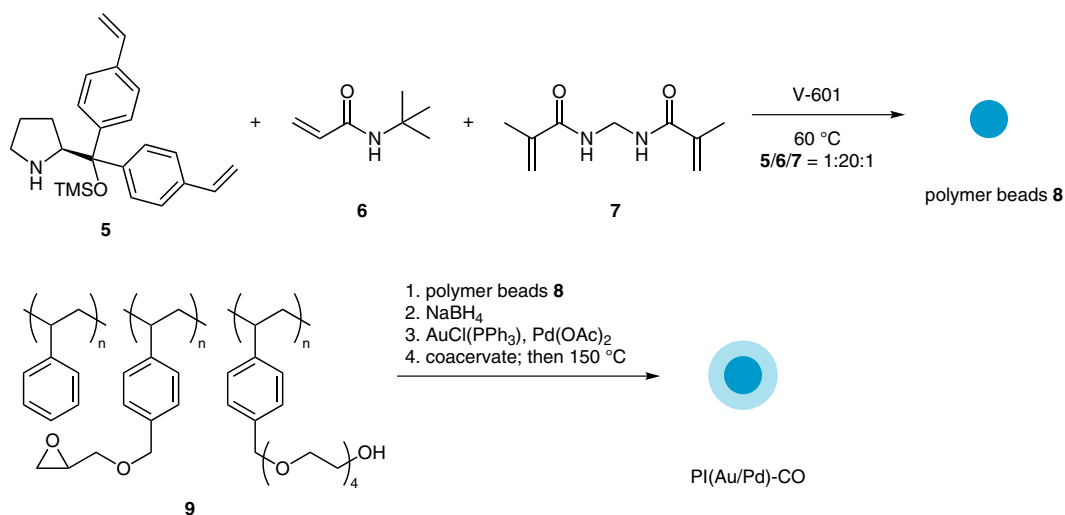
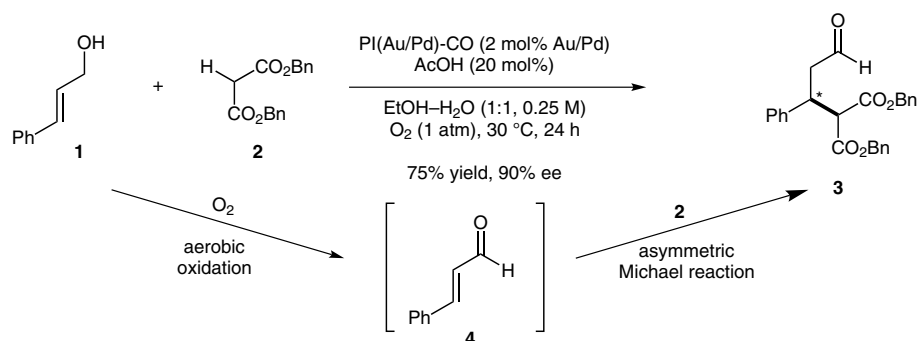
SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Aya Ohno
Synfacts 2014, 10(1), 0101 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340379; Reg-No.: Y13213SF

H. MIYAMURA, G. C. Y. CHOO, T. YASUKAWA, W.-J. YOO, S. KOBAYASHI* (THE UNIVERSITY OF TOKYO, JAPAN)

A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation

Chem. Commun. **2013**, *49*, 9917–9919.

A Heterogeneous Bifunctional Au/Pd Nanoparticle Organocatalyst



Significance: The preparation of a polymer-incarcerated Au/Pd-coated organocatalyst [PI(Au/Pd)-CO] for the sequential aerobic oxidation–Michael reaction between γ -substituted allylic alcohols and dibenzylmalonate was described. The reaction of 3-phenyl-2-propen-1-ol (**1**) and dibenzylmalonate (**2**) proceeded in the presence of PI(Au/Pd)-CO to give dibenzyl 2-(3-oxo-1-phenylpropyl)propane-1,3-dioate (**3**) in 75% yield with 90% ee (other 9 examples: 34–83% yield, 74–91% ee).

Comment: The Au/Pd organocatalyst was prepared by the copolymerization of monomers **5**, **6** and **7** in the presence of V-601 [dimethyl 2,2'-azobis(2-methylpropionate)] as a radical initiator followed by the formation of the cross-linked shell layer of a polymer **9** in which bimetallic Au/Pd nanoparticles were incorporated. Thus, PI(Au/Pd)-CO was composed of an organocatalytic resin core and a polymeric Au/Pd nanoparticle shell.

SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Takuma Sato

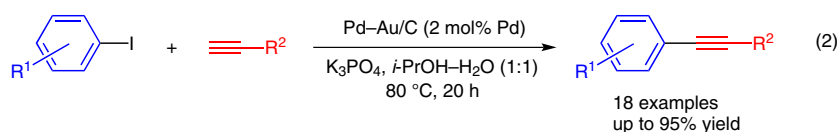
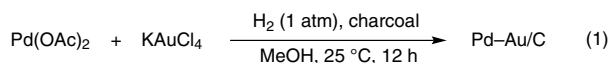
Synfacts 2014, 10(1), 0102 Published online: 13.12.2013

DOI: 10.1055/s-0033-1340401; Reg-No.: Y14213SF

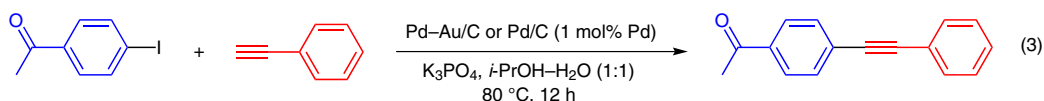
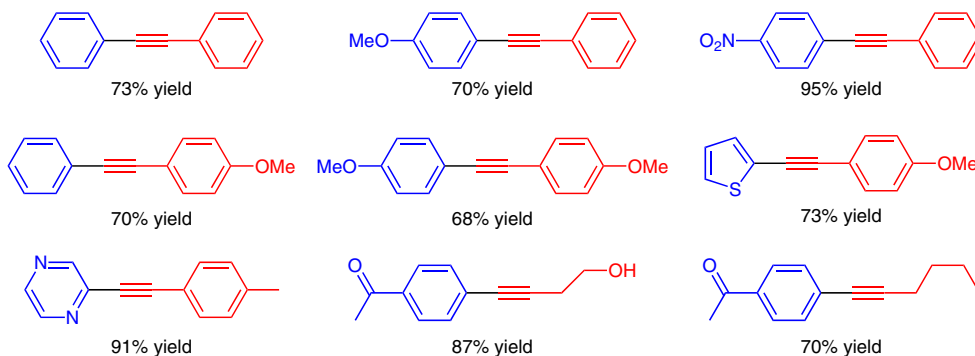
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C. ROSSY, J. MAJIMEL, E. FOUQUET, C. DELACÔTE, M. BOUJITA, C. LABRUGÈRE, M. TRÉGUER-DELAPIERRE,* F.-X. FELPIN* (UNIVERSITÉ DE NANTES, UNIVERSITÉ DE BORDEAUX, TALENCE AND UNIVERSITÉ DE BORDEAUX, PESSAC, FRANCE)
 Stabilisation of Carbon-Supported Palladium Nanoparticles through the Formation of an Alloy with Gold:
 Application to the Sonogashira Reaction
Chem. Eur. J. **2013**, *19*, 14024–14029.

Sonogashira Coupling with Bimetallic Pd–Au Nanoparticles on Carbon



Selected results:



	1 st run	2 nd run	3 rd run	4 th run	5 th run
Pd–Au/C	85	74	71	68	65
Pd/C	86	68	46	50	49

Significance: Bimetallic palladium–gold nanoparticles on carbon (Pd–Au/C) were prepared by treatment of a mixture of Pd(OAc)₂, KAuCl₄ and charcoal in methanol with H₂ (eq. 1). Pd–Au/C catalyzed the Sonogashira coupling of aryl iodides with terminal alkynes under copper-free conditions to give the corresponding diaryl alkynes in up to 95% yield (18 examples, eq. 2).

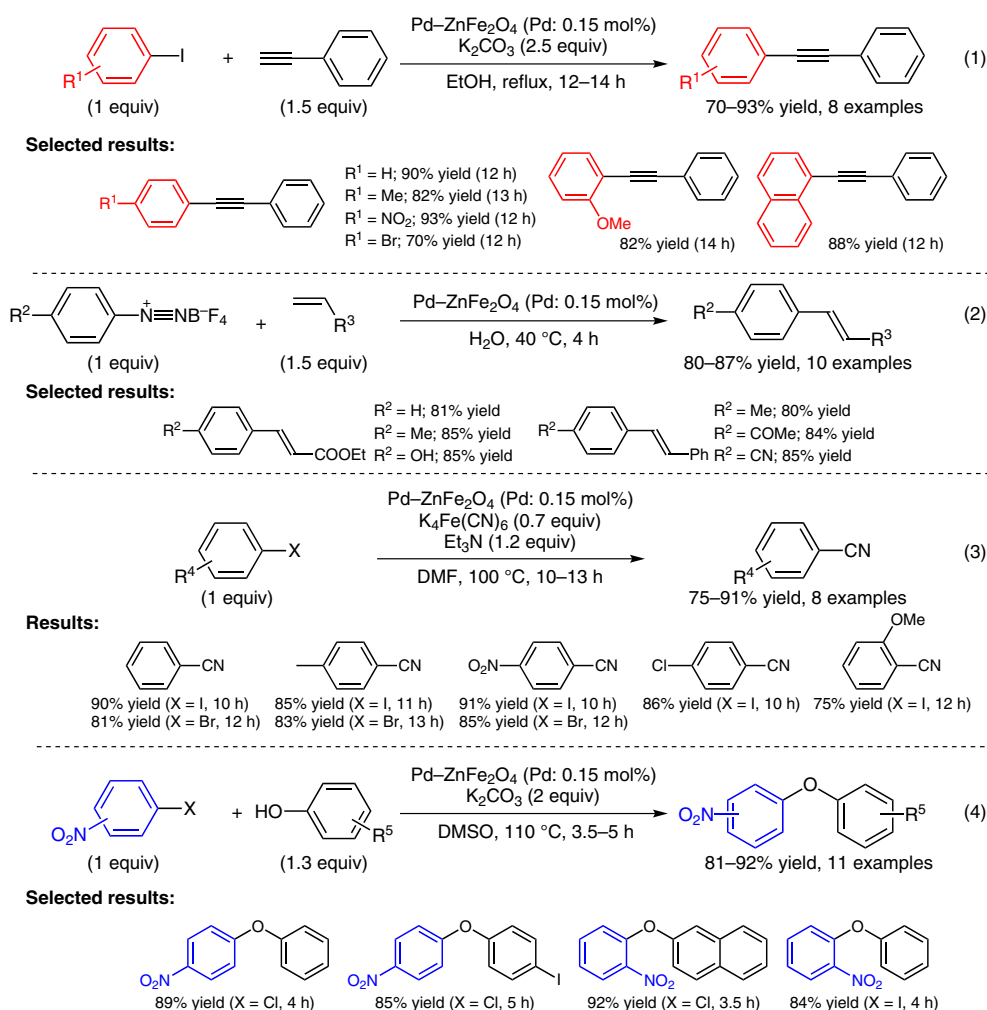
Comment: The Pd–Au/C nanoparticles were characterized by TEM, XRD, STEM-EDX, XPS and CV analyses. Though the catalytic activity of fresh Pd–Au/C was similar to that of fresh Pd/C, Pd–Au/C showed high stability during the recycling experiments (eq. 3). TEM analysis showed that the morphology of the recovered Pd–Au/C was unchanged after the third run.

SYNFACTS Contributors: Yasuhiro Uozumi, Hiroaki Tsuji
 Synfacts 2014, 10(1), 0103 Published online: 13.12.2013
 DOI: 10.1055/s-0033-1340382; Reg-No.: Y13513SF

A. S. SINGH, S. S. SHENDAGE, J. M. NAGARKAR* (INSTITUTE OF CHEMICAL TECHNOLOGY, MUMBAI, INDIA)

Palladium Supported on Zinc Ferrite: An Efficient Catalyst for Ligand-Free C–C and C–O Cross-Coupling Reactions
Tetrahedron Lett. **2013**, *54*, 6319–6323.

Ligand-Free C–C and C–O Cross-Couplings with Pd–ZnFe₂O₄

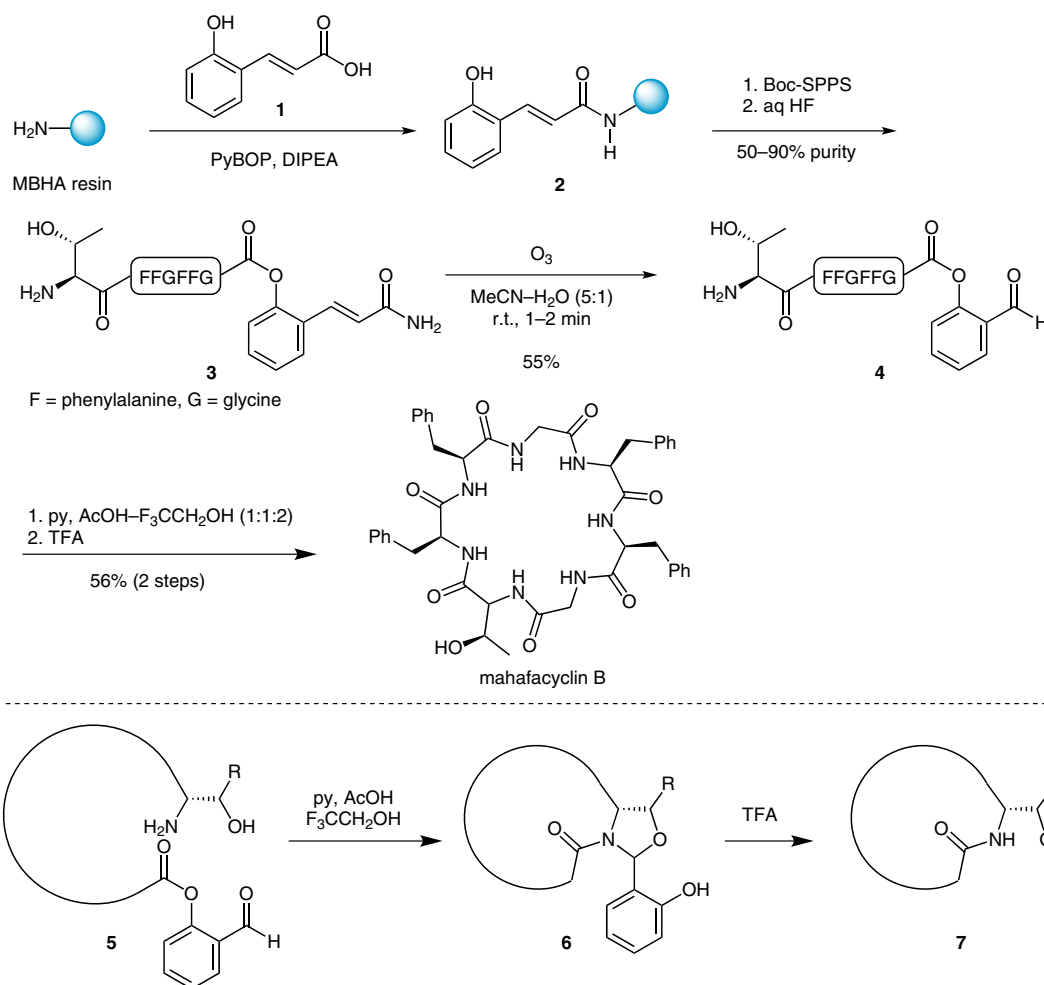


Significance: The superparamagnetic Pd–ZnFe₂O₄ catalyst was prepared by adding palladium nanoparticles into a suspension of ZnFe₂O₄ magnetic nanoparticles in water. Pd–ZnFe₂O₄ catalyzed the Sonogashira coupling (8 examples, eq. 1), the Heck–Matsuda coupling (10 examples, eq. 2), the cyanation of aryl halides (8 examples, eq. 3) and the Ullman coupling (11 examples, eq. 4).

SYNFACTS Contributors: Yasuhiro Uozumi, Aya Tazawa
Synfacts 2014, 10(1), 0104 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340396; Reg-No.: Y13713SF

Comment: In the Sonogashira coupling of iodo-benzene with phenylacetylene and the Ullmann coupling of 4-nitrochlorobenzene with phenol, the catalyst was recovered and reused twice without significant loss of catalytic activity.

Cyclic Peptide Synthesis Using Peptidyl Salicylaldehyde Esters



Significance: A protocol for the solid-phase synthesis of cyclopeptides was described. Starting from MBHA resin and **1**, peptide **3** was prepared in 50–90% purity utilizing Boc-SPPS. Ozonolysis of **3** afforded a salicylaldehyde ester peptide **4** in 55% yield (other 15 examples: 42–89% yield). The reaction of **4** in the mixture of pyridine, acetic acid and 2,2,2-trifluoroethanol (1:1:2) followed by TFA treatment gave mahafacyclin B in 56% yield over two steps (other 7 examples: 29–65% yield).

Comment: The present cyclization of salicylaldehyde ester peptides bearing a Thr or Ser N-terminal residue (**5**) proceeds via the formation of salicylidene *N,O*-acetals **6**. Li's group reported a similar approach on the cyclic peptide synthesis independently (C. T. T. Wong et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 10212).

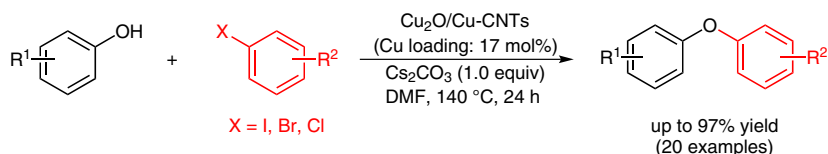
SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Takuma Sato
 Synfacts 2014, 10(1), 0105 Published online: 13.12.2013
 DOI: 10.1055/s-0033-1340400; Reg-No.: Y14113SF

Y.-P. ZHANG,* Y.-C. JIAO, Y.-S. YANG,* C.-L. LI (LANZHOU UNIVERSITY OF TECHNOLOGY, P. R. OF CHINA)

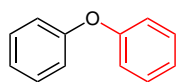
Ligand-Free Catalytic System for the Synthesis of Diarylethers over Cu₂O/Cu-CNTs as Heterogeneous Reusable Catalyst

Tetrahedron Lett. **2013**, 54, 6494–6497.

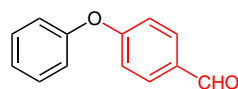
Cu₂O/Cu-CNTs Catalyzed the O-Arylation of Phenols with Aryl Halides



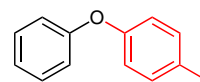
Selected examples:



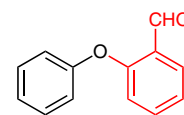
94% yield (X = I)
96% yield (X = Br)
32% yield (X = Cl)



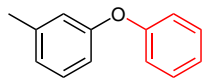
83% yield (X = Br)



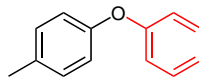
45% yield (X = Cl)



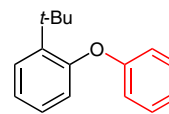
50% yield (X = Cl)



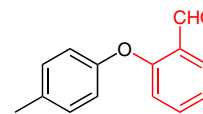
77% yield (X = I)
65% yield (X = Br)



97% yield (X = Br)



42% yield (X = I)
25% yield (X = Br)

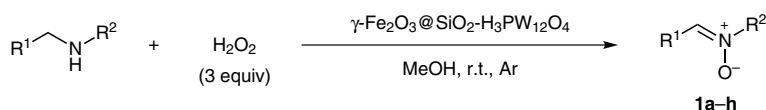


55% yield (X = Cl)

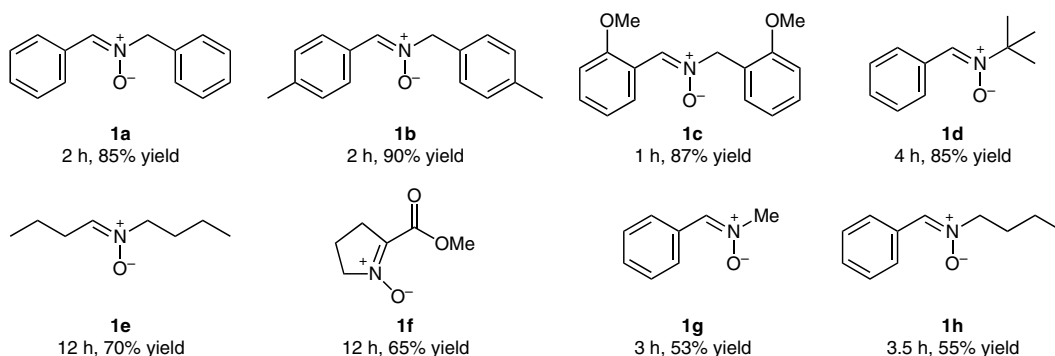
Significance: Cu₂O/Cu-Coated carbon nano-tubes (Cu₂O/Cu-CNTs) catalyzed the O-arylation of phenols with aryl halides under ligand-free conditions to give the corresponding diaryl ethers in up to 97% yield (20 examples).

Comment: Cu₂O/Cu-CNTs were recovered by filtration and reused three times without significant loss of catalytic activity. Lee and co-workers have previously reported the preparation and characterization of Cu₂O/Cu-CNTs (*Scr. Mater.* **2008**, 58, 1010).

Preparation of Nitrones Using γ -Fe₂O₃@SiO₂-H₃PW₁₂O₄₀



Results:



Significance: The oxidation of secondary amines by superparamagnetic tungstophosphoric acid supported on silica-encapsulated γ -Fe₂O₃ (γ -Fe₂O₃@SiO₂-H₃PW₁₂O₄₀) was carried out with an aqueous hydrogen peroxide as oxidant to give the corresponding nitrones **1a–h** in up to 90% yield.

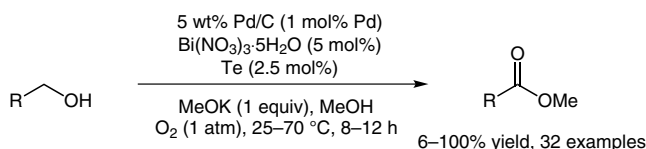
Comment: The γ -Fe₂O₃@SiO₂-H₃PW₁₂O₄₀ nanoparticles were readily recovered by an external magnet and reused three times without significant loss of catalytic activity (1st reuse: **1a** 85% yield, 3rd reuse: **1a** 80% yield). The authors previously reported the preparation of γ -Fe₂O₃@SiO₂-H₃PW₁₂O₄₀ and its application to the synthesis of formamidines (*J. Mol. Struct.* **2012**, 1027, 156).

A. B. POWELL, S. S. STAHL* (UNIVERSITY OF WISCONSIN-MADISON, USA)

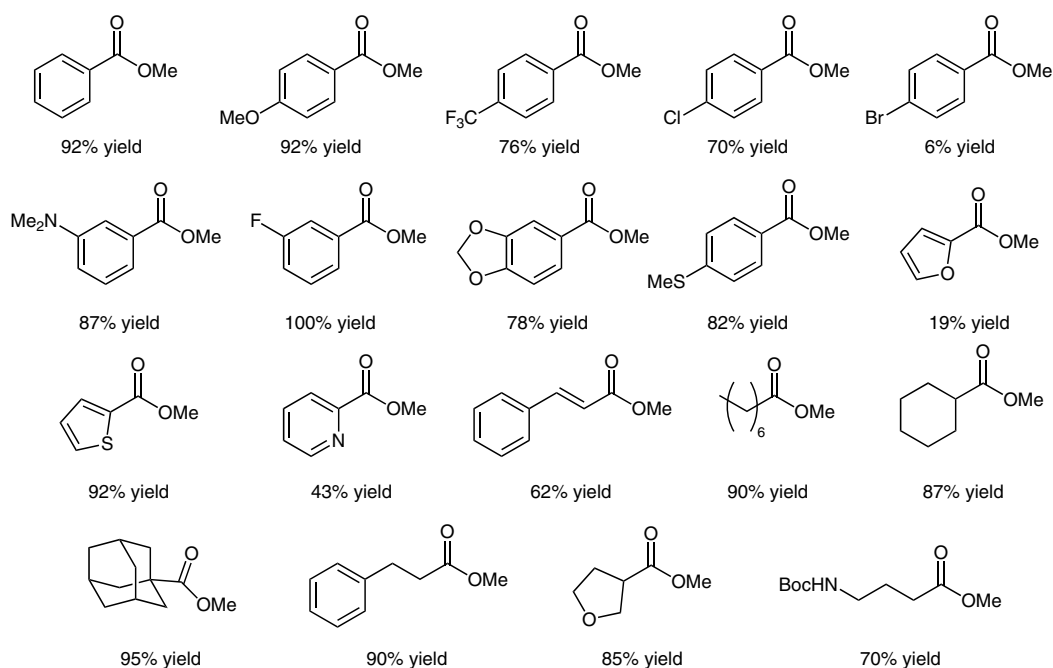
Aerobic Oxidation of Diverse Primary Alcohols to Methyl Esters with a Readily Accessible Heterogeneous Pd/Bi/Te Catalyst

Org. Lett. **2013**, *15*, 5072–5075.

Oxidative Esterification of Primary Alcohols with a Pd/Bi/Te Catalyst



Typical results:



Significance: Palladium on activated charcoal (Pd/C, 5 wt%, purchased from Sigma-Aldrich) in combination with $\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and Te catalyzed the aerobic oxidative esterification of primary alcohols to give the corresponding methyl esters in 6–100% yield (32 examples, eq. 1).

Comment: In the absence of $\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and Te, the oxidative esterification of 1-octanol gave methyl octanoate in 16% yield. The catalytic activity of palladium on activated charcoal was superior to that of palladium on carbon and alumina (purchased from Sigma-Aldrich).