Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 64 (2008) 1943–1954
Tetrahedron
www.elsevier.com/locate/tet

Cp*Ir-catalyzed N-alkylation of amines with alcohols. A versatile and atom economical method for the synthesis of amines

Ken-ichi Fujita [a,b,*], Youichiro Enoki [a], Ryohei Yamaguchi [a,*]

[a] *Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan*
[b] *Graduate School of Global Environmental Studies, Kyoto University, Kyoto 606-8501, Japan*

Received 21 October 2007; received in revised form 21 November 2007; accepted 21 November 2007
Available online 21 December 2007

This paper is dedicated to the memory of the late Professor Yoshihiko Ito

Abstract

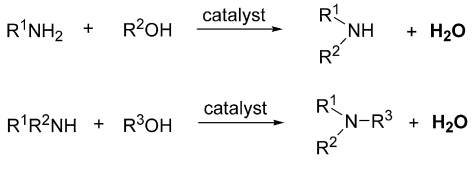
A versatile and highly atom economical catalytic system consisting of $[Cp^*IrCl_2]_2/NaHCO_3$ (Cp*=pentamethylcyclopentadienyl) for the N-alkylation of amines with primary and secondary alcohols as alkylating reagents has been developed. For example, the reaction of equimolar amounts of aniline and benzyl alcohol in the presence of $[Cp^*IrCl_2]_2$ (1.0 mol % Ir) and $NaHCO_3$ (1.0 mol %) in toluene at 110 °C gives *N*-benzylaniline in 94% yield. The present catalytic system is applicable to the N-alkylation of both primary and secondary amines, and only harmless water is produced as co-product. A wide variety of secondary and tertiary amines can be synthesized with high atom economy under mild and less-toxic conditions. One-pot sequential N-alkylation leading to tertiary amines bearing three different substituents is also described.

Keywords: Iridium catalyst; Hydrogen transfer; N-Alkylation; Amine; Alcohol

1. Introduction

The development of versatile and efficient methods for the synthesis of amines has still been an active area of research,[1] because a variety of amines play an important role in many fields of organic chemistry including such as biological, medicinal, agrochemical, dyes, and polymer chemistry. In recent years, a number of transition metal catalyzed reactions for the synthesis of amines, such as hydroamination of alkenes or alkynes,[2] and amination of aryl halides,[3] have been developed. On the other hand, there have been a couple of traditional methods for the synthesis of amines: the N-alkylation with alkyl halides[4] and the reductive amination with carbonyl compounds.[5] However, these conventional reactions suffer disadvantages as follows; (1) the use of alkyl halides or strong reducing reagents is undesirable from an environmental point of view and (2) these reactions generate equimolar amounts of wasteful salts as co-products.

The N-alkylation of amines with alcohols (Scheme 1) is an attractive candidate for the synthesis of amines because, (1) it does not generate any harmful and/or wasteful co-products (only H_2O as co-product), (2) alcohols are more readily available than corresponding halides or carbonyl compounds in many cases, and (3) if the reaction proceeds efficiently by the employment of equimolar amounts of starting materials, extremely high atom economical system[6] can be realized. Although several catalytic systems for the N-alkylation of amines with alcohols have been studied using ruthenium[7] and other transition metal catalysts,[8–10] most of them require



Scheme 1.

* Corresponding authors. Fax: +81 75 753 6634.
E-mail addresses: fujitak@kagaku.mbox.media.kyoto-u.ac.jp (K.-i. Fujita), yama@kagaku.mbox.media.kyoto-u.ac.jp (R. Yamaguchi).

0040-4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.11.083

a high reaction temperature (>150 °C) and/or an excess use of alcohols to obtain high yields of the product. Additionally, applicable amines and alcohols are relatively restricted; there have been no reports on the efficient systems for the N-alkylation with secondary alcohols.[11]

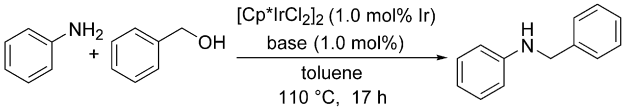
In the course of our studies on the chemistry of pentamethylcyclopentadienyl (Cp*) iridium complexes,[12] we found their high catalytic activities toward hydrogen transfer reactions including the Oppenauer-type oxidation of alcohols,[13] carbon–nitrogen bond formations,[14] and carbon–carbon bond formations.[15] In this paper, we wish to report a full account of Cp*Ir-catalyzed N-alkylation of primary and secondary amines with primary and secondary alcohols.[16] As described below, a variety of amines can be synthesized in atom economical manner under mild and less-toxic conditions.

2. Results and discussion

2.1. Reaction of aniline with benzyl alcohol: optimization of the reaction conditions

Initially, we studied the reaction of aniline with benzyl alcohol as a model reaction. The reaction was carried out using equimolar amounts of aniline and benzyl alcohol in toluene (0.1 mL) in the presence of $[Cp^*IrCl_2]_2$ as catalyst (1.0 mol % Ir) and base (1.0 mol %) at 110 °C for 17 h.[17] The results are summarized in Table 1. In each reaction, mono-alkylated *N*-benzylaniline was formed selectively; no formation of di-alkylated *N*,*N*-dibenzylaniline was observed. When the reaction was carried out without a base, *N*-benzylaniline was formed in 32% yield (entry 1). The reaction was considerably accelerated by the addition of a weak base (entries 2–5 and 8). When the reaction was carried out in the presence of $NaHCO_3$, *N*-benzylaniline was formed in an excellent yield (94%), which we considered to be the choice of the base (entry 2). Other weak bases, such as Na_2CO_3, $KHCO_3$, K_2CO_3, and CH_3COONa, were also effective (entries 3–5 and 8), while Li_2CO_3 was not (entry 6). On the other hand, addition of stronger bases, such as Cs_2CO_3 and NaO^{t}Bu, retarded the reactions (entries 7 and 9). We also examined the reaction in the absence of solvent using $NaHCO_3$ as a base; however, the yield was moderate (entry 10).

Table 1
N-Alkylation of aniline with benzyl alcohol catalyzed by $[Cp^*IrCl_2]_2$ and various bases[a]



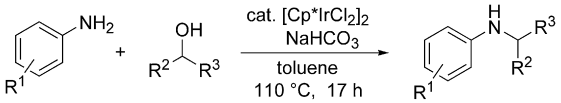
Entry	Base	Yield[b] (%)
1	None	32
2	$NaHCO_3$	94
3	Na_2CO_3	85
4	$KHCO_3$	82
5	K_2CO_3	85
6	Li_2CO_3	40
7	Cs_2CO_3	11
8	CH_3COONa	83
9	NaO^{t}Bu	1
10[c]	$NaHCO_3$	67

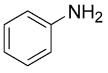
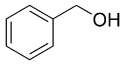
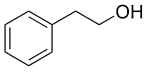
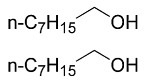
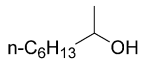
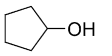
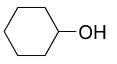
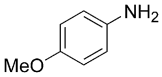
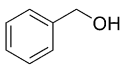
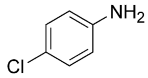
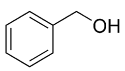
[a] The reaction was carried out with aniline (1.0 mmol), benzyl alcohol (1.0 mmol), $[Cp^*IrCl_2]_2$ (0.0050 mmol, 1.0 mol % Ir), and base (0.01 mmol, 1.0 mol %) in toluene (0.1 mL) at 110 °C for 17 h.
[b] Determined by GC.
[c] The reaction was carried out without solvent.

2.2. N-Alkylation of anilines with primary and secondary alcohols

On the basis of the optimization of the reaction conditions, N-alkylation of anilines with various primary and secondary alcohols was conducted. The results are summarized in Table 2. The reactions of aniline with primary alcohols (benzyl alcohol, 2-phenylethanol, and 1-octanol) resulted in the selective mono-alkylation in high to excellent yields (entries 1–3), although the reaction with 2-phenylethanol required higher temperature to obtain a high yield (entry 2).[18] When the reaction of aniline with 1-octanol was performed using an excess amount of 1-octanol (2.6 equiv) in the presence of 5.0%

Table 2
N-Alkylation of anilines with various primary and secondary alcohols[a]



Entry	Amine	Alcohol	Catalyst (mol % Ir)	Yield[b] (%)
1			1.0	94
2[c,d]			3.0	88
3			2.0	97
4[e]			5.0	63+36[f]
5[c]			3.0	91
6			1.0	93
7			3.0	92
8			1.0	94
9			1.0	92

[a] The reaction was carried out with aniline (1.0 mmol), alcohol (1.0 mmol), $[Cp^*IrCl_2]_2$ (1.0–3.0 mol % Ir), and $NaHCO_3$ (same equivalent as that of the iridium catalyst) in toluene (0.1 mL) at 110 °C for 17 h.
[b] Isolated yield.
[c] At 130 °C.
[d] K_2CO_3 was used as base.
[e] The reaction was carried out using aniline (1.0 mmol), 1-octanol (2.6 mmol), $[Cp^*IrCl_2]_2$ (5.0 mol % Ir), and K_2CO_3 (5.0 mol %) in toluene (0.5 mL) at 110 °C for 40 h.
[f] *N*-Octylaniline (63%) and *N*,*N*-dioctylaniline (36%) were isolated.

catalysts for 40 h, the di-alkylated product was obtained in 36% yield along with the mono-alkylated product (63%) (entry 4), indicating that the second alkylation is sufficiently slow. Secondary alcohols such as 2-octanol, cyclopentanol, and cyclohexanol were also good alkylating reagents; *N*-(2-octyl)aniline, *N*-cyclopentylaniline, and *N*-cyclohexylaniline could be obtained in excellent yields (entries 5–7). Anilines bearing methoxy and chloro substituent were also applicable to this N-alkylation system (entries 8 and 9). The reactions using tertiary alcohol (*tert*-butyl alcohol) and phenol were also examined; however, those resulted in no reaction.

2.3. N-Alkylation of aniline with benzyl alcohols bearing functional groups

To evaluate the usefulness of the present N-alkylation system, the reactions of aniline with benzyl alcohols bearing various functional groups were explored. The results are summarized in Table 3. Methyl, methoxy, chloro, bromo, nitro, cyano, and ester substituents were tolerant in the present N-alkylation system. All of these reactions resulted in the selective formation of mono-alkylated aniline in high to excellent yields. Even with a benzyl alcohol bearing a substituent at *ortho*-position, the reaction proceeded in an excellent yield (entry 2). In the reactions using benzyl alcohols with electron-withdrawing substituents, relatively larger amounts of the catalyst were required to obtain high yields (entries 6–9).

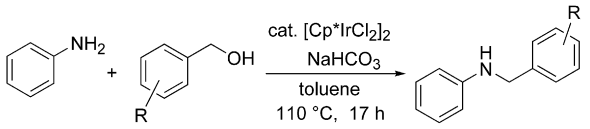
2.4. N-Alkylation of benzylamine, phenethylamine, and octylamine with primary and secondary alcohols

We also examined the N-alkylation of other primary amines. The results are summarized in Table 4. The reactions of benzylamine with several primary and secondary alcohols proceeded in good to excellent yields (entries 1–6). In the reactions using 1-octanol and cyclohexanol (entries 3 and 6), high yields were obtained even at lower temperature (90 °C).[19] When the reaction of benzylamine with 1-octanol was performed using an excess amount of 1-octanol (2.6 equiv) in the presence of 5.0% catalysts for 40 h, *N*,*N*-dioctylbenzylamine was obtained in 80% yield (entry 4), indicating that di-alkylation of benzylamine is easier than that of aniline (see entry 4 in Table 2).[20] Phenethylamine and octylamine could be also alkylated by the present catalytic system, although relatively higher catalyst loading and/or higher reaction temperature were required (entries 7–9).

2.5. N-Alkylation of various secondary amines with benzyl alcohol

We next turned our attention to the N-alkylation of secondary amines with alcohols. At first, the reactions of various secondary amines with benzyl alcohol catalyzed by $[Cp^*IrCl_2]_2$/$NaHCO_3$ were studied. The results are summarized in Table 5. In the alkylation of secondary amines, basicity and steric

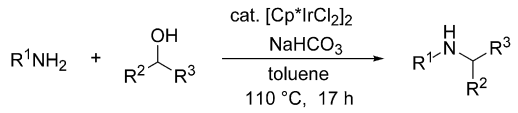
Table 3
N-Alkylation of aniline with benzyl alcohols bearing functional groups[a]

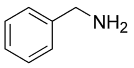
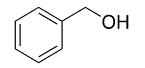
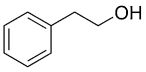
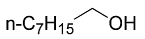
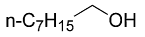
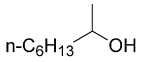
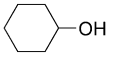
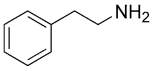
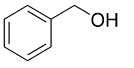
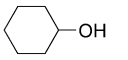
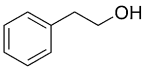


Entry	R	Catalyst (mol % Ir)	Yield[b] (%)
1	4-Me	1.0	92
2	2-OMe	2.0	93
3	3-OMe	2.0	97
4	4-OMe	1.0	92
5	4-Cl	1.0	96
6	4-Br	3.0	98
7	4-NO_2	3.0	84
8	3-CN	3.0	87
9	4-COOMe	3.0	96

[a] The reaction was carried out with aniline (1.0 mmol), benzyl alcohols (1.0 mmol), $[Cp^*IrCl_2]_2$ (1.0–3.0 mol % Ir), and $NaHCO_3$ (same equivalent as that of the iridium catalyst) in toluene (0.1 mL) at 110 °C for 17 h.
[b] Isolated yield.

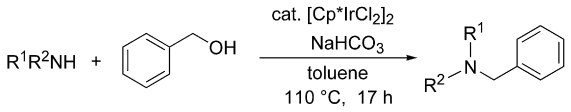
Table 4
N-Alkylation of benzylamine, phenethylamine, and octylamine with primary and secondary alcohols[a]

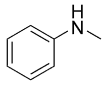
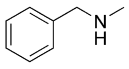
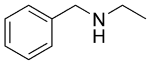
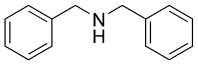
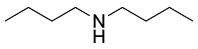
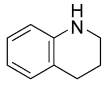


Entry	Amine	Alcohol	Catalyst (mol % Ir)	Yield[b] (%)
1			1.0	93
2			1.0	80
3[c]			1.0	86
4[d]			5.0	80[e]
5			2.0	86
6[c]			1.0	98
7			3.0	86
8[f]			3.0	71
9[g]	n-$C_8H_{17}NH_2$		3.0	76

[a] The reaction was carried out with primary amine (1.0 mmol), alcohols (1.0 mmol), $[Cp^*IrCl_2]_2$ (1.0–3.0 mol % Ir), and $NaHCO_3$ (same equivalent as that of the iridium catalyst) in toluene (0.1 mL) at 110 °C for 17 h.
[b] Isolated yield.
[c] At 90 °C.
[d] The reaction was carried out using benzylamine (1.0 mmol), 1-octanol (2.6 mmol), $[Cp^*IrCl_2]_2$ (5.0 mol % Ir), and K_2CO_3 (5.0 mol %) in toluene (0.5 mL) at 110 °C for 40 h.
[e] *N*,*N*-Dioctylbenzylamine (80%) was isolated.
[f] At 130 °C.
[g] At 100 °C for 40 h.

Table 5
N-Alkylation of various secondary amines with benzyl alcohol[a]



Entry	Amine	Catalyst (mol % Ir)	Yield[b] (%)
1		4.0	91
2		1.0	95
3		2.0	87
4		3.0	75
5		5.0	81
6		1.0	92
7		2.0	93
8		5.0	83
9		5.0	72

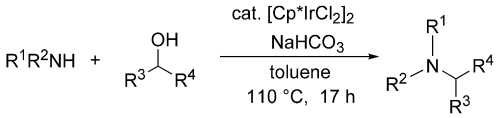
[a] The reaction was carried out with secondary amine (1.0 mmol), benzyl alcohol (1.0 mmol), $[Cp^*IrCl_2]_2$ (1.0–5.0 mol % Ir), and $NaHCO_3$ (same equivalent as that of the iridium catalyst) in toluene (0.1 mL) at 110 °C for 17 h.
[b] Isolated yield.

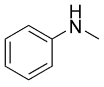
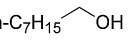
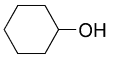
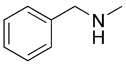
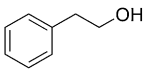
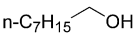
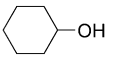
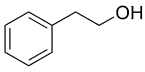
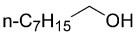
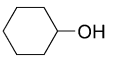
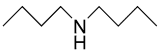
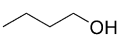
factor of amine substrates were important: the reaction of *N*-methylaniline with benzyl alcohol required higher catalyst loading (4.0 mol % Ir) to obtain an excellent yield (entry 1), while the reaction of more basic and sterically unhindered *N*-methylbenzylamine required only 1.0 mol % Ir of the catalyst (entry 2). Additionally, while *N*-methylbenzylamine and *N*-ethylbenzylamine were applicable to this N-alkylation system, the reaction of *N*-isopropylbenzylamine resulted in a poor yield (<30%), indicating the importance of steric hindrance around the nitrogen atom in amines. Other aromatic, aliphatic, and cyclic secondary amines could be also benzylated in good to excellent yields by the present catalytic system (entries 4–9).

2.6. N-Alkylation of N-methylaniline, N-methylbenzylamine, pyrrolidine, and dibutylamine with various primary and secondary alcohols

We also examined the N-alkylation of other secondary amines with various primary and secondary alcohols. The results are summarized in Table 6. The reaction of *N*-methylaniline with 1-octanol gave *N*-methyl-*N*-octylaniline in 66% yield although larger amounts of catalyst (5.0 mol % Ir) and higher temperature (130 °C) were required (entry 1). The reaction of *N*-methylaniline with secondary alcohol (cyclohexanol) also

Table 6
N-Alkylation of *N*-methylaniline, *N*-methylbenzylamine, pyrrolidine, and dibutylamine with various primary and secondary alcohols[a]



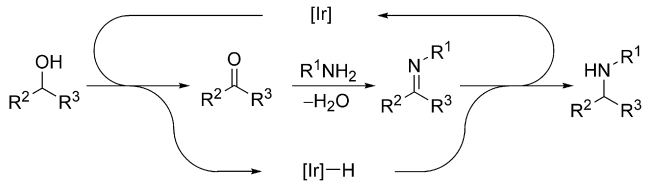
Entry	Amine	Alcohol	Catalyst (mol % Ir)	Yield[b] (%)
1[c]			5.0	66
2			4.0	83
3			1.0	88
4			1.0	95
5			4.0	44
6			5.0	77
7[d]			2.0	96
8[e]			5.0	88
9[f,g]			3.0	91[h]

[a] The reaction was carried out with secondary amine (1.0 mmol), alcohol (1.0 mmol), $[Cp^*IrCl_2]_2$ (1.0–5.0 mol % Ir), and $NaHCO_3$ (same equivalent as that of the iridium catalyst) in toluene (0.1 mL) at 110 °C for 17 h.
[b] Isolated yield.
[c] At 130 °C.
[d] 1-Octanol (2.0 mmol) was used.
[e] Pyrrolidine (2.0 mmol) and 4.0 mmol of cyclohexanol were used.
[f] 1-Butanol (5.0 mmol) was used.
[g] At 90 °C.
[h] GC yield.

gave the tertiary amine in good yield (entry 2). The N-alkylation of *N*-methylbenzylamine with primary alcohols proceeded smoothly (entries 3 and 4), while the reaction with cyclohexanol gave a relatively low yield: *N*-cyclohexyl-*N*-methylbenzylamine was formed in only 44% yield (entry 5). Pyrrolidine and dibutylamine were also applicable to this catalytic system (entries 6–9). In some cases, employment of excess amounts of alcohols gave excellent results (entries 7–9).[21]

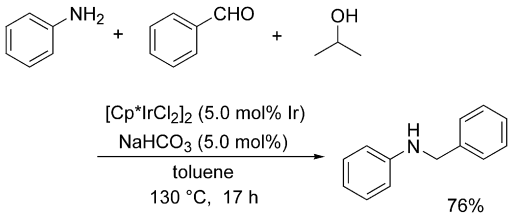
2.7. Possible mechanisms

We have previously reported the hydrogen transfer (Oppenauer-type) oxidation of primary and secondary alcohols to aldehydes or ketones catalyzed by $[Cp^*IrCl_2]_2$/base system.[13a] Thus, we propose that the initial stage of the reaction would be the oxidation of alcohols to a carbonyl intermediate accompanied by the transitory generation of an iridium hydride. Then, the carbonyl intermediate would readily react with an amine to afford an imine or an iminium species with concomitant formation of water. Transfer hydrogenation of the imine or the iminium species with the iridium hydride would follow to give an alkylated amine as a product (Scheme 2).



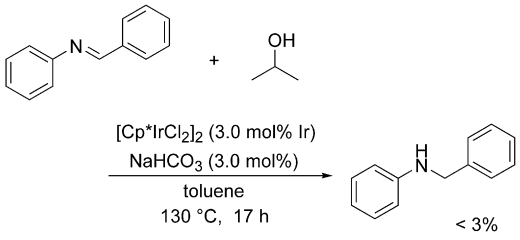
Scheme 2.

To obtain an information concerning the reaction mechanism, the reaction of an amine with an aldehyde in the presence of a hydrogen donor (2-propanol) under the catalytic condition was undertaken: the reaction of aniline (1.0 mmol) with benzaldehyde (1.0 mmol) and 2-propanol (3.0 mmol) in the presence of catalytic amounts of $[Cp^*IrCl_2]_2$ and $NaHCO_3$ in toluene at 130 °C for 17 h gave *N*-benzylaniline in 76% yield (Eq. 1). This result obviously supports our proposal described above.



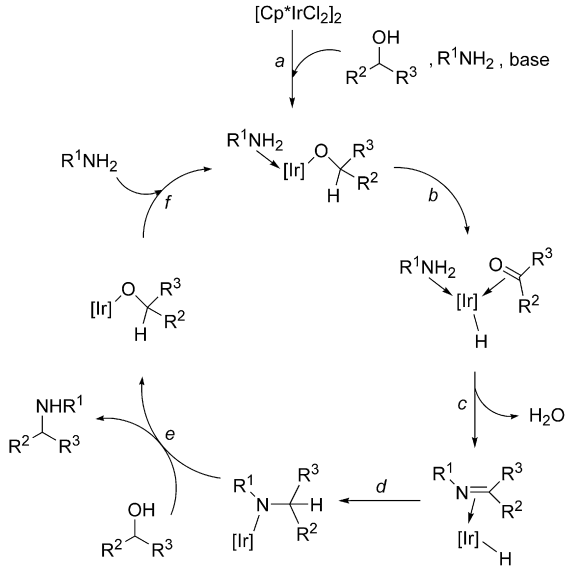
(1)

On the other hand, the reaction of an imine in the presence of a hydrogen donor under catalytic condition hardly gave an amine: the reaction of benzylideneaniline (1.0 mmol) with 2-propanol (5.0 mmol) in the presence of catalytic amounts of $[Cp^*IrCl_2]_2$ and $NaHCO_3$ resulted in the formation of a trace amount of *N*-benzylaniline (Eq. 2). This result indicates that uncoordinated imine could not be transfer hydrogenated by the present catalytic system and that the formation of benzylideneaniline by the reaction of aniline with benzaldehyde must occur in the coordination sphere of iridium to give *N*-benzylaniline.



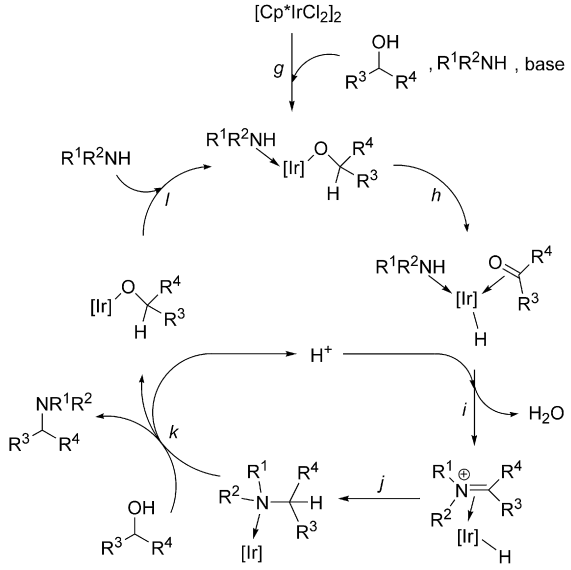
(2)

On the basis of these experimental results,[22] a possible mechanism for the Cp*Ir-catalyzed N-alkylation of primary amines with primary and secondary alcohols is illustrated in Scheme 3. The first step of the reaction would involve the formation of alkoxo iridium species coordinated with an amine (step *a*).[23] β-Hydrogen elimination of alkoxo moiety would occur to afford an iridium hydride coordinated with the amine and the aldehyde (or ketone) (step *b*). Condensation between the amine and the aldehyde (or ketone) in the coordination sphere of iridium would lead to the formation of an imine-coordinated iridium hydride (step *c*). Insertion of a C=N of the imine into iridium–hydride bond (step *d*), amide–alkoxide exchange[24] accompanied by the release of the product (step *e*), and coordination of the amine (step *f*) would successively occur to regenerate the catalytically active species.[25]



Scheme 3.

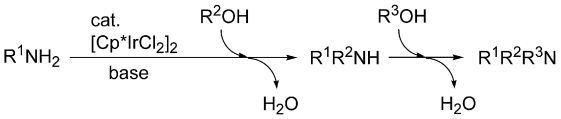
A possible mechanism for the Cp*Ir-catalyzed N-alkylation of secondary amines with primary and secondary alcohols is illustrated in Scheme 4. This mechanism is closely similar to that for the reaction of primary amines. However, the condensation between a secondary amine and an aldehyde (or ketone) would be affected by a proton to afford an iridium hydride coordinated with iminium ion (step *i*). Then, insertion of a C=N of the iminium ion into iridium–hydride bond (step *j*), release of the product (step *k*), and regeneration of active species (step *l*) would successively occur.[25]



Scheme 4.

2.8. One-pot sequential N-alkylation of benzylamine leading to tertiary amines bearing three different substituents

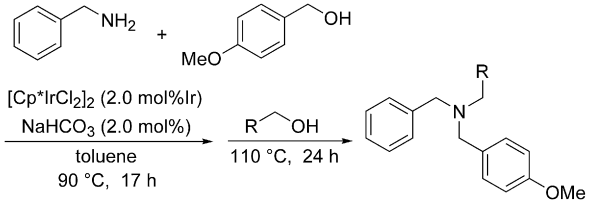
As described above, the present N-alkylation system catalyzed by $[Cp^*IrCl_2]_2$ is highly selective for mono-alkylation of primary amines, and it also exhibits a high activity for the alkylation of secondary amines to give tertiary amines. Thus, it could be anticipated that sequential addition of two kinds of alcohols to the reaction system would lead up to the selective formation of tertiary amines having three different substituents (Eq. 3).

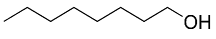
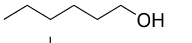
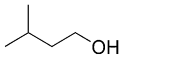
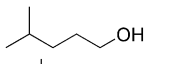
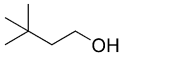
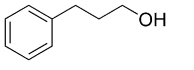
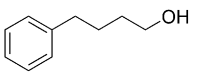


(3)

First, the reaction of benzylamine with 4-methoxybenzyl alcohol was carried out in the presence of $[Cp^*IrCl_2]_2$ (2.0 mol % Ir) and $NaHCO_3$ (2.0 mol %) at 90 °C for 17 h. Then, 1-octanol (1.2 equiv) was added to the reaction mixture, and that was stirred at 110 °C for additional 24 h. By this simple procedure, *N*-benzyl-*N*-octyl-4-methoxybenzylamine was obtained in 87% yield (Table 7, entry 1). Thus, several tertiary amines bearing benzyl, 4-methoxybenzyl, and another alkyl substituent could be synthesized by the sequential alkylation methodology. The results are summarized in Table 7.

Table 7
One-pot sequential N-alkylation of benzylamine leading to tertiary amines[a]



Entry	Alcohol	Yield[b] (%)
1		87
2		88
3		50
4		86
5[c]		65
6		42
7		86

[a] The reaction was carried out with benzylamine (1.0 mmol), 4-methoxybenzyl alcohol (1.0 mmol), $[Cp^*IrCl_2]_2$ (0.010 mmol, 2.0 mol % Ir), and $NaHCO_3$ (0.020 mmol, 2.0 mol %) in toluene (0.1 mL) at 90 °C for 17 h. Then, another alcohol (1.2 mmol) was added and stirred at 110 °C for 24 h.
[b] Isolated yield.
[c] 3,3-Dimethyl-1-butanol (3.0 mmol) was used.

In summary, we have developed a new and efficient system for the synthesis of amines catalyzed by a Cp*Ir complex. It should be noted that the employment of equimolar amounts of starting materials (amine and alcohol) is sufficient to obtain high yields of the desired products, and only harmless water is produced as co-product in these reactions. A wide variety of secondary and tertiary amines can be synthesized with high atom economy under mild and less-toxic conditions. The present new catalytic system can provide an environmentally benign and versatile protocol for the synthesis of amines.

3. Experimental section

3.1. General

All reactions and manipulations were carried out under an atmosphere of argon by means of standard Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded on JEOL A-500 and EX-270 spectrometers. Gas chromatography (GC) analyses were performed on a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences TC-17) and on a Shimadzu GC-14A gas chromatograph with a capillary column (Shimadzu CBP1-M25-025). High-performance liquid chromatography (HPLC) analysis was performed with a TOSOH model CCPS pumping system with a chiral column (Daicel CHIRALCEL OD-H). Column chromatography was carried out by using Wako-gel C-200. Preparative thin layer chromatography was carried out by using Merck Silica gel 60 F_{254} (layer thickness 1 mm). Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Solvents were dried by standard procedures and distilled prior to use. The catalyst $[Cp^*IrCl_2]_2$ (Cp*=pentamethylcyclopentadienyl), was prepared according to the literature method.[26] All other reagents are commercially available and were used as received.

3.2. N-Alkylation of aniline with benzyl alcohol catalyzed by $[Cp^*IrCl_2]_2$ and various bases (Table 1)

In a heavy-walled glass reactor under an atmosphere of argon were suspended $[Cp^*IrCl_2]_2$ (4.0 mg, 0.0050 mmol, 1.0 mol % Ir) and base (0.01 mmol, 1.0 mol %) in toluene (0.1 mL). Then aniline (93.1 mg, 1.0 mmol) and benzyl alcohol (108.1 mg, 1.0 mmol) were added, and the mixture was stirred at 110 °C for 17 h in the sealed reactor. The yield of *N*-benzylanilne was determined by GC analysis using undecane as an internal standard.

3.3. N-Alkylation of anilines with various primary and secondary alcohols (Table 2)

In a heavy-walled glass reactor under an atmosphere of argon were suspended $[Cp^*IrCl_2]_2$ (0.0050–0.0150 mmol, 1.0–3.0 mol % Ir) and $NaHCO_3$ (same equivalent to the iridium catalyst) in toluene (0.1 mL). Then aniline (1.0 mmol) and alcohol (1.0 mmol) were added, and the mixture was stirred at 110 °C for 17 h in the sealed reactor. After evaporation of

the solvent, the products were isolated by column chromatography (eluent: hexane/ethyl acetate/triethylamine).

3.3.1. N-Benzylaniline (Table 2, entry 1)[27]

^{1}H NMR ($CDCl_3$) δ 7.39–7.12 (m, 7H, aromatic), 6.73–6.61 (m, 3H, aromatic), 4.28 (s, 2H, CH_2), 4.00 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 148.0, 139.3, 129.1, 128.5, 127.4, 127.1, 117.5, 112.8, 48.4.

3.3.2. N-Phenethylaniline (Table 2, entry 2)[28]

^{1}H NMR ($CDCl_3$) δ 7.30–7.10 (m, 7H, aromatic), 6.67 (t, J=7 Hz, 1H, aromatic), 6.55 (d, J=8 Hz, 2H, aromatic), 3.58 (br, 1H, NH), 3.32 (t, J=7 Hz, 2H, CH_2), 2.83 (t, J=7 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 147.8, 139.1, 129.1, 128.6, 128.4, 126.2, 117.2, 112.8, 45.0, 35.5.

3.3.3. N-Octylaniline (Table 2, entry 3)[29]

^{1}H NMR ($CDCl_3$) δ 7.21–7.13 (m, 2H, aromatic), 6.70–6.56 (m, 3H, aromatic), 3.52 (br, 1H, NH), 3.07 (t, J=7 Hz, 2H, CH_2), 1.65–1.54 (m, 2H, CH_2), 1.28 (br, 10H, CH_2), 0.88 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 148.3, 129.0, 116.9, 112.5, 43.9, 31.9, 29.6, 29.5, 29.3, 27.2, 22.7, 14.2.

3.3.4. N,N-Dioctylaniline (Table 2, entry 4)[30]

^{1}H NMR ($CDCl_3$) δ 7.20–7.17 (m, 2H, aromatic), 6.63–6.59 (m, 3H, aromatic), 3.23 (t, J=7 Hz, CH_2), 1.56 (br, 4H, CH_2), 1.31–1.29 (m, 20H, CH_2), 0.88 (t, J=7 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 148.2, 129.2, 115.0, 111.7, 51.0, 31.8, 29.5, 29.3, 27.24, 27.20, 22.7, 14.1.

3.3.5. N-(2-Octyl)aniline (Table 2, entry 5)[31]

^{1}H NMR ($CDCl_3$) δ 7.16–7.10 (m, 2H, aromatic), 6.66–6.52 (m, 3H, aromatic), 3.45–3.39 (m, 2H, CH and NH), 1.53–1.27 (m, 10H, CH_2), 1.14 (d, J=6 Hz, 3H, CH_3), 0.87 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 147.6, 129.1, 116.6, 112.9, 48.4, 37.3, 31.9, 29.4, 26.2, 22.7, 20.8, 14.1.

3.3.6. N-Cyclopentylaniline (Table 2, entry 6)[32]

^{1}H NMR ($CDCl_3$) δ 7.18–7.11 (m, 2H, aromatic), 6.66 (t, J=7 Hz, 1H, aromatic), 6.58 (d, J=7 Hz, 2H, aromatic), 3.81–3.72 (m, 1H, CH), 3.59 (br, 1H, NH), 2.03–1.94 (m, 2H, CH_2), 1.76–1.41 (m, 6H, CH_2). ^{13}C NMR ($CDCl_3$) δ 147.9, 129.0, 116.7, 113.0, 54.6, 33.6, 24.1.

3.3.7. N-Cyclohexylaniline (Table 2, entry 7)[33]

^{1}H NMR ($CDCl_3$) δ 7.20–7.09 (m, 2H, aromatic), 6.67–6.55 (m, 3H, aromatic), 3.49 (br, 1H, NH), 3.27–3.18 (m, 1H, CH), 2.06–2.01 (m, 2H, CH_2), 1.77–1.62 (m, 3H, CH_2), 1.42–1.05 (m, 5H, CH_2). ^{13}C NMR ($CDCl_3$) δ 147.2, 129.1, 116.7, 113.0, 51.6, 33.5, 26.0, 25.1.

3.3.8. N-Benzyl-4-methoxyaniline (Table 2, entry 8)[7d]

^{1}H NMR ($CDCl_3$) δ 7.36–7.20 (m, 5H, aromatic), 6.76 (d, J=9 Hz, 2H, aromatic), 6.57 (d, J=9 Hz, 2H, aromatic), 4.25 (s, 2H, CH_2), 3.71 (s, 3H, OCH_3), 3.58 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 152.0, 142.3, 139.5, 128.4, 127.4, 127.0, 114.8, 114.0, 55.8, 49.2.

3.3.9. N-Benzyl-4-chloroaniline (Table 2, entry 9)[7d]

^{1}H NMR ($CDCl_3$) δ 7.35–7.21 (m, 5H, aromatic), 7.06 (d, J=9 Hz, 2H, aromatic), 6.49 (d, J=9 Hz, 2H, aromatic), 4.25 (s, 2H, CH_2), 4.00 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 146.5, 138.8, 128.9, 128.5, 127.25, 127.21, 121.9, 113.8, 48.2.

3.4. N-Alkylation of aniline with benzyl alcohols bearing functional groups (Table 3)

In a heavy-walled glass reactor under an atmosphere of argon were suspended $[Cp^*IrCl_2]_2$ (0.0050–0.0150 mmol, 1.0–3.0 mol % Ir) and $NaHCO_3$ (same equivalent to the iridium catalyst) in toluene (0.1 mL). Then aniline (1.0 mmol) and benzyl alcohol (1.0 mmol) were added, and the mixture was stirred at 110 °C for 17 h in the sealed reactor. After evaporation of the solvent, the products were isolated by column chromatography (eluent: hexane/ethyl acetate/triethylamine).

3.4.1. N-(4-Methylbenzyl)aniline (Table 3, entry 1)[34]

^{1}H NMR ($CDCl_3$) δ 7.26–7.12 (m, 6H, aromatic), 6.73–6.60 (m, 3H, aromatic), 4.26 (s, 2H, CH_2), 3.95 (br, 1H, NH), 2.33 (s, 3H, Me). ^{13}C NMR ($CDCl_3$) δ 147.9, 136.4, 136.1, 129.0, 128.9, 127.2, 117.2, 112.6, 47.8, 21.0.

3.4.2. N-(2-Methoxybenzyl)aniline (Table 3, entry 2)[35]

^{1}H NMR ($CDCl_3$) δ 7.29–7.10 (m, 4H, aromatic), 6.87 (t, J=8 Hz, 2H, aromatic), 6.69–6.61 (m, 3H, aromatic), 4.31 (s, 2H, CH_2), 4.09 (br, 1H, NH), 3.82 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ 157.2, 148.2, 129.0, 128.7, 128.1, 127.2, 120.3, 117.1, 112.9, 110.1, 55.3, 43.4.

3.4.3. N-(3-Methoxybenzyl)aniline (Table 3, entry 3)[5c]

^{1}H NMR ($CDCl_3$) δ 7.34–7.20 (m, 3H, aromatic), 7.03–6.67 (m, 6H, aromatic), 4.35 (s, 2H, CH_2), 4.07 (br, 1H, NH), 3.84 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ 159.7, 147.9, 141.0, 129.4, 129.1, 119.6, 117.4, 112.9, 112.7, 112.5, 55.1, 48.2.

3.4.4. N-(4-Methoxybenzyl)aniline (Table 3, entry 4)[36]

^{1}H NMR ($CDCl_3$) δ 7.25–7.10 (m, 4H, aromatic), 6.85–6.56 (m, 5H, aromatic), 4.19 (s, 2H, CH_2), 3.88 (br, 1H, NH), 3.74 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ 158.6, 148.0, 131.2, 129.0, 128.6, 117.3, 113.9, 112.7, 55.2, 47.7.

3.4.5. N-(4-Chlorobenzyl)aniline (Table 3, entry 5)[37]

^{1}H NMR ($CDCl_3$) δ 7.25–7.11 (m, 6H, aromatic), 6.73–6.54 (m, 3H, aromatic), 4.25 (s, 2H, CH_2), 3.98 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 147.6, 137.9, 132.7, 129.1, 128.6, 128.5, 117.6, 112.8, 47.6.

3.4.6. N-(4-Bromobenzyl)aniline (Table 3, entry 6)

^{1}H NMR ($CDCl_3$) δ 7.40–7.09 (m, 6H, aromatic), 6.71–6.51 (m, 3H, aromatic), 4.18 (s, 2H, CH_2), 3.94 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 147.6, 138.4, 131.4, 129.1, 128.8,

120.7, 117.6, 112.7, 47.5. Anal. Calcd for $C_{13}H_{12}BrN$: C, 59.56; H, 4.61; N, 5.34. Found: C, 59.43; H, 4.64; N, 5.15.

3.4.7. N-(4-Nitrobenzyl)aniline (Table 3, entry 7)[36]

^{1}H NMR ($CDCl_3$) δ 8.11–8.08 (m, 2H, aromatic), 7.49–7.44 (m, 2H, aromatic), 7.18–7.10 (m, 2H, aromatic), 6.73–6.53 (m, 3H, aromatic), 4.40 (s, 2H, CH_2), 4.29 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 147.4, 147.1, 146.7, 129.1, 127.4, 123.5, 117.8, 112.7, 47.4.

3.4.8. N-(3-Cyanobenzyl)aniline (Table 3, entry 8)

^{1}H NMR ($CDCl_3$) δ 7.65–7.39 (m, 4H, aromatic), 7.23–7.12 (m, 2H, aromatic), 6.76–6.55 (m, 3H, aromatic), 4.38 (s, 2H, CH_2), 4.17 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 147.2, 141.2, 131.4, 130.7, 130.5, 129.25, 129.22, 118.7, 118.0, 112.8, 112.6, 47.5. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.50; H, 6.00; N, 13.20.

3.4.9. N-(4-Methoxycarbonylbenzyl)aniline (Table 3, entry 9)[38]

^{1}H NMR ($CDCl_3$) δ 7.98 (d, J=8 Hz, 2H, aromatic), 7.40 (d, J=8 Hz, 2H, aromatic), 7.14 (t, J=7 Hz, 2H, aromatic), 6.70 (t, J=7 Hz, 1H, aromatic), 6.58 (d, J=7 Hz, 2H, aromatic), 4.37 (d, J=4 Hz, 2H, CH_2), 4.13 (br, 1H, NH), 3.88 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ 166.7, 147.6, 144.8, 129.8, 129.1, 128.9, 127.0, 117.7, 112.8, 52.0, 47.9.

3.5. N-Alkylation of benzylamine, phenethylamine, and octylamine with primary and secondary alcohols (Table 4)

In a heavy-walled glass reactor under an atmosphere of argon were suspended $[Cp^*IrCl_2]_2$ (0.0050–0.0150 mmol, 1.0–3.0 mol % Ir) and $NaHCO_3$ (same equivalent to the iridium catalyst) in toluene (0.1 mL). Then primary amine (1.0 mmol) and alcohol (1.0 mmol) were added, and the mixture was stirred at 110 °C for 17 h in the sealed reactor. After evaporation of the solvent, the products were isolated by column chromatography (eluent: hexane/ethyl acetate/triethylamine).

3.5.1. Dibenzylamine (Table 4, entry 1)[39]

^{1}H NMR ($CDCl_3$) δ 7.40–7.18 (m, 10H, aromatic), 3.79 (s, 4H, CH_2), 1.76 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 140.2, 128.3, 128.0, 126.8, 53.1.

3.5.2. N-Benzylphenethylamine (Table 4, entry 2)[40]

^{1}H NMR ($CDCl_3$) δ 7.33–7.15 (m, 10H, aromatic), 3.84 (s, 2H, CH_2), 2.93–2.77 (m, 4H, CH_2), 1.45 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 140.1, 139.9, 128.6, 128.3, 128.0, 127.9, 126.7, 126.0, 53.9, 50.6, 36.4.

3.5.3. N-Octylbenzylamine (Table 4, entry 3)[4b]

^{1}H NMR ($CDCl_3$) δ 7.33–7.15 (m, 10H, aromatic), 3.77 (s, 2H, CH_2), 2.61 (t, J=7 Hz, 2H, CH_2), 1.52–1.45 (m, 2H, CH_2), 1.32 (br, 1H, NH), 1.27 (m, 10H, CH_2), 0.88 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 140.4, 128.19, 128.16, 126.6, 54.1, 49.5, 31.8, 30.2, 29.6, 29.3, 27.4, 22.7, 14.1.

3.5.4. N,N-Dioctylbenzylamine (Table 4, entry 4)[41]

^{1}H NMR ($CDCl_3$) δ 7.32–7.21 (m, 5H, aromatic), 3.53 (s, 2H, CH_2), 2.38 (t, J=7 Hz, 4H, CH_2), 1.45 (br, 4H, CH_2), 1.29–1.25 (m, 20H, CH_2), 0.88 (t, J=7 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 140.3, 128.8, 128.0, 126.5, 58.6, 53.8, 31.9, 29.6, 29.3, 27.5, 27.0, 22.7, 14.1.

3.5.5. N-(2-Octyl)benzylamine (Table 4, entry 5)[4b]

^{1}H NMR ($CDCl_3$) δ 7.33–7.19 (m, 5H, aromatic), 3.82 (d, J=13 Hz, 1H, CH_2), 3.72 (d, J=13 Hz, 1H, CH_2), 2.70–2.61 (m, 1H, CH), 1.52–1.47 (m, 1H, CH_2), 1.37–1.27 (m, 9H, CH_2), 1.07 (d, J=7 Hz, 3H, CH_3), 0.88 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 140.8, 128.2, 128.0, 126.6, 52.5, 51.4, 37.2, 31.9, 29.6, 26.0, 22.7, 20.4, 14.2.

3.5.6. N-Cyclohexylbenzylamine (Table 4, entry 6)[1b]

^{1}H NMR ($CDCl_3$) δ 7.33–7.19 (m, 5H, aromatic), 3.80 (s, 2H, CH_2), 2.53–2.43 (m, 1H, CH), 1.93–1.89 (m, 2H, CH_2), 1.75–1.70 (m, 2H, CH_2), 1.63–1.59 (m, 1H, NH), 1.35–1.04 (m, 6H, CH_2). ^{13}C NMR ($CDCl_3$) δ 140.8, 128.2, 128.0, 126.6, 56.2, 51.0, 33.6, 26.2, 25.0.

3.5.7. N-Cyclohexylphenethylamine (Table 4, entry 8)[42]

^{1}H NMR ($CDCl_3$) δ 7.31–7.19 (m, 5H, aromatic), 2.89 (t, J=6 Hz, 2H, CH_2), 2.78 (t, J=7 Hz, 2H, CH_2), 2.41 (tt, J=10, 4 Hz, 1H, CH), 1.87–1.60 (m, 5H, NH and CH_2), 1.31–0.98 (m, 6H, CH_2). ^{13}C NMR ($CDCl_3$) δ 140.0, 128.5, 128.2, 125.9, 56.7, 48.2, 36.7, 33.6, 26.2, 25.1.

3.5.8. N-Octylphenethylamine (Table 4, entry 9)[43]

^{1}H NMR ($CDCl_3$) δ 7.31–7.16 (m, 5H, aromatic), 2.85 (m, 2H, CH_2), 2.81 (m, 2H, CH_2), 2.59 (t, J=7 Hz, 2H, CH_2), 1.45 (br, 2H, CH_2), 1.26 (br, 10H, CH_2), 0.87 (t, J=7 Hz, 3H,CH_3). ^{13}C NMR ($CDCl_3$) δ 140.0, 128.5, 128.3, 125.9, 51.3, 50.0, 36.5, 31.9, 30.2, 29.6, 29.3, 27.4, 22.7, 14.1.

3.5.9. N-Benzyl-(1-phenylethyl)amine (Ref. 22)[44]

^{1}H NMR ($CDCl_3$) δ 7.34–7.21 (m, 10H, aromatic), 3.80 (q, J=7 Hz, 1H, CH), 3.65 (d, J=13 Hz, 1H, CH_2), 3.58 (d, J=13 Hz, 1H, CH_2), 1.35 (d, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 145.6, 140.6, 128.4, 128.3, 128.1, 126.9, 126.8, 126.6, 57.5, 51.6, 24.5.

3.6. N-Alkylation of various secondary amines with benzyl alcohol (Table 5)

In a heavy-walled glass reactor under an atmosphere of argon were suspended $[Cp^*IrCl_2]_2$ (0.0050–0.0250 mmol, 1.0–5.0 mol % Ir) and $NaHCO_3$ (same equivalent to the iridium catalyst) in toluene (0.1 mL). Then secondary amine (1.0 mmol) and benzyl alcohol (1.0 mmol) were added, and the mixture was stirred at 110 °C for 17 h in the sealed reactor. After evaporation of the solvent, the products were isolated by column chromatography (eluent: hexane/ethyl acetate/triethylamine).

3.6.1. N-Benzyl-N-methylaniline (Table 5, entry 1)[45]

^{1}H NMR ($CDCl_3$) δ 7.31–7.15 (m, 7H, aromatic), 6.73–6.65 (m, 3H, aromatic), 4.48 (s, 2H, CH_2), 3.03 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 149.5, 138.8, 129.0, 128.4, 126.7, 126.6, 116.4, 112.2, 56.6, 38.5.

3.6.2. N,N-Dibenzylmethylamine (Table 5, entry 2)[46]

^{1}H NMR ($CDCl_3$) δ 7.37–7.18 (m, 10H, aromatic), 3.51 (s, 4H, CH_2), 2.17 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 139.2, 128.8, 128.1, 126.8, 61.9, 42.3.

3.6.3. N,N-Dibenzylethylamine (Table 5, entry 3)[47]

^{1}H NMR ($CDCl_3$) δ 7.41–7.17 (m, 10H, aromatic), 3.56 (s, 4H, CH_2), 2.48 (q, J=7 Hz, 2H, CH_2), 1.05 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 139.9, 128.6, 128.0, 126.6, 57.8, 47.1, 12.0.

3.6.4. Tribenzylamine (Table 5, entry 4)[48]

^{1}H NMR ($CDCl_3$) δ 7.42–7.18 (m, 15H, aromatic), 3.55 (s, 6H, CH_2). ^{13}C NMR ($CDCl_3$) δ 139.5, 128.6, 128.1, 126.7, 57.9.

3.6.5. N,N-Dibutylbenzylamine (Table 5, entry 5)[4b]

^{1}H NMR ($CDCl_3$) δ 7.34–7.16 (m, 5H, aromatic), 3.53 (s, 2H, CH_2), 2.39 (t, J=7 Hz, 4H, CH_2), 1.49–1.35 (m, 4H, CH_2), 1.32–1.21 (m, 4H, CH_2), 0.87 (t, J=7 Hz, 4H, CH_3). ^{13}C NMR ($CDCl_3$) δ 140.3, 128.7, 127.9, 126.4, 58.7, 53.6, 29.4, 20.7, 14.2.

3.6.6. 1-Benzylpyrrolidine (Table 5, entry 6)[14b]

^{1}H NMR ($CDCl_3$) δ 7.35–7.19 (m, 5H, aromatic), 3.60 (s, 2H, CH_2), 2.53–2.42 (m, 4H, CH_2), 1.84–1.70 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ 139.3, 128.8, 128.0, 126.7, 60.7, 54.2, 23.5.

3.6.7. 1-Benzylpiperidine (Table 5, entry 7)[14b]

^{1}H NMR ($CDCl_3$) δ 7.32–7.18 (m, 5H, aromatic), 3.46 (s, 2H, CH_2), 2.38–2.34 (m, 4H, CH_2), 1.60–1.52 (m, 4H, CH_2), 1.45–1.37 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 138.5, 129.1, 127.9, 126.7, 63.9, 54.5, 26.1, 24.5.

3.6.8. 4-Benzylmorpholine (Table 5, entry 8)[45]

^{1}H NMR ($CDCl_3$) δ 7.49–7.20 (m, 5H, aromatic), 3.70 (t, J=5 Hz, 4H, CH_2), 3.49 (s, 2H, CH_2), 2.43 (t, J=5 Hz, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ 137.6, 129.0, 128.1, 127.0, 67.0, 63.4, 53.6.

3.6.9. 1-Benzyl-1,2,3,4-tetrahydroquinoline (Table 5, entry 9)[49]

^{1}H NMR ($CDCl_3$) δ 7.32–7.18 (m, 5H, aromatic), 6.97–6.64 (m, 2H, aromatic), 6.58–6.46 (m, 2H, aromatic), 4.44 (s, 2H, CH_2), 3.36–3.32 (m, 2H, CH_2), 2.82–2.77 (m, 2H, CH_2), 2.03–1.94 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 145.4, 138.8, 128.9, 128.4, 127.0, 126.6, 126.4, 122.1, 115.7, 110.9, 55.2, 49.9, 28.3, 22.5.

3.7. N-Alkylation of N-methylaniline, N-methylbenzylamine, pyrrolidine, and dibutylamine with various primary and secondary alcohols (Table 6)

In a heavy-walled glass reactor under an atmosphere of argon were suspended $[Cp^*IrCl_2]_2$ (0.0050–0.0250 mmol, 1.0–5.0 mol % Ir) and $NaHCO_3$ (same equivalent to the iridium catalyst) in toluene (0.1 mL). Then secondary amine (1.0 mmol) and alcohol (1.0 mmol) were added, and the mixture was stirred at 110 °C for 17 h in the sealed reactor. After evaporation of the solvent, the products were isolated by column chromatography (eluent: hexane/ethyl acetate/triethylamine).

3.7.1. N-Methyl-N-octylaniline (Table 6, entry 1)[50]

^{1}H NMR ($CDCl_3$) δ 7.23–7.17 (m, 2H, aromatic), 6.69–6.62 (m, 3H, aromatic), 3.27 (t, J=7 Hz, 2H, CH_2), 2.90 (s, 3H, NCH_3), 1.54 (m, 2H, CH_2), 1.28–1.27 (m, 10H, CH_2), 0.87 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 149.2, 129.0, 115.6, 111.9, 52.8, 38.3, 31.9, 29.6, 29.4, 27.3, 26.7, 22.7, 14.2.

3.7.2. N-Cyclohexyl-N-methylaniline (Table 6, entry 2)[51]

^{1}H NMR ($CDCl_3$) δ 7.24–6.64 (m, 5H, aromatic), 3.55 (m, 1H, CH), 2.75 (s, 3H, NCH_3), 1.84–1.09 (m, 10H, CH_2). ^{13}C NMR ($CDCl_3$) δ 150.0, 128.9, 116.1, 113.0, 58.1, 31.2, 30.1, 26.3, 26.0.

3.7.3. N-Benzyl-N-methylphenethylamine (Table 6, entry 3)[2g]

^{1}H NMR ($CDCl_3$) δ 7.32–7.14 (m, 10H, aromatic), 3.53 (s, 2H, CH_2), 2.83–2.78 (m, 2H, CH_2), 2.69–2.60 (m, 2H, CH_2), 2.27 (s, 3H, NCH_3). ^{13}C NMR ($CDCl_3$) δ 140.4, 138.9, 128.7, 128.6, 128.1, 128.0, 126.8, 125.7, 62.2, 59.2, 42.2, 34.0.

3.7.4. N-Benzyl-N-methyloctylamine (Table 6, entry 4)[52]

^{1}H NMR ($CDCl_3$) δ 7.30–7.17 (m, 5H, aromatic), 3.46 (s, 2H, CH_2), 2.34 (t, J=7 Hz, 2H, CH_2), 2.17 (s, 3H, NCH_3), 1.52–1.47 (m, 2H, CH_2), 1.26 (br, 10H, CH_2), 0.87 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 139.2, 128.9, 128.0, 126.6, 62.4, 57.6, 42.3, 31.9, 29.6, 29.4, 27.5, 27.5, 22.7, 14.2.

3.7.5. N-Cyclohexyl-N-methylbenzylamine (Table 6, entry 5)[53]

^{1}H NMR ($CDCl_3$) δ 7.33–7.17 (m, 5H, aromatic), 3.55 (s, 2H, CH_2), 2.47–2.38 (m, 1H, CH), 2.18 (s, 3H, NCH_3), 1.94–1.78 (m, 4H, CH_2), 1.65–1.60 (m, 1H, CH_2), 1.37–1.08 (m, 5H, CH_2). ^{13}C NMR ($CDCl_3$) δ 140.3, 128.6, 128.0, 126.5, 62.5, 57.9, 37.7, 28.8, 26.5, 26.1.

3.7.6. 1-Phenethylpyrrolidine (Table 6, entry 6)[14b]

^{1}H NMR ($CDCl_3$) δ 7.27–7.20 (m, 5H, aromatic), 2.86–2.80 (m, 4H, CH_2), 2.74–2.52 (m, 4H, CH_2), 1.86–1.72 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ 140.3, 128.4, 128.1, 125.8, 58.3, 54.2, 35.9, 23.4.

3.7.7. 1-Octylpyrrolidine (Table 6, entry 7)[14b]

^{1}H NMR ($CDCl_3$) δ 2.48–2.38 (m, 6H, CH_2), 1.79–1.77 (m, 4H, CH_2), 1.51 (br, 2H, CH_2), 1.28 (br, 10H, CH_2), 0.88 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 56.8, 54.3, 31.9, 29.6, 29.3, 29.2, 27.8, 23.5, 22.7, 14.1.

3.7.8. 1-Cyclohexylpyrrolidine (Table 6, entry 8)[54]

^{1}H NMR ($CDCl_3$) δ 2.51–2.45 (m, 4H, CH_2), 1.90–1.85 (m, 3H, CH_2), 1.76–1.66 (m, 6H, CH_2), 1.55–1.51 (m, 1H, CH_2), 1.26–1.06 (m, 6H, CH_2). ^{13}C NMR ($CDCl_3$) δ 63.7, 51.4, 32.1, 26.0, 25.2, 23.2.

3.8. One-pot sequential N-alkylation of benzylamine leading to tertiary amines (Table 7)

In a septum-capped glass tube under an atmosphere of argon were suspended $[Cp^*IrCl_2]_2$ (8.0 mg, 0.010 mmol, 2.0 mol % Ir) and $NaHCO_3$ (0.020 mmol, 2.0 mol %) in toluene (0.1 mL). Benzylamine (1.0 mmol) and 4-methoxybenzyl alcohol (1.0 mmol) were added, and the mixture was stirred at 90 °C for 17 h. Then primary alcohol (1.2 mmol) was added to the reaction mixture, and that was stirred at 110 °C for additional 24 h. After evaporation of the solvent, the products were isolated by preparative thin layer chromatography (entries 1, 3 and 5–7) or column chromatography (entries 2 and 4).

3.8.1. N-Benzyl-N-octyl-4-methoxybenzylamine (Table 7, entry 1)

^{1}H NMR ($CDCl_3$) δ 7.35–7.19 (m, 7H, aromatic), 6.84 (d, J=8 Hz, 2H, aromatic), 3.78 (s, 3H, OCH_3), 3.52 (s, 2H, CH_2), 3.47 (s, 2H, CH_2), 2.38 (t, J=7 Hz, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.22 (br, 10H, CH_2), 0.87 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 158.3, 140.0, 131.9, 129.7, 128.6, 128.0, 126.5, 113.4, 58.2, 57.6, 55.2, 53.2, 31.9, 29.5, 29.4, 27.4, 27.0, 22.7, 14.2. Anal. Calcd for $C_{23}H_{33}NO$: C, 81.37; H, 9.80; N, 4.13. Found: C, 81.50; H, 9.51; N, 4.17.

3.8.2. N-Benzyl-N-hexyl-4-methoxybenzylamine (Table 7, entry 2)

^{1}H NMR ($CDCl_3$) δ 7.36–7.20 (m, 7H, aromatic), 6.84 (d, J=8 Hz, 2H, aromatic), 3.77 (s, 3H, OCH_3), 3.51 (s, 2H, CH_2), 3.47 (s, 2H, CH_2), 2.37 (t, J=7 Hz, 2H, CH_2), 1.48–1.45 (m, 2H, CH_2), 1.24–1.20 (m, 6H, CH_2), 0.84 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 158.3, 140.1, 131.9, 129.7, 128.7, 128.0, 126.5, 113.4, 58.1, 57.6, 55.2, 53.3, 31.8, 27.2, 27.0, 22.7, 14.2. Anal. Calcd for $C_{21}H_{29}NO$: C, 80.98; H, 9.38; N, 4.50. Found: C, 80.96; H, 9.41; N, 4.54.

3.8.3. N-Benzyl-N-(3-methylbutyl)-4-methoxybenzylamine (Table 7, entry 3)

^{1}H NMR ($CDCl_3$) δ 7.36–7.17 (m, 7H, aromatic), 6.83 (d, J=8 Hz, 2H, aromatic), 3.77 (s, 3H, OCH_3), 3.51 (s, 2H, CH_2), 3.47 (s, 2H, CH_2), 2.40 (t, J=7 Hz, 2H, CH_2), 1.63–1.53 (m, 1H, CH), 1.43–1.35 (m, 2H, CH_2), 0.79–0.74 (d, J=6 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 158.3, 140.0, 131.8, 129.8, 128.7, 128.0, 126.5, 113.4, 58.1, 57.5, 55.2, 51.4, 36.0, 26.1, 22.8. Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.71. Found: C, 80.80; H, 9.36; N, 4.74.

3.8.4. N-Benzyl-N-(4-methylpentyl)-4-methoxybenzylamine (Table 7, entry 4)

^{1}H NMR ($CDCl_3$) δ 7.36–7.21 (m, 7H, aromatic), 6.84 (d, J=8 Hz, 2H, aromatic), 3.79 (s, 3H, OCH_3), 3.52 (s, 2H, CH_2), 3.48 (s, 2H, CH_2), 2.36 (t, J=7 Hz, 2H, CH_2), 1.59–1.40 (m, 3H, CH_2), 1.16–1.08 (m, 2H, CH_2), 0.84–0.82 (d, J=7 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 158.2, 140.0, 131.9, 129.7, 128.6, 128.0, 126.5, 113.4, 58.1, 57.5, 55.2, 53.6, 36.5, 27.9, 24.8, 22.7. Anal. Calcd for $C_{21}H_{29}NO$: C, 80.98; H, 9.48; N, 4.50. Found: C, 80.68; H, 9.38; N, 4.54.

3.8.5. N-Benzyl-N-(3,3-dimethylbutyl)-4-methoxybenzylamine (Table 7, entry 5)

^{1}H NMR ($CDCl_3$) δ 7.36–7.21 (m, 7H, aromatic), 6.83 (d, J=7 Hz, 2H, aromatic), 3.79 (s, 3H, OCH_3), 3.54 (s, 2H, CH_2), 3.50 (s, 2H, CH_2), 2.43 (t, J=8 Hz, 2H, CH_2), 1.45 (t, J=6 Hz, 2H, CH_2), 0.80 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$) δ 158.2, 140.0, 131.8, 129.7, 128.6, 128.0, 126.5, 113.4, 58.0, 57.4, 55.2, 49.0, 40.2, 29.9, 29.6. Anal. Calcd for $C_{21}H_{29}NO$: C, 80.98; H, 9.48; N, 4.50. Found: C, 80.80; H, 9.51; N, 4.47.

3.8.6. N-Benzyl-N-(4-methoxybenzyl)-3-phenylpropylamine (Table 7, entry 6)

^{1}H NMR ($CDCl_3$) δ 7.36–7.07 (m, 12H, aromatic), 6.84 (d, J=8 Hz, 2H, aromatic), 3.79 (s, 3H, OCH_3), 3.54 (s, 2H, CH_2), 3.49 (s, 2H, CH_2), 2.57 (t, J=8 Hz, 2H, CH_2), 2.45 (t, J=7 Hz, 2H, CH_2), 1.86–1.78 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 158.3, 142.5, 139.9, 131.7, 129.8, 128.7, 128.3, 128.1, 128.0, 126.6, 125.5, 113.4, 58.1, 57.6, 55.3, 52.8, 33.6, 29.1. Anal. Calcd for $C_{24}H_{27}NO$: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.42; H, 8.00; N, 4.05.

3.8.7. N-Benzyl-N-(4-methoxybenzyl)-4-phenylbutylamine (Table 7, entry 7)

^{1}H NMR ($CDCl_3$) δ 7.36–7.08 (m, 12H, aromatic), 6.86–6.80 (m, 2H, aromatic), 3.77 (s, 3H, OCH_3), 3.50 (s, 2H, CH_2), 3.46 (s, 2H, CH_2), 2.58–2.38 (m, 4H, CH_2), 1.62–1.52 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ 158.3, 142.5, 139.9, 131.8, 129.7, 128.6, 128.3, 128.1, 128.0, 126.6, 125.5, 113.4, 58.2, 57.6, 55.2, 52.9, 35.7, 29.0, 26.6. Anal. Calcd for $C_{25}H_{29}NO$: C, 83.52; H, 8.13; N, 3.90. Found: C, 83.67; H, 8.30; N, 3.94.

Acknowledgements

We thank Mr. Y. Kida for his valuable technical assistance.

References and notes

1. For example, see: (a) Salvatore, R. N.; Yoon, C. H.; Jung, K. W. *Tetrahedron* **2001**, *57*, 7785; (b) Chiappe, C.; Pieraccini, D. *Green Chem.* **2003**, *5*, 193.
2. (a) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708; (b) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675; (c)

Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Herwig, J.; Müller, T. E.; Thiel, O. R. *Chem.—Eur. J.* **1999**, *5*, 1306; (d) Nobis, M.; Driessen-Hölscher, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3983; (e) Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 5608; (f) Ryu, J.-S.; Li, G. Y.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 12584; (g) Utsunomiya, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 2702; (h) Tillack, A.; Jiao, H.; Castro, I. G.; Hartung, C. G.; Beller, M. *Chem.—Eur. J.* **2004**, *10*, 2409; (i) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828.

3. (a) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348; (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609; (c) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133; (d) Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6054; (e) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805; (f) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852; (g) Hartwig, J. F. *Pure Appl. Chem.* **1999**, *71*, 1417; (h) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158; (i) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553; (j) Shekhar, S.; Ryberg, P.; Hartwig, J. F.; Mathew, J. S.; Blackmond, D. G.; Strieter, E. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 3584; (k) Navarro, O.; Marion, N.; Mei, J.; Nolan, S. P. *Chem.—Eur. J.* **2006**, *12*, 5142.
4. (a) Smith, M. B.; March, J. *Advanced Organic Chemistry*, 5th ed.; Wiley: New York, NY, 2001; p 499; (b) Salvatore, R. N.; Nagle, A. S.; Jung, K. W. *J. Org. Chem.* **2002**, *67*, 674; (c) Romera, J. L.; Cid, J. M.; Trabanco, A. A. *Tetrahedron Lett.* **2004**, *45*, 8797. See also Ref. 1.
5. (a) Smith, M. B.; March, J. *Advanced Organic Chemistry*, 5th ed.; Wiley: New York, NY, 2001; p 1187; (b) Bhattacharyya, S. *J. Org. Chem.* **1995**, *60*, 4928; (c) Abdel-Magid, A. F.; Carson, K. G.; Harris, B. D.; Maryanoff, C. A.; Shah, R. D. *J. Org. Chem.* **1996**, *61*, 3849; (d) Mizuta, T.; Sakagushi, S.; Ishii, Y. *J. Org. Chem.* **2005**, *70*, 2195.
6. Trost, B. M. *Science* **1991**, *254*, 1471.
7. (a) Watanabe, Y.; Tsuji, Y.; Ohsugi, Y. *Tetrahedron Lett.* **1981**, *22*, 2667; (b) Arcelli, A.; Khai, B.-T.; Porzi, G. *J. Organomet. Chem.* **1982**, *235*, 93; (c) Murahashi, S.-I.; Kondo, K.; Hakata, T. *Tetrahedron Lett.* **1982**, *23*, 229; (d) Watanabe, Y.; Tsuji, Y.; Ige, H.; Ohsugi, Y.; Ohta, T. *J. Org. Chem.* **1984**, *49*, 3359; (e) Marsella, J. A. *J. Org. Chem.* **1987**, *52*, 467; (f) Jenner, G. *J. Mol. Catal.* **1989**, *55*, 241; (g) Bitsi, G.; Schleiffer, E.; Antoni, F.; Jenner, G. *J. Organomet. Chem.* **1989**, *373*, 343; (h) Ganguly, S.; Roundhill, D. M. *Polyhedron* **1990**, *9*, 2517; (i) Watanabe, Y.; Morisaki, Y.; Kondo, T.; Mitsudo, T. *J. Org. Chem.* **1996**, *61*, 4214; (j) Abbenhuis, R. A. T. M.; Boersma, J.; van Koten, G. *J. Org. Chem.* **1998**, *63*, 4282; (k) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599; (l) Del Zotto, A.; Baratta, W.; Sandri, M.; Verardo, G.; Rigo, P. *Eur. J. Inorg. Chem.* **2004**, 524.
8. Grigg, R.; Mitchell, T. R. B.; Sutthivaiyakit, S.; Tongpenyai, N. *J. Chem. Soc., Chem. Commun.* **1981**, 611.
9. Heterogeneously catalyzed reactions are also known. (a) Valot, F.; Fache, F.; Jacquot, R.; Spagnol, M.; Lemaire, M. *Tetrahedron Lett.* **1999**, *40*, 3689; (b) Narayanan, S.; Deshpande, K. *Appl. Catal., A: General* **2000**, *199*, 1.
10. Williams et al. reported iridium- and ruthenium-catalyzed N-alkylation reactions of amines with alcohols under mild conditions, which proceed sufficiently with the use of equimolar amounts of starting materials. However, only primary amines and primary alcohols can be used in their catalytic system. (a) Cami-Kobeci, G.; Slatford, P. A.; Whittlesey, M. K.; Williams, J. M. J. *Bioorg. Med. Chem. Lett.* **2005**, 535; (b) Hamid, M. H. S. A.; Williams, J. M. J. *Chem. Commun.* **2007**, 725.
11. Quite recently, Beller et al. reported a new ruthenium-catalyzed system for the N-alkylation of primary amines under mild conditions, in which both primary and secondary alcohols can be used. However, excess amounts (5 equiv) of alcohols have to be employed in these reactions. (a) Tillack, A.; Hollmann, D.; Michalik, D.; Beller, M. *Tetrahedron Lett.* **2006**, *47*, 8881; (b) Hollmann, D.; Tillack, A.; Michalik, D.; Jackstell, R.; Beller, M. *Chem. Asian J.* **2007**, *2*, 403.
12. Fujita, K.; Yamaguchi, R. *Synlett* **2005**, 560.
13. (a) Fujita, K.; Furukawa, S.; Yamaguchi, R. *J. Organomet. Chem.* **2002**, *649*, 289; (b) Hanasaka, F.; Fujita, K.; Yamaguchi, R. *Organometallics* **2004**, *23*, 1490; (c) Hanasaka, F.; Fujita, K.; Yamaguchi, R. *Organometallics* **2005**, *24*, 3422.
14. (a) Fujita, K.; Yamamoto, K.; Yamaguchi, R. *Org. Lett.* **2002**, *4*, 2691; (b) Fujita, K.; Fujii, T.; Yamaguchi, R. *Org. Lett.* **2004**, *6*, 3525.
15. Fujita, K.; Asai, C.; Yamaguchi, T.; Hanasaka, F.; Yamaguchi, R. *Org. Lett.* **2005**, *7*, 4017.
16. For a preliminary report, see: Fujita, K.; Li, Z.; Ozeki, N.; Yamaguchi, R. *Tetrahedron Lett.* **2003**, *44*, 2687.
17. Reactions using other catalysts such as $[Cp^*IrHCl]_2$, [IrCl(1,5-cyclopentadiene)]$_2$ and $[Cp^*RhCl_2]_2$ were also carried out. However, these reactions gave inferior results compared to the reactions using $[Cp^*IrCl_2]_2$ as the catalyst. See Ref 16.
18. When the reaction was carried out at 110 °C, the yield was 63%.
19. In the case of the reaction with 1-octanol, a better result was obtained at 90 °C than at 110 °C. When the reaction was carried out at 110 °C, formation of a considerable amount of di-alkylated product (*N*,*N*-dioctylbenzylamine) was observed.
20. We also conducted a competitive reaction using benzylamine (1.0 mmol) and dibenzylamine (1.0 mmol) with 4-chlorobenzyl alcohol (1.0 mmol) in the presence of $[Cp^*IrCl_2]_2$ (1.0 mol % Ir) and $NaHCO_3$ (1.0 mol %) at 110 °C for 17 h. In this reaction, the selective formation of *N*-(4-chlorobenzyl)benzylamine was observed without any formation of *N*-(4-chlorobenzyl)dibenzylamine. This result indicates that the alkylations of primary amines are sufficiently faster than those of secondary amines, which rationalizes the high selectivity for mono-alkylation of primary amines to secondary amines.
21. (a) The reaction of pyrrolidine (1.0 mmol) with 1-octanol (1.0 mmol) gave 65% of 1-octylpyrrolidine; (b) The reaction of dibutylamine (1.0 mmol) with 1-butanol (1.0 mmol) at 110 °C gave 72% of tributylamine.
22. The reaction of benzylamine with chiral secondary alcohol was also carried out: the reaction of benzylamine (1.0 mmol) and (*S*)-1-phenylethanol (1.0 mmol) in the presence of $[Cp^*IrCl_2]_2$ (5.0 mol % Ir) and $NaHCO_3$ (5.0 mol %) at 110 °C for 17 h gave racemic *N*-benzyl-(1-phenylethyl)-amine in 74% isolated yield. The enantiomeric excess of the product was determined to be <1% by chiral HPLC analysis using a Chiralcel OD-H (Daicel) column. This result also supports that the first stage of the catalytic cycle involves the transitory oxidation of alcohols, which causes racemization.
23. It has been reported that the reaction of $[Cp^*IrCl_2]_2$ with an amine results in the formation of mononuclear $Cp^*Ir(amine)Cl_2$. Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.
24. A similar amide–alkoxide exchange reaction for Cp*Ir complexes has been reported by Bergman. Glueck, D. S.; Winslow, L. J. N.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462.
25. In the present reaction, catalytic intermediates would be trivalent iridium species. There are many examples of Cp*Ir-catalyzed hydrogen transfer reactions, in which catalytic intermediates are trivalent iridium species. (a) Suzuki, T.; Yamada, T.; Watanabe, K.; Katoh, T. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 2583; (b) Ogo, S.; Makihara, N.; Watanabe, Y. *Organometallics* **1999**, *18*, 5470; (c) Mashima, K.; Abe, T.; Tani, K. *Chem. Lett.* **1998**, 1201.
26. White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.
27. Xu, L.; Zhu, D.; Wu, F.; Wang, R.; Wan, B. *Tetrahedron* **2005**, *61*, 6553.
28. Beller, M.; Thiel, O. R.; Trauthwein, H.; Hartung, C. G. *Chem.—Eur. J.* **2000**, *6*, 2513.
29. Yokozawa, T.; Asai, T.; Sugi, R.; Ishigooka, S.; Hiraoka, S. *J. Am. Chem. Soc.* **2000**, *122*, 8313.
30. Chen, H.; Farahat, M. S.; Law, K.-Y.; Whitten, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 2584.
31. Khedkar, V.; Tillack, A.; Beller, M. *Org. Lett.* **2003**, *5*, 4767.
32. Zhang, Z.; Mao, J.; Zhu, D.; Wu, F.; Chen, H.; Wan, B. *Tetrahedron* **2006**, *62*, 4435.
33. Barluenga, J.; Bayon, A. M.; Perez-Prieto, J.; Asensio, G. *Tetrahedron* **1984**, *40*, 5053.
34. Frimer, A. A.; Aljadeff, G.; Ziv, J. *J. Org. Chem.* **1983**, *48*, 1700.
35. Schepartz, A.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 1814.
36. Apodaca, R.; Xiao, W. *Org. Lett.* **2001**, *3*, 1745.

37. Heydari, A.; Khaksar, S.; Esfandyari, M.; Tajbakhsh, M. *Tetrahedron* **2007**, *63*, 3363.
38. Cho, B. T.; Kang, S. K. *Tetrahedron* **2005**, *61*, 5725.
39. Cicchi, S.; Bonanni, M.; Cardona, F.; Revuelta, J.; Goti, A. *Org. Lett.* **2003**, *5*, 1773.
40. Yu, Z.; Alesso, S.; Pears, D.; Worthington, P. A.; Luke, R. W. A.; Bradley, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1947.
41. Lopez, R. M.; Fu, G. C. *Tetrahedron* **1997**, *53*, 16349.
42. Blackburn, L.; Taylor, R. J. K. *Org. Lett.* **2001**, *3*, 1637.
43. Almena, J.; Foubelo, F.; Yus, M. *J. Org. Chem.* **1994**, *59*, 3210.
44. Wehn, P. M.; Du Bois, J. *Org. Lett.* **2005**, *7*, 4685.
45. Zhang, M.; Moore, J. D.; Flynn, D. L.; Hanson, P. R. *Org. Lett.* **2004**, *6*, 2657.
46. Bull, S. D.; Davies, S. G.; Fenton, G.; Mulvaney, A. W.; Prasad, R. S.; Smith, A. D. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3765.
47. Berman, A. M.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 5680.
48. Loris, A.; Perosa, A.; Selva, M.; Tundo, P. *J. Org. Chem.* **2004**, *69*, 3953.
49. Wolfe, J. P.; Rennels, R. A.; Buchwald, S. L. *Tetrahedron* **1996**, *52*, 7525.
50. Buwalda, R. T.; Stuart, M. C. A.; Engberts, J. B. F. N. *Langmuir* **2002**, *18*, 6507.
51. Kawakami, T.; Sugimoto, T.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *J. Org. Chem.* **1995**, *60*, 2677.
52. Apice, P. J. *J. Org. Chem.* **1961**, *26*, 261.
53. Glover, S. A.; Warkentin, J. *J. Org. Chem.* **1993**, *58*, 2115.
54. Flaniken, J. M.; Collins, C. J.; Lanz, M.; Singaram, B. *Org. Lett.* **1999**, *1*, 799.