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Switching the Cleavage Sites in Palladium on Carbon-Catalyzed Carbon−Carbon Bond Disconnection

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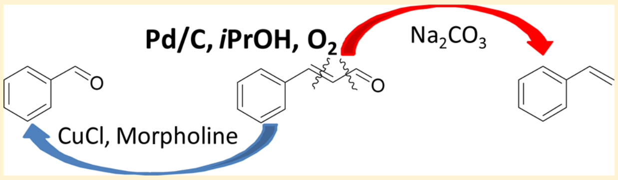
Supporting Information

ABSTRACT: We have demonstrated a palladium on carbon-catalyzed approach to regioselectively alter the cleavage sites of the C−C bonds of cinnamaldehyde derivatives by a slight change in the reaction conditions in isopropanol under an O_2 atmosphere. Styrene derivatives could be selectively formed by the addition of Na_2CO_3 in association with the dissociation of carbon monoxide, while benzaldehyde derivatives were generated by the addition of CuCl and morpholine instead of Na_2CO_3.

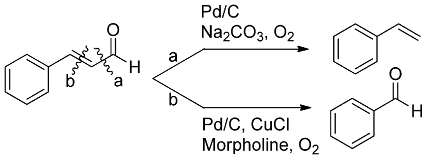


INTRODUCTION

Carbon−carbon (C−C) bonds are the most fundamental and important structural unit of organic compounds, and the selective cleavage of the C−C bonds of molecules could be used to construct different types of structural units. Therefore, the development of selective C−C bond cleavage methods is exceedingly important for synthetic organic chemistry, including the total synthesis of natural products,[1] while the thermodynamic stability of the C−C bonds makes their cleavage difficult, especially in a regioselective manner. A couple of C−C cleavage reactions based on the decarbonylation of aromatic and aliphatic aldehydes using a homogeneous rhodium[2] or iridium[3] catalyst have been reported. Furthermore, Maiti and co-workers recently accomplished the decarbonylation of aldehydes using a palladium catalyst [$Pd(OAc)_2$],[4] and the heterogeneous decarbonylation of biomass-derived molecules, such as furfural, was reported as the only example using palladium nanoparticles deposited on SBA-15 mesoporous silica as a catalyst.[5] Among the available supported catalysts, palladium on carbon (Pd/C) is one of the catalysts most frequently used for industrial processes because of its low price, high stability, easy removal from the reaction mixture, and ability to be reused.

We now report an additive-dependent regioselective control method between two types of Pd/C-catalyzed C−C cleavage reactions of cinnamaldehyde derivatives (Scheme 1, a and b).

Scheme 1. Regioselective C−C Bond Cleavage Catalyzed by 10% Pd/C



The addition of Na_2CO_3 promotes the decarbonylation for the formation of styrene derivatives (Scheme 1, a), although the C═C bonds are cleaved in the presence of Cu species and morpholine as additives to produce the corresponding benzaldehyde derivatives (Scheme 1, b).

RESULTS AND DISCUSSION

We initially realized that a C−C bond of 4-methoxycinnamaldehyde was cleaved leading to the formation of a styrene derivative in the presence of 10% Pd/C and Na_2CO_3 in *N*,*N*-dimethylacetamide (DMA) under an O_2 atmosphere (Table 1, entries 1−4), while the use of $Pd(OAc)_2$, substituted for 10% Pd/C, was not effective (entry 5). The reaction efficiency was improved in isopropanol (*i*PrOH) as a solvent, and the conversion yield increased to 89% (entries 3 and 6−8). Furthermore, the temperature of the external heating equipment (aluminum block) could be decreased from 140 to 120 °C in *i*PrOH without any loss of reaction efficiency (entries 8 and 9), although further reduction of the temperature caused a significant decrease in the reaction efficiency (entries 10 and 11).

Encouraged by these results, we applied the present optimal conditions to the decarbonylation of various cinnamaldehydes (Table 2). The cinnamaldehydes bearing either the electron-donating methoxy and/or hydroxyl groups or the electron-withdrawing nitro group on the benzene ring could be efficiently converted into the corresponding styrene derivative (entries 2−6).[6] The phenyl substituent at the β-position of the alkene moiety never suppressed the decarbonylation, while the β-methylated cinnamaldehyde had a critical influence on the reaction efficiency (entries 7 and 8).[7] Furthermore, 4-phenylbenzaldehyde, which has an aldehyde group directly on

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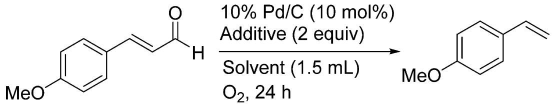
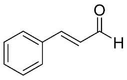
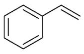
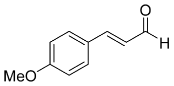
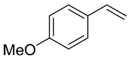
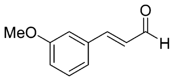
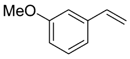
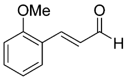
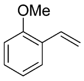
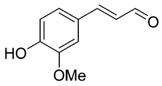
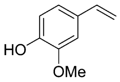
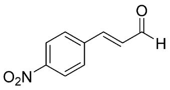
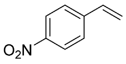
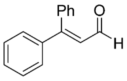
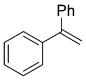
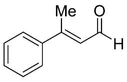
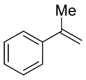
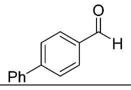
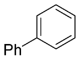
Table 1. Effects of Solvent and Additive on the 10% Pd/C-Catalyzed Decarbonylation of (*E*)-4′-Methoxycinnamaldehyde



entry	additive	solvent	temperature (°C)	yield (%)[a]
1	–	DMA	140	3
2	NaO*t*Bu	DMA	140	0
3	Na_2CO_3	DMA	140	75
4	TFA	DMA	140	0
5[b]	Na_2CO_3	DMA	140	39
6	Na_2CO_3	DMSO	140	3
7	Na_2CO_3	MeOH	140	59
8	Na_2CO_3	*i*PrOH	140	89
9	Na_2CO_3	*i*PrOH	120	86[c]
10	Na_2CO_3	*i*PrOH	100	57
11	Na_2CO_3	*i*PrOH	80	45

[a]Determined by ^1H NMR using terephthalonitrile as an internal standard. [b]$Pd(OAc)_2$ was used instead of 10% Pd/C. [c]Isolated yield.

Table 2. 10% Pd/C-Catalyzed Decarbonylation of Cinnamaldehydes to Styrene Derivatives[a]

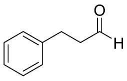
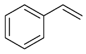
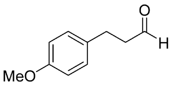
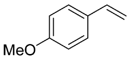
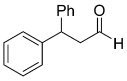
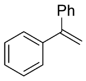
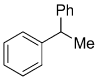
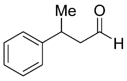
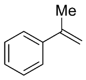
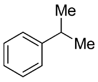
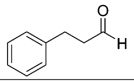
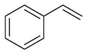
entry	aldehyde	product	yield (%)[b,c]
1			76
2			86
3			80
4			72
5			41
6			94
7[d]			87
8[d]			34
9			99

[a]Reaction conditions: aldehyde (0.25 mmol), Na_2CO_3 (0.5 mmol), 10% Pd/C (0.025 mmol) in *i*PrOH (1.5 mL) at 120 °C under O_2 for 24 h. [b]Isolated yield. [c]All reactions proceeded cleanly, and no byproducts were detected. Substrates were completely consumed in entries 1−4, 6, 7, and 9 (in entries 5 and 8, 51 and 41% of the substrates remained unchanged, respectively, as determined by ^1H NMR analysis of the crude reaction mixture). [d]One millimole of Na_2CO_3 was added.

the aromatic ring, smoothly underwent the corresponding decarbonylation (entry 9).

The decarbonylation of the dihydrocinnamaldehyde derivatives also smoothly proceeded in association with the dehydrogenation of the ethylene moiety to afford the corresponding styrene derivatives in good yields (Table 3, entries 1 and 2). For the substrates possessing a methyl or phenyl substituent at the benzylic position of dihydrocinnamaldehyde, 1,1-disubstituted ethenes were obtained along with the formation of an ∼10% yield of saturated 1,1-disubstituted ethane derivatives as minor products (entries 3 and 4).[8] The decarbonylation could also be completed under an argon atmosphere without oxygen gas, although the styrene yield significantly decreased because of the generation of the corresponding ethylbenzene (entry 5).

Table 3. 10% Pd/C-Catalyzed Decarbonylation of Dihydrocinnamaldehydes[a]

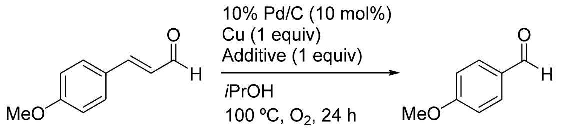
entry	aldehyde	product	yield (%)[b,c]
1			68
2			78
3[d]			71
			9
4[d]			35
			12
5[e]			41

[a]Reaction conditions: aldehyde (0.25 mmol), Na_2CO_3 (0.5 mmol), 10% Pd/C (0.025 mmol) in *i*PrOH (1.5 mL) at 120 °C under O_2 for 24 h. [b]Isolated yield. [c]All reactions proceeded cleanly, and no byproducts were detected. Substrates were completely consumed in entries 1−3 and 5 (for entry 4, 41% of the substrate remained unchanged as determined by ^1H NMR analysis of the crude reaction mixture). [d]One millimole of Na_2CO_3 was added. [e]Under an Ar atmosphere instead of O_2.

The synthesis of benzaldehyde from cinnamaldehyde via the C═C cleavage could be achieved using hydrogen peroxide (H_2O_2).[9−11] Several methods without H_2O_2 in the presence of water were also reported using cyclodextrins,[12] hydrotalcite as a catalyst,[13] microwave heating,[14] or secondary amine.[15] We then investigated the benzaldehyde synthesis by the Pd/C-catalyzed C═C cleavage of cinnamaldehyde in anticipation of switching the cleavage sites of the same compound by using different additives.

The effect of amines as additives was specifically investigated in the presence of CuBr. The presence of amines was found to be essential for the C═C bond cleavage reaction (Table 4, entry 1). The addition of cyclic aliphatic amines was especially effective (entries 2−5). The screening of copper species revealed that (1) the reaction hardly took place without copper species (entry 6) and (2) the reaction was completed within 24 h by using $CuBr_2$ (entry 7) or monovalent copper species, such

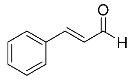
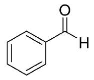
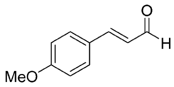
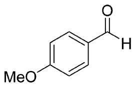
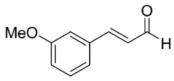
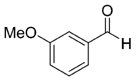
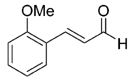
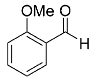
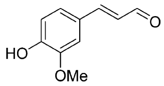
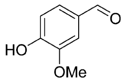
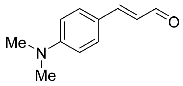
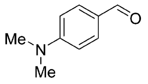
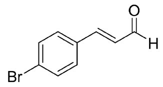
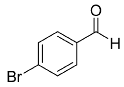
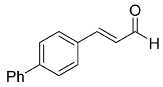
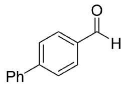
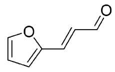
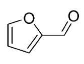
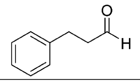
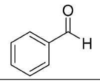
Table 4. Effect of Amine and Copper as a C=C Cleavage Reaction



entry	amine	copper	substrate:product ratio	yield (%)[a]
1	–	CuBr	100:0	99[b]
2	NEt_3	CuBr	99:trace	–
3	propylamine	CuBr	99:trace	–
4	pyrrolidine	CuBr	0:100	38
5	morpholine	CuBr	0:100	84
6	morpholine	–	87:13	–
7	morpholine	$CuBr_2$	0:100	84
8	morpholine	$CuCl_2$	7:93	–
9	morpholine	CuCl	0:100	85
10[c]	morpholine	$CuBr_2$	80:20	–
11[c]	morpholine	CuBr	55:45	–
12[c]	morpholine	CuCl	16:84	–
13[d]	morpholine	CuCl	38:62	–
14[e]	morpholine	CuCl	100:0	–
15[f]	morpholine	CuCl	51:49	–
16[e,f]	morpholine	CuCl	66:34	–

[a] Isolated yield. [b] Yield of recovered starting material. [c] Five hours. [d] A half equivalent of morpholine was used. [e] Without 10% Pd/C. [f] H_2O was used as a solvent instead of *i*PrOH.

Table 5. Scope of Cinnamaldehyde Derivatives for the Benzaldehyde Synthesis[a]

entry	aldehyde	product	yield (%)[b,c]
1			87
2			84
3			80
4			70
5			42
6			87
7			92
8			76
9			54
10[d]			0

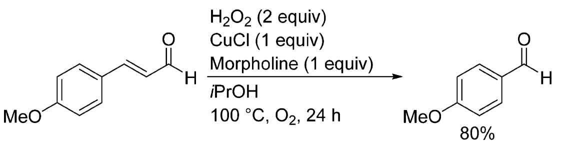
[a] Reaction conditions: aldehyde (0.25 mmol), CuCl (0.25 mmol), morpholine (0.25 mmol), 10% Pd/C (0.025 mmol) in *i*PrOH (1.5 mL) at 100 °C under O_2 for 24 h. [b] Isolated yield. [c] All reactions proceeded cleanly, and no byproducts were detected. Substrates were completely consumed in entries 1−3 and 6−8 (in entries 4, 5, and 9, 13, 38, and 31% of the substrates remained unchanged, respectively, as determined by ^1H NMR analysis of the crude reaction mixture). [d] No reaction took place.

as CuBr and CuCl (entries 5 and 9, respectively). CuCl was finally selected as the appropriate copper salt after comparison of the conversion ratios of 4-methoxybenzaldehyde for 5 h in the presence of $CuBr_2$ (entry 10), CuBr (entry 11), or CuCl (entry 12), and the reaction efficiency decreased via the reduction of the morpholine usage to 0.5 equiv (entry 13). No reaction took place without 10% Pd/C in *i*PrOH (entry 14), while the reaction partially proceeded in H_2O regardless of the presence of 10% Pd/C (entry 15) or its absence (entry 16). These results indicated that a Pd/C-catalyzed mechanism, which is different from the water-mediated reactions,[12−15] would have strong control over the present reaction effectively proceeding only in the presence of Pd/C and amine in *i*PrOH.

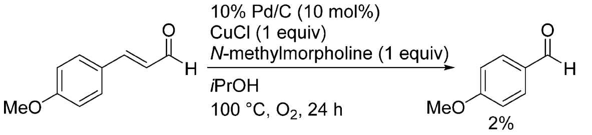
Electron-neutral and electron-sufficient cinnamaldehydes were smoothly converted to the corresponding benzaldehydes in high yields under the conditions presented here (Table 5, entries 1−6).[16] A bromine as a substituent on the aromatic ring of the substrate was tolerant under the reaction conditions (entry 7). While the replacement of the benzene ring of cinnamaldehyde with a furan ring hardly affected the reaction progress, the desired furfural could be obtained in 54% yield (entry 9). Interestingly, benzaldehyde was never obtained using dihydrocinnamaldehyde as the substrate (entry 10).

We recently reported that the Pd/C-, Rh/C-, or Pt/C-catalyzed dehydrogenation of *i*PrOH effectively generated H_2 gas and acetone,[17] and Pd/C catalyzed the hydrogenation of oxygen gas to directly generate H_2O_2.[18] The generation of H_2O_2 in *i*PrOH in the presence of 10% Pd/C and O_2, CuCl, and morpholine at 100 °C was confirmed by iodometry of the filtrate obtained after the removal of 10% Pd/C by hot filtration, indicating that the Pd/C-catalyzed hydrogenation of O_2 gas by the H_2, which was generated via the Pd/C-catalyzed dehydrogenation of *i*PrOH, took place during the present C=C cleavage reaction of cinnamaldehydes to benzaldehydes. Furthermore, 4-methoxybenzaldehyde could be synthesized from 4-methoxycinnamaldehyde in 80% yield in the presence of 30% aqueous H_2O_2 (2 equiv) even without 10% Pd/C (eq 1). Because the reaction was strongly suppressed by using *N*-methylmorpholine instead of morpholine, the secondary amine moiety of morpholine should be important (eq 2). In addition, the in situ-generated H_2O_2 would not oxidize morpholine during the reaction, because the addition of morpholine *N*-oxide was not efficient (eq 3). While 51% CO was detected in the reaction vessel during the styrene synthesis by gas chromatography (eq 4), CO was hardly detected under the benzaldehyde synthesis conditions (eq 5).

The decarbonylation of cinnamaldehyde would proceed like the Rh-catalyzed reaction reported in the literature, although the role of Na_2CO_3 is unclear.[17,19] Pd(0)/C would be oxidatively inserted into the C(O)−H bond of the aldehyde to form an acyl Pd(II) hydride complex (**A**). Subsequently, Pd would migrate to form a vinyl Pd(II) hydride complex (**B**), and reductive elimination of styrene would take place to generate CO and Pd(0)/C (Scheme 2). Similarly, phenethyl Pd(II) hydride (**B′**) (Scheme 3) would form from dihydrocinnamaldehyde, and styrene would be afforded together with H_2 via the *β*-hydrogen elimination. The alkene moiety could be partially hydrogenated by the H_2 gas generated from **B′** and/or *i*PrOH.



(1)



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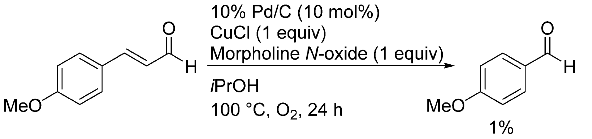
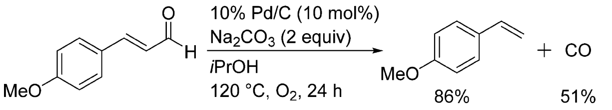


(3)



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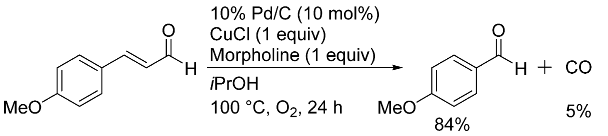


(5)

For benzaldehyde formation, we propose a H_2O_2-mediated mechanism; thus, an epoxy−iminium intermediate (**C**) could be initially generated from cinnamaldehyde in the presence of morpholine and CuCl via the in situ-generated H_2O_2-mediated oxidation of the alkene moiety as with the organocatalytic epoxidation of α,β-unsaturated aldehydes using H_2O_2.[20] A further nucleophilic attack of H_2O_2 on the epoxide and iminium moieties of **C** would lead to the formation of a five-membered ring intermediate, and the subsequent ring opening reaction gave the desired benzaldehyde, glyoxal, and morpholine.

10% Pd/C could be recovered and reused for both decarbonylation (Table 6) and C═C cleavage reaction (Table 7) of (*E*)-4′-methoxycinnamaldehyde at least until the third runs without any change in the catalyst activity, although the decreased reaction efficiency was observed in the fourth run of only the decarbonylation reaction.

Scheme 3. Proposed Mechanism for the Synthesis of Styrene from Dihydrocinnamaldehyde

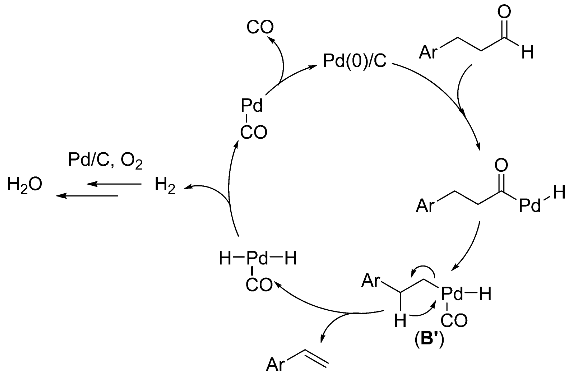
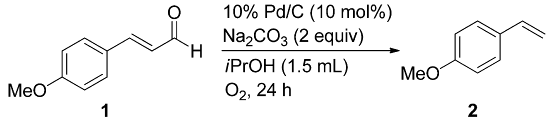


Table 6. Reuse Test of 10% Pd/C for the Decarbonylation of (*E*)-4′-Methoxycinnamaldehyde

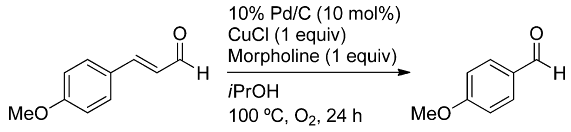


1 2

	first run	second run	third run	fourth run
1:2 ratio[a]	0:100	0:100	0:100	42:58
yield (%)[b]	91	89	88	50

[a] Determined by ^{1}H NMR. No byproducts were observed. [b] Isolated yield.

Table 7. Reuse Test of 10% Pd/C for the C═C Cleavage Reaction of (*E*)-4′-Methoxycinnamaldehyde

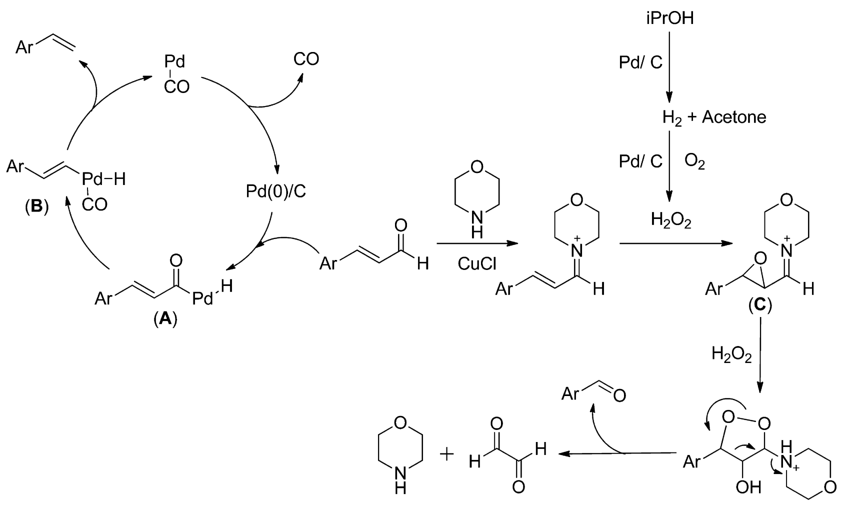


1 3

	first run	second run	third run	fourth run
1:3 ratio[a]	0:100	0:100	0:100	0:100
yield (%)[b]	92	90	91	89

[a] Determined by ^{1}H NMR. No byproducts were observed. [b] Isolated yield.

Scheme 2. Proposed Catalytic Cycle for the C−C Cleavage Reactions



■ CONCLUSION

In conclusion, we have developed two types of Pd/C-catalyzed efficient regioselective carbon−carbon bond cleavage reactions of cinnamaldehyde derivatives. Styrene and benzaldehyde derivatives could be selectively synthesized in high yields using different additives, i.e., Na_2CO_3 for the synthesis of the styrene derivatives and CuCl and morpholine for the synthesis of the benzaldehyde derivatives.

■ EXPERIMENTAL SECTION

General. All solvents and reagents were obtained from commercial sources and used without further purification. Chemical shifts (δ) of ^{1}H NMR (400 MHz, $CDCl_3$) are expressed in parts per million and are internally referenced (0.00 ppm for tetramethylsilane). Presented products in this manuscript were all known, and their ^{1}H NMR and MS spectra were identical to those in the literature.

General Procedure for the Synthesis of Styrene Derivatives (Tables 1−3). A mixture of 10% Pd/C (26.6 mg, 25.0 μmol), a cinnamaldehyde derivative (250 μmol), and Na_2CO_3 (53.0 mg, 50.0 μmol) in *i*PrOH (1.5 mL) in a 17 mL test tube was stirred using a personal organic synthesizer Chemistation (EYELA, Tokyo, Japan) or ChemistPlaza (Shibata Scientific Technology, Ltd., Tokyo, Japan) at 120 °C under an O_2 atmosphere for 24 h. The mixture was passed through a membrane filter (Millipore Corp., Billerica, MA; Millex-LH, 0.45 μm) to remove the insoluble catalyst, and the filtered residue was washed with Et_2O (30 mL). The combined filtrate was washed with H_2O (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane) or preparative TLC (hexane) to afford the corresponding styrene derivative.

Styrene (Table 2, entry 1, and Table 3, entries 1 and 5).[21] ^{1}H NMR δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.71 (dd, *J* = 17.2, 11.2 Hz, 1H), 5.74 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 11.2 Hz, 1H); MS (EI) *m*/*z* 104 (M$^+$, 100), 78 (76).

4-Methoxystyrene (Table 2, entry 2, and Table 3, entry 2).[22] ^{1}H NMR δ 7.35 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 18.0, 10.4 Hz, 1H), 5.52 (d, *J* = 18.0 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 3.81 (s, 3H); MS (EI) *m*/*z* 134 (M$^+$, 100), 119 (51), 103 (2), 91 (71).

3-Methoxystyrene (Table 2, entry 3).[22] ^{1}H NMR δ 7.24 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.95 (s, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.69 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 3.81 (s, 3H); MS (EI) *m*/*z* 134 (M$^+$, 100), 119 (3), 104 (25), 91 (62).

2-Methoxystyrene (Table 2, entry 4).[22] ^{1}H NMR δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 18.0, 10.8 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 5.76 (d, *J* = 18.0 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 3.86 (s, 3H); MS (EI) *m*/*z* 134 (M$^+$, 27), 119 (28), 103 (3), 91 (100), 78 (9).

4-Hydroxy-3-methoxyphenylethene (Table 2, entry 5).[23] ^{1}H NMR δ 6.95−6.88 (m, 3H), 6.63 (dd, *J* = 18.0, 10.8 Hz, 1H), 5.63 (d, *J* = 8.8 Hz, 1H), 5.57 (s, 1H), 5.13 (d, *J* = 8.8 Hz, 1H), 3.92 (s, 3H); MS (EI) *m*/*z* 150 (M$^+$, 100), 135 (80), 77 (66).

4-Nitrostyrene (Table 2, entry 6).[24] ^{1}H NMR δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.78 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.93 (d, *J* = 17.6 Hz, 1H), 5.50 (d, *J* = 10.8 Hz, 1H); MS (EI) *m*/*z* 149 (M$^+$, 46), 133 (1), 119 (11), 103 (11), 91 (21), 77 (100).

1,1-Diphenylethylene (Table 2, entry 7, and Table 3, entry 3).[25] ^{1}H NMR δ 7.32−7.28 (m, 10H), 5.43 (s, 2H); MS (EI) *m*/*z* 180 (M$^+$, 100), 165 (64).

1,1-Diphenylethane (Table 3, entry 3).[26] ^{1}H NMR δ 7.29−7.15 (m, 10H), 4.14 (q, *J* = 7.6 Hz, 1H), 1.63 (d, *J* = 7.6 Hz, 3H); MS (EI) *m*/*z* 182 (M$^+$, 70), 167 (100), 152 (34), 77 (58).

α-Methylstyrene (Table 2, entry 8, and Table 3, entry 4).[27] ^{1}H NMR δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 5.36 (s, 1H), 5.07 (s, 1H), 2.14 (s, 3H); MS (EI) *m*/*z* 118 (M$^+$, 100), 103 (38), 90 (13), 77 (43).

2-Phenylpropane (Table 3, entry 4).[26] ^{1}H NMR δ 7.18−7.32 (m, 5H), 2.91 (sept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); MS (EI) *m*/*z* 120 (M$^+$, 45), 105 (100), 77 (35).

Biphenyl (Table 2, entry 9).[28] ^{1}H NMR δ 7.62−7.58 (m, 4H), 7.48−7.25 (m, 6H); MS (EI) *m*/*z* 154 (M$^+$, 100).

General Procedure for Synthesis of Benzaldehyde Derivatives (Tables 4 and 5). A mixture of 10% Pd/C (26.6 mg, 25.0 μmol), a cinnamaldehyde derivative (250 μmol), CuCl (25.0 mg, 250 μmol), and morpholine (21.6 μL, 250 μmol) in *i*PrOH (1.5 mL) in a 17 mL test tube was stirred using a personal organic synthesizer Chemistation (EYELA) or ChemistPlaza (Shibata Scientific Technology, Ltd.) at 100 °C under an O_2 atmosphere for 24 h. The mixture was passed through a membrane filter (Millipore Corp.; Millex-LH, 0.45 μm) to remove the insoluble catalyst, and the filtered residue was washed with Et_2O (30 mL). The combined filtrate was washed with H_2O (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane) or preparative TLC (hexane) to afford the corresponding benzaldehyde derivative.

Benzaldehyde (Table 5, entry 1).[29] ^{1}H NMR δ 10.02 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H); MS (EI) *m*/*z* 105 (M$^+$, 57), 77 (100).

4-Methoxybenzaldehyde (Table 4 and Table 5, entry 2).[30] ^{1}H NMR δ 9.89 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); MS (EI) *m*/*z* 135 (M$^+$, 100), 107 (9), 92 (21), 77 (64).

3-Methoxybenzaldehyde (Table 5, entry 3).[30] ^{1}H NMR δ 9.98 (s, 1H), 7.46−7.42 (m, 2H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.18 (m, 1H), 3.87 (s, 3H); MS (EI) *m*/*z* 136 (M$^+$, 100), 119 (2), 107 (19), 92 (6), 77 (49).

2-Methoxybenzaldehyde (Table 5, entry 4).[30] ^{1}H NMR δ 10.47 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.04−6.98 (m, 2H), 3.93 (s, 1H); MS (EI) *m*/*z* 136 (M$^+$, 56), 118 (18), 104 (5), 92 (15), 77 (100).

4-Hydroxy-3-methoxybenzaldehyde (Table 5, entry 5).[31] ^{1}H NMR δ 9.89 (s, 1H), 7.40−7.45 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.25 (s, 1H), 3.99 (s, 3H); MS (EI) *m*/*z* 151 (M$^+$, 100).

4-(*N*,*N*-Dimethylamino)benzaldehyde (Table 5, entry 6).[32] ^{1}H NMR δ 9.74 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 3.09 (s, 6H); MS (EI) *m*/*z* 149 (M$^+$, 100).

4-Bromobenzaldehyde (Table 5, entry 7).[29] ^{1}H NMR δ 9.98 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H); MS (EI) *m*/*z* 184 (M$^+$, 100), 156 (13), 75 (23).

4-Phenylbenzaldehyde (Table 5, entry 8).[33] ^{1}H NMR δ 10.06 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.65−7.42 (m, 5H); MS (EI) *m*/*z* 181 (M$^+$, 100), 152 (32).

Furan-2-carbaldehyde (Table 5, entry 9).[32] ^{1}H NMR δ 9.67 (s, 1H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 6.63 (dd, *J* = 3.6, 1.2 Hz, 1H); MS (EI) *m*/*z* 96 (M$^+$, 100), 39 (52).

Procedure for the Confirmation of H_2O_2 Generation by Iodometry. A mixture of 10% Pd/C (26.6 mg, 25.0 μmol), CuCl (25.0 mg, 250 μmol), and morpholine (21.6 μL, 250 μmol) in *i*PrOH (1.5 mL) in a 17 mL test tube was stirred using a personal organic synthesizer ChemistPlaza (Shibata Scientific Technology, Ltd.) at 100 °C under an O_2 atmosphere for 6 h. The mixture was passed through a membrane filter (Millipore Corp.; Millex-LH, 0.45 μm) without cooling to remove the insoluble catalyst. The remaining H_2O_2 in the resulting filtrate was mesured by iodometry using 0.01 M $Na_2S_2O_3$ (f = 0.996) for the titration; 6.50 mL of 0.01 M $Na_2S_2O_3$ corresponding to 32.4 μmol H_2O_2 detection was consumed by the titration.

General Procedure for the Reuse Test of 10% Pd/C for the Decarbonylation of (*E*)-4′-Methoxycinnamaldehyde (Table 6). Three test tubes were prepared, and (*E*)-4′-methoxycinnamaldehyde (40.6 mg, 0.250 mmol), 10% Pd/C (26.6 mg, 25.0 μmol, 10 mol %), Na_2CO_3 (53.0 mg, 0.500 mmol), and *i*PrOH (1.5 mL) were placed in each test tube. The mixture in each test tube was stirred under O_2 (balloon) at 120 °C for 24 h, and then the combined mixture was filtered using a Kiriyama funnel (1 μm filter paper). The catalyst on the filter paper was washed with EtOAc (20 mL), H_2O (20 mL), and MeOH (20 mL), and the filtrate was concentrated *in vacuo* to give 4-

methoxystyrene (95.5 mg, 0.682 mmol, 91%). The recovered catalyst was dried at room temperature under reduced pressure for 24 h and then weighed [79.7 mg, 100%, 79.7/(26.6 × 3) × 100]. The reaction for the second run was conducted in the same manner as the first run. 4-Methoxystyrene was obtained in 89% yield (89.6 mg, 0.668 mmol), and the catalyst was recovered [70.5 mg, 88%, 70.5/(26.6 × 3) × 100]. The reactions for the third and fourth runs were performed in the same manner as the first run, but using two test tubes because of the slight loss of the recovered 10% Pd/C during the filtration [total substrate amount, 81.2 mg (40.6 mg × 2), 0.500 mmol (0.250 mmol × 2); total catalyst amount, 53.2 mg (26.2 mg × 2), 50.0 μmol (25.0 μmol × 2); total Na_2CO_3 amount, 106 mg (53.0 mg × 2), 1.00 mmol (0.500 mmol × 2)]. The yields of 4-methoxystyrene in the third and fourth runs were 88% (59.0 mg, 0.440 mmol) and 50% (33.2 mg, 0.247 mmol), respectively. The catalyst was quantitatively recovered in the third run [53.2 mg, 53.2/(26.6 × 2) × 100] and the fourth run [53.0 mg, 53.0/(26.6 × 2) × 100].

General Procedure for the Reuse Test of 10% Pd/C for the C═C Cleavage Reaction of (*E*)-4′-Methoxycinnamaldehyde (Table 7). Three test tubes were prepared, and (*E*)-4′-methoxycinnamaldehyde (40.6 mg, 0.250 mmol), 10% Pd/C (26.6 mg, 25.0 μmol, 10 mol %), CuCl (24.0 mg, 0.250 mmol), morpholine (22.0 μL, 0.250 mmol), and *i*PrOH (1.5 mL) were placed in each test tube. The mixture in each test tube was stirred under O_2 (balloon) at 100 °C for 24 h, and then the combined mixture was filtered using a Kiriyama funnel (1 μm filter paper). The catalyst on the filter paper was washed with EtOAc (20 mL), H_2O (20 mL), and MeOH (20 mL), and the filtrate was concentrated *in vacuo* to give 4-methoxybenzaldehyde (93.8 mg, 0.690 mmol, 92%). The recovered catalyst was dried at room temperature under reduced pressure for 24 h and then weighed [79.8 mg, 100%, 100/(26.6 × 3) × 100]. The reaction for the second to fourth runs was performed in the same manner as the first run. The yields of 4-methoxybenzaldehyde in the second to fourth runs were 90% (91.8 mg, 0.670 mmol), 91% (92.9 mg, 0.683 mmol), and 89% (91.3 mg, 0.671 mmol), respectively. The catalyst were quantitatively recovered in the second to fourth runs {100% for the second run [80.0 mg, 80.0/(26.6 × 3) × 100], 100% for the third run [79.8 mg, 79.8/(26.6 × 3) × 100], and 98% for the fourth run [78.2 mg, 78.2/(26.6 × 3) × 100]}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02632.

Copies of ^1H spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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