Gold(I)-Catalyzed Synthesis of γ-Hydroxyketones from 5-Allyloxy-1-yneS

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I. General Information

All commercially available chemicals were used without further purification. All solvents were dried and distilled according to the standard methods before use. Au(PPh₃)Cl and AgSbF₆ were purchased from Aldrich Chemicals and stored in a dry-keeper. Au[t-Bu₂P(o-biphenyl)]Cl and Au[P(C₆F₅)₃]Cl were prepared according to the literature procedures. Experiments were performed in flame-dried glasswares with rubber septa under a positive pressure of nitrogen. Reactions were monitored by thin-layer chromatography using UV light as a visualizing agent and acidic p-anisaldehyde, PMA/EtOH and heat as developing agent. ¹H and ¹³C NMR spectra were recorded with 300 MHz spectrometer. ¹H NMR spectra were referenced to CDCl₃ (7.26 ppm) and reported as follows; chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, quint = quintet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets). Chemical shifts of the ¹³C NMR spectra were measured relative to CDCl₃ (77.23 ppm).

II. General procedure for the gold(I)-catalyzed reaction

**Compound 10**

To a solution of AgSbF₆ (2.5 mg, 0.0073 mmol) in dry CH₂Cl₂ (1 mL) was added a solution of 11a (5.6 mg, 0.0073 mmol) in dry CH₂Cl₂ (1 mL). The solution was stirred for 10 min. The resulting solution was filtered through a pad of celite and concentrated. The residue was dried over high vacuum for 2 hours and then cooled to 0°C. To this residue was added the solution of 8 (56 mg, 0.37mmol) in CH₂Cl₂ : H₂O = 10 : 1 (7.4 mL, pre-cooled to 0°C). The resulting green solution was stirred for 30 min. Triethylamine (1 mL) was added and the solution was stirred for 5 min. The resulting solution was filtered through a pad of silica and concentrated. The crude oil was purified by flash chromatography on silica gel (eluted with hexane : ethyl acetate = 70 : 30) to give the compound 10 as a colorless oil (60mg, 0.35mmol, 95% yield). RF = 0.08 (hexane : ethyl acetate = 80 : 20); ¹H NMR (300 MHz, CDCl₃): δ = 1.10 (s, 6H), 1.77 (quint, J = 6.3 Hz, 2H), 2.03 (br s, 1H), 2.32 - 2.55 (m, 4H), 2.67 - 2.76 (m, 1H), 3.62 (t, J = 6.1 Hz, 2H), 4.90 – 5.00 (m, 2H), 5.89 (ddd, J = 17.2 Hz, J = 10.3 Hz, J = 6.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 26.5, 27.2, 36.6, 41.8, 54.5, 62.4, 111.1, 143.0, 210.7; IR: (cm⁻¹) ν 3397, 2966, 1640, 1456, 1371; HRMS calcd for C₁₀H₁₈O₂: 170.1307. found: 170.1308.

**Compound 13**

Using the representative procedure (performed at rt), a mixture of 12 (25 mg, 0.18 mmol), gold complex 11a (6.7 mg, 0.0087 mmol) and AgSbF₆ (3.0 mg, 0.0087 mmol) were reacted to give 13 as a colorless oil. (25 mg, 0.16 mmol, 90 % yield). RF = 0.17 (hexane: ethyl acetate = 70:30); ¹H NMR (300 MHz, CDCl₃): δ = 1.00 (d, J = 6.7 Hz, 3H), 1.81 (quint, J = 6.5 Hz, 2H), 2.03 (s, 1H), 2.32 - 2.55 (m, 4H), 2.67 - 2.76 (m, 1H), 3.62 (t, J = 6.1 Hz, 2H), 4.90 – 5.00 (m, 2H), 5.73 (ddd, J = 17.2 Hz, J = 10.3 Hz, J = 6.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 20.0, 26.5, 33.6, 40.4, 49.7, 62.4, 113.3, 143.0, 210.7;
IR: (cm$^{-1}$) ν 3420, 3081, 2958, 1717, 1641, 1419, 1373, 915; HRMS calcd for C$_9$H$_{16}$O$_2$: 156.1150, found: 156.1153.

**Compound 15**

Using the representative procedure (performed at -15°C), a mixture of 14 (38 mg, 0.17 mmol), gold complex 11a (6.7 mg, 0.0087 mmol) and AgSbF$_6$ (3.0 mg, 0.0087 mmol) were reacted to give 15 as a colorless oil (30 mg, 0.13 mmol, 75 % yield). R$_f$ = 0.09 (hexane: ethyl acetate = 80:20); $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.09 (s, 3H), 1.32 - 1.48 (m, 2H), 1.56 (s, 3H), 1.65 (s, 3H), 1.77 (quint, $J$ = 6.5 Hz, 2H), 1.81 - 1.90 (m, 2H), 2.03 (s, 1H), 2.37 - 2.57 (m, 4H), 3.59 (t, $J$ = 6.1 Hz, 2H), 4.92 (dd, $J$ = 17.5 Hz, $J$ = 1.0 Hz, 1H), 5.02 (dd, $J$ = 10.8 Hz, $J$ = 1.1 Hz, 1H), 5.02 - 5.08 (m, 1H), 5.82 (dd, $J$ = 17.5, 10.8 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 17.8, 23.0, 23.0, 25.8, 26.5, 39.7, 41.0, 41.9, 52.9, 62.4, 112.4, 124.6, 131.6, 146.0, 210.8; IR: (cm$^{-1}$) ν 3419, 3079, 3020, 2965, 2926, 1700, 1375, 1060; HRMS calcd for C$_{15}$H$_{26}$O$_2$: 238.1933, found: 238.1930.

**Compound 17**

Using the representative procedure (performed at rt), a mixture of 16 (50 mg, 0.24 mmol), gold complex 11a (18.4 mg, 0.024 mmol) and AgSbF$_6$ (8.2 mg, 0.024 mmol) were reacted to give 17 (mixed with cyclized form in CDCl$_3$ solution) as a white solid (25 mg, 0.11 mmol, 46 % yield). R$_f$ = 0.30 (hexane: ethyl acetate = 80:20), m.p = 39 – 41°C; $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.87 (t, $J$ = 6.8 Hz, 3H), 1.27 - 1.42 (m, 12H), 1.52 - 2.00 (m, 5H), 2.09 - 2.24 (m, 1H), 2.28 - 2.51 (m, 2H), 2.51 - 2.59 (m, 4H), 3.53 - 3.58 (m, 1H), 4.93 - 5.08 (m, 2H), 5.73 - 5.93 (m, 1H); {distinctive signals for cyclized form} δ = 3.92 - 4.02 (m, 1H), 4.13 - 4.22 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 14.3, 22.8, 25.8, 28.0, 29.5, 31.1, 32.0, 38.0, 39.4, 42.1, 71.6, 115.4, 137.3, 211.2; {distinctive signals for cyclized form} δ = 26.1, 26.3, 29.1, 29.1, 29.6, 30.4, 30.8, 35.9, 35.9, 37.0, 37.8, 39.9, 40.0, 78.9, 81.3, 106.6, 106.8, 114.7, 114.8, 138.7; IR: (cm$^{-1}$) ν 3419, 3079, 2928, 2857, 1714, 1456, 1377; HRMS calcd for C$_{14}$H$_{27}$O$_2$ (FAB$^+$): 227.2011, found: 227.2014.

**Compound 19**

Using the representative procedure, a mixture of 18 (50 mg, 0.23 mmol), gold complex 11a (3.4 mg, 0.0044 mmol) and AgSbF$_6$ (1.5 mg, 0.0044 mmol) were reacted to give 19 as a colorless oil (45 mg, 0.19 mmol, the mixture of diastereomers = 1 : 1, 83 % yield). R$_f$ = 0.12 (hexane: ether = 70:30); $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.87 (t, $J$ = 6.7 Hz, 3H), 1.01 (d, $J$ = 6.8 Hz, 3H), 1.21 - 1.43 (m, 10H), 210.2.
1.55 - 1.68 (m, 1H), 1.73 - 1.84 (m, 2H), 2.33 - 2.50 (m, 2H), 2.55 (t, J = 7.0 Hz, 2H), 2.68 - 2.77 (m, 1H), 3.50 - 3.60 (m, 1H), 4.91 - 5.02 (m, 1H), 5.69 - 5.80 (m, 1H); 13C NMR (75 MHz, CDCl3): δ = 14.3, 20.0, 20.0, 22.8, 25.8, 29.5, 31.0, 32.0, 33.6, 38.0, 40.0, 40.0, 49.8, 71.7, 113.3, 113.3, 143.1, 143.1, 211.0; IR: (cm⁻¹) ν 3422, 3082, 2957, 2929, 2858, 1712; HRMS calcd for C15H28O2: 240.2089. found: 240.2087.

**Compound 21**

Using the representative procedure, a mixture of 20 (87 mg, 0.37 mmol), gold complex 11a (5.6 mg, 0.0073 mmol) and AgSbF6 (2.5 mg, 0.0073 mmol) were reacted to give 21 as a colorless oil. (83 mg, 0.33 mmol, 89 % yield). Rf = 0.32 (hexane: ethyl acetate = 80:20); 1H NMR (300 MHz, CDCl3): δ = 0.87 (t, J = 6.6 Hz, 3H), 1.10 (s, 6H), 1.20 - 1.41 (m, 10H), 1.51 - 1.64 (m, 1H), 1.70 - 1.80 (m, 2H), 2.42 (s, 2H), 2.53 (t, J = 6.9 Hz, 2H), 3.50 - 3.60 (m, 1H), 4.91 - 4.97 (m, 2H), 5.90 (dd, J = 17.6 Hz, J = 10.5 Hz, 1H); 13C NMR (75 MHz, CDCl3): δ = 14.3, 22.8, 25.8, 27.2, 27.3, 27.3, 29.5, 30.9, 32.0, 36.7, 38.0, 41.4, 54.5, 71.6, 111.0, 147.4, 211.0; IR: (cm⁻¹) ν 3418, 2958, 2929, 2858, 1710, 1468, 1363, 913; HRMS calcd for C16H30O2: 254.2246. found: 254.2247.

**Compound 23**

Using the representative procedure (performed at rt), a mixture of 22 (33 mg, 0.14 mmol), gold complex 11a (5.3 mg, 0.0069 mmol) and AgSbF6 (2.4 mg, 0.0069 mmol) were reacted to give 23 as a white solid. (28 mg, 0.11 mmol, 77 % yield). Rf = 0.13 (hexane: ethyl acetate = 80:20), m.p = 46 – 47°C; 1H NMR (300 MHz, CDCl3): δ = 0.87 (t, J = 6.9 Hz, 3H), 1.25 - 1.30 (m, 12H), 1.78 - 1.98 (m, 5H), 2.48 - 2.57 (m, 4H), 3.64 (t, J = 6.0 Hz, 2H), 5.31 - 5.46 (m, 2H); 13C NMR (75 MHz, CDCl3): δ = 14.3, 22.9, 26.7, 27.1, 29.4, 29.5, 29.7, 32.1, 32.7, 39.8, 43.0, 62.6, 128.3, 131.9, 211.3; IR: (cm⁻¹) ν 3341, 2954, 2918, 2849, 1704, 1463, 1437, 1056, 969; HRMS calcd for C16H30O2: 254.2246. found: 254.2248.

**Compound 25**

Using the representative procedure, a mixture of 24 (24 mg, 0.15 mmol), gold complex 11a (5.6 mg, 0.0073 mmol) and AgSbF6 (2.5 mg, 0.0073 mmol) were reacted to give 25 as a colorless oil. (25 mg, 0.14 mmol, 93 % yield). Rf = 0.12 (hexane: ethyl acetate = 80:20); 1H NMR (300 MHz, CDCl3): δ = 1.12 - 1.22 (m, 1H), 1.47 - 1.93 (m, 7H), 2.32 - 2.40 (m, 3H), 2.50 - 2.60 (m, 3H), 3.60 (t, J = 6.1 Hz,
2H), 5.42 - 5.46 (m, 1H), 5.64 - 5.67 (m, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 21.2, 25.2, 26.6, 29.1, 31.4, 40.4, 49.4, 62.4, 128.2, 130.6, 211.2\); IR: (cm\(^{-1}\)) \(\nu = 3397, 2925, 1700, 1448, 1371, 1058\); HRMS calcd for C\(_{11}\)H\(_{18}\)O\(_2\): 182.1307. found: 182.1309.

**Compound 27**

Using the representative procedure, a mixture of 26 (29 mg, 0.19 mmol), gold complex 11a (6.9 mg, 0.0090 mmol) and AgSbF\(_6\) (3.1 mg, 0.0090 mmol) were reacted to give 27 as a colorless oil. (28 mg, 0.16 mmol, 85 % yield). \(R_f = 0.07\) (hexane: ethyl acetate = 80:20); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.97\) (d, \(J = 6.7\) Hz, 3H), 1.61 (d, \(J = 5.9\) Hz, 3H), 1.80 (quint, \(J = 6.5\) Hz, 2H), 2.06 (s, 1H), 2.32 (dd, \(J = 15.5\) Hz, \(J = 7.2\) Hz, 1H), 2.42 (dd, \(J = 15.6\) Hz, \(J = 7.0\) Hz, 1H), 2.51 (t, \(J = 6.9\) Hz, 2H), 2.60 - 2.69 (m, 1H), 3.61 (t, \(J = 6.1\) Hz, 2H), 5.26 - 5.44 (m, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 18.0, 20.7, 26.6, 33.0, 40.3, 50.3, 62.4, 124.0, 135.7, 211.1\); IR: (cm\(^{-1}\)) \(\nu = 3419, 3027, 2958, 2881, 1710, 1410, 1373, 1059\); HRMS calcd for C\(_{10}\)H\(_{18}\)O\(_2\): 170.1307. found: 170.1310.

**Compound 29**

Using the representative procedure, a mixture of 28 (83 mg, 0.37 mmol), gold complex 11a (5.6 mg, 0.0073 mmol) and AgSbF\(_6\) (2.5 mg, 0.0073 mmol) were reacted to give 29 as a colorless oil. (77 mg, 0.32 mmol, 85 % yield). \(R_f = 0.13\) (hexane: ethyl acetate = 80:20); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.86\) (t, \(J = 6.3\) Hz, 3 H), 1.10 - 1.30 (m, 10H), 1.62 (dd, \(J = 6.3, J = 1.4\) Hz, 3H), 1.80 (quint, \(J = 6.5\) Hz, 2H), 1.92 (s, 1H), 2.36 - 2.53 (m, 5H), 3.61 (t, \(J = 6.1\) Hz, 2H), 5.12 - 5.20 (m, 1H), 5.35 - 5.43 (m, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 14.3, 18.1, 22.8, 26.5, 27.2, 29.4, 32.0, 35.5, 39.0, 40.5, 49.1, 62.5, 125.6, 134.3, 211.4\); IR: (cm\(^{-1}\)) \(\nu = 3423, 3027, 1645, 1456, 967\); HRMS calcd for C\(_{15}\)H\(_{28}\)O\(_2\): 240.2089. found: 240.2088.

**Compound 31**

Using the representative procedure, a mixture of 30 (83 mg, 0.37 mmol), gold complex 11a (5.6 mg, 0.0073 mmol) and AgSbF\(_6\) (2.5 mg, 0.0073 mmol) were reacted to give 31 as a colorless oil. (74 mg, 0.31 mmol, 83 % yield). \(R_f = 0.22\) (hexane: ethyl acetate = 70:30); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.87\) (t, \(J = 6.5\) Hz, 2H), 0.98 (d, \(J = 6.7\) Hz, 3H), 1.20 – 1.35 (m, 8H), 1.77 – 1.86 (m, 3H), 1.91 – 1.97 (m, 2H), 2.30 – 2.47 (m, 2H), 2.52 (t, \(J = 6.9\) Hz, 2H), 2.59 – 2.70 (m, 1H), 3.63 (t, \(J = 6.0\) Hz, 2H), 5.25 – 5.44 (m, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 14.3, 20.9, 22.8, 26.6, 29.0, 29.7, 31.9, 32.7, 33.1, 40.4, 50.5, 62.6, 129.7, 134.5, 211.1\); IR: (cm\(^{-1}\)) \(\nu = 3419, 3026, 1645, 1456, 967\); HRMS calcd for C\(_{15}\)H\(_{28}\)O\(_2\): 240.2089. found: 240.2086.

**Mixture of 33 and 34**
Using the representative procedure (performed at rt), a mixture of 32 (41 mg, 0.17 mmol), gold complex 11a (6.7 mg, 0.0087 mmol) and AgSbF$_6$ (3.0 mg, 0.0087 mmol) were reacted to give mixture of 33 and 34 as a colorless oil. (32 mg, 0.13 mmol, the mixture of constitutional isomers = 1.3 : 1, 72% yield). $R_f$ = 0.32 (hexane: ethyl acetate = 70:30); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.83 – 0.88 (m, 6H), 1.07 (s, 6H), 1.24 - 1.35 (m, 16H), 1.69 - 1.82 (m, 4H), 1.93 - 2.00 (m, 4H), 2.26 - 2.41 (m, 4H), 2.47 - 2.52 (m, 4H), 2.72 - 2.75 (m, 1H), 3.60 (t, $J = 6.1$ Hz, 2H), 5.27 - 5.36 (m, 1H), 5.44 - 5.49 (m, 1H); {distinctive signals for [1,3]-product 34} 1.60 (d, $J = 1.0$, 3H), 1.66 (d, $J = 1.0$, 3H), 4.77 - 4.80 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 14.3, 18.4, 22.8, 26.0, 26.6, 26.7, 27.3, 27.9, 29.0, 29.6, 29.8, 31.9, 32.0, 32.8, 34.8, 36.2, 40.6, 42.0, 49.4, 55.1, 62.5, 127.1, 128.4, 132.3, 138.9, 211.2, 211.6; IR: (cm$^{-1}$) ν 3419, 2957, 2926, 2856, 1710, 1456, 1377, 1059, 973; HRMS calcd for C$_{16}$H$_{30}$O$_2$: 254.2246. found: 254.2247.

III. Representative procedure for the gold(I)-catalyzed reaction with methanol

**Compound 35**

To a solution of AgSbF$_6$ (2.5 mg, 0.0073 mmol) in dry CH$_2$Cl$_2$ (1 mL) was added a solution of Au[P(C$_6$F$_5$)$_3$]Cl (5.6 mg, 0.0073 mmol) in dry CH$_2$Cl$_2$ (1 mL). The solution was stirred for 10 min. The resulting solution was filtered through a pad of celite and concentrated. The residue was dried over high vacuum for 2 - 3 hours. To this residue was added the solution of 22 (34 mg, 0.14 mmol) and methanol (30 μL, 0.74 mmol) in dry CH$_2$Cl$_2$ (3.0 mL) at rt. The reaction mixture was stirred for 20 min. Triethylamine (1 mL) was added and the solution was stirred for 5 min. The resulting solution was concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel ( deactivated by triethylamine before use, eluted with hexane : ethyl acetate = 95 : 5) to give the compound 35 as a colorless oil (28 mg, 0.10 mmol, 71% yield). $R_f$ = 0.63 (hexane : ethyl acetate = 80 : 20); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.88 (t, $J = 6.7$ Hz, 3H), 1.26 - 1.32 (m, 12H), 1.53 - 2.07 (m, 10H), 3.17 (s, 3H), 3.84 - 3.90 (m, 2H), 5.37 - 5.44 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 14.3, 22.9, 24.5, 28.1, 29.4, 29.5, 29.7, 29.8, 32.1, 32.8, 34.3, 35.7, 48.3, 67.5, 109.5, 129.7, 130.9; IR: (cm$^{-1}$) ν 2925, 2854, 1457, 1092, 1043, 966; HRMS calcd for C$_{17}$H$_{32}$O$_2$: 268.2402. found: 268.2404.

IV. Representative procedure for the preparation of substrates

**Procedure A (substrate 8)**
The literature procedure was modified. A solution of 4-pentyn-1-ol (800 mg, 9.51 mmol) in THF (4mL) was added dropwise to a suspension of sodium hydride (60% dispersion in mineral oil, 418 mg, 11 mmol) in THF (15 mL) at 0°C. After stirring for 30 min this temperature, prenyl bromide (1.29 mL, 9.99 mmol) was added. The reaction mixture was stirred for 15 hr at rt, then quenched with water. THF was removed under reduced pressure. The crude oil was extracted with Et₂O, dried over Na₂SO₄, concentrated and purified by flash chromatography on silica gel (pentane : ether = 90 : 10) to give the compound 8 as a colorless oil (1.20 g, 7.88 mmol, 83% yield). Rf = 0.69 (pentane : ether = 90 : 10). This spectral data was consistent with the literature value.²; ¹H NMR (300 MHz, CDCl₃): δ = 1.68 (s, 3H), 1.75 (s, 3H), 1.80 (quint, J = 6.5 Hz, 2H), 1.94 (t, J = 2.6 Hz, 1H), 2.29 (td, J = 7.1 Hz, J = 2.6 Hz, 2H), 3.51 (t, J = 6.2 Hz, 2H), 3.95 (d, J = 6.8 Hz, 2H), 5.33 - 5.37 (m, 1H).

Substrate 12

Procedure A: Yield = 76% (mixture of olefin isomers); ¹H NMR (300 MHz, CDCl₃): δ = 1.66 - 1.84 (m, 5H), 1.94 (t, J = 2.6 Hz, 1H), 2.26 - 2.31 (m, 2H), 3.50 (t, J = 6.3 Hz, 2H), 3.89 (d, J = 6.2 Hz, 2H), 5.51 - 5.62 (m, 1H), 5.66 - 5.77 (m, 1H); {distinctive signals for Z-isomer} δ = 4.03 (d, J = 6.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ = 13.4, 15.5, 18.0, 28.9, 66.4, 68.6, 68.6, 68.8, 71.8, 84.2, 127.2, 127.9, 128.0, 129.6; IR: (cm⁻¹) ν 3306, 3020, 2938, 2857, 2119, 1446, 1363, 1109, 967; HRMS calcd for C₉H₁₄O: 138.1045. found: 138.1045.

Substrate 14

Procedure A: Yield = 72%; ¹H NMR (300 MHz, CDCl₃): δ = 1.60 (s, 3H), 1.67 - 1.71 (m, 6H), 1.80 (quint, J = 6.7 Hz, 2H), 1.94 (t, J = 2.7 Hz, 1H), 2.00 - 2.14 (m, 4H), 2.29 (td, J = 7.1 Hz, J = 2.6 Hz, 2H), 3.51 (t, J = 6.2 Hz, 2H), 3.98 (d, J = 6.7 Hz, 2H), 5.07 - 5.12 (m, 1H), 5.32 - 5.37 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 15.5, 16.7, 17.9, 25.9, 26.6, 28.9, 39.8, 67.6, 68.6, 68.6, 84.3, 121.1, 124.2, 131.8, 140.3; IR: (cm⁻¹) ν 3311, 2926, 2857, 1669, 1436, 1377, 1107; HRMS calcd for C₁₅H₂₄O: 220.1827. found: 220.1826.
Procedure A: Yield = 76%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.87 (t, $J = 6.6$ Hz, 3H), 1.28 - 1.54 (m, 10H), 1.65 - 1.72 (m, 2H), 1.92 (t, $J = 2.6$ Hz, 1H), 2.49 (td, $J = 7.2$ Hz, $J = 2.6$ Hz, 2H), 3.42 (quint, $J = 5.9$ Hz, 1H), 3.92 - 4.04 (m, 2H), 5.11 - 5.15 (m, 1H), 5.22 - 5.29 (m, 1H), 5.85 - 5.98 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 14.2, 14.8, 22.8, 25.4, 29.6, 32.0, 33.1, 33.9, 68.4, 70.4, 77.7, 84.7, 116.7, 135.5; IR: (cm$^{-1}$) $\nu$ 3313, 2930, 2859, 2120, 1647, 1459, 1342, 1134; HRMS calcd for C$_{15}$H$_{24}$O(MH$^+$): 209.1905. found: 209.1902.

Substrate 18

Procedure A: Yield = 84% (mixture of olefin isomers); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.88 (t, $J = 6.6$ Hz, 3H), 1.25 - 1.51 (m, 10H), 1.60 - 1.71 (m, 5H), 1.92 (t, $J = 2.6$ Hz, 1H), 2.24 - 2.29 (m, 2H), 3.35 - 3.43 (m, 1H), 3.58 - 4.07 (m, 2H), 5.52 - 5.73 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 13.4, 14.3, 14.8, 18.0, 22.8, 25.5, 29.7, 32.0, 33.2, 34.1, 64.5, 68.3, 68.4, 70.2, 77.4, 84.8, 127.6, 127.6, 128.3, 129.3; IR: (cm$^{-1}$) $\nu$ 3314, 2930, 2858, 1456, 1094, 966; HRMS calcd for C$_{15}$H$_{26}$O: 222.1984. found: 222.1982.

Substrate 20

Procedure A: Yield = 68%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.88 (t, $J = 6.6$ Hz, 3H), 1.25 - 1.54 (m, 10H), 1.65 - 1.72 (m, 5H), 1.74 (s, 3H), 1.93 (t, $J = 2.6$ Hz, 1H), 2.25 - 2.31 (m, 2H), 3.39 (quint, $J = 5.9$ Hz, 1H), 3.93 - 3.99 (m, 2H), 5.33 - 5.38 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 14.3, 14.9, 18.2, 22.8, 25.5, 26.0, 29.7, 32.1, 33.3, 34.1, 65.8, 68.3, 77.4, 84.8, 121.8, 136.8; IR: (cm$^{-1}$) $\nu$ 3314, 2930, 2858, 1447, 1377, 1069; HRMS calcd for C$_{16}$H$_{28}$O: 236.2140. found: 236.2137.

Procedure B (substrate 22)
A solution of undec-1-en-3-ol (380 mg, 2.23 mmol) in DMF (1 mL) was added dropwise to a suspension of sodium hydride (60 w% in mineral oil, 107 mg, 2.7 mmol) in DMF (1 mL) at 0°C. After stirring for 30 min this temperature, a solution of homopropargyl bromide (295 mg, 2.01 mmol) in DMF (0.5 mL) was added. The reaction mixture was stirred for 20 hr at rt, then diluted with water and extracted with Et₂O. The organic layer was dried over Na₂SO₄, concentrated and purified by flash chromatography on silica gel (hexane : ethyl acetate = 9 : 5) to give the compound 22 as a colorless oil (192 mg, 0.812 mmol, 40% yield, 50% of starting material was recovered). Rf = 0.63 (hexane : ethyl acetate = 90 : 10); ¹H NMR (300 MHz, CDCl₃): δ = 0.88 (t, J = 6.6 Hz, 3H), 1.26 - 1.59 (m, 14H), 1.77 (quint, J = 6.6 Hz, 2H), 1.93 (t, J = 2.6 Hz, 1H), 2.29 (td, J = 7.2 Hz, J = 2.6 Hz, 2H), 3.31 - 3.38 (m, 1H), 3.54 - 3.63 (m, 1H), 3.5 - 3.65 (m, 1H), 5.13 - 5.19 (m, 2H), 5.61 - 5.72 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 14.3, 15.6, 22.9, 25.6, 29.1, 29.5, 29.8, 29.8, 32.1, 35.7, 66.9, 68.5, 81.7, 84.4, 116.5, 139.7; IR: (cm⁻¹) ν 3314, 3078, 2926, 2856, 1467, 1323, 1102, 993, 924; HRMS calcd for C₁₆H₂₉O (MH⁺): 237.2218. found: 237.2221.

Substrate 24

Procedure B: Yield = 20%; ¹H NMR (300 MHz, CDCl₃): δ = 1.53 - 1.83 (m, 6H), 1.93 (t, J = 2.6 Hz, 1H), 1.95 - 2.03 (m, 2H), 2.3 (td, J = 7.0 Hz, J = 2.6 Hz, 2H), 3.52 - 3.65 (m, 1H), 3.83 - 3.85 (m, 1H), 5.74 - 5.78 (m, 1H), 5.82 - 5.87 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 15.5, 19.5, 25.5, 28.5, 29.3, 66.7, 68.5, 73.1, 84.4, 128.1, 131.0; IR: (cm⁻¹) ν 3306, 3027, 2937, 2862, 1436, 1319, 1100; HRMS calcd for C₁₁H₁₇O (MH⁺): 165.1279. found: 165.1281.

Substrate 26

Procedure B: Yield = 30%; ¹H NMR (300 MHz, CDCl₃): δ = 1.21 (d, J = 6.3 Hz, 3H), 1.67 (dd, J = 9.1 Hz, J = 1.5 Hz, 3H), 1.76 (quint, J = 6.7 Hz, 2H), 1.93 (t, J = 2.7 Hz, 1H), 2.25 - 2.30 (m, 2H), 3.33 - 3.43 (m, 1H), 3.47 - 3.55 (m, 1H), 3.76 (quint, J = 6.7 Hz, 1H), 5.36 - 5.39 (m, 1H), 5.57 - 5.64 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 15.5, 17.8, 21.7, 29.1, 66.4, 68.4, 76.7, 84.4, 127.3, 133.7; IR: (cm⁻¹) ν 3311, 2930, 2858, 1446, 1371, 1102, 967; HRMS calcd for C₁₀H₁₆O: 152.1201. found: 152.1201.
Substrate 28

Procedure B: Yield = 42%; $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.88 (t, $J$ = 6.7 Hz, 3H), 1.21 (d, $J$ = 6.3 Hz, 3H), 1.23 - 1.39 (m, 9H), 1.76 (quint, $J$ = 6.7 Hz, 2H), 1.92 (t, $J$ = 2.6 Hz, 1H), 1.99 - 2.05 (m, 2H), 2.25 - 2.31 (m, 2H), 3.33 - 3.40 (m, 1H), 3.47 - 3.56 (m, 1H), 3.77 (quint, $J$ = 6.7 Hz, 1H), 5.31 (ddt, $J$ = 15.4 Hz, $J$ = 7.7 Hz, $J$ = 1.4 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 14.3, 15.6, 21.9, 22.8, 29.0, 29.1, 29.4, 31.9, 32.4, 66.4, 68.4, 76.8, 84.4, 132.3, 133.0; IR: (cm$^{-1}$) ν 3314, 2928, 2856, 1456, 1370, 1102, 969; HRMS calcd for C$_{15}$H$_{26}$O: 222.1984. found: 222.1981.

Substrate 30

Procedure B: Yield = 37%; $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.87 (t, $J$ = 6.6 Hz, 3H), 1.26 - 1.59 (m, 10H), 1.65 - 1.79 (m, 5H), 1.92 (t, $J$ = 2.6 Hz, 1H), 2.27 (td, $J$ = 7.2 Hz, $J$ = 2.5 Hz, 2H), 3.27 - 3.36 (m, 1H), 3.50 - 3.58 (m, 2H), 5.24 - 5.32 (m, 1H), 5.52 - 5.64 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 14.3, 15.6, 17.9, 22.8, 25.7, 29.1, 29.5, 32.1, 35.9, 66.5, 68.4, 81.2, 84.5, 128.1, 132.7; IR: (cm$^{-1}$) ν 3314, 2930, 2858, 2121, 1671, 1456, 1100, 968; HRMS calcd for C$_{15}$H$_{27}$O (MH$^+$): 223.2062. found: 223.2057.

Substrate 32

Procedure B: Yield = 29%; $^1$H NMR (300 MHz, CDCl$_3$): δ = 0.87 (t, $J$ = 6.4 Hz, 3H), 1.20 - 1.58 (m, 10H), 1.65 (s, 3H), 1.69 - 1.78 (m, 5H), 1.91 (t, $J$ = 2.6 Hz, 1H), 2.24 - 2.29 (m, 2H), 3.28 - 3.36 (m, 1H), 3.47 - 3.54 (m, 1H), 3.87 - 3.94 (m, 1H), 4.99 - 5.02 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 14.3, 15.6, 18.5, 22.9, 25.6, 26.1, 29.2, 29.6, 32.1, 36.0, 66.3, 68.4, 76.2, 84.5, 127.0, 135.3; IR: (cm$^{-1}$) ν 3314, 2930, 2858, 1446, 1377, 1100; HRMS calcd for C$_{16}$H$_{28}$O: 236.2140. found: 236.2137.

References: