JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
J. Am. Chem. Soc., 1997, 119(42), 10014-10027, DOI:10.1021/ja9716160

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Supporting Information for:

Intramolecular Cyclization of 2,7- or 2,8-Bis-unsaturated Esters Mediated by (η^2-Propene)Ti(O-*i*-Pr)$_2$. Facile Construction of Mono- and Bicyclic Skeletons with Stereoselective Introduction of a Side Chain. A Synthesis of *d*-Sabinene

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Typical procedure for the preparation of a starting material in the mono-cyclization. *t*-Butyl 8-(trimethylsilyl)-(*E*)-2-octen-7-ynoate (6). To a stirred solution of NaH (0.15 g, 55 % suspension in mineral oil, 3.5 mmol, washed with hexane) in THF (15 mL) was added $(EtO)_2P(O)CH_2CO_2$-*t*-Bu (0.90 mL, 3.9 mmol) at 0 °C under an argon atmosphere. After the solution was stirred at rt for 30 min, 6-(trimethylsilyl)-5-hexynal (0.540 g, 3.21 mmol) was added at -78 °C. Then the mixture was stirred for 10 min at rt. The reaction was terminated by the addition of aqueous NH_4Cl solution and Et_2O. The organic layer was separated, washed with 1 M HCl and aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated *in vacuo* to an oil. The crude compound was purified on silica gel (hexane-ether) to give the title compound (0.708 g, 83%) as an oil: ^{1}H NMR δ 0.14 (s, 9H), 1.47 (s, 9H), 1.66 (quintet, J = 6.9 Hz, 2H), 2.17-2.33 (m, 4H), 5.85 (br d, J = 15.3 Hz, 1H), 6.95 (dt, J = 15.3, 6.9 Hz, 1H); ^{13}C NMR δ 0.11, 19.31, 26.94, 28.15, 30.86, 80.07, 85.26, 106.39, 123.70, 146.66, 165.92; IR (neat) 2960, 2900 (sh), 2160, 1720, 1650, 1370, 1320, 1280, 1250, 1220, 1150, 980, 840, 760, 640 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_2Si$: C, 67.62; H, 9.84. Found: C, 67.24; H, 9.86.

***t*-Butyl 8-(trimethylsilyl)-(*Z*)-2-octen-7-ynoate (*Z*-6).** This was prepared from 6-(trimethylsilyl)-5-hexynal and *t*-butyl (trimethylsilyl)acetate [Hartzell, S. L.; Sullivan, D. F.; Rathke, M. W. *Tetrahedron Lett.* **1974**, 1403. See also: Larson, G. L.; Quiroz, F.; Suárez, J. *Synth. Commun.* **1983**, *13*, 833]. ^{1}H NMR δ 0.14 (s, 9H), 1.47 (s, 9H), 1.66 (quintet, J = 7.6

Hz, 2H), 2.26 (t, J = 7.6 Hz, 2H), 2.69 (q, J = 7.6 Hz, 2H), 5.68 (br d, J = 11 Hz, 1H), 6.12 (dt, J = 11, 7.6 Hz, 1H); ^{13}C NMR δ -0.02, 19.49, 27.99, 28.09, 28.13, 80.13, 84.84, 106.96, 122.30, 147.58, 166.00; IR (neat) 2960, 2940 (sh), 2170, 1720, 1640, 1410, 1370, 1250, 1220, 1150, 840, 760, 700, 640 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_2Si$: C, 67.62; H, 9.84. Found: C, 67.22; H, 9.60.

***t*-Butyl (*E*)-2-tridecen-7-ynoate (15).** This was prepared from 5-undecyn-1-ol by Swern oxidation and the Horner-Emmons reaction in 75 % overall yield. ^{1}H NMR δ 0.89 (t, J = 7.1 Hz, 3H), 1.22-1.54 (m, 6H), 1.47 (s, 9H), 1.62 (quintet, J = 7 Hz, 2H), 2.08-2.22 (m, 4H), 2.28 (br q, J = 7.1 Hz, 2H), 5.76 (dt, J = 15.6, 1.5 Hz, 1H), 6.84 (dt, J = 15.6, 7.1 Hz, 1H); ^{13}C NMR δ 13.88, 18.16, 18.60, 22.11, 27.36, 28.05, 28.69, 30.89, 30.98, 79.12, 80.06, 81.12, 123.56, 147.22, 166.20; IR (neat) 2940, 2930, 2860, 1720, 1650, 1460, 1370, 1330, 1290, 1260, 1220, 980 cm^{-1}. Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.15; H, 10.68.

***t*-Butyl 9-(trimethylsilyl)-(*E*)-2-nonen-8-ynoate (17).** This was prepared from 6-(trimethylsilyl)-5-hexyn-1-ol in 44% overall yield *via* the following sequence: (*i*) MsCl, Et_3N; (*ii*) NaCN; (*iii*) Dibal-H; (*iv*) $(EtO)_2P(O)CH_2CO_2$-*t*-Bu, NaH. ^{1}H NMR δ 0.06 (s, 9H), 1.36-1.67 (m, 4H), 1.47 (s, 9H), 2.08-2.31 (m, 4H), 5.74 (br d, J = 15.8 Hz, 1H), 6.84 (dt, J = 15.8, 7.0 Hz, 1H); ^{13}C NMR δ 0.01, 19.51, 27.05, 27.88, 28.06, 31.34, 80.02, 84.76, 107.01, 123.35, 147.55, 166.21; IR (neat) 2960, 2940, 2900 (sh), 2860, 2180, 1720, 1650, 1370, 1320, 1290, 1250, 1160, 1140, 980, 840, 760, 640 cm^{-1}. Anal. Calcd for $C_{16}H_{28}O_2Si$: C, 68.52; H, 10.06. Found: C, 68.24; H, 10.09.

***N*,*N*-Diethyl-(*E*)-2-tridecen-7-ynamide (21).** This was prepared from 5-undecyn-1-ol by Swern oxidation and the Horner-Emmons reaction (NaH, $(EtO)_2P(O)CH_2CONEt_2$, 1,2-DME) in 73% overall yield [Landor, P. D.; Landor, S. R.; Odyek, O. *J. Chem. Soc., Perkin I.* **1977**, 93]. ^{1}H NMR δ 0.86 (t, J = 6.9 Hz, 3H), 1.11 (t, J = 7.5 Hz, 3H), 1.17 (t, J = 7.6 Hz, 3H), 1.21-1.38 (m, 4H), 1.39-1.52 (m, 2H), 1.61 (quintet, J = 7.2 Hz, 2H), 2.04-2.21 (m, 4H), 2.29 (q, J = 7.2 Hz, 2H), 3.34 (q, J = 7.5 Hz, 2H), 3.39 (q, J = 7.6 Hz, 2H), 6.19 (br d, J = 14.9 Hz, 1H), 6.85 (dt, J = 14.9, 7.2 Hz, 1H); ^{13}C NMR δ 13.11, 13.92, 14.79, 18.19, 18.65, 22.14, 27.69, 28.76, 31.01, 31.35, 40.73, 42.08, 79.18, 80.94, 121.07, 144.95, 165.75; IR

(neat) 2980, 2930, 2860, 2370, 1660, 1620, 1450 (sh), 1430, 1380, 1360, 1280, 1250, 1220, 1140, 1100, 970 cm^{-1}. Anal. Calcd for $C_{17}H_{29}ON$: C, 77.51; H, 11.10; N, 5.32. Found: C, 77.34; H, 10.93; N, 5.25.

Ethyl 8-(trimethylsilyl)-(*E*)-2-octen-7-ynoate (28). This was prepared from 6-(trimethylsilyl)-5-hexyn-1-ol by Swern oxidation and the Horner-Emmons reaction in 67% overall yield. ^1H NMR δ 0.15 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.68 (quintet, *J* = 7.1 Hz, 2H), 2.26 (t, *J* = 7.1 Hz, 2H), 2.32 (dq, *J* = 1.4, 7.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 5.85 (dt, *J* = 15.6, 1.4 Hz, 1H), 6.95 (dt, *J* = 15.6, 7.1 Hz, 1H); ^{13}C NMR δ 0.09, 14.24, 19.27, 26.86, 31.00, 60.16, 85.35, 106.26, 122.00, 147.96, 166.54; IR (neat) 2960, 2940 (sh), 2900 (sh), 2180, 1720, 1660, 1270 (sh), 1250, 1190, 1150, 1040, 840, 760 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.17; H, 9.43.

Ethyl 8-(trimethylsilyl)-(*Z*)-2-octen-7-ynoate (37). This was prepared from 6-(trimethylsilyl)-5-hexynal by a literature method [Taguchi, H.; Shimoji, K.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2529]. ^1H NMR δ 0.15 (s, 9H), 1.28 (t, *J* = 7.7 Hz, 3H), 1.68 (quintet, *J* = 7.7 Hz, 2H), 2.27 (t, *J* = 7.7 Hz, 2H), 2.74 (q, *J* = 7.7 Hz, 2H), 4.16 (q, *J* = 7.7 Hz, 2H), 5.78 (d, *J* = 11.0 Hz, 1H), 6.20 (dt, *J* = 11.0, 7.7 Hz, 1H); ^{13}C NMR δ 0.17, 14.27, 19.59, 28.11, 28.22, 59.79, 84.92, 106.46, 122.46, 148.91, 166.25; IR (neat) 3050, 2980, 2940, 2880, 2180, 1730, 1650, 1260, 1200, 850, 760, 700 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.66; H, 9.32.

Ethyl (*E*)-2-tridecen-7-ynoate (38). This was prepared from 5-undecynal by the Horner-Emmons reaction in 73 % yield. ^1H NMR δ 0.90 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.24-1.42 (m, 4H), 1.42-1.54 (m, 2H), 1.64 (quintet, *J* = 7.1 Hz, 2H), 2.19-2.23 (m, 4H), 2.31 (dq, *J* = 1.5, 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 5.69 (dt, *J* = 15.6, 1.5 Hz, 1H), 6.96 (dt, *J* = 15.6, 7.1 Hz, 1H); ^{13}C NMR δ 13.90, 14.20, 18.21, 18.64, 22.14, 27.39, 28.74, 31.02, 31.06, 60.06, 78.95, 81.13, 121.80, 148.23, 166.51; IR (neat) 2950, 2860, 2220, 1720, 1650, 1450, 1380, 1320, 1270, 1200, 1160, 1100, 1040, 980, 860 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.19; H, 10.35.

Ethyl 9-(trimethylsilyl)-(*E*)-2-nonen-8-ynoate (40). This was prepared from 6-(trimethylsilyl)-5-hexyn-1-ol in 53% overall yield *via* the following sequence: (*i*) MsCl, Et_3N; (*ii*)

NaCN; (*iii*) Dibal-H; (*iv*) $(EtO)_2P(O)CH_2CO_2Et$, NaH. ^1H NMR δ 0.14 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H), 1.46-1.63 (m, 4H), 2.16-2.28 (m, 4H), 4.18 (q, J = 7.1 Hz, 2H), 5.82 (dt, J = 15.7, 1.5 Hz, 1H), 6.95 (dt, J = 15.7, 6.9 Hz, 1H); ^{13}C NMR δ 0.13, 14.25, 19.61, 27.07, 27.93, 31.57, 60.13, 84.80, 106.87, 121.58, 148.69, 166.64; IR (neat) 2970 (sh), 2950, 2910, 2870, 2180, 1720, 1660, 1370, 1310, 1270, 1250, 1190, 1150, 1050, 980, 850, 760 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.16; H, 9.75.

Methyl 6-[(*t*-butyl)dimethylsiloxy]-8-(trimethylsilyl)-(*E*)-2-octen-7-ynoate (**42**): ^1H NMR δ 0.10 (s, 3H), 0.13 (s, 3H), 0.15 (s, 9H), 0.89 (s, 9H), 1.69-1.88 (m, 2H), 2.22-2.46 (m, 2H), 3.72 (s, 3H), 4.36 (t, J = 6.2 Hz, 1H), 5.84 (br d, J = 15.7 Hz, 1H), 6.95 (dt, J = 15.7, 6.9 Hz, 1H); ^{13}C NMR δ -4.94, -4.40, 0.11, 18.21, 25.79, 27.91, 36.66, 51.37, 62.52, 89.32, 106.91, 121.25, 148.78, 167.01; IR (neat) 2950, 2990, 2930, 2860, 2170, 1730, 1660, 1440, 1330, 1250, 1200, 1160, 1100, 1050, 840, 880, 760 cm^{-1}. Anal. Calcd for $C_{18}H_{34}O_3Si_2$: C, 60.96; H, 9.66. Found: C, 60.71; H, 9.60.

Ethyl 4-[(*t*-butyl)dimethylsiloxy]-8-(trimethylsilyl)-(*E*)-2-octen-7-ynoate (**44**). This was prepared from 6-(trimethylsilyl)-5-hexyn-1-ol *via* the following sequence: (*i*) $(ClCO)_2$, DMSO, Et_3N; (*ii*) TMSCN, cat. ZnI_2; (*iii*) H^+; (*iv*) TBSCl, Et_3N, cat. DMAP; (*v*) Dibal-H; (*vi*) $(EtO)_2P(O)CH_2CO_2Et$, NaH. ^1H NMR δ 0.04 (s, 3H), 0.08 (s, 3H), 0.14 (s, 9H), 0.91 (s, 9H), 1.29 (t, J = 6.8 Hz, 3H), 1.64-1.78 (m, 2H), 2.16-2.40 (m, 2H), 4.18 (q, J = 6.8 Hz, 1H), 4.19 (q, J = 6.8 Hz, 1H), 4.45 (br q, J = 5.4 Hz, 1H), 5.97 (dd, J = 1.7, 15.7 Hz, 1H), 6.90 (dd, J = 5.4, 15.7 Hz, 1H); ^{13}C NMR δ -5.11, -4.67, 0.06, 14.12, 15.53, 18.05, 25.75, 35.96, 60.33, 70.14, 85.40, 106.49, 120.47, 150.26, 166.65; IR (neat) 2960, 2930, 2900, 2860, 2180, 1720, 1660, 1470, 1370, 1250, 1160, 1120, 1090, 1050, 980, 840, 780, 760, 640 cm^{-1}. Anal. Calcd for $C_{19}H_{36}O_3Si_2$: C, 61.90; H, 9.84. Found: C, 61.45; H, 9.80.

Ethyl 4-butyl-8-(trimethylsilyl)-(*E*)-2-octen-7-ynoate (**46**). This was prepared from 6-(trimethylsilyl)-5-hexyn-1-ol *via* the following sequence: (*i*) Jones reagent; (*ii*) $(ClCO)_2$; (*iii*) EtOH, Et_3N; (*iv*) LDA, BuI, HMPA; (*v*) $LiAlH_4$; (*vi*) $(ClCO)_2$, DMSO, Et_3N; (*vii*) $(EtO)_2P(O)CH_2CO_2Et$, NaH. ^1H NMR δ 0.14 (s, 9H), 0.87 (t, J = 6.9 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.14-1.59 (m, 7H), 1.68 (br ddt, J = 5.2, 13.5, 7.9 Hz, 1H), 2.04-2.36 (m, 3H), 4.18 (q, J = 7.2 Hz, 2H), 5.80 (dd, J = 0.8, 15.7 Hz, 1H), 6.68 (dd, J = 9.3, 15.7 Hz, 1H); ^{13}C

NMR δ -0.04, 13.83, 14.15, 17.67, 22.49, 29.16, 32.91, 33.72, 41.43, 60.20, 85.04, 106.75, 121.89, 152.39, 166.72; IR (neat) 2960, 2930, 2860, 2180, 1720, 1650, 1370, 1310, 1270, 1250, 1210, 1160, 1040, 840, 760 cm^{-1}. Anal. Calcd for $C_{17}H_{30}O_2Si$: C, 69.33; H, 10.27. Found: C, 69.20; H, 10.15.

Ethyl (*E*)-2,7-octadienoate (50). This was prepared from 5-hexenal by the Horner-Emmons reaction in 55% yield. ^1H NMR δ 1.29 (t, *J* = 7.0 Hz, 3H), 1.56 (quintet, *J* = 7.2 Hz, 2H), 2.09 (br q, *J* = 7.2 Hz, 2H), 2.22 (dq, *J* = 1.4, 7.2 Hz, 2H), 4.19 (q, *J* = 7.0 Hz, 2H), 4.98 (dd, *J* = 1.4, 10.2 Hz, 1H), 5.05 (dq, *J* = 17.0, 1.4 Hz, 1H), 5.79 (ddt, *J* = 10.2, 17.0, 7.2 Hz, 1H), 5.82 (dt, *J* = 15.4, 1.4 Hz, 1H), 6.96 (dt, *J* = 15.4, 7.2 Hz, 1H); ^{13}C NMR δ 14.26, 27.19, 31.48, 33.06, 60.13, 115.07, 121.58, 137.99, 148.85, 166.69; IR (neat) 3100, 3000, 2950, 2880, 1730, 1660, 1460, 1380, 1320 (sh), 1280, 1200, 1180, 1050, 990, 920 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.53; H, 9.98.

Ethyl 4,5-benzo-(*E*)-2,7-octadienoate (52). This was prepared from *o*-bromobenzaldehyde *via* the following sequence: (*i*) $HOCH_2CH_2OH$, H^+; (*ii*) *t*-BuLi, $Li_2Cu(CN)$(2-thienyl), allyl bromide; (*iii*) H^+; (*iv*) $(EtO)_2P(O)CH_2CO_2Et$, NaH. ^1H NMR δ 1.34 (t, *J* = 7.1 Hz, 3H), 3.52 (br d, *J* = 6.1 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.99 (dq, *J* = 17.0, 1.6 Hz, 1H), 5.09 (dq, *J* = 10.1, 1.6 Hz, 1H), 5.96 (ddt, *J* = 10.1, 17.0, 6.1 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 7.19-7.37 (m, 3H), 7.58 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.99 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR δ 14.26, 37.40, 60.38, 116.28, 119.60, 126.55, 126.77, 130.04, 130.18, 133.39, 136.47, 139.17, 142.07, 166.87; IR (neat) 3070, 2990, 2940 (sh), 2900 (sh), 1720, 1640, 1600, 1480, 1450, 1370, 1320, 1280, 1270, 1220, 1170, 1040, 980, 920, 760 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.63; H, 7.45.

Ethyl (2*E*,7*Z*)-2,7-tridecadienoate (55) (93-94% *Z*). This was prepared from (*Z*)-4-decen-1-ol (93-94% *Z*) *via* the following sequence: (*i*) MsCl, Et_3N; (*ii*) NaCN; (*iii*) Dibal-H; (*iv*) $(EtO)_2P(O)CH_2CO_2Et$, NaH. ^1H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.16-1.40 (m, 6H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.51 (quintet, *J* = 6.8 Hz, 2H), 1.92-2.11 (m, 4H), 2.20 (dq, *J* = 1.6, 6.8 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 5.24-5.47 (m, 2H), 5.81 (dt, *J* = 15.4, 1.6 Hz, 1H), 6.96 (dt, *J* = 15.4, 6.8 Hz, 1H); ^{13}C NMR δ 14.01, 14.25, 22.52, 26.59, 27.22, 28.04, 29.35, 31.49, 31.65, 60.08, 121.45, 128.63, 130.86, 149.01, 166.66; IR (neat) 2980, 2930, 2860, 1720,

1650, 1460, 1370, 1310, 1270, 1190, 1150, 1040, 980 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.49; H, 11.06.

A preparation of a starting material for Type II tandem cyclization. Ethyl 7-octen-2-ynoate (56). To a stirred solution of CBr_4 (29.1 g, 87.7 mmol) in CH_2Cl_2 (60 mL) was added PPh_3 (45.9 g, 175 mmol) in CH_2Cl_2 (40 mL) and 5-hexenal (2.15g, 21.9 mmol) in this order at 0 °C under an argon atmosphere. After the solution was stirred for 30 min at 0 °C, the reaction was terminated by the addition of H_2O and Et_2O. The organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified on silica gel (hexane) to give 1,1-dibromo-1,6-heptadiene (4.86 g, 87%). To a stirred solution of this dibromide (4.37 g, 17.2 mmol) in THF (60 mL) was added BuLi (13.3 mL, 2.85 M solution in hexane, 37.8 mmol) at -78 °C under an argon atmosphere. The solution was kept for 1 h at this temperature and stirred for 1 h at rt. Then ethyl chloroformate (2.30 mL, 24.1 mmol) was added at -78 °C. After stirring for 30 min at -78 °C, the reaction was terminated by the addition of H_2O and Et_2O. The organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo* to an oil. The crude oil was purified on silica gel to give the title compound (2.80 g, 88%): ^1H NMR δ 1.31 (t, J = 7.1 Hz, 3H), 1.69 (quintet, J = 7.1 Hz, 2H), 2.17 (tq, J = 1.5, 7.1 Hz, 2H), 2.35 (t, J = 7.1 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 5.01 (br d, J = 10.3 Hz, 1H), 5.06 (dq, J = 17.0, 1.5 Hz, 1H), 5.77 (ddt, J = 10.3, 17.0, 7.1 Hz, 1H); ^{13}C NMR δ 14.01, 17.96, 26.66, 32.61, 61.72, 73.41, 88.89, 115.71, 137.08, 153.78; IR (neat) 2980, 2930, 2860, 2240, 1700, 1640, 1450, 1360, 1250, 1070, 1010, 990, 910, 750 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.86; H, 8.60.

Ethyl 4-(*N*-benzyl-*N*-allylamino)-2-butynoate (67). This was prepared from the corresponding acetylene *via* lithiation with BuLi (1.1 equiv, THF, -78 °C, 20 min) and the addition of $ClCO_2Et$ (1.1 equiv, -78 °C→r.t.) in 94 % yield. ^1H NMR δ 1.34 (t, J = 7.7 Hz, 3H), 3.19 (d, J = 7.0 Hz, 2H), 3.45 (s, 2H), 3.66 (s, 2H), 4.25 (q, J = 7.7 Hz, 2H), 5.19 (d, J = 9.0 Hz, 1H), 5.29 (d, J = 17.0 Hz, 1H), 5.85 (ddd, J = 7.0, 9.0, 17.0 Hz, 1H), 7.22-7.38 (m, 5H); ^{13}C NMR δ 14.04, 41.30, 56.70, 57.48, 61.92, 77.80, 83.41, 118.35, 127.28, 128.36, 129.01, 135.09, 138.16, 153.44; IR (neat) 3080, 3040, 2990, 2940, 2830, 2230, 1720, 1460, 1370, 1250, 1060, 750, 700 cm^{-1}. Anal. Calcd for $C_{16}H_{19}O_2N$: N, 5.44. Found: N, 5.21.

Ethyl 4-(allyloxy)-2-nonynoate (69). This was prepared analogously in 84 % yield from the corresponding terminal acetylene. ^{1}H NMR δ 0.88 (t, *J* = 7.5 Hz, 3H), 1.30 (m, 7H), 1.45 (quintet, *J* = 7.5 Hz, 2H), 1.75 (m, 2H), 3.96 (dd, *J* = 6.0, 14.0 Hz, 1H), 4.14-4.31 (m, 4H), 5.22 (d, *J* = 9.0 Hz, 1H), 5.32 (d, *J* = 17.0 Hz, 1H), 5.89 (ddd, *J* = 6.0, 9.0, 17.0 Hz, 1H); ^{13}C NMR δ 13.91, 13.97, 22.41, 24.75, 31.37, 34.95, 61.98, 68.45, 70.08, 77.42, 86.30, 117.72, 133.91, 153.31; IR (neat) 3080, 2950, 2860, 2230, 1720, 1470, 1250, 1080 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.31; H, 9.27.

Ethyl 6-[(*tert*-butyl)dimethylsiloxy]-7-octen-2-ynoate (72). This was prepared from 1-(trimethylsilyl)-4-iodo-1-butyne in 36% overall yield *via* the following reactions: i) lithiation of the iodide (*t*-BuLi, ether) followed by the addition of acrolein, ii) protection of the hydroxy group (ethyl vinyl ether, cat. TsOH•H_2O, ether), iii) desilylation (TBAF), iv) ethoxycarbonylation (BuLi, $ClCO_2Et$, THF), v) deprotection of the EE ether (ether-THF-3 N HCl (1:1:1), r. t.), and vi) silylation (TBS-Cl, imidazole, DMF). ^{1}H NMR δ 0.02 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 1.29 (t, *J* = 7 Hz, 3 H), 1.74 (q, *J* = 7.5 Hz, 2 H), 2.32 (dt, *J* = 14, 7.5 Hz, 1 H), 2.40 (dt, *J* = 14, 7.5 Hz, 1 H), 4.20 (q, *J* = 7 Hz, 2 H), 5.07 (d, *J* = 9 Hz, 1 H), 5.18 (d, *J* = 16 Hz, 1 H), 5.75 (ddd, *J* = 7, 9, 16 Hz, 1 H); ^{13}C NMR δ -5.01, -4.43, 13.98, 14.34, 18.12, 25.79, 35.54, 61.61, 72.00, 73.33, 89.06, 114.60, 140.46, 153.70; IR (neat) 2960, 2930, 2900, 2860, 2240, 1715, 1470, 1360, 1250, 1130, 1070, 1020, 990, 920, 840, 780, 750, 680 cm^{-1}. Anal. Calcd for $C_{16}H_{28}O_3Si$: C, 64.82; H, 9.52. Found: C, 65.09; H, 9.92.

Ethyl 6-vinyl-2-decynoate (74): ^{1}H NMR δ 0.87 (t, *J* = 7 Hz, 3 H), 1.24 (m, 6 H), 1.28 (t, *J* = 7.5 Hz, 3 H), 1.44 (m, 1 H), 1.67 (m, 1 H), 2.04 (m, 1 H), 2.21 (dd, *J* = 7.5, 16.5 Hz, 1 H), 2.32 (ddd, *J* = 6.8, 7.5, 16.5 Hz, 1 H), 4.20 (q, *J* = 7.5 Hz, 2 H), 4.99 (d, *J* = 17 Hz, 1 H), 5.01 (d, *J* = 9 Hz, 1 H), 5.44 (dt, *J* = 17, 9 Hz, 1 H); ^{13}C NMR δ 13.90 (2 peaks), 16.45, 22.58, 29.14, 32.43, 34.39, 43.29, 61.70, 73.11, 89.49, 115.78, 141.67, 154.00; IR (neat) 3080, 2960, 2920, 2880, 2860, 2240, 1715, 1640, 1460, 1420, 1365, 1300 (sh), 1250, 1070, 1000, 920, 860, 750 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.33; H, 10.05.

Ethyl 6-[[(*tert*-butyl)dimethylsiloxy]methyl]-7-octen-2-ynoate (76). This is a racemic form of **86**. For physical properties, see those of **86**.

Ethyl (*E*)-7-tridecen-2-ynoate (78) (>98-99% *E*). This was prepared from commercially available ethyl *E*-4-decenoate *via* the following reactions: i) reduction ($LiAlH_4$, ether, 100%), ii) tosylation (TsCl, py) and iodination (NaI, acetone, 92% for 2 steps), iii) alkylation of (trimethylsilyl)acetylene (BuLi, THF-HMPA) and desilylation (TBAF, 84% for 2 steps), and iv) ethoxycarbonylation (BuLi, $ClCO_2Et$, THF, 96%). The isomeric purity was determined in comparison with an authentic sample of the *Z*-isomer by ^{13}C NMR analysis. ^1H NMR δ 0.87 (t, *J* = 7 Hz, 3 H), 1.26 (m, 6 H), 1.29 (t, *J* = 7.5 Hz, 3 H), 1.62 (quintet, *J* = 7 Hz, 2 H), 1.95 (q, *J* = 7 Hz, 2 H), 2.08 (q, *J* = 7 Hz, 2 H), 2.30 (t, *J* = 7 Hz, 2 H), 4.20 (q, *J* = 7.5 Hz, 2 H), 5.31 (dt, *J* = 15.4, 7 Hz, 1 H), 5.44 (dt, *J* = 15.4, 7 Hz, 1 H); ^{13}C NMR δ 13.91, 17.83, 22.41, 27.30, 29.09, 31.28, 31.41 (2 peaks), 32.41, 61.53, 73.26, 89.01, 128.17, 132.02, 153.67; IR (neat) 2960, 2920, 2860, 2240, 1720, 1460, 1360, 1250, 1070, 970, 750 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 75.89; H, 10.27.

Ethyl (*Z*)-7-tridecen-2-ynoate (80) (93-94% *Z*). This was prepared from commercially available *Z*-4-decen-1-ol *via* the following reactions: i) tosylation (TsCl, py) and iodination (NaI, acetone, 90% for 2 steps), ii) alkylation with (trimethylsilyl)acetylene (BuLi, THF-HMPA) and desilylation (TBAF, 86% for 2 steps), and iii) ethoxycarbonylation (BuLi, $ClCO_2Et$, THF, 93%). The isomeric purity was determined in comparison with an authentic sample of the *E*-isomer by ^{13}C NMR analysis. ^1H NMR δ 0.88 (t, *J* = 7 Hz, 3 H), 1.25 (m, 6 H), 1.28 (t, *J* = 7.5 Hz, 3 H), 1.63 (quintet, *J* = 7 Hz, 2 H), 2.01 (q, *J* = 7 Hz, 2 H), 2.15 (q, *J* = 7 Hz, 2 H), 2.31 (t, *J* = 7 Hz, 2 H), 4.20 (q, *J* = 7.5 Hz, 2 H), 5.27 (dt, *J* = 10, 7 Hz, 1 H), 5.41 (dt, *J* = 10, 7 Hz, 1 H); ^{13}C NMR δ 13.92 (2 peaks), 17.97, 22.44, 26.10, 27.13, 27.46, 29.28, 31.41, 61.55, 73.29, 88.95, 127.63, 131.57, 153.66; IR (neat) 2960, 2930, 2860, 2240, 1715, 1460, 1360, 1250, 1080, 750 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 76.32; H, 10.07.

(4*S*)-3-[(2*S*)-2-Vinyl-4-pentenoyl]-4-isopropyl-2-oxazolidinone (88). To diisopropylamine (1.56 mL, 11.2 mmol) in 40 mL of THF was added BuLi (4.67 mL of a 2.40 M solution in hexane, 11.2 mmol) at -78 °C. After 10 min, hexamethylphosphoric triamide (1.95 mL, 11.2 mmol) in 5 mL of THF was added, and the mixture was stirred for 30 min at -78 °C. The oxazolidinone **87** [Ref. 33a in text] (2.0 g, 10.2 mmol) in 20 mL of THF was added at that

temperature, followed 15 min later by allyl bromide (2.65 mL, 30.6 mmol). After the stirring was continued for 20 min at -78 °C, the solution was gradually allowed to come to -10 °C over 30 min, and was kept at this temperature for 1 h. Dilute hydrochloric acid was added and the organic products were extracted with ether-hexane (1:1). Combined organic extracts were washed with aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated to an oil, which was purified by silica gel chromatography to afford the title compound (1.47 g, 61%) as an inseparable 9:1 mixture of diastereoisomers.

Major isomer: ^1H NMR δ 0.85 (d, *J* = 7.5 Hz, 3 H), 0.89 (d, *J* = 7.5 Hz, 3 H), 2.30 (m, 2 H), 2.58 (dt, *J* = 14, 7.5 Hz, 1 H), 4.18 (dd, *J* = 3, 8 Hz, 1 H), 4.23 (t, *J* = 8 Hz, 1 H), 4.41 (dt, *J* = 8, 3.5 Hz, 1 H), 4.58 (q, *J* = 7.5 Hz, 1 H), 5.00 (d, *J* = 10 Hz, 1 H), 5.06 (d, *J* = 18 Hz, 1 H), 5.13 (d, *J* = 10 Hz, 1 H), 5.18 (d, *J* = 18 Hz, 1 H), 5.76 (ddt, *J* = 10, 18, 7 Hz, 1 H), 5.88 (ddd, *J* = 8, 10, 18 Hz, 1 H); ^{13}C NMR δ 14.53, 17.84, 28.36, 36.79, 46.81, 58.61, 63.08, 117.22, 117.92, 134.89, 135.58, 153.73, 173.68; IR (neat) 3080, 2960, 2930, 2880, 1780, 1700, 1640, 1490, 1460, 1440, 1390, 1370, 1300, 1230, 1200, 1140, 1120, 1100, 1060, 1020, 990, 920, 770, 750, 720, 660 cm^{-1} for a 9:1 mixture of the diastereoisomers. Anal. Calcd for $C_{13}H_{19}O_3N$: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.64; H, 8.08; N, 5.74 for a 9:1 mixture of the diastereoisomers.

Minor isomer. The following peaks are characteristic of the minor diastereoisomer. ^1H NMR δ 0.82 (d, *J* = 7.5 Hz, 3H), 5.26 (d, *J* = 18 Hz, 1 H); ^{13}C NMR δ 14.46, 17.76, 28.20, 35.72, 46.71, 58.27, 117.04, 118.14, 135.24, 135.73.

(*tert*-Butyl)dimethylsilyl ether of (*S*)-2-vinyl-4-penten-1-ol (89). To $LiAlH_4$ (0.706 g, 18.6 mmol) in 20 mL of THF was added the allylated oxazolidinone **88** (1.47 g, 6.20 mmol) in 4 mL of THF at 0 °C. After stirring at 0 °C for 30 min, the solution was diluted with dry ether. Water (0.71 mL), 15% aqueous NaOH solution (0.71 mL), and water (2.2 mL) were cautiously added in this order with vigorous stirring. The organic layer was filtered to remove solid materials, dried (Na_2SO_4), and concentrated to give an oil. A mixture of this crude alcohol, TBS-Cl (1.40 g, 9.3 mmol), and imidazole (0.844 g, 12.4 mmol) in DMF (3 mL) was stirred at room temperature for 1 h. The solution was diluted with pentane-ether (1:1) and the organic phase was washed successively with 1 N HCl and aqueous $NaHCO_3$ solution. Drying (Na_2SO_4) and

concentration of the organic layer afforded a crude oil, which was purified on silica gel (ether-hexane) to give the title compound (1.19 g, 85%): ^{1}H NMR δ 0.03 (s, 6 H), 0.89 (s, 9 H), 2.06 (m, 1 H), 2.27 (m, 2 H), 3.50 (dd, *J* = 5.8, 9.7 Hz, 1 H), 3.55 (dd. *J* = 5.8, 9.7 Hz, 1 H), 4.96-5.08 (m, 4 H), 5.62-5.85 (m, 2 H); ^{13}C NMR δ -5.54, -5.50, 18.21, 25.81, 35.23, 45.94, 65.84, 115.53, 115.88, 136.95, 139.78; IR (neat) 3080, 2960, 2930, 2900, 2860, 1640, 1470, 1440, 1420, 1380, 1360, 1250, 1100, 990, 910, 840, 780, 660 cm^{-1}. $[\alpha]_D^{23}$ +7.9 (*c* 2, $CHCl_3$) for a sample of 80% ee. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.89; H, 11.62.

(*S*)-4-[[(*tert*-Butyl)dimethylsiloxy]methyl]-5-hexen-1-ol (90). To the diene **89** (1.15 g, 5.08 mmol) in 25 mL of THF was added 9-BBN (13.2 mL of a 0.5 M solution of THF, 6.6 mmol) at -20 °C. The solution was stirred at 0 °C for 14.5 h and was allowed to warm to 15 °C over 6 h. Then, water (1.68 mL) was cautiously added, followed by 3 N-NaOH (3.36 mL) and aqueous 35% H_2O_2 (3.36 mL) with occasional cooling. The heterogeneous mixture was stirred at room temperature for 1.5 h. Extractive workup with ether-hexane (1:1) gave an organic phase, which was washed with brine, dried (Na_2SO_4), and finally chromatographed on silica gel to furnish the starting material (221 mg, 19% recovery), the pure title compound (0.58 g, 47% or 58% based on conversion) as a colorless oil, and regioisomeric 3-[[(*tert*-butyl)dimethylsiloxy]methyl]-5-hexen-1-ol (**97**) (91 mg, **97**:**90** = 8:2). ^{1}H NMR δ 0.03 (s, 6 H), 0.88 (s, 9 H), 1.25 (m, 1 H), 1.34 (br s, 1 H), 1.45-1.70 (m, 3 H), 2.18 (m, 1 H), 3.48 (dd, *J* = 7.5, 9 Hz, 1 H), 3.54 (dd, *J* = 6, 9 Hz, 1 H), 3.62 (t, *J* = 5.6 Hz, 2 H), 5.02 (m, 2 H), 5.61 (m, 1 H); ^{13}C NMR δ -5.51, 18.21, 25.79, 26.69, 30.12, 46.26, 62.96, 66.55, 115.82, 140.08; IR (neat) 3350 (br), 3080, 2960, 2930, 2890, 2860, 1640, 1470, 1250, 1100, 1060, 910, 840, 770 cm^{-1}. $[\alpha]_D^{23}$ +13.6 (*c* 2.1, $CHCl_3$) for a sample of 80% ee. Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.54. Found: C, 63.93; H, 11.59.

(*S*)-4-[[(*tert*-Butyl)dimethylsiloxy]methyl]-5-hexenal. To a mixture of the alcohol **90** (0.55 g, 2.25 mmol), DMSO (3.2 mL, 45 mmol), and NEt_3 (3.15 mL, 22.5 mmol) in 3.3 mL of CH_2Cl_2 was added SO_3•pyridine (2.16 g, 13.6 mmol) in portions at 0 °C. The cooling bath was removed and the mixture was stirred at room temperature for 15 min. After the reaction mixture was diluted with dry ether-hexane (1:1), the reaction was terminated by the addition of ice

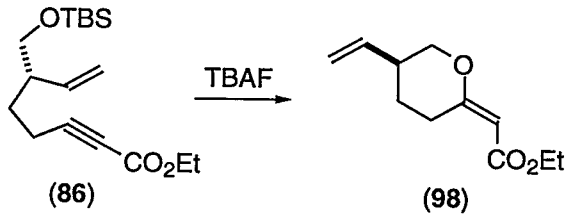
and water. The organic layer was separated, washed twice with 1 N HCl and twice with aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated to leave a crude oil of the title aldehyde (0.531 g), which was directly used in the next step without further purification. ^1H NMR δ 0.02 (s, 6 H), 0.87 (s, 9 H), 1.54 (m, 1 H), 1.89 (m, 1 H), 2.15 (m, 1 H), 2.38 (ddd, J = 1.5, 8, 16 Hz, 1 H), 2.48 (ddd, J = 1.5, 8, 16 Hz, 1 H), 3.48 (dd, J = 6, 9 Hz, 1 H), 3.57 (dd, J = 5, 9 Hz, 1 H), 5.04 (d, J = 16.5 Hz, 1 H), 5.06 (d, J = 9 Hz, 1 H), 5.57 (ddd, J = 7.5, 9, 16.5 Hz, 1 H), 9.76 (t, J = 1.5 Hz, 1 H).

(*S*)-1,1-Dibromo-4-[[(*tert*-butyl)dimethylsiloxy]methyl]-1,6-heptadiene. To a CH_2Cl_2 solution (1.9 mL) of CBr_4 (1.50 g, 4.5 mmol) was added a solution of PPh_3 (2.36 g, 9.0 mmol) in CH_2Cl_2 (5.0 mL) at 0 °C. After being stirred at 0 °C for 15 min, the mixture was cooled to -78 °C and the above crude aldehyde (0.531 g) in 3 mL of CH_2Cl_2 was added. After the mixture was stirred at -78 °C for 1 h, it was allowed to come to room temperature over 20 min and was diluted with hexane. Celite and a small amount of powdered $NaHCO_3$ were added, and the suspension was filtered. The combined filtrate and hexane washings were concentrated and chromatographed on silica gel to afford the title compound (685 mg, 76% overall yield from the alcohol) as a pale yellow oil, which was immediately used in the next step. ^1H NMR δ 0.04 (s, 6 H), 0.88 (s, 9 H), 1.34 (m, 1 H), 1.66 (m, 1 H), 1.98-2.22 (m, 3 H), 3.49 (dd, J = 7.5, 10.5 Hz, 1 H), 3.56 (dd, J = 6.8, 10.5 Hz, 1 H), 5.06 (d, J = 16.5 Hz, 1 H), 5.08 (d, J = 11.3 Hz, 1 H), 5.61 (m, 1 H), 6.39 (t, J = 7.5 Hz, 1 H).

Ethyl (*S*)-6-[[(*tert*-butyl)dimethylsiloxy]methyl]-7-octen-2-ynoate (86). To the above dibromide (685 mg, 1.71 mmol) in 20 mL of THF was added BuLi (1.57 mL of a 2.40 M hexane solution, 3.76 mmol) at -78 °C. After the mixture was stirred at -78 °C for 1 h, ethyl chloroformate (0.213 mL, 2.22 mmol) was injected. The mixture was stirred at -78 °C for 10 min, allowed to warm to room temperature over 20 min, and was further stirred for 30 min at the same temperature. The reaction was terminated by the addition of aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were dried (Na_2SO_4) and concentrated to give an oil, which was purified on silica gel to afford the title compound (0.536 g, quant.) as a colorless oil: ^1H NMR δ 0.03 (s, 6 H), 0.88 (s, 9 H), 1.29 (t, J = 7.3 Hz, 3 H), 1.50 (m, 1 H), 1.85 (m, 1 H), 2.20-2.45 (m, 3 H), 3.49 (dd, J =

7.3, 9.2 Hz, 1 H), 3.57 (dd, J = 5.4, 9.2 Hz, 1 H), 4.20 (q, J = 7.3 Hz, 2 H), 5.08 (d, J = 11.5 Hz, 1 H), 5.09 (d, J = 15 Hz, 1 H), 5.57 (dt, J = 15, 11 Hz, 1 H); ^{13}C NMR δ -5.72, -5.68, 13.77, 16.16, 17.99, 25.63, 28.58, 45.39, 61.19, 65.91, 73.14, 88.56, 116.49, 138.25, 153.31; IR (neat) 3080, 2960, 2930, 2900, 2860, 2240, 1715, 1470, 1365, 1250, 1110, 1080, 1010, 920, 840, 780, 750 cm^{-1}. $[\alpha]_D^{23}$ +22.8 (c 2.1, $CHCl_3$) for a sample of 80% ee. Anal. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74. Found: C, 65.56; H, 9.68. The enantiopurity of this sample (80% ee) was determined by the derivatization to a cyclic product **98** followed by chiral shift study on ^1H NMR spectroscopy (*vide infra*).

Determination of the enantiomeric excess of 86. 2-[(Ethoxycarbonyl)-methylene]-5-vinyl-2*H*-tetrahydropyran (98).



(86) (98)

The TBS ether **86** (10 mg, 0.032 mmol) was treated with TBAF (0.035 mL of a 1 M solution in THF, 0.035 mmol) in THF (1 mL) at room temperature for 1.5 h. Usual workup and purification afforded the cyclization product (4 mg, 63%) virtually as a single olefinic stereoisomer. We have not attempted to assign its stereochemistry. ^1H NMR δ 1.26 (t, J = 7.5 Hz, 3 H), 1.95 (br dd, J = 9, 16.5 Hz, 1 H), 2.13 (br dt, J = 16.5, 4.5, 1 H), 2.53 (m, 1 H), 3.01 (br s, 2 H), 3.66 (t, J = 10.5 Hz, 1 H), 4.05 (ddd, J = 1.5, 3.8, 10.5 Hz, 1 H), 4.16 (q, J = 7.5 Hz, 2 H), 4.68 (dd, J = 3, 4.5 Hz, 1 H), 5.07 (d, J = 10 Hz, 1 H), 5.12 (d, J = 17 Hz, 1 H), 5.74 (ddd, J = 6.8, 10, 17 Hz, 1 H). Chiral shift study was performed with (+)-$Eu(hfc)_3$. The terminal olefinic protons were separated as follows: 100 mol% of Eu: major enantiomer: δ 5.165 (ddd, J = 1.2, 1.4, 10.6 Hz, 1 H), 5.256 (dt, J = 17, 1.4 Hz, 1 H); minor enantiomer: δ 5.15 (ddd, J = 1.2, 1.4, 10.6 Hz, 1 H), 5.243 (dt, J = 17, 1.4 Hz, 1 H). 120 mol% of Eu: major enantiomer: δ 5.176 (ddd, J = 1.2, 1.4, 10.6 Hz, 1 H), 5.274 (dt, J = 17, 1.4 Hz, 1 H); minor enantiomer: δ 5.158 (ddd, J = 1.2, 1.4, 10.6 Hz, 1 H), 5.258 (dt, J = 17, 1.4 Hz, 1 H). The integration of these peaks at 120 mol% of the Eu reagent determined the enantiopurity of **98**, hence that of **86**, to be 80% ee.