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Chemoselective Oxidation of Alcohols by a H_2O_2–Pt Black System under Organic Solvent- and Halide-Free Conditions

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: Environmentally benign oxidation of allylic alcohols by platinum black catalyst with aqueous hydrogen peroxide to give the corresponding α,β-unsaturated carbonyl compounds in high yield is presented. Reactions are carried out under organic solvent- and halide-free conditions. The platinum black catalyst is commercially available and is found to be reusable at least seven times before significant loss of catalytic activity. The operation is very simple, even in a hectogram-scale synthesis, and gives corresponding carbonyl compounds in over 90% yield. The effective oxidation of benzyl and secondary alcohols are also described.

Keywords: alcohols · green chemistry · oxidation · peroxides · platinum

Introduction

Chemoselective oxidation has been widely used in organic synthetic chemistry, especially in the laboratory[1] and in chemical manufacturing,[2] as well as in regio- and stereo-selective oxidation.[3] One of the central issues in chemoselective oxidation is the discrimination between olefinic double bonds and hydroxy groups. In particular, oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds has long been of interest. At the time of the realisation concerning the necessity for the effective organic synthesis of α,β-unsaturated carbonyl compounds from allylic alcohols, the discovery by Ball, Goodwin, and Morton of almost quantitative conversion of Vitamin A into retinene by an active manganese compound in 1948 was already well-known.[4,5a] Then, various oxidants with high chemoselectivity, such as MnO_2 and CrO_3, were developed and are frequently used in organic synthesis until now.[5] However, the atom efficiency of these oxidants is low, and they generate chemical waste containing polluting heavy metals and deoxidized compounds to get the same amount of useful oxidized compounds. As a part of the green concept, toxic and/or flammable organic solvents are being replaced by alternative non-toxic media, or the reactions are carried out without the use of any solvent.[6,7]

Hydrogen peroxide (H_2O_2) is a cheap and environmentally benign oxidant because the atom efficiency is excellent and water is theoretically the sole co-product.[8] However, its oxidizing ability is quite weak and requires catalytic activation. The first example of catalytic activity for oxidation of alcohols with tungsten and molybdenum peroxo complexes was reported by Jacobson et al. in 1979.[9] Since then, many kinds of metal catalysts, such as Mo, Ru, Pd, Pt, W, and their polyoxo compounds, which accelerate the oxidation of alcohols with H_2O_2, have been reported.[10] All of them, however, suffer from the necessity for a high concentration or a large excess of H_2O_2, or the use of an organic solvent, or the requirement of long reaction times. An efficient procedure for alcohol oxidation reactions with aqueous 3–30% H_2O_2 with tungsten catalyst under organic solvent-free conditions have also appeared;[11,12] however, these processes have disadvantages regarding the reuse and recycling of catalysts. Air and/or dioxygen are environmentally ideal oxidants owing to their low cost and high abundance. A huge amount of O_2 oxidation of alcohols with heterogeneous catalysts has been reported and energetically investigated.[11] Although the oxidation of cinnamyl alcohol to cinnamaldehyde with O_2 (or air) has been reported, organic solvents and/or bases are necessary to achieve high yield and selectivity.[13,14a–j] The oxidation of cinnamyl alcohols under organic solvent- and base-free conditions was reported, but

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Table 1. Oxidation of allylic alcohols with aqueous solution of H_2O_2.[a]

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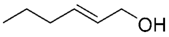
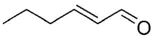
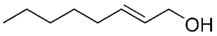
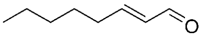
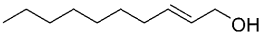
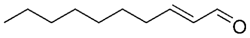
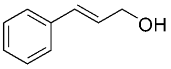
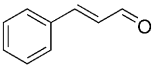
1			81
2			93
3			90
4[c]			94[d]
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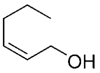
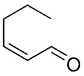
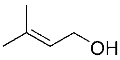
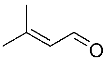
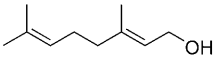
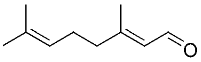
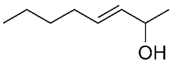
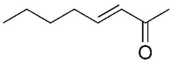
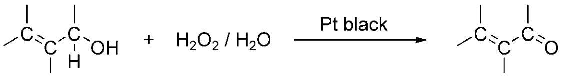
6[e]			84
7			91
8[f]			97
9[f,g]			97

[a] Unless otherwise stated, the reaction was run using alcohol (10 mmol), 5% H_2O_2, and Pt black in a 100:110:1 molar ratio at 90°C for 3 h. [b] Determined by GC analysis. Based on alcohol charged. [c] Reaction was run using alcohol (100 g, 0.745 mol). [d] Yield of isolated product after distillation. [e] Alcohol/H_2O_2/Pt = 33:100:1. [f] Alcohol/H_2O_2/Pt = 33:67:1. [g] 30% H_2O_2 was used.

the yield of cinnamaldehyde was lower than that obtained with organic solvent and/or base conditions.[14i,j] To our knowledge, there have been few reports of the completely chemoselective alcohol oxidation of allylic alcohols with H_2O_2 under organic solvent-free conditions and using recyclable catalysts.[15] In general, epoxidation of allylic alcohols proceeds easily with H_2O_2, and few α,β-unsaturated carbonyl compounds have been observed.[16]

We have recently reported a practical method for the synthesis of α,β-unsaturated carbonyl compounds from the selective oxidation of allylic alcohols using aqueous H_2O_2 catalyzed with easily recyclable platinum black under halide and organic solvent-free conditions with high yield and selectivity [Eq. (1)].[17] This method demonstrated a convenient H_2O_2 oxidation process using platinum black as a catalyst.



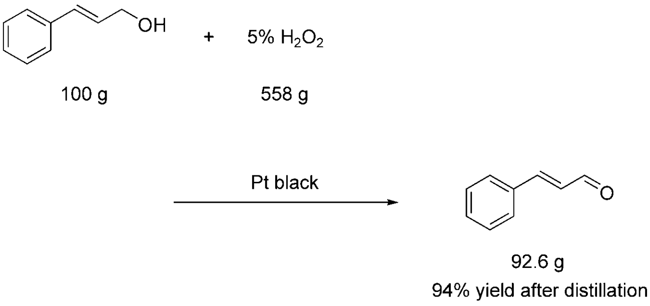
(1)

Herein, we report the detailed H_2O_2 oxidation experiment of allylic and benzyl alcohols with platinum black, and the application of this procedure to the oxidation of secondary alcohols. Although H_2O_2 is generally decomposed in the presence of trace transition metals,[1b] Pt black works surprisingly well as a catalyst in the present method. The application of various supported metals and platinum complexes instead of Pt black is also discussed.

Results and Discussion

The oxidation of cinnamyl alcohol in a hectogram-scale synthesis successfully provided a corresponding cinnamaldehyde, as shown in Scheme 1. The operation is very simple; cinnamyl alcohol (100 g) and a 0.01 molar amount of Pt black were stirred in the open air at 90°C for 10 min, and then a 1.1 molar amount of aqueous H_2O_2 (5%) was slowly added dropwise. The mixture was stirred at 90°C for 3 h to give cinnamaldehyde in a 94% yield (92.6 g). Interestingly, an epoxidized compound of cinnamyl alcohol was not observed. Without the use of H_2O_2 (under an air atmosphere), cinnamaldehyde was obtained in only <10% yield.[18]

This chemoselective-oxidation system is applicable to various allylic alcohols to yield α,β-unsaturated carbonyl compounds. These results are shown in Table 1.[19,20] Primary allylic alcohols were chemoselectively oxidized to form the corresponding α,β-unsaturated aldehydes (Table 1, entries 1–8). Secondary allylic alcohol also underwent oxidation by H_2O_2 to give the corresponding α,β-unsaturated ketone (Table 1, entry 9). The oxidation of allylic alcohols having a terminal double bond, like 1-hexen-3-ol, did not proceed at all. While the oxidation of *trans*-2-hexen-1-ol with H_2O_2 catalyzed by Pt black resulted in the formation of *trans*-2-hexenal in an 81% yield (Table 1, entry 1), the addition of 1-hexen-3-ol or 1-hexene retarded the oxidation of *trans*-2-hexen-1-ol (*trans*-2-hexenal in 43% yield with 1-hexen-3-ol and 26% yield with 1-hexene). This result indicates that the strong coordination of terminal olefin to Pt^0



Scheme 1. Hectogram-scale oxidation of cinnamyl alcohol

Abstract in Japanese:

過酸化水素と白金黒触媒を用いることで環境にやさしく且つ化学選択的にアリルアルコールを不飽和カルボニル化合物に酸化する反応を見出した。本手法は100 gスケールに対応可能なうえ、７回触媒の回収再使用を行っても９０％以上の収率で目的物を与えた。

largely retards the alcohol oxidation of allylic alcohols.[21] The oxidation of cinnamyl alcohol was completely stopped by the removal of Pt black from the reaction solution. This result indicates that any Pt species that may have leached into the reaction solution were not active homogeneous catalysts.

Pt black catalyst was easily reused in the oxidation of cinnamyl alcohol. After the first alcohol oxidation, the catalyst was filtrated and washed with water, then reused for the second reaction. Seven cycles of oxidation could be catalyzed by the reused Pt black without any decrease in its catalytic activity. Yields of each reaction were mostly over 90%, as shown in Table 2.

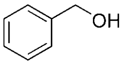
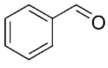
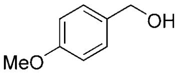
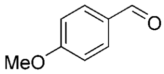
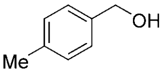
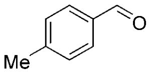
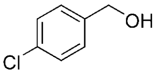
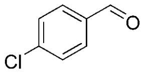
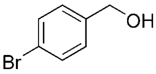
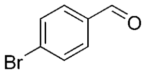
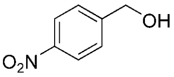
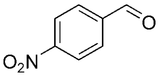
Table 2. Oxidation of cinnamyl alcohol with H_2O_2 catalyzed by Pt black.[a]

Reused number	1	2	3	4	5	6	7
% yield of cinnamaldehyde[b]	96	92	90	90	91	97	97

[a] Reaction was run using cinnamyl alcohol (10 mmol), 5% H_2O_2, and Pt black in a 30:33:1 molar ratio at 90°C for 5 h. [b] Determined by GC analysis. Based on alcohol charged.

Benzyl alcohols were also oxidized at 90°C with H_2O_2 (30%) in the presence of Pt black to give the corresponding benzaldehydes in good yields (Table 3). Although the selective oxidation of benzyl alcohols to benzaldehydes is not easy,[10f,12b] Pt black successfully catalyzed the selective oxidation of benzyl alcohols to generate the corresponding benzaldehyde in high yields, with little corresponding carboxylic acid produced. Benzyl alcohol, *p*-methoxy benzyl alcohol, and *p*-methyl benzyl alcohol were successfully oxidized to give the corresponding aldehydes in 86–95% yields (Table 3, entries 1–3). Oxidation of *p*-chloro, *p*-bromo-, and *p*-nitrobenzyl alcohol are more difficult, in this order (Table 3, entries 4–6). The reactivity of *p*-substituted benzyl alcohols is dependent on the electric properties of the substituents. Competitive experiments using a 1:1 mixture of benzyl alcohol and *p*-substituted benzyl alcohol in the presence of Pt black and H_2O_2 (5%) at 25°C, showed that the Hammett linear free-energy relationship, $\sigma+$, gave a good correlation with $\rho = -0.44$ (Table 4 and Figure 1). The correlation with $\sigma+$ implies a direct interaction through resonance between the substituent and the reaction site. This relatively small negative ρ value suggests the formation of a partial positive charge on the benzyl α-carbon in the transition state of the oxidation path. A similar substituent effect, $\rho = -0.31$, has been observed with benzyl alcohol oxidation of H_2O_2 with tungsten catalysts.[12c]

Table 3. Oxidation of benzyl alcohols with aqueous solution of H_2O_2.[a]

Entry	Alcohol	Carbonyl compound	Yield[b] [%]
1			90
2			86
3			95
4[c]			75
5[c]			63
6[c]			18

[a] Unless otherwise stated, the reaction was run using alcohol (10 mmol), 30% H_2O_2, and Pt black in a 100:110:1 molar ratio at 90°C for 2 h. [b] Determined by GC analysis. Based on alcohol charged. [c] Alcohol (2 mmol) was used.

Table 4. Competitive oxidation of *p*-substituted benzyl alcohols[a]

Entry	*p*-Substituents (X)	Yield of *p*-X [%][b]	Yield of *p*-H [%][b]
1	Me	6.2	4.4
2	Cl	6.2	8.6
3	OMe	10	4.5
4	NO_2	1.2	2.6

[a] Reaction was run using a 1:1 mixture of benzyl alcohol and *p*-substituted benzyl alcohols (2.4 mmol), 5% H_2O_2, and Pt black in a 100:110:1 molar ratio at 25°C for 0.5 h. [b] Determined by GC analysis. Based on alcohol charged.

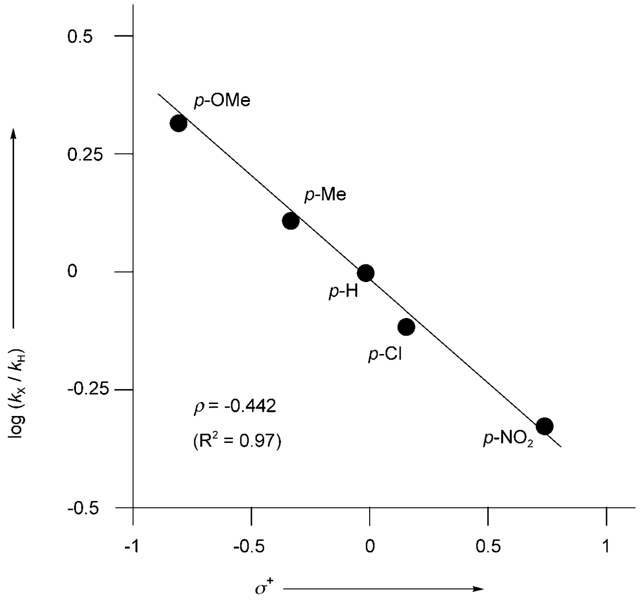
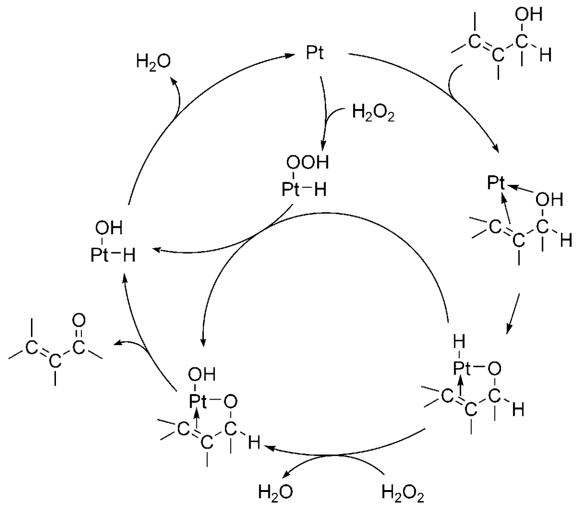


Figure 1. Hammett plot for oxidation of *p*-substituted benzyl alcohols, *p*-$XC_6H_4CH_2OH$.

The proposed mechanism of this catalytic chemoselective oxidation is shown in Scheme 2. The oxidative addition of a hydroxy group can function by the coordination of allylic alcohol to Pt^0, to form Pt^{II} hydridoalkoxide.[22] The Pt^{II} complex may be attacked by H_2O_2 or the Pt^{II} hydridoperoxide



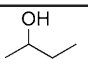
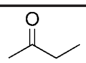
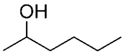
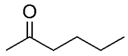
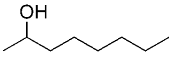
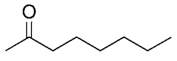
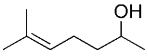
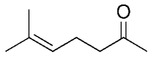
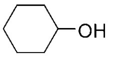
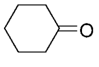
Scheme 2. Proposed mechanism of the chemoselective oxidation.

complex generated from the reaction of Pt^0 with H_2O_2, to form Pt^{II} bisalkoxide; the α,β-unsaturated carbonyl compound can then be liberated by β-elimination. Pt^0 can be regenerated through reductive elimination.

Various supported metals (a 0.03 molar amount of metal with a metal/support ratio of 0.05) also worked as catalysts in the oxidation of cinnamyl alcohol (catalyst, yield of cinnamaldehyde: Pt/C, 80%; Pd/C, 43%; Rh/C, 40%; Ru/C, 70%; Re/C, 16%). However, $[Pt(PPh_3)_4]$, $[Pt(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphanyl)ethane), $[PtCl_2(PPh_3)_2]$, PtO_2, and $Na_2[Pt(OH)_6]$ did not work as catalysts (yields of cinnamaldehyde were 0–4%).[23]

Furthermore, the oxidation of not only allylic alcohols but also secondary alcohols, resulted in the formation of ketones in this catalytic system (Table 5). Hectogram-scale oxidation of 2-octanol was performed with a 1.1 molar amount of aqueous H_2O_2 (30%) in the presence a 0.01 molar amount of Pt black at 90 °C for 4–5 h to give a 91% yield of 2-octanone (89.6 g) (Table 5, entry 3). The chemoselective oxidation of alcohols containing a double bond at the not-allylic position proceeded smoothly, resulting in the formation of the corresponding ketone (Table 5, entry 5). 1-Octen-4-ol, containing a terminal double bond, did not oxidize in this catalytic system. Pt black catalyst was also easily reused in the oxidation of 2-octanol for seven cycles, with the yield of each reaction being primarily over 97%.

Table 5. Oxidation of secondary alcohols with aqueous solution of H_2O_2.[a]

Entry	Alcohol	Carbonyl compound	Yield[b] [%]
1			> 99
2			94
3[c]			91[d]
4			> 99
5[e]			80
6			94

[a] Unless otherwise stated, the reaction was run using alcohol (10 mmol), 30% H_2O_2, and Pt black in a 100:110:1 molar ratio at 90 °C for 2 h. [b] Determined by GC analysis. Based on alcohol charged. [c] Reaction was run using 100 g of alcohol (0.768 mol). [d] Yield of isolated product after distillation. [e] Alcohol/H_2O_2/Pt = 100:300:1. Reaction for 5 h.

Conclusions

We have shown a facile chemoselective catalytic oxidation of allylic alcohols to form α,β-unsaturated carbonyl compounds in high yields. In particular, the use of H_2O_2 as oxidant under organic solvent and halide-free conditions allows the development of green sustainable chemical processes. This catalytic system is applicable to various allylic alcohols, benzyl alcohols, and secondary alcohols to provide the corresponding carbonyl compounds with good selectivity. Only alcohols having a terminal olefin cannot be oxidized in this catalytic system, which shows that the strong coordination of a terminal olefin to Pt^0 largely retards the alcohol oxidation of allylic alcohols. The Pt black catalyst is easily reusable with simple manipulation. This green process is straightforward, effective, and environmentally conscious, meeting the requirements of modern organic synthesis.

Experimental Section

General

^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a JEOL winLambda-500 NMR spectrometers. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^1H, and relative to residual $CHCl_3$ at 77.0 ppm for ^{13}C unless otherwise noted. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-17 A using a TC-FFAP column (0.25 mm × 30 m, GL Sciences Inc.).

All the materials obtained from commercial suppliers were used as received without further purification. Cinnamyl alcohol, *trans*-2-hexen-1-ol, trans-2-octen-1-ol, *trans*-2-decen-1-ol, *cis*-2-hexen-1-ol, 3-methyl-2-buten-1-ol, geraniol, *trans*-3-octen-2-ol, benzyl alcohol, 1-hexen-3-ol, 1-octen-4-ol, 2-hexanol, and 2-octanol were obtained from Tokyo Chemical Industry Co., Ltd. 2-Butanol and cyclohexanol were obtained from Wako Pure Chemicals Ind., Ltd. Hydrogen peroxide (30%) was obtained from Kanto Chemical Co., Inc. 6-Methyl-5-hepten-2-ol was obtained from Aldrich Chemical Co. Platinum black, $[Pt(dba)_2]$, and various supported metals were obtained from N.E. CHEMCAT Co. $[Pt(PPh_3)_4]$, $[PtCl_2(PPh_3)_2]$, and PtO_2 were obtained from STREM. $Na_2[Pt(OH)_6]$ was obtained from Alfa.

Syntheses

Hectogram-scale oxidation of cinnamyl alcohol: A 1-liter round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was slowly charged with cinnamyl alcohol (100 g, 0.745 mol) and Pt black (1.45 g, 7.45 mmol). After the mixture was vigorously stirred at 90 °C for 10 min, an aqueous solution of H_2O_2 (5%, 558 g, 0.820 mol) was added dropwise. The mixture was heated at 90 °C for 3 h, and then cooled to room temperature. The organic phase was separated and washed with saturated aqueous solution of $Na_2S_2O_3$ (50 mL). After distillation, cinnamaldehyde (92.6 g, 0.701 mol, 94%) was obtained as a colorless liquid.

Hectogram-scale oxidation of 2-octanol: A 0.5-liter round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was slowly charged with 2-octanol (100 g, 0.768 mol) and Pt black (1.50 g, 7.69 mmol). After the mixture was vigorously stirred at 90 °C for 10 min, an aqueous solution of H_2O_2 (30 %, 95.8 g, 0.845 mol) was added dropwise over the course of 1 h. The mixture was heated at 90 °C for 4 h, and then cooled to room temperature. The organic phase was separated and washed with a saturated aqueous solution of $Na_2S_2O_3$ (50 mL). After distillation, 2-octanone (89.6 g, 0.699 mol, 91 %) was obtained as a colorless liquid.

General procedure for oxidation of allylic alcohol: A round-bottomed flask (30 mL) equipped with a magnetic stirring bar and a reflux condenser was charged with allylic alcohol (10.0 mmol) and Pt black (19.5 mg, 0.100 mmol). After the mixture was vigorously stirred at 90 °C for 10 min, an aqueous solution of H_2O_2 (5 %, 7.48 g, 11.0 mmol) was added dropwise over the course of 1 h. The mixture was heated at 90 °C for 2 h, and then cooled to room temperature. The organic phase was separated and washed with a saturated aqueous solution of $Na_2S_2O_3$ (2.5 mL). The conversion and yield were determined by GC with an internal standard (4 mmol), typically biphenyl.

General procedure for oxidation of benzyl alcohol: A round-bottomed flask (30 mL) equipped with a magnetic stirring bar and a reflux condenser was charged with benzyl alcohol (10.0 mmol) and Pt black (19.5 mg, 0.100 mmol). After the mixture was vigorously stirred at 90 °C for 10 min, an aqueous solution of H_2O_2 (30 %, 1.25 g, 11.0 mmol) was added dropwise over the course of 30 min. The mixture was heated at 90 °C for 2 h, and then cooled to room temperature. The organic phase was separated and washed with a saturated aqueous solution of $Na_2S_2O_3$ (2.5 mL). The conversion and yield were determined by GC with an internal standard (4 mmol), typically biphenyl.

Hammett plot for oxidation of *p*-substituted benzyl alcohols: A round-bottomed flask (30 mL) equipped with a magnetic stirring bar and a reflux condenser was charged with *p*-substituted benzyl alcohol (2.4 mmol), benzyl alcohol (2.4 mmol), and Pt black (4.7 mg, 0.02 mmol). After the mixture was vigorously stirred at 25 °C for 5 min, an aqueous solution of H_2O_2 (5 %, 1.80 g, 2.6 mmol) was added dropwise over the course of 30 min, and Pt black was then separated by filtration. The conversion of substrates was kept below 10 %. The disappearance of the substrates was monitored by GC analysis with an internal standard (4 mmol), typically biphenyl. Initial relative rates ($\log(k_X/k_H)$) were 0.35 (*p*-OMe), 0.15 (*p*-Me), 0.00 (*p*-H), −0.14 (*p*-Cl), and −0.34 (*p*-NO_2).

Oxidation of cinnamyl alcohol with various supported metals: A round-bottomed flask (30 mL) equipped with a magnetic stirring bar and a reflux condenser was charged with cinnamyl alcohol (1.342 g, 10.0 mmol) and supported metal (0.30 mmol). After the mixture was vigorously stirred at 90 °C for 10 min, an aqueous solution of H_2O_2 (5 %, 7.48 g, 11.0 mmol) was added dropwise. The mixture was heated at 90 °C for 5 h, and then cooled to room temperature. The organic phase was separated and washed with a saturated aqueous solution of $Na_2S_2O_3$ (2.5 mL). The conversion and yield were determined by GC with an internal standard (4 mmol), typically biphenyl.

Oxidation of cinnamyl alcohol with platinum complexes: A round-bottomed flask (30 mL) equipped with a magnetic stirring bar and a reflux condenser was charged with a cinnamyl alcohol (1.342 g, 10.0 mmol) and platinum complex (0.30 mmol). After the mixture was vigorously stirred at 90 °C for 10 min, an aqueous solution of H_2O_2 (5 %, 7.48 g, 11.0 mmol) was added dropwise. The mixture was heated at 90 °C for 5 h, and then cooled to room temperature. The organic phase was separated and washed with a saturated aqueous solution of $Na_2S_2O_3$ (2.5 mL). The conversion and yield were determined by GC with an internal standard (4 mmol), typically biphenyl.

General procedure for oxidation of secondary alcohol: A round-bottomed flask (30 mL) equipped with a magnetic stirring bar and a reflux condenser was charged with secondary alcohol (10.0 mmol) and Pt black (19.5 mg, 0.100 mmol). After the mixture was vigorously stirred at 90 °C for 10 min, an aqueous solution of H_2O_2 (30 %, 1.25 g, 11.0 mmol) was added dropwise over the course of 1 h. The mixture was heated at 90 °C for 1 h, and then cooled to room temperature. The organic phase was separated and washed with a saturated aqueous solution of $Na_2S_2O_3$ (2.5 mL). The conversion and yield were determined by GC analysis with an internal standard (4 mmol), typically biphenyl.

Cinnamaldehyde:[24] b.p.: 104 °C/7 mmHg; ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta =$ 6.52 (dd, $^3J(H,H) = 15.9$, 7.6 Hz, 1H), 7.21–7.26 (m, 4H), 7.34–7.37 (m, 2H), 9.51 ppm (d, 1H, $^3J(H,H) = 7.6$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 128.4$, 129.2, 131.1, 133.9, 152.8, 193.5 ppm.

***trans*-2-Hexenal**:[25] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 0.96$ (t, $^3J(H,H) = 8.8$ Hz, 3H), 1.49–1.57 (m, 2H), 2.27–2.34 (m, 2H), 6.11 (ddt, $^3J(H,H) = 1.4$, 7.9, 15.6 Hz, 1H), 6.84 (dt, $^3J(H,H) = 6.7$, 15.6 Hz, 1H), 9.50 ppm (d, $^3J(H,H) = 7.9$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 13.6$, 21.1, 34.6, 133.0, 158.5, 193.9 ppm.

***trans*-2-Octenal**:[26] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 0.91$ (t, $^3J(H,H) = 7.8$ Hz, 3H), 1.29–1.37 (m, 4H), 1.47–1.55 (m, 2H), 2.30–2.37 (m, 2H), 6.12 (ddt, $^3J(H,H) = 1.4$, 6.9, 15.4 Hz, 1H), 6.86 (dt, $^3J(H,H) =$ 6.7, 15.4 Hz, 1H), 9.51 ppm (d, $^3J(H,H) = 6.9$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 13.9$, 22.3, 27.5, 31.3, 32.6, 132.9, 158.8, 193.9 ppm.

***trans*-2-Decenal**:[27] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 0.89$ (t, $^3J(H,H) = 6.7$ Hz, 3H), 1.25–1.35 (m, 8H), 1.45–1.53 (m, 2H) , 2.30–2.37 (m, 2H), 6.12 (dd, $^3J(H,H) = 7.9$, 15.6 Hz, 1H), 6.86 (dt, $^3J(H,H) = 6.9$, 15.6 Hz, 1H), 9.51 ppm (d, $^3J(H,H) = 7.9$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 14.0$, 22.6, 27.9, 29.0, 29.1, 31.7, 32.7, 132.9, 158.7, 193.8 ppm.

***cis*-2-Hexenal**:[28] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 0.94$ (t, $^3J(H,H) = 6.2$ Hz, 3H), 1.46–1.58 (m, 2H), 2.18–2.23 (m, 2H), 5.90–6.05 (m, 1H), 6.60 (dt, $^3J(H,H) = 6.7$, 15.4 Hz, 1H), 10.05 ppm (d, $^3J(H,H) =$ 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 13.6$, 21.0, 34.6, 130.0, 153.0, 191.1 ppm.

3-Methyl-2-butenal:[29] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 1.99$ (s, 3H), 2.18 (s, 3H), 5.89 (dq, $^3J(H,H) = 6.7$, 2.4 Hz, 1H), 9.96 ppm (d, $^3J(H,H) = 6.7$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 18.9$, 28.1, 128.1, 160.3, 190.8 ppm.

***trans*-3,7-Dimethylocta-2,6-dienal (Geranial)**:[30] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 1.61$ (s, 3H), 1.69 (s, 3H), 2.17 (s, 3H), 2.17–2.26 (m, 4H), 5.00–5.10 (m, 1H), 5.88 (d, $^3J(H,H) = 8.5$ Hz, 1H), 10.00 ppm (d, $^3J(H,H) = 8.5$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta =$ 17.7, 17.8, 25.7, 25.8, 40.6, 122.5, 127.4, 132.9, 163.9, 191.3 ppm.

***trans*-3-Octen-2-one**:[31] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 0.91$ (t, $^3J(H,H) = 7.0$ Hz, 3H), 1.35 (tq, $^3J(H,H) = 7.0$, 7.2 Hz, 2H), 1.43–1.47 (m, 2H), 2.10–2.25 (m, 5H), 6.07 (dt, $^3J(H,H) = 1.5$, 15.8 Hz, 1H), 6.80 (dt, $^3J(H,H) = 6.7$, 15.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 13.8$, 22.2, 26.7, 30.2, 32.1, 131.3, 148.5, 198.6 ppm.

Benzaldehyde:[12c] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 7.53$ (dd, $^3J(H,H) = 7.5$, 7.8 Hz, 2H), 7.63 (dt, $^3J(H,H) = 1.5$, 7.5 Hz, 1H), 7.88 (dd, $^3J(H,H) = 1.5$, 7.8 Hz, 2H), 10.03 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 128.9$, 129.7, 134.4, 136.4, 192.3 ppm.

2-Butanone:[32] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 1.05$ (t, $^3J(H,H) = 7.6$ Hz, 3H), 2.14 (s, 3H), 2.46 ppm (q, $^3J(H,H) = 7.6$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 7.8$, 29.4, 36.8, 209.2 ppm.

2-Hexanone:[33] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 0.90$ (t, $^3J(H,H) = 7.5$ Hz, 3H), 1.32 (tq, $^3J(H,H) = 7.3$, 7.5 Hz, 2H), 1.55 (sep, $^3J(H,H) = 7.3$ Hz, 2H), 2.13 (s, 3H), 2.43 ppm (t, $^3J(H,H) = 7.3$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 13.8$, 22.3, 26.0, 29.7, 43.5, 208.8 ppm.

2-Octanone:[31] b.p.: 173 °C; ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 0.88$ (t, $^3J(H,H) = 6.8$ Hz, 3H), 1.27–1.29 (m, 6H), 1.52–1.59 (m, 2H), 2.13 (s, 3H), 2.42 ppm (t, $^3J(H,H) = 7.4$ Hz, 2H), ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 13.9$, 22.4, 23.7, 28.7, 29.7, 31.5, 43.7, 209.2 ppm.

6-Methyl-5-hepten-2-one:[34] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 1.62$ (s, 3H), 1.68 (s, 3H), 2.14 (s, 3H), 2.25 (q, $^3J(H,H) = 7.3$ Hz, 2H), 2.45 (t, $^3J(H,H) = 7.3$ Hz, 2H), 5.00–5.08 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 17.6$, 22.6, 25.6, 29.7, 43.7, 122.7, 132.6, 208.3 ppm.

Cyclohexanone:[31] ^1H NMR (500 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 1.70$–1.75 (m, 2H), 1.85–1.93 (m, 4H), 2.34 ppm (t, $^3J(H,H) = 6.8$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 24.8$, 26.8, 41.7, 211.9 ppm.

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[1] a) R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**, pp. 350–357; b) M. Hudlicky, *Oxidation in Organic Chemistry*, ACS Monograph Ser. 186, American Chemical Society, Washington, DC, **1990**, pp. 114–163; c) G. Procter in *Comprehensive Organic Synthesis 1st ed., Vol. 7* (Eds.: B. M. Trost, I. Fleming, S. V. Ley), Academic Press, Oxford, **1991**, pp. 251–289, 305–327; d) J. March, *Advanced Organic Chemistry, 4th ed.*, Wiley, New York, **1992**; e) R. C. Larock, *Comprehensive Organic Transformations, 2nd ed.*, Wiley, New York, **1999**, pp. 1646–1650.

[2] a) G. Franz, R. A. Sheldon in *Ullmann's Encyclopedia of Industrial Chemistry, 5th ed., Vol. A18* (Eds.: B. Elvers, S. Hawkins, G. Schulz), VCH, Weinheim, **1991**, pp. 261–311; b) S. Caron, R. W. Dugger, S. G. Ruggeri, J. A. Ragan, D. H. B. Ripin, *Chem. Rev.* **2006**, *106*, 2943–2989.

[3] R. A. Sheldon, *CHEMTECH* **1991**, 566–576.

[4] S. Ball, T. W. Goodwin, R. A. Morton, *Biochem. J.* **1948**, *42*, 516–523.

[5] For review on alcohol oxidation with MnO_2, see: a) A. J. Fatiadi, *Synthesis* **1976**, 65–104; oxidation of allylic alcohol with CrO_2Cl_2, see: b) K. B. Sharpless, K. Akashi, *J. Am. Chem. Soc.* **1975**, *97*, 5927–5928; oxidation with DMSO-trifluoroacetic acid anhydride, see: c) K. Omura, A. K. Sharma, D. Swern, *J. Org. Chem.* **1976**, *41*, 957–962; oxidation with $(C_5H_5NH)_2Cr_2O_7$, see: d) E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1979**, *20*, 399–402.

[6] a) B. M. Trost, *Science* **1991**, *254*, 1471–1477; b) R. A. Sheldon, *Chem. Ind.* **1992**, 903–906.

[7] a) J. O. Metzger, *Angew. Chem.* **1998**, *110*, 3145–3148; *Angew. Chem. Int. Ed.* **1998**, *37*, 2975–2978; b) P. T. Anastas, J. C. Warner, *Green Chemistry, Theory and Practice*, Oxford University Press, New York, **1998**; c) W. M. Nelson in *Green Chemical Syntheses and Processes* (Eds.: P. T. Anastas, L. G. Heine, T. C. Williamson), American Chemical Society, Washington, DC, **2000**, pp. 313–328; d) M. Eissen, J. O. Metzger, E. Schmidt, U. Schneidewind, *Angew. Chem.* **2002**, *114*, 402–425; *Angew. Chem. Int. Ed.* **2002**, *41*, 414–436.

[8] a) G. Strukul, *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic Publishers, Netherland, **1992**; b) R. A. Sheldon, *Green Chem.* **2000**, *2*, G1-G4; c) P. T. Anastas, L. B. Bartlett, M. M. Kirchhoff, T. C. Williamson, *Catal. Today* **2000**, *55*, 11–22; d) R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* **2003**, 1977–1986; e) For international regulations, see regulations concerning the International Carriage of Dangerous Goods by Rail (RID), European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR).

[9] S. E. Jacobson, D. A. Muccigrosso, F. Mares, *J. Org. Chem.* **1979**, *44*, 921–924.

[10] a) B. M. Trost, Y. Masuyama, *Tetrahedron Lett.* **1984**, *25*, 173–176; b) O. Bortolini, V. Conte, F. Di Furia, G. Modena, *J. Org. Chem.* **1986**, *51*, 2661–2663; c) G. Barak, J. Dakka, Y. Sasson, *J. Org. Chem.* **1988**, *53*, 3553–3555; d) Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 3587–3593; e) R. Zennaro, F. Pinna, G. Strukul, H. Arzoumanian, *J. Mol. Catal.* **1991**, *70*, 269–275; f) C. Venturello, M. Gambaro, *J. Org. Chem.* **1991**, *56*, 5924–5931; g) A. C. Dengel, W. P. Griffith, B. C. Parkon, *J. Chem. Soc. Dalton Trans.* **1993**, 2683–2688; h) R. Neumann, M. Gara, *J. Am. Chem. Soc.* **1995**, *117*, 5066–5074.

[11] For a review of catalytic oxidation of alcohols with H_2O_2, see: R. A. Sheldon, I. W. C. E. Arends, A. Dijksman, *Catal. Today* **2000**, *57*, 157–166.

[12] a) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *J. Org. Chem.* **1996**, *61*, 8310–8311; b) K. Sato, M. Aoki, J. Takagi, R. Noyori, *J. Am. Chem. Soc.* **1997**, *119*, 12386–12387; c) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Penyella, R. Noyori, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 905–915; d) K. Sato, M. Aoki, R. Noyori, *Science* **1998**, *281*, 1646–1647; e) K. Sato, J. Takagi, M. Aoki, R. Noyori, *Tetrahedron Lett.* **1998**, *39*, 7549–7552; f) K. Sato, M. Aoki, J. Takagi, K. Zimmermann, R. Noyori, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2287–2306; g) K. Sato, M. Hyodo, J. Takagi, M. Aoki, R. Noyori, *Tetrahedron Lett.* **2000**, *41*, 1439–1442; h) K. Sato, M. Hyodo, M. Aoki, X.-Q. Zheng, R. Noyori, *Tetrahedron* **2001**, *57*, 2469–2476; i) Y. Usui, K. Sato, *Green Chem.* **2003**, *5*, 373–375; j) Y. Usui, K. Sato, M. Tanaka, *Angew. Chem.* **2003**, *115*, 5781–5783; *Angew. Chem. Int. Ed.* **2003**, *42*, 5623–5625.

[13] For a review of catalytic oxidation of cinnamyl alcohols with O_2, see: T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037–3058.

[14] a) M. Matsumoto, N. Watanabe, *J. Org. Chem.* **1984**, *49*, 3435–3436; b) J.-E. Bäckvall, R. L. Chowdhury, U. Karlsson, *J. Chem. Soc. Chem. Commun.* **1991**, 473–475; c) K. Kaneda, M. Fujii, K. Morioka, *J. Org. Chem.* **1996**, *61*, 4502–4503; d) I. E. Markó, P. G. Giles, M. Tsukazaki, S. M. Brown, C. J. Urch, *Science* **1996**, *274*, 2044–2046; e) G. J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639; f) A. F. Lee, J. J. Gee, H. J. Theyers, *Green Chem.* **2000**, *2*, 279–282; g) K. Yamaguchi, N. Mizuno, *Angew. Chem.* **2002**, *114*, 4720–4724; *Angew. Chem. Int. Ed.* **2002**, *41*, 4538–4542; h) K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2002**, *124*, 11572–11573; i) A. Abad, P. Concepción, A. Corma, H. García, *Angew. Chem.* **2005**, *117*, 4134–4137; *Angew. Chem. Int. Ed.* **2005**, *44*, 4066–4069; j) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362–365; k) G. An, M. Lim, K.-S. Chun, H. Rhee, *Synlett* **2007**, 95–98.

[15] a) A. J. H. P. van der Pol, J. H. C. van Hooff, *Appl. Catal. A* **1993**, *106*, 97–113; b) F. Maspero, U. Romano, *J. Catal.* **1994**, *146*, 476–482; c) A. Bhaumik, R. Kumar, *J. Chem. Soc. Chem. Commun.* **1995**, 349–350; d) R. Anderson, K. Griffin, P. Johnston, P. L. Alsters, *Adv. Synth. Catal.* **2003**, *345*, 517–523; e) C. A. Marsh, *J. Chem. Soc.* **1952**, 1578–1582; f) T. Matsumoto, M. Ueno, N. Wang, S. Kobayashi, *Chem. Asian J.* **2008**, *3*, 196–214.

[16] a) T. Hori, K. B. Sharpless, *J. Org. Chem.* **1978**, *43*, 1689–1697; b) C. Venturello, M. Gambaro, *J. Org. Chem.* **1991**, *56*, 5924–5931; c) P. Kumar, R. Kumar, B. Pandey, *Synlett* **1995**, 289–298; d) C. Baccin, A. Gusso, F. Pinna, G. Strukul, *Organometallics* **1995**, *14*, 1161–1167; e) I. W. C. E. Arends, R. A. Sheldon, M. Wallau, U. Schuchardt, *Angew. Chem.* **1997**, *109*, 1190–1211; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1144–1163; f) T. Tatsumi, K. A. Koyano, N. Igarashi, *Chem. Commun.* **1998**, 325–326; g) I. W. C. E. Arends, R. A. Sheldon, *Top. Catal.* **2002**, *19*, 133–141.

[17] Y. Kon, Y. Usui, K. Sato, *Chem. Commun.* **2007**, 4399–4400.

[18] Complex mixture containing benzaldehyde, benzoic acid, and other carboxylic acids was formed.

[19] Reaction rate was observed for the oxidation of cinnamyl alcohol; cinnamyl alcohol conversion (cinnamaldehyde selectivity) was 34% (100%) for 20 min, 71% (100%) for 40 min, 95% (96%) for 1 h, 97% (95%) for 2 h, 98% (94%) for 3 h, respectively.

[20] The oxidation of cinnamyl alcohol had a TOF of 2000 h^{-1}.

[21] For coordination ability of terminal double bond to Ni^0 complex, see: C. A. Tolman, *J. Am. Chem. Soc.* **1974**, *96*, 2780–2789.

[22] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 10657–10666.

[23] The complexes having the ligands coordinate to Pt strongly, like $[Pt(PPh_3)_4]$, $[Pt(dppe)_2]$, $[PtCl_2(PPh_3)_2]$, PtO_2, and $Na_2[Pt(OH)_6]$, show low catalytic activities for alcohol oxidation because the coordination of olefin to Pt surface would be a key step in this reaction.

[24] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*, *1st ed.* Vol. 2, Aldrich Chemical, Milwaukee, **1993**, p. 926-C.

[25] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^1H FT NMR Spectra*, *1st ed.* Vol. 1, Aldrich Chemical, Milwaukee, **1993**, p. 736-C.

[26] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, *1st ed*. Vol. 1, Aldrich Chemical, Milwaukee, **1993**, p. 738-A.

[27] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, *1st ed*. Vol. 1, Aldrich Chemical, Milwaukee, **1993**, p. 739-B.

[28] B. K. Eya, T. Otsuka, I. Kubo, D. L. Wood, *Tetrahedron* **1990**, *46*, 2695–2706.

[29] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, *1st ed*. Vol. 1, Aldrich Chemical, Milwaukee, **1993**, p. 735-B.

[30] S. Fielder, D. D. Rowan, M. S. Sherburn, *Tetrahedron* **1998**, *54*, 12907–12922.

[31] SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/ (National Institute of Advanced Industrial Science and Technology, Apr. 12, 2007).

[32] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, *1st ed*. Vol. 1, Aldrich Chemical, Milwaukee, **1993**, p. 631-C.

[33] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, *1st ed*. Vol. 1, Aldrich Chemical, Milwaukee, **1993**, p. 635-B.

[34] C. J. Pouchert, J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, *1st ed*. Vol. 1, Aldrich Chemical, Milwaukee, **1993**, p. 646-B.

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