# Supporting information

# Substrate-controlled stereoselectivity in the Yamamoto aldol reaction

*Nadin Schläger and Andreas Kirschning**

Institute of Organic Chemistry and Center of Biomolecular Drug Research (BMWZ),
Schneiderberg 1b, 30167 Hannover.
Fax: +49(0)511 7623011; Tel: +49 (0)511 7624614;
E-mail: andreas.kirschning@oci.uni-hannover.de

## General Remarks

Unless otherwise stated, all chemicals and solvents were purchased in per analysis quality and used as received. $^1$H NMR spectra were recorded at 400 MHz or 500 MHz and $^{13}$C NMR spectra were recorded at 100 MHz or 125 MHz with a BRUKER Avance 400, DPX 400 or DRX 500. Chemical shift values of NMR data are reported as values in ppm relative to (residual undeuterated) solvent signal as internal standard. Multiplicities for $^1$H NMR signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; where appropriate with the addition of b = broad. $^{13}$C Multiplicities refer to the resonances in the off-resonance decoupled spectra and were elucidated using the distortionless enhancement by polarisation transfer (DEPT) spectral editing technique. Multiplicities for $^{13}$C NMR signals are reported using the following abbreviation: q = quaternary ($CR_4$), t = tertiary ($R_3CH$), secondary = s ($R_2CH_2$) and primary = p ($RCH_3$). Mass spectra were obtained with a type LCT (ESI) (Micromass) equipped with a lockspray dual ion source in combination with a WATERS Alliance 2695 LC system, or with a type Q-TOF premier (Micromass) spectrometer (ESI mode) in combination with a WATERS Acquity UPLC system equipped with a Waters BEH C18 1.7 µm (SN 01473711315545) column (solvent A: water + 0.1 % (v/v) formic acid, solvent B: MeOH + 0.1 % (v/v) formic acid; flow rate = 0.4 mL/min; gradient (t [min]/solvent B [%]): (0:5) (2.5:95) (6.5:95) (6.6:5) (8:5)). Ion mass signals (m/z) are reported as values in atomic mass units. Optical rotations were measured on a Perkin-Elmer polarimeter type 341 or 241 in a quartz glass cuvette at l = 589 nm (Na D-line). The optical rotation is given in [° ml·g-1·dm-1] with *c* = 1 corresponding to 10 mg ml$^{-1}$. Flash-chromatography was done with silica gel (Acros, particle size 35-70 µm) by applying moderate pressure. Preparative HPLC was operated at a MERCK HITACHI

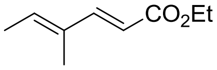
LaChrome HPLC (Pump L7150 or L7100, Interface D-7000, Diode Array Detector L-7450) respectively at a BECKMANN system Gold HPLC (Solvent Module 125, Detector 166). Solvents, columns, operating procedures and retention times are given with the corresponding experimental and analytical data.

## General procedure for the YAMAMOTO-aldol reaction

*Introductory remarks*: YAMAMOTO aldol reactions were carried out under different conditions. Parameters like “temperature“ and “reaction time“ were varied. The general procedure is given below. All changes according to the general procedure are stated in the main paper.

**Solution A**: 2,6-Diphenylphenol (6.6 eq) was dissolved in toluene ($c$ = 0.28 mol/l, with respect to $AlMe_3$) and $AlMe_3$ ($c$ = 2 mol/l in toluene, 2.2 eq) was slowly added over 30 min after which time the yellow solution was stirred for 30 min at rt and then cooled to -78 °C. The ester (2.0 eq) was dissolved in toluene ($c$ = 1 mol/l) and slowly added. The resulting solution was stirred for 30 min at -78 °C. **Solution B (LTMP-solution 8)**: 2,2,6,6-Tetramethyl-piperidine (2.3 eq) was dissolved in THF ($c$ = 0.19 mol/l) and cooled to -78 °C. *n*-BuLi ($c$ = 2.5 mol/l in hexane, 2.3 eq) was added dropwise. The resulting solution was stirred for 20 min at -78 °C and slowly added to **solution A**. The resulting mixture was stirred for 40 min at -78 °C. **Solution C**: 2,6-Diphenylphenol (6.0 eq) was dissolved in toluene ($c$ = 0.28 mol/l with respect to $AlMe_3$) and $AlMe_3$ ($c$ = 2 mol/l in toluene, 2.0 eq) was slowly added over 45 min. Afterwards the solution was stirred for 30 min at rt and then cooled to -78 °C. The aldehyde (1.0 eq) was dissolved in toluene ($c$ = 1 mol/l) and added dropwise. The solution was stirred for 30 min at -78 °C. **Solution C** was added over 10 min to **solution A** and the resulting reaction mixture was stirred at -78 °C over night. The reaction was terminated by addition of aq. $NH_4Cl$, warmed up to rt and stirred for 3 h after the addition of a solution of Na-K-tartrate. The layers were separated and the aqueous layer extracted with EE. The combined, organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography (petroleum ether:ethyl acetate; ratios are given).

### (2*E*,4*E*)-Ethyl-4-methylhexa-2,4-dienoate (6)

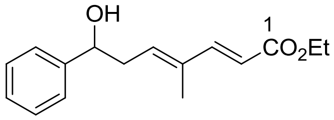


**6**

*trans*-2-Methyl-butenal (**13**) (2.8 ml, 29.0 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (30 ml) and (1-ethoxycarbonylmethyliden)triphenylphosphorane (**14**) (15 g, 43.1 mmol, 1.5 eq) was added. The solution was stirred for 13 d at rt. The crude product was adsorbed on silica gel and purified by flash chromatography (petroleum ether : ethyl acetate = 20:1). (2*E*,4*E*)-Ethyl-4-methylhexa-2,4-dienoate (**6**) (4.36 g, 28.3 mmol, 98%) was obtained as a colourless liquid.

$R_f$ = 0.54 (PE:EE = 10:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.31 (d, 1H, *J* = 15.7 Hz, H-3), 5.98 (q, 1H, *J* = 7.1 Hz, H-5), 5.78 (d, 1H, *J* = 15.7 Hz, H-2), 4.20 (q, 2H, *J* = 7.2 Hz, H-8), 1.81 (d, 3H, *J* = 7.1 Hz, H-6), 1.77 (s, 3H, H-7), 1.30 (t, 3H, *J* = 7.2 Hz, H-9) ppm; **HRMS** (EI): *m/z*: calculated for $C_9H_{14}O_2$: 154.0994 $M^+$ , found: 154.0994 $M^+$. The analytical data is in accordance with the literature.[S1]

**Test reaction: (2*E*,4*E*)-Ethyl-7-hydroxy-4-methyl-7-phenylhepta-2,4-dienoate (S1)**



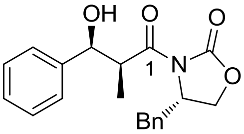
**S1**

For checking the quality of all components, a test reaction with benzaldehyde was conducted prior to use of chiral aldehydes.

Thus, 2,6-diphenylphenol (1.19 g, 4.9 mmol, 9.9 eq) was dissolved in toluene (6 ml) and $AlMe_3$ (0.81 ml, *c* = 2 mol/l in hexane, 1.6 mmol, 3.3 eq) was slowly added. The solution was stirred for 30 min at rt and then cooled to -78 °C. Benzaldehyde (**S2**) (0.05 ml, 0.5 mmol, 1.0 eq) and ester **6** (151 mg, 1.0 mmol, 2.0 eq) were added and the solution was stirred for 35 min at -78 °C. For preparation of the LTMP-solution, 2,2,6,6-tetramethylpiperidine (0.19 ml, 1.1 mmol, 2.3 eq) was dissolved in THF (6 ml) and cooled to -78 °C. *n*-BuLi (0.45 ml, *c* = 2.5 mol/l in hexane, 1.2 mmol, 2.3 eq) was slowly added and stirring was continued for 30 min. The LTMP-solution (**8**) was added and the reaction was stirred for 30 min at -78 °C. The reaction was terminated by addition of aq. $NH_4Cl$, Na-K-tartrate and the mixture was stirred overnight. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 2:1) and product **S1** (127 mg, 0.5 mmol, 99%) was obtained as colourless oil.

$R_f$ = 0.44 (PE:EE = 2:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-2.37 (m, 5H, Ph), 7.29 (d, 1H, *J* = 15.5 Hz, H-3), 5,91 (dd, 1H, *J* = 7.4, 7.3 Hz, H-5), 5.79 (d, 1H, *J* = 15.5 Hz, H-2), 4.80 (dd, 1H, *J* = 6.7, 6.3 Hz, H-7), 4.20 (q, 2H, *J* = 7.1 Hz, H-9), 2.73 (ddd, 1H, *J* = 14.6, 7.4, 6.7 Hz, H-$6_a$), 2.64 (ddd, 1H, *J* = 14.6, 7.3, 6.3 Hz, H-$6_b$), 1.72 (s, 3H, H-8), 1.29 (t, 3H, *J* = 7.1 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.2 (t, C-3), 143.8 (q, C-4), 136.7 (t, C-5), 135.4 (q, Ph), 128.7 (t, Ph), 128.0 (q, Ph), 125.9 (t, Ph), 116.5 (t, C-2), 73.9 (t, C-7), 60.4 (s, C-9), 38.7 (s, C-6), 14.5 (p, C-10), 12.5 (p, C-8) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{21}O_3$ and $C_{16}H_{20}O_3Na$: 261.1491 $[M + H]^+$ and 283.1310 $[M + Na]^+$, found: 261.1490 $[M + H]^+$ und 283.1299 $[M + Na]^+$.

### (*S*)-7-Benzyl-3-[(2*S*,3*S*)-3-hydroxy-2-methyl-3-phenylpropanoyl]oxazolidin-2-one (S3)

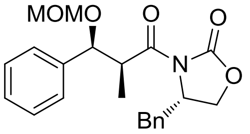


**S3**

Propionated (*S*)-Evans auxiliary **S4**[S2] (1.00 g, 4.3 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (16 ml) and the solution was cooled to 0 °C. $Et_3N$ (0.7 ml, 5.2 mmol, 1.2 eq) was added. Afterwards, *n*-$Bu_2BOTf$ (5.2 ml, *c* = 1 mol/l in $CH_2Cl_2$, 5.2 mmol, 1.2 eq) was added over a peiod of 10 min. The solution was stirred for 2 h at 0 °C. After cooling to -78 °C, benzaldehyde (**S2**) (0.7 ml, 6.4 mmol, 1.5 eq) in $CH_2Cl_2$ (1.6 ml) was added over a period of 5 min. The solution was stirred for 2 h at -78 °C and then overnight at 0 °C. The reaction was terminated by addition of MeOH (20 ml), phosphate buffer (pH = 7, 6.2 ml) and a solution of MeOH (14 ml) and aq. $H_2O_2$ (30%; 7 ml). After stirring for 4 h at rt, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 2:1). Product **S3** (1.40 g, 4.1 mmol, 96%) was obtained as a colourless oil.

$R_f$ = 0.39 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +60.3 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.16-7.41 (m, 10H, Ph), 5.10 (d, 1H, *J* = 4.1 Hz, H-3), 4.56-4.63 (m, 1H, H-7), 4.04-4.16 (m, 3H, H-2 + H-6), 3.25 (dd, 1H, *J* = 13.3, 3.1 Hz, H-$8_a$), 2.78 (dd, 1H, *J* = 13.3, 9.6 Hz, H-$8_b$), 1.23 (d, 3H, J = 6.8 Hz, H-4) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 176.9 (q, C-1), 153.0 (q, C-5), 141.4 (q, Ph), 135.2 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 128.4 (t, Ph), 127.7 (t, Ph), 127.6 (t, Ph), 126.3 (t, Ph), 74.0 (t, C-3), 66.3 (s, C-6), 55.4 (t, C-7), 44.7 (t, C-2), 37.9 (s, C-8), 11.1 (p, C-4) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{21}NaNO_4$: 362.1368 $[M + Na]^+$, found: 362.1369 $[M + Na]^+$. The analytical data are in accordance with those reported in the literature.[S3]

### ($S$)-7-Benzyl-3-[(2$S$,3$S$)-3-(methoxymethoxy)-2-methyl-3-phenylpropanoyl]oxazolidin-2-one (S5)

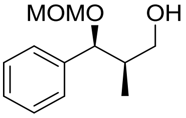


**S5**

Alcohol **S3** (500 mg, 1.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (30 ml) and cooled to 0 °C. $^i$Pr$_2$NEt (3.4 ml, 14.7 mmol, 10.0 eq) and MOMCl (0.6 ml, 7.35 mmol, 5.0 eq) were added. The reaction mixture was stirred for 30 min at 0 °C and then for 7 d at rt after which time the reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl ($c$ = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1) and furnished product **S5** (528 mg, 1.4 mmol, 94%) as a colourless oil.

R$_f$ = 0.43 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +6.8 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.15-7.39 (m, 10H, Ph), 4.82 (d, 1H, $J$ = 7.5 Hz, H-3), 4.53 (d, 1H, $J$ = 6.8 Hz, MOM), 4.51 (d, 1H, $J$ = 6.8 Hz, MOM), 4.22-4.36 (m, 2H, H-7 + H-2), 4.00 (dd, 1H, $J$ = 8.4, 1.9 Hz, H-6$_a$), 3.72 (dd, 1H, $J$ = 8.4, 8.1 Hz, H-6$_b$), 3.35 (s, 3H, MOM), 3.21 (dd, 1H, $J$ = 13.2, 3.1 Hz, H-8$_a$), 2.69 (dd, 1H, $J$ = 13.2, 10.0 Hz, H-8$_b$), 1.38 (d, 3H, J = 6.7 Hz, H-4) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.4 (q, C-1), 153.1 (q, C-5), 139.7 (q, Ph), 135.4 (q, Ph), 129.6 (t, Ph), 129.0 (t, Ph), 128.3 (t, Ph), 128.1 (t, Ph), 127.6 (t, Ph), 127.4 (t, Ph), 94.4 (s, MOM), 79.3 (t, C-3), 66.0 (s, C-6), 55.9 (t, C-7), 55.8 (p, MOM), 44.7 (t, C-2), 37.8 (s, C-8), 13.3 (p, C-4) ppm; **HRMS** (ESI): $m/z$: calculated for $C_{22}H_{25}NaNO_5$: 406.1630 $[M + Na]^+$, found: 406.1630 $[M + Na]^+$.

### (2$R$,3$S$)-3-(Methoxymethoxy)-2-methyl-3-phenylpropan-1-ol (S6)

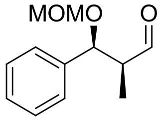


**S6**

Oxazolidinone **S5** (528 mg, 1.38 mmol, 1.0 eq) was dissolved in $Et_2O$ (27 ml) and cooled to 0 °C. $H_2O$ (0.03 ml, 1.66 mmol, 1.2 eq) and $LiBH_4$ (150 mg, 6.89 mmol, 5.0 eq) were added. The solution was stirred overnight at rt. The reaction was terminated by addition of aq. $NH_4Cl$ and stirred for 2 h at RT. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 2:1) to furnish alcohol **S6** (259 mg, 1.23 mmol, 89%) as a colourless oil.

R$_f$ = 0.30 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -174.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.78 (d, 1H, *J* = 5.1 Hz, H-3), 4.58 (d, 1H, *J* = 6.5 Hz, MOM), 4.54 (d, 1H, *J* = 6.5 Hz, MOM), 3.61 (dd, 1H, *J* = 11.0, 7.3 Hz, H-1$_a$), 3.49 (dd, 1H, *J* = 11.0, 5.1 Hz, H-1$_b$), 3.41 (s, 3H, MOM), 2.25 (brs, 1H, OH), 2.02-2.13 (m, 1H, H-2), 0.87 (d, 3H, *J* = 6.8 Hz, H-4) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 140.1 (q, Ph), 128.4 (t, Ph), 127.7 (t, Ph), 127.3 (t, Ph), 95.0 (s, MOM), 79.9 (t, C-3), 65.5 (s, C-1), 56.0 (p, MOM), 41.9 (t, C-2), 11.9 (p, C-4) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{18}NaO_3$: 233.1154 [M + Na]$^+$, found: 233.1154 [M + Na]$^+$.

### (2*S*,3*S*)-3-(Methoxymethoxy)-2-methyl-3-phenylpropanal (15)

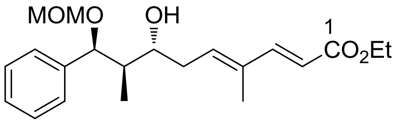


**15**

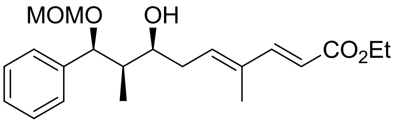
Alcohol **S6** (130 mg, 0.52 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (10 ml) and $NaHCO_3$ (20 mg) and DESS-MARTIN periodinane (266 mg, 0.63 mmol, 1.2 eq) were added. Stirring was continued for 2 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and the mixture was stirred for 2 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **15** (94 mg, 0.45 mmol, 87%) as a colourless oil, which was used immediately in the next step.

R$_f$ = 0.63 (PE:EE = 2:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.77 (d, 1H, *J* = 1.0 Hz, H-1), 7.27-7.40 (m, 5H, Ph), 5.11 (d, 1H, *J* = 4.8 Hz, H-3), 4.57 (d, 1H, *J* = 6.8 Hz, MOM), 4.55 (d, 1H, *J* = 6.8 Hz, MOM), 3.35 (s, 3H, MOM), 2.70 (m, 1H, H-2), 1.11 (d, 3H, *J* = 7.2 Hz, H-4) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 203.5 (t, C-1), 139.0 (q, Ph), 128.7 (t, Ph), 128.1 (t, Ph), 127.2 (t, Ph), 94.4 (s, MOM), 76.9 (t, C-3), 56.1 (p, MOM), 53.0 (t, C-2), 8.6 (p, C-4) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{16}NaO_3$: 231.0997 [M + Na]$^+$, found: 231.0995 [M + Na]$^+$.

### (2*E*,4*E*,7*S*,8*R*,9*S*)-Ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethyl-9-phenylnona-2,4-dienoate (7,8-*syn*,8,9-*syn* 17a) and (2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethyl-9-phenylnona-2,4-dienoate (7,8-*anti*,8,9-*syn* 17b)



7,8-*anti*,8,9-*syn* **17b**



7,8-*syn*,8,9-*syn* **17a**

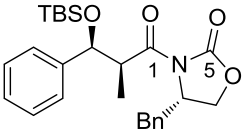
Following the general procedure aldehyde **15** (41 mg, 0.20 mmol, 1.0 eq) was reacted with ester **6** (62 mg, 0.40 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 5:1) to furnish alcohols 7,8-*syn*,8,9-*syn* **17a** and 7,8-*anti*,8,9-*syn* **17b** (*d.r.*: 1:5.2 (**17b**:**17a**), 63 mg, 0.17 mmol, 88%) as a yellow oil.

$R_f$ = 0.13 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{21}H_{30}NaO_5$: 385.1991 $[M + Na]^+$, found: 385.1991 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **17a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.23-7.39 (m, 6H, H-3 + Ph), 5.86 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.79 (d, 1H, *J* = 15.7 Hz, H-2), 4.80 (d, 1H, *J* = 5.5 Hz, H-9), 4.55 (d, 1H, *J* = 6.5 Hz, MOM), 4.52 (d, 1H, *J* = 6.5 Hz, MOM), 4.20 (q, 2H, *J* = 7.1 Hz, H-12), 3.79-3.85 (m, 1H, H-7), 3.40 (s, 3H, MOM), 2.28-2.55 (m, 2H, H-6), 1.77-1.83 (m, 1H, H-8), 1.76 (s, 3H, H-10), 1.29 (t, 3H, *J* = 7.1 Hz, H-13), 0.97 (d, 3H, *J* = 7.2 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.3 (t, C-3), 140.0 (q, Ph), 137.7 (t, C-5), 134.7 (q, C-4), 128.5 (t, Ph), 127.8 (t, Ph), 127.2 (t, Ph), 116.3 (t, C-2), 94.6 (s, MOM), 82.0 (t, C-9), 73.5 (t, C-7), 60.3 (s, C-12), 56.3 (p, MOM), 43.8 (t, C-8), 34.7 (s, C-6), 14.4 (p, C-13), 12.5 (p, C-10), 7.0 (p, C-11) ppm.

7,8-*anti*,8,9-*syn* **17b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.23-7.39 (m, 6H, H-3 + Ph), 6.07 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 5.04 (d, 1H, *J* = 3.4 Hz, H-9), 4.63 (d, 1H, *J* = 6.5 Hz, MOM), 4.52 (d, 1H, *J* = 6.5 Hz, MOM), 4.20 (q, 2H, *J* = 7.1 Hz, H-12), 3.71 (ddd, 1H, *J* = 7.9, 7.9, 3.8 Hz, H-7), 3.41 (s, 3H, MOM), 2.28-2.55 (m, 2H, H-6), 1.83-1.90 (m, 1H, H-8), 1.76 (s, 3H, H-10), 1.29 (t, 3H, *J* = 7.1 Hz, H-13), 0.77 (d, 3H, *J* = 6.8 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 139.9 (q, Ph), 138.4 (t, C-5), 134.5 (q, C-4), 128.3 (t, Ph), 127.5 (t, Ph), 127.0 (t, Ph), 116.0 (t, C-2), 95.5 (s, MOM), 79.5 (t, C-9), 72.9 (t, C-7), 60.3 (s, C-12), 56.2 (p, MOM), 44.7 (t, C-8), 34.1 (s, C-6), 14.4 (p, C-13), 12.6 (p, C-10), 11.1 (p, C-11) ppm.

### (*S*)-7-Benzyl-3-[(2*S*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-2-methyl-3-phenylpropanoyl]-oxazolidin-2-one (S7)

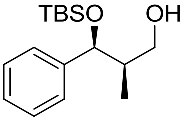


**S7**

Alcohol **S3** (500 mg, 1.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (30 ml) and cooled to 0 °C. 2,6-Lutidine (0.48 ml, 4.4 mmol, 3.0 eq) and TBSOTf (0.47 ml, 2.2 mmol, 1.5 eq) were added and the reaction mixture was stirred for 3 h at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl ($c$ = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish product **S7** (632 mg, 1.4 mmol, 95%) as a colourless oil.

$R_f$ = 0.52 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +67.4 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.15-7.38 (m, 10H, Ph), 4.84 (d, 1H, H-3), 4.22-4.29 (m, 1H, H-7), 4.12-4.20 (m, 1H, H-2), 3.99 (dd, 1H, $J$ = 8.5, 1.7 Hz, H-6$_a$), 3.69 (dd, 1H, $J$ = 8.5, 8.0 Hz, H-6$_b$), 3.20 (dd, 1H, $J$ = 13.3, 3.1 Hz, H-8$_a$), 2.69 (dd, 1H, $J$ = 13.3, 9.9 Hz, H-8$_b$), 1.30 (d, 3H, $J$ = 6.5 Hz, H-4), 0.88 (s, 9H, TBS), 0.02 (s, 3H, TBS), -0.23 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.7 (q, C-1), 153.0 (q, C-5), 143.0 (q, Ph), 135.5 (q, Ph), 129.6 (t, Ph), 129.0 (t, Ph), 128.0 (t, Ph), 127.6 (t, Ph), 127.4 (t, Ph), 126.8 (t, Ph), 76.7 (t, C-3), 66.0 (s, C-6), 55.9 (t, C-7), 46.8 (t, C-2), 37.9 (s, C-8), 25.9 (p, TBS), 18.3 (q, TBS), 13.0 (p, C-4), -4.5 (p, TBS), -5.1 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{26}H_{35}NO_4Si$: 454.2414 $[M + H]^+$, found: 454.2411 $[M + H]^+$.

### (2*R*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-2-methyl-3-phenylpropan-1-ol (S8)

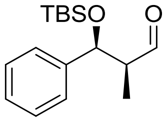


**S8**

Oxazolidinone **S7** (625 mg, 1.38 mmol, 1.0 eq) was dissolved in $Et_2O$ (28 ml) and cooled to 0 °C. $H_2O$ (0.03 ml, 1.68 mmol, 1.2 eq) and $LiBH_4$ (150 mg, 6.89 mmol, 5.0 eq) were added and the reaction mixture was stirred for 2 h at 0 °C and then overnight at rt. The reaction was terminated by addition of aq. $NH_4Cl$ and stirring was continued for 2 h at rt. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish alcohol **S8** (200 mg, 0.71 mmol, 40%) as a colourless liquid.

R$_f$ = 0.35 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -57.7 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.22-7.37 (m, 5H, Ph), 4.83 (d, 1H, *J* = 4.3 Hz, H-3), 3.58 (dd, 1H, *J* = 10.8, 8.2 Hz, H-1$_a$), 3.44 (dd, 1H, *J* = 10.8, 4.7 Hz, H-1$_b$), 2.26 (brs, 1H, OH), 2.01-2.12 (m, 1H, H-2), 0.90 (s, 9H, TBS), 0.77 (d, 3H, *J* = 7.0 Hz, H-4), 0.05 (s, 3H, TBS), -0.18 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 142.4 (q, Ph), 128.0 (t, Ph), 127.3 (t, Ph), 126.9 (t, Ph), 77.7 (t, C-3), 65.7 (s, C-1), 43.0 (t, C-2), 26.0 (p, TBS), 18.3 (q, TBS), 12.1 (p, C-4), -4.5 (p, TBS), -5.2 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{28}NaO_2Si$: 303.1756 $[M + Na]^+$, found: 303.1757 $[M + Na]^+$.

**(2*S*,3*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-methyl-3-phenylpropanal (16)**

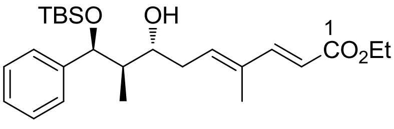


**16**

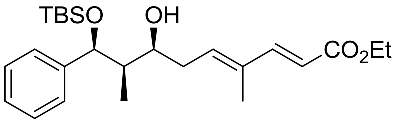
Alcohol **S8** (101 mg, 0.36 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7 ml) and $NaHCO_3$ (15 mg) was added. DESS-MARTIN periodinane (184 mg, 0.43 mmol, 1.2 eq) was added and stirring was continued for 70 min at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ at rt. After 1 h the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **16** (82 mg, 0.30 mmol, 83%) as a colourless liquid, which was directly used in the next step.

R$_f$ = 0.62 (PE:EE = 5:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.76 (d, 1H, *J* = 1.1 Hz, H-1), 7.23-7.37 (m, 5H, Ph), 5.15 (d, 1H, *J* = 4.5 Hz, H-3), 2.59 (qdd, 1H, *J* = 6.8, 4.5, 1.1 Hz, H-2), 1.04 (d, 1H, *J* = 6.8 Hz, H-4), 0.89 (s, 9H, TBS), 0.03 (s, 3H, TBS), -0.18 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 204.5 (t, C-1), 142.4 (q, Ph), 128.3 (t, Ph), 127.6 (t, Ph), 126.4 (t, Ph), 74.4 (t, C-3), 54.9 (t, C-2), 25.9 (p, TBS), 18.3 (q, TBS), 8.1 (p, C-4), -4.4 (p, TBS), -5.1 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{26}NaO_2Si$: 301.1600 $[M + Na]^+$, found: 301.1606 $[M + Na]^+$.

### (2*E*,4*E*,7*S*,8*R*,9*S*)-Ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethyl-9-phenylnona-2,4-dienoate (7,8-*syn*,8,9-*syn* 18a) and (2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethyl-9-phenylnona-2,4-dienoate (7,8-*anti*,8,9-*syn* 18b)



7,8-*anti*,8,9-*syn* **18b**



7,8-*syn*,8,9-*syn* **18a**

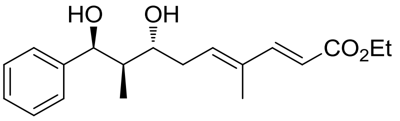
Following the general procedure aldehyde **16** (37 mg, 0.13 mmol, 1.0 eq) was reacted with ester **6** (40 mg, 0.26 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols 7,8-*syn*,8,9-*syn* **18a** and 7,8-*anti*,8,9-*syn* **18b** [*d.r.*: 1:2 (**18b**:**18a**), 28 mg, 0.06 mmol, 49%] as a yellow liquid.

$R_f$ = 0.39 (PE:EE = 5:1); diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{25}H_{40}NaO_4Si$: 455.2594 [M + Na]$^+$, found: 455.2589 [M + Na]$^+$.

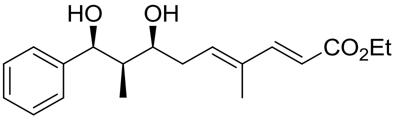
7,8-*syn*,8,9-*syn* **18a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.21-7.39 (m, 6H, H-3 + Ph), 5.86 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.79 (d, 1H, *J* = 15.7 Hz, H-2), 4.81 (d, 1H, *J* = 4.4 Hz, H-9), 4.20 (q, 2H, *J* = 7.1 Hz, H-12), 3.81-3.88 (m, 1H, H-7), 2.26-2.50 (m, 2H, H-6), 1.76 (s, 3H, H-10), 1.65-1.74 (m, 1H, H-8), 1.30 (t, 3H, *J* = 7.1 Hz, H-13), 0.89-0.93 (m, 12H, TBS + H-11), 0.07 (s, 3H, TBS), 0.06 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.3 (t, C-3), 143.4 (q, Ph), 137.8 (t, C-5), 134.7 (q, C-4), 128.2 (t, Ph), 127.4 (t, Ph), 126.6 (t, Ph), 116.3 (t, C-2), 79.5 (t, C-9), 73.6 (t, C-7), 60.4 (s, C-12), 45.0 (t, C-8), 34.9 (s, C-6), 26.0 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-13), 12.6 (p, C-10), 6.7 (p, C-11), -4.3 (p, TBS), -5.0 (p, TBS) ppm.

7,8-*anti*,8,9-*syn* **18b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.21-7.39 (m, 6H, H-3 + Ph), 6.06 (dd, 1H, *J* = 7.3, 7.0 Hz, H-5), 5.79 (d, 1H, *J* = 15.7 Hz, H-2), 4.95 (d, 1H, *J* = 3.4 Hz, H-9), 4.20 (q, 2H, *J* = 7.1 Hz, H-12), 3.62-3.69 (m, 1H, H-7), 2.26-2.50 (m, 2H, H-6), 1.89-1.95 (m, 1H, H-8), 1.77 (s, 3H, H-10), 1.30 (t, 3H, *J* = 7.1 Hz, H-13), 0.91 (s, 9H, TBS), 0.72 (d, 3H, *J* = 6.8 Hz, H-11), 0.07 (s, 3H, TBS), 0.06 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): 167.7 (q, C-1), 149.6 (t, C-3), 141.4 (q, Ph), 138.0 (t, C-5), 134.6 (q, C-4), 128.0 (t, Ph), 127.4 (t, Ph), 127.2 (t, Ph), 115.9 (t, C-2), 78.6 (t, C-9), 72.4 (t, C-7), 60.3 (s, C-12), 44.9 (t, C-8), 34.5 (s, C-6), 25.9 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-13), 12.6 (p, C-10), 12.4 (p, C-11), -4.5 (p, TBS), -5.2 (p, TBS) ppm.

### **(2*E*,4*E*,7*S*,8*R*,9*S*)-Ethyl-7,9-dihydroxy-4,8-dimethyl-9-phenyl-nona-2,4-dienoate** **(**7,8-*syn*,8,9-*syn* **S9a)** and **(2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-7,9-dihydroxy-4,8-dimethyl-9-phenylnona-2,4-dienoate** **(**7,8-*anti*,8,9-*syn* **S9b)**



7,8-*anti*,8,9-*syn* **S9b**



7,8-*syn*,8,9-*syn* **S9a**

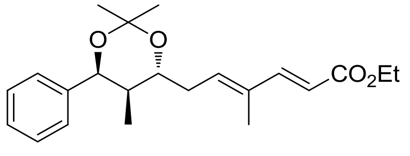
A mixture of alcohols **18** [*d.r.*: 1:2 (**18b**:**18a**), 10 mg, 23 µmol, 1.0 eq] was dissolved in THF (0.4 ml) and cooled to 0 °C. TBAF·3$H_2O$ (11 mg, 35 µmol, 1.5 eq) was dissolved in THF (0.3 ml) and added to the solution of alcohols **18a**,**b**. The solution was stirred for 2 ¼ h at 0 °C and the reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 1:1) to furnish diols 7,8-*syn*,8,9-*syn* **S9a** and 7,8-*anti*,8,9-*syn* **S9b** [*d.r.*: 1:2 (**S9b**:**S9a**) 6.8 mg, 21 µmol, 93%] as a colourless oil.

$R_f$ = 0.27 (PE:EE = 2:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{19}H_{26}NaO_4$: 341.1729 $[M + Na]^+$, found: 341.1721 $[M + Na]^+$.

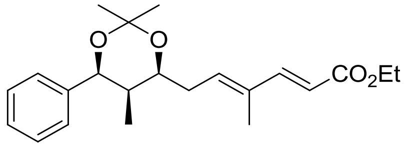
7,8-*syn*,8,9-*syn* **S9a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.24-7.39 (m, 6H, H-3 + Ph), 5.91 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.83 (d, 1H, *J* = 15.7 Hz, H-2), 5.04 (d, 1H, *J* = 2.7 Hz, H-9), 4.21 (q, 2H, *J* = 7.1 Hz, H-12), 4.10 (ddd, 1H, *J* = 7.4, 6.2, 1.5 Hz, H-7), 2.48-2.59 (m, 1H, H-$6_a$), 2.31-2.40 (m, 1H, H-$6_b$), 2.21 (brs, 2H, OH), 1.76-1.82 (m, 1H, H-8), 1.80 (s, 3H, H-10), 1.30 (t, 3H, *J* = 7.1 Hz, H-13), 0.86 (d, 3H, *J* = 6.8 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.1 (t, C-3), 143.2 (q, Ph), 137.1 (t, C-5), 135.2 (q, C-4), 128.4 (t, Ph), 127.4 (t, Ph), 125.8 (t, Ph), 116.6 (t, C-2), 78.7 (t, C-9), 75.6 (t, C-7), 60.4 (s, C-12), 43.6 (t, C-8), 35.0 (s, C-6), 14.5 (p, C-13), 12.6 (p, C-10), 4.8 (p, C-11) ppm.

7,8-*anti*,8,9-*syn* **S9b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.24-7.39 (m, 6H, H-3 + Ph), 6.00 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.84 (d, 1H, *J* = 15.7 Hz, H-2), 5.16 (d, 1H, *J* = 2.4 Hz, H-9), 4.21 (q, 2H, *J* = 7.1 Hz, H-12), 3.64-3.74 (m, 1H, H-7), 2.48-2.59 (m, 1H, H-$6_a$), 2.31-2.40 (m, 1H, H-$6_b$), 2.21 (brs, 2H, OH), 1.88-1.98 (m, 1H, H-8), 1.80 (s, 3H, H-10), 1.30 (t, 3H, *J* = 7.1 Hz, H-13), 0.84 (d, 3H, *J* = 7.2 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.1 (t, C-3), 142.7 (q, Ph), 137.1 (t, C-5), 135.4 (q, C-4), 128.3 (t, Ph), 127.3 (t, Ph), 126.1 (t, Ph), 116.6 (t, C-2), 74.8 (t, C-9), 74.6 (t, C-7), 60.4 (s, C-12), 43.7 (t, C-8), 35.1 (s, C-6), 14.5 (p, C-13), 12.7 (p, C-10), 11.3 (p, C-11) ppm.

**Acetonides 19** (7,8-*syn*,8,9-*syn* **19a** and 7,8-*anti*,8,9-*syn* **19b**)



7,8-*anti*,8,9-*syn* **19b**



7,8-*syn*,8,9-*syn* **19a**

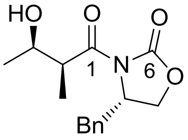
A mixture of diols **S9** [*d.r.*: 1:2 (**S9b**:**S9a**), 6.5 mg, 20 µmol, 1 eq] was dissolved in $CH_2Cl_2$ (0.6 ml). 2,2-Dimethoxypropane (0.06 ml) and PPTS (1 mg, catalytic) were added and the reaction mixture was stirred for 3 h at rt. The solvent was removed under reduced pressure and flash chromatography (petroleum ether : ethyl acetate = 20:1) yielded acetonides 7,8-*syn*,8,9-*syn* **19a** and 7,8-*anti*,8,9-*syn* **19b** [*d.r.*: 1:2 (**19b**:**19a**), 3.5 mg, 10 µmol, 50%] as a colourless oil.

$R_f$ = 0.79 (PE:EE = 2:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{31}O_4$: 359.2222 $[M + H]^+$, found: 359.2217 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **19a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.20-7.39 (m, 6H, H-3 + Ph), 5.91 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.82 (d, 1H, *J* = 15.7 Hz, H-2), 5.09 (d, 1H, *J* = 2.7 Hz, H-9), 4.22 (q, 2H, *J* = 7.1 Hz, H-12), 4.16-4.22 (m, 1H, H-7), 2.42-2.53 (m, 1H, H-6$_a$), 2.30-2.40 (m, 1H, H-6$_b$), 1.81 (s, 3H, H-10), 1.66-1.74 (m, 1H, H-8), 1.54 (s, 3H, H-15$_a$), 1.53 (s, 3H, H-15$_b$), 1.31 (t, 3H, *J* = 7.1 Hz, H-13), 0.65 (d, 3H, *J* = 6.8 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 141.1 (q, Ph), 137.0 (t, C-5), 134.7 (q, C-4), 128.2 (t, Ph), 127.0 (t, Ph), 125.6 (t, Ph), 116.3 (t, C-2), 99.6 (q, C-14), 74.8 (t, C-9), 72.8 (t, C-7), 60.4 (s, C-12), 37.1 (t, C-8), 32.8 (s, C-6), 30.1 (p, C-15$_a$), 19.8 (p, C-15$_b$), 14.5 (p, C-13), 12.6 (p, C-10), 5.2 (p, C-11) ppm.

7,8-*anti*,8,9-*syn* **19b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.20-7.39 (m, 6H, H-3 + Ph), 6.02 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.82 (d, 1H, *J* = 15.7 Hz, H-2), 5.17 (d, 1H, *J* = 2.7 Hz, H-9), 4.22 (q, 2H, *J* = 7.1 Hz, H-12), 3.48 (ddd, 1H, *J* = 7.4, 7.4, 4.9 Hz, H-7), 2.42-2.53 (m, 1H, H-6$_a$), 2.30-2.40 (m, 1H, H-6$_b$), 1.94-2.05 (m, 1H, H-8), 1.81 (s, 3H, H-10), 1.45 (s, 3H, H-15$_a$), 1.40 (s, 3H, H-15$_b$), 1.31 (t, 3H, *J* = 7.1 Hz, H-13), 0.53 (d, 3H, *J* = 6.8 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 141.1 (q, Ph), 138.0 (t, C-5), 134.7 (q, C-4), 128.2 (t, Ph), 126.1 (t, Ph), 126.0 (t, Ph), 116.1 (t, C-2), 100.7 (q, C-14), 74.7 (t, C-9), 70.8 (t, C-7), 60.4 (s, C-12), 41.7 (t, C-8), 29.8 (s, C-6), 25.1 (p, C-$15_a$), 24.1 (p, C-$15_b$), 14.5 (p, C-13), 12.6 (p, C-10), 12.6 (p, C-11) ppm.

### (*S*)-8-Benzyl-3-[(2*S*,3*R*)-3-hydroxy-2-methylbutanoyl]oxazolidin-2-one (S10)

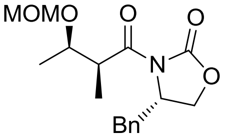


**S10**

Propionated (*S*)-EVANS auxiliary **S4**[S2] (2.0 g, 8.6 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (34 ml) and the reaction mixture was cooled to 0 °C. $Et_3N$ (1.5 ml, 10.3 mmol, 1.2 eq) and *n*-$Bu_2BOTf$ (10.3 ml, *c* = 1 mol/l in $CH_2Cl_2$, 10.3 mmol, 1.2 eq) were added. The solution was stirred for 1 h at -78 °C and for 1 h at 0 °C after which time it was cooled to -78 °C. Acetaldehyde (**S11**) (1.0 ml, 17.2 mmol, 2.0 eq) was dissolved in $CH_2Cl_2$ (5 ml) and added to the solution, which was stirred for 2 h at -78 °C and then overnight at 0 °C. The reaction was terminated by addition of MeOH (150 ml), $NH_4OAc$ (6.5 g), aq. $H_2O_2$ (6 ml, 30%ig) and stirring was continued for 2 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 2:1) to furnish product **S10** (2.1 g, 7.5 mmol, 87%) as a colourless oil.

$R_f$ = 0.36 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +51.1 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.26-7.37 (m, 3H, Ph), 7.18-7.23 (m, 2H, Ph), 4.68-4.76 (m, 1H, H-8), 4.14-4.27 (m, 3H, H-3 + H-7), 3.74 (qd, 1H, *J* = 7.1, 3.0 Hz, H-2), 3.25 (dd, 1H, *J* = 13.4, 3.1 Hz, H-$9_a$), 2.79 (dd, 1H, *J* = 13.4, 9.4 Hz, H-$9_b$), 1.27 (d, 3H, *J* = 7.1 Hz, H-5), 1.21 (d, 3H, *J* = 6.1 Hz, H-4) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 177.5 (q, C-1), 153.3 (q, C-6), 135.2 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.6 (t, Ph), 67.8 (t, C-3), 66.3 (s, C-7), 55.2 (t, C-8), 43.2 (t, C-2), 38.0 (s, C-9), 19.7 (p, C-4), 10.7 (p, C-5) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_{20}NO_4$ und $C_{15}H_{19}NNaO_4$: 278.1392 $[M + H]^+$ and 300.1212 $[M + Na]^+$, found: 278.1388 $[M + H]^+$ and 300.1201 $[M + Na]^+$.[S4]

### (*S*)-8-Benzyl-3-[(2*S*,3*R*)-3-(methoxymethoxy)-2-methylbutanoyl]oxazolidin-2-one (S12)

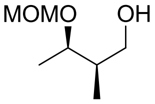


**S12**

Alcohol **S10** (1.0 g, 3.6 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (70 ml) and cooled to 0 °C. $^i$Pr$_2$NEt (6.5 ml, 36.4 mmol, 10 eq) was added. Then, MOMCl (1.4 ml, 18.2 mmol, 5 eq) was added slowly and the reaction mixture was warmed to rt. The solution was stirred for 4 d at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl ($c$ = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 2:1). MOM-ether **S12** (1.1 g, 3.3 mmol, 91%) was obtained as a colourless oil.

$R_f$ = 0.46 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +71.5 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.19-7.38 (m, 5H, Ph), 4.58-4.69 (m, 3H, H-8 + MOM), 4.14-4.22 (m, 2H, H-7), 3.92-4.02 (m, 1H, H-2 + H-3), 3.34 (s, 3H, MOM), 3.30 (dd, 1H, $J$ = 13.4, 3.2 Hz, H-9$_a$), 2.77 (dd, 1H, $J$ = 13.4, 9.6 Hz, H-9$_b$), 1.26 (d, 3H, $J$ = 6.8 Hz, H-5), 1.24 (d, 3H, $J$ = 6.2 Hz, H-4) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 175.0 (q, C-1), 153.4 (q, C-6), 135.5 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.5 (t, Ph), 95.4 (s, MOM), 74.3 (t, C-3), 66.2 (s, C-7), 55.9 (p, MOM), 55.7 (t, C-8), 43.0 (t, C-2), 37.9 (s, C-9), 18.1 (p, C-4), 12.5 (p, C-5) ppm; **HRMS** (ESI): $m/z$: calculated for $C_{17}H_{23}NaNO_5$: 344.1474 $[M + Na]^+$, found: 344.1464 $[M + Na]^+$.

### (2*R*,3*R*)-3-(Methoxymethoxy)-2-methylbutan-1-ol (S13)



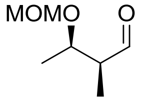
**S13**

Oxazolidinone **S12** (1.0 g, 3.2 mmol, 1.0 eq) was dissolved in $Et_2O$ (64 ml) and cooled to 0 °C. $LiBH_4$ (280 mg, 12.8 mmol, 4.0 eq) was slowly added and the solution was warmed to rt overnight. The reaction was terminated by addition of aq. $NH_4Cl$ and stirring was continued for 2.5 h at rt. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 2:1) to yield alcohol **S13** (410 mg, 2.8 mmol, 87%) as a colourless liquid.

$R_f$ = 0.25 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -62.8 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.69 (d, 1H, $J$ = 6.8 Hz, MOM), 4.61 (d, 1H, $J$ = 6.8 Hz, MOM), 3.90 (qd, 1H, $J$ = 6.5, 3.6 Hz, H-3), 3.68 (dd, 1H, $J$ = 11.0, 8.5 Hz, H-1$_a$), 3.54 (dd, 1H, $J$ = 11.0, 4.9 Hz, H-1$_b$), 3.39 (s, 3H, MOM), 2.31 (brs, 1H, OH), 1.85-1.96 (m, 1H, H-2), 1.17 (d, 3H,

*J* = 6.5 Hz, H-4), 0.87 (d, 3H, *J* = 6.8 Hz, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 95.4 (s, MOM), 75.4 (t, C-3), 65.5 (s, C-1), 55.8 (p, MOM), 40.0 (t, C-2), 16.2 (p, C-4), 11.6 (p, C-5) ppm; **HRMS** (ESI): *m/z*: calculated for $C_7H_{16}NaO_3$: 171.0997 $[M + Na]^+$, found: 171.0994 $[M + Na]^+$.

### (2*S*,3*R*)-3-(Methoxymethoxy)-2-methylbutanal (20)

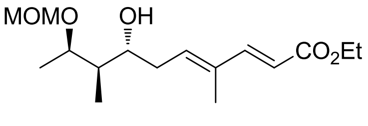


**20**

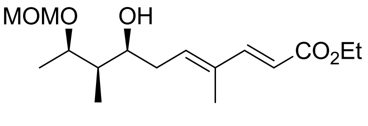
Alcohol **S13** (60 mg, 0.4 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (8 ml) and $NaHCO_3$ (20 mg) added. DESS-MARTIN periodinane (206 mg, 0.5 mmol, 1.2 eq) was added and stirring ws continued for 1 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and the solution was stirred for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish aldehyde **20** (42 mg, 0.3 mmol, 72%) as a colourless liquid, which was used immediately in the next step.

$R_f$ = 0.65 (PE:EE = 2:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.78 (d, 1H, *J* = 0.9 Hz, H-1), 4.71 (d, 1H, *J* = 7.2 Hz, MOM), 4.60 (d, 1H, *J* = 7.2 Hz, MOM), 4.16 (qd, 1H, *J* = 6.4, 4.2 Hz, H-3), 3.34 (s, 2H, MOM), 2.49 (qdd, 1H, *J* = 7.1, 4.2, 0.9 Hz, H-2), 1.24 (d, 3H, *J* = 6.4 Hz, H-4), 1.13 (d, 3H, *J* = 7.1 Hz, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 204.5 (t, C-1), 95.3 (s, MOM), 72.6 (t, C-3), 55.7 (p, MOM), 51.9 (t, C-2), 17.8 (p, C-4), 8.4 (p, C-5) ppm; **HRMS** (ESI): *m/z*: Compound **20** could not be detected by mass spectrometry.

### (2*E*,4*E*,7*S*,8*R*,9*R*)-Ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethyldeca-2,4-dienoate (7,8-*syn*,8,9-*syn* 26a) and (2*E*,4*E*,7*R*,8*R*,9*R*)-ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethyldeca-2,4-dienoate (7,8-*anti*,8,9-*syn* 26b)



7,8-*anti*,8,9-*syn* **26b**



7,8-*syn*,8,9-*syn* **26a**

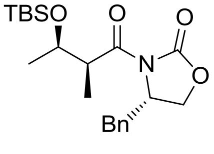
Following the general procedure, aldehyde **20** (36 mg, 0.25 mmol, 1 eq) was reacted with ester **6** (74 mg, 0.48 mmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 2:1) and furnished alcohols 7,8-*syn*,8,9-*syn* **26a** and 7,8-*anti*,8,9-*syn* **26b** (*d.r.*: 1:3.2 (**26b**:**26a**), 53 mg, 0.18 mmol, 72%) as a yellow oil.

R$_f$ = 0.19 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{28}NaO_5$: 323.1834 $[M + Na]^+$, found: 323.1825 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **26a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.5 Hz, H-3), 5.92 (dd, 1H, *J* = 7.7, 7.7 Hz, H-5), 5.81 (d, 1H, *J* = 15.5 Hz, H-2), 4.74 (d, 1H, *J* = 6.8 Hz, MOM), 4.61 (d, 1H, *J* = 6.8 Hz, MOM), 4.20 (q, 2H, *J* = 7.0 Hz, H-13), 3.90-3.97 (m, 2H, H-7 + H-9), 3.38 (s, 3H, MOM), 2.43-2.54 (m, 1H, H-6$_a$), 2.30-2.41 (m, 1H, H-6$_b$), 1.80 (s, 3H, H-11), 1.47-1.55 (m, 1H, H-8), 1.29 (t, 3H, *J* = 7.0 Hz, H-14), 1.19 (d, 3H, *J* = 6.5 Hz, H-10), 0.98 (d, 3H, *J* = 7.2 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 138.0 (t, C-5), 134.4 (q, C-4), 116.2 (t, C-2), 94.7 (s, MOM), 77.6 (t, C-9), 75.0 (t, C-7), 60.3 (s, C-13), 56.0 (p, MOM), 42.1 (t, C-8), 34.6 (s, C-6), 17.7 (p, C-10), 14.5 (p, C-14), 12.6 (p, C-11), 5.9 (p, C-12) ppm.

7,8-*anti*,8,9-*syn* **26b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.36 (d, 1H, *J* = 14.8 Hz, H-3), 6.09 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 14.8 Hz, H-2), 4.69 (d, 1H, *J* = 7.0 Hz, MOM), 4.62 (d, 1H, *J* = 7.0 Hz, MOM), 4.20 (q, 2H, *J* = 7.0 Hz, H-13), 4.02 (qd, 1H, *J* = 6.6, 2.8 Hz, H-9), 3.73 (ddd, 1H, *J* = 8.0, 8.0, 4.1 Hz, H-7), 3.39 (s, 3H, MOM), 2.43-2.54 (m, 1H, H-6$_a$), 2.30-2.41 (m, 1H, H-6$_b$), 1.80 (s, 3H, H-11), 1.63-1.74 (m, 1H, H-8), 1.29 (t, 3H, *J* = 7.0 Hz, H-14), 1.19 (d, 3H, *J* = 6.6 Hz, H-10), 0.87 (d, 3H, *J* = 7.2 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.6 (t, C-3), 138.4 (t, C-5), 134.3 (q, C-4), 115.9 (t, C-2), 95.4 (s, MOM), 75.5 (t, C-9), 72.9 (t, C-7), 60.3 (s, C-13), 55.9 (p, MOM), 42.4 (t, C-8), 34.4 (s, C-6), 16.1 (p, C-10), 14.5 (p, C-14), 12.6 (p, C-11), 12.1 (p, C-12) ppm.

### (*S*)-8-Benzyl-3-[(2*S*,3*R*)-3-(*tert*-butyldimethylsilyloxy)-2-methylbutanoyl]oxazolidin-2-one (S14)

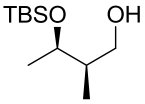


**S14**

Alcohol **S10** (1.0 g, 3.6 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (50 ml) and the solution was cooled to 0 °C. 2,6-Lutidine (1.3 ml, 10.9 mmol, 3.0 eq) and TBSOTf (1.3 ml, 5.5 mmol, 1.5 eq) were added and the reaction mixture was stirred for 2 h. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 9:1 → 2:1) to furnish alcohol **S14** (1.4 g, 3.5 mmol, 97%) as a colourless oil.

$R_f$ = 0.80 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +49.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.37 (m, 3H, Ph), 7.20-7.24 (m, 2H, Ph), 4.59-4.67 (m, 1H, H-8), 4.14-4.19 (m, 2H, H-7), 4.05-4.12 (m, 1H, H-3), 3.79-3.88 (m, 1H, H-2), 3.29 (dd, 1H, *J* = 13.3, 3.4 Hz, H-$9_a$), 2.77 (dd, 1H, *J* = 13.3, 9.6 Hz, H-$9_b$), 1.22 (d, 3H, *J* = 6.8 Hz, H-5), 1.18 (d, 3H, *J* = 6.1 Hz, H-4), 0.88 (s, 9H, TBS), 0.05 (s, 3H, TBS), 0.02 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 175.5 (q, C-1), 153.3 (q, C-6), 135.5 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.5 (t, Ph), 69.8 (t, C-3), 66.1 (s, C-7), 55.8 (t, C-8), 45.1 (t, C-2), 37.9 (s, C-9), 25.9 (p, TBS), 21.8 (p, C-4), 18.1 (q, TBS), 12.7 (p, TBS), -4.4 (p, TBS), -4.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{21}H_{34}NO_4Si$ and $C_{21}H_{33}NNaO_4Si$: 392.2257 $[M + H]^+$ and 414.2077 $[M + Na]^+$, found: 392.2256 $[M + H]^+$ and 414.2063 $[M + Na]^+$.

### (2*R*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylbutan-1-ol (S15)

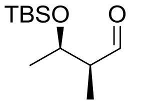


**S15**

Oxazolidinone **S14** (1.4 g, 3.5 mmol, 1.0 eq) was dissolved in $Et_2O$ (70 ml) and the solution was cooled to 0 °C. $LiBH_4$ (303 mg, 13.9 mmol, 4.0 eq) was slowly added and stirring was continued overnight at rt. The reaction was terminated by addition of aq. $NH_4Cl$. After stirrinf for 1 h at rt, the layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish alcohol **S15** (263 mg, 1.2 mmol, 35%) as a colourless oil.

$R_f$ = 0.69 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -10.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.00 (qd, 1H, *J* = 6.4, 3.5 Hz, H-3), 3.72 (dd, 1H, *J* = 10.8, 9.0 Hz, H-$1_a$), 3.51 (dd, 1H, *J* = 10.8, 4.6 Hz, H-$1_b$), 1.91-2.01 (m, 1H, H-2), 1.15 (d, 3H, *J* = 6.4 Hz, H-4), 0.89 (s, 9H, TBS), 0.79 (d, 3H, *J* = 7.2 Hz, H-5), 0.08 (s, 3H, TBS), 0.08 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 72.5 (t, C-3), 65.9 (s, C-1), 41.0 (t, C-2), 26.0 (p, TBS), 18.4 (p, C-4), 18.2 (q, TBS), 12.6 (p, C-5), -4.3 (p, TBS), -4.8 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{11}H_{27}O_2Si$ and $C_{21}H_{33}NNaO_4Si$: 219.1780 $[M + H]^+$ and 241.1600 $[M + Na]^+$, found: 219.1781 $[M + H]^+$ and 241.1602 $[M + Na]^+$.

### (2*S*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylbutanal (21)

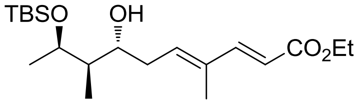


**21**

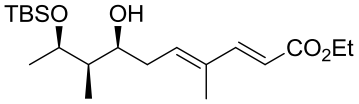
Alcohol **S15** (60 mg, 275 µmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (5.5 ml) and $NaHCO_3$ (15 mg) added. DESS-MARTIN periodinane (140 mg, 330 µmol, 1.2 eq) was added and the reaction mixture was stirred 1 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and the solution was stirred for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **21** (46 mg, 213 µmol, 77%) as a colourless liquid, which was used immediately in the next step.

$R_f$ = 0.72 (PE:EE = 2:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.77 (d, 1H, *J* = 1.4 Hz, H-1), 4.26 (qd, 1H, *J* = 6.2, 4.4 Hz, H-3), 2.34-2.42 (m, 1H, H-2), 1.18 (d, 3H, *J* = 6.2 Hz, H-4), 1.07 (d, 3H, *J* = 6.8 Hz, H-5), 0.86 (s, 9h, TBS), 0.07 (s, 3H, TBS), 0.05 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 205.5 (t, C-1), 68.3 (t, C-3), 53.6 (t, C-2), 25.9 (p, TBS), 21.3 (p, C-4), 18.1 (q, TBS), 8.3 (p, C-5), -4.1 (p, TBS), -4.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: Compound **21** could not be detected by mass spectrometry.

### (2*E*,4*E*,7*S*,8*R*,9*R*)-Ethyl-9-(*tert*-butyldimethyl-silyloxy)-7-hydroxy-4,8-dimethyldeca-2,4-dienoate (7,8-*syn*,8,9-*syn* 27a) and (2*E*,4*E*,7*R*,8*R*,9*R*)-ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethyldeca-2,4-dienoate (7,8-*anti*,8,9-*syn* 27b)



7,8-*anti*,8,9-*syn* **27b**



7,8-*syn*,8,9-*syn* **27a**

Following the general procedure, aldehyde **21** (35 mg, 0.16 mmol, 1 eq) was reacted with ester **6** (49 mg, 0.32 mmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols

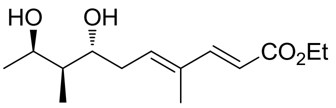
7,8-*syn*,8,9-*syn* **27a** and 7,8-*anti*,8,9-*syn* **27b** [*d.r.*: 1:1.9 (**27b**:**27a**), 53 mg, 0.14 mmol, 89%] as a yellow oil.

$R_f$ = 0.27 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{39}O_4Si$: 371.2618 $[M + H]^+$, found: 371.2616 $[M + H]^+$.

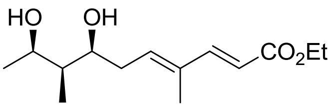
7,8-*syn*,8,9-*syn* **27a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.38 (d, 1H, *J* = 15.7 Hz, H-3), 5.91 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.20 (q, 2H, *J* = 7.2 Hz, H-13), 4.08 (qd, 1H, *J* = 6.4, 2.7 Hz, H-9), 3.90 (ddd, 1H, *J* = 6.9, 6.9, 1.8 Hz, H-7), 2.28-2.50 (m, 2H, H-6), 1.80 (s, 3H, H-11), 1.70-1.83 (m, 1H, H-8), 1.30 (t, 3H, *J* = 7.2 Hz, H-14), 1.16 (d, 3H, *J* = 6.5 Hz, H-10), 0.93 (d, 3H, *J* = 7.2 Hz, H-12), 0.89 (s, 9H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 138.1 (t, C-5), 134.5 (q, C-4), 116.1 (t, C-2), 75.2 (t, C-9), 74.0 (t, C-7), 60.3 (s, C-13), 42.8 (t, C-8), 34.6 (s, C-6), 26.0 (p, TBS), 21.9 (p, C-10), 18.1 (q, TBS), 14.5 (p, C-14), 12.6 (p, C-11), 5.4 (p, C-12), -3.4 (p, TBS), -4.7 (p, TBS) ppm.

7,8-*anti*,8,9-*syn* **27b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 6.11 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.79 (d, 1H, *J* = 15.7 Hz, H-2), 4.20 (q, 2H, *J* = 7.2 Hz, H-13), 4.01 (qd, 1H, *J* = 6.6, 3.2 Hz, H-9), 3.82 (ddd, 1H, *J* = 9.5, 6.4, 3.3 Hz, H-7), 2.28-2.50 (m, 2H, H-6), 1.80 (s, 3H, H-11), 1.37-1.46 (m, 1H, H-8), 1.30 (t, 3H, *J* = 7.2 Hz, H-14), 1.18 (d, 3H, *J* = 6.6 Hz, H-10), 0.89 (s, 9H, TBS), 0.77 (d, 3H, *J* = 7.2 Hz, H-12), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.8 (q, C-1), 149.7 (t, C-3), 138.4 (t, C-5), 134.2 (q, C-4), 115.7 (t, C-2), 73.6 (t, C-9), 72.8 (t, C-7), 60.3 (s, C-13), 43.1 (t, C-8), 34.8 (s, C-6), 25.9 (p, TBS), 18.0 (q, TBS), 17.8 (p, C-10), 14.5 (p, C-14), 13.6 (p, C-12), 12.6 (p, C-11), -4.5 (p, TBS), -5.0 (p, TBS) ppm.

**(2*E*,4*E*,7*S*,8*S*,9*R*)-Ethyl-7,9-dihydroxy-4,8-dimethyldeca-2,4-dienoate**
**(**7,8-*syn*,8,9-*syn* **S16a)** and
**(2*E*,4*E*,7*R*,8*S*,9*R*)-ethyl-7,9-dihydroxy-4,8-dimethyldeca-2,4-dienoate**
**(**7,8-*anti*,8,9-*syn* **S16b)**



7,8-*anti*,8,9-*syn* **S16b**



7,8-*syn*,8,9-*syn* **S16a**

A mixture of alcohols **27** (21 mg, 57 μmol, 1.0 eq) was dissolved in THF (1.0 ml) and cooled to 0 °C. $TBAF\cdot 3H_2O$ (27 mg, 86 μmol, 1.5 eq) was added and the solution was stirred for 1 h while it warmed up from 0 °C to rt. The reaction was terminated by addition of aq. $NH_4Cl$.

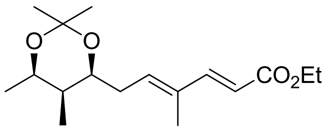
The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 2:1 → 1:1) to furnish diols 7,8-*syn*,8,9-*syn* S**16a** and 7,8-*anti*,8,9-*syn* **S16b** (13 mg, 50 µmol, 89%) as a colourless oil.

$R_f$ = 0.2 (PE:EE = 2:1); **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{24}NaO_4$: 279.1572 $[M + Na]^+$, found: 279.1569 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **S16a**: $[\alpha]_D^{20}$ = -7.1 (*c* = 0.4, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, *J* = 15.5 Hz, H-3), 5.89 (dd, 1H, *J* = 7.5, 7.4 Hz, H-5), 5.82 (d, 1H, *J* = 15.5 Hz, H-2), 4.21 (q, 2H, *J* = 7.1 Hz, H-13), 4.10 (qd, 1H, *J* = 6.4, 2.1 Hz, H-9), 3.98 (ddd, 1H, *J* = 7.6, 6.8, 1.9 Hz, H-7), 2.50 (ddd, 1H, *J* = 14.9, 7.6, 7.5 Hz, H-$6_a$), 2.34 (ddd, 1H, *J* = 14.9, 7.4, 6.8 Hz, H-$6_b$), 1.81 (s, 3H, H-11), 1.47 (qdd, 1H, *J* = 7.1, 2.1, 1.9 Hz, H-8), 1.30 (t, 3H, *J* = 7.1 Hz, H-14), 1.21 (d, 3H, *J* = 6.4 Hz, H-10), 0.96 (d, 3H, *J* = 7.1 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.2 (t, C-3), 137.3 (t, C-5), 135.1 (q, C-4), 116.5 (t, C-2), 76.3 (t, C-9), 73.0 (t, C-7), 60.4 (s, C-13), 41.8 (t, C-8), 34.8 (s, C-6), 21.7 (p, C-10), 14.5 (p, C-14), 12.6 (p, C-11), 4.2 (p, C-12) ppm.

7,8-*anti*,8,9-*syn* **S16b**: $[\alpha]_D^{20}$ = +21.2 (*c* = 0.4, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, *J* = 15.7 Hz, H-3), 5.99 (dd, 1H, *J* = 7.5, 7.2 Hz, H-5), 5.83 (d, 1H, *J* = 15.7 Hz, H-2), 4.21 (q, 2H, *J* = 7.1 Hz, H-13), 4.16 (qd, 1H, *J* = 6.5, 2.3 Hz, H-9), 3.79 (ddd, 1H, *J* = 6.5, 6.1, 6.1 Hz, H-7), 2.45-2.51 (m, 2H, H-6), 1.82 (s, 3H, H-11), 1.68 (dqd, 1H, *J* = 7.1, 6.5, 2.3 Hz, H-8), 1.30 (t, 3H, *J* = 7.1 Hz, H-14), 1.21 (d, 3H, *J* = 6.5 Hz, H-10), 0.94 (d, 3H, *J* = 7.1 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.2 (t, C-3), 137.3 (t, C-5), 135.3 (q, C-4), 116.5 (t, C-2), 74.8 (t, C-9), 69.6 (t, C-7), 60.4 (s, C-13), 42.4 (t, C-8), 35.2 (s, C-6), 19.6 (p, C-10), 14.5 (p, C-14), 12.6 (p, C-11), 12.0 (p, C-12) ppm.

**Acetonide** (7,8-*syn*,8,9-*syn* **S17a**)

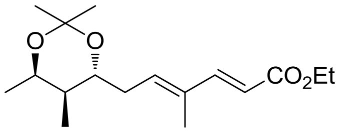


7,8-*syn*,8,9-*syn* **S17a**

Diol 7,8-*syn*,8,9-*syn* **S16a** (3.9 mg, 15 µmol, 1 eq) was dissolved in $CH_2Cl_2$ (2.0 ml). 2,2-Dimethoxypropane (0.2 ml) and CSA (2 mg, catalytic) were added and the solution was stirred for 1.5 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 8:1 → 3:1). Acetonide 7,8-*syn*,8,9-*syn* **S17a** (3.8 mg, 13 μmol, 91%) was obtained as a colourless oil.

R$_f$ = 0.66 (PE:EE = 2:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, *J* = 15.7 Hz, H-3), 5.86 (dd, 1H, *J* = 7.3, 7.2 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2 ), 4.21 (q, 2H, *J* = 7.2 Hz, H-13), 4.08 (qd, 1H, *J* = 6.4, 2.3 Hz, H-9), 3.97 (ddd, 1H, *J* = 7.3, 7.2, 2.0 Hz, H-7), 2.41 (ddd, 1H, *J* = 15.1, 7.2, 7.2 Hz, H-6$_a$), 2.34 (ddd, 1H, *J* = 15.1, 7.3, 7.3 Hz, H-6$_b$), 1.80 (s, 3H, H-11), 1.44 (s, 3H, H-16$_a$), 1.40 (s, 3H, H-16$_b$), 1.26-1.35 (m, 1H, H-8), 1.30 (t, 3H, *J* = 7.2 Hz, H-14), 1.13 (d, 3H, *J* = 6.4 Hz, H-10), 0.87 (d, 3H, *J* = 6.8 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 137.3 (t, C-5), 134.5 (q, C-4), 116.2 (t, C-2), 99.1 (q, C-15), 72.9 (t, C-9), 69.1 (t, C-7), 60.4 (s, C-13), 41.8 (t, C-8), 35.9 (s, C-6), 30.2 (p, C-16$_a$), 19.8 (p, C-10), 19.1 (p, C-16$_b$), 14.5 (p, C-14), 12.6 (p, C-11), 4.6 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{17}H_{28}NaO_4$: 319.1885 $[M + Na]^+$, found: 319.1883 $[M + Na]^+$.

**Acetonide** (7,8-*anti*,8,9-*syn* **S17b**)

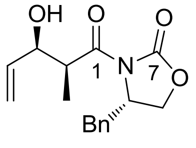


7,8-*anti*,8,9-*syn* **S17b**

Diol 7,8-*anti*,8,9-*syn* **S16b** (3.9 mg, 15 μmol, 1 eq) was dissolved in $CH_2Cl_2$ (2.0 ml). 2,2-Dimethoxypropane (0.2 ml) and CSA (2 mg, catalytic) were added and the solution was stirred for 1.5 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 8:1 → 3:1). Acetonide 7,8-*anti*,8,9-*syn* **S17b** (3.8 mg, 13 μmol, 91%) was obtained as a colourless oil.

R$_f$ = 0.65 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -7.2 (*c* = 0.2, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$= 7.16 ppm): δ 7.69 (d, 1H, *J* = 15.6 Hz, H-3), 5.98 (d, 1H, *J* = 15.6 Hz, H-2 ), 5.88 (dd, 1H, *J* = 7.8, 6.3 Hz, H-5), 4.11 (q, 2H, *J* = 7.1 Hz, H-13), 3.94 (qd, 1H, *J* = 6.6, 6.2 Hz, H-9), 3.19-3.26 (m, 1H, H-7), 2.10-2.25 (m, 2H, H-6), 1.52 (s, 3H, H-11), 1.33 (s, 3H, H-16$_a$), 1.28 (s, 3H, H-16$_b$), 1.25-1.38 (m, 1H, H-8), 1.02 (t, 3H, *J* = 7.1 Hz, H-14), 0.98 (d, 3H, *J* = 6.6 Hz, H-10), 0.65 (d, 3H, *J* = 6.9 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$ = 128.06 ppm): δ 167.1 (q, C-1), 149.3 (t, C-3), 138.3 (t, C-5), 134.3 (q, C-4), 116.8 (t, C-2), 100.5 (q, C-15), 74.3 (t, C-9), 64.9 (t, C-7), 60.1 (s, C-13), 40.4 (t, C-8), 34.1 (s, C-6), 25.3 (p, C-16$_a$), 24.1 (p, C-16$_b$), 16.7 (p, C-10), 14.4 (p, C-14), 12.3 (p, C-11), 11.8 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{17}H_{28}NaO_4$: 319.1885 $[M + Na]^+$, found: 319.1883 $[M + Na]^+$.

**(*S*)-9-Benzyl-3-[(2*S*,3*R*)-3-hydroxy-2-methylpent-4-enoyl]oxazolidin-2-one (S18)**

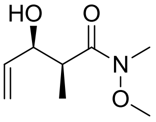


**S18**

Propionated (*S*)-EVANS auxiliary **S4**[S2] (8.0 g, 34 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (120 ml) and cooled to 0 °C. $^{i}Pr_2NEt$ (6 ml, 41 mmol, 1.2 eq) and *n*-$Bu_2BOTf$ (38 ml, *c* = 1 mol/l in $CH_2Cl_2$, 38 mmol, 1.1 eq) were added. The solution was stirred for 75 min at 0 °C, cooled to -78 °C and freshly distillated acroleine (**S19**) (11 ml, 172 mmol, 5.0 eq) was added. The solution was stirred for 30 min at -78 °C and then for 2.5 h at 0 °C. The reaction was terminated by addition of MeOH (160 ml), $H_2O$ (46 ml) and phosphate buffer (pH = 7, 2 ml) and a solution of MeOH (110 ml) and aq. $H_2O_2$ (55 ml, 30%ig) added. The mixture was stirred for 15 min during which time the temperature raised form 0 °C to rt. The solvent was removed under reduced pressure and dissolved in $H_2O$ (250 ml). The aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. $NaHCO_3$, aq. NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product purified by flash chromatography (petroleum ether : ethyl acetate = 3:1 → 2:1) to furnish product **S18** (7.5 g, 26 mmol, 76%) as a colourless oil.

$R_f$ = 0.21 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +59.2 (*c* = 1.0, $CHCl_3$) [ref. S5.: +92.6 (*c* = 1.0, $CH_2Cl_2$)]; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.37 (m, 2H, Ph), 7.18-7.23 (m, 2H, Ph), 5.86 (ddd, 1H, *J* = 17.2, 10.6, 5.4 Hz, H-4), 5.36 (ddd, 1H, *J* = 17.2, 1.5, 1.4 Hz, H-$5_a$), 5.23 (ddd, 1H, *J* = 10.6, 1.4, 1.4 Hz, H-$5_b$), 4.68-4.75 (m, 1H, H-9), 4.49-4.54 (m, 1H, H-3), 4.17-4.26 (m, 2H, H-8), 3.88 (qd, 1H, *J* = 6.9, 3.5 Hz, H-2), 3.26 (dd, 1H, *J* = 13.5, 3.2 Hz, H-$10_a$), 2.86 (d, 1H, *J* = 3.1 Hz, OH), 2.80 (dd, 1H, *J* = 13.5, 9.4 Hz, H-$10_b$), 1.25 (d, 3H, *J* = 6.9 Hz, H-6) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 176.8 (q, C-1), 153.2 (q, C-7), 137.4 (t, C-4), 135.1 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.6 (t, Ph), 116.5 (s, C-5), 72.7 (t, C-3), 66.4 (s, C-8), 55.3 (t, C-9), 42.6 (t, C-2), 37.9 (s, C-10), 11.1 (p, C-6) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{19}NaO_4$: 312.1212 $[M + Na]^+$, found: 312.1215 $[M + Na]^+$. The analytical data are in accordance with those reported in the literature.[S5]

### (2*S*,3*R*)-3-Hydroxy-*N*-methoxy-*N*,2-dimethylpent-4-enamide (S19)

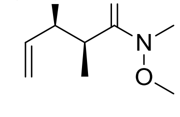


**S19**

*N*,*O*-Dimethylhydroxylamine hydrochloride (6.2 g, 63.2 mmol, 10.7 eq) was suspended in THF (10 ml) and cooled to -30 °C. $AlMe_3$ (32 ml, *c* = 2 mol/l in hexane, 63.2 mmol, 10.7 eq) was added over a period of 30 min. The slurry was warmed up to rt and stirred for 25 min. The solution was cooled to -10 °C. Alcohol **S18** (1.7 g, 5.9 mmol, 1.0 eq) was dissolved in THF (25 ml) and added to the first solution over a period of 10 min. The reaction was stirred for 2 h at 0 °C. The mixture was slowly transferred into a solution at 0 °C of aq. Na-K-tartrate (165 ml), aq. $NaHCO_3$ (90 ml), ethyl acetate (265 ml) and stirred 1 h at 0 °C and 45 min at rt. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 2:1) and furnished Weinreb amide **S19** (472 mg, 2.7 mmol, 46%) as colourless liquid.

$R_f$ = 0.33 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +31.1 (*c* = 1.0, $CHCl_3$) [ref. S6.: +46.3 (*c* = 1.4, $CH_2Cl_2$)]; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 5.81 (ddd, 1H, *J* = 17.1, 10.7, 5.1 Hz, H-4), 5.35 (d, 1H, *J* = 17.1 Hz, H-$5_a$), 5.20 (d, 1H, *J* = 10.7 Hz, H-$5_b$), 4.42-4.47 (m, 1H, H-3), 3.77-3.82 (m, 1H, H-2), 3.71 (s, 3H, H-8), 3.20 (s, 3H, H-7), 2.95 (brs, 1H, OH), 1.17 (d, 3H, *J* = 7.2 Hz, H-6) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 177.9 (q, C-1), 137.9 (t, C-4), 115.9 (s, C-5), 72.6 (t, C-3), 61.7 (p, C-8), 39.4 (t, C-2), 31.9 (p, C-7), 10.7 (p, C-6) ppm; **HRMS** (ESI): *m/z*: calculated for $C_8H_{15}NaNO_3$: 196.0950 $[M + Na]^+$, found: 196.0955 $[M + Na]^+$. The analytical data are in accordance with those reported in the literature.[S6]

### (2*S*,3*R*)-*N*-Methoxy-3-(methoxymethoxy)-*N*,2-dimethylpent-4-enamide (S20)

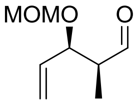


**S20**

Alcohol **S19** (150 mg, 0.9 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (10 ml) and ´the solution was cooled to 0 °C. $^i$Pr$_2$NEt (2.01 ml, 12.1 mmol, 14.0 eq) and MOMCl (0.46 ml, 6.1 mmol, 7.0 eq) were added and stirring was continued for 8 d at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 2:1) to furnish alcohol **S20** (172 mg, 0.8 mmol, 91%) as a colourless oil.

$R_f$ = 0.33 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -80.4 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 5.75 (ddd, 1H, *J* = 16.6, 9.5, 7.8 Hz, H-4), 5.25 (d, 1H, *J* = 16.6 Hz, H-$5_a$), 5.22 (d, 1H, *J* = 9.5 Hz, H-$5_b$), 4.70 (d, 1H, *J* = 6.7 Hz, MOM), 4.54 (d, 1H, *J* = 6.7 Hz, MOM), 4.16 (dd, 1H, *J* = 8.0, 7.8 Hz, H-3), 3.68 (s, 3H, H-8), 3.38 (s, 3H, MOM), 3.16 (s, 4H, H-2 + H-7), 1.24 (d, 3H, *J* = 6.8 Hz, H-6) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 175.3 (q, C-1), 136.3 (t, C-4), 118.9 (s, C-5), 94.1 (s, MOM), 79.1 (t, C-3), 61.6 (p, C-8), 55.8 (p, MOM), 40.6 (t, C-2), 32.2 (p, C-7), 14.3 (p, C-6) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{10}H_{19}NaO_4N$: 240.1212 $[M + Na]^+$, found: 240.1212 $[M + Na]^+$.

### (2*S*,3*R*)-3-(Methoxymethoxy)-2-methylpent-4-enal (22)

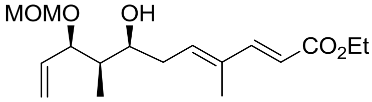


**22**

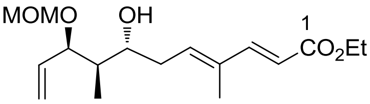
Weinreb amide **S20** (144 mg, 0.7 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ and cooled to -78 °C. DIBAL-H (1.11 ml, *c* = 1.2 mol/l in toluene, 1.3 mmol, 2.0 eq) was added dropwise and the solution was stirred for 1.5 h at -78 °C. More DIBAL-H (0.65 ml, *c* = 1.2 mol/l in toluene, 0.8 mmol, 1.2 eq) was added and stirring was continued for 2 h at -78 °C. The reaction was terminated by addition of etyl acetate and after addition of aq. Na-K-tartrate the mixture was stirred for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish aldehyde **22** (85 mg, 0.5 mmol, 81%) as a colourless oil, which was used immediately in the next step.

$R_f$ = 0.64 (PE:EE = 2:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.78 (d, 1H, *J* = 1.0 Hz, H-1), 5.75 (ddd, 1H, *J* = 16.6, 12.1, 7.5 Hz, H-4), 5.32 (d, 1H, *J* = 16.6 Hz, H-$5_a$), 5.32 (d, 1H, *J* = 12.1 Hz, H-$5_b$), 4.71 (d, 1H, *J* = 6.8 Hz, MOM), 4.53 (d, 1H, *J* = 6.8 Hz, MOM), 4.46 (dd, 1H, *J* = 7.5, 4.4 Hz, H-3), 3.35 (s, 3H, MOM), 2.53-2.61 (m, 1H, H-2), 1.13 (d, 3H, *J* = 7.2 Hz, H-6) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 203.6 (t, C-1), 135.1 (t, C-4), 119.3 (s, C-5), 94.1 (s, MOM), 55.9 (p, MOM), 50.9 (t, C-3), 8.7 (p, C-6) ppm.

**(2*E*,4*E*,7*S*,8*R*,9*R*)-Ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethyl-undeca-2,4,10-trienoate (**7,8-*syn*,8,9-*syn* **28a)** and
**(2*E*,4*E*,7*R*,8*R*,9*R*)-ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethylundeca-2,4,10-trienoate (**7,8-*anti*,8,9-*syn* **28b)**



7,8-*syn*,8,9-*syn* **28a**

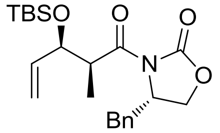


7,8-*anti*,8,9-*syn* **28b**

Following the general procedure aldehyde **22** (76 mg, 0.5 mmol, 1.0 eq) was reacted with ester **6** (148 mg, 1.0 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 2:1) to furnish alcohols 7,8-*syn*,8,9-*syn* **28a** and 7,8-*anti*,8,9-*syn* **28b** (*d.r.*: 1:1, 138 mg, 0.4 mmol, 91%) as a colourless oil.

$R_f$ = 0.16 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.36 (d, 1H, *J* = 15.4 Hz, H-$3_1$), 7.32 (d, 1H, *J* = 15.4 Hz, H-$3_2$), 6.08 (dd, 1H, *J* = 7.2, 7.2 Hz, H-$5_1$), 5.92 (dd, 1H, *J* = 7.3, 7.3 Hz, H-$5_2$), 5.81 (d, 1H, *J* = 15.4 Hz, H-$2_1$), 5.80 (d, 1H, *J* = 15.4 Hz, H-$2_2$), 5.69-5.83 (m, 2H, H-$10_{1,2}$), 5.27 (d, 2H, *J* = 9.6 Hz, H-$11_{a,1,2}$), 5.25 (d, 2H, *J* = 17.4 Hz, H-$11_{b,1,2}$), 4.70 (d, 1H, *J* = 6.8 Hz, $MOM_{a,1}$), 4.66 (d, 1H, *J* = 6.5 Hz, $MOM_{b,1}$), 4.58 (d, 1H, *J* = 6.5 Hz, $MOM_{b,2}$), 4.54 (d, 1H, *J* = 6.8 Hz, $MOM_{a,2}$), 4.33 (dd, 1H, *J* = 6.8, 3.1 Hz, H-$9_1$), 4.17-4.21 (m, 1H, H-$9_2$), 4.20 (q, 4H, *J* = 7.2 Hz, H-$14_{1,2}$), 3.93-3.99 (m, 1H, H-$7_2$), 3.67-3.75 (m, 1H, H-$7_1$), 3.54 (s, 1H, $OH_1$), 3.40 (s, 3H, $MOM_1$), 3.39 (s, 3H, $MOM_2$), 2.72 (s, 1H, $OH_2$), 2.43-2.54 (m, 2H, H-$6_{a,1,2}$), 2.31-2.41 (m, 2H, H-$6_{b,1,2}$), 1.80 (s, 6H, H-$12_{1,2}$), 1.61-1.69 (m, 1H, H-$8_2$), 1.29 (t, 6H, *J* = 7.2 Hz, H-$15_{1,2}$), 1.01 (d, 3H, *J* = 7.2 Hz, H-$13_2$), 0.87 (d, 3H, J = 6.8 Hz, H-$13_1$) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-$1_1$), 167.6 (q, C-$1_2$), 149.6 (t, C-$3_1$), 149.3 (t, C-$3_2$), 138.3 (t, C-$5_1$), 137.8 (t, C-$5_2$), 136.3 (t, C-$10_1$), 135.4 (t, C-$10_2$), 134.7 (q, C-$4_1$), 134.4 (q, C-$4_2$), 118.6 (s, C-$11_1$), 118.2 (s, C-$11_2$), 116.3 (t, C-$2_1$), 115.9 (t, C-$2_2$), 94.8 (s, MOM), 94.0 (s, MOM), 81.7 (t, C-$9_1$), 79.9 (t, C-$9_2$), 73.9 (t, C-$7_1$), 73.0 (t, C-$7_2$), 60.4 (s, C-$14_1$), 60.3 (s, C-$14_2$), 56.1 (p, MOM), 42.4 (t, C-$8_1$), 41.8 (t, C-$8_2$), 34.5 (s, C-$6_1$), 34.2 (s, C-$6_2$), 14.5 (p, C-$15_{1,2}$), 12.6 (p, C-$12_1$), 12.6 (p, C-$12_2$), 11.9 (p, C-$13_1$), 6.9 (p, C-$13_2$) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{17}H_{28}NaO_5$: 335.1834 $[M + Na]^+$, found: 335.1832 $[M + Na]^+$.

### (*S*)-4-Benzyl-3-[(2*S*,3*R*)-3-(*tert*-butyldimethylsilyloxy]-2-methylpent-4-enoyl)oxazolidin-2-one (S21)

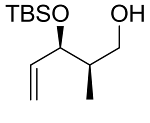


**S21**

(*S*)-EVANS aldol product **S18** (2.5 g, 8.6 mmol, 1.5 eq) was dissolved in $CH_2Cl_2$ (180 ml) and cooled to 0 °C. 2,6-Lutidine (3 ml, 25.8 mmol, 3.0 eq) and TBSOTf (3 ml, 13.1 mmol, 1.5 eq) were added and the mixture was stirred for 2 h at 0 °C and for 1.5 h at rt. The reaction was terminated by addition of aq. $NaHCO_3$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl ($c$ = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) and furnished product **S21** (2.5 g, 6.2 mmol, 72%) as a colourless solid.

$R_f$ = 0.76 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +51.5 ($c$ = 1.0, $CHCl_3$); m.p. = 42 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 5.85 (ddd, 1H, $J$ = 17.1, 10.3, 6.3 Hz, H-4), 5.20 (d, 1H, $J$ = 17.1 Hz, H-5$_a$), 5.11 (d, 1H, $J$ = 10.3 Hz, H-5$_b$), 4.60 (dddd, 1H, $J$ = 8.0, 6.4, 6.4, 3.2 Hz, H-9), 4.33 (dd, 1H, $J$ = 6.4, 6.3 Hz, H-3), 4.09-4.19 (m, 2H, H-8), 3.98 (qd, 1H, $J$ = 6.7, 6.4 Hz, H-2), 3.28 (dd, 1H, $J$ = 13.3, 3.2 Hz, H-10$_a$), 2.77 (dd, 1H, $J$ = 13.3, 8.0 Hz, H-10$_b$), 1.21 (d, 3H, $J$ = 6.7 Hz, H-6), 0.89 (s, 9H, TBS), 0.02 (s, 3H, TBS), 0.01 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.8 (q, C-1), 153.4 (q, C-7), 139.4 (t, C-4), 135.5 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.5 (q, Ph), 115.9 (s, C-5), 75.3 (t, C-3), 66.1 (s, C-8), 55.8 (t, C-9), 44.2 (t, C-2), 37.9 (s, C-10), 25.9 (p, TBS), 18.3 (q, TBS), 12.6 (p, C-6), -4.3 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): $m/z$: calculated for $C_{22}H_{33}NaNO_4Si$: 426.2077 $[M + Na]^+$, found: 426.2086 $[M + Na]^+$.

### (2*R*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylpent-4-en-1-ol (S22)



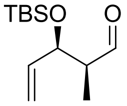
**S22**

Oxazolidinone **S21** (1.46 g, 3.3 mmol, 1 eq) was dissolved in $Et_2O$ (70 ml) and $LiBH_4$ (158 mg, 7.3 mmol, 2 eq) was added. The solution was stirred for 2 h at rt. The reaction was terminated by addition of aq. $NH_4Cl$ and stirred for 1 h. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$

and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1) to furnish alcohol **S22** (592 mg, 2.6 mmol, 71%) as a colourless oil.

R$_f$ = 0.42 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +10.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 5.88 (ddd, 1H, *J* = 17.1, 10.6, 5.8 Hz, H-4), 5.23 (d, 1H, *J* = 17.1 Hz, H-5$_a$), 5.19 (d, 1H, *J* = 10.6 Hz, H-5$_b$), 4.25 (dd, 1H, *J* = 5.8, 4.6 Hz, H-3), 3.65 (dd, 1H, *J* = 10.7, 8.9 Hz, H-1$_a$), 3.49 (dd, 1H, *J* = 10.7, 4.3 Hz, H-1$_b$), 2.77 (brs, 1H, OH), 1.95-2.05 (m, 1H, H-2), 0.91 (s, 9H, TBS), 0.81 (d, 3H, *J* = 7.2 Hz, H-6), 0.08 (s, 3H, TBS), 0.05 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 137.8 (t, C-4), 116.1 (s, C-5), 77.6 (t, C-3), 65.9 (s, C-1), 41.0 (t, C-2), 26.0 (p, TBS), 18.3 (q, TBS), 12.5 (p, C-6), -4.3 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{26}NaO_2Si$: 253.1600 $[M + Na]^+$, found: 253.1602 $[M + Na]^+$.

### (2*S*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylpent-4-enal (23)



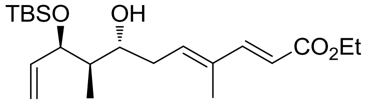
**23**

Alcohol **S22** (110 mg, 0.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (3.5 ml). $NaHCO_3$ (30 mg) and DESS-MARTIN periodinane (243 mg, 0.6 mmol, 1.2 eq) were added. The slurry was stirred for 1 h at rt; the reaction was terminated by addition of aq. $Na_2S_2O_3$ and the mixture was stirred for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **23** (83 mg, 0.4 mmol, 77%) as a colourless liquid.

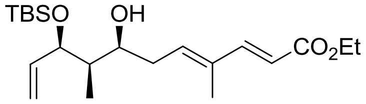
R$_f$ = 0.69 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +20.0 (*c* = 0.2, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.76 (d, 1H, *J* = 1.2 Hz, H-1), 5.82 (ddd, 1H, *J* = 16.9, 10.6, 6.0 Hz, H-4), 5.25 (ddd, 1H, *J* = 16.9, 1.2, 1.2 Hz, H-5$_a$), 5.17 (d, 1H, *J* = 10.6 Hz, H-5$_b$), 4.53 (dd, 1H, *J* = 6.0, 4.5 Hz, H-3), 2.47 (qdd, 1H, *J* = 6.9, 4.5, 1.2 Hz, H-2), 1.07 (d, 3H, *J* = 6.9 Hz, H-6), 0.88 (s, 9H, TBS), 0.05 (s, 3H, TBS), 0.03 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 204.8 (t, C-1), 138.5 (t, C-4), 116.1 (s, C-5), 73.7 (t, C-3), 52.6 (t, C-2), 25.9 (p, TBS), 18.3 (q, TBS), 8.4 (p, C-6), -4.1 (p, TBS), -4.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: Compound **23** could not be detected by mass spectrometry.

**(2*E*,4*E*,7*S*,8*R*,9*R*)-Ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4,10-trienoate (**7,8-*syn*,8,9-*syn* **29a)** and

**(2*E*,4*E*,7*R*,8*R*,9*R*)-ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4,10-trienoate (**7,8-*anti*,8,9-*syn* **29b)**



7,8-*anti*,8,9-*syn* **29b**



7,8-*syn*,8,9-*syn* **29a**

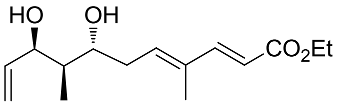
Following the general procedure, aldehyde **23** (72 mg, 0.3 mmol, 1.0 eq) was reacted with ester **6** (97 mg, 0.6 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols 7,8-*syn*,8,9-*syn* **29a** and 7,8-*anti*,8,9-*syn* **29b** [*d.r.*: 1.7:1 (**29a**:**29b**), 108 mg, 0.3 mmol, 90%] as a colourless oil.

$R_f$ = 0.3 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{21}H_{38}NaO_2Si$: 405.2437 $[M + Na]^+$, found: 405.2433 $[M + Na]^+$.

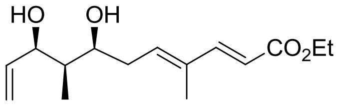
7,8-*syn*,8,9-*syn* **29a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.5 Hz, H-3), 5.88-5.93 (m, 1H, H-5), 5.84-95 (m, 1H, H-10), 5.80 (d, 1H, *J* = 15.5 Hz, H-2), 5.20 (d, 1H, *J* = 17.4 Hz, H-11$_a$), 5.13 (d, 1H, *J* = 10.2 Hz, H-11$_b$), 4.21-4.32 (m, 1H, H-9), 4.20 (q, 2H, *J* = 7.2 Hz, H-14), 3.94-4.00 (m, 1H, H-7), 2.65 (d, 1H, *J* = 2.1 Hz, OH), 2.39-2.50 (m, 1H, H-6$_a$), 2.26-2.38 (m, 1H, H-6$_b$), 1.79 (s, 3H, H-12), 1.52-1.61 (m, 1H, H-8), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 0.96 (d, 3H, *J* = 6.8 Hz, H-13), 0.91 (s, 9H, TBS), 0.08 (s, 3H, TBS), 0.04 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 140.0 (t, C-10), 138.1 (t, C-5), 134.6 (q, C-4), 116.2 (t, C-2), 115.5 (s, C-11), 78.7 (t, C-9), 73.6 (t, C-7), 60.3 (s, C-14), 43.3 (t, C-8), 34.6 (s, C-6), 26.0 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 6.9 (p, C-13), -3.7 (p, TBS), -4.8 (p, TBS) ppm.

7,8-*anti*,8,9-*syn* **29b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.36 (d, 1H, *J* = 15.4 Hz, H-3), 6.09 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.84-95 (m, 1H, H-10), 5.79 (d, 1H, *J* = 15.4 Hz, H-2), 5.24 (d, 1H, *J* = 14.7 Hz, H-11$_a$), 5.21 (d, 1H, *J* = 9.9 Hz, H-11$_b$), 4.21-4.32 (m, 1H, H-9), 4.20 (q, 2H, *J* = 7.2 Hz, H-14), 3.69-3.77 (m, 1H, H-7), 2.39-2.50 (m, 1H, H-6$_a$), 2.26-2.38 (m, 1H, H-6$_b$), 1.74-1.85 (m, 4H, H-12 + H-8), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 0.90 (s, 9H, TBS), 0.79 (d, 3H, *J* = 7.2 Hz, H-13), 0.10 (s, 3H, TBS), 0.06 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.7 (t, C-3), 138.3 (t, C-10), 136.8 (t, C-5), 134.3 (q, C-4), 116.7 (t, C-2), 115.8 (s, C-11), 78.7 (t, C-9), 73.2 (t, C-7), 60.3 (s, C-14), 43.4 (t, C-8), 34.6 (s, C-6), 26.0 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-15), 13.2 (p, C-13), 12.6 (p, C-12), -4.4 (p, TBS), -5.0 (p, TBS) ppm.

### (2*E*,4*E*,7*S*,8*R*,9*R*)-Ethyl-7,9-dihydroxy-4,8-dimethylundeca-2,4,10-trienoate
### (7,8-*syn*,8,9-*syn* S23a) and
### (2*E*,4*E*,7*R*,8*R*,9*R*)-ethyl-7,9-dihydroxy-4,8-dimethylundeca-2,4,10-trienoate
### (7,8-*anti*,8,9-*syn* S23b)



7,8-*anti*,8,9-*syn* **S23b**



7,8-*syn*,8,9-*syn* **S23a**

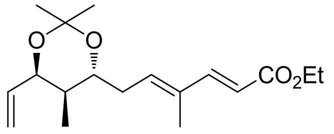
A mixture of alcohols **29** [*d.r.*: 1.7:1 (**29a**:**29b**), 107 mg, 280 μmol, 1.0 eq] was dissolved in THF (6 ml) and cooled to 0 °C. TBAF·3 $H_2O$ (133 mg, 400 □mol, 1.5 eq) was dissolved in THF (2 ml) and added to the first solution. Stirring was continued for 1 h at 0 °C and for 10 min at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 2:1) to furnish diols 7,8-*syn*,8,9-*syn* **S23a** and 7,8-*anti*,8,9-*syn* **S23b** [*d.r.*: ~2:1 (**S23a**:**S23b**), 66 mg, 250 μmol, 88%] as a colourless oil.

$R_f$ = 0.25 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_{24}NaO_4$: 291.1572 $[M + Na]^+$, found: 291.1567 $[M + Na]^+$.

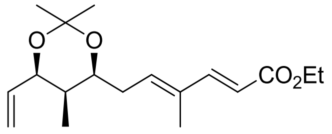
7,8-*syn*,8,9-*syn* **S23a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.31 (d, 1H, *J* = 15.7 Hz, H-3), 5.83-5.93 (m, 2H, H-5 + H-10), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 5.26 (d, 1H, *J* = 17.1 Hz, H-$11_a$), 5.16 (d, 1H, *J* = 10.6 Hz, H-$11_b$), 4.37-4.43 (m, 1H, H-9), 4.19 (q, 2H, *J* = 7.2 Hz, H-14), 3.99-4.05 (m, 1H, H-7), 3.10 (brs, 1H, OH), 2.42-2.55 (m, 1H, H-$6_a$), 2.30-2.39 (m, 1H, H-$6_b$), 1.80 (s, 3H, H-12), 1.57-1.65 (m, 1H, H-8), 1.29 (t, 3H, *J* = 7.2 Hz, H-15), 0.93 (d, 3H, *J* = 7.2 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 139.6 (t, C-10), 137.5 (t, C-5), 134.9 (q, C-4), 116.4 (t, C-2), 114.9 (s, C-11), 77.4 (t, C-9), 75.5 (t, C-7), 60.4 (s, C-14), 41.2 (t, C-8), 34.8 (s, C-6), 14.4 (p, C-15), 12.6 (p, C-12), 5.1 (p, C-13) ppm.

7,8-*anti*,8,9-*syn* **S23b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.96-6.02 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.83-5.95 (m, 1H, H-10), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 5.28 (d, 1H, *J* = 17.1 Hz, H-$11_a$), 5.20 (d, 1H, J = 10.6 Hz, H-$11_b$), 4.37-4.43 (m, 1H, H-9), 4.19 (q, 2H, $J$ = 7.2 Hz, H-14), 3.72-3.78 (m, 1H, H-7), 2.77 (brs, 1H, OH), 2.42-2.55 (m, 2H, H-6), 1.75-1.84 (m, 4H, H-12 + H-8), 1.29 (t, 3H, $J$ = 7.2 Hz, H-15), 0.89 (d, 3H, $J$ = 7.2 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 138.3 (t, C-10), 137.4 (t, C-5), 135.2 (q, C-4), 116.3 (t, C-2), 115.7 (s, C-11), 74.9 (t, C-9), 74.4 (t, C-7), 60.4 (s, C-14), 42.1 (t, C-8), 35.0 (s, C-6), 14.4 (p, C-15), 12.6 (p, C-12), 12.2 (p, C-13) ppm.

**Acetonides** (7,8-*syn*,8,9-*syn* **47a**) and (7,8-*anti*,8,9-*syn* **47b**)



7,8-*anti*,8,9-*syn* **47b**



7,8-*syn*,8,9-*syn* **47a**

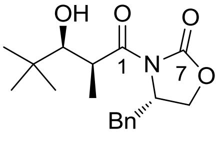
A mixture of diols **S23** [*d.r.*: ~2:1 (**S23a**:**S23b**), 33 mg, 0.13 mmol, 1.0 eq] was dissolved in $CH_2Cl_2$ (7.5 ml). 2,2-Dimethoxypropane (1.4 ml) and PPTS (3 mg, catalytic) were added and the solution was stirred for 75 min at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1). Diols 7,8-*anti*,8,9-*syn* **47b** and 7,8-*syn*,8,9-*syn* **47a** [*d.r.*: ~1.8:1 (**47a**:**47b**), 38 mg, 0.12 mmol, 99%) were obtained as a colourless oil.

$R_f$ = 0.82 (PE:EE = 2:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{18}H_{28}NaO_4$: 331.1885 $[M + Na]^+$, found: 331.1888 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **47a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, $J$ = 15.7 Hz, H-3), 5.86 (dd, 1H, $J$ = 7.3, 7.3 Hz, H-5), 5.81 (d, 1H, $J$ = 15.7 Hz, H-2), 5.73-5.83 (m, 1H, H-10), 5.25 (d, 1H, $J$ = 17.4 Hz, H-11$_a$), 5.16 (d, 1H, $J$ = 10.6 Hz, H-11$_b$), 4.44-4.48 (m, 1H, H-9), 4.21 (q, 2H, $J$ = 7.2 Hz, H-14), 4.02 (ddd, 1H, $J$ = 7.1, 7.1, 2.1 Hz, H-7), 2.37-2.52 (m, 1H, H-6$_a$), 2.26-2.36 (m, 1H, H-6$_b$), 1.80 (s, 3H, H-12), 1.42-1.50 (m, 4H, H-8 + H-17$_a$), 1.44 (s, 3H, H-17$_b$), 1.30 (t, 3H, $J$ = 7.2 Hz, H-15), 0.87 (d, 3H, $J$ = 7.2 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 137.4 (t, C-5), 137.0 (t, C-10), 134.6 (q, C-4), 116.2 (t, C-2), 115.4 (s, C-11), 99.3 (q, C-16), 74.2 (t, C-9), 72.5 (t, C-7), 60.4 (s, C-14), 35.7 (t, C-8), 32.6 (s, C-6), 30.1 (p, C-17$_a$), 19.8 (p, C-17$_b$), 14.5 (p, C-15), 12.6 (p, C-12), 5.4 (p, C-13) ppm.

7,8-*anti*,8,9-*syn* **47b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, $J$ = 15.7 Hz, H-3), 5.98 (dd, 1H, $J$ = 6.8, 6.5 Hz, H-5), 5.81 (d, 1H, $J$ = 15.7 Hz, H-2), 5.73-5.83 (m, 1H, H-10), 5.25 (d, 1H, $J$ = 17.4 Hz, H-11$_a$), 5.16 (d, 1H, $J$ = 10.6 Hz, H-11$_b$), 4.42 (dd, 1H, $J$ = 5.8, 5.8 Hz, H-9), 4.21 (q, 2H, $J$ = 7.2 Hz, H-14), 3.40 (ddd, 1H, $J$ = 8.0, 8.0, 4.3 Hz, H-7), 2.37-2.52 (m, 1H, H-6$_a$), 2.26-2.36 (m, 1H, H-6$_b$), 1.72-1.81 (m, 4H, H-12 + H-8), 1.36 (s, 6H, H-17), 1.30 (t, 3H, $J$ = 7.2 Hz, H-15), 0.84 (d, 3H, $J$ = 7.2 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 138.0 (t, C-5), 135.8 (t, C-10), 134.3 (q, C-4), 116.1 (t, C-2), 115.9 (s, C-11), 100.9 (q, C-16), 74.2 (t, C-7), 70.8 (t, C-9), 60.4 (s, C-14), 40.4 (t, C-8), 33.8 (s, C-6), 25.3 (p, C-17$_a$), 24.1 (p, C-17$_b$), 14.5 (p, C-15), 12.8 (p, C-13), 12.6 (p, C-12) ppm.

**Oxazolidinone S24**

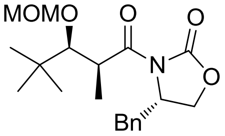


**S24**

Propionated ($S$)-Evans auxiliary **S4**[S2] (1.00 g, 4.3 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (16 ml) and cooled to 0 °C. $Et_3N$ (0.7 ml, 5.2 mmol, 1.2 eq) and $n$-$Bu_2BOTf$ (5.2 ml, $c$ = 1 mol/l in $CH_2Cl_2$, 5.2 mmol, 1.2 eq) were slowly added. The solution was stirred for 2 h at 0 °C, cooled to -78 °C and pivaldehyde (**S25**) (0.7 ml, 6.4 mmol, 1.5 eq) in $CH_2Cl_2$ (2 ml) was added over a period of 5 min. After stirring for 2 h at -78 °C the solution was left at 0 °C overnight. The reaction was terminated by addition of MeOH (20 ml), phosphate buffer (pH = 7, 6.2 ml) and a solution of MeOH (14 ml) and aq. $H_2O_2$ (7 ml, 30%ig). The mixture was stirred for 4.5 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 5:1) to furnish product **S24** (1.28 g, 4.0 mmol, 93%) as a colourless oil.

$R_f$ = 0.48 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +36.9 ($c$ = 1.0, $CHCl_3$); mp. = 108 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.37-7.18 (m, 5H, Ph), 4.68 (dddd, 1H, $J$ = 9.7, 6.9, 3.2, 3.1 Hz, H-9), 4.15-4.25 (m, 2H, H-8), 4.09, (qd, 1H, $J$ = 6.9, 3.1 Hz, H-2), 3.67 (d, 1H, $J$ = 3.1 Hz, H-3), 3.26 (dd, 1H, $J$ = 13.3, 3.1 Hz, H-10$_a$), 2.77 (dd, 1H, $J$ = 13.3, 9.7 Hz, H-10$_b$), 1.30 (d, 3H, $J$ = 6.9 Hz, H-6), 0.97 (s, 9H, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 178.5 (q, C-1), 153.0 (q, C-7), 135.2 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.6 (q, Ph), 77.8 (t, C-3), 66.2 (s, C-8), 55.3 (t, C-9), 38.9 (t, C-2), 38.0 (s, C-10), 35.8 (q, C-4), 27.0 (p, C-5), 12.9 (p, C-6) ppm; **HRMS** (ESI): $m/z$: calculated for $C_{18}H_{26}O_4N$: 320.1862 $[M + H]^+$, found: 320.1859 $[M + H]^+$.

## MOM-protected oxazolidinone S26

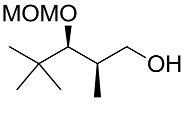


**S26**

Alcohol **S24** (500 mg, 1.6 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (26 ml) and cooled to 0 °C. $^{i}Pr_2NEt$ (3.5 ml, 21.9 mmol, 14.0 eq) and MOMCl (0.8 ml, 11.0 mmol, 7.0 eq) were added. The solution was stirred for 20 min at 0 °C and then for 6 d at RT. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1) to furnish product **S26** (503 mg, 1.4 mmol, 88%) as a colourless solid.

$R_f$ = 0.36 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +62.3 (*c* = 1.0, $CHCl_3$); m.p. = 47 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.19-7.36 (m, 5H, Ph), 4.81 (d, 1H, *J* = 6.5 Hz, MOM), 4.69 (d, 1H, *J* = 6.5 Hz, MOM), 4.60-4.67 (m, 1H, H-9), 4.14-4.22 (m, 2H, H-8), 4.07-4.14 (m, 1H, H-2), 3.72 (d, 1H, *J* = 5.5 Hz, H-3), 3.43 (s, 3H, MOM), 3.28 (dd, 1H, *J* = 13.4, 3.2 Hz, H-$10_a$), 2.76 (dd, 1H, *J* = 13.4, 9.6 Hz, H-$10_b$), 1.26 (d, 3H, *J* = 7.2 Hz, H-6), 0.92 (s, 9H, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 177.1 (q, C-1), 153.1 (q, C-5), 135.5 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.5 (t, Ph), 98.9 (s, MOM), 85.4 (t, C-3), 66.2 (s, C-8), 56.8 (p, MOM), 55.8 (t, C-9), 39.6 (t, C-2), 38.0 (s, C-10), 36.5 (q, C-4), 26.6 (p, C-5), 14.8 (p, C-6) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{29}NaNO_5$: 386.1943 $[M + Na]^+$, found: 386.1943 $[M + Na]^+$.

## Alcohol S27

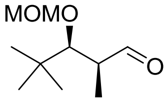


**S27**

Oxazolidinone **S26** (500 mg, 1.38 mmol, 1.0 eq) was dissolved in $Et_2O$ (28 ml) and cooled to 0 °C. $H_2O$ (0.03 ml, 1.68 mmol, 1.2 eq) and $LiBH_4$ (150 mg, 6.88 mmol, 5.0 eq) were added and the solution was stirred for 2 h at 0 °C and then overnight at rt. The reaction was terminated by addition of aq. $NH_4Cl$ and stirred for 1.5 h at rt. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1) to furnish alcohol **S27** (214 mg, 1.12 mmol, 82%) as a colourless liquid.

R$_f$ = 0.34 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -93.5 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.69 (s, 2H, MOM), 3.47-3.51 (m, 2H, H-1), 3.42 (s, 3H, MOM), 3.31 (d, 1H, *J* = 1.6 Hz, H-3), 2.16 (brs, 1H, OH), 1.92-2.03 (m, 1H, H-2), 0.93 (s, 9H, H-5), 0.91 (d, 3H, *J* = 7.0 Hz, H-6) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 99.6 (s, MOM), 87.1 (t, C-3), 67.4 (s, C-1), 56.3 (p, MOM), 36.6 (q, C-4), 36.2 (t, C-2), 27.1 (p, C-5), 12.1 (p, C-6) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{10}H_{22}NaO_3$: 213.1467 $[M + Na]^+$, found: 213.1463 $[M + Na]^+$.

**Aldehyde 24**



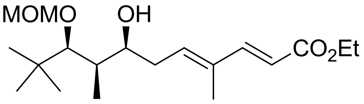
**24**

Alcohol **S27** (107 mg, 0.56 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (11 ml) and $NaHCO_3$ (20 mg) was added. DESS-MARTIN periodinane (286 mg, 0.67 mmol, 1.2 eq) was added and stirring was continued for 75 min at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and mixture was stirred for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **24** (86 mg, 0.46 mmol, 81%) as a colourless liquid, which was used immediately in the next step.

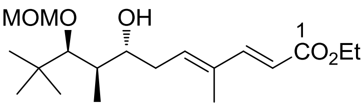
R$_f$ = 0.72 (PE:EE = 2:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.58 (s, 1H, H-1), 4.50 (d, 1H, *J* = 6.8 Hz, MOM), 4.43 (d, 1H, *J* = 6.8 Hz, MOM), 3.63 (d, 1H, *J* = 2.0 Hz, H-3), 3.20 (s, 3H, MOM), 2.44 (qd, 1H, *J* = 7.0, 2.0 Hz, H-2), 1.10 (d, 3H, *J* = 7.0 Hz, H-6), 0.87 (s, 9H, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 204.7 (t, C-1), 98.3 (s, MOM), 83.6 (t, C-3), 56.2 (p, MOM), 47.8 (t, C-2), 36.4 (q, C-4), 27.1 (p, C-5), 9.3 (p, C-6) ppm; **HRMS** (ESI): *m/z*: Compound **24** could not be detected by mass spectrometry.

**(2*E*,4*E*,7*S*,8*R*,9*S*)-Ethyl-7-hydroxy-9-(methoxymethoxy)-4,8,10,10-tetramethylundeca-2,4-dienoate (**7,8-*syn*,8,9-*syn* **30a)** and

**(2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-7-hydroxy-9-(methoxymethoxy)-4,8,10,10-tetramethylundeca-2,4-dienoate (**7,8-*anti*,8,9-*syn* **30b)**



7,8-*syn*,8,9-*syn* **30a**

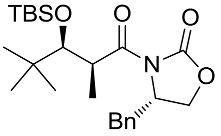


7,8-*anti*,8,9-*syn* **30b**

Following the general procedure aldehyde **24** (36 mg, 0.19 µmol, 1.0 eq) was reacted with ester **6** (59 mg, 0.38 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 5:1) to furnish alcohols 7,8-*syn*,8,9-*syn* **30a** and 7,8-*anti*,8,9-*syn* **30b** (*d.r.*: 1:5.9 (**30b**:**30a**), 45 mg, 0.13 mmol, 69%) as a yellow oil.

$R_f$ = 0.16 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; 7,8-*syn*,8,9-*syn* **30a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.93 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.76 (d, 1H, *J* = 6.5 Hz, MOM), 4.71 (d, 1H, *J* = 6.5 Hz, MOM), 4.20 (q, 2H, *J* = 7.2 Hz, H-14), 3.72-3.78 (m, 1H, H-7), 3.42 (s, 3H, MOM), 3.15 (d, 1H, *J* = 1.4 Hz, H-9), 2.39-2.49 (m, 1H, H-$6_a$), 2.28-2.39 (m, 1H, H-$6_b$), 1.79-1.88 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.29 (t, 3H, *J* = 7.2 Hz, H-15), 0.96 (d, 3H, *J* = 7.2 Hz, H-13), 0.87 (s, 9H, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 138.3 (t, C-5), 134.5 (q, C-4), 116.1 (t, C-2), 100.3 (s, MOM), 92.3 (t, C-9), 77.5 (t, C-7), 60.3 (s, C-14), 56.3 (p, MOM), 37.7 (t, C-8), 37.3 (q, C-10), 34.7 (s, C-6), 26.3 (p, C-11), 14.5 (p, C-15), 12.6 (p, C-12), 8.1 (p, C-13) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{19}H_{34}NaO_5$: 365.2304 $[M + Na]^+$, found: 365.2301 $[M + Na]^+$.

## Oxazolidinone S28

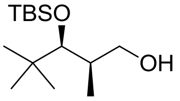


**S28**

Alcohol **S24** (500 mg, 1.6 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (30 ml) and cooled to 0 °C. 2,6-Lutidine (0.55 ml, 4.7 mmol, 3.0 eq) and TBSOTf (0.54 ml, 2.3 mmol, 1.5 eq) were added and stirred for 3 h at 0 °C. Additional 2,6-lutidine (0.30 ml, 2.6 mmol, 1.6 eq) and TBSOTf (0.35 ml, 1.5 mmol, 1.0 eq) were added and stirring was continued overnight at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish product **S28** (660 mg, 1.5 mmol, 97%) as a colourless, waxy solid.

R$_f$ = 0.51 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +28.5 (*c* = 1.0, $CHCl_3$); mp. = 83 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.19-7.36 (m, 5H, Ph), 4.63-4.70 (m, 1H, H-9), 4.12-4.22 (m, 2H, H-8), 3.97-4.06 (m, 1H, H-2), 3.94-3.97 (m, 1H, H-3), 3.26 (dd, 1H, *J* = 13.4, 3.4 Hz, H-10$_a$), 2.74 (dd, 1H, *J* = 13.4, 9.7 Hz, H-10$_b$), 1.22 (d, 3H, *J* = 6.8 Hz, H-6), 0.95 (s, 9H, H-5), 0.87 (s, 9H, TBS), 0.14 (s, 3H, TBS), 0.13 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 177.5 (q, C-1), 153.0 (q, C-7), 135.4 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.5 (t, Ph), 78.0 (t, C-3), 66.1 (s, C-8), 55.5 (t, C-9), 40.0 (t, C-2), 38.1 (q, C-4), 37.0 (s, C-10), 26.5 (p, C-5), 26.4 (p, TBS), 18.8 (q, TBS), 15.1 (p, C-6), -3.0 (p, TBS), -4.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{24}H_{39}NaNO_4Si$: 456.2546 $[M + Na]^+$, found: 456.2555 $[M + Na]^+$.

**Alcohol S29**

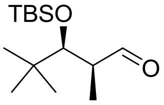


**S29**

Oxazolidinone **S28** (630 mg, 1.45 mmol, 1.0 eq) was dissolved in $Et_2O$ (28 ml) and cooled to 0 °C. $H_2O$ (0.03 ml, 1.68 mmol, 1.1 eq) and $LiBH_4$ (158 mg, 7.27 mmol, 5.0 eq) were added. The solution was stirred for 2 h at 0 °C and then overnight at rt. The reaction was terminated by addition of aq. $NH_4Cl$ and stirred for 1.75 h at rt. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 5:1) to furnish alcohol **S29** (279 mg, 1.07 mmol, 74%) as a colourless liquid.

R$_f$ = 0.42 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -7.4 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 3.42-3.50 (m, 2H, H-1), 3.37 (d, 1H, *J* = 1.4 Hz, H-3), 1.96 (qddd, 1H, *J* = 7.1, 7.0, 6.9, 1.4 Hz, H-2), 1.43 (brs, 1H, OH), 0.92 (s, 9H, H-5), 0.89 (s, 9H, TBS), 0.87 (d, 3H, *J* = 7.1 Hz, H-6), 0.06 (s, 3H, TBS), 0.05 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 78.8 (s, C-3), 67.8 (t, C-1), 37.6 (t, C-2), 36.7 (q, C-4), 27.1 (p, C-5), 26.5 (p, TBS), 18.9 (q, TBS), 12.3 (p, C-6), -2.9 (p, TBS), -3.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{32}NaO_2Si$: 283.2069 $[M + Na]^+$, found: 283.2075 $[M + Na]^+$.

### Aldehyde 25

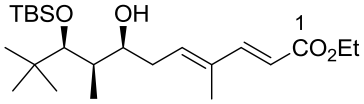


**25**

Alcohol **S29** (120 mg, 0.46 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (9.2 ml) and $NaHCO_3$ (20 mg) added. DESS-MARTIN periodinane (234 mg, 0.55 mmol, 1.2 eq) was added and the mixture was stirred for 75 min at RT. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 1 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1) to furnish aldehyde **25** (104 mg, 0.40 mmol, 88%) as a colourless liquid, which was immediately used in the next step.

$R_f$ = 0.69 (PE:EE = 5:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.67 (s, 1H, H-1), 3.92 (d, 1H, *J* = 2.0 Hz, H-3), 2.52 (qd, 1H, *J* = 7.4, 2.0 Hz, H-2), 1.18 (d, 3H, *J* = 7.4 Hz, H-6), 0.92 (s, 9H, H-5), 0.90 (s, 9H, TBS), 0.07 (s, 3H, TBS), -0.09 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 205.8 (t, C-1), 76.4 (t, C-3), 48.8 (t, C-2), 36.8 (q, C-4), 27.0 (p, C-5), 26.3 (p, TBS), 18.6 (q, TBS), 9.5 (p, C-6), -3.4 (p, TBS), -4.4 (p, TBS) ppm; **HRMS** (ESI): *m/z*: Compound **25** could not be detected by mass spectrometry.

### YAMAMOTO aldol product 7,8-*syn*,8,9-*syn* 31a

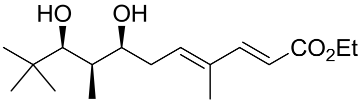


7,8-*syn*,8,9-*syn* **31a**

Following the general procedure, aldehyde **25** (48 mg, 0.18 mmol, 1.0 eq) was reacted with ester **6** (56 mg, 0.36 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohol 7,8-*syn*,8,9-*syn* **31a** (*d.r.*: >10:1, 46 mg, 0.11 μmol, 62%) as a yellow oil.

$R_f$ = 0.23 (PE:EE = 10:1); $[\alpha]_D^{20}$ = -13.0 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.96 (dd, 1H, *J* = 7.5, 7.2 Hz, H-5), 5.82 (d, 1H, *J* = 15.7 Hz, H-2), 4.20 (q, 2H, *J* = 7.3 Hz, H-14), 3.55 (ddd, 1H, *J* = 6.2, 6.2, 6.2 Hz, H-7), 3.33 (d, 1H, *J* = 2.4 Hz, H-9), 2.40-2.48 (m, 1H, H-$6_a$), 2.28-2.39 (m, 1H, H-$6_b$), 1.79-1.90 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.54 (brs, 1H, OH), 1.29 (t, 3H, *J* = 7.3 Hz, H-15), 0.88-0.96 (m, 12H, H-11 + H-13), 0.86 (s, 9H, TBS), 0.08 (s, 3H, TBS), 0.05 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.2 (t, C-3), 137.9 (t, H-5), 135.0 (q, C-4), 116.4 (t, C-2), 80.2 (t, C-9), 75.4 (t, C-7), 60.4 (s, C-14), 39.8 (t, C-8), 37.2 (q, C-10), 35.3 (s, C-6), 26.7 (p, C-11), 26.5 (p, TBS), 18.9 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 10.2 (p, C-13), -2.8 (p, TBS), -4.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{23}H_{45}O_4Si$: 413.3087 $[M + H]^+$, found: 413.3075 $[M + H]^+$.

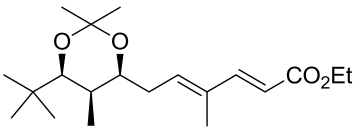
**Diol** 7,8-*syn*,8,9-*syn* **S31a**



7,8-*syn*,8,9-*syn* **S31a**

Alcohol 7,8-*syn*,8,9-*syn* **31a** (15 mg, 36 □mol, 1.0 eq) was dissolved in THF (0.6 ml) and cooled to 0 °C. TBAF·$3H_2O$ (17 mg, 55 □mol, 1.5 eq) was dissolved in THF (0.4 ml) and slowly added. The solution was stirred for 2 h at 0 °C and then for 1.5 h at rt. An additional portion of TBAF·$3H_2O$ (10 mg, 32 □mol, 0.9 eq) was added and stirring was continued for 2 h at rt. I final portion of TBAF·$3H_2O$ (10 mg, 32 □mol, 0.9 eq) was added and the reaction mixture was stirred overnight at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 2:1) to furnish diol 7,8-*syn*,8,9-*syn* **S31a** (5 mg, 17 □mol, 47%) as a colourless liquid. $R_f$ = 0.32 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -5.4 (*c* = 0.4, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.90 (dd, 1H, *J* = 7.3, 6.7 Hz, H-5), 5.83 (d, 1H, *J* = 15.7 Hz, H-2), 4.21 (q, 2H, *J* = 7.3 Hz, H-14), 3.81-3.87 (m, 1H, H-7), 3.49 (s, 1H, H-9), 2.42-2.54 (m, 1H, H-6$_a$), 2.27-2.37 (m, 1H, H-6$_b$), 1.80-1.90 (m, 1H, H-8), 1.81 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.3 Hz, H-15), 0.97 (d, 3H, *J* = 7.2 Hz, H-13), 0.95 (s, 9H, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.5 (q, C-1), 149.2 (t, C-3), 137.5 (t, C-5), 135.0 (q, C-4), 116.5 (t, C-2), 84.2 (t, C-9), 78.1 (t, C-7), 60.4 (s, C-14), 37.2 (t, C-8), 35.9 (q, C-10), 34.4 (s, C-6), 27.0 (p, C-11), 14.5 (p, C-15), 12.6 (p, C-12), 6.5 (p, C-13) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{17}H_{31}O_4$: 299.2222 $[M + H]^+$, found: 299.2224 $[M + H]^+$.

### **Acetonide** (7,8-*syn*,8,9-*syn* **S32a**)

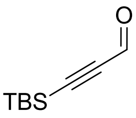


7,8-*syn*,8,9-*syn* **S32a**

Diol 7,8-*syn*,8,9-*syn* **S31a** (4.5 mg, 15 µmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (0.5 ml) and 2,2-dimethoxypropane (0.05 ml) was added. PPTS (0.5 mg, catalytic) was added and stirring was continued for 2 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1). Acetonide 7,8-*syn*,8,9-*syn* **S32a** (3.3 mg, 10 µmol, 65%) was obtained as a colourless liquid.

$R_f$ = 0.85 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -10.3 ($c$ = 0.3, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, $J$ = 15.7 Hz, H-3), 5.90 (dd, 1H, $J$ = 7.2, 6.8 Hz, H-5), 5.81 (d, 1H, $J$ = 15.7 Hz, H-2), 4.21 (q, 2H, $J$ = 7.1 Hz, H-14), 3.87 (td, 1H, $J$ = 7.0, 1.7 Hz, H-7), 3.43 (d, 1H, $J$ = 2.1 Hz, H-9), 2.34-2.44 (m, 1H, H-$6_a$), 2.23-2.32 (m, 1H, H-$6_b$), 1.79 (s, 3H, H-12), 1.47-1.57 (m, 1H, H-8), 1.40 (s, 3H, H-$17_a$), 1.38 (s, 3H, H-$17_b$), 1.30 (t, 3H, $J$ = 7.1 Hz, H-15), 0.89-0.95 (m, 12H, H-11 + H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 137.6 (t, C-5), 134.4 (q, C-4), 116.5 (t, C-2), 99.2 (q, C-16), 80.6 (t, C-9), 74.6 (t, C-7), 60.4 (s, C-14), 34.3 (q, C-10), 33.9 (t, C-8), 32.6 (s, C-6), 30.0 (p, C-$17_a$), 27.1 (p, C-11), 19.5 (p, C-$17_b$), 14.5 (p, C-15), 12.6 (p, C-12), 6.8 (p, C-13) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{35}O_4$: 339.2535 $[M + H]^+$, found: 339.2533 $[M + H]^+$.

### **3-(*tert*-Butyldimethylsilyl)propionaldehyde (S33)**



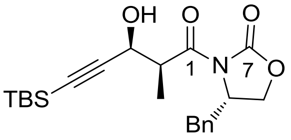
**S33**

TBS-Acetylene (**S34**) (2.1 ml, 11.3 mmol, 1.0 eq) was dissolved in THF (25 ml) and cooled to 0 °C. *n*-BuLi (4.7 ml, $c$ = 2.5 mol/l in hexane, 11.8 mmol, 1.1 eq) was added and the solution was stirred for 20 min during which time the temperature was raised from 0 °C to rt. The solution was cooled to 0 °C and DMF (0.9 ml, 11.8 mmol, 1.1 eq.) was added. After warming to rt over a period of 20 min, the solution was heated to reflux for 1 h. The solution was cooled to 0 °C and the reaction was terminated by addition of aq. $H_2SO_4$ (20 ml, 5%ig). The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure.

The crude product was purified by distillation under reduced pressure (13 mbar, 66 °C) to furnish aldehyde **S33** (1.37 g, 8.1 mmol, 72%) as a colourless liquid.

$^{1}$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.18 (s, 1H, H-1), 0.97 (s, 9H, TBS), 0.20 (s, 6H, TBS) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 176.8 (t, C-1), 103.2 (q, C-2), 102.1 (q, C-3), 26.1 (p, TBS), 16.7 (q, TBS), -5.1 (p, TBS) ppm. The NMR-data is in accordance with literature.[S7]

## (*S*)-9-Benzyl-3-[(2*S*,3*S*)-5-(*tert*-butyldimethylsilyl)-3-hydroxy-2-methylpent-4-ynoyl]-oxazolidin-2-one (S35)

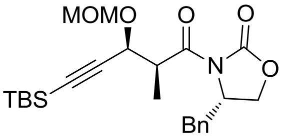


**S35**

Propionated (*S*)-EVANS auxiliary **S4**[S2] (12.9 g, 55 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (205 ml) and cooled to -78 °C. $Et_3N$ (8.6 ml, 61 mmol, 1.1 eq) and *n*-$Bu_2BOTf$ (61.0 ml, *c* = 1 mol/l in $CH_2Cl_2$, 61 mmol, 1.1 eq) were added. The solution was stirred for 1 h at -78 °C during which time the temperature was raised to 0 °C before it was cooled to -78 °C. Aldehyde **S33** (10.2 g, 61 mmol, 1.1 eq) was dissolved in $CH_2Cl_2$ (20 ml) and the solution was added over a period of 20 min to the first solution. It was stirred for 2 h at -78 °C and then at 0 °C overnight. The reaction was terminated by addition of MeOH (660 ml), NaOAc (36 g), aq. $H_2O_2$ (40 ml, 30%ig) and stirred 2 h. The layers were separated and the aqueous layer extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), aq. NaCl, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish aldol product **S35** (19.7 g, 49 mmol, 89%) as a colourless solid.

$R_f$ = 0.64 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +55.6 (*c* =1.0, $CHCl_3$); m.p. = 113 °C; $^{1}$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.37 (m, 3H, Ph), 7.18-7.22 (m, 2H, Ph), 4.73 (dd, 1H, *J* = 4.8, 4.7 Hz, H-3), 4.65-4.75 (m, 1H, H-9), 4.18-4.26 (m, 2H, H-8), 3.96 (qd, 1H, *J* = 6.9, 4.7 Hz, H-2), 3.24 (dd, 1H, *J* = 13.5, 3.2 Hz, H-$10_a$), 2.81 (dd, 1H, *J* = 13.5, 9.4 Hz, H-$10_b$), 2.77 (d, 1H, *J* = 4.8 Hz, OH), 1.42 (d, 3H, *J* = 6.9 Hz, H-6), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 175.5 (q, C-1), 153.0 (q, C-7), 135.1 (q, Ph), 129.6 (t, Ph), 129.2 (t, Ph), 127.6 (t, Ph), 104.5 (q, C-4), 89.0 (q, C-5), 66.4 (s, C-8), 63.9 (t, C-3), 55.2 (t, C-9), 44.2 (t, C-2), 37.9 (s, C-10), 26.2 (p, TBS), 16.6 (q, TBS), 12.4 (p, C-6), -4.6 (p, TBS), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{31}NNaO_4Si$: 424.1920 $[M + Na]^+$, found: 424.1938 $[M + Na]^+$.

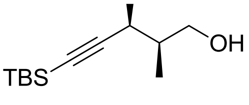
### **(*S*)-9-Benzyl-3-[(2*S*,3*S*)-5-(*tert*-butyldimethylsilyl)-3-(methoxymethoxy)-2-methylpent-4-ynoyl]oxazolidin-2-one (S36)**



**S36**

Alcohol **S35** (1.0 g, 3.1 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (50 ml) and cooled to 0 °C. $^i Pr_2NEt$ (5.1 ml, 30.7 mmol, 10.0 eq) was added and the solution was stirred for 30 min at 0 °C. MOMCl (1.2 ml, 15.4 mmol, 5.0 eq) was added and stirring was continued for 2 d at rt. More $^i Pr_2NEt$ (5.1 ml, 30.7 mmol, 10.0 eq) and MOMCl (1.2 ml, 15.4 mmol, 5.0 eq) were added and the solution was stirred for another 4 d. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 10:1) to furnish alcohol **S36** (1.1 g, 2.4 mmol, 78%) as a colourless solid.
$R_f$ = 0.68 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -36.0 (*c* = 1.0, $CHCl_3$); mp. = 109 °C; $^1$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.36 (m, 3H, Ph), 7.19-7.23 (m, 2H, Ph), 4.95 (d, 1H, *J* = 6.8 Hz, MOM), 4.62-4.69 (m, 1H, H-9), 4.61 (d, 1H, *J* = 6.8 Hz, MOM), 4.58 (d, 1H, *J* = 7.2 Hz, H-3), 4.13-4.23 (m, 3H, H-2 + H-8), 3.37 (s, 3H, MOM), 3.28 (dd, 1H, *J* = 13.4, 3.2 Hz, H-$10_a$), 2.80 (dd, 1H, *J* = 13.4, 9.6 Hz, H-$10_b$), 1.38 (d, 3H, *J* = 6.8 Hz, H-6), 0.92 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.09 (s, 3H, TBS) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 173.4 (q, C-1), 153.1 (q, C-7), 135.4 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.5 (t, Ph), 102.9 (q, C-4), 94.3 (s, MOM), 90.0 (q, C-5), 67.3 (t, C-3), 66.2 (s, C-8), 56.0 (p, MOM), 55.7 (t, C-9), 43.2 (t, C-2), 37.9 (s, C-10), 26.2 (p, TBS), 16.6 (q, TBS), 13.6 (p, C-6), -4.6 (p, TBS), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{24}H_{35}NNaO_5Si$: 468.2182 $[M + Na]^+$, found: 468.2180 $[M + Na]^+$.

### **(2*R*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(methoxymethoxy)-2-methylpent-4-yn-1-ol (S37)**

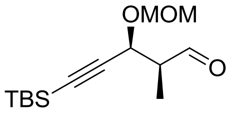


**S37**

(*S*)-EVANS aldol product **S36** (2.14 g, 4.8 mmol, 1.0 eq) was dissolved in $Et_2O$ (100 ml), cooled to 0 °C and $H_2O$ (0.1 ml, 4.8 mmol, 1.0 eq) added. $LiBH_4$ (250 mg, 11.5 mmol, 2.9 eq) was added and the reaction mixture was stirred for 1 h at 0 °C and 75 min at rt. The reaction was terminated by addition of aq. $NH_4Cl$ and stirring was continued for 30 min. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1) and furnished alcohol **S37** (1.16 mg, 4.3 mmol, 89%) as a colourless liquid.

$R_f$ = 0.49 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -167.4 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.97 (d, 1H, *J* = 6.7 Hz, MOM), 4.60 (d, 1H, *J* = 6.7 Hz, MOM), 4.48 (d, 1H, *J* = 4.4 Hz, H-3), 3.81 (ddd, 1H, *J* = 11.3, 7.4, 4.2 Hz, H-$1_a$), 3.60 (ddd, 1H, *J* = 11.3, 7.2, 4.3 Hz, H-$1_b$), 3.39 (s, 3H, MOM), 2.32 (dd, 1H, *J* = 7.2, 4.2 Hz, OH), 2.04-2.15 (m, 1H, H-2), 1.01 (d, 3H, *J* = 7.2 Hz, H-6), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 102.9 (q, C-4), 94.3 (s, MOM), 90.7 (q, C-5), 69.7 (t, C-3), 65.5 (s, C-1), 56.0 (p, MOM), 40.0 (t, C-2), 26.2 (p, TBS), 16.6 (q, TBS), 12.9 (p, C-6), -4.5 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{28}NaO_3Si$: 295.1705 $[M + Na]^+$, found: 295.1707 $[M + Na]^+$.

### (2*S*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(methoxymethoxy)-2-methylpent-4-ynal (32)

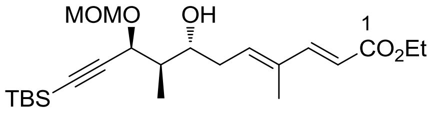


**32**

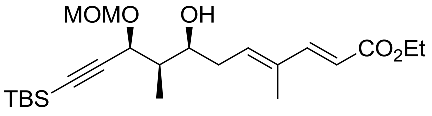
Alcohol **S37** (20 mg, 0.1 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (1.5 ml). $NaHCO_3$ (5 mg) and DESS-MARTIN periodinane (41 mg, 0.1 mmol, 1.3 eq) were added and the reaction mixture was stirred at rt overnight. The reaction was terminated by addition of aq. $Na_2SO_3/NaHCO_3$ and stirring was continued for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish aldehyde **32** (20 mg, 0.1 mmol, 99%) as a colourless oil.

$R_f$ = 0.63 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -124.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.80 (d, 1H, *J* = 0.9 Hz, H-1), 4.99 (d, 1H, *J* = 6.8 Hz, MOM), 4.78 (d, 1H, *J* = 5.4 Hz, H-3), 4.59 (d, 1H, *J* = 6.8 Hz, MOM), 3.36 (s, 3H, MOM), 2.64 (qdd, 1H, *J* = 7.0, 5.4, 0.9 Hz, H-2), 1.25 (d, 3H, *J* = 7.0 Hz, H-6), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 202.8 (t, C-1), 101.8 (q, C-4), 94.2 (s, MOM), 91.8 (q, C-5), 66.1 (t, C-3), 56.1 (p, MOM), 50.4 (t, C-2), 26.2 (p, TBS), 16.6 (q, TBS), 9.6 (p, C-6), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{26}NaO_3Si$: 293.1549 $[M + Na]^+$, found: 293.1544 $[M + Na]^+$.

### (2*E*,4*E*,7*S*,8*R*,9*S*)-Ethyl-11-(*tert*-butyldimethylsilyl)-7-hydroxy-9-(methoxymethoxy)-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*syn*,8,9-*syn* 33a) and (2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-11-(*tert*-butyldimethylsilyl)-7-hydroxy-9-(methoxymethoxy)-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*anti*,8,9-*syn* 33b)



7,8-*anti*,8,9-*syn* **33b**



7,8-*syn*,8,9-*syn* **33a**

Following the general procedure, aldehyde **32** (33 mg, 120 µmol, 1.0 eq) was reacted with ester **6** (37 mg, 240 µmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 5:1) to furnish alcohols 7,8-*syn*,8,9-*syn* **33a** and 7,8-*anti*,8,9-*syn* **33b** [*d.r.*: 1.4:1 (**33b**:**33a**), 41 mg, 97 µmol, 80%] as a yellow oil.

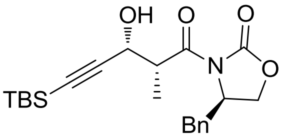
$R_f$ = 0.32 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{25}H_{39}NaO_5Si$: 447.2543 $[M + Na]^+$, found: 447.2536 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **33a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.36 (d, 1H, *J* = 15.7 Hz, H-3), 5.94 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 5.00 (d, 1H, *J* = 6.8 Hz, MOM), 4.60 (d, 1H, *J* = 6.8 Hz, MOM), 4.44 (d, 1H, *J* = 4.4 Hz, H-9), 4.20 (q, 2H, *J* = 7.1 Hz, H-14), 4.04-4.10 (m, 1H, H-7), 3.38 (s, 3H, MOM), 2.70 (d, 1H, *J* = 2.4 Hz, OH), 2.44-2.55 (m, 1H, $H-6_a$), 2.30-2.42 (m, 1H, $H-6_b$), 1.80-1.92 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.1 Hz, H-15), 1.11 (d, 3H, *J* = 7.2 Hz, H-13), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.3 (t, C-3), 137.8 (t, C-5), 134.7 (q, C-4), 116.3 (t, C-2), 103.3 (q, C-10), 94.2 (s, MOM), 91.3 (q, C-11), 72.8 (t, C-7), 70.1 (t, C-9), 60.3 (s, C-14), 56.2 (p, MOM), 41.9 (t, C-8), 34.5 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 8.3 (p, C-13), -4.5 (p, TBS) ppm.

7,8-*anti*,8,9-*syn* **33b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 6.06 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.96 (d, 1H, *J* = 6.5 Hz, MOM), 4.63 (d, 1H, *J* = 3.4 Hz, H-9), 4.61 (d, 1H, *J* = 6.5 Hz, MOM), 4.20

(q, 2H, $J$ = 7.1 Hz, H-14), 3.85-3.93 (m, 1H, H-7), 3.40 (s, 3H, MOM), 3.06 (d, 1H, $J$ = 3.4 Hz, OH), 2.44-2.55 (m, 1H, H-$6_a$), 2.30-2.42 (m, 1H, H-$6_b$), 1.80-1.92 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.30 (t, 3H, $J$ = 7.1 Hz, H-15), 1.02 (d, 3H, $J$ = 7.2 Hz, H-13),0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.5 (t, C-3), 137.8 (t, C-5), 134.7 (q, C-4), 116.1 (t, C-2), 102.7 (q, C-10), 94.5 (s, MOM), 91.0 (q, C-11), 72.8 (t, C-7), 69.5 (t, C-9), 60.3 (s, C-14), 56.2 (p, MOM), 42.7 (t, C-8), 34.1 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.7 (p, C-13), 12.6 (p, C-12), -4.5 (p, TBS) ppm.

### (*R*)-9-Benzyl-3-[(2*R*,3*R*)-5-(*tert*-butyldimethylsilyl)-3-hydroxy-2-methylpent-4-ynoyl]-oxazolidin-2-one (*ent*-S35)

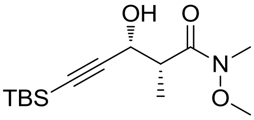


*ent*-**S35**

Propionated (*R*)-EVANS auxiliary *ent*-**S4**[S2] (300 mg, 1.29 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (5 ml) and the solution was cooled to -78 °C. $Et_3N$ (0.2 ml, 1.42 mmol, 1.1 eq) and *n*-$Bu_2BOTf$ (1.42 ml, $c$ = 1 mol/l in $CH_2Cl_2$, 1.42 mmol, 1.1 eq) were added. The solution was stirred for 1 h during which time the temperature was raised from -78 °C to 0 °C. Then, the reaction was cooled again down to -78 °C and aldehyde **S33** (260 mg, 1.54 mmol, 1.2 eq) dissolved in $CH_2Cl_2$ (0.5 ml) was added. The solution was stirred for 2 h at -78 °C and then for 16 h at 0 °C. The reaction was terminated by addition of MeOH (17 ml), NaOAc (1.0 g) and aq. $H_2O_2$ (1 ml, 30%ig) and stirring was continued for 2 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish product *ent*-**S35** (446 mg, 1.11 mmol, 86%) as a colourless solid.

$R_f$ = 0.65 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -51.9 ($c$ = 1.0, $CHCl_3$); m.p. = 76 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.37 (m, 3H, Ph), 7.18-7.23 (m, 2H, Ph), 4.73 (d, 1H, $J$ = 4.5 Hz, H-3), 4.65-4.72 (m, 1H, H-9), 4.15-4.26 (m, 2H, H-8), 3.96 (qd, 1H, $J$ = 6.9, 4.5 Hz, H-2), 3.24 (dd, 1H, $J$ = 13.2, 3.1 Hz, H-$10_a$), 2.81 (dd, 1H, $J$ = 13.2, 9.1 Hz, H-$10_b$), 1.43 (d, 3H, $J$ = 6.9 Hz, H-6), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 175.5 (q, C-1), 153.0 (q, C-7), 135.1 (q, Ph), 129.6 (t, Ph), 129.2 (t, Ph), 127.6 (t, Ph), 104.5 (q, C-4), 89.0 (q, C-5), 66.4 (s, C-8), 63.9 (t, C-3), 55.2 (t, C-9), 44.2 (t, C-2), 37.9 (s, C-10), 26.2 (p, TBS), 16.6 (q, TBS), 12.4 (p, C-6), -4.6 (p, TBS), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{32}NO_4Si$: 402.2101 [M + Na]$^+$, found: 402.2086 [M + Na]$^+$.

### (2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-3-hydroxy-*N*-methoxy-*N*,2-dimethylpent-4-ynamide (S38)

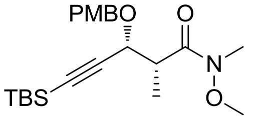


**S38**

*N*,*O*-Dimethylhydroxylamine hydrochloride (2.44 g, 25.1 mmol, 9.0 eq) was suspended in THF (4.0 ml), cooled to -30 °C and $AlMe_3$ (12.5 ml, *c* = 2 mol/l in hexane, 25.1 mmol, 9.0 eq) was added over 5 min. The solution was warmed up to rt, stirred for 15 min and then cooled to -10 °C. Alcohol *ent*-**S35** (0.91 g, 2.8 mmol, 1.0 eq) was dissolved in THF (10.0 ml) and added to the first solution. The reaction mixture was stirred for 2 h at 0 °C. The slurry was slowly transferred into a solution of aq. Na-K-tartrate (75 ml), aq. $NaHCO_3$ (30 ml) and ethyl acetate (100 ml) and stirred for 1 h, while the temperature was slowly raised from 0 °C to rt. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 3:1) to furnish Weinreb amide **S38** (584 mg, 2.1 mmol, 74%) as a colourless liquid.

$R_f$ = 0.17 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -10.5 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.72 (dd, 1H, *J* = 3.2, 3.2 Hz, H-3), 3.77 (s, 1H, OH), 3.73 (s, 3H, H-8), 3.19 (s, 3H, H-7), 2.98-3.08 (m, 1H, H-2), 1.35 (d, 3H, *J* = 7.2 Hz, H-6), 0.93 (s, 9H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.4 (q, C-1), 105.1 (q, C-4), 88.1 (q, C-5), 64.0 (t, C-3), 61.8 (p, C-8), 40.9 (t, C-2), 32.0 (p, C-7), 26.2 (p, TBS), 16.6 (q, TBS), 11.6 (p, C-6), -4.5 (p, TBS), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{28}NO_3Si$: 286.1838 [M + H]$^+$, found: 286.1832 [M + H]$^+$.

### (2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-*N*-methoxy-3-(4-methoxybenzyloxy)-*N*,2-dimethyl-pent-4-ynamide (S39)

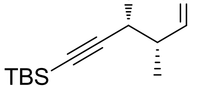


**S39**

Alcohol **S38** (580 mg, 2.9 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7 ml). PMB-trichloroacetimidate (1.15 g, 4.1 mmol, 2.0 eq) was dissolved in $CH_2Cl_2$ (3 ml) and added to the first solution. CSA (38.0 mg, 0.2 mmol, 0.1 eq) was added and stirring was continued for 2 d at rt. A second portion of PMB-trichloroacetimidate (287 mg, 1.0 mmol, 0.5 eq) was added and the mixture was stirred for additional 3 d. The reaction was terminated by addition of aq. $NaHCO_3$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. $NaHCO_3$ and aq. NaCl, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 2:1) and to furnish Weinreb amide **S39** (668 mg, 1.7 mmol, 81%) as a colourless oil.

$R_f$ = 0.25 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +62.9 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.25-7.29 (m, 2H, PMB), 6.85-6.88 (m, 2H, PMB), 4.74 (d, 1H, *J* = 11.3 Hz, PMB), 4.46 (d, 1H, *J* = 11.3 Hz, PMB), 4.20 (d, 1H, *J* = 9.2 Hz, H-3), 3.80 (s, 3H, PMB), 3.70 (s, 3H, H-8), 3.21-3.33 (m, 1H, H-2), 3.17 (s, 3H, H-7), 1.22 (d, 3H, *J* = 6.8 Hz, H-6), 0.93 (s, 9H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.7 (q, C-1), 159.5 (q, PMB), 129.9 (t, PMB), 129.4 (q, PMB), 114.0 (t, PMB), 104.4 (q, C-4), 89.6 (q, C-5), 70.6 (s, PMB), 70.5 (t, C-3), 61.7 (p, C-8), 55.4 (p, PMB), 41.6 (t, C-2), 32.1 (p, C-7), 26.2 (p, TBS), 16.6 (q, TBS), 14.4 (p, C-6), -4.5 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{37}NO_4Si$ and $C_{20}H_{36}NNaO_4Si$: 406.2414 $[M + H]^+$ and 428.2233 $[M + Na]^+$, found: 406.2409 $[M + H]^+$ and 428.2246 $[M + Na]^+$.

### (2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-3-(4-methoxybenzyloxy)-2-methylpent-4-ynal (35)

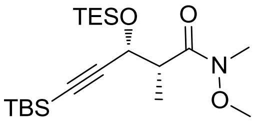


**35**

Weinreb amide **S39** (100 mg, 0.3 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (4 ml) and the solution was cooled to -78 °C. DIBAL-H (0.42 ml, *c* = 1.2 mol/l in toluene, 0.5 mmol, 2.0 eq) was added and stirring was continued for 1 h at -78 °C. More DIBAL-H (0.1 ml, *c* = 1.2 mol/l in toluene, 0.1 mmol, 0.5 eq) was added and the solution was stirred for 1 h. The reaction was terminated by addition of ethyl acetate and the mixture was warmed up to rt. Then, aq. Na-K-tartrate was added and the mixture was stirred for 2 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Aldehyde **35** was used in the next step without further purification.

R$_f$ = 0.82 (PE:EE = 2:1).

### (2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-*N*-methoxy-*N*,2-dimethyl-3-(triethylsilyloxy)pent-4-ynamide (S40)

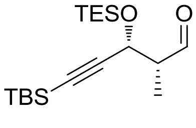


**S40**

Alcohol **S38** (150 mg, 0.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (10 ml) and cooled to -78 °C. 2,6-Lutidine (0.25 ml, 2.1 mmol, 4.0 eq) was added and after 5 min TESOTf (0.24 ml, 1.1 mmol, 2.0 eq). The solution was stirred for 2.5 h at -78 °C. The reaction was terminated by addition of aq. $NaHCO_3$ and warmed to rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 2:1) to furnish Weinreb amide **S40** (104 mg, 0.3 mmol, 50%) as a colourless oil.

R$_f$ = 0.48 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +65.0 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.47 (d, 1H, *J* = 9.6 Hz, H-3), 3.72 (s, 3H, H-8), 3.14-3.22 (m, 4H, H-2 + H-7), 1.20 (d, 3H, *J* = 6.8 Hz, H-6), 0.98 (t, 9H, *J* = 8.0 Hz, TES), 0.89 (s, 9H, TBS), 0.57-0.76 (m, 6H, TES), 0.05 (s, 3H, TBS), 0.05 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.9 (q, C-1), 107.2 (q, C-4), 87.4 (q, C-5), 64.9 (t, C-3), 61.7 (p, C-8), 43.9 (t, C-2), 32.1 (p, C-7), 26.1 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-6), 6.9 (p, TES), 4.9 (s, TES), -4.6 (p, TBS), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{42}NO_3Si_2$: 400.2703 $[M + Na]^+$, found: 400.711 $[M + Na]^+$.

### (2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-2-methyl-3-(triethylsilyloxy)pent-4-ynal (36)



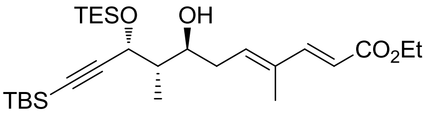
**36**

Weinreb amide **S40** (50 mg, 130 µmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (2.0 ml) and cooled to -78 °C. DIBAL-H (0.3 ml, *c* = 1.2 mol/l in toluene, 0.4 mmol, 2.5 eq) was added and the mixture was stirred for 4 h at -78 °C. The reaction was terminated by addition of ethyl acetate and after addition of Na-K-tartrate stirred 3 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash

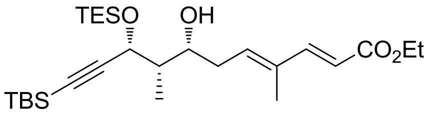
chromatography (petroleum ether : ethyl acetate = 30:1) to furnish aldehyde **36** (33 mg, 0.1 mmol, 77%) as a colourless liquid, which was used immediately in the next step.
$R_f$ = 0.85 (PE:EE = 2:1).

**(2*E*,4*E*,7*R*,8*S*,9*R*)-Ethyl-11-(*tert*-butyldimethylsilyl)-9-(triethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (**7,8-*syn*,8,9-*syn* **41a)** and

**(2*E*,4*E*,7*S*,8*S*,9*R*)-ethyl-11-(*tert*-butyldimethylsilyl)-9-(triethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (**7,8-*anti*,8,9-*syn* **41b)**



7,8-*anti*,8,9-*syn* **41b**



7,8-*syn*,8,9-*syn* **41a**

Following the general procedure, aldehyde **36** (38 mg, 0.11 mmol, 1.0 eq) was reacted with ester **6** (37 mg, 0.24 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols 7,8-*syn*,8,9-*syn* **41a** and 7,8-*anti*,8,9-*syn* **41b** (*d.r.*: 1:1, 30 mg, 0.06 μmol, 55%) as a colourless liquid.

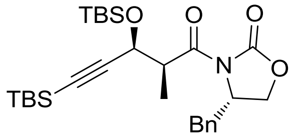
$R_f$ = 0.31 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{27}H_{50}NaO_4Si_2$: 517.3145 $[M + Na]^+$, found: 517.3134 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **41a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.93 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.53 (d, 1H, *J* = 3.8 Hz, H-9), 4.20 (q, 4H, *J* = 7.1 Hz, H-14), 4.03-4.09 (m, 1H, H-7), 3.02 (s, 1H, O*H*), 2.42-2.53 (m, 2H, H-$6_a$), 2.29-2.41 (m, 2H, H-$6_b$), 1.80 (s, 6H, H-12), 1.68-1.76 (m, 1H, H-8), 1.30 (t, 6H, *J* = 7.1 Hz, H-15), 1.07 (d, 3H, *J* = 7.2 Hz, H-13), 0.98 (t, 9H, *J* = 8.0 Hz, TES), 0.93 (s, 18H, TBS), 0.59-0.76 (m, 12H, TES), 0.10 (s, 12H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 138.0 (t, C-5), 134.6 (q, C-4), 116.2 (t, C-2), 106.5 (q, C-10), 89.5 (q, C-11), 73.3 (t, C-7), 67.9 (t, C-9), 60.3 (s, C-14), 43.4 (t, C-8), 34.5 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 7.6 (p, C-13), 6.9 (p, TES), 5.0 (s, TES), -4.6 (p, TBS) ppm.

7,8-*anti*,8,9-*syn* **41b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.37 (d, 1H, *J* = 15.7 Hz, H-3), 6.10 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.59 (d, 1H, *J* = 3.8 Hz, H-9), 4.20 (q, 4H, *J* = 7.1 Hz, H-14), 3.97-4.03 (m, 1H, H-7), 3.97 (s, 1H, O*H*), 2.42-2.53 (m, 2H, H-$6_a$), 2.29-2.41 (m, 2H, H-$6_b$), 1.80-1.90 (m, 1H, H-8), 1.80 (s, 6H, H-12), 1.30 (t, 6H, *J* = 7.1 Hz, H-15), 0.98 (t, 9H, *J* = 7.9 Hz, TES), 0.93 (s, 18H, TBS), 0.91

(d, 3H, *J* = 7.2 Hz, H-13), 0.59-0.76 (m, 12H, TES), 0.10 (s, 12H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.7 (t, C-3), 138.2 (t, C-5), 134.4 (q, C-4), 115.8 (t, C-2), 104.9 (q, C-10), 89.9 (q, C-11), 73.3 (t, C-7), 68.3 (t, C-9), 60.3 (s, C-14), 43.6 (t, C-8), 34.5 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 13.1 (p, C-13), 12.6 (p, C-12), 6.9 (p, TES), 4.79 (s, TES), -4.7 (p, TBS) ppm.

### (*S*)-9-Benzyl-3-[(2*S*,3*S*)-5-(*tert*-butyldimethylsilyl)-3-(*tert*-butyldimethylsilyloxy)-2-methylpent-4-ynoyl]oxazolidin-2-one (S41)

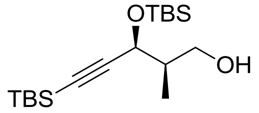


**S41**

Alcohol **S35** (8.2 g, 20 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (300 ml) and cooled to 0 °C. 2,6-Lutidine (11.7 ml, 101 mmol, 5.0 eq) and TBSOTf (11.6 ml, 50 mmol, 2.5 eq) were added and the mixture was stirred for 2 h at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish product **S41** (10.0 g, 19 mmol, 95%) as a colourless solid.

$R_f$ = 0.67 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +22.3 (*c* = 1.0, $CHCl_3$); m.p.: 91 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.28-7.42 (m, 3H, Ph), 7.16-7.22 (m, 2H, Ph), 4.58-4.65 (m, 1H, H-9), 4.58 (d, 1H, *J* = 7.9 Hz, H-3), 4.05-4.20 (m, 3H, H-2 + H-8), 3.27 (dd, 1H, *J* = 13.5, 3.2 Hz, H-$10_a$), 2.80 (dd, 1H, *J* = 13.5, 9.4 Hz, H-$10_b$), 1.31 (d, 3H, *J* = 7.2 Hz, H-6), 0.90 (s, 9H, TBS), 0.90 (s, 9H, TBS), 0.15 (s, 3H, TBS), 0.11 (s, 3H, TBS), 0.07 (s, 3H, TBS), 0.07 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.0 (q, C-1), 153.1 (q, C-7), 135.4 (q, Ph), 129.6 (t, Ph), 129.1 (t, Ph), 127.5 (t, Ph), 106.4 (q, C-4), 88.2 (q, C-5), 66.2 (s, C-8), 64.9 (t, C-3), 55.7 (t, C-9), 45.5 (p, C-2), 37.9 (s, C-10), 26.2 (p, TBS), 25.8 (p, TBS), 18.4 (q, TBS), 16.6 (q, TBS), 13.7 (p, C-6), -4.4 (p, TBS), -4.7 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{28}H_{45}NNaO_4Si_2$: 538.2785 $[M + Na]^+$, found: 538.2786 $[M + Na]^+$.

### (2*R*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(*tert*-butyldimethylsilyloxy)-2-methylpent-4-yn-1-ol (S42)

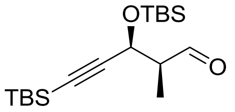


**S42**

Alcohol **S41** (1.2 g, 2.3 mmol, 1.0 eq) was dissolved in $Et_2O$ (46 ml), cooled to 0 °C and $H_2O$ (0.04 ml, 2.3 mmol, 1.0 eq) added. $LiBH_4$ (250 mg, 11.5 mmol, 5.0 eq) was added. The solution was stirred for 2 h at 0 °C and overnight at rt. The reaction was terminated by addition of aq. $NH_4Cl$ and stirring was continued for 3 h. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish alcohol **S42** (591 mg, 1.7 mmol, 75%) as a colourless liquid.

$R_f$ = 0.58 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -45.5 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.49 (d, 1H, *J* = 4.4 Hz, H-3), 3.81-3.88 (m, 1H, H-$1_a$), 3.52-3.59 (m, 1H, H-$1_b$), 2.72 (brs, 1H, OH), 1.98-2.09 (m, 1H, H-2), 0.93 (s, 9H, TBS), 0.92 (d, 3H, *J* = 7.2 Hz, H-6), 0.90 (s, 9H, TBS), 0.16 (s, 3H, TBS), 0.13 (s, 3H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 105.7 (q, C-4), 89.4 (q, C-5), 67.9 (t, C-3), 65.9 (s, C-1), 41.4 (t, C-2), 26.2 (p, TBS), 25.8 (p, TBS), 18.2 (q, TBS), 16.6 (q, TBS), 12.8 (p, C-6), -4.4 (p, TBS), -4.6 (p, TBS), -5.1 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{18}H_{38}NaO_2Si_2$: 365.2308 $[M + Na]^+$, found: 365.2305 $[M + Na]^+$.

### (2*S*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(*tert*-butyldimethylsilyloxy)-2-methylpent-4-ynal (37)

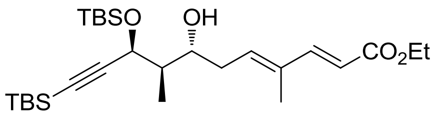


**37**

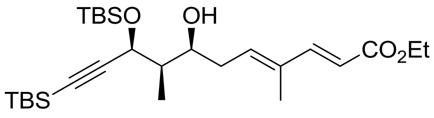
Alcohol **S42** (478 mg, 1.4 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (28 ml) and $NaHCO_3$ (100 mg) was added. DESS-MARTIN periodinane (890 mg, 2.1 mmol, 1.5 eq) was added and the reaction mixture was stirred for 1 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 1.5 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **37** (416 mg, 1.2 mg, 87%) as a colourless liquid.

$R_f$ = 0.56 (PE:EE = 20:1); $[\alpha]_D^{20}$ = -33.2 ($c$ = 0.4 in $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.79 (d, 1H, $J$ = 1.4 Hz, H-1), 4.71 (d, 1H, $J$ = 4.4 Hz, H-3), 2.50-2.58 (m, 1H, H-2), 1.19 (d, 3H, $J$ = 6.8 Hz, H-6), 0.93 (s, 9H, TBS), 0.88 (s, 9H, TBS), 0.16 (s, 3H, TBS), 0.12 (s, 3H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 203.7 (t, C-1), 105.3 (q, C-4), 89.9 (q, C-5), 63.8 (t, C-3), 52.6 (t, C-2), 26.2 (p, TBS), 25.8 (p, TBS), 18.3 (q, TBS), 16.6 (q, TBS), 9.3 (p, C-6), -4.3 (p, TBS), -4.7 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): $m/z$: calculated for $C_{18}H_{36}NaO_2Si_2$: 363.2152 $[M + Na]^+$, found: 363.2148 $[M + Na]^+$.

**(2*E*,4*E*,7*S*,8*R*,9*S*)-Ethyl-11-(*tert*-butyldimethylsilyl)-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (**7,8-*syn*,8,9-*syn* **42a)** and **(2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-11-(*tert*-butyldimethylsilyl)-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (**7,8-*anti*,8,9-*syn* **42b)**



7,8-*anti*,8,9-*syn* **42b**



7,8-*syn*,8,9-*syn* **42a**

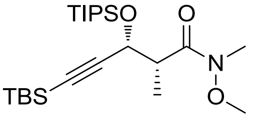
Following the general procedure, aldehyde **37** (401 mg, 1.2 mmol, 1.0 eq) was reacted with ester **6** (364 mg, 2.36 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) and to furnish alcohols 7,8-*syn*,8,9-*syn* **42a** and 7,8-*anti*,8,9-*syn* **42b** [*d.r.*: 3.4:1 (**42b**:**42a**), 466 mg, 0.94 mmol, 80%] as a colourless oil.

$R_f$ = 0.38 (PE:EE = 10:1); **HRMS** (ESI): $m/z$: calculated for $C_{27}H_{50}NaO_4Si_2$: 517.3145 $[M + Na]^+$, found: 517.3140 $[M + Na]^+$.

7,8-*anti*,8,9-*syn* **42b**: $[\alpha]_D^{20}$ = -8.0 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.37 (d, 1H, $J$ = 15.7 Hz, H-3), 6.09 (dd, 1H, $J$ = 7.2, 5.8 Hz, H-5), 5.79 (d, 1H, $J$ = 15.7 Hz, H-2), 4.58 (d, 1H, $J$ = 3.4 Hz, H-9), 4.20 (q, 2H, $J$ = 7.1 Hz, H-14), 3.95-4.01 (m, 1H, H-7), 3.81 (d, 1H, $J$ = 1.7 Hz, OH), 2.47 (ddd, 1H, $J$ = 15.5, 5.8, 4.7 Hz, H-$6_a$), 2.36 (ddd, 1H, $J$ = 15.5, 7.6, 7.2 Hz, H-$6_b$), 1.77-1.88 (m, 1H, H-8), 1.79 (s, 3H, H-12), 1.29 (t, 3H, $J$ = 7.1 Hz, H-15), 0.91-0.95 (m, 12H, TBS + H-13), 0.90 (s, 9H, TBS), 0.18 (s, 3H, TBS), 0.14 (s, 3H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.6 (t, C-3), 138.1 (t, C-5), 134.4 (q, C-4), 115.8 (t, C-2), 105.1 (q, C10), 90.0 (q, C-11), 73.2 (t, C-7), 68.3 (t, C-9), 60.3 (s, C-14), 43.7 (t, C-8), 34.3 (s, C-6), 26.2 (p, TBS), 25.8 (p, TBS), 18.2 (q, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.9 (p, C-13), 12.6 (p, C-12), -4.4 (p, TBS), -4.6 (p, TBS), -5.1 (p, TBS) ppm.

7,8-*syn*,8,9-*syn* **42a**: Isolated as a mixture with 7,8-*anti*,8,9-*syn* **42b**; **$^1$H-NMR** (500 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 16.1 Hz, H-3), 5.92 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 16.1 Hz, H-2), 4.49 (d, 1H, *J* = 4.2 Hz, H-9), 4.20 (q, 2H, *J* = 7.1 Hz, H-14), 4.03-4.09 (m, 1H, H-7), 2.89 (s, 1H, OH), 2.42-2.51 (m, 1H, H-$6_a$), 2.30-2.40 (m, 1H, H-$6_b$), 1.80 (s, 3H, H-12), 1.68-1.77 (m, 1H, H-8), 1.30 (t, 3H, *J* = 7.1 Hz, H-15), 1.06 (d, 3H, *J* = 7.1 Hz, H-13), 0.93 (s, 9H, TBS), 0.90 (s, 9H, TBS), 0.14 (s, 6H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (125 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 138.0 (t, C-5), 134.6 (q, C-4), 116.2 (t, C-2), 106.6 (q, C10), 89.7 (q, C-11), 73.1 (t, C-7), 67.9 (t, C-9), 60.6 (s, C-14), 43.4 (s, C-6), 26.2 (p, TBS), 25.8 (p, TBS), 18.2 (q, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 7.8 (p, C-13), -4.1 (p, TBS), -4.4 (p, TBS), -4.9 (p, TBS) ppm.

### (2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-*N*-methoxy-*N*,2-dimethyl-3-(triisopropylsilyloxy)-pent-4-ynamide (S43)

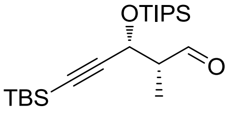


**S43**

Alcohol **S38** (150 mg, 0.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7 ml) and cooled to -78 °C. 2,6-Lutidine (0.24 ml, 2.1 mmol, 4.0 eq) was added and after 5 min TIPSOTf (0.28 ml, 1.1 mmol, 2.0 eq). The solution was stirred for 3 h at -78 °C. The reaction was terminated by addition of aq. $NaHCO_3$ and warmed to rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish Weinreb amide **S43** (229 mg, 0.5 mmol, 99%) as a colourless liquid.

$R_f$ = 0.51 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +44.3 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.63 (d, 1H, *J* = 8.9 Hz, H-3), 3.73 (s, 3H, H-8), 3.14-3.23 (m, 4H, H-2 + H-7), 1.24 (d, 3H, *J* = 6.8 Hz, C-6), 1.13-1.23 (m, 3H, TIPS), 1.06-1.12 (m, 18H, TIPS), 0.89 (s, 9H, TBS), 0.05 (s, 3H, TBS), 0.04 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.9 (q, C-1), 107.6 (q, C-4), 87.7 (q, C-5), 65.2 (t, C-3), 61.7 (p, C-8), 44.4 (t, C-2), 32.1 (p, C-7), 26.1 (p, TBS), 18.3 (p, TIPS), 18.3 (p, TIPS), 16.6 (q, TBS), 14.5 (p, C-6), 12.5 (t, TIPS), -4.6 (p, TBS), -4.7 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{23}H_{48}NO_3Si_2$ and $C_{23}H_{47}NNaO_3Si_2$: 442.3173 $[M + H]^+$ and 464.2992 $[M + Na]^+$, found: 442.3181 $[M + H]^+$ and 464.3003 $[M + Na]^+$.

### (2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-2-methyl-3-(triisopropylsilyloxy)pent-4-ynal (38)

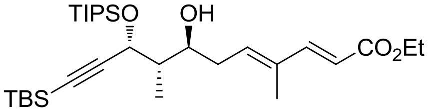


**38**

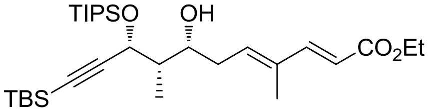
Weinreb amide **S43** (114 mg, 0.3 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (4.0 ml) and cooled to -78 °C. DIBAL-H (1.3 ml, *c* = 1.2 mol/l in toluene, 1.5 mmol, 6.0 eq.) was slowly added and stirred for 4 h at -78 °C. The reaction was terminated by addition of ethyl acetate and after the addition of Na-K-tartrate stirring was continued overnight. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 20:1) to furnish aldehyde **38** (46 mg, 120 µmol, 47%) as a colourless liquid, which was used immediately in the next step.

$R_f$ = 0.70 (PE:EE = 20:1).

### (2*E*,4*E*,7*R*,8*S*,9*R*)-Ethyl-11-(*tert*-butyl-dimethylsilyl)-7-hydroxy-4,8-dimethyl-9-(triisopropylsilyloxy)undeca-2,4-dien-10-ynoate (7,8-*syn*,8,9-*syn* 43a) and (2*E*,4*E*,7*S*,8*S*,9*R*)-Ethyl-11-(*tert*-butyldimethylsilyl)-7-hydroxy-4,8-dimethyl-9-(triisopropylsilyloxy)undeca-2,4-dien-10-ynoate (7,8-*anti*,8,9-*syn* 43b)



7,8-*anti*,8,9-*syn* **43b**



7,8-*syn*,8,9-*syn* **43a**

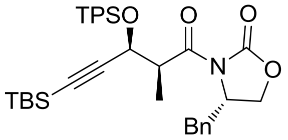
Following the general procedure, aldehyde **38** (23 mg, 60 µmol, 1.0 eq) was reacted with ester **6** (19 mg, 120 µmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 50:1 → 20:1) to furnish alcohols 7,8-*syn*,8,9-*syn* **43a** and 7,8-*anti*,8,9-*syn* **43b** [*d.r.*: 2:1 (**43b**:**43a**), 14 mg, 25 µmol, 43%] as a colourless liquid.

$R_f$ = 0.36 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{30}H_{56}NaO_4Si_2$: 559.3615 [M + Na]$^+$, found: 559.3608 [M + Na]$^+$.

7,8-*syn*,8,9-*syn* **43a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.93 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.57 (d, 1H, *J* = 3.8 Hz, H-9), 4.20 (q, 2H, *J* = 7.2 Hz, H-14), 4.14-4.20 (m, 1H, H-7), 2.90 (s, 1H, OH), 2.44-2.53 (m, 1H, H-6$_a$), 2.28-2.41 (m, 1H, H-6$_b$), 1.80 (s, 3H, H-12), 1.73-1.79 (m, 1H, H-8), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 1.12-1.22 (m, 3H, TIPS), 1.05-1.12 (m, 21H, TIPS + H-13), 0.93 (s, 9H, TBS), 0.10 (s, 6H, TBS) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): 167.6 (q, C-1), 149.4 (t, C-3), 138.1 (t, C-5), 134.6 (q, C-4), 116.1 (t, C-2), 106.9 (q, C10), 89.8 (q, C-11), 72.2 (t, C-7), 67.7 (t, C-9), 60.3 (s, C-14), 43.8 (t, C-8), 34.5 (s, C-6), 26.2 (p, TBS), 18.2 (p, TIPS), 16.6 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 12.5 (t, TIPS), 8.4 (p, C-13), -4.7 (p, TBS) ppm.

7,8-*anti*,8,9-*syn* **43b**: $^{1}$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.37 (d, 1H, *J* = 15.7 Hz, H-3), 6.12 (dd, 1H, *J* = 6.8, 6.8 Hz, H-5), 5.79 (d, 1H, *J* = 15.7 Hz, H-2), 4.66 (d, 1H, *J* = 3.4 Hz, H-9), 4.20 (q, 2H, *J* = 7.2 Hz, H-14), 4.03-4.10 (m, 1H, H-7), 3.17 (s, 1H, OH), 2.44-2.53 (m, 1H, $H\text{-}6_a$), 2.28-2.41 (m, 1H, $H\text{-}6_b$), 1.85-1.96 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 1.12-1.22 (m, 3H, TIPS), 1.05-1.12 (m, 18H, TIPS), 0.92-0.95 (m, 12H, TBS + H-13), 0.10 (s, 6H, TBS) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.7 (t, C-3), 138.3 (t, C-5), 134.3 (q, C-4), 115.8 (t, C-2), 104.8 (q, C10), 90.2 (q, C-11), 73.3 (t, C-7), 69.3 (t, C-9), 60.3 (s, C-14), 43.8 (t, C-8), 34.3 (s, C-6), 26.2 (p, TBS), 18.1 (p, TIPS), 16.6 (q, TBS), 14.5 (p, C-15), 13.4 (p, C-13), 12.5 (p, C-12), 12.2 (t, TIPS), -4.6 (p, TBS) ppm.

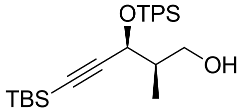
### (*S*)-9-Benzyl-3-[(2*S*,3*S*)-5-(*tert*-butyldimethylsilyl)-3-(triphenylsilyloxy)-2-methylpent-4-ynoyl]oxazolidin-2-one (S44)



**S44**

EVANS aldol product **S35** (300 mg, 0.9 mmol, 1.0 eq) was dissolved in DMF (3.8 ml) and imidazole (201 mg, 3.0 mmol, 3.2 eq) was added. TPSCl (353 mg, 1.2 mmol, 1.3 eq) was added and the slurry was stirred for 4 d. Additional TPSCl (177 mg, 0.6 mmol, 0.7 eq) and imidazole (100 mg, 1.5 mmol, 1.6 eq) were added and the reaction mixture was stirred overnight. The reaction was diluted with $Et_2O$. The organic layer was washed with aq. HCl (*c* = 1 mol/l) and aq. NaCl, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 50:1 → 10:1) to furnish product **S44** (544 mg, 0.8 mmol, 90%) as a colourless oil.[S8] $R_f$ = 0.60 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -3.5 (*c* = 1.0, $CHCl_3$); $^{1}$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.62-7.69 (m, 8H, Ph), 7.24-7.50 (m, 10H, Ph), 7.14-7.18 (m, 2H, Ph), 4.82 (d, 1H, *J* = 6.6 Hz, H-3), 4.34-4.41 (m, 1H, H-9), 4.18 (dq, 1H, *J* = 6.7, 6.6 Hz, H-2), 4.04 (dd, 1H, *J* = 8.6, 2.0 Hz, $H\text{-}8_a$), 3.85 (dd, 1H, *J* = 8.6, 8.4 Hz, $H\text{-}8_b$), 3.22 (dd, 1H, *J* = 13.4, 2.9 Hz, H-10$_a$), 2.73 (dd, 1H, *J* = 13.4, 9.6 Hz, H-10$_b$), 1.40 (d, 3H, *J* = 6.7 Hz, H-6), 0.86 (s, 9H, TBS), -0.03 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 173.5 (q, C-1), 153.1 (q, C-7), 127.5-135.9 (t+q, Ph), 105.3 (C-4), 89.5 (q, C-5), 66.1 (s, C-8), 65.5 (t, C-3), 55.5 (t, C-9), 45.4 (C-2), 37.8 (s, C-10), 26.2 (p, TBS), 16.5 (q, TBS), 13.1 (p, C-6), -4.8 (p, TBS), -4.8 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{42}H_{44}NNaO_4Si_2$: 682.2785 $[M + Na]^+$, found: 682.2798 $[M + Na]^+$.

### (2*R*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(triphenylsilyloxy)-2-methylpent-4-yn-1-ol (S45)

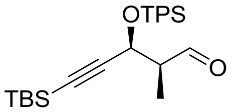


**S45**

EVANS aldol product **S44** (530 mg, 0.8 mmol, 1.0 eq) was dissolved in $Et_2O$ (18 ml), cooled to 0 °C and $H_2O$ (0.02 ml, 0.8 mmol, 1.0 eq) was added. $LiBH_4$ (36 mg, 1.6 mmol, 2.0 eq) was added and the reaction mixture was stirred for 1 h at 0 °C and then for 75 min at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 2:1) and furnished alcohol **S45** (331 mg, 0.7 mmol, 85%) as a colourless liquid.

$R_f$ = 0.51 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -55.3 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.63-7.70 (m, 6H, Ph), 7.34-7.49 (m, 9H, Ph), 4.58 (d, 1H, *J* = 4.1 Hz, H-3), 3.87 (ddd, 1H, *J* = 11.2, 7.6, 3.8 Hz, H-1$_a$), 3.61 (ddd, 1H, *J* = 11.2, 7.3, 4.1 Hz, H1$_b$), 2.23-2.30 (m, 1H, OH), 2.03-2.13 (m, 1H, H-2), 0.94 (d, 3H, *J* = 6.8 Hz, H-6), 0.87 (s, 9H, TBS), -0.002 (s, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 127.8-135.3 (q+t, Ph), 105.2 (q, C-4), 90.2 (q, C-5), 68.0 (t, C-3), 65.4 (s, C-1), 41.9 (t, C-2), 26.2 (p, TBS), 16.6 (q, TBS), 12.8 (p, C-6), -4.7 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{30}H_{38}NaO_2Si_2$: 509.2308 $[M + Na]^+$, found: 509.2298 $[M + Na]^+$.

### (2*S*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(triphenylsilyloxy)-2-methylpent-4-ynal (39)



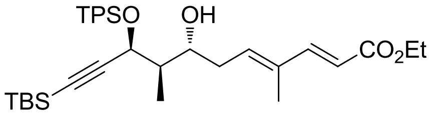
**39**

Alcohol **S45** (75 mg, 150 µmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (3 ml) and $NaHCO_3$ (10 mg) was added. DESS-MARTIN periodinane (98 mg, 230 µmol, 1.5 eq) was added und the mixture was stirred for 2 h at rt. The reaction was terminated by addition of aq. $NaHCO_3/Na_2SO_3$ and the solution was stirred for 75 min. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 10:1) to furnish aldehyde **39** (59 mg, 120 µmol, 80%) as a colourless liquid.

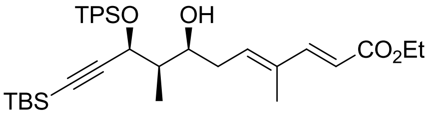
$R_f$ = 0.67 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -60.4 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.88 (d, 1H, *J* = 1.0 Hz, H-1), 7.62-7.67 (m, 6H, TPS), 7.41-7.49 (m, 3H, TPS), 7.34-7.41 (m, 6H, TPS), 4.76 (d, 1H, *J* = 4.4 Hz, H-3), 2.56-2.65 (m, 1H, H-2), 1.20 (d, 3H, *J* = 7.2 Hz, H-6), 0.86 (s, 9H, TBS), -0.02 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 203.5 (t, C-1), 127.8-135.7 (q+t, TPS), 104.1 (q, C-4), 91.2 (q, C-5), 65.0 (t, C-3), 52.6 (t, C-2), 26.1 (p, TBS), 16.5 (q, TBS), 9.7 (p, C-6), -4.8 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{30}H_{36}NaO_2Si_2$: 507.2152 $[M + Na]^+$, found: 507.2165 $[M + Na]^+$.

**(2*E*,4*E*,7*S*,8*R*,9*S*)-Ethyl-11-(*tert*-butyldimethylsilyl)-9-(triphenylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (**7,8-*syn*,8,9-*syn* **44a)** and

**(2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-11-(*tert*-butyldimethylsilyl)-9-(triphenylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (**7,8-*anti*,8,9-*syn* **44b)**



7,8-*anti*,8,9-*syn* **44b**



7,8-*syn*,8,9-*syn* **44a**

Following the general procedure, aldehyde **39** (40 mg, 80 µmol, 1.0 eq) was reacted with ester **6** (25 mg, 160 µmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols 7,8-*anti*,8,9-*syn* **44b** and 7,8-*syn*,8,9-*syn* **44a** [*d.r.*: 2.2:1 (**44b**:**44a**), 40 mg, 62 µmol, 78%] as a colourless liquid.

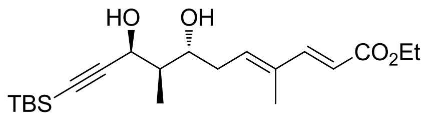
$R_f$ = 0.26 (PE:EE = 2:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{39}H_{50}NaO_4Si_2$: 661.3145 $[M + Na]^+$, found: 661.3143 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **44a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.61-7.69 (m, 6H, TPS), 7.32-7.48 (m, 10H, TPS + H-3), 5.88 (dd, 1H, *J* = 7.5, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.49 (d, 1H, *J* = 4.4 Hz, H-9), 4.26-4.33 (m, 1H, H-7), 4.22 (q, 2H, *J* = 7.3 Hz, H-14), 2.65 (d, 1H, *J* = 2.1 Hz, OH), 2.42-2.52 (m, 1H, $H\text{-}6_a$), 2.26-2.39 (m, 1H, $H\text{-}6_b$), 1.76 (s, 4H, H-12 + H-8), 1.31 (t, 3H, *J* = 7.3 Hz, H-15), 1.03 (d, 3H, *J* = 6.8 Hz, H-13), 0.86 (s, 9H, TBS), -0.02 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ =

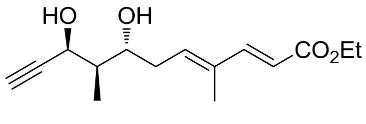
77.16 ppm): δ 167.6 (q, C-1), 149.4 (t, C-3), 137.9 (t, C-5), 135.7 (t, TPS), 134.7 (q, C-4), 133.8 (q, TPS), 130.4 (t, TPS), 128.1 (t, TPS), 116.2 (t, C-2), 106.1 (q, C-10), 91.1 (q, C-11), 71.5 (t, C-7), 67.9 (t, C-9), 60.3 (s, C-14), 43.6 (t, C-8), 34.4 (s, C-6), 26.1 (p, TBS), 16.5 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 9.0 (p, C-13), -4.7 (p, TBS), -4.8 (p, TBS) ppm.

7,8-*anti*,8,9-*syn* **44b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.61-7.69 (m, 6H, TPS), 7.32-7.48 (m, 10H, TPS + H-3), 6.02 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.70 (d, 1H, *J* = 3.4 Hz, H-9), 4.22 (q, 2H, *J* = 7.3 Hz, H-14), 3.93-4.00 (m, 1H, H-7), 3.19 (d, 1H, *J* = 2.7 Hz, OH), 2.42-2.52 (m, 1H, H-6$_a$), 2.26-2.39 (m, 1H, H-6$_b$), 1.80-1.89 (m, 1H, H-8), 1.76 (s, 3H, H-12), 1.31 (t, 3H, *J* = 7.3 Hz, H-15), 0.93 (d, 3H, *J* = 6.8 Hz, H-13), 0.87 (s, 9H, TBS), -0.01 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.6 (t, C-3), 138.0 (t, C-5), 135.1 (t, TPS), 134.5 (q, C-4), 133.5 (q, TPS), 130.3 (t, TPS), 128.1 (t, TPS), 115.9 (t, C-2), 104.8 (q, C-10), 90.6 (q, C-11), 72.8 (t, C-7), 68.4 (t, C-9), 60.3 (s, C-14), 44.2 (t, C-8), 34.2 (s, C-6), 26.1 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.7 (p, C-13), 12.5 (p, C-12), -4.7 (p, TBS) ppm.

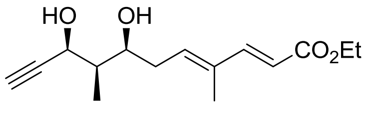
**(2*E*,4*E*,7*R*,8*R*,9*S*)-Ethyl-11-(*tert*-butyldimethylsilyl)-7,9-dihydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (**7,8-*anti*,8,9-*syn* **S46b),**
**(2*E*,4*E*,7*S*,8*R*,9*S*)-ethyl-7,9-dihydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate**
**(**7,8-*syn*,8,9-*syn* **45a)** and
**(2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-7,9-dihydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate**
**(**7,8-*anti*,8,9-*syn* **45b)**



7,8-*anti*,8,9-*syn* **S46b**



7,8-*anti*,8,9-*syn* **45b**



7,8-*syn*,8,9-*syn* **45a**

A mixture of alcohols **42** [*d.r.*: 3.4:1 (**42b**:**42a**), 80 mg, 0.16 mmol, 1.0 eq] was dissolved in THF (3 ml) and cooled to 0 °C. TBAF·3$H_2O$ (102 mg, 0.32 mmol, 2.0 eq) was dissolved in THF (2 ml) and added to the first solution. The reaction mixture was stirred for 2 h and the reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 2:1) to furnish diols 7,8-*anti*,8,9-*syn* **S46b** [42 mg, 0.11 mmol, 69% (92% referring to the 7,8-*anti*,8,9-*syn*-diastereomer)] and 7,8-*anti*,8,9-*syn* **45b** and 7,8-*syn*,8,9-*syn* **45a** (~1:1, 7 mg, 0.03 mmol, 17%) as colourless liquids.

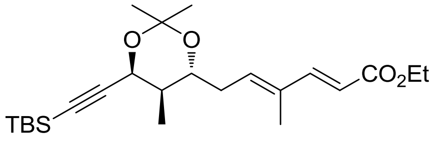
7,8-*anti*,8,9-*syn* **S46b**: $R_f$ = 0.5 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -3.3 ($c$ = 1.0 in $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, $J$ = 15.7 Hz, H-3), 6.00 (dd, 1H, $J$ = 7.6, 6.6 Hz, H-5), 5.82 (d, 1H, $J$ = 15.7 Hz, H-2), 4.55 (dd, 1H, $J$ = 6.0, 2.9 Hz, H-9), 4.21 (q, 2H, $J$ = 7.2 Hz, H-14), 3.93-4.01 (m, 1H, H-7), 3.45-3.60 (m, 1H, $OH_{C9}$), 2.73-2.83 (m, 1H, $OH_{C7}$), 2.50 (ddd, 1H, $J$ = 15.5, 6.6, 4.4 Hz, H-$6_a$), 2.42 (ddd, 1H, $J$ = 15.5, 7.9, 7.6 Hz, H-$6_b$), 1.87-1.98 (m, 1H, H-8), 1.81 (s, 3H, H-12), 1.30 (t, 3H, $J$ = 7.2 Hz, H-15), 0.98 (d, 3H, $J$ = 7.2 Hz, H-13), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.2 (t, C-3), 136.8 (t, C-5), 135.6 (q, C-4), 116.5 (t, C-2), 105.5 (q, C-10), 89.3 (q, C-11), 74.2 (t, C-7), 67.1 (t, C-9), 60.5 (s, C-14), 43.0 (t, C-8), 34.9 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.4 (p, C-15), 13.3 (p, C-13), 12.6 (p, C-12), -4.5 (p, TBS), -4.5 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{21}H_{36}NaO_3Si$: 403.2281 $[M + Na]^+$, found: 403.2269 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **45a** and 7,8-*anti*,8,9-*syn* **45b**: $R_f$ = 0.23 (PE:EE = 2:1); the diastereomers could not be separated; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_{22}NaO_4$: 289.1416 $[M + Na]^+$, found: 289.1407 $[M + Na]^+$.

7,8-*syn*,8,9-*syn* **45a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, $J$ = 15.7 Hz, H-3), 5.90 (dd, 1H, $J$ = 7.3, 7.3 Hz, H-5), 5.83 (d, 1H, $J$ = 15.7 Hz, H-2), 4.60 (dd, 1H, $J$ = 3.6, 2.3 Hz, H-9), 4.21 (q, 2H, $J$ = 7.2 Hz, H-14), 4.07 (ddd, 1H, $J$ = 7.2, 6.5, 1.4 Hz, H-7), 2.53 (d, 1H, $J$ = 2.3 Hz, H-11), (m, 2H, H-6), 1.81 (s, 3H, H-12), 1.77-1.83 (m, 1H, H-8), 1.30 (t, 3H, $J$ = 7.2 Hz, H-15), 1.13 (d, 3H, $J$ = 6.8 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.1 (t, C-3), 137.0 (t, C-5), 135.2 (q, C-4), 116.7 (t, C-2), 83.6 (q, C-10), 74.3 (t, C-7), 73.9 (t, C-11), 66.9 (t, C-9), 60.4 (s, C-14), 42.6 (t, C-8), 34.7 (s, C-6), 14.5 (p, C-15), 6.9 (p, C-13), 12.6 (p, C-12) ppm.

7,8-*anti*,8,9-*syn* **45b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.35 (d, 1H, $J$ = 15.7 Hz, H-3), 5.99 (dd, 1H, $J$ = 7.5, 7.5 Hz, H-5), 5.85 (d, 1H, $J$ = 15.7 Hz, H-2), 4.54 (dd, 1H, $J$ = 2.4, 2.2 Hz, H-9), 4.22 (q, 2H, $J$ = 7.2 Hz, H-14), 4.00 (ddd, 1H, $J$ = 8.2, 8.2, 3.8 Hz, H-7), 2.50 (d, 1H, $J$ = 2.2 Hz, H-11), 2.32-2.55 (m, 2H, H-6), 1.91-2.00 (m, 1H, H-8), 1.82 (s, 3H, H-12), 1.30 (t, 3H, $J$ = 7.2 Hz, H-15), 1.00 (d, 3H, $J$ = 7.2 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 148.9 (t, C-3), 136.3 (t, C-5), 136.0 (q, C-4), 116.8 (t, C-2), 83.1 (q, C-10), 74.3 (t, C-7), 73.9 (t, C-11), 66.7 (t, C-9), 60.5 (s, C-14), 42.9 (t, C-8), 35.0 (s, C-6), 14.4 (p, C-15), 13.3 (p, C-13), 12.7 (p, C-12) ppm.

**(2*E*,4*E*,7*R*,8*R*,9*S*)-Acetonide** (7,8-*anti*,8,9-*syn* **S47b**)

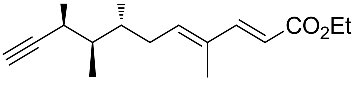


**S47b**

Diol **S46b** (997 mg, 2.6 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (160 ml). 2,2-Dimethoxypropane (32 ml) and PPTS (20 mg, catalytic) were added. The solution was stirred for 2 h at rt. The solvent was removed under reduced pressure and the crude product purified by flash chromatography (petroleum ether : ethyl acetate = 10:1). Acetonide **S47b** (1.0 g, 2.5 mmol, 95%) was obtained as a yellow liquid.

$R_f$ = 0.8 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +22.2 ($c$ = 1.0, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, $J$ = 15.7 Hz, H-3), 6.00 (dd, 1H, $J$ = 7.6, 6.5 Hz, H-5), 5.81 (d, 1H, $J$ = 15.7 Hz, H-2), 4.64 (d, 1H, $J$ = 6.2 Hz, H-9), 4.21 (q, 2H, $J$ = 7.0 Hz, H-14), 3.75 (ddd, 1H, $J$ = 9.5, 7.6, 3.5 Hz, H-7), 2.50 (ddd, 1H, $J$ = 15.9, 6.5, 3.5 Hz, H-$6_a$), 2.35 (ddd, 1H, $J$ = 15.9, 7.6, 7.6 Hz, H-$6_b$), 1.87 (dqd, 1H, $J$ = 9.5, 7.7, 6.2 Hz, H-8), 1.79 (s, 3H, H-12), 1.59 (s, 3H, H-$17_a$), 1.36 (s, 3H, H-$17_b$), 1.30 (t, 3H, $J$ = 7.0 Hz, H-15), 0.95 (d, 3H, $J$ = 7.7 Hz, H-13), 0.94 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 137.5 (t, C-5), 134.4 (q, C-4), 116.0 (q, C-2), 104.4 (q, C-10), 100.5 (q, C-16), 91.4 (q, C-11), 71.7 (t, C-7), 65.4 (t, C-9), 60.4 (s, C-14), 37.6 (t, C-8), 32.7 (s, C-6), 29.1 (p, C-$17_a$), 26.2 (p, TBS), 23.5 (p, C-$17_b$), 16.7 (q, TBS), 14.5 (p, C-13), 13.4 (p, C-15), 12.6 (p, C-12), -4.6 (p, TBS), -4.7 (p, TBS) ppm; **HRMS** (ESI): *m/z*: Compound **S47b** could not be detected by mass spectrometry.

**(2*E*,4*E*,7*R*,8*R*,9*S*)-Acetonide** (7,8-*anti*,8,9-*syn* **46b**)



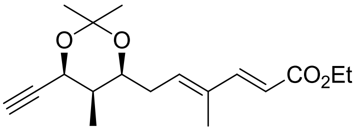
7,8-*anti*,8,9-*syn* **46b**

Acetonide **S47b** (203 mg, 0.48 mmol, 1.0 eq) was dissolved in THF (10 ml) and cooled to 0 °C. A solution of TBAF·3$H_2O$ (259 mg, 0.82 mmol, 1.7 eq) in THF (5 ml) was slowly added and stirring was continued for 25 min at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$.

The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish alkyne **46b** (141 mg, 0.46 mmol, 96%) as a colourless liquid.

$R_f$ = 0.59 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +33.7 (*c* = 1.0, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, *J* = 15.7 Hz, H-3), 5.99 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.66 (dd, 1H, *J* = 5.5, 2.4 Hz, H-9), 4.21 (q, 2H, *J* = 7.1 Hz, H-14), 3.71 (ddd, 1H, *J* = 9.0, 8.0, 3.6 Hz, H-7), 2.51 (d, 1H, *J* = 2.4 Hz, H-11), 2.45-2.54 (m, 1H, H-$6_a$), 2.31-2.40 (m, 1H, H-$6_b$), 1.82-1.93 (m, 1H, H-8), 1.78 (s, 3H, H-12), 1.55 (s, 3H, H-$17_a$), 1.37 (s, 3H, H-$17_b$), 1.30 (t, 3H, *J* = 7.1 Hz, H-15), 0.98 (d, 3H, *J* = 7.2 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 137.3 (t, C-5), 134.4 (q, C-4), 116.1 (t, C-2), 100.8 (q, C-16), 81.6 (q, C-10), 76.2 (t, C-11), 72.0 (t, C-7), 64.3 (t, C-9), 60.4 (s, C-14), 37.8 (t, C-8), 32.8 (s, C-6), 28.4 (p, C-$17_a$), 23.5 (p, C-$17_b$), 14.5 (p, C-15), 13.3 (p, C-13), 12.6 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{18}H_{26}NaO_4$: 329.1729 $[M + Na]^+$, found: 329.1741 $[M + Na]^+$.

**(2*E*,4*E*,7*S*,8*R*,9*S*)-Acetonide** (7,8-*syn*,8,9-*syn* **46a**)

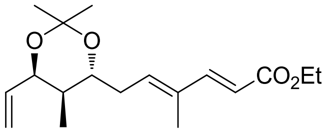


7,8-*syn*,8,9-*syn* **46a**

Diol **45a** (7.3 mg, 27 µmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (1 ml) and 2,2-dimethoxypropane (0.2 ml) was added. Then PPTS (0.5 mg, catalytic) was added and the reaction mixture was stirred for 3 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 3:1 → 10:1). Acetonide **46a** (6.9 mg, 23 µmol, 85%) was obtained as a yellow liquid.

$R_f$ = 0.42 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +18.5 (*c* = 0.6, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.31 (d, 1H, *J* = 15.5 Hz, H-3), 5.81-5.86 (m, 1H, H-5), 5.82 (d, 1H, *J* = 15.5 Hz, H-2), 4.79 (dd, 1H, *J* = 2.2, 2.1 Hz, H-9), 4.21 (q, 2H, *J* = 7.2 Hz, H-14), 3.98 (ddd, 1H, *J* = 7.4, 7.1, 1.7 Hz, H-7), 2.49 (d, 1H, *J* = 2.1 Hz, H-11), 2.43 (ddd, 1H, *J* = 15.0, 7.4, 7.4 Hz, H-$6_a$), 2.31 (ddd, 1H, *J* = 15.0, 7.4, 7.1 Hz, H-$6_b$), 1.80 (s, 3H, H-12), 1.55-1.63 (m, 1H, H-8), 1.46 (s, 3H, H-$17_a$), 1.44 (s, 3H, H-$17_b$), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 1.13 (d, 3H, *J* = 6.8 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.1 (t, C-3), 136.4 (t, C-5), 134.9 (q, C-4), 116.5 (t, C-2), 99.9 (q, C-16), 81.6 (q, C-10), 74.2 (t, C-11), 71.8 (t, C-7), 65.6 (t, C-9), 60.4 (s, C-14), 35.7 (t, C-8), 32.6 (s, C-6), 30.0 (p, C-17$_a$), 19.3 (p, C-17$_b$), 14.5 (p, C-15), 12.6 (p, C-12), 6.4 (p, C-13) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{18}H_{26}NaO_4$: 329.1729 $[M + Na]^+$, found: 329.1745 $[M + Na]^+$.

### **Acetonide** (7,8-*anti*,8,9-*syn* **47b**)

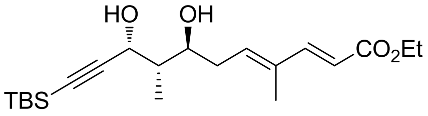


7,8-*anti*,8,9-*syn* **47b**

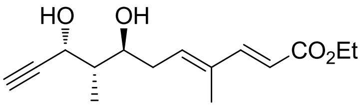
Alkyne **46b** (12.0 mg, 33 µmol, 1 eq) was dissolved in $CH_2Cl_2$ (2.4 ml) and LINDLAR-catalyst (2.5 mg, 5 % Pd, 1 µmol, 3 mol%) was added. The flask was filled with $H_2$ and the solution stirred for 105 min at rt. The mixture was filtered through Celite™ and the solvent removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish alkene **47b** (7.7 mg, 25 µmol, 75%) as a colourless liquid. In addition alkyne **46b** (~3.0 mg, ~1 µmol, 25%) was reisolated.

$R_f$ = 0.64 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -4.0 (*c* = 0.6, $CHCl_3$); $^1$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, *J* = 15.7 Hz, H-3), 5.98 (t, 1H, *J* = 7.0 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 5.79 (ddd, 1H, *J* = 17.2, 10.8, 6.1 Hz, H-10), 5.25 (d, 1H, *J* = 17.2 Hz, H-11$_a$), 5.17 (d, 1H, *J* = 10.8 Hz, H-11$_b$), 4.42 (dd, 1H, *J* = 6.1, 5.6 Hz, H-9), 4.21 (q, 2H, *J* = 7.2 Hz, H-14), 3.40 (td, 1H, *J* = 7.9, 4.1 Hz, H-7), 2.35-2.52 (m, 2H, H-6), 1.78 (s, 4H, H-12), 1.71-1.77 (m, 1H, H-8), 1.36 (s, 6H, H-17), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 0.84 (d, 3H, *J* = 6.8 Hz, H-13) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CHCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 138.0 (t, C-5), 135.8 (t, C-10), 134.3 (q, C-4), 116.1 (t, C-2), 115.9 (s, C-11), 101.0 (q, C-16), 74.2 (t, C-7), 70.9 (t, C-9), 60.4 (s, C-14), 40.4 (t, C-8), 33.8 (s, C-6), 25.3 (p, C-17$_a$), 24.1 (p, C-17$_b$), 14.5 (p, C-15), 12.8 (p, C-12), 12.6 (p, C-13) ppm; **HRMS** (ESI): Compound **47b** could not be detected by mass spectrometry.

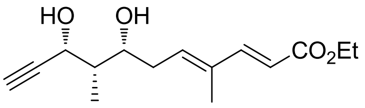
### **(2*E*,4*E*,7*S*,8*S*,9*R*)-Ethyl-11-(*tert*-butyldimethylsilyl)-7,9-dihydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (***ent*-7,8-*anti*,8,9-*syn*-**S46b)**



*ent*-7,8-*anti*,8,9-*syn* **S46b**



*ent*-7,8-*anti*,8,9-*syn* **45b**

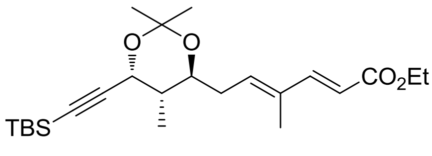


*ent*-7,8-*syn*,8,9-*syn* **45a**

A mixture of alcohols **43** [*d.r.*: 2:1 (7,8-*anti*,8,9-*syn*:7,8-*syn*,8,9-*syn*), 13 mg, 24 µmol, 1.0 eq] was dissolved in THF (0.4 ml) and cooled to 0 °C. TBAF·$3H_2O$ (15 mg, 50 µmol, 2.0 eq) was dissolved in THF (0.3 ml) and added slowly. The solution was stirred for 1 h and the reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 5:1) and furnished diols *ent*-7,8-*anti*,8,9-*syn* **S46b** (5 mg, 14 µmol, 57%) and a mixture of *ent*-7,8-*anti*,8,9-*syn* **45b** and *ent*-7,8-*syn*,8,9-*syn* **45a** (*d.r.*: ~1.1, 1.5 mg, 5.6 µmol, 24%) as colourless liquids.

*ent*-7,8-*anti*,8,9-*syn* **S46b**: $R_f$ = 0.48 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +0.8 (*c* = 0.6, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.35 (d, 1H, *J* = 15.7 Hz, H-3), 5.99 (dd, 1H, *J* = 7.5, 7.5 Hz, H-5), 5.84 (d, 1H, *J* = 15.7 Hz, H-2), 4.55 (d, 1H, *J* = 3.1 Hz, H-9), 4.22 (q, 2H, *J* = 7.1 Hz, H-14), 3.97 (ddd, 1H, J = 8.2, 8.2, 3.8 Hz, H-7), 2.35-2.55 (m, 2H, H-6), 1.88-1.98 (m, 1H, H-8), 1.81 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.0 Hz, H-15), 0.99 (d, 3H, *J* = 7.1 Hz, H-13), 0.94 (s, 9H, TBS), 0.12 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.0 (t, C-3), 136.6 (t, C-5), 135.8 (q, C-4), 116.7 (t, C-2), 105.5 (q, C-10), 89.4 (q, C-11), 74.3 (t, C-7), 67.1 (t, C-9), 60.4 (s, C-14), 43.1 (t, C-8), 34.9 (s, C-6), 26.2 (p, TBS), 16.7 (q, TBS), 14.5 (p, C-15), 13.3 (p, C-13), 12.7 (p, C-12), -4.5 (p, TBS), -4.5 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{21}H_{36}NaO_4Si$: 403.2281 $[M + Na]^+$, found: 403.2276 $[M + Na]^+$.

**(2*E*,4*E*,7*S*,8*S*,9*R*)-Acetonide** (*ent*-7,8-*anti*,8,9-*syn* **S47b**)

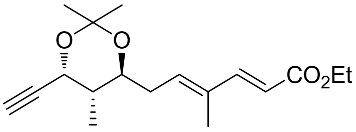


*ent*-7,8-*anti*,8,9-*syn* **S47b**

Diol **S46b** (6.1 mg, 16 µmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (1 ml). 2,2-Dimethoxypropane (0.2 ml) and PPTS (0.5 mg, catalytic) were added. The solution was stirred for 2 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1). Acetonide **S47b** (4.3 mg, 10 µmol, 64%) was obtained as a colourless liquid.

$R_f$ = 0.8 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -21.8 (*c* = 0.4, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.35 (d, 1H, *J* = 15.7 Hz, H-3), 6.00 (dd, 1H, *J* = 7.3, 6.6 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.65 (d, 1H, *J* = 5.8 Hz, H-9), 4.21 (q, 2H, *J* = 7.2 Hz, H-14), 3.75 (ddd, 1H, *J* = 9.6, 7.6, 3.5 Hz, H-7), 2.50 (ddd, 1H, *J* = 15.8, 6.6, 3.5 Hz, H-$6_a$), 2.36 (ddd, 1H, $J$ = 15.8, 7.6, 7.3 Hz, H-6$_b$), 1.82-1.93 (m, 1H, H-8), 1.79 (s, 3H, H-12), 1.60 (s, 3H, H-17$_a$), 1.36 (s, 3H, H-17$_b$), 1.21-1.34 (m, 3H, H-15), 0.94 (s, 9H, TBS), 0.84-0.91 (m, 3H, H-13), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 137.5 (t, C-5), 134.4 (q, C-4), 116.0 (q, C-2), 104.4 (q, C-10), 100.5 (q, C-16), 91.4 (q, C-11), 71.7 (t, C-7), 65.4 (t, C-9), 60.4 (s, C-14), 37.6 (t, C-8), 32.7 (s, C-6), 29.2 (p, C-17$_a$), 26.2 (p, TBS), 23.5 (p, C-17$_b$), 16.7 (q, TBS), 14.5 (p, C-13), 14.2 (p, C-15), 12.6 (p, C-12), -4.6 (p, TBS), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: Compound **S47b** could not be detected by mass spectrometry.

**(2*E*,4*E*,7*S*,8*S*,9*R*)-Acetonide** (*ent*-7,8-*anti*,8,9-*syn* **46b**)

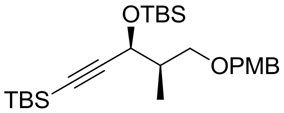


*ent*-7,8-*anti*,8,9-*syn* **46b**

Acetonide **45b** (7.5 mg, 18 μmol, 1.0 eq) was dissolved in THF (0.3 ml) and cooled to 0 °C. TBAF·3$H_2O$ (8.0 mg, 20 μmol, 1.3 eq) was dissolved in THF (0.4 ml) and added to the first solution. The reaction mixture was stirred for 1 h at 0 °C and terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alkyne **46b** (4.2 mg, 14 μmol, 77%) as a colourless liquid.

$R_f$ = 0.50 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -19.2 ($c$ = 0.5, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, $J$ = 15.7 Hz, H-3), 5.99 (dd, 1H, $J$ = 6.8, 6.8 Hz, H-5), 5.81 (d, 1H, $J$ = 15.7 Hz, H-2), 4.67 (dd, 1H, $J$ = 5.8, 2.4 Hz, H-9), 4.22 (q, 2H, $J$ = 7.1 Hz, H-14), 3.71 (ddd, 1H, $J$ = 9.1, 7.9, 3.7 Hz, H-7), 2.52 (d, 1H, $J$ = 2.4 Hz, H-11), 2.44-2.55 (m, 1H, H-6$_a$), 2.31-2.41 (m, 1H, H-6$_b$), 1.83-1.94 (m, 1H, H-8), 1.79 (s, 3H, H-12), 1.55 (s, 3H, H-17$_a$), 1.37 (s, 3H, H-17$_b$), 1.30 (t, 3H, $J$ = 7.1 Hz, H-15), 0.98 (d, 3H, $J$ = 7.2 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 137.3 (t, C-5), 134.5 (q, C-4), 116.1 (t, C-2), 100.8 (q, C-16), 81.6 (q, C-10), 76.2 (t, C-11), 72.0 (t, C-7), 64.3 (t, C-8), 60.4 (s, C-14), 37.8 (t, C-8), 32.8 (s, C-6), 28.4 (p, C-17$_a$), 23.5 (p, C-17$_b$), 14.5 (p, C-15), 13.3 (p, C-13), 12.6 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{18}H_{26}NaO_4$: 329.1729 $[M + Na]^+$, found: 329.1741 $[M + Na]^+$.

## Alkyne S48

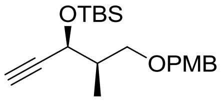


**S48**

Alcohol **S42** (1.0 g, 2.92 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7 ml). PMB-trichloroacetimidate (3.3 g, 11.68 mmol, 4.0 eq) was dissolved in $CH_2Cl_2$ (3 ml) and added to the solution. Then, CSA (68 mg, 0.29 mmol, 0.1 eq) was added and the reaction mixture stirred for 5 d at rt. A second portion of PMB-trichloroacetimidate (1.2 g, 4.3 mmol, 1.5 eq) was added and stirring was continued for another 2 d. The reaction was terminated by addition of aq. $NaHCO_3$ and the mixture was stirred for 3 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1). A second purification by flash chromatography (petroleum ether : ethyl acetate = 40:1 → 10:1) furnished PMB-protected alcohol **S48** (1.0 g, 2.28 mmol, 78%) as a colourless liquid. Additionally, alcohol **S42** (200 mg, 0.58 mmol, 20%) was reisolated.

$R_f$ = 0.71 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -24.9 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.22-7.28 (m, 2H, PMB), 6.85-6.90 (m, 2H, PMB), 4.51 (d, 1H, $J$ = 4.2 Hz, H-3), 4.43 (d, 1H, $J$ = 11.4 Hz, PMB), 4.38 (d, 1H, $J$ = 11.4 Hz, PMB), 3.80 (s, 3H, PMB), 3.48 (dd, 1H, $J$ = 9.1, 7.0 Hz, H-$1_a$), 3.33 (dd, 1H, $J$ = 9.1, 7.0 Hz, H-$1_b$), 1.99 (dqdd, 1H, $J$ = 7.0, 6.7, 6.3, 4.2 Hz, H-2), 1.00 (d, 3H, $J$ = 6.7 Hz, H-6), 0.92 (s, 9H, TBS), 0.89 (s, 9H, TBS), 0.13 (s, 3H, TBS), 0.08 (s, 3H, TBS), 0.07 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 159.2 (q, PMB), 130.9 (q, PMB), 129.3 (t, PMB), 113.9 (t, PMB), 107.8 (q, C-4), 87.3 (q, C-5), 72.9 (s, PMB), 71.8 (s, C-1), 63.9 (t, C-3), 55.4 (p, PMB), 40.8 (t, C-2), 26.2 (p, TBS), 25.9 (p, TBS), 18.4 (q, TBS), 16.6 (q, TBS), 12.0 (p, C-6), -4.3 (p, TBS), -4.6 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{26}H_{46}NaO_3Si_2$: 485.2883 $[M + Na]^+$, found: 485.2871 $[M + Na]^+$.

## Alkyne S50



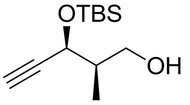
**S50**

Alkyne **S48** (100 mg, 0.22 mmol, 1 eq) was dissolved in THF (4 ml) and cooled to 0 °C. TBAF·$3H_2O$ (205 mg, 0.65 mmol, 3 eq) was dissolved in THF (2 ml) and added. The solution was stirred 1.5 h at 0 °C and rt respectively. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 3:1) to furnish alkyne **S49** (50 mg, 0.22 mmol, 99%) as a colourless liquid.

Alkyne **S49** (50 mg, 0.21 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (3.5 ml) and cooled to 0 °C. 2,6-Lutidine (0.07 ml, 0.63 mmol, 3 eq) and TBSOTf (0.07 ml, 0.32 ml, 1.5 eq) were added and the reaction mixture was stirred for 2 h at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl ($c$ = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 40:1) to furnish alkyne **S50** (68 mg, 0.20 mmol, 94%) as a colourless liquid.

$R_f$ = 0.77 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -22.4 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.22-7.28 (m, 2H, PMB), 6.69-6.85 (m, 2H, PMB), 4.54 (dd, 1H, $J$ = 3.9, 2.1 Hz, H-4), 4.44 (d, 1H, $J$ = 11.6 Hz, PMB), 4.38 (d, 1H, $J$ = 11.6 Hz, PMB), 3.81 (s, 3H, PMB), 3.47 (dd, 1H, $J$ = 9.1, 7.1 Hz, H-$1_a$), 3.34 (dd, 1H, $J$ = 9.1, 6.4 Hz, H-$1_b$), 2.34 (d, 1H, $J$ = 2,1 Hz, H-5), 2.00 (dqdd, 1H, $J$ = 7.1, 6.9, 6.4, 3.9 Hz, H-2), 1.01 (d, 2H, $J$ = 6.9 Hz, H-6), 0.89 (s, 9H, TBS), 0.14 (s, 3H, TBS), 0.09 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 159.3 (q, PMB), 130.8 (q, PMB), 129.4 (t, PMB), 114.0 (t, PMB), 85.0 (q, C-4), 72.9 (s, PMB), 72.6 (t, C-5), 71.6 (t, C-3), 63.1 (s, C-1), 55.4 (p, PMB), 40.7 (t, C-2), 25.9 (p, TBS), 18.3 (q, TBS), 11.7 (p, C-6), -4.4 (p, TBS), -5.1 (p, TBS) ppm; **HRMS** (ESI): $m/z$: calculated for $C_{20}H_{32}NaO_3Si$: 371.2018 $[M + Na]^+$, found: 371.2026 $[M + Na]^+$.

### (2*R*,3*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylpent-4-yn-1-ol (S51)



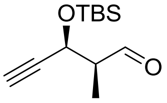
**S51**

Alkyne **S50** (66 mg, 0.19 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$/phosphate buffer (pH = 7) (6.6 ml, 10:1) at rt. DDQ (52 mg, 0.23 mmol, 1.2 eq) was added and the mixture was stirred for 3 h. The reaction was terminated by addition of aq. $NaHCO_3$ and stirring was continued for 20 min. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was dissolved in MeOH/$CH_2Cl_2$ (15 ml, 1:2) and $NaBH_4$ (~20 mg) was added. The reaction was terminated after 30 min by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure.

The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 10:1) to furnish alcohol **S51** (30 mg, 0.13 mmol, 68%) as a colourless liquid.

R$_f$ = 0.46 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -45.1 (*c* = 1.0, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.51 (dd, 1H, *J* = 5.3, 2.1 Hz, H-3), 3.83 (dd, 1H, *J* = 11.0, 7.7 Hz, H-1$_a$), 3.57 (dd, 1H, *J* = 11.0, 4.0 Hz, H-1$_b$), 2.55 (brs, 1H, OH), 2.44 (d, 1H, *J* = 2.1 Hz, H-5), 2.04 (dqdd, 1H, *J* = 7.7, 7.2, 5.3, 4.0 Hz, H-2), 0.93 (d, 3H, *J* = 7.2 Hz, H-6), 0.90 (s, 9H, TBS), 0.17 (s, 3H, TBS), 0.13 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 83.1 (q, C-4), 74.2 (t, C-5), 66.9 (t, C-3), 65.6 (s, C-1), 41.4 (t, C-2), 25.8 (p, TBS), 18.2 (q, TBS), 12.5 (p, C-6), -4.5 (p, TBS), -5.2 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{24}NaO_2Si$: 251.1443 $[M + Na]^+$, found: 251.1442 $[M + Na]^+$.

### (2*S*,3*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylpent-4-ynal (48)

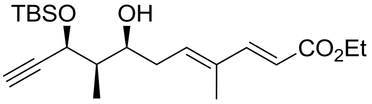


**48**

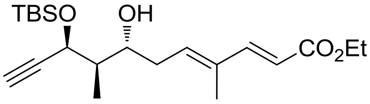
Alcohol **S51** (21 mg, 0.09 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (5 ml) and $NaHCO_3$ (10 mg) and DESS-MARTIN periodinane (47 mg, 0.11 mmol, 1.2 eq) were added and the reaction mixture was stirred for 1 h at rt. The reaction was terminated by addition of an aq. $Na_2S_2O_3$ solution and stirring was continued for 1 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **48** (18 mg, 0.08 mmol, 87%) as a colourless liquid, which was used immediately in the next step.

R$_f$ = 0.71 (PE:EE = 5:1).

### (2*E*,4*E*,7*S*,8*R*,9*S*)-Ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*syn*,8,9-*syn* 49a) and (2*E*,4*E*,7*R*,8*R*,9*S*)-ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*anti*,8,9-*syn* 49b)



7,8-*syn*,8,9-*syn* **49a**



7,8-*anti*,8,9-*syn* **49b**

Following the general procedure, aldehyde **48** (18 mg, 0.08 mmol, 1 eq) was reacted with ester **6** (25 mg, 0.16 mmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 8:1) to furnish alcohols

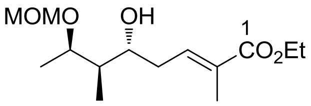
7,8-*syn*,8,9-*syn* **49a** and 7,8-*anti*,8,9-*syn* **49b** (*d.r.*: 1:1, 23 mg, 0.06 mmol, 77%) as yellow liquids.

**HRMS** (ESI): *m/z*: calculated for $C_{21}H_{36}NaO_4Si$: 403.2281 $[M + Na]^+$, found: 403.2261 $[M + Na]^+$.

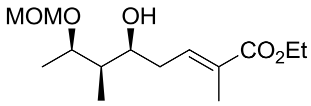
7,8-*syn*,8,9-*syn* **49a**: $R_f$ = 0.39 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -21.5 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, *J* = 15.7 Hz, H-3), 5.92 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.50 (dd, 1H, *J* = 3.4, 2.1 Hz, H-9), 4.20 (q, 2H, *J* = 7.2 Hz, H-14), 4.06 (ddd, 1H, *J* = 7.5, 6.5, 1.4 Hz, H-7), 2.67 (brs, 1H, OH), 2.48 (d, 1H, *J* = 2.1 Hz, H-11), 2.43-2.52 (m, 1H, H-6$_a$), 2.36 (ddd, 1H, J = 7.5, 7.4, 7.3 Hz, H-6$_b$), 1.70-1.77 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 1.07 (d, 3H, *J* = 7.2 Hz, H-13), 0.90 (s, 9H, TBS), 0.18 (s, 3H, TBS), 0.15 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.3 (t, C-3), 137.7 (t, C-5), 134.7 (q, C-4), 116.3 (t, C-2), 84.7 (q, C-10), 74.5 (t, C-7), 73.0 (t, C-11), 67.3 (t, C-9), 60.3 (s, C-14), 43.4 (t, C-8), 34.6 (s, C-6), 25.8 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 7.7 (p, C-13), -4.5 (p, TBS), -5.2 (p, TBS) ppm.

7,8-*anti*,8,9-*syn* **49b**: $R_f$ = 0.48 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -3.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.37 (d, 1H, *J* = 15.7 Hz, H-3), 6.10 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.60 (dd, 1H, *J* = 3.4, 2.2 Hz, H-9), 4.20 (q, 2H, *J* = 7.1 Hz, H-14), 3.98 (ddd, 1H, *J* = 7.9, 7.9, 3.8 Hz, H-7), 3.69 (brs, 1H, OH), 2.47 (d, 1H, *J* = 2.2 Hz, H-11), 2.43-2.52 (m, 1H, H-6$_a$), 2.32-2.41 (m, 1H, H-6$_b$), 1.81-1.90 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.1 Hz, H-15), 0.89-0.94 (m, 3H, H-13), 0.91 (s, 9H, TBS), 0.18 (s, 3H, TBS), 0.15 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.6 (t, C-3), 137.9 (t, C-5), 134.5 (q, C-4), 116.0 (t, C-2), 82.6 (q, C-10), 74.8 (t, C-7), 72.9 (t, C-11), 67.6 (t, C-9), 60.3 (s, C-14), 43.7 (t, C-8), 34.3 (s, C-6), 25.8 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-15), 12.8 (p, C-13), 12.6 (p, C-12), -4.5 (p, TBS), -5.2 (p, TBS) ppm.

### (5*S*,6*R*,7*R*,*E*)-Ethyl-5-hydroxy-7-(methoxymethoxy)-2,6-dimethyloct-2-enoate (5,6-*syn*,6,7-*syn*-**51a**) and (5*R*,6*R*,7*R*,*E*)-ethyl-5-hydroxy-7-(methoxymethoxy)-2,6-dimethyloct-2-enoate (5,6-*anti*,6,7-*syn*-**51b**)



5,6-*anti*,6,7-*syn* **51b**



5,6-*syn*,6,7-*syn* **51a**

Following the general procedure, aldehyde **20** (33 mg, 0.23 mmol, 1 eq) was reacted with ethyl-*trans*-2-methyl-2-butenoate (**50**) (0.06 ml, 0.46 mmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 2:1) to furnish alcohols 5,6-*anti*,6,7-*syn* **51b** and 5,6-*syn*,6,7-*syn* **51a** [*d.r.*: 1:2.7 (**51b**:**51a**), 45 mg, 0.16 mmol, 72%] as a yellow liquid.

$R_f$ = 0.31 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{26}NaOi$: 297.1678 $[M + Na]^+$, found: 297.1678 $[M + Na]^+$.

5,6-*syn*,6,7-*syn* **51a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.78 (ddd, 1H, *J* = 7.7, 7.0, 1.0 Hz, H-3), 4.75 (d, 1H, *J* = 6.8 Hz, MOM), 4.61 (d, 1H, *J* = 6.8 Hz, MOM), 4.19 (q, 2H, *J* = 7.1 Hz, H-11), 3.90-4.00 (m, 2H, H-5 + H-7), 3.39 (s, 3H, MOM), 2.40-2.50 (m, 1H, H-$4_a$), 2.27-2.38 (m, 1H, H-$4_b$), 1.86 (s, 3H, H-9), 1.49-1.56 (m, 1H, H-6), 1.29 (t, 3H, *J* = 7.1 Hz, H-12), 1.20 (d, 3H, *J* = 6.5 Hz, H-8), 0.98 (d, 3H, *J* = 7.2 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.2 (q, C-1), 138.4 (t, C-3), 129.7 (q, C-2), 94.7 (s, MOM), 77.6 (t, C-5), 74.7 (t, C-7), 60.7 (s, C-11), 56.0 (p, MOM), 42.1 (t, C-6), 34.5 (s, C-4), 17.7 (p, C-8), 14.4 (p, C-12), 12.8 (p, C-9), 5.9 (p, C-10) ppm.

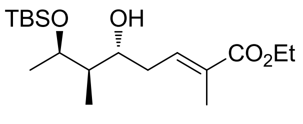
5,6-*anti*,6,7-*syn* **51b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.94 (ddd, 1H, *J* = 7.9, 6.5, 1.4 Hz, H-3), 4.69 (d, 1H, *J* = 7.2 Hz, MOM), 4.63 (d, 1H, *J* = 7.2 Hz, MOM), 4.19 (q, 2H, *J* = 7.1 Hz, H-11), 4.03 (qd, 1H, *J* = 6.5, 2.8 Hz, H-7), 3.77 (ddd, 1H, *J* = 8.2, 8.2, 8.2 Hz, H-5), 3.39 (s, 3H, MOM), 2.40-2.50 (m, 1H, H-$4_a$), 2.27-2.38 (m, 1H, H-$4_b$), 1.86 (s, 3H, H-9), 1.66-1.76 (m, 1H, H-6), 1.29 (t, 3H, *J* = 7.1 Hz, H-12), 1.19 (d, 3H, *J* = 6.5 Hz, H-8), 0.88 (d, 3H, *J* = 7.2 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.2 (q, C-1), 138.8 (t, C-3), 129.4 (q, C-2), 95.4 (s, MOM), 75.6 (t, C-5), 72.7 (t, C-7), 60.6 (s, C-11), 55.9 (p, MOM), 42.5 (t, C-6), 34.4 (s, C-4), 16.1 (p, C-8), 14.4 (p, C-12), 12.8 (p, C-9), 12.1 (p, C-10) ppm.

### (5*S*,6*R*,7*R*,*E*)-Ethyl-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,6-dimethyloct-2-enoate

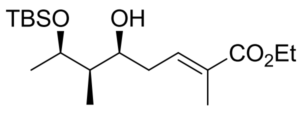
**(**5,6-*syn*,6,7-*syn* **52a)** and

### (5*R*,6*R*,7*R*,*E*)-ethyl-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,6-dimethyloct-2-enoate

**(**5,6-*anti*,6,7-*syn* **52b)**



5,6-*anti*,6,7-*syn* **52b**



5,6-*syn*,6,7-*syn* **52a**

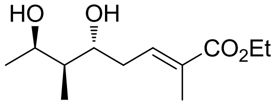
Following the general procedure, aldehyde **21** (38 mg, 0.18 mmol, 1 eq) was reacted with ethyl-*trans*-2-methyl-2-butenoate (**50**) (0.05 ml, 0.35 mmol, 2 eq) in accordance with the general procedure at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnished alcohols 5,6-*syn*,6,7-*syn* **52a** and 5,6-*anti*,6,7-*syn* **52b** [*d.r.*: 1:2.4 (**52b**:**52a**), 48 mg, 0.14 mmol, 80%] as a yellow liquid.

$R_f$ = 0.32 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography, **HRMS** (ESI): *m/z*: calculated for $C_{18}H_{37}O_4Si$: 345.2461 [M + H]$^+$, found: 345.2453 [M + Na]$^+$.

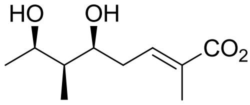
5,6-*syn*,6,7-*syn* **52a**: **$^{1}$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.66 (ddd, 1H, *J* = 7.7, 7.2, 0.9 Hz, H-3), 4.09 (q, 2H, *J* = 7.1 Hz, H-11), 3.99 (qd, 1H, *J* = 6.2, 2.7 Hz, H-7), 3.85 (ddd, 1H, *J* = 7.0, 7.0, 1.9 Hz, H-5), 2.15-2.37 (m, 2H, H-4), 1.76 (s, 3H, H-9), 1.28-1.37 (m, 1H, H-6), 1.19 (t, 3H, *J* = 7.1 Hz, H-12), 1.07 (d, 3H, *J* = 6.2 Hz, H-8), 0.83 (d, 3H, *J* = 7.2 Hz, H-10), 0.79 (s, 9H, TBS), 0.01 (s, 3H, TBS), 0.00 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.2 (q, C-1), 138.5 (t, C-3), 129.7 (q, C-2), 74.8 (t, C-5), 74.0 (t, C-7), 60.5 (s, C-11), 42.8 (t, C-6), 34.5 (s, C-4), 26.0 (p, TBS), 21.9 (p, C-8), 18.1 (q, TBS), 14.4 (p, C-12), 12.8 (p, C-9), 5.5 (p, C-10), -3.4 (p, TBS), -4.6 (p, TBS) ppm.

5,6-*anti*,6,7-*syn* **52b**: **$^{1}$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.87 (ddd, 1H, *J* = 7.5, 6.7, 1.0 Hz, H-3), 4.08 (q, 2H, *J* = 7.1 Hz, H-11), 3.91 (qd, 1H, *J* = 6.4, 3.2 Hz, H-7), 3.75 (ddd, 1H, *J* = 9.6, 6.7, 3.5 Hz, H-5), 2.15-2.37 (m, 2H, H-4), 1.76 (s, 3H, H-9), 1.60-1.71 (m, 1H, H-6), 1.18 (t, 3H, *J* = 7.1 Hz, H-12), 1.09 (d, 3H, *J* = 6.4 Hz, H-8), 0.79 (s, 9H, TBS), 0.68 (d, 3H, *J* = 7.2 Hz, H-10), 0.01 (s, 3H, TBS), 0.00 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.2 (q, C-1), 138.8 (t, C-3), 129.3 (q, C-2), 73.7 (t, C-5), 72.7 (t, C-7), 60.4 (s, C-11), 43.1 (t, C-6), 34.8 (s, C-4), 25.9 (p, TBS), 18.0 (q, TBS), 17.7 (p, C-8), 14.4 (p, C-12), 13.8 (p, C-10), 12.9 (p, C-9), -4.5 (p, TBS), -5.0 (p, TBS) ppm.

**(5*S*,6*S*,7*R*,*E*)-Ethyl 5,7-dihydroxy-2,6-dimethyloct-2-enoate (**5,6-*syn*,6,7-*syn* **S52a)** and **(5*R*,6*S*,7*R*,*E*)-ethyl-5,7-dihydroxy-2,6-dimethyloct-2-enoate (**5,6-*anti*,6,7-*syn* **S52b)**



5,6-*anti*,6,7-*syn* **S52b**



5,6-*syn*,6,7-*syn* **S52a**

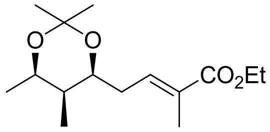
A mixture of alcohols **52** [*d.r.*: 1:2.4 (**52b**:**52a**), 18 mg, 52 μmol, 1.0 eq] was dissolved in THF (1.2 ml) and cooled to 0 °C. $TBAF\cdot 3H_2O$ (21 mg, 65 μmol, 1.5 eq) was added and the mixture was stirred for 1 h while the temperature was raised from °C to rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 2:1) to furnish diols 5,6-*syn*,6,7-*syn* **S52a** and 5,6-*anti*,6,7-*syn* **S52b** [*d.r.*: 1:2 (**S52b**:**S52a**), 12 mg, 51 □mol, 98%] as a colourless liquid.

$R_f$ = 0.23 (PE:EE = 2:1); the diastereomer could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{23}O_4$ and $C_{12}H_{22}NaO_4$: 231.1596 $[M + H]^+$ and 253.1416 $[M + Na]^+$, found: 231.1595 $[M + H]^+$ and 253.1405 $[M + Na]^+$.

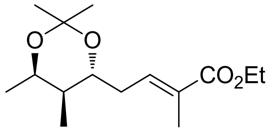
5,6-*syn*,6,7-*syn* **S52a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.75 (ddd, 1H, *J* = 7.5, 7.5, 1.4 Hz, H-3), 4.19 (q, 2H, *J* = 7.1 Hz, H-11), 3.99 (qd, 1H, *J* = 6.4, 2.0 Hz, H-7), 4.03 (ddd, 1H, *J* = 7.4, 6.4, 1.7 Hz, H-5), 2.41-2.51 (m, 1H, H-$4_a$), 2.25-2.39 (m, 1H, H-$4_b$), 1.87 (s, 3H, H-9), 1.47 (qdd, 1H, *J* = 7.1, 2.0, 1.7 Hz, H-6), 1.30 (t, 3H, *J* = 7.1 Hz, H-12), 1.21 (d, 3H, *J* = 6.4 Hz, H-8), 0.96 (d, 3H, *J* = 7.1 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.1 (q, C-1), 137.9 (t, C-3), 130.2 (q, C-2), 76.0 (t, C-5), 73.0 (t, C-7), 60.8 (s, C-11), 41.8 (t, C-6), 34.7 (s, C-4), 21.8 (p, C-8), 14.4 (p, C-12), 12.8 (p, C-9), 4.2 (p, C-10) ppm.

5,6-*anti*,6,7-*syn* **S52b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.85 (ddd, 1H, *J* = 7.3, 7.3, 1.2 Hz, H-3), 4.19 (q, 2H, *J* = 7.1 Hz, H-11), 4.15-4.21 (m, 1H, H-7), 3.80-3.86 (m, 1H, H-5), 2.41-2.51 (m, 1H, H-$4_a$), 2.25-2.39 (m, 1H, H-$4_b$), 1.87 (s, 3H, H-9), 1.68 (qdd, 1H, *J* = 7.1, 6.8, 2.6 Hz, H-6), 1.30 (t, 3H, *J* = 7.1 Hz, H-12), 1.21 (d, 3H, *J* = 6.5 Hz, H-8), 0.94 (d, 3H, *J* = 7.1 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.1 (q, C-1), 138.0 (t, C-3), 130.3 (q, C-2), 74.5 (t, C-5), 69.6 (t, C-7), 60.8 (s, C-11), 42.4 (t, C-6), 35.1 (s, C-4), 19.6 (p, C-8), 14.4 (p, C-12), 12.9 (p, C-9) 12.1 (p, C-10), ppm.

**Acetonides (**5,6-*syn*,6,7-*syn* **S53a**) and (5,6-*anti*,6,7-*syn* **S53b**)



5,6-*syn*,6,7-*syn* **S53a**



5,6-*anti*,6,7-*syn* **S53b**

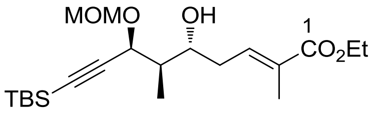
A mixture of diols **S52** [*d.r.*: 1:2 (**S52b**:**S52a**), 14 mg, 61 □mol, 1 eq] was dissolved in $CH_2Cl_2$ (1.0 ml). 2,2-Dimethoxypropane (0.2 ml) and CSA (2 mg, catalytic) were added and stirred for 3 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1). Acetonides

5,6-*syn*,6,7-*syn* **S53a** and 5,6-*anti*,6,7-*syn* **S53b** [*d.r.*: ~1:2.5 (**S53b**:**S53a**), 15 mg, 56 □mol, 91%] were obtained as a colourless liquid.

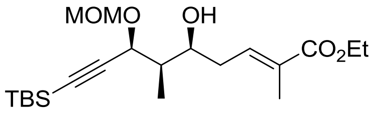
$R_f$ = 0.22 (PE:EE = 20:1); the diastereomers could not be separated by column chromatography; 5,6-*syn*,6,7-*syn* **S53a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.70 (ddd, 1H, *J* = 7.6, 6.7, 1.1 Hz, H-3), 4.19 (q, 2H, *J* = 7.2 Hz, H-11), 4.09 (qd, 1H, *J* = 6.4, 2.3 Hz, H-7), 4.01 (ddd, 1H, *J* = 7.2, 7.2, 2.1 Hz, H-5), 2.24-2.40 (m, 2H, H-4), 1.86 (s, 3H, H-9), 1.27.1.35 (m, 1H, H-6), 1.44 (s, 3H, H-$14_a$), 1.40 (s, 3H, H-$14_b$), 1.29 (t, 3H, *J* = 7.2 Hz, H-12), 1.13 (d, 3H, *J* = 6.4 Hz, H-8), 0.87 (d, 3H, *J* = 6.8 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.2 (q, C-1), 137.6 (t, C-3), 129.8 (q, C-2), 99.1 (q, C-13), 72.6 (t, C-5), 69.0 (t, C-7), 60.7 (s, C-11), 35.8 (t, C-6), 32.5 (s, C-4), 30.1 (p, C-$14_a$), 19.8 (p, C-8), 19.1 (p, C-$14_b$), 14.4 (p, C-12), 12.9 (p, C-9), 4.5 (p, C-10) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_{26}NaO_4$: 293.1729 $[M + Na]^+$, found: 293.1726 $[M + Na]^+$.

### **(2*E*,5*S*,6*R*,7*S*)-Ethyl-9-(*tert*-butyldimethylsilyl)-5-hydroxy-7-(methoxymethoxy)-2,6-dimethylnon-2-en-8-ynoate (**5,6-*syn*,6,7-*syn* **53a)** and

### **(2*E*,5*R*,6*R*,7*S*)-ethyl-9-(*tert*-butyldimethylsilyl)-5-hydroxy-7-(methoxymethoxy)-2,6-dimethylnon-2-en-8-ynoate (**5,6-*anti*,6,7-*syn* **53b)**



5,6-*anti*,6,7-*syn* **53b**



5,6-*syn*,6,7-*syn* **53a**

Following the general procedure, aldehyde **32** (36 mg, 130 μmol, 1.0 eq) was reacted with ethyl-*trans*-2-methyl-2-butenoate (**50**) (0.04 ml, 280 μmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 5:1) to furnish alcohols 5,6-*syn*,6,7-*syn* **53a** and 5,6-*anti*,6,7-*syn* **53b** [*d.r.*: 1:3.8 (**53b**:**53a**), 38 mg, 0.1 mmol, 70%] as a colourless liquid.

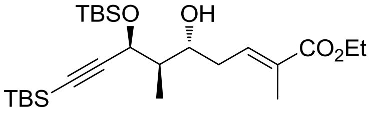
$R_f$ = 0.31 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{21}H_{38}NaO_5Si$: 421.2386 $[M + Na]^+$, found: 421.2386 $[M + Na]^+$.

5,6-*syn*,6,7-*syn* **53a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.79 (dd, 1H, *J* = 6.8, 6.8 Hz, H-3), 5.00 (d, 1H, *J* = 6.8 Hz, MOM), 4.60 (d, 1H, *J* = 6.8 Hz, MOM), 4.45 (d, 1H, *J* = 4.4 Hz, H-7), 4.18 (q, 2H, *J* = 7.5 Hz, H-12), 4.07-4.4.14 (m, 1H, H-5), 3.38 (s, 3H, MOM), 2.73 (s, 1H, OH), 2.41-2.50 (m, 1H, H-$4_a$), 2.29-2.39 (m, 1H, H-$4_b$), 1.87-1.97 (m, 1H, H-6), 1.86 (s, 3H, H-10), 1.29 (t, 3H, *J* = 7.5 Hz, H-13), 1.11 (d, 3H, *J* = 7.2 Hz, H-

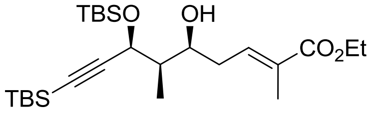
11), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.1 (q, C-1), 138.3 (t, C-3), 129.8 (q, C-2), 103.2 (q, C-8), 94.2 (s, MOM), 91.2 (q, C-9), 72.5 (t, C-5), 70.1 (t, C-7), 60.6 (s, C-12), 56.1 (p, MOM), 42.0 (t, C-6), 34.4 (s, C-4), 26.2 (p, TBS), 16.6 (q, TBS), 14.4 (p, C-13), 12.8 (p, C-10), 8.3 (p, C-11), -4.6 (p, TBS) ppm.

5,6-*anti*,6,7-*syn* **53b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.91 (dd, 1H, *J* = 6.7, 6.7 Hz, H-3), 4.96 (d, 1H, *J* = 6.7 Hz, MOM), 4.64 (d, 1H, *J* = 3.4 Hz, H-7), 4.60 (d, 1H, *J* = 6.7 Hz, MOM), 4.18 (q, 2H, *J* = 7.5 Hz, H-12), 3.88-3.96 (m, 1H, H-5), 3.40 (s, 3H, MOM), 3.10 (s, 1H, OH), 2.41-2.50 (m, 1H, H-4$_a$), 2.29-2.39 (m, 1H, H-4$_b$), 1.87-1.97 (m, 1H, H-6), 1.86 (s, 3H, H-10), 1.29 (t, 3H, *J* = 7.5 Hz, H-13), 1.03 (d, 3H, *J* = 7.2 Hz, H-11), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.1 (q, C-1), 138.3 (t, C-3), 129.8 (q, C-2), 102.7 (q, C-8), 94.5 (s, MOM), 91.0 (q, C-9), 72.5 (t, C-5), 69.5 (t, C-7), 60.6 (s, C-12), 56.2 (p, MOM), 42.8 (t, C-6), 34.1 (s, C-4), 26.2 (p, TBS), 16.6 (q, TBS), 14.4 (p, C-13), 12.8 (p, C-10), 12.7 (p, C-11), -4.6 (p, TBS) ppm.

**(5*S*,6*R*,7*S*,*E*)-Ethyl-9-(*tert*-butyldimethylsilyl)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,6-dimethylnon-2-en-8-ynoate (**5,6-*syn*,6,7-*syn* **54a)** and
**(5*R*,6*R*,7*S*,*E*)-ethyl-9-(*tert*-butyldimethylsilyl)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,6-dimethylnon-2-en-8-ynoate (**5,6-*anti*,6,7-*syn* **54b)**



5,6-*anti*,6,7-*syn* **54b**



5,6-*syn*,6,7-*syn* **54a**

Following the general procedure, aldehyde **37** (48 mg, 140 μmol, 1.0 eq) was reacted with ethyl-*trans*-2-methyl-2-butenoate (**50**) (0.05 ml, 360 μmol, 2.6 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols 5,6-*syn*,6,7-*syn* **54a** and 5,6-*anti*,6,7-*syn* **54b** [*d.r.*: 2.5:1 (**54b**: **54a**), 57 mg, 122 μmol, 87%] as a yellow liquid.

R$_f$ = 0.17 (PE:EE = 20:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{25}H_{48}NaO_4Si_2$: 491.2989 [M + Na]$^+$, found: 491.2983 [M + Na]$^+$.

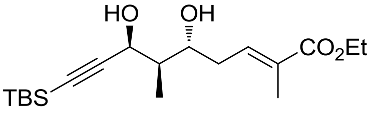
5,6-*syn*,6,7-*syn* **54a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.78 (dd, 1H, *J* = 7.7, 7.3 Hz, H-3), 4.50 (d, 1H, *J* = 4.1 Hz, H-7), 4.19 (q, 2H, *J* = 7.1 Hz, H-12), 4.08-4.15 (m, 1H, H-5), 2.38-2.49 (m, 1H, H-4$_a$), 2.28-2.38 (m, 1H, H-4$_b$), 1.86 (s, 3H, H-10), 1.69-1.78

(m, 1H, H-6), 1.29 (t, 3H, *J* = 7.1 Hz, H-13), 1.06 (d, 3H, *J* = 7.2 Hz, H-11), 0.90 (s, 18H, TBS), 0.18 (s, 6H, TBS), 0.15 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, CDCl$_3$, CDCl$_3$ = 77.16 ppm): δ 168.2 (q, C-1), 138.4 (t, C-3), 129.7 (q, C2), 106.7 (q, C-8), 89.8 (q, C-9), 72.6 (t, C-5), 67.9 (t, C-7), 60.6 (s, C-12), 43.5 (t, C-6), 34.4 (s, C-4), 25.8 (p, TBS), 18.2 (q, TBS), 16.6 (q, TBS), 14.4 (p, C-13), 12.8 (p, C-10), 8.0 (p, C-11), -4.1 (p, TBS), -4.6 (p, TBS), -4.9 (p, TBS) ppm.

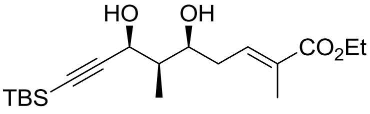
5,6-*anti*,6,7-*syn* **54b**: **$^{1}$H-NMR** (400 MHz, CDCl$_3$, CHCl$_3$ = 7.26 ppm): δ 6.95 (dd, 1H, *J* = 7.2, 7.0 Hz, H-3), 4.59 (d, 1H, *J* = 3.4 Hz, H-7), 4.19 (q, 2H, *J* = 7.1 Hz, H-12), 4.01 (ddd, 1H, J = 7.9, 7.9, 3.8 Hz, H-5), 2.38-2.49 (m, 1H, H-4$_a$), 2.28-2.38 (m, 1H, H-4$_b$), 1.86 (s, 3H, H-10), 1.80-1.86 (m, 1H, H-6), 1.29 (t, 3H, *J* = 7.1 Hz, H-13), 0.93 (s, 18H, TBS), 0.88-0.92 (m, 3H, H-11), 0.10 (s, 12H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, CDCl$_3$, CDCl$_3$ = 77.16 ppm): δ 168.2 (q, C-1), 138.6 (t, C-3), 129.5 (q, C2), 105.1 (q, C-8), 90.1 (q, C-9), 73.0 (t, C-5), 68.4 (t, C-7), 60.6 (s, C-12), 43.8 (t, C-6), 34.4 (s, C-4), 26.2 (p, TBS), 18.2 (q, TBS), 16.6 (q, TBS), 14.4 (p, C-13), 13.0 (p, C-11), 12.8 (p, C-10), -4.4 (p, TBS), -4.6 (p, TBS), -5.1 (p, TBS) ppm.

**(2*E*,5*S*,6*R*,7*S*)-Ethyl-9-(*tert*-butyldimethylsilyl)-5,7-dihydroxy-2,6-dimethylnon-2-en-8-ynoate (**5,6-*syn*,6,7-*syn* **S54a)** and

**(2*E*,5*R*,6*R*,7*S*)-ethyl-9-(*tert*-butyldimethylsilyl)-5,7-dihydroxy-2,6-dimethylnon-2-en-8-ynoate (**5,6-*anti*,6,7-*syn* **S54b)**



5,6-*anti*,6,7-*syn* **S54b**



5,6-*syn*,6,7-*syn* **S54a**

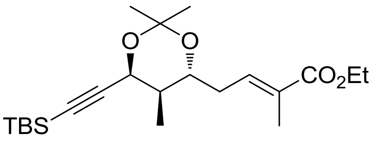
A mixture of alcohols **53** [*d.r.*: 1:3.8 (**53b**:**53a**), 10 mg, 25 µmol, 1.0 eq] was dissolved in EtOH (0.8 ml) and cooled to 0 °C. Concentrated aq. HCl (~0.1 ml) was added dropwise over a period of 6 d until tlc revealed complete transformation. The reaction was terminated by addition of aq. NaHCO$_3$. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined, organic layers were dried over MgSO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 5:1) to furnish diols 5,6-*syn*,6,7-*syn* **S54a** and 5,6-*anti*,6,7-*syn* **S54b** [*d.r.*: 1:4 (**S54b**:**S54a**), 8.6 mg, 24 µmol, 97%] as a colourless liquid.

R$_f$ = 0.19 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for C$_{19}$H$_{34}$NaO$_4$Si: 377.2124 [M + Na]$^+$, found: 377.2116 [M + Na]$^+$.

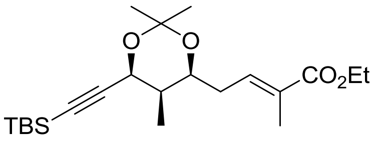
5,6-*syn*,6,7-*syn* **S54a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.77 (ddd, 1H, *J* = 7.6, 7.1, 0.9 Hz, H-3), 4.55-4.60 (m, 1H, H-7), 4.19 (q, 2H, *J* = 7.1 Hz, H-12), 4.06-4.15 (m, 1H, H-5), 2.68 (d, 1H, *J* = 1.7 Hz, $OH_5$), 2.39-2.52 (m, 1H, H-$4_a$), 2.28-2.39 (m, 1H, H-$4_b$), 1.87 (s, 3H, H-10), 1.76-1.84 (m, 1H, H-6), 1.29 (t, 3H, *J* = 7.1 Hz, H-13), 1.12 (d, 3H, *J* = 6.8 Hz, H-11), 0.94 (s, 9H, TBS), 0.12 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.1 (q, C-1), 137.9 (t, C-3), 130.1 (q, C-2), 106.0 (q, C-8), 89.8 (q, C-9), 73.3 (t, C-5), 67.4 (t, C-7), 60.7 (s, C-12), 42.7 (t, C-6), 34.5 (s, C-4), 26.2 (p, TBS), 16.6 (q, TBS), 14.4 (p, C-13), 12.8 (p, C-10), 7.3 (p, C-11), -4.6 (p, TBS) ppm.

5,6-*anti*,6,7-*syn* **S54b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.85 (ddd, 1H, *J* = 7.7, 7.0, 0.9 Hz, H-3), 4.55-4.60 (m, 1H, H-7), 4.20 (q, 2H, *J* = 7.1 Hz, H-12), 3.97-4.05 (m, 1H, H-5), 3.33 (d, 1H, *J* = 6.8 Hz, $OH_7$), 2.61 (d, 1H, *J* = 3.1 Hz, $OH_5$), 2.39-2.52 (m, 1H, H-$4_a$), 2.28-2.39 (m, 1H, H-$4_b$), 1.89-1.99 (m, 1H, H-6), 1.87 (s, 3H, H-10), 1.30 (t, 3H, *J* = 7.1 Hz, H-13), 0.99 (d, 3H, *J* = 6.8 Hz, H-11), 0.94 (s, 9H, TBS), 0.12 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.1 (q, C-1), 137.3 (t, C-3), 130.1 (q, C-2), 105.4 (q, C-8), 89.4 (q, C-9), 74.0 (t, C-5), 67.1 (t, C-7), 60.8 (s, C-12), 43.1 (t, C-6), 34.8 (s, C-4), 26.2 (p, TBS), 16.6 (q, TBS), 14.4 (p, C-13), 13.3 (p, C-11), 12.9 (p, C-10), -4.6 (p, TBS) ppm.

**Acetonides** (5,6-*syn*,6,7-*syn* **S55a**) and (5,6-*anti*,6,7-*syn* **S55b**)



5,6-*anti*,6,7-*syn* **S55b**



5,6-*syn*,6,7-*syn* **S55a**

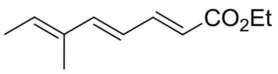
A mixture of diols **S54** [*d.r.*: 1:4 (**S54b**:**S54a**), 8.6 mg, 24 µmol, 1.0 eq] was dissolved in $CH_2Cl_2$ (1.0 ml) and 2,2-dimethoxypropane (0.2 ml) was added. After addition of PPTS (0.5 mg, catalytic), the solution was stirred for 4 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1). Acetonides 5,6-*anti*,6,7-*syn* **S55b** and 5,6-*syn*,6,7-*syn* **S55a** [*d.r.*: 1:4 (**S55b**:**S55a**), 6.8 mg, 17 µmol, 72%] were obtained as a colourless liquid.

$R_f$ = 0.57 (PE:EE = 5:1); $[\alpha]_D^{20}$ = the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{38}NaO_4Si$: 417.2437 $[M + Na]^+$, found: 417.2435 $[M + Na]^+$.

5,6-*syn*,6,7-*syn* **S55a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.68 (dd, 1H, *J* = 6.7, 6.7 Hz, H-3), 4.81 (d, 1H, *J* = 2.1 Hz, H-7), 4.20 (q, 2H, *J* = 7.2 Hz, H-12), 4.01 (ddd, 1H, *J* = 7.1, 7.1, 2.1 Hz, H-5), 2.24-2.50 (m, 2H, H-4), 1.86 (s, 3H, H-10), 1.57-1.63 (m, 1H, H-6), 1.45 (s, 3H, H-15$_b$), 1.44 (s, 3H, H-15$_a$), 1.30 (t, 3H, *J* = 7.2 Hz, H-13), 1.12 (d, 3H, *J* = 6.8 Hz, H-11), 0.94 (s, 9H, TBS), 0.12 (s, 3H, TBS), 0.11 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.1 (q, C-1), 137.0 (t, C-3), 130.1 (q, C-2), 103.9 (q, C-8), 99.8 (q, C-14), 88.8 (q, C-9), 71.5 (t, C-5), 66.1 (t, C-7), 60.7 (s, C-12), 36.1 (t, C-6), 32.6 (s, C-4), 30.0 (p, C-15$_a$), 26.2 (p, TBS), 19.4 (p, C-15$_b$), 16.7 (q, TBS), 14.4 (p, C-13), 12.9 (p, C-10), 6.5 (p, C-11), -4.5 (p, TBS) ppm.

5,6-*anti*,6,7-*syn* **S55b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 6.84 (dd, 1H, *J* = 6.3, 6.3 Hz, H-3), 4.66 (d, 1H, *J* = 5.8 Hz, H-7), 4.20 (q, 2H, *J* = 7.2 Hz, H-12), 3.79 (ddd, 1H, *J* = 9.9, 7.2, 3.2 Hz, H-5), 2.24-2.50 (m, 2H, H-4), 1.85 (s, 3H, H-10), 1.61 (s, 3H, H-15$_b$), 1.86-1.93 (m, 1H, H-6), 1.37 (s, 3H, H-15$_a$), 1.30 (t, 3H, *J* = 7.2 Hz, H-13), 0.93-0.98 (m, 3H, H-11), 0.94 (s, 9H, TBS), 0.12 (s, 3H, TBS), 0.11 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 168.1 (q, C-1), 137.9 (t, C-3), 130.1 (q, C-2), 104.3 (q, C-8), 100.6 (q, C-14), 91.4 (q, C-9), 71.4 (t, C-5), 65.4 (t, C-7), 60.6 (s, C-12), 37.5 (t, C-6), 32.7 (s, C-4), 29.2 (p, C-15$_a$), 26.2 (p, TBS), 23.5 (p, C-15$_b$), 16.7 (q, TBS), 14.4 (p, C-13), 13.4 (p, C-11), 12.8 (p, C-10), -4.6 (p, TBS), -4.6 (p, TBS) ppm.

### (2*E*,4*E*,6*E*)-Ethyl-6-methylocta-2,4,6-trienoate (55)

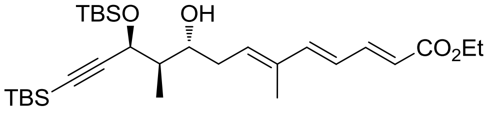


**55**

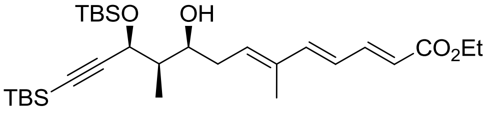
Ester **6** (500 mg, 3.2 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (60 ml) and cooled to -78 °C. DIBAL-H (*c* = 1.2 mol/l in toluene, 11 ml, 13.0 mmol, 4.0 eq) was slowly added and the reaction mixture was stirred for 30 min. The reaction was terminated by addition of ethyl acetate, warmed to rt and after addition of Na-K-tartrate stirring was continued for 1 h. The layers were separated and the aqueous layer extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (100% petroleum ether → petroleum ether : ethyl acetate = 5:1). The resulting alcohol was dissolved in $CH_2Cl_2$ (65 ml) and $NaHCO_3$ (1 g) and the DESS-MARTIN periodinane (1.65 g, 3.9 mmol, 1.2 eq) were added and the solution was stirred for 45 min at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and the mixture was stirred for another 1 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was dissolved in $CHCl_3$ (4 ml) and (1-ethoxycarbonylmethyliden)-triphenylphosphorane (**14**) (2.3 g, 6.5 mmol, 2.0 eq) was added. The solution was stirred for 4 d. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 50:1). Ester **55** (367 mg, 2.0 mmol, 64%) was obtained as a yellow liquid.

R$_f$ = 0.59 (PE:EE = 5:1); The ester was obtained as *all-E*-isomer (*E:Z*> 10:1). **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.36 (dd, 1H, *J* = 15.3, 11.1 Hz, H-3), 6.60 (d, 1H, *J* = 15.3 Hz, H-5), 6.25 (dd, 1H, *J* = 15.3, 11.1 Hz, H-4), 5.88 (d, 1H, *J* = 15.3 Hz, H-2), 5.81 (q, 1H, *J* = 6.7 Hz, H-7), 4.22 (q, 2H, *J* = 7.2 Hz, H-10), 1.81 (d, 3H, *J* = 6.7 Hz, H-8), 1.80 (s, 3H, H-9), 1.32 (t, 3H, *J* = 7.2 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.5 (q, C-1), 145.9 (t, C-5), 145.6 (t, C-3), 134.8 (q, C-6), 132.8 (t, C-7), 123.6 (t, C-4), 119.8 (t, C-2), 60.3 (s, C-10), 14.5 (p, C-11), 14.5 (p, C-8), 12.0 (p, C-9) ppm; **HRMS** (ESI): Compound **55** could not be detected by mass spectrometry.

**(2*E*,4*E*,6*E*,9*S*,10*R*,11*S*)-Ethyl-13-(*tert*-butyldimethylsilyl)-11-(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,10-dimethyltrideca-2,4,6-trien-12-ynoate (**9,10-*syn,*10,11-*syn* **56a)** and **(2*E*,4*E*,6*E*,9*R*,10*R*,11*S*)-ethyl-13-(*tert*-butyldimethylsilyl)-11-(*tert*-butyldimethysilyloxy)-9-hydroxy-6,10-dimethyltrideca-2,4,6-trien-12-ynoate (**9,10-*anti*,10,11-*syn* **56b)**



9,10-*anti*,10,11-*syn* **56b**



9,10-*syn*,10,11-*syn* **56a**

Following the general procedure, aldehyde **37** (67 mg, 0.20 mmol, 1 eq) was reacted with ester **55** (72 mg, 0.40 mmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols 9,10-*syn,*10,11-*syn* **56a** and 9,10-*anti,*10,11-*syn* **56b** [*d.r.*: 2.8:1 (**56b**:**56a**), 85 mg, 0.16 mmol, 83%] as a yellow liquid.

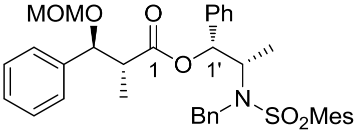
R$_f$ = 0.33 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{29}H_{52}NaO_4Si_2$: 543.3302 $[M + Na]^+$, found: 543.3297 $[M + Na]^+$.

9,10-*syn,*10,11-*syn* **56a**: **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 7.57 (dd, 1H, *J* = 15.3, 11.1 Hz, H-3), 6.27 (d, 1H, *J* = 15.3 Hz, H-5), 6.06 (dd, 1H, *J* = 15.3, 11.1 Hz, H-4), 5.98 (d, 1H, *J* = 15.3 Hz, H-2), 5.61 (dd, 1H, *J* = 7.5, 7.5 Hz, H-7), 4.48 (d, 1H, *J* = 4.8 Hz, H-11), 4.11 (q, 2H, *J* = 7.2 Hz, H-16), 4.03-4.10 (m, 1H, H-9), 2.39 (d, 1H, *J* = 2.7 Hz, OH), 2.35-2.45 (m, 1H, H-8$_a$), 2.12-2.24 (m, 1H, H-8$_b$), 1.67-1.77 (m, 1H, H-10), 1.54 (s, 3H, H-14), 1.21 (d, 3H, *J* = 7.2 Hz, H-15), 0.99-1.05 (m, 3H, H-17), 1.00 (s, 9H. TBS), 0.96 (s, 9H, TBS), 0.25 (s, 3H, TBS), 0.14 (s, 3H, TBS), 0.12 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$ = 128.06 ppm): δ 166.9 (q, C-1), 145.7 (t, C-5), 145.5 (t, C-3), 135.6

(q, C-6), 134.5 (t, C-7), 124.5 (t, C-4), 120.7 (t, C-2), 107.9 (q, C-12), 89.3 (q, C-13), 72.8 (t, C-9), 67.9 (t, C-11), 60.1 (s, C-16), 44.4 (t, C-10), 34.9 (s, C-8), 26.2 (p, TBS), 25.9 (p, TBS), 18.4 (q, TBS), 16.7 (q, TBS), 14.4 (p, C-17), 12.4 (p, C-14), 8.5 (p, C-15), -4.0 (p, TBS), -4.6 (p, TBS), -4.9 (p, TBS) ppm.

9,10-*anti*,10,11-*syn* **56b**: **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 7.57 (dd, 1H, *J* = 15.3, 11.1 Hz, H-3), 6.25 (d, 1H, *J* = 15.3 Hz, H-5), 6.06 (dd, 1H, *J* = 15.3, 11.1 Hz, H-4), 5.98 (d, 1H, *J* = 15.3 Hz, H-2), 5.72 (dd, 1H, *J* = 7.3, 7.3 Hz, H-7), 4.83 (d, 1H, *J* = 3.1 Hz, H-11), 4.11 (q, 2H, *J* = 7.2 Hz, H-16), 3.86-3.94 (m, 1H, H-9), 2.61 (d, 1H, *J* = 3.8 Hz, OH), 2.26-2.35 (m, 1H, H-8$_a$), 2.12-2.24 (m, 1H, H-8$_b$), 1.76-1.84 (m, 1H, H-10), 1.54 (s, 3H, H-14), 0.99-1.05 (m, 6H, H-15 + H-17), 1.02 (s, 9H. TBS), 0.98 (s, 9H, TBS), 0.27 (s, 3H, TBS), 0.16 (s, 3H, TBS), 0.14 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$ = 128.06 ppm): δ 166.9 (q, C-1), 145.7 (t, C-5), 145.5 (t, C-3), 135.8 (q, C-6), 134.1 (t, C-7), 124.4 (t, C-4), 120.7 (t, C-2), 107.5 (q, C-12), 89.0 (q, C-13), 72.6 (t, C-9), 66.5 (t, C-11), 60.1 (s, C-16), 45.1 (t, C-10), 34.5 (s, C-8), 26.3 (p, TBS), 26.0 (p, TBS), 18.4 (q, TBS), 16.8 (q, TBS), 14.4 (p, C-17), 12.5 (p, C-14), 12.1 (p, C-15), -4.5 (p, TBS), -4.5 (p, TBS), -5.0 (p, TBS) ppm.

### MOM-protected MASAMUNE aldol product S56

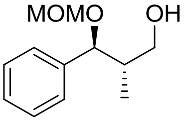


**S56**

Alcohol **S57** (300 mg, 0.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (8 ml) and cooled to 0 °C. $^i$Pr$_2$NEt (1.2 ml, 7.2 mmol, 14.0 eq) and MOMCl (0.27 ml, 3.6 mmol, 7.0 eq) were added and the reaction mixture was stirred for 10 d at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 10:1) to furnish product **S56** (324 mg, 0.5 mmol, 99%) as a colourless solid.

R$_f$ = 0.68 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -9.0 (*c* = 1.0, $CHCl_3$); mp. = 53 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.47-7.11 (m, 13H, Ph), 6.93 (s, 2H, Mes), 6.73-6.77 (m, 2H, Ph), 5.87 (d, 1H, *J* = 4.0 Hz, H-5), 4.99 (d, 1H, *J* = 16.7 Hz, H-8$_a$), 4.70 (d, 1H, *J* = 10.2 Hz, H-3), 4.68 (d, 1H, *J* = 16.7 Hz, H-8$_b$), 4.42 (s, 2H, MOM), 4.07 (qd, 1H, *J* = 6.7, 4.0 Hz, H-6), 3.24 (s, 3H, MOM), 2.97 (dq, 1H, *J* = 10.2, 7.2 Hz, H-2), 2.52 (s, 6H, Mes), 2.32 (s, 3H, Mes), 1.13 (d, 3H, *J* = 6.7 Hz, H-7), 0.81 (d, 3H, *J* = 7.2 Hz, H-4) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.1 (q, C-1), 142.7 (q, Ph), 140.4 (q, Ph), 139.3 (q, Ph), 138.6 (q, Ph), 138.6 (q, Ph), 133.7 (q, Ph), 132.3 (t, Ph), 128.7 (t, Ph), 128.6 (t, Ph), 128.5 (t, Ph), 128.5 (t, Ph), 128.1 (t, Ph), 128.1 (t, Ph), 127.9 (t, Ph), 127.3 (t, Ph), 125.9 (t, Ph), 94.0 (s, MOM), 80.2 (t, C-3), 78.3 (t, C-5), 57.1 (t, C-6), 56.1 (p, MOM), 48.2 (s, C-8), 47.0 (t, C-2), 23.0 (p, Mes), 21.1 (p, Mes), 14.3 (p, C-4), 13.8 (p, C-7) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{37}H_{43}NaNO_6S$: 652.2709 $[M + Na]^+$, found: 652.2731 $[M + Na]^+$.

### (2*S*,3*S*)-3-(Methoxymethoxy)-2-methyl-3-phenylpropan-1-ol (S58)

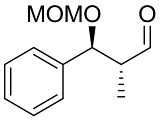


**S58**

Ester **S56** (320 mg, 0.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7 ml) and cooled to -78 °C. DIBAL-H (1.7 ml, *c* = 1.2 mol/l in toluene, 2.0 mmol, 4.0 eq) was slowly added and the solution was stirred for 2.5 h. The reaction was terminated by addition of ethyl acetate and the mixture was stirred overnight at rt after the addition of aq. Na-K-tartrate. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 5:1) to furnish alcohol **S58** (106 mg, 0.5 mmol, 98%) as a colourless liquid.

$R_f$ = 0.26 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -161.8 (*c* = 1.0, $CHCl_3$); $^1$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.38 (m, 5H, Ph), 4.48 (s, 2H, MOM), 4.44-4.46 (m, 1H, H-3), 3.68-3.78 (m, 2H, H-1), 3.40 (s, 3H, MOM), 2.98 (s, 1H, OH), 2.05-2.15 (m, 1H, H-2), 0.73 (d, 3H, *J* = 6.8 Hz, H-4) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 104.2 (q, Ph), 128.5 (t, Ph), 128.2 (t, Ph), 127.9 (t, Ph), 94.1 (s, MOM), 83.5 (t, C-3), 67.3 (s, C-1), 56.1 (p, MOM), 41.8 (t, C-2), 14.1 (p, C-4) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{18}NaO_3$: 233.1154 $[M + Na]^+$, found: 233.1156 $[M + Na]^+$.

### (2*R*,3*S*)-3-(Methoxymethoxy)-2-methyl-3-phenylpropanal (57)



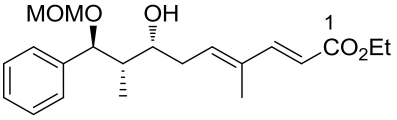
**57**

Alcohol **S58** (100 mg, 0.48 mmol, 1.0 eq) was dissoved in $CH_2Cl_2$ (9.5 ml) and $NaHCO_3$ (50 mg) and the DESS-MARTIN periodinane (242 mg, 0.57 mmol, 1.2 eq) were added and the reaction mixture was stirred for 2 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and the solution was stirred for 75 min. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish aldehyde **57** (88 mg, 0.42 mmol, 89%) as a colourless liquid. The aldehyde was immediately used in the next step.

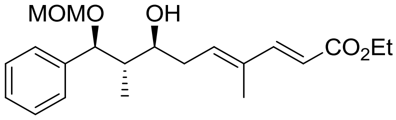
$R_f$ = 0.69 (PE:EE = 2:1); **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{16}NaO_3Si$: 231.1021 $[M + Na]^+$, found: 231.0994 $[M + Na]^+$.

### (2*E*,4*E*,7*R*,8*S*,9*S*)-Ethyl-7-hydroxy-9-(methoxy-methoxy)-4,8-dimethyl-9-phenylnona-2,4-dienoate (7,8-*anti*,8,9-*anti* 65a) and

### (2*E*,4*E*,7*S*,8*S*,9*S*)-ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethyl-9-phenylnona-2,4-dienoate (7,8-*syn*,8,9-*anti* 65b)



7,8-*syn*,8,9-*anti* **65b**

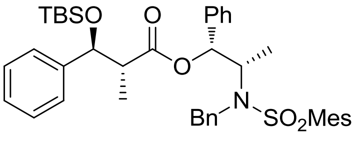


7,8-*anti*,8,9-*anti* **65a**

Following the general procedure, aldehyde **57** (38 mg, 0.18 mmol, 1.0 eq) was reacted with ester **6** (59 mg, 0.38 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 2:1) to furnish alcohols 7,8-*anti*,8,9-*anti* **65a** and 7,8-*syn*,8,9-*anti* **65b** (*d.r.*: 1:1, 49 mg, 0.13 mmol, 74%) as a colourless liquid.

$R_f$ = 0.13 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.41 (m, 12H, $Ph_{1,2}$ + H-$3_{1,2}$), 6.12 (dd, 1H, *J* = 7.0, 7.0 Hz, H-$5_1$), 5.91 (dd, 1H, *J* = 7.2, 7.2 Hz, H-$5_2$), 5.80 (d, 1H, *J* = 15.7 Hz, H-$2_1$), 5.79 (d, 1H, *J* = 15.7 Hz, H-$2_2$), 4.60 (d, 1H, *J* = 7.5 Hz, H-$9_1$), 4.48-4.54 (m, 3H, H-$9_2$ + MOM), 4.43-4.47 (m, 2H, MOM), 4.21 (q, 4H, *J* = 7.2 Hz, H-$12_{1,2}$), 4.07-4.13 (m, 1H, H-$7_1$), 3.94 (s, 1H, $OH_1$), 3.83-3.90 (m, 1H, H-$7_2$), 3.40 (s, 3H, $MOM_1$), 3.39 (s, 3H, $MOM_2$), 2.92 (d, 1H, *J* = 3.8 Hz, $OH_2$), 2.48-2.58 (m, 2H, H-$6_{a,1,2}$), 2.37-2.48 (m, 1H, H-$6_{b,1}$), 2.22-2.34 (m, 1H, H-$6_{b,2}$), 2.00-2.11 (m, 1H, H-$8_1$), 1.87-1.97 (m, 1H, H-$8_2$), 1.81 (s, 3H, H-$10_1$), 1.77 (s, 3H, H-$10_2$), 1.30 (t, 6H, *J* = 7.2 Hz, H-$13_{1,2}$), 0.84 (d, 3H, *J* = 7.2 Hz, H-$11_1$), 0.62 (d, 3H, *J* = 7.2 Hz, H-$11_2$) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-$1_1$), 167.7 (q, C-$1_2$), 149.6 (t, C-$3_1$), 149.5 (t, C-$3_2$), 140.4 (q, Ph), 139.7 (q, Ph), 138.4 (t, C-$5_1$), 138.1 (t, C-$5_2$), 134.5 (q, C-$4_1$), 134.3 (q, C-$4_2$), 128.6 (t, Ph), 128.5 (t, Ph), 128.3 (t, Ph), 128.2 (t, Ph), 128.0 (t, Ph), 127.5 (t, Ph), 116.1 (t, C-$2_1$), 115.9 (t, C-$2_2$), 94.9 (s, MOM), 93.8 (s, MOM), 83.3 (t, C-$9_1$), 82.1 (t, C-$9_2$), 74.7 (t, C-$7_1$), 70.4 (t, C-$7_2$), 60.3 (s, C-$12_1$), 60.3 (s, C-$12_2$), 56.3 (p, $MOM_1$), 56.3 (p, $MOM_2$), 44.4 (t, C-$8_1$), 43.6 (t, C-$8_2$), 33.8 (s, C-$6_{1,2}$), 14.5 (p, C-$13_{1,2}$), 13.0 (p, C-$11_1$), 12.6 (p, C-$10_1$), 12.5 (p, C-$10_2$), 10.8 (p, C-$11_2$) ppm. **HRMS** (ESI): *m/z*: calculated for $C_{21}H_{30}NaO_5$: 385.1991 $[M + Na]^+$, found: 385.1985 $[M + Na]^+$.

### TBS-protected MASAMUNE aldol product S59

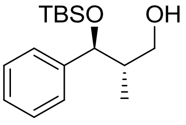


**S59**

Alcohol **S57** (300 mg, 0.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (6.5 ml) and cooled to 0 °C. 2,6-Lutidine (0.24 ml, 2.1 mmol, 4.0 eq) and TBSOTf (0.24 ml, 1.0 mmol, 2.0 eq) were added and the mixture was stirred for 1.5 h at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl ($c$ = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 10:1) to furnish alcohol **S59** (341 mg, 0.5 mmol, 95%) as a colourless solid.

$R_f$ = 0.61 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +21.3 ($c$ = 1.0, $CHCl_3$); m.p. = 52 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.46-7.04 (m, 13H, Ph), 6.89 (s, 2H, Mes), 6.66-6.70 (m, 2H, Ph), 5.73 (d, 1H, $J$ = 5.9 Hz, H-5), 4.89 (d, 1H, $J$ = 16.7 Hz, H-$8_a$), 4.76 (d, 1H, $J$ = 8.3 Hz, H-3), 4.46 (d, 1H, $J$ = 16.7 Hz, H-$8_b$), 4.02 (qd, 1H, $J$ = 6.7, 5.9 Hz, H-6), 2.75 (dq, 1H, $J$ = 8.3, 7.4 Hz, H-2), 2.44 (s, 6H, Mes), 2.31 (s, 3H, Mes), 1.15 (d, 3H, $J$ = 6.7 Hz, H-7), 0.77 (s, 9H, TBS), 0.70 (d, 3H, $J$ = 7.4 Hz, H-4), -0.06 (s, 3H, TBS), -0.25 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 173.5 (q, C-1), 142.6 (q, Ph), 142.1 (q, Ph), 140.6 (q, Ph), 138.9 (q, Ph), 138.4 (q, Ph), 133.2 (q, Ph), 132.3 (t, Ph), 128.6 (t, Ph), 128.5 (t, Ph), 128.4 (t, Ph), 128.3 (t, Ph), 127.9 (t, Ph), 127.9 (t, Ph), 127.5 (t, Ph), 127.3 (t, Ph), 126.5 (t, Ph), 77.9 (t, C-5), 77.0 (t, C-3), 56.9 (t, C-6), 49.0 (s, C-8), 48.4 (t, C-2), 26.0 (p, TBS), 23.1 (p, Mes), 21.1 (p, Mes), 18.3 (q, TBS), 14.7 (p, C-4), 13.8 (p, C-7), -4.6 (p, TBS), -4.8 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{41}H_{53}NaNO_5SiS$: 722.3311 $[M + Na]^+$, found: 722.3311 $[M + Na]^+$.

### (2*S*,3*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-methyl-3-phenylpropan-1-ol (S60)

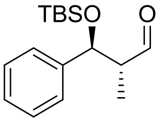


**S60**

Ester **S59** (335 mg, 0.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7 ml) and cooled to -78 °C. DIBAL-H (1.6 ml, $c$ = 1.2 mol/l in toluene, 1.9 mmol, 4.0 eq) was added and the reaction mixture was stirred for 2.5 h. The reaction was terminated by addition of ethyl acetate and after addition of aq. Na-K-tartrate stirring was continued overnight at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 10:1) to furnish alcohol **S60** (101 mg, 0.4 mmol, 75%) as a colourless liquid.

$R_f$ = 0.45 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -65.7 ($c$ = 1.0, $CHCl_3$) [Lit.: -28.6 ($c$ = 0.2, $CHCl_3$)]; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.38-7.21 (m, 5H, Ph), 4.56 (d, 1H, $J$ = 6.8 Hz, H-3), 3.68 (ddd, 1H, $J$ = 11.0, 6.0, 3.5 Hz, H-1$_a$), 3.60 (ddd, 1H, $J$ = 11.0, 6.8, 5.4 Hz, H-1$_b$), 2.93 (dd, 1H, $J$ = 6.0, 5.4 Hz, OH), 1.93 (qddd, 1H, $J$ = 7.0, 6.8, 6.8, 3.5 Hz, H-2), 0.89 (s, 9H, TBS), 0.85 (d, 3H, $J$ = 7.0 Hz, H-4), 0.04 (s, 3H, TBS), -0.26 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 143.7 (q, Ph), 128.2 (t, Ph), 127.6 (t, Ph), 126.8 (t, Ph), 81.3 (t, C-3), 66.5 (s, C-1), 43.2 (t, C-2), 26.0 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-4), -4.4 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{28}NaO_2Si$: 303.1756 $[M + Na]^+$, found: 303.1752 $[M + Na]^+$. The analytical data is in accordance with the literature.[S9]

### (2*R*,3*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-methyl-3-phenylpropanal (58)



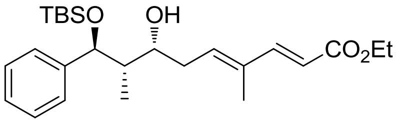
**58**

Alcohol **S60** (100 mg, 0.36 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7 ml) and $NaHCO_3$ (30 mg) and the DESS-MARTIN periodinane (181 mg, 0.2 mmol, 1.2 eq) were added and the mixture was stirred for 2 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 1 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **58** (71 mg, 0.25 mmol, 70%) as a colourless liquid. The aldehyde was used immediately in the next step.

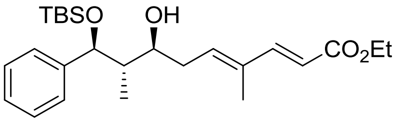
R$_f$ = 0.63 (PE:EE = 10:1); **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{26}NaO_2Si$: 301.1600 [M + Na]$^+$, found: 301.1416 [M + Na]$^+$.

**(2*E*,4*E*,7*S*,8*S*,9*S*)-Ethyl-9-(*tert*-butyldimethyl-silyloxy)-7-hydroxy-4,8-dimethyl-9-phenyl-nona-2,4-dienoate (**7,8-*anti*,8,9-*anti* **66a)** and

**(2*E*,4*E*,7*R*,8*S*,9*S*)-ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethyl-9-phenyl-nona-2,4-dienoate (**7,8-*syn*,8,9-*anti* **66b)**



7,8-*syn*,8,9-*anti* **66b**



7,8-*anti*,8,9-*anti* **66a**

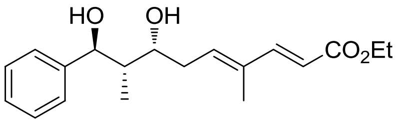
Following the general procedure, aldehyde **58** (34 mg, 0.12 mmol, 1.0 eq) was reacted with ester **6** (37 mg, 0.24 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 5:1) to furnish alcohols 7,8-*anti*,8,9-*anti* **66a** and 7,8-*syn*,8,9-*anti* **66b** [*d.r.*: 2:1 (**66a**:**66b**), 42 mg, 0.10 mmol, 79%] as a yellow liquid.

R$_f$ = 0.40 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{25}H_{40}NaO_4Si$: 455.2594 [M + Na]$^+$, found: 455.2589 [M + Na]$^+$.

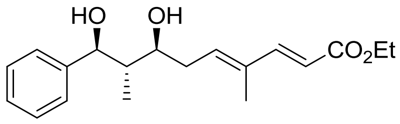
7,8-*anti*,8,9-*anti* **66a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.22-7.40 (m, 6H, Ph + H-3), 6.10 (dd, 1H, *J* = 6.8, 6.8 Hz, H-5), 5.79 (d, 1H, *J* = 16.0 Hz, H-2), 4.54 (d, 1H, *J* = 8.5 Hz, H-9), 4.20 (q, 2H, *J* = 7.0 Hz, H-12), 3.92 (s, 1H, OH), 3.78-3.84 (m, 1H, H-7), 2.45-2.53 (m, 1H, H-6$_a$), 2.32-2.43 (m, 1H, H-6$_a$), 1.89-1.99 (m, 1H, H-8), 1.78 (s, 3H, H-10), 1.30 (t, 3H, *J* = 7.0 Hz, H-13), 0.87 (s, 9H, TBS), 0.62 (d, 3H, *J* = 6.8 Hz, H-11), 0.02 (s, 3H, TBS), -0.32 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.6 (t, C-3), 143.3 (q, Ph), 138.3 (t, C-5), 134.4 (q, C-4), 128.3 (t, Ph), 127.8 (t, Ph), 127.5 (t, Ph), 115.8 (t, C-2), 81.5 (t, C-9), 74.4 (t, C-7), 60.3 (s, C-12), 46.2 (t, C-8), 33.8 (s, C-6), 26.0 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-13), 12.8 (p, C-11), 12.6 (p, C-10), -4.3 (p, TBS), -5.0 (p, TBS) ppm.

7,8-*syn*,8,9-*anti* **66b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.22-7.40 (m, 6H, Ph + H-3), 5.72-5.78 (m, 1H, H-5), 5.75 (d, 1H, *J* = 15.7 Hz, H-2), 4.81 (d, 1H, *J* = 3.8 Hz, H-9), 4.20 (q, 2H, *J* = 7.0 Hz, H-12), 3.88-3.94 (m, 1H, H-7), 3.58 (s, 1H, OH), 2.32-2.43 (m, 1H, H-6$_a$), 2.12-2.22 (m, 1H, H-6$_b$), 1.66-1.73 (m, 4H, H-8 + H-10), 1.28 (t, 3H, *J* = 7.0 Hz, H-13), 1.06 (d, 3H, *J* = 6.8 Hz, H-11), 0.92 (s, 9H, TBS), 0.08 (s, 3H, TBS), -0.21 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 143.2 (q, Ph), 138.2 (t, C-5), 134.3 (q, C-4), 128.3 (t, Ph), 127.5 (t, Ph), 126.2 (t, Ph), 115.9 (t, C-2), 80.6 (t, C-9), 69.9 (t, C-7), 60.3 (s, C-12), 44.0 (t, C-8), 34.2 (s, C-6), 26.0 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-13), 12.5 (p, C-10), 11.6 (p, C-11), -4.5 (p, TBS), -5.1 (p, TBS) ppm.

**(2*E*,4*E*,7*S*,8*S*,9*S*)-Ethyl-7,9-dihydroxy-4,8-dimethyl-9-phenylnona-2,4-dienoate (**7,8-*anti*,8,9-*anti* **S61a)** and
**(2*E*,4*E*,7*R*,8*S*,9*S*)-ethyl-7,9-dihydroxy-4,8-dimethyl-9-phenylnona-2,4-dienoate (**7,8-*syn*,8,9-*anti* **S61b)**



7,8-*syn*,8,9-*anti* **S61b**



7,8-*anti*,8,9-*anti* **S61a**

A mixture of alcohols **66** [*d.r.*: 2:1 (**66a**:**66b**), 11 mg, 26 µmol, 1.0 eq] was dissoved in THF (0.4 ml) and the solution was cooled to 0 °C. TBAF·$3H_2O$ (15 mg, 48 µmol, 1.8 eq) was dissolved in THF (0.3 ml) and added to the first solution. The reaction mixture was stirred for 1 h at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 2:1) to furnish diols 7,8-*anti*,8,9-*anti* **S61a** and 7,8-*syn*,8,9-*anti* **S61b** [*d.r.*: 2:1 (**S61a**:**S61b**), 8.3 mg, 26 µmol, 99%] as a colourless liquid.

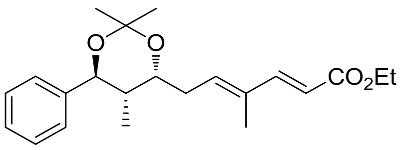
$R_f$ = 0.26 (PE:EE = 2:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{19}H_{26}NaO_4$: 341.1729 $[M + Na]^+$, found: 341.1729 $[M + Na]^+$.

7,8-*anti*,8,9-*anti* **S61a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.26-7.40 (m, 6H, Ph + H-3), 6.10 (dd, 1H, *J* = 7.5, 7.2 Hz, H-5), 5.82 (d, 1H, *J* = 15.7 Hz, H-2), 4.57 (d, 1H, *J* = 8.9 Hz, H-9), 4.21 (q, 2H, *J* = 7.0 Hz, H-12), 3.88 (ddd, 1H, *J* = 7.7, 7.7, 3.6 Hz, H-7), 3.67 (brs, 1H, OH), 2.89 (brs, 1H, OH), 2.50-2.59 (m, 1H, H-$6_a$), 2.39-2.50 (m, 1H, H-$6_b$), 1.90-2.02 (m, 1H, H-8), 1.81 (s, 3H, H-10), 1.30 (t, 3H, *J* = 7.2 Hz, H-13), 0.59 (d, 3H, *J* = 7.2 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 143.2 (q, Ph), 137.5 (t, C-5), 135.1 (q, C-4), 128.7 (t, Ph), 128.2 (t, Ph), 127.2

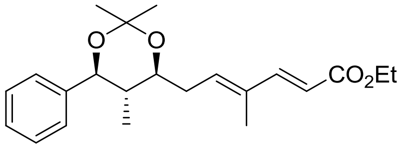
(t, Ph), 116.2 (t, C-2), 80.9 (t, C-9), 76.2 (t, C-7), 60.4 (s, C-12), 44.6 (t, C-8), 34.6 (s, C-6), 14.5 (p, C-13), 13.6 (p, C-11), 12.6 (p, C-10) ppm.

7,8-*syn*,8,9-*anti* **S61b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.26-7.40 (m, 6H, Ph + H-3), 5.87 (dd, 1H, *J* = 7.5, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.74 (d, 1H, *J* = 6.5 Hz, H-9), 4.20 (q, 2H, *J* = 7.1 Hz, H-12), 3.93-3.98 (m, 1H, H-7), 3.19 (brs, 1H, OH), 2.73 (brs, 1H, OH), 2.50-2.59 (m, 1H, H-6$_a$), 2.27-2.36 (m, 1H, H-6$_b$), 1.90-2.02 (m, 1H, H-8), 1.78 (s, 3H, H-10), 1.29 (t, 3H, *J* = 7.1 Hz, H-13), 0.92 (d, 3H, *J* = 6.8 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 143.6 (q, Ph), 137.9 (t, C-5), 134.9 (q, C-4), 128.6 (t, Ph), 127.8 (t, Ph), 126.4 (t, Ph), 116.3 (t, C-2), 78.4 (t, C-9), 71.9 (t, C-7), 60.4 (s, C-12), 44.7 (t, C-8), 33.7 (s, C-6), 14.5 (p, C-13), 12.6 (p, C-10), 11.7 (p, C-11) ppm.

**Acetonids** 7,8-*anti*,8,9-*anti* **S62a and** 7,8-*syn*,8,9-*anti* **S62b**



7,8-*syn*,8,9-*anti* **S62b**



7,8-*anti*,8,9-*anti* **S62a**

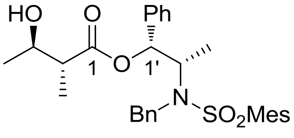
A mixture of diols **S61** [*d.r.*: 2:1 (**S61a**:**S61b**), 7 mg, 22 µmol, 1.0 eq] was dissolved in $CH_2Cl_2$ (1.3 ml). 2,2-Dimethoxypropane (0.25 ml) and PPTS (0.5 mg, catalytic) were added and stirring was continued for 3 h at RT. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1). Diols 7,8-*anti*,8,9-*anti* **S62a** and 7,8-*syn*,8,9-*anti* **S62b** [*d.r.*: 2:1 (**S62a**:**S62b**), 8 mg, 22 µmol, 99%] were isolated as a colourless liquid.

$R_f$ = 0.82 (PE:EE = 2:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{30}NaO_4$: 381.2042 $[M + Na]^+$, found: 381.2032 $[M + Na]^+$.

7,8-*anti*,8,9-*anti* **S62a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.41 (m, 6H, Ph + H-3), 6.08 (dd, 1H, *J* = 7.0, 7.0 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.41 (d, 1H, *J* = 10.2 Hz, H-9), 4.22 (q, 2H, *J* = 7.0 Hz, H-12), 4.16 (ddd, 1H, *J* = 10.1, 7.2, 3.1 Hz, H-7), 2.56 (ddd, 1H, *J* = 15.8, 7.2, 3.1 Hz, H-6$_a$), 2.27-2.47 (m, 1H, H-6$_b$), 1.78 (s, 3H, H-10), 1.56-1.66 (m, 1H, H-8), 1.55 (s, 3H, H-15$_a$), 1.47 (s, 3H, H-15$_b$), 1.31 (t, 3H, *J* = 7.0 Hz, H-13), 0.65 (d, 3H, *J* = 6.5 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.8 (q, C-1), 149.6 (t, C-3), 140.6 (q, Ph), 137.9 (t, C-5), 134.2 (q, C-4), 128.5 (t, Ph), 128.2 (t, Ph), 127.9 (t, Ph), 115.9 (t, C-2), 98.9 (q, C-14), 78.5 (t, C-9), 74.5 (t, C-7), 60.4 (s, C-12), 40.3 (t, C-8), 32.8 (s, C-6), 30.3 (p, C-$15_a$), 19.8 (p, C-$15_b$), 14.5 (p, C-13), 12.6 (p, C-11), 12.4 (p, C-10) ppm.

7,8-*syn*,8,9-*anti* **S62b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.27-7.41 (m, 6H, Ph + H-3), 5.92 (dd, 1H, *J* = 6.7, 6.7 Hz, H-5), 5.82 (d, 1H, *J* = 15.7 Hz, H-2), 4.26 (d, 1H, *J* = 6.8 Hz, H-9), 4.21 (q, 2H, *J* = 7.1 Hz, H-12), 4.12-4.18 (m, 1H, H-7), 2.27-2.47 (m, 2H, H-6), 2.03-2.12 (m, 1H, H-8), 1.81 (s, 3H, H-10), 1.45 (s, 3H, H-$15_a$), 1.43 (s, 3H, H-$15_b$), 1.30 (t, 3H, *J* = 7.2 Hz, H-13), 0.91 (d, 3H, *J* = 6.5 Hz, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 141.8 (q, Ph), 137.9 (t, C-5), 134.3 (q, C-4), 128.6 (t, Ph), 127.9 (t, Ph), 127.2 (t, Ph), 116.1 (t, C-2), 101.4 (q, C-14), 77.7 (t, C-9), 69.1 (t, C-7), 60.4 (s, C-12), 41.9 (t, C-8), 30.5 (s, C-6), 25.0 (p, C-$15_a$), 24.1 (p, C-$15_b$), 14.5 (p, C-13), 12.7 (p, C-10), 11.6 (p, C-11) ppm.

### MASAMUNE aldol product S63



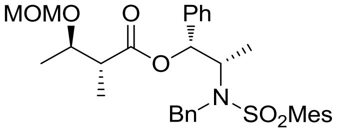
**S63**

Propionated MASAMUNE auxiliary **S64**[S10] (3.0 g, 6.3 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (30 ml) and cooled to -78 °C. $Et_3N$ (2.1 ml, 15.0 mmol, 2.4 eq) and $(cy)_2BOTf$ (13.8 ml, *c* = 1 mol/l in hexane, 13.8 mmol, 2.2 eq) were added. The solution was stirred 2 h at -78 °C. Acetaldehyde (**S11**) (1.4 ml, 25.0 mmol, 4.0 eq) was dissolved in $CH_2Cl_2$ (5 ml) and added to the first solution. The reaction mixture was stirred for 1 h during which time the temperature was raised from -78 °C to rt. The reaction was terminated by the addition of phosphate buffer (pH = 7, 26 ml), MeOH (128 ml) and aq. $H_2O_2$ (13 ml, 30%ig) and stirring was continued for 16 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 15:1 → 5:1) to furnish ester **S63** (*d.r.* > 20:1, 3.1 g, 5.9 mmol, 94%,) as a colourless solid.

$R_f$ = 0.11 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +10.1 (*c* = 1.0, $CHCl_3$); m.p. = 139 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.15-7.31 (m, 8H, Ph), 6.84-6.93 (m, 4H, Ph), 5.86 (d, 1H, *J* = 4.4 Hz, H-1'), 4.74 (d, 1H, *J* = 16.5 Hz, H-$4_a$'), 4.55 (d, 1H, *J* = 16.5 Hz, H-$4_b$'), 4.12 (qd, 1H, *J* = 6.6, 4.4 Hz, H-2'), 3.83 (dq, 1H, *J* = 7.0, 6.6 Hz, H-3), 2.49 (s, 6H, Mes), 2.37 (qd, 1H, *J* = 7.4, 7.0 Hz, H-2), 2.28 (s, 3H, Mes), 1.18 (d, 3H, *J* = 6.6 Hz, H-3'+H-4), 1.12 (d, 3H, *J* = 7.4 Hz, H-6) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ

174.6 (q, C-1), 142.7 (q, Ph), 140.4 (q, Ph), 138.6 (q, Ph), 138.3 (q, Ph), 133.5 (q, Ph), 132.3 (t, Ph), 128.6 (t, Ph), 128.5 (t, Ph), 128.1 (t, Ph), 127.7 (t, Ph), 127.3 (t, Ph), 126.1 (t, Ph), 78.4 (t, C-1’), 69.4 (t, C-3), 56.9 (t, C-2’), 48.4 (s, C-4’), 47.2 (t, C-2), 23.1 (p, Mes), 21.0 (p, Mes), 20.7 (p, C-4), 14.1 (p, C-3’), 13.5 (p, C-5) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{30}H_{37}NaNO_5S$: 546.2290 $[M + Na]^+$, found: 546.2288 $[M + Na]^+$.

### MOM-protected MASAMUNE aldol product S65

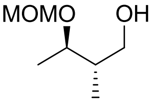


**S65**

Alcohol **S63** (1.0 g, 1.9 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (30 ml) and the solution was cooled to 0 °C. $^{i}Pr_2NEt$ (3.4 ml, 19.1 mmol, 10 eq) and MOMCl (0.73 ml, 9.5 mmol, 5 eq) were added. The solution was warmed up to rt and stirred for 7 d at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1) to furnish MOM-ether **S65** (1.1 g, 1.9 mmol, 98%) as a colourless oil.

$R_f$ = 0.29 (PE:EE = 4:1); $[\alpha]_D^{20}$ = +28.8 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33-7.39 (m, 2H, Ph), 7.12-7.28 (m, 6H, Ph), 6.88-6.92 (m, 2H, Ph), 6.76-6.81 (m, 2H, Ph), 5.78 (d, 1H, *J* = 4.4 Hz, H-1‘), 4.87 (d, 1H, *J* = 16.7 Hz, H-4‘), 4.53-4.61 (m, 3H, H-4‘ + MOM), 4.02-4.10 (m, 1H, H-2‘), 3.87 (dq, 1H, *J* = 6.8, 6.6 Hz, H-3), 3.32 (s, 3H, MOM), 2.63 (qd, 1H, *J* = 7.1, 6.8 Hz, H-2), 2.48 (s, 6H, Mes), 2.30 (s, 3H, Mes), 1.78 (d, 3H, *J* = 6.6 Hz, H-4), 1.30 (d, 3H, *J* = 7.2 Hz, H-3‘), 1.06 (d, 3H, *J* = 7.1 Hz, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 173.64 (q, C-1), 142.7 (q, Ph), 140.4 (q, Ph), 139.0 (q, Ph), 138.5 (q, Ph), 133.6 (q, Ph), 132.3 (t, Ph), 128.5 (t, Ph), 128.4 (t, Ph), 128.0 (t, Ph), 127.2 (t, Ph), 126.1 (t, Ph), 95.7 (s, MOM), 78.1 (t, C-1‘), 75.4 (t, C-3), 56.9 (t, C-2‘), 55.7 (p, MOM), 48.2 (s, C-4‘), 46.4 (t, C-2), 23.0 (p, Mes), 21.0 (p, Mes), 17.5 (p, C-4), 13.8 (p, C-3‘), 13.1 (p, C-5) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{32}H_{41}NaNO_6S$: 590.2552 $[M + Na]^+$, found: 590.2550 $[M + Na]^+$.

### (2*S*,3*R*)-3-(Methoxymethoxy)-2-methylbutan-1-ol (S66)

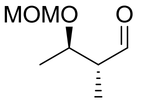


**S66**

Ester **S65** (1.0 g, 1.8 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (25 ml) and cooled to -78 °C. DIBAL-H (6.1 ml, $c = 1.2$ mol/l in toluene, 7.3 mmol, 4 eq) was slowly added and the reaction mixture was stirred for 1.5 h at -78 °C. The reaction was terminated by addition of ethyl acetate and the mixture was warmed up to rt. Then, aq. Na-K-tartrate was added and the solution was stirred for 16 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 3:1) to furnish alcohol **S66** (250 mg, 1.7 mmol, 92%) as a colourless liquid.

$R_f = 0.07$ (PE:EE = 2:1); $[\alpha]_D^{20} = -68.4$ ($c = 1.0$, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.73 (d, 1H, $J = 6.8$ Hz, MOM), 4.61 (d, 1H, $J = 6.8$ Hz, MOM), 3.72 (dd, 1H, $J = 11.1, 3.8$ Hz, H-$1_a$), 3.65 (dq, 1H, $J = 6.7, 6.5$ Hz, H-3), 3.57 (dd, 1H, $J = 11.1, 6.5$ Hz, H-$1_b$), 3.40 (s, 3H, MOM), 2.47 (brs, 1H, OH), 1.74 (qddd, 1H, $J = 6.9, 6.7, 6.5, 3.8$ Hz, H-2), 1.20 (d, 3H, $J = 6.5$ Hz, H-4), 0.95 (d, 3H, $J = 6.9$ Hz, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 95.2 (s, MOM), 77.8 (t, C-3), 66.3 (s, C-1), 55.9 (p, MOM), 41.3 (t, C-2), 18.1 (p, C-4), 14.1 (p, C-5) ppm; **HRMS** (ESI): $m/z$: calculated for $C_7H_{16}NaO_3$: 171.0997 $[M + Na]^+$, found: 171.1002 $[M + Na]^+$.

### (2*R*,3*R*)-3-(Methoxymethoxy)-2-methylbutanal (59)

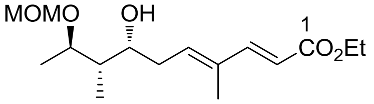


**59**

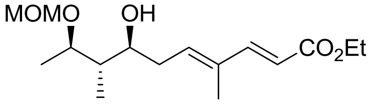
Alcohol **S66** (50 mg, 0.34 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (6.5 ml) and $NaHCO_3$ (15 mg) added. DESS-MARTIN periodinane (172 mg, 0.41 mmol, 1.2 eq) was added and the reaction mixture was stirred for 75 min at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1). Aldehyde **59** (19 mg, 0.13 mmol, 38%) was obtained as a colourless liquid and used immediately in the next step.

### (2*E*,4*E*,7*S*,8*S*,9*R*)-Ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethyldeca-2,4-dienoate (7,8-*anti*,8,9-*anti* 67a) and

## (2*E*,4*E*,7*R*,8*S*,9*R*)-ethyl-7-hydroxy-9-(methoxymethoxy)-4,8-dimethyldeca-2,4-dienoate (7,8-*syn*,8,9-*anti* 67b)



7,8-*syn*,8,9-*anti* **67b**



7,8-*anti*,8,9-*anti* **67a**

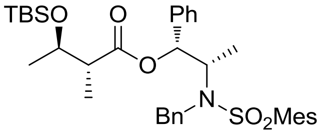
Following the general procedure, aldehyde **59** (15 mg, 10 µmol, 1 eq) was reacted with ester **6** (31 mg, 20 µmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 1.7:1) to furnish alcohols 7,8-*anti*,8,9-*anti* **67a** and 7,8-*syn*,8,9-*anti* **67b** [*d.r.*: 1:2.3 (**67a**:**67b**), 26 mg, 9 µmol, 87%] as a colourless liquid.

$R_f$ = 0.15 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{28}NaO_5$: 323.1834 $[M + Na]^+$, found: 323.1833 $[M + Na]^+$.

7,8-*anti*,8,9-*anti* **67a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.35 (d, 1H, *J* = 15.7 Hz, H-3), 6.05 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.73 (d, 1H, *J* = 7.7 Hz, MOM), 4.62 (d, 1H, *J* = 7.7 Hz, MOM), 4.20 (q, 2H, *J* = 7.2 Hz, H-13), 3.74-3.82 (m, 1H, H-7), 3.67-3.75 (m, 1H, H-9), 3.38 (s, 3H, MOM), 2.42-2.52 (m, 1H, H-$6_a$), 2.33-2.41 (m, 1H, H-$6_b$), 1.80 (s, 3H, H-12), 1.69-1.79 (m, 1H, H-8), 1.29 (t, 3H, *J* = 7.2 Hz, H-14), 1.19 (d, 3H, *J* = 6.1 Hz, H-10), 0.86 (d, 3H, *J* = 7.2 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 138.1 (t, C-5), 134.8 (q, C-4), 116.1 (t, C-2), 95.0 (s, MOM), 76.8 (t, C-7), 74.0 (t, C-9), 60.3 (s, C-13), 55.9 (p, MOM), 44.2 (t, C-8), 34.0 (s, C-6), 17.5 (p, C-10), 14.5 (p, C-14), 12.6 (p, C-11), 12.4 (p, C-12) ppm.

7,8-*syn*,8,9-*anti* **67b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.94 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.70 (d, 1H, *J* = 6.8 Hz, MOM), 4.60 (d, 1H, *J* = 6.8 Hz, MOM), 4.20 (q, 2H, *J* = 7.2 Hz, H-13), 4.09-4.15 (m, 1H, H-9), 3.67-3.75 (m, 1H, H-7), 3.39 (s, 3H, MOM), 2.42-2.52 (m, 1H, H-$6_a$), 2.24-2.33 (m, 1H, H-$6_b$), 1.80 (s, 3H, H-12), 1.48-1.56 (m, 1H, H-8), 1.29 (t, 3H, *J* = 7.2 Hz, H-14), 1.23 (d, 3H, *J* = 6.5 Hz, H-10), 0.97 (d, 3H, *J* = 7.2 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 138.5 (t, C-5), 134.3 (q, C-4), 116.1 (t, C-2), 95.7 (s, MOM), 77.8 (t, C-7), 70.1 (t, C-9), 60.3 (s, C-13), 56.0 (p, MOM), 42.7 (t, C-8), 33.9 (s, C-6), 18.7 (p, C-10), 14.5 (p, C-14), 12.6 (p, C-11), 10.7 (p, C-12) ppm.

### TBS-protected MASAMUNE aldol product S67

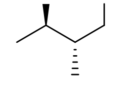


**S67**

Alcohol **S63** (1.5 g, 2.7 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (40 ml) and cooled to 0 °C. 2,6-Lutidine (1.3 ml, 11.5 mmol, 4 eq) and TBSOTf (1.3 ml, 5.7 mmol, 2 eq) were added and the reaction mixture was stirred for 2 h. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish alcohol **S67** (1.8 g, 2.8 mmol, 99%) as a colourless liquid.

$R_f$ = 0.63 (PE:EE = 4:1); $[\alpha]_D^{20}$ = +18.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.31-7.37 (m, 2H, Ph), 7.10-7.29 (m, 6H, Ph), 6.80-6.89 (m, 4H, Ph), 5.74 (d, 1H, *J* = 5.1 Hz, H-1‘), 4.82 (d, 1H, *J* = 16.6 Hz, H-$4_a$‘), 4.49 (d, 1H, *J* = 16.6 Hz, H-$4_b$‘), 3.99-4.14 (m, 2H, H-2‘ + H-3), 2.41-2.49 (m, 7H, Mes + H-2), 2.29 (s, 3H, Mes), 1.17 (d, 3H, *J* = 7.2 Hz, H-3‘), 1.02 (d, 3H, *J* = 7.2 Hz, H-5), 1.02 (d, 3H, *J* = 6.1 Hz, H-4), 0.86 (s, 9H, TBS), 0.04 (s, 3H, TBS), 0.03 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 173.0 (q, C-1), 142.6 (q, Ph), 140.5 (q, Ph), 138.6 (q, Ph), 138.5 (q, Ph), 133.4 (q, Ph), 132.3 (t, Ph), 128.5 (t, Ph), 128.4 (t, Ph), 128.0 (t, Ph), 128.0 (t, Ph), 127.4 (t, Ph), 126.4 (t, Ph), 78.1 (t, C-1‘), 69.3 (t, C-3), 56.9 (t, C-2‘), 48.3 (s, C-4‘), 47.6 (t, C-2), 26.0 (p, TBS), 23.1 (p, Mes), 21.0 (p, Mes), 20.1 (p, C-4), 18.2 (q, TBS), 14.2 (p, C-3‘), 11.7 (p, C-5), -4.5 (p, TBS), -4.7 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{36}H_{51}NaNO_5SiS$: 660.3155 $[M + Na]^+$, found: 660.3173 $[M + Na]^+$.

### (2*S*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylbutan-1-ol (S68)

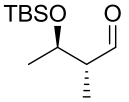


**S68**

Ester **S67** (1.8 g, 2.8 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (40 ml) and cooled to -78 °C. DIBAL-H (9.3 ml, *c* = 1.2 mol/l in toluene, 11.1 mmol, 4 eq) was slowly added and stirring was continued for 1.5 h at -78 °C. The reaction was terminated by addition of ethyl acetate and warmed up to rt. Then, aq. Na-K-tartrate was added and the mixture was stirred for 16 at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The

combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 50:1 → 10:1) to furnish alcohol **S68** (0.6 g, 2.8 mmol, 99%) as a colourless liquid.
$R_f$ = 0.33 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -22.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 3.59-3.67 (m, 2H, H-$1_a$ + H-3), 3.48 (dd, 1H, *J* = 10.6, 5.8 Hz, H-$1_b$), 1.95 (brs, 1H, OH), 1.42-1.53 (m, 1H, H-2), 1.02 (d, 3H, *J* = 6.2 Hz, H-4), 0.94 (s, 9H, TBS), 0.85 (d, 3H, *J* = 6.8 Hz, H-5), 0.04 (p, 3H, TBS), 0.01 (p, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$ = 128.06 ppm): δ 72.6 (t, C-3), 65.4 (s, C-1), 42.6 (t, C-2), 26.0 (p, TBS), 21.5 (p, C-4), 18.2 (q, TBS), 14.0 (p, C-5), -4.2 (p, TBS), -4.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{11}H_{27}O_2Si$: 219.1780 $[M + H]^+$, found: 219.1776 $[M + H]^+$.

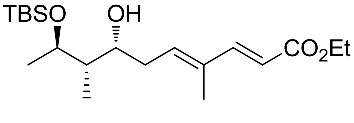
### (2*R*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylbutanal (60)



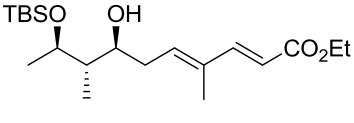
**60**

Alcohol **S68** (120 mg, 0.55 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (5 ml) and $NaHCO_3$ (30 mg) was added. DESS-MARTI periodinane (280 mg, 0.66 mmol, 1.2 eq) was added and the reaction mixture was stirred for 1 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **60** (110 mg, 0.51 mmol, 92%) as a colourless liquid, which was used immediately in the next step.
$R_f$ = 0.65 (PE:EE = 5:1).

### (2*E*,4*E*,7*S*,8*S*,9*R*)-Ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethyldeca-2,4-dienoate (7,8-*anti*,8,9-*anti* 68a) and (2*E*,4*E*,7*R*,8*S*,9*R*)-ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethyldeca-2,4-dienoate (7,8-*syn*,8,9-*anti* 68b)



7,8-*syn*,8,9-*anti* **68b**



7,8-*anti*,8,9-*anti* **68a**

Following the general procedure, aldehyde **60** (11 mg, 50 µmol, 1 eq) was reacted with ester **6** (15 mg, 100 µmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 5:1) to furnish alcohols 7,8-*anti*,8,9-*anti* **68a** and 7,8-*syn*,8,9-*anti* **68b** [*d.r.*: 2:1 (**68b**:**68a**), 15 mg, 39 µmol, 79%] as colourless liquids.

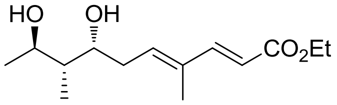
**HRMS** (ESI): *m/z*: calculated for $C_{20}H_{39}O_4Si$: 371.2618 $[M + H]^+$, found: 371.2612 $[M + H]^+$.

7,8-*anti*,8,9-*anti* **68a**: $R_f$ = 0.07 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -15.7 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 7.37 (d, 1H, *J* = 15.7 Hz, H-3), 6.08 (dd, 1H, *J* = 7.3, 6.3 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.21 (q, 2H, *J* = 7.2 Hz, H-13), 3.80 (qd, 1H, *J* = 6.3, 6.3 Hz, H-9), 3.70 (ddd, 1H, *J* = 7.7, 7.7, 3.8 Hz, H-7), 2.47 (ddd, 1H, *J* = 15.7, 6.3, 3.8 Hz, H-$6_a$), 2.35 (ddd, 1H, *J* = 15.7, 7.7, 7.3 Hz, H-$6_b$), 1.80 (s, 3H, H-12), 1.55-1.65 (m, 1H, H-8), 1.30 (t, 3H, *J* = 7.2 Hz, H-14), 1.20 (d, 3H, *J* = 6.3 Hz, H-10), 0.90 (s, 9H, TBS), 0.82 (d, 3H, *J* = 6.8 Hz, H-12), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$ = 128.06 ppm): δ 167.7 (q, C-1), 149.6 (t, C-3), 138.4 (t, C-5), 134.5 (q, C-4), 115.9 (t, C-2), 74.1 (t, C-7), 73.7 (t, C-9), 60.3 (s, C-13), 45.7 (t, C-8), 34.0 (s, C-6), 26.0 (p, TBS), 22.3 (p, C-10), 18.1 (q, TBS), 14.5 (p, C-14), 13.3 (p, C-12), 12.6 (p, C-11), -4.0 (p, TBS), -4.7 (p, TBS) ppm.

7,8-*syn*,8,9-*anti* **68b**: $R_f$ = 0.12 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -3.7 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.92 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.15-4.24 (m, 3H, H-7 + H-13), 3.96 (qd, 1H, *J* = 6.4, 2.6 Hz, H-9), 2.46 (ddd, 1H, *J* = 15.0, 7.3, 7.3 Hz, H-$6_a$), 2.27 (ddd, 1H, *J* = 15.0, 7.4, 7.3 Hz, H-$6_b$), 1.80 (s, 3H, H-12), 1.36-1.44 (m, 1H, H-8), 1.29 (t, 3H, *J* = 7.2 Hz, H-14), 1.26 (d, 3H, *J* = 6.4 Hz, H-10), 1.02 (d, 3H, *J* = 6.8 Hz, H-12), 0.89 (s, 9H, TBS), 0.09 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$ = 128.06 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 138.3 (t, C-5), 134.3 (q, C-4), 116.0 (t, C-2), 74.7 (t, C-7), 70.1 (t, C-9), 60.3 (s, C-13), 42.0 (t, C-8), 34.2 (s, C-6), 25.9 (p, TBS), 22.2 (p, C-10), 18.0 (q, TBS), 14.5 (p, C-14), 12.6 (p, C-11), 11.6 (p, C-12), -4.2 (p, TBS), -5.0 (p, TBS) ppm.

### (2*E*,4*E*,7*R*,8*R*,9*R*)-Ethyl-7,9-dihydroxy-4,8-dimethyldeca-2,4-dienoate

**(**7,8-*syn*,8,9-*anti* **S69b)**



7,8-*syn*,8,9-*anti* **S69b**

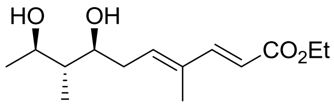
Alcohol 7,8-*syn*,8,9-*anti* **68b** (17 mg, 46 µmol, 1.0 eq) was dissolved in THF (1.3 ml) and the solution was cooled to 0 °C. TBAF·3$H_2O$ (19 mg, 60 µmol, 1.3 eq) was added and the reaction mixture was stirred for 2 h at 0 °C. The reaction was terminated by addition of aq.

$NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 5:1 → 1:1) to furnish diol 7,8-*syn*,8,9-*anti* **S69b** (8 mg, 32 μmol, 70%) as a colourless liquid.

$R_f$ = 0.13 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +15.4 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.95 (dd, 1H, *J* = 7.5, 7.0 Hz, H-5), 5.82 (d, 1H, *J* = 15.7 Hz, H-2), 4.21 (q, 2H, *J* = 7.4 Hz, H-13), 4.06 (ddd, 1H, *J* = 8.2, 5.5, 2.2 Hz, H-7), 3.88 (qd, 1H, *J* = 6.5, 6.5 Hz, H-9), 2.50 (ddd, 1H, *J* = 15.3, 8.2, 7.5 Hz, H-$6_a$), 2.43 (brs, 1H, OH), 2.33 (ddd, 1H, *J* = 15.3, 7.0, 5.5 Hz, H-$6_b$), 1.81 (s, 3H, H-11), 1.59 (qdd, 1H, *J* = 7.0, 6.5, 2.2 Hz, H-8), 1.30 (t, 3H, *J* = 7.4 Hz, H-14), 1.27 (d, 3H, *J* = 6.5 Hz, H-10), 0.96 (d, 3H, *J* = 7.0 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 138.0 (t, C-5), 134.9 (q, C-4), 116.4 (t, C-2), 72.3 (t, C-7), 71.7 (t, C-9), 60.4 (s, C-13), 43.3 (t, C-8), 33.4 (s, C-6), 22.4 (p, C-10), 14.5 (p, C-14), 12.6 (p, C-11), 11.9 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{25}O_4$ and $C_{14}H_{24}NaO_4$: 257.1753 $[M + H]^+$ and 279.1572 $[M + Na]^+$, found: 257.1745 $[M + H]^+$ and 279.1573 $[M + Na]^+$.

### (2*E*,4*E*,7*S*,8*R*,9*R*)-Ethyl-7,9-dihydroxy-4,8-dimethyldeca-2,4-dienoate

**(**7,8-*anti*,8,9-*anti* **S69a)**



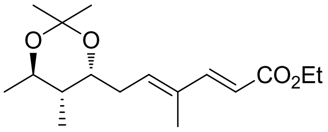
7,8-*anti*,8,9-*anti* **S69a**

Alcohol 7,8-*anti*,8,9-*anti* **68a** (12 mg, 32 μmol, 1.0 eq) was dissolved in THF (0.9 ml) and the solution was cooled to 0 °C. TBAF·3$H_2O$ (13 mg, 41 μmol, 1.3 eq) was added and stirring was continued for 2 h at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 2:1) to furnish diol 7,8-*anti*,8,9-*anti* **S69a** (4 mg, 14 μmol, 44%) as a colourless liquid.

$R_f$ = 0.11 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -16.9 (*c* = 1.0, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 7.65 (d, 1H, *J* = 15.7 Hz, H-3), 5.97 (d, 1H, *J* = 15.7 Hz, H-2), 5.82 (dd, 1H, *J* = 7.6, 6.6 Hz, H-5), 4.12 (q, 2H, *J* = 7.2 Hz, H-13), 3.46-3.55 (m, 1H, H-9), 3.38 (ddd, 1H,

$J$ = 7.8, 7.8, 3.6 Hz, H-7), 2.15 (ddd, 1H, $J$ = 15.2, 6.6, 3.6 Hz, H-$6_a$), 2.06 (ddd, 1H, $J$ = 15.2, 7.8, 7.6 Hz, H-$6_b$), 1.52 (s, 3H, H-11), 1.39-1.41 (m, 1H, H-8), 1.04 (t, 3H, $J$ = 7.2 Hz, H-14), 0.99 (d, 3H, $J$ = 6.3 Hz, H-10), 0.49 (d, 3H, $J$ = 6.9 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$, = 128.0 ppm): δ 167.2 (q, C-1), 149.5 (t, C-3), 138.1 (t, C-5), 134.9 (q, C-4), 116.7 (t, C-2), 75.7 (t, C-7), 72.4 (t, C-9), 60.2 (s, C-13), 45.3 (t, C-8), 34.7 (s, C-6), 21.9 (p, C-10), 14.4 (p, C-14), 12.9 (p, C-11), 12.3 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{25}O_4$ and $C_{14}H_{24}NaO_4$: 257.1753 $[M + H]^+$ and 279.1572 $[M + Na]^+$, found: 257.1745 $[M + H]^+$ and 279.1573 $[M + Na]^+$.

**Acetonide** 7,8-*syn*,8,9-*anti* **S70b**

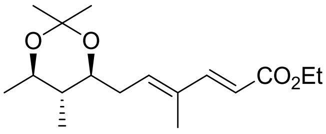


7,8-*syn*,8,9-*anti* **S70b**

Diol 7,8-*syn*,8,9-*anti* **S69b** (8 mg, 31 μmol, 1 eq) was dissolved in $CH_2Cl_2$ (1.0 ml) and 2,2-dimethoxypropane (0.2 ml) and PPTS (1 mg, catalytic) were added and the reaction mixture was stirred for 2 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1). Acetonide 7,8-*syn*,8,9-*anti* **S70b** (7 mg, 25 mmol, 81%) was obtained as a colourless liquid.

$R_f$ = 0.87 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -4.3 ($c$ = 0.7, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 7.67 (d, 1H, $J$ = 15.5 Hz, H-3), 5.97 (d, 1H, $J$ = 15.5 Hz, H-2), 5.69 (dd, 1H, $J$ = 7.3, 6.7 Hz, H-5), 4.11 (q, 2H, $J$ = 7.1 Hz, H-13), 3.78 (ddd, 1H, $J$ = 8.3, 5.9, 5.2 Hz, H-7), 3.31 (qd, 1H, $J$ = 6.5, 6.5 Hz, H-9), 2.10 (ddd, 1H, $J$ = 15.4, 8.3, 7.3 Hz, H-$6_a$), 1.94 (ddd, 1H, $J$ = 15.4, 6.7, 5.9 Hz, H-$6_b$), 1.49 (s, 3H, H-11), 1.32 (s, 3H, H-$16_a$), 1.29 (s, 3H, H-$16_b$), 1.24-1.33 (m, 1H, H-8), 1.14 (d, 3H, $J$ = 6.5 Hz, H-10), 1.03 (t, 3H, $J$ = 7.1 Hz, H-14), 0.62 (d, 3H, $J$ = 6.9 Hz, H-12) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$, = 128.0 ppm): δ 167.1 (q, C-1), 149.3 (t, C-3), 138.2 (t, C-5), 134.2 (q, C-4), 116.7 (t, C-2), 100.6 (q, C-15), 70.9 (t, C-9), 68.6 (t, C-7), 60.1 (s, C-13), 41.7 (t, C-8), 30.6 (s, C-6), 25.1 (p, C-$16_a$), 24.1 (p, C-$16_b$), 20.6 (p, C-10), 14.4 (p, C-14), 12.3 (p, C-11), 11.9 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{17}H_{28}NaO_4$: 319.1885 $[M + Na]^+$, found: 319.1880 $[M + Na]^+$.

**Acetonide** (7,8-*anti*,8,9-*anti* **S70a**)

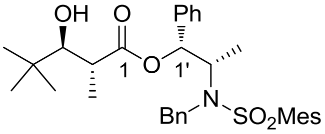


7,8-*anti*,8,9-*anti* **S70a**

Diol **S69a** (3 mg, 12 µmol, 1 eq) was dissolved in $CH_2Cl_2$ (0.5 ml) and 2,2-dimethoxypropane (0.1 ml) and PPTS (0.5 mg, catalytic) were added and the reaction mixture was stirred for 2 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1). Acetonide 7,8-*anti*,8,9-*anti* **S70a** (3 mg, 9 mmol, 73%) was obtained as a colourless liquid.

$R_f$ = 0.85 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -14.4 ($c$ = 0.3, $CH_2Cl_2$); $^1$**H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 7.69 (d, 1H, $J$ = 15.7 Hz, H-3), 5.95-6.01 (m, 2H, H-2 + H-5), 4.11 (q, 2H, $J$ = 7.1 Hz, H-13), 3.32-3.40 (m, 1H, H-9), 3.29 (ddd, 1H, $J$ = 10.2, 7.4, 2.9 Hz, H-7), 2.23 (ddd, 1H, $J$ = 15.7, 6.6, 2.9 Hz, H-$6_a$), 2.13 (ddd, 1H, $J$ = 15.7, 7.6, 7.4 Hz, H-$6_b$), 1.53 (s, 3H, H-11), 1.49 (s, 3H, H-$16_a$), 1.26 (s, 3H, H-$16_b$), 1.07-1.16 (m, 1H, H-8), 1.12 (d, 3H, $J$ = 6.0 Hz, H-10), 1.02 (t, 3H, $J$ = 7.1 Hz, H-14), 0.41 (d, 3H, $J$ = 7.2 Hz, H-12) ppm; $^{13}$**C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$, = 128.0 ppm): δ 167.1 (q, C-1), 149.4 (t, C-3), 138.1 (t, C-5), 134.2 (q, C-4), 116.6 (t, C-2), 98.0 (q, C-15), 74.2 (t, C-7), 70.7 (t, C-9), 60.1 (s, C-13), 40.6 (t, C-8), 32.9 (s, C-6), 30.4 (p, C-$16_a$), 20.1 (p, C-10), 19.7 (p, C-$16_b$), 14.4 (p, C-14), 12.3 (p, C-12), 12.3 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{17}H_{28}NaO_4$: 319.1885 $[M + Na]^+$, found: 319.1885 $[M + Na]^+$.

### MASAMUNE aldol produkt S71

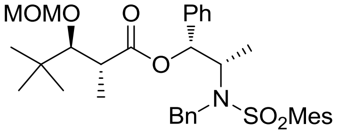


**S71**

Propionated MASAMUNE auxiliary **S64**[S10] (5.0 g, 10.4 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (70 ml) and the reaction mixture was cooled to -78 °C. $Et_3N$ (3.3 ml, 22.9 mmol, 2.2 eq) and $(cy)_2BOTf$ (22.9 ml, $c$ = 1 mol/l in hexane, 22.9 mmol, 2.2 eq) were slowly added. The solution was stirred for 2 h at -78 °C. Pivaldehyde (**S25**) (2.9 ml, 26.3 mmol, 2.5 eq) was dissolved in $CH_2Cl_2$ (20 ml) and added to the first solution. The reaction mixture was stirred for 2 h at -78 °C and for 16 h at 0 °C. The reaction was terminated by addition of phosphate buffer (pH = 7, 50 ml), MeOH (250 ml) and aq. $H_2O_2$ (30 ml, 30%ig) and stirring was continued overnight at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10.:1) to furnish ester **S71** (5.0 g, 8.8 mmol, 85%, *d.r.* > 20:1) as a colourless solid.

R$_f$ = 0.32 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +20.7 (*c* = 1.0, $CHCl_3$); mp.: 183 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.19-7.32 (m, 6H, Ph), 7.11-7.17 (m, 2H, Ph), 6.79-6.85 (m, 4H, Ph), 5.69 (d, 1H, *J* = 6.2 Hz, H-1'), 4.80 (d, 1H, *J* = 16.0 Hz, H-4'), 4.50 (d, 1H, *J* = 16.0 Hz, H-4'), 4.17 (qd, 1H, *J* = 7.0, 6.2 Hz, H-2'), 3.16 (d, 1H, *J* = 2.4 Hz, H-3), 2.75 (qd, 1H, *J* = 7.2, 2.4 Hz, H-2), 2.40 (s, 6H, Mes), 2.29 (s, 3H, Mes), 1.25 (d, 3H, *J* = 7.0 Hz, H-3'), 1.20 (d, 3H, *J* = 7.2 Hz, H-6), 0.90 (s, 9H, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 176.1 (q, C-1), 142.7 (q, Ph), 140.5 (q, Ph), 138.4 (q, Ph), 137.7 (q, Ph), 133.2 (q, Ph), 132.2 (t, Ph), 128.5 (t, Ph, 2x), 128.3 (t, Ph), 128.2 (t, Ph), 127.5 (t, Ph), 126.6 (t, Ph), 82.6 (t, C-3), 78.5 (t, C-1‘), 56.5 (t, C-2‘), 48.3 (s, C-4‘), 39.0 (t, C-2), 36.1 (q, C-4), 26.5 (p, C-5), 23.0 (p, Mes), 21.0 (p, Mes), 17.9 (p, C-6), 14.9 (p, C-3‘) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{33}H_{43}NaNO_5S$: 588.2760 $[M + Na]^+$, found: 588.2755 $[M + Na]^+$.[S10]

### MOM-protected MASAMUNE aldol product S72



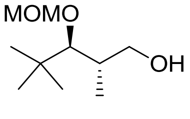
**S72**

Alcohol **S71** (1.9 g, 3.4 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (70 ml) and the solution was cooled to 0 °C. $^i$Pr$_2$NEt (6.2 ml, 34.3 mmol, 10.0 eq) and MOMCl (1.3 ml, 17.1 mmol, 5.0 eq) were added and the reaction mixture was stirred for 3 h at 0 °C and then for 7 d at rt. MOMCl (0.5 ml, 6.6 mmol, 1.9 eq) was added and stirring was continued for 2 d at rt. A second portion of MOMCl (0.3 ml, 3.3 mmol, 1.0 eq) was added and the reaction mixture was stirred for 2 d at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish product **S72** (1.6 g, 2.9 mmol, 85%) as a colourless oil.

R$_f$ = 0.43 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +30.5 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.30-7.35 (m, 2H, Ph), 7.11-7.24 (m, 6H, Ph), 6.80-6.86 (m, 4H, Ph), 5.82 (d, 1H, *J* = 5.7 Hz, H-1‘), 4.86 (d, 1H, *J* = 16.6 Hz, H-4‘$_a$), 4.63 (d, 1H, *J* = 7.0 Hz, MOM), 4.57

(d, 1H, *J* = 16.6 Hz, H-4’$_b$), 4.46 (d, 1H, *J* = 7.0 Hz, MOM), 4.16 (qd, 1H, *J* = 7.0, 5.7 Hz, H-2‘), 3.32 (s, 3H, MOM), 3.23 (d, 1H, *J* = 4.9 Hz, H-3), 2.85 (qd, 1H, *J* = 7.1, 4.9 Hz, H-2), 2.43 (s, 6H, Mes), 2.28 (s, 3H, Mes), 1.24 (d, 3H, *J* = 7.0 Hz, H-3‘), 1.14 (d, 3H, *J* = 7.1 Hz, H-6), 0.94 (s, 9H, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 173.3 (q, C-1‘), 142.5 (q, Ph), 140.4 (q, Ph), 138.8 (q, Ph), 138.7 (q, Ph), 133.7 (q, Ph), 132.2 (t, Ph), 128.4 (t, Ph), 128.3 (t, Ph), 128.0 (t, Ph), 128.0 (t, Ph), 127.2 (t, Ph), 126.5 (t, Ph), 98.8 (s, MOM), 89.7 (t, C-3), 78.3 (t, C-1‘), 57.0 (p, MOM), 56.5 (t, C-2‘), 48.1 (s, C-4‘), 42.7 (t, C-2), 36.3 (q, C-4), 26.6 (p, C-5), 23.0 (p, Mes), 21.0 (p, Mes), 18.0 (p, C-3‘), 14.4 (p, C-6) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{35}H_{47}NaNO_6S$: 632.3022 $[M + Na]^+$, found: 632.3011 $[M + Na]^+$.

**Alcohol S73**

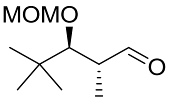


**S73**

Ester **S72** (1.6 g, 2.6 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (77 ml) and cooled to -78 °C. DIBAL-H (8.8 ml, *c* = 1.2 mol/l in toluene, 10.6 mmol, 4 eq) was added over a period of 1.5 h and the solution was stirred for another 1.5 h at -78 °C. The reaction was terminated by addition of ethyl acetate and aq. Na-K-tartrate. The solution was stirred overnight at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 5:1) to furnish alcohol **S73** (422 mg, 2.2 mmol, 85%) as a colourless liquid.

$R_f$ = 0.21 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -42.0 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.74 (d, 1H, *J* = 6.1 Hz, MOM), 4.62 (d, 1H, *J* = 6.1 Hz, MOM), 3.64 (dd, 1H, *J* = 11.3, 4.4 Hz, H-1$_a$), 3.59 (dd, 1H, *J* = 11.3, 6.5 Hz, H-1$_b$), 3.43 (s, 3H, MOM), 3.05 (d, 1H, *J* = 4.1 Hz, H-3), 2.53 (brs, 1H, OH), 1.03 (d, 3H, *J* = 7.2 Hz, H-6), 0.93 (s, 9H, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 100.2 (s, MOM), 93.8 (t, C-3), 66.2 (s, C-1), 56.6 (p, MOM), 36.6 (q, C-4), 36.0 (t, C-2), 26.4 (p, C-5), 18.8 (p, C-6) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{10}H_{22}NaO_3$: 213.1467 $[M + Na]^+$, found: 213.1463 $[M + Na]^+$.

**Aldehyde 61**

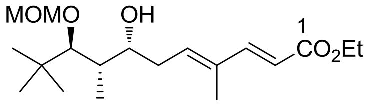


**61**

Alcohol **S73** (66 mg, 0.35 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7 ml) and $NaHCO_3$ (20 mg) and DESS-MARTIN periodinane (177 mg, 0.42 mmol, 1.2 eq) were added and the reaction mixture was stirred for 75 min at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 75 min at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish aldehyde **61** (54 mg, 0.29 mmol, 83%) as a colourless liquid, which was used immediately in the next step.

$R_f$ = 0.62 (PE:EE = 5:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): $\delta$ 9.81 (d, 1H, *J* = 2.1 Hz, H-1), 4.65 (d, 1H, *J* = 6.8 Hz, MOM), 4.59 (d, 1H, *J* = 6.8 Hz, MOM), 3.35 (s, 3H, MOM), 3.21 (d, 1H, *J* = 1.8 Hz, H-3), 2.68 (qdd, 1H, *J* = 7.0, 2.1, 1.8 Hz, H-2), 1.20 (d, 3H, *J* = 7.0 Hz, H-6), 0.98 (s, 9H, H-5) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): $\delta$ 204.4 (t, C-1), 99.0 (s, MOM), 91.2 (t, C-3), 56.4 (p, MOM), 47.3 (t, C-2), 36.6 (q, C-4), 26.5 (p, C-5), 14.7 (p, C-6) ppm; **HRMS** (ESI): *m/z*: Compound **61** could not be detected by mass spectrometry.

### **YAMAMOTO aldol product** 7,8-*syn*,8,9-*anti* **69b**



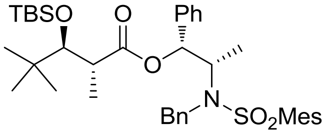
7,8-*syn*,8,9-*anti* **69b**

Following the general procedure, aldehyde **61** (48 mg, 0.26 μmol, 1 eq) was reacted with ester **6** (79 mg, 0.51 μmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 2:1) to furnish 7,8-*syn*,8,9-*anti* **69b** (*d.r.*: >10:1, 55 mg, 0.16 μmol, 63%) as a yellow liquid.

$R_f$ = 0.25 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -1.4 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): $\delta$ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.96 (dd, 1H, *J* = 7.5, 7.4 Hz, H-5), 5.79 (d, 1H, *J* = 15.7 Hz, H-2), 4.78 (d, 1H, *J* = 5.3 Hz, MOM), 4.53 (d, 1H, *J* = 5.3 Hz, MOM), 4.19 (q, 2H, *J* = 7.1 Hz, H-14), 4.11-4.17 (m, 1H, H-7), 3.80 (brs, 1H, OH), 3.40 (s, 3H, MOM), 2.95 (d, 1H, *J* = 2.7 Hz, H-9), 2.44 (ddd, 1H, *J* = 14.8, 7.4, 7.3 Hz, H-$6_a$), 2.28 (ddd, 1H, *J* = 14.8, 7.5, 7.4 Hz, H-$6_b$), 1.75-1.83 (m, 4H, H-8 + H-12), 1.29 (t, 3H, *J* = 7.2 Hz, H-15), 1.05 (d, 3H, *J* = 7.2 Hz, H-13) 0.88 (s, 9H, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$

= 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 138.8 (t, H-5), 134.2 (q, C-4), 115.9 (t, C-2), 100.7 (s, MOM), 94.9 (t, C-9), 69.6 (t, C-7), 60.3 (s, C-14), 55.9 (p, MOM), 37.1 (t, C-8), 36.9 (q, C-10), 34.3 (s, C-6), 26.5 (p, C-11), 14.4 (p, C-15), 13.8 (p, C-13), 12.5 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{19}H_{34}NaO_5$: 365.2304 [M + Na]$^+$, found 365.2297 [M + Na]$^+$.

### TBS-protected MASAMUNE aldol product S74

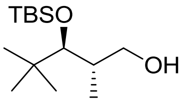


**S74**

Alcohol **S71** (2.3 g, 4.1 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (60 ml) and cooled to 0 °C. 2,6-Lutidine (1.43 ml, 12.3 mmol, 3.0 eq) and TBSOTf (1.42 ml, 6.1 mmol, 1.5 eq) were added and the reaction mixture was stirred for 3 h at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish product **S74** (2.7 g, 3.9 mmol, 96%) as a colourless solid.

$R_f$ = 0.53 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +30.5 (*c* = 1.0, $CHCl_3$); m.p. = 172 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.31-7.35 (m, 2H, Ph), 7.15-7.29 (m, 4H, Ph), 7.04-7.10 (m, 2H, Ph), 6.79-6.84 (m, 4H, Ph), 5.69 (d, 1H, *J* = 7.0 Hz, H-1‘), 4.77 (d, 1H, *J* = 16.4 Hz, H-4’$_a$), 4.42 (d, 1H, *J* = 16.4 Hz, H-4’$_b$), 4.16 (dq, 1H, *J* = 7.0, 6.8 Hz, H-2‘), 3.70 (d, 1H, *J* = 3.1 Hz, H-3), 2.60 (qd, 1H, *J* = 7.2, 3.1 Hz, H-2), 2.35 (s, 6H, Mes), 2.28 (s, 3H, Mes), 1.28 (d, 3H, *J* = 6.8 Hz, H-3‘), 1.12 (d, 3H, *J* = 7.2 Hz, H-6), 0.90 (s, 9H, TBS), 0.72 (p, 9H, H-5), 0.08 (p, 3H, TBS), 0.05 (p, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 172.6 (q, C-1), 142.5 (q, Ph), 140.6 (q, Ph), 138.3 (q, Ph), 137.8 (q, Ph), 133.1 (q, Ph), 132.3 (t, Ph), 128.6 (t, Ph), 128.3 (t, Ph), 128.2 (t, Ph), 128.0 (t, Ph), 127.6 (t, Ph), 127.3 (t, Ph), 80.8 (t, C-3), 78.0 (t, C-1‘), 56.5 (t, C-2‘), 48.2 (s, C-4‘), 45.8 (t, C-2), 36.9 (q, C-4), 27.3 (p, C-5), 26.2 (p, TBS), 23.0 (p, Mes), 21.0 (p, Mes), 18.4 (q, TBS), 15.6 (p, C-3‘), 13.3 (p, C-6), -3.8 (p, TBS), -4.2 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{39}H_{57}NaNO_{5S}Si$: 702.3624 [M + Na]$^+$, found: 702.3633 [M + Na]$^+$.

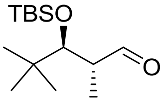
### Alcohol S75



**S75**

Ester **S74** (2.6 g, 3.9 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (95 ml) and cooled to -78 °C. DIBAL-H (13.0 ml, *c* = 1.2 mol/l in toluene, 15.6 mmol, 4 eq) was added over a period of 1.5 h and the reaction mixture was stirred for 30 min at -78 °C. The reaction was terminated by addition of ethyl acetate and aq. Na-K-tartrate. The solution was stirred at rt overnight after which time the layers were separated and the aqueous layer extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1) to furnish alcohol **S75** (998 mg, 3.8 mmol, 99%) as a colourless liquid.
$R_f$ = 0.56 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -4.1 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 3.65 (dd, 1H, *J* = 11.1, 8.7 Hz, H-$1_a$), 3.40 (dd, 1H, *J* = 11.1, 5.3 Hz, H-$1_b$), 3.25 (d, 1H, *J* = 3.8 Hz, H-3), 2.45 (brs, 1H, OH), 2.01-2.13 (m, 1H, H-2), 0.94 (s, 9H, TBS), 0.92 (d, 3H, *J* = 7.2 Hz, H-6), 0.91 (s, 9H, C-5), 0.14 (s, 3H, TBS), 0.09 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 86.1 (t, C-3), 66.5 (s, C-1), 36.7 (q, C-4), 36.2 (t, C-2), 26.5 (p, TBS), 26.5 (p, C-5), 18.9 (p, C-6), 18.5 (q, TBS), -2.7 (p, TBS), -3.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{32}NaO_2Si$: 283.2069 $[M + Na]^+$, found: 283.2057 $[M + Na]^+$.

## Aldehyde 62

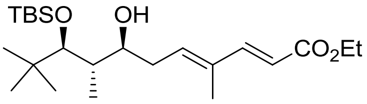


**62**

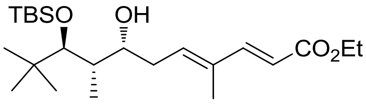
Alcohol **S75** (60 mg, 0.23 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (4.6 ml) and $NaHCO_3$ (20 mg) and the DESS-MARTIN periodinane (117 mg, 0.28 mmol, 1.2 eq) were added and the reaction mixture was stirred for 90 min at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 75 min at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1) to furnish aldehyde **62** (59 mg, 0.23 mmol, 99%) as a colourless liquid, which was used immediately in the next step.
$R_f$ = 0.66 (PE:EE = 10:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.83 (d, 1H, *J* = 1.8 Hz, H-1), 3.40 (d, 1H, *J* = 1.8 Hz, H-3), 2.66 (qdd, 1H, *J* = 7.2, 1.8, 1.8 Hz, H-2), 1.16

(d, 3H, *J* = 7.2 Hz, H-6), 0.95 (s, 9H, TBS), 0.90 (s, 9H, H-5), 0.06 (s, 3H, TBS), 0.06 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, CDCl$_3$, CDCl$_3$ = 77.16 ppm): δ 204.9 (t, C-1), 84.6 (t, C-3), 48.0 (t, C-2), 36.9 (q, C-4), 26.6 (p, TBS), 26.3 (p, C-5), 18.6 (q, TBS), 14.9 (p, C-6), -3.1 (p, TBS), -4.1 (p, TBS) ppm; **HRMS** (ESI): *m/z*: Compound **62** could not be detected by mass spectrometry.

### **YAMAMOTO aldol products** 7,8-*anti*,8,9-*anti* **70a** and 7,8-*syn*,8,9-*anti* **70b**



7,8-*anti*,8,9-*anti* **70a**

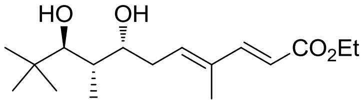


7,8-*syn*,8,9-*anti* **70b**

Following the general procedure, aldehyde **62** (52 mg, 20 μmol, 1 eq) was reacted with ester **6** (62 mg, 40 μmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols 7,8-*anti*,8,9-*anti* **70a** and 7,8-*syn*,8,9-*anti* **70b** (*d.r.*: 1:7 (**70a**:**70b**), 64 mg, 15 μmol, 77%) as a yellow liquid.

$R_f$ = 0.28 (PE:EE = 10:1); the diastereomers could not be separated by column chromatography; 7,8-*syn*,8,9-*anti* **70b**: **$^{1}$H-NMR** (400 MHz, CDCl$_3$, CHCl$_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.91 (dd, 1H, *J* = 7.7, 7.0 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 3.55 (ddd, 1H, *J* = 7.3, 7.0, 1.7 Hz, H-7), 4.20 (q, 2H, *J* = 7.1 Hz, H-14), 3.49 (brs, 1H, OH), 3.44 (d, 1H, *J* = 1.4 Hz, H-9), 2.42 (ddd, 1H, *J* = 15.0, 7.0, 7.0 Hz, H-6$_a$), 2.28 (ddd, 1H, *J* = 15.0, 7.7, 7.3 Hz, H-6$_b$), 1.79-1.88 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.29 (t, 3H, *J* = 7.1 Hz, H-15), 1.05 (d, 3H, *J* = 7.2 Hz, H-13) 0.96 (s, 9H, H-11), 0.95 (s, 9H, TBS), 0.17 (s, 3H, TBS), 0.14 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, CDCl$_3$, CDCl$_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 138.1 (t, H-5), 134.4 (q, C-4), 116.1 (t, C-2), 88.0 (t, C-9), 71.0 (t, C-7), 60.3 (s, C-14), 36.8 (t, C-8), 36.6 (q, C-10), 34.6 (s, C-6), 28.0 (p, C-11), 26.6 (p, TBS), 18.9 (q, TBS), 14.5 (p, C-15), 14.0 (p, C-13), 12.6 (p, C-12), -2.7 (p, TBS), -3.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{23}H_{45}O_4Si$: 413.3087 [M + H]$^+$, found: 413.3075 [M + H]$^+$.

### **Diol** 7,8-*syn*,8,9-*anti* **S76b**

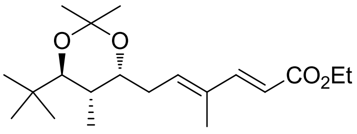


7,8-*syn*,8,9-*anti* **S76b**

Alcohol **70b** (15 mg, 36 μmol, 1.0 eq) was dissolved in THF (1.2 ml) and cooled to 0 °C. TBAF·3$H_2O$ (17 mg, 54 μmol, 1.5 eq) was added and the reaction mixture was stirred for 1.5 h at 0 °C. A second portion of TBAF·3$H_2O$ (10 mg, 32 μmol, 0.9 eq) was added and stirring was continued for 1.5 h at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 8:1 → 2:1) to furnish diol 7,8-*syn*,8,9-*anti* **S76b** (7 mg, 25 μmol, 69%) as a colourless oil.

$R_f$ = 0.15 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +2.2 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.93 (dd, 1H, *J* = 7.5, 7.4 Hz, H-5), 5.82 (d, 1H, *J* = 15.7 Hz, H-2), 4.21 (q, 2H, *J* = 7.2 Hz, H-14), 4.14-4.21 (m, 1H, H-7), 3.28 (d, 1H, *J* = 2.7 Hz, H-9), 2.48 (ddd, 1H, *J* = 14.9, 7.5, 7.5 Hz, H-$6_a$), 2.31 (ddd, 1H, *J* = 14.9, 7.4, 7.3 Hz, H-$6_b$), 1.77-1.85 (m, 4H, H-8 + H-12), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 1.06 (d, 3H, *J* = 7.2 Hz, H-13) 0.93 (s, 9H, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 138.0 (t, H-5), 134.8 (q, C-4), 116.3 (t, C-2), 85.2 (t, C-9), 71.4 (t, C-7), 60.4 (s, C-14), 36.6 (t, C-8), 36.2 (q, C-10), 34.2 (s, C-6), 26.4 (p, C-11), 14.5 (p, C-15), 14.1 (p, C-13), 12.6 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{17}H_{31}O_4$ and $C_{17}H_{30}NaO_4$: 299.2222 $[M + H]^+$ and 321.2028 $[M + Na]^+$, found: 299.2213 $[M + H]^+$ and 321.2028 $[M + Na]^+$.

### **Acetonide** 7,8-*syn*,8,9-*anti* **S77b**

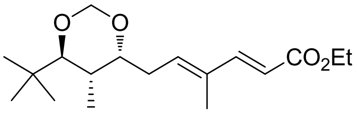


7,8-*syn*,8,9-*anti* **S77b**

Diol **S76b** (7 mg, 23 μmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (0.5 ml), 2,2-dimethoxypropane (0.1 ml) and CSA (1 mg, catalytic) were added and the reaction mixture was stirred for 2 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish acetonide 7,8-*syn*,8,9-*anti* **S77b** (4 mg, 12 μmol, 51%) as a colourless liquid.

$R_f$ = 0.35 (PE:EE = 20:1); $[\alpha]_D^{20}$ = -5.1 (*c* = 0.4, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.88 (dd, 1H, *J* = 6.8, 6.8 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.21 (q, 2H, *J* = 7.1 Hz, H-14), 3.78 (ddd, 1H, *J* = 8.8, 5.6, 3.5 Hz, H-7), 2.97 (d, 1H, *J* = 6.5 Hz, H-9), 2.28-2.38 (m, 1H, H-$6_a$), 2.17-2.28 (m, 1H, H-$6_b$), 1.71-1.79 (m, 4H, H-8 + H-12), 1.32 (s, 3H, H-17$_a$), 1.30 (t, 3H, *J* = 7.1 Hz, H-15), 1.29 (s, 3H, H-17$_b$), 0.88-0.91 (m, 12H, H-13 + H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.8 (q, C-1), 149.5 (t, C-3), 138.3 (t, H-5), 134.2 (q, C-4), 115.9 (t, C-2), 100.2 (q, C-16), 81.9 (t, C-9), 69.2 (t, C-7), 60.4 (s, C-14), 34.8 (t, C-8), 34.7 (q, C-10), 30.7 (s, C-6), 26.2 (p, C-17$_a$), 25.7 (p, C-11), 23.4 (p, C-17$_b$), 14.5 (p, C-15), 13.9 (p, C-13), 12.6 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{34}NaO_4$: 361.2355 [M + Na]$^+$, found: 361.2341 [M + Na]$^+$.

### Oxolane S78b

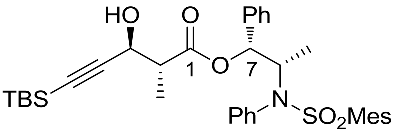


**S78b**

Alcohol **69b** (17 mg, 50 μmol, 1.0 eq) was dissolved in EtOH (1.5 ml) and concentrated HCl (0.1 ml) was added. The solution was stirred overnight and the reaction was terminated by addition of aq. $NaHCO_3$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish oxolane **S78b** (13 mg, 42 mmol, 84%) as a colourless liquid.

R$_f$ = 0.67 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -7.7 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.91 (dd, 1H, *J* = 7.5, 7.1 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 5.06 (d, 1H, *J* = 3.9 Hz, H-16$_a$), 4.84 (d, 1H, *J* = 3.9 Hz, H-16$_b$), 4.21 (q, 2H, *J* = 7.2 Hz, H-14), 3.91 (ddd, 1H, *J* = 8.5, 6.4, 3.5 Hz, H-7), 2.91 (d, 1H, *J* = 6.2 Hz, H-9), 2.50 (ddd, 1H, *J* = 15.3, 8.5, 7.5 Hz, H-6$_a$), 2.26 (ddd, 1H, *J* = 15.3, 7.1, 6.4 Hz, H-6$_b$), 1.98 (qdd, 1H, *J* = 6.9, 6.2, 3.5 Hz, H-8), 1.81 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 0.94 (d, 3H, *J* = 6.9 Hz, H-13), 0.93 (s, 9H, H-11) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 137.6 (t, H-5), 134.4 (q, C-4), 116.2 (t, C-2), 90.9 (s, C-16), 87.9 (t, C-9), 71.0 (t, C-7), 60.4 (s, C-14), 35.1 (q, C-10), 34.7 (t, C-8), 29.9 (s, C-6), 26.0 (p, C-11), 15.0 (p, C-13), 14.5 (p, C-15), 12.6 (p, C-12) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{18}H_{30}NaO_4$: 333.2042 [M + Na]$^+$, found: 333.2040 [M + Na]$^+$.

### MASAMUNE aldol product S79

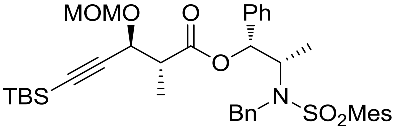


**S79**

Propionated MASAMUNE auxiliary **S64**[S10] (3.0 g, 6.3 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (30 ml) and cooled to -78 °C. $Et_3N$ (2.1 ml, 15.0 mmol, 2.4 eq) and $(cy)_2BOTf$ (13.8 ml, $c = 1$ mol/l in hexane, 13.8 mmol, 2.2 eq) were added and the solution was stirred for 2 h at -78 °C. Aldehyde **S33** (1.6 g, 9.4 mmol, 1.5 eq) was dissolved in $CH_2Cl_2$ (5 ml) and added dropwise to the first solution. The reaction mixture was stirred for 2 h at -78 °C and for 16 h at rt. Then, the reaction was terminated by addition of phosphate buffer (pH = 7, 26 ml), MeOH (128 ml), aq. $H_2O_2$ (13 ml, 30%ig) and stirring was continued for 2 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1 → 5:1) to furnish ester **S79** (4.0 g, 6.2 mmol, 99%, *d.r.*> 20:1) as a colourless solid.

$R_f = 0.36$ (PE:EE = 5:1); $[\alpha]_D^{20} = +26.7$ ($c = 1.0$, $CHCl_3$); m.p.: 54 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.28-7.33 (m, 2H, Ph), 7.14-7.27 (m, 6H, Ph), 6.82-6.89 (m, 4H, Ph), 5.83 (d, 1H, $J = 4.8$ Hz, H-1'), 4.76 (d, 1H, $J = 16.2$ Hz, H-$4_a$'), 4.52 (d, 1H, $J = 16.2$ Hz, H-$4_b$'), 4.51 (d, 1H, $J = 7.9$ Hz, H-3), 4.06-4.15 (m, 1H, H-2'), 2.68 (dq, 1H, $J = 7.9$, 7.2 Hz, H-2), 2.47 (s, 6H, Mes), 2.28 (s, 3H, Mes), 1.21 (d, 3H, $J = 7.2$ Hz, H-3'), 1.18 (d, 3H, $J = 7.2$ Hz, H-6), 0.92 (s, 9H, TBS), 0.09 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 173.1 (q, C-1), 142.7 (q, Ph), 140.5 (q, Ph), 138.6 (q, Ph), 138.2 (q, Ph), 133.5 (q, Ph), 132.3 (t, Ph), 128.6 (t, Ph), 128.5 (t, Ph), 128.1 (t, Ph), 127.9 (t, Ph), 127.4 (t, Ph), 126.2 (t, Ph), 104.6 (q, C-10), 89.8 (q, C-11), 78.6 (t, C-1'), 64.9 (t, C-3), 56.9 (t, C-2'), 48.4 (s, C-4'), 46.6 (t, C-2), 26.2 (p, TBS), 23.1 (p, Mes), 21.0 (p, Mes), 16.6 (q, TBS), 14.0 (p, C-3'), 13.8 (p, C-6), -4.6 (p, TBS), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{37}H_{49}NaNO_5SiS$: 670.2998 $[M + Na]^+$, found: 670.2973 $[M + Na]^+$.

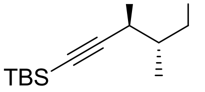
## MOM-protected MASAMUNE aldol product S80



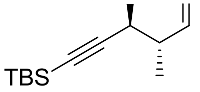
**S80**

Ester **S79** (1.0 g, 1.5 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (30 ml) and cooled to 0 °C. $^{i}Pr_2NEt$ (2.8 ml, 15.4 mmol, 10 eq) and MOMCl (0.6 ml, 7.7 mmol, 5 eq) were added and the solution was stirred for 3 d at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1) to furnish alcohol **S80** (1.0 g, 1.4 mmol, 93%) as a colourless solid.
$R_f$ = 0.52 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -11.5 ($c$ = 1.0, $CHCl_3$); m.p. = 49 °C; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32-7.37 (m, 2H, Ph), 7.12-7.27 (m, 6H, Ph), 6.87-6.90 (m, 2H, Ph), 6.75-6.80 (m, 2H, Ph), 5.81 (d, 1H, $J$ = 4.4 Hz, H-1'), 4.94 (d, 1H, $J$ = 6.5 Hz, MOM), 4.87 (d, 1H, $J$ = 16.4 Hz, H-$4_a$'), 4.48-4.60 (m, 3H, H-$4_b$' + MOM + H-3), 4.07 (m, 1H, H-2'), 3.33 (s, 3H, MOM), 2.68 (m, 1H, H-2), 2.47 (s, 6H, Mes), 2.30 (s, 3H, Mes), 1.21 (d, 3H, $J$ = 7.2 Hz, H-6), 1.13 (d, 3H, $J$ = 7.2 Hz, H-3'), 0.93 (s, 9H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 172.7 (q, C-1), 142.7 (q, Ph), 140.4 (q, Ph), 139.0 (q, Ph), 138.4 (q, Ph), 133.7 (q, Ph), 132.3 (t, Ph), 128.5 (t, Ph), 128.4 (t, Ph), 128.1 (t, Ph), 128.0 (t, Ph), 127.3 (t, Ph), 126.1 (t, Ph), 102.2 (q, C-4), 94.2 (s, MOM), 91.2 (q, C-5), 78.4 (t, C-1'), 68.3 (t, C-3), 56.9 (t, C-2'), 56.2 (p, MOM), 48.2 (s, C-4'), 45.5 (t, C-2), 26.2 (p, TBS), 23.0 (p, Mes), 21.1 (p, Mes), 16.6 (q, TBS), 14.0 (p, C-6), 13.8 (p, C-3'), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{39}H_{53}NO_6SSiNa$: 714.3261 $[M + Na]^+$; found: 714.3244 $[M + Na]^+$.

### **(2*S*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(methoxymethoxy)-2-methylpent-4-yn-1-ol (S81)** and **(2R,3S)-5-(*tert*-Butyldimethylsilyl)-3-(methoxymethoxy)-2-methylpent-4-ynal (63)**



**S81**



**63**

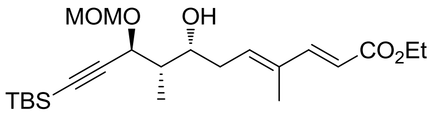
Ester **S80** (940 mg, 1.4 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (20 ml) and the solution was cooled to -78 °C. DIBAL-H (4.5 ml, $c$ = 1.2 mol/l in toluene, 5.4 mmol, 4 eq) was added and stirring was continued for 2 h at -78 °C. The reaction was terminated by addition of ethyl acetate and Na-K-tartrate was added. The mixture was stirred overnight at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 2:1) to yield aldehyde **63** (260 mg, 1.0 mmol, 72%) and alcohol **S81** (100 mg, 0.4 mmol, 27%) as colourless liquids.

**S81**: $R_f$ = 0.17 (PE:EE = 4:1); $[\alpha]_D^{20}$ = -84.6 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.99 (d, 1H, *J* = 6.8 Hz, H-3), 4.60 (d, 1H, *J* = 6.5 Hz, MOM), 4.36 (d, 1H, *J* = 6.5 Hz, MOM), 3.74 (dd, 1H, *J* = 11.1, 4.1 Hz, H-$1_a$), 3.65 (dd, 1H, *J* = 11.1, 6.8 Hz, H-$1_b$), 3.40 (s, 3H, MOM), 2.06 (qddd, 1H, *J* = 6.8, 6.8, 6.8, 4.1 Hz, H-2), 1.06 (d, 3H, *J* = 6.8 Hz, H-6), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 103.5 (q, C-4), 94.3 (s, MOM), 90.3 (q, C-5), 70.0 (t, C-3), 65.9 (s, C-1), 56.0 (p, MOM), 40.6 (t, C-2), 26.2 (p, TBS), 16.6 (q, TBS), 13.4 (p, C-6), -4.5 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{29}O_3Si$: 273.1886 $[M + H]^+$, found: 273.1892 $[M + H]^+$.

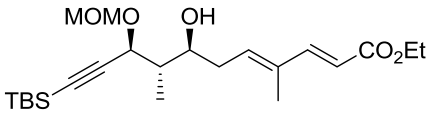
**63**: $R_f$ = 0.36 (PE:EE = 4:1); $[\alpha]_D^{20}$ = -106.6 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.81 (s, 1H, H-1), 4.98 (d, 1H, *J* = 6.8 Hz, MOM), 4.61 (d, 1H, *J* = 7.0 Hz, H-3), 4.58 (d, 1H, *J* = 6.8 Hz, MOM), 3.37 (s, 3H, MOM), 2.72 (qdd, 1H, *J* = 7.0, 6.9, 1.5 Hz, H-2), 1.21 (d, 3H, *J* = 6.9 Hz, H-6), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 202.5 (t, C-1), 102.0 (q, C-4), 94.2 (s, MOM), 91.7 (q, C-5), 66.6 (t, C-3), 56.1 (p, MOM), 50.9 (t, C-2), 26.2 (p, TBS), 16.6 (q, TBS), 10.8 (p, C-6), -4.6 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{26}NaO_3Si$: 293.1549 $[M + Na]^+$, found: 293.1550 $[M + Na]^+$.

### (2E,4E,7S,8S,9S)-Ethyl 11-(*tert*-butyldimethylsilyl)-7-hydroxy-9-(methoxymethoxy)-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*anti*,8,9-*anti*-71a) and

### (2*E*,4*E*,7*R*,8*S*,9*S*)-ethyl-11-(*tert*-butyldimethylsilyl)-7-hydroxy-9-(methoxymethoxy)-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*syn*,8,9-*anti* 71b)



7,8-*syn*,8,9-*anti* **71b**



7,8-*anti*,8,9-*anti* **71a**

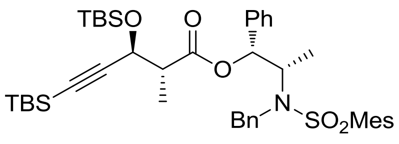
Following the general procedure, aldehyde **63** (40 mg, 0.15 mmol, 1.0 eq) was reacted with ester **6** (46 mg, 0.30 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 5:1) to furnish alcohols 7,8-*anti*,8,9-*anti* **71a** and 7,8-*syn*,8,9-*anti* **71b** [*d.r.*: 1:2 (**71b**:**71a**), 37 mg, 0.09 mmol, 58%] as a yellow liquid. In addition, another isomer was detected by NMR spectroscopy, which we propose to be the 4*Z*-isomer. However, clear analytical proof could not be collected.

R$_f$ = 0.25 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{23}H_{41}O_5Si$: 425.2723 $[M + H]^+$, found: 425.2729 $[M + H]^+$.

7,8-*anti*,8,9-*anti* **71a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.35 (d, 1H, *J* = 15.7 Hz, H-3), 6.04 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.99 (d, 1H, *J* = 6.7 Hz, MOM), 4.61 (d, 1H, *J* = 6.7 Hz, MOM), 4.53 (d, 1H, *J* = 6.1 Hz, H-9), 4.20 (q, 2H, *J* = 7.2 Hz, H-14), 3.74 (ddd, 1H, *J* = 7.9, 7.9, 3.4 Hz, H-7), 3.38 (s, 3H, MOM), 2.64 (s, 1H, OH), 2.30-2.56 (m, 2H, H-6), 1.91-2.01 (m, 1H, H-8), 1.81 (s, 3H, H-12), 1.29 (t, 3H, *J* = 7.2 Hz, H-15), 1.03 (d, 3H, *J* = 6.8 Hz, H-13), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.3 (t, C-3), 137.6 (t, C-5), 135.1 (q, C-4), 116.3 (t, C-2), 103.1 (q, C-10), 94.3 (s, MOM), 90.8 (q, C-11), 73.6 (t, C-9), 69.3 (t, C-7), 60.4 (s, C-14), 56.1 (p, MOM), 43.4 (t, C-8), 34.1 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-13), 12.6 (p, C-12), -4.5 (p, TBS), -4.6 (p, TBS) ppm.

7,8-*syn*,8,9-*anti* **71b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, *J* = 15.5 Hz, H-3), 5.92 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.81 (d, 1H, *J* = 15.5 Hz, H-2), 4.96 (d, 1H, *J* = 6.7 Hz, MOM), 4.60 (d, 1H, *J* = 6.7 Hz, MOM), 4.39 (d, 1H, *J* = 4.8 Hz, H-9), 4.19-4.27 (m, 1H, H-7), 4.20 (q, 2H, *J* = 7.2 Hz, H-14), 3.38 (s, 3H, MOM), 2.30-2.56 (m, 2H, H-6), 2.28 (s, 1H, OH), 1.82-1.90 (m, 1H, H-8), 1.81 (s, 3H, H-12), 1.29 (t, 3H, *J* = 7.2 Hz, H-15), 1.08 (d, 3H, *J* = 6.8 Hz, H-13), 0.93 (s, 9H, TBS), 0.11 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.0 (t, C-3), 137.8 (t, C-5), 134.7 (q, C-4), 116.3 (t, C-2), 103.7 (q, C-10), 94.4 (s, MOM), 90.7 (q, C-11), 71.0 (t, C-9), 70.5 (t, C-7), 60.4 (s, C-14), 56.1 (p, MOM), 42.1 (t, C-8), 34.1 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 10.0 (p, C-13), -4.5 (p, TBS), -4.6 (p, TBS) ppm.

### TBS-protected MASAMUNE aldol product S82



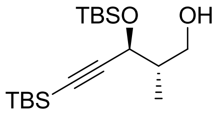
**S82**

Aldol product **S79** (2.0 g, 3.1 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (45 ml) and the solution was cooled to 0 °C. 2,6-Lutidine (1.4 ml, 12.3 mmol, 4 eq) and TBSOTf (1.4 ml, 6.2 mmol, 2 eq) were added and the reaction mixture was stirred for 1.5 h. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with

$CH_2Cl_2$. The combined, organic layers were washed with aq. HCl ($c$ = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohol **S82** (2.3 g, 3.0 mmol, 96%) as a colourless oil.

$R_f$ = 0.50 (PE:EE = 5:1); $[\alpha]_D^{20}$ = +17.6 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.35-7.40 (m, 2H, Ph), 7.15-7.33 (m, 4H, Ph), 7.07-7.14 (m, 2H, Ph), 6.87-6.90 (m, 2H, Ph), 6.71-6.75 (m, 2H, Ph), 5.70 (d, 1H, $J$ = 5.8 Hz, H-1’), 4.85 (d, 1H, $J$ = 16.4 Hz, H-4$_a$’), 4.57 (d, 1H, H-3), 4.43 (d, 1H, $J$ = 16.4 Hz, H-4$_b$’), 4.04 (qd, 1H, $J$ = 6.6, 5.8 Hz, H-2’), 2.65 (dq, 1H, $J$ = 7.8, 7.3 Hz, H-2), 2.43 (s, 6H, Mes), 2.31 (s, 3H, Mes), 1.15 (d, 3H, $J$ = 6.6 Hz, H-3’), 1.11 (d, 3H, $J$ = 7.3 Hz, H-6), 0.91 (s, 9H, TBS), 0.86 (s, 9H, TBS), 0.13 (s, 3H, TBS), 0.08 (s, 3H, TBS), 0.07 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 172.1 (q, C-1), 142.5 (q, Ph), 140.4 (q, Ph), 138.6 (q, Ph), 138.2 (q, Ph), 133.2 (q, Ph), 132.2 (t, Ph), 128.4 (t, Ph), 128.3 (t, Ph), 128.2 (t, Ph), 127.9 (t, Ph), 127.3 (t, Ph), 126.3 (t, Ph), 105.5 (q, C-4), 89.4 (q, C-5), 77.9 (t, C-1’), 65.2 (t, C-3), 56.7 (t, C-2’), 48.2 (s, C-4’), 47.5 (t, C-2), 26.0 (p, TBS), 25.8 (p, TBS), 22.9 (p, Mes), 20.9 (p, Mes), 18.2 (q, TBS), 16.4 (q, TBS), 14.5 (p, C-3’), 13.2 (p, C-6), -4.7 (p, TBS), -4.8 (p, TBS), -4.9 (p, TBS) ppm; **HRMS** (ESI): $m/z$: calculated for $C_{34}H_{63}NNaO_5Si_2S$: 784.3863 $[M + Na]^+$, found: 784.3870 $[M + Na]^+$.

### (2*S*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(*tert*-butyldimethylsilyloxy)-2-methylpent-4-yn-1-ol (S83)

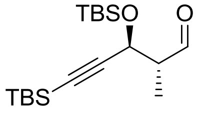


**S83**

Ester **S82** (2.2 g, 2.9 mmol, 1 eq) was dissolved in $CH_2Cl_2$ (40 ml) and the solution was cooled to -78 °C. DIBAL-H (9.5 ml, $c$ = 1.2 mol/l in toluene, 11.4 mmol, 4 eq) was slowly added and stirring was continued for 1.5 h at -78 °C. The reaction was terminated by addition of ethyl acetate and aq. Na-K-tartrate was added and the mixture was stirred overnight at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 50:1 → 10:1) to furnish alcohol **S83** (925 mg, 2.7 mmol, 94%) as a colourless liquid.

$R_f$ = 0.50 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -45.3 ($c$ = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.34 (d, 1H, $J$ = 6.2 Hz, H-3), 3.81 (dd, 1H, $J$ = 10.9, 3.5 Hz, H-1$_a$), 3.63 (dd, 1H, $J$ = 10.9, 6.5 Hz, H-$1_b$), 2.10 (brs, 1H, OH), 1.93 (qddd, 1H, $J$ = 6.9, 6.5, 6.2, 3.5 Hz, H-2), 1.02 (d, 3H, $J$ = 6.9 Hz, H-6), 0.93 (s, 9H, TBS), 0.91 (s, 9H, TBS), 0.17 (s, 3H, TBS), 0.14 (s, 3H, TBS), 0.10 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 107.0 (q, C-4), 88.8 (q, C-5), 68.1 (t, C-3), 66.0 (s, C-1), 42.1 (t, C-2), 26.2 (p, TBS), 25.9 (p, TBS), 18.3 (q, TBS), 16.6 (q, TBS), 13.6 (p, C-6), -4.3 (p, TBS), -4.6 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{18}H_{39}O_2Si_2$: 343.2484 $[M + H]^+$, found: 343.2480 $[M + H]^+$.

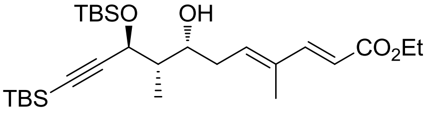
### (2*R*,3*S*)-5-(*tert*-Butyldimethylsilyl)-3-(*tert*-butyldimethylsilyloxy)-2-methylpent-4-ynal (64)



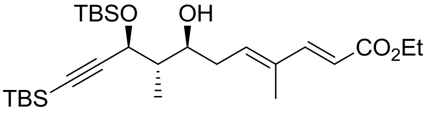
**64**

Alcohol **S83** (60 mg, 0.18 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (3.5 ml) and $NaHCO_3$ (10 mg) as well as DESS-MARTIN periodinane (90 mg, 0.21 mmol, 1.2 eq) were added and the solution was stirred for 1 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1) to furnish aldehyde **64** (58 mg, 0.17 mmol, 96%) as a colourless liquid, which was used immediately in the next step.
$R_f$ = 0.73 (PE:EE = 10:1).

### (2*E*,4*E*,7*S*,8*S*,9*S*)-Ethyl-11-(*tert*-butyldimethylsilyl)-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*anti*,8,9-*anti* 72a) and (2*E*,4*E*,7*R*,8*S*,9*S*)-ethyl-11-(*tert*-butyldimethylsilyl)-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*syn*,8,9-*anti* 72b)



7,8-*syn*,8,9-*anti* **72b**



7,8-*anti*,8,9-*anti* **72a**

Following the general procedure, aldehyde **64** (57 mg, 0.17 mmol, 1 eq) was reacted with ester **6** (52 mg, 0.34 mmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohols 7,8-

*anti*,8,9-*anti* **72a** and 7,8-*syn*,8,9-*anti* **72b** (*d.r.*: 1:1, 73 mg, 0.15 mmol, 88%) as yellow liquids.

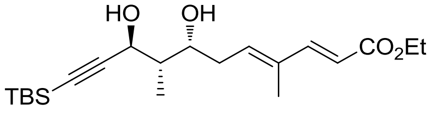
**HRMS** (ESI): *m/z*: calculated for $C_{27}H_{51}O_4Si_2$ and $C_{27}H_{50}NaO_4Si_2$: 495.3326 $[M + H]^+$ and 517.3145 $[M + Na]^+$, found: 495.3344 $[M + H]^+$ and 517.3138 $[M + Na]^+$.

7,8-*anti*,8,9-*anti* **72a**: $R_f$ = 0.38 (PE:EE = 10:1); $[\alpha]_D^{20}$ = -1.4 (*c* = 0.4, $CH_2Cl_2$); $^1$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.37 (d, 1H, *J* = 15.7 Hz, H-3), 6.07 (dd, 1H, *J* = 6.8, 6.8 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.46 (d, 1H, *J* = 6.5 Hz, H-9), 4.21 (q, 2H, *J* = 7.0 Hz, H-14), 3.75 (ddd, 1H, *J* = 7.5, 7.5, 36 Hz, H-7), 3.03 (brs, 1H, OH), 2.47-2.56 (m, 1H, H-6$_a$), 2.35-2.45 (m, 1H, H-6$_b$), 1.81-1.91 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.0 Hz, H-15), 0.97 (d, 3H, *J* = 6.8 Hz, H-13), 0.93 (s, 9H, TBS), 0.91 (s, 9H, TBS), 0.18 (s, 3H, TBS), 0.15 (s, TBS), 0.10 (s, 6H, TBS) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 138.0 (t, C-5), 134.7 (q, C-4), 116.0 (t, C-2), 106.8 (q, C-10), 89.4 (q, C-11), 73.9 (t, C-9), 67.5 (t, C-7), 60.3 (s, C-14), 45.2 (t, C-8), 34.2 (s, C-6), 26.2 (p, TBS), 25.9 (p, TBS), 18.3 (q, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.8 (p, C-13), 12.6 (p, C-12), -4.2 (p, TBS), -4.6 (p, TBS), -4.9 ppm.

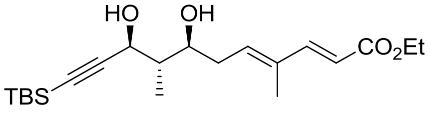
7,8-*syn*,8,9-*anti* **72b**:$R_f$ = 0.39 (PE:EE = 10:1); $[\alpha]_D^{20}$ = +0.4 (*c* = 0.6, $CH_2Cl_2$); $^1$**H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, *J* = 15.7 Hz, H-3), 5.92 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.80 (d, 1H, *J* = 15.7 Hz, H-2), 4.36-4.44 (m, 2H, H-9 + H-7), 4.21 (q, 2H, *J* = 7.2 Hz, H-14), 3.16 (brs, 1H, OH), 2.41-2.52 (m, 1H, H-6$_a$), 2.25-2.35 (m, 1H, H-6$_b$), 1.65-1.75 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 1.04 (d, 3H, *J* = 6.8 Hz, H-13), 0.93 (s, 9H, TBS), 0.90 (s, 9H, TBS), 0.18 (s, 3H, TBS), 0.13 (s, 3H, TBS), 0.01 (s, 6H, TBS) ppm; $^{13}$**C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.4 (t, C-3), 138.0 (t, C-5), 134.6 (q, C-4), 116.2 (t, C-2), 106.6 (q, C-10), 89.4 (q, C-11), 71.3 (t, C-9), 69.0 (t, C-7), 60.3 (s, C-14), 42.8 (t, C-8), 34.2 (s, C-6), 26.2 (p, TBS), 25.8 (p, TBS), 18.2 (q, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.5 (p, C-12), 10.1 (p, C-13), -4.4 (p, TBS), -4.6 (p, TBS), -4.6 (p, TBS), -5.3 (p, TBS) ppm.

### (2*E*,4*E*,7*S*,8*S*,9*S*)-Ethyl-11-(tert-butyldimethylsilyl)-7,9-dihydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*anti*,8,9-*anti* S84a) and

### (2*E*,4*E*,7*R*,8*S*,9*S*)-ethyl-11-(*tert*-butyldimethylsilyl)-7,9-dihydroxy-4,8-dimethylundeca-2,4-dien-10-ynoate (7,8-*syn*,8,9-*anti* S84b)



7,8-*syn*,8,9-*anti* **S84b**



7,8-*anti*,8,9-*anti* **S84a**

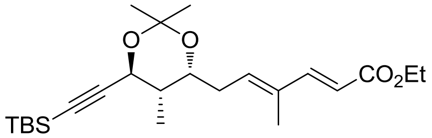
A mixture of alcohols **71** [*d.r.*: 1:2 (**71b**:**71a**), 10 mg, 23 μmol, 1 eq] was dissolved in EtOH (1 ml) and concentrated aq. HCl (0.04 ml) was added. The solution was stirred for 5 d at rt. A second portion of concentrated aq. HCl (0.02 ml) was added and stirring was continued for 1 d at rt. The reaction was terminated by addition of aq. $NaHCO_3$, the layers were separated, the aqueous layer was extracted with $CH_2Cl_2$ and the combined, organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 2:1). Diols 7,8-*syn*,8,9-*anti* **S84b** and 7,8-*anti*,8,9-*anti* **S84a** [*d.r.*: 1:2 (**S84b**:**S84a**), 7 mg, 17 mmol, 75%) were obtained as a colourless liquid.

$R_f$ = 0.4 (PE:EE = 2:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{21}H_{37}O_4Si$: 381.2461 $[M + H]^+$, found: 381.2460 $[M + H]^+$.

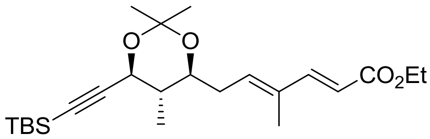
7,8-*anti*,8,9-*anti* **S84a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.35 (d, 1H, *J* = 15.5 Hz, H-3), 6.02 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.83 (d, 1H, *J* = 15.5 Hz, H-2), 4.54 (d, 1H, *J* = 6.8 Hz, H-9), 4.21 (q, 2H, *J* = 7.2 Hz, H-14), 3.73 (ddd, 1H, *J* = 7.9, 7.8, 3.7 Hz, H-7), 2.42-2.58 (m, 2H, H-6), 1.83-1.93 (m, 1H, H-8), 1.81 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 1.02 (d, 3H, *J* = 6.8 Hz, H-13), 0.94 (s, 9H, TBS), 0.12 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.2 (t, C-3), 137.0 (t, C-5), 135.5 (q, C-4), 116.5 (t, C-2), 105.8 (q, C-10), 89.7 (q, C-11), 74.8 (t, C-9), 66.9 (t, C-7), 60.4 (s, C-14), 44.5 (t, C-8), 34.6 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.9 (p, C-12), 12.7 (p, C-13), -4.5 (p, TBS), -4.5 (p, TBS) ppm.

7,8-*syn*,8,9-*anti* **S84b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, *J* = 15.7 Hz, H-3), 5.91 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.83 (d, 1H, *J* = 15.7 Hz, H-2), 4.44 (d, 1H, *J* = 5.5 Hz, H-9), 4.28 (ddd, 1H, *J* = 7.8, 7.8, 6.1 Hz, H-7), 4.21 (q, 2H, *J* = 7.2 Hz, H-14), 2.30-2.51 (m, 2H, H-6), 1.46-1.64 (m, 1H, H-8), 1.81 (s, 3H, H-12), 1.30 (t, 3H, *J* = 7.2 Hz, H-15), 1.09 (d, 3H, *J* = 6.8 Hz, H-13), 0.94 (s, 9H, TBS), 0.12 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.1 (t, C-3), 137.2 (t, C-5), 135.2 (q, C-4), 116.6 (t, C-2), 106.5 (q, C-10), 89.5 (q, C-11), 71.7 (t, C-9), 67.1 (t, C-7), 60.4 (s, C-14), 42.8 (t, C-8), 34.2 (s, C-6), 26.2 (p, TBS), 16.6 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 10.1 (p, C-13), -4.5 (p, TBS), -4.5 (p, TBS) ppm.

### **Acetonide** (7,8-*anti*,8,9-*anti* **S85a**) and (7,8-*syn*,8,9-*anti* **S85b**)



7,8-*syn*,8,9-*anti* **S85b**



7,8-*anti*,8,9-*anti* **S85a**

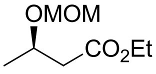
A mixture of diols **S84** [*d.r.*: 1:2 (**S84b**:**S84a**), 6.0 mg, 16 µmol, 1 eq) was dissolved in $CH_2Cl_2$ (0.8 ml) and 2,2-dimethoxypropane (0.08 ml) and PPTS (1 mg, catalytic) were added. The reaction mixture was stirred for 3 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1). Acetonides 7,8-*syn*,8,9-*anti* **S85b** and 7,8-*anti*,8,9-*anti* **S85a** [*d.r.*: 1:1.5 (**S85b**:**S85a**), 3.4 mg, 8 µmol, 50%) were obtained as a colourless liquid.

$R_f$ = 0.56 (PE:EE = 5:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{24}H_{49}NaO_4Si$: 443.2594 $[M + Na]^+$, found: 443.2585 $[M + Na]^+$.

7,8-*anti*,8,9-*anti* **S85a**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, *J* = 15.6 Hz, H-3), 6.00 (dd, 1H, *J* = 7.3, 6.9 Hz, H-5), 5.80 (d, 1H, *J* = 15.6 Hz, H-2), 4.28 (d, 1H, *J* = 10.5 Hz, H-9), 4.21 (q, 2H, *J* = 7.1 Hz, H-14), 3.58 (ddd, 1H, *J* = 10.3, 7.4, 3.3 Hz, H-7), 2.51 (ddd, 1H, *J* = 16.0, 6.9, 3.3 Hz, H-$6_a$), 2.35 (ddd, 1H, *J* = 16.0, 7.4, 7.3 Hz, H-$6_b$), 1.77 (s, 3H, H-12), 1.59-1.70 (m, 1H, H-8), 1.43 (s, 3H, H-$17_a$), 1.43 (s, 3H, H-$17_b$), 1.31 (q, 3H, *J* = 7.1 Hz, H-14), 0.96 (d, 3H, *J* = 6.7 Hz, H-13), 0.93 (s, 9H, TBS), 0.11 (s, 3H, TBS), 0.11 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 137.4 (t, C-5), 134.4 (q, C-4), 116.0 (t, C-2), 104.1 (q, C-10), 99.1 (q, C-16), 88.5 (q, C-11), 74.1 (t, C-7), 67.1 (t, C-9), 60.4 (s, C-14), 39.6 (t, C-8), 32.6 (s, C-6), 30.1 (p, C-$17_a$), 26.3 (p, TBS), 19.4 (p, C-$17_b$), 16.7 (q, TBS), 14.5 (p, C-15), 13.0 (p, C-13), 12.6 (p, C-12), -4.5 (p, TBS), -4.6 (p, TBS) ppm.

7,8-*syn*,8,9-*anti* **S85b**: **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, *J* = 15.7 Hz, H-3), 5.87 (dd, 1H, *J* = 7.7, 7.7 Hz, H-5), 5.82 (d, 1H, *J* = 15.7 Hz, H-2), 4.34 (d, 1H, *J* = 4.1 Hz, H-9), 4.21-4.30 (m, 1H, H-7), 4.22 (q, 2H, *J* = 7.0 Hz, H-14), 2.40 (ddd, 1H, *J* = 15.1, 7.7, 7.4 Hz, H-$6_a$), 2.29 (ddd, 1H, *J* = 15.1, 7.7, 7.2 Hz, H-$6_b$), 1.81-1.89 (m, 1H, H-8), 1.80 (s, 3H, H-12), 1.37 (s, 3H, H-$17_a$), 1.31 (q, 3H, *J* = 7.0 Hz, H-14), 1.25 (s, 3H, H-$17_b$), 1.06 (d, 3H, *J* = 6.8 Hz, H-13), 0.93 (s, 9H, TBS), 0.11 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.3 (t, C-3), 137.0 (t, C-5), 134.7 (q, C-4), 116.3 (t, C-2), 104.3 (q, C-10), 101.0 (q, C-16), 89.3 (q, C-11), 68.0 (t, C-7), 67.4 (t, C-9), 60.4 (s, C-14), 38.7 (t, C-8), 31.7 (s, C-6), 28.4 (p, C-$17_a$), 26.2 (p, TBS), 23.7 (p, C-$17_b$), 16.7 (q, TBS), 14.5 (p, C-15), 12.6 (p, C-12), 11.6 (p, C-13), -4.7 (p, TBS), -4.7 (p, TBS) ppm.

### (*R*)-Ethyl-3-(methoxymethoxy)butanoate (S86)

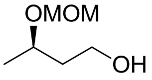


**S86**

Ethyl (*R*)-(-)-3-hydroxybutyrate (**S87**) (0.49 ml, 3.8 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (50 ml), cooled to 0 °C and $^i$$Pr_2NEt$ (6.26 ml, 37.8 mmol, 10.0 eq) was added. MOMCl (1.44 ml, 18.9 mmol, 5.0 eq) was added dropwise and the reaction mixture was stirred at rt overnight. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl ($c$ = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 10:1) to furnish alcohol **S86** (630 mg, 3.6 mmol, 95%) as a colourless liquid.

$R_f$ = 0.69 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -11.1 ($c$ = 1.0, $CHCl_3$) [Lit.: -88.1 ($c$ = 1.0, $CHCl_3$)]; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.67 (d, 1H, $J$ = 7.0 Hz, MOM), 4.65 (d, 1H, $J$ = 7.0 Hz, MOM), 4.14 (q, 2H, $J$ = 7.1 Hz, H-5), 4.10-4.19 (m, 1H, H-3), 3.35 (s, 3H, MOM), 2.59 (dd, 1H, $J$ = 15.2, 7.5 Hz, H-$2_a$), 2.41 (dd, 1H, $J$ = 15.2, 5.5 Hz, H-$2_b$), 1.26 (t, 3H, $J$ = 7.1 Hz, H-6), 1.25 (d, 3H, $J$ = 6.2 Hz, H-4) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 171.4 (q, C-1), 95.5 (s, MOM), 70.5 (t, C-3), 60.6 (s, C-5), 55.5 (p, MOM), 42.6 (s, C-2), 20.7 (p, C-4), 14.4 (p, C-6) ppm; **HRMS** (ESI): *m/z*: calculated for $C_8H_{16}NaO_4$: 199.0946 $[M + Na]^+$, found: 199.0950 $[M + Na]^+$. The analytical data are in accordance with those reported in the literature.[S11]

### (*R*)-3-(Methoxymethoxy)butan-1-ol (S88)

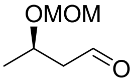


**S88**

Ester **S86** (611 mg, 3.5 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (50 ml) and the solution was cooled to -78 °C. DIBAL-H (8.7 ml, $c$ = 1.2 mol/l in toluene, 10.4 mmol, 3.0 eq) was added dropwise and stirring was continued for 2 h. The solution was warmed up to -50 °C and stirred for another 1.5 h. A second portion of DIBAL-H (3.0 ml, $c$ = 1.2 mol/l in toluene, 3.6 mmol, 1.0 eq) was added and the mixture was stirred for 1.5 h. The reaction was terminated by addition of ethyl acetate and warmed up to rt. Then, aq. Na-K-tartrate was added and after stirring overnight, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 2:1) to furnish alcohol **S88** (327 mg, 2.4 mmol, 70%) as a colourless liquid.

R$_f$ = 0.16 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -77.6 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.71 (d, 1H, *J* = 6.7 Hz, MOM), 4.62 (d, 1H, *J* = 6.7 Hz, MOM), 3.88-3.97 (m, 1H, H-3), 3.76-3.84 (m, 1H, H-1$_a$), 3.69-3.76 (m, 1H, H-1$_b$), 3.38 (s, 3H, MOM), 2.40-2.48 (m, 1H, OH), 1.67-1.81 (m, 2H, H-2), 1.20 (d, *J* = 6.5 Hz, H-4) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 95.1 (s, MOM), 72.4 (t, C-3), 60.3 (s, C-1), 55.7 (p, MOM), 39.3 (s, C-2), 20.4 (p, C-4) ppm; **HRMS** (ESI): *m/z*: Compound **S88** could not be detected by mass spectrometry.

### (*R*)-3-(Methoxymethoxy)butanal (73)

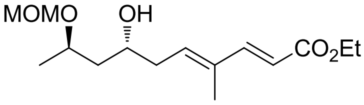


**73**

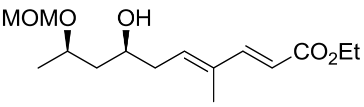
Alcohol **S88** (53 mg, 0.4 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7.0 ml) and $NaHCO_3$ (20 mg) and the DESS-MARTIN periodinane (200 mg, 0.5 mmol, 1.2 eq) were added. The reaction mixture was stirred for 1 h at rt and the reaction was terminated by addition of aq. $Na_2SO_3$/$NaHCO_3$. After 1 h at rt, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 2:1) to furnish aldehyde **73** (27 mg, 0.2 mmol, 51%) as a colourless liquid, which was used immediately in the next step.

R$_f$ = 0.43 (PE:EE = 2:1); **$^1$H-NMR** (200 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.80 (dd, 1H, *J* = 2.6, 1.7 Hz, H-1), 4.71 (d, 1H, *J* = 7.0 Hz, MOM), 4.63 (d, 1H, *J* = 7.0 Hz, MOM), 4.18-4.33 (m, 1H, H-3), 3.35 (s, 3H, MOM), 2.68 (ddd, 1H, *J* = 16.4, 7.3, 2.6 Hz, H-2$_a$), 2.51 (ddd, 1H, *J* = 16.4, 5.0, 1.7 Hz, H-1$_b$), 1.27 (d, 3H, *J* = 6.3 Hz, H-4) ppm.

### (2*E*,4*E*,7*S*,9*R*)-Ethyl-7-hydroxy-9-(methoxymethoxy)-4-methyldeca-2,4-dienoate (7,9-*syn* 75a) and (2*E*,4*E*,7*R*,9*R*)-ethyl-7-hydroxy-9-(methoxymethoxy)-4-methyldeca-2,4-dienoate (7,9-*anti* 75b)



7,9-*anti* **75b**



7,9-*syn* **75a**

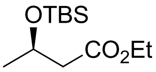
Following the general procedure, aldehyde **73** (27 mg, 0.2 mmol, 1.0 eq.) was reacted with ester **6** (62 mg, 0.4 mmol, 2.0 eq.) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 1:1) to furnish alcohols 7,9-*anti* **75b** and 7,9-*syn* **75a** [*d.r.*: 1.6:1 (**75a**:**75b**), 32 mg, 0.1 mmol, 56%] as yellow liquids.

**HRMS** (ESI): *m/z*: calculated for $C_{15}H_{26}NaO_5$: 309.1678 $[M + Na]^+$, found: 309.1679 $[M + Na]^+$.

7,9-*syn* **75a**: $R_f$ = 0.26 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -36.3 (*c* = 0.8, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, *J* = 15.7 Hz, H-3), 5.95 (dd, 1H, *J* = 7.9, 7.2 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.76 (d, 1H, *J* = 7.0 Hz, MOM), 4.62 (d, 1H, *J* = 7.0 Hz, MOM), 4.20 (q, 2H, *J* = 7.2 Hz, H-12), 3.88-4.00 (m, 2H, H-7 + H-9), 3.39 (s, 3H, MOM), 2.31-2.47 (m, 2H, H-6), 1.80 (s, 3H, H-11), 1.55-1.73 (m, 2H, H-8), 1.29 (t, 3H, *J* = 7.2 Hz, H-13), 1.20 (d, 3H, *J* = 6.2 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.4 (t, C-3), 137.4 (t, C-5), 134.8 (q, C-4), 116.3 (t, C-2), 94.6 (s, MOM), 73.9 (t, C-7), 71.1 (t, C-9), 60.3 (s, C-12), 56.0 (p, MOM), 43.7 (s, C-8), 37.0 (s, C-6), 20.5 (p, C-10), 14.5 (p, C-13), 12.6 (p, C-11) ppm.

7,9-*anti* **75b**: $R_f$ = 0.24 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -24.1 (*c* = 0.6, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, *J* = 15.7 Hz, H-3), 5.97 (dd, 1H, *J* = 8.4, 7.3 Hz, H-5), 5.81 (d, 1H, *J* = 15.7 Hz, H-2), 4.70 (d, 1H, *J* = 6.7 Hz, MOM), 4.62 (d, 1H, *J* = 6.7 Hz, MOM), 4.21 (q, 2H, *J* = 7.1 Hz, H-12), 3.95-4.07 (m, 2H, H-7 + H-9), 3.40 (s, MOM), 2.32-2.50 (m, 2H, H-6), 1.80 (s, 3H, H-11), 1.59-1.65 (m, 2H, H-8), 1.30 (t, 3H, *J* = 7.1 Hz, H-13), 1.22 (d, 3H, *J* = 6.2 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.6 (q, C-1), 149.4 (t, C-3), 137.6 (t, C-5), 134.8 (q, C-4), 116.3 (t, C-2), 95.6 (s, MOM), 71.5 (t, C-9), 67.8 (t, C-7), 60.4 (s, C-12), 55.8 (p, MOM), 43.4 (s, C-8), 36.9 (s, C-6), 20.4 (p, C-10), 14.5 (p, C-13), 12.6 (p, C-11) ppm.

### (*R*)-Ethyl-3-(*tert*-butyldimethylsilyloxy)butanoate (S89)

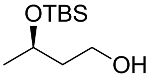


**S89**

Ethyl (*R*)-(-)-3-hydroxybutyrate (**S87**) (0.3 ml, 2.3 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (30 ml), cooled to 0 °C and 2,6-lutidine (1.05 ml, 9.1 mmol, 4.0 eq) and TBSOTf (1.04 ml, 4.5 mmol, 2.0 eq) were successively added. The reaction mixture was stirred for 1 h 0 °C and then for 1.5 h at rt. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were washed with aq. HCl (*c* = 1 mol/l), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1) to furnish alcohol **S89** (529 mg, 2.2 mmol, 95%) as a colourless liquid.

R$_f$ = 0.34 (PE:EE = 20:1); $[\alpha]_D^{20}$ = -19.2 (*c* = 1.0, $CHCl_3$) [Lit. S12.: -28.0 (*c* = 1.1, $CHCl_3$)]; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.23-4.32 (m, 1H, H-3), 4.05-4.18 (m, 2H, H-5), 2.47 (dd, 1H, *J* = 14.5, 7.7 Hz, H-2$_a$), 2.36 (dd, 1H, *J* = 14.5, 5.3 Hz, H-2$_b$), 1.26 (t, 3H, *J* = 7.2 Hz, H-6), 1.19 (d, 3H, *J* = 6.2 Hz, H-4), 0.86 (s, 9H, TBS), 0.06 (s, 3H, TBS), 0.04 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 171.8 (q, C-1), 66.0 (t, C-3), 60.4 (s, C-5), 45.1 (s, C-2), 25.9 (p, TBS), 24.1 (p, C-4), 18.1 (q, TBS), 14.3 (p, C-6), -4.4 (p, TBS), -4.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{26}NaO_3Si$: 269.1549 $[M + Na]^+$, found: 269.1550 $[M + Na]^+$. The analytical data are in accordance with those reported in the literature.[S12]

**(*R*)-3-(*tert*-Butyldimethylsilyloxy)butan-1-ol (S90)**



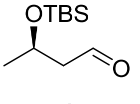
**S90**

Ester **S89** (510 mg, 2.1 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (40 ml) and cooled to -78 °C. DIBAL-H (5.2 ml, *c* = 1.2 mol/l in toluene, 6.2 mmol, 3.0 eq) was added dropwise and the reaction mixture was stirred for 2 h. The solution was warmed to -50 °C and stirring was continued for 1.5 h. A second portion of DIBAL-H (1.8 ml, *c* = 1.2 mol/l in toluene, 2.2 mmol, 1.0 eq) was added and the reaction mixture was stirred for another 1.5 h. The reaction was terminated by addition of ethyl acetate, warmed to rt, aq. Na-K-tartrate was added and stirring was continued overnight. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 5:1) to furnish alcohol **S90** (317 mg, 1.6 mmol, 75%) as a colourless liquid.

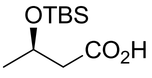
R$_f$ = 0.58 (PE:EE = 2:1); $[\alpha]_D^{20}$ = -26.6 (*c* = 1.0, $CHCl_3$) [Lit. S13.: -28.0 (*c* = 2.1, $CHCl_3$)]; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.11 (dqd, 1H, *J* = 6.6, 6.2, 4.1 Hz, H-3), 3.79-3.88 (m, 1H, H-1$_a$), 3.67-3.75 (m, 1H, H-1$_b$), 2.52-2.58 (m, 1H, OH), 1.78 (dddd, 1H, *J* = 14.1, 8.1, 4.1, 4.1 Hz, H-2$_a$), 1.63 (dddd, 1H, *J* = 14.1, 6.9, 6.6, 4.0 Hz, H-2$_b$), 1.20 (d, *J* = 6.2 Hz, H-4), 0.89 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.08 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 68.6 (t, C-3), 60.7 (s, C-1), 40.6 (s, C-2), 25.9 (p, TBS), 23.6 (p, C-4), 18.1 (q, TBS), -4.2 (p, TBS), -4.8 (p, TBS) ppm; **HRMS** (ESI): *m/z*:

calculated for $C_{10}H_{24}NaO_2Si$: 227.1443 $[M + Na]^+$, found: 227.1433 $[M + Na]^+$. The analytical data are in accordance with those reported in the literature.[S13]

### (*R*)-3-(*tert*-Butyldimethylsilyloxy)butanal (74)



**74**



**S91**

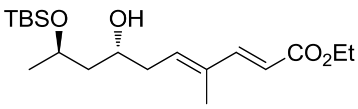
Alcohol **S90** (77 mg, 0.4 mmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (7.5 ml) and $NaHCO_3$ (40 mg) and the DESS-MARTIN periodinane (240 mg, 0.6 mmol, 1.5 eq) were added and the reaction mixture was stirred for 75 min. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 50 min. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 2:1) to furnish aldehyde **74** (40.1 mg, 0.20 mmol, 53%) and the corresponding acid **S91** (31.1 mg, 140 µmol, 38%) as colourless liquids. Aldehyde **74** was used immediately in the next step.

**74**: $R_f$ = 0.67 (PE:EE = 5:1); **$^1$H-NMR** (200 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 9.80 (dd, 1H, *J* = 2.4, 2.2 Hz, H-1), 4.53 (ddq, 1H, *J* = 6.2, 6.1, 6.0 Hz, H-3), 2.38-2.63 (m, 2H, H-2), 1.24 (d, 3H, *J* = 6.2 Hz, H-4), 0.87 (s, 9H, TBS), 0.08 (s, 3H, TBS), 0.06 (s, 3H, TBS) ppm. The NMR-data are in accordance with those reported in the literature.[S12,S13]

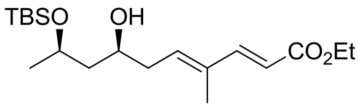
**S91**: $R_f$ = 0.25 (PE:EE = 5:1); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 4.28 (qdd, 1H, *J* = 6.0, 5.9, 5.9 Hz, H-3), 2.42-2.57 (m, 2H, H-2), 1.25 (d, 3H, *J* = 6.0 Hz, H-4), 0.89 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.09 (s, 3H, TBS); **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 174.9 (q, C-1), 65.9 (t, C-3), 43.9 (s, C-2), 25.8 (p, TBS), 23.6 (p, C-4), 18.1 (q, TBS), -4.4 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{10}H_{21}O_3Si$: 217.1260 $[M - H]^-$, found: 217.1259 $[M - Na]^-$.

### (2*E*,4*E*,7*S*,9*R*)-Ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4-methyldeca-2,4-dienoate (7,9-*syn* 76a) and

### (2*E*,4*E*,7*R*,9*R*)-ethyl-9-(*tert*-butyldimethylsilyloxy)-7-hydroxy-4-methyldeca-2,4-dienoate (7,9-*anti* 76b)



7,9-*anti* **76b**



7,9-*syn* **76a**

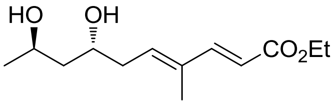
Following the general procedure, aldehyde **74** (40 mg, 0.2 mmol, 1.0 eq) was reacted with ester **6** (61 mg, 0.4 mmol, 2.0 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 40:1 → 2:1) to furnish alcohols 7,9-*anti* **76b** and 7,9-*syn* **76a** [*d.r.*: 1:3 (**76b**:**76a**), 56 mg, 0.2 mmol, 79%] as a colourless liquid.

$R_f$ = 0.36 (PE:EE = 2:1); the diastereomers could not be separated by column chromatography; **HRMS** (ESI): *m/z*: calculated for $C_{19}H_{36}NaO_4Si$: 379.2281 [M + Na]$^+$, found: 379.2280 [M + Na]$^+$.

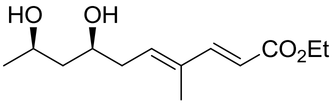
7,9-*syn* **76a**: **$^{1}$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, *J* = 15.9 Hz, H-3), 5.96 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.80 (d, 1H, *J* = 15.9 Hz, H-2), 4.20 (q, 2H, *J* = 7.1 Hz, H-12), 4.02-4.14 (m, 1H, H-9), 3.85-3.93 (m, 1H, H-7), 3.69 (s, 1H, OH), 2.28-2.47 (m, 2H, H-6), 1.79 (s, 3H, H-11), 1.56 (dd, 2H, *J* = 6.2, 6.1 Hz, H-8), 1.29 (t, 3H, *J* = 7.1 Hz, H-13), 1.17 (d, 3H, *J* = 6.2 Hz, H-10), 0.90 (s, 9H, TBS), 0.12 (s, 3H, TBS), 0.11 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 137.6 (t, C-5), 134.7 (q, C-4), 116.2 (t, C-2), 71.3 (t, C-7), 70.5 (t, C-9), 60.3 (s, C-12), 45.2 (s, C-8), 37.0 (s, C-6), 25.9 (p, TBS), 24.8 (p, C-10), 18.0 (q, TBS), 14.5 (p, C-13), 12.6 (p, C-11), -3.7 (p, TBS), -4.7 (p, TBS) ppm.

7,9-*anti* **76b**: **$^{1}$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.34 (d, 1H, *J* = 15.9 Hz, H-3), 5.96 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.80 (d, 1H, *J* = 15.9 Hz, H-2), 4.20 (q, 2H, *J* = 7.1 Hz, H-12), 4.18-4.24 (m, 1H, H-9), 4.02-4.14 (m, 1H, H-9), 3.57 (s, 1H, OH), 2.28-2.47 (m, 2H, H-6), 1.79 (s, 3H, H-11), 1.56 (dd, 2H, *J* = 6.2, 6.1 Hz, H-8), 1.29 (t, 3H, *J* = 7.1 Hz, H-13), 1.23 (d, 3H, *J* = 6.5 Hz, H-10), 0.89 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.08 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.5 (t, C-3), 137.7 (t, C-5), 134.7 (q, C-4), 116.2 (t, C-2), 68.1 (t, C-7), 67.8 (t, C-9), 60.3 (s, C-12), 43.7 (s, C-8), 37.3 (s, C-6), 25.9 (p, TBS), 22.8 (p, C-10), 18.1 (q, TBS), 14.5 (p, C-13), 12.6 (p, C-11), -4.4 (p, TBS), -4.9 (p, TBS) ppm.

### **(2*E*,4*E*,7*S*,9*R*)-Ethyl-7,9-dihydroxy-4-methyldeca-2,4-dienoate (**7,9-*syn* **S92a)** and **(2*E*,4*E*,7*R*,9*R*)-ethyl-7,9-dihydroxy-4-methyldeca-2,4-dienoate (**7,9-*anti* **S92b)**



7,9-*anti* **S92b**



7,9-*syn* **S92a**

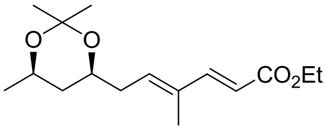
A mixture of alcohols **76** [*d.r.*: 1:3 (**76b**:**76a**), 28 mg, 79 μmol, 1.0 eq] was dissolved in THF (1.4 ml) and cooled to 0 °C. TBAF·3$H_2O$ (32 mg, 0.1 mmol, 1.3 eq) was dissolved in THF (0.9 ml) and added to the first solution. The reaction was terminated after 45 min by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 1:1) to furnish diols 7,9-*anti* **S92b** and 7,9-*syn* **S92a** [*d.r.*: ~1:2.5 (**S92b**:**S92a**), 18 mg, 75 μmol, 83%] as colourless liquids.

$R_f$ = 0.20 (PE:EE = 2:1); **HRMS** (ESI): *m/z*: Compound **S92** could not be detected by mass spectrometry.

7,9-*syn* **S92a**: $[\alpha]_D^{20}$ = -2.8 (*c* = 0.4, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, *J* = 15.5 Hz, H-3), 5.93 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.82 (d, 1H, *J* = 15.5 Hz, H-2), 4.20 (q, 2H, *J* = 7.0 Hz, H-12), 4.02-4.10 (m, 1H, H-9), 3.94-4.01 (m, 1H, H-7), 2.31-2.52 (m, 2H, H-6), 1.79 (s, 3H, H-11), 1.47-1.66 (m, 2H, H-8), 1.29 (t, 3H, *J* = 7.0 Hz, H-13), 1.21 (d, 3H, *J* = 6.2 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.2 (t, C-3), 136.9 (t, C-5), 135.2 (q, C-4), 116.5 (t, C-2), 72.4 (t, C-7), 69.3 (t, C-9), 60.4 (s, C-12), 44.3 (s, C-8), 37.5 (s, C-6), 24.5 (p, C-10), 14.5 (p, C-13), 12.6 (p, C-11) ppm.

7,9-*anti* **S92b**: $[\alpha]_D^{20}$ = -0.9 (*c* = 0.4, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.32 (d, 1H, *J* = 15.5 Hz, H-3), 5.93 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.82 (d, 1H, *J* = 15.5 Hz, H-2), 4.20 (q, 2H, *J* = 7.0 Hz, H-12), 4.14-4.22 (m, 1H, H-9), 4.02-4.10 (m, 1H, H-7), 2.31-2.52 (m, 2H, H-6), 1.79 (s, 3H, H-11), 1.47-1.66 (m, 2H, H-8), 1.29 (t, 3H, *J* = 7.0 Hz, H-13), 1.24 (d, 3H, *J* = 6.2 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.2 (t, C-3), 137.3(t, C-5), 135.1 (q, C-4), 116.5 (t, C-2), 68.8 (t, C-7), 65.6 (t, C-9), 60.4 (s, C-12), 43.8 (s, C-8), 37.0 (s, C-6), 23.7 (p, C-10), 14.5 (p, C-13), 12.6 (p, C-11) ppm.

**Acetonide** (7,9-*syn* **S93a**)

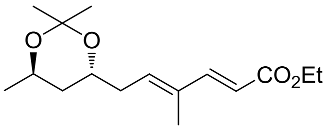


7,9-*syn* **S93a**

Diol 7,9-*syn* **S92a** (8.6 mg, 19 μmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (2 ml) and 2,2-dimethoxypropane (0.2 ml) as well as PPTS (2 mg, catalytic) were added. The reaction mixture was stirred for 1 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 8:1 → 2:1) to furnish acetonide 7,9-*syn* **S93a** (2.3 mg, 8 µmol, 42%) as a colourless liquid.

$R_f$ = 0.76 (PE:EE = 1:1); $[\alpha]_D^{20}$ = +2.5 ($c$ = 0.2, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.33 (d, 1H, $J$ = 15.7 Hz, H-3), 5.92 (dd, 1H, $J$ = 7.2, 7.2 Hz, H-5), 5.81 (d, 1H, $J$ = 15.7 Hz, H-2), 4.21 (q, 2H, $J$ = 7.2 Hz, H-12), 3.86-4.02 (m, 2H, H-9 + H-7), 2.28-2.49 (m, 2H, H-6), 1.78 (s, 3H, H-11), 1.46-1.55 (m, 2H, H-8), 1.45 (s, 3H, H-$15_a$), 1.41 (s, 3H, H-$15_b$), 1.30 (t, 3H, $J$ = 7.2 Hz, H-13), 1.17 (d, 3H, $J$ = 5.8 Hz, H-10) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.4 (t, C-3), 136.9 (t, C-5), 134.7 (q, C-4), 116.2 (t, C-2), 98.8 (q, C-14), 68.6 (t, C-7), 65.2 (t, C-9), 60.4 (s, C-12), 38.5 (s, C-8), 35.9 (s, C-6), 30.4 (p, C-$15_b$), 22.4 (p, C-10), 20.0 (p, C-$15_a$), 14.5 (p, C-13), 12.6 (p, C-11) ppm; **HRMS** (ESI): $m/z$: calculated for $C_{16}H_{26}NaO_4$: 305.1729 $[M + Na]^+$, found: 305.1726 $[M + Na]^+$.

**Acetonide** (7,9-*anti* **S93b**)



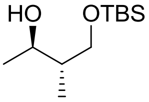
7,9-*anti* **S93b**

Diol 7,9-*anti* **S92b** (4.8 mg, 20 µmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (2 ml) and 2,2-dimethoxypropane (0.2 ml) as well as PPTS (2 mg, catalytic) were added. The reaction mixture was stirred for 1 h at rt. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 8:1 → 2:1). Acetonide 7,9-*anti* **S93b** (2.7 mg, 10 µmol, 48%) was obtained as a colourless liquid.

$R_f$ = 0.75 (PE:EE = 1:1); $[\alpha]_D^{20}$ = -18.3 ($c$ = 0.3, $CH_2Cl_2$); **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 7.65 (d, 1H, $J$ = 15.6 Hz, H-3), 5.97 (d, 1H, $J$ = 15.6 Hz, H-2), 5.72 (dd, 1H, $J$ = 7.1, 7.0 Hz, H-5), 4.11 (q, 2H, $J$ = 7.1 Hz, H-12), 3.75-3.86 (m, 1H, H-9), 3.65-3.74 (m, 1H, H-7), 2.21 (ddd, 1H, $J$ = 15.0, 7.0, 6.9 Hz, H-$6_a$), 2.05 (ddd, 1H, $J$ = 15.0, 6.7, 6.7 Hz, H-$6_b$), 1.48 (s, 3H, H-11), 1.34 (s, 3H, H-$15_a$), 1.32 (s, 3H, H-$15_b$), 1.16-1.38 (m, 2H, H-8), 1.09 (d, 3H, $J$ = 6.3 Hz, H-10), 1.03 (t, 3H, $J$ = 7.1 Hz, H-13) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$ = 128.06 ppm): δ 167.0 (q, C-1), 149.3 (t, C-3), 137.4 (t, C-5), 134.5 (q, C-4), 116.9 (t, C-2), 100.2 (q, C-14), 66.1 (t, C-7), 62.7 (t, C-9), 60.1 (s, C-12), 39.9 (s, C-8), 35.5 (s, C-6), 25.2 (p, C-$15_b$), 25.2 (p, C-$15_a$), 22.0 (p, C-10), 14.4 (p, C-13), 12.3 (p, C-11) ppm;

**HRMS** (ESI): *m/z*: calculated for $C_{16}H_{26}NaO_4$: 305.1729 [M + Na]$^+$, found: 305.1729 [M + Na]$^+$.

### Alcohol S94

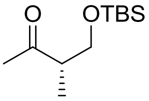


**S94**

Alcohol **S94** was isolated from the reaction mixture of alcohol **77/S68** after acid treatment. It is supposed to be formed by a proton-mediated silyl shift.

R$_f$ = 0.4 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +8.4 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 3.78 (dd, 1H, *J* = 10.1, 3.9 Hz, H-1$_a$), 3.63-3.74 (m, 1H, H-3), 3.55 (dd, 1H, *J* = 10.1, 8.4 Hz, H-1$_b$), 1.59-1.71 (m, 1H, H-2), 1.18 (d, 3H, *J* = 6.2 Hz, H-4), 0.90 (s, 9H, TBS), 0.80 (d, 3H, *J* = 6.8 Hz, H-5), 0.08 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 73.4 (t, C-3), 69.2 (s, C-1), 41.5 (t, C-2), 26.0 (p, TBS), 21.5 (p, C-4), 18.2 (q, TBS), 13.5 (p, C-5), -5.5 (p, TBS), -5.5 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{11}H_{26}NaO_2Si$: 241.1600 [M + Na]$^+$, found: 241.1598 [M + Na]$^+$.

### (*S*)-4-(*tert*-Butyldimethylsilyloxy)-3-methylbutan-2-one (78)



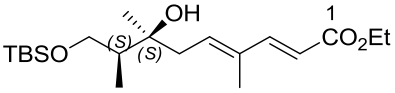
**78**

Alcohol **S94** (41 mg, 188 µmol, 1.0 eq) was dissolved in $CH_2Cl_2$ (4 ml) and $NaHCO_3$ (20 mg) as well as the DESS-MARTIN periodinane (96 mg, 226 µmol, 1.2 eq) were added. The reaction mixture was stirred for 1 h at rt. The reaction was terminated by addition of aq. $Na_2S_2O_3$ and stirring was continued for 1 h at rt. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 20:1) to furnish ketone **78** (26 mg, 121 µmol, 64%) as a colourless liquid.

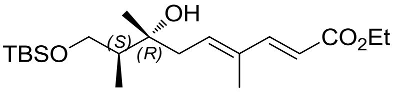
R$_f$ = 0.53 (PE:EE = 2:1); $[\alpha]_D^{20}$ = +13.7 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $C_6D_6$, $C_6D_5H$ = 7.16 ppm): δ 3.62 (dd, 1H, *J* = 9.9, 7.1 Hz, H-4$_a$), 3.45 (dd, 1H, *J* = 9.9, 5.6 Hz, H-4$_b$), 2.41

(qdd, 1H, *J* = 7.1, 7.1, 5.6 Hz, H-3), 1.84 (s, 3H, H-1), 0.92 (s, 9H, TBS), 0.86 (d, 3H, *J* = 7.1 Hz, H-5), 0.00 (s, 3H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $C_6D_6$, $C_6D_6$ = 128.06 ppm): δ 209.0 (q, C-2), 65.7 (s, C-4), 49.2 (t, C-3), 29.2 (p, C-1), 26.2 (p, TBS), 18.4 (q, TBS), 13.0 (p, C-5), -5.4 (p, TBS) ppm.

**Alcohols** (7*S*)-**79a and** (7R)-**79b**



(7*S*)-**79a**



(7*R*)-**79b**

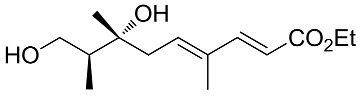
Following the general procedure, ketone **78** (23 mg, 0.11 mmol, 1.0 eq) was reacted with ester **6** (34 mg, 0.22 mmol, 2 eq) at -78 °C overnight. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 30:1 → 5:1) to furnish alcohols (7*S*)-**79a** and (7*R*)-**79b** [*d.r.*: 1:1.5 (**79b**:**79a**), 22 mg, 0.06 mmol, 54%] as colourless liquids.

**HRMS** (ESI): *m/z*: calculated for $C_{20}H_{38}NaO_4Si$: 393.2461 $[M + Na]^+$, found: 393.2449 $[M + Na]^+$.

(7*R*)-**79b**: R$_f$ = 0.43 (PE:EE = 5:1); Mixture with 7,8-*syn*,8,9-*anti* **68b**; **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.38 (d, 1H, *J* = 15.7 Hz, H-3), 6.14 (dd, 1H, *J* = 7.2, 7.2 Hz, H-5), 5.79 (d, 1H, *J* = 15.7 Hz, H-2), 4.38 (brs, 1H, OH), 4.20 (q, 2H, *J* = 7.2 Hz, H-13), 3.76 (dd, 1H, *J* = 10.2, 4.4 Hz, H-9$_a$), 3.65 (dd, 1H, *J* = 10.2, 8.5 Hz, H-9$_b$), 2.40 (d, 1H, *J* = 4.8 Hz, H-6$_a$), 2.38 (d, 1H, *J* = 4.8 Hz, H-6$_b$), 1.80-1.90 (m, 1H, H-8), 1.79 (s, 3H, H-10), 1.29 (t, 3H, *J* = 7.2 Hz, H-14), 1.14 (s, 3H, H-11), 0.90 (s, 9H, TBS), 0.80 (d, 3H, *J* = 7.2 Hz, H-12), 0.09 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.9 (t, C-3), 138.1 (t, C-5), 134.1 (q, C-4), 115.7 (t, C-2), 75.5 (t, C-7), 67.0 (t, C-9), 60.3 (s, C-13), 41.4 (t, C-8), 40.9 (s, C-6), 25.9 (p, TBS), 22.9 (p, C-11), 18.2 (q, TBS), 14.5 (p, C-14), 12.7 (p, C-12), 12.6 (p, C-10), -5.5 (p, TBS), -5.6 (p, TBS) ppm.

(7*S*)-**79a**: R$_f$ = 0.37 (PE:EE = 5:1); $[\alpha]_D^{20}$ = -10.0 (*c* = 1.0, $CHCl_3$); **$^1$H-NMR** (400 MHz, $CDCl_3$, $CHCl_3$ = 7.26 ppm): δ 7.36 (d, 1H, *J* = 15.5 Hz, H-3), 6.06 (dd, 1H, *J* = 7.3, 7.3 Hz, H-5), 5.79 (d, 1H, *J* = 15.5 Hz, H-2), 4.20 (q, 2H, *J* = 7.1 Hz, H-13), 4.08 (brs, 1H, OH), 3.88 (dd, 1H, *J* = 10.2, 4.1 Hz, H-9$_a$), 3.65 (dd, 1H, *J* = 10.2, 6.5 Hz, H-9$_b$), 2.36-2.41 (m, 1H, H-6), 1.79 (s, 3H, H-10), 1.71-1.78 (m, 1H, H-8), 1.29 (t, 3H, *J* = 7.1 Hz, H-14), 1.19 (s, 3H, H-11), 0.95 (d, 3H, *J* = 6.8 Hz, H-12), 0.90 (s, 9H, TBS), 0.09 (s, 6H, TBS) ppm; **$^{13}$C-NMR** (100 MHz, $CDCl_3$, $CDCl_3$ = 77.16 ppm): δ 167.7 (q, C-1), 149.8 (t, C-3), 138.0 (t, C-5), 134.4 (q, C-4), 115.8 (t, C-2), 75.5 (t, C-7), 67.0 (t, C-9), 60.3 (s, C-13), 42.6 (t, C-8), 37.5 (s, C-6), 26.6 (p, C-11), 25.9 (p, TBS), 18.2 (q, TBS), 14.5 (p, C-14), 12.7 (p, C-12), 12.6 (p, C-10), -5.6 (p, TBS), -5.6 (p, TBS) ppm.

### **Diol** (7*R*)-**S95b**

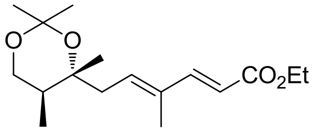


(7*R*)-**S95b**

Alcohol (7*R*)-**79b** (15 mg, 40 µmol, 1.0 eq) was dissolved in THF (1.5 ml) and the solution was cooled to 0 °C. TBAF·$3H_2O$ (15 mg, 50 µmol, 1.2 eq) was added and the reaction mixture was stirred for 1 h at 0 °C. The reaction was terminated by addition of aq. $NH_4Cl$. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined, organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether : ethyl acetate = 7:1 → 2:1) to furnish diol (7*R*)-**S95b** (5 mg, 20 µmol, 49%) as a colourless liquid.

$R_f$ = 0.20 (PE:EE = 1:1); $[\alpha]_D^{20}$ = -0.6 (*c* = 0.2, MeOH); **$^1$H-NMR** (500 MHz, $CD_3OD$, $CD_2HOD$ = 3.31 ppm): δ 7.36 (d, 1H, *J* = 15.5 Hz, H-3), 6.14 (dd, 1H, *J* = 7.6, 7.4 Hz, H-5), 5.42 (d, 1H, *J* = 15.5 Hz, H-2), 4.19 (q, 2H, *J* = 7.1 Hz, H-13), 3.81 (dd, 1H, *J* = 10.5, 6.1 Hz, H-$9_a$), 3.47 (dd, 1H, *J* = 10.5, 7.0 Hz, H-$9_b$), 2.47 (dd, 1H, *J* = 15.2, 7.6 Hz, H-$6_a$), 2.41 (dd, 1H, *J* = 15.2, 7.4 Hz, H-$6_b$), 1.82 (s, 3H, H-10), 1.77 (dqd, 1H, *J* = 7.0, 6.8, 6.1 Hz, H-8), 1.29 (t, 3H, *J* = 7.1 Hz, H-14), 1.13 (s, 3H, H-12), 0.92 (d, 3H, *J* = 6.8 Hz, H-11) ppm; **$^{13}$C-NMR** (500 MHz, $CD_3OD$, $CD_3OD$ = 77.16 ppm): δ 169.3 (q, C-1), 151.0 (t, C-3), 139.2 (t, C-5), 135.7 (q, C-4), 116.5 (t, C-2), 76.2 (q, C-7), 65.3 (s, C-9), 61.4 (s, C-13), 44.6 (s, C-6), 41.0 (t, C-8), 23.3 (p, C-12), 14.6 (p, C-14), 12.9 (p, C-10), 12.6 (p, C-11) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{24}NaO_4$: 279.1572 $[M + Na]^+$, found: 279.1573 $[M + Na]^+$.

### **Acetonide** (7*R*)-**80b**



(7*R*)-**80b**

Diol (7*R*)-**S95b** (2 mg, 8 µmol, 1.0 eq.) was dissolved in $CH_2Cl_2$ (0.70 ml) and cooled to 0 °C and 2,2-dimethoxypropane (0.07 ml) as well as PPTS (0.2 mg, catalytic) were added and stirring was continued for 1 h at rt. The reaction was terminated by addition of $Et_3N$ and the solvent was removed under reduced pressure. The crude product was purified by RP-HPLC (Macherey-Nagel NUCLEODUR C18 ISIS 5 µm, column: 250 mm x 8 mm, gradient: 50/50 water/MeOH → 100 MeOH in 60 min, flow: 3.5 ml/min, $t_r$ = 37.5 min). Diol (7*R*)-**80b** (1.5 mg, 5 µmol, 64%) was obtained as a colourless liquid.

$R_f$ = 0.8 (PE:EE = 1:1); $[\alpha]_D^{20}$ = -5.9 (*c* = 0.1, MeOH); **$^1$H-NMR** (500 MHz, $CD_3OD$, $CD_2HOD$ = 3.31 ppm): δ 7.34 (d, 1H, *J* = 15.7 Hz, H-3), 6.12 (dd, 1H, *J* = 8.0, 7.2 Hz, H-5), 5.83 (d, 1H, *J* = 15.7 Hz, H-2), 4.19 (q, 2H, *J* = 7.2 Hz, H-13), 3.70 (dd, 1H, *J* = 11.7, 11.1 Hz, H-$9_a$), 3.60 (dd, 1H, *J* = 11.7, 4.9 Hz, H-$9_e$), 2.45 (dd, 1H, *J* = 15.2, 8.0 Hz, H-$6_a$), 2.39 (dd, 1H, *J* = 15.2, 7.2 Hz, H-$6_b$), 1.85-1.94 (m, 1H, H-8), 1.81 (s, 3H, H-10), 1.43 (s, 3H, H-12), 1.33 (s, 3H, H-$16_e$), 1.29 (t, 3H, *J* = 7.2 Hz, H-14), 1.27 (p, 3H, H-$16_a$), 0.80 (d, 3H, *J* = 7.1 Hz, H-11) ppm; **$^{13}$C-NMR** (500 MHz, $CD_3OD$, $CD_3OD$ = 77.16 ppm): δ 169.3 (q, C-1), 151.2 (t, C-3), 139.5 (t, C-5), 135.6 (q, C-4), 116.4 (t, C-2), 99.4 (q, C-15), 78.1 (q, C-7), 63.5 (s, C-9), 61.4 (s, C-13), 42.1 (s, C-6), 36.6 (t, C-8), 31.1 (p, C-$16_e$), 25.3 (p, C-12), 22.6 (C-$16_a$), 14.6 (p, C-14), 12.6 (p, C-10), 12.4 (p, C-11) ppm; **HRMS** (ESI): *m/z*: calculated for $C_{17}H_{28}NaO_4$: 319.1885 $[M + Na]^+$, found: 319.1892 $[M + Na]^+$.

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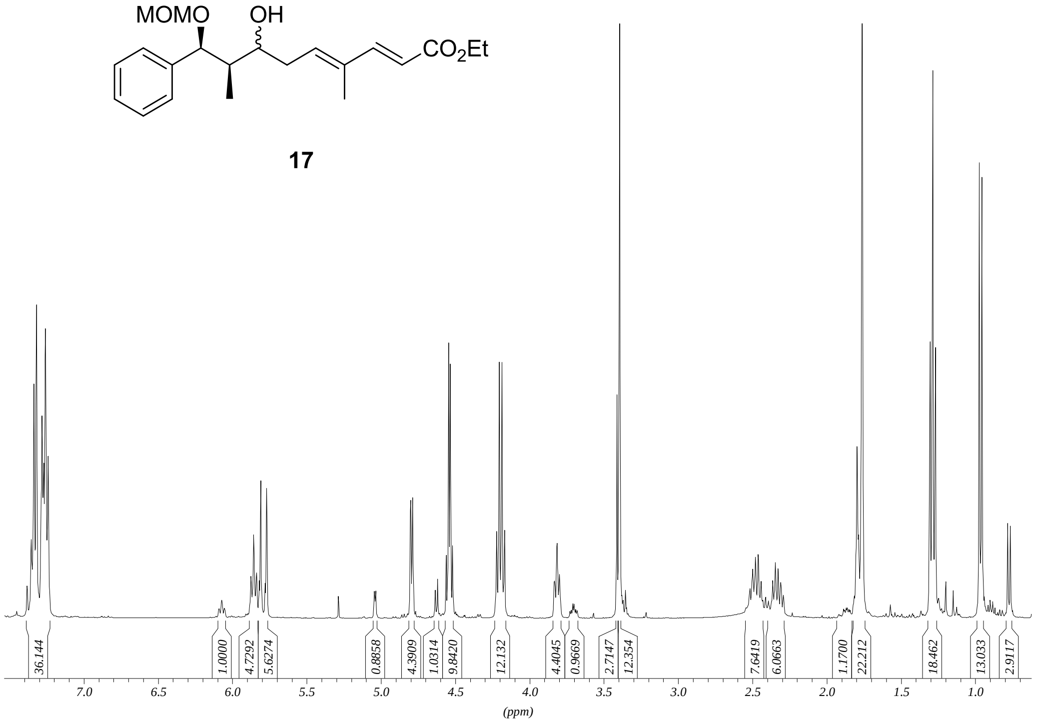
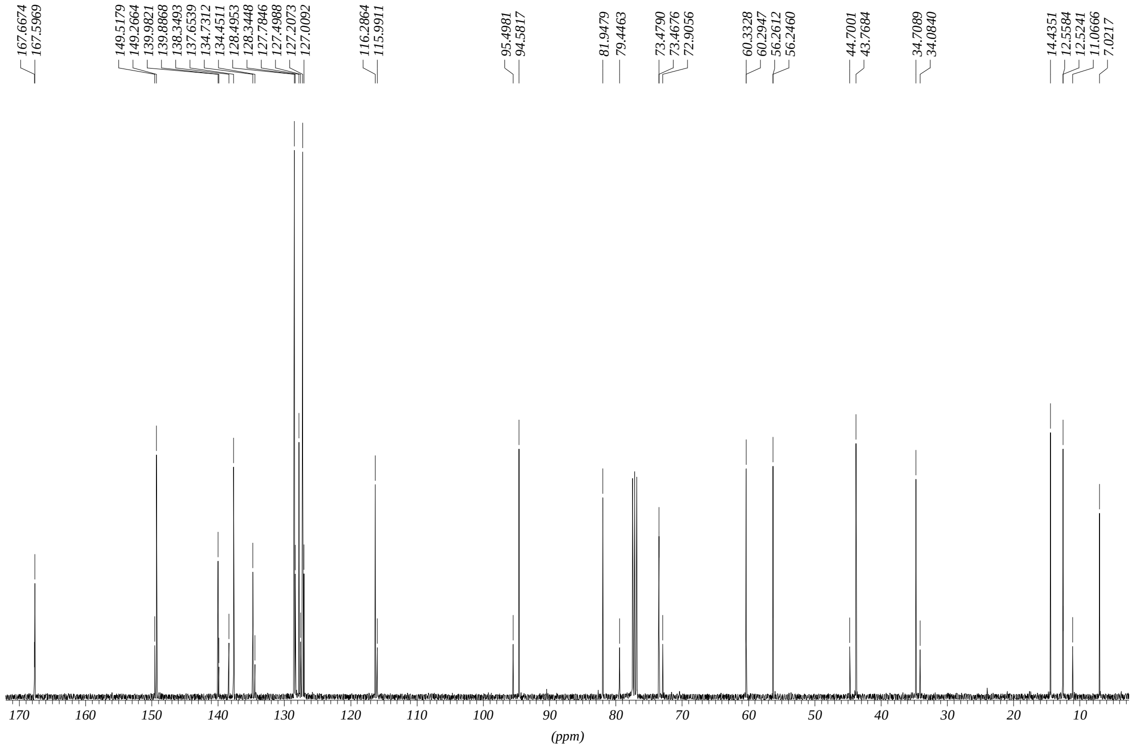
# Attachement: representative NMR spectra



**17**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110
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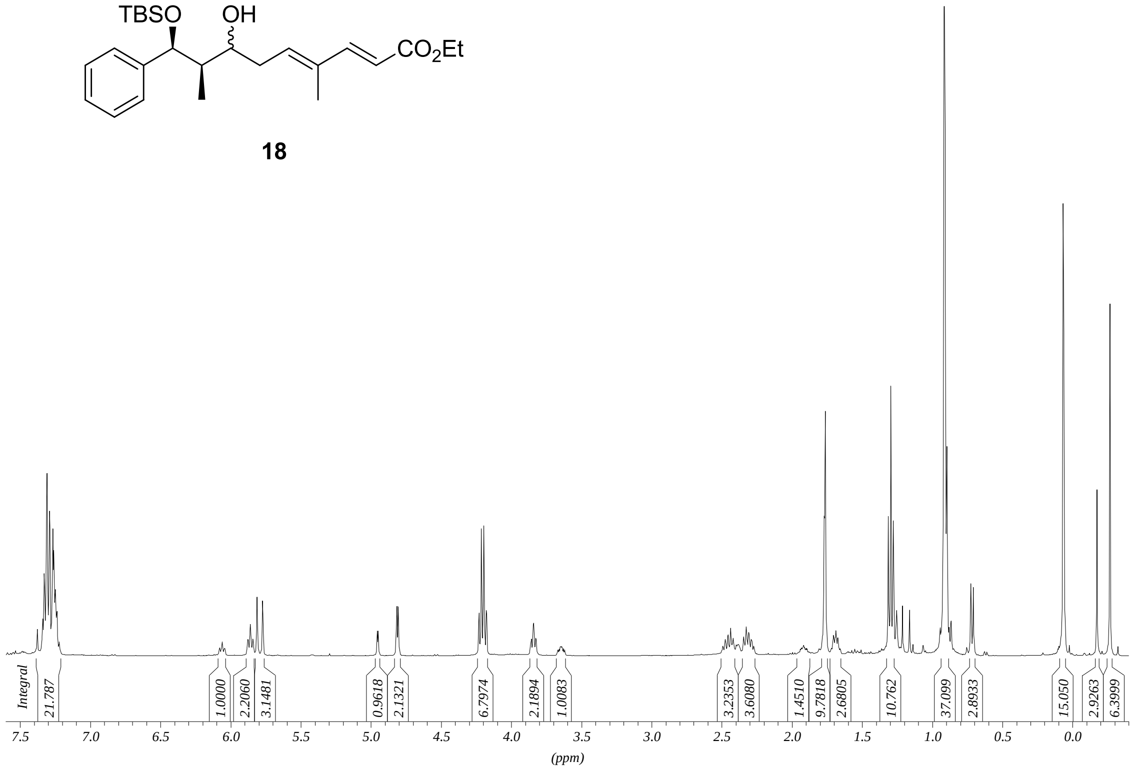
(ppm)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6.5
6.0
5.5
5.0
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3.0
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1.5
1.0
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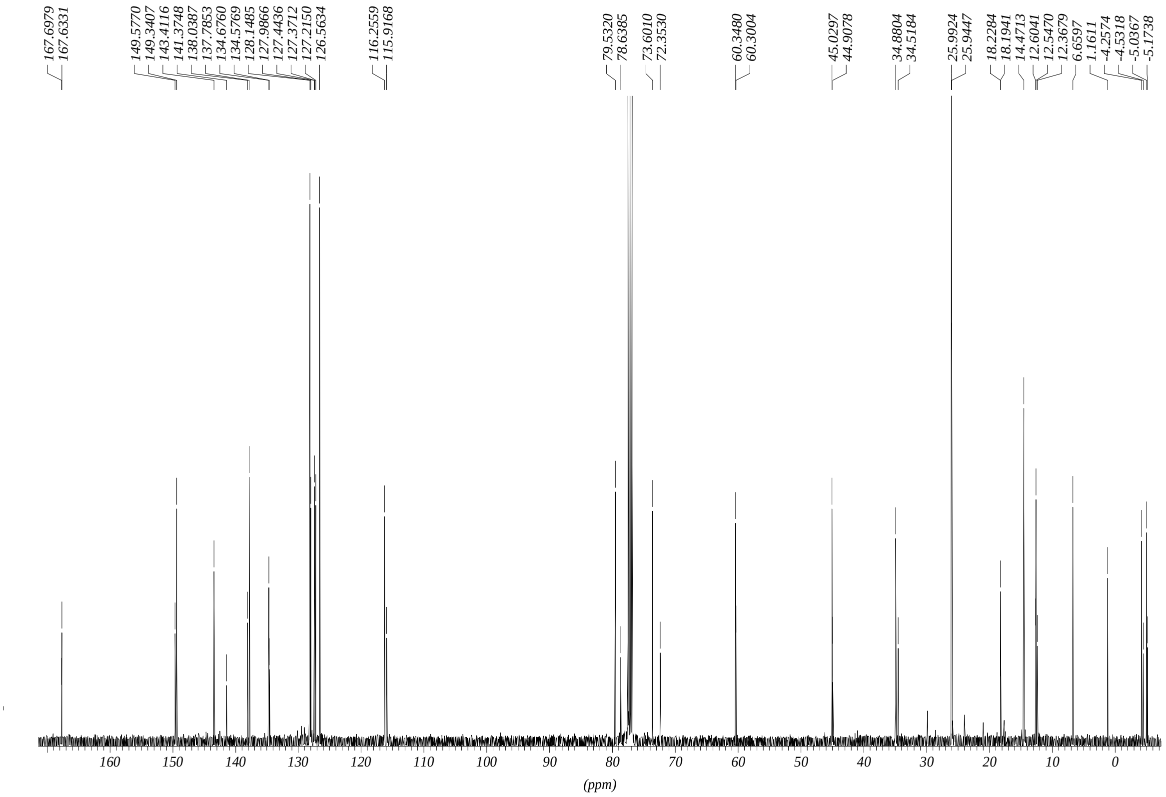
(ppm)

**18**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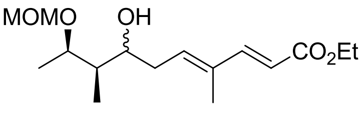
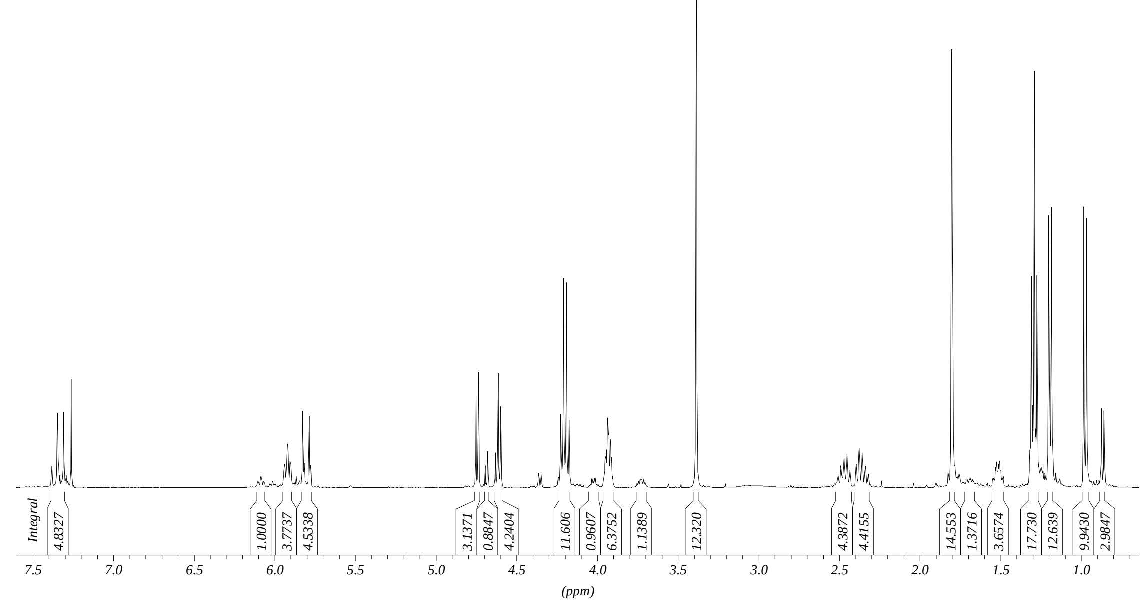
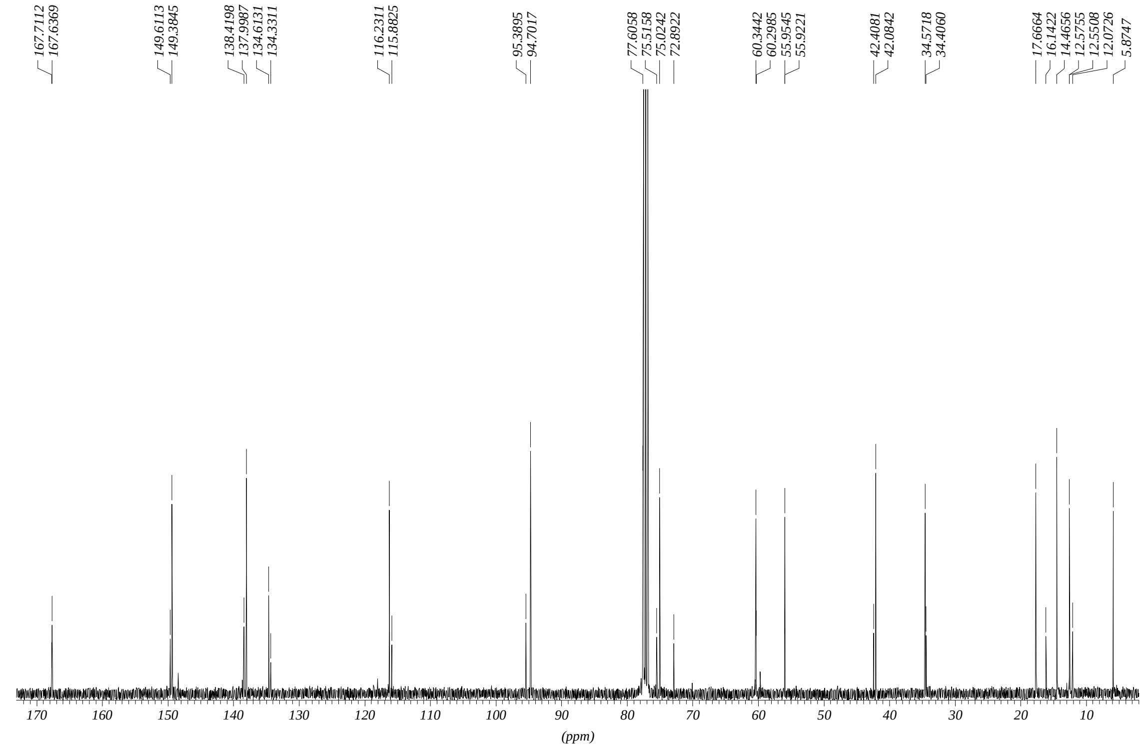
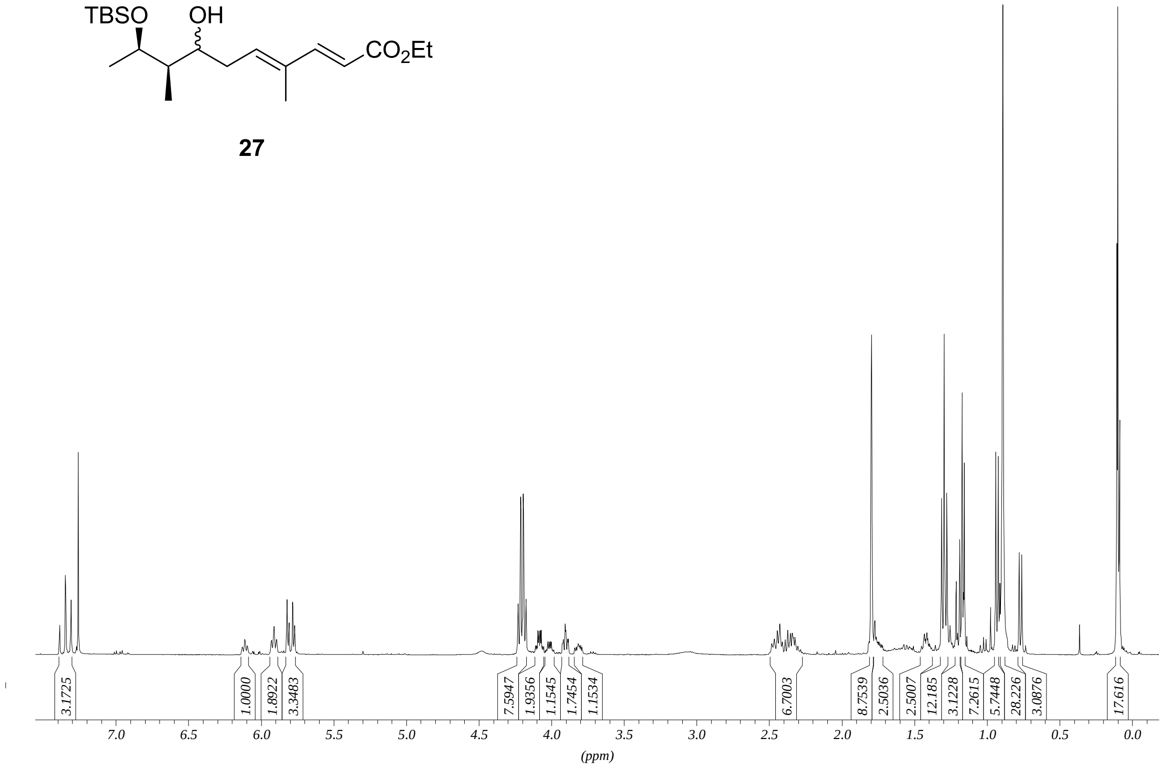
34.8804
34.5184
25.9924
25.9447
18.2284
18.1941
14.4713
12.6041
12.5470
12.3679
6.6597
1.1611
-4.2574
-4.5318
-5.0367
-5.1738
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


MOMO
OH
CO2Et

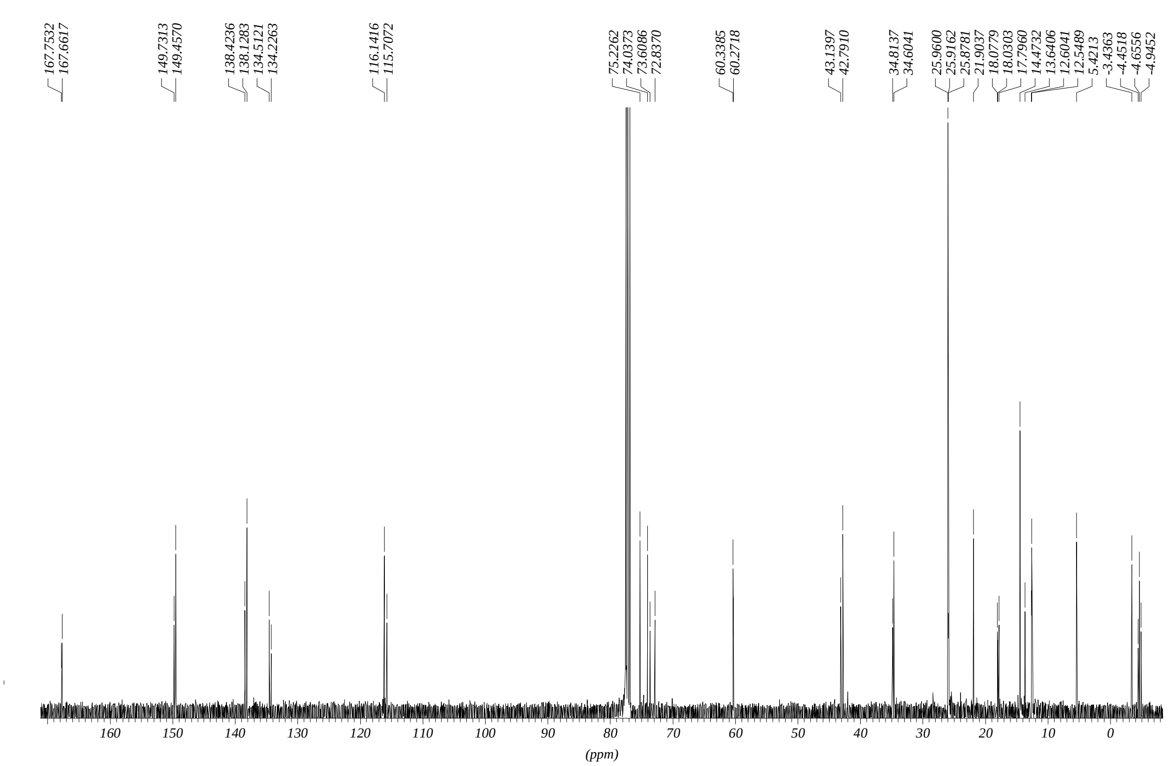
**26**

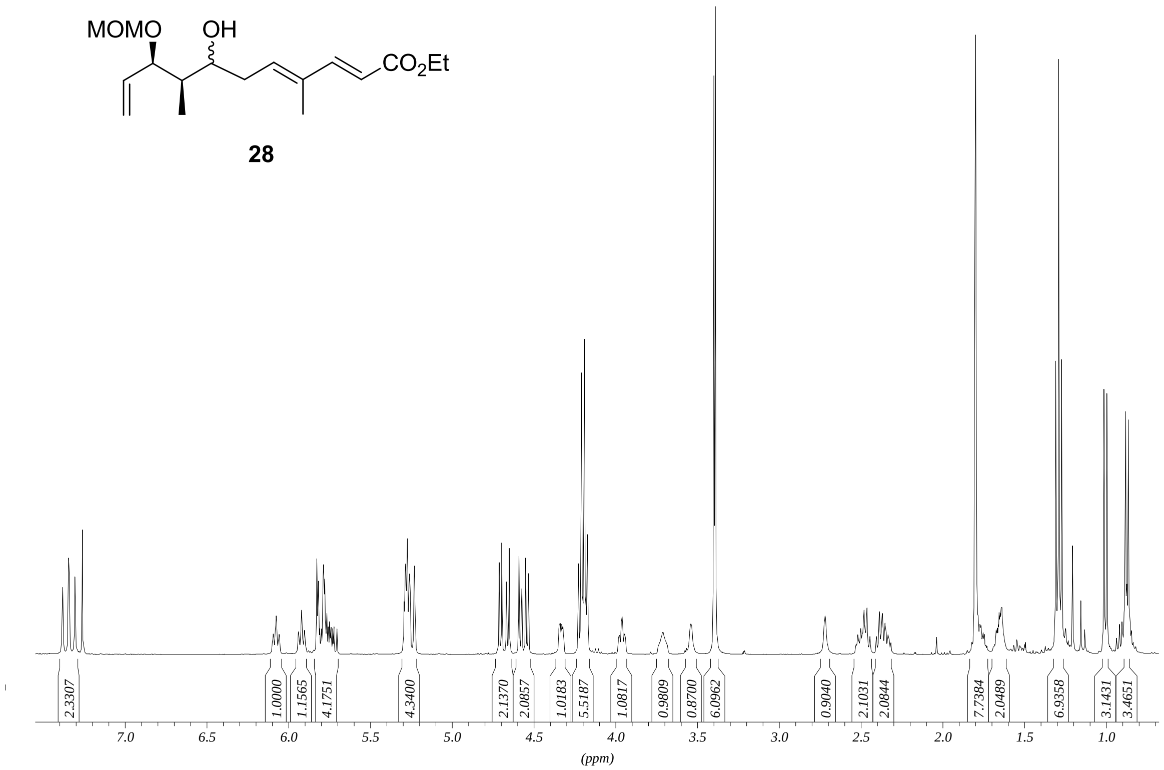

Integral
4.8327
1.0000
3.7737
4.5338
3.1371
0.8847
4.2404
11.606
0.9607
6.3752
1.1389
12.320
4.3872
4.4155
14.553
1.3716
3.6574
17.730
12.639
9.9430
2.9847
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)


167.7112
167.6369
149.6113
149.3845
138.4198
137.9987
134.6131
134.3311
116.2311
115.8825
95.3895
94.7017
77.6058
75.5158
75.0242
72.8922
60.3442
60.2985
55.9545
55.9221
42.4081
42.0842
34.5718
34.4060
17.6664
16.1422
14.4656
12.5755
12.5508
12.0726
5.8747
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

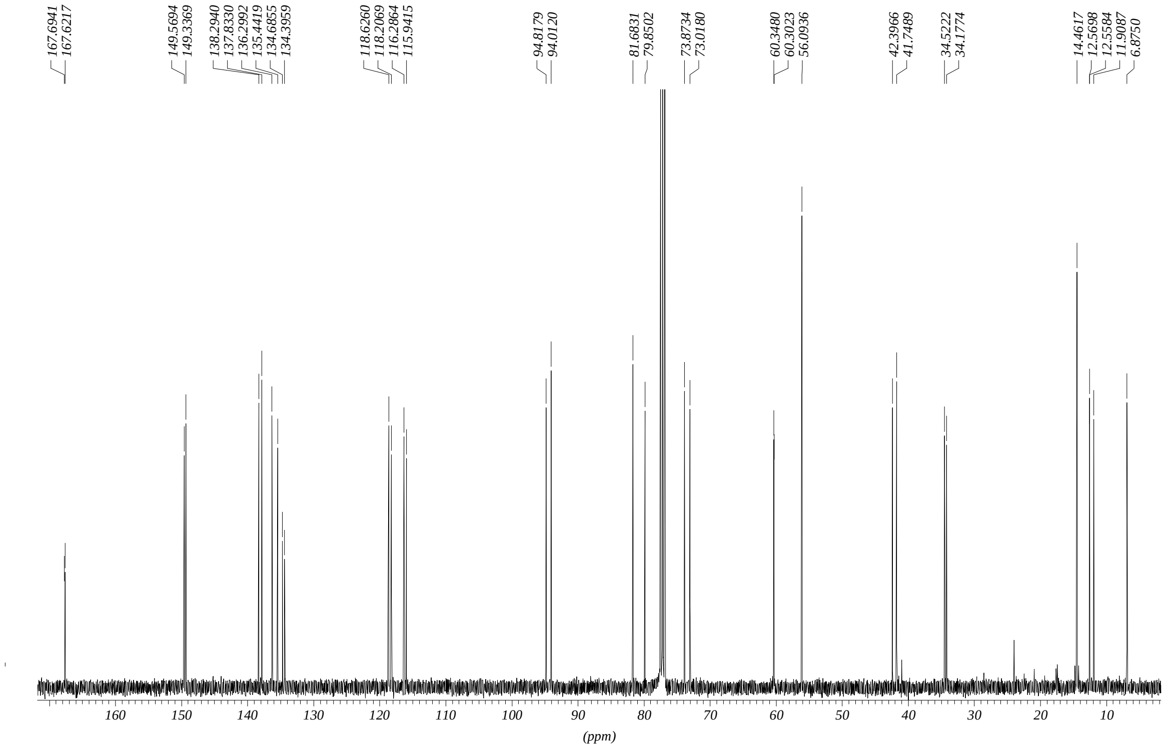

TBSO
OH
CO2Et
3.1725
1.0000
1.8922
3.3483
7.5947
1.9356
1.1545
1.7454
1.1534
6.7003
8.7539
2.5036
2.5007
12.185
3.1228
7.2615
5.7448
28.226
3.0876
17.616
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

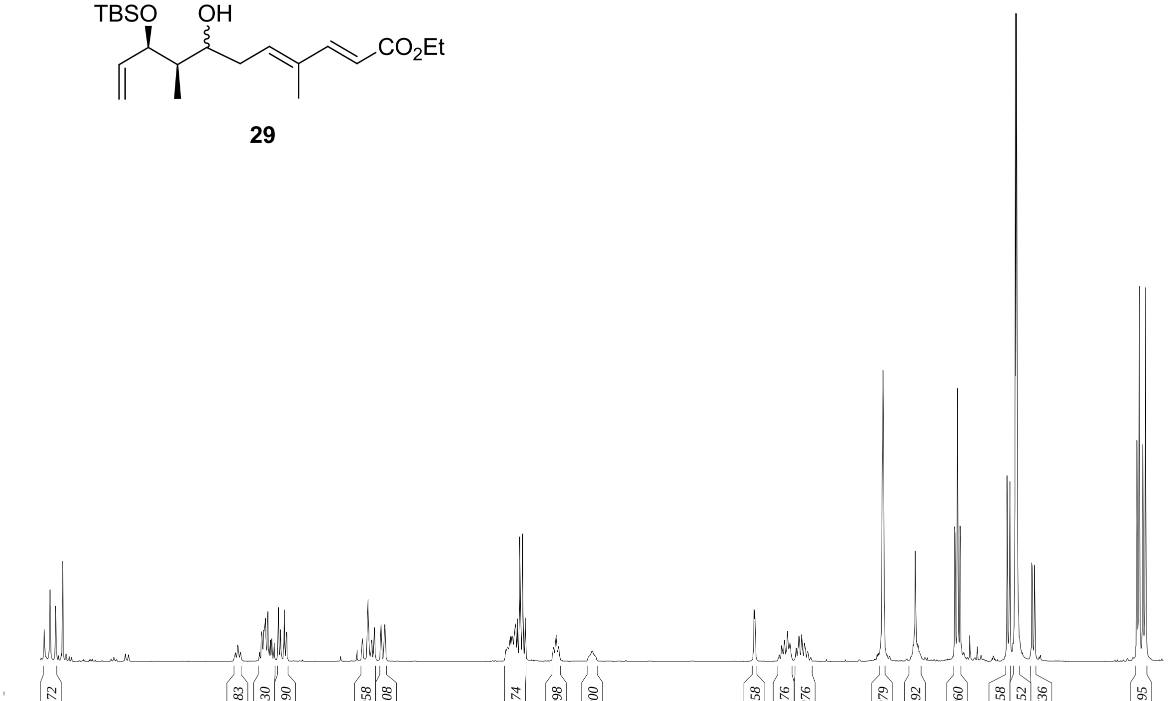
**27**


167.7532
167.6617
149.7313
149.4570
138.4236
138.1283
134.5121
134.2263
116.1416
115.7072
75.2262
74.0373
73.6086
72.8370
60.3385
60.2718
43.1397
42.7910
34.8137
34.6041
25.9600
25.9162
25.8781
21.9037
18.0779
18.0303
17.7960
14.4732
13.6406
12.6041
12.5489
5.4213
-3.4363
-4.4518
-4.6556
-4.9452
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

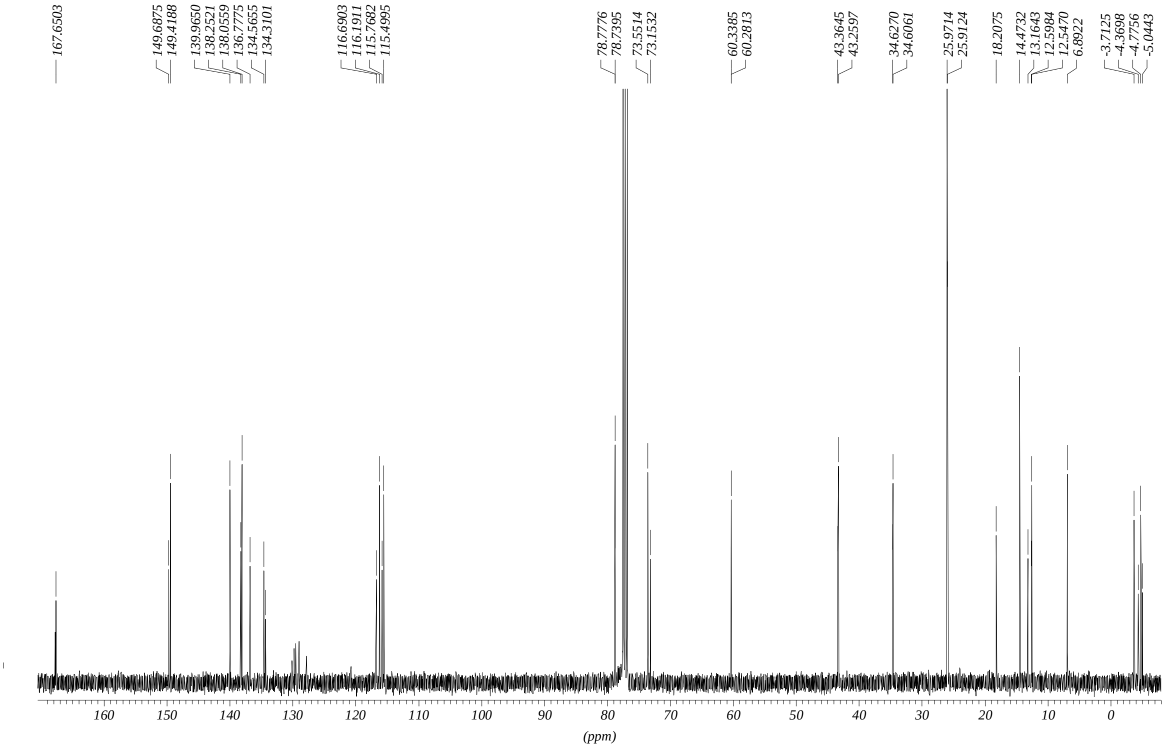

MOMO
OH
CO2Et
2.3307
1.0000
1.1565
4.1751
4.3400
2.1370
2.0857
1.0183
5.5187
1.0817
0.9809
0.8700
6.0962
0.9040
2.1031
2.0844
7.7384
2.0489
6.9358
3.1431
3.4651
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

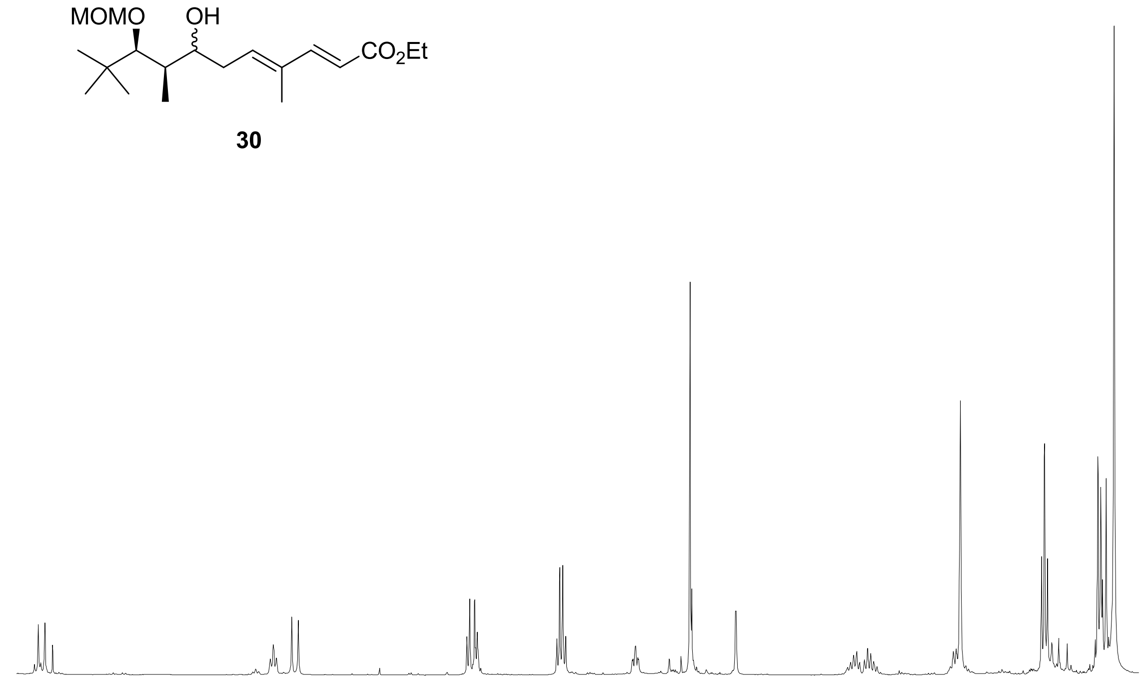
**28**


167.6941
167.6217
149.5694
149.3369
138.2940
137.8330
136.2992
135.4419
134.6855
134.3959
118.6260
118.2069
116.2864
115.9415
94.8179
94.0120
81.6831
79.8502
73.8734
73.0180
60.3480
60.3023
56.0936
42.3966
41.7489
34.5222
34.1774
14.4617
12.5698
12.5584
11.9087
6.8750
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

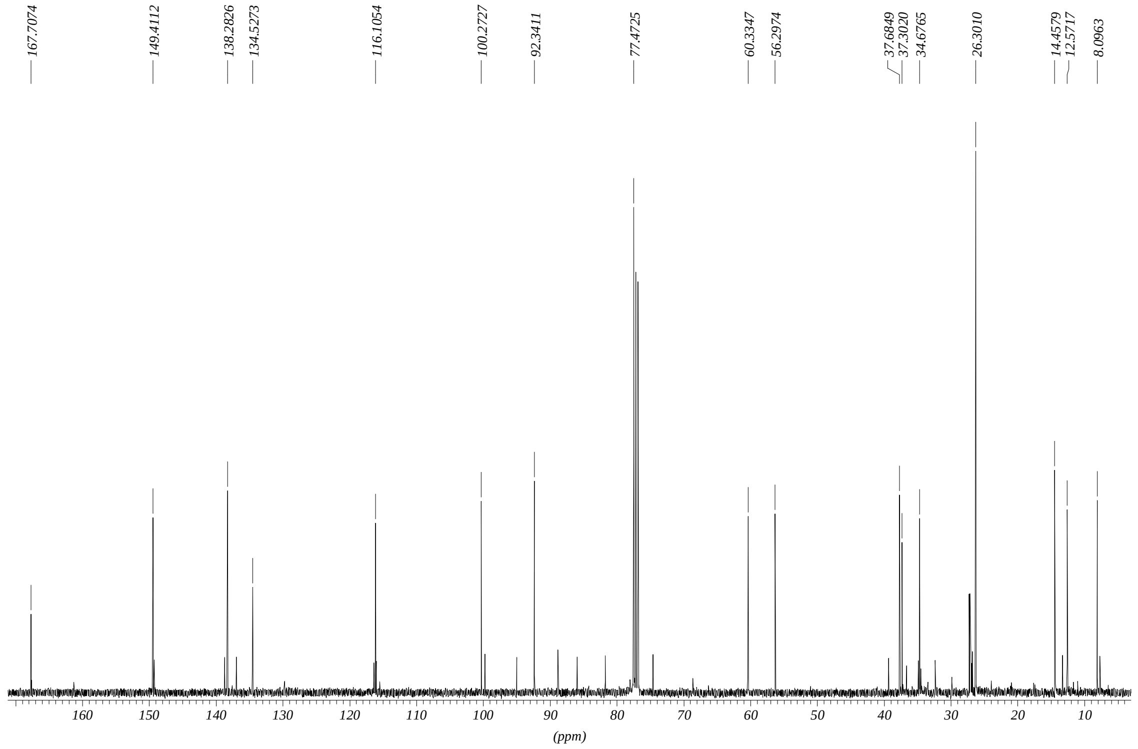

TBSO
OH
CO2Et
3.0372
0.9483
4.5430
2.7290
3.8058
1.8308
9.3574
1.7098
1.0000
1.5258
2.7576
2.8076
8.7079
3.4192
8.5060
4.8558
25.452
2.9636
16.295
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

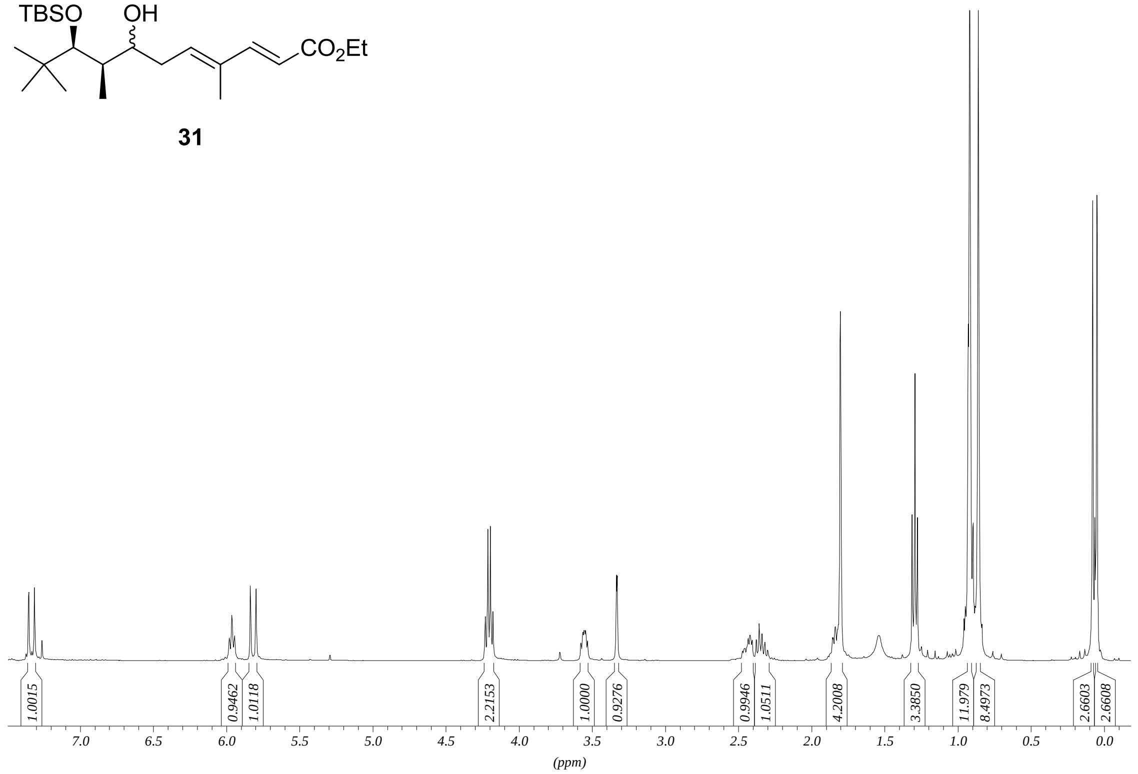
**29**


167.6503
149.6875
149.4188
139.9650
138.2521
138.0559
136.7775
134.5655
134.3101
116.6903
116.1911
115.7682
115.4995
78.7776
78.7395
73.5514
73.1532
60.3385
60.2813
43.3645
43.2597
34.6270
34.6061
25.9714
25.9124
18.2075
14.4732
13.1643
12.5984
12.5470
6.8922
-3.7125
-4.3698
-4.7756
-5.0443
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

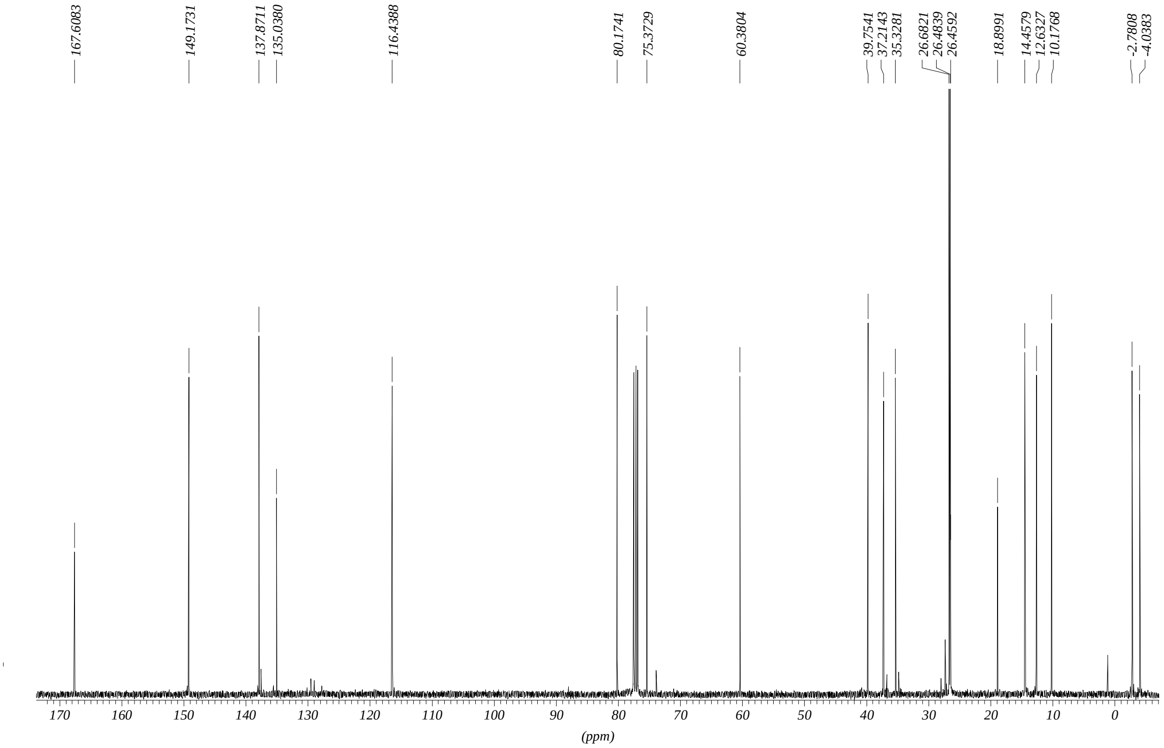

MOMO
OH
CO2Et
7.5277
1.0000
5.6083
6.5023
5.5415
7.5016
14.938
5.6561
19.438
5.1795
6.7250
6.7522
28.571
23.971
22.230
48.172
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

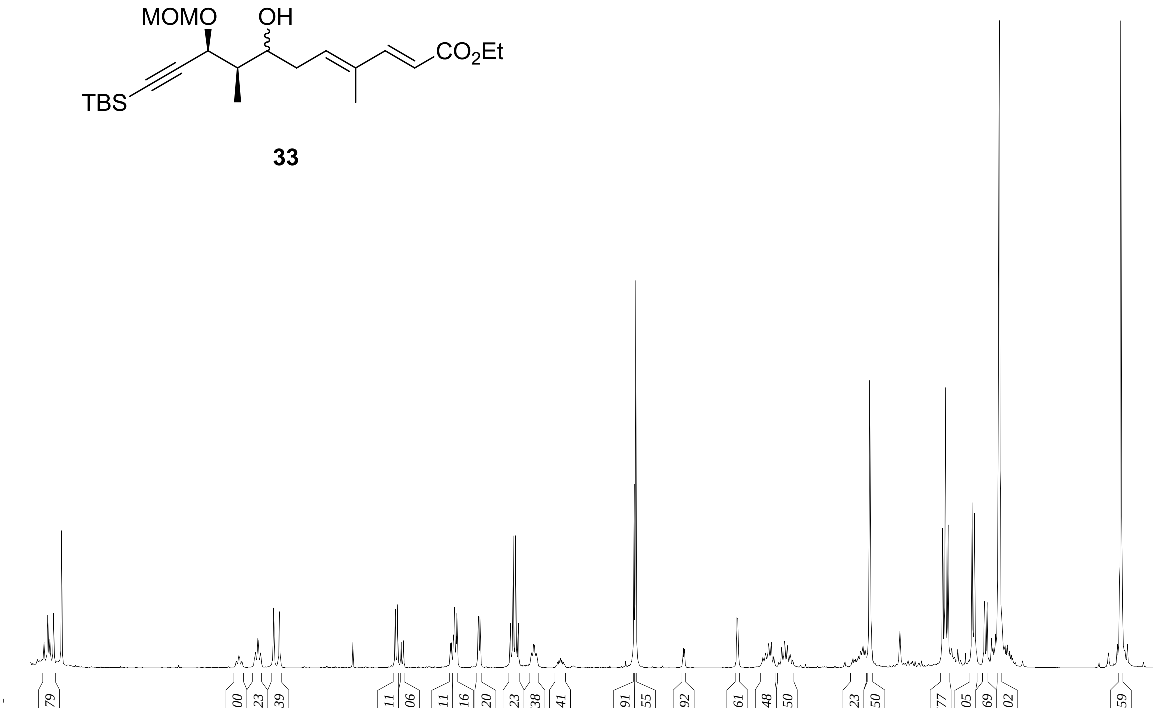
**30**


167.7074
149.4112
138.2826
134.5273
116.1054
100.2727
92.3411
77.4725
60.3347
56.2974
37.6849
37.3020
34.6765
26.3010
14.4579
12.5717
8.0963
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

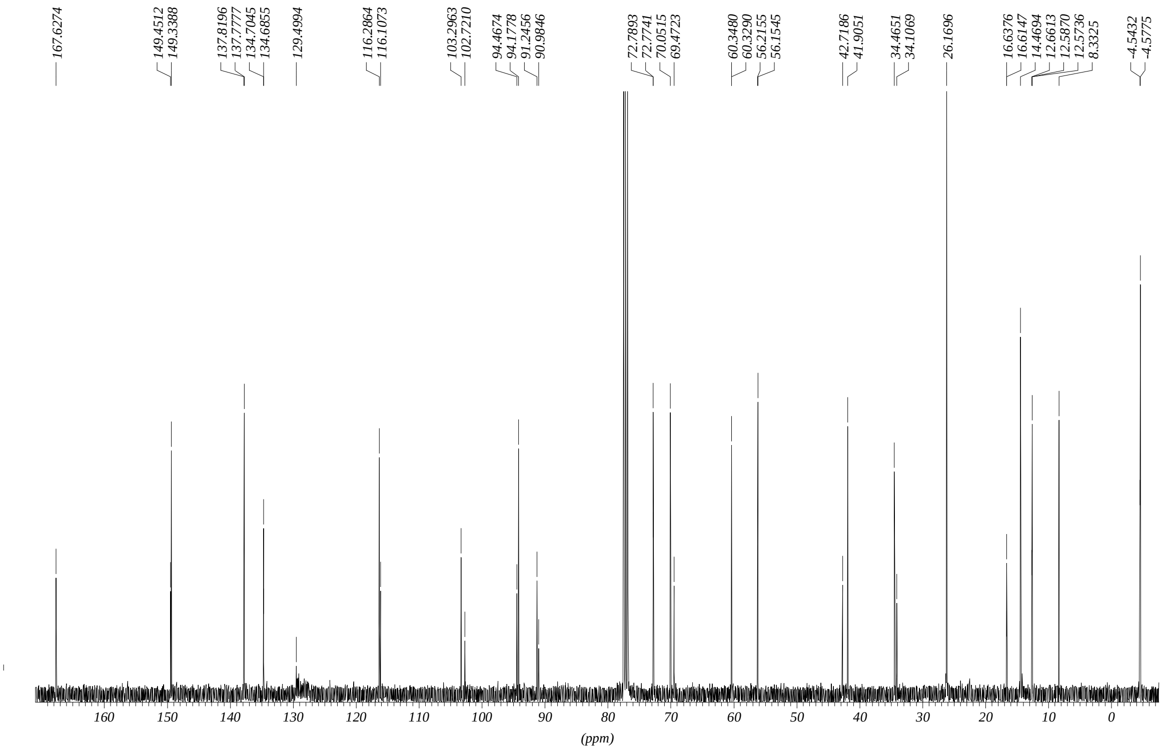

TBSO
OH
CO2Et
1.0015
0.9462
1.0118
2.2153
1.0000
0.9276
0.9946
1.0511
4.2008
3.3850
11.979
8.4973
2.6603
2.6608
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

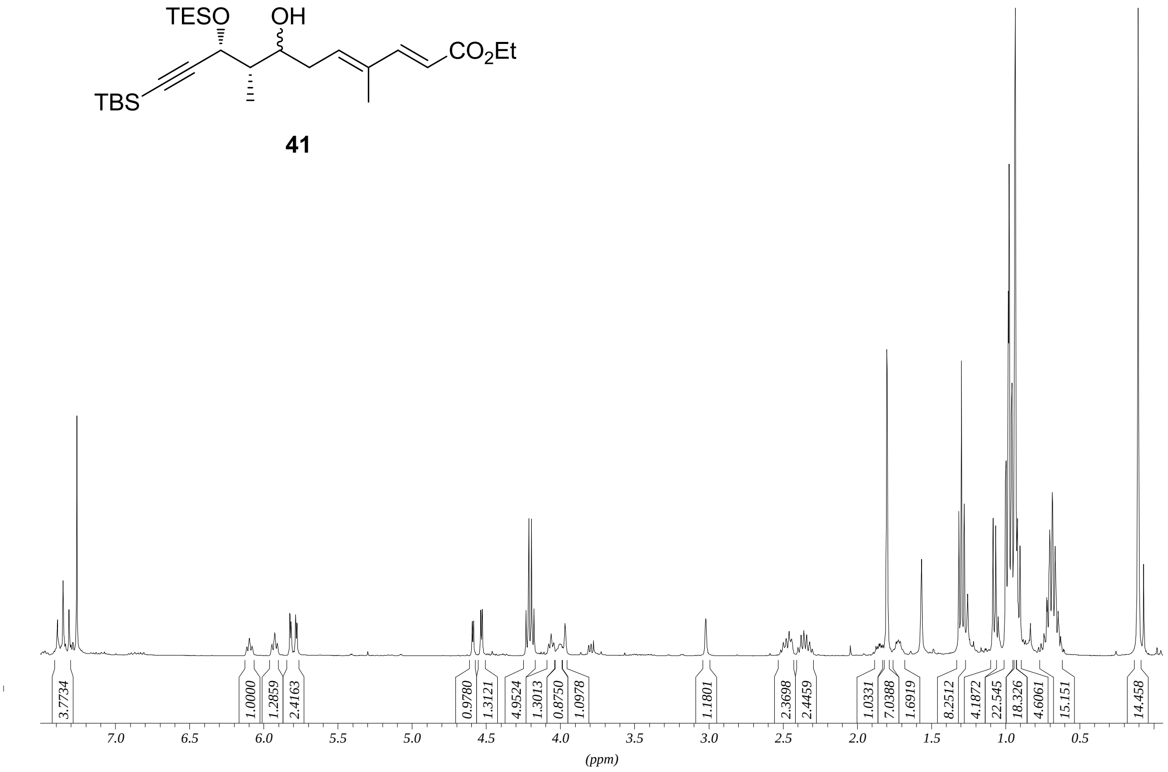
**31**


167.6083
149.1731
137.8711
135.0380
116.4388
80.1741
75.3729
60.3804
39.7541
37.2143
35.3281
26.6821
26.4839
26.4592
18.8991
14.4579
12.6327
10.1768
-2.7808
-4.0383
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

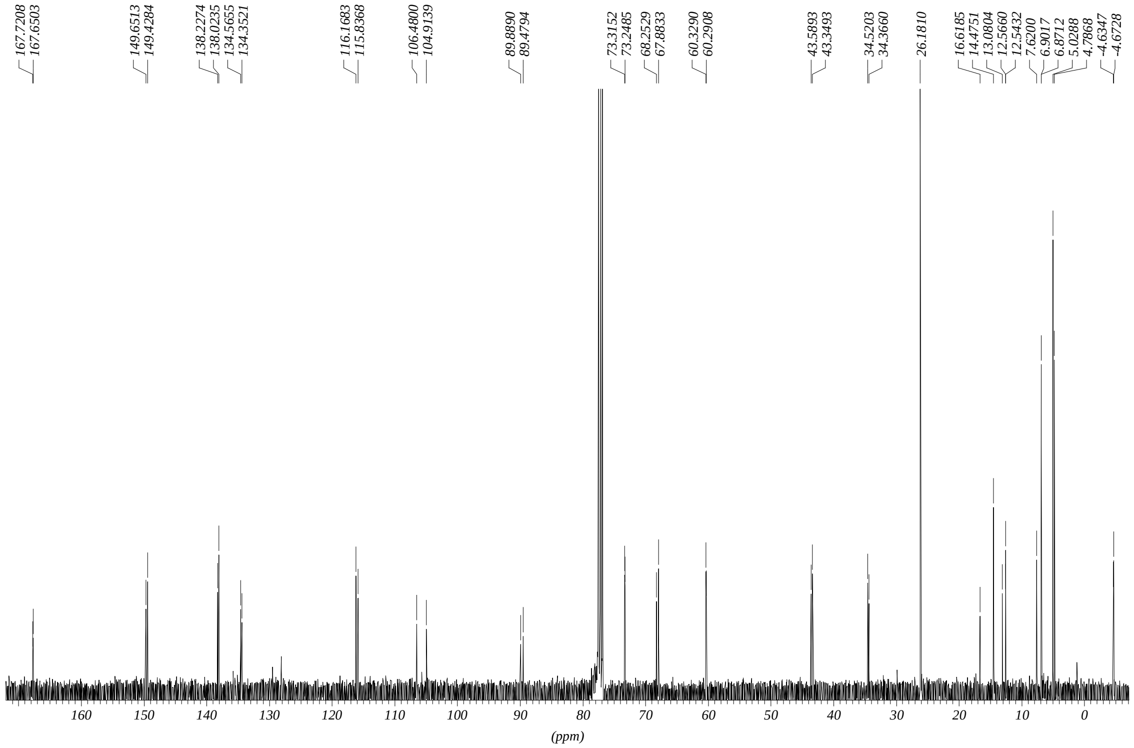

MOMO
OH
CO2Et
TBS
4.6679
1.0000
2.2623
3.3139
2.2111
0.9106
0.9611
3.1616
2.1520
7.1123
2.2738
0.9541
2.7291
5.7655
0.8192
2.0261
3.3948
3.4350
3.5223
9.9450
11.777
7.4505
3.0269
31.202
19.659
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

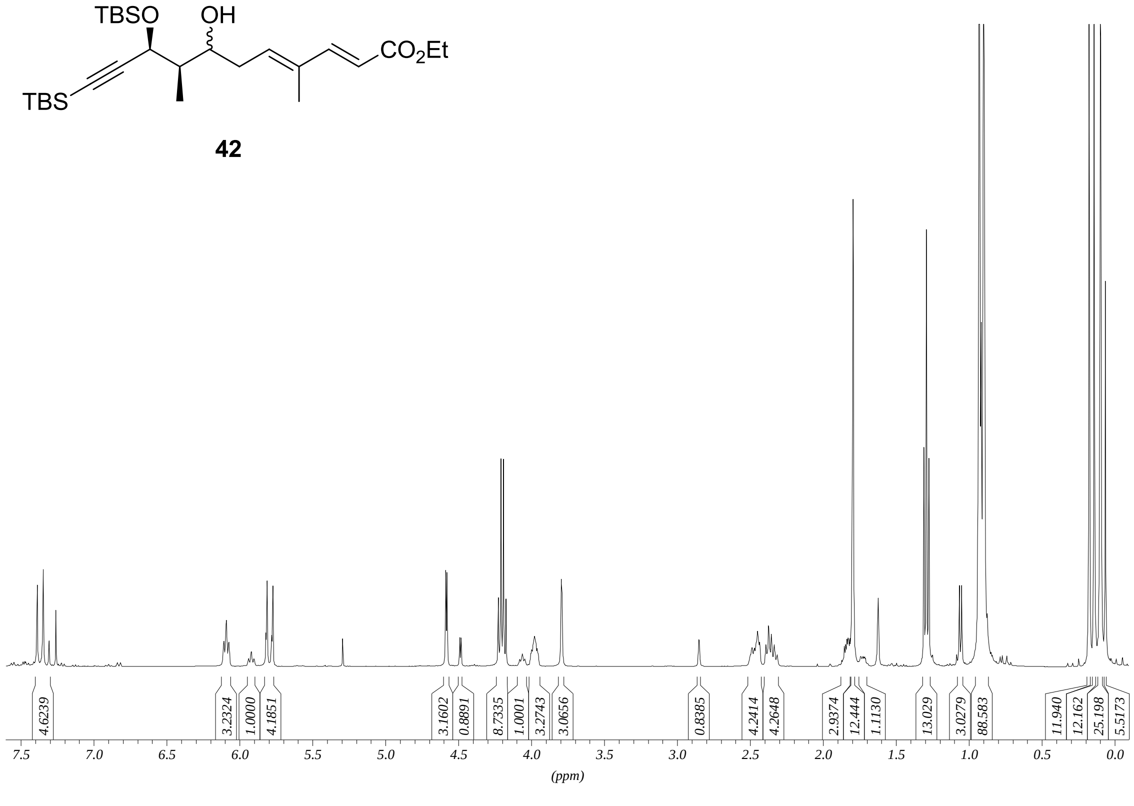
**33**


167.6274
149.4512
149.3388
137.8196
137.7777
134.7045
134.6855
129.4994
116.2864
116.1073
103.2963
102.7210
94.4674
94.1778
91.2456
90.9846
72.7893
72.7741
70.0515
69.4723
60.3480
60.3290
56.2155
56.1545
42.7186
41.9051
34.4651
34.1069
26.1696
16.6376
16.6147
14.4694
12.6613
12.5870
12.5736
8.3325
-4.5432
-4.5775
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

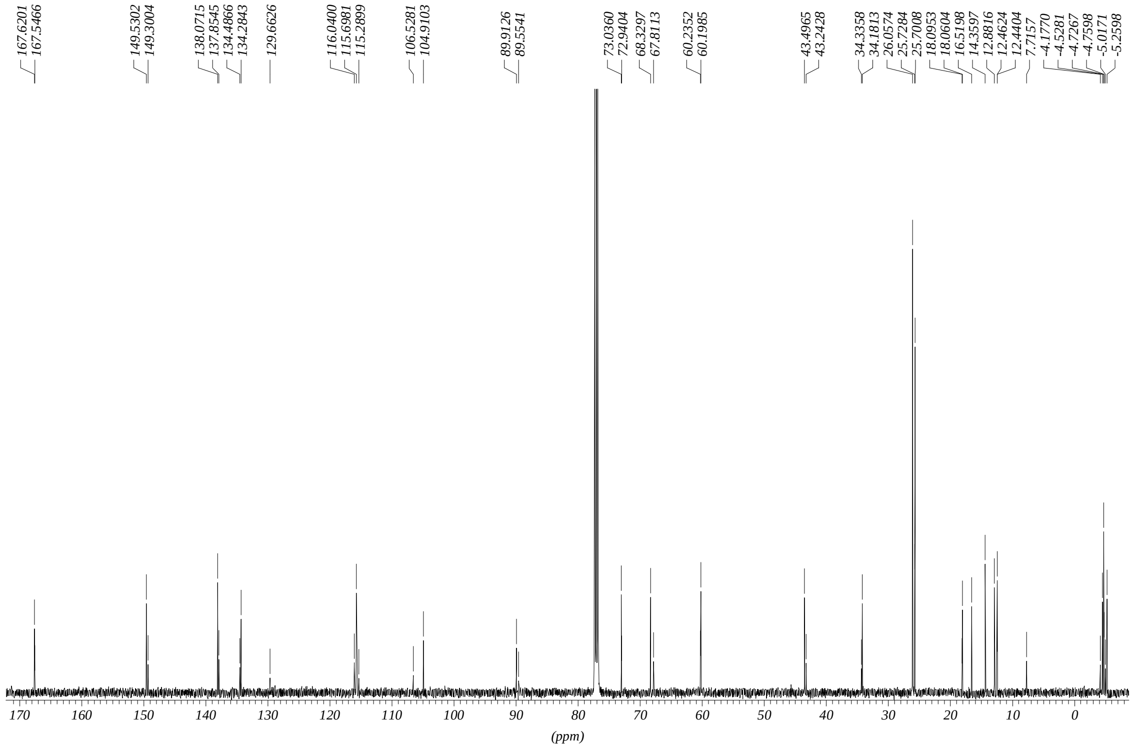

TESO
OH
CO2Et
TBS
3.7734
1.0000
1.2859
2.4163
0.9780
1.3121
4.9524
1.3013
0.8750
1.0978
1.1801
2.3698
2.4459
1.0331
7.0388
1.6919
8.2512
4.1872
22.545
18.326
4.6061
15.151
14.458
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

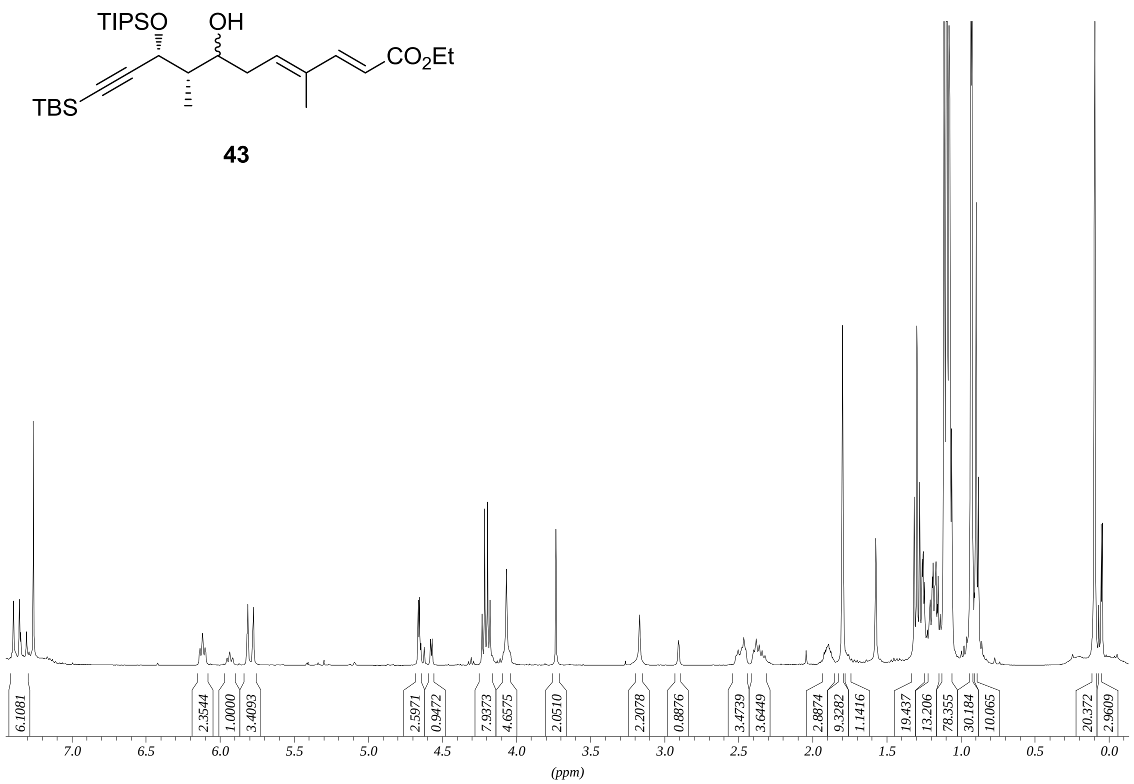
**41**


167.7208
167.6503
149.6513
149.4284
138.2274
138.0235
134.5655
134.3521
116.1683
115.8368
106.4800
104.9139
89.8890
89.4794
73.3152
73.2485
68.2529
67.8833
60.3290
60.2908
43.5893
43.3493
34.5203
34.3660
26.1810
16.6185
14.4751
13.0804
12.5660
12.5432
7.6200
6.9017
6.8712
5.0288
4.7868
-4.6347
-4.6728
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

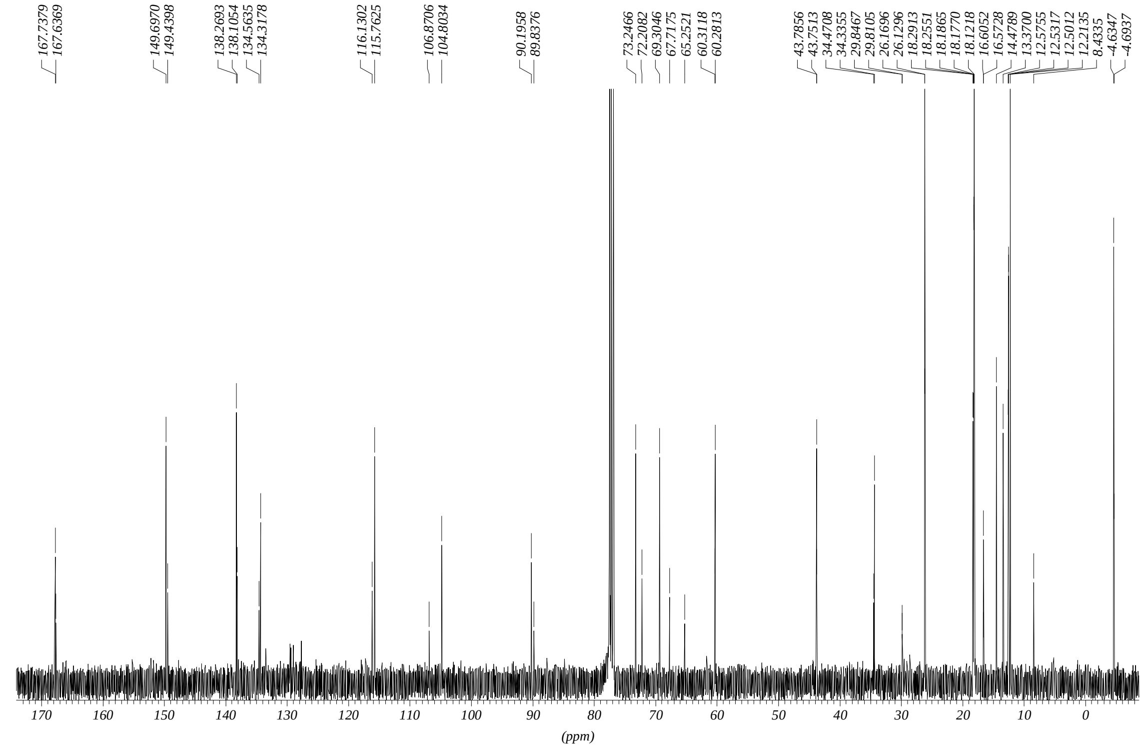

TBSO
OH
CO2Et
TBS
4.6239
3.2324
1.0000
4.1851
3.1602
0.8891
8.7335
1.0001
3.2743
3.0656
0.8385
4.2414
4.2648
2.9374
12.444
1.1130
13.029
3.0279
88.583
11.940
12.162
25.198
5.5173
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

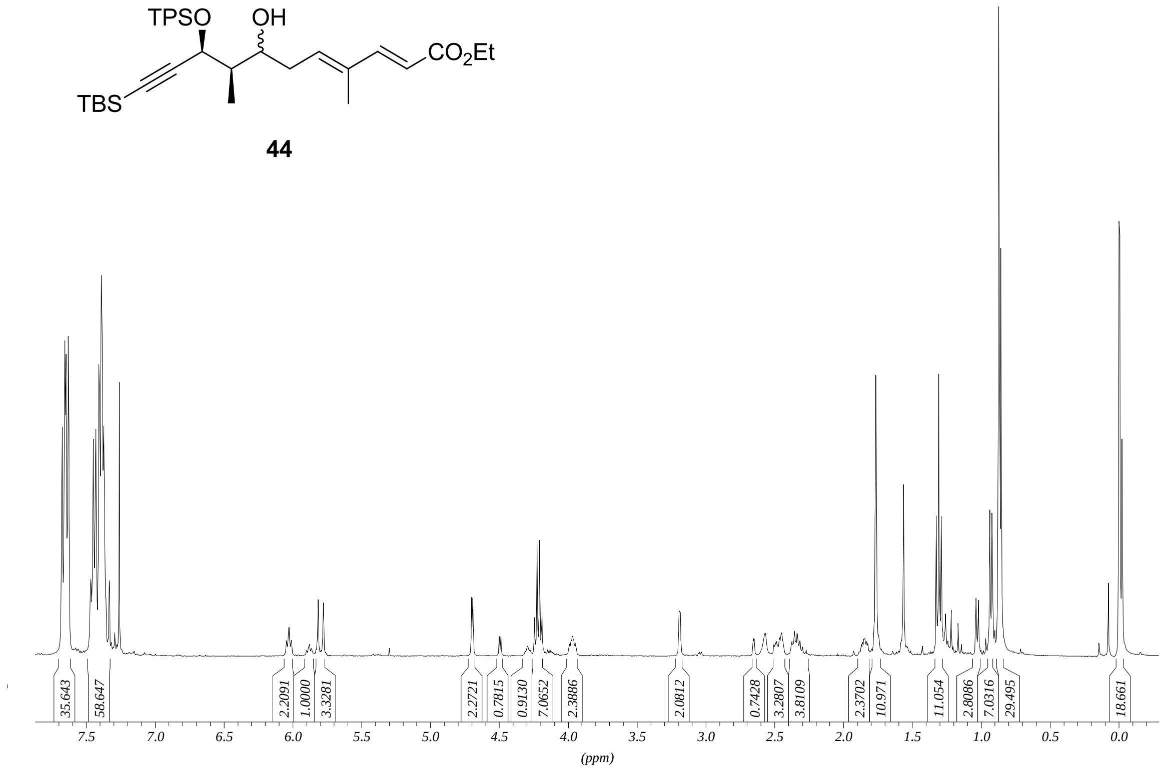
**42**


167.6201
167.5466
149.5302
149.3004
138.0715
137.8545
134.4866
134.2843
129.6626
116.0400
115.6981
115.2899
106.5281
104.9103
89.9126
89.5541
73.0360
72.9404
68.3297
67.8113
60.2352
60.1985
43.4965
43.2428
34.3358
34.1813
26.0574
25.7284
25.7008
18.0953
18.0604
16.5198
14.3597
12.8816
12.4624
12.4404
7.7157
-4.1770
-4.5281
-4.7267
-4.7598
-5.0171
-5.2598
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

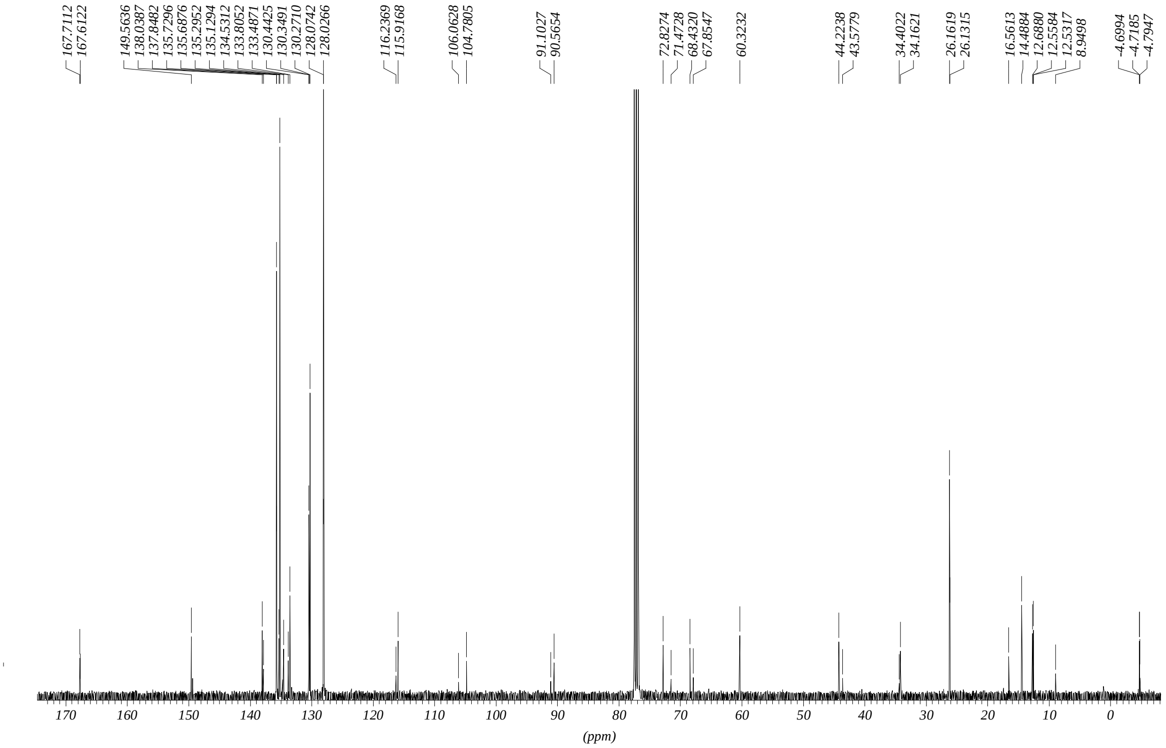

TIPSO
OH
CO2Et
TBS
6.1081
2.3544
1.0000
3.4093
2.5971
0.9472
7.9373
4.6575
2.0510
2.2078
0.8876
3.4739
3.6449
2.8874
9.3282
1.1416
19.437
13.206
78.355
30.184
10.065
20.372
2.9609
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

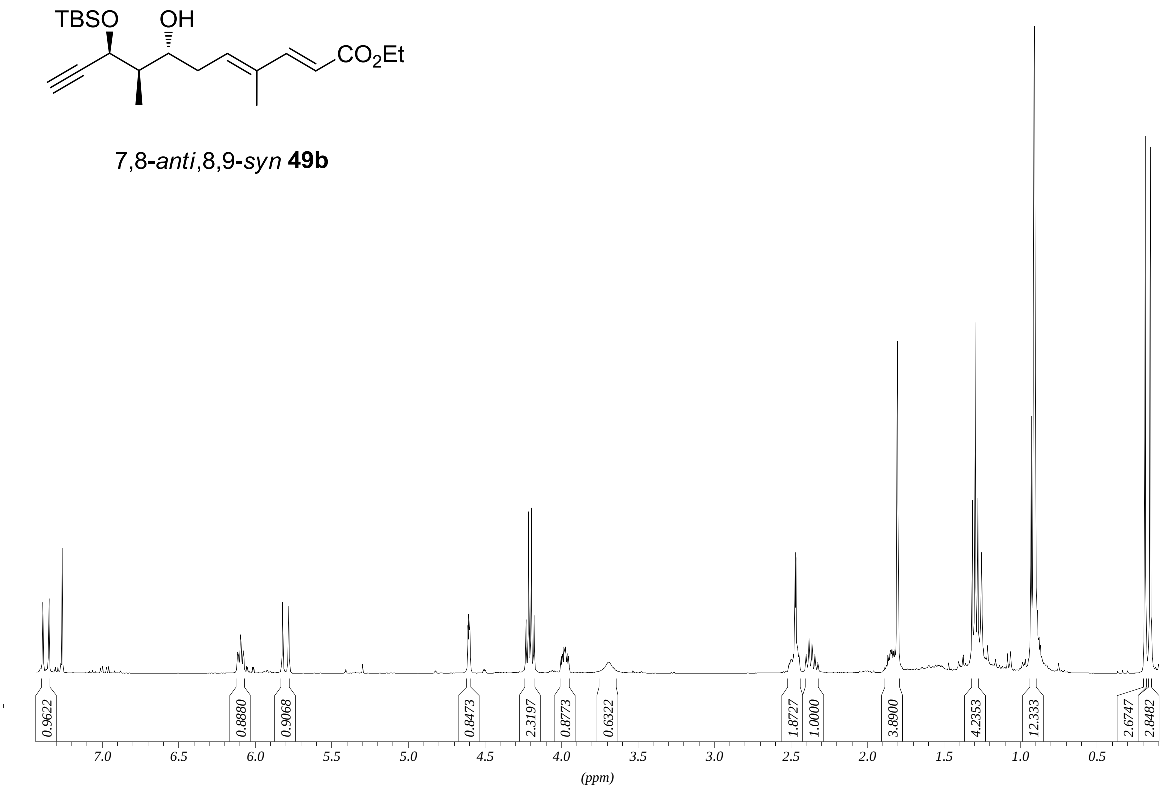
**43**


167.7379
167.6369
149.6970
149.4398
138.2693
138.1054
134.5635
134.3178
116.1302
115.7625
106.8706
104.8034
90.1958
89.8376
73.2466
72.2082
69.3046
67.7175
65.2521
60.3118
60.2813
43.7856
43.7513
34.4708
34.3355
29.8467
29.8105
26.1696
26.1296
18.2913
18.2551
18.1865
18.1770
18.1218
16.6052
16.5728
14.4789
13.3700
12.5755
12.5317
12.5012
12.2135
8.4335
-4.6347
-4.6937
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

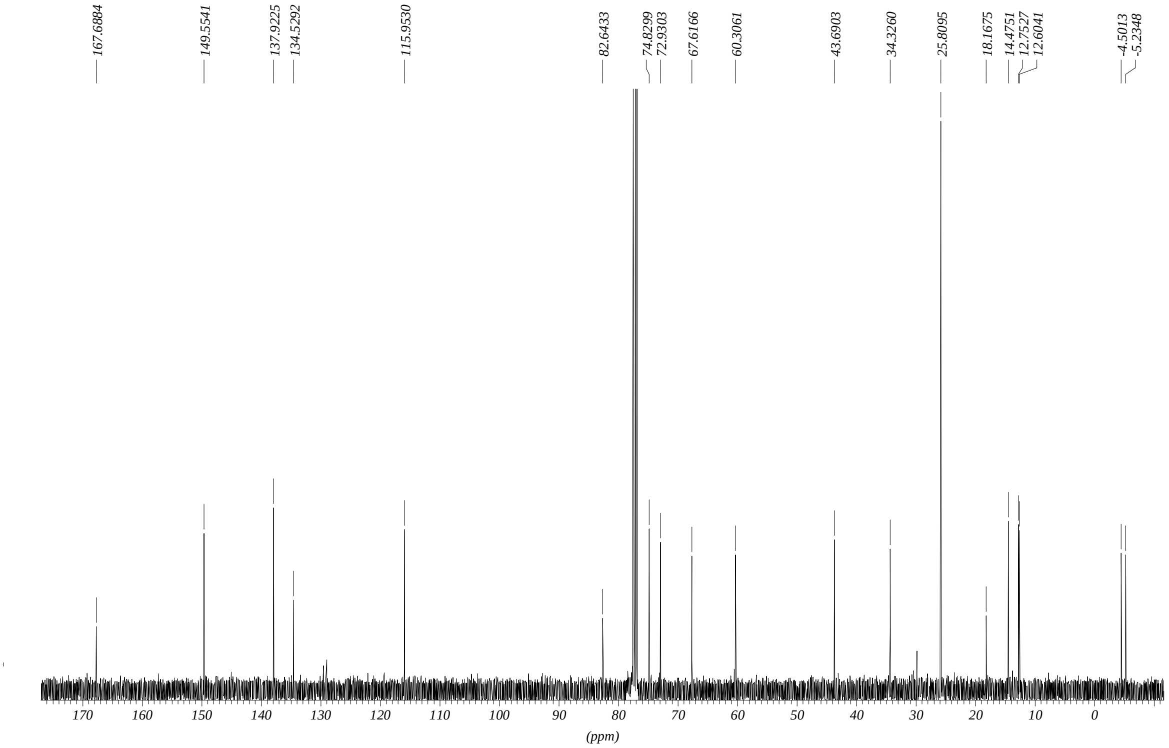

TPSO
OH
CO2Et
TBS
35.643
58.647
2.2091
1.0000
3.3281
2.2721
0.7815
0.9130
7.0652
2.3886
2.0812
0.7428
3.2807
3.8109
2.3702
10.971
11.054
2.8086
7.0316
29.495
18.661
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

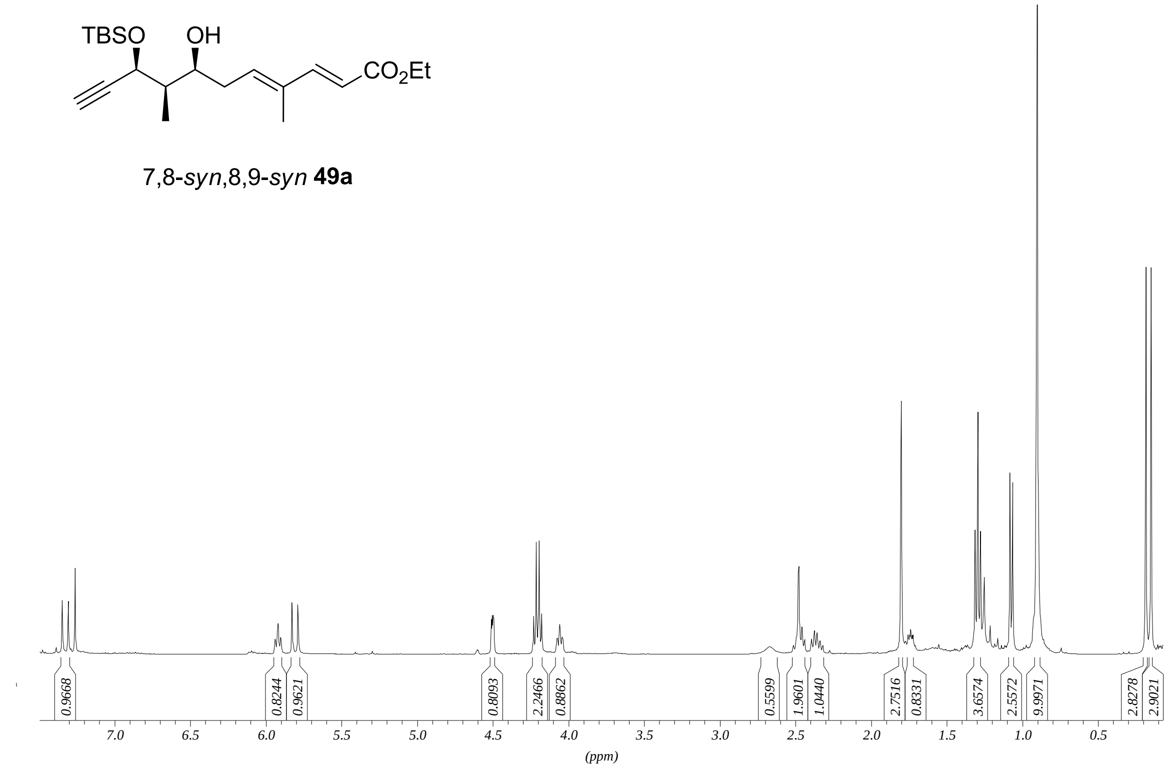
**44**



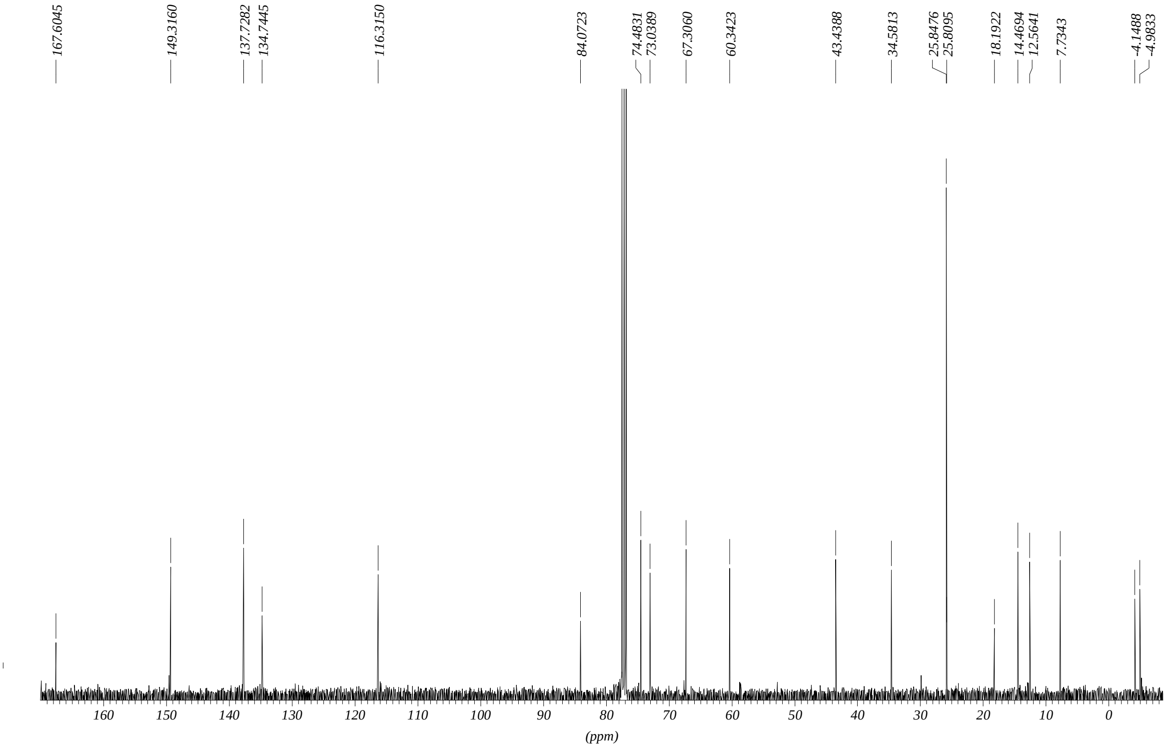


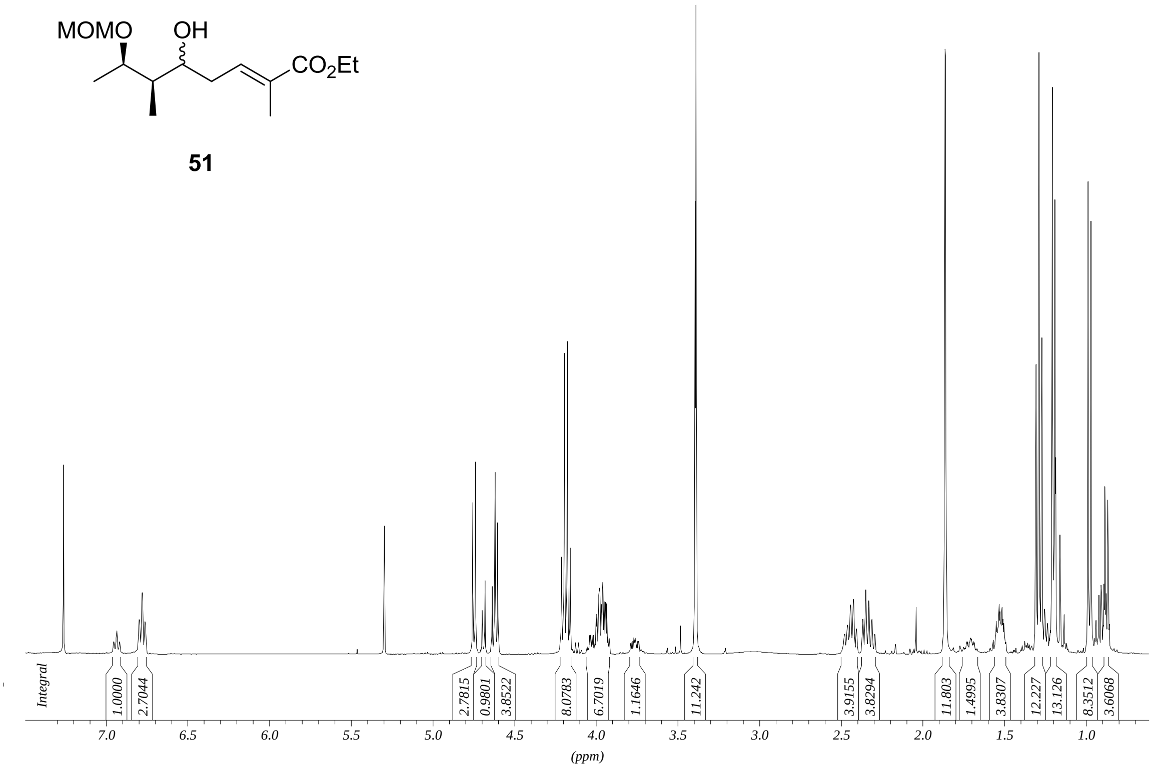
7,8-*anti*,8,9-*syn* **49b**



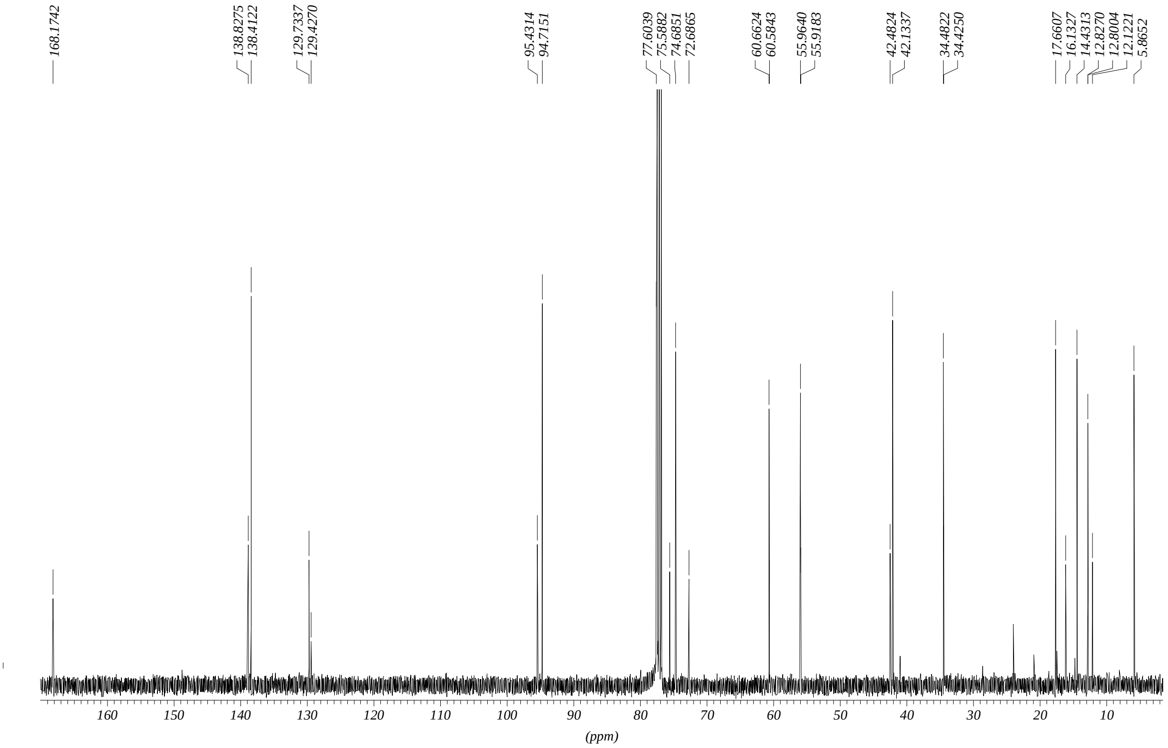


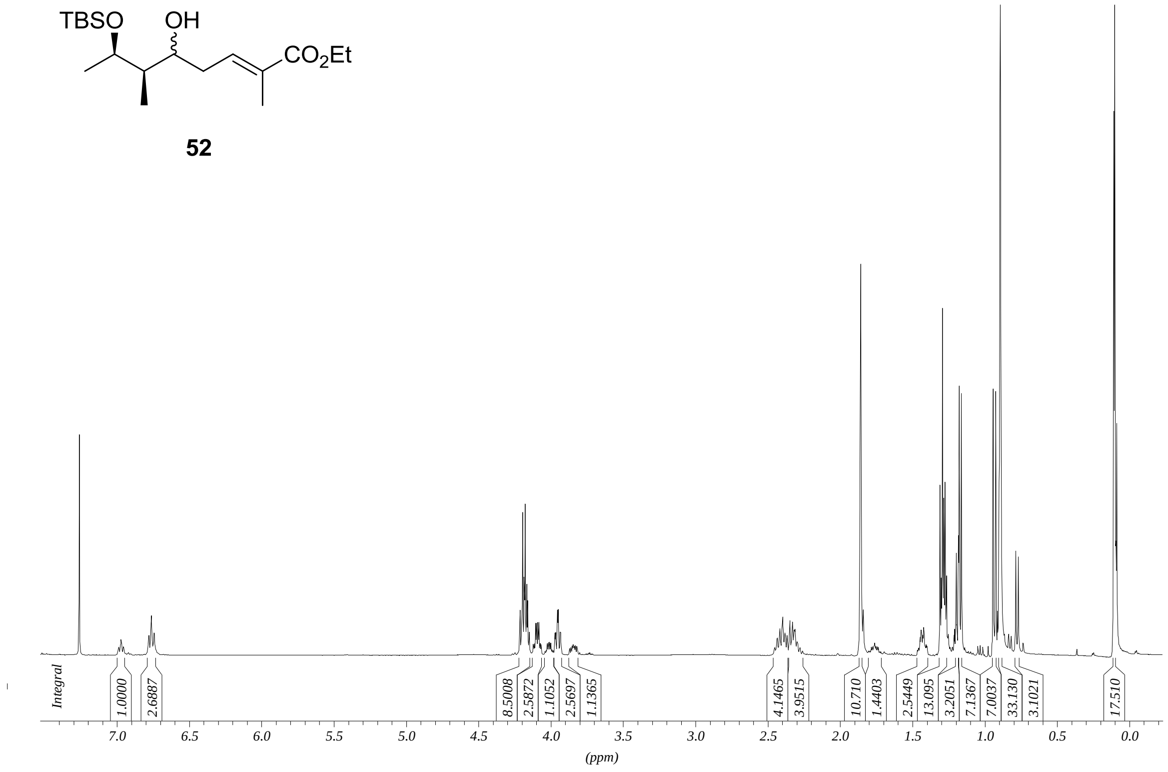
7,8-*syn*,8,9-*syn* **49a**


167.6045
149.3160
137.7282
134.7445
116.3150
84.0723
74.4831
73.0389
67.3060
60.3423
43.4388
34.5813
25.8476
25.8095
18.1922
14.4694
12.5641
7.7343
-4.1488
-4.9833
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

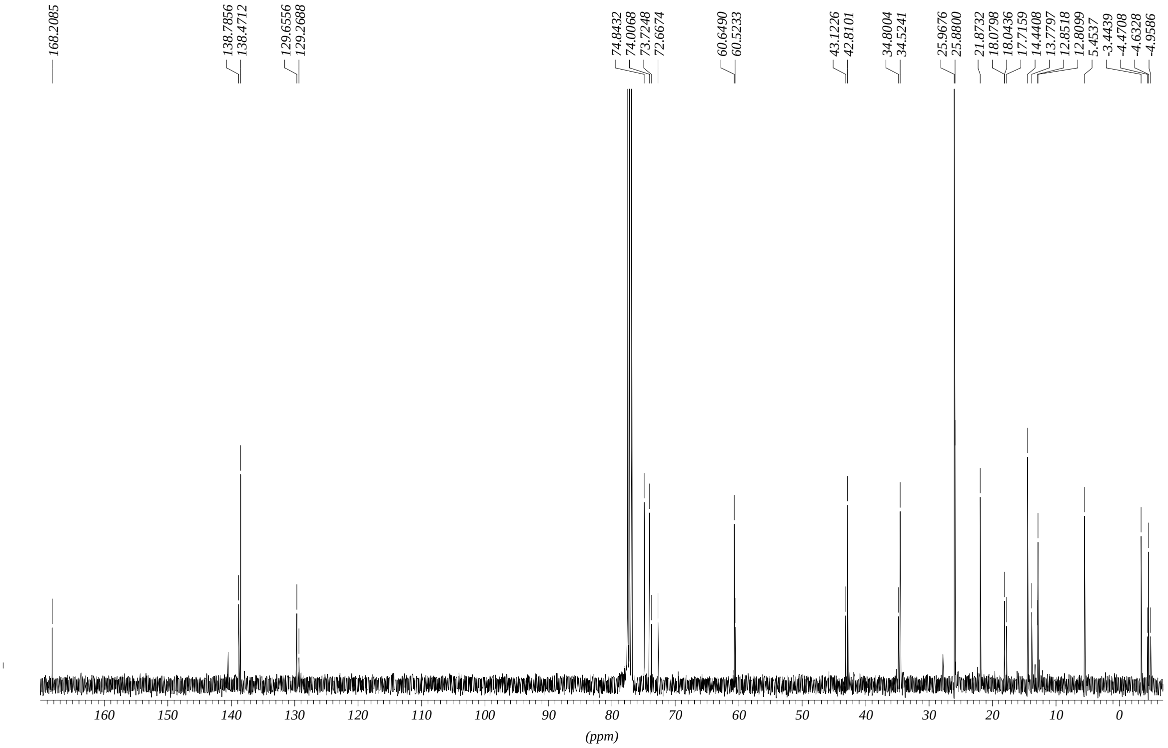

MOMO
OH
CO2Et
Integral
1.0000
2.7044
2.7815
0.9801
3.8522
8.0783
6.7019
1.1646
11.242
3.9155
3.8294
11.803
1.4995
3.8307
12.227
13.126
8.3512
3.6068
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

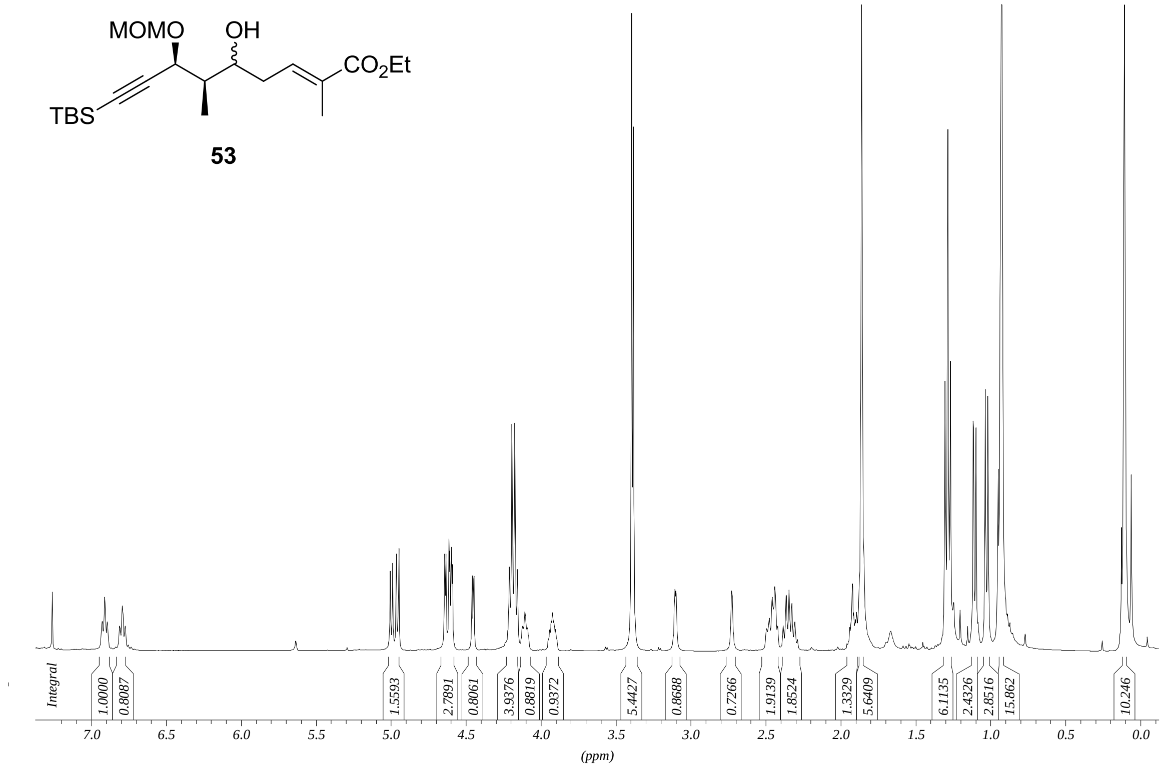
**51**


168.1742
138.8275
138.4122
129.7337
129.4270
95.4314
94.7151
77.6039
75.5882
74.6851
72.6865
60.6624
60.5843
55.9640
55.9183
42.4824
42.1337
34.4822
34.4250
17.6607
16.1327
14.4313
12.8270
12.8004
12.1221
5.8652
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

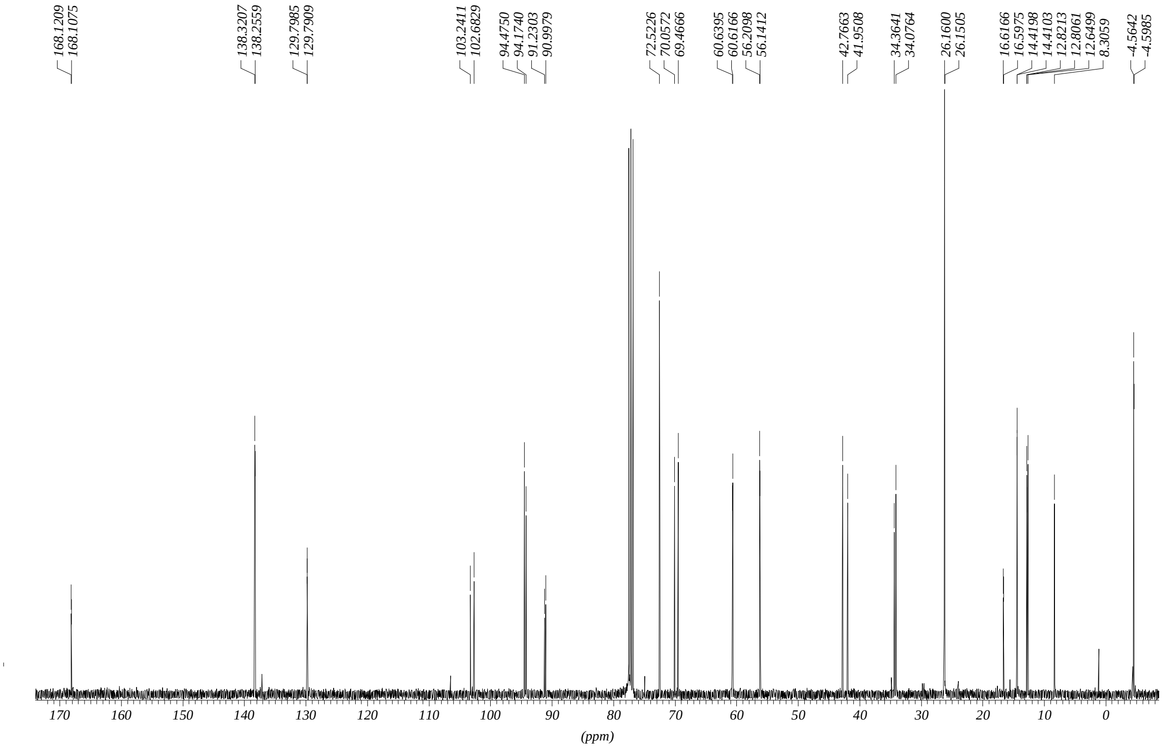

TBSO
OH
$CO_2Et$
Integral
1.0000
2.6887
8.5008
2.5872
1.1052
2.5697
1.1365
4.1465
3.9515
10.710
1.4403
2.5449
13.095
3.2051
7.1367
7.0037
33.130
3.1021
17.510
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

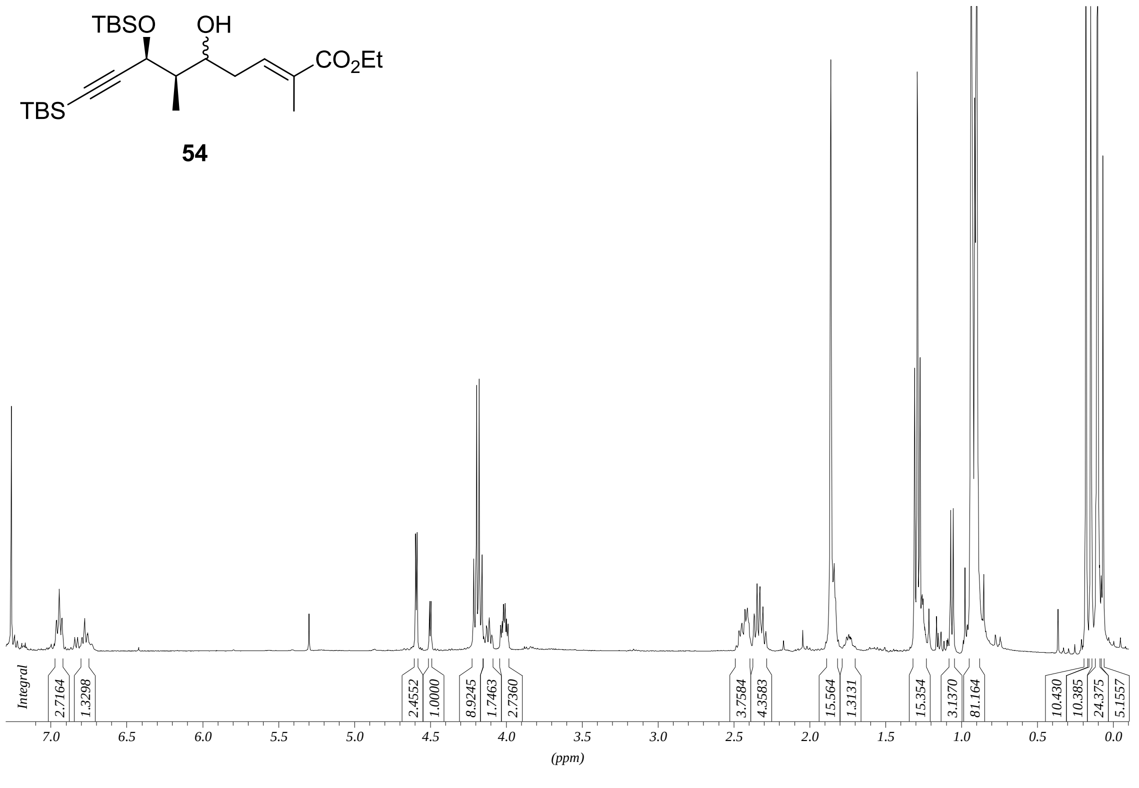
**52**


168.2085
138.7856
138.4712
129.6556
129.2688
74.8432
74.0068
73.7248
72.6674
60.6490
60.5233
43.1226
42.8101
34.8004
34.5241
25.9676
25.8800
21.8732
18.0798
18.0436
17.7159
14.4408
13.7797
12.8518
12.8099
5.4537
-3.4439
-4.4708
-4.6328
-4.9586
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

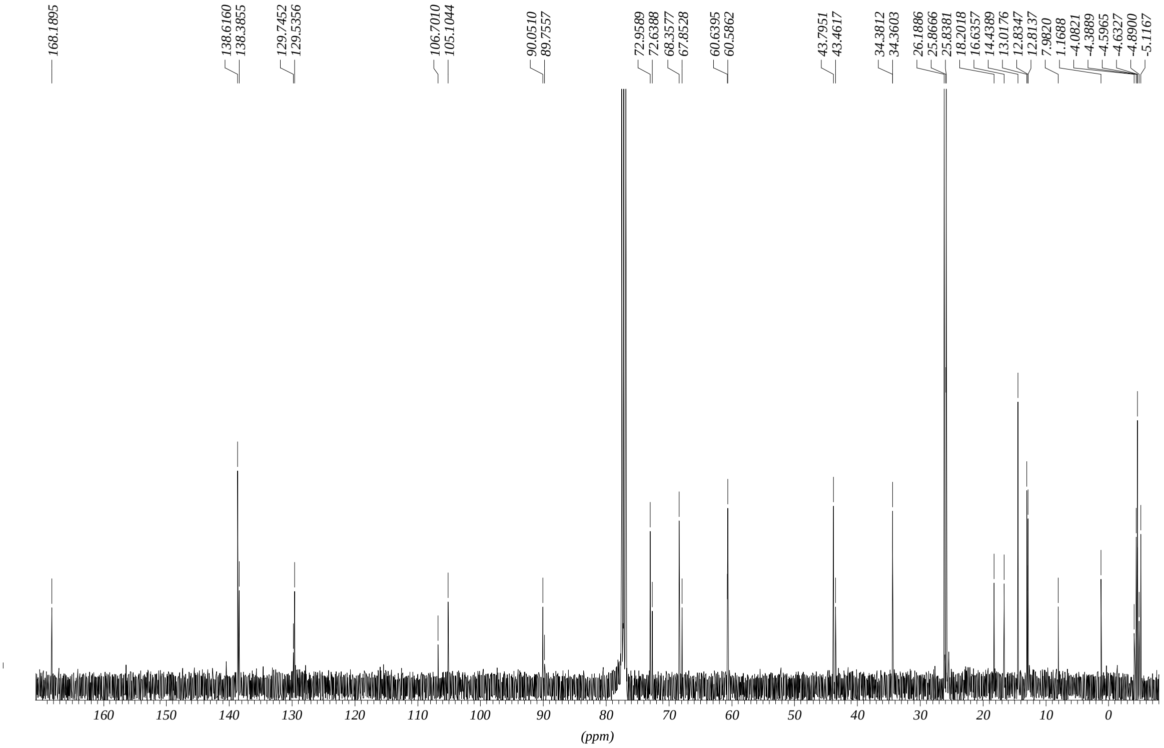

MOMO
OH
CO2Et
TBS
Integral
1.0000
0.8087
1.5593
2.7891
0.8061
3.9376
0.8819
0.9372
5.4427
0.8688
0.7266
1.9139
1.8524
1.3329
5.6409
6.1135
2.4326
2.8516
15.862
10.246
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

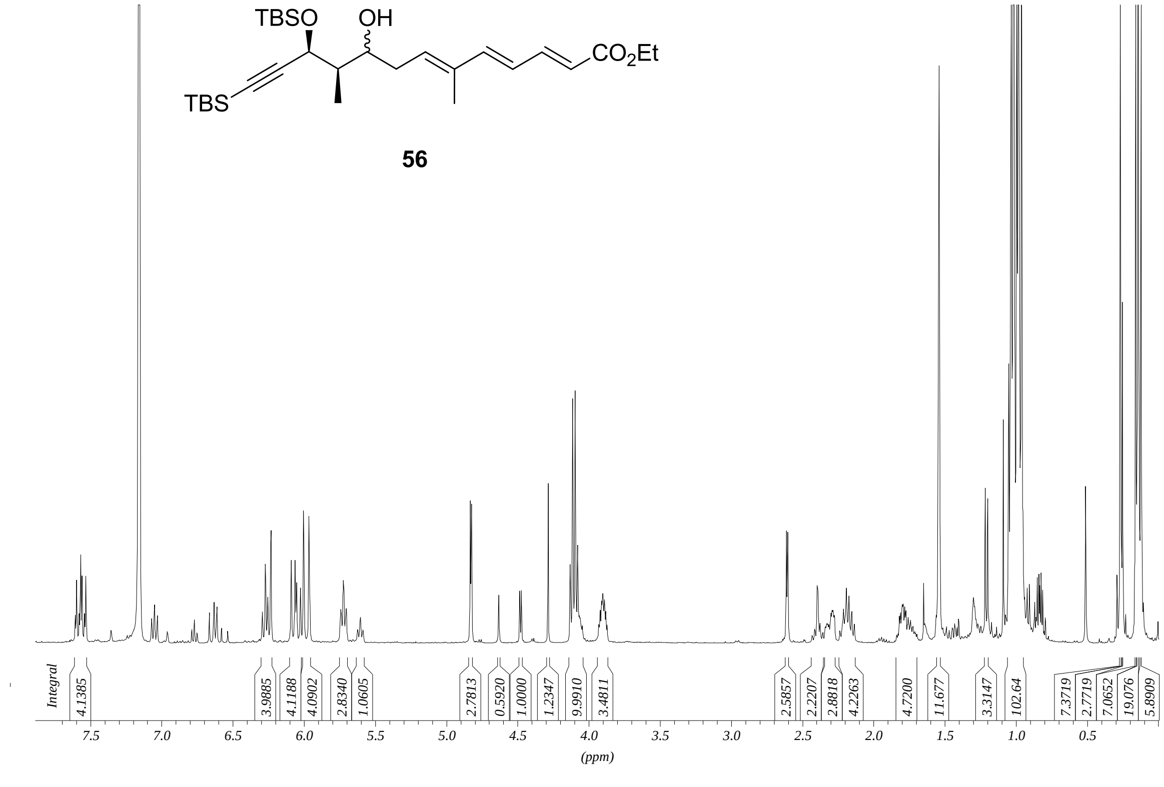
**53**


168.1209
168.1075
138.3207
138.2559
129.7985
129.7909
103.2411
102.6829
94.4750
94.1740
91.2303
90.9979
72.5226
70.0572
69.4666
60.6395
60.6166
56.2098
56.1412
42.7663
41.9508
34.3641
34.0764
26.1600
26.1505
16.6166
16.5975
14.4198
14.4103
12.8213
12.8061
12.6499
8.3059
-4.5642
-4.5985
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

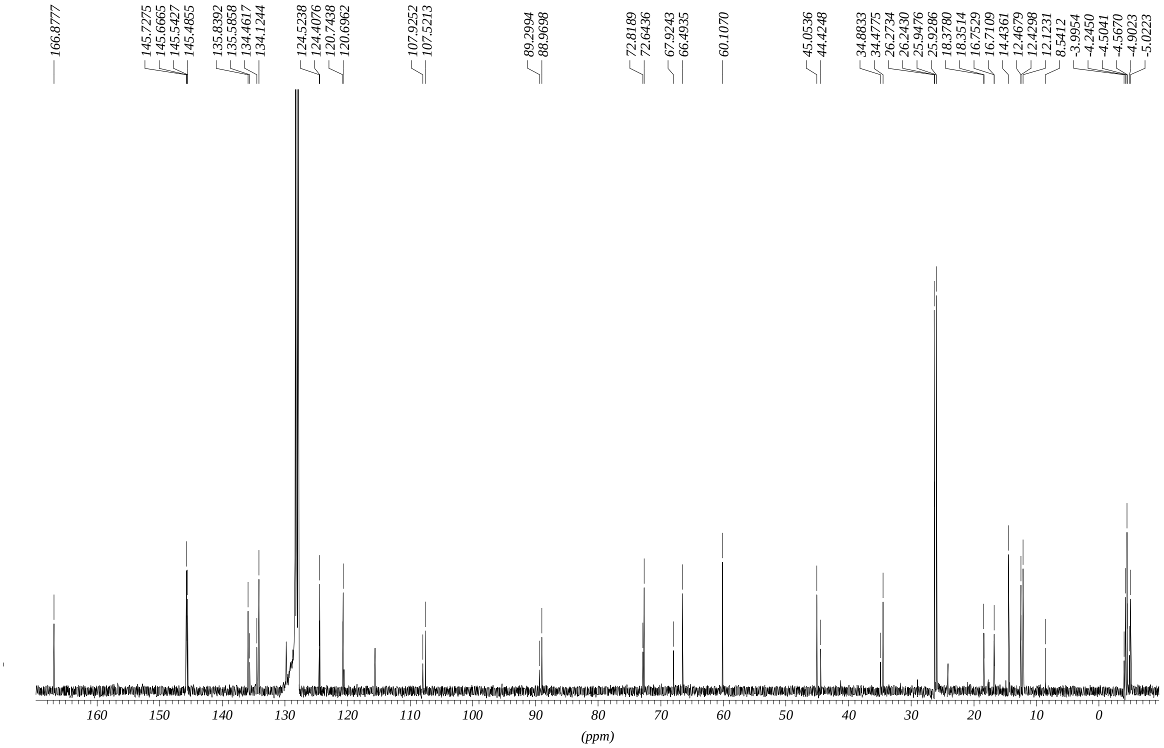

TBSO
OH
CO2Et
TBS
Integral
2.7164
1.3298
2.4552
1.0000
8.9245
1.7463
2.7360
3.7584
4.3583
15.564
1.3131
15.354
3.1370
81.164
10.430
10.385
24.375
5.1557
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

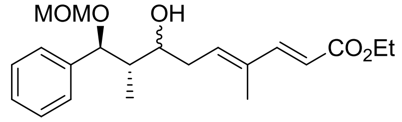
**54**


168.1895
138.6160
138.3855
129.7452
129.5356
106.7010
105.1044
90.0510
89.7557
72.9589
72.6388
68.3577
67.8528
60.6395
60.5862
43.7951
43.4617
34.3812
34.3603
26.1886
25.8666
25.8381
18.2018
16.6357
14.4389
13.0176
12.8347
12.8137
7.9820
1.1688
-4.0821
-4.3889
-4.5965
-4.6327
-4.8900
-5.1167
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

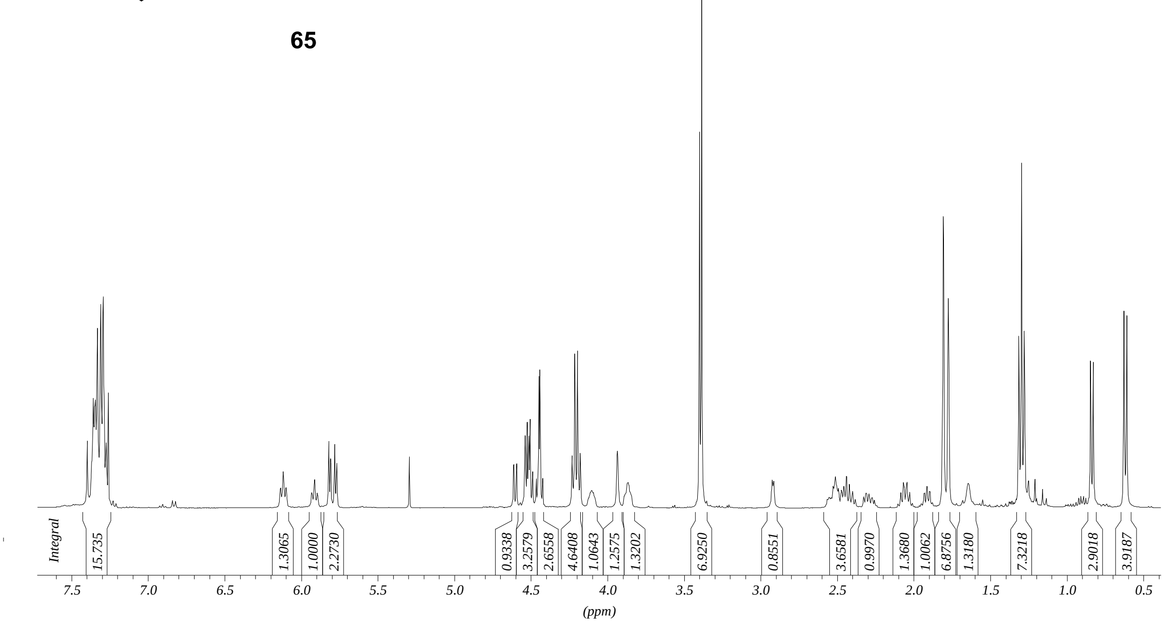

TBSO
OH
CO2Et
TBS
Integral
4.1385
3.9885
4.1188
4.0902
2.8340
1.0605
2.7813
0.5920
1.0000
1.2347
9.9910
3.4811
2.5857
2.2207
2.8818
4.2263
4.7200
11.677
3.3147
102.64
7.3719
2.7719
7.0652
19.076
5.8909
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

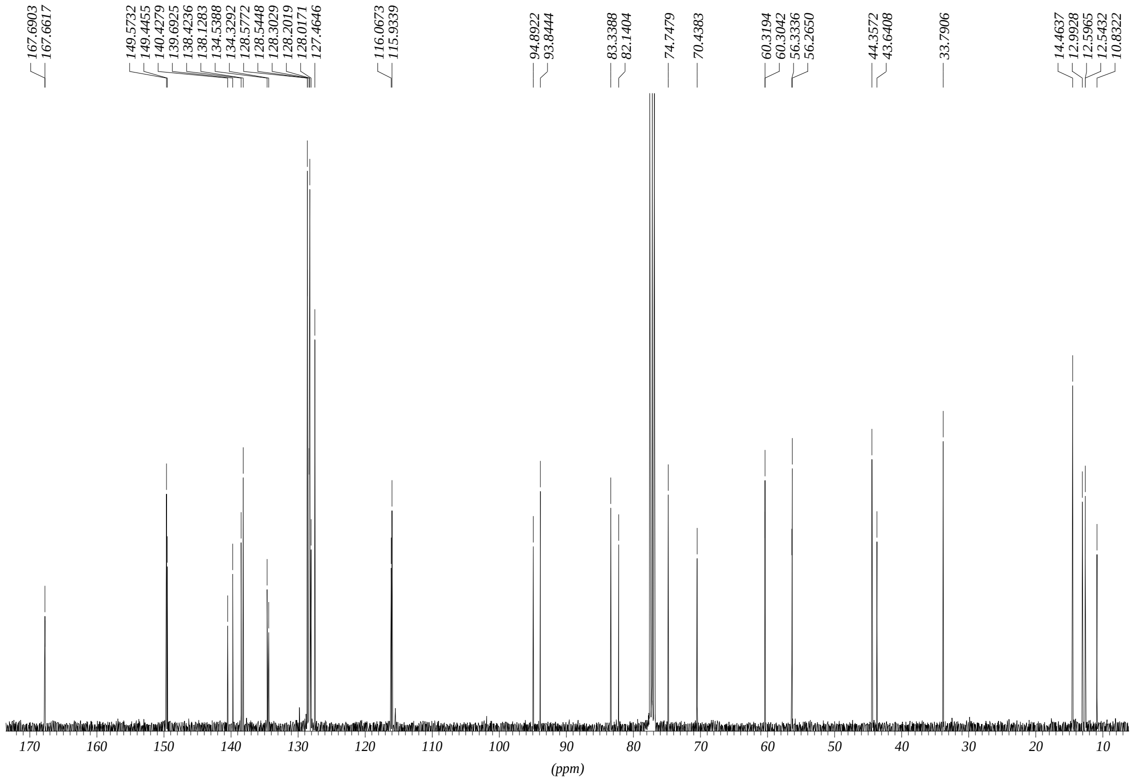
**56**

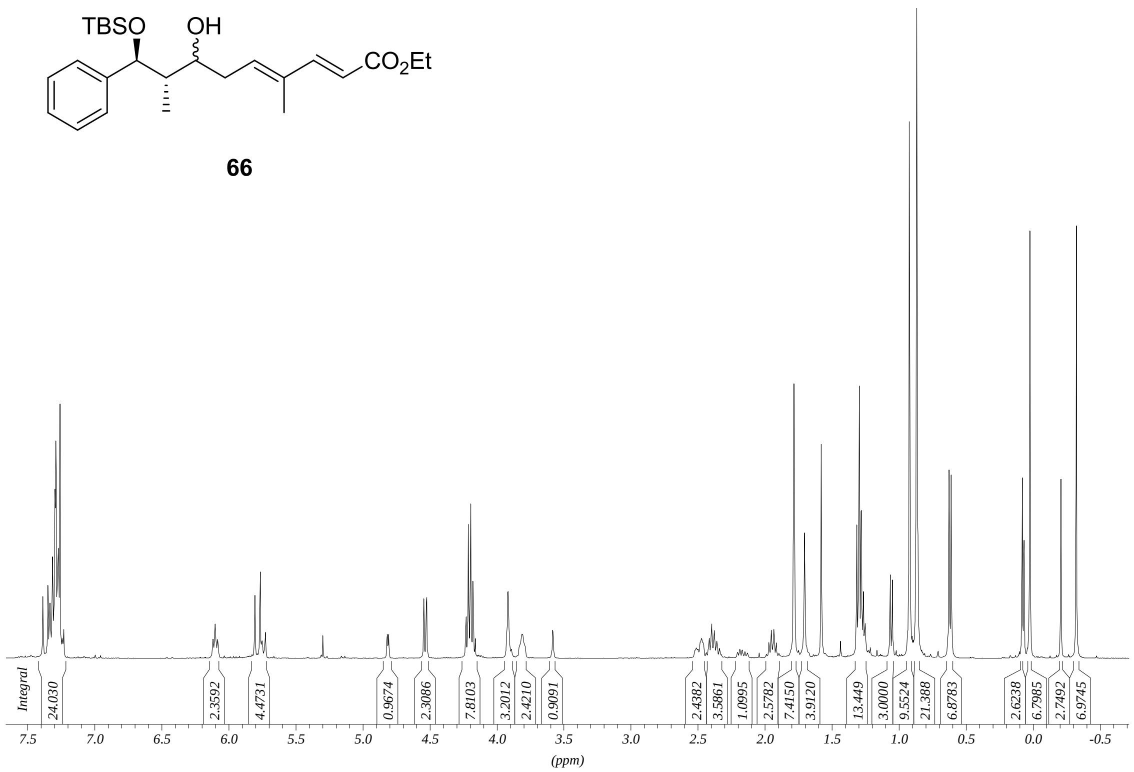

166.8777
145.7275
145.6665
145.5427
145.4855
135.8392
135.5858
134.4617
134.1244
124.5238
124.4076
120.7438
120.6962
107.9252
107.5213
89.2994
88.9698
72.8189
72.6436
67.9243
66.4935
60.1070
45.0536
44.4248
34.8833
34.4775
26.2734
26.2430
25.9476
25.9286
18.3780
18.3514
16.7529
16.7109
14.4361
12.4679
12.4298
12.1231
8.5412
-3.9954
-4.2450
-4.5041
-4.5670
-4.9023
-5.0223
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


MOMO
OH
CO2Et

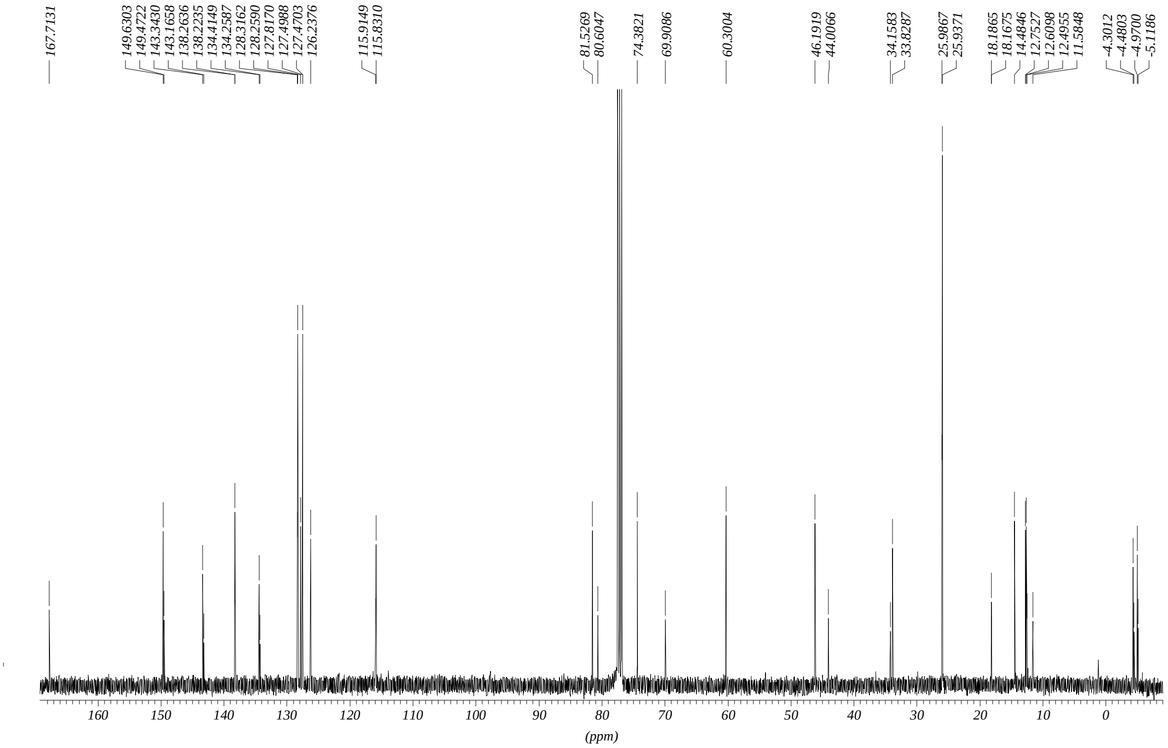
**65**

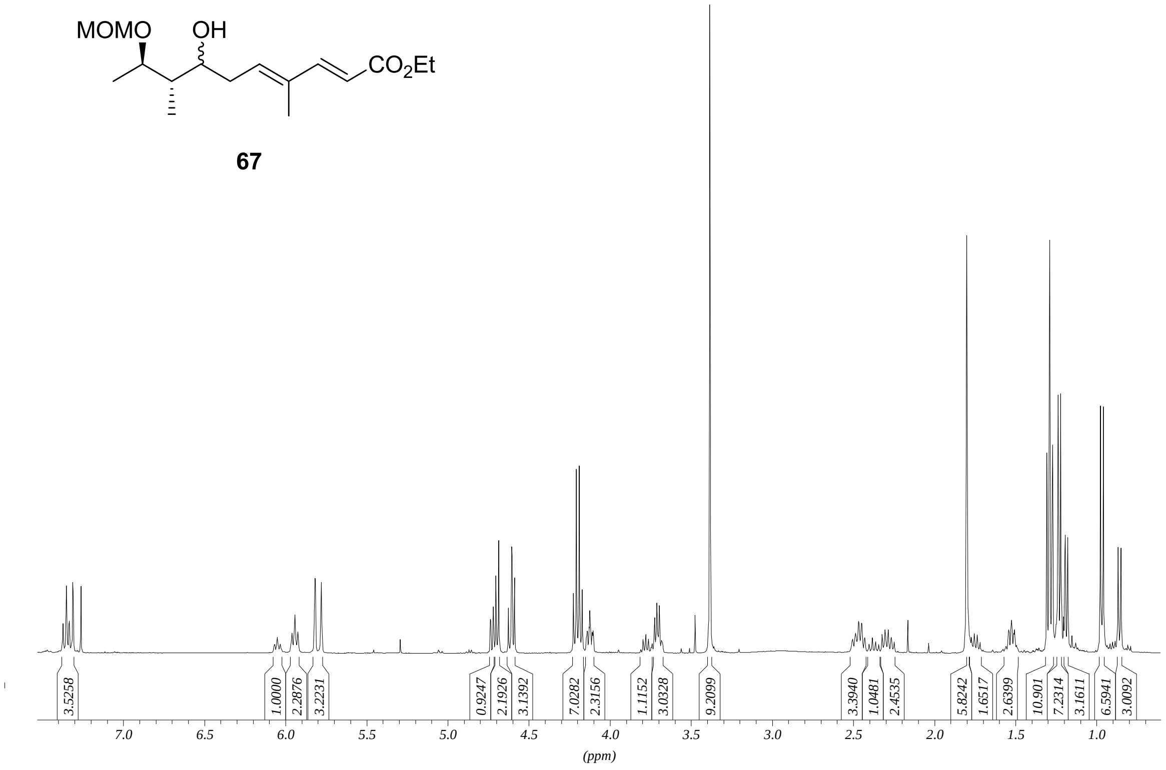

Integral
15.735
1.3065
1.0000
2.2730
0.9338
3.2579
2.6558
4.6408
1.0643
1.2575
1.3202
6.9250
0.8551
3.6581
0.9970
1.3680
1.0062
6.8756
1.3180
7.3218
2.9018
3.9187
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


167.6903
167.6617
149.5732
149.4455
140.4279
139.6925
138.4236
138.1283
134.5388
134.3292
128.5772
128.5448
128.3029
128.2019
128.0171
127.4646
116.0673
115.9339
94.8922
93.8444
83.3388
82.1404
74.7479
70.4383
60.3194
60.3042
56.3336
56.2650
44.3572
43.6408
33.7906
14.4637
12.9928
12.5965
12.5432
10.8322
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

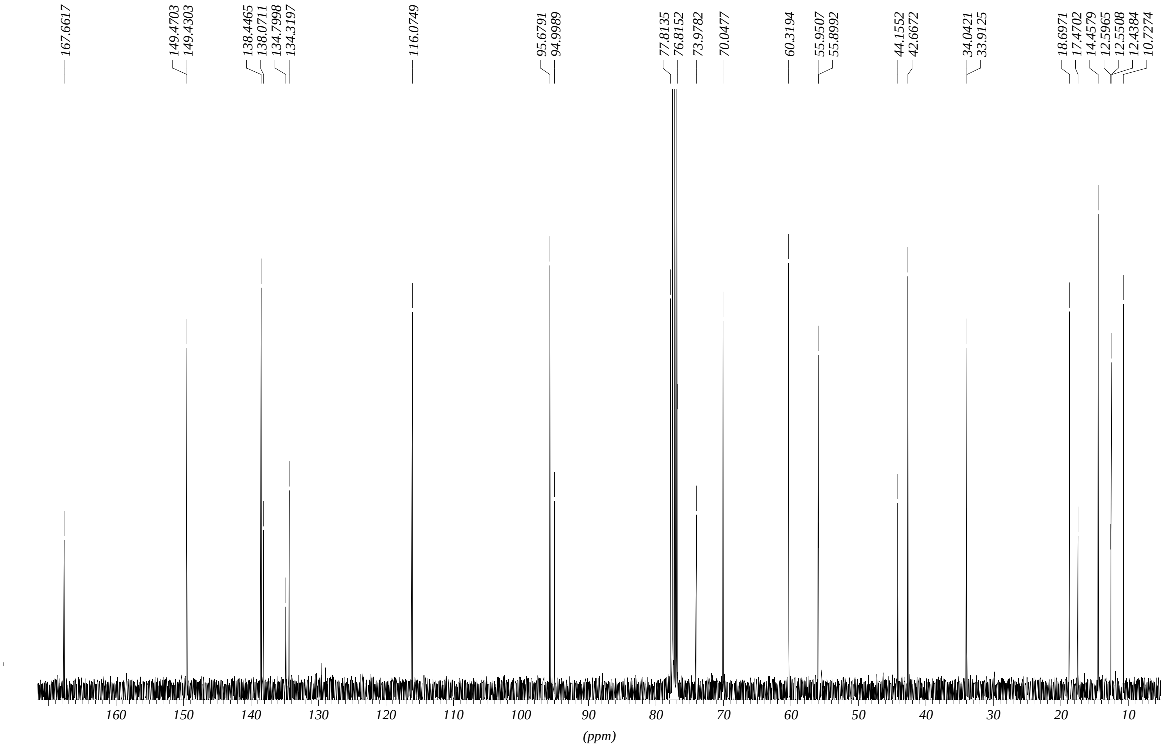

TBSO
OH
$CO_2Et$
Integral
24.030
2.3592
4.4731
0.9674
2.3086
7.8103
3.2012
2.4210
0.9091
2.4382
3.5861
1.0995
2.5782
7.4150
3.9120
13.449
3.0000
9.5524
21.388
6.8783
2.6238
6.7985
2.7492
6.9745
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
(ppm)

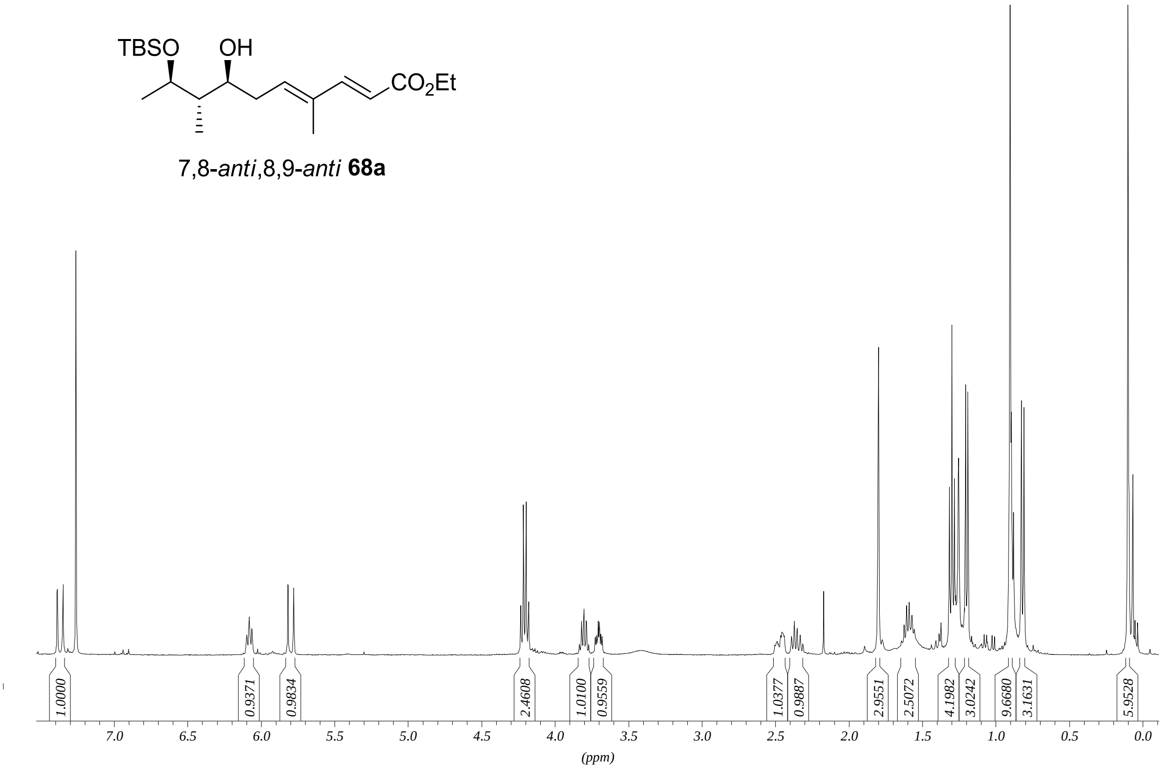
**66**


167.7131
149.6303
149.4722
143.3430
143.1658
138.2636
138.2235
134.4149
134.2587
128.3162
128.2590
127.8170
127.4988
127.4703
126.2376
115.9149
115.8310
81.5269
80.6047
74.3821
69.9086
60.3004
46.1919
44.0066
34.1583
33.8287
25.9867
25.9371
18.1865
18.1675
14.4846
12.7527
12.6098
12.4955
11.5848
-4.3012
-4.4803
-4.9700
-5.1186
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

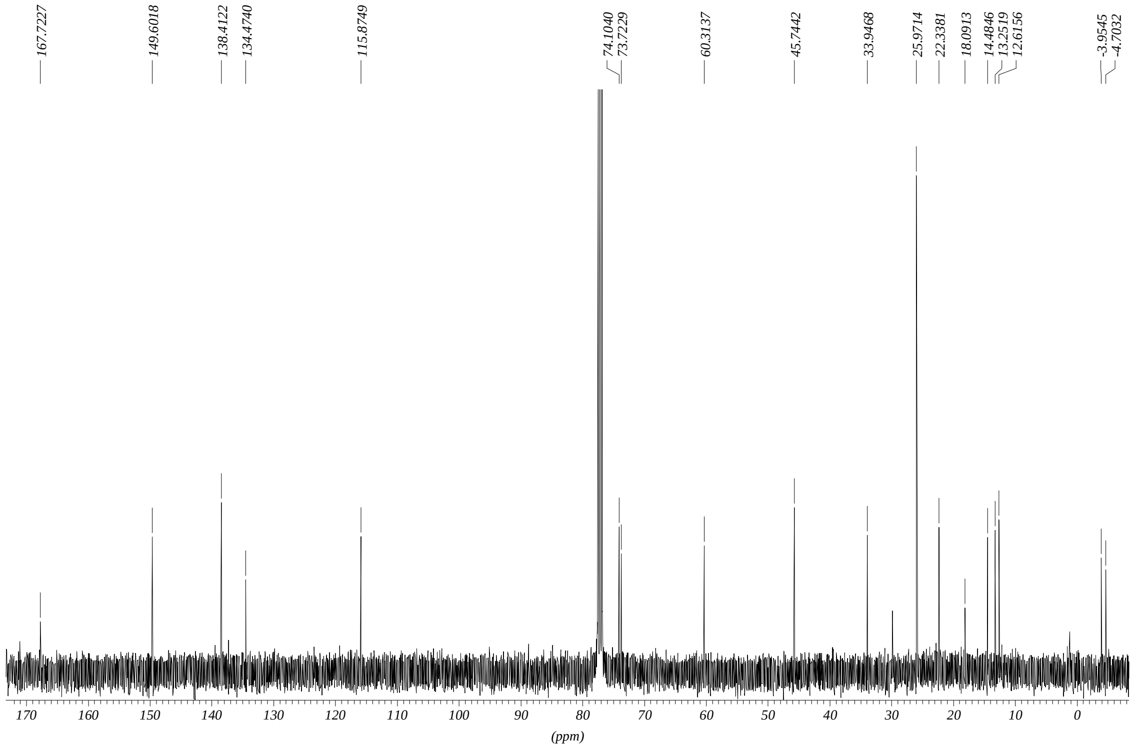

MOMO
OH
CO2Et
3.5258
1.0000
2.2876
3.2231
0.9247
2.1926
3.1392
7.0282
2.3156
1.1152
3.0328
9.2099
3.3940
1.0481
2.4535
5.8242
1.6517
2.6399
10.901
7.2314
3.1611
6.5941
3.0092
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

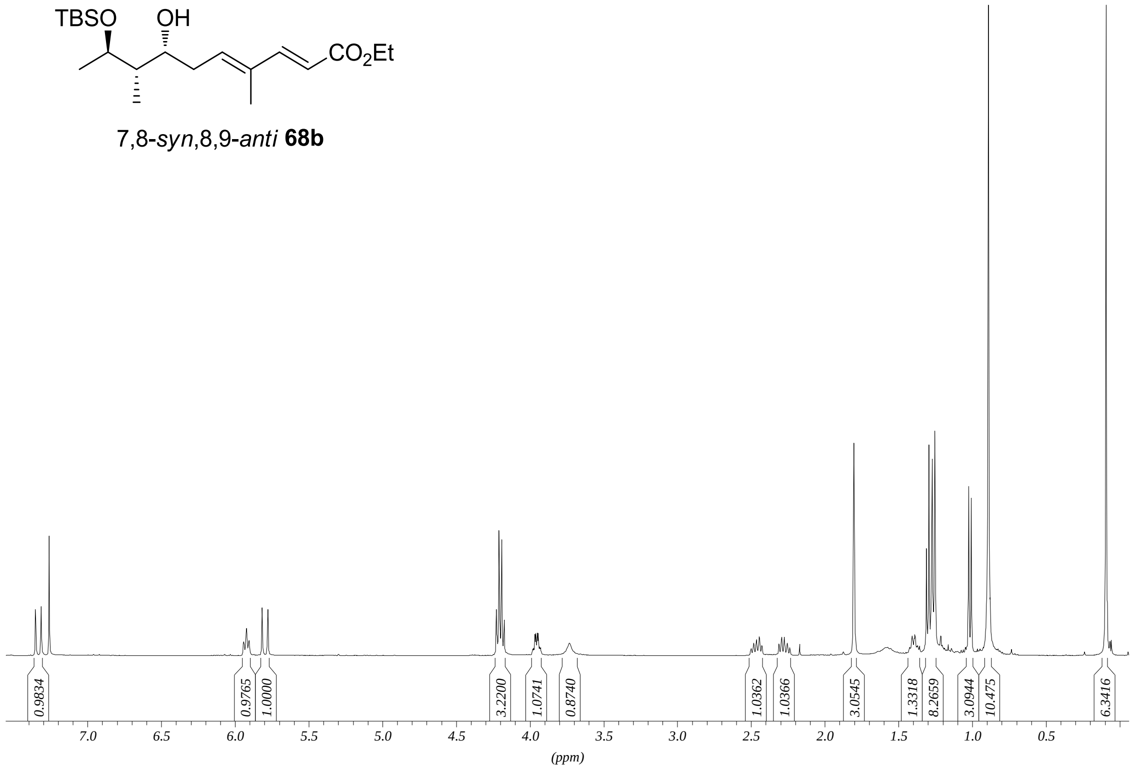
**67**



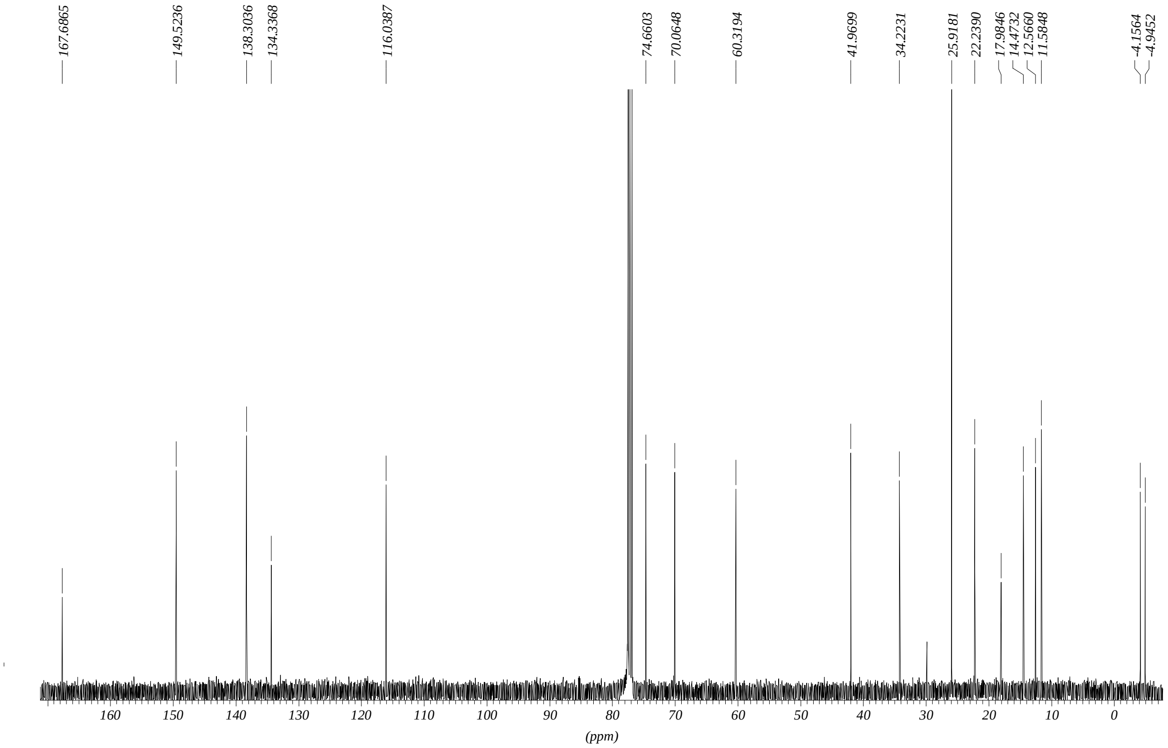


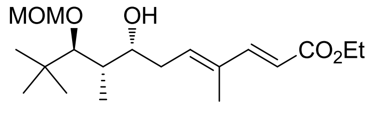
7,8-*anti*,8,9-*anti* **68a**



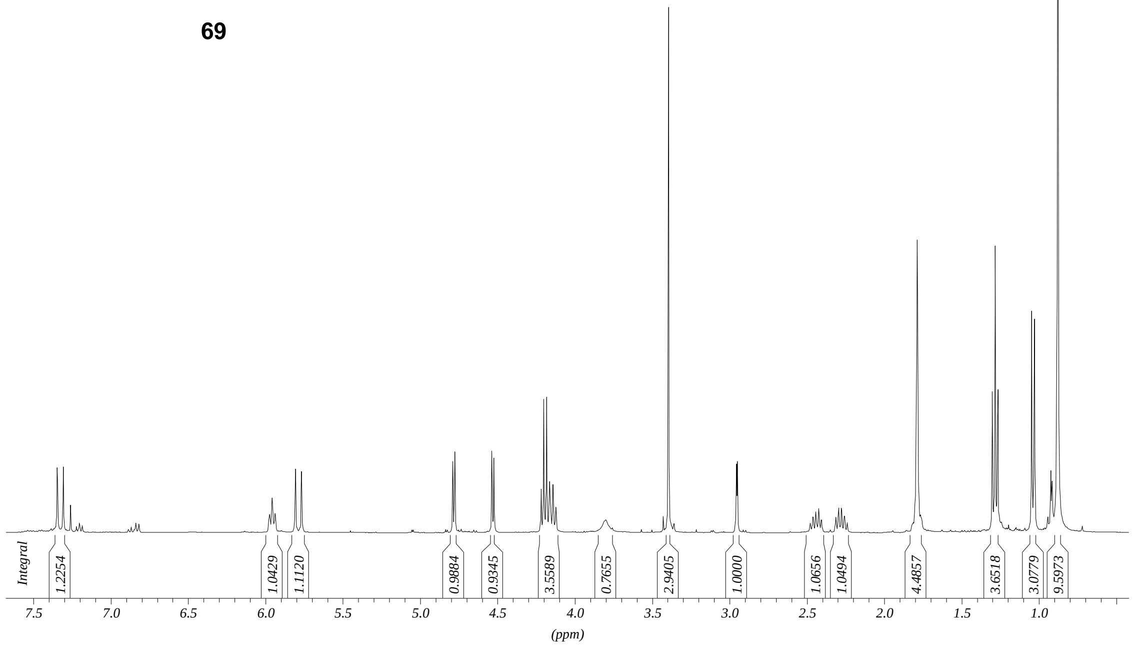


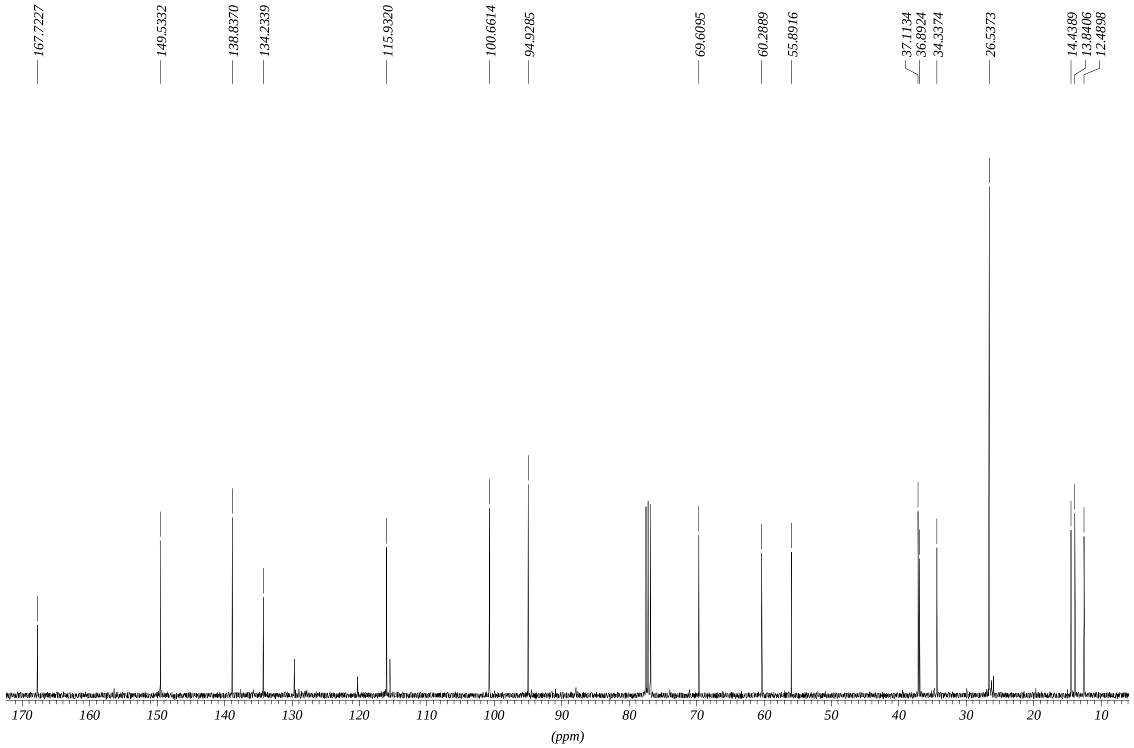
7,8-*syn*,8,9-*anti* **68b**

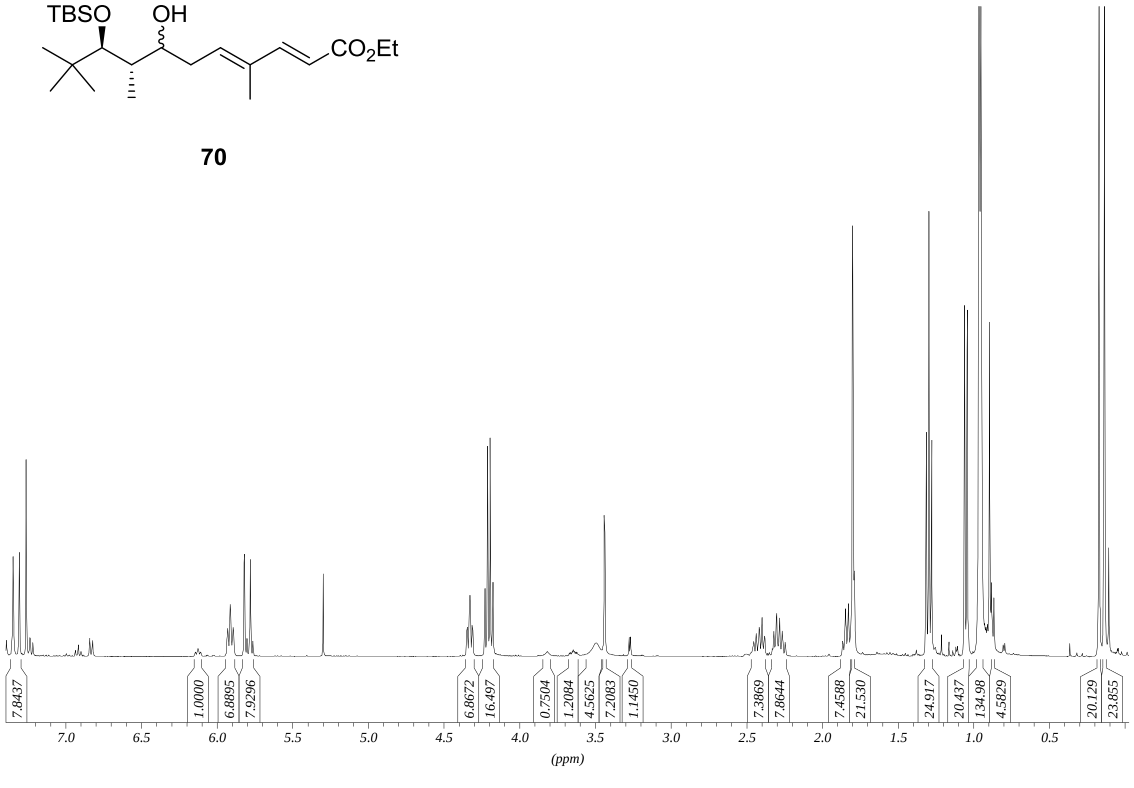

167.6865
149.5236
138.3036
134.3368
116.0387
74.6603
70.0648
60.3194
41.9699
34.2231
25.9181
22.2390
17.9846
14.4732
12.5660
11.5848
-4.1564
-4.9452
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


MOMO
OH
CO2Et

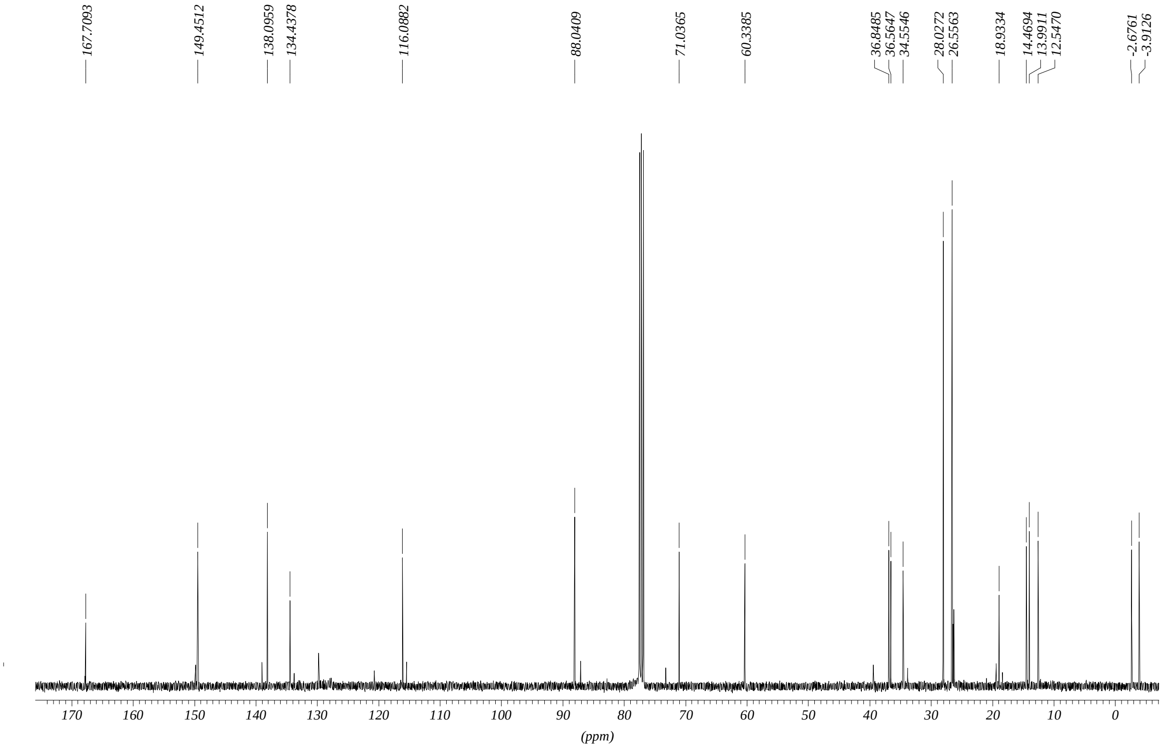
**69**

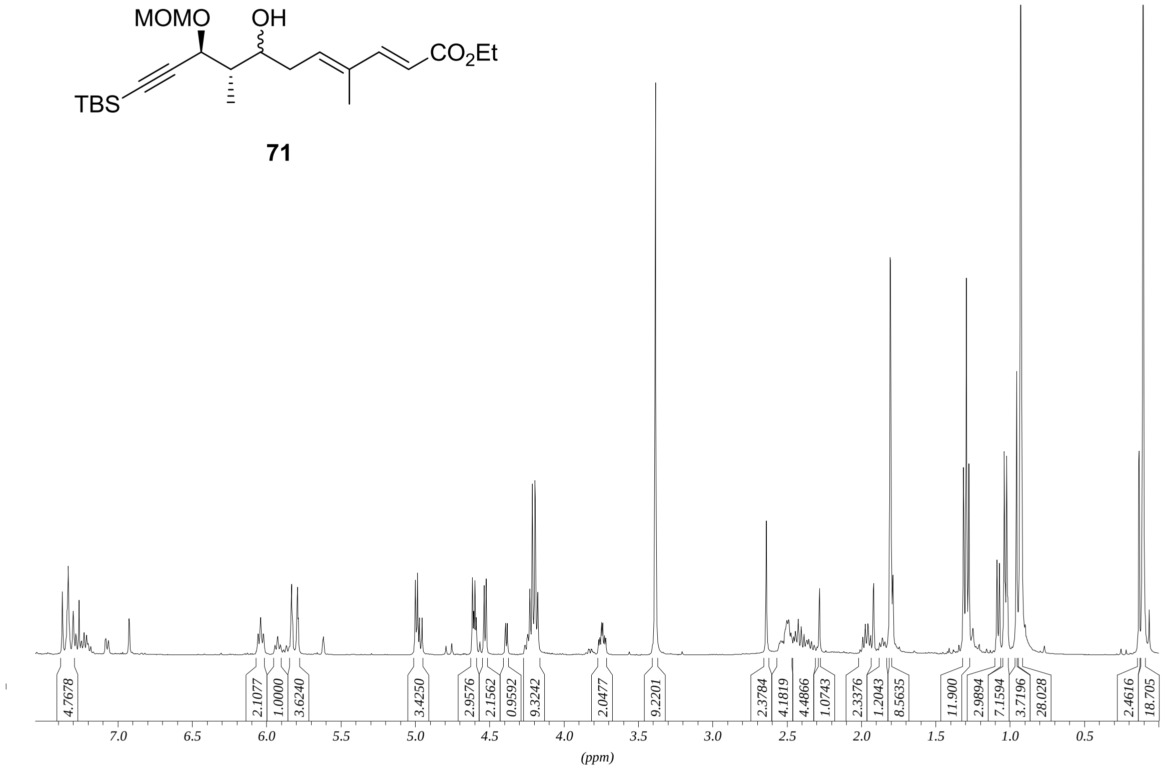

Integral
1.2254
1.0429
1.1120
0.9884
0.9345
3.5589
0.7655
2.9405
1.0000
1.0656
1.0494
4.4857
3.6518
3.0779
9.5973
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)


167.7227
149.5332
138.8370
134.2339
115.9320
100.6614
94.9285
69.6095
60.2889
55.8916
37.1134
36.8924
34.3374
26.5373
14.4389
13.8406
12.4898
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

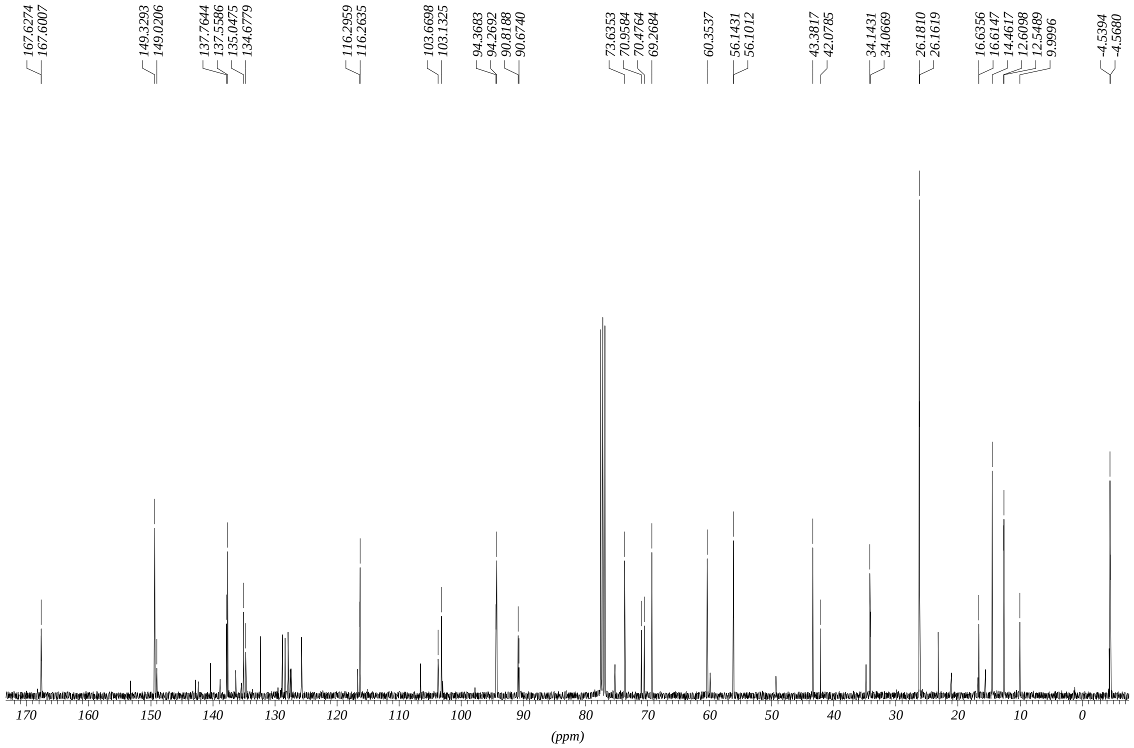

TBSO
OH
CO2Et
7.8437
1.0000
6.8895
7.9296
6.8672
16.497
0.7504
1.2084
4.5625
7.2083
1.1450
7.3869
7.8644
7.4588
21.530
24.917
20.437
134.98
4.5829
20.129
23.855
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

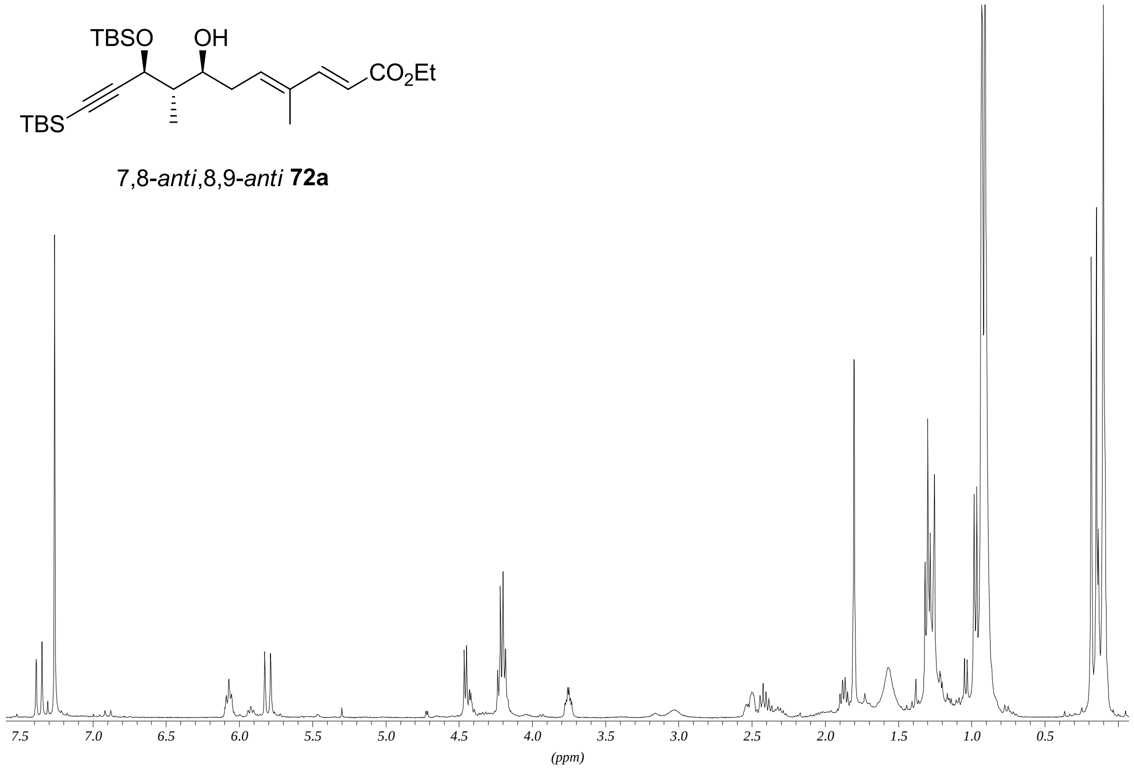
**70**


167.7093
149.4512
138.0959
134.4378
116.0882
88.0409
71.0365
60.3385
36.8485
36.5647
34.5546
28.0272
26.5563
18.9334
14.4694
13.9911
12.5470
-2.6761
-3.9126
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

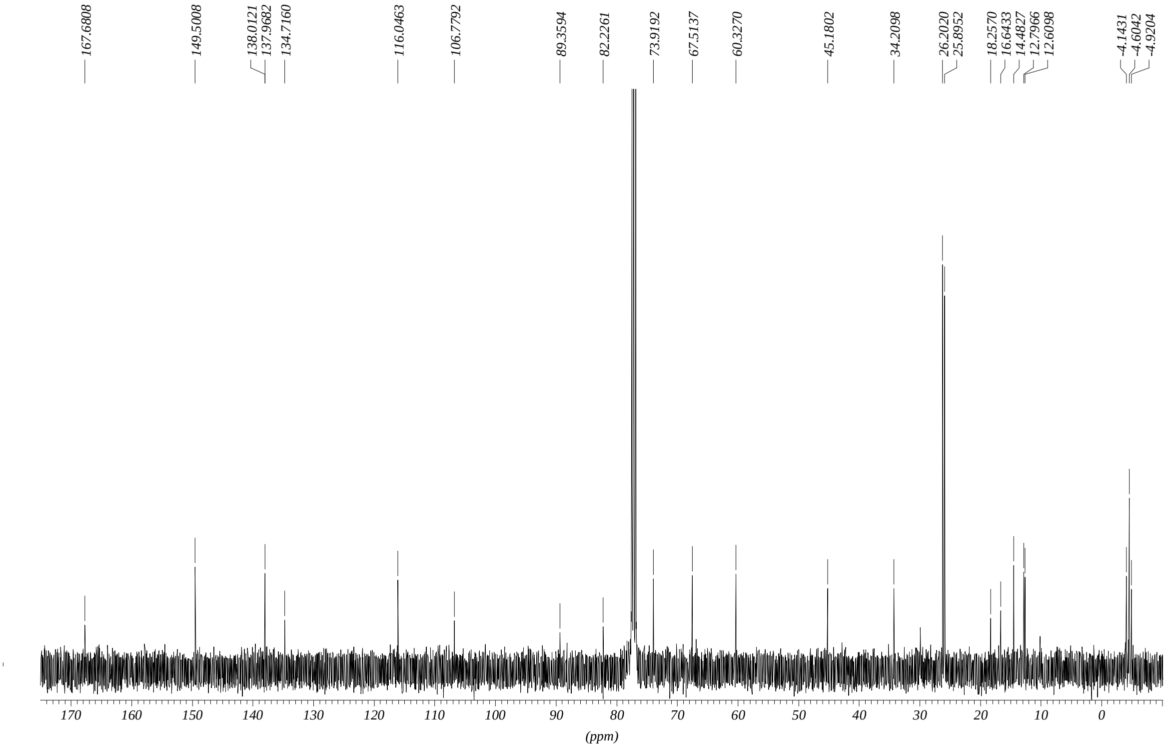

MOMO
OH
CO2Et
TBS
4.7678
2.1077
1.0000
3.6240
3.4250
2.9576
2.1562
0.9592
9.3242
2.0477
9.2201
2.3784
4.1819
4.4866
1.0743
2.3376
1.2043
8.5635
11.900
2.9894
7.1594
3.7196
28.028
2.4616
18.705
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

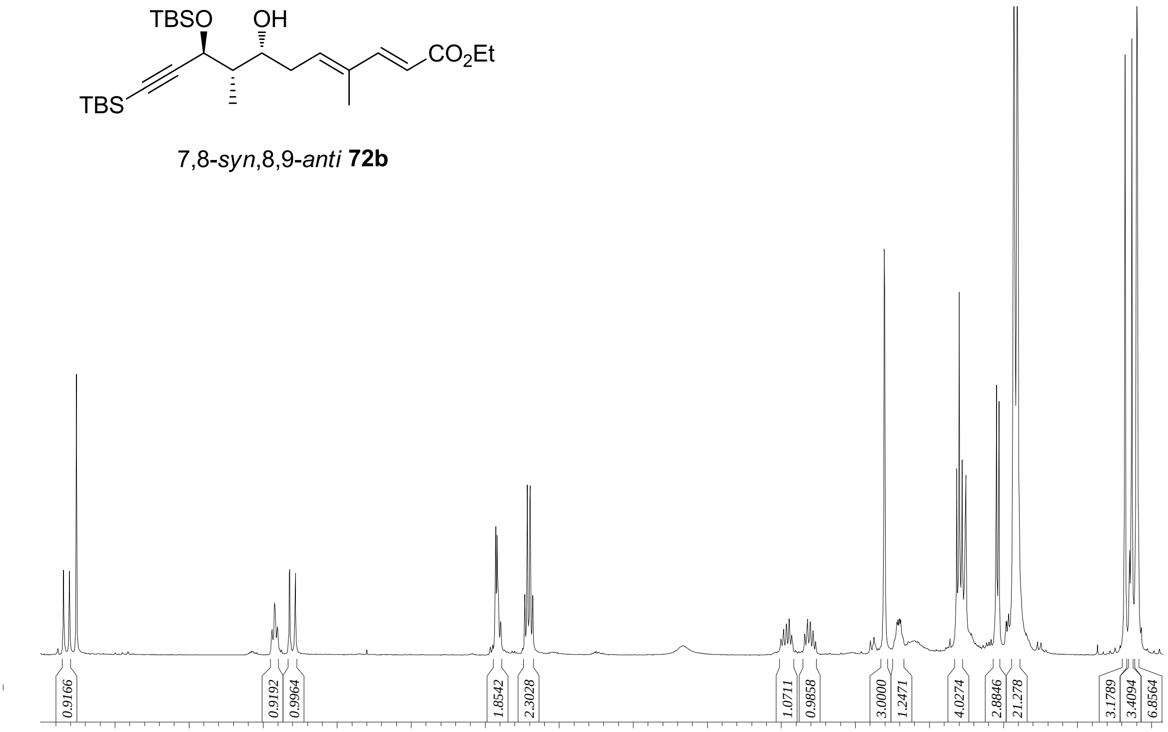
**71**



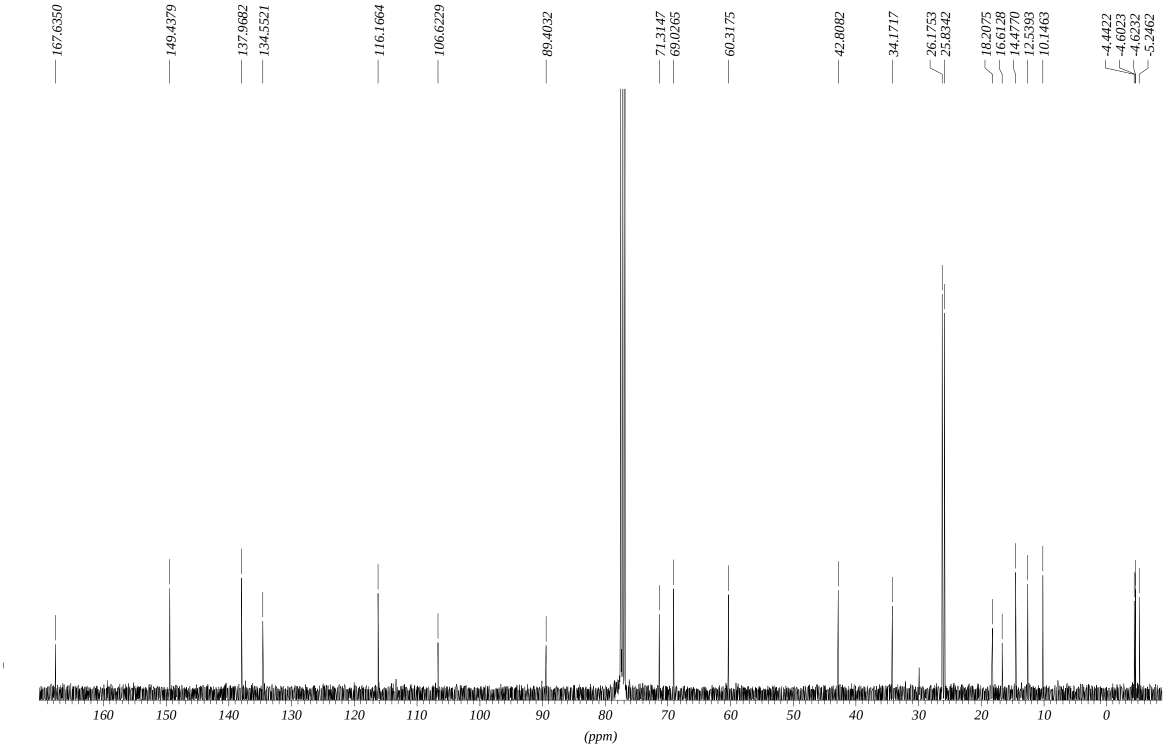


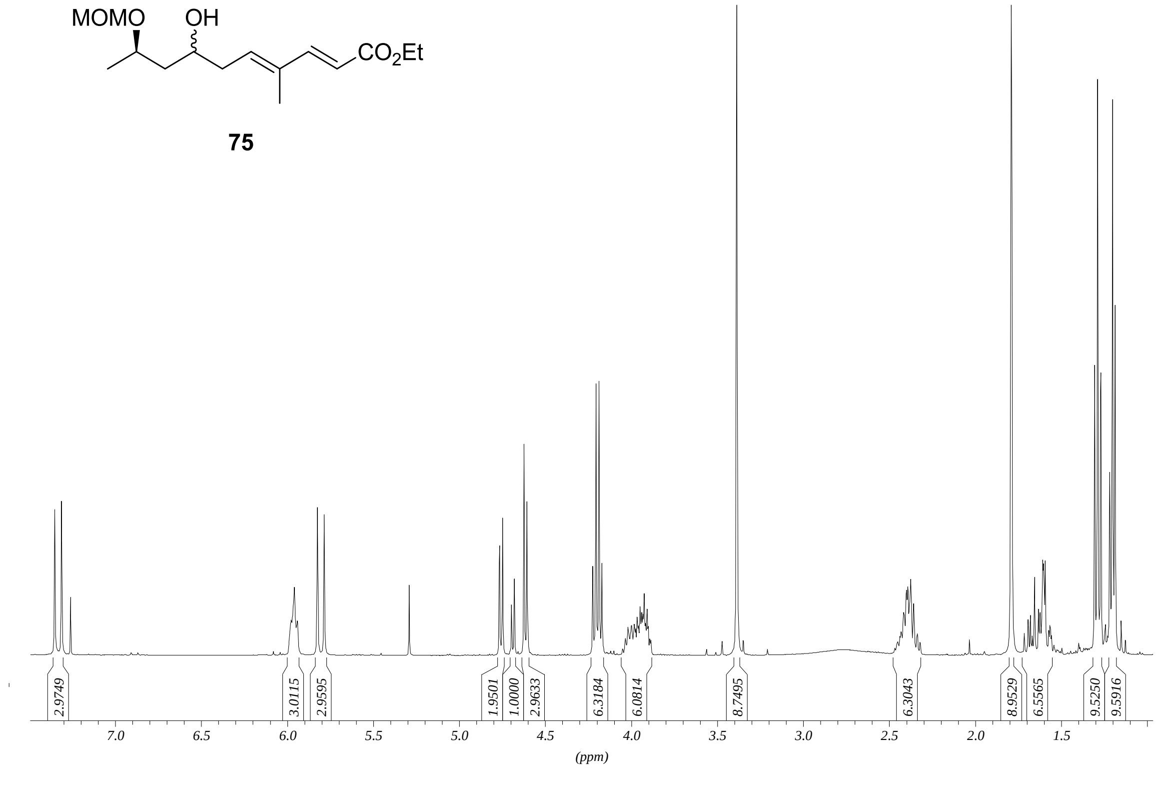
7,8-*anti*,8,9-*anti* **72a**



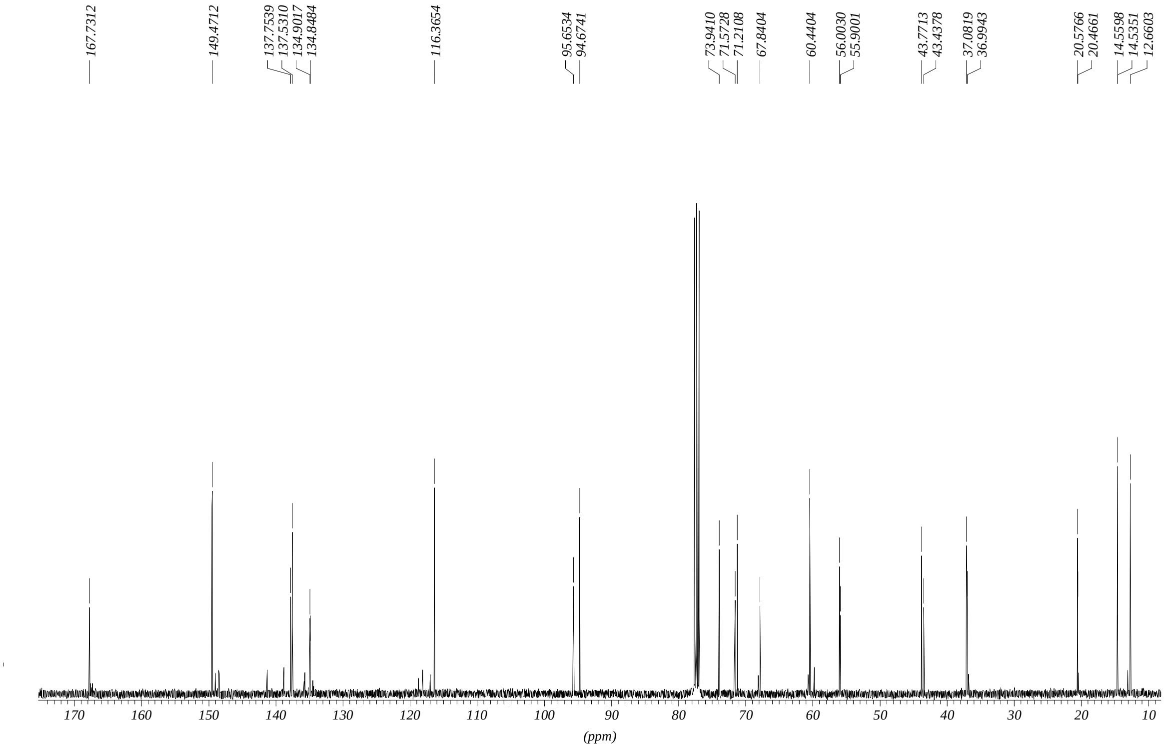


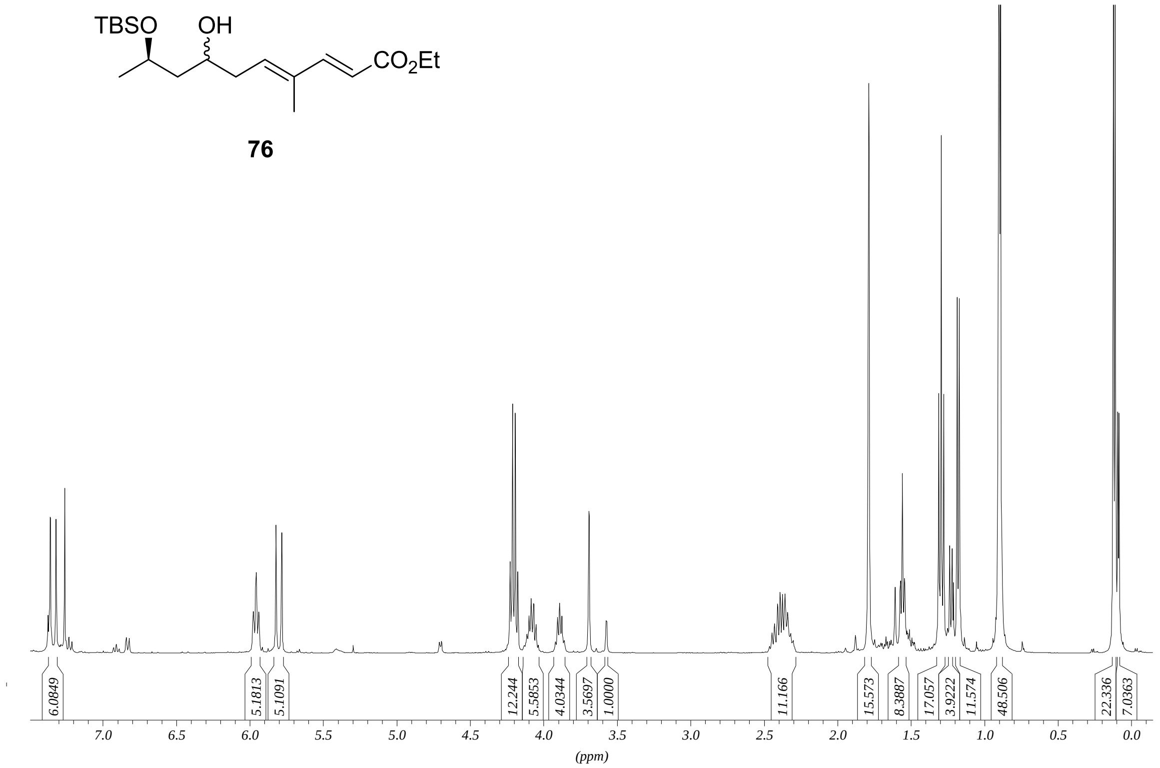
7,8-*syn*,8,9-*anti* **72b**


167.6350
149.4379
137.9682
134.5521
116.1664
106.6229
89.4032
71.3147
69.0265
60.3175
42.8082
34.1717
26.1753
25.8342
18.2075
16.6128
14.4770
12.5393
10.1463
-4.4422
-4.6023
-4.6232
-5.2462
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

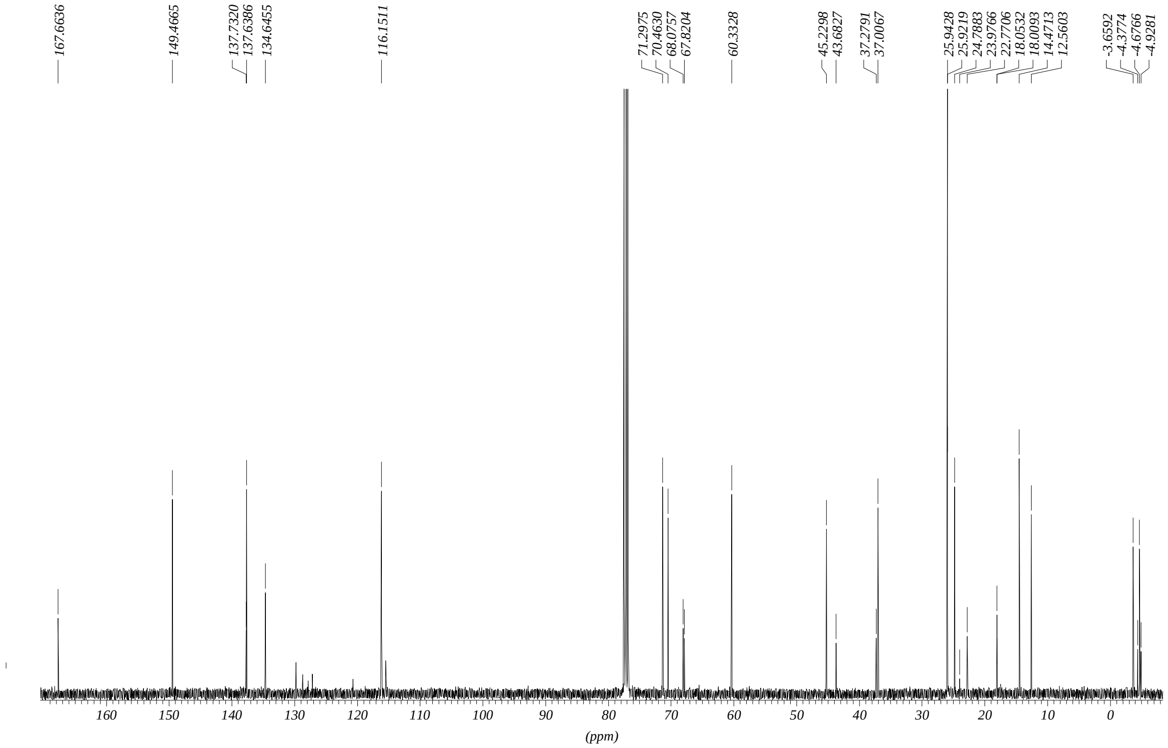

MOMO
OH
CO2Et
2.9749
3.0115
2.9595
1.9501
1.0000
2.9633
6.3184
6.0814
8.7495
6.3043
8.9529
6.5565
9.5250
9.5916
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)

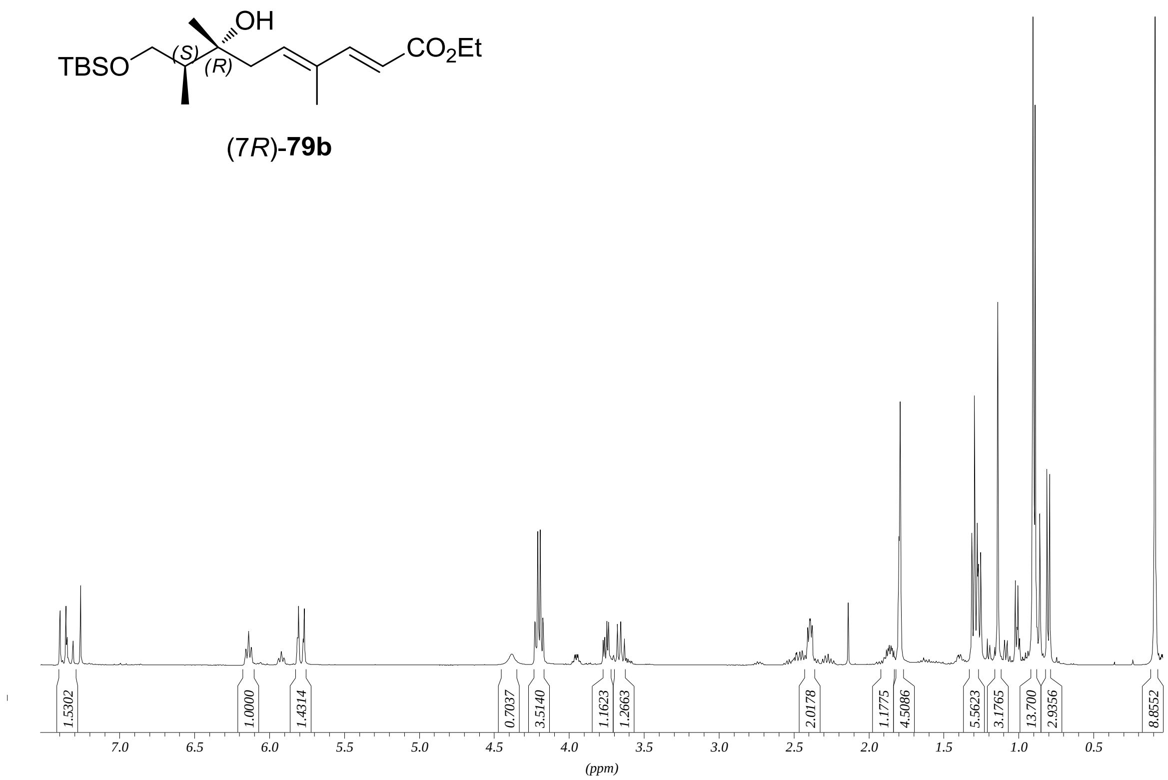
**75**


167.7312
149.4712
137.7539
137.5310
134.9017
134.8484
116.3654
95.6534
94.6741
73.9410
71.5728
71.2108
67.8404
60.4404
56.0030
55.9001
43.7713
43.4378
37.0819
36.9943
20.5766
20.4661
14.5598
14.5351
12.6603
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

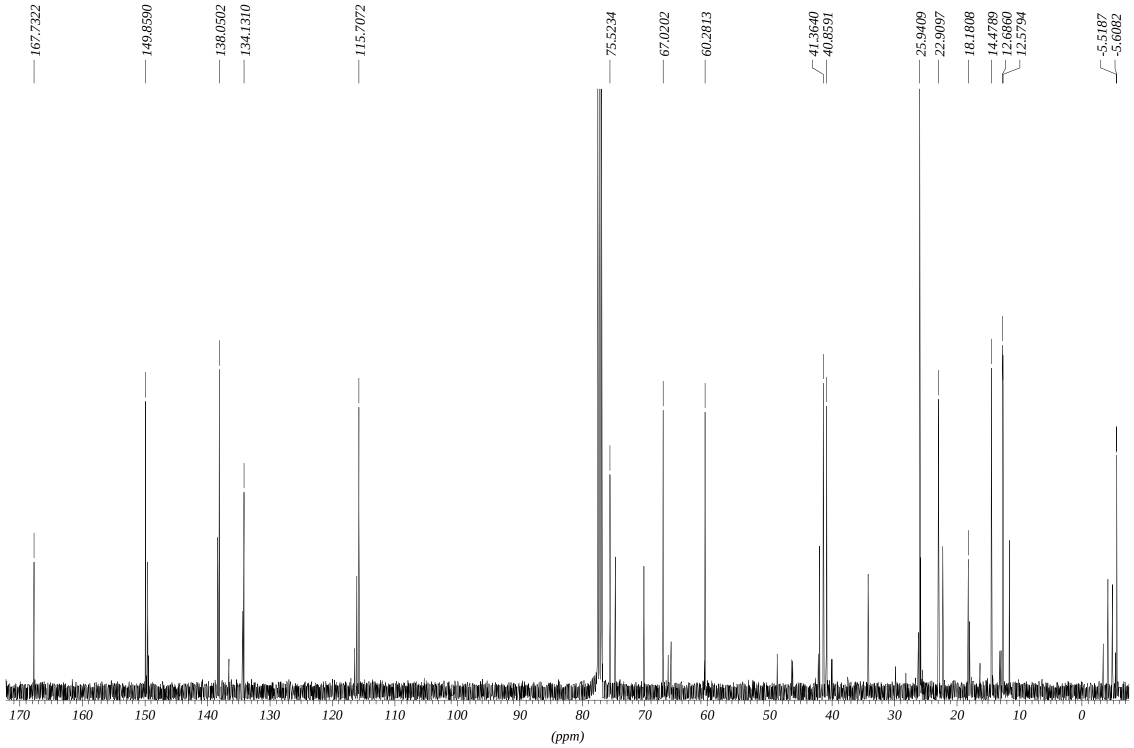

TBSO
OH
$CO_2Et$
6.0849
5.1813
5.1091
12.244
5.5853
4.0344
3.5697
1.0000
11.166
15.573
8.3887
17.057
3.9222
11.574
48.506
22.336
7.0363
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

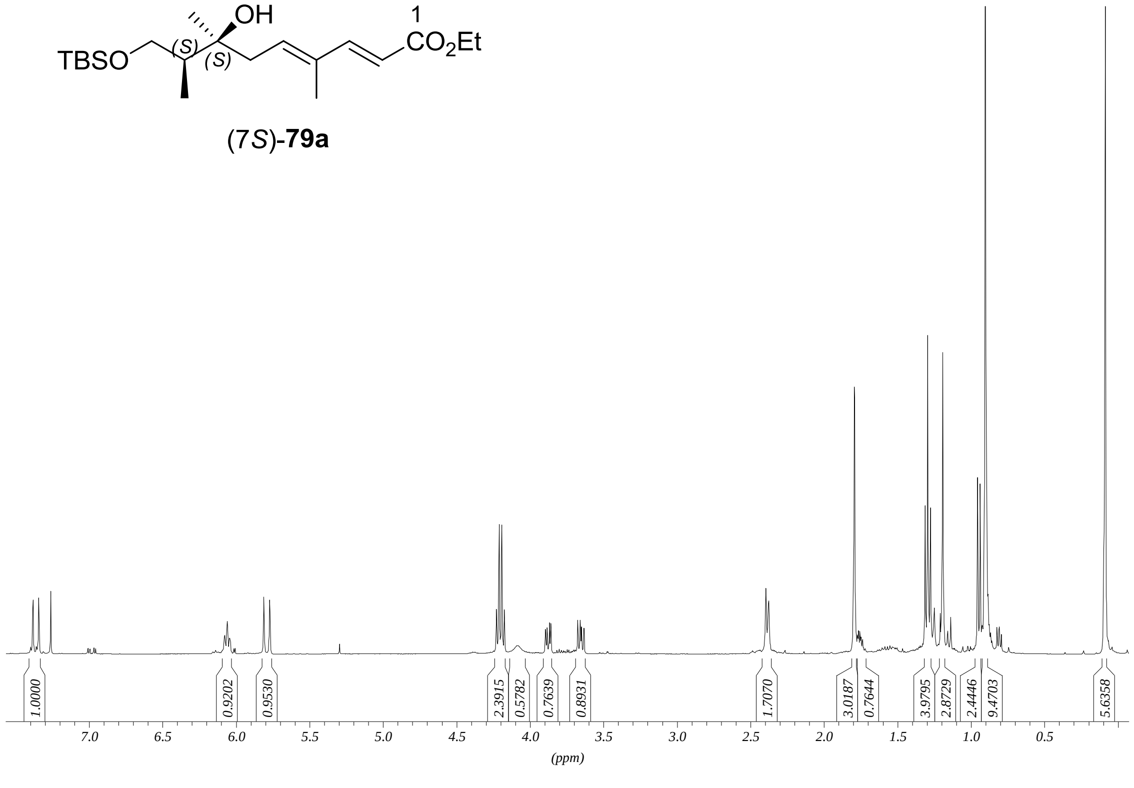
**76**


167.6636
149.4665
137.7320
137.6386
134.6455
116.1511
71.2975
70.4630
68.0757
67.8204
60.3328
45.2298
43.6827
37.2791
37.0067
25.9428
25.9219
24.7883
23.9766
22.7706
18.0532
18.0093
14.4713
12.5603
-3.6592
-4.3774
-4.6766
-4.9281
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

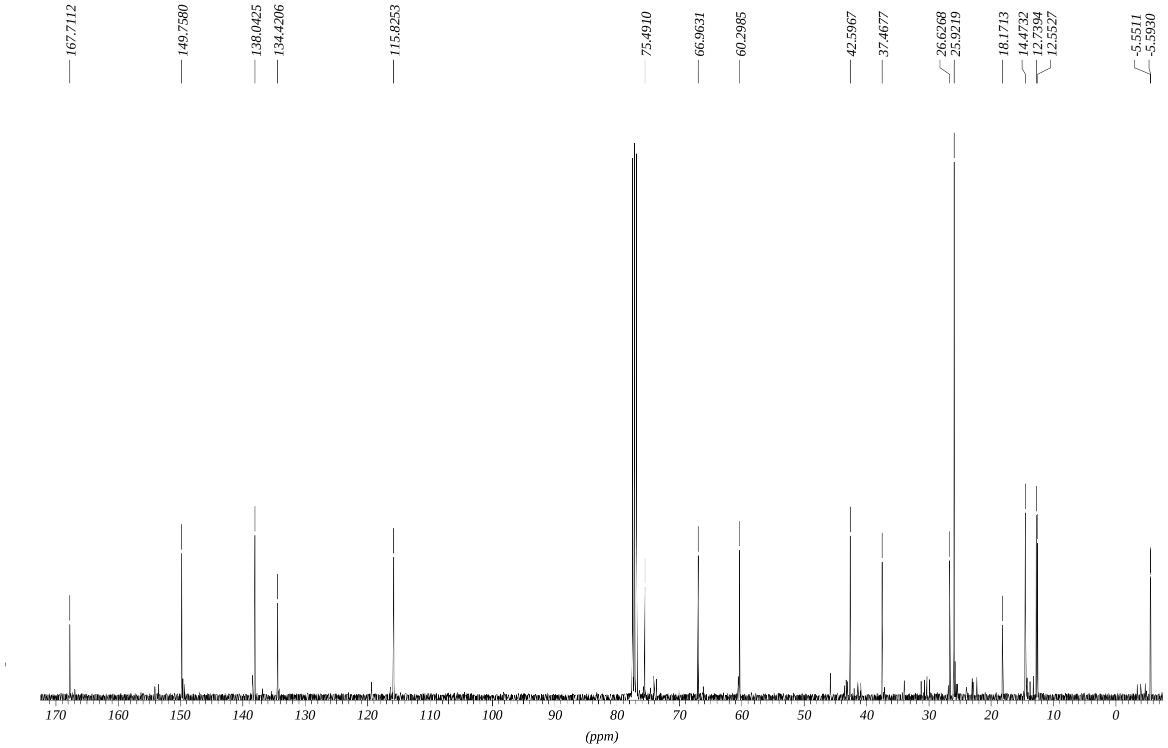

TBSO
(S)
(R)
OH
CO2Et
1.5302
1.0000
1.4314
0.7037
3.5140
1.1623
1.2663
2.0178
1.1775
4.5086
5.5623
3.1765
13.700
2.9356
8.8552
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

(7*R*)-**79b**


167.7322
149.8590
138.0502
134.1310
115.7072
75.5234
67.0202
60.2813
41.3640
40.8591
25.9409
22.9097
18.1808
14.4789
12.6860
12.5794
-5.5187
-5.6082
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


TBSO
(S)
(S)
OH
1
CO2Et
1.0000
0.9202
0.9530
2.3915
0.5782
0.7639
0.8931
1.7070
3.0187
0.7644
3.9795
2.8729
2.4446
9.4703
5.6358
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

(7*S*)-**79a**


167.7112
149.7580
138.0425
134.4206
115.8253
75.4910
66.9631
60.2985
42.5967
37.4677
26.6268
25.9219
18.1713
14.4732
12.7394
12.5527
-5.5511
-5.5930
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)