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Alkylative Amination of Aldehydes via Carbon-Carbon Bond Formation Based on Radical Addition to Carbon-Nitrogen Double Bond

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Abstract: Alkylative amination of aldehydes was achieved *via* a carbon-carbon bond formation by the intermolecular alkyl radical addition to the carbon-nitrogen double bond of oxime ethers generated *in situ* from aldehydes and benzyloxyamine. Alkyl radical addition to oxime ethers *via* a route involving the iodine atom-transfer process was found to be largely dependent on the reaction temperature and eliminated the tedious workup to remove excess tin-residues from the reaction mixture.
Keywords: radical addition, oxime ether, atom-transfer, one-pot, amination

INTRODUCTION

The reaction of imines with *C*-nucleophiles provides a useful route for preparing a variety of amines.[1] The reactions are generally carried out by using moisture-sensitive organometallic reagents, except for a few outstanding examples.[2,3] These methods necessitate strictly anhydrous reaction conditions and additional protection-deprotection steps. Employment of a moisture-resistant radical species would eliminate the cumbersome operations involved in conventional ionic reactions and successfully integrate a multi-step reaction into a one-step reaction. Following our studies on free radical-mediated one-pot synthesis of α-amino acids,[4] we describe herein the first practical alkylative amination reaction of various aldehydes based on the radical addition to the carbon-nitrogen double bond. As shown below, the success of this process reflects the overall difference in the reactivity of alkyl radicals between aldehydes and oxime ethers. The alkyl radical is well known to be inert to aldehydes due to the instability of the resulting intermediate alkoxy radical, while oxime ethers are excellent radical acceptors.[5] Thus, the free radical-mediated alkylative amination reaction of aldehydes afforded selectively the alkylated amines with no formation of alkylated alcohols by the alkyl radical addition to aldehydes.

RESULTS AND DISCUSSION

As a preliminary experiment, we investigated the ethylative amination of benzaldehyde **1a** using benzyloxyamine and triethylborane as an ethyl radical source (Table 1, entry 1). The intermediate oxime ether was easily available by stirring a 1:1 mixture of benzaldehyde **1a** and benzyloxyamine in the presence of $MgSO_4$

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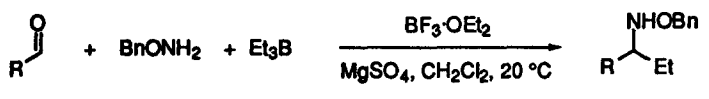
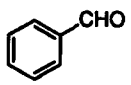
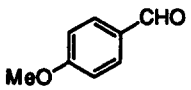
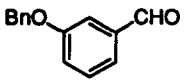
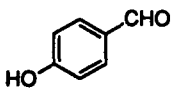
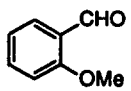
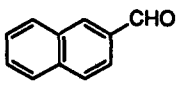
Table 1. Ethylative amination of aldehydes **1a-g**[a]



1a-g **2aA-gA**

a : R = Ph
b : R = 4-MeO-C_6H_4
c : R = 3-BnO-C_6H_4
d : R = 4-HO-C_6H_4
e : R = 2-MeO-C_6H_4
f : R = 2-Naph
g : R = *n*-Bu

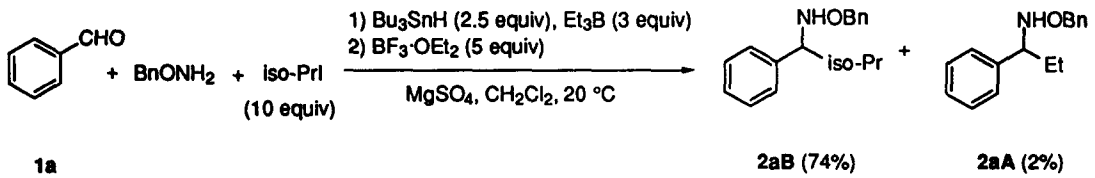
Entry	Aldehyde		Time (h)[b]	Product	Yield (%)[c]
1		**1a**	24	**2aA**	83
2		**1b**	48	**2bA**	89
3		**1c**	48	**2cA**	76
4		**1d**	48	**2dA**	88
5		**1e**	48	**2eA**	92
6		**1f**	24	**2fA**	56
7	*n*-Bu–CHO	**1g**	24	**2gA**	79

[a] To a solution of oxime ether in CH_2Cl_2 were added BF_3·OEt_2 (5 equiv) and 1M Et_3B in hexane (4 equiv) at 20 °C.
[b] Time for the preparation of oxime ethers from aldehyde (1 equiv) and benzyloxyamine (1 equiv) in the presence of $MgSO_4$ in CH_2Cl_2 at 20 °C. [c] Isolated yields.

in CH_2Cl_2 at 20 °C for 24 h. To the reaction vessel containing the oxime ether was added commercially available 1.0 M solution of Et_3B in hexane (4 equiv) in the presence of BF_3·OEt_2 (5 equiv), and then the reaction mixture was stirred at 20 °C for 5 min.[6] This quite simple procedure in one-pot afforded, as expected, the ethylated amine **2aA** in 83% yield.[7] It was found that a nonpolar aromatic solvent such as toluene is also effective for this process, although a typical solvent is dichloromethane. In this reaction, triethylborane acts as not only a radical initiator but also a terminator to trap the resulting benzyloxyaminyl radical; thus, the radical reaction cycle proceeds through the regeneration of the ethyl radical.[4,8] We also examined the ethylative amination of the aryl aldehydes **1b-f** bearing a variety of substituents (entries 2-6). Preparation of the intermediate oxime ethers from

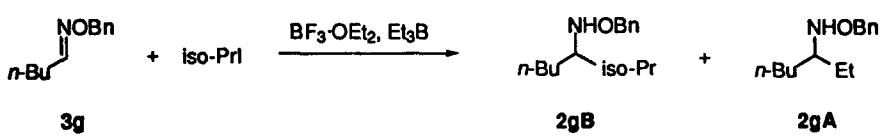
the aldehydes **1b-e** containing an electron-donating substituent was also readily accomplished by stirring in the presence of $MgSO_4$ at 20 °C for 48 h, and the subsequent radical reaction of the oxime ethers completed in 5 min.[9] High chemical yields were observed in the alkylative amination reaction of aryl aldehydes **1b-d** having not only alkoxy groups but also a 4-hydroxyl group with no protection (entry 4). Sterically hindered 2-methoxybenzaldehyde **1e** worked well under similar reaction conditions to give the ethylated amine **2eA** in 92% yield (entry 5). It is known that a radical acceptor having electron-donating substituents shows low reactivity toward nucleophilic alkyl radicals because of the high LUMO energy of the radical acceptor. Therefore, it is noteworthy that the ethylative amination reaction of less reactive aldehydes **1b-e** proceeded smoothly under mild reaction conditions to give the corresponding amines **2bA-eA** with excellent yield. The reaction of enolizable imines and related compounds with organometallic reagents is frequently plagued by the aldol-type self condensation reaction and so on.[1] In this study, we have also found that the ethylative amination of the aliphatic aldehyde **1g** having sensitive α-hydrogens proceeds under similar reaction conditions (entry 7).

The alkylative amination of benzaldehyde **1a** using isopropyl iodide was also studied under the stannyl radical-induced radical reaction conditions (Scheme 1). Treatment of preformed intermediate oxime ether with Bu_3SnH, isopropyl iodide, and Et_3B in CH_2Cl_2 at 20 °C followed by the addition of $BF_3{\cdot}OEt_2$ gave the isopropylated product **2aB** in 74% yield and the ethylated product **2aA** in 2% yield.

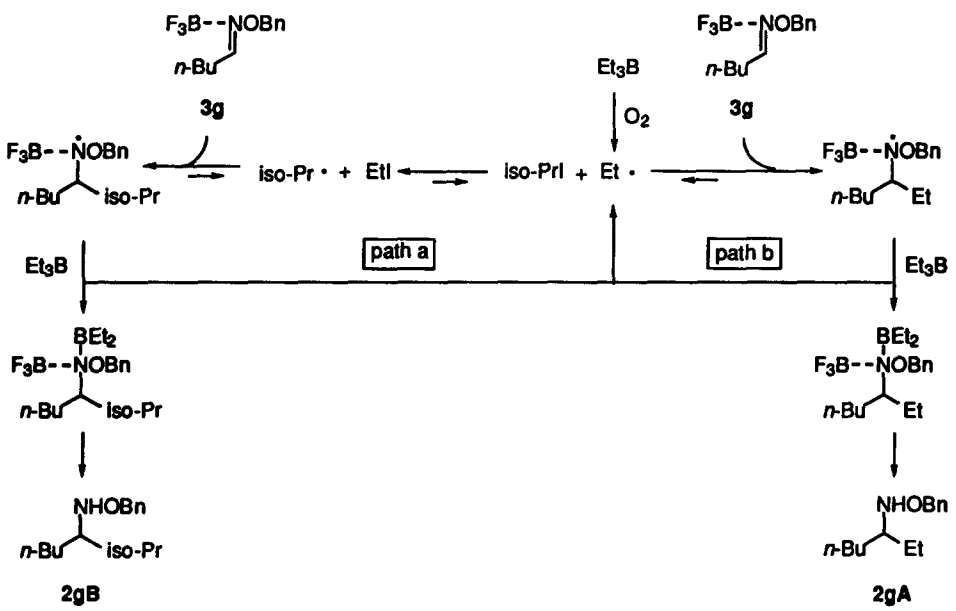


Scheme 1

Free radical synthetic methods largely relied on toxic organomercury or organotin chemistry. Therefore, the radical reactions including atom- and group-transfer processes or single-electron transfer (SET) processes have been a subject of current interest.[10] Based on our investigations toward the stannyl radical-induced radical addition to oxime ethers,[4,6] we next examined the alkyl radical addition *via* a route involving the iodine atom-transfer process in the absence of tin hydride (Scheme 2). The isopropyl radical addition to oxime ether **3g** was run by using iso-PrI (10 equiv) and Et_3B (2.5 equiv) in the presence of $BF_3{\cdot}OEt_2$ (2 equiv). As expected, the reaction proceeded smoothly in the absence of tributyltin hydride to give the desired isopropylated product **2gB** (*via* path a) accompanying by the ethylated product **2gA** (*via* path b), which was formed by a competitive reaction with the ethyl radical generated from Et_3B (Scheme 3). The formation of **2gB** was found to be dependent on the reaction temperature and solvent used, thus changing the temperature from -78 °C (in CH_2Cl_2) to 60 °C (in toluene) led to an effective increase in the ratio **2gB/2gA** to 17.9 (Figure 1). These results indicated that the reaction proceeded effectively at 60 °C *via* a route involving the iodine atom-transfer process between the



Scheme 2



Scheme 3

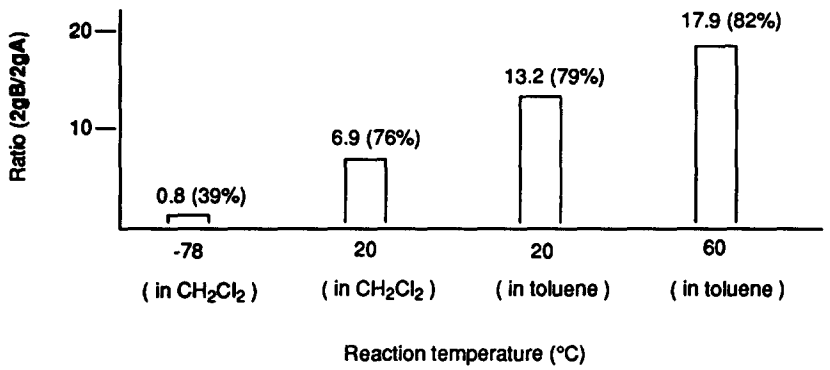


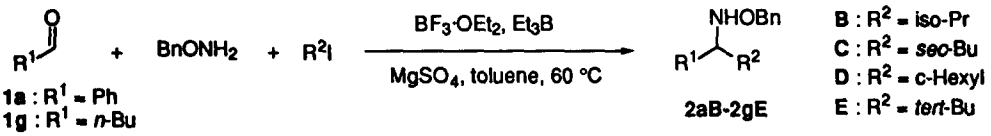
Figure 1. Ratio of **2gB** to **2gA** and reaction temperature in the radical addition to **3g**. Yields in parentheses are for the isolated **2gB**.

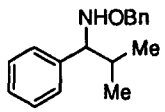
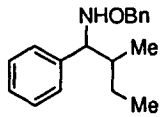
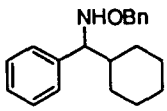
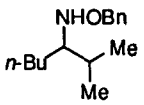
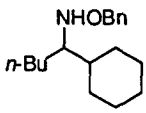
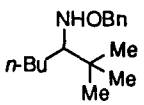
isopropyl iodide and the ethyl radical, and the predominant addition of the more nucleophilic and stable isopropyl radical was observed. This radical reaction has a tremendous practical advantage over the stannyl radical-induced reaction which requires the tedious work-up to remove the tin-residues from the reaction mixture.

The present procedure was successfully extended to a three-component reaction using different radical precursors such as isopropyl, *sec*-butyl, cyclohexyl, and *tert*-butyl iodides, allowing facile incorporation of structural variability (Table 2). In the case of the alkylative amination of benzaldehyde **1a** using isopropyl iodide, to the reaction vessel containing the preformed intermediate oxime ether in toluene were successively added isopropyl iodide, BF_3•OEt_2 and Et_3B as a radical initiator at 60 °C to give the isopropylated amine **2aB** in 82%

yield (entry 1). Alkylative amination of *n*-valeraldehyde **1g** proceeded to give a good yield of alkylated products **2gB-2gE** under the same reaction conditions (entries 4-6).

Table 2. Alkylative amination of aldehydes **1a** and **1g**[a]



Entry	Aldehyde	R^2	Product		Yield (%)[b]
1	**1a**	iso-Pr		**2aB**	82
2	**1a**	*sec*-Bu		**2aC**	81
3	**1a**	c-Hexyl		**2aD**	70
4	**1g**	iso-Pr		**2gB**	56
5	**1g**	c-Hexyl		**2gD**	54
6	**1g**	*tert*-Bu		**2gE**	60

[a] To a solution of oxime ether in toluene were added R^2I (10 equiv), BF_3•OEt_2 (10 equiv), and 1M Et_3B in hexane (2.5 equiv) at 60 °C. [b] Isolated yields.

CONCLUSION

We have demonstrated that the use of a moisture-resistant radical species provides direct access to various types of alkylated amines from aldehydes. The advantages of this procedure are that the tedious isolation of the intermediate oxime ethers is unnecessary and both aromatic and aliphatic aldehydes having functional groups

participate readily as substrates. Additionally, this one-pot method involves both carbon-nitrogen and carbon-carbon bond-forming reactions through the condensation of aldehydes with benzyloxyamine, followed by the alkyl radical addition to the resulting oxime ethers.

EXPERIMENTAL SECTION

General. ^1H and ^{13}C NMR spectra were measured using Varian Gemini-200 (200 and 50 MHz, respectively) instrument in $CDCl_3$. Chemical shifts (δ scale) are relative to TMS as internal reference. IR spectra were measured with a Perkin Elmer 1600 FTIR machine and mass spectra were taken by Hitachi M-4100 spectrometer. For flash column chromatography, E. Merck Kieselgel 60 (230-400 mesh) was used. Preparative TLC separations were carried out on precoated silica gel plates (E. Merck $60F_{254}$). Triethylborane proved to be an effective radical initiator in the presence of trace amount of oxygen.[8]

General Procedure for the Ethylative Amination.

To a solution of aldehyde (60 mg) in CH_2Cl_2 (1 mL) were added a 3.79 M solution of benzyloxyamine in CH_2Cl_2 (1 equiv) and $MgSO_4$ (10 mg) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 24 h (in the case of aldehydes **1a**, **1f**, and **1g**) or 48 h (in the case of aldehydes **1b-e**), CH_2Cl_2 (5 mL), BF_3•OEt_2 (5 equiv), and Et_3B (1.0 M in hexane, 4 equiv) were added at the same temperature. After being stirred at the same temperature for 5 min, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ and then extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure.

***O*-Benzyl-*N*-(1-phenylpropyl)hydroxylamine (2aA).**
Purification of the residue by preparative TLC (hexane/AcOEt 50:1) afforded **2aA**.[6]

***O*-Benzyl-*N*-[1-(4-methoxyphenyl)propyl]hydroxylamine (2bA).** Purification of the residue by preparative TLC (hexane/AcOEt 50:1, twofold development) afforded **2bA** as a colorless oil. IR ($CHCl_3$): ν = 2965, 1514, 1455 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.30-7.22 (7H, m), 6.87 (2H, br d, J = 8.6 Hz), 4.61 (1H, d, J = 11.4 Hz), 4.56 (1H, d, J = 11.4 Hz), 3.84 (1H, br dd, J = 8.6, 5.3 Hz), 3.79 (3H, s), 1.92-1.50 (2H, m), 0.79 (3H, t, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 158.8, 137.8, 133.5, 128.8, 128.3, 128.2, 127.6, 113.5, 76.6, 66.7, 55.1, 26.4, 10.4. HRMS: Calcd for $C_{17}H_{21}NO_2$ (M^+) : 271.1571, Found : 271.1554.

***O*-Benzyl-*N*-[1-(3-benzyloxyphenyl)propyl]hydroxylamine (2cA).** Purification of the residue by preparative TLC (hexane/AcOEt 30:1, twofold development) afforded **2cA** as a colorless oil. IR ($CHCl_3$): ν = 2967, 1487, 1453 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.45-7.20 (11H, m), 6.97-6.86 (3H, m), 5.04 (2H, s), 4.60 (1H, d, J = 11.5 Hz), 4.56 (1H, d, J = 11.5 Hz), 3.86 (1H, br dd, J = 8.2, 5.6 Hz), 1.85-1.55 (2H, m), 0.79 (3H, t, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 158.7, 143.3, 137.8, 137.0, 129.1, 128.4, 128.3, 128.2, 127.8, 127.6, 127.4, 120.4, 114.2, 113.6, 76.6, 69.8, 67.3, 26.5, 10.4. HRMS: Calcd for $C_{23}H_{25}NO_2$ (M^+) : 347.1884, Found : 347.1901.

***O*-Benzyl-*N*-[1-(4-hydroxyphenyl)propyl]hydroxylamine (2dA).** Purification of the residue by preparative TLC (hexane/AcOEt 5:1) afforded **2dA**.[6]

***O*-Benzyl-*N*-[1-(2-methoxyphenyl)propyl]hydroxylamine (2eA).** Purification of the residue by preparative TLC (hexane/AcOEt 50:1, twofold development) afforded **2eA**.[6]

***O*-Benzyl-*N*-[1-(2-naphthyl)propyl]hydroxylamine (2fA).** Purification of the residue by preparative TLC (hexane/AcOEt 50:1, twofold development) afforded **2fA** as a colorless oil. IR ($CHCl_3$): ν = 2967, 1485, 1451 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.85-7.76 (4H, m), 7.53-7.43 (3H, m), 7.27-7.21 (5H, m), 4.61 (1H, d, *J* = 11.5 Hz), 4.56 (1H, d, *J* = 11.5 Hz), 4.07 (1H, br dd, *J* = 8.4, 5.5 Hz), 1.90-1.71 (2H, m), 0.82 (3H, t, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 139.1, 137.7, 133.2, 132.9, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 126.9, 125.8, 125.6, 125.5, 76.7, 67.5, 26.4, 10.5. HRMS: Calcd for $C_{20}H_{21}NO$ (M^+) : 291.1622, Found : 291.1616.

***O*-Benzyl-*N*-(3-heptyl)hydroxylamine (2gA).** Purification of the residue by preparative TLC (hexane/AcOEt 50:1, twofold development) afforded **2gA** as a colorless oil. IR ($CHCl_3$): ν = 2962, 1455 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.37-7.26 (5H, m), 4.70 (2H, s), 2.78 (1H, m), 1.53-1.27 (8H, m), 0.90 (6H, br t, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 138.0, 128.2, 127.6, 76.4, 61.7, 30.9, 28.0, 24.4, 22.8, 13.9, 9.9. HRMS: Calcd for $C_{14}H_{23}NO$ (M^+) : 221.1778, Found : 221.1794.

Alkylative Amination of 1a using Bu_3SnH

To a solution of aldehyde **1a** (60 mg, 0.565 mmol) in CH_2Cl_2 (1 mL) were added a 4.09 M solution of benzyloxyamine in CH_2Cl_2 (0.138 mL, 0.565 mmol) and $MgSO_4$ (10 mg) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 24 h, CH_2Cl_2 (5 mL), Bu_3SnH (0.38 mL, 1.41 mmol), isopropyl iodide (0.562 mL, 5.65 mmol), and Et_3B (1.0 M in hexane, 1.7 mL, 1.70 mol) were added at the same temperature. After being stirred at the same temperature for 90 sec, $BF_3{\cdot}OEt_2$ (0.356 mL, 2.83 mmol) was added to the reaction mixture. After being stirred at the same temperature for 5 min, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ and then extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by preparative TLC (hexane/AcOEt 50:1, twofold development) afforded **2aB** (106 mg, 74%) as a colorless oil and **2aA**[6] (3 mg, 2%) as a colorless oil.

***O*-Benzyl-*N*-(2-methyl-1-phenylpropyl)hydroxylamine (2aB).** IR ($CHCl_3$): ν = 2964, 1495, 1454 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.32-7.16 (10H, m), 4.57 (1H, d, *J* = 11.4 Hz), 4.52 (1H, d, *J* = 11.4 Hz), 3.73 (1H, br d, *J* = 7.3 Hz), 1.98 (1H, m), 0.96 (3H, d, *J* = 6.8 Hz), 0.74 (3H, d, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ = 141.0, 137.7, 128.4, 128.2, 128.1, 127.8, 127.6, 127.0, 76.4, 71.6, 30.8, 19.8, 18.9. HRMS: Calcd for $C_{17}H_{21}NO$ (M^+) : 255.1622, Found : 255.1635.

Pentanal *O*-Benzyloxime (3g). To a solution of *n*-valeraldehyde (10 g, 116 mmol) in pyridine (40 mL) was added *O*-benzylhydroxylamine hydrochloride (20.4 g, 128 mmol) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 18 h, the reaction mixture was diluted with Et_2O. The organic phase was washed with water and brine, dried over $MgSO_4$ and concentrated at reduced pressure. Purification of the residue by flash column chromatography (hexane/AcOEt 10:1) afforded **3g** (22 g, 99%) as a colorless oil and a 3:2 mixture of *E*/*Z*-oxime ether. IR ($CHCl_3$): ν = 2961, 1497, 1466, 1455 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.44 (3/5H, t, *J* = 6.2 Hz), 7.40-7.21 (5H, m), 6.66 (2/5H, t, *J* = 5.5 Hz), 5.10 (4/5H, s), 5.05 (6/5H, s), 2.38 (4/5H, m), 2.18 (6/5H, m), 1.56-1.21 (4H, m), 0.90 (9/5H, t, *J* = 7.4 Hz), 0.89 (6/5H, t, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 152.4, 151.4, 138.1, 137.6, 128.2, 128.1, 127.7, 127.6, 127.5, 75.5, 75.3, 29.0, 28.6, 28.2, 25.4, 22.3, 22.0, 13.6. HRMS: Calcd for $C_{12}H_{17}NO$ (M^+) : 191.1309, Found : 191.1298.

Isopropyl Radical Addition to 3g. To a solution of oxime ether **3g** (100 mg, 0.52 mmol) in CH_2Cl_2 or toluene (10 mL) were added $BF_3{\cdot}OEt_2$ (0.13 mL, 1.05 mmol), iso-PrI (0.52 mL, 5.2 mmol) and Et_3B (1.0 M in hexane, 1.3 mL, 1.31 mmol) under a nitrogen atmosphere at -78, 20, or 60 °C. After being stirred at the same temperature for 5 min, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ and then extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and concentrated at reduced pressure. Purification of the residue by preparative TLC (hexane/AcOEt 50:1, twofold development) afforded **2gB** as a colorless oil and **2gA**. Yields of **2gB** are shown in Figure 1.

***O*-Benzyl-*N*-(2-methyl-3-heptyl)hydroxylamine (2gB).** IR ($CHCl_3$): ν = 2960, 1469, 1454 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.38-7.21 (5H, m), 4.68 (2H, s), 2.63 (1H, m), 1.95 (1H, m), 1.50-1.15 (6H, m), 0.95-0.82 (9H, m). ^{13}C NMR ($CDCl_3$): δ = 138.1, 128.26, 128.18, 127.5, 76.2, 65.7, 28.9, 28.6, 27.4, 22.8, 18.8, 17.7, 13.9. HRMS: Calcd for $C_{15}H_{25}NO$ (M^+) : 235.1935, Found : 235.1933.

General Procedure for the Alkylative Amination.
To a solution of aldehyde **1a** or **1g** (80 mg) in toluene (1 mL) were added benzyloxyamine (0.55 M in toluene, 1 equiv) and $MgSO_4$ (10 mg) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 1 day, toluene (5 mL), RI (10 equiv), $BF_3{\cdot}OEt_2$ (10 equiv), and Et_3B (1.0 M in hexane, 2.5 equiv) were added at 60 °C. After being stirred at the same temperature for 5 min, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ and then extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by preparative TLC (hexane/AcOEt 50:1, twofold development) afforded alkylative amines **2aB-2gE**.

***O*-Benzyl-*N*-(2-methyl-1-phenylbutyl)hydroxylamine (2aC).** (as a 1:1 diastereomeric mixture) IR ($CHCl_3$): ν = 2965, 1495, 1454 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.43-7.17 (10H, m), 4.63-4.49 (2H, m), 3.89 (1/2H, d, *J* = 6.7 Hz), 3.83 (1/2H, d, *J* = 6.7 Hz), 1.89-0.95 (3H, m), 0.94-0.71 (6H, m). ^{13}C NMR ($CDCl_3$): δ = 141.4, 140.7, 137.83, 137.79, 130.9, 129.9, 128.38, 128.36, 128.3, 128.2, 127.83, 127.77, 127.6, 127.0, 126.9, 76.8, 76.4, 70.3, 69.6, 37.7, 37.2, 26.2, 25.4, 15.7, 15.0, 11.3, 11.2. HRMS: Calcd for $C_{18}H_{23}NO$ (M^+) : 269.1778, Found : 269.1759.
***O*-Benzyl-*N*-(1-cyclohexyl-1-phenylmethyl)hydroxylamine (2aD).** IR ($CHCl_3$): ν = 2929, 1495, 1454 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40-7.20 (10H, m), 4.55 (1H, d, *J* = 11.4 Hz), 4.50 (1H, d, *J* = 11.4 Hz), 3.76 (1H, br d, *J* = 7.5 Hz), 1.94-0.78 (11H, m). ^{13}C NMR ($CDCl_3$): δ = 141.3, 137.8, 128.4, 128.2, 128.1, 127.8, 127.8, 127.6, 126.9, 76.4, 70.9, 40.7, 30.3, 29.3, 26.3, 26.05, 26.04. HRMS: Calcd for $C_{20}H_{25}NO$ (M^+) : 295.1935, Found : 295.1936.
***O*-Benzyl-*N*-(1-cyclohexylpentyl)hydroxylamine (2gD).** IR ($CHCl_3$): ν = 2929, 1452 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.41-7.22 (5H, m), 4.68 (2H, s), 2.62 (1H, m), 1.80-0.85 (20H, m). ^{13}C NMR ($CDCl_3$): δ = 138.1, 128.3, 128.2, 127.5, 76.2, 65.3, 39.1, 29.3, 28.9, 28.6, 28.0, 26.6, 26.53, 26.48, 22.8, 13.9. HRMS: Calcd for $C_{18}H_{29}NO$ (M^+) : 275.2248, Found : 275.2250.
***O*-Benzyl-*N*-(2,2-dimethyl-3-heptyl)hydroxylamine (2gE).** IR ($CHCl_3$): ν = 2959, 1455 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40-7.23 (5H, m), 4.68 (1H, d, *J* = 11.6 Hz), 4.66 (1H, d, *J* = 11.6 Hz), 2.45 (1H, m), 1.60-1.20 (6H, m), 0.93 (9H, s), 0.91 (3H, t, *J* = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 138.1, 128.2, 128.1,

127.5, 75.6, 69.4, 34.2, 30.3, 28.2, 27.2, 22.9, 14.0. HRMS: Calcd for $C_{16}H_{27}NO$ (M^+) : 249.2091, Found : 249.2066.

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