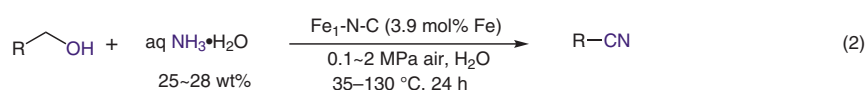
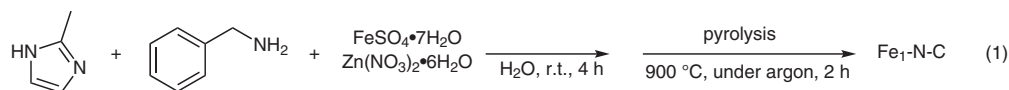


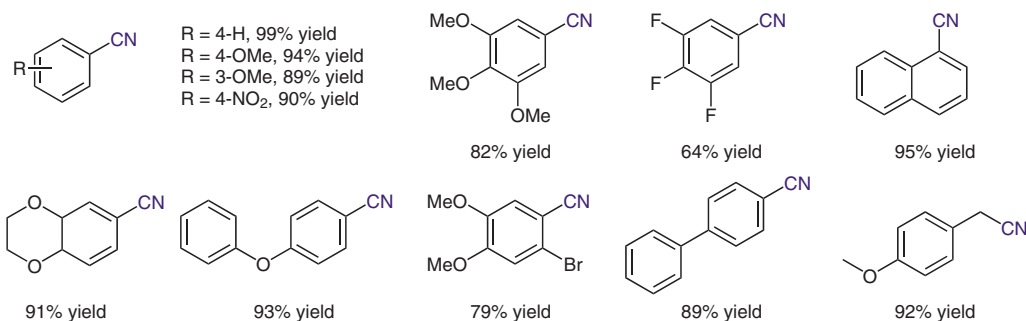
K. SUN, H. SHAN, H. NEUMANN*, G.-P. LU*, M. BELLER* (NANJING UNIVERSITY OF SCIENCE AND TECHNOLOGY, P. R. OF CHINA, AND LEIBNIZ-INSTITUTE FÜR KATALYSE, ROSTOCK, GERMANY)

Efficient Iron Single-Atom Catalysts for Selective Ammoxidation of Alcohols to Nitriles
Nat. Commun. **2022**, *13*, 1848 DOI: 10.1038/s41467-022-29074-1.

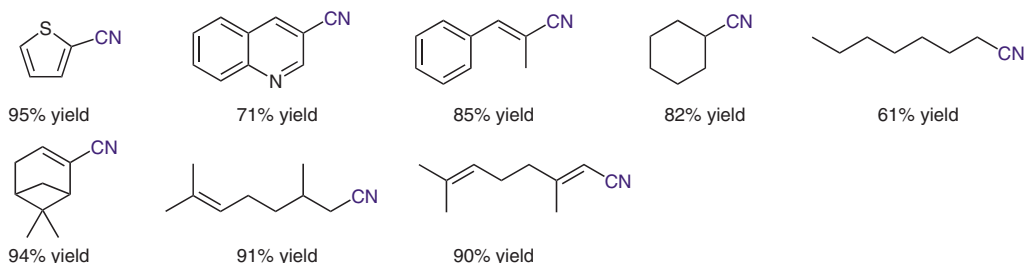
Ammoxidation of Alcohols with Aqueous Ammonia Using an Iron Single-Atom Catalyst



Selected examples:



Heterocyclic nitriles, allylic nitriles, and aliphatic nitriles:



Significance: Iron atoms supported on nitrogen-doped porous carbon derived from a benzylamine-modified zeolitic imidazolate framework (**Fe₁-N-C**) were prepared according to equation 1. **Fe₁-N-C** catalyzed the selective ammoxidation of alcohols with ammonium hydroxide under air to afford the corresponding nitriles in ≤99% yield (eq. 2; 20 examples).

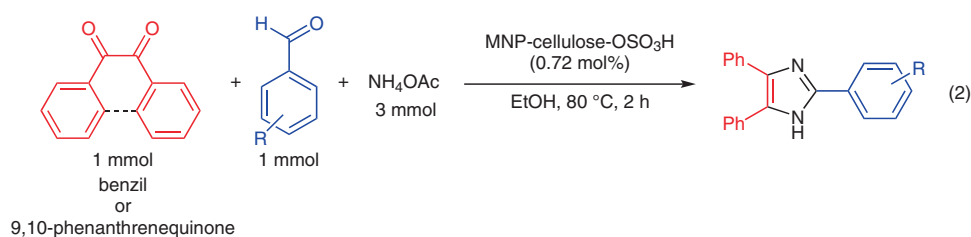
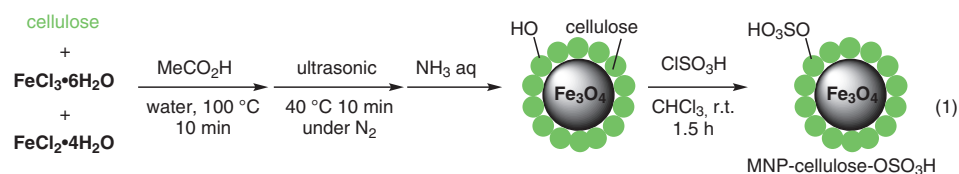
Comment: The **Fe₁-N-C** catalyst was characterized by means of PXRD, SEM, STEM, EDX, XRD, BET, XANES, FTXAFS, EXAFS, XPS, Raman, and ICP-OES analyses. In the reaction of benzyl alcohol with aqueous ammonia, the catalyst was recovered and reused five times without significant loss of its catalytic activity. ICP analysis showed that no iron leached into the solution during the reaction.

S. SAEEDI, A. RAHMATI* (UNIVERSITY OF ISFAHAN, IRAN)

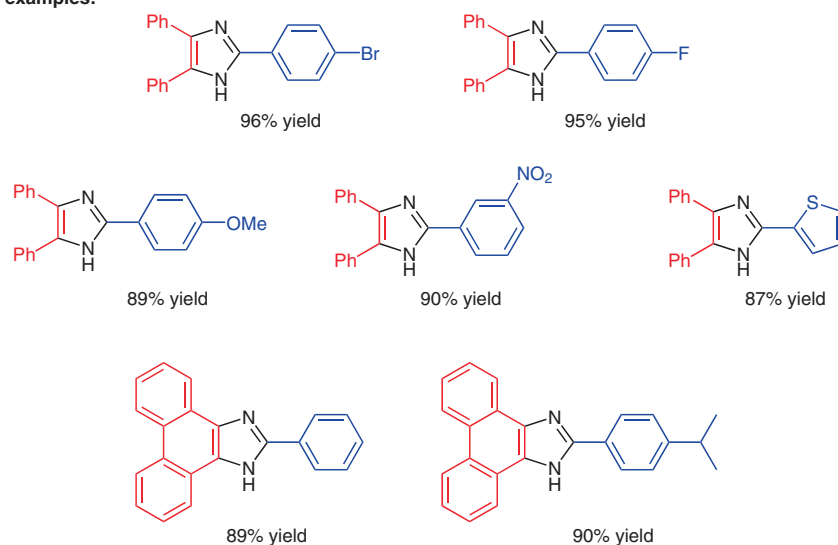
MNP-Cellulose-OSO₃H as an Efficient and Biodegradable Heterogeneous Catalyst for Green Synthesis of Trisubstituted Imidazoles

RSC Adv. 2022, 12, 11740–11749, DOI: 10.1039/d2ra01348g.

Synthesis of Trisubstituted Imidazoles by Sulfonated Magnetic Cellulose-Nanoparticles



Selected examples:



Significance: Sulfonated magnetic cellulose nanoparticles (MNP-cellulose-OSO₃H), prepared according to equation 1, catalyzed the three-component reaction of benzil or 9,10-phenanthrenequinone with aromatic aldehydes and ammonium acetate to give the corresponding imidazoles in ≤96% yield (eq. 2).

Comment: The MNP-cellulose-OSO₃H catalyst was characterized by means of FTIR, elemental analysis, ICP-OES, XRD, SEM, EDX, TEM, zeta potential analysis, VSM and TGA. In the reaction of benzil, benzaldehyde, and ammonium acetate, the catalyst was recovered and reused four times without significant loss of its catalytic activity.

Hydrothiolation of Alkenes and Alkynes on Carbon Nanotube-Supported Ru–Rh Nanoparticles

Category

Polymer-Supported Synthesis

Key words

ruthenium catalysis

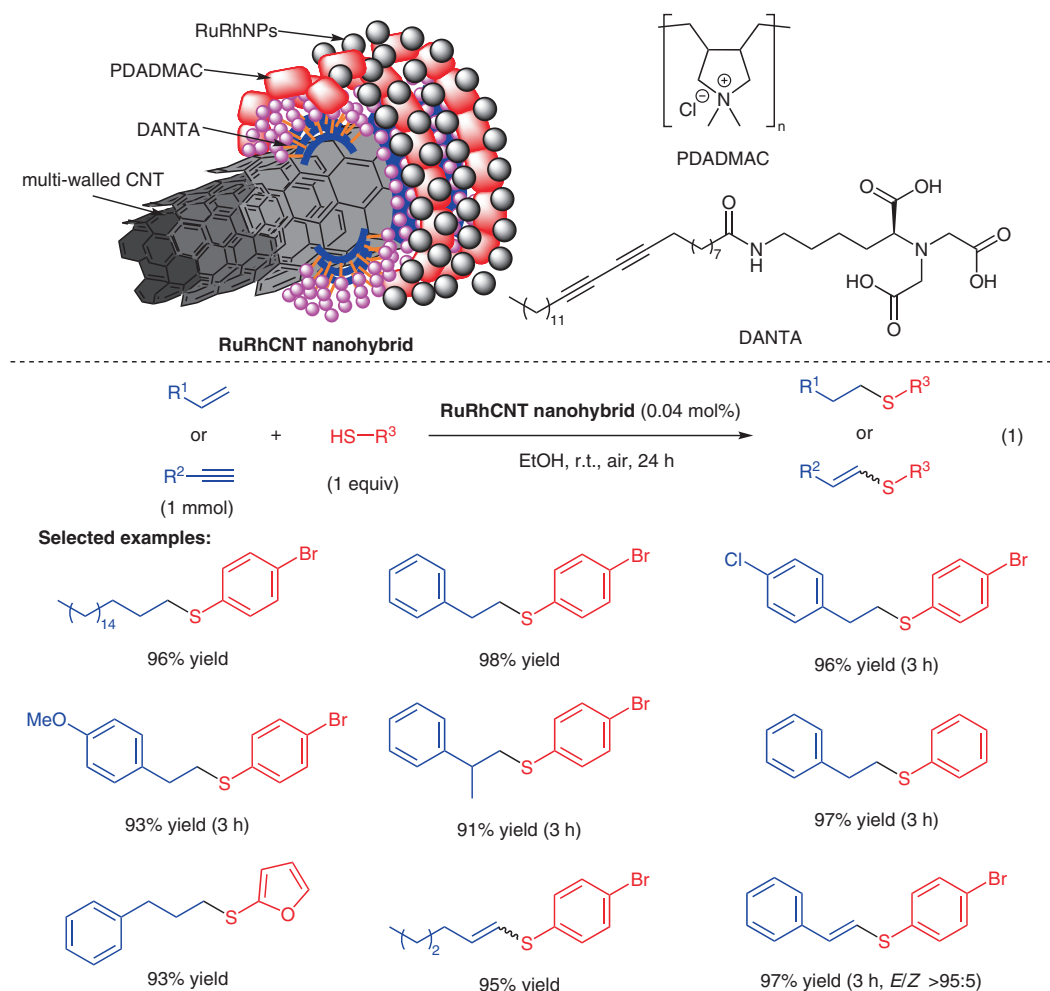
rhodium catalysis

bimetallic nanoparticles

carbon nanotubes

hydrothiolation

alkenes



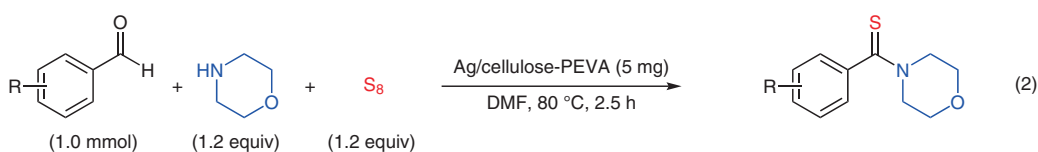
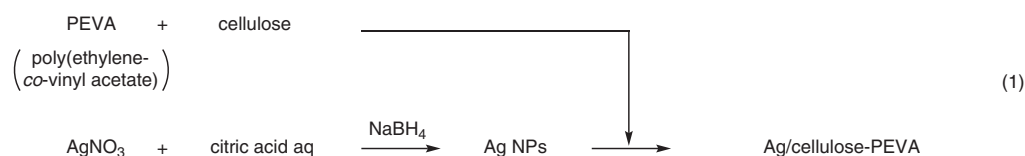
Significance: Bimetallic ruthenium–rhodium nanoparticles immobilized on multiwalled carbon nanotubes (RuRhCNT nano hybrid) catalyzed the hydrothiolation of alkenes and alkynes with thiols in ethanol at room temperature under air to give the corresponding thioethers in $\leq 98\%$ and $\leq 97\%$ yields, respectively (eq. 1).

Comment: The RuRhCNT nano hybrid was prepared according to previous reports (Y. Wang, J. Ren, K. Deng, L. Gui, Y. Tang *Chem. Mater.* **2000**, *12*, 1622; J. John et al. *Angew. Chem. Int. Ed.* **2011**, *50*, 7533). In the reaction of octadec-1-ene with 4-bromothiophenol, the catalyst was recovered and reused five times without significant loss of its catalytic activity.

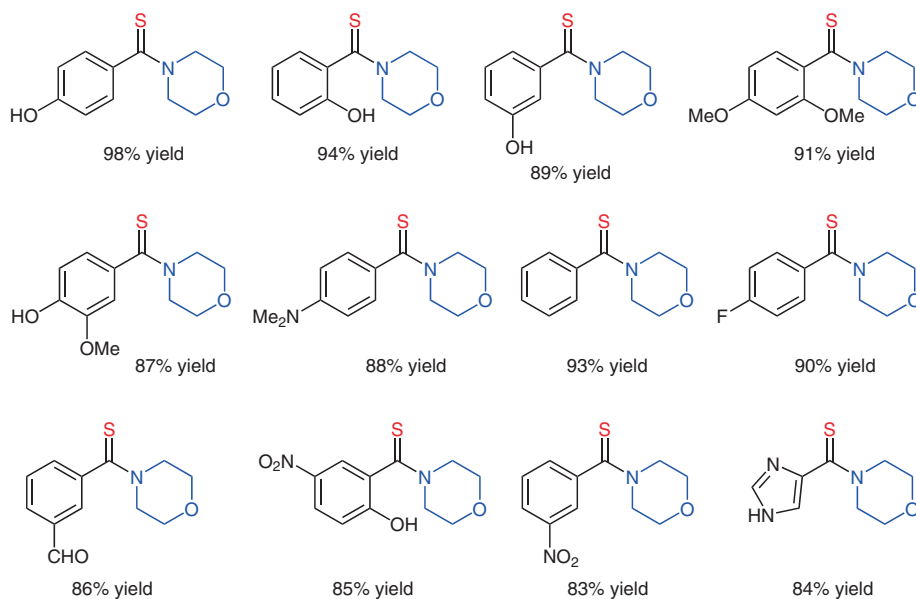
A. SINGH, S. SAINI, N. SINGH*, N. KAUR*, D. O. JANG* (INDIAN INSTITUTE OF TECHNOLOGY ROPAR, PANJAB UNIVERSITY, CHANDIGARH, INDIA AND YONSEI UNIVERSITY, WONJU, SOUTH KOREA)

Cellulose-Reinforced Poly(Ethylene-co-Vinyl Acetate)-Supported Ag Nanoparticles with Excellent Catalytic Properties: Synthesis of Thioamides Using the Willgerodt–Kindler Reaction
RSC Adv. 2022, 12, 6659–6667, DOI: 10.1039/d1ra09225a.

Willgerodt–Kindler Reaction on Supported Silver Nanoparticles



Results:



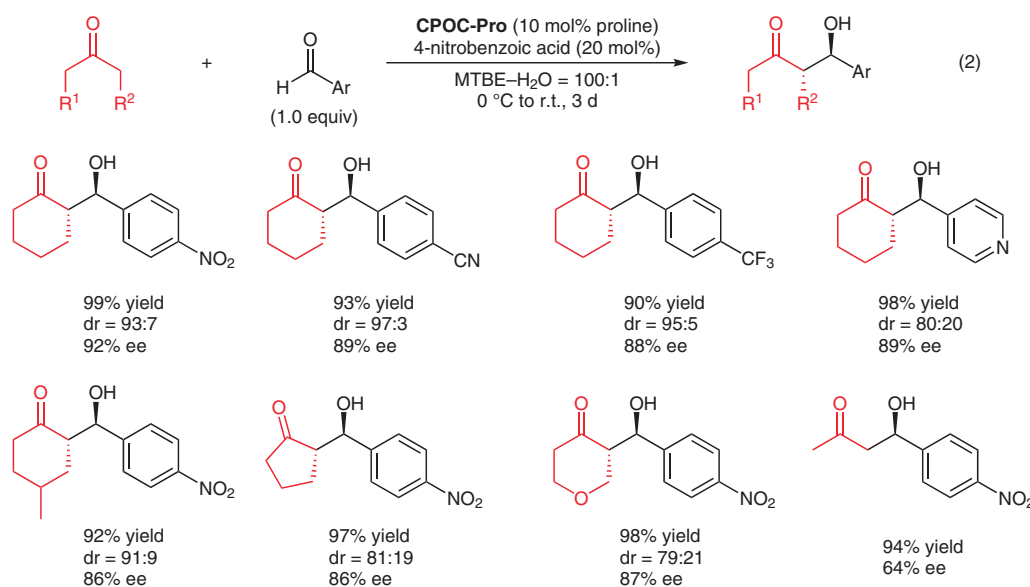
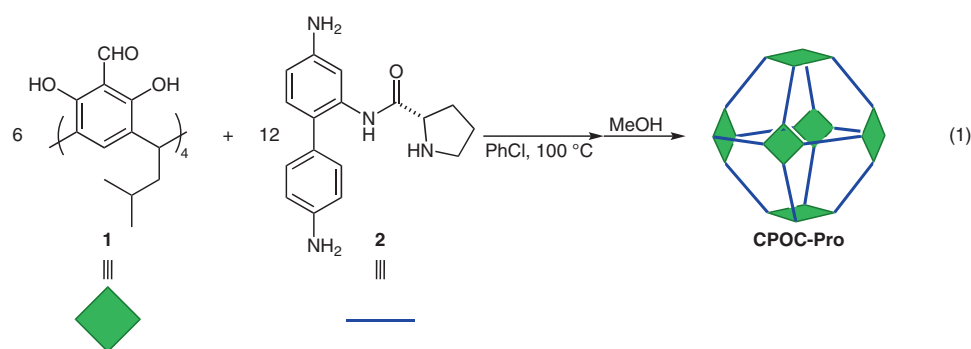
Significance: Silver nanoparticles supported on cellulose-reinforced poly(ethylene-co-vinyl acetate) (**Ag/cellulose-PEVA**), prepared according to equation 1, catalyzed the Willgerodt–Kindler reaction of benzaldehydes, morpholine, and S₈ to give the corresponding thioamides (eq. 2).

Comment: In the Willgerodt–Kindler reaction of 4-hydroxybenzaldehyde, morpholine, and S₈, the **Ag/cellulose-PEVA** catalyst was reused seven times without significant loss of its catalytic activity (first run: 98% yield, eighth run: 94%).

SYNFACTS Contributors: Yasuhiro Uozumi, Ryoko Niimi
Synfacts 2022, 18(07), 0776 Published online: 15.06.2022
DOI: 10.1055/s-0041-1737656; Reg-No.: Y05122SF

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Asymmetric Aldol Reaction Catalyzed by a Chiral Proline-Substituted Porous Organic Cage

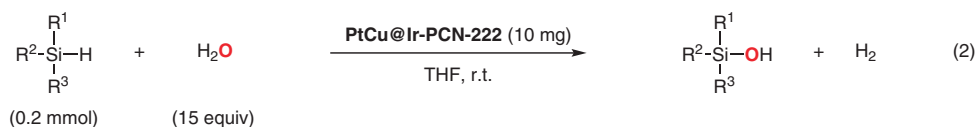
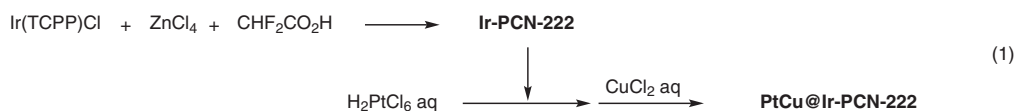


Significance: The chiral porous organic cage **CPOC-Pro** was prepared by self-assembly of the tetraformyl-functionalized calix[4]resorcinarene **1** with the proline-substituted diamine **2** (eq. 1). **CPOC-Pro** catalyzed the asymmetric aldol reaction of ketones with aromatic aldehydes to give the corresponding β -hydroxy ketones in up to 99% yield, 97:3 dr, and 92% ee (eq. 2).

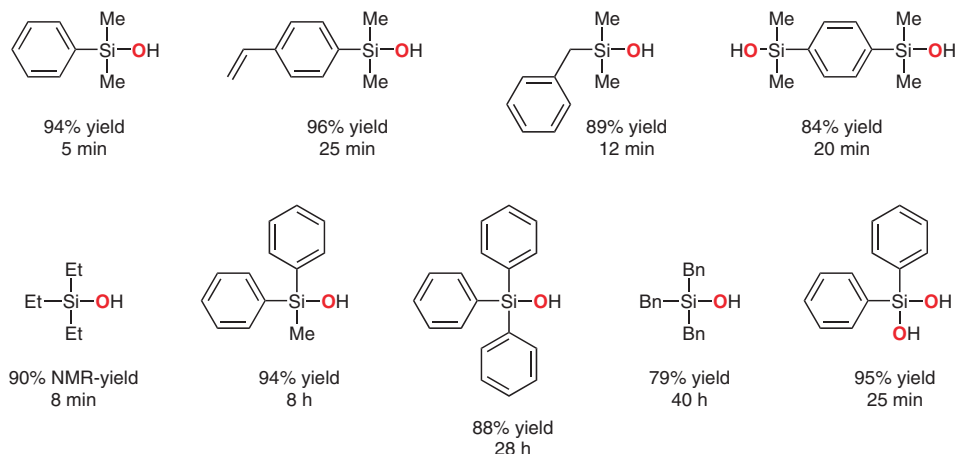
Comment: In the model reaction of 4-nitrobenzaldehyde with cyclohexanone, the catalyst was recovered and reused four times without a significant loss of its catalytic performance. **CPOC-Pro** showed a higher catalytic activity and greater diastereoselectivity and enantioselectivity than L-proline (10 d; 80% yield, dr = 45:55, and 77% ee in the model reaction).

C. CHEN, Q. MO, J. FU, Q. YANG*, L. ZHANG*, C.-Y. SU (BEIJING UNIVERSITY OF CHEMICAL TECHNOLOGY AND SUN YAT-SEN UNIVERSITY, GUANGZHOU, P. R. OF CHINA)
PtCu@Ir-PCN-222: Synergistic Catalysis of Bimetallic PtCu Nanowires in Hydrosilane-Concentrated Interspaces of an Iridium(III)-Porphyrin-Based Metal–Organic Framework
ACS. Cat **2022**, 12, 3604–3614, DOI: 10.1021/acscatal.1c05922.

Hydrolytic Oxidation of Hydrosilanes on PtCu Nanowires Encapsulated in Ir(III) Porphyrinic MOFs



Results:



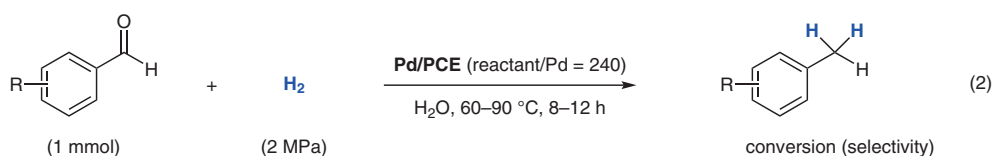
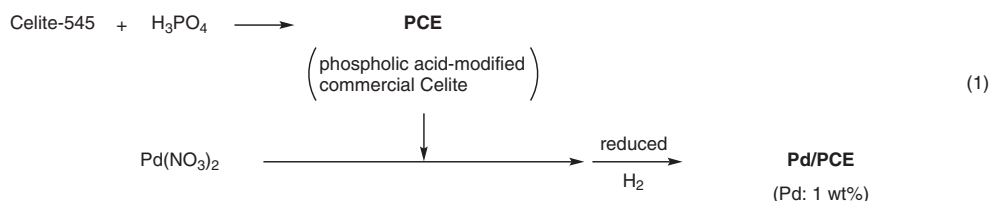
Significance: Platinum–copper nanowires encapsulated in an iridium(III) porphyrinic metal–organic framework (**PtCu@Ir-PCN-222**), prepared according to equation 1, catalyzed the hydrolytic oxidation of hydrosilanes to give the corresponding silanols in $\leq 96\%$ yield (eq. 2).

Comment: In the hydrolytic oxidation of dimethyl(phenyl)silane, **PtCu@Ir-PCN-222** was reused nine times without significant loss of its catalytic activity. TEM and PXRD analysis of the used catalyst revealed that its morphology remained intact during the reaction.

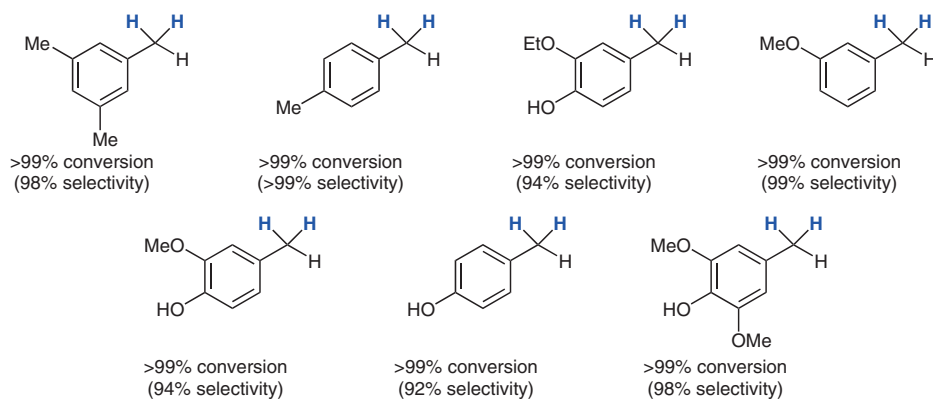
R. YANGCHENG, J. RAN, Z. LIU*, Y. CUI, J. WANG* (CHONGQING UNIVERSITY, P. R. OF CHINA)

Phosphoric Acid-Modified Commercial Kieselguhr Supported Palladium Nanoparticles as Efficient Catalysts for Low-Temperature Hydrodeoxygenation of Lignin Derivatives in Water
Green Chem. **2022**, *24*, 1570–1577, DOI: 10.1039/d1gc04243b.

Hydrodeoxygenation of Lignin Derivatives Catalyzed by Kieselguhr-Supported Palladium Nanoparticles



Results:



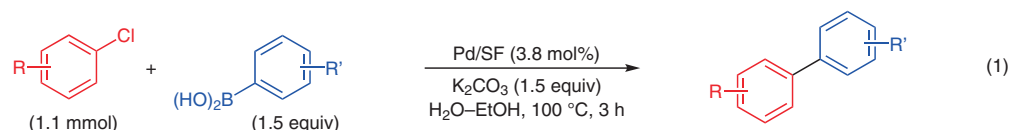
Significance: Palladium nanoparticles supported on phosphoric acid-modified commercial Celite (Pd/PCE) were prepared according to equation 1. Pd/PCE catalyzed the hydrodeoxygenation of lignin derivatives to give the corresponding toluene derivatives (eq. 2).

Comment: Without phosphoric acid modification, the turnover frequency of the catalyst for the hydrodeoxygenation reaction to give vanillyl alcohol was significantly decreased.

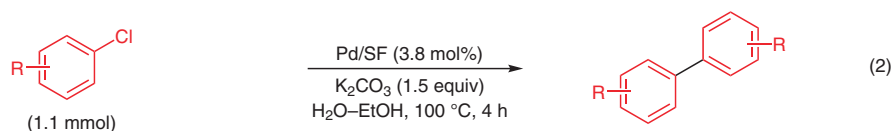
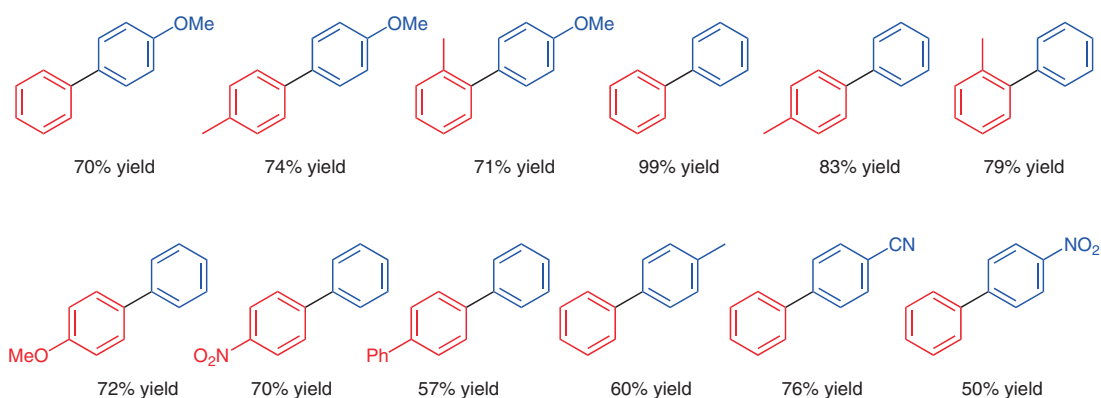
G. RIZZO, G. ALBANO, T. SIBILLANO, C. GIANNINI, R. MUSIO, F. G. OMENETTO, G. M. FARINOLA* (UNIVERSITÀ DEGLI STUDI DI BARI ALDO MORO, ITALY AND TUFTS UNIVERSITY, MEDFORD, USA)

Silk-Fibroin-Supported Palladium Catalyst for Suzuki–Miyaura and Ullmann Coupling Reactions of Aryl Chlorides
Eur. J. Org. Chem. **2022**, --9, DOI: 10.1002/ejoc.202101567.

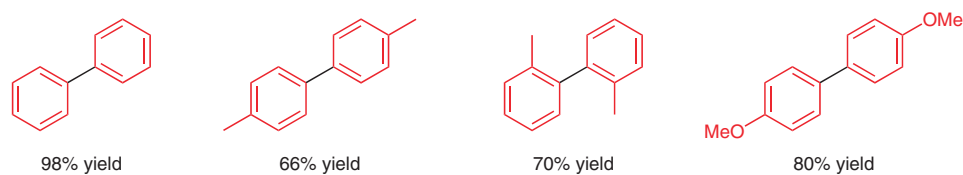
Suzuki–Miyaura and Ullmann Couplings of Aryl Chlorides Catalyzed by Silk-Fibroin-Supported Pd



Results:



Results:



Significance: A palladium catalyst supported on silk fibroin (**Pd/SF**) promoted the Suzuki–Miyaura coupling (eq. 1) and Ullmann coupling (eq. 2) reactions of aryl chlorides to give the corresponding bi-phenyls in $\leq 99\%$ yield.

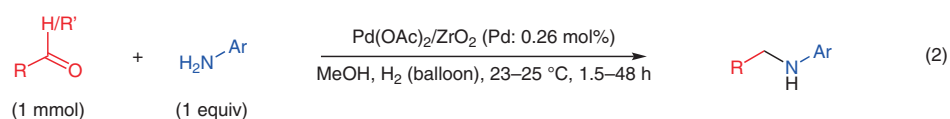
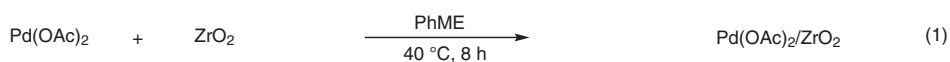
Comment: The authors have previously reported the preparation of **Pd/SF** (*Eur. J. Org. Chem.* **2020**, 6992). WAXS investigations of **Pd/SF** suggested that monoatomic palladium species form stable complexes with the silk-fibroin.

Z. ZHANG, T. IKEDA, H. MURAYAMA, T. HONMA, M. TOKUNAGA, Y. MOTOYAMA*
(TOYOTA TECHNOLOGICAL INSTITUTE, NAGOYA, JAPAN)

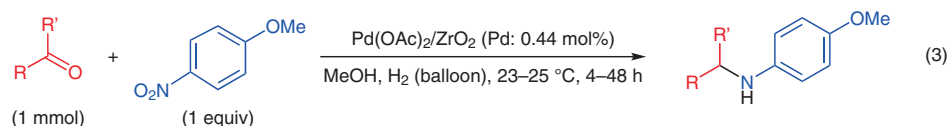
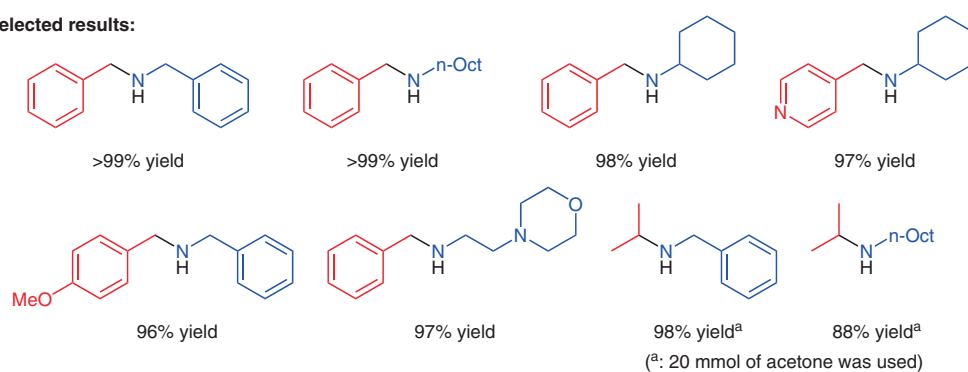
Anchored Palladium Complex-Generated Clusters on Zirconia: Efficiency in Reductive N-Alkylation of Amines with Carbonyl Compounds under Hydrogen Atmosphere

Chem. Asian J. **2022**, *17*, e202101243 DOI: 10.1002/asia.202101243.

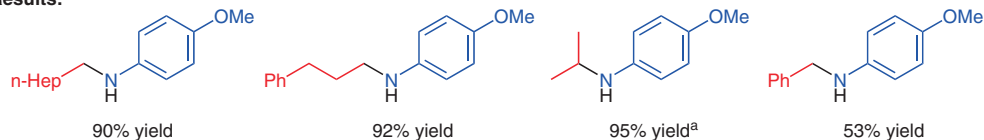
Reductive N-Alkylation of Amines with Aldehydes and Ketones on a Zirconia-Supported Pd Catalyst



Selected results:



Results:



Significance: A zirconia-supported palladium catalyst [Pd(OAc)₂/ZrO₂] was readily prepared by mixing palladium acetate and zirconium oxide (eq. 1). Pd(OAc)₂/ZrO₂ catalyzed the N-alkylation of amines with aldehydes and ketones under a H₂ atmosphere to give the corresponding N-alkylamines in ≤99% yield (eqs. 2 and 3).

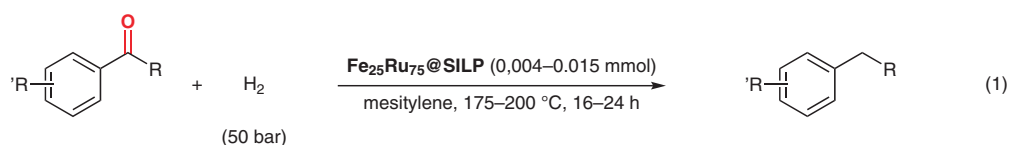
Comment: In the N-alkylation of octylamine with benzaldehyde, Pd(OAc)₂/ZrO₂ was reused five times with gradual loss of its catalytic activity [fresh: >99% yield (4 h), sixth run: 49% (4 h)].

L. GOCLIK, H. WALSCHUS, A. BORDET*, W. LEITNER* (MAX PLANCK INSTITUTE FOR CHEMICAL ENERGY CONVERSION, MÜLHEIM AN DER RUHR AND RWTH AACHEN UNIVERSITY, GERMANY)

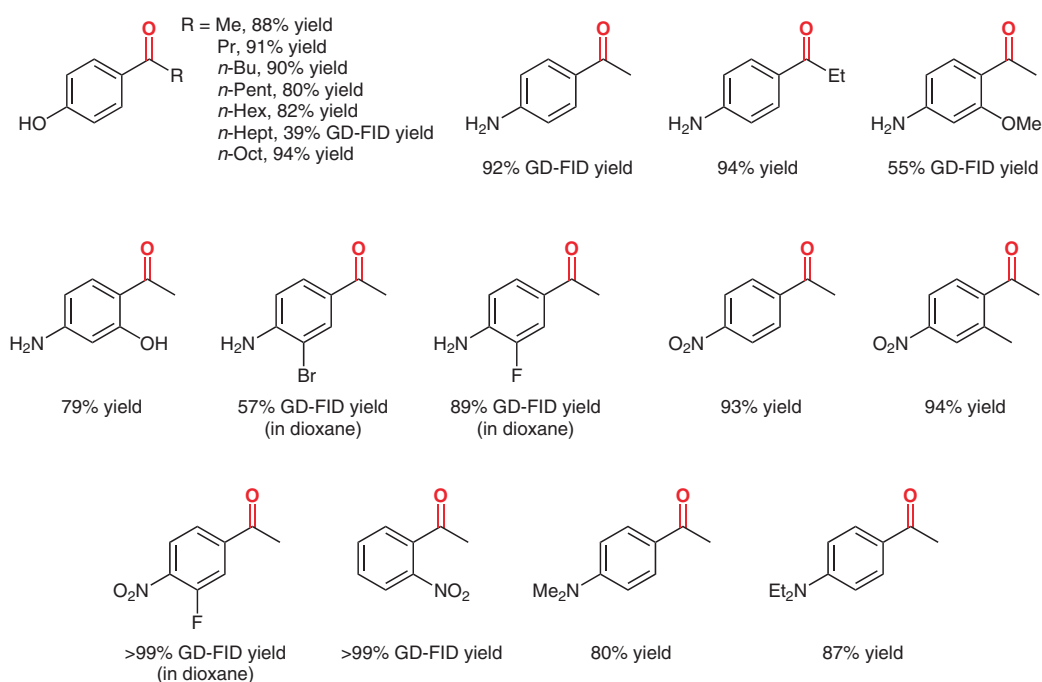
Selective Hydrodeoxygenation of Acetophenone Derivatives Using a $\text{Fe}_{25}\text{Ru}_{75}$ @SILP Catalyst: A Practical Approach to the Synthesis of Alkyl Phenols and Anilines

Green Chem. **2022**, *24*, 2937–2945, DOI: 10.1039/d1gc04189d.

Hydrodeoxygenation of Acetophenone Derivatives on a an Iron–Ruthenium Bimetallic Catalyst



Results:



Significance: Bimetallic iron–ruthenium nanoparticles immobilized on an imidazolium-based supported ionic liquid phase ($\text{Fe}_{25}\text{Ru}_{75}$ @SILP) catalyzed the hydrodeoxygenation of hydroxy, amino, and nitro derivatives of acetophenone to give the corresponding alkyl products in up to 94% yield (eq. 1).

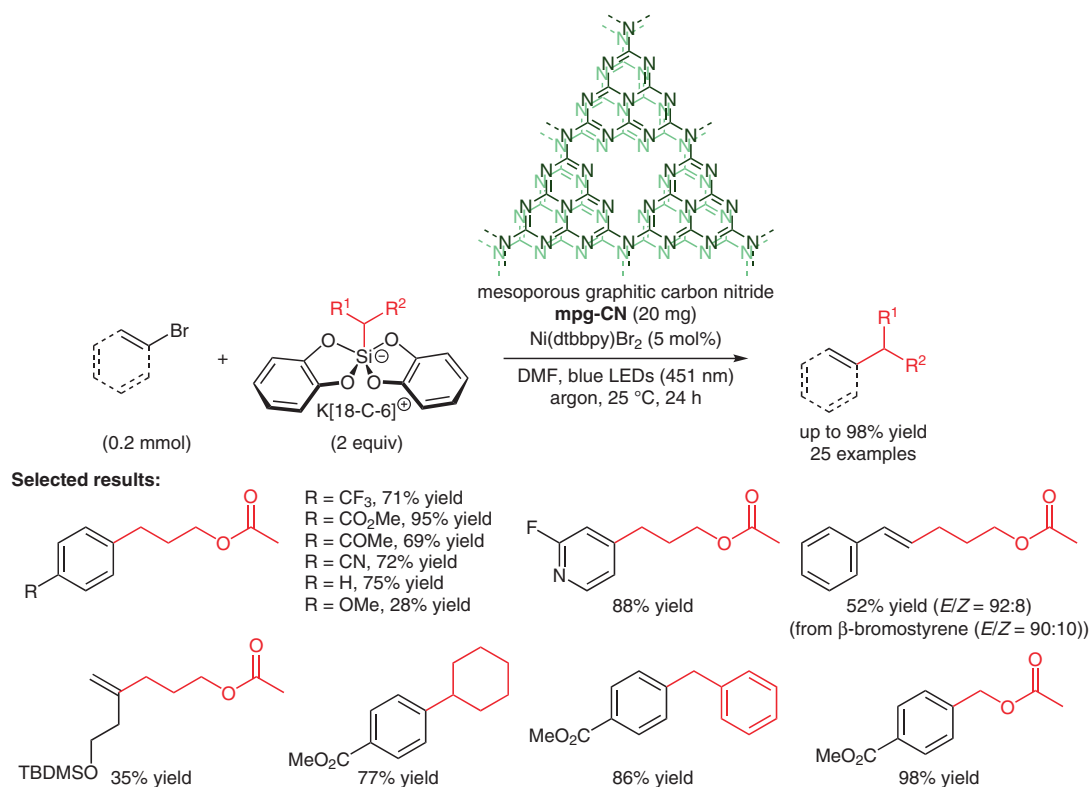
Comment: The authors have previously reported the preparation of $\text{Fe}_{25}\text{Ru}_{75}$ @SILP (*Chem. Commun.* **2020**, *56*, 9509). The catalyst was characterized by means of STEM-HAADF and SEM-EDX analyses. The hydrodeoxygenation of 4-hydroxyacetophenone in flow [175 °C, 50 bar H_2 , 0.6 mL/min substrate flow (25 mmol anisole soln), 17 s residence time] gave a 90–95% yield of 4-ethylphenol during five hours.

T. E. SCHIRMER, M. ABDELLAOUI, A. SAVATEEV, C. OLLIVIER*, M. ANTONIETTI, L. FENSTERBANK*, B. KÖNIG* (UNIVERSITY OF REGENSBURG, GERMANY AND SORBONNE UNIVERSITÉ, PARIS, FRANCE)

Mesoporous Graphitic Carbon Nitride as a Heterogeneous Organic Photocatalyst in the Dual Catalytic Arylation of Alkyl Bis(catecholato)silicates

Org. Lett. 2022, 24, 2483–2487, DOI: 10.1021/acs.orglett.2c00529.

Photocatalytic Cross-Coupling of Alkyl Silicates with Aryl or Alkenyl Bromides



Significance: A mesoporous graphitic carbon nitride (mpg-CN) and Ni(dtbbpy)Br₂ (dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) catalyzed the cross-coupling reaction of aryl or alkenyl bromides with potassium [18-Crown-6] bis(catecholato) alkylsilicates under irradiation by LEDs (451 nm) to afford the corresponding alkylated products in ≤98% yield (25 examples).

Comment: The authors have previously reported the the synthesis of mpg-CN and its application in such reactions as the C–H functionalization of arenes (*Science* 2019, 365, 360) and the cross-coupling of aryl bromides with alkyl borates (*ACS Catal.* 2020, 10, 3526). In the formation of 3-[4-(trifluoromethyl)phenyl]propyl acetate, the Ni/mpg-CN catalytic system was reused three times (second run: 76% yield, third run: 77%, fourth run: 43%).

SYNFACTS Contributors: Yasuhiro Uozumi, Aya Tazawa
Synfacts 2022, 18(07), 0783 Published online: 15.06.2022
DOI: 10.1055/s-0041-1737655; Reg-No.: Y05022SF

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Category

Polymer-Supported Synthesis

Key words

carbon nitride
nickel catalysis
arylation
alkenylation
alkyl silicates