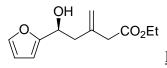
## **Experimental Section**

All reactions were carried out under an atmosphere of nitrogen. Glassware for all reactions was oven dried at 125 °C and cooled in a desiccator prior to use. Liquid reagents and solvents were introduced by oven dried syringes or cannulas through septa sealed flasks under a nitrogen atmosphere. Solvents were purified according to the guidelines in Purification of Common Laboratory Chemicals (Perrin, Armoarego, and Perrin, Pergomon; Oxford, 1966). Yields were calculated for material judged homogenous by thin layer chromatography and NMR. Thin layer chromatography was performed on Merck Kieselgel 60  $F_{254}$  plates eluting with the solvents indicated, visualized by a 254 nm UV lamp, and stained with a ethanolic solution of 12molybdophosphoric acid or potassium permanganate. Flash column chromatography was performed with Davisil 62 silica gel, slurry packed with the eluting solvent indicated. Nuclear magnetic resonance spectra were acquired at 300 MHz for <sup>1</sup>H, and 75 MHz for <sup>13</sup>C. Chemical shifts for proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra are reported in parts per million in reference to the singlet of CHCl<sub>3</sub> at 7.26 ppm. Chemical shifts for carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra are reported in parts per million in reference to the center line of the triplet of  $CDCl_3$  at 77.23 ppm. The abbreviations s, d, t, q, brs, and appt. s, stand for the resonance multiplicities singlet, doublet, triplet, quartet, broad singlet, and apparent singlet respectively. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. Optical rotations were obtained using a micro cell with a 1 dm path length. Concentrations are reported in g / 100 ml. For the determination of the enantiomeric excess of UV active samples, analysis was accomplished by HPLC using a 25 cm CHIRACEL OD-H column and isopropanol / hexanes as the mobile phase with a UV detector. The enantiomeric excess for non-UV active samples was determined by conversion to the Mosher MTPA ester, followed by <sup>19</sup>F NMR, <sup>1</sup>H NMR measurement. Analysis of samples using both HPLC and <sup>19</sup>F NMR of the derived Mosher ester gave results within experimental error of one another.

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 $\$  SnBu<sub>3</sub> <u>Preparation of Ethyl 3-(2,2-dibutyl-2-stannahexyl)but-3-enoate (6)</u>: A solution of 3-tributylstannyl-2-[(tributylstannyl)methyl]propene (10.0 g, 15.8 mmol) in 60 ml of freshly distilled ethylchloroformate was heated at reflux for 7 h, then cooled to rt and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel column (5 × 25 cm) which was slurry packed with 1% Et<sub>3</sub>N / EtOAc and flushed with 150 ml hexane prior to use. Elution with 2% EtOAc / hexane gave 4.5 g (68%) of **6** as a colorless liquid: R<sub>f</sub> 0.36 (5% EtOAc / hexane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.69 (appt. s with Sn satellites, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 2.94 (appt. s with Sn satellites, 2H), 1.85 (appt. s with Sn satellites, 2H), 1.62-1.42 (m, 6H), 1.36-1.22 (m, 9H), 1.00-0.75 (m, 15H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 171.7, 143.1, 109.2, 60.8, 44.3, 29.3, 27.6, 19.2, 14.4, 13.9, 9.7; IR (neat) 1739, 1630, 1461 cm<sup>-1</sup>; Anal. Calcd for C<sub>19</sub>H<sub>36</sub>O<sub>2</sub>Sn: C, 54.70; H, 9.18. Found: C, 54.88; H, 9.02.

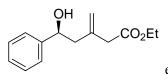
Representative experimental procedure for the reaction of aldehydes with ethyl 3-(2,2dibutyl-2-stannahexyl)but-3-enoate (6)using method B catalyst



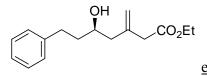
## Preparation of ethyl 3-((2S)-2-cyclopenta-1,3-dienyl-2-

hydroxyethyl)but-3-enoate (12): A mixture of S-(-)-1,1'-binaphthol (115 mg, 0.401 mmol), 1M Ti(O-i-Pr)<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> (0.20 ml, 0.20 mmol), 0.1M CF<sub>3</sub>CO<sub>2</sub>H in CH<sub>2</sub>Cl<sub>2</sub> (60  $\mu$ l, 6.0 × 10<sup>-3</sup> mmol), and oven-dried 4Å molecular sieves (1.50 g) in 15 ml of CH<sub>2</sub>Cl<sub>2</sub> was heated at reflux for 1 h. The resulting red-brown mixture was cooled to rt and 2furylaldehyde (192 mg, 2.00 mmol) was added. This mixture was stirred at rt for 10 min before it was cooled to -78 °C and ethyl 3-(2,2-dibutyl-2-stannahexyl)but-3-enoate (1.67 g, 4.00 mmol) was then added. The reaction flask was then placed in a -20 °C freezer for 72 h without stirring. The resulting mixture was quenched by the addition of 10 ml of saturated NaHCO<sub>3</sub> solution and stirred for 5 min at rt, then filtered through a plug of Celite. The filtrate was diluted with 200 ml of CH<sub>2</sub>Cl<sub>2</sub> and washed with 100 ml of water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The residue was purified by flash chromatography on a silica gel column ( $2.8 \times 25$  cm), eluting with acetone / EtOAc / hexane (1.5:1:10) to give 448 mg (100%) of the product as a colorless oil. The enantiomeric excess was determined to be 99% by conversion to the Mosher MTPA ester, and <sup>19</sup>F NMR measurement.  $R_f$  0.13 (20% EtOAc / hexane);  $[\alpha]_D^{24} = -31.8$ (c 2.32, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (dd, J = 2.0, 0.7 Hz, 1H), 6.32 (dd, J = 3.2, 2.0 Hz, 1H), 6.26 (ddd, J = 3.2, 0.7, 0.7 Hz, 1H), 5.11 (dd, J = 1.0, 1.0 Hz, 1H), 5.07 (dd, J = 1.0, 1.0 Hz, 1H), 4.85 (dd, J = 7.8, 5.9 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.12 (dd, J = 15.9, 1.0 Hz, 1 H), 3.05 (dd, J = 15.6, 1.0 Hz, 1H), 2.72-2.60 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  172.1, 156.1, 142.1, 138.4, 118.4,

110.4, 106.2, 65.0, 61.6, 42.8, 41.8, 14.3; IR (neat) 3250 (br), 3081, 1732, 1650, 1501, cm<sup>-1</sup>; Anal. Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>: C, 64.27; H, 7.19. Found: C, 64.18; H, 7.21.

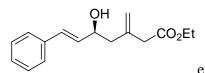


ethyl 3-((2S)-2-hydroxy-2-phenylethyl)but-3-enoate:  $R_f 0.19$ (20% EtOAc / hexane);  $[\alpha]_D^{23.5} = -45.0$  (c 2.64, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ 7.40-7.23 (m, 5H), 5.12 (d, J = 1.0 Hz, 1H), 5.09 (d, J = 0.7 Hz, 1H), 4.83 (ddd, J = 9.0, 4.2, 2.2 Hz, 1 H), 4.16 (q, J = 7.1 Hz, 2H), 3.16 (dd, J = 15.6, 0.7 Hz, 1 H), 3.09 (dd, J =15.6, 0.7 Hz, 1H), 2.64 (brd, J = 2.3 Hz, 1H), 2.56 (ddd, J = 14.4, 4.4, 1.0 Hz, 1H), 2.49 (ddd, J = 14.4, 9.3, 0.7 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ 172.0, 144.1, 139.1, 128.5, 127.6, 125.8, 118.1, 71.9, 61.1, 46.8, 41.9, 14.3; IR (neat) 3440 (br), 1733, 1648, 1493 cm<sup>-1</sup>; Anal. Calcd for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>: C, 71.77; H, 7.74. Found: C, 71.67; H, 7.72.



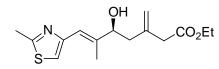
ethyl 3-((2R)-2-hydroxy-4-phenylbutyl)but-3-enoate: R<sub>f</sub>

0.16 (20% EtOAc / hexane);  $[\alpha]_D^{22} = +15.7$  (c 1.50, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.31-7.15 (m, 5H), 5.08 (d, J = 0.7 Hz, 1H), 5.06 (s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.78-3.66 (m, 1H), 3.12 (d, J = 15.4 Hz, 1H), 3.02 (d, J = 15.5 Hz, 1H), 2.82 (ddd, J = 13.7, 9.3, 6.6 Hz, 1H), 2.70 (ddd, J = 13.7, 9.3, 7.3 Hz, 1H), 2.39-2.31 (m, 2H), 2.20 (ddd, J = 14.2, 9.5, 0.7 Hz, 1H), 1.84-1.73 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  172.2, 142.3, 139.4, 128.7, 128.6, 126.0, 118.1, 68.5, 61.2, 45.2, 41.9, 39.0, 32.3, 14.4; IR (neat) 3402 (br), 1733, 1648, 1603, 1495 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>22</sub>O<sub>3</sub>: C, 73.25; H, 8.45. Found: C, 73.01; H, 8.36.

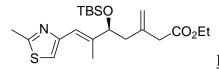


ethyl (6E)(5S)-5-hydroxy-3-methylene-7-phenylhept-6enoate:  $R_f 0.13 (20\% EtOAc / hexane); [\alpha]_D^{23} = +17.8 (c 1.97, CHCl_3); {}^{1}H NMR (300 MHz, CDCl_3) \delta 7.40-7.19 (m, 5H), 6.64 (dd,$ *J*= 15.9, 1.2 Hz, 1H), 6.23 (dd,*J*= 15.9, 5.9 Hz, 1H), 5.13 (dd,*J*= 1.0, 1.0 Hz, 1H), 5.09 (dd,*J*= 1.0, 1.0 Hz, 1H), 4.50-4.40 (m, 1H), 4.16 (q,*J*= 7.1 Hz, 2H), 3.18 (dd, J = 15.6, 0.7 Hz, 1H), 3.11 (dd,*J*= 15.6, 0.7 Hz, 1H), 2.50 (ddd,*J*= 14.4, 4.4, 0.7 Hz, 1H), 2.43 (brs, 1H), 2.39 (ddd,*J*= 14.4, 8.8, 0.7 Hz, 1H), 1.26 (t,*J* $= 7.1 Hz, 3H); {}^{13}C NMR (75 MHz, CDCl_3) \delta 172.0, 138.7, 136.8, 131.6, 130.2, 128.7, 127.7, 126.6, 118.3, 70.4, 61.1, 44.8, 42.0, 14.3; IR (neat) 3517 (br), 1734, 1649, 1493 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>: C, 73.82; H, 7.74. Found: C, 73.55; H, 7.86.$ 

Bn  $O_{2}^{\text{O}}$   $CO_{2}^{\text{Et}}$  ethyl 3-((2S)-2-hydroxy-3-phenoxypropyl)but-3-enoate: R<sub>f</sub> 0.34 (EtOAc / hexane: 40%);  $[\alpha]_{D}^{22} = +2.2$  (c 1.24, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.39-7.26 (m, 5H), 5.05 (d, J = 1.0 Hz, 1H), 5.02 (brs, 1H), 4.55 (s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 4.03-3.92 (m, 1H), 3.50 (dd, J = 9.5, 3.7 Hz, 1H), 3.40 (dd, J = 9.5, 7.1 Hz, 1H), 3.14 (dd, J = 15.6, 0.7 Hz, 1H), 3.08 (dd, J = 15.6, 0.7 Hz, 1H), 2.67 (d, J =3.4 Hz, 1H), 2.34 (dd, J = 14.4, 4.4 Hz, 1H), 2.26 (ddd, J = 14.4, 8.6, 0.7 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.9, 139.0, 138.1, 128.6, 127.9 (two peaks), 117.3, 74.2, 73.5, 68.6, 60.9, 41.9, 40.4, 14.3; IR (neat) 3316 (br), 1733, 1648, 1452 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>22</sub>NO<sub>4</sub>: C, 69.04; H, 7.97. Found: C, 69.16, H, 8.00.



thiazol-4-yl))-3-methylenehept-6-enoate (**8**):  $R_f 0.10$  (Acetone / EtOAc / hexane: 1:1:8); [ $\alpha$ ]  $_D^{23} = -15.8$  (c 1.24, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.93 (s, 1H), 6.58 (s, 1H), 5.10 (d, J = 0.7 Hz, 1H), 5.06 (brs, 1H), 4.29 (ddd, J = 9.3, 3.2, 2.7 Hz, 1H), 4.15 (q, J =7.1 Hz, 2H), 3.17 (dd, J = 15.6, 0.7 Hz, 1H), 3.10 (dd, J = 15.6, 0.7 Hz, 1H), 2.70 (s, 3H), 2.60 (brs, 1H), 2.50 (dd, J = 13.7, 3.2 Hz, 1H), 2.36 (ddd, J = 14.2, 9.3, 0.7 Hz, 1H), 2.04 (d, J = 1.3 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  172.0, 164.7, 153.1, 141.6, 139.3, 119.0, 117.8, 115.8, 75.3, 61.1, 43.0, 42.0, 19.4, 14.7, 14.4; IR (neat) 3279 (br),1733, 1647, 1506 cm<sup>-1</sup>; Anal. Calcd for C<sub>15</sub>H<sub>21</sub>NO<sub>3</sub>S: C, 60.99; H, 7.17; N, 4.74. Found: C, 60.83; H, 7.26; N, 4.67.

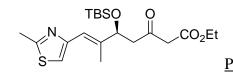


Preparation of ethyl (6E)(5S)-6-methyl-7-(2-methyl(1,3-

ethyl (6E)(5S)-5-hydroxy-6-methyl-7-(2-methyl(1,3-

<u>thiazol-4-yl))-3-methylene-5-(1,1,2,2-tetramethyl-1-silapropoxy)hept-6-enoate (9)</u>: To a solution of alcohol **8** (321 mg, 1.09 mmol) in 2.4 ml of DMF, was added imidazole (148 mg, 2.18 mmol), followed by *tert*-butyldimethylchlorosilane (247 mg, 1.63 mmol). The resulting mixture was stirred at rt for 2 h, then diluted with 100 ml of 70% EtOAc /

hexane and washed with water (2 × 100 ml). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The residue was purified by flash chromatography on a silica gel column (1.3 × 30 cm), eluting with 10% EtOAc / hexane to give 429 mg (96%) of **9** as a colorless oil:  $R_f 0.40$  (20% EtOAc / hexane);  $[\alpha]_D^{23.5} = +2.3$  (c 1.71, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.93 (s, 1H), 6.48 (s, 1H), 4.97 (s, 2H), 4.27 (dd, J = 6.8, 6.0 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.10 (s, 2H), 2.71 (s, 3H), 2.42 (dd, J = 13.9, 6.5 Hz, 1H), 2.37 (dd, J = 13.9, 5.5 Hz, 1H), 2.01 (d, J = 0.8 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 164.6, 153.2, 142.1, 139.5, 119.3, 117.0, 115.4, 78.0, 60.8, 43.3, 42.4, 26.0, 19.4, 18.4, 14.4, 14.1, -4.4, -4.9; IR (neat) 1736, 1649, 1505 cm<sup>-1</sup>; Anal. Calcd for C<sub>21</sub>H<sub>35</sub>NO<sub>3</sub>SSi: C, 61.57; H, 8.61; N, 3.42. Found: C, 61.36; H, 8.56; N, 3.48.



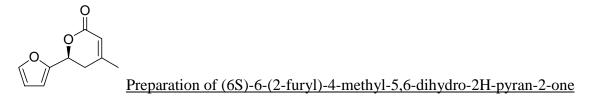
thiazol-4-yl))-3-oxo-5-(1,1,2,2-tetramethyl-1-silapropoxy)hept-6-enoate (**10**): To a stirring solution of olefin **9** (200 mg, 0.49 mmol) and 4-methylmorpholine N-oxide (57 mg, 0.49 mmol) in 10 ml of THF / t-BuOH / H<sub>2</sub>O (5:5:1), maintained at 0 °C. was added OsO<sub>4</sub> solution (4% wt in THF, 0.35 ml, 0.049 mmol). The reaction mixture was stirred at 0 °C for 14 h. It was then diluted with 10 ml of THF / H<sub>2</sub>O (3:2) and NaIO<sub>4</sub> (1.03 g, 4.9 mmol) was added. The resulting mixture was stirred at 0 °C for 2 h and then filtered. The filtrate was diluted with 70% EtOAc / hexane (80 ml), then washed with 5% NaHSO<sub>3</sub> aqueous solution (80 ml) and brine (50 ml). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The residue was purified by flash

chromatography on a silica gel column (1.3 × 30 cm), eluting with 15% EtOAc / hexane to give 160 mg (80%) of **10** as a colorless oil:  $R_f 0.19$  (15% EtOAc / hexane); [α]  $D^{22.5}_{D} = -$ 44.4 (c 1.27, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.92 (s, 1H), 6.52 (s, 1H), 4.65 (dd, J = 9.0, 3.2 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.49 (s, 2H), 2.91 (dd, J = 14.9, 9.0 Hz, 1H), 2.70 (s, 3H), 2.57 (dd, J = 14.9, 3.4 Hz, 1H), 2.02 (d, J = 1.0 Hz, 3H), 1.25 (t, J =7.1 Hz, 3H), 0.86 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 201.5, 167.2, 164.8, 152.9, 140.9, 119.5, 116.0, 75.2, 61.5, 51.2, 49.9, 26.0, 19.4, 18.3, 14.3, 14.2, -4.5, -5.1. IR (neat) 3434,1747, 1719, 1651, 1504 cm<sup>-1</sup>; Anal. Calcd for  $C_{20}H_{33}NO_4SSi:$  C, 58.36; H, 8.08; N, 3.40. Found: C, 58.41; H, 7.98; N, 3.41. A very minor set of signals resulting from the tautomeric form of the β-ketoester were also detected by both proton and carbon NMR spectroscopy but are not reported here due to the complexity of the spectrum and an insufficient signal / noise ratio.

<u>1-silapropoxy)ethyl]but-3-enoate (15)</u>: To a solution of alcohol **12** (302 mg, 1.35 mmol) in 1 ml of DMF, was added imidazole (186 mg, 2.70 mmol), followed by *tert*butyldimethylchlorosilane (264 mg, 1.75 mmol). The resulting mixture was stirred at rt for 10 h, then diluted with 70 ml of 70% EtOAc / hexane and washed with water (2 × 70 ml). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The residue was purified by flash chromatography on a silica gel column (1.3 × 30 cm), eluting with 10% EtOAc / hexane to give 410 mg (90%) of **15** as a colorless oil:  $R_f$  0.32 (5% EtOAc / hexane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (dd, *J* = 1.9, 0.7 Hz, 1H), 6.28 (dd, J = 3.2, 1.9 Hz, 1H), 6.17 (ddd, J = 3.2, 0.5, 0.5 Hz, 1H), 4.95-4.93 (m, 2H), 4.83 (dd, J = 6.6, 6.6 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.02 (s, 2H), 2.63 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 0.85 (s, 9H), 0.03 (s, 3H), -0.10 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.6, 156.7, 141.5, 139.0, 117.2, 110.2, 106.3, 67.8, 60.8, 43.3, 42.3, 25.9, 18.4, 14.4, -4.8, -5.0.

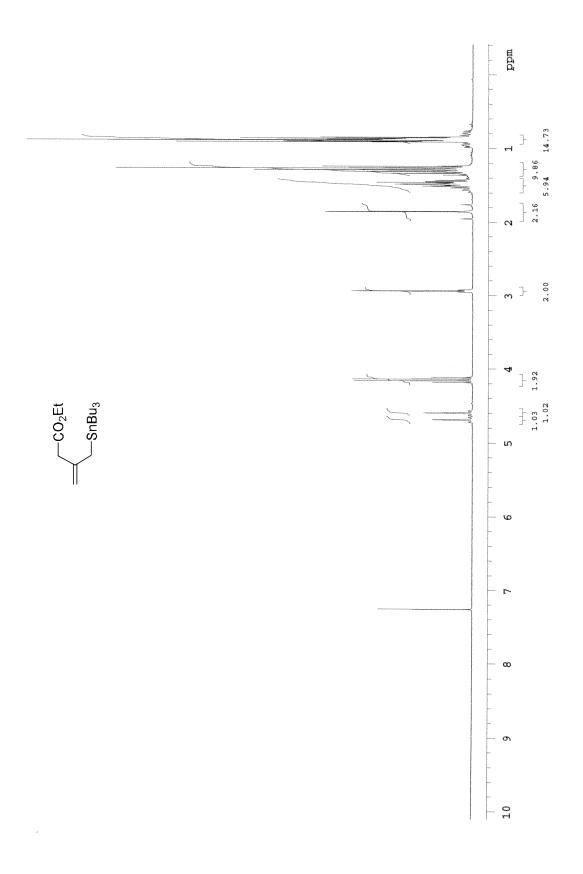
## Preparation of ethyl (2E)(5S)-5-(2-furyl)-3-methyl-5-(1,1,2,2-

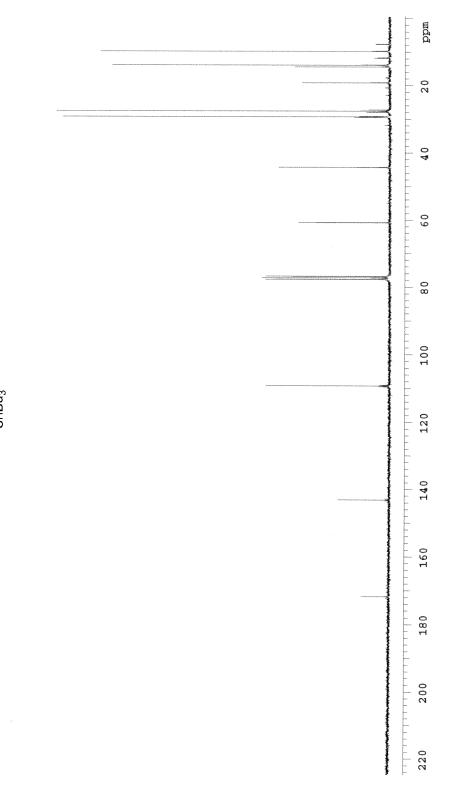
tetramethyl-1-silapropoxy)pent-2-enoate (14): To a solution of 15 (123 mg, 0.364 mmol) in 6 ml of THF was added NaH (8.6 mg, 0.36 mmol). The reaction mixture was stirred at rt for 6h, then diluted with 60 ml of 50% EtOAc / hexane and washed with water (2 × 20 ml). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The residue was purified by flash chromatography on a silica gel column (1.3 × 30 cm), eluting with 5% EtOAc / hexane to give 114 mg (93%) of 14 as a colorless oil:  $R_f$  0.37 (5% EtOAc / hexane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34 (dd, *J* = 2.0, 0.8 Hz, 1H), 6.29 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.17 (ddd, *J* = 3.2, 0.7, 0.7 Hz, 1H), 5.71-5.67 (m, 1H), 4.84 (dd, *J* = 8.1, 5.1 Hz, 1H), 4.21-4.05 (m, 2H), 2.63 (ddd, *J* = 13.2, 8.1, 1.0 Hz, 1H), 2.54 (ddd, *J* = 13.2, 5.1, 0.7 Hz, 1H), 2.15 (d, *J* = 1.2 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.84 (s, 9H), 0.01 (s, 3H), -0.11 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 166.7, 156.4, 155.6, 141.7, 118.9, 110.3, 106.3, 67.2, 59.6, 48.5, 25.9, 19.3, 18.3, 14.5, -4.8, -5.1.



(13): To a solution of alcohol 12 (27 mg, 0.12 mmol) in 1.5 ml of MeOH, was added

Na2CO3 (29 mg, 0.27 mmol). The reaction mixture was stirred at rt for 1h, then diluted with 30 ml of 50% EtOAc / hexane and washed with water (10 ml) and brine (10 ml). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated. The residue was purified by flash chromatography on a silica gel column ( $1.3 \times 30$  cm), eluting with 25% EtOAc / hexane to give 20 mg (85%) of **13** as a colorless oil: R<sub>f</sub> 0.20 (30% EtOAc / hexane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (dd, J = 1.7, 0.7 Hz, 1H), 6.43 (dd, J = 3.3, 0.7, 0.7 Hz, 1H), 6.37 (dd, J = 3.2, 1.8 Hz, 1H), 5.89-5.86 (m, 1H), 5.45 (dd, J = 11.2, 4.4 Hz, 1H), 2.96-2.84 (m, 1H), 2.50 (dd, J = 17.8, 4.4 Hz, 1H), 2.04 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  164.3, 156.9, 150.9, 143.2, 116.8, 110.7, 109.0, 72.0, 33.0, 23.2.





CO2Et

