Convergent and Stereospecific Synthesis of Skipped Polyenes and Polyunsaturated Fatty Acids

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SUPPORTING INFORMATION:
**General.** All reactions were conducted in flame-dried glassware under an argon atmosphere with dry solvents, unless otherwise noted. Dry diethyl ether (Et$_2$O), tetrahydrofuran (THF), dichloromethane (CH$_2$Cl$_2$), N$_2$N-dimethylformamide (DMF) and toluene (PhMe) were obtained by passing HPLC grade solvents through activated alumina columns. Anhydrous solutions of acetonitrile (MeCN) and benzene (PhH) were freshly distilled from calcium hydride and sodium / benzophenone respectively. Chlorotitanium triisopropoxide was obtained as a 1M solution in hexanes from Aldrich and used as purchased. n-Butyllithium solution was purchased from Aldrich and titrated monthly against N-benzylbenzamide. c-C$_5$H$_9$MgCl was purchased from Aldrich and titrated monthly using 1,10-phenatholine / s-butanol. [Pd(PPh$_3$)$_4$] was purchased from Strem. Reactions were monitored by thin-layer chromatography (TLC) carried out on 250 µm E. Merck silica gel plates (60F-254) and visualized using p-anisaldehyde or phosphomolybdic acid stain with heat as a developing agent. Silica gel for flash column chromatography was purchased from Silicycle (P60, particle size 40-63 µm). $^1$H and $^{13}$C NMR data were recorded at 400 and 100 MHz using a Bruker AM-400 instrument with chemical shifts relative to residual CHCl$_3$ (7.24 and 77.16 ppm). Infrared spectra were recorded on a PerkinElmer SpectrumOne FT-IR instrument. Low resolution mass spectrometry were performed on a Shimadzu QP2010S (RTX-5 column) GCMS using EI and Varian 500-MS IT LCMS (ESI) using soft negative ionization. HRMS data (TOF ionization) were obtained by the University of Florida Mass Spectrometry lab, usually as (M + H$^+$) or (M + Na$^+$) ions. Yields refer to chromatographically and spectroscopically ($^1$H NMR) homogeneous materials, unless otherwise stated and all compounds purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise. Relative stereochemistry was defined using the R*/S* convention proposed by IUPAC. Brine refers to a saturated aqueous solution of NaCl.

**General Procedure A: Corey-Myers Diazoacetic Ester Cyclopropanation**

To a dry, argon flushed 3-neck RBF fitted with a condenser and drip funnel containing Cu(TBS)$_2$ (0.05 mmol) in PhMe (25 mL) at 120 °C is added diazoacetic ester (1 mmol, prepared as described by Corey from allylic alcohols and glyoxyllic acid chloride tosylhydrazone) in

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1 See [http://www.ux1.eiu.edu/~cfthb/research/handbook/TLCstains.htm](http://www.ux1.eiu.edu/~cfthb/research/handbook/TLCstains.htm) for the recipe.

2 Corey, E. J.; Myers, A. G. *Tetrahedron Lett.* 1984, 25, 3559 – 3562.

3 Sacconi, L.; Ciampolini, M. *J. Chem. Soc.* 1964, 274 – 280.
PhMe (10 mL) from the drip funnel (1 drop / 8-10 seconds) until the addition is complete and the reaction is stirred for an additional 30 min. The reaction is cooled, concentrated, and purified by flash column chromatography (EtOAc or Et₂O in hexanes) to yield pure bicyclic lactone.

(1R*,5S*)-6,6-Dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (12b)

The titled compound was prepared according to Procedure A using the following quantities of reagents: 3,3-Dimethylallyl 2-diazoacetate (12) (2.0 g, 12.98 mmol) in PhMe (130 mL) and Cu(TBS)₂ (270 mg, 0.65 mmol) in PhMe (325 mL). After column chromatography (50% Et₂O in hexanes) 12b was isolated as a colourless oil (1.32 g, 81%). Spectroscopic data was in full accordance to that found in the literature.⁴

(1S*,5R*,6S*)-6-Propyl-3-oxabicyclo[3.1.0]hexan-2-one (13b)

The titled compound was prepared according to Procedure A using the following quantities of reagents: (Z)-Hex-2-enyl 2-diazoacetate (13) (2.0 g, 11.9 mmol) in PhMe (120 mL) and Cu(TBS)₂ (250 mg, 0.60 mmol) in PhMe (300 mL). After column chromatography (30% EtOAc in hexanes) 13b was isolated as a colourless oil (1.35 g, 81%). Spectroscopic data was in full accordance to that found in the literature for the non-racemic compound.⁵

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⁴ Hirao, T.; Harano, Y.; Yamana, Y.; Hamada, Y; Nagata, S.; Agawa, T. Bull. Chem. Soc. Jpn. 1986, 59, 1341 – 1347.

⁵ Doyle, M. P.; Patterson, C. S.; Zhou, Q.-L.; Nishiyama, H. Chem. Comm. 1997, 2, 211 – 212.
(1S*,5R*)-4,4-Dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (14b)

\[
\text{Me} \quad \text{Me} \quad \text{O} \quad \text{N}_2
\]

\[
\text{Cu(TBS)}_2, \text{PhMe} \quad 70\%
\]

\[
\text{H} \quad \text{Me} \quad \text{Me}
\]

The titled compound was prepared according to Procedure A using the following quantities of reagents: 1,1-Dimethylallyl 2-diazoacetate (14) (1.5 g, 9.74 mmol) in PhMe (100 mL) and Cu(TBS)_2 (203 mg, 0.49 mmol) in PhMe (250 mL). After column chromatography (50% Et_2O in hexanes) 14b was isolated as a colourless oil that slowly solidified at RT (850 mg, 70%). Spectroscopic data was in full accordance to that found in the literature.\(^4\)

(1S*,5R*)-5-Methyl-3-oxabicyclo[3.1.0]hexan-2-one (15b)

\[
\text{Me} \quad \text{O} \quad \text{N}_2
\]

\[
\text{Cu(TBS)}_2, \text{PhMe} \quad 76\%
\]

\[
\text{Me}
\]

The titled compound was prepared according to Procedure A using the following quantities of reagents: 2-Methylallyl 2-diazoacetate (15) (2.0 g, 14.27 mmol) in PhMe (150 mL) and Cu(TBS)_2 (300 mg, 0.71 mmol) in PhMe (350 mL). After column chromatography (30% EtOAc in hexanes) 15b was isolated as a colourless oil (1.22 g, 76%). Spectroscopic data was in full accordance to that found in the literature.\(^6\)

(1R*,5S*,6S*)-6-Propyl-3-oxabicyclo[3.1.0]hexan-2-one (16b)

\[
\text{Me} \quad \text{Me} \quad \text{O} \quad \text{N}_2
\]

\[
\text{Cu(TBS)}_2, \text{PhMe} \quad 76\%
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6 Hirao, T.; Harano, Y.; Yamana, Y.; Hamada, Y, Nagata, S.; Agawa, T. Bull. Chem. Soc. Jpn. 1986, 59, 1341 – 1347.
The titled compound was prepared according to Procedure A using the following quantities of reagents:  (E)-Hex-2-enyl 2-diazoacetate (16) (2.0 g, 11.9 mmol) in PhMe (120 mL) and Cu(TBS)_2 (250 mg, 0.60 mmol) in PhMe (300 mL). After column chromatography (30% EtOAc in hexanes) 16b was isolated as a colourless oil (1.28 g, 76%). Spectroscopic data was in full accordance to that found in the literature for the non-racemic compound.  

(1S*,5R*,6S*)-6-Propyl-3-oxabicyclo[3.1.0]hexan-2-ol (13c)

To a RBF containing 6-propyl-3-oxabicyclo[3.1.0]hexan-2-one (13b) (420 mg, 3.0 mmol) in CH₂Cl₂ (6 mL) at -78 °C was added DIBAL (4.5 mL, 4.5 mmol, 1.0 M in hexanes) dropwise by syringe. After 1 h, MeOH (2 mL) and saturated aqueous sodium potassium tartrate (5 mL) were added and the reaction was allowed to warm and stir overnight. The phases were separated and the aqueous phase extracted with CH₂Cl₂, organic extracts combined, filtered through MgSO₄, concentrated \textit{in vacuo}, and purified by flash column chromatography (30% EtOAc in hexanes) to yield pure 13c (358 mg, 84%) as a light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 5.20 (bs, 1H), 4.15 (dd, J = 3.3, 8.5, 1H), 3.75 (d, J = 8.5, 1H), 3.02 (bd, J = 25.1, 1H), 1.72 – 1.69 (m, 2H), 1.39 – 1.26 (m, 4H), 0.90 (t, J = 7.1, 3H), 0.92 – 0.86 (m, 1H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 98.0, 66.8, 27.4, 23.7, 23.5, 19.8, 19.5, 14.1 ppm; IR (thin film, NaCl) 3390, 2958, 2927, 2873, 1682, 1463, 1307, 1074, 1016, 989, 904 cm⁻¹; LRMS (EI) calcd for C₈H₁₄O₂ 142.2 (M⁺, m/z), observed 142.1 (M⁺), 28 (100%).

Doyle, M. P.; Austin, R. E.; Bailey, A. S.; Dwyer, M. P.; Dyatkin, A. B.; Kalinin, A. V.; Kwan, M. M. Y.; Liras, S.; Oalmann, C. J.; Pieters, R. J.; Protopopova, M. N.; Raab, C. E.; Roos, G. H. P.; Zhou, Q.-L.; Martin, S. F. J. Am. Chem. Soc. 1995, 117, 5763 – 5775.
(1S*,5R*,6R*)-6-Propyl-3-oxabicyclo[3.1.0]hexan-2-ol (16c)

To a RBF containing 6-propyl-3-oxabicyclo[3.1.0]hexan-2-one (16b) (500 mg, 3.6 mmol) in CH$_2$Cl$_2$ (7 mL) at -78 °C was added DIBAL (5.4 mL, 5.4 mmol, 1.0 M in hexanes) dropwise by syringe. After 1 h, MeOH (2 mL) and saturated aqueous sodium potassium tartrate (5 mL) were added and the reaction was allowed to warm and stir overnight. The phases were separated and the aqueous phase extracted with CH$_2$Cl$_2$, organic extracts combined, filtered through MgSO$_4$, concentrated in vacuo, and purified by flash column chromatography (50% EtOAc in hexanes) to yield pure 16c (431 mg, 85%) as a light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.24 (d, $J$ = 4.2, 1H), 3.96 (dt, $J$ = 1.5, 8.0, 1H), 3.77 (dd, $J$ = 0.4, 8.1, 1H), 2.89 (d, $J$ = 4.4, 1H), 1.43 (dd, $J$ = 1.6, 3.6, 2H), 1.39 – 1.33 (m, 3H), 1.22 – 1.17 (m, 2H), 0.88 (t, $J$ = 7.3, 3H), 0.58 – 0.52 (m, 1H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 98.5, 68.0, 33.0, 22.3, 22.2, 20.4, 13.9 ppm; IR (thin film, NaCl) 3391, 2958, 2926, 2873, 1698, 1464, 1294, 1063, 1008, 896 cm$^{-1}$; LRMS (EI) calcd for C$_8$H$_{14}$O$_2$ 142.2 (M$^+$, m/z), observed 141.9 (M$^+$), 28 (100%).

((1R*,3S*)-2,2-dimethyl-3-vinylcyclopropyl)methanol (17)

To a RBF containing 6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (12b) (500 mg, 3.96 mmol) in CH$_2$Cl$_2$ (10 mL) at -78 °C was added DIBAL (6.0 mL, 6.0 mmol, 1.0 M in hexanes) dropwise by syringe. After 1 h, MeOH (3 mL) and saturated aqueous sodium potassium tartrate (5 mL) were added, the bath was removed and then solution was stirred for 2 hours. The phases were separated and the aqueous phase extracted with CH$_2$Cl$_2$, organic extracts combined, filtered
through MgSO₄, concentrated in vacuo to afford the crude lactol that was used directly in the following reaction. To a RBF containing methyltriphenylphosphonium bromide (2.12 g, 6.0 mmol) in THF (15 mL) at 0 °C was added n-BuLi (2.2 mL, 5.8 mmol, 2.5 M in hexanes). The bath was removed and the orange mixture stirred for 30 min. After recooing to 0 °C, the crude lactol in THF (2 mL) was added by cannula and the bath removed. The solution was then stirred for an additional 3 h. Saturated aqueous NH₄Cl was added and the reaction diluted with Et₂O, layers separated, aqueous phase extracted with Et₂O, organic extracts combined, filtered through MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (40% Et₂O in hexanes) to yield pure 17 (365 mg, 73%) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.58 (dt, J = 10.2, 16.9, 1H), 5.17 (ddd, J = 0.6, 2.1, 16.9, 1H), 5.02 (ddd, J = 0.6, 2.1, 10.3, 1H), 3.68 (ddd, J = 7.9, 11.6, 28.2, 2H), 1.48 (bs, 1H), 1.40 (t, J = 9.3, 1H), 1.14 – 1.08 (m, 1H), 1.09 (s, 3H), 1.07 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 135.0, 116.3, 60.3, 32.5, 31.6, 28.9, 22.1, 15.6 ppm; IR (thin film, NaCl) 3347, 2946, 1632, 1454, 1376, 1019, 988, 896 cm⁻¹; LRMS (EI) calecd for C₈H₁₄O 126.2 (M⁺, m/z), observed 126.1 (M⁺), 95 (100%).

**((1S*,2S*,3R*)-2-Propyl-3-vinylcyclopropyl)methanol (18)**

![Chemical Structure]

To a RBF containing methyltriphenylphosphonium bromide (3.98 g, 11.2 mmol) in THF (80 mL) at RT was added NaHMDS (9.7 mL, 9.7 mmol, 1.0 M in THF) dropwise by syringe and the bright yellow mixture was stirred for 90 min before the addition of 6-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (13c) (1.043 g, 7.4 mmol) in THF (12 mL) by cannula. After 2 h the mixture was diluted with CH₂Cl₂ (75 mL), filtered through silica, and concentrated in vacuo. The residue was purified by flash column chromatography (30% EtOAc in hexanes) to yield pure 18 (772 mg, 75%) as a light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 5.65 (dt, J = 10.2, 16.9, 1H), 5.26 – 5.22 (m, 1H), 5.06 (dd, J = 2.0, 10.3, 1H), 3.79 (dd, J = 7.3, 11.5, 1H), 3.68 (dd, J =
8.6, 11.5, 1H), 1.68 (dd, J = 9.0, 18.4, 1H), 1.43 – 1.32 (m, 5H), 1.29 – 1.24 (m, 1H), 1.17 – 1.11 (m, 1H), 0.90 (t, J = 6.9, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 134.1, 116.7, 59.9, 26.3, 24.3, 23.2, 23.0, 22.5, 14.2; IR (thin film, NaCl) 3351, 2958, 2931, 2872, 1633, 1465, 1021, 897 cm$^{-1}$; LRMS (EI) calcd for C$_9$H$_{16}$O 140.2 (M$^+$, m/z), observed 140.1 (M$^+$), 55 (100%).

2-((15*,25*)-2-vinylcyclopropyl)propan-2-ol (19)

![](image)

To a RBF containing 4,4-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (14b) (745 mg, 5.91 mmol) in CH$_2$Cl$_2$ (15 mL) at -78 °C was added DIBAL (8.9 mL, 8.87 mmol, 1.0 M in hexanes) dropwise by syringe. After 1 h, MeOH (4 mL) and saturated aqueous sodium potassium tartrate (6 mL) are added and the bath removed. The solution is then stirred for an additional 2 hours. The phases were separated and the aqueous phase extracted with CH$_2$Cl$_2$, organic extracts combined, filtered through MgSO$_4$, concentrated in vacuo to afford the crude lactol that was used directly in the following reaction. To a RBF containing methyltriphenylphosphonium bromide (5.28 g, 14.8 mmol) in THF (25 mL) at 0 °C is added n-BuLi (5.67 mL, 14.2 mmol, 2.5 M in hexanes) and the bath was removed and the orange mixture stirred for 30 min. After recooling to 0 °C, the crude lactol in THF (3 mL) was added by cannula and the bath removed. The solution was then stirred for an additional 3 h. Saturated aqueous NH$_4$Cl was added and the reaction diluted with Et$_2$O, layers separated, aqueous phase extracted with Et$_2$O, organic extracts combined, filtered through MgSO$_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (40% Et$_2$O in hexanes) to yield pure 19 (580 mg, 78%) as a colourless oil. Spectroscopic data was in full accordance to that found in the literature.$^8$

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$^8$ Apparu, M.; Barrelle, M. *Tetrahedron* **1978**, *34*, 1691 – 1679.
((1R*,2R*)-1-Methyl-2-((Z)-prop-1-enyl)cyclopropyl)methanol (20)

![Chemical structure](image)

To a RBF containing 5-methyl-3-oxabicyclo[3.1.0]hexan-2-one (15b) (366 mg, 3.27 mmol) in CH₂Cl₂ (6 mL) at -78 °C was added DIBAL (4.9 mL, 4.9 mmol, 1.0 M in hexanes) dropwise by syringe. After 1 h, MeOH (3 mL) and saturated aqueous sodium potassium tartrate (5 mL) are added and the reaction was allowed to warm and stir for 2 hours. The phases were separated and the aqueous phase extracted with CH₂Cl₂, organic extracts combined, filtered through MgSO₄, concentrated in vacuo to afford the crude lactol that was used directly in the following reaction.

To a RBF containing ethyltriphenylphosphonium bromide (1.32 g, 3.95 mmol) in THF (5 mL) at -78 °C is added NaHMDS (3.9 mL, 3.95 mmol, 1.0 M in THF) and the bath was removed and the orange mixture stirred for 30 min. After recooling to -78 °C, the crude lactol in THF (2 mL) was added by canula and the bath removed allowing stirring for 3 h. Saturated aqueous NH₄Cl was added and the reaction diluted with EtOAc, layers separated, aqueous phase extracted with EtOAc, organic extracts combined, filtered through MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (40% Et₂O in hexanes) to yield 20 (235 mg, 57%, Z:E = 94:6) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ 1H NMR (400 MHz, CDCl₃) δ 5.52 (dqd, J = 1.2, 6.8, 10.7, 1H), 5.14 (ddq, J = 1.7, 9.2, 10.8, 1H), 3.61 (dd, J = 6.6, 11.5, 1H), 3.40 (d, J = 11.6, 1H), 1.71 (dd, J = 1.7, 6.8, 3H), 1.46 (td, J = 5.7, 8.6, 1H), 1.35 (bs, 1H), 1.19 (s, 3H), 0.78 (dd, J = 4.6, 8.2, 1H), 0.50 (t, J = 5.0, 1H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 129.8, 126.0, 68.2, 25.5, 22.4, 22.4, 20.7, 13.4 ppm; IR (thin film, NaCl) 3366, 2952, 2868, 1672, 1445, 1385, 1035, 1020 cm⁻¹; LRMS (EI) calcd for C₈H₁₄O 126.2 (M⁺, m/z), observed 126.1 (M⁺), 67 (100%).
(E)-Methyl 3-((1S*,2R*,3R*)-2-(hydroxymethyl)-3-propylcyclopropyl)acrylate (13d)

A RBF containing an enantiomeric mixture of 6-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (13c) (500 mg, 3.52 mmol) and methyl (triphenylphoranylidene) acetate (1.53 g, 4.58 mmol) in benzene (18 mL) was heated to 90 °C for 6 h. The concentrated residue was purified by flash column chromatography (40% EtOAc in hexanes) to yield pure 13d (550 mg, 79%) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.76 (dd, J = 11.2, 15.3, 1H), 5.95 (d, J = 15.3, 1H), 3.81 (dd, J = 7.3, 11.6, 1H), 3.70 (dd, J = 8.2, 11.6, 1H), 3.65 (s, 3H), 2.17 (s, 1H), 1.75 (dt, J = 8.4, 11.1, 1H), 1.60 – 1.51 (m, 1H), 1.51 – 1.37 (m, 2H), 1.38 – 1.27 (m, 3H), 0.86 (t, J = 7.2, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 167.1, 147.3, 121.5, 59.0, 51.5, 27.2, 26.3, 25.3, 23.1, 22.6, 14.0 ppm; IR (thin film, NaCl) 3418, 2957, 2872, 1716, 1699, 1639, 1436, 1266, 1148, 1025 cm⁻¹; LRMS (EI) calcd for C₁₁H₁₈O₃ 198.2 (M⁺, m/z), observed 198.1 (M⁺), 81 (100%).

((1R*,2S*,3R*)--2-((E)-3-(4-Methoxybenzyloxy)prop-1-enyl)-3-propylcyclopropyl)methanol (21)

A RBF containing (E)-methyl 3-(2-(hydroxymethyl)-3-propylcyclopropyl)acrylate 13d (450 mg, 2.27 mmol), TBSCI (376 mg, 2.5 mmol), imidazole (170 mg, 2.5 mmol) in DMF (11 mL) is stirred at RT for 20 h. The reaction was then diluted with water (60 mL) and extracted twice with Et₂O, organic extracts combined, washed with brine, filtered through MgSO₄, and concentrated in vacuo to afford the crude product that was then dissolved in THF (11 mL), cooled to 0 °C, and treated by syringe with LAH (2.3 mL, 2.3 mmol, 1 M in THF). The mixture
was allowed to warm to RT and stirred for 1 h, recooled to 0 °C, and quenched slowly with saturated aqueous sodium potassium tartrate (10 mL). After rapid stirring for 1 h at RT, the layers are separated and the aqueous layer is extracted twice with Et₂O, organic extracts combined, filtered through MgSO₄, concentrated *in vacuo*, and purified by flash column chromatography (20% EtOAc in hexanes) to yield pure product (220 mg) and impure fractions (405 mg) which contained a small amount of over reduction product. This pure product (220 mg, 0.77 mmol) was mixed in a RBF with PMBCl (147 μL, 1.1 mmol), TBAI (28 mg, 0.08 mmol) in DMF (5 mL) and NaH (62 mg, 1.54 mmol, 60% in mineral oil) was added in one portion at RT. After 20 h of stirring, the mixture was quenched with saturated aqueous NH₄Cl (5 mL) and diluted with water (20 mL), extracted twice with Et₂O, organic extracts combined, washed with brine, filtered through MgSO₄, concentrated *in vacuo*, and purified by flash column chromatography (10% EtOAc in hexanes) to yield the product. This product was then dissolved in THF (5 mL) and treated by syringe at RT with TBAF (950 μL, 0.95 mmol, 1 M in THF, dried by stirring in Na₂SO₄ for 30 min), and stirred for 4 h. The reaction was then quenched with solid CaCO₃ (~50 mg) and saturated aqueous NH₄Cl (5 mL), layers separated, aqueous layer extracted twice with Et₂O, organic extracts combined, filtered through MgSO₄, concentrated *in vacuo*, and purified by flash column chromatography (20 to 40% EtOAc in hexanes) to yield pure 21 (160 mg, 58% over 4 steps) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.18 (m, 2H), 6.89 – 6.80 (m, 2H), 5.80 (dt, J = 6.3, 15.2, 1H), 5.52 (ddt, J = 1.2, 10.0, 15.2, 1H), 4.41 (s, 2H), 3.94 (dt, J = 1.1, 6.4, 2H), 3.78 (s, 3H), 3.74 (dd, J = 3.8, 11.2, 1H), 3.66 (dd, J = 8.3, 11.6, 1H), 1.68 (dd, J = 8.8, 18.5, 1H), 1.44 (bs, 1H), 1.42 – 1.28 (m, 5H), 1.20 – 1.09 (m, 1H), 0.94 – 0.84 (m, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 159.5, 130.6, 130.0, 129.6, 128.8, 114.0, 71.6, 70.7, 59.7, 55.4, 26.3, 24.2, 23.2, 22.4, 21.6, 14.2 ppm; IR (thin film, NaCl) 3418, 2956, 2859, 1614, 1514, 1463, 1302, 1248, 1173, 1035, 820 cm⁻¹; HRMS (GC-CI) calcd for C₁₈H₂₇O₃, 291.1963 (M + H)⁺ m/z; observed, 291.1962 (M + H)⁺ m/z.
((1S*,2R*,3R*)-2-((Z)-Prop-1-enyl)-3-propylcyclopropyl) methanol (22)

To a RBF containing ethyltriphenylphosphonium bromide (1.2 g, 3.21 mmol) in THF (5 mL) at -78 °C was added NaHMDS (3.21 mL, 3.21 mmol, 1.0 M in THF). The bath was removed and the orange mixture was stirred for 30 min. After recooling to -78 °C, 6-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (13c) (300 mg, 2.14 mmol) in THF (2 mL) was added by cannula. The bath was removed and the solution was stirred for 3 h. Saturated aqueous NH₄Cl was added and the reaction was diluted with EtOAc, layers separated, aqueous phase extracted with EtOAc, organic extracts combined, filtered through MgSO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (35% Et₂O in hexanes) to yield 22 (270 mg, 75%, Z:E = 95:5) as a colourless oil;¹H NMR (400 MHz, CDCl₃) δ 5.49 (ddq, J = 1.1, 6.8, 10.7, 1H), 5.13 (ddq, J = 1.7, 9.4, 11.0, 1H), 3.75 (dd, J = 6.3, 11.6, 1H), 3.43 (dd, J = 9.0, 11.6, 1H), 1.70 (dd, J = 1.7, 6.8, 3H), 1.45 – 1.23 (m, 6H), 1.12 (tdd, J = 5.1, 6.3, 8.8, 1H), 0.88 (t, J = 7.1, 3H), 0.70 (dq, J = 5.0, 6.5, 1H) ppm;¹³C NMR (126 MHz, CDCl₃) δ 129.0, 125.4, 63.6, 35.7, 28.4, 26.6, 21.5, 14.0, 13.3 ppm; IR (thin film, NaCl) 3351, 2957, 2919, 2873, 1651, 1464, 1408, 1033 724 cm⁻¹; LRMS (EI) calcd for C₁₀H₁₈O 154.2 (M⁺, m/z), observed 154.1 (M⁺), 81 (100%).

General Procedure B: Coupling of Vinylsilane with Vinylecyclopropanes

To a RBF containing ClTi(Oi-Pr)₃ (3 mmol, 1.0 M in hexanes) and chlorodimethylvinylsilane (3 mmol) in Et₂O (0.1 M) at -78 °C is added c-C₃H₆MgCl (6 mmol) by syringe and the mixture is warmed to -50 °C and stirred for 1 h becoming deep brown in colour. In a separate RBF containing vinylecyclopropane (1 mmol) in THF (~0.2 M) at -78 °C is added n-BuLi (1.2 mmol) by syringe and the mixture was warmed to 0 °C over 20 min and then added by cannula to the titanium complex that had been re-cooled to -70 °C. The mixture is then slowly warmed to RT over 2–3 h and treated with 1N HCl (~5 mL / mmol vinylecyclopropane) with rapid stirring.
After 10 min the now colourless mixture is further diluted with EtOAc and then filtered through a pad of silica rinsing with additional EtOAc. After concentration in vacuo, the non-polar product fractions were separated from the unreacted vinylcyclopropane by flash column chromatography (15% EtOAc in hexanes followed by flushing with EtOAc) and used directly in the following Tamao oxidation. To a cooled (0 °C) solution of tBuOOH (30 mmol, 70% in H2O) in DMF (0.2 M) is added CsOH • H2O (25 mmol). After the mixture is warmed to RT, a solution of crude isopropoxysilane / silanol in THF (~0.5 M) was added. After 10 min, TBAF (10 mmol, 1.0 M in THF) is added, the mixture is heated to 70 °C, and stirred at that temperature for 6 h. The mixture is then cooled to RT, and saturated aqueous Na2S2O3 was slowly added with rapid stirring. The mixture is then further diluted with water and extracted twice with Et2O. The organic extracts are then combined and filtered through MgSO4, concentrated in vacuo, and purified by flash column chromatography (EtOAc or Et2O in hexanes) to yield pure 1,4-dienyl alcohol. Alternatively the crude product could be oxidized by stirring with KF (8 mmol), KHCO3 (4 mmol), and H2O2 (5 mmol, 30%) in MeOH / THF (0.1 M, 50:50) for 1-2 days. This reaction is then quenched by the slow addition of saturated aqueous Na2S2O3, diluted with E2O and water, layers separated, aqueous extracted with Et2O, organic extracts combined and filtered through MgSO4, concentrated in vacuo, and purified by flash column chromatography (EtOAc or Et2O in hexanes).

(E)-6,6-Dimethylocta-4,7-dien-1-ol (23)

\[
\begin{align*}
\text{Me}_3\text{SiMe}_2\text{Cl, } \text{ClTi(O-i-Pr)}_3, \text{c-C}_5\text{H}_9\text{MgCl, Et}_2\text{O} & \\
\text{tBuOOH, CsOH • H}_2\text{O, TBAF, DMF} & \\
\text{58% over 2 steps} & \\
(82% \text{ based on recovered s.m.})
\end{align*}
\]

The titled compound was prepared according to Procedure B using the following quantities of reagents: ClTi(Oi-Pr)3 (3.0 mL, 3.0 mmol), chlorodimethylvinylsilane (310 µL, 2.25 mmol), c-C5H9MgCl (3.0 mL, 6.0 mmol, 2.0 M in Et2O) in Et2O (7.5 mL), and 2,2-dimethyl-3-vinylcyclopropyl) methanol 17 (95 mg, 0.75 mmol), n-BuLi (360 µL, 0.9 mmol, 2.5 M in
hexanes) in THF (2 mL). Unreacted vinylcyclopropane was recovered (28 mg). Oxidation: alkyl silane in THF (2 mL), \(t\)BuOOH (3.2 mL, 22.5 mmol), CsOH • H_2O (3.3 g, 18.8 mmol), TBAF (7.5 mL, 7.5 mmol) in DMF (5 mL). After workup, flash column chromatography (40% Et_2O in hexanes) to yield 23 (67 mg, 58%, >20:1 E:Z, 82% brsm) as a colourless oil; \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 5.78 (dd, \(J = 10.6, 17.4, 1H\)), 5.43 (dt, \(J = 1.0, 15.6, 1H\)), 5.33 (dt, \(J = 6.5, 15.6, 1H\)), 4.94 – 4.84 (m, 2H), 3.61 (t, \(J = 6.5, 2H\)), 2.06 (td, \(J = 1.0, 7.4, 2H\)), 1.60 (td, \(J = 6.7, 13.8, 2H\)), 1.05 (s, 6H) ppm; \(^{13}\)C NMR (126 MHz, CDCl_3) \(\delta\) 147.7, 139.6, 126.1, 110.5, 62.7, 39.2, 32.6, 29.2, 27.3 ppm; IR (thin film, NaCl) 3352, 2961, 2869, 1470, 1360, 1059, 911 cm\(^{-1}\); HRMS (GC-Cl) calcd for C_{10}H_{19}O, 155.1436 (M + H)^+ m/z; observed, 155.1429 (M + H)^+ m/z.

Alkene geometry at C4-C5 was assigned by nOe:

\((E)-6\)-Vinylnon-4-en-1-ol (24)

The titled compound was prepared according to Procedure B using the following quantities of reagents: ClTi(Oi-Pr)_3 (2.14 mL, 2.14 mmol), chlorodimethylvinylsilane (295 \(\mu\)L, 2.14 mmol), \(c\)-C_5H_9MgCl (2.1 mL, 4.28 mmol, 2.01 M in Et_2O) in Et_2O (7 mL), and (2-propyl-3-vinylecyclopropyl)methanol 18 (100 mg, 0.71 mmol), \(n\)-BuLi (240 \(\mu\)L, 0.86 mmol, 2.5 M in hexanes) in THF (3 mL). Oxidation: alkyl silane in DMF (2 mL), \(t\)BuOOH (3.0 mL, 21 mmol), CsOH • H_2O (2.5 g, 14.2 mmol), TBAF (7.0 mL, 7.0 mmol) in DMF (5 mL). After workup, flash column chromatography (15% EtOAc in hexanes) yielded 24 (65 mg, 54%, >20:1 E:Z) as a colourless oil; \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 5.72 – 5.64 (m, 1H), 5.44 – 5.29 (m, 2H), 4.97 – 4.94 (m, 1H), 4.93 – 4.91 (m, 1H), 3.63 (t, \(J = 6.5, 3H\)), 2.65 – 2.61 (m, 1H), 2.08 (dd, \(J = 6.9, 13.9, 2H\)), 1.66 – 1.59 (m, 2H), 1.34 – 1.17 (m, 5H), 0.86 (t, \(J = 7.1, 3H\)) ppm; \(^{13}\)C NMR (126 MHz, CDCl_3) \(\delta\) 142.4, 133.9, 129.6, 113.6, 62.8, 46.7, 37.2, 32.6, 29.2, 26.2, 20.5, 14.2 ppm; IR
(thin film, NaCl) 3351, 2957, 2930, 2872, 1635, 1270, 1126, 1059, 911, 771 cm⁻¹; HRMS (GC-Cl) calcd for C₁₁H₂₁O, 169.1592 (M + H)⁺ m/z; observed, 169.1592 (M + H)⁺ m/z.

Alkene geometry at C4-C5 was assigned by nOe:

(E)-8-Methylnona-4,7-dien-1-ol (25)

The titled compound was prepared according to Procedure B using the following quantities of reagents: ClTi(Oi-Pr)₃ (1.9 mL, 1.9 mmol), chlorodimethylvinylsilane (262 µL, 1.9 mmol), c-C₅H₉MgCl (1.9 mL, 3.8 mmol, 2.0 M in Et₂O) in Et₂O (7 mL), and 2-(2-vinylcyclopropyl)propan-2-ol 19 (80 mg, 0.63 mmol), n-BuLi (300 µL, 0.76 mmol, 2.5 M in hexanes) in THF (2 mL). Oxidation: alkyl silane, KF (290 mg, 5.07 mmol), KHCO₃ (260 mg, 2.54 mmol), H₂O₂ (360 µL, 3.17 mmol) in MeOH/THF (6 mL, 50:50) for 48 h. After workup, flash column chromatography (40% Et₂O in hexanes) to yield pure 25 (49 mg, 50%, >20:1 E:Z) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ ¹H NMR (400 MHz, CDCl₃) δ 5.43 (dq, J = 1.8, 1.3 Hz, 2H), 5.13 (tdt, J = 7.2, 2.8, 1.4 Hz, 1H), 3.66 (d, J = 6.4 Hz, 2H), 2.68 (dd, J = 2.1, 1.1 Hz, 2H), 2.13 – 2.04 (m, 2H), 1.71 (d, J = 1.1 Hz, 3H), 1.68 – 1.60 (m, 2H), 1.61 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 132.4, 129.7, 129.6, 122.5, 62.8, 32.5, 31.4, 30.5, 29.0, 17.8 ppm; IR (thin film, NaCl) 3338, 2927, 2875, 1448, 1376, 1055, 966 cm⁻¹; LRMS (EI) calcd for C₁₁H₁₈O 154.2 (M⁺, m/z), observed 154.1 (M⁺), 67 (100%).

Alkene geometry at C4-C5 was assigned by analogy to other examples (see 23, 24, 26 and 27).
(E)-3,7-Dimethylocta-4,7-dien-1-ol (26)

The titled compound was prepared according to Procedure B using the following quantities of reagents: ClTi(Oi-Pr)$_3$ (3.0 mL, 3.0 mmol), chlorodimethylvinylsilane (310 µL, 2.25 mmol), c-C$_5$H$_9$MgCl (3.0 mL, 6.0 mmol, 2.0 M in Et$_2$O) in Et$_2$O (7.5 mL), and methyl-2-((Z)-prop-1-enyl)cyclopropyl)methanol 20 (95 mg, 0.75 mmol), n-BuLi (360 µL, 0.9 mmol, 2.5 M in hexanes) in THF (2 mL). Oxidation: alkyl silane in THF (2 mL), tBuOOH (3.2 mL, 22.5 mmol), CsOH • H$_2$O (3.3 g, 18.8 mmol), TBAF (7.5 mL, 7.5 mmol) in DMF (5 mL). After workup, flash column chromatography (40% Et$_2$O in hexanes) to yield 26 (70 mg, 61%, >20:1 E:Z) as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 5.46 – 5.25 (m, 2H), 4.67 (d, $J = 11.5$, 2H), 3.67 – 3.56 (m, 2H), 2.65 (d, $J = 6.6$, 2H), 2.25 (dt, $J = 7.2$, 14.3, 1H), 1.67 (s, 3H), 1.58 – 1.48 (m, 2H), 0.98 (d, $J = 6.8$, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$) δ 145.3, 137.8, 126.8, 110.5, 61.5, 41.3, 39.9, 34.0, 22.5, 21.3 ppm; IR (thin film, NaCl) 3334, 2961, 2929, 1651, 1455, 1373, 1128, 1050 971, 888 cm$^{-1}$; HRMS (GC-Cl) calcd for C$_{10}$H$_{19}$O, 155.1436 (M + H)$^+$ m/z; observed, 155.1438 (M + H)$^+$ m/z.

Alkene geometry at C4-C5 was assigned by nOe:

For Compound 26: The 1,4-diene product isolated was contaminated with a minor product of unknown structure. If this minor product is the Z-alkene isomer, selectivity for this process can be calculated to be $\geq 10:1$ (based on integration in the $^1$H NMR spectrum).

(3$R^*$,6$S^*$,E)-3-((4-Methoxybenzyloxy)methyl)-6-vinlnon-4-en-1-ol (27)

For Compound 27: The 1,4-diene product isolated was contaminated with a minor product of unknown structure. If this minor product is the Z-alkene isomer, selectivity for this process can be calculated to be $\geq 10:1$ (based on integration in the $^1$H NMR spectrum).
The titled compound was prepared according to Procedure B using the following quantities of reagents: ClTi(Oi-Pr)_3 (630 µL, 0.63 mmol), chlorodimethylvinylsilane (310 µL, 0.63 mmol), c-C_5H_9MgCl (630 µL, 1.26 mmol, 2.0 M in Et_2O) in Et_2O (3 mL), and an enantiomeric mixture of 2,2-dimethyl-3-vinylcyclopropyl)methanol 21 (60 mg, 0.21 mmol), n-BuLi (100 µL, 0.25 mmol, 2.5 M in hexanes) in THF (1 mL). Oxidation: alkyl silane in THF (2 mL), tBuOOH (0.9 mL, 6.3 mmol), CsOH • H_2O (930 mg, 5.3 mmol), TBAF (2.1 mL, 2.1 mmol) in DMF (2 mL). After workup, flash column chromatography (30 to 40% EtOAc in hexanes) to yield pure 27 (37 mg, 55%, >20:1 E:Z, >20:1 dr) as a colourless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.20 (m, 3H), 6.89 – 6.81 (m, 2H), 5.67 (ddd, J = 7.3, 10.6, 16.9, 1H), 5.37 (dd, J = 7.4, 15.7, 1H), 5.26 (dd, J = 8.5, 15.8, 1H), 5.00 – 4.94 (m, 1H), 4.93 (d, J = 1.1, 1H), 4.42 (s, 2H), 3.78 (s, 3H), 3.69 – 3.64 (m, 1H), 3.62 – 3.56 (m, 1H), 3.40 (dd, J = 5.2, 9.2, 1H), 3.32 (dd, J = 7.6, 9.2, 1H), 2.63 (dd, J = 7.1, 14.1, 1H), 2.51 – 2.37 (m, 1H), 2.10 (s, 1H), 1.74 (ddt, J = 5.8, 7.5, 13.4, 1H), 1.65 – 1.53 (m, 2H), 1.37 – 1.22 (m, 5H), 0.86 (t, J = 7.1, 3H) ppm; ^13C NMR (126 MHz, CDCl_3) δ 159.4, 142.1, 134.7, 130.9, 130.4, 129.5, 114.0, 113.9, 74.3, 73.0, 61.5, 55.5, 46.7, 40.9, 37.2, 36.0, 20.5, 14.2 ppm; IR (thin film, NaCl) 3380, 2956, 2930, 2871, 1608, 1513, 1250, 1103, 1025 cm^-1; HRMS (GC-Cl) calcd for C_{20}H_{31}O_3, 319.2273 (M + H)^+ m/z; observed, 319.2265 (M + H)^+ m/z.

Alkene geometry at C4-C5 was assigned by nOe:

(3S^*,6R^*,E)-3-Methyl-6-vinylnon-4-en-1-ol (28)

The titled compound was prepared according to Procedure B using the following quantities of reagents: ClTi(Oi-Pr)_3 (1.56 mL, 1.56 mmol), chlorodimethylvinylsilane (215 µL, 1.56 mmol), c-C_5H_9MgCl (1.56 mL, 3.12 mmol, 2.0 M in Et_2O) in Et_2O (5 mL), and 2-((Z)-prop-1-enyl)-3-propylcyclopropyl)methanol 22 (80 mg, 0.52 mmol), n-BuLi (230 µL, 0.63 mmol, 2.5 M in
hexanes) in THF (2 mL). Oxidation: alkyl silane in THF (2 mL), tBuOOH (2 mL, 15.6 mmol), CsOH • H2O (2.3 g, 13 mmol), TBAF (5.2 mL, 5.2 mmol) in DMF (5 mL). After workup, flash column chromatography (15% EtOAc in hexanes) to yield pure 28 (49 mg, 52%, >20:1 E:Z, >20:1 dr) as a colourless oil; 1H NMR (400 MHz, CDCl3) δ 5.68 (ddd, J = 7.24, 10.4, 25.2, 1H), 5.32 – 5.23 (m, 2H), 4.97 – 4.91 (m, 1H), 4.92 – 4.91 (m, 1H), 3.67 – 3.58 (m, 2H), 2.64 – 2.59 (m, 1H), 2.28 – 2.21 (m, 1H), 1.61 – 1.46 (m, 2H), 1.34 – 1.23 (m, 4H), 0.98 (d, J = 6.8, 3H), 0.86 (t, J = 7.1, 4H) ppm; 13C NMR (126 MHz, CDCl3) δ 142.4, 135.8, 132.1, 113.6, 61.7, 46.6, 40.1, 37.3, 34.2, 21.4, 20.5, 14.2 ppm; IR (thin film, NaCl) 3338, 2958, 2928, 2872, 1457, 1128, 1052, 971, 911, 772 cm\(^{-1}\); HRMS (GC-Cl) calcd for C12H23O, 183.1749 (M + H)\(^+\) m/z; observed, 183.1752 (M + H)\(^+\) m/z.

Alkene geometry at C4-C5 was assigned by analogy to other examples (see assignments for compounds 23, 24, 26, and 27).

(Z)-2-Methylnona-1,3-dien-5-ol (29)

\[
\text{OH} \quad \text{Me} \quad \text{1. n-BuZnBr, THF} \quad \text{OH} \quad \text{Me} \\
\text{I} \quad \text{2. 2-Isopropenyl-ZnBr, [Pd(PPh3)4], THF} \quad \text{97%} \\
\]

To a solution of n-butylzinc bromide [prepared from n-BuLi (9.17 mL, 22.9 mmol, 2.5 M in hexanes) and zinc bromide (22.9 mL, 22.9 mmol, 1 M in THF) in THF (10 mL)], a solution of (Z)-1-iodohept-1-en-3-ol\(^9\) (5.0 g, 20.8 mmol) in THF (10 mL) was added dropwise at 0 °C. After 20 min at this temperature, the reaction mixture was cannulated into a solution of isopropenylzinc bromide [prepared from isopropenylmagnesium bromide (84 mL, 42 mmol, 0.5 M in THF) and zinc bromide (42 mL, 42 mmol, 1 M in THF)]. [Pd(PPh3)4] (1.2 g, 1.02 mmol) was added in one portion and the mixture was warmed and heat to 70 °C for 1 h. The reaction was cooled and quenched by addition of saturated aqueous NH4Cl, diluted with water and Et2O, layers separated, aqueous phase extracted with Et2O, organic extracts combined, washed with brine, filtered through MgSO4, concentrated in vacuo, and purified by flash column

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\(^9\) I. Marek; C. Meyer; J.-F. Normant, Org. Synth. 1997, 74, 194 – 204.
chromatography (25 to 30 % Et₂O in hexanes) to yield 29 (3.1 g, 97%) as a light yellow oil of adequate purity for characterization and use in the following step; ¹H NMR (400 MHz, CDCl₃) δ 5.91 (d, J = 11.8 Hz, 1H), 5.39 (dd, J = 11.8, 9.2 Hz, 1H), 5.02 – 4.93 (m, 1H), 4.87 (s, 1H), 4.60 (dt, J = 8.2, 6.4 Hz, 1H), 1.86 (s, 3H), 1.75 (s, 1H), 1.64 – 1.53 (m, 1H), 1.45 (ddt, J = 9.8, 6.7, 5.6 Hz, 1H), 1.39 – 1.24 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 141.3, 133.8, 132.5, 116.5, 68.0, 37.6, 27.7, 23.2, 22.8, 14.1 ppm; IR (thin film, NaCl) 3421, 2958, 2933, 2872, 1458, 1378, 1121, 1055 cm⁻¹; LRMS (EI) calcd for C₁₁H₁₈O₁₅₄.2 (M⁺, m/z), observed 154.1 (M⁺), 97 (100%).

(R*)-1-((1R*,2S*)-2-(prop-1-en-2-yl)cyclopropyl)pentan-1-ol (30)

![Chemical structure of 29 and 30]

To a suspension of samarium powder (10 g, 97.25 mmol) and HgCl₂ (3.6 g, 19.45 mmol) dispensed in a glovebox in THF (260 mL) was added (Z)-2-methylnona-1,3-dien-5-ol (2.05 g, 19.45 mmol). To the vigorously stirred mixture, ICH₂Cl (4.8 mL, 97.25 mmol) was added dropwise at -50 °C. The reaction mixture was gradually allowed to warm to RT over a period of 2 h. It was then poured into cold saturated aqueous K₂CO₃ solution (200 mL) overlaid with diethyl ether (200 mL). After stirring for 20 min, the resulting mixture was filtered through Celite and the removed solids were thoroughly washed with Et₂O. The layers were separated, aqueous layer extracted with Et₂O, organic extracts combined, washed with brine, filtered through MgSO₄, concentrated in vacuo, and purified by flash column chromatography (30% Et₂O in hexanes) to yield pure 30 (1.9 g, 85%, >99 de) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ 4.88 – 4.75 (m, 1H), 4.63 (s, 1H), 3.17 – 3.03 (m, 1H), 1.80 (s, 3H), 1.55 – 1.38 (m, 4H), 1.36 – 1.23 (m, 4H), 1.10 (ddd, J = 17.5, 8.7, 5.8 Hz, 1H), 0.87 (t, J = 7.2 Hz, 1H), 0.79 – 0.69 (m, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 142.7, 110.9, 71.3, 37.8, 28.0, 25.3, 24.5, 23.2, 22.8, 14.2, 7.2 ppm; IR (thin film, NaCl) 3352, 2957, 2932, 2859, 1646, 1455, 1377, 1035,
The titled compound was prepared according to Procedure B using the following quantities of reagents: \( \text{ClTi(O}i\text{-Pr)}_3 \) (1.78 mL, 1.78 mmol), chlorodimethylvinylsilane (246 \( \mu \text{L}, 1.78 \text{mmol}), \text{c-C}_5\text{H}_9\text{MgCl} \) (1.78 mL, 3.56 mmol, 2.0 M in Et\(_2\)O) in Et\(_2\)O (6 mL), and 2-(prop-1-en-2-yl)cyclopropyl)pentan-1-ol 30 (100 mg, 0.59 mmol), \( \text{n-BuLi} \) (286 \( \mu \text{L}, 0.71 \text{mmol, 2.5 M in hexanes}) in THF (2 mL). Oxidation: crude alkyl silane in THF (2 mL), \( \text{tBuOOH} \) (2.55 mL, 17.8 mmol), \( \text{CsOH} \cdot \text{H}_2\text{O} \) (2.63 g, 14.9 mmol), TBAF (6 mL, 6 mmol) in DMF (6 mL). After workup, flash column chromatography (20% EtOAc in hexanes) yielded pure 31 (60.5 mg, 52%, >20:1 E:Z, >20:1 dr) as a colourless oil; \( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta 5.43 – 5.26 \text{ (m, 2H), 5.21 – 5.12 \text{ (m, 1H), 3.63 (t, J = 6.5 Hz, 2H), 2.73 (dd, J = 7.1, 6.5 Hz, 2H), 2.06 (q, J = 7.5 Hz, 4H), 1.73 – 1.66 \text{ (m, 2H), 1.64 (s, 3H), 1.37 – 1.29 \text{ (m, 5H), 0.94 – 0.86 \text{ (m, 3H) ppm;}} ^{13}\text{C NMR (126 MHz, CDCl}_3 \) \( \delta 135.1, 130.1, 128.2, 123.5, 63.0, 36.1, 32.0, 30.9, 27.1, 26.4, 22.5, 16.0, 14.1 \text{ ppm; IR (thin film, NaCl) 3399, 2956, 2933, 2872, 1458, 1377, 1252, 1047 979 cm}^{-1}; \text{LRMS (EI) calcd for C}_{13}\text{H}_{24}\text{O 196.2 (M}^+, \text{m/z), observed 196.1 (M}^+, \text{28 (100%).}}

Alkene geometry at C4-C5 and C7-C8 was assigned by nOe:
(S*)-1-((1R*,2S*)-2-(prop-1-en-2-yl)cyclopropyl)pentan-1-ol (32)

To a vigorously stirred mixture of 30 (700 mg, 4.15 mmol) and 4Å powdered molecular sieves (3 g) in CH$_2$Cl$_2$ (40 mL) was added PDC (3.1 g, 8.3 mmol). After 15 h at RT, the reaction mixture was filtered through Florisil and washed with CH$_2$Cl$_2$. Concentration in vacuo yielded the cyclopropyl ketone (630 mg, 91%) as a colourless oil that was of sufficient purity for the following step. To this crude ketone (600 mg, 3.61 mmol) in THF (20 mL) at -78 °C was added L-selectride (5.4 mL, 5.4 mmol, 1M in THF) and the reaction was stirred for 30 min. The reaction was quenched with MeOH and diluted with water and Et$_2$O, layers separated, aqueous layer extracted with Et$_2$O, organic extracts combined, washed with brine, filtered through MgSO$_4$, concentrated in vacuo, and purified by flash column chromatography (5 to 10 % EtOAc in hexanes) to yield pure 32 (460 mg, 76%) as a colourless oil along with pure 30 (70 mg, 12%); $^1$H NMR (400 MHz, CDCl$_3$) δ 4.92 – 4.84 (m, 1H), 4.65 (s, 1H), 3.11 (dt, $J = 12.2, 4.4$ Hz, 1H), 1.97 – 1.87 (m, 3H), 1.63 – 1.55 (m, 2H), 1.53 – 1.26 (m, 5H), 1.12 (ddd, $J = 18.2, 8.9, 5.7$ Hz, 1H), 0.91 (t, $J = 7.1$ Hz, 3H), 0.83 – 0.73 (m, 1H), 0.52 (dd, $J = 11.5, 5.6$ Hz, 1H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.9, 110.7, 71.9, 37.4, 28.1, 25.6, 24.7, 23.0, 22.2, 14.2, 7.8 ppm; IR (thin film, NaCl) 3368, 2957, 2931, 2860, 1647, 1455, 1037, 884 cm$^{-1}$; HRMS (GC-CI) calcd for C$_{11}$H$_{21}$O, 169.1592 (M + H)$^+$ m/z; observed, 169.1597 (M + H)$^+$ m/z.

(4E,7E)-4-Methyldodeca-4,7-dien-1-ol (33)
The titled compound was prepared according to Procedure B using the following quantities of reagents: ClTi(O-i-Pr)_3 (1.78 mL, 1.78 mmol), chlorodimethylvinylsilane (246 µL, 1.78 mmol), c-C_5H_9MgCl (1.78 mL, 3.56 mmol, 2.0 M in Et_2O) in Et_2O (6 mL), and 2-(prop-1-en-2-yl)cyclopropylpentan-1-ol 32 (100 mg, 0.59 mmol), n-BuLi (300 µL, 0.71 mmol, 2.4 M in hexanes) in THF (2 mL). Oxidation: alkyl silane, KF (202 mg, 3.56 mmol), KHCO_3 (190 mg, 1.78 mmol), H_2O_2 (680 µL, 5.94 mmol) in MeOH / THF (10 mL, 50:50) for 32 h. After workup, flash column chromatography (20% Et_2O in hexanes) yielded pure 33 (49 mg, 42%, >20:1 E:Z, >20:1 dr) as a colourless oil; ^1H NMR (400 MHz, CDCl_3) δ ^1H NMR (400 MHz, CDCl_3) δ 5.47 – 5.29 (m, 2H), 5.22 – 5.14 (m, 1H), 3.64 (dd, J = 8.5, 4.3 Hz, 2H), 2.73 – 2.64 (m, 2H), 2.13 – 2.06 (m, 2H), 1.98 (dd, J = 12.6, 7.0 Hz, 2H), 1.76 – 1.63 (m, 2H), 1.57 (s, 3H), 1.35 – 1.26 (m, 5H), 0.88 (t, J = 7.1 Hz, 3H) ppm; ^13C NMR (126 MHz, CDCl_3) δ 135.4, 130.7, 128.5, 123.2, 63.0, 36.1, 32.4, 31.9, 31.3, 30.9, 22.4, 16.0, 14.1 ppm; IR (thin film, NaCl) 3356, 2956, 2926, 2857, 1455, 1363, 1059, 966 cm⁻¹; LRMS (EI) calcd for C_{13}H_{24}O 196.2 (M⁺, m/z), observed 196.1 (M⁺), 28 (100%).

Alkene geometry at C4-C5 and C7-C8 was assigned by nOe:

(1^R*,5^S*,6^S*)-4-Butyl-6-methyl-3-oxabicyclo[3.1.0]hexan-2-one

The titled compound was prepared according to Procedure A using the following quantities of reagents: (E)-oct-2-en-4-yl 2-diazoacetate (2.8 g, 14.27 mmol) in PhMe (140 mL) and Cu(TBS)_2 (300 mg, 0.71 mmol) in PhMe (350 mL) yielded after column chromatography (30% Et_2O in hexanes) the product (1.6 g, 67%, 3:1 dr) as a colourless oil of inseparable diastereomers that were used directly in the following reduction / olefination step.
(S*)-1-(((1R*,2S*,3S*)-2-Methyl-3-((Z)-prop-1-enyl)cyclopropyl)pentan-1-ol (40) and (R*)-1-(((1R*,2S*,3S*)-2-methyl-3-((Z)-prop-1-enyl)cyclopropyl)pentan-1-ol (34)

To a RBF containing a 4-butyl-6-methyl-3-oxabicyclo[3.1.0]hexan-2-one (1.3 g, 7.73 mmol) in CH$_2$Cl$_2$ (40 mL) at -78 °C was added DIBAL (11.6 mL, 11.6 mmol, 1.0 M in hexanes) dropwise by syringe. After 1 h, MeOH (5 mL) and saturated aqueous sodium potassium tartrate (20 mL) were added and the reaction was allowed to warm and stir for 2 hours. The phases were separated and the aqueous phase extracted with CH$_2$Cl$_2$, organic extracts combined, filtered through MgSO$_4$, concentrated in vacuo to afford the crude lactol that was used directly in the following reaction. To a RBF containing ethyltriphenylphosphonium bromide (6.6 g, 17.8 mmol) in THF (20 mL) at -78 °C was added NaHMDS (17.8 mL, 17.8 mmol, 1.0 M in THF). The bath was removed and the orange mixture stirred for 30 min. After recooling to -78 °C, the crude lactol in THF (5 mL) was added by cannula. The bath was removed and the solution was stirred for 3 h. Saturated aqueous NH$_4$Cl was added and the reaction diluted with Et$_2$O, layers separated, aqueous phase extracted with Et$_2$O, organic extracts combined, filtered through MgSO$_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (40% Et$_2$O in hexanes) to yield 40 (1.05 g, 75%, Z:E = 94:6) as a colourless oil and 34 (190 mg, 14%, Z:E = 91:9) as a colourless oil; 40: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.56 (dqd, $J$ = 10.7, 6.8, 1.1 Hz, 1H), 5.25 – 5.16 (m, 1H), 3.32 – 3.08 (m, 1H), 1.75 (dd, $J$ = 6.8, 1.7 Hz, 3H), 1.68 (d, $J$ = 1.9 Hz, 1H), 1.65 – 1.51 (m, 2H), 1.45 – 1.30 (m, 5H), 1.11 (d, $J$ = 6.0 Hz, 3H), 0.91 (dd, $J$ = 8.4, 5.9 Hz, 3H), 0.89 – 0.83 (m, 1H), 0.76 (dd, $J$ = 11.0, 5.1 Hz, 1H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 129.5, 125.7, 73.4, 37.1, 34.8, 28.0, 23.0, 22.2, 21.5, 18.3, 14.2, 13.4 ppm; IR (thin film, NaCl) 3419, 2954, 2928, 2861, 1650, 1447, 1409, 1379, 1005, 727 cm$^{-1}$; LRMS (EI) calcd for C$_{12}$H$_{22}$O 182.3 (M$^+$, $m/z$), observed 182.2 (M$^+$), 82 (100%). 34: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.46 (dqd, $J$ = 10.7, 6.8, 1.1 Hz, 1H), 5.03 (ddq, $J$ = 10.9, 9.3, 1.7 Hz, 1H), 3.22 (dt, $J$ = 8.9, 6.0
Hz, 1H), 1.68 (dd, J = 6.8, 1.7 Hz, 3H), 1.53 – 1.45 (m, 3H), 1.45 – 1.39 (m, 2H), 1.36 – 1.23 (m, 4H), 1.13 (d, J = 5.7 Hz, 3H), 0.90 – 0.86 (m, 3H), 0.86 – 0.79 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 129.5, 124.8, 72.8, 37.0, 34.0, 27.6, 23.3, 22.9, 20.4, 18.7, 14.1, 13.2 ppm; IR (thin film, NaCl) 3357, 2955, 2929, 2861, 1651, 1458, 1408, 1379, 1001, 728 cm⁻¹; LRMS (EI) calcd for C₁₂H₂₂O 182.3 (M⁺, m/z), observed 182.1 (M⁺), 82 (100%).

General Procedure C: Synthesis of Synthetic Fatty Acids by Coupling Alkynes with Vinylcyclopropane Carbinols

To a RBF containing alkyne (2 mmol) and ClTi(Oiri-Pr)₃ (2 – 2.5 mmol, 1.0 M in hexanes) in PhMe (0.1 M) at -78 °C is added c-C₅H₉MgCl (4 – 5 mmol) by syringe and the mixture is warmed to -30 °C and stirred for 1 h (becoming deep brown in colour). In a separate RBF containing a vinylcyclopropane carbinol (1 mmol) in Et₂O (< 0.3 M) at -78 °C is added n-BuLi (1.2 mmol) by syringe and the mixture is warmed to 0 °C over 20 min and then added by cannula to the titanium complex that had been re-cooled to -78 °C. The mixture is then slowly warmed to RT over 3 h and treated with 1N HCl (~5 mL / mmol vinylcyclopropane) with rapid stirring. After 10 min the now colourless mixture is further diluted with EtOAc and then filtered through a pad of silica rinsing with additional EtOAc. After concentration in vacuo, the non-polar product fractions are separated from the unreacted vinylcyclopropane by flash column chromatography (0 to 5% Et₂O in hexanes followed by flushing with EtOAc) and used directly in the following reaction. To this crude product in a plastic vial dissolved in MeCN / CH₂Cl₂ (5 mL, 1:1) at 0 °C is added HF • pyridine by plastic syringe in 1 mL / 5 min increments. When the reaction is complete (indicated by TLC), the reaction mixture is poured slowly into a plastic beaker containing stirred saturated aqueous NaHCO₃ (100 mL) at 0 °C, then diluted with Et₂O. The layers are separated, the aqueous phase extracted with Et₂O, organic extracts combined and filtered through MgSO₄, concentrated in vacuo, and purified by flash column chromatography (10 – 15% EtOAc in hexanes). The resultant alcohol which could contain small amounts of reduction side products was used directly in the following oxidation. The purified skipped polyene alcohol (ie 0.5 mmol) in DMF (3 mL) is added PDC (2.0 mmol) and two drops of water at RT and the reaction is stirred for 12 h. The reaction mixture is then poured into brine (15 mL) and extracted three times with Et₂O, extracts combined, washed with brine, filtered through
MgSO₄, concentrated *in vacuo*, and purified by flash column chromatography (20% EtOAc in hexanes) to yield the pure product.

(4E,6E,9Z)-5,8-dimethyl-4-((trimethylsilyl)methylene)tetradeca-6,9-dien-1-ol (36)

The titled compound was prepared according to Procedure C using the following quantities of reagents: CITi(Oi-Pr)₃ (1.5 mL, 1.5 mmol), *tert*-butyldimethyl(5-(trimethylsilyl)pent-4-enyloxy)silane¹⁰ (325 mg, 1.2 mmol), c-C₅H₉MgCl (1.6 mL, 3.0 mmol, 1.9 M in Et₂O) in PhMe (6 mL), and (S)-1-(2-methyl-3-((Z)-prop-1-enyl)cyclopropyl)pentan-1-ol 34 (110 mg, 0.6 mmol), n-BuLi (270 µL, 0.66 mmol, 2.5 M in hexanes) in Et₂O (2 mL). Unreacted vinylcyclopropane 34 was recovered (66 mg) and the oily product fractions were dissolved in THF (2 mL), treated with TBAF (2.76 mL, 2.4 mmol) at 0 °C and stirred to 20 °C over 3 h. The reaction was quenched with solid CaCO₃ (~50 mg) and saturated aqueous NaHCO₃, diltured with Et₂O, layers separated, aqueous phase extracted with Et₂O, organic extracts combined, washed with brine, filtered through MgSO₄, concentrated *in vacuo*, and purified by flash column chromatography (10 – 15% EtOAc in hexanes) to yield pure 36 (64 mg, 34% over 2 steps, 82% brsm) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.40 – 5.10 (m, 5H), 3.66 – 3.61 (m, 2H), 3.56 (dt, J = 8.8, 4.8 Hz, 1H), 3.12 (dd, J = 15.6, 6.6 Hz, 1H), 2.80 (pent, J = 6.9 Hz, 1H), 2.22 – 2.16 (m, 2H), 2.07 – 1.99 (m, 2H), 1.67 (ddd, J = 9.2, 8.1, 4.1 Hz, 2H), 1.34 – 1.22 (m, 6H), 1.08 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H), 0.90 (dd, J = 4.2, 2.9 Hz, 3H), 0.10 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 162.7, 134.2, 133.8, 132.9, 128.8, 122.2, 63.4, 43.9, 34.7, 32.8, 32.1, 31.9,

¹⁰ Page, P. C. B.; Rosenthal, S. *Tetrahedron* 1990, 46, 2573 – 2586.
The stereochemical assignment for skipped triene 36 was made based on the following analysis:

1) alkene geometry at C1-C2 was assigned by nOe (see below),
2) alkene geometry at C7-C8 was assigned by nOe (see below),
3) alkene geometry at C4-C5 was assigned based on analogy to previous examples (see assignments for compounds 23, 24, 26, and 27),
4) relative stereochemistry at C3 was assigned based on the combination of the model established for the stereospecific coupling and syn carbometallation.

(6E,9Z)-6-Methyl-4-methylenetetradeca-6,9-dienoic acid (37)

The titled compound was prepared according to Procedure C using the following quantities of reagents: ClTi(Oi-Pr)₃ (1.2 mL, 1.2 mmol), tert-butylidimethyl(5-(trimethylsilyl)pent-4-ynyloxy)silane⁸ (325 mg, 1.2 mmol), c-C₆H₆MgCl (1.26 mL, 2.4 mmol, 1.9 M in Et₂O) in PhMe (6 mL), and 2-(prop-1-en-2-yl)cyclopropyl)pentan-1-ol (34, 100 mg, 0.6 mmol), n-BuLi (270 µL, 0.66 mmol, 2.5 M in hexanes) in Et₂O (2 mL). Unreacted vinylcyclopropane 30 was recovered (34 mg). Desilylation: HF • pyridine (2 mL, 70%) in MeCN / CH₂Cl₂ (5 mL, 1:1). Oxidation: crude alcohol (75 mg, 0.32 mmol), PDC (482 mg, 1.28 mmol) in DMF (2 mL) and water (1 drop) yielded 37 (63 mg, 38% over 3 steps, 57% brsm) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.43 – 5.29 (m, 2H), 5.26 (t, J = 7.1 Hz, 1H), 4.80 (d, J = 8.1 Hz, 2H), 2.78 (s, 2H), 2.74 (t, J = 7.0 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 2.31 (t, J = 7.5 Hz, 2H), 2.04 (q, J = 6.5 Hz, 2H), 1.64 (d, J = 1.2 Hz, 3H), 1.38 – 1.28 (m, 3H), 0.93 – 0.88 (m, 3H) ppm; ¹³C NMR (126
MHz, CDCl$_3$) $\delta$ 179.5, 145.2, 132.7, 130.3, 128.1, 125.8, 110.8, 39.2, 32.6, 32.0, 30.5, 27.1, 26.5, 23.4, 22.5, 14.1 ppm; IR (thin film, NaCl) 2959, 2928, 2859, 1713, 1442, 1249, 894 cm$^{-1}$; LRMS (ESI) calcd for C$_{16}$H$_{25}$O$_2$ 250.4 (M$^+$, m/z), observed 249.8 (M − H)$^+$. 

Alkene geometry at C6-C7 and C9-C10 was assigned by nOe:

**(E)-tert-Butyldimethyl-(9-(trimethylsilyl)non-5-en-8-ynyloxy)silane (38)**

To a RBF containing 1-trimethylsilyl-1-propyne (1.97 mL, 13.2 mmol) and TMEDA (2.12 mL, 14.1 mmol) in THF (20 mL) at -78 °C was added n-BuLi (5.7 mL, 14.1 mmol, 2.5 M in hexanes). This transparent yellow reaction was then allowed to warm to 0 °C, stirred for 45 min, then transfer by cannula to a mixture of CuI (2.86 g, 15.0 mmol) in THF (10 mL) at -78 °C. After stirring for an additional 30 min PBu$_3$ (3.26 mL, 13.2 mmol) was added and the reaction was allowed to warm slowly to −20 °C over 20 min. **(E)-tert-Butyldimethyl(9-(trimethylsilyl)non-5-en-8-ynyloxy)silane**$^{11}$ (3.0 g, 8.82 mmol) was then added by syringe and the dark brown mixture was left to warm slowly to RT over night. The reaction was quenched by addition of saturated aqueous NH$_4$Cl, diluted with water and Et$_2$O, layers separated, aqueous phase extracted with Et$_2$O, organic extracts combined, washed with brine, filtered through MgSO$_4$, concentrated in vacuo, and purified by flash column chromatography (1 to 3 % Et$_2$O in hexanes) to yield pure 38 (2.56 g, 90%) as a light yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.67 (dtt, $J = 15.2, 6.8, 1.7$ Hz, 1H), 5.39 (dtt, $J = 15.2, 5.5, 1.4$ Hz, 1H), 3.60 (t, $J = 6.4$ Hz, 2H), 2.95 (ddd, $J = 5.5, 2.9, 1.3$ Hz, 2H), 2.04 (ddd, $J = 8.2, 7.3, 1.3$ Hz, 2H), 1.56 – 1.49 (m, 2H), 1.45 – 1.39 (m, 2H), 0.89 (s, 9H), 0.16 (s, 9H), 0.05 (s, 6H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 132.4, 123.9, 104.9, 86.3, 63.2, 32.5, 32.2, 26.1, 25.6, 23.2, 18.5, 0.3, -5.1 ppm; IR (thin film, NaCl)

$^{11}$ Piers, E.; Coish, P. D. G. *Synthesis* 2001, 2, 251–261.
2955, 1608, 1456, 1247, 1058, 836 cm⁻¹; LRMS (EI) calcd for C₂₈H₃₈OSi 324.6 (M⁺, m/z), observed 309.1 (M – CH₃)+, 147 (100%).

(5E,10E,13Z)-10-Methyl-8-methyleneoctadeca-5,10,13-trienoic acid (39)

The titled compound was prepared according to Procedure C using the following quantities of reagents: ClTi(O-i-Pr)₃ (1.5 mL, 1.5 mmol), (E)-tert-butyldimethyl(9-(trimethylsilyl)non-5-en-8-ynyloxy)silane (38, 390 mg, 1.2 mmol), c-C₅H₉MgCl (1.6 mL, 3.0 mmol, 1.9 M in Et₂O) in PhMe (6 mL), and (R)-1-(2-methyl-3-((Z)-prop-1-enyl)cyclopropyl)pentan-1-ol 30 (110 mg, 0.6 mmol), n-BuLi (270 µL, 0.66 mmol, 2.5 M in hexanes) in Et₂O (2 mL). Unreacted vinylecyclopropane 30 was recovered (31 mg). Desilylation: HF • pyridine (3 mL, 70%) in MeCN / CH₂Cl₂ (4 mL, 1:1). Oxidation: crude alcohol (84 mg, 0.29 mmol), PDC (435 mg, 1.16 mmol) in DMF (2 mL) and water (1 drop) yielded 39 (65 mg, 36% over 3 steps, 53% brsm) as a colourless oil; ¹H NMR (400 MHz, CDCl₃) δ 5.52 – 5.27 (m, 4H), 5.24 (t, J = 7.2 Hz, 1H), 4.76 (d, J = 5.7 Hz, 2H), 2.76 – 2.68 (m, 4H), 2.65 (d, J = 5.2 Hz, 2H), 2.37 – 2.32 (m, 2H), 2.11 – 1.98 (m, 4H), 1.73 (dd, J = 14.8, 7.4 Hz, 2H), 1.64 (d, J = 1.2 Hz, 3H), 1.35 – 1.30 (m, 4H), 0.93 – 0.88 (m, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 179.5, 146.2, 133.07, 131.1, 130.1, 129.1, 128.3, 125.5, 110.8, 45.0, 39.3, 38.8, 32.0, 31.9, 27.1, 26.6, 24.7, 23.6, 22.5, 14.1 ppm; IR (thin film, NaCl) 2957, 2927, 1709, 1436, 1247, 970, 894, 838 cm⁻¹; LRMS (ESI) calcd for C₂₀H₃₁ O₂ 304.5 (M⁺, m/z), observed 303.9 (M – H)+.

Alkene geometry at C10-C11 and C13-C14 was assigned by nOe:
For Compound 39: The 1,4-diene product isolated was contaminated with a minor product of unknown structure. If this minor product is an olefin isomer, selectivity for this process can be calculated to be $= 20:1$ (based on integration in the 1H NMR spectrum).

(6E,9E)-5,8-Dimethyl-4-methylene tetradeca-6,9-dienoic acid (41)

The titled compound was prepared according to Procedure C using the following quantities of reagents: ClTi(O-i-Pr)$_3$ (1.2 mL, 1.2 mmol), tert-butyldimethyl(5-(trimethylsilyl)pent-4-ynyloxy)silane$^8$ (325 mg, 1.2 mmol), c-C$_5$H$_9$MgCl (1.26 mL, 2.4 mmol, 1.9 M in Et$_2$O) in PhMe (6 mL), and (R)-1-(2-methyl-3-((Z)-prop-1-enyl)cyclopropyl)pentan-1-ol 40 (110 mg, 0.6 mmol), n-BuLi (270 µL, 0.66 mmol, 2.5 M in hexanes) in Et$_2$O (2 mL). Unreacted vinylcyclopropane 40 was recovered (60 mg). Desilylation: HF • pyridine (3 mL, 70%) in MeCN / CH$_2$Cl$_2$ (4 mL, 1:1). Oxidation: crude alcohol (48 mg, 0.18 mmol), PDC (271 mg, 0.72 mmol) in DMF (2 mL) and water (1 drop) yielded pure 41 (39 mg, 23% over 3 steps, 52% brsm) as a colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.45 – 5.22 (m, 4H), 4.84 (s, 1H), 4.74 (d, $J = 1.0$ Hz, 1H), 2.83 – 2.71 (m, 2H), 2.55 – 2.47 (m, 2H), 2.37 – 2.29 (m, 2H), 1.99 (dd, $J = 12.0$, 7.1 Hz, 2H), 1.35 – 1.26 (m, 4H), 1.12 (d, $J = 6.9$ Hz, 3H), 1.04 (d, $J = 6.9$ Hz, 3H), 0.89 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 179.4, 151.8, 134.7, 134.6, 132.3, 129.1, 108.5, 42.9, 39.3, 32.8, 32.4, 31.9, 29.0, 22.3, 20.8, 19.4, 14.1 ppm; IR (thin film, NaCl) 2961, 2927, 2872, 1712, 1455, 1295, 970, 895 cm$^{-1}$; LRMS (ESI) calcd for C$_{17}$H$_{27}$O$_2$ 264.4 (M$^+$, m/z), observed 263.8 (M – H)$^+$. The stereochemical assignment for the polyunsaturated fatty acid 41 was made by analogy to previous examples (i.e. 36).
Figure S1: \( ^1H \) (400 MHz, CDCl\(_3\)) and \( ^{13}C \) CPD (100 MHz, CDCl\(_3\)) of 13c
Figure S2: $^1$H (400 MHz, CDCl$_3$) and $^{13}$CPT (100 MHz, CDCl$_3$) of 16c
Figure S3: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$APT (100 MHz, CDCl$_3$) of 17
Figure S4: $^1H$ (400 MHz, CDCl$_3$) and $^{13}$CPT (100 MHz, CDCl$_3$) of 18
Figure S5: H\textsuperscript{1} (400 MHz, CDCl\textsubscript{3}) and C\textsuperscript{13}CPT (100 MHz, CDCl\textsubscript{3}) of 20 (Z:E = 94:6)
Figure S6: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$CPT (100 MHz, CDCl$_3$) of 13d
Figure S7: $\text{H}^1$ (400 MHz, CDCl$_3$) and $\text{C}^{13}$PT (100 MHz, CDCl$_3$) of 21
Figure S8: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$PT (100 MHz, CDCl$_3$) of 22 ($Z:E = 95:5$)
Figure S9: $^1$H (400 MHz, CDCl$_3$) and $^{13}$CPT (100 MHz, CDCl$_3$) of 23
Figure S10: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$PT (100 MHz, CDCl$_3$) of 24
Figure S11: $^1\text{H}$ (400 MHz, CDCl$_3$) and $^{13}\text{C}$PT (100 MHz, CDCl$_3$) of 25
Figure S12: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$PT (100 MHz, CDCl$_3$) of 26
Figure S13: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$CPT (100 MHz, CDCl$_3$) of 27
Figure S14: $^1\text{H}$ (400 MHz, CDCl$_3$) and $^{13}\text{C}$ CPT (100 MHz, CDCl$_3$) of 28
Figure S15: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$PT (100 MHz, CDCl$_3$) of 29
Figure S16: H$^1$ (400 MHz, CDCl$_3$) and C$^{13}$CPT (100 MHz, CDCl$_3$) of 30
Figure S17: \textsuperscript{1}H (400 MHz, CDCl\textsubscript{3}) and C\textsuperscript{13}PT (100 MHz, CDCl\textsubscript{3}) of 31
Figure S18: $\text{H}^1$ (400 MHz, CDCl$_3$) and $\text{C}^{13}$CPT (100 MHz, CDCl$_3$) of 32
Figure S19: $^1$H (400 MHz, CDCl$_3$) and $^{13}$CPT (100 MHz, CDCl$_3$) of 33
Figure S20: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$ (100 MHz, CDCl$_3$) of 40 ($Z:E = 94:6$)
Figure S21: $^1$H (400 MHz, CDCl$_3$) and $^{13}$CPT (100 MHz, CDCl$_3$) of 34 ($Z:E = 91:9$)
Figure S22: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$PT (100 MHz, CDCl$_3$) of 36
**Figure S23:** $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$PT (100 MHz, CDCl$_3$) of 37

![NMR spectra](image-url)
Figure S24: $^1\text{H}$ (400 MHz, CDCl$_3$) and $^{13}\text{C}$PT (100 MHz, CDCl$_3$) of 38
Figure S25: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$PT (100 MHz, CDCl$_3$) of 39
Figure S26: $^1H$ (400 MHz, CDCl$_3$) and $^{13}C$PT (100 MHz, CDCl$_3$) of 41