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Semireduction of Alkynes Using Formic Acid with Reusable Pd-Catalysts

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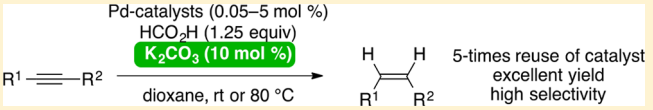
Supporting Information

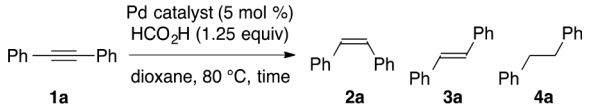
ABSTRACT: The treatment of $PdCl_2$ with K_2CO_3 and HCO_2H in dioxane gives black precipitates, which are an effective catalyst for the semireduction of alkynes to alkenes using formic acid as a reductant. Even 0.05 mol % Pd promoted the reduction reaction of tolane in high yield with high selectivity.



The semireduction of alkynes to alkenes is an important transformation in organic chemistry. A typical catalyst for reduction reactions of alkynes is Pd/C and their analogues under a H_2 atmosphere as a reductant.[1−3] In contrast, several studies have considered the use of formic acid as a reductant for the semireduction of alkynes to alkenes.[4] In these previous reports, the use of formic acid with a base, such as amine bases, was effective in the presence of homogeneous and heterogeneous Pd,[5] Ni,[6] Ru,[7] Au,[8] and Ti[9] catalysts. The use of a stable and inexpensive liquid reductant, formic acid, as a substitute for a flammable H_2 gas stored in a cylinder, is convenient in common transformations, such as reduction reactions. We here describe easily prepared and reusable heterogeneous Pd-catalysts for the semireduction of alkynes using formic acid as a reductant.

The initial approach in the present study exemplified the drastic effect of bases containing potassium atoms (Table 1) (screening of bases and reductants; see the Supporting Information). The typical reaction of tolane (**1a**) and HCO_2H (1.25 equiv) was conducted in the presence of a Pd-catalyst in dioxane at 80 °C. The reaction in the presence of $PdCl_2$ did not give the desired products; trimerization slightly took place to give hexaphenylbenzene (entry 1). The reaction in the presence of $Pd(OAc)_2$ or $PdCl_2(PPh_3)_2$ as a catalyst gave the desired products **2a** and **3a** in low yields (entries 2 and 3). Typical catalysts for reduction reactions using H_2 gas, such as Pd/C or Lindlar's catalyst, showed a good catalytic activity using HCO_2H, but chemo- and stereoselective reduction failed (entries 4 and 5). In contrast, the reaction proceeded in the presence of $PdCl_2$ (5 mol %) and K_2CO_3 (10 mol %) to predominantly give the desired product **2a** in excellent yield; the trimerization product, hexaphenylbenzene, was not obtained at all (entry 6). The reaction efficiently took place even at room temperature (entry 7). The use of $Pd(OAc)_2$ (5 mol %) or $PdCl_2(PPh_3)_2$ (5 mol %) as a catalyst with K_2CO_3 (10 mol %) also promoted the reaction (entries 8 and 9). Typical catalysts, Pd/C or Lindlar's catalyst, with K_2CO_3 (10 mol %) showed moderate yields and selectivities, respectively (entries 10 and 11).

Table 1. Effect of K_2CO_3



entry[a]	Pd-salt	time (h)	2a	3a	4a
	Without K_2CO_3				
1[b]	$PdCl_2$	18		1	
2	$Pd(OAc)_2$	15	9	2	
3	$PdCl_2(PPh_3)_2$	15	1	1	
4	Pd/C	3	78	9	11
5	Lindlar's catalyst	42	74	16	10
	With K_2CO_3 (10 mol %)				
6	$PdCl_2$	3	97	2	1
7[c]	$PdCl_2$	33	96	3	1
8	$Pd(OAc)_2$	3	98	2	
9	$PdCl_2(PPh_3)_2$	3	87	9	
10	Pd/C	3	67	14	19
11	Lindlar's catalyst	42	60	8	

[a]NMR yields. [b]Cyclotrimerization product, hexaphenylbenzene, was obtained. [c]The reaction was conducted at room temperature.

The present reaction typically gave heterogeneous mixtures including black precipitates, indicating the generation of Pd-heterogeneous catalysts during the reaction. Thus, precatalysts and the preparation methods might influence the catalytic performance (Scheme 1, Table 2). We examined the treatment of $PdCl_2$ (5 mol %) in dioxane with HCO_2H (1.25 equiv), but there was no change (catalyst A, entry 1). In contrast, the

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Scheme 1. Preparation of Catalysts

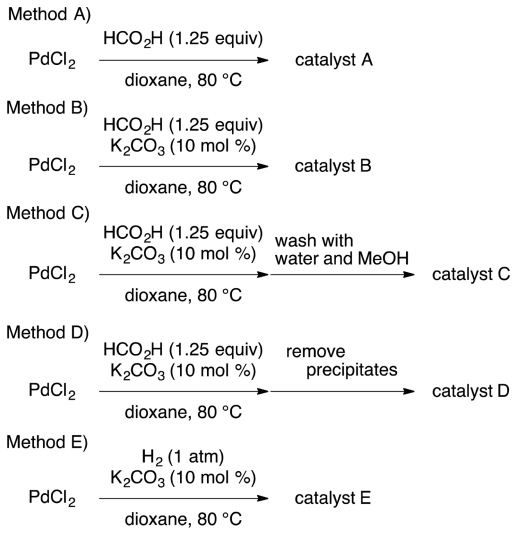
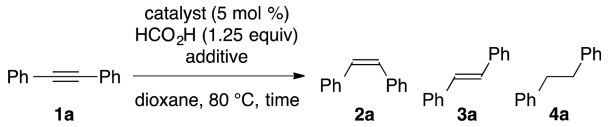


Table 2. Confirmation of Catalytic Activity



entry[a]	catalyst	additive	2a	3a	4a
1	A				
2	B		97	2	1
3	B	HCO_2H (1.25 equiv)	94	3	2
4	B	H_2 (1 equiv)	76	5	19
5	B	H_2 (1 atm)	6	8	86
6	C				
7	C	K_2CO_3 (10 mol %)	98	1	1
8	C	Na_2CO_3 (10 mol %)	53	2	
9[b]	C	H_2 (1 atm) K_2CO_3 (10 mol %)	81	7	12
10	D				
11	E		29	1	1

[a]NMR yields. The reaction time for entries 1−7 and 9, 3 h; entry 8, 19 h; entry 10, 15 h; entry 11, 24 h. [b]HCO_2H was not used.

treatment of $PdCl_2$ (5 mol %) in dioxane with HCO_2H (1.25 equiv) in the presence of K_2CO_3 (10 mol %) at 80 °C gave black precipitates, which showed a catalytic activity for the semireduction of tolane (**1a**) without the further addition of HCO_2H (catalyst B, entry 2). Therefore, the present method does not require an alkyne to obtain active Pd-catalysts.[10] The use of an excess amount of HCO_2H gave similar results; over-reduction hardly took place (catalyst B, entry 3). The addition of H_2 (1 equiv) or H_2 (1 atm) increased the amount of alkane **4a** as a byproduct (catalyst B, entries 4 and 5). We assume that the Pd-intermediates derived from H_2 would readily react with alkenes **2a** and **3a** for the generation of alkane **4a**, although Ohkuma reported that Pd-nanoparticles promoted the semi-reduction of alkynes under a H_2 atmosphere at high pressure (8 atm).[10] The precipitates prepared from $PdCl_2$ (5 mol %), K_2CO_3 (10 mol %), and HCO_2H (1.25 equiv) in dioxane were recovered and repeatedly washed with ultrapure water and MeOH for use as catalyst C. The reaction using catalyst C in the absence of K_2CO_3 (10 mol %) did not take place at all (catalyst C, entry 6). In contrast, the reaction using catalyst C in the presence of K_2CO_3 (10 mol %) took place to give the desired product **2a** (catalyst C, entry 7). The present results suggest that the reaction requires K_2CO_3 for the preparation of catalyst as well as the reduction of alkynes.[11] The reaction using Na_2CO_3 (10 mol %) in the presence of catalyst C gave the desired product **2a** in moderate yield with high stereoselectivity; thus, the catalyst prepared using K_2CO_3 shows catalytic activity using other bases in the reduction of alkynes (entry 8). The use of catalyst C under H_2 (1 atm) without HCO_2H showed catalytic activity, but the chemo-selectivity decreased (entry 9). We wondered whether ultrasmall nanoparticles in the supernatant of catalyst B could be acting as active catalysts. The supernatant of catalyst prepared using $PdCl_2$ (5 mol %), K_2CO_3 (10 mol %), and HCO_2H (1.25 equiv) was transferred into a reaction vessel as catalyst D for the semireduction of tolane (**1a**); the reaction did not take place at all (entry 10). The results indicated that the black precipitates were active catalysts. The preparation of effective catalysts required formic acid; catalyst E prepared under a H_2 atmosphere showed low catalytic activity (entry 11).[12] The purity of K_2CO_3, such as >99.9% or >99.997%, did not influence the catalytic performance. To confirm the presence of active catalysts in solution or not, the filtration of the reaction mixture at 80 °C to remove precipitates was conducted after 25% conversion (Scheme 2). The filtrate was heated at 80 °C for an additional 3 h, which gave 25% conversion; thus, the elution of a Pd at 80 °C would not play a crucial role in the present reaction.

The screening of alkynes under the optimized conditions is described in Table 3. The purification by silica-gel column chromatography decreased the yields, since alkynes, alkenes, and alkanes show similar polarity and volatility. Carbonyl groups can be tolerated under the present conditions (entries 1−4). Alkyne **1e** bearing a C−F bond gave the desired product **2e** (entry 5). There was no change in reactivity with the electron-rich alkynes **1f** and **1g** (entries 6 and 7). Heteroaromatic alkynes showed unique reactivity and selectivity; the use of 2-alkynylpyridine derivative **1h** gave an *E*-geometry as a major product (entry 8). The coordinative moiety might affect the stereoselectivity of the product. The use of 3-alkynyl or 4-alkynylpyridine derivatives **1i** and **1j** gave the desired products, but the yields were moderate (entries 9 and 10). The alkyne **1k** bearing a thiophene moiety gave the desired product **2k** in high yield (entry 11). The propiolate derivative **1l** gave the desired product **2l**, but unidentified side products were observed (entry 12). The aliphatic alkynes **1m** and **1n** gave the desired products **2m** and **2n** in acceptable

Scheme 2. Conversion after Hot Filtration

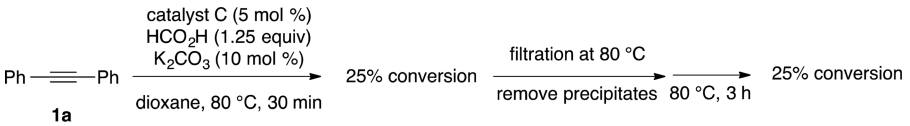


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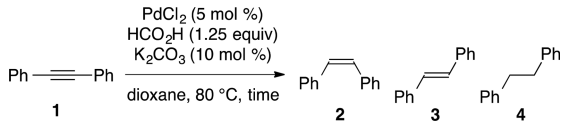
Table 3. Scope of Alkynes



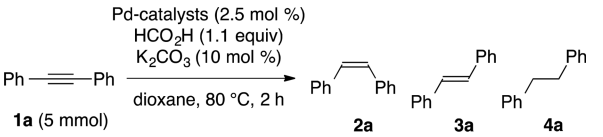
entry[a,b]	alkynes **1**	**2**	**3**	**4**
1	Ph—≡—Ph **1a**	**2a** 97 (93)	**3a** 2	**4a** 1
2	O, H_3C, Ph **1b**	**2b** 80 (79)	**3b** ND	**4b** ND
3	O, MeO, Ph **1c**	**2c** 86 (75)	**3c** trace	**4c** 2
4[c]	O, H, Ph **1d**	**2d** 74 (66)	**3d** ND	**4d** ND
5	F, Ph **1e**	**2e** 85 (79)	**3e** trace	**4e** 4
6	Me, Ph **1f**	**2f** 83 (83)	**3f** 2	**4f** ND
7	MeO, Ph **1g**	**2g** 93 (85)	**3g** 2	**4g** ND
8	N, Ph **1h**	**2h** ND	**3h** 77 (72)	**4h** 21
9	N, Ph **1i**	**2i** 34 (37)	**3i** ND	**4i** ND
10	N, Ph **1j**	**2j** 51 (51)	**3j** trace	**4j** 8
11	S, Ph **1k**	**2k** 80 (69)	**3k** trace	**4k** trace
12	O, EtO, Ph **1l**	**2l** 84 (71)	**3l** 4	**4l** trace
13	Ph **1m**	**2m** 81 (78)	**3m** trace	**4m** trace
14	n-C_5H_{11}—≡—n-C_5H_{11} **1n**	**2n** 92 (79)	**3n** trace	**4n** trace

[a]NMR yields. The yields after column chromatography are described in parentheses. [b]Entry 1, 3 h; entry 2, 5 h; entry 3, 8 h; entry 4, 15 h; entry 5, 4 h; entry 6, 2 h; entry 7, 4 h; entry 8, 14 h; entry 9, 39 h; entry 10, 10 h; entry 11, 4 h; entry 12, 4 h; entry 13, 6 h; entry 14, 2 h. [c]$PdCl_2$ (10 mol %), K_2CO_3 (20 mol %), and HCO_2H (10 equiv) were used.

yields, respectively (entries 13 and 14). The use of terminal alkynes gave unidentified side products; further modification of catalyst is required.

Simple workup after the reaction realized the reuse of catalyst (Table 4). The black precipitates in the reaction mixture were dried under a vacuum after washing with acetone, MeOH, and water, which was used for the next reaction. We used the Pd-catalysts (2.5 mol %) five times, and excellent yields and selectivities were obtained in all cases.[13,14] The reused Pd-catalysts (second to fifth runs) showed almost similar catalytic activity compared to the freshly prepared Pd-catalysts from $PdCl_2$. The Pd-catalysts (0.5 mol %) were also used twice, but the second run required a longer reaction time. The loss of catalytic activity in air might be problematic; thus, the Pd-catalysts should be stored in Ar. The catalyst loading (0.05 mol % Pd) was enough for the reaction to run to completion (Scheme 3).

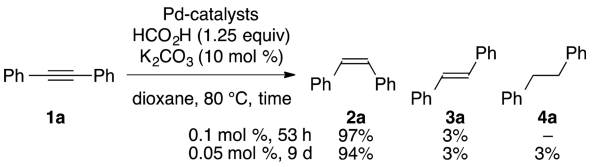
Table 4. Reuse of Catalyst



run[a]	first	second	third	fourth	fifth
2a (%)	92 (97)	97 (97)	97	96	98
3a (%)	5 (3)	3 (3)	3	2	2
4a (%)	3 (−)			2	

[a]NMR yields. [b]The yields in parentheses are the use of Pd-clusters (0.5 mol %) for 11 h in the first run and for 50 h in the second run.

Scheme 3. Example of Low Catalyst Loading



In conclusion, we succeeded in establishing an easy approach to Pd-catalysts using commercially available chemicals, $PdCl_2$, K_2CO_3, and HCO_2H, via a simple operation. These Pd-catalysts show good catalytic activity for the semireduction of alkynes using formic acid. The reuse of catalyst (2.5 mol % Pd) for five times was not associated with a decrease in catalytic performance. The use of Pd-clusters (0.1 or 0.05 mol % Pd) achieved high yield with high selectivity. The reaction took place efficiently even at room temperature. Although the mechanism is still unclear, the use of potassium bases plays an important role in the preparation of the present Pd-catalysts. The present Pd-catalysts and other heterogeneous metal catalysts are being studied further to achieve novel catalytic performance.

EXPERIMENTAL SECTION

General Experimental Information. All reactions dealing with air, moisture, and light sensitive compounds were carried out in a dry reaction vessel covered with foil under positive pressure of argon. All liquids and solutions were transferred via a syringe. Analytical thin-layer chromatography was performed on an aluminum plate coated with silica gel containing a fluorescent indicator (Silica Gel 60 F254, Merck). The plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in a basic staining solution of $KMnO_4$ followed by heating with a heat gun. Organic solutions were concentrated by a rotary evaporator. Flash column chromatography was performed employing Kanto Silica gel 60N (spherical, neutral). Proton nuclear magnetic resonance (^{1}H NMR, 399 MHz), carbon nuclear magnetic resonance (^{13}C{^{1}H} NMR, 100 MHz), and fluorine nuclear magnetic resonance (^{19}F NMR, 375 MHz) spectra were recorded with JEOL JNM-ECZ400S spectrometers. Proton nuclear magnetic resonance (^{1}H NMR, 300 MHz) and carbon nuclear magnetic resonance (^{13}C{^{1}H} NMR, 75 MHz) spectra were recorded with JEOL JNM-ECS300 spectrometers. ^{1}H NMR spectra in $CDCl_3$ were referenced internally to tetramethylsilane (δ = 0.00 ppm) as a standard, and ^{13}C{^{1}H} NMR spectra, to the solvent resonance ($CDCl_3$ δ = 77.0 ppm). ^{19}F NMR spectra in $CDCl_3$ were referenced externally to trifluoroacetic acid (δ = −76.5 ppm) as a standard. Data are presented as follows: chemical shift, spin multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant in Hz, and signal area integration in natural numbers.

All reagents were purchased as commercially available sources. Internal alkynes except for diphenylacetylene and 6-dodecyne were prepared according to either method reported in the literature.[15−25]

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J. Org. Chem. XXXX, XXX, XXX−XXX

General Procedure for Reduction of Alkynes Using HCO_2H. Alkyne (0.20 mmol), $PdCl_2$ (1.8 mg, 0.010 mmol), K_2CO_3 (5.5 mg, 0.020 mmol), and 1,4-dioxane (1.0 mL) were added to a flame-dried Schlenk tube under an argon atmosphere. Within a minute, formic acid (11 μL, 0.25 mmol) was added to this suspension at once. The resulting reaction mixture containing black precipitates and white powder (K_2CO_3) was stirred at 80 °C (the reaction was monitored by GC-MS analysis). After the reaction was complete, Pd-catalyst and K_2CO_3 were removed by filtration with acetone. The solvent was concentrated at reduced pressure. The resulting crude product was purified by silica gel column chromatography (hexane/ethyl acetate) and/or GPC (JAI, LC-9210 II NEXT) to give the product. The products are literature known.

Representative Procedure for Semireduction of Internal Alkynes (0.05 mol % Pd). Tolane (**1a**) (20 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol, 0.05 mol %), K_2CO_3 (276 mg, 2 mmol, 10 mol %), and 1,4-dioxane (20 mL) were added to a flame-dried Schlenk tube under an argon atmosphere. Within a minute, formic acid (1.08 mL, 25 mmol) was added to this suspension at once. The resulting reaction mixture containing black precipitates and white powder (K_2CO_3) was stirred at 80 °C for 9 d. After the reaction was complete, Pd-catalyst and K_2CO_3 were removed by filtration with acetone. The solvent was concentrated at reduced pressure. The yields were determined by ^1H NMR analysis.

Preparation of Pd-Catalysts. The mixture of $PdCl_2$ (9 mg, 0.05 mmol), K_2CO_3 (13.8 mg, 0.1 mmol), and HCO_2H (57.5 mg, 1.25 mmol) in 5 mL of dioxane was stirred at 80 °C for 1 h under Ar. The black precipitates with white powder obtained after filtration were washed with acetone, MeOH, and ultrapure water. Subsequent dryness under a vacuum gave the desired Pd-catalysts quantitatively. Pd-catalysts should be stored under Ar in a refrigerator.

The Reuse of Catalyst. After the reduction reaction was complete, the solution mixture was transferred to another vessel using a pipet. The residue, including black precipitates, was washed with acetone, MeOH, and water under air. After the dryness of black precipitates under reduced pressure, the next run was conducted.

*(Z)-Stilbene (**2a**).*[5h] Eluent for column chromatography, hexane only; colorless oil, 33.5 mg, 93%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.18−7.26 (m, 10H), 6.60 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.2, 130.2, 128.9, 128.2, 127.1.

*(Z)-1-(4-Styrylphenyl)ethanone (**2b**).*[5h] Eluent for column chromatography, hexane/ethyl acetate = 9/1; pale yellow oil, 35.1 mg, 79%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.23−7.26 (m, 5H), 6.72 (d, J = 12.3 Hz, 1H), 6.60 (d, J = 12.3 Hz, 1H), 2.57 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.6, 142.2, 136.6, 135.6, 132.4, 129.1, 129.0, 128.8, 128.3, 128.3, 127.5, 26.5.

*(Z)-4-Styrylmethylbenzoate (**2c**).*[26] Eluent for column chromatography, hexane/ethyl acetate = 9/1; colorless oil, 35.7 mg, 75%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.20−7.24 (m, 5H), 6.71 (d, J = 12.3 Hz, 1H), 6.61 (d, J = 12.3 Hz, 1H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 142.1, 136.6, 132.2, 129.5, 129.2, 128.8, 128.6, 128.3, 127.5, 52.0.

*(Z)-4-Styrylbenzaldehyde (**2d**).*[2c] Eluent for column chromatography, hexane/ethyl acetate = 9/1; pale yellow oil, 27.5 mg, 66%; ^1H NMR (399 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.23−7.26 (m, 5H), 6.76 (d, J = 12.3 Hz, 1H), 6.62 (d, J = 12.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.7, 143.7, 136.5, 134.9, 132.9, 129.7, 129.5, 128.9, 128.8, 128.4, 127.7.

*(Z)-1-Fluoro-4-styrylbenzene (**2e**).*[2d] Eluent for column chromatography, hexane/Et_3N = 99/1; colorless oil, 31.3 mg, 79%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.18−7.24 (m, 7H), 6.90 (t, J = 8.7 Hz, 2H), 6.59 (d, J = 12.3 Hz, 1H), 6.54 (d, J = 12.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (76 MHz, $CDCl_3$) δ 161.8 (d, J = 246 Hz), 137.0, 133.1 (d, J = 3 Hz), 130.5 (d, J = 8 Hz), 130.2, 129.0, 128.8, 128.3, 127.2, 115.1 (d, J = 22 Hz); ^{19}F NMR (375 MHz, $CDCl_3$) δ −117.84.

*(Z)-1-Methyl-4-styrylbenzene (**2f**).*[27] Eluent for column chromatography, hexane only; colorless oil, 32.2 mg, 83%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.18−7.28 (m, 5H), 7.14 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 6.55 (s, 2H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.5, 136.9, 134.3, 130.2, 129.5, 128.9, 128.8, 128.8, 128.2, 127.0, 21.2.

*(Z)-1-Methoxy-4-styrylbenzene (**2g**).*[28] Eluent for column chromatography, hexane/ethyl acetate = 9/1; yellow oil, 35.7 mg, 85%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.17−7.28 (m, 7H), 6.74−6.77 (m, 2H), 6.48−6.55 (m, 2H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.7, 137.6, 130.1, 129.7, 129.6, 128.8, 128.7, 128.2, 126.9, 113.6, 55.2.

*(E)-2-Styrylpyridine (**3h**).*[29] Eluent for column chromatography, hexane/ethyl acetate/Et_3N = 70/30/1; off-white solid, 26.1 mg, 72%; ^1H NMR (301 MHz, $CDCl_3$) δ 8.61 (d, J = 3.8 Hz, 1H), 7.64−7.70 (m, 2H), 7.58−7.62 (m, 3H), 7.36−7.43 (m, 3H), 7.29−7.33 (m, 1H), 7.14−7.21 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.6, 149.7, 136.6, 136.5, 132.7, 128.7, 128.3, 127.9, 127.1, 122.1.

*(Z)-3-Styrylpyridine (**2i**).*[30] Eluent for column chromatography, hexane/ethyl acetate/Et_3N = 70/30/1; yellow oil, 13.4 mg, 37%; ^1H NMR (399 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.37−8.42 (m, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.20−7.27 (m, 5H), 7.10−7.15 (m, 1H), 6.75 (d, J = 12.3 Hz, 1H), 6.55 (d, J = 12.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.0, 148.0, 136.4, 135.7, 132.8, 132.5, 128.6, 128.4, 127.5, 126.3, 122.9.

*(Z)-4-Styrylpyridine (**2j**).*[31] Eluent for column chromatography, hexane/ethyl acetate/Et_3N = 70/30/1; yellow oil, 18.5 mg, 51%; ^1H NMR (399 MHz, $CDCl_3$) δ 8.45 (d, J = 5.5 Hz, 2H), 7.20−7.29 (m, 5H), 7.11 (d, J = 5.5 Hz, 2H), 6.80 (d, J = 12.3 Hz, 1H), 6.50 (d, J = 12.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.8, 144.9, 136.1, 134.0, 128.7, 128.4, 127.8, 127.5, 123.5.

*(Z)-2-Styrylthiophene (**2k**).*[5h] Eluent for column chromatography, hexane only; colorless oil, 25.7 mg, 69%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.27−7.37 (m, 5H), 7.08 (dd, J = 5.0, 0.9 Hz, 1H), 6.96 (d, J = 3.7 Hz, 1H), 6.88 (dd, J = 5.2, 3.4 Hz, 1H), 6.70 (d, J = 11.9 Hz, 1H), 6.58 (d, J = 11.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.3, 128.9, 128.8, 128.5, 128.1, 127.5, 126.4, 125.5, 123.3.

*(Z)-3-Phenyl-2-propenoic Acid Ethyl Ester (**2l**).*[32] GPC was used for purification; pale yellow oil, 25.1 mg, 71%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.58 (d, J = 6.8 Hz, 2H), 7.30−7.37 (m, 3H), 6.95 (d, J = 12.3 Hz, 1H), 5.95 (d, J = 12.3 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 142.9, 134.8, 129.7, 128.9, 127.9, 119.9, 60.3, 14.1.

*(Z)-(2-Cyclohexylvinyl)benzene (**2m**).*[30] Eluent for column chromatography, hexane only; pale yellow oil, 29 mg, 78%; ^1H NMR (399 MHz, $CDCl_3$) δ 7.20−7.35 (m, 5H), 6.31 (d, J = 11.9 Hz, 1H), 5.48 (dd, J = 11.9, 11.4 Hz, 1H), 2.54−2.63 (m, 1H), 1.64−1.82 (m, 5H), 1.11−1.33 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.9, 137.9, 128.6, 128.2, 126.8, 126.4, 36.9, 33.3, 26.0, 25.7.

*(Z)-6-Dodecene (**2n**).*[2a] Eluent for column chromatography, hexane only; colorless oil, 26.6 mg, 79%; ^1H NMR (399 MHz, $CDCl_3$) δ 5.31−5.39 (m, 2H), 1.97−2.06 (m, 4H), 1.24−1.38 (m, 12H), 0.89 (t, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 129.9, 31.6, 29.5, 27.2, 22.6, 14.1.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b02169.

Screening of bases and reductants, TEM images, and NMR spectra of products (PDF)

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Notes

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J. Org. Chem. XXXX, XXX, XXX−XXX

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(12) The treatment of HCO_2H and K_2CO_3 in dioxane in the presence of catalyst C in Scheme 1 did not give a detectable amount of H_2. It is still unclear if the generation of H_2 from HCO_2H is important or not. The reduction using an excess amount of HCO_2H gave alkenes, followed by the reduction under a H_2 atmosphere which gave an alkane. Accordingly, intermediates may be different between the use of HCO_2H and H_2.

(13) The Pd-catalysts washed with water and MeOH often gave a higher chemoselectivity. The reason is unclear, but the invisible small Pd-particles showing a low selectivity might be rinsed out during washing.

(14) Black precipitates were tentatively subjected to TEM analysis. TEM images and the SAED pattern indicated that the present black precipitates are Pd-clusters (10−50 nm) of face-centered cubic (fcc) Pd-nanocrystals. The aggregates of Pd-clusters show large Pd-particles. K atoms can be omitted due to the low detection limit. Further analysis using TEM should be required for details. See the Supporting Information.

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