

Supplementary Information

(E)-4-Oxo-2-hexenal Dimers in the Scent Glands of the Bark Bug *Phloea subquadrata* (Heteroptera, Phloeidae)

Francine S. A. da Fonseca,^{a,b} Marília Medeiros,^a Adriana T. Salomão,^c
João Vasconcellos-Neto^d and Anita J. Marsaioli*^a

^aInstituto de Química, Universidade Estadual de Campinas, CP 6154, 13083-970
Campinas-SP, Brazil

^bInstituto de Ciências Agrárias, Universidade Federal de Minas Gerais,
Montes Claros-MG, Brazil

^cPrograma de Pós-Graduação em Ecologia and ^dDepartamento de Biologia Animal, Instituto de
Biologia, Universidade Estadual de Campinas, CP 6109, 13083-970 Campinas-SP, Brazil

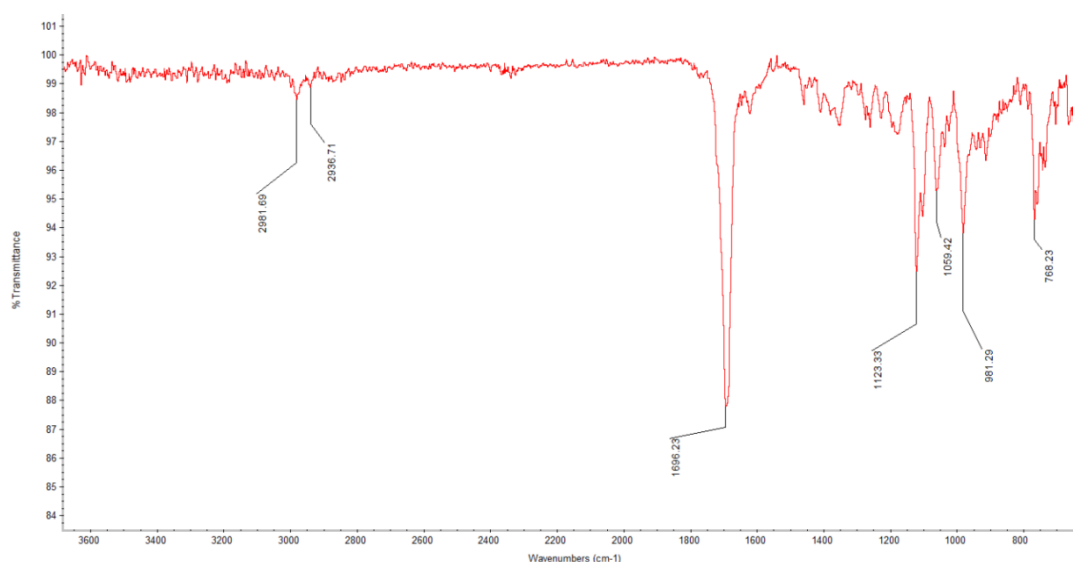


Figure S1. Infrared spectrum of synthetic (*E*)-4-oxo-2-hexenal.

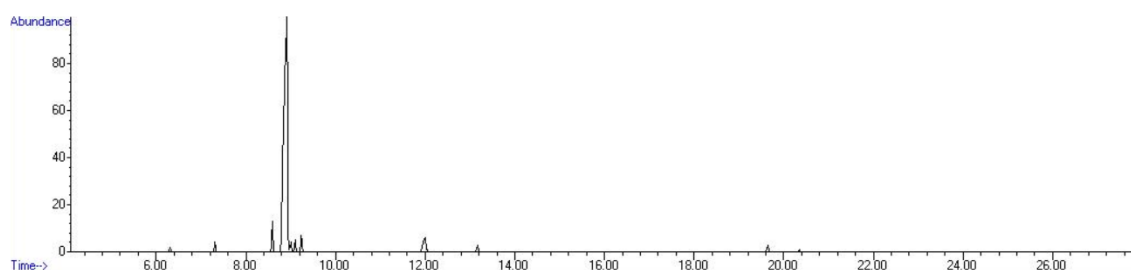


Figure S2. GC chromatogram of synthetic (*E*)-4-oxo-2-hexenal (retention time 9.005 min, HP-5 column).

*e-mail: anita@iqm.unicamp.br

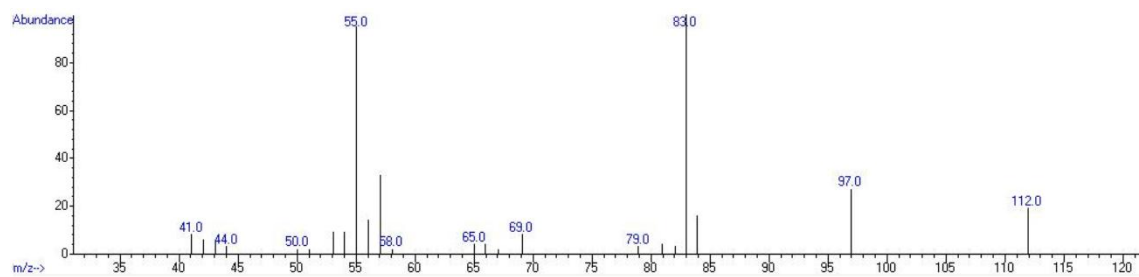


Figure S3. EI-MS spectrum of synthetic (*E*)-4-oxo-2-hexenal.

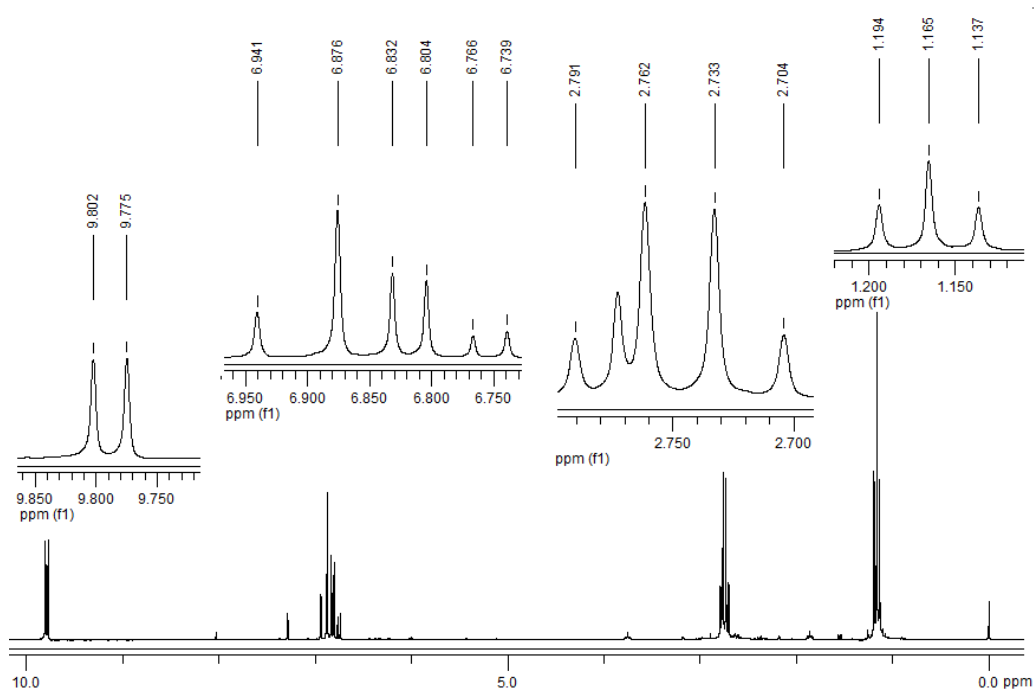


Figure S4. ^1H NMR spectrum (250.13 MHz, CDCl_3) of synthetic (*E*)-4-oxo-2-hexenal.

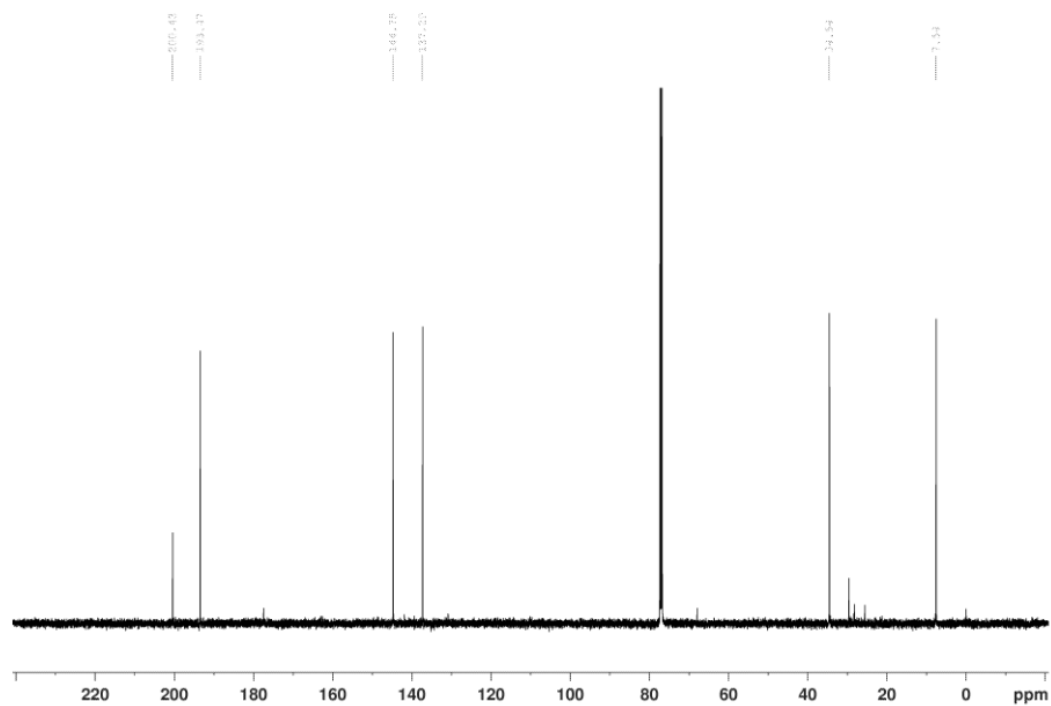


Figure S5. ^{13}C NMR spectrum (62.90 MHz, CDCl_3) of synthetic (*E*)-4-oxo-2-hexenal.

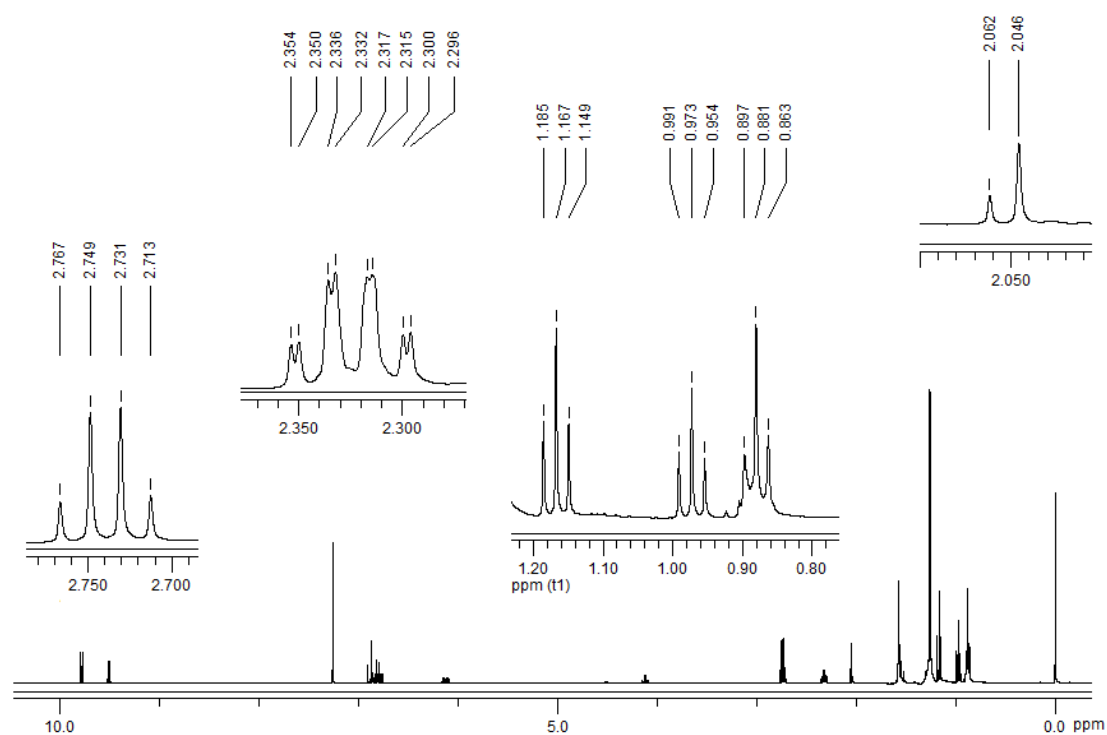


Figure S6. ^1H NMR spectrum (250.13 MHz, CDCl_3) of metathoracic gland content of *Phloea subquadrata* males.

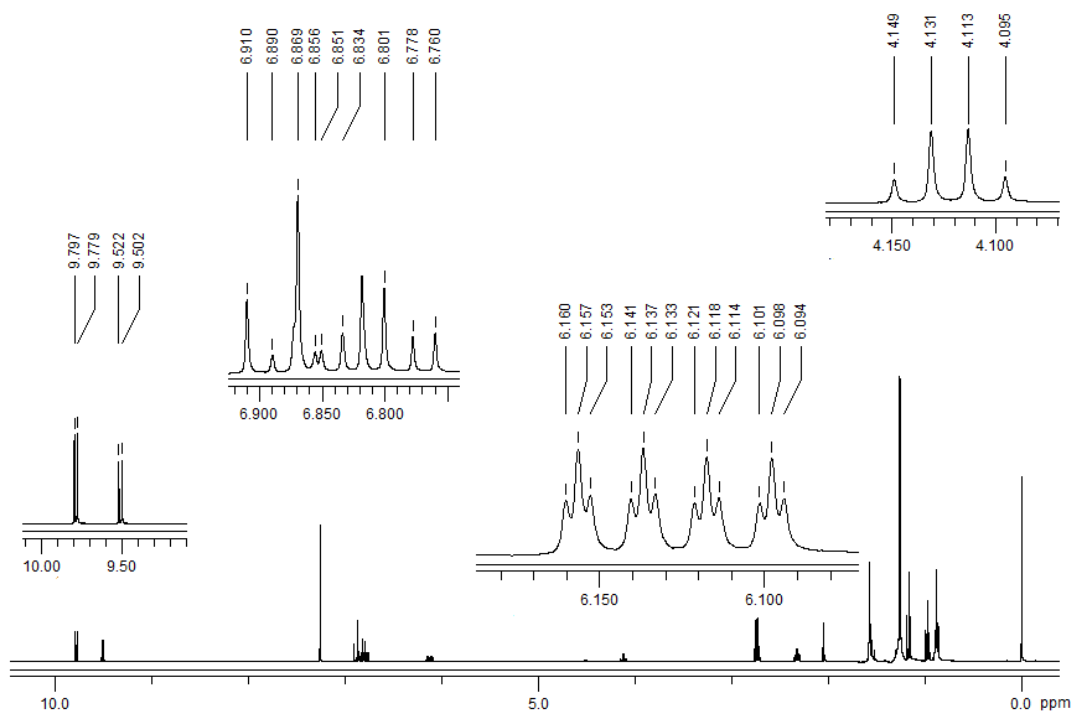


Figure S7. ^1H NMR spectrum (250.13 MHz, CDCl_3) of metathoracic gland content of *Phloea subquadrata* males.

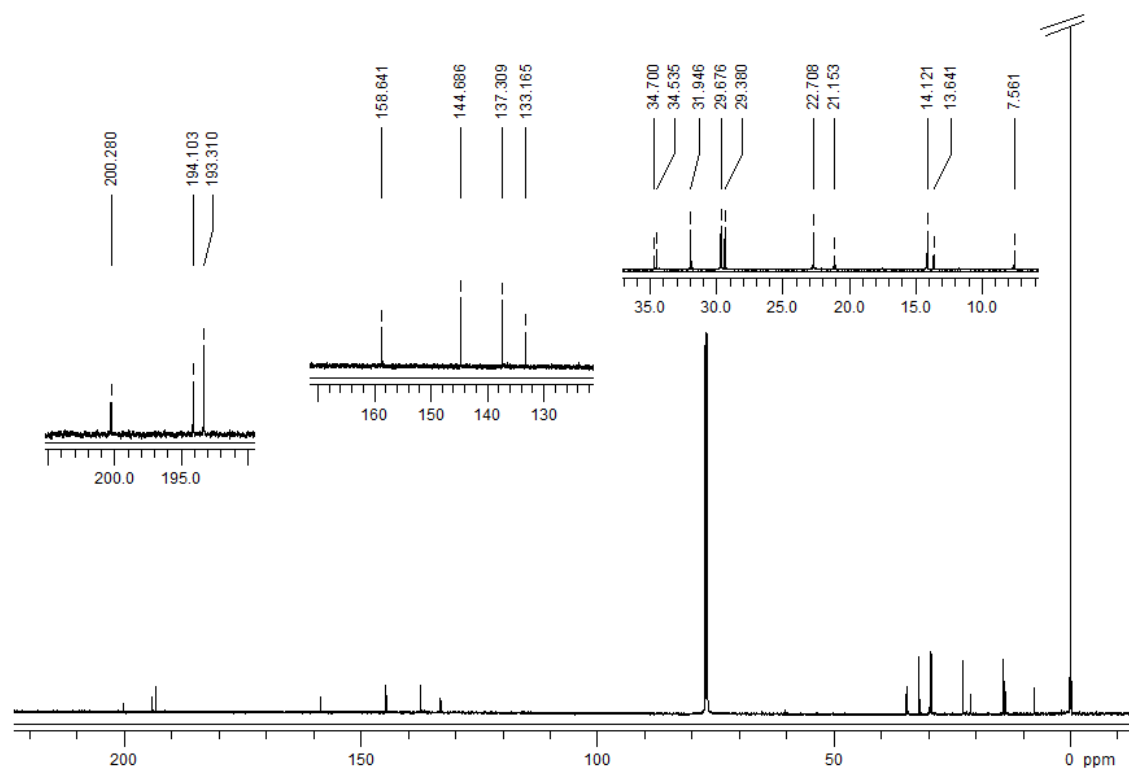


Figure S8. ^{13}C NMR spectrum (62.90 MHz, CDCl_3) of spectra of metathoracic gland content of *Phloea subquadrata* males.

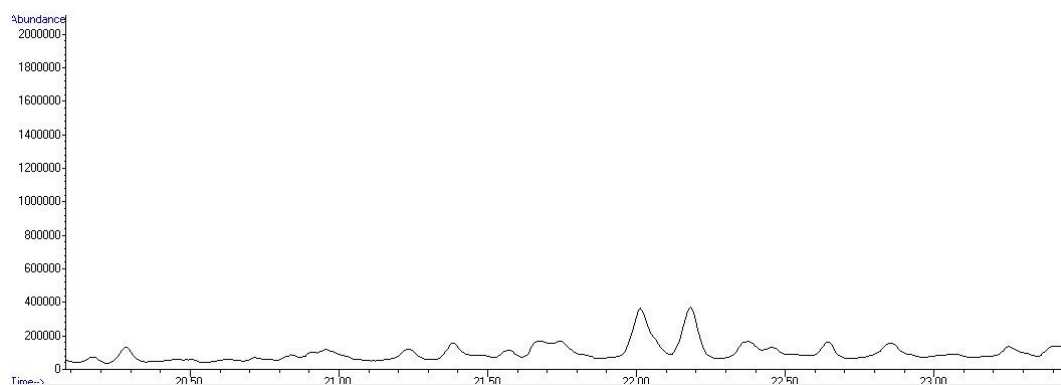


Figure S9. GC chromatogram of natural dimers (HP-5 column).

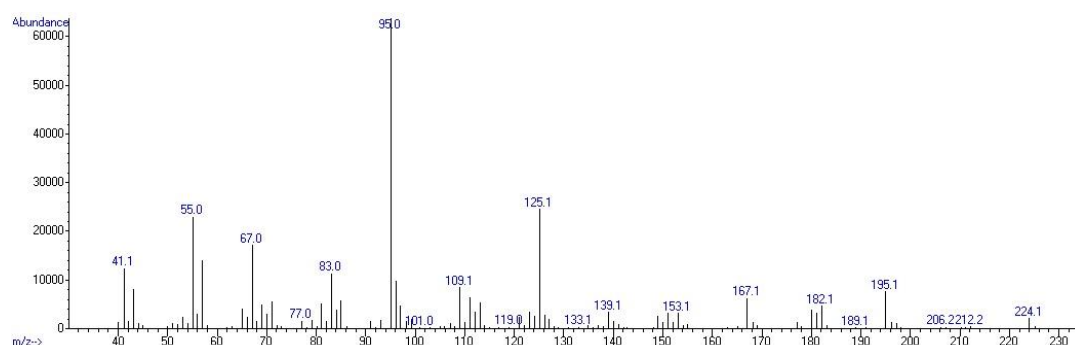


Figure S10. EI-MS of natural dimers (retention time 22.018 min).

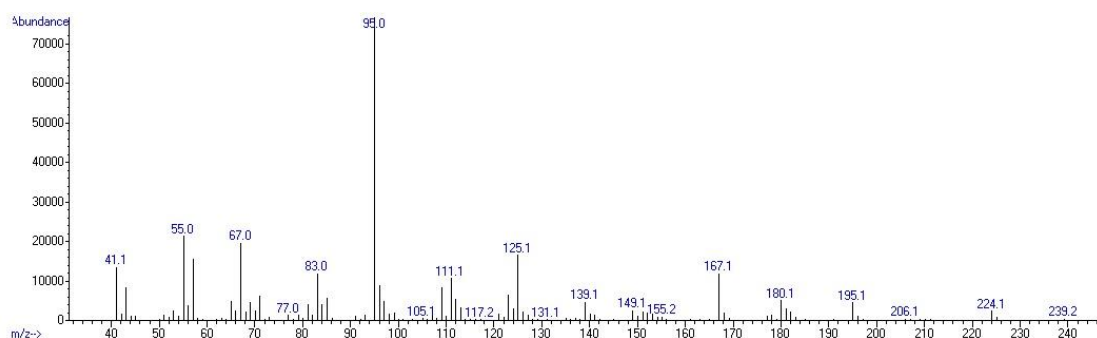


Figure S11. Mass fragmentation analysis of natural dimers (retention time 22.183 min).

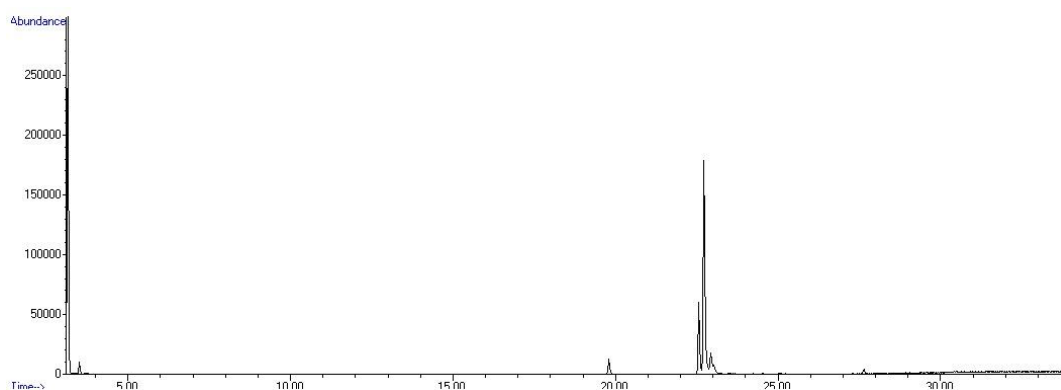


Figure S12. GC chromatogram of synthetic dimers (HP-5 column).

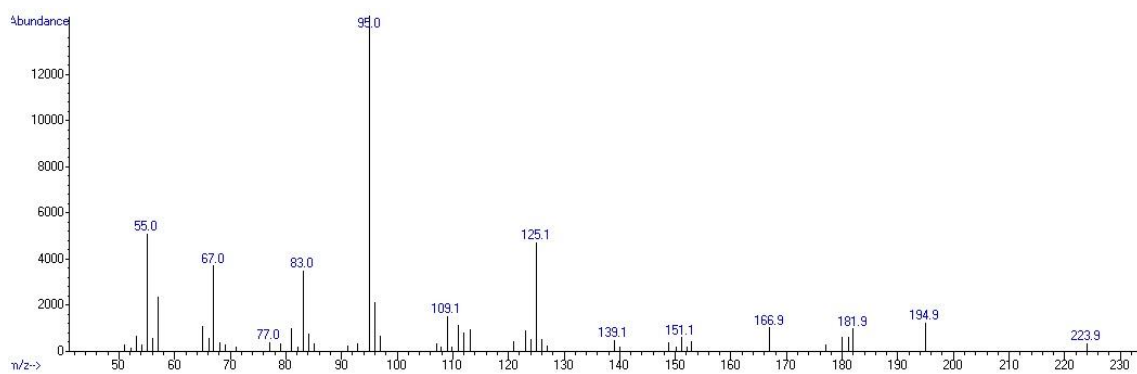


Figure S13. EI-MS of synthetic dimers (retention time 22.563 min).

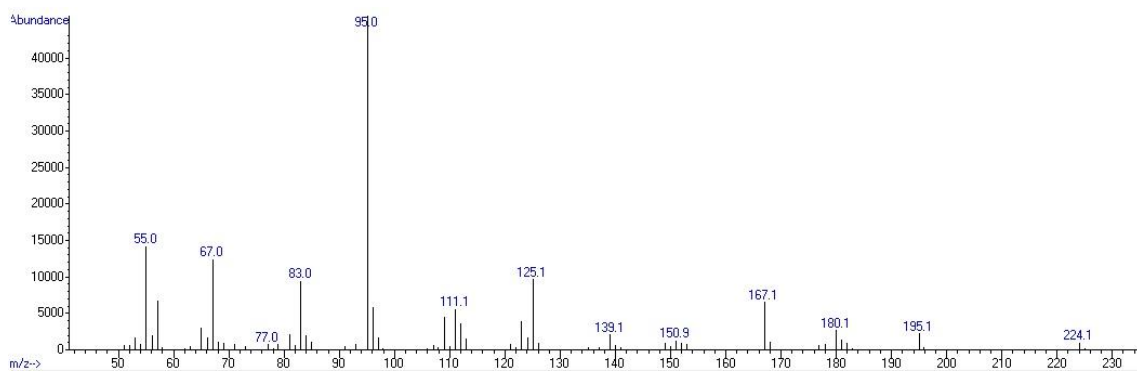


Figure S14. EI-MS of synthetic dimers (retention time 22.723 min).

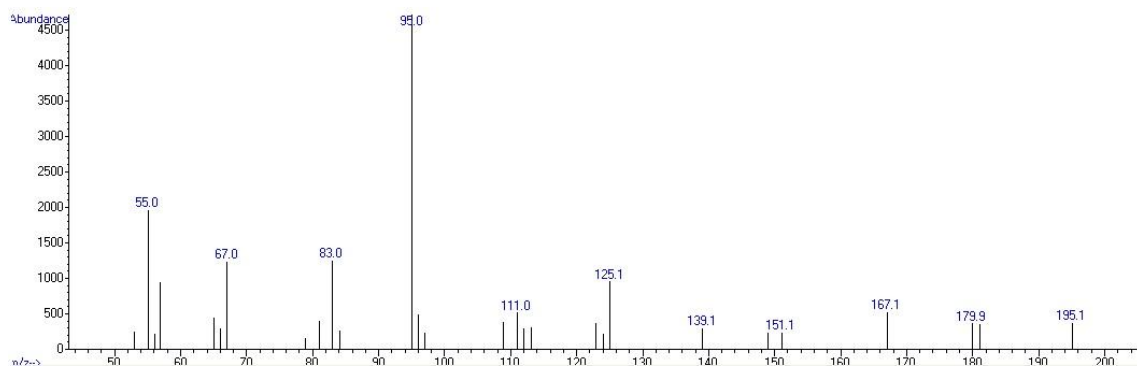


Figure S15. EI-MS of synthetic dimers (retention time 22.929 min).

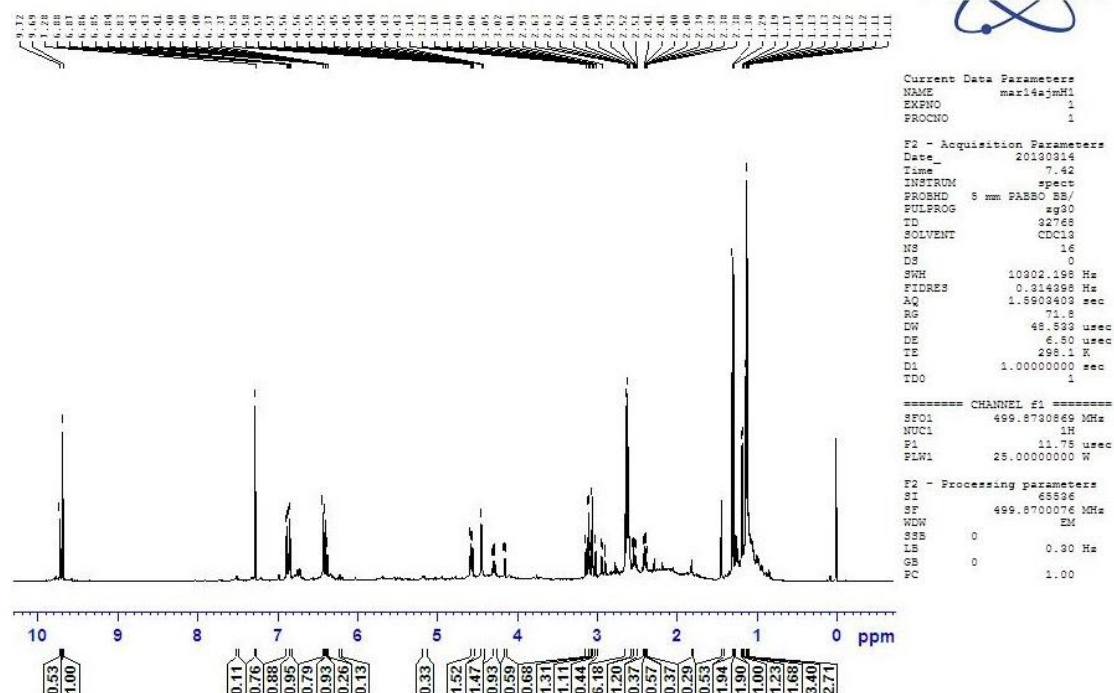


Figure S16. ¹H NMR spectrum (499.9 MHz, CDCl₃) of synthetic (*E*)-4-oxo-2-hexenal dimers.

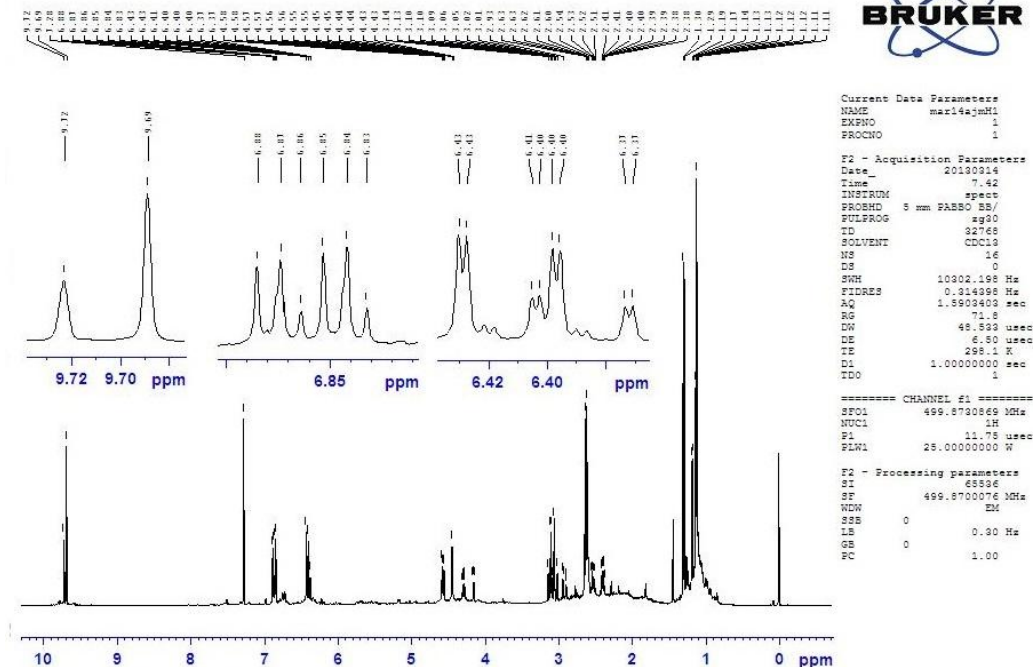


Figure S17. ¹H NMR spectrum (499.9 MHz, CDCl₃) of synthetic (*E*)-4-oxo-2-hexenal dimers.

Marilia - DIMEROS 2 - CDCl₃ - Avance 500 MHz - mar14ajmH1

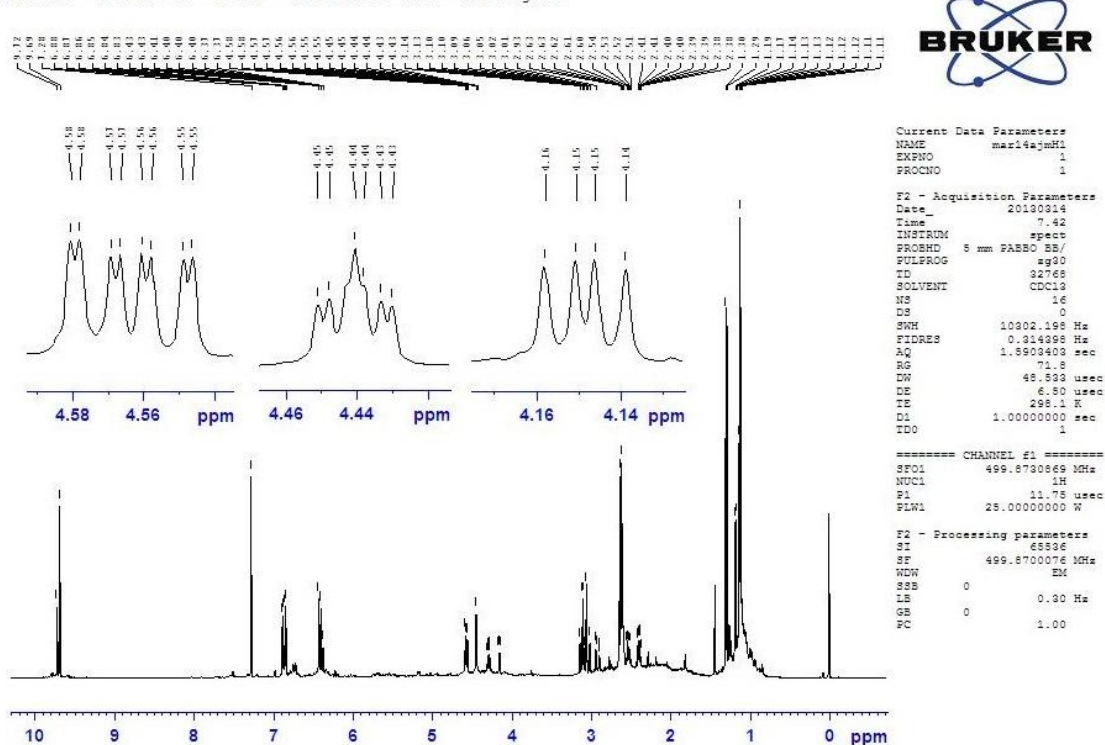


Figure S18. ¹H NMR spectrum (499.9 MHz, CDCl₃) of synthetic (*E*)-4-oxo-2-hexenal dimers.

Marilia - DIMEROS 2 - CDCl₃ - Avance 500 MHz - mar14ajmH1

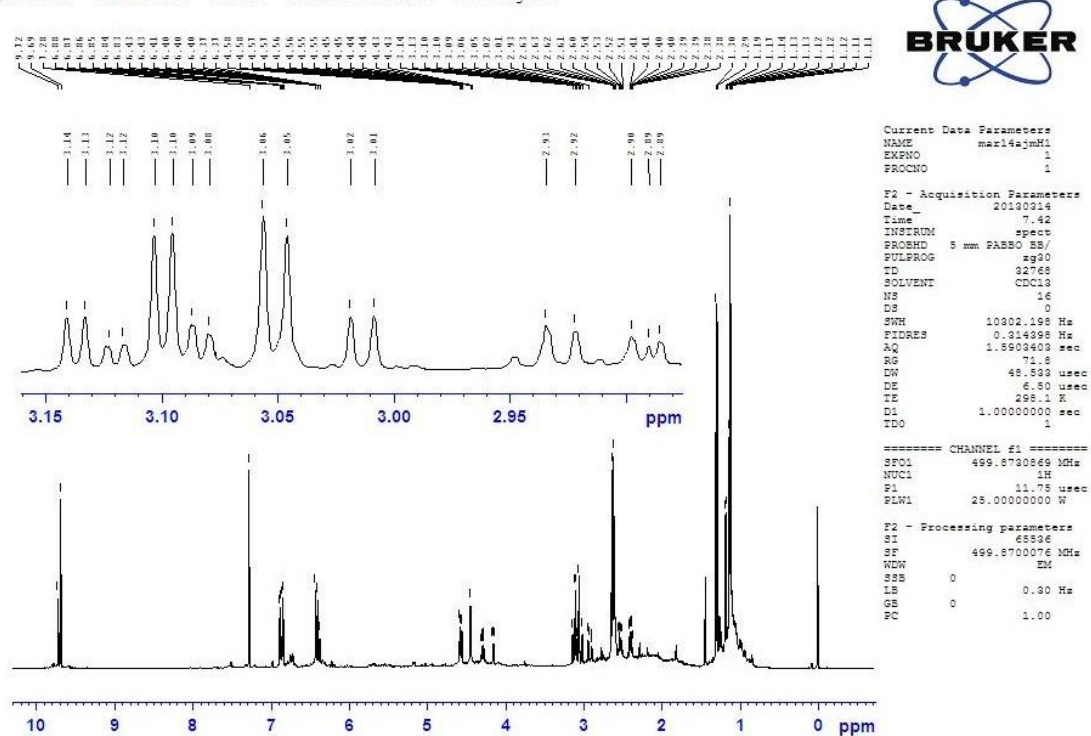


Figure S19. ¹H NMR spectrum (499.9 MHz, CDCl₃) of synthetic (*E*)-4-oxo-2-hexenal dimers.

Marilia - DIMEROS 2 - CDCl₃ - Avance 500 MHz - mar14ajmH1

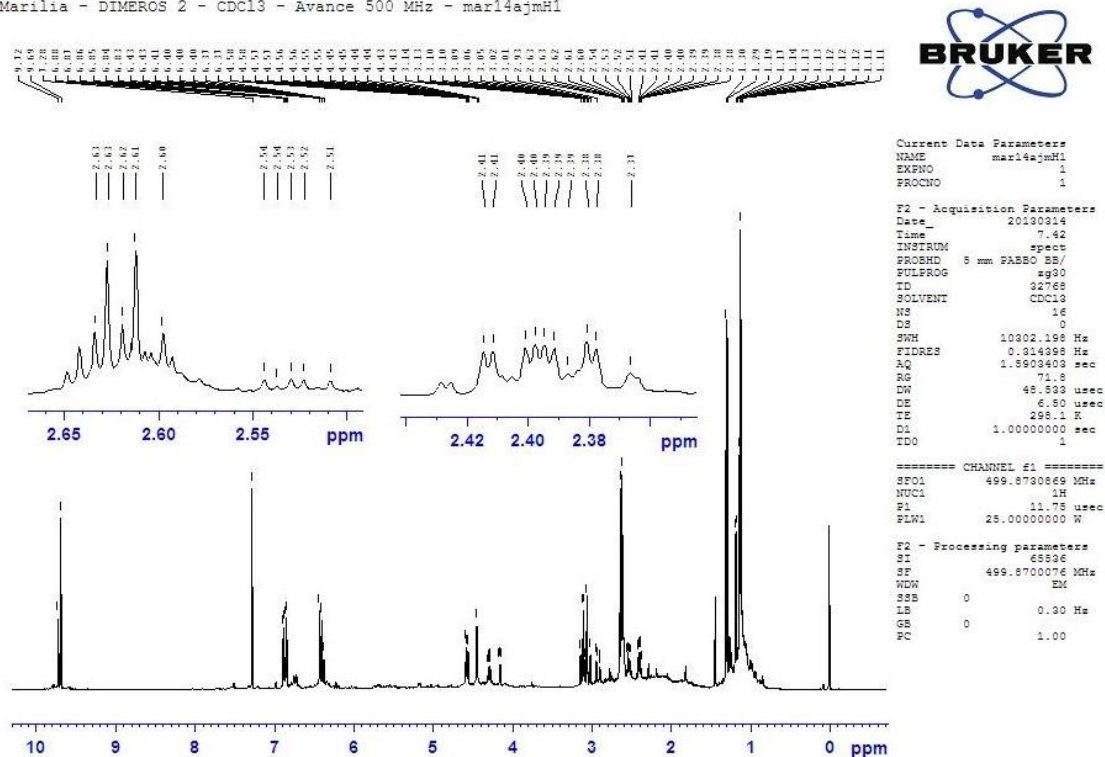


Figure S20. ¹H NMR spectrum (499.9 MHz, CDCl₃) of synthetic (*E*)-4-oxo-2-hexenal dimers.

Marilia - DIMEROS 2 - CDCl₃ - Avance 500 MHz - mar14ajmH1

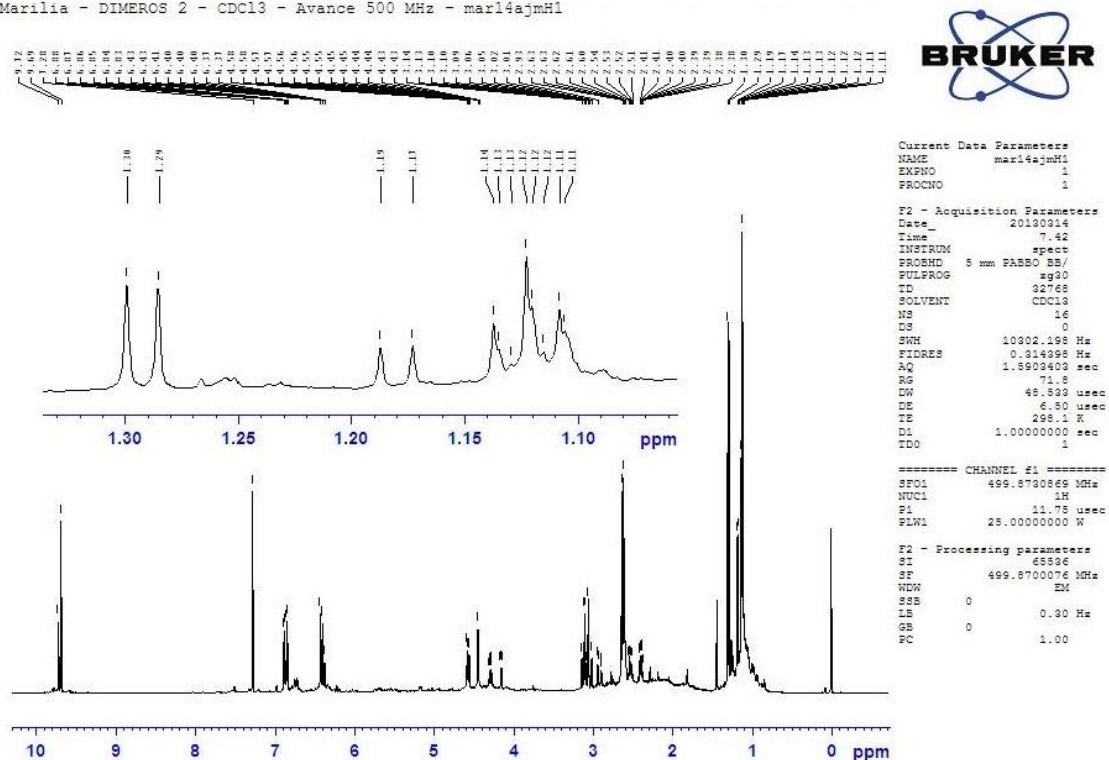
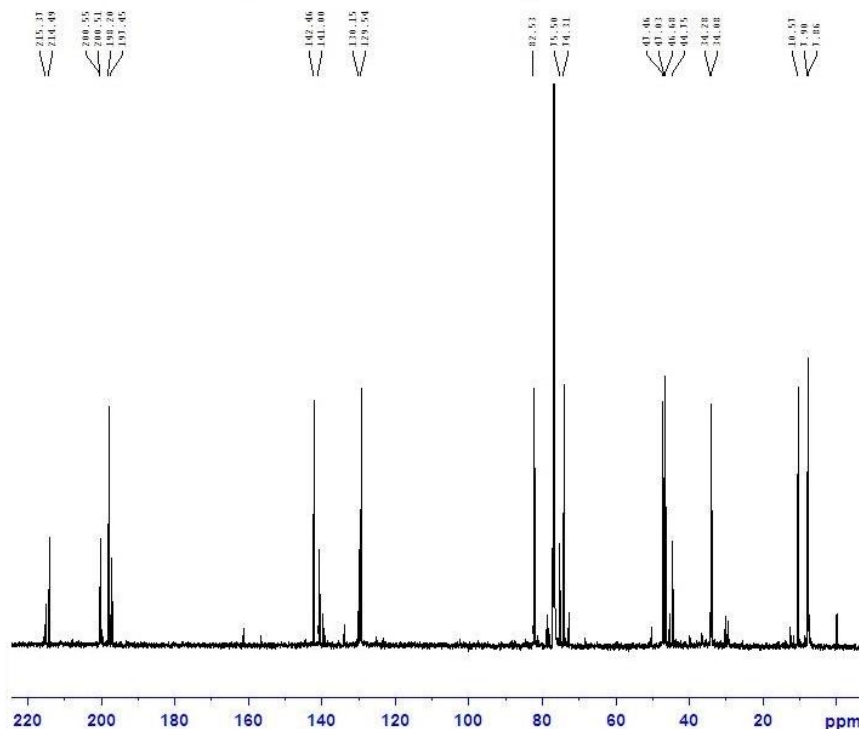


Figure S21. ¹H NMR spectrum (499.9 MHz, CDCl₃) of synthetic (*E*)-4-oxo-2-hexenal dimers.

Marilia - DIMEROS 2 - CDCl₃ - Avance 500 MHz - mar14ajmH1 - 13C



Current Data Parameters
NAME mar14ajmH1
EXFNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130314
Time_ 8.54
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl₃
NS 5120
DS 0
SWH 32594.738 Hz
FIDRES 1.002868 Hz
AQ 0.4980736 sec
RG 875
DW 18.200 usec
DE 6.80 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

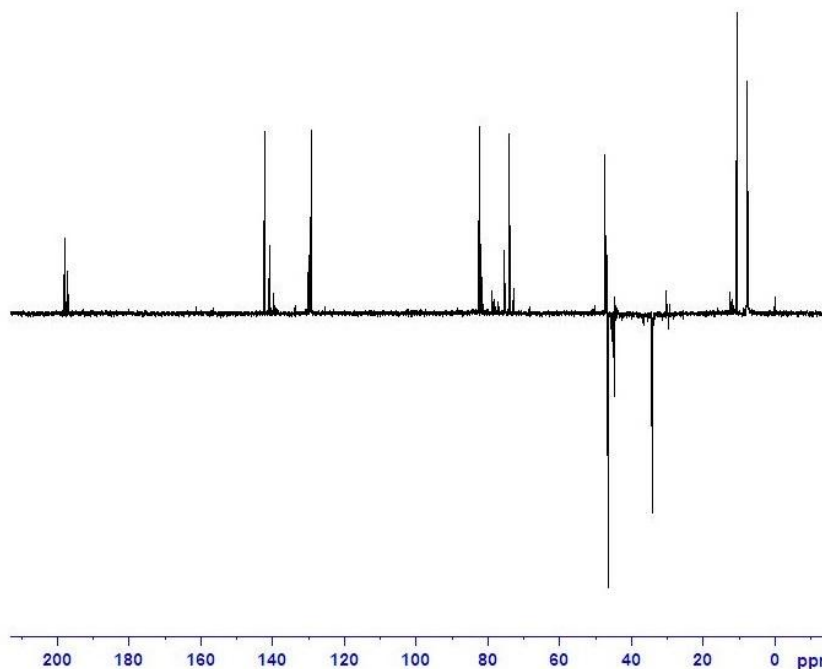
===== CHANNEL f1 =====
SFO1 125.7062372 MHz
NUC1 13C
P1 10.00 usec
PLW1 91.00000000 W

===== CHANNEL f2 =====
SFO2 499.8719995 MHz
NUC2 1H
CDEPRG12 waltz16
PCPD2 20.00 usec
PLW2 26.85300064 W
PLW12 0.57928002 W
PLW13 0.97074000 W

F2 - Processing parameters
SI 131072
SF 125.6924187 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

Figure S22. ¹³C NMR spectrum (125.7 MHz, CDCl₃) of (*E*)-4-oxo-2-hexenal dimers.

Marilia - DIMEROS 2 - CDCl₃ - Avance 500 MHz - mar14ajmH1 - DEPT 135



Current Data Parameters
NAME mar14ajmH1
EXFNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130314
Time_ 19.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG dept135
TD 32768
SOLVENT CDCl₃
NS 2048
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505024 sec
RG 2050
DW 16.800 usec
DE 6.80 usec
TE 298.2 K
CNST2 145.0000000
D1 2.00000000 sec
D2 0.00344222 sec
D12 0.00002000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 125.7049807 MHz
NUC1 13C
P1 10.00 usec
F2 20.00 usec
PLW1 91.00000000 W

===== CHANNEL f2 =====
SFO2 499.8719986 MHz
NUC2 1H
CDEPRG12 waltz16
P3 11.75 usec
P4 23.50 usec
PCPD2 20.00 usec
PLW2 26.85300064 W
PLW12 0.57928002 W

F2 - Processing parameters
SI 32768
SF 125.6924180 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S23. DEPT 135 spectrum (125.7 MHz, CDCl₃) of (*E*)-4-oxo-2-hexenal dimers.

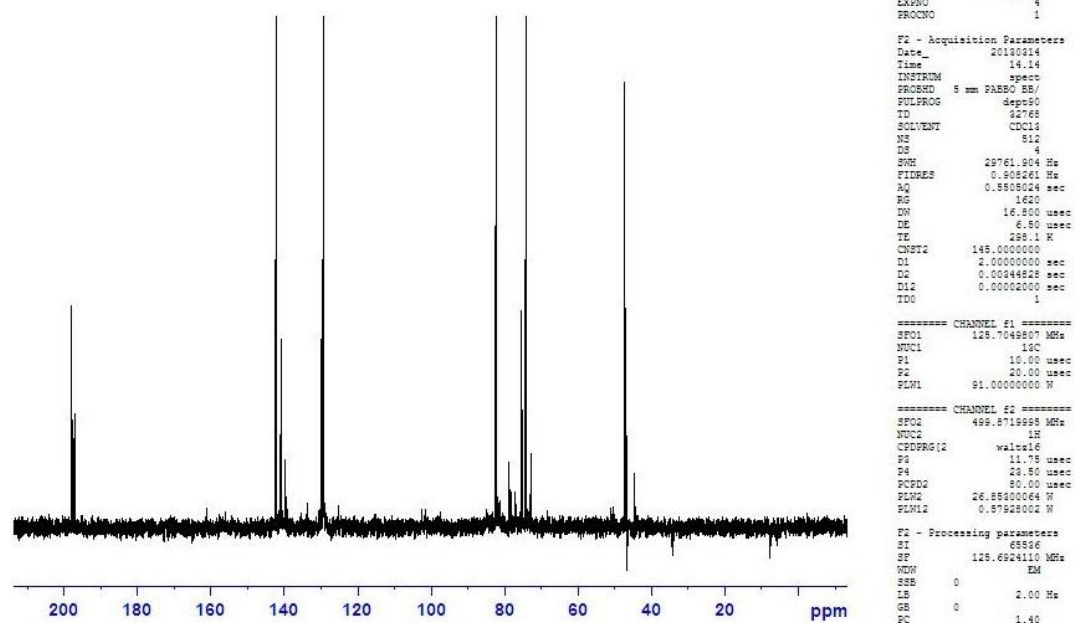


Figure S24. DEPT 90 spectrum (125.7 MHz, CDCl₃) of (*E*)-4-oxo-2-hexenal dimers.

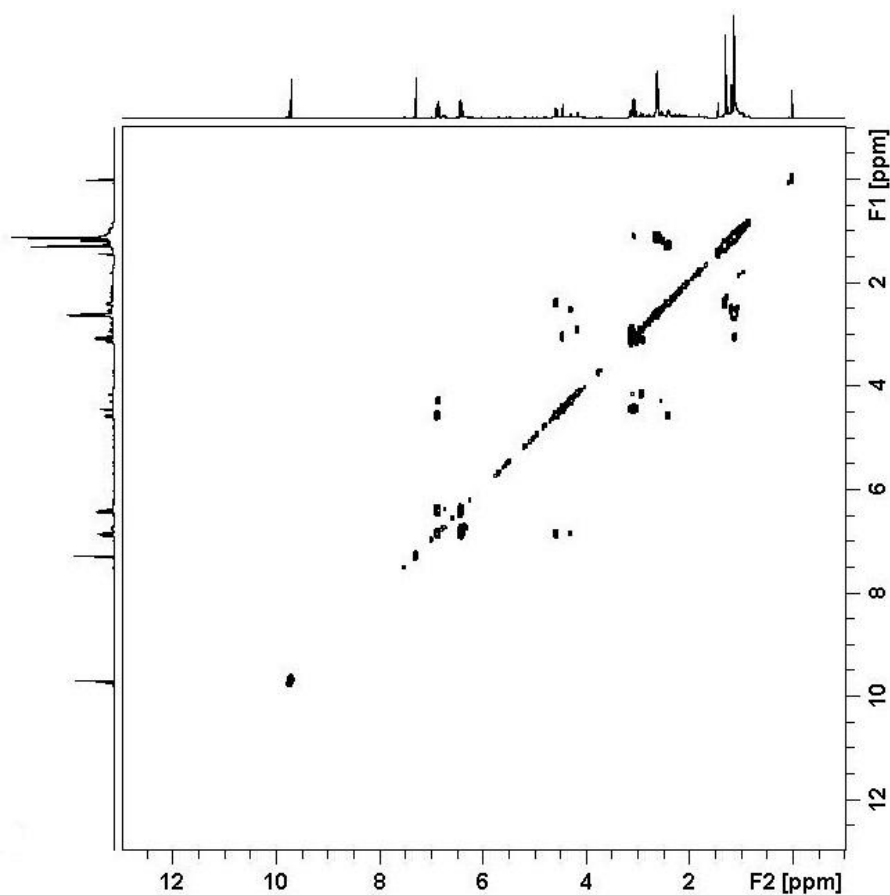


Figure S25. ¹H-¹H COSY spectrum (499.9 MHz, CDCl₃) of (*E*)-4-oxo-2-hexenal dimers.

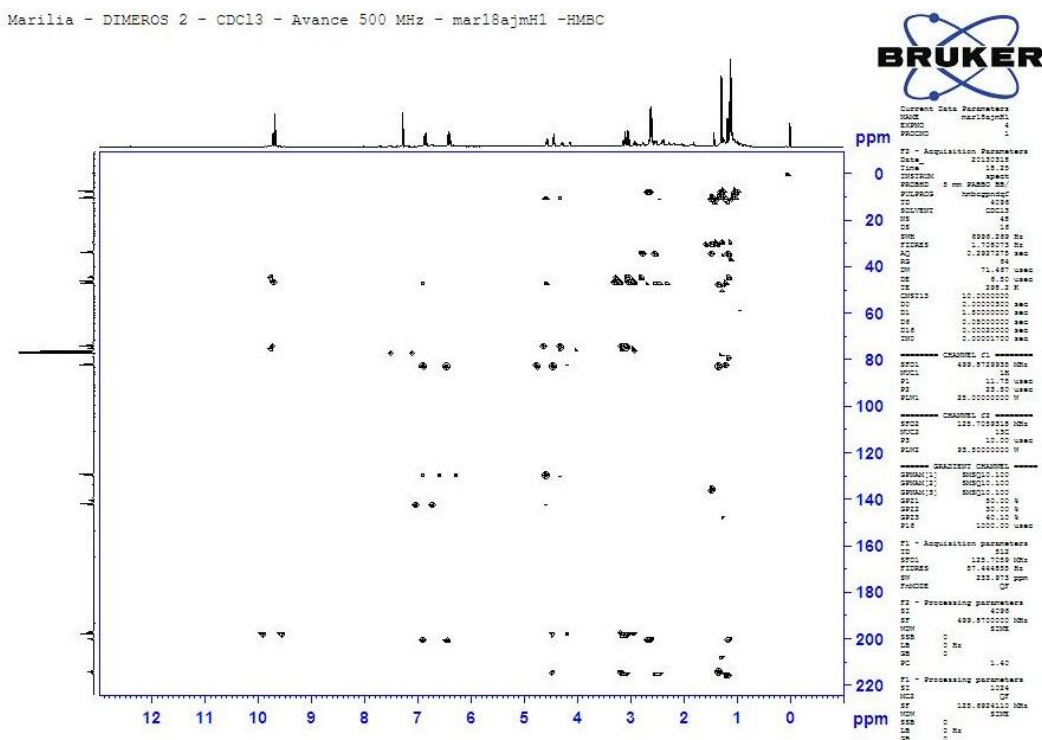
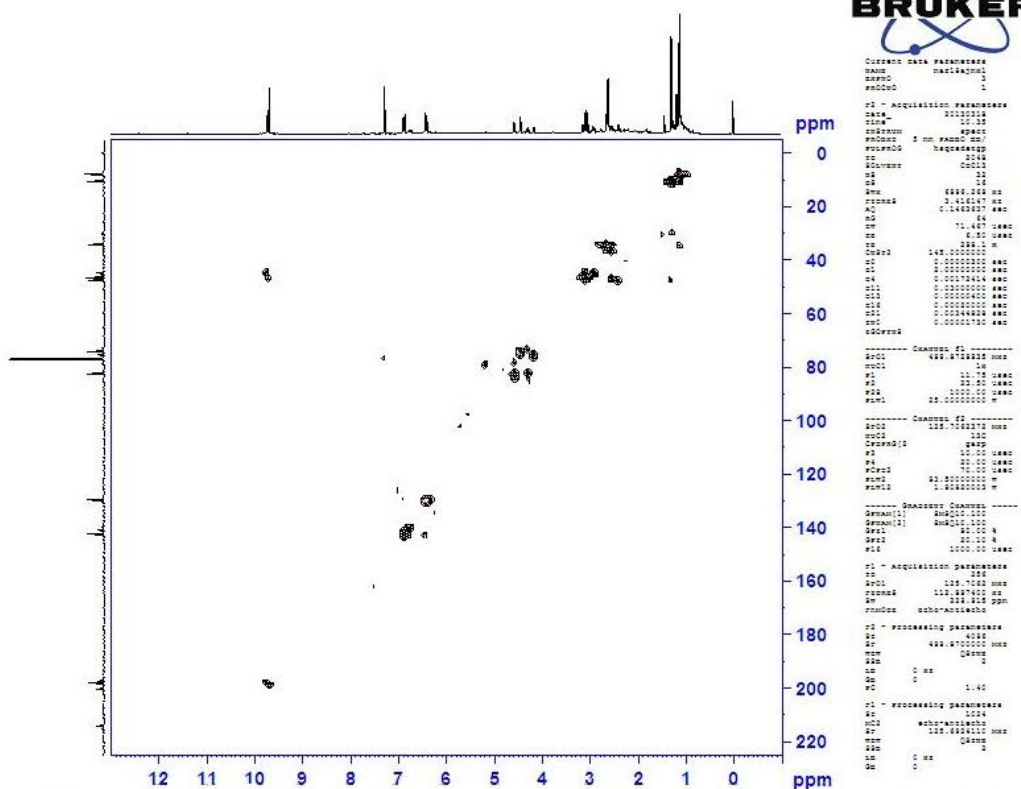


Figure S27. ^1H , ^{13}C HMBC spectrum (499.9 MHz, 125.7 MHz, CDCl_3) of (*E*)-4-oxo-2-hexenal dimers.

Anita - Faixa 3 - CDCl₃ - Av 400 MHz - mail2ajmh2

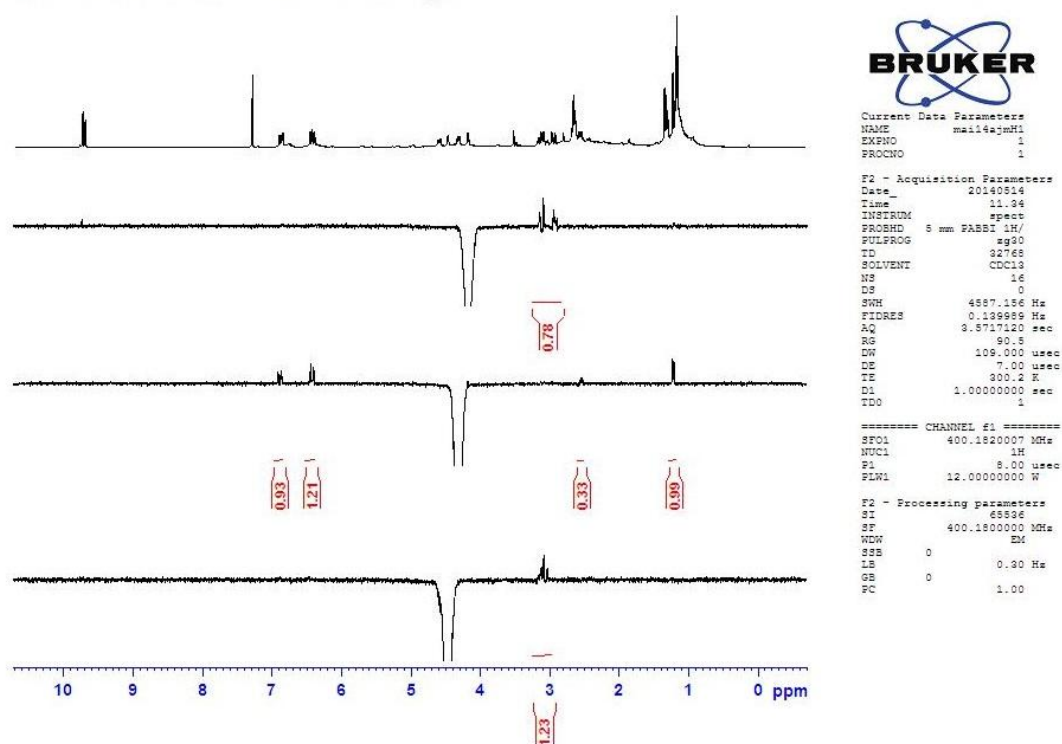


Figure S28. 1D NOESY spectrum (400.18 MHz, CDCl₃) of (*E*)-4-oxo-2-hexenal dimers.