Supporting Information for:

Facile Preparation of Various Heteroaromatic Compounds via Azatitanacyclopentadiene Intermediates

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Experimental Section

General. ^1H and ^{13}C NMR spectra were taken on a Varian Gemini-300 spectrometer at 300 and 75 MHz, respectively. CDCl_3 was used as the solvent. Chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^1H) or based on the middle peak of the solvent (CDCl_3) (δ 77.00 ppm for ^{13}C NMR) as an internal standard. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (J) are given in hertz. Infrared (IR) spectra were recorded on a JASCO A-100 spectrometer and are reported in wave numbers (cm^{-1}). $\text{Ti}(\text{O}-i\text{-Pr})_4$ was distilled and stocked under argon atmosphere. Isopropylmagnesium chloride was prepared in Et_2O as a 1.3-1.7 M solution from isopropyl chloride and magnesium turnings by the usual procedure, titrated, and stocked under an argon atmosphere. All reactions were carried out under argon. Dry solvents (THF, ethyl ether, CH_2Cl_2) were purchased from Kanto Chemicals Co. (Japan). Chemicals were purified or dried in a standard manner, if necessary.

(*E*)-3-Butyl-1-methoxy-3-octen-2-one (8). To a stirred solution of 5-decyne (0.030 mL, 0.168 mmol) and $\text{Ti}(\text{O}-i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.58 M in Et_2O , 0.278 mL, 0.437 mmol) at $-78\text{ }^\circ\text{C}$ under argon to give a yellow homogeneous solution. The solution was warmed to $-50\text{ }^\circ\text{C}$ over 30 min, during which period its color turned black. After stirring at $-50\text{ }^\circ\text{C}$ for 3 h, α -methoxyacetonitrile (0.010 mL, 0.134 mmol) was introduced to the reaction mixture at $-50\text{ }^\circ\text{C}$ and the solution was stirred for 3 h. After the reaction was terminated by

the addition of 3*N* HCl (1.5 mL) and quickly warmed up to room temperature, the resulting mixture was vigorously stirred for 3 h. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO₃, dried over Na₂SO₄, and concentrated to a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (21 mg, 74%) as a colorless oil.

¹H NMR δ 0.89 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 6.9 Hz, 3H), 1.18-1.53 (m, 8H), 2.24 (q, *J* = 7.5 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 3.42 (s, 3H), 4.39 (s, 2H), 6.51 (t, *J* = 7.2 Hz, 1H). Irradiation of the proton at δ 6.51 ppm (C=CH) showed 6% nOe enhancement to the peak at δ 4.39 ppm (CH₂OMe). Thus, the stereochemistry has been confirmed.

¹³C NMR δ 13.76, 13.79, 22.40, 22.68, 25.26, 28.39, 30.91, 31.33, 59.15, 74.45, 140.34, 143.10, 197.41.

IR (neat) 2960, 2929, 2862, 1682 (C=O), 1637, 1458, 1385, 1262, 1197, 1103, 930, 850, 700 cm⁻¹.

Anal. Calcd for C₁₃H₂₄O₂: C, 73.54; H, 11.39. Found: C, 73.33; H, 11.52.

(*E*)-3-Butyl-4-deuterio-1-methoxy-3-octen-2-one (8-*d*)

¹H NMR δ 0.89 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 6.9 Hz, 3H), 1.18-1.53 (m, 8H), 2.24 (t, *J* = 7.5 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 3.42 (s, 3H), 4.39 (s, 2H). The peak at δ 6.51 ppm (C=CH) of (*E*)-3-butyl-1-methoxy-3-octen-2-one (**8**) disappeared to show 98% deuterium incorporation.

3,4-Dibutyl-2-(methoxymethyl)pyridine (18). To a stirred solution of 5-decyne (0.030 mL, 0.168 mmol) and Ti(O-*i*-Pr)₄ (0.062 mL, 0.210 mmol) in 1.5 mL of Et₂O was added *i*-PrMgCl (1.575 M in Et₂O, 0.278 mL, 0.437 mmol) at -78 °C under argon to give a yellow homogeneous solution. The solution was warmed to -50 °C over 30 min, during which period its color turned black. After stirring at -50 °C for an additional 3 h, α-methoxyacetonitrile (0.015 mL, 0.202 mmol) was introduced to the reaction mixture at -50 °C and the solution was stirred for another 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (24 mg, 0.134 mmol) was added and the reaction mixture was stirred for 3 h at -30 °C. The reaction was terminated by the addition of water (0.06 mL) and quickly warmed up to room temperature. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ¹H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (24 mg, 76%) as a colorless oil, which was fully characterized by ¹H and ¹³C NMR, IR, and elemental analyses.

^1H NMR δ 0.95 (t, J = 6.9 Hz, 3H), 0.97 (t, J = 6.9 Hz, 3H), 1.30-1.65 (m, 8H), 2.60 (t, J = 7.8 Hz, 2H), 2.86 (t, J = 7.8 Hz, 2H), 3.44 (s, 3H), 4.59 (s, 2H), 7.02 (d, J = 4.8 Hz, 1H), 8.31 (d, J = 4.8 Hz, 1H).

^{13}C NMR δ 13.72, 13.77, 22.63, 23.15, 27.32, 31.55, 32.51, 32.95, 58.52, 74.63, 123.92, 135.66, 146.31, 150.61, 155.07.

IR (neat) 3049, 2957, 2927, 2870, 2821, 1586, 1560, 1458, 1376, 1099, 955, 920, 830, 725 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{NO}$: C, 76.55; H, 10.71. Found: C, 76.22; H, 10.36.

3,4-Dibutyl-6-deuterio-2-(methoxymethyl)pyridine (18-d).

^1H NMR δ 0.95 (t, J = 6.9 Hz, 3H), 0.97 (t, J = 6.9 Hz, 3H), 1.30-1.65 (m, 8H), 2.60 (t, J = 7.8 Hz, 2H), 2.86 (t, J = 7.8 Hz, 2H), 3.44 (s, 3H), 4.59 (s, 2H), 7.02 (s, 1H). The peak at δ 8.31 ppm (Py-H) of 3,4-dibutyl-2-(methoxymethyl)pyridine (**18**) disappeared to show 98% deuterium incorporation.

3,4-Dibutyl-2-(1-methoxynonyl)pyridine (21). To a stirred solution of 5-decyne (0.103 mL, 0.576 mmol) and $\text{Ti}(\text{O}-i\text{-Pr})_4$ (0.213 mL, 0.720 mmol) in 6 mL of Et_2O was added $i\text{-PrMgCl}$ (1.575 M in Et_2O , 0.950 mL, 1.50 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for an additional 3 h, 2-methoxydecenenitrile (0.145 mL, 0.692 mmol) was introduced to the reaction mixture at -50°C and the solution was stirred for another 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (73 mg, 0.403 mmol) was added and the reaction mixture was stirred for 3 h at -30°C . The reaction was terminated by the addition of water (0.2 mL) and quickly warmed up to room temperature. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (89 mg, 63%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.86 (t, J = 6.9 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 6.9 Hz, 3H), 1.15-1.75 (m, 21H), 1.92 (symmetric m, 1H), 2.60 (t, J = 7.2 Hz, 2H), 2.66 (symmetric m, 2H), 3.22 (s, 3H), 4.51 (d/d, J = 5.1, 7.8 Hz, 1H), 6.97 (d, J = 5.1 Hz, 1H), 8.39 (d, J = 5.1 Hz, 1H).

^{13}C NMR δ 13.75, 13.80, 13.96, 22.54, 22.69, 23.15, 26.01, 26.83, 29.16, 29.40, 29.54, 31.74, 31.77, 32.65, 33.16, 35.64, 56.50, 80.73, 123.00, 134.40, 146.97, 150.16, 158.54.

IR (neat) 3041, 2960, 2927, 2854, 1559, 1458, 1262, 1107, 846 cm^{-1} .

Anal. Calcd for C₂₃H₄₁NO: C, 79.48; H, 11.89. Found: C, 79.43; H, 12.00.

3-Hexyl-2-(methoxymethyl)-4-(trimethylsilyl)pyridine (23). To a stirred solution of 1-(trimethylsilyl)-1-octyne (31 mg, 0.168 mmol) and Ti(O-*i*-Pr)₄ (0.062 mL, 0.210 mmol) in 1.5 mL of Et₂O was added *i*-PrMgCl (1.575 M in Et₂O, 0.278 mL, 0.437 mmol) at -78 °C under argon to give a yellow homogeneous solution. The solution was warmed to -50 °C over 30 min, during which period its color turned black. After stirring at -50 °C for an additional 3 h, α-methoxyacetonitrile (0.015 mL, 0.202 mmol) was introduced to the reaction mixture at -50 °C and the solution was stirred for another 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (21 mg, 0.118 mmol) was added and the reaction mixture was stirred for 3 h at -30 °C. The reaction was terminated by the addition of water (0.06 mL) and quickly warmed up to room temperature. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ¹H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (19 mg, 58%) as a colorless oil, which was fully characterized by ¹H and ¹³C NMR, IR, and elemental analyses.

¹H NMR δ 0.33 (s, 9H), 0.91 (t, *J* = 6.9 Hz, 3H), 1.15-1.55 (m, 8H), 2.76 (t, *J* = 7.2 Hz, 2H), 3.46 (s, 3H), 4.60 (s, 2H), 7.28 (d, *J* = 4.8 Hz, 1H), 8.40 (d, *J* = 4.8 Hz, 1H). Irradiation of the proton at δ 0.33 ppm (SiMe₃) showed 12% nOe enhancement to the peak at δ 7.28 ppm (Py-H). Irradiation of the proton at δ 4.60 ppm (CH₂OMe) showed 3% nOe enhancement to the peak at δ 2.76 ppm (PyCH₂). Thus, the regiochemistry has been confirmed.

¹³C NMR δ 0.07, 13.91, 22.51, 29.86, 31.52, 32.27, 32.62, 58.71, 74.17, 128.98, 142.50, 145.89, 149.28, 154.42.

IR (neat) 3060, 3041, 2960, 2926, 2862, 2821, 1559, 1457, 1251, 1104, 837, 764 cm⁻¹.

Anal. Calcd for C₁₆H₂₉NOSi: C, 68.76; H, 10.46. Found: C, 68.51; H, 10.29.

6-Deuterio-3-hexyl-2-(methoxymethyl)-4-(trimethylsilyl)pyridine (23-*d*). ¹H NMR δ 0.33 (s, 9H), 0.91 (t, *J* = 6.9 Hz, 3H), 1.15-1.55 (m, 8H), 2.76 (t, *J* = 7.2 Hz, 2H), 3.46 (s, 3H), 4.60 (s, 2H), 7.28 (s, 1H). The peak at δ 8.40 ppm (Py-H) of 3-hexyl-2-(methoxymethyl)-3-(trimethylsilyl)pyridine (**23**) disappeared to show 94% deuterium incorporation.

3-Hexyl-6-iodo-2-(methoxymethyl)-4-(trimethylsilyl)pyridine (24). To a stirred solution of 1-

(trimethylsilyl)-1-octyne (105 mg, 0.576 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.213 mL, 0.720 mmol) in 6 mL of Et_2O was added $i\text{-PrMgCl}$ (1.575 M in Et_2O , 0.950 mL, 1.50 mmol) at $-78\text{ }^\circ\text{C}$ under argon to give a yellow homogeneous solution. The solution was warmed to $-50\text{ }^\circ\text{C}$ over 30 min, during which period its color turned black. After stirring at $-50\text{ }^\circ\text{C}$ for an additional 3 h, α -methoxyacetonitrile (0.051 mL, 0.692 mmol) was introduced to the reaction mixture at $-50\text{ }^\circ\text{C}$ and the solution was stirred for another 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (73 mg, 0.403 mmol) was added. After stirring for 3 h at $-30\text{ }^\circ\text{C}$, I_2 (585 mg, 2.31 mmol) in 6 mL of THF was added and the solution was rapidly warmed up to room temperature. After being stirred for 1 h at that temperature, aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (1.0 mL) was added. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (82 mg, 50%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.32 (s, 9H), 0.90 (t, $J = 6.9\text{ Hz}$, 3H), 1.12-1.55 (m, 8H), 2.70 (t, $J = 6.9\text{ Hz}$, 2H), 3.42 (s, 3H), 4.51 (s, 2H), 7.64 (s, 1H).

^{13}C NMR δ -0.11, 13.89, 22.46, 29.79, 31.45, 31.96, 32.12, 58.65, 73.88, 115.24, 139.97, 142.33, 153.03, 156.71.

IR (neat) 2960, 2926, 2862, 1515, 1458, 1409, 1252, 1197, 1123, 1107, 840, 764 cm^{-1} .

Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{INOSi}$: C, 47.40; H, 6.96. Found: C, 47.49; H, 7.11.

3-Hexyl-2-(1-methoxynonyl)-4-(trimethylsilyl)pyridine (25). To a stirred solution of 1-(trimethylsilyl)-1-octyne (105 mg, 0.576 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.213 mL, 0.720 mmol) in 6 mL of Et_2O was added $i\text{-PrMgCl}$ (1.575 M in Et_2O , 0.950 mL, 1.50 mmol) at $-78\text{ }^\circ\text{C}$ under argon to give a yellow homogeneous solution. The solution was warmed to $-50\text{ }^\circ\text{C}$ over 30 min, during which period its color turned black. After stirring at $-50\text{ }^\circ\text{C}$ for an additional 3 h, 2-methoxydecanenitrile (0.145 mL, 0.692 mmol) was introduced to the reaction mixture at $-50\text{ }^\circ\text{C}$ and the solution was stirred for another 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (73 mg, 0.403 mmol) was added and the reaction mixture was stirred for 3 h at $-30\text{ }^\circ\text{C}$. The reaction was terminated by the addition of water (0.2 mL) and quickly warmed up to room temperature. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was

chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (87 mg, 57%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.34 (s, 9H), 0.86 (t, J = 6.9 Hz, 3H), 0.91 (t, J = 6.9 Hz, 3H), 1.10-1.82 (m, 21H), 1.95 (symmetric m, 1H), 2.71 (symmetric m, 2H), 3.23 (s, 3H), 4.51 (d/d, J = 4.8, 8.1 Hz, 1H), 7.23 (d, J = 4.8 Hz, 1H), 8.48 (d, J = 4.8 Hz, 1H). Irradiation of the proton at δ 0.34 ppm (SiMe_3) showed 18% nOe enhancement to the peak at δ 7.23 ppm (Py-H). Irradiation of the proton at δ 4.51 ppm (CH_2OMe) showed 3% nOe enhancement to the peak at δ 2.71 ppm (PyCH_2). Thus, the regiochemistry has been confirmed.

^{13}C NMR δ 0.12, 13.90, 13.97, 22.51, 22.55, 26.03, 29.17, 29.42, 29.55, 29.82, 31.55, 31.77, 32.48 (2 peaks), 35.76, 56.42, 79.44, 128.13, 141.14, 146.66, 148.66, 158.03.

IR (neat) 3061, 3029, 2960, 2927, 2856, 1559, 1453, 1252, 1065, 974, 915, 754, 698 cm^{-1} .

Anal. Calcd for $\text{C}_{24}\text{H}_{45}\text{NOSi}$: C, 73.59; H, 11.58. Found: C, 73.42; H, 11.26.

2-(Chloromethyl)-3-hexyl-4-(trimethylsilyl)pyridine (27). To a stirred solution of 1-(trimethylsilyl)-1-octyne (105 mg, 0.576 mmol) and $\text{Ti}(\text{O}-i\text{-Pr})_4$ (0.213 mL, 0.720 mmol) in 6 mL of Et_2O was added $i\text{-PrMgCl}$ (1.575 M in Et_2O , 0.950 mL, 1.50 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for an additional 3 h, α -chloroacetonitrile (0.044 mL, 0.692 mmol) was introduced to the reaction mixture at -50°C and the solution was stirred for another 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (73 mg, 0.403 mmol) was added and the reaction mixture was stirred for 3 h at -30°C . The reaction was terminated by the addition of water (0.2 mL) and quickly warmed up to room temperature. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (61 mg, 53%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.35 (s, 9H), 0.91 (t, J = 6.9 Hz, 3H), 1.15-1.70 (m, 8H), 2.80 (t, J = 7.5 Hz, 2H), 4.73 (s, 2H), 7.31 (d, J = 4.8 Hz, 1H), 8.41 (d, J = 4.8 Hz, 1H). Irradiation of the proton at δ 0.35 ppm (SiMe_3) showed 12% nOe enhancement to the peak at δ 7.31 ppm (Py-H). Irradiation of the proton at δ 4.73 ppm (CH_2Cl) showed 3% nOe enhancement to the peak at δ 2.80 ppm (PyCH_2). Thus, the regiochemistry has been confirmed.

^{13}C NMR δ 0.04, 13.92, 22.51, 29.84, 31.52, 32.47, 32.88, 45.16, 129.65, 142.24, 146.54, 150.16, 153.90.

IR (neat) 3060, 3041, 2960, 2925, 2854, 1559, 1458, 1395, 1252, 1135, 1089, 914, 840, 759, 701 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{ClNSi}$: C, 63.46; H, 9.23. Found: C, 63.33; H, 9.18.

2-(Methoxymethyl)-3-phenyl-4-(trimethylsilyl)pyridine (29). To a stirred solution of 1-phenyl-2-(trimethylsilyl)acetylene (0.113 mL, 0.576 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.213 mL, 0.720 mmol) in 6 mL of Et_2O was added $i\text{-PrMgCl}$ (1.575 M in Et_2O , 0.950 mL, 1.50 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for an additional 3 h, α -methoxyacetonitrile (0.051 mL, 0.692 mmol) was introduced to the reaction mixture at -50°C and the solution was stirred for another 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (73 mg, 0.403 mmol) was added and the reaction mixture was stirred for 3 h at -30°C . The reaction was terminated by the addition of water (0.2 mL) and quickly warmed up to room temperature. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (61 mg, 56%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ -0.60 (s, 9H), 3.27 (s, 3H), 4.22 (s, 2H), 7.18-7.24 (m, 2H), 7.35-7.43 (m, 3H), 7.41 (d, $J = 4.8$ Hz, 1H), 8.59 (d, $J = 4.8$ Hz, 1H). Irradiation of the proton at δ -0.60 ppm (SiMe_3) showed 12% nOe enhancement to the peak at δ 7.41 ppm (Py-H). Irradiation of the proton at δ 4.22 ppm (CH_2OMe) showed 3% nOe enhancement to the peak at δ 7.18-7.24 ppm (Ph-H). Thus, the regiochemistry has been confirmed.

^{13}C NMR δ -0.45, 58.53, 73.53, 127.85, 127.96, 129.94, 139.31, 142.62, 147.47, 149.62, 153.85.

IR (neat) 3058, 3033, 2960, 2926, 2854, 2821, 1457, 1376, 1250, 1097, 841, 578 cm^{-1} .

Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NOSi}$: C, 70.80; H, 7.80. Found: C, 70.99; H, 7.75.

(S)-3,4-Dibutyl-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]pyridine (32). To a stirred solution of 5-decyne (0.030 mL, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.575 M in Et_2O , 0.267 mL, 0.420 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its

color turned black. After stirring at -50 °C for 3 h, (*S*)-2-[(*tert*-butyl)dimethylsilyloxy]propanenitrile (34 mg, 0.185 mmol) in 1 mL of Et₂O was introduced to the reaction mixture at -50 °C and the solution was stirred for 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (24 mg, 0.134 mmol) was added and the reaction mixture was stirred for 3 h at -30 °C. The reaction was terminated by the addition of water (0.06 mL) and quickly warmed up to room temperature. The resulting heterogeneous mixture was dried with anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil, careful analysis of which by ¹H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (34 mg, 73%) as a yellow oil.

¹H NMR δ -0.03 (s, 3H), -0.02 (s, 3H), 0.84 (s, 9H), 0.92-1.00 (m, 6H), 1.34-1.61 (m, 8H), 1.51 (d, *J* = 6.6 Hz, 3H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.75 (m, 2H), 5.19 (q, *J* = 6.6 Hz, 1H), 6.95 (d, *J* = 4.8 Hz, 1H), 8.31 (d, *J* = 4.8 Hz, 1H). Irradiation of the proton at δ 5.19 ppm (CHMe) showed 2% nOe enhancement to the peak at δ 1.51 ppm (CHMe) and 3% nOe enhancement to the peak at δ 2.75 ppm (PyCH₂). Irradiation of the proton at δ 6.95 ppm (Py-β-H) showed 2% nOe enhancement to the peak at δ 2.59 ppm (PyCH₂) and 8% nOe enhancement to the peak at δ 8.31 ppm (Py-β-H). Thus, the regiochemistry has been confirmed.

¹³C NMR δ -4.74, -4.65, 13.72, 13.80, 18.18, 22.65, 23.25, 24.15, 25.83, 26.96, 31.62, 32.69, 33.37, 70.63, 123.00, 133.30, 146.31, 150.56, 160.95.

IR (neat) 3047, 2956, 2929, 2858, 1584, 1463, 1253, 1092, 972, 938, 835, 812, 776, 669 cm⁻¹.

Anal. Calcd for C₂₁H₃₉NOSi: C, 71.79; H, 10.78. Found: C, 71.79; H, 10.78.

[α]_D²⁸ -7.5 (c 0.43, CHCl₃) for a sample of >99% ee.

(*S*)-3,4-Dibutyl-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]-6-deuteriopyridine (32-d**).**

¹H NMR δ -0.03 (s, 3H), -0.02 (s, 3H), 0.84 (s, 9H), 0.92-1.00 (m, 6H), 1.34-1.61 (m, 8H), 1.51 (d, *J* = 6.6 Hz, 3H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.75 (m, 2H), 5.19 (q, *J* = 6.6 Hz, 1H), 6.95 (s, 1H). The peak at δ 8.31 ppm (Py-α-H) of (*S*)-3,4-dibutyl-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]pyridine (**32**) disappeared to show 97% deuterium incorporation.

(*S*)-3,4-Dibutyl-2-[1-(hydroxy)ethyl]pyridine (for Determination of the Enantiopurity of **32).**

To a stirred solution of (*S*)-3,4-dibutyl-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]pyridine (**32**) (20 mg, 0.057 mmol) in 1 mL of THF was added a 1.0 M solution of tetra(*n*-butyl)ammonium fluoride (0.1 mL, 0.1 mmol) at room temperature under argon. After stirring at room temperature for 3 h, 1 mL of water was

added. The organic phase was separated, and the aqueous layer was extracted with ether. The combined organic layers were dried (Na_2SO_4) and concentrated to a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (12 mg, 87%) as a colorless oil.

^1H NMR δ 0.93-0.99 (m, 6H), 1.35-1.63 (m, 8H), 1.41 (d, $J = 6.3$ Hz, 3H), 2.47-2.68 (m, 4H), 4.73 (s, 1H), 5.00 (q, $J = 6.3$ Hz, 1H), 7.01 (d, $J = 4.8$ Hz, 1H), 8.28 (d, $J = 4.8$ Hz, 1H).

^{13}C NMR δ 13.68, 13.79, 22.68, 23.15, 25.23, 26.68, 31.55, 32.60, 32.78, 65.86, 123.24, 131.93, 145.49, 150.76, 160.67.

IR (neat) 3393, 3049, 2958, 2929, 2871, 1589, 1457, 1388, 1125, 1085, 1014, 834, 669 cm^{-1} .

$[\alpha]_{\text{D}}^{28}$ -27.8 (c 0.23, CHCl_3) for a sample of >99% ee.

The ee value of this sample was determined to be more than 99% based on the Mosher ester method.

A characteristic peak of the (*R*)-MTPA ester from (*S*)-MTPACl and (*S*)-3,4-dibutyl-2-[1-(hydroxy)ethyl]pyridine: ^1H NMR δ 8.36 (d, $J = 5.1$ Hz, 1H, Py- α -H).

A characteristic peak of the (*S*)-MTPA ester from (*R*)-MTPACl and (*S*)-3,4-dibutyl-2-[1-(hydroxy)ethyl]pyridine: ^1H NMR δ 8.26 (d, $J = 5.1$ Hz, 1H, Py- α -H).

Thus, the enantiopurity of **32** was determined to be at least 99% ee.

(*S*)-3,4-Dibutyl-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]6-iodopyridine (33). To a stirred solution of 5-decyne (0.030 mL, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added *i*-PrMgCl (1.575 M in Et_2O , 0.267 mL, 0.420 mmol) at -78 $^\circ\text{C}$ under argon to give a yellow homogeneous solution. The solution was warmed to -50 $^\circ\text{C}$ over 30 min, during which period its color turned black. After stirring at -50 $^\circ\text{C}$ for 3 h, (*S*)-2-[(*tert*-butyl)dimethylsilyloxy]propanenitrile (34 mg, 0.185 mmol) in 1 mL of Et_2O was introduced to the reaction mixture at -50 $^\circ\text{C}$ and the solution was stirred for 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (24 mg, 0.134 mmol) was added. After stirring for 3 h at -30 $^\circ\text{C}$, I_2 (170 mg, 0.672 mmol) in 1.5 mL of THF was added and the solution was rapidly warmed up to room temperature. After being stirred for 1 h at that temperature, an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (0.25 mL) was added. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated to a crude oil, careful analysis of which by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl ether) to afford the title compound (44 mg, 69%) as a colorless oil.

^1H NMR δ -0.04 (s, 3H), -0.02 (s, 3H), 0.84 (s, 9H), 0.92-0.97 (m, 6H), 1.33-1.58 (m, 8H), 1.48 (d, J = 6.6 Hz, 3H), 2.50 (t, J = 7.8 Hz, 2H), 2.71 (m, 2H), 5.09 (q, J = 6.6 Hz, 1H), 7.38 (s, 1H).

^{13}C NMR δ -4.65, -4.52, 13.70, 13.75, 18.13, 22.62, 23.22, 23.92, 25.79, 26.65, 31.07, 32.48, 33.13, 71.48, 114.33, 133.65, 133.84, 153.31, 163.10.

IR (neat) 2957, 2928, 2857, 1560, 1540, 1465, 1424, 1253, 1102, 969, 938, 853, 835, 812, 776, 669 cm^{-1} .

Anal. Calcd for $\text{C}_{21}\text{H}_{38}\text{INOSi}$: C, 53.04; H, 8.05. Found: C, 52.82; H, 7.73.

$[\alpha]_{\text{D}}^{28}$ -59.6 (c 0.55, CHCl_3).

(*S*)-3,4-Dibutyl-2-[[(*tert*-butyl)dimethylsilyloxy](phenyl)methyl]pyridine (34**).**

^1H NMR δ -0.18 (s, 3H), 0.10 (s, 3H), 0.69 (t, J = 7.2 Hz, 3H), 0.91 (s, 9H, CMe_3), 0.89-1.57 (m, 11H), 2.33-2.62 (m, 3H), 2.88 (m, 1H), 6.16 (s, 1H), 7.01 (d, J = 4.8 Hz, 1H), 7.16-7.41 (m, 5H), 8.31 (d, J = 4.8 Hz, 1H).

^{13}C NMR δ -5.29, -5.04, 13.52, 13.77, 18.22, 22.58, 23.28, 25.82, 26.84, 31.03, 31.84, 32.62, 79.96, 123.60, 125.41, 126.44, 127.91, 135.71, 144.16, 145.32, 152.10, 160.59.

IR (neat) 3047, 3017, 2956, 2918, 2862, 1584, 1463, 1252, 1089, 1066, 868, 836, 778, 706 cm^{-1} .

Anal. Calcd for $\text{C}_{27}\text{H}_{45}\text{NOSi}_2$: C, 75.85; H, 10.04. Found: C, 75.84; H, 9.90.

$[\alpha]_{\text{D}}^{25}$ -93.3 (c 1.25, CHCl_3) for a sample of >99% ee.

(*S*)-3,4-Dibutyl-2-[phenyl(hydroxy)methyl]pyridine (for Determination of the Enantiopurity of **34).** This was prepared in 88% yield by the desilylation of (*S*)-3,4-dibutyl-2-[[(*tert*-butyl)dimethylsilyloxy](phenyl)methyl]pyridine (**34**) with tetra(*n*-butyl)ammonium fluoride, according to the procedure from (*S*)-3,4-dibutyl-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]pyridine (**32**) to 3,4-dibutyl-2-(1-hydroxyethyl)pyridine.

^1H NMR δ 0.83 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.22-1.60 (m, 8H), 2.44 (t, J = 8.1 Hz, 2H), 2.57 (m, 2H), 5.79 (s, 1H), 6.16 (s, 1H), 7.08 (d, J = 4.8 Hz, 1H), 7.22-7.31 (m, 5H), 8.37 (d, J = 4.8 Hz, 1H).

^{13}C NMR δ 13.60, 13.76, 22.65, 23.16, 26.88, 31.30, 31.58, 32.51, 72.36, 123.65, 127.70, 127.84, 128.62, 133.36, 143.86, 144.63, 151.30, 157.52.

IR (neat) 3337, 3060, 3029, 2957, 2927, 2871, 1590, 1456, 1429, 1394, 1192, 1076, 1048, 829, 760, 700 cm^{-1} .

$[\alpha]_{\text{D}}^{25}$ 11.1 (c 0.85, CHCl_3) for a sample of >99% ee.

The ee value of this sample was determined to be more than 99% based on the Mosher ester method.

Characteristic peaks of the (*R*)-MTPA ester from (*S*)-MTPACl and (*S*)-3,4-dibutyl-2-[phenyl(hydroxy)methyl]pyridine: ^1H NMR δ 3.52 (s, 3H, OMe), 7.01 (d, J = 4.8 Hz, 1H, Py- β -H), 7.20 (s, 1H, CHPh), 8.40 (d, J = 4.8 Hz, 1H, Py- α -H).

Characteristic peaks of the (*S*)-MTPA ester from (*R*)-MTPACl and (*S*)-3,4-dibutyl-2-[phenyl(hydroxy)methyl]pyridine: ^1H NMR δ 3.60 (s, 3H, OMe), 7.05 (d, J = 4.8 Hz, 1H, Py- β -H), 7.22 (s, 1H, CHPh), 8.29 (d, J = 4.8 Hz, 1H, Py- α -H).

Thus, the enantiopurity of **34** was determined to be at least 99% ee.

(*S*)-2-[1-[(*tert*-Butyl)dimethylsilyloxy]ethyl]-3-hexyl-4-(trimethylsilyl)pyridine (35). To a stirred solution of 1-(trimethylsilyl)-1-octyne (31 mg, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added *i*-PrMgCl (1.575 M in Et_2O , 0.278 mL, 0.437 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for 3 h, (*S*)-2-[(*tert*-butyl)dimethylsilyloxy]propanenitrile (34 mg, 0.185 mmol) in 1 mL of Et_2O was introduced to the reaction mixture at -50°C and the solution was stirred for 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (21 mg, 0.118 mmol) was added and the reaction mixture was stirred for 3 h at -30°C . The reaction was terminated by the addition of water (0.06 mL) and quickly warmed up to room temperature. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated to a crude oil, careful analysis of which by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (30 mg, 65%) as a colorless oil.

^1H NMR δ -0.04 (s, 3H), -0.03 (s, 3H), 0.32 (s, 9H), 0.83 (s, 9H), 0.91 (m, 3H), 1.32-1.44 (m, 8H), 1.53 (d, J = 6.6 Hz, 3H), 2.78 (m, 2H), 5.21 (q, J = 6.6 Hz, 1H), 7.21 (d, J = 4.5 Hz, 1H), 8.43 (d, J = 4.5 Hz, 1H). Irradiation of the proton at δ 0.32 ppm (SiMe_3) showed 15% nOe enhancement to the peak at δ 7.21 ppm (Py- β -H). Irradiation of the proton at δ 5.21 ppm (CHMe) showed 2% nOe enhancement to the peak at δ 1.53 ppm (CHMe) and 4% nOe enhancement to the peak at δ 2.78 ppm (Py CH_2). Thus, the regiochemistry has been confirmed.

^{13}C NMR δ -4.73, -4.47, 0.10, 13.90, 18.19, 22.53, 24.19, 25.80, 29.86, 31.56, 32.64, 32.88, 68.57, 128.06, 139.82, 146.12, 148.94, 160.20.

IR (neat) 3034, 2955, 2928, 2856, 1577, 1472, 1399, 1363, 1252, 1116, 1032, 965, 835, 775 cm^{-1} .

Anal. Calcd for $\text{C}_{22}\text{H}_{43}\text{NOSi}_2$: C, 67.11; H, 11.01. Found: C, 67.30; H, 10.85.

$[\alpha]_{\text{D}}^{29}$ -1.79 (c 0.63, CHCl_3) for a sample of >99% ee.

(S)-2-[1-[(*tert*-Butyl)dimethylsilyloxy]ethyl]-6-deuterio-3-hexyl-4-(trimethylsilyl)pyridine

(35-d).

^1H NMR δ -0.04 (s, 3H), -0.03 (s, 3H), 0.32 (s, 9H), 0.83 (s, 9H), 0.91 (m, 3H), 1.32-1.44 (m, 8H), 1.53 (d, J = 6.6 Hz, 3H), 2.78 (m, 2H), 5.21 (q, J = 6.6 Hz, 1H), 7.21 (s, 1H). The peak at δ 8.43 ppm (Py- α -H) of 2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]-3-hexyl-4-(trimethylsilyl)pyridine (**35**) disappeared to show 97% deuterium incorporation.

(S)-3-Hexyl-2-(1-hydroxyethyl)pyridine (for Determination of the Enantiopurity of 35). To a stirred solution of (S)-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]-3-hexyl-4-(trimethylsilyl)pyridine (**35**) (20 mg, 0.051 mmol) in 1 mL of THF was added a 1.0 M solution of tetra(*n*-butyl)ammonium fluoride (0.2 mL, 0.2 mmol) at room temperature under argon. After stirring at room temperature for 3 h, 1 mL of water was added. The organic phase was separated, and the aqueous layer was extracted with ether. The combined organic layers were dried (Na_2SO_4) and concentrated to a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (7.6 mg, 72%) and (S)-3-hexyl-2-(1-hydroxyethyl)-4-(trimethylsilyl)pyridine (1.7 mg, 12%).

^1H NMR δ 0.89 (t, J = 6.9 Hz, 3H), 1.25-1.65 (m, 8H), 1.41 (d, J = 6.6 Hz, 3H), 2.57 (m, 2H), 4.79 (s, 1H), 5.02 (q, J = 6.6 Hz, 1H), 7.15 (dd, J = 4.8 Hz, 7.8 Hz, 1H), 7.49 (dd, J = 1.8 Hz, 7.8 Hz, 1H), 8.39 (dd, J = 1.8 Hz, 4.8 Hz, 1H).

^{13}C NMR δ 13.92, 22.46, 24.73, 29.16, 30.38, 30.46, 31.54, 65.66, 122.39, 133.74, 137.17, 145.71, 160.40.

IR (neat) 3414, 3055, 2956, 2928, 2857, 1458, 1400, 1094, 1012, 902, 782 cm^{-1} .

$[\alpha]_{\text{D}}^{29}$ -46.3 (c 0.08, CHCl_3) for a sample of >99% ee.

The ee value of this sample was determined to be more than 99% based on the Mosher ester method.

A characteristic peak of the (*R*)-MTPA ester from (S)-MTPACl and (S)-3-hexyl-2-(1-hydroxyethyl)pyridine: ^1H NMR δ 8.38 (dd, J = 1.8 Hz, 4.5 Hz, 1H, Py- α -H).

A characteristic peak of the (S)-MTPA ester from (*R*)-MTPACl and (S)-3-hexyl-2-(1-hydroxyethyl)pyridine: ^1H NMR δ 8.48 (dd, J = 1.8 Hz, 4.5 Hz, 1H, Py- α -H).

Thus, the enantiopurity of **35** was determined to be at least 99% ee.

(S)-2-[1-[(*tert*-Butyl)dimethylsilyloxy]ethyl]-3-hexyl-6-iodo-4-(trimethylsilyl)pyridine (36**).**

To a stirred solution of 1-(trimethylsilyl)-1-octyne (31 mg, 0.168 mmol) and $\text{Ti}(\text{O}-i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added *i*-PrMgCl (1.575 M in Et_2O , 0.278 mL, 0.437 mmol) at -

78 °C under argon to give a yellow homogeneous solution. The solution was warmed to -50 °C over 30 min, during which period its color turned black. After stirring at -50 °C for 3 h, (S)-2-[(*tert*-butyl)dimethylsilyloxy]propanenitrile (34 mg, 0.185 mmol) in 1 mL of Et₂O was introduced to the reaction mixture at -50 °C and the solution was stirred for 3 h. Then, pulverized ethynyl *p*-tolyl sulfone (21 mg, 0.118 mmol) was added. After stirring for 3 h at -30 °C, I₂ (170 mg, 0.672 mmol) in 1.5 mL of THF was added and the solution was rapidly warmed up to room temperature. After being stirred for 1 h at that temperature, an aqueous solution of Na₂S₂O₃ (0.25 mL) was added. The resulting heterogeneous mixture was dried with anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated to a crude oil, careful analysis of which by ¹H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl ether) to afford the title compound (30 mg, 49%) as a colorless oil.

¹H NMR δ -0.08 (s, 3H), -0.02 (s, 3H), 0.32 (s, 9H), 0.83 (s, 9H), 0.89 (m, 3H), 1.25-1.46 (m, 8H), 1.51 (d, *J* = 6.6 Hz, 3H), 2.72 (*J* = 7.8 Hz, 2H), 5.09 (q, *J* = 6.6 Hz, 1H), 7.57 (s, 1H).

¹³C NMR δ -4.42, -4.38, -0.04, 0.88, 13.90, 18.15, 22.51, 23.90, 25.77, 29.83, 31.56, 32.82, 69.49, 115.82, 139.02, 138.72, 152.97, 162.61.

IR (neat) 2956, 2928, 2856, 1506, 1472, 1415, 1362, 1253, 1186, 1033, 962, 837, 813, 775 cm⁻¹.

Anal. Calcd for C₂₂H₄₂INOSi₂: C, 50.85; H, 8.15. Found: C, 51.09; H, 8.23.

[α]_D²⁹ -58.6 (c 0.43, CHCl₃).

(S)-2-[(*tert*-Butyl)dimethylsilyloxy(phenyl)methyl]-3-hexyl-4-(trimethylsilyl)pyridine (37).

¹H NMR δ -0.18 (s, 3H), 0.08 (s, 3H), 0.29 (s, 9H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.91 (s, 9H), 0.98-1.26 (m, 8H), 2.45 (m, 1H), 3.03 (m, 1H), 6.18 (s, 1H), 7.17-7.45 (m, 5H), 7.28 (d, *J* = 4.8 Hz, 1H), 8.39 (d, *J* = 4.8 Hz, 1H).

¹³C NMR δ -5.20, -5.07, 0.25, 13.91, 18.21, 22.44, 25.80, 29.83, 31.59, 31.88, 32.41, 79.32, 125.58, 126.57, 127.97, 128.62, 142.94, 144.13, 144.78, 150.64, 159.62.

IR (neat) 3060, 3030, 2954, 2919, 2856, 1471, 1390, 1252, 1097, 1065, 838, 778, 700 cm⁻¹.

Anal. Calcd for C₂₇H₄₅NOSi₂: C, 71.14; H, 9.95. Found: C, 71.08; H, 9.67.

[α]_D²⁴ -106.8 (c 1.0, CHCl₃) for a sample of >99% ee.

(S)-3-Hexyl-2-[phenyl(hydroxy)methyl]pyridine (for Determination of the Enantiopurity of 37). This was prepared in 76% yield by the desilylation of (S)-2-[(*tert*-butyl)dimethylsilyloxy(phenyl)methyl]-3-hexyl-4-(trimethylsilyl)pyridine (37) with tetra(*n*-butyl)ammonium fluoride, according to the procedure from (S)-2-[1-[(*tert*-

butyl)dimethylsilyloxy]ethyl]-3-hexyl-4-(trimethylsilyl)pyridine (**35**) to (*S*)-3-hexyl-2-(1-hydroxyethyl)pyridine.

^1H NMR δ 0.85 (t, J = 6.9 Hz, 3H), 1.18-1.58 (m, 8H), 2.32 (m, 1H), 2.48 (m, 1H), 5.81 (s, 1H), 6.06 (s, 1H), 7.17-7.45 (m, 6H), 7.48 (dd, J = 1.5 Hz, 7.5 Hz, 1H), 8.48 (dd, J = 1.5 Hz, 4.8 Hz, 1H).

^{13}C NMR δ 13.90, 22.36, 29.07, 29.55, 30.54, 31.45, 72.22, 122.84, 127.79, 127.83, 128.62, 135.19, 137.55, 143.33, 144.96, 157.48.

IR (neat) 3372, 3060, 3029, 2960, 2926, 2856, 1577, 1493, 1456, 1405, 1043. 916, 799, 762, 699 cm^{-1} .

Anal. Calcd for $\text{C}_{27}\text{H}_{45}\text{NOSi}_2$: C, 71.14; H, 9.95. Found: C, 71.08; H, 9.67.

$[\alpha]_{\text{D}}^{24}$ 25.0 (c 1.2, CHCl_3) for a sample of >99% ee.

The ee value of this sample was determined to be more than 99% based on the Mosher ester method.

Characteristic peaks of the (*R*)-MTPA ester from (*S*)-MTPACl and (*S*)-3-hexyl-2-[phenyl(hydroxy)methyl]pyridine: ^1H NMR δ 3.54 (s, 3H, OMe), 8.40 (dd, J = 1.5 Hz, 4.8 Hz, 1H, Py-H).

Characteristic peaks of the (*S*)-MTPA ester from (*R*)-MTPACl and (*S*)-3-hexyl-2-[phenyl(hydroxy)methyl]pyridine: ^1H NMR δ 3.60 (s, 3H, OMe), 8.50 (dd, J = 1.5 Hz, 4.8 Hz, 1H, Py-H).

Thus, the enantiopurity of **37** was determined to be at least 99% ee.

(*S*)-2-[1-[(*tert*-Butyl)dimethylsilyloxy]ethyl]-3-phenyl-4-(trimethylsilyl)pyridine (38**).**

^1H NMR δ -0.18 (s, 3H), -0.16 (s, 3H), -0.08 (s, 9H), 0.77 (s, 9H), 1.34 (d, J = 6.3 Hz, 3H), 4.71 (q, J = 6.3 Hz, 1H), 7.12 (m, 1H), 7.22 (m, 1H), 7.37-7.41 (m, 3H), 7.35 (d, J = 4.5 Hz, 1H), 8.64 (d, J = 4.5 Hz, 1H). Irradiation of the proton at δ -0.08 ppm (SiMe_3) showed 13% nOe enhancement to the peak at δ 7.35 ppm (Py- β -H), 5% nOe enhancement to the peak at δ 7.12 ppm (Ph-H), and 5% nOe enhancement to the peak at δ 7.22 ppm (Ph-H). Irradiation of the proton at δ 1.34 ppm (CHMe) showed 14% nOe enhancement to the peak at δ 4.71 ppm (CHMe), 5% nOe enhancement to the peak at δ 7.12 ppm (Ph-H), and 1% nOe enhancement to the peak at δ 7.22 ppm (Ph-H). Thus, the regiochemistry has been confirmed.

^{13}C NMR δ -4.91, -4.71, -0.33, 18.15, 24.41, 25.82, 67.99, 127.30, 127.84, 127.86, 127.90, 132.10, 130.56, 139.64, 139.91, 148.03, 149.09, 159.86.

IR (neat) 3057, 3026, 2955, 2927, 2895, 2855, 1472, 1362, 1250, 1112, 961, 863, 836, 774, 758, 705 cm^{-1} .

Anal. Calcd for C₂₂H₃₅NOSi₂: C, 68.51; H, 9.15. Found: C, 68.55; H, 8.97.

[α]_D²⁸ -4.4 (c 0.61, CHCl₃) for a sample of >99% ee.

(S)-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]-6-deuterio-3-phenyl-4-(trimethylsilyl)pyridine (38-d).

¹H NMR δ -0.18 (s, 3H), -0.16 (s, 3H), -0.08 (s, 9H), 0.77 (s, 9H), 1.34 (d, *J* = 6.3 Hz, 3H), 4.71 (q, *J* = 6.3 Hz, 1H), 7.12 (m, 1H), 7.21 (m, 1H), 7.37-7.41 (m, 3H), 7.35 (s, 1H). The peak at δ 8.64 ppm (Py- α -H) of (S)-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]-3-phenyl-4-(trimethylsilyl)pyridine (**38**) disappeared to show 97% deuterium incorporation.

(S)-2-(1-Hydroxyethyl)-3-phenylpyridine (for Determination of the Enantiopurity of 38).

This was prepared in 76% yield by the desilylation of (S)-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]-3-phenyl-4-(trimethylsilyl)pyridine (**38**) with tetra(n-butyl)ammonium fluoride, according to the procedure from (S)-2-[1-[(*tert*-butyl)dimethylsilyloxy]ethyl]-3-hexyl-4-(trimethylsilyl)pyridine (**35**) to (S)-3-hexyl-2-(1-hydroxyethyl)pyridine.

¹H NMR δ 1.18 (d, *J* = 6.6 Hz, 3H), 4.52 (s, 1H), 5.04 (q, *J* = 6.6 Hz, 1H), 7.28-7.48 (m, 5H), 7.29 (dd, *J* = 4.8 Hz, 7.5 Hz, 1H), 7.55 (dd, *J* = 1.8 Hz, 7.5 Hz, 1H), 8.58 (dd, *J* = 1.8 Hz, 4.8 Hz, 1H).

¹³C NMR δ 24.14, 66.13, 122.24, 127.95, 128.72 (o- or m-Ph), 128.98, 135.14, 138.14, 138.47, 147.37, 160.20.

IR (neat) 3392, 3049, 2957, 2929, 2872, 1589, 1458, 1388, 1125, 1085, 1013, 834 cm⁻¹.

[α]_D²⁸ -53.8 (c 0.16, CHCl₃) for a sample of >99% ee.

The ee value of this sample was determined to be more than 99% based on the Mosher ester method.

A characteristic peak of the (*R*)-MTPA ester from (S)-MTPACl and (S)-2-(1-hydroxyethyl)-3-phenylpyridine: ¹H NMR δ 8.55 (dd, *J* = 1.8 Hz, 4.8 Hz, 1H, Py- α -H).

A characteristic peak of the (S)-MTPA ester from (R)-MTPACl and (S)-2-(1-hydroxyethyl)-3-phenylpyridine: ¹H NMR δ 8.64 (dd, *J* = 1.8 Hz, 4.8 Hz, 1H, Py- α -H).

Thus, the enantiopurity of **38** was determined to be at least 99% ee.

(S)-2-[1-[(*tert*-Butyl)dimethylsilyloxy]ethyl]-6-iodo-3-phenyl-4-(trimethylsilyl)pyridine (39).

¹H NMR δ -0.17 (s, 3H), -0.13 (s, 3H), -0.08 (s, 9H), 0.79 (s, 9H), 1.30 (d, *J* = 6.3 Hz, 3H), 4.60 (q, *J* = 6.3 Hz, 1H), 7.11 (m, 1H), 7.18 (m, 1H), 7.39-7.41 (m, 3H), 7.72 (s, 1H).

¹³C NMR δ -4.60, -0.45, 18.15, 24.09, 25.77, 68.34, 118.44, 127.99, 128.03, 128.15, 129.87, 130.54, 138.39, 139.31, 152.74, 162.26.

IR (neat) 3059, 3024, 2954, 2927, 2895, 2855, 1505, 1415, 1251, 1177, 1142, 964, 838, 776, 705 cm^{-1} .
Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{INOSi}_2$: C, 51.65; H, 6.70. Found: C, 51.71; H, 6.47.
 $[\alpha]_{\text{D}}^{29}$ -43.4 (*c* 2.4, CHCl_3).

(S)-2-[1-((*t*-Butyl)dimethylsiloxy)ethyl]-3-[(*t*-butyl)dimethylsiloxy)methyl]-6-iodo-4-(trimethylsilyl)pyridine (42). To a stirred solution of 3-[(*t*-butyl)dimethylsiloxy]-1-(trimethylsilyl)-1-propyne (500 mg, 2.06 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.760 mL, 2.58 mmol) in 25 mL of Et_2O was added *i*-PrMgCl (1.46 M in Et_2O , 3.53 mL, 5.16 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for an additional 3 h, (S)-2-[(*t*-butyl)dimethylsiloxy]propanenitrile (**30**) (0.491 mL, 2.27 mmol) was introduced to the reaction mixture at -50°C and the solution was warmed to -30°C and stirred for 4 h. Then, pulverized ethynyl *p*-tolyl sulfone (**14**) (260 mg, 1.44 mmol) was added. After stirring for 3 h at -30°C , I_2 (2.10 g, 8.25 mmol) in 15 mL of THF was added and the solution was rapidly warmed up to room temperature. After being stirred for 1 h at that temperature, an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (5 mL) was added. The resulting heterogeneous mixture was dried over anhydrous sodium sulfate and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (391 mg, 47%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

$[\alpha]_{\text{D}}^{24}$ -39.7 (*c* 1.00, CHCl_3) for a sample of 99% ee.

^1H NMR δ -0.07 (s, 6H), -0.05 (s, 6H), 0.34 (s, 9H), 0.84 (s, 9H), 0.90 (s, 9H), 1.53 (d, $J = 6.6$ Hz, 3H), 4.69 (d, $J = 11.4$ Hz, 1H), 4.92 (d, $J = 11.4$ Hz, 1H), 5.15 (q, $J = 6.6$ Hz, 1H), 7.63 (s, 1H).

^{13}C NMR δ -5.31, -5.29, -4.69, -4.49, 0.02, 18.05, 18.07, 24.25, 25.69, 25.86, 60.78, 70.04, 118.00, 136.17, 138.83, 153.94, 164.55.

IR (neat) 2960, 2929, 2886, 2857, 1507, 1472, 1410, 1362, 1254, 1181, 1096, 1004, 964, 838, 776, 669 cm^{-1} .

Anal. Calcd for $\text{C}_{23}\text{H}_{46}\text{INO}_2\text{Si}_3$: C, 47.65; H, 8.00. Found: C, 47.72; H, 7.91.

(S)-6-[1-((*t*-Butyl)dimethylsiloxy)ethyl]-5-[(*t*-butyl)dimethylsiloxy)methyl]-4-(trimethylsilyl)-2-pyridinecarboxaldehyde (43). To a stirred solution of (S)-2-[1-((*t*-

butyl)dimethylsiloxy)ethyl]-3-(((*t*-butyl)dimethylsiloxy)methyl)-6-iodo-4-(trimethylsilyl)pyridine (**42**) (224 mg, 0.386 mmol) in 3 mL of THF was added *t*-BuLi (1.40 M in pentane, 0.662 mL, 0.927 mmol) at -78 °C under argon. After stirring at -78 °C for 15 min, DMF (0.036 mL, 0.464 mmol) was introduced to the reaction mixture at -78 °C and the solution was warmed to room temperature and stirred for 1 h. The reaction was terminated by the addition of an aqueous solution of NH₄Cl and the organic products were extracted with ether. The combined organic layers were dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (134mg, 72%) as a colorless oil, which was fully characterized by IR, ¹H and ¹³C NMR, and elemental analyses.

$[\alpha]_D^{23}$ -13.2 (*c* 1.00, CHCl₃) for a sample of 99% ee.

¹H NMR δ -0.06 (s, 6H), -0.05 (s, 6H), 0.38 (s, 9H), 0.83 (s, 9H), 0.91 (s, 9H), 1.60 (d, *J* = 6.6 Hz, 3H), 4.82 (d, *J* = 11.4 Hz, 1H), 4.99 (d, *J* = 11.4 Hz, 1H), 5.35 (q, *J* = 6.6 Hz, 1H), 7.95 (s, 1H), 10.11 (s, 1H).

¹³C NMR δ -5.30, -5.28, -4.69, -4.56, 0.07, 18.09, 18.18, 24.32, 25.70, 25.84, 61.35, 69.56, 125.40, 141.69, 150.21, 152.02, 163.16, 194.78.

IR (neat) 2959, 2929, 2903, 1713 (C=O), 1570, 1472, 1362, 1255, 1146, 1115, 1062, 1005, 966, 934, 837, 775, 669 cm⁻¹.

Anal. Calcd for C₂₄H₄₇NO₃Si₃: C, 59.82; H, 9.83. Found: C, 59.86; H, 9.61.

(S)-2-(1-Hydroxyethyl)-3-(hydroxymethyl)-6-(dimethoxymethyl)pyridine (44). To a stirred solution of (S)-6-[1-((*t*-butyl)dimethylsiloxy)ethyl]-5-(((*t*-butyl)dimethylsiloxy)methyl)-4-(trimethylsilyl)-2-pyridinecarboxaldehyde (**43**) (172 mg, 0.357 mmol) in 4.5 mL of MeOH were added trimethoxymethane (0.117 mL, 1.07 mmol) and pyridium *p*-toluenesulfonate (18 mg, 0.071 mmol) at room temperature and refluxed for 10 h. After cooling to room temperature, the reaction mixture was evaporated. Then, Et₂O and an aqueous solution of NaHCO₃ were added to the residue and the organic products were extracted with ether. The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo* to give a crude oil. This crude product was dissolved in 5 mL of THF and then, TBAF (1.00 M in THF, 1.43 mL, 1.43 mmol) was added at room temperature under argon. After stirring at room temperature for 1 h, the reaction was terminated by the addition of an aqueous solution of NH₄Cl and the organic products were extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the

title compound (69 mg, 85%) as a colorless oil, which was fully characterized by IR, ^1H and ^{13}C NMR, and elemental analyses.

$[\alpha]_{\text{D}}^{25}$ -19.0 (c 0.80, CHCl_3) for a sample of 99% ee. lit. $[\alpha]_{\text{D}}^{26}$ -11.1 (c 0.98, CHCl_3) for a sample of 96% ee [Endoh, N.; Yonezawa, Y.; Shin, C. *Bull. Chem. Soc. Jpn.* **2003**, 76, 643-644].

^1H NMR δ 1.42 (d, J = 6.3 Hz, 3H), 2.77 (br s, 1H), 3.37 (s, 3H), 3.40 (s, 3H), 4.66 (d, J = 13.2 Hz, 1H), 4.69 (br s, 1H), 4.74 (d, J = 13.2 Hz, 1H), 5.00 (m, 1H), 5.34 (s, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H).

^{13}C NMR δ 23.96, 53.54, 53.62, 60.37, 66.35, 103.76, 120.00, 132.41, 136.97, 154.67, 159.42.

IR (neat) 3390, 2976, 2935, 2832, 1580, 1447, 1398, 1362, 1194, 1161, 1110, 1058, 992, 892, 847, 813 cm^{-1} .

Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_4$: C, 58.14; H, 7.54. Found: C, 58.27; H, 7.45.

Spectroscopic data of the compound were identical to those reported [Endoh, N.; Yonezawa, Y.; Shin, C. *Bull. Chem. Soc. Jpn.* **2003**, 76, 643-644. Shin, C.; Okabe, A.; Ito, A.; Yonezawa, Y. *Bull. Chem. Soc. Jpn.* **2002**, 75, 1583-1596].

(S)-3-[(*t*-Butyl)diphenylsiloxy)methyl]-2-(1-hydroxyethyl)-6-(dimethoxymethyl)pyridine

(**45**). The title compound was prepared from (S)-2-(1-hydroxyethyl)-3-(hydroxymethyl)-6-(dimethoxymethyl)pyridine (**44**) according to the reported procedure [Shin, C.; Okabe, A.; Ito, A.; Yonezawa, Y. *Bull. Chem. Soc. Jpn.* **2002**, 75, 1583-1596].

$[\alpha]_{\text{D}}^{27}$ -15.1 (c 0.98, CHCl_3) for a sample of 99% ee.

^1H NMR δ 1.08 (s, 9H), 1.27 (d, J = 6.3 Hz, 3H), 3.40 (s, 3H), 3.44 (s, 3H), 4.70 (d, J = 13.2 Hz, 1H), 4.71 (d, J = 13.2 Hz, 1H), 4.72 (br s, 1H), 4.80 (q, J = 6.3 Hz, 1H), 5.36 (s, 1H), 7.35-7.46 (m, 6H), 7.50 (d, J = 7.8 Hz, 1H), 7.62-7.70 (m, 4H), 7.91 (d, J = 7.8 Hz, 1H).

^{13}C NMR δ 19.14, 24.18, 26.68, 53.68, 53.90, 61.42, 65.58, 104.18, 119.89, 127.97, 130.07, 131.89, 132.83, 132.90, 135.59, 136.19, 154.54, 158.85. Some aromatic peaks inevitably overlap.

IR (neat) 3447, 3066, 3041, 2960, 2932, 2895, 1473, 1429, 1363, 1192, 1113, 1075, 1001, 863, 823, 741, 702 cm^{-1} .

Anal. Calcd for $\text{C}_{27}\text{H}_{35}\text{NO}_4\text{Si}$: C, 69.64; H, 7.58. Found: C, 69.89; H, 7.55.

Spectroscopic data of the compound were identical to those of racemic 3-[(*t*-butyl)diphenylsiloxy)methyl]-2-(1-hydroxyethyl)-6-(dimethoxymethyl)pyridine reported earlier [Shin, C.; Okabe, A.; Ito, A.; Yonezawa, Y. *Bull. Chem. Soc. Jpn.* **2002**, 75, 1583-1596.].

The enantiomeric excess (ee) of the title compound was determined to be 99% ee by ^1H NMR

analysis of the derived MTPA ester.

¹H NMR of the (*R*)-MTPA ester from (*S*)-MTPACl: δ 1.08 (s, 9H, *t*-BuSiPh₂), 1.60 (d, *J* = 6.3 Hz, 3H, Me), 3.28 (s, 3H, OMe), 3.38 (s, 3H, OMe), 3.45 (s, 3H, OMe), 4.76 (d, *J* = 13.2 Hz, 1H, CH₂OSi), 4.94 (d, *J* = 13.2 Hz, 1H, CH₂OSi), 5.18 (s, 1H, CH(OMe)₂), 6.13 (q, *J* = 6.3 Hz, 1H, MeCHPy), 7.20-7.50 (m, 11H, Ph- and Py-H), 7.60-7.75 (m, 6H, Ph- and Py-H).

¹H NMR of the (*S*)-MTPA ester from (*R*)-MTPACl: (only characteristic peaks are shown) δ 4.80 (d, *J* = 13.2 Hz, 1H, CH₂OSi), 5.00 (d, *J* = 13.2 Hz, 1H, CH₂OSi), 5.31 (s, 1H, CH(OMe)₂), 6.04 (q, *J* = 6.3 Hz, 1H, MeCHPy).

3,4-Dibutyl-2-(methoxymethyl)-5-phenylfuran (51). To a stirred solution of 5-decyne (0.030 mL, 0.168 mmol) and Ti(O-*i*-Pr)₄ (0.062 mL, 0.210 mmol) in 1.5 mL of Et₂O was added *i*-PrMgCl (1.33 M in Et₂O, 0.33 mL, 0.437 mmol) at -78 °C under argon to give a yellow homogeneous solution. The solution was warmed to -50 °C over 30 min, during which period its color turned black. After stirring at -50 °C for an additional 3 h, α-methoxyacetonitrile (0.010 mL, 0.134 mmol) was introduced to the reaction mixture at -50 °C and the solution was stirred for another 3 h. Then, benzaldehyde (0.020 mL, 0.202 mmol) was added and the reaction mixture was gradually warmed to room temperature over 3 h. The reaction was terminated by the addition of 1N HCl and vigorously stirred at room temperature for 10 h. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO₃, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane-Et₂O) to afford the title compound (22 mg, 68%) as a colorless oil, which was fully characterized by ¹H and ¹³C NMR, IR, and elemental analyses.

¹H NMR δ 0.95 (t, *J* = 7.2 Hz, 6H), 1.20-1.62 (m, 8H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 3.39 (s, 3H), 4.41 (s, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H).

¹³C NMR δ 13.75, 13.81, 22.59, 22.86, 23.10, 23.92, 32.28, 33.21, 57.80, 64.77, 122.29, 125.60, 126.25, 126.77, 128.49, 132.02, 146.23, 148.08.

IR (neat) 3090, 3058, 3035, 2960, 2930, 2862, 2820, 1490, 1457, 1377, 1360, 1180, 1150, 1090, 1040, 1015, 970, 950, 910, 781, 694 cm⁻¹.

Anal. Calcd for C₂₀H₂₈O₂: C, 79.96; H, 9.39. Found: C, 80.18; H, 9.32.

3,4-Dibutyl-2-(methoxymethyl)-5-octylfuran (52). To a stirred solution of 5-decyne (0.030

mL, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.33 M in Et_2O , 0.330 mL, 0.437 mmol) at $-78\text{ }^\circ\text{C}$ under argon to give a yellow homogeneous solution. The solution was warmed to $-50\text{ }^\circ\text{C}$ over 30 min, during which period its color turned black. After stirring at $-50\text{ }^\circ\text{C}$ for an additional 3 h, α -methoxyacetonitrile (0.010 mL, 0.134 mmol) was introduced to the reaction mixture at $-50\text{ }^\circ\text{C}$ and the solution was stirred for another 3 h. Then, nonanal (0.035 mL, 0.202 mmol) was added and the reaction mixture was gradually warmed to room temperature over 3 h. The reaction was terminated by the addition of 1N HCl and vigorously stirred at room temperature for 10 h. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO_3 , dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane- Et_2O) to afford the title compound (27 mg, 60%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.87 (t, $J = 6.9$ Hz, 3H), 0.91 (t, $J = 6.9$ Hz, 3H), 0.92 (t, $J = 6.9$ Hz, 3H), 1.14-1.66 (m, 20H), 2.26 (t, $J = 7.2$ Hz, 2H), 2.34 (t, $J = 7.2$ Hz, 2H), 2.50 (t, $J = 7.2$ Hz, 2H), 3.33 (s, 3H), 4.30 (s, 2H).

^{13}C NMR δ 13.81, 13.82, 13.97, 22.56, 22.59 (2 peaks), 23.20, 23.33, 26.26, 28.57, 29.13, 29.25, 29.31, 31.78, 33.05, 33.14, 57.57, 64.72, 119.34, 124.47, 144.57, 151.36.

IR (neat) 2929, 2859, 1458, 1378, 1270, 1205, 1122, 1029, 935, 790, 730 cm^{-1} .

Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{O}_2$: C, 78.51; H, 11.98. Found: C, 78.40; H, 11.93.

3,4-Dibutyl-2-(1-methoxynonyl)-5-phenylfuran (53). To a stirred solution of 5-decyne (0.030 mL, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.50 M in Et_2O , 0.290 mL, 0.437 mmol) at $-78\text{ }^\circ\text{C}$ under argon to give a yellow homogeneous solution. The solution was warmed to $-50\text{ }^\circ\text{C}$ over 30 min, during which period its color turned black. After stirring at $-50\text{ }^\circ\text{C}$ for an additional 3 h, 2-methoxydecanenitrile (25 mg, 0.134 mmol) in 1 mL of Et_2O was introduced to the reaction mixture at $-50\text{ }^\circ\text{C}$ and the solution was stirred for another 3 h. Then, benzaldehyde (0.020 mL, 0.202 mmol) was added and the reaction mixture was gradually warmed to room temperature over 3 h. The reaction was terminated by the addition of 1N HCl and vigorously stirred at room temperature for 10 h. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO_3 , dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane- Et_2O) to afford the title compound (30 mg, 57%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.86 (t, J = 6.9 Hz, 3H), 0.93 (t, J = 6.9 Hz, 3H), 0.96 (t, J = 6.9 Hz, 3H), 1.15-1.65 (m, 20 H), 1.80-2.08 (m, 2H), 2.41 (t, J = 7.2 Hz, 2H), 2.59 (t, J = 7.2 Hz, 2H), 3.22 (s, 3H), 4.21 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.62 (t, J = 7.8 Hz, 2H).

^{13}C NMR δ 0.88, 13.79, 13.83, 13.97, 22.55, 22.78, 22.90, 22.92, 23.95, 25.77, 29.15, 29.38, 31.78, 32.29, 33.49, 33.85, 55.96, 75.00, 122.03, 125.38, 125.74, 126.57, 128.48, 132.18, 147.45, 147.50.

IR (neat) 3058, 3033, 2960, 2928, 2858, 2821, 1491, 1465, 1378, 1262, 1098, 1034, 911, 765, 693 cm^{-1} .

Anal. Calcd for $\text{C}_{28}\text{H}_{44}\text{O}_2$: C, 81.50; H, 10.75. Found: C, 81.26; H, 10.75.

3-Hexyl-2-(methoxymethyl)-5-phenyl-4-(trimethylsilyl)furan (54). To a stirred solution of 1-(trimethylsilyl)-1-octyne (31 mg, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.33 M in Et_2O , 0.33 mL, 0.437 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for an additional 3 h, α -methoxyacetonitrile (0.010 mL, 0.134 mmol) was introduced to the reaction mixture at -50°C and the solution was stirred for another 3 h. Then, benzaldehyde (0.020 mL, 0.202 mmol) was added and the reaction mixture was gradually warmed to room temperature over 3 h. The reaction was terminated by the addition of 1N HCl and vigorously stirred at room temperature for 10 h. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO_3 , dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane- Et_2O) to afford the title compound (25 mg, 57%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.15 (s, 9H), 0.91 (t, J = 6.9 Hz, 3H), 1.20-1.62 (m, 8H), 2.49 (t, J = 7.8 Hz, 2H), 3.40 (s, 3H), 4.41 (s, 2H), 7.28-7.40 (m, 3H), 7.42-7.50 (m, 2H). Irradiation of the proton at δ 4.41 ppm (CH_2OMe) showed 3% nOe enhancement to the peak at δ 2.49 ppm (furyl CH_2). Thus, the regiochemistry has been confirmed.

^{13}C NMR δ 0.84, 13.96, 22.63, 25.51, 29.28, 31.65, 32.01, 57.95, 64.40, 115.07, 127.87, 128.39, 129.38, 130.40, 133.44, 147.27, 159.50.

IR (neat) 3074, 3035, 2960, 2926, 2862, 1458, 1254, 1099, 854, 760, 699 cm^{-1} .

Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{O}_2\text{Si}$: C, 73.20; H, 9.36. Found: C, 72.94; H, 9.17.

3-Hexyl-2-(methoxymethyl)-5-octyl-4-(trimethylsilyl)furan (55). To a stirred solution of 1-

(trimethylsilyl)-1-octyne (31 mg, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.33 M in Et_2O , 0.33 mL, 0.437 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for an additional 3 h, α -methoxyacetonitrile (0.010 mL, 0.134 mmol) was introduced to the reaction mixture at -50°C and the solution was stirred for another 3 h. Then, nonanal (0.035 mL, 0.202 mmol) was added and the reaction mixture was gradually warmed to room temperature over 3 h. The reaction was terminated by the addition of 1N HCl and vigorously stirred at room temperature for 10 h. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO_3 , dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane- Et_2O) to afford the title compound (27 mg, 55%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.24 (s, 9H), 0.87 (t, $J = 6.9$ Hz, 3H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.10-1.68 (m, 20H), 2.37 (t, $J = 7.8$ Hz, 2H), 2.58 (t, $J = 7.8$ Hz, 2H), 3.35 (s, 3H), 4.31 (s, 2H).

^{13}C NMR δ 0.78, 13.93, 13.97, 22.52, 22.55, 25.45, 29.01, 29.12, 29.27, 29.31, 29.41, 29.43, 31.62, 31.75, 32.23, 57.70, 64.31, 112.31, 129.08, 145.58, 161.55.

IR (neat) 2960, 2927, 2854, 1539, 1465, 1385, 1249, 1190, 1094, 950, 839, 772, 712, 688 cm^{-1} .

Anal. Calcd for $\text{C}_{23}\text{H}_{44}\text{O}_2\text{Si}$: C, 72.57; H, 11.65. Found: C, 72.91; H, 11.59.

3-Hexyl-2-(1-methoxynonyl)-5-phenyl-4-(trimethylsilyl)furan (56). To a stirred solution of 1-(trimethylsilyl)-1-octyne (31 mg, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.50 M in Et_2O , 0.29 mL, 0.437 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for an additional 3 h, 2-methoxydecanenitrile (25 mg, 0.134 mmol) in 1 mL of Et_2O was introduced to the reaction mixture at -50°C and the solution was stirred for another 3 h. Then, benzaldehyde (0.020 mL, 0.202 mmol) was added and the reaction mixture was gradually warmed to room temperature over 3 h. The reaction was terminated by the addition of 1N HCl and vigorously stirred at room temperature for 10 h. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO_3 , dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane- Et_2O) to afford the title compound (33 mg, 54%) as a colorless oil, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 0.16 (s, 9H), 0.86 (t, $J = 7.2$ Hz, 3H), 1.15-1.60 (m, 20H), 1.75-2.03 (m, 2H), 2.47 (t, $J = 7.5$ Hz, 2H), 3.24 (s, 3H), 4.24 (t, $J = 7.2$ Hz, 1H), 7.30-3.40 (m, 3H), 7.40-7.50 (m, 2H). Irradiation of the proton at δ 4.24 ppm (FuCH $\underline{\text{O}}$ Me) showed 5% nOe enhancement to the peak at δ 2.47 ppm (FuCH $\underline{\text{H}}$ $_2$). Thus, the regiochemistry has been confirmed.

^{13}C NMR δ 0.97, 13.95, 13.97, 22.56 (2 peaks), 25.29, 25.82, 29.16, 29.38, 29.47, 31.70, 31.78, 32.28, 33.85, 56.03, 74.62, 114.46, 127.81, 128.21, 129.31, 129.76, 133.56, 148.49, 159.05.

IR (neat) 3066, 3033, 2960, 2925, 2856, 1465, 1376, 1250, 1099, 1034, 842, 760, 697 cm^{-1} .

Anal. Calcd for $\text{C}_{29}\text{H}_{48}\text{O}_2\text{Si}$: C, 76.25; H, 10.59. Found: C, 76.17; H, 10.66.

2-(Methoxymethyl)-3,4, 5-triphenylfuran (58). To a stirred solution of diphenylacetylene (30 mg, 0.168 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.062 mL, 0.210 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.33 M in Et_2O , 0.33 mL, 0.437 mmol) at -78°C under argon to give a yellow homogeneous solution. The solution was warmed to -50°C over 30 min, during which period its color turned black. After stirring at -50°C for an additional 3 h, α -methoxyacetonitrile (0.010 mL, 0.134 mmol) was introduced to the reaction mixture at -50°C and the solution was stirred for another 3 h. Then, benzaldehyde (0.020 mL, 0.202 mmol) was added and the reaction mixture was gradually warmed to room temperature over 3 h. The reaction was terminated by the addition of 1N HCl and vigorously stirred at room temperature for 10 h. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO_3 , dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a crude oil. The crude product was chromatographed on silica gel (hexane- Et_2O) to afford the title compound (30 mg, 66%) as a white solid, which was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses.

^1H NMR δ 3.38 (s, 3H), 4.38 (s, 2H), 7.00-7.28 (m, 13H), 7.32-7.42 (m, 2H).

^{13}C NMR δ 58.14, 65.09, 122.76, 126.21, 127.04, 127.27, 127.50, 128.11, 128.15, 128.32, 128.57, 129.84, 130.49, 130.88, 132.13, 133.32, 147.40, 148.82.

IR (nujol) 3180, 2731, 1303, 1164, 1092, 1017, 954, 895, 822, 763, 726, 692 cm^{-1} .

Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{O}_2$: C, 84.68; H, 5.92. Found: C, 84.58; H, 6.06.

m.p. 126-127 $^\circ\text{C}$.

3,4-Dibutyl-5-(methoxymethyl)pyrrole-2-carboxaldehyde (61). To a stirred solution of 5-decyne (0.036 mL, 0.200 mmol) and $\text{Ti}(\text{O-}i\text{-Pr})_4$ (0.074 mL, 0.250 mmol) in 1.5 mL of Et_2O was added $i\text{-PrMgCl}$ (1.60 M in Et_2O , 0.313 mL, 0.500 mmol) at -78°C under argon to give a yellow

homogeneous solution. The solution was warmed to -50 °C over 30 min, during which period its color turned black. After stirring at -50 °C for 3 h, α -methoxyacetonitrile (0.045 mL, 0.600 mmol) was introduced at -50 °C and the mixture was stirred for another 3 h. The solution was allowed to warm to room temperature and was stirred overnight. After the reaction was terminated by the addition of 1N HCl (1.5 mL), the resulting mixture was vigorously stirred for 15 min. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO₃, dried over Na₂SO₄, and concentrated to a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (29 mg, 68%) as a brown oil.

¹H NMR δ 0.92 (t, J = 7.5 Hz, 6H), 1.25-1.41 (m, 6H), 1.54 (quintet, J = 7.5 Hz, 2H), 2.38 (t, J = 7.7 Hz, 2H), 2.67 (t, J = 7.8 Hz, 2H), 3.38 (s, 3H), 4.42 (s, 2H), 9.33 (s, 1H), 9.55 (s, 1H).

¹³C NMR δ 13.76, 13.81, 22.56 (2 peaks), 23.27, 23.39, 33.51, 34.86, 58.49, 65.79, 123.04, 128.39, 134.29, 136.38, 177.21.

IR (neat) 3396, 2959, 2927, 2853, 1653 (C=O), 1458, 1363, 1250, 1093, 668 cm⁻¹.

Anal. Calcd for C₁₅H₂₅NO₂: C, 71.67; H, 10.02. Found: C, 71.93; H, 9.82.

3-Butyl-5-(1-methoxynonyl)-4-phenylpyrrole-2-carboxaldehyde (68). To a stirred solution of 1-phenyl-1-hexyne (0.035 mL, 0.200 mmol) and Ti(O-*i*-Pr)₄ (0.074 mL, 0.250 mmol) in 1.5 mL of Et₂O was added *i*-PrMgCl (1.60 M in Et₂O, 0.313 mL, 0.500 mmol) at -78 °C under argon to give a yellow homogeneous solution. The solution was warmed to -50 °C over 30 min, during which period its color turned black. After stirring at -50 °C for 3 h, 2-methoxydecenenitrile (0.045 mL, 0.200 mmol) was introduced to the reaction mixture at -50 °C and the solution was stirred for 5 h. Then, methoxyacetonitrile (0.012 mL, 0.160 mmol) was added and the solution was allowed to warm to room temperature and was stirred overnight. After the reaction was terminated by the addition of 1N HCl (1.5 mL), the resulting mixture was vigorously stirred for 15 min. The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO₃, dried over Na₂SO₄, and concentrated to a crude oil, ¹H NMR analysis of which did not show the presence of the regioisomer. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (41 mg, 54%) as a brown oil.

¹H NMR δ 0.79 (t, J = 7.5 Hz, 3H), 0.86 (t, J = 6.75 Hz, 3H), 1.17-1.26 (m, 14H), 1.43 (q, J = 6 Hz, 2H), 1.62 (quintet, J = 6 Hz, 2H), 2.66 (t, J = 7.8 Hz, 2H), 3.21 (s, 3H), 4.17 (t, J = 6.9 Hz, 1H), 7.19-7.43 (m, 5H), 9.20 (s, 1H), 9.66 (s, 1H). Irradiation of the proton at δ 9.66 ppm (aldehyde) showed 8% nOe enhancement to the peak at δ 2.66 ppm (pyrrole-CH₂). Thus, the regiochemistry has been

confirmed.

^{13}C NMR δ 13.56, 13.94, 22.27, 22.50, 23.25, 25.10, 29.05, 29.13, 29.22, 31.70, 34.64, 35.84, 56.99, 75.41, 125.95, 127.11, 128.31, 128.47, 130.23, 133.94, 135.95, 138.31, 177.71.

IR (neat) 3441, 3278, 2952, 2927, 2862, 1653 (C=O), 1539, 1246, 1107, 707 cm^{-1} .

Anal. Calcd for $\text{C}_{25}\text{H}_{37}\text{NO}_2$: C, 78.28; H, 9.72. Found: C, 78.23; H, 9.80.

5-(Benzyloxymethyl)-3,4-dibutylpyrrole-2-carboxaldehyde (69).

^1H NMR δ 0.96 (t, J = 6.6 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.30-1.48 (m, 6H), 1.58 (quintet, J = 6 Hz, 2H), 2.39 (t, J = 7.7 Hz, 2H), 2.66 (t, J = 7.8 Hz, 2H), 4.45 (s, 2H), 4.60 (s, 2H), 7.34-7.44 (m, 5H), 9.17 (s, 1H), 9.59 (s, 1H).

^{13}C NMR δ 13.78 (2 peaks), 22.56 (2 peaks), 23.29, 23.40, 33.48, 34.87, 63.30, 72.81, 123.16, 127.05, 127.71, 128.06, 128.61, 134.32, 134.52, 137.51, 177.20.

IR (neat) 3441, 3249, 2928, 2860, 1653 (C=O), 1570, 1458, 1363, 1091, 669 cm^{-1} .

Anal. Calcd for $\text{C}_{21}\text{H}_{29}\text{NO}_2$: C, 77.02; H, 8.93. Found: C, 76.77; H, 8.62.

3,4-Dibutyl-5-(1-methoxynonyl)pyrrole-2-carboxaldehyde (70).

^1H NMR δ 0.86 (t, J = 6.6 Hz, 3H), 0.93 (t, J = 7.2 Hz, 6H), 1.18-1.31 (m, 18H), 1.38 (q, J = 6.5, 2H), 1.55 (quintet, J = 7.5 Hz, 2H), 2.37 (t, J = 7.8 Hz, 2H), 2.67 (t, J = 7.5 Hz, 2H), 3.21 (s, 3H), 4.24 (dd, J = 5.7, 7.5 Hz, 1H), 8.95 (s, 1H), 9.55 (s, 1H).

^{13}C NMR δ 13.77 (2 peaks), 13.81, 13.94, 22.51, 22.62, 22.71, 23.25, 23.44, 25.39, 29.10, 29.30, 31.72, 33.72, 34.95, 36.20, 57.02, 75.66, 123.28, 128.21, 136.31, 138.06, 177.13.

IR (neat) 3442, 3252, 2956, 2930, 1634 (C=O), 1521, 1456, 1357, 1247, 1190, 948 cm^{-1} .

Anal. Calcd for $\text{C}_{23}\text{H}_{41}\text{NO}_2$: C, 75.98; H, 11.37. Found: C, 75.73; H, 10.97.

3,4-Bis[4-(benzyloxy)butyl]-5-(methoxymethyl)pyrrole-2-carboxaldehyde (71).

^1H NMR δ 1.50-1.67 (m, 8H), 2.40 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 7.7 Hz, 2H), 3.36 (s, 3H), 3.47 (t, J = 6.6 Hz, 4H), 4.42 (s, 2H), 4.48 (s, 4H), 7.26-7.34 (m, 10H), 9.27 (s, 1H), 9.54 (s, 1H).

^{13}C NMR δ 23.35, 23.46, 27.83, 29.50, 29.23, 58.52, 65.79, 70.00, 70.07, 72.93, 122.58, 127.60, 127.67, 128.42, 134.33, 135.85, 138.59, 138.62, 177.17. Several peaks apparently overlap due to the pseudo-symmetry of the molecule.

IR (neat) 3441, 3253, 2925, 2861, 1653 (C=O), 1457, 1368, 1101, 1041, 669 cm^{-1} .

Anal. Calcd for $\text{C}_{29}\text{H}_{37}\text{NO}_4$: C, 75.13; H, 8.04. Found: C, 75.10; H, 8.13.

An 80:20 Mixture of 3-[3-[(*tert*-Butyl)dimethylsiloxy]propyl]-5-(1-methoxynonyl)-4-methylpyrrole-2-carboxaldehyde (**72**) and 4-[3-[(*tert*-Butyl)dimethylsiloxy]propyl]-5-(1-methoxynonyl)-3-methylpyrrole-2-carboxaldehyde.

3-[3-[(*tert*-Butyl)dimethylsiloxy]propyl]-5-(1-methoxynonyl)-4-methylpyrrole-2-carboxaldehyde (72**).**

¹H NMR δ 0.03 (s, 6H), 0.75-0.90 (m, 12H), 1.08-1.24 (m, 12H), 1.42-1.66 (m, 4H), 1.96 (s, 3H), 2.69 (t, *J* = 7.5 Hz, 2H), 3.21 (s, 3H), 3.62 (t, *J* = 6.3 Hz, 2H), 4.25 (t, *J* = 6.6 Hz, 1H), 9.07 (s, 1H), 9.52 (s, 1H). Irradiation of the proton at δ 9.52 ppm (aldehyde) showed 6% nOe enhancement to the peak at δ 2.69 ppm (pyrrole-CH₂). Thus, the regiochemistry has been confirmed.

¹³C NMR δ 8.31 (2 peaks), 13.95 (2 peaks), 18.18, 22.52, 23.41, 25.20, 25.82, 27.91, 29.11, 29.32, 31.72, 32.41, 35.70, 57.10, 62.77, 75.95, 117.71, 128.11, 136.72, 138.31, 177.01.

IR (neat) 3461, 3269, 2926, 2853, 1625 (C=O), 1457, 1262, 1106, 838 cm⁻¹ for an 80:20 mixture of **72** and its regioisomer.

Anal. Calcd for C₂₅H₄₇NO₃Si: C, 68.60; H, 10.82. Found: C, 68.21; H, 10.96 for an 80:20 mixture of **72** and its regioisomer.

4-[3-[(*tert*-Butyl)dimethylsiloxy]propyl]-5-(1-methoxynonyl)-3-methylpyrrole-2-carboxaldehyde. Regioisomer of **72.**

¹H NMR (only characteristic peaks are shown) δ 2.27 (s, 3H), 9.55 (s, 1H).

3-Hexyl-5-(1-methoxynonyl)-4-(4-chlorophenyl)pyrrole-2-carboxaldehyde (73**).**

¹H NMR δ 0.82 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H), 1.15-1.30 (m, 18H), 1.41 (q, *J* = 6.9 Hz, 2H), 1.62 (br m, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 3.20 (s, 3H), 4.14 (t, *J* = 6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 9.23 (s, 1H), 9.65 (s, 1H). Irradiation of the proton at δ 9.65 ppm (aldehyde) showed 7% nOe enhancement to the peak at δ 2.63 ppm (pyrrole-CH₂). Thus, the regiochemistry has been confirmed.

¹³C NMR δ 13.84, 13.94, 22.33, 22.51, 23.47, 25.11, 28.85, 29.07, 29.13, 29.24, 31.24, 31.71, 32.34, 35.79, 57.03, 75.44, 124.50, 128.39, 128.77, 131.51, 132.52, 133.23, 135.79, 138.27, 177.73.

IR (neat) 3447, 3261, 2926, 2731, 1653 (C=O), 1436, 1240, 1093, 833 cm⁻¹.

Anal. Calcd for C₂₇H₄₀ClNO₂: C, 72.70; H, 9.04. Found: C, 72.75; H, 9.25.

3-Butyl-5-(1-methoxynonyl)-4-(4-methoxyphenyl)pyrrole-2-carboxaldehyde (74**).**

¹H NMR δ 0.79 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 6.6 Hz, 3H), 1.05-1.25 (m, 14H), 1.41 (q, *J* = 7.2 Hz,

2H), 1.55-1.72 (br m, 2H), 2.64 (t, $J = 7.8$ Hz, 2H), 3.21 (s, 3H), 3.86 (s, 3H), 4.14 (t, $J = 6$ Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 8.1$ Hz, 2H), 9.15 (s, 1H), 9.64 (s, 1H). Irradiation of the proton at δ 9.64 ppm (aldehyde) showed 7% nOe enhancement to the peak at δ 2.64 ppm (pyrrole-CH₂). Thus, the regiochemistry has been confirmed.

¹³C NMR δ 13.62 (2 peaks), 22.31, 22.51, 23.30, 25.14, 29.08, 29.16, 29.25, 31.71, 34.64, 35.80, 55.15, 56.96, 75.45, 113.89, 125.60, 126.04, 128.24, 131.31, 136.20, 138.43, 158.80, 177.66.

IR (neat) 3441, 3277, 2926, 2862, 1653 (C=O), 1559, 1437, 1248, 1174, 1095, 835 cm⁻¹.

Anal. Calcd for C₂₅H₃₇NO₂: C, 75.50; H, 9.50. Found: C, 75.31; H, 9.20.

4-(2-Furyl)-3-hexyl-5-(1-methoxynonyl)pyrrole-2-carboxaldehyde (75).

¹H NMR δ 0.87 (t, $J = 6.6$ Hz, 3H), 0.88 (t, $J = 6.6$ Hz, 3H), 1.20-1.38 (m, 18H), 1.58 (q, $J = 6.6$ Hz, 2H), 1.68 (quintet, $J = 7.4$ Hz, 2H), 2.83 (t, $J = 8.0$ Hz, 2H), 3.28 (s, 3H), 4.58 (t, $J = 6.3$ Hz, 1H), 6.26 (d, $J = 3.3$ Hz, 1H), 6.48 (dd, $J = 3.3, 1.5$ Hz, 1H), 7.45 (d, $J = 1.5$ Hz, 1H), 9.24 (s, 1H), 9.64 (s, 1H). Irradiation of the proton at δ 9.64 ppm (aldehyde) showed 6% nOe enhancement to the peak at δ 2.83 ppm (pyrrole-CH₂). Thus, the regiochemistry has been confirmed.

¹³C NMR δ 13.90, 13.97, 22.43, 22.53, 24.13, 25.14, 29.07, 29.10, 29.19, 29.29, 31.40, 31.68, 31.74, 35.97, 57.67, 76.39, 106.85, 111.03, 113.90, 114.14, 128.34, 139.84, 141.23, 148.44, 177.59.

IR (neat) 3441, 3265, 2926, 2856, 1652 (C=O), 1464, 1097, 729 cm⁻¹.

Anal. Calcd for C₂₅H₃₉NO₃: C, 74.77; H, 9.79. Found: C, 74.44; H, 9.88.

3,4-(1,10-Decylidene)-5-(methoxymethyl)pyrrole-2-carboxaldehyde (76).

¹H NMR δ 1.20-1.58 (m, 14H), 1.72 (br m, 2H), 2.41 (t, $J = 7.2$ Hz, 2H), 2.68 (t, $J = 7.5$ Hz, 2H), 3.39 (s, 3H), 4.44 (s, 2H), 9.29 (s, 1H), 9.58 (s, 1H).

¹³C NMR δ 20.61, 20.93, 22.52, 22.69, 25.01, 25.38, 25.73, 26.16, 28.87, 31.43, 58.52, 65.98, 123.30, 128.29, 134.47, 136.95, 177.35.

IR (neat) 3440, 3244, 2923, 2853, 1638 (C=O), 1457, 1376 cm⁻¹.

Anal. Calcd for C₁₇H₂₇NO₂: C, 73.61; H, 9.81. Found: C, 73.25; H, 9.83.

3,4-(1,10-Decylidene)-5-(1-methoxynonyl)pyrrole-2-carboxaldehyde (77).

¹H NMR δ 0.85 (t, $J = 6.6$ Hz, 3H), 1.16-1.38 (m, 14H), 1.40-1.80 (m, 16H), 2.41 (t, $J = 7.8$ Hz, 2H), 2.67 (t, $J = 7.8$ Hz, 2H), 3.19 (s, 3H), 4.62 (t, $J = 6.6$ Hz, 1H), 9.21 (s, 1H), 9.57 (s, 1H).

¹³C NMR δ 13.92, 20.71, 21.05, 22.49, 22.56, 22.71, 25.36, 25.48, 25.67, 26.13, 26.41, 29.09, 29.23, 29.29, 29.31, 31.47, 31.70, 36.15, 56.94, 75.77, 123.68, 128.22, 136.78, 138.42, 177.30.

IR (neat) 3447, 3258, 2925, 2855, 1635 (C=O), 1444, 1240, 1095 cm⁻¹.

Anal. Calcd for C₂₅H₄₃NO₂: C, 75.50; H, 11.12. Found: C, 75.10; H, 10.83.

3,4-Dibutyl-5-methylpyrrole-2-carboxaldehyde (78). To a suspension of NaI (12 mg, 0.079 mmol) in CH₃CN (1 mL) was added Me₃SiCl (0.010 mL, 0.079 mmol) at room temperature and the mixture was stirred for 30 min. Then, 5-(benzyloxymethyl)-3,4-dibutylpyrrole-2-carboxaldehyde (**69**) (10 mg, 0.031 mmol) in CH₃CN (1 mL) was added at room temperature. After the mixture was stirred for 5 min, the reaction was terminated by the addition of water (0.2 mL). The organic products were extracted with ether. The combined organic layers were washed with an aqueous solution of NaHCO₃ and Na₂S₂O₃, dried over Na₂SO₄, and concentrated to a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (6.0 mg, 89%) as a colorless oil.

¹H NMR δ 0.93 (t, *J* = 7.8 Hz, 6H), 1.30-1.46 (m, 6H), 1.53 (quintet, *J* = 7.5 Hz, 2H), 2.25 (s, 3H), 2.35 (t, *J* = 8.1 Hz, 2H), 2.65 (t, *J* = 8.1 Hz, 2H), 9.42 (s, 1H), 9.98 (s, 1H).

¹³C NMR δ 11.62, 13.77, 13.83, 22.56, 22.59, 23.44, 23.57, 33.15, 34.97, 122.92, 127.58, 136.17, 137.71, 175.89.

IR (neat) 3445, 3249, 2923, 2862, 1628 (C=O), 1437, 1374, 1267, 1036 cm⁻¹.

Anal. Calcd for C₁₄H₂₃NO: C, 75.97; H, 10.47. Found: C, 76.04; H, 10.58.

3,4-Dibutyl-5-[(*E*)-1-nonenyl]pyrrole-2-carboxaldehyde (79). This was carried out according to the literature [Grieco, P. A.; Nishizawa, M.; Oguri, T.; Burke, S. D.; Marinovic, N. *J. Am. Chem. Soc.* **1977**, 99, 5773-5779]. To a stirred solution of 3,4-dibutyl-5-(1-methoxynonyl)pyrrole-2-carboxaldehyde (**70**) (17 mg, 0.046 mmol) in 1.2 mL of CH₂Cl₂ was added BBr₃ (0.044 mL, 0.464 mmol) at -78 °C under argon to give a black solution. The resulting mixture was stirred at -78 °C for 1 h, allowed to warm to -12 °C, and was further stirred for 5 h at the same temperature. After the reaction was terminated by the addition of ether (2 mL) and aqueous 1*N* NaOH (1.0 mL), the reaction mixture was warmed to room temperature and vigorously stirred for 1 h. The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated to a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (13 mg, 84%) as a brown oil.

¹H NMR δ 0.88 (t, *J* = 6.9 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 6H), 1.16-1.56 (m, 18H), 2.21 (q, *J* = 6.3 Hz, 2H), 2.41 (t, *J* = 8.4 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 6.01 (dt, *J* = 15.9, 7.2 Hz, 1H), 6.26 (d, *J* = 15.9 Hz, 1H), 8.98 (s, 1H), 9.54 (s, 1H).

^{13}C NMR δ 13.77, 13.83, 13.96, 22.57, 22.72, 23.22, 23.32, 28.97, 29.04, 29.12, 29.32, 31.74, 33.16, 33.66, 34.83, 118.07, 124.02, 128.46, 132.40, 134.93, 136.94, 176.63.

IR (neat) 3460, 3279, 2926, 2856, 1629 (C=O), 1444, 1378, 1260, 1100 cm^{-1} .

Anal. Calcd for $\text{C}_{22}\text{H}_{37}\text{NO}$: C, 79.70; H, 11.25. Found: C, 79.50; H, 10.89.