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# A novel aminomethylation reaction of gaseous alkanes with tert-methylamine *N*-oxides via C–H bond activation by copper(II) salts

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**Abstract**

The $Cu(OAc)_2/CF_3COOH$ (TFA) system catalyzes the aminomethylation of gaseous alkanes such as propane and ethane with trimethylamine *N*-oxide to give *N,N*-dimethylisobutylamine (**1**) and *N,N*-dimethylpropylamine (**7**), respectively. The corresponding trifluoroacetates are also formed as by-products from the reactions of methane and propane.

*Keywords:* Copper acetate; Aminomethylation; Amine *N*-oxide; C–H bond activation; C–C bond formation; Alkane

## 1. Introduction

One of the most important and challenging problems in modern chemistry is the activation of the C–H bond by transition metal complexes [1]. In 1967, we reported the palladium-catalyzed reaction of olefins with aromatic compounds to give aromatic substituted olefins [2,3]. The substitution proceeds via an Ar–PdL $\sigma$-complex intermediate, which is derived from direct thermal activation of a C–H aromatic bond by electrophilic substitution by Pd(II). The Ar–PdL $\sigma$-complex can react with CO and $O_2$ to give carboxylic acids [4] and phenols [5], respectively. Unreactive C–H bonds of saturated hydrocarbons can be also activated by transition metal complexes. We have reported that the $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8/$ trifluoroacetic acid (TFA) system can cause the carboxylation of alkanes such as cyclohexane, propane, ethane, and methane to give the corresponding alkanoic acids in high yields [6]. Furthermore, we also developed the $NiCl_2$-catalyzed ethylation of a cycloalkane with ethylene [7]. These reactions serve as novel C–C bond forming reactions via the alkane C–H bond activation by transition metal complexes. Although carbon–oxygen bond forming reactions to afford ketones, alcohols and esters from hydrocarbons by using various oxidants have been extensively studied [1,8,9], little is known about C–C bond forming reactions [10]. Recently, the mercury-photosensitized amination of alkanes have been reported by Crabtree et al. and a trace amount of aminomethylated product was obtained as a by-product [11]. In continuing studies on exploring synthetic reactions via thermal activation of alkane C–H bonds by transition metals, we have found that trimethylamine *N*-oxides react with alkanes such as ethane and propane in the presence of a catalytic amount of $Cu(OAc)_2$, giving the corresponding aminomethylated products.

Herein we report a novel reaction of tert-methylamine *N*-oxides with gaseous alkanes such as ethane and propane in the presence of a catalytic amount of $Cu(OAc)_2$ to afford the corresponding aminomethylated alkanes and esters (Eq. (1)).

$$C_nH_{2n+2} + CH_3R_2N \rightarrow O \xrightarrow[CF_3COOH]{Cu(OAc)_2cat} C_nH_{2n+1}CH_2NR_2 + H_2O \quad (1)$$

## 2. Results and discussion

First, we examined the reaction of propane (10 atm in an autoclave; 41 mmol) with anhydrous trimethylamine *N*-oxide (5 mmol) and $K_2S_2O_8$ in TFA (5 ml)

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Table 1
Reaction of propane with $(CH_3)_3NO$ by the $Cu(OAc)_2$ [a]

| Entry | Catalyst (0.05 mmol) | $K_2S_2O_8$ (mmol) | Products and yield (%) [b] | |
|---|---|---|---|---|
| | | | 1 | 2 |
| 1 | none | 9.0 | – (3.0) [c] | – (7.3) |
| 2 | $Cu(OAc)_2$ | 9.0 | 1020 (10.2) | 3140 (31.4) |
| 3 | $Pd(OAc)_2$ | 9.0 | 360 (3.6) | 440 (4.4) |
| 4 | $Cu(OAc)_2$ /$Pd(OAc)_2$ [d] | 9.0 | 920 (9.2) | 300 (3.0) |
| 5 | $CuCl_2$ | 9.0 | 540 (5.4) | 1500 (15.0) |
| 6 | CuCl | 9.0 | 520 (5.2) | 800 (8.0) |
| 7 | $CuSO_4$ | 9.0 | 720 (7.2) | 1860 (18.6) |
| 8 | Cu powder | 9.0 | 900 (9.0) | 1140 (11.4) |
| 9 | $Cu(OAc)_2$ | none | 740 (7.4) | 6200 (62.0) |
| 10 | $Cu(OAc)_2$ | 0.5 | 860 (8.6) | 580 (5.8) |
| 11 | $Cu(OAc)_2$ | 1.0 | 1400 (14.0) | 520 (5.2) |
| 12 | $Cu(OAc)_2$ | 3.0 | 1320 (13.2) | 1440 (14.4) |
| 13 | $Cu(OAc)_2$ | 5.0 | 1060 (10.6) | 1020 (10.2) |
| 14 | $Cu(OAc)_2$ | 7.0 | 1160 (11.6) | 1280 (12.8) |

[a] Reaction conditions: $C_3H_8$ (10 atm), $(CH_3)_3NO$ (5.0 mmol), catalyst (0.05 mmol), TFA (5 ml), 150 °C, 20 h.
[b] $^1$H-NMR yield based on catalyst. Numbers in parentheses are the yields based on $(CH_3)_3NO$.
[c] *N,N*-Dimethylbutylamine (**3**) was also formed in 3.0% yield.
[d] 0.05 mmol each.

using various copper and palladium salts (0.05 mmol) at 150 °C for 20 h (Eq. (2)), and the results are summarized in Table 1. As is apparent from the table, the

$$C_3H_8 + (CH_3)_3N \rightarrow O + CF_3COOH \xrightarrow{Cu(OAc)_2 cat} \underset{\mathbf{1}}{(CH_3)_2CHCH_d2N(CH_3)_2} + \underset{\mathbf{2}}{(CH_3)_2CHOCOCF_3} + (CH_3)_3N + H_2O \quad (2)$$

$Cu(OAc)_2/K_2S_2O_8$/TFA system gives the highest yield of aminomethylated product **1**. The reaction proceeded catalytically to give *N,N*-di-methylisobutylamine (**1**) and isopropyl trifluoroacetate (**2**) along with large amounts of trimethylamine. In this copper-catalyzed reaction of propane with trimethylamine *N*-oxide, *N,N*-dimethylbutylamine (**3**) was not obtained. In the absence of the copper salt, the products **1**, **2** and **3** were formed in 3.0, 7.3 and 3.0% yields based on trimethylamine *N*-oxide, respectively (entry 1). The similar formation of ester **2** from gaseous alkanes was reported by Sen et al. [9a,b] and Moiseev et al. [9f]. Of the catalysts tested, $Cu(OAc)_2$ is the best, giving **1** and **2** in 1020 and 3140% yields based on Cu, respectively (entry 2). When the amount of $Cu(OAc)_2$ is increased from 0.05 mmol to 0.5 mmol, the yields of **1** and **2** decrease to 40 and 98% yields based on Cu, respectively. $Pd(OAc)_2$ alone and $Cu(OAc)_2/Pd(OAc)_2$ mixed catalysts have lower catalytic activity (entries 3 and 4). Addition of a small amount of $K_2S_2O_8$ (1 mmol) gave the best result for the yield of **1** (1400% on Cu) with the highest selectivity (**1**/**2**), and addition of larger amounts of $K_2S_2O_8$ had no effect on yields of the products (entries 12–14). In the absence of $K_2S_2O_8$ the yield of **2** goes up to 62.0% based on trimethylamine *N*-oxide, but the yield of aninomethylated product **1** is very low (entry 9). Use of $KHSO_4$ (or $K_2SO_4$) (1 mmol) instead of $K_2S_2O_8$ under the conditions of entry 11 in the table also decreased the yield of ester **2** to 940% (640%) along with amine **1** in 1100% (740%) yield. Thus, esterification of propane to **2** with trimethylamine *N*-oxide in TFA was retarded by an addition of pottasium salts such as $K_2S_2O_8$, $KHSO_4$, and $K_2SO_4$. As a result of the suppression of the side reaction by pottasium salts, the yield of amine **1** seems to increase moderately.

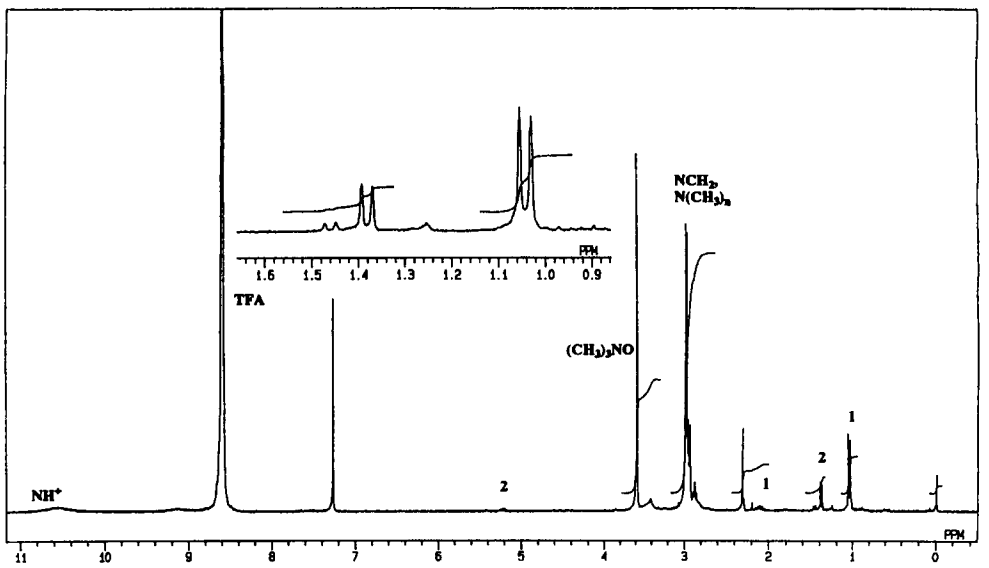


Fig. 1. $Cu(OAc)_2$-catalyzed reaction of propane with trimethylamine *N*-oxide.

The amine *N*-oxide has two roles: one is to form the Mannich base [12], and the other is to oxidize propane to give ester **2** and trimethylamine.

The solvent effect was also examined, and it was found that the use of formic, acetic and hydochloric acids resulted in no reaction. Trifluoroacetic acid (TFA) is the best solvent for the reaction of propane. From these results, the best reaction conditions are determined to be 150 °C for 20 h under 10 atm $C_3H_8$ for the aminomethylation of propane. In order to investigate the reaction mechanism, we performed the reaction with the use of a radical scavenger. The reaction conducted under the conditions of entry 11 of the table was retarded by an addition of 4-tert-butylcatechol (1.1 mmol); the yields of **1** and **2** decreased to 320 and 260% on Cu, respectively.

A control experiment using amine **1** in the absence of propane under similar conditions resulted in no reaction. Generally, the C–H bonds of methylamine *N*-oxides and methylamines are stabilized by the neighboring nitrogen atom and they are transformed to *N*-hydroxyammonium and ammonium salts, respectively, by protonation with TFA. These ammonium salts would not be attacked by the catalyst because of the electrostatic and/or the steric effects.

In addition to trimethylamine *N*-oxide, other tertiary methylamine *N*-oxides such as *N*-methylpiperidine, *N*-methylpyrroridine and *N*-methylmorpholine *N*-oxides were found to react with propane to afford the corresponding *N*-isobutyl-piperidine (**4**), -pyrrolidine (**5**) and -morpholine (**6**) in 660, 180 and 28% yields based on Cu, respectively. Regioselectivity for aminomethylation exclusively on the *N*-methyl group of amine *N*-oxide was observed.

Fig. 1 shows the $^1$H NMR spectrum of the reaction mixture of propane with trimethylamine *N*-oxide. For amine **1**, the doublet at $\delta = 1.04$ and the septet at 2.10 are assigned as methyl and methyne protons of the isobutyl group, respectively. Signals at 2.8–3.1 are assignable as methyl and methylene groups of **1** and large amounts of trimethylamine. Signals of the doublet at 1.38 and the septet at 5.21 are assignable as the isopropyl group of ester **2**. The spectra of these products were in fair agreement with those of the authentic samples. Furthermore, the spectrum shows that the reaction is clean and no other by-products are formed.

Ethane also reacts with trimethylamine *N*-oxide, giving *N, N*-dimethylpropylamine (**7**) exclusively without the formation of ethyl trifluoroacetate. For example, the reaction of trimethylamine *N*-oxide (5 mmol) with ethane (10 atm) in the presence of a catalytic amount of $Cu(OAc)_2$ (0.05 mmol) in TFA (5 ml) at 150 °C for 20 h gave *N,N*-dimethylpropylamine (**7**) in 1460% yield based on Cu (14.6% on amine *N*-oxide) as sole product. The similar reaction of *N*-methylpiperidine *N*-oxide with ethane under these conditions also takes place to give *N*-*n*-propylpiperidine (**8**) in 340% yield based on Cu. In these reactions of ethane, an addition of $K_2S_2O_8$ had no effect on the yield of products.

Methane is the least reactive alkane, but one of the most abundant, and so selective conversion to useful chemical products is very valuable [6d–g]. However, this is difficult to achieve because of its low reactivity. We tried the reaction of methane (40 atm) with trimethylamine *N*-oxide (5.0 mmol) and $K_2S_2O_8$ (9 mmol) in the presence of $Cu(OAc)_2$ (0.05 mmol) in TFA (5 ml) at 150 °C for 20 h (Eq. (3)). From the reaction, methyl trifluoroacetate (9) was obtained in 760% yield based

$$CH_4 + CF_3COOH \xrightarrow[K_2S_2O_8]{Cu(OAc)_2cat} \underset{\mathbf{9}}{CH_3OCOCF_3} \qquad (3)$$

on $Cu(OAc)_2$ as sole product without the formation of *N,N*-dimethylethylamine. In the absence of $K_2S_2O_8$, the esterification did not occur. For the production of **9**, trimethylamine *N*-oxide is not necessary. The presence of $K_2S_2O_8$ acting as reoxidant of the catalyst is essential. In the aminomethylation of other alkanes such as propane and ethane, the methyl ester **9** was not observed. Therefore, it is clear that the methyl group of ester **9** is not derived from trimethylamine *N*-oxide but from methane.

Although the details of the mechanism of copper(II)-catalyzed reaction are not yet clear, the reaction would proceed via an alkylcopper species and the Mannich bases generated from methylamine *N*-oxides and TFA [12] as intermediates.

## 3. Experimental section

### 3.1. General

Analytical GLC evaluations of product mixtures were performed on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector by using a 5 m × 3.2 mm $\phi$ glass column packed with a 5% Silicone OV-17 on 60–80 mesh Chromosorb W with an injection temperature of 280 °C and detector temperature of 280 °C. Mass spectra were obtained on a Shimadzu GC-MS QP-1000 by using a 5 m × 3.2 mm $\phi$ glass column packed with a 5% Silicone OV-17 on 60–80 mesh Chromosorb W. IR spectra were recorded on a Perkin-Elmer 1600-FTIR spectrophotometer. $^1$H-NMR spectra were obtained on JEOL JNM-FX-90A and JEOL JNM-FX-270 spectrometers; chemical shifts ($\delta$) were expressed in parts per million downfield from sodium 3-(trimethylsilyl)propanesulfonate (DSS).

### 3.2. Materials

Commercial trimethylamine *N*-oxide hydrate was dried at 120 °C for 1 h under reduced pressure (1

mmHg) prior to use. The authentic *N,N*-dimethylisobutylamine (**1**), *N,N*-dimethylbutylamine (**3**) and *N,N*-dimethylpropylamine (**7**) were prepared by the literature procedure [13]. *N*-Isobutylpiperidine (**4**), *N*-isobutylpyrrolidine (**5**), *N*-isobutylmorpholine (**6**) and *N*-propylpiperidine (**8**) were prepared by the alkylation of piperidine, pyrrolidine and morpholine with isobutyl and propyl bromides, respectively. Isopropyl trifluoroacetate (**2**) was prepared by the reaction of the 2-propanol with trifluoroacetic anhydride in pyridine.

### 3.3. Typical procedure for the reaction of gaseous alkanes with trimethylamine N-oxide catalyzed by $Cu(OAc)_2$

A 50 ml centrifuge glass tube (100 mm × 30 mm $\phi$) equipped with a Teflon-coated magnetic stirring bar (20 mm × 7 mm $\phi$) was charged with $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), trimethylamine *N*-oxide (0.376g, 5.0 mmol), potassium persulfate (0.270 g, 1.0 mmol), and trifluoroacetic acid (5.0 ml). The glass tube capped with a rubber septum with a glass needle was placed in a 100 ml stainless steel autoclave. The autoclave was closed, flushed with a gaseous alkane three times and pressurized to 10 atm. The reaction mixture was heated at 150 °C with stirring for 20 h. After cooling and venting of the residual gas, the autoclave was opened. Sodium 3-(trimethylsilyl)propanesulfonate (DSS) (21.8 mg, 0.1 mmol) was added to the reaction mixture, and a few drops of the resulting mixture were dissolved in $CDCl_3$. The identification of reaction products was proved by comparison with the authentic samples. The yields of **1**, **2** and **3** were determined by $^1$H-NMR analyses. These results are listed in Table 1.

### 3.4. N,N-Dimethylisobutylamine (1)

Colorless oil. b.p. 82–83 °C; MS (70 eV) *m/e* 58 (100%, $M^+ - CH(CH_3)_2$), 101 (4.3%, $M^+$); IR (neat) 2952(s), 2871(m), 2815(s), 2764(s), 2723(m), 1472(m), 1386(m), 1365(m), 1265(m), 1163(m), 1110(m), 1040(s), 843(m), 824(w) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 270 MHz) $\delta$ 0.90 (d, $J = 6.6$ Hz, 6 H), 1.73 (tsept, $J = 7.6$ and 6.6 Hz, 1 H), 2.00 (d, $J = 7.6$ Hz, 2 H), 2.20 (s, 6 H): $^{13}$C-NMR ($CDCl_3$, 67.8 MHz) $\delta$ 20.8, 26.1, 45.9, 68.5 [Registry No. 7239-24-9].

### 3.5. Isopropyl trifluoroacetate (2)

Colorless oil. b.p. 45–59 °C; IR (neat) 2991(m), 1168.2, 1785(s), 1675(m), 1490(m), 1383(m), 1333(m), 1168(s), 862(w), 757(w) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 90 MHz) $\delta$ 1.38 (d, $J = 6.4$ Hz, 6 H), 5.21 (sept, $J = 6.4$ Hz, 1 H); $^{13}$C-NMR ($CDCl_3$, 67.8 Hz) $\delta$ 21.2, 73.2, 114.6 (d, $J_{C\text{-}F} = 286$ Hz), 157.0 (d, $J_{C\text{-}F} = 42$ Hz) [Registry No. 400-38-4].

### 3.6. N,N-Dimethylbutylamine (3)

Colorless oil. b.p. 91–94 °C; MS (70 eV) *m/e* 58 (100%, $M^+ - (CH_2)_2CH_3$), 101 (2.9%, $M^+$); IR (neat) 2970(s), 1455(s), 1376(s), 1338(w), 1306(m), 1264(s), 1243(m), 1198(m), 1164(m), 1103(m), 1070(m), 1042(s), 1000(m), 979(m), 890(w), 841(m), 792(m), 733(m) $cm^{-1}$; $^1$H-NMR (270 MHz, $CDCl_3$) $\delta$ 0.91 (t, $J = 7.3$ Hz, 3 H), 1.25–1.50 (m, 4 H), 2.21 (s, 6 H), 2.25 (t, $J = 7.3$ Hz, 2 H); $^{13}$C-NMR (22.3 MHz, $CDCl_3$) $\delta$ 13.0, 19.8, 29.1, 44.5, 58.8 [Registry No. 927-62-8].

### 3.7. N-Isobutylpiperidine (4)

Colorless oil. b.p. 63–64 °C at 27 mmHg; MS (70 eV) *m/e* 98 (100%, $M^+ - CH(CH_3)_2$), 141 (9.0%, $M^+$); IR (neat) 2934(s), 2869(s), 2854(s), 2799(s), 2775(s), 2734(s), 2690(m), 1468(m), 1442(m), 1379(m), 1364(m), 1298(m), 1156(s), 1100(s), 1058(m), 1040(m), 1003(m), 963(w), 858(w), 785(m) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 0.88 (d, $J = 6.6$ Hz, 6 H), 1.41 (ddd, $J = 5.0$, 5.0 and 5.0 Hz, 2 H), 1.56 (dt, $J = 5.5$ and 5.5 Hz, 4 H), 1.78 (tsept, $J = 7.3$ and 6.6 Hz, 1 H), 2.03 (d, $J = 7.3$ Hz, 2 H), 2.18–2.49 (m, 4 H). $^{13}$C NMR ($CDCl_3$, 67.8 MHz) $\delta$ 21.1, 24.6, 25.5, 26.6, 55.1, 67.9 [Registry No. 10315-89-6].

### 3.8. N-Isobutylpyrrolidine (5)

Colorless oil. b.p. 40–42 °C at 18 mmHg; MS (70 eV) *m/e* 84 (100%, $M^+ - CH(CH_3)_2$), 127 (23.5%, $M^+$); IR (neat) 2954(s), 2783(s), 1459(m), 1389(m), 1364(m), 1352(m), 1334(m), 1300(m), 1196(m), 1153(m), 1117(m), 1089(m), 912(w), 872(w) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 270 MHz) $\delta$ 0.92 (d, $J = 6.6$ Hz, 6 H), 1.74 (tsept, $J = 7.6$ and 6.6, 1 H), 1.76 (dd, $J = 5.6$ and 5.6 Hz, 4 H), 2.21 (d, $J = 7.6$ Hz, 2 H), 2.44 (dd, $J = 5.6$ and 5.6 Hz, 4 H); $^{13}$C-NMR ($CDCl_3$, 67.8 MHz) $\delta$ 21.1, 23.4, 27.6, 54.5, 65.3 [Registry No. 39198-81-7].

### 3.9. N-Isobutylmorpholine (6)

Colorless oil. b.p. 68–71 °C at 30 mmHg; MS (70 eV) *m/e* 100 (100%, $M^+ - CH(CH_3)_2$), 143 (2.1%, $M^+$); IR (neat) 2955(s), 2853(s), 2806(s), 1469(s), 1456(m), 1398(m), 1378(m), 1365(m), 1309(m), 1293(s), 1273(m), 1250(m), 1152(s), 1119(s), 1071(m), 1036(m), 1016(s), 961(w), 948(w), 931(w), 898(m), 864(s), 800(w), 630(m) $cm^{-1}$; $^1$H-NMR (CDCl3, 270 MHz) $\delta$ 0.90 (d, $J = 6.6$ Hz, 6 H), 1.78 (tsept., $J = 6.6$ and 7.6 Hz, 1H), 2.07 (d, $J = 7.6$ MHz, 2 H), 2.36 (dd, $J = 4.6$ and 4.6 Hz, 4H), 3.70 (dd, $J = 4.6$ and 4.6 Hz, 4 H); $^{13}$C-NMR ($CDCl_3$, 67.8 MHz) $\delta$ 20.8, 25.0, 54.1, 67.1, 67.3 [Registry No. 10315-98-7].

### 3.10. N,N-Dimethylpropylamine (7)

Colorless oil. b.p. 58–61 °C; IR (neat) 2935(s), 2874(s), 2852(s), 2800(s), 2769(s), 2734(s), 2691(m), 2668(m), 1468(m), 1456(m), 1443(m), 1376(m), 1350(m), 1301(m), 1158(m), 1144(m), 1133(m), 1098(m), 1054(w), 1041(w), 978(w), 858(w), 783(w) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 270 MHz) $\delta$ 0.90 (t, $J = 7.6$ Hz, 3 H), 1.48 (sept, $J = 7.6$ Hz, 2 H), 2.21 (t, $J = 7.6$ Hz, 2 H), 2.21 (s, 6 H); $^{13}$C-NMR ($CDCl_3$, 67.8 MHz) $\delta$ 11.8, 20.8, 45.4, 61.8 [Registry No. 926-63-6].

### 3.11. N-Propylpiperidine (8)

Colorless oil. b.p. 44–46 °C at 18 mmHg; MS (70 eV) $m/e$ 98 (100%, $M^+ - CH_2CH_3$), 127 (10.8%, $M^+$); IR (neat) 2973(s), 2773(s), 1459(m), 1381(m), 1340(w), 1265(m), 1207(m), 1163(m), 1102(m), 1055(m), 1019(m), 995(m), 913(w), 888(w), 838(w), 743(w) $cm^{-1}$; $^1$H-NMR ($CDCl_3$, 270 MHz) $\delta$ 0.88 (t, $J = 7.6$ Hz, 3 H), 1.42–1.62 (m, 8 H), 2.21–2.27 (m, 2 H), 2.36 (dd, $J = 3.0$ and 3.0 Hz, 4 H); $^{13}$C-NMR ($CDCl_3$, 67.8 MHz) $\delta$ 12.0, 20.0, 24.5, 26.0, 54.6, 61.6 [Registry No. 5470-02-0].

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