

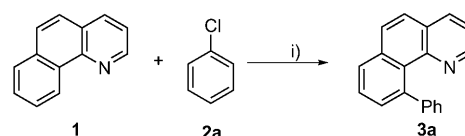
RuCl₃·xH₂O-Catalyzed Direct Arylation of Arenes with Aryl Chlorides in the Presence of Triphenylphosphine

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Development of a catalytic system utilizing inexpensive and readily available catalysts and reagents has been a challenge in organic synthesis. Direct arylation of arenes with organic coupling reagents through C–H bond activation has recently emerged as a promising alternative to traditional cross-coupling reactions using organometallic reagents and coupling partners such as aryl iodides, bromides, triflates, and other electrophiles^[1] due to generation of less toxic wastes.^[2,3] Aryl chlorides are considered as the ideal coupling partners for an economically attractive cross-coupling process because they are usually cheap and readily available. However, given that they are much less reactive than other coupling reagents, their utilization requires the implementation of specific experimental conditions. To date, ruthenium still shows the greatest potential for the direct regioselective functionalization of arenes under C–H activation,^[4] even though palladium and rhodium have been also applied for the same purpose.^[5] [[RuCl₂(*p*-cymene)]₂] and Ru^{IV} complexes were reported to catalyze arylation of arenes with aryl chlorides in the presence of K₂CO₃^[6–8] or KOAc.^[9] RuCl₃ is known to mediate the oxidative arylation of arenes with aryl iodides.^[10] RuCl₃·xH₂O was documented to promote arylation of arenes with aryl bromides,^[11] but it is inefficient for the same goal with aryl chlorides, although it can effect alkylation of activated C(sp³)–H bonds with alcohols.^[12] Herein, we report an economically attractive cata-

lytic system RuCl₃·xH₂O/PPh₃/Na₂CO₃/*N*-methyl-2-pyrrolidone for direct arylation of arenes with aryl chlorides.

In our initial studies, the phenylation of benzo[*h*]quinoline (**1**) with chlorobenzene (**2a**) was investigated (Scheme 1).



Scheme 1. i) Ru catalyst, ligand, base, solvent.

Using 5 mol % RuCl₃·xH₂O and 10 mol % PPh₃, the reaction of **1** and **2a** in *N*-methyl-2-pyrrolidone (NMP) formed **3a** as the only product in 86–93% yields at 120–130 °C in the presence of K₂CO₃; **3a** was quantitatively formed when Na₂CO₃ was used as the base (Table 1, entries 1–5). Thus, Na₂CO₃ acts more effectively than K₂CO₃ as a base for this reaction. Without the PPh₃ ligand the reaction did not occur (entry 6). The presence of an excess of ligand (15–20 mol %) did not affect formation of **3a**, whereas sub-stoichiometric

Table 1. Screening conditions for the reaction of benzo[*h*]quinoline (**1**) and chlorobenzene (**2a**).^[a]

	Catalyst/ [mol %]	Ligand/ [mol %]	Base	<i>T</i> [°C]	<i>t</i> [h]	Conv. ^[b] [%]
1	RuCl ₃ ·xH ₂ O/5	PPh ₃ /10	K ₂ CO ₃	120	24	86
2	RuCl ₃ ·xH ₂ O/5	PPh ₃ /10	K ₂ CO ₃	130	18	93
3	RuCl ₃ ·xH ₂ O/5	PPh ₃ /10	Na ₂ CO ₃	120	24	99
4	RuCl ₃ ·xH ₂ O/5	PPh ₃ /10	Na ₂ CO ₃	130	18	>99
5	RuCl ₃ ·xH ₂ O/5	PPh ₃ /10	Na ₂ CO ₃	140	16	100 ^[c]
6	RuCl ₃ ·xH ₂ O/5		Na ₂ CO ₃	140	22	0
7	RuCl ₃ ·xH ₂ O/5	PPh ₃ /5	Na ₂ CO ₃	140	24	68
8	RuCl ₃ ·xH ₂ O/2.5	PPh ₃ /5	Na ₂ CO ₃	140	24	32
9	RuCl ₃ ·xH ₂ O/5	PPh ₃ /10	KF	130	22	90
10	RuCl ₃ ·xH ₂ O/5	PPh ₃ /10	K ₃ PO ₄	130	22	99
11	[[RuCl ₂ (<i>p</i> -cymene)] ₂]/2.5	PPh ₃ /10	Na ₂ CO ₃	130	22	99
12	[RuCl ₂ (PPh ₃) ₃]/5		Na ₂ CO ₃	130	22	99

[a] Conditions: **1** (0.50 mmol), **2a** (0.75 mmol), base (1.00 mmol), NMP (2 mL). [b] Conversion of **1** by GC analysis. [c] Isolated yield, 99%.

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














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ligand amounts led to a reduced conversion for **1** (entry 7). KF and K₃PO₄ can also be used as bases for the reaction (entries 9 and 10), and both [[RuCl₂(*p*-cymene)]₂] and [RuCl₂(PPh₃)₃] promoted the arylation but with less efficiency than RuCl₃·*x*H₂O (entries 11 and 12). Eventually, the reaction conditions were optimized to: 5 mol % RuCl₃·*x*H₂O as catalyst, 10 mol % PPh₃ as ligand, Na₂CO₃ as base, 130 °C or 140 °C in NMP under nitrogen atmosphere.

Next, the arylation and benzylation of **1** with various aryl chlorides was explored. Under the optimized conditions, the desired products **3** were obtained in 73–99 % (Table 2).

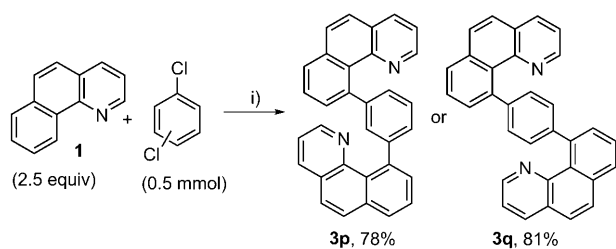
Table 2. Arylation of benzo[*h*]quinoline (**1**) with aryl chlorides (**2**).^[a]

 3a , 99 %	 3b , 75 %	 3c , 80 %	 3d , 83 %	 3e , 73 % ^[b]
 3f , 75 %	 3g , 76 %	 3h , 39 %	 3i , 87 %	 3j , 86 %
 3k , 73 %	 3l , 81 %	 3m , 75 %	 3n , 0 %	 3o , 62 % ^[c]

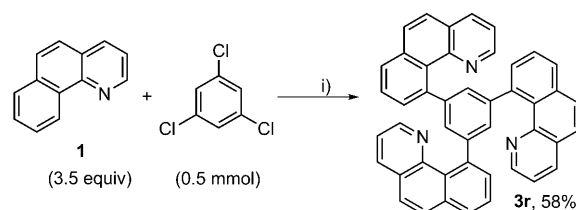
[a] Conditions: **1** (0.50 mmol), **2** (0.75 mmol), RuCl₃·*x*H₂O (5 mol %), PPh₃ (10 mol %), Na₂CO₃ (1.00 mmol), NMP (2 mL), 140 °C, 16 h; isolated yields. [b] 24 h. [c] RuCl₃·*x*H₂O (10 mol %), PPh₃ (20 mol %), 24 h.

However, 2'-chloroacetophenone exhibited a low reactivity to form **3h** (39 %) presumably due to the steric hindrance of its 2-substituent, and 4-chloronitrobenzene did not undergo the reaction. Unexpectedly, with 10 mol % catalyst benzylation of **1** with benzyl chloride occurred to afford **3o** in 62 % yield. Interestingly, polychlorobenzenes underwent direct polyarylation to give polyarene products. Thus, polyarenes **3p** (78 %), **3q** (81 %), and **3r** (58 %) were obtained from the reactions of **1** with dichloro-benzenes and 1,3,5-trichlorobenzene in a 2:1 and 3:1 molar ratios, respectively (Schemes 2 and 3). It should be noted that 1,2-dichlorobenzene exhibited no reactivity.

With 2-phenylpyridine (**4a**) as the arene substrate, a remarkable base effect was also observed in its reaction with

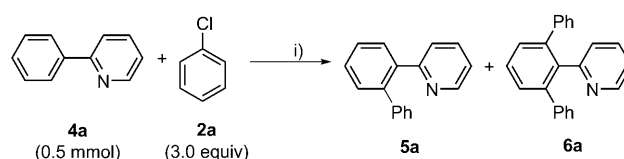


Scheme 2. i) RuCl₃·*x*H₂O (10 mol %), PPh₃ (20 mol %), Na₂CO₃ (3.0 equiv), NMP, 140 °C, 16 h.



Scheme 3. i) RuCl₃·*x*H₂O (15 mol %), PPh₃ (30 mol %), Na₂CO₃ (4.0 equiv), NMP, 140 °C, 16 h.

2a (Scheme 4, Table 3). Treatment of **4a** with an excess of **2a** was expected to form the diarylation product **6a**, but the mono-arylation product **5a** was also formed. With 5 mol %



Scheme 4. i) RuCl₃·*x*H₂O (10 mol %), PPh₃ (20 mol %), base (4.0 equiv), NMP (2 mL), 140 °C, 22 h.

Table 3. Base effect in the diphenylation of 2-phenylpyridine (**4a**) with chlorobenzene (**2a**).

	Catalyst[mol %]	Base	Yield ^[a] [%]	
			5a	6a
1	RuCl ₃ · <i>x</i> H ₂ O/5	K ₂ CO ₃	63	19
2	RuCl ₃ · <i>x</i> H ₂ O/5	Na ₂ CO ₃	28	70
3	RuCl ₃ · <i>x</i> H ₂ O/10	K ₂ CO ₃	50 (40) ^[b]	47 (35) ^[b]
4	RuCl ₃ · <i>x</i> H ₂ O/10	Na ₂ CO ₃	0	100 (99) ^[b]
5	RuCl ₃ · <i>x</i> H ₂ O/10	KF	62 (49) ^[b]	6
6	RuCl ₃ · <i>x</i> H ₂ O/10	K ₃ PO ₄	56	38
7	RuCl ₃ · <i>x</i> H ₂ O/10	Cs ₂ CO ₃	69	23
8	RuCl ₃ · <i>x</i> H ₂ O/10	NaHCO ₃	60	5
9	RuCl ₃ · <i>x</i> H ₂ O/10	DBU	34	9
10	RuCl ₃ · <i>x</i> H ₂ O/10	Et ₃ N	<1	<1
11 ^[c]	RuCl ₃ · <i>x</i> H ₂ O/10	Na ₂ CO ₃	25	2
12 ^[d]	RuCl ₃ · <i>x</i> H ₂ O/10	Na ₂ CO ₃	55	41
13 ^[e]	RuCl ₃ · <i>x</i> H ₂ O/10	Na ₂ CO ₃	4	95
14	[[RuCl ₂ (<i>p</i> -cymene)] ₂]/5	Na ₂ CO ₃	2	95
15 ^[f]	[RuCl ₂ (PPh ₃) ₃]/10	Na ₂ CO ₃	64	34

[a] Determined by GC analysis. [b] Isolated yields in parentheses. [c] PPh₃ (10 mol %). [d] In *o*-xylene. [e] 130 °C, 30 h. [f] Without PPh₃.

RuCl₃·*x*H₂O as catalyst, the reaction of **4a** and **2a** in a 1:3 molar ratio afforded **5a** (63 %) as the major product by using K₂CO₃ base, while **6a** was formed in 70 % yield in the presence of Na₂CO₃ (entries 1 and 2). Using 10 mol % catalyst the reaction proceeded more efficiently: with K₂CO₃ as the base **5a** and **6a** in almost equally amounts, while **4a** was quantitatively transformed to **6a** by using Na₂CO₃ base (entries 3 and 4). Other bases were much less effective than Na₂CO₃. It is worth noting that K₂CO₃ instead of Na₂CO₃ has usually been used as the base in a cross-coupling reaction,^[13] and more attention might be paid to Na₂CO₃ base to develop a new catalytic system for cross-couplings.^[5],14] The methodology was then applied in a variety of reactions of 2-

arylpiperidines (**4**) with aryl chlorides (**2**), affording the desired products **6** in good to excellent yields (55–99%; Table 4), among which tridentate terpyridine **6o** was obtained in 55% yield. 1-Phenylpyrazole and 2-phenyloxazo-

Table 4. Diarylation of 2-arylpiperidines (**4**) with aryl chlorides (**2**).^[a]

6a , 99%	6b , 60%	6c , 74%	6d , 78%	6e , 56%
6f , 82%	6g , 85%	6h , 0%	6i , 67%	6j , 95%
6k , 81%	6l , 0%	6m , 71%	6n , 58%	6o , 55% ^[b]
6p , 81%	6q , 70%	6r , 76%	6s , 85%	6t , 80% ^[c]

[a] Conditions: **4** (0.5 mmol) **2** (1.5 mmol) RuCl₃·xH₂O (10 mol %), PPh₃ (20 mol %), Na₂CO₃ (2.0 mmol), NMP (2 mL), 140 °C, 22 h. [b] 36 h. [c] RuCl₃·xH₂O (20 mol %), PPh₃ (40 mol %), 48 h.

line were also directly diarylated, forming **6q–t** in 70–85% yields. In a similar fashion, monoarylation products **5a–k** and **5o,p** were synthesized in 45–68% yields (Scheme 5,



Scheme 5. i) RuCl₃·xH₂O (10 mol %), PPh₃ (20 mol %), base (1.5 equiv), NMP (2 mL), 140 °C, 22 h.

Table 5, entries 1–13) with minor formation of the diarylation products **6** (8–25%; see the Supporting Information) by treating **4a** with equimolar amount of **2a–k** and **2o**, respectively. However, reactions of functionalized arenes **4c–e** only formed monoarylation products **5t–v** (57–75%; entries 14–16).

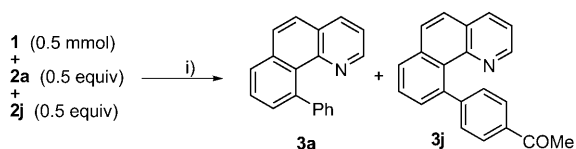
Competition reactions were studied to identify the reactivity of substrates. Reaction of **1** and **2a/2j** (1:1) in a 1:1 molar ratio reached 93% conversion for **1** in NMP at 140 °C within 16 h to form **3j** as the major product, revealing that

Table 5. Monoarylation of 2-arylpiperidines (**4**) with aryl chlorides (**2**).

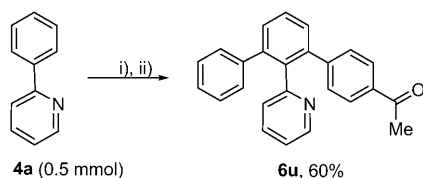
	4	ArCl	Product	Yield ^[a] [%]
1			5a	68
2	4a		5b	45
3	4a		5c	58
4	4a		5d	65
5	4a		5e	50
6	4a		5f	55
7	4a		5g	55
8	4a		5h	0
9	4a		5i	59
10	4a		5j	58
11	4a		5k	45
12	4a		5l	52
13		2a	5p	63
14 ^[b]		2a	5t	59
15 ^[c]		2a	5u	75
16 ^[c]		2a	5v	57 ^[d]

[a] Isolated yields. [b] **2a** (3.0 equiv), Na₂CO₃ (4.0 equiv). [c] **2a** (1.5 equiv), Na₂CO₃ (2.0 equiv). [d] 36 h.

4'-chloroacetophenone (**2j**) is more reactive than **2a** (Scheme 6). Treatment of **1/4a** (1:1) with **2a** in a 1:1 molar ratio under similar conditions produced a mixture of **3a**, **5a**, and **6a** (59:33:8), suggesting that **1** is more reactive than **4a** (see the Supporting Information). From a two-step one-pot reaction of **4a** with **2a** and then with **2j** (Scheme 7), diarylation product **6u** was obtained in 60% yield with minor formation of **6a** and **6j** (**6a/6j/6u** = 20:7:73), while the one-pot reaction of **4a**, **2a** and **2j** only produced a mixture of **5a**, **5j**, **6a**, **6j**, and **6u** (12:37:6:19:25; see the Supporting Informa-



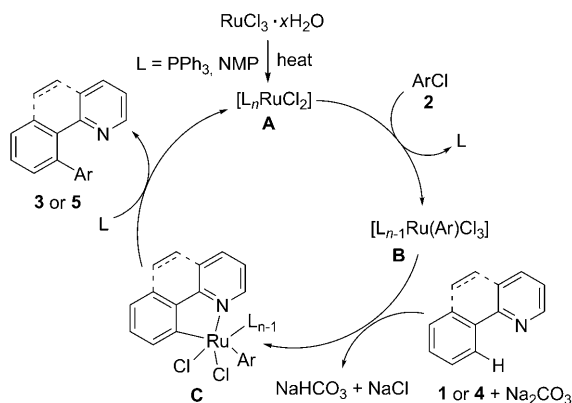
Scheme 6. i) $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (5 mol %), PPh_3 (10 mol %), Na_2CO_3 (2.0 equiv), NMP, 140°C , 16 h; 93% conversion for **1** (**3a/3j** = 43:57).



Scheme 7. i) $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (10 mol %), PPh_3 (20 mol %), **2a** (0.5 mmol), Na_2CO_3 (2.0 equiv), NMP, 140°C , 22 h; ii) **2j** (0.75 mmol), 140°C , 18 h; > 99% conversion for **4a** (**6a/6j/6u** = 20:7:73).

tion), further confirming that **2j** is more reactive than **2a**. This protocol thus provides a new route to mixed arylated arenes.

$^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the reaction mixture of **1** and **2a** under the reaction conditions or a mixture of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, Ph_3P and Na_2CO_3 in NMP heated at 140°C for two hours revealed formation of Ph_3PO and presence of free Ph_3P in the mixtures, suggesting that reduction of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ occurred during the reaction. Thus, a reaction mechanism is proposed in Scheme 8. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ is presumably reduced to Ru^{II}



Scheme 8. Proposed mechanism.

species **A** in situ with PPh_3 and a base by heating. It has been known that in refluxing methanol $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ can be reduced to Ru^{II} complexes in the presence of PPh_3 .^[15] Oxidative addition of aryl chloride to **A** leads to Ru^{IV} intermediate **B**, thus activating the $\text{C}(\text{sp}^2)\text{--Cl}$ bond. **B** reacts with arene **1** or **4** in the presence of Na_2CO_3 base to form Ru^{IV} species **C** through arene C–H bond activation. Reductive elimination by coordination of a ligand to **C** affords the desired product **3** or **5** and regenerates the catalytically active

Ru^{II} species **A**. Compound **5** is further arylated following the same mechanism to produce the diarylation product **6**.

In conclusion, a simple, efficient and economically attractive catalytic system has been developed for the direct arylation of arenes with aryl chlorides by using the catalytic system $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/\text{PPh}_3/\text{Na}_2\text{CO}_3/\text{NMP}$. Here, using Na_2CO_3 as a base instead of K_2CO_3 was found to result in a significant enhancement of the efficiency of the system. Our proposed mechanism suggests that the direct arylation of arenes is possibly initiated by an in situ generated Ru^{II} species from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in the presence of PPh_3 and Na_2CO_3 base.

Experimental Section

A typical procedure for the arylation of benzo[*h*]quinoline (1**) with aryl chlorides (**2**)—phenylation of **1** with chlorobenzene (**2a**):** Under nitrogen atmosphere, a mixture of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (7 mg, 0.025 mmol), **1** (90 mg, 0.50 mmol), chlorobenzene **2a** (85 mg, 0.75 mmol), PPh_3 (13 mg, 0.05 mmol), and Na_2CO_3 (106 mg, 1 mmol) in NMP (2 mL) was stirred at 140°C for 16 h. After cooled to ambient temperature, Et_2O (30 mL) and H_2O (20 mL) were added. The organic phase was separated and the aqueous layer was extracted with Et_2O (2×20 mL). The combined organic phase was washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4 , and then concentrated under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether (60– 90°C)/ EtOAc = 8:1, v/v), affording the target product **3a** as a white solid (126 mg, 99%). The product was characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and further confirmed by comparison with the reported authentic NMR data.

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Keywords: arenes • aryl chlorides • arylation • C–H activation • ruthenium

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