Single Isomer Tetrasubstituted Olefins from Regio- and Stereoselective Palladium-Catalyzed Couplings of β -Chloro- α -Iodo- α,β -Unsaturated Esters

Alison B. Lemay, Katarina S. Vulic, and William W. Ogilvie*

Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, Canada, K1N 6N5

Email wogilvie@science.uottawa.ca

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General. Reactions were performed under nitrogen in flame-dried glassware equipped with a magnetic stirbar and a rubber septum unless otherwise indicated. Solvents were freshly distilled prior to use as follows: THF over sodium/benzophenone; dichloromethane and DMF over calcium hydride. Triethylamine and diisopropylethylamine were freshly distilled over calcium hydride. All other reagents were used without further purification unless otherwise indicated. Reactions were monitored by TLC analysis using glass plates precoated (250 μ m thickness) with silica gel 60 F₂₅₄. TLC plates were visualized using ultraviolet light, potassium permanganate, ceric ammonium molybdate, and/or *p*-anisaldehyde stains. Flash chromatography was carried out on 230-400 mesh silica gel 60, or preparatory TLC glass plates precoated with silica gel (Si250F). ¹H and ¹³C NMR spectra were acquired on a 300 MHz or 500 MHz spectrometer in the specified solvent. Infrared spectra were acquired on a FTIR spectrometer. High resolution mass spectra were obtained using an Analytical Concept spectrometer. Melting points were determined using an Electrothermal Meltemp apparatus and are uncorrected.

General procedure for the conversion of 2-alkynyl esters into (*E*)- β -chloro- α -iodo- α,β -unsaturated esters (Table 1, compounds 1-5).

(*E*)-Methyl 3-chloro-2-iodoacrylate (1). A solution of methyl-2-propiolate (250 mg, 2.98 mmol, 1 eq) in dichloroethane (25 mL) and tetrabutylammonium iodide (3.25 g, 8.95 mmol, 3 eq) was heated at reflux for 18 h. The reaction was cooled, diluted with EtOAc and washed with NaHSO₃ (20 % wt solution), saturated NaHCO₃ and brine. The organic phase was then dried over MgSO₄, filtered and concentrated *in vacuo*. The pure product was obtained by column chromatography on silica gel eluting with hexanes then 5 % EtOAc in hexanes to give the title compound as a colourless oil (528 mg, 72%). ¹H NMR (300 MHz, CDCl₃) δ 7.00 (s, 1H), 3.79 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 162.6 (C), 129.4 (CH), 84.3 (C), 53.2 (CH₃); IR (neat) 1728, 1567 cm⁻¹; MS (EI) 246 (M⁺); HRMS Calcd for C₄H₄ClIO₂ (M⁺) 245.8945, found 245.8926.

(*E*)-Ethyl 3-chloro-2-iodobut-2-enoate (2). Prepared from ethyl-2-butynoate (1.0 g, 8.93 mmol) using a procedure similar to that described above for compound **1** that provided the title product as a colorless oil (2.23 g, 91%). ¹H NMR (300 MHz, CDCl₃) δ 4.17 (q, *J* = 3.6 Hz, 2H), 1.95 (s, 3H), 1.26 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 164.8 (C), 134.8 (C), 80.8 (C), 62.4 (CH), 29.5 (CH₃), 13.8 (CH₃); IR (neat) 1727, 1627 cm⁻¹; MS (EI) 274 (M⁺); HRMS calcd for C₆H₈ClIO₂ (M⁺) 273.9258, found 273.9294.

(*E*)-Ethyl 3-chloro-3-cyclohexyl-2-iodoacrylate (3).

Prepared from ethyl 3-cyclohexylpropiolate (200 mg, 1.11 mmol) using a procedure similar to that described above for compound **1** that provided the title product as a colourless oil (256 mg, 62 %). ¹H NMR (400 MHz, C₆D₆) δ 3.99 (q, *J* = 7.2 Hz, 2H), 2.93 (tt, *J* = 11.2, 3.6 Hz,

1H), 1.31-1.52 (m, 6H), 0.85-1.08 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 165.1 (C), 142.0 (C), 79.7 (C), 62.2 (CH_2), 48.3 (CH), 29.8 (CH_2), 25.7 (CH_2), 25.6 (CH_2), 13.8 (CH_3); **IR** (neat) 1730, 1611, cm^{-1} ; **MS** (EI) 342 (M^+); **HRMS** calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{ClI}$ (M^+) 341.9884, found 341.9897.

(E)-Ethyl 5-(tert-butyldimethylsilyloxy)-3-chloro-2-iodopent-2-enoate (4). Prepared from ethyl 5-(tert-butyldimethylsilyloxy)pent-2-ynoate (500 mg, 2.07 mmol) using a procedure similar to that described above for compound **1** that provided the title product as a colorless oil (537 mg, 67%). ^1H NMR (300 MHz, C_6D_6) δ 3.95 (q, $J = 7.2$ Hz, 2H), 3.58 (t, $J = 6.3$ Hz, 2H), 2.59 (t, $J = 6.3$ Hz, 2H), 0.93 (t, $J = 7.2$ Hz, 3H), 0.92 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ 164.8 (C), 135.0 (C), 83.3 (C), 62.1 (CH_2), 59.8 (CH_2), 44.4 (CH_2), 26.1 (CH_3), 18.4 (C), 13.8 (CH_3), -5.3 (CH_3); **IR** (neat) 1734, 1622 cm^{-1} ; **MS** (EI) 360 ($\text{M}^+ - \text{tBu}$); **HRMS** Calcd for $\text{C}_9\text{H}_{15}\text{ClIO}_3\text{Si}$ ($\text{M}^+ - 57$) 360.9524, found 360.9528.

(E)-Ethyl 3-chloro-2-iodo-3-phenylacrylate (5). Prepared from ethyl phenylpropiolate (500 mg, 2.87 mmol) using a procedure similar to that described above for compound **1** that provided the title product as a colorless oil (647 mg, 67%). ^1H NMR (400 MHz, C_6D_6) δ 7.06 (d, $J = 7.6$ Hz, 1H), 6.90-6.93 (m, 4H), 4.02 (q, $J = 7.2$ Hz, 2H), 0.96 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 163.7 (C), 141.3 (C), 129.7 (CH), 129.0 (CH), 129.0 (CH), 128.4 (C), 122.3 (C), 62.6 (CH_2), 13.8 (CH_3); **IR** (neat) 1729, 1628, cm^{-1} ; **MS** (EI) 336 (M^+); **HRMS** Calcd for $\text{C}_{11}\text{H}_{10}\text{ClIO}_2$ (M^+) 335.9414, found 335.9435.

General procedure for the Sonogashira coupling of (E)- β -chloro- α -iodo- α,β -unsaturated esters (Table 2, compounds 9-16):

(Z)-Ethyl 3-chloro-2-(2-phenylethynyl)but-2-enoate (9). A flask was charged with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (13 mg, 0.018 mmol, 0.10 eq) and copper iodide (5.1 mg, 0.027 mmol, 0.15 eq). To this was added dichloromethane (2 mL) and diisopropylethylamine (0.13 mL, 0.72 mmol, 4 eq) via syringe. (E)-ethyl 3-chloro-2-iodobut-2-enoate (**2**) (50 mg, 0.18 mmol, 1 eq) was then introduced, and the resulting yellow solution was carefully sparged with nitrogen for 10 minutes. Phenyl acetylene (0.06 mL, 0.55 mmol, 3 eq) was then added via syringe and the resulting black solution was stirred for 2 h. The mixture was partitioned between water and EtOAc and the organic layer collected then dried over MgSO_4 , filtered and concentrated. The product was purified by column chromatography on silica gel eluting with hexanes then 5% EtOAc in hexanes to afford the title product (35 mg, 78 %) as a clear, tan oil. ^1H NMR (300 MHz, CDCl_3) δ 7.48-7.46 (m, 2H), 7.35-7.34 (m, 3H), 4.33 (q, $J = 7.0$ Hz, 2H), 2.52 (s, 3H), 1.37 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.5 (C), 146.6 (C), 131.4 (CH), 128.8 (CH), 128.3 (CH), 122.5 (C), 115.3 (C), 96.8 (C), 83.0 (C), 61.7 (CH_2), 26.2

(CH₃), 14.0 (CH₃); **IR** (neat) 2201, 1734, 1612 cm⁻¹; **MS** (EI) 248 (M⁺); **HRMS** calcd for C₁₄H₁₃ClO₂ (M⁺) 248.0604, found 248.0617.

(Z)-Ethyl 3-chloro-2-(2-(4-fluorophenyl)ethynyl)but-2-enoate (10). Prepared from compound **2** (50 mg, 0.18 mmol) using a procedure similar to that described above for compound **9** that provided the title product as a pale yellow oil (37 mg, 77%). **¹H NMR** (500 MHz, CDCl₃) δ 7.17 (dd, *J* = 5.5, 9.0 Hz, 2H), 6.67 (dd, *J* = 9.0, 9.0 Hz, 2H), 4.17 (q, *J* = 7.5 Hz, 2H), 2.18 (s, 3H), 1.10 (t, *J* = 7.5 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 164.0 (C), 163.3 (C), 162.0 (C), 146.2 (C), 133.7 (CH), 133.6 (CH), 119.0 (C), 115.9 (CH), 115.7 (CH), 96.0 (C), 83.6 (C), 61.7 (CH₂), 25.5 (CH₃), 14.0 (CH₃); **IR** (neat) 2140, 1733, 1600 cm⁻¹; **MS** (EI) 266 (M⁺); **HRMS** calcd for C₁₄H₁₂ClFO₂ (M⁺) 266.0510, found 266.0490.

(Z)-Ethyl 3-chloro-2-(2-(trimethylsilyl)ethynyl)but-2-enoate (11). Prepared from compound **2** (50 mg, 0.18 mmol) using a procedure similar to that described above for compound **9** that provided the title product as a pale yellow oil (30 mg, 68%). **¹H NMR** (300 MHz, C₆D₆) δ 3.96 (q, *J* = 7.2 Hz, 2H), 2.04 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.10 (s, 9H); **¹³C NMR** (75 MHz, C₆D₆) δ 163.0 (C), 147.6 (C), 116.5 (C), 102.8 (C), 99.0 (C), 61.6 (CH₂), 25.5 (CH₃), 13.9 (CH₃), -0.3 (CH₃); **IR** (neat) 2147, 1736, 1586 cm⁻¹; **MS** (EI) 244 (M⁺); **HRMS** calcd for C₁₁H₁₇ClO₂Si (M⁺) 244.0686, found 244.0668.

(Z)-Ethyl 2-(1-chloroethylidene)hex-3-ynoate (12). Prepared from compound **2** (50 mg, 0.18 mmol) using a procedure similar to that described above for compound **9** that provided the title product as a pale yellow oil (34 mg, 74%). **¹H NMR** (500 MHz, C₆D₆) δ 4.15 (q, *J* = 7.5 Hz, 2H), 2.20 (s, 3H), 2.19 (t, *J* = 7.0 Hz, 2H), 1.45-1.40 (m, 2H), 1.36-1.32 (m, 2H), 1.31-1.26 (m, 2H), 1.23-1.19 (m, 2H), 1.09 (t, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H); **¹³C NMR** (125 MHz, C₆D₆) δ 163.9 (C), 144.0 (C), 116.9 (C), 98.6 (C), 75.5 (C), 61.4 (CH₂), 31.5 (CH₂), 28.7 (CH₂), 28.6 (CH₂), 25.2 (CH₃), 22.8 (CH₂), 19.8 (CH₂), 14.2 (CH₃), 14.0 (CH₃); **IR** (neat) 2223, 1735, 1587 cm⁻¹; **MS** (EI) 256 (M⁺); **HRMS** calcd for C₁₄H₂₁ClO₂ (M⁺) 256.1231, found 256.1232.

(Z)-Ethyl 5-(tert-butyldimethylsilyloxy)-2-(1-chloroethylidene)pent-3-ynoate (13). Prepared from compound **2** (50 mg, 0.18 mmol) using a procedure similar to that described above for compound **9** that provided the title product as a pale yellow oil (43 mg, 76%). **¹H NMR** (500 MHz, C₆D₆) δ 4.22 (s, 2H), 4.02 (q, *J* = 7.0 Hz, 2H), 2.03 (s, 3H), 0.97 (t, *J* = 7.0

Hz, 3H), 0.94 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 163.2 (C), 146.6 (C), 100.2 (C), 96.1 (C), 79.1 (C), 61.5 (CH_2), 52.1 (CH_2), 25.9 (CH_3), 25.4 (CH_3), 18.3 (C), 14.0 (CH_3), -5.1 (CH_3); **IR** (neat) 1737, 1586 cm^{-1} ; **MS** (EI) 301 ($\text{M}^+ - \text{Me}$); **HRMS** calcd for $\text{C}_{11}\text{H}_{16}\text{ClO}_3\text{Si}$ ($\text{M}^+ - 57$) 259.0557, found 259.0553.

(Z)-Ethyl 6-(tert-butyldimethylsilyloxy)-2-(1-chloroethylidene)hex-3-ynoate (14).

Prepared from compound **2** (50 mg, 0.18 mmol) using a procedure similar to that described above for compound **9** that provided the title product as a pale yellow oil (42.8 mg, 72%). ^1H NMR (500 MHz, C_6D_6) δ 4.04 (q, $J = 7.0$ Hz, 2H), 3.5 (t, $J = 7.0$ Hz, 2H), 2.32 (t, $J = 7.0$ Hz, 2H), 2.93 (s, 3H), 0.98 (t, $J = 7.0$ Hz, 3H), 0.91 (s, 9H), -0.02 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 163.7 (C), 144.6 (C), 116.7 (C), 95.7 (C), 76.2 (C), 61.7 (CH_2), 61.5 (CH_2), 26.0 (CH_3), 25.2 (CH_3), 24.3 (CH_2), 18.4 (C), 14.0 (CH_3), -5.3 (CH_3); **IR** (neat) 2224, 1736, 1587 cm^{-1} ; **MS** (EI) 315 ($\text{M}^+ - \text{Me}$); **HRMS** calcd for $\text{C}_{12}\text{H}_{18}\text{ClO}_3\text{Si}$ ($\text{M}^+ - 57$) 273.0714, found 273.0752.

(Z)-Ethyl 2-(chloro(cyclohexyl)methylene)-4-phenylbut-3-ynoate (15). Prepared from compound **3** (100 mg, 0.305 mmol) using a procedure similar to that described above for compound **9** that provided the title product as a yellow oil (74 mg, 68 %). ^1H NMR (400 MHz, C_6D_6) δ 7.39-7.30 (m, 2H), 6.94-6.92 (m, 3H), 4.07 (q, $J = 7.2$ Hz, 2H), 3.38-3.32 (m, 1H), 1.67-1.22 (m, 10H), 0.98 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) 163.7 (C), 153.9 (C), 131.7 (CH), 128.9 (CH), 128.6 (CH), 123.1 (CH), 123.1 (C), 115.0 (C), 97.3 (C), 92.1 (C), 61.7 (CH_2), 45.7 (CH), 30.3 (CH_2), 26.0 (CH_2), 24.6 (CH_2), 14.0 (CH_3); δ **IR** (neat) 2237, 1710 cm^{-1} ; **HRMS** calcd for $\text{C}_{19}\text{H}_{21}\text{ClO}_2$ (M^+) 316.1230, found 316.1241.

(Z)-Ethyl 5-(tert-butyldimethylsilyloxy)-3-chloro-2-(2-(trimethylsilyl)ethynyl)pent-2-enoate (16). Prepared from compound **4** (30 mg, 0.072 mmol) using a procedure similar to that described above for compound **9** that provided the title product as a colourless oil (22 mg, 79%). ^1H NMR (400 MHz, C_6D_6) δ 3.96 (q, $J = 7.2$ Hz, 2H), 3.69 (t, $J = 6.4$ Hz, 2H), 2.82 (t, $J = 6.4$ Hz, 2H), 0.97 (s, 9H), 0.92 (t, $J = 7.2$ Hz, 3H), 0.15 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 163.2 (C), 148.4 (C), 118.2 (C), 102.6 (C), 99.0 (C), 61.6 (CH_2), 60.1 (CH_2), 41.9 (CH_2), 26.0 (CH_3), 18.3 (C), -0.3 (CH_3), -5.3 (CH_3); **IR** (neat) 2148, 1738 cm^{-1} ; **HRMS** calcd for $\text{C}_{14}\text{H}_{24}\text{ClO}_3\text{Si}_2$ ($\text{M}^+ - t\text{-Bu}$) 331.0950, found 331.0977.

(Z)-Ethyl 3-methyl-5-phenyl-2-(2-phenylethynyl)pent-2-en-4-ynoate (17). A flame-dried round bottom flask under nitrogen was charged with Pd(PPh₃)₂Cl₂ (51 mg, 0.073 mmol, 0.1 eq) and CuI (28 mg, 0.146 mmol, 0.15 eq). Dichloromethane (7.3 mL), DIPEA (0.51 mL, 2.92 mmol, 4 eq), and (*E*)-ethyl 3-chloro-2-iodobut-2-enoate (**2**) (200 mg, 0.73 mmol, 1 eq) were then introduced sequentially. The solution was sparged for 5 minutes with N₂ before the addition of phenylacetylene (0.24 mL, 2.19 mmol, 3 eq). The reaction was stirred for 18 h and then was partitioned between water and EtOAc. The layers were separated and the combined organic phases were washed with HCl (10 %), saturated NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. The product was purified by column chromatography eluting with hexanes then 5 % EtOAc in hexanes affording the title product as a yellow oil (130 mg, 55%). ¹H NMR (500 MHz, C₆D₆) δ 7.59 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.43 (dd, *J* = 8.0, 1.5 Hz, 2H), 6.96-6.97 (m, 6H), 4.12 (q, *J* = 7.0 Hz, 2H), 2.27 (s, 3H), 1.02 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, C₆D₆) δ 163.7 (C), 136.7 (C), 132.3 (CH), 131.7 (CH), 129.2 (CH), 128.7 (C), 128.6 (CH), 128.6 (CH), 128.3 (CH), 123.7 (C), 121.5 (C), 104.9 (C), 101.5 (C), 91.0 (C), 86.5 (C), 61.1 (CH₂), 24.0 (CH₃), 14.2 (CH₃); IR (neat) 2209, 2186, 1723, 1597 cm⁻¹; MS (EI) 314 (M⁺); HRMS calcd for C₂₂H₁₈O₂ (M⁺) 314.1307, found 314.1276.

(Z)-Ethyl 3-methyl-5-phenyl-2-(2-(trimethylsilyl)ethynyl)pent-2-en-4-ynoate (18). A flame-dried round bottom flask was charged with Pd(PPh₃)₂Cl₂ (23 mg, 0.033 mmol, 0.1 eq) and CuI (9.4 mg, 0.050 mmol, 0.15 eq). Dioxane (3.0 mL), (*Z*)-ethyl 3-chloro-2-(2-(trimethylsilyl)ethynyl)but-2-enoate (**11**) (80 mg, 0.33 mmol, 1 eq) and DIPEA (0.17 mL, 0.99 mmol, 3 eq) were added sequentially and the solution was sparged for 10 min with N₂. Phenylacetylene (0.10 mL, 0.99 mmol, 3 eq) was then added and the resulting black reaction mixture was stirred for 1 hour at which time an addition portion of phenylacetylene (0.10 mL, 0.99 mmol, 3 eq) was introduced. The reaction mixture was stirred for an additional 12 h, after which it was partitioned between water and EtOAc. The layers were separated and the organic phase washed with H₂O. The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. The product was purified by column chromatography on silica gel eluting with hexanes then 2% Et₂O in hexanes to give the desired product (43 mg, 42 %) as a yellow oil. ¹H NMR (500 MHz, C₆D₆) δ 7.55-7.53 (m, 2H), 6.98-6.93 (m, 3H), 4.05 (q, *J* = 7.0 Hz, 2H), 2.24 (s, 3H), 0.98 (t, *J* = 7.0 Hz, 3H), 0.19 (s, 9H); ¹³C NMR (125 MHz, C₆D₆) δ 163.6 (C), 138.0 (C), 132.3 (CH), 129.2 (CH), 128.6 (CH), 123.5 (C), 121.5 (C), 107.1 (C), 105.3 (C), 101.4 (C), 90.6 (C), 61.1 (CH₂), 24.0 (CH₃), 14.1 (CH₃), -0.1 (CH₃); IR (neat) 2196, 2140, 1727, 1598 cm⁻¹; MS (EI) 310 (M⁺); HRMS calcd for C₁₉H₂₂O₂Si (M⁺) 310.1389, found 310.1389.

General procedure for the Suzuki coupling of β-chloro-α-alkynyl-α,β-unsaturated esters (Table 3, compounds 19-25)

(Z)-Ethyl 3-phenyl-2-(2-(trimethylsilyl)ethynyl)but-2-enoate (19). A flame-dried round bottom flask was charged with a solution of (*Z*)-ethyl 3-chloro-2-(2-(trimethylsilyl)ethynyl)but-2-enoate (**11**) (50 mg, 0.20 mmol, 1 eq) in 1,4-dioxane (2 mL) and

the solution was sparged for 10 minutes with N₂. Pd₂(dba)₃ (9.2 mg, 0.010 mmol, 0.05 eq), phenyl boronic acid (49 mg, 0.40 mmol, 2 eq), and tri-*tert*-butyl phosphine tetrafluoroborate (11.6 mg, 0.040 mmol, 0.20 eq) were then added. The solution was sparged for an additional 5 minutes with N₂ before the addition of Cs₂CO₃ (130 mg, 0.40 mmol, 2 eq). The resulting black solution was stirred for 2 h after which water was added. The mixture was extracted with EtOAc and the organic layer was dried over MgSO₄, filtered and concentrated. The product was purified by column chromatography on silica gel, eluting with hexanes then 5% EtOAc in hexanes affording the product as a pale yellow oil (44 mg, 77%). ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.30 (m, 3H), 7.29-7.16 (m, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.26 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 165.7 (C), 156.4 (C), 141.3 (C), 128.1 (CH), 128.0 (CH), 126.6 (CH), 115.0 (C), 101.5 (C), 100.5 (C), 61.0 (CH₂), 24.5 (CH₃), 13.5 (CH₃), -0.1 (CH₃); IR (neat) 2146, 1728, 1592 cm⁻¹; MS (EI) 286 (M⁺); HRMS calcd for C₁₇H₂₂O₂Si (M⁺) 286.1389, found 286.1366.

(Z)-Ethyl 3-*p*-tolyl-2-(2-(trimethylsilyl)ethynyl)but-2-enoate (20). Prepared from compound **11** (50 mg, 0.20 mmol) using a procedure similar to that described above for compound **19** using *p*-tolyl boronic acid (109 mg, 0.80 mmol, 4 eq), which provided the title product as a pale yellow oil (45 mg, 75%). ¹H NMR (300 MHz, C₆D₆) δ 7.03 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 3.80 (q, *J* = 7.0 Hz, 2H), 2.26 (s, 3H), 2.02 (s, 3H), 0.70 (t, *J* = 7.0 Hz, 3H), 0.21 (s, 9H); ¹³C NMR (75 MHz, C₆D₆) δ 165.8 (C), 154.9 (C), 138.8 (C), 137.9 (C), 128.9 (CH), 127.2 (CH), 116.0 (C), 102.1 (C), 101.3 (C), 60.8 (CH₂), 24.0 (CH₃), 21.1 (CH₃), 13.7 (CH₃), -0.03 (CH₃); IR (neat) 2145, 1728, 1594 cm⁻¹; MS (EI) 300 (M⁺); HRMS calcd for C₁₈H₂₄O₂Si (M⁺) 300.1546; found 300.1547.

(Z)-Ethyl 3-(4-fluorophenyl)-2-(2-(trimethylsilyl)ethynyl)but-2-enoate (21). Prepared from compound **11** (50 mg, 0.20 mmol) using a procedure similar to that described above for compound **19**, using *p*-fluorophenyl boronic acid (112 mg, 0.80 mmol, 4 eq), which provided the title product as a pale yellow oil (43 mg, 72%). ¹H NMR (500 MHz, C₆D₆) δ 6.82 (dd, *J* = 5.5, 9.0 Hz, 2H), 6.66 (dd, *J* = 8.5, 8.5 Hz, 2H), 3.74 (q, *J* = 7.0 Hz, 2H), 2.15 (s, 3H), 0.66 (t, *J* = 7.0 Hz, 3H), 0.20 (s, 9H); ¹³C NMR (125 MHz, C₆D₆) δ 165.4 (C), 164.5 (C), 161.2 (C), 153.9 (C), 137.5 (C), 129.1 (CH), 128.9 (CH), 115.3 (CH), 115.0 (CH), 101.8 (C), 101.7 (C), 60.9 (CH₂), 24.1 (CH₃), 13.6 (CH₃), -0.1 (CH₃); IR (neat) 2147, 1728, 1601 cm⁻¹; MS (EI) 304 (M⁺); HRMS calcd for C₁₇H₂₁FO₂Si (M⁺) 304.1295, found 304.1279.

(2Z,4E)-Ethyl 3-methyl-5-phenyl-2-(2-(trimethylsilyl)ethynyl)penta-2,4-dienoate (22). Prepared from compound **11** (50 mg, 0.20 mmol) using a procedure similar to that described above for compound **19**, using S-phos (16.4 mg, 0.04 mmol, 0.20 eq) instead of $P(t\text{-Bu})_3\text{HBF}_4$ and K_2CO_3 (55.3 mg, 0.40 mmol, 2 eq) as base, which provided the title product as a pale yellow oil (41.5 mg, 67%). $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 8.62 (d, $J = 16.0$ Hz, 1H), 7.38 (d, $J = 7.5$ Hz, 2H), 7.06-7.00 (m, 3H), 6.74 (d, $J = 16$ Hz, 1H), 4.04 (q, $J = 7.0$ Hz, 2H), 2.34 (s, 3H), 1.01 (t, $J = 7.0$ Hz, 3H); 0.24 (s, 9H); $^{13}\text{C NMR}$ (125 MHz, C_6D_6) δ 165.1 (C), 153.6 (C), 137.2 (C), 136.2 (CH), 128.9 (CH), 128.9 (CH), 128.3 (CH), 127.0 (CH), 114.8 (C), 103.9 (C), 103.7 (C), 61.0 (CH_2), 18.3 (CH_3), 14.1 (CH_3), 0.04 (CH_3); **IR** (neat) 2138, 1713, 1610, 1575 cm^{-1} ; **MS** (EI) 312 (M^+); **HRMS** calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{Si}$ (M^+) 312.1546, found 312.1562.

(2Z,4E)-Ethyl 3-methyl-2-(2-(trimethylsilyl)ethynyl)undeca-2,4-dienoate (23). Prepared from compound **11** (50 mg, 0.20 mmol) using a procedure similar to that described above for compound **19**, using S-Phos (16.4 mg, 0.04 mmol, 0.20 eq) as ligand and K_2CO_3 (55.3 mg, 0.40 mmol, 2 eq) as base, which provided the title product as a pale yellow oil (41 mg, 64%). $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 7.77 (dt, $J = 16.0, 1.6$ Hz, 1H), 5.93 (dt, $J = 15.0, 6.8$ Hz, 1H), 4.01 (q, $J = 7.2$ Hz, 2H), 2.20 (s, 3H), 2.00 (q, $J = 6.8$ Hz, 2H), 1.14-1.26 (m, 10H), 0.98 (t, $J = 7.2$, 3H), 0.86 (t, $J = 7.2$, 3H); 0.23 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, C_6D_6) δ 165.2 (C), 153.7 (C), 139.7 (CH), 129.0 (CH), 113.3 (C), 103.5 (C), 102.6 (C), 60.8 (CH_2), 33.8 (CH_2), 32.0 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 22.9 (CH_2), 18.5 (CH_3), 14.3 (CH_3), 14.1 (CH_3), 0.1 (CH_3); **IR** (neat) 2140, 1716, 1625, 1426 cm^{-1} ; **MS** (EI) 320 (M^+); **HRMS** calcd for $\text{C}_{19}\text{H}_{32}\text{O}_2\text{Si}$ (M^+) 320.2172, found 320.2185.

(Z)-Ethyl 2-(cyclohexyl(phenyl)methylene)-4-phenylbut-3-ynoate (24). Prepared from compound **15** (28 mg, 0.078 mmol) using a procedure similar to that described above for compound **19** that provided the title product as a yellow solid (21 mg, 62%). **MP** 79-80 $^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 7.53-7.51 (m, 2H), 7.12-7.06 (m, 5H), 6.98-6.94 (m, 3H), 3.76 (q, $J = 7.2$ Hz, 2H), 3.40 (tt, $J = 3.2, 12.0$ Hz, 1H), 1.78 (dd, $J = 1.6, 13.2$ Hz, 2H), 1.59 (dt, $J = 2.8, 12.8$ Hz, 2H), 1.47-1.10 (m, 6H), 0.65 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, C_6D_6) δ 165.4 (C), 163.2 (C), 139.2 (C), 131.8 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 127.7 (CH), 127.3 (CH), 123.8 (C), 116.3 (C), 100.2 (C), 96.5 (C), 85.8 (C), 60.7 (CH_2), 45.6 (CH), 31.1 (CH_2), 26.7 (CH_2); **IR** (neat) 1725 cm^{-1} ; **HRMS** calcd for $\text{C}_{25}\text{H}_{26}\text{O}_2$ (M^+) 258.1933, found 358.1946.

(Z)-Ethyl 5-(tert-butyldimethylsilyloxy)-3-phenyl-2-(2-(trimethylsilyl)ethynyl)pent-2-enoate (25). Prepared from compound **16** (7 mg, 0.018 mmol) using a procedure similar to that described above for compound **19** that provided the title product as a yellow oil (4 mg, 52%). ¹H NMR (400 MHz, C₆D₆) δ 7.18 (d, *J* = 1.6 Hz, 1H), 7.05-6.98 (m, 4H), 3.73 (q, *J* = 7.2 Hz, 2H), 3.67 (t, *J* = 6.8 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H), 0.96 (s, 9H), 0.62 (t, *J* = 7.2 Hz, 3H), 0.23 (s, 9H), 0.02 (s, 6H); ¹³C NMR (100 MHz, C₆D₆) δ 165.6 (C), 155.8 (C), 140.5 (C), 128.2 (CH), 128.1 (CH), 127.7 (CH), 117.9 (C), 101.6 (C), 101.4 (C), 60.9 (CH₂), 60.8 (CH₂), 41.0 (CH₂), 26.1 (CH₃), 18.4 (C), 13.5 (CH₃), -0.07 (CH₃), -5.2 (CH₃); IR (neat) 2146, 1725 cm⁻¹; HRMS calcd for C₂₀H₂₉O₃Si₂ (M⁺ - *t*-Bu) 373.1655, found 373.1665.

PROOF of STEREOCHEMISTRY:

General procedure for the reduction of (*E*)-β-chloro-α-iodo-α,β-unsaturated esters to the corresponding (*E*)-alcohols

(*E*)-3-Chloro-2-iodobut-2-en-1-ol (7). To a solution of ester **2** (100 mg, 0.36 mmol, 1 eq) in CH₂Cl₂ (3 mL) at 0 °C was added diisobutylaluminum hydride as a 1 M solution in hexanes (0.80 mL, 0.80 mmol). The reaction was warmed to room temperature, and stirred for 2 h. Methanol (1 mL) was carefully added dropwise to quench the reaction. Ether (5 mL) and a saturated solution of Rochelle's salt (3 mL) were then introduced, and the resulting mixture was stirred until both layers became clear. The layers were separated, and the organic phase was dried over MgSO₄, filtered, and concentrated. Purification by column chromatography on silica gel eluting with 10 % EtOAc in hexanes gave the desired compound as a colourless oil (68 mg, 81 %). ¹H NMR (300 MHz, CDCl₃) δ 4.42 (s, 2H), 2.37 (s, 3H), 2.16 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 129.6 (C), 99.4 (C), 67.6 (CH₂), 30.6 (CH₃); IR (neat) 3341, 1626 cm⁻¹; MS (EI) 232 (M⁺); MS (EI) 232 (M⁺); HRMS calcd for C₄H₆ClIO (M⁺) 231.9152; found 231.9169.

(*E*)-3-Chloro-2-iodoprop-2-en-1-ol. Prepared from ester **1** (50 mg, 0.20 mmol) using a procedure similar to that described above for (*E*)-3-chloro-2-iodobut-2-en-1-ol which gave the title compound as a colorless oil (32.7 mg, 75 %). ¹H NMR (500 MHz, C₆D₆): δ 5.96 (s, 1H), 3.81 (d, *J* = 1.0 Hz, 2H), 1.12 (br s, 1H); ¹³C NMR (125 MHz, C₆D₆): δ 119.5 (CH), 104.2 (C), 63.3 (CH₂); IR (neat) 3338, 1603 cm⁻¹; MS (EI) 218 (M⁺); HRMS calcd for C₃H₄ClIO (M⁺) 217.8995; found 217.9019.

(E)-3-Chloro-3-cyclohexyl-2-iodoprop-2-en-1-ol. Prepared from ester **3** (50 mg, 0.28) using a procedure similar to that described above for (E)-3-chloro-2-iodobut-2-en-1-ol which gave the title compound as a colorless oil (49 mg, 64 %). ¹H NMR (400 MHz, C₆D₆): δ 3.99 (q, *J* = 7.2 Hz, 2H), 2.93 (tt, *J* = 11.2, 4.5 Hz, 1H), 1.30-1.52 (m, 6H), 0.89-1.09 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, C₆D₆): δ 165.1 (C), 142.0 (C), 79.7 (C), 62.2 (CH₂), 48.3 (CH), 29.8 (CH₂), 25.7 (CH₂), 25.6 (CH₂), 13.8 (CH₃); IR (neat) 3342, 1607, 1449 cm⁻¹; MS (EI) 300 (M⁺); HRMS calcd for C₉H₁₄ClIO (M⁺) 299.9778, found 299.9765.

(E)-5-(tert-butyldimethylsilyloxy)-3-chloro-2-iodopent-2-en-1-ol. Prepared from ester **4** (75 mg, 0.18 mmol) using a procedure similar to that described above for (E)-3-chloro-2-iodobut-2-en-1-ol which gave the title compound as a colorless oil (51 mg, 91 %). ¹H NMR (500 MHz, C₆D₆): δ 4.11 (d, *J* = 7.0 Hz, 2H), 3.67 (t, *J* = 7.0 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 2H), 1.32 (t, *J* = 7.0 Hz, 1H), 0.95 (s, 9H), 0.04 (s, 6H); ¹³C NMR (125 MHz, C₆D₆): δ 130.0 (C), 103.2 (C), 67.3 (CH₂), 60.0 (CH₂), 46.3 (CH₂), 26.1 (CH₃), 18.4 (C), -5.2 (CH₃); IR (neat) 3360, 1618 cm⁻¹; MS (EI) 319 (M⁺ - ^tBu); HRMS calcd for C₇H₁₃ClIO₂Si (M⁺ - ^tBu) 318.9420, found 318.9413.

(E)-3-Chloro-2-iodo-3-phenylprop-2-en-1-ol. Prepared from ester **5** (10 mg, 0.030 mmol) using a procedure similar to that described above for (E)-3-chloro-2-iodobut-2-en-1-ol which gave the title compound as a colorless oil (7 mg, 79 %). ¹H NMR (400 MHz, C₆D₆): δ 7.31 (dd, *J* = 8.4, 1.6 Hz, 2H), 6.91-7.03 (m, 3H), 4.22 (d, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, C₆D₆): δ 136.7 (C), 129.1 (C), 129.0 (CH), 129.0 (CH), 128.9 (CH), 67.2 (C), 63.4 (CH₂); IR (neat) 3362, 1662 cm⁻¹; MS (EI) 294 (M⁺).

General procedure for the reduction of (Z)-β-chloro-α-iodo-α,β-unsaturated esters to the corresponding (Z)-alcohols

(Z)-3-Chloro-2-iodobut-2-en-1-ol (8). A solution of ester **2** (85 mg, 0.31 mmol) was subjected to UV light (350 nm) for 1 hour, thereby isomerizing to the (Z)-β-chloro-α-iodo-α,β-unsaturated ester. To a solution of the crude product (85 mg, 0.31 mmol, 1 eq) in

CH₂Cl₂ (3 mL) was added diisobutylaluminum hydride as a 1 M solution in hexanes (0.77 mL, 2.5 eq). The reaction was stirred for 2 h. Methanol (1 mL) was carefully added dropwise to quench the reaction. Ether (5 mL) and a saturated solution of Rochelle's salt (3 mL) were then introduced, and the resulting mixture was stirred until both layers became clear. The layers were separated, and the organic phase was dried over MgSO₄, filtered, and concentrated. Purification by column chromatography on silica gel eluting with 10 % EtOAc in hexanes gave the desired compound as a colourless oil (15 mg, 21 %) **¹H NMR** (500 MHz, C₆D₆): δ 3.72 (s, 2H), 1.62 (s, 3H), 1.16 (br s, 1H); **¹³C NMR** (125 MHz, C₆D₆): δ 138.4 (C), 103.7 (C), 67.6 (CH₂), 21.9 (CH₃); **IR** (neat) 3382, 1627 cm⁻¹; **MS** (EI) 232 (M⁺); **HRMS** calcd for C₄H₆ClIO (M⁺) 231.9152; found 231.9147.

(Z)-3-Chloro-2-iodoprop-2-en-1-ol. Prepared from ester **1** (113 mg, 0.46 mmol) using a procedure similar to that described above for (Z)-3-chloro-2-iodobut-2-en-1-ol which gave the title compound as a colorless oil (13 mg, 13 %). **¹H NMR** (500 MHz, C₆D₆): δ 6.05 (t, *J* = 1.5 Hz, 1H), 3.58 (dd, *J* = 5.0, 1.5 Hz, 2H), 1.20 (br s, 1H); **¹³C NMR** (125 MHz, C₆D₆): δ 124.5 (CH), 110.1 (C), 69.7 (CH₂); **IR** (neat) 3338, 1590 cm⁻¹; **MS** (EI) 218 (M⁺); **HRMS** calcd for C₃H₄ClIO (M⁺) 217.8995; found 217.8923.

(Z)-3-Chloro-3-cyclohexyl-2-iodoprop-2-en-1-ol. Prepared from ester **3** (25 mg, 0.073 mmol) using a procedure similar to that described above for (Z)-3-chloro-2-iodobut-2-en-1-ol which gave the title compound as a colorless oil (5 mg, 23 %). **¹H NMR** (400 MHz, C₆D₆): δ 4.12 (d, *J* = 6.9 Hz, 2H), 2.63 (m, 1H), 0.91-1.96 (m, 10H); **¹³C NMR** (100 MHz, C₆D₆): δ 149.1 (C), 103.8 (C), 67.7 (CH₂), 43.6 (CH), 31.6 (CH₂), 26.1 (CH₂), 25.6 (CH₂); **IR** (neat) 3354, 1595 cm⁻¹; **MS** (EI) 300 (M⁺); **HRMS** Calcd for C₉H₁₄ClIO (M⁺) 299.9778; found 299.9773.

(Z)-5-(tert-butyldimethylsilyloxy)-3-chloro-2-iodopent-2-en-1-ol. Prepared from ester **4** (115 mg, 0.28 mmol) using a procedure similar to that described above for (Z)-3-chloro-2-iodobut-2-en-1-ol which gave the title compound as a colorless oil (51 mg, 51 %). **¹H NMR** (500 MHz, C₆D₆): δ 4.21 (d, *J* = 6.5 Hz, 2H), 3.37 (t, *J* = 5.5 Hz, 2H), 2.59 (t, *J* = 6.5 Hz, 1H), 2.30 (t, *J* = 5.5 Hz, 2H), 0.85 (s, 9H), -0.04 (s, 6H); **¹³C NMR** (125 MHz, C₆D₆): δ 130.0 (C), 103.2 (C), 69.2 (CH₂), 56.0 (CH₂), 38.8 (CH₂), 26.0 (CH₃ x 3), 18.4 (C), -5.5 (CH₃ x 2); **IR** (neat): 3360, 1471 cm⁻¹; **MS** (EI) 319 (M⁺ - *t*-Bu). **HRMS** calcd for C₇H₁₃ClIO₂Si (M⁺ - *t*-Bu) 318.9420; found 318.9413.

(Z)-3-Chloro-2-iodo-3-phenylprop-2-en-1-ol. Prepared from ester **5** (50 mg, 0.15 mmol) using a procedure similar to that described above for (Z)-3-chloro-2-iodobut-2-en-1-ol which gave the title compound as a colorless oil (19 mg, 45 %). $^1\text{H NMR}$ (400 MHz, C_6D_6): δ 7.20 (dd, $J = 8.4, 1.6$ Hz, 2H), 6.90-7.03 (m, 3H), 3.76 (d, $J = 6.8$ Hz, 2H), 1.27 (t, $J = 6.8$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, C_6D_6): δ 136.7 (C), 129.2 (C), 129.0 (CH), 129.0 (CH), 128.8 (CH), 67.2 (C), 63.5 (CH_2); **IR** (neat) 3356, 1444 cm^{-1} ; **MS** (EI) 294 (M^+).

General procedure for the reduction of polysubstituted- α,β -unsaturated esters:

(Z)-3-Chloro-2-(2-(4-fluorophenyl)ethynyl)but-2-en-1-ol. To a solution of (Z)-ethyl 3-chloro-2-(2-(4-fluorophenyl)ethynyl)but-2-enoate **10** (20 mg, 0.08 mmol) in CH_2Cl_2 (1.0 mL) was added diisobutylaluminum hydride (0.16 mL, 0.16 mmol, 2.2 eq, 1.0 M solution in hexanes). After 2 hours, and additional portion of diisobutylaluminum hydride (0.16 mL, 0.16 mmol, 2.2 eq) was introduced. The reaction was stirred for an additional 15 minutes, upon which time the reaction mixture was quenched via dropwise addition of a saturated solution of Rochelle's salt (~2 mL). Ether (~3 mL) was added, and the mixture was stirred until two clear layers were apparent. The layers were separated, the organic layer was dried over MgSO_4 , filtered, and concentrated. The product was purified by column chromatography on silica gel, eluting with 5% EtOAc in hexanes then 10% EtOAc in hexanes affording the title product (26 mg, 99%) as a clear, colourless oil. $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 7.06 (dd, $J = 5.5, 9.0$ Hz, 2H), 6.58 (dd, $J = 9.0, 9.0$ Hz, 2H), 4.25 (s, 2H), 2.12 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, C_6D_6) δ 163.9 (C), 161.9 (C), 138.8 (C), 133.6 (CH), 133.5 (CH), 121.3 (C), 115.9 (CH), 115.7 (CH), 95.2 (C), 85.8 (C), 62.2 (CH_2), 24.9 (CH_3); **IR** (neat) 3357, 1598 cm^{-1} ; **MS** (EI) 224 (M^+); **HRMS** calcd for $\text{C}_{12}\text{H}_{10}\text{ClFO}$ (M^+) 224.0404, found 224.0397.

(Z)-3-Phenyl-2-(2-(trimethylsilyl)ethynyl)but-2-en-1-ol (27). Prepared from compound **19** (123 mg, 0.43 mmol) using a procedure similar to that described above for (Z)-3-chloro-2-(2-(4-fluorophenyl)ethynyl)but-2-en-1-ol that provided the title product as a clear colorless oil (100 mg, 95 %). $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 6.99-7.05 (m, 5H), 4.03 (d, $J = 6.0$ Hz, 2H), 2.26 (s, 3H), 1.51 (t, $J = 6.0$ Hz, 1H), 0.23 (s, 9H); $^{13}\text{C NMR}$ (125 MHz, C_6D_6) δ 147.6 (C), 141.1 (C), 128.4 (CH), 127.9 (CH), 127.7 (CH), 120.9 (C), 105.3 (C), 100.0 (C), 62.4 (CH_2), 24.0 (CH_3), 0.2 (CH_3); **IR** (neat) 3399, 1492 cm^{-1} ; **MS** (EI) 244 (M^+); **HRMS** calcd for $\text{C}_{15}\text{H}_{20}\text{OSi}$ (M^+) 244.1283; found 244.1288.

(Z)-3-*p*-Tolyl-2-(2-(trimethylsilyl)ethynyl)but-2-en-1-ol. Prepared from compound **20** (30 mg, 0.11 mmol) using a procedure similar to that described above for (Z)-3-chloro-2-(2-(4-fluorophenyl)ethynyl)but-2-en-1-ol that provided the title product as a clear colorless oil (29 mg, 99%). ¹H NMR (500 MHz, C₆D₆) δ 6.98 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.10 (s, 2H), 2.29 (s, 3H), 2.05 (s, 3H), 0.24 (s, 9H); ¹³C NMR (125 MHz, C₆D₆) δ 147.8 (C), 138.2 (C), 137.4 (C), 129.1 (CH), 127.9 (CH), 120.6 (C), 105.5 (C), 99.9 (C), 62.5 (CH₂), 24.1 (CH₃), 21.0 (CH₃), 0.2 (CH₃); IR (neat) 3399, 2140, 1513 cm⁻¹; MS (EI) 258 (M⁺); HRMS calcd for C₁₆H₂₂OSi (M⁺) 258.1440, found 258.1430.

(2Z,4E)-3-Methyl-5-phenyl-2-(2-(trimethylsilyl)ethynyl)penta-2,4-dien-1-ol. Prepared from compound **22** (50 mg, 0.16 mmol) using a procedure similar to that described above for (Z)-3-chloro-2-(2-(4-fluorophenyl)ethynyl)but-2-en-1-ol that provided the title product as a clear, colorless oil (37 mg, 86 %). ¹H NMR (400 MHz, C₆D₆) δ 7.26 (d, *J* = 14.8, 1H), 7.23 (d, *J* = 6.0 Hz, 1H), 7.03-7.11 (m, 4H), 6.58 (d, *J* = 16 Hz, 1H), 4.29 (s, 2H), 2.21 (s, 3H), 0.23 (s, 9H); ¹³C NMR (100 MHz, C₆D₆) δ 142.6 (C), 137.5 (D), 132.3 (CH), 128.9 (CH), 127.2 (CH), 125.7 (CH), 122.4 (C), 106.5 (C), 102.7 (C), 61.0 (CH₂), 19.0 (CH₃), 0.1 (CH₃); IR (neat) 3366, 2129, 1492, 1447 cm⁻¹; MS (EI) 270 (M⁺); HRMS calcd for C₁₇H₂₂OSi (M⁺) 270.1440, found 270.1431.

(E)-3-Phenyl-2-(2-(trimethylsilyl)ethynyl)but-2-en-1-ol (28**).** A solution of ester **19** (60 mg, 0.21 mmol) in dichloromethane (2.0 mL) was exposed to UV light (350 nm). After one hour, the solution was reduced using a procedure similar to that described above for (Z)-3-chloro-2-(2-(4-fluorophenyl)ethynyl)but-2-en-1-ol that provided the title product as a clear, colorless oil (16 mg, 31 %). ¹H NMR (400 MHz, C₆D₆) δ 7.43 (d, *J* = 7.0 Hz, 2H), 7.09-7.72 (m, 3H), 4.23 (d, *J* = 6.5 Hz, 2H), 1.76 (s, 3H), 0.88 (t, *J* = 6.5 Hz, 1H), 0.06 (s, 9H); ¹³C NMR (100 MHz, C₆D₆) δ 146.4 (C), 143.1 (C), 128.4 (CH), 127.9 (CH), 127.7 (CH), 120.2 (C), 105.7 (C), 97.9 (C), 62.0 (CH₂), 19.6 (CH₃), -0.2 (CH₃); IR (neat) 3373, 2134, 1248 cm⁻¹; MS (EI) 244 (M⁺); HRMS calcd for C₁₅H₂₀OSi (M⁺) 244.1283, found 244.1275.

(2*E*,4*E*)-3-Methyl-5-phenyl-2-(2-(trimethylsilyl)ethynyl)penta-2,4-dien-1-ol. A solution of ester **22** (70 mg, 0.22 mmol) in dichloromethane (2.0 mL) was exposed to UV light (350 nm). After one hour, the solution was reduced using a procedure similar to that described above for (Z)-3-chloro-2-(2-(4-fluorophenyl)ethynyl)but-2-en-1-ol that provided the title product as a white solid (15 mg, 25 %). **MP** 75-76 °C; **¹H NMR** (500 MHz, C₆D₆) δ 8.03 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.13-7.16 (m, 2H), 7.03 (m, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 4.14 (d, *J* = 6.0 Hz, 2H), 1.65 (s, 3H), 1.38 (t, *J* = 6.0 Hz, 1H), 0.23 (s, 9H); **¹³C NMR** (125 MHz, C₆D₆) δ 142.9 (C), 137.9 (C), 131.5 (CH), 130.5 (CH), 129.0 (CH), 127.9 (CH), 122.8 (C), 104.9 (C), 61.8 (CH₂), 13.4 (CH₃), 0.1 (CH₃); **IR** (neat) 3327, 2132, 1732 cm⁻¹; **MS** (EI) 255 (M⁺-Me); **HRMS** calcd for C₁₆H₁₉OSi (M⁺ - Me) 255.1205, found 255.1142.

Table 1. Proof of stereochemistry *via* nOe analysis of alcohols

Original Isomer

6.996

3.794

98.0

3.00

ppm (t1)

S16

4.312
4.289
4.265
4.241

2.432

1.343
1.319
1.296

S18

3

4.019
4.001
3.983
3.965

2.970
2.961
2.953
2.941
2.933
2.924
2.913
2.904
2.895

2.00

0.94

4.00

3.50

3.00

ppm (f1)

S21

1.077
1.054
1.044
1.035
1.021
1.012
1.003
0.980
0.942
0.924
0.907
0.863

1.498
1.490
1.483
1.480
1.475
1.472
1.458
1.450
1.411
1.403
1.398
1.394
1.390
1.382
1.372
1.363
1.352
1.344
1.320

S22

165.062

141.967

79.710

62.188

48.324

29.788

25.683

25.562

13.774

ppm (f1)

150

100 **S23**

50

7.150
7.068
7.049
6.932
6.914
6.908
6.902
6.895

4.044
4.026
4.020
4.002

0.976
0.958
0.940
0.403

17.04

2.00

3.23
1.12

129.628

99.400

77.252

76.997

76.743

67.598

30.586

8

7.150

3.722

1.615

2.00

3.64

1.11

ppm (t1)

S30

8

138.430

103.682

67.615

21.914

S31

150

100

50

ppm (t1)

7.481
 7.476
 7.471
 7.468
 7.466
 7.461
 7.353
 7.349
 7.343
 7.339

4.346
 4.332
 4.318
 4.304

2.518

1.386
 1.372
 1.357

2.00
 2.00

2.00

96.2

3.11

S32

ppm (t1)

163.507
 146.577
 131.391
 128.768
 128.338
 122.456
 115.279
 96.762
 83.047
 77.254
 76.999
 76.745
 61.717
 26.162
 14.040

2.045
1.864

0.957
0.934
0.910

0.167
0.113
0.101
0.089

S36

S38

S44

S47

18

7.549
7.543
7.540
7.533
7.530
7.150
6.935
6.932

4.072
4.058
4.044
4.030

2.242

0.995
0.981
0.967

0.187

ppm (f1)

S48

19

7.364
7.358
7.350
7.345
7.334
7.331
7.328
7.323
7.314
7.309
7.300
7.292
7.187
7.178
7.172
7.168
7.161
7.155
4.020
3.996
3.972
3.949
2.389
1.000
0.976
0.953
0.257

7.150
7.040
7.013
6.871
6.844

3.839
3.816
3.792
3.768

2.264
2.021

0.722
0.698
0.674
0.213

ppm (f1)

S56

7.798
7.794
7.791
7.759
7.755
7.751

5.962
5.945
5.927
5.923
5.905
5.888

4.042
4.024
4.006
3.988

2.198
2.019
2.016
2.001
1.998
1.982
1.965
1.263
1.246
1.230
1.216
1.163
1.155
1.153
1.147
1.136
1.002
0.984
0.966
0.880
0.863
0.845
0.230

1.00

1.04

2.16

3.07
2.14

11.02

7.74

9.84

S60

7.183
7.179
7.054
7.049
7.032
7.014
7.000
6.982

3.759
3.741
3.723
3.705
3.691
3.673
3.656
3.109
3.091
3.074

0.961
0.636
0.618
0.600
0.229
0.015

ppm (t1)

S61

165.565
 155.806
 140.483
 128.241
 128.121
 128.000
 127.880
 127.759
 117.940
 101.577
 101.393
 60.891
 60.852
 41.011
 26.071
 18.369
 13.543
 -0.070
 -5.240

7.150
7.046
7.043
7.032
7.031
7.027
7.023
7.012
7.010
6.995

4.036
4.025

2.255

1.520
1.507
1.495

0.231

5.07

2.00

2.92

0.97

8.87

ppm (t1)

S63

7.433
7.419
7.416
7.166
7.150

4.147
4.135

1.761

0.893
0.879
0.865

0.057

28

146.448
143.108

128.748

128.366

127.910

120.233

105.724

97.856

62.024

19.558

-0.196

ppm (f1)

150

100

S66

50

0