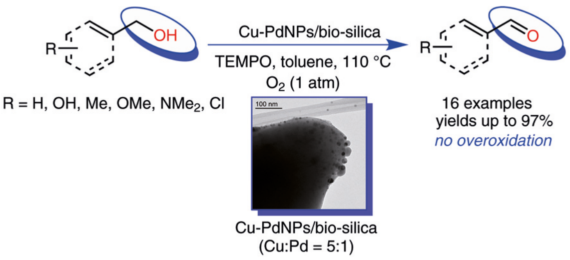
Bimetallic Cu-Pd Nanoparticles Supported on Bio-silica as an Efficient Catalyst for Selective Aerobic Oxidation of Benzylic Alcohols

Eduardo Buxaderas[a]
Marilyn Graziano-Mayer[a]
María Alicia Volpe[b]
Gabriel Radivoy*[a]

[a] Instituto de Química del Sur (INQUISUR-CONICET), Departamento de Química, Universidad Nacional del Sur, Avda. Alem 1253, 8000 Bahía Blanca, Argentina
gradivoy@criba.edu.ar
[b] Planta Piloto de Ingeniería Química, PLAPIQUI (CONICET-UNS), Camino La Carrindanga Km 7, CC 717, 8000 Bahía Blanca, Argentina



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Abstract A new bimetallic heterogeneous catalyst consisting of copper and palladium nanoparticles supported on bio-silica is presented. The use of TEMPO as co-catalyst allowed the aerobic oxidation of primary benzylic alcohols into the corresponding aldehydes with excellent selectivity and good activity. The methodology could be applied to the oxidation of allylic and heterobenzylic alcohols. The catalyst is easy to prepare from commercial starting materials and can be recovered and reused without apparent loss of activity.

Key words benzylic alcohols, aerobic oxidation, benzaldehydes, copper-palladium nanoparticles, TEMPO

Selective alcohol oxidation for the synthesis of carbonyl compounds is a fundamental and valuable transformation both in nature and in organic chemistry. In particular, oxidation of benzylic alcohols is essential for laboratory and industrial chemistry since benzaldehydes and benzoic acids are key compounds in the production of many fine chemicals.[1]

Traditional methods for the oxidation of alcohols involve the use of stoichiometric inorganic oxidants such as permanganate and chromate, with the concomitant formation of undesirable amounts of waste and by-products. Thus, in the last decades the development of aerobic oxidation methods has gained increasing interest and a wide range of transition-metal-catalyzed oxidizing systems have been reported (Pd,[2] Ru,[3] Pt,[4] Ni,[5] Co,[6] Os,[7] Fe,[8] Cu,[9] among others[10]). Most of these oxidizing agents consist of homogeneous catalysts based on the use of expensive and/or toxic metals in conjunction with appropriate ligands and different additives. From a green perspective, the use of oxygen as oxidant in combination with a heterogeneous metal catalyst is the more attractive alternative since the atom efficiency is high, water is the major by-product and, in many cases, the catalyst can be recovered and reused.[11–13] In this scenario, supported metal nanoparticles arise as promising catalysts; consequently, many noble-metal-heterogeneous catalytic systems for the oxidation of alcohols involving the use of metal nanoparticles have been reported in the last years,[14] most of them based on PdNPs or AuNPs nanoparticles. In many of these catalytic systems, the use of a base for deprotonation of the alcohol and/or for the regeneration of metal active species is mandatory.[15] Moreover, the beneficial synergistic effect of using bimetallic Au-PdNPs catalysts has been suggested recently.[16]

On the other hand, the use of less expensive, CuNPs-based heterogeneous catalysts for the selective oxidation of benzylic alcohols has rarely been reported.[17] This could be attributed to the intrinsic lower activity of copper catalysts for alcohol oxidation when compared with palladium or gold catalysts, even in homogeneous catalytic systems. In this sense, the use of stable nitroxyl radicals such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), in combination with copper (salts or complexes) and oxygen as terminal oxidant, has been demonstrated to be a very efficient and selective approach for the oxidation of a wide variety of alcohols. Since the pioneering work by Semmelhack[18] on this kind of homogeneous catalytic systems, the use of copper/nitroxyl catalysts for the aerobic oxidation of alcohols have been studied in depth, among others by the research groups of Stahl, Sheldon, and Koskinen.[19]

It is noteworthy that most of the catalytic systems mentioned above oxidize both primary and secondary alcohols, although a few of them showed over-oxidation of primary alcohols to the corresponding carboxylic acids.

In the last years we were involved in the development of new nanocatalysts based on the preparation of naked or supported copper nanoparticles (CuNPs) for their use as catalysts in different synthetic transformations, mainly in reduction and coupling reactions.[20] Prompted by our inter-

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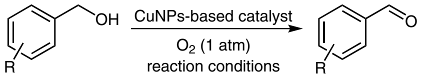
est in expanding the synthetic applications of these heterogeneous nanocatalysts, we decided to study the performance of CuNPs-based catalysts in the selective oxidation of primary benzylic alcohols to benzaldehydes under aerobic conditions (Scheme 1).

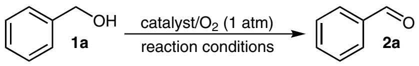


Scheme 1 Aerobic oxidation of benzylic alcohols catalyzed by CuNPs-based catalysts

Initially, benzyl alcohol (**1a**) was chosen as a model compound for testing the performance of a variety of catalysts consisting of CuNPs or bimetallic Cu-PdNPs supported on different materials (Table 1). All catalysts were prepared as previously reported by us.[20d] Briefly, metal nanoparticles were generated in THF at room temperature by fast reduction of the corresponding anhydrous metal chlorides with lithium powder and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB), and were then stirred in the presence of the support for one hour. The bimetallic Cu-Pd catalysts were prepared with a charged Cu/Pd ratio of 5:1. Oxidation reactions were carried out in toluene as solvent and stirring overnight under O_2 atmosphere (balloon). In all cases, the metal loading (copper or copper-palladium) was 18 mol%. The metal composition of the mono- and bimetallic catalysts was measured by atomic absorption spectroscopy.

As shown in Table 1, monometallic copper catalysts showed excellent selectivity to the desired benzaldehyde but low activities were observed with all catalysts tested (Table 1, entries 1–4). On the other hand, monometallic palladium catalysts, although very active, were less selective, giving considerable amounts of benzoic acid as over-oxidation by-product (entries 5 and 6). The best results were obtained by working at 110 °C and using the bimetallic Cu-Pd catalysts supported on bio-silica (Celite) or MCM-48 (entries 7 and 8), with Cu-PdNPs/bio-silica being the catalyst that showed the best performance.

Table 1 Screening of Cu- and Pd-Based Nanocatalysts[a]



Entry	Catalyst	Conversion (%)[b]	Selectivity (%)[c]
1	CuNPs@MagSilica	20	100
2	CuNPs@bio-silica	14	100
3	CuNPs@CeO$_2$	12	100
4	CuNPs@MCM-48	27	100
5	PdNPs@bio-silica	78	65
6	PdNPs@CeO$_2$	80	61
7	Cu-PdNPs@bio-silica[d]	97 (65,[e] 74,[f] 96[g])	100
8	Cu-PdNPs@MCM-48[d]	84	100

[a] Reaction conditions: **1a** (0.5 mmol), nanocatalyst (80 mg, metal loading: 18 mol%), toluene (3 mL), 110 °C, overnight.
[b] GC-MS conversion of the starting benzylic alcohol.
[c] Selectivity expressed as yield (%) of benzaldehyde based on the starting benzyl alcohol.
[d] Catalyst metal loading: 15 mol% Cu and 3 mol% Pd.
[e] Reaction performed with 40 mg catalyst (metal loading: 9 mol%).
[f] Reaction performed with 60 mg catalyst (metal loading: 13.5 mol%).
[g] Reaction performed with 100 mg catalyst (metal loading: 22.5 mol%).

As shown in Table 1, the use of higher catalyst loading did not lead to any improvement in catalytic activity, whereas the conversion dropped significantly at lower catalyst loadings (entry 7, footnotes e–g). On the other hand, screening of reaction solvents showed that toluene was the solvent of choice. Thus, the reaction carried out in THF or H_2O led to low conversions of the starting benzyl alcohol (23 and 5%, respectively), and the use of DMF resulted in low catalyst selectivity and to a 4:1 mixture of benzaldehyde and benzoic acid, although with comparable results to that of toluene in terms of conversion (88%).

Analysis by TEM of the Cu-PdNPs/bio-silica catalyst showed spherical nanoparticles with an average size of 10 ± 2 nm (Figure 1). XPS analysis of the Cu-PdNPs/bio-silica catalyst showed Cu (2p3/2) peaks at 932.3, 934.6, 936.2, 941.5, and 944.7 eV, with the last two peaks being a satellite shake-up feature characteristic of Cu^{2+} species. On the other hand, XPS analysis revealed the presence of Pd (3d5/2) and Pd (3d3/2) peaks that, after deconvolution, showed two contributions at 336.2/337.6 eV for Pd (3d5/2) peak, and 341.3/342.9 eV for Pd (3d3/2) peak. From these results it could be concluded that metallic copper and palladium coexist with oxidized copper and palladium species at the surface of the nanocatalyst.[21]

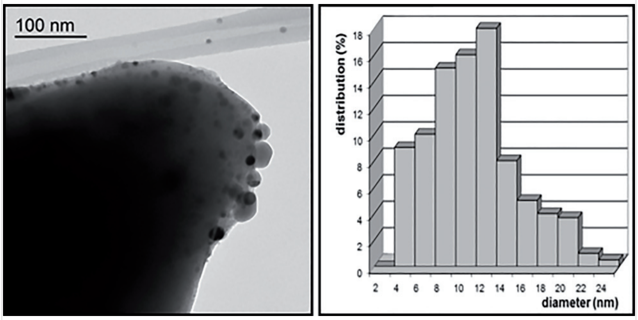


Figure 1 TEM micrograph and size distribution graphic for Cu-Pd-NPs/bio-silica catalyst.

We then examined the scope of the reaction with the optimal catalyst by testing the oxidation of a variety of benzylic alcohols. However, as shown in Table 2, the results for most of the substrates tested were not very encouraging. Although some starting alcohols, such as *p*-chloro-, *p*-methoxy-, *p*-hydroxy-, and *p*-dimethylamino benzylic alcohols were oxidized to the corresponding benzaldehydes in good to moderate yield (entries 2, 4, 6, and 9), other starting benzylic alcohols bearing substituents such as *o*-chloro, *o*-meth-

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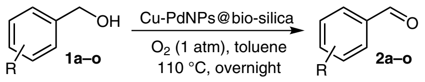
oxy, *m*-hydroxy, *o*-hydroxy, or *p*-methyl were rather unreactive (entries 3, 5, 7, 8, and 10). Attempts to improve the oxidation rate by modifying the reaction conditions (temperature, substrate/catalyst ratio, etc.) were unsuccessful.

It is known that a general drawback of palladium catalysts is the slow reoxidation of Pd(0) to Pd(II). To circumvent this problem, Cu(II) is often used as co-catalyst, which reoxidizes Pd(0) to Pd (II) while generating Cu(I) species that need to be oxidized to Cu(II) to restart the catalytic cycle. On the other hand, the studies by Sheldon and co-workers mentioned above have established that the Cu(I)/Cu(II) couple, in combination with TEMPO, allows the aerobic oxidation of alcohols to carbonyl compounds under homogeneous conditions. Therefore, we decided to study the effect of the addition of a catalytic amount of TEMPO to the reaction mixture. Thus, the oxidation of *p*-methylbenzyl alcohol, under the optimized conditions, with TEMPO (5 mg, 0.03 mmol) as additive, led to the desired *p*-methylbenzaldehyde with a remarkable increase in yield (90%) when compared with that obtained in the absence of TEMPO (Table 2, entry 10). Similarly, the oxidation of *o*-chlorobenzylic alcohol gave 71% of *o*-chlorobenzaldeyde in contrast to 9% yield obtained without using TEMPO. As can be seen in Table 2, except for *p*-*N*,*N*-dimethylaminobenzyl alcohol **1i** (entry 9), all of the substrates tested gave good to excellent yields of the corresponding aldehydes by using TEMPO as additive. Moreover, the use of TEMPO allowed the oxidation of other π-conjugated alcohols such as naphthalen-2-ylmethanol, cinnamyl alcohol, and thiophen-2-ylmethanol (entries 11–13) in high yields. In contrast, aliphatic primary and secondary alcohols gave low yields of the corresponding carbonyl compounds, both in the presence and in the absence of the nitroxyl radical (entries 14 and 15). A similar lack of reactivity was observed when a secondary benzylic alcohol (1-phenylethanol) was reacted under the optimized conditions, giving only 13% conversion into acetophenone (entry 16). On the other hand, the oxidation of electron-poor primary alcohols, such as 4-nitrobenzyl alcohol or 3-pyridinemethanol, gave low conversions (10–15%) into the corresponding overoxidized products.

Table 2 Scope of the Oxidation Reaction Catalyzed by Cu-PdNPs@bio-silica[a]



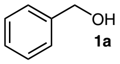
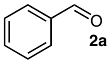
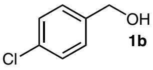
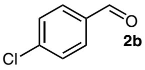
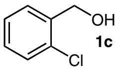
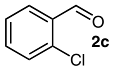
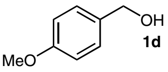
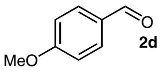
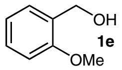
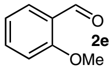
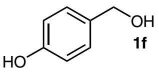
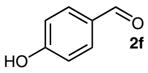
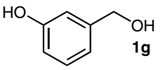
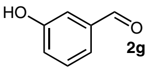
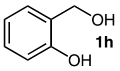
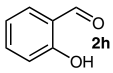
Entry	Starting alcohol	Product	Yield (%)	
			Cu-PdNPs[b]	Cu-PdNPs-TEMPO[c]
1	 **1a**	 **2a**	97	98
2	 **1b**	 **2b**	73	75
3	 **1c**	 **2c**	9	71
4	 **1d**	 **2d**	52	78
5	 **1e**	 **2e**	32	76
6	 **1f**	 **2f**	73	99
7	 **1g**	 **2g**	18	80
8	 **1h**	 **2h**	17	99

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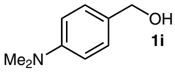
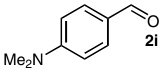
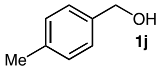
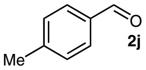
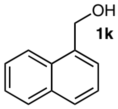
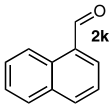
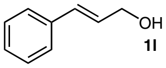
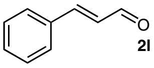
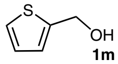
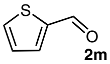
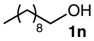
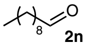
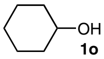
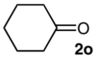
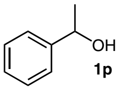
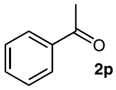
Table 2 (continued)

Entry	Starting alcohol	Product	Yield (%)	
			Cu-PdNPs[b]	Cu-PdNPs-TEMPO[c]
9	 **1i**	 **2i**	67	47[d]
10	 **1j**	 **2j**	30	90
11	 **1k**	 **2k**	20	99
12	 **1l**	 **2l**	48	81
13	 **1m**	 **2m**	56	83
14	 **1n**	 **2n**	18	18
15	 **1o**	 **2o**	7	9
16	 **1p**	 **2p**	6[e]	13[e]

[a] Reaction conditions: alcohol (0.5 mmol), Cu-PdNPs catalyst (80 mg, 15 mol% Cu and 3 mol% Pd), toluene (3 mL), stirred, 110 °C, overnight.
[b] Isolated yield after column chromatography (silica gel; hexane/EtOAc).
[c] TEMPO (5 mg, 0.03 mmol) was added to the reaction mixture.
[d] The corresponding aldehyde product along with a complex mixture of condensation products was observed.
[e] Determined by GC-MS analysis using an internal standard.

The use of TEMPO as additive also allowed the recovery and reuse of the catalyst in three consecutive cycles without apparent loss of activity. As an example, after the oxidation of benzyl alcohol (**1a**) was completed (97% yield in the first cycle), the reaction mixture was centrifuged, and the catalyst was filtered off, washed with the reaction solvent, and reused in a second cycle, giving 93% aldehyde **2a**, and 90% yield after a third cycle.

With the aim to get some information on the possible reaction pathway and the exact role of TEMPO in the catalytic system, we conducted some additional experiments. The oxidation of **1a** conducted only in the presence of TEMPO (no catalyst), gave 58% yield of benzaldehyde (**2a**) after 24 hours reaction time. We then conducted the oxidation of **1a** by using the monometallic copper or palladium nanocatalysts and TEMPO as additive. Thus, the reaction with CuNPs/bio-silica as catalyst rendered 30% conversion into **2a** as the only reaction product, whereas the oxidation of **1a** catalyzed by PdNPs/bio-silica gave 85% yield of benzoic acid together with minor amounts of aldehyde **2a**. Finally, the oxidation of **1a** under the optimized conditions, but working under nitrogen atmosphere, gave only 47% yield of aldehyde **2a**. From these results it can be inferred that, although the nitroxyl radical could be involved both as an oxidant for the alcoholic hydroxyl group and as reoxidant of the metal catalyst back to its original oxidation state, an oxygen atmosphere is crucial for the oxidation to take place at a reasonable rate. On the other hand, although PdNPs showed higher catalytic activity in the presence of TEMPO, copper would provide the selectivity to the bimetallic catalytic system. It can be proposed that TEMPO could be acting as reoxidant for reduced copper species in the catalyst, and that the fivefold excess of copper present in the bimetallic catalyst could passivate the high activity of palladium, leading to a catalytic system with high selectivity and good activity.

In summary, we have described herein a new heterogeneous Cu-PdNPs bimetallic catalyst that, in the presence of TEMPO as co-catalyst, can be used to selectively oxidize primary benzylic and allylic alcohols to the corresponding al-

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dehydes in good to excellent yields. The catalyst is readily prepared from commercial starting materials under mild conditions. In addition, the catalyst can be recovered and reused without apparent loss of activity. Further studies aimed at gaining a better understanding of the mechanism involved in the catalysis are underway.

All moisture-sensitive reactions for the preparation of metal nanoparticles were carried out under a nitrogen atmosphere. Anhydrous tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl. Other solvents were treated prior to use by standard methods. All starting materials were of the best available grade (Aldrich, Fluka, Merck) and were used without further purification. Commercially available copper(II) chloride dihydrate was dehydrated upon heating in an oven (150 °C, 45 min) prior to use for the preparation of CuNPs and Cu-PdNPs. Column chromatography was performed with Merck silica gel 60 (0.040–0.063 μm, 240–400 mesh). Reactions were monitored by thin-layer chromatography on silica gel plates (60F-254) visualized under UV light and/or by using 5% phosphomolybdic acid in ethanol. NMR spectra were recorded with a Bruker ARX-300 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (TMS) using the residual solvent resonance ($CDCl_3$: δ = 7.26 ppm for ^1H NMR, δ = 77.16 ppm for ^{13}C NMR). Multiplicities are abbreviated as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard HP-5890 GC/MS instrument equipped with a HP-5972 selective mass detector. FTIR spectra were obtained with a Nicolet-Nexus spectrophotometer. The purity of volatile compounds and the chromatographic analyses (GC) were determined with a Shimadzu GC-14B instrument equipped with a flame-ionization detector and a 30 m column (HP-5MS, 0.25mm, 0.25 μm), using nitrogen as carrier gas.

The freshly prepared catalyst was characterized by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Copper and palladium content in the supported catalysts were determined by atomic absorption spectroscopy (AAS). The heterogeneity of the catalytic process and the absence of metal leaching were determined by a hot filtration test followed by AAS analysis (see the Supporting Information).

Aerobic Oxidation of Alcohols 1a–o; Typical Procedure

Starting alcohol **1** (0.5 mmol) was added to a suspension of the Cu-PdNPs/bio-silica catalyst (80 mg) and TEMPO (5 mg, 0.03 mmol) in toluene (3 mL). The reaction flask was purged and filled with oxygen (1 atm) and heated at 110 °C overnight. The reaction mixture was then centrifuged and the supernatant was removed. The solvent was evaporated in vacuo, and the crude product was purified by flash column chromatography (silica gel; hexane/EtOAc). The recovered solid catalyst was washed with toluene (3 × 2 mL) and dried in an oven (100 °C, 4 h) for its reuse. The following known compounds included in Table 2 were characterized by comparison of their chromatographic and spectroscopic data (FTIR, ^1H NMR, ^{13}C NMR, and MS) with those described previously.

Benzaldehyde (2a)[22]

Yield: 52 mg (0.49 mmol, 98%); colorless oil.

IR (neat): 2820, 2738, 1703, 1204, 828, 746, 688 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 10.05 (s, 1 H), 7.93–7.90 (m, 2 H), 7.66 (m, 1 H), 7.58–7.55 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.4, 136.4, 134.4, 129.7, 129.0.

MS: *m*/*z* = 106 (100) $[M]^+$, 105 (94), 78 (16), 77 (93), 52 (10), 51 (37), 50 (18).

p-Chlorobenzaldehyde (2b)[23]

Yield: 53 mg (0.38 mmol, 75%); pale-yellow solid; mp 45–47 °C.

IR (KBr): 2860, 1693, 1209, 841, 817 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.99 (s, 1 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.3, 140.4, 134.2, 130.4, 128.9.

MS: *m*/*z* = 142 (23) $[M^++2]$, 141 (37) $[M^++1]$, 140 (73) $[M^+]$, 139 (100), 113 (21), 112 (14), 111 (65), 77 (32), 76 (17), 75 (52), 74 (30), 51 (36), 50 (53), 38 (11), 37 (10).

o-Chlorobenzaldehyde (2c)[8e]

Yield: 50 mg (0.36 mmol, 71%); pale-yellow oil.

IR (neat): 2869, 1698, 1593, 1268, 768 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 10.4 (s, 1 H), 7.88 (m, 1 H), 7.52 (m, 1 H), 7.42 (m, 1 H), 7.37 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.5, 137.8, 135.1, 132.5, 130.6, 129.3, 127.3.

MS: *m*/*z* = 142 (25) $[M^++2]$, 141 (38) $[M^++1]$, 140 (76) $[M^+]$, 139 (100), 113 (14), 111 (42), 77 (21), 76 (22), 75 (25), 74 (12), 51 (16), 50 (24).

p-Methoxybenzaldehyde (2d)[24]

Yield: 53 mg (0.39 mmol, 78%); colorless oil.

IR (neat): 2841, 1698, 1684, 1601, 1261, 1151 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.86 (s, 1 H), 7.81 (d, *J* = 8.8 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.8, 164.6, 131.9, 129.9, 114.3, 55.6.

MS: *m*/*z* = 136 (75) $[M^+]$, 135 (100), 107 (19), 92 (20), 77 (38), 65 (13), 64 (12), 63 (12), 51 (10), 39 (13).

o-Methoxybenzaldehyde (2e)[25]

Yield: 52 mg (0.38 mmol, 76%); pale-yellow solid; mp 35–37 °C.

IR (KBr): 2846, 1689, 1601, 1247, 759 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 10.40 (s, 1 H), 7.75 (d, *J* = 3.9 Hz, 1 H), 7.48 (t, *J* = 8.4 Hz, 1 H), 6.94 (m, 2 H), 3.84 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.5, 161.6, 135.8, 128.2, 124.6, 120.4, 111.5, 55.4.

MS: *m*/*z* = 136 (100) $[M^+]$, 135 (54), 121 (15), 119 (27), 118 (25), 107 (13), 105 (18), 104 (22), 92 (22), 91 (14), 90 (15), 79 (17), 78 (23), 77 (56), 76 (29), 65 (22), 64 (11), 63 (15), 51 (15), 50 (13), 39 (18), 28 (13), 18 (14).

p-Hydroxybenzaldehyde (2f)[26]

Yield: 60 mg (0.49 mmol, 99%); yellow solid; mp 113–116 °C.

IR (KBr): 3171, 1669, 1604, 1291, 1164 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.61 (s, 1 H), 7.60 (d, *J* = 8.3 Hz, 2 H), 6.73 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.8, 164.2, 130.1, 128.0, 115.9.

MS: *m*/*z* = 122 (93) $[M^+]$, 121 (100), 93 (41), 65 (42), 39 (30).

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m-Hydroxybenzaldehyde (2g)[27]

Yield: 49 mg (0.40 mmol, 80%); pale-yellow solid; mp 100–103 °C.

IR (KBr): 3219, 1673, 1584, 1287 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.94 (s, 1 H), 7.43 (m, 2 H), 7.32 (m, 1 H), 7.13 (m, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 192.8, 156.6, 137.8, 130.4, 123.6, 122.3, 114.8.

MS: *m*/*z* = 122 (100) [M$^+$], 121 (88), 93 (50), 66 (10), 65 (44), 39 (32).

o-Hydroxybenzaldehyde (2h)[26]

Yield: 60 mg (0.49 mmol, 99%); colorless oil.

IR (neat): 3189, 1665, 1581, 1279, 767 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.80 (s, 1 H), 7.72 (d, *J* = 9.1 Hz, 1 H), 7.51 (m, 1 H), 7.15 (m, 1 H), 6.61 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 196.5, 161.6, 136.9, 133.7, 120.7, 119.8, 117.5.

MS: *m*/*z* = 122 (100) [M$^+$], 121 (93), 104 (16), 93 (24), 76 (25), 66 (14), 65 (41), 63 (12), 50 (11), 39 (41), 38 (11).

p-Dimethylaminobenzaldehyde (2i)[28]

Yield: 51 mg (0.34 mmol, 67%); yellow solid; mp 72–75 °C.

IR (KBr): 2909, 1678, 1606, 1169 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.70 (s, 1 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 6.64 (d, *J* = 8.4 Hz, 2 H), 3.00 (s, 6 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 190.1, 154.3, 131.9, 125.1, 111.0, 40.0.

MS: *m*/*z* = 149 (85) [M$^+$], 148 (100), 77 (13), 42 (11).

p-Methylbenzaldehyde (2j)[23]

Yield: 48 mg (0.40 mmol, 90%); colorless oil.

IR (neat): 2827, 2734, 1702, 1608, 1169, 810 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.97 (s, 1 H), 7.78 (d, *J* = 7.9 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 2.44 (s, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 191.6, 145.1, 133.8, 129.5, 129.3, 21.5.

MS: *m*/*z* = 120 (91) [M$^+$], 119 (96), 92 (11), 91 (100), 65 (29), 63 (14), 51 (10), 39 (19).

1-Naphthaldehyde (2k)[29]

Yield: 76 mg (0.49 mmol, 99%); pale-yellow oil.

IR (neat): 3051, 2726, 1688, 1170, 1056, 803, 772 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 10.38 (s, 1 H), 9.26 (d, *J* = 8.6 Hz, 1 H), 8.08 (d, *J* = 8.2 Hz, 1 H), 7.96 (dd, *J* = 7.1, 1.1 Hz, 1 H), 7.91 (d, *J* = 8.2 Hz, 1 H), 7.69 (t, *J* = 7.2 Hz, 1 H), 7.60 (q, *J* = 7.2 Hz, 2 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 193.6, 136.8, 135.4, 133.8, 131.4, 130.6, 129.1, 128.5, 127.0, 124.9.

MS: *m*/*z* = 157 (12) [M$^+$+1], 156 (100) [M$^+$], 155 (59), 128 (79), 127 (79), 126 (16), 77 (13), 75 (10), 51 (11).

Cinnamaldehyde (2l)[23]

Yield: 54 mg (0.41 mmol, 81%); yellow oil.

IR (neat): 3062, 2814, 1678, 1627, 1124, 689 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.68 (d, *J* = 7.7 Hz, 1 H), 7.55 (dd, *J* = 6.4, 2.7 Hz, 2 H), 7.45 (d, *J* = 16.1 Hz, 1 H), 7.41 (dd, *J* = 5.1, 1.6 Hz, 3 H), 6.70 (dd, *J* = 15.9, 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 193.7, 152.8, 134.0, 131.3, 129.1, 128.6, 128.5.

MS: *m*/*z* = 132 (74) [M$^+$], 131 (100), 104 (29), 103 (57), 78 (32), 77 (42), 51 (32), 50 (13).

2-Thiophenecarboxaldehyde (2m)[23]

Yield: 47 mg (0.42 mmol, 83%); light-brown oil.

IR (neat): 3106, 2837, 1674, 1420, 1216, 1047, 768, 730, 665 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.92 (s, 1 H), 7.70 (m, 2 H), 7.19 (t, *J* = 4.3 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 183.1, 144.0, 136.5, 135.2, 128.4.

MS: *m*/*z* = 113 (10) [M$^+$+1], 112 (91) [M$^+$], 111 (100), 83 (12), 58 (10), 45 (15), 39 (29), 51 (32), 50 (13).

Decanal (2n)[28]

Yield: 14 mg (0.09 mmol, 18%); colorless oil.

IR (neat): 2967, 2928, 1730, 1467 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.74 (t, *J* = 1.8 Hz, 1 H), 2.39 (td, *J* = 7.4, 1.8 Hz, 2 H), 1.68–1.56 (m, 2 H), 1.37–1.19 (m, 12 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 202.9, 43.9, 31.8, 29.4, 29.3, 29.2, 29.1, 22.6, 22.1, 14.1.

MS: *m*/*z* = 156 (1) [M$^+$], 112 (22), 110 (12), 96 (15), 95 (17), 84 (16), 83 (28), 82 (33), 81 (22), 71 (34), 70 (47), 69 (30), 68 (34), 67 (26), 57 (62), 56 (43), 55 (62), 54 (15), 45 (17), 44 (54), 43 (100), 42 (30), 41 (81), 39 (19), 29 (51), 27 (34).

Cyclohexanone (2o)[25]

Yield: 5 mg (0.05 mmol, 9%); colorless oil.

IR (neat): 2941, 1716, 1222 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.29 (t, *J* =6.8 Hz, 4 H), 1.85–1.79 (m, 4 H), 1.70–1.64 (m, 2 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 212.1, 41.9, 26.9, 24.9.

MS: *m*/*z* = 98 (92) [M$^+$], 83 (16), 70 (27), 69 (34), 56 (10), 55 (100), 42 (54), 41 (31), 39 (24), 28 (23), 27 (14).

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Supporting Information

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