Electronic Supplementary Information

Synthesis of fatty ketoesters by tandem epoxidation-rearrangement with heterogeneous catalysis

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1. Chromatographic conditions and typical chromatograms from the epoxidation and Meinwald rearrangement reactions.

The reactions were monitored using an Agilent 7890A and an Agilent 6890N chromatographs, both equipped with FID detectors. The capillary column was a ZB-5HT Inferno: 30 m × 0.25 mm × 0.25 µm. Helium was used as carrier gas at 17 psi in column head.

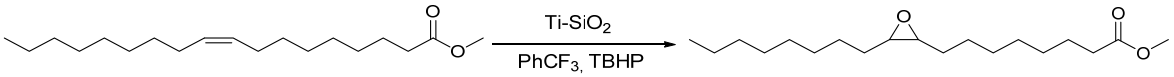
Injector temperature: 280 °C.

Detector temperature: 250 °C.

Oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C (0 min) and 5 °C min^{-1} to 250 °C (15 min).

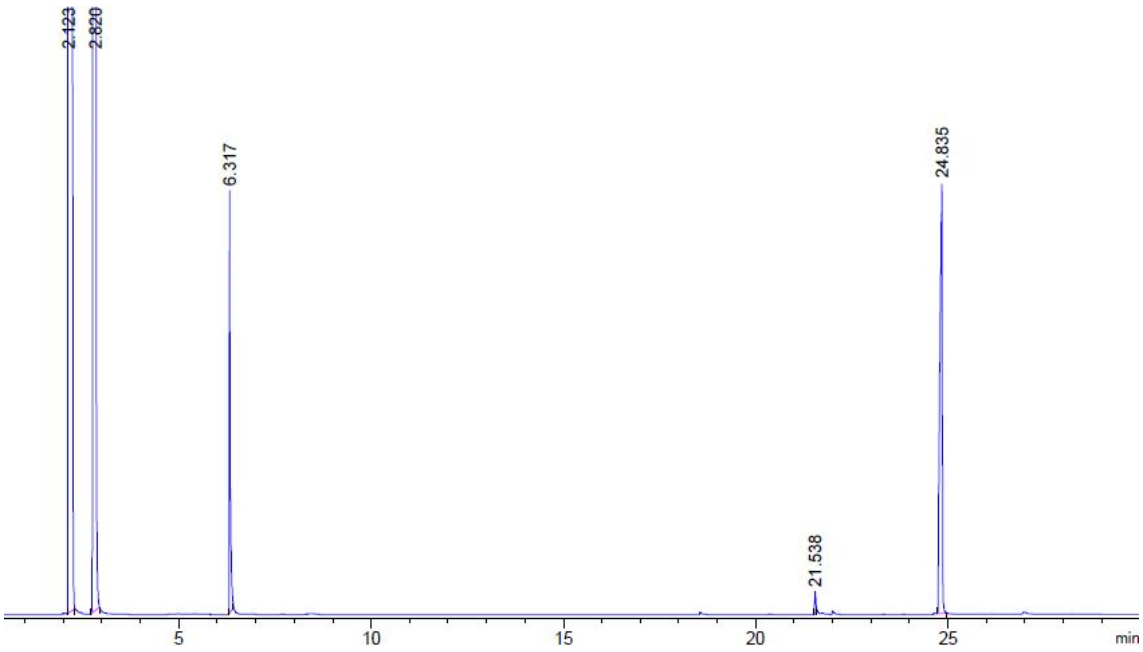
1.1. Epoxidation reactions

1.1.1. Reaction with methyl oleate

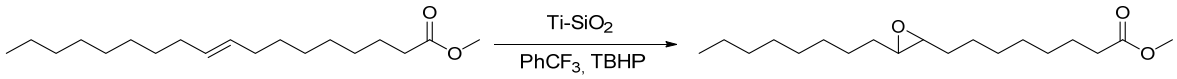


Retention times:

- decane: 6.3 min
- methyl oleate: 21.5 min
- methyl *cis*-9,10-epoxystearate: 24.8 min

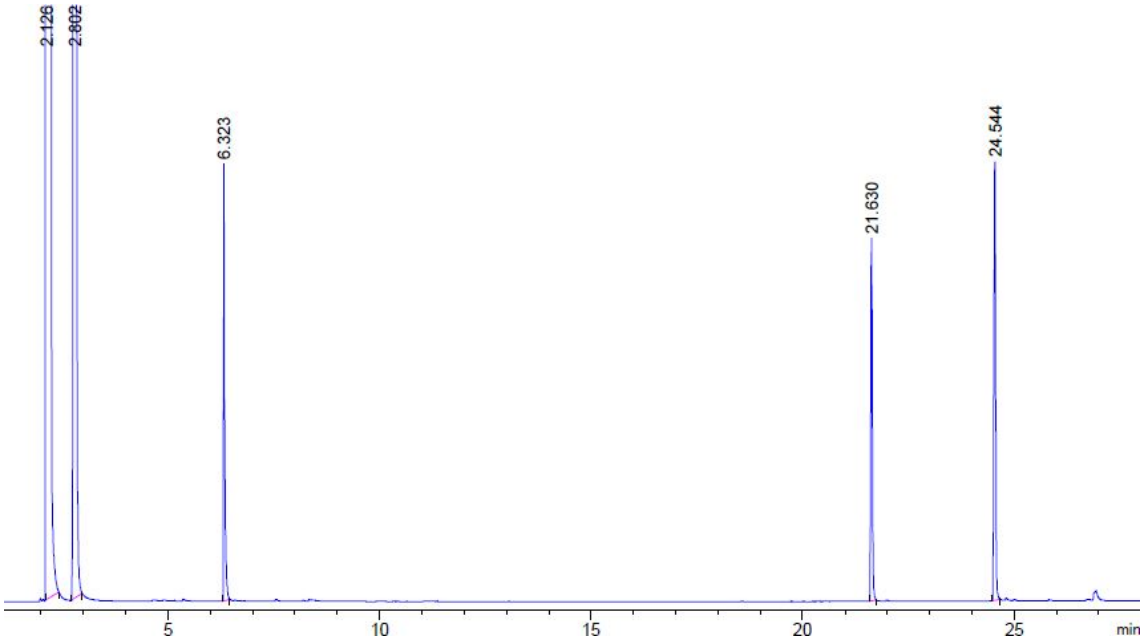


1.1.2. Reaction with methyl elaidate

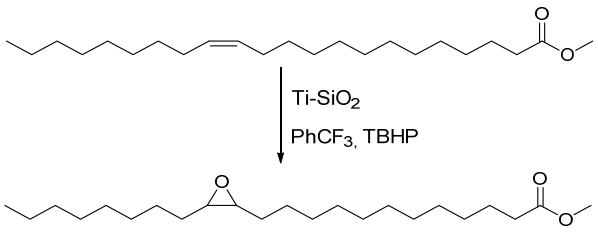


Retention times:

- Decane: 6.3 min
- methyl elaidate: 21.6 min
- methyl *trans*-9,10-epoxystearate: 24.5 min

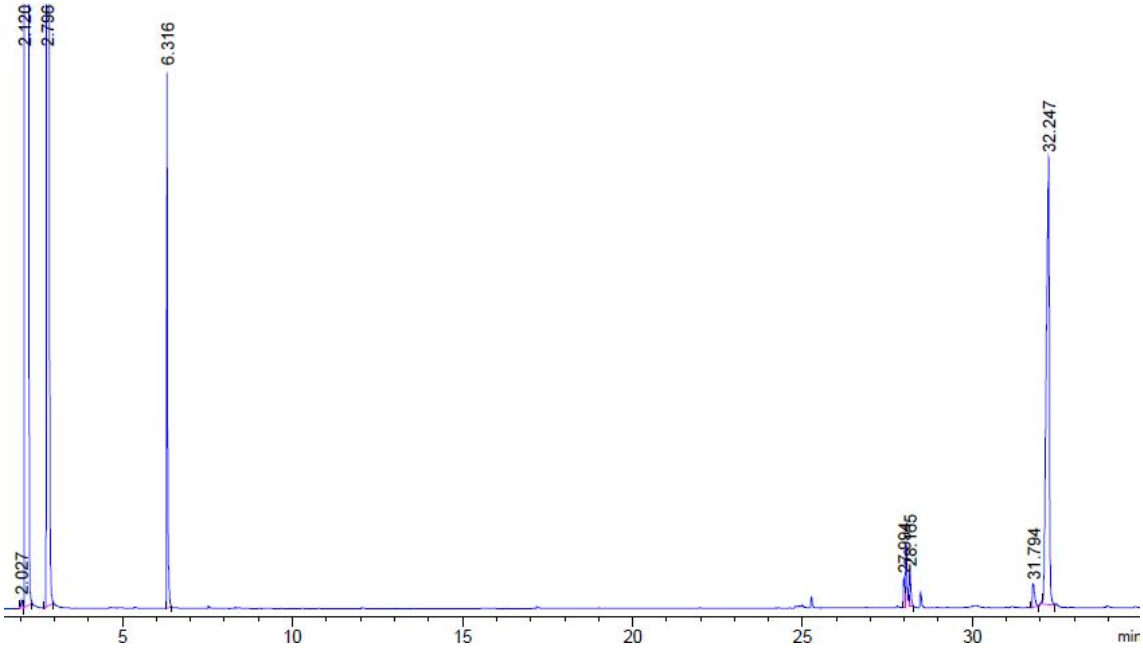


1.1.3. Reaction with methyl erucate

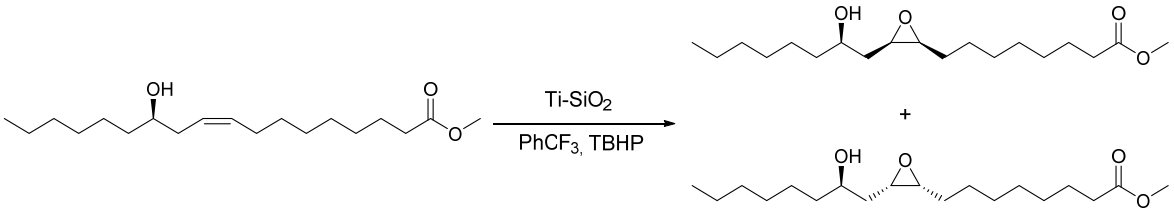


Retention times:

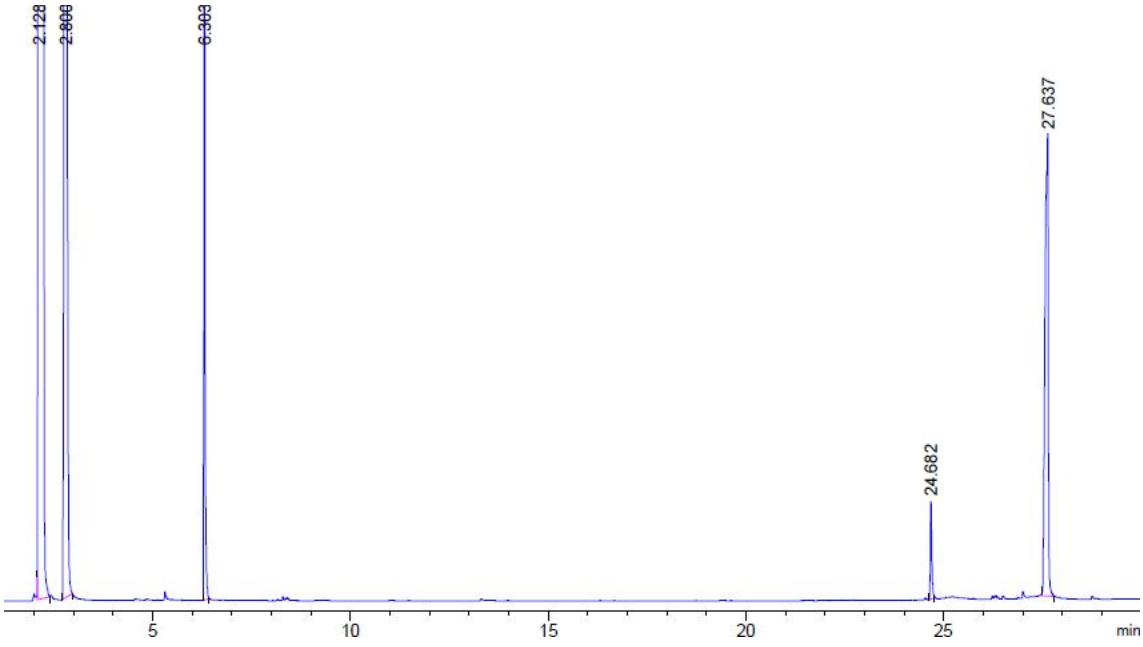
- decane: 6.3 min
- methyl erucate: 28.1 min
- impurities in the commercial starting material: 27.9 min
- epoxidized impurities: 31.7 min
- methyl *cis*-13,14-epoxydocosanoate: 32.2 min



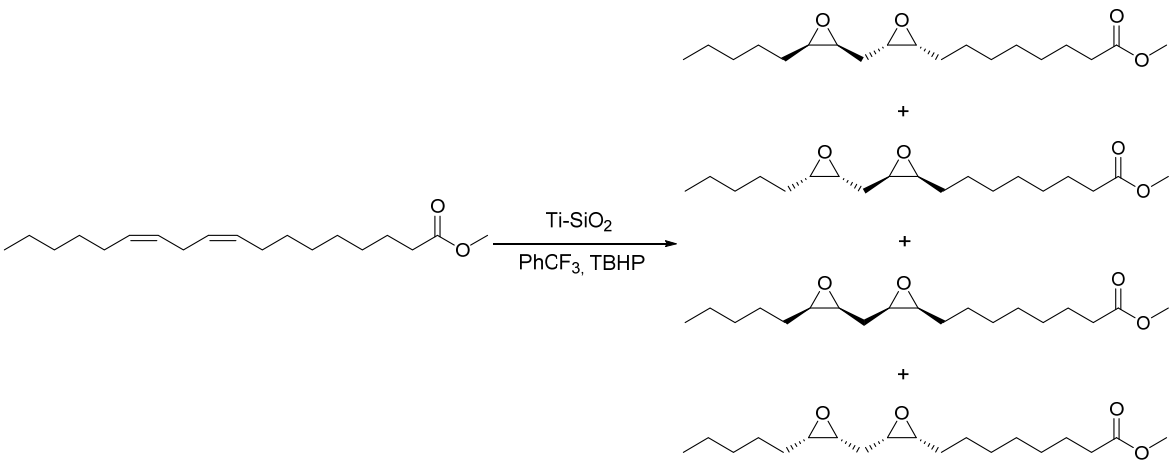
1.1.4. Reaction with methyl ricinoleate



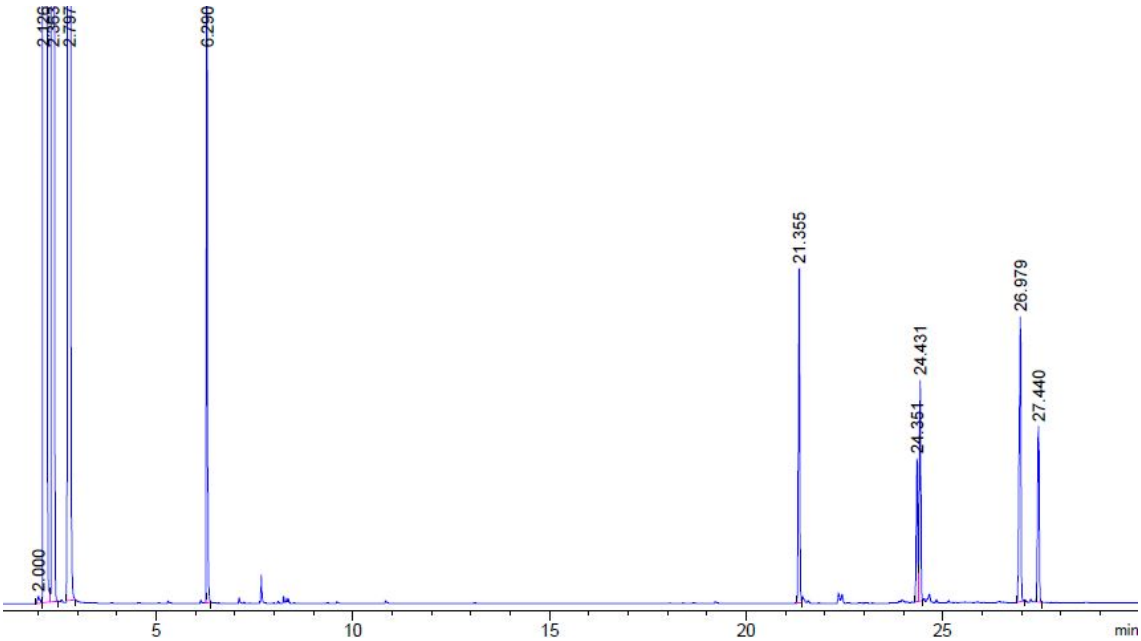
- decane: 6.3 min
- methyl ricinoleate: 24.6 min
- methyl *cis*-9,10-epoxy-12(*R*)-hydroxystearate: 27.6 min



1.1.5. Reaction with methyl linoleate

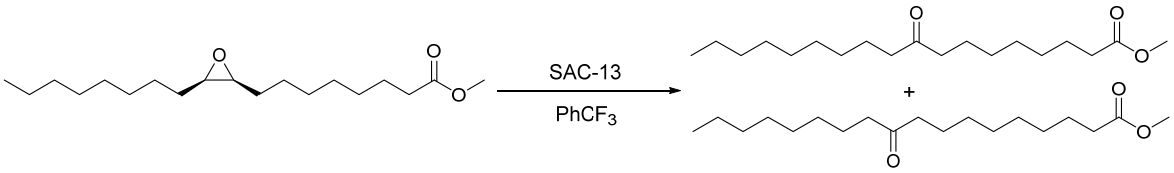


- decane: 6.3 min
- methyl linoleate: 21.3 min
- methyl *cis*-9,10(12,13)-epoxy-*cis*-12(9)-octadecenoate: 24.3 and 24.4 min
- methyl *cis*,*cis*-9,10:12,13-diepoxystearates: 26.9 and 27.4 min

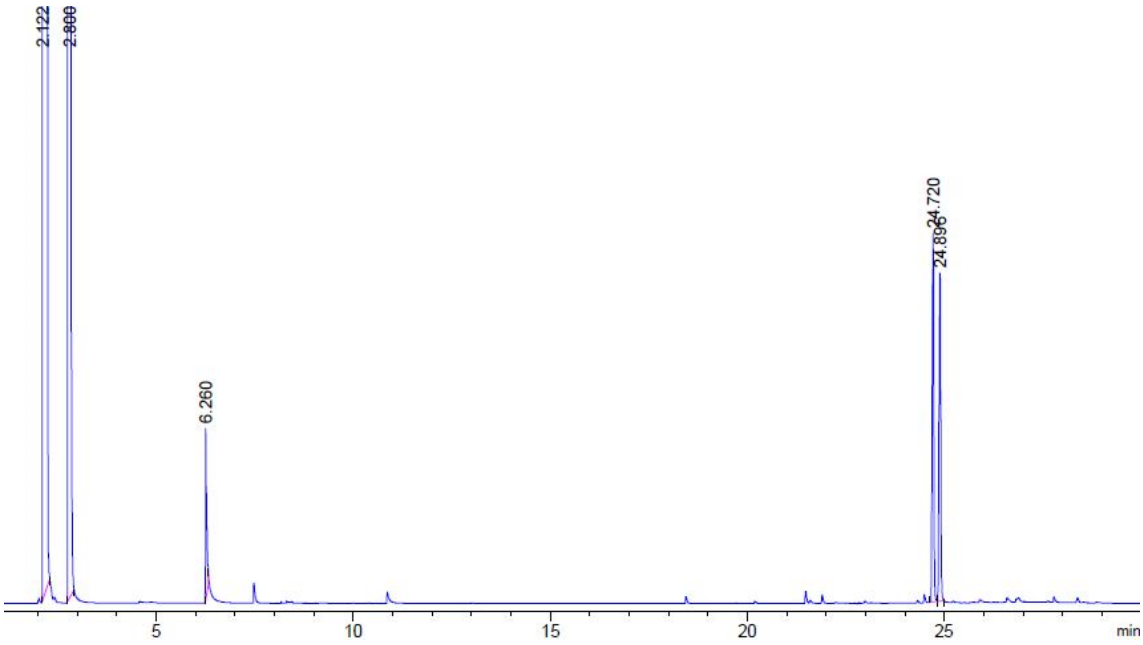


1.2. Meinwald rearrangement reactions

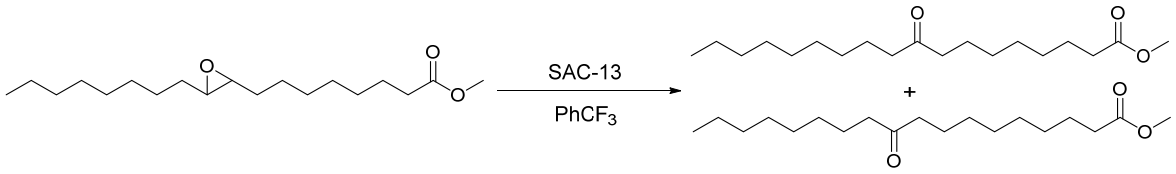
1.2.1. Reaction with methyl *cis*-9,10-epoxystearate



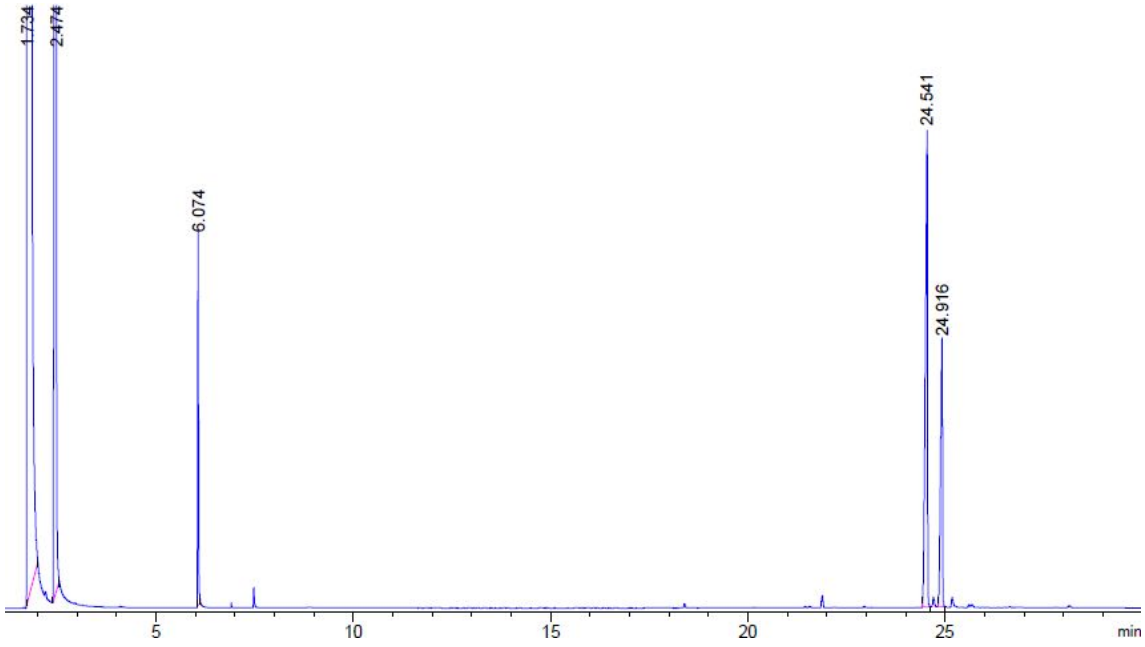
- benzonitrile: 6.2 min
- methyl *cis*-9,10-epoxystearate: 24.7 min
- methyl 9(10)-oxostearate: 24.9 min



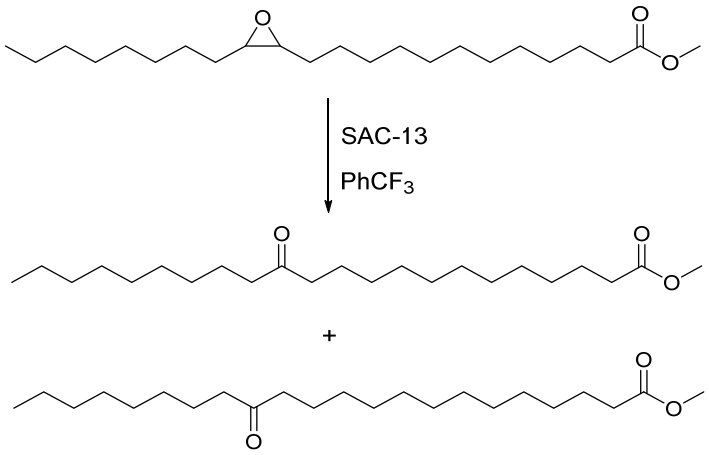
1.2.2. Reaction with methyl *trans*-9,10-epoxystearate



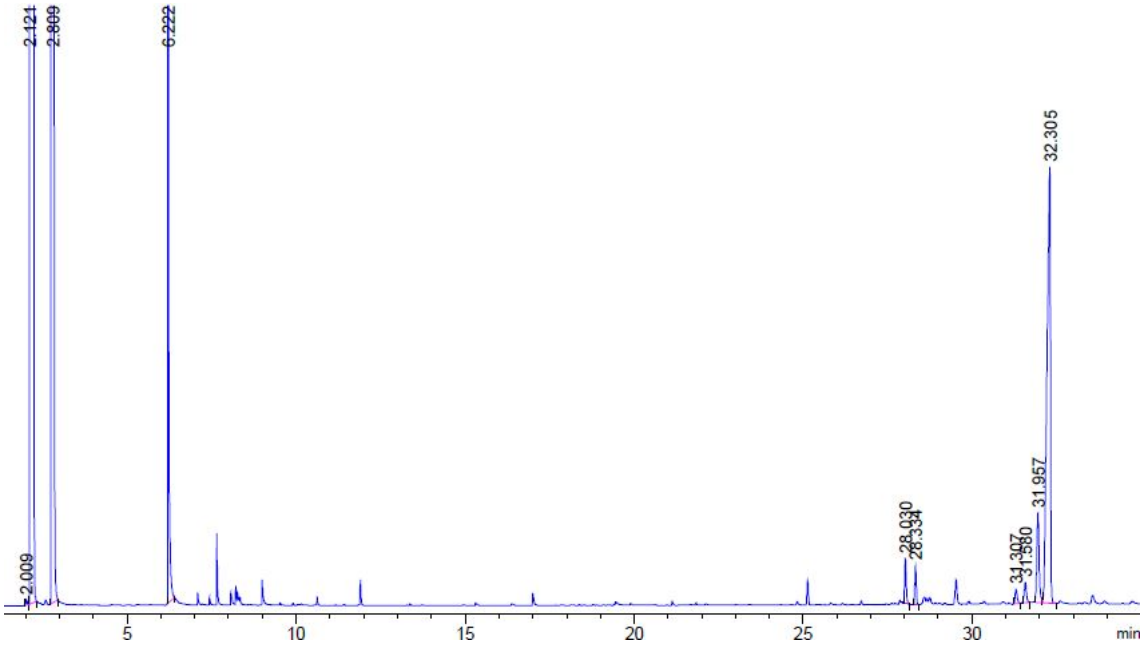
- benzonitrile: 6.1 min
- methyl *trans*-9,10-epoxystearate: 24.5 min
- methyl 9(10)-oxostearate: 24.9 min



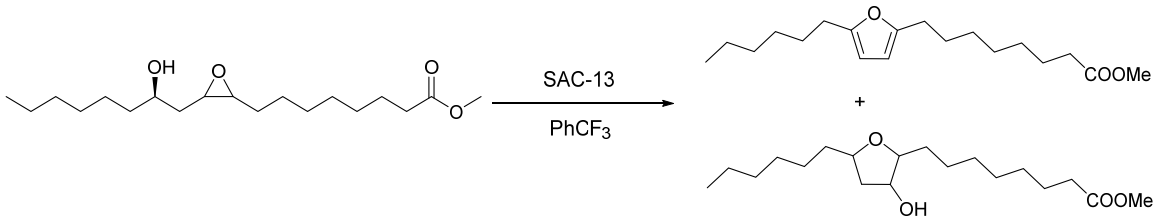
1.2.3. Reaction with methyl *cis*-13,14-epoxydocosanoate



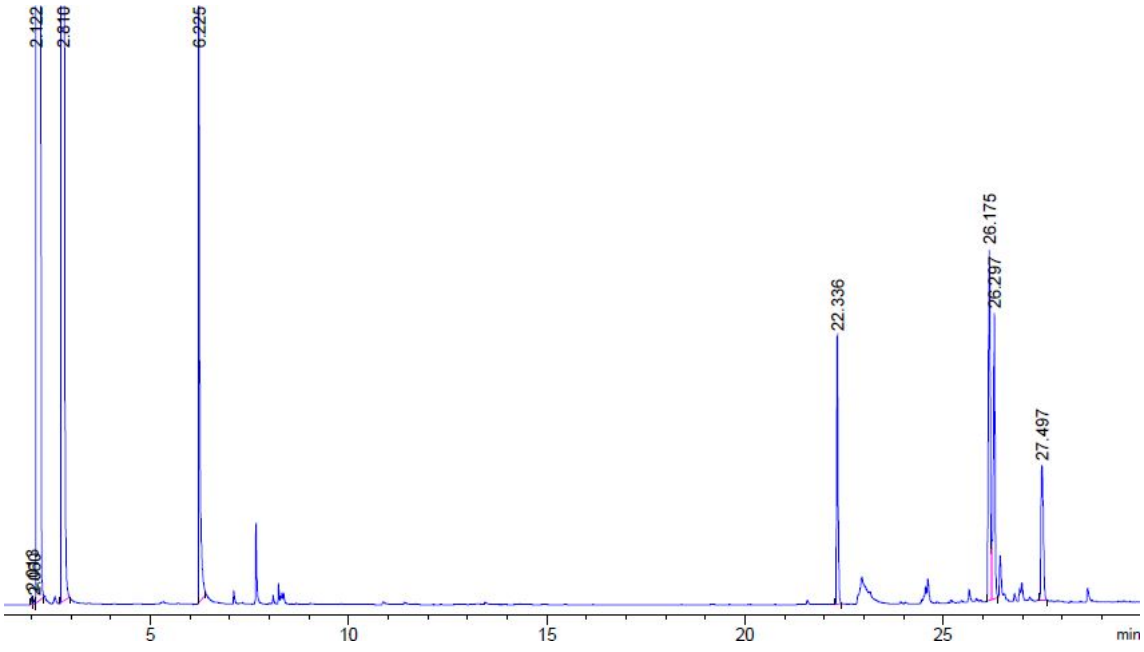
- benzonitrile: 6.2 min
- impurities in the commercial starting material: 28,0 and 28,3 min
- epoxidized impurities or impurities with ketone groups: 31,3 and 31,6 min
- methyl *cis*-13,14-epoxydocosanoate: 31,9 min
- methyl 13(14)-oxodocosanoate: 32,3 min



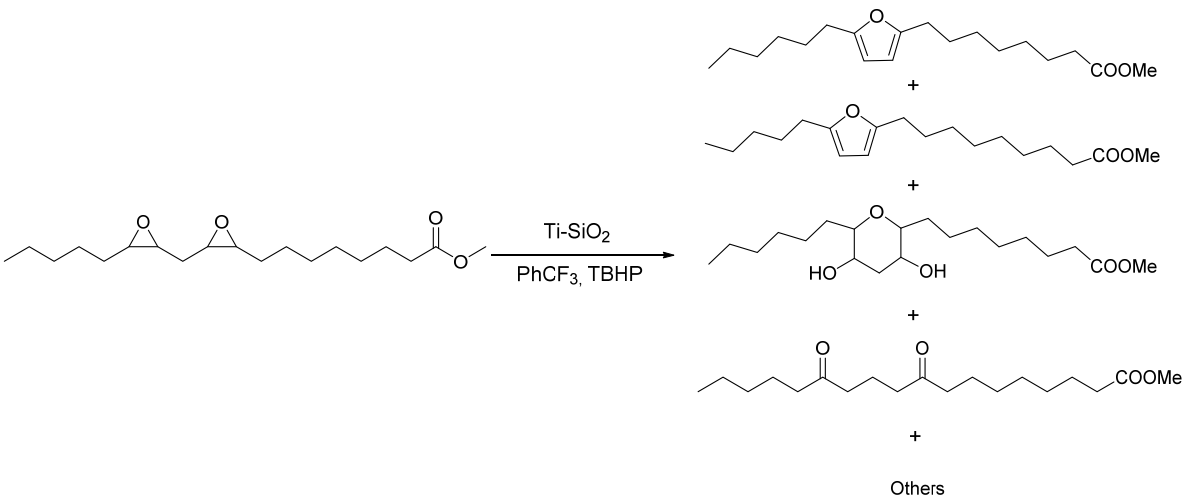
1.2.4. Reaction with methyl *cis*-9,10-epoxy-12(*R*)-hydroxystearate



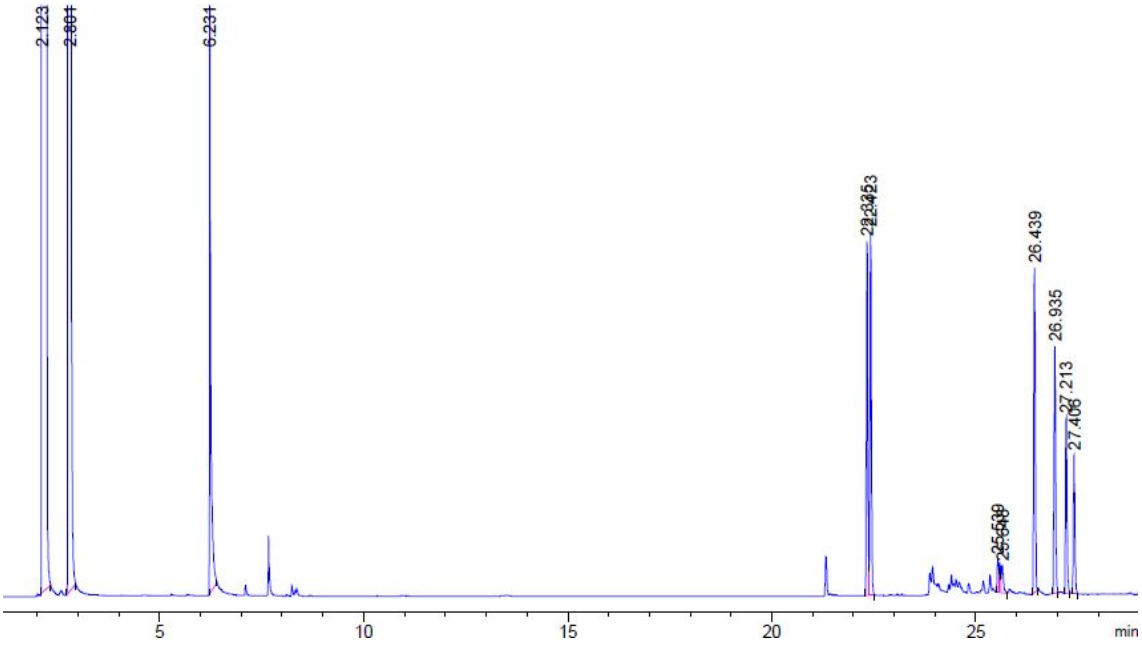
- benzonitrile: 6.2 min
- methyl 8-(5-hexylfuran-2-yl)octanoate: 22.3 min
- methyl 8-(5-hexyl-3-hydroxytetrahydrofuran-2-yl)octanoates: 26.1-26.4 min
- methyl *cis*-9,10-epoxy-12(*R*)-hydroxystearate: 27.5 min



1.2.5. Reaction with methyl *cis*,*cis*-9,10:12,13-diepoxystearate

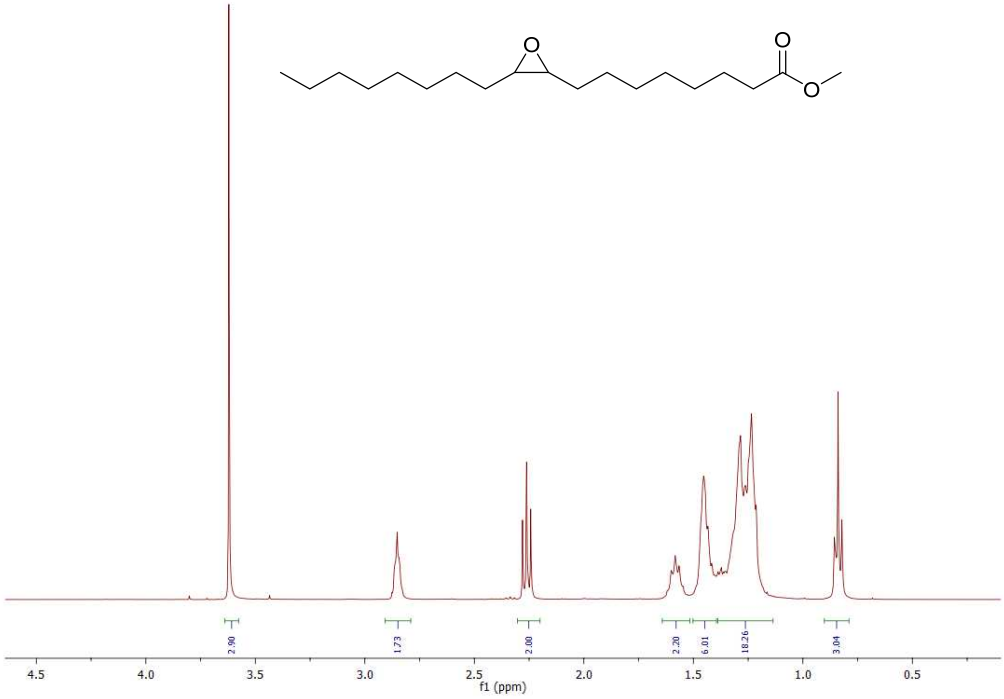


- benzonitrile: 6.2 min
- methyl 8-(5-hexylfuran-2-yl)octanoate: 22.3 min
- methyl 9-(5-pentylfuran-2-yl)nonanoate: 22.4 min
- others: 23.8-25.6 min
- methyl 8-(6-hexyl-3,5-dihydroxytetrahydro-2H-pyran-2-yl)octanoate: 26.4 min
- methyl 9,13-dioxostearate: 27.2 min
- methyl *cis*,*cis*-9,10:12,13-diepoxystearate: 26.9 and 27.4 min

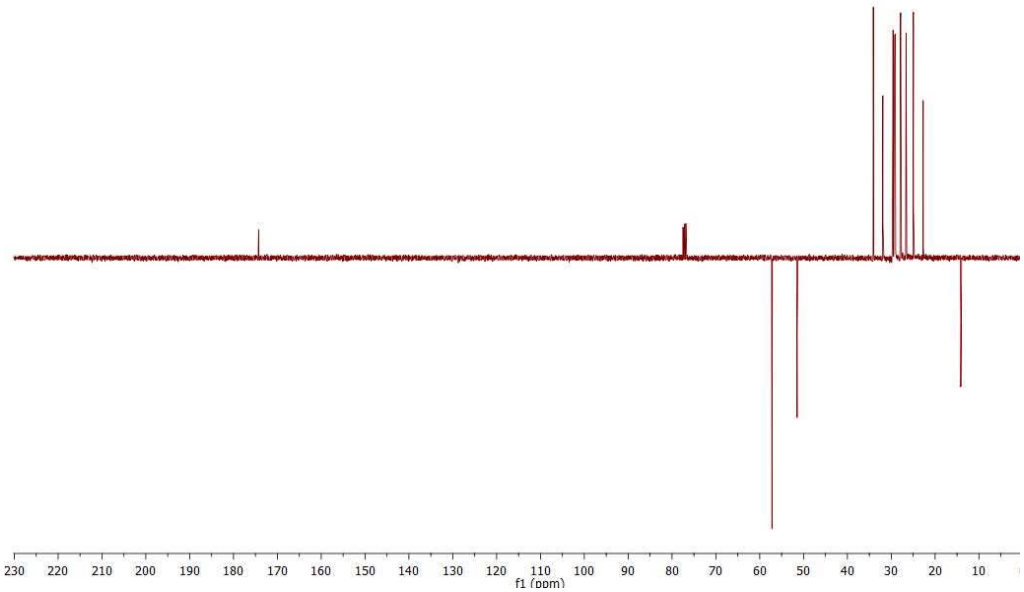


2. NMR spectra of the products

2.1. Methyl *cis*-9,10-epoxystearate.

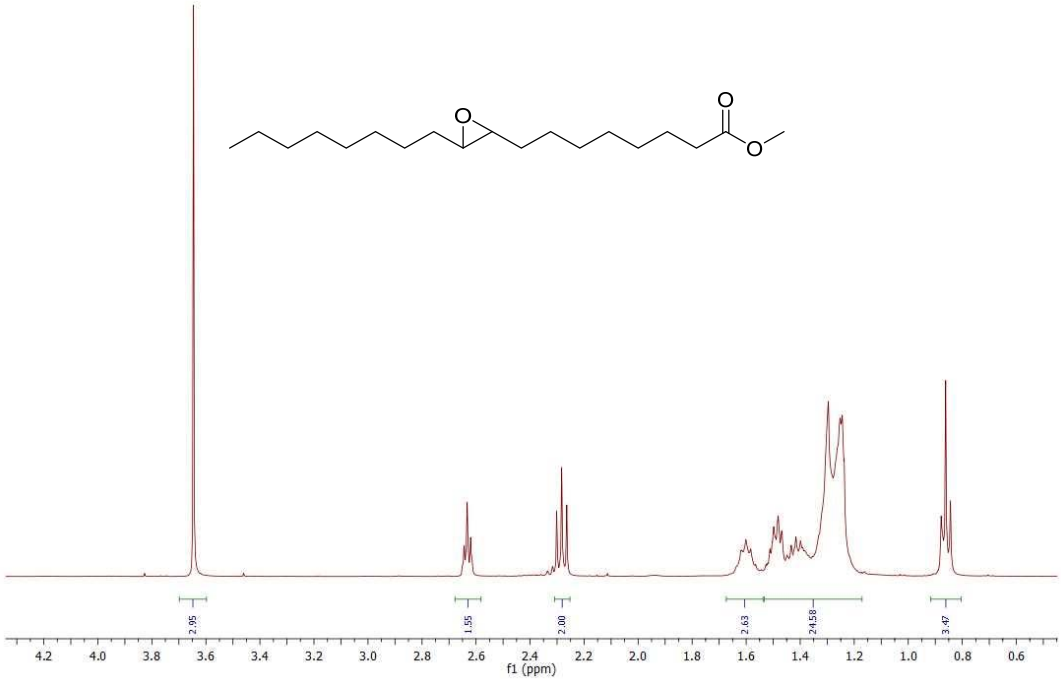


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 3.62 (s, 3H), 2.85 (m, 2H), 2.26 (t, 2H, *J*=7.6 Hz), 1.58 (m, 2H), 1.50-1.21 (m, 24H), 0.84 (t, 3H, *J*=7.6 Hz).

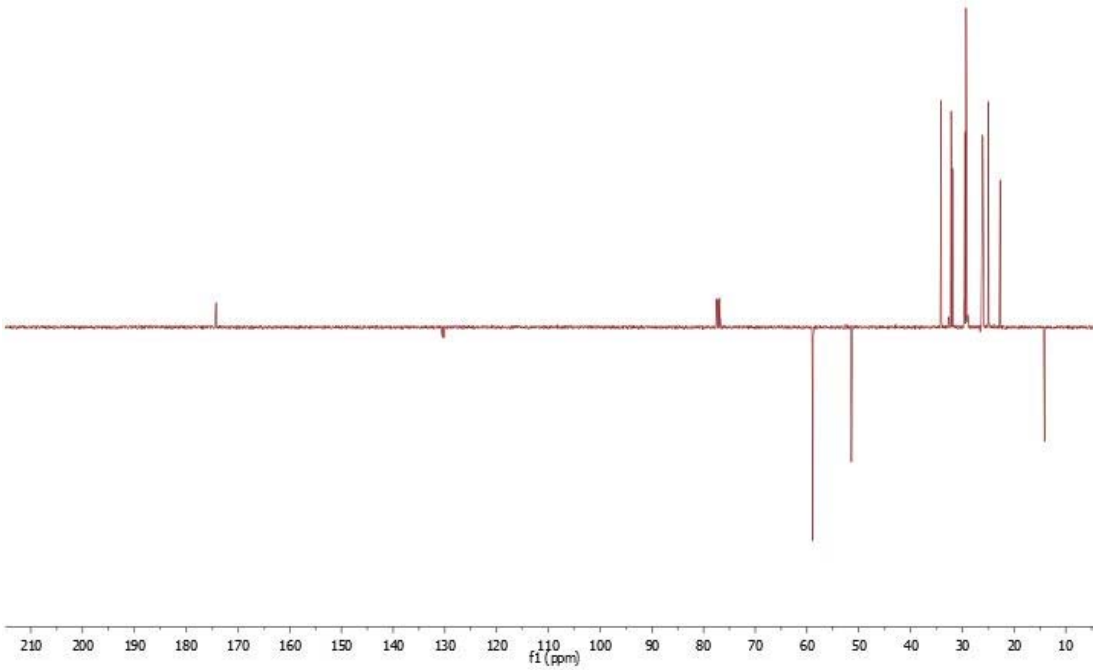


^{13}C-NMR ($CDCl_3$, δ ppm, 100 MHz): 174.2, 57.25, 57.21, 51.5, 34.1, 31.9, 29.61, 29.59, 29.4, 29.28, 29.23, 29.1, 27.89, 27.85, 26.66, 26.62, 24.95, 22.72,14.1.

2.2. Methyl *trans*-9,10-epoxystearate

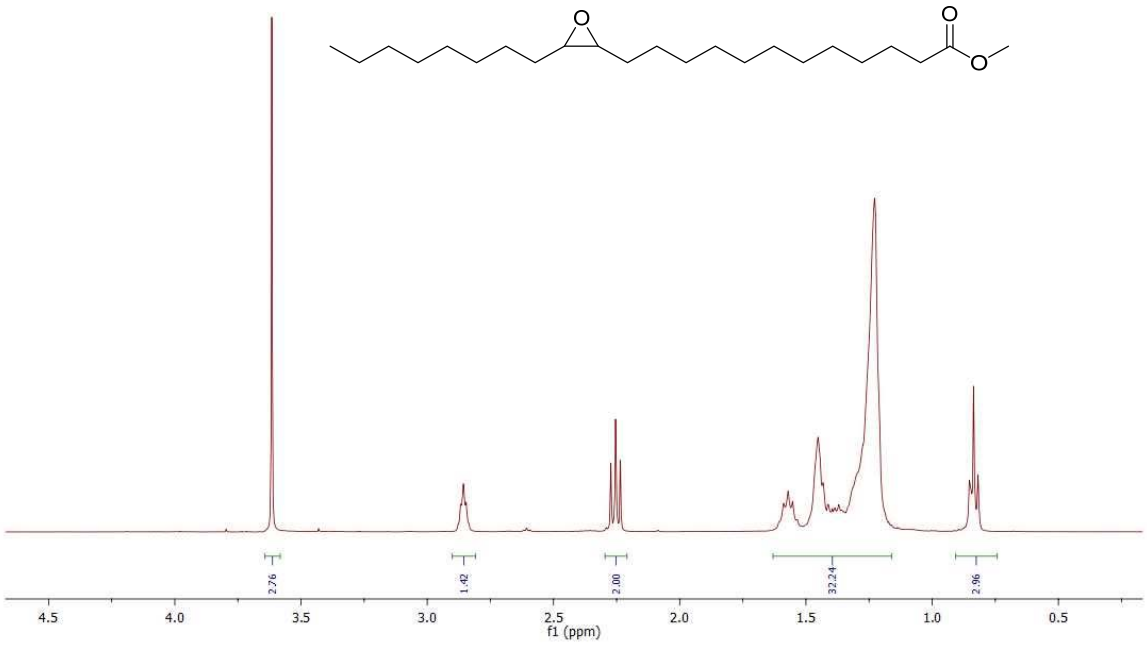


^{1}H-RMN ($CDCl_3$, δ ppm, 400 MHz): 3.65 (s, 3H), 2.63 (m, 2H), 2.28 (t, 2H, *J*=7.6 Hz), 1.58 (m, 2H), 1.50-1.24 (m, 24H), 0.86 (t, 3H, *J*=7.5 Hz).

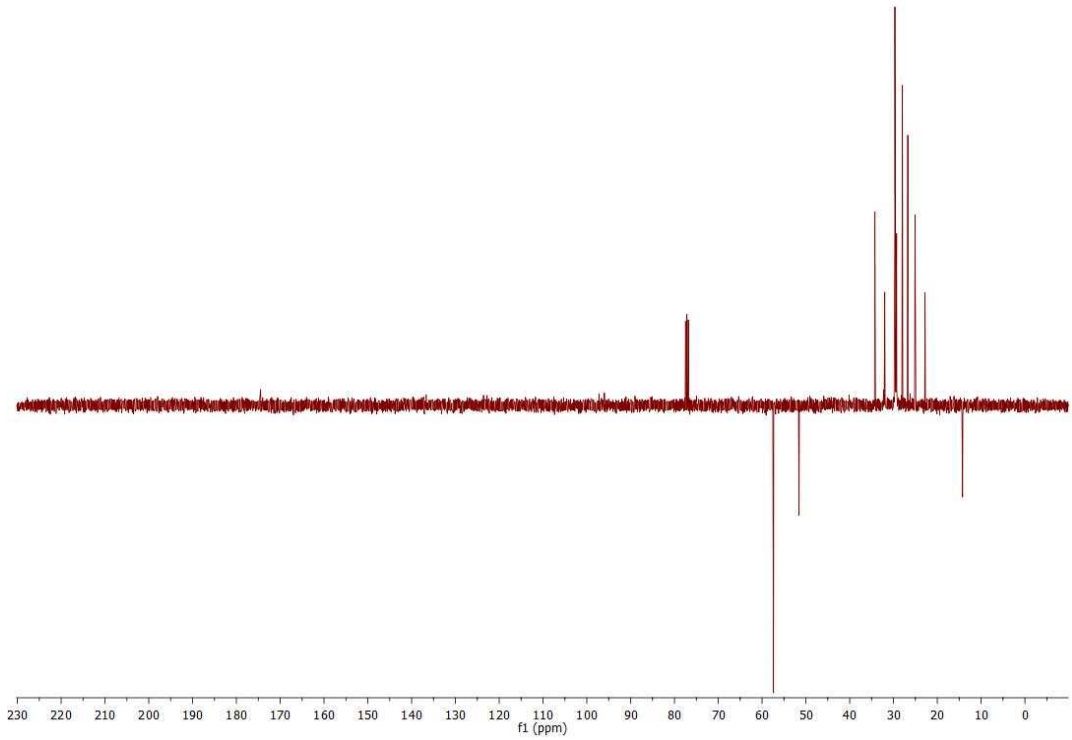


^{13}C-RMN ($CDCl_3$, δ ppm, 100 MHz): 174.4, 59.08, 59.03, 51.6, 34.2, 32.25, 32.22, 31.98, 29.6, 29.5, 29.36, 29.35, 29.3, 29.2, 26.2, 26.1, 25.0, 22.8, 14.2.

2.3. Methyl *cis*-13,14-epoxydocosanoate

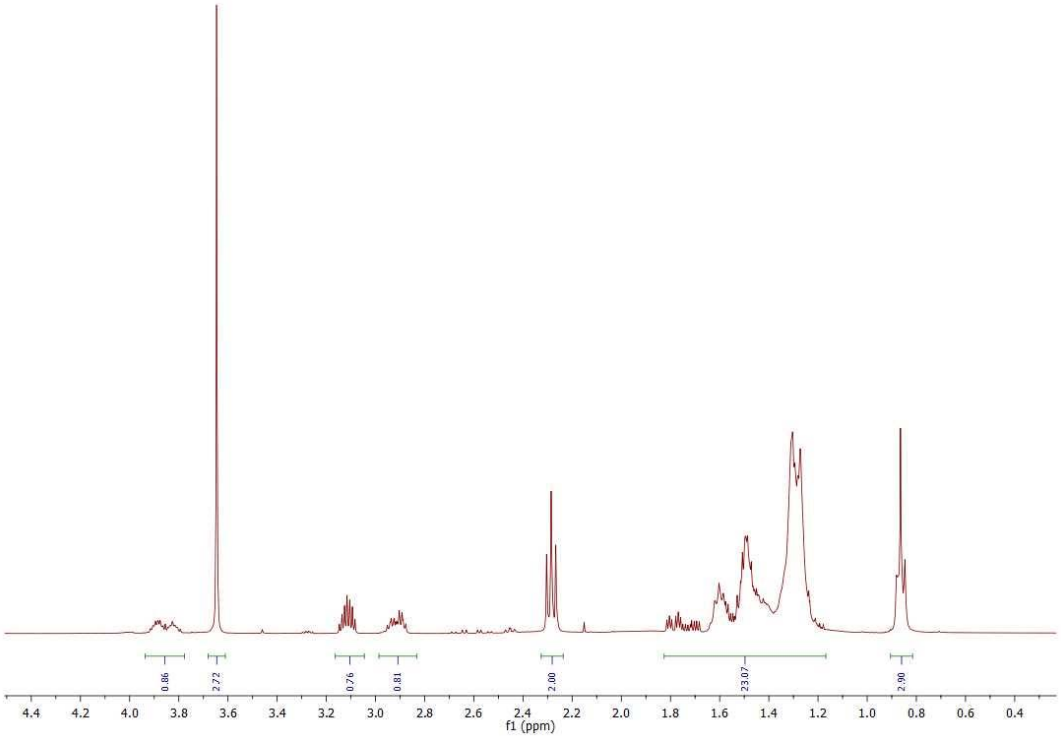


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 3.62 (s, 3H), 2.86 (m, 2H), 2.25 (t, 2H, *J*=7.6 Hz), 1.59-1.23 (m, 34H), 0.84 (t, 3H, *J*=7.5 Hz).

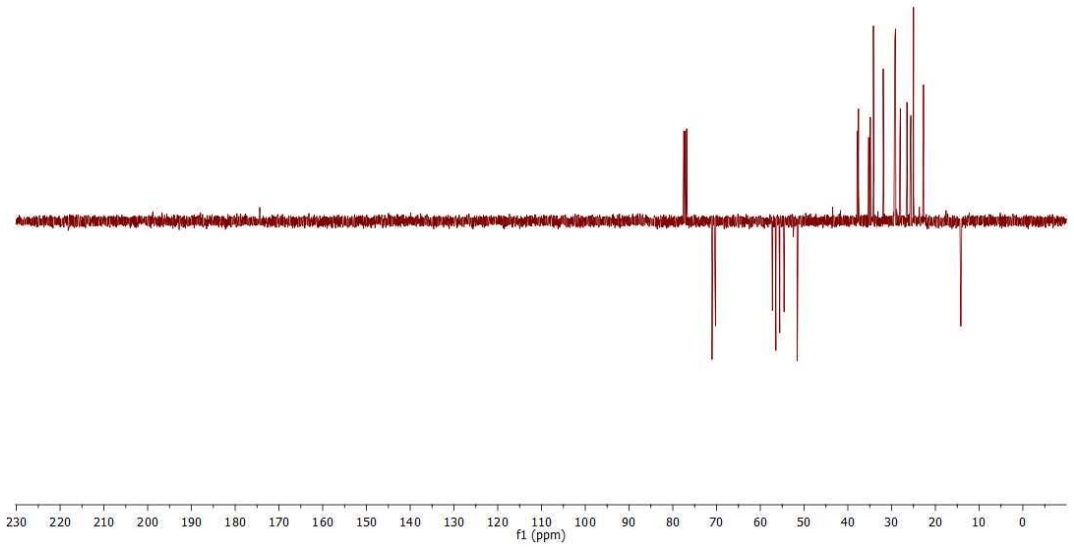


^{13}C-NMR ($CDCl_3$, δ ppm, 100 MHz): 174.4, 57.3, 51.5, 34.2, 32.06, 31.99, 29.79, 29.68, 29.56, 29.5, 29.38, 29.36, 29.28, 27.9, 26.7, 25.1, 22.8, 14.2.

2.4. Methyl *cis*-9,10-epoxy-12(*R*)-hydroxystearates

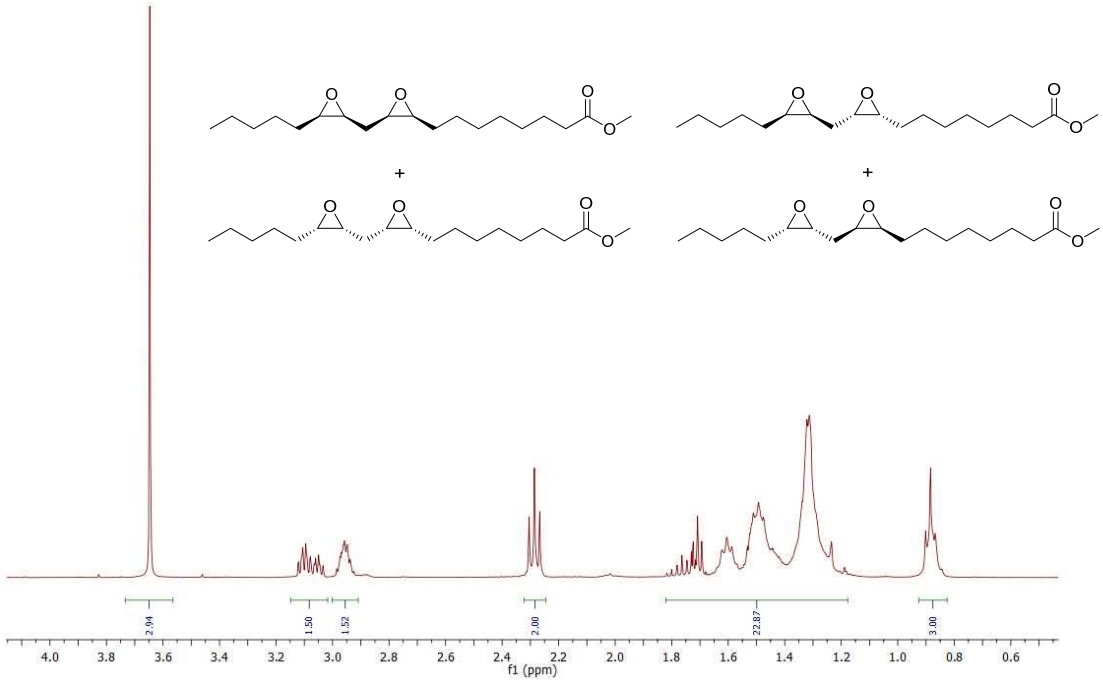


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 3.86 (m, 1H), 3.65 (s, 3H), 3.12 (m, 1H), 2.92 (m, 1H), 2.29 (t, 2H, *J*=7.6 Hz), 1.81-1.23 (m, 24H), 0.86 (t, 3H, *J*=7.4 Hz).

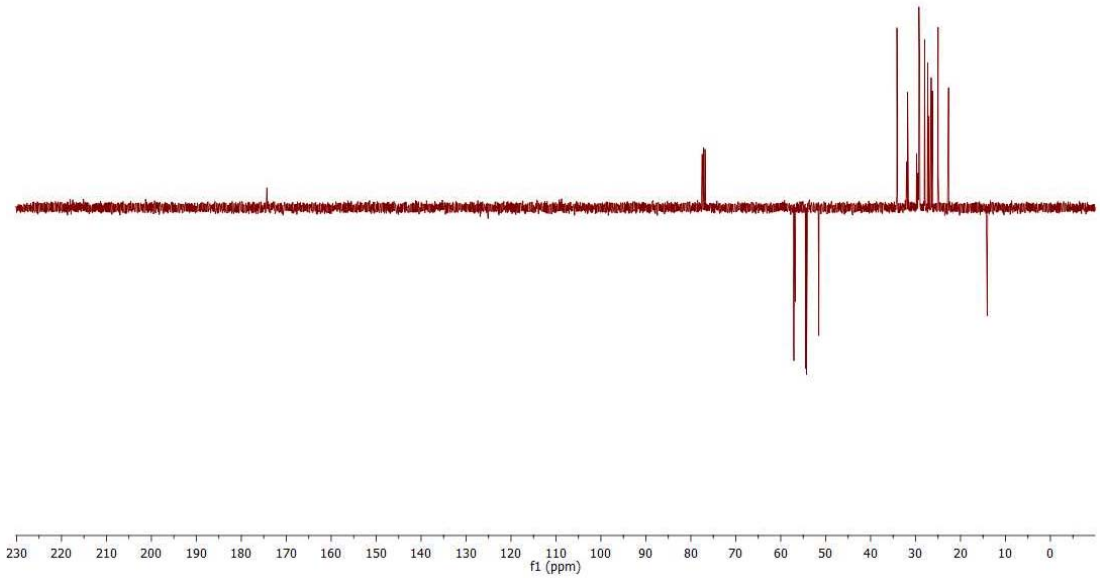


^{13}C-NMR ($CDCl_3$, δ ppm, 100 MHz): 174.4, 71.0, 71.2, 57.2, 56.6, 56.4, 56.5, 54.5, 52.4, 51.5, 37.8, 37.5, 36.2, 34.8, 34.1, 31.9, 29.40, 29.36, 29.25, 29.11, 28.92, 28.11, 28.06, 28.0, 26.53, 26.49, 25.7, 25.6, 24.98, 22.7, 14.1.

2.5. Methyl *cis,cis*-9,10:12,13-diepoxystearates

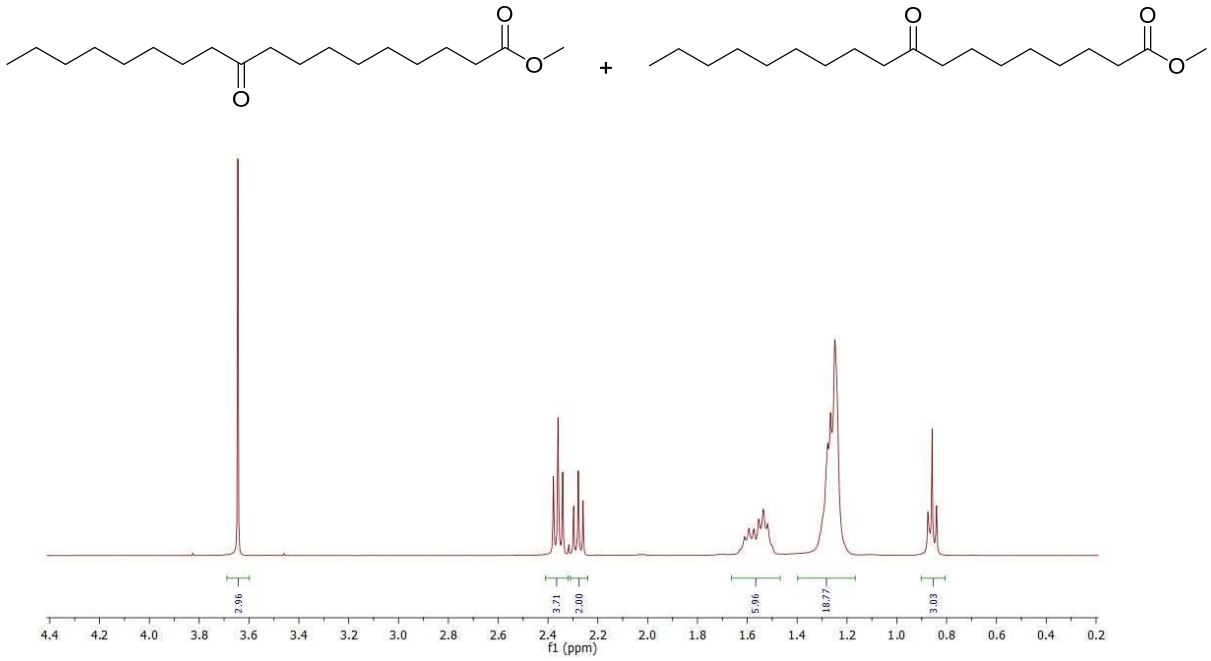


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 3.65 (s, 3H), 3.06 (m, 2H), 2.96 (m, 2H), 2.29 (t, 2H, *J*=7.6 Hz), 1.80-1.22 (m, 22H), 0.88 (t, 3H, *J*=7.5 Hz).

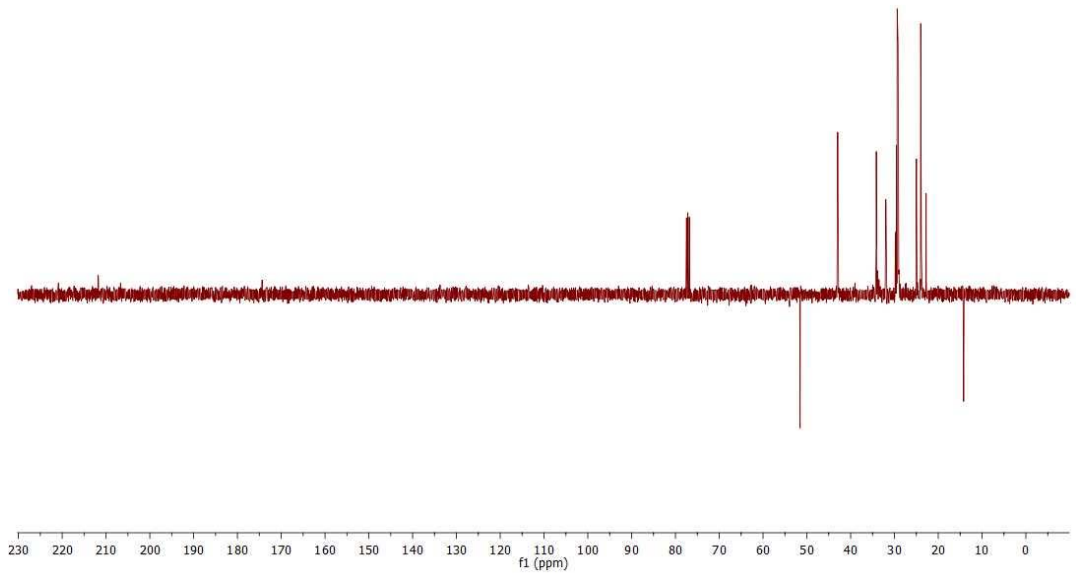


^{13}C-NMR ($CDCl_3$, δ ppm, 100 MHz): 174.3, 57.10, 57.05, 56.82, 56.76, 54.45, 54.43, 54.28, 51.52, 34.14, 32.0, 31.7, 29.7, 29.45, 29.38, 29.2, 29.1, 27.99, 27.98, 27.91, 27.3, 27.0, 26.6, 26.5, 26.3, 24.9, 22.78, 22.66, 14.2, 14.07.

2.6. Methyl 9(10)-oxostearate.

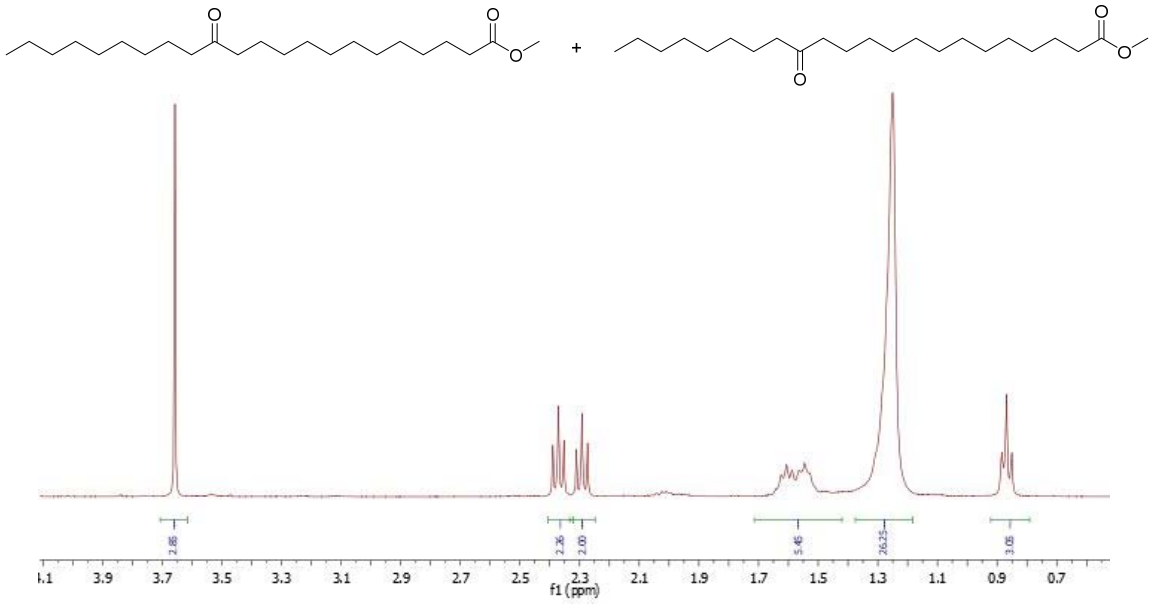


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 3.64 (s, 3H), 2.36 (t, 4H, *J*=8 Hz), 2.28 (t, 2H, *J*=7.6 Hz), 1.61-1.52 (m, 6H), 1.28-1.25 (m, 18H), 0.86 (t, 3H, *J*=7.5 Hz).

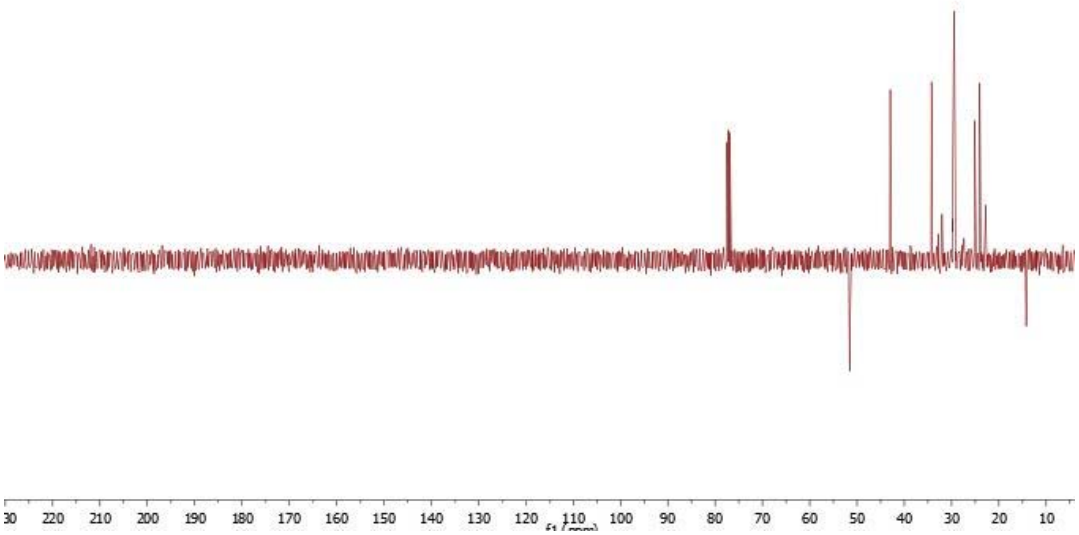


^{13}C-NMR ($CDCl_3$, δ ppm, 100 MHz): 211.78, 211.72, 174.36, 174.34, 51.5, 42.95, 42.94, 42.86, 42.81, 34.17, 34.15, 31.97, 31.93, 29.8, 29.7, 29.54, 29.53, 29.48, 29.38, 29.31, 29.28, 29.25, 29.17, 29.15, 29.05, 29.98, 25.01, 24.97, 24.0, 23.92, 23.86, 22.76, 22. 74, 14.19.

2.7. Methyl 13(14)-oxodocosanoate.

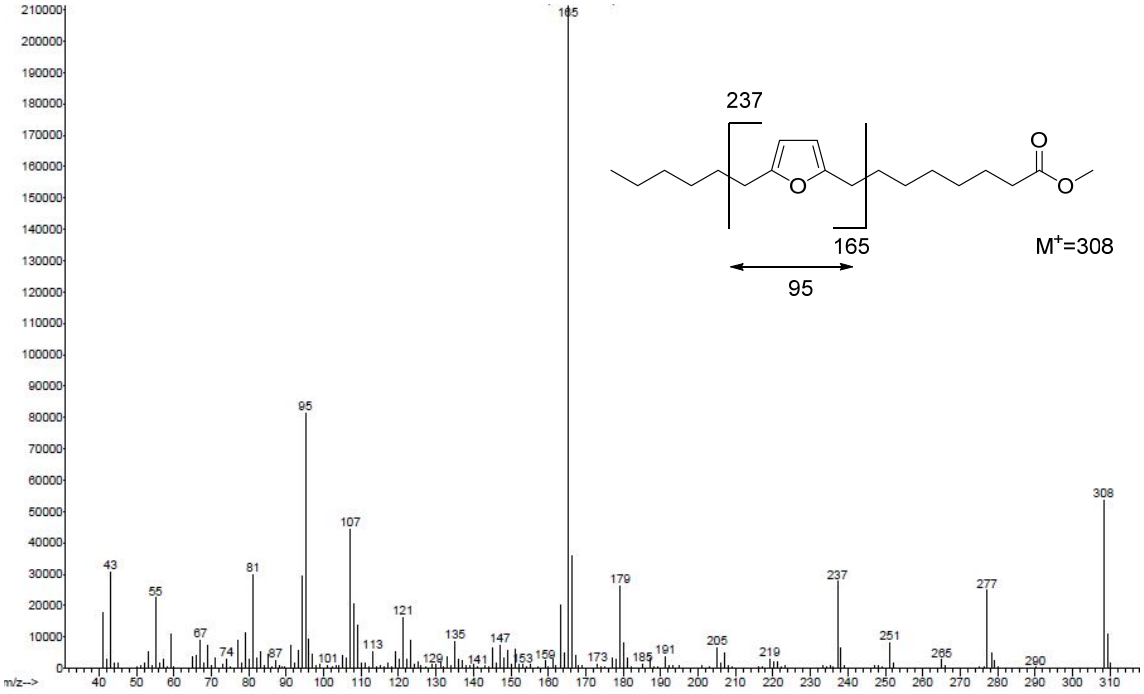


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 3.65 (s, 3H), 2.37 (t, 4H, *J*=7.5 Hz), 2.29 (t, 2H, *J*=7.6 Hz), 1.66-1.50 (m, 6H), 1.34-1.20 (m, 26H), 0.86 (t, 3H, *J*=6.8 Hz).

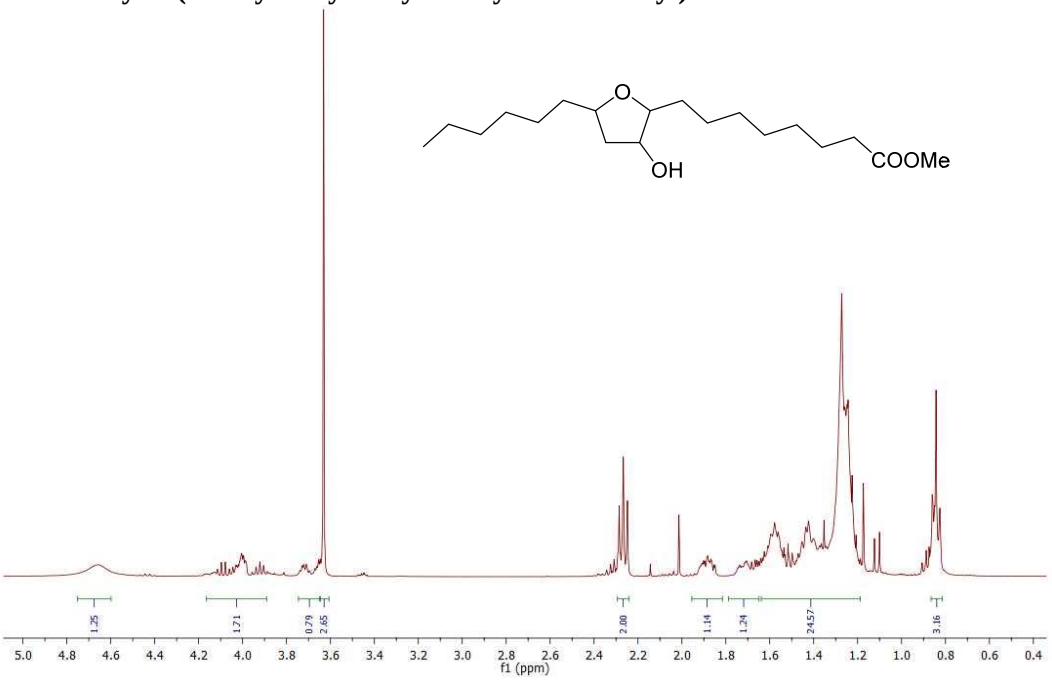


^{13}C-NMR ($CDCl_3$, δ ppm, 100 MHz): 211.2, 174.5, 51.5, 42.9, 34.2, 32.7, 32.0, 31.9, 29.9, 29.7, 29.65, 29.57, 29.4, 29.3, 27.3, 25.1, 24.0, 22.8, 14.2.

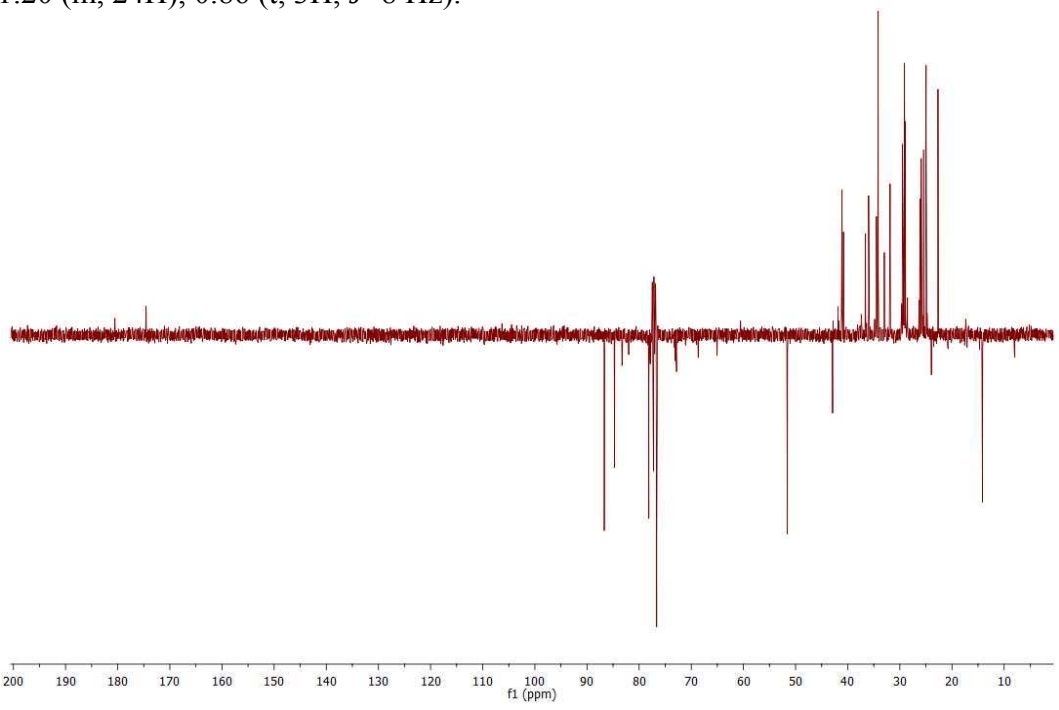
2.8. Methyl 8-(5-hexylfuran-2-yl)octanoate



2.9. Methyl 8-(5-hexyl-3-hydroxytetrahydrofuran-2-yl)octanoate

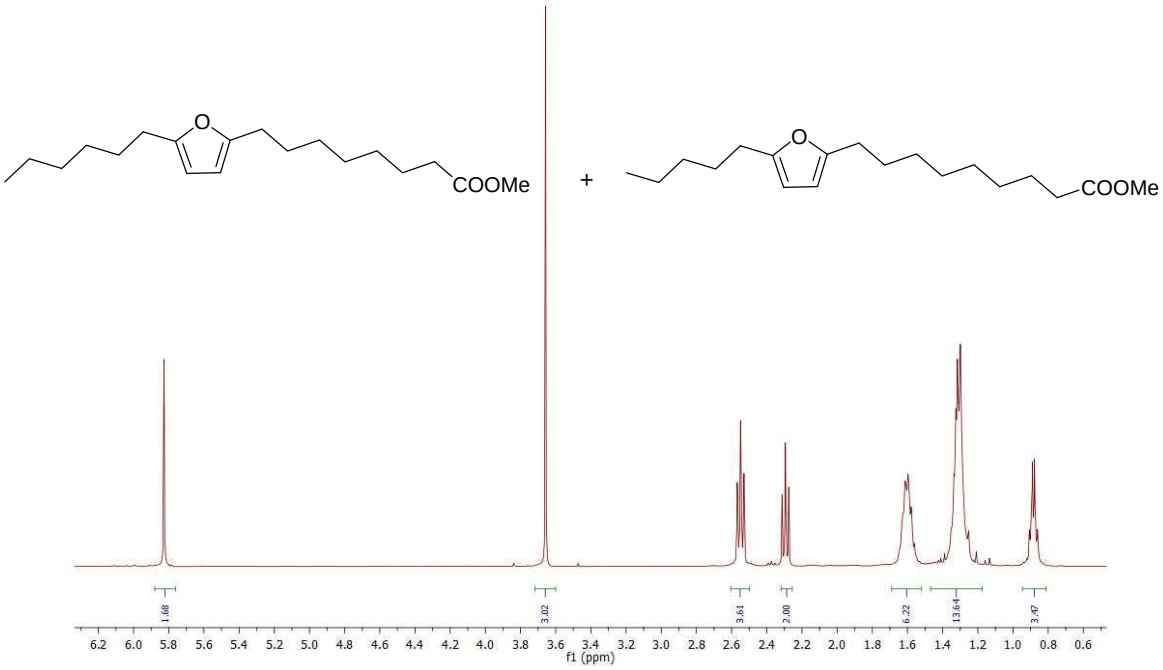


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 4.75-4.60 (bs, 1H), 4.10-3.90 (m, 2H), 3.74-3.64 (m, 1H), 3.63 (s, 3H), 2.26 (t, 2H, *J*=7.6 Hz), 1.95-1.85 (m, 1H), 1.76-1.65 (m, 1H), 1.65-1.20 (m, 24H), 0.86 (t, 3H, *J*=8 Hz).

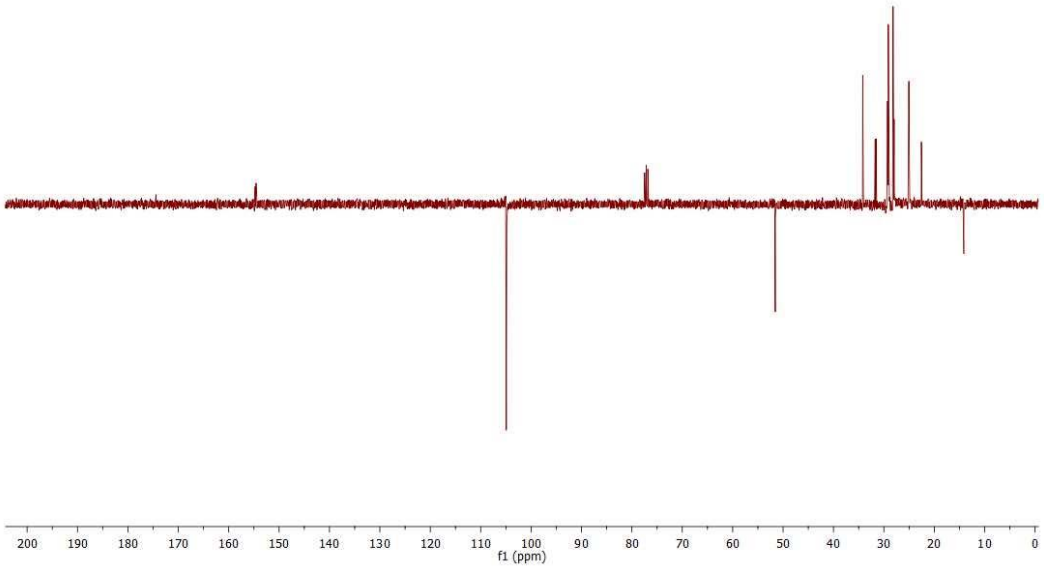


^{13}C-NMR (APT) ($CDCl_3$, δ ppm, 100 MHz): 174.56, 86.7, 84.7, 78.1, 77.2, 76.6, 51.5, 42.9, 41.08, 41.01, 40.8, 36.7, 36.6, 36.4, 35.9, 34.5, 34.1, 32.9, 31.89, 31.87, 29.65, 29.50, 29.45, 29.39, 29.34, 29.19, 29.11, 28.9, 26.29, 26.13, 26.10, 26.01, 25.9, 25.8, 25.54, 25.45, 24.9, 24.7, 22.6, 14.1.

2.10. Methyl 8-(5-hexylfuran-2-yl)octanoate and methyl 9-(5-pentylfuran-2-yl)nonanoate (1:1)

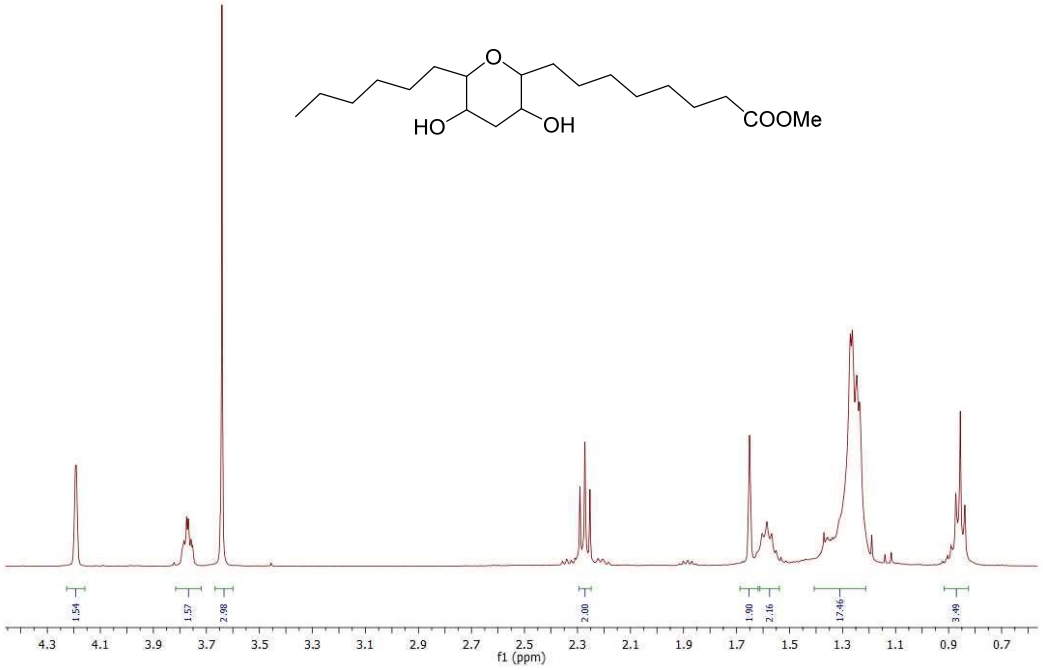


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 5.82 (s, 2H), 3.65 (s, 3H), 2.54 (t, 4H, *J*=7.6 Hz), 2.29 (t, 2H, *J*=7.6 Hz), 1.65-1.55 (m, 6H), 1.40-1.24 (m, 12H), 0.86 (t, 3H, *J*=7.6 Hz).

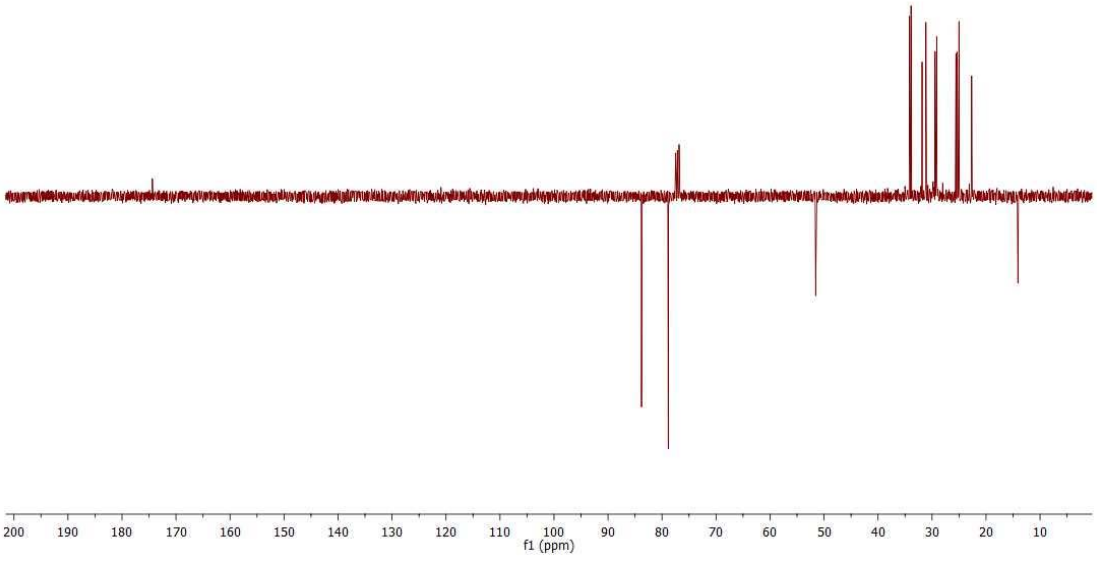


^{13}C-NMR (APT) ($CDCl_3$, δ ppm, 100 MHz): 174.4, 154.78, 154.76, 154.65, 154.57, 104.97, 104.94, 104.91, 104.82, 51.5, 34.22, 34.20, 31.7, 31.5, 29.30, 29.28, 29.24, 29.18, 29.12, 28.23, 28.2, 28.17, 28.15, 25.06, 25.05, 22.7, 22.5, 14.19, 14.14.

2.11. Methyl 8-(6-hexyl-3,5-dihydroxytetrahydro-2H-pyran-2-yl)octanoate

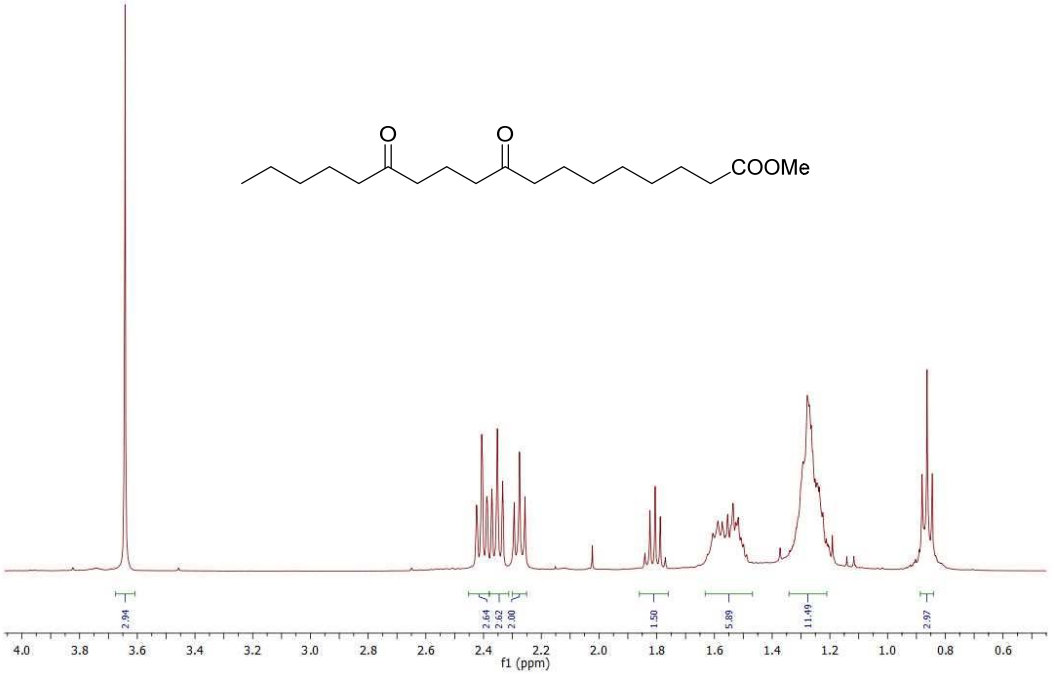


^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 4.19 (d, 2H, *J*=1.4 Hz), 3.77 (td, 2H, *J*=6.5, 2.3 Hz), 3.64 (s, 3H), 2.27 (t, 2H, *J*=7.6 Hz), 1.65 (t, 2H, *J*=1.2 Hz), 1.62-1.54 (m, 2H), 1.40-1.22 (m, 18H), 0.86 (t, 3H, *J*=7.4 Hz).

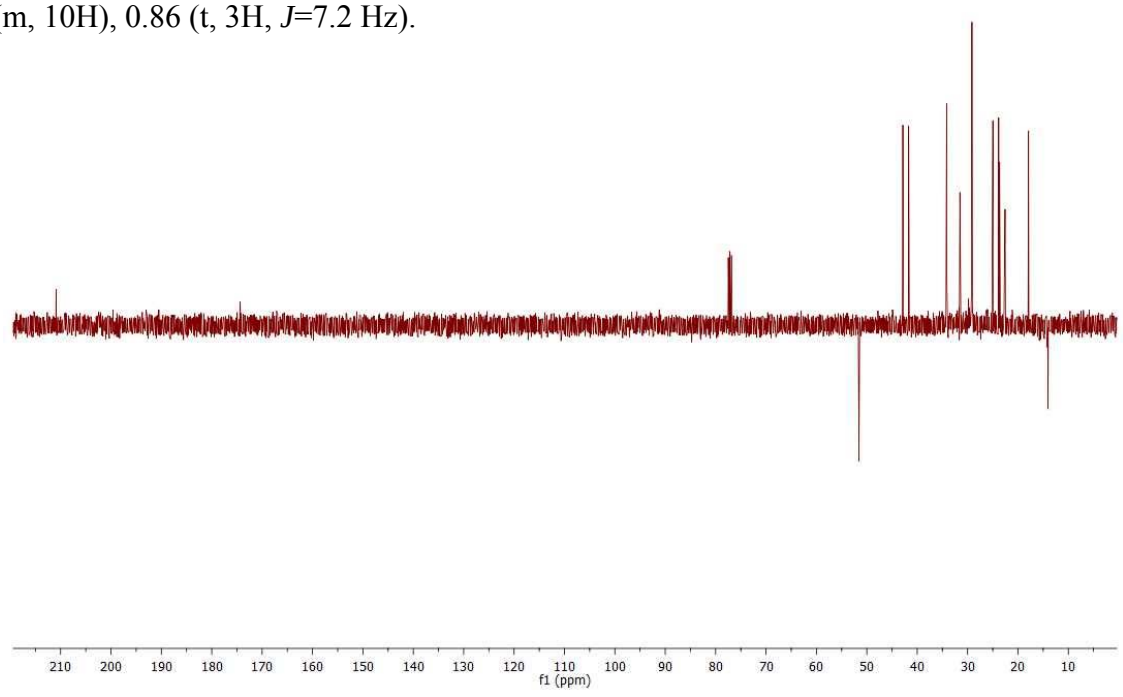


^{13}C-NMR (APT) ($CDCl_3$, δ ppm, 100 MHz): 174.3, 83.8, 83.7, 78.86, 78.85, 51.5, 34.1, 33.89, 33.88, 31.84, 31.14, 29.8, 29.4, 29.2, 29.1, 28.0, 25.5, 25.3, 25.0, 23.1, 22.6, 14.1.

2.12. Methyl 9,13-dioxostearate



^{1}H-NMR ($CDCl_3$, δ ppm, 400 MHz): 3.64 (s, 3H), 2.40 (t, 4H, *J*=7.2 Hz), 2.35 (t, 4H, *J*=7.2 Hz), 2.27 (t, 2H, *J*=7.6 Hz), 1.81 (q, 2H, *J*=7.1 Hz), 1.63-1.47 (m, 6H), 1.34-1.20 (m, 10H), 0.86 (t, 3H, *J*=7.2 Hz).



^{13}C-NMR (APT) ($CDCl_3$, δ ppm, 100 MHz): 211.0, 210.8, 174.3, 51.5, 42.9, 42.8, 41.7, 41.6, 34.1, 31.5, 29.8, 29.1, 29.0, 24.9, 23.8, 23.6, 22.5, 17.9, 14.0.