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Palladium on carbon-catalyzed solvent-free and solid-phase hydrogenation and Suzuki–Miyaura reaction

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ABSTRACT

The solvent-free and solid-phase hydrogenation of various reducible functionalities was efficiently catalyzed by heterogeneous palladium on carbon (Pd/C) under ambient hydrogen pressure and temperature. The Pd/C-catalyzed Suzuki–Miyaura coupling reaction between solid aryl bromides and solid arylboronic acids to generate the corresponding solid biaryls was also achieved under the totally solid-phase conditions.

1. Introduction

One of the main purposes of green sustainable chemistry is the elimination or reduction of using and generating hazardous substances during organic syntheses.[1] Waste prevention is also a key green sustainable chemistry principle, and the elimination of organic solvents is the ultimate goal.[2] The use of catalysts instead of stoichiometric amounts of reagents is also highly recommended,[3] and heterogeneous catalysts have especially significant advantages due to their air-stability, recoverability, reusability, non-residual property, etc.[4] The development of a heterogeneously catalyzed, solvent-free reaction could achieve an economically and environmentally friendly process based on a significant energy savings since only the appropriate and small amount of solvent is required to separate the catalyst from the reaction mixture, and the size of the reaction vessels could be reduced.

Palladium on charcoal (Pd/C), which has been commonly used as a hydrogenation catalyst, is finding wide applications in various types of reactions including cross-coupling reactions.[5,6] We recently developed the Pd/C-catalyzed cross-coupling reactions between aromatic halides and various types of nucleophilic species, such as aromatic boronic acids (Suzuki–Miyaura reaction),[7] monosubstituted alkynes (Sonogashira reaction),[8] or amines (Buchwald–Hartwig reaction) as liquid-phase reactions.[9] The Suzuki–Miyaura coupling reaction is particularly useful and effective for the preparation of biaryl units, which are contained as a partial structure of a wide variety of functional materials, such as pharmaceuticals, agrochemicals, liquid crystals, and so on.

The heterogeneously catalyzed solvent-free hydrogenation of aromatic nuclei, alkenes, and alkynes as well as the hydrogenolysis of epoxides using conventional catalysts, such as rhodium on carbon, platinum oxide, platinum on carbon, or Pd/C, has been reported.[10] The studies of these solvent-free catalyses mainly focused on the elucidation of mechanistic aspects, e.g., whether the reactions proceeded in the fused state or in the solid state, while their utility was not well-demonstrated. Furthermore, these reactions required pretreatment of the catalyst with a high heat, prior grinding of a mixture of the substrate and catalyst using a mortar and pestle, or/and use of a vast amount of catalyst, and basically achieved a very low conversion yield. Employment of newly developed transition-metal nanoparticles supported on molecular sieves,[11] nanozeolites,[12] activated carbon fibers,[13] carbon nanotubes,[14] or zinc (II) oxide[15] for the hydrogenation of alkenes, alkynes, nitro groups, or aromatics in the absent of solvents has recently been reported, although these reactions were carried out under pressurized hydrogen (0.5–4 MPa) except for the Ru(0)/nanozeolite-catalyzed hydrogenation of arenes (≤0.3 MPa),[12] and all substrates were liquid under the given reaction conditions.[11–15]

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Solvent-free Suzuki–Miyaura reactions have been achieved by stirring at 100 °C[16] or grinding,[17] but these are not solid-phase reactions since only liquid aryl halides were applicable to the former case and liquid Et_3N was used as a solvent and base in the latter case. Microwave reactors[18] or ball-milling equipment[19] have also been employed. However, solvent-free Suzuki–Miyaura reactions in a totally solid-phase using solid substrates and a heterogeneous palladium catalyst together with a solid inorganic base have never been reported in the literature, although $PdCl_2$, a homogeneous catalyst, was employed as only an example for the solid-phase Suzuki–Miyaura reaction.[20]

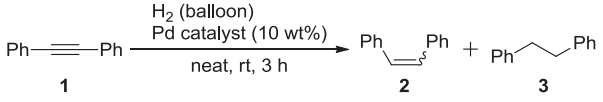
In this study, we demonstrate that the solvent-free and solid-phase Pd/C-catalyzed hydrogenation of various reducible functionalities as well as Suzuki–Miyaura coupling reactions efficiently proceeded without any liquid components.

2. Results and discussion

2.1. Solvent-free Pd/C-catalyzed hydrogenation

Several palladium species were screened as a catalyst for the solvent-free and solid-phase hydrogenation of diphenylacetylene (**1**) (Table 1). The hydrogenation smoothly proceeded at room temperature under ordinary hydrogen pressure using a variety of heterogeneous catalysts [10 percent of the weight of the substrate (**1**)], such as commercially available 10% Pd/C, 5% palladium on barium sulfate, 5% palladium on alumina, and our handmade 5% palladium on HP20,[21] which was developed as the alternative to Pd/C (entries 1 vs 2–5), to afford the corresponding solid alkane, diphenylethane (**3**) in 100% conversion within 3 h, although the intermediary *cis*-stilbene (**2**) remained under palladium black-catalyzed conditions (entry 6). Furthermore, the reaction progress was found to depend on neither the suppliers nor types of 10% Pd/C products (entries 2 and 7–9). On the basis of these results, Pd/C was chosen as the catalyst for the substrate screening (Table 2).[22,23]

Table 1
Screening of heterogeneous palladium catalysts

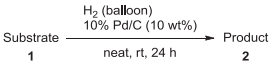


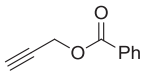
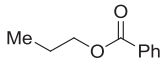
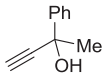
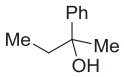
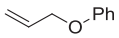
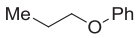
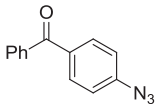
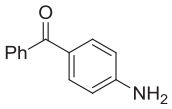
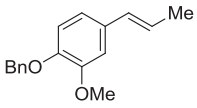
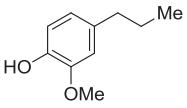
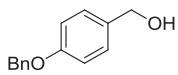
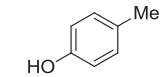
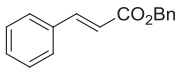
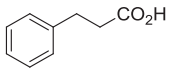
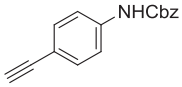
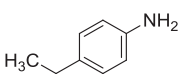
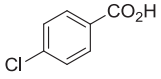
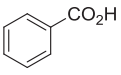
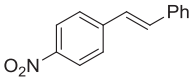
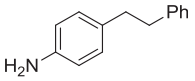
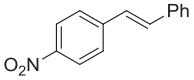
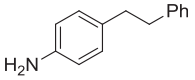
Entry	Pd catalyst (supplier)	Product ratio (%)[a]
		1:**2**:**3**
1	—	100:0:0
2	10% Pd/C (Aldrich)	0:0:100
3	5% Pd/$BaSO_4$ (Aldrich)	0:0:100
4	5% Pd/Al_2O_3 (Aldrich)	0:0:100
5	5% Pd/HP20	0:0:100
6	Pd black (Aldrich)	0:37:63
7	10% Pd/C (Wako Pure Chemical)	0:0:100
8	10% Pd/C [N.E. Chemcat (K-type)]	0:0:100
9	10% Pd/C [N.E. Chemcat (NX-type)]	0:0:100

[a] Determined by ^1H NMR.

Since it was difficult to monitor the reaction progress unlike in liquid reactions, the reaction time was fixed at 24 h. Alkyne, alkene, and azide derivatives were readily hydrogenated to the corresponding alkanes and amines (entries 1–7, 10, 11, and 15). The hydrogenolysis of either benzyl ethers or esters, *N*-Cbz and aromatic chloride[24] functionalities smoothly proceeded (entries 7–13). Although the hindered benzylic alcohols and diphenylketones were not reduced (entries 4 and 6), 4-benzyloxybenzylalcohol underwent deoxygenation of the benzylic alcohol moiety to afford the volatile *p*-cresol with the hydrogenolysis of the

Table 2
Scope and limitation of solvent-free Pd/C-catalyzed hydrogenation

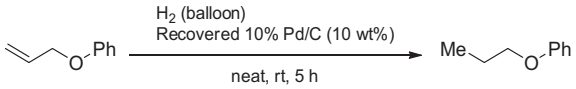


Entry	Substrate	Product	Yield (%)[a]
1	1-Dodecyne	Dodecane	83
2	6-Dodecyne	Dodecane	84
3			73
4			89
5			83
6			89
7			100
8			75[b]
9	$PhCO_2Bn$	$PhCO_2H$	92
10			100
11			84
12	Cbz-Gly–OH	Gly–OH	90
13[c]			82
14			—[d]
15[e]			90

[a] Isolated yield. No other products were obtained.
[b] Determined by GC.
[c] K_2CO_3 (1.2 equiv) was added. The reaction was carried out at 50 °C.
[d] The yield was not determined. A mixture of 4-nitrostilbene and 4-phenethylaniline was obtained in the ratio of 65 to 35, respectively.
[e] The reaction was carried out at 80 °C.

O-benzyl group (entry 8). The nitro group was also hydrogenated in a similar manner, although mild heat conditions at 80 °C were necessary for the effective conversion (entries 14 and 15). It should be noted that a couple of solid substrates were converted to the corresponding solid reduced products without any liquid sources under the simple mixing conditions of Pd/C and substrates in hydrogen atmosphere (entries 6 and 13).[25] Furthermore, 10% Pd/C was successfully recovered and reused at least until the fifth run without any significant loss in catalytic activity (Table 3).

Table 3
Reuse test of 10% Pd/C

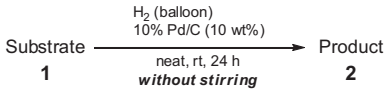


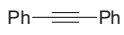
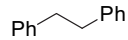
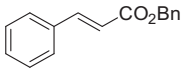
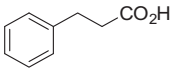
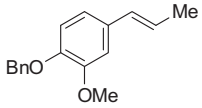
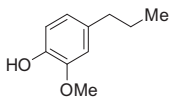
Run	First	Second	Third	Fourth	Fifth
Yield (%) of propoxybenzene[a]	81	82	88	80	79
Yield (%) of recovered 10% Pd/C	100	93	90	95	88

[a] Isolated yield. Propoxybenzene was obtained as the sole product.

During the course of our study, it was found that the reaction mixtures had not been sufficiently stirred at the edges of the flask. Such observation suggested that the solvent-free hydrogenation could take place with even poor contact between palladium metal of the catalyst and the substrate. To elucidate the stirring effect on the reaction progress, the mixed substrate and 10% Pd/C (gently shaken in the flask by hand for 10 s)[26] were only left under hydrogen atmosphere at room temperature without stirring. As the result, both hydrogenations of the carbon–carbon multiple bonds and hydrogenolyses of benzyl ethers and esters surprisingly proceeded and quantitatively afforded the fully reduced products (Table 4, entries 1–3).

Table 4
Solvent-free Pd/C-catalyzed hydrogenation without stirring



Entry	Substrate	Product	Yield (%)[a]
1			99
2			98
3			97

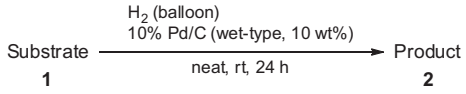
[a] Isolated yield. No other products were obtained.

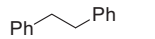
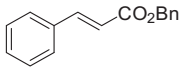
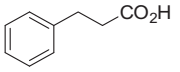
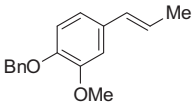
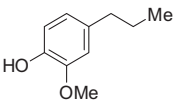
Although dry-type Pd/Cs are extensively used in laboratory-scale reactions due to their easy handling and storage, they are likely to be avoided in large scale reactions for industrial applications owing to their potential risk of ignition. The wet-type Pd/Cs, which contain approximately 50 wt % water, are desired for practical use because of the significant risk reduction. As shown in Table 5, wet-type 10% Pd/C (N.E. Chemcat, K-type) was compatible with the corresponding dry-type for the solvent-free hydrogenation.

2.2. Solvent- and ligand-free Pd/C-catalyzed Suzuki–Miyaura reaction

The solvent- and ligand-free Pd/C-catalyzed Suzuki–Miyaura reactions were next investigated. When the cross-coupling reactions between bromobenzene and phenylboronic acid derivatives at 80 °C were carried out in a test tube using an organic synthesizer, which could control the stirring and heating,[27] the desired biaryl compounds were obtained in moderate to good yields. After careful observation of the reaction process, we found

Table 5
Employment of wet-type 10% Pd/C for the solvent-free hydrogenation

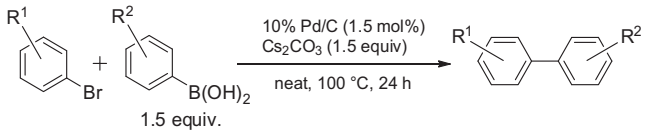


Entry	Substrate	Product	Yield (%)[a]
1			83
2			94
3			88

[a] Isolated yield. No other products were obtained.

that a significant quantity of sublimed aryl bromides adhered to the upper part of the test tube. Since such aryl bromides were not able to contact with the arylboronic acids, 10% Pd/C, and base, the yields varied depending on the kinds of bromides. To keep the continuous contact of these materials at the same temperature, they were sealed in a small glass vial and the mixture was shaken in a constant-temperature incubator (TAITEC Bioshaker BR-23FH). When 1.5 equiv of phenylboronic acid was used for the cross-coupling with 4-bromonitrobenzene in the presence of 1.5 mol % of 10% Pd/C and 1.5 equiv of Cs_2CO_3 as the base at 100 °C, the desired 4-nitrobiphenyl was obtained in 92% isolated yield (Table 6, entry 2), while the lower yield (73%) was achieved using 1.1 equiv of phenylboronic acid (entry 1). The solvent- and ligand-free conditions promoted the cross-coupling of the arylboronic acids bearing either an electron-withdrawing or -donating group with a variety of aryl bromides to afford the corresponding biaryls in moderate to excellent yields (entries 2–15) only except for the combination of

Table 6
The solvent- and ligand-free, heterogeneous Pd/C-catalyzed Suzuki–Miyaura coupling

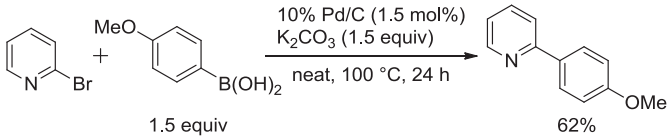


Entry	R^1	R^2	Yield (%)[a]
1[b]	4-NO_2	H	73
2	4-NO_2	H	92
3	4-NO_2	4-MeO	90
4	4-NO_2	3-MeO	94
5	4-NO_2	2-MeO	100
6	4-NO_2	4-Me	74
7	4-NO_2	4-COMe	100
8	4-CHO	4-MeO	100
9[c]	4-CN	4-MeO	88
10	4-CO_2Et	4-MeO	77
11	4-OH	4-MeO	85
12	4-NH_2	4-MeO	55
13	2-Me	4-MeO	50
14	4-MeO	H	81
15	1-Br–naphthalene	4-MeO	57
16	4-OH	4-Ac	23
17	4-MeO	4-Ac	10
18	4-Cl–nitrobenzene	4-MeO	51

[a] Isolated yield.
[b] Phenylboronic acid (1.1 equiv) was used.
[c] 4-Methoxyphenylboronic acid (1.1 equiv) was used.

electron-deficient arylboronic acids and electron-sufficient aryl bromides (entries 16 and 17). Furthermore, 4-chloronitrobenzene underwent the cross-coupling with 4-methoxyphenylboronic acid, although chloroarenes were generally less reactive (entry 18). It is noteworthy that solid arylboronic acids could be smoothly cross-coupled with solid aryl bromides at 100 °C without any liquid materials to give the corresponding solid coupling products (entries 1–3, 6, 7, and 9).[28]

We recently developed an efficient and wide-range applicable protocol for the liquid-phase Pd/C-catalyzed Suzuki–Miyaura cross-coupling reaction involving heteroarenes in a solvent, although the hetero-Suzuki–Miyaura coupling reactions were generally sluggish due to the catalyst poison effect caused by heteroatoms possessing a lone pair.[7e,f] The Pd/C-catalyzed Suzuki–Miyaura reaction between 4-methoxyphenylboronic acid and 2-bromopyridine effectively proceeded even under solvent- and ligand-free conditions (Scheme 1).



Scheme 1. Solvent- and ligand-free Pd/C-catalyzed Suzuki–Miyaura reaction between 4-methoxyphenylboronic acid and 2-bromopyridine.

3. Conclusion

We have developed the solvent-free and solid-phase Pd/C-catalyzed hydrogenation and Suzuki–Miyaura coupling reaction. A variety of reducible functionalities could be hydrogenated under ambient hydrogen pressure and temperature without any liquid materials. The cross-coupling between solid aryl halides and solid arylboronic acids in the presence of solid 10% Pd/C and Cs_2CO_3 or K_2CO_3 leading to the formation of solid biaryls has been achieved under the absolute solid-phase conditions. These methodologies can provide facile, efficient, and environmentally-benign heterogeneous processes due to the simplicity and wide applicability of the substrates without ligands and solvents.

4. Experimental

4.1. General

All reagents were obtained from commercial sources and used without further purification. Analytical thin-layer chromatography (TLC) was carried out on pre-coated Silica gel 60 F_{254} plates (32–63 μm particle size) and visualized with UV light (254 nm). The 10% Pd/C was obtained from the N.E. Chemcat Co. (Tables 2–5 and Scheme 1). Flash column chromatography was performed with Silica gel 60 (40–63 μm particle size, Merck & Co., Inc.) or Silica gel 60 N (100–210 μm, Kanto Chemical Co., Inc.). ^{1}H and ^{13}C NMR spectra were recorded by a JEOL JNM EX-400 or AL-400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) using $CDCl_3$ as the solvent. Chemical shifts (δ) are expressed in parts per million and are internally referenced [0.00 ppm for $CDCl_3$ (tetramethylsilane) or D_2O (sodium 3-(trimethylsilyl)propionate-2,2′,3,3′-d_4) or 2.04 ppm for acetone-d_6 for ^{1}H NMR and 77.0 ppm for $CDCl_3$, 0.00 ppm D_2O (sodium 3-(trimethylsilyl)propionate-2,2′,3,3′-d_4), or 29.8 ppm for acetone-d_6 for ^{13}C NMR]. The NMR spectra of all compounds were identical with those reported in the literature or those of the commercial products from Sigma–Aldrich Co. (Sigma–Aldrich) or Tokyo Chemical Industry Co. Ltd. (TCI). Mass spectra were taken on a JEOL JMS-SX102A instrument.

4.2. General procedure for the solvent-free Pd/C-catalyzed hydrogenation

In a 25-mL round-bottom flask were placed the substrate (1.00 mmol) and 10% Pd/C (10 wt % of the substrate), and the mixture was stirred using a magnetic stirrer at room temperature under a hydrogen atmosphere (balloon) for 24 h Et_2O (20 mL) was added, and the mixture was passed through a membrane filter (Millipore, Millex-LH, 0.45 μm) to remove the catalyst. The filtrate was concentrated in vacuo to give the pure product.

4.2.1. Bibenzyl (Table 1; Tables 3 and 4, entry 1). ^{1}H NMR ($CDCl_3$): δ 2.89 (4H, s), 7.14–7.18 (6H, m), 7.25 (4H, t, J=7.7 Hz); ^{13}C NMR ($CDCl_3$): δ 37.9, 125.9, 128.2, 128.3, 141.7. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) m/z (%): 182 (M^+, 41), 91 (100).

4.2.2. Dodecane (Table 2, entries 1 and 2). ^{1}H NMR ($CDCl_3$): δ 0.88 (6H, m), 1.26 (20H, m); ^{13}C NMR ($CDCl_3$): δ 32.0, 29.8, 29.7, 22.8, 14.1. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) m/z (%): 170 (M^+, 6), 85 (67), 71 (82), 57 (100).

4.2.3. Propyl benzoate (Table 2, entry 3). ^{1}H NMR ($CDCl_3$): δ 1.03 (3H, t, J=7.0 Hz), 1.79 (2H, sext, J=7.0 Hz), 4.28 (2H, t, J=7.0 Hz), 7.43 (2H, t, J=7.7 Hz), 7.54 (1H, t, J=7.7 Hz), 8.04 (2H, d, J=7.7 Hz); ^{13}C NMR ($CDCl_3$): δ 10.4, 22.0, 66.4, 128.2, 129.4, 132.7, 166.6. The NMR spectra were identical with those of the commercial products from Aldrich. MS (EI) m/z (%): 164 (M^+, 2), 105 (100).

4.2.4. 2-Phenyl-2-butanol (Table 2, entry 4). ^{1}H NMR ($CDCl_3$): δ 0.81 (3H, t, J=7.2 Hz), 1.55 (3H, s), 2.06 (2H, m), 7.24 (1H, t, J=7.7 Hz), 7.34 (2H, dd, J=7.7, 7.2 Hz), 7.44 (2H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 8.2, 29.5, 36.6, 74.8, 125.1, 126.6, 128.2, 147.7. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) m/z (%): 150 (M^+, 3), 121 (100).

4.2.5. Propoxybenzene (Table 2, entry 5)[36]. ^{1}H NMR ($CDCl_3$): δ 1.02 (3H, t, J=7.2 Hz), 1.79 (2H, sext, J=7.2 Hz), 3.90 (2H, t, J=7.2 Hz), 6.88–6.93 (3H, m), 7.26 (2H, t, J=8.0 Hz); ^{13}C NMR ($CDCl_3$): δ 10.5, 22.6, 69.4, 114.5, 120.5, 129.4, 159.2. MS (EI) m/z (%): 136 (M^+, 32), 94 (100).

4.2.6. 4-Aminobenzophenone (Table 2, entry 6). ^{1}H NMR ($CDCl_3$): δ 4.19 (2H, br s), 6.66 (2H, d, J=8.2 Hz), 7.43–7.55 (3H, m), 7.70–7.73 (4H, m); ^{13}C NMR ($CDCl_3$): δ 113.6, 127.3, 128.0, 129.5, 131.4, 132.9, 138.8, 151.0, 195.3. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) m/z (%): 197 (M^+, 74), 120 (100).

4.2.7. 2-Methoxy-4-propylphenol (Table 2, entry 7; Tables 3 and 4, entry 3)[37]. ^{1}H NMR ($CDCl_3$): δ 0.92 (3H, t, J=7.2 Hz), 1.59 (2H, dd, J=7.2, 7.7 Hz), 2.50 (2H, t, J=7.7 Hz), 3.81 (3H, s), 6.63 (1H, br s), 6.63–6.65 (2H, m), 6.81 (1H, d, J=8.2 Hz); ^{13}C NMR ($CDCl_3$): δ 13.7, 24.7, 37.6, 55.7, 111.0, 114.1, 120.9, 134.5. MS (EI) m/z (%): 166 (M^+, 27), 137 (100).

4.2.8. p-Cresol (Table 2, entry 8). ^{1}H NMR ($CDCl_3$): δ 2.32 (3H, s), 5.78 (1H, br s), 6.79 (2H, d, J=8.1 Hz), 7.07 (2H, d, J=8.1 Hz); ^{13}C NMR ($CDCl_3$): δ 20.4, 115.1, 130.0, 152.9 (one signal could not be located because of its overlap with another signal). The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) m/z (%): 108 (M^+, 88), 107 (100), 77 (62).

4.2.9. Benzoic acid (Table 2, entries 9 and 13). ^{1}H NMR ($CDCl_3$): δ 7.47 (2H, dd, J=7.2, 7.7 Hz), 7.61 (1H, t, J=7.2 Hz), 8.14 (2H, d, J=7.7 Hz), 12.7 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 128.4, 129.3, 130.2,

133.8, 172.6. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) *m*/*z* (%): 122 (M^+, 86), 105 (100), 77 (62).

4.2.10. Hydrocinnamic acid (Table 2, entry 10, Tables 3 and 4, entry 2). ^{1}H NMR ($CDCl_3$): δ 2.65 (2H, t, *J*=7.7 Hz), 2.93 (2H, t, *J*=7.7 Hz), 7.17–7.29 (5H, m), 9.75 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 30.5, 35.5, 126.3, 128.2, 128.5, 140.1, 179.0. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) *m*/*z* (%): 150 (M^+, 46), 104 (54), 91 (100).

4.2.11. 4-Ethylaniline (Table 2, entry 11). ^{1}H NMR ($CDCl_3$): δ 1.18 (3H, t, *J*=7.5 Hz), 2.53 (2H, q, *J*=7.5 Hz), 3.48 (2H, br s), 6.60 (2H, d, *J*=8.2 Hz), 6.98 (2H, d, *J*=8.2 Hz); ^{13}C NMR ($CDCl_3$): δ 15.9, 27.9, 115.2, 128.5, 134.3, 144.0. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) *m*/*z* (%): 121 (M^+, 44), 106 (100).

4.2.12. Glycine (Table 2, entry 12). ^{1}H NMR (D_2O): δ 3.57 (2H, s); ^{13}C NMR: δ 44.2, 179.2. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (FAB^+, NBA) *m*/*z* (%): 75 (M^+, a peak for the product was observed in matrix peaks).

4.2.13. 4-Aminodibenzyl (Table 2, entries 13 and 14)[38]. ^{1}H NMR ($CDCl_3$): δ 2.75–2.86 (4H, m), 6.55 (2H, d, *J*=8.5 Hz), 6.93 (2H, d, *J*=8.5 Hz), 7.13–7.17 (3H, m), 7.24 (2H, t, *J*=8.2 Hz); ^{13}C NMR ($CDCl_3$): δ 37.0, 38.2, 115.1, 125.7, 128.2, 128.4, 129.1, 131.7, 142.0, 144.3. MS (EI) *m*/*z* (%): 197 (M^+, 16), 106 (100).

4.3. Reuse test of 10% Pd/C for the hydrogenation of allyl phenyl ether (Table 3)

Five 50-mL round-bottom flasks were prepared. In each flask were placed ally phenyl ether (132 μL, 1.00 mmol) and 10% Pd/C (13.4 mg, 10 wt % of allyl phenyl ether), and the mixtures were stirred using a magnetic stirrer at room temperature under a hydrogen atmosphere (balloon) for 5 h H_2O (10 mL) and Et_2O (10 mL) were added to each flask, and the mixtures of all flasks were passed through a filter paper [Kiriyama, No. 5C (1 μm)]. The filtrate was separated into two layers, and the organic layer was concentrated in vacuo to give propoxybenzene (554 mg, 81%). 10% Pd/C was recovered in 100% yield (67.0 mg), and the recovered Pd/C catalyst (67.0 mg) was divided into five portions and used for the second run. Five 50-mL round-bottom flasks were prepared. In each flask were placed ally phenyl ether (132 μL, 1.00 mmol) and 10% Pd/C (13.4 mg), and the mixtures were treated in the same way as the first run to give propoxybenzene (558 mg, 82%). 10% Pd/C was recovered in 93% yield (62.3 mg), and the recovered Pd/C catalyst (53.6 mg) was divided into four portions and used for the third run. Four 50-mL round-bottom flasks were prepared. In each flask were placed ally phenyl ether (132 μL, 1.00 mmol) and 10% Pd/C (13.4 mg), and the mixtures were treated in the same way as the first run to give propoxybenzene (479 mg, 88%). 10% Pd/C was recovered in 90% yield (48.2 mg), and the recovered Pd/C catalyst (40.2 mg) was divided into three portions and used for the fourth run. Three 50-mL round-bottom flasks were prepared. In each flask was placed ally phenyl ether (132 μL, 1.00 mmol) and 10% Pd/C (13.4 mg), and the mixtures were treated in the same way as the first run to give propoxybenzene (327 mg, 80%). 10% Pd/C was recovered in 95% yield (38.2 mg), and the recovered Pd/C catalyst (26.8 mg) was divided into two portions and used for the fifth run. Two 50-mL round-bottom flasks were prepared. In each flask were placed ally phenyl ether (132 μL, 1.00 mmol) and 10% Pd/C (13.4 mg), and the mixtures were treated in the same way as the first run to give propoxybenzene (216 mg, 79%). 10% Pd/C was recovered in 88% yield (23.5 mg).

4.4. General procedure for the solvent- and ligand-free Pd/C-catalyzed Suzuki–Miyaura reaction

In a 10-mL glass vial were placed the aryl halide (0.500 mmol), the arylboronic acid (0.750 mmol), 10% Pd/C (0.80 mg, 1.5 mol %), and Cs_2CO_3 (244 mg, 0.750 mmol), and the mixture in a constant-temperature incubator (Taitec Bioshaker BR-23FH) was shaken with 200 rpm at 100 °C for 24 h H_2O (10 mL) and Et_2O (10 mL) were added, and the mixture was passed through a membrane filter (Millipore, Millex-LH, 0.45 μm) to remove the catalyst. The aqueous layer of the filtrate was extracted with Et_2O (8 mL), and the combined organic layers were washed with brine (8 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc) to give the corresponding biaryl, the structure of which was confirmed by comparison to the literature structure.

4.4.1. 4-Nitro-1,1′-biphenyl (Table 6, entries 1 and 2)[7c]. ^{1}H NMR ($CDCl_3$): δ 7.43–7.53 (3H, m), 7.63 (2H, d, *J*=6.8 Hz), 7.74 (2H, d, *J*=8.8 Hz), 8.30 (2H, t, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 124.1, 127.4, 127.8, 128.9, 129.1, 138.7, 147.1, 147.6. MS (EI) *m*/*z* (%): 199 (M^+, 100), 152 (80).

4.4.2. 4-Methoxy-4′-nitro-1,1′-biphenyl (Table 6, entries 3 and 18). ^{1}H NMR ($CDCl_3$): δ 3.86 (3H, s), 7.01 (2H, d, *J*=9.0 Hz), 7.57 (2H, d, *J*=9.0 Hz), 7.67 (2H, d, *J*=8.8 Hz), 8.24 (2H, d, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 55.3, 114.5, 124.1, 127.0, 128.5, 130.9, 146.4, 147.1, 160.4. The NMR spectra were identical with those of the commercial products from TCI. MS (EI) *m*/*z* (%): 229 (M^+, 100), 199 (17).

4.4.3. 3-Methoxy-4′-nitro-1,1′-biphenyl (Table 6, entry 4)[39]. ^{1}H NMR ($CDCl_3$): δ 3.87 (3H, s), 6.97 (1H, dd, *J*=2.0, 8.0 Hz), 7.12 (1H, m), 7.19 (1H, d, *J*=8.0 Hz), 7.40 (1H, t, *J*=8.0 Hz), 7.70 (2H, d, *J*=8.8 Hz), 8.26 (2H, d, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 55.8, 113.7, 114.5, 120.2, 124.5, 128.2, 130.6, 140.6, 147.5, 147.9, 160.6. MS (EI) *m*/*z* (%): 229 (M^+, 100), 199 (40).

4.4.4. 2-Methoxy-4′-nitro-1,1′-biphenyl (Table 6, entry 5)[7d]. ^{1}H NMR ($CDCl_3$): δ 3.86 (3H, s), 7.01 (1H, d, *J*=8.3 Hz), 7.06 (1H, t, *J*=7.6 Hz), 7.32 (1H, d, *J*=7.6 Hz), 7.39 (1H, dd, *J*=7.6, 8.3 Hz), 7.68 (2H, d, *J*=8.8 Hz), 8.23 (2H, d, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 55.5, 111.3, 121.0, 123.1, 128.1, 130.1, 130.2, 130.6, 145.4, 146.5, 156.3. MS (EI) *m*/*z* (%): 229 (M^+, 100), 214 (47), 168 (52).

4.4.5. 4-Methyl-4′-nitro-1,1′-biphenyl (Table 6, entry 6)[7d]. ^{1}H NMR ($CDCl_3$): δ 2.42 (3H, s), 7.30 (2H, d, *J*=8.4 Hz), 7.51 (2H, d, *J*=8.4 Hz), 7.71 (2H, d, *J*=9.0 Hz), 8.27 (2H, d, *J*=9.0 Hz); ^{13}C NMR ($CDCl_3$): δ 21.2, 124.1, 127.2, 127.4, 129.9, 135.8, 139.1, 146.9, 147.6. MS (EI) *m*/*z* (%): 213 (M^+, 100), 183 (26), 165 (31), 152 (41).

4.4.6. 4-Acetyl-4′-nitrobiphenyl (Table 6, entry 7)[7b]. ^{1}H NMR ($CDCl_3$): δ 2.67 (3H, s), 7.73 (2H, d, *J*=8.3 Hz), 7.78 (2H, d, *J*=8.8 Hz), 8.09 (2H, d, *J*=8.3 Hz), 8.33 (2H, d, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 26.7, 124.2, 127.6, 128.1, 129.1, 137.1, 143.1, 146.2, 147.6, 197.4. MS (EI) *m*/*z* (%): 241 (M^+, 38), 226 (100), 152 (24).

4.4.7. 4′-Methoxy-[1,1′-biphenyl]-4-carboxaldehyde (Table 6, entry 8)[7d]. ^{1}H NMR ($CDCl_3$): δ 3.86 (3H, s), 7.01 (2H, d, *J*=8.7 Hz), 7.58 (2H, d, *J*=8.7 Hz), 7.71 (2H, d, *J*=8.2 Hz), 7.92 (2H, d, *J*=8.2 Hz), 10.03 (1H, s); ^{13}C NMR ($CDCl_3$): δ 55.4, 114.5, 127.1, 128.5, 130.3, 132.1, 134.7, 146.8, 160.1, 191.9. MS (EI) *m*/*z* (%): 212 (M^+, 100), 197 (15).

4.4.8. 4′-Methoxy-1,1′-biphenyl-4-carbonitrile (Table 6, entry 9)[34]. ^{1}H NMR ($CDCl_3$): δ 3.85 (3H, s), 6.99 (2H, d, *J*=8.7 Hz), 7.52 (2H, d, *J*=8.7 Hz), 7.62 (2H, d, *J*=8.2 Hz), 7.67 (2H, d, *J*=8.2 Hz); ^{13}C NMR

($CDCl_3$): δ 55.3, 110.0, 114.5, 119.0, 127.0, 128.3, 131.4, 132.5, 145.1, 160.2. MS (EI) *m*/*z* (%): 209 (M^+, 100), 194 (31), 166 (44).

4.4.9. Ethyl 4′-methoxy-1,1′-biphenyl-4-carboxylate (Table 6, entry 10)[40]. ^1H NMR ($CDCl_3$): δ 1.40 (3H, t, *J*=7.2 Hz), 3.84 (3H, s), 4.39 (2H, q, *J*=7.2 Hz), 6.98 (2H, d, *J*=8.2 Hz), 7.55 (2H, d, *J*=8.2 Hz), 7.60 (2H, d, *J*=8.2 Hz), 8.07 (2H, d, *J*=8.2 Hz); ^{13}C NMR ($CDCl_3$): δ 14.3, 55.3, 60.8, 114.3, 126.4, 128.3, 128.6, 130.0, 132.4, 145.0, 159.8, 166.5. MS (EI) *m*/*z* (%): 256 (M^+, 100), 211 (56).

4.4.10. 4-Hydroxy-4′-methoxy-1,1′-biphenyl (Table 6, entry 11). ^1H NMR (acetone-d_6): δ 3.79 (3H, s), 6.92 (2H, d, *J*=8.8 Hz), 6.95 (2H, d, *J*=8.8 Hz), 7.44 (2H, d, *J*=8.6 Hz), 7.49 (2H, d, *J*=8.6 Hz), 8.38 (1H, s); ^{13}C NMR (acetone-d_6): δ 55.5, 114.9, 116.5, 128.1, 128.3, 132.9, 134.2, 157.3, 159.6. The NMR spectra were identical with those of the commercial products from TCI. MS (EI) *m*/*z* (%): 200 (M^+, 100), 185 (52).

4.4.11. 4-Amino-4′-methoxybiphenyl (Table 6, entry 12)[41]. ^1H NMR ($CDCl_3$): δ 3.68 (2H, br s), 3.81 (3H, s), 6.72 (2H, d, *J*=8.2 Hz), 6.93 (2H, d, *J*=8.5 Hz), 7.35 (2H, d, *J*=8.2 Hz), 7.44 (2H, d, *J*=8.5 Hz); ^{13}C NMR ($CDCl_3$): δ 29.7, 55.3, 114.1, 115.4, 127.4, 131.3, 133.8, 145.3, 158.4. MS (EI) *m*/*z* (%): 199 (M^+, 100), 184 (84).

4.4.12. 2-Methyl-4′-methoxy-1,1′-biphenyl (Table 6, entry 13)[7d]. ^1H NMR ($CDCl_3$): δ 2.27 (3H, s), 3.84 (3H, s), 6.94 (2H, d, *J*=8.2 Hz), 7.21–7.26 (6H, m); ^{13}C NMR ($CDCl_3$): δ 20.5, 55.2, 113.5, 125.7, 126.9, 129.9, 130.2, 134.4, 135.5, 141.5, 158.5. MS (EI) *m*/*z* (%): 198 (M^+, 100), 183 (25).

4.4.13. 4-Methoxy-1,1′-biphenyl (Table 6, entry 14). ^1H NMR ($CDCl_3$): δ 3.81 (3H, s), 6.96 (2H, d, *J*=8.7 Hz), 7.28 (1H, t, *J*=7.7 Hz), 7.39 (2H, t, *J*=7.7 Hz), 7.51 (2H, d, *J*=8.7 Hz), 7.54 (2H, d, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 55.3, 114.2, 126.6, 126.7, 128.1, 128.7, 133.7, 140.8, 159.1. The NMR spectra were identical with those of the commercial products from Sigma–Aldrich. MS (EI) *m*/*z* (%): 184 (M^+, 100), 169 (36), 141 (45).

4.4.14. 1-(4-Methoxyphenyl)naphthalene (Table 6, entry 15)[42]. ^1H NMR ($CDCl_3$): δ 3.86 (3H, s), 7.01 (2H, d, *J*=8.8 Hz), 7.38–7.50 (6H, m), 7.81 (1H, d, *J*=8.3 Hz), 7.87 (1H, d, *J*=7.8 Hz), 7.92 (1H, d, *J*=8.3 Hz); ^{13}C NMR ($CDCl_3$): δ 55.3, 113.7, 125.4, 125.7, 125.9, 126.0, 126.9, 127.3, 128.2, 131.1, 131.8, 133.1, 133.8, 139.9, 158.9. MS (EI) *m*/*z* (%): 234 (M^+, 100), 219 (24).

4.4.15. 4-Acetyl-4′-hydroxy-1,1′-biphenyl (Table 6, entry 16)[43]. ^1H NMR ($CDCl_3$): δ 2.64 (3H, s), 5.06 (1H, br s), 6.95 (2H, d, *J*=8.4 Hz), 7.54 (2H, d, *J*=8.4 Hz), 7.64 (2H, d, *J*=8.4 Hz), 8.02 (2H, d, *J*=8.4 Hz); ^{13}C NMR ($CDCl_3$): δ 26.6, 115.9, 126.6, 128.6, 129.0, 132.5, 135.3, 145.3, 155.9. 197.8. MS (EI) *m*/*z* (%): 212 (M^+, 57), 197 (100).

4.4.16. 4-Acetyl-4′-methoxy-1,1′-biphenyl (Table 6, entry 17)[7c]. ^1H NMR ($CDCl_3$): δ 2.63 (3H, s), 3.86 (3H, s), 7.00 (2H, d, *J*=8.8 Hz), 7.58 (2H, d, *J*=8.8 Hz), 7.64 (2H, d, *J*=8.4 Hz), 8.01 (2H, d, *J*=8.4 Hz); ^{13}C NMR ($CDCl_3$): δ 26.6, 55.4, 114.4, 126.6, 128.4, 128.9, 132.2, 135.3, 145.4, 159.9. 197.9. MS (EI) *m*/*z* (%): 226 (M^+, 58), 211 (100).

4.4.17. 2-(4-Methoxyphenyl)pyridine (Scheme 1)[7e]. ^1H NMR ($CDCl_3$): δ 3.83 (3H, s), 6.98 (2H, d, *J*=6.8 Hz), 7.14 (1H, ddd, *J*=1.5, 4.9, 6.8 Hz), 7.64 (1H, m), 7.68 (1H, m), 7.94 (2H, d, *J*=8.8 Hz), 8.64 (1H, m); ^{13}C NMR ($CDCl_3$): δ 55.3, 114.1, 119.7, 121.3, 128.1, 132.0, 136.6, 149.5, 157.1, 160.4. MS (EI) *m*/*z* (%): 185 (M^+, 100), 170 (24).

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22. 10% Pd/C [N.E. Chemcat (K-type)] was used in Tables 2–6 and Scheme 1. The palladium particle size and carbon surface area of the 10% Pd/C [N.E. Chemcat (K-type)] are approximately 5 nm and 1100 m^2/g, respectively.
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28. The melting points of both substrates and products are over 100 °C in Table 6, entries 1–3, 6, 7, and 9. The melting points of 4-nitrobromobenzene (entries 1–3, 6, and 7),[29] 4-bromobenzonitrile (entry 9),[30] phenylboronic acid (entries 1 and 2),[31] 4-methoxyphenylboronic acid (entries 3 and 9),[31] *p*-tolylboronic acid (entry 6),[32] 4-acetylphenylboronic acid (entry 7),[33] 4-nitrobiphenyl (entries 1 and 2),[7a] 4-methoxy-4′-nitrobiphenyl (entry 3),[7a] 4-methyl-4'nitrobiphenyl (entry 6),[34] 4-acetyl-4′-nitrobiphenyl (entry 7),[7a] and 4-cyano-4′-methoxybiphenyl (entry 9)[35] are 127 °C, 113.5 °C, 215.5–219 °C, 202–206 °C, 242–245 °C, 231–233 °C, 113–114 °C, 107–108 °C, 142.5–143 °C, 151–152 °C, and 104 °C, respectively.
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