Challenging cyclopropanation reactions on non-activated double bonds of fatty esters

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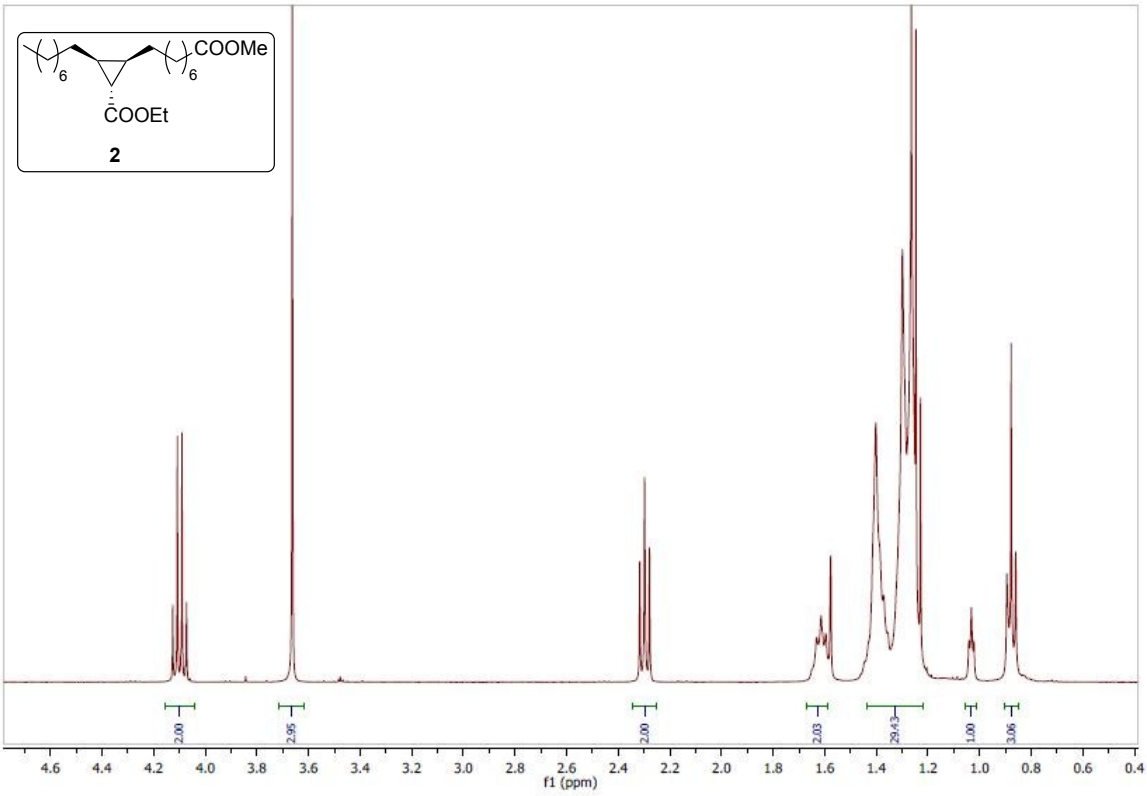
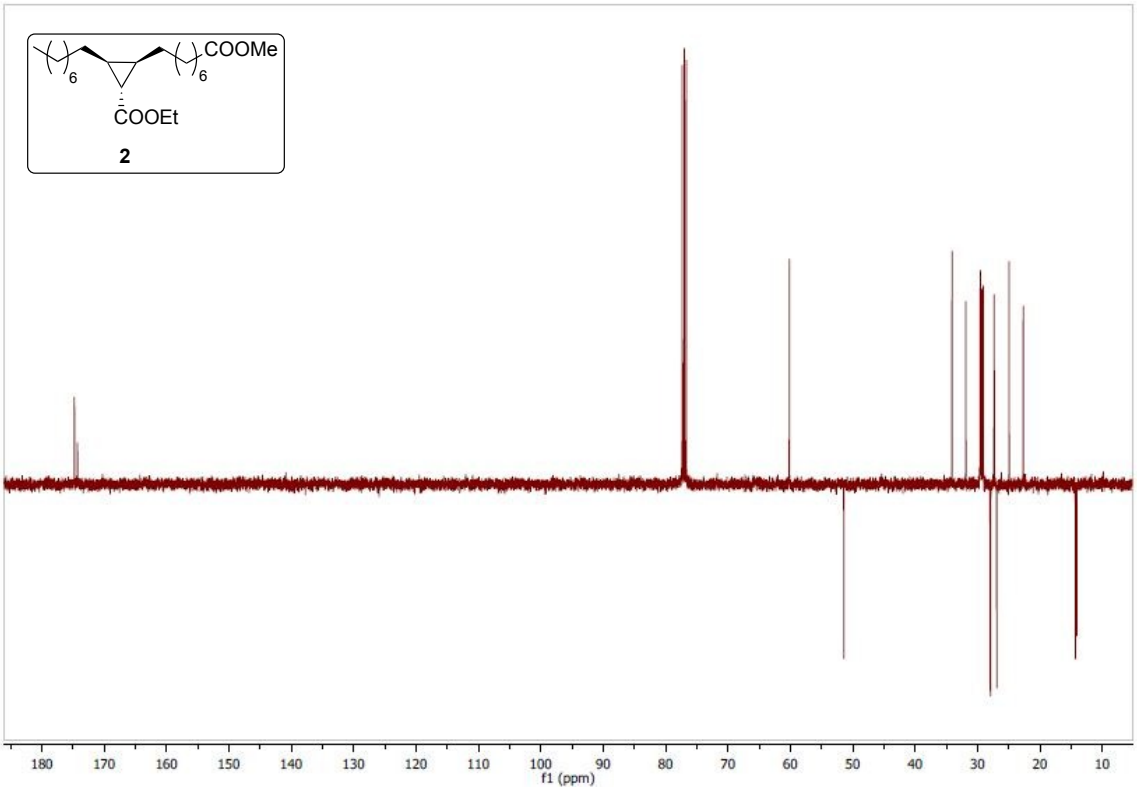
NMR spectra of products

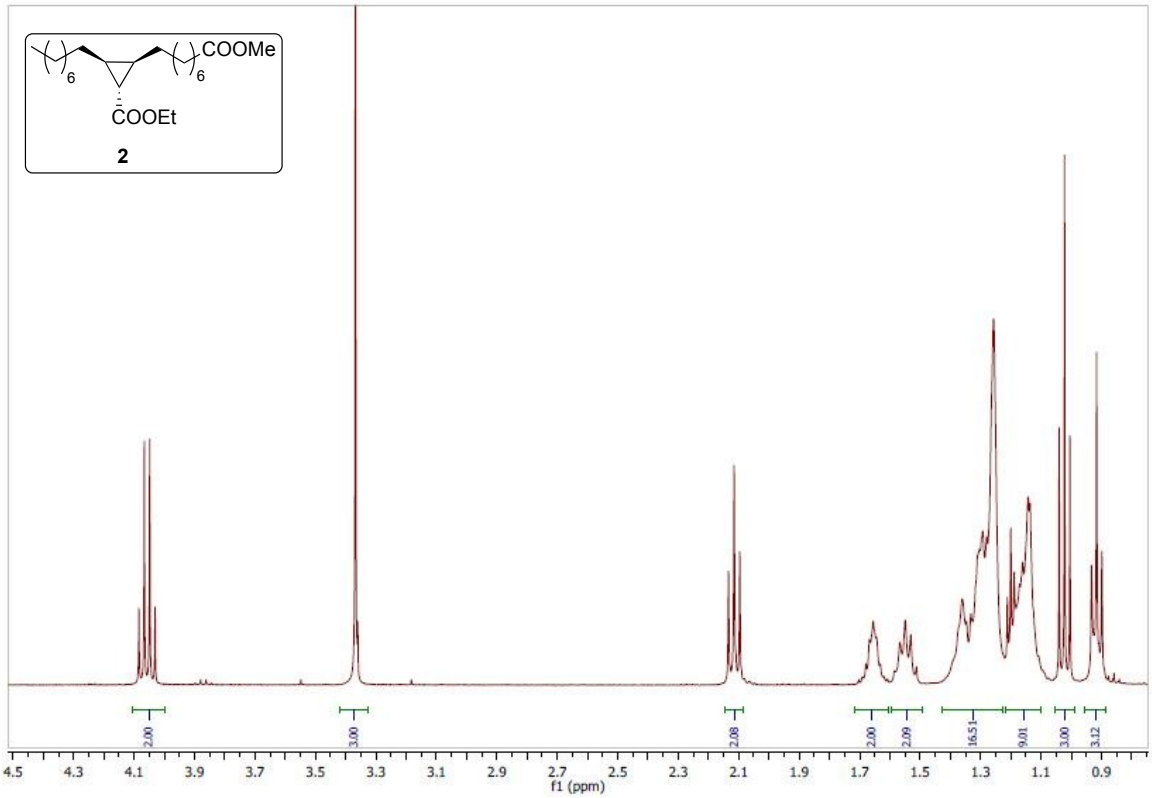
^{1}H-RMN ($CDCl_3$, δ ppm, 400 MHz)



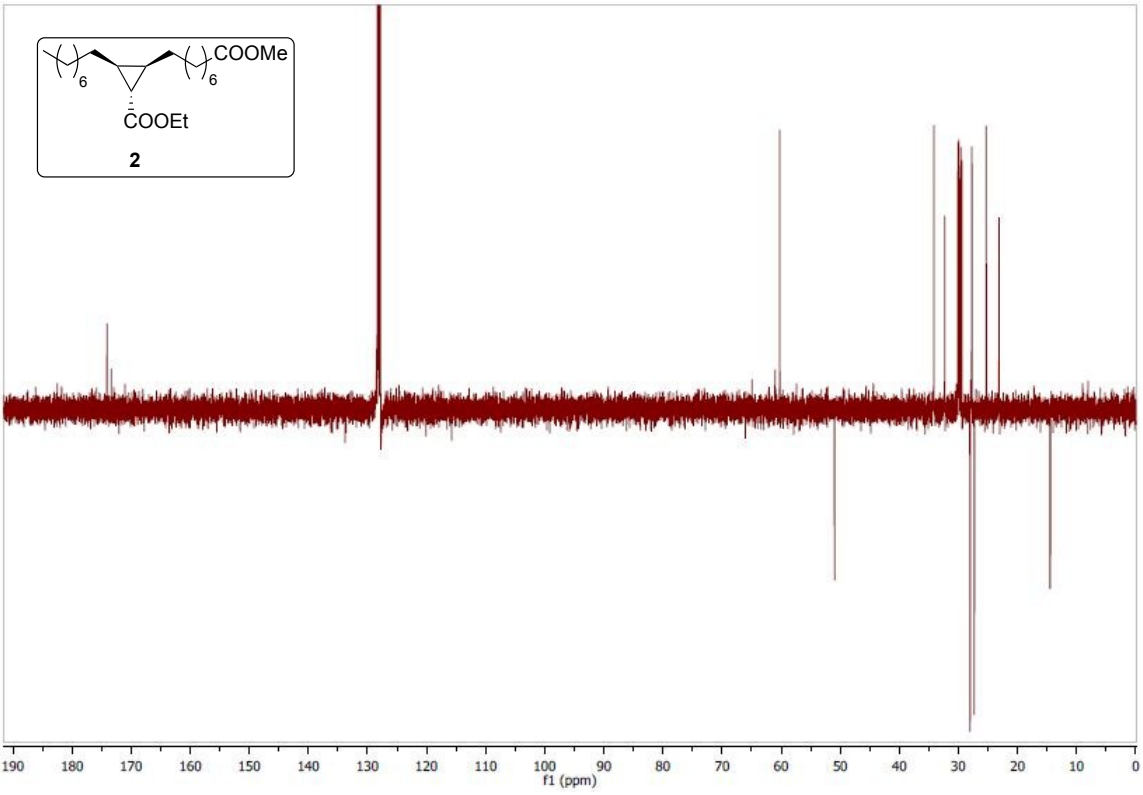
^{13}C-RMN (APT) ($CDCl_3$, δ ppm, 100 MHz)



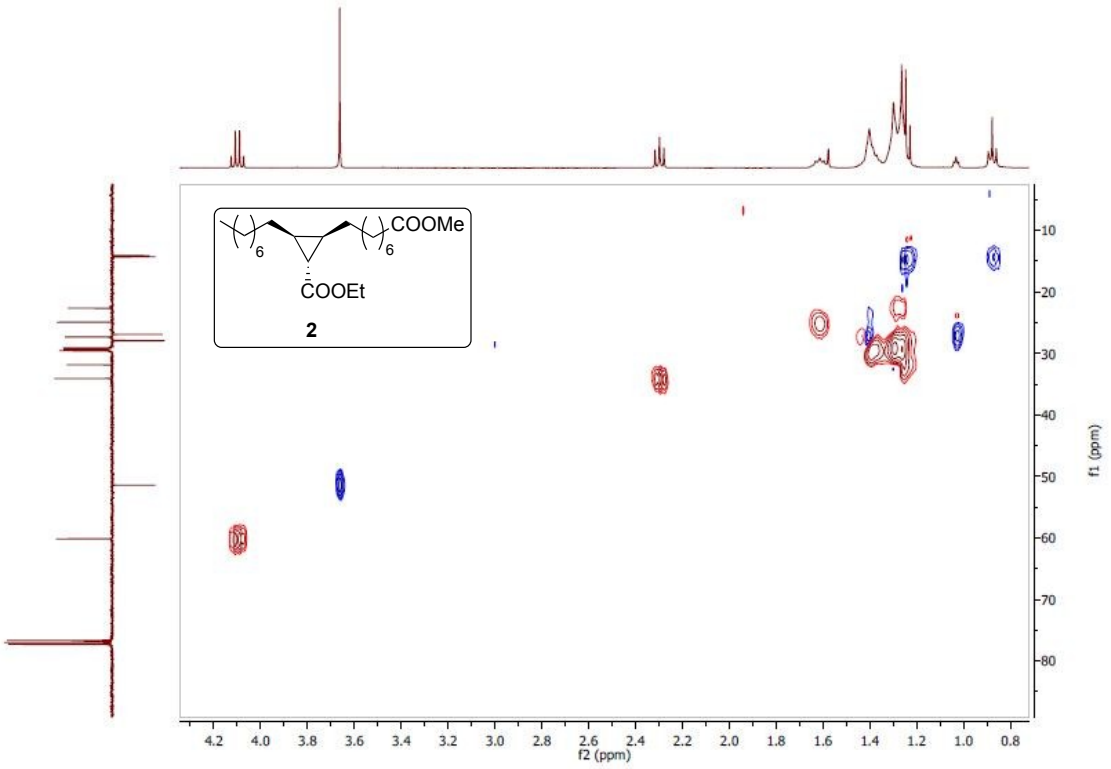
^{1}H-RMN (C_6D_6, δ ppm, 400 MHz)



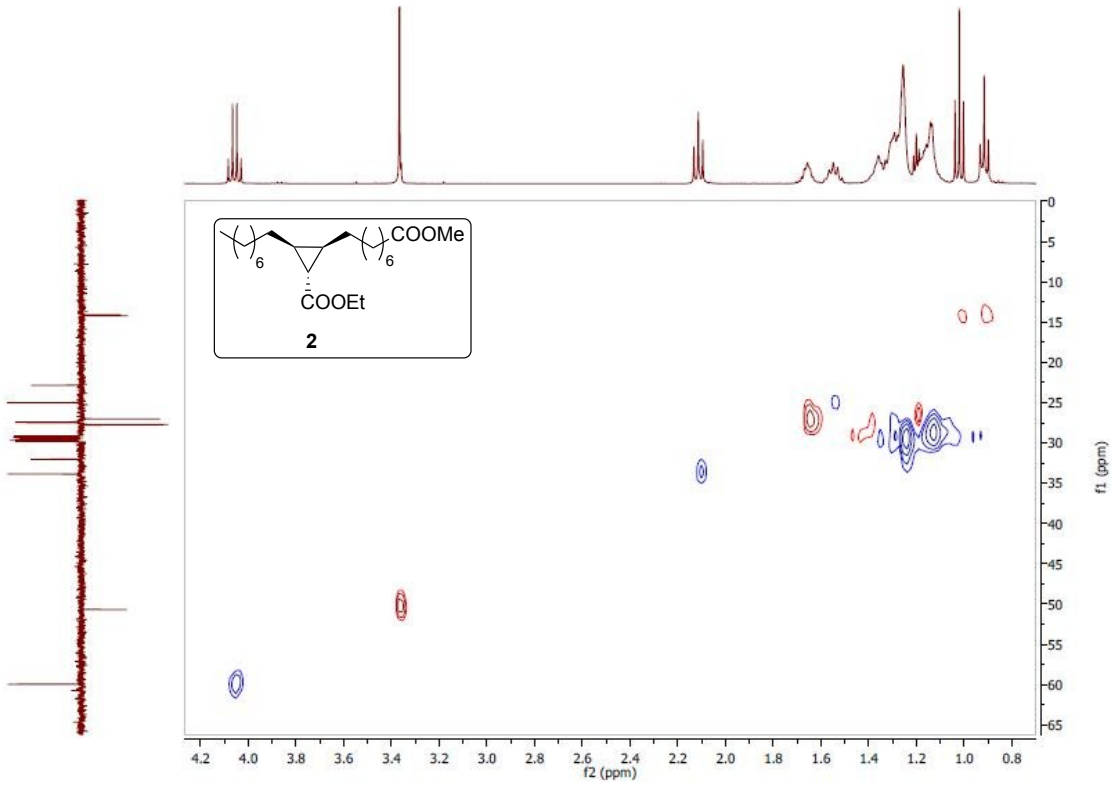
^{13}C-RMN (APT) (C_6D_6, δ ppm, 100 MHz)



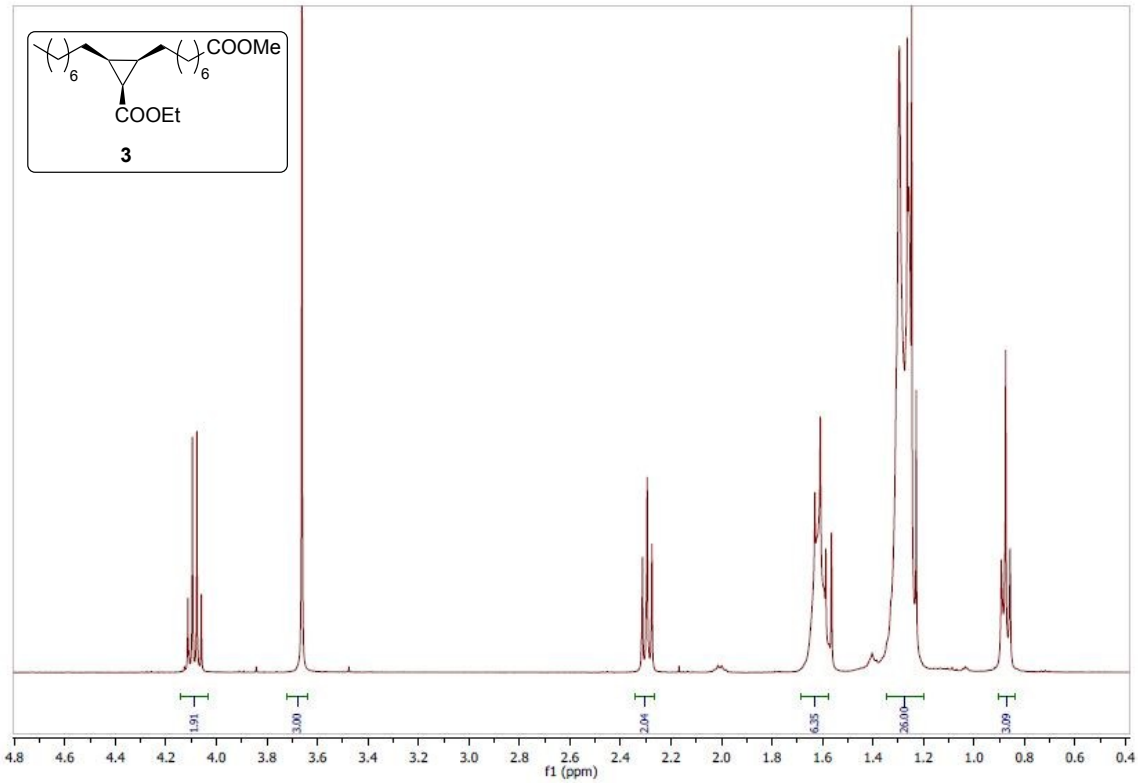
^{1}H-^{13}C HSQC ($CDCl_3$, δ ppm)



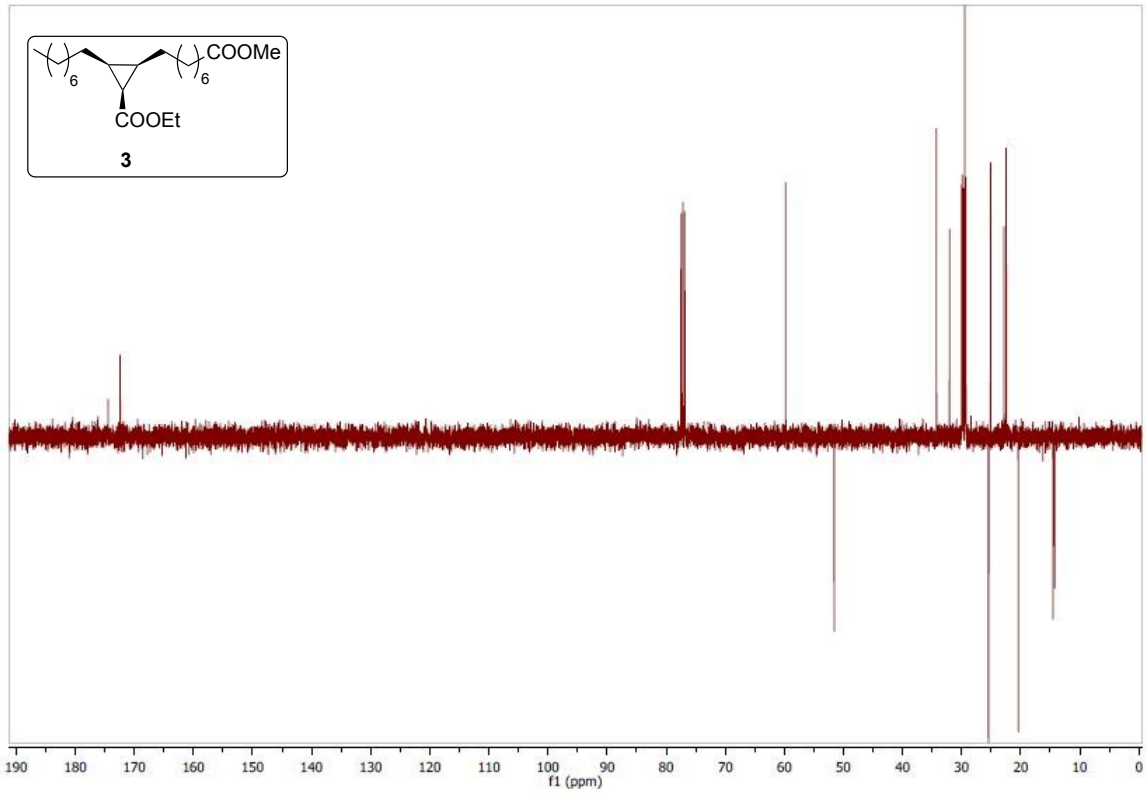
^{1}H-^{13}C HSQC (C_6D_6, δ ppm)



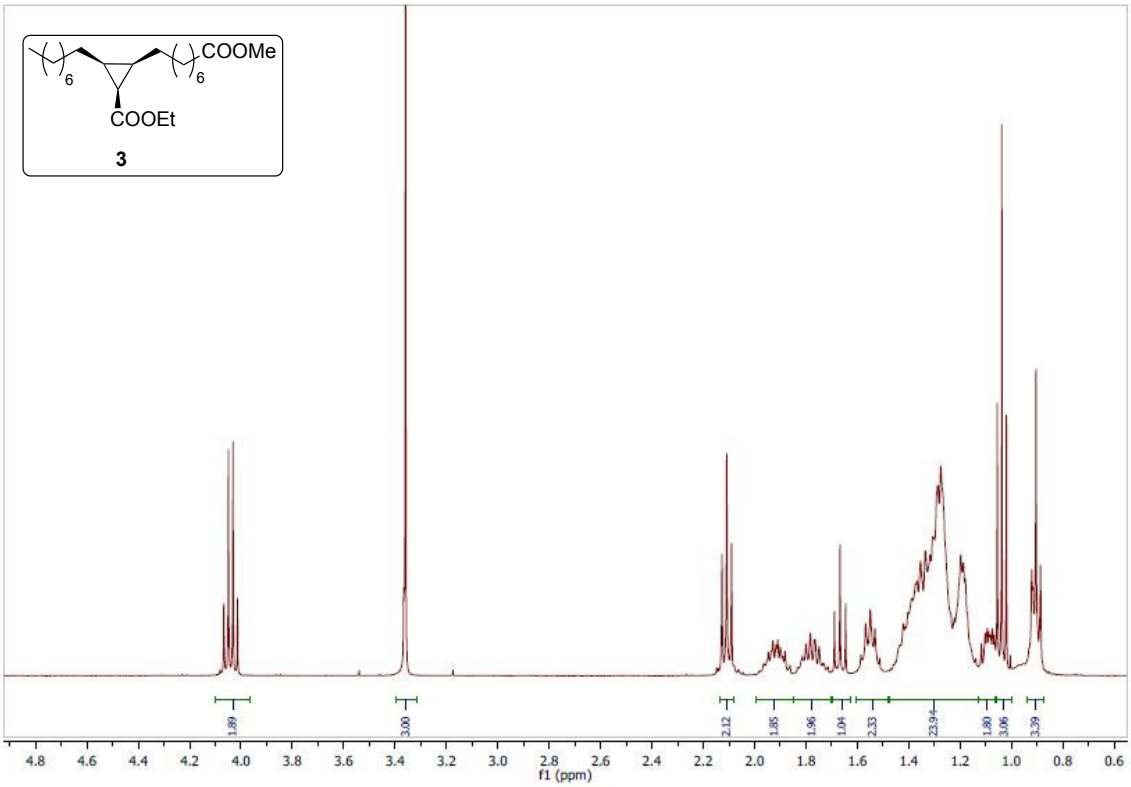
^{1}H-RMN ($CDCl_3$, δ ppm, 400 MHz)



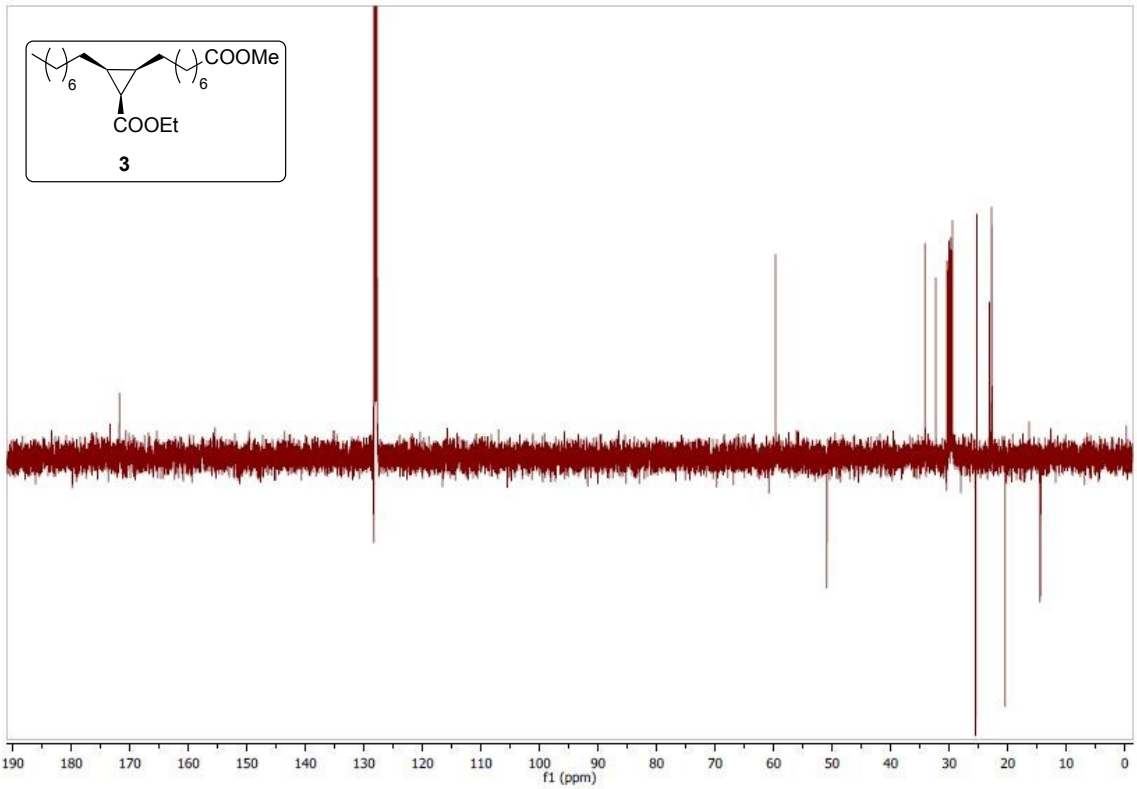
^{13}C-RMN (APT) ($CDCl_3$, δ ppm, 100 MHz)



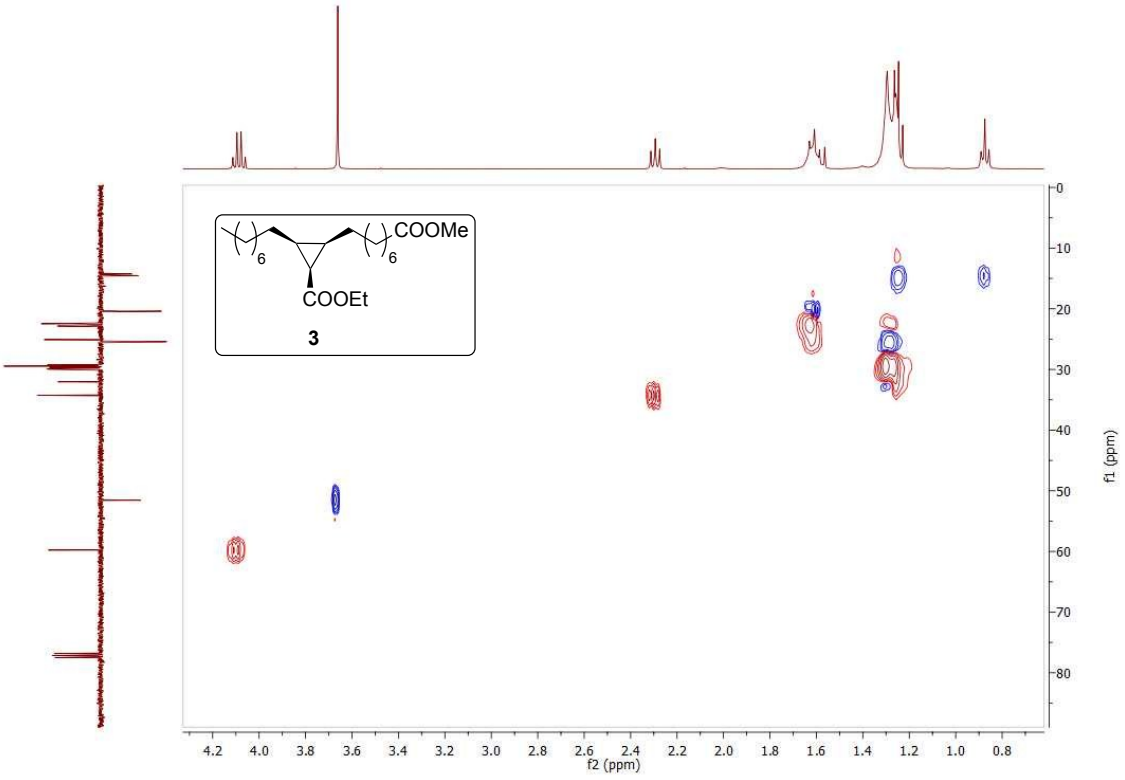
^{1}H-RMN (C_6D_6, δ ppm, 400 MHz)



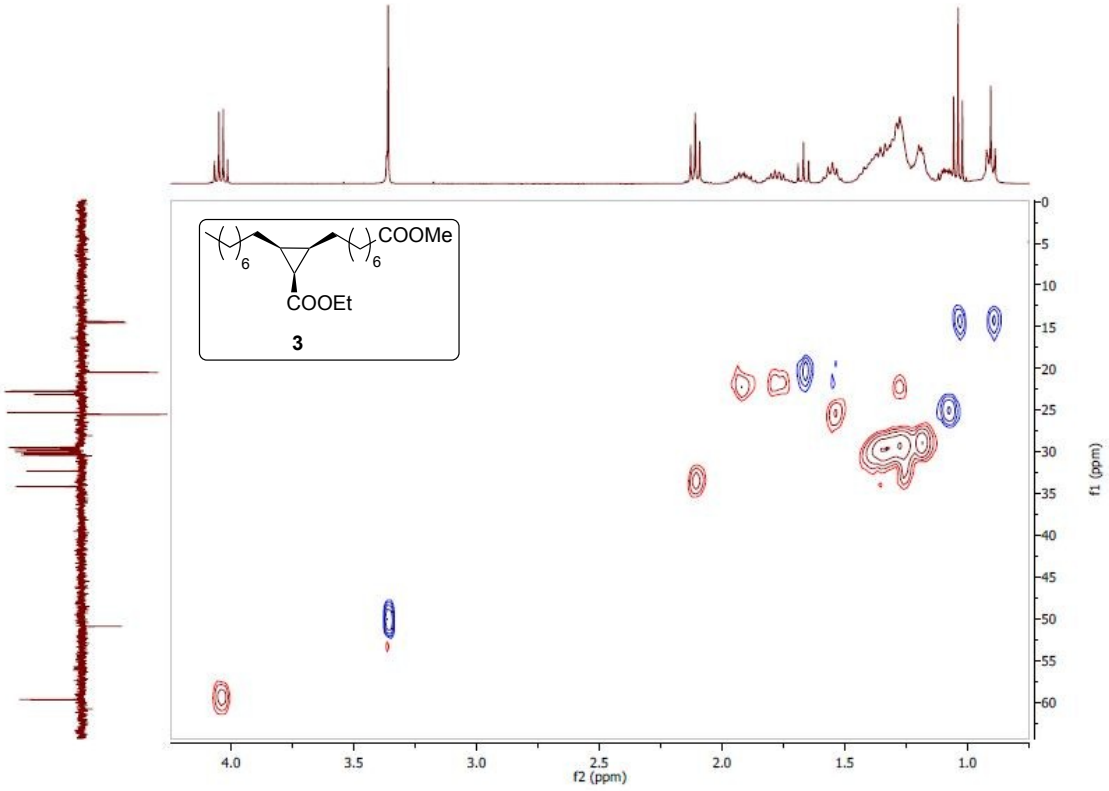
^{13}C-RMN (APT) (C_6D_6, δ ppm, 100 MHz)



^{1}H-^{13}C HSQC ($CDCl_3$, δ ppm)



^{1}H-^{13}C HSQC (C_6D_6, δ ppm)



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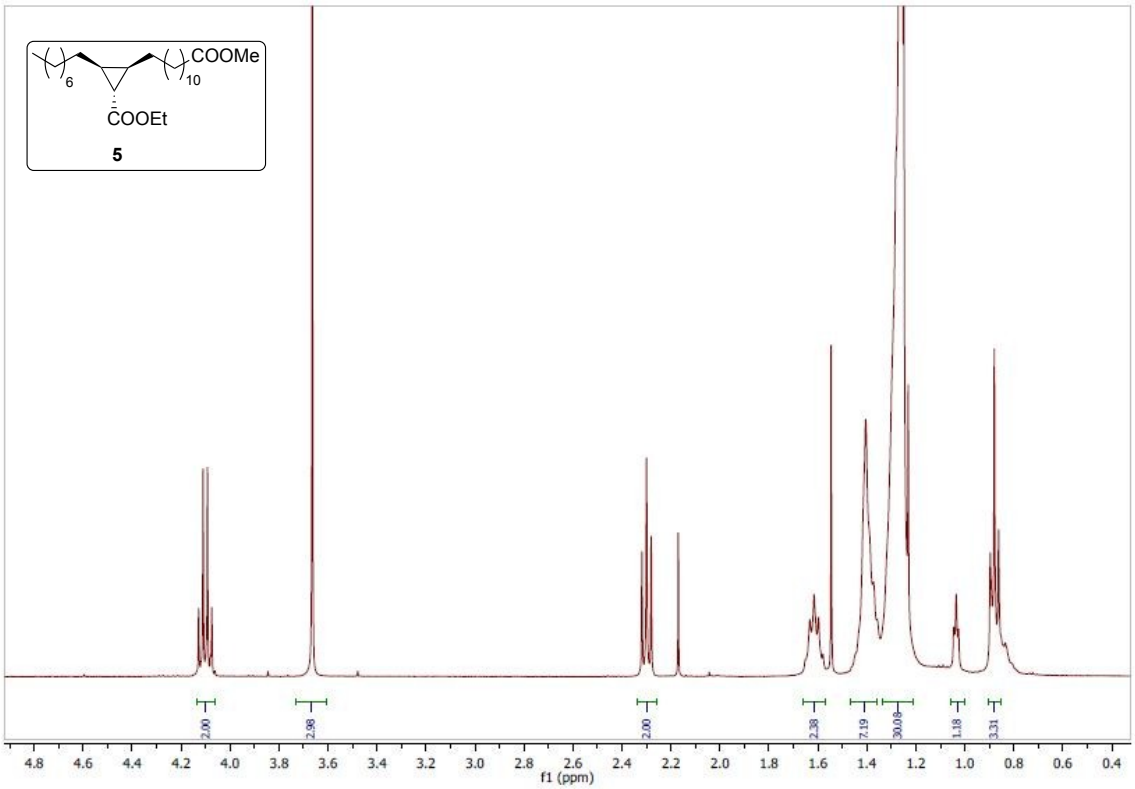

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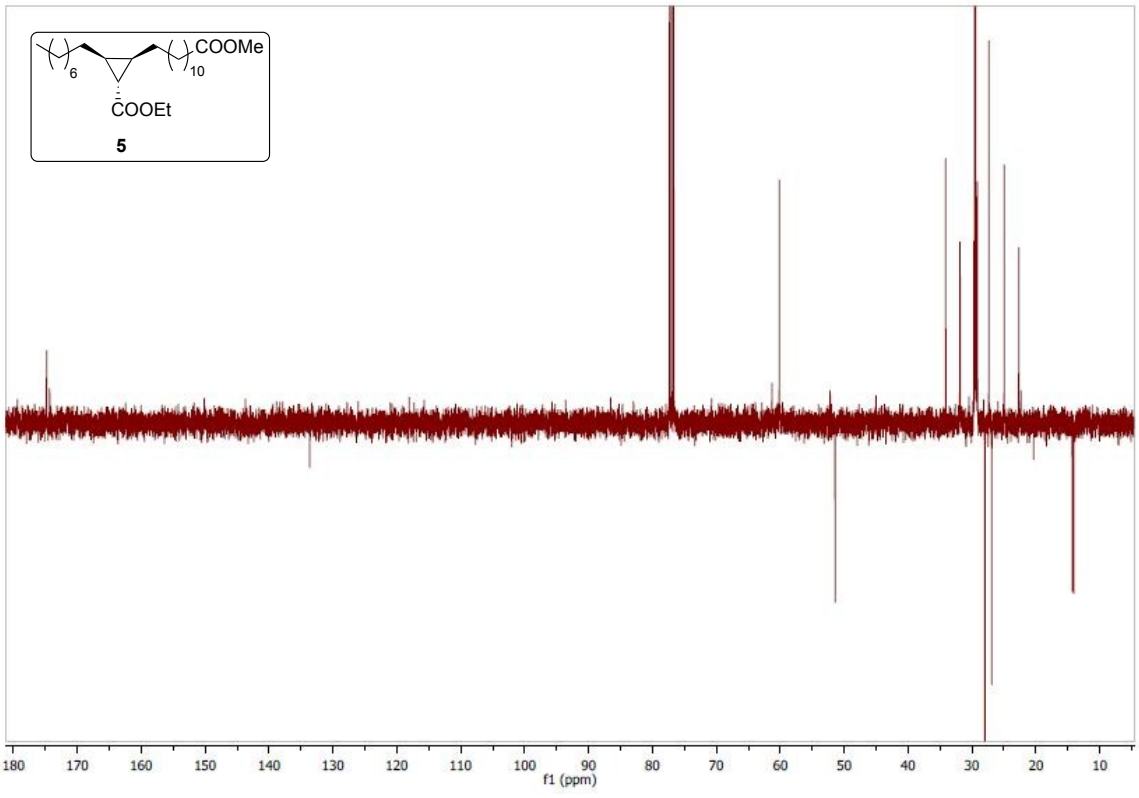

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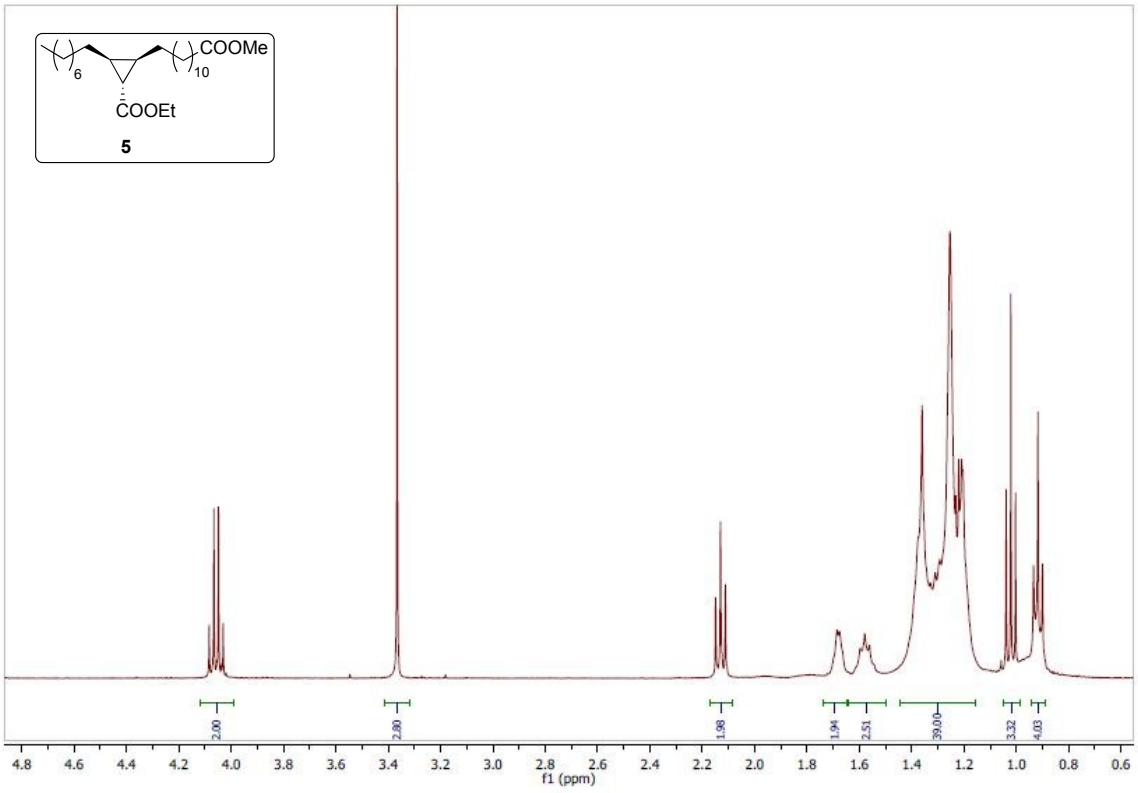

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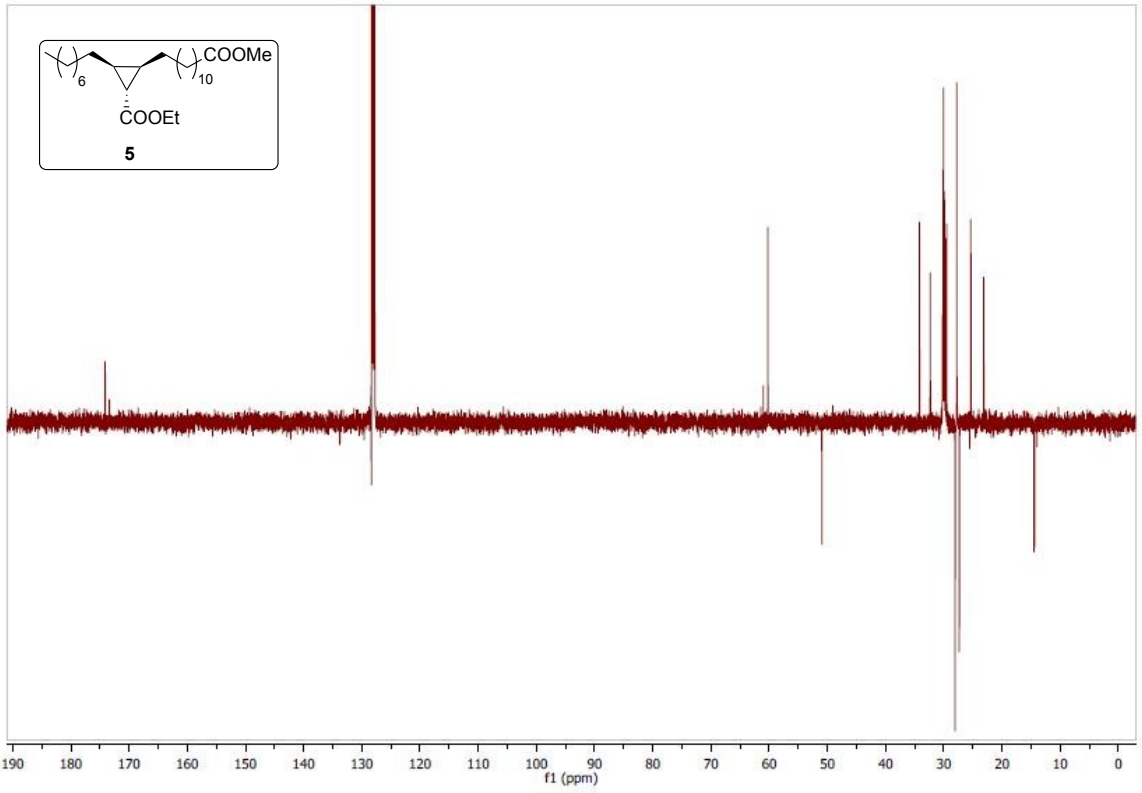

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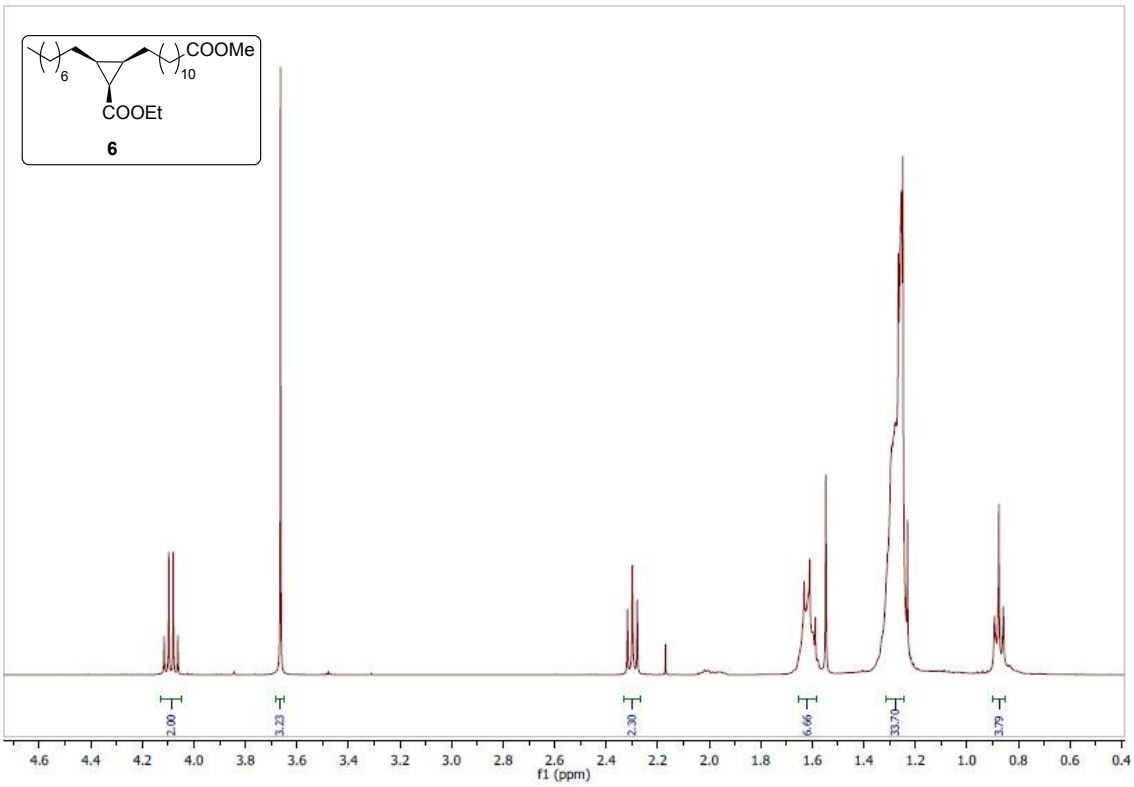

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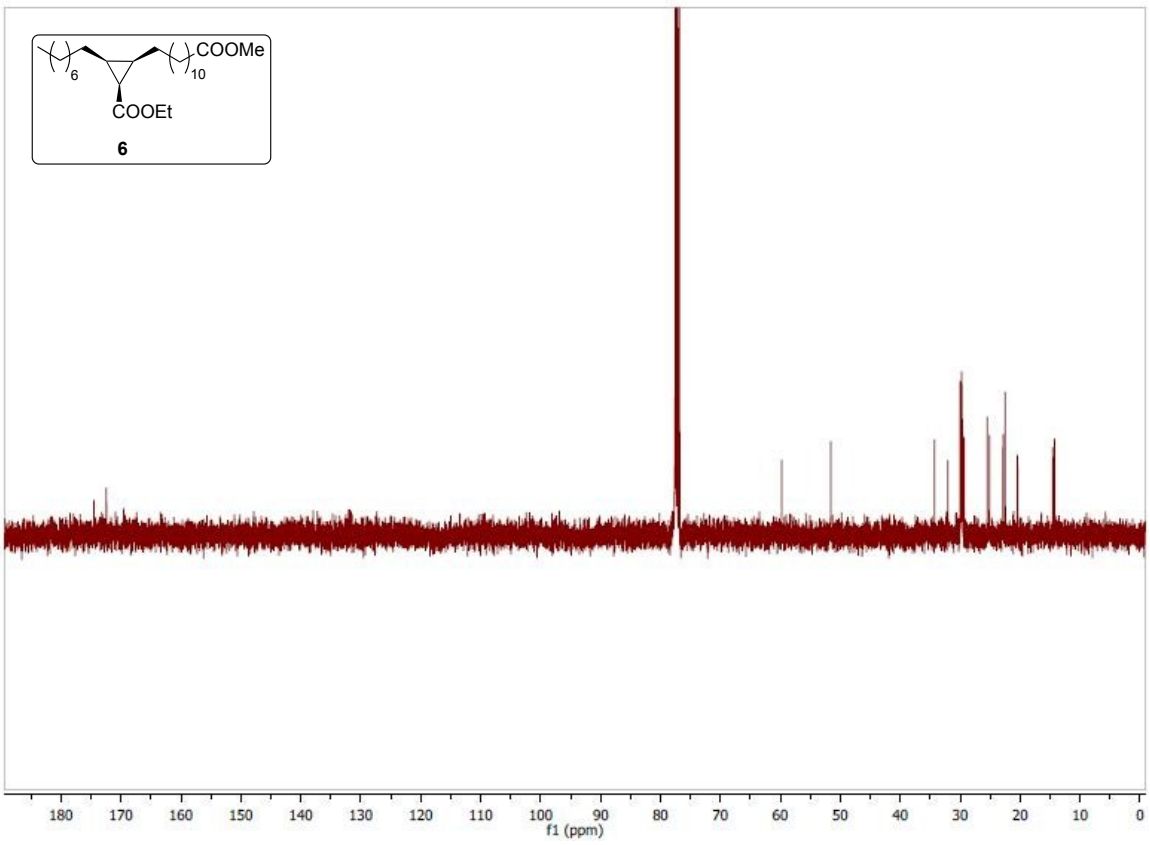

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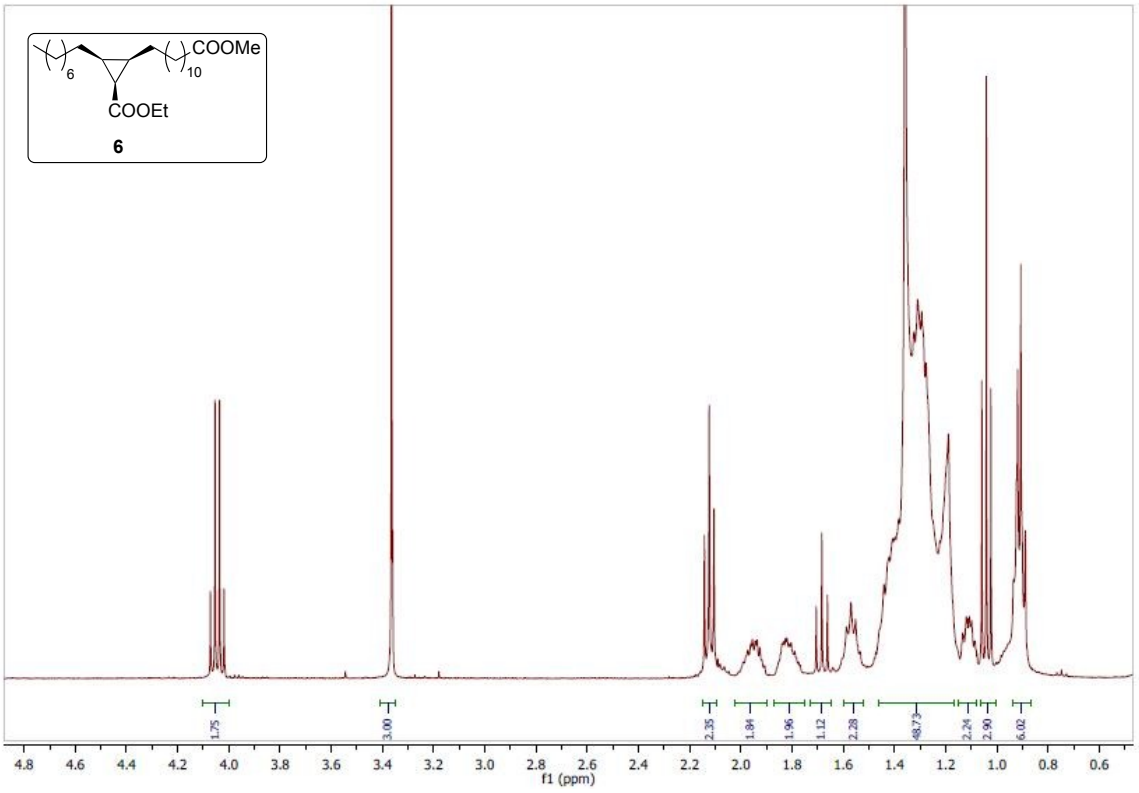

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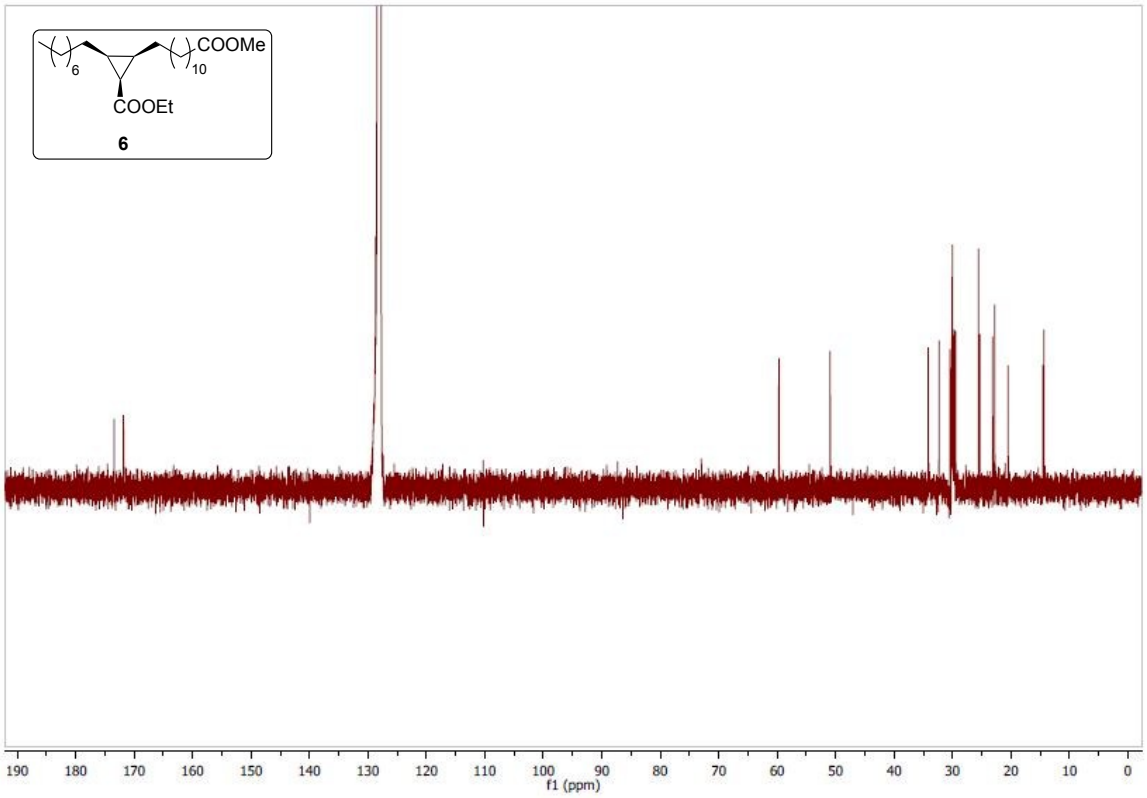
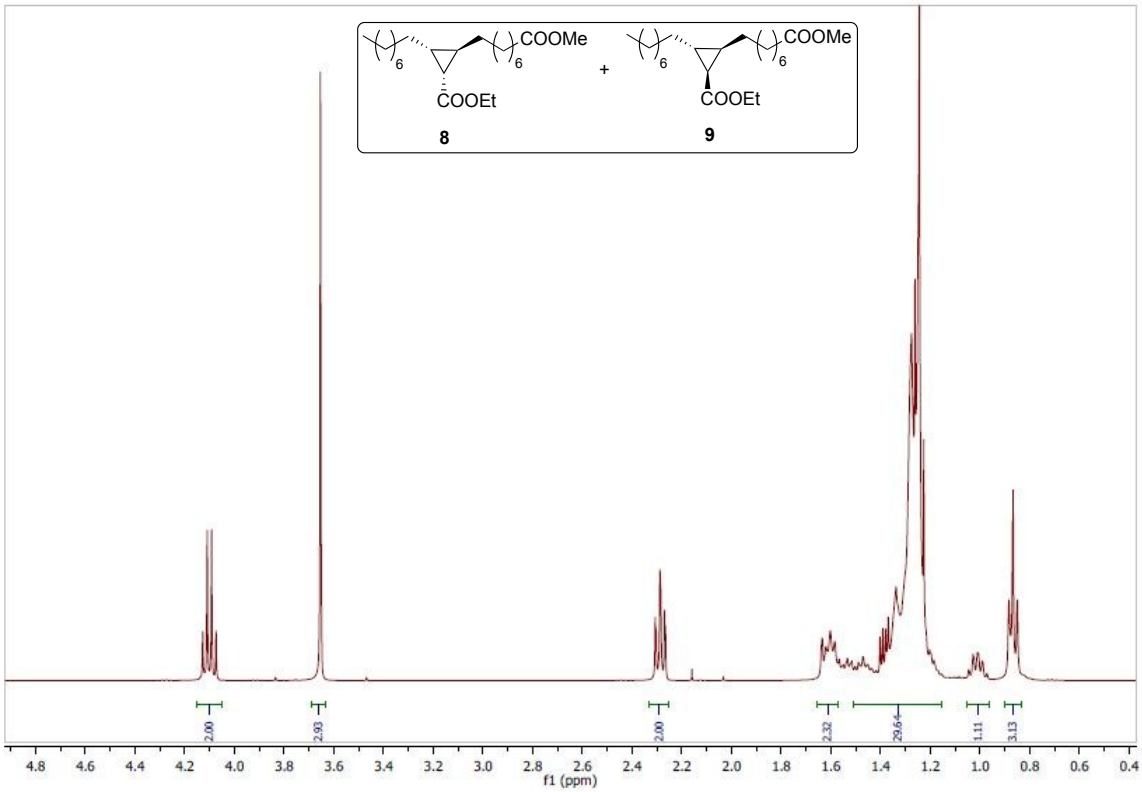
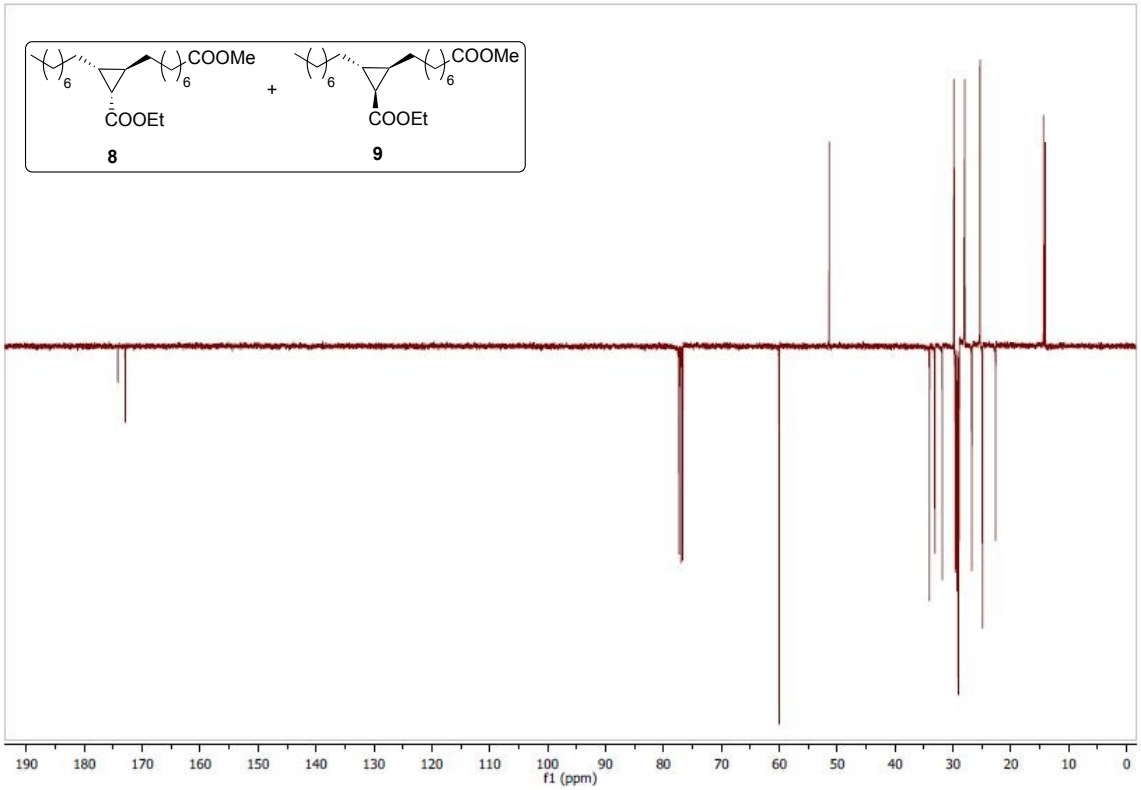


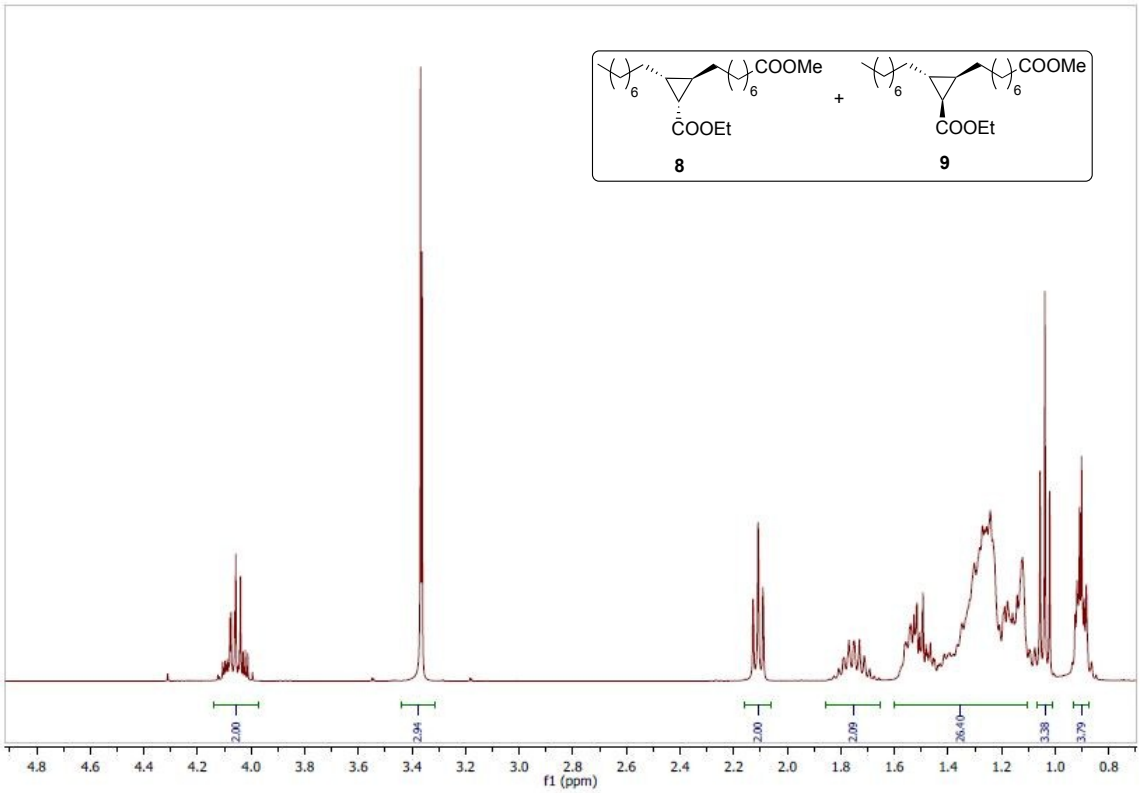
^{1}H-RMN ($CDCl_3$, δ ppm, 400 MHz)



^{13}C-RMN (APT) ($CDCl_3$, δ ppm, 100 MHz)



^{1}H-RMN (C_6D_6, δ ppm, 400 MHz)



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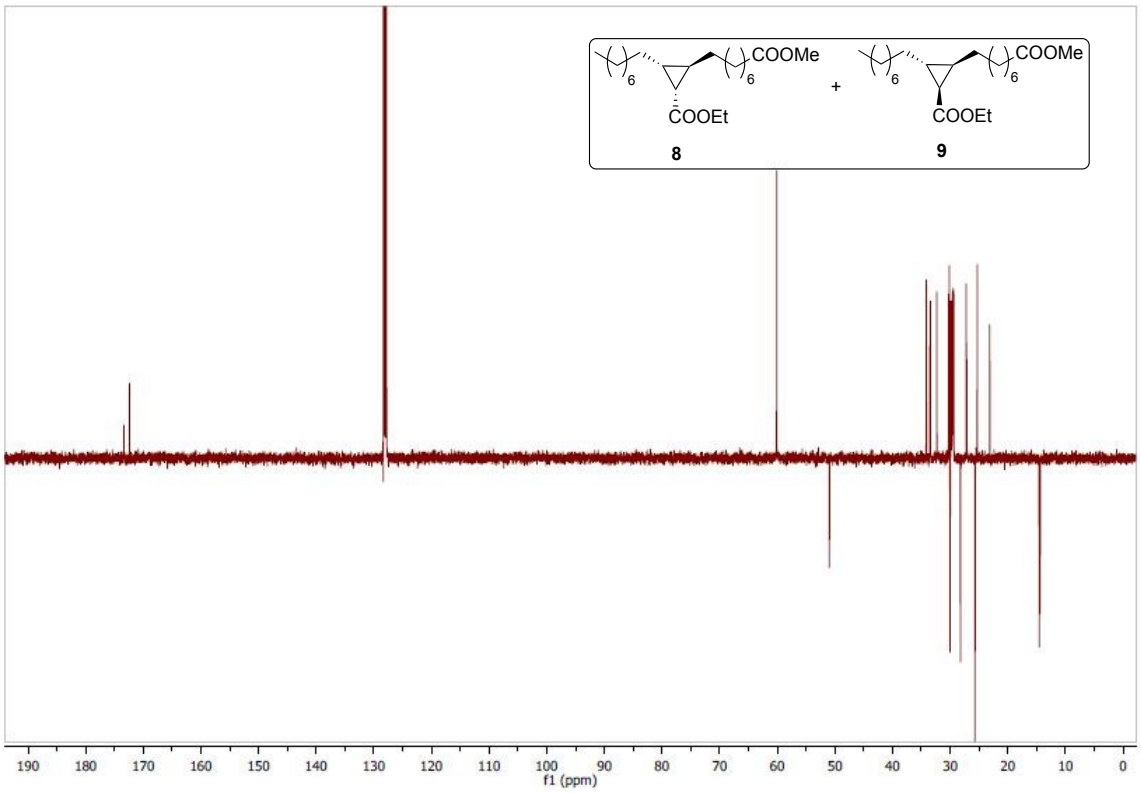
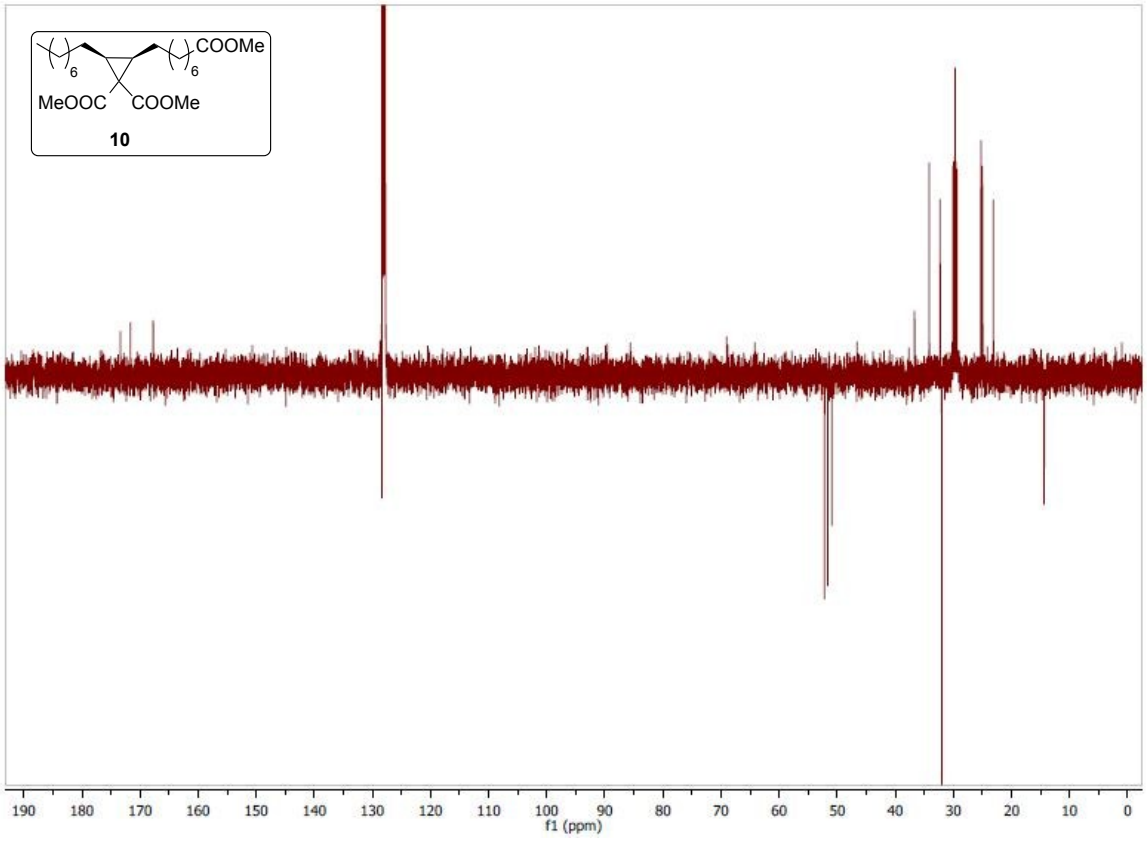


^{1}H-RMN (C_6D_6, δ ppm, 400 MHz)

^{13}C-RMN (APT) (C_6D_6, δ ppm, 100 MHz)



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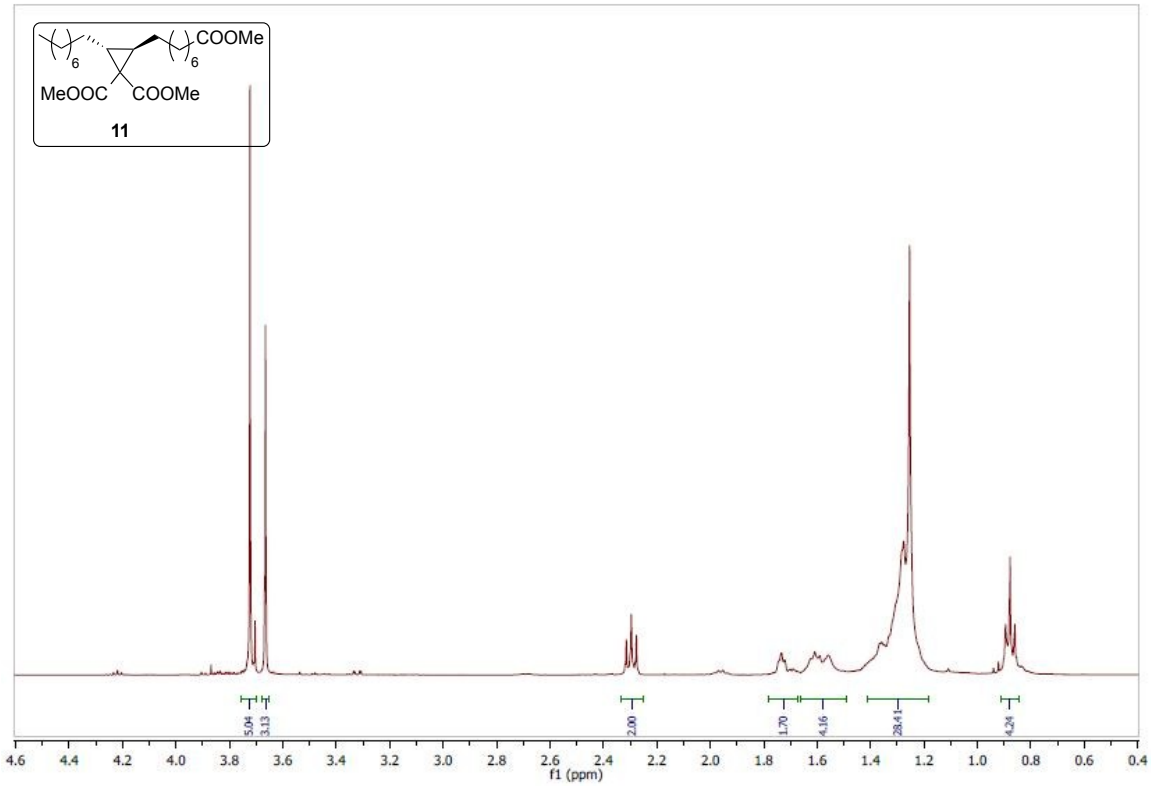

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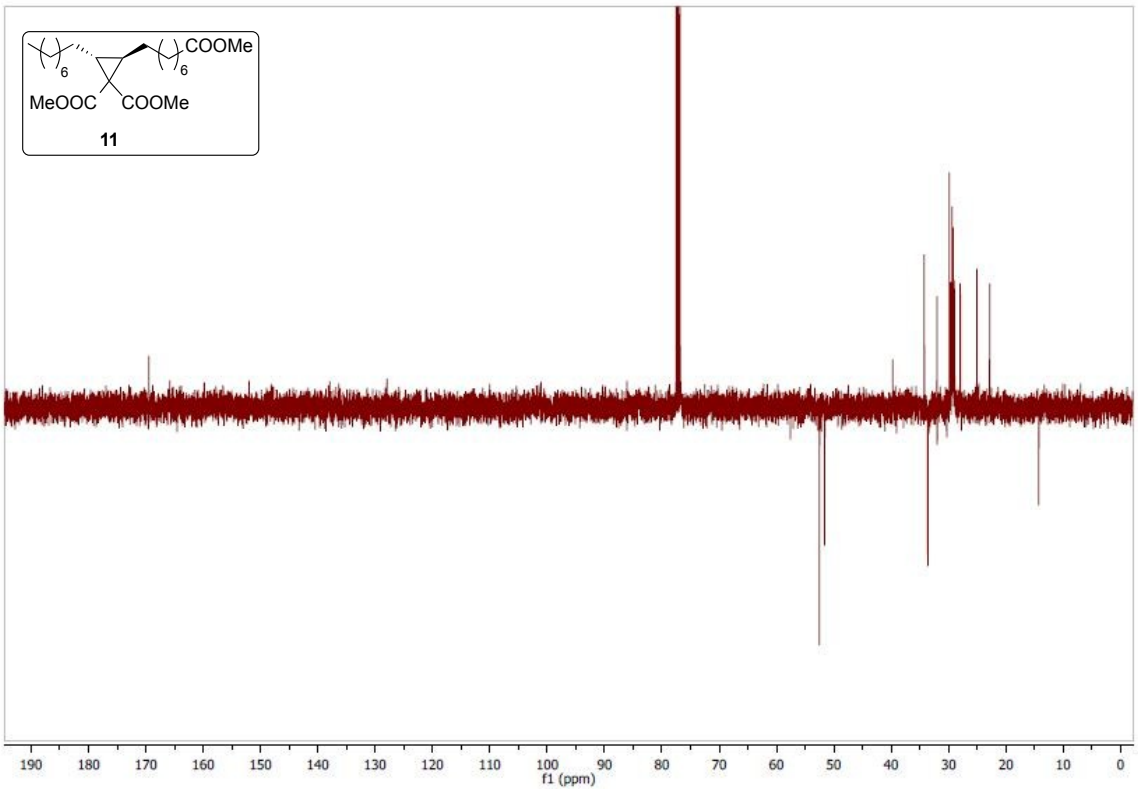
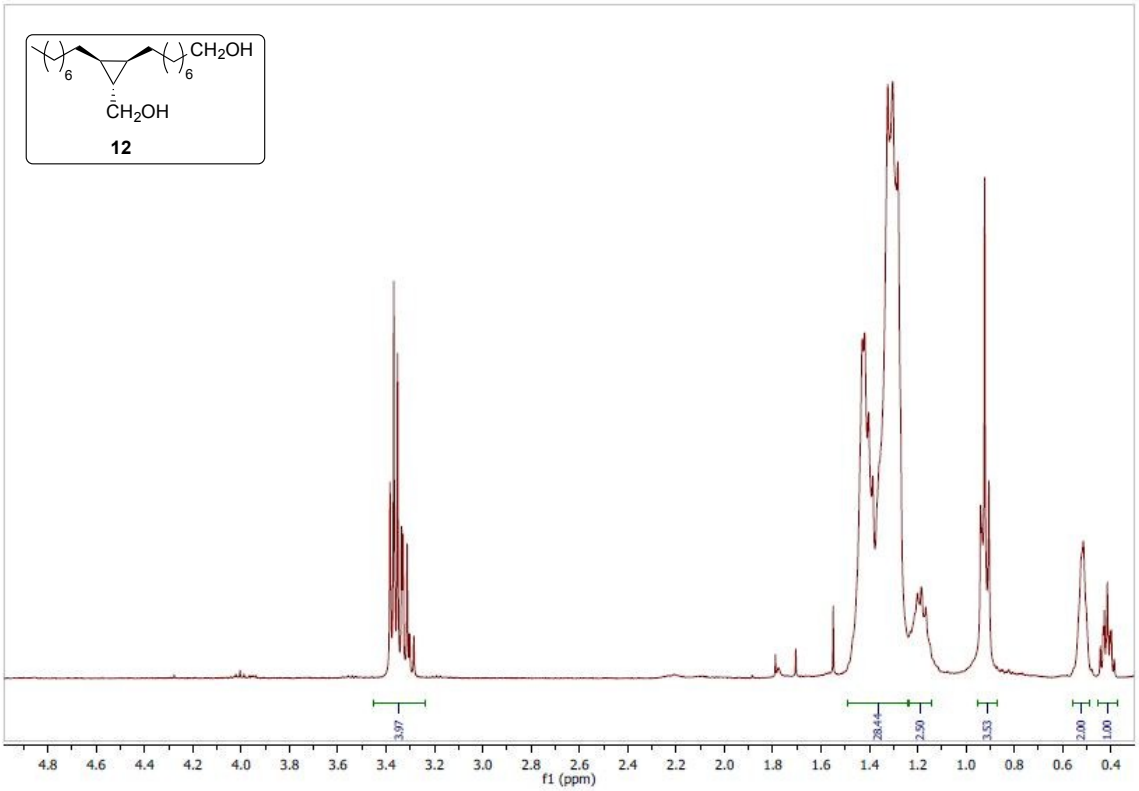
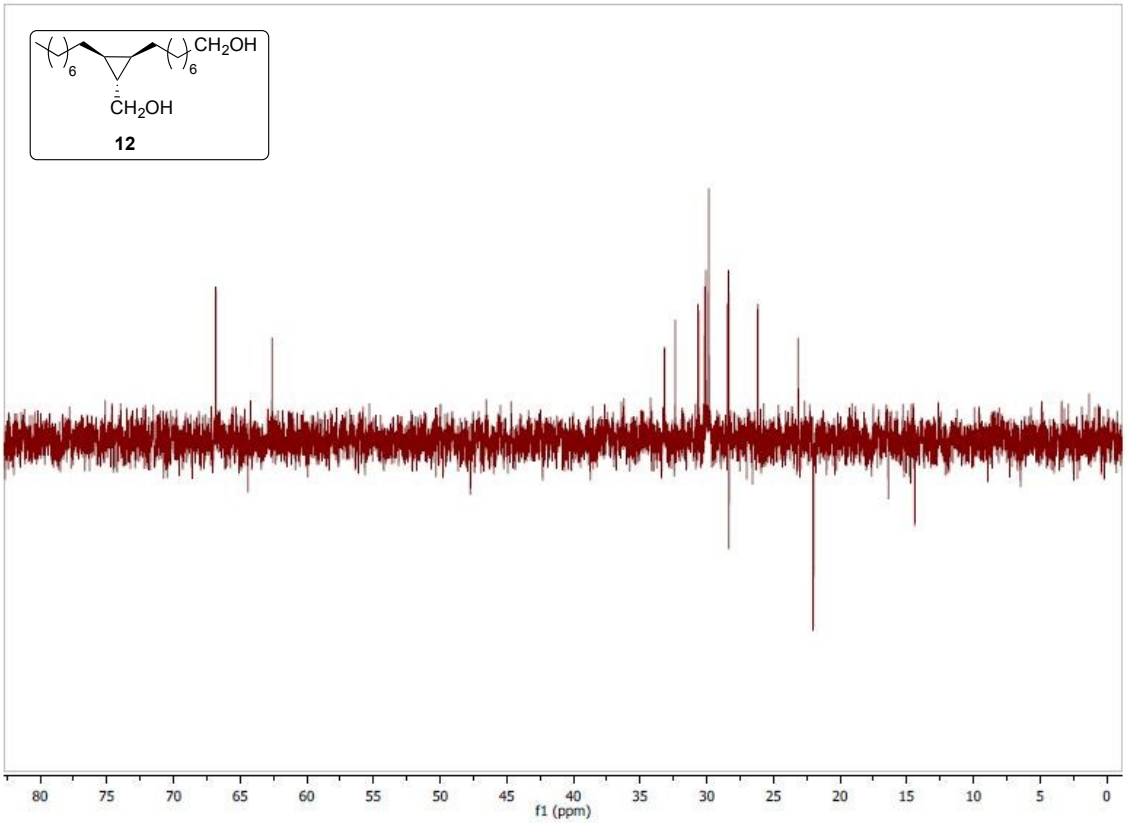


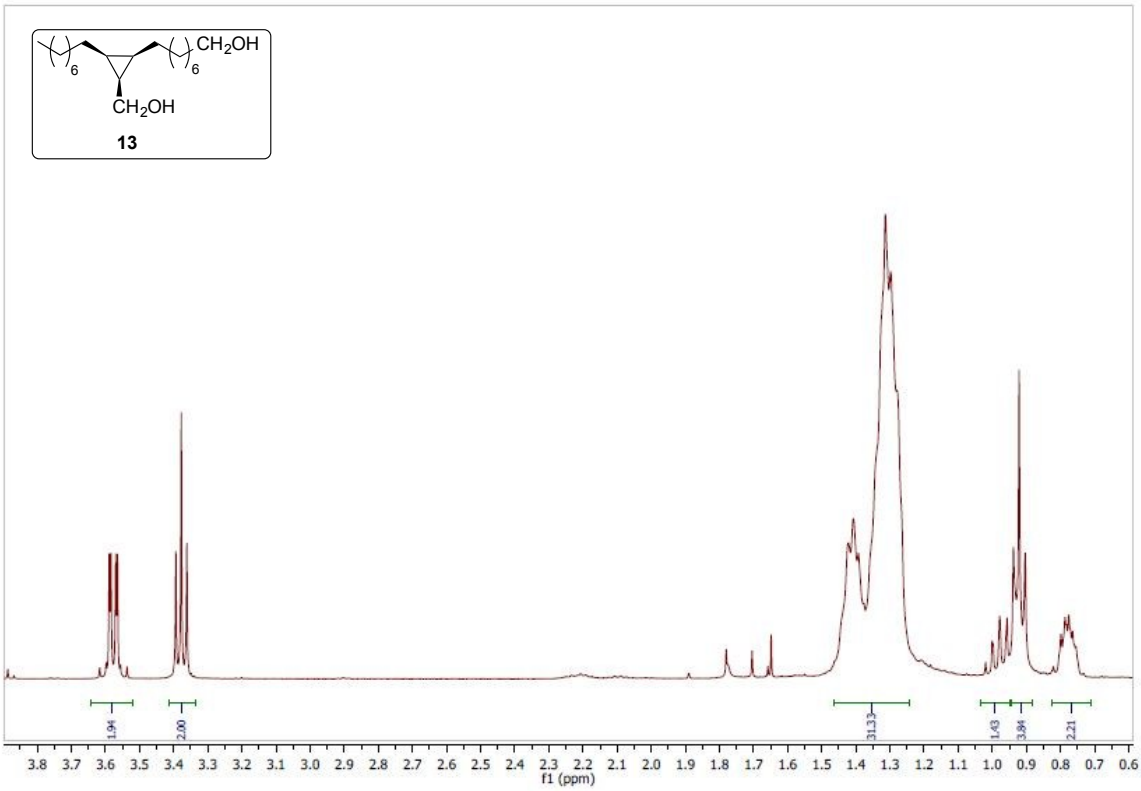
^{1}H-RMN (C_6D_6, δ ppm, 400 MHz)



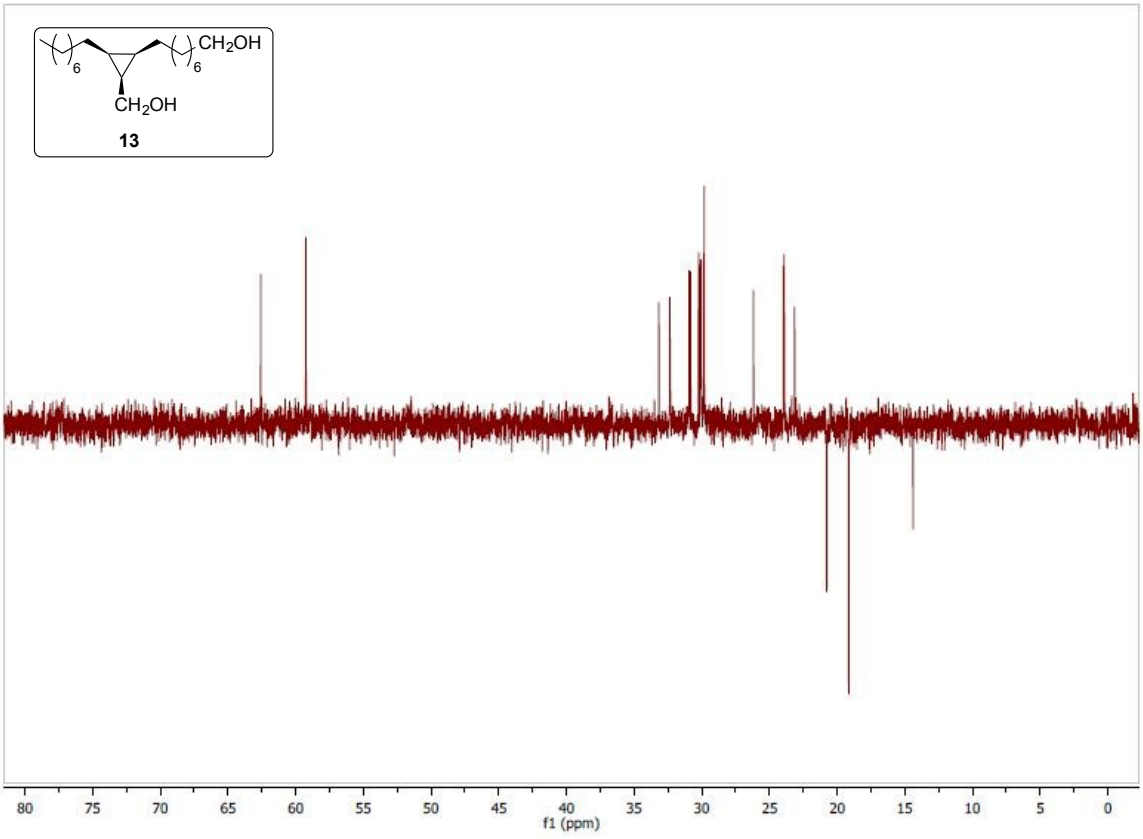
^{13}C-RMN (APT) (C_6D_6, δ ppm, 100 MHz)



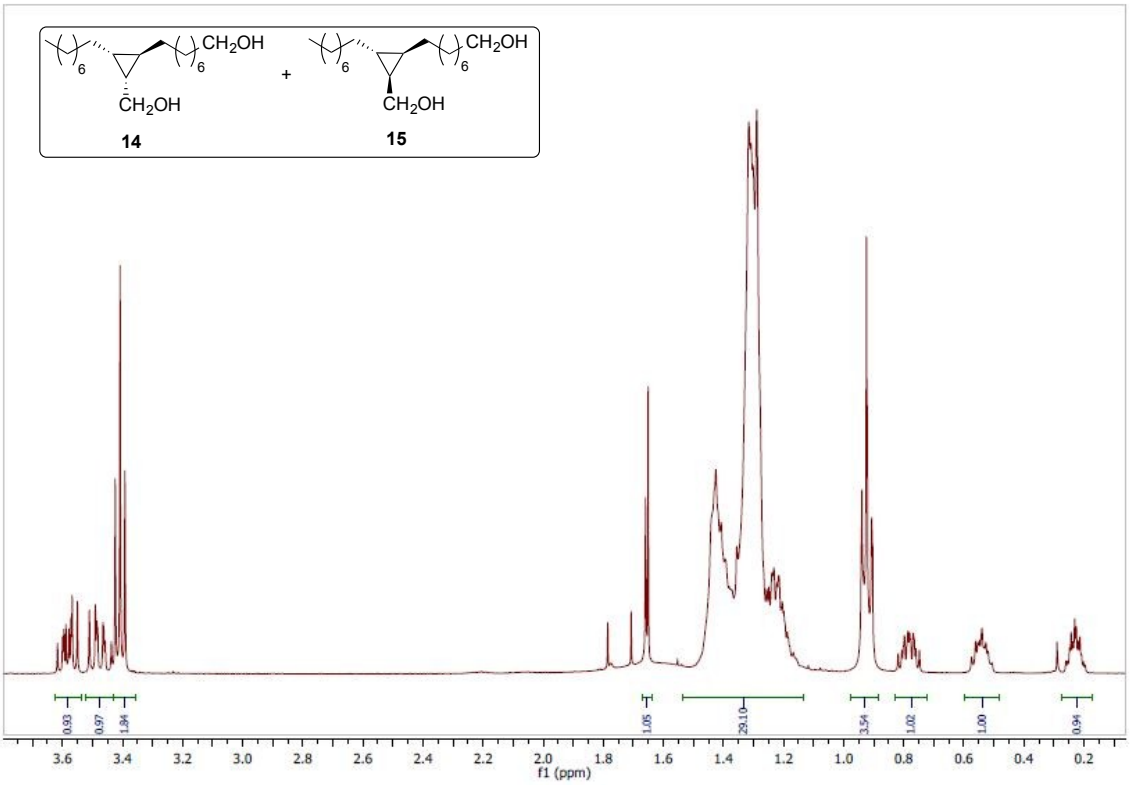
^{1}H-RMN (C_6D_6, δ ppm, 400 MHz)



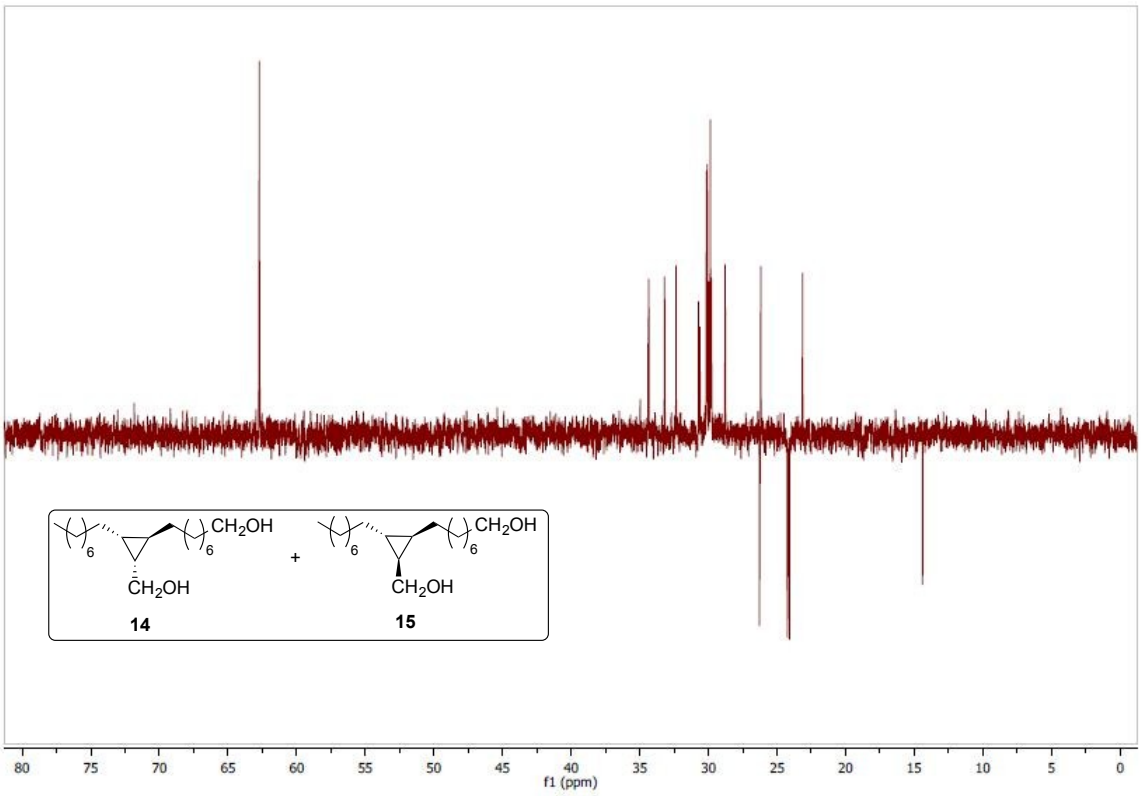
^{13}C-RMN (APT) (C_6D_6, δ ppm, 100 MHz)



^{1}H-RMN (C_6D_6, δ ppm, 400 MHz)



^{13}C-RMN (APT) (C_6D_6, δ ppm, 100 MHz)



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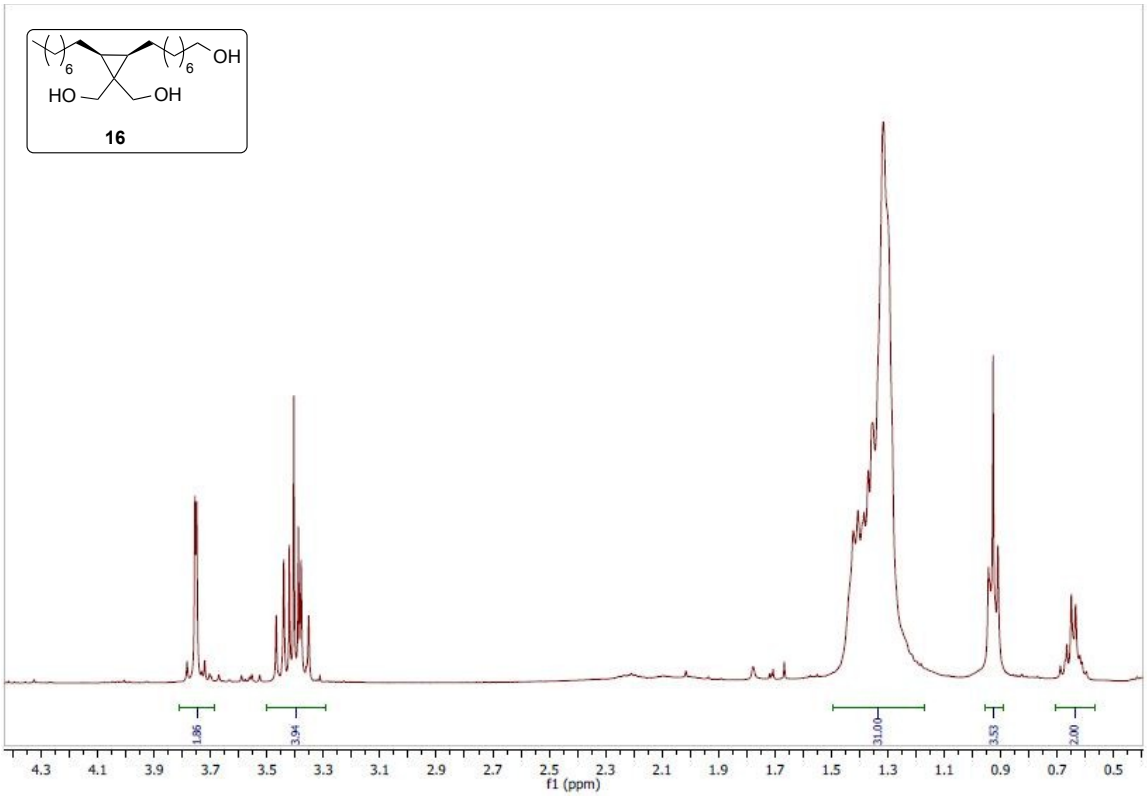

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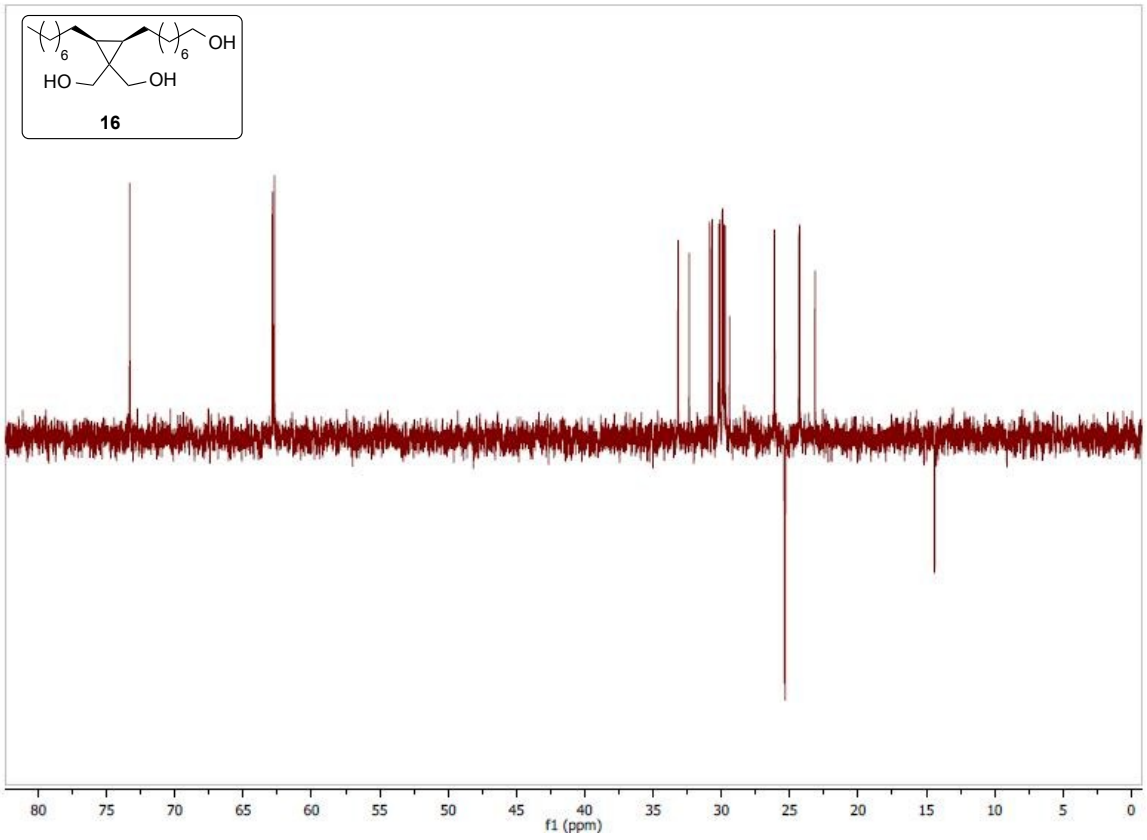
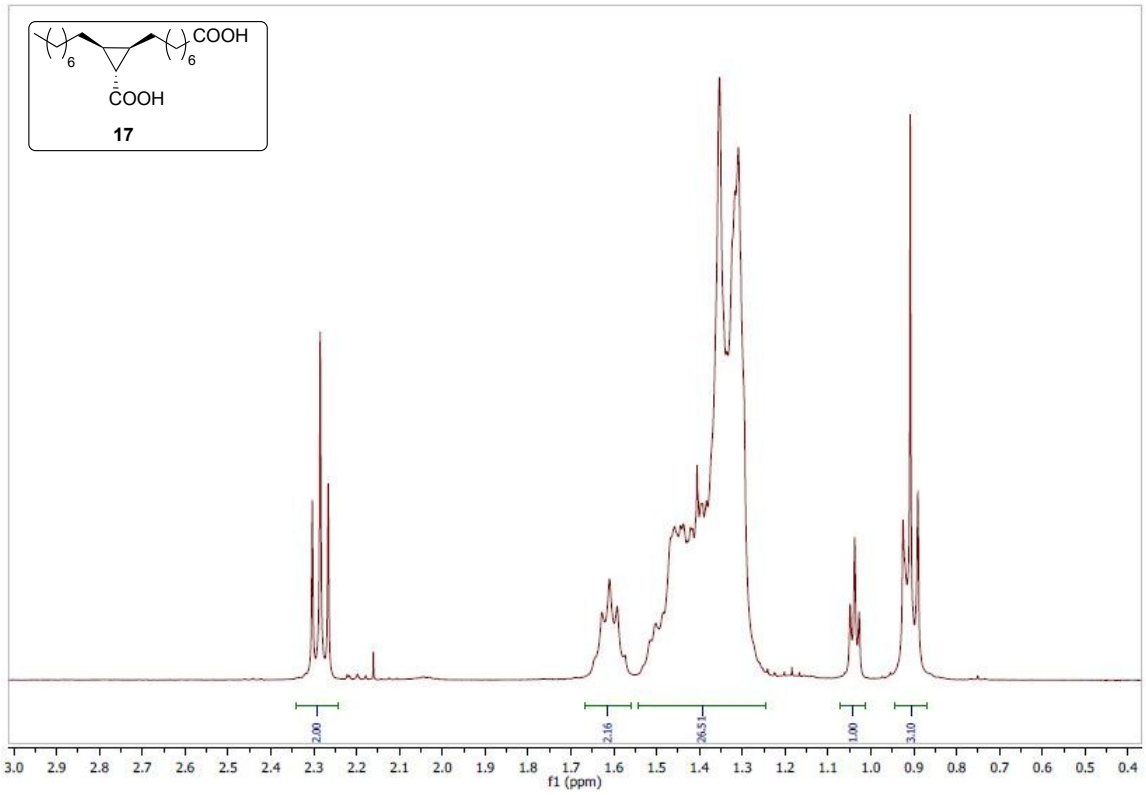
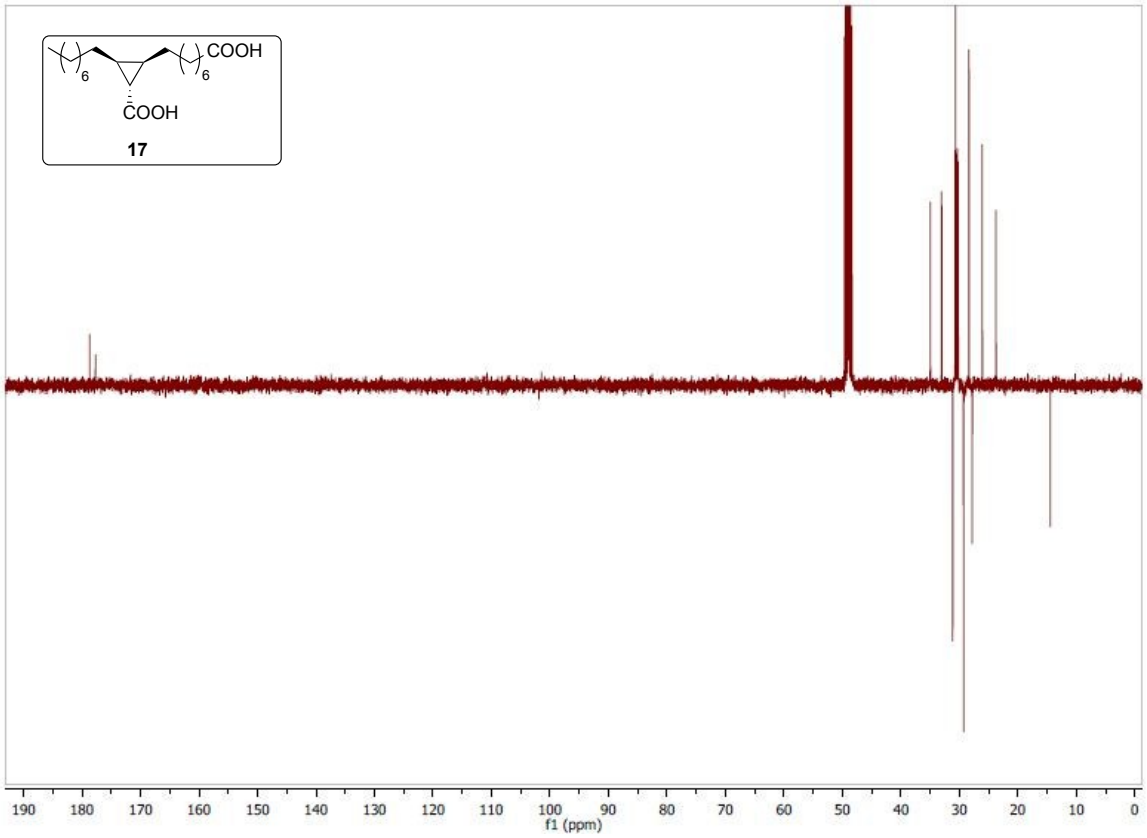


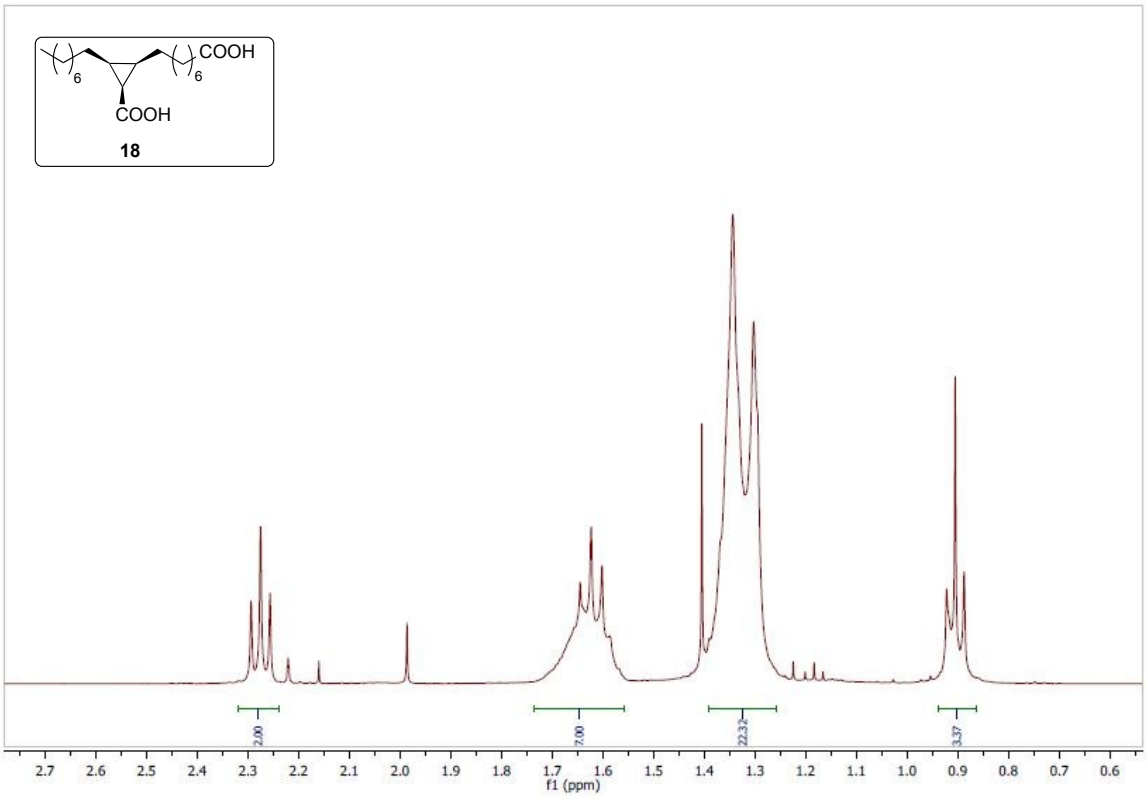
^{1}H-RMN (MeOD, δ ppm, 400 MHz)



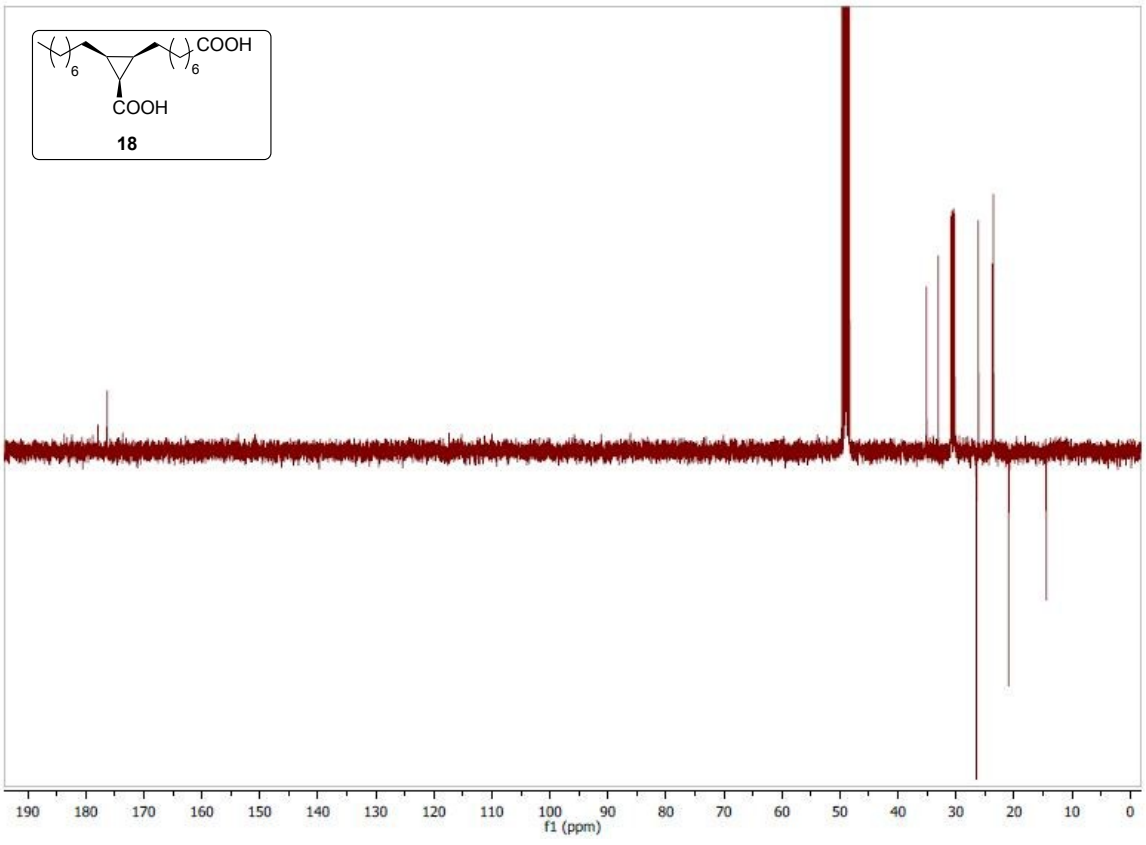
^{13}C-RMN (APT) (MeOD, δ ppm, 100 MHz)



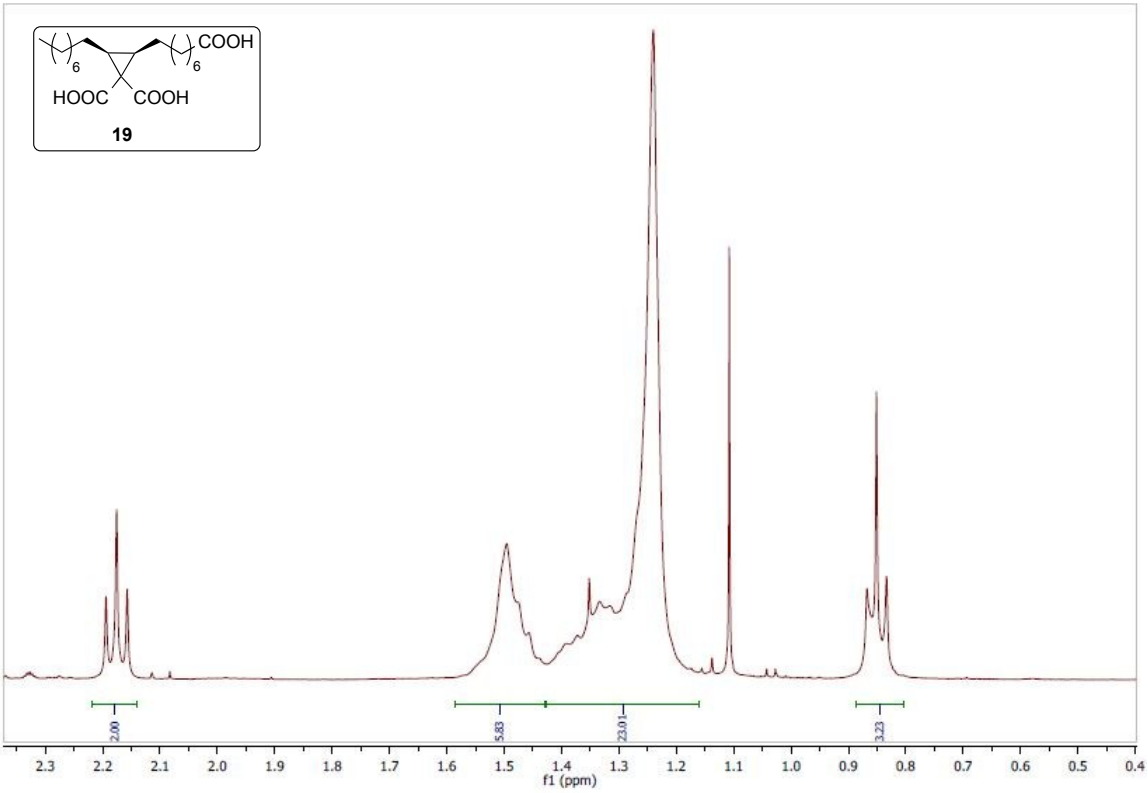
^{1}H-RMN (MeOD, δ ppm, 400 MHz)



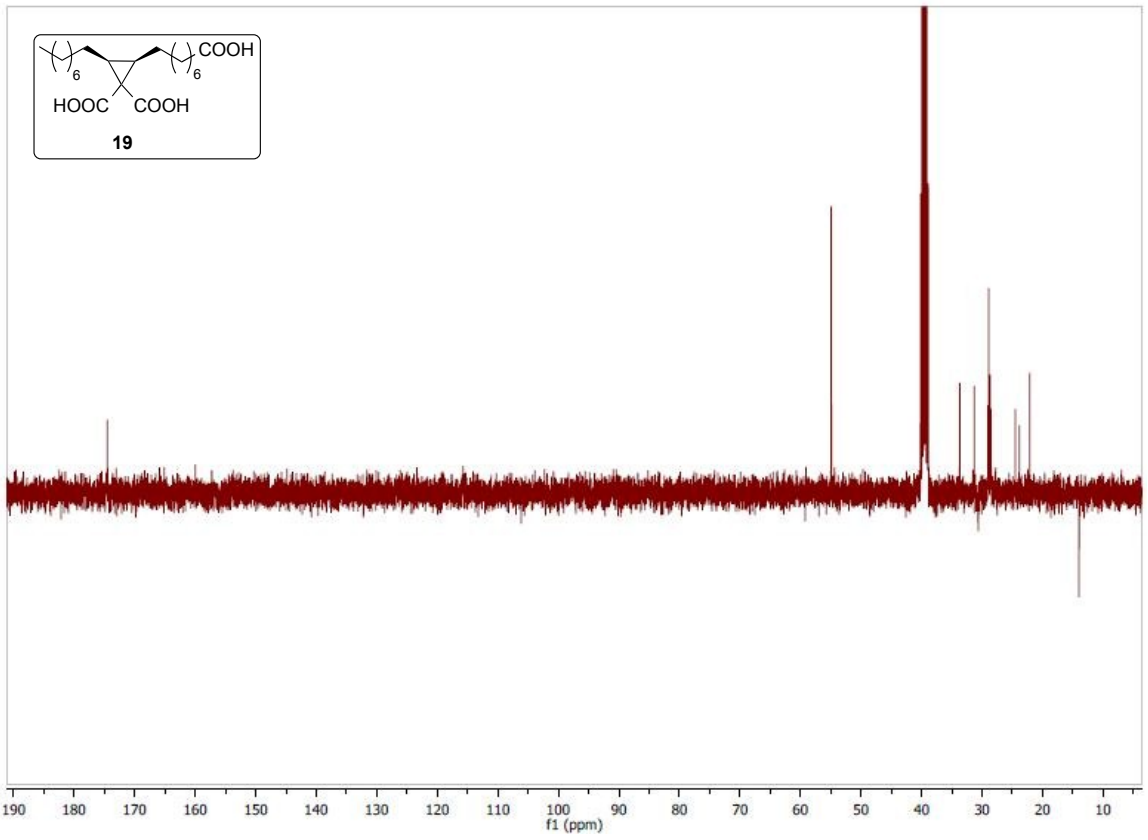
^{13}C-RMN (APT) (MeOD, δ ppm, 100 MHz)



^{1}H-RMN (DMSO, δ ppm, 400 MHz)

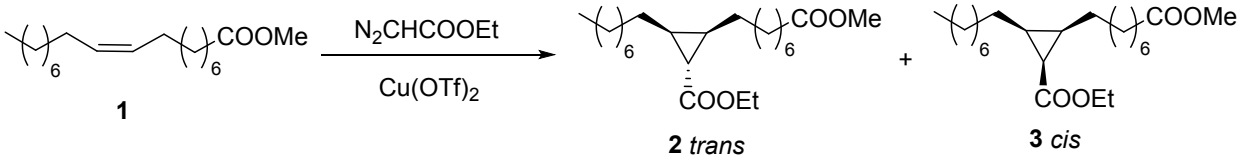


^{13}C-RMN (APT) (DMSO, δ ppm, 100 MHz)

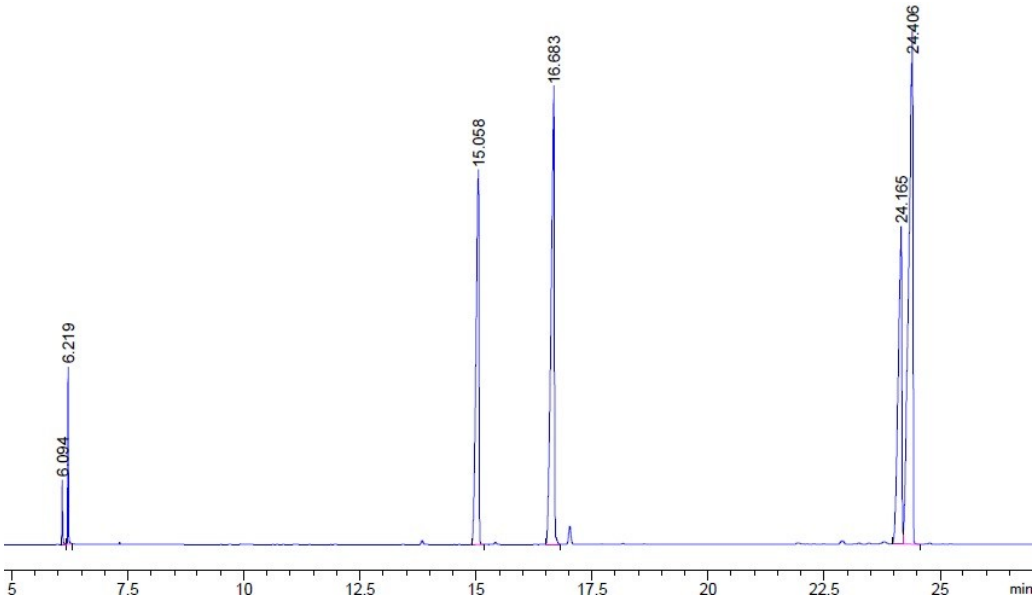


Chromatographic conditions and typical chromatograms

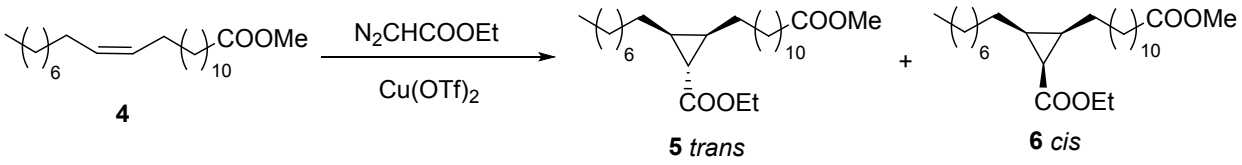
A) Cyclopropanation of methyl oleate (1) and EDA



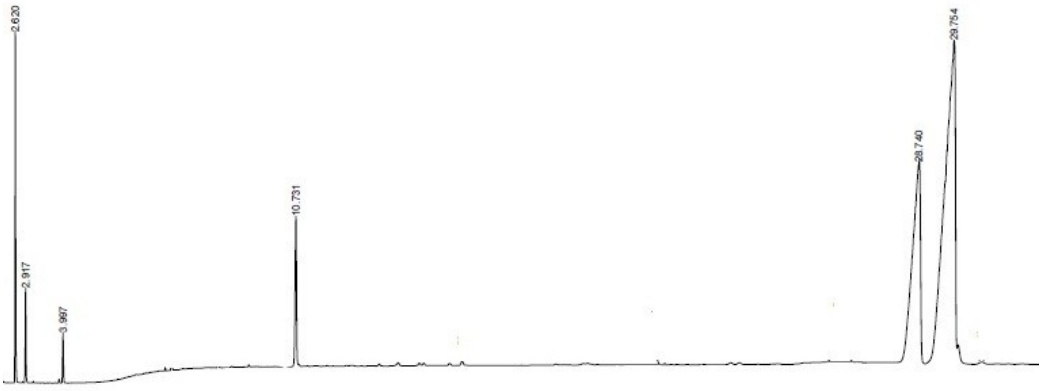
FID detector, HP5 column: 30 m × 0.25 mm × 0.25 µm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 300 °C; oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C, 5 °C min^{-1} to 250 °C (20 min); retention times: ethyl diazoacetate 2.0 min, diethyl maleate 6.1 min, diethyl fumarate 6.2 min, eicosane (internal standard) 15.1 min, methyl oleate 16.7 min, *cis* cyclopropane **3** 24.2 min, *trans* cyclopropane **2** 24.4 min.



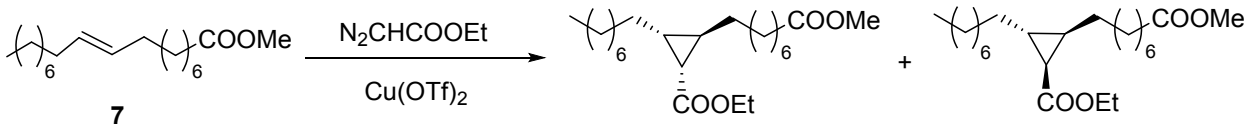
B) Cyclopropanation of methyl erucate (4) and EDA



FID detector, OMEGAWAX™ 250 column: 30 m × 0.25 mm × 0.25 µm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 300 °C; oven program: 200 °C (4 min), 35 °C min^{-1} to 260 °C (30 min); retention times: ethyl diazoacetate 2.0 min, diethyl maleate 2.6 min, diethyl fumarate 2.9 min, eicosane (internal standard) 4.0 min, methyl erucate 10.8 min, *cis* cyclopropane **6** 28.7 min, *trans* cyclopropane **5** 29.7 min.



C) Cyclopropanation of methyl elaidate (7) and EDA



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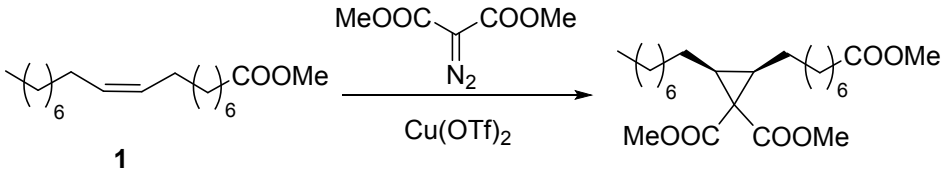
FID detector, OMEGAWAX™ 250 column: 30 m × 0.25 mm × 0.25 µm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 300 °C; oven program: 205 °C (5 min), 20 °C min^{-1} to 250 °C (20 min); retention times: ethyl diazoacetate 2.0 min, diethyl maleate 2.6 min, diethyl fumarate 2.8 min, eicosane (internal standard) 3.7 min, methyl elaidate 7.9 min, cyclopropane **8** 17.9 min, cyclopropane **9** 18.1 min.

D) Cyclopropanation of methyl oleate (1) with DDM



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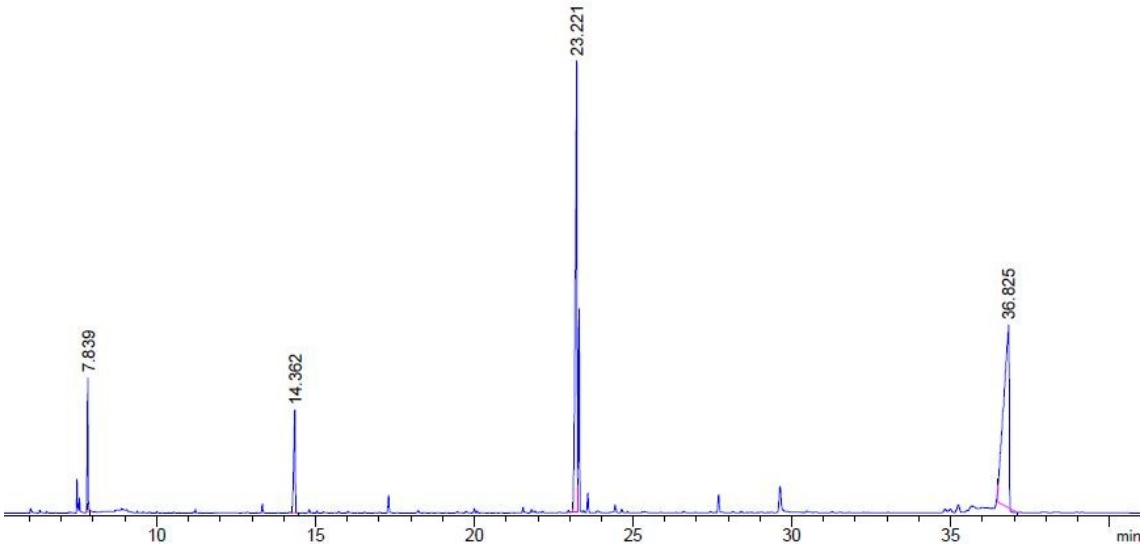
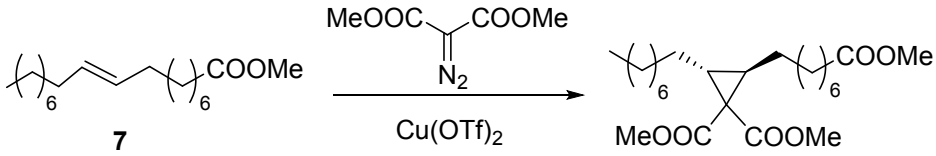
FID detector, Zebron ZB-5HT Inferno column: 30 m × 0.25 mm × 0.25 µm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 250 °C; oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C, 5 °C min^{-1} to 250 °C (20 min); retention times: dimethyl 2-diazomalonate 7.8 min, methyl oleate 23.2 min, cyclopropane **10** 36.8 min.

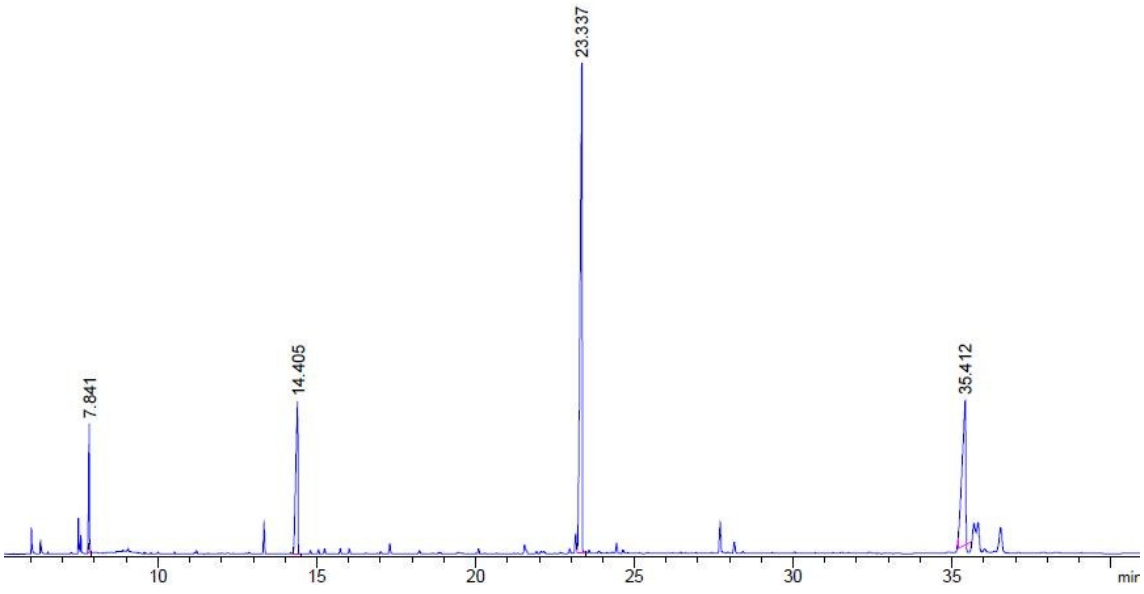


E) Cyclopropanation of methyl elaidate (7) with DDM

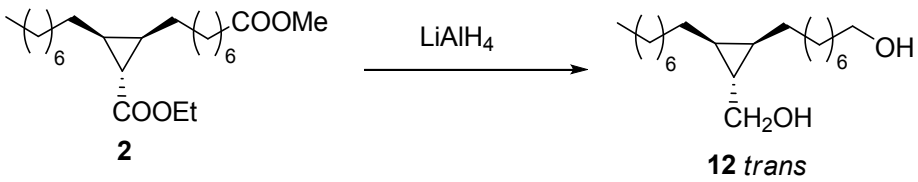


7 **11**

FID detector, Zebron ZB-5HT Inferno column: 30 m × 0.25 mm × 0.25 µm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 250 °C; oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C, 5 °C min^{-1} to 250 °C (20 min); retention times: dimethyl 2-diazomalonate 7.8 min, methyl elaidate 23.4 min, cyclopropane **11** 35.4 min.

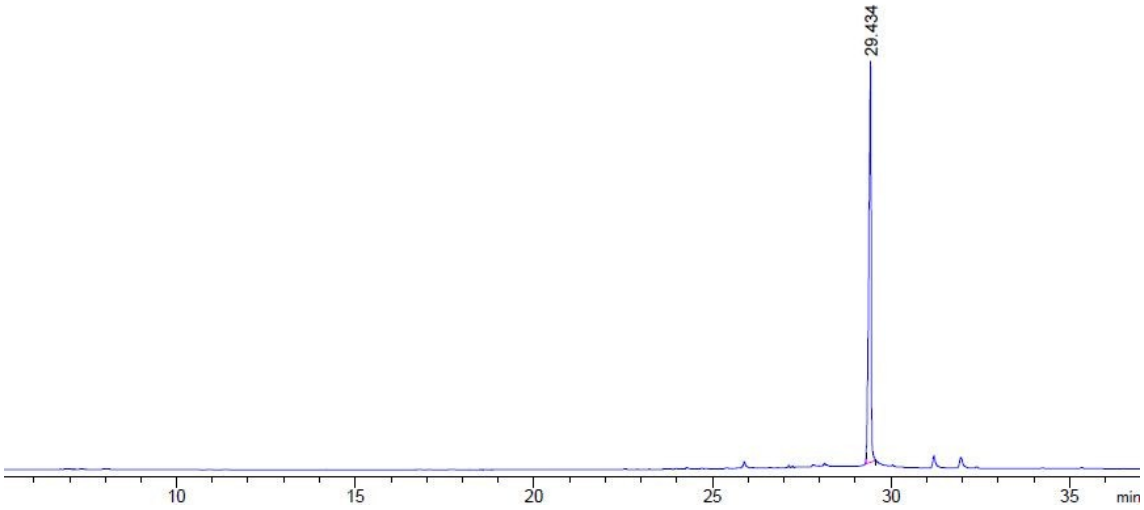


F) Reduction of the *trans* cyclopropane (2) to product 12

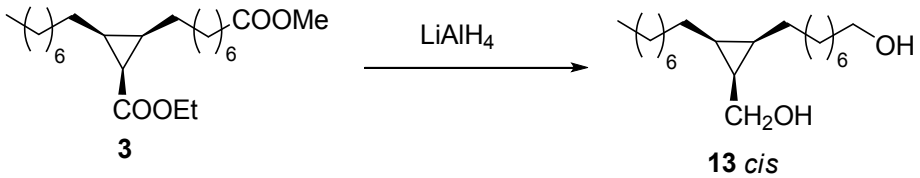


2 **12** *trans*

FID detector, Zebron ZB-5HT Inferno column: 30 m × 0.25 mm × 0.25 µm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 250 °C; oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C, 5 °C min^{-1} to 250 °C (20 min); retention times: *trans* cyclopropane **2** 32.5 min, diol **12** 29.4 min.

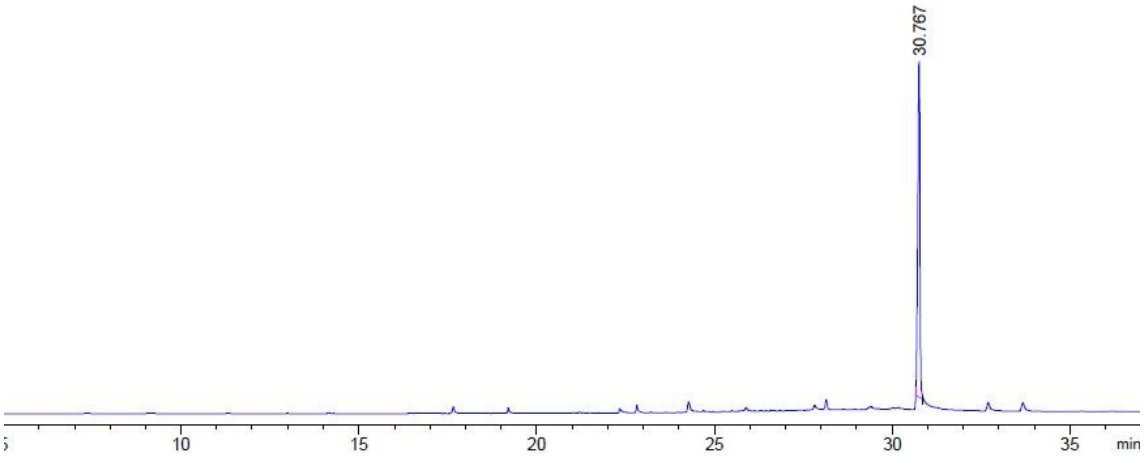


G) Reduction of the *cis* cyclopropane (3) to product 13

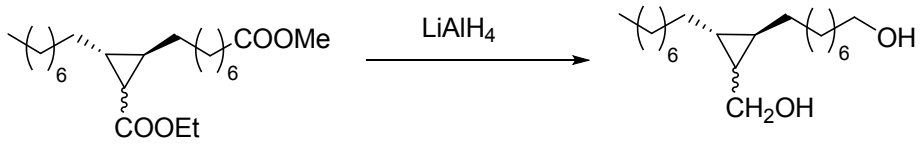


3 **13** *cis*

FID detector, Zebron ZB-5HT Inferno column: 30 m × 0.25 mm × 0.25 µm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 250 °C; oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C, 5 °C min^{-1} to 250 °C (20 min); retention times: *cis* cyclopropane **3** 32.3 min, diol **13** 30.7 min.



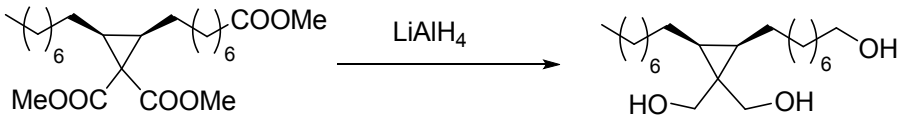
H) Reduction of the cyclopropanes (8+9) to products 14 and 15



8 + **9** **14** + **15**

FID detector, Zebron ZB-5HT Inferno column: 30 m × 0.25 mm × 0.25 µm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 250 °C; oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C, 5 °C min^{-1} to 250 °C (20 min); retention times: cyclopropanes **8+9** 32.4 min, diols **14+15** 29.4 min.

I) Reduction of the cyclopropane 10 to the triol 16



10 **16**

FID detector, Zebron ZB-5HT Inferno column: 30 m × 0.25 mm × 0.25 μm; helium as carrier gas; injector temperature: 280 °C; detector temperature: 250 °C; oven program: 70 °C (4 min), 25 °C min^{-1} to 150 °C, 5 °C min^{-1} to 250 °C (20 min); retention times: cyclopropane **10** 36.8 min, triol **16** 20.6 min.