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Rhodium-catalyzed cross-coupling of aryl carbamates with arylboron reagents

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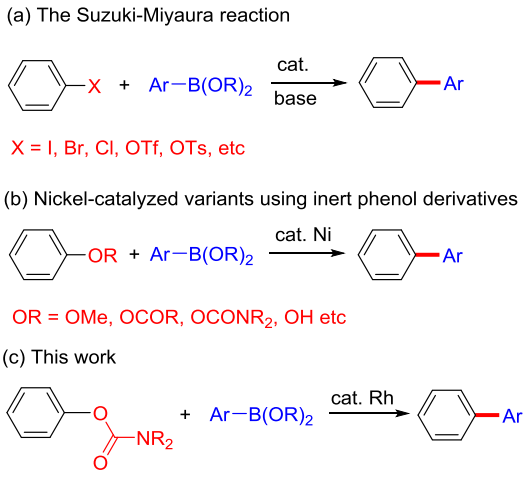
ABSTRACT

A new method has been developed for the rhodium-catalyzed cross-coupling of aryl carbamates with organoboron reagents. The use of an NHC ligand bearing a 2-adamantyl group, i.e., I(2-Ad), is essential to the success of the reaction. The reaction involves the rhodium-mediated activation of the relatively inert C(aryl)-O bond of aryl carbamates.

1. Introduction

Cross-coupling reactions between organic halides and organometallic reagents are recognized as one of the most powerful methods for the formation of carbon–carbon bonds, especially C(aryl)-C(aryl) bonds.[1] Among them, the Suzuki-Miyaura reaction represents one of the most useful processes, largely because of the functional group compatibility and stability of organoboron nucleophiles.[2] Although this reaction has seen significant advancement since it was first discovered in 1979,[2a,b] the scope of the electrophilic coupling partner still remains rather limited to organic halides and sulfonates (Scheme 1a). In 2004, the use of anisoles containing an ortho directing group in the cross-coupling reaction with organoboron nucleophiles was reported to proceed with a ruthenium catalyst.[3] In this reaction, an inert C(aryl)-OMe bond is activated through a chelation-assisted oxidative addition. The scope of the electrophile used in Suzuki-Miyaura type reactions was significantly expanded by the use of nickel catalysts,[4] which allowed for the cross-coupling of simple unactivated phenol derivatives such as aryl ethers,[5] esters,[6] carbamates,[7] carbonates,[8] and naphtholate[9] (Scheme 1b). The success of these reactions indicated that low valent nickel species possess exceptionally high levels of reactivity towards C(aryl)-O bonds that could not otherwise be activated under conventional palladium-catalyzed conditions.[10] From a fundamental perspective, it would be intriguing to know whether transition metals other than nickel could be used to promote the Suzuki-Miyaura reaction of such unactivated phenol derivatives. It has also been reported that the C(aryl)-O bonds of aryl esters and pivalates can be activated by iron[11] and cobalt[12] catalysts, although these reactions require the addition of more than



Scheme 1. Aryl electrophiles for use in the Suzuki-Miyaura reaction.

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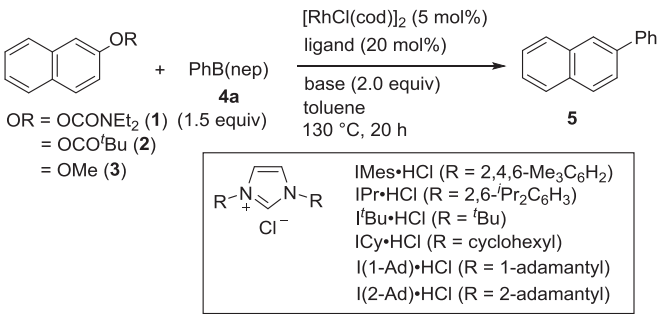
a stoichiometric amount of Grignard reagents.[13,14] Furthermore, these catalysts cannot be used to affect cross-coupling reactions with organoboron reagents. Our group recently found that the rhodium-catalyzed reaction of aryl pivalates with a diboron reagent resulted in the formation of borylated products.[15] The use of a diboron reagent in this reaction was found to be essential to promote the cleavage of the C(aryl)-O bond of aryl pivalates under these rhodium-catalyzed conditions (i.e., $[RhCl(cod)]_2$/P(4-$MeOC_6H_4)_3$), and the catalyst system was therefore only applicable to carbon–boron bond-forming reactions. Based on these results, it was envisaged that the Suzuki-Miyaura reaction of inert phenol derivatives could be realized by identifying an appropriate rhodium catalyst system. Ozerov et al.[16] reported that a rhodium complex bearing a PNP-pincer ligand could be used to mediate the oxidative addition of phenyl pivalate and carbamate, and this observation also encouraged us to investigate the development of a new rhodium-catalyzed reaction. Pleasingly, our investigative efforts in this area culminated in the development of a rhodium-catalyzed cross-coupling of aryl carbamates with arylboronic esters, which we report herein (Scheme 1c).

2. Results and discussion

At the outset of our studies, we decided to investigate the reaction of 2-naphthyl carbamates **1** with boronic ester **4a** (nep=neopentylglycolate) in the presence of $[RhCl(cod)]_2$ as a catalyst and NaOEt as a base (Table 1). However, virtually none of the desired cross-coupling product **5** was formed in the absence of a ligand (Entry 1) and in the presence of phosphine ligands, such as PPh_3 (Entry 2) and PCy_3 (Entry 3). Based on our experience of nickel-catalyzed C(aryl)-O bond activation processes[5b,17] as well as related reports from others[18] it was assumed that a stronger σ-donor would provide a better ligand candidate, and we therefore preceded to examine a series of NHC ligands. As expected, the use of IMes as a ligand led to the formation of **5** in 25% yield (Entry 4). Although the use of an NHC ligand bearing bulkier aryl groups (i.e., IPr) inhibited the arylation (Entry 5), the use of a ^{t}Bu-substituted NHC ligand (I^{t}Bu) led to a significant increase in the yield of **5**—77% (Entry 6). Furthermore, the use of an NHC ligand bearing adamantyl groups led to even higher catalytic activity, with the 2-adamantyl derivative I(2-Ad) (Entry 9) performing much more effectively than the 1-adamantyl isomer I(1-Ad) (Entry 8). In terms of the base, NaOEt could be replaced with CsF, although this led to a slight decrease in the yield of **5** from 98 to 74% (Entry 10). The boronic acid $PhB(OH)_2$ could also be used as an arylating reagent under these conditions, without any discernible decrease in the efficiency of the reaction (Entry 11), whereas the use of the bulkier PhB(pin) resulted in a much lower yield of **5** (Entry 12). The cross-coupling of aryl pivalate **2** with **4a** did not occur under these conditions, but resulted instead in the exclusive formation of a hydrolyzed naphthol product (Entry 13). The use of the corresponding *tert*-butyl carbonate also led to the formation of 2-naphthol (see ESI for details). Aryl methyl ether **3** was found to be completely unreactive under the current conditions (Entry 14).

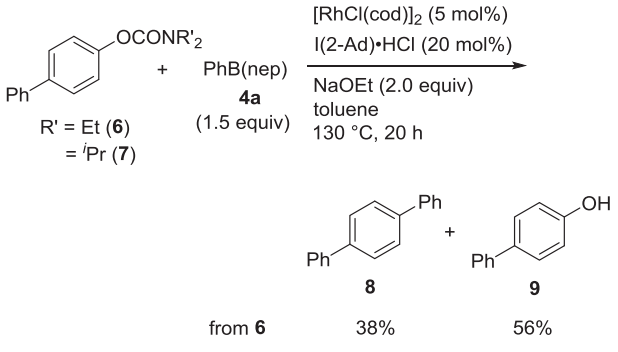
Having identified I(2-Ad) as the optimal ligand for the reaction (Table 1, Entry 9), we preceded to examine the scope of aryl carbamates. Although 2-naphthyl carbamate **1** underwent the cross-coupling with **4a** to form **5** in excellent yield, use of less reactive substrates led to a significant reduction in the yield. For example, phenyl carbamate **6** underwent the cross-coupling with **4a** to afford **8** in only 38% yield, with the hydrolyzed compound **9** being formed as the major product in 56% yield (Scheme 2). This undesired hydrolysis could be suppressed completely by increasing the steric bulk of the carbamate moiety, as exemplified by the use of an $OCON^iPr_2$ group, which delivered **8** in 86% yield. Based on these results, the bulky diisopropyl carbamate group (-$OCON^iPr_2$) was selected as the best group for further exploration. It is noteworthy that this carbamate moiety can be readily introduced at a phenolic hydroxyl group by the reaction of the appropriate phenol with $ClCON^iPr_2$, which is commercially available (See Experimental Section for details).

Table 1
Optimization studies[a]



Entry	Substrate	Ligand	Base	Yield/%[b]
1	**1**	None	NaOEt	8
2	**1**	PPh_3	NaOEt	0
3	**1**	PCy_3	NaOEt	0
4	**1**	IMes·HCl	NaOEt	25
5	**1**	IPr·HCl	NaOEt	3
6	**1**	I^{t}Bu·HCl	NaOEt	77
7	**1**	ICy·HCl	NaOEt	5
8	**1**	I(1-Ad)·HCl	NaOEt	54
9	**1**	I(2-Ad)·HCl	NaOEt	94
10	**1**	I(2-Ad)·HCl	CsF	74
11[c]	**1**	I(2-Ad)·HCl	NaOEt	73
12[d]	**1**	I(2-Ad)·HCl	NaOEt	16
13	**2**	I(2-Ad)·HCl	NaOEt	3
14	**3**	I(2-Ad)·HCl	NaOEt	0

[a] Reaction conditions: substrate (0.30 mmol), **4a** (0.45 mmol), $[RhCl(cod)]_2$ (0.015 mmol), ligand (0.060 mmol), and base (0.60 mmol) in toluene (1.0 mL) at 130 °C for 20 h in a sealed tube.
[b] GC yield of **5** based on the substrate.
[c] *p*-TolylB$(OH)_2$ was used instead of **4a**.
[d] *p*-TolylB(pin) was used instead of **4a**.



Scheme 2. Effect of the substituent of the carbamoyl group.

The scope of the rhodium/I(2-Ad)-catalyzed cross-coupling of aryl carbamates with boronic ester **4a** is shown in Table 2. Phenyl carbamate **12** (Entry 2) proved to be significantly less reactive than the naphthyl substrate **10** (Entry 1), as is often observed in nickel-catalyzed C(aryl)-O bond activation reactions.[19] Interestingly, the introduction of a phenyl group to the substrate led to a significant improvement in the yield of the product, as evidenced by biphenyl carbamates **14** (Entry 3) and **16** (Entry 4), which reacted successfully under the optimized conditions to give **15** and **17** in 86 and 82% yields, respectively. Several biaryl derivatives bearing CF_3 and

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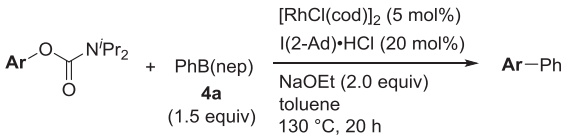
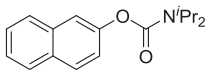
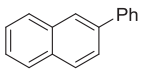
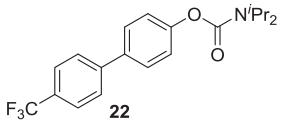
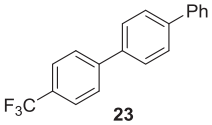
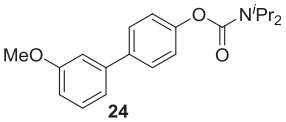
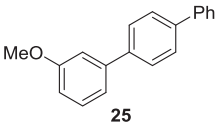
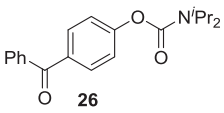
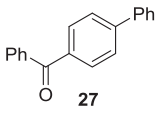
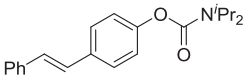
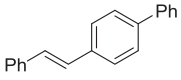
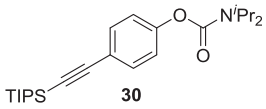
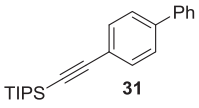
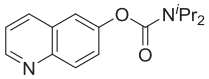
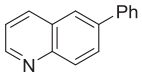
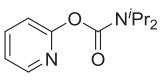
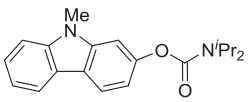
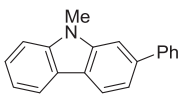
Table 2
Rh(I)/NHC-catalyzed cross-coupling of aryl carbamates with **4a**[a]



Entry	Aryl carbamate	Product	Yield/%[b]
1	 **10**	 **11**	80
2	R=*p*-^{t}Bu **12**	**13**	18
3	R=*p*-Ph **14**	**15**	86
4	R=*m*-Ph **16**	**17**	82
5	R=*o*-Ph **18**	**19**	0
6	R=*p*-CF_3 **20**	**21**	79
7[c]	 **22**	 **23**	97
8[c]	 **24**	 **25**	61
9[d]	 **26**	 **27**	63
10[e]	 **28**	 **29**	60
11[f]	 **30**	 **31**	82
12[e]	 **32**	 **33**	81
13	 **34**	 **35**	40
14	 **36**	 **37**	90

[a] Reaction conditions: aryl carbamates (0.30 mmol), **4a** (0.45 mmol), [RhCl(cod)]$_2$ (0.015 mmol), I(2-Ad)·HCl (0.060 mmol), and NaOEt (0.60 mmol) in toluene (1.0 mL) at 130 °C for 20 h in a sealed tube.
[b] Isolated yield after column chromatography.
[c] Toluene (1.5 mL) was used.
[d] NaO^{t}Bu (0.060 mmol) and CsF (0.60 mmol) was used instead of NaOEt.
[e] Toluene (2 mL) was used.
[f] NaOEt (0.45 mmol) was used.

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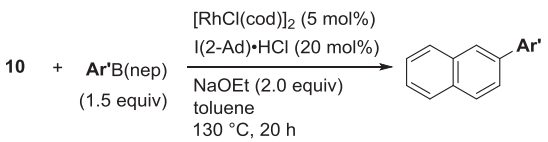
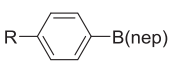
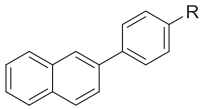
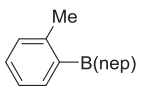
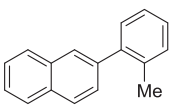
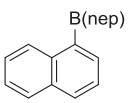
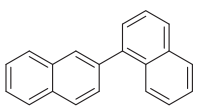
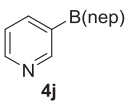
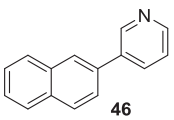
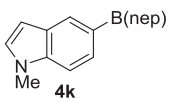
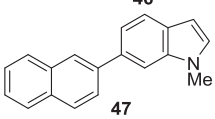
MeO groups also performed effectively as substrates for the coupling reactions (Entries 7 and 8), whereas the *o*-phenyl-substituted substrate **18** (Entry 5) was found to be completely unreactive, most likely because of its steric bulk. Given the minor inductive effect of a phenyl group (σ_p=0.05, σ_m=0.05),[20] the significant enhancement observed in the reactivity of the biaryl carbamates could be attributed to the extension of their π-conjugation. Indeed, stryrenyl (Entry 10) and alkynyl (Entry 11) groups also exerted a positive effect on the efficiency of the reaction and exhibited higher levels of reactivity compared with the simple alkyl-substituted substrate **12** (Entry 2). It is noteworthy that carbamate **30** could not be arylated under the previously reported nickel-catalyzed conditions (see ESI for details). Inductive effects can also have an important impact on this cross-coupling, as exemplified by the electron-deficient aryl carbamate **20** with no extended π-system, which gave rise to the arylated product **21** in 79% yield (Entry 6). Notably, several heteroaromatic substrates, including π-deficient quinoline (Entry 12) and pyridine (Entry 13) rings and a π-rich carbazole (Entry 14), all reacted smoothly to provide the corresponding phenylated products. Aryl bromides and chlorides were found to be incompatible with these conditions and reacted instead to give the arylated products.[21]

The scope with respect to boronic esters is shown in Table 3. The electronic nature of the aryl group in the boronic ester was found to have a profound impact on the outcome of the reaction. Arylboronic esters bearing an electron-donating group, such as a Me (Entry 1), NMe_2 (Entry 2) or an OMe (Entry 3) group, performed as excellent aryl donors to efficiently form the corresponding biaryl derivatives. In contrast, arylboronic esters bearing an electron-deficient CF_3 group on its phenyl ring, i.e., **4e** reacted poorly to afford the desired biaryl product in only 17% yield (Entry 4). The presence of ester and Boc groups was also well tolerated under these rhodium/I(2-Ad)-catalyzed conditions (Entries 5 ad 6). The sterically hindered *o*-tolylboronic ester **4h** (Entry 7) and 1-naphthylboronic ester **4i** (Entry 8) also reacted smoothly with **10** to form the corresponding congested biaryl frameworks. Heteroarylboronic esters, including those containing a pyridine or a indole ring, could also be used in this arylation, although the product was formed in a relatively low yield (Entries 9 and 10).

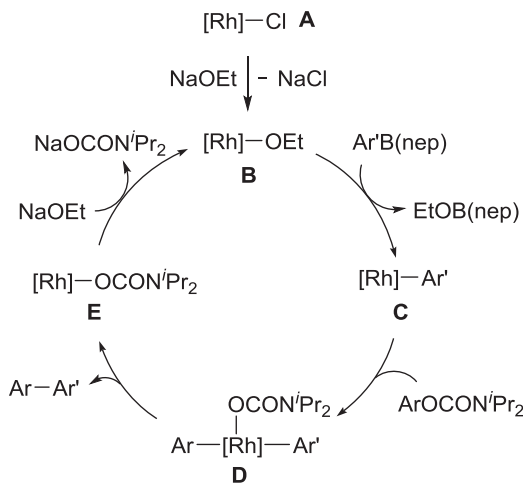
Table 3
Scope of the boronic ester in the Rh(I)/NHC-catalyzed cross-coupling of **10**[a]



Entry	Boronic ester	Product	Yield/%[b]
			
1	R=Me **4b**	**38**	98
2	R=NMe_2 **4c**	**39**	81
3	R=OMe **4d**	**40**	82
4	R=CF_3 **4e**	**41**	17
5	R=CO_2Et **4f**	**42**	62
6	R=NMeBoc **4g**	**43**	73
7	 **4h**	 **44**	81
8	 **4i**	 **45**	79
9	 **4j**	 **46**	49
10[c]	 **4k**	 **47**	93

[a] Reaction conditions: **10** (0.30 mmol), arylboronic ester (0.45 mmol), $[RhCl(cod)]_2$ (0.015 mmol), I(2-Ad)·HCl (0.060 mmol), and NaOEt (0.60 mmol) in toluene (1.0 mL) at 130 °C for 20 h in a sealed tube.
[b] Isolated yield after column chromatography.
[c] NaOEt (0.45 mmol) was used.

Based on the results reported by Ozerov,[16] we have proposed a mechanism for the current rhodium-catalyzed cross-coupling of aryl carbamates with aryl boronic esters, which is depicted in Scheme 3 The catalyst precursor **A** would initially react with NaOEt to give the catalytically competent rhodium ethoxide complex **B**, which would subsequently undergo transmetalation with an aryl boronic ester Ar'B(OR)$_2$ to give the arylrhodium species **C**. The oxidative addition of a carbamate substrate to the arylrhodium **C** would activate the C(aryl)-O bond of the carbamate, leading to the formation of a rhodium(III) intermediate **D**, which would release an arylated product through reductive elimination. The resulting rhodium carbamate **E** would then be converted to rhodium ethoxide **B** via ligand exchange with NaOEt. A direct transmetalation pathway from **E** to **C** was considered to be unlikely because the use of excess NaOEt was essential for an efficient cross-coupling under these conditions.[22] The key to achieving the difficult oxidative addition of the C(aryl)-O bond of the aryl carbamate (i.e., **C**→**D**) could be attributed to the electron-rich nature of the rhodium center generated through the addition of the I(2-Ad) ligand.[23] The electronic effects observed for the boronic ester most likely originated from the electronic effect of the oxidative addition step (**C**→**D**) rather than the effect of the transmetalation step (**B**→**C**), because it is well known that the latter of these two steps can proceed with a wide range of electronically different organoboron compounds.[24] The use of electron-deficient boronic esters would lead to a decrease in the electron density of the rhodium center in **C**, which would in turn lead to reduction in the efficiency of the oxidative addition.[25]



Scheme 3. Possible mechanism.

3. Conclusion

In summary, we have developed a new rhodium-catalyzed cross-coupling reaction of aryl carbamates with organoboron reagents, which involves the cleavage of a relatively inert C(aryl)-O bond. Although C(aryl)-O bonds of this type can be activated using nickel-based catalysts,[5–9] the reaction described herein represents the first use of a rhodium-based catalyst in a Suzuki-Miyaura type reaction. The choice of an appropriate ligand was found to be essential for efficient catalysis, and an NHC ligand bearing a 2-adamantyl group was found to be optimal. It is envisaged that this rhodium-mediated C(aryl)-O bond activation reaction could be applied to a range of other catalytic transformations, when considering a diverse reactivity of organorhodium intermediates, such as C–H activation.[26] Studies aimed at a better understanding of the scope and limitations of this rhodium-mediated C(aryl)-O bond activation strategy are currently underway in our laboratory.

4. Experimental section

4.1. General

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMTC-400/54/ss spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data have been reported as follows: chemical shift in parts per million (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, and m=multiplet), coupling constant (Hertz), and integration. Infrared spectra (IR) were obtained on a JASCO FT/IR-4000; absorptions have been reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were recorded on a Shimadzu GC–MS-QP 2010 instrument with an ionization voltage of 70 eV. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 [Merck SilicaGel 60 (230–400 mesh) or Silycycle Silica Flash F60 (230–400 mesh)]. Gel permeation chromatography (GPC) was performed using LC-9210NEXT HPLC or LC9225NEXT HPLC system. All of the reactions were carried out in 10 mL sample vials with Teflon-sealed screw caps. All of the chemicals used in the current study were manipulated in a glovebox filled with nitrogen.

4.2. Materials

I(1-Ad)·HCl were purchased from Strem Chemicals and used as received. NaO^{t}Bu, NaOEt, IMes·HCl, IPr·HCl and diisopropylcarbamoyl chloride were purchased from TCI and used as received. Toluene (for Organic Synthesis), $[RhCl(cod)]_2$, PPh_3, **4a**, **4b** and **4j** were purchased from Wako Chemicals and used as received. PCy_3 and CsF were purchased from Aldrich and used as received. NaH was purchased from nacalai tesque and used as received. Compounds **12**,[27] **16**,[28] **34**,[29] **4c**,[5b] **4d**,[30] **4e**,[5b] **4f**,[31] **4g**,[5b] **4h**,[5b] **4i**[5b] and **4k**[32] were synthesized according to the reported procedures.

4.3. [1,1′-Biphenyl]-4-yl diisopropylcarbamate (14)

[1,1′-Biphenyl]-4-ol (1.7 g, 10 mmol), diisopropylcarbamic chloride (2.5 g, 15 mmol) and K_2CO_3 (2.1 g, 15 mmol) were refluxed in MeCN for 12 h. The resulting mixture was cooled to room temperature, and the solvent was removed in vacuo. The purification by flash column chromatography over silica gel (hexane/EtOAc=2/1) gave the title compound **14** as a white solid (2.7 g, 91%); R_f (hexane/EtOAc=3/1) 0.67; mp 76 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): 1.31 (br s, 6H), 1.36 (br s, 6H), 3.97 (br s, 1H), 4.13 (br s, 1H), 7.20 (d, J=8.8 Hz, 2H), 7.34 (t, J=7.4H, 1H), 7.43 (t, J=7.8 Hz, 2H), 7.56–7.58 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 20.4, 21.5, 46.0, 46.9, 122.1, 127.0, 127.9, 128.7, 138.0, 140.6, 150.8, 153.7; HRMS (FAB): Calcd for $C_{19}H_{23}NO_2+H^+$298.1802, Found 298.1801.

4.4. 1,1′:4′,1″-Terphenyl (15)

$[RhCl(cod)]_2$ (7.4 mg, 0.015 mmol), I(2-Ad)·HCl (22 mg, 0.060 mmol), NaOEt (41 mg, 0.60 mmol) and toluene (0.40 mL) were added to a 10 mL sample vial with a Teflon sealed screwcap in a glovebox filled with nitrogen, and the resulting mixture was stirred for 10 min [1,1′-Biphenyl]-4-yl diisopropylcarbamate (**14**, 89 mg, 0.30 mmol), 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**4a**, 86 mg, 0.45 mmol) and toluene (0.60 mL) were then added to the vial, and the resulting mixture was sealed in the vessel and heated at 130 °C for 20 h on an aluminum block. The mixture was then cooled to room temperature and purified directly by flash column chromatography over silica gel (eluent: hexane/EtOAc=10:1) to give the title compound **15** as a white solid (59 mg, 86%); R_f (hexane/EtOAc=3/1) 0.75; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.37 (t, J=7.4 Hz, 2H), 7.47 (t, J=7.4 Hz, 4H), 7.65 (d, J=7.6 Hz, 4H), 7.68 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 127.0, 127.3, 127.5, 128.8, 140.0, 140.7; HRMS (EI): Calcd for $C_{18}H_{14}$ 230.1096, Found 230.1089.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.02.088.

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