

Supporting Information

Synthesis of the fungus metabolite cladosin C

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TOC

¹H NMR and ¹³C NMR spectra

S2-14

Gas chromatograms, ¹H and ¹³C NMR spectra of the *R*-MTPA esters of
R-**10** and *S*-**10**

S15-17

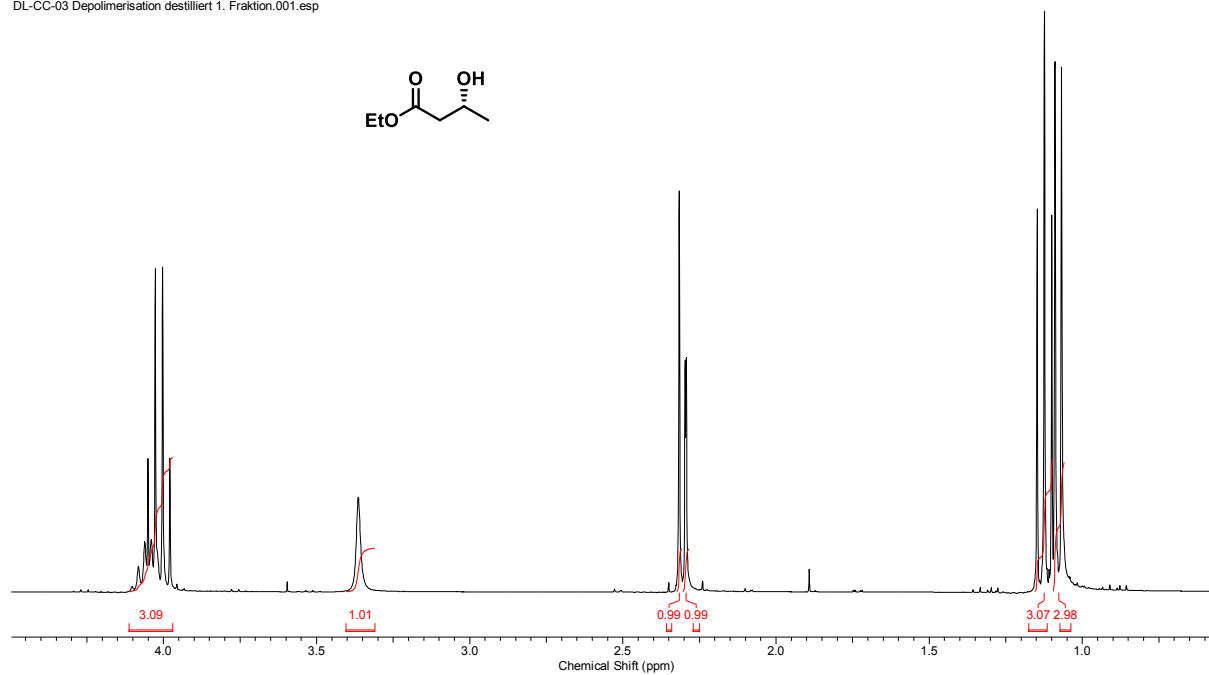


Figure S1 (*R*)-Ethyl-3-hydroxy butyrate (*R*-10) ¹H NMR (300 MHz, CDCl₃).

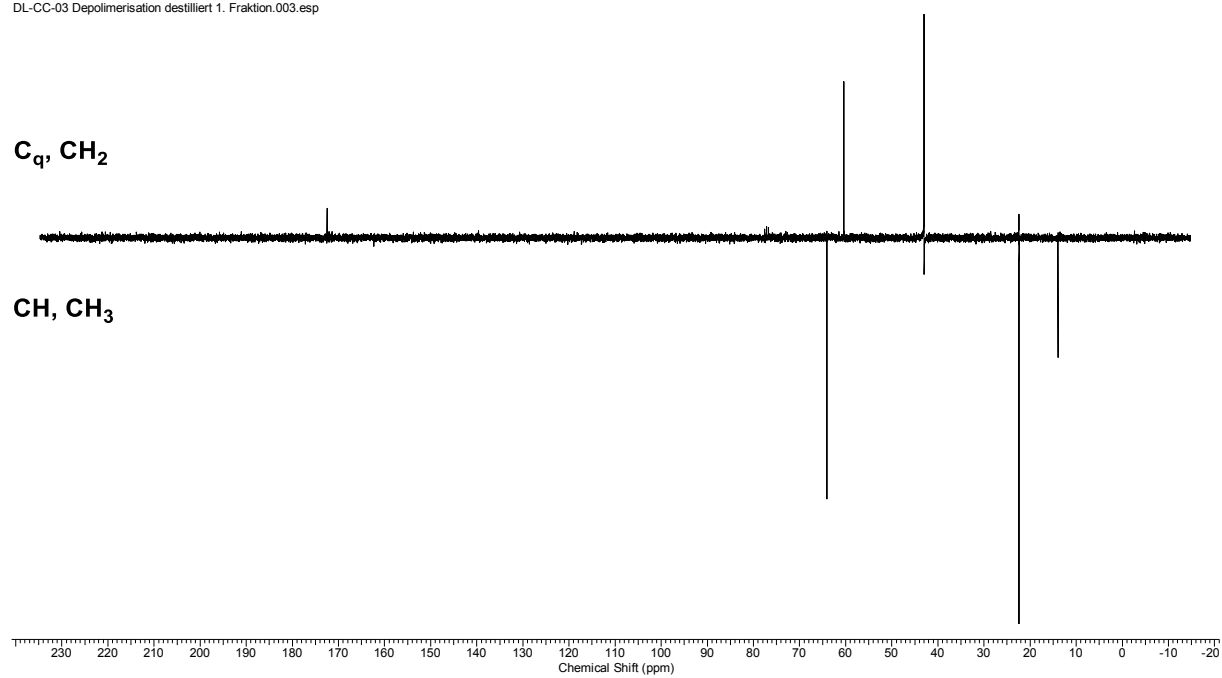


Figure S2 (*R*)-Ethyl-3-hydroxy butyrate (*R*-10) ¹³C NMR (75 MHz, CDCl₃).

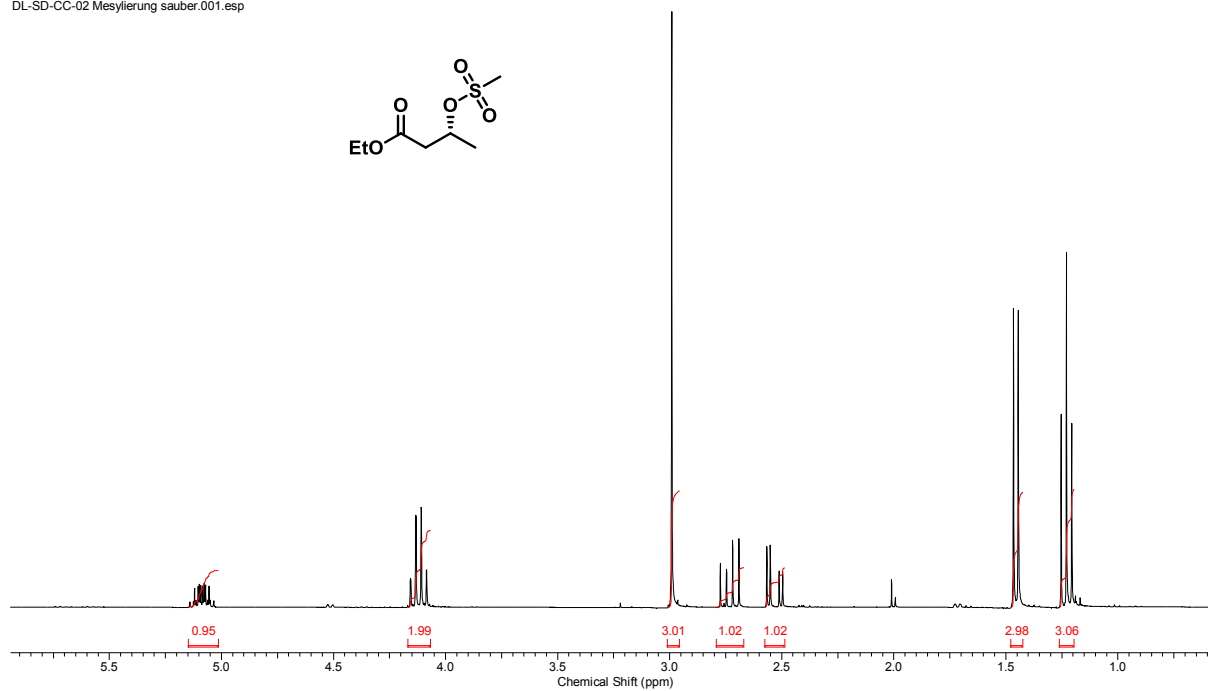


Figure S3 (*R*)-Ethyl-3-mesyloxy butyrate (**11**) ¹H NMR (300 MHz, CDCl₃).

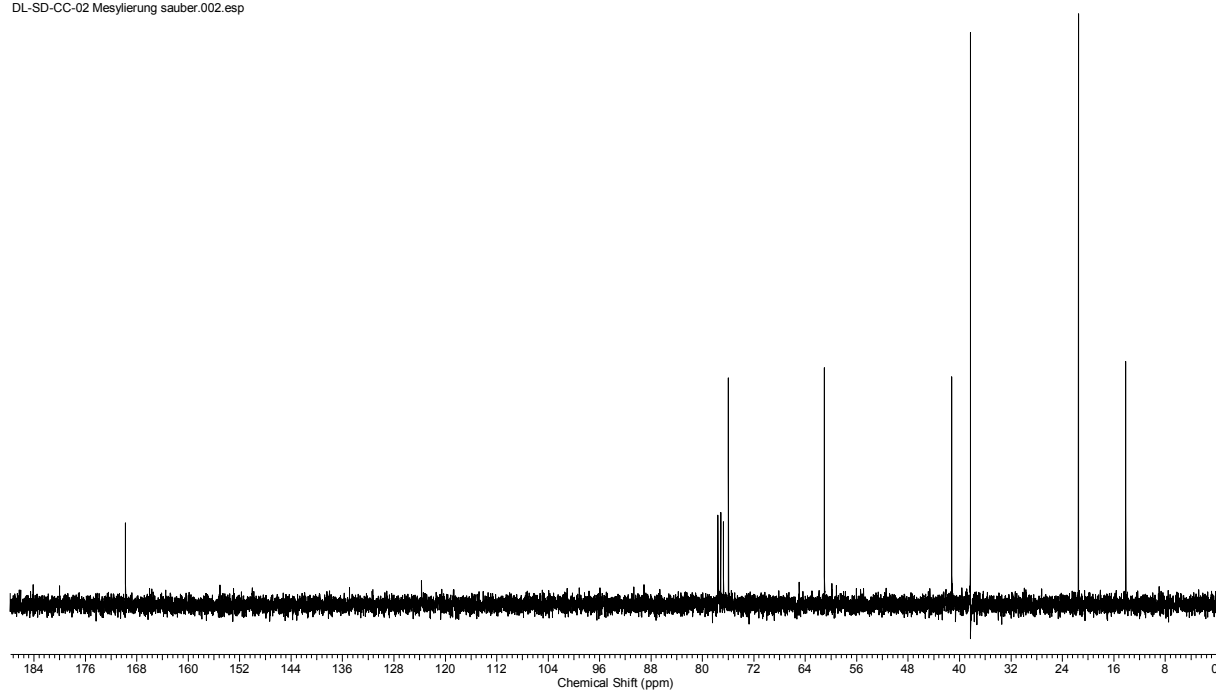


Figure S4 (*R*)-Ethyl-3-mesyloxy butyrate (**11**) ¹³C NMR (75 MHz, CDCl₃).

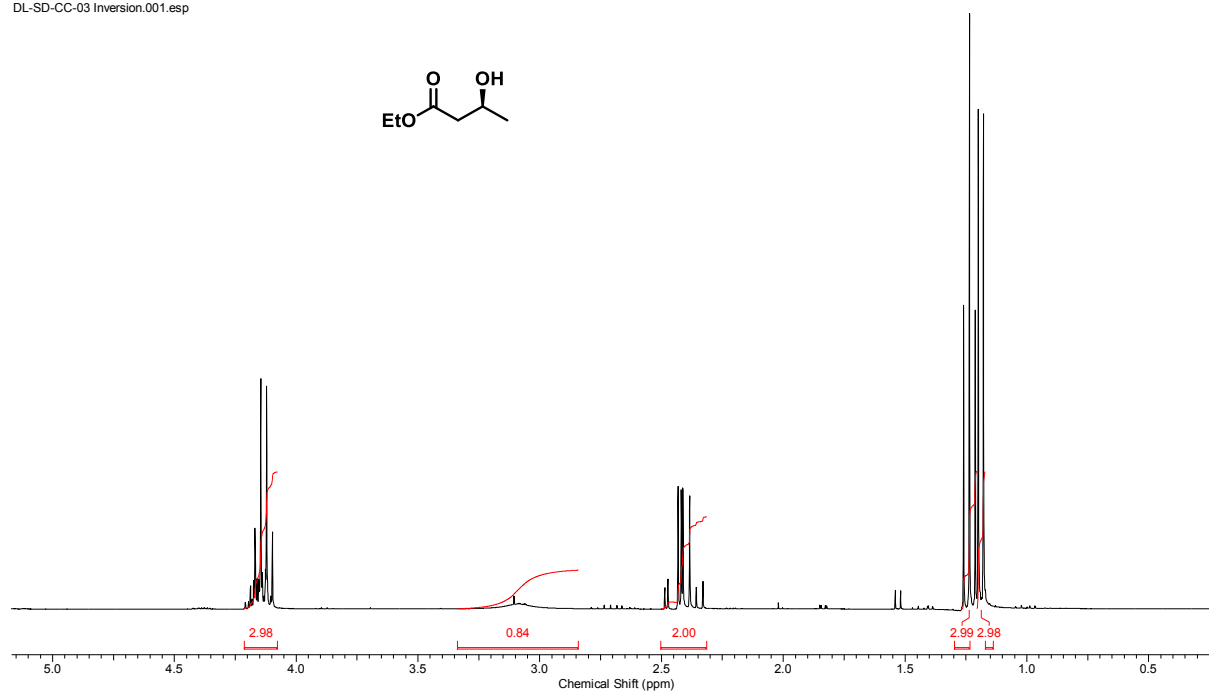


Figure S5 (S)-Ethyl-3-hydroxy butyrate (S-10) ¹H NMR (500 MHz, CDCl₃).

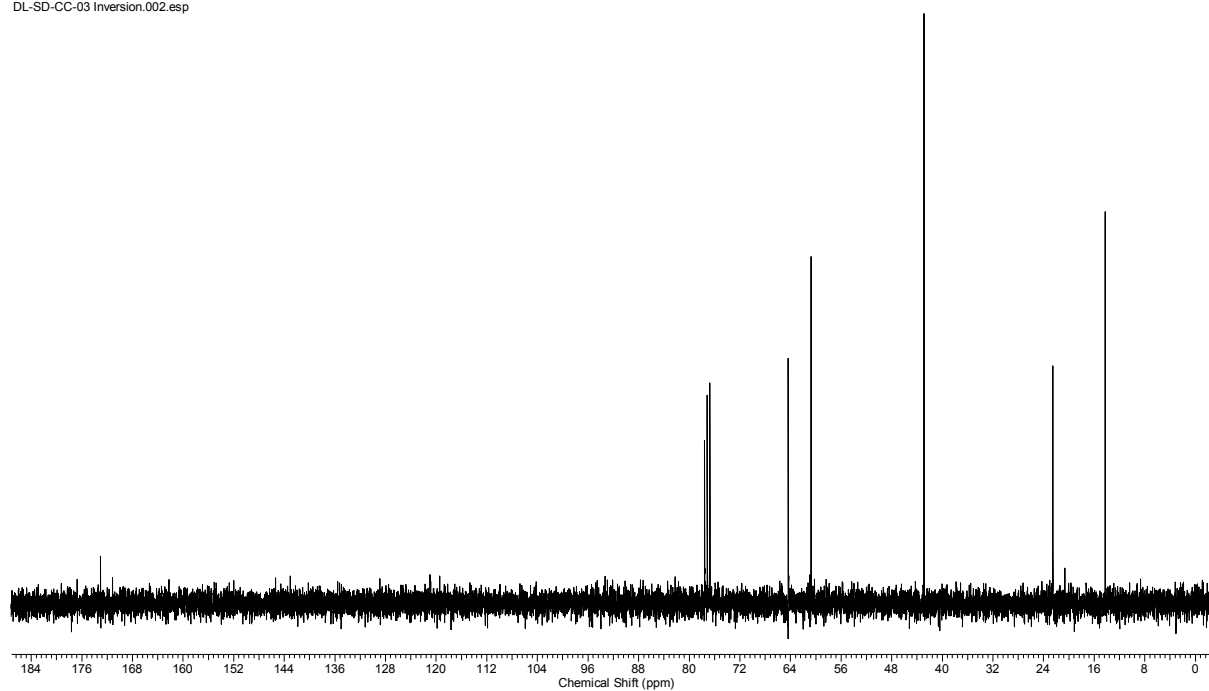


Figure S6 (S)-Ethyl-3-hydroxy butyrate (S-10) ¹³C NMR (75 MHz, CDCl₃).

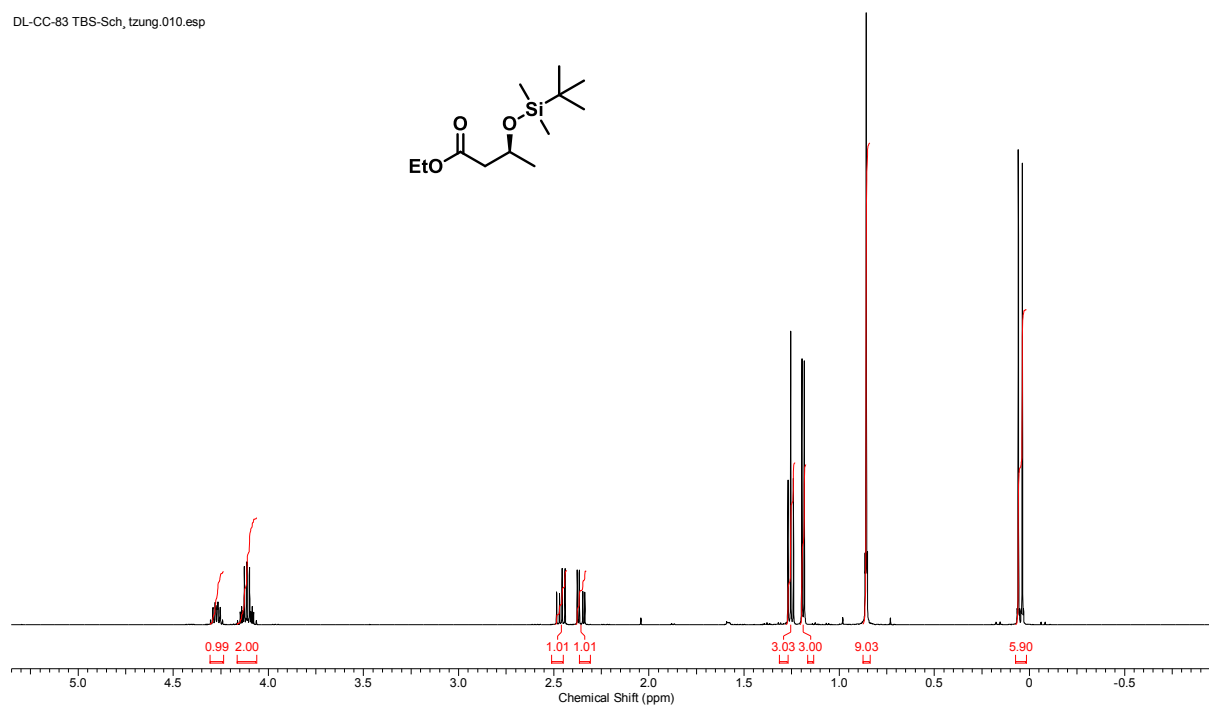


Figure S7 (S)-Ethyl-3-(*tert*-butyldimethylsilyloxy)-butyrate (**12**) ^1H NMR (300 MHz, CDCl_3).

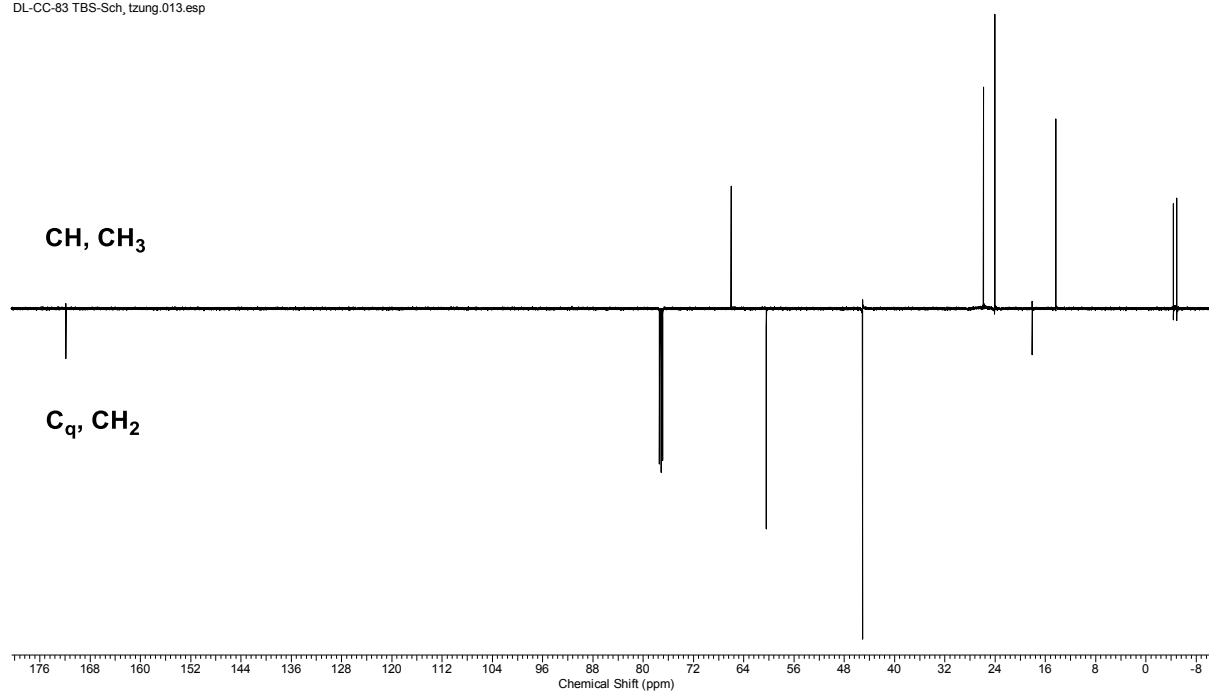


Figure S8 (S)-Ethyl-3-(*tert*-butyldimethylsilyloxy)-butyrate (**12**) ^{13}C NMR (75 MHz, CDCl_3).

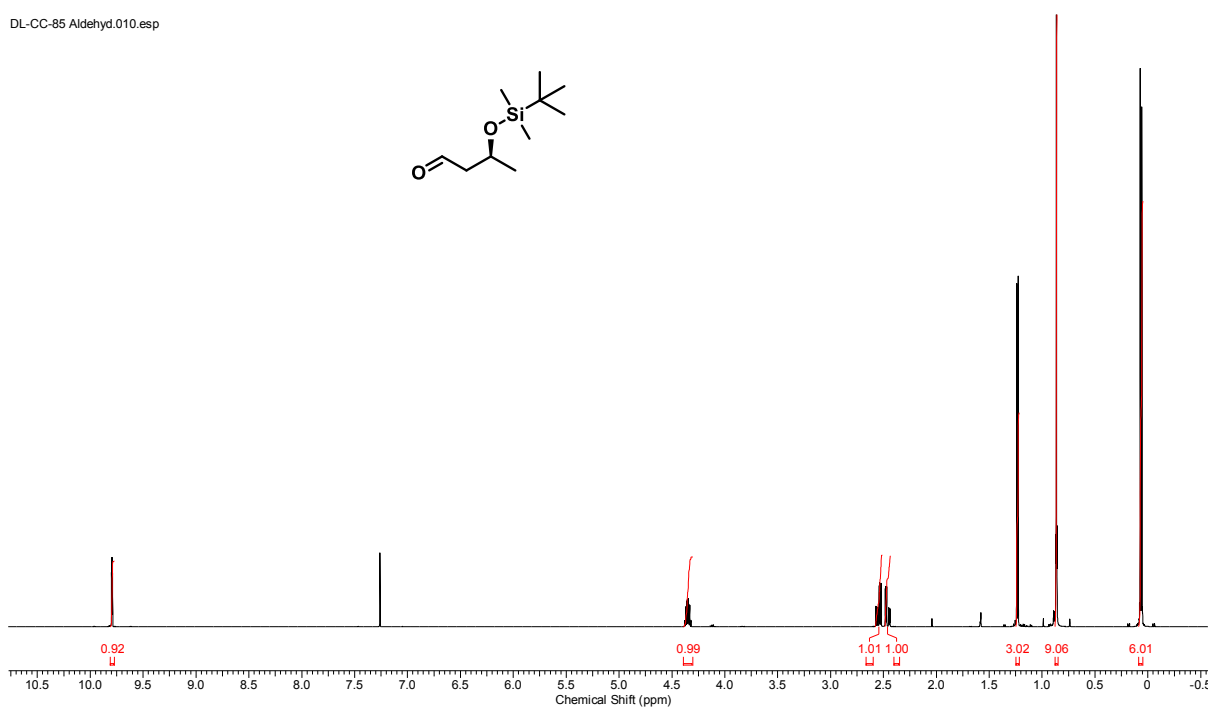


Figure S9 (S)-3-(*tert*-Butyldimethylsilyloxy)-butanale (13) ^1H NMR (300 MHz, CDCl_3).

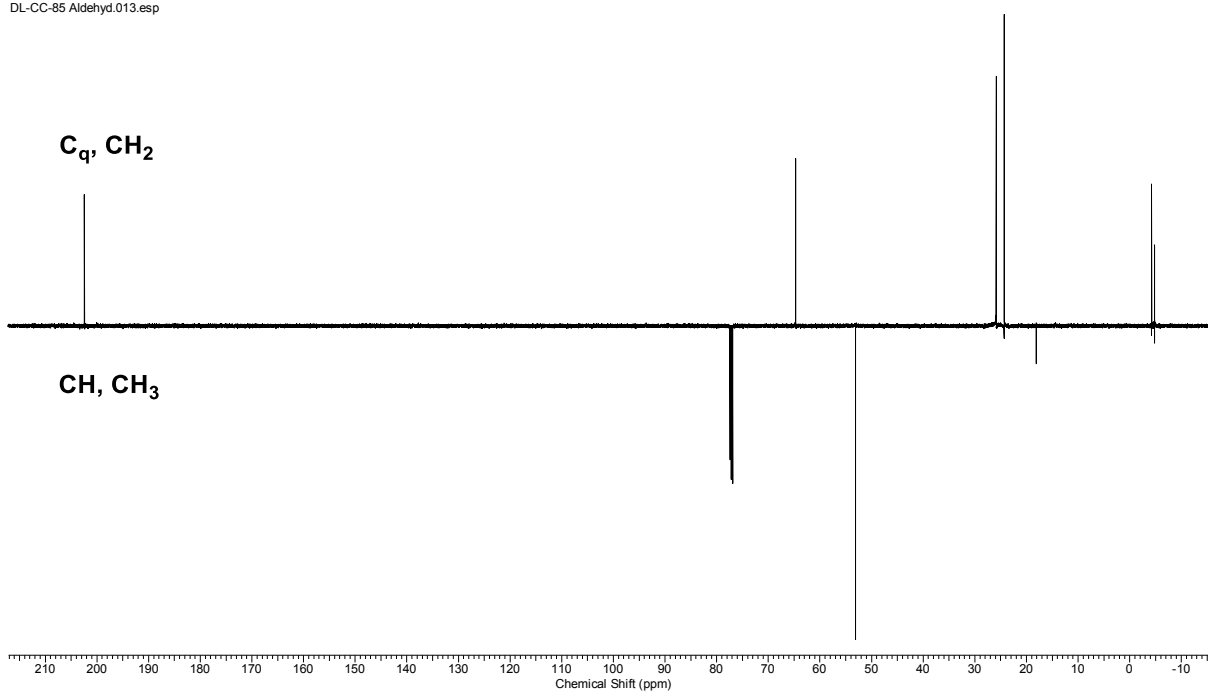


Figure S10 (S)-3-(*tert*-Butyldimethylsilyloxy)-butanale (13) ^{13}C NMR (75 MHz, CDCl_3).

DL-CC-BocMeValinEster.001.esp

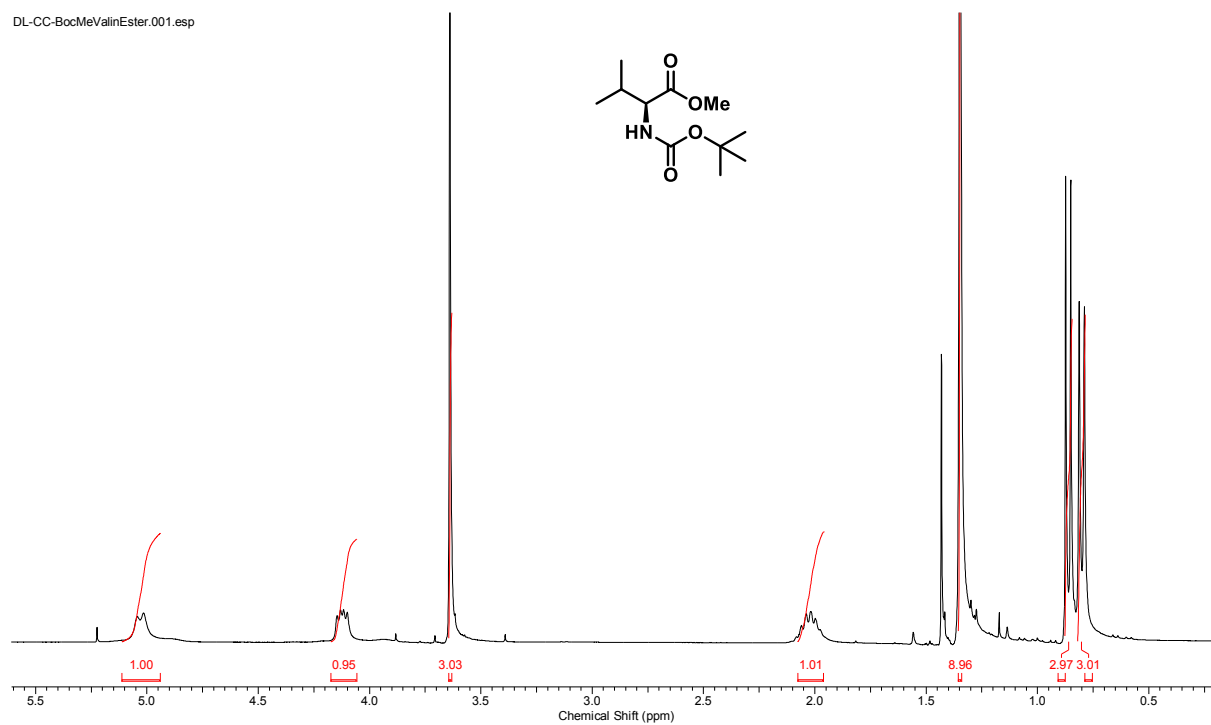


Figure S11 L-N-(*tert*-Butyloxycarbonyl)-valine methyl ester (**16**) ¹H NMR (300 MHz, CDCl₃).

DL-CC-BocMeValinEster.003.esp

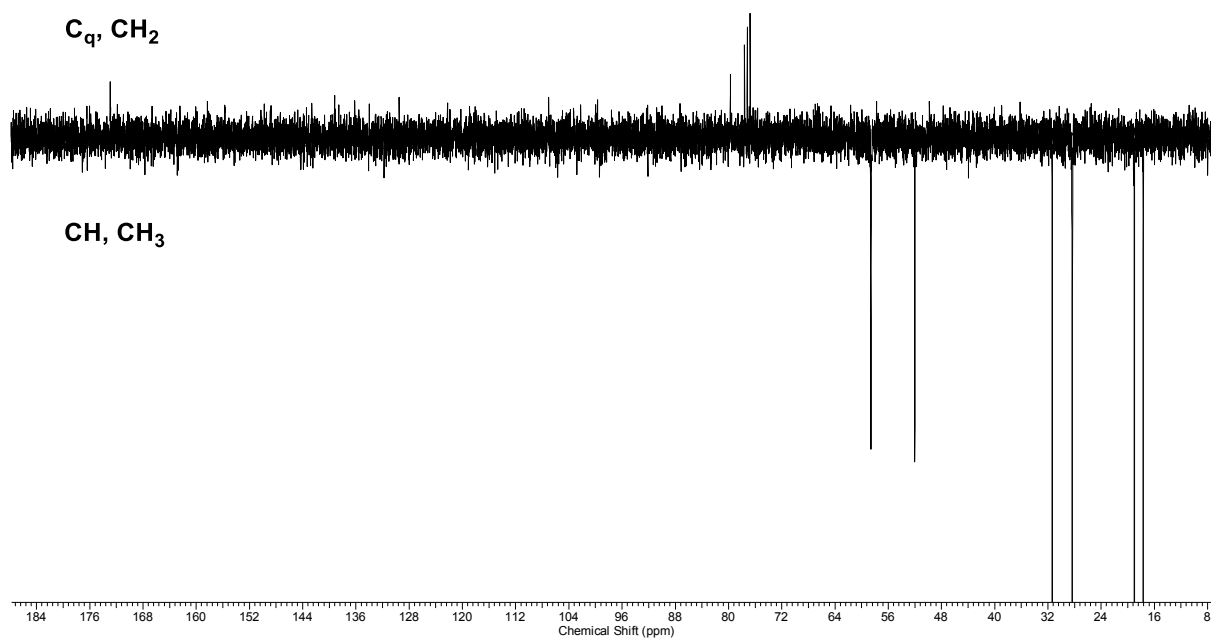


Figure S12 L-N-(*tert*-Butyloxycarbonyl)-valine methyl ester (**16**) ¹³C NMR (75 MHz, CDCl₃).

DL-CC-13 N-Chlorierung.001.esp

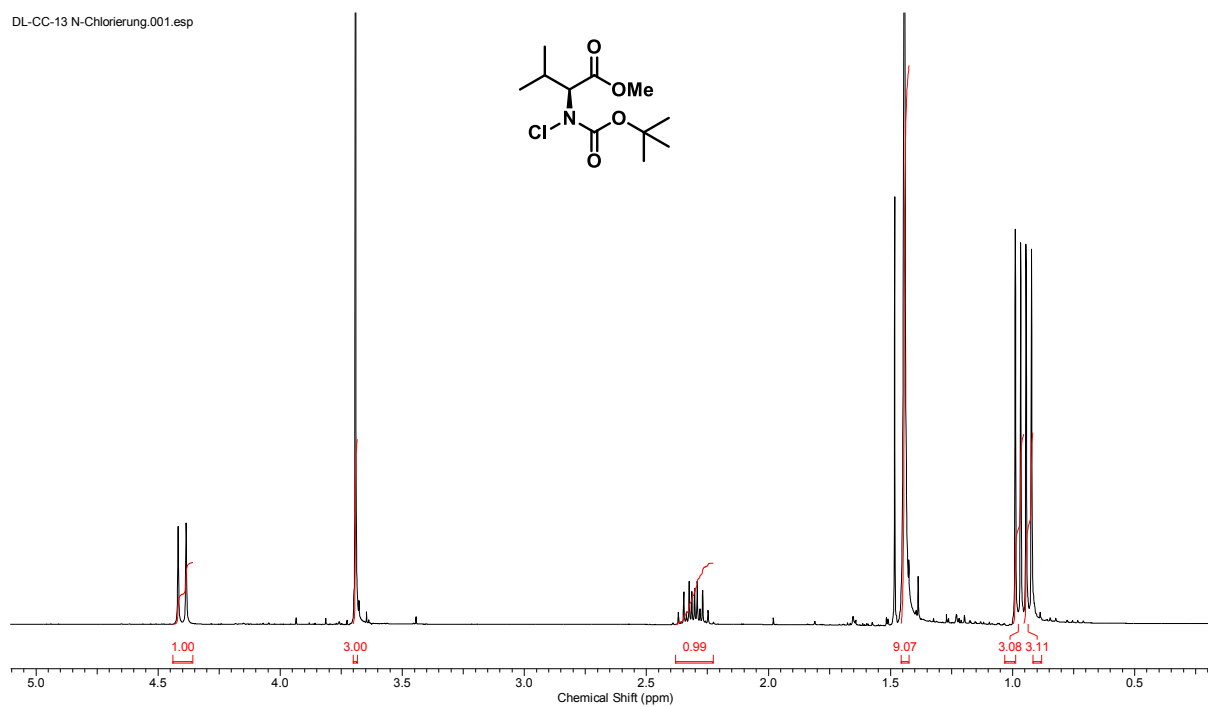


Figure S13 L-N-Chloro-N-(*tert*-butyloxycarbonyl)-valine methyl ester (**17**) ¹H NMR (300 MHz, CDCl₃).

DL-CC-13 N-Chlorierung.003.esp

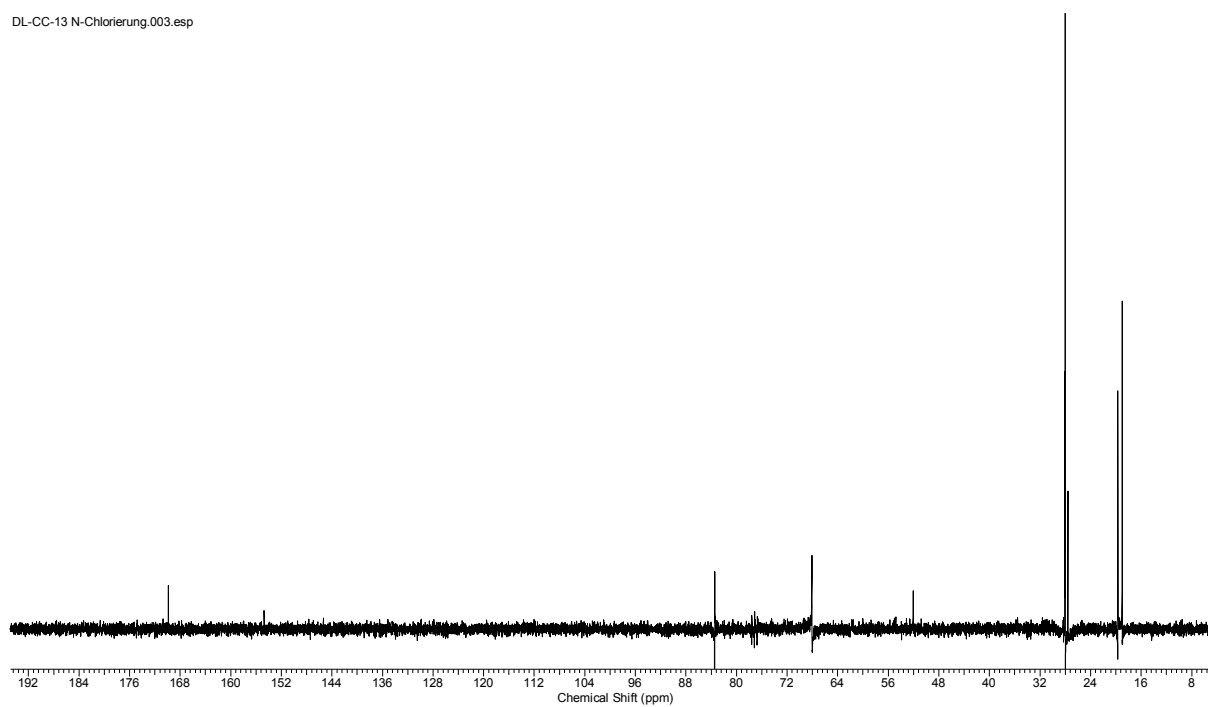


Figure S14 L-N-Chloro-N-(*tert*-butyloxycarbonyl)-valine methyl ester (**17**) ¹³C NMR (75 MHz, CDCl₃).

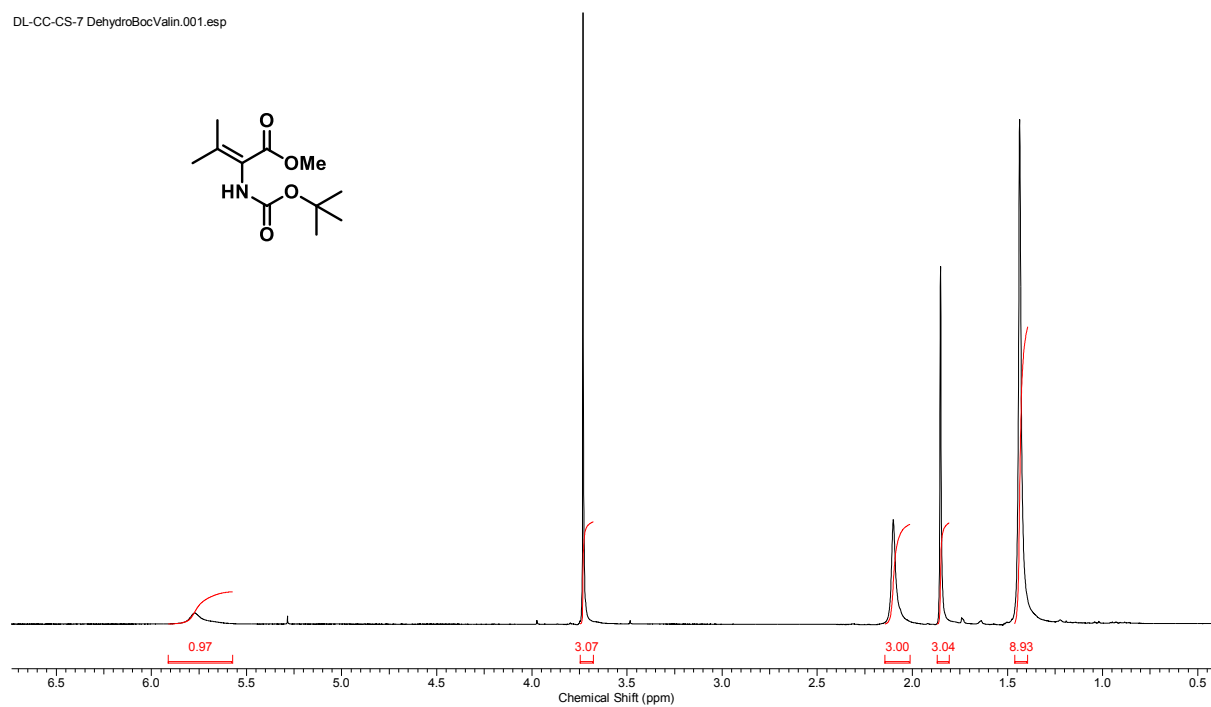


Figure S15 *N*-(*tert*-Butyloxocarbonyl)-dehydrovaline methyl ester (**18**) ¹H NMR (300 MHz, CDCl₃).

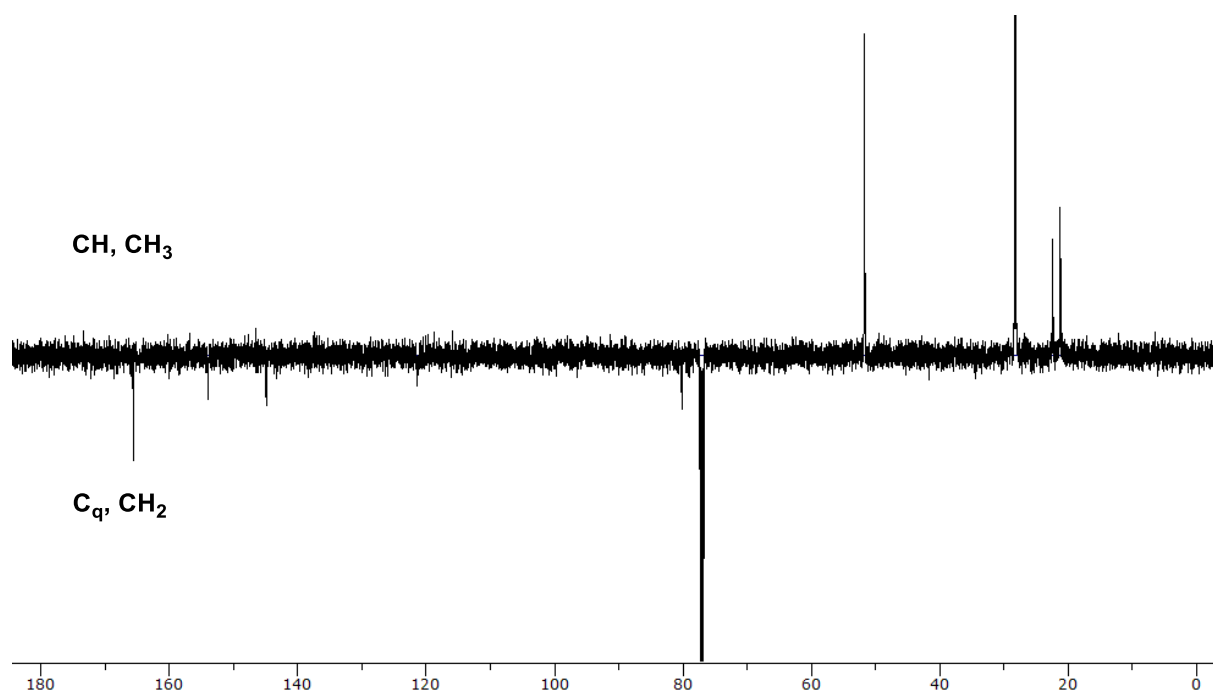


Figure S16 *N*-(*tert*-Butyloxocarbonyl)-dehydrovaline methyl ester (**18**) ¹³C NMR (75 MHz, CDCl₃).

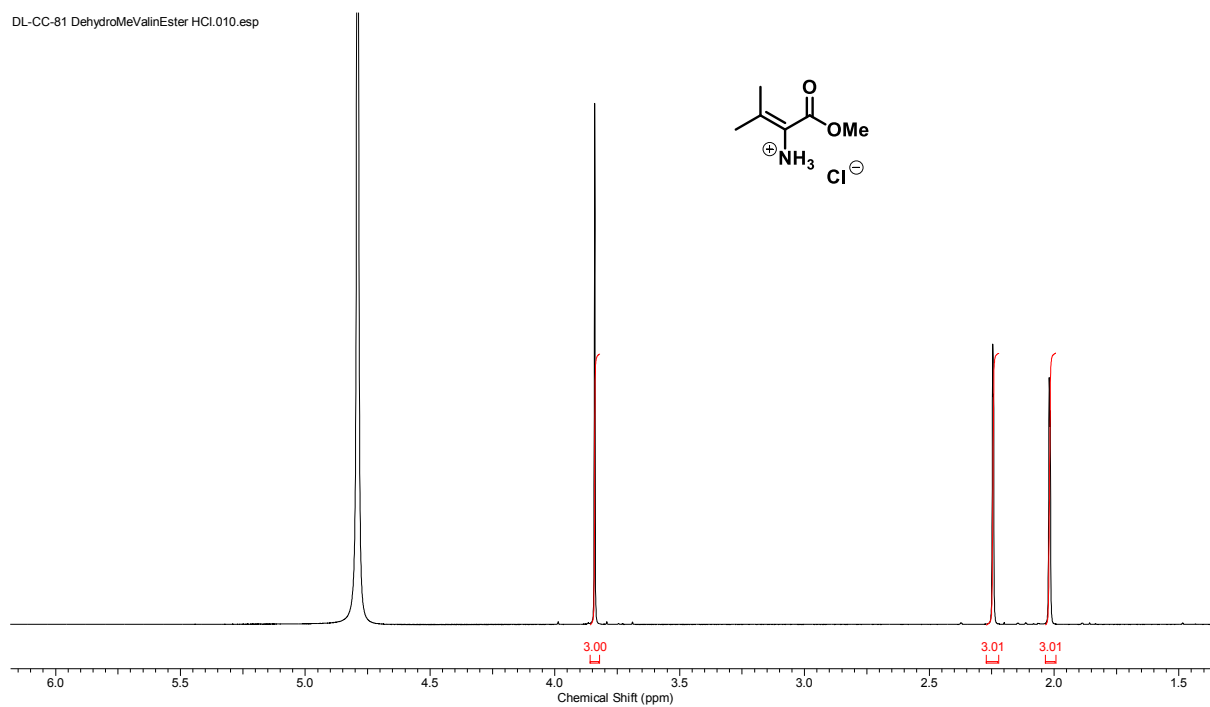


Figure S17 Dehydrovaline methyl ester hydrochloride ($8\times\text{HCl}$) ^1H NMR (300 MHz, D_2O).

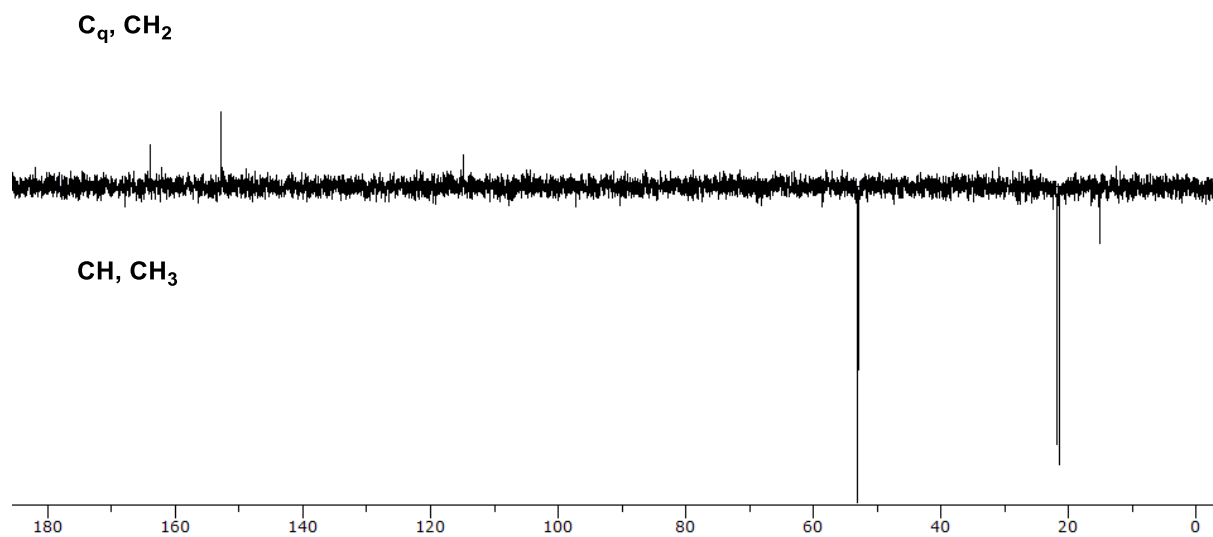


Figure S18 Dehydrovaline methyl ester hydrochloride ($8\times\text{HCl}$) ^{13}C NMR (75 MHz, D_2O).

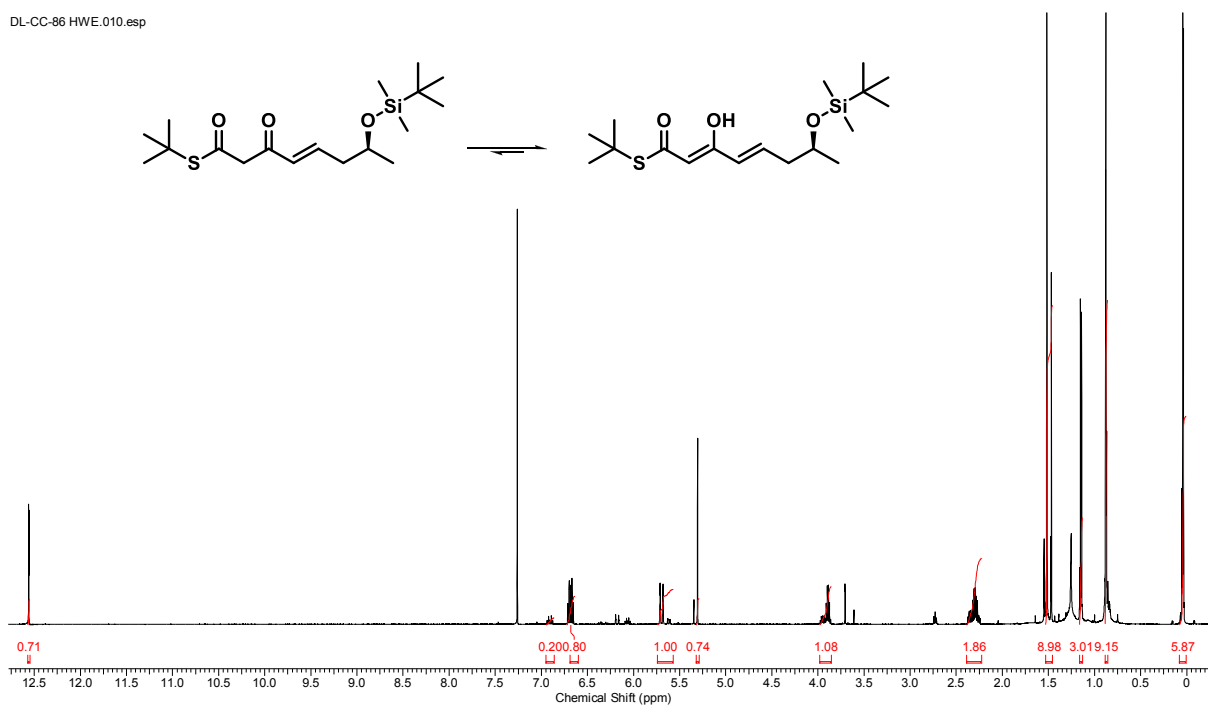


Figure S19 *(S,E)*-*S*-*tert*-Butyl-7-(*tert*-butyldimethylsilyloxy)-3-oxo-oct-4-entioate (7) ^1H NMR (300 MHz, CDCl_3).

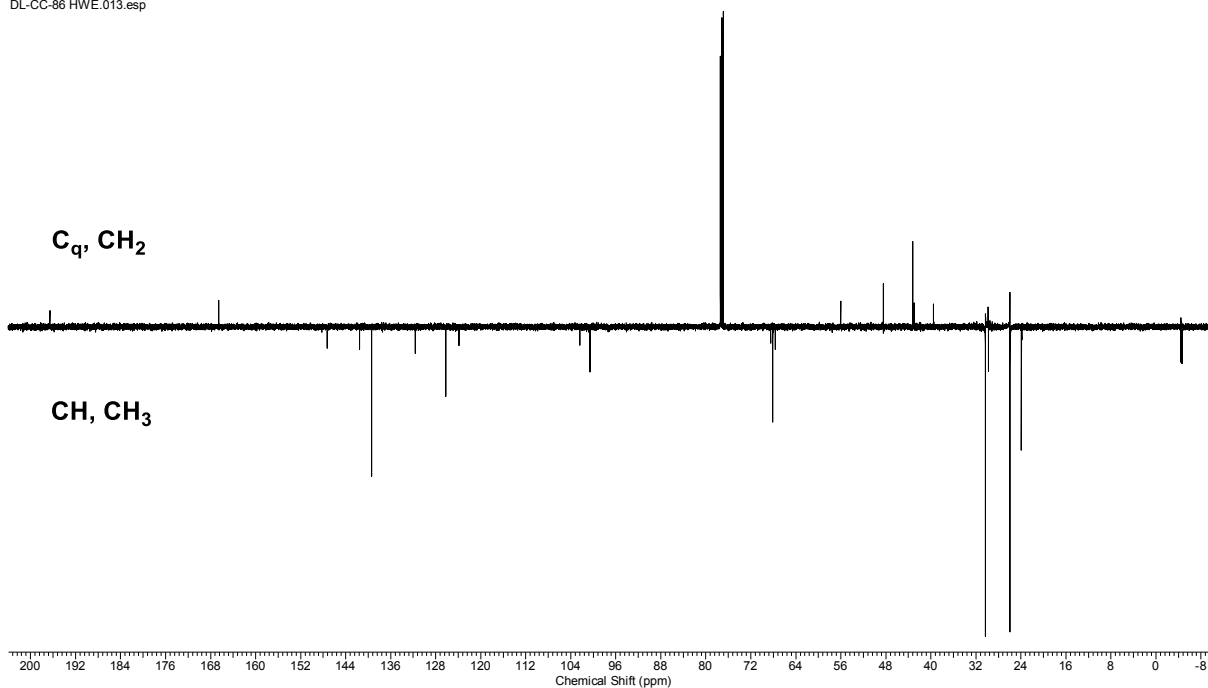


Figure S20 *(S,E)*-*S*-*tert*-Butyl-7-(*tert*-butyldimethylsilyloxy)-3-oxo-oct-4-entioate (7) ^{13}C NMR (75 MHz, CDCl_3).

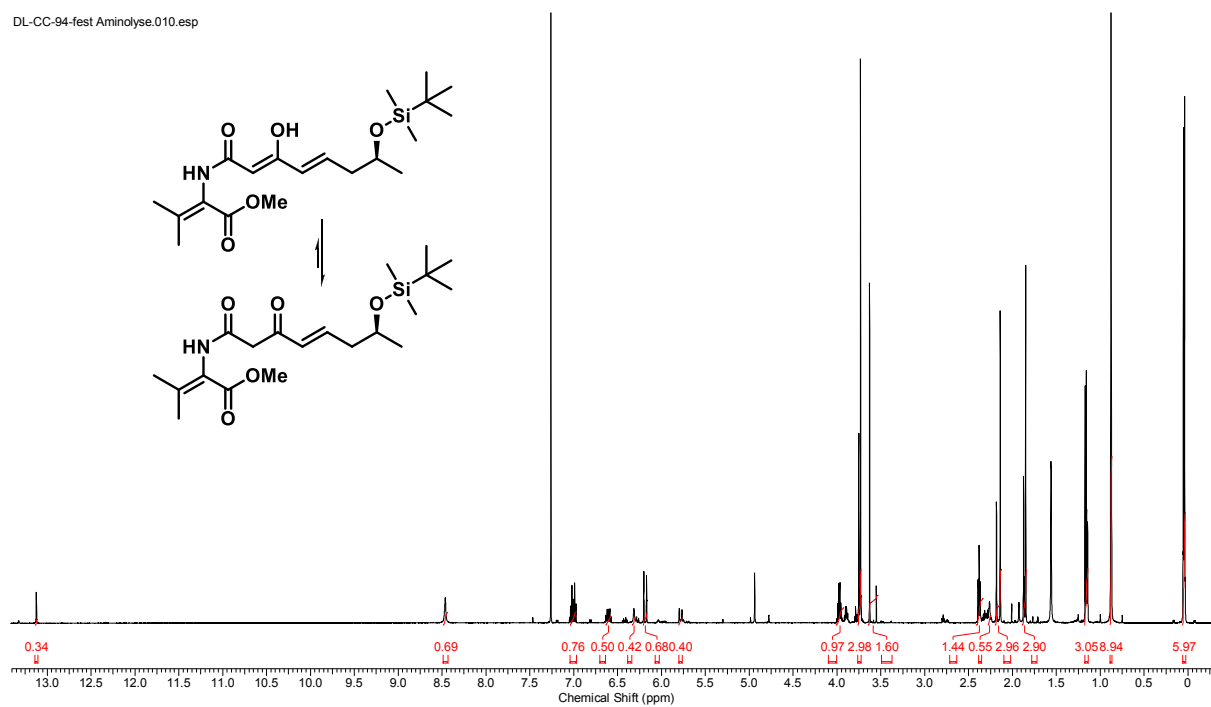


Figure S21 (*S,E*)-*N*-[7-(*tert*-Butyldimethylsilyloxy)-1,3-dioxo-oct-4-en]-dehydrovaline methyl ester (**6**)
¹H NMR (300 MHz, CDCl₃).

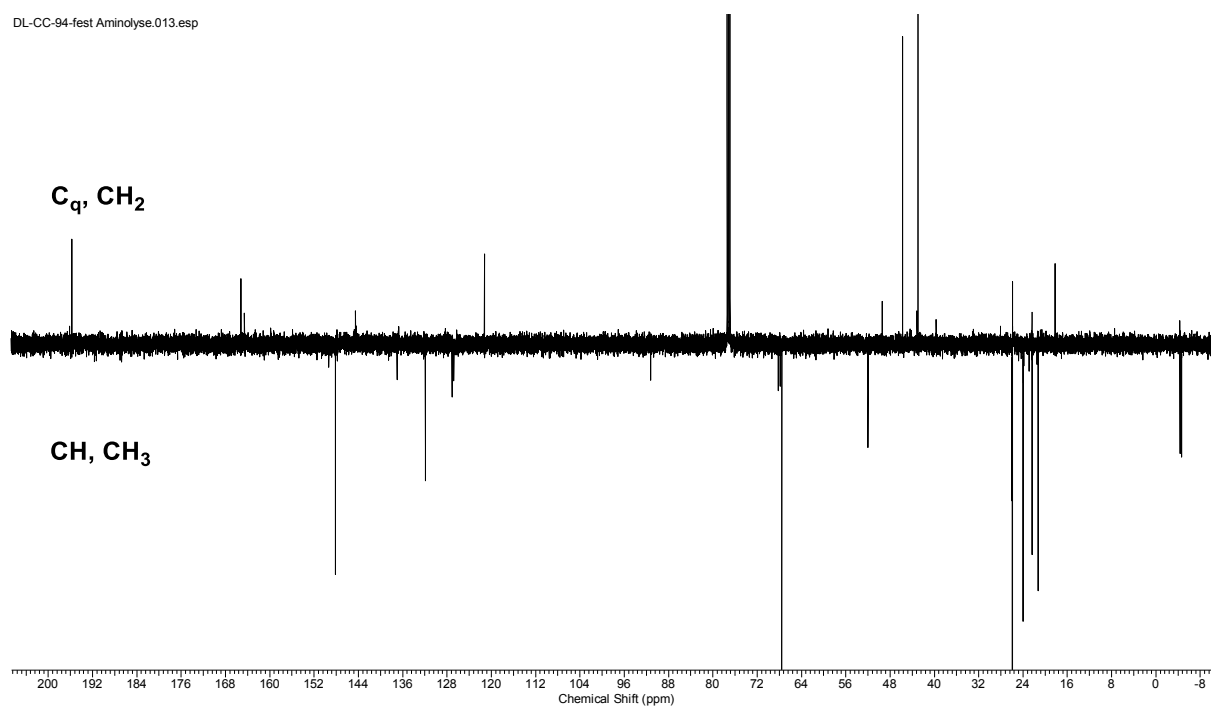


Figure S22 (*S,E*)-*N*-[7-(*tert*-Butyldimethylsilyloxy)-1,3-dioxo-oct-4-en]-dehydrovaline methyl ester (**6**)
¹³C NMR (75 MHz, CDCl₃).

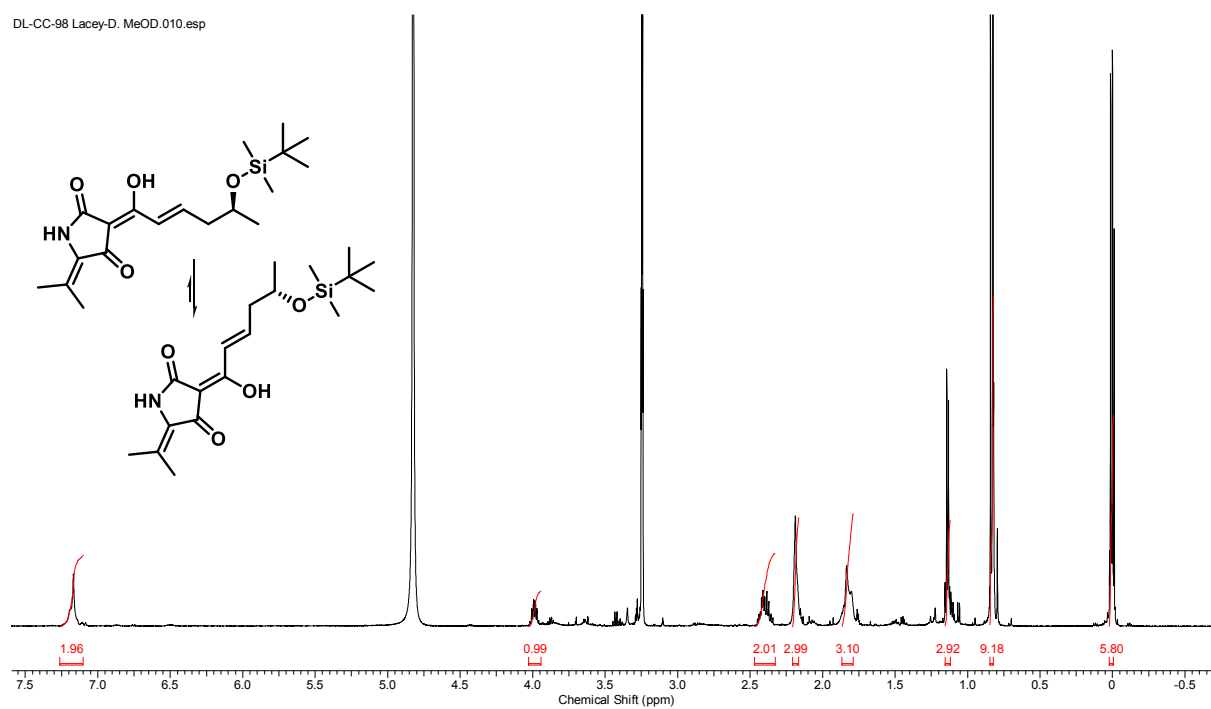


Figure S23 3-[(*S,E*)-5-(*tert*-Butyldimethylsilyloxy)-1-hydroxyhex-2-enoyl]-5-(propan-2-ylidene)-pyrrolidin-2,4-dione (**5**) ^1H NMR (500 MHz, MeOD).

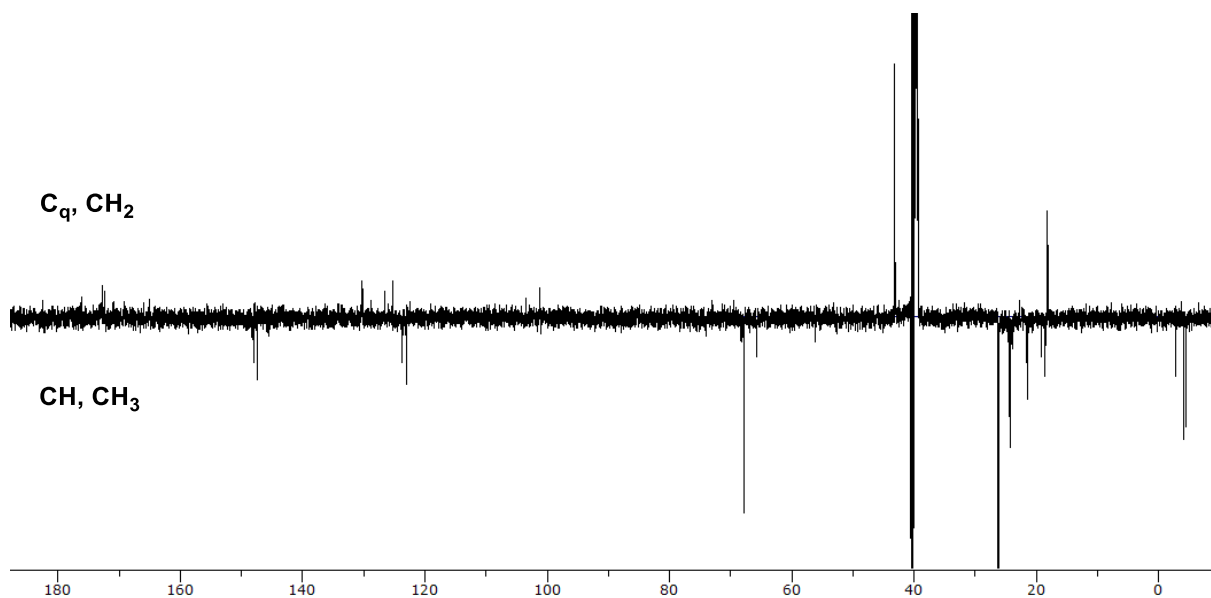


Figure S24 3-[(*S,E*)-5-(*tert*-Butyldimethylsilyloxy)-1-hydroxyhex-2-enoyl]-5-(propan-2-ylidene)-pyrrolidin-2,4-dione (**5**) ^{13}C NMR (75 MHz, DMSO- d_6).

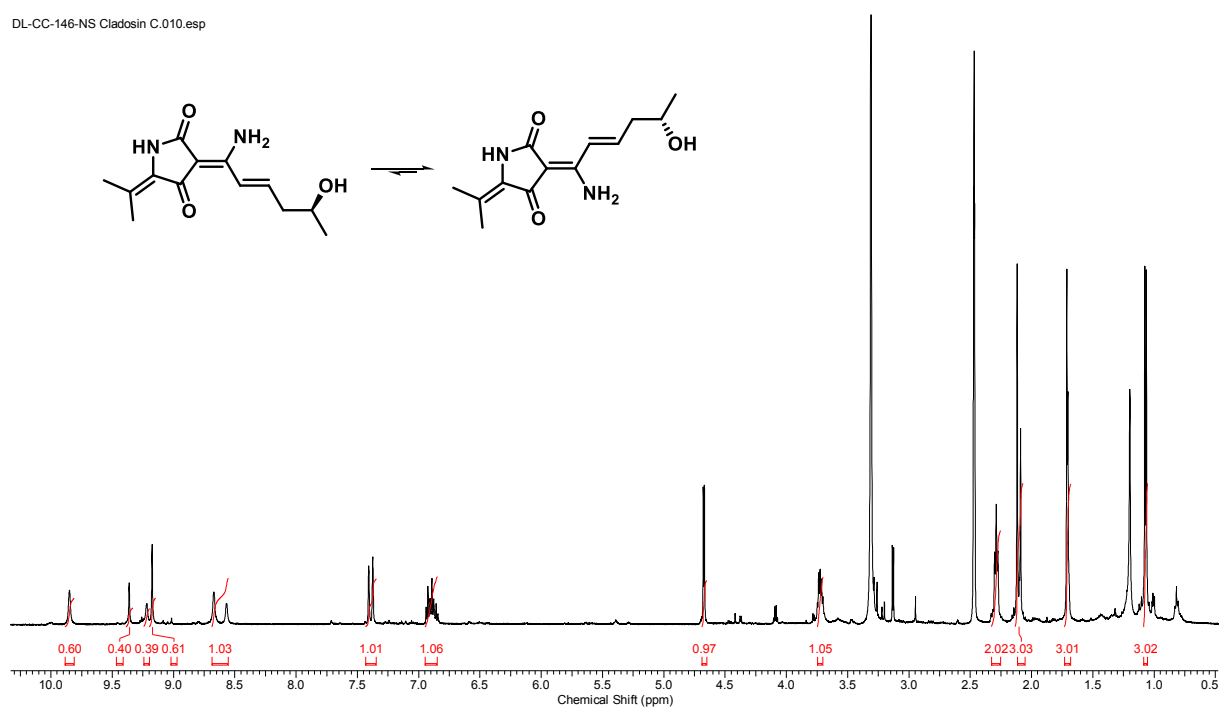


Figure S25 Cladosin C (3) ^1H NMR (500 MHz, DMSO-d_6).

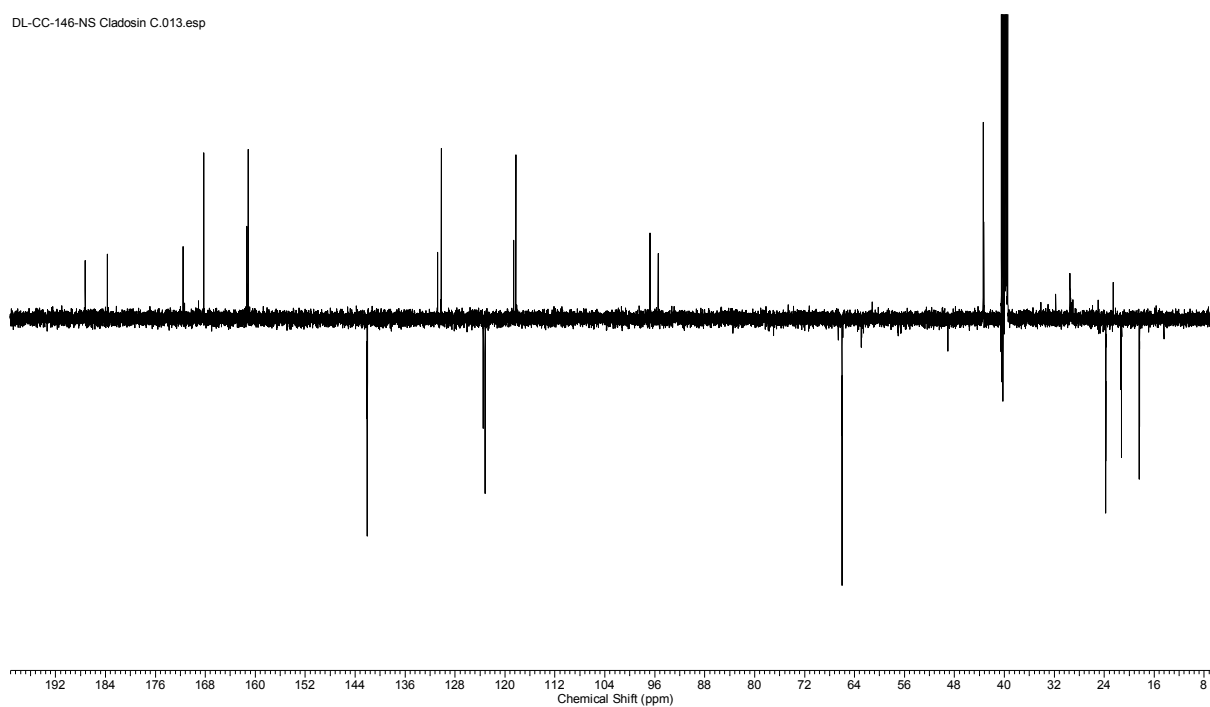


Figure S26 Cladosin C (3) ^{13}C NMR (75 MHz, DMSO-d_6).

Gas chromatography of *R*-Mosher esters of alcohols **10**:

Shimadzu GC 2010 with autosampler AOC 20i and FID,
column: Macherey-Nagel Lipodex A 25 m × 0.25 mm, df = 0.25 μm
T injector: 250 °C, split 1:100, carrier gas H₂, constant flow, velocity = 40 cm/s
T-gradient: begin 60 °C, hold time 0.5 min, rate 10 °C / min to 200 °C, hold time 10 min

Results: Fig S27: Mosher ester of *R*-**10**: $t_{(Ret)}$ = 14.423 min
Fig S28: Mosher ester of *S*-**10**: $t_{(Ret)}$ = 14.473 min
with area *R,R*-diastereomer = 532 (1.6 %), area *R,S*-diastereomer = 32876 (98.4 %)

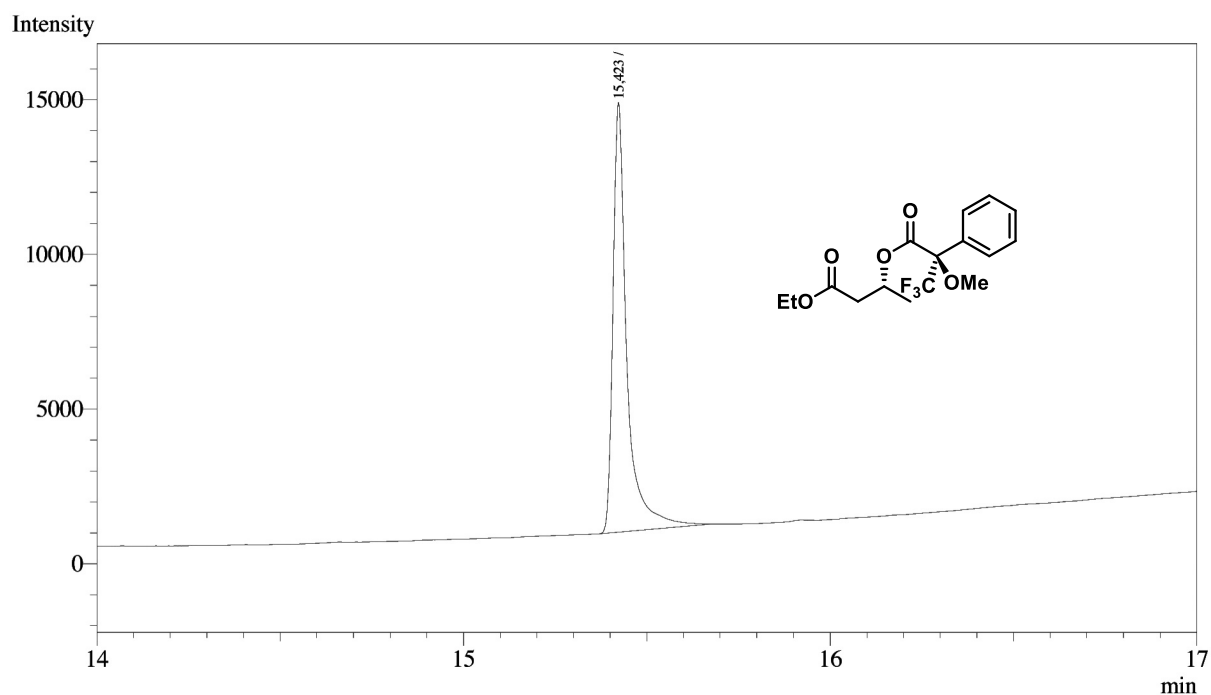


Figure S27 GC of the *R*-MTPA ester of *R*-**10**

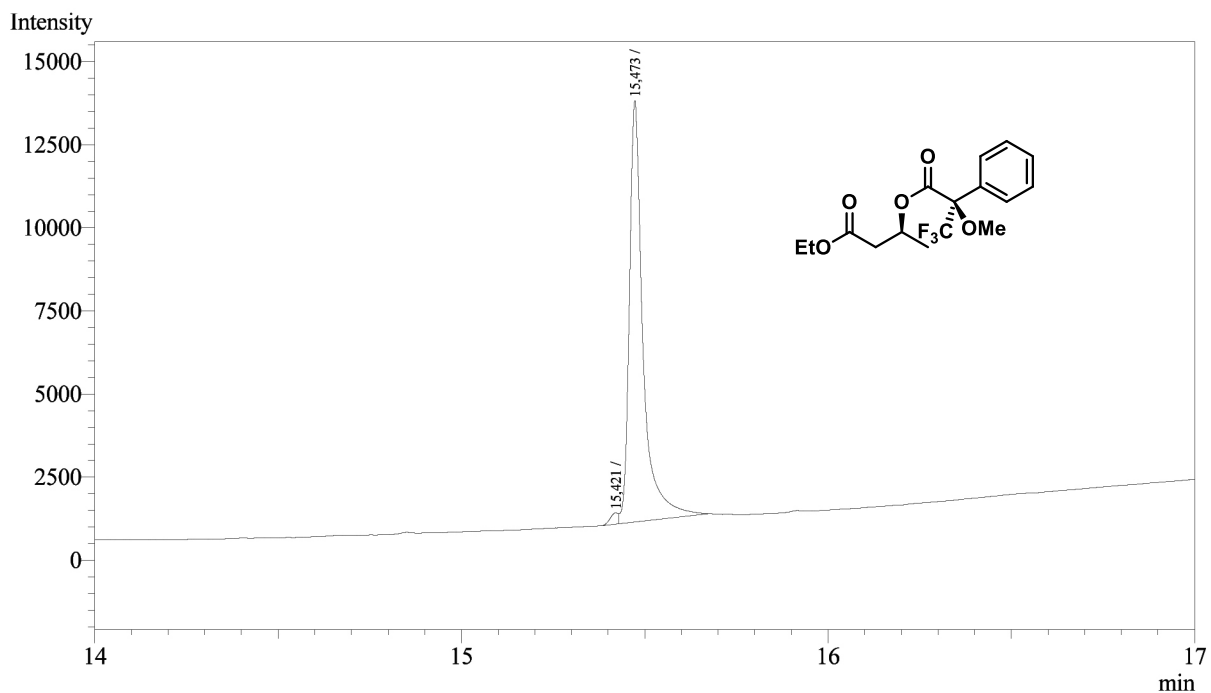


Figure S28 Gas chromatogram of the *R*-MTPA ester of *S*-**10**.

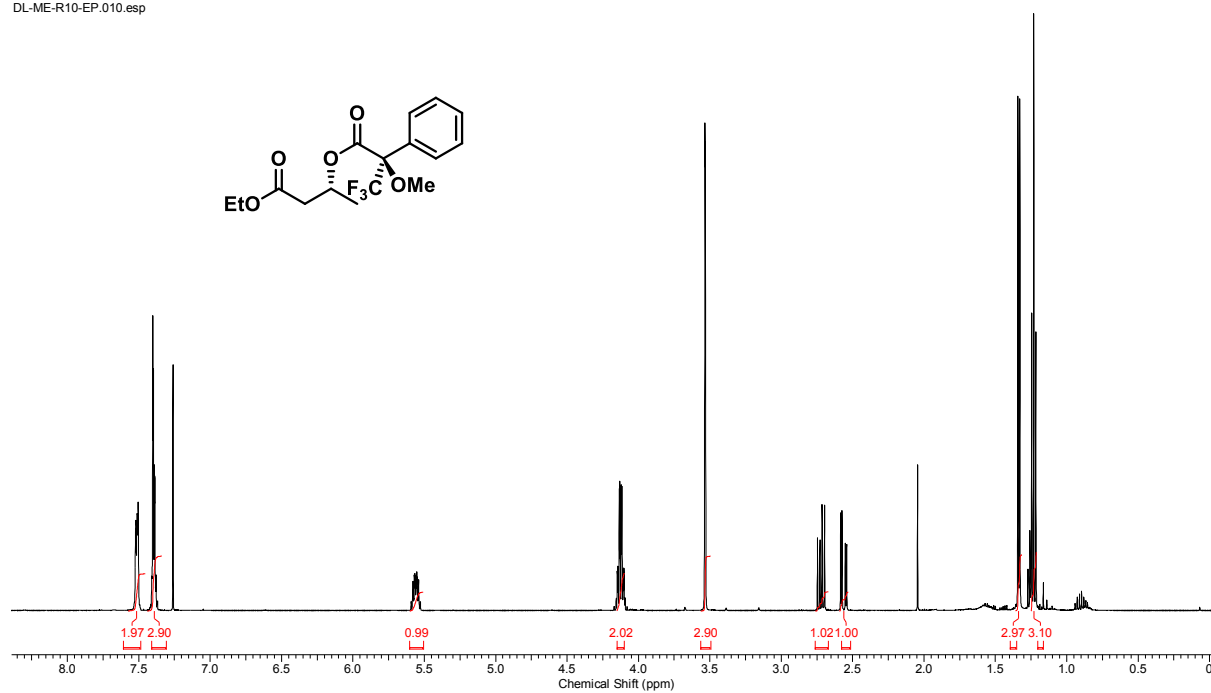


Figure S29 *R*-MTPA ester of *R*-10 ((*R*)-Ethyl 3-((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyloxy)butanoate) ¹H NMR (500 MHz, CDCl₃).

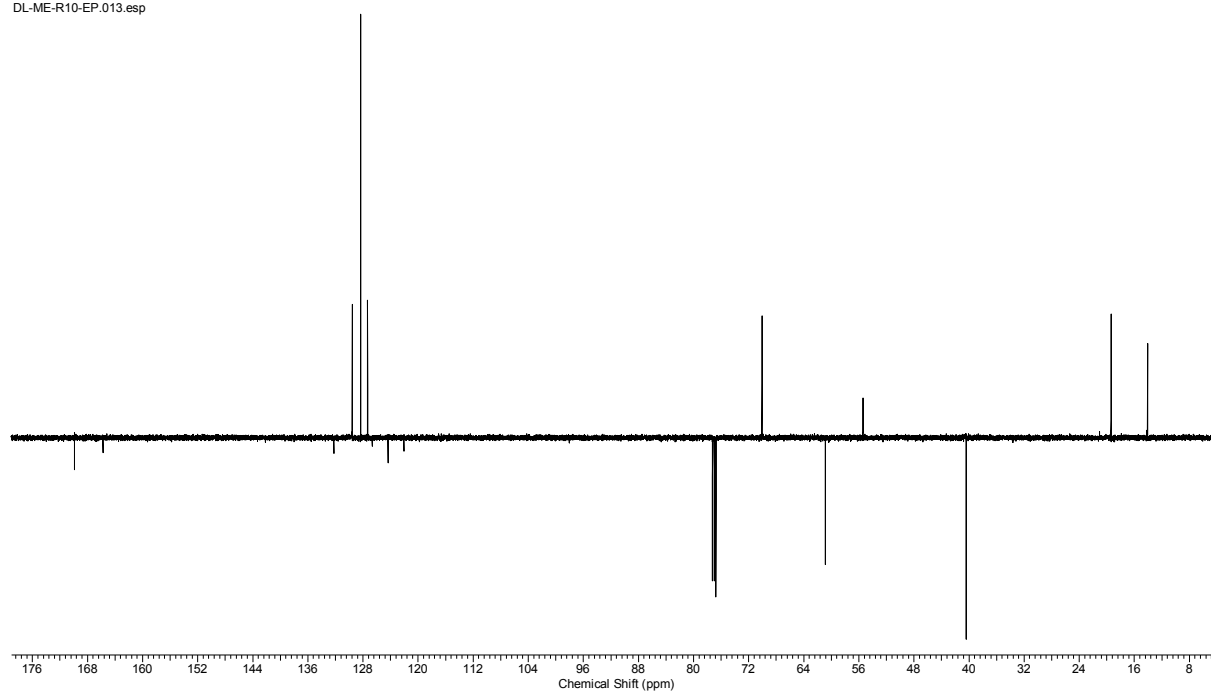


Figure S30 *R*-MTPA ester of *R*-10 ((*R*)-Ethyl 3-((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyloxy)butanoate) ¹³C NMR (75 MHz, CDCl₃).

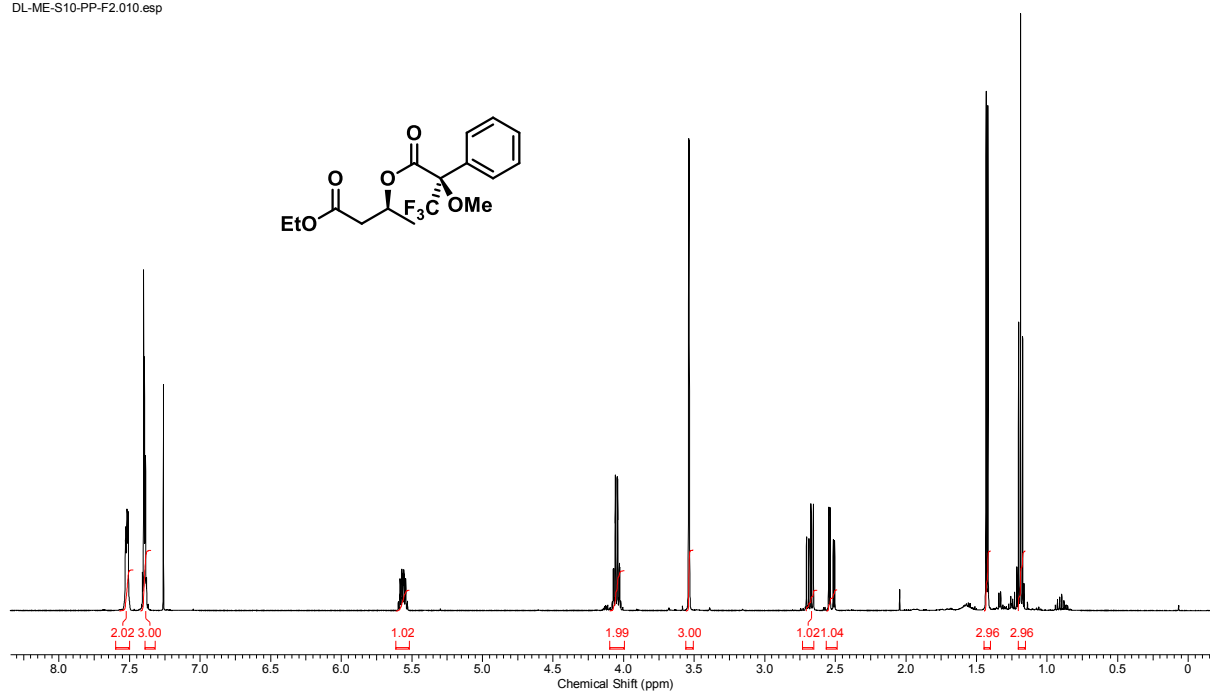


Figure S31 *R*-MTPA ester of *S*-10 ((*S*)-Ethyl 3-((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyloxy)butanoate) ¹H NMR (500 MHz, CDCl₃).

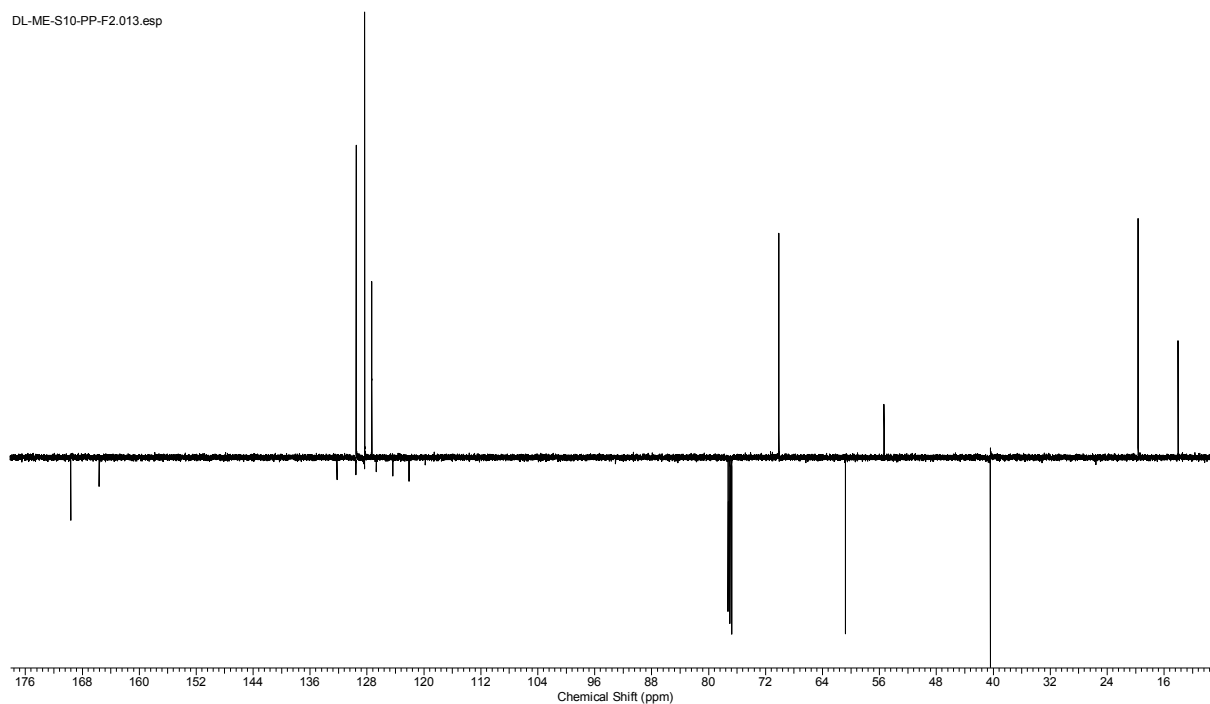


Figure S32 *R*-MTPA ester of *S*-10 ((*S*)-Ethyl 3-((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyloxy)butanoate) ¹³C NMR (75 MHz, CDCl₃).