

Supporting Information

Convergent Synthesis of Degradable Dendrons based on L-Malic acid

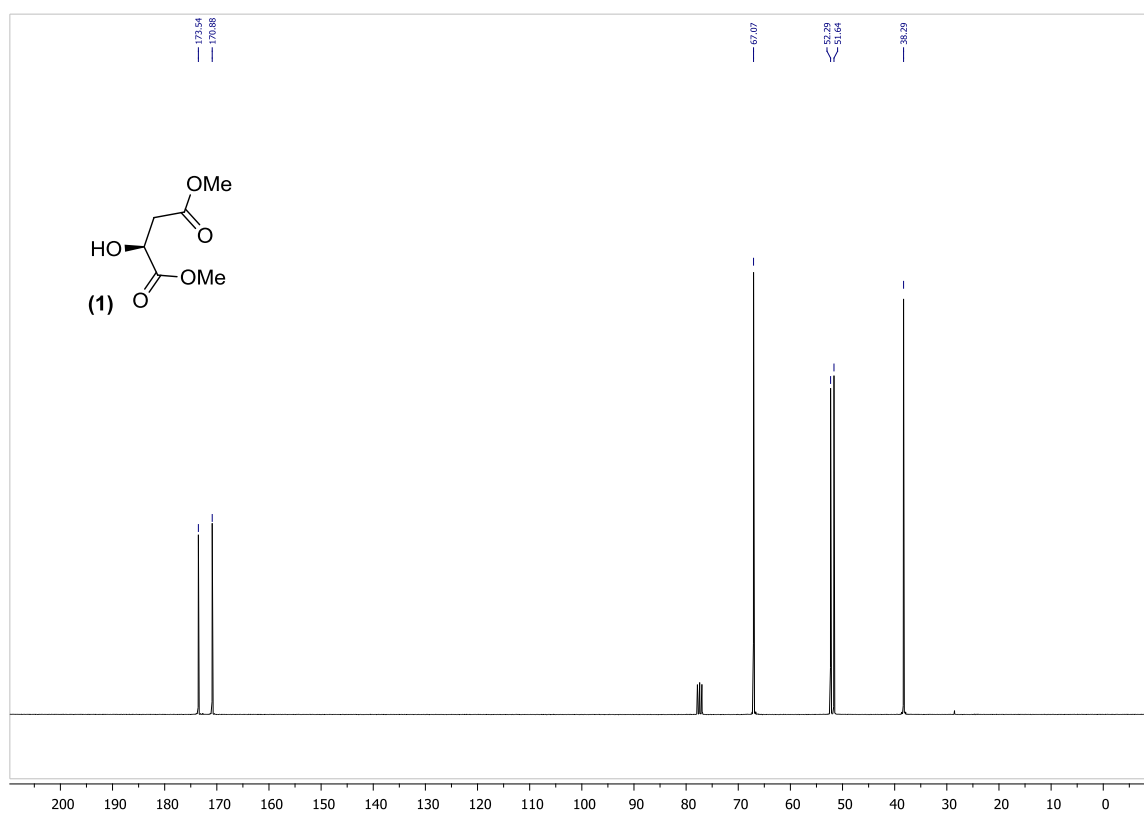
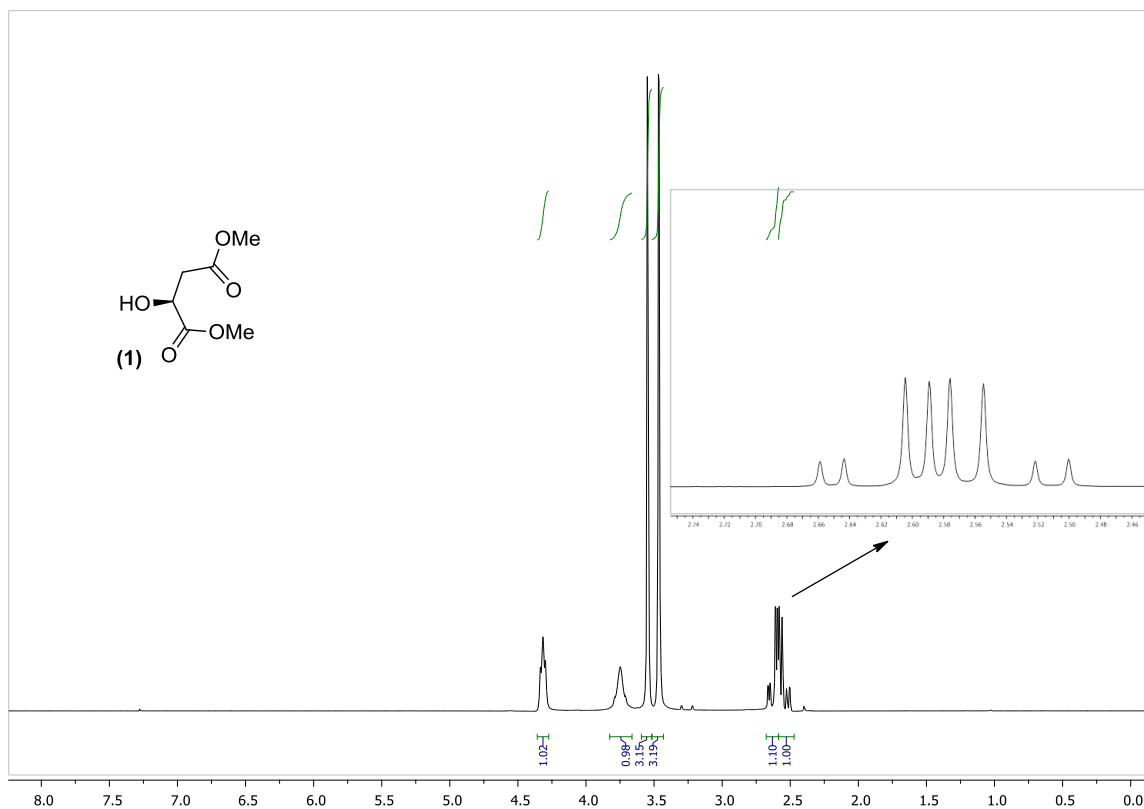
Ulrich Meyhoff,[†] Ulla Riber[‡] and Ulrik Boas^{‡,*}

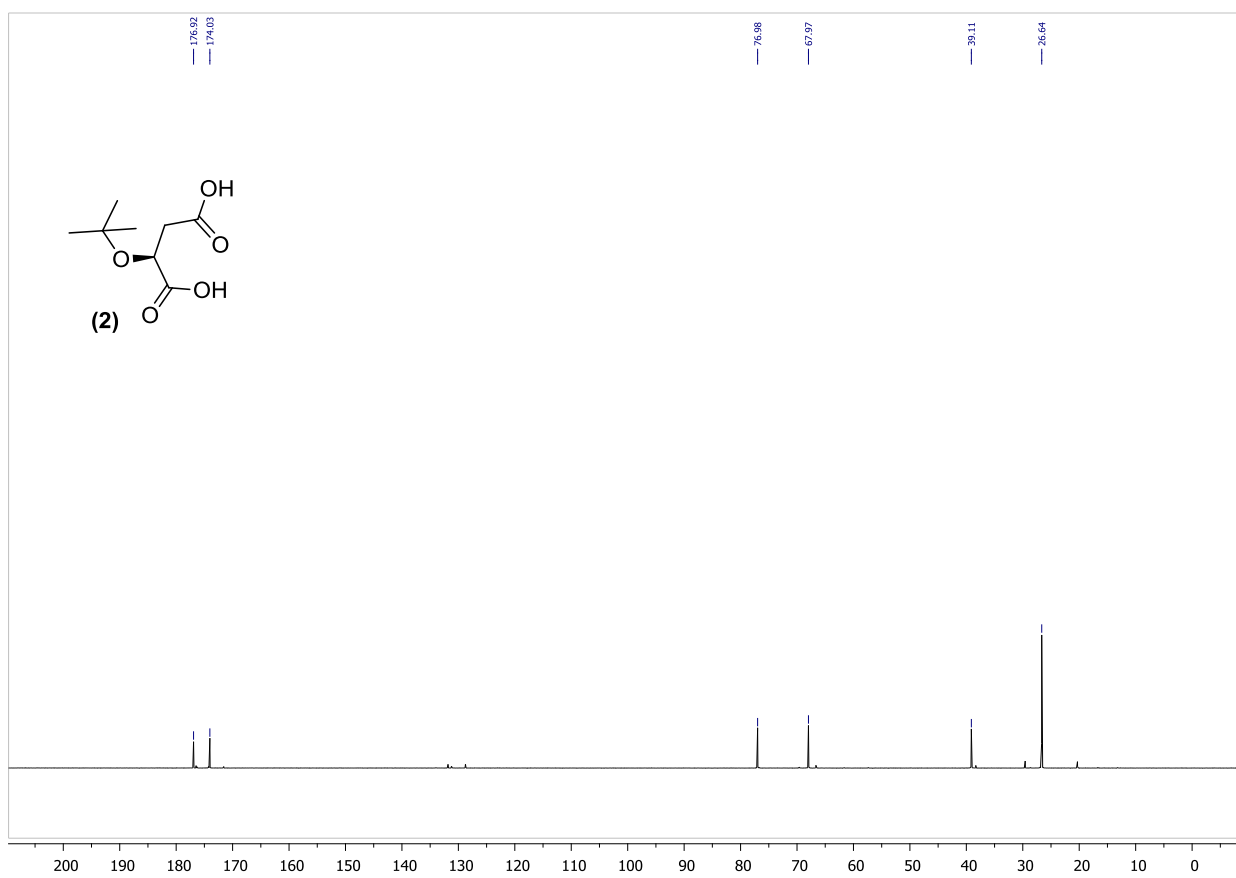
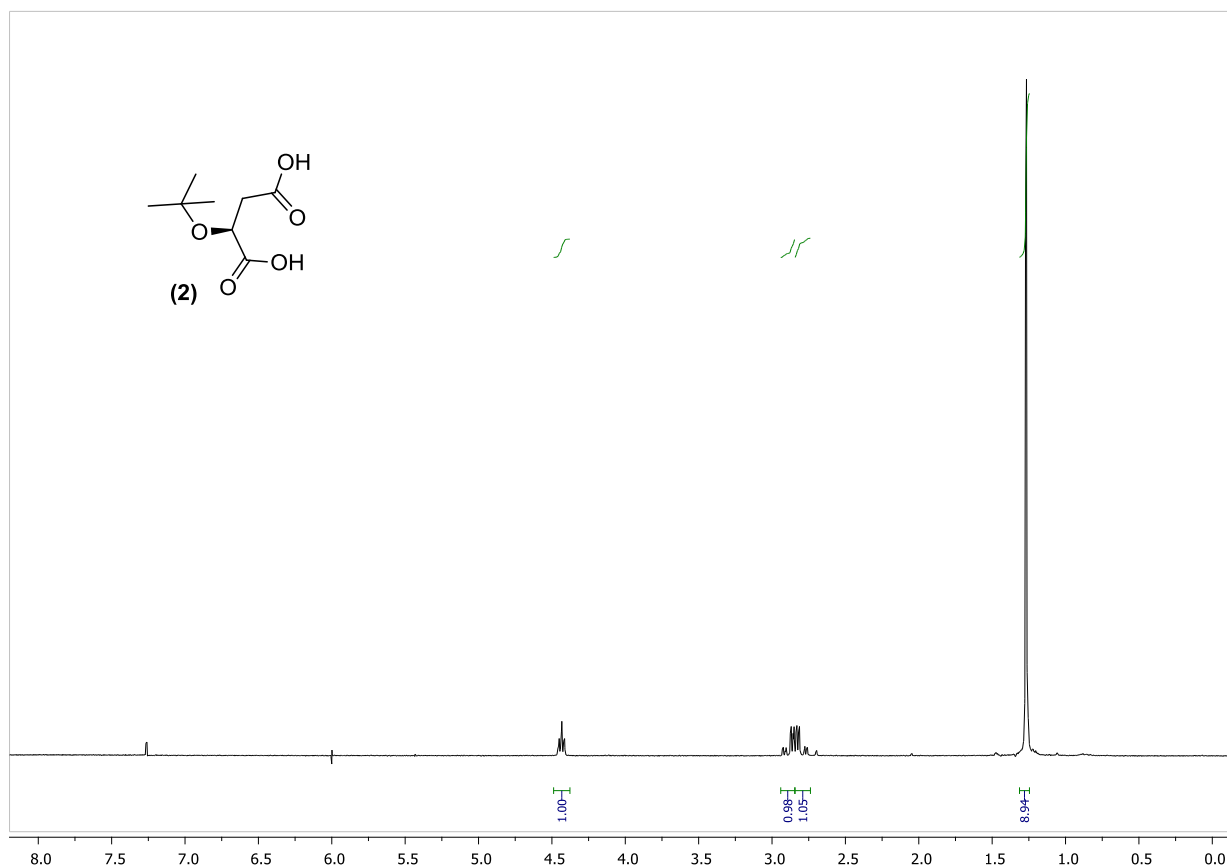
[†]*Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark*

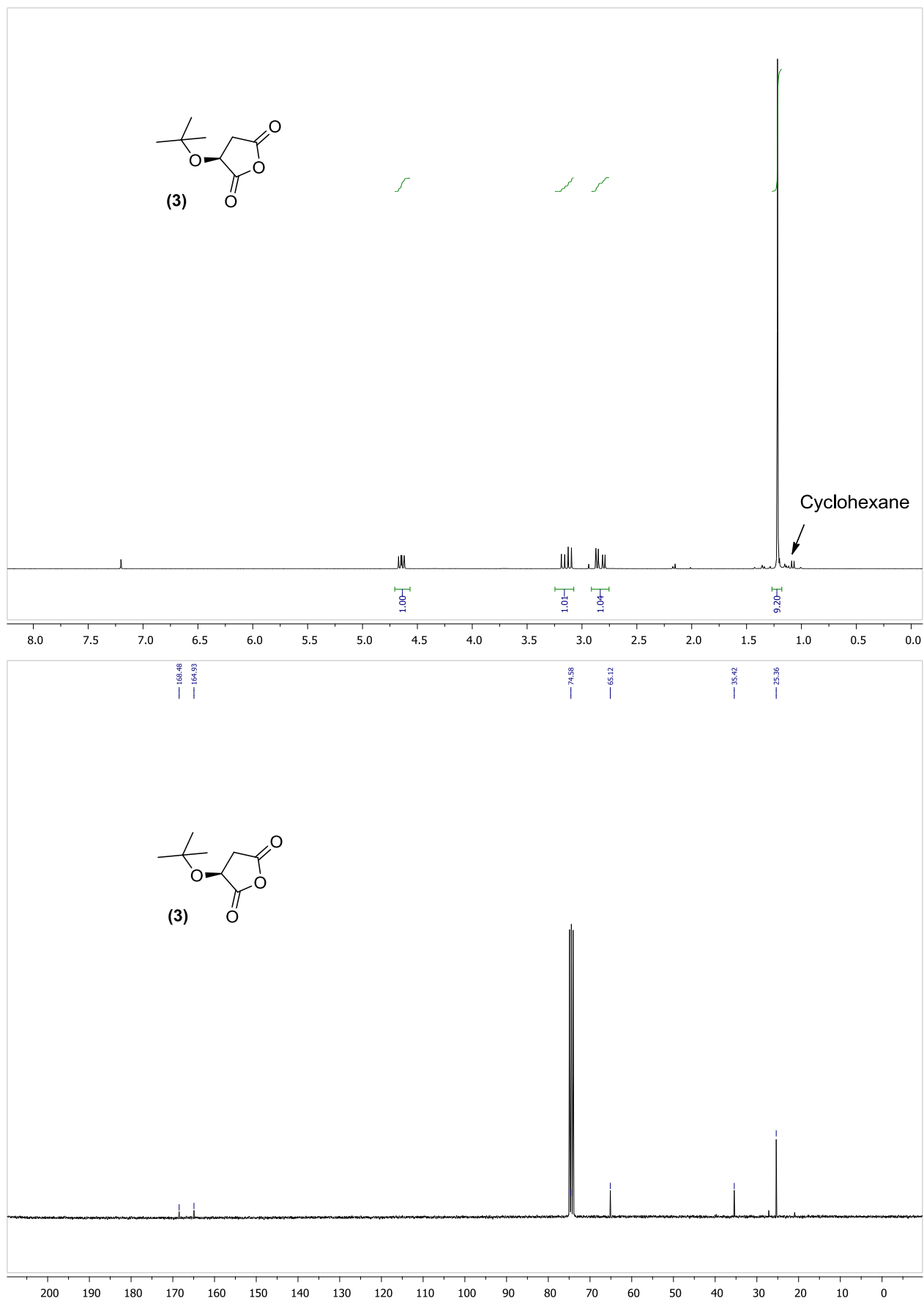
[‡]*Section of Immunology and Vaccinology, National Veterinary Institute, Technical University of Denmark (DTU), Bülowsvej 27, DK 1870 Frederiksberg C.*

* *uboa@vet.dtu.dk*

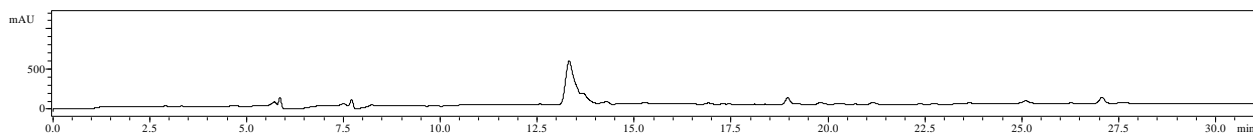
NMR and MS spectra and HPLC chromatograms on selected compounds





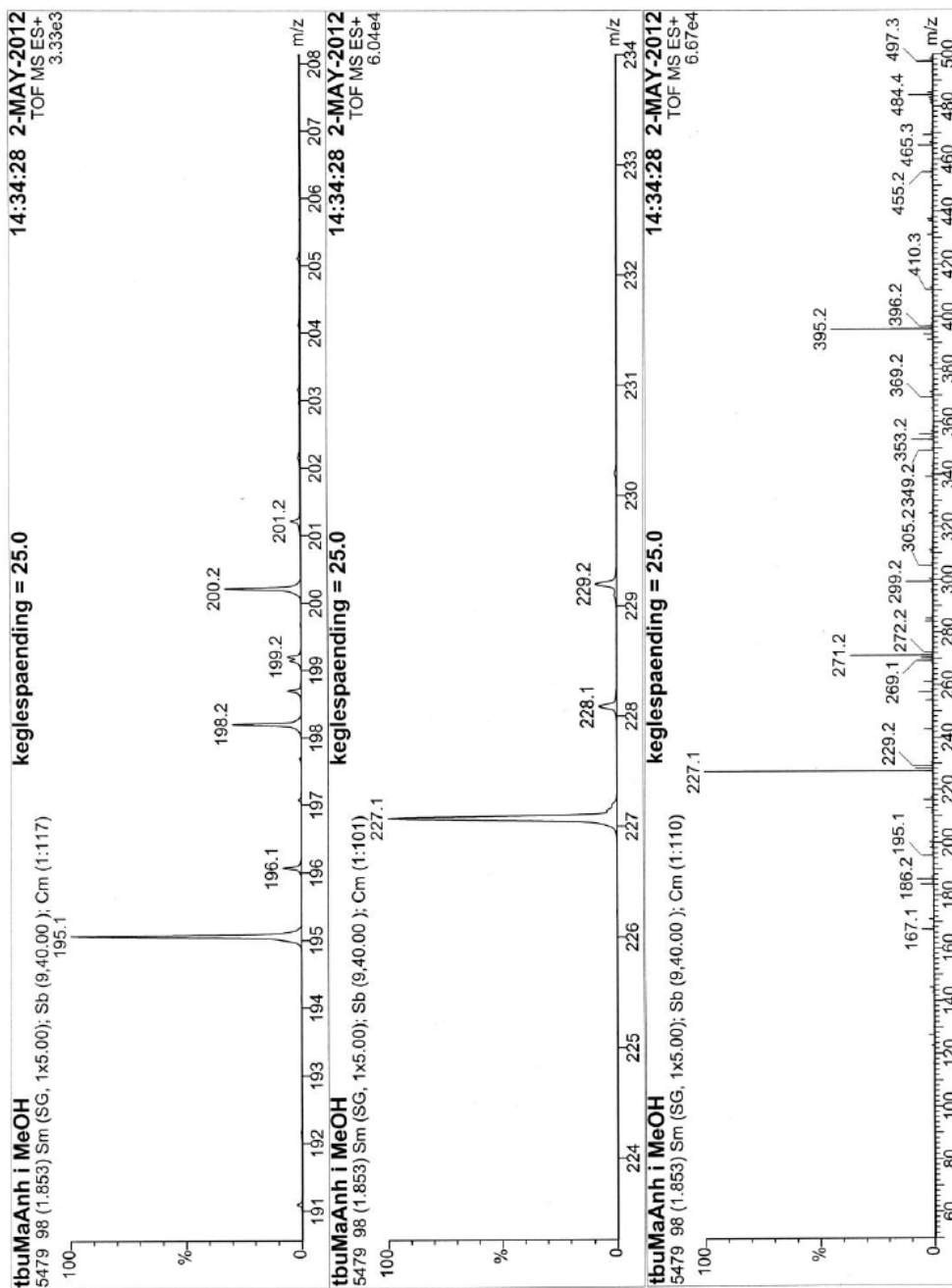


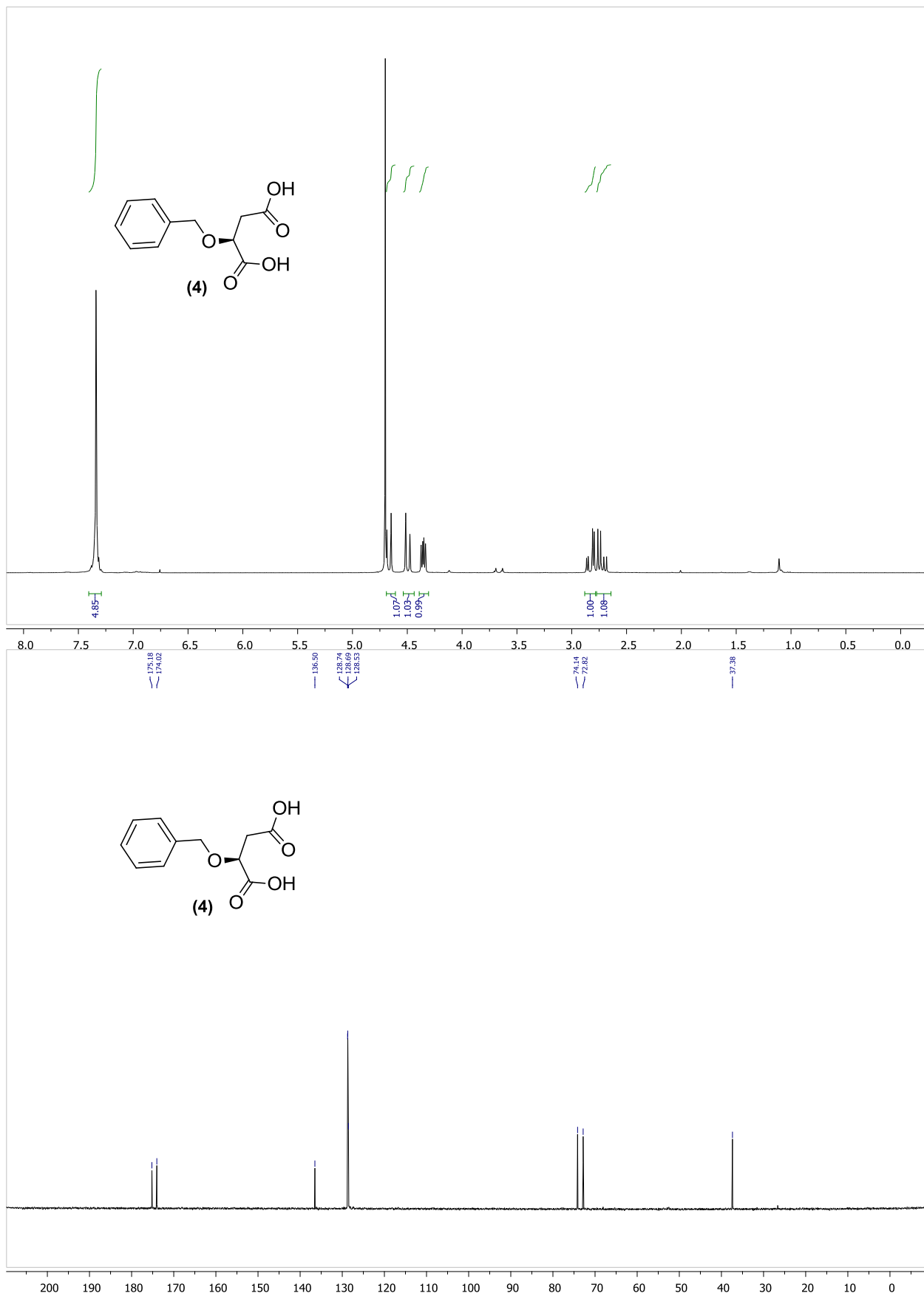
HPLC (reversed phase) of (3) hydrolyzed to the corresponding acid and MS (TOF ESI+) of (3)

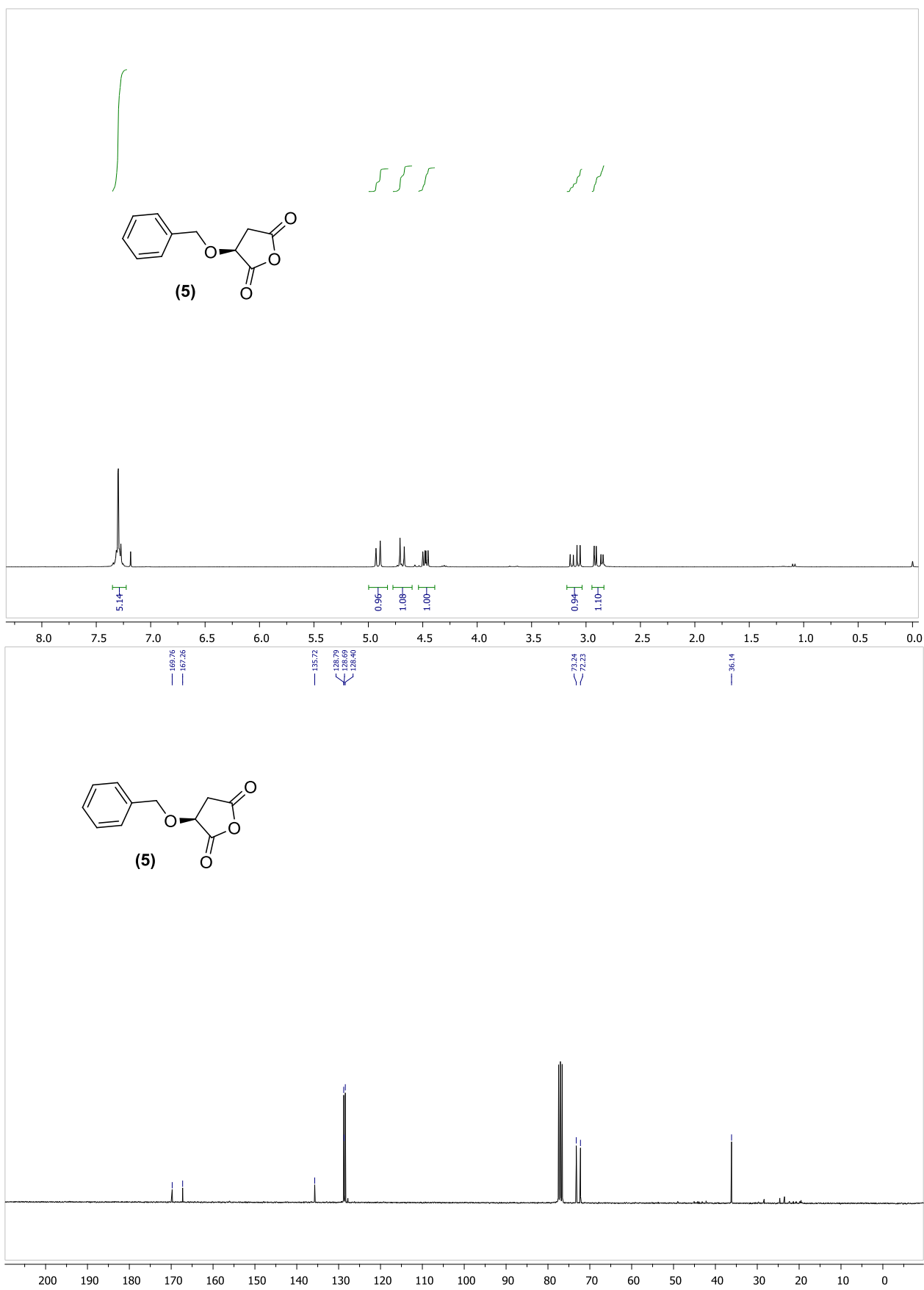


MS (TOF ESI+)

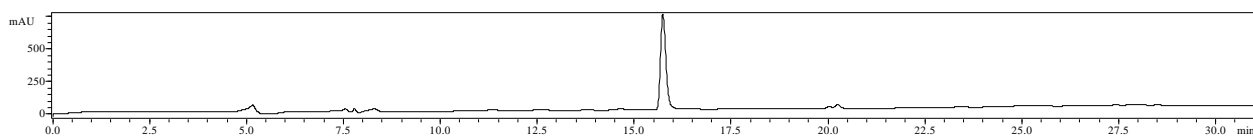
Opløst i MeOH. MS (TOF ESI+) m/z 195 $[M+Na]^+$, 227 $[M+MeOH+Na]^+$.





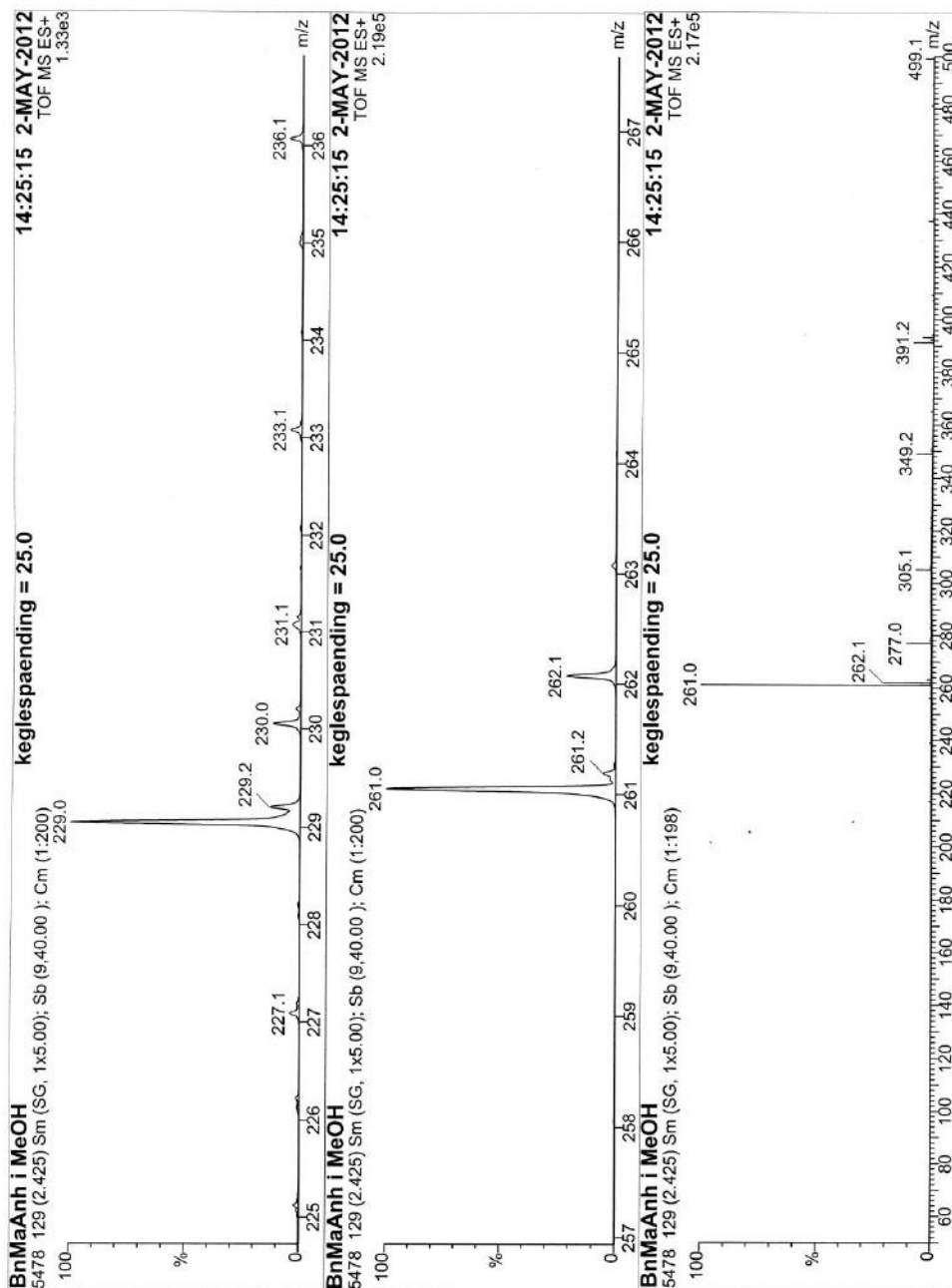


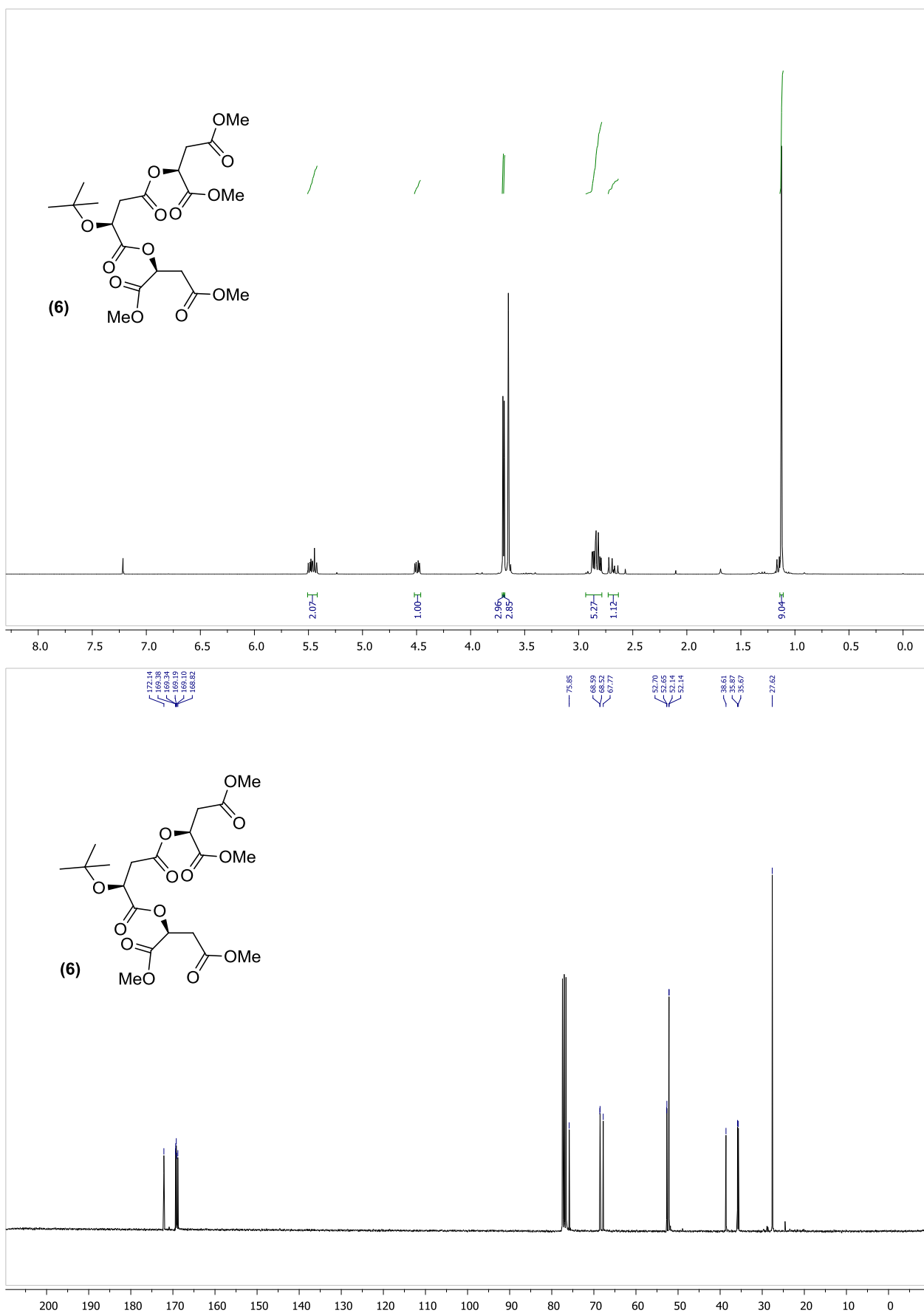
HPLC (reversed-phase) of (5) hydrolyzed to the corresponding acid and MS (TOF ESI+) of (5)

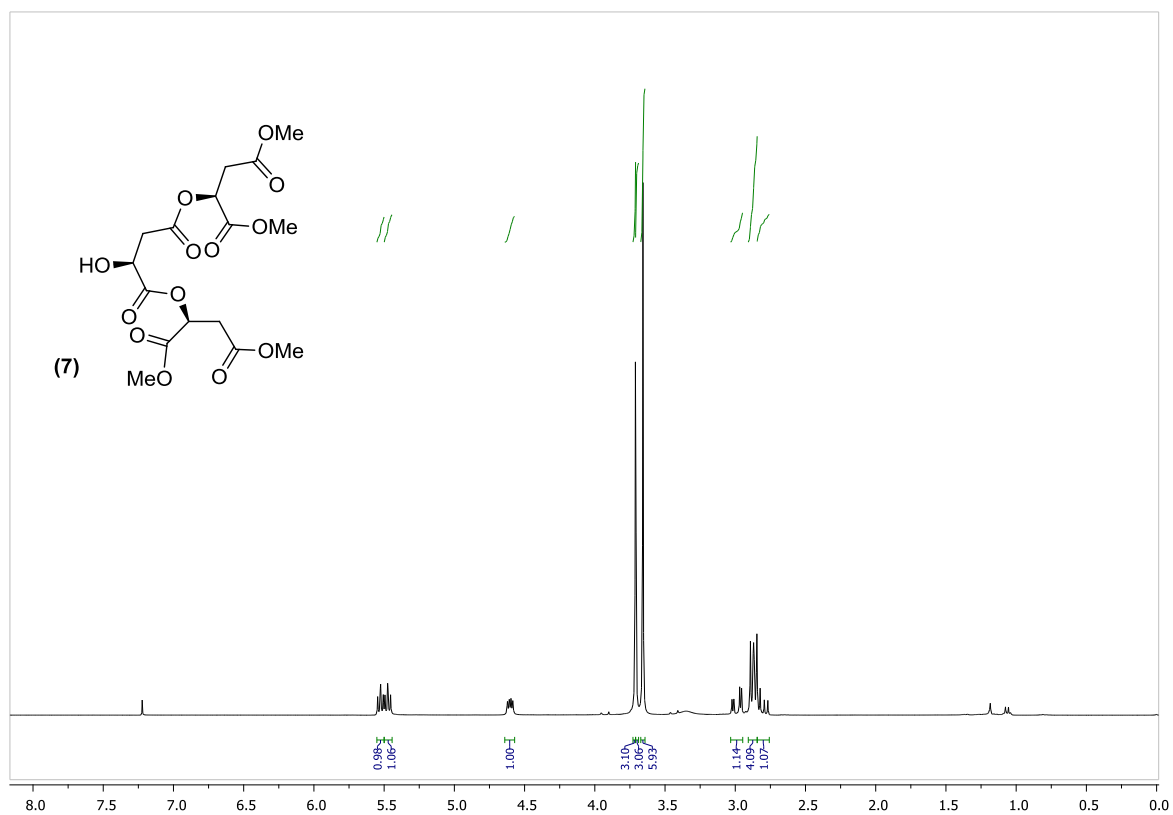
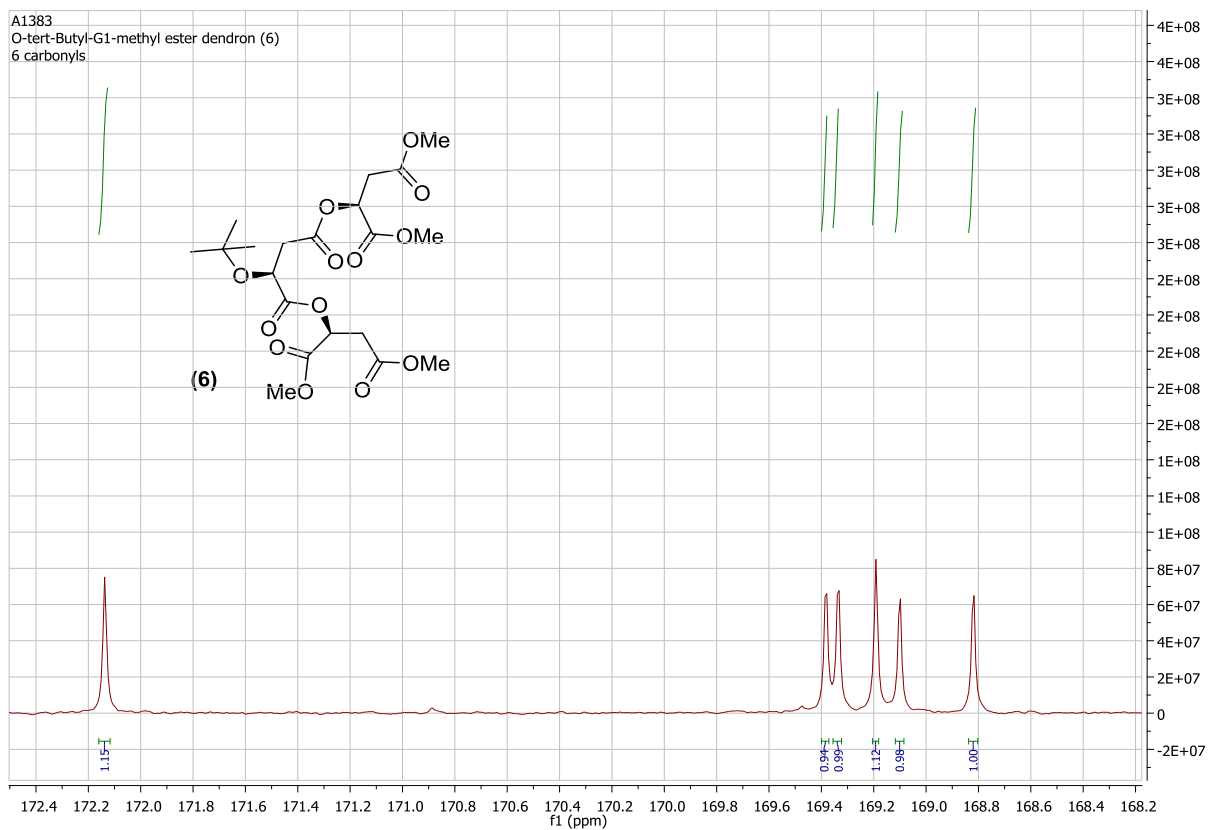


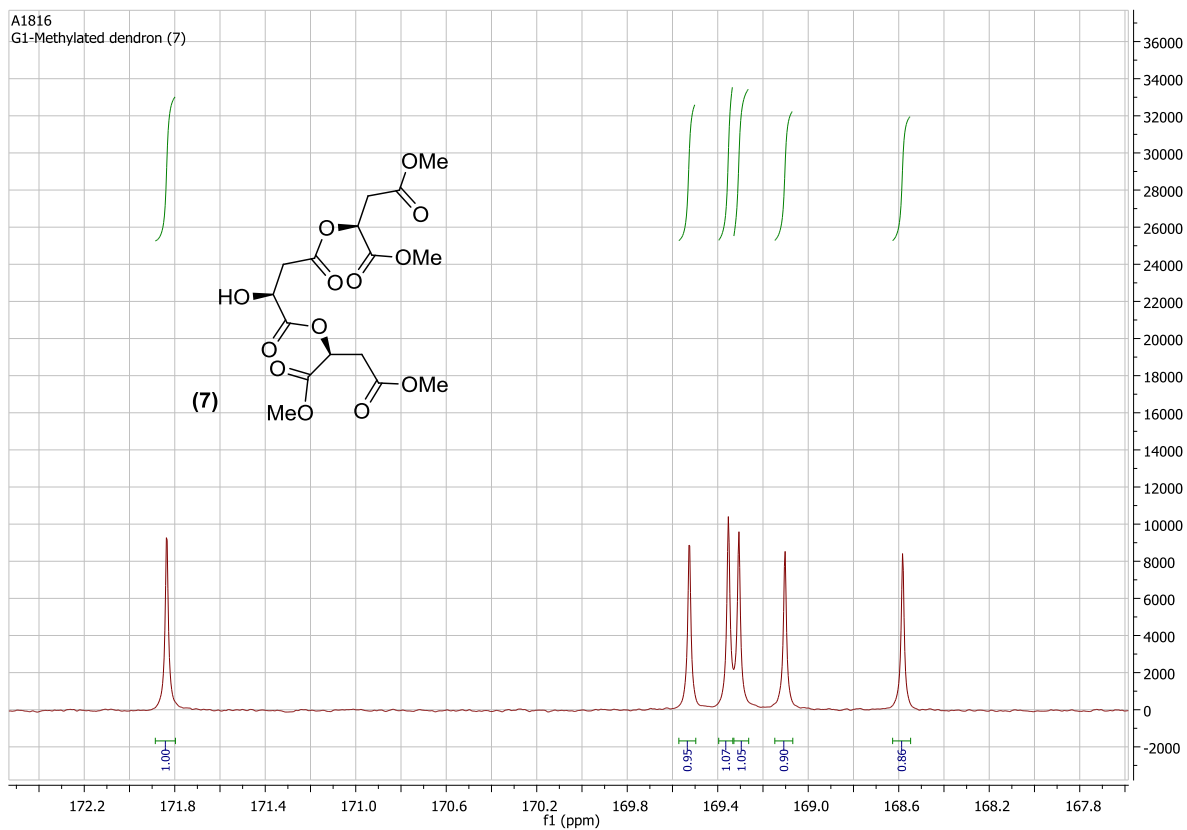
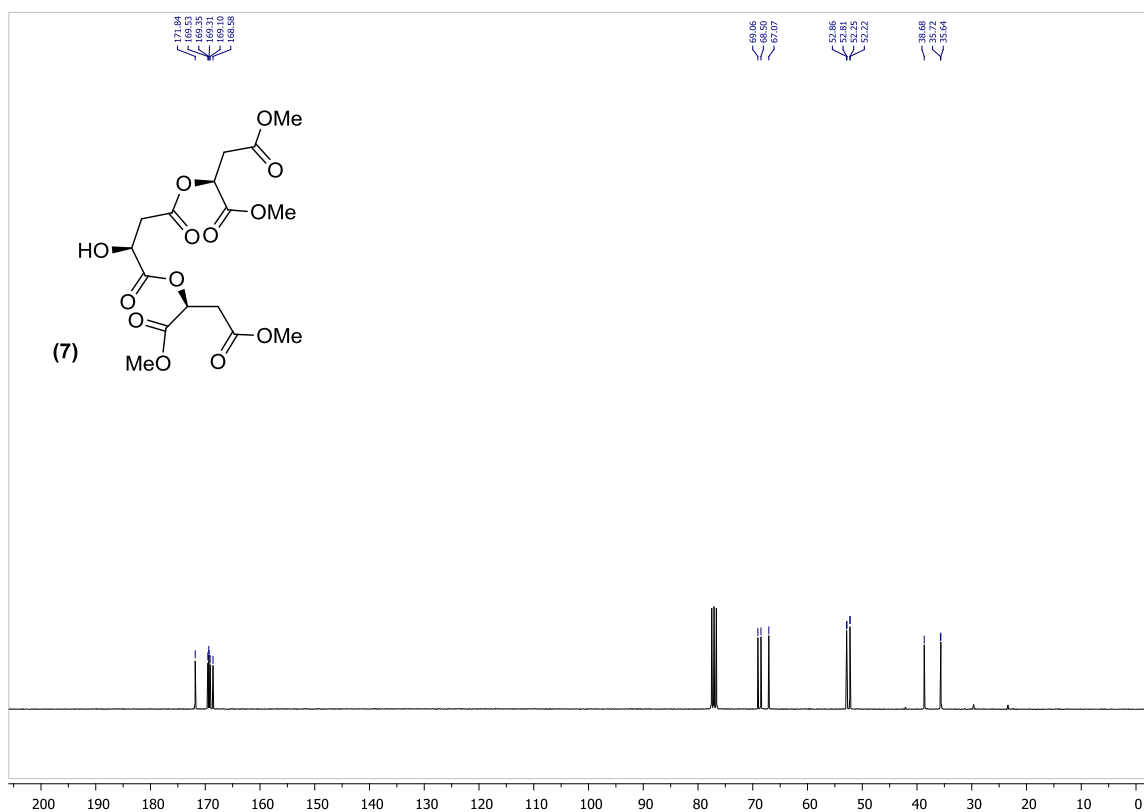
MS (TOF ESI+)

Opløst i MeOH. (TOF ESI⁺) m/z 229 [M+Na]⁺, 261 [M+MeOH+Na]⁺.

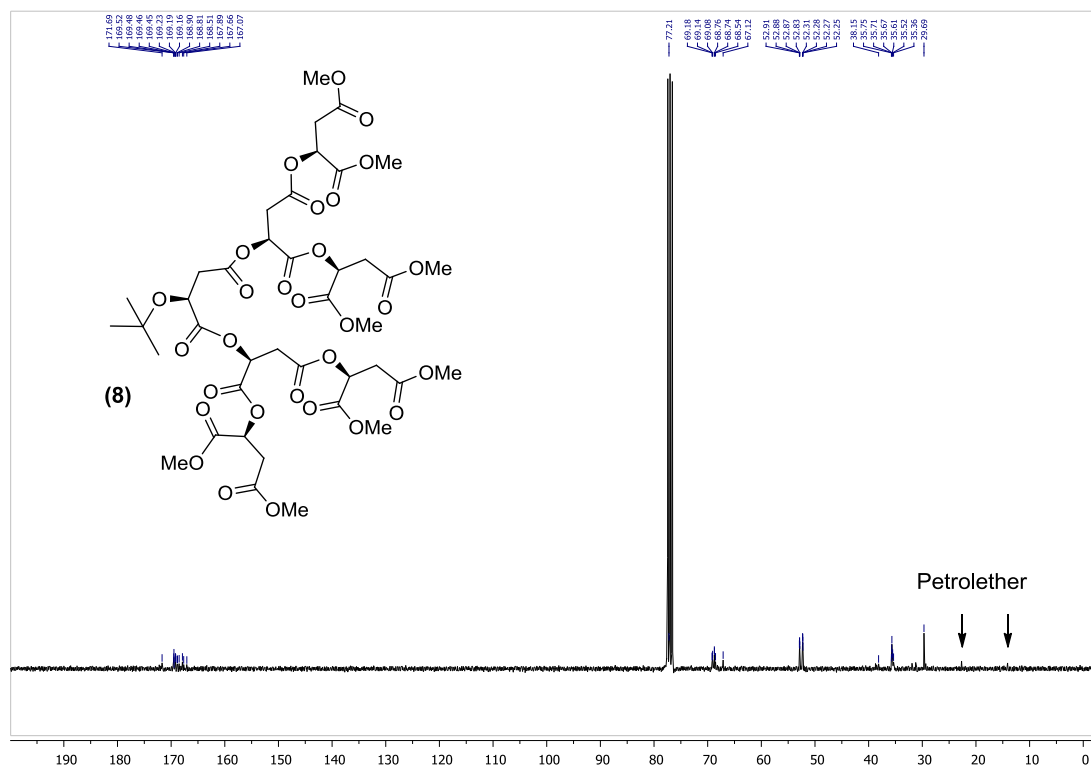
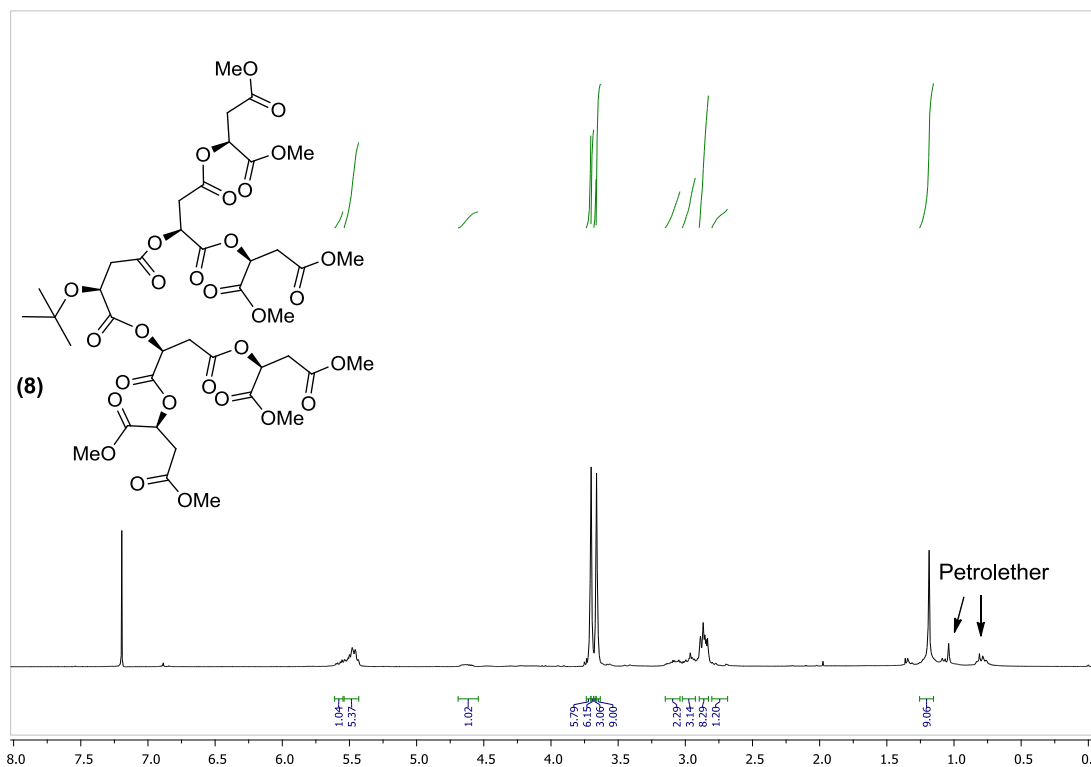
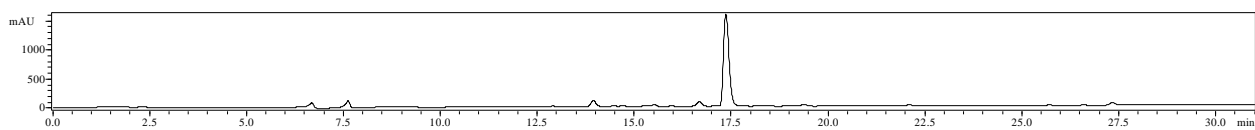


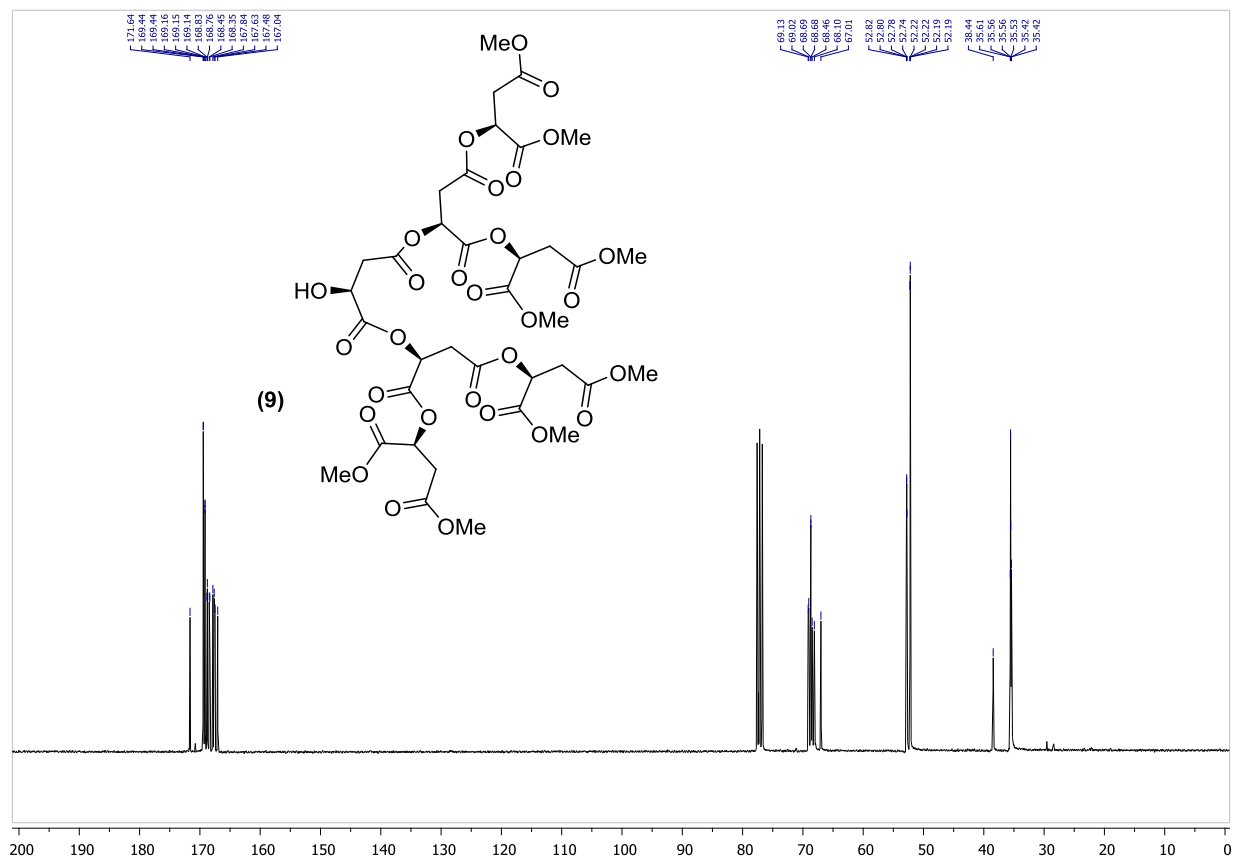
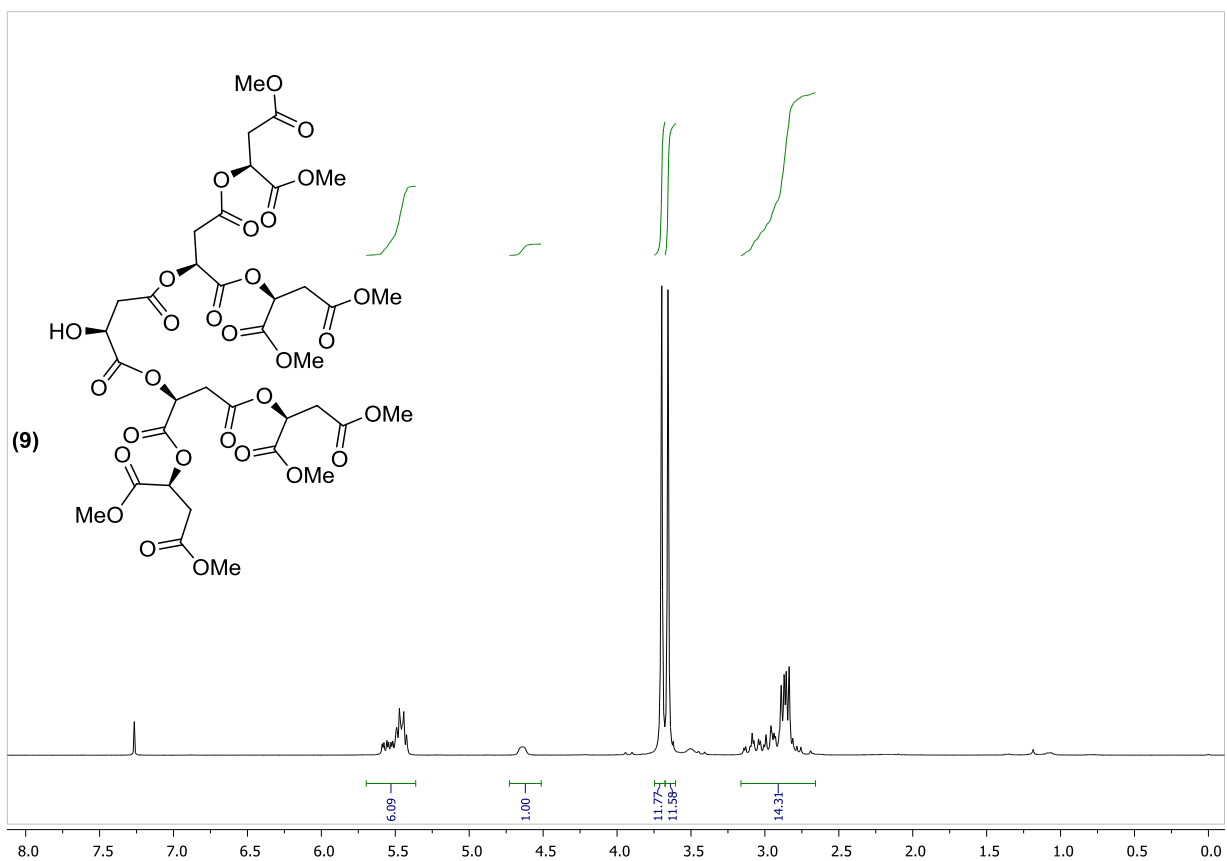


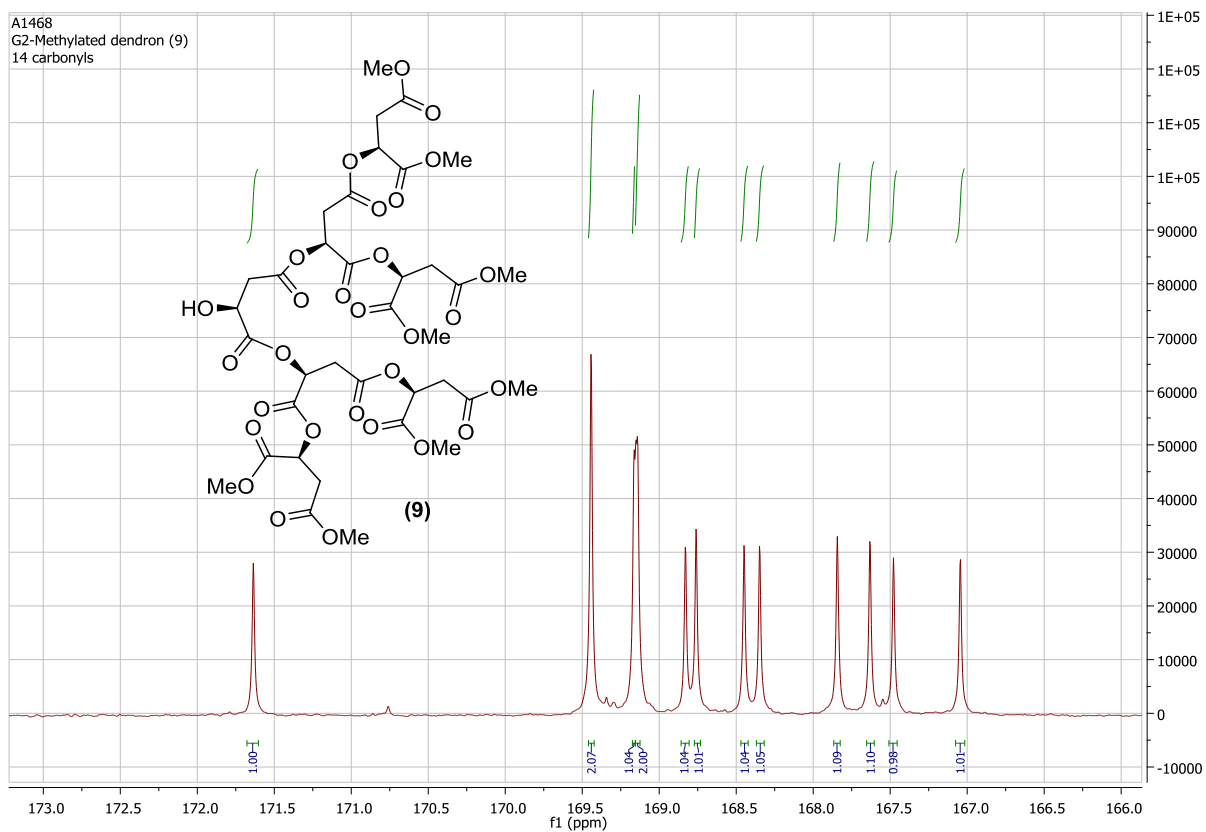




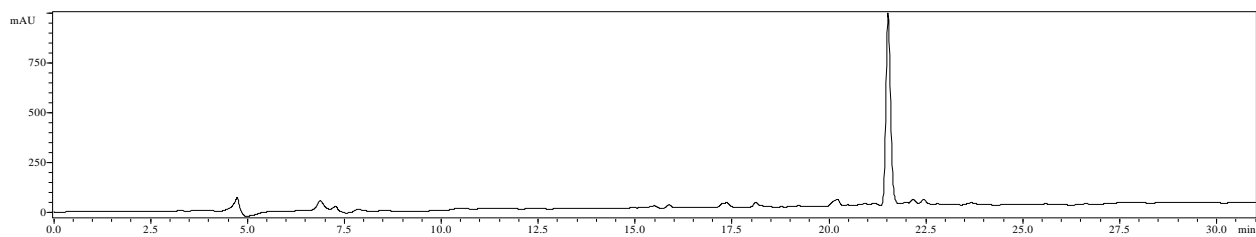
HPLC (reversed-phase) of (7)







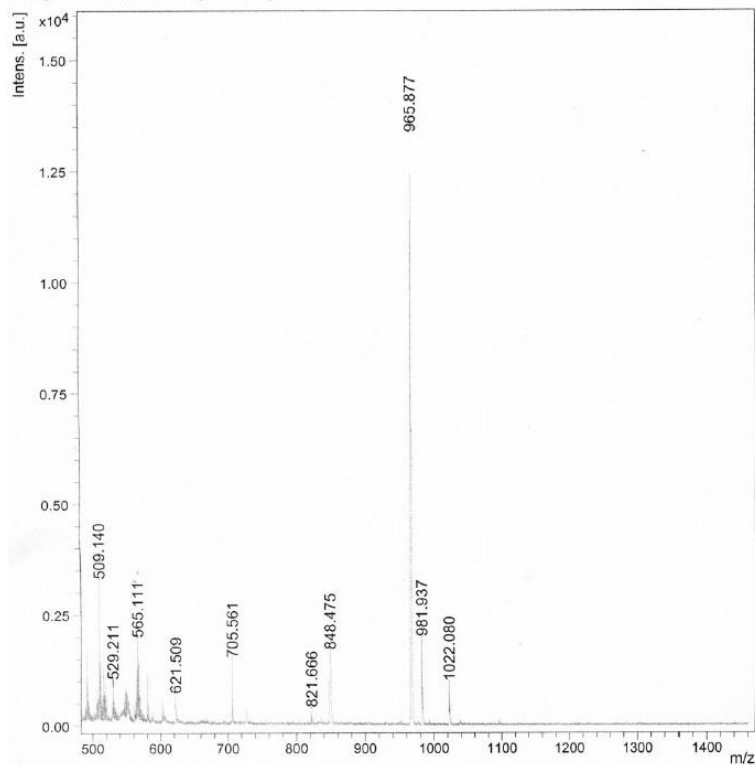
HPLC (reversed-phase) and MS (MALDI-TOF) of (9)



MS (MALDI-TOF) m/z 965 $[M+Na]^+$

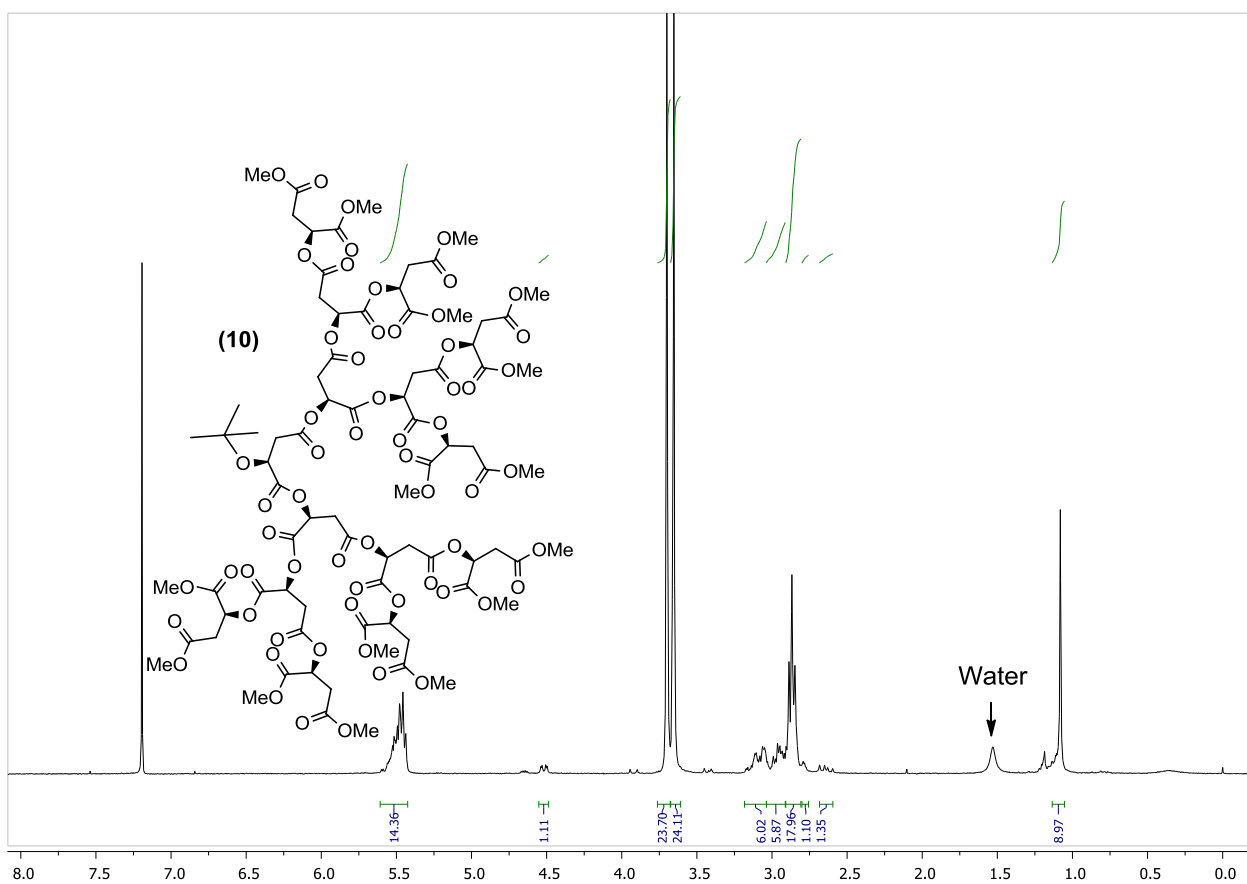
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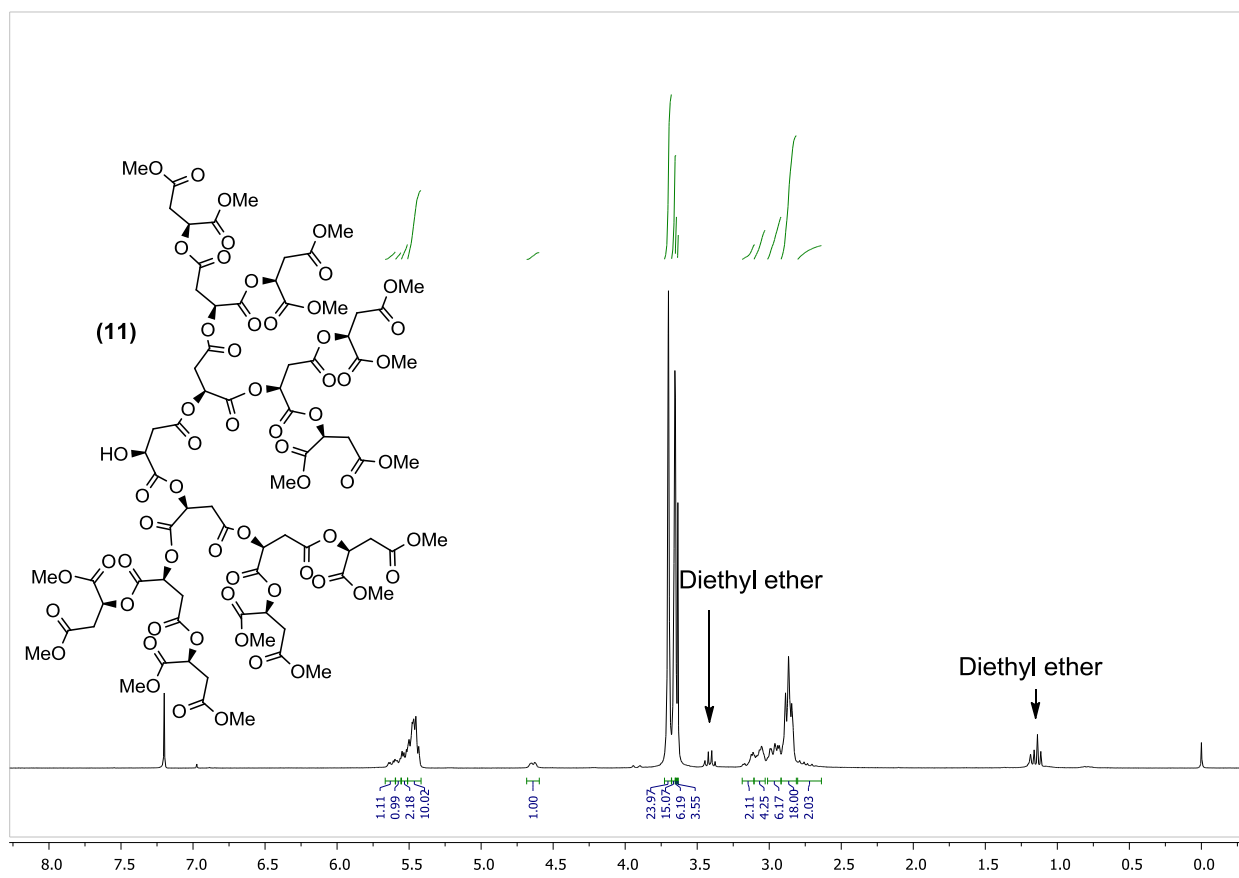
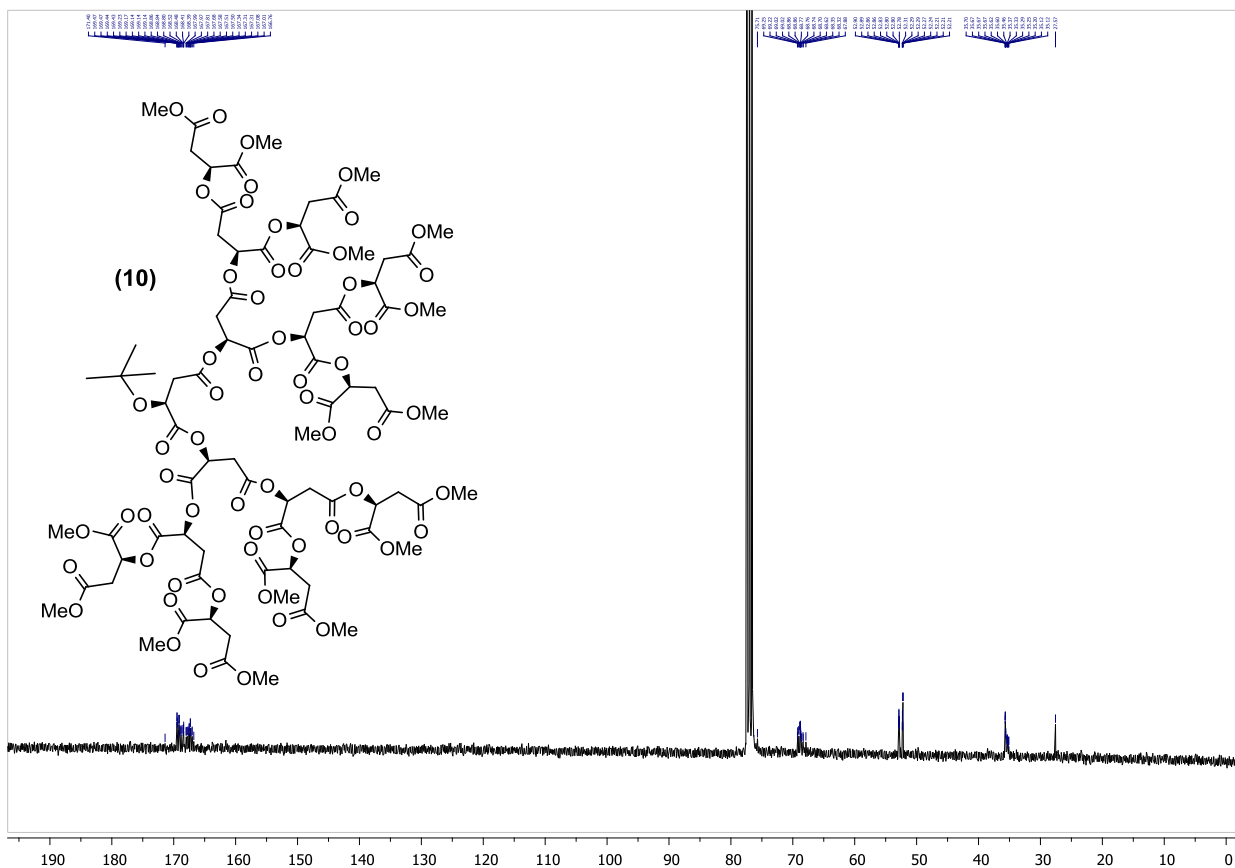
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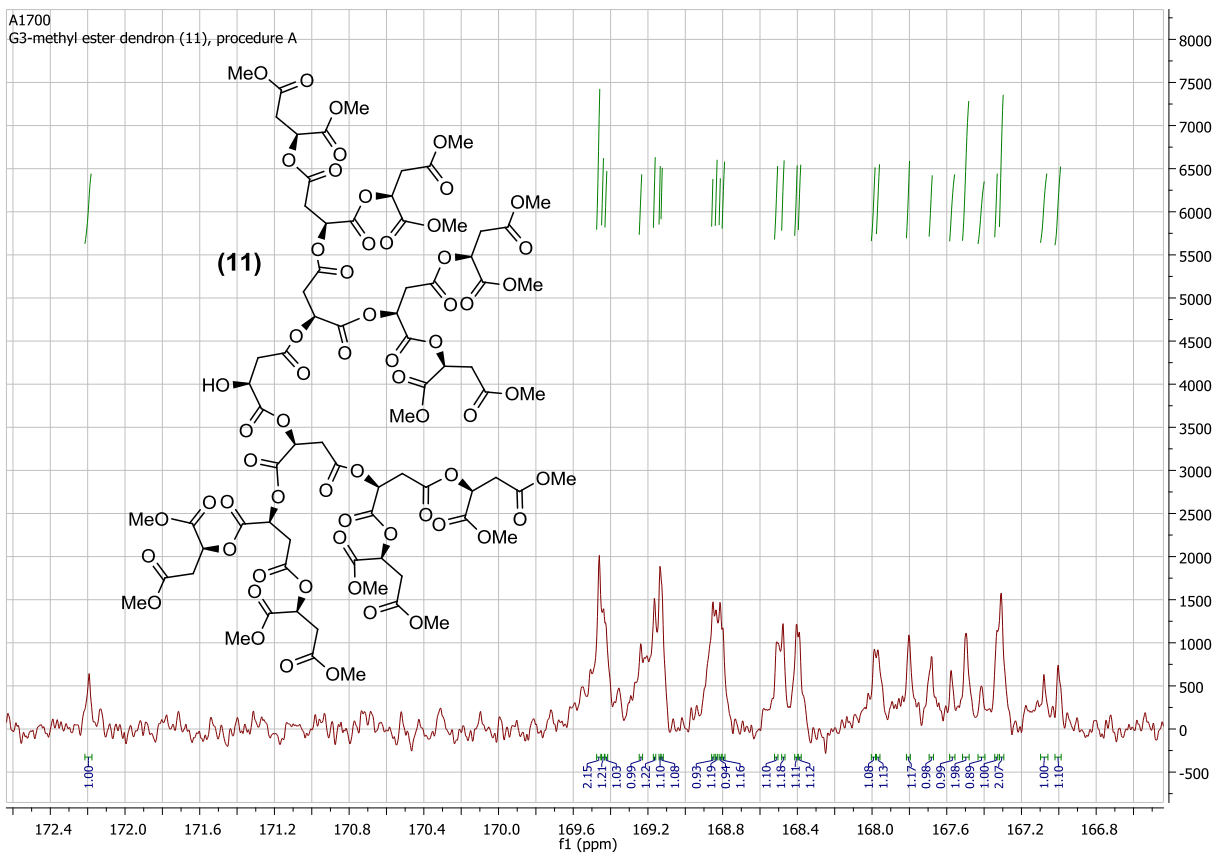
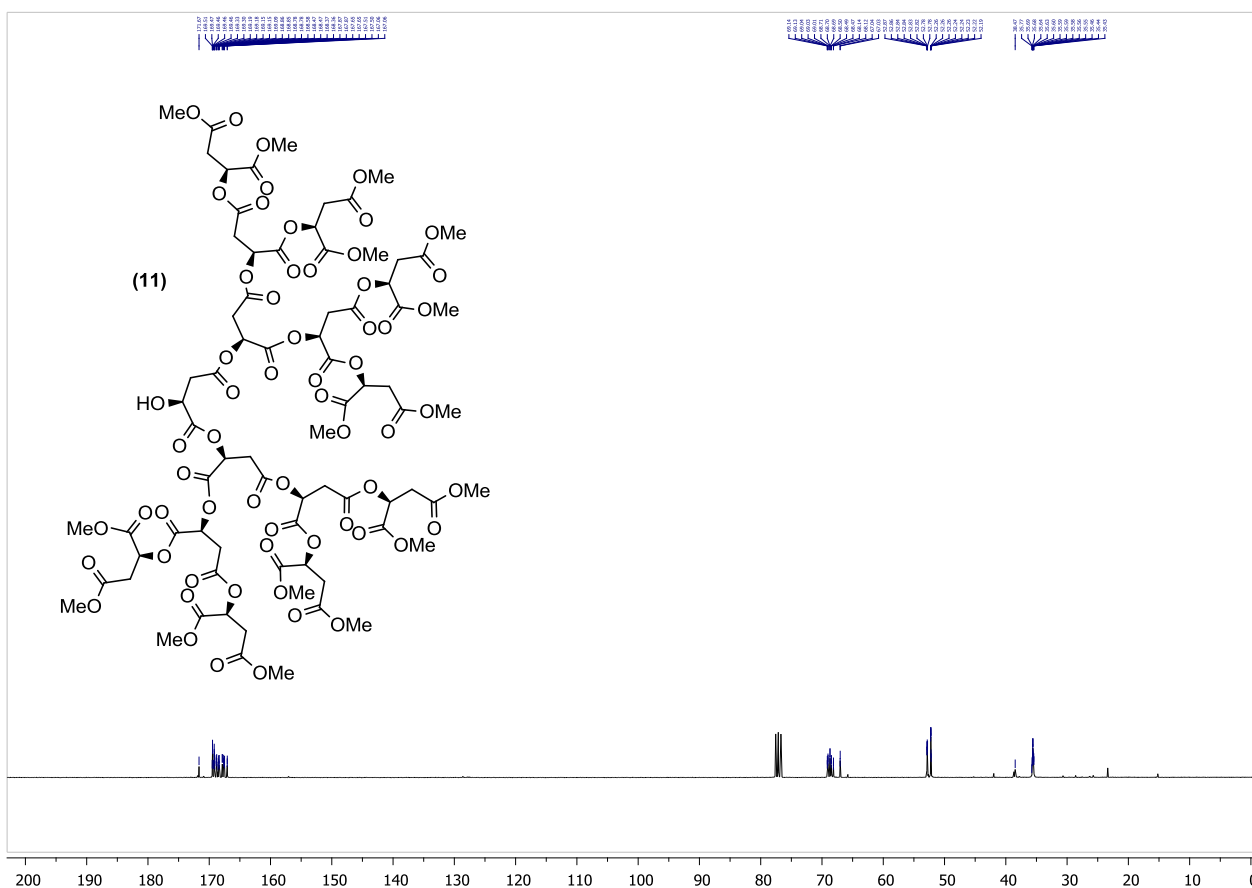


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Number of shots 100

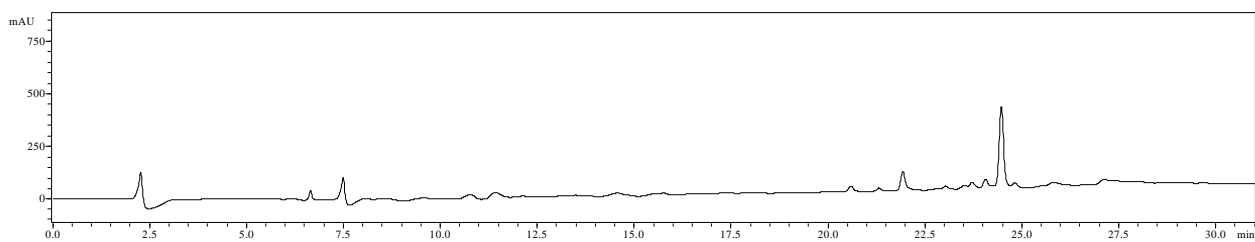
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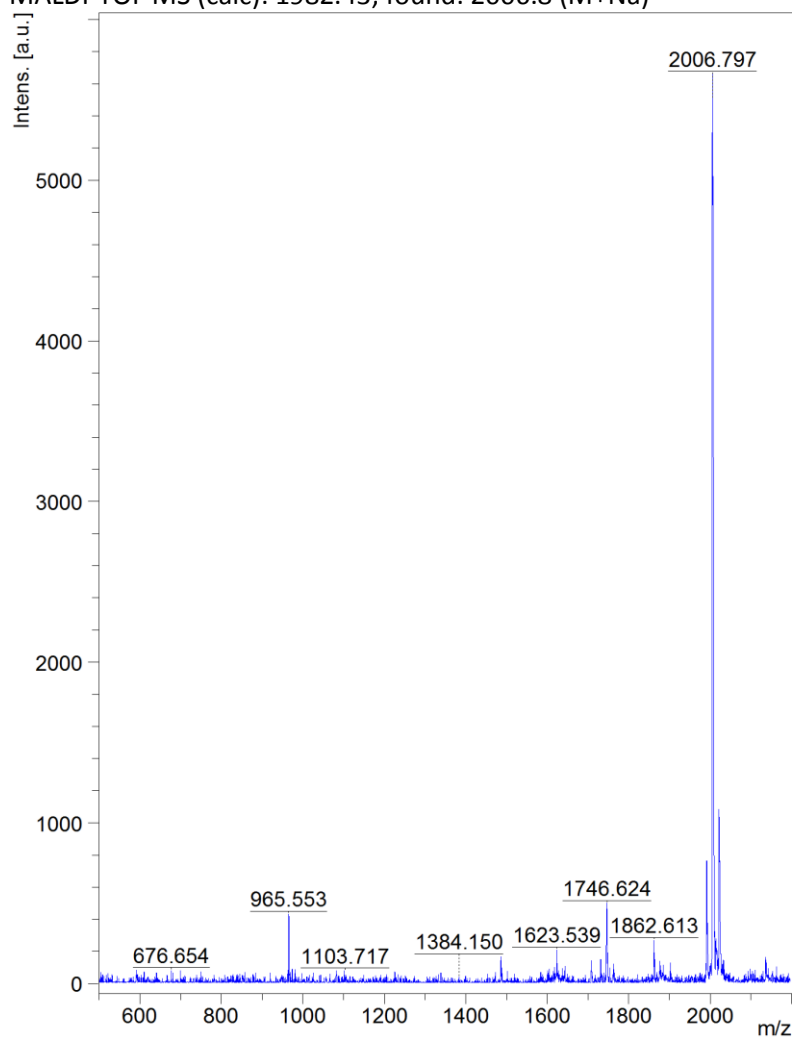


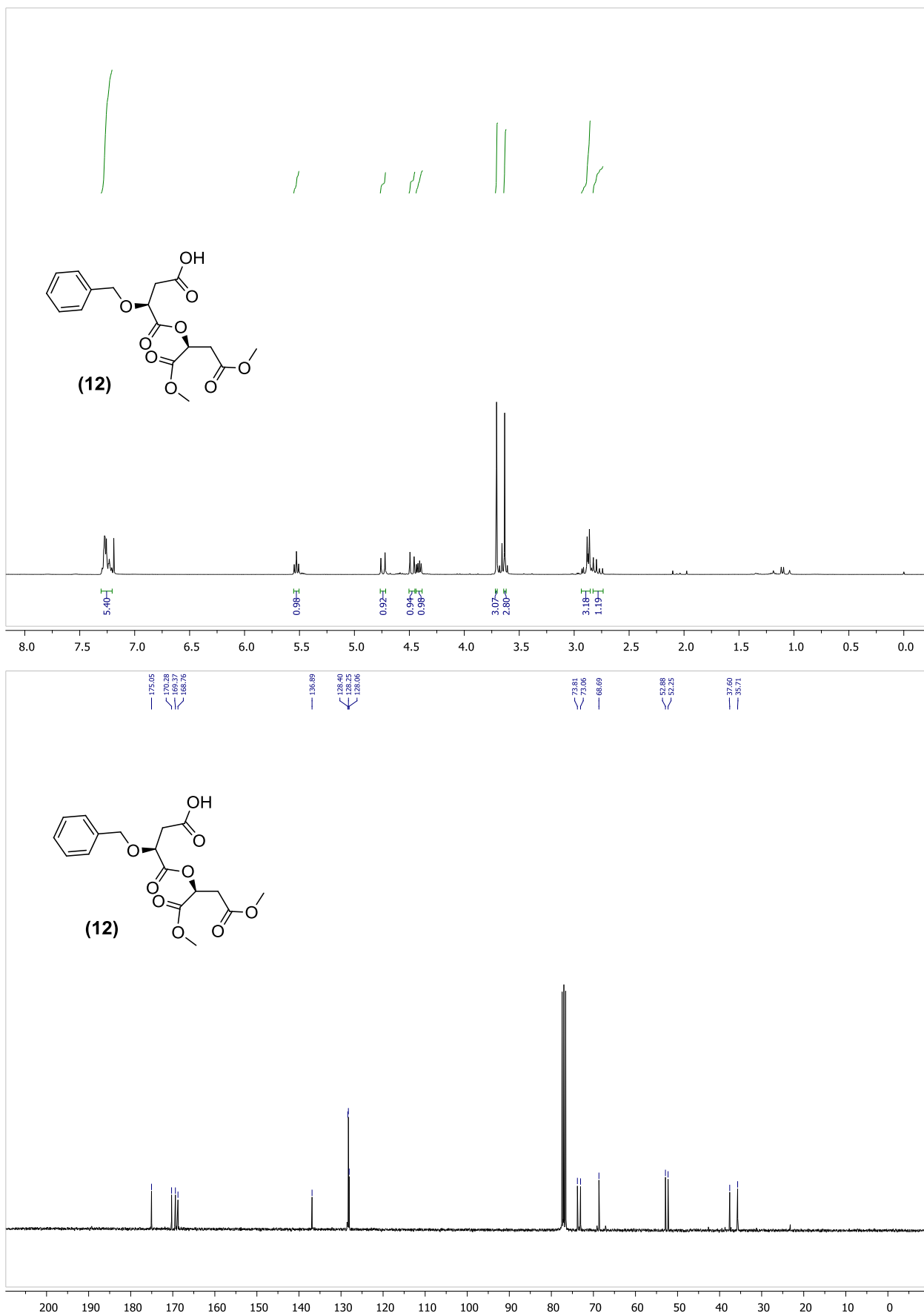


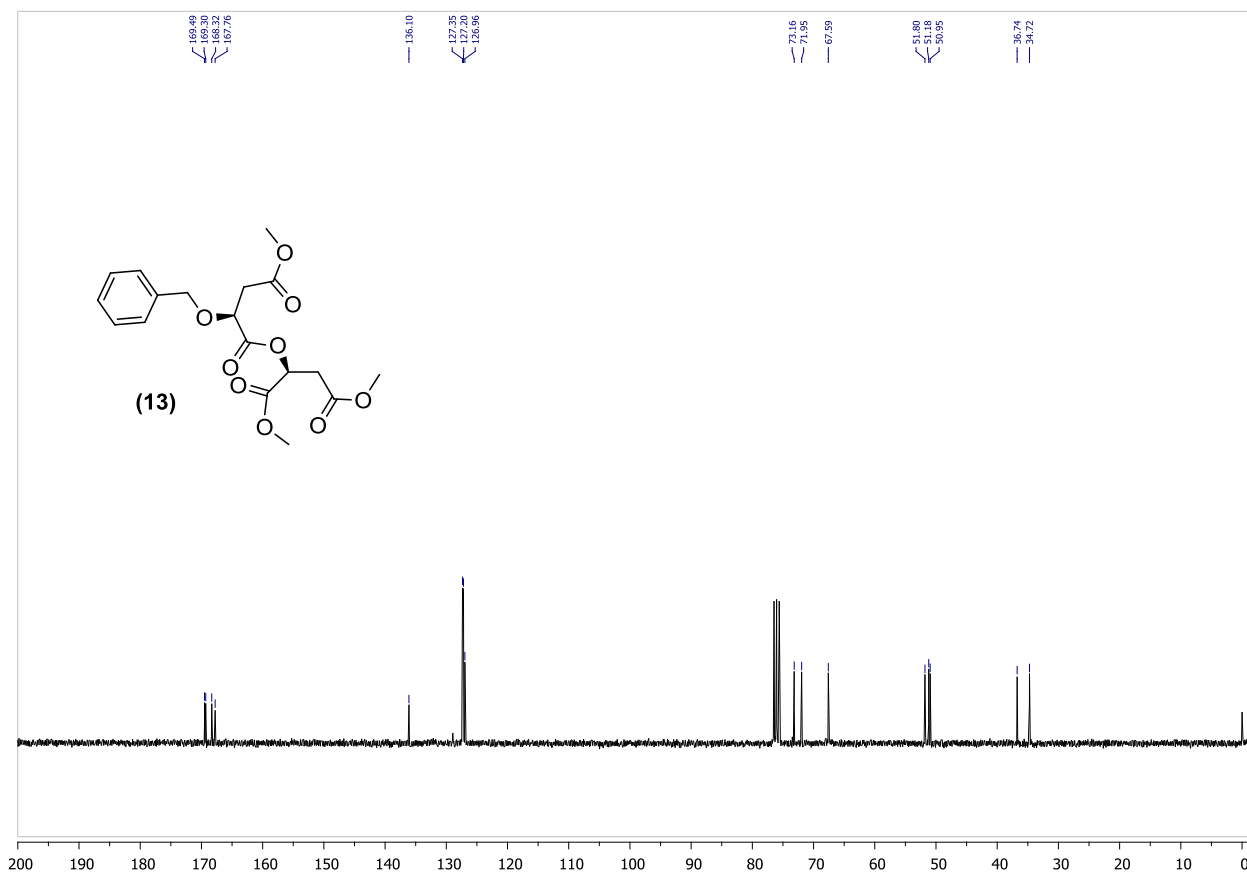
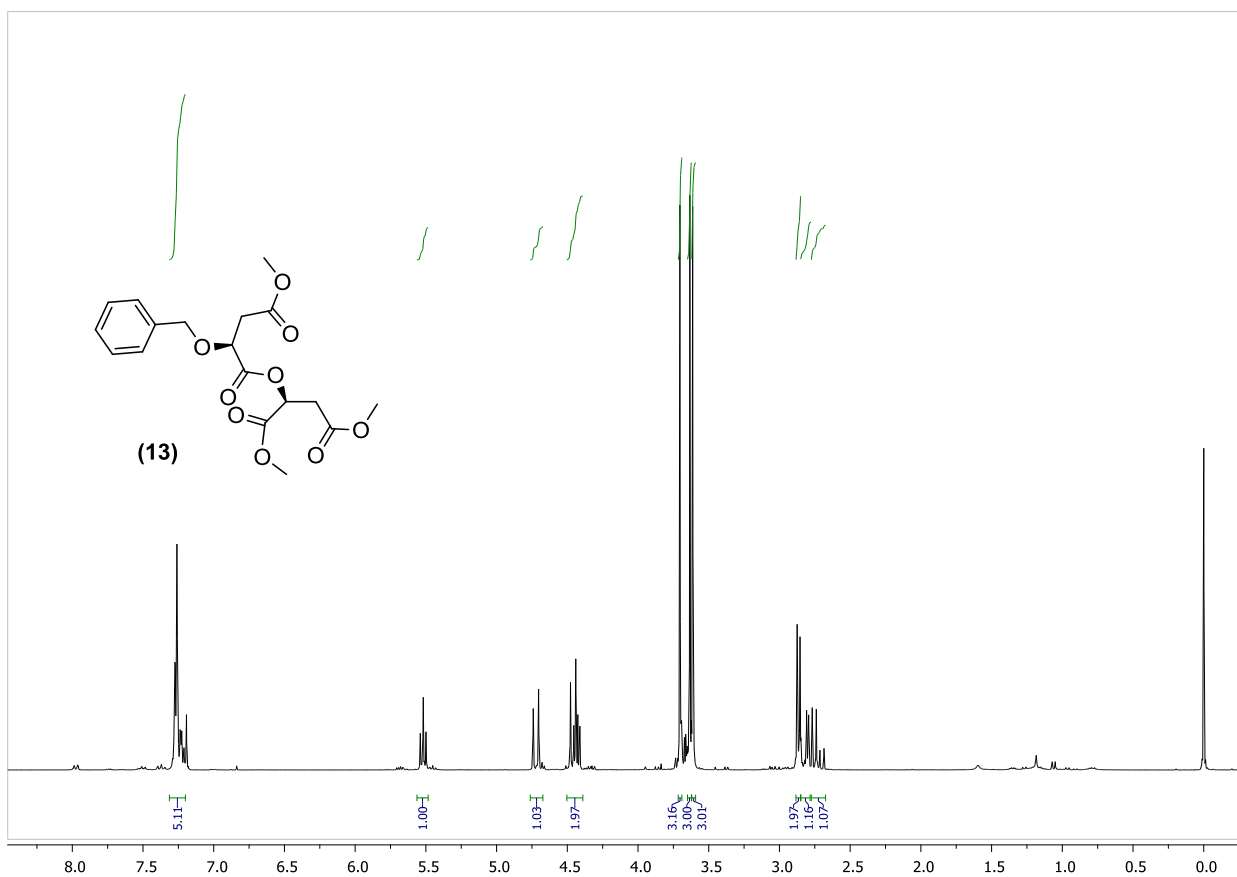
HPLC (reversed phase) and MS (MALDI-TOF) of **(11)**

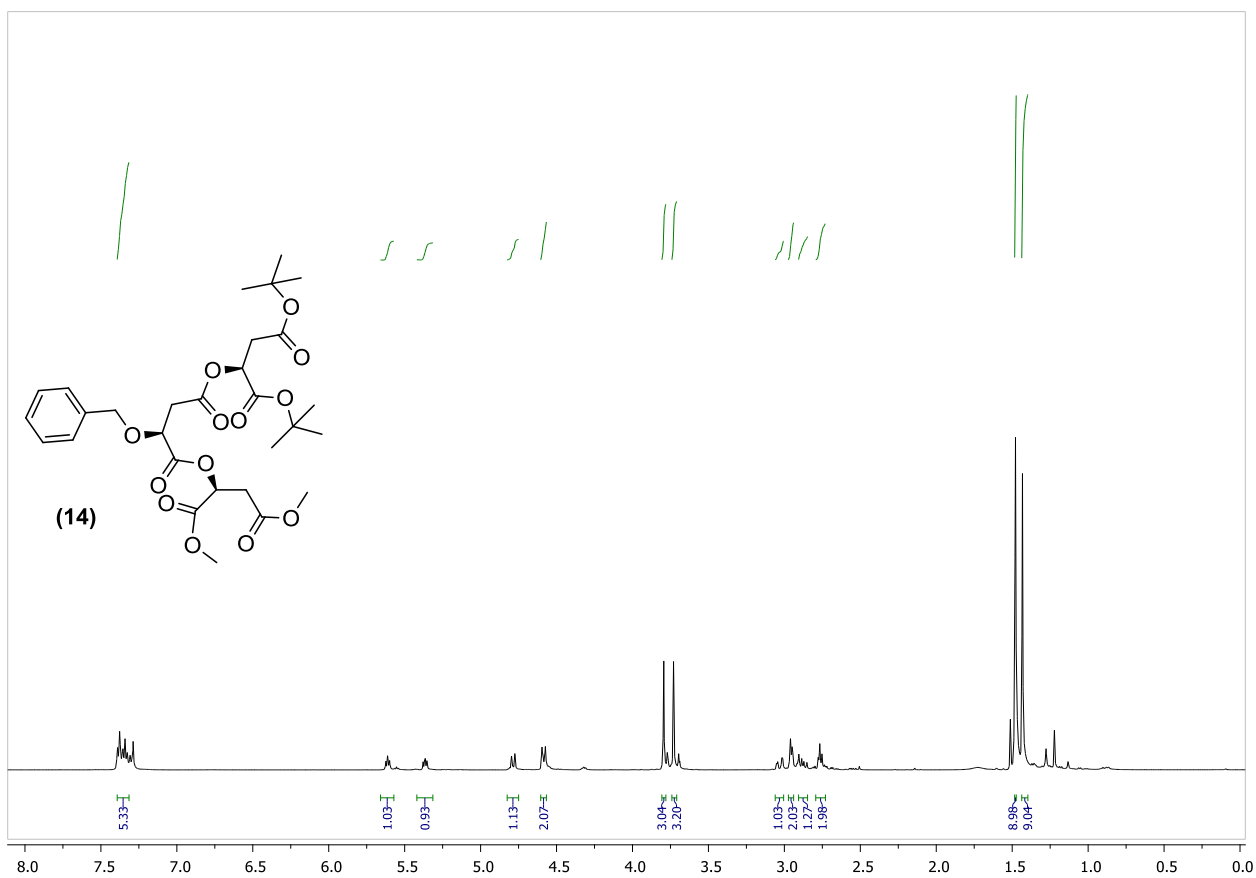
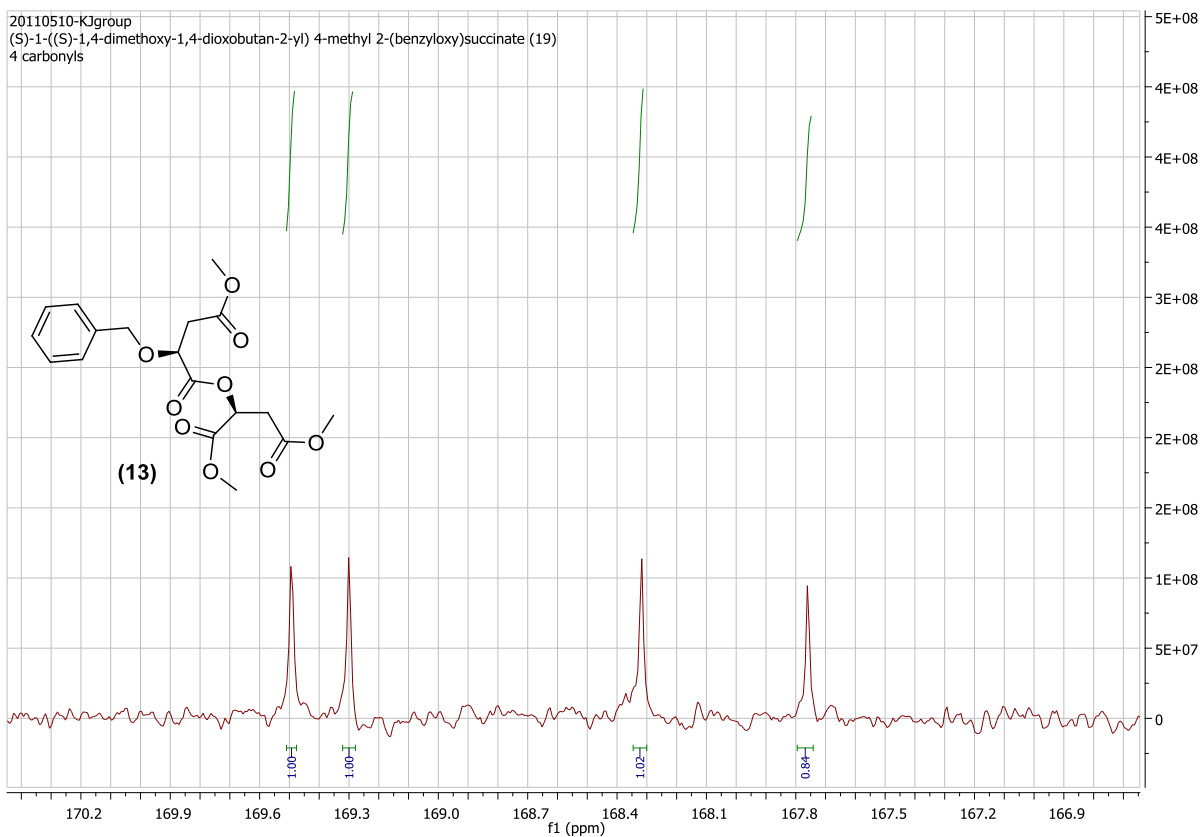


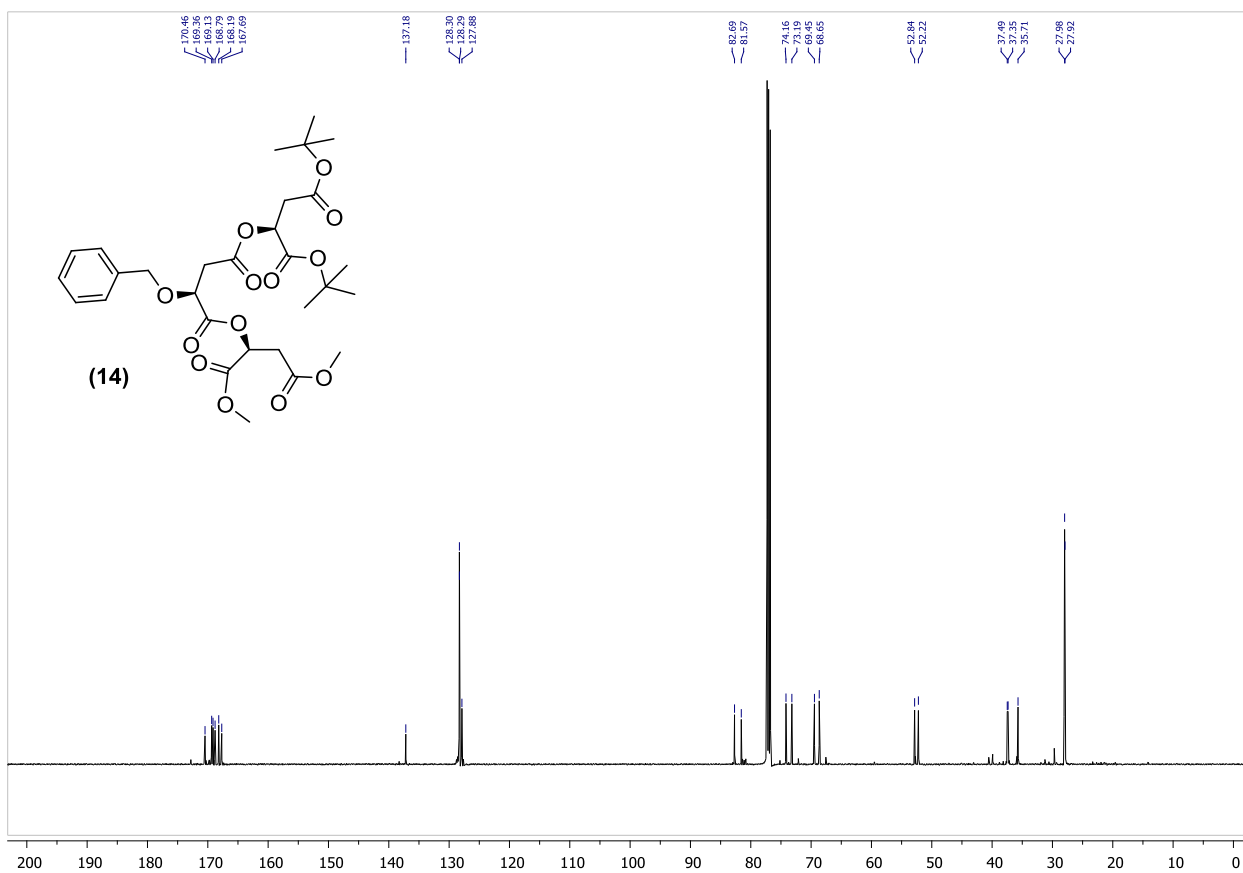
MALDI-TOF MS (calc): 1982.43, found: 2006.8 (M+Na)



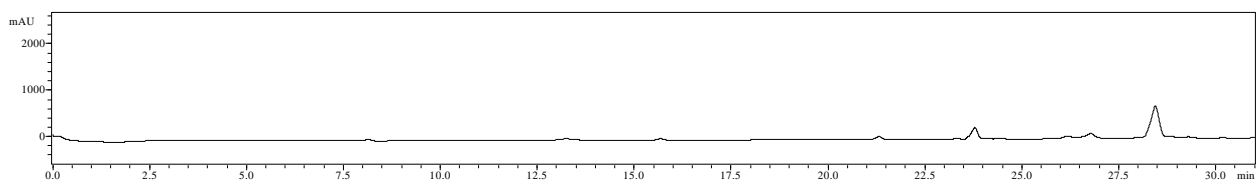




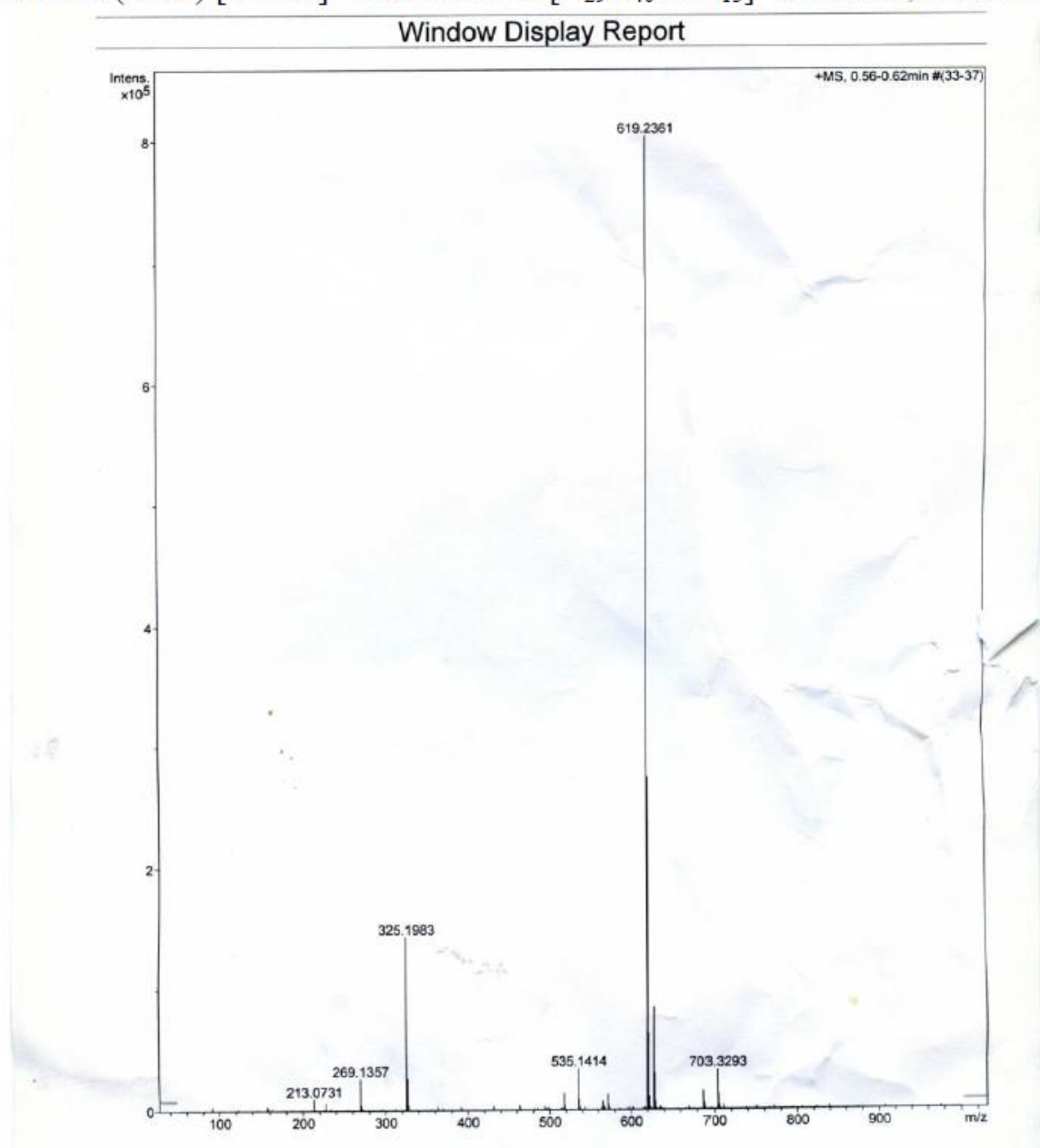


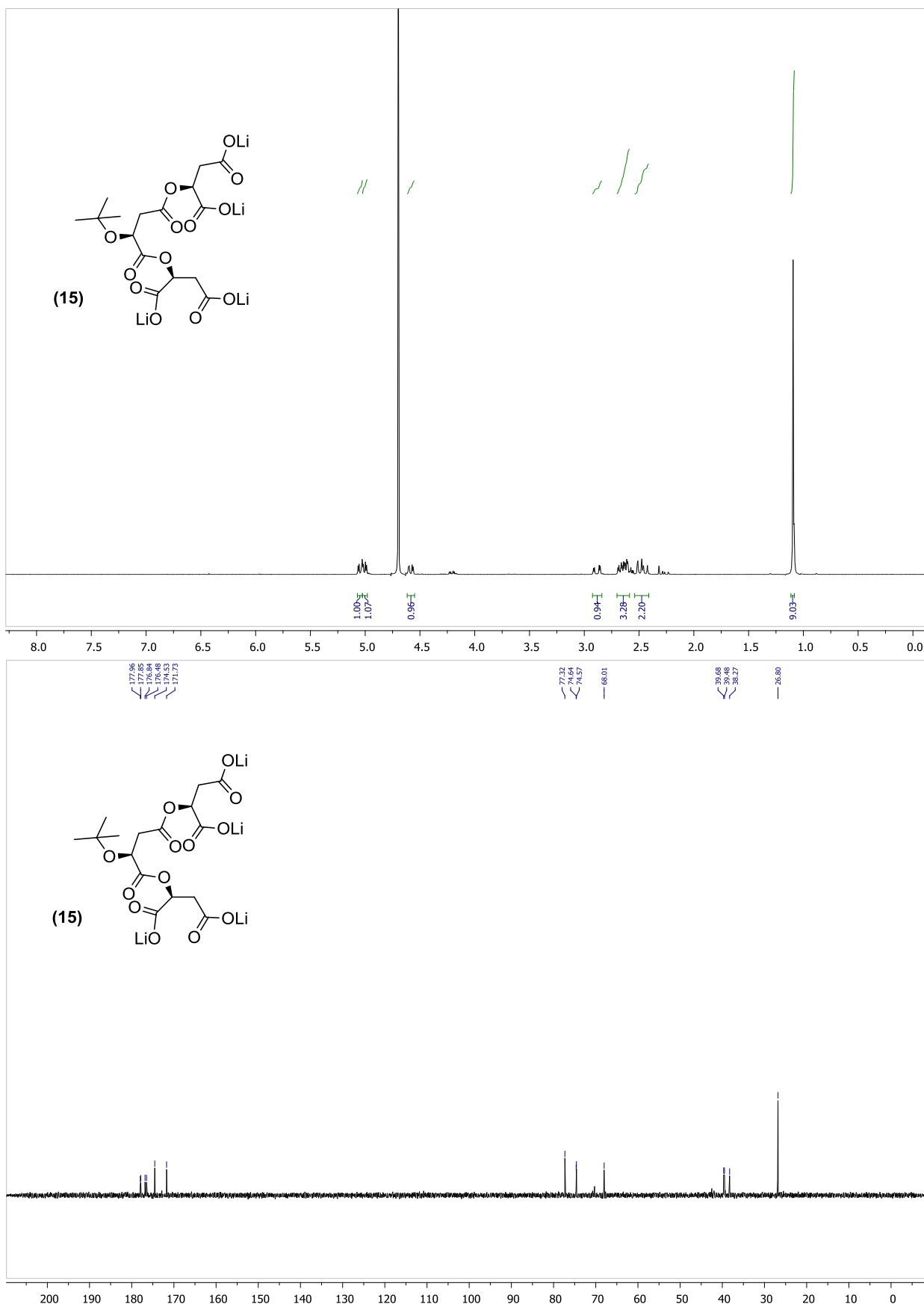


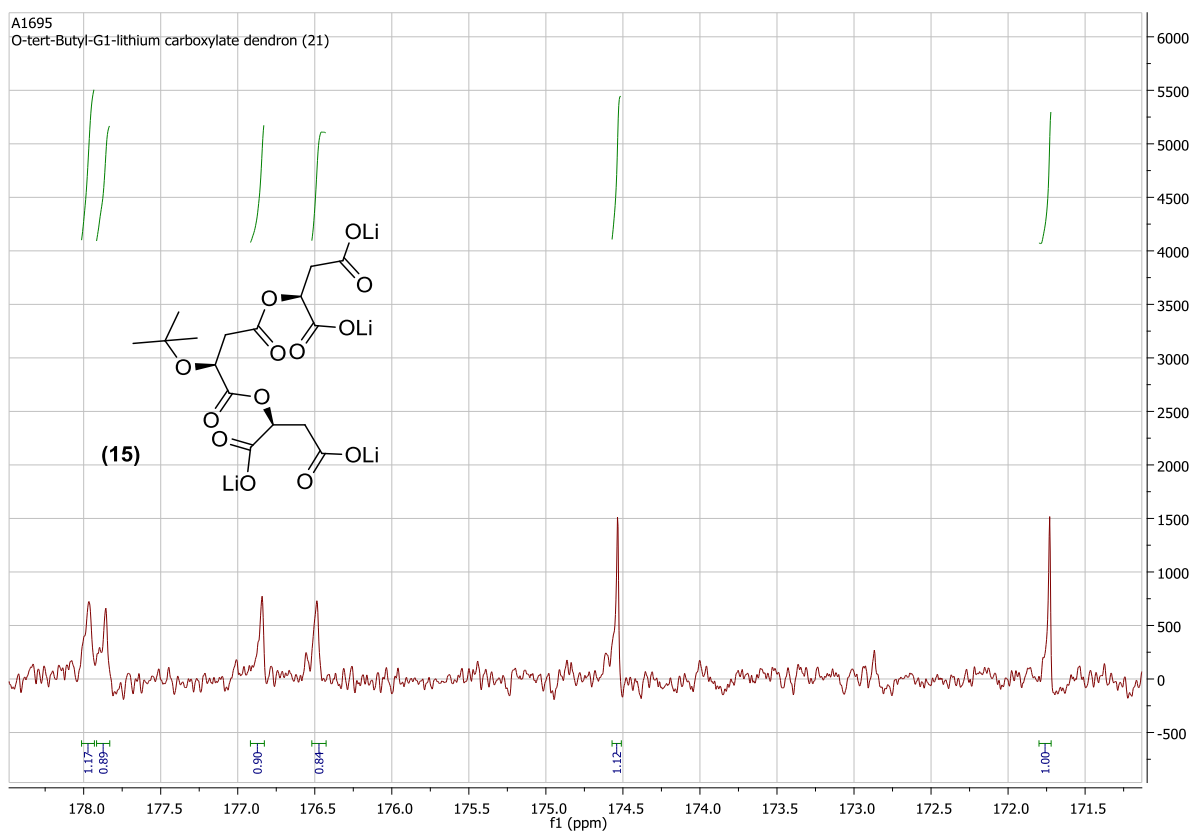
HPLC (reversed-phase) and MS of (14)



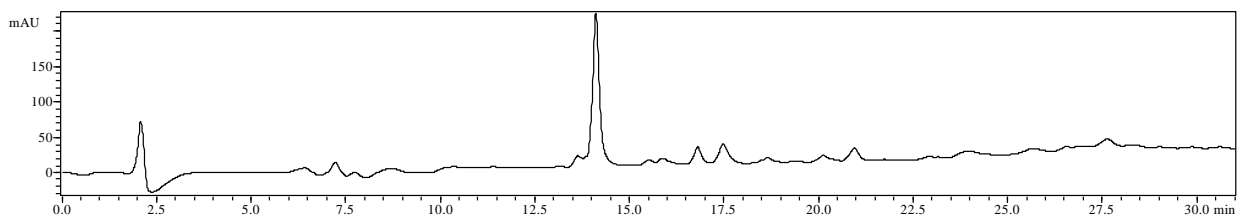
HRMS (ESI+) $[M+Na]^+$ calculated for $[C_{29}H_{40}NaO_{13}]^+$ 619.2361, found 619.2361.



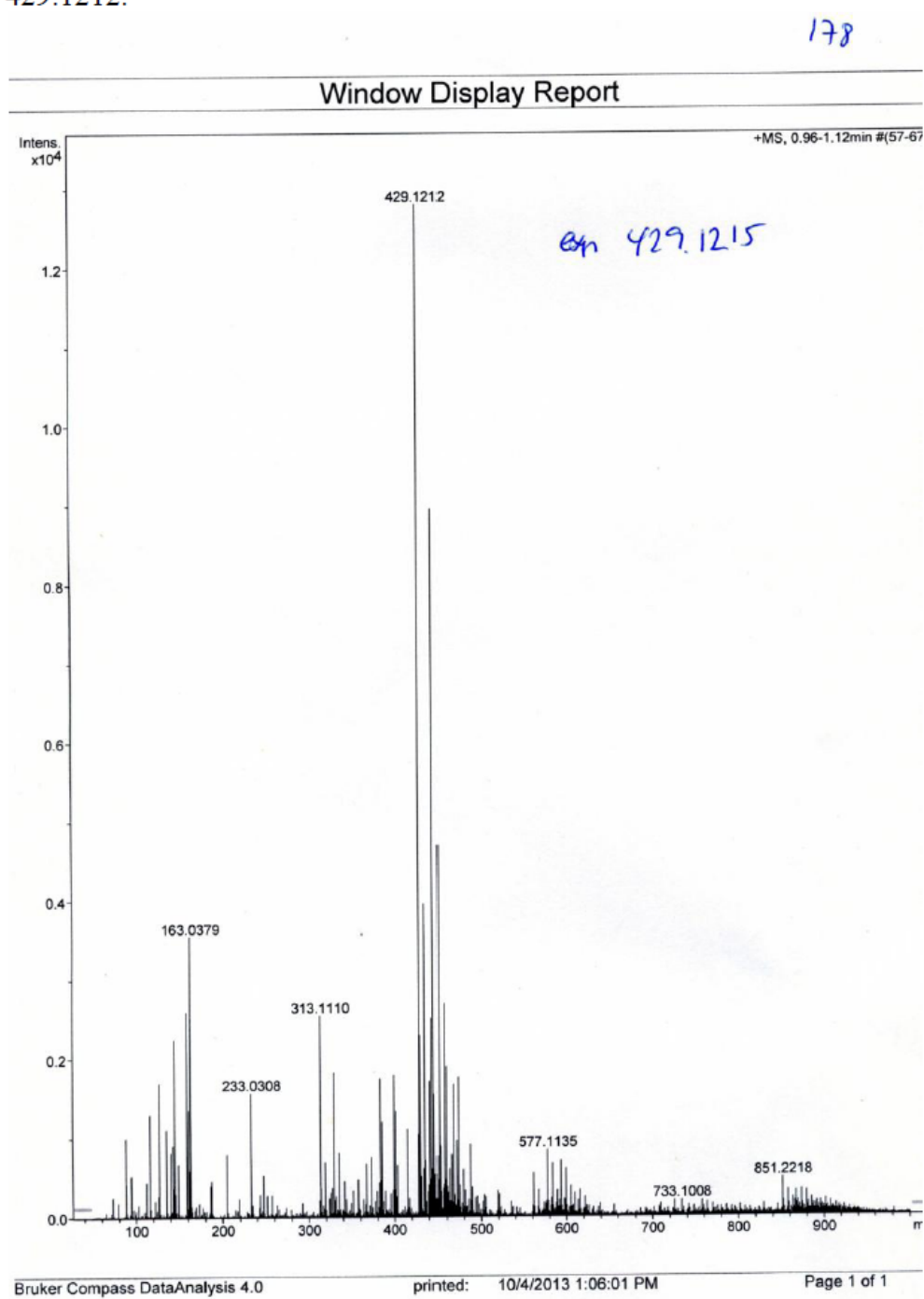


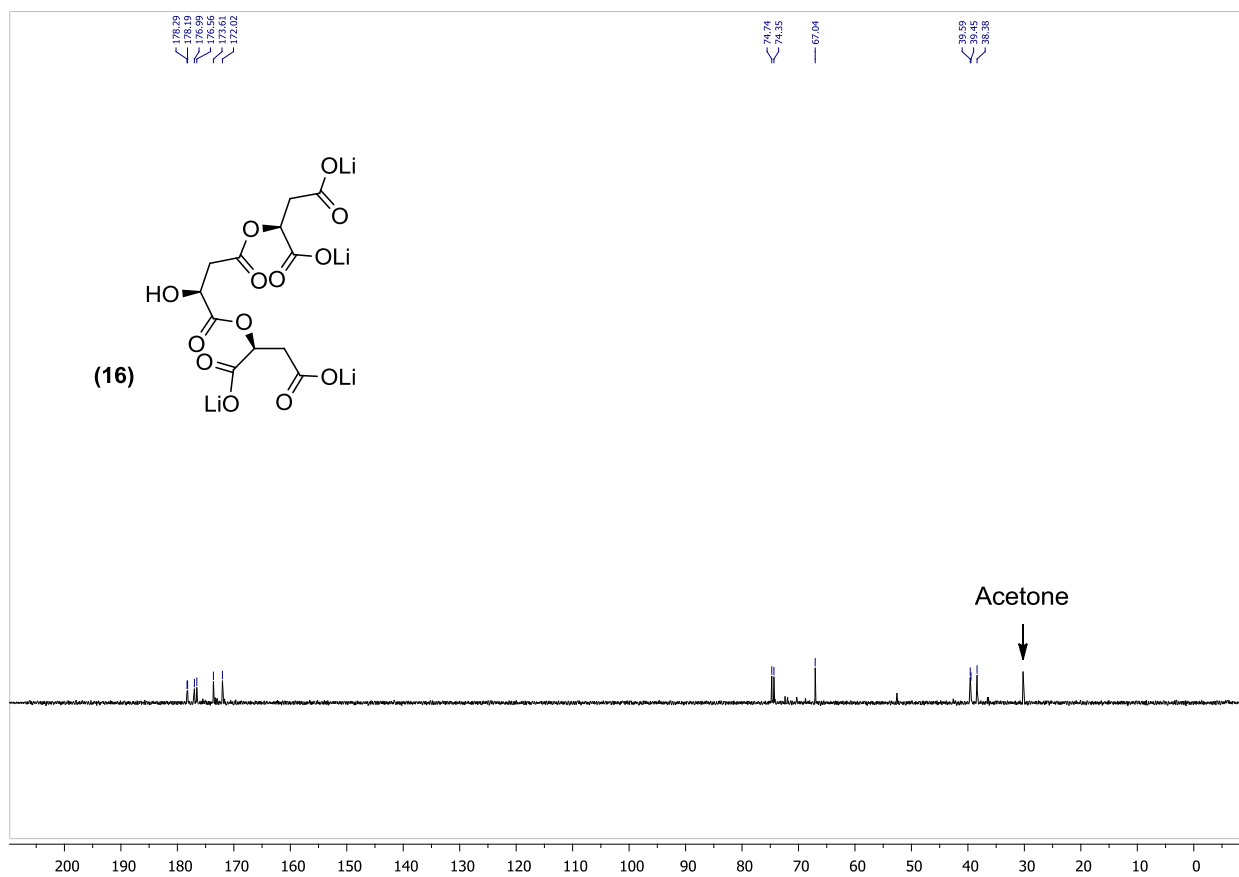
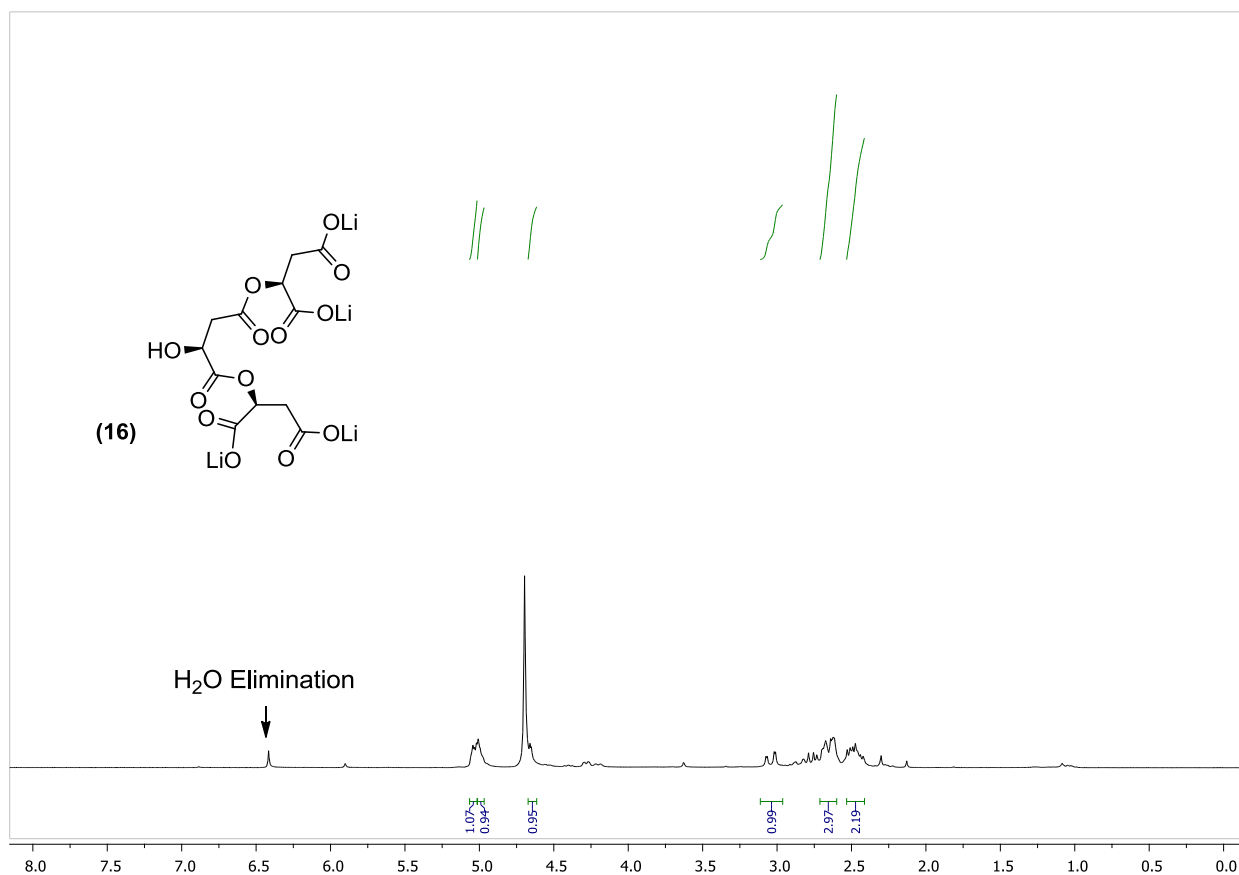


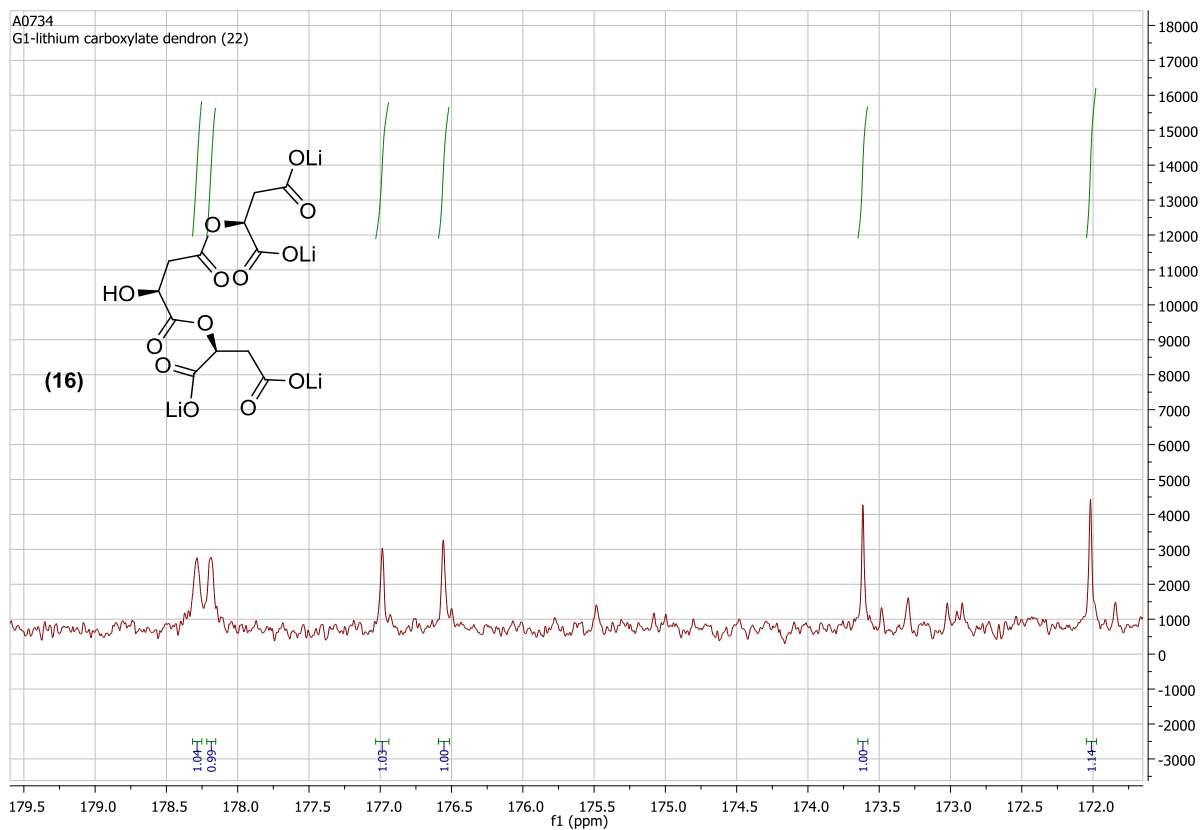
HPLC (reversed-phase, protonated compound) and MS of (15)



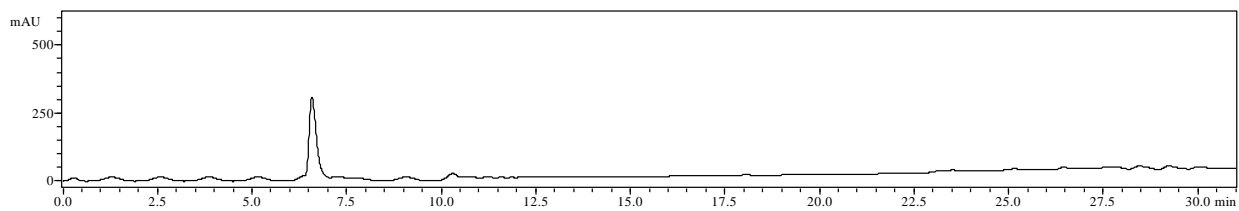
HRMS (ESI⁺) (protonated with TFA) [M+Li]⁺ calculated for [C₁₆H₂₂LiO₁₃]⁺ 429.1215, found 429.1212.





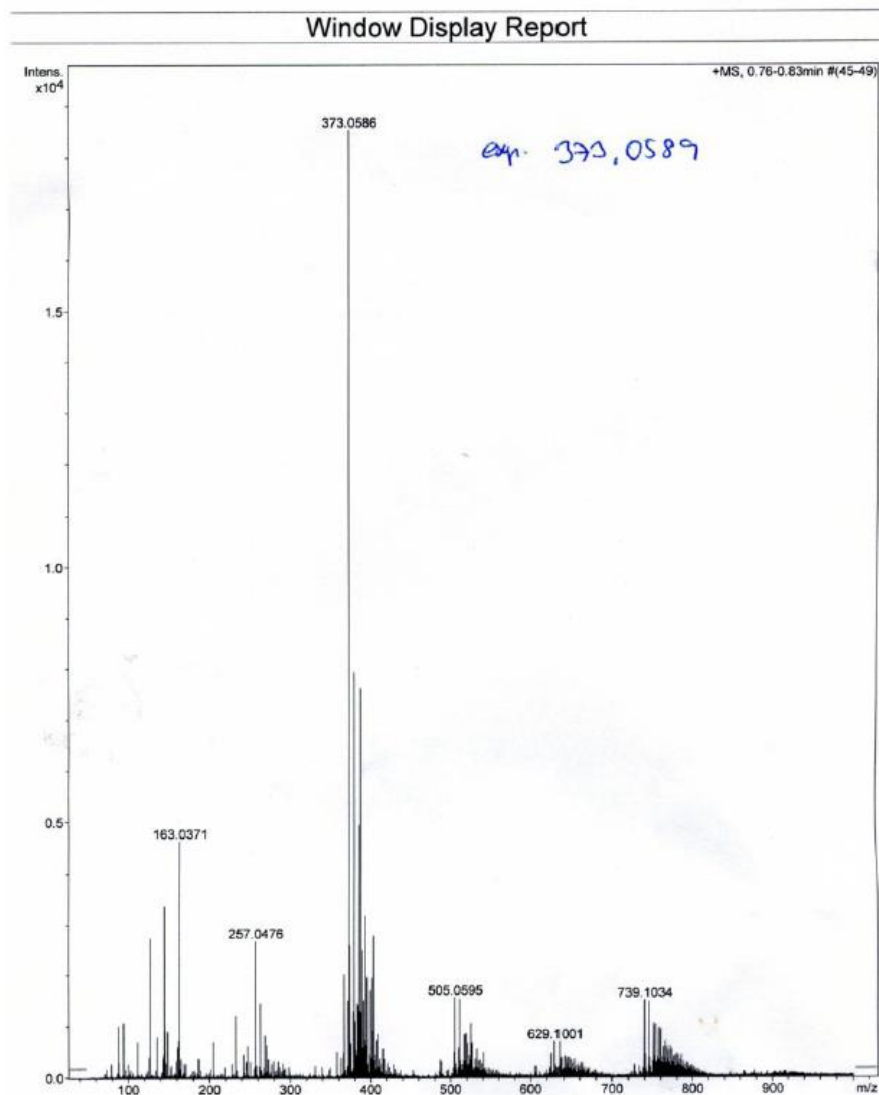


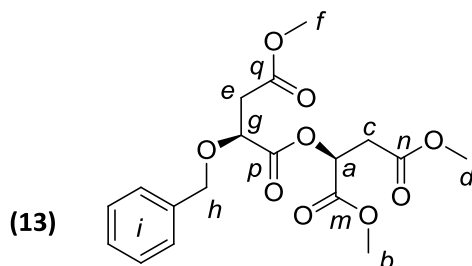
HPLC (reversed-phase, protonated form) and MS of (16)



HRMS (ESI+) (protonated with TFA) $[M+Li]^+$ calculated for $C_{12}H_{14}LiO_{13}^+$ 373.0589, found 373.0586.

177



Assigned HMBC-NMR for (S)-1-((S)-1,4-dimethoxy-1,4-dioxobutan-2-yl) 4-methyl 2-(benzyloxy)succinate (13):

^1H NMR (300 MHz, CDCl_3 , δ in ppm) H_i 7.54 – 7.02 (m, 5H), H_a 5.52 (t, $J = 6.1$ Hz, 1H), H_h 4.72 (d, $^1J = 11.3$ Hz, 1H), H_g 4.46 (d, $^1J = 11.2$ Hz, 1H), H_g 4.43 (dd, $J = 8.6, 4.3$ Hz, 1H), H_b 3.70 (s, 3H), H_d 3.63 (s, 3H), H_f 3.61 (s, 3H), H_c 2.86 (d, $J = 6.1$ Hz, 2H), H_e 2.83 (dd, $^1J = 16.3, 4.2$ Hz, 1H), 2.73 (dd, $^1J = 16.3, 8.7$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm) HMBC

C_q 169.49 $^3J_{\text{H}_f-\text{C}_q}$ (3.61, 169.49), $^2J_{\text{H}_e-\text{C}_q}$ (2.73 & 2.83, 169.49), $^3J_{\text{H}_g-\text{C}_q}$ (4.43, 169.49)

C_p 169.30 $^2J_{\text{H}_g-\text{C}_p}$ (2.86, 169.30), $^3J_{\text{H}_a-\text{C}_p}$ (5.52, 169.30), $^3J_{\text{H}_e-\text{C}_n}$ (2.73 & 2.83, 169.30), $^4J_{\text{H}_c-\text{C}_p}$ (2.86, 169.30)

C_n 168.32 $^3J_{\text{H}_d-\text{C}_n}$ (3.63, 168.32), $^2J_{\text{H}_c-\text{C}_n}$ (2.86, 168.32), $^3J_{\text{H}_a-\text{C}_n}$ (5.52, 168.32)

C_m 167.76 $^3J_{\text{H}_b-\text{C}_m}$ (3.70, 167.76), $^2J_{\text{H}_a-\text{C}_m}$ (5.52, 167.76), $^3J_{\text{H}_c-\text{C}_m}$ (2.86, 167.76)

C_i 136.10, 127.35, 127.20, 126.96, $^{2,4}J_{\text{H}_h-\text{C}_i}$ (4.72 & 4.46, 136.10 & ca. 126), $^{1,4}J_{\text{H}_f-\text{C}_i}$ (7.54 – 7.02, 136.10 & ca. 127)

C_g 73.16 $^4J_{\text{H}_h-\text{C}_g}$ (4.72 & 4.46, 73.16), $^1J_{\text{H}_g-\text{C}_g}$ (4.43, 73.16), $^2J_{\text{H}_e-\text{C}_g}$ (2.83 & 2.73, 73.16)

C_h 71.95 $^1J_{\text{H}_h-\text{C}_h}$ (4.72 & 4.46, 71.95), $^3J_{\text{H}_g-\text{C}_h}$ (4.43, 71.95), $^4J_{\text{H}_e-\text{C}_h}$ (2.83 & 2.73, 71.95), $^{3,4}J_{\text{H}_f-\text{C}_h}$ (7.54 – 7.02, 71.95)

C_a 67.59 $^4J_{\text{H}_b-\text{C}_a}$ (3.70, 67.59), $^1J_{\text{H}_a-\text{C}_a}$ (5.52, 67.59), $^2J_{\text{H}_c-\text{C}_a}$ (2.86, 67.59)

C_b 51.80 $^1J_{\text{H}_b-\text{C}_b}$ (3.70, 51.80)

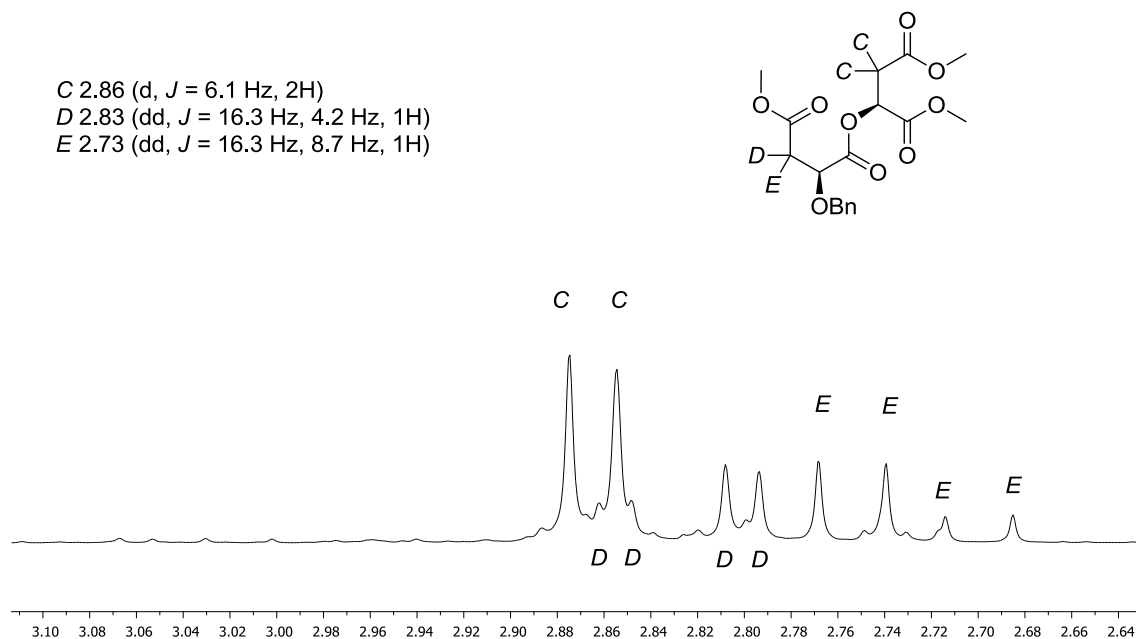
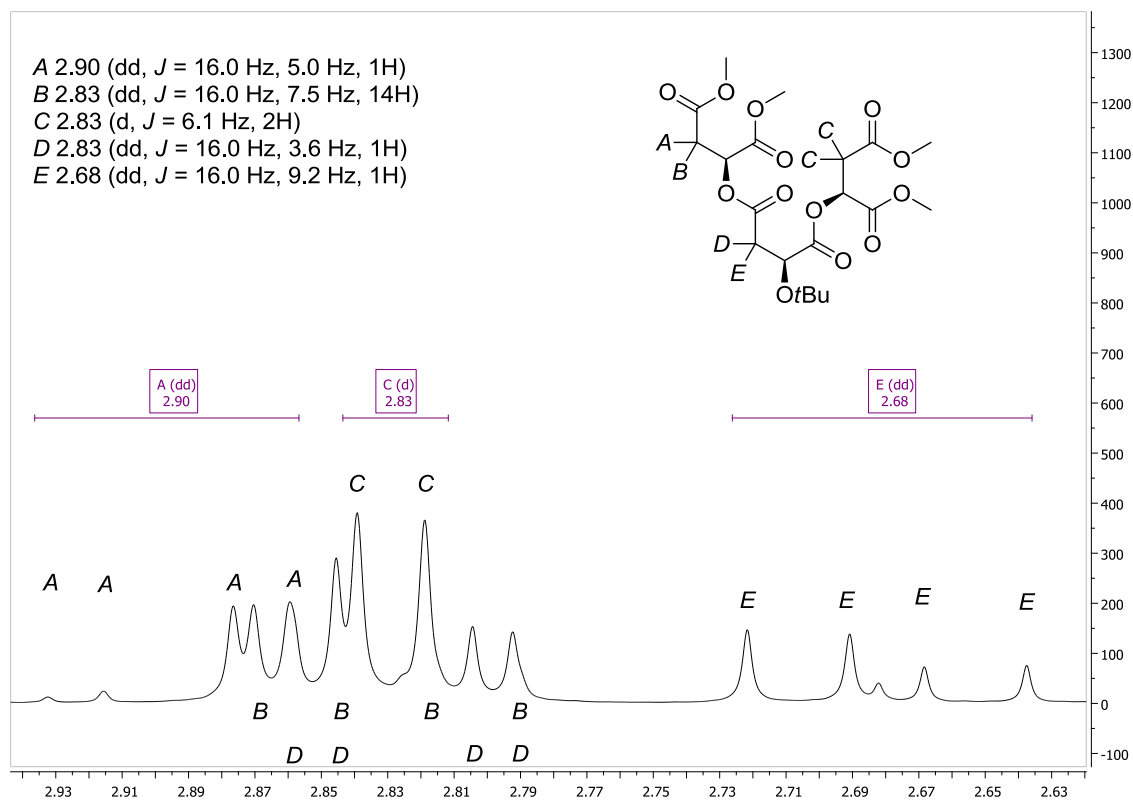
C_d 51.18 $^1J_{\text{H}_d-\text{C}_d}$ (3.63, 51.18)

C_f 50.95 $^1J_{\text{H}_f-\text{C}_f}$ (3.61, 50.95)

C_e 36.74 $^4J_{\text{H}_f-\text{C}_e}$ (3.61, 36.74), $^1J_{\text{H}_e-\text{C}_e}$ (2.73 & 2.86, 36.74), $^2J_{\text{H}_g-\text{C}_e}$ (4.43, 36.74)

C_c 34.72 $^4J_{\text{H}_d-\text{C}_c}$ (3.63, 34.72), $^1J_{\text{H}_c-\text{C}_c}$ (2.86, 34.72), $^2J_{\text{H}_a-\text{C}_c}$ (5.52, 34.72)

Assignment of diastereotopic protons in compound 6 and compound 13 by NMR to determine the epimerization extent:



Degradation of G1-methyl ester dendron at pH 9 analyzed by NMR (HSQC and H,H-COSY).

