Experimental Section

Materials. All reagents and the solvents were dried and purified before use by the usual procedures. Allylic esters were prepared by the reaction of the corresponding alcohols with acetyl chloride or methyl chloroformate. (*Z*)-2-Nonen-1-ol, (*Z*)-2-undecen-1-ol, (*Z*)-6-phenyl-2-hexen-1-ol, (*Z*)-2,8-nonadien-1-ol, (*Z*)-5-ethyl-2-nonen-1-ol and (*Z*)-3-phenyl-2-propen-1-ol were prepared by the hydrogenation of the corresponding 2-alkyn-1-ol. (*Z*)-2-Nonyn-1-ol, (*Z*)-2-undecyn-1-ol and (*Z*)-6-phenyl-2-hexyn-1-ol were prepared by the reaction of 1-alkynyl lithium with paraformaldehyde.[1] (*Z*)-2-Nonyn-8-en-1-ol and (*Z*)-5-ethyl-2-nonyn-1-ol were prepared by the reaction of dilithiated propargyl alcohol with the corresponding alkyl bromide in liquid ammonia.[2] (*Z*)-4-Buthoxy-2-buten-1-ol was prepared by the reaction of monosodio-(*Z*)-2-buten-1,4-diol with 1-iodobutane. $[Ir(COD)Cl]_2$,[3] $[Ir(COD)_2]BF_4$[4] and $[Ir(COD)OMe]_2$[5] were prepared according to the published method. Lindlar catalyst was purchased from Wako chemicals.

General Methods. ^1H NMR spectra were measured on a JEOL-EX-270 spectrometer or a Brucker AVANCE-400 spectrometer using Me_4Si as an internal standard. ^{13}C NMR spectra were measured on a JEOL-EX-270 spectrometer using Me_4Si as an internal standard. Samples were dissolved in $CDCl_3$ or d_6-benzene solutions. GC analyses were performed on a Shimadzu GC-14A by using a 3-mm x 2-m glass columns packed with either 5% PEG-HT on 60/80 mesh chromosorb w AW-DMCS, 5% PEG-HT + 1% KOH on 60/80 mesh uniport HP or 5% OV-17 on 60/80 mesh chromosorb w AW-DMCS. Column chromatography was carried out on 70 - 230 mesh silica gel (Merk; Silica Gel 60). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Allylic Amination of Allylic Esters. A typical procedure is described for the reaction of $\mathbf{1a}_1$ with piperidine. A mixture of methyl (*Z*)-2-nonenyl carbonate $\mathbf{1a}_1$ (400 mg, 2.0 mmol), triphenylphosphite (49.6 mg, 0.16 mmol), $[Ir(COD)Cl]_2$ (26.9 mg, 0.04 mmol) and piperidine (5.0 mL) were stirred at 50°C for 2 h under Ar atmosphere. The progress of the reaction was monitored by GLC. After $\mathbf{1a}_1$ was consumed, the reaction mixture was diluted with ether. The etheral solution was extracted with 6 M HCl. Combined acidic layers were neutralized with

NaOH, and extracted with ether. The organic layer was dried with $MgSO_4$ and filtered. After evaporation of the solvent, the residue was purified by column chromatography (*n*-hexane/ethyl acetate (70/30)) to give (*Z*)-**3a** and **4a** (360 mg; Yield 86%).

(*Z*)-1-(2-Nonenyl)piperidine ((*Z*)-3a): ^{1}H-NMR (400 MHz, C_6D_6) δ 1.00 (t, *J* = 7.0 Hz, 3H), 1.30-1.51 (m, 10H), 1.66 (quintet, *J* = 5.1 Hz, 4H), 2.19 (q, *J* = 7.1 Hz, 2H), 2.48 (t, *J* = 5.1 Hz, 4H), 3.09 (d, *J* = 6.7 Hz, 2H), 5.64 (dtt, *J* = 11.0, 7.3, 1.6 Hz, 1H), 5.77 (dtt, *J* = 11.0, 6.7, 1.5 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 14.0, 22.6, 24.4, 26.0 (2C), 27.4, 28.9, 29.5, 31.7, 54.5 (2C), 55.9, 126.4, 132.8. Anal. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69. Found: C, 80.07; H, 13.01; N, 6.65.

(*E*)-1-(2-Nonenyl)piperidine ((*E*)-3a): Compound (*E*)-**3a** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*Z*)-**3a**. ^{1}H-NMR (400 MHz, C_6D_6) δ 5.69 (dt, *J* = 15.2, 5.5 Hz, 1H), 5.74 (dt, *J* = 15.2, 5.2 Hz, 1H).

1-(1-*n*-Hexyl-2-propenyl)piperidine (4a): Compound **4a** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*Z*)-**3a**. ^{1}H-NMR (400 MHz, C_6D_6) δ 5.12 (dd, *J* = 17.2, 2.2 Hz, 1H), 5.21 (dd, *J* = 10.3, 2.2 Hz, 1H), 5.83 (ddd, *J* = 17.2, 10.3, 6.9 Hz, 1H).

(*Z*)-1-(2-Nonenyl)pyrrolidine ((*Z*)-3b): ^{1}H-NMR (400 MHz, C_6D_6) δ 1.00 (t, *J* = 6.8 Hz, 3H), 1.31-1.51 (m, 8H), 1.71-1.77 (m, 4H), 2.20 (q, *J* = 7.0 Hz, 2H), 2.54-2.63 (m, 4H), 3.26 (d, *J* = 6.7 Hz, 2H), 5.62 (dtt, *J* = 11.0, 7.3, 1.6 Hz, 1H), 5.83 (dtt, *J* = 11.0, 6.7, 1.6 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 14.0, 22.6, 23.4 (2C), 27.5, 28.9, 29.5, 31.7, 52.5, 54.0 (2C), 126.8, 132.0. Anal. Calcd for $C_{13}H_{25}N$: C, 79.93; H, 12.90; N, 7.17. Found: C, 80.01; H, 12.98; N, 7.14.

1-(1-*n*-Hexyl-2-propenyl)pyrrolidine (4b): Compound **4b** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*Z*)-**3b**. ^{1}H-NMR (400 MHz, C_6D_6) δ 5.15 (dd, *J* = 10.2, 2.3 Hz, 1H), 5.18 (dd, *J* = 16.3, 2.5 Hz, 1H), 5.90 (ddd, *J* = 16.3, 10.2, 7.1 Hz, 1H).

(*Z*)-1-(2-Nonenyl)morpholine ((*Z*)-3c): ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.29-1.34 (m, 8H), 2.06 (q, *J* = 6.9 Hz, 2H), 2.44-2.55 (m, 4H), 3.01 (d, *J* =

6.4 Hz, 2H), 3.72 (t, J = 4.6 Hz, 4H), 5.44 (dt, J = 10.9, 6.9 Hz, 1H), 5.58 (dt, J = 11.2, 6.9 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 14.0, 22.6, 27.5, 28.9, 29.5, 31.7, 53.6 (2C), 55.5, 67.0 (2C), 125.3, 133.8. Anal. Calcd for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63; O, 7.57. Found: C, 74.13; H, 12.08; N, 6.80.

1-(1-*n*-Hexyl-2-propenyl)morpholine (4c): Compound **4c** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*Z*)-**3c**. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.07 (dd, J = 16.3, 2.0 Hz, 1H), 5.18 (dd, J = 10.2, 2.0 Hz, 1H), 5.65 (ddd, J = 16.3, 10.2, 7.9 Hz, 1H).

(*Z*)-*N*-(2-Nonenyl)diethylamine ((*Z*)-3d): ^{1}H-NMR (400 MHz, C_6D_6) δ 1.00 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 6H), 1.34-1.50 (m, 8H), 2.19 (q, J = 7.1 Hz, 2H), 2.59 (q, J = 7.1 Hz, 4H), 3.24 (d, J = 6.6 Hz, 2H), 5.63 (dtt, J = 11.0, 7.1, 1.6 Hz, 1H), 5.75 (dtt, J = 11.0, 6.6, 1.5 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 11.8 (2C), 14.0, 22.6, 27.5, 29.0, 29.6, 31.7, 46.7 (2C), 49.6, 126.7, 132.5. Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 79.14; H, 13.75; N, 7.12.

***N*-(1-*n*-Hexyl-2-propenyl)diethylamine (4d):** Compound **4d** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*Z*)-**3d**. ^{1}H-NMR (400 MHz, C_6D_6) δ 5.11 (dd, J = 17.2, 2.1 Hz, 1H), 5.20 (dd, J = 10.4, 2.2 Hz, 1H), 5.81 (ddd, J = 17.2, 10.4, 6.9 Hz, 1H).

(*Z*)-*N*-(2-Nonenyl)butylamine ((*Z*)-3e): ^{1}H-NMR (400 MHz, C_6D_6) δ 0.97-1.03 (m, 6H), 1.36-1.53 (m, 12H), 2.17 (q, J = 7.3 Hz, 2H), 2.65 (t, J = 5.9 Hz, 2H), 3.17 (d, J = 5.7 Hz, 1H), 3.37 (d, J = 6.6 Hz, 2H), 5.60 (dt, J = 10.9, 7.3 Hz, 1H), 5.68 (dt, J = 10.6, 6.6 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 13.9, 14.0, 20.5, 22.6, 27.4, 28.9, 29.6, 31.7, 32.2, 46.3, 49.2, 128.0, 131.9. Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 79.11; H, 14.03; N, 7.01.

***N*-(1-*n*-Hexyl-2-propenyl)butylamine (4e):** Compound **4e** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*Z*)-**3e**. ^{1}H-NMR (400 MHz, C_6D_6) δ 5.07 (d, J = 15.2 Hz, 1H), 5.07 (d, J = 11.9 Hz, 1H), 5.56 (ddd, J = 15.2, 11.9, 8.6 Hz, 1H).

(Z)-1-(2-Undecenyl)piperidine ((Z)-3f): ^{1}H-NMR (400 MHz, C_6D_6) δ 1.0 (t, J = 6.7 Hz, 3H), 1.39-1.48 (m, 14H), 1.66 (quintet, J = 5.7 Hz, 4H), 2.20 (q, J = 7.3 Hz, 2H), 2.48 (t, J = 5.1 Hz, 4H), 3.10 (d, J = 6.7 Hz, 2H), 5.64 (dtt, J = 11.0, 7.3, 1.6 Hz, 1H), 5.77 (dtt, J = 11.0, 6.7, 1.5 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 14.1, 22.6, 24.4, 26.0 (2C), 27.4, 29.3 (2C), 29.4, 29.5, 31.8, 54.5 (2C), 55.9, 126.3, 132.8. Anal. Calcd for $C_{16}H_{31}N$: C, 80.94; H, 13.16; N, 5.90. Found: C, 80.81; H, 13.10; N, 5.74.

1-(1-*n*-Octyl-2-propenyl)piperidine (4f): Compound **4f** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (Z)-**3f**. ^{1}H-NMR (400 MHz, C_6D_6) δ 5.13 (dd, J = 17.2, 2.2 Hz, 1H), 5.21 (dd, J = 10.3, 2.2 Hz, 1H), 5.84 (ddd, J = 17.2, 10.3, 6.9 Hz, 1H).

(Z)-1-(6-Phenyl-2-hexenyl)piperidine ((Z)-3g): ^{1}H-NMR (400 MHz, C_6D_6) δ 1.42-1.47 (m, 2H), 1.64 (quintet, J = 5.4 Hz, 4H), 1.72 (quintet, J = 7.5 Hz, 2H), 2.15 (q, J = 7.3 Hz, 2H), 2.42-2.45 (m, 4H), 2.62 (t, J = 7.6 Hz, 2H), 3.02 (d, J = 6.7 Hz, 2H), 5.60 (dtt, J = 11.0, 7.3, 1.6 Hz, 1H), 5.76 (dtt, J = 11.0, 6.7, 1.4 Hz, 1H), 7.17-7.30 (m, 5H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 24.3, 25.9 (2C), 27.0, 31.2, 35.4, 54.5 (2C), 55.9, 125.6, 126.9, 128.2 (2C), 128.4 (2C), 132.1, 142.3. Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.64; H, 10.65; N, 5.67.

1-(1-(3-Phenylpropyl)-2-propenyl)piperidine (4g): Compound **4g** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (Z)-**3g**. ^{1}H-NMR (400 MHz, C_6D_6) δ 5.07 (dd, J = 17.2, 2.1 Hz, 1H), 5.17 (dd, J = 10.0, 2.1 Hz, 1H).

(Z)-1-(2,8-Nonadienyl)piperidine ((Z)-3h): ^{1}H-NMR (400 MHz, C_6D_6) δ 1.41-1.48 (m, 6H), 1.65 (quintet, J = 5.4 Hz, 4H), 2.08 (q, J = 6.9 Hz, 2H), 2.14 (q, J = 7.2 Hz, 2H), 2.46 (t, J = 5.2 Hz, 4H), 3.07 (d, J = 6.7 Hz, 2H), 5.08 (dq, J = 10.2, 2.1 Hz, 1H), 5.13 (dq, J = 17.1, 1.9 Hz, 1H), 5.60 (dtt, J = 11.0, 7.3, 1.5 Hz, 1H), 5.74 (dtt, J = 11.0, 6.7, 1.5 Hz, 1H), 5.88 (ddt, J = 17.0, 10.3, 6.9 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 24.3, 26.0 (2C), 27.3, 28.5, 29.0, 33.6, 54.5 (2C), 55.9, 114.3, 126.6, 132.5, 138.9. Anal. Calcd for $C_{14}H_{25}N$: C, 81.09; H, 12.15; N, 6.75. Found: C, 80.83; H, 12.42; N, 6.74.

(*Z*)-1-(5-Ethyl-2-nonenyl)piperidine ((*Z*)-3i): ^{1}H-NMR (400 MHz, C_6D_6) δ 0.99 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 6.7 Hz, 3H), 1.38-1.47 (m, 11H), 1.66 (quintet, *J* = 5.6 Hz, 4H), 2.18-2.20 (m, 2H), 2.49 (t, *J* = 5.2 Hz, 4H), 3.12 (d, *J* = 6.7 Hz, 2H), 5.65 (dtt, *J* = 11.1, 7.3, 1.6 Hz, 1H), 5.81 (dtt, *J* = 11.1, 6.7, 1.5 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 11.0, 14.1, 23.0, 24.4, 25.8, 26.0 (2C), 29.0, 31.1, 32.7, 39.5, 54.6 (2C), 56.1, 127.2, 131.4. Anal. Calcd for $C_{16}H_{31}N$: C, 80.94; H, 13.16; N, 5.90. Found: C, 80.99; H, 13.12; N, 5.84.

(*Z*)-1-(4-*n*-Buthoxy-2-butenyl)piperidine ((*Z*)-3j): ^{1}H-NMR (400 MHz, C_6D_6) δ 0.99 (t, *J* = 7.3 Hz, 3H), 1.42-1.50 (m, 4H), 1.61-1.66 (m, 6H), 2.41 (t, *J* = 4.9 Hz, 4H), 3.01 (d, *J* = 6.6 Hz, 2H), 3.45 (t, *J* = 6.4 Hz, 2H), 4.12 (d, *J* = 6.0 Hz, 2H), 5.79 (dtt, *J* = 11.2, 6.6, 1.5 Hz, 1H), 5.89 (dtt, *J* = 11.2, 6.1, 1.5 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 13.9, 19.3, 24.2, 25.9 (2C), 31.8, 54.5 (2C), 56.0, 66.4, 70.2, 129.3, 129.7. Anal. Calcd for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63; O, 7.57. Found: C, 73.58; H, 11.91; N, 6.49.

1-(*n*-Buthoxylmethyl-2-propenyl)piperidine (4j): Compound **4j** could not be isolated in pure form. Partial ^{1}H-NMR spectra was obtained from the mixture of (*Z*)-**3j**. ^{1}H-NMR (400 MHz, C_6D_6) δ 5.16 (d, *J* = 9.8 Hz, 1H), 5.18 (d, *J* = 18.8 Hz, 1H), 5.88 (ddd, *J* = 18.8, 9.8, 7.3 Hz, 1H).

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