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Tsuji–Wacker Oxidation of Terminal Olefins using a Palladium–Carbon Nanotube Nanohybrid

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Palladium nanoparticles supported on carbon nanotubes were used in the Tsuji–Wacker oxidation. The palladium-based nanohybrid was found to be very active in combination with cuprous chloride for the selective oxidation of terminal olefins into methyl ketones. The co-catalytic system operates under very mild and sustainable conditions (room temperature, atmospheric pressure, low catalyst loading), as opposed to previously reported catalysts, and can be recycled without any loss in activity.

The Tsuji–Wacker oxidation is a practical method for the transformation of terminal olefins into ketones. It usually involves catalytic amounts of palladium together with stoichiometric amounts of cuprous salts under aerobic conditions.[1] Recent efforts have been devoted to improving the process by tuning the catalysts,[2] oxidants,[3] and/or solvents.[4] To recycle the costly palladium catalyst and to facilitate isolation of the products, supported catalysis has also been investigated, including the use of palladium on iron oxide[5] or TiO_2,[6] dendrimer–palladium complexes,[7] palladium on montmorillonite,[8] and palladium on charcoal.[9] Although efficient, these heterogeneous systems suffer from some drawbacks such as high temperatures and/or high catalyst loadings.

With these critical features in mind, we sought to develop a catalyst that would operate under mild and sustainable conditions. Our laboratories recently reported supramolecular assemblies of metallic nanoparticles on carbon nanotubes (CNTs). This protocol afforded densely coated CNTs that were used in the catalysis of various organic transformations.[10] In the course of our investigations, we demonstrated that CNTs acted as a synergistic support capable of boosting the performance of the catalytic metal, as nanotubes provide high specific surface area and excellent nanoparticle dispersion. In addition, nanotubes are electronically active, and stabilization of transient higher oxidation states of Pd is anticipated. We therefore wanted to expand the use of CNT-supported palladium to the catalysis of the Tsuji–Wacker oxidation reaction (Figure 1).

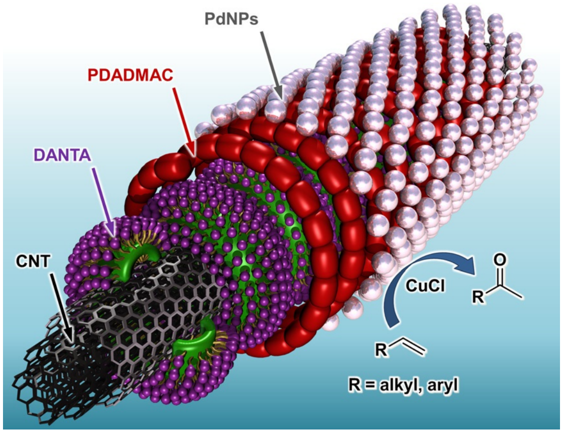

Figure 1. Overview of the Tsuji–Wacker oxidation over PdCNT.

The supported palladium catalyst was prepared by using a layer-by-layer approach.[10b] First, carbon nanotubes were sonicated in the presence of amphiphilic nitrilotriacetic-diyne (DANTA) surfactants in water, and this resulted in the formation of nanoring-like structures at the surface of the CNTs. The rings were then polymerized by UV irradiation, which reinforced the cohesion of the supramolecular assembly. In a second step, a polycationic polymer [i.e., polydiallyldimethylammonium chloride (PDADMAC)] layer was deposited on the primary coating, and palladium nanoparticles (PdNPs) were added to afford the final hybrid (i.e., PdCNT). Although other anchoring methods of PdNPs on CNTs are described in the literature, they usually do not provide such a dense and homogeneous covering of the nanotube surface.[11] Blank experiments were conducted with either bare nanotubes or DANTA-coated nanotubes. However, no PdNPs could be detected on the naked nanotubes and poor Pd-covering was observed with DANTA nanotubes. These control experiments highlight the importance of the layer-by-layer assembly, for which the polyammonium network provided robust anchoring and stabilization of the palladium nanoparticles.

Transmission electron microscopy (TEM) indicated that the PdNPs were of spherical shape, and size evaluation by statistical measurement gave a mean particle diameter of approximately 2 nm (Figure S1, Supporting Information). The volume of the aqueous PdCNT suspension was adjusted to a Pd concentration of 14 mᴍ [as determined by inductively coupled plasma mass spectrometry (ICP-MS)]. X-ray photoelectron spectroscopy (XPS) analysis indicated that the particles were composed of a mixture of palladium metal and palladium oxide in an approximate ratio of 1:1 (Figure S2).

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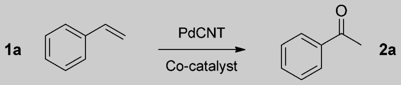
Preliminary studies on the catalytic activity of the PdCNT nanohybrid in the Tsuji–Wacker oxidation were conducted by using styrene as a model substrate. Its conversion into acetophenone was investigated under different conditions (Table 1).

Table 1. Optimization of the Tsuji–Wacker oxidation of styrene into acetophenone.[a]

1a



2a

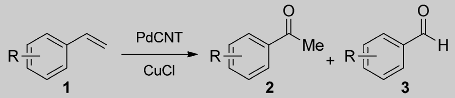
Entry	Solvent	Co-catalyst [mol %]	Atmosphere	Time [h]	Yield [%][b]
1	THF/H_2O (4:1)	$KBrO_3$ (100)	air	36	–
2	THF/H_2O (4:1)	$CuBr_2$ (10)	air	48	59
3	THF/H_2O (4:1)	CuCl (10)	air	48	85
4	EtOH/H_2O (1:1)	CuCl (10)	air	48	–
5	toluene/H_2O (1:1)	CuCl (10)	air	48	–
6	DMF/H_2O (8:1)	CuCl (10)	air	48	68
7[c]	THF/H_2O (4:1)	CuCl (5)	air	48	82
8[c]	THF/H_2O (4:1)	CuCl (5)	O_2[d]	24	93
9[e]	THF/H_2O (4:1)	CuCl (10)	O_2[d]	36	–
10	THF/H_2O (4:1)	–	O_2[d]	36	–

[a] Conditions: **1a** (0.1 mmol), co-catalyst (5–100 mol %), PdCNT (1 mol %), solvent (0.5 mL), RT. [b] Yield of purified, isolated product. [c] Reaction was performed with 0.56 mol % of PdCNT. [d] O_2 (101.3 kPa). [e] Reaction was performed without PdCNT.

We first looked at the nature of the co-catalysts; whereas no product was detected with $KBrO_3$ in THF/H_2O (Table 1, entry 1), cupric and cuprous salts proved to be better co-catalysts, as acetophenone was isolated in moderate ($CuBr_2$; Table 1, entry 2) to good yields (CuCl; Table 1, entry 3). CuCl was selected as the co-catalyst, and solvent effects were investigated, but neither EtOH/H_2O nor toluene/H_2O gave satisfactory conversion after 48 h (Table 1, entries 4 and 5). DMF/H_2O (Table 1, entry 6) was found to be more efficient (68 % conversion), but the best system remained THF/H_2O. Using this solvent system, the catalyst and co-catalyst loadings (initially 1 and 10 mol %, respectively) could be lowered to 0.56 and 5 mol %, respectively (Table 1, entry 7). Working under an oxygen atmosphere gave optimal results with 93 % conversion after 24 h of reaction (Table 1, entry 8). Control experiments run in the absence of either the catalyst (Table 1, entry 9) or the co-catalyst (Table 1, entry 10) led to no product formation, highlighting the cooperative effect between the two metals.

We next expanded the scope of the above process to the oxidation of variously substituted styrenes. Surprisingly, the Tsuji–Wacker oxidation of substituted styrenes under an oxygen atmosphere led to some side formation of benzaldehyde derivatives resulting from oxidative cleavage of the alkene unit (Table 2, entries 3, 5, 7, and 9). The formation of these unwanted products could, however, be minimized by working in air, as we observed in this case better selectivity towards acetophenone, although longer reaction times were required to reach satisfactory conversion yields (Table 2, entries 4, 6, 8, and 10).

Table 2. PdCNT-catalyzed Tsuji–Wacker oxidation of styrene derivatives.[a]

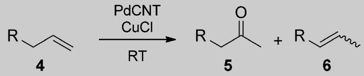


Entry	1	R	Atmosphere	Time [h]	Yield of 2[b] [%]	Selectivity 2/3[c]
1	**1a**	H	O_2	24	93	100:0
2			air	48	82	100:0
3	**1b**	4-CH_2Cl	O_2	36	67	68:32
4			air	48	89	94:6
5	**1c**	4-Cl	O_2	36	69	71:29
6			air	48	89	95:5
7	**1d**	3-NO_2	O_2	36	39	46:54
8			air	48	76	81:19
9	**1e**	4-*t*Bu	O_2	36	73	77:23
10			air	48	96	99:1

[a] Conditions: **1** (0.1 mmol), CuCl (5 mol %), PdCNT (0.56 mol %), THF/H_2O (4:1, 0.5 mL), RT. [b] Yield of isolated product. [c] Determined by analysis of the crude mixture by ^1H NMR spectroscopy.

The selectivity of the catalytic oxidation of aliphatic alkenes, on the other hand, followed another trend: experiments conducted in air led mainly to isomerization of the double bond, whereas reactions run under an O_2 atmosphere afforded the desired ketones. For example, the reaction of tetradec-1-ene with PdCNT and CuCl in air afforded a 30:70 mixture of tetradecan-2-one (**5a**) and isomeric alkene **6a** in 90 % yield (Table 3, entry 1). The same reaction conducted under an oxygen atmosphere afforded exclusively the Tsuji–Wacker oxidation product (i.e., **5a**) in 95 % yield (Table 3, entry 2). It thus clearly appeared that dioxygen was needed for substrates bearing an isomerizable double bond. With these reaction conditions in hand, we further examined the scope of the reaction of terminal olefins.

Table 3. Scope of the PdCNT-catalyzed Tsuji–Wacker oxidation.[a]

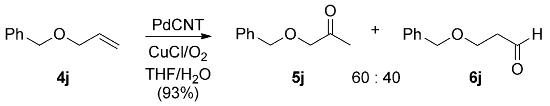


Entry	4	R	Product	Time [h]	Yield[b] [%]	Selectivity 5/6[c,d]
1[e]	**4a**	$Me(CH_2)_{10}$	**5a**; **6a**	36	90	30:70
2	**4a**	$Me(CH_2)_{10}$	**5a**	36	92	100:0
3	**4b**	$MeO_2C(CH_2)_7$	**5b**	36	96	98:2
4	**4c**	$HO_2C(CH_2)_7$	**5c**	36	92	95:5
5	**4d**	$OHC(CH_2)_7$	**5d**	36	97	100:0
6	**4e**	$HO(CH_2)_8$	**5e**	36	93	98:2
7	**4f**	$Br(CH_2)_8$	**5f**	36	93	96:4
8	**4g**	$N_3(CH_2)_8$	**5g**	36	95	99:1
9	**4h**	$O_2N(CH_2)_8$	**5h**	36	94	100:0
10	**4i**	$I(CH_2)_8$	**5i**	36	93	98:2

[a] Conditions: **4** (0.1 mmol), CuCl (5 mol %), PdCNT (0.56 mol %), THF/H_2O (4:1, 0.5 mL), RT, O_2 (101.3 kPa). [b] Yield of isolated product. [c] Determined by analysis of the crude mixture by ^1H NMR spectroscopy. [d] Compound **6** was obtained as a mixture of isomeric alkenes. [e] Reaction was performed in air.

The process was found to tolerate a large number of functional moieties such as ester (Table 3, entry 3), carboxylic acid (Table 3, entry 4), aldehyde (Table 3, entry 5), alcohol (Table 3, entry 6), bromide (Table 3, entry 7), azide (Table 3, entry 8), nitro (Table 3, entry 9), and iodide (Table 3, entry 10) groups. Products were obtained in excellent yields with high selectivity. Noteworthy, no alcohol or aldehyde oxidation was detected (Table 3, entries 5 and 6) under the PdCNT/CuCl-mediated conditions.

The observed selectivity towards methyl ketone formation was good to excellent in all the above cases. However, the reaction of (allyloxy)methylbenzene with PdCNT/CuCl under an O_2 atmosphere afforded a 60:40 mixture of expected methyl ketone **5j** and aldehyde **6j** (Scheme 1) that resulted from oxidation of the terminal carbon atom (93% yield, 24 h). The formation of the aldehyde can be ascribed to palladium coordination to the allylic oxygen atom, which causes water to attack the terminal position.[12]



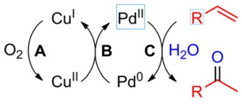
Scheme 1. Reactivity of (allyloxy)methylbenzene in the Tsuji–Wacker oxidation.

The performance of our PdCNT/CuCl system was compared to that of a reference system. An oxidation reaction of tetradec-1-ene was thus set with $PdCl_2/CuCl/O_2$ in THF/H_2O. Under these conditions, the $PdCl_2$-based system afforded a 1:2 mixture of expected methyl ketone **5a** and isomerized olefin **6a** in approximately 90% yield after 36 h of reaction. Although the yields of products were satisfactory, selectivity was poor. This selectivity has to be compared to that of PdCNT (**5a**/**6a** = 100:0), which highlights the superiority of the CNT-supported palladium catalyst.

To better understand the nature of the catalysis, an oxidation reaction of tetradec-1-ene was set up under the above-mentioned conditions (0.56 mol% PdCNT, 5 mol% CuCl, O_2 atmosphere). After stirring for 12 h, the PdCNT catalyst was removed by centrifugation. At this point, approximately 40% conversion was reached, as determined by ^{1}H NMR spectroscopy. The catalyst-free supernatant was then stirred for an additional 24 h, but no further conversion was detected, which thus demonstrated the heterogeneous nature of the catalyst.

Finally, the recyclability of the palladium catalyst was assessed by using styrene as the substrate. At the end of the reaction, the mixture was centrifuged and the supernatant was worked-up to isolate acetophenone. The Pd/CNT catalyst was washed with water and THF and resuspended in THF/H_2O. Styrene and CuCl were added, and the mixture was stirred for 24 h at room temperature under an O_2 atmosphere. The overall process was repeated four times. No significant decrease in the catalytic activity was observed throughout the five cycles, as the yields of the isolated product remained nearly constant (90–93%). No palladium that might have leached out of the CNTs could be detected by ICP-MS analysis of the above mixtures. In addition, TEM analysis of the catalyst after the fifth cycle indicated no morphological alteration, except for some occasional bare areas. These results substantiate the robustness of the Pd tethering.

A proposed mechanism (Scheme 2) for the above co-catalytic transformation involves initial aerobic oxidation of Cu^I into Cu^{II} (path A), followed by the copper(II)-mediated oxidation of Pd^0 (path B). The activated Pd^{II} species then undergoes complexation with the olefinic substrate before nucleophilic attack of water (path C) and subsequent release of the ketone product together with Pd^0, which then enters a new catalytic cycle.



Scheme 2. Proposed mechanism for the PdCNT/CuCl-mediated Tsuji–Wacker oxidation of terminal olefins.

In summary, a heterogeneous catalyst was assembled by stabilization of palladium nanoparticles on carbon nanotubes.[11] The resulting nanohybrid was used in the co-catalytic Tsuji–Wacker oxidation of olefins in the presence of cuprous chloride. The system proved very efficient on all the investigated substrates, demonstrated high selectivity toward methyl ketone formation, tolerated various functional groups, operated with minimal amounts of the co-catalysts at room temperature, and could be readily recycled.

Experimental Section

Typical procedure for Tsuji–Wacker oxidation

Pd/CNT (40 μL of a 14 mM suspension, 0.56 mol%) and CuCl (0.5 mg, 5 mol%) were added to THF/H_2O (4:1, 0.5 mL). Oxygen was bubbled into the mixture for 15 min and styrene (10.4 mg, 0.1 mmol) was added. The mixture was stirred at room temperature under an oxygen (balloon) atmosphere until completion. Water (2 mL) was added, and the aqueous phase was extracted with EtOAc (3×3 mL). The combined organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by chromatography (silica gel, petroleum ether/EtOAc = 90:10) to afford **2a** as a colorless oil (11.2 mg, 93%).

Characterization data

Acetophenone (**2a**): ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.95$ (d, $J = 7.4$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.4$ Hz, 2H), 2.59 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 198.3$, 137.2, 133.2, 128.7, 128.4, 26.7 ppm.

4-(Chloromethyl)acetophenone (**2b**): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.95$ (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 4.62 (s, 2H), 2.61 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 197.7$, 142.6, 137.2, 129.4, 128.9, 45.5, 26.9 ppm.

4-Chloroacetophenone (**2c**): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.87$ (dt, $J = 8.6$ Hz, $J = 2.0$ Hz, 2H), 7.42 (dt, $J = 8.6$ Hz, $J = 2.0$ Hz, 2H), 2.58 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 197.0$, 139.7, 135.6, 129.9, 129.0, 26.7 ppm.

3-Nitroacetophenone (**2 d**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=8.77–8.76 (m, 1 H), 8.42 (d, J=8.0 Hz, 1 H), 8.28 (d, J=8.0 Hz, 1 H), 7.69 (t, J=8.0 Hz, 1 H), 2.69 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=195.8, 148.4, 138.4, 133.9, 130.0, 127.6, 123.4, 26.6 ppm.

4-(*tert*-Butyl)acetophenone (**2 e**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=7.90 (d, J=8.4 Hz, 2 H), 7.48 (d, J=8.4 Hz, 2 H), 2.59 (s, 3 H), 1.35 ppm (s, 9 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=197.8, 156.8, 134.6, 128.2, 125.4, 35.1, 31.0, 26.5 ppm.

4-(Chloromethyl)benzaldehyde (**3 b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=10.0 (s, 1 H), 7.88 (d, J=8.2 Hz, 2 H), 7.56 (d, J=8.2 Hz, 2 H), 4.63 ppm (s, 2 H).

4-Chlorobenzaldehyde (**3 c**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=9.98 (s, 1 H), 7.83 (dt, J=8.6 Hz, J=2.0 Hz, 2 H), 7.51 ppm (dt, J=8.6 Hz, J=1.7 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=191.1, 141.2, 134.9, 129.7, 129.1 ppm.

3-Nitrobenzaldehyde (**3 d**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=10.13 (s, 1 H), 8.73 (t, J=1.6 Hz, 1 H), 8.49 (dd, J=7.8 Hz, J=1.6 Hz, 1 H), 8.24 (dd, J=7.8 Hz, J=1.6 Hz, 1 H), 7.77 ppm (t, J=7.8 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=189.6, 148.7, 137.3, 134.5, 130.3, 128.5, 124.5 ppm.

4-*tert*-Butylbenzaldehyde (**3 e**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=9.99 (s, 1 H), 7.82 (d, J=8.4 Hz, 2 H), 7.55 (d, J=8.4 Hz, 2 H), 1.36 ppm (s, 9 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=192.0, 158.4, 134.0, 129.6, 125.9, 35.3, 31.0 ppm.

2-Tetradecanone (**5 a**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=2.41 (t, J=7.5 Hz, 2 H), 2.13 (s, 3 H), 1.55–1.60 (m, 2 H), 1.20–1.32 (m, 18 H), 0.87 ppm (t, J=8.6 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=209.7, 44.0, 32.1, 30.4, 30.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 24.1, 22.9, 14.3 ppm.

Methyl 10-oxoundecanoate (**5 b**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=3.64 (s, 3 H), 2.39 (t, J=7.4 Hz, 2 H), 2.27 (t, J=7.4 Hz, 2 H), 2.11 (s, 3 H), 1.61–1.51 (m, 4 H), 1.29–1.22 ppm (m, 8 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=209.5, 174.5, 51.6, 43.9, 34.2, 30.0, 29.3, 29.2 (3C), 25.0, 23.9 ppm.

10-Oxoundecanoic acid (**5 c**): ^{1}H NMR (500 MHz, CDCl$_3$) δ=2.41 (t, J=7.4 Hz, 2 H), 2.36 (t, J=7.4 Hz, 2 H), 2.13 (s, 3 H), 1.64–1.54 (m, 4 H), 1.31–1.24 ppm (m, 8 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ=209.6, 178.7, 43.9, 30.0, 29.9, 29.3, 29.2 (2C), 29.1, 24.8, 24.0 ppm.

10-Oxoundecanal (**5 d**): ^{1}H NMR (500 MHz, CDCl$_3$) δ=9.76 (t, J=1.8 Hz, 1 H), 2.43–2.39 (m, 4 H), 2.13 (s, 3 H), 1.65–1.54 (m, 4 H), 1.33–1.24 ppm (m, 8 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ=209.5, 203.1, 44.0, 43.9, 30.0, 29.3 (2C), 29.2 (2C), 23.9, 22.2 ppm.

11-Hydroxyundecan-2-one (**5 e**): ^{1}H NMR (500 MHz, CDCl$_3$) δ=3.62 (t, J=6.6 Hz, 2 H), 2.40 (t, J=7.5 Hz, 2 H), 2.12 (s, 3 H), 1.74 (br s, 1 H), 1.56–1.51 (m, 4 H), 1.37–1.22 ppm (m, 10 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ=209.7, 63.2, 44.0, 32.9, 30.1, 29.6, 29.5, 29.5, 29.3, 25.9, 25.0 ppm.

11-Bromoundecan-2-one (**5 f**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=3.40 (t, J=6.9 Hz, 2 H), 2.41 (t, J=7.4 Hz, 2 H), 2.13 (s, 3 H), 1.84 (quint., J=7.2 Hz, 2 H), 1.60–1.54 (m, 2 H), 1.44–1.38 (m, 2 H), 1.32–1.22 ppm (m, 8 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=209.6, 44.0, 34.2, 33.0, 30.1, 29.4 (2C), 29.3, 28.9, 28.3, 24.0 ppm.

11-Azidoundecan-2-one (**5 g**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=3.24 (t, J=7.0 Hz, 2 H), 2.41 (t, J=7.4 Hz, 2 H), 2.13 (s, 3 H), 1.62–1.54 (m, 4 H); 1.38–1.25 ppm (m, 10 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=209.6, 51.6, 43.9, 30.0, 29.4 (2C), 29.3, 29.2, 29.0, 26.8, 24.0 ppm.

11-Nitroundecan-2-one (**5 h**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=4.37 (t, J=7.1 Hz, 2 H), 2.41 (t, J=7.4 Hz, 2 H), 2.13 (s, 3 H), 1.99 (quint., J=7.2 Hz, 2 H), 1.61–1.52 (m, 2 H), 1.38–1.21 ppm (m, 10 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=209.5, 75.9, 43.9, 31.1, 29.9, 29.4, 29.2, 28.9, 27.6, 26.4, 23.9 ppm.

11-Iodoundecan-2-one (**5 i**): ^{1}H NMR (400 MHz, CDCl$_3$) δ=3.18 (t, J=7.0 Hz, 2 H), 2.41 (t, J=7.4 Hz, 2 H), 2.13 (s, 3 H), 1.81 (quint., J=7.2 Hz, 2 H), 1.59–1.54 (m, 2 H), 1.39–1.22 ppm (m, 10 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=209.2, 43.7, 33.5, 33.0, 30.4, 29.8, 29.2, 29.1, 29.0, 28.4, 23.7 ppm.

Recycling experiment

A typical oxidation reaction of styrene was set up as above starting from styrene (0.1 mmol), CuCl (5 mol %), and PdCNT (0.56 mol %) in THF/H$_2$O (4:1, 0.5 mL). The mixture was stirred at room temperature under an oxygen atmosphere for 24 h. The catalyst was recovered by centrifugation, and the supernatant was worked up as above. The recovered catalyst was washed with water and reused in a subsequent oxidation reaction of styrene with added CuCl.

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Keywords: heterogeneous catalysis · olefins · nanoparticles · nanotubes · oxidation

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