# An Efficient and Recyclable Catalyst for N-Alkylation of Amines and β-Alkylation of Secondary Alcohols with Primary Alcohols: SBA-15 Supported N-Heterocyclic Carbene Iridium Complex

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Abstract: A mesoporous silica (SBA-15)-supported pyrimidine-substituted N-heterocyclic carbene iridium complex was prepared and used as a catalyst for both environmentally friendly N-alkylation of amines and  $\beta$ -alkylation of secondary alcohols with primary alcohols. The structure of the supported iridium catalyst was characterized by Fourier transform infrared (FT-IR), <sup>13</sup>C and <sup>29</sup>Si solid-state nuclear magnetic resonance (NMR), small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), iridium K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopic analyses which demonstrated that the coordination environment of the iridium centre and the 3-dimensional-hexagonal pore structure of SBA-15 were retained after the immobilization. The catalyst was found to be highly efficient for both kinds of reaction on a wide range of substrates under mild conditions. Moreover, the sup-

ported iridium catalyst was obviously superior to the unsupported one in the N-alkylation of aniline and  $\beta$ -alkylation of 1-phenylethanol with benzyl alcohol as substrate, which indicated that not only the iridium complex moiety but also the support material contributed to the catalytic activity of the supported iridium catalyst in these reactions. The supported iridium catalyst can be easily recycled by simple washing without chemical treatment, and exhibited excellent recycling performance without notable decrease in catalytic efficiency even after twelve test cycles for N-alkylation of aniline with benzyl alcohol, nine cycles for N-alkylation of different amines with different alcohols, and eight cycles for  $\beta$ -alkylation of 1-phenylethanol with benzyl alcohol, respectively.

**Keywords:** β-alkylation of secondary alcohols; immobilization; iridium; N-alkylation of amines; N-heterocyclic carbenes

### Introduction

Recently, much attention has been focused on the strategy of redox processes in the formation of C–N or C–C bonds through the use of alcohols to replace toxic halides.<sup>[1]</sup> In addition, reactions such as N-alkylation of amines with alcohols and  $\beta$ -alkylation of secondary alcohols with primary alcohols produce water as sole by-products and are thus environmentally-benign.<sup>[2]</sup> Since the first homogeneous catalysts for the N-alkylation of amines were introduced by Grigg and Watanabe in 1981,<sup>[3]</sup> various catalytic systems em-

ploying  $Ir^{[4]}$  or  $Ru^{[4c-g,5]}$  complexes, for example,  $[Cp*IrCl_2]_2$  (Cp\*=pentamethylcyclopentadienyl anion),  $[Ru(p-cymene)Cl_2]_2$ , Cp\*Ir(NHC) (NHC=N-heterocyclic carbene) and Ir(P, N ligand) have been developed. Although they are very efficient catalysts, separating the products from the reaction mixtures still remains a challenge. Furthermore, the lack of recyclability of these homogenous catalysts hindered their applications. In the last few years, heterogeneous catalysts such as Pd/MgO or  $Fe_2O_3$ ,  $^{[6]}$  Ag/Mo or Ag/Al<sub>2</sub>O<sub>3</sub>,  $^{[7]}$  Au/TiO<sub>2</sub><sup>[8]</sup> and CuAl-HT (copper-aluminum hydrotalcite)<sup>[9]</sup> were also developed for the N-alkyla-

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tion of amines. However, most of them required harsh reaction conditions. Thus, we are interested in the immobilization of metal complexes on support surfaces which combines the advantages of homogeneous and heterogeneous catalysis.

A recent computational study on the mechanism of N-alkylation of amines with alcohols catalyzed by Cp\*Ir shows three sequential steps: (i) metal-catalyzed oxidation of alcohols to aldehydes, (ii) condensation of the aldehydes with amines to form imines, and (iii) metal-catalyzed reduction of the imines to the final products, secondary amines.<sup>[4a]</sup> It is crucial that the same catalyst has to dehydrogenate alcohols and hydrogenate imines. Dehydrating agents in the catalytic system are needed to promote the condensation of aldehydes with amines. Mesoporous silica (SBA-15) provides an ideal support for homogenous catalyst immobilization owing to the ordered structures, very high surface area, as well as uniform and large pore diameter.<sup>[10]</sup> Several catalytic processes using SBA-15 immobilized complexes as catalysts were developed.<sup>[11]</sup> However, in these catalysts, SBA-15 just plays a support role, but does not promote the reactions.

We designed a silica-supported catalyst, consisting of a Cp\*Ir(NHC) moiety, which proved to be efficient for the N-alkylation of amines with alcohols and mesoporous silica (SBA-15) providing water-locking function. Herein, we describe the synthesis and characterization of SBA-15-immobilized N-heterocyclic carbene iridium complex **1**, and its application in catalyzing both the N-alkylation of amines with alcohols and the  $\beta$ -alkylation of secondary alcohols with primary alcohols with remarkably high reactivity and exceptional recycleability. In addition, the support material, SBA-15, in catalyst **1** obviously promots the mentioned reactions as has now been proved.

### **Results and Discussion**

The reaction of *N*-(2-pyrimidyl) imidazole and 3-iodopropyl(trimethoxy)silane affords the corresponding pyrimidine imidazolium salt. Then, the SBA-15-supported N-heterocyclic carbene iridium complex **1** is obtained by *in situ* transmetalation from the silver carbene complex of the imidazolium salt with [Cp\*IrCl<sub>2</sub>]<sub>2</sub>, followed by the addition of SBA-15 (Scheme 1). For comparison, pyrimidine-substituted N-heterocyclic carbene chelated iridium complex **2** (Scheme 2) was synthesized according to a literature method.<sup>[4c]</sup>

In the FT-IR spectrum of **1** (see Supporting Information, Figure S1), the characteristic bands of SBA-15 around 1085 and 462 cm<sup>-1</sup> for v(Si–O) and  $\delta$ (Si– O) are maintained and the band around 937 cm<sup>-1</sup> assigned to Si–OH stretching of silanols on the surface almost disappears.<sup>[12]</sup> These indicate that the Ir complex is tethered onto SBA-15 surface, which is further confirmed by solid state NMR spectra. The <sup>29</sup>Si CP/ MAS NMR spectrum of **1** (see the Supporting Information, Figure S4) exhibited strong signals (–101.3, –109.9 ppm) originating from network structures of SBA-15 and weak signals (–50.2, –57.7 ppm) derived from silyl ether groups of the iridium complex moiety.<sup>[13]</sup> In the solid-state <sup>13</sup>C CP/MAS NMR spec-



Scheme 2. Ir complex 2.



**Scheme 1.** Synthesis of SBA-15 supported Ir complex **1**. *Reaction conditions*: (a) toluene, reflux, 24 h; (b) Ag<sub>2</sub>O,  $CH_2Cl_2$ , room temperature, 16 h; then  $[Cp*IrCl_2]_2$ , room temperature, overnight; (c) SBA-15, toluene, reflux, 48 h.



Figure 1. The <sup>13</sup>C CP/MAS NMR spectrum of SBA-15-supported Ir complex 1.



**Figure 2.** Normalized Ir  $L_3$  edge XANES spectra (a) and Fourier transform EXAFS spectra (b) for **1**, **2**, and **3** (catalyst recycled from  $\beta$ -alkylation of 1-phenylethanol with benzyl alcohol for eight times).

trum Figure 1), signals at 8 and 92 ppm indicate the present of the Cp\* ring while resonances at 158–116 ppm and 58–16 ppm are attributed to aromatic carbons and aliphatic carbons respectively, which are consistent with those of complex **2**. The loading level of the immobilized iridium was measured to be 3.26:96.74 (Ir:Si atomic%) by EDS (see Supporting Information, Figure S2).

From the Ir  $L_3$  edge XANES and EXAFS spectra (Figure 2) of 1 and 2, it is clear that the metal centre

of the supported Ir complex **1** has the same coordination environment as complex **2**. The SAXS patterns (Figure 3) of **1** show one similar intense  $d_{100}$  diffraction peak along with two similar weak diffraction peaks ( $d_{110}$ ,  $d_{200}$ ), suggesting that the dimensional-hexagonal pore structure observed in SBA-15 is preserved after the immobilization, which can also be demonstrated by the TEM image (Figure 4). All these characterization findings of the supported Ir complex **1** confirm the retention of both its original coordina-



Figure 3. The SAXS patterns for SBA-15 (a), 1 (b) and 3 (c).



Figure 4. TEM images of 1 (a) and 3 (b) viewed along the [100] direction.

tion environment of the Ir centre and the dimensional-hexagonal pore structure of SBA-15.

With the well-defined supported Ir complex 1 in hand, its abilities to catalyze the N-alkylation of amines (Table 1) and the  $\beta$ -alkylation of secondary alcohols (Table 2) with alcohols were examined. The unsupported Ir complex 2 and SBA-15 were also used in these catalytic processes for comparison. For the N-alkylation of aniline with benzyl alcohol (Table 1, entries 1–3) and the  $\beta$ -alkylation of 1-phenylethanol with benzyl alcohol (Table 2, entries 1-3), 1 was obviously superior to 2 and SBA-15 alone did not work, which indicates that the Ir complex moiety in catalyst **1** is crucial and the support material SBA-15 also plays an important role in promoting the reactions.

Results obtained from the N-alkylation of various amines with primary and secondary alcohols are summarized in Table 1. Benzyl alcohols with electronpoor and electron-rich groups (Table 1, entries 1, 4, and 5) and secondary alcohol (Table 1, entry 6) react with aniline to give the desired products in high yields, even an aliphatic alcohol (Table 1, entry 7) gives a moderate yield in the same conditions. The

F	$R^{1}-NH_{2} + R^{2}OH$	1, NaHCO <sub>3</sub>	
		toluene, 110 °C, 48 h	Н
Entry	Amine	Alcohol	Yield [%] <sup>[b]</sup>
1	NH <sub>2</sub>	ОН	93
2 <sup>[c]</sup>	NH <sub>2</sub>	ОН	80
3 <sup>[d]</sup>	NH <sub>2</sub>	ОН	0
4	NH <sub>2</sub>	СІОН	93
5	NH <sub>2</sub>	Ме	94
6	NH <sub>2</sub>	ОН	78
7	NH <sub>2</sub>	ОН	52
8	CI NH2	ОН	94
9	CI NH2	СІ	99
10	CI NH2	Ме	91
11	MeO	ОН	89
12	NH <sub>2</sub>	ОН	81
13	NH <sub>2</sub>	ОН	90
14	N NH <sub>2</sub>	ОН	70

[a] conditions: alcohol (1.0 mmol), Reaction amine (1.1 mmol), 1 (Ir: 1.5 mol%), NaHCO<sub>3</sub> (0.5 mmol), toluene (0.5 mL), 110 °C, 48 h.

[b] Isolated yield.

[c] 2 (1.5 mol%) as catalyst.

<sup>[d]</sup> SBA-15 as catalyst.

transformation of substituted anilines with substituted benzyl alcohols, with both electron-poor and electronrich groups, afforded the corresponding secondary amines in excellent yields (Table 1, entries 8-11). Aliphatic (Table 1, entries 12 and 13) and heterocyclic amines (Table 1, entry 14), which are difficult to react, could also participate smoothly to generate the corresponding amines in good to excellent yields.

We found that 1 was surprisingly versatile, it was also efficient for the  $\beta$ -alkylation of secondary alco-

O	Н	<b>1</b> , KOH	ОН
R <sup>1</sup> ∕∕	+ HO R <sup>2</sup> tolue	ene, 110 °C, 24 h R	$1 - R^2$
Entry	Secondary alcohol	Primary alcohol	Yield [%] <sup>[b]</sup>
1	OH	ОН	93
2 <sup>[c]</sup>	ОН	ОН	75
3 <sup>[d]</sup>	ОН	ОН	0
4	OH CI	ОН	93
5	OH H <sub>3</sub> C	ОН	92
6	ОН	СІ	94
7	ОН	Ме	91
8	OH CI	СІОН	90
9	OH	ОН	61
10	OH	ОН	70
11	ОН	ЛЛОН	58

<b>Table 2.</b> $\beta$ -Alkylation	of secondary	alcohols	with	primary	al-
cohols. <sup>[a]</sup>	-				

<sup>[a]</sup> Reaction conditions: secondary alcohol (1.0 mmol), primary alcohol (1.1 mmol), 1 (Ir: 1.5 mol%), KOH (1.0 mmol), toluene (0.5 mL), 110°C, 24 h.

- <sup>[b]</sup> Isolated yield.
- <sup>[c]</sup> 2 (1.5 mol%) as catalyst.

<sup>[d]</sup> SBA-15 as catalyst.

hols with primary alcohols and the desired products were obtained in moderate to excellent isolated yields (Table 2). Aromatic methyl secondary alcohols react with aromatic primary alcohols to give the desired products in excellent yields (Table 2, entries 1, 4–8), with both electron-poor and electron-rich groups. The reactions of 1-(naphthalen-2-yl)ethanol or 4-phenylbutan-2-ol with benzyl alcohol (Table 2, entries 9 and 10) and 1-phenylethanol with *n*-hexyl alcohol (Table 2, entry 11), which are difficult to react, give the corresponding products in moderate to good yields.

Recycling studies for the two reactions were then performed, and the results are shown in Figure 5. After being simply filtered and washed with  $CH_2Cl_2$ , catalyst **1** could be used repetitively twelve times for the N-alkylation of aniline with benzyl alcohol and eight times for the  $\beta$ -alkylation of 1-phenylethanol with benzyl alcohol without significant decreases in isolated yields, from 93 to 83% and 94 to 82%, respectively.

In order to compare the activity of the fresh and reused catalysts, we performed kinetic experiments for the N-alkylation of aniline with 4-methylbenzyl alcohol and the  $\beta$ -alkylation of 1-(*p*-tolyl)ethanol with benzyl alcohol by using gas chromatography (Figure 6). The kinetic profiles show that both the fresh and reused catalysts have induction periods in the two reactions and the reused catalyst has longer induction periods in comparison to the fresh one.<sup>[14]</sup> We also notice that the activity of the fresh catalyst is slightly lower in the early stage but higher after the induction period than that of the fresh one.

From XANES spectra (Figure 2), there is no apparent difference between the fresh catalyst 1 and the recovered catalyst 3, which indicates that most Ir in 3 retains the same electronic structure as 1. From the EXAFS spectra (Figure 2), the intensity of the main peak at ~1.6 Å of 3 is lower than that of 1. This can be attributed to the loss and decomposition of the catalyst, which are unavoidable after the 8 cycles of reaction. This is a common phenomenon in supported organometallic catalysts. On the other hand, from the TEM observation of 3 (Figure 4), there is no obvious change in the morphology and size compared with fresh catalyst 1, which is also confirmed by the SAXS pattern (Figure 3).

In order to further investigate the reusability of catalyst **1**, we used different combinations of substrates in nine recycle tests of the N-alkylation of amines with alcohols. As shown in Table 3, over 90% isolated yields were achieved in all of the sequential runs, which supports that the SBA-15-supported Ir complex **1** possesses extremely high efficiency and excellent recycle ability in the N-alkylation of amines with primary alcohols.



**Figure 5.** Yields in the recycling of **1** for the N-alkylation of aniline with benzyl alcohol (a) and  $\beta$ -alkylation of 1-phenylethanol with benzyl alcohol (b). *Reaction conditions:* the same with those shown in Table 1 and Table 1 2.



**Figure 6.** Kinetic profiles for N-alkylation of aniline with 4-methylbenzyl alcohol (a) and  $\beta$ -alkylation of 1-(*p*-tolyl)ethanol with benzyl alcohol (b). *Reaction conditions:* catalyst **1** (20 mg), toluene (0.1 mL), and dodecane (0.05 mmol) as an internal standard. For (a) aniline (0.22 mmol), 4-methylbenzyl alcohol (0.20 mmol), NaHCO<sub>3</sub> (0.10 mmol); (b) 1-(*p*-tolyl)ethanol (0.20 mmol), benzyl alcohol (0.22 mmol), KOH (0.20 mmol).

Table 3. Reusability of 1 for	N-alkylation	of amines	reaction
with different substrates. <sup>[a]</sup>	-		

		1, NaHCO <sub>3</sub>		
	12 + HO R-	toluene, 110 °C, 48 h	H H	
Run <sup>[b]</sup>	$\mathbb{R}^1$	$\mathbb{R}^2$	Yield [%] <sup>[c]</sup>	
1	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	93	
2	$4 - Cl(C_6H_4)$	$C_6H_5$	94	
3	$(CH_2)_5CH$	$C_6H_5$	90	
4	$C_6H_5$	$C_6H_5$	91	
5	$C_6H_5$	$4-Cl(C_6H_4)$	93	
6	$C_6H_5$	$4 - MeO(C_6H_4)$	92	
7	$4 - MeO(C_6H_4)$	$C_6H_5$	91	
8	$4-Cl(C_6H_4)$	$4-Cl(C_6H_4)$	95	
9	$C_6H_5$	$C_6H_5$	93	

<sup>[a]</sup> Reaction conditions: see Table 1.

<sup>[b]</sup> The catalyst used was recycled from the last entry.

<sup>[c]</sup> Isolated yield.

the observed catalysis was due to the heterogeneous catalyst 1 or the leached iridium species in solution. The reaction of 1-phenylethanol with benzyl alcohol was completely terminated by the removal of **1** from the reaction mixture after 50% conversion of 1-phenylethanol under the conditions as in Table 2 entry 1. Further treatment of the filtrate under the same reaction conditions did not improve the yield. Moreover, ICP analysis of the filtrate confirmed that the Ir content was below the detection limit (<0.10 ppm). These findings indicate that the catalysis is heterogeneous.

An experiment was carried out to verify whether

## Conclusions

In summary, we have successfully prepared a mesoporous SBA-15-supported pyrimidine-substituted N-heterocyclic carbene iridium complex **1**, in which the integrity of both the organometallic moiety and the inorganic support remain unchanged. The well-defined catalyst **1** was obviously superior to Ir-catalyzed homogenous system for the clean and atom-efficient Nalkylation of amines with alcohols and β-alkylation of secondary alcohols with primary alcohols in the same conditions. That the support material SBA-15 in catalyst **1** also promotes the mentioned reactions was proven. It must be noted that the catalyst could be recovered by simple filtration and used repetitively for twelve times (N-alkylation of aniline with benzyl alcohol) and eight times ( $\beta$ -alkylation of 1-phenylethanol with benzyl alcohol) without significant loss of its catalytic activity. Furthermore, the use of recycled 1 for N-alkylation reactions with different substrates also produces the desired products in high yields. The fact that the integrity and bifunctionality of both the organometallic moiety and the inorganic support are maintained nicely in consecutive catalysis runs meets the objective set to merge the properties of a homogeneous and a heterogeneous catalytic system into one sustainable hybrid catalyst system.

# **Experimental Section**

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, toluene) or calcium hydride (dichloromethane), and methanol was distilled over Mg/I<sub>2</sub>. The starting materials 2-(1-imidazolyl)pyrimidine<sup>[15]</sup> and [Cp\*IrCl<sub>2</sub>]<sup>[16]</sup> were synthesized according to the literature procedures. Other chemical reagents were obtained from commercial sources and used without further purification. FT-IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer using KBr discs in the range of 4000-400 cm<sup>-1</sup>. SEM analyses and EDS patterns were performed with a JEOL JSM-6380LV instrument. TEM studies were performed on a JEOL JEM2010 electron microscope, operated at an acceleration voltage of 200 kV. The SAXS patterns were recorded with a Bruker D4 powder X-ray diffractometer using Cu Ka radiation (40 kV, 40 mA). Nuclear magnetic resonance (NMR) spectra were recorded using Bruker spectrometers operating at 400 MHz (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C) in CDCl<sub>3</sub>. Solid state <sup>13</sup>C and <sup>29</sup>Si CP MAS NMR spectra were recorded at 100.6 MHz using a Bruker AV-400 spectrometer. EI mass spectra were recorded by an Agilent 5973N mass spectrometer. High resolution mass spectrometry (HR-MS) was performed using the Waters Micromass GCT Permier. Ir K-edge X-ray absorption nearedge structure (XANES) and spectroscopic signal extended X-ray absorption fine structure (EXAFS) spectroscopic analyses were performed at room temperature in transmission mode using ion chambers filled with N<sub>2</sub>/Ar at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with an Si (311) double crystal monochromator. During the measurement, the synchrotron was operated at an energy of 3.5 GeV and a current between 150-210 mA. Data processing was performed using the program ATHENA. All fits to the EXAFS data were performed using the program ARTE-MIS.<sup>[17]</sup> A gas chromatography-mass spectra (Thermo Focus ISQ) was also used.

#### **Preparation of 1A**

To a 50-mL Schlenk tube containing 10 mL of toluene, was added N-(2-pyrimidyl)imidazole (62 mg, 0.42 mmol) and 3iodopropyl(trimethoxy)silane<sup>[18]</sup> (121 mg, 0.42 mmol). The mixture was refluxed for 24 h, followed by the removal of the solvent using a rotary evaporator. Addition of *n*-hexane (10 mL) gave the product as an oily brown solid. Solvent was decanted and the product was washed with ether several times and dried in vacuum; yield: 174 mg (95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 10.37$  (s, 1H, N-CH-N), 8.89 (d, J = 4.8, 2H, H<sub>pyrimidine</sub>), 8.24 (s, 1H, imidazole<sub>backbone</sub>), 7.91 (s, 1H, imidazole<sub>backbone</sub>), 7.61 (m, 1H, H<sub>pyrimidine</sub>), 4.71 (d, 2H, NCH<sub>2</sub> of silane), 3.55 (s, 9H, OCH<sub>3</sub>), 2.00 (m, 2H, CH<sub>2</sub> of silane), 0.72 (m, 2H, SiCH<sub>2</sub> of silane); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 159.74, 147.23, 135.07, 124.13, 122.40, 118.69, 52.78,$ 50.77, 23.93, 5.68; HR-MS (ESI<sup>+</sup>): m/z = 309.20, calcd. for **[1A**-I]<sup>+</sup>: 309.14.

### **Preparation of 1B**

The imidazolium iodide 1A (170 mg, 0.39 mmol) was dissolved in  $CH_2Cl_2$  (10 mL) and added to a Schlenk vessel containing activated 3Å molecular sieves (50 mg) and Ag<sub>2</sub>O (55 mg, 0.23 mmol). The reaction mixture was refluxed in the absence of light for 12 h and filtered, after cooling to room temperature, into a 50-mL Schlenk vessel. [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (81 mg, 1.0 mmol) was added, and the reaction mixture was stirred at room temperature in the absence of light for 6 h. After filtration, the filtrate was concentrated under vaccuum, the resulting solid was purified by column chromatography on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/20) to afford a dark yellow solid **1B**; yield: 156 mg (78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 9.23$  (m, 1H, H<sub>pyrimidine</sub>), 8.94 (m, 1H, H<sub>pyrimidine</sub>), 8.09 (s, 1 H, imidazole<sub>backbone</sub>), 7.92 (s, 1 H, imidazole<sub>backbone</sub>), 7.62 (m, 1H, H<sub>pyrimidine</sub>), 4.91 (m, 2H, CH<sub>2</sub>N), 3.58 (s, 9H, OCH<sub>3</sub>), 2.13 (m, 2H, CH<sub>2</sub>), 1.89 (s, 15H, H<sub>Cp\*</sub>), 0.70 (m, 2H, CH<sub>2</sub>Si); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 165.0$ , 160.8, 160.5, 157.1, 124.5, 122.2, 117.8, 92.7, 52.8, 50.7, 29.6, 24.4, 9.71, 6.31; HR-MS (ESI<sup>+</sup>): m/z = 478.18, calcd. for [1B-Cl]<sup>+</sup>: 478.22.

#### **Preparation of 1**

A suspension of **1B** (154 mg, 0.30 mmol) and SBA-15 (1.0 g) in toluene (10 mL) was refluxed for 48 h, the solid was filtered and washed sequently with CH<sub>2</sub>Cl<sub>2</sub>, ethanol and ether, and then vacuum-dried to give a bright yellow soild. <sup>13</sup>C CP-MAS NMR (100.6 Hz, solid state):  $\delta$ =158, 149, 133, 124, 120, 116, 92, 58, 50, 26, 16, 8; <sup>29</sup>Si CP-MAS NMR (100.6 Hz, solid state):  $\delta$ =-50.2, -57.7, -101.3, -109.9.

#### **Preparation of 2**

This was prepared according to a literature procedure.<sup>[4c]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.88-8.84$  (m, 2H), 7.86 (d, 1H), 7.63 (t, 1H), 7.32 (m, 1H), 4.30-4.28 (m, 2H), 1.92 (m, 2H), 1.80 (s, 15H), 1.40-1.35 (m, 2H), 0.98 (t, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta = 159.97$ , 152.53, 136.99, 123.91, 122.37, 118.80, 93.00, 50.99, 32.50, 19.68, 13.72.

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# General Procedure for N-Alkylation of Amines with Primary Alcohols

Alcohol (1.0 mmol) and amine (1.1 mmol), were weighed into an oven-dried Schlenk flask. Sodium bicarbonate (41 mg, 0.50 mmol) was added, followed by dry toluene (0.50 mL). The mixture was put under an atmosphere of nitrogen, and catalyst (110 mg, Ir: 1.5 mol%) was added before stoppering the flask and immersing it in a preheated oil bath (110 °C) for 48 h. The reaction mixture was cooled and diluted with 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, and filtered over a pad of Celite. The filtrate was concentrated under reduced pressure, purified by column chromatography on silica gel (Et<sub>3</sub>N/*n*-hexane = from 1/100 to 1/20) to give the products.

# General Procedure for β-Alkylation of Secondary Alcohols with Primary Alcohols

Secondary alcohol (1.0 mmol), primary alcohol (1.1 mmol), KOH (56 mg, 1.00 mmol), catalyst **1** (100 mg, Ir: 1.5 mol%), were combined in an oven-dried Schlenk flask. Dry toluene (0.5 mL) was added, and the mixture was refluxed under nitrogen for 24 h. The reaction mixture was cooled and diluted with 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, and filtered. The filtrate was concentrated under reduced pressure, purified by column chromatography on silica gel (EtOAc/*n*-hexane = from 1/50 to 1/20) to give the products.

# General Procedure for Recycling Use of the Supported Catalyst 1

According to the general procedure for the N-alkylation of amines or  $\beta$ -alkylation of secondary alcohols with premary alcohols, the first run reaction was carried out. After completion of the reaction, the catalyst **1** was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> and water, and then vacuum-dried. The recovered catalyst was used for consecutive reactions under the same condition.

### **Supporting Information**

The Supporting Information for this article contains IR spectra of 1 and 2, EDS patterns of 1, TEM images of 1 and 3 viewed along the [001] directions, and NMR spectra of the products.

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