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SUPPLEMENTARY MATERIALS

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**A Highly Stereoselective Saucy-Marbet Rearrangement Using
Chiral Ynamides. Synthesis of
Highly Substituted Chiral Homoallenyl Alcohols.**

authored by

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General procedure for propargyl alcohol addition / Saucy-Marbet rearrangement:

Ynamide (0.2 mmol), anhy *p*-nitrobenzenesulfonic acid (0.2 equiv), propargyl alcohol (1-2 equiv), and anhydrous toluene (4 mL) were combined in a flame-dried 25 mL sealed tube under nitrogen atmosphere. The tube was sealed and the reaction mixture was heated at 100 °C for 24-48 h. The reaction was followed with TLC and/or LCMS analysis. Once completed by TLC analysis, the reaction was cooled to room temperature, filtered through celite, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (gradient: 0% to 25% EtOAc in hexanes) to provide the rearranged products in yields indicated in the text.

General procedure for reductive removal of chiral auxiliary

Allene (0.1 mmol), LiBH₄ (3 equiv), and anhy THF (10 mL) were combined in a flame-dried RB-flask. The reaction mixture was allowed to stir overnight at rt. The reaction was quenched with H₂O (10 mL) extracted with ether (3 x 5 mL), dried over Na₂SO₄, and concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (gradient: 0% to 25% EtOAc in hexanes) to provide homo allenyl alcohols in yields as indicated in the text.

Allene 9

R_f = 0.38 [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23}$ – 68.2 (c 0.51, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 1.62 (dd, 3 H, *J* = 3.0, 7.0 Hz), 3.66 (ddq, 2 H, *J* = 2.5, 7.0, 18.0 Hz), 4.31 (dd, 1 H, *J* = 3.5, 9.0 Hz), 4.71 (t, 1 H, *J* = 9.0 Hz), 5.09-5.16 (m, 1 H), 5.21 (dddd, 1 H, *J* = 2.5, 3.0, 7.0, 7.0), 5.44 (dd, 1 H, *J* = 3.5, 9.0 Hz), 7.27-7.47 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 36.1, 57.5, 70.0, 82.5, 86.7, 125.9, 128.6, 129.0, 138.7, 153.2, 170.4, 205.9; IR (thin film) cm⁻¹ 2970 (m), 2961 (m), 2925 (m), 2870 (w), 1776 (s), 1705 (s); mass spectrum (APCI): *m/e* (% relative intensity) 258 (23) (M + H)⁺, 164 (28), 146 (26), 120 (100), 95 (92), 87 (21).

Allene 10

R_f = 0.38 [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23}$ – 51.6 (c 0.60, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 1.62 (dd, 3 H, *J* = 3.0, 7.0 Hz), 3.66 (ddq, 2 H, *J* = 2.5, 7.0, 18.0 Hz), 4.31 (dd, 1 H, *J* = 3.5, 9.0 Hz), 4.71 (t, 1 H, *J* = 9.0 Hz), 5.09-5.16 (m, 1 H), 5.21 (dddd, 1 H, *J* = 2.5, 3.0, 7.0, 7.0), 5.44 (dd, 1 H, *J* = 3.5, 9.0 Hz), 7.27-7.47 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 36.1, 57.5, 70.0, 82.5, 86.7, 125.9, 128.6, 129.0, 138.7, 153.2, 170.4, 205.9; IR (thin film) cm⁻¹ 2970 (m), 2961 (m), 2925 (m), 2870 (w), 1776 (s), 1705 (s); mass spectrum (APCI): *m/e* (% relative intensity) 258 (23) (M + H)⁺, 164 (28), 146 (26), 120 (100), 95 (92), 87 (21).

Allene 12

R_f = 0.42 [25% EtOAc in hexanes]; mp = 92-94 °C; $[\alpha]_D^{23}$ – 122.0 (c 0.91, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 0.86-0.89 (m, 3 H), 1.25-1.32 (m, 4 H), 1.49-1.56 (m, 1 H), 1.70 (dd, 3 H, *J* = 3.0, 7.0 Hz), 1.71-1.77 (m, 1 H), 4.23 (dq, 1 H, *J* = 1.0, 7.5 Hz), 4.41 (dd, 1 H, *J* = 3.0, 9.0 Hz), 4.44 (t, 1 H, *J* = 9.0 Hz), 4.72 (d, 1 H, *J* = 5.5 Hz), 5.05 (ddt, 1 H, *J* = 3.5, 7.5, 11.5 Hz), 5.22 (ddq, 1 H, *J* = 2.0, 7.5, 7.5 Hz), 5.34 (ddd, 1 H, *J* = 3.5, 5.5, 8.5 Hz), 7.10-7.15 (m, 4 H), 7.25-7.33 (m, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 14.2, 29.1, 31.0, 43.3, 50.4, 56.2, 64.5, 87.3, 89.0, 126.9, 127.7, 128.2, 128.6, 128.7, 129.4, 137.8, 139.4, 152.8, 174.1, 205.4 (missing 1 signal due to overlap of the terminal allene carbons); IR (thin film) cm⁻¹ 2956 (m), 2922 (m), 2854 (w), 1781 (s), 1691 (s); mass spectrum (APCI): *m/e* (% relative intensity) 404 (75) (M + H)⁺, 378 (21), 360 (20), 254 (33), 193 (18), 151 (100).

Allene 13

R_f = 0.42 [25% EtOAc in hexanes]; clear oil; ¹H NMR (500 MHz, CDCl₃) Major isomer: δ 0.86-0.89 (m, 3 H), 1.24-1.32 (m, 4 H), 1.51-1.59 (m, 1 H), 1.70 (dd, 3 H, *J* = 3.0, 7.0 Hz), 1.71-1.78 (m, 1 H), 4.15 (dq, 1 H, *J* = 1.0, 7.5 Hz), 4.36-4.46 (m, 2 H), 4.74 (d, 1 H, *J* = 5.0 Hz), 5.08-5.14 (m, 1 H), 5.20 (ddq, 1 H, *J* = 2.0, 7.5, 7.5 Hz), 5.30-5.34 (m, 1 H), 7.10-7.15 (m, 4 H), 7.25-7.33 (m, 6 H); Minor isomer: δ 0.86-0.89 (m, 3 H), 1.24-1.32 (m, 4 H), 1.51-1.59 (m, 1 H), 1.63 (dd, 3 H, *J* = 3.0, 7.0 Hz), 1.71-1.78 (m, 1 H), 4.10 (dq, 1 H, *J* = 1.0, 7.5 Hz),

4.36-4.46 (m, 2 H), 4.69 (d, 1 H, $J = 5.0$ Hz), 5.08-5.14 (m, 1 H), 5.20 (ddq, 1 H, $J = 2.0, 7.5, 7.5$ Hz), 5.30-5.34 (m, 1 H), 7.10-7.15 (m, 4 H), 7.25-7.33 (m, 6 H); IR (thin film) cm^{-1} 2956 (m), 2922 (m), 2854 (w), 1781 (s), 1691 (s); mass spectrum (APCI): m/e (% relative intensity) 404 (75) ($M + H$)⁺, 378 (21), 360 (20), 254 (33), 193 (18), 151 (100).

Allene 21

$R_f = 0.41$ [25% EtOAc in hexanes]; mp = 74-75°C; $[\alpha]_D^{23} - 16.7$ (c 1.26, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.89 (m, 3 H), 1.25-1.27 (m, 4 H), 1.51 (dd, 3 H, $J = 3.5, 7.0$ Hz), 1.53-1.57 (m, 1 H), 1.73-1.80 (m, 1 H), 4.26 (dd, 1 H, $J = 4.5, 9.0$ Hz), 4.26-4.30 (m, 1 H), 4.69 (t, 1 H, $J = 9.0$ Hz), 5.11-5.17 (m, 2 H), 5.45 (dd, 1 H, $J = 4.5, 9.0$ Hz), 7.29-7.39 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.4, 29.2, 30.9, 43.2, 57.7, 69.7, 87.7, 88.6, 125.8, 128.5, 129.0, 138.8, 153.1, 173.4, 205.3 (missing 1 signal due to overlap of the terminal allene carbons); IR (thin film) cm^{-1} 2960 (m), 2927 (m), 2859 (w), 1780 (s), 1704 (s); mass spectrum (APCI): m/e (% relative intensity) 314 (33) ($M + H$)⁺, 270 (15), 164 (20), 151 (100), 123 (36), 120 (46).

Allene *ent*-21

$R_f = 0.41$ [25% EtOAc in hexanes]; mp = 74-75°C; $[\alpha]_D^{23} + 16.7$ (c 0.24, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.89 (m, 3 H), 1.25-1.27 (m, 4 H), 1.51 (dd, 3 H, $J = 3.5, 7.0$ Hz), 1.53-1.57 (m, 1 H), 1.73-1.80 (m, 1 H), 4.26 (dd, 1 H, $J = 4.5, 9.0$ Hz), 4.26-4.30 (m, 1 H), 4.69 (t, 1 H, $J = 9.0$ Hz), 5.11-5.17 (m, 2 H), 5.45 (dd, 1 H, $J = 4.5, 9.0$ Hz), 7.29-7.39 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.4, 29.2, 30.9, 43.2, 57.7, 69.7, 87.7, 88.6, 125.8, 128.5, 129.0, 138.8, 153.1, 173.4, 205.3 (missing 1 signal due to overlap of the terminal allene carbons); IR (thin film) cm^{-1} 2960 (m), 2927 (m), 2859 (w), 1780 (s), 1704 (s); mass spectrum (APCI): m/e (% relative intensity) 314 (33) ($M + H$)⁺, 270 (15), 164 (20), 151 (100), 123 (36), 120 (46).

Allene 22

$R_f = 0.39$ [25% EtOAc in hexanes]; mp = 50-51°C; $[\alpha]_D^{23} - 18.4$ (c 0.38, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3 H, $J = 7.0$ Hz), 0.90 (t, 3 H, $J = 7.0$ Hz), 1.22-1.25 (m, 4 H), 1.26-1.36 (m, 6 H), 1.52-1.56 (m, 1 H), 1.74-1.79 (m, 1 H), 1.84-1.89 (m, 2 H), 4.25 (dd, 1 H, $J = 4.0, 9.0$ Hz), 4.29 (dq, 1 H, $J = 2.5, 8.0$ Hz), 4.69 (t, 1 H, $J = 9.0$ Hz), 5.14-5.19 (m, 2 H), 5.45 (dd, 1 H, $J = 4.0, 9.0$ Hz), 7.14-7.39 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 13.9, 22.3, 22.4, 28.4, 28.6, 29.2, 30.8, 31.1, 43.3, 57.6, 69.6, 89.1, 93.1, 125.7, 128.4, 128.9, 138.7, 153.1, 173.4, 204.5; IR (thin film) cm^{-1} 2965 (m), 2930 (m), 2925 (m), 2860 (w), 1777 (s), 1702 (s); mass spectrum (APCI): m/e (% relative intensity) 370 (40) ($M + H$)⁺, 326 (7), 207 (100), 164 (6), 120 (12).

Allene *ent*-22

$R_f = 0.39$ [25% EtOAc in hexanes]; mp = 52-53°C; $[\alpha]_D^{23} + 13.0$ (c 0.40, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3 H, $J = 7.0$ Hz), 0.90 (t, 3 H, $J = 7.0$ Hz), 1.22-1.25 (m, 4 H), 1.26-1.36 (m, 6 H), 1.52-1.56 (m, 1 H), 1.74-1.79 (m, 1 H), 1.84-1.89 (m, 2 H), 4.25 (dd, 1 H, $J = 4.0, 9.0$ Hz), 4.29 (dq, 1 H, $J = 2.5, 8.0$ Hz), 4.69 (t, 1 H, $J = 9.0$ Hz), 5.14-5.19 (m, 2 H), 5.45 (dd, 1 H, $J = 4.0, 9.0$ Hz), 7.14-7.39 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 13.9, 22.3, 22.4, 28.4, 28.6, 29.2, 30.8, 31.1, 43.3, 57.6, 69.6, 89.1, 93.1, 125.7, 128.4, 128.9, 138.7, 153.1, 173.4, 204.5; IR (thin film) cm^{-1} 2965 (m), 2930 (m), 2925 (m), 2860 (w), 1777 (s), 1702 (s); mass spectrum (APCI): m/e (% relative intensity) 370 (40) ($M + H$)⁺, 326 (7), 207 (100), 164 (6), 120 (12).

Allene 23

$R_f = 0.43$ [25% EtOAc in hexanes]; mp = 95-97°C; $[\alpha]_D^{23} - 8.7$ (c 0.60, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.86-1.02 (m, 5 H), 1.06-1.20 (m, 2 H), 1.24-1.36 (m, 4 H), 1.49-1.63 (m, 6 H), 1.70-1.88 (m, 3 H), 4.25 (dd, 1 H, $J = 4.0, 9.0$ Hz), 4.27 (dq, 1 H, $J = 2.0, 6.5$ Hz), 4.69 (t, 1 H, $J = 9.0$ Hz), 5.20 (dt, 1 H, $J = 4.0, 6.0$ Hz), 5.23 (dt, 1 H, $J = 4.0, 6.0$ Hz), 5.45 (dd, 1 H, $J = 4.0, 9.0$ Hz), 7.26-7.40 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 22.6, 26.0, 26.1, 29.4, 30.5, 32.8, 32.9, 37.0, 37.2, 43.2, 57.7, 69.8, 90.0, 99.5, 125.9, 128.6, 129.1, 138.9, 153.4, 173.5, 203.7; IR (thin film) cm^{-1} 2924 (m), 2859 (w), 1785 (s), 1707 (s), 1457 (m), 1379 (m); mass spectrum (APCI): m/e (% relative intensity) 382 (66) ($M + H$)⁺, 219 (100), 191 (6), 164 (8), 120 (9).

Allene 24

$R_f = 0.38$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} + 55.6$ (c 0.63, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.84-1.40 (m, 6 H), 1.54 (dd, 3 H, $J = 3.0, 7.0$ Hz), 1.64-1.76 (m, 4 H), 1.86 (d, 1 H, $J = 7.0$ Hz), 4.24 (dd, 1 H, $J = 4.0, 8.5$ Hz), 4.25 (t, 1 H, $J = 9.0$ Hz), 4.68 (t, 1 H, $J = 8.5$ Hz), 4.97 (septet, 1 H, $J = 3.0$ Hz), 5.09 (quintet, 1 H, $J = 7.0$ Hz), 5.45 (dd, 1 H, $J = 4.0, 9.0$ Hz), 7.27-7.39 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 26.0, 26.2, 29.5, 31.2, 38.3, 39.7, 49.5, 57.6, 69.5, 86.6, 87.4, 125.7, 128.4, 128.9, 138.8, 153.1, 173.2, 205.8; IR (thin film) cm^{-1} 2924 (m), 2854 (w), 1783 (s), 1700 (m), 1386 (m); mass spectrum (APCI): m/e (% relative intensity) 340 (48) ($\text{M} + \text{H}$) $^+$, 177 (100), 164 (14), 149 (87), 87 (62).

Allene 25

$R_f = 0.27$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} - 88.7$ (c 0.37, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 1.23 (d, 3 H, $J = 7.0$ Hz), 1.52 (dd, 3 H, $J = 3.0, 7.0$ Hz), 4.27 (dd, 1 H, $J = 4.5, 9.0$ Hz), 4.33 (ddt, 1 H, $J = 2.5, 7.0, 7.0$ Hz), 4.70 (t, 1 H, $J = 9.0$ Hz), 5.17 (ddt, 1 H, $J = 2.5, 7.0, 7.0$ Hz), 5.29 (ddd, 1 H, $J = 3.0, 7.0, 7.0$ Hz), 5.45 (dd, 1 H, $J = 4.5, 9.0$ Hz), 7.32-7.34 (m, 3 H), 7.35-7.40 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 15.9, 37.4, 57.6, 69.7, 88.5, 89.9, 125.8, 128.5, 128.9, 129.0, 153.1, 173.7, 204.7; IR (thin film) cm^{-1} 2955 (m), 2940 (m), 2870 (w), 1776 (s), 1703 (s); mass spectrum (APCI): m/e (% relative intensity) 272 (15) ($\text{M} + \text{H}$) $^+$, 228 (14), 164 (19), 120 (54), 109 (100).

Allene 26

$R_f = 0.24$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} + 7.1$ (c 0.34, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 1.31 (d, 3 H, $J = 7.0$ Hz), 4.26 (dd, 1 H, $J = 4.5, 9.0$ Hz), 4.51 (ddt, 1 H, $J = 3.0, 7.0, 7.0$ Hz), 4.71 (t, 1 H, $J = 9.0$ Hz), 5.46 (dd, 1 H, $J = 4.5, 9.0$ Hz), 5.83 (t, 1 H, $J = 7.0$ Hz), 6.22 (dd, 1 H, $J = 3.0, 7.0$ Hz), 7.12-7.40 (m, 10 H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.8, 37.8, 57.8, 69.8, 94.8, 97.4, 125.8, 126.7, 126.9, 128.4, 128.5, 129.0, 133.7, 138.5, 153.4, 173.2, 203.2; IR (thin film) cm^{-1} 2963 (m), 2935 (m), 2866 (w), 1781 (s), 1706 (s), 1391 (m); mass spectrum (APCI): m/e (% relative intensity) 334 (13) ($\text{M} + \text{H}$) $^+$, 261 (54), 247 (38), 229 (43), 171 (100), 147 (36), 115 (35).

Allene 27

$R_f = 0.41$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} - 30.9$ (c 0.59, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, 3 H, $J = 7.0$ Hz), 1.28-1.39 (m, 8 H), 1.58-1.62 (m, 1 H), 1.68 (dd, 3 H, $J = 3.0, 7.0$ Hz), 1.79-1.83 (m, 1 H), 2.73 (dd, 1 H, $J = 10.0, 13.5$ Hz), 3.30 (dd, 1 H, $J = 3.5, 13.5$ Hz), 4.16 (dd, 1 H, $J = 3.0, 7.0$ Hz), 4.20 (t, 1 H, $J = 9.0$ Hz), 4.27 (dq, 1 H, $J = 2.0, 7.0$ Hz), 4.66-4.71 (m, 1 H), 5.22 (dq, 1 H, $J = 2.0, 7.0$ Hz), 5.28-5.32 (m, 1 H), 7.22-7.35 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 14.2, 22.5, 27.0, 29.0, 31.6, 31.7, 37.6, 43.3, 55.2, 65.8, 87.7, 89.2, 127.1, 128.8, 129.3, 135.2, 152.7, 174.0, 204.9; IR (thin film) cm^{-1} 2952 (m), 2930 (m), 2865 (w), 1786 (s), 1706 (s), 1460 (m); mass spectrum (APCI): m/e (% relative intensity) 356 (43) ($\text{M} + \text{H}$) $^+$, 330 (25), 312 (12), 179 (100), 117 (22).

Allene 28

$R_f = 0.42$ [25% EtOAc in hexanes]; mp = 152-154°C; $[\alpha]_D^{23} + 27.2$ (c 0.34, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, 3 H, $J = 7.0$ Hz), 1.25-1.36 (m, 4 H), 1.61-1.68 (m, 1 H), 1.77-1.84 (m, 1 H), 4.38-4.44 (m, 2 H), 4.45 (t, 1 H, $J = 9.0$ Hz), 4.77 (d, 1 H, $J = 6.0$ Hz), 5.38 (ddd, 1 H, $J = 3.5, 6.0, 7.5$ Hz), 5.48 (dd, 1 H, $J = 7.0, 8.0$ Hz), 6.28 (dd, 1 H, $J = 2.0, 6.5$), 7.14-7.35 (m, 15 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.4, 29.4, 31.0, 43.5, 50.7, 56.3, 64.7, 93.7, 96.3, 126.5, 126.8, 127.0, 127.8, 128.3, 128.5, 128.6, 128.8, 129.3, 134.1, 137.8, 139.4, 152.8, 173.7, 205.8; IR (thin film) cm^{-1} 3031 (w), 2957 (m), 2930 (m), 2870 (w), 1784 (s), 1700 (s); mass spectrum (APCI): m/e (% relative intensity) 466 (71) ($\text{M} + \text{H}$) $^+$, 276 (8), 254 (22), 213 (100), 193 (13).

Allene 30

$R_f = 0.71$ (40% EtOAc in hexanes); oil; $[\alpha]_D^{23} - 36.7$ (c 0.22, EtOH); ^1H NMR (500 MHz, CDCl_3) major/minor mostly overlapped δ 0.88 (t, $J = 6.5$ Hz, 3H), 0.91 (s, 3H), 1.02 (s, 3H), 1.26-1.36 (m, 4H), 1.45 (s, 3H), 1.47 (s, 1H), 1.64 (m, 1H), 1.63 (dd, $J = 3.3, 6.8$ Hz, 3H) 1.72-1.85 (m, 2H), 1.96-2.10 (m, 2H), 2.36 (d, $J = 4.0$ Hz,

1H), 4.17 (m, 1H), 5.10-5.20 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) major only δ 13.1, 13.5, 13.9, 14.2, 14.3, 17.5, 18.5, 22.5, 23.6, 29.1, 30.3, 32.0, 46.4, 55.3, 87.1, 90.0, 176.0, 177.7, 205.0; IR (thin film) cm^{-1} 2957m, 2927m, 1743s, 1699s; mass spectrum [EI]; m/e (%relative intensity) 303 (1) M^+ , 246 (43), 220 (47), 166 (56), 136 (45), 110 (100).

Allene 31

$R_f = 0.71$ (40% EtOAc in hexanes); oil; $[\alpha]_D^{23} -89.4$ (c 0.26, EtOH); ^1H NMR (300 MHz, CDCl_3) major/minor mostly overlapped δ 0.89 (t, $J = 3.3$ Hz, 3H), 0.91 (s, 3H), 1.02 (s, 3H), 1.27-1.42 (m, 4H), 1.44 (s, 3H), 1.48 (s, 1H), 1.62-1.66 (m, 4H), 1.72-1.87 (m, 2H), 1.94-2.10 (m, 2H), 2.36 (d, $J = 4.2$ Hz, 1H), 4.18 (m, 1H), 5.12-5.15 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) major/minor δ 13.5, 13.7, 13.8, 14.2, 14.5, 14.6, 17.8, 17.9, 18.9, 19.4, 22.7, 23.9, 24.0, 24.5, 26.1, 29.4, 29.5, 30.6, 32.3, 32.4, 32.8, 39.1, 46.7, 47.7, 55.5, 55.6, 73.3, 87.1, 87.4, 89.1, 90.4, 112.5, 176.4, 178.1, 205.4; IR (thin film) cm^{-1} 2960m, 2932m, 1743s, 1699s; mass spectrum [EI]: m/e (%relative intensity) 303 (1) M^+ , 246 (60), 220 (60), 166 (62), 136 (50), 110 (100).

Allene 32

$R_f = 0.25$ [25% EtOAc in hexanes]; mp = 84-86°C; $[\alpha]_D^{23} + 98.7$ (c 0.46, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, 3 H, $J = 7.0$ Hz), 1.29-1.40 (m, 4 H), 1.61-1.64 (m, 1 H), 1.83-1.85 (m, 1 H), 4.25 (dd, 1 H, $J = 4.0$, 9.0 Hz), 4.45 (dq, 1 H, $J = 2.0$, 7.0 Hz), 4.70 (t, 1 H, $J = 9.0$ Hz), 5.45 (dd, 1 H, $J = 4.0$, 9.0 Hz), 5.70 (t, 1 H, $J = 7.0$ Hz), 6.19 (dd, 1 H, $J = 2.0$, 7.0 Hz), 7.13-7.32 (m, 10 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 22.6, 29.6, 30.8, 43.5, 57.9, 69.9, 93.7, 97.0, 126.0, 126.7, 126.9, 128.6, 128.7, 129.1, 134.0, 140.2, 153.4, 173.2, 205.6; IR (thin film) cm^{-1} 2964 (m), 2933 (m), 2865 (w), 1781 (s), 1707 (m), 1385 (m); mass spectrum (APCI): m/e (% relative intensity) 376 (20) ($\text{M} + \text{H}^+$), 332 (8), 213 (100), 185 (16), 120 (7).

Allene 33

$R_f = 0.25$ [25% EtOAc in hexanes]; mp = 95-97°C; $[\alpha]_D^{23} - 150.8$ (c 0.39, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, 3 H, $J = 7.0$ Hz), 1.26-1.40 (m, 4 H), 1.58-1.65 (m, 1 H), 1.83-1.89 (m, 1 H), 4.29 (dd, 1 H, $J = 4.0$, 9.0 Hz), 4.42 (dq, 1 H, $J = 2.0$, 7.0 Hz), 4.70 (t, 1 H, $J = 9.0$ Hz), 5.47 (dd, 1 H, $J = 4.0$, 8.5 Hz), 5.73 (t, 1 H, $J = 7.0$ Hz), 6.00 (dd, 1 H, $J = 2.0$, 7.0 Hz), 7.15-7.56 (m, 10 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 22.6, 29.5, 31.3, 43.5, 57.7, 69.8, 93.6, 96.8, 126.0, 126.6, 126.8, 128.6, 128.7, 129.2, 133.8, 138.8, 153.3, 172.8, 205.5; IR (thin film) cm^{-1} 2964 (m), 2933 (m), 2865 (w), 1781 (s), 1707 (m), 1385 (m); mass spectrum (APCI): m/e (% relative intensity) 376 (20) ($\text{M} + \text{H}^+$), 332 (8), 213 (100), 185 (16), 120 (7).

Allene 34

$R_f = 0.25$ [25% EtOAc in hexanes]; mp = 86-87°C; $[\alpha]_D^{23} - 99.1$ (c 0.54, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, 3 H, $J = 7.0$ Hz), 1.29-1.40 (m, 4 H), 1.61-1.64 (m, 1 H), 1.83-1.85 (m, 1 H), 4.25 (dd, 1 H, $J = 4.0$, 9.0 Hz), 4.45 (dq, 1 H, $J = 2.0$, 7.0 Hz), 4.70 (t, 1 H, $J = 9.0$ Hz), 5.45 (dd, 1 H, $J = 4.0$, 9.0 Hz), 5.70 (t, 1 H, $J = 7.0$ Hz), 6.19 (dd, 1 H, $J = 2.0$, 7.0 Hz), 7.13-7.32 (m, 10 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 22.6, 29.6, 30.8, 43.5, 57.9, 69.9, 93.7, 97.0, 126.0, 126.7, 126.9, 128.6, 128.7, 129.1, 134.0, 140.2, 153.4, 173.2, 205.6; IR (thin film) cm^{-1} 2964 (m), 2933 (m), 2865 (w), 1781 (s), 1707 (m), 1385 (m); mass spectrum (APCI): m/e (% relative intensity) 376 (20) ($\text{M} + \text{H}^+$), 332 (8), 213 (100), 185 (16), 120 (7).

Allene 35

$R_f = 0.25$ [25% EtOAc in hexanes]; mp = 81-83°C; $[\alpha]_D^{23} + 126.5$ (c 0.80, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, 3 H, $J = 7.0$ Hz), 1.26-1.40 (m, 4 H), 1.58-1.65 (m, 1 H), 1.83-1.89 (m, 1 H), 4.29 (dd, 1 H, $J = 4.0$, 9.0 Hz), 4.42 (dq, 1 H, $J = 2.0$, 7.0 Hz), 4.70 (t, 1 H, $J = 9.0$ Hz), 5.47 (dd, 1 H, $J = 4.0$, 8.5 Hz), 5.73 (t, 1 H, $J = 7.0$ Hz), 6.00 (dd, 1 H, $J = 2.0$, 7.0 Hz), 7.15-7.56 (m, 10 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 22.6, 29.5, 31.3, 43.5, 57.7, 69.8, 93.6, 96.8, 126.0, 126.6, 126.8, 128.6, 128.7, 129.2, 133.8, 138.8, 153.3, 172.8, 205.5; IR (thin film) cm^{-1} 2964 (m), 2933 (m), 2865 (w), 1781 (s), 1707 (m), 1385 (m); mass spectrum (APCI): m/e (% relative intensity) 376 (20) ($\text{M} + \text{H}^+$), 332 (8), 213 (100), 185 (16), 120 (7).

Allene 38

$R_f = 0.50$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} - 94.0$ (c 0.90, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.86 (t, 3 H, $J = 7.0$ Hz), 0.92 (t, 3 H, $J = 7.0$ Hz), 1.24-1.28 (m, 2 H), 1.32-1.42 (m, 6 H), 1.52-1.55 (m, 2 H), 1.71-1.92 (m, 4 H), 4.18 (dd, 1 H, $J = 4.5, 9.0$ Hz), 4.65 (t, 1 H, $J = 9.0$ Hz), 5.05 (dt, 1 H, $J = 2.0, 7.0$ Hz), 5.44 (dd, 1 H, $J = 4.5, 9.0$ Hz), 5.53 (dt, 1 H, $J = 2.0, 7.0$), 7.18-7.45 (m, 10 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.3, 22.6, 28.4, 29.0, 29.8, 31.3, 31.6, 43.5, 57.8, 65.5, 69.5, 90.1, 96.5, 125.7, 126.3, 128.1, 128.2, 128.8, 131.5, 136.5, 138.4, 153.4, 173.3, 204.5; IR (thin film) cm^{-1} 2960 (m), 2932 (m), 2862 (w), 1784 (s), 1702 (s); mass spectrum (APCI): m/e (% relative intensity) 446 (8) ($\text{M} + \text{H}$) $^+$, 284 (22), 283 (100).

Allene 39

$R_f = 0.48$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} - 47.5$ (c 0.40, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.82 (t, 3 H, $J = 7.0$ Hz), 0.92 (t, 3 H, $J = 7.0$ Hz), 0.94-0.97 (m, 2 H), 1.07-1.32 (m, 12 H), 1.55-1.80 (m, 9 H), 4.24 (dd, 1 H, $J = 4.5, 8.5$ Hz), 4.41 (t, 1 H, $J = 7.0$ Hz), 4.67 (t, 1 H, $J = 8.5$ Hz), 5.16-5.18 (m, 1 H), 5.46 (dd, 1 H, $J = 4.5, 8.5$ Hz), 7.28-7.36 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 18.2, 22.2, 22.5, 25.8, 26.0, 27.9, 29.5, 29.6, 30.2, 30.7, 33.0, 37.5, 44.2, 46.2, 57.7, 67.3, 100.1, 103.1, 125.9, 128.4, 128.8, 138.8, 153.3, 173.6, 200.9; IR (thin film) cm^{-1} 2958 (m), 2940 (m), 2856 (w), 1784 (s), 1701 (s); mass spectrum (APCI): m/e (% relative intensity) 438 (73) ($\text{M} + \text{H}$) $^+$, 394 (7), 340 (10), 275 (100), 177 (17).

Allene 40

$R_f = 0.39$ [25% EtOAc in hexanes]; clear oil; ^1H NMR (500 MHz, CDCl_3) Major isomer: δ 0.81-0.91 (m, 6 H), 1.21-1.57 (m, 11 H), 1.70-2.01 (m, 3 H), 4.26 (dd, 1 H, $J = 4.2, 9.0$ Hz), 4.31-4.36 (m, 1 H), 4.68 (t, 1 H, $J = 9.0$ Hz), 5.19-5.25 (m, 2 H), 5.45 (t, 1 H, $J = 9.0$ Hz), 7.27-7.40 (m, 5 H); Minor isomer: δ 0.81-0.91 (m, 6 H), 1.21-1.57 (m, 11 H), 1.70-2.01 (m, 3 H), 4.28 (dd, 1 H, $J = 4.2, 9.0$ Hz), 4.31-4.36 (m, 1 H), 4.70 (t, 1 H, $J = 9.0$ Hz), 4.98 (dq, 1 H, $J = 1.8, 6.6$ Hz), 5.20-5.25 (m, 1 H), 5.44 (t, 1 H, $J = 9.0$ Hz), 7.27-7.40 (m, 5 H); IR (thin film) cm^{-1} 2965 (m), 2930 (m), 2925 (m), 2860 (w), 1777 (s), 1702 (s); mass spectrum (APCI): m/e (% relative intensity) 370 (46) ($\text{M} + \text{H}$) $^+$, 326 (9), 207 (100), 120 (26), 87 (12).

Hydrogenated Product 41

$R_f = 0.39$ [25% EtOAc in hexanes]; clear oil; ^1H NMR (500 MHz, CDCl_3) Major isomer: δ 0.77 (t, 3 H, $J = 6.9$ Hz), 0.85-0.91 (m, 3 H), 0.88 (t, 3 H, $J = 6.9$ Hz), 0.98-1.08 (m, 4 H), 1.14-1.29 (m, 8 H), 1.36-1.46 (m, 3 H), 1.51-1.67 (m, 2 H), 3.77-3.86 (m, 1 H), 4.26 (dd, 1 H, $J = 3.9, 9.0$ Hz), 4.68 (t, 1 H, $J = 9.0$ Hz), 5.46 (dd, 1 H, $J = 3.9, 9.0$ Hz), 7.27-7.40 (m, 5 H); Minor isomer: δ 0.77 (t, 3 H, $J = 6.9$ Hz), 0.85-0.91 (m, 3 H), 0.88 (t, 3 H, $J = 6.9$ Hz), 0.98-1.08 (m, 4 H), 1.14-1.29 (m, 8 H), 1.36-1.46 (m, 3 H), 1.51-1.67 (m, 2 H), 3.77-3.86 (m, 1 H), 4.27 (dd, 1 H, $J = 3.9, 9.0$ Hz), 4.68 (t, 1 H, $J = 9.0$ Hz), 5.46 (dd, 1 H, $J = 3.9, 9.0$ Hz), 7.27-7.40 (m, 5 H); IR (thin film) cm^{-1} 2955 (m), 2942 (m), 2862 (w), 1782 (s), 1703 (s); mass spectrum (APCI): m/e (% relative intensity) 374 (100) ($\text{M} + \text{H}$) $^+$, 282 (22), 211 (22), 183 (75), 164 (82), 120 (23).

Hydrogenated Product 42

$R_f = 0.25$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} - 32.9$ (c 0.42, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 0.88 (t, 3 H, $J = 6.9$ Hz), 1.24-1.28 (m, 4 H), 1.33-1.52 (m, 4 H), 1.54-1.70 (m, 2 H), 2.48 (t, 2 H, $J = 7.5$ Hz), 3.89 (dddd, 1 H, $J = 5.1, 7.8, 10.5, 13.2$ Hz), 4.27 (dd, 1 H, $J = 6.9, 9.0$ Hz), 4.69 (t, 1 H, $J = 9.0$ Hz), 5.46 (dd, 1 H, $J = 6.9, 9.0$ Hz), 7.03-7.05 (m, 2 H), 7.18-7.37 (m, 8 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.8, 28.5, 29.5, 31.5, 32.4, 35.8, 42.5, 57.8, 69.6, 125.6, 126.0, 128.2, 128.3, 128.7, 129.1, 139.2, 142.1, 153.4, 176.4; IR (thin film) cm^{-1} 2955 (m), 2942 (m), 2862 (w), 1782 (s), 1703 (s); mass spectrum (APCI): m/e (% relative intensity) 380 (100) ($\text{M} + \text{H}$) $^+$, 217 (22), 189 (73), 164 (49), 87 (41).

Homo Allenyl Alcohol 45

$R_f = 0.39$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} - 65.6$ (c 0.39, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, 3 H, $J = 7.0$ Hz), 0.90 (t, 3 H, $J = 7.0$ Hz), 1.26-1.38 (m, 8 H), 1.39-1.47 (m, 4 H), 1.97-2.04 (m, 2 H), 2.18-2.23 (m, 1 H), 3.48 (dd, 1 H, $J = 7.5, 10.5$ Hz), 3.58-3.61 (m, 1 H), 4.95 (dq, 1 H, $J = 3.0, 6.5$ Hz), 5.17 (dq, 1

H, $J = 2.0, 6.5$, Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.4, 22.6, 28.7, 28.8, 29.2, 30.8, 31.2, 42.4, 66.1, 91.7, 92.0, 204.0 (missing 1 signal due to overlap of the terminal allene carbons); IR (thin film) cm^{-1} 3332 (brs), 2963 (m), 2932 (s), 2857 (m); mass spectrum (APCI): m/e (% relative intensity) 211 (100) ($\text{M} + \text{H}$) $^+$, 193 (27), 113 (41), 85 (17).

Homo Allenyl Alcohol 46

$R_f = 0.32$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} + 40.4$ (c 0.46, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.91 (t, 3 H, $J = 7.0$ Hz), 1.32-1.56 (m, 6 H), 2.35-2.42 (m, 1 H), 3.60 (t, 1 H, $J = 7.0$ Hz), 3.65-3.70 (m, 1 H), 5.49 (t, 1 H, $J = 6.5$ Hz), 6.22 (dd, 1 H, $J = 2.0, 6.5$ Hz), 7.19-7.39 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.6, 29.3, 30.8, 42.4, 66.1, 95.2, 96.3, 126.4, 126.7, 128.5, 135.6, 204.3; IR (thin film) cm^{-1} 3340 (brs), 2961 (m), 2935 (s), 2861 (m); mass spectrum (APCI): m/e (% relative intensity) 217 (93) ($\text{M} + \text{H}$) $^+$, 199 (12), 143 (17), 117 (15), 91 (100).

Homo Allenyl Alcohol 47

$R_f = 0.50$ [25% EtOAc in hexanes]; clear oil; $[\alpha]_D^{23} + 20.0$ (c 0.10, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 0.86-0.92 (m, 6 H), 1.30-1.37 (m, 8 H), 1.47-1.56 (m, 3 H), 1.72-1.86 (m, 1 H), 2.12 (q, 2 H, $J = 7.0$ Hz), 2.78 (quintet, 1 H, $J = 6.0$ Hz), 3.64-3.70 (m, 2 H), 5.60 (dt, 1 H, $J = 1.5, 7.0$ Hz), 7.19-7.22 (m, 1 H), 7.30-7.34 (m, 2 H), 7.40-7.42 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.5, 22.8, 24.8, 29.0, 29.3, 30.6, 31.3, 37.7, 62.9, 65.6, 95.8, 126.2, 128.1, 128.3, 131.5, 203.1 (missing 1 signal); IR (thin film) cm^{-1} 3320 (brs), 2960 (m), 2940 (s), 2870 (m); mass spectrum (APCI): m/e (% relative intensity) 287 (100) ($\text{M} + \text{H}$) $^+$, 269 (68), 257 (39), 187 (96), 117 (86), 87 (38).

$R_f = 0.43$ [25% EtOAc in Hexanes]; clear oil; ^1H NMR (500 MHz, CDCl_3) Major isomer: δ 0.86-1.02 (m, 5 H), 1.06-1.20 (m, 2 H), 1.24-1.36 (m, 4 H), 1.49-1.63 (m, 6 H), 1.70-1.88 (m, 3 H), 4.28 (dd, 1 H, $J = 4.0, 9.0$ Hz), 4.34 (dq, 1 H, $J = 2.0, 6.5$ Hz), 4.67 (t, 1 H, $J = 9.0$ Hz), 5.20 (dt, 1 H, $J = 2.0, 6.0$ Hz), 5.26-5.31 (m, 1 H), 5.43 (dd, 1 H, $J = 4.0, 9.0$ Hz), 7.26-7.40 (m, 5 H); Minor Isomer: δ 0.86-1.02 (m, 5 H), 1.06-1.20 (m, 2 H), 1.24-1.36 (m, 4 H), 1.49-1.63 (m, 6 H), 1.70-1.88 (m, 3 H), 4.26 (dd, 1 H, $J = 4.0, 9.0$ Hz), 4.34 (dq, 1 H, $J = 2.0, 6.5$ Hz), 4.67 (t, 1 H, $J = 9.0$ Hz), 4.96 (dt, 1 H, $J = 2.0, 6.5$ Hz), 5.23-5.26 (m, 1 H), 5.45 (dd, 1 H, $J = 4.0, 9.0$ Hz), 7.26-7.40 (m, 5 H); IR (thin film) cm^{-1} 2924 (m), 2859 (w), 1785 (s), 1707 (s), 1457 (m), 1379 (m); mass spectrum (APCI): m/e (% relative intensity) 382 (66) ($\text{M} + \text{H}$) $^+$, 219 (100), 191 (6), 164 (8), 120 (9).