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Heterogeneous Pd/C-catalyzed ligand-free Suzuki–Miyaura coupling reaction using aryl boronic esters

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Abstract—Heterogeneous Pd/C-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl boronic esters with aryl bromides was successfully carried out in aqueous media at room temperature without the use of a ligand such as phosphine derivatives.

1. Introduction

The Suzuki–Miyaura coupling reaction is a common and convenient tool for C–C bond formation during the construction of biaryls. Because biaryl moieties are used as the building block of a wide range of pharmaceuticals, herbicides, natural products, polymers, etc., much effort has been spent on the development of simple and practical conditions for the Suzuki–Miyaura coupling reaction.[1] Suzuki–Miyaura coupling reactions have been traditionally employed using homogeneous palladium catalysts in the presence of phosphine ligands.[2] Such catalysts are not reusable and the resulting products are often contaminated by Pd metal and ligands.[2d] On the other hand, reusable heterogeneous catalysts have recently attracted much attention due to the increasing international momentum for the development of an environmentally friendly reaction in terms of green chemistry.[3,4] Pd/C is one of the most suitable catalysts for this type of reaction with the advantages of being inexpensive, stable, removable, and reusable.[5] Although some interesting results of the Suzuki–Miyaura coupling reaction catalyzed by Pd/C have been reported,[6–8] most of the procedures were limited to substrates, and required heating and additives such as phosphine ligands or quaternary ammonium salts.[7] A few additive-free Pd/C-catalyzed Suzuki–Miyaura coupling reactions at room temperature have been developed, but these methodologies are only applicable to the coupling of a narrow range of substrates, such as halophenols and iodocycloenones.[8] We have recently reported a mild and efficient ligand-free Pd/C-catalyzed Suzuki–Miyaura coupling reaction at room temperature in the presence of an inorganic mild base in aqueous or alcoholic media: $NaHCO_3$/MeOH, Na_2CO_3/50% EtOH, and Na_3PO_4/50% *i*-PrOH.[9] This method is applicable to a wide variety of aryl and aryl vinyl boronic acids with good to excellent yields. It is also known that boronic esters are applicable to the Suzuki–Miyaura coupling reaction in place of boronic acids.[2h,10] The use of boronic esters has some advantages, such as a high stability to heat and high solubility in organic solvents, when compared to boronic acids. For the preparation of aryl boronic esters, the developed methods are chiefly categorized under the following two types: the palladium-catalyzed boration of aryl halides or triflates using dialkoxyboranes[11] and the iridium- or rhodium-catalyzed boration of arenes with dialkoxyboranes.[12] Therefore, we now disclose the Pd/C-catalyzed and ligand-free Suzuki–Miyaura coupling reaction using aryl boronic esters instead of aryl boronic acids at room temperature in aqueous media and their synthetic application for the preparation of a pesticide (bifenazate[13]).

2. Results and discussion

As part of an ongoing program involving the Pd/C-catalyzed Suzuki–Miyaura coupling reaction using aryl boronic esters with an aryl bromide,[9] we found that the reaction smoothly proceeded at room temperature. When the reaction of 4-bromonitrobenzene and 1.1 equiv of phenylboronic acid neopentylglycol ester was carried out in the presence of 2.5 mol % of 10% Pd/C using 2.5 equiv of Na_2CO_3 as the base at room temperature in 50% EtOH, the desired 4-nitrobiphenyl was obtained in 94% yield within only 2 h (Table 1, entry 1). Among the key factors, the use of Pd/C (as Pd metal) and Na_2CO_3 was quite important for suppressing the reaction time. The amount of 10% Pd/C could be reduced

Keywords: Suzuki–Miyaura coupling reaction; Aryl boronic ester; Pd/C; Heterogeneous; Ligand-free.
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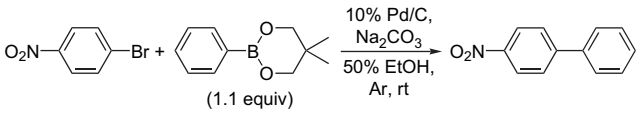
Table 1. Optimization of the reaction conditions



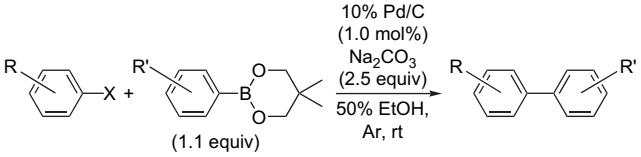
Entry	10% Pd/C (mol %)	Na_2CO_3 (equiv)	Time (h)	Yield[a] (%)
1	2.5	2.5	2	94
2	1.5	2.5	2	95
3	1.0	2.5	2	96
4	0.5	2.5	4	91
5	1.0	2.0	4	93
6	1.0	1.5	5	90

[a] Isolated yields.

to 1.0 mol % without any significant reduction of the reactivity (Table 1, entries 1–4) while the dosage reduction of Na_2CO_3 caused an extension of the reaction time (Table 1, entries 5 and 6). Therefore, we chose the use of 1.0 mol % of 10% Pd/C and 2.5 equiv of Na_2CO_3 as the optimized conditions.

Further investigation of the present Pd/C-catalyzed Suzuki–Miyaura coupling reaction shows it to have a good degree of generality (Table 2). Aryl bromides bearing an electron-withdrawing group as well as an electron-donating group can be employed to generate biphenyls by coupling with phenylboronic acid neopentylglycol ester in high yields accompanied by a *trace* amount of the homocoupling products of the boronic ester as the sole side-reaction product (Table 2, entries 1–4). Regarding the aryl boronic acid neopentylglycol esters, the coupling reaction using electron-rich boronic esters proceeded quite efficiently when compared with electron-neutral boronic esters (Table 2, entries 5, 6, 10, and 11 versus entries 1 and 2). On the other hand, the electron-poor boronic esters indicated that a rather lower reactivity and lower reaction times were required for the reaction completion, although the desired coupling products were obtained in nearly quantitative yields (Table 2, entries 7–9 and 12–14). It is noteworthy that the use of aryl triflates, which usually provide a lower reactivity in comparison to the corresponding bromides, also provide the desired biphenyls in excellent yields (Table 2, entries 15 and 16).

Table 2. Suzuki–Miyaura coupling reaction using aryl boronic acid neopentylglycol esters



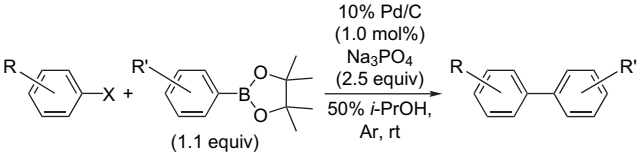
Entry	R	X	R′	Time (h)	Yield[a] (%)
1	4-NO_2	Br	H	2	96
2	4-OMe	Br	H	12	92
3	2-Me	Br	H	3	91
4	4-Ph	Br	H	6	95
5	4-NO_2	Br	2-MeO	1	93
6	4-NO_2	Br	4-Me	1	93
7	4-NO_2	Br	4-F	3	98
8	4-NO_2	Br	3-COMe	4	95
9	4-NO_2	Br	4-CHO	4	95
10	4-OMe	Br	2-MeO	6	98
11	4-OMe	Br	4-Me	7	94
12	4-OMe	Br	4-F	18	93
13	4-OMe	Br	3-COMe	24	90
14	4-OMe	Br	4-CHO	24	97
15[b]	4-NO_2	OTf	H	24	93
16[b]	4-OMe	OTf	H	48	90

[a] Isolated yields.
[b] Phenylboronic acid neopentylglycol ester (1.5 equiv) was used.

We explored a similar application of the present method to the coupling using aryl boronic acid pinacol esters (Table 3). Although the reaction of phenylboronic acid pinacol ester with 4-bromoanisole was incomplete within 24 h under the conditions shown in Table 2 (Table 3, entry 1), the drawback of the coupling reaction was solved by the use of Na_3PO_4 as a base in 50% *i*-PrOH, and then the reaction was successfully completed within 24 h at room temperature (Table 3, entry 2).[14] Reactions using a wide array of aryl boronic acid pinacol esters with various aryl bromides bearing an electron-withdrawing group as well as an electron-donating group gave the desired coupling products in excellent yields (Table 3, entries 2–13). Regarding 4-nitrophenyl triflate, the coupling product was obtained in a moderate yield because the hydrolysis of the aryl triflate to form the corresponding 4-nitrophenol competed with the coupling (Table 3, entry 14).

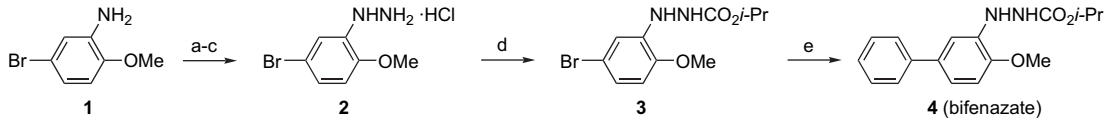
This chemistry can be extended to the synthesis of the bioactive substance, bifenazate, which is an acaricide effective against pest mites. Four different synthetic processes have been reported for the preparation of bifenazate using the biphenyl skeleton as a starting building block.[15–18] We have now developed a new synthetic route toward bifenazate using the present Pd/C-catalyzed Suzuki–Miyaura cross-coupling in the final step, starting from 5-bromo-2-methoxyaniline (**1**) (Scheme 1). Conversion of aniline (**1**) into phenylhydrazine (**2**) via the corresponding diazonium intermediate,[19] and acylation using isopropyl chloroformate

Table 3. Suzuki–Miyaura coupling reaction using aryl boronic acid pinacol esters



Entry	R	X	R′	Time (h)	Yield[a] (%)
1[b]	4-OMe	Br	H	24	73[c]
2	4-OMe	Br	H	24	96
3	4-NO_2	Br	H	6	98
4	2-Me	Br	H	8	92
5	4-Ph	Br	H	18	90
6	4-NO_2	Br	3,5-OMe	1	96
7	4-NO_2	Br	3-CO_2Me	6	90
8	4-NO_2	Br	4-NHAc	10	91
9	4-NO_2	Br	4-OH	8	95
10	4-OMe	Br	3,5-OMe	5	100
11	4-OMe	Br	3-CO_2Me	36	93
12	4-OMe	Br	4-NHAc	72	92
13	4-OMe	Br	4-OH	48	96
14[d]	4-NO_2	OTf	H	24	50 (32[e])

[a] Isolated yields.
[b] Na_2CO_3 (2.5 equiv) and 50% EtOH were used.
[c] The reaction was incomplete.
[d] Phenylboronic acid pinacol ester (1.5 equiv) was used.
[e] The yield of 4-nitrophenol.



Scheme 1. Application for the synthesis of bifenazate. Reagents and conditions: (a) concd HCl, 0 °C; (b) $NaNO_2$, 0 °C; (c) $SnCl_2/2H_2O$, HCl, 0 °C 80% (three steps); (d) *i*-PrCOCl, Et_3N, THF, 0 °C→rt, 65%; (e) $PhB(OCH_2)_2CMe_2$, 10% Pd/C, Na_2CO_3, 50% EtOH, 80 °C, 87%.

afforded the hydrazine carboxylate (**3**),[20] which was used as the Suzuki–Miyaura cross-coupling partner of phenylboronic acid neopentylglycol ester. The desired bifenazate (**4**) was obtained in 87% yield (45% five steps total yield from **1**), although the heating reaction conditions at 80 °C were required for this exceptional coupling reaction.

3. Conclusion

In conclusion, we have developed a ligand-free and heterogeneous Pd/C-catalyzed Suzuki–Miyaura coupling reaction using aryl boronic esters under mild reaction conditions. A variety of aryl bromides and triflates underwent the coupling reaction in good to high yields at room temperature. The present method was also applicable to the synthesis of bifenazate. This methodology can provide a facile, efficient and environmentally friendly heterogeneous process for the Suzuki–Miyaura coupling reaction together with a wide applicability to various substrates, the use of less toxic reagents, and mild reaction conditions in aqueous or alcoholic media. The simplicity of this method makes it an attractive new tool for the Suzuki–Miyaura coupling reaction.

4. Experimiental

4.1. General

All reactions were carried out under an argon atmosphere, unless otherwise noted. All reagents and solvents except two aryl boronic acid neopentylglycol esters were obtained from commercial sources and used without further purification. Aryl bromides were purchased from Tokyo Chemical Industry Co., Ltd. Aryl boronic acid esters were purchased from Aldrich Chemical Co., Inc., Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd. or prepared according to the known procedure.[21] Pd/C was gifted by N. E. Chemcat Co. Bases and solvents were purchased from Nacalai Tasque, Inc. or Wako Pure Chemical Industries, Ltd.

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM EX-400 or JEOL JNM AL-400 spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR). Chemical shifts (δ) are expressed in parts per million and internally referenced (0.00 ppm for tetramethylsilane (TMS)/$CDCl_3$ and TMS/acetone-d_6, 2.49 ppm for DMSO-d_6, or 3.30 ppm for CD_3OD for ^1H NMR and 77.0 ppm for $CDCl_3$, 29.8 ppm for acetone-d_6, 39.5 ppm for DMSO-d_6, or 49.0 ppm for CD_3OD for ^{13}C NMR). EI mass spectra were taken on a JEOL JMS-SX102A instrument. Elemental analyses were performed by YANACO MT-5 instrument. Flash column chromatography was performed using Kanto Chemical Co., Inc. silica gel 60N, spherical neutral (63–210 μm).

4.1.1. Preparation of aryl boronic acid neopentylglycol ester.[21] To aryl boronic acid (3.0 mmol) and 2,2-dimethylpropan-1,3-diol (3.3 mmol) in CH_2Cl_2 (6.0 mL) was added $MgSO_4$ (4.0 g) and the mixture was stirred at room temperature overnight. The reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc, 10:1) to give the corresponding aryl boronic acid neopentylglycol ester.

4.1.1.1. 5,5-Dimethyl-2-(2-methoxyphenyl)-1,3,2-dioxaborinane. Colorless oil; ^1H NMR ($CDCl_3$) δ 7.87, 7.66 (each d, J=7.8 Hz, 1H), 7.41, 7.35 (each t, J=7.8 Hz, 1H), 7.01, 6.93 (each t, J=7.8 Hz, 1H), 6.85 (t, J=7.8 Hz, 1H), 3.83, 3.80 (each s, 3H), 3.77 (s, 4H), 1.01 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 164.3, 163.5, 136.7, 135.6, 132.6, 131.5, 121.0, 120.0, 110.2, 109.7, 72.2, 55.4, 55.2, 31.5, 21.6; MS (EI) *m/z* 220 (M^+, 100%). HRMS (EI) calcd for $C_{12}H_{17}BO_3$ (M^+): 220.1271. Found: 220.1261.

4.1.1.2. 5,5-Dimethyl-2-(3-acetylphenyl)-1,3,2-dioxaborinane. Colorless solid; mp 117–119 °C; ^1H NMR ($CDCl_3$) δ 8.37 (s, 1H), 8.04 (d, J=7.6 Hz, 1H), 7.99 (d, J=7.6 Hz, 1H), 7.45 (t, J=7.6 Hz, 1H), 3.79 (s, 4H), 2.64 (s, 3H), 1.04 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 198.7, 138.6, 136.4, 134.0, 130.2, 127.9, 72.3, 31.9, 26.7, 21.9; MS (EI) *m/z* 232 (M^+, 15%). HRMS (EI) calcd for $C_{13}H_{17}BO_3$ (M^+): 232.1271. Found: 232.1262. Anal. Calcd for $C_{13}H_{17}BO_3$: C, 67.28; H, 7.38. Found: C, 67.20; H, 7.35.

4.1.2. General procedure for Suzuki–Miyaura cross-coupling reaction using aryl boronic acid neopentylglycol ester. To a test tube with a stir bar were added aryl bromide (500 μmol), aryl boronic acid neopentylglycol ester (550 μmol), Na_2CO_3 (133 mg, 1.25 mmol), 10% Pd/C (5.3 mg, 5.00 μmol), H_2O (1 mL), and EtOH (1 mL) and the system was sealed with a septum. The air inside was replaced with argon (balloon) by three vacuum/argon cycles and the mixture was stirred at room temperature. After a certain period, the mixture was diluted with H_2O (10 mL) and Et_2O (10 mL), and passed through a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was separated into two layers and the aqueous layer was extracted with Et_2O (2×10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc, 50:1) to give the corresponding biaryl.

4.1.2.1. General procedure for Suzuki–Miyaura cross-coupling reaction using aryl boronic acid pinacol ester. To a test tube with a stir bar were added aryl bromide (500 μmol), aryl boronic acid pinacol ester (550 μmol), $Na_3PO_4\cdot12H_2O$ (475 mg, 1.25 mmol), 10% Pd/C (5.3 mg,

5.00 μmol), H_2O (1 mL), and *i*-PrOH (1 mL) and the system was sealed with a septum. The air inside was replaced with argon (balloon) by three vacuum/argon cycles and the mixture was stirred at room temperature. After a certain period, the mixture was diluted with H_2O (10 mL) and Et_2O (10 mL), and passed through a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was separated into two layers and the aqueous layer was extracted with Et_2O (2×10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc, 50:1) to give the corresponding biaryl.

4.1.2.2. 4-Nitrobiphenyl[22] (Table 1, entries 1–6; Table 2, entries 1 and 15; Table 3, entries 3 and 14). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 8.30 (d, J=8.8 Hz, 2H), 7.74 (d, J=8.8 Hz, 2H), 7.63 (d, J=6.8 Hz, 2H), 7.53–7.43 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 147.6, 147.1, 138.7, 129.1, 128.9, 127.8, 127.4, 124.1; MS (EI) *m*/*z* 199 (M^+, 100%). HRMS (EI) calcd for $C_{12}H_9NO_2$ (M^+): 199.0633. Found: 199.0625.

4.1.2.3. 4-Methoxybiphenyl[22,23,25,28,29,33] (Table 2, entries 2 and 16; Table 3, entries 1 and 2). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 7.56–7.52 (m, 4H), 7.41 (t, J=7.6 Hz, 2H), 7.30 (t, J=7.6 Hz, 1H), 6.97 (d, J=8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3; MS (EI) *m*/*z* 184 (M^+, 100%). HRMS (EI) calcd for $C_{13}H_{12}O$ (M^+): 184.0888. Found: 184.0891.

4.1.2.4. 2-Methylbiphenyl[22,23] (Table 2, entry 3; Table 3, entry 4). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.35–7.32 (m, 3H), 7.28–7.24 (m, 3H), 7.19–7.16 (m, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 141.9, 135.3, 130.3, 129.8, 129.2, 128.7, 128.0, 127.2, 126.7, 125.7, 20.5; MS (EI) *m*/*z* 168 (M^+, 100%). HRMS (EI) calcd for $C_{13}H_{12}$ (M^+): 168.0939. Found: 168.0947.

4.1.2.5. *p*-Terphenyl[23] (Table 2, entry 4; Table 3, entry 5). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 7.67–7.63 (m, 8H), 7.45–7.35 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 140.7, 140.1, 128.8, 127.5, 127.3, 127.0; MS (EI) *m*/*z* 230 (M^+, 100%). HRMS (EI) calcd for $C_{14}H_{14}O_2$ (M^+): 230.1096. Found: 230.1090.

4.1.2.6. 2-Methoxy-4′-nitrobiphenyl[24] (Table 2, entry 5). Pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 8.24 (d, J=9.0 Hz, 2H), 7.68 (d, J=9.0 Hz, 2H), 7.40 (t, J=8.0 Hz, 1H), 7.32 (d, J=8.0 Hz, 1H), 7.06 (t, J=8.0 Hz, 1H), 7.01 (d, J=8.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 156.3, 146.6, 145.4, 130.6, 130.3, 130.1, 128.2, 123.1, 121.0, 111.4, 55.5; MS (EI) *m*/*z* 229 (M^+, 100%). HRMS (EI) calcd for $C_{13}H_{11}NO_3$ (M^+): 229.0739. Found: 229.0732.

4.1.2.7. 4-Methyl-4′-nitrobiphenyl[25] (Table 2, entry 6). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 8.24 (d, J=8.2 Hz, 2H), 7.68 (d, J=8.2 Hz, 2H), 7.50 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 147.4, 146.7, 139.0, 135.7, 129.8, 127.3, 127.1, 124.0, 21.1; MS (EI) *m*/*z* 213 (M^+, 100%). HRMS (EI) calcd for $C_{13}H_{11}NO_2$ (M^+): 213.0790. Found: 213.0797.

4.1.2.8. 4-Fluoro-4′-nitrobiphenyl[26] (Table 2, entry 7). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 8.26 (d, J=8.8 Hz, 2H), 7.68 (d, J=8.8 Hz, 2H), 7.60 (dd, J=8.5, 5.0 Hz, 2H), 7.18 (t, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 163.4 (d, J=250 Hz), 147.1, 146.6, 134.9, 129.2 (d, J=8.0 Hz), 125.9, 116.2 (d, J=21 Hz); MS (EI) *m*/*z* 217 (M^+, 100%); HRMS (EI) calcd for $C_{12}H_8NO_2F$ (M^+): 217.0539. Found: 217.0532.

4.1.2.9. 3-Acetyl-4′-nitrobiphenyl (Table 2, entry 8). Pale yellow solid; mp 106–108 °C, ^{1}H NMR ($CDCl_3$) δ 8.30 (d, J=8.8 Hz, 2H), 8.22 (s, 1H), 8.02 (d, J=7.2 Hz, 1H), 7.83 (d, J=7.2 Hz, 1H), 7.77 (d, J=8.8 Hz, 2H), 7.62 (t, J=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 179.5, 147.3, 146.3, 139.1, 137.8, 131.7, 129.4, 128.7, 127.8, 126.9, 124.1, 26.6; MS (EI) *m*/*z* 241 (M^+, 49%). HRMS (EI) calcd for $C_{14}H_{11}NO_3$ (M^+): 241.0739. Found: 241.0732. Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.93; H, 4.92; N, 5.44.

4.1.2.10. 4-Nitrobiphenyl-4-carbaldehyde[27] (Table 2, entry 9). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 10.10 (s, 1H), 8.33 (d, J=9.0 Hz, 2H), 8.02 (d, J=9.0 Hz, 2H), 7.82–7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 191.5, 147.6, 145.9, 144.3, 136.1, 130.3, 128.1, 128.0, 124.1; MS (EI) *m*/*z* 227 (M^+, 100%). HRMS (EI) calcd for $C_{13}H_9NO_3$ (M^+): 227.0583. Found: 227.0574.

4.1.2.11. 2,4′-Dimethoxybiphenyl[28] (Table 2, entry 10). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 7.47 (d, J=8.8 Hz, 2H), 7.31–7.27 (m, 2H), 7.03–6.94 (m, 4H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 158.6, 156.4, 130.8, 130.6, 130.5, 130.2, 128.1, 120.8, 113.4, 111.1, 55.4, 55.2; MS (EI) *m*/*z* 214 (M^+, 100%). HRMS (EI) calcd for $C_{14}H_{14}O_2$ (M^+): 214.0994. Found: 214.0999.

4.1.2.12. 4-Methoxy-4′-methylbiphenyl[23,28,29] (Table 2, entry 11). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 7.49 (d, J=8.4 Hz, 2H), 7.43 (d, J=8.4 Hz, 2H), 7.20 (d, J=8.6 Hz, 2H), 6.94 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 159.0, 138.0, 136.3, 133.8, 129.4, 127.9, 126.6, 114.2, 55.3, 29.7, 21.0; MS (EI) *m*/*z* 198 (M^+, 100%). HRMS (EI) calcd for $C_{14}H_{14}O$ (M^+): 198.1045. Found: 198.1037.

4.1.2.13. 4-Fluoro-4′-methoxybiphenyl[29] (Table 2, entry 12). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 7.48–7.43 (m, 4H), 7.07 (t, J=8.4 Hz, 2H), 6.94 (d, J=8.4 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 162.5 (d, J=247 Hz), 159.2, 137.0, 132.8, 128.2 (d, J=8.0 Hz), 128.0, 115.5 (d, J=21 Hz), 114.4, 55.3; MS (EI) *m*/*z* 202 (M^+, 100%). HRMS (EI) calcd for $C_{13}H_{11}OF$ (M^+): 202.0794. Found: 202.0785.

4.1.2.14. 3-Acetyl-4′-methoxybiphenyl[30] (Table 2, entry 13). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 8.14 (s, 1H), 7.88 (d, J=7.8 Hz, 1H), 7.75 (d, J=7.8 Hz, 1H), 7.56 (d, J=8.4 Hz, 2H), 7.50 (t, J=7.8 Hz, 1H), 7.00 (d, J=8.4 Hz, 2H), 3.86 (s, 3H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 198.2, 159.5, 141.3, 137.6, 132.6, 131.3, 128.9, 128.2, 126.6, 126.4, 114.3, 55.3, 26.7; MS (EI) *m*/*z* 226 (M^+, 100%). HRMS (EI) calcd for $C_{15}H_{14}O_2$ (M^+): 226.0994. Found: 226.1001.

4.1.2.15. 4-Methoxybiphenyl-4-carbaldehyde[30] (Table 2, entry 14). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 10.0 (s, 1H), 7.93 (d, J=8.2 Hz, 2H), 7.72 (d, J=8.2 Hz, 2H), 7.60 (d, J=8.8 Hz, 2H), 7.01 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 191.9, 160.0, 146.7, 134.6, 132.0, 130.3, 128.5, 127.0, 114.4, 55.4; MS (EI) m/z 212 (M^+, 100%). HRMS (EI) calcd for $C_{14}H_{12}O_2$ (M^+): 212.0837. Found: 212.0845.

4.1.2.16. 3,5-Dimethoxy-4′-nitrobiphenyl (Table 3, entry 6). Colorless solid; mp 116–118 °C, ^{1}H NMR ($CDCl_3$) δ 8.23 (d, J=8.8 Hz, 2H), 7.68 (d, J=8.8 Hz, 2H), 6.71 (s, 2H), 6.52 (s, 1H), 3.85 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 161.2, 147.4, 147.1, 140.7, 127.7, 123.9, 105.6, 100.4, 55.4; MS (EI) m/z 259 (M^+, 100%). HRMS (EI) calcd for $C_{14}H_{13}NO_4$ (M^+): 259.0845. Found: 259.0852. Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.74; H, 5.00; N, 5.18.

4.1.2.17. Methyl (4′-nitrobiphenyl-3-yl)carboxylate (Table 3, entry 7). Colorless solid; mp 119–121 °C; ^{1}H NMR ($CDCl_3$) δ 8.32 (d, J=8.8 Hz, 2H), 8.12 (d, J=8.0 Hz, 1H), 7.82 (d, J=8.0 Hz, 1H), 7.78 (d, J=8.8 Hz, 2H), 7.58 (t, J=8.0 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.5, 147.4, 146.4, 139.0, 131.6, 131.3, 129.9, 129.3, 128.5, 127.9, 124.2, 52.3; MS (EI) m/z 257 (M^+, 94%). HRMS (EI) calcd for $C_{14}H_{11}NO_4$ (M^+): 257.0688. Found: 257.0680. Anal. Calcd for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.44. Found: C, 65.74; H, 4.67; N, 5.02.

4.1.2.18. 4′-Nitrophenyl-4-acetanilide (Table 3, entry 8). Pale yellow solid; mp 257–259 °C; ^{1}H NMR (DMSO-d_6) δ 10.2 (s, 1H), 8.24 (d, J=7.6 Hz, 2H), 7.89 (d, J=7.6 Hz, 2H), 7.75–7.71 (m, 4H), 2.08 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 168.6, 146.1, 140.3, 131.9, 127.6, 127.0, 124.0, 119.3, 24.0; MS (EI) m/z 256 (M^+, 62%). HRMS (EI) calcd for $C_{14}H_{12}N_2O_3$ (M^+): 256.0848. Found: 256.0859. Anal. Calcd for $C_{14}H_{12}N_2O_3\cdot 5/7H_2O$: C, 62.48; H, 5.03; N, 10.41. Found: C, 62.81; H, 4.78; N, 10.02.

4.1.2.19. 4-Hydroxy-4′-nitrobiphenyl (Table 3, entry 9). Pale yellow solid; mp 211–213 °C; ^{1}H NMR (acetone-d_6) δ 8.80 (s, 1H), 8.25 (d, J=9.0 Hz, 2H), 7.85 (d, J=9.0 Hz, 2H), 7.64 (d, J=8.6 Hz, 2H), 6.98 (d, J=8.6 Hz, 2H); ^{13}C NMR (acetone-d_6) δ 206.2, 159.5, 148.2, 147.3, 130.5, 129.5, 127.7, 124.8, 116.9; MS (EI) m/z 215 (M^+, 76%). HRMS (EI) calcd for $C_{12}H_9NO_3$ (M^+): 215.0583. Found: 215.0576. Anal. Calcd for $C_{12}H_9NO_3\cdot 6/7H_2O$: C, 62.49; H, 4.68; N, 6.07. Found: C, 62.14; H, 4.23; N, 5.74.

4.1.2.20. 3,4′,5-Trimethoxybiphenyl[31] (Table 3, entry 10). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J=8.6 Hz, 2H), 6.96 (d, J=8.6 Hz, 2H), 6.69 (s, 2H), 6.43 (s, 1H), 3.84 (s, 6H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 161.0, 159.3, 143.1, 133.7, 128.2, 114.1, 105.1, 98.7, 55.4, 55.3; MS (EI) m/z 244 (M^+, 100%). HRMS (EI) calcd for $C_{15}H_{16}O_3$ (M^+): 244.1100. Found: 244.1095.

4.1.2.21. Methyl (4′-methoxybiphenyl-3-yl)carboxylate[32] (Table 3, entry 11). Colorless solid; ^{1}H NMR ($CDCl_3$) δ 8.23 (s, 1H), 7.96 (d, J=8.0 Hz, 1H), 7.72 (d, J=8.0 Hz, 1H), 7.55 (d, J=8.8 Hz, 2H), 7.44 (t, J=8.0 Hz, 1H), 6.98 (d, J=8.8 Hz, 2H), 3.93 (s, 3H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 159.5, 141.0, 132.5, 131.0, 130.6, 128.7, 128.1, 127.7, 114.3, 55.3, 52.1; MS (EI) m/z 242 (M^+, 100%). HRMS (EI) calcd for $C_{15}H_{14}O_3$ (M^+): 242.0943. Found: 242.0932.

4.1.2.22. 4′-Methoxyphenyl-4-acetanilide[33] (Table 3, entry 12). Colorless solid; ^{1}H NMR (DMSO-d_6) δ 9.98 (s 1H), 7.64 (d, J=8.8 Hz, 2H), 7.56–7.52 (m, 4H), 6.98 (d, J=8.8 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 168.2, 158.5, 138.2, 134.4, 132.2, 127.2, 126.3, 119.3, 114.3, 55.1, 24.0; MS (EI) m/z 241 (M^+, 100%). HRMS (EI) calcd for $C_{15}H_{15}NO_2$ (M^+): 241.1103. Found: 241.1093.

4.1.2.23. 4-Hydroxy-4′-methoxybiphenyl[34] (Table 3, entry 13). Colorless solid; ^{1}H NMR (acetone-d_6) δ 8.38 (s, 1H), 7.49 (d, J=8.6 Hz, 2H), 7.44 (d, J=8.6 Hz, 2H), 6.95 (d, J=8.8 Hz, 2H), 6.92 (d, J=8.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (acetone-d_6) δ 206.5, 159.5, 157.3, 134.2, 132.9, 128.3, 128.1, 116.4, 114.9, 55.5; MS (EI) m/z 200 (M^+, 100%). HRMS (EI) calcd for $C_{13}H_{12}O_2$ (M^+): 200.0837. Found: 200.0846.

4.1.3. Synthesis of Bifenazate.

4.1.3.1. 5-Bromo-2-methoxyphenylhydrazine hydrochloride. The reaction mixture was maintained at 0 °C during this procedure. 5-Bromo-2-methoxyaniline (2.00 g, 10.0 mmol) was added to vigorously stirred concentrated HCl (17 mL) and aged for 10 min. A solution of $NaNO_2$ (691 mg, 10.0 mmol) in distilled water (4 mL) was added dropwise over 10 min and the mixture was stirred for an additional 15 min. A solution of $SnCl_2\cdot H_2O$ (498 mg, 22.0 mol) in concentrated HCl (5 mL) was added dropwise. The reaction mixture was stirred for 30 min and filtered. The product was dried in vacuo overnight to afford 5-bromo-2-methoxyphenylhydrazine hydrochloride as a brown solid (2.03 g, 80%); ^{1}H NMR (CD_3OD) δ 7.19–7.15 (m, 2H), 6.95 (d, J=8.8 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (CD_3OD) δ 149.6, 136.3, 127.5, 119.3, 113.9, 113.8, 56.6.

4.1.3.2. Isopropyl 3-(5-bromo-2-methoxyphenyl)carbazate. A solution of 5-bromo-2-methoxyphenylhydrazine hydrochloride (2.00 g, 7.90 mmol) and triethylamine (2.28 mL, 16.6 mmol) in CH_2Cl_2 (16 mL) was cooled to 0 °C and a solution of isopropyl chloroformate (0.93 mL, 8.08 mmol) in CH_2Cl_2 (8 mL) was added dropwise at a rate that maintained a temperature below 0 °C. When the addition was complete, the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred for 3 h and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc, 2:1) to afford isopropyl 3-(5-bromo-2-methoxyphenyl)carbazate as a colorless solid (1.55 g, 65%); mp 117–119 °C; ^{1}H NMR ($CDCl_3$) δ 6.97 (s, 1H), 6.93 (d, J=8.2 Hz, 1H), 6.66 (d, J=8.2 Hz), 4.97 (heptet, J=6.4 Hz, 1H), 3.83 (s, 3H), 1.27 (br m, 6H); ^{13}C NMR ($CDCl_3$) δ 156.4, 145.8, 136.3, 138.8, 122.4, 114.7, 113.4, 111.4, 69.6, 55.6, 21.8; MS (EI) m/z 302 (M^+, 63%). HRMS (EI) calcd for $C_{11}H_{15}N_2O_3Br$ (M^+): 302.0266. Found: 302.0273. Anal. Calcd for $C_{11}H_{15}N_2O_3Br$: C, 43.58; H, 4.99; N, 9.24. Found: C, 44.02; H, 4.93; N, 8.91.

4.1.3.3. Bifenazate.[15a] To a 50-mL round-bottom flask with a stir bar were added isopropyl 3-(5-bromo-2-methoxyphenyl)carbazate (1.51 g, 5.00 mmol), 5,5-dimethyl-2-

phenyl-1,3,2-dioxaborinane (1.05 g, 5.50 mmol), Na_2CO_3 (1.33 g, 12.5 mmol), 10% Pd/C (53 mg, 50.0 μmol), H_2O (10 mL), and EtOH (10 mL) and the system was sealed with a septum. The air inside was replaced with argon (balloon) by three vacuum/argon cycles and the mixture was stirred at 80 °C for 12 h. The mixture was diluted with H_2O (50 mL) and Et_2O (50 mL), and filtered through a Celite pad. The filtrate was separated into two layers and the aqueous layer was extracted with EtOAc (2×50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc, 50:1∼5:1) to afford bifenazate as a yellow solid (1.3 g, 87%); ^{1}H NMR ($CDCl_3$) δ 7.52 (d, J=7.2 Hz, 2H), 7.39 (t, J=7.2 Hz, 2H), 7.28 (t, J=7.2 Hz, 1H), 7.10–7.06 (m, 2H), 6.88 (d, J=8.0 Hz, 1H), 6.38 (br s, 1H), 6.29 (br s, 1H), 4.97 (heptet, J=6.4 Hz, 1H), 3.90 (s, 3H), 1.26 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 146.6, 137.7, 134.3, 128.5, 126.8, 126.6, 122.6, 119.1, 114.9, 111.5, 111.1, 110.4, 69.5, 55.7, 22.0; MS (EI) *m/z* 300 (M^+, 100%). HRMS (EI) calcd for $C_{17}H_{20}N_2O_3$ (M^+): 300.1474. Found: 300.1466.

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