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$Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura cross-coupling reaction in DMF

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Abstract—The scope and limitations of the $Pd(OAc)_2$/DABCO (1,4-diaza-bicyclo[2.2.2]octane)-catalyzed Suzuki–Miyaura cross-coupling reactions have been demonstrated. The results showed that the effect of solvent had a fundamental influence on the reaction. In the presence of $Pd(OAc)_2$ and DABCO, both aryl bromides and aryl chlorides all worked well with arylboronic acids to form biaryls, heteroaryl-aryls, and biheteroaryls in moderate to excellent yields using DMF as the solvent. Additionally, the reactions of aryl bromides were conducted under relatively mild conditions.

1. Introduction

Palladium-catalyzed cross-coupling of aryl halides with organoboronic acids, namely Suzuki–Miyaura cross-coupling reaction, is a versatile and utilized reaction for the selective formation of carbon–carbon bonds, in particular for the synthesis of biaryls.[1–7] Recently, efforts have been focused on the development of efficient and selective catalytic systems for the Suzuki–Miyaura reaction. However, many catalytic systems are limited to the couplings of aromatic iodides and bromides.[2] In recent years, employing readily available aryl chlorides in these transformations have received increasing attention, and a number of effective catalytic systems have been developed for this purpose.[2–4] In these processes, the use of sterically hindered and electron-rich ligands played crucial roles in the coupling of these challenging substrates. One of the notable examples is the use of bulky trialkylphosphines.[4] However, many of those phosphine ligands are sensitive to air and/or moisture besides expensive, which place significant limits on their synthetic applications. Very recently, we have reported that DABCO (1,4-diaza-bicyclo[2.2.2]octane) was an inexpensive, stable, and highly efficient ligand for the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction.[6] After checking our previous results carefully, we found that the scopes of the Suzuki–Miyaura reactions catalyzed by our catalytic system relied on the solvents. In the presence of $Pd(OAc)_2$ and DABCO, only aryl iodides and bromides were coupled with arylboronic acids efficiently using acetone as the solvent,[6a] whereas the scope was extended to the activated aryl chlorides when PEG-400[6b] or H_2O[6c] was used as the media. Furthermore, the deactivated aryl chlorides could be coupled smoothly with PEG-400 to afford moderate yields with the aid of TBAB (tetrabutylammonium bromide). The results encouraged us to further explore the effects of the solvents on the scope and limitations of the $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura cross-coupling reactions.[2] We were happy to discover that the scope of the protocol could be extended to aryl chlorides to construct biaryls, heteroaryl-aryl, and biheteroaryls when DMF was employed as the media. Moreover, the couplings of aryl bromides in DMF could be conducted under relatively mild conditions. Here, we wish to report the results of this methodology in detail (Eq. 1).

$$\mathrm{Ar{-}X} + \mathrm{Ar'{-}B(OH)_2} \xrightarrow[\mathrm{Cs_2CO_3,\ DMF}]{\mathrm{Pd(OAc)_2/DABCO}} \mathrm{Ar{-}Ar'} \quad (1)$$

Ar, Ar' = aryl, heteroaryl
X = Br, Cl

2. Results and discussion

2.1. Effect of solvents on the $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura reaction

The $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura reaction between 1-chloro-4-nitro-benzene (**1a**) and phenylboronic acid (**2a**) was chosen as a model reaction to evaluate the effects of the solvents, and the results are summarized in

Keywords: $Pd(OAc)_2$/DABCO; Suzuki–Miyaura cross-coupling reaction; Aryl halide; Arylboronic acids.
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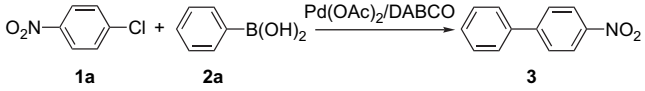
Table 1. Effect of solvents on $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura cross-coupling reaction of 1-chloro-4-nitrobenzene with phenylboronic acid[a]



1a 2a 3

Entry	Solvent	Time (h)	Isolated yield (%)
1	Acetone (5 mL)	2	18 (Ref. 6a)
2[b]	Acetone (5 mL)	2	40
3	PEG-400 (2 g)	3	60 (Ref. 6b)
4[c]	PEG-400 (2 g)	3	92 (Ref. 6b)
5	Dioxane (3 mL)	19	45
6[b]	H_2O (5 mL)	24	Trace (Ref. 6c)
7[b]	CH_3CH_2OH/H_2O (1:4; 5 mL)	24	50 (Ref. 6c)
8	DMF (3 mL)	19	100
9[d]	DMF (3 mL)	17	100
10[d,e]	DMF (3 mL)	33	94
11[d,f]	DMF (3 mL)	42	72

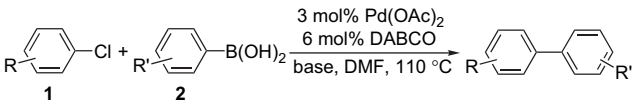
[a] Reaction conditions: **1** (0.5 mmol), **2** (0.7 mmol), $Pd(OAc)_2$ (3 mol %), DABCO (6 mol %), and K_2CO_3 (3 equiv) at 110 °C.
[b] PEG-400 (0.2 equiv).
[c] TBAB (0.1 equiv).
[d] Cs_2CO_3 (3 equiv).
[e] $Pd(OAc)_2$ (1 mol %) and DABCO (2 mol %).
[f] $Pd(OAc)_2$ (0.1 mol %) and DABCO (0.2 mol %).

Table 1. In our initial communication,[6a] acetone was used as the media. Unfortunately, only an 18% yield of the target product **3** was isolated in acetone when 1-chloro-4-nitrobenzene (**1a**) was treated with phenylboronic acid (**2a**), $Pd(OAc)_2$ (3 mol %), DABCO (6 mol %), and K_2CO_3 (3 equiv) at 110 °C (entry 1). We found that the yield of **3** was enhanced to 40% when 0.2 equiv of PEG-400 was added (entry 2). Thus, PEG-400 employed as the medium was tested, and a 60% yield was provided (entry 3).[6b] It was interesting to observe that the yield of **3** was increased sharply to 92% using PEG-400 as the media and TBAB as an additional promoter (entry 4). Dioxane, the reported excellent solvent by Tao and Boykin,[5] gave only a 45% yield of **3** (entry 5). The reaction performed in aqueous media was also investigated.[6c] Trace amount of **3** was isolated in water (entry 6), but the yield was increased to 50% when ethanol was used as the co-solvent (entry 7). We were happy to see that the quantitative yield of **3** was obtained when the reaction was carried out in DMF (entry 8). The results also indicated that effects of bases could affect the reaction to some extent. Cs_2CO_3 in place of K_2CO_3 as the base could shorten the reaction time (entries 8 and 9). It is noteworthy that the reaction performed in DMF can be conducted at 0.1 mol % loading Pd together with a good yield after prolonged reaction time (94% yield at 1 mol % Pd and 72% yield at 0.1 mol % Pd; entries 10 and 11).

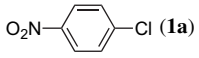
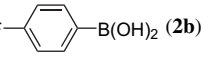
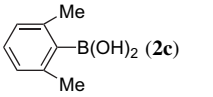
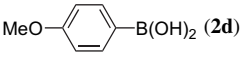
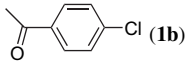
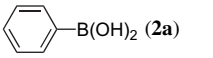
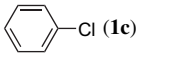
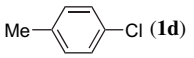
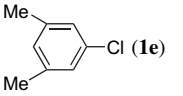
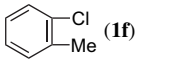
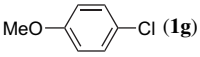
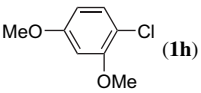
2.2. $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura reaction to synthesize biaryls

The coupling reaction between a range of substrates and several arylboronic acids was then conducted to explore the general effectiveness of the $Pd(OAc)_2$/DABCO/DMF system (Table 2). Under the above optimized reaction conditions, a wide range of aryl chlorides **1a–h**, whether electron-rich or electron-deficient, all worked well with arylboronic acids **2a–d**. Moreover, *ortho*-substituents on the aromatic rings could also be tolerated as well, leading to the corresponding hindered coupling products in moderate yields. As shown in Table 2, the $Pd(OAc)_2$/DABCO/DMF system was proved exceptionally active for the couplings of the activated chlorides **1a** and **1b**, but the yields relied on arylboronic acids. For example, treatment of **1a** with boronic acid **2b** or **2d** afforded the target products in excellent yields (a 99% yield for **2b** and a 93% yield for **2d**; entries 1 and 3), whereas only a moderate yield was observed when **1a** reacted with the hindered boronic acid **2c** (entry 2). Although the efficiency of the $Pd(OAc)_2$/DABCO/DMF system was also decreased for more challenging deactivated aryl chlorides, moderate yields of the corresponding hindered coupling products were still achieved (entries 7–9 and 14). Unfortunately, an attempt to coupling of the deactivated

Table 2. $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl chlorides with arylboronic acids in DMF[a]



1 2

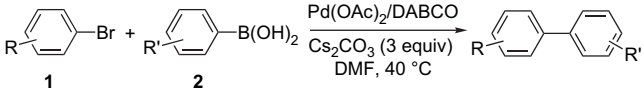
Entry	ArX	$ArB(OH)_2$	Yield (%)[b]
1	 (**1a**)	 (**2b**)	99 (**4**)
2	(**1a**)	 (**2c**)	52 (**5**)
3	(**1a**)	 (**2d**)	93 (**6**)
4[c]	 (**1b**)	 (**2a**)	100 (**7**)
5	 (**1c**)	(**2a**)	65 (**8**)
6	 (**1d**)	(**2a**)	53 (**9**)
7	 (**1e**)	(**2a**)	64 (**10**)
8	 (**1f**)	(**2a**)	60 (**11**)
9	(**1f**)	(**2d**)	58 (**12**)
10	 (**1g**)	(**2a**)	61 (**13**)
11	(**1g**)	(**2b**)	71 (**14**)
12	(**1g**)	(**2c**)	Trace (**15**)
13	(**1g**)	(**2d**)	52 (**16**)
14	 (**1h**)	(**2a**)	63 (**17**)
15	1-Iododecane (**1i**)	(**2a**)	— (**18**)

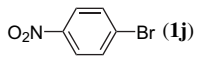
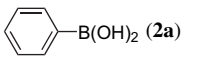
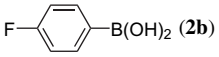
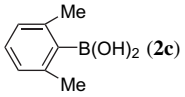
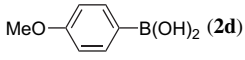
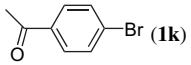
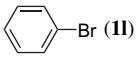
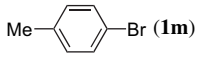
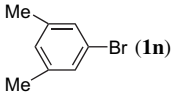
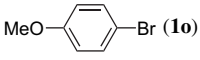
[a] Unless otherwise indicated, the reaction conditions were as follows: **1** (0.5 mmol), **2** (0.7 mmol), $Pd(OAc)_2$ (3 mol %), DABCO (6 mol %), and Cs_2CO_3 (3 equiv) in DMF (3 mL) at 110 °C for 19 h.
[b] Isolated yield.
[c] For 17 h.

chloride **1g** with the bulky boronic acid **2c** was unsuccessful (entry 12). Finally, we also screened the reaction between 1-iododecane (**1i**) and phenylboronic acid (**2a**), but no target product was obtained (entry 15).

With the excellent reaction conditions in hand, we then decided to explore the couplings of aryl bromides again. Gratifyingly, the reactions between aryl bromides and arylboronic acids were able to conduct under mild conditions (Table 3). At 40 °C, aryl bromides **1j–m** and **1o** reacted well with **2a** to afford the corresponding cross-coupling products in excellent yields (entries 2–8 and 11). The hindered bromide **1n** required higher reaction temperature.

Table 3. $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura cross-coupling reactions of aryl bromides with arylboronic acids in DMF[a]



Entry	ArX	$ArB(OH)_2$	Yield (%)[b]
1[c]	 (**1j**)	 (**2a**)	Trace (**3**)
2	(**1j**)	(**2a**)	100 (**3**)
3	(**1j**)	 (**2b**)	81 (**3**)
4	(**1j**)	 (**2c**)	Trace (**5**)
5	(**1j**)	 (**2d**)	90 (**3**)
6	 (**1k**)	(**2a**)	96 (**7**)
7	 (**1l**)	(**2a**)	94 (**8**)
8	 (**1m**)	(**2a**)	89 (**9**)
9	 (**1n**)	(**2a**)	40 (**10**)
10[d]	(**1n**)	(**2a**)	92 (**10**)
11	 (**1o**)	(**2a**)	90 (**13**)
12	(**1o**)	(**2b**)	37 (**14**)
13[d]	(**1o**)	(**2b**)	82 (**14**)
14	(**1o**)	(**2d**)	30 (**16**)
15[d,e]	(**1o**)	(**2d**)	96 (**16**)

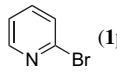
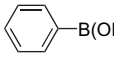
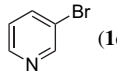
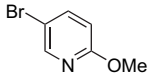
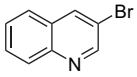
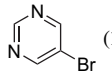
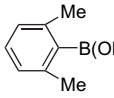
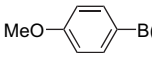
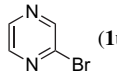
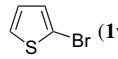
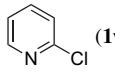
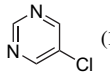
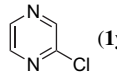
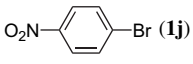
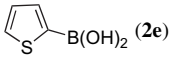
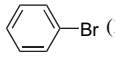
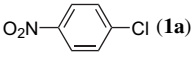
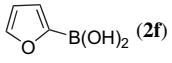
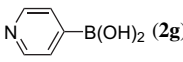
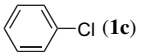
[a] Unless otherwise indicated, the reaction conditions were as follows: **1** (0.5 mmol), **2** (0.7 mmol), $Pd(OAc)_2$ (3 mol %), DABCO (6 mol %), and Cs_2CO_3 (3 equiv) in DMF (3 mL) at 40 °C for 16 h.
[b] Isolated yield.
[c] At room temperature.
[d] At 80 °C.
[e] For 25 h.

Only a 40% yield of the target product **10** was isolated from the reaction of **1n** with **1a** at 40 °C, but the yield of **10** was enhanced to 92% when the reaction was performed at 80 °C (entries 9 and 10). The couplings of the substrates **1j** and **1o** with the other boronic acids were also examined. The results demonstrated that the yields of the desired products were varied with different boronic acids (entries 3–5 and 12–15). The bromide **1j** treated with **2b–d**, $Pd(OAc)_2$, DABCO, and Cs_2CO_3 at 40 °C to offer the corresponding products in 81%, trace, and 90% yields, respectively (entries 3–5). We also observed that bromide **1o** with the other boronic acid **2b** or **2d** required the couplings performing at higher temperature to produce good results (entries 12–15). For example, the reaction of bromide **1o** with **2b** provided only 37% of the desired coupled product **14** at 40 °C (entry 12). However, the yield was increased to 82% when the reaction was carried out at 80 °C (entries 13).

2.3. $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura reaction to synthesize heteroaryl-aryls and biheteroaryls

Construction of biaryl containing heteroaryl rings via the palladium-catalyzed Suzuki–Miyaura reaction is another interesting area.[2,7] There are a few transformations for general cross-coupling reactions of both aryl halides and heteroaryl halides with arylboronic acids including heteroarylboronic acids to synthesize biaryls containing heteroaryl rings. However, most of the transformations required the phosphine ligands to improve them as well as limited to aryl bromides. To our delight, the $Pd(OAc)_2$/DABCO/DMF system was also effective for the reactions of aryl halides with heteroarylboronic acids (Table 4). Solvent was also found to play a crucial role in the reaction (entries 1–4). In acetone, treatment of **1p** with **2a**, $Pd(OAc)_2$, DABCO, and Cs_2CO_3 afforded a 34% yield of the target product **19** in 48 h. In dioxane, the yield of **19** was increased slightly to 49% for 48 h (entry 2). We were happy to find that the yield of **19** was enhanced to 66% for 22 h when the reaction was conducted in DMF. Under the same optimized reaction conditions, the other heteroaryl bromides **1q–v**, including nitrogen- or sulfur-containing heteroaryl bromides, coupled with arylboronic acids were carried out efficiently to produce the corresponding products in moderate to excellent yields (entries 4–12). For example, 5-bromopyrimidine **1t** reacted with three kinds of arylboronic acids, including a challenging boronic acid **2d**, smoothly to give the corresponding desired products **23–25** in 98, 50, and 98% yields, respectively (entries 7–9). The sulfur-containing substrate **1v** coupled with **2a** offered a moderate yield of the target product **27** under the same reaction conditions (entry 11). It was pleased to find that the yield of **27** was increased sharply to 98% when K_2CO_3 was employed as the base (entry 12). However, the best base for the couplings of heteroaryl chlorides **1w–y** was KOH (entries 13–17). Treatment of chloride **1w** with **2a**, $Pd(OAc)_2$, DABCO, and Cs_2CO_3 provided a 40% of the desired product **19** (entry 13), whereas the yield of **19** was enhanced dramatically to 58% using KOH as the base (entry 14). In the presence of $Pd(OAc)_2$, DABCO, KOH, and DMF, the other chlorides **1x** and **1y** underwent the coupling with **2a** smoothly to afford the corresponding products in moderate yields (entries 15 and 16).

Table 4. $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides with heteroarylboronic acids to synthesize heteroaryl-aryls[a]

Entry	ArX	$ArB(OH)_2$	Time (h)	Yield (%)[b]
1[c]	 (**1p**)	 (**2a**)	48	34 (**19**)
2[d]	(**1p**)	(**2a**)	48	49 (**19**)
3	(**1p**)	(**2a**)	22	66 (**19**)
4	 (**1q**)	(**2a**)	22	81 (**20**)
5	 (**1r**)	(**2a**)	21	65 (**21**)
6	 (**1s**)	(**2a**)	22	94 (**22**)
7	 (**1t**)	(**2a**)	4	98 (**23**)
8	(**1t**)	 (**2c**)	12	50 (**24**)
9	(**1t**)	 (**2d**)	10	98 (**25**)
10	 (**1u**)	(**2a**)	46	94 (**26**)
11	 (**1v**)	(**2a**)	22	65 (**27**)
12[e]	(**1v**)	(**2a**)	22	98 (**27**)
13	 (**1w**)	(**2a**)	48	40 (**19**)
14[f]	(**1w**)	(**2a**)	46	58 (**19**)
15[f]	 (**1x**)	(**2a**)	46	52 (**23**)
16[f]	 (**1y**)	(**2a**)	46	54 (**26**)
17	 (**1j**)	 (**2e**)	10	98 (**28**)
18	 (**1l**)	(**2e**)	12	95 (**27**)
19	 (**1a**)	(**2e**)	19	93 (**28**)
20	(**1a**)	 (**2f**)	19	90 (**29**)
21	(**1a**)	 (**2g**)	24	58 (**30**)
22	 (**1c**)	(**2e**)	24	88 (**27**)
23	(**1c**)	(**2f**)	24	74 (**31**)

[a] Unless otherwise indicated, the reaction conditions were as follows: **1** (0.5 mmol), **2** (0.7 mmol), $Pd(OAc)_2$ (3 mol %), DABCO (6 mol %), and Cs_2CO_3 (3 equiv) in DMF (3 mL) at 110 °C.
[b] Isolated yield.
[c] In acetone (3 mL).
[d] In dioxane (3 mL).
[e] K_2CO_3 (3 equiv) instead of Cs_2CO_3.
[f] KOH (3 equiv) instead of Cs_2CO_3.

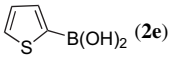
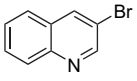
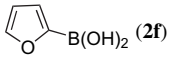
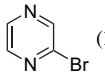
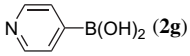
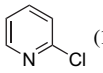
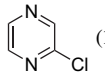
Subsequently, the couplings between aryl halides and heteroarylboronic acids were conducted under the same optimized conditions. The results indicated that the reactions of aryl bromides **1j** or **1l** with heteroarylboronic acid **2e** produced the corresponding products in excellent yields using $Pd(OAc)_2$/DABCO as the catalytic system and DMF as the solvent (entries 17 and 18). Moderate to good yields were still achieved when aryl chlorides **1a** or **1c** were treated with heteroarylboronic acids under the same reaction conditions (entries 19–23). For example, the reaction of substrate **1a** with **2e–g** afforded the corresponding products **28–30** in 93, 90, and 58%, respectively, in the presence of $Pd(OAc)_2$, DABCO, Cs_2CO_3, and DMF (entries 19–21).

The reactions of heteroaryl halides with heteroarylboronic acids were also performed smoothly under the $Pd(OAc)_2$/DABCO/DMF system and the results are summarized in Table 5. In the presence of $Pd(OAc)_2$ and DABCO, a number of heteroaryl bromides reacted with sulfur- and oxygen-containing heteroarylboronic acids to afford the corresponding products in high yields using KOH or K_2CO_3 as the base and DMF as the solvent (entries 1–6), but with nitrogen-containing heteroarylboronic acid (**2g**) provided a moderate yield (entry 7). For example, the reaction of substrate **1u** with **2e** gave the desired product **37** in a 98% yield, whereas treatment of **1u** with **2g**, a nitrogen-containing heteroarylboronic acid, produced only a 65% yield of the target product **38** (entries 6 and 7). To our surprise, only a 16% yield of the desired coupled product **32** was isolated together with a 56% yield of 2-(pyridin-2-yl)pyridine, a homocoupling product of 2-bromopyridine (**1p**) (entry 1). Under the same reaction conditions, the reaction of 2-chloropyridine **1w** was also unsuccessful (entry 8). However, another chloride **1y** coupled with **2e** was carried out smoothly to offer the desired product **37** in a moderate yield (entry 9).

3. Conclusion

In summary, we have discussed the effect of solvents on the scope and limitations of the $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura cross-coupling reaction. On the base of the results, several features are established: (1) the effect of the solvents has a fundamental influence on the scope and limitations of the current reaction, and the results demonstrate the broad substrate scope of the $Pd(OAc)_2$/DABCO/DMF system for the Suzuki–Miyaura coupling. In acetone,

Table 5. $Pd(OAc)_2$/DABCO-catalyzed Suzuki–Miyaura cross-coupling reactions of heteroaryl halides with heteroarylboronic acids to provide biheteroaryls[a]

Entry	ArX	$ArB(OH)_2$	Time (h)	Yield (%)[b]
1	 (**1p**)	 (**2e**)	39	16 (**32**)
2	 (**1s**)	(**2e**)	23	93 (**33**)
3	(**1s**)	 (**2f**)	21	98 (**34**)
4[c]	 (**1t**)	(**2e**)	17	96 (**35**)
5[c]	(**1t**)	(**2f**)	22	93 (**36**)
6	 (**1u**)	(**2e**)	23	98 (**37**)
7	(**1u**)	 (**2g**)	23	65 (**38**)
8	 (**1w**)	(**2e**)	41	Trace (**32**)
9	 (**1y**)	(**2e**)	38	50 (**37**)

[a] Unless otherwise indicated, the reaction conditions were as follows: **1** (0.5 mmol), **2** (0.7 mmol), $Pd(OAc)_2$ (3 mol %), DABCO (6 mol %), and KOH (3 equiv) in DMF (3 mL) at 110 °C.
[b] Isolated yield.
[c] K_2CO_3 (3 equiv) instead of KOH.

only aryl iodides and bromides were coupled with arylboronic acids efficiently,[6a] whereas in PEG-400[6b] or PEG-400/H_2O[6c] the scope was extended to the activated aryl chlorides. In addition, some deactivated aryl chlorides could be coupled smoothly when TBAB was added to PEG-400.[6b] However, DMF was proved here to be the more effective solvent for a wide range of aryl halides including the deactivated aryl chlorides and heteroaryl halides. Moreover, the couplings of aryl bromides in DMF were conducted under mild conditions. The reason that DMF is the most effective medium here may be that DMF is a highly polar solvent and may play as a ligand to promote the reaction.[2] (2) The reaction showed excellent substituent tolerance on the aromatic rings. (3) DABCO is considerably inexpensive and readily available, which emerged as an attractive alternative to the phosphine ligand for the Suzuki–Miyaura cross-coupling reaction. Given these advantage, design, and application of these ligands on the base of the DABCO skeleton in other palladium-catalyzed cross-coupling transformations should be attractive.

4. Experimental

4.1. Typical experimental procedure for the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction in DMF

A mixture of aryl halide **1** (0.5 mmol), arylboronic acid **2** (0.7 mmol), $Pd(OAc)_2$ (3 mol %), DABCO (6 mol %), base (3 equiv), and DMF (3 mL) was stirred at the indicated reaction temperature for the desired time until complete consumption of starting material as monitored by TLC. After the mixture was poured into diethyl ether, then washed with water, extracted with diethyl ether, dried by anhydrous Na_2SO_4, and evaporated under vacuum, the residue was purified by flash column chromatography (hexane or hexane/ethyl acetate) to afford the desired coupled products **3**–**14**, **16**, **17**, and **19**–**38**.

4.1.1. 4-Nitro-biphenyl (3).[3] Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, J=8.8 Hz, 2H), 7.74 (d, J=8.8 Hz, 2H), 7.64 (d, J=6.9 Hz, 2H), 7.52–7.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 147.1, 138.8, 129.2, 128.91, 127.8, 127.4, 124.1; LRMS (EI, 20 eV) m/z (%): 199 (M^+, 100).

4.1.2. 4-Nitro-4′-fluorobiphenyl (4).[3] Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, J=8.8 Hz, 2H), 7.70 (d, J=8.8 Hz, 2H), 7.59 (dd, J=5.6 Hz, 5.6 Hz, 2H), 7.20 (t, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.6, 162.1, 146.5, 134.9, 129.1 (d, J=8.6 Hz, 1C), 127.6, 124.2, 116.2 (d, J=21.7 Hz, 1C); LRMS (EI, 20 eV) m/z (%): 217 (M^+, 100).

4.1.3. 4-Nitro-2′,6′-dimethylbiphenyl (5).[3] Yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.31 (d, J=9.0 Hz, 2H), 7.35 (d, J=8.7 Hz, 2H), 7.25–7.20 (m, 1H), 7.15–7.13 (m, 2H), 2.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.4, 146.8, 139.5, 135.3, 130.7, 128.0, 127.6, 123.8, 20.7; LRMS (EI, 20 eV) m/z (%): 227 (M^+, 100).

4.1.4. 4-Nitro-4′-methoxybiphenyl (6).[3] Yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.25 (d, J=9.0 Hz, 2H), 7.68 (d, J=9.0 Hz, 2H), 7.57 (d, J=9.0 Hz, 2H), 7.02 (d, J=8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.4, 147.2, 146.5, 131.0, 128.5, 127.0, 124.1, 114.6, 55.4; LRMS (EI, 20 eV) m/z (%): 229 (M^+, 100).

4.1.5. 1-Biphenyl-4-yl-ethanone (7).[3] White solid; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.04 (d, J=8.4 Hz, 2H), 7.69 (d, J=8.4 Hz, 2H), 7.64 (d, J=7.6 Hz, 2H), 7.50–7.40 (m, 3H), 2.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.1, 146.1, 140.2, 136.2, 130.1, 129.2, 128.6, 127.6, 118.5, 27.0; LRMS (EI, 20 eV) m/z (%): 196 (M^+, 100).

4.1.6. Biphenyl (8).[3] White solid; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.59 (d, J=8.4 Hz, 4H), 7.43 (t, J=7.2 Hz, 4H), 7.36 (t, J=7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 141.6, 129.1, 127.6, 127.5; LRMS (EI, 20 eV) m/z (%): 154 (M^+, 100).

4.1.7. 4-Methyl-biphenyl (9).[3] White solid; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59 (t, J=7.6 Hz, 2H), 7.49 (d, J=8.0 Hz, 2H), 7.42 (t, J=7.6 Hz, 2H), 7.31 (t, J=7.6 Hz, 1H), 7.24 (d, J=8.0 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 138.3, 137.0, 129.5, 128.7, 127.3, 127.2, 127.0, 21.1; LRMS (EI, 20 eV) m/z (%): 168 (M^+, 100).

4.1.8. 3,5-Dimethyl-biphenyl (10).[3] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, J=8.4 Hz, 2H), 7.44–7.40 (m, 2H), 7.31–7.28 (m, 1H), 7.19 (d, J=8.4 Hz, 2H), 6.98 (d, J=9.2 Hz, 1H), 2.35 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.5, 138.1, 128.9, 128.7, 127.9,

127.2, 127.1, 125.1, 21.4; LRMS (EI, 20 eV) *m/z* (%): 182 (M^+, 100).

4.1.9. 2-Methyl-biphenyl (11).[3] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (t, J=7.2 Hz, 2H), 7.32 (t, J=6.8 Hz, 3H), 7.25–7.23 (m, 4H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 125.6, 20.4; LRMS (EI, 20 eV) *m/z* (%): 168 (M^+, 100).

4.1.10. 2-Methyl-4′-methoxy-biphenyl (12).[3] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26–7.22 (m, 6H), 6.95 (d, J=8.4 Hz, 2H), 3.85 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 141.5, 135.5, 134.3, 130.3, 130.2, 129.9, 127.0, 125.8, 113.5, 55.3, 20.6; LRMS (EI, 20 eV) *m/z* (%): 198 (M^+, 100).

4.1.11. 4-Methoxy-biphenyl (13).[3] White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.54 (t, J=8.4 Hz, 4H), 7.42 (t, J=7.8 Hz, 2H), 7.31 (t, J=7.5 Hz, 1H), 6.98 (d, J=9.0 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3; LRMS (EI, 20 eV) *m/z* (%): 184 (M^+, 100).

4.1.12. 4-Fluoro-4′-methoxy-biphenyl (14).[3] White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.50–7.45 (m, 4H), 7.09 (t, J=8.4 Hz, 2H), 6.96 (d, J=8.7 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7, 160.4, 159.0, 132.7, 128.2 (d, J=9.3 Hz, 1C), 128.0, 115.5 (d, J=28.2 Hz, 1C), 114.2, 55.3; LRMS (EI, 20 eV) *m/z* (%): 202 (M^+, 100).

4.1.13. 4,4′-Dimethoxy-biphenyl (16).[3] White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.48 (d, J=8.4 Hz, 4H), 6.95 (d, J=8.87 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 133.5, 127.7, 114.1, 59.3; LRMS (EI, 20 eV) *m/z* (%): 214 (M^+, 100).

4.1.14. 2,4-Dimethoxy-biphenyl (17).[3] Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53 (d, J=8.1 Hz, 2H), 7.40 (t, J=7.5 Hz, 2H), 7.34 (t, J=9.0 Hz, 1H), 6.95–6.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.6, 138.3, 129.4, 128.0, 127.0, 116.6, 116.0, 113.0, 112.8, 112.5, 56.2, 55.8; LRMS (EI, 20 eV) *m/z* (%): 214 (M^+, 100).

4.1.15. 2-Phenylpyridine (19).[3] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (d, J=4.8 Hz, 1H), 7.99 (d, J=6.8 Hz, 2H), 7.78–7.71 (m, 2H), 7.48 (t, J=8.8 Hz, 2H), 7.42 (t, J=7.2 Hz, 1H), 7.26–7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4, 149.6, 139.3, 136.7, 128.9, 128.7, 126.9, 122.1, 120.5; LRMS (EI, 20 eV) *m/z* (%): 155 (M^+, 100).

4.1.16. 3-Phenylpyridine (20).[3] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (s, 1H), 8.59 (d, J=6.4 Hz, 1H), 7.88 (d, J=12.0 Hz, 1H), 7.60 (d, J=8.4 Hz, 2H), 7.49 (t, J=7.2 Hz, 2H), 7.43–7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 148.3, 137.8, 136.6, 134.3, 129.0, 128.1, 127.1, 123.5; LRMS (EI, 20 eV) *m/z* (%): 155 (M^+, 100).

4.1.17. 2-Methoxy-5-phenylpyridine (21). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (s, 1H), 7.79 (d, J=2.8 Hz, 1H), 7.54–7.52 (m, 2H), 7.46 (t, J=7.2 Hz, 2H), 7.35 (t, J=7.6 Hz, 1H), 6.82 (d, J=8.8 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.6, 145.0, 137.9, 137.4, 130.1, 128.9, 127.3, 126.7, 110.8, 53.5; LRMS (EI, 20 eV) *m/z* (%): 185 (M^+, 100); HRMS (EI) for $C_{12}H_{11}NO$ (M^+): calcd, 185.0841; found, 185.0840.

4.1.18. 3-Phenylquinoline (22).[8] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.19 (s, 1H), 8.30 (s, 1H), 8.15 (d, J=8.8 Hz, 1H), 7.88 (d, J=8.0 Hz, 1H), 7.72 (d, J=7.2 Hz, 3H), 7.60–7.51 (m, 3H), 7.44 (t, J=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9, 147.3, 137.8, 133.8, 133.2, 129.4, 129.2, 129.1, 128.1, 128.0 (2C), 127.4, 127.0; LRMS (EI, 20 eV) *m/z* (%): 205 (M^+, 100).

4.1.19. 5-Phenylpyrimidine (23).[3] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.21 (s, 1H), 8.96 (s, 2H), 7.58 (d, J=8.8 Hz, 2H), 7.53 (t, J=8.8 Hz, 2H), 7.47 (t, J=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3, 154.8, 134.2, 134.1, 129.3, 128.9, 126.7; LRMS (EI, 20 eV) *m/z* (%): 156 (M^+, 100).

4.1.20. 5-(2,6-Dimethylphenyl)pyrimidine (24). White solid, mp 50–52 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.23 (s, 1H), 8.60 (s, 2H), 7.26 (t, J=8.0 Hz, 1H), 7.17 (d, J=8.4 Hz, 2H), 2.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3, 157.1, 136.4, 134.6, 133.8, 128.7, 127.8, 21.0; LRMS (EI, 20 eV) *m/z* (%): 184 (M^+, 100); HRMS (EI) for $C_{12}H_{12}N_2$ (M^+): calcd, 184.1001; found, 184.1000.

4.1.21. 5-(4-Methoxyphenyl)pyrimidine (25). White solid, mp 91–93 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.16 (s, 1H), 8.92 (s, 2H), 7.53 (d, J=8.4 Hz, 2H), 7.05 (d, J=8.4 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 156.8, 154.3, 133.8, 128.0, 126.4, 114.8, 55.3; LRMS (EI, 20 eV) *m/z* (%): 186 (M^+, 100); HRMS (EI) for $C_{11}H_{10}N_2O$ (M^+): calcd, 186.0793; found, 186.0791.

4.1.22. 2-Phenylpyrazine (26).[9] White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.04 (d, J=1.6 Hz, 2H), 8.65 (s, 1H), 8.52 (d, J=2.4 Hz, 1H), 8.02 (d, J=8.0 Hz, 2H), 7.51 (t, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8, 144.2, 142.9, 142.2, 136.3, 129.9, 129.0, 126.9; LRMS (EI, 20 eV) *m/z* (%): 156 (M^+, 100).

4.1.23. 2-Phenylthiophene (27).[10] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61–7.57 (m, 2H), 7.35 (t, J=7.6 Hz, 2H), 7.29–7.23 (m, 2H), 7.05 (t, J=4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4, 134.3, 128.8, 127.9, 127.4, 125.9, 124.7, 123.0; LRMS (EI, 20 eV) *m/z* (%): 160 (M^+, 100).

4.1.24. 2-(4-Nitrophenyl)thiophene (28).[11] Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, J=8.8 Hz, 2H), 7.74 (d, J=9.6 Hz, 2H), 7.48 (d, J=4.0 Hz, 1H), 7.44 (d, J=5.2 Hz, 1H), 7.15 (t, J=4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.6, 141.6, 140.6, 128.7, 127.7, 126.0, 125.7, 124.4; LRMS (EI, 20 eV) *m/z* (%): 205 (M^+, 100).

4.1.25. 2-(4-Nitrophenyl)furan (29).[11] Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (d, J=8.8 Hz, 2H), 7.78 (d, J=7.8 Hz, 2H), 7.57 (d, J=1.2 Hz, 1H), 6.87

(d, J=2.4 Hz, 1H), 6.55 (t, J=3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.7, 146.4, 144.1, 136.4, 124.3, 123.3, 112.4, 108.6; LRMS (EI, 20 eV) m/z (%): 189 (M^+, 100).

4.1.26. 4-(4-Nitrophenyl)pyridine (30). Yellow solid, mp 128.4–129.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (d, J=6.0 Hz, 2H), 8.36 (d, J=8.8 Hz, 2H), 7.81 (d, J=8.8 Hz, 2H), 7.55 (d, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.6, 148.1, 145.7, 144.4, 127.9, 124.3, 121.7; LRMS (EI, 20 eV) m/z (%): 200 (M^+, 100).

4.1.27. 2-Phenylfuran (31).[12] White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.67 (d, J=8.8 Hz, 1H), 7.60 (d, J=8.8 Hz, 2H), 7.46–7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.0, 128.7, 128.6, 127.3, 127.2, 127.1, 123.7, 111.6; LRMS (EI, 20 eV) m/z (%): 144 (M^+, 100).

4.1.28. 3-(Thiophen-2-yl)quinoline (33). White solid, mp 73.4–73.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.18 (s, 1H), 8.21 (s, 1H), 8.08 (d, J=8.0 Hz, 1H), 7.77 (d, J=8.4 Hz, 1H), 7.66 (t, J=7.6 Hz, 1H), 7.51 (t, J=7.6 Hz, 1H), 7.45 (s, 1H), 7.35 (d, J=4.8 Hz, 1H), 7.12 (t, J=4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.5, 147.1, 140.6, 131.2, 129.2, 129.1, 128.3, 127.8, 127.7, 127.4, 127.1, 126.0, 124.3; LRMS (EI, 20 eV) m/z (%): 211 (M^+, 100); HRMS (EI) for $C_{13}H_9NS$ (M^+): calcd, 211.0456; found, 211.0455.

4.1.29. 3-(Furan-2-yl)quinoline (34). Pale solid, mp 81.7–82.0 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.21 (s, 1H), 8.33 (s, 1H), 8.07 (d, J=8.4 Hz, 1H), 7.81 (d, J=8.0 Hz, 1H), 7.66 (t, J=8.8 Hz, 1H), 7.56–7.51 (m, 2H), 6.85 (d, J=3.2 Hz, 1H), 6.54 (d, J=5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.3, 147.1, 143.1, 129.3, 129.2, 129.0, 127.9, 127.8, 127.1, 124.0, 111.9, 106.7; LRMS (EI, 20 eV) m/z (%): 195 (M^+, 100); HRMS (EI) for $C_{13}H_9NO$ (M^+): calcd, 195.0684; found, 195.0684.

4.1.30. 5-(Thiophen-2-yl)pyrimidine (35). White solid, mp 77.2–78.0 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.13 (s, 1H), 8.96 (s, 1H), 7.46 (d, J=6.0 Hz, 2H), 7.43 (d, J=5.2 Hz, 1H), 7.18 (t, J=3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.2, 153.4, 136.2, 128.6 (2C), 127.3, 125.2; LRMS (EI, 20 eV) m/z (%): 162 (M^+, 100); HRMS (EI) for $C_8H_6N_2S$ (M^+): calcd, 162.0252; found, 162.0251.

4.1.31. 5-(Furan-2-yl)pyrimidine (36).[13] Slight yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10 (s, 1H), 9.01 (s 2H), 7.59 (d, J=1.6 Hz, 1H), 6.85 (d, J=3.6 Hz, 1H), 6.55 (t, J=1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.0, 151.3, 147.9, 144.0, 125.0, 112.1, 107.9; LRMS (EI, 20 eV) m/z (%): 146 (M^+, 100).

4.1.32. 2-(Thiophen-2-yl)pyrazine (37).[13] Slight yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.96 (s, 1H), 8.51 (s, 1H), 8.40 (s, 1H), 7.69 (d, J=4.0 Hz, 1H), 7.49 (d, J=5.6 Hz, 1H), 7.16 (t, J=4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.5, 143.9, 142.3, 141.3, 140.6, 129.0, 128.4, 125.7; LRMS (EI, 20 eV) m/z (%): 162 (M^+, 100).

4.1.33. 2-(Pyridin-4-yl)pyrazine (38). Slight yellow solid, mp 87.6–88.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.11 (s, 1H), 8.79 (d, J=6.0 Hz, 2H), 8.72 (s, 1H), 8.64 (s, 1H), 7.93 (d, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7, 150.1, 144.7, 144.6, 143.5, 142.3, 120.9; LRMS (EI, 20 eV) m/z (%): 157 (M^+, 100); HRMS (EI) for $C_9H_7N_3$ (M^+): calcd, 157.0640; found, 157.0640.

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Supplementary data

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