# Supporting Information 

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

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## Table of Contents

1. General methods and materials S1
2. Synthesis and characterization S2
3. Spectra S10
4. General materials and methods. Infrared (IR) spectra were obtained using Thermo-Nicolet 6700 infrared spectrometer. Proton and carbon nuclear magnetic resonance ( ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR) spectra were recorded on the following instruments: Bruker model Avance-III $\left({ }^{1} \mathrm{H}\right.$ at $500 \mathrm{MHz},{ }^{13} \mathrm{C}$ at 125 MHz$)$, Bruker model Avance $\left({ }^{1} \mathrm{H}\right.$ at $400 \mathrm{MHz},{ }^{13} \mathrm{C}$ at 100 MHz ), and Bruker model Avance-III $\left({ }^{1} \mathrm{H}\right.$ at $300 \mathrm{MHz},{ }^{13} \mathrm{C}$ 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)



10a

To a solution of propargyl alkyne $9(18.79 \mathrm{~g}, 60.90 \mathrm{mmol})$ in THF ( 200 mL ) at $-78{ }^{\circ} \mathrm{C}$ was added a solution of n - BuLi ( 1.6 M in THF, $16.95 \mathrm{~mL}, 60.90 \mathrm{mmol}$ ) dropwise. The mixture was stirred at $-78{ }^{\circ} \mathrm{C}$ for 15 min and followed by addition of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(7.49$ $\mathrm{mL}, 60.90 \mathrm{mmol})$. The resulting mixture was stirred for 10 min and followed by addition of a solution of $(-)-(R)$-benzyl glyosidic ether $8(5.00 \mathrm{~g}, 30.45 \mathrm{mmol})$. The reaction mixture was stirred further at $-78{ }^{\circ} \mathrm{C}$ for 1 h before it was quenched with saturated aq. $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The reaction mixture was allowed to warm to room temperature and diluted with ether. The organic layer was separated, washed with $\mathrm{H}_{2} \mathrm{O}$, brine, dried over $\mathrm{MgSO}_{4}$, and concentrated. The crude residue was purified by flash column chromatography on silica gel ( $10-20 \% \mathrm{EtOAc}$ in hexanes) to afford the product $\mathbf{1 0 a}$ ( $12.09 \mathrm{~g}, 84 \%$ yield) as a colorless oil:
$[\alpha]^{25}{ }_{\mathrm{D}}=-7.0\left(c 7.02, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.69-7.65(\mathrm{~m}, 4 \mathrm{H}), 7.45$ $-7.25(\mathrm{~m}, 11 \mathrm{H}), 4.52(\mathrm{~s}, 2 \mathrm{H}), 3.92-3.85(\mathrm{~m}, 1 \mathrm{H}), 3.73$ (t, $J=7 \mathrm{~Hz}, 2 \mathrm{H}), 3.57$ (dd, $J=$ $4,9 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.46 (dd, $J=4,9 \mathrm{~Hz}, 1 \mathrm{H}$ ), $2.47-2.35$ (m, 5 H ), 1.05 ( $\mathrm{s}, 9 \mathrm{H}$ ); IR (neat) 3447, 3069, 2931, 2857, 1738, 1472, 1454, 1389, 1362, 1243, 1029, 941, $823 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{30} \mathrm{H}_{36} \mathrm{O}_{3} \mathrm{Si}\left[\mathrm{M}+\mathrm{Na}^{+}\right] 495.2326$ found 495.2320.

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



10b
To a solution of propargyl alcohol $10 \mathrm{a}(6.70 \mathrm{~g}, 14.17 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(100 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ was added $\mathrm{Et}_{3} \mathrm{~N}$ ( $4.98 \mathrm{~mL}, 35.43 \mathrm{mmol}$ ) and 4-DMAP ( $5 \mathrm{mg}, 0.04 \mathrm{mmol}$ ), followed by the dropwise addition of $\mathrm{Ac}_{2} \mathrm{O}(1.47 \mathrm{~mL}, 15.59 \mathrm{mmol})$. The reaction was stirred from 0 ${ }^{\circ} \mathrm{C}$ to room temperature over 24 h before it was quenched with saturated aq. $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The reaction mixture was diluted with ether. The organic layer was separated, washed with $\mathrm{H}_{2} \mathrm{O}$, brine, dried over $\mathrm{MgSO}_{4}$, and concentrated. The crude residue was purified by flash column chromatography on silica gel ( $10-20 \%$ EtOAc in hexanes) to afford the product $\mathbf{1 0 b}(5.82 \mathrm{~g}, 80 \%$ yield) as a colorless oil:
$[\alpha]^{25}{ }_{\mathrm{D}}=-12.2\left(c 7.85, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.68-7.66(\mathrm{~m}, 4 \mathrm{H}), 7.44$ $-7.35(\mathrm{~m}, 6 \mathrm{H}), 7.33-7.23(\mathrm{~m}, 4 \mathrm{H}), 5.30-5.00(\mathrm{~m}, 1 \mathrm{H}), 4.52(\mathrm{dd}, J=12.1,8.2 \mathrm{~Hz}, 2$ H), 3.73 (t, $J=11.3 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.61 (d, $J=2.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), $2.57-2.43(\mathrm{~m}, 2 \mathrm{H}), 2.41-2.36$ (m, 2 H ), $2.10(\mathrm{~s}, 3 \mathrm{H}), 2.03(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{Mz}, \mathrm{CDCl}_{3}\right) \delta 170.8,138.5,138.4$, 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, $737 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{32} \mathrm{H}_{38} \mathrm{O}_{4} \mathrm{Si}[\mathrm{M}+$ $\mathrm{Na}^{+}$] 537.2432 found 537.2421.

## 2-Acetyloxy-( $E, R$ )-1-Benzyloxy-7-[(tert-butyldiphenylsilyl)oxy]-4-triethylsilyl-hept-4-ene (11a) <br> and <br> 2-Acetyloxy-( $\boldsymbol{R}, \boldsymbol{E}$ )-1-Benzyloxy-7-[(tert-butyldiphenylsilyl)oxy]-5-triethylsilyl-hept-4-ene (11b)



11a


11b

To a flask containing alkyne $\mathbf{1 0 b}(9.80 \mathrm{~g}, 20.98 \mathrm{mmol})$ and $\mathrm{Et}_{3} \mathrm{SiH}(4.02 \mathrm{~mL}, 25.18$ mmol ) at room temperature was added $\mathrm{H}_{2} \mathrm{PtCl}_{6} \cdot \mathrm{H}_{2} \mathrm{O}$ catalyst ( $52 \mathrm{mg}, 0.12 \mathrm{mmol}$ ). The resulting mixture was heated at $80{ }^{\circ} \mathrm{C}$ for 40 min before it was cooled to room temperature and purified by flash column chromatography on silica gel ( $1-2 \% \mathrm{EtOAc}$ in hexanes) to provide a mixture of products ( $13.08 \mathrm{~g}, 99 \%$ yield, $11 \mathbf{a}: \mathbf{1 1 b}=1.8: 1$ ) 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)


7a


7b

To a solution of acetates $\mathbf{1 1 a}$ and $\mathbf{1 1 b}(5.98 \mathrm{~g}, 9.48 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(100 \mathrm{~mL})$ at $-78{ }^{\circ} \mathrm{C}$ was added dropwise a solution of DIBAL-H ( 1.0 M in toluene, $14.22 \mathrm{~mL}, 1.50 \mathrm{mmol}$ ). 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 $\mathrm{H}_{2} \mathrm{O}$, brine, dried over $\mathrm{MgSO}_{4}$ and concentrated. The crude residue was purified by flash column chromatography on silica gel ( $10 \% \mathrm{EtOAc}$ in hexanes) to provide a regioisomeric mixture of alcohols $\mathbf{7 a}$ and $\mathbf{7 b}(5.26 \mathrm{~g}, 94 \%$ yield, $7 \mathbf{a}: 7 \mathbf{b}=1.8$ : 1) as a colorless oil. A portion of this product mixture was re-purified using the same condition above to give $\mathbf{7 a}$ first and then the more polar $\mathbf{7 b}$ :

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

7b: $[\alpha]^{25}{ }_{\mathrm{D}}=-3.1\left(c 11.70, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.68-7.63(\mathrm{~m}, 4 \mathrm{H})$, $7.42-7.27(\mathrm{~m}, 11 \mathrm{H}), 5.73(\mathrm{t}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.51(\mathrm{~s}, 2 \mathrm{H}), 3.80-3.71(\mathrm{~m}, 1 \mathrm{H}), 3.52$ $3.43(\mathrm{~m}, 2 \mathrm{H}), 3.37(\mathrm{dd}, J=9.5,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.24(\mathrm{dd}, J=9.4,7.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.38(\mathrm{t}, J=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.21-2.15(\mathrm{~m}, 3 \mathrm{H}), 1.04(\mathrm{~s}, 9 \mathrm{H}), 0.0 .80(\mathrm{t}, J=7.9 \mathrm{~Hz}, 9 \mathrm{H}), 0.43(\mathrm{q}, J=$ $3.8 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{Mz}, \mathrm{CDCl}_{3}$ ) $\delta 139.1$, 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, $823 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{36} \mathrm{H}_{52} \mathrm{O}_{3} \mathrm{Si}_{2}[\mathrm{M}+\mathrm{H}] 589.3527$ found 589.3533.
(2R,3R,5R)-5-(Benzyloxymehyl)-2-\{[2-(tert-butyldiphenylsilyl)oxy]-ethyl\}-3-triethylsilyl-tetrahydrofuran (12a)
and
(2S,3S,5R)-5-(Benzyloxymethyl)-2-\{[2-(tert-butyldiphenylsilyl)oxy]-ethyl\}-3-triethylsilyl-tetrahydrofuran (12b)


12a


12b

To a solution of a mixture of alcohols $\mathbf{7 a}$ and $\mathbf{7 b}(1.26 \mathrm{~g}, 2.20 \mathrm{mmol})$ in $\mathrm{CHCl}_{3}(80 \mathrm{~mL})$ at room temperature was added $\mathrm{TsOH} \cdot \mathrm{H}_{2} \mathrm{O}(41 \mathrm{mg}, 0.22 \mathrm{mmol})$. The reaction was then heated at $60^{\circ} \mathrm{C}$ for 7 h and then at $70^{\circ} \mathrm{C}$ for 15 h before it was allowed to cool to ambient
temperature. $\mathrm{Et}_{3} \mathrm{~N}$ ( 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 ( $72 \mathrm{mg}, 6 \%$ yield) first and followed by the more polar $\mathbf{1 2 b}(637 \mathrm{mg}, 51 \%$ yield) as colorless oils:

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

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


To a solution of allylic alcohol $7 \mathbf{a}(5.78 \mathrm{~g}, 10.09 \mathrm{mmol})$ in $\mathrm{CHCl}_{3}(200 \mathrm{~mL})$ at room temperature was added $\mathrm{TsOH}(100 \mathrm{mg}, 0.53 \mathrm{mmol})$. The reaction was then heated at 55 ${ }^{\circ} \mathrm{C}$ 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 ( $723 \mathrm{mg}, 13 \%$ yield) first and followed by the more polar $\mathbf{1 2 b}(3.80 \mathrm{~g}$, $66 \%$ yield). In addition, the starting material 7 a was also recovered ( 0.43 g ).

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



13
To a solution of silyl ether $\mathbf{1 2 a}(1.56 \mathrm{~g}, 2.65 \mathrm{mmol})$ in THF $(80 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ was added dropwise a solution of TBAF ( 1.0 M in THF, $3.97 \mathrm{~mL}, 3.97 \mathrm{mmol}$ ). The reaction was then stirred from $0{ }^{\circ} \mathrm{C}$ to room temperature over 3 h before it was quenched with saturated aq. $\mathrm{NH}_{4} \mathrm{Cl}$ solution. The reaction mixture was then extracted with EtOAc. The organic layer was washed with brine, dried over $\mathrm{MgSO}_{4}$ and concentrated. The crude residue was purified by flash column chromatography on silica gel ( $10-40 \% \mathrm{EtOAc}$ in hexanes) to provide alcohol $\mathbf{1 3}$ ( $932 \mathrm{mg}, 100 \%$ yield) as a colorless oil:
$[\alpha]^{25}{ }_{\mathrm{D}}=47.2\left(c 4.79, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.37-7.24(\mathrm{~m}, 5 \mathrm{H}), 4.59-$ $4.44(\mathrm{~m}, 3 \mathrm{H}), 4.28-4.21(\mathrm{~m}, 1 \mathrm{H}), 3.87-3.72(\mathrm{~m}, 2 \mathrm{H}), 3.43-3.32(\mathrm{~m}, 2 \mathrm{H}), 2.08-$ $1.96(\mathrm{~m}, 1 \mathrm{H}), 1.90-1.82(\mathrm{~m}, 1 \mathrm{H}), 1.76-1.53(\mathrm{~m}, 2 \mathrm{H}), 1.46-1.38(\mathrm{~m}, 1 \mathrm{H}), 0.98-$ $0.92(\mathrm{~m}, 9 \mathrm{H}), 0.66-0.54(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{Mz}, \mathrm{CDCl}_{3}\right) \delta 138.6,128.7$, 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, $697 \mathrm{~cm}^{-1} ;$ HRMS (EI) calcd for $\mathrm{C}_{20} \mathrm{H}_{34} \mathrm{O}_{3} \mathrm{Si}[\mathrm{M}+\mathrm{H}] 351.2350$ found 351.2348 .

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



6
To a solution of alcohol $\mathbf{1 3}(0.88 \mathrm{~g}, 2.51 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(25 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ was added $\mathrm{NaHCO}_{3}(0.53 \mathrm{~g}, 6.28 \mathrm{mmol})$ and followed by Dess-Martin periodinane ( $1.38 \mathrm{~g}, 3.26$ $\mathrm{mmol})$ in small portions. The reaction was then stirred from $0{ }^{\circ} \mathrm{C}$ to room temperature over 1 h before it was diluted with EtOAc. The organic layer was washed with $\mathrm{H}_{2} \mathrm{O}$, brine, dried over $\mathrm{MgSO}_{4}$ and concentrated to yield the crude aldehyde $6(0.84 \mathrm{~g}, 96 \%$ yield) as a colorless oil:
$[\alpha]^{25}{ }_{\mathrm{D}}=69.6\left(c 6.98, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR (300 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 9.77-9.75(\mathrm{~m}, 1 \mathrm{H}), 7.37-$ $7.24(\mathrm{~m}, 5 \mathrm{H}), 4.80-4.73(\mathrm{~m}, 1 \mathrm{H}), 4.54(\mathrm{~s}, 2 \mathrm{H}), 4.07-3.99(\mathrm{~m}, 1 \mathrm{H}), 3.56-3.46(\mathrm{~m}, 2$ H), 2.51 (ddd, $J=14.8,11.3,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.31-2.20(\mathrm{~m}, 1 \mathrm{H}), 2.09-1.98(\mathrm{~m}, 1 \mathrm{H})$, $1.78-1.62(\mathrm{~m}, 2 \mathrm{H}), 0.94(\mathrm{t}, J=7.9 \mathrm{~Hz}, 9 \mathrm{H}), 0.63-0.53(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 75 Mz , $\left.\mathrm{CDCl}_{3}\right) \delta 202.8,138.7,128.8,128.1,128.0,80.0,77.6,73.9,73.3,50.1,30.9,30.1,8.1$, 4.1; IR (neat) 3064, 3030, 2954, 2910, 2875, 2732, 1727, 1455, 1418, 1363, 1310, 1241, 1192, 1098, 1076, 1017, 948, 732, $698 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{20} \mathrm{H}_{32} \mathrm{O}_{3} \mathrm{Si}[\mathrm{M}+\mathrm{H}]$ 349.2194 found 349.2192 .

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


15
To a solution of ethyl diazoacetate ( $196 \mathrm{mg}, 1.72 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(6 \mathrm{~mL})$ at room temperature was added anhydrous $\mathrm{SnCl}_{2}(27 \mathrm{mg}, 0.14 \mathrm{mmol})$. The cloudy reaction mixture was stirred for 15 min and followed by addition of a solution of aldehyde 6 (500 $\mathrm{mg}, 1.43 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(6 \mathrm{~mL})$. 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 ( $436 \mathrm{mg}, 70 \%$ yield) and the more polar oxocene $4(104 \mathrm{mg}, 23 \%$ yield) both as colorless oils:
$\beta$-keto ester 15: $[\alpha]^{25}{ }_{\mathrm{D}}=90.5\left(c\right.$ 4.31, $\left.\mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.36$ $7.26(\mathrm{~m}, 5 \mathrm{H}), 4.69-4.62(\mathrm{~m}, 1 \mathrm{H}), 4.54(\mathrm{~s}, 2 \mathrm{H}), 4.18-4.10(\mathrm{~m}, 2 \mathrm{H}), 4.06-3.93(\mathrm{~m}, 1$ H), $3.58-3.47$ (m, 4 H ), 2.69 (dd, $J=13.9,11.3 \mathrm{~Hz}, 1 \mathrm{H}$ ), $2.38(\mathrm{dd}, J=13.9,2.6 \mathrm{~Hz}, 1$ H), $2.03-1.95(\mathrm{~m}, 1 \mathrm{H}), 1.77-1.63(\mathrm{~m}, 2 \mathrm{H}), 1.27-1.19(\mathrm{~m}, 3 \mathrm{H}), 1.00-0.92(\mathrm{~m}, 9 \mathrm{H})$, $0.65-0.52(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{Mz}, \mathrm{CDCl}_{3}$ ) $\delta 202.7$, 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, $733,698 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{24} \mathrm{H}_{38} \mathrm{O}_{5} \mathrm{Si}[\mathrm{M}+\mathrm{H}] 457.2381$ found 457.2373.
(2S,3S,8R,Z)-8-(Benzyloxymethyl)-3-hydroxy-3,4,7,8-tetrahydro-(2H)-oxocine-2carboylic acid ethyl ester (4)

$[\alpha]^{25}{ }_{\mathrm{D}}=32.5\left(c 3.43, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.35-7.27(\mathrm{~m}, 5 \mathrm{H}), 5.96-$ 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 ), $3.74-3.66$ $(\mathrm{m}, 1 \mathrm{H}), 3.60(\mathrm{dd}, J=5.5,4.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.45(\mathrm{dd}, J=5.4,4.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.00(\mathrm{~m}, 1 \mathrm{H})$, $2.83-2.74(\mathrm{~m}, 1 \mathrm{H}), 2.44-2.22(\mathrm{~m}, 3 \mathrm{H}), 1.25(\mathrm{t}, J=7 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 Mz , $\mathrm{CDCl}_{3}$ ) $\delta 174.2,138.6,138.5,129.6,129.6,128.8,128.0,82.7,81.3,73.7,73.3,73.0$, 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, $698 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{O}_{5}[\mathrm{M}+\mathrm{H}]$ 321.1697 found 321.1694 .

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



13b
$[\alpha]^{25}{ }_{\mathrm{D}}=-29.3\left(c 6.10, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.36-7.27(\mathrm{~m}, 5 \mathrm{H}), 4.55$ (dd, $J=12,17 \mathrm{~Hz}, 2 \mathrm{H}), 4.5-4.45(\mathrm{~m}, 1 \mathrm{H}), 4.28-4.22(\mathrm{~m}, 1 \mathrm{H}), 3.87-3.73(\mathrm{~m}, 2 \mathrm{H})$, $3.42-3.18(\mathrm{~m}, 2 \mathrm{H}), 3.16(\mathrm{dd}, J=2,9 \mathrm{~Hz}, 1 \mathrm{H}), 2.07-1.99(\mathrm{~m}, 1 \mathrm{H}), 1.89-1.83(\mathrm{~m}, 1$ H), $1.75-1.64(\mathrm{~m}, 1 \mathrm{H}), 1.62-1.55(\mathrm{~m}, 1 \mathrm{H}), 1.45-1.38(\mathrm{~m}, 1 \mathrm{H}), 0.97(\mathrm{t}, J=8 \mathrm{~Hz}, 9$ H), $0.65-0.55(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{Mz}, \mathrm{CDCl}_{3}$ ) $\delta 138.6$, 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, $697 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{20} \mathrm{H}_{34} \mathrm{O}_{3} \mathrm{Si}[\mathrm{M}+\mathrm{H}] 351.2350$ found 351.2351 .
[(2S,3S,5R)-5-(Benzyloxymethyl)-3-triethylsilyl-tetrahydro-furan-2-yl]-acetaldehyde (6b)


6b
$[\alpha]^{25}{ }_{\mathrm{D}}=-47.9\left(c 4.70, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 9.79-9.78(\mathrm{~m}, 1 \mathrm{H}), 7.35$ $-7.26(\mathrm{~m}, 5 \mathrm{H}), 4.85-4.80(\mathrm{~m}, 1 \mathrm{H}), 4.54(\mathrm{dd}, J=12,17 \mathrm{~Hz}, 2 \mathrm{H}), 4.27-4.20(\mathrm{~m}, 1 \mathrm{H})$, $3.42-3.33(\mathrm{~m}, 2 \mathrm{H}), 2.51$ (ddd, $J=15,11,3 \mathrm{~Hz}, 1 \mathrm{H}), 2.30-2.26(\mathrm{~m}, 1 \mathrm{H}), 2.05-1.88$ $(\mathrm{m}, 2 \mathrm{H}), 1.72-1.62(\mathrm{~m}, 1 \mathrm{H}), 0.96(\mathrm{t}, J=8 \mathrm{~Hz}, 9 \mathrm{H}), 0.63-0.53(\mathrm{~m}, 6 \mathrm{H}){ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{Mz}, \mathrm{CDCl}_{3}\right) \delta 202.2,138.6,128.7,128.1,128.0,77.9,76.4,73.7,73.0,65.2,48.2$, 30.1, 28.2, 8.1, 4.0; IR (neat) 3030, 2953, 2910, 2875, 2732, 1727, 1454, 1415, 1241, 1161, 1096, 1017, 803, 733, $698 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{20} \mathrm{H}_{32} \mathrm{O}_{3} \mathrm{Si}[\mathrm{M}+\mathrm{H}]$ 349.2194 found 349.2194 .
(2R,3R,8R,Z)-8-(Benzyloxymethyl)-3-hydroxy-3,4,7,8-tetrahydro-(2H)-oxocine-2carboylic acid ethyl ester (20)


20
${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.36-7.27(\mathrm{~m}, 5 \mathrm{H}), 5.91-5.74(\mathrm{~m}, 2 \mathrm{H}), 4.53(\mathrm{~s}, 2 \mathrm{H})$, $4.22-4.15(\mathrm{~m}, 3 \mathrm{H}), 4.02-3.91(\mathrm{~m}, 2 \mathrm{H}), 3.64$ (ddd, $J=6,10,17 \mathrm{~Hz}, 2 \mathrm{H}), 2.75(\mathrm{~d}, J=$ $4.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.59-2.53(\mathrm{~m}, 1 \mathrm{H}), 2.43-2.31(\mathrm{~m}, 3 \mathrm{H}), 1.24(\mathrm{t}, J=7 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{Mz}, \mathrm{CDCl}_{3}$ ) $\delta 173.4,138.3,128.9,128.8,128.8,128.1,128.0,77.6,76.0,75.5,73.6$, $72.5,71.2,65.0,61.7,33.3,29.3,14.5$; IR (neat) 3462, 3027, 2980, 2932, 1740, 1497, 1454, 1373, 1323, 1245, 1182, 1097, 1041, 737, $698 \mathrm{~cm}^{-1}$; HRMS (EI) calcd for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{O}_{5}[\mathrm{M}+\mathrm{H}] 321.1697$ found 321.1693.



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