Regio- and Enantioselective Hydrogenation Using a Peptide Catalyst

Significance: The amphiphilic resin-supported peptide 1 catalyzed the regio- and enantioselective transfer hydrogenation of (2E,4E)-α,β,γ,δ-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 (2E,4E)-2b and (2Z,4E)-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).

Selected examples:

3a R = H, 79% yield, 99% ee
3b R = NO2, 75% yield, 97% ee
3c R = Cl, 79% yield, 97% ee
3d R = Br, 71% yield, 98% ee
3e R = OMe, 65% yield, 98% ee
3f 74% yield, 98% ee
3g 71% yield, 98% ee
3h 64% yield, 98% ee
3i 65% yield, 97% ee
3j 47% yield, 97% ee
3k 60% yield, 87% ee
3l 87% yield, dr = 57:43, 93% ee for major diastereomer
95% ee for minor diastereomer

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Dehydrative Alkylation of 2-Methylquinoline with Alcohols Using Pt/Al₂O₃

**Significance:** The Al₂O₃-supported platinum nanoclusters (Pt/Al₂O₃) were prepared by mixing Al₂O₃ and an aqueous HNO₃ solution of Pt(NO₃)₂(NH₃)₂ followed by reduction with hydrogen (eq. 1). Pt/Al₂O₃ 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 Pt/Al₂O₃ nanoclusters were characterized by XANES, EXAFS and CO adsorption analyses. In the reaction of 2-methylquinoline with benzyl alcohol, the catalytic activity of Pt/Al₂O₃ was superior to that of the other Al₂O₃-supported metal catalysts (Ir/Al₂O₃: 53% yield, Rh/Al₂O₃: 31% yield, Pd/Al₂O₃: 32% yield, Ag/Al₂O₃: 5% yield) and Pt nanoclusters supported on the other solid supports (Pt/Nb₂O₅: 20% yield, Pt/C: 7% yield, Pt/ZrO₂: 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 NaHCO₃ 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).

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Copper Ferrite Nanoparticles: An Efficient and Reusable Nanocatalyst for a Green One-Pot, Three-Component Synthesis of Spirooxindoles in Water


Synthesis of Spirooxindoles Using CuFe$_2$O$_4$ Nanoparticles

**Significance:** CuFe$_2$O$_4$ 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 (1$^{\text{st}}$ reuse: 90% yield, 2$^{\text{nd}}$ reuse: 89% yield, 3$^{\text{rd}}$ reuse: 88% yield, 4$^{\text{th}}$ reuse: 80% yield).
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.

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


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-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′-azo-bis[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.
Stabilisation of Carbon-Supported Palladium Nanoparticles through the Formation of an Alloy with Gold: Application to the Sonogashira Reaction


Sonogashira Coupling with Bimetallic Pd–Au Nanoparticles on Carbon

\[
Pd(OAc)_2 + KAuCl_4 \xrightarrow{H_2 (1 \text{ atm}), \text{charcoal}} \xrightarrow{\text{MeOH, } 25 \degree C, 12 \text{ h}} Pd-Au/C \quad (1)
\]

\[
\begin{array}{c}
R^1 \quad \text{I} \\
+ \quad \text{H} \\
\end{array} + \begin{array}{c}
\quad \text{R}^2 \\
\end{array} \xrightarrow{Pd-Au/C (2 \text{ mol}\% Pd)} \xrightarrow{K_3PO_4, i-\text{PrOH-H}_2\text{O (1:1)}} \xrightarrow{80 \degree C, 20 \text{ h}} R^1 \quad \text{R}^2 \quad \text{(2)
}\]

Selected results:

<table>
<thead>
<tr>
<th>Aryl Iodide</th>
<th>Terminal Alkyne</th>
<th>Coupling Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R^1)</td>
<td>(R^2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(73%)</td>
<td>(70%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(91%)</td>
<td>(87%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(70%)</td>
<td>(95%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{array}{c}
\quad \text{O} \\
\end{array} + \begin{array}{c}
\quad \text{MeO} \\
\end{array} \xrightarrow{Pd-Au/C or Pd/C (1 \text{ mol}\% Pd)} \xrightarrow{K_3PO_4, i-\text{PrOH-H}_2\text{O (1:1)}} \xrightarrow{80 \degree C, 12 \text{ h}} \text{(3)
}\]

<table>
<thead>
<tr>
<th>Run</th>
<th>1st run</th>
<th>2nd run</th>
<th>3rd run</th>
<th>4th run</th>
<th>5th run</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Au/C</td>
<td>85</td>
<td>74</td>
<td>71</td>
<td>68</td>
<td>65</td>
</tr>
<tr>
<td>Pd/C</td>
<td>86</td>
<td>68</td>
<td>46</td>
<td>50</td>
<td>49</td>
</tr>
</tbody>
</table>

**Significance:** Bimetallic palladium–gold nanoparticles on carbon (Pd–Au/C) were prepared by treatment of a mixture of Pd(OAc)\(_2\), KAuCl\(_4\) and charcoal in methanol with H\(_2\) (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.
Palladium Supported on Zinc Ferrite: An Efficient Catalyst for Ligand-Free C–C and C–O Cross-Coupling Reactions


Ligand-Free C–C and C–O Cross-Couplings with Pd–ZnFe$_2$O$_4$

Significance: The superparamagnetic Pd–ZnFe$_2$O$_4$ catalyst was prepared by adding palladium nanoparticles into a suspension of ZnFe$_2$O$_4$ magnetic nanoparticles in water. Pd–ZnFe$_2$O$_4$ 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).

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.

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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).
Cu$_2$O/Cu-CNTs Catalyzed the O-Arylation of Phenols with Aryl Halides

**Significance:** Cu$_2$O/Cu-Coated carbon nanotubes (Cu$_2$O/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:** Cu$_2$O/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 Cu$_2$O/Cu-CNTs (Scr. Mater. **2008**, **58**, 1010).

**Selected examples:**

- $\text{Ph} - \text{Ph}$ (X = I), 94% yield (X = I);
- $\text{Ph} - \text{Ph}$ (X = Br), 96% yield (X = Br);
- $\text{Ph} - \text{Ph}$ (X = Cl), 52% yield (X = Cl);
- $\text{Ph} - \text{Ph}$ (X = I), 97% yield (X = Br);
- $\text{Ph} - \text{Ph}$ (X = Br), 65% yield (X = Cl);
- $\text{Ph} - \text{Ph}$ (X = Cl), 42% yield (X = Br);
- $\text{Ph} - \text{Ph}$ (X = Cl), 25% yield (X = Br);
- $\text{Ph} - \text{Ph}$ (X = Cl), 55% yield (X = Cl).

**Diagram:**

Cu$_2$O/Cu-CNTs (Cu loading: 17 mol%)

Cs$_2$CO$_3$ (1.0 equiv)

DMF, 140 °C, 24 h

up to 97% yield

(20 examples)
Preparation of Nitrones Using $\gamma$-Fe$_2$O$_3$@SiO$_2$-H$_3$PW$_{12}$O$_{40}$

Results:

- **1a**: 2 h, 85% yield
- **1b**: 2 h, 90% yield
- **1c**: 1 h, 87% yield
- **1d**: 4 h, 85% yield
- **1e**: 12 h, 70% yield
- **1f**: 12 h, 65% yield
- **1g**: 3 h, 53% yield
- **1h**: 3.5 h, 55% yield

**Significance:** The oxidation of secondary amines by superparamagnetic tungstophosphoric acid supported on silica-encapsulated $\gamma$-Fe$_2$O$_3$ ($\gamma$-Fe$_2$O$_3$@SiO$_2$-H$_3$PW$_{12}$O$_{40}$) was carried out with an aqueous hydrogen peroxide as oxidant to give the corresponding nitrones **1a**–**h** in up to 90% yield.

**Comment:** The $\gamma$-Fe$_2$O$_3$@SiO$_2$-H$_3$PW$_{12}$O$_{40}$ 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 $\gamma$-Fe$_2$O$_3$@SiO$_2$-H$_3$PW$_{12}$O$_{40}$ and its application to the synthesis of formamidines (J. Mol. Struct. 2012, 1027, 156).
Oxidative Esterification of Primary Alcohols with a Pd/Bi/Te Catalyst

**Significance:** Palladium on activated charcoal (Pd/C, 5 wt%, purchased from Sigma-Aldrich) in combination with Bi(NO₃)₃·5H₂O 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 Bi(NO₃)₃·5H₂O 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).

**Typical results:**

<table>
<thead>
<tr>
<th>R</th>
<th>OMe</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>OMe</td>
<td>92%</td>
</tr>
<tr>
<td>MeO</td>
<td>OMe</td>
<td>92%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>76%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>70%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>6%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>87%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>100%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>78%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>82%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>19%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>92%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>43%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>62%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>90%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>87%</td>
</tr>
<tr>
<td>C₆H₅</td>
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<td>C₆H₅</td>
<td>OMe</td>
<td>90%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>85%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>70%</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>OMe</td>
<td>62%</td>
</tr>
</tbody>
</table>

**Oxidative Esterification of Primary Alcohols**

**Organic Letters**

2013, 15, 5072–5075.

**Equation:**

\[
\text{R-OH + MeOK (1 equiv), MeOH} \quad \xrightarrow{\text{O}_2 (1 \text{ atm}), \text{25–70} \degree \text{C, 8–12 h}} \quad \text{R-OMe}
\]

**Conditions:**

- 5 wt% Pd/C (1 mol% Pd)
- Bi(NO₃)₃·5H₂O (5 mol%)
- Te (2.5 mol%)
- MeOK (1 equiv), MeOH
- O₂ (1 atm), 25–70 °C, 8–12 h

6–100% yield, 32 examples