# N-Alkylation of carbamates and amides with alcohols catalyzed by a Cp*Ir complex

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## ARTICLE INFO

## ABSTRACT

New atom-economical catalytic systems consisting of [Cp*IrCl$_2$]$_2$/NaOAc (Cp*=pentamethylcyclopentadienyl) for the N-alkylation of carbamates and amides using alcohols as alkylating agents under solvent-free conditions have been developed. For example, the reaction of $n$-butyl carbamate with benzyl alcohol in the presence of [Cp*IrCl$_2$]$_2$ (5.0 mol% Ir) and NaOAc (5.0 mol%) at 130 °C under the absence of solvent gives $n$-butyl $N$-benzylcarbamate in the yield of 94%. The present catalytic system is applicable to not only carbamates but also amides, and only harmless water is produced as co-product.

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## 1. Introduction

Carbamates are a highly important class of compounds because of their multiple applications as synthetic intermediates for the production of a variety of biologically active compounds.[1] Carbamate moiety can be found in a number of agrochemicals and pharmaceuticals.[2] Therefore, it is quite important to develop efficient methods for the introduction of substituents in carbamates, since those must provide useful protocols for rapid screening of biologically active compounds. Meanwhile, carbamates can be regarded as ammonia equivalents, because the protecting alkoxy carbonyl group on nitrogen can be readily removed by simple procedure.[3] Thus, the N-alkylation on nitrogen in carbamates would lead to an easy access to the synthesis of primary amines.

N-Alkylations of carbamates are usually performed by the reductive amination with carbonyl compounds[4] or the reaction with alkyl halides.[5] However, both of these reactions have some disadvantages from an environmental point of view, because they generate equimolar amounts of wasteful salts as co-products. Additionally, the latter is only applicable for the alkylation of secondary carbamates.

Recently, much attention has been focused on the transition metal-catalyzed N-alkylation reactions using alcohols as alkylating agents based on the catalytic hydrogen transfer.[6–8] Such methodologies using alcohols are apparently attractive because, (1) they do not generate wasteful co-products (water is produced as co-product), (2) alcohols are more readily available compared to other alkylating agents such as alkyl halides and carbonyl compounds in many cases. Several efficient systems for the alkylation of amines[7] or ammonium salts[7k,m] with alcohols have been reported so far. In contrast, there have been only two reports on the catalytic N-alkylation of amides with alcohols, in both of which high reaction temperature (>180 °C) is needed.[9] Furthermore, to the best of our knowledge, the N-alkylation of carbamates with alcohols has not been reported in spite of its importance as described above.

We have recently revealed the high catalytic performance of [Cp*IrCl$_2$]$_2$ (Cp*=pentamethylcyclopentadienyl) in the hydrogen transfer reactions,[6b,d] and developed catalytic systems for the N-alkylation of amines and ammonium salts using alcohols as alkylating agents.[7l,m] We report here the first catalytic system for the N-alkylation of carbamates catalyzed by [Cp*IrCl$_2$]$_2$, which can be conducted without solvent under relatively mild conditions (at 130 °C). The N-alkylation of amides is also demonstrated.

## 2. Results and discussion

Initially, we examined the reactions of $n$-butyl carbamate (**1**) with benzyl alcohol (**2a**) under various conditions. The results are summarized in Table 1. When the reaction of **1** (1.0 mmol) and **2a** (2.0 mmol) was carried out in the presence of [Cp*IrCl$_2$]$_2$ (5.0 mol% Ir) at 130 °C for 17 h, $n$-butyl $N$-benzylcarbamate **3a** was formed in 57% yield (entry 1). The reaction was selective for mono-alkylation; no dialkylated product was observed. Other catalysts, [IrCl(cod)]$_2$,

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**Table 1**
N-Alkylation of n-butyl carbamate (**1**) with benzyl alcohol (**2a**) under various conditions[a]



| Entry | Catalyst | Base | Temp (°C) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | [Cp*IrCl₂]₂ | None | 130 | 57 (46[c]) |
| 2 | [IrCl(cod)]₂ | None | 130 | Trace |
| 3 | [Cp*RhCl₂]₂ | None | 130 | Trace |
| 4 | RuCl₂(PPh₃)₃ | None | 130 | 17 |
| 5 | [Cp*IrCl₂]₂ | NaHCO₃ | 130 | 72 |
| 6 | [Cp*IrCl₂]₂ | t-BuONa | 130 | 71 |
| 7 | [Cp*IrCl₂]₂ | NaOAc | 130 | 78 |
| 8 | [Cp*IrCl₂]₂ | NaOAc | 120 | 59 |
| 9 | [Cp*IrCl₂]₂ | NaOAc | 140 | 46 |
| 10[d] | [Cp*IrCl₂]₂ | NaOAc | 130 | 94 |

[a] The reaction was carried out with **1** (1.0 mmol), **2a** (2.0 mmol), catalyst (5.0 mol % metal), and base (5.0 mol %) for 17 h.
[b] Determined by GC.
[c] Isolated yield.
[d] 4.0 mmol of **2a** was used.

[Cp*RhCl₂]₂, and RuCl₂(PPh₃)₃, which have been used as catalysts in hydrogen transfer reactions, showed inferior activity for the present reaction at 130 °C (entries 2–4). The reaction was considerably accelerated by the addition of a base. When the reaction was carried out in the presence of NaHCO₃ (5.0 mol %), the yield of **3a** was improved to 72% (entry 5). Stronger base (t-BuONa) was also effective (entry 6). We finally found that NaOAc was the base of choice, and the yield of **3a** was increased up to 78% (entry 7). The optimum reaction temperature was 130 °C; the reactions at lower (120 °C) or higher (140 °C) temperatures resulted in the lower yields (entries 8 and 9). An excellent yield of **3a** (94%) was obtained by the reaction using 4 equiv of **2a** (entry 10).[10]

On the basis of the optimization of the reaction conditions, the N-alkylation reactions of **1** with various primary alcohols were conducted. The results are summarized in Table 2. The reactions with benzyl alcohols bearing electron-donating (**2b,c**) and electron-withdrawing (**2d–h**) substituents at the aromatic ring proceeded to give the corresponding products (**3b–h**) in moderate to good yields (entries 2–8), although the higher catalyst loadings (10 mol % Ir) were required in some cases (entries 5, 6, and 8). Chloro- and bromo-substituents were tolerant in this catalytic system, which is promising for further transformation of the products. Other aromatic alcohols such as 2-naphthylmethanol (**2i**) and 2-pyridylmethanol (**2j**), and an aliphatic alcohol such as 1-butanol (**2k**) could be also used as alkylating agents (entries 9–11). We also carried out the reaction of methyl carbamate (**4**) with **2a**, which gave methyl N-benzylcarbamate (**5a**) in 46% yield (entry 12).[11] The reactions of **1** with secondary alcohols (1-phenylethanol, 1-phenyl-2-propanol, and 2-butanol) were also attempted, but the alkylation did not proceed in such reactions.

The n-butoxycarbonyl moiety in the N-alkylated n-butyl carbamate could be easily removed by simply refluxing in MeOH/H₂O under the basic condition (Eq. 1). Thus, n-butyl carbamate (**1**) can be regarded as an ammonia equivalent, and the present catalytic system provides a new protocol for the transformation of an alcohol to a primary amine.



(1)
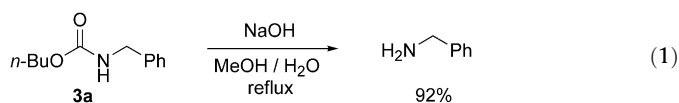
We next studied the N-alkylation of amides (**6** and **7**) with alcohols. The results are summarized in Table 3.[11] When the reaction

**Table 2**
N-Alkylation of n-butyl carbamate (**1**) and methyl carbamate (**4**) with various alcohols[a]



| Entry | Carbamate | Alcohol | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 | R¹=n-Bu (**1**) | **2a** | **3a** | 87 (94[c]) |
| 2 | R¹=n-Bu (**1**) | **2b** | **3b** | 92 |
| 3 | R¹=n-Bu (**1**) | **2c** | **3c** | 67 |
| 4 | R¹=n-Bu (**1**) | **2d** | **3d** | 55 |
| 5[d] | R¹=n-Bu (**1**) | **2e** | **3e** | 67 |
| 6[d] | R¹=n-Bu (**1**) | **2f** | **3f** | 58 |
| 7 | R¹=n-Bu (**1**) | **2g** | **3g** | 53 |
| 8[d] | R¹=n-Bu (**1**) | **2h** | **3h** | 57 |
| 9 | R¹=n-Bu (**1**) | **2i** | **3i** | 69 |
| 10[d] | R¹=n-Bu (**1**) | **2j** | **3j** | 50 |
| 11[d] | R¹=n-Bu (**1**) | **2k** | **3k** | 65 |
| 12 | R¹=Me (**4**) | **2a** | **5a** | 46 |

[a] The reaction was carried out with carbamate (1.0 mmol), alcohol (4.0 mmol), [Cp*IrCl₂]₂ (5.0 mol % Ir), and NaOAc (5.0 mol %) at 130 °C for 17 h.
[b] Isolated yield.
[c] GC yield.
[d] [Cp*IrCl₂]₂ (10 mol % Ir) and NaOAc (10 mol %) were used.

of benzamide (**6**) with benzyl alcohol (**2a**) was conducted in the presence of [Cp*IrCl₂]₂ (5.0 mol % Ir) and NaOAc (5.0 mol %) at 130 °C for 17 h, N-benzylbenzamide (**8a**) was obtained in the isolated yield of 81% (entry 1). The reaction of **6** with 4′-methylbenzyl alcohol (**2b**) also gave **8b** in excellent yield (entry 2). Other benzyl alcohols bearing electron-donating and electron-withdrawing substituent (**2c** and **2d**) could be also used as alkylating agents (entries 3 and 4). Similar reactions of **6** with aliphatic primary alcohols such as 1-butanol (**2k**), 1-hexanol (**2l**), and 3-methyl-1-butanol (**2m**) also proceeded to give the corresponding N-alkylated benzamides in moderate to high yields (entries 5–7). The reactions of acetamide (**7**) with **2a** and **2b** were also carried out. The products

**Table 3**
N-Alkylation of benzamide (**6**) and acetamide (**7**) with various alcohols[a]



| Entry | Carbamate | Alcohol | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 | R$^1$=Ph (**6**) | **2a** | **8a** | 81 |
| 2 | R$^1$=Ph (**6**) | **2b** | **8b** | 91 |
| 3 | R$^1$=Ph (**6**) | MeO 〜 **2c** | **8c** | 59 |
| 4[c] | R$^1$=Ph (**6**) | Cl 〜 **2d** | **8d** | 67 |
| 5 | R$^1$=Ph (**6**) | **2k** | **8k** | 82 |
| 6 | R$^1$=Ph (**6**) | **2l** | **8l** | 66 |
| 7 | R$^1$=Ph (**6**) | **2m** | **8m** | 70 |
| 8 | R$^1$=Me (**7**) | **2a** | **9a** | 64 |
| 9 | R$^1$=Me (**7**) | **2b** | **9b** | 66 |

[a] The reaction was carried out with amide (1.0 mmol), alcohol (4.0 mmol), [Cp*IrCl$_2$]$_2$ (5.0 mol % Ir), and NaOAc (5.0 mol %) at 130 °C for 17 h.
[b] Isolated yield.
[c] [Cp*IrCl$_2$]$_2$ (10 mol % Ir) and NaOAc (10 mol %) were used.

**9a** and **9b** were obtained in 64 and 66% yield, respectively (entries 8 and 9), which were slightly lower than those in the corresponding reactions of **6**.

Although the mechanism for the present reaction is not completely clear yet, a possible reaction pathway is shown in Scheme 1. A similar reaction mechanism has been proposed for the ruthenium-catalyzed N-alkylation of amides with alcohols by Watanabe et al.[9a,12] The first step of the reaction would involve the hydrogen transfer oxidation of a primary alcohol through an alkoxo iridium species **A** to the corresponding aldehyde **B** accompanied by the formation of a hydrido iridium species **C**.[13] Then, the condensation of the aldehyde **B** with a carbamate or an amide would occur to afford an N-acyl imine **D**.[14] Addition of the hydrido iridium **C** to a carbon–nitrogen double bond of **D** would occur to give an amido iridium species **E**. The species **E** would react with an alcohol to give the product and regenerate the catalytically active alkoxo iridium species **A**. The base (NaOAc) would stimulate the formation of the alkoxo iridium species **A** by trapping hydrogen chloride generated at the first step of the reaction.

To support the proposed reaction pathway shown above, the transfer hydrogenation of N-benzylidenebenzamide **10** (this corresponds to the possible intermediate **D**) using an alcohol as a hydrogen source was carried out. When the reaction of **10** with 3 equiv of 2-propanol was conducted in the presence of [Cp*IrCl$_2$]$_2$
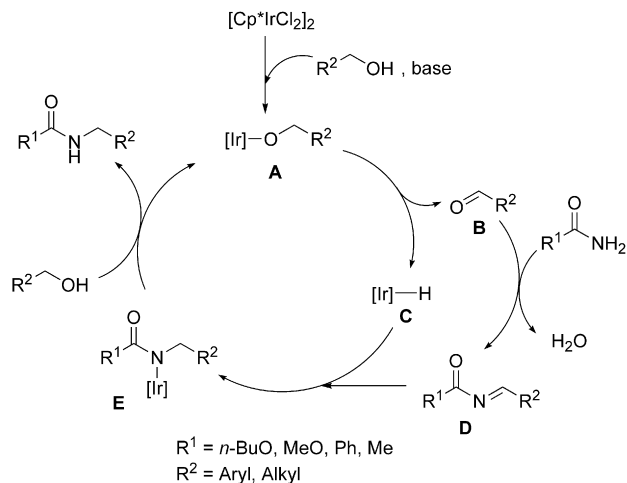


**Scheme 1.**

(5.0 mol % Ir) and NaOAc (5.0 mol %) in toluene at 130 °C for 17 h, N-benzylbenzamide (**8a**) was formed in 78% yield (Eq. 2). This result indicates that the iminic species **D** would be incorporated in the catalytic cycle, supporting the proposed reaction pathway.
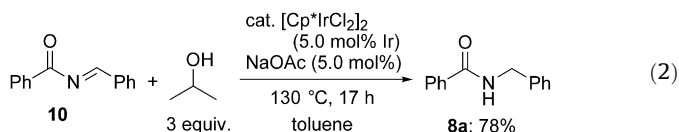


In summary, we have developed new atom-economical catalytic systems for the N-alkylation of carbamates and amides using alcohols as alkylating agents under solvent-free conditions. The present study is, to the best of our knowledge, the first example of the N-alkylation of carbamates with alcohols. Additionally, the N-alkylation of amides were also achieved under relatively mild conditions (at 130 °C) compared to the known systems catalyzed by ruthenium.

## 3. Experimental section

### 3.1. General

All reactions and manipulations were carried out under an atmosphere of argon by means of standard Schlenk techniques. $^1$H 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). Column chromatography was carried out by using Wako-gel C-200. 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.[15] All other reagents are commercially available and were used as received.

### 3.2. Optimization of the reaction of n-butyl carbamate (1) with benzyl alcohol (2a) (Table 1)

In a heavy-walled glass reactor under an atmosphere of argon were placed the catalyst (5.0 mol % metal), base (5.0 mol %), **1** (1.0 mmol), and **2a** (2.0 mmol). The mixture was stirred at 130 °C for 17 h in the sealed reactor. The yield of n-butyl N-benzylcarbamate (**3a**) was determined by GC analysis using undecane as an internal standard.

## 3.3. N-Alkylation of carbamates with various alcohols (Table 2)

In a heavy-walled glass reactor under an atmosphere of argon were placed [Cp*IrCl₂]₂ (0.025 mmol, 5.0 mol % Ir), NaOAc (0.050 mmol, 5.0 mol %), carbamate **1** or **4** (1.0 mmol), and alcohol (4.0 mmol). The mixture was stirred at 130 °C for 17 h in the sealed reactor. After cooled to room temperature, the products were isolated by column chromatography (eluent: hexane/ethyl acetate). The products **3a**,[16] **3k**,[17] and **5a**[18] were known compounds, which were identified by spectral comparison with literature data. The NMR and elemental analysis data of other products are as follows.

### 3.3.1. n-Butyl N-(4′-methylbenzyl)carbamate (3b)

$^1$H NMR (CDCl₃) δ 7.24–7.10 (m, 4H, aromatic), 5.06 (br s, 1H, NH), 4.29 (d, J=6 Hz, 2H, NCH₂), 4.07 (t, J=7 Hz, 2H, OCH₂), 2.32 (s, 3H, Me), 1.58 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.92 (t, J=8 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 156.6, 136.9, 135.5, 129.1, 127.3, 64.8, 44.7, 31.1, 21.1, 19.1, 13.8. Anal. Calcd for C₁₃H₁₉NO₂: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.81; H, 8.50; N, 6.25.

### 3.3.2. n-Butyl N-(3′-methoxylbenzyl)carbamate (3c)

$^1$H NMR (CDCl₃) δ 7.24 (t, J=8 Hz, 1H, aromatic), 6.88–6.79 (m, 3H, aromatic), 5.05 (br s, 1H, NH), 4.33 (d, J=6 Hz, 2H, NCH₂), 4.09 (t, J=7 Hz, 2H, OCH₂), 3.79 (s, 3H, OMe), 1.61 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.92 (t, J=7 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 159.8, 156.8, 140.2, 129.6, 119.6, 113.0, 112.8, 64.9, 55.1, 44.9, 31.0, 19.0, 13.7. Anal. Calcd for C₁₃H₁₉NO₃: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.97; H, 7.94; N, 5.77.

### 3.3.3. n-Butyl N-(4′-chlorobenzyl)carbamate (3d)

$^1$H NMR (CDCl₃) δ 7.30–7.19 (m, 4H, aromatic), 5.14 (br s, 1H, NH), 4.30 (d, J=6 Hz, 2H, NCH₂), 4.07 (t, J=7 Hz, 2H, OCH₂), 1.61 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.92 (t, J=7 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 156.6, 137.1, 133.0, 128.65, 128.55, 65.0, 44.3, 31.1, 19.1, 13.8. Anal. Calcd for C₁₂H₁₆ClNO₂: C, 59.63; H, 6.67; N, 5.79. Found: C, 59.58; H, 6.47; N, 5.73.

### 3.3.4. n-Butyl N-(3′-chlorobenzyl)carbamate (3e)

$^1$H NMR (CDCl₃) δ 7.27–7.16 (m, 4H, aromatic), 5.20 (br s, 1H, NH), 4.32 (d, J=6 Hz, 2H, NCH₂), 4.08 (t, J=7 Hz, 2H, OCH₂), 1.59 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.92 (t, J=7 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 156.6, 140.7, 134.3, 129.7, 127.4, 127.3, 125.4, 65.0, 44.4, 31.0, 19.1, 13.8. Anal. Calcd for C₁₂H₁₆ClNO₂: C, 59.63; H, 6.67; N, 5.79. Found: C, 59.56; H, 6.66; N, 5.80.

### 3.3.5. n-Butyl N-(3′,4′-dichlorobenzyl)carbamate (3f)

$^1$H NMR (CDCl₃) δ 7.39–7.10 (m, 3H, aromatic), 5.15 (br s, 1H, NH), 4.30 (d, J=6 Hz, 2H, NCH₂), 4.08 (t, J=7 Hz, 2H, OCH₂), 1.61 (m, 2H, CH₂), 1.38 (m, 2H, CH₂), 0.93 (t, J=7 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 156.6, 139.1, 132.6, 131.3, 130.5, 129.2, 126.7, 65.1, 43.8, 31.0, 19.0, 13.7. Anal. Calcd for C₁₂H₁₅Cl₂NO₂: C, 52.19; H, 5.47; N, 5.07. Found: C, 52.16; H, 5.37; N, 5.02.

### 3.3.6. n-Butyl N-(4′-bromobenzyl)carbamate (3g)

$^1$H NMR (CDCl₃) δ 7.43 (d, J=8 Hz, 2H, aromatic), 7.16 (d, J=8 Hz, 2H, aromatic), 5.02 (br s, 1H, NH), 4.30 (d, J=6 Hz, 2H, NCH₂), 4.08 (t, J=6 Hz, 2H, OCH₂), 1.62 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.92 (t, J=7 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 156.6, 137.6, 131.6, 129.0, 121.1, 65.0, 44.4, 31.1, 19.1, 13.8. Anal. Calcd for C₁₂H₁₆BrNO₂: C, 50.37; H, 5.64; N, 4.89. Found: C, 50.56; H, 5.52; N, 4.92.

### 3.3.7. n-Butyl N-(3′-bromobenzyl)carbamate (3h)

$^1$H NMR (CDCl₃) δ 7.43–7.37 (m, 2H, aromatic), 7.27–7.18 (m, 2H, aromatic), 5.14 (br s, 1H, NH), 4.32 (d, J=5 Hz, 2H, NCH₂), 4.09 (t, J=8 Hz, 2H, OCH₂), 1.61 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.93 (t, J=8 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 156.8, 141.0, 130.4, 130.3, 130.1, 126.0, 122.6, 65.0, 44.3, 30.1, 19.0, 13.7. Anal. Calcd for C₁₂H₁₆BrNO₂: C, 50.37; H, 5.64; N, 4.89. Found: C, 51.06; H, 5.69; N, 4.84.

### 3.3.8. n-Butyl N-(2-naphthylmethyl)carbamate (3i)

$^1$H NMR (CDCl₃) δ 7.82–7.70 (m, 3H, aromatic), 7.70 (s, 1H, aromatic), 7.48–7.38 (m, 3H, aromatic), 5.08 (br s, 1H, NH), 4.51 (d, J=5 Hz, 2H, NCH₂), 4.11 (t, J=8 Hz, 2H, OCH₂), 1.63 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.93 (t, J=8 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 156.8, 136.0, 133.3, 132.7, 128.4, 127.7, 127.6, 126.2, 126.0, 125.8, 125.7, 65.0, 45.2, 31.1, 19.0, 13.7. Anal. Calcd for C₁₆H₁₉NO₂: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.70; H, 7.51; N, 5.35.

### 3.3.9. n-Butyl N-(2-pyridylmethyl)carbamate (3j)

$^1$H NMR (CDCl₃) δ 8.53 (d, J=5 Hz, 1H, aromatic), 7.69–7.63 (m, 1H, aromatic), 7.29 (d, J=8 Hz, 1H, aromatic), 7.20–7.16 (m, 1H, aromatic), 5.96 (br s, 1H, NH), 4.49 (d, J=6 Hz, 2H, NCH₂), 4.09 (t, J=6 Hz, 2H, OCH₂), 1.61 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 0.92 (t, J=7 Hz, 3H, CH₃). $^{13}$C NMR (CDCl₃) δ 157.2, 156.9, 149.0, 136.7, 122.2, 121.7, 64.8, 45.9, 31.0, 19.0, 13.6. Anal. Calcd for C₁₁H₁₆N₂O₂: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.14; H, 7.53; N, 13.31.

## 3.4. Conversion of n-butyl N-benzylcarbamate (3a) to benzylamine (Eq. 1)

In a flask, **3a** (227.2 mg, 1.096 mmol), NaOH (991.2 mg, 24.8 mmol), methanol (3.0 mL), and water (3.0 mL) were placed. The mixture was heated under reflux for 41 h. After cooled to room temperature, the product was extracted with dichloromethane. The yield of benzylamine was determined by GC analysis using undecane as an internal standard.

## 3.5. N-Alkylation of amides with various alcohols (Table 3)

In a heavy-walled glass reactor under an atmosphere of argon were placed [Cp*IrCl₂]₂ (0.025 mmol, 5.0 mol % Ir), NaOAc (0.050 mmol, 5.0 mol %), amide **6** or **7** (1.0 mmol), and alcohol (4.0 mmol). The mixture was stirred at 130 °C for 17 h in the sealed reactor. After cooled to room temperature, the products were isolated by column chromatography (eluent: hexane/ethyl acetate). The products **8a**,[19] **8b**,[20] **8d**,[21] **8k**,[22] **8l**,[9a] **8m**,[23] **9a**,[24] and **9b**[25] were known compounds, which were identified by spectral comparison with literature data. The NMR data of **8c**[26] are as follows.

### 3.5.1. N-(3′-Methoxylbenzyl)benzamide (8c)

$^1$H NMR (CDCl₃) δ 7.78 (d, J=7 Hz, 2H, aromatic), 7.51–7.37 (m, 3H, aromatic), 7.25 (t, J=8 Hz, 1H, aromatic), 6.93–6.81 (m, 3H, aromatic), 6.62 (br s, 1H, NH), 4.59 (d, J=6 Hz, 2H, CH₂), 3.78 (s, 3H, OMe). $^{13}$C NMR (CDCl₃) δ 167.3, 159.9, 139.8, 134.3, 131.5, 129.7, 128.5, 126.9, 120.0, 113.4, 112.9, 55.2, 44.0. Anal. Calcd for C₁₅H₁₅NO₂: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.55; H, 6.32; N, 5.66.

## 3.6. Preparation of N-benzylidenebenzamide (10)

In a flask, benzamide (2.03 g, 16.8 mmol), PhSO₂Na (5.54 g, 33.7 mmol), methanol (16 mL), and water (32 mL) were placed. Benzaldehyde (3 mL) was then added in one portion, followed by formic acid (1.3 mL). The mixture was stirred at 50 °C for 120 h. The precipitate was isolated by Büchner funnel filtration and purified by washing with water. Then, the white solid was transferred to a flask, K₂CO₃ (1.89 g, 13.7 mmol), Na₂SO₄ (2.29 g, 16.1 mmol), and toluene (30 mL) were added. The mixture was heated under reflux for 15 h. After the mixture was filtered through a pad of Celite and evaporation of the filtrate gave **10** (161.7 mg, 0.7730 mmol, 4.6%).

$^{1}$H NMR (CDCl$_3$) $\delta$ 8.77 (s, 1H, iminic CH), 8.17 (d, $J$=7 Hz, 2H, aromatic), 7.97 (d, $J$=7 Hz, 2H, aromatic), 7.59–7.45 (m, 6H, aromatic). $^{13}$C NMR (CDCl$_3$) $\delta$ 180.9, 164.5, 134.6, 133.5, 133.4, 133.3, 130.1, 130.0, 129.0, 128.5.

### 3.7. Transfer hydrogenation of 10 catalyzed by [Cp*IrCl$_2$]$_2$ (Eq. 2)

In a heavy-walled glass reactor under an atmosphere of argon were placed [Cp*IrCl$_2$]$_2$ (14.4 mg, 0.0181 mmol, 5.0 mol % Ir), NaOAc (3.0 mg, 0.0366 mmol, 5.0 mol %), **10** (150.7 mg, 0.7202 mmol), 2-propanol (128.1 mg, 2.131 mmol, 3 equiv), and toluene (1.0 mL). The mixture was stirred at 130 °C for 17 h in the sealed reactor. The yield of **8a** was determined by GC analysis using undecane as an internal standard.

### Acknowledgements

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