

Structure determination of liquid biofuels *via in situ* cryocrystallisation and single crystal X-ray diffraction

Siriyara Jagannatha Prathapa, Cara Slabbert,^{a,b} Manuel A. Fernandes and Andreas Lemmerer^{*a}

a. Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg 2050, South Africa. Fax: +27 11 717 6749; Tel: +27 11 717 6711; E-mail: Andreas.Lemmerer@wits.ac.za; cara.slabbert@up.ac.za

b. Department of Chemistry, University of Pretoria, Pretoria, 0002, South Africa.

Supplementary Information

Table of Contents

A. <i>In-Situ</i> Cryocrystallization via OHCD technique	2
B. <i>ORTEP</i> and Packing / Hydrogen Bonding Diagrams of FAMEs	4
C. DSC Scans	19
D. Hirshfeld surfaces analysis	26

A. *In-Situ* Cryocrystallization via OHCD technique:

Single crystals of the liquid FAMES were grown *via in-situ* crystallization in a 0.3 mm diameter Lindemann (X-ray transparent glass) capillary using an Optical Heating and Crystallization Device (OHCD III). In this technique samples are loaded into a capillary, sealed on both sides and mounted vertically in the diffractometer (D8 VENTURE) then cooled down to crystallization temperature (just below the melting temperature) using a cold stream of liquid nitrogen. Diffraction quality crystals are created using a zone-melting technique where a small region of the capillary is heated with a CO₂ IR laser to create a molten zone. The laser intensity was increased from zero in 3 minutes to create the molten zone which is sample dependent (Table S1). Then the molten zone is slowly moved along the length of the capillary at about 3cm/30min by adjusting the position of the laser, allowing recrystallization of the molten zone.^{1,2} After each cycle intensity was reduced back to zero in 3 minutes. This cycle is repeated several times until a single crystal amenable for diffraction is obtained. Crystals successfully grown this way are then analysed at the atomic level by X-ray diffraction. The number of cycles, cycle time and laser intensity required to obtain a good quality single crystal is sample dependent, and the whole process, which is labour intensive, can take several days. (For a few compounds several attempts have been required resulting in weeks of work). Since the samples are sensitive to temperature and melt easily, the whole experiment is carried out in the measurement device (a diffractometer) hence the term *in situ*.

Table S1. Values of Zone-Melting temperature and the corresponding laser intensity used in the method of *In-Situ* Cryocrystallization of FAMES.

FAMES	Zone-Melting Temperature (°)	Laser Intensity
C ₅	-114	21
C ₆	-77	19
C ₇	-70	20
C ₈	-46	18
C ₉	-44.5	19
C ₁₀	-23	21
C ₁₁	-25	20
C ₁₂	-5	24
C ₁₃	-8	22

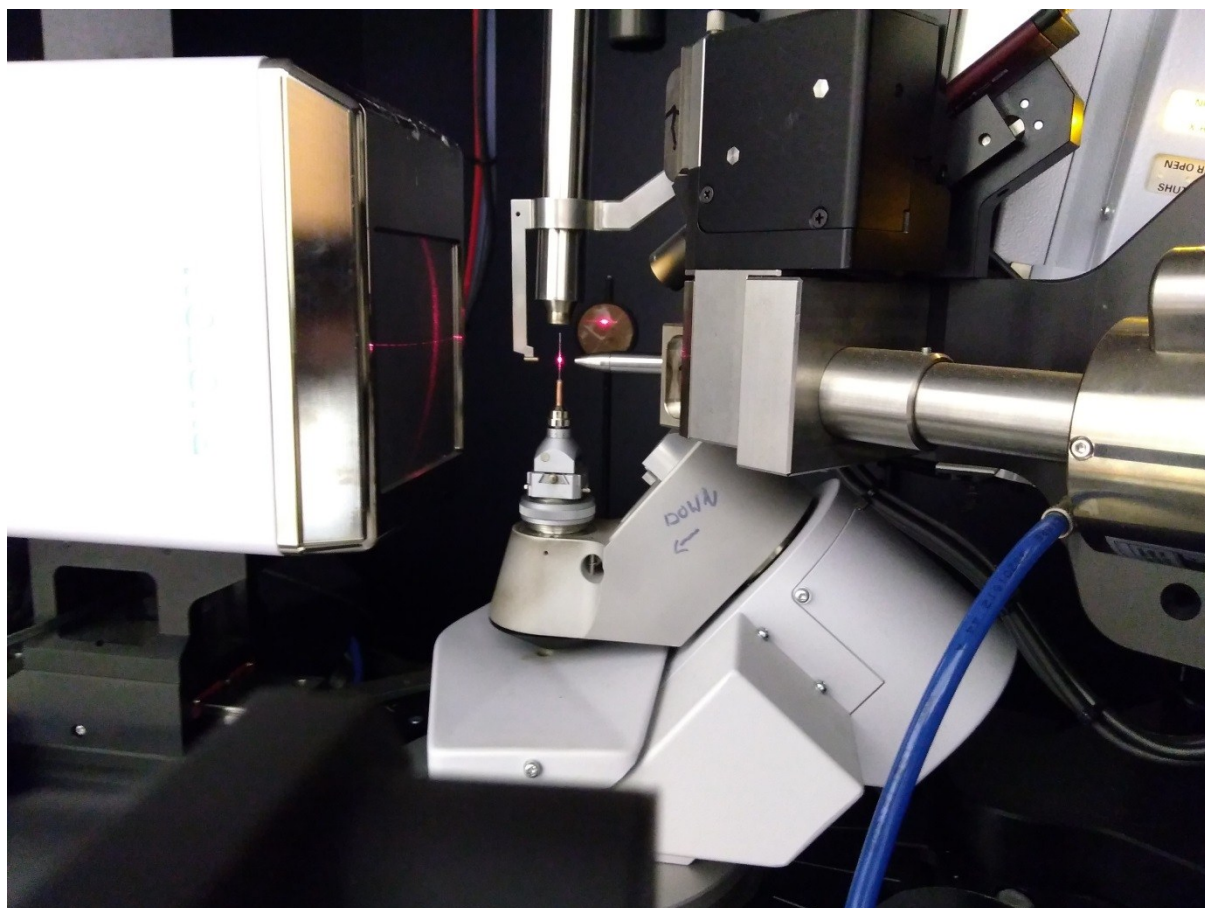


Figure S1. Experimental set up of In-Situ Cryocrystallization via OHCD technique on BRUKER D8 VENTURE X-ray diffractometer.

B. ORTEP and Packing Diagrams of FAMEs

B.1 ORTEP and Packing Diagrams for C₅ Methyl Ester:

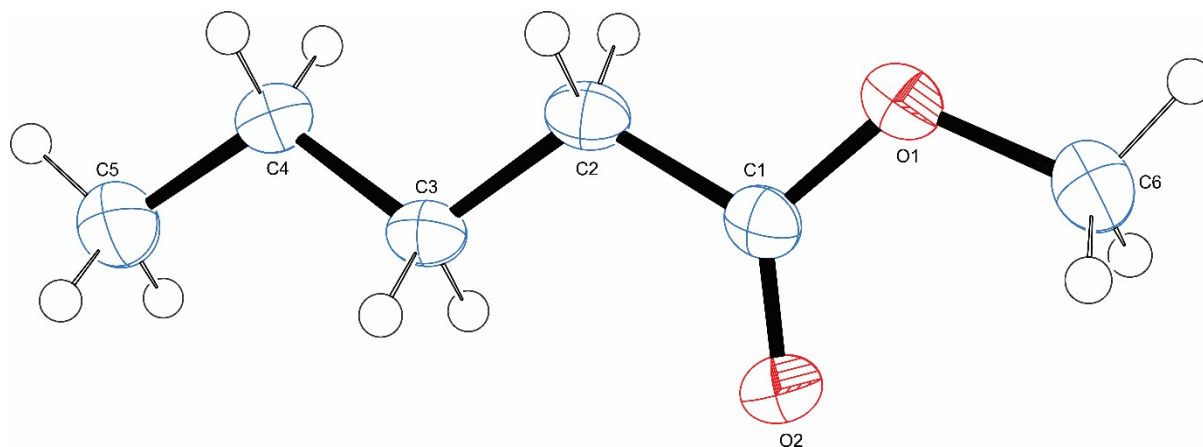


Figure S2. The ORTEP diagram of C₅ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

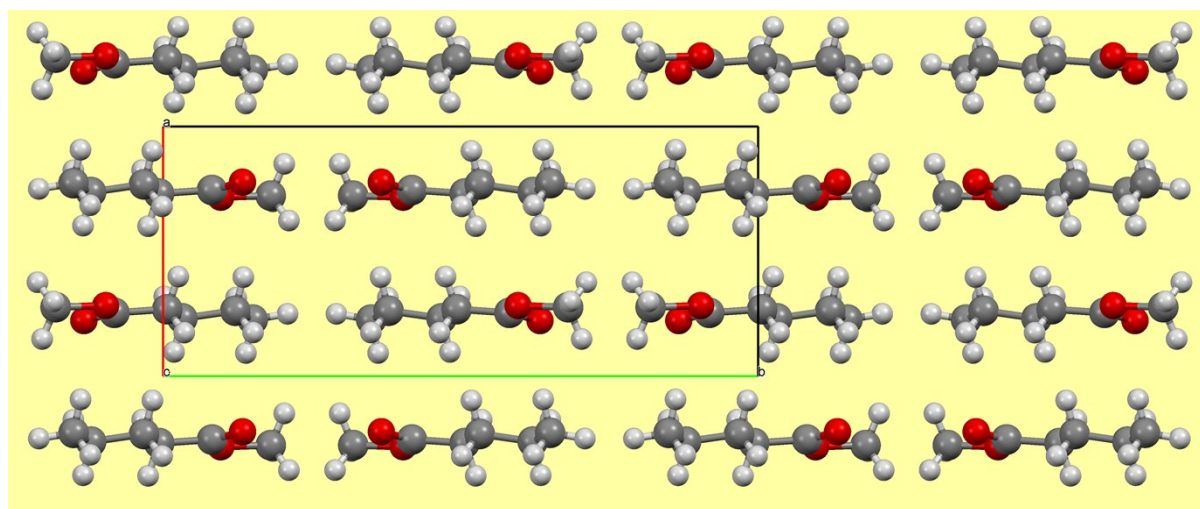


Figure S3. Packing diagram of C₅ methyl ester down the c-axis, showing the head-to-head arrangement.

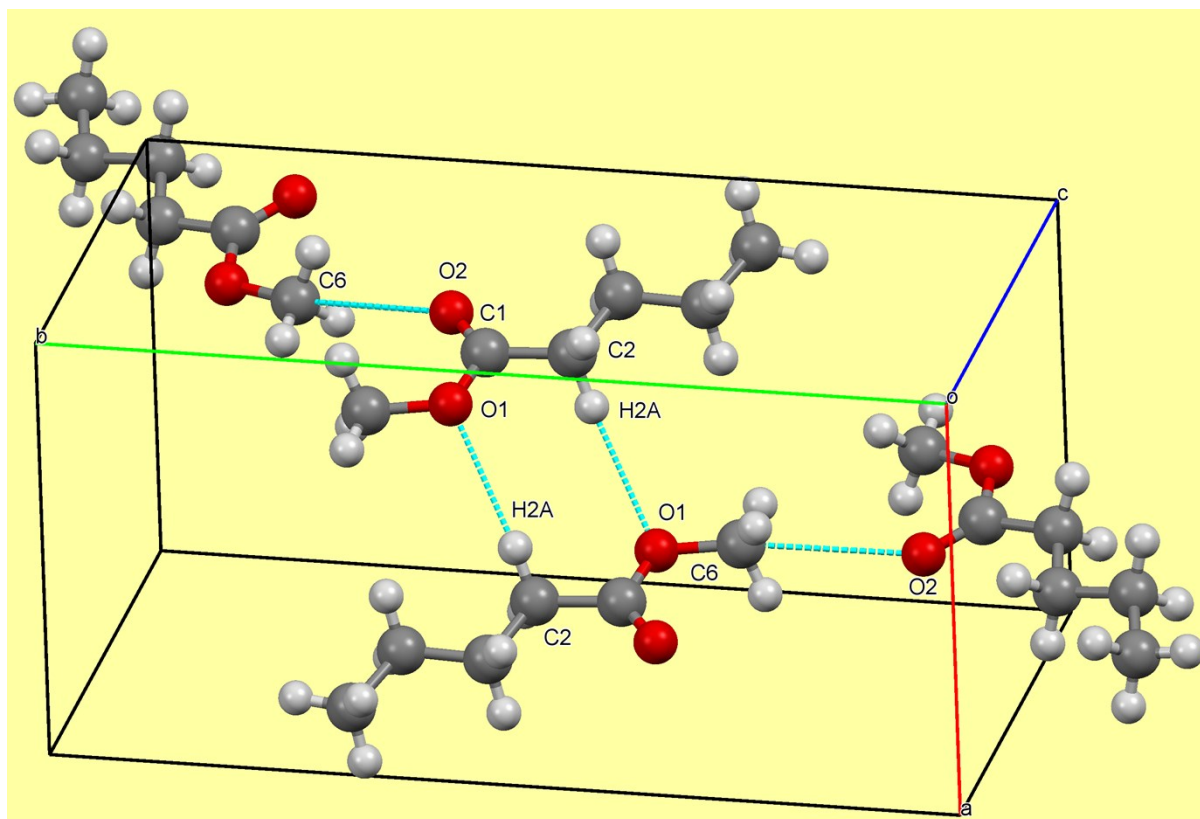


Figure S4. Hydrogen bonding and short contact packing diagram of C₅ methyl ester, , showing the C2-H2A...O1 hydrogen bond and C6...O2 short contact.

B.2 ORTEP and Packing Diagrams for C₆ Methyl Ester:

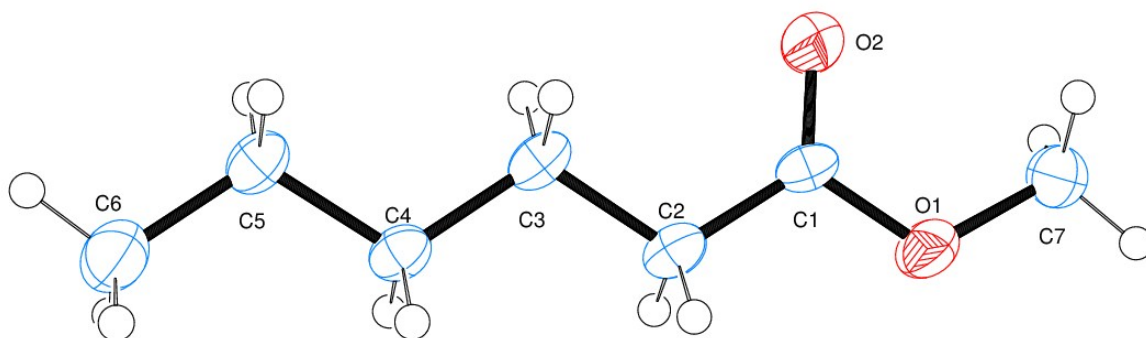


Figure S5. The ORTEP diagram of C₆ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

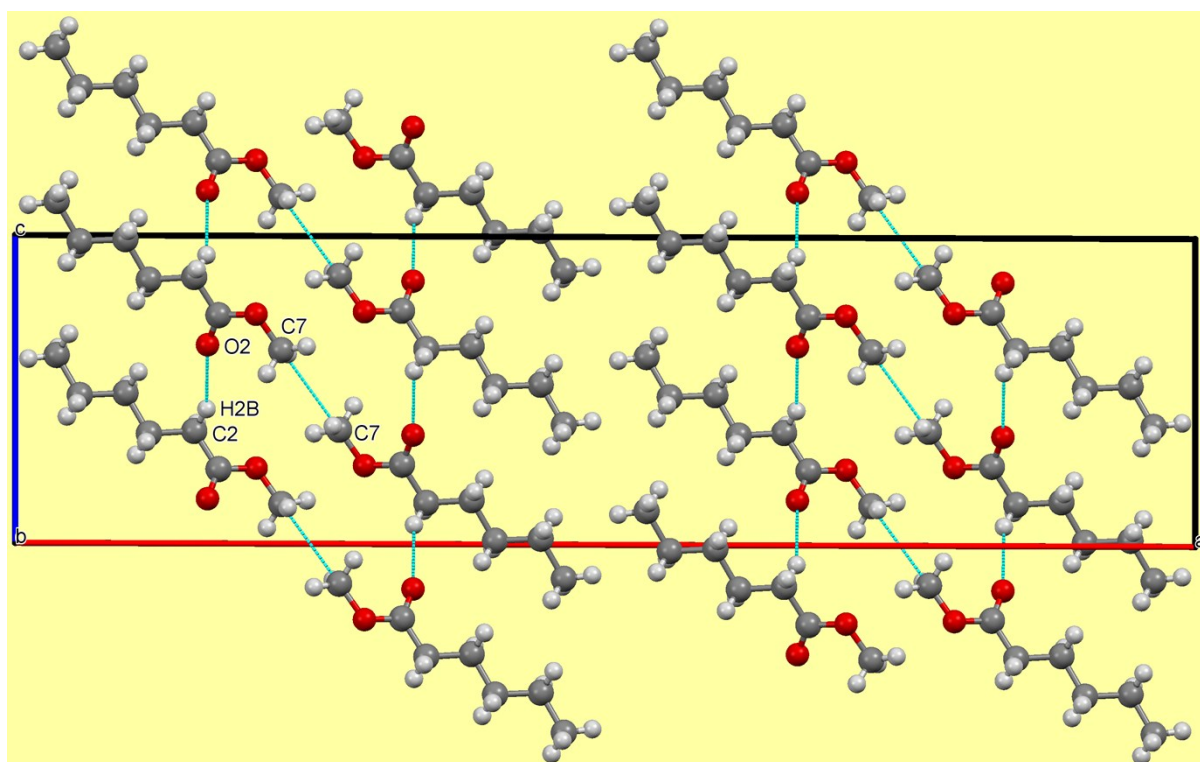


Figure S6. Crystal packing diagram of C₆ methyl ester viewed along the *b*-axis, showing the C(2)-H(2B)···O(2) hydrogen bond and C(7)···C(7) short contact.

B.3 ORTEP and Packing Diagrams for C₇ Methyl Ester:

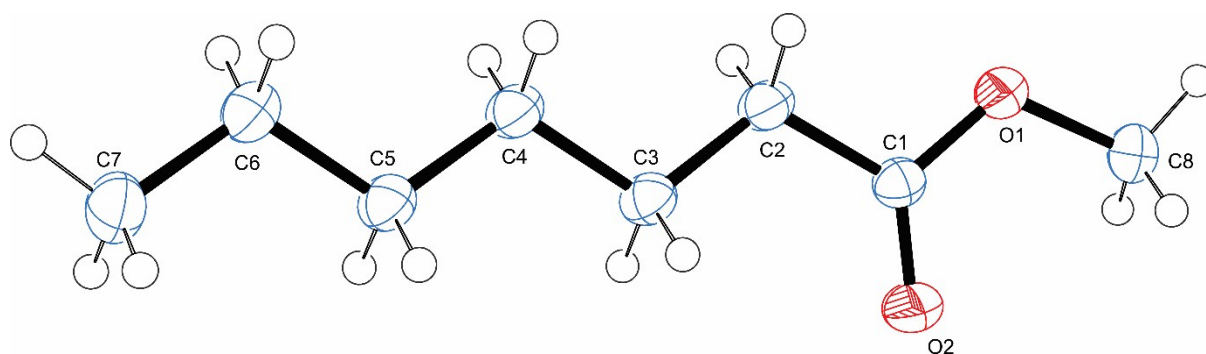


Figure S7. The ORTEP diagram of C₇ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

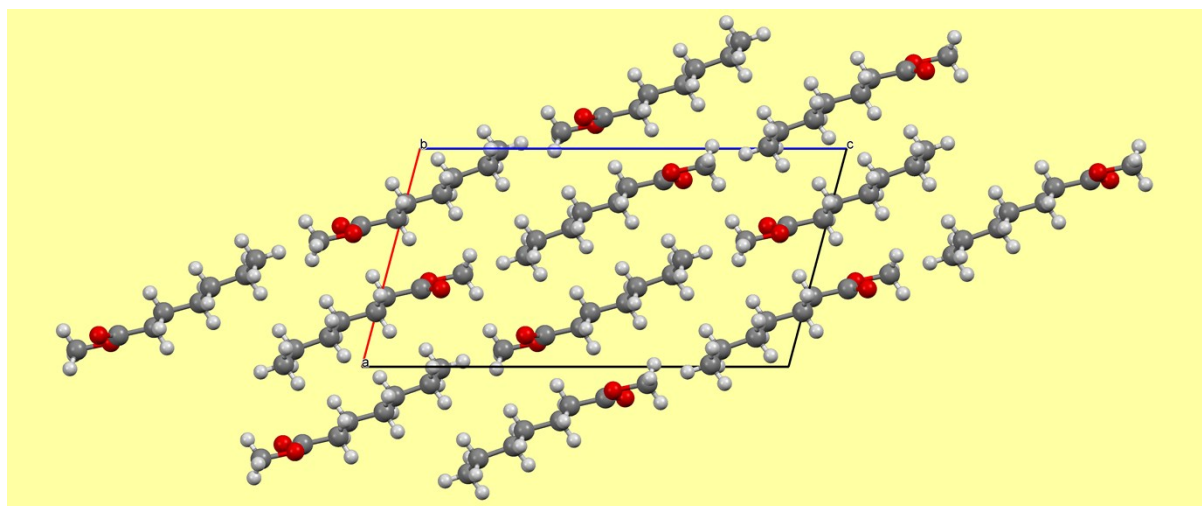


Figure S8. Packing diagram of C₇ methyl ester down the c-axis, showing the head-to-tail arrangement.

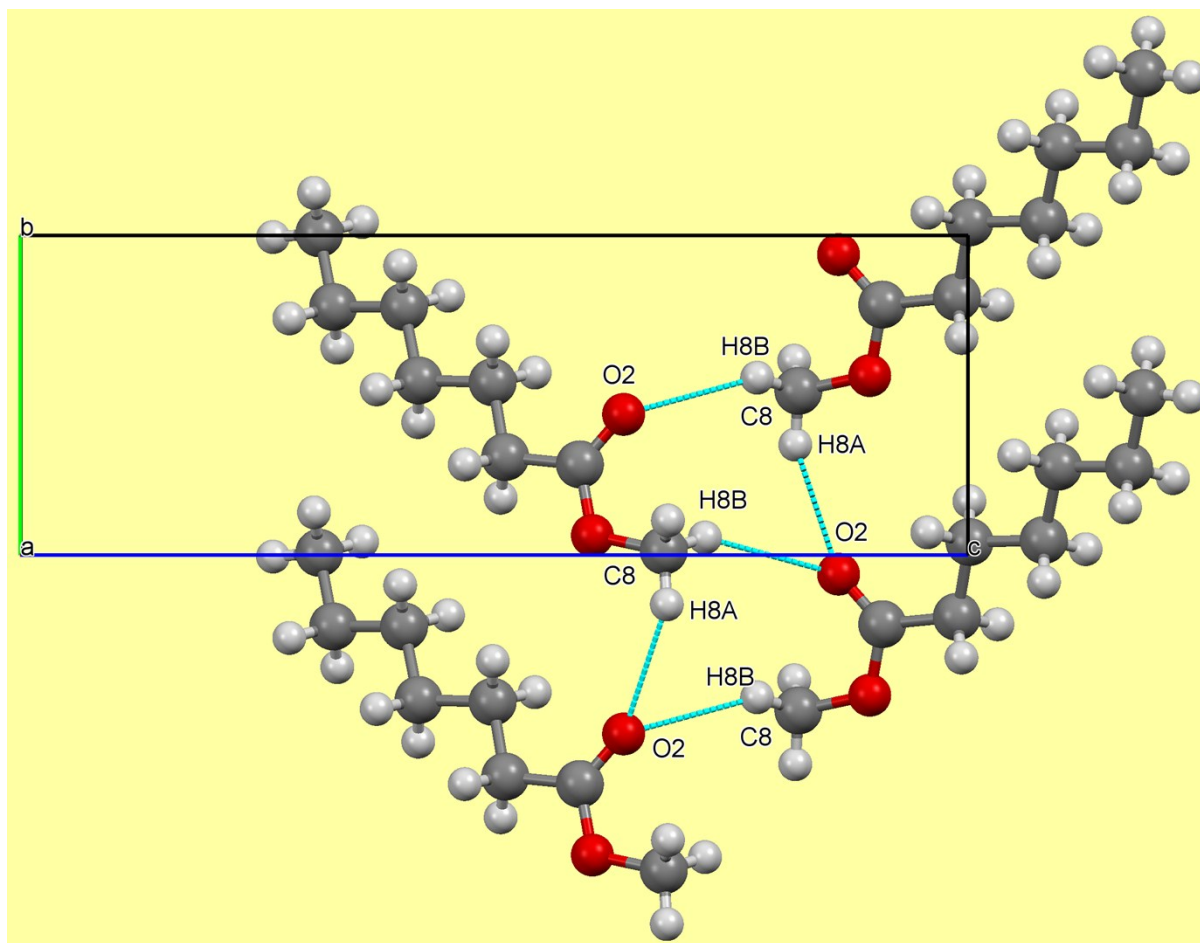


Figure S9. Hydrogen bonding diagram of C₇ methyl ester, showing the C8-H8A...O2 and C8-H8B...O2 hydrogen bonds.

B.4 ORTEP and Packing Diagrams for C₈ Methyl Ester:

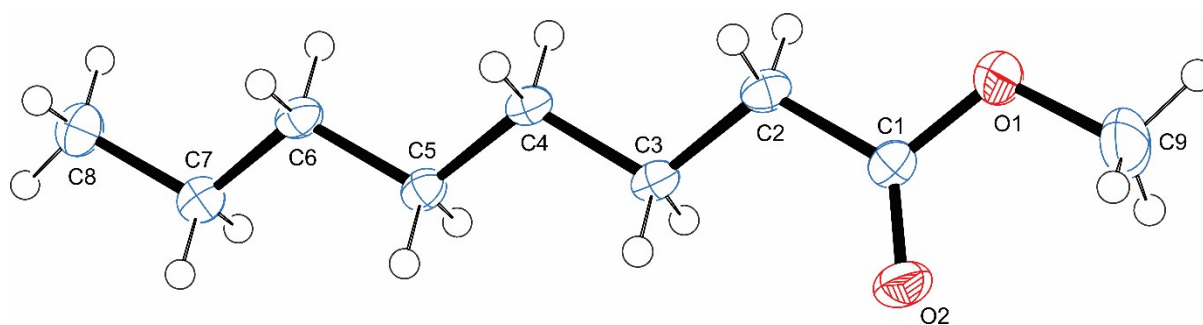


Figure S10. The ORTEP diagram of C₈ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

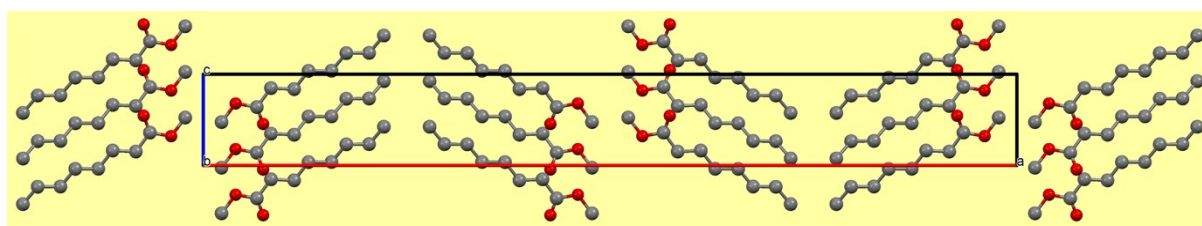


Figure S11. Crystal packing diagram of C₈ methyl ester viewed down *b*-axis, showing the herringbone packing arrangement and the head-to-head arrangement. H atoms omitted for clarity.

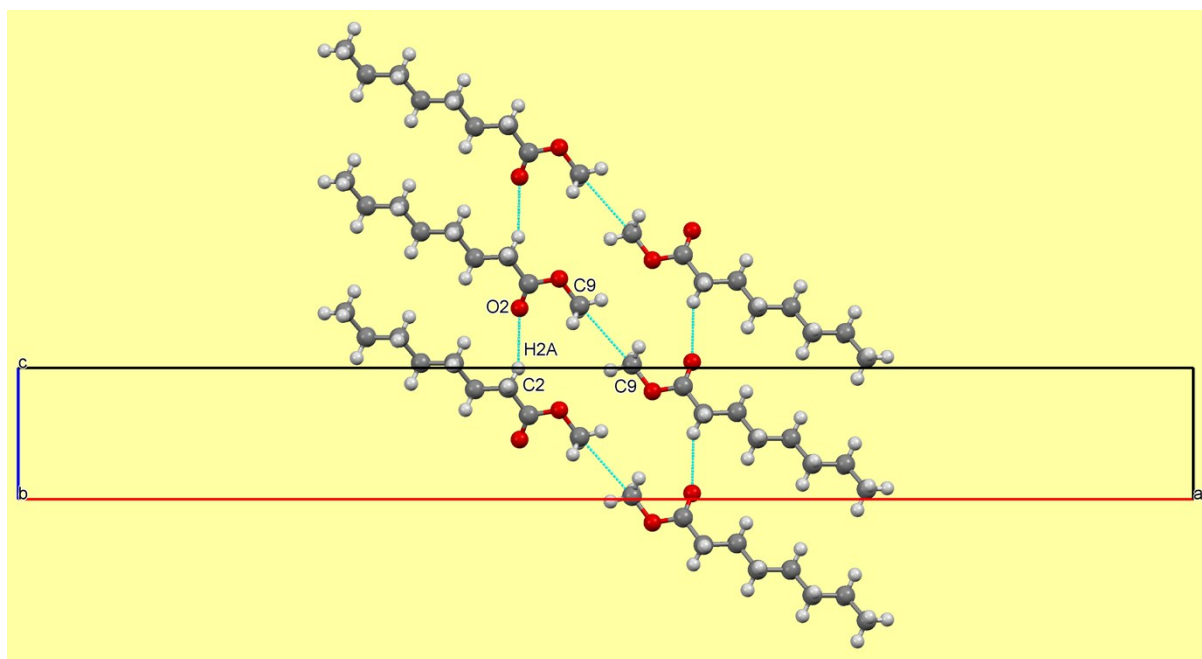


Figure S12. Hydrogen bonding and short contact packing diagram of C₈ methyl ester, showing the C₂-H2A...O₂ hydrogen bond and C₉...C₉ short contact.

B.5 ORTEP and Packing Diagrams for C₉ Methyl Ester:

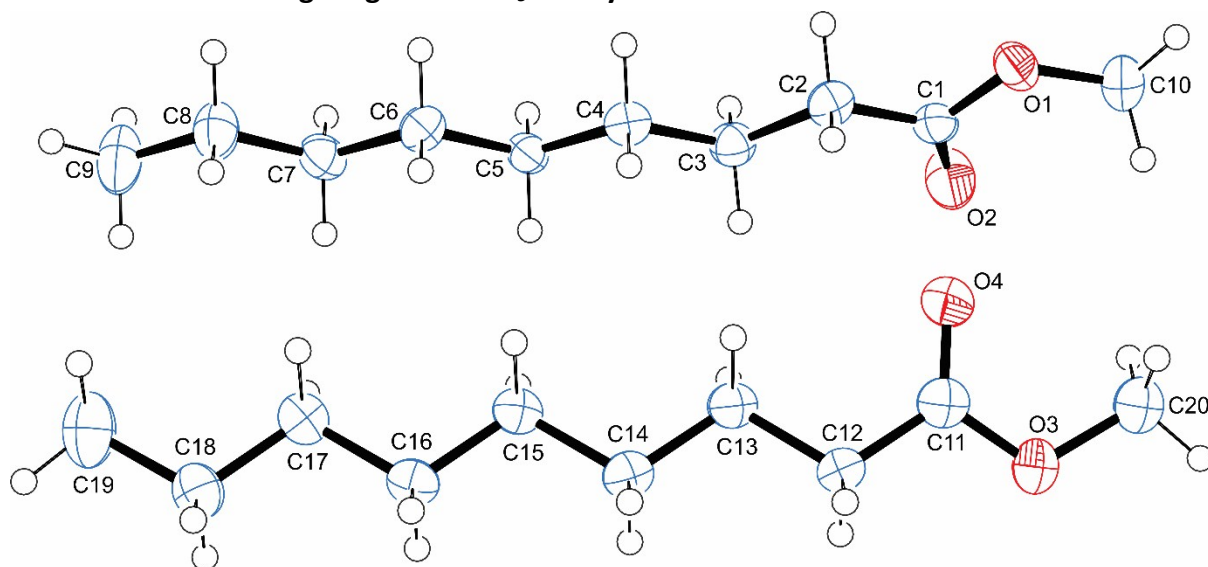


Figure S13. The ORTEP diagram of C₉ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

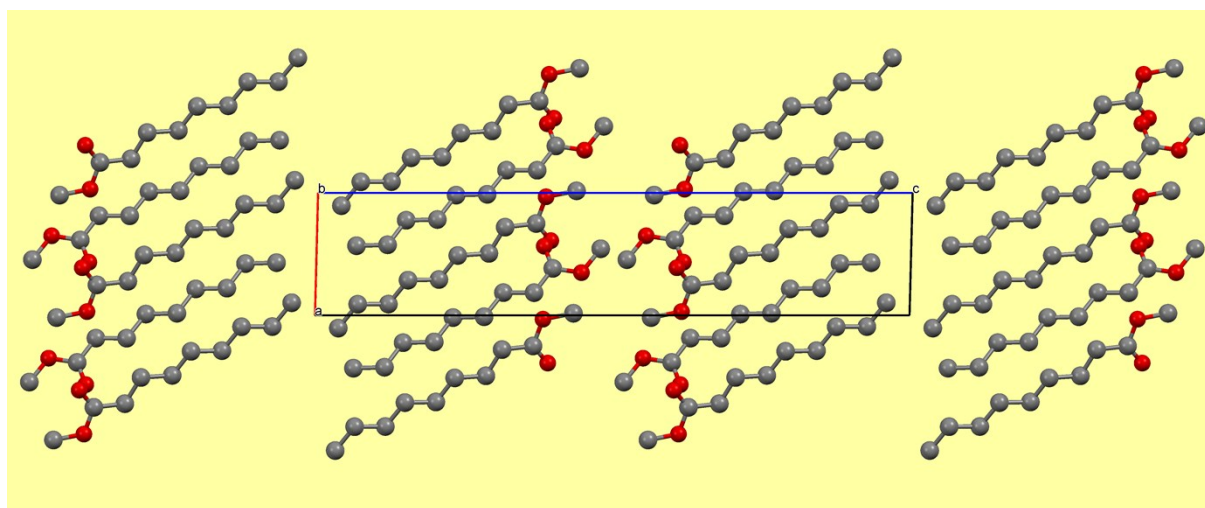


Figure S14. Crystal packing diagram of C₉ methyl ester viewed down *b*-axis, showing the head-to-head parallel stacking.

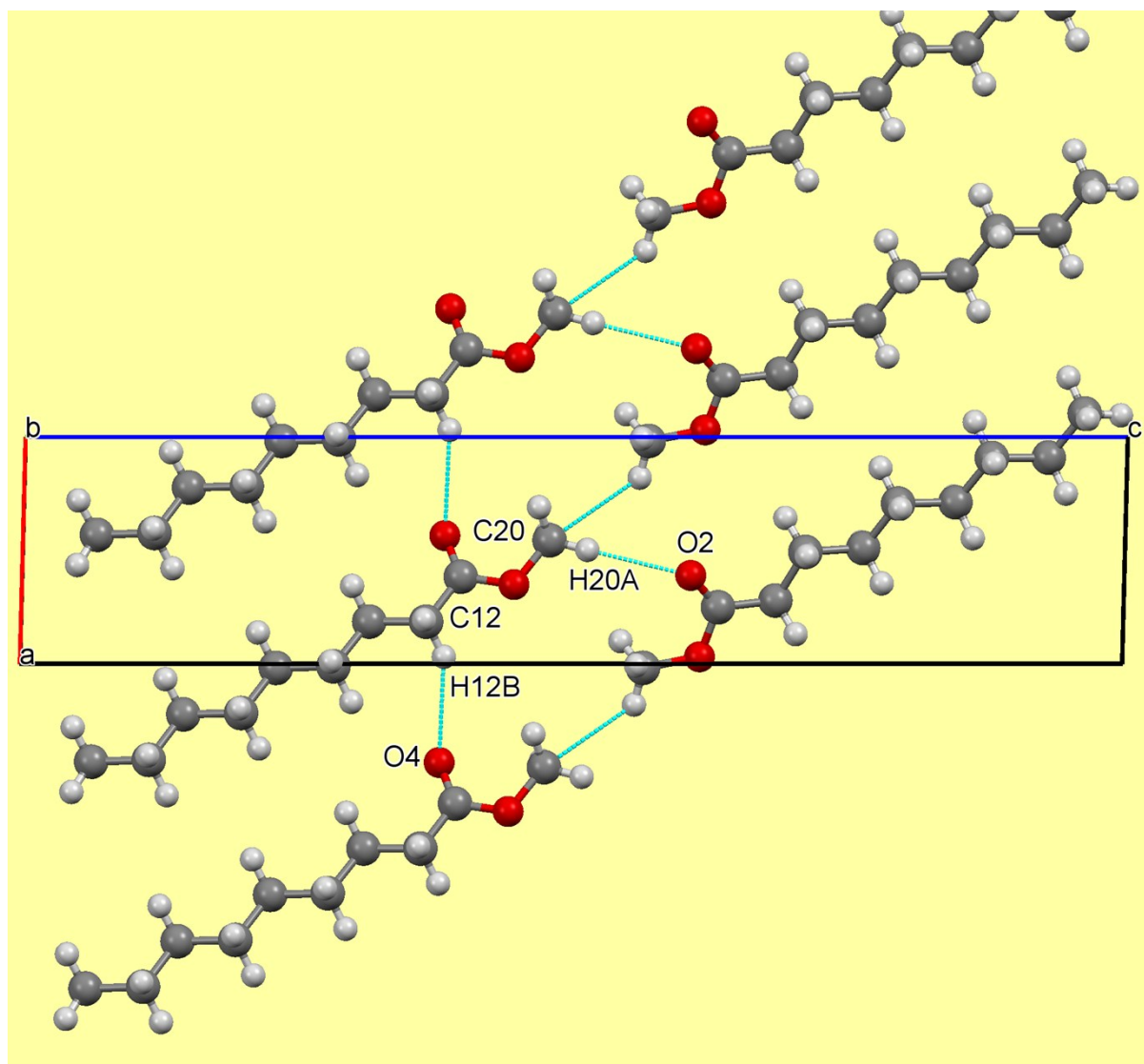


Figure S15. Hydrogen bonding and short contact packing diagram of C₉ methyl ester, showing the C12-H12B $\cdots$ O4 and C20-H20A $\cdots$ O2 hydrogen bond.

B.6 ORTEP and Packing Diagrams for C₁₀ Methyl Ester:

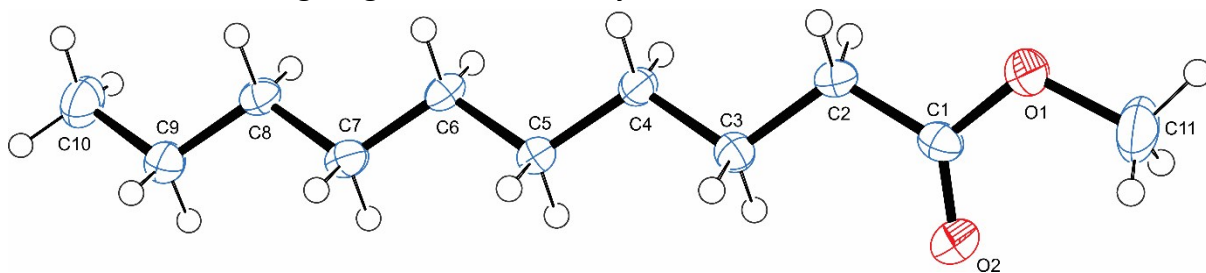


Figure S16. The ORTEP diagram of C₁₀ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

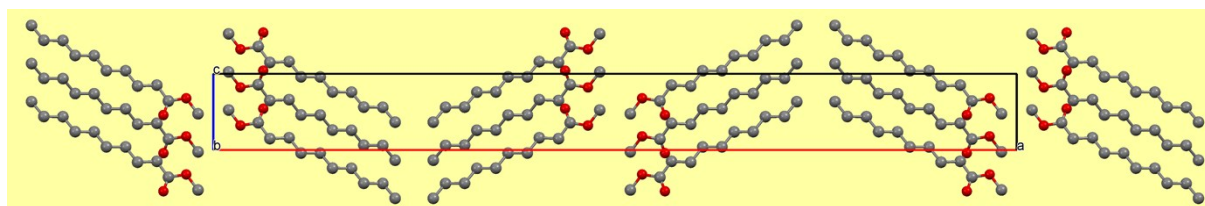


Figure S17. Crystal packing diagram of C₁₀ methyl ester viewed down *b*-axis, showing the herringbone packing arrangement and the head-to-head arrangement. H atoms omitted for clarity.

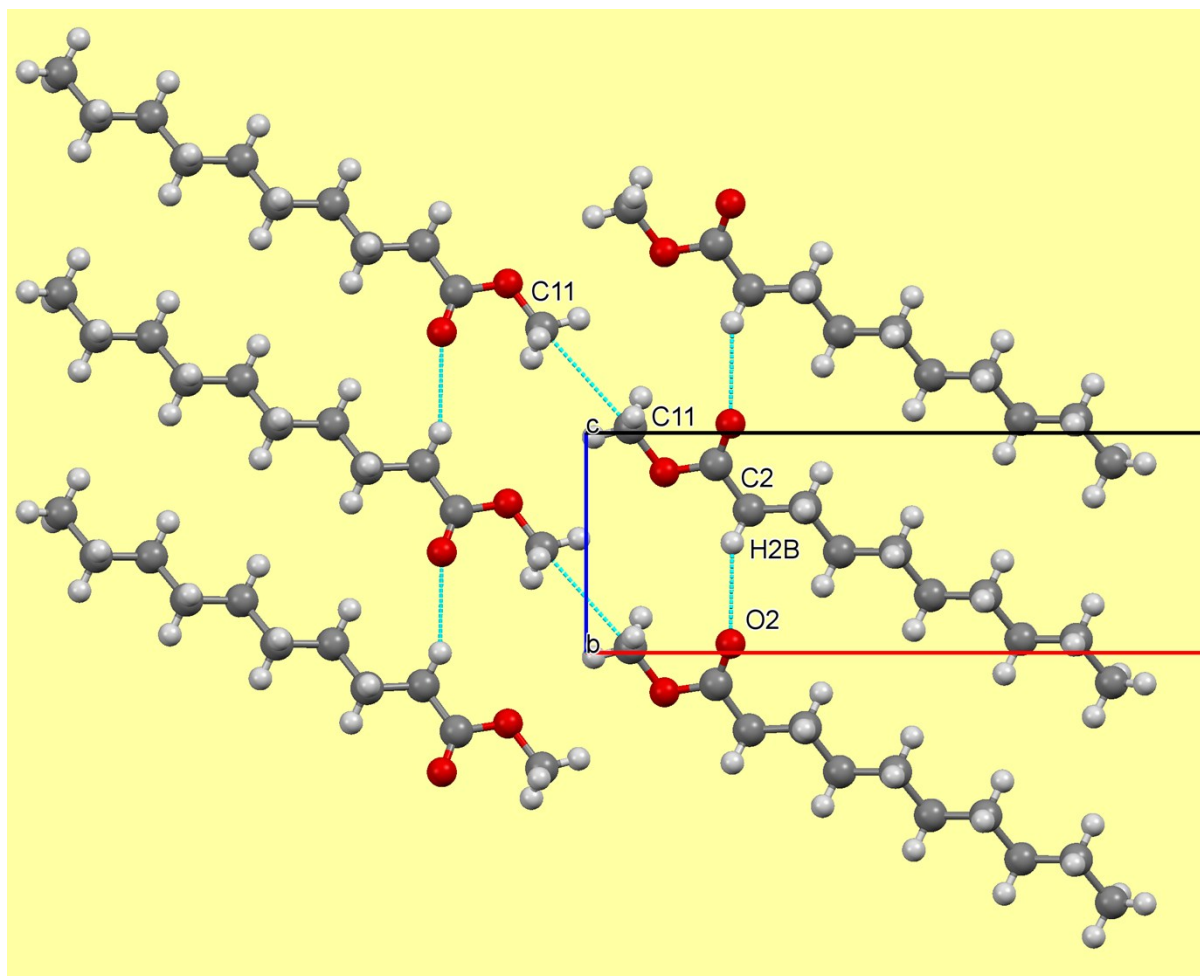


Figure S18. Hydrogen bonding and short contact packing diagram of C₁₀ methyl ester, showing the C2-H2B...O2 hydrogen bond and C11...C11 short contact.

B.7 ORTEP and Packing Diagrams for C₁₁ Methyl Ester:

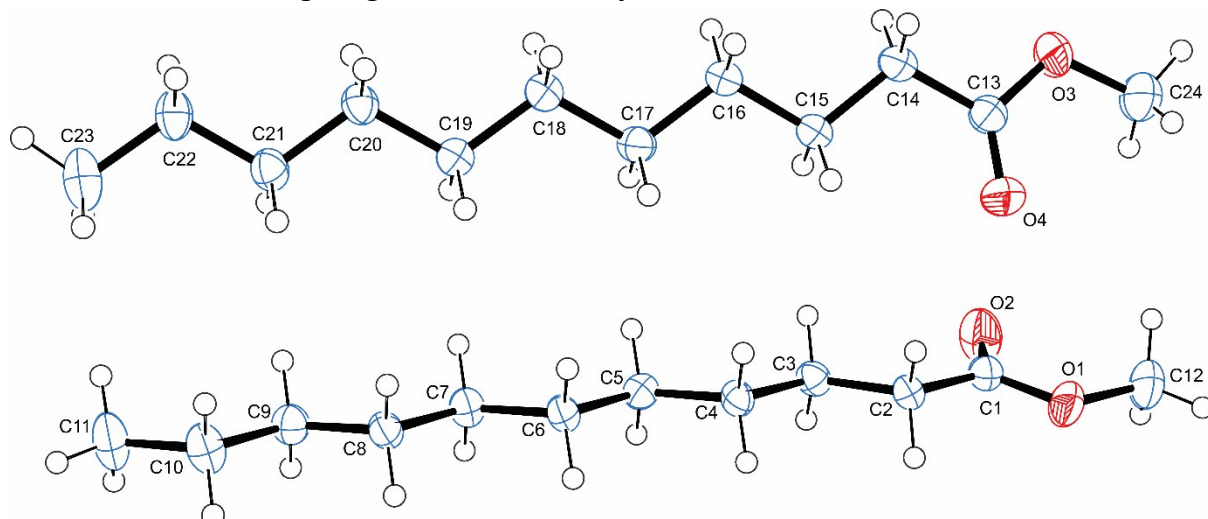


Figure S19. The ORTEP diagram of C₁₁ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

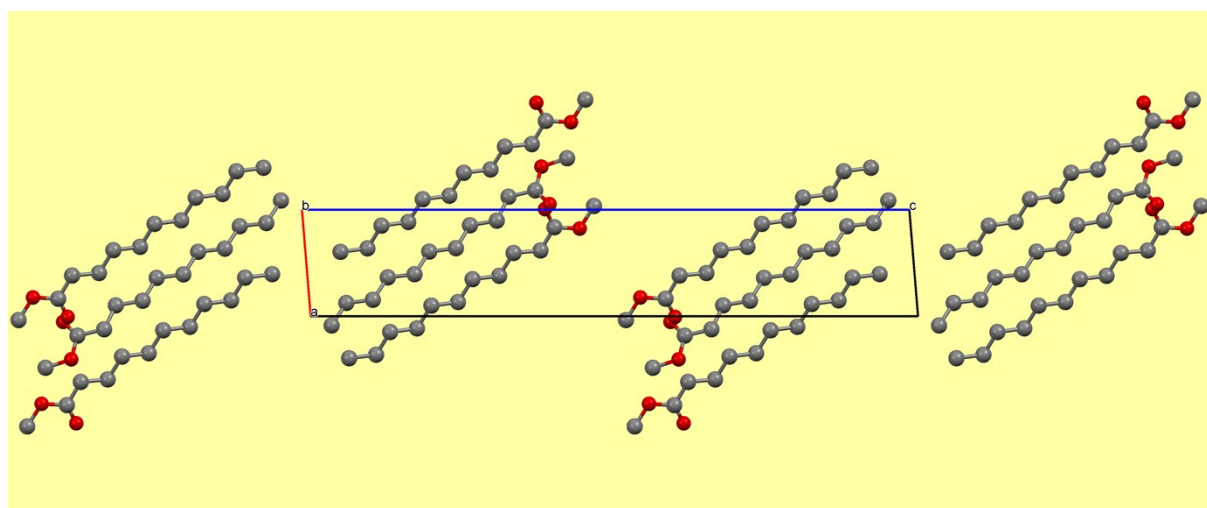


Figure S20. Crystal packing diagram of C₁₁ methyl ester viewed down *b*-axis, showing the head-to-head parallel stacking.

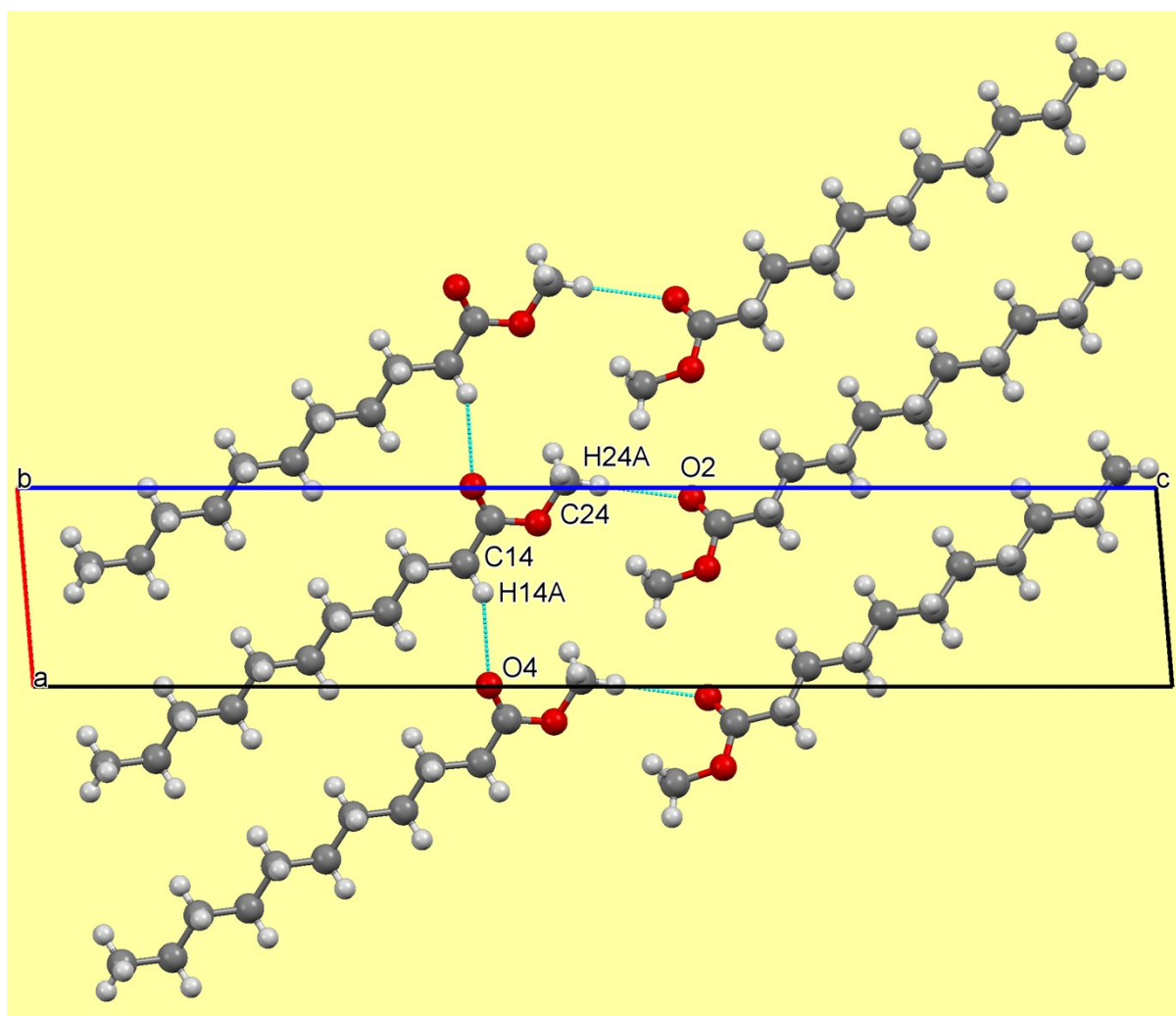


Figure S21. Hydrogen bonding and short contact packing diagram of C₁₁ methyl ester, showing the C14-H14A...O4 and C24-H24A...O2 hydrogen bond.

B.8 ORTEP and Packing Diagrams for C₁₂ Methyl Ester:

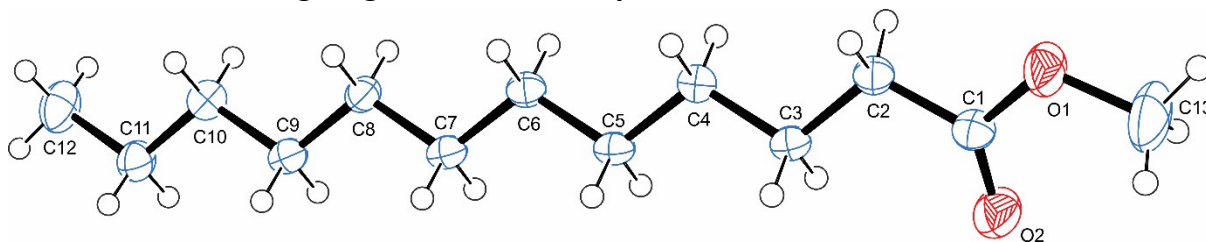


Figure S22. The ORTEP diagram of C₁₂ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

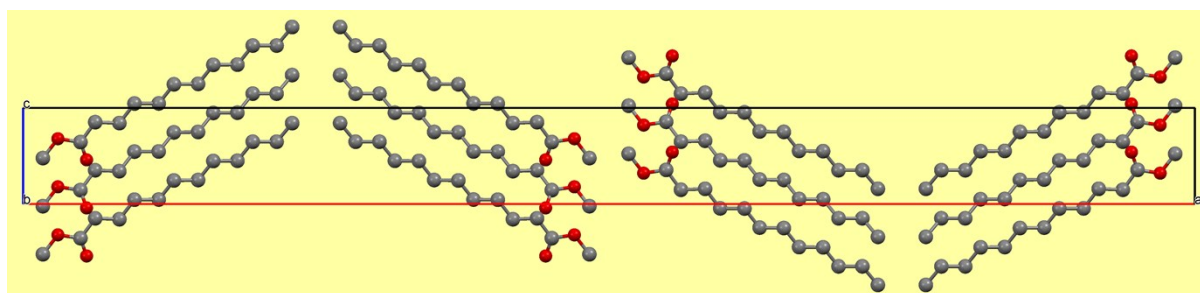


Figure S23. Crystal packing diagram of C₁₂ methyl ester viewed down *b*-axis, showing the herringbone packing arrangement and the head-to-head arrangement. H atoms omitted for clarity.

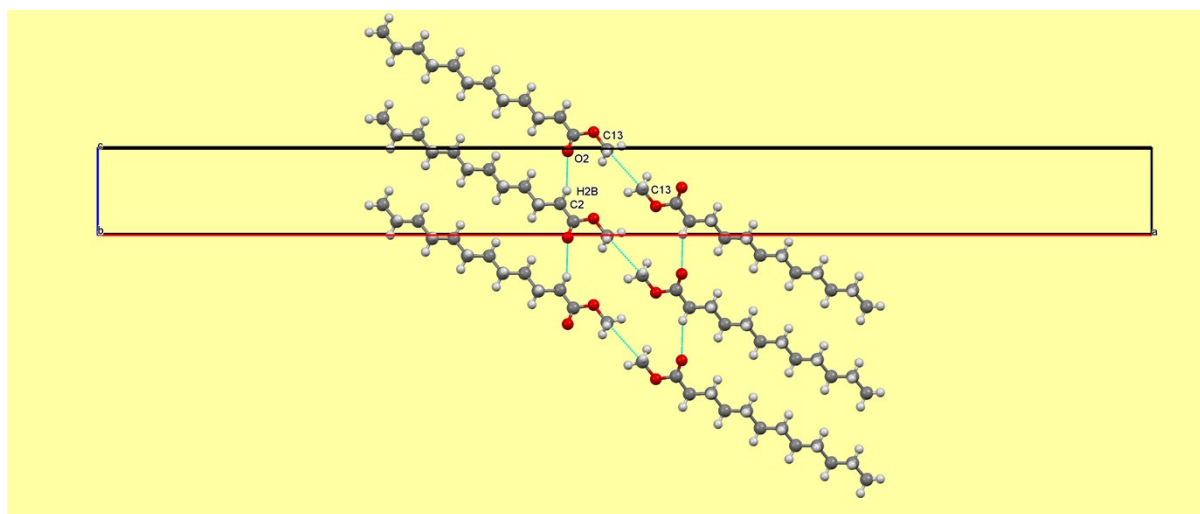


Figure S24. Hydrogen bonding diagram of C₁₂ methyl ester, showing the C2-H2B...O2 hydrogen bond.

B.9 ORTEP and Packing Diagrams for C₁₃ Methyl Ester:

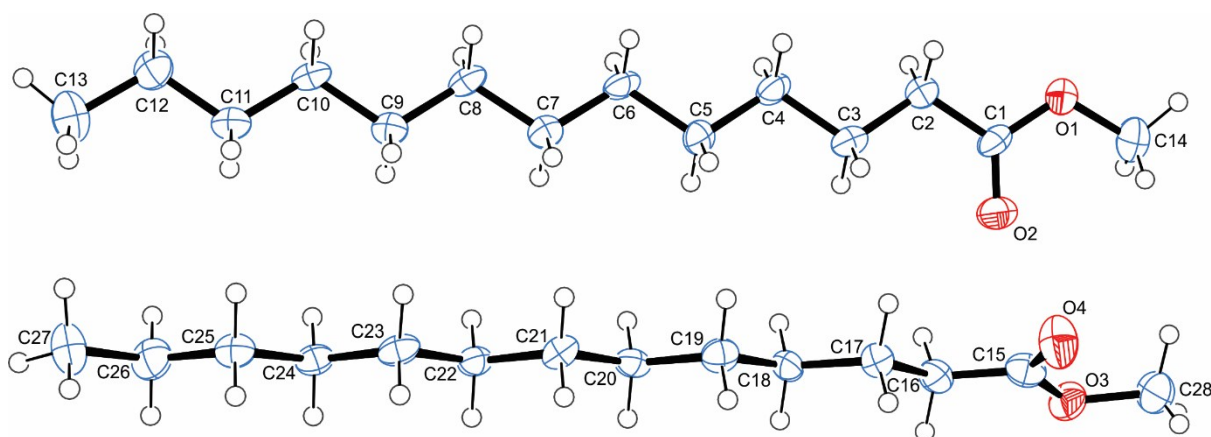


Figure S25. The ORTEP diagram of C₁₃ methyl ester with displacement ellipsoids drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

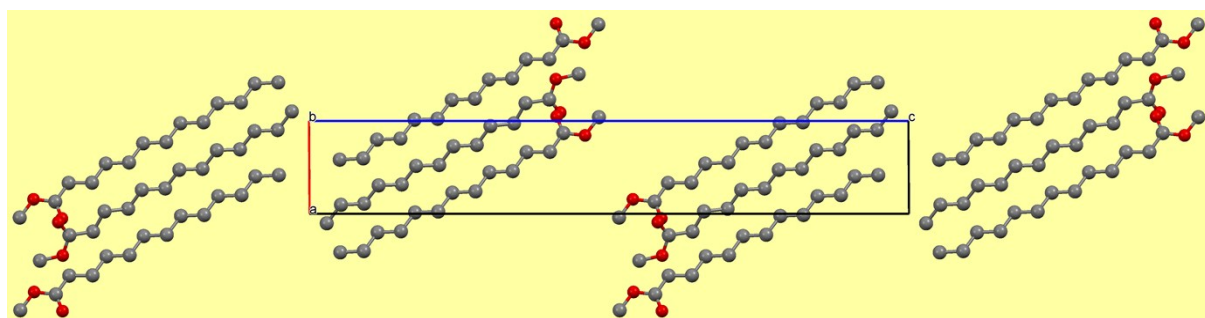


Figure S26. Crystal packing diagram of C₁₃ methyl ester viewed down *b*-axis, showing the head-to-head parallel stacking.

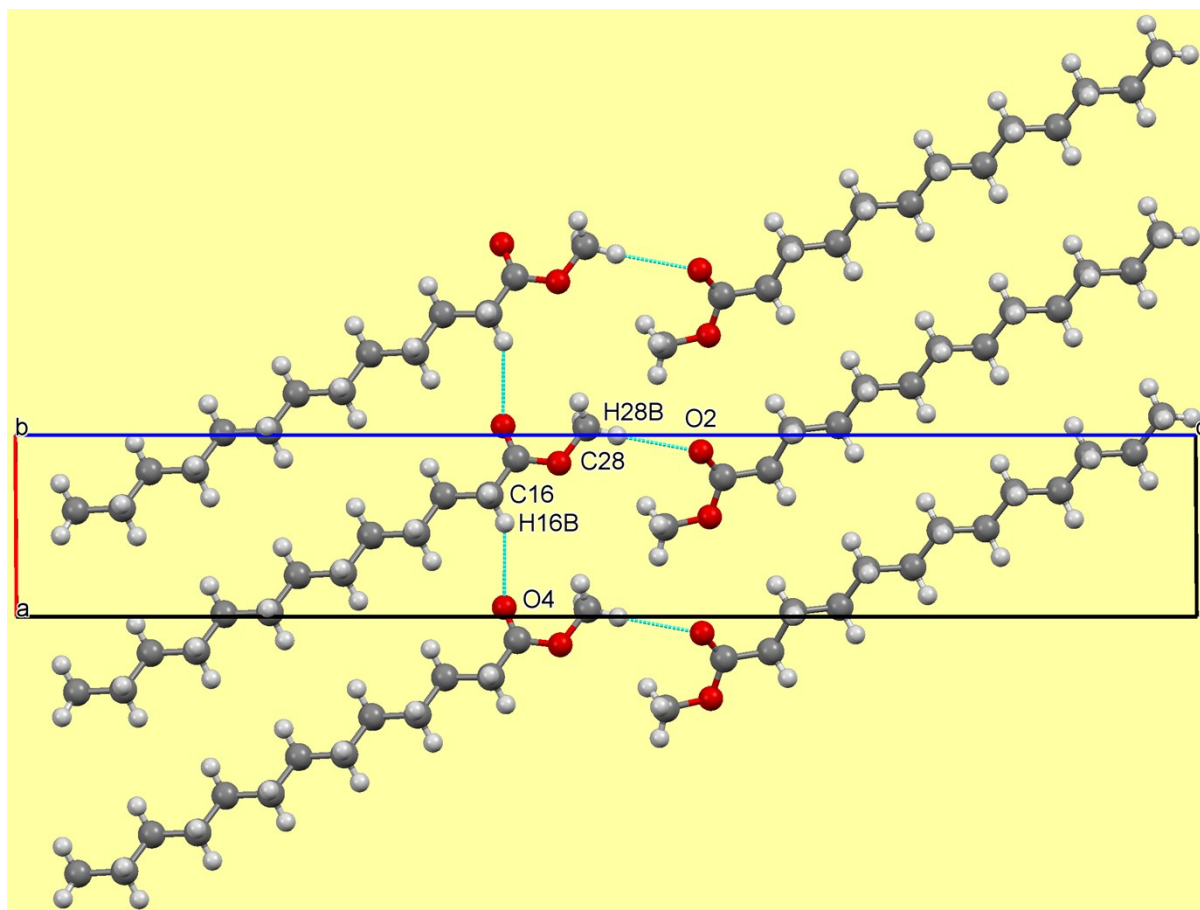


Figure S27. Hydrogen bonding and short contact packing diagram of C₁₃ methyl ester, showing the C16-H16B...O4 and C28-H28B...O2 hydrogen bond.

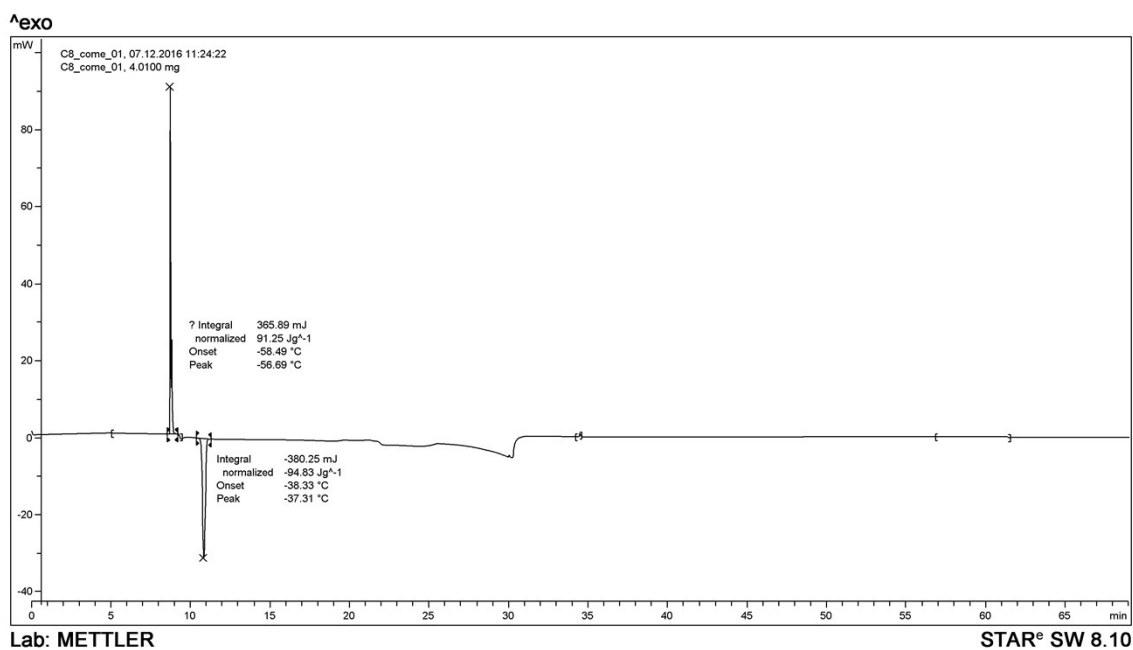
C. DSC Scans for FAME

Table S2 Literature and experimental melting point determined by DSC

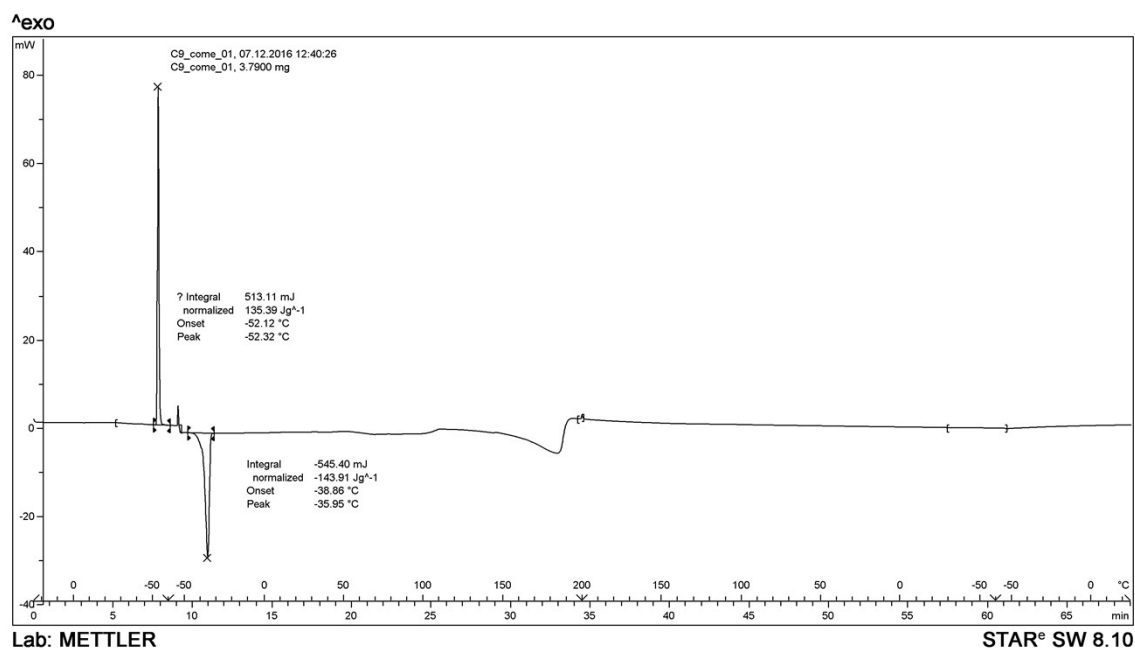
Methyl ester	CAS	Melting Point Literature ¹ / °C	Melting Point (DSC) / °C
C ₅	624-24-8	-90.65	-
C ₆	106-70-7	-69.55	-
C ₇	106-73-0	-55.75	-
C ₈	111-11-5	-36.65	-38.3
C ₉	1731-84-6	-34.35	-38.9
C ₁₀	111-42-9	-12.75	-14.8
C ₁₁	1731-86-8	-11.35	-14.2
C ₁₂	111-82-0	4.85	+4.1
C ₁₃	1731-88-0	5.85	+3.1

- 1 N. Adriaanse, H. Dekker and J. Coops, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 557.

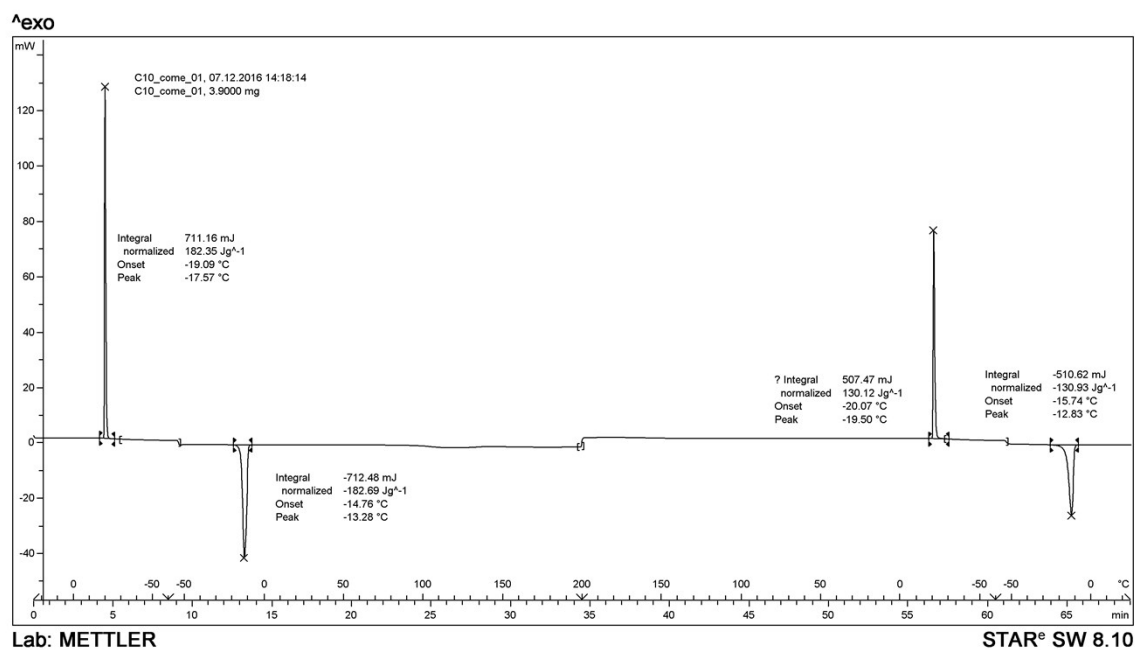
C.1 C₈ Methyl Ester



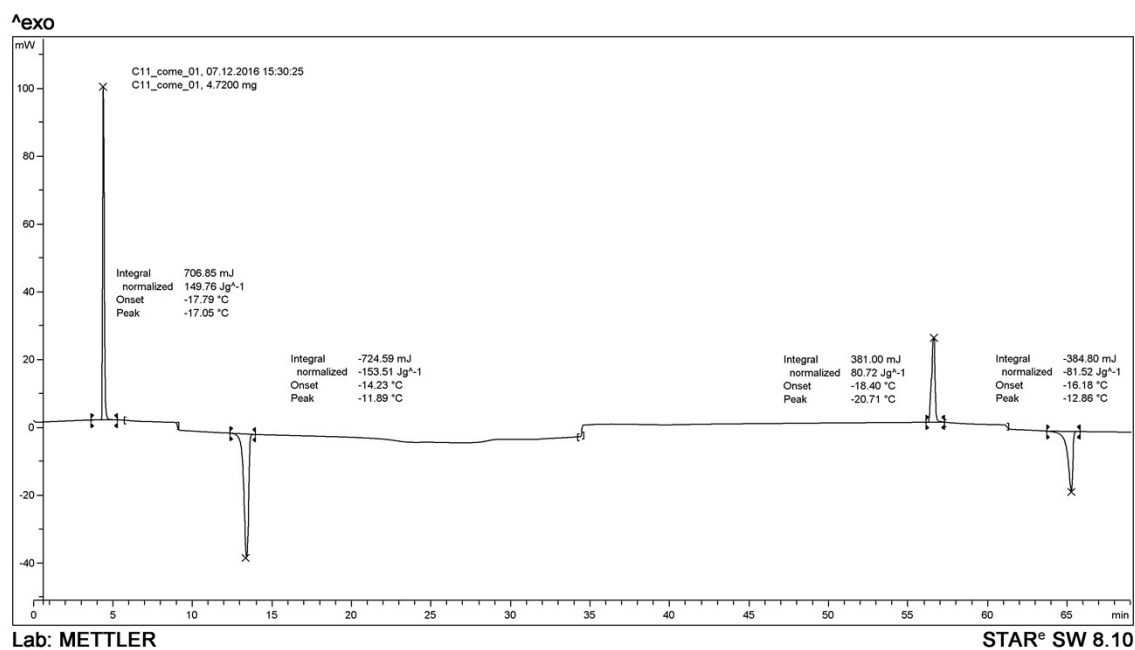
C.2 C₉ Methyl Ester



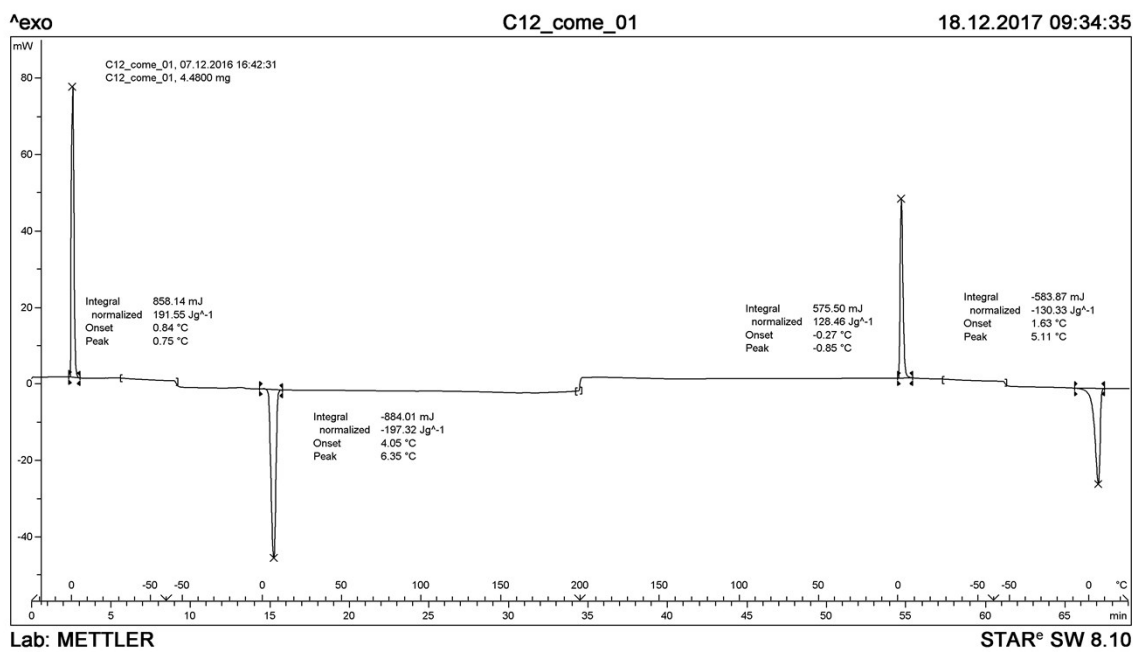
C.3 C₁₀ Methyl Ester



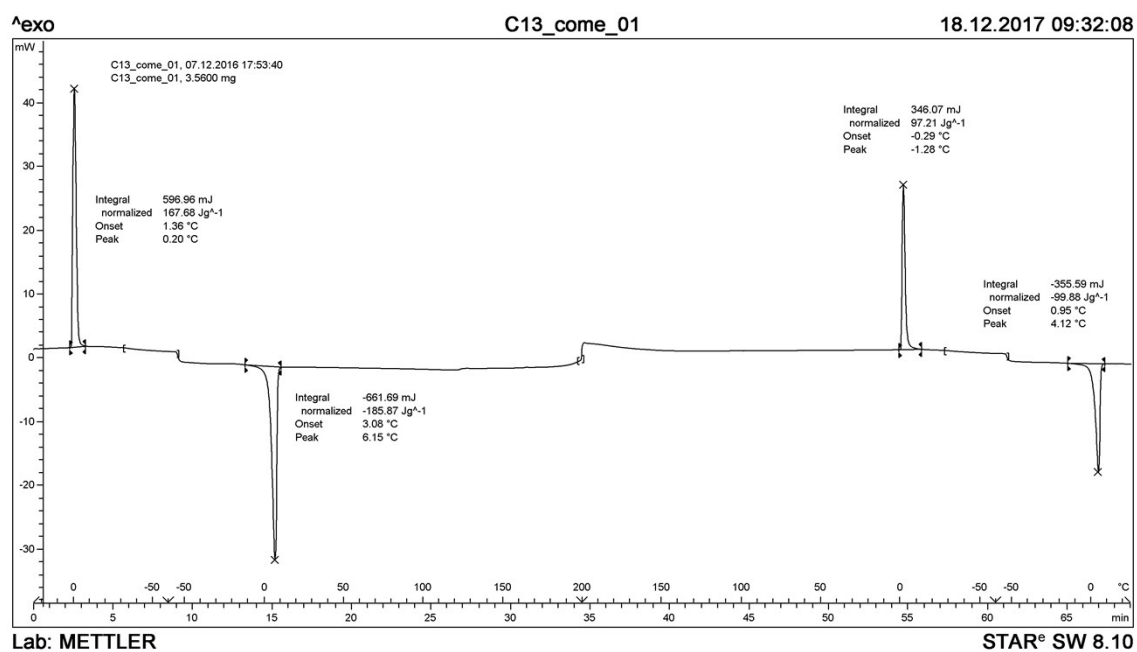
C.4 C₁₁ Methyl Ester



C.5 C₁₂ Methyl Ester



C.6 C₁₃ Methyl Ester



D.1 Hirshfeld surfaces analysis – Fingerprint plots

Figure S20. Fingerprint plots for the C_5 to C_7 FAMEs, resolved into O...H (left) and H...H contacts (right), with the full fingerprint plot as a grey shadow beneath each decomposed plot.

Figure S21. Fingerprint plots for the even- (left) and odd-numbered members (right) of the C_8 to C_{13} FAMEs, resolved into O...H (left) and H...H contacts (right), with the full fingerprint plot as a grey shadow beneath each decomposed plot.