### **Supporting Information**

### An Expedient Enantioselective Synthesis of the $\Delta^4$ -Oxocene Cores of (+)-Laurencin and (+)-Prelaureatin

Jim Li\*, Judy M. Suh and Elbert Chin

Department of Medicinal Chemistry, Roche Palo Alto LLC, 3431 Hillview Avenue, Palo Alto, CA 94034

jim.li@roche.com

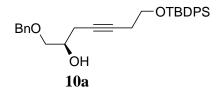
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**1. General materials and methods.** Infrared (IR) spectra were obtained using Thermo-Nicolet 6700 infrared spectrometer. Proton and carbon nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR) spectra were recorded on the following instruments: Bruker model Avance-III (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz), Bruker model Avance (<sup>1</sup>H at 400 MHz, <sup>13</sup>C at 100 MHz), and Bruker model Avance-III (<sup>1</sup>H at 300 MHz, <sup>13</sup>C at 75 MHz). Optical rotations were determined using a Perkin-Elmer 341 polarimeter. High resolution mass spectroscopic data were obtained in ESI mode using Thermo LTQ Orbitrap. All chemicals and solvents were purchased from commercial sources and used directly without further treatment.

### 2. Synthesis and characterization

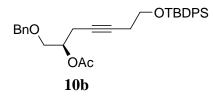
(R)-1-Benzyloxy-7-[(tert-butyldiphenylsilyl)oxy]-hept-4-yn-2-ol (10a)



To a solution of propargyl alkyne **9** (18.79 g, 60.90 mmol) in THF (200 mL) at -78 °C was added a solution of n-BuLi (1.6 M in THF, 16.95 mL, 60.90 mmol) dropwise. The mixture was stirred at -78 °C for 15 min and followed by addition of BF<sub>3</sub>•OEt<sub>2</sub> (7.49 mL, 60.90 mmol). The resulting mixture was stirred for 10 min and followed by addition of a solution of (-)–(*R*)–benzyl glyosidic ether **8** (5.00 g, 30.45 mmol). The reaction mixture was stirred further at -78 °C for 1 h before it was quenched with saturated aq. NH<sub>4</sub>Cl solution. The reaction mixture was allowed to warm to room temperature and diluted with ether. The organic layer was separated, washed with H<sub>2</sub>O, brine, dried over MgSO<sub>4</sub>, and concentrated. The crude residue was purified by flash column chromatography on silica gel (10 – 20% EtOAc in hexanes) to afford the product **10a** (12.09 g, 84% yield) as a colorless oil:

 $[\alpha]_{D}^{25} = -7.0 \ (c \ 7.02, \ CHCl_3); \ ^1H \ NMR \ (400 \ MHz, \ CDCl_3) \ \delta \ 7.69 - 7.65 \ (m, \ 4 \ H), \ 7.45 - 7.25 \ (m, \ 11 \ H), \ 4.52 \ (s, \ 2 \ H), \ 3.92 - 3.85 \ (m, \ 1 \ H), \ 3.73 \ (t, \ J = 7 \ Hz, \ 2 \ H), \ 3.57 \ (dd, \ J = 4, \ 9 \ Hz, \ 1 \ H), \ 3.46 \ (dd, \ J = 4, \ 9 \ Hz, \ 1 \ H), \ 2.47 - 2.35 \ (m, \ 5 \ H), \ 1.05 \ (s, \ 9 \ H); \ IR \ (neat) \ 3447, \ 3069, \ 2931, \ 2857, \ 1738, \ 1472, \ 1454, \ 1389, \ 1362, \ 1243, \ 1029, \ 941, \ 823 \ cm^{-1}; \ HRMS \ (EI) \ calcd \ for \ C_{30}H_{36}O_3Si \ [M + Na^+] \ 495.2326 \ found \ 495.2320.$ 

#### 2-Acetyloxy-(*R*)-1-benzyloxy-7-[(*tert*-butyldiphenylsilyl)oxy]-hept-4-yne (10b)



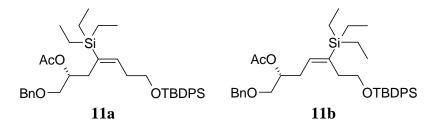
To a solution of propargyl alcohol **10a** (6.70 g, 14.17 mmol) in  $CH_2Cl_2$  (100 mL) at 0 °C was added  $Et_3N$  (4.98 mL, 35.43 mmol) and 4-DMAP (5 mg, 0.04 mmol), followed by the dropwise addition of Ac<sub>2</sub>O (1.47 mL, 15.59 mmol). The reaction was stirred from 0 °C to room temperature over 24 h before it was quenched with saturated aq. NH<sub>4</sub>Cl solution. The reaction mixture was diluted with ether. The organic layer was separated, washed with H<sub>2</sub>O, brine, dried over MgSO<sub>4</sub>, and concentrated. The crude residue was purified by flash column chromatography on silica gel (10 – 20% EtOAc in hexanes) to afford the product **10b** (5.82 g, 80% yield) as a colorless oil:

 $[α]^{25}{}_{D} = -12.2$  (*c* 7.85, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.68 – 7.66 (m, 4 H), 7.44 – 7.35 (m, 6 H), 7.33 – 7.23 (m, 4 H), 5.30 – 5.00 (m, 1 H), 4.52 (dd, *J* = 12.1, 8.2 Hz, 2 H), 3.73 (t, *J* = 11.3 Hz, 2 H), 3.61 (d, *J* = 2.4 Hz, 2 H), 2.57 – 2.43 (m, 2 H), 2.41 – 2.36 (m, 2 H), 2.10 (s, 3 H), 2.03 (s, 9 H) ; <sup>13</sup>C NMR (100 Mz, CDCl<sub>3</sub>) δ 170.8, 138.5, 138.4, 134.1, 130.1, 128.8, 128.1, 128.0, 79.7, 77.6, 76.5, 73.6, 71.5, 70.0, 63.1, 27.2, 23.3, 21.5, 21.5, 19.6; IR (neat) 3070, 3030, 2931, 2858, 1740, 1589, 1496, 1472, 1454, 1428, 1373, 1237, 1110, 1057, 1028, 960, 916, 823, 737 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>32</sub>H<sub>38</sub>O<sub>4</sub>Si [M + Na<sup>+</sup>] 537.2432 found 537.2421.

# 2-Acetyloxy-(*E*,*R*)-1-Benzyloxy-7-[(*tert*-butyldiphenylsilyl)oxy]-4-triethylsilyl-hept-4-ene (11a)

#### and

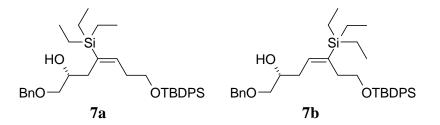
2-Acetyloxy-(*R*,*E*)-1-Benzyloxy-7-[(*tert*-butyldiphenylsilyl)oxy]-5-triethylsilyl-hept-4-ene (11b)



To a flask containing alkyne **10b** (9.80 g, 20.98 mmol) and Et<sub>3</sub>SiH (4.02 mL, 25.18 mmol) at room temperature was added H<sub>2</sub>PtCl<sub>6</sub>•H<sub>2</sub>O catalyst (52 mg, 0.12 mmol). The resulting mixture was heated at 80 °C for 40 min before it was cooled to room temperature and purified by flash column chromatography on silica gel (1 – 2% EtOAc in hexanes) to provide a mixture of products (13.08 g, 99% yield, **11a** : **11b** = 1.8 : 1) as colorless oils. This mixture was used directly in the next step.

## (*R*,*E*)-1-Benzyloxy-7-[(*tert*-butyldiphenylsilyl)oxy]-5-triethylsilyl-hex-4-en-2-ol (7a) and

(*R*,*E*)-1-Benzyloxy-7-[(*tert*-butyldiphenylsilyl)oxy]-4-triethylsilyl-hex-4-en-2-ol (7b)



To a solution of acetates **11a** and **11b** (5.98 g, 9.48 mmol) in  $CH_2Cl_2$  (100 mL) at -78 °C was added dropwise a solution of DIBAL-H (1.0 M in toluene, 14.22 mL, 1.50 mmol). The reaction was stirred at the same temperature for 1 h before it was quenched with *i*-

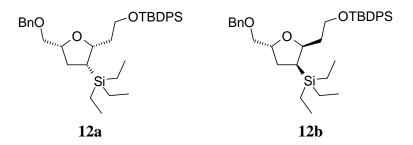
PrOH. The reaction mixture was diluted with EtOAc and 25% aq. Rocelle's salt solution and stirred at room temperature over a period of 3 h. The organic layer was separated, washed with H<sub>2</sub>O, brine, dried over MgSO<sub>4</sub> and concentrated. The crude residue was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to provide a regioisomeric mixture of alcohols **7a** and **7b** (5.26 g, 94% yield, **7a** : **7b** = 1.8 : 1) as a colorless oil. A portion of this product mixture was re-purified using the same condition above to give **7a** first and then the more polar **7b**:

**7a**:  $[\alpha]_{D}^{25} = 8.8 \ (c \ 9.72, \ CHCl_3); {}^{1}H \ NMR \ (400 \ MHz, \ CDCl_3) \ \delta \ 7.68 - 7.66 \ (m, 4 \ H), 7.43 - 7.26 \ (m, 11 \ H), 5.98 \ (t, J = 6.8 \ Hz, 1 \ H), 4.54 \ (dd, J = 17.5, 5.6 \ Hz, 2 \ H), 3.84 - 3.77 \ (m, 1 \ H), 3.69 \ (t, J = 6.3 \ Hz, 2 \ H), 3.48 - 3.35 \ (m, 2 \ H), 2.55 - 2.41 \ (1 \ H), 2.40 - 2.26 \ (m, 3 \ H), 1.04 \ (s, 9 \ H), 0.91 \ (t, J = 7.9 \ Hz, 9 \ H), 0.58 \ (q, J = 3.8 \ Hz, 6 \ H); {}^{13}C \ NMR \ (100 \ Mz, \ CDCl_3) \ \delta \ 141.9, 138.6, 136.0, 135.8, 134.2, 130.0, 128.8, 128.1, 128.1, 128.0, 74.6, 73.8, 70.5, 63.8, 34.6, 32.7, 27.2, 19.5, 7.8, 3.7; \ IR \ (neat) \ 3584, 3463, 3070, 2953, 2872, 1608, 1589, 1496, 1472, 1456, 1388, 1237, 1007, 939, 823 \ cm^{-1}; \ HRMS \ (EI) \ calcd for C_{36}H_{52}O_3Si_2 \ [M + H] \ 589.3527 \ found \ 589.3533.$ 

**7b**:  $[\alpha]_{D}^{25} = -3.1 (c \ 11.70, CHCl_3)$ ; <sup>1</sup>H NMR (400 MHz, CDCl\_3)  $\delta$  7.68 – 7.63 (m, 4 H), 7.42 – 7.27 (m, 11 H), 5.73 (t, *J* = 6.9 Hz, 1 H), 4.51 (s, 2 H), 3.80 – 3.71 (m, 1 H), 3.52 – 3.43 (m, 2 H), 3.37 (dd, *J* = 9.5, 3.2 Hz, 1 H), 3.24 (dd, *J* = 9.4, 7.6 Hz, 1 H), 2.38 (t, *J* = 8.3 Hz, 1 H), 2.21 – 2.15 (m, 3 H), 1.04 (s, 9 H), 0.0.80 (t, *J* = 7.9 Hz, 9 H), 0.43 (q, *J* = 3.8 Hz, 6 H); <sup>13</sup>C NMR (100 Mz, CDCl\_3)  $\delta$  139.1, 138.4, 136.4, 136.0, 134.4, 130.0, 128.9, 128.2, 128.2, 128.0, 74.2, 73.8, 70.6, 63.4, 33.9, 32.9, 27.3, 19.5, 7.8, 3.2; IR (neat) 3584, 3456, 3070, 3030, 2999, 1610, 1589, 1496, 1472, 1456, 1421, 1390, 1361, 1237, 1007, 823 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>36</sub>H<sub>52</sub>O<sub>3</sub>Si<sub>2</sub> [M + H] 589.3527 found 589.3533.

(2*R*,3*R*,5*R*)-5-(Benzyloxymehyl)-2-{[2-(*tert*-butyldiphenylsilyl)oxy]-ethyl}-3triethylsilyl-tetrahydrofuran (12a) and

(2*S*,3*S*,5*R*)-5-(Benzyloxymethyl)-2-{[2-(*tert*-butyldiphenylsilyl)oxy]-ethyl}-3-triethylsilyl-tetrahydrofuran (12b)

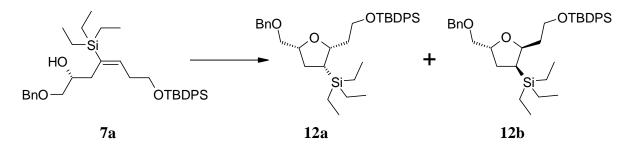


To a solution of a mixture of alcohols **7a** and **7b** (1.26 g, 2.20 mmol) in CHCl<sub>3</sub> (80 mL) at room temperature was added TsOH•H<sub>2</sub>O (41 mg, 0.22 mmol). The reaction was then heated at 60 °C for 7 h and then at 70 °C for 15 h before it was allowed to cool to ambient

temperature. Et<sub>3</sub>N (5 drops) was added to the reaction mixture before it was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (2 – 15% EtOAc in hexanes) to provide furan **12a** (72 mg, 6% yield) first and followed by the more polar **12b** (637 mg, 51% yield) as colorless oils:

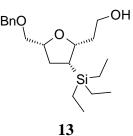
**12a**:  $[\alpha]_{D}^{25} = -27.5$  (*c* 3.57, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 – 7.69 (m, 4 H), 7.47 – 7.27 (m, 11 H), 4.57 (dd, *J* = 17.9, 12.2 Hz, 2 H), 4.48 – 4.40 (m, 1 H), 4.12 – 4.04 (m, 1 H), 3.89 – 3.76 (m, 2 H), 3.42 – 3.33 (m, 2 H), 1.96 – 1.78 (m, 2 H), 1.60 – 1.46 (m, 3 H), 1.08 (s, 9 H), 0.98 (t, *J* = 8.2 Hz, 9 H), 0.64 – 0.52 (m, 6 H); <sup>13</sup>C NMR (75 Mz, CDCl<sub>3</sub>)  $\delta$  138.5, 135.6, 135.5, 134.2, 134.0, 129.5, 129.5, 128.3, 127.7, 127.6, 127.5, 78.9, 75.2, 73.3, 73.0, 61.7, 36.6, 29.9, 27.9, 19.2, 7.8, 3.7; IR (neat) 3070, 3049, 2953, 2875, 2856, 1472, 1455, 1428, 1389, 1361, 1241, 1197, 1111, 1016, 940, 823, 701 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>36</sub>H<sub>52</sub>O<sub>3</sub>Si<sub>2</sub> [M + H] 611.3347 found 611.3336.

**12b**:  $[\alpha]_{D}^{25} = 54.4 (c \ 3.09, CHCl_3); {}^{1}H \ NMR (300 \ MHz, CDCl_3) \delta 7.74 - 7.68 (m, 4 H), 7.46 - 7.26 (m, 11 H), 4.52 (dd,$ *J*= 17.9, 12.2 Hz, 2 H), 4.45 - 4.38 (m, 1 H), 4.05 - 3.97 (m, 1 H), 3.88 - 3.77 (m, 2 H), 3.47 - 3.38 (m, 2 H), 2.06 - 1.98 (m, 1 H), 1.70 - 1.46 (m, 4 H), 1.07 (s, 9 H), 1.00 (t,*J* $= 8.9 Hz, 9 H), 0.64 - 0.56 (m, 6 H); {}^{13}C \ NMR (75 \ Mz, CDCl_3) \delta 137.6, 134.7, 134.7, 133.3, 133.1, 128.5, 127.3, 126.6, 126.5, 77.9, 77.4, 73.1, 72.3, 60.7, 38.0, 30.1, 28.7, 25.9, 18.2, 6.8, 2.8; IR (neat) 3070, 2954, 2875, 1589, 1496, 1472, 1455, 1428, 1389, 1361, 1306, 1240, 1192, 1016, 939, 823, 701 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>36</sub>H<sub>52</sub>O<sub>3</sub>Si<sub>2</sub> [M + H] 611.3347 found 611.3336.$ 



To a solution of allylic alcohol **7a** (5.78 g, 10.09 mmol) in CHCl<sub>3</sub> (200 mL) at room temperature was added TsOH (100 mg, 0.53 mmol). The reaction was then heated at 55 °C for 2 days before it was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (2 – 15% EtOAc in hexanes) to provide furan **12a** (723 mg, 13% yield) first and followed by the more polar **12b** (3.80 g, 66% yield). In addition, the starting material **7a** was also recovered (0.43 g).

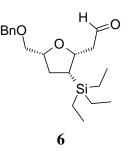
**2-**[(*2R*,*3R*,*5R*)-**5-**(Benzyloxymethyl)-**3-**triethylsilyl-tetrahydro-furan-**2**-yl]-ethanol (13)



To a solution of silvl ether **12a** (1.56 g, 2.65 mmol) in THF (80 mL) at 0 °C was added dropwise a solution of TBAF (1.0 M in THF, 3.97 mL, 3.97 mmol). The reaction was then stirred from 0 °C to room temperature over 3 h before it was quenched with saturated aq. NH<sub>4</sub>Cl solution. The reaction mixture was then extracted with EtOAc. The organic layer was washed with brine, dried over MgSO<sub>4</sub> and concentrated. The crude residue was purified by flash column chromatography on silica gel (10 – 40% EtOAc in hexanes) to provide alcohol **13** (932 mg, 100% yield) as a colorless oil:

$$\begin{split} & [\alpha]^{25}{}_D = 47.2 \ (c \ 4.79, \ CHCl_3); \ ^1H \ NMR \ (100 \ MHz, \ CDCl_3) \ \delta \ 7.37 - 7.24 \ (m, \ 5 \ H), \ 4.59 - 4.44 \ (m, \ 3 \ H), \ 4.28 - 4.21 \ (m, \ 1 \ H), \ 3.87 - 3.72 \ (m, \ 2 \ H), \ 3.43 - 3.32 \ (m, \ 2 \ H), \ 2.08 - 1.96 \ (m, \ 1 \ H), \ 1.90 - 1.82 \ (m, \ 1 \ H), \ 1.76 - 1.53 \ (m, \ 2H), \ 1.46 - 1.38 \ (m, \ 1 \ H), \ 0.98 - 0.92 \ (m, \ 9 \ H), \ 0.66 - 0.54 \ (m, \ 6 \ H); \ ^{13}C \ NMR \ (75 \ Mz, \ CDCl_3) \ \delta \ 138.6, \ 128.7, \ 128.0, \ 128.0, \ 83.9, \ 76.2, \ 73.7, \ 73.1, \ 62.8, \ 35.6, \ 30.3, \ 28.7, \ 8.1, \ 4.1; \ IR \ (neat) \ 3441, \ 3064, \ 3030, \ 2952, \ 2875, \ 1496, \ 1454, \ 1417, \ 1375, \ 1240, \ 1067, \ 1016, \ 732, \ 697 \ cm^{-1}; \ HRMS \ (EI) \ calcd for \ C_{20}H_{34}O_3Si \ [M + H] \ 351.2350 \ found \ 351.2348. \end{split}$$

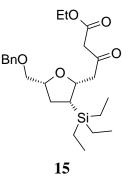
## [(2*R*,3*R*,5*R*)-5-(Benzyloxymethyl)-3-triethylsilyl-tetrahydro-furan-2-yl] acetaldehyde (6)



To a solution of alcohol **13** (0.88 g, 2.51 mmol) in  $CH_2Cl_2$  (25 mL) at 0 °C was added NaHCO<sub>3</sub> (0.53 g, 6.28 mmol) and followed by Dess-Martin periodinane (1.38 g, 3.26 mmol) in small portions. The reaction was then stirred from 0 °C to room temperature over 1 h before it was diluted with EtOAc. The organic layer was washed with H<sub>2</sub>O, brine, dried over MgSO<sub>4</sub> and concentrated to yield the crude aldehyde **6** (0.84 g, 96% yield) as a colorless oil:

[α]<sup>25</sup><sub>D</sub> = 69.6 (*c* 6.98, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.77 – 9.75 (m, 1 H), 7.37 – 7.24 (m, 5 H), 4.80 – 4.73 (m, 1 H), 4.54 (s, 2 H), 4.07 – 3.99 (m, 1 H), 3.56 – 3.46 (m, 2 H), 2.51 (ddd, J = 14.8, 11.3, 3.2 Hz, 1 H), 2.31 – 2.20 (m, 1 H), 2.09 – 1.98 (m, 1 H), 1.78 – 1.62 (m, 2 H), 0.94 (t, J = 7.9 Hz, 9 H), 0.63 – 0.53 (m, 6 H); <sup>13</sup>C NMR (75 Mz, CDCl<sub>3</sub>) δ 202.8, 138.7, 128.8, 128.1, 128.0, 80.0, 77.6, 73.9, 73.3, 50.1, 30.9, 30.1, 8.1, 4.1; IR (neat) 3064, 3030, 2954, 2910, 2875, 2732, 1727, 1455, 1418, 1363, 1310, 1241, 1192, 1098, 1076, 1017, 948, 732, 698 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>20</sub>H<sub>32</sub>O<sub>3</sub>Si [M + H] 349.2194 found 349.2192.

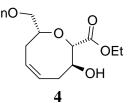
#### 4-[(2*R*,3*R*,5*R*)-5-(Benzyloxymethyl)-3-triethylsilyl-tetrahydro-furan-2-yl]-3-oxobutyric acid ethyl ester (15)



To a solution of ethyl diazoacetate (196 mg, 1.72 mmol) in  $CH_2Cl_2$  (6 mL) at room temperature was added anhydrous  $SnCl_2$  (27 mg, 0.14 mmol). The cloudy reaction mixture was stirred for 15 min and followed by addition of a solution of aldehyde **6** (500 mg, 1.43 mmol) in  $CH_2Cl_2$  (6 mL). The resulting mixture was stirred for 2 h before it was concentrated. The crude residue was purified by flash column chromatography on silica gel (10 – 15% EtOAc in hexanes) to provide  $\beta$ -keto ester **15** (436 mg, 70% yield) and the more polar oxocene **4** (104 mg, 23% yield) both as colorless oils:

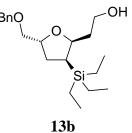
β-keto ester **15**:  $[\alpha]^{25}_{D} = 90.5$  (*c* 4.31, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.26 (m, 5 H), 4.69 – 4.62 (m, 1 H), 4.54 (s, 2 H), 4.18 – 4.10 (m, 2 H), 4.06 – 3.93 (m, 1 H), 3.58 –3.47 (m, 4 H), 2.69 (dd, *J* = 13.9, 11.3 Hz, 1 H), 2.38 (dd, *J* = 13.9, 2.6 Hz, 1 H), 2.03 – 1.95 (m, 1 H), 1.77 – 1.63 (m, 2 H), 1.27 – 1.19 (m, 3 H), 1.00 – 0.92 (m, 9 H), 0.65 – 0.52 (m, 6 H); <sup>13</sup>C NMR (75 Mz, CDCl<sub>3</sub>) δ 202.7, 167.8, 138.7, 128.8, 128.1, 128.0, 79.7, 79.0, 72.9, 61.5, 50.5, 49.5, 30.7, 30.2, 14.5, 8.1, 4.1; IR (neat) 3030, 2954, 2910, 2875, 1745, 1717, 1653, 1496, 1455, 1416, 1368, 1240, 1196, 1096, 1029, 802, 733, 698 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>24</sub>H<sub>38</sub>O<sub>5</sub>Si [M + H] 457.2381 found 457.2373.

(2*S*,3*S*,8*R*,*Z*)-8-(Benzyloxymethyl)-3-hydroxy-3,4,7,8-tetrahydro-(2*H*)-oxocine-2carboylic acid ethyl ester (4)



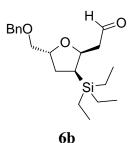
[α]<sup>25</sup><sub>D</sub> = 32.5 (*c* 3.43, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.27 (m, 5 H), 5.96 – 5.85 (m, 2 H), 4.57 (s, 2 H), 4.25 – 4.13 (m, 3 H), 3.90 (d, J = 9.4 Hz, 1 H), 3.74 – 3.66 (m, 1 H), 3.60 (dd, J = 5.5, 4.3 Hz, 1 H), 3.45 (dd, J = 5.4, 4.3 Hz, 1 H), 3.00 (m, 1H), 2.83 – 2.74 (m, 1 H), 2.44 – 2.22 (m, 3 H), 1.25 (t, J = 7 Hz, 3 H); <sup>13</sup>C NMR (100 Mz, CDCl<sub>3</sub>) δ 174.2, 138.6, 138.5, 129.6, 129.6, 128.8, 128.0, 82.7, 81.3, 73.7, 73.3, 73.0, 65.0, 61.8, 31.6, 31.0, 14.5; IR (neat) 3462, 3027, 2980, 2932, 1740, 1497, 1454, 1373, 1323, 1245, 1182, 1097, 1041, 737, 698 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>18</sub>H<sub>24</sub>O<sub>5</sub> [M + H] 321.1697 found 321.1694.

### **2-**[(2*S*,3*S*,5*R*)-**5-**(Benzyloxymethyl)-**3-**triethylsilyl-tetrahydro-furan-**2-**yl]-ethanol (13b)



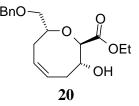
[α]<sup>25</sup><sub>D</sub> = -29.3 (*c* 6.10, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 -7.27 (m, 5 H), 4.55 (dd, *J* = 12, 17 Hz, 2 H), 4.5 -4.45 (m, 1 H), 4.28 -4.22 (m, 1 H), 3.87 -3.73 (m, 2 H), 3.42 -3.18 (m, 2 H), 3.16 (dd, *J* = 2, 9 Hz, 1 H), 2.07 -1.99 (m, 1 H), 1.89 -1.83 (m, 1 H), 1.75 -1.64 (m, 1 H), 1.62 -1.55 (m, 1 H), 1.45 -1.38 (m, 1 H), 0.97 (t, *J* = 8 Hz, 9 H), 0.65 -0.55 (m, 6 H); <sup>13</sup>C NMR (100 Mz, CDCl<sub>3</sub>) δ 138.6, 128.7, 128.0, 83.9, 76.1, 73.7, 73.1, 62.7, 35.6, 30.2, 28.6, 8.1, 4.1; IR (neat) 3441, 3063, 3030, 2950, 2909, 2875, 1496, 1454, 1417, 1374, 1241, 1090, 1047, 1017, 732, 697 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>20</sub>H<sub>34</sub>O<sub>3</sub>Si [M + H] 351.2350 found 351.2351.

[(2*S*,3*S*,5*R*)-5-(Benzyloxymethyl)-3-triethylsilyl-tetrahydro-furan-2-yl]-acetaldehyde (6b)

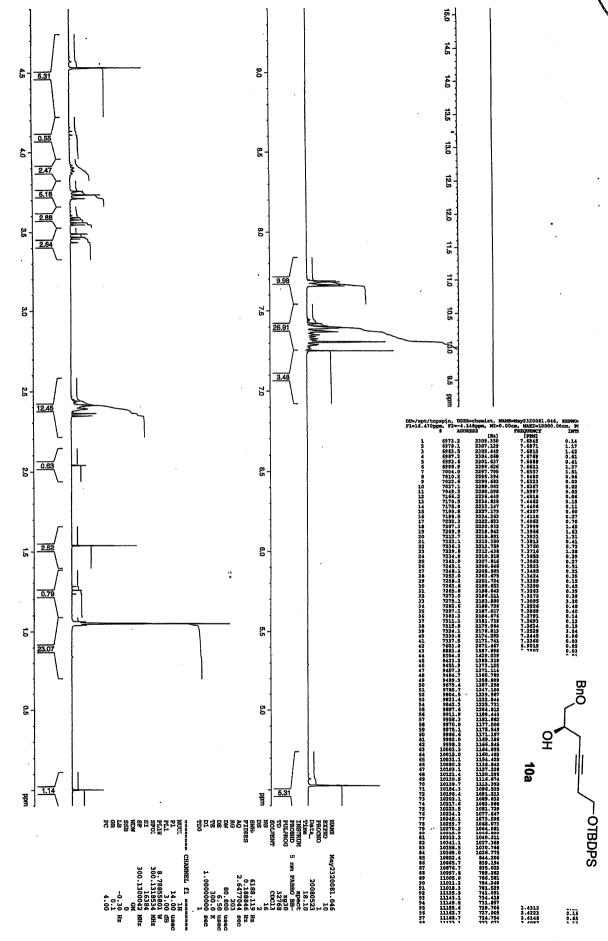


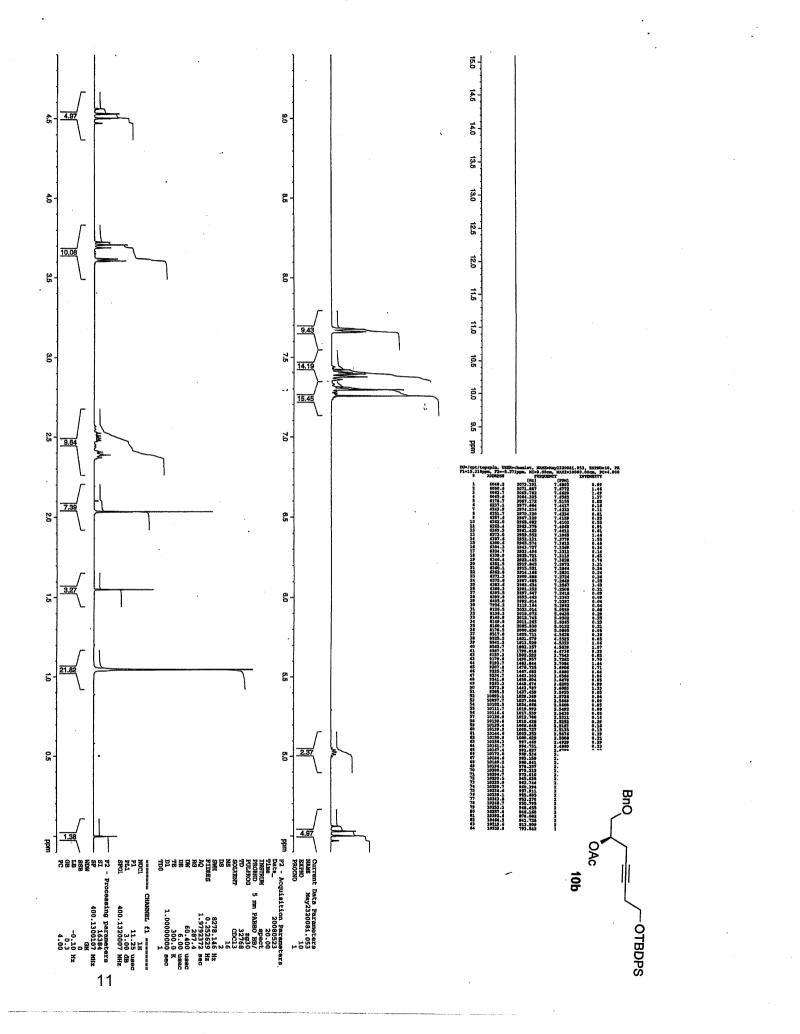
[α]<sup>25</sup><sub>D</sub> = -47.9 (*c* 4.70, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.79 – 9.78 (m, 1 H), 7.35 – 7.26 (m, 5 H), 4.85 – 4.80 (m, 1 H), 4.54 (dd, *J* = 12, 17 Hz, 2 H), 4.27 – 4.20 (m, 1 H), 3.42 – 3.33 (m, 2 H), 2.51 (ddd, *J* = 15, 11, 3 Hz, 1 H), 2.30 – 2.26 (m, 1 H), 2.05 – 1.88 (m, 2 H), 1.72 – 1.62 (m, 1 H), 0.96 (t, *J* = 8 Hz, 9 H), 0.63 – 0.53 (m, 6 H); <sup>13</sup>C NMR (100 Mz, CDCl<sub>3</sub>) δ 202.2, 138.6, 128.7, 128.1, 128.0, 77.9, 76.4, 73.7, 73.0, 65.2, 48.2, 30.1, 28.2, 8.1, 4.0; IR (neat) 3030, 2953, 2910, 2875, 2732, 1727, 1454, 1415, 1241, 1161, 1096, 1017, 803, 733, 698 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>20</sub>H<sub>32</sub>O<sub>3</sub>Si [M + H] 349.2194 found 349.2194.

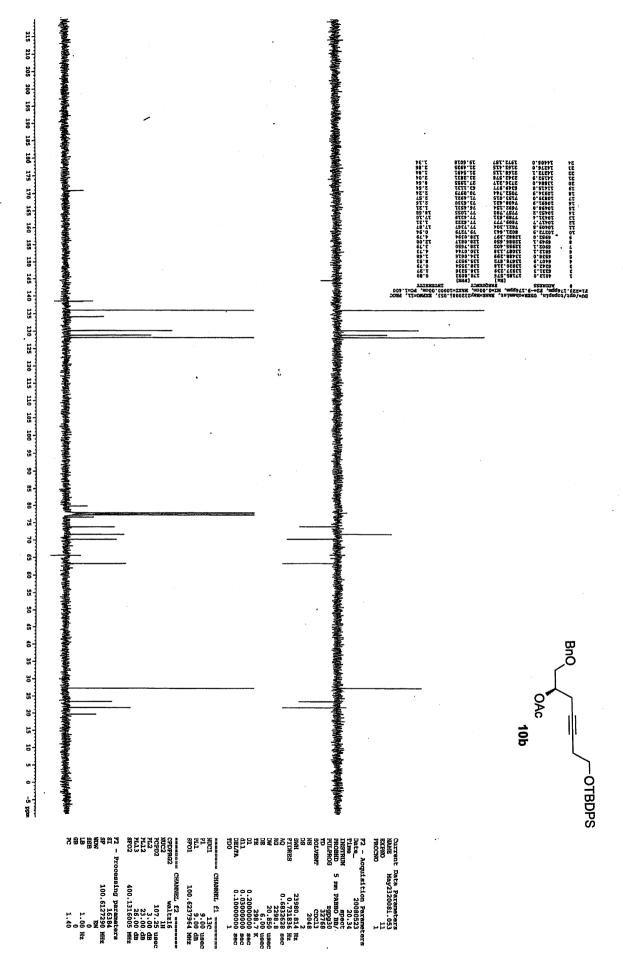
#### (2*R*,3*R*,8*R*,*Z*)-8-(Benzyloxymethyl)-3-hydroxy-3,4,7,8-tetrahydro-(2*H*)-oxocine-2carboylic acid ethyl ester (20)

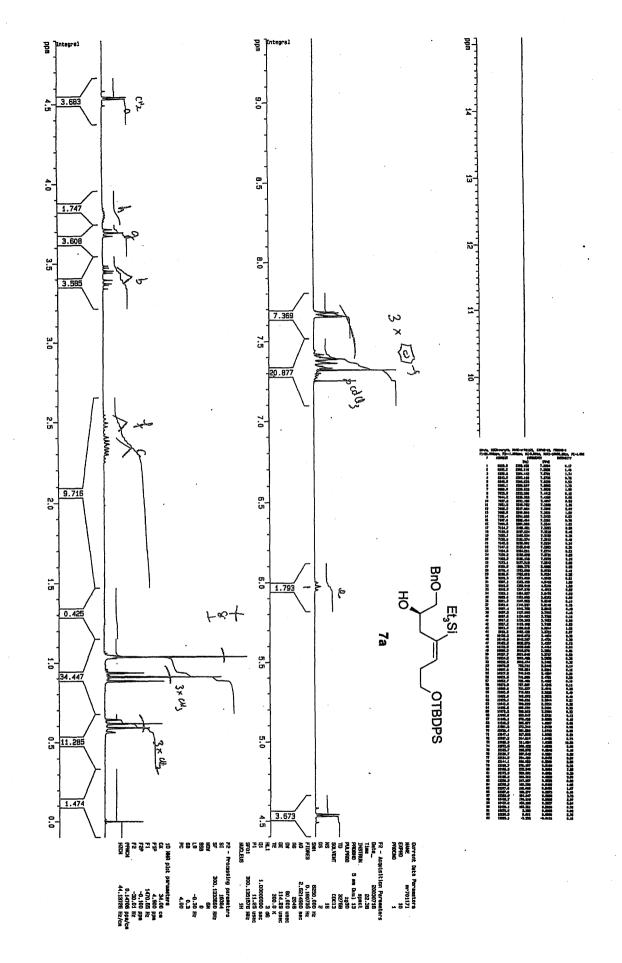


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.27 (m, 5 H), 5.91 – 5.74 (m, 2 H), 4.53 (s, 2 H), 4.22 – 4.15 (m, 3 H), 4.02 – 3.91 (m, 2 H), 3.64 (ddd, *J* = 6, 10, 17 Hz, 2 H), 2.75 (d, *J* = 4.5 Hz, 1 H), 2.59 – 2.53 (m, 1 H), 2.43 – 2.31 (m, 3H), 1.24 (t, *J* = 7 Hz, 3 H); <sup>13</sup>C NMR (100 Mz, CDCl<sub>3</sub>)  $\delta$  173.4, 138.3, 128.9, 128.8, 128.8, 128.1, 128.0, 77.6, 76.0, 75.5, 73.6, 72.5, 71.2, 65.0, 61.7, 33.3, 29.3, 14.5; IR (neat) 3462, 3027, 2980, 2932, 1740, 1497, 1454, 1373, 1323, 1245, 1182, 1097, 1041, 737, 698 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>18</sub>H<sub>24</sub>O<sub>5</sub> [M + H] 321.1697 found 321.1693.

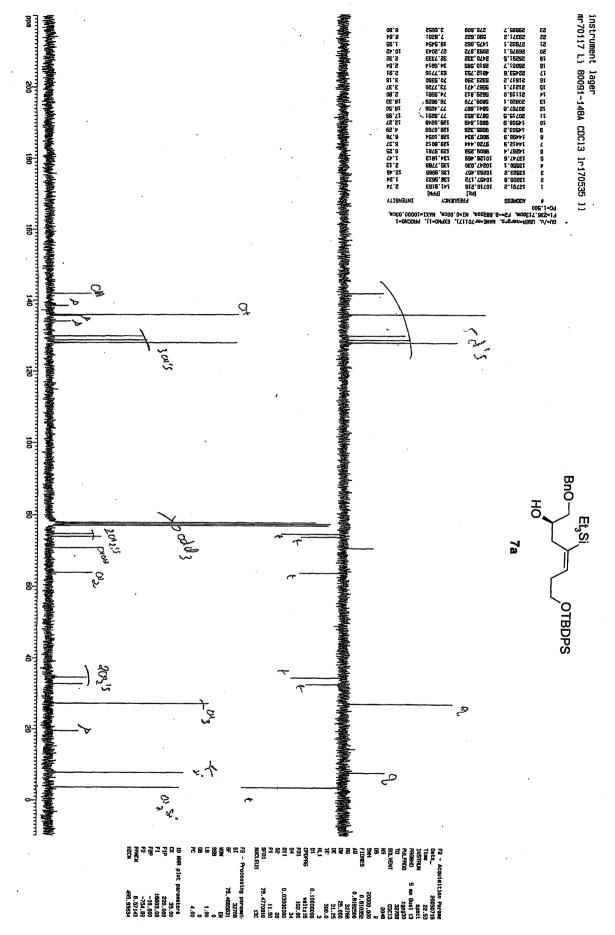


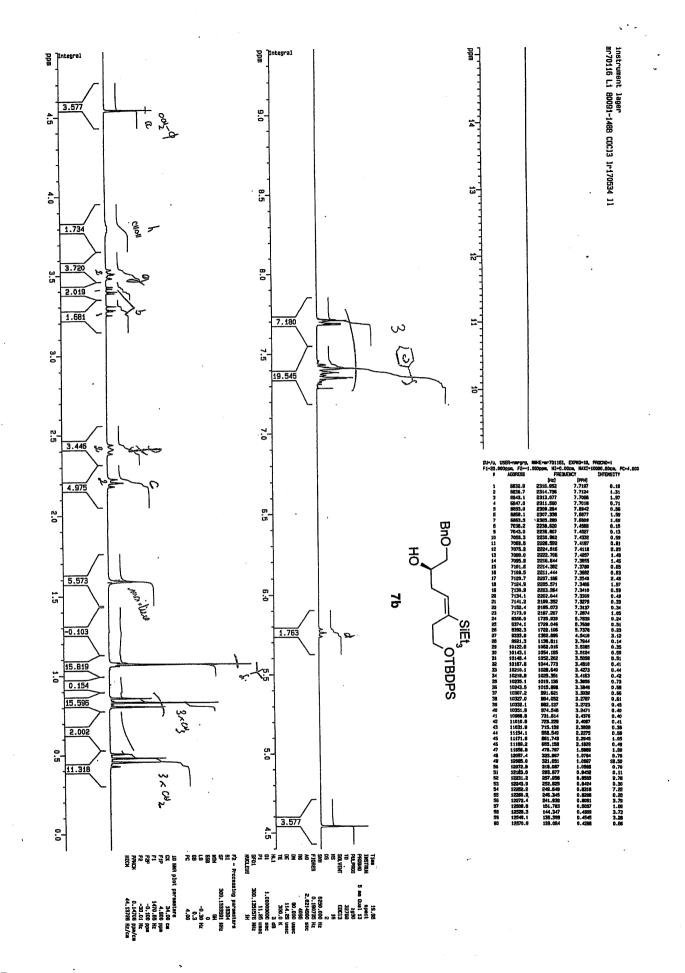


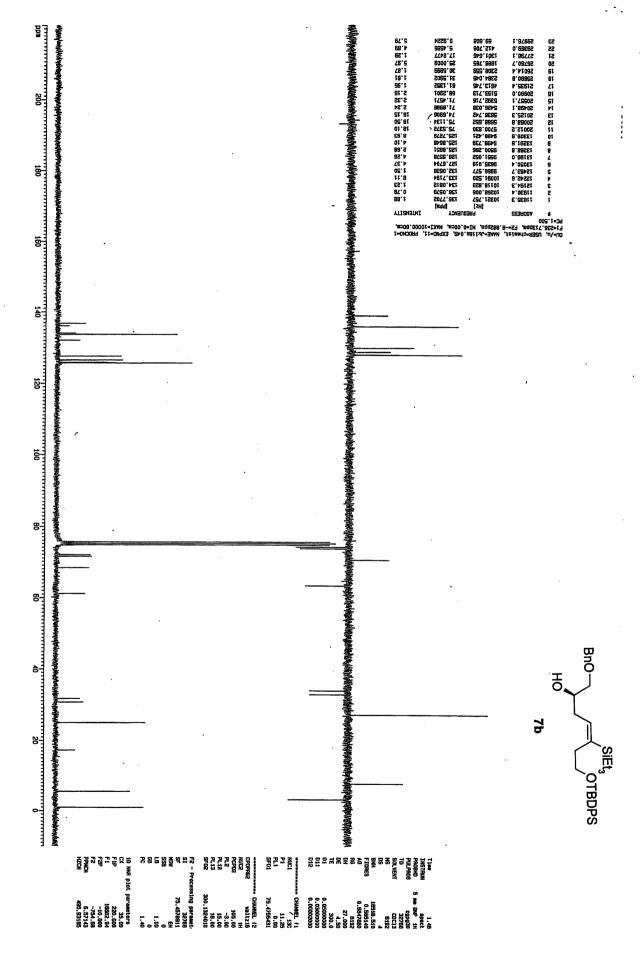


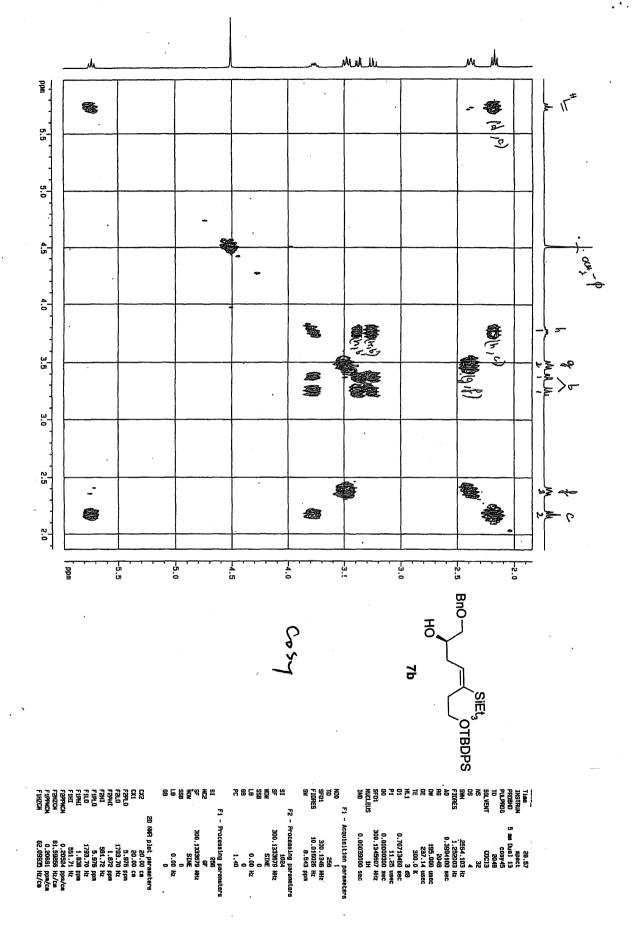


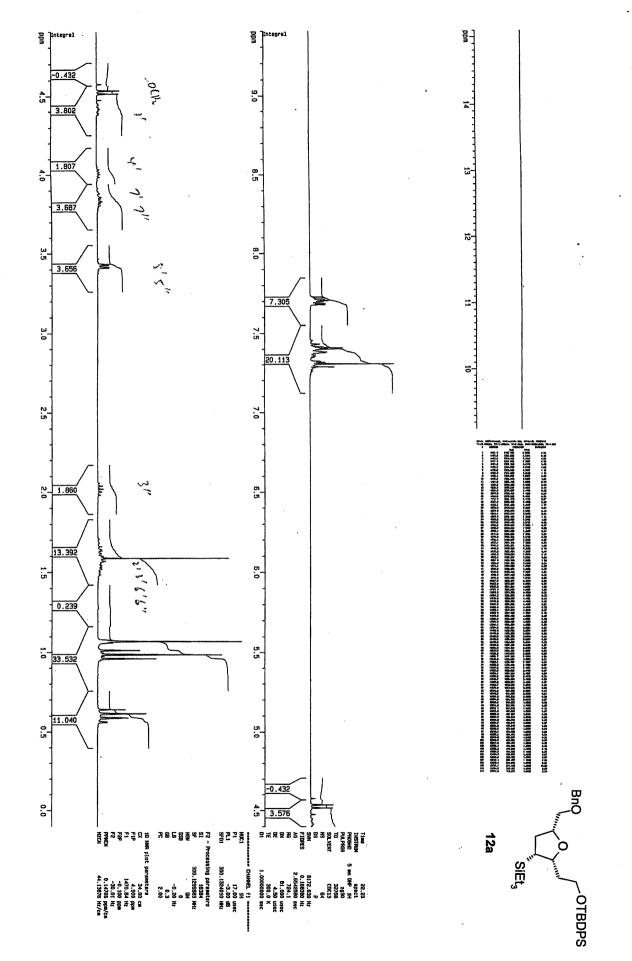
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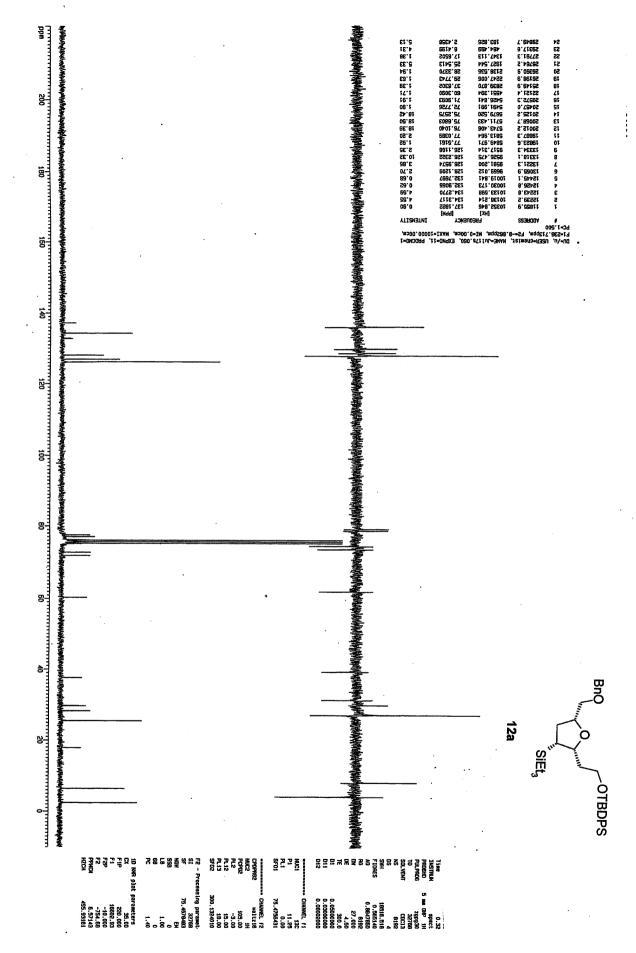




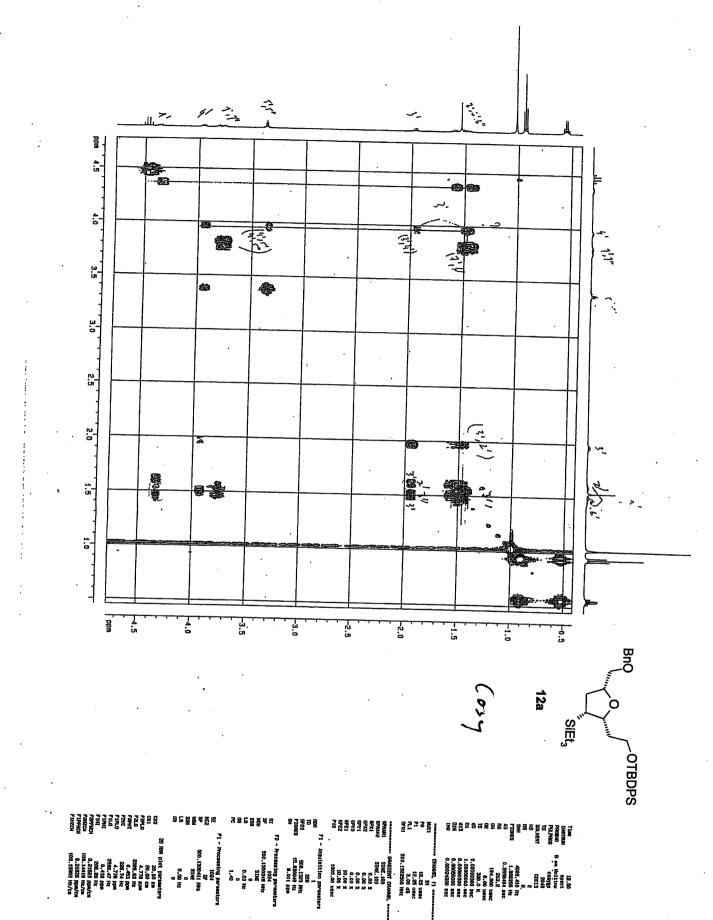




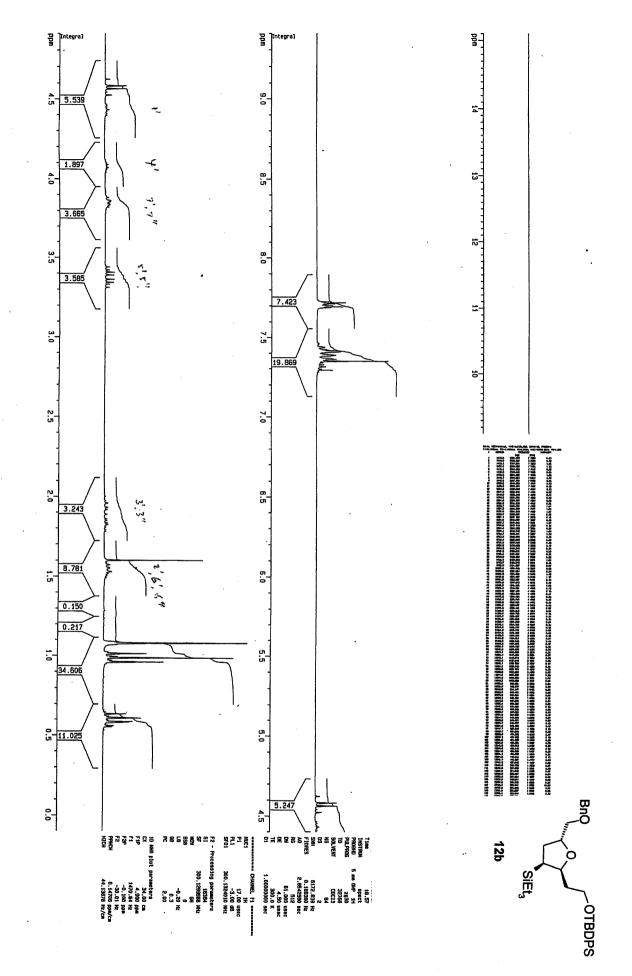


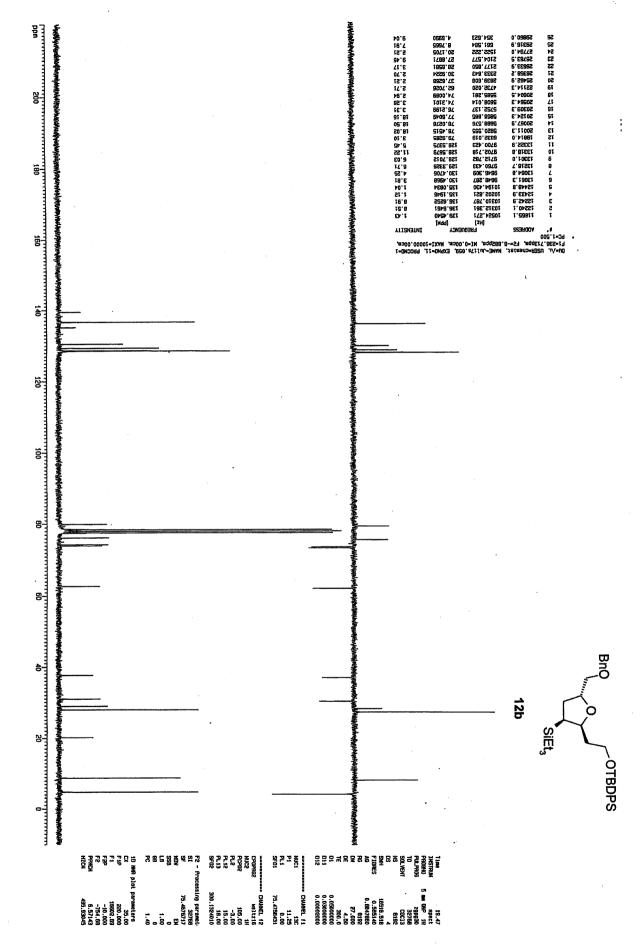


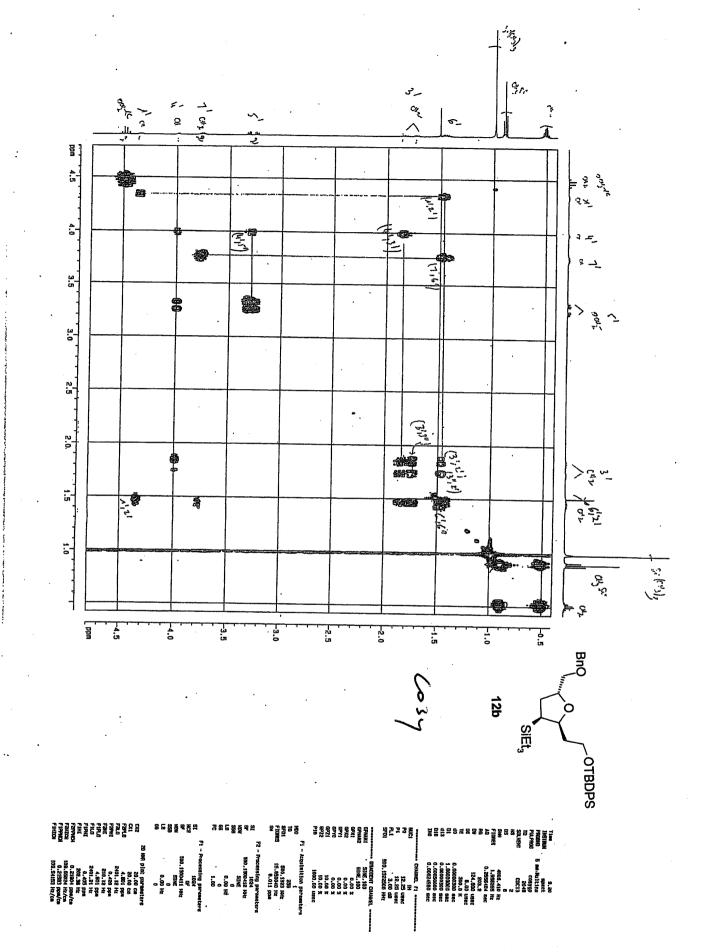
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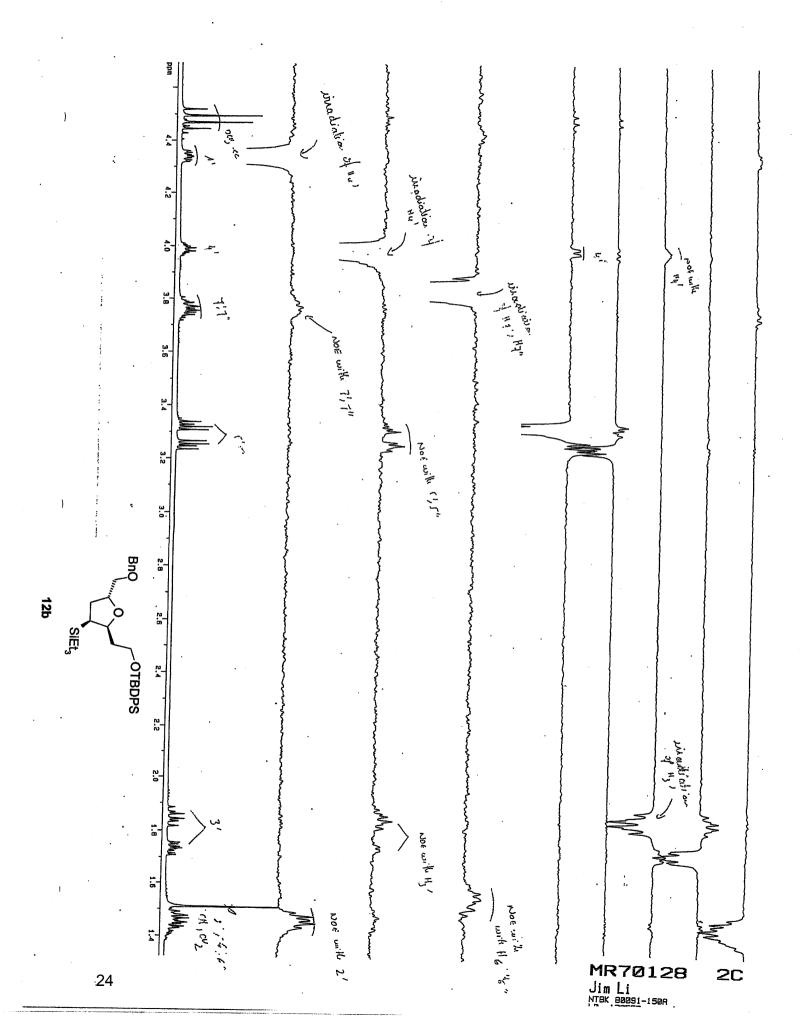
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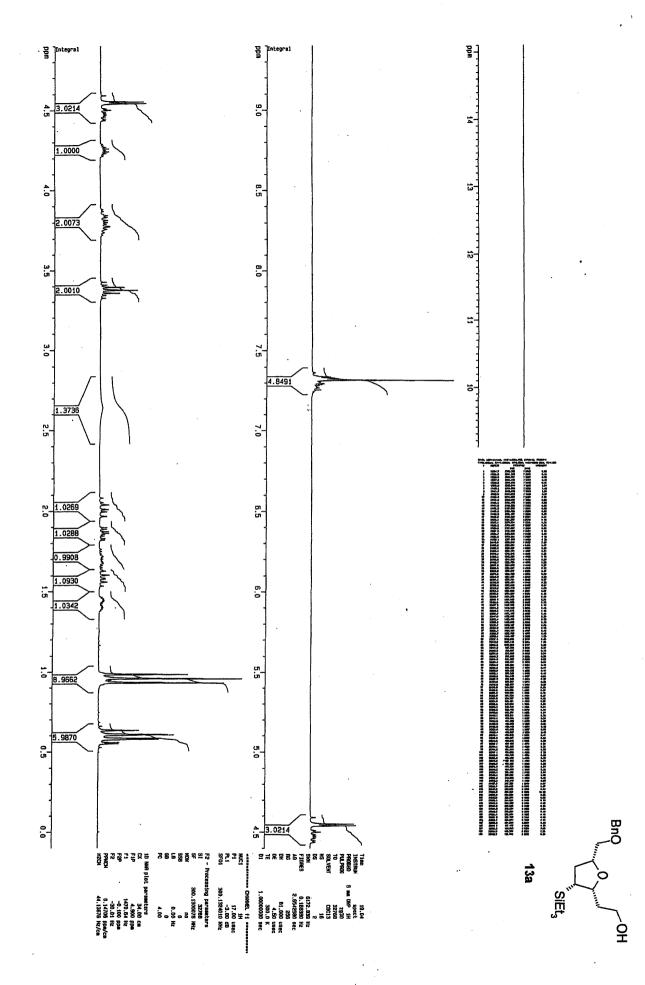


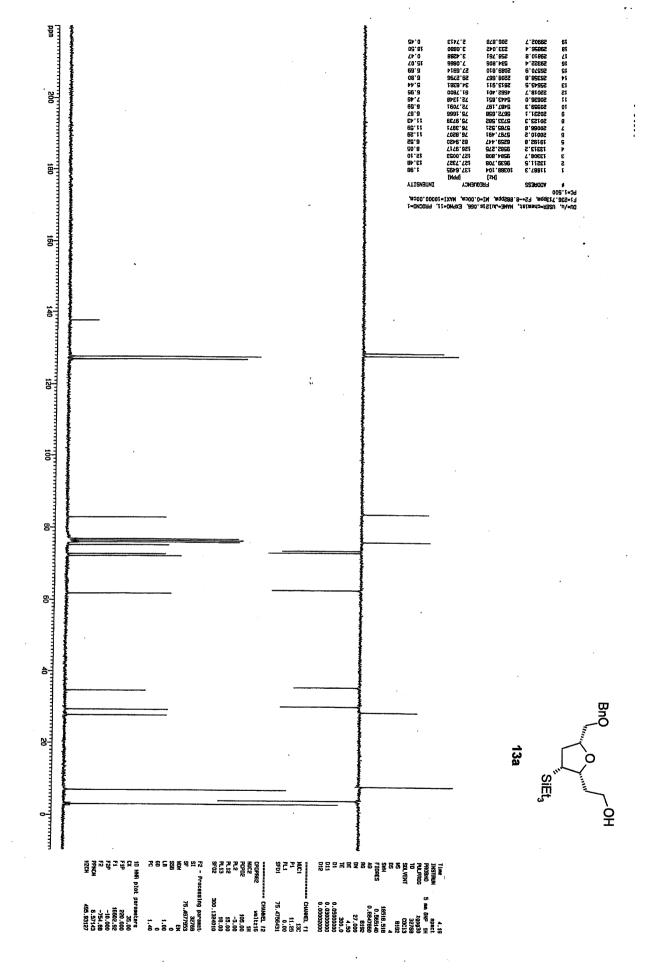


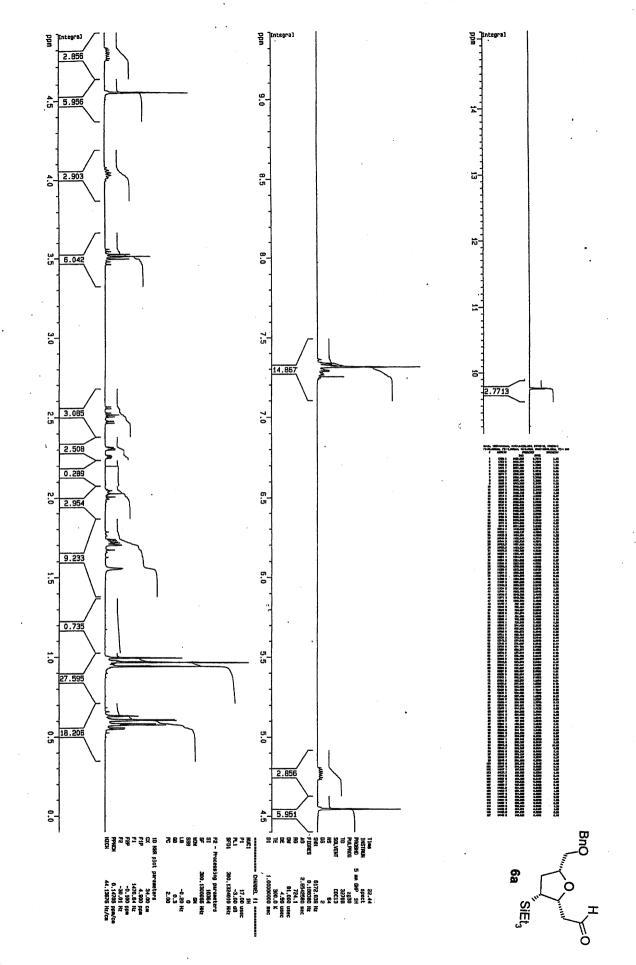


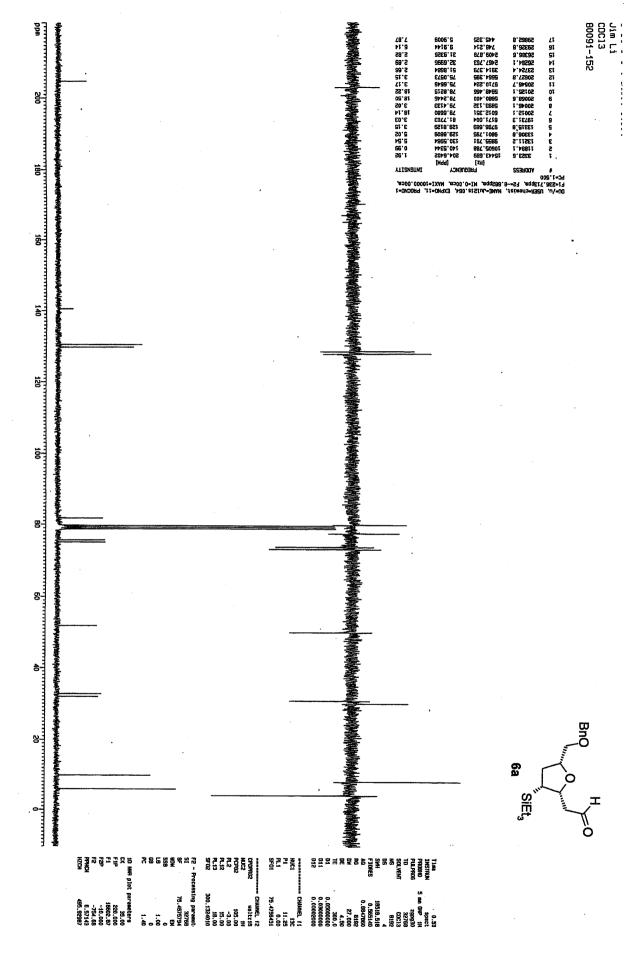
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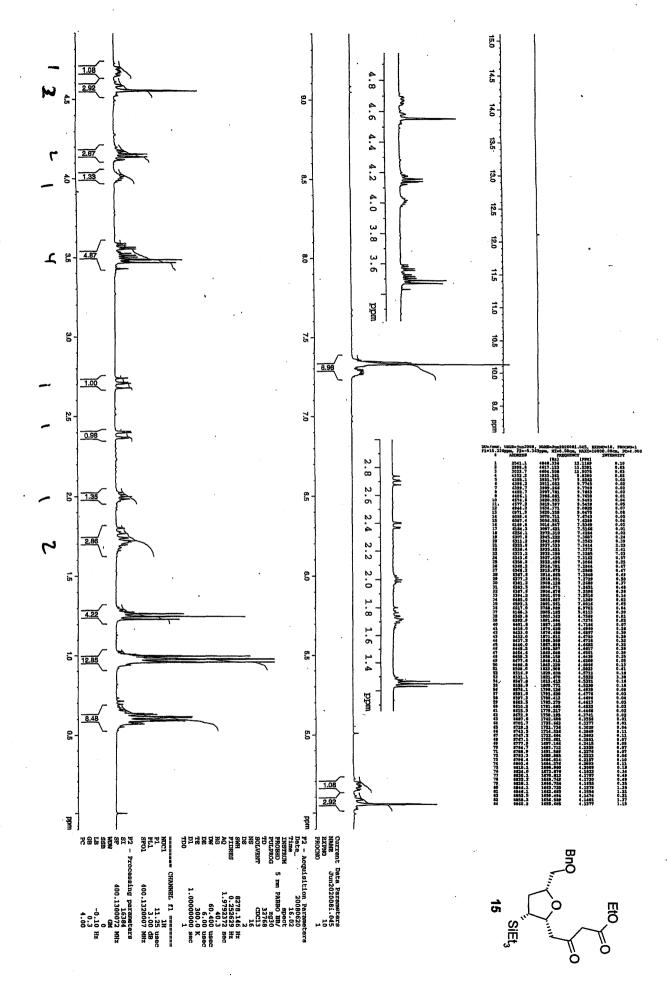


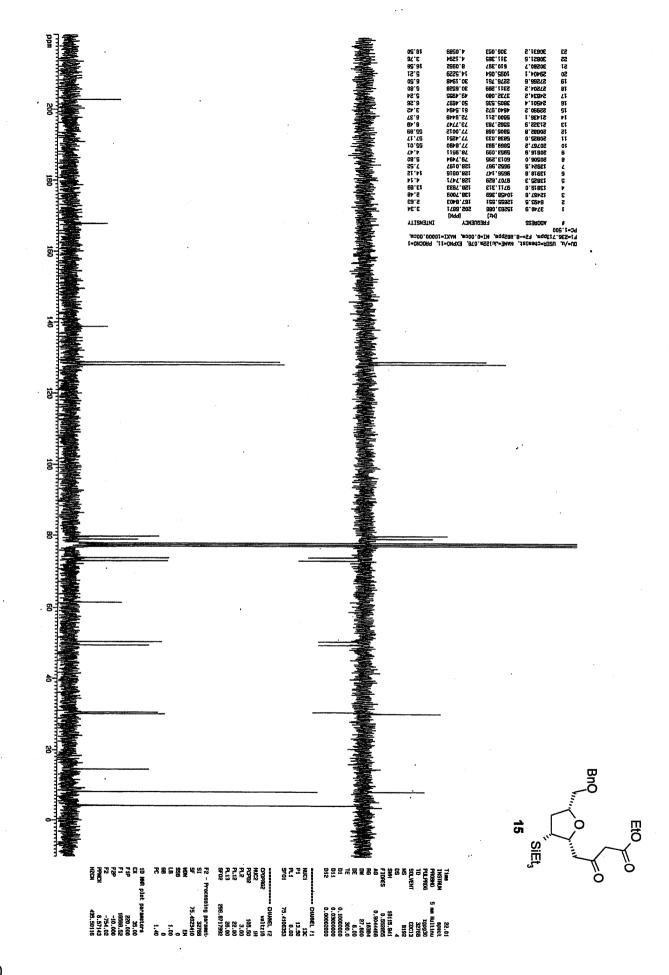


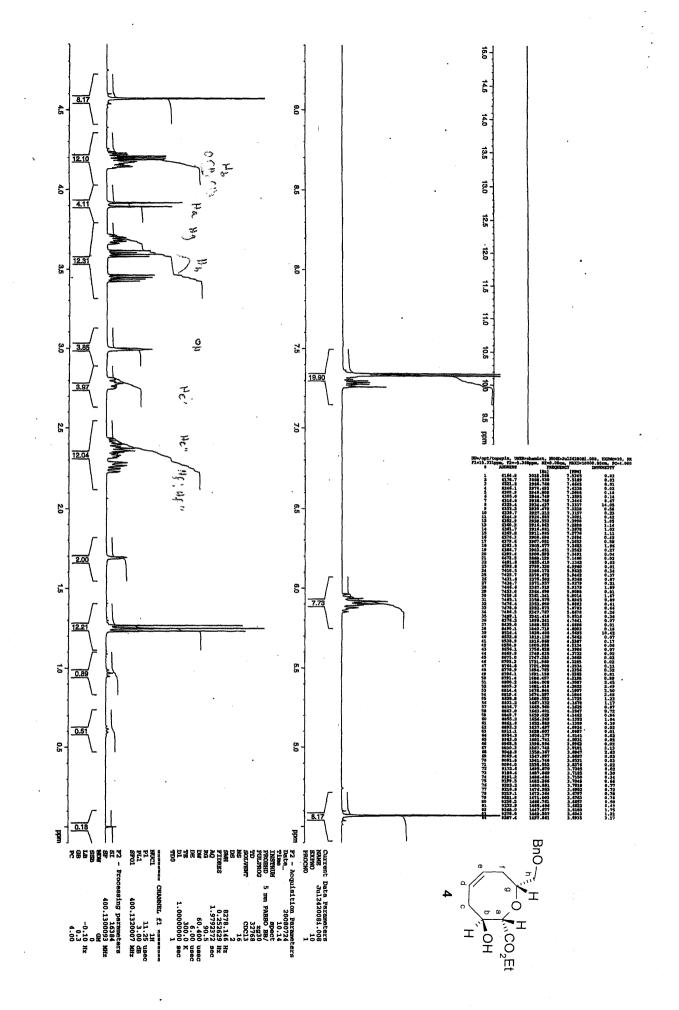


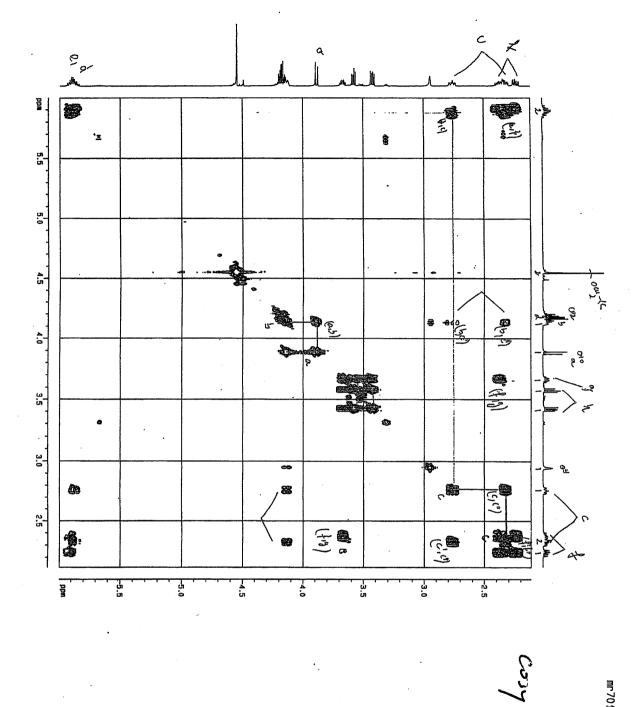


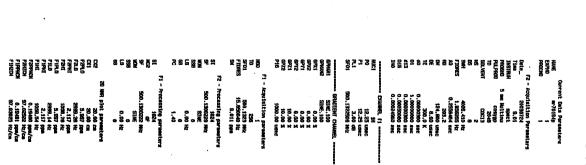




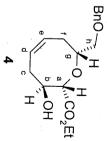


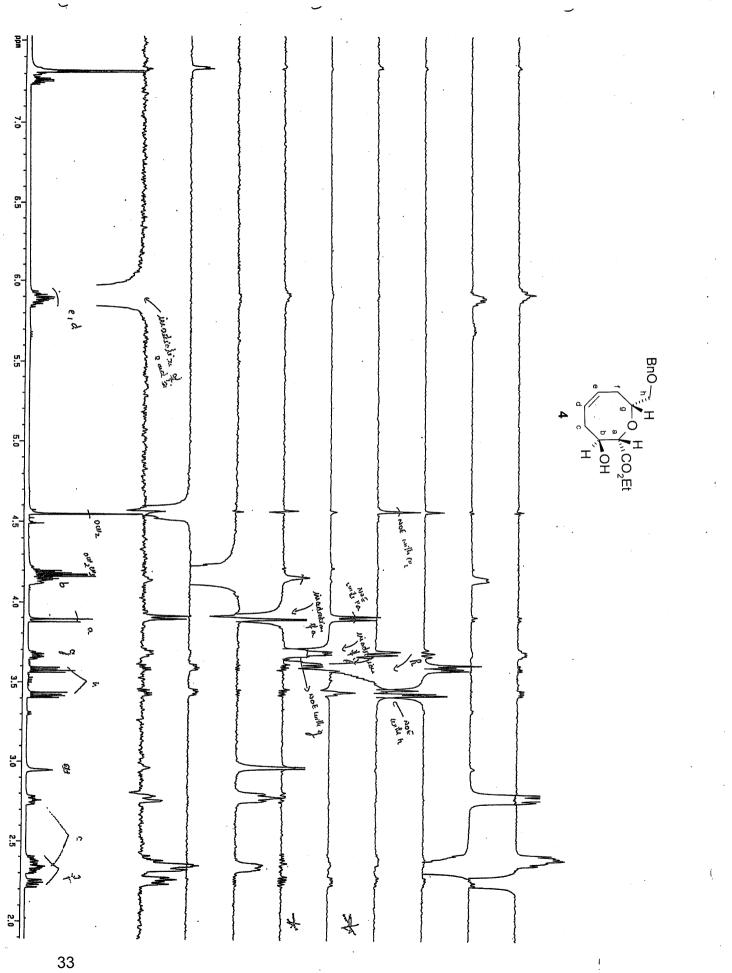


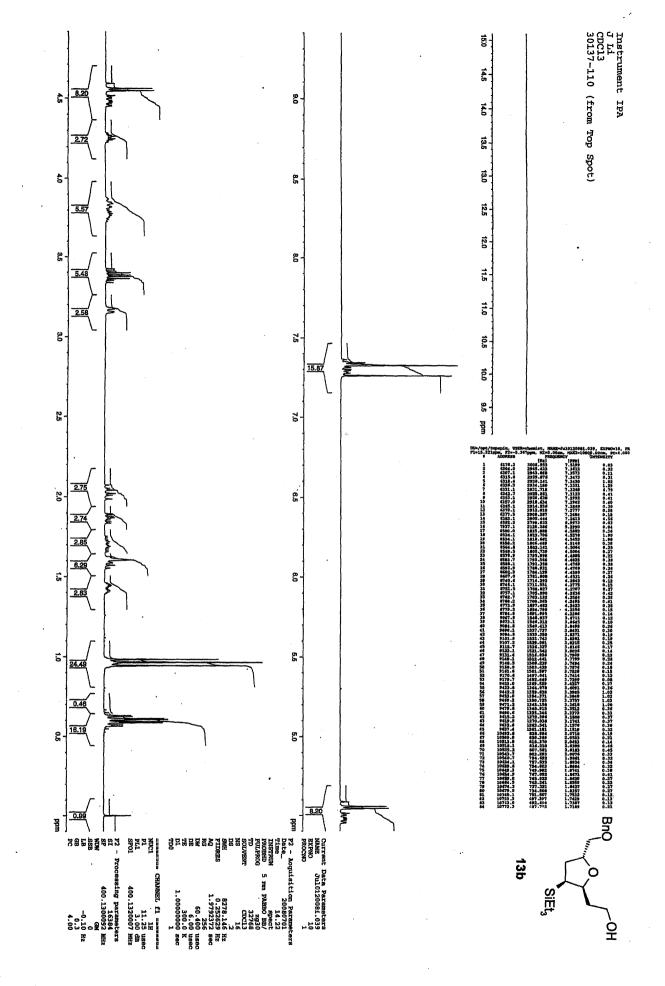


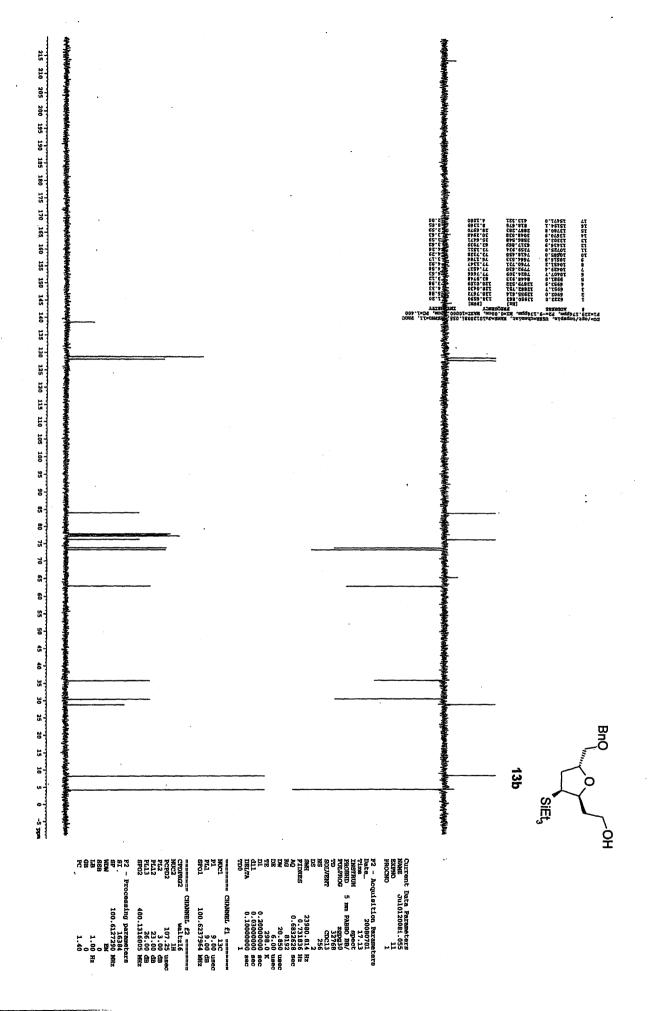


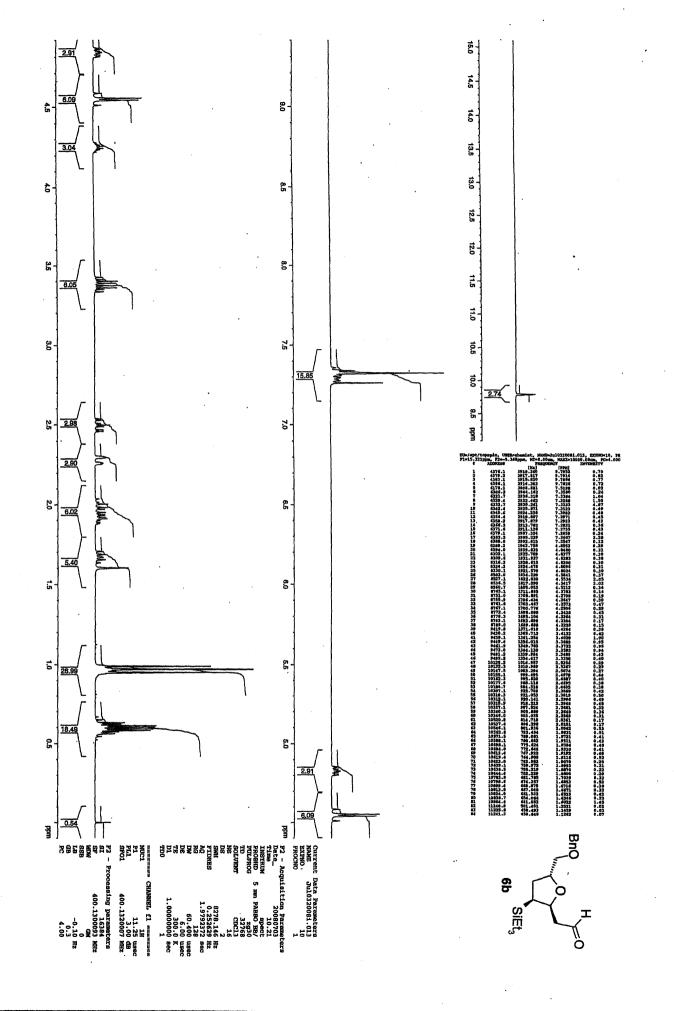
Instrument amb mr70184 Li 80091-1538 cdcl3 lr 170640

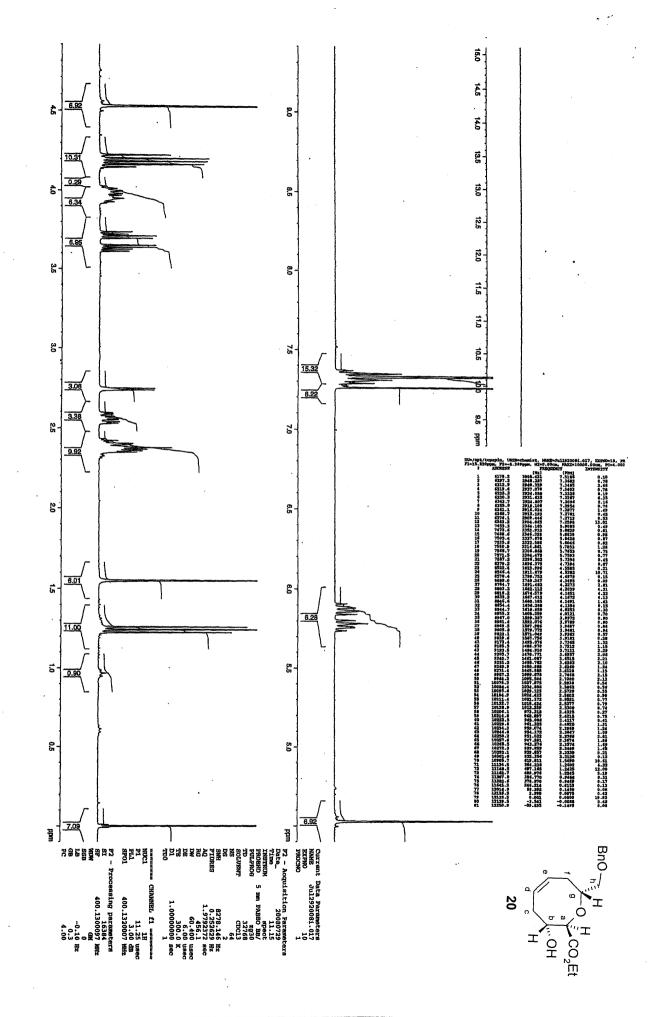


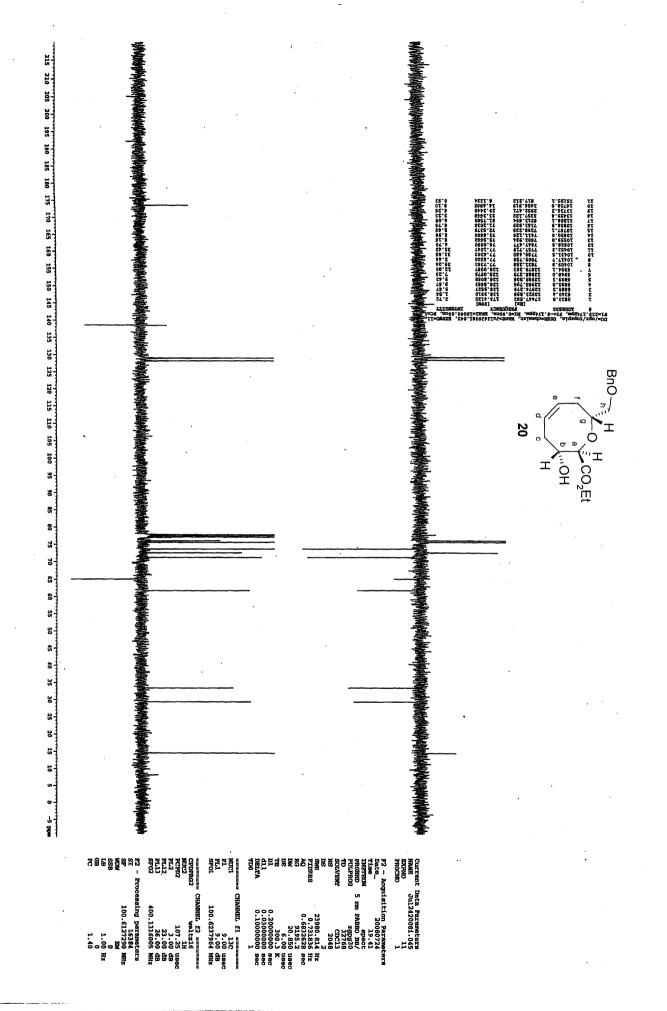


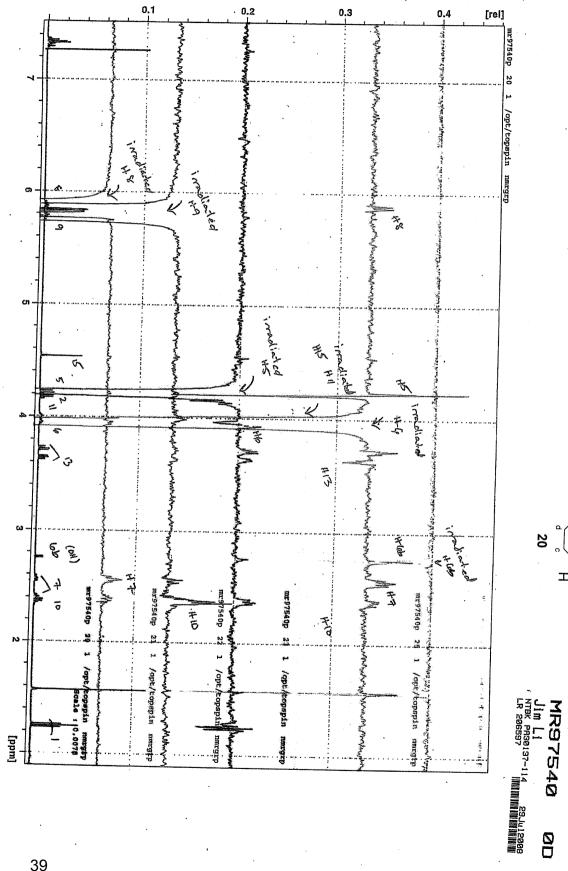


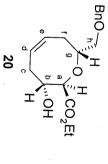












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