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Chemoselective control of hydrogenation among aromatic carbonyl and benzyl alcohol derivatives using Pd/C(en) catalyst

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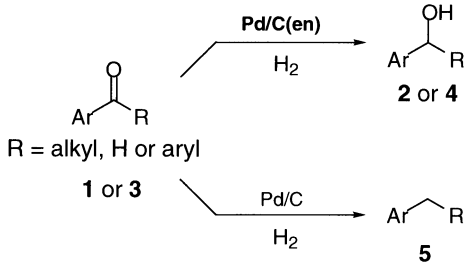
Abstract—The hydrogenolysis of aromatic ketones and aldehydes quite smoothly give the corresponding methylene compounds via the formation of the intermediary benzyl alcohols in the presence of Pd/C as a catalyst. Therefore, it is extremely difficult to isolate the intermediary benzyl alcohol selectively. This paper describes a mild and chemoselective hydrogenation method of an aromatic carbonyl compound to benzyl alcohol using the 10% Pd/C(en) catalyst and its application to the chemoselective deacetoxylation reaction at the benzylic position in the presence of the benzyl alcohol functionality within the molecule.

The development of new catalytic reductions of ketones and aldehydes to alcohols using highly specific catalysts has been a challenging area in organic synthetic chemistry.[1] Although the transformation of ketones and aldehydes to alcohols has been mainly accomplished by stoichiometric metal hydride reagents,[2] the reaction is usually accompanied with formation of a large quantity of metal sludge. Catalytic hydrogenation or a hydrogen transfer method of carbonyl compounds using a homogeneous catalyst[3–5] has been studied extensively during recent years because of the low cost and no formation of metal sludge. Despite the recent progress in the homogeneous hydrogenation process, there are few hydrogenation methods of ketones and aldehydes to alcohols using a heterogeneous catalyst.[6,7] Industry in particular requires high yield, high selectivity, sufficient productivity, low cost, safety, operational simplicity and environmental consciousness among other technical factors.[8] In this context, the general advantages associated with a heterogeneous catalyst for hydrogenolysis are the favorable and 'greener' properties such as low cost, operational simplicity, easy separation, production of no sludge and possible recycling. Although palladium on carbon (Pd/C), which is the most frequently available heterogeneous hydrogenation catalyst in academia and industrial production, does not easily catalyze the hydrogenation of non-aromatic carbonyls, aromatic carbonyls (**1** or **3**) are quite smoothly hydrogenolyzed to methylene compounds (**5**) via the formation of the intermediary benzyl alcohols (**2** or **4**) (Scheme 1).[1,9] Therefore, it is extremely difficult to isolate the intermediary benzyl alcohol (**2** or **4**) selectively when hydrogenating aromatic carbonyl compounds using the Pd/C catalyst.[10] While Ram and Spicer reported a transfer hydrogenation method for the partial reduction of aromatic carbonyls using 10% Pd/C and ammonium formate, the main reduction tends to be accompanied with a reductive amination reaction with nucleophilic ammonia released from the ammonium formate.[7a] Therefore, the development of heterogeneous palladium catalysts with excellent chemoselectivity between aromatic carbonyls and the intermediary benzyl alcohols is highly desirable because of the potential practical benefits of the methodology.

We have recently developed a heterogeneous Pd–ethylenediamine [Pd/C(en)] complex catalyst that possesses less catalytic activity than commercial Pd/C because the coordinated ethylenediamine (en) acts as a mild catalyst-poison. Pd/C(en) selectively catalyzed the hydrogenation of various reducible functional groups such as olefin, benzyl ester, azide and nitro groups, without the hydrogenolysis of the O-benzyl, N-Cbz and O-TBS protective groups and epoxides.[11] During the course of our studies intended at extension of the applicability of the Pd/C(en) complexes as catalysts for selective hydrogenation, we found that no hydrogenolysis of benzyl alcohols (**2** or **4**) to methylene compounds (**5**) occurred when the 10% Pd/C(en) catalyst



Scheme 1.

Keywords: heterogeneous catalysis; 10% Pd/C(en); selective hydrogenation; aromatic carbonyl; deacetoxylation.

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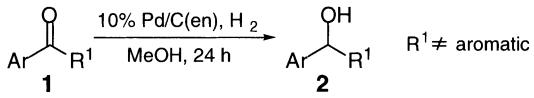
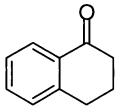
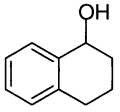
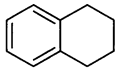
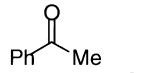
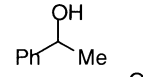
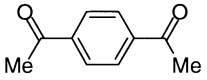
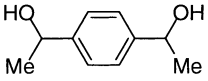
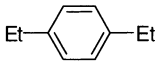
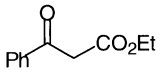
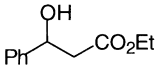
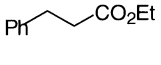
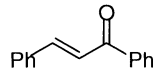
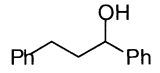
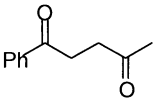
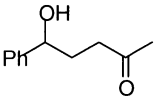
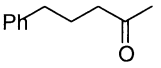
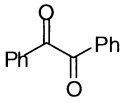
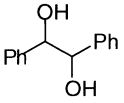
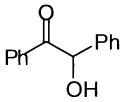
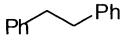
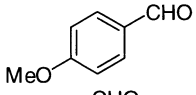
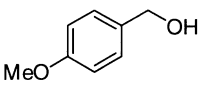
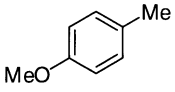
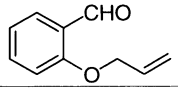
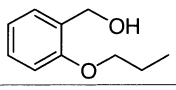
Table 1. 10% Pd/C(en)-catalyzed partial hydrogenation of *mono*-aromatic ketones and aldehydes to benzyl alcohols



	Substrate (**1**)	Product (**2**)	Yield (%)[a]	Product (**5**) upon the use of commercial 10% Pd/C[b,c]	
a			91		(92%)
b			93	—[d]	
c			97		(72%)[e]
d			98		(95%)
e			99	—[d]	
f			91		(76%)[e]
g			95[f]	—[d]	
h		**2g**	97[g]		(96%)
i			94		(84%)[e]
j			99	—[d]	

The reaction was carried out using 0.5 mmol of the substrate (**1**) in MeOH (2 mL) with 10% Pd/C(en) (10% of the weight of the substrate) under a hydrogen atmosphere (balloon) for 24 h.

[a] Isolated yield.

[b] Upon the use of commercial 10% Pd/C instead of 10%Pd/C(en), the hydrogenolysis of **1** readily proceeded to give fully hydrogenolyzed methylene products.

[c] The numbers in parentheses indicate isolated yield.

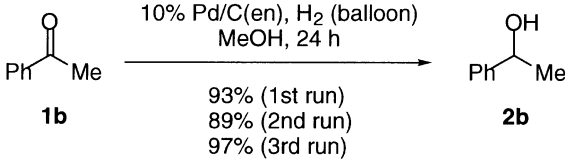
[d] Not tested.

[e] Because of the volatile nature, relatively lower yields were observed.

[f] *meso*/*dl*=71/29.

[g] *meso*/*dl*=76/24.

used and, consequently, it can be applied to selective hydrogenation of aromatic ketones and aldehydes to benzyl alcohols.[12] Moreover, we also found that through acetylation of benzyl alcohols, benzyl alcohols (**2** or **4**) were easily transformed to methylene compounds (**5**) by the hydrogenolysis using the 10% Pd/C(en) catalyst although it did not catalyze the hydrogenolysis of benzyl alcohols (**2** or **4**) directly. Therefore, we applied this reaction to the selective dehydroxylation (deacetoxylation) of the benzyl alcohol functionality coexisting with the carbonyl or other benzyl alcohol functionality (such as benzoin, aldol product and so on).



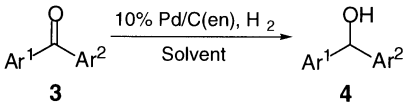
Scheme 2.

Herein we report detailed discussion of highly selective hydrogenation of aromatic ketones and aldehydes to benzyl alcohols using the 10% Pd/C(en) catalyst and its application to the deacetoxylation.

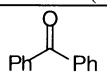
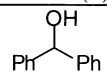
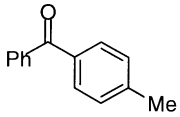
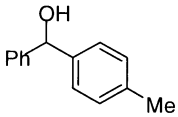
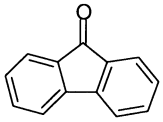
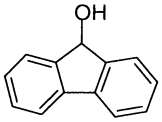
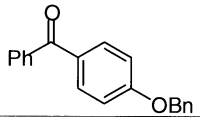
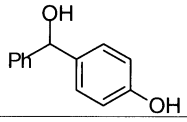
1. Results and discussion

First, the hydrogenations of *mono*-aromatic ketones (**1a–h**) and aldehydes (**1i–j**) were carried out smoothly using the

Table 2. 10% Pd/C(en)-catalyzed partial hydrogenation of *bis*-aromatic ketones to benzyl alcohols



3 **4**

Run		Substrate (**3**)	Solvent	t (h)	Product (**4**)[a]	Yield (%)[b]
1	**a**		MeOH	3		96
2			MeOH	17		80[c]
3			THF	6		100
4			THF	17		99
5	**b**		THF	16		97
6	**c**		THF	16		100
7	**d**		THF	24		91[d]

The reaction was carried out using 0.5 mmol of the substrate (**3**) in MeOH or THF (2 mL) with 10% Pd/C(en) (10% of the weight of the substrate) under a hydrogen atmosphere (balloon) for the given reaction time.

[a] Upon the use of commercial 5 or 10% Pd/C instead of 10%Pd/C(en), the hydrogenolysis of **3** readily proceeded to give fully hydrogenolyzed methylene products in excellent yields.

[b] Isolated yield.

[c] The yield of **4** was determined by ^{1}H NMR.

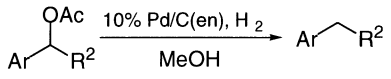
[d] An *O*-benzyl protective group of 4-(benzyloxy)benzophenone (**3d**), which possesses electron withdrawing benzoyl group at the *p*-position, did not survive under these conditions (see Ref. 11).

10% Pd/C(en) catalyst (10% of the weight of the substrate) in MeOH under hydrogen atmosphere (balloon) for 24 h to provide partially reduced benzyl alcohols (**2a–j**) in excellent isolated yield without formation of the fully hydrogenolyzed methylene compounds (**5**) (Table 1). The reactions of the *mono*-aromatic ketones and aldehydes (**1**) were very clean, and no chromatographic separation was required to obtain spectrally pure products. However, upon using a commercial 10% Pd/C catalyst such selective hydrogenation failed, and fully hydrogenolyzed methylene compounds (**5**) were easily formed as the sole product (Table 1).

The hydrogenation of olefin and ketone (**1e**) or aldehyde (**1j**) functionalities simultaneously occurred to give the corresponding saturated benzyl alcohol derivative (**2e** or **2j**) in 99% yield, respectively. No competitive hydrogenation of aliphatic ketone of 1-phenyl-1,4-pentadione (**1f**) possessing aromatic and aliphatic ketones within the molecule was observed.[13] The hydrogenation of ketones of benzil (**1g**) and benzoin (**1h**) proceeded chemoselectively, and hydrobenzoin (**2g**) was obtained in 95 and 97% yield, respectively (*meso*/*dl*=71/29 and 76/24). The partial hydrogenation of the aldehydes of **1i** and **1j** occurred also in analogy with aromatic ketones to give the corresponding benzyl alcohol derivatives (**2i** and **2j**), in 94 and 99% yield, respectively. The catalyst could be recovered almost quantitatively after simple filtration and it could be reused. The recovered 10% Pd/C(en) was also effective in the second and third reactions, and the yields and selectivity of the second and third runs were comparable to those of the first run (Scheme 2).

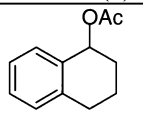
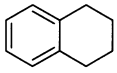
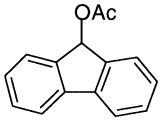
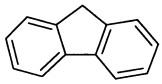
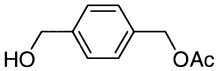
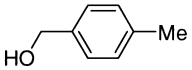
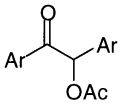
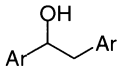
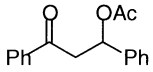
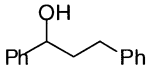
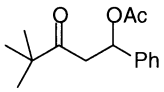
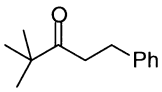
Next, we examined selective hydrogenation of *bis*-aromatic ketones (**3**) using the 10% Pd/C(en) catalyst (Table 2). Although the hydrogenation of benzophenone (**3a**) using the 10% Pd/C(en) catalyst in MeOH for 3 h gave benzhydrol (**4a**) in 96% yield (run 1), the resulting products from **3a** were contaminated by a significant quantity of an over-reduction product (20%), diphenylmethane, by the continuous hydrogenation for 17 h (run 2). We considered that a search for optimal reaction conditions needed to establish a general chemoselective hydrogenation method of *bis*-aromatic ketones (**3**). We recently reported a chemoselective method for the hydrogenation using a combination of the Pd/C(en) catalyst and THF as a solvent.[11c] THF is extremely important as a solvent to achieve dramatic suppressive effect toward the hydrogenolysis of the epoxides. Similarly, the use of THF as a solvent in the hydrogenation of **3a** resulted in the highly selective hydrogenation of the *bis*-aromatic ketone function to give **4a** in 100 or 99% yield regardless of its reaction time (6 or 17 h) (run 3 and 4).[12] To explore the scope of this method, the hydrogenation of some other *bis*-aromatic ketones (**3b–d**) in THF was investigated (Table 2). The results shown in runs 5–7 demonstrate that the reaction can be carried out using either acyclic or cyclic *bis*-aromatic ketones. The chemoselectivity of the hydrogenation could be attributable to the difference in the coordination affinity between longer-conjugated aromatic carbo-nyls and benzyl alcohols to

Table 3. 10% Pd/C(en)-catalyzed deacetoxylation



6 **5**

R^2 = alkyl or aromatic

	Substrate (**6**)	t (h)	Product (**5**)	Yield (%)[a]
k		3		91
l		3		95
m		1		76[b]
n	 Ar = Ph	12		98
o	Ar = 4-Tol	16		100
p	Ar = 4-MeOPh	24		98
q	Ar = 2-pyridyl	24		89
r		6		94
s		1.5		99

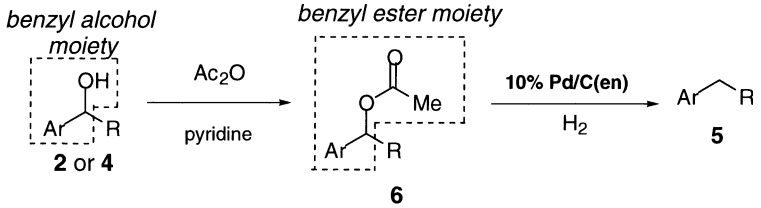
The reaction was carried out using 0.5 mmol of the substrate (**6**) in MeOH (2 mL) with 10% Pd/C(en) (10% of the weight of the substrate) under a hydrogen atmosphere (balloon) for the given reaction time.

[a] Isolated yield.

[b] Because of the low boiling point of the product, the quantitative conversion was observed by ^{1}H NMR in CD_3OD.

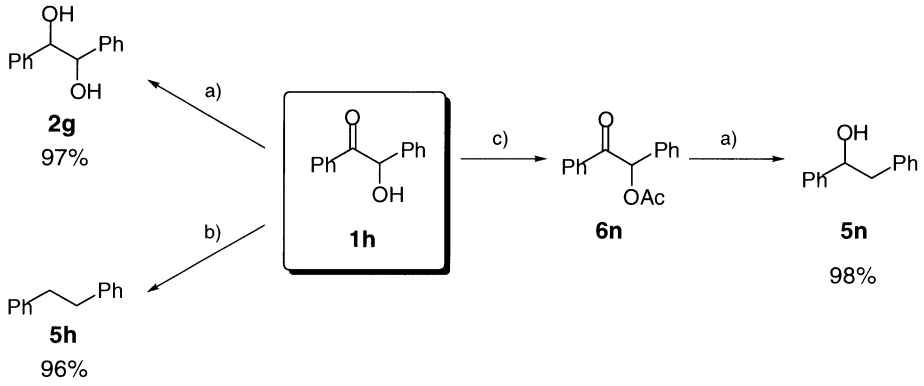
ethylenediamine-coordinated palladium. In the Pd/C(en) catalyst, the original affinity of palladium to the π-electron should be reasonably reduced by ethylenediamine.[11a]

It is worth noting that the acetate (**6**) prepared by the acetylation of the corresponding benzyl alcohol (**2** or **4**) according to the conventional method[14] was readily converted to methylene compound (**5**) by the hydrogenolysis using even the 10% Pd/C(en) catalyst while the mother benzyl alcohol (**2** or **4**) was not hydrogenolyzed directly under the same conditions as mentioned above. The hydrogenolysis of acetates (**6k–s**) using the 10% Pd/C(en) catalyst in methanol smoothly proceeded to give the corresponding methylene compounds (**5k–s**) in excellent yields, respectively (Table 3). In the case of **6m** possessing both alcohol and acetoxy functionalities on the benzylic position within the molecule, the selective deacetoxylation occurred without hydrogenolysis of the benzyl alcohol function to give **5m** in 76% yield. When acetyl benzoin derivatives (**6n–p**) and α-pyridoin (**6q**) were hydrogenated, the selective deacetoxylation and hydrogenation of the ketones functionalities to benzyl alcohols occurred to give **5n–q** in



2 or **4** **6** **5**

Scheme 3.



Scheme 4. (a) 10% Pd/C(en), H_2, MeOH; (b) 10% Pd/C, H_2 MeOH; (c) Ac_2O, pyridine.

89–100% yields, respectively. **6r** and **6s** were obtained by acetylation of β-hydroxy ketones which were accessible from the corresponding silyl enol ethers and benzaldehydes with $TiCl_4$ by the Mukaiyama aldol reaction.[15] The ketone and the acetoxy functionalities of **6r** were successfully and selectively transformed under these conditions to give the benzyl alcohol (**5r**) in 94% yield. The reaction tolerates the aliphatic ketone of **6s** to give the corresponding ketone (**5s**, 99%). It is certain that the conversion of the benzyl alcohol moiety of **2** or **4** into the benzylic acetate (acetic acid benzyl ester) moiety of **6**, which is easily hydrogenolyzed using the Pd/C(en) catalyst,[11] accounts for the easy deacetoxylation (Scheme 3). These results demonstrated that our methodology enabled the diverse and selective transformations of molecules possessing plural benzyl alcohols and/or aromatic ketones. For example, although the hydrogenation of benzoin (**1h**) using a commercial 10% Pd/C gave only diphenylethane (**5h**), the use of the 10% Pd/C(en) catalyst selectively gave hydrobenzoin (**2g**), and 1,2-diphenylethanol (**5n**) was obtained using the acetyl-protected benzoin (**6n**) as the starting material (Scheme 4).

2. Conclusion

We have developed a mild and chemoselective hydrogenation method of aromatic ketones and aldehydes to benzyl alcohols using the heterogeneous 10% Pd/C(en) catalyst. The reaction is applicable to the chemoselective deacetoxylation reaction. The reaction is general for an acetoxy function on the benzyl position and tolerates the benzyl alcohol. The outstanding chemoselectivity and the general utility of this method make it an attractive new tool for the organic chemist.

3. Experimental

3.1. General

^1H NMR and ^{13}C NMR spectroscopy: JEOL JNM GX-270 and JEOL JNM EX-400 (^1H NMR: 270 and 400 MHz; ^{13}C NMR: 100 MHz); MS: JMS-SX 102A; TLC (thin-layer chromatography): 0.25 mm Silica Gel 60 F_{254} plates (Art 5715, Merck) using UV light as a visualizing agent and 7% ethanolic phosphomolybdic acid or *p*-anisaldehyde solution, and heat as developing agent; column chromatography: Silica Gel 60 (230–400 mesh, Merck). Melting points were determined on a Yanagimoto melting point apparatus and were uncorrected. MeOH of HPLC grade was used without further purification. THF was distilled from sodium benzophenone ketyl immediately prior to use. 10% Pd/C was purchased from Aldrich. All substrates (**1** and **3**) were commercially available and used without further purification. Aldol products were prepared exactly according to the previously outlined procedure.[15]

3.2. The preparation of 10% Pd/C(en) catalyst[11a,b,12]

A suspension of commercial 10% Pd/C (300 mg, 0.28 mmol of Pd metal) and ethylenediamine (1.2 mL, 19.74 mmol) in methanol (10 mL) under a rigorous argon atmosphere to prevent ignition (Pd/C is highly pyrophoric) was stirred for 48 h at ambient temperature. The solid was filtered, washed vigorously with methanol (20 mL×5) and ether (20 mL×2), and dried under a vacuum pump at room temperature for 48 h to give the 10% Pd/C(en) anal. found: C, 74.10; H, 2.64; N, 3.01.

3.3. 10% Pd/C(en)-catalyzed partial hydrogenation of *mono*-aromatic ketones and aldehyde to benzyl alcohols (Table 1)

After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the substrate **1** (0.5 mmol), 10% Pd/C(en) or 10% Pd/C (10% of the weight of **1**, 1.1~2.0 mol%) in MeOH (2 mL) was hydrogenated at ambient pressure (balloon) and temperature (ca. 20°C) for 24 h. The reaction mixture was filtered using a celite cake or a membrane filter (MILLIPORE, LCR13-LG) and the filtrate was concentrated in vacuo. The quantitative conversion of **1** was confirmed by ^1H NMR of the crude mixture in $CDCl_3$. In this reaction no chromatographic separation was required to obtain spectrally pure products. The products, α-tetralol (**2a**), 1-phenylethanol (**2b**), ethyl mandelate (**2d**), hydrobenzoin (**2g**), 4-methoxybenzyl alcohol (**2i**), tetralin® (**5a** [**5k**]), 1,4-diethylbenzene (**5c**), ethyl hydrocinnamate (**5d**), bibenzyl (**5h**) and 4-methylanisole (**5i**), agreed with the analytical data of commercially available samples.

3.3.1. 1,4-Bis(1-hydroxyethyl)benzene (2c). The product **2c** was afforded in 97% yield from **1c** as a white solid. Mp 78°C; ^1H NMR (400 MHz, rt, $CDCl_3$): δ=1.51, 1.80

(each d, J=6.4 Hz, 3H×2), 4.91 (q, J=6.4 Hz, 2H), 7.37 (s, 4H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=25.1, 70.1, 125.5, 145.0; HRMS (EI) calcd for $C_{10}H_{14}O_2$ [M^+] 166.0994, found 166.0987.

3.3.2. 1,3-Diphenylpropanol (2e). The product **2e** was afforded in 99% yield from **1e** as a colorless oil. ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=1.85 (brs, 1H), 2.04–2.15 (m, 2H), 2.63–2.75 (m, 2H), 4.65–4.73 (m, 1H), 7.16–7.36 (m, 10H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=32.1, 40.5, 73.9, 125.9, 125.90, 127.6, 128.4, 128.4, 128.5, 141.8, 144.6; HRMS (EI) calcd for $C_{15}H_{16}O$ [M^+] 212.1201, found 212.1191.

3.3.3. 5-Hydroxy-5-phenyl-2-pentanone (2f). The product **2f** was afforded in 91% yield from **1f** as a colorless oil. ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.03 (t, J=6.8 Hz, 2H), 2.14 (s, 3H), 2.41 (d, J=3.9 Hz, 1H), 2.56 (t, J=6.8 Hz, 2H), 4.73 (q, J=3.9 Hz, 1H), 7.26–7.35 (m, 5H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=29.7, 32.5, 39.5, 72.9, 125.5, 127.2, 128.1, 144.1, 209.5; HRMS (EI) calcd for $C_{11}H_{14}O_2$ [M^+] 178.0994, found 178.0989.

3.3.4. 2-Propoxybenzyl alcohol (2j). The product **2j** was afforded in 99% yield from **1j** as a colorless oil. ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=1.06 (t, J=6.9 Hz, 3H), 1.84 (hex, J=6.9 Hz, 2H), 2.39 (t, J=6.7 Hz, 1H), 3.99 (t, J=6.9 Hz, 2H), 4.70 (d, J=6.7 Hz, 2H), 6.87 (d, J=8.3 Hz, 1H), 6.92 (d, J=7.5 Hz, 1H), 7.23–7.27 (m, 2H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=10.6, 22.6, 62.4, 69.5, 111.1, 120.5, 128.7, 128.9, 129.2, 157.0; HRMS (EI) calcd for $C_{10}H_{14}O_2$ [M^+] 166.0994, found 166.0987.

3.3.5. 5-Phenyl-2-pentanone (5f). The product was afforded in 76% yield from **1f** as a colorless oil. ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=1.91 (pen, J=7.5 Hz, 2H), 2.12 (s, 3H), 2.44 (t, J=7.5 Hz, 2H), 2.62 (t, J=7.5 Hz, 2H), 7.16–7.30 (m, 5H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ= 25.2, 29.9, 35.0, 42.8, 125.9, 128.4, 128.4, 141.5, 208.7; HRMS (EI) calcd for $C_{11}H_{14}O$ [M^+] 162.1045, found 162.1047.

3.4. 10% Pd/C(en)-catalyzed partial hydrogenation of *bis*-aromatic ketones to benzyl alcohols (Table 2)

After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the substrate **3** (0.5 mmol), 10% Pd/C(en) (10% of the weight of **3**, 1.7∼2.7 mol%) in MeOH or THF (2 mL) was hydrogenated at ambient pressure (balloon) and temperature (ca. 20°C) for the given reaction time. The reaction mixture was filtered using a celite cake or a membrane filter (MILLIPORE, LCR13-LG) and the filtrate was concentrated in vacuo. The quantitative conversion of **3** was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$. In this reaction no chromatographic separation was required to obtain spectrally pure products. The products, benzhydrol (**4a**), 4-methylbenzhydrol (**4b**) and 9-hydroxyfluorene (**4c**), agreed with the analytical data of commercially available samples.

3.4.1. 4-Hydroxy benzhydrol (4d). The product **4d** was afforded in 91% yield from **3d** as a white solid. Mp 168°C; ^{1}H NMR (400 MHz, rt, CD_3OD): δ=5.68 (s, 1H), 6.71 (d, J=2.4 Hz, 2H), 7.13–7.34 (m, 7H); ^{13}C NMR (100 MHz, rt, CD_3OD): δ=76.7, 116.0, 127.6, 128.0, 129.1, 136.9, 146.2, 157.7; MS (EI) m/z (%) 220 (33) [M^+]; anal. calcd for $C_{13}H_{12}O_2$: C 77.98, H 6.04; found: C 77.90, H 6.16.

3.5. 10% Pd/C(en)-catalyzed deacetoxylation (Table 3)

Benzyl alcohol derivatives were acetylated using acetic anhydride in pyridine.[14] After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the substrate **6** (0.5 mmol), 10% Pd/C(en) (10% of the weight of **6**, 1.7∼2.5 mol%) in MeOH (2 mL) was hydrogenated at ambient pressure (balloon) and temperature (ca. 20°C) for the given reaction time. The reaction mixture was filtered using a celite cake or a membrane filter (MILLIPORE, LCR13-LG) and the filtrate was poured into saturated aqueous $NaHCO_3$ (15 mL) and extracted with ethyl acetate (15 mL). The organic layer was washed with water (15 mL) and brine (15 mL) and dried over anhydrous magnesium sulfate. After filtration, the solvents were evaporated to afford **5**. The products, tetralin® (**5k** [**5a**]), fluorene (**5l**) and 4-methylbenzylalcohol (**5m**), agreed with the analytical data of commercially available samples.

3.5.1. 1-*O*-Acetyl-1,2,3,4-tetrahydronaphthol (6k). ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=1.74–2.01 (m, 4H), 2.06 (s, 3H), 2.68–2.90 (m, 2H), 5.98–6.01 (m, 1H), 7.08–7.28 (m, 4H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=18.7, 21.4, 28.9, 29.0, 69.9, 126.0, 128.0, 129.0, 129.3, 134.5, 137.8, 170.6; HRMS (EI) calcd for $C_{12}H_{14}O_2$ [M^+] 190.0994, found 190.1000.

3.5.2. 9-Acetoxyfluorene (6l). Mp 67°C; ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.19 (s, 3H), 6.80 (s, 1H), 7.30 (t, J=7.8 Hz, 2H), 7.41 (t, J=7.3 Hz, 2H), 7.55 (d, J= 7.3 Hz, 2H), 7.67 (d, J=7.8 Hz, 2H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=21.2, 75.1, 120.0, 125.9, 127.8, 129.5, 141.0, 142.0, 171.7; HRMS (EI) calcd for $C_{15}H_{12}O_2$ [M^+] 224.0837, found 224.0842.

3.5.3. 4-Acetoxymethyl benzyl alcohol (6m). ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.15 (s, 3H), 4.75 (s, 2H), 5.15 (s, 1H), 7.32–7.41 (m, 4H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=21.3, 65.2, 66.4, 127.4, 128.8, 135.6, 141.3, 171.2; HRMS (EI) calcd for $C_{10}H_{12}O_3$ [M^+] 180.0786, found 180.0790.

3.5.4. *O*-Acetylbenzoin (6n). Mp 81°C; ^{1}H NMR (270 MHz, rt, $CDCl_3$): δ=2.21 (s, 3H), 6.86 (s, 1H), 7.26–7.54 (m, 8H), 7.93 (d, J=7.3 Hz, 2H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=20.7, 77.6, 128.6, 128.7, 128.7, 129.1, 129.3, 133.4, 133.6, 134.6, 170.4, 193.7; MS (EI) m/z (%) 254 (2) [M^+]; anal. calcd for $C_{16}H_{14}O_3$: C 75.58, H 5.55; found: C 75.45, H 5.68.

3.5.5. *O*-Acetyl-4,4′-dimethybenzoin (6o). ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.19, 2.30, 2.33 (each s, 3H×3), 6.83 (s, 1H), 7.15–7.18 (m, 4H), 7.34 (d, J=8.1 Hz, 2H), 7.83 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=20.6, 21.0, 21.4, 77.3, 128.5, 128.7, 129.1, 129.6, 130.8, 132.0, 139.0, 144.1, 170.3, 193.1; HRMS (EI) calcd for $C_{18}H_{18}O_3$ [M^+] 282.1256, found 282.1265.

3.5.6. *O*-Acetyl-4,4′-dimmethoxybenzoin (*O*-acetylanisoin) (6p). Mp 96°C; ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.19, 3.77, 3.82 (each s, 3H×3), 6.80 (s, 1H), 6.85–6.89 (m, 4H), 7.38 (d, *J*=9.0 Hz, 2H), 7.91 (d, *J*=9.0 Hz, 2H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=20.8, 55.3, 55.4, 77.1, 113.9, 114.6, 126.1, 127.5, 130.2, 131.1, 160.3, 163.7, 170.5, 192.1; MS (EI) *m/z* (%) 314 (5) [M^+]; anal. calcd for $C_{18}H_{18}O_5$: C 68.78, H 5.77; found: C 68.77, H 5.84.

3.5.7. *O*-Acetyl-α-pyridoin (6q). Mp 122°C; ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.24 (s, 3H), 7.18–7.21 (m, 1H), 7.38–7.41 (m, 1H), 7.57 (s, 1H), 7.62 (d, *J*=7.8 Hz, 1H), 7.71 (dt, *J*=2.0 and 7.8 Hz, 1H), 7.80 (dt, *J*=1.5 and 7.8 Hz, 1H), 8.09 (d, *J*=7.8 Hz, 1H), 8.52 (d, *J*=3.9 Hz, 1H), 8.58 (d, *J*=3.9 Hz, 1H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=20.6, 78.0, 122.7, 123.2, 124.4, 127.2, 136.8, 136.8, 148.8, 149.5, 151.6, 154.5, 170.2, 193.4; MS (EI) *m/z* (%) 256 (1) [M^+]; anal. calcd for $C_{14}H_{12}N_2O_3$: C 65.62, H 4.72, N 10.93; found: C 65.62, H 4.72, N 10.89.

3.5.8. 3-Acetoxy-3-phenylpropiophenone (6r). ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.02 (s, 3H), 3.32 (dd, *J*=4.9 and 16.7 Hz, 1H), 3.71 (dd, *J*=8.3 and 16.7 Hz, 1H), 6.40 (dd, *J*=4.9 and 8.3 Hz, 1H), 7.25–7.58 (m, 8H), 7.93 (d, *J*=7.3 Hz, 2H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=21.0, 45.1, 71.9, 126.5, 128.1, 128.2, 128.6, 128.6, 133.3, 136.7, 140.0, 169.8, 196.1; HRMS (EI) calcd for $C_{17}H_{16}O_3$ [M^+] 268.1092, found 268.1099.

3.5.9. 1-Acetoxy-4,4-dimethyl-1-phenyl-3-pentanone (6s). ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=1.09 (s, 9H), 2.02 (s, 3H), 2.82 (dd, *J*=4.9 and 16.9 Hz, 1H), 3.20 (dd, *J*=8.3 and 16.9 Hz, 1H), 6.21 (dd, *J*=4.9 and 8.3 Hz, 1H), 7.26–7.35 (m, 5H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=21.0, 25.9, 43.2, 44.2, 72.1, 126.5, 128.1, 128.5, 140.2, 169.7, 211.6; HRMS (EI) calcd for $C_{15}H_{20}O_3$ [M^+] 248.1412, found 248.1414.

3.5.10. 1,2-Diphenylethanol (5n). The product **5n** was afforded in 98% yield from **6n** as a white crystal. Mp 65°C; ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=1.93 (d, *J*=2.4 Hz, 1H), 2.99 (dd, *J*=8.3 and 13.4 Hz, 1H), 3.05 (dd, *J*=4.9 and 13.4 Hz, 1H), 4.88–4.93 (m, 1H), 7.19–7.38 (m, 10H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=46.1, 75.3, 125.9, 126.6, 127.6, 128.4, 128.5, 129.5, 138.0, 143.8; MS (EI) *m/z* (%) 198 (3) [M^+]; anal. calcd for $C_{14}H_{14}O$: C 84.81, H 7.12; found: C 84.62, H 7.22.

3.5.11. 1,2-Di-4-methylphenylethanol (5o). The product **5o** was afforded in 100% yield from **6o** as a white crystal. Mp 67°C; ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.32 and 2.35 (each s, 3H×2), 2.92 (dd, *J*=8.6 and 13.7 Hz, 1H), 2.99 (dd, *J*=4.6 and 13.7 Hz, 1H), 4.82 (dd, *J*=4.6 and 8.6 Hz, 1H), 7.08–7.10 (m, 4H), 7.15 and 7.25 (each d, *J*=7.8 Hz, 2H×2); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=21.0, 21.1, 45.6, 75.2, 125.8, 129.1, 129.2, 129.3, 135.0, 136.1, 137.2, 140.9; MS (EI) *m/z* (%) 226 (1) [M^+]; anal. calcd for $C_{16}H_{18}O$: C 84.91, H 8.02; found: C 84.79, H 8.18.

3.5.12. 1,2-Di-4-methoxyphenylethanol (5p). The product **5p** was afforded in 98% yield from **6p** as a white crystal. Mp 113°C; ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=2.92–2.94 (m, 2H), 3.77 and 3.79 (each s, 3H×2), 4.79 (t, *J*=6.6 Hz, 1H), 6.82 (d, *J*=8.8 Hz, 2H), 6.86 (d, *J*=8.8 Hz, 2H), 7.07 and 7.25 (each d, *J*=8.8 Hz, 2H×2); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=45.1, 55.2, 55.2, 75.0, 113.7, 113.9, 127.1, 130.1, 130.4, 136.0, 158.3, 159.0; MS (EI or FAB) *m/z* (%) no [M^+] ([M^++1]) peak; anal. calcd for $C_{16}H_{18}O_3$: C 74.40, H 7.02; found: C 74.45, H 7.09.

3.5.13. 1,2-Di-2-pyridylethanol (5q). The product **5q** was afforded in 99% yield from **6q** as a light brown oil. ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=3.14 (dd, *J*=9.1 and 16.0 Hz, 1H), 3.36 (dd, *J*=3.2 and 16.0 Hz, 1H), 5.22 (dd, *J*=3.2 and 9.1 Hz, 1H), 7.14–7.17 (m, 3H), 7.50 (d, *J*=7.8 Hz, 1H), 7.59 (dt, *J*=2.0 and 7.8 Hz, 1H), 7.66 (dt, *J*=1.5 and 7.8 Hz, 1H), 8.49–8.53 (m, 2H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=44.4, 73.5, 120.3, 121.6, 122.0, 124.0, 136.6, 136.7, 148.3, 148.4, 159.3, 162.4; HRMS (EI) calcd for $C_{12}H_{12}N_2O$ [M^+] 200.0950, found 200.0946.

3.5.14. 1,3-Diphenylpropanol (5r). The product **5r** agreed with the analytical data of **2e**.

3.5.15. 1-Phenyl-4,4-dimethyl-3-pentanone (5s). The product **5s** was afforded in 99% yield from **6s** as a pale yellow oil. ^{1}H NMR (400 MHz, rt, $CDCl_3$): δ=1.11 (s, 9H), 2.78–2.88 (m, 4H), 7.19–7.29 (m, 5H); ^{13}C NMR (100 MHz, rt, $CDCl_3$): δ=26.3, 30.1, 38.5, 44.1, 126.0, 128.4, 128.4, 141.6, 214.9; HRMS (EI) calcd for $C_{13}H_{18}O$ [M^+] 190.1358, found 190.1355.

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