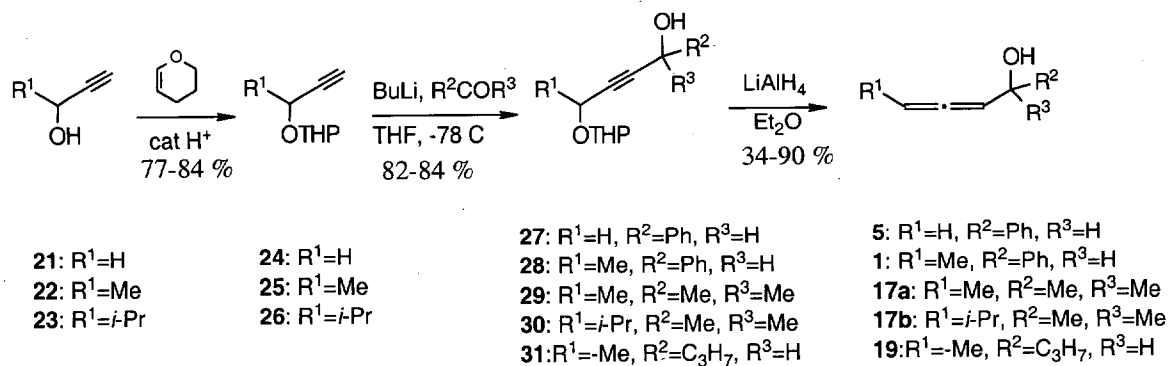


## Experimental Section

$^1\text{H}$  NMR (300 or 500 MHz) and  $^{13}\text{C}$  NMR (75 or 125 MHz) spectra were recorded on a Varian GEM-300 or on an Inova 500 spectrometer using the residual peak of  $\text{CHCl}_3$  in  $\text{CDCl}_3$  (7.26 ppm for  $^1\text{H}$  and 77.0 ppm for  $^{13}\text{C}$ ) as the internal standard. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. IR Spectra were obtained using a Perkin-Elmer 500 FT-IR instrument and the samples were examined as thin films or  $\text{CDCl}_3$  solutions. EM Science silica gel 60 (230-400 mesh) was used for flash chromatography and analytical thin-layer chromatography was performed on Merck precoated silica gel 60-F<sub>254</sub> plates. Melting points (mp) were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Mass spectra were recorded on a Thermoquest GC-MS instrument at 70 eV. Elemental analysis was performed by M-H-W laboratories of Phoenix, AZ. Tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl prior to use. Diethyl ether, and toluene were dried by pressing them through a column of activated alumina under argon. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was distilled from calcium hydride. Petroleum ether refers to that fraction boiling in the range 35 – 60 °C. All reactions were run under an atmosphere of argon in flame-dried glassware. Anhydrous solvents were transferred by an oven-dried syringe or cannula. Unless otherwise noted, all material were obtained from commercial suppliers and used without further purification.  $\text{VO}(\text{OSiPh}_3)_3$ <sup>1</sup> and 2-pyrrolecarbaldehyde<sup>2</sup> were prepared according to literature procedures.

### Preparation of starting material:

The allenic alcohols **1**, **5**, **17a**, **17b** and **19** were prepared according to the procedure shown in Scheme 1.<sup>3</sup> The starting propargylic alcohols are commercially available. The propargylic alcohols were treated with dihydropyran to form the THP protected alcohols **24-26**. The derivatives **27-31** were prepared by the reaction of the lithium acetylide of **24-26** generated by treatment with butyllithium, with an appropriate aldehyde or ketone. Reaction of **27-31** with  $\text{LiAlH}_4$  gives the allenic alcohols in good yields.



Scheme 1

### Preparation of Tetrahydropyranyl Ethers of propargylic Alcohols (24-26).

All preparations were carried out according to the procedure by Landor<sup>4</sup>. The preparation of **1-methyl-2-propynyl tetrahydro-2H-2-pyranyl ether (25)**<sup>5</sup> is representative. To a mixture of 3-butyn-2-ol (**22**) (30 g, 0.43 mol) and dihydropyran (39.2 g 0.47 mol) was added a few drops of concentrated hydrochloric acid, and the mixture was allowed to stir for 1.5 h. The mixture was then dried (K<sub>2</sub>CO<sub>3</sub>-MgSO<sub>4</sub>), filtered and distilled to give the product **25** in 84 % yield (55.6 g). Bp 98-101 °C (20 mm Hg). The NMR spectra were complicated due to the presence of diastereomers. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.92 (dd, *J* = 4.4, 2.9 Hz, 0.5 H), 4.75 (t, *J* = 3.2 Hz, 0.5 H), 4.53 (dq, *J* = 6.7, 2.0 Hz, 0.5 H), 4.44 (dq, *J* = 6.7, 2.0 Hz, 0.5 H), 3.97 (m, 0.5 H), 3.80 (m, 0.5 H), 3.51 (m, 1H), 2.41 (d, *J* = 2.0 Hz, 0.5 H), 2.36 (d, *J* = 2.0 Hz, 0.5 H), 1.89-1.62 (m, 2 H), 1.60-1.46 (m, 4 H), 1.46 (d, *J* = 6.7 Hz, 1.5 H), 1.42 (d, *J* = 6.7 Hz, 1.5 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (97.1, 95.7), (84.6, 83.6), (72.4, 71.8), (62.4, 62.2), (62.1, 60.5), (30.46, 30.43), (25.37, 25.30), (21.9, 21.8), (19.4, 19.0). IR (neat): 3292, 2943, 2871, 2110, 1453, 1442, 1372, 1334, 1202, 1184, 1123, 1094, 1076, 1023, 984. cm<sup>-1</sup>.

**2-propynyl tetrahydro-2H-2-pyranyl ether (24)** was prepared from propargyl alcohol **21** according to the general procedure in 92% yield. Bp 78-80 °C (20 mm Hg). NMR data were in accordance with previously reported data.<sup>6</sup>

**1-isopropyl-2-propynyl tetrahydro-2H-2-pyranyl ether (26)** was prepared from 4-methyl-1-pentyn-3-ol (**23**) according to the general procedure in 77% yield. Bp 55-58° C (1 mm Hg). The NMR spectra looked complicated due to the presence of diastereomers. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.98 (t, *J* = 3.3 Hz, 0.5 H), 4.70 (t, *J* = 3.4

Hz, 0.5 H), 4.18 (dd,  $J = 6.1, 2.0$  Hz, 0.5 H), 4.06 (dd,  $J = 5.8, 2.0$  Hz, 0.5 H), 4.02 (m, 0.5 H), 3.78 (m, 0.5 H), 3.52 (m, 1 H), 2.41 (d,  $J = 2.0$  Hz, 0.5 H), 2.36 (d,  $J = 2.0$  Hz, 0.5 H), 1.94 (m, 1H), 1.52-1.83 (m, 6 H), 1.04 (d,  $J = 6.8$  Hz, 1.5 H), 1.02 (d,  $J = 6.7$  Hz, 1.5 H), 1.00 (d,  $J = 6.8$  Hz, 1.5 H), 0.98 (d,  $J = 6.7$  Hz, 1.5 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (98.8, 95.2), (82.5, 81.6), (73.8, 73.1), (72.6, 70.0), (62.2, 62.1), (32.9, 32.6), (30.38, 30.31), (25.4, 25.3), (19.2, 19.0), (18.5, 18.2), (17.9, 17.3). IR (neat): 3292, 2943, 2871, 2110, 1453, 1442, 1372, 1334, 1202, 1184, 1123, 1094, 1076, 1023, 984.  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{11}\text{H}_{18}\text{O}_2$ : C, 72.49; H, 9.95; Found: C, 72.38; H, 10.16.

**General Procedure<sup>7</sup> for the 4-(Tetrahydropyranyloxy)-butyn-1-ol Derivatives 27-31.** To a solution of the appropriate 3-(tetrahydro-2-pyranyloxy)-1-propyne derivative **24-26** (38 mmol) in dry THF (38 mL) at  $-78^\circ\text{C}$  was added BuLi (1.6 M in hexane 42.2 mmol) and the reaction mixture was stirred for 2h at the same temperature. An appropriate aldehyde or ketone (43.6 mmol) was added at  $-78^\circ\text{C}$  and the mixture was stirred at the same temperature for 2h. After allowing the solution to warm to room temperature, sat  $\text{NH}_4\text{Cl}$  (15 mL) was added and the mixture was extracted with ether (3 x 25 mL). The combined extracts were dried ( $\text{MgSO}_4$ ), filtered and distilled to afford 4-(Tetrahydropyranyloxy)-butyn-1-ol derivatives **27-31**.

**1-phenyl-4-(tetrahydro-2H-2-pyranyloxy)-2-butyn-1-ol (27).** Purified by flash chromatography (ether/petroleum ether 1:4). 80% yield. The NMR data were in accordance with previously reported values.<sup>7</sup>

**1-phenyl-4-(tetrahydro-2H-2-pyranyloxy)-2-pentyn-1-ol (28).** Purified by flash chromatography (ether/petroleum ether 1:5). 84% yield. The NMR spectra looked complicated due to the presence of diastereomers.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.53 (m, 2H), 7.41-7.28 (m, 3H), 5.49 (m, 1H), 4.95 (dd,  $J = 4.2, 2.8$  Hz, 0.5 H), 4.78 (t,  $J = 3.3$  Hz, 0.5 H), 4.64 (dq,  $J = 6.6, 1.5$  Hz, 0.5 H), 4.52 (dq,  $J = 6.6, 1.5$  Hz, 0.5 H), 3.96 (m, 0.5 H), 3.80 (m, 0.5 H), 3.49 (m, 1 H), 2.39 (br s, OH), 1.92-1.66 (m, 2 H), 1.65-1.45 (m, 4 H), 1.49 (dd,  $J = 6.6, 1.0$  Hz, 1.5 H), 1.46 (dd,  $J = 6.6, 1.0$  Hz, 1.5 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (140.6, 140.5), (128.5, 128.4), (128.3, 128.2), (126.65, 126.62), (97.4, 95.8), (87.4, 86.4), (84.4, 83.6), (64.4, 64.9), (62.4, 62.1), 60.8, (30.5, 30.4), (25.34, 25.29), (21.9, 21.8), (19.3, 19.0). IR (neat): 3396, 3062, 2943, 2870, 2360, 1493, 1453,

1379, 1333, 1201, 1186, 1156, 1069, 994  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{16}\text{H}_{20}\text{O}_3$ : C, 73.82; H, 7.74; Found: C, 73.76; H, 7.51.

**2-methyl-5-(tetrahydro-2H-2-pyranyloxy)-3-hexyn-2-ol (29).** Purified by flash chromatography (ether/petroleum ether 1:4). 83% yield. The NMR spectra looked complicated due to the presence of diastereomers.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.91 (dd,  $J = 4.1, 2.9$  Hz, 0.5 H), 4.78 (t,  $J = 3.2$  Hz, 0.5 H), 4.55 (dq,  $J = 6.7$  Hz, 0.5 H) 4.46 (q,  $J = 6.7$  Hz, 0.5 H), 3.98 (m, 0.5 H), 3.80 (m, 0.5 H), 3.52 (m, 1 H), 2.00 (br s, OH), 1.88-1.66 (m, 2 H), 1.65-1.45 (m, 4 H), 1.51 (s, 6 H), 1.44 (d,  $J = 6.7$  Hz, 1.5 H), 1.41 (d,  $J = 6.7$  Hz, 1.5 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (100.2, 95.6), (97.1, 95.3), (89.6, 88.7), (82.5, 81.2), (64.77, 64.75), (62.9, 62.1), (61.8, 60.5), (31.35, 31.29), (30.5, 30.3), 25.3, 22.0, (19.1, 18.8). IR (neat): 3420, 2982, 2940, 2870, 2212, 1454, 1442, 1371, 1335, 1233, 1202, 1166, 1127, 1036, 993, 969.  $\text{cm}^{-1}$ .

**2,6-dimethyl-5-(tetrahydro-2H-2-pyranyloxy)-3-heptyn-2-ol (30).** Bulb to bulb distillation (1mm Hg) oven temperature: 160-180  $^\circ\text{C}$ , 82% yield. The NMR spectra looked complicated due to the presence of diastereomers.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.97 (t,  $J = 3.4$  Hz, 0.5 H), 4.73 (t,  $J = 3.4$  Hz, 0.5 H), 4.18 (d,  $J = 6.4$  Hz, 0.5 H) 4.04 (d,  $J = 5.9$  Hz, 0.5 H), 4.03 (m, 0.5 H), 3.78 (ddd,  $J = 11.2, 9.0, 3.2$  Hz, 0.5 H), 3.53 (m, 1 H), 2.15 (br s, OH), 1.91 (m, 1 H), 1.85-1.53(m, 6 H), 1.51 (s, 6 H), 1.03 (d,  $J = 6.7$  Hz, 1.5 H), 1.02 (d,  $J = 6.7$  Hz, 1.5 H), 0.97 (d,  $J = 6.7$  Hz, 1.5 H), 0.95 (d,  $J = 6.7$  Hz, 1.5 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (98.6, 95.0), (90.84, 90.89), (80.8, 79.6), (72.9, 70.0), 65.1, 61.9, (33.1, 32.8), (31.51, 31.49), (31.42, 31.41), (30.40, 30.35), (25.49, 25.44), (19.1, 18.9), (18.7, 18.4), (18.1, 17.6) IR (neat): 3415, 2872, 2360, 1469, 1455, 1367, 1233, 1202, 1168, 1020  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{24}\text{O}_3$ : C, 69.96; H, 10.06; Found: C, 69.96; H.9.88.

**7-(tetrahydro-2H-2-pyranyloxy)-5-octyn-4-ol (31).** Purified by flash chromatography (ether/petroleumether 1:3). 56% yield. The NMR spectra looked complicated due to the presence of diastereomers.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 4.92 (dt,  $J = 4.1, 3.4$  Hz, 0.5 H), 4.76 (t,  $J = 3.3$  Hz, 0.5 H), 4.56 (dq,  $J = 6.6, 1.7$  Hz, 0.5 H), 4.43 (dq,  $J = 6.6, 1.7$  Hz, 0.5 H), 4.40 (t,  $J = 6.6$  Hz, 1 H), 3.97 (m, 0.5 H), 3.81 (m, 0.5 H), 3.52 (m, 1 H), 1.86 (br s, OH), 1.84-1.47 (m, 10 H), 1.45 (d,  $J = 6.6$  Hz, 1.5 H), 1.41 (d,  $J = 6.6$  Hz, 1.5 H), 0.93 (t,  $J = 7.1$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (97.2, 95.6),

(85.8, 85.4), (85.0, 84.2), (62.6, 62.4), (62.14, 60.67), 60.0, (39.77, 39.70), (30.51, 30.42), (25.35, 25.32) (22.07, 21.89), (19.37, 19.04), 18.4, 13.7. IR (neat): 3421, 2939, 2873, 1454, 1379, 1334, 1202, 1164, 1074  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{13}\text{H}_{22}\text{O}_3$ : C, 68.99; H, 9.80; Found: C, 68.79; H, 9.68.

**General Procedure for the preparation of 2,3-Butadienyl Alcohols 1, 5, 17a, 17b and 19.**<sup>4</sup> To a slurry of  $\text{LiAlH}_4$  (1.12 g, 29.5 mmol) in dry diethylether (45 ml) at 0 °C was added the appropriate derivative of 4-(tetrahydro-2-pyranyloxy)-2-butyne-1-ols **29-33** (27 mmol) dissolved in dry ether (15 mL) over a period of 45 minutes. The mixture was refluxed for 4h and the excess  $\text{LiAlH}_4$  was decomposed by adding aqueous THF dropwise until the gray slurry turned white. Water was then added and the phases were separated. The aqueous phase was extracted with ether (3x 50 mL) and the combined organic fractions were dried ( $\text{MgSO}_4$ ) and filtered. After evaporation of the solvent the residue was purified by distillation or flash chromatography.

**1-Phenyl-2,3-butadienol (5).** Purified by flash chromatography ( $\text{Et}_2\text{O}$ /petroleum ether, gradient 1:6→1:2), 75% yield. The NMR data were in accordance with previously reported data.<sup>8</sup>

**1-phenyl-2,3-pentadien-1-ol**<sup>9</sup> (**1**). Purified by flash chromatography ( $\text{EtOAc}$ /petroleum ether, gradient 1:9→1:6), 90% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43-7.28 (m, 5 H), 5.36 (m, 2 H), 5.22 (m, 1 H), 2.16 (br s, OH) 1.73 (dd,  $J = 6.7, 3.4$  Hz, 3 H), 1.70 (dd,  $J = 6.7, 3.4$  Hz, 1.5 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.9, 143.0, 128.4, 127.7, 126.1, 95.5, (89.78, 89.68), (72.19, 72.11), (14.24, 14.37). IR (neat): 3362, 3062, 3029, 2926, 2859, 1968, 1492, 1452, 1407, 1371, 1278, 1194, 1073, 1030, 970.  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_{11}\text{H}_{12}\text{O}$ : 160.0888. Found: 160.0882.

**2-methyl-3,4-hexadien-2-ol. (17a).** Purified by flash chromatography ( $\text{Et}_2\text{O}$ /Petroleumether 1:3) to give **9** in 34% yield<sup>10</sup>. The NMR data were in accordance with previously reported data<sup>11</sup>

**5,6-octadien-4-ol. (19).** Purified by flash chromatography ( $\text{Et}_2\text{O}$ /petroleum ether, 1:3), 65% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.22 (m, 1H), 5.16 (m, 1H), 4.11 (m, 1H), 1.78 (br s, OH), 1.69 (app dt  $J = 7.1, 3.2$  Hz, 3H), 1.51 (m, 2H), 1.42 (m, 2H), 0.91 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.8, (95.07, 95.00), (88.6, 88.4), (69.9,

69.6), (39.5, 39.48), 18.6, 14.3, 13.8. IR (neat): 3355, 2950, 2873, 1967, 1458, 1372, 1320, 1117, 1068, 1003.  $\text{cm}^{-1}$ . HRMS Calcd for  $\text{C}_8\text{H}_{14}\text{O}$ : 126.1044. Found: 126.1040.

**2,6-dimethyl-3,4-heptadien-2-ol (17b).** Purified by distillation Bp 75 °C (18 mmHg), 75% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.35 (m, 2 H), 2.31 (m, 1 H), 1.67 (br s, OH) 1.33 (s, 6 H), 1.02 (d,  $J = 6.7$  Hz, 3 H), 1.01 (d,  $J = 6.7$  Hz, 3 H)  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.7, 102.44, 102.41, 69.5, 30.0, 29.9, 27.9, 22.4, 22.3. IR (neat): 3361, 2965, 2290, 1960, 1464, 1363, 1299, 1237, 1150, 1069, 970.  $\text{cm}^{-1}$ .

#### Preparation of the catalyst.

**Tris(triphenylsilyl)vanadate.(4)** To a solution of triphenyl silanol (9.66 g, 34.93 mmol), triethylamine (3.00 mL) and pyridine (2.00 mL) in toluene (200 mL) was added  $\text{VOCl}_3$  (2.00 g, 1.20 mmol) slowly at room temperature under argon. The mixture was stirred for 16 h. The resulting suspension was heated to 60°C and filtered through a cannula with a cotton plug at the same temperature to remove precipitated triethylamine hydrochloride. The filtrate was concentrated in *vacuo* and 120 mL of diethyl ether was added. The precipitate was collected by filtration and washed with small amounts of diethyl ether. Acetonitrile (200 mL) was added to the solid and heated to reflux. Then THF (54 mL) was added to initiate the precipitation. After cooling to room temperature the precipitate was collected by filtration under argon, washed with acetonitrile and dried in *vacuo* to give  $\text{VO}(\text{OSiPh}_3)_3$  (5.45 g, 51%) as a white solid. m.p.: 225 - 227 °C. (litt 224-226 °C).<sup>1</sup>  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50-7.44 (m, 2 H), 7.41-7.32 (m, 1 H), 7.16-7.25 (m, 2 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  135.2, 134.3, 130.1, 127.8. IR (KBr): 3068, 1589, 1429, 1118, 1005, 894, 740, 713, 698  $\text{cm}^{-1}$ .

**Reaction of Allenic Alcohols with Aldehydes in the Presence of VO(OSiPh<sub>3</sub>)<sub>3</sub>**

The reactions were carried out in a flame dried 5 mL Screw-top V-vial sealed with a Miniert Syringe Valve under an Argon atmosphere. Typically, to a solution of VO(OSiPh<sub>3</sub>)<sub>3</sub> (5 %) in dichloromethane (2.5 M) freshly distilled aldehyde (1.2 equiv) and then allenic alcohol (1 equiv.) was added. The reaction mixture was stirred at room temperature for 24-48 hours. The solvent was removed in *vacuo* and the residue purified by flash chromatography.

**(E)-5-hydroxy-4-methyl-1,5-diphenyl-1-penten-3-one (2).** Allenic alcohol **1** (100 mg, 0.62 mmol) and benzaldehyde (79.6 mg, 0.75 mmol) was added to a solution of VO(OSiPh<sub>3</sub>)<sub>3</sub> (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL). The mixture was stirred at room temperature for 30 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/Et<sub>2</sub>O (3:1) as the eluent to give **2** (0.14 mg, 86%) as a mixture of *syn*- and *anti*-isomers (80:20). *Syn*-**2**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.60 (d, *J* = 16.0 Hz, 1 H), 7.53 (m, 2 H), 7.44-7.22 (m, 8 H), 6.75 (d, *J* = 16.0 Hz, 1 H), 5.18 (d, *J* = 3.6 Hz, 1 H), 3.30 (br s, OH), 3.18 (dq, *J* = 7.3, 3.6 Hz, 1 H), 1.18 (d, *J* = 7.3 Hz, 3 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 204.6, 143.7, 141.7, 134.1, 130.7, 128.9, 128.4, 128.1, 127.2, 125.9, 124.6, 72.9, 50.5, 10.6. *Anti*-**2**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.63 (d, *J* = 16.0 Hz, 1 H), 7.53 (m, 2 H), 7.44-7.22 (m, 8 H), 6.83 (d, *J* = 16.0 Hz, 1 H), 4.90 (d, *J* = 8.2 Hz, 1 H), 3.30 (br s, OH), 3.29 (dq, *J* = 8.2, 7.3 Hz, 1 H), 1.03 (d, *J* = 7.3 Hz, 3 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 203.9, 143.4, 142.0, 134.2, 130.5, 128.8, 128.3, 127.7, 126.5, 125.9, 125.4, 76.4, 51.2, 14.8. IR (neat): 3461, 3061, 3029, 2976, 2876, 2248, 1680, 1650, 1606, 1576, 1495, 1450, 1332, 1200, 1161, 1051, 980. cm<sup>-1</sup>. Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>: C, 81.17; H, 6.81; Found: C, 80.94; H, 6.69.

**(E)-5-hydroxy-5-(4-methoxyphenyl)-4-methyl-1-phenyl-1-penten-3-one (6).** Allenic alcohol **1** (100 mg, 0.62 mmol) and anis aldehyde (111 mg, 0.82 mmol) was added to a solution of VO(OSiPh<sub>3</sub>)<sub>3</sub> (30.5 mg, 0.034 mmol) in dichloromethane (0.27 mL). The mixture was stirred at room temperature for 48 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using CHCl<sub>3</sub>/benzene/EtOAc/petroleum ether (0.5/0.5/1/8) as the eluent to give **6** (0.157 mg,

83%) as a mixture of *syn*- and *anti*-isomers (42:58). *syn*-**6**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (d,  $J = 16.2$  Hz, 1 H), 7.55 (m, 2 H), 7.40 (m, 3 H), 7.31 (t,  $J = 8.5$  Hz, 2 H), 6.89 (m, 2 H), 6.73 (d,  $J = 16.2$  Hz, 1 H), 5.12 (d,  $J = 3.8$  Hz, 1 H), 3.79 (s, 3 H), 3.38 (br s, OH), 3.13 (dq,  $J = 7.2, 3.8$  Hz, 1 H), 1.17 (d,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.7, 158.8, 143.7, 134.2, 133.9, 130.8, 129.0, 128.5, 127.9, 127.2, 113.6, 72.9, 55.3, 50.6, 10.9. *anti*-**6**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (d,  $J = 16.2$  Hz, 1 H), 7.55 (m, 2 H), 7.40 (m, 3 H), 7.31 (t,  $J = 8.5$  Hz, 2 H), 6.89 (m, 2 H), 6.83 (d,  $J = 16.2$  Hz, 1 H), 4.86 (dd,  $J = 8.2, 3.3$  Hz, 1 H), 3.80 (s, 3 H), 3.25 (dq,  $J = 8.2, 7.2$  Hz, 1 H), 2.92 (d,  $J = 3.3$  Hz, OH), 1.02 (d,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.1, 159.2, 143.5, 134.4, 134.2, 130.6, 128.9, 128.4, 127.9, 125.5, 113.8, 76.2, 55.3, 51.5, 14.9. IR ( $\text{CDCl}_3$ ): 3437, 3029, 2969, 2837, 1681, 1651, 1607, 1450, 1330, 1303, 1249, 1175, 1035  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_3$ : C, 77.00; H, 6.80; Found: C, 76.86; H, 6.68.

**(E)- 5-Furan-5-yl-5-hydroxy-4-methyl-1-phenyl-pent-1-en-3-one (7)** Allenic alcohol (**1**) (80.0 mg, 0.50 mmol) and 2-furaldehyde (49.7  $\mu\text{L}$ , 0.60 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (22.3 mg, 0.03 mmol) in dichloromethane (0.2 mL). After 36 hours water (1 mL) was added and the aqueous layer was extracted with diethylether (3x 2 mL). The organic layer was then dried ( $\text{MgSO}_4$ ) and the solvent was evaporated in *vacuo*. The residue was purified by flash chromatography using pet.ether/ethyl acetat (gradient 10:1 $\rightarrow$ 6:1) to give **7** (115.8 mg, 89 %) as a mixture of *syn*- and *anti*- isomers (73:27). *Syn*-(**7**):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (d,  $J = 16.0$  Hz, 1 H), 7.61-7.53 (m, 2 H), 7.41-7.34 (m, 4 H), 6.74 (d,  $J = 16.0$  Hz, 1 H), 6.33-6.29 (m, 2 H), 5.12 (app t,  $J = 3.8$  Hz, 1 H), 3.40 (dq,  $J = 7.2, 3.8$  Hz, 1 H), 3.28 (d,  $J = 3.8$  Hz, OH), 1.27 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.7, 154.4, 143.9, 141.7, 134.2, 130.8, 128.5, 129.0, 124.5, 110.2, 106.7, 68.5, 47.8, 11.7. *Anti*-(**7**):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65 (d,  $J = 16.0$  Hz, 1 H), 7.63-7.53 (m, 2 H), 7.41-7.34 (m, 4 H), 6.80 (d,  $J = 16.0$  Hz, 1 H), 6.33-6.29 (m, 2 H), 4.92 (dd,  $J = 7.5, 6.2$  Hz, 1 H), 3.53 (dq,  $J = 7.5, 7.2$  Hz, 1 H), 3.28 (m,  $J = 6.2$  Hz, OH), 1.14 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.7, 154.4, 143.9, 142.2, 134.2, 130.8, 129.0, 128.5, 124.5, 110.3, 107.5, 70.0, 48.0, 14.7. IR (film): 3442 (s), 2974 (s), 2935 (m), 2361 (m), 1683 (s), 1652 (s), 1607 (s), 1576 (m),



1496 (m), 1450 (s), 1374 (b), 1332 (m), 1129 (m), 864 (m)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_3$ : C, 74.98; H, 6.29; Found: C, 75.03; H, 6.41.

**(E)-5-hydroxy-4-methyl-1-phenyl-5-(2-thienyl)-1-penten-3-one (8)** Allenic alcohol **1** (100 mg, 0.62 mmol) and 2-thiophenecarboxaldehyde (83 mg, 0.75 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (30.5 mg, 0.034 mmol) in dichloromethane (0.27 mL). The mixture was stirred at room temperature for 36 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using EtOAc/petroleum ether (1/4) as the eluent to give **8** (0.145 mg, 86%) as a mixture of *syn*- and *anti*-isomers (68:32). *syn*-**8**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.61 (d,  $J = 16.1$  Hz, 1 H), 7.56 (m, 2 H), 7.40 (m, 3 H), 7.22 (m, 1 H), 6.97 (m, 2 H), 6.76 (d,  $J = 16.1$  Hz, 1 H), 5.40 (dd,  $J = 4.2, 2.6$  Hz, 1 H), 3.60 (m, OH), 3.26 (dq,  $J = 7.2, 4.2$  Hz, 1 H), 1.29 (d,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.9, 145.7, 143.9, 134.1, 130.8, 128.9, 128.4, 126.5, 124.5, 124.2, 123.5, 70.3, 50.9, 15.0. *anti*-**8**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (d,  $J = 16.1$  Hz, 1 H), 7.56 (m, 2 H), 7.40 (m, 3 H), 7.27 (dd,  $J = 3.8, 1.3$  Hz, 1 H), 7.01 (m, 1 H), 6.97 (m, 1 H), 6.83 (d,  $J = 16.1$  Hz, 1 H), 5.16 (dd,  $J = 7.9, 7.2$  Hz, 1 H), 3.49 (m, OH), 3.32 (dq,  $J = 7.9, 7.2$  Hz, 1 H), 1.14 (d,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.7, 146.2, 143.8, 134.2, 130.7, 128.9, 128.5, 126.5, 125.3, 124.9, 124.8, 72.5, 51.4, 11.5. IR ( $\text{CDCl}_3$ ): 3448, 3061, 2973, 2876, 1680, 1650, 1605, 1575, 1495, 1331, 1181, 1175, 1035  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}$ : C, 70.56; H, 5.92; Found: C, 70.41; H, 5.92.

**(E)-5-[1-(2,2-Dimethyl-propionyl)-1H-pyrrol-2-yl]-5-hydroxy-4-methyl-1-phenyl-pent-1-en-3-one (9)**. Allenic alcohol **1** (80.0 mg, 0.5 mmol) and 1-(2,2-Dimethyl-propionyl)-1H-pyrrole-2-carbaldehyde<sup>2</sup> (117.6 mg, 0.602 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (22.3 mg, 0.03 mmol) in of dichloromethane (0.2 ml). After 30 hours water (1 mL) was added and the aqueous layer was extracted with diethylether (3x 2 mL). The organic layer was then dried ( $\text{MgSO}_4$ ) and the solvent was evaporated in *vacuo*. The residue was purified by flash chromatography using pet.ether/ethyl acetate (gradient 10:1→4:1) to give **9** (156.8 mg, mmol, 88 %) as a mixture of *syn*- and *anti*-isomers (71:29). *Syn*-(**9**):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (d  $J = 16.0$  Hz, 1 H), 7.58-7.53 (m, 2 H), 7.41-7.39 (m, 3 H), 7.12 (m, 1 H), 6.74 (d,  $J = 16.0$  Hz, 1 H), 6.18 (m, 1 H), 6.05 (m,  $J = 3.3$  Hz, 1 H), 5.30 (dd,  $J = 7.2, 5.4$  Hz, 1 H), 4.06 (d,  $J = 5.4$  Hz, OH),

3.52 (app quintet,  $J = 7.2$  Hz, 1 H), 1.60 (s, 9 H), 1.32 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.1, 150.1, 143.0, 134.5, 130.5, 128.9, 128.3, 125.2, 121.9, 113.9, 112.9, 110.4, 84.5, 68.1, 47.8, 27.9, 13.2. *Anti*-(9):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63 (d,  $J = 16.1$  Hz, 1 H), 7.66-7.53 (m, 2 H), 7.41-7.39 (m, 3 H), 7.19-7.17 (m, 1 H), 6.50 (d,  $J = 16.1$  Hz, 1 H), 6.24 (m, 1 H), 6.11 (dd,  $J = 3.6, 3.0$  Hz, 1 H), 5.11 (app triplet,  $J = 8.8$  Hz, 1 H), 4.43 (d,  $J = 8.8$  Hz, OH), 3.61 (dq,  $J = 8.8, 7.2$  Hz, 1 H), 1.60 (s, 9 H), 1.06 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.8, 150.1, 143.1, 135.6, 130.4, 128.9, 128.5, 126.4, 122.4, 113.9, 112.9, 110.4, 84.8, 70.9, 47.8, 27.9, 15.29. IR (film): 3478 (s), 2978 (s), 2935 (m), 2875 (m), 1732 (s), 1688 (m), 1660 (m), 1608 (s), 1576 (m), 1495 (m), 1450 (s), 1337 (b), 1165 (m), 1129 (m), 864 (m)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{21}\text{H}_{25}\text{NO}_4$ : C, 70.96; H, 7.09; N, 3.94; Found: C, 70.85; H, 7.18; N, 3.85.

**(E)-5-hydroxy-4-methyl-1-phenyl-1-octen-3-one (10).** Allenic alcohol **1** (150 mg, 0.94 mmol) and butyraldehyde (81 mg, 1.12 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (50.1 mg, 0.056 mmol) in dichloromethane (0.37 mL). The mixture was stirred at room temperature for 48 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using  $\text{CHCl}_3$ /benzene/EtOAc/petroleum ether (0.5/0.5/1/8) as the eluent to give **10** (0.17 mg, 79 %) as a mixture of *syn*- and *anti*-isomers (78:22). *Syn*-**10**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (d,  $J = 15.9$  Hz, 1 H), 7.57 (m, 2 H), 7.40 (m, 3 H), 6.79 (d,  $J = 15.9$  Hz, 1 H), 4.01 (ddd,  $J = 8.4, 4.2, 3.1$  Hz, 1 H), 2.89 (dq,  $J = 7.2, 3.1$  Hz, 1 H), 2.65 (br s, OH), 1.52 (m, 2 H), 1.36 (m, 2 H), 1.22 (d,  $J = 7.2$  Hz, 3 H), 0.94 (t,  $J = 7.1$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.0, 143.6, 134.2, 130.7, 128.9, 128.4, 124.8, 70.8, 48.2, 36.3, 19.2, 14.0, 10.3. *Anti*-**10**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (d,  $J = 15.9$  Hz, 1 H), 7.57 (m, 2 H), 7.40 (m, 3 H), 6.79 (d,  $J = 15.9$  Hz, 1 H), 3.79 (m, 1 H), 2.97 (dq,  $J = 7.2, 6.1$  Hz, 1 H), 2.65 (br s, OH), 1.52 (m, 2 H), 1.36 (m, 2 H), 1.23 (d,  $J = 7.2$  Hz, 3 H), 0.93 (t,  $J = 7.1$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.0, 143.5, 134.2, 130.3, 128.9, 128.4, 125.5, 73.5, 49.2, 36.9, 18.9, 14.7, 10.3. IR (neat): 3448, 3065, 2959, 2933, 1680, 1648, 1606, 1575, 1450, 1331, 1184  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{15}\text{H}_{20}\text{O}_2$ : C, 77.55; H, 8.68; Found: C, 77.38; H, 8.61.

**(E)-5-hydroxy-4-methyl-1,6,6-triphenyl-1-hexen-3-one (11)** To a mixture of  $\text{VO}(\text{OSiPh}_3)_3$  (22.3 mg, 0.03 mmol) in dichloromethane (0.2 mL) was added diphenylacetaldehyde (117.0 mg, 0.60 mmol). The reaction mixture was stirred for one

hour then allenyl alcohol **1** (68.7 mg, 0.42 mmol) was added over a period of 6 h. The mixture was stirred at room temperature for an additional 48 h. The solution was poured into 5 ml of water and extracted with Et<sub>2</sub>O (3x5 mL). The combined organic layers were washed with saturated aqueous NaCl solution, dried over MgSO<sub>4</sub> and concentrated in *vacuo*. The residue was purified by flash chromatography using CDCl<sub>3</sub>/benzene/petroleum ether/ethyl acetat (0.5:0.5:8:1) to give **11** (106.2 mg, 71 %) as a mixture of *anti*- and *syn*-isomers (80:20). *Syn*-(**11**): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.51-7.18 (m, 16 H), 6.60 (d, *J* = 16.2 Hz, 1 H), 4.86 (dt, *J* = 9.7, 2.7 Hz, 1 H), 4.05 (d, *J* = 9.7 Hz, 1 H), 2.96 (d, *J* = 2.7 Hz, OH), 2.85 (dq, *J* = 6.9, 2.7 Hz, 1 H), 1.28 (d, *J* = 6.9 Hz, 3 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 204.3, 143.5, 141.8, 134.3, 130.8, 130.7, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 126.8, 126.6, 124.6, 72.8, 55.0, 45.5, 9.7. *Anti*-(**11**): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.52-7.22 (m, 16 H), 6.63 (d, *J* = 16.2 Hz, 1 H), 4.48 (dt, *J* = 8.7, 4.2 Hz, 1 H), 4.09 (d, *J* = 8.7 Hz, 1 H), 3.50 (d, *J* = 8.7 Hz, OH), 3.00 (dq, *J* = 7.5, 4.2 Hz, 1 H), 1.34 (d, *J* = 7.5 Hz, 3 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 205.8, 143.7, 142.5, 141.5, 134.2, 130.8, 129.0, 128.9, 128.7, 128.5, 128.4, 127.9, 126.8, 126.4, 125.7, 77.4, 56.3, 44.9, 15.1. IR (film): 3477 (s), 2988 (s), 2975 (s), 2875 (s), 1955 (s), 1888 (s), 1807 (s), 1673 (m), 1608 (s), 1450 (m), 1332 (m), 1187 (s) cm<sup>-1</sup>. Anal. Calcd. for C<sub>25</sub>H<sub>24</sub>O<sub>2</sub>: C, 84.24; H, 6.79; Found: C, 84.02; H, 6.79.

**(E)-1-Cyclohexyl-1-hydroxy-2-methyl-hex-4-en-3-one (12)** To a suspension of VO(OSiPh<sub>3</sub>)<sub>3</sub> (24.4 mg, 0.027 mmol) in dichloromethane (0.20 mL) was added cyclohexylcarboxyaldehyde (72.0 μl, 0.60 mmol) and allenyl alcohol (**1**) (76.1 mg, 0.47 mmol). Reaction mixture was stirred at room temperature for 48 h. The solution was poured into 5 ml of water and extracted with 3x5 ml of Et<sub>2</sub>O. The combined organic layers were washed with saturated aqueous NaCl solution, dried over MgSO<sub>4</sub> and concentrated in *vacuo*. The residue was purified by flash chromatography using petroleum ether/ethyl acetat (15:1) to give **12** (78.7 mg, 61 %) as a mixture of *syn*- and *anti*- isomers (66:33). *Syn*-(**12**): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.62 (d, *J* = 15.6 Hz, 1 H), 7.60-7.56 (m, 2 H), 7.42-7.40 (m, 3 H), 6.80 (d, *J* = 15.6 Hz, 1 H), 3.68 (app dt, *J* = 8.4, 2.7, 1 H), 3.06 (dq, *J* = 7.2, 2.7 Hz, 1 H), 3.01 (d, *J* = 2.7 Hz, OH), 2.10 (m, 1 H), 1.79-1.58 (m, 5 H), 1.30-1.12 (m, 5 H), 1.20 (d, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 205.1, 143.5, 134.3, 130.7, 128.9, 128.5, 124.7, 75.1, 45.2, 40.0, 29.4, 29.0,

26.4, 26.1, 25.8, 9.81. *Anti*-(**12**):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65-7.56 (m, 3 H), 7.43-7.34 (m, 3 H), 6.80 (d,  $J = 15.9$  Hz, 1 H), 3.50 (m, 1 H), 3.14 (dq,  $J = 7.2, 6.0$  Hz, 1 H), 2.90 (d,  $J = 8.1$  Hz, 1 H), 1.91 (m, 1 H) 1.79-1.62 (m, 5 H), 1.49-1.12 (m, 5 H), 1.25 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.1, 143.5, 133.3, 128.5, 127.9, 126.4, 120.0, 78.5, 45.5, 41.2, 30.2, 27.5, 26.4, 26.1, 25.8, 15.4. IR (film): 3456 (s), 2926 (s), 2852 (s), 1681 (m), 1651 (m), 1606 (s), 1576 (m), 1494 (m), 1450 (s), 1330 (m), 1184 (m), 1118 (s), 978.5 (m), 764 (m), 709 (m)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{24}\text{O}_2$ : C, 79.37; H, 8.88; Found: C, 79.50; H, 9.04.

**(*E*)-5-hydroxy-1,5-diphenyl-1-penten-3-one (13)** Allenic alcohol **5** (150 mg, 1.03 mmol) and benzaldehyde (130 mg, 1.23 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (45.8 mg, 0.051 mmol) in dichloromethane (0.41 mL). The mixture was stirred at room temperature for 48 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using EtOAc/petroleum ether (gradient 1/8 $\rightarrow$ 1/6) as the eluent to give **13** (220.1 mg 85 % yield) as a white solid mp = 49-51  $^\circ\text{C}$ . NMR data were in accordance with previously reported values<sup>12</sup>

**(*E*)-5-hydroxy-1,7-diphenyl-1-hepten-3-one (14)** Allenic alcohol **5** (150 mg, 1.03 mmol) and hydrocinnamaldehyde (165 mg, 1.23 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (45.8 mg, 0.051 mmol) in dichloromethane (0.41 mL). The mixture was stirred at room temperature for 40 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using EtOAc/petroleum ether (gradient 1/8 $\rightarrow$ 1/6) as the eluent to give **14** (201.6 mg 70 % yield) as a white solid mp = 83-85  $^\circ\text{C}$  (litt 82-83  $^\circ\text{C}$ ). NMR data were in accordance with previously reported values<sup>12</sup>

**(*E*)-5-hydroxy-5-(4-nitrophenyl)-1-phenyl-1-penten-3-onen (15)** Allenic alcohol **5** (100 mg, 0.69 mmol) and 4-nitrobenzaldehyde (124 mg, 0.82 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (30.5 mg, 0.034 mmol) in dichloromethane (0.27 mL). The mixture was stirred at room temperature for 36 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using EtOAc/petroleum ether (gradient 1/5) as the eluent to give **15** (169 mg 83 % yield) as a white solid (mp = 106-108  $^\circ\text{C}$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.24 (d,  $J = 8.8$  Hz, 2 H), 7.60 (d,  $J = 8.8$  Hz, 2 H), 7.59 (d,  $J = 16.3$  Hz, 1 H), 7.54 (m, 2 H), 7.42 (m, 3 H), 6.74 (d,  $J = 16.3$  Hz, 1 H), 5.39 (dt,  $J = 9.2, 3.1$  Hz, 1 H), 3.90 (d,  $J = 3.1$  Hz, OH), 3.13 (dd,  $J = 17.4, 3.1$  Hz, 1

H), 3.06 (dd,  $J = 17.4, 9.2$  Hz, 1 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.5, 150.1, 147.3, 144.6, 133.8, 131.1, 129.1, 128.5, 126.5, 125.7, 123.8, 69.2, 48.4. IR ( $\text{CDCl}_3$ ): 3436, 3026, 2928, 1677, 1627, 1606, 1577, 1520, 1348, 1103, 1065  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{17}\text{H}_{15}\text{NO}_4$ : C, 68.68; H, 5.09; N, 4.71; Found: C, 68.63; H, 5.03; N, 4.72

**(E)-5-hydroxy-5-(4-methoxyphenyl)-1-phenyl-1-penten-3-one (16)**

Allenic alcohol **5** (150 mg, 1.03 mmol) and anisaldehyde (167 mg, 1.23 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (45.8 mg, 0.051 mmol) in dichloromethane (0.41 mL). The mixture was stirred at room temperature for 40 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using EtOAc/petroleum ether (gradient 1/8 $\rightarrow$ 1/4) as the eluent to give **16** (183.8 mg, 64 % yield) as a white solid mp = 104–106 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.57 (d,  $J = 16.3$  Hz, 1 H), 7.54 (m, 2 H), 7.41 (m, 3 H), 7.35 (d,  $J = 8.7$  Hz, 2 H), 6.91 (d,  $J = 8.7$  Hz, 2 H), 6.73 (d,  $J = 16.3$  Hz, 1 H) 5.22 (ddd,  $J = 8.2, 3.9, 2.7$  Hz, 1 H), 3.81 (s, 3 H), 3.52 (d,  $J = 2.7$  Hz, OH), 3.11 (dd,  $J = 17.3, 8.2$  Hz, 1 H), 3.06 (dd,  $J = 17.3, 3.9$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  200.3, 159.1, 143.9, 135.1, 134.1, 130.8, 129.0, 128.4, 126.9, 126.2, 113.9, 69.8, 55.3, 48.8. IR ( $\text{CDCl}_3$ ): 3425, 2947, 2829, 1649, 1609, 1513, 1449, 1247, 1175, 1034.  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_3$ : C, 76.57; H, 6.43; Found: C, 76.70; H, 6.39.

**(E)-1-hydroxy-2,5-dimethyl-1-phenyl-4-hexen-3-one (18a).** Allenic alcohol **17a** (70 mg, 0.62 mmol) and benzaldehyde (79.5 mg, 0.75 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (27.8 mg, 0.031 mmol) in dichloromethane (0.25 mL). The mixture was stirred at room temperature for 36 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/EtOAc/ $\text{CHCl}_3$ /benzene (10:1:0.5:0.5) as the eluent to give **18a** (118 mg, 86%) as a mixture of *syn*- and *anti*-isomers (77:23). *Syn*-**18a**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32 (m, 4 H), 7.26 (m, 1 H), 6.09 (m, 1 H), 5.16 (d,  $J = 3.0$  Hz, 1 H), 3.22 (br s, OH) 2.77 (dq,  $J = 7.2, 3.0$  Hz, 1 H), 2.17 (d,  $J = 1.0$  Hz, 3 H), 1.91 (d,  $J = 1.0$  Hz, 3 H), 1.03 (d,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.6, 158.2, 141.9, 128.1, 127.0, 125.8, 122.9, 72.7, 52.5, 27.9, 21.0, 9.9. *Anti*-**18a**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33 (m, 4 H), 7.29 (m, 1 H), 6.11 (septet,  $J = 1.3$  Hz, 1 H), 4.79 (d,  $J = 8.0$  Hz, 1 H), 3.33 (br s, OH), 2.88 (dq,  $J = 8.0, 7.2$  Hz, 1 H), 2.17 (d,  $J = 1.3$  Hz, 3 H), 1.90 (d,  $J = 1.3$  Hz, 3 H), 0.96 (d,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.6, 157.5, 142.2, 128.3, 127.7, 126.6,

123.6, 76.5, 53.6, 27.9, 20.9, 14.6. IR (neat): 3456, 3030, 2935, 2876, 1675, 1615, 1551, 1379, 1232, 1204, 1105, 1028, 982  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{O}_2$ : C, 77.03; H, 8.31; Found: C, 76.87; H, 8.51.

**(E)-1-hydroxy-2-methyl-1-phenyl-4-octen-3-one (20)** Allenic alcohol **19** (73 mg, 0.57 mmol) and benzaldehyde (75.7 mg, 0.71 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (53.1 mg, 0.059 mmol) in dichloromethane (0.24 mL). The mixture was stirred at 60 °C for 24 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using  $\text{CHCl}_3$ /benzene/EtOAc/petroleum ether (0.5/0.5/1/30) as the eluent to give **20** (0.096 mg, 72%) as a mixture of *syn*- and *anti*-isomers (55:45). *syn*-**20**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35-7.32 (m, 5 H), 6.92 (dt,  $J$  = 15.8, 6.9 Hz, 1 H), 6.11 (d,  $J$  = 15.8, 1.6 Hz, 1 H) 5.12 (dd,  $J$  = 3.2, 1.8 Hz, 1 H), 3.32 (d,  $J$  = 1.8 Hz, OH), 3.05 (dq,  $J$  = 7.2, 3.2 Hz, 1 H), 2.20 (ddt,  $J$  = 7.2, 6.9, 1.6 Hz, 2 H), 1.48 (sextet,  $J$  = 7.2 Hz, 2 H), 0.97 (d,  $J$  = 7.2 Hz, 3 H), 0.93 (t,  $J$  = 7.2 Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.1, 149.1, 141.7, 130.1, 128.1, 127.7, 125.9, 72.9, 49.4, 34.5, 21.5, 13.7, 10.5. *anti*-**20**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35-7.32 (m, 5H), 6.90 (dt,  $J$  = 15.8, 6.9 Hz, 1H), 6.15 (d,  $J$  = 15.8, 1.6 Hz, 1H) 4.85 (dd,  $J$  = 7.9, 4.5 Hz, 1H), 3.17 (dq,  $J$  = 7.9, 7.2 Hz, 1H), 3.05 (d,  $J$  = 4.6 Hz, OH), 2.19 (ddt,  $J$  = 7.2, 6.9, 1.6 Hz, 2H), ) 1.48 (sextet,  $J$  = 7.2 Hz, 2H) 0.99 (d,  $J$  = 7.2 Hz, 3H), 0.93 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.4, 148.9, 142.1, 129.7, 128.3, 127.7, 126.5, 76.4, 50.2, 34.5, 21.5, 15.0, 13.7; IR ( $\text{CDCl}_3$ ): 3442, 3064, 2961, 2874, 1684, 1656, 1623, 1454, 1375, 1337, 1247, 1186, 1118, 1040  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{15}\text{H}_{20}\text{O}_2$ : C, 77.55; H, 6.68; Found: C, 77.78; H, 8.63.

**(E)-5-[hydroxy(phenyl)methyl]-2,6-dimethyl-2-hepten-4-one (18b)** Allenic alcohol **17b** (150 mg, 1.07 mmol) and benzaldehyde (136 mg, 1.29 mmol) was added to a solution of  $\text{VO}(\text{OSiPh}_3)_3$  (47.8 mg, 0.053 mmol) in dichloromethane (0.43 mL). The mixture was stirred at 35 °C for 28 hours. The solvent was removed in *vacuo* and the residue was purified by flash chromatography using petroleum ether/ $\text{Et}_2\text{O}$  (4:1) as the eluent to give **18b** as a mixture of *syn*- and *anti*-isomers (88:12). The mixture was then distilled (bulb to bulb distillation, (0.1 mm Hg, oven temp: 150-160 °C) to give **18b** in 57 % yield (0.151g). *Syn*-**18b**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43-7.18 (m, 5 H), 5.90 (septet,  $J$  = 1,3 Hz, 1 H), 5.04 (d,  $J$  = 6.5 Hz, 1 H), 2.85 (dd,  $J$  = 6.5, 4.4 Hz, 1 H), 2.75

(br s, OH) 2.22 (d septet,  $J = 7.0, 4.4$  Hz, 1 H), 2.00 (d,  $J = 1.3$  Hz, 3 H), 1.80 (d,  $J = 1.3$  Hz, 3 H), 1.00 (d,  $J = 7.0$  Hz, 3 H), 0.95 (d,  $J = 7.0$  Hz, 3 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.7, 155.5, 142.7, 128.1, 127.3, 126.4, 125.6, 73.4, 63.6, 27.6, 27.3, 22.5, 20.6, 19.1; **Anti-18b**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43-7.18 (m, 5H), 5.73 (septet,  $J = 1.3$  Hz, 1 H), 4.99 (d,  $J = 4.4$  Hz, 1 H), 2.65 (dd,  $J = 8.4, 4.4$  Hz, 1 H), 2.75 (br s, OH) 2.13 (m, 1 H), 2.01 (d,  $J = 1.3$  Hz, 3 H), 1.73 (d,  $J = 1.3$  Hz, 3 H), 1.10 (d,  $J = 7.0$  Hz, 3 H), 0.90 (d,  $J = 7.0$  Hz, 3 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.9, 155.5, 143.3, 128.1, 126.9, 126.5, 126.3, 73.1, 64.5, 28.9, 27.6, 21.1, 20.7, 20.6. IR (neat): 3443, 2960, 2873, 1575, 1615, 1493, 1447, 1383, 1281, 1203, 1133, 1040  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_2$ : C, 78.01; H, 9.00; Found: C, 77.86; H, 8.89.

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