Cyclopalladated ferrocenylimines:highly active catalysts for Suzuki-Miyaura Reaction

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Dedicated to Academician Chengye Yuan on the Occasion of his 80th birthday

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Abstract

Cyclopalladated ferrocenylimines were found to be efficient phosphine-free catalysts for the Suzuki-Miyaura reaction of aryl iodides, bromides or chlorides with arylboronic acids. Moderate to excellent yields and high turnover numbers were obtained under certain reaction conditions. The stability, efficiency and activity of the catalyst **1** [$\{PdCl[C_5H_5FeC_5H_3C(CH_3)=N-(C_6H_4-CH_3)]\}_2$] were studied.

Keywords: Phosphine-free, cyclopalladated ferrocenylimine, Suzuki-Miyaura, cross-coupling

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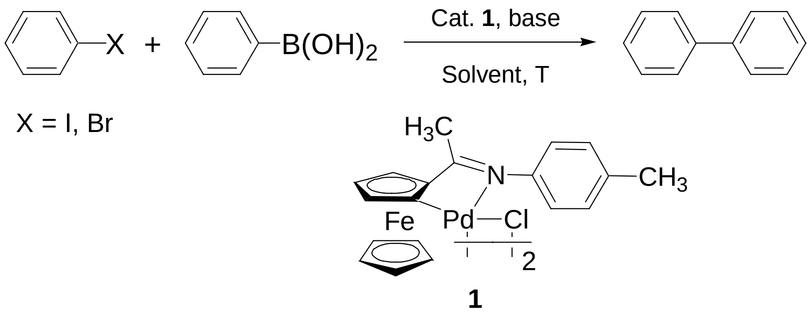
Introduction

The palladium-catalyzed Suzuki-Miyaura cross-coupling reaction between organoboron compounds and organic halides provides a powerful and general methodology for the formation of new carbon-carbon bonds. In the case of reaction of arylboronic acids and aryl halides, biaryls[1] are formed, which are an important class of compounds for many applications including pharmaceuticals, polymers, advanced materials, liquid crystals, and ligand synthesis.[2] The extension of the scope of Suzuki-Miyaura reaction and the search for more efficient catalyst have been one of the most popular aims of research for organic chemists,[3] and some recent progress has been made in this reaction. Buchwald[4] and Fu[5] have used sterically demanding, electron-rich tertiary phosphine as the catalyst modifier and made possible the activation of inexpensive aryl chlorides as coupling partners. Nolan[6] and Herrmann[7] have reported the use of nucleophilic N-heterocyclic carbenes (NHC) as auxiliary ligands in palladium-mediated Suzuki-Miyaura cross-coupling reactions of aryl halides or aryl triflates with arylboronic acids. However, palladacycles have been by far the most developed and extensively studied catalysts. They are presently the most successful and the most promising catalysts in C-C bond-forming reaction[7a, 8] because of their structural versatility and easy synthetic accessibility. Among them, phosphapalladacycles[9] and NHC[6a, 7a, 10] are able to catalyze the Suzuki-Miyaura cross-couplings of aryl bromides and chlorides with phenylboronic acids in good yields but generally under inert atmosphere. Bedford[11] has prepared orthometallated monomeric amine complexes as very active catalysts for the Suzuki-Miyaura cross-couplings both activated and nonactivated aryl chlorides, while tricyclohexylphosphine had to be used as ligands. Milstein[12] has shown that phosphine-free cyclometallated imine dimers are able to mediate Suzuki-Miyaura reaction involving aryl bromides with high TONs. However, this system was sterile when using inexpensive and readily accessible aryl chlorides.

We have found that cyclopalladated ferrocenylimines are a novel kind of efficient phosphine-free catalyst for the Heck reaction and the dimerization of arylmercurials.[13] Our interest in studies of the catalytic efficiency of cyclopalladated ferrocenylimines has prompted us to survey their efficiency in Suzuki-Miyaura reaction. The results indicated that cyclopalladated ferrocenylimines are also novel, highly efficient catalysts for this reaction.

Results and Discussion

Initially, we performed a brief investigation on the reactivity of catalyst **1** in the presence of different bases and solvents. The cross-coupling reaction of iodobenzene and bromobenzene with phenylboronic acid were used as the test systems (Scheme 1, Table 1).



Scheme 1. Investigation of the effect of bases and solvents on the reaction.

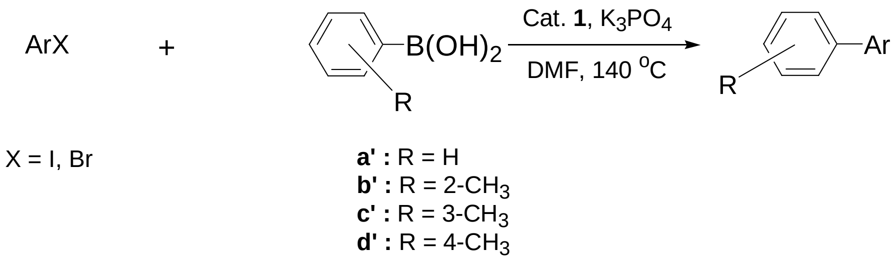
As shown in table **1**, with 10^{-2} mol % of Pd catalyst **1,** in general the reaction proceeded smoothly in DMF and the best results were obtained with potassium phosphate in DMF (entries 2, 7). The relevant conditions were then used for all subsequent Suzuki-Miyaura reactions with different substrates.

Table 1. Investigation of the Suzuki-Miyaura reaction conditions

Entry[a]	PhX	Base	Yield[b] (%)		
			DMF (140 ^{o}C)	Dioxane (101 ^{o}C)	Xylene (130 ^{o}C)
1	C_6H_5I[c]	K_2CO_3	88	69	45
2	C_6H_5I[c]	K_3PO_4	94	92	51
3	C_6H_5I[c]	Cs_2CO_3	89	91	44
4	C_6H_5I[c]	KF	89	77	25
5	C_6H_5I[c]	NaOH	10	78	21
6	C_6H_5Br[d]	K_2CO_3	87	7	81
7	C_6H_5Br[d]	K_3PO_4	89	12	80
8	C_6H_5Br[d]	Cs_2CO_3	89	59	87
9	C_6H_5Br[d]	KF	87	11	32
10	C_6H_5Br[d]	NaOH	63	31	60

[a] Reaction stoichiometry: PhX 2.0 mmol, $PhB(OH)_2$ 3.0 mmol, base 4.0 mmol except entries 4, 9 (6.6 mmol), solvent 7 mL, 2.0×10^{-4} mmol of Pd of catalyst **1**. [b] Average results of two runs determined by HPLC based on PhX. [c] reaction time 4 h. [d] reaction time 6 h.

Under the optimized conditions, we studied the activity of catalyst **1** towards different aryl halides and arylboronic acids. As expected, cyclopalladated ferrocenylimine **1** was found to efficiently catalyze the coupling of a wide range of aryl iodides or bromides with arylboronic acids (Scheme 2). Good to excellent yields and high turnover numbers were obtained regardless of substituent effect on the arylhalides. The experimental results are listed in Table 2.



Scheme 2. Suzuki-Miyaura reaction of aryl iodides and bromides with arylboronic acids.

Table 2. Suzuki-Miyaura reaction of aryl iodides and bromides with arylboronic acids

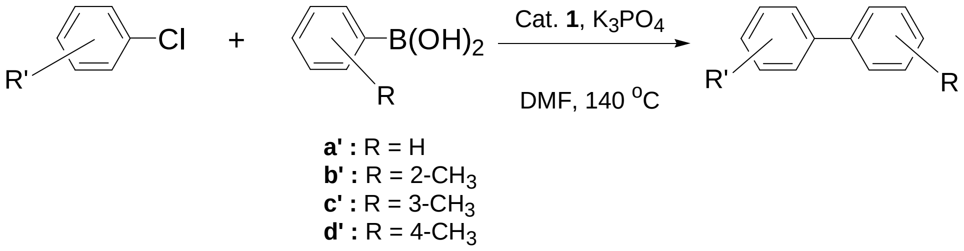
Entry[a]	ArX	ArB(OH)$_2$	Catalyst **1** (mmol% of Pd)	Time (h)	Yield (%)	TON
1 [d]	C_6H_5I	$C_6H_5B(OH)_2$	10^{-2}	1	94[b]	9400
2 [d]	3-$CH_3C_6H_4I$	$C_6H_5B(OH)_2$	10^{-2}	1	.93[c]	9300
3 [d]	4-$CH_3C_6H_4I$	$C_6H_5B(OH)_2$	10^{-2}	1	100[c]	10000
4 [d]	4-$CH_3OC_6H_4I$	$C_6H_5B(OH)_2$	10^{-2}	3	97[c]	9700
5 [f]	4-$CH_3OC_6H_4I$	3-$CH_3C_6H_5B(OH)_2$	10^{-2}	1	99[c]	9900
6 [f]	4-$CH_3OC_6H_4I$	4-$CH_3C_6H_5B(OH)_2$	10^{-2}	1	99[c]	9900
7 [d]	4-$NH_2C_6H_4I$	$C_6H_5B(OH)_2$	10^{-2}	7	95[c]	9500
8 [d]	4-ClC_6H_4I	$C_6H_5B(OH)_2$	10^{-2}	1	96[c]	9600
9 [d]	4-ClC_6H_4I	$C_6H_5B(OH)_2$	1.66×10^{-3}	3	80[b]	48200
10 [d]	2-iodothiophene	$C_6H_5B(OH)_2$	10^{-2}	10	93[c]	9300
11 [d]	C_6H_5Br	$C_6H_5B(OH)_2$	10^{-2}	6	89[b]	8900
12 [d]	4-$NO_2C_6H_4Br$	$C_6H_5B(OH)_2$	10^{-2}	6	93[b]	9300
13 [d]	4-$NO_2C_6H_4Br$	$C_6H_5B(OH)_2$	10^{-3}	10	77[b]	77000
14 [d]	4-$NO_2C_6H_4Br$	2-$CH_3C_6H_4B(OH)_2$	10^{-2}	6	99[c]	9900
15 [d]	4-$CF_3C_6H_4Br$	$C_6H_5B(OH)_2$	10^{-2}	6	98[c]	9800
16 [e]	4-$CF_3C_6H_4Br$	2-$CH_3C_6H_4B(OH)_2$	10^{-2}	6	89[c]	8900
17 [e]	4-$CF_3C_6H_4Br$	3-$CH_3C_6H_4B(OH)_2$	10^{-3}	6	99[c]	99000
18 [d]	4-CNC_6H_4Br	$C_6H_5B(OH)_2$	10^{-1}	6	81[b]	810
19 [e]	4-CNC_6H_4Br	2-$CH_3C_6H_4B(OH)_2$	10^{-2}	6	88[c]	8800
20 [d]	4-$CH_3COC_6H_4Br$	$C_6H_5B(OH)_2$	10^{-2}	6	80[b]	8000
21 [d]	4-$CH_3COC_6H_4Br$	2-$CH_3C_6H_4B(OH)_2$	10^{-3}	6	100[c]	100000
22 [d]	4-$CH_3COC_6H_4Br$	3-$CH_3C_6H_4B(OH)_2$	10^{-3}	6	99[c]	99000
23 [d]	4-$CH_3COC_6H_4Br$	4-$CH_3C_6H_4B(OH)_2$	10^{-3}	6	100[b]	100000
24 [d]	4-ClC_6H_4Br	$C_6H_5B(OH)_2$	10^{-2}	6	100[b]	10000
25 [d]	4-$CH_3OC_6H_4Br$	$C_6H_5B(OH)_2$	10^{-2}	6	93[c]	9300
26 [e]	4-$CH_3OC_6H_4Br$	2-$CH_3C_6H_4B(OH)_2$	10^{-2}	6	100[c]	10000

[a] Reaction conditions: ArX 2.0 mmol, ArB(OH)$_2$ 3.0 mmol, K_3PO_4 4.0 mmol, 7 mL of DMF, reflux. [b] Average results of two runs determined by HPLC based on ArX. [c] Isolated yields based on ArX. The compounds were purified by preparative TLC on silica gel. [d] The products of these reactions were characterized by comparison of m.p. or n_D^{20} with those in literature.[16a] [e] The products of these reactions were characterized by comparison of the ^{1}H NMR data with those in literature.[16d, 16e, 16f, 16g] [f] The products of these reactions were characterized by elemental analysis.

Here it can be seen that electron-donating methyl group on the phenyl ring of the arylboronic acid can improve the cross-coupling reaction in most cases (entries 5, 6, 14, 17, 19, 21, 22, 23, 26). When 1.66×10^{-3} mol % of Pd of catalyst **1** was used to catalyze the cross-coupling of 4-

chloroiodobenzene with phenylboronic acid, the optimal result was obtained with 4.82×10^4 turnover number and 80% yield (entry 9). In the reaction of 4-bromoacetophenone with 2- and 4-methyl-phenylboronic acids, the highest TON obtained was 1×10^5 with the yield of 100 % (entries 21, 23).

We next investigated the catalytic activity of this catalyst towards the Suzuki-Miyaura reaction of arylchlorides with arylboronic acid, because arylchlorides are inexpensive, readily available in bulk quantities and most suitable for application in industrial synthesis (Scheme 3). As shown in Table 3, moderate to good yields and higher turnover numbers were obtained with electron-poor aryl chlorides. In the reaction of *m*-nitrochlorobenzene with *m*-methylphenylboronic acids, the highest TON obtained was 9.1×10^4 with the yield of 91 % (entry 3).



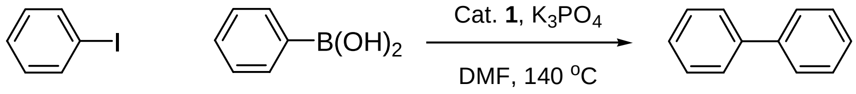
Scheme 3. Suzuki-Miyaura reaction of arylchlorides with arylboronic acids.

Table 3. Suzuki-Miyaura reaction of arylchlorides with arylboronic acids

Entry[a]	ArCl	$ArB(OH)_2$	Catalyst **1** (mmol % of Pd)	Time (h)	Yield (%)	TON
1 [d]	$4\text{-}NO_2C_6H_4Cl$	$C_6H_5B(OH)_2$	10^{-1}	10	91[b]	910
2 [d]	$3\text{-}NO_2C_6H_4Cl$	$C_6H_5B(OH)_2$	10^{-1}	20	.90[b]	900
3 [d]	$3\text{-}NO_2C_6H_4Cl$	$3\text{-}CH_3C_6H_4B(OH)_2$	10^{-3}	20	91[c]	91000
4 [d]	$3\text{-}CF_3C_6H_4Cl$	$C_6H_5B(OH)_2$	10^{-1}	20	74[c]	740
5 [d]	$4\text{-}CH_3COC_6H_4Cl$	$C_6H_5B(OH)_2$	10^{-1}	20	.64[b]	640
6 [d]	$4\text{-}CH_3COC_6H_4Cl$	$2\text{-}CH_3C_6H_4B(OH)_2$	10^{-3}	20	.60[c]	60000
7 [d]	$4\text{-}CH_3COC_6H_4Cl$	$3\text{-}CH_3C_6H_4B(OH)_2$	10^{-3}	20	59[c]	59000
8 [d]	$2,4\text{-}(NO_2)_2C_6H_3Cl$	$C_6H_5B(OH)_2$	10^{-1}	10	.98[c]	980
9 [d]	$2,4\text{-}(NO_2)_2C_6H_3Cl$	$C_6H_5B(OH)_2$	10^{-2}	20	66[c]	6600

[a] Reaction conditions: ArCl 2.0 mmol, $ArB(OH)_2$ 3.0 mmol, K_3PO_4 4.0 mmol, 7 mL of DMF, reflux. [b] Average results of two runs determined by HPLC based on ArCl. [c] Isolated yields based on ArCl. All compounds were purified by flash chromatography on silica gel [d] The products of these reactions were characterized by comparison of m.p. with those in literature.[16a]

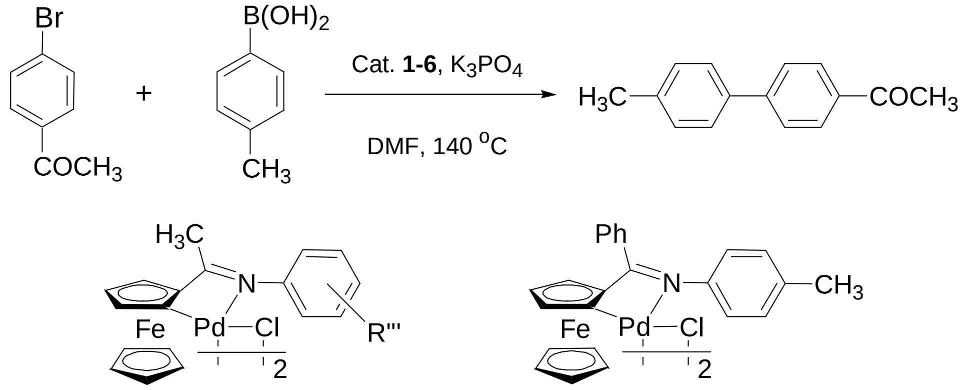
Apart from high catalytic efficiency, palladacycles **1** also demonstrated pronounced thermal stability. No significant deactivation of the recovered catalyst was observed in subsequent catalytic runs of cross-coupling iodobenzene with phenylboronic acid under typical conditions (2×10^{-2} mol % of Pd of catalyst **1**). HPLC analyses of five cycles yielded a constant rate of conversion of iodobenzene after addition of fresh reagents to the solution (Scheme 4).



First cycle: 100%, 0.5hr
Second cycle: 100%, 0.5hr
Third cycle: 100%, 0.5hr
Fourth cycle: 95.4%, 0.5hr
Fifth cycle: 90.1%, 0.5hr

Scheme 4. Stability of catalyst **1**.

In order to study the catalytic activity of different kinds of cyclopalladated ferrocenylimines **1-6**, we choose as a model the cross-coupling between *p*-methylphenylboronic acid and *p*-bromoacetophenone under the optimized conditions with a catalyst loading of 10^{-3} mol % of Pd of catalyst (Scheme 5, Table 4). The reaction provided very similar results and quantitative conversion in air for nearly all the dimeric complexes with reaction periods within 5 h.



1- 5 **6**

R''' = *p*-CH_3 (**1**), *p*-OCH_3 (**2**),
p-Cl (**3**), *o*-Cl (**4**), *m*-Cl (**5**)

Scheme 5. A catalyst survey.

Table 4. Suzuki-Miyaura reaction: catalyst study

Entry[a]	Catalyst (10^{-3} mol % Pd)	Time(h)	Yield[b](%)	TON
1	**1**	5	100	100000
2	**2**	5	99	99000
3	**3**	5	100	100000
4	**4**	5	.99	99000
5	**5**	5	100	100000
6	**6**	5	98	98000

[a] Reaction soichiometry: 4-$BrC_6H_4COCH_3$ 2.0 mmol, 4-$CH_3C_6H_4B(OH)_2$ 3.0 mmol, K_3PO_4 4.0 mmol, solvent 7 mL, catalyst **1**. [b] Average results of two runs determined by HPLC based on PhX.

In summary, cyclopalladated ferrocenylimines were found to be a very efficient kind of phosphine-free catalysts for the Suzuki-Miyaura reaction of aryl iodides, bromides and chlorides with arylboronic acids. Moderate to excellent yields and higher turnover numbers were obtained under optimized conditions. The variety of substrates, high stability, efficiency and activity after repeated uses make them an excellent kind of practical catalyst for Suzuki-Miyaura reaction, and further studies of their applicability in other organic transformations are in progress.

Experimental Section

General Procedures. Melting points were measured on a WC-1 microscopic apparatus and are uncorrected. Elemental analyses were determined with a Carlo-Erba 1106. ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer, using $CDCl_3$ as solvent and TMS as an internal reference standard. HPLC analyses were carried out on a Waters 600E type instrument equipped with a Nava-Pak (R) C8 60Å HPLC Cartridge column (3.9×150 mm, 4 μm), and UV detector for determination of the products. Preparative TLC was performed on dry silica gel plates developed with dichloromethane/petroleum.

All solvents were dried according to the standard methods. The aryl halides for Suzuki-Miyaura reaction were obtained from commercial sources and were generally used without further purification. The arylboronic acids were obtained according to the literature.[14]

Cyclopalladated ferrocenylimines **1-6** in which the metal center is stabilized by a five-membered ring were synthesized according to the literature method.[13a, 15]

The biaryls for HPLC external standard were prepared *via* Suzuki-Miyaura reaction and characterized by comparison of melting points or ^{1}H NMR spectra with the literatures values.[16]

Preparation of arylboronic acids

Synthesis of *tri-n*-butyl borate. A 500mL round-bottom flask equipped with a Dean-Stark trap with a condenser and a stirring bar was charged with boric acid (0.5 mol, 30.9 g) and 1-butanol (2.3 mol, 206 mL). The solution was heated at 120 °C in an oil bath and the water formed was separated using a Dean-Stark apparatus. The reaction was finished after 2.5 h while the solution went from cloudy white to clear. The solution was then transferred to a Claisen flask and distilled under vacuum to give a colorless oil at 103-105 °C/ 7 mmHg (lit[17]. 103-105 °C/ 8 mmHg), yield: 96 %.

Synthesis of phenylboronic acid. Under an argon atmosphere, a 250 mL three-neck flask equipped with a temperature probe and a mechanic stirrer bar was charged with THF (60 mL) and Grignard reagent (PhMgBr/THF, 0.3 mol/60 mL). The solution was cooled to –70 °C using a liquid nitrogen/ethanol bath. Tri-n-butyl-borate (0.3 mol, 81 mL) was added dropwise *via* a dropping funnel over 1 h and the mixture was stirred for an additional 1 h at –70 °C. Then the cold bath was removed and the reaction mixture was allowed to warm to –20 °C before 20 mL of H_2O was added. A 2N HCl solution was then added to bring the solution to pH 6, and the mixture was separated. The aqueous phase was extracted three times with ether and the combined organic phases were dried over Na_2SO_4. After removal of the solvent *in vacuo* the phenylboronic acid was obtained as a white powder, which was recrystallized from ethanol/water as white needles, m.p. 217-219 °C (Lit[14]. 217-221 °C), yield: 70 %.

Synthesis of methyl-substituted phenylboronic acids. Under an argon atmosphere, a 50 mL three-necked flask equipped with a 10 mL dropping funnel and a stirring bar was charged with $B(O^nBu)_3$ (0.1 mol, 2.298 g) and 10 mL THF. The solution was cooled to –10 °C using an ice/salt bath. Grignard reagent 2-$CH_3C_6H_4MgBr$/THF (0.3 mol/60 mL) was added dropwise *via* a 10 mL dropping funnel over 1 h and the solution was stirred for an additional 1 h. The cold bath was then removed and the mixture was allowed to warm to room temperature before H_2SO_4 (10%) was added to pH 6. The mixture was separated and the aqueous phase was extracted three times with ether. The combined organic phases were dried over Na_2SO_4. After removal of the solvent *in vacuo*, a yellow precipitate was obtained, which was recrystallized from ethanol/water as white plate crystals (2-$CH_3C_6H_4B(OH)_2$), m.p. 160-162 °C (Lit[14]. 162-164 °C), yield: 75 %.

Using the same procedure, 3-$CH_3C_6H_4B(OH)_2$, white plate crystals, m.p. 158-160°C (Lit[14]. 160-162 °C), and 4-$CH_3C_6H_4B(OH)_2$, white needles, m.p. 260-263°C (Lit[14]. 256-263 °C) were prepared.

General procedure for Suzuki-Miyaura reaction

Typical experimental procedure for Suzuki-Miyaura reaction (Table 1, entry 1): A 15 mL round-bottom flask was charged with iodobenzene (2.0 mmol, 0.408 g), phenylboronic acid (3.0 mmol, 0.366 g), potassium phosphate (4.0 mmol, 0.849 g), 10^{-4} catalyst **1** (0.5mL of a solution (1.832×10^{-1} mg, 2×10^{-4} mmol in 1 mL of dioxane)), and 6.5 mL of dioxane. The mixture was stirred at 100 °C in air and the reaction yield was determine by HPLC.

Typical experimental procedure for Suzuki-Miyaura reaction (Table 4, entry 1): A 15 mL round-bottom flask was charged with 4-acetyl bromobenzene (2.0 mmol, 0.398 g), 4-methylphenylboronic acid (3 mmol, 0.408 g), potassium phosphate (4.0 mmol, 0.849 g), 10^{-5} catalyst **1** (0.5mL of a solution (1.832×10^{-2} mg, 2×10^{-5} mmol in 1 mL of DMF)), and 6.5 mL of DMF. The mixture was stirred at 140 ^{o}C in air and the reaction progress was monitored by TLC. After the completion of the reaction, the mixture was diluted with 2N HCl and extracted with CH_2Cl_2 for three times. The combined organic phases were dried over Na_2SO_4. After removal of the solvent *in vacuo*, the product was isolated by preparative TLC and the yield was calculated based on ArX.

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