ChemBioChem

Supporting Information

Identification and Composition of Clasper Scent Gland Components of the Butterfly *Heliconius erato* and Its Relation to Mimicry

Stephanie Ehlers, Daiane Szczerbowski, Tim Harig, Matthew Stell, Susan Hötling, Kathy Darragh, Chris D. Jiggins, and Stefan Schulz*

Content

Figures

1. Total ion chromatograms

Some TICs of representative individuals are shown in the next Figures to illustrate variation within individual CSG gland composition of *H. erato*.

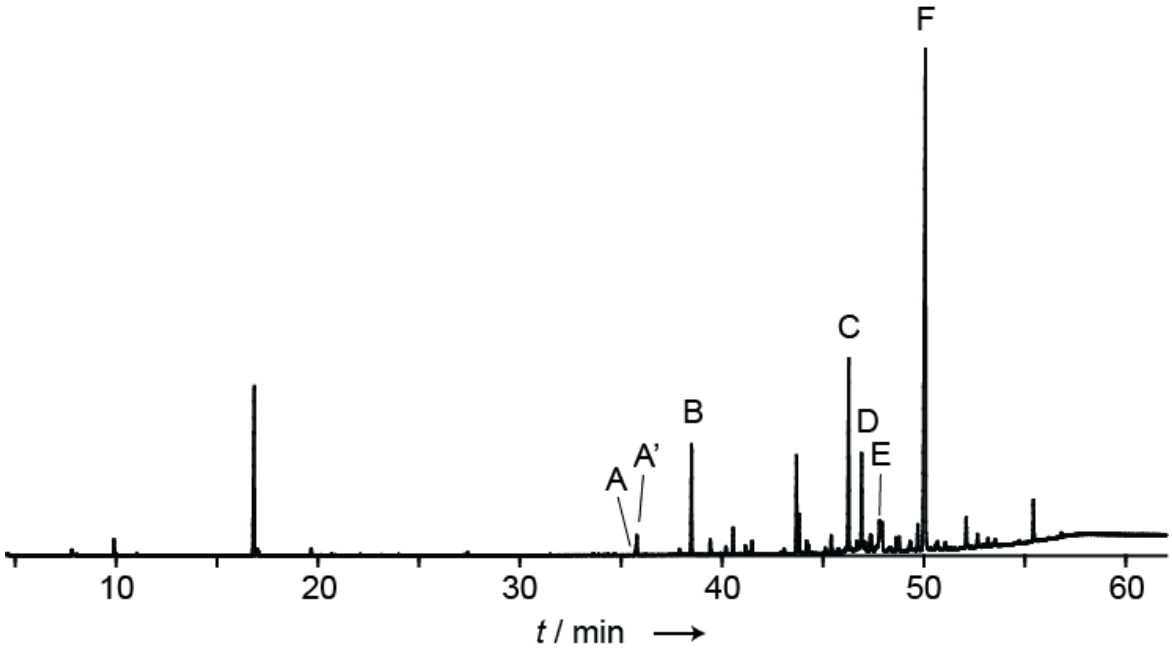


Figure S1. Total ion chromatogram (TIC) of H. erato lativitta *from Colombia, dennis-ray mimicry pattern.*

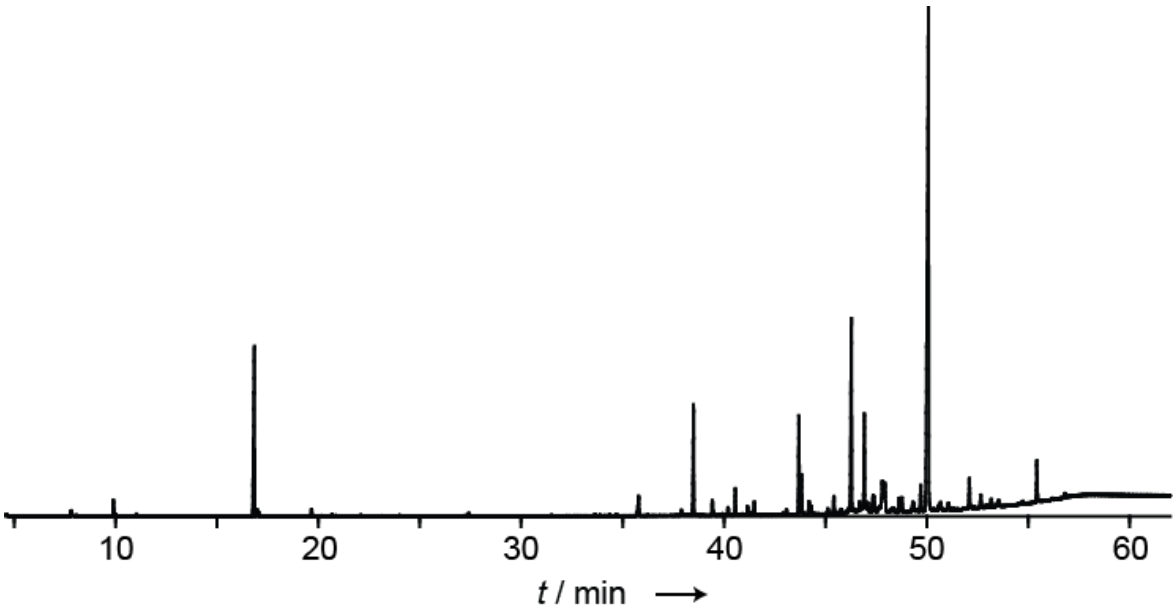


Figure S2. TIC of H. erato lativitta *from East Ecuador, dennis-ray mimicry pattern.*

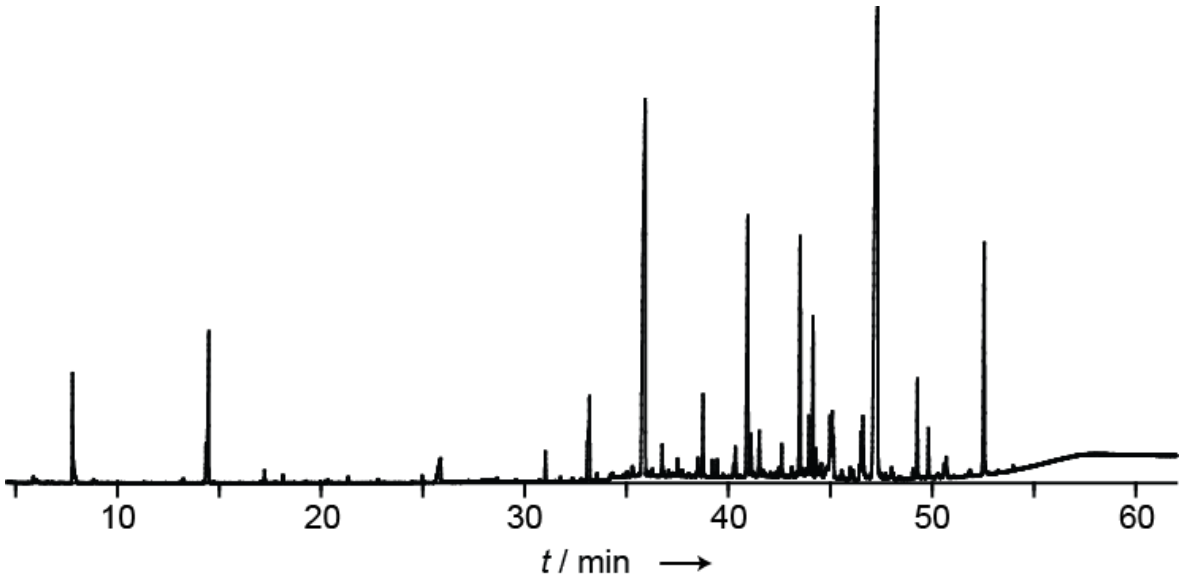


Figure S3. TIC of H. erato cyrbia *from West Ecuador, iridescent mimicry pattern.*

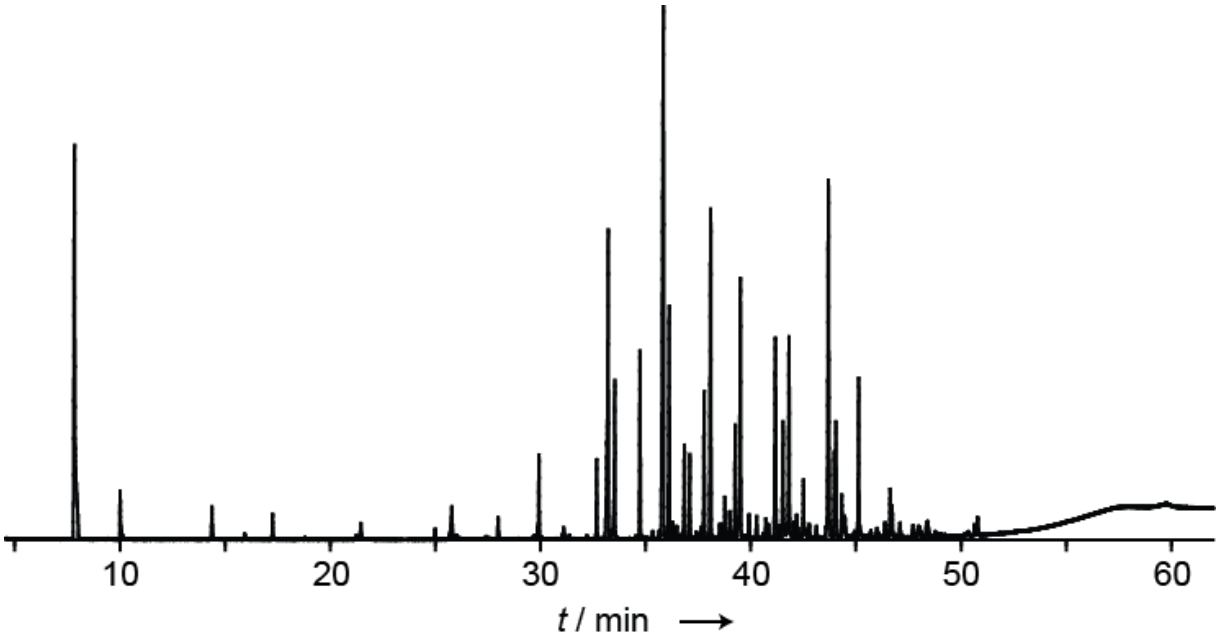


Figure S4. TIC of H. erato amphitrite *from Peru, red band mimicry pattern.*

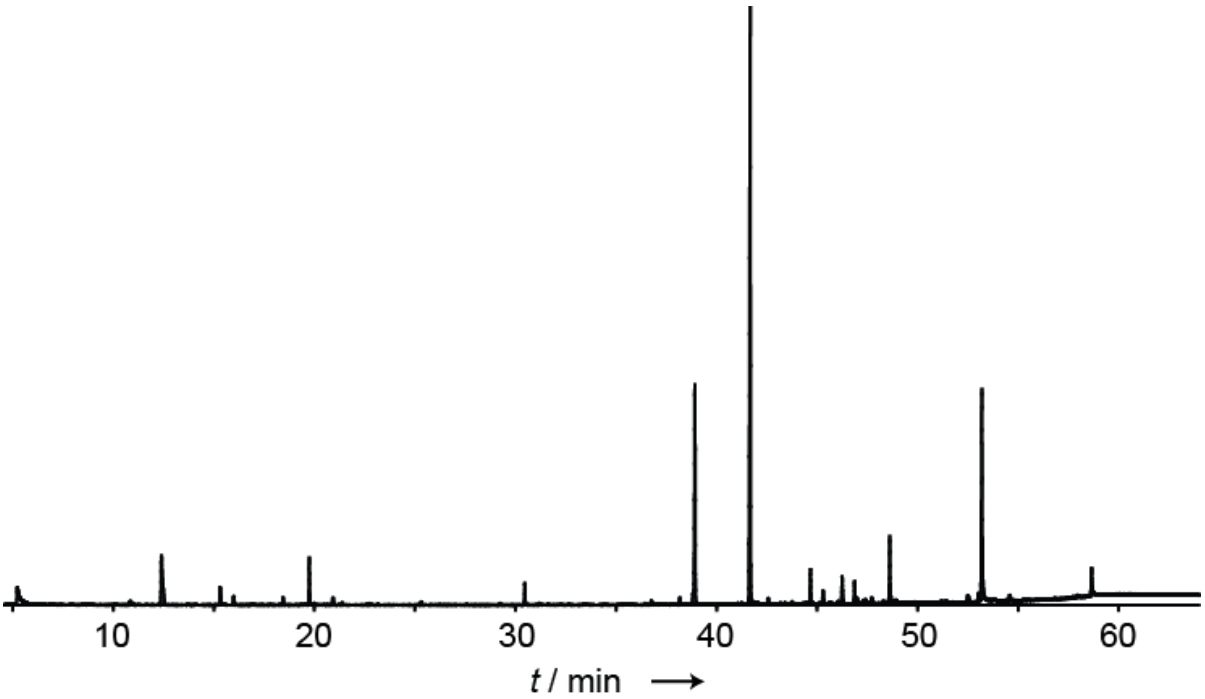


Figure S5. TIC of H. erato demophoon *from Peru, red band mimicry pattern.*

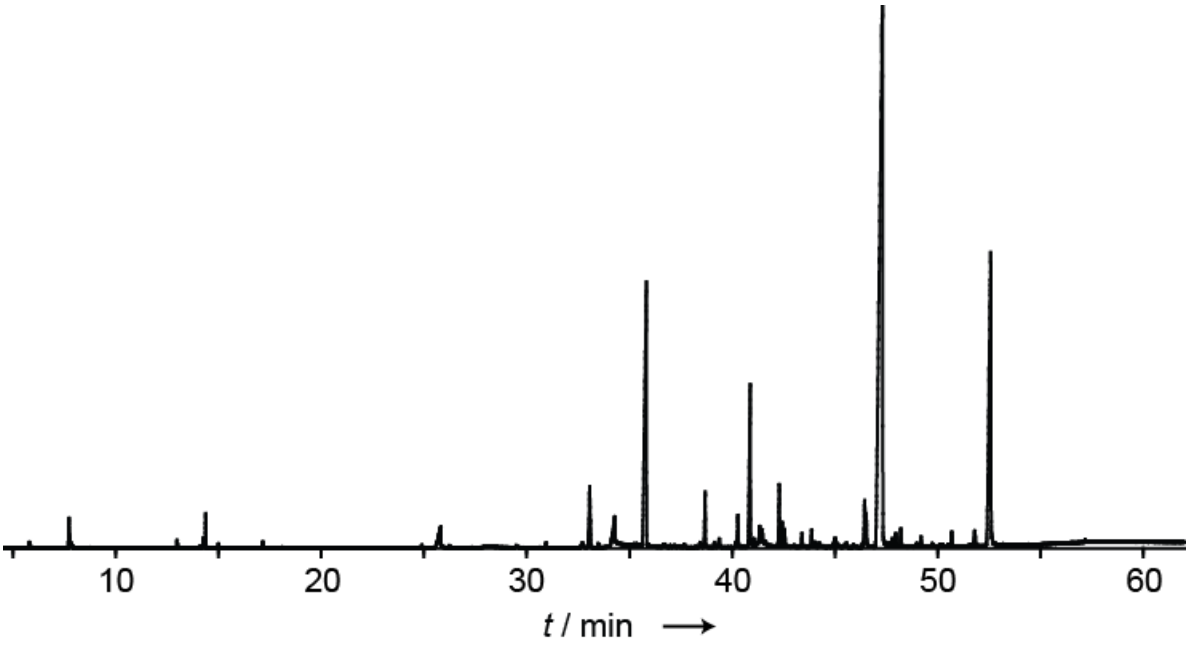


Figure S6. TIC of H. erato amazona *from Brazil, dennis-ray mimicry pattern.*

2. Mass Spectrometry

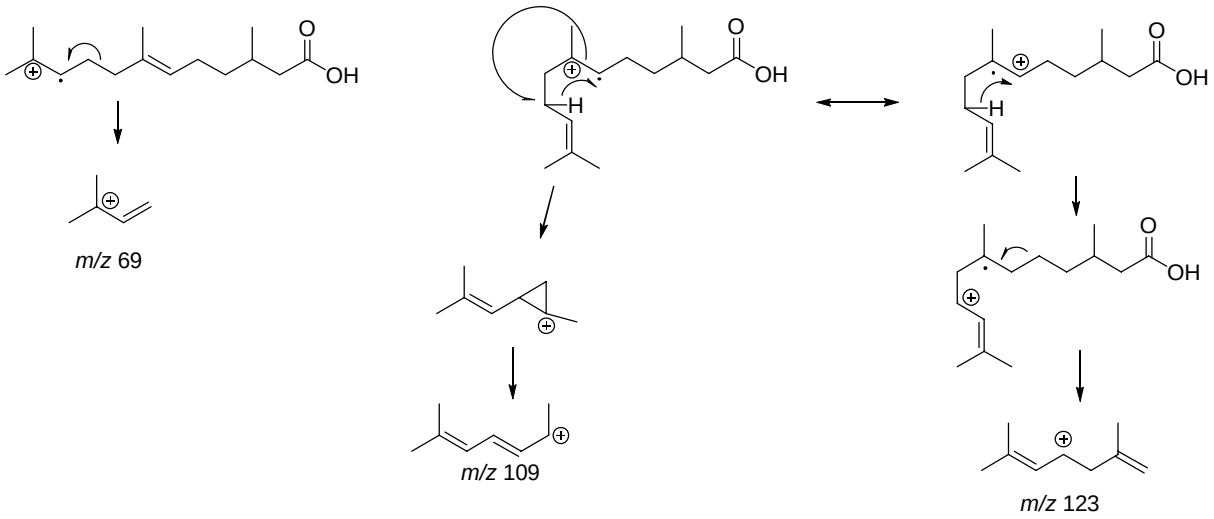


Figure S7. Proposed mass spectrometric fragmentation of 2,3-dihydrofarnesoic acid (8a) leading to various characteristic ions.

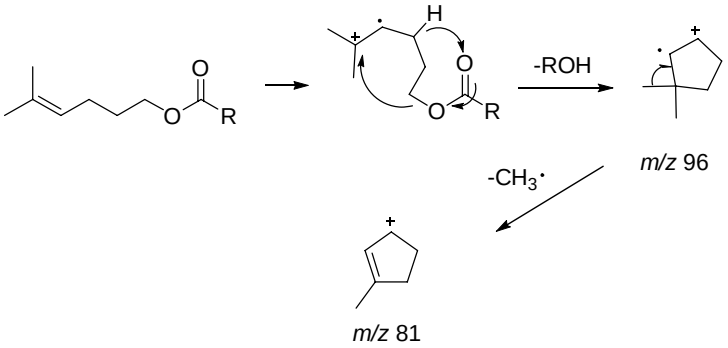


Figure S8. Proposed mass spectrometric fragmentation of 5-methyl-4-hexenyl esters leading to the two dominating ions.

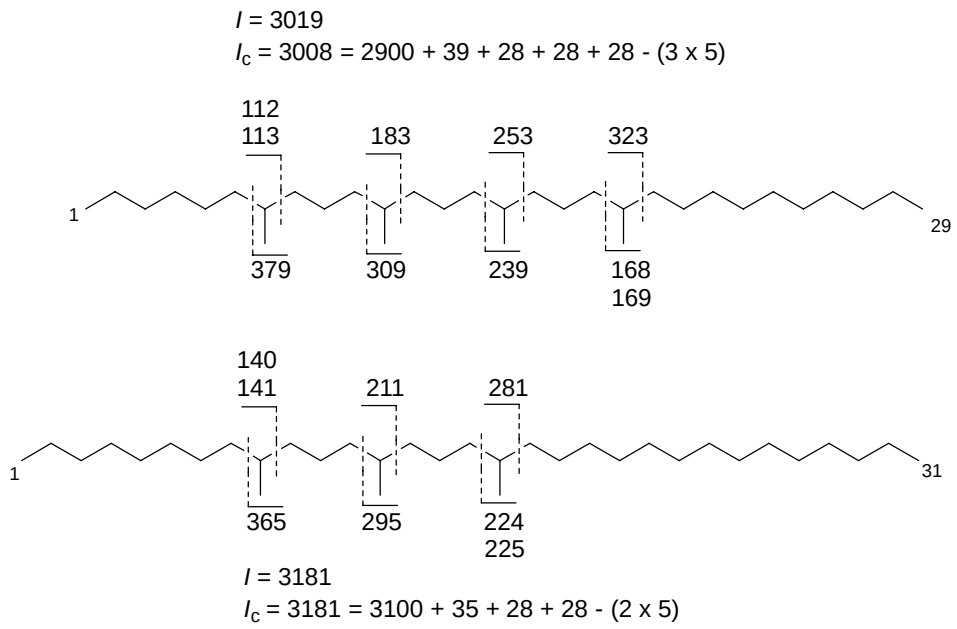


Figure S9. Mass spectrometric fragmentation of long chain branched methylalkanes.

Terminal branches are detectable by characteristic double peaks, while internal methyl group positions are indicated by enhanced single ions. The gas chromatographic retention index can be calculated.[1] The chain length gives the basis, for each methyl group an increment is added, with varying values near to the ends of the compounds. For each 1,5-arrangmement a small steric component has to be deduced.

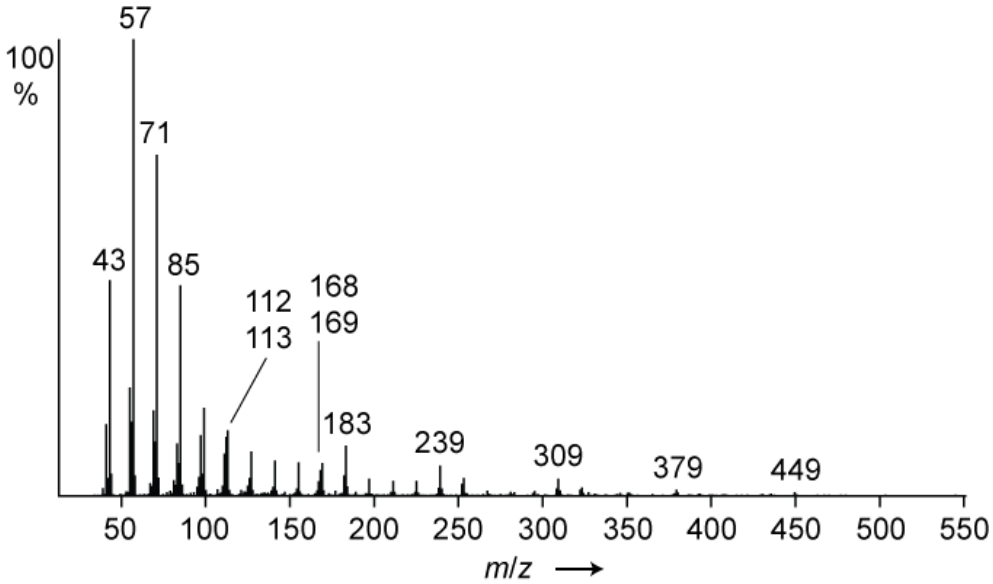


Figure S10. Mass spectrum of 7,11,15,19-tetramethylnonacosane.

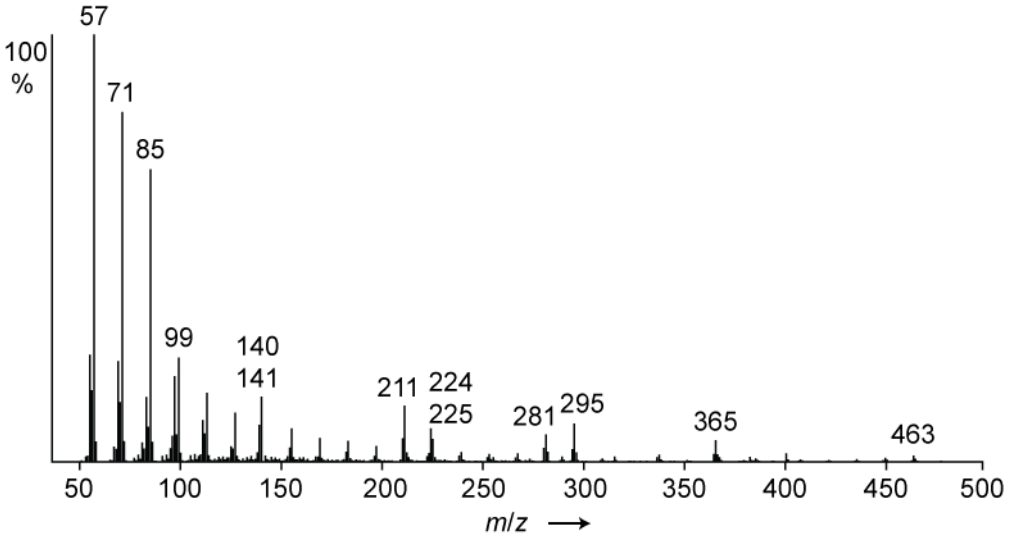


Figure S11. Mass spectrum of 9,13,17-trimethylhentriacontane.

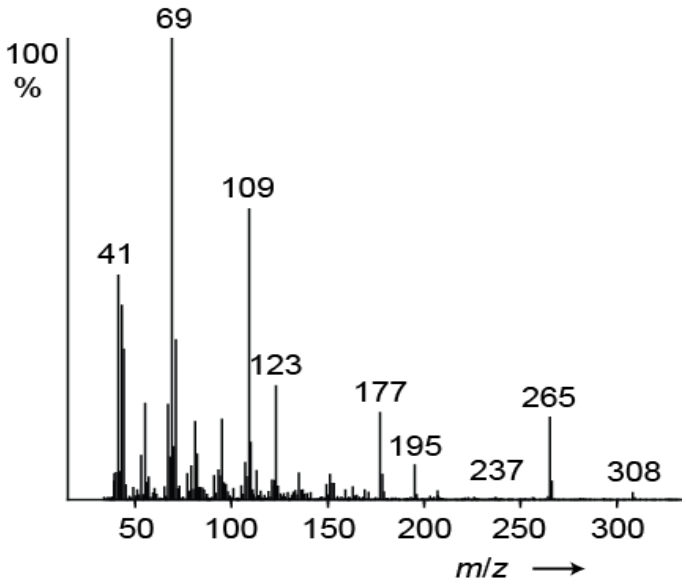


Figure S12. Mass spectrum of 3-methylbutyl (E)-2,3-dihydrofarnesoate (8h).

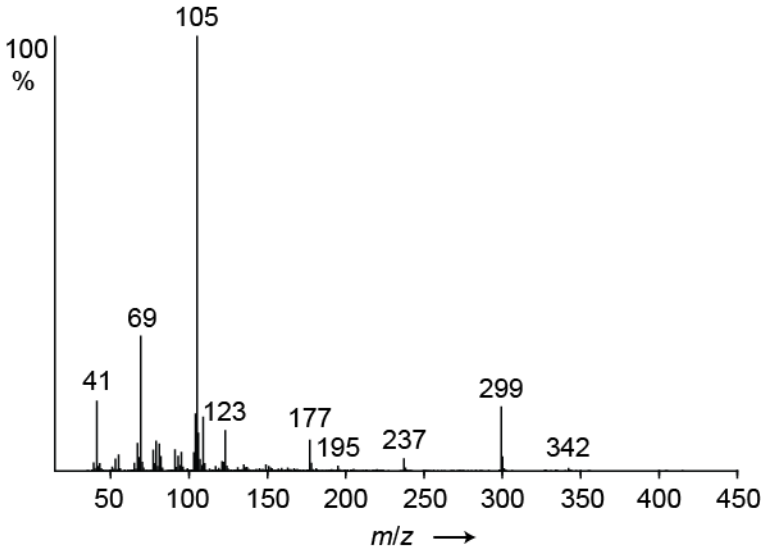


Figure S13. Mass spectrum of 2-phenylethyl (E)-2,3-dihydrofarnesoate (8p).

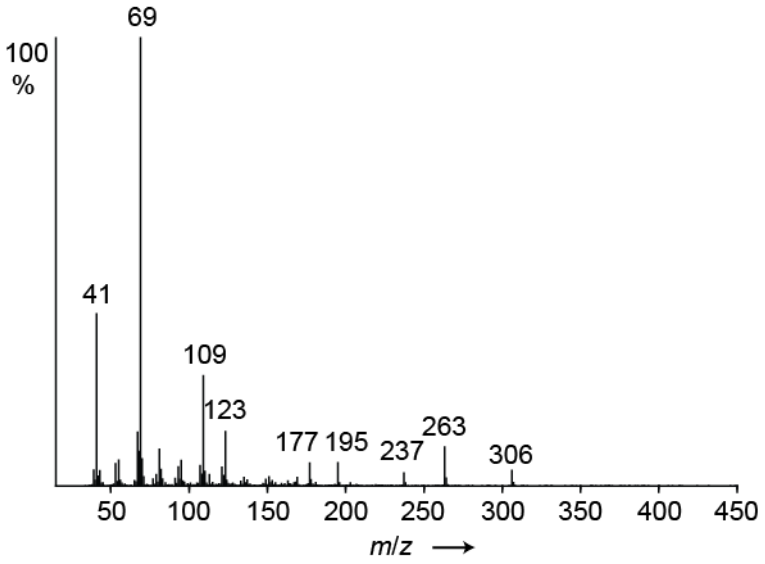


Figure S14. Mass spectrum of isoprenyl (E)-2,3-dihydrofarnesoate (8f).

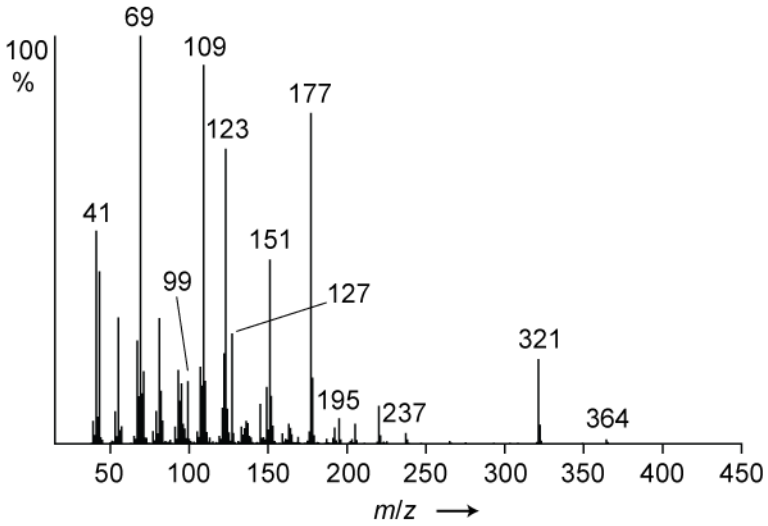


Figure S15. Mass spectrum of 3-oxooctyl (E)-2,3-dihydrofarnesoate (8n).

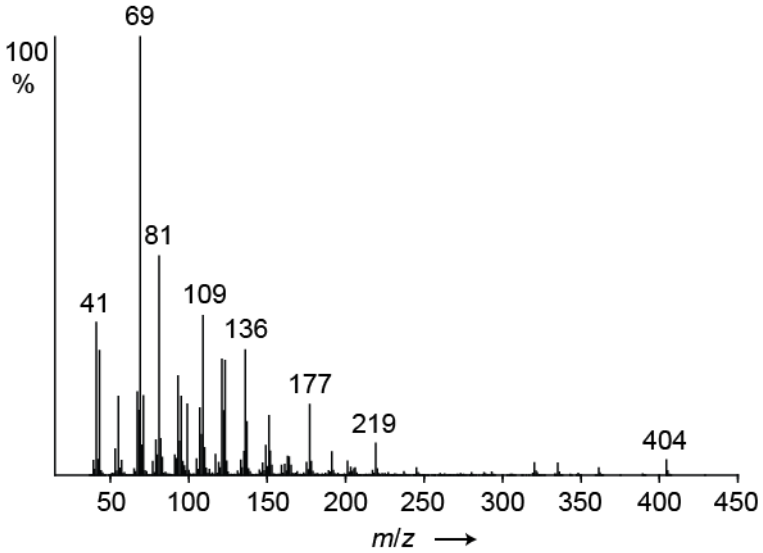


Figure S16. Mass spectrum of 3-oxohexyl geranlycitronellate (9l).

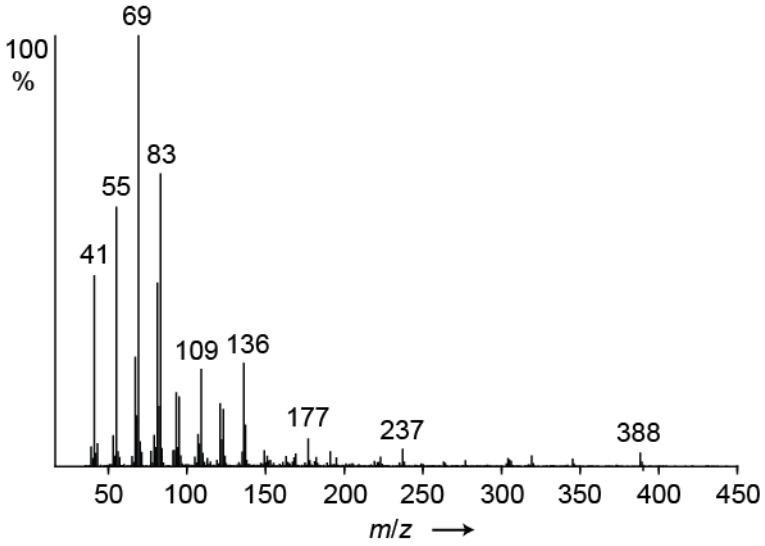


Figure S17. Mass spectrum of (Z)-3-hexenyl geranylcitronellate (9i).

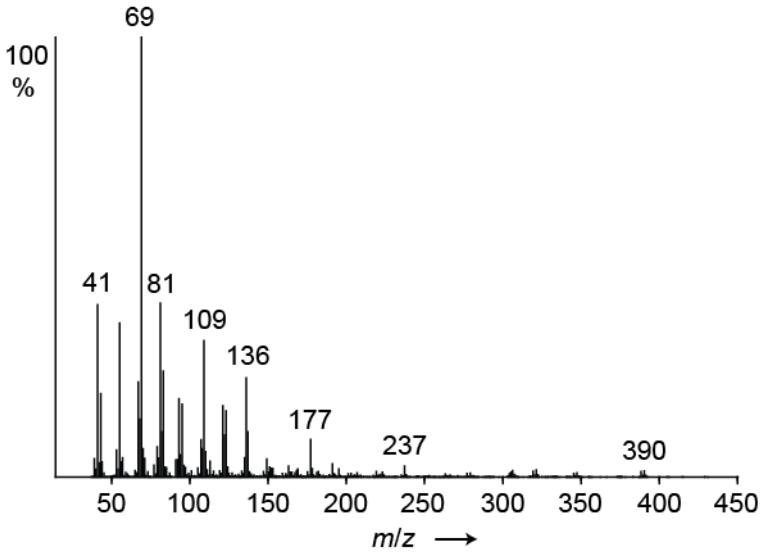


Figure S18. Mass spectrum of hexyl geranylcitronellate (9j).

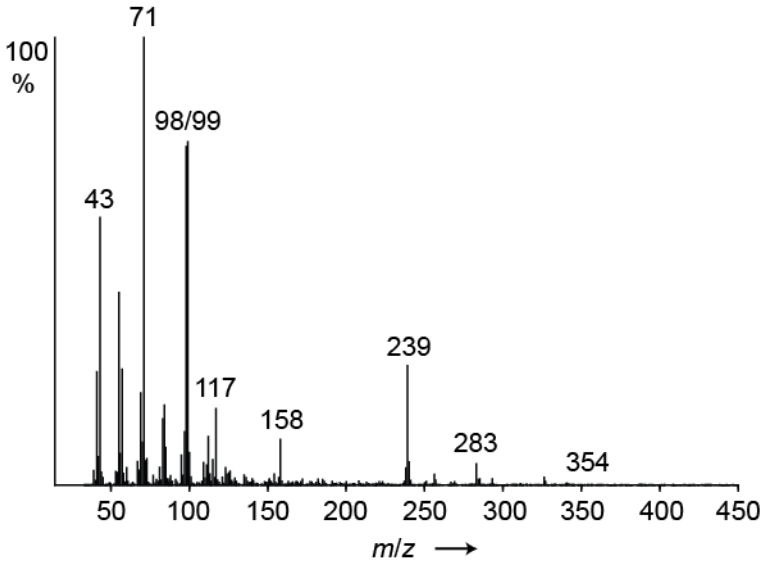


Figure S19. Mass spectrum of 3-oxohexyl hexadecanoate (19l).

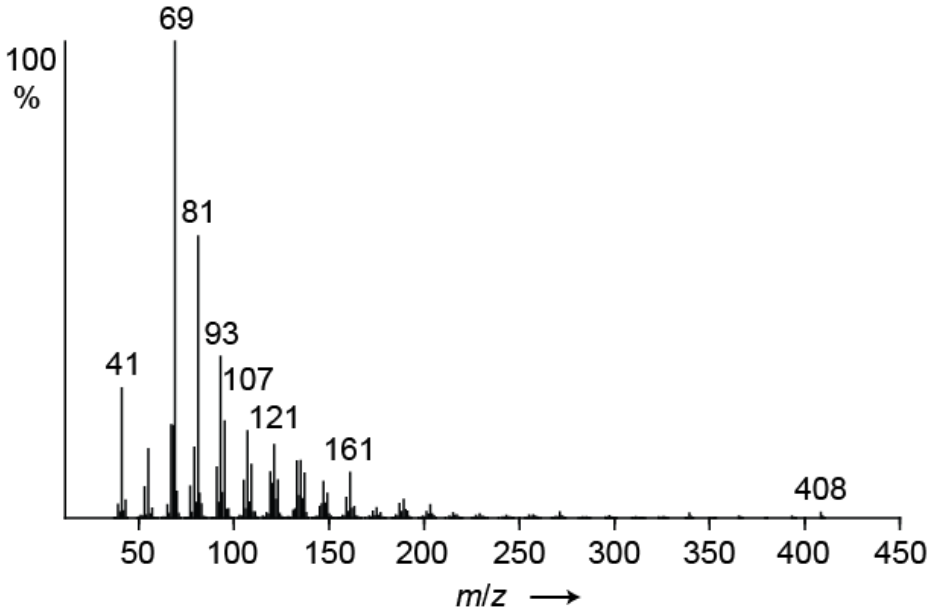


*Figure S20. Mass spectrum of unknown compound C, identified to be (*E,E,E,E*)-β-farnesylfarnesene (28).*

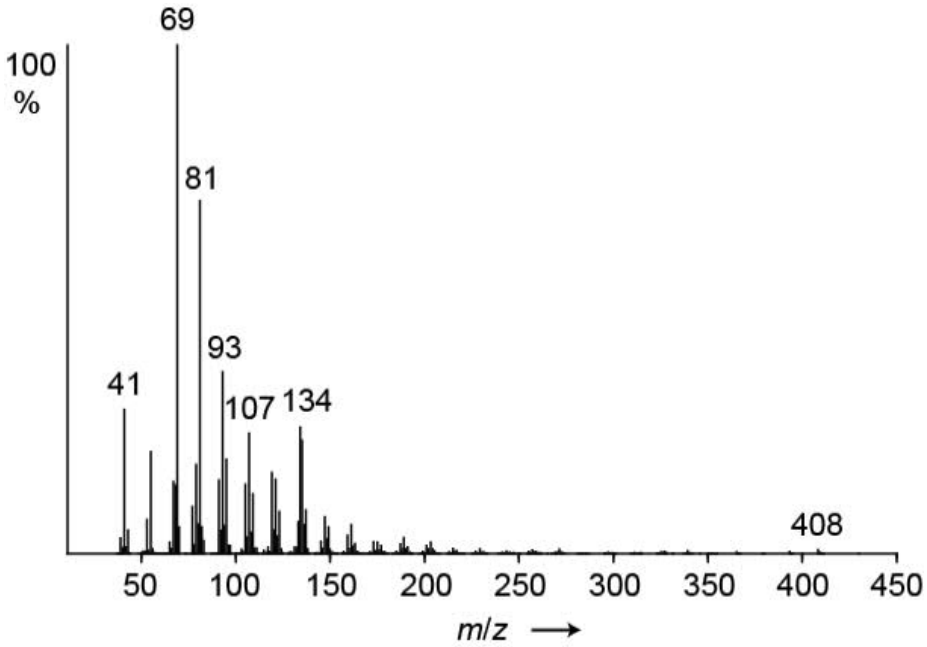


*Figure S21. Mass spectrum of unknown compound D, identified to be (*E,E,E,E*)-α-farnesylfarnesene (29).*

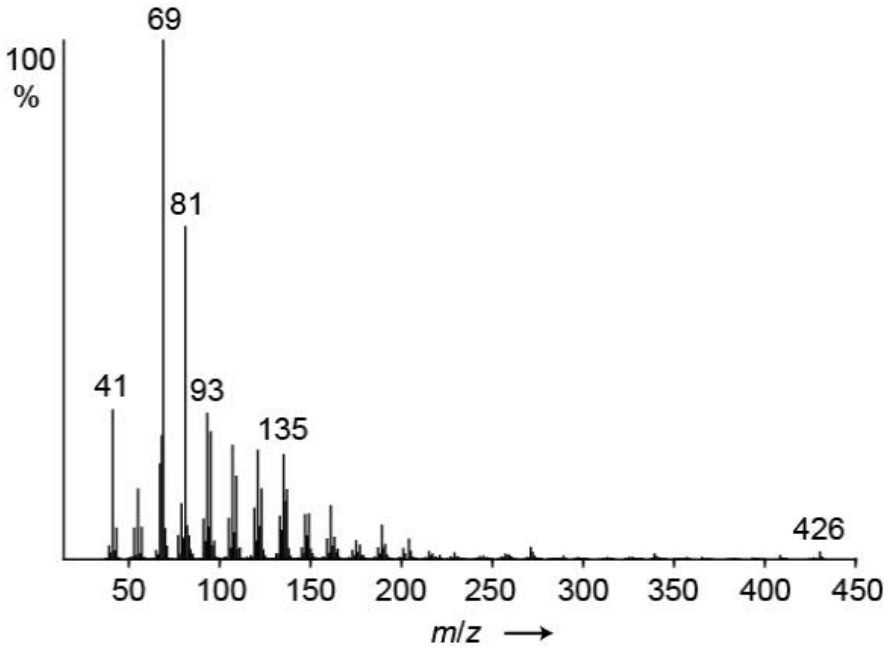


*Figure S22. Mass spectrum of unknown compound F, identified to be (*E,E,E,E*)-farnesylfarnesol (30).*

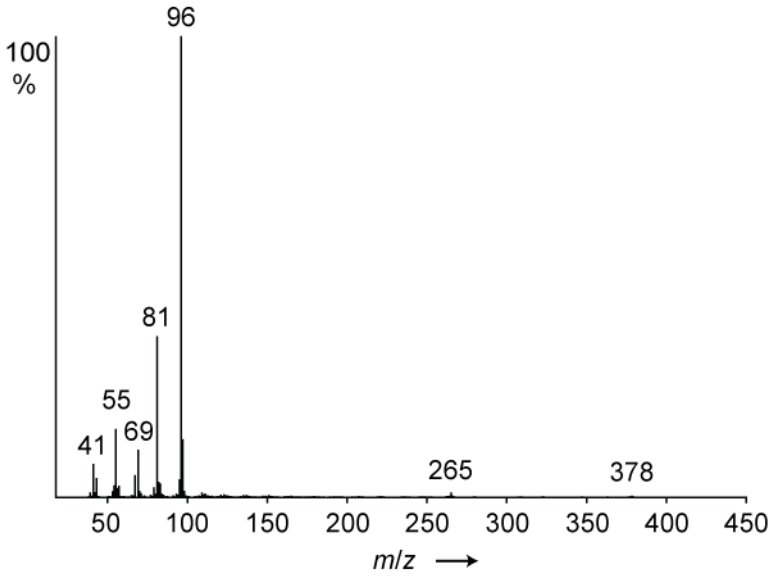


Figure S23. Mass spectrum of 5-methyl-4-hexenyl (Z)-9-octadecenoate. The ion m/z *265 is the acylium ion.*

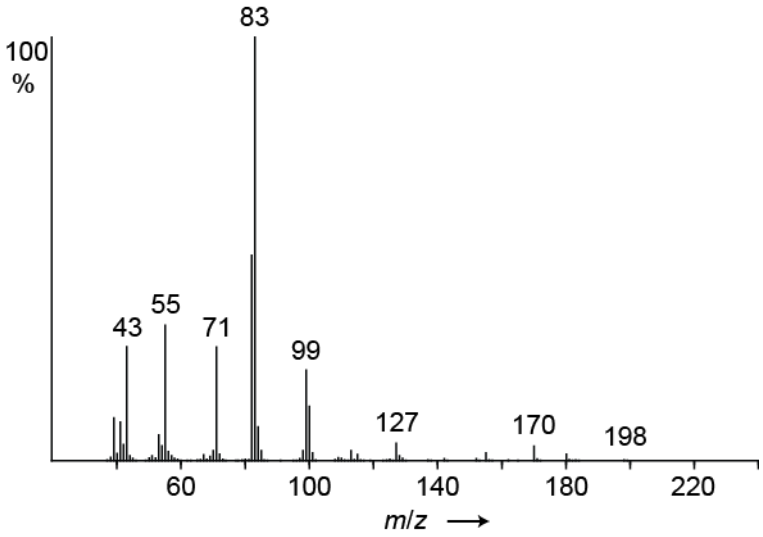


Figure S24. Mass spectrum of 3-oxohexyl 3-methyl-2-butenoate (34).

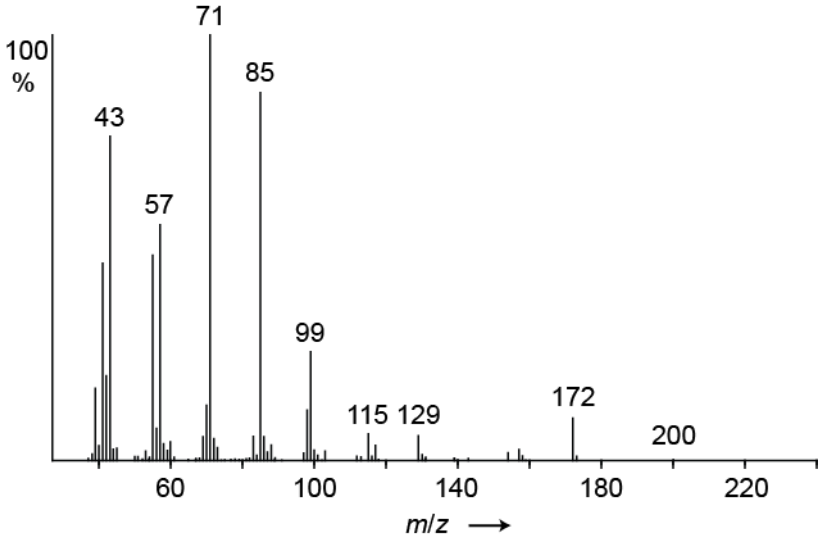


Figure S25. Mass spectrum of 3-oxohexyl 3-methylbutanoate (33).

3. IR spectra

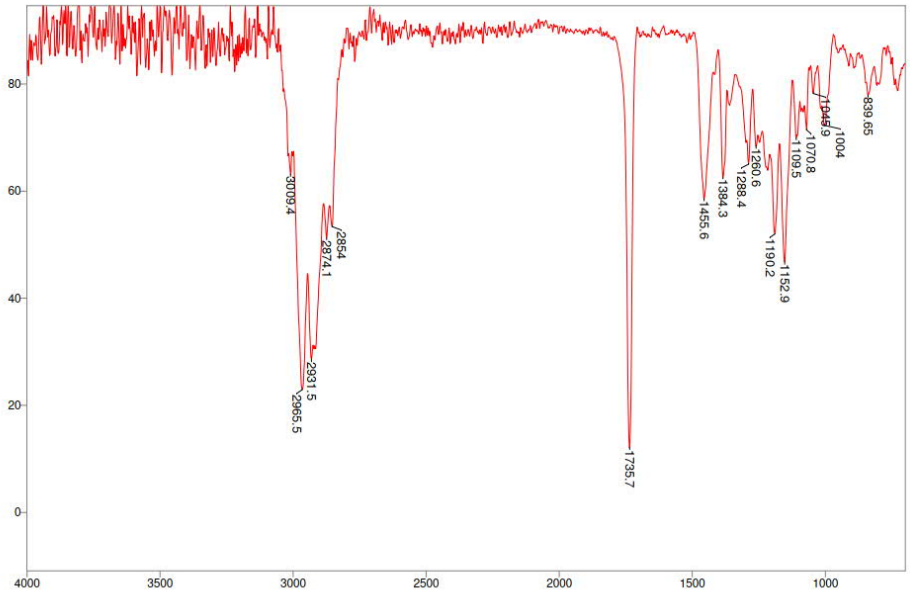


Figure S26. DD-IR spectrum of compound A/A', identified to be a mixture of hexyl and (Z)-3-hexenyl 2,3-dihydrofarnesoate (8j, 8i).

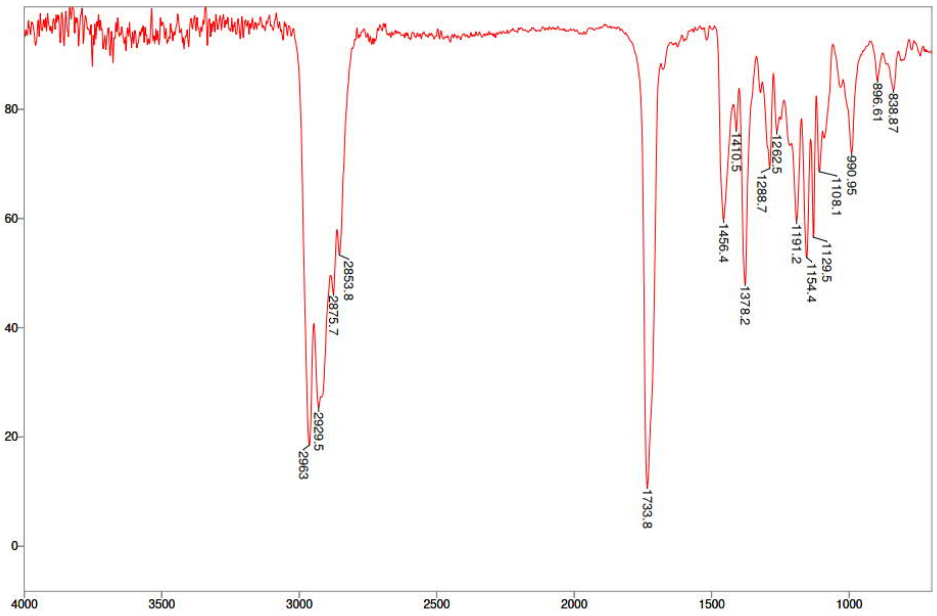


Figure S27. DD-IR spectrum of compound B, identified to be 3-oxohexyl 2,3-dihydrofarnesoate (8l).

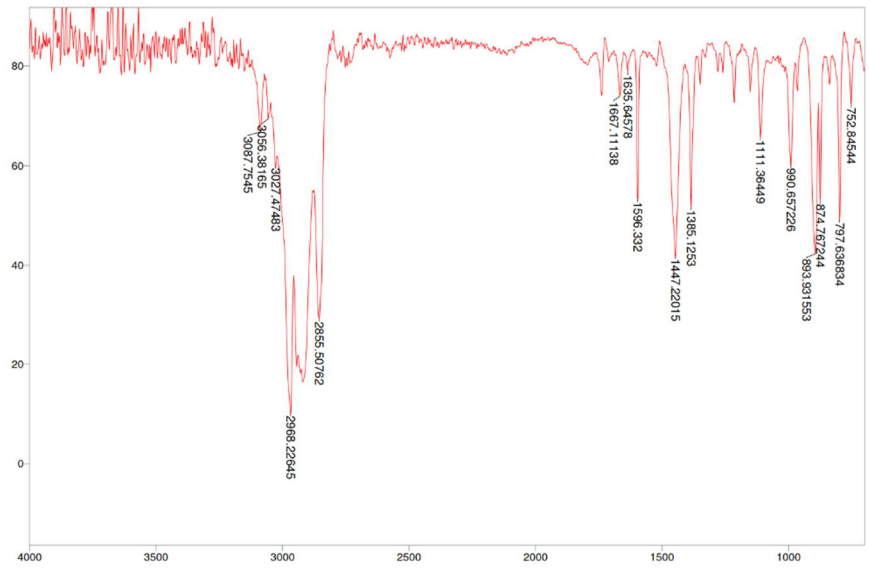


Figure S28. DD-IR spectrum of (E,E,E)-*β-farnesylfarnesene (28).*

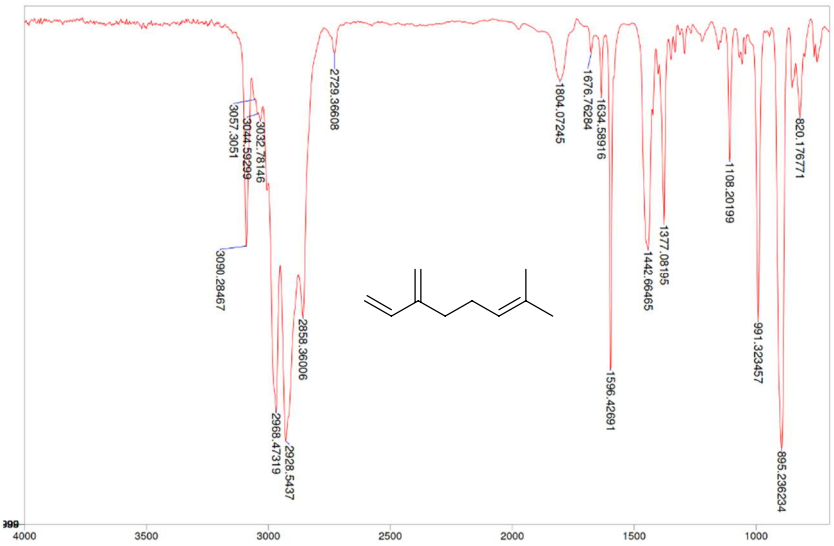


Figure S29. DD-IR spectrum of myrcene.

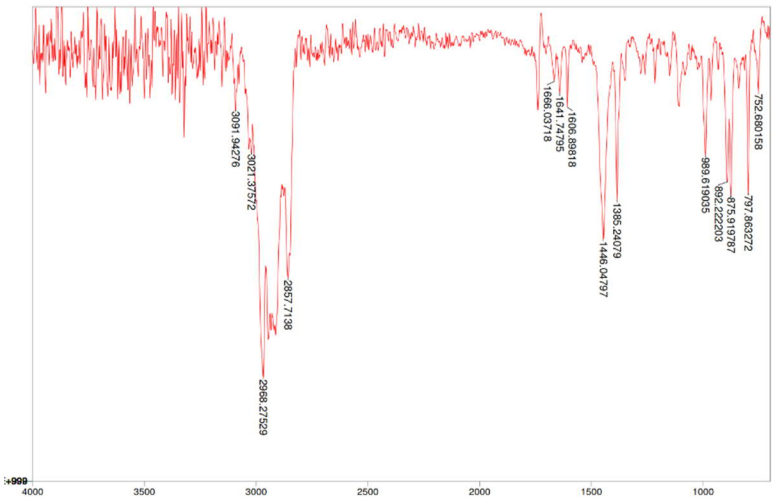


Figure S30. DD-IR spectrum of (E,E,E,E,E)-α*-farnesylfarnesene (29).*

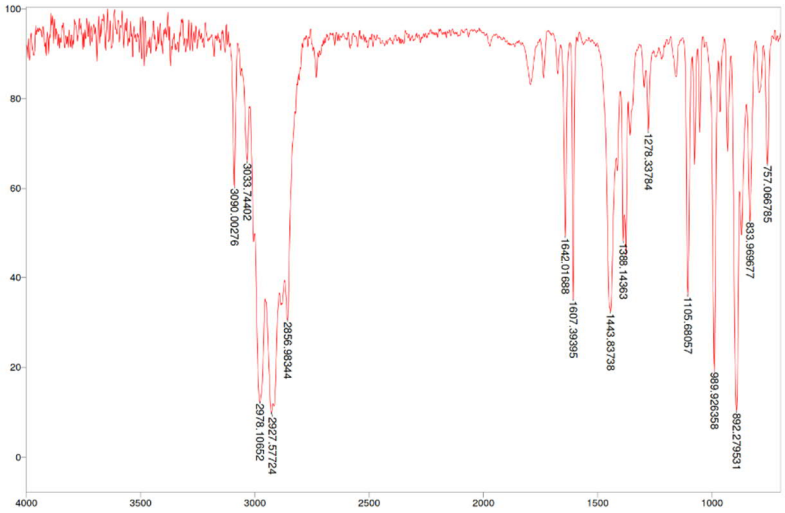


Figure S31. DD-IR spectrum of (E)-β*-ocimene (1).*

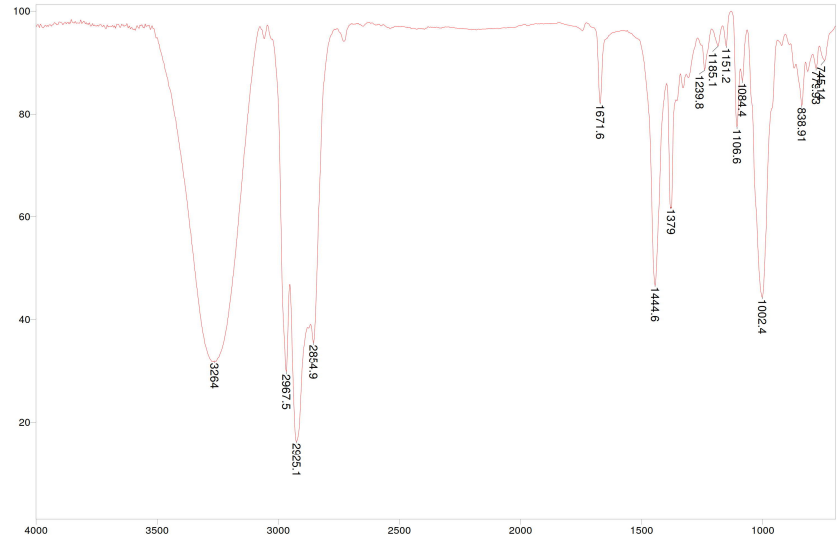


*Figure S32. DD-IR Spectrum of synthetic (*E,E*)-farnesol.*

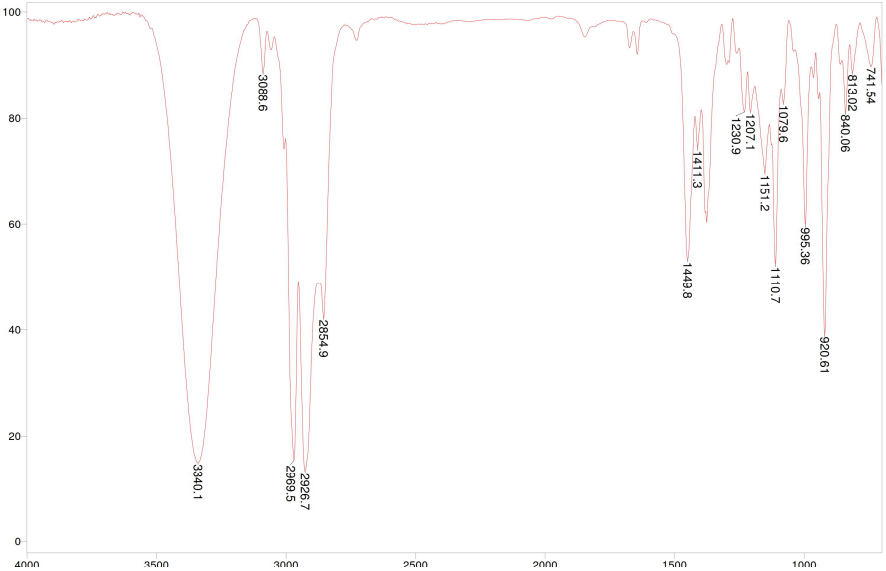


*Figure S33. DD-IR Spectrum of synthetic (*E*)-nerolidol.*

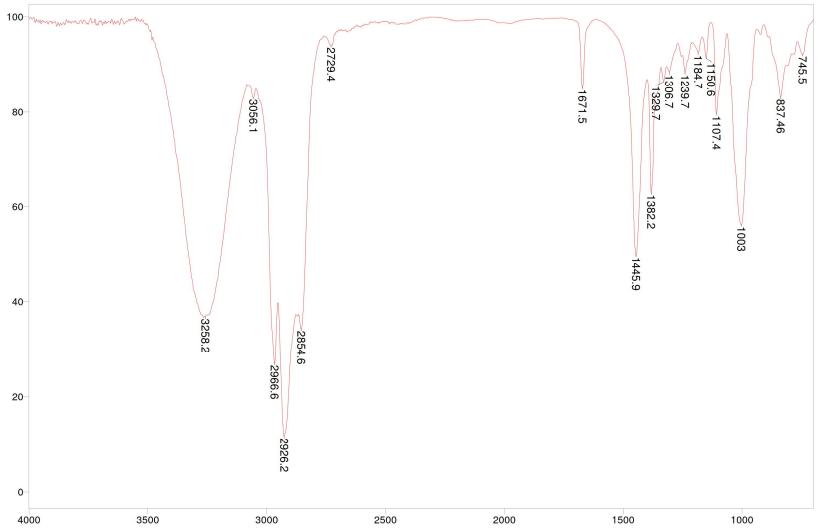


Figure S34. DD-IR Spectrum of synthetic (E,E,E)*-geranylgeraniol.*

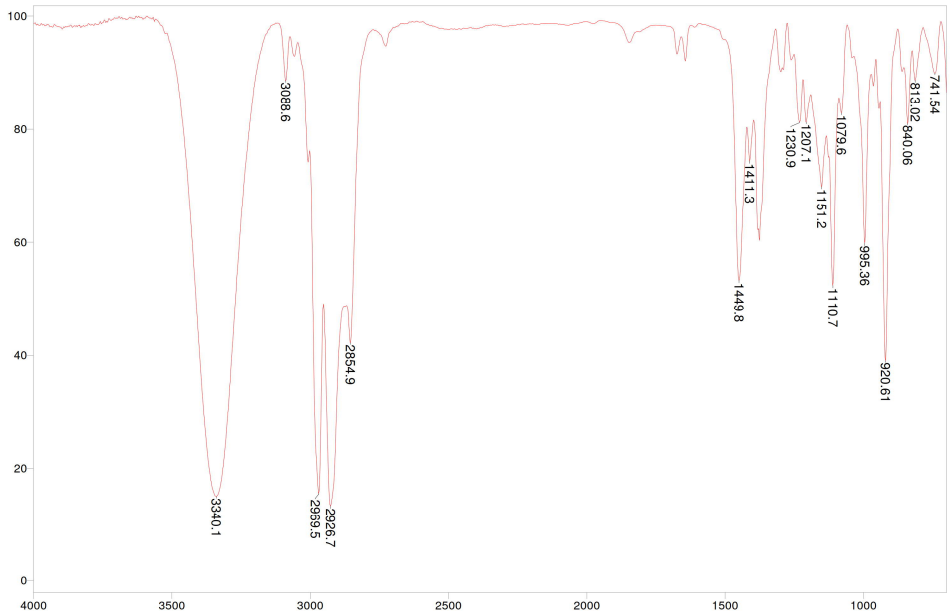


Figure S35. DD-IR Spectrum of synthetic (E,E)*-geranyllinalool.*

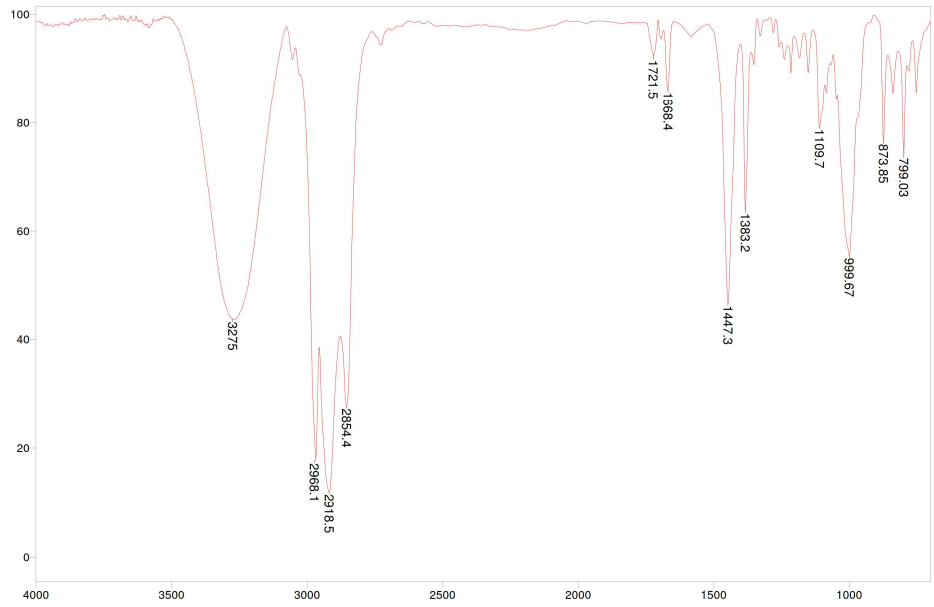


*Figure S36. DD-IR Spectrum of (*E,E,E,E,E*)-farnesylfarnesol (30).*

4. Gas chromatography on chiral phases

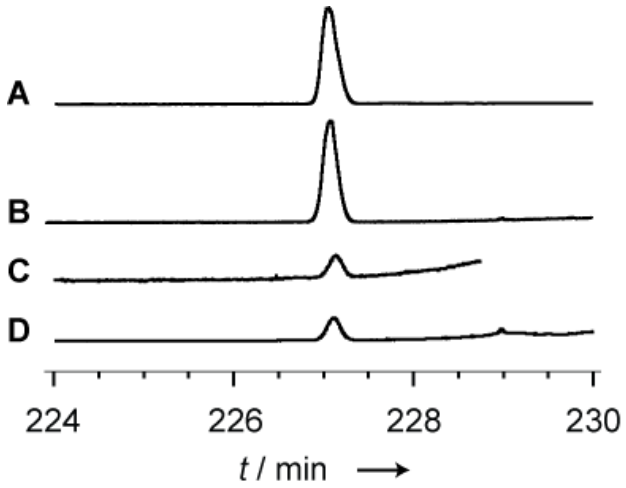


Figure S37. Gas chromatograms of 8b obtained by transesterification with trimethylsulfonium hydroxide on a chiral Hydrodex-6-TBDMS phase. A: H. erato lativitta*; B:* H. erato microclea*; C:* H. erato emma hybrid*; D:* H. erato venustus.

5. Phylogeny of Terpene Synthases of *Heliconius*

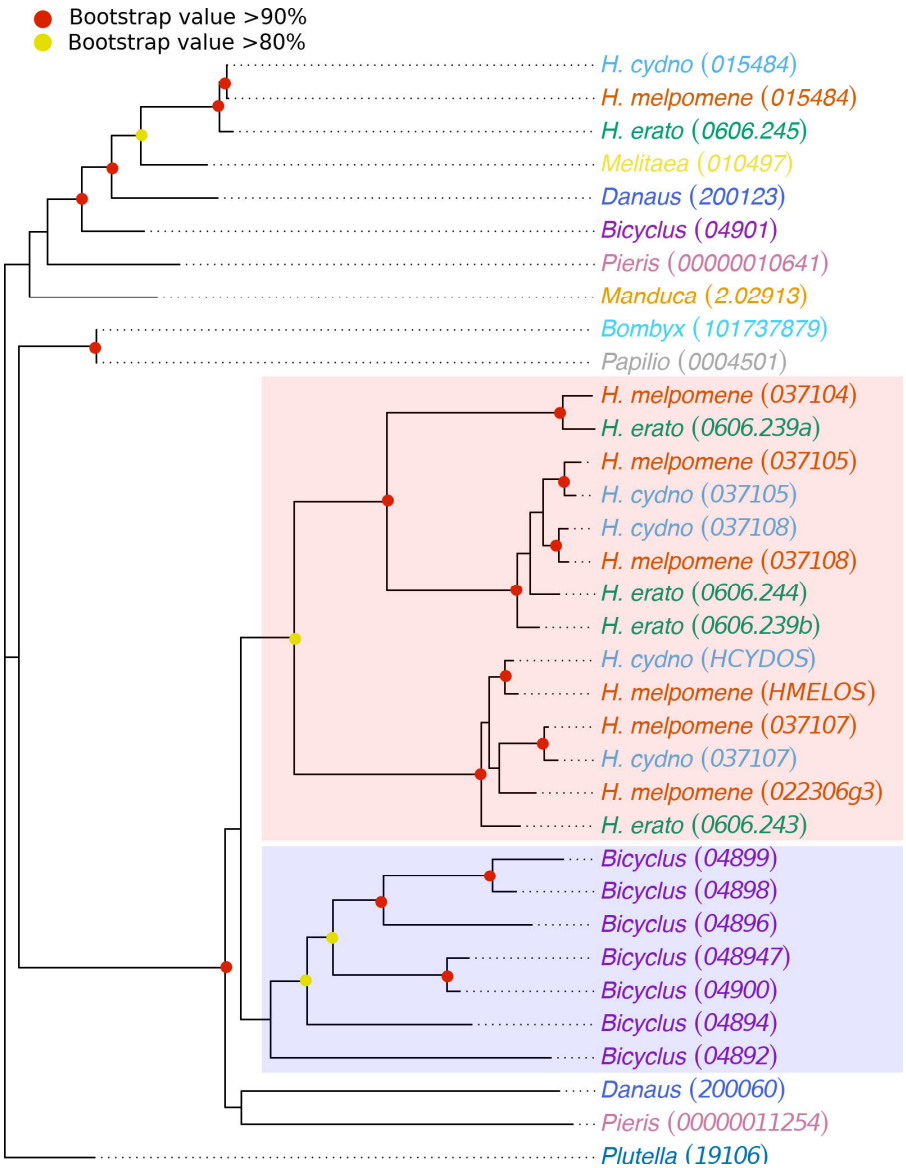


Figure S38. Phylogenetic tree of the GGPPS family of H. melpomene, H. cydno *and* H. erato *and its relation to those of other butterfly families. This figure was published by us earlier.*[S2]

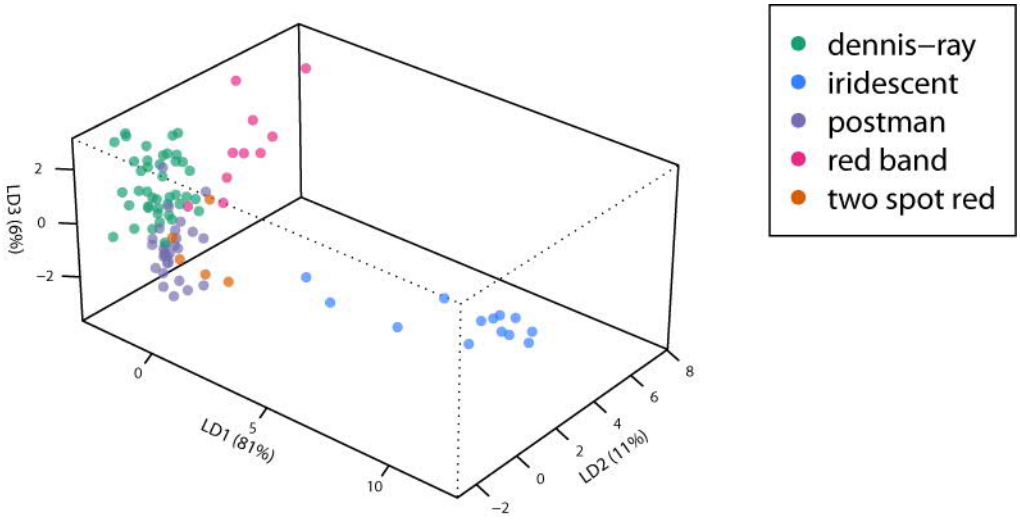


Figure S39. DAPC analysis of different mimicry rings comprising all compounds occurring in at least three samples.

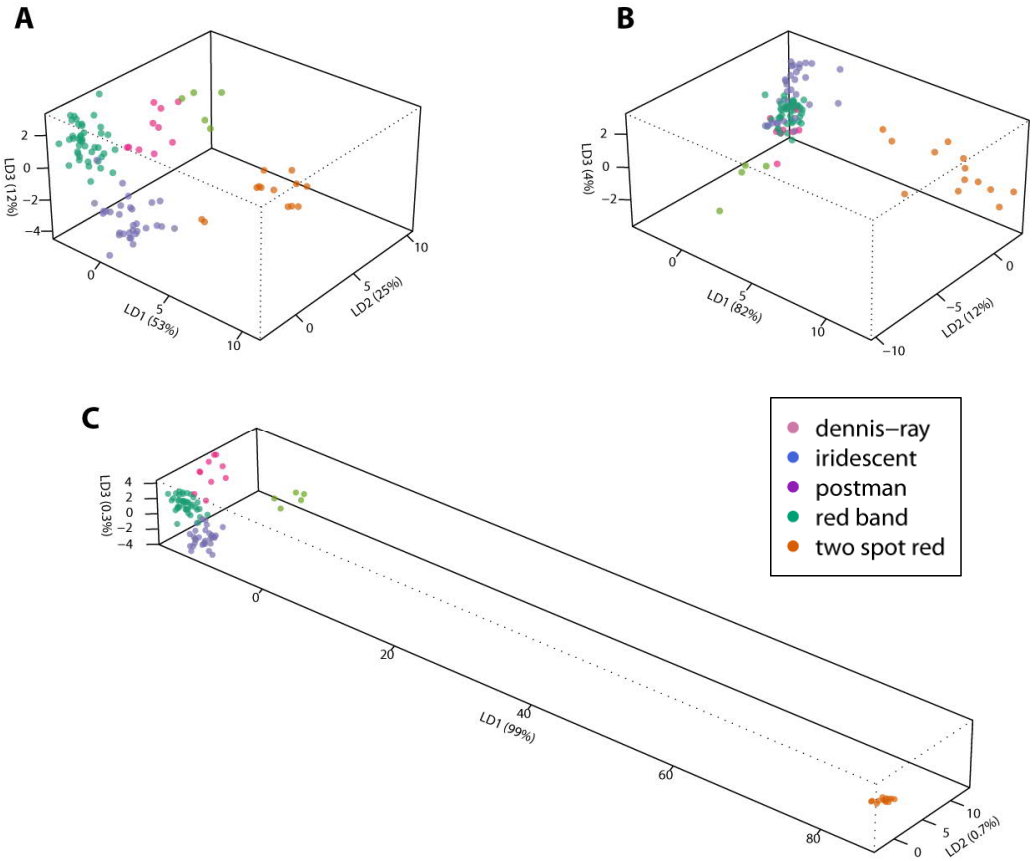


Figure S40. DAPC analysis of different mimicry rings comprising all compounds occurring in at least three samples, normalized within samples. A: volatile compounds; B: compounds with low volatility; C: non-volatile compounds.

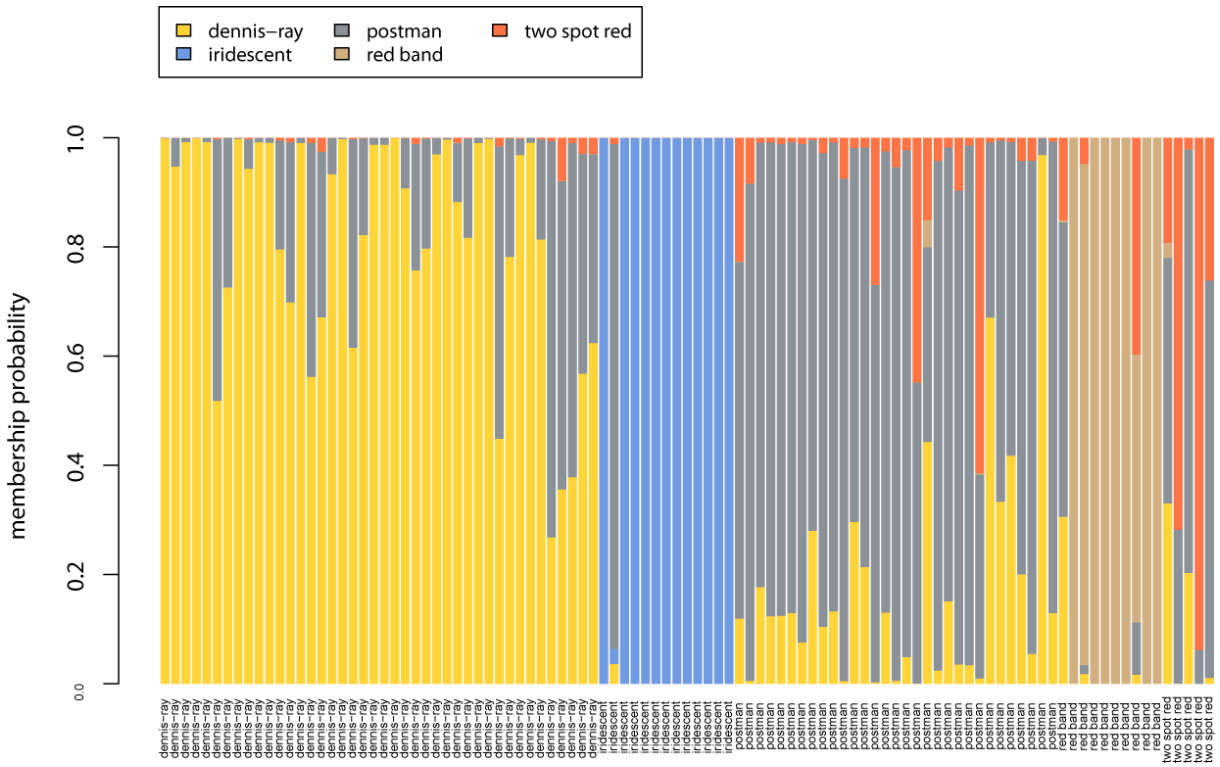


Figure S41. Model predictions by DAPC for mimicry groups based on all compounds occurring at least three times in the samples, natural concentrations.

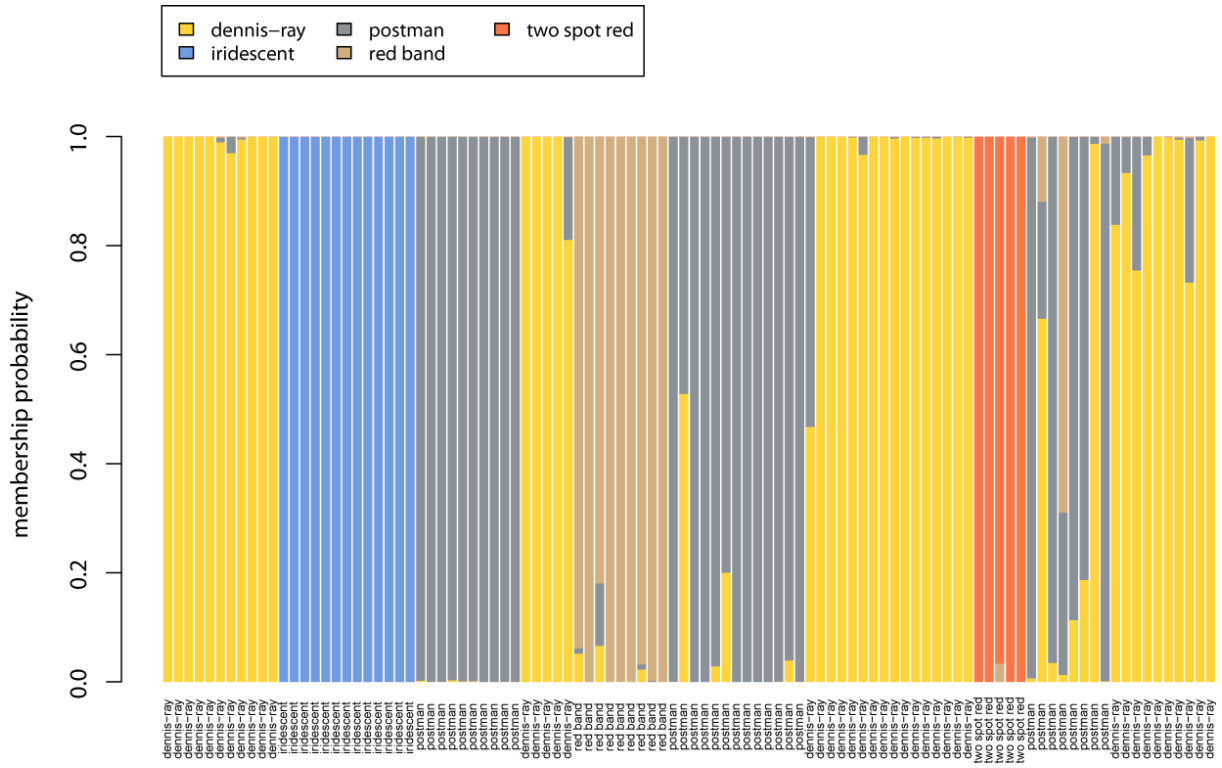


Figure S42. Model predictions by DAPC for mimicry groups based on all compounds occurring at least three times in the samples, amounts normalized within samples.

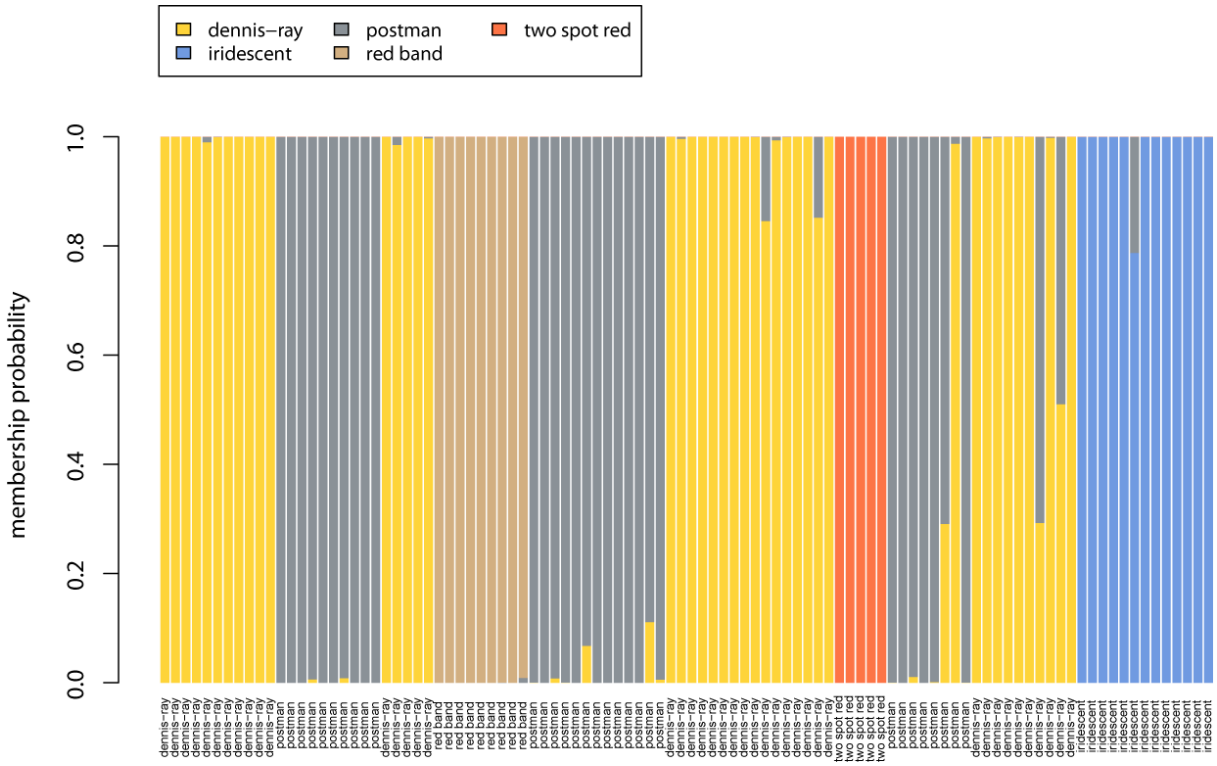


Figure S43. Model predictions by DAPC for mimicry groups for volatile compounds (I < 1750) occurring at least three times in the samples, amounts normalized within samples.

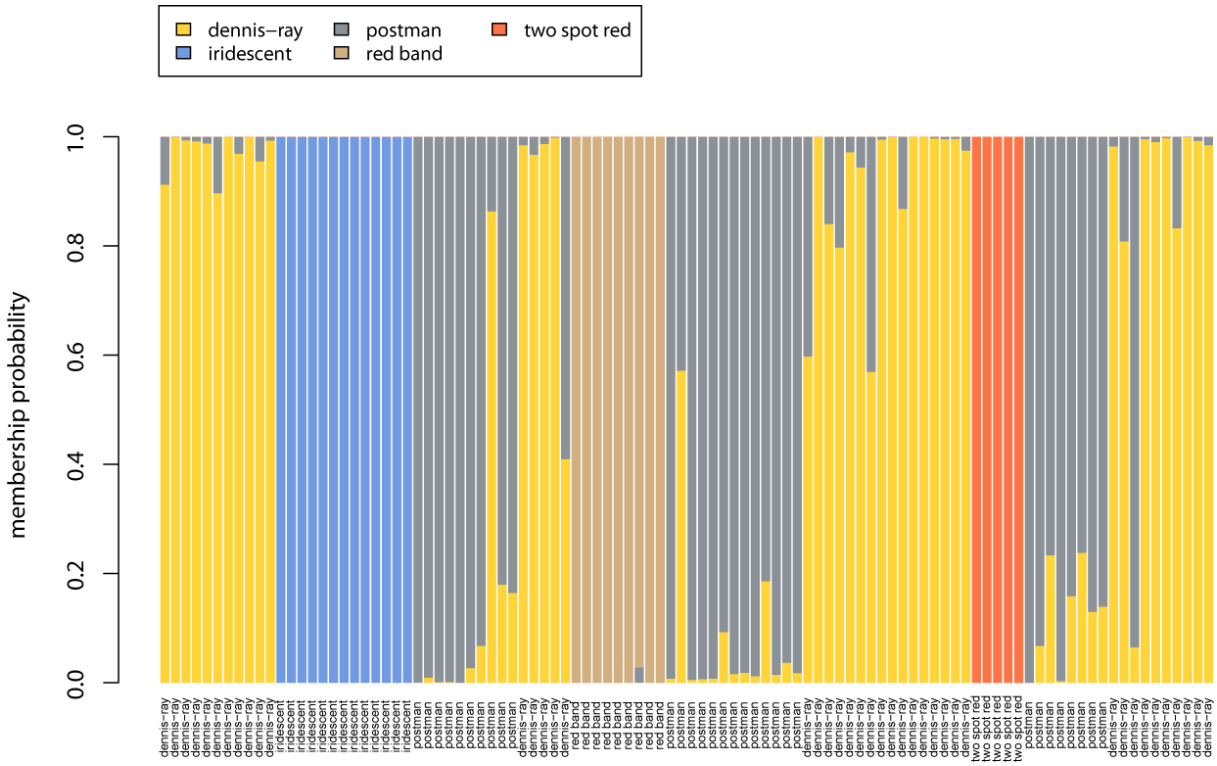


Figure S44. Model predictions by DAPC for mimicry groups for compounds with low volatility (1750 > I < 2500) occurring at least three times in the samples, amounts normalized within samples.

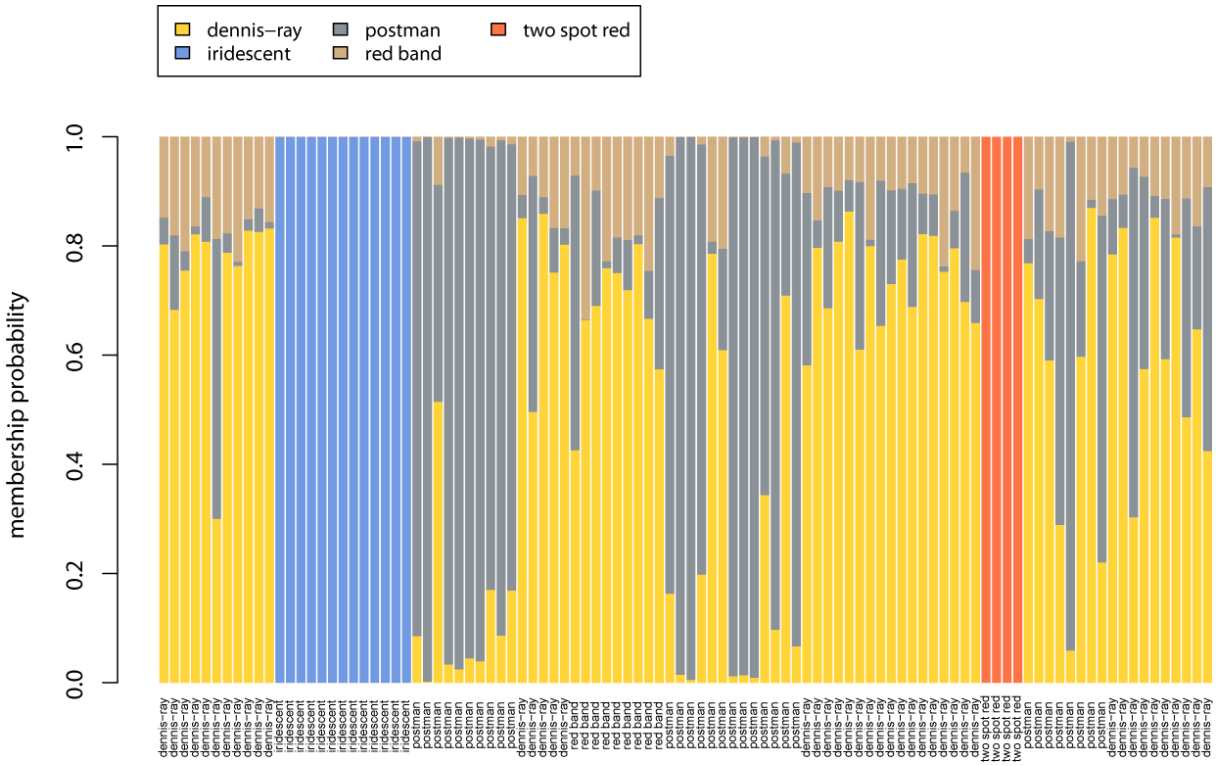


Figure S45. Model predictions by DAPC for mimicry groups for non-volatile compounds (I > 2500) occurring at least three times in the samples, amounts normalized within samples.

A scores

```
"mean a-score" all compounds, non-normalized.
[1] 0.266
[1] "a-scores of groups"
  dennis-ray   iridescent      postman     red band two spot red
  0.09966667   0.51153846   0.27290323   0.49740000  -0.05160000
$`Median and Confidence Interval for Random Chance`
     2.5%       50%     97.5%
0.1305654 0.2007042 0.2796297

$`Mean Successful Assignment by Number of PCs of PCA`
       10        20        30        40        50        60        70
0.5913889 0.5883333 0.6516667 0.5944444 0.5908333 0.5569444 0.5758333

$`Number of PCs Achieving Highest Mean Success`
[1] "30"

$`Root Mean Squared Error by Number of PCs of PCA`
       10        20        30        40        50        60        70
0.4280852 0.4319101 0.3726097 0.4196835 0.4294511 0.4601806 0.4467397

$`Number of PCs Achieving Lowest MSE`
[1] "30"


"mean a-score" all compounds, normalized.
[1] 0.269
[1] "a-scores of groups"
  dennis-ray   iridescent      postman     red band two spot red
   0.1399048    0.3638462    0.1732258    0.2786000    0.3900000
$`Median and Confidence Interval for Random Chance`
     2.5%       50%     97.5%
0.1280949 0.2045480 0.2796297

$`Mean Successful Assignment by Number of PCs of PCA`
       10        20        30        40        50        60
0.5977778 0.5630556 0.6158333 0.7297222 0.7336111 0.6641667
       70
0.6036111

$`Number of PCs Achieving Highest Mean Success`
[1] "50"

$`Root Mean Squared Error by Number of PCs of PCA`
       10        20        30        40        50        60
0.4148125 0.4478731 0.3988670 0.2918610 0.2847961 0.3528882
       70
0.4185485

$`Number of PCs Achieving Lowest MSE`
[1] "50"


"mean a-score" volatile compounds, normalized.
[1] "mean a-score"
[1] 0.213
[1] "a-scores of groups"
  dennis-ray   iridescent      postman     red band two spot red
   0.1416667    0.3647692    0.2011613    0.1882000    0.1680000
$`Median and Confidence Interval for Random Chance`
     2.5%       50%     97.5%
0.1372584 0.1955347 0.2873707

$`Mean Successful Assignment by Number of PCs of PCA`
       10        20        30        40        50        60        70
0.4927778 0.6652778 0.6541667 0.6977778 0.7130556 0.6280556 0.4286111

$`Number of PCs Achieving Highest Mean Success`
[1] "50"

$`Root Mean Squared Error by Number of PCs of PCA`
       10        20        30        40        50        60        70
```

```
0.5183842 0.3571589 0.3710377 0.3294215 0.3099096 0.3909834 0.5894069

$`Number of PCs Achieving Lowest MSE`
[1] "50"


[1] "mean a-score" low volatile compounds, normalized.
[1] 0.328
[1] "a-scores of groups"
  dennis-ray   iridescent      postman     red band two spot red
   0.1498140    0.7247692    0.2643226   -0.1878000    0.6890000
$`Median and Confidence Interval for Random Chance`
     2.5%       50%     97.5%
0.1307407 0.1988216 0.2813890

$`Mean Successful Assignment by Number of PCs of PCA`
       10        20        30        40        50        60        70
0.5454545 0.7605556 0.7207828 0.6493434 0.5795707 0.5456061 0.4747222

$`Number of PCs Achieving Highest Mean Success`
[1] "20"

$`Root Mean Squared Error by Number of PCs of PCA`
       10        20        30        40        50        60        70
0.4656988 0.2512001 0.2971951 0.3762051 0.4417977 0.4683674 0.5486713

$`Number of PCs Achieving Lowest MSE`
[1] "20"


[1] "mean a-score" non-volatile compounds, normalized.
[1] 0.188
[1] "a-scores of groups"
  dennis-ray   iridescent      postman     red band two spot red
  0.06447619   0.26076923   0.17187097   0.16880000   0.27640000
$`Median and Confidence Interval for Random Chance`
     2.5%       50%     97.5%
0.1274383 0.2006310 0.2915109

$`Mean Successful Assignment by Number of PCs of PCA`
       10        20        30        40        50        60        70
0.5697222 0.6052778 0.6755556 0.7013889 0.7038889 0.7447222 0.6175000

$`Number of PCs Achieving Highest Mean Success`
[1] "60"

$`Root Mean Squared Error by Number of PCs of PCA`
       10        20        30        40        50        60        70
0.4432075 0.4130146 0.3462431 0.3281930 0.3189174 0.2660627 0.4070473

$`Number of PCs Achieving Lowest MSE`
[1] "60"
```

7. Loadings of individual compounds for linear discriminants

Table S1. Loadings of individual components of DAPC of all compounds contributing more than 2%. Bold style indicates the component to be one of the 50 most abundant components, while italics indicate part of the 50 most important volatile components.

	LD1	LD2	LD3
2-Phenylethyl tetradecanoate	14.2		
2-Phenylethyl dodecanoate	8.3		
Hexyl-9-octadecenoate and (Z)-3-Hexenyl-9-octadecenoate	7.7		
(*E*)-2,3-Dihydrofarnesoic acid	6.1		
2-Phenylethyl octadecenoate_isomer_1	6.0		
3-Oxohexyl geranylcitronellate	6.0		
3-Oxohexyl tetradecanoate	4.3		
3-Oxohexyl-9-octadecenoate	3.6		
(*Z*)-3-Hexenyl (*E*)-2,3-dihydrofarnesoate	3.1		
2-Phenylethyl (*E*)-2,3-dihydrofarnesoate	2.4		
Benzyl cyanide	2.4		
Unknown B95_8	2.0		
(2*E*,6*E*,10*E*,14*E*)-Geranylfarnesyl acetate		18.6	
9,13,17-Trimethylhentriacontane		16.5	6.3
9,13,17-Trimethylnonacosane		11.0	
7,11,15,19-Tetramethylnonacosane		8.8	
7,11,15-Trimethylnonacosane		7.8	
Tetracosen-1-ol		2.4	4.9
3-Oxohexyl geranylcitronellate			6.5
13-Docosenamide			5.1
2-(Nitroethyl)benzene			4.9
3-Oxohexyl hexadecanaote			4.8
Geranylcitronellic_acid			4.4
Unknown B135_5			4.2
Farnesylfarnesene_isomer_3			4.1
5,9,13,17-Tetramethylnonacosane			3.3
Mellein			2.6
(*E*)-2,3-Dihydrogeranylfarnesoic acid			2.5
(*Z*)-9-Octadecenyl-9-octadecenoate			2.5
(*Z*)-3-Hexenyl (*E*)-2,3-dihydrogeranylfarnesoate			2.3
Unknown B135_6			2.1
1,3-Docosanediol			2.1

Table S2. Loadings of individual components of DAPC of all compounds contributing more than 2%, normalized within samples. Bold style indicates the component to be one of the 50 most abundant components, while italics indicate part of the 50 most important volatile components.

	LD1	LD2	LD3
Benzyl cyanide	15.4		
3-Oxohexyl tetradecanoate	8.5		
Unknown B95_8	7.1		
Hexyl geranylcitronellate	5.9		2.6
Isoprenyl (*E*)-2,3-dihydrofarnesoate	5.4	6.3	
3-Oxooctyl (*E*)-2,3-dihydrofarnesoate	4.2		
Hexyl-3-methylbutyrate	3.1	3.5	3.4
2-Phenylethyl 3-methyl-2-butenoate	1.9		
Unknown (*E*)-2,3-dihydrofarnesylfarnesoate		13.5	
(Z)-3-Hexenyl 3-methylbutyrate		5.9	
Heneicosane		5.3	
9,13,17-Trimethylhentriacontane		4.7	
Geranylcitronellic acid		3.7	
Unknown B135_5		3.6	4.6
Hexacosen-1-ol		3.2	
2-Phenylethyl (*E*)-2,3-dihydrogeranylfarnesoate		2.5	
α-Tocopherol		2.4	
7,11,15-Trimethylnonacosane		2.1	
Hexyl (*E*)-2,3-dihydrogeranylfarnesoate			5.4
(*Z*)-3-Hexenyl (*E*)-2,3-dihydrogeranylfarnesoate			0.053
2-Phenylethyl geranylcitronellate			4.3
Unknown B135_6			4
5,9,13,17-Tetramethylnonacosane			3.7
7,11,15,19-Tetramethylhentriacontane			3.7
Farnesylfarnesene isomer_3			2.9
Mellein			2.7
Unknown B135_12			2.4
3,7,11,15-Tetramethylnonacosane			2.3
1,3-Docosanediol			2.3
Octacosenol			2.3
2-(Nitroethyl)benzene			2.2

Table S3. Loadings of individual components of DAPC of volatile compounds contributing more than 2%, normalized within samples. Bold style indicates the component to be one of the 50 most abundant components, while italics indicate part of the 50 most important volatile components.

	LD1	LD2	LD3
Unknown 71_4	7.3		9.7
3-Methylbutyl 3-methylbutanoate	6.3		2.2
(E)-Nerolidol	5.9		
Unknown hydrocarbon 6	5.7		1.1
1-Hepten-3-one	4.7		
(*E*)-Geranylacetone	4.5		
Unknown B91-1	4.4	5.8	3.9
7,8-Dihydro-β-ionol	4.0	13.5	7.0
Gylcerol triacetate	3.4		2.0
2-Phenylethanol	3.3	2.9	1.5
Germacrene D	3.3		
T-Cadinol	3.1		1.2
α-Terpinyl acetate	3.0		
Isogeranial	2.9		
β-Cyclocitral	2.9	10.1	13.0
Unknown B163-2	2.5	4.9	3.6
Cyclopentane-1,3-diol	2.2	7.4	2.6
Unknown B71-5	2.1		2.5
β–Caryophyllene	1.7	4.1	
Hexyl 3-methyl-2-butenoate	1.7	2.5	4.2
Undecenyl acetate		3.8	
Unknown 3-oxohexyl ester 1		3.5	
Linalool		2.4	
Limonene		2.4	1.5
Unknown B95 1		1.8	14.3
Methoxyphenyl oxime		1.6	2.7
3-Oxohexyl 3-methylbutanoate			8.7

Table S4. Loadings of individual components of DAPC of compounds of low volatility contributing more than 2%, normalized within samples. Bold style indicates the component to be one of the 50 most abundant components, while italics indicate part of the 50 most important volatile components.

	LD1	LD2	LD3
3-Oxohexyl tetradecanoate	13.9	3.8	1.6
Unknown B95_8	11.6	14.2	
3-Methylbutyl (*E*)-2,3-dihydrofarnesoate	10.7	2.3	18.1
1-Docosanol	7.6		
Isoprenyl (*E*)-2,3-dihydrofarnesoate	6.6	55.2	
(6*E*,10*E*,14*E*)-β-Geranylfarnesene	5.1	1.3	
(*Z*)-3-Hexenyl (*E*)-2,3-dihydrofarnesoate	4.6		1.9
2-Phenylethyl dodecanoate	3.8	2.2	
Pentacosene 1	3.7		6.1
Ethyl 9-octadecenoate	3.6	0.5	2.1
Hexadecadienolide	2.7	2.5	10.1
Octadecenolide 1	2.6		1.5
9-Octadecenamide isomer 2	2.4	3.1	2.0
Geranylcitronellic acid	2.2	0.6	1.0
(6*E*,10*E*,14*E*)-Geranylnerolidol	1.6		18.5
Octadecan 1-ol	1.5		4.0
9-Octadecenamide isomer 1		2.1	3.1
Heneicosane		0.7	5.0
Hexyl (*E*)-2,3-dihydrofarnesoate			5.6
Isoprenyl 9-octadecenoate			4.3

Table S5. Loadings of individual components of DAPC of non-volatile compounds contributing more than 2%, normalized within samples. Bold style indicates the component to be one of the 50 most abundant components, while italics indicate part of the 50 most important volatile components.

	LD1	LD2	LD3
1,3-Tetracosanediol	10.7	1.7	1.0
1-Hexacosanol	6.7		3.8
2-Phenylethyl octadecanoate	6.1	1.7	1.5
Unknown terpene 37	5.0		7.7
Unknown B116 3	4.6		
Unknown B79 2	4.0		
trans-2-Nonyl-5-octadecyltetrahydrofuran	3.5	1.9	8.0
7,11,15-Trimethylhentriacontane	3.2	4.9	1.0
branched Hydrocarbon 12	3.0		
11,15,19-Trimethylhentriacontane	2.9		
Hexenyl ocatdecatrienoate and (*Z*)-3-Hexenyl octadecatrienoate	2.8		
Unknown B116 1	2.4		
1,3-Docosanediol	2.0		
5,9,13,17-Tetramethylheptacosane	1.6	3.6	
Ergostenol	1.4	2.1	
2-Eicosyl-5-heptyltetrahydrofuran	1.4	2.6	6.3
Unknown (*E*)-2,3-dihydrofarnesylfarnesoate 2		25.7	6.4
7,11,15-Trimethylnonacosane bH 14		6.0	20.1
(*Z*)-3-Hexenyl (*E*)-2,3-dihydrofarnesylfarnesoate		3.7	
2-Phenylethyl (*E*)-2,3-dihydrogeranylfarnesoate		2.9	1.7
cis-2-Nonyl-5-octadecyltetrahydrofuran		2.2	
Unknown B135 6			3.6
11,15-Dimethylnonacosane bH 10			3.6
Unknown B135 11			2.6

Table S6. Loadings of individual components of DAPC of iridescent mimics against all other mimetic groups. Compounds contributing more than 3%, normalized within samples. Bold style indicates the component to be one of the 50 most abundant components, while italics indicate part of the 50 most important volatile components.

2-Phenylethyl (*E*)-2,3-dihydrofarnesoate	25.2
2-Phenylethyl tetradecanoate	17.6
2-Phenylethyl octadecenoate	10.9
2-Phenylethyl hexadecanoate	4.8
3-Undecanone	3.9

8. Heatmaps

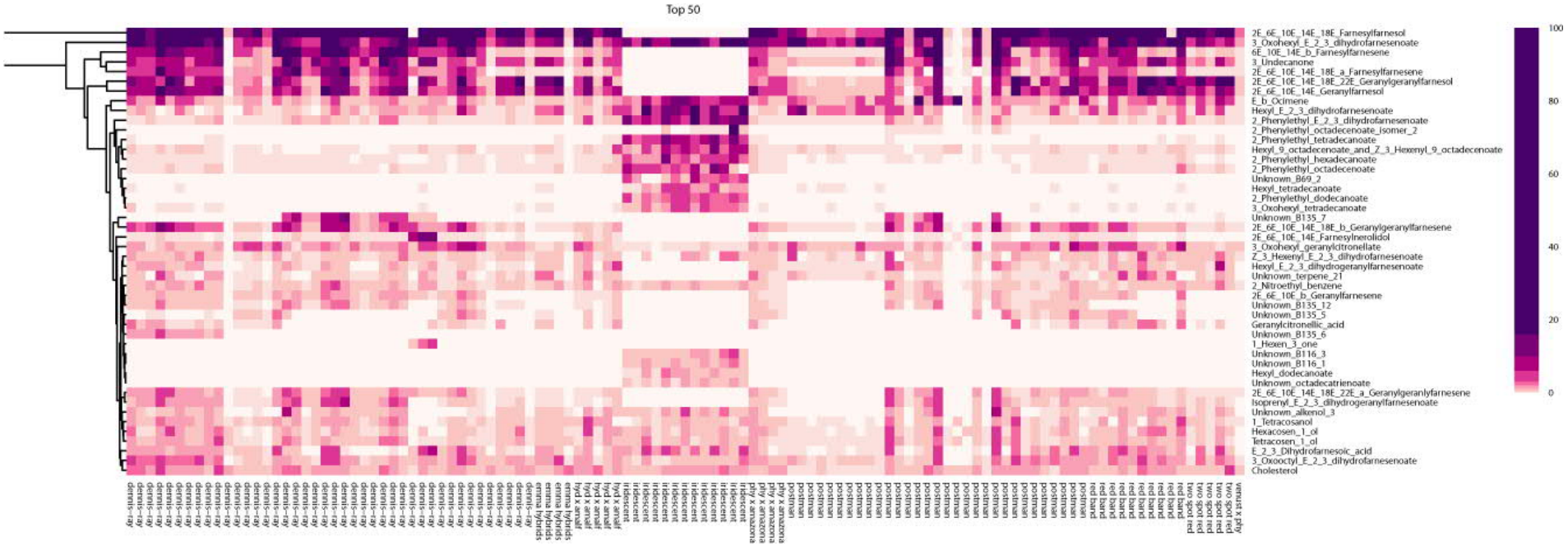


Figure S46. Heatmap of the 50 compounds occurring in highest concentrations. Please note that slight differences to Table 1 occur because hybrid specimens are not included here.

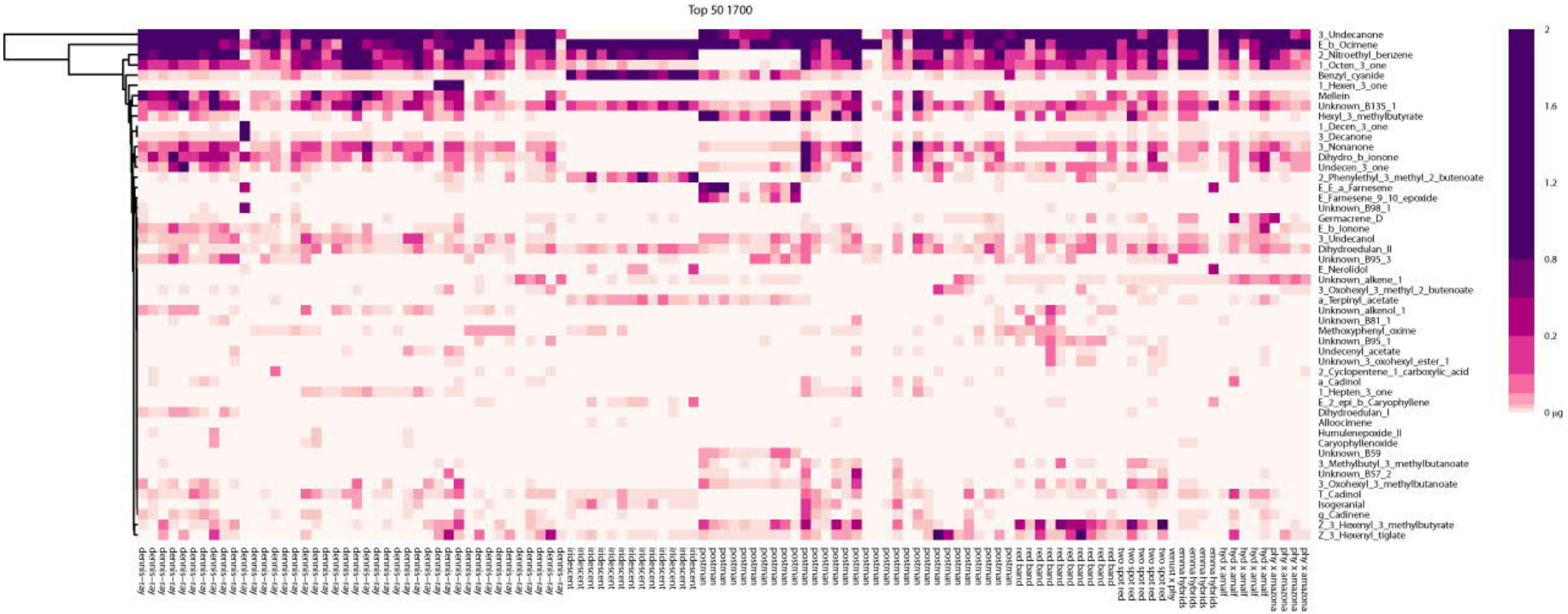


Figure S47. Heatmap of the 50 volatile compounds occurring in highest concentrations. Please note that slight differences to Table 4 occur because hybrid specimens are not included here.

9. R code

```
library(ggplot2)
require(scales)
require(gridExtra)
require(ggtext)
require(ggsci)
library(brew)
require(plotly)
require(MASS)
require(adegenet)
library(readr)
library("dplyr")
#DAPC analysis
#Import data and formation
setwd("E:/R_Projekte/Heliconius")
library(readxl)
Rohdaten_2 <- read_excel("E:/file", sheet = "Table 1", range = "AX:XY")

sums<- rowSums(Rohdaten_2[5:ncol(Rohdaten_2)])
norm<- Rohdaten_2[5:ncol(Rohdaten_2)]/sums
rowSums(norm) #check all add up to one

#if no conversion to relative proportions (norm): remove #  next line
#norm<- Rohdaten_2[5:ncol(Rohdaten_2)]

df<-Rohdaten_2
df[1:4]<-df[1:4] %>% mutate_if(is.character,as.factor)
df[5:ncol(df)]<-df[5:ncol(df)] %>% mutate_if(is.double,as.numeric)
colnames(df)[colnames(df) == "Spezies-alt"] <- "Salinispora"

#Selection
daten<-"Mimicry" #Define factor for discriminant analysis

if(daten == "name"){
  d<-4
} else if(daten == "Subspecies"){
  d<-2
} else if(daten == "Mimicry"){
  d<-3
} else if(daten == "Location"){
  d<-1
}
#DAPC complete
# data not scaled, but centered. If otherwise, set appropriate scale and center values
set.seed(23)
dapc.daten<-dapc(norm, grp = df[[daten]], var.contrib = T, center = T, scale = F, n.da=3, n.pca = 100)
xval <- xvalDapc(norm, df[[daten]], n.pca.max = 300, training.set = 0.9,
                 result = "groupMean", center = TRUE, scale = FALSE,
                 n.pca = NULL, n.rep = 30, xval.plot = TRUE)
k<-seq(1,50)
ascore<-c()
stemp<-c()
for (i in k){
  temp<-a.score(dapc.daten)
  mtemp<-temp$mean
  stemp<-cbind(stemp,temp$pop.score)
  ascore<-c(ascore, mtemp)
}
score<-round(mean(ascore),3)
einzel_score<-apply(stemp, 1, mean)
print(score)
print(einzel_score)
print(xval[1:6])

n_pcs <- as.numeric(readline(prompt="How many PCs should be used?: "))

dapc.daten<-dapc(norm, grp = df[[daten]], var.loadings = T, var.contrib = T, center = T, scale = F,
n.da=3, n.pca = n_pcs)
k<-seq(1,50)
ascore<-c()
stemp<-c()
for (i in k){
```

```
  temp<-a.score(dapc.daten)
  mtemp<-temp$mean
  stemp<-cbind(stemp,temp$pop.score)
  ascore<-c(ascore, mtemp)
}
score<-round(mean(ascore),3)
einzel_score<-apply(stemp, 1, mean)
pca.scaled<-prcomp(norm, center = T, scale = F) # scalieren T, nicht skalieren F, beides mal
pcs<-pca.scaled$x[,1:n_pcs]
pcs<-as.data.frame(cbind(df[1:4],pcs))
f<-paste(names(pcs)[d], "~", paste(names(pcs)[-c(1:4)], collapse = " + "))
pca.lda<-lda(as.formula(paste(f)), data = pcs)
prop.lda<-pca.lda$svd^2/sum(pca.lda$svd^2)
lda.result<-predict(pca.lda)

my_log <- file("my_log.txt") # File name of output log
sink(my_log, append = TRUE, type = "output") # Writing console output to log file
print('mean a-score')
print(score)
print('a-scores of groups')
print(einzel_score)
print(xval[2:6])
ta <- dapc.daten$var.contr
ta<-as.data.frame(ta)
Lodta1 <- ta[order(-ta$LD1),]
Lodta2 <- ta[order(-ta$LD2),]
Lodta3 <- ta[order(-ta$LD3),]
print('Loadings LD1')
print(head(Lodta1, 20))
print('')
print('Loadings LD2')
print(head(Lodta2, 20))
print('')
print('Loadings LD3')
print(head(Lodta3, 20))

closeAllConnections() # Close connection to log file

i1<-ggplot(as.data.frame(lda.result$x), aes(x=lda.result$x[,1], y=lda.result$x[,2])) +
  geom_point(aes(color=factor(df[[daten]])),size=5, alpha=0.7) +
  labs(x= paste("LD1 (", percent(prop.lda[1]), ")", sep=""),
       y= paste("LD2 (", percent(prop.lda[2]), ")", sep=""),
       color="Spezies", shape="Spezies") +
  scale_color_simpsons() +
  ggtitle("", subtitle = paste("a-score: ",score, sep = "")) +
  theme(legend.text = element_text(size=12),
        plot.background = element_blank(),
        panel.background = element_blank(),
        panel.border = element_blank(),
        #panel.grid.major = element_blank(),
        #panel.grid.minor = element_line(size = 0.25, linetyp = "solid", colour = "lightgrey"),
        axis.line = element_line(colour = "black"),
        axis.text = element_text(size=12),
        legend.key = element_blank(),
        legend.title = element_blank(),
        plot.title = element_text(hjust = 0, vjust=2, size=14),
        plot.subtitle = element_text(hjust = 0, vjust=2, size=12))
i1
i2<-ggplot(as.data.frame(lda.result$x), aes(x=lda.result$x[,1], y=lda.result$x[,3])) +
  geom_point(aes(color=factor(df[[daten]])),size=5, alpha=0.7) +
  labs(x= paste("LD1 (", percent(prop.lda[1]), ")", sep=""),
       y= paste("LD3 (", percent(prop.lda[3]), ")", sep=""),
       color="Spezies", shape="Spezies") +
  scale_color_simpsons() +
 ggtitle("", subtitle = paste("a-score: ",score, sep = "")) +
  theme(legend.text = element_text(size=12),
        plot.background = element_blank(),
        panel.background = element_blank(),
        panel.border = element_blank(),
        #panel.grid.major = element_blank(),
        #panel.grid.minor = element_line(size = 0.25, linetyp = "solid", colour = "lightgrey"),
        axis.line = element_line(colour = "black"),
        axis.text = element_text(size=12),
        legend.key = element_blank(),
        legend.title = element_blank(),
```

```
        plot.title = element_text(hjust = 0, vjust=2, size=14),
        plot.subtitle = element_text(hjust = 0, vjust=2, size=12))
i2
i3<-ggplot(as.data.frame(lda.result$x), aes(x=lda.result$x[,2], y=lda.result$x[,3])) +
  geom_point(aes(color=factor(df[[daten]])),size=5, alpha=0.7) +
  labs(x= paste("LD2 (", percent(prop.lda[2]), ")", sep=""),
       y= paste("LD3 (", percent(prop.lda[3]), ")", sep=""),
       color="Spezies", shape="Spezies") +
  scale_color_simpsons() +
 ggtitle("", subtitle = paste("a-score: ",score, sep = "")) +
  theme(legend.text = element_text(size=12),
        plot.background = element_blank(),
        panel.background = element_blank(),
        panel.border = element_blank(),
        #panel.grid.major = element_blank(),
        #panel.grid.minor = element_line(size = 0.25, linetyp = "solid", colour = "lightgrey"),
        axis.line = element_line(colour = "black"),
        axis.text = element_text(size=12),
        legend.key = element_blank(),
        legend.title = element_blank(),
        plot.title = element_text(hjust = 0, vjust=2, size=14),
        plot.subtitle = element_text(hjust = 0, vjust=2, size=12))
i3


temp <- which(apply(dapc.daten$posterior, 1, function(e) all(e < 0.9)))
compoplot(dapc.daten,
          n.col = 3,
          cleg = 0.8, #legend size
          cex.names = 0.35, #Gr??e der X-Achsen Beschriftung
          #subset = temp, #only samples with more than 90 % propability
          show.lab=T, #Labels x axis: T ein, F aus
          lab = df$Mimicry,
          cex.lab = 1,
          srt = 60,
          posi=list(x=0,y=1.24), #change position of legend
          #axis(side = 1, at=seq_len(length(txt[[daten]]) + 1),labels = T),
          col=pal_simpsons(),
          txt.leg = colnames(dapc.daten)
          )

LD_1<-paste("LD1 (", percent(prop.lda[1]), ")", sep="")
LD_2<-paste("LD2 (", percent(prop.lda[2]), ")", sep="")
LD_3<-paste("LD3 (", percent(prop.lda[3]), ")", sep="")

fig<-plot_ly(x=lda.result$x[,1],
        y=lda.result$x[,2],
        z=lda.result$x[,3],
        text = paste("Location: ", df$Location,
                     "<br>Sub: ", df$Subspecies,
                     "<br>Mimicry: ", df$Mimicry,
                     "<br>Name: ", df$name),
        #name = df$name,
       # colors=c("#911eb4", "#42d4f4", "#4363d8",  "#56B4E9", "#009E73","#D55E07","#E69F00","#F0E442",
"#a9a9a9",  "#CC79A7", "#0072B2", "#4363d8"),
        colors="Dark2",
       type="scatter3d",
        mode="markers",
        color=factor(df[[daten]]),
        size = 5)
fig<-fig %>% layout(scene = list(
  xaxis = list(title = LD_1),
  yaxis = list(title = LD_2),
  zaxis = list(title = LD_3)))
fig<-fig %>% layout(legend =list(font = list(size = 10)))
fig<-fig %>% layout(legend =list(itemsizing = list(size = 10)))
fig

##############################'
##############################'
##############################'
#Heatmap
library(pheatmap)
library(RColorBrewer)
library(gplots)
```

```
library(readr)
Rohdaten_2 <- read_excel("E:/data",
                         sheet = "Top 50", range = "Ax:YZ")
Rohdaten_2<-as.data.frame(Rohdaten_2)
head(Rohdaten_2)
rnames <- Rohdaten_2[,3]
head(rnames)
mat_data <- data.matrix(Rohdaten_2[,5:ncol(Rohdaten_2)])
rownames(mat_data) <- rnames
mimic <- mat_data[,3]
head(mimic)
mimic_ann <- mat_data(sample = rep(c("Mimicry"), c(4)))


my_palette <- colorRampPalette(c("red", "yellow", "green"))(n = 299)
col_groups <- substr(colnames(mat_data), 1, 1)
table(col_groups)
head (rnames)

# 90Â° rotation: pheatmap(mat_data,
pheatmap(t(mat_data),
         cellnote = mat_data,  # same data set for cell labels
         #main = "Correlation", # heat map title
         #notecol="black",      # change font color of cell labels to black
         #density.info="none",  # turns off density plot inside color legend
         trace="none",         # turns off trace lines inside the heat map
         margins =c(12,9),     # widens margins around plot
         color= brewer.pal(9,"RdPu"),       # use on color palette defined earlier
         border_color=NA,
         cluster_rows = T,
         cluster_cols = F,
         #scale = "column",
         fontsize = 4,
         #breaks= c(0, 0.0002, 0.2, 0.5, 1, 2, 3, 4,  10, 20),
         #colors top 50: (1, 5, 10, 15, 30, 50, 80, 130, 200),
         breaks= c(0, 0.0002, 1, 5, 10, 15, 30, 50, 80, 130, 500),
         # breaks=seq(0, 100, length.out=10),   # enable color transition at specified limits
         #dendrogram="row",     # only draw a row dendrogram
         #Colv="NA"            # turn off column clustering
         main              = "Top 50",
         show_rownames     = TRUE,
         #annotation_row = mimic,
         cellwidth = 4, cellheight = 4)


################################
################################
#pie charts
piedata<-read.csv("piechart.csv")
library(ggplot2)
piedata$Class <- factor(piedata$Class, levels = c("U", "Ar", "Ac",
"Al","Am","H","M","O","SE","ST","T","C","S","P"))
pie<- ggplot(data=piedata, aes(x=" ", y=Value, group=Class, colour=Class, fill=Class)) +
  geom_bar(width = 1, size=0.1, stat = "identity", position="fill", color="white") +
  scale_fill_manual(values=c("#585859","#41a629","#e6352d","#be0925","#ec7405","#7c4d25",
"#fcea0d","#f8b334","#e20079","#23bae2","#0b71b6","#a20d59","#b07f48","#97bf0d"))+

  coord_polar("y", start=0) +
  facet_grid(.~ Species) +
  theme_void()  +guides(fill=guide_legend(ncol=1))
pie
pdf(file="piecharts.pdf", width=10, height=4)
pie
dev.off()
```

10. Experimental

10.1 General Information

Unless otherwise stated, all chemicals were obtained from commercial suppliers and used without further purification. All air or moisture-sensitive reactions were conducted in flame dried glassware under nitrogen atmosphere. Conventionally dried solvents were distilled before use. Purification of synthetic compounds was performed by column chromatography with silica (silica gel 60, particle size 0.040–0.063 mm, mesh 230–440 ASTM, Fluka) using ethyl acetate, pentane, and diethyl ether as solvents. Thin layer chromatography was performed using silica coated plates Polygram SIL G/UV254 (Macherey & Nagel) with molybdatophosphoric acid (10 % in ethanol) for detection. ^{1}H NMR- and ^{13}C NMR spectra were acquired with the following instruments (Bruker): AV II-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C), DRX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C), AV III-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) and AV II-600 (600 MHz for ^{1}H and 150 MHz for ^{13}C). Tetramethylsilane was used as an internal standard (TMS, δ = 0 ppm). Multiplicities of the protons are described as singlets (s), doublets (d), triplets (t), quartets (q), quintets (quint), sextets (sext), septets (sept), or multiplets (m). GC/MS analyses of synthetic products were performed with a GC HP6890/MSD HP5973 combination (Hewlett Packard) and natural samples were analyzed with a GC 7890A/MSD 5975C combination (Agilent Technologies). Mass spectrometry was performed in electron ionization mode (EI) with 70 eV. Fused-silica capillary columns HP-5MS (Agilent Technologies, 30 m, 0.25 mm i.d., 0.25 µm film thickness) were used with helium as the carrier gas. EI-HRMS spectra were obtained by GC/MS under the following conditions: An Agilent 6890 gas chromatograph was equipped with a 30 m analytical column (Phenomenex ZB1-MS, 30 m × 0.25 mm ID, tf = 0.25 µm). A split injection port at 270 °C was used for sample introduction, and the split ratio was set to 10:1. The temperature program was 50 °C (3 min)–10 °C/min–310 °C (3 min). Helium was used as carrier gas and was set to a 1.0 mL/min flow rate (constant flow mode). The transfer line was kept at 270 °C. High-resolution mass spectra were obtained with a JMS-T100GC (GCAccuTOF, JEOL, Japan) time-of-flight mass spectrometer in electron ionization (EI) mode at 70 eV JEOL MassCenter workstation software. The source and transfer line temperatures were set at 200 and 270 °C, respectively. The detector voltage was set at 2050 V. The acquisition range was from *m/z* 41 to 600 with a spectrum recording interval of 0.4 s. The system was tuned with PFK to achieve a resolution of 6000 (FWHM) at *m/z* 292.9824. CI-HRMS spectra were obtained by GC/MS under the following conditions: A TRACE 1310 Series GC coupled to an Exactive GC Orbitrap mass spectrometer (Thermo Scientific) was used. Samples were injected (1 µL) in the gas chromatograph system with a split inlet of 1:20 and an injector temperature of 270 °C. The system was equipped with a ZB5MS capillary column (30 m × 25 mm ID × 0.25 µm f.t.; Phenomenex, Aschaffenburg, Germany), and helium was used as carrier gas at a flow rate of 1.0 mL/min. The temperature gradient used was

50 °C (3 min)–10 °C/min–310 °C (3 min). Mass spectral data were acquired in full scan mode (40–650 *m*/*z*), and the automatic gain control (AGC) was set to 1E6. The ion source and transfer line temperatures were set at 250 and 290 °C, respectively. The analyzer resolution settings were 60,000 at *m*/*z* 200 (full width at half-maximum (FWHM)) and 2 microscans averaging. For positive chemical ionization (CI) high-purity methane (99.995%; Westfalen AG) as CI-reagent gas was used at a flow rate of 1.7 mL/min. Internal lock masses (149.02332 or 207.03235) were used for spectrum mass correction. Xcalibur software V 4.4 (Thermo Scientific) was used for data processing. Enantiomer separation of methyl (*E*)-2,3-dihydrofarnesoate (8b) was achieved by GC/FID on 7820A gas chromatographs (Agilent) using hydrogen as carrier gas and a Hydrodex-6-TBDMS capillary column (Macherey-Nagel, 25 m × 0.25 mm × 0.25 µm film thickness). A starting temperature of 100 °C was held for 225 min. Then, the temperature was raised at a rate of 20 °C/min to 180 °C and was hold for 5 min. IR spectra were acquired with a Tensor 27 (Bruker) by using the diamond-ATR-technique. GC/IR analysis was performed using a GC 7890B (Agilent Technologies) gas chromatograph coupled to a DiscovIR instrument (Dani Instruments). The samples eluting from the GC column were deposited on a cooled ZnSe disc at – 40 °C using a disc speed of 4 mm/min. The gas chromatograph was equipped with an Agilent HP-5 column (30 m, 0.25 mm i.d., 0.25 µm film thickness) with helium as the carrier gas. The resulting infrared spectra had a resolution of 4 wavenumbers and were normalized and processed using GRAMS/AI 9.2 software by Thermo Fisher Scientific Inc. modified with workbooks provided by Dani Instruments. The peaks are listed with wave numbers in cm^{-1}. Intensities are described with s (strong), m (medium), w (weak) and br (broad). Optical rotation was measured with an Anton Paar MCP-150 polarimeter with 100 mm cuvettes at a wavelength of 589 nm. Melting points were aquired with a Büchi Melting Point M-560.

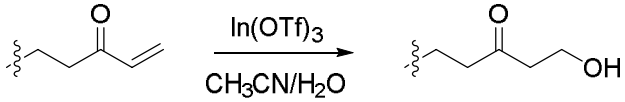
Readily detectable contaminants were excluded from analyses. They were detected by analyzing control samples treated as natural samples, but did not contain any biological material. Such compounds are typically plasticizers such as phthalates or adipates, sunscreen compounds [3], insect repellents, trace mineral oils, or a few unknown compounds occurring in many samples of insects.

10.2 Derivatization of natural extracts

Transesterifications with trimethyl sulfonium hydroxide (TMSH) in methanol were performed according to Müller et al.[4] The location of double bonds were identified by dimethyl disulfide (DMDS) derivatization according to Schulz et al.[5]

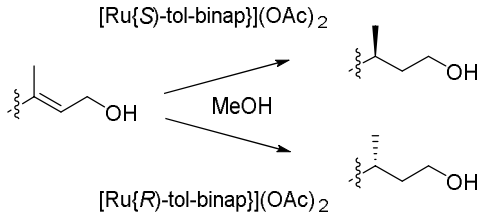
10.3 General Synthetic Procedures

General Procedure 1 (GP1) – Hydration of **α**,**β**-Unsaturated Ketones



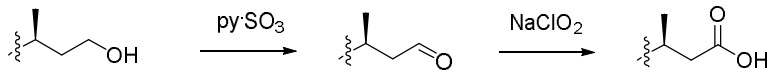
A solution of an α,β-unsaturated ketone (1.0 mmol, 1.0 equiv.) and $In(OTf)_3$ (0.20 mmol, 20 mol%) in CH_3CN/H_2O (1 mL/2 mL) was stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After removal of the solvents, column chromatography (pentane/Et_2O) yielded the desired β-hydroxyl carbonyl compound.[6]

General Procedure 2 (GP2) – Enantioselective Hydrogenation



The catalyst diacetato-[(*R*)-(+)-2,2′-bis-(di-*p*-tolylphosphino)-1,1′–binaphthyl]-ruthenium(II) ([Ru{*R*)-tol-binap}](OAc)$_2$, 0.02 equiv.) was added to a solution of the terpene alcohol (1.0 equiv.) in degassed MeOH (1.95 mL/mmol) in a 40 mL cylindrical glass vial equipped with a magnetic stir bar. The vial was transferred to a Teflon-lined high pressure hydrogenation autoclave, which was first purged with nitrogen and then filled with hydrogen gas (35 bar). The solution was stirred for 5 h at room temperature. Afterwards the crude reaction mixture was stirred for 15 min with added silica (1000 wt.-% of catalyst) and activated charcoal (400 wt.-% of starting material), and filtered through a short silica plug. The resulting (*S*)-alcohol was used without further purification. The corresponding (*R*)-alcohol was obtained when [Ru{*S*)-tol-binap}](OAc)$_2$ was used.[7]

General Procedure 3 (GP3) – Synthesis of 2,3-Dihydroterpene aldehydes



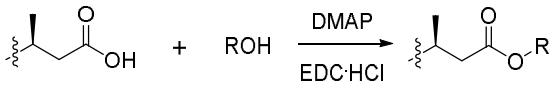
Pyridine·SO_3 (3.0 equiv.) was dissolved in DMSO (11.2 mL/mmol) and stirred for 15 min at room temperature. This solution was added to a solution of a 2,3-dihydroterpene alcohol (1.0 equiv.) and NEt_3 (10.0 equiv.) in CH_2Cl_2 (33.7 mL/mmol) at 0 °C. The reaction was terminated after stirring for 3 h at room temperature by adding water (22.5 mL/mmol). The aqueous phase was extracted with

CH_2Cl_2 (3 x 50 mL) and the combined organic phases were dried with anhydrous Na_2SO_4. After removal of the solvents the aldehyde was directly used in the next reaction step.[7]

General Procedure 4 (GP4) – of 2,3-Dihydroterpenoic acids

A 2,3-dihydroterpene aldehyde (1.0 equiv.) was added to a solution of NaH_2PO_4 (10.0 equiv.), 2-methyl-2-butene (4.5 mL/mmol), *tert*-butanol (3.37 mL/mmol) in THF (11.33 mL/mmol) and water (11.23 mL/mmol). Sodium chlorite (5.0 equiv.) was added partially in three equal portions every 45 min. After the last portion was added, the mixture was stirred for an additional hour. Water (50 mL) was added and the aqueous phase was extracted with ethyl acetate (3 x 75 mL). The combined organic phases were washed with brine (50 mL), dried with anhydrous Na_2SO_4 and the solvents were removed. The obtained acid was used without further purification in the following esterifications. Yields were determined after esterification.[7]

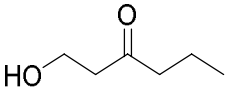
General Procedure 5 (GP5) – Esterification



4-(Dimethylamino)pyridine (DMAP, 1 equiv.) was added to a solution of the required alcohol (1.5 equiv.) and acid (1.0 equiv.) in CH_2Cl_2 (18.9 mL/mmol). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide-HCl (EDC-HCl, 1.5 equiv.) was added at 0 °C and the mixture was stirred for one hour at 0 °C and then overnight at room temperature. The reaction was neutralized with a saturated solution of $NaHCO_3$ (5 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were washed with brine (5 mL) and dried with anhydrous Na_2SO_4. After removal of the solvents, column chromatography (pentane/Et_2O) yielded the desired esters.

10.3. Synthetic Procedures

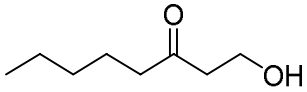
1-Hydroxyhexan-3-one (40)



Following GP1, 40 was prepared using 1-hexen-3-one (196.3 mg, 2.0 mmol) and $In(OTf)_3$ (224.8 mg, 0.4 mmol, 20 mol%), affording the desired compound after column chromatography (pentane/Et_2O, 2:1) as a colorless oil (218.1 mg, 1.88 mmol, 94%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, 3H), 1.63 (sext, $^3J_{H,H}$ = 7.5 Hz, 2H), 2.43 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 2.67 (t, $^3J_{H,H}$ = 5.4 Hz, 2H), 3.85 (t, $^3J_{H,H}$ = 5.4 Hz, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.8, 17.2, 44.4, 45.4, 58.0, 212.0 ppm. MS (EI, 70 eV): *m*/*z* (%): 116 (<1, $[M]^+$), 88 (25), 73 (94), 71 (78), 58 (8), 55 (16), 45 (21), 43 (100), 42 (14), 41 (24), 39 (11). IR (GC-IR): $\tilde{\nu}$ = 3425 (m), 3366 (br. s), 2968 (m), 2957 (s), 2929 (m), 2909 (m), 2876 (m), 1699 (s), 1470 (m), 1449 (m), 1425 (m), 1407 (m), 1046 (s), 1005 (w) cm^{-1}.

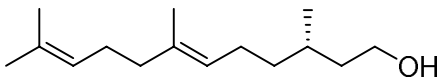
1-Hydroxyoctane-3-one (S1)



Following GP1, S1 was prepared using 1-octen-3-one (506.4 mg, 4.0 mmol) and $In(OTf)_3$ (449.6 mg, 0.8 mmol, 20 mol%), affording the desired compound after column chromatography (pentane/Et_2O, 2:1) as a light yellow oil (331.4 mg, 2.30 mmol, 57%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 3H), 1.21–1.39 (m, 4H), 1.54–1.64 (m, 2H), 2.44 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 2.59 (br. s, 1H), 2.67 (t, $^3J_{H,H}$ = 5.4 Hz, 2H), 3.85 (t, $^3J_{H,H}$ = 5.4 Hz, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0, 22.6, 23.5, 31,5, 43.5, 44.4, 58.0, 212.2 ppm. MS (EI, 70 eV): *m*/*z* (%): 144 (<1, $[M]^+$), 99 (63), 88 (70), 73 (85), 71 (53), 70 (49), 55 (38), 45 (19), 43 (100), 42 (20), 41 (24). IR (GC-IR): $\tilde{\nu}$ = 3430 (br. s), 3366 (br. s), 2964 (s), 2954 (s), 2929 (s), 2872 (s), 2860 (s), 1701 (s), 1472 (m), 1424 (m), 1390 (m), 1064 (m), 1047 (m), 976 (m) cm^{-1}.

(*S*,*E*)-2,3-Dihydrofarnesol ((*S*)-6)



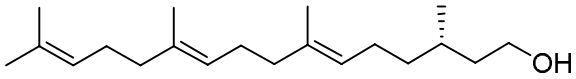
According to GP2, (*S*)-6 was prepared using (*E*,*E*)-farnesol (2.0 g, 8.99 mmol) and [Ru{*R*)-tol-binap}]$(OAc)_2$ (161.6 mg, 0.18 mmol), affording the desired compound as a light yellow oil (1.73 g, 7.73 mmol, 86%).

(*R*,*E*)-2,3-Dihydrofarnesol ((*R*)-6) was obtained in 97% yield by using [Ru{*S*)-tol-binap}]$(OAc)_2$ (161.6 mg, 0.18 mmol) as the catalyst.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.13–1.44 (m, 5H), 1.60 (s, 6H), 1.68 (s, 3H), 1.95–2.10 (m, 6H), 3.62–3.75 (m, 2H), 5.06–5.13 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 16.1, 17.8,

19.7, 25.5, 25.8, 26.9, 29.3, 37.9, 39.9, 40.1, 61.4, 124.5, 124.7, 131.4, 135.0 ppm. MS (EI, 70 eV): *m*/*z* (%): 224 (<1, $[M]^+$), 181 (24), 123 (47). 109 (16), 99 (14), 95 (36), 81 (59), 69 (100), 67 (21), 55 (22), 41 (40). IR (GC-IR): $\tilde{\nu}$ = 3282 (br. s), 2963 (br. s). 2931 (br. s), 2920 (br. s), 2873 (br. s), 2857 (br. s), 1452 (m), 1377 (m), 1107 (w), 1060 (m), 1013 (w), 956 (w), 837 (w), 740 (w) cm^{-1}. (*S*)-6: $[\alpha]_D^{25.0}$ = - 3.42 (*c* = 1.03 in CH_2Cl_2). (*R*)-6: $[\alpha]_D^{25.0}$ = +3.25 (*c* = 1.02 in CH_2Cl_2).

(*S*)-Geranylcitronellol ((*S*)-7)

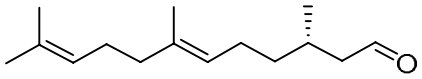


According to GP2, (*S*)-7 was prepared using (*E*,*E*)-geranylfarnesol obtained from annato seeds (1.16 g, 4.0 mmol) and [Ru{*R*}-tol-binap}](OAc)$_2$ (71.8 mg, 0.08 mmol), affording the desired compound as a light yellow oil (661.7 mg, 72.26 mmol, 57%).

(*R*)-Geranylcitronellol ((*R*)-7) was obtained in 54% yield by using [Ru{*S*)-tol-binap}](OAc)$_2$ (17.9 mg, 0.02 mmol) as the catalyst.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.10–1.44 (m, 5H), 1.60 (s, 9H), 1.68 (s, 3H), 1.95–2.11 (m, 10H), 3.61–3.74 (m, 2H), 5.07–5.14 (m, 3H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 16.1, 16.2, 17.8, 19.7, 25.5, 25.8, 26.8, 26.9, 29.4, 37.4, 39.9, 40.1, 61.4, 124.4, 124.5, 124.7, 131.4, 135.0, 135.1 ppm. MS (EI, 70 eV): *m*/*z* (%): 292 (<1, $[M]^+$), 136 (13), 121 (12). 95 (27), 93 (15), 81 (61), 69 (100), 68 (19), 67 (26), 55 (21), 41 (47). IR (GC-IR): $\tilde{\nu}$ = 3282 (br. s), 2962 (br. s), 2927 (br. s), 2871 (br. s), 2860 (br. s), 1451 (m), 1378 (m), 1109 (w), 1061 (m), 1017 (w), 843 (w), 739 (w) cm^{-1}. (*S*)-7: $[\alpha]_D^{25.0}$ = -3.43 (*c* = 1.02 in CH_2Cl_2). (*R*)-7: $[\alpha]_D^{25.0}$ = +3.17 (*c* = 1.01 in CH_2Cl_2).

(*S*,*E*)-2,3-Dihydrofarnesal ((*S*)-S2)



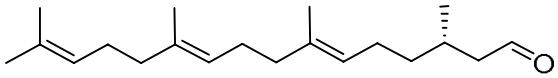
According to GP3, (*S*)-S2 was prepared using (*S*)-6 (1.0 g, 4.46 mmol) affording the desired compound as a light yellow oil (882.6 mg, 3.97 mmol, 89%).

(*R*,*E*)-2,3-Dihydrofarnesol ((*R*)-S2) was obtained in 91% yield by using (*R*)-6 (600 mg, 2.67 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.13–1.44 (m, 3H), 1.60 (s, 6H), 1.68 (s, 3H), 1.96–2.13 (m, 6H), 2.23 (ddd, $^3J_{H,H}$ = 2.6 Hz, 7.9 Hz, 15.9 Hz, 1H), 2.41 (ddd, $^3J_{H,H}$ = 2.1 Hz, 5.6 Hz, 15.9 Hz, 1H) 5.05–5.12 (m, 2H), 9.75 (t, $^3J_{H,H}$ = 2.3 Hz, 1H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 16.1, 17.8, 20.0, 25.4, 25.8, 26.8, 27.9, 37.1, 39.8, 51.1, 124.1, 124.4, 131.5, 135.5, 203.2 ppm. MS (EI, 70 eV):

m/*z* (%): 222 (<1, $[M]^+$), 179 (28), 161 (11), 123 (26). 109 (31), 93 (13), 81 (16), 69 (100), 67 (20), 55 (14), 41 (40). IR (GC-IR): $\tilde{\nu}$ = 2965 (s), 2917 (br. s), 2853 (s), 2723 (m), 1726 (s), 1450 (m), 1381 (m), 1108 (w), 986 (w), 838 (w) cm^{-1}. (*S*)-S2: $[\alpha]_D^{25.0}$ = -10.94 (*c* = 1.03 in CH_2Cl_2). (*R*)-S2: $[\alpha]_D^{25.0}$ = +11.63 (*c* = 0.98 in CH_2Cl_2).

(*S*)-Geranylcitronellal ((*S*)-S3)

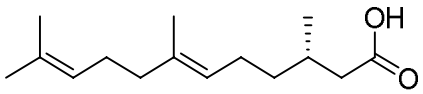


According to GP3, (*S*)-S3 was prepared using (*S*)-7 (614.0 mg, 2.1 mmol) and Pyridine·SO_3 (1.00 g, 6.3 mmol) affording the desired compound as a light yellow oil (515.0 mg, 1.77 mmol, 84%).

(*R*)-Geranylcitronellal ((*R*)-S3) was obtained in 83% yield by using (*R*)-7 (120 mg, 0.4 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.21–1.44 (m, 2H), 1.60 (s, 10H), 1.68 (s, 3H), 1.94–2.13 (m, 10H), 2.23 (ddd, $^3J_{H,H}$ = 2.6 Hz, 7.9 Hz, 15.9 Hz, 1H), 2.41 (ddd, $^3J_{H,H}$ = 2.1 Hz, 5.6 Hz, 15.9 Hz, 1H), 5.06–5.13 (m, 3H), 9.75 (dd, $^3J_{H,H}$ = 2.1 Hz, 2.6 Hz, 1H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 16.2, 17.8, 20.0, 25.5, 25.8, 26.7, 26.9, 28.0, 37.1, 39.8, 39.9, 51.1, 124.1, 124.3, 124.5, 131.4, 135.1, 135.6, 203.2 ppm. MS (EI, 70 eV): *m*/*z* (%): 290 (<1, $[M]^+$), 136 (12), 109 (14). 95 (14), 93 (13), 81 (39), 69 (100), 68 (13), 67 (22), 55 (16), 41 (47). IR (GC-IR): $\tilde{\nu}$ = 2966 (s), 2916 (br. s), 2852 (s), 2724 (m), 1726 (s), 1449 (s), 1382 (s), 1100 (w), 986 (w), 842 (w) cm^{-1}. (*S*)-S3: $[\alpha]_D^{25.0}$ = -6.54 (*c* = 1.04 in CH_2Cl_2). (*R*)-S3: $[\alpha]_D^{25.0}$ = +11.14 (*c* = 1.05 in CH_2Cl_2).

(*S*,*E*)-2,3-Dihydrofarnesoic acid ((*S*)-8a)



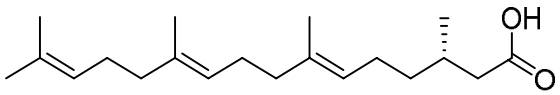
According to GP4, (*S*)-8a was prepared using (*S*)-S2 (850 mg, 3.82 mmol) affording the desired compound as a colorless oil.

(*R*,*E*)-2,3-Dihydrofarnesoic acid ((*R*)-8a) was obtained by using (*R*)-S2 (500 mg, 2.25 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.20–1.45 (m, 3H), 1.60 (s, 6H), 1.68 (s, 3H), 1.92–2.10 (m, 6H), 2.16 (dd, $^3J_{H,H}$ = 8.2 Hz, 14.9 Hz, 1H), 2.38 (dd, $^3J_{H,H}$ = 5.8 Hz, 14.9 Hz, 1H), 5.06–5.13 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 16.1, 17.8, 19.7, 25.4, 25.8, 26.8, 30.0, 36.8, 39.9, 41.6, 124.2, 124.5, 131.5, 135.4, 179.3 ppm. MS (EI, 70 eV, MSTFA-Derivativ): *m*/*z* (%):.310 (<1, $[M]^+$), 267 (35), 177 (38), 143 (17), 123 (27), 117 (18), 109 (100), 75 (36), 73 (70), 69 (58), 41 (25). IR (GC-IR): $\tilde{\nu}$ = 2967 (br. s), 2919 (br. s), 2854 (s), 2686 (br. m), 2577 (br. w), 1706 (s), 1442 (br. m), 1382 (w), 1307

(m), 1232 (w), 1109 (w), 852 (br. m), 834 (w) cm^{-1}. (*S*)-8a: $[\alpha]_D^{25.0}$ = -3.46 (*c* = 0.93 in CH_2Cl_2). (*R*)-8a: $[\alpha]_D^{25.0}$ = +4.72 (*c* = 0.98 in CH_2Cl_2).

(*S*)-Geranylcitronellic acid ((*S*)-9a)

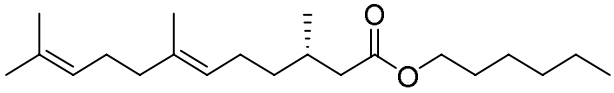


According to GP4, (*S*)-9a was prepared using (*S*)-S3 (460 mg, 1.58 mmol) affording the desired compound as a colorless oil.

(*R*)-Geranylcitronellic acid ((*R*)-9 a) was obtained by using (*R*)-S3 (180 mg, 0.62 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.21–1.45 (m, 3H), 1.60 (s, 9H), 1.68 (s, 3H), 1.94–2.09 (m, 10H), 2.15 (dd, $^3J_{H,H}$ = 8.2 Hz, 14.9 Hz, 1H), 2.38 (dd, $^3J_{H,H}$ = 5.8 Hz, 14.9 Hz, 1H), 5.06–5.13 (m, 3H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 16.1, 17.8, 19.8, 25.5, 25.9, 26.8, 26.9, 30.0, 36.9, 39.9, 41.6, 124.2, 124.3, 124.6, 131.4, 135.1, 135.4, 179.4 ppm. MS (EI, 70 eV, MSTFA-Derivativ): *m*/*z* (%):.378 (<1, $[M]^+$), 121 (17), 109 (41), 95 (15), 93 (20), 81 (37), 75 (32), 73 (61), 69 (100), 67 (19), 41 (38). IR (GC-IR): $\tilde{\nu}$ = 2967 (s), 2922 (br. s), 2853 (s), 2703 (br. m), 2577 (br. m), 1707 (s), 1445 (m), 1382 (m), 1306 (m), 1232 (w), 1164 (w), 1109 (w), 951 (br. m), 837 (w) cm^{-1}. (*S*)-9a: $[\alpha]_D^{25.0}$ = -3.76 (*c* = 1.41 in CH_2Cl_2). (*R*)-9a: $[\alpha]_D^{25.0}$ = +4.46 (*c* = 0.88 in CH_2Cl_2).

Hexyl (*S*,*E*)-2,3-dihydrofarnesoate ((*S*)-8j)



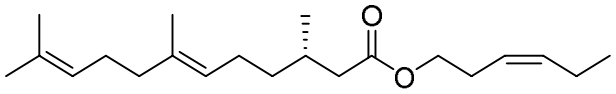
According to GP5, (*S*)-8j was prepared using (*S*)-8a (50 mg, 0.21 mmol) and 1-hexanol (32.2 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 40:1) as a colorless oil (55.1 mg, 0.17 mmol, 81%).

Hexyl (*R*,*E*)-2,3-dihydrofarnesoate ((*R*)-8j) was obtained by using (*R*)-8a (134 mg, 0.56 mmol) and 1-hexanol (85.8 mg, 0.84 mmol) after stirring overnight and column chromatography (pentane/Et_2O, 40:1) in 76% yield (137 mg, 0.42 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 0.95 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.18–1.40 (m, 9H), 1.59 (s, 6H), 1.68 (s, 3H), 1.91–2.09 (m, 8H), 2.11 (dd, $^3J_{H,H}$ = 8.2 Hz, 14.5 Hz, 1H), 2.31 (dd, $^3J_{H,H}$ = 5.9 Hz, 14.5 Hz, 1H), 4.06 (t, $^3J_{H,H}$ = 6.7 Hz, 2H), 5.06–5.12 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 14.1, 16.1, 17.8, 19.8, 22.7, 25.5, 25.8, 25.8, 26.9, 28.8, 30.3, 31.6, 36.9, 39.9, 42.0, 64.5, 124.3, 124.5, 131.4,

135.3, 173.5 ppm. HRMS (EI-TOF) *m/z*: $[M+H]^+$ Calculated for $C_{21}H_{38}O_2$ 322.2872; Found 322.2885. MS (EI, 70 eV): *m/z* (%): 322 (<1, $[M]^+$), 279 (67), 177 (39). 123 (35), 109 (100), 95 (19), 81 (17), 69 (99), 67 (16), 43 (32), 41 (36). IR (GC-IR): $\tilde{\nu}$ = 2959 (br. s), 2931 (br. s), 2860 (s), 1736 (s), 1456 (m), 1378 (m), 1288 (w), 1190 (m), 1152 (m), 1101 (w), 988 (w), 836 (w), 730 (w) cm^{-1}. (*S*)-8j: $[\alpha]_D^{25.0}$ = -3.20 (*c* = 1.03 in CH_2Cl_2). (*R*)-8j: $[\alpha]_D^{25.0}$ = +2.93 (*c* = 1.13 in CH_2Cl_2).

(Z)-3-Hexenyl (*S*,*E*)-2,3-dihydrofarnesoate ((*S*)-8i)

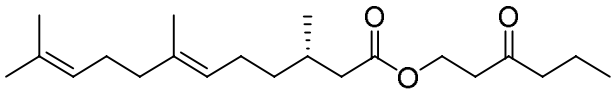


According to GP5, (*S*)-8i was prepared using (*S*)-8a (50 mg, 0.21 mmol) and (*Z*)-3-hexenol (31.6 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 60:1) as a colorless oil (54.2 mg, 0.18 mmol, 84%).

(Z)-3-Hexenyl (*R*,*E*)-2,3-dihydrofarnesoate ((*R*)-8i) was obtained by using (*R*)-8a (134 mg, 0.56 mmol) and (*Z*)-3-hexenol (84.2 mg, 0.84 mmol) after stirring overnight and column chromatography (pentane/Et_2O, 60:1) in 74% yield (134 mg, 0.42 mmol).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (d, $^3J_{H,H}$ = 6.7 Hz, 3H), 0.97 (d, $^3J_{H,H}$ = 7.5 Hz, 3H), 1.18–1.40 (m, 2H), 1.59 (s, 6H), 1.68 (s, 3H), 1.91–2.09 (m, 9H), 2.11 (dd, $^3J_{H,H}$ = 8.2 Hz, 14.5 Hz, 1H), 2.31 (dd, $^3J_{H,H}$ = 5.9 Hz, 14.5 Hz, 1H), 2.34–2.40 (m, 2H), 4.07 (t, $^3J_{H,H}$ = 6.9 Hz, 2H), 5.06–5.12 (m, 2H), 5.28–5.35 (m, 1H), 5.46–5.53 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 14.4, 16.1, 17.8, 19.8, 20.8, 25.5, 25.8, 26.9, 27.0, 30.2, 36.9, 39.9, 42.0, 63.9, 124.0, 124.3, 124.5, 131.5, 134.6, 135.3, 173.4 ppm. HRMS (EI-TOF) *m/z*: $[M+H]^+$ Calculated for $C_{21}H_{36}O_2$ 320.2715; Found 320.2701. MS (EI, 70 eV): *m/z* (%): 320 (<1, $[M]^+$), 277 (34), 195 (22). 123 (35), 109 (62), 83 (70), 82 (24), 69 (100), 67 (37), 55 (67), 41 (48). IR (GC-IR): $\tilde{\nu}$ = 3011 (m), 2964 (br. s), 2930 (br. s), 2874 (br. s), 2854 (br. s), 1736 (s), 1455 (m), 1384(m), 1288 (m), 1218 (m), 1188 (m), 1153 (m), 1108 (w), 1071 (w), 1044 (w), 1003 (w), 839 (w), 735 (w) cm^{-1}. (*S*)-8i: $[\alpha]_D^{25.0}$ = -2.72 (*c* = 1.03 in CH_2Cl_2). (*R*)-8i: $[\alpha]_D^{25.0}$= +2.44 (*c* = 1.06 in CH_2Cl_2).

3-Oxohexyl (*S*,*E*)-2,3-dihydrofarnesoate ((*S*)-8l)

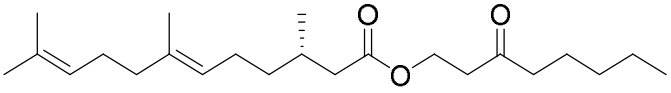


According to GP5, (*S*)-8l was prepared using (*S*)-8a (50 mg, 0.21 mmol) and f19 (36.6 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 20:1) as a colorless oil (40.7 mg, 0.17 mmol, 57%).

3-Oxohexyl (*R*,*E*)-2,3-dihydrofarnesoate ((*R*)-8l) was obtained by using (*R*)-8a (134 mg, 0.56 mmol) and 40 (97.6 mg, 0.84 mmol) after stirring overnight and column chromatography (pentane/Et_2O, 20:1) in 64% yield (121 mg, 0.36 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, $^3J_{H,H}$ = 7.5 Hz, 3H), 0.92 (d, $^3J_{H,H}$ = 6.4 Hz, 3H), 1.16–1.38 (m, 3H), 1.57–1.67 (m, 10H), 1.89–2.07 (m, 7H), 2.08 (dd, $^3J_{H,H}$ = 8.3 Hz, 14.6 Hz, 1H), 2.29 (dd, $^3J_{H,H}$ = 5.9 Hz, 14.6 Hz, 1H), 2.41 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 4.33 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 5.06–5.10 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 13.8, 16.1, 17.2, 17.8, 19.7, 25.4, 25.8, 26.8, 30.2, 36.9, 39.9, 41.5, 41.8, 45.2, 59.3, 124.2, 124.5, 131.4, 135.3, 173.2, 208.0 ppm. HRMS (EI-TOF) *m*/*z*: $[M+H]^+$ Calculated for $C_{21}H_{36}O_3$ 336.2817; Found 336.2788. MS (EI, 70 eV): *m*/*z* (%): 336 (<1, $[M]^+$), 293 (33), 177 (82). 151 (49), 123 (75), 109 (100), 81 (33), 69 (94), 55 (35), 43 (39), 41 (46). IR (GC-IR): $\tilde{\nu}$ = 2963 (br. s), 2928 (br. s), 2879 (br. s), 2854 (br. s), 1734 (s), 1457 (m), 1378 (m), 1288 (m), 1191 (m), 1154 (m), 1129 (m), 1108 (w), 991 (w), 897 (w), 835 (w) cm^{-1}. (*S*)-8i: $[\alpha]_D^{25.0}$ = -1.85 (*c* = 0.81 in CH_2Cl_2). (*R*)-8i: $[\alpha]_D^{25.0}$ = +2.51 (*c* = 1.08 in CH_2Cl_2).

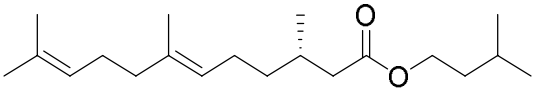
3-Oxooctyl (*S*,*E*)-2,3-dihydrofarnesoate ((*S*)-8n)



According to GP5, (*S*)-8n was prepared using (*S*)-8a (50 mg, 0.21 mmol) and S1 (36.6 mg, 0.32 mmol) affording the desired compound after stirring overnight and column chromatography (pentane/Et_2O, 10:1) as a colorless oil (268 mg, 0.74 mmol, 74%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 3H), 0.92 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.14–1.40 (m, 8H), 1.59 (s, 6H), 1.67 (s, 3H), 1.87–2.08 (m, 7H), 2.08 (dd, $^3J_{H,H}$ = 8.2 Hz, 14.6 Hz, 1H), 2.29 (dd, $^3J_{H,H}$ = 5.8 Hz, 14.7 Hz, 1H), 2.42 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 2.72 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 4.33 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 5.05–5.11 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 14.1, 16.1, 17.8, 19.7, 22.6, 23.4, 25.5, 25.8, 26.9, 30.2, 31.5, 36.9, 39.9, 41.5, 41.8, 43.4, 59.3, 124.3, 124.5, 131.5, 135.3, 173.2, 208.2 ppm. HRMS (CI-Orbitrap) *m*/*z*: $[M+H]^+$ Calculated for $C_{23}H_{40}O_3$ 364.2977; Found 364.2976. MS (EI, 70 eV): *m*/*z* (%): 364 (<1, $[M]^+$), 177 (93), 151 (50). 123 (73), 109 (100), 81 (32), 70 (74), 69 (97), 55 (89), 43 (54), 41 (53). IR (GC-IR): $\tilde{\nu}$ = 2959 (br. s), 2931 (br. s), 2870 (br. s), 2859 (br. s), 1734 (s), 1705 (s), 1468 (m), 1424 (m), 1378 (s), 1326 (m), 1300 (m), 1197 (m), 1158 (m), 1130 (m), 1108 (m), 1070 (w), 1010 (w), 981 (m), 838 (w), 735 (w) cm^{-1}. (*S*)-8n: $[\alpha]_D^{25.0}$ = -1.73 (*c* = 1.10 in CH_2Cl_2).

3-Methylbutyl (*S*,*E*)-2,3-dihydrofarnesoate ((*S*)-8h)

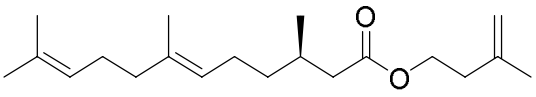


According to GP5, (*S*)-8h was prepared using (*S*)-8a (50 mg, 0.21 mmol) and 3-methylbutanol (27.8 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 50:1) as a colorless oil (55.9 mg, 0.18 mmol, 86%).

3-Methylbutyl (*R*,*E*)-2,3-dihydrofarnesoate ((*R*)-8h) was obtained by using (*R*)-8a (83.4 mg, 0.35 mmol) and 3-methylbutanol (46.3 mg, 0.53 mmol) after stirring overnight and column chromatography (pentane/Et_2O, 50:1) in 48% yield (51.4 mg, 0.17 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, $^3J_{H,H}$ = 6.6 Hz, 6H), 0.94 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.11–1.42 (m, 3H), 1.51 (q, $^3J_{H,H}$ = 6.8 Hz, 2H), 1.60 (s, 6H), 1.68 (s, 3H), 1.88–2.08 (m, 7H), 2.10 (dd, $^3J_{H,H}$ = 8.1 Hz, 14.5 Hz, 1H), 2.31 (dd, $^3J_{H,H}$ = 5.9 Hz, 14.5 Hz, 1H), 4.10 (t, $^3J_{H,H}$ = 6.9 Hz, 2H), 5.06–5.12 (m, 2H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 16.1, 17.8, 19.8, 22.6, 25.2, 25.5, 25.8, 26.9, 30.2, 36.9, 37.5, 39.9, 42.1, 63.0, 124.3, 124.5, 131.5, 135.3, 173.5 ppm. HRMS (EI-TOF) *m*/*z*: $[M+H]^+$ Calculated for $C_{20}H_{36}O_2$ 308.2715; Found 308.2704. MS (EI, 70 eV): *m*/*z* (%): 308 (<1, $[M]^+$), 265 (51), 177 (37). 123 (33), 109 (92), 95 (20), 71 (39), 69 (100), 67 (21), 43 (67), 41 (50). IR (GC-IR): $\tilde{\nu}$ = 3079 (w), 2967 (br. s), 2916 (br. s), 2854 (s), 1735 (s), 1654 (m), 1451 (m), 1377 (m), 1289 (m), 1189 (m), 1152 (m), 1108 (w), 1036 (w), 985 (w), 892 (m), 837 (w) cm^{-1}. (*S*)-8h: $[\alpha]_D^{25.0}$ = -2.96 (*c* = 1.08 in CH_2Cl_2). (*R*)-8h: $[\alpha]_D^{25.0}$ = +3.08 (*c* = 1.04 in CH_2Cl_2).

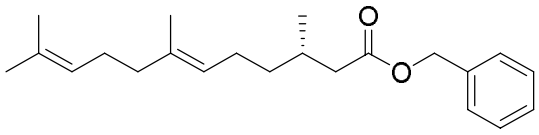
Isoprenyl (*R*,*E*)-2,3-dihydrofarnesoate ((*R*)-8f)



According to GP5, (*R*)-8f was prepared using (*R*)-8a (200 mg, 0.84 mmol) and isoprenol (109 mg, 1.26 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 40:1) as a colorless oil (94.8 mg, 0.31 mmol, 37%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.15–1.41 (m, 2H), 1.59 (s, 6H), 1.68 (s, 3H), 1.75 (s, 3H), 1.90–2.14 (m, 8H), 2.27–2.40 (m, 3H), 4.19 (t, $^3J_{H,H}$ = 6.8 Hz, 2H), 4.72–4.84 (m, 2H), 5.05–5.12 (m, 2H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 16.1, 17.8, 19.8, 22.6, 25.5, 25.8, 26.9, 30.2, 36.9, 36.9, 39.9, 42.0, 62.5, 112.3, 124.3, 124.5, 131.4, 135.2, 141.8, 173.4 ppm. HRMS (EI-TOF) *m*/*z*: $[M+H]^+$ Calculated for $C_{20}H_{34}O_2$ 306.2559; Found 306.2563. MS (EI, 70 eV): *m*/*z* (%): 306 (<1, $[M]^+$), 263 (10), 123 (15). 109 (27), 95 (7), 81 (10), 69 (100), 68 (11), 67 (17), 53 (7), 41 (43). IR (GC-IR): $\tilde{\nu}$ = 3077 (w), 2967 (br. s), 2917 (br. s), 2854 (s), 1735 (s), 1654 (m), 1451 (m), 1378 (m), 1289 (m), 1188 (m), 1152 (m), 1109 (w), 1036 (w), 985 (w), 892 (m), 836 (w) cm^{-1}. (*R*)-8f: $[\alpha]_D^{25.0}$ = +3.20 (*c* = 1.00 in CH_2Cl_2).

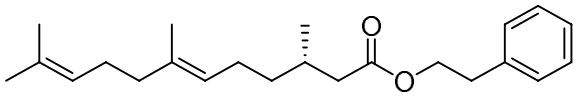
Benzyl (*S*,*E*)-2,3-dihydrofarnesoate ((*S*)-8o)



According to GP5, (*S*)-8o was prepared using (*S*)-8a (50 mg, 0.21 mmol) and benzylalcohol (34.1 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 50:1) as a colorless oil (60.4 mg, 0.18 mmol, 88%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, $^3J_{H,H}$ = 6.7 Hz, 3H), 1.16–1.42 (m, 2H), 1.58 (s, 3H), 1.60 (s, 3H), 1.67 (s, 3H), 1.75 (s, 3H), 1.94–2.07 (m, 6H), 2.17 (dd, $^3J_{H,H}$ = 8.1 Hz, 14.6 Hz, 1H), 2.37 (dd, $^3J_{H,H}$ = 5.9 Hz, 14.6 Hz, 1H), 5.05–5.09 (m, 2H), 5.11 (s, 2H), 7.29–7.37 (m, 5H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 16.1, 17.8, 19.8, 25.4, 25.8, 26.8, 30.2, 36.9, 39.9, 41.9, 66.2, 124.3, 124.5, 128.3, 128.3, 128.7, 131.5, 135.3, 136.3, 173.2 ppm. HRMS (CI-Orbitrap) *m*/*z*: $[M-H]^+$ Calculated for $C_{22}H_{31}O_2$ 327.2330; Found 327.2320. MS (EI, 70 eV): *m*/*z* (%): 328 (<1, $[M]^+$), 237 (10), 109 (13). 95 (10), 92 (10), 91 (100), 81 (14), 69 (81), 67 (14), 65 (10), 41 (35). IR (GC-IR): $\tilde{\nu}$ = 3091 (w), 3065 (w), 3036 (w), 2965 (br. s), 2922 (br. s), 2853 (s), 1734 (s), 1499 (m), 1456 (m), 1383 (m), 1359 (w), 1287 (m), 1261 (m), 1216 (m), 1187 (m), 1149 (m), 1108 (m), 987 (m), 837 (w), 739 (m) cm^{-1}. (*S*)-8o: $[\alpha]_D^{25.0}$ = -0.82 (*c* = 1.22 in CH_2Cl_2).

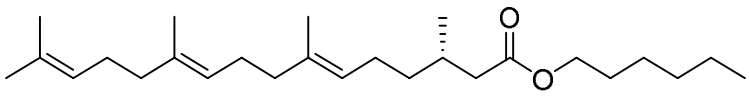
2-Phenylethyl (*S*,*E*)-2,3-dihydrofarnesoate ((*S*)-8p)



According to GP5, (*S*)-8p was prepared using (*S*)-8a (50 mg, 0.21 mmol) and 2-phenylethanol (38.5 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 60:1) as a colorless oil (60.7 mg, 0.18 mmol, 84%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.14–1.40 (m, 2H), 1.61 (s, 6H), 1.68 (s, 3H), 1.88–2.12 (m, 7H), 2.10 (dd, $^3J_{H,H}$ = 8.1 Hz, 14.6 Hz, 1H), 2.31 (dd, $^3J_{H,H}$ = 5.9 Hz, 14.6 Hz, 1H), 2.94 (t, $^3J_{H,H}$ = 7.1 Hz, 2H), 4.30 (t, $^3J_{H,H}$ = 7.1 Hz, 2H), 5.06–5.12 (m, 2H), 7.20–7.33 (m, 5H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 16.1, 17.8, 19.7, 25.5, 25.8, 26.8, 30.2, 35.3, 36.9, 39.9, 41.9, 64.8, 124.3, 124.5, 126.7, 128.6, 129.0, 131.5, 135.3, 138.0, 173.3 ppm. HRMS (CI-Orbitrap) *m*/*z*: $[M+H]^+$ Calculated for $C_{23}H_{34}O_2$ 342.2559; Found 342.2555. MS (EI, 70 eV): *m*/*z* (%): 342 (<1, $[M]^+$), 123 (8), 109 (13), 106 (9). 105 (100), 104 (19), 91 (10), 79 (12), 69 (46), 67 (11), 41 (31). IR (GC-IR): $\tilde{\nu}$ = 3061 (w), 3030 (w), 2962 (br. s), 2925 (br. s), 2875 (s), 2855 (s), 1734 (s), 1606 (w), 1498 (w), 1455 (m), 1384 (m), 1362 (w), 1287 (m), 1188 (m), 1151 (m), 1110 (m), 1089 (m), 1001(m), 836 (w), 752 (m) cm^{-1}. (*S*)-8p: $[\alpha]_D^{25.0}$ = -3.12 (*c* = 1.25 in CH_2Cl_2).

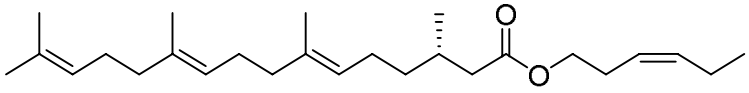
Hexyl (*S*)-geranylcitronellate ((*S*)-9j)



According to GP5, (*S*)-9j was prepared using (*S*)-9a (64.4 mg, 0.21 mmol) and 1-hexanol (32.2 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 50:1) as a colorless oil (60.0 mg, 0.15 mmol, 73%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 0.95 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 1.16–1.42 (m, 9H), 1.60 (s, 10H), 1.68 (s, 3H), 1.91–2.08 (m, 11H), 2.10 (dd, $^3J_{H,H}$ = 8.2 Hz, 14.5 Hz, 1H), 2.31 (dd, $^3J_{H,H}$ = 5.9 Hz, 14.5 Hz, 1H), 4.06 (t, $^3J_{H,H}$ = 6.7 Hz, 2H), 5.06–5.13 (m, 3H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 14.1, 16.1, 16.1, 17.8, 19.8, 22.7, 25.5, 25.8, 25.8, 26.8, 26.9, 28.8, 30.3, 31.6, 36.9, 39.9, 42.0, 64.5, 124.4, 124.5, 131.4, 135.1, 135.3, 173.5 ppm. HRMS (EI-TOF) *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{46}O_2$ 390.3498; Found 390.3489. MS (EI, 70 eV): *m/z* (%): 390 (<1, $[M]^+$), 136 (32), 123 (22). 121 (25), 109 (49), 95 (22), 93 (22), 81 (43), 69 (100), 43 (27), 41 (28). IR (GC-IR): $\tilde{\nu}$ = 2958 (br. s), 2929 (br. s), 2857 (s), 1735 (s), 1670 (w), 1454 (m), 1378 (m), 1287 (w), 1189 (m), 1151 (m), 1108 (w), 1089 (w), 1070 (w), 988 (w), 839 (w), 728 (w) cm^{-1}. (*S*)-9j: $[\alpha]_D^{25.0}$ = -3.01 (*c* = 1.03 in CH_2Cl_2).

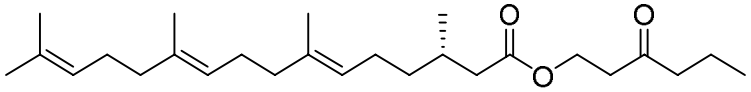
(*Z*)-3-Hexenyl (*S*)-geranylcitronellate ((*S*)-b11i)



According to GP5, (*S*)-9i was prepared using (*S*)-9a (64.4 mg, 0.21 mmol) and (*Z*)-3-hexenol (31.6 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 60:1) as a colorless oil (54.2 mg, 0.18 mmol, 84%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, $^3J_{H,H}$ = 6.6 Hz, 3H), 0.97 (d, $^3J_{H,H}$ = 7.5 Hz, 3H), 1.18–1.40 (m, 2H), 1.59 (s, 6H), 1.68 (s, 3H), 1.90–2.14 (m, 14H), 2.28–2.41 (m, 3H), 4.07 (t, $^3J_{H,H}$ = 6.9 Hz, 2H), 5.06–5.13 (m, 3H), 5.26–5.36 (m, 1H), 5.45–5.55 (m, 1H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 14.4, 16.1, 16.2, 17.8, 19.8, 20.8, 25.5, 25.8, 26.8, 26.9, 30.2, 36.9, 39.9, 42.0, 63.9, 124.0, 124.3, 124.4, 124.5, 131.4, 134.6, 135.1, 135.3, 173.4 ppm. HRMS (CI-Orbitrap) *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{44}O_2$ 388.3351; Found 388.3338. MS (EI, 70 eV): *m/z* (%): 388 (<1, $[M]^+$), 109 (20), 95 (15). 93 (17), 83 (40), 82 (15), 81 (41), 69 (100), 67 (35), 55 (61), 41 (49). IR (GC-IR): $\tilde{\nu}$ = 3010 (m), 2964 (br. s), 2930 (br. s), 2876 (br. s), 2853 (br. s), 1736 (s), 1452 (m), 1384(m), 1288 (m), 1218 (m), 1189 (m), 1153 (m), 1109 (w), 1090 (w), 1071 (w), 1045 (w), 1002 (w), 838 (w), 796 (w), 737 (w) cm^{-1}. (*S*)-9i: $[\alpha]_D^{25.0}$ = -3.01 (*c* = 1.03 in CH_2Cl_2).

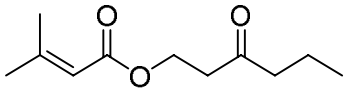
3-Oxohexyl (*S*)-geranylcitronellate ((*S*)-9l)



According to GP5, (*S*)-9l was prepared using (*S*)-9a (50 mg, 0.21 mmol) and f19 (36.6 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 20:1) as a colorless oil (40.7 mg, 0.17 mmol, 57%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89–0.94 (m, 6H), 1.15–1.40 (m, 3H), 1.58–1.63 (m, 10H), 1.67 (s, 3H), 1.92–2.12 (m, 12H), 2.29 (dd, $^3J_{H,H}$ = 5.8 Hz, 14.6 Hz, 1H), 2.41 (t, $^3J_{H,H}$ = 7.3 Hz, 2H), 4.33 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 5.06–5.12 (m, 3H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): 13.8, 16.1, 16.2, 17.2, 17.8, 19.7, 25.5, 25.9, 26.8, 26.9, 30.2, 36.9, 39.9, 41.5, 41.8, 45.3, 59.3, 124.2, 124.3, 124.5, 131.4, 135.1, 135.4, 173.2, 208.0 ppm. HRMS (EI-TOF) *m*/*z*: $[M+H]^+$ Calculated for $C_{26}H_{44}O_3$ 404.3290; Found 404.3288. MS (EI, 70 eV): *m*/*z* (%): 404 (<1, $[M]^+$), 177 (23), 136 (37). 123 (33), 121 (34), 109 (44), 93 (26), 81 (55), 69 (100), 43 (26), 41 (31). IR (ATR): $\tilde{\nu}$ = 2962 (br. s), 2920 (br. s), 2856 (br. s), 1731 (s), 1449 (m), 1378 (m), 1292 (m), 1256 (m), 1185 (m), 1152 (m), 1093 (m), 990 (w), 833 (w), 737 (w), 540 (m) cm^{-1}. (*S*)-9i: $[\alpha]_D^{25.0}$ = -2.52 (*c* = 1.03 in CH_2Cl_2).

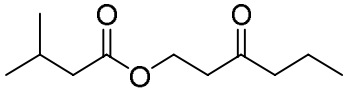
3-Oxohexyl 3-methyl-2-butenoate (S4)



According to GP5, S4 was prepared using 3-methyl-2-butenoic acid (75.1 mg, 0.75 mmol) and 40 (58.1 mg, 0.50 mmol) affording the desired compound after stirring overnight and column chromatography (pentane/Et_2O, 5:1) as a colorless oil (30.4 mg, 0.15 mmol, 50%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, $^3J_{H,H}$ = 7.4 Hz, 3H), 1.61 (sex, $^3J_{H,H}$ = 7.4 Hz, 2H), 1.88 (d, $^3J_{H,H}$ = 1.3 Hz, 3H), 2.14 (d, $^3J_{H,H}$ = 1.3 Hz, 3H), 2.41 (t, $^3J_{H,H}$ = 7.3 Hz, 2H), 2.73 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 4.35 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 5.63 (sep, $^3J_{H,H}$ = 1.3 Hz, 1H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 13.8, 17.2, 20.4, 27.5, 41.7, 45.3, 58.7, 115.8, 157.3, 166.6, 208.4 ppm. HRMS (EI-TOF) *m*/*z*: $[M+H]^+$ Calculated for $C_{11}H_{18}O_3$ 198.1256; Found 198.1259. MS (EI, 70 eV): *m*/*z* (%): 198 (<1, $[M]^+$), 100 (13), 99 (21). 84 (8), 83 (100), 82 (48), 71 (27), 55 (32), 43 (27), 41 (9), 39 (10). IR (GC-IR): $\tilde{\nu}$ = 2964 (s), 2938 (s), 2916 (m), 2878 (m), 1717 (s), 1653 (m), 1448 (m), 1379 (m), 1350 (m), 1233 (s), 1153 (s), 1130 (m), 1108 (w), 1084 (m), 994 (w), 853 (m) cm^{-1}.

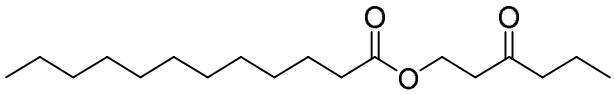
3-Oxohexyl 3-methylbutanoate (33)



According to GP5, 33 was prepared using 3-methylbutanoic acid (53.6 mg, 0.53 mmol) and 40 (40.7 mg, 0.35 mmol) affording the desired compound after stirring overnight and column chromatography (pentane/Et_2O, 30:1) as a colorless oil (62.7 mg, 0.31 mmol, 89%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, $^3J_{H,H}$ = 7.4 Hz, 3H), 0.92 (d, $^3J_{H,H}$ = 6.6 Hz, 6H), 1.60 (sex, $^3J_{H,H}$ = 7.4 Hz, 2H), 1.98–2.11 (m, 1H), 2.13–2.15 (m, 2H), 2.40 (t, $^3J_{H,H}$ = 7.3 Hz, 2H), 2.71 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 4.32 (t, $^3J_{H,H}$ = 6.3 Hz, 2H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 13.8, 17.2, 22.5, 25.8, 41.5, 43.4, 45.2, 59.3, 173.1, 208.1 ppm. HRMS (EI-TOF) *m/z*: $[M+H]^+$ Calculated for $C_{11}H_{20}O_3$ 200.1412; Found 200.1410. MS (EI, 70 eV): *m/z* (%): 200 (<1, $[M]^+$), 99 (26), 85 (87). 71 (100), 70 (13), 57 (55), 55 (44), 43 (77), 42 (17), 41 (46), 39 (17). IR (GC-IR): $\tilde{\nu}$ = 2959 (s), 2934 (s), 2875 (m), 1731 (s), 1699 (s), 1469 (m), 1425 (m), 1366 (m), 1299 (w), 1199 (m), 1115 (m), 999 (w), 964 (w), 889 (w), 833 (w), 772 (w), 725 (w) cm^{-1}.

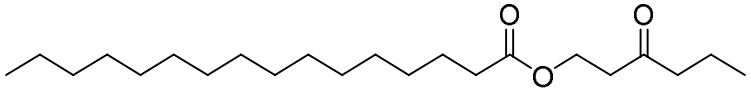
3-Oxohexyl dodecanoate (17l)



According to GP5, 17l was prepared using dodecanoic acid (105 mg, 0.53 mmol) and 40 (40.7 mg, 0.35 mmol) affording the desired compound after stirring overnight and column chromatography (pentane/Et_2O, 30:1) as a colorless solid (64.9 mg, 0.22 mmol, 63%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{H,H}$ = 6.7 Hz, 3H), 0.91 (t, $^3J_{H,H}$ = 7.4 Hz, 3H), 1.25 (s, 16H), 1.53–1.67 (m, 4H), 2.26 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 2.41 (t, $^3J_{H,H}$ = 7.2 Hz, 2H), 2.71 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 4.33 (t, $^3J_{H,H}$ = 6.3 Hz, 2H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 13.8, 14.3, 17.2, 22.8, 25.0, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0, 41.5, 45.3, 59.4, 173.9, 208.1 ppm. HRMS (EI-TOF) *m/z*: $[M+H]^+$ Calculated for $C_{18}H_{34}O_3$ 298.2508; Found 298.2519. MS (EI, 70 eV): *m/z* (%): 298 (<1, $[M]^+$), 183 (51), 117 (14). 99 (63), 98 (50), 84 (17), 71 (100), 57 (23), 55 (47), 43 (60), 41 (29). IR (GC-IR): $\tilde{\nu}$ = 2959 (s), 2920 (s), 2874 (m), 2850 (s), 1739 (s), 1701 (s), 1464 (m), 1385 (m), 1330 (m), 1299 (m), 1270 (m), 1239 (s), 1211 (s), 1187 (s), 1130 (m), 1109 (w), 1089 (w), 1002 (w), 901 (w), 720 (w) cm^{-1}. Melting point: 26.5 °C.

3-Oxohexyl hexadecanoate (18l)



According to GP5, 18l was prepared using hexadecanoic acid (53.8 mg, 0.21 mmol) and 40 (32.2 mg, 0.32 mmol) affording the desired compound after 2 days stirring and column chromatography (pentane/Et_2O, 30:1) as a colorless solid (64.9 mg, 0.22 mmol, 63%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{H,H}$ = 6.8 Hz, 3H), 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 3H), 1.25 (s, 24H), 1.55–1.68 (m, 4H), 2.26 (t, $^3J_{H,H}$ = 7.4 Hz, 2H), 2.41 (t, $^3J_{H,H}$ = 7.3 Hz, 2H), 2.72 (t, $^3J_{H,H}$ = 6.3 Hz, 2H), 4.33 (t, $^3J_{H,H}$ = 6.3 Hz, 2H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 13.8, 14.3, 17.2, 22.8, 25.1, 29.3, 29.4, 29.5, 29.6, 29.8, 29.8, 29.8, 32.1, 41.5, 45.3, 59.4, 173.9, 208.1 ppm. HRMS (EI-TOF) *m*/*z*: $[M-H]^+$ Calculated for $C_{22}H_{41}O_3$ 353.3061; Found 353.3054. MS (EI, 70 eV): *m*/*z* (%): 354 (<1, $[M]^+$), 239 (12), 99 (46). 98 (50), 83 (19), 71 (61), 70 (21), 57 (14), 55 (100), 43 (39), 41 (19). IR (GC-IR): $\tilde{\nu}$ = 2958 (m), 2919 (s), 2873 (m), 2851 (s), 1738 (s), 1702 (m), 1464 (m), 1382 (m), 1331 (m), 1288 (m), 1266 (m), 1243 (s), 1211 (s), 1199 (s), 1183 (s), 1130 (m), 1102 (w), 1016 (w), 989 (w), 900 (w), 721 (w) cm^{-1}. Melting point: 47.0 °C.

5-Methylhex-4-enyl (Z)-9-octadecenoate (22k)

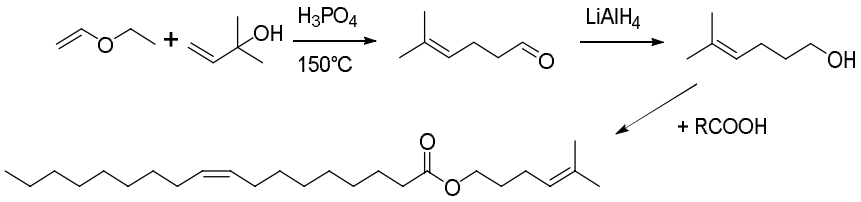


Figure S48. Synthesis of 5-hexen-4-enyl 9-octadecenoate (22k).

According to GP5, 22k was prepared using oleic acid (56.5 mg, 0.20 mmol) and 5-methylhex-4-en-1-ol (34.3 mg, 0.30 mmol), prepared according to Yonova et al.,[8] affording the desired compound after stirring overnight and column chromatography (pentane/Et_2O, 50:1) as a colorless oil (53.9 mg, 0.14 mmol, 71%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 3H), 1.25–1.30 (m, 20H), 1.59–1.70 (m, 10H), 1.97–2.08 (m, 6H), 2.29 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 4.05 (t, $^3J_{H,H}$ = 6.6 Hz, 2H), 5.09 (tquint, $^3J_{H,H}$ = 1.4 Hz, 7.2 Hz, 14.4 Hz, 1H), 5.29–5.40 (m, 2H) ppm. ^{13}C NMR (75.7 MHz, $CDCl_3$): 14.3, 17.8, 22.8, 24.5, 25.2, 25.8, 27.3, 27.4, 28.9, 29.3, 29.3, 29.5, 29.7, 29.8, 29.8, 29.9, 32.1, 34.6, 64.0, 123.4, 129.9, 130.1, 132.6, 174.1 ppm. HRMS (EI-TOF) *m*/*z*: $[M+H]^+$ Calculated for $C_{25}H_{46}O_2$ 378.3498; Found 378.3492. MS (EI, 70 eV): *m*/*z* (%): 378 (<1, $[M]^+$), 97 (13), 96 (100). 81 (46), 69 (19), 67 (9), 57 (6), 55 (34), 54 (6), 43 (12), 41 (22). IR (GC-IR): $\tilde{\nu}$ = 3005 (m), 2953 (m), 2919 (s), 2870 (m), 2853 (s), 1736 (s), 1473 (m), 1377 (w), 1335 (w), 1298 (w), 1254 (m), 1210 (m), 1176 (s), 1116 (w), 1035 (w), 832 (w), 720 (w) cm^{-1}.

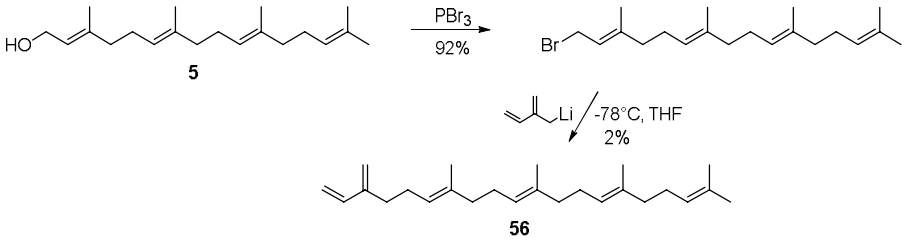
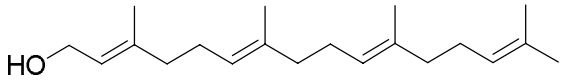


*Figure S49. Synthesis of (*E,E,E*)-β-geranylfarnesene (56).*

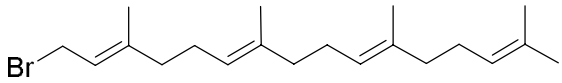
(2*E*,6*E*,10*E*)-3,7,11,15-Tetramethylhexadeca-2,6,10,14-tetraen-1-ol (5, geranylgeraniol)



Geranylgeraniol was isolated from Annatto seeds that contain about 80 % of this compound.[9]

R_f: 0.24 (pentane/diethyl ether 5:1). Yield 1.8 g (6.22 mmol), 96%. GC (BPX-5): *I* = 2215. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): δ = 1.60 (s, 3 H, CH_3), 1.61 (s, 6 H, 2 x CH_3), 1.68 (s, 3 H, CH_3), 1.96 – 2.13 (m, 12 H, 6 x CH_2), 4.15 (dd, $^3J_{H,H}$ = 6.9 Hz, 0.5 Hz, 2 H, CH_2), 5.11 (m, 3 H, 3 x CH), 5.42 (tq, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H, CH) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 15.99 (s, CH_3), 16.00 (s, CH_3), 16.3 (s, CH_3), 17.7 (s, CH_3), 25.7 (s, CH_3), 26.3 (s, CH_2), 26.6 (s, CH_2), 26.7 (s, CH_2), 39.5 (s, CH_2), 39.67 (s,CH_2), 39.70 (s, CH_2), 59.4 (s, CH_2), 123.3 (s, CH), 123.7 (s, CH), 124.2 (s, CH), 124.4 (s, CH), 131.3 (s, C_q), 134.9 (s, C_q), 135.4 (s, C_q), 139.8 (s, C_q) ppm. MS (EI, 70 eV): *m/z* (%): 290 (1) [M^+], 272 (2), 257 (2), 229 (4), 221 (4), 204 (5), 203 (6), 191 (4), 189 (8), 177 (6), 161 (12), 159 (5), 149 (8), 148 (6), 147 (11), 137 (15), 136 (20), 135 (21), 134 (8), 133 (13), 123 (18), 122 (10), 121 (28), 120 (8), 119 (18), 109 (22), 108 (9), 107 (38), 105 (20), 97 (6), 96 (5), 95 (35), 94 (12), 93 (50), 92 (10), 91 (31), 84 (6), 83 (10), 82 (11), 81 (66), 80 (11), 79 (32), 78 (6), 77 (24), 71 (10), 70 (15), 69 (100), 68 (41), 67 (55), 66 (6), 65 (13), 57 (20), 55 (32), 53 (36), 43 (19), 42 (10), 41 (90), 40 (9), 39 (27). IR (ATR): $\tilde{\nu}$ = 3325 (m), 2966 (m), 2917 (s), 2854 (m), 1668 (w), 1443 (m), 1238 (m), 999 cm^1 (s).

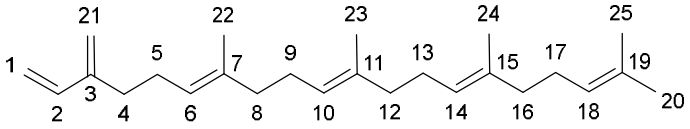
(2*E*,6*E*,10*E*)-1-Bromo-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraene (S5)



(2*E*,6*E*,10*E*)-Geranylgeraniol (1.8 g, 6.22 mmol)[9] was dissolved in abs. diethyl ether (7 mL) and cooled to -30°C according to the synthesis of GAMPE *et al*.[10] PBr_3 (0.3 mL, 3.11 mmol) was then added. The reaction mixture was stirred for 3h at rt, hydrolyzed with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and the solvent was removed. The crude product was used without further purification. Yield: 2.03 g (5.75 mmol), 92%. GC (BPX-5): *I* = 1917. ^{1}H-NMR (300 MHz, $CDCl_3$, TMS): δ = 1.60 – 1.78 (m, 15 H, 5 x CH_3), 1.98 – 2.15 (m, 12 H, 6 x CH_2), 4.02 (d, $^3J_{H,H}$ = 8.3 Hz,

2 H, CH_2), 5.09 (m, 3 H, 3 x CH), 5.53 (t, $^3J_{H,H}$ = 8.3 Hz, 1 H, CH) ppm. ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 15.96 (s, CH_3), 16.00 (s, CH_3), 16.04 (s, CH_3), 17.7 (s, CH_3), 25.7 (s, CH_3), 26.1 (s, CH_2), 26.6 (s, CH_2), 26.7 (s, CH_2), 29.7 (s, CH_2), 39.5 (s,CH_2), 39.6 (s, CH_2), 39.7 (s, CH_2), 120.5 (s, CH), 123.4 (s, CH), 124.2 (s, CH), 124.4 (s, CH), 131.2 (s, C_q), 134.9 (s, C_q), 135.6 (s, C_q), 143.6 (s, C_q) ppm. MS (EI, 70 eV): *m/z* (%): 353 (<1) [M^+], 272 (2), 257 (2), 229 (2), 203 (2), 187 (5), 161 (10), 159 (6), 147 (8), 135 (6), 134 (7), 133 (23), 132 (5), 123 (6), 121 (12), 120 (19), 119 (14), 109 (8), 107 (20), 105 (14), 95 (16), 94 (7), 93 (49), 92 (7), 91 (26), 81 (40), 79 (27), 77 (19), 70 (6), 69 (100), 68 (19), 67 (37), 65 (10), 55 (16), 53 (18), 41 (58), 39 (12).

(6*E*,10*E*,14*E*)-7,11,15,19-Tetramethyl-3-methylenheneicosa-1,6,10,14,18-pentaene (56, β-geranylfarnesene)



Diisopropylamine (0.8 mL, 5.65 mmol) was added to a solution of KOtBu (0.6 g, 5.65 mmol) in abs. THF (8 mL). The reaction mixture wss cooled to -78°C and *n*-BuLi (1.6 M, 3.8 mL) was added. After stirring for 10 min, isoprene (5.08 mmol, 0.5 mL) was added. Finally, after formation of a strong red color, (2*E*,6*E*,10*E*)-1-Bromo-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraene (S5, 2.0 g, 5.65 mmol) was added.[11] The reaction mixture was stirred for 24h at rt, hydrolyzed with water and acidified with 6 M H_2SO_4 solution. The aqueous phase was extracted three times with diethyl ether and the combined organic phases were washed several times with sat. NaCl solution. The organic phase was dried with $MgSO_4$ and the solvent was removed with a rotary evaporator. Single column chromatographic purification on silica gel yields the desired terpene 56 as a colorless oil. R_f: 0.4 (pentane). Yield: 30.6 mg (0.09 mmol), 2% (*E/Z*, 5:1). GC (BPX-5): *I* = 2382. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): δ = 1.43 (s, 3 H, H-22), 1.60 (s, 9 H, H-23, H-24, H-25), 1.68 (s, 3 H, H-20), 1.96 – 2.09 (m, 12 H, 6 x CH_2), 2.17 – 2.27 (m, 4 H, H-5, H-4), 5.00 (s, 1 H, H-21), 5.01 (s, 2 H, H-21), 5.04 – 5.18 (m, 5 H, H-1, H-6, H-10, H-14, H-18), 5.15 (d, $^2J_{H,H}$ = 17.6 Hz, 1 H, H-1b), 6.38 (dd, $^3J_{H,H}$ = 17.6 Hz, 10.8 Hz, 1 H, H-2) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 16.00 (s, CH_3, C-22), 16.02 (s, CH_3, C-23), 16.04 (s, CH_3, C-24), 17.7 (s, CH_3,C-25), 25.7 (s, CH_3, C-20), 26.6 (s, CH_2, C-13), 26.7 (s, CH_2, C-17), 26.76 (s, CH_2, C-9), 31.4 (s, CH_2, C-5), 39.7 (s, 4 x CH_2, C-16, C-12, C-8, C-4), 113.1 (s, CH_2, C-1), 115.7 (s, CH_2, C-21), 124.0 (s, CH, C-6), 124.2 (s, CH, C-14), 124.3 (s, CH, C-10), 124.4 (s, CH, C-18), 131.3 (s, C_q, C-19), 134.9 (s, C_q, C-15), 135.0 (s, C_q, C-11), 135.4 (s, C_q, C-7), 139.0 (s, CH, C-2), 146.1 (s, C_q, C-3) ppm. MS (EI, 70 eV): *m/z* (%): 340 (3) [M^+], 271 (2), 203 (3), 187 (5), 175 (3), 163 (2), 162 (3), 161 (13), 159 (6), 149 (4), 148 (5), 147 (11), 146 (4), 137 (6), 135 (10), 134 (7), 133 (18), 132 (4), 123 (8), 121 (15), 120 (12), 119 (13), 109 (10), 107 (23), 105 (13), 95 (21), 94 (7), 93 (45), 92 (5), 91 (22), 81 (50), 79 (24), 77 (14), 70 (7), 69 (100), 68 (22), 67 (31),

65 (7), 55 (16), 53 (13), 41 (41). IR (ATR): $\tilde{\nu}$ = 2963 (m), 2923 (s), 2857 (m), 1446 (s), 1378 (m), 891 cm^{1} (s). UV/VIS (PE): λ_{max}(log ε) = 284 (3.02), 197 (4.55).

11. NMR Spectra

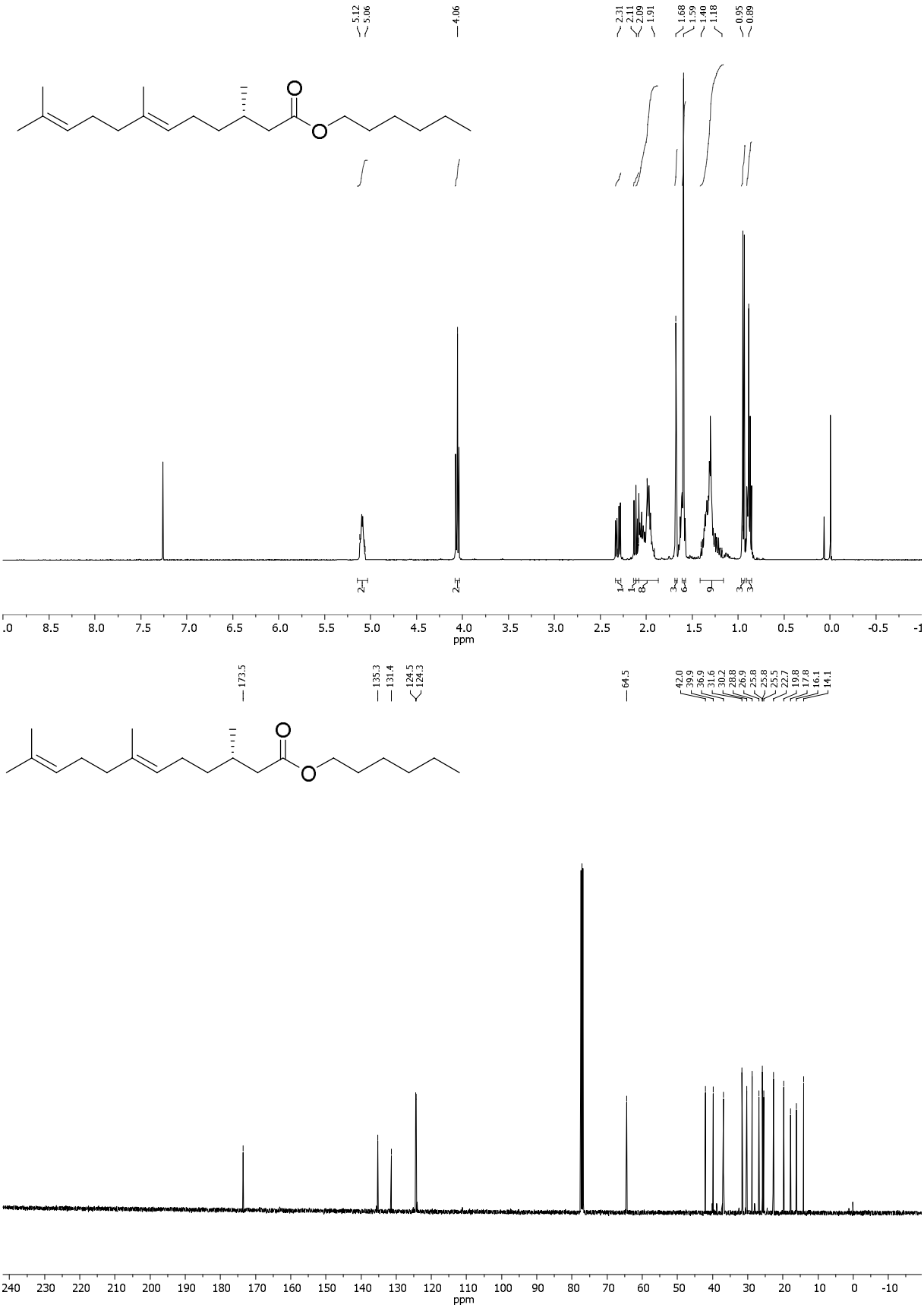


Figure S50. ^{1}H- and ^{13}C-NMR spectra of hexyl (S,E)-2,3-dihydrofarnesoate ((S)-8i).

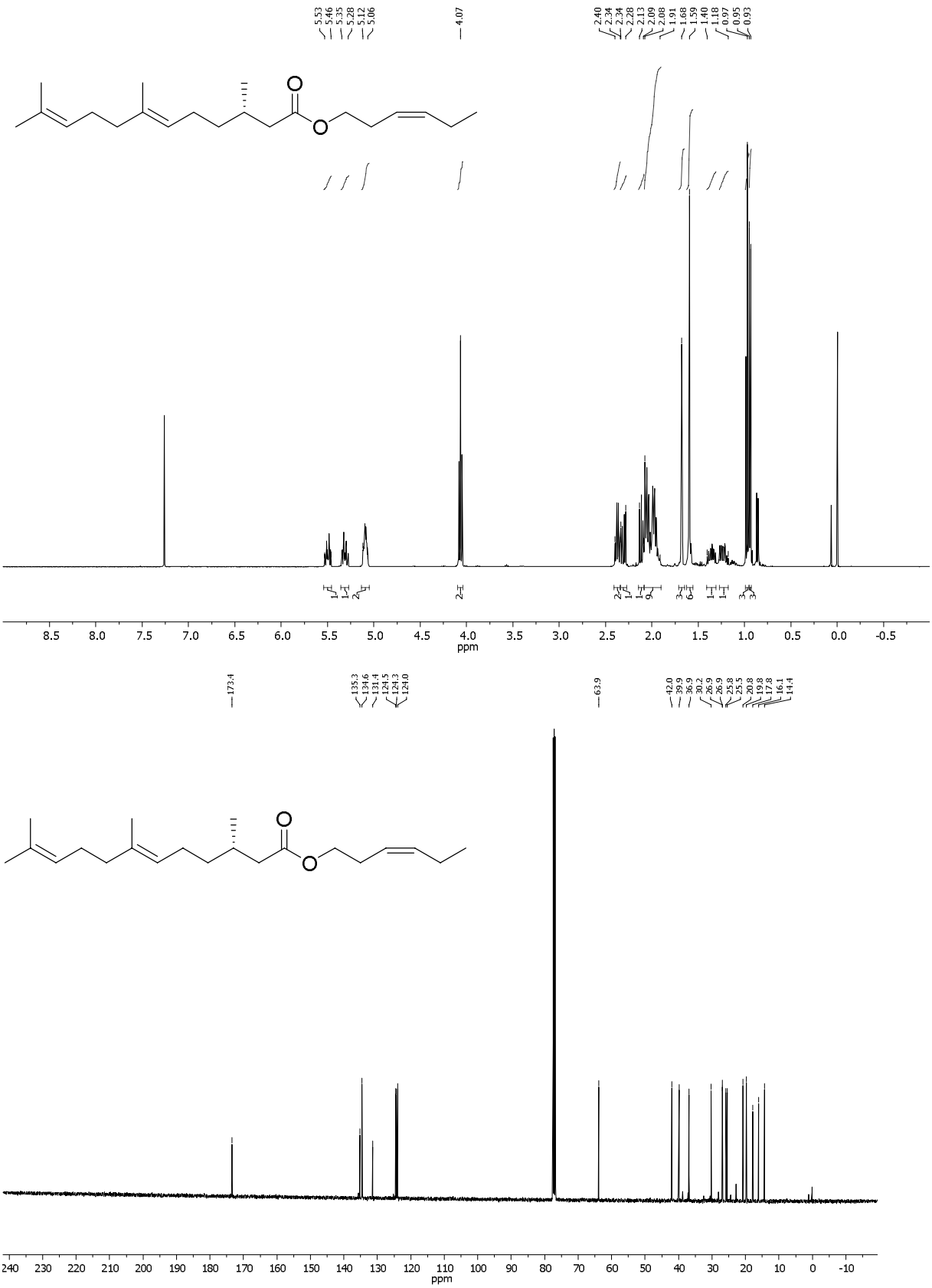


Figure S51. ^{1}H- and ^{13}C-NMR spectra of (Z)-3-hexenyl (S,E)-2,3-dihydrofarnesoate ((S)-8i).

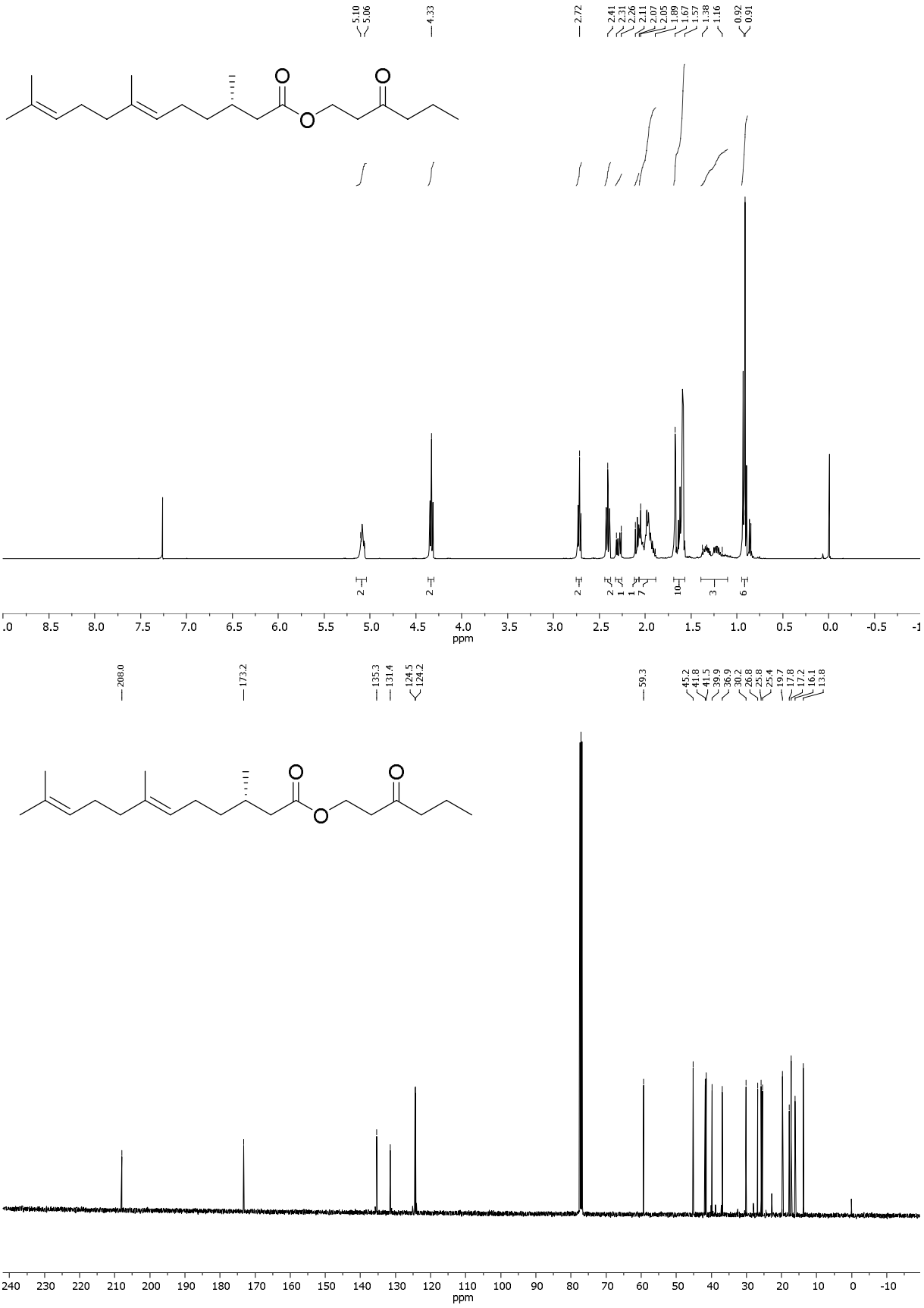


Figure S52. ^{1}H- and ^{13}C-NMR spectra of 3-oxohexyl (S,E)-2,3-dihydrofarnesoate ((S)-8l).

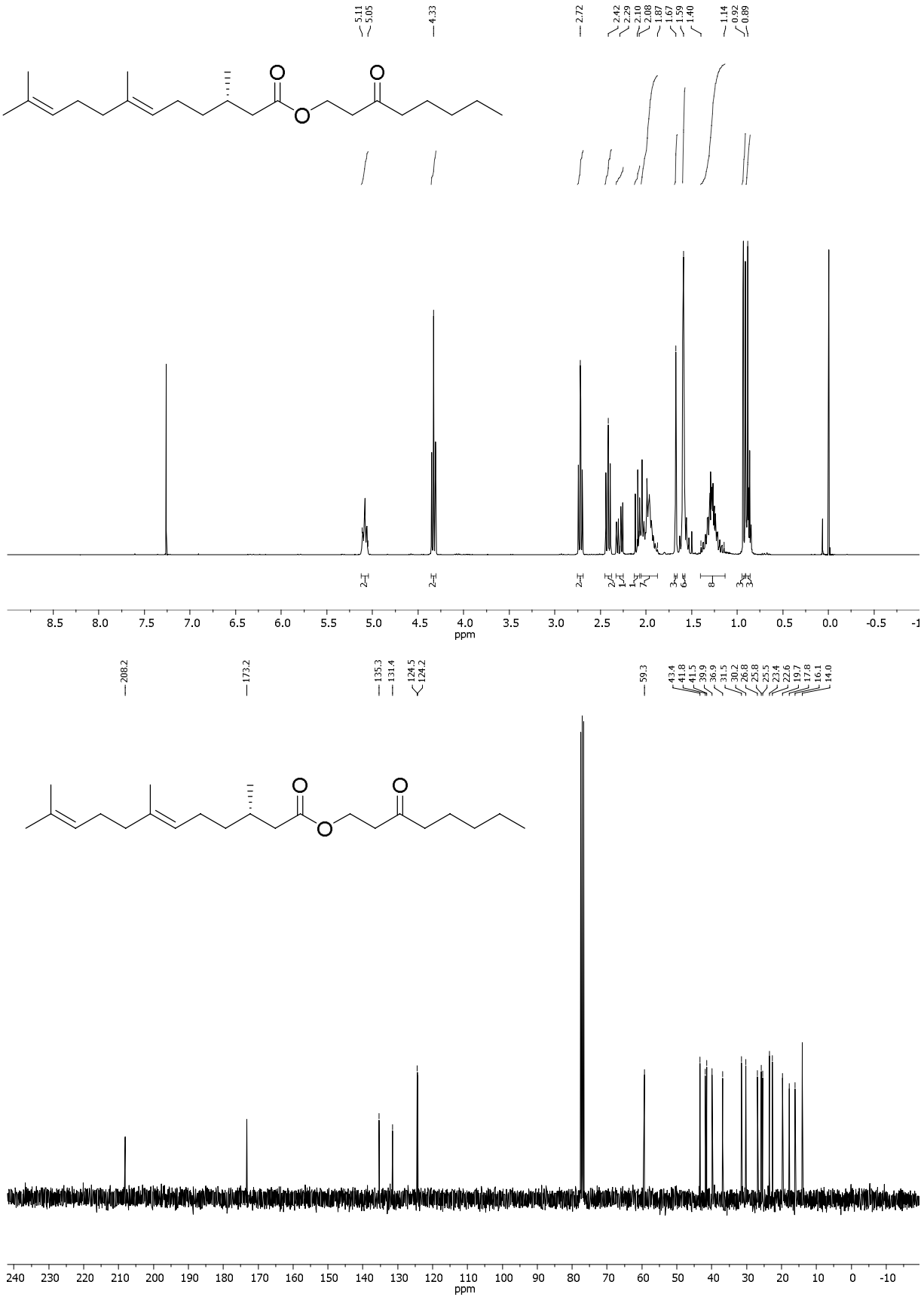


Figure S53. ^{1}H- and ^{13}C-NMR spectra of 3-oxooctyl (S,E)-2,3-dihydrofarnesoate ((S)-8n).

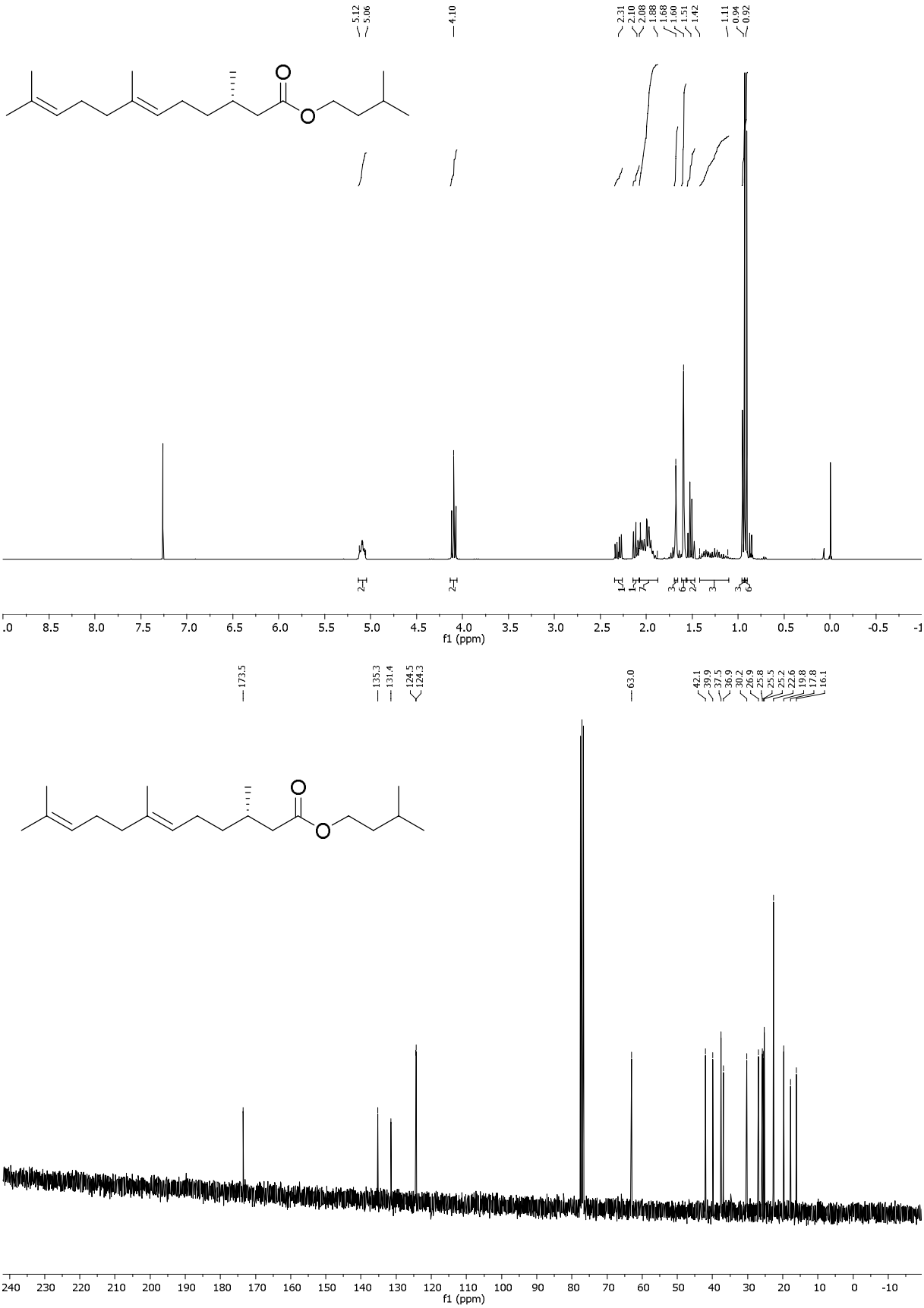


Figure S54. ^{1}H- and ^{13}C-NMR spectra of 3-methylbutyl (S,E)-2,3-dihydrofarnesoate ((S)-8h).

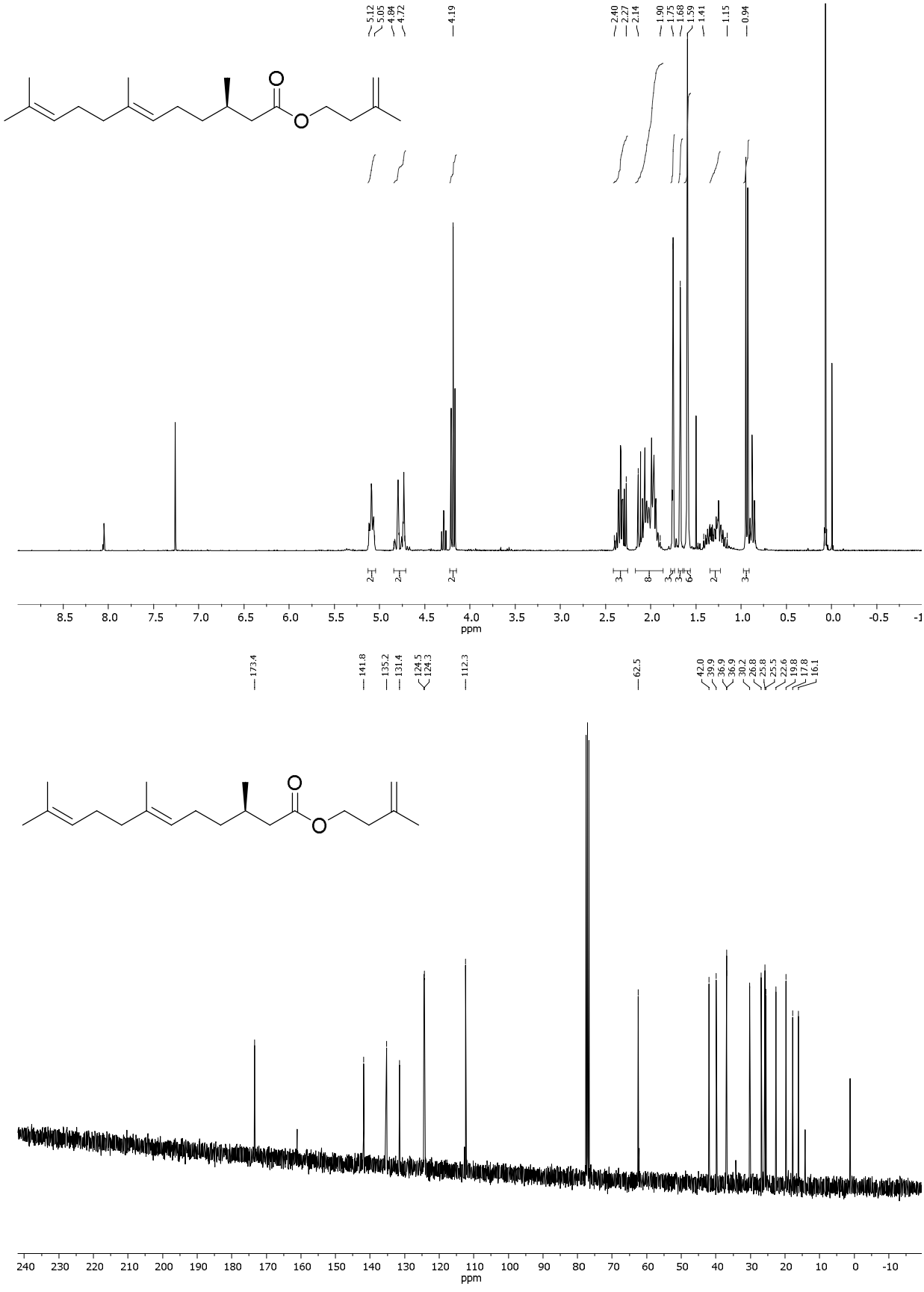


*Figure S55. ^{1}H- and ^{13}C-NMR spectra of isoprenyl (*R,E*)-2,3-dihydrofarnesoate ((R)-8f).*

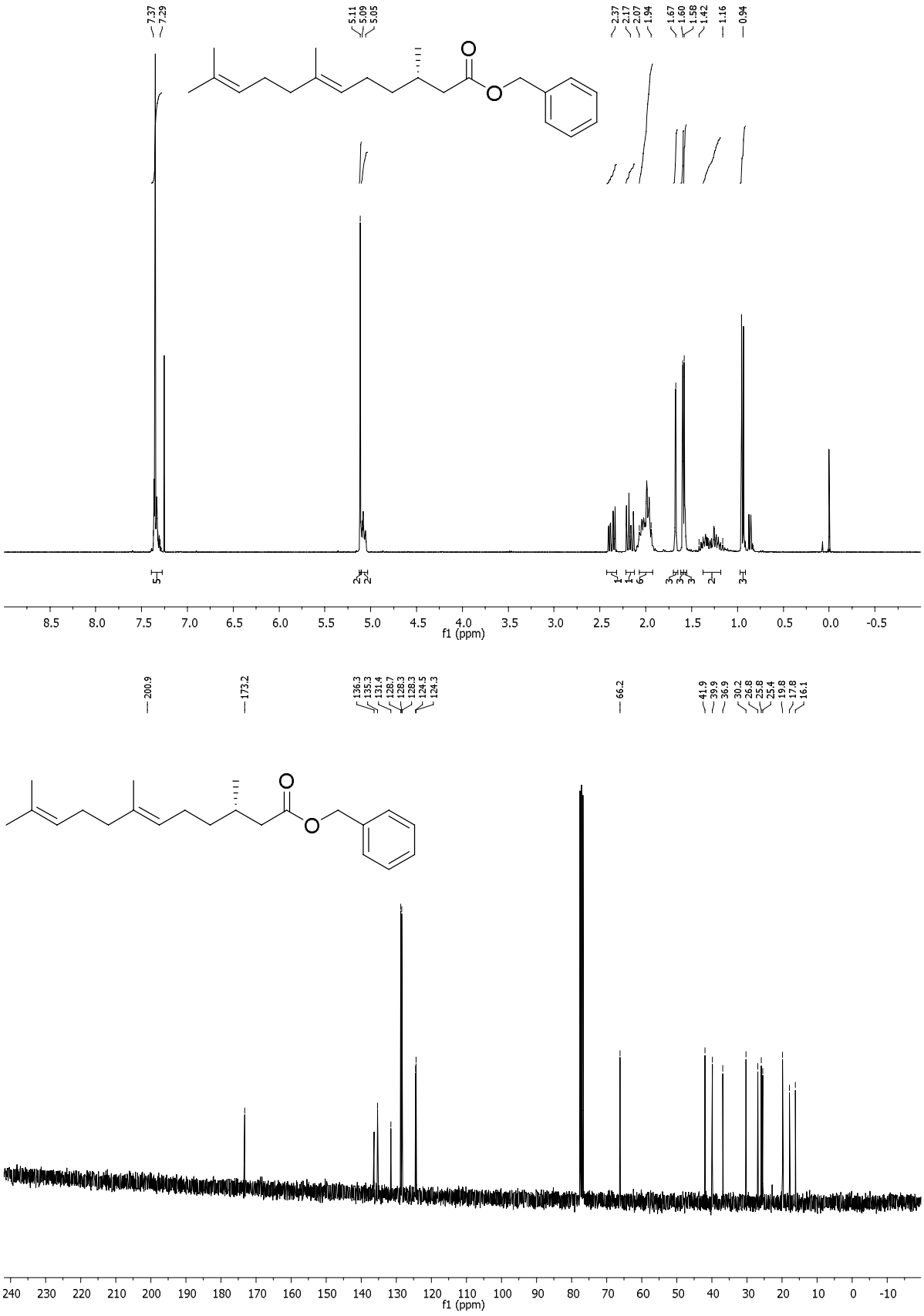


Figure S56. ^{1}H- and ^{13}C-NMR spectra of benzyl (S,E)-2,3-dihydrofarnesoate ((S)-8o).

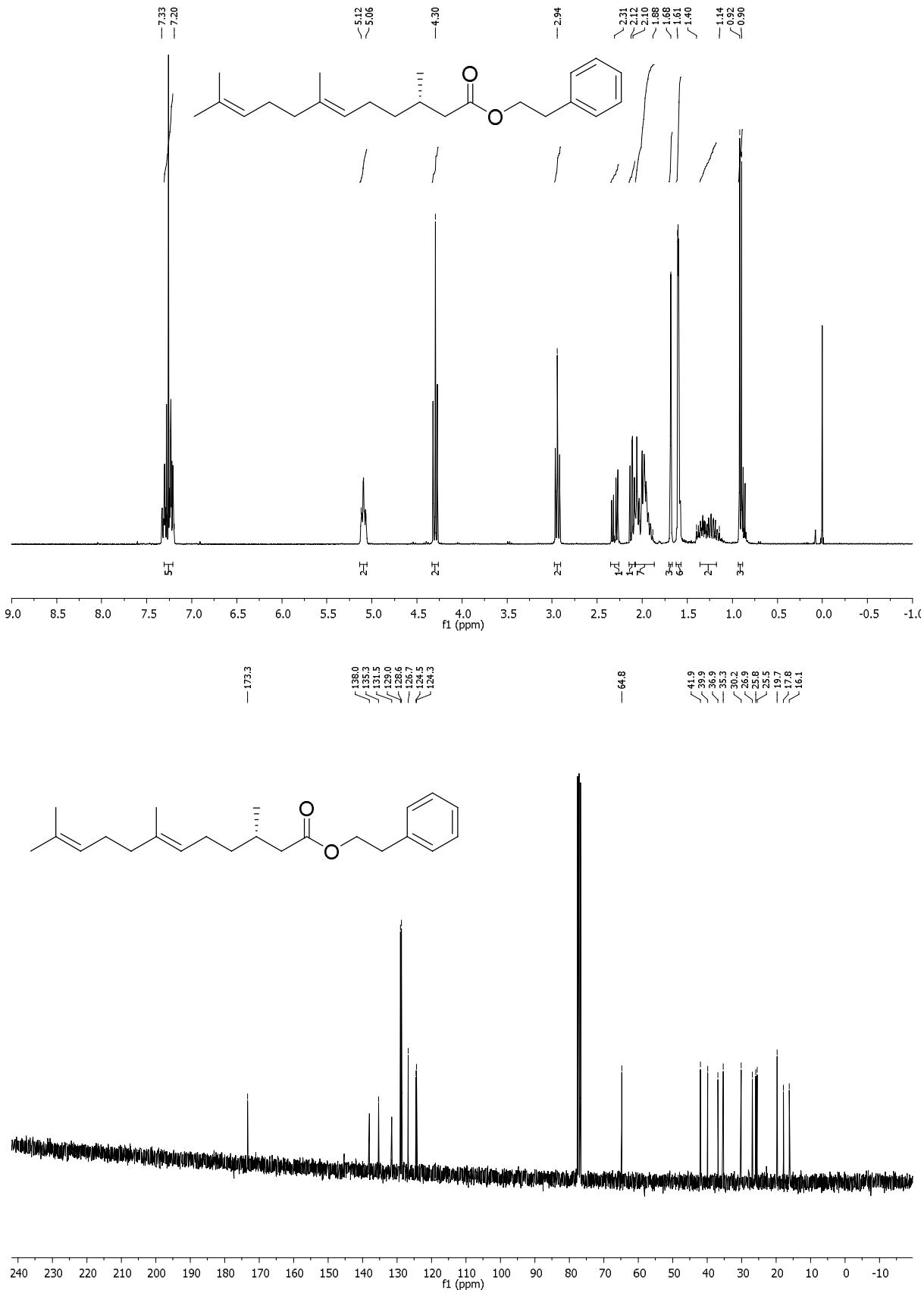


Figure S57. ^{1}H- and ^{13}C-NMR spectra of 2-phenylethyl (S,E)-2,3-dihydrofarnesoate ((S)-8p).

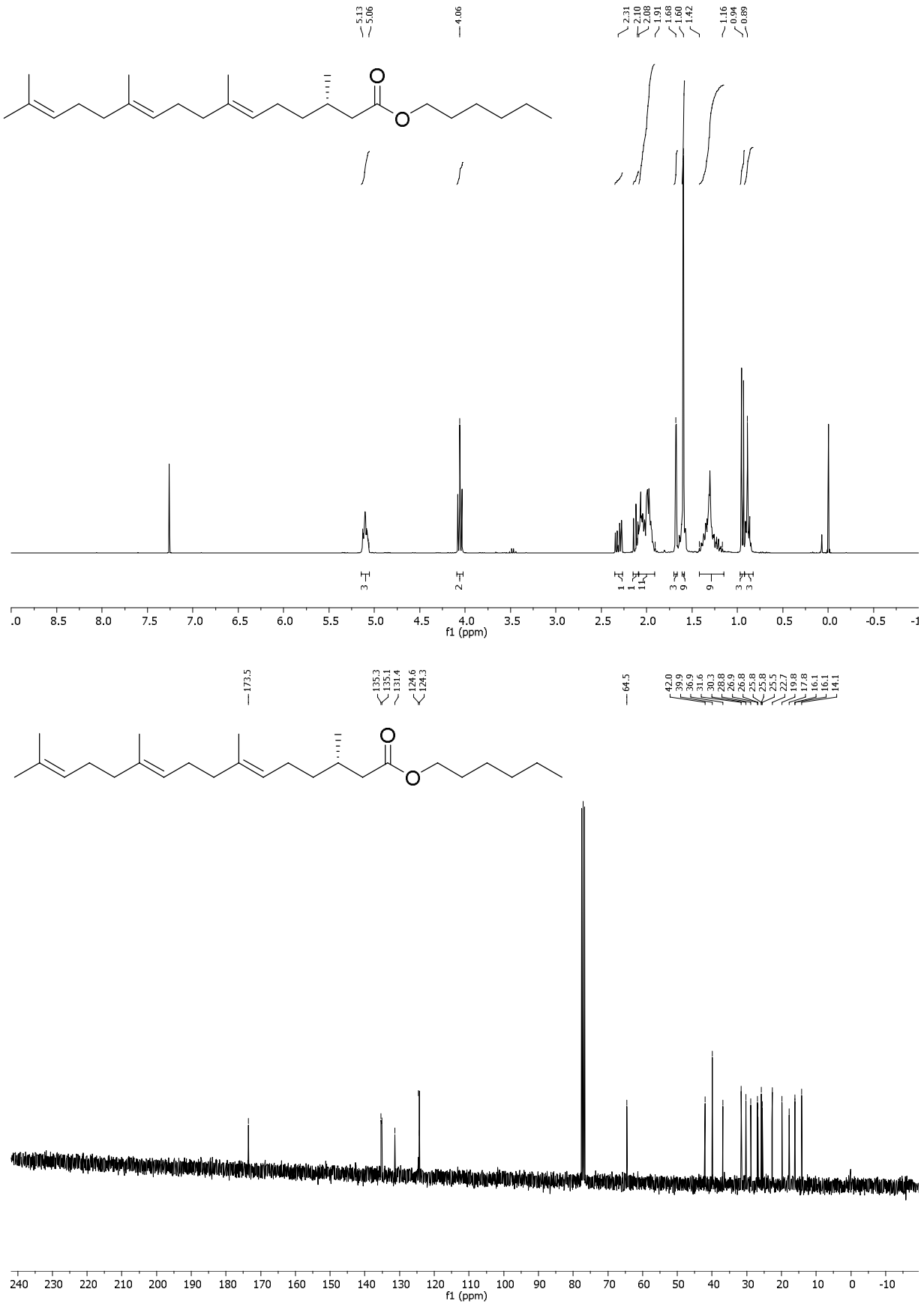


Figure S58. ^{1}H- and ^{13}C-NMR spectra of hexyl (S)-geranylcitronellate ((S)-9j).

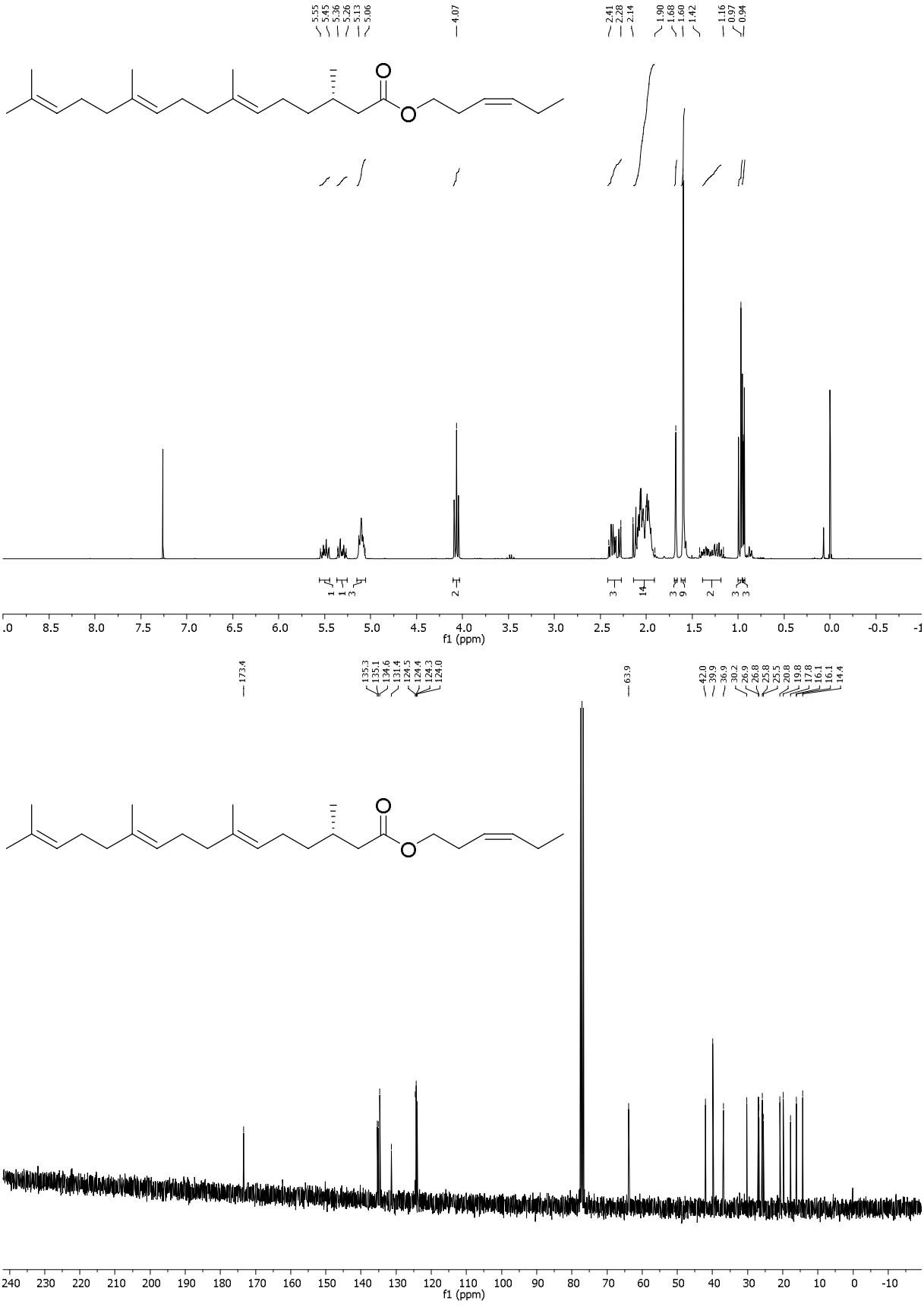


Figure S59. ^{1}H- and ^{13}C-NMR spectra of (Z)-3-hexenyl (S)-geranylcitronellate ((S)-9i).

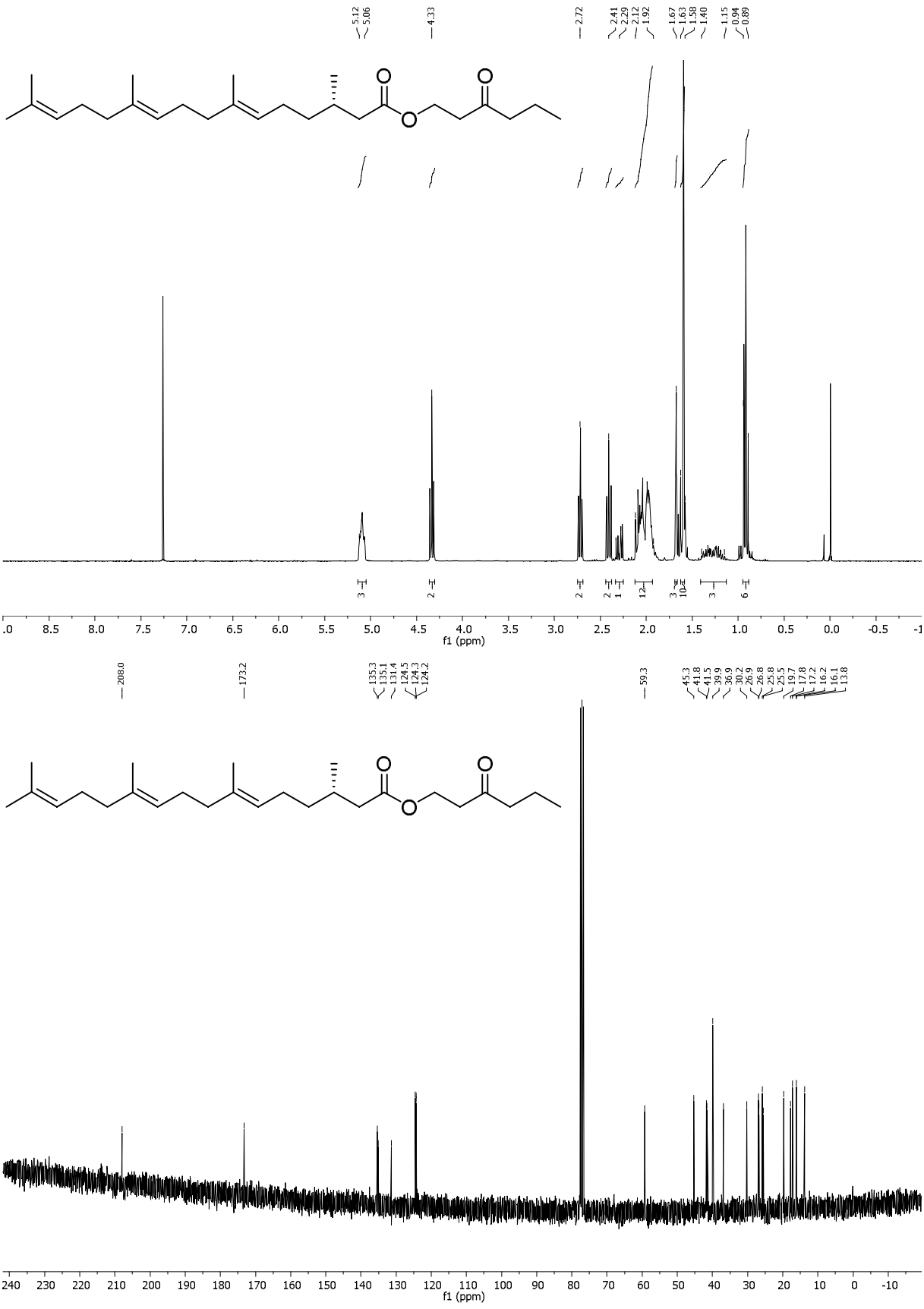


Figure S60. ^{1}H- and ^{13}C-NMR spectra of 3-oxohexyl (S)-geranylcitronellate ((S)-9l).

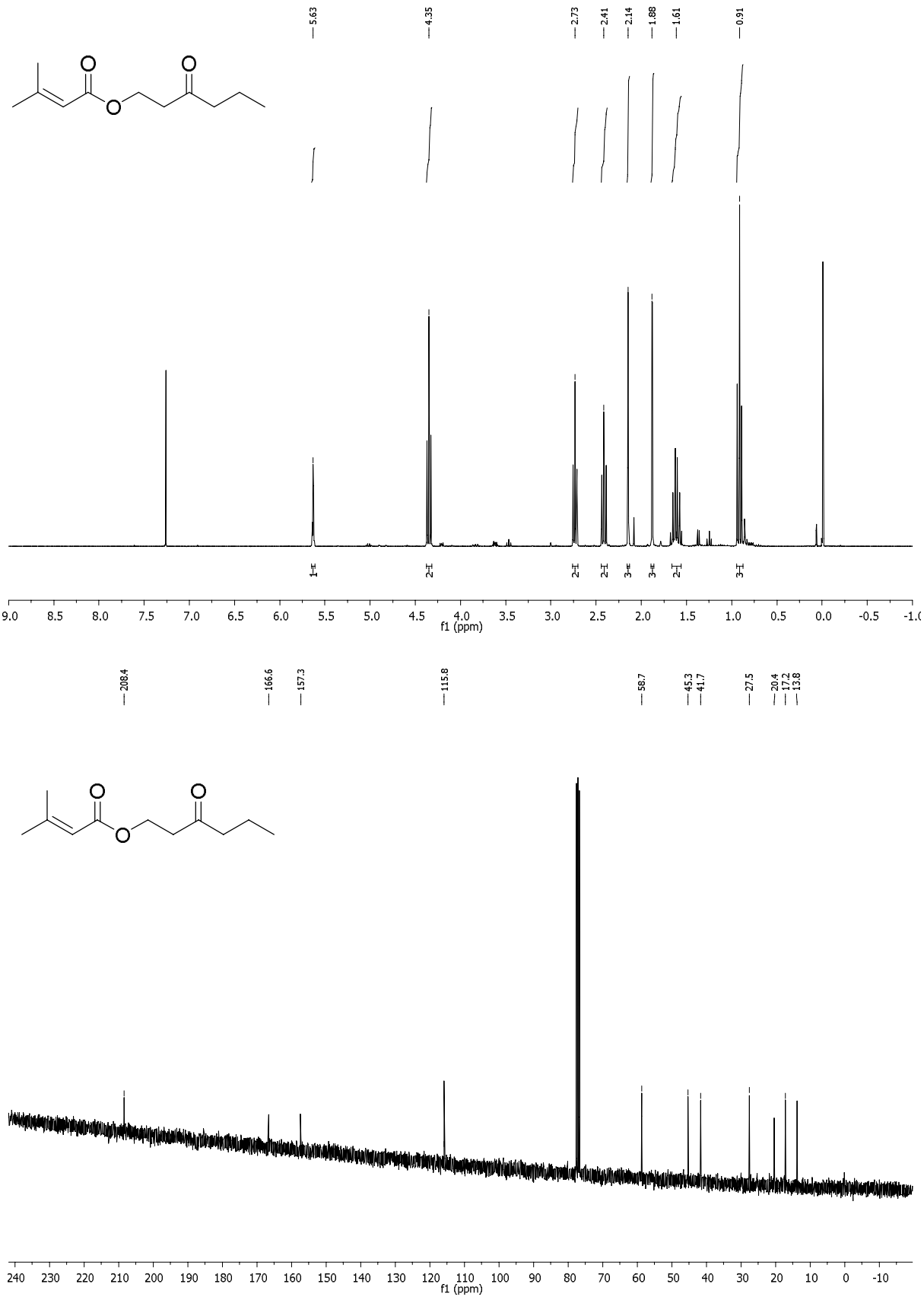


Figure S61. ^{1}H- and ^{13}C-NMR spectra of 3-oxohexyl 3-methyl-2-butenoate (S4).

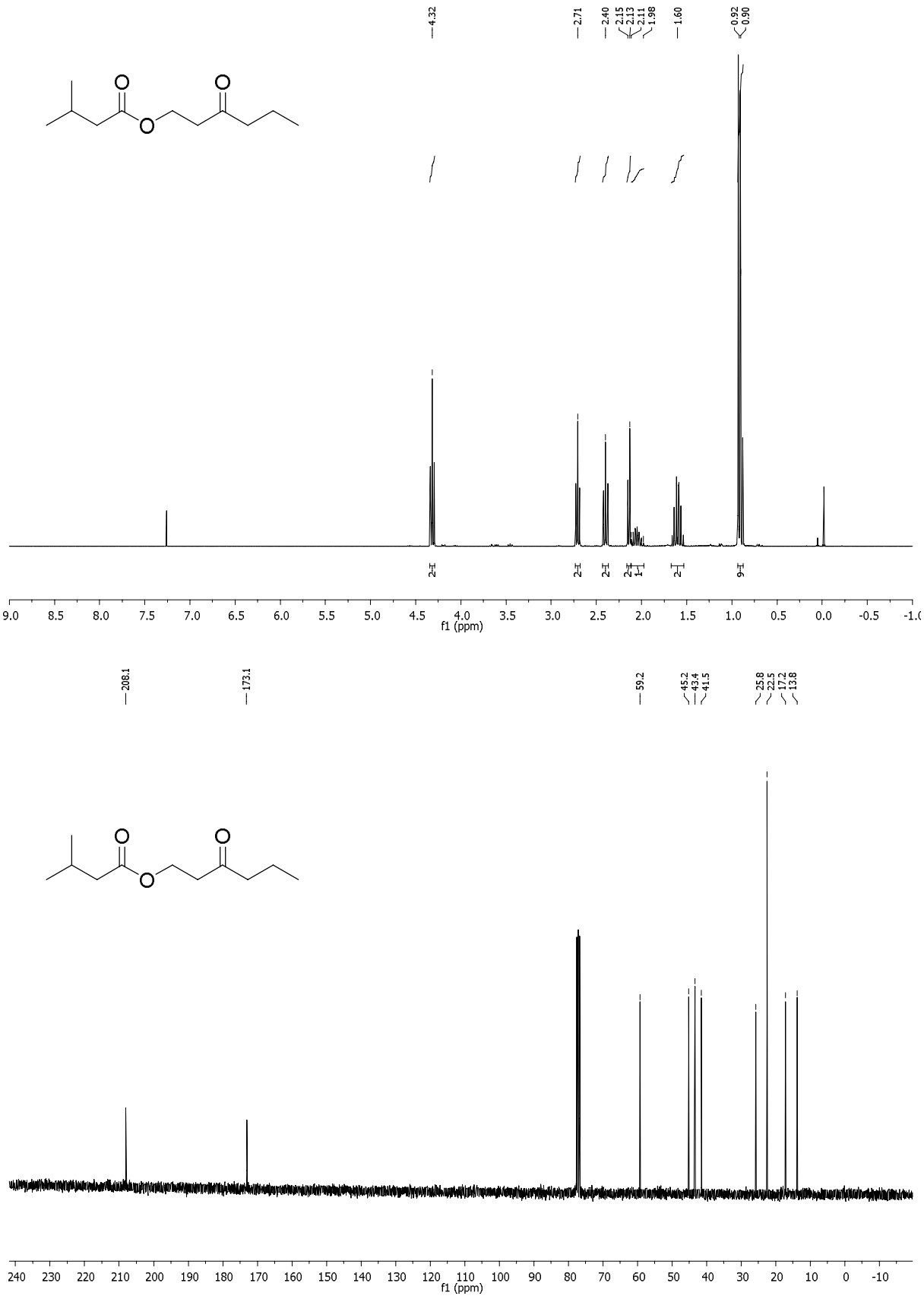


Figure S62. ^{1}H- and ^{13}C-NMR spectra of 3-oxohexyl 3-methylbutanoate (33).

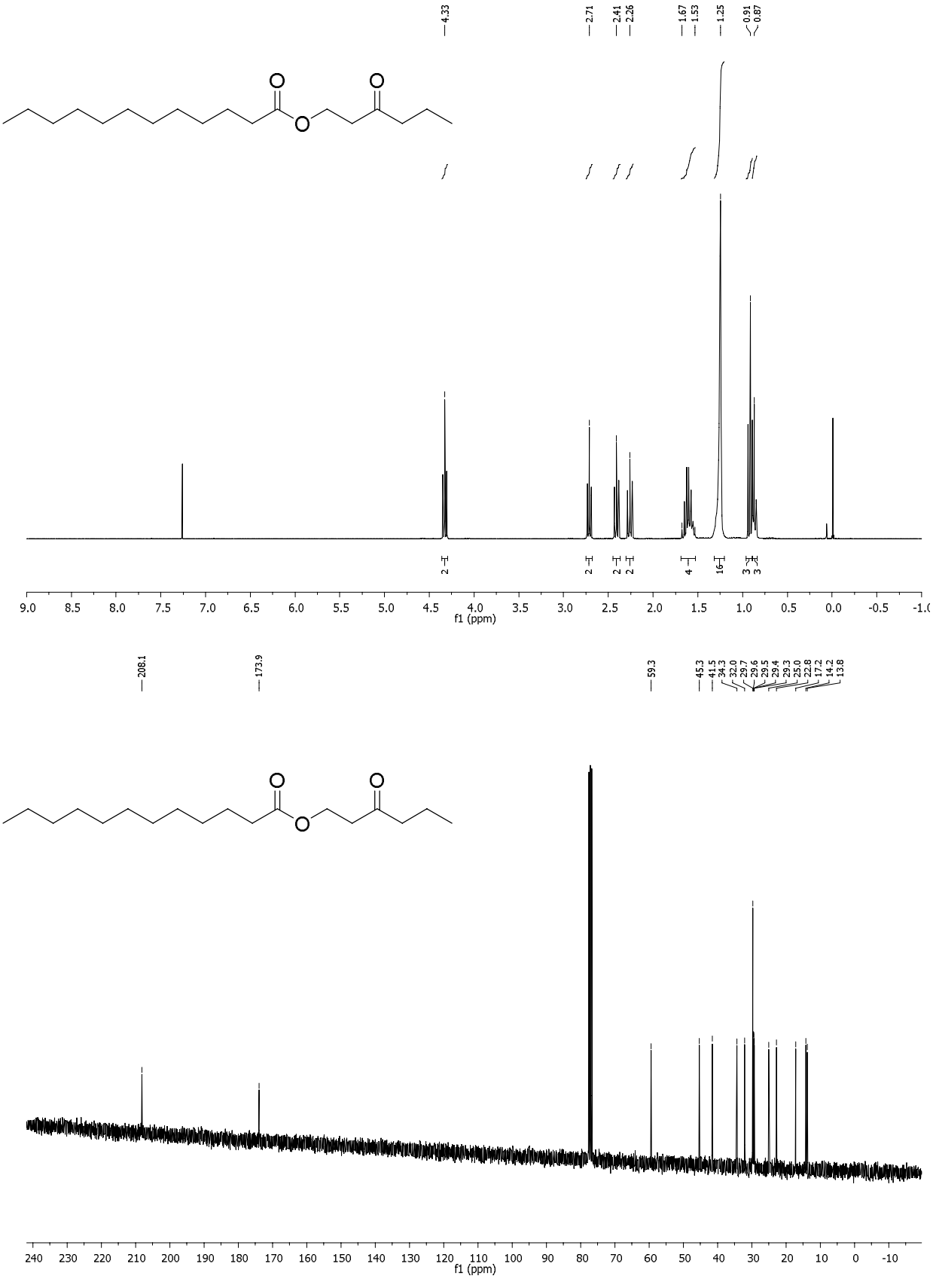


Figure S63. ^{1}H- and ^{13}C-NMR spectra of 3-oxohexyl dodecanoate (17l).

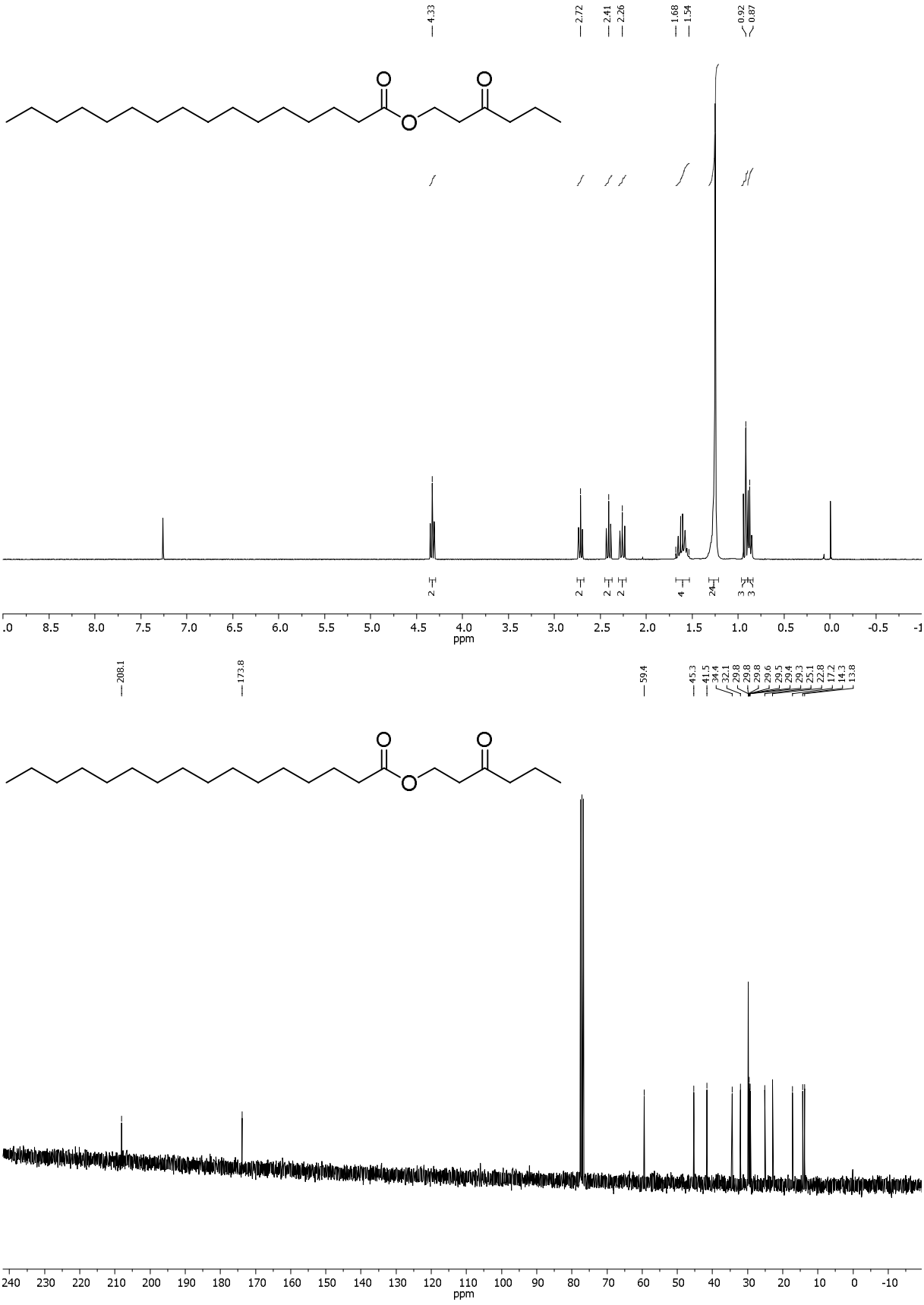


Figure S64. ^{1}H- and ^{13}C-NMR spectra of 3-oxohexyl hexadecanoate (18l).

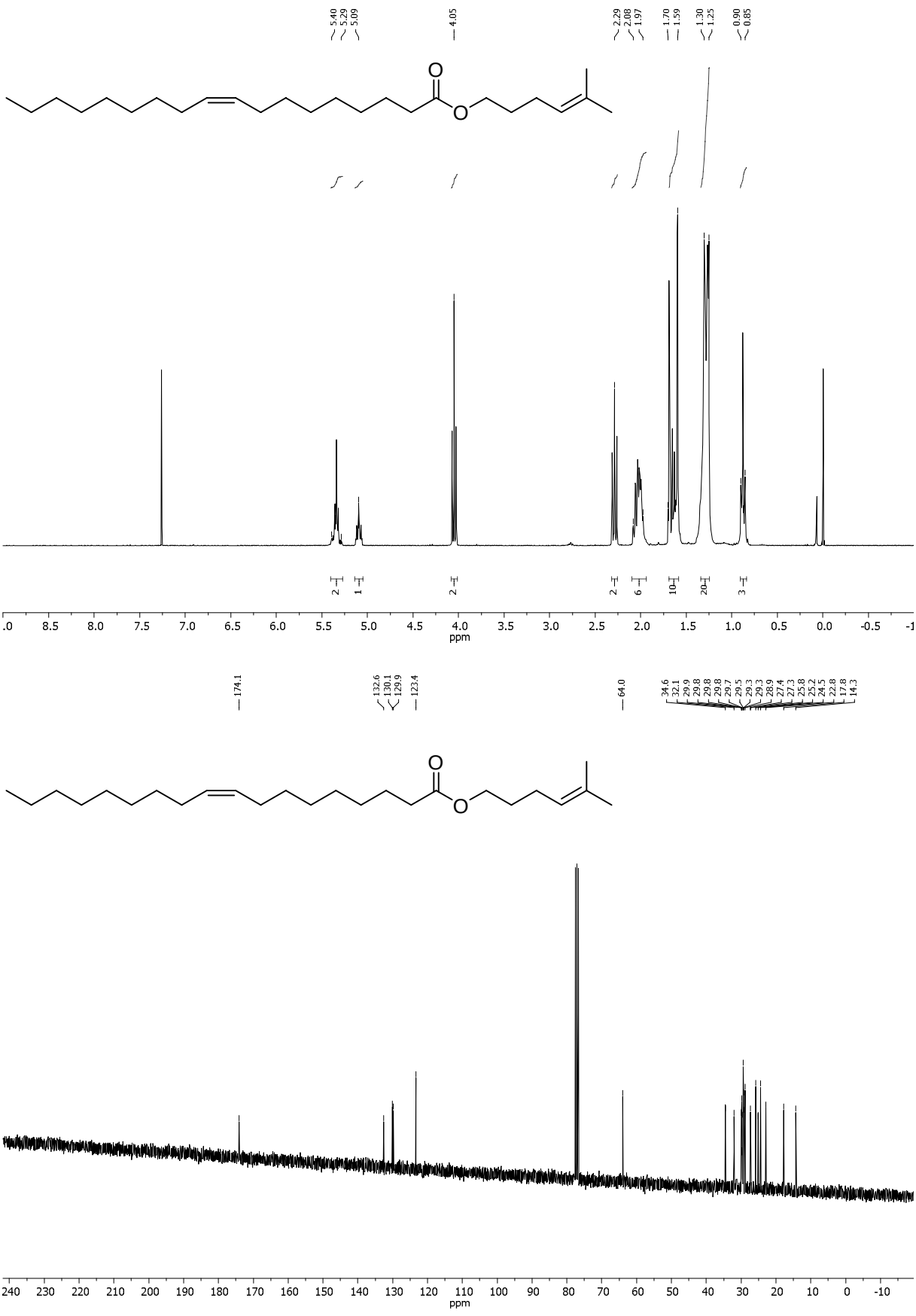


Figure S65. ^{1}H- and ^{13}C-NMR spectra of 5-methylhex-4-enyl (Z)-9-octadecenoate (22k).

12. References

[S1] S. Schulz, *Lipids* 2001, *36*, 637–647.

[S2] K. Darragh, A. Orteu, D. Black, K. J. R. P. Byers, D. Szczerbowski, I. A. Warren, P. Rastas, A. Pinharanda, J. W. Davey, S. Fernanda Garza, D. Abondano Almeida, R. M. Merrill, W. O. McMillan, S. Schulz, C. D. Jiggins, *PLOS Biol.* 2021, *19*, e3001022.

[S3] F. Mann, S. Vanjari, N. Rosser, S. Mann, K. K. Dasmahapatra, C. Corbin, M. Linares, C. Pardo-Diaz, C. Salazar, C. Jiggins, S. Schulz, *J. Chem. Ecol.* 2017, *43*, 843–857.

[S4] K. -D. Müller, H. Husmann, H. P. Nalik, G. Schomburg, *Chromatographia* 1990, *30*, 245–248.

[S5] S. Schulz, C. Arsene, M. Tauber, J. N. McNeil, *Phytochemistry* 2000, *54*, 325–336.

[S6] J.-J. Yun, M.-L. Zhi, W.-X. Shi, X.-Q. Chu, Z.-L. Shen, T.-P. Loh, *Adv. Synth. Catal.* 2018, *360*, 2632–2637.

[S7] M. Menke, K. Melnik, P. S. Peram, I. Starnberger, W. Hödl, M. Vences, S. Schulz, *Eur. J. Org. Chem.* 2018, 2651–2656.

[S8] a) R. Wang, Y. Chen, M. Shu, W. Zhao, M. Tao, C. Du, X. Fu, A. Li, Z. Lin, *Chem. Eur. J.* 2020, *26*, 1941–1946; b) I. M. Yonova, A. G. Johnson, C. A. Osborne, C. E. Moore, N. S. Morrissette, E. R. Jarvo, *Angew. Chem. Int. Ed.* 2014, *53*, 2422–2427.

[S9] K. Preece, R. Glávits, J. R. Foster, T. Murbach, J. R. Endres, G. Hirka, A. Vértesi, E. Béres, I. P. Szakonyiné, *Regul. Toxicol. Pharmacol.* 2021, *124*, 104975.

[S10] C. M. Gampe, H. Tsukamoto, T.-S. A. Wang, S. Walker, D. Kahne, *Tetrahedron* 2011, *67*, 9771–9778.

[S11] P. A. A. Klusener, L. Tip, L. Brandsma, *Tetrahedron* 1991, *47*, 2041–2064.