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Palladium-catalyzed ligand-free and efficient Suzuki–Miyaura reaction of *N*-methyliminodiacetic acid boronates in water

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Abstract: A green and efficient protocol has been developed for the $Pd(OAc)_2$-catalyzed ligand-free Suzuki–Miyaura reaction of *N*-methyliminodiacetic acid (MIDA) boronates in water. In the presence of $Pd(OAc)_2$ as a catalyst and $(i\text{-Pr})_2NH$ as a base, the cross-coupling reactions of aryl bromides with aryl MIDA boronates proceeded smoothly in water without any surfactant, and various functional groups were tolerated under the optimized conditions.

Key words: Palladium, ligand-free, Suzuki–Miyaura reaction, *N*-methyliminodiacetic acid boronates, water

1. Introduction

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction has been considered as one of the most powerful and popular tools for preparation of biaryl compounds, which are important structural moieties in natural products and pharmaceutical and functional materials.[1−5] Arylboronic acids are the most common nucleophilic reagents for the Suzuki–Miyaura reaction.[6,7] However, superstoichiometric loadings (1.5–2.0 eq.) of arylboronic acids are often required in aqueous Suzuki–Miyaura cross-coupling catalytic systems due to the undesired side reactions of homocoupling[8,9] and protodeboronation.[10,11] In addition, some of the organoboronic acids, such as 2-heteroarylboronic acids, are unstable, which limits their application in cross-coupling reactions.[12−14] Since the first report in the early 1980s, the *N*-methyliminodiacetic acid (MIDA) boronates have emerged as an attractive and promising alternative to organoboronic acids in cross-coupling reactions.[15,16] The MIDA boronates are nontoxic, biodegradable, and crystalline solids that are stable for storage indefinitely on the benchtop in air without decomposition.[17] These bench-stable boronates can be easily prepared from corresponding organoboronic acids, and many MIDA boronates are currently commercially available.[17,18] In recent years, Suzuki–Miyaura systems involving MIDA boronates have been developed by the research groups of Burke,[13,17,19−21] Wu,[22] Yudin,[23] and many others. Among these systems, ligands including phosphines and carbenes were used for promoting the cross-coupling reaction. However, compared with the ligand-promoted Suzuki–Miyaura reaction systems, only a few ligand-free protocols are reported for the Suzuki–Miyaura reaction of MIDA boronates.[24] In 2014, da Silva et al.[25] reported a phosphine-free Suzuki–Miyaura cross-coupling system for aryl or (2-pyridyl) MIDA boronates in aqueous ethanol using polyurea microencapsulated palladium (Pd EnCat30) as the catalyst. Very recently, we reported the palladium-catalyzed ligand-free cross-couplings of heteroaryl halides with aryl MIDA boronates.[26] In the present paper, we report a simple and efficient catalytic system for the Suzuki–Miyaura

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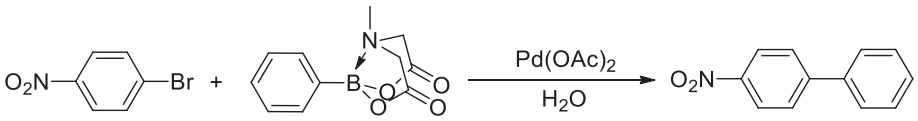
reaction of aryl MIDA boronates with aryl halides in pure water without any additive. This catalytic system, using $Pd(OAc)_2$ as the catalyst and $(i\text{-}Pr)_2NH$ as the base, is highly efficient for a broad range of substrates.

2. Results and discussion

Initially, the effects of various bases on the cross-coupling reaction were investigated. The cross-coupling of 4-bromonitrobenzene with phenylboronic acid MIDA ester was chosen as a model reaction. As shown in Table 1, the most efficient base in the present catalytic system was diisopropylamine, which provided a 94% yield in 4 h (Table 1, entry 1). The other bases, such as Et_3N, K_2CO_3, Cs_2CO_3, $K_3PO_4{\cdot}3H_2O$, and KOH (Table 1, entries 2–6), gave disappointing results. Thus, we chose diisopropylamine as the base for further study. Recently, we found that the cross-coupling reactions of aryl halides with arylboronic acids could be performed with good yields in pure water.[27] To compare the reactivity of the organoboron reagents in this system, the cross-coupling reaction of 4-bromonitrobenzene with phenylboronic acid or phenylboronic acid pinacol cyclic ester was carried out and a 93% or 62% yield was obtained in 4 h under air, respectively (Table 1, entries 7 and 8). It is obvious that both phenylboronic acid and the phenylboronic acid MIDA ester are very active, while the phenylboronic acid pinacol cyclic ester is less active.

Table 1. The effect of base on the Suzuki–Miyaura reaction.[a]

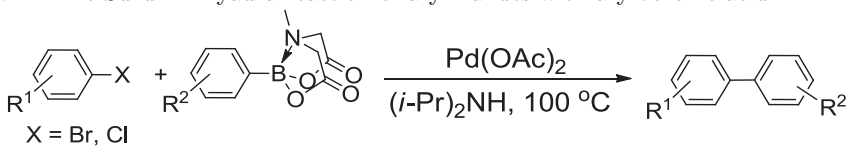


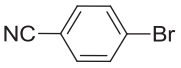
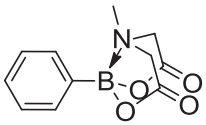
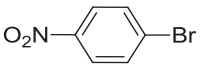
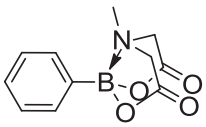
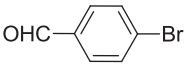
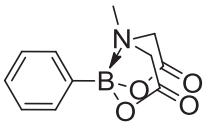
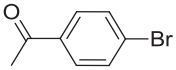
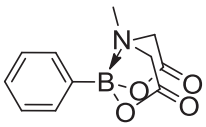
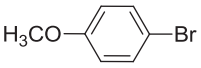
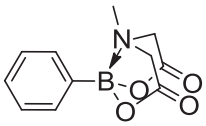
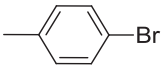
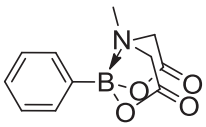
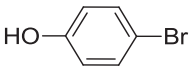
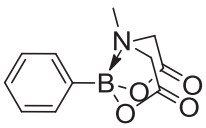
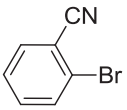
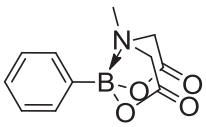
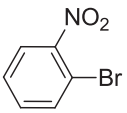
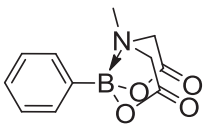
Entry	Base	Yield[b]
1	$(i\text{-}Pr)_2NH$	94
2	Et_3N	52
3	K_2CO_3	54
4	Cs_2CO_3	51
5	$K_3PO_4{\cdot}3H_2O$	48
6	KOH	16
7	$(i\text{-}Pr)_2NH$	93[c]
8	$(i\text{-}Pr)_2NH$	62[d]

[a] Reaction conditions: 4-bromonitrobenzene (0.5 mmol), arylboronic acid MIDA ester (0.6 mmol), base (1.0 mmol), $Pd(OAc)_2$ (2 mol%), H_2O (1 mL), 100 °C, 4 h, under air. [b] Isolated yields. [c] Phenylboronic acid (0.6 mmol). [d] Phenylboronic acid pinacol cyclic ester (0.6 mmol).

We next explored the generality of the cross-couplings between aryl halides with a variety of arylboronic acid MIDA esters using 2 mol% $Pd(OAc)_2$ and two equivalents of diisopropylamine at 100 °C in water. The results are shown in Table 2. Various 4-substituted aryl bromides, bearing either electron-donating or electron-withdrawing groups, provided the corresponding products in good to excellent yields (Table 2, entries 1–7). A broad range of functional groups, such as –CN, $–NO_2$, –CHO, $–COCH_3$, –OMe, –Me, and –OH, were tolerated in the catalytic system. Sterically demanding aryl bromides could be coupled with phenylboronic acid MIDA esters to give good to excellent yields of the desired products (Table 2, entries 8–11). To further investigate the scope and limitations of this methodology, we carried out cross-couplings of aryl halides with different arylboronic acid MIDA esters under the optimized conditions. The arylboronic acid MIDA esters bearing election-donating groups underwent Suzuki–Miyaura coupling smoothly to afford the desired products in excellent yields (Table 2,

Table 2. The Suzuki–Miyaura reaction of aryl halides with arylboronic acid MIDA ester.



Entry	Ar-X	MIDA boronate	Time	Yield[b]
1			1.0 h	95
2			4.0 h	93
3			1.5 h	92
4			1.0 h	95
5			1.0 h	95
6			1.0 h	85
7			1.0 h	92
8			1.5 h	95
9			1.5 h	90

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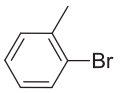
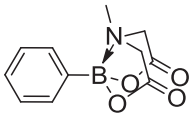
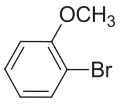
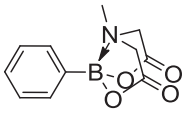
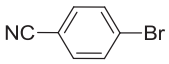
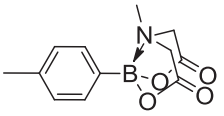
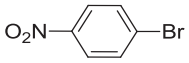
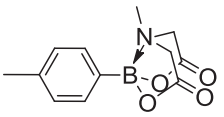
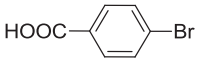
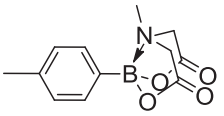
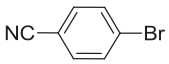
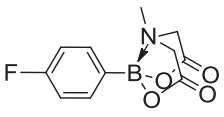
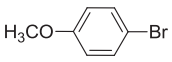
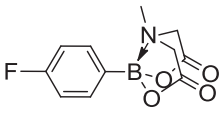
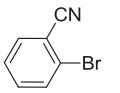
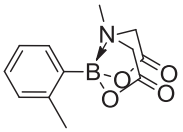
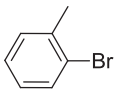
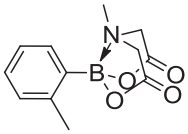
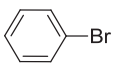
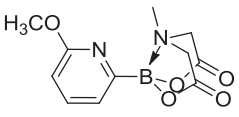
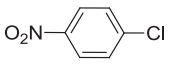
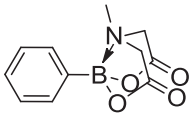
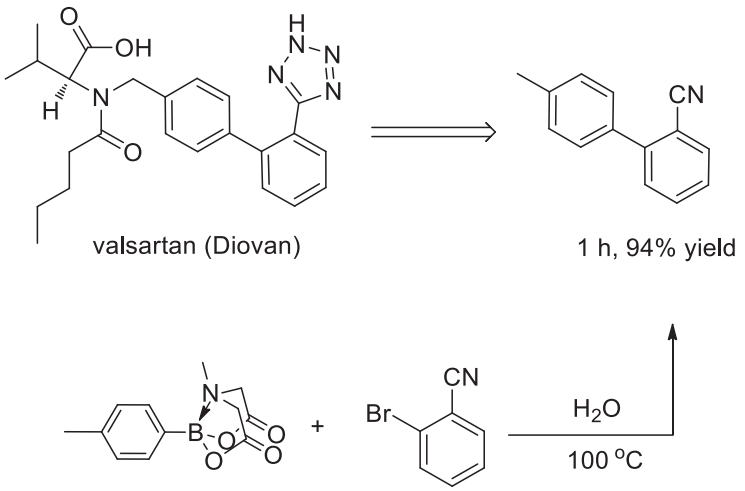
10			2.0 h	89
11			1.5 h	94
12			1.0 h	94
13			1.0 h	92
14			2.0 h	91
15			1.0 h	88
16			1.5 h	85
17			2.5 h	92
18			3.0 h	83
19			12 h	42
20			12 h	34[c]

[a] Reaction conditions: aryl bromides (0.5 mmol), arylboronic acid MIDA ester (0.6 mmol), $Pd(OAc)_2$ (2 mol%), H_2O (1 mL), $(i\text{-Pr})_2NH$ (1 mmol), under air, 100 °C. [b] Isolated yields. [c] $Pd(OAc)_2$ (4 mol%).

entries 12–14), while arylboronic acid MIDA esters bearing election-withdrawing substituents gave slight lower yields (Table 2, entries 15 and 16). Sterically demanding arylboronic acid MIDA esters were also effective in the coupling reaction to afford the corresponding biaryls in good yields (Table 2, entries 17 and 18). The cross-coupling reaction of 6-methoxy-2-pyridylboronic acid MIDA ester and bromobenzene afforded a 42% yield of the desired product in 12 h (Table 2, entry 19). The cross-coupling of 4-chloronitrobenzene with phenylboronic acid MIDA ester provided a 34% yield of product after 12 h (Table 2, entry 20).

2-Cyano-4'-methylbiphenyl is an important unit in valsartan (Diovan), a drug that is therapeutically useful in treating congestive heart failure and high blood pressure.[28] As shown in the Scheme, in this catalytic system, 2-bromobenzonitrile coupled with 4-methylphenylboronic acid MIDA ester to give the product of 2-cyano-4'-methylbiphenyl in 94% yield in 1 h.



Scheme. Synthesis of the biaryl core within valsartan. Reaction conditions: 2-bromobenzonitrile (0.5 mmol), 4-methylphenylboronic acid MIDA ester (0.6 mmol), $(i\text{-Pr})_2NH$ (1 mmol), $Pd(OAc)_2$ (2 mol%), H_2O (1 mL), in air, 1 h, 100 °C.

3. Experimental

3.1. General remarks

All commercially available reagents (from Acros, Aldrich, and Fluka) were used without further purification. MIDA boronates were prepared from corresponding arylboronic acids following the method reported in the literature.[21] All reactions were carried out in air. NMR spectra were recorded on a Bruker Avance II 400 spectrometer using TMS as the internal standard (400 MHz for ^1H NMR). The isolated yields of products were obtained by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60-90 °C), unless otherwise noted. Compounds described in the literature were characterized by ^1H NMR spectra compared with reported data.

3.2. General procedure for the Suzuki–Miyaura reaction

A mixture of aryl halide (0.5 mmol), MIDA boronates (0.6 mmol), $(i\text{-Pr})_2NH$ (1 mmol), $Pd(OAc)_2$ (2 mol%), and H_2O (1 mL) was stirred at 100 °C in air for the indicated time. The reaction mixture was added to brine

(10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were concentrated in vacuo and the product was isolated by short chromatography.

4-Cyanodiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H, Ar-H), 7.68 (d, J = 8.2 Hz, 2H, Ar-H), 7.59 (d, J = 7.2 Hz, 2H, Ar-H), 7.48 (t, J = 7.3 Hz, 2H, Ar-H), 7.42 (t, J = 7.2 Hz, 1H, Ar-H).

4-Nitrobiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.8 Hz, 2H, Ar-H), 7.74 (d, J = 8.9 Hz, 2H, Ar-H), 7.63 (d, J = 7.0 Hz, 2H, Ar-H), 7.50 (t, J = 7.2 Hz, 2H, Ar-H), 7.45 (dd, J = 8.4, 5.9 Hz, 1H, Ar-H).

4-Biphenylcarbaldehyde[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H, CHO), 7.96 (d, J = 8.2 Hz, 2H, Ar-H), 7.76 (d, J = 8.2 Hz, 2H, Ar-H), 7.64 (d, J = 7.1 Hz, 2H, Ar-H), 7.49 (t, J = 7.4 Hz, 2H, Ar-H), 7.42 (t, J = 7.3 Hz, 1H, Ar-H).

4-Acetylbiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.3 Hz, 2H, Ar-H), 7.69 (d, J = 8.3 Hz, 2H, Ar-H), 7.63 (d, J = 7.3 Hz, 2H, Ar-H), 7.47 (t, J = 7.5 Hz, 2H, Ar-H), 7.40 (t, J = 7.3 Hz, 1H, Ar-H), 2.64 (s, 3H, CH_3).

4-Methoxybiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (t, J = 8.3 Hz, 4H, Ar-H), 7.41 (t, J = 7.7 Hz, 2H, Ar-H), 7.31 (t, J = 7.3 Hz, 1H, Ar-H), 6.98 (d, J = 8.8 Hz, 2H, Ar-H), 3.85 (s, 3H, OCH_3).

4-Methylbiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ7.58 (d, J= 7.6 Hz, 2H, Ar-H), 7.49 (d, J = 8.4 Hz, 2H, Ar-H), 7.42 (dd, 2H, Ar-H), 7.32 (t, J = 6.8 Hz, 1H, Ar-H), 7.25 (t, J = 3.2 Hz, 2H, Ar-H), 2.41 (s, 3H, CH_3).

4-Hydroxybiphenyl[27]**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.9 Hz, 2H, Ar-H), 7.47 (d, J = 8.3 Hz, 2H, Ar-H), 7.41 (t, J = 7.5 Hz, 2H, Ar-H), 7.29 (t, J = 7.3 Hz, 1H, Ar-H), 6.91 (d, J = 8.3 Hz, 2H, Ar-H), 4.73 (s, 1H, OH).

2-Phenylbenzonitrile[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J= 6.8 Hz, 1H, Ar-H), 7.63 (t, J= 8.4 Hz, 1H, Ar-H), 7.40–7.55 (m, 7H, Ar-H).

2-Nitrobiphenyl[29]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8 Hz, 1H, Ar-H), 7.61 (t, J = 7.5 Hz, 1H, Ar-H), 7.50–7.49 (m, 5H, Ar-H), 7.33–7.31 (m, 2H, Ar-H).

2-Methylbiphenyl[30]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.43 (m, 2H, Ar-H), 7.31–7.35 (m, 3H, Ar-H), 7.24–7.26 (m, 4H, Ar-H), 2.25 (s, 3H, CH_3).

2-Methoxylbiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ7.53 (d, J = 7.0 Hz, 2H, Ar-H), 7.40 (t, J = 7.5 Hz, 2H, Ar-H), 7.32 (dd, J = 15.7, 1.5 Hz, 3H, Ar-H), 7.03 (t, J = 7.5 Hz, 1H, Ar-H), 7.00–6.95 (m, 1H, Ar-H), 3.80 (s, 3H, OCH_3).

4-Cyano-4'-methylbiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (q, J = 8.5 Hz, 4H, Ar-H), 7.49 (d, J = 8.1 Hz, 2H, Ar-H), 7.28 (d, J = 8.0 Hz, 2H, Ar-H), 2.18 (s, 3H, CH_3).

4-Methoxy-4'-methylbiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ7.51 (d, J = 8.7 Hz, 2H, Ar-H), 7.45 (d, J = 8.0 Hz, 2H, Ar-H), 7.23 (d, J = 8.0 Hz, 2H, Ar-H), 6.97 (d, J = 8.6 Hz, 2H, Ar-H), 3.85 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3).

4'-Methylbiphenyl-4-carboxylic acid[27]: ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ 12.90 (br, 1H, COOH), 8.01 (d, J = 8.0 Hz, 2H, Ar-H), 7.78 (d, J = 8.4 Hz, 2H, Ar- H), 7.64 (d, J = 8.0 Hz, 2H, Ar- H), 7.31 (d, J = 8.0 Hz, 2H, Ar-H), 2.36 (s, 3H, CH_3).

4-Cyano-4'-fluorobiphenyl[31]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.5 Hz, 2H, Ar-H), 7.64 (d, J = 8.4 Hz, 2H, Ar-H), 7.60–7.53 (m, 2H, Ar-H), 7.22–7.13 (m, 2H, Ar-H).

4-Methoxyl-4'-fluorobiphenyl[31]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 4H, Ar-H), 7.10 (t, J = 8.8 Hz, 2H, Ar-H), 6.98 (d, J = 8.8 Hz, 2H, Ar-H), 3.85 (s, 3H, CH_3).

2-Cyano-2'-methylbiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.7 Hz, 1H, Ar-H), 7.59 (t, J = 7.7 Hz, 1H, Ar-H), 7.41 (t, J = 7.7 Hz, 1H, Ar-H), 7.37–7.31 (m, 1H, Ar-H), 7.25 (t, J = 7.1 Hz, 2H, Ar-H), 7.18 (d, J = 7.3 Hz, 1H, Ar-H), 2.18 (s, 3H, CH_3).

2,2'-Dimethylbiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.17 (m, 6H, Ar-H), 7.10 (d, J = 6.9 Hz, 2H, Ar-H), 2.05 (s, 6H, CH_3).

2-Methoxy-6-phenylpyridine[32]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.03 (m, 2H, Ar-H), 7.60 (t, J= 7.6 Hz, 1H, Ar-H), 7.45 (t, J= 7.6 Hz, 2H, Ar-H), 7.40–7.36 (m, 1H, Py-H), 7.33 (d, J= 7.2 Hz, 1H, Py-H), 6.68 (d, J= 7.6 Hz, 1H, Py-H), 4.03 (s, 3H, OCH_3).

2-Cyano-4'-methylbiphenyl[27]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.6 Hz, Ar-H), Ar-H, 7.61 (t, J = 7.6 Hz, 1H, Ar-H), 7.48 (d, J = 8.0 Hz, 1H, Ar-H), 7.45 (d, J = 8.0 Hz, 2H, Ar-H), 7.40 (t, J= 7.6 Hz, 1H, Ar-H), 7.28 (d, J= 8.0 Hz, 2H, Ar-H), 2.41 (s, 3H, CH_3).

4. Conclusion

In summary, we have developed a green and efficient ligand-free protocol for the palladium-catalyzed Suzuki–Miyaura cross-couplings of aryl bromides with arylboronic acid MIDA esters in pure water and a wide range of groups could be tolerated in this system. This aqueous protocol is in accordance with the concept of green chemistry and is of great interest for practical production.

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