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Iron Catalyzed Regio- and Stereoselective Carbolithiation of Alkynes

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Experimental Section

Boiling points listed in the section for compound data were determined with Kugelrohr distillation apparatus. Gas chromatography was carried out with Shimadzu GC-8A (column; 15% of SE-30 on Chromosorb W AW-DMCS 60-80 mesh, 3 mm x 2.0 m, rate of flow; 60 mL/min). ^{1}H NMR spectra at 270 MHz and ^{13}C NMR spectra at 67.7 MHz were determined on a JEOL JNM-EX270 instrument with tetramethylsilane (δ = 0.00 ppm) or chloroform (^{1}H, 7.26 ppm; ^{13}C, 77.0 ppm) as an internal standard. Infrared spectra were measured with a Shimadzu IR-460 spectrophotometer. Mass spectra were measured (by EI method) on a Shimadzu GCMS-QP2000, QP5000 and JEOL JMS-GCMATE (HRMS) instruments. Microanalyses were performed by the Analysis Center of University of Tsukuba.

Solvents and Reagents. Unless otherwise specified, the following solvents and reagents (reagent grade) were used without further purification: sodium iodide (Kishida Chemical Co., Ltd.); $Fe(III)Cl_3$, $Fe(III)Cl_3 \cdot 6H_2O$, $Fe(III)(acac)_3$, $Fe(II)Cl_2$, magnesium, lithium lump, Cu(I)I, sodium hydride, paraformaldehyde, ammonia (Wako Pure Chemical Industries Ltd.); $Hg(II)Cl_2$, butyl alcohol, 1,3-diphenylpropane-1,3-dione, benzyl bromide, iodomethane (Tokyo Chemical Industry Co., Ltd.). A solution of butyllithium in hexane was purchased from (Kanto Chemical Co., Inc.) and used without purification. *o*-Iodoanisole was distilled prior to use. Propanal and propiophenone were distilled over molecular sieves (4A) under nitrogen atmosphere. Chlorotrimethylsilane and chlorodimethylsilane were distilled from *N,N*-diethylaniline. Hexane, toluene, hexamethylphosphoric triamide (HMPA), ethanol, 3-pentyn-1-ol, 2,2-dimethyl-4-hexyn-1-ol, 1-bromo-3-phenylpropane, 1-pentyne, 6-dodecyne, benzaldehyde, propargyl bromide, and diethylamine were distilled over calcium hydride under nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried and distilled from benzophenone and sodium immediately prior to use under nitrogen atmosphere.

Preparation of Tris(dibenzoylmethido)iron(III) , Fe(DBM)$_3$[1]. A 200 mL two-necked round bottom flask containing $Fe(III)Cl_3 \cdot 6H_2O$ (1.2 g, 4.4 mmol), water (10 mL) and a magnetic stirring

bar was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with nitrogen. The mixture was stirred with external heating until the mixture became homogeneous. A solution of 1,3-diphenylpropane-1,3-dione (3.7 g, 16.5 mmol) in ethanol (35 mL) was added. The mixture was heated to homogeneous. Ammonia (25%) was added dropwise to adjust the mixture to pH 8. After 3 h, resultant red precipitate was filtered, and the precipitate was dried under reduced pressure. After recrystallization from benzene-hexane, purple needle was obtained in 85% yield (2.7 g, 3.7 mmol).

3-Pentynyl 3-phenylpropyl ether (**1a**). A 200 mL two-necked round bottom flask containing NaH (2.4 g with oil, 60 mmol) and a magnetic stirring bar was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with nitrogen. Under a reduced pressure this flask was dried by heating with a heat-gun, and after cooling down, nitrogen was introduced. Mineral oil of the NaH suspension was washed with two portions of dry THF (10 mL) using a syringe. Dry THF (100 mL) and HMPA (10 mL) were introduced to the flask and the suspension was cooled to 0 °C. To this suspension, 3-pentyn-1-ol (4.2 g, 50 mmol) was added, and the mixture was stirred for 1.5 h at room temperature. The flask was again cooled to 0 °C, and NaI (7.5 g, 50 mmol) and 1-bromo-3-phenylpropane (9.9 g, 50 mmol) were added to the mixture. The mixture was stirred at room temperature for 3 h. A saturated NH_4Cl solution was added to the mixture. After extraction with ether (20 mL x 3), drying over Na_2SO_4, evaporation of solvents, and purification by chromatography on silica gel (hexane/ ethyl acetate = 30:1), pure 3-pentynyl 3-phenylpropyl ether (**1a**) was obtained. 38% yield (3.8 g, 19 mmol). Bp 200 °C / 0.5 mmHg. ^{1}H NMR ($CDCl_3$) δ 1.79 (t, *J* = 2.6 Hz, 3H), 1.90 (tt, *J* = 7.6, 6.6 Hz, 2H), 2.42 (tq, *J* = 7.3, 2.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.51 (t, *J* = 7.3 Hz, 2H), 7.18-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 3.5 (CH_3), 20.1 (CH_2), 31.2 (CH_2), 32.2 (CH_2), 69.4 (CH_2), 69.9 (CH_2), 76.0 (quart.), 77.2 (quart.), 125.7 (CH), 128.3 (CH x 2), 128.5 (CH x 2), 141.9 (quart.), 142.1 (quart.); IR (neat) 3060 (m), 2920 (s), 2860 (s), 1600 (w), 1497 (m), 1452 (m), 1370 (m), 1218 (w), 1115 (s), 754 (s), 699 (s) cm^{-1}; mass spectrum *m/z* (% relative intensity) 202 (M^+, 1), 187 (2), 118 (67), 91 (100). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.20; H, 9.23.

3-Pentynyl benzyl ether (**1b**). This compound was prepared in the same way as **1a**, but without HMPA, using benzyl bromide instead of 1-bromo-3-phenylpropane. 99% yield (8.6 g, 50 mmol). Bp 150 °C / 0.4 mmHg. ^{1}H NMR ($CDCl_3$) δ 1.78 (t, *J* = 2.6 Hz, 3H), 2.45 (tq, *J* = 6.9, 2.6 Hz, 2H), 3.55 (t, *J* = 6.9 Hz, 2H), 4.55 (s, 2H), 7.25-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 3.4 (CH_3), 20.1 (CH_2), 68.7 (CH_2), 72.8 (CH_2), 75.8 (quart.), 76.6 (quart.), 127.5 (CH), 127.6 (CH x 2), 128.3 (CH x 2), 138.1 (quart.); IR (neat) 3020 (w), 2985 (s), 2860 (s), 1495 (m), 1456 (s), 1364 (s), 1204 (m), 1101 (s), 1028 (m), 737 (s), 698 (s), 660 (w) cm^{-1}; mass spectrum *m/z* (% relative intensity) 174 (M^+, 1), 173 (4), 159 (40), 129 (10), 91 (100). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10.

Found: C, 82.76; H, 8.13.

2,2-Dimethyl-4-hexynyl benzyl ether (**1c**). This compound was prepared from 2,2-dimethyl-4-hexyn-1-ol and benzyl bromide like as the preparation of **1b**. 95% yield (4.1 g, 19 mmol) Bp 230 °C / 0.5 mmHg. ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 6H), 1.78 (t, *J* = 2.3 Hz, 3H), 2.13 (q, *J* = 2.3 Hz, 2H), 3.22 (s, 2H), 4.53 (s, 2H), 7.26-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 3.5 (CH_3), 24.3 (CH_3 x 2), 29.1 (CH_2), 35.1 (quart.), 73.2 (CH_2), 76.9 (quart.), 76.9 (quart.), 78.1 (CH_2), 127.3 (CH x 3), 128.2 (CH x 2), 139.0 (quart.); IR (neat) 3030 (w), 3000 (s), 2855 (s), 1494 (w), 1379 (w), 1364 (m), 1204 (w), 1099 (s), 1027 (w), 756 (s), 740 (s), 696 (s), 661 (w) cm^{-1}; mass spectrum *m/z* (% relative intensity) 216 (M^+, 2), 215 (11), 201 (13), 91 (100). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.17; H, 9.59.

3-Pentynyldiethylamine (**1d**). *Butyl N,N-diethylaminomethyl ether*[2]. A 300 mL three-necked round bottom flask containing a magnetic stirring bar was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with nitrogen. Under a reduced pressure this flask was dried by heating with a heat-gun, and after cooling down, nitrogen was introduced. Paraformaldehyde (30 g, 1 mol) and water (55 mL) were introduced to the flask, and the mixture was stirred until the mixture became homogeneous. Diethylamine (55 g, 0.753 mol) was added to the mixture at 0 °C, and the mixture was stirred for 5 min. Butyl alcohol (74 g, 1 mol) was added and Na_2CO_3 was introduced to the flask to saturation. After stirring the mixture at 0 °C for 1 h, a water layer was separated. The organic layer was dried on anhydrous K_2CO_3 for overnight. By the careful distillation, butyl *N,N*-diethylaminomethyl ether (bp 165 °C) was obtained. After measuring NMR, this aminomethyl ether was immediately subjected to the next reaction. 50% yield (79.5 g, 0.50 mol). ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.08 (t, *J* = 2.6 Hz, 6H), 1.37 (tq, *J* = 7.3, 6.9 Hz, 2H), 1.54 (tt, *J* = 6.9, 6.6 Hz, 2H), 2.72 (q, *J* = 7.3 Hz, 4H), 3.38 (t, *J* = 6.6 Hz, 2H), 4.18 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.1 (CH_3 x 2), 13.9 (CH_3), 19.4 (CH_2), 32.0 (CH_2), 45.3 (CH_2 x 2), 67.8 (CH_2), 84.2 (CH_2); mass spectrum *m/z* (% relative intensity) 168 (M^+-1, 2), 143 (46), 129 (65), 69 (100). *3-Butynyldiethylamine*[3]. A 300 mL three-necked round bottom flask containing a magnetic stirring bar was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with nitrogen. Under a reduced pressure this flask was dried by heating with a heat-gun, and after cooling down, nitrogen was introduced. A solution of propargylmagnesium bromide[4] in ether prepared from propargyl bromide (11.9 g, 100 mmol) and ether (100 mL) was introduced to the flask at 0 °C. A solution of butyl diethylaminomethyl ether (8.0 g, 50 mmol) in ether (100 mL) was added to a solution of the Grignard reagent, and the temperature of the mixture was raised to room temperature. After stirring the mixture at room temperature for 15 h, saturated NH_4Cl solution was added to the mixture, and an organic layer was separated. The pH of a water layer was adjusted to 12 with 20% NaOH solution and organics were extracted from the water layer with ether

(20 mL x 3). Combined organic layers were dried on K_2CO_3 and solvents were evaporated, and a residue was distilled (74 °C/ 68 mmHg) to obtain 3-butynyldiethylamine in 66% yield (4.1 g, 33 mmol). This compound was used for the next reaction without further purification. *3-Pentynyldiethylamine* (**1d**). A 300 mL three-necked round bottom flask containing a magnetic stirring bar was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with nitrogen. Under a reduced pressure this flask was dried by heating with a heat-gun, and after cooling down, nitrogen was introduced. After cooling the flask to -78 °C, NH_3 (ca. 100 mL) was introduced through a rubber septum. Lithium lump (0.28 g, 40 mmol) was added, and the mixture was stirred until the mixture became a dark blue homogeneous solution. 3-Butynyldiethylamine (4.13 g, 33 mmol) was added to the solution over 15 min. The mixture was stirred further for 15 min. Iodomethane (5.68 g, 40 mmol) was added to the mixture. A cooling bath was removed and a three-way stopcock was opened. After removing NH_3, ether (100 mL), ice (50 g),and saturated NH_4Cl solution (100 mL) were added at 0 °C. After extraction with ether (20 mL x 3), drying on K_2CO_3, and evaporation of solvents, a crude product was subjected to purification by chromatography on basic alumina (hexane/ ethyl acetate = 10:1). 72% yield (3.3 g, 24 mmol). Bp 130 °C / 10 mmHg. ^{1}H NMR ($CDCl_3$) δ 1.03 (t, *J* = 7.3 Hz, 6H), 1.78 (t, *J* = 2.6 Hz, 3H), 2.25 (tq, *J* = 7.6, 2.6 Hz, 2H), 2.54 (q, *J* = 7.3 Hz, 4H), 2.65 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 3.5 (CH_3), 11.9 (CH_3 x 2), 17.0 (CH_2), 46.9 (CH_2 x 2), 52.0 (CH_2), 76.1 (quart.), 77.6 (quart.); IR (neat) 2975 (s), 2800 (s), 1466 (m), 1384 (m), 1291 (w), 1203 (m), 1161 (w), 1118 (w), 1067 (m), 661 (w) cm^{-1}; mass spectrum *m/z* (% relative intensity) 139 (M^+, 1), 124 (1), 108 (1), 86 (34), 43 (100). Anal. Calcd for $C_9H_{17}N$: C, 77.63; H, 12.31; N, 10.06. Found: C, 77.42; H, 12.74; N, 10.11.

2-(1-Pentynyl)anisole (**1e**)[5]. A 500 mL three-necked round bottom flask containing a magnetic stirring bar, bis(triphenylphosphine)dichloropalladium(II) (0.175 g, 0.250 mmol), and CuI (0.095 g, 0.500 mmol) was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with argon. Under a reduced pressure this flask was dried by heating with a heat-gun, and after cooling down, argon was introduced. Diethylamine (150 mL), *o*-iodoanisole (11.7 g, 50 mmol), and 1-pentyne (3.4 g, 50 mmol) were introduced, and the mixture was stirred at room temperature for 3 days. After confirmation of disappearance of starting materials by TLC, water (100 mL) was added to the flask. Extraction with ether (30 mL x 3), drying on Na_2SO_4, and evaporation of solvents, and purification by chromatography on silica gel (hexane/ ethyl acetate = 30:1) gave 2-(1-pentynyl)anisole (**1e**). 54% yield (4.7 g, 27 mmol). Bp 170 °C / 0.6 mmHg. ^{1}H NMR ($CDCl_3$) δ 1.06 (t, *J* = 7.3 Hz, 3H), 1.65 (tq, *J* = 6.9, 7.3 Hz, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 3.87 (s, 3H), 6.85 (brd, *J* = 8.2 Hz, 1H), 6.87 (ddd, *J* = 7.6, 7.6,1.0 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.6, 1.7 Hz, 1H), 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 21.7 (CH_2), 22.2 (CH_2), 55.7 (CH_3), 76.7 (quart.), 94.4 (quart.), 110.5 (CH), 113.1 (quart.), 120.3 (CH), 128.8 (CH), 133.6 (CH), 159.7

(quart.); IR (neat) 2965 (m), 1595 (w), 1580 (w), 1494 (s), 1465 (m), 1435 (m), 1294 (m), 1261 (s), 1180 (w), 1117 (m), 1049 (w), 1026 (m), 797 (w), 751 (s), 660 (w) cm^{-1}; mass spectrum *m/z* (% relative intensity) 174 (M^+, 100), 159 (25), 145 (31), 131 (46), 115 (80), 91 (48). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.39; H, 8.17.

Carbolithiation of Alkynyl Ethers or Alkynylamine (1) in the Presence of an Iron Salt. A 50 mL two-necked round bottom flask containing a magnetic stirring bar was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with argon. Under a reduced pressure this flask was dried by heating with a heat-gun, and after cooling down, argon was introduced. A solution of $Fe(acac)_3$ in toluene (0.025 M, 0.025 mmol, 1.0 mL), toluene (4.0 mL) and a substrate **1** (0.50 mmol) were introduced to the flask. The flask was cooled to -40 °C and a solution of butyllithium in hexane (1.50 M, 1.50 mmol) was added to the mixture. Reaction temperature was immediately raised to -20 °C and the mixture was stirred at -20 °C for 2 h. The reaction was quenched with 1N HCl. The reaction mixture was diluted with saturated NH_4Cl. After extraction with ether (10 mL x 3), washing the combined organic layer with saturated $NaHCO_3$, drying on $MgSO_4$, and evaporation of solvents, the residue was subjected to chromatography on silica gel (hexane/ ethyl acetate) to obtain a pure product.

(*E*)-4-Methyl-3-octenyl 3-phenylpropyl ether (**2a**). 97% yield (126 mg, 0.49 mmol). Bp 200 °C / 0.3 mmHg, R_f = 0.25 (hexane/ethyl acetate = 30:1). ^1H NMR ($CDCl_3$) δ 0.82 (t, *J* = 7.3 Hz, 3H), 1.13-1.36 (m, 4H), 1.54 (s, 3H), 1.82 (tt, *J* = 7.9, 6.6 Hz, 2H), 1.91 (t, *J* = 6.9 Hz, 2H), 2.22 (dt, *J* = 7.3, 7.3 Hz, 2H), 2.62 (t, *J* = 7.9 Hz, 2H), 3.32 (t, *J* = 7.3 Hz, 2H), 3.36 (t, *J* = 6.6 Hz, 2H), 5.06 (brt, *J* = 7.3 Hz, 1H), 7.08-7.24 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 16.0 (CH_3), 22.3 (CH_2), 28.6 (CH_2), 30.1 (CH_2), 31.3 (CH_2), 32.3 (CH_2), 39.4 (CH_2), 69.9 (CH_2), 70.7 (CH_2), 119.9 (CH), 125.7 (CH), 128.3 (CH x 2), 128.5 (CH x 2), 137.5 (quart.), 142.1 (quart.); IR (neat) 2920 (s), 2850 (s), 1491 (m), 1453 (m), 1369 (m), 1178 (w), 1114 (s), 1039 (m), 745 (m), 698 (s), 659 (w) cm^{-1}; mass spectrum *m/z* (% relative intensity) 260 (M^+, 1), 232 (1), 156 (13), 118 (74), 91 (100), 69 (53). Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 83.03; H, 11.03.

(*E*)-4-Methyl-3-octenyl benzyl ether (**2b**). 97% yield (113 mg, 0.49 mmol). Bp 190 °C / 0.3 mmHg, R_f = 0.18 (hexane/ethyl acetate = 30:1). ^1H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.9 Hz, 3H), 1.22-1.40 (m, 4H), 1.60 (s, 3H), 1.98 (t, *J* = 7.3 Hz, 2H), 2.33 (dt, *J* = 6.9, 6.9 Hz, 2H), 3.46 (t, *J* = 6.9 Hz, 2H), 4.52 (s, 2H), 5.14 (brt, *J* = 6.9 Hz, 1H), 7.27-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 16.0 (CH_3), 22.4 (CH_2), 28.7 (CH_2), 30.1 (CH_2), 39.4 (CH_2), 70.2 (CH_2), 72.8 (CH_2), 119.9 (CH), 127.5 (CH), 127.6 (CH x 2), 128.3 (CH x 2), 137.6 (quart.), 138.6 (quart.); IR (neat) 2915 (s), 2820 (s), 1493 (w), 1448 (m), 1360 (m), 1200 (w), 1100 (s), 1026 (w), 734 (m), 689 (m), 659 (w) cm^{-1}; mass spectrum *m/z* (% relative intensity) 232 (M^+, 2), 175 (6), 141 (13), 123 (13), 107 (17),

91 (100), 69 (75). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.77; H, 10.51.

(*E*)-2,2-Dimethyl-5-methyl-4-nonenyl benzyl ether (**2c**). 99% yield (136 mg, 0.50 mmol). Bp 220 °C / 0.3 mmHg, R_f = 0.34 (hexane/ethyl acetate = 30:1). ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 6H), 0.89 (t, *J* = 7.9 Hz, 3H), 1.22-1.43 (m, 4H), 1.57 (s, 3H), 1.98 (d, *J* = 7.4 Hz, 2H), 1.98 (t, *J* = 6.6 Hz, 2H), 3.12 (s, 2H), 4.50 (s, 2H), 5.15 (brt, *J* = 7.9 Hz, 1H), 7.26-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3), 16.2 (CH_3), 22.6 (CH_2), 24.8 (CH_3 x 2), 36.0 (quart.), 37.4 (CH_2), 40.0 (CH_2), 73.4 (CH_2), 79.3 (CH_2), 120.9 (CH), 127.5 (CH x 2), 128.5 (CH x 2), 137.2 (quart.), 139.4 (quart.); IR (neat) 2912 (s), 2850 (s), 1489 (w), 1464 (m), 1442 (m), 1376 (m), 1354 (m), 1201 (w), 1090 (s), 1027 (w), 731 (m), 688 (m), 661 (m) cm^{-1}; mass spectrum *m/z* (% relative intensity) 274 (M^+, 1), 162 (18), 109 (6), 91 (100), 69 (29). Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.24; H, 11.27.

(*E*)-Diethyl(4-Methyl-3-octenyl)amine (**2d**). 72% yield (71 mg, 0.36 mmol). Bp 150 °C / 0.3 mmHg. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.3 Hz, 3H), 1.03 (t, *J* = 7.3 Hz, 6H), 1.23-1.40 (m, 4H), 1.60 (s, 3H), 1.97 (t, *J* = 6.9 Hz, 2H), 2.14 (dt, *J* = 7.3, 8.6 Hz, 2H), 2.43 (t, *J* = 8.6 Hz, 2H), 2.55 (q, *J* = 7.3 Hz, 4H), 5.09 (brt, *J* = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.8 (CH_3 x 2), 14.0 (CH_3), 16.0 (CH_3), 22.4 (CH_2), 25.6 (CH_2), 30.2 (CH_2), 39.4 (CH_2), 46.9 (CH_2 x 2), 52.8 (CH_2), 121.8 (CH), 136.5 (quart.); IR (neat) 2965 (s), 2865 (s), 1464 (m), 1381 (m), 1291 (w), 1150 (w), 1113 (w), 1063 (m), 661 (m) cm^{-1}; mass spectrum *m/z* (% relative intensity) 196 (M^+-H, 1), 180 (1), 86 (100), 58 (28). Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 79.15; H, 14.19; N, 7.10.

2-(2-Propyl-1-hexenyl)anisole (**2e**). 55% yield (69 mg, 0.28 mmol), as an 82/ 18 mixture of stereoisomers. major isomer ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 6.6 Hz, 3H), 1.23-1.62 (m, 6H), 2.12-2.23 (m, 4H), 3.81 (s, 3H), 6.26 (brs, 1H), 6.82-6.94 (m, 2H), 7.11-7.21 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 13.8 (CH_3), 21.0 (CH_2), 22.1 (CH_2), 29.9 (CH_2), 32.6 (CH_2), 36.1 (CH_2), 54.9 (CH_3), 109.9 (CH), 119.5 (CH), 119.8 (CH), 126.8 (CH), 127.2 (quart.), 129.7 (CH), 142.9 (quart.), 156.6 (quart.); mass spectrum *m/z* (% relative intensity) 232 (M^+, 45), 189 (24), 147 (78), 121 (100), 91 (37).

(*E*)-3-Dimethylsilyl-4-methyl-3-octenyl benzyl ether (**3a**). 73% yield (106 mg, 0.37 mmol). Bp 225 °C / 0.3 mmHg. ^{1}H NMR ($CDCl_3$) δ 0.14 (t, *J* = 3.6 Hz, 6H), 0.90 (t, *J* = 6.9 Hz, 3H), 1.26-1.40 (m, 4H), 1.73 (s, 3H), 2.15 (t, *J* = 8.2 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 3.34 (t, *J* = 8.2 Hz, 2H), 4.23 (sept, *J* = 3.6 Hz, 1H), 4.51 (s, 2H), 7.26-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ - 2.8 (CH_3 x 2), 14.1 (CH_3), 18.3 (CH_3), 22.8 (CH_2), 31.2 (CH_2), 32.2 (CH_2), 38.8 (CH_2), 69.8 (CH_2), 72.8 (CH_2), 126.0 (quart), 127.5 (CH), 127.6 (CH x 2), 128.3 (CH x 2), 138.7 (quart.), 151.0 (quart.); mass spectrum *m/z* (% relative intensity) 289 (M^+-1, 1), 199 (4), 183 (9), 165 (9), 124 (14), 91 (100), 75

(78), 59 (54).

(*E*)-3-(1-Hydroxy-1-phenylmethyl)-4-methyl-3-octenyl benzyl ether (**3b**). 83% yield (140 mg, 0.42 mmol). Bp 260 °C / 0.3 mmHg, R_f = 0.10 (hexane/ethyl acetate = 20:1). ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.3 Hz, 3H), 1.24-1.45 (m, 4H), 1.62 (s, 3H), 2.00 (dd, *J* = 15.5, 2.0 Hz, 1H), 2.14-2.26 (m, 2H), 2.20 (d, *J* = 15.5 Hz, 1H), 3.33 (d, *J* = 3.6 Hz, 1H), 3.36 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.28 (d, *J* = 5.3 Hz, 1H), 4.40 (d, *J* = 12.2 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 5.67 (d, *J* = 5.3 Hz, 1H), 7.08-7.30 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 18.9 (CH_3), 22.9 (CH_2), 28.1 (CH_2), 31.3 (CH_2), 34.3 (CH_2), 69.2 (CH_2), 70.9 (CH_2), 73.1 (CH_2), 125.8 (CH x 2), 126.3 (CH), 127.6 (CH x 2), 127.7 (CH), 127.9 (CH x 2), 128.5 (CH x 2), 132.1 (quart.), 135.8 (quart.), 137.5 (quart.), 144.7 (quart.); IR (neat) 3405 (m), 2920 (s), 2855 (s), 1492 (m), 1447 (m), 1364 (m), 1087 (s), 1023 (s), 735 (s), 697 (s), 661 (w) cm^{-1}; mass spectrum *m/z* (% relative intensity) 281 (M^+-C_4H_9, 4), 229 (8), 211 (28), 129 (22), 91 (100). Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.77; H, 9.13.

(*E*)-3-(1-Hydroxypropyl)-4-methyl-3-octenyl benzyl ether (**3c**). 80% yield (116 mg, 0.40 mmol). Bp 230 °C / 0.3 mmHg, R_f = 0.19 (hexane/ethyl acetate = 8:1). ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 6.9 Hz, 3H), 1.18-1.35 (m, 4H), 1.41 (dq, *J* = 6.8, 6.9 Hz, 2H), 1.64 (s, 3H), 1.97-2.17 (m, 2H), 2.41 (dd, *J* = 8.3, 5.3 Hz, 2H), 3.47 (brs, 1H), 3.47 (dt, *J* = 8.6, 8.3 Hz, 1H), 3.57 (dt, *J* = 8.6, 5.3 Hz, 1H), 4.46 (brt, *J* = 6.8 Hz, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 7.20-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.4 (CH_3), 14.1 (CH_3), 18.9 (CH_3), 22.8 (CH_2), 27.0 (CH_2), 29.4 (CH_2), 31.1 (CH_2), 33.7 (CH_2), 69.7 (CH_2), 71.4 (CH), 73.2 (CH_2), 127.6 (CH), 127.7 (CH x 2), 128.4 (CH x 2), 132.2 (quart.), 134.1 (quart.), 137.8 (quart.); IR (neat) 3435 (m), 2920 (s), 2855 (s), 1448 (m), 1371 (m), 1362 (m), 1095 (s), 1021 (m), 998 (m), 958 (m), 733 (m), 694 (m), 660 (w) cm^{-1}; mass spectrum *m/z* (% relative intensity) 261 (M^+-C_2H_5, 3), 181 (6), 153 (17), 91 (100). Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.56; H, 10.75.

(*E*)-3-(1-Hydroxy-1-phenylpropyl)-4-methyl-3-octenyl benzyl ether (**3d**). 69% yield (126 mg, 0.35 mmol). Bp 260 °C / 0.1 mmHg. ^{1}H NMR ($CDCl_3$) δ 0.65 (t, *J* = 6.9 Hz, 3H), 0.72-1.02 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 3H), 1.59-1.70 (m, 2H), 1.69 (s, 3H), 2.02 (ddt, *J* = 13.5, 2.0, 7.3 Hz, 1H), 2.20 (dt, *J* = 13.5, 7.3 Hz, 1H), 2.58 (dt, *J* = 14.2, 4.6 Hz, 1H), 2.83 (ddd, *J* = 14.2, 8.9, 5.9 Hz, 1H), 3.64 (s, 1H), 3.61-3.72 (m, 2H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 7.13-7.26 (m, 8H), 7.40-7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 8.6 (CH_3), 13.8 (CH_3), 19.7 (CH_3), 23.0 (CH_2), 29.4 (CH_2), 30.7 (CH_2), 33.1 (CH_2), 35.9 (CH_2), 71.0 (CH_2), 73.4 (CH_2), 78.2 (quart.), 126.1 (CH), 126.3 (CH x 2), 127.7 (CH), 127.8 (CH x 4), 128.4 (CH x 2), 133.7 (quart.), 136.6 (quart.), 137.6 (quart.), 149.6 (quart.); IR (neat) 3455 (m), 2930 (s), 1741 (s), 1493 (m), 1449 (m), 1373 (m), 1240 (s), 1096 (s), 1047 (m), 966 (m), 767 (m), 734 (m), 698 (s) cm^{-1}; mass spectrum *m/z* (% relative

intensity) 348 (M^+-H_2O, 2), 257 (7), 239 (12), 213 (33), 183 (17), 171 (11), 157 (19), 143 (30), 129 (19), 105 (16), 91 (100), 77 (13). Anal. Calcd for $C_{25}H_{34}O_2$: C, 81.92; H, 9.35. Found: C, 81.77; H, 9.53.

Ethylation and Hexylation of 1b in the Presence of $Fe(acac)_3$ (reference 12). Reactions were conducted in the same way as in the reactions with a solution of butyllithium in hexane (1.50 M, 1.50 mmol), except for using ethyllithium in ether (1.46 M, 1.0 mL, 1.46 mmol) or hexyllithium in hexane (1.19 M, 1.3 mL, 1.50 mmol). Both ethyllithium and hexyllithium were prepared in ether. The prepared solution of ethyllithium in ether (0.86 M) was once transferred to another flask, and concentrated to 1.46 M by removal of ether under reduced pressure at room temperature and the 1.46 M solution in ether was used for the carbometalation. For hexyllithium, after removal of ether in other flask under reduced pressure at room temperature, hexane was introduced to prepare the solution in hexane. The solution was again transferred to another flask, and the 1.19 M solution in hexane was used for the carbolithiation.

(*E*)-4-Methyl-3-hexenyl benzyl ether. 81% yield (83 mg, 0.41 mmol). Bp 180 °C / 0.3 mmHg, R_f = 0.18 (hexane/ethyl acetate = 30:1). ^{1}H NMR ($CDCl_3$) δ 0.99 (t, *J* = 7.3 Hz, 3H), 1.62 (s, 3H), 2.00 (q, *J* = 7.3 Hz, 2H), 2.33 (dt, *J* = 6.9, 6.9 Hz, 2H), 3.46 (t, *J* = 6.9 Hz, 2H), 4.52 (s, 2H), 5.14 (brt, *J* = 6.9 Hz, 1H), 7.26-7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.7 (CH_3), 16.0 (CH_3), 28.6 (CH_2), 32.3 (CH_2), 70.2 (CH_2), 72.8 (CH_2), 118.7 (CH), 127.4 (CH), 127.6 (CH x 2), 128.3 (CH x 2), 138.6 (quart.), 139.0 (quart.); IR (neat) 2960 (s), 2855 (s), 1454 (m), 1359 (m), 1100 (s), 735 (m), 695 (m) cm^{-1}; mass spectrum *m/z* (% relative intensity) 204 (M^+, 2), 175 (4), 113 (6), 107 (5), 91 (73), 55 (100).

(*E*)-4-Methyl-3-decen-1-yl benzyl ether. 92% yield (120 mg, 0.46mmol). R_f = 0.27 (hexane/ethyl acetate = 30:1). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.27-1.37 (m, 8H), 1.54 (s, 3H), 1.97 (t, *J* = 7.4 Hz, 2H), 2.33 (dt, *J* = 6.3, 7.2 Hz, 3H), 3.46 (t, *J* = 7.2 Hz, 2H), 4.52 (s, 2H), 5.13 (brt, *J* = 6.3 Hz, 1H), 7.26-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 16.0 (CH_3), 22.6 (CH_2), 27.9 (CH_2), 28.6 (CH_2), 29.0 (CH_2), 31.8 (CH_2), 39.7 (CH_2), 70.2 (CH_2), 72.8 (CH_2), 119.8 (CH), 127.4 (CH), 127.6 (CH x 2), 128.3 (CH x 2), 137.6 (quart.), 138.6 (quart.); IR (neat) 2927 (s), 2854 (s), 1496 (m), 1454 (m), 1361 (m), 1203 (w), 1103 (s), 1027 (m), 732 (s), 696 (s) cm^{-1}; mass spectrum *m/z* (% relative intensity) 260 (M^+, 0.1), 232 (0.1), 175 (2), 169 (1), 152 (3), 91 (100), 83 (20), 69 (24), 65 (25), 55 (54).

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