

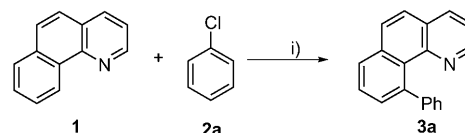
# RuCl<sub>3</sub>·xH<sub>2</sub>O-Catalyzed Direct Arylation of Arenes with Aryl Chlorides in the Presence of Triphenylphosphine

Ning Luo<sup>[a]</sup> and Zhengkun Yu<sup>\*[a, b]</sup>

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<sup>[1]</sup> due to generation of less toxic wastes.<sup>[2,3]</sup> 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,<sup>[4]</sup> even though palladium and rhodium have been also applied for the same purpose.<sup>[5]</sup> [[RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>] and Ru<sup>IV</sup> complexes were reported to catalyze arylation of arenes with aryl chlorides in the presence of K<sub>2</sub>CO<sub>3</sub><sup>[6–8]</sup> or KOAc.<sup>[9]</sup> RuCl<sub>3</sub> is known to mediate the oxidative arylation of arenes with aryl iodides.<sup>[10]</sup> RuCl<sub>3</sub>·xH<sub>2</sub>O was documented to promote arylation of arenes with aryl bromides,<sup>[11]</sup> but it is inefficient for the same goal with aryl chlorides, although it can effect alkylation of activated C(sp<sup>3</sup>)–H bonds with alcohols.<sup>[12]</sup> Herein, we report an economically attractive cata-

lytic system RuCl<sub>3</sub>·xH<sub>2</sub>O/PPh<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>/*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 % RuCl<sub>3</sub>·xH<sub>2</sub>O and 10 mol % PPh<sub>3</sub>, 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 K<sub>2</sub>CO<sub>3</sub>; **3a** was quantitatively formed when Na<sub>2</sub>CO<sub>3</sub> was used as the base (Table 1, entries 1–5). Thus, Na<sub>2</sub>CO<sub>3</sub> acts more effectively than K<sub>2</sub>CO<sub>3</sub> as a base for this reaction. Without the PPh<sub>3</sub> 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**).<sup>[a]</sup>

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

[a] N. Luo, Prof. Dr. Z. K. Yu  
Dalian Institute of Chemical Physics  
Chinese Academy of Sciences  
457 Zhongshan Road, Dalian 116023 (P. R. China)  
Fax: (+86)411-8437-9227  
E-mail: zkyu@dicp.ac.cn
















[b] Prof. Dr. Z. K. Yu  
State Key Laboratory of Organometallic Chemistry  
Shanghai Institute of Organic Chemistry  
Chinese Academy of Sciences  
354 Fenglin Road, Shanghai 200032 (P. R. China)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200902612>.

ligand amounts led to a reduced conversion for **1** (entry 7). KF and  $K_3PO_4$  can also be used as bases for the reaction (entries 9 and 10), and both  $[RuCl_2(p\text{-cymene})_2]$  and  $[RuCl_2(PPh_3)_3]$  promoted the arylation but with less efficiency than  $RuCl_3 \cdot xH_2O$  (entries 11 and 12). Eventually, the reaction conditions were optimized to: 5 mol %  $RuCl_3 \cdot xH_2O$  as catalyst, 10 mol %  $PPh_3$  as ligand,  $Na_2CO_3$  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).

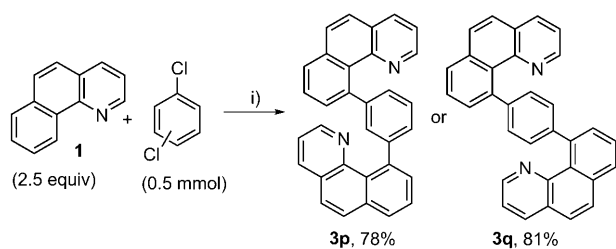
Table 2. Arylation of benzo[*h*]quinoline (**1**) with aryl chlorides (**2**).<sup>[a]</sup>

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

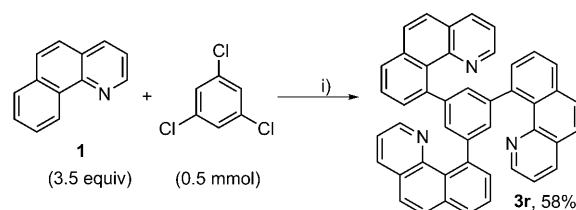
[a] Conditions: **1** (0.50 mmol), **2** (0.75 mmol),  $RuCl_3 \cdot xH_2O$  (5 mol %),  $PPh_3$  (10 mol %),  $Na_2CO_3$  (1.00 mmol), NMP (2 mL), 140 °C, 16 h; isolated yields. [b] 24 h. [c]  $RuCl_3 \cdot xH_2O$  (10 mol %),  $PPh_3$  (20 mol %), 24 h.

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

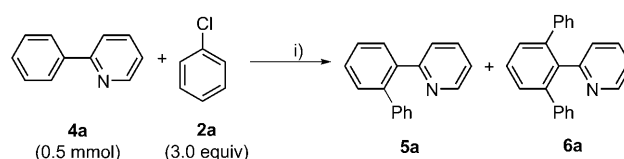


Scheme 2. i)  $RuCl_3 \cdot xH_2O$  (10 mol %),  $PPh_3$  (20 mol %),  $Na_2CO_3$  (3.0 equiv), NMP, 140 °C, 16 h.



Scheme 3. i)  $RuCl_3 \cdot xH_2O$  (15 mol %),  $PPh_3$  (30 mol %),  $Na_2CO_3$  (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)  $RuCl_3 \cdot xH_2O$  (10 mol %),  $PPh_3$  (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 <sup>[a]</sup> [%]	
			<b>5a</b>	<b>6a</b>
1	$RuCl_3 \cdot xH_2O/5$	$K_2CO_3$	63	19
2	$RuCl_3 \cdot xH_2O/5$	$Na_2CO_3$	28	70
3	$RuCl_3 \cdot xH_2O/10$	$K_2CO_3$	50 (40) <sup>[b]</sup>	47 (35) <sup>[b]</sup>
4	$RuCl_3 \cdot xH_2O/10$	$Na_2CO_3$	0	100 (99) <sup>[b]</sup>
5	$RuCl_3 \cdot xH_2O/10$	KF	62 (49) <sup>[b]</sup>	6
6	$RuCl_3 \cdot xH_2O/10$	$K_3PO_4$	56	38
7	$RuCl_3 \cdot xH_2O/10$	$Cs_2CO_3$	69	23
8	$RuCl_3 \cdot xH_2O/10$	$NaHCO_3$	60	5
9	$RuCl_3 \cdot xH_2O/10$	DBU	34	9
10	$RuCl_3 \cdot xH_2O/10$	$Et_3N$	<1	<1
11 <sup>[c]</sup>	$RuCl_3 \cdot xH_2O/10$	$Na_2CO_3$	25	2
12 <sup>[d]</sup>	$RuCl_3 \cdot xH_2O/10$	$Na_2CO_3$	55	41
13 <sup>[e]</sup>	$RuCl_3 \cdot xH_2O/10$	$Na_2CO_3$	4	95
14	$[RuCl_2(p\text{-cymene})_2]/5$	$Na_2CO_3$	2	95
15 <sup>[f]</sup>	$[RuCl_2(PPh_3)_3]/10$	$Na_2CO_3$	64	34

[a] Determined by GC analysis. [b] Isolated yields in parentheses. [c]  $PPh_3$  (10 mol %). [d] In *o*-xylene. [e] 130 °C, 30 h. [f] Without  $PPh_3$ .

$RuCl_3 \cdot xH_2O$  as catalyst, the reaction of **4a** and **2a** in a 1:3 molar ratio afforded **5a** (63%) as the major product by using  $K_2CO_3$  base, while **6a** was formed in 70% yield in the presence of  $Na_2CO_3$  (entries 1 and 2). Using 10 mol % catalyst the reaction proceeded more efficiently: with  $K_2CO_3$  as the base **5a** and **6a** in almost equally amounts, while **4a** was quantitatively transformed to **6a** by using  $Na_2CO_3$  base (entries 3 and 4). Other bases were much less effective than  $Na_2CO_3$ . It is worth noting that  $K_2CO_3$  instead of  $Na_2CO_3$  has usually been used as the base in a cross-coupling reaction,<sup>[13]</sup> and more attention might be paid to  $Na_2CO_3$  base to develop a new catalytic system for cross-couplings.<sup>[5],14]</sup> 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**).<sup>[a]</sup>

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

[a] Conditions: **4** (0.5 mmol) **2** (1.5 mmol) RuCl<sub>3</sub>·xH<sub>2</sub>O (10 mol %), PPh<sub>3</sub> (20 mol %), Na<sub>2</sub>CO<sub>3</sub> (2.0 mmol), NMP (2 mL), 140 °C, 22 h. [b] 36 h. [c] RuCl<sub>3</sub>·xH<sub>2</sub>O (20 mol %), PPh<sub>3</sub> (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) RuCl<sub>3</sub>·xH<sub>2</sub>O (10 mol %), PPh<sub>3</sub> (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).

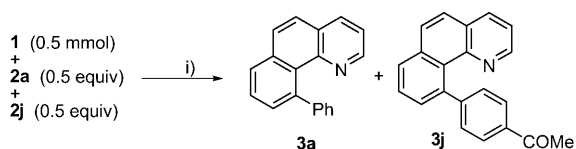
Competition reactions were studied to identify the reactivity of substrates. Reaction of **1** and **2a/2j** (1:1) in a 1:1 molar ratio reached 93% conversion for **1** in NMP at 140 °C within 16 h to form **3j** as the major product, revealing that

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

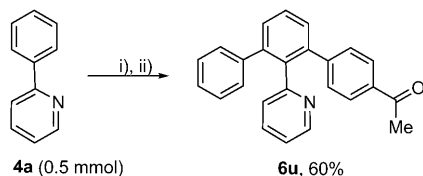
	<b>4</b>	ArCl	Product	Yield <sup>[a]</sup> [%]
1			<b>5a</b>	68
2	<b>4a</b>		<b>5b</b>	45
3	<b>4a</b>		<b>5c</b>	58
4	<b>4a</b>		<b>5d</b>	65
5	<b>4a</b>		<b>5e</b>	50
6	<b>4a</b>		<b>5f</b>	55
7	<b>4a</b>		<b>5g</b>	55
8	<b>4a</b>		<b>5h</b>	0
9	<b>4a</b>		<b>5i</b>	59
10	<b>4a</b>		<b>5j</b>	58
11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

[a] Isolated yields. [b] **2a** (3.0 equiv), Na<sub>2</sub>CO<sub>3</sub> (4.0 equiv). [c] **2a** (1.5 equiv), Na<sub>2</sub>CO<sub>3</sub> (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-



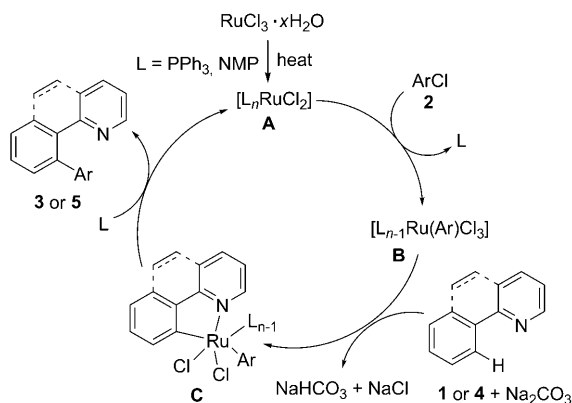
Scheme 6. i)  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (5 mol %),  $\text{PPh}_3$  (10 mol %),  $\text{Na}_2\text{CO}_3$  (2.0 equiv), NMP,  $140^\circ\text{C}$ , 16 h; 93% conversion for **1** (**3a/3j** = 43:57).



Scheme 7. i)  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (10 mol %),  $\text{PPh}_3$  (20 mol %), **2a** (0.5 mmol),  $\text{Na}_2\text{CO}_3$  (2.0 equiv), NMP,  $140^\circ\text{C}$ , 22 h; ii) **2j** (0.75 mmol),  $140^\circ\text{C}$ , 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  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{Ph}_3\text{P}$  and  $\text{Na}_2\text{CO}_3$  in NMP heated at  $140^\circ\text{C}$  for two hours revealed formation of  $\text{Ph}_3\text{PO}$  and presence of free  $\text{Ph}_3\text{P}$  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  $\text{Ru}^{\text{II}}$



Scheme 8. Proposed mechanism.

species **A** in situ with  $\text{PPh}_3$  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  $\text{Ru}^{\text{II}}$  complexes in the presence of  $\text{PPh}_3$ .<sup>[15]</sup> Oxidative addition of aryl chloride to **A** leads to  $\text{Ru}^{\text{IV}}$  intermediate **B**, thus activating the  $\text{C}(\text{sp}^2)\text{--Cl}$  bond. **B** reacts with arene **1** or **4** in the presence of  $\text{Na}_2\text{CO}_3$  base to form  $\text{Ru}^{\text{IV}}$  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

$\text{Ru}^{\text{II}}$  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  $\text{Na}_2\text{CO}_3$  as a base instead of  $\text{K}_2\text{CO}_3$  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  $\text{Ru}^{\text{II}}$  species from  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in the presence of  $\text{PPh}_3$  and  $\text{Na}_2\text{CO}_3$  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),  $\text{PPh}_3$  (13 mg, 0.05 mmol), and  $\text{Na}_2\text{CO}_3$  (106 mg, 1 mmol) in NMP (2 mL) was stirred at  $140^\circ\text{C}$  for 16 h. After cooled to ambient temperature,  $\text{Et}_2\text{O}$  (30 mL) and  $\text{H}_2\text{O}$  (20 mL) were added. The organic phase was separated and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  ( $2 \times 20$  mL). The combined organic phase was washed with  $\text{H}_2\text{O}$  (20 mL) and brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$ , and then concentrated under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether (60– $90^\circ\text{C}$ )/ $\text{EtOAc}$  = 8:1, v/v), affording the target product **3a** as a white solid (126 mg, 99%). The product was characterized by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy and further confirmed by comparison with the reported authentic NMR data.

## Acknowledgements

We are grateful to the National Basic Research Program of China (2009CB825300), the National Natural Science Foundation of China (20772124, 20972157), and the Knowledge Innovation Program of the Chinese Academy of Sciences (DICP K2009D04) for support of this research.

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

- [1] *Transition Metals for Organic Synthesis*, 2nd ed. (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**.
- [2] Selected recent reviews on direct arylation, see: a) G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447; b) J. C. Lewis, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013; c) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173; d) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; e) L. Ackermann, *Top. Organomet. Chem.* **2008**, *24*, 35; f) T. Satoh, M. Miura, *Top. Organomet. Chem.* **2008**, *24*, 61; g) L. Ackermann, *Synlett* **2007**, 507; h) J.-Q. Yu, R. Giri, X. Chen, *Org. Biomol. Chem.* **2006**, *4*, 4041; i) O. Daugulis, V. G. Zaitsev, D. Shabashov, Q. N. Pham, A. Lazareva, *Synlett* **2006**, 3382; j) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731.
- [3] Selected recent reports on cross-couplings of two arenes, see: a) S. H. Cho, S. J. Hwang, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 9254; b) T. Dohi, M. Ito, K. Morimoto, M. Iwata, Y. Kita, *Angew. Chem.* **2008**, *120*, 1321; *Angew. Chem. Int. Ed.* **2008**, *47*, 1301; c) B.-

- J. Li, S.-L. Tian, Z. Fang, Z.-J. Shi, *Angew. Chem.* **2008**, *120*, 1131; *Angew. Chem. Int. Ed.* **2008**, *47*, 1115; d) D. R. Stuart, K. Fagnou, *Science* **2007**, *316*, 1172; e) D. R. Stuart, E. Villemure, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 12072; f) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 11904; g) Y.-Z. Li, B.-J. Li, X.-Y. Lu, S. Lin, Z.-J. Shi, *Angew. Chem.* **2009**, *121*, 3875; *Angew. Chem. Int. Ed.* **2009**, *48*, 3817; h) Y.-X. Jia, E. P. Kündig, *Angew. Chem.* **2009**, *121*, 1664; *Angew. Chem. Int. Ed.* **2009**, *48*, 1636; i) G. Deng, L. Zhao, C.-J. Li, *Angew. Chem.* **2008**, *120*, 6374; *Angew. Chem. Int. Ed.* **2008**, *47*, 6278.
- [4] Selected recent leading reports on Ru-catalyzed direct arylation of arenes, see: a) R. Martínez, M.-O. Simon, R. Chevalier, C. Pautigny, J.-P. Genet, S. Darses, *J. Am. Chem. Soc.* **2009**, *131*, 7887; b) T. Kochi, S. Urano, H. Seki, E. Mizushima, M. Sato, F. Kakiuchi, *J. Am. Chem. Soc.* **2009**, *131*, 2792; c) I. Özdemir, S. Demir, B. Cetinkaya, C. Gourlaouen, F. Maseras, C. Bruneau, P. H. Dixneuf, *J. Am. Chem. Soc.* **2008**, *130*, 1156; d) L. Ackermann, M. Mulzer, *Org. Lett.* **2008**, *10*, 5043; e) S. J. Pastine, D. V. Gribkov, D. Sames, *J. Am. Chem. Soc.* **2006**, *128*, 14220; f) S. Oi, E. Aizawa, Y. Ogino, Y. Inoue, *J. Org. Chem.* **2005**, *70*, 3113.
- [5] Selected recent reports on palladium and rhodium-catalyzed direct arylation of arenes, see: a) M. Miyasaka, A. Fukushima, T. Satoh, K. Hirano, M. Miura, *Chem. Eur. J.* **2009**, *15*, 3674; b) Y.-H. Zhang, B.-F. Shi, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 5072; c) C. Wang, I. Piel, F. Glorius, *J. Am. Chem. Soc.* **2009**, *131*, 4194; d) X. D. Zhao, E. Dimitrijević, V. M. Dong, *J. Am. Chem. Soc.* **2009**, *131*, 3466; e) L.-C. Campeau, D. R. Stuart, J.-P. Leclerc, M. Bertrand-Laperlé, E. Villemure, H.-Y. Sun, S. Lasserre, N. Guimond, M. Lecavallier, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 3291; f) L. Ackermann, A. Althammer, S. Fenner, *Angew. Chem.* **2009**, *121*, 207; *Angew. Chem. Int. Ed.* **2009**, *48*, 201; g) Z.-H. Guan, Z.-H. Ren, S. M. Spinella, S. Yu, Y.-M. Liang, X.-M. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 729; h) J. Canivet, J. Yamaguchi, I. Ban, K. Itami, *Org. Lett.* **2009**, *11*, 1733; i) A. M. Berman, J. C. Lewis, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 14926; j) X. D. Zhao, Z. K. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 8136.
- [6] a) L. Ackermann, A. Althammer, R. Born, *Angew. Chem.* **2006**, *118*, 2681; *Angew. Chem. Int. Ed.* **2006**, *45*, 2619; b) L. Ackermann, *Org. Lett.* **2005**, *7*, 3123.
- [7] L. Ackermann, R. Vicente, A. Althammer, *Org. Lett.* **2008**, *10*, 2299.
- [8] L. Ackermann, R. Born, P. Álvarez-Bercedo, *Angew. Chem.* **2007**, *119*, 6482; *Angew. Chem. Int. Ed.* **2007**, *46*, 6364.
- [9] F. Požgan, P. H. Dixneuf, *Adv. Synth. Catal.* **2009**, *351*, 1737.
- [10] K. Cheng, Y. H. Zhang, J. L. Zhao, C. S. Xie, *Synlett* **2008**, *9*, 1325.
- [11] L. Ackermann, A. Althammer, R. Born, *Tetrahedron* **2008**, *64*, 6115.
- [12] T. Jensen, R. Madsen, *J. Org. Chem.* **2009**, *74*, 3990.
- [13] L. Ackermann, P. Novák, R. Vicente, N. Hofmann, *Angew. Chem.* **2009**, *121*, 6161; *Angew. Chem. Int. Ed.* **2009**, *48*, 6045.
- [14] W. W. Jin, Z. K. Yu, W. He, W. J. Ye, W.-J. Xiao, *Org. Lett.* **2009**, *11*, 1317.
- [15] T. A. Stephenson, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

Received: September 23, 2009  
Published online: December 8, 2009