Supplementary Information

FOR

From Plant to Probe: Semi-Synthesis of Labelled Undecaprenol Analogues Allows Rapid Access to Probes for Antibiotic Targets

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TABLE OF CONTENTS

Supplemental Figures.....S3

Figure S1: Equipment used in large-scale Soxhlet extraction.....S3

Figure S2: ^{1}H-NMR analysis after Soxhlet extraction.....S4

Figure S3: 2D-NMR analysis of ω-epoxide.....S4

Figure S4: Structure of activated phosphate **21**.....S4

General Experimental Information.....S5

Solvents and Reagents.....S5

Chromatography.....S5

Spectroscopy.....S5

Experimental Procedures and Characterization of Products.....S6

Large Scale Extraction of Undecaprenol from Bay Leaves.....S6

Und-OAc (2).....S7

Und-OH (1).....S7

Undecaprenyl α-aldehyde (3).....S8

***d*$_1$-Und-OH (4)**.....S9

Und-OAc (ω-epoxide) (5).....S9

Und-OAc (ω-aldehyde) (6).....S10

Und-OH (ω-2-aminobenzamide) (7).....S11

Und-OH (ω-4-nitroaniline) (8).....S12

Representative procedure for synthesis of compounds 9 – 14 via reductive amination.....S13

Und-OH (ω-1-pyrenemethylamine) (9).....S13
Und-OH (ω-3-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]-benzylamine) (10).....S14
Und-OH (ω-(4-amino-TEMPO)) (11).....S14
Und-OH (ω-(4-azidoaniline)) (12).....S15
Und-OH (ω-(3-ethynylaniline)) (13).....S16
Und-OH (ω-propargylamine) (14).....S16
Und-OH (ω-epoxide) (15).....S17
Undecaprenyl α-THP ether (ω-alcohol) (16).....S18
Und-OH (ω-thioacetate) (17) S19
Und-OH (ω-azide) (18).....S20
***d_1*-Und-P (20)**.....S20
***d_1*-Lipid II (19)**.....S22
Expression and purification of UdpK.....S23
UdpK Activity Assay.....S24
References.....S24
NMR Spectra.....S25

Supplemental Figures

A

B

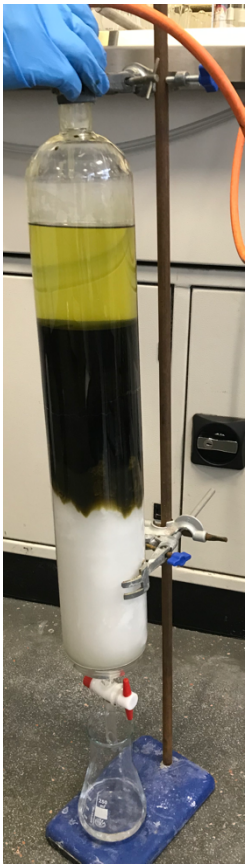

Figure S1: Equipment used in large-scale Soxhlet extraction. **A)** Large-scale Soxhlet extraction of bay leaves into a 5L round-bottomed flask. **B)** Partial purification of undecaprenol by flash column-chromatography. Column diameter is 10 cm and height is 45 cm.

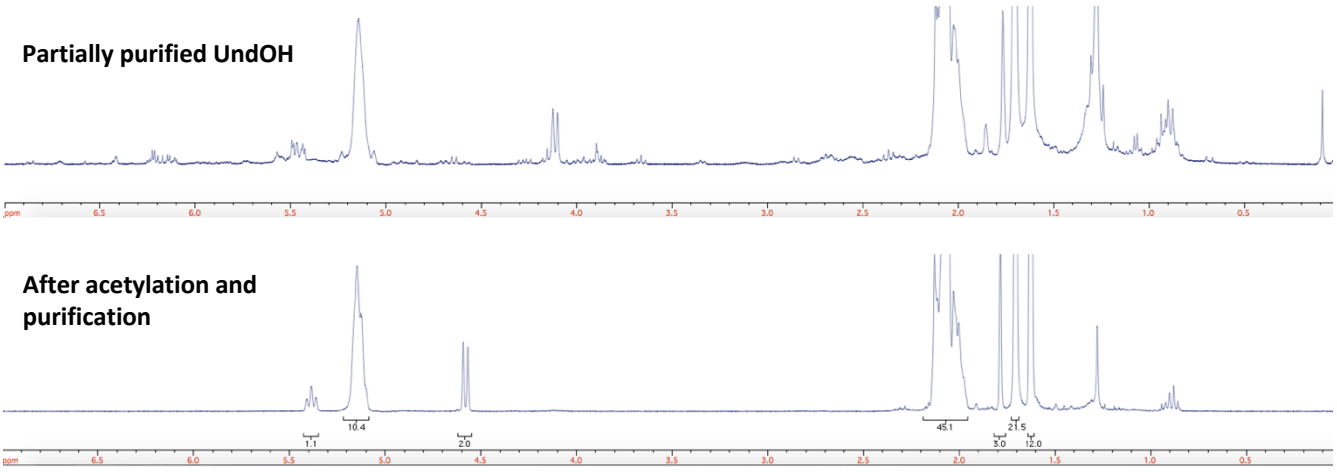

Figure S2: ^{1}H-NMR analysis after Soxhlet extraction. **Top:** ^{1}H-NMR of partially purified undecaprenol. **Bottom:** ^{1}H-NMR of purified undecaprenyl acetate.

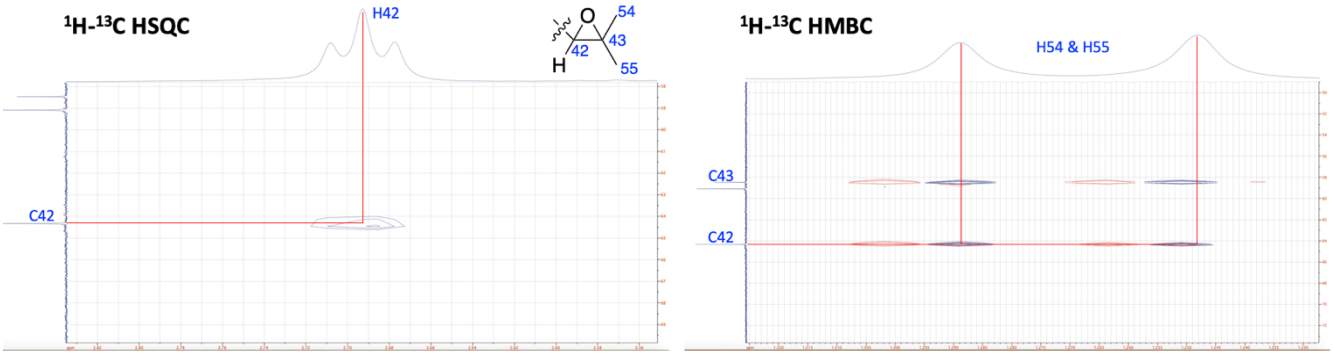

Figure S3: 2D-NMR analysis confirms that epoxidation occurs selectively on the ω-isoprene unit.

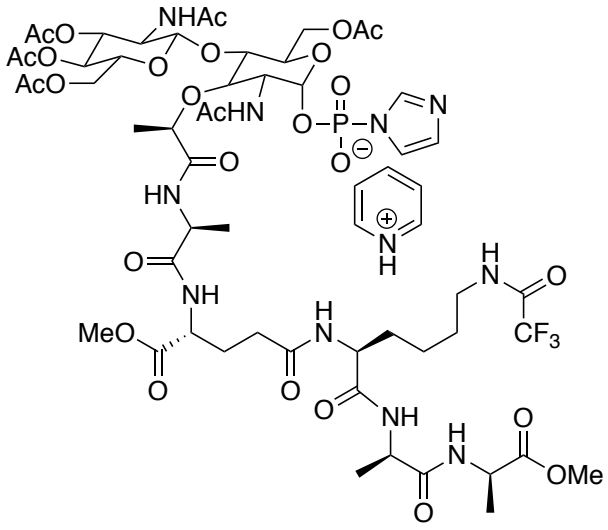

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Figure S4: Structure of activated phosphate **21**.

General Experimental Information

Solvents and Reagents

Reactions were performed under an inert atmosphere (Ar) in flame-dried glassware unless otherwise stated. Appropriate measures were taken to ensure that all air- and moisture-sensitive reagents were added under an inert atmosphere. All dry solvents were prepared from HPLC grade solvents by addition of 20% w/v freshly activated 3 Å molecular sieves (MS) under an inert atmosphere and standing for 24 h. All other solvents and reagents were used directly as received from commercial suppliers.

Chromatography

Reactions were monitored using thin-layer chromatography (TLC), which was performed using Merck Kieselgel 60 F254 (230-400 mesh) fluorescent treated silica plates, with visualization by UV light (254 and/or 365 nm) or staining with aqueous potassium permanganate or phosphomolybdic acid solutions. Flash column chromatography was performed using Fluorochem 60 40-63 micron silica gel.

Spectroscopy

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker 600 or 400 MHz spectrometer running TopSpin^{TM} software and are quoted in parts per million (ppm) for measurement against tetramethylsilane. Samples were prepared by dissolution of material in $CDCl_3$ (~ 0.7 mL) and spectra referenced relative to the residual $CHCl_3$ solvent peaks at 7.26 (^{1}H-NMR) and 77.16 (^{13}C-NMR). All spectra were acquired at 298 K. iNMR was used for processing and viewing NMR data. Chemical shifts (δ) are given in ppm, and coupling constants (J) are given in Hertz (Hz). The ^{1}H NMR spectra are reported using the following format: δ / ppm (number of protons, multiplicity, coupling constant J / Hz (where appropriate), assignment). Multiplicity is abbreviated as follows: app. = apparent, br. = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. The 13C NMR spectra are reported in δ / ppm. Where necessary or appropriate, two-dimensional (COSY, HSQC and HMBC) NMR experiments were used to assist the assignment of signals in the ^{1}H-NMR spectra. Due to the presence of multiple chemically similar isoprene units in undecaprenol and its synthetic derivatives, complete resolution of all signals was not possible. Due to the extremely hydrophobic nature of the described undecaprenol derivatives, removal of trace solvents used during purification and hydrocarbon impurities from these solvents proved very difficult, even under high vacuum for several days. Such impurities appear below 1.5 ppm and are present in most ^{1}H-NMR spectra. In all cases coincidental overlap of signals in ^{13}C-NMR

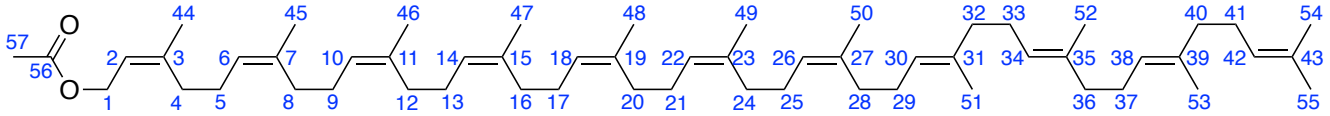
spectra mean not all expected ^{13}C-signals are visible. High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier ToF mass spectrometer using the electrospray ionization (ESI) technique.

Experimental Procedures and Characterization of Products

Large Scale Extraction of Undecaprenol from Bay Leaves

The Soxhlet extraction of ground bay leaves (purchased from Buy Whole Foods Online https://www.buywholefoodsonline.co.uk/bay-leaves-ground-1kg.html) was setup as shown in **Fig S1**. An absorbent cotton pad (~13 cm diameter) was placed at the bottom of a large Soxhlet extractor and ~900 grams of ground bay leaves added, followed by another absorbent cotton pad on top. The Soxhlet extractor was attached to a 3-necked 5 L flask and petroleum ether (PE) added to the top of the leaves until extract started to enter the flask (~1.5 L). A further 2.5 L of PE was added through one of the flask side-necks. The solvent was heated to reflux for 48 h, during which time the contents of the flask became a deep green color. The power was turned off and the extract allowed to cool. The spent bay leaves were then removed and replaced with a fresh batch of ~900 grams and the Soxhlet extraction continued for a further 48 h. The heating was then switched off and the Soxhlet extractor disconnected from the flask. Methanol (500 mL) and anhydrous K_2CO_3 (40 g) were added and the resulting mixture stirred for 72 h at room temperature. Solids were then removed from the extract solution by filtration through glass wool and the extract concentrated to yield a sticky green tar. This crude extract was suspended in 5:95 EtOAc:PE (~400 mL) and stirred to dissolve the majority of material. This entire mixture was added on top of silica gel (1 kg) pre-wetted with 5:95 EtOAc:PE in a glass column for purification by column chromatography. Due to the large amount of material, loading required regular piercing of the top of the silica gel with a glass rod until the eluent flowed freely out of the column. Undecaprenol-containing fractions were identified by comparison with a commercial standard from American Radiolabeled Chemicals, combined and concentrated *in vacuo* to yield 18.8 g of crude undecaprenol **1** as an orange oil (~ 1% w/w bay leaves).

Und-OAc (2)



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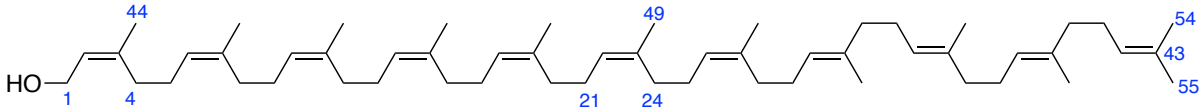
*Full numbering system used for undecaprenol derivatives is shown above. Future figures will contain simplified numbering.

Crude undecaprenol obtained by Soxhlet-extraction (18.80 g) was dissolved in pyridine (10 mL) and acetic anhydride (20 mL) and stirred at ambient temperature for 5 h. The resulting mixture was diluted with 2:1 brine:water (100 mL) and extracted with EtOAc (3 x 50 mL). The organic phase was washed with 1M HCl (100 mL), saturated aqueous $NaHCO_3$ (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude material was then purified by flash column chromatography (silica gel (800 g), 3:97 EtOAc:PE) to yield undecaprenyl acetate (**2**) as a light-yellow oil (10.20 g, 51.4%). δH (300 MHz, $CDCl_3$): 5.36 (1H, td, *J* 7.2, 1.1, H2), 5.17-5.06 (10H, m, H6, H10, H14, H18, H22, H26, H30, H34, H38 & H42), 4.56 (2H, d, *J* 7.3, H1), 2.11-1.95 (43H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40, H41 & H57), 1.76 (3H, s, H44), 1.70-1.67 (21H, m, H45, H46, H47, H48, H49, H50 & H55), 1.62-1.59 (12H, m, H51, H52, H53 & H54); δC (75 MHz, $CDCl_3$): 171.19, 142.74, 135.95, 135.50, 135.44, 135.36, 135.33, 135.09, 135.02, 131.38, 125.15, 125.14, 125.06, 124.53, 124.42, 124.39, 124.36, 124.26, 124.29, 119.29, 61.23, 39.91, 39.89, 39.87, 32.51, 32.37, 32.34, 32.13, 26.91, 26.81, 26.78, 26.55, 26.48, 25.85, 23.69, 23.59, 23.54, 21.21, 17.84, 16.17, 16.15; HRMS (ESI+): found 826.7435; $C_{57}H_{96}NO_2$, $[M+NH_4]^+$ requires 826.7441.

Und-OH (1)

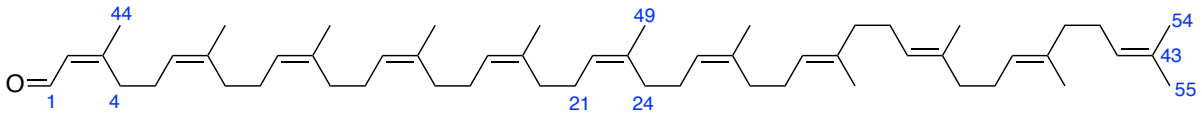


1

Und-OAc (**2**) (1.10 g, 1.36 mmol) was dissolved in 3:2 THF:MeOH (12 mL) and anhydrous K_2CO_3 (1.00 g, 7.24 mmol) was added. The resulting suspension was stirred for 18 h at ambient temperature, diluted with PE (100 mL) and washed with water (50 mL) and brine (50 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to yield undecaprenol (**1**) as a light-yellow oil (1.00 g, 96%). δH (400 MHz, $CDCl_3$): 5.45 (1H, td, *J* 7.3, 1.0, H2), 5.17-5.06 (10H, m, H6, H10, H14, H18, H22, H26,

H30, H34, H38 & H42), 4.09 (2H, d, *J* 7.2, H1), 2.11-1.95 (40H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40 & H41), 1.75 (3H, s, H44), 1.70-1.67 (21H, m, H45, H46, H47, H48, H49, H50 & H55), 1.62-1.59 (12H, m, H51, H52, H53 & H54); *δC* (75 MHz, $CDCl_3$): 140.04, 136.23, 135.52, 135.43, 135.40, 135.39, 135.38, 135.35, 135.12, 135.05, 131.39, 125.18, 125.17, 125.15, 125.09, 125.04, 124.68, 124.61, 124.56, 124.42, 124.39, 124.29, 59.19, 39.93, 39.89, 32.40, 32.37, 32.35, 32.16, 29.86, 26.94, 26.85, 26.81, 26.57, 26.53, 26.48, 25.85, 23.61, 23.59, 23.52, 17.84, 16.17, 16.15; HRMS (ESI+): found 784.7323; $C_{55}H_{94}NO$, $[M+NH_4]^+$ requires 784.7335.

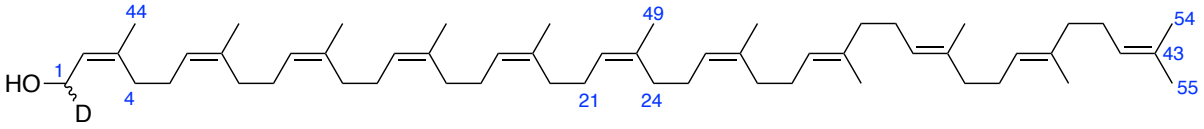
Undecaprenyl α-aldehyde (3)



3

Undecaprenol (**1**) (300 mg, 0.39 mmol) was dissolved in CH_2Cl_2 (9 mL) and cooled to 0 °C. MnO_2 (2.00 g, 23.00 mmol) was added and the resulting suspension warmed to ambient temperature and stirred for 48 h. The mixture was then filtered through celite, washed with CH_2Cl_2 (20 mL), concentrated *in vacuo* and purified by flash column chromatography (Silica gel, 5:95 EtOAc:PE) to yield Undecaprenyl α-aldehyde (**3**) as a light-yellow oil (238 mg, 80%). *δH* (400 MHz, $CDCl_3$): 9.90 (1H, d, *J* 8.2, H1), 5.89-5.86 (1H, m, H2), 5.17-5.06 (10H, m, H6, H10, H14, H18, H22, H26, H30, H34, H38 & H42), 2.58 (2H, t, *J* 7.5, H4), 2.24 (2H, app. qd, *J* 7.4, 0.8, H5), 2.11-1.95 (39H, m, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40, H41 & H44), 1.70-1.67 (21H, m, H45, H46, H47, H48, H49, H50 & H55), 1.62-1.59 (12H, m, H51, H52, H53 & H54); *δC* (75 MHz, $CDCl_3$): 190.87, 163.80, 137.37, 135.70, 135.52, 135.51, 135.45, 135.44, 135.39, 135.38, 135.37, 135.34, 135.10, 135.03, 131.38, 128.83, 125.16, 125.14, 125.08, 124.81, 124.55, 124.41, 124.38, 124.28, 123.14, 39.92, 39.88, 33.01, 32.39, 32.36, 32.35, 32.14, 29.85, 26.97, 26.93, 26.84, 26.79, 26.56, 26.53, 26.39, 25.84, 25.68, 25.19, 23.61, 23.58, 23.48, 17.83, 16.16, 16.15; HRMS (ESI+): found 787.6724; $C_{55}H_{88}NaO$, $[M+Na]^+$ requires 787.6727.

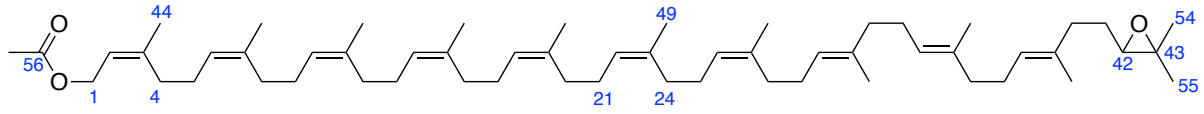
d_1-Und-OH (4)



4

Undecaprenyl α-aldehyde (**3**) (220 mg, 0.29 mmol) was dissolved in THF (1.5 mL) and MeOH (1.5 mL) and cooled to 0 °C under argon. $CeCl_3.7H_2O$ (118 mg, 0.32 mmol) was added, followed by $NaBD_4$ (14 mg, 0.34 mmol). The resulting mixture was stirred for 10 min, quenched with water (2 mL) and warmed to ambient temperature. The mixture was then extracted with Et_2O (3 x 3 mL), which was then washed with brine (3 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo* to yield d_1-undecaprenol (**4**) as a light-yellow oil (193 mg, 88%). δH (400 MHz, $CDCl_3$): 5.44 (1H, d, *J* 7.2, H2), 5.17-5.06 (10H, m, H6, H10, H14, H18, H22, H26, H30, H34, H38 & H42), 4.10-4.06 (1H, m, H1), 2.11-1.95 (40H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40 & H41), 1.75-1.74 (3H, m, H44), 1.70-1.67 (21H, m, H45, H46, H47, H48, H49, H50 & H55), 1.62-1.59 (12H, m, H51, H52, H53 & H54); δC (75 MHz, $CDCl_3$): 140.08, 136.22, 135.51, 135.42, 135.39, 135.34, 135.10, 135.04, 131.39, 125.16, 125.14, 125.07, 125.02, 124.66, 124.54, 124.41, 124.38, 124.28, 39.91, 39.88, 34.27, 32.36, 32.14, 26.91, 26.83, 26.79, 26.55, 26.52, 26.46, 25.84, 23.61, 23.58, 23.52, 22.49, 17.83, 16.14, 14.21; HRMS (ESI+): found 790.6947; $C_{55}H_{89}DNaO$, $[M+Na]^+$ requires 790.6952.

Und-OAc (ω-epoxide) (5)

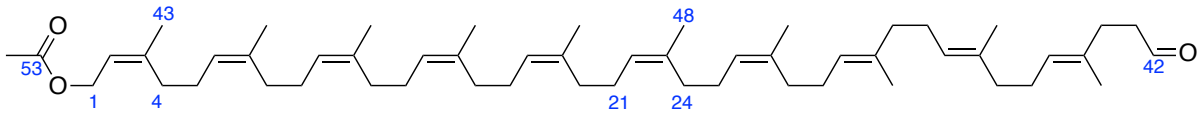


5

Und-OAc (**2**) (2.85 g, 3.53 mmol) was dissolved in 9:1 THF:water (175 mL) and cooled to 0 °C. *N*-Bromosuccinimide (0.67 g, 3.79 mmol) was added in parts over 15 minutes and the resulting solution stirred at 0 °C for 5 h. The reaction mixture was concentrated *in vacuo* to remove THF, followed by the addition of brine (10 mL). The resulting mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic layers dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting material was then dissolved in 3:2 THF:MeOH (50 mL) and anhydrous K_2CO_3 (3.43 g, 24.80 mmol) was added. The resulting

suspension was stirred for 16 h at ambient temperature. Brine (11 mL) and water (22 mL) were then added, followed by extraction of the aqueous layer with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to yield crude epoxide. This crude product was then re-dissolved in CH_2Cl_2 (47 mL), followed by the addition of DIPEA (1.63 mL, 9.38 mmol), acetic anhydride (0.81 mL, 8.53 mmol) and DMAP (52 mg, 0.426 mmol) and stirred for 16 h at ambient temperature. Brine (30 mL) was then added and the aqueous layer extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. This crude material was purified by flash column chromatography (silica gel (150 g), 1:9 EtOAc:PE) to afford epoxide **5** as a clear oil (1.22 g, 42% over 3 steps). δH (400 MHz, $CDCl_3$): 5.35 (1H, td, *J* 7.3, 1.3, H2), 5.18-5.08 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.55 (2H, d, *J* 7.0, H1), 2.69 (1H, t, *J* 6.2, H42), 2.15-1.95 (43H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40, H41 & H57), 1.75 (3H, d, *J* 0.9, H44), 1.70-1.65 (18H, m, H45, H46, H47, H48, H49 & H50), 1.62-1.59 (9H, m, H51, H52 & H53), 1.29 (3H, s, CH_3), 1.25 (3H, s, CH_3); δC (75 MHz, $CDCl_3$): 171.12, 142.67, 135.92, 135.45, 135.41, 135.33, 135.32, 135.27, 134.92, 134.09, 125.15, 125.13, 125.07, 125.06, 125.04, 125.01, 124.45, 124.42, 124.28, 119.32, 64.30, 61.20, 58.40, 39.88, 39.87, 39.78, 36.44, 32.51, 32.36, 32.34, 32.12, 29.82, 27.61, 26.82, 26.77, 26.54, 26.50, 26.47, 25.02, 23.65, 23.59, 23.56, 23.51, 21.16, 18.86, 16.12; HRMS (ESI+): found 847.6934; $C_{57}H_{92}O_3Na$, $[M+Na]^+$ requires 847.6944.

Und-OAc (ω-aldehyde) (6)

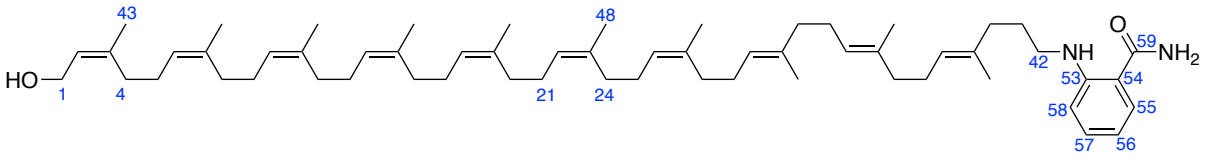


6

Epoxide **5** (320 mg, 0.39 mmol) was dissolved in 9:1 THF:water (5 mL) and cooled to 0 °C. Periodic acid (30 mg, 0.133 mmol) was then added slowly, and the reaction allowed to warm to room temperature. When all starting material was consumed (~5 h as indicated by TLC), the reaction mixture was diluted with water (10 mL) and EtOAc (10 mL). The organic and aqueous layers were separated, and the aqueous phase extracted with EtOAc (2 x 10 mL). The combined organic extracts were washed with aqueous saturated $NaHCO_3$ (50 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting crude aldehyde **6** was used in subsequent steps without further purification. δH (600 MHz,

$CDCl_3$): 9.75 (1H, td, *J* 1.9, H42), 5.36 (1H, td, *J* 7.1, 1.3, H2), 5.18-5.08 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.55 (2H, dd, *J* 7.3, 0.8, H1), 2.52-2.48 (2H, m, H41), 2.31 (2H, t, *J* 7.44, H40), 2.11-1.95 (39H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37 & H54), 1.76 (3H, q, *J* 1.2, H43), 1.70-1.65 (18H, m, H44, H45, H46, H47, H48 & H49), 1.62-1.58 (9H, m, H50, H51 & H52); δC (75 MHz, $CDCl_3$): 202.67, 171.12, 142.67, 135.92, 135.45, 135.41, 135.34, 135.32, 135.26, 134.75, 132.97, 125.55, 125.16, 125.15, 125.14, 125.08, 125.06, 124.59, 124.42, 124.29, 119.32, 61.20, 42.28, 39.87, 39.63, 32.51, 32.36, 32.34, 32.33, 32.32, 32.11, 31.99, 26.80, 26.77, 26.71, 26.54, 26.47, 23.66, 23.59, 23.56, 23.55, 23.51, 21.16, 16.21, 16.12, 16.09; HRMS (ESI+): found 805.6469; $C_{54}H_{86}O_3Na$, $[M+Na]^+$ requires 805.6475.

Und-OH (ω-2-aminobenzamide) (7)

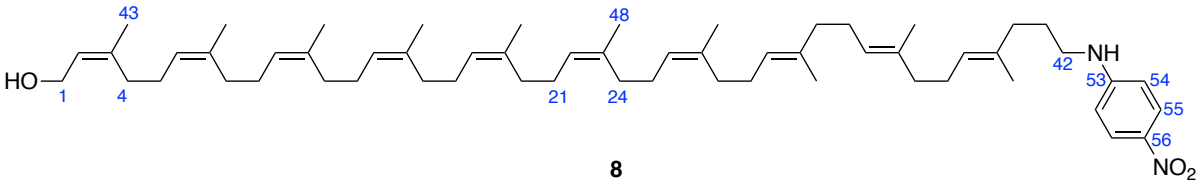


7

Anthranilamide (20 mg, 0.146 mmol) was dissolved in dichloroethane (DCE) (0.5 mL) and acetic acid (10.6 µL, 0.186 mmol). To this mixture was added a solution of aldehyde **6** (104 mg, 0.133 mmol) in DCE (1 mL), followed by sodium triacetoxyborohydride (42 mg, 0.199 mmol). The reaction was left to stir at ambient temperature for 16 h. Upon completion, aqueous saturated $NaHCO_3$ (50 mL) was added and the resulting mixture extracted with Et_2O (3 x 10 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting crude yellow solid was then dissolved in 1:2.5 THF:methanol (3.5 mL) and anhydrous K_2CO_3 (100 mg, 0.724 mmol) was added. After stirring at ambient temperature for 16 h, water (5 mL) was added and the reaction mixture extracted with Et_2O (3 x 10 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was then purified by flash column chromatography (Silica gel, 1:2 EtOAc:PE + 0.1% NEt_3) to afford amine **7** as a yellow oil (53 mg, 46%). δH (600 MHz, $CDCl_3$): 7.80 (1H, s, NH), 7.36 (1H, dd, *J* 7.9, 1.5, H55), 7.30 (1H, ddd, *J* 8.5, 7.1, 1.5, H57), 6.68 (1H, dd, *J* 8.4, 0.7, H58), 6.54 (1H, ddd, *J* 7.9, 7.1, 1.0, H56), 5.44 (1H, td, *J* 7.1, 1.2, H1), 5.18-5.10 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.09 (2H, d, *J* 7.2, H2), 3.12 (2H, q, *J* 5.8, H42), 2.11-1.95 (38H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40), 1.78-1.74 (5H, m, H41 & H43), 1.70-1.65

(18H, m, H44, H45, H46, H47, H48 & H49), 1.62-1.58 (9H, m, H50, H51 & H52); *δC* (75 MHz, $CDCl_3$): 172.32, 150.62, 139.92, 136.17, 135.49, 135.48, 135.40, 135.36, 135.34, 135.04, 134.15, 133.62, 128.42, 125.15, 125.15, 125.13, 125.07, 125.02, 124.67, 124.62, 124.39, 124.24, 114.16, 112.73, 111.88, 59.13, 42.56, 39.89, 39.82, 37.21, 32.37, 32.36, 32.35, 32.32, 32.13, 29.83, 27.43, 26.85, 26.84, 26.78, 26.54, 26.51, 26.46, 23.60, 23.59, 23.57, 23.50, 16.15, 16.13, 16.04; HRMS (ESI+): found 861.7258; $C_{59}H_{93}N_2O_2$, $[M+H]^+$ requires 861.7237.

Und-OH (ω-4-nitroaniline) (8)



8

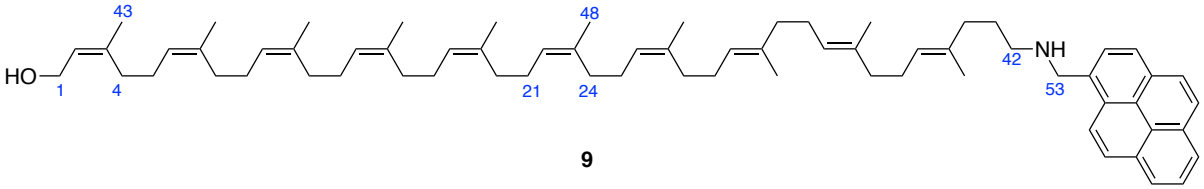
4-Nitroaniline (15 mg, 0.11 mmol) was dissolved in dichloroethane (DCE) (0.5 mL) and acetic acid (8.0 µL, 0.14 mmol). To this mixture was added a solution of aldehyde **6** (78 mg, 0.10 mmol) in DCE (1 mL), followed by sodium triacetoxyborohydride (32 mg, 0.15 mmol). The reaction was left to stir at ambient temperature for 16 h. Upon completion, aqueous saturated $NaHCO_3$ (50 mL) was added and the resulting mixture extracted with Et_2O (3 x 10 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting crude yellow solid was then dissolved in 1:2.5 THF:methanol (3.5 mL) and anhydrous K_2CO_3 (100 mg, 0.724 mmol) was added. After stirring at ambient temperature for 16 h, water (5 mL) was added and the reaction mixture extracted with Et_2O (3 x 10 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was then purified by flash column chromatography (Silica gel, 1:2 EtOAc:PE + 0.1% NEt_3) to afford amine **8** as a yellow oil (59 mg, 68%). *δH* (600 MHz, $CDCl_3$): 8.09-8.06 (2H, m, H55), 6.51-6.48 (2H, m, H54), 5.44 (1H, td, *J* 7.2, 1.2, H2), 5.18-5.09 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.53-4.47 (1H, m, NH), 4.09 (2H, d, *J* 6.6, H1), 3.18 (2H, q, *J* 6.4, H42), 2.11-1.95 (38H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40), 1.77-1.72 (5H, m, H41 & H43), 1.69-1.66 (18H, m, H44, H45, H46, H47, H48 & H49), 1.62-1.59 (9H, m, H50, H51 & H52); *δC* (75 MHz, $CDCl_3$): 153.48, 140.02, 138.00 136.20, 135.50, 135.47, 135.40, 135.36, 135.35, 135.26, 134.87, 133.75, 126.60, 125.71, 125.19, 125.17, 125.15, 125.10, 125.09, 125.04, 124.68, 124.61, 124.59, 124.34, 111.02, 59.17, 43.05, 39.91, 39.77, 37.01, 32.38, 32.37, 32.36, 32.33, 32.13, 29.85, 27.13, 26.84,

26.79, 26.74, 26.57, 26.56, 26.52, 26.47, 23.61, 23.60, 23.58, 23.51, 16.14, 15.99; HRMS (ESI+): found 863.7030; $C_{58}H_{91}N_2O_3$, $[M+H]^+$ requires 863.7030.

Representative procedure for synthesis of compounds 9 – 14 via reductive amination

To a solution of aldehyde **6** (97 mg, 0.124 mmol) in CH_2Cl_2 (3 mL) was added 4-amino TEMPO (25.5 mg, 0.149 mmol) followed by sodium triacetoxyborohydride (52.5 mg, 0.248 mmol) and acetic acid (12.8 µL). The reaction mixture was stirred at ambient temperature for 16 h and then saturated aqueous $NaHCO_3$ (50 mL) was added. The aqueous phase was extracted with EtOAc (2 x 50 mL) and the combined organic extracts dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting crude reaction mixture was re-dissolved in 3:2 THF:methanol (10 mL), anhydrous K_2CO_3 added (124 mg, 0.896 mmol) added, and the resulting suspension stirred for 16 h at ambient temperature. Water (20 mL) was added, the layers were separated, and the aqueous phase extracted with EtOAc (2 x 20 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting yellow oil was purified by flash column chromatography (Silica gel, gradient 1:9 EtOAc:PE → EtOAc) to yield amine **11** as a yellow oil (47 mg, 42%).

Und-OH (ω-1-pyrenemethylamine) (9)

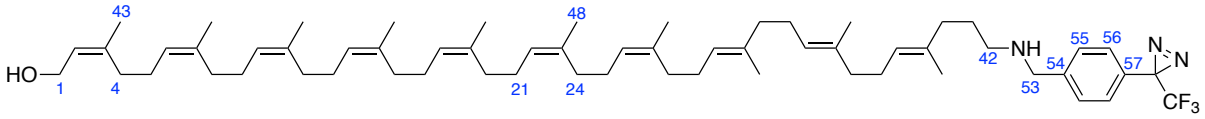


9

Amine **9** was synthesized according to the representative procedure described above and purified by flash column chromatography (Silica gel, gradient 1:9 EtOAc:PE → 1:1 EtOAc:PE) to yield the product as a yellow oil (38 mg, 39%). *δH* (600 MHz, $CDCl_3$): 8.38 (1H, d, *J* 9.2, Ar-H), 8.19-8.17 (2H, m, Ar-H), 8.15-8.13 (2H, m, Ar-H), 8.05-8.04 (2H, m, Ar-H), 8.02-7.99 (2H, m, Ar-H), 5.44 (1H, td, *J* 7.1, 1.3, H1), 5.15-5.08 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.49 (2H, s, H53), 4.09 (2H, dd, *J* 7.2, 0.8, H2), 2.78 (2H, t, *J* 7.2, H42), 2.11-1.95 (41H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40 & H41), 1.74-1.73 (3H, m, H43), 1.70-1.65 (18H, m, H44, H45, H46, H47, H48 & H49), 1.62-1.58 (9H, m, H50, H51 & H52); *δC* (75 MHz, $CDCl_3$): 139.95, 136.19, 135.50, 135.42, 135.38, 135.37, 135.36, 135.34, 135.06, 134.69, 131.48, 131.00, 130.80, 129.21, 127.77, 127.61,

127.19, 127.16, 126.00, 125.21, 125.20, 125.17, 125.16, 125.14, 125.12, 125.08, 125.03, 124.84, 124.76, 124.68, 124.64, 124.36, 124.28, 123.31, 59.14, 52.00, 49.78, 39.92, 39.83, 37.54, 32.38, 32.36, 32.36, 32.33, 32.14, 28.41, 26.85, 26.84, 26.79, 26.55, 26.52, 26.47, 23.61, 23.60, 23.58, 23.51, 16.15, 16.03; HRMS (ESI+) Found 956.7643; $C_{69}H_{98}NO$, $[M+H]^+$ requires 956.7648.

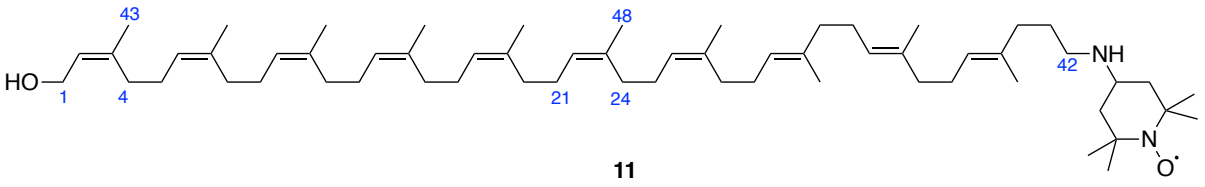
Und-OH (ω-3-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]-benzylamine) (10)



10

Amine **10** was synthesized according to the representative procedure described above and purified by flash column chromatography (Silica gel, gradient 1:4 EtOAc:PE → 2:5 EtOAc:PE) to yield the product as a yellow oil (39 mg, 38%). *δH* (600 MHz, $CDCl_3$): 7.36 (2H, d, *J* 8.6, H56), 7.15 (2H, d, *J* 8.0, H55), 5.44 (1H, td, *J* 7.1, 1.3, H2), 5.18-5.10 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.10-4.08 (2H, m, H1), 3.80 (2H, s, H53), 2.58 (2H, t, *J* 7.2, H42), 2.11-1.95 (38H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40), 1.75-1.74 (3H, m, H43), 1.69-1.65 (18H, m, H44, H45, H46, H47, H48 & H49), 1.63-1.57 (11H, m, H41, H50, H51 & H52); *δC* (75 MHz, $CDCl_3$): 139.95, 136.20, 135.51, 135.50, 135.41, 135.38, 135.37, 135.36, 135.33, 135.02, 134.58, 134.32, 129.77, 128.68, 127.86, 126.67, 126.56, 125.18, 125.17, 125.14, 125.09, 125.03, 124.89, 124.80, 124.68, 124.64, 124.42, 124.38, 124.29, 59.14, 53.44, 49.16, 39.92, 39.84, 37.43, 32.38, 32.36, 32.34, 32.14, 29.85, 28.22, 26.85, 26.82, 26.80, 26.56, 26.52, 26.47, 23.61, 23.58, 23.51, 16.15, 16.00; *δF* (600 MHz, $CDCl_3$): -65.31; HRMS (ESI+) Found 940.7259 $C_{61}H_{93}F_3N_3O$, $[M+H]^+$ requires 940.7272.

Und-OH (ω-(4-amino-TEMPO)) (11)



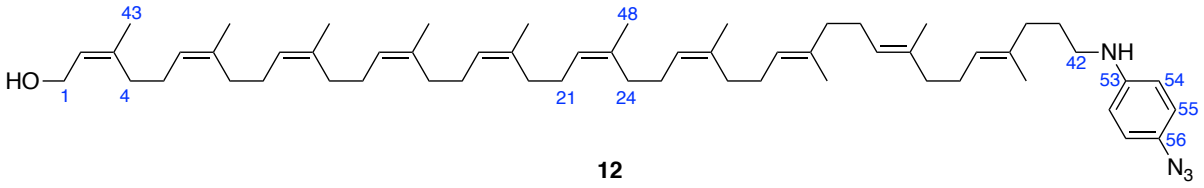
11

Amine **11** was synthesized according to the representative procedure described above and purified by flash column chromatography (Silica gel, gradient 1:9 EtOAc:PE → EtOAc) to yield the product as a yellow oil (47 mg, 42%). *δH** (600 MHz, $CDCl_3$): 5.52 (1H, br. s, H2), 5.27-5.11 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.22 (2H, br. s, H1), 2.21-2.00 (40H, m, H4, H5, H8, H9, H12, H13, H16, H17,

H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40 & H41), 1.82 (3H, s, H43), 1.78-1.74 (18H, m, H44, H45, H46, H47, H48 & H49), 1.71-1.66 (9H, m, H50, H51 & H52); δC (75 MHz, $CDCl_3$): 138.52, 134.77, 134.09, 134.07, 134.00, 133.96, 133.91, 57.79, 38.59, 38.48, 36.62, 31.05, 31.02, 30.09, 30.97, 30.81, 28.45, 25.52, 25.48, 25.45, 25.22, 25.18, 25.17, 25.14, 22.34, 22.32, 22.30, 22.27, 22.21, 22.20, 14.93, 14.90, 14.67; HRMS (ESI+) Found 896.8086; $C_{61}H_{104}N_2O_2^{\cdot}$, $[M+H]^+$ requires 896.8098.

*The paramagnetic nitroso species drastically reduces relaxation times, which lead to significant line-broadening in the 1H-NMR spectra, such that signals from the TEMPO unit were not observed.

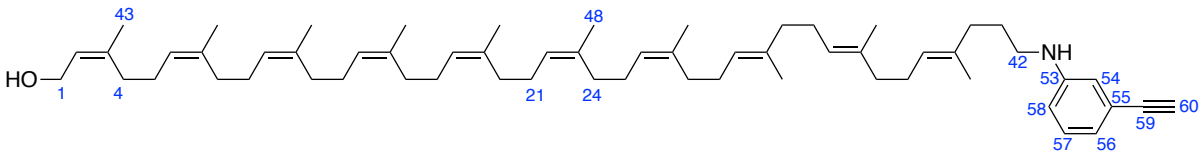
Und-OH (ω-(4-azidoaniline)) (12)



12

Amine **12** was synthesized according to the representative procedure described above and purified by flash column chromatography (Silica gel, gradient 5:95 EtOAc:PE → 1:9 EtOAc:PE) to yield the product as a yellow oil (25 mg, 24%). δH (600 MHz, $CDCl_3$): 6.86-6.83 (2H, m, H55), 6.58-6.57 (2H, m, H54), 5.44 (1H, td, *J* 7.2, 1.4, H2), 5.18-5.10 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.09 (2H, d, *J* 7.1, H1), 3.06 (2H, t, *J* 7.1, H42), 2.11-1.95 (38H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40), 1.75-1.74 (3H, m, H43), 1.72-1.67 (20H, m, H41, H44, H45, H46, H47, H48 & H49), 1.62-1.59 (9H, m, H50, H51 & H52); δC (75 MHz, $CDCl_3$): 146.14, 140.02, 136.22, 135.51, 135.50, 135.42, 135.38, 135.37, 135.32, 134.96, 134.25, 128.73, 125.20, 125.18, 125.17, 125.15, 125.10, 125.04, 124.68, 124.61, 124.52, 124.31, 120.11, 113.90, 59.18, 43.98, 39.92, 39.82, 37.23, 32.39, 32.37, 32.37, 32.34, 32.15, 31.74, 27.61, 26.85, 26.80, 26.79, 26.56, 26.53, 26.47, 23.62, 23.61, 23.59, 23.52, 16.15, 16.04, 14.27; HRMS (ESI+) Found 859.7209; $C_{58}H_{91}N_4O$, $[M+H]^+$ requires 859.7193.

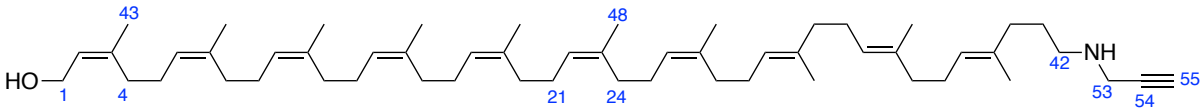
Und-OH (ω-(3-ethynylaniline)) (13)



13

Amine **13** was synthesized according to the representative procedure described above and purified by flash column chromatography (Silica gel, gradient 1:4 EtOAc:PE → EtOAc) to yield the product as a yellow oil (35 mg, 35%). *δH* (600 MHz, $CDCl_3$): 7.09 (1H, t, *J* 7.9, H57), 6.82 (1H, dt, *J* 7.5, 1.2, H58), 6.70 (1H, dd, *J* 2.3, 1.5, H54), 6.57 (1H, ddd, *J* 8.2, 2.4, 0.9, H56), 5.44 (1H, td, *J* 7.2, 1.4, H2), 5.18-5.09 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.09 (2H, d, *J* 6.9, H1), 3.07 (2H, t, *J* 7.1, H42), 3.00 (1H, s, H60), 2.11-1.95 (38H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40), 1.75-1.74 (3H, m, H43), 1.73-1.67 (20H, m, H41, H44, H45, H46, H47, H48 & H49), 1.62-1.59 (9H, m, H50, H51 & H52); *δC* (75 MHz, $CDCl_3$): 148.35, 140.02, 136.21, 135.51, 135.42, 135.38, 135.37, 135.37, 135.33, 134.97, 134.23, 129.25, 125.21, 125.18, 125.17, 125.14, 125.09, 125.03, 124.67, 124.61, 124.50, 124.29, 122.80, 121.13, 115.81, 113.81, 84.51, 76.24, 59.17, 43.51, 39.91, 39.80, 37.20, 32.38, 32.37, 32.36, 32.36, 32.34, 32.15, 27.55, 26.85, 26.80, 26.79, 26.56, 26.52, 26.47, 23.62, 23.61, 23.58, 23.52, 16.15, 16.04; HRMS (ESI+) Found 842.7179; $C_{60}H_{92}NO$, $[M+H]^+$ requires 842.7179.

Und-OH (ω-propargylamine) (14)

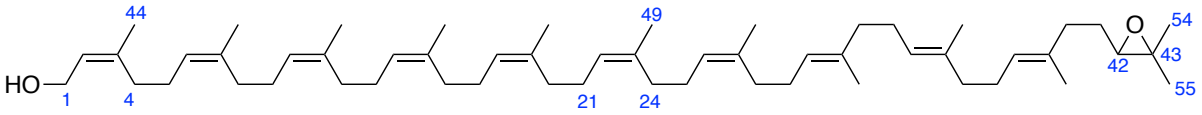


14

Amine **14** was synthesized according to the representative procedure described above and purified by flash column chromatography (Silica gel, gradient 1:4 EtOAc:PE → 3:7 EtOAc:PE) to yield the product as a yellow oil (30 mg, 41%). *δH* (600 MHz, $CDCl_3$): 5.44 (1H, td, *J* 7.2, 1.4, H2), 5.18-5.08 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.09 (2H, dd, *J* 7.2, 0.9, H1), 3.42 (2H, d, *J* 2.4, H53), 2.66 (2H, t *J* 7.2, H42), 2.20 (1H, t, *J* 2.4, H55), 2.11-1.95 (38H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37 & H40), 1.75-1.74 (3H, m, H43), 1.70-1.67 (18H, m, H44, H45, H46, H47, H48 & H49), 1.62-1.56 (11H, m, H41, H50, H51 & H52); *δC* (75 MHz, $CDCl_3$): 139.96, 136.20, 135.51, 135.42, 135.38, 135.37, 135.34, 135.05, 134.60, 125.18, 125.17, 125.14, 125.09, 125.04, 124.78,

124.68, 124.65, 124.42, 124.29, 82.39, 71.36, 59.14, 48.52, 39.92, 39.84, 38.30, 37.45, 32.38, 32.36, 32.34, 32.15, 30.47, 29.85, 28.13, 26.85, 26.83, 26.80, 26.56, 26.52, 26.47, 23.62, 23.61, 23.58, 23.55, 23.52, 16.16, 16.01; HRMS (ESI+) Found 780.7020; $C_{55}H_{90}NO^+$, $[M+H]^+$ requires 780.7022.

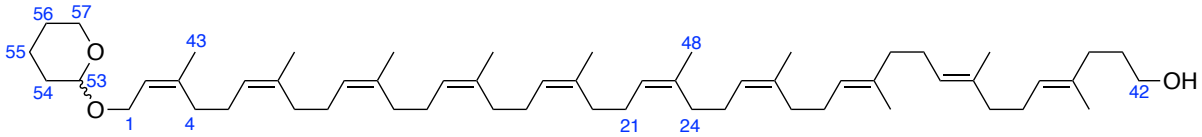
Und-OH (ω-epoxide) (15)



15

Und-OAc (**2**) (0.96 g, 1.19 mmol) was dissolved in 9:1 THF:water (100 mL) and cooled to 0 °C. *N*-Bromosuccinimide (232 mg, 1.30 mmol) was added in parts over 15 minutes and the resulting solution stirred at 0 °C for 5 h. Brine (100 mL) was added, the layers separated and the aqueous phase extracted with EtOAc (2 x 50 mL). The combined organic layers dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting material was then dissolved in 3:2 THF:MeOH (100 mL) and anhydrous K_2CO_3 (1.15 g, 8.30 mmol) was added. The resulting suspension was stirred for 16 h at ambient temperature. Brine (50 mL) and water (50 mL) were then added, followed by extraction of the aqueous layer with EtOAc (2 x 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to yield crude epoxide. This crude material was purified by flash column chromatography (silica gel, 5:95 EtOAc:PE) to afford epoxide **15** as a clear oil (470 mg, 36% over 3 steps). δH (400 MHz, $CDCl_3$): 5.43 (1H, d, *J* 6.9, H2), 5.18-5.08 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.08 (2H, d, *J* 7.0, H1), 2.69 (1H, t *J* 6.2, H42), 2.11-1.95 (40H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40 & H41), 1.73 (3H, s, H44), 1.70-1.67 (18H, m, H45, H46, H47, H48, H49 & H50), 1.62-1.59 (9H, m, H51, H52 & H53), 1.29 (3H, s, H55), 1.25 (3H, s, H54); δC (75 MHz, $CDCl_3$): 139.82, 136.12, 135.44, 135.35, 135.31, 135.25, 134.91, 134.07, 125.14, 125.12, 125.06, 125.04, 125.01, 124.66, 124.64, 124.45, 124.27, 64.33, 59.09, 58.47, 39.87, 39.76, 36.43, 32.35, 32.33, 32.31, 32.10, 27.58, 26.80, 26.76, 26.53, 26.49, 26.45, 25.00, 23.57, 23.55, 23.48, 18.85, 16.11; HRMS (ESI+) Found 805.6837; $C_{55}H_{90}NaO_2$, $[M+Na]^+$ requires 805.6833.

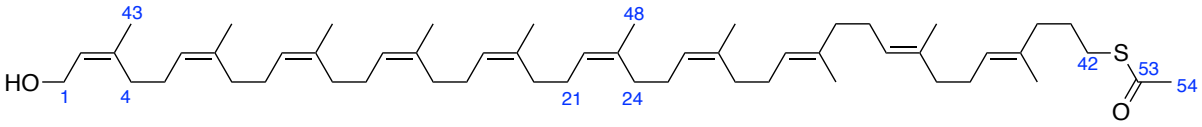
Undecaprenyl α-THP ether (ω-alcohol) (16)



16

Epoxide **5** (600 mg, 0.766 mmol) was dissolved in THF (4.5 mL), cooled to 0 °C and water (0.25 mL) added. To this cooled solution was added periodic acid (192 mg, 0.843 mmol) in water (0.25 mL), and allowed to warm to ambient temperature after 30 mins at 0 °C. After stirring for 2.5 h at ambient temperature, the reaction was diluted with brine (5 mL) and extracted with EtOAc (2 x 10 mL). Combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. This crude mixture was dissolved in CH_2Cl_2 (5 mL) and dihydropyran (105 µL, 1.15 mmol) added, followed by pyridinium *p*-toluenesulfonate (19.0 mg, 0.077 mmol). The reaction mixture stirred for 16 h. Aqueous saturated $NaHCO_3$ (5 mL) was added, followed by extraction with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting material was then dissolved in dry Et_2O (2.3 mL) and sodium borohydride (43 mg, 1.15 mmol) added along with methanol (50 µL). The resulting suspension was stirred for 6 h. Water (5 mL) and Et_2O (5 mL) were added to the reaction mixture, the layers were separated, and the aqueous layer extracted with Et_2O (2 x 10 mL). Combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Crude product was purified by flash column chromatography (SiO_2, 1:9 EtOAc:pentane) to yield the alcohol product **16** as a clear oil (325 mg, 51%). δH (400 MHz, $CDCl_3$): 5.39-5.35 (1H, m, H2), 5.18-5.08 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.82 (0.2H, dd, *J* 5.0, 2.9, β-THP H53), 4.63 (0.8H, t, *J* 3.7, α-THP H53), 4.21 (1H, ddd, *J* 11.8, 6.5, 1.1, H1), 3.98 (1H, ddd, *J* 11.8, 7.5, 0.8, H1'), 3.88 (1H, ddd, *J* 11.3, 8.2, 3.1, α-THP & β-THP H57), 3.63 (2H, t, *J* 6.5, H42), 3.56 (0.2H, m, H57), 3.58-3.54 (0.2H, m, β-THP H57'), 3.52-3.49 (0.8H, m, α-THP H57'), 2.11-1.96 (40H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40 & H41), 1.89-1.76 (2H, m, 2xTHP-H) 1.76-1.74 (3H, m, H43), 1.70-1.65 (18H, m, H44, H45, H46, H47, H48 & H49), 1.62-1.49 (13H, m, H50, H51, H52 & 4xTHP-H); δC (75 MHz, $CDCl_3$): 140.56, 135.66, 135.49, 135.38, 135.36, 135.35, 135.31, 134.95, 134.71, 125.17, 125.16, 125.13, 125.09, 124.97, 124.77, 124.50, 124.29, 121.76, 98.63, 98.00, 63.59, 63.51, 62.97, 62.29, 60.54, 39.89, 39.79, 36.15, 32.58, 32.38, 32.35, 32.34, 32.14, 30.86, 26.82, 26.79, 26.75, 26.68, 25.55, 26.51, 25.66, 23.72, 23.61, 23.58, 23.54, 19.70, 16.14, 16.12, 16.00; HRMS (ESI+) Found 844.7562; $C_{57}H_{98}NO_3$, $[M+NH_4]^+$ requires 844.7547.

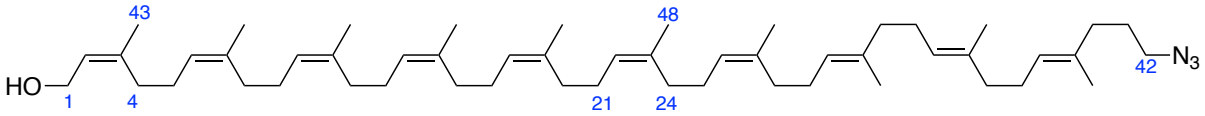
Und-OH (ω-thioacetate) (17)



17

Alcohol **16** (100 mg, 0.121 mmol) was dissolved in CH_2Cl_2 (0.2 mL), cooled to 0 °C, and triethylamine (20.2 µL, 0.145 mmol) added. After stirring for 10 min, mesyl chloride (18.7 µL, 0.242 mmol) was added, and the reaction mixture stirred at ambient temperature for 2 h. The reaction mixture was diluted with CH_2Cl_2 (1 mL) and water (1 mL), the phase separated and the aqueous phase extracted with CH_2Cl_2 (2 x 1 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude mesylate was dissolved in dry DMF (0.75 mL), and heated to 60 °C, at which point potassium thioacetate (27.6 mg, 0.242 mmol) was added. After 1 h, the reaction mixture was concentrated and CH_2Cl_2 (5 mL) and water (5 mL) were added. The phases were separated and the aqueous phase extracted with CH_2Cl_2 (2 x 5 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to yield crude thioacetate (100 mg, 93%), which was used in the subsequent step without further purification (HRMS (ESI+) Found 902.7418; $C_{59}H_{100}NO_3S^+$, $[M+NH_4]^+$ requires 902.7443). This crude material was dissolved in THF (1 mL) and a solution of *p*-toluene sulfonic acid (5 mg, 0.024 mmol) in MeOH (1 mL) added dropwise over 1 min. The reaction mixture was stirred at ambient temperature for 1 h and then saturated aqueous Na_2SO_4 (2.5 mL) and water (2.5 mL) were added. The aqueous layer was extracted with Et_2O (2 x 5 mL) and the combined organic layers dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (SiO_2, 1:9 EtOAc:pentane) to yield thioacetate **17** as a clear oil (50 mg, 50%). δ_H (600 MHz, $CDCl_3$): 5.44 (1H, td, *J* 7.2, 1.3, H2), 5.16-5.09 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.09 (2H, dd, *J* 7.2, 0.8, H1), 2.82 (2H, t, *J* 7.4, H42), 2.31 (3H, s, H54), 2.10-1.96 (38H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40), 1.75-1.73 (3H, m, H43), 1.70-1.63 (20H, m, H41, H44, H45, H46, H47, H48 & H49), 1.61 (3H, s, CH3), 1.59 (3H, s, CH3), 1.58 (3H, s, H52); δ_C (75 MHz, $CDCl_3$): 196.05, 139.95, 136.18, 135.49, 135.40, 135.36, 135.35, 135.32, 134.94, 133.68, 125.50, 125.16, 125.15, 125.13, 125.07, 125.02, 124.67, 124.62, 124.48, 124.26, 59.14, 39.88, 39.77, 32.35, 32.32, 32.13, 30.76, 28.74, 27.84, 26.82, 26.79, 26.76, 26.55, 26.51, 26.46, 23.61, 23.59, 23.57, 23.50, 16.14, 16.11, 15.91; HRMS (ESI+) Found 818.6726; $C_{54}H_{92}NO_2S$, $[M+NH_4]^+$ requires 818.6849.

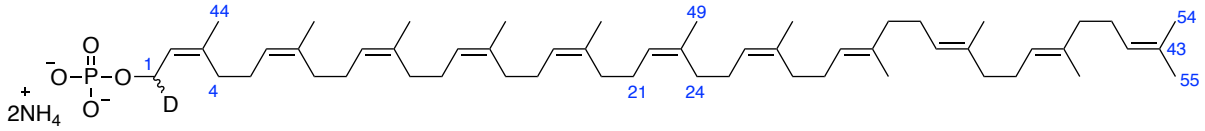
Und-OH (ω-azide) (18)



18

The ω-mesylate was synthesized as described above. This material (45 mg, 0.063 mmol) was dissolved in THF (0.5 mL). To this solution was added *p*-toluene sulphonic acid (1.15 mg, 0.0067 mmol) in MeOH (0.5 mL) over 1 min and the resulting reaction mixture was stirred for 16 h at ambient temperature. Aqueous saturated $NaHCO_3$ (2 mL) was added, the phase separated and the aqueous phase extracted with CH_2Cl_2 (2 x 1 mL). Combined organic extracts were then dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. This crude material was purified by flash column chromatography (SiO_2, 1:9 EtOAc:PE) to yield azide **18** as a clear oil (25 mg, 53%).δH (600 MHz, $CDCl_3$): 5.44 (1H, td, *J* 7.2, 1.4, H2), 5.16-5.09 (9H, m, H6, H10, H14, H18, H22, H26, H30, H34 & H38), 4.09 (2H, app. t, *J* 6.1, H1), 3.23 (2H, t, *J* 7.0, H42), 2.10-1.95 (38H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40), 1.76-1.74 (3H, m, H43), 1.70-1.67 (20H, m, H41, H44, H45, H46, H47, H48 & H49), 1.62-1.59 (9H, m, H50, H51 & H52); δC (75 MHz, $CDCl_3$): 134.00, 136.20, 135.51, 135.51, 135.42, 135.38, 135.37, 135.31, 134.90, 133.42, 125.73, 125.20, 125.19,125.17, 125.11, 125.06, 124.69, 124.66, 124.58, 124.33, 59.19, 51.07, 39.91, 39.77, 36.66, 32.40, 32.38, 32.36, 32.16, 27.17, 26.86, 26.81, 26.79, 26.57, 26.54, 26.50, 23.60, 23.59, 23.57, 23.51, 16.16, 16.12, 15.94; HRMS (ESI+) Found 790.6592; $C_{52}H_{85}N_3NaO$, $[M+Na]^+$ requires 790.6590.

***d₁*-Und-P (20)**

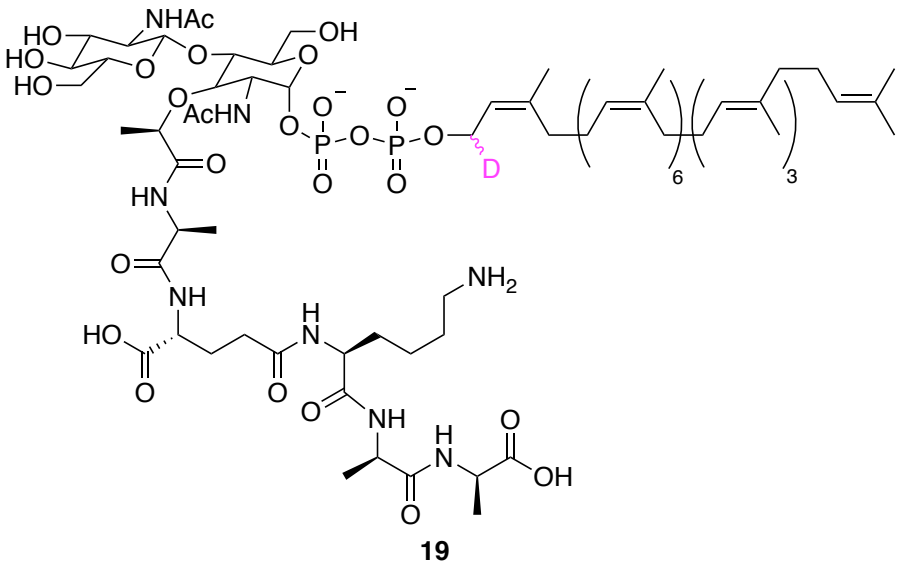


20

d₁-Und-OH (**4**) (180 mg, 0.234 mmol) was dissolved in dry CH_2Cl_2 (3 mL) and added rapidly via syringe to a vigorously stirred suspension of 5-ethylthio-1*H*-tetrazole (143 mg, 1.101 mmol) and bis(2-cyanoethyl)-*N*,*N*'-diisopropylphosphoramidite (190 mg, 0.703 mmol) in dry CH_2Cl_2 (3 mL). The reaction mixture became homogeneous within a few min. After 3 h, the mixture was diluted with CH_2Cl_2 (40 mL) and washed with aqueous saturated $NaHCO_3$ (30 mL), water (30 mL) and brine (30 mL). The organic solution was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to yield the phosphite as a yellow

oil. The product was dissolved in THF (6 mL) and cooled to -78 °C. Hydrogen peroxide (30%, 0.6 mL) was added dropwise via syringe to the vigorously stirred solution. After the addition was complete, the ice bath was removed and the mixture was allowed to warm to ambient temperature over 2 h. The reaction mixture was then diluted with ice-cold saturated sodium sulfite (5 mL) and stirred at 0 °C for 5 min. The reaction mixture was then extracted with EtOAc (50 mL) and the organic layer was washed with saturated aqueous $NaHCO_3$ (25 mL), water (25 mL) and brine (25 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to yield the phosphate as a yellow oil. The crude phosphate was suspended in anhydrous MeOH (4.5 mL) and petroleum ether (1 mL) and a 25% NaOMe in MeOH solution (0.175 mL) was added. The resulting suspension was stirred at ambient temperature for 16 h. The reaction mixture was diluted with CH_2Cl_2 (7 mL) and carefully neutralized with DOWEX 50WX8 H^+ form resin. The resin was removed by filtration and the filtrate concentrated *in vacuo*. The resulting yellow oil was purified by column chromatography (SiO_2, 90:10:0:0.1 to 65:25:5:0.1 $CHCl_3$:MeOH:H_2O:NH_4OH) to yield the product as an off-white foam (120 mg, 58%). δH (400 MHz, $CDCl_3$): 5.34 (1H, br. s, *J* 7.2, H2), 5.19-5.01 (10H, m, H6, H10, H14, H18, H22, H26, H30, H34, H38 & H42), 4.37 (1H, br. s, H1), 2.09-1.94 (40H, m, H4, H5, H8, H9, H12, H13, H16, H17, H20, H21, H24, H25, H28, H29, H32, H33, H36, H37, H40 & H41), 1.71-1.54 (36H, m, H44, H45, H46, H47, H48, H49, H50, H51, H52, H53, H54 & H55); δC (75 MHz, $CDCl_3$): 145.47, 135.31, 135.08, 135.01, 131.35, 125.18, 125.17, 125.08, 124.55, 124.41, 124.38, 124.29, 68.63, 39.91, 39.88, 32.37, 32.35, 32.33, 32.15, 26.92, 26.83, 26.80, 26.55, 26.52, 26.49, 26.40, 25.84, 23.62, 23.57, 23.50, 17.83, 16.16, 16.15, 16.14; δP (400 MHz, $CDCl_3$): 0.71; HRMS (ESI-): found 846.6643; $C_{55}H_{89}DO_4P$, $[M-H]^-$ requires 846.6639.

***d*$_1$-Lipid II (19)**



19

Dibenzyl phosphate **21** (synthesized as previously described[1]) (50 mg, 33 µmol) was dissolved in anhydrous MeOH (6 mL) and the flask flushed with an argon baloon. Pd/C (10 % w/w, 106 mg, 99 µmol) was added and the resulting suspension stirred under a H_2 atmosphere for 3 h. The suspension was then filtered through celite, which was washed with MeOH (2 x 3 mL). Pyridine (1 mL) was added to the filtrate, which was then concentrated *in vacuo* and dried by high vacuum for 1 h to yield the sugar phosphate salt as a white solid. This salt was dissolved in dry DMF (1 mL) and dry THF (1 mL) and carbonyl diimidazole (26.8 mg, 165 µmol) was added. The resulting clear solution was stirred at ambient temperature for 2 h, at which point analysis by ESI showed complete product formation ($[M-H]^-$ = 1388.4). Excess carbonyl diimidazole was destroyed by the addition of dry MeOH (5.34 µL, 132 µmol) and stirring continued for 45 min. The reaction mixture was then concentrated *in vacuo* and dried under high vac for 1 h. To resulting activated phosphate was added a solution of *d*$_1$-Und-P (29 mg, 33 µmol) in THF (2 mL) and 5-ethylthio-1*H*-tetrazole (4.3 mg, 33 µmol). The resulting solution was stirred for 96 h under argon at ambient temperature and concentrated *in vacuo*. To this crude mixture was added 1,4-dioxane (1 mL) and a solution of sodium hydroxide (40 mg, 1 mmol) in water (1 mL). The resulting mixture was stirred at 37 °C for 2 h and filtered through an aqueous filter disc, which was washed with 1:1 H_2O/1,4-dioxane (2 mL). Lipid II was then purified by HPLC: column = Phenomenex Luna C_{18}(2) 100 Å prep-scale column; flow-rate = 20 mL/min, UV = 220 nm, method: solvent A = 50 mM NH_4HCO_3(aq), solvent B = MeOH, gradient = 2 to 98 % B over 30 min, 98 % B for 10 min, 98 to 2 % B over 1 min and 2 % B for 4 min. *d*$_1$-Lipid II eluted between 33.7 – 34.4 min. Product containing fractions were concentrated by rotary evaporator and diluted with H_2O, frozen and lyophilized to yield *d*$_1$-lipid II (**19**)

as a fluffy white power (17.7 mg, 29%). HRMS (ESI-): found 1875.0588; $C_{94}H_{153}DN_8O_{26}P_2$, $[M-H]^-$ requires 1875.0596.

Expression and purification of UdpK

The DNA for UdpK WT from *Streptococus mutans* was cloned into the pETDuet vector to produce an expression construct with an N-terminal TEV-cleavable hexahistidine-tag. For expression, chemically competent C43(DE3) cells were transformed with the pETDuet vector and grown in ampicillin-supplemented (50 µg/mL) LB agar plates. The transformed C43(DE3) cells were used to prepare an overnight (16 h) starter culture with which to inoculate TB medium. Cultures were grown at 180 rpm and 37 °C to an OD_{600} of 0.6 and cooled to 20 °C on ice. Expression of UdpK WT was induced with 1 mM IPTG and cells were grown for 20 h at 20 °C post-induction. Cells were harvested at 6,000 x *g* for 10 min at 4 °C, resuspended in buffer A (75 mM Tris-HCl, 300 mM NaCl, 2 mM EDTA, final pH 7.8) and lysed at 1,000-1,750 bar using an EmulsiFlex-C5 homogeniser (Avestin, Canada) at 4 °C. Cell debris was removed by centrifugation at 9,000 x *g* for 25 min. Membranes were pelleted by centrifugation at 120,000 x *g* for 1 h at 4 °C, solubilized in buffer B (75 mM Tris-HCl, 300 mM NaCl, 2 mM EDTA, 3 %(v/v) Empigen, final pH 7.8) for 30 min at 4 °C followed by centrifugation at 9,000 x *g* for 20 min at 4 °C. The supernatant was mixed with Ni-NTA resin (Qiagen, Germany) on a mixer for 60 min at 4 °C. The resin was washed with 50 mL of buffer C (40 mM HEPES, 300 mM NaCl, 1.5 %(v/v) Empigen, 40 mM Imidazole, 10 µM BHT, final pH 7.5). The Empigen detergent was exchanged to decyl maltoside (DM) by pulse washing the resin with 50 mL of buffer D (20 mM HEPES, 0.25 %(w⁄v) DM, 100 mM NaCl, final pH 7.5). Protein was eluted with buffer E (10 mM Tris-HCl, 100 mM NaCl, 0.5 %(w/v) DM, 400 mM Imidazole, final pH 7.4). The hexahistidine-tag was cleaved by incubation for 16 h with TEV protease at 4 °C. The TEV protease and any uncleaved UdpK WT were removed by reverse IMAC using Ni-NTA resin. The cleaved UdpK protein was further purified using a HiLoad 16/60 Superdex 200 column (GE Healthcare, UK) equilibrated in buffer F (10 mM Tris-HCl, 150 mM NaCl, 0.25 %(w/v) DM, final pH 7.4). The purified protein was concentrated in a 50 kDa MWCO Amicon Ultra 15 concentrator (Millipore, USA) to 12 mg/mL, aliquoted, snap frozen in liquid nitrogen and stored at -80 °C for subsequent use in functional assays.

Kinase activity assay

Each of the compounds tested was solubilized by sonication using 15 mM LDAO in 2 %(v/v) DMSO[2] to a concentration of 2.5 mM. The assay mix contained 75 mM PIPES pH 6.9, 50 mM LiCl, 0.1 mM EGTA, 0.1 mM EDTA, 1 %(w⁄v) DM, 1 mM PEP, 3 mM ATP, 15 mM magnesium acetate, 0.2 mM DTT, 0.25 mM NADH, 20 U⁄mL PK and LDH. To eliminate any ADP in the system and for thermal equilibration, the reaction mixture was incubated at 30 °C for 10 min prior to assay. The kinase reaction, in triplicate, was initiated by adding 0.2 mL Assay Mix to 0.4 µL UdpK solution of a 1.2 mg/mL stock, purified protein in Buffer F. Immediately, the plate was placed in a SpectraMax M5e plate reader (Molecular Devices) pre-warmed to 30 °C. A340 was recorded every 15 s with mixing for 2 s between each reading. UdpK-free blanks were run with each assay using Buffer F in place of protein solution. Background rates, corresponding to non-enzymatic hydrolysis of ATP and NADH photobleaching, were subtracted from those recorded in the presence of UdpK.[3]

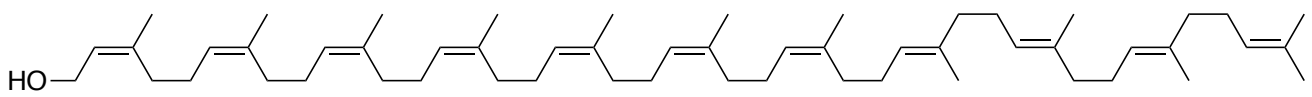
References

1) Y. Y. Dong, H. Wang, A. C. W. Pike, S. A. Cochrane, S. Hamedzadeh, F. J. Wyszyński, S. R. Bushell, S. F. Royer, D. A. Widdick, A. Sajid, H. I. Boshoff, Y. Park, R. Lucas, W-M. Liu, S. S. Lee, T. Machida, L. Minall, S. Mehmood, K. Belaya, W-W. Liu, A. Chu, L. Shrestha, S. M.M. Mukhopadhyay, C. Strain-Damerell, R. Chalk, N. A. Burgess-Brown, M. J. Bibb, C. E. Barry 3rd, C. V. Robinson, D. Beeson, B. G. Davis, E. P. Carpenter. *Cell* **2018**, *175*, 1045.

2) L. Y. Huang, S. H. Huang, Y. C. Chang, W. C. Cheng, T. J. R. Cheng and C. H. Wong. *Angew. Chem. Int. Ed*. **2014**, *53*, 8060.

3) D. Li and M. Caffrey. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 8639.

NMR Spectra



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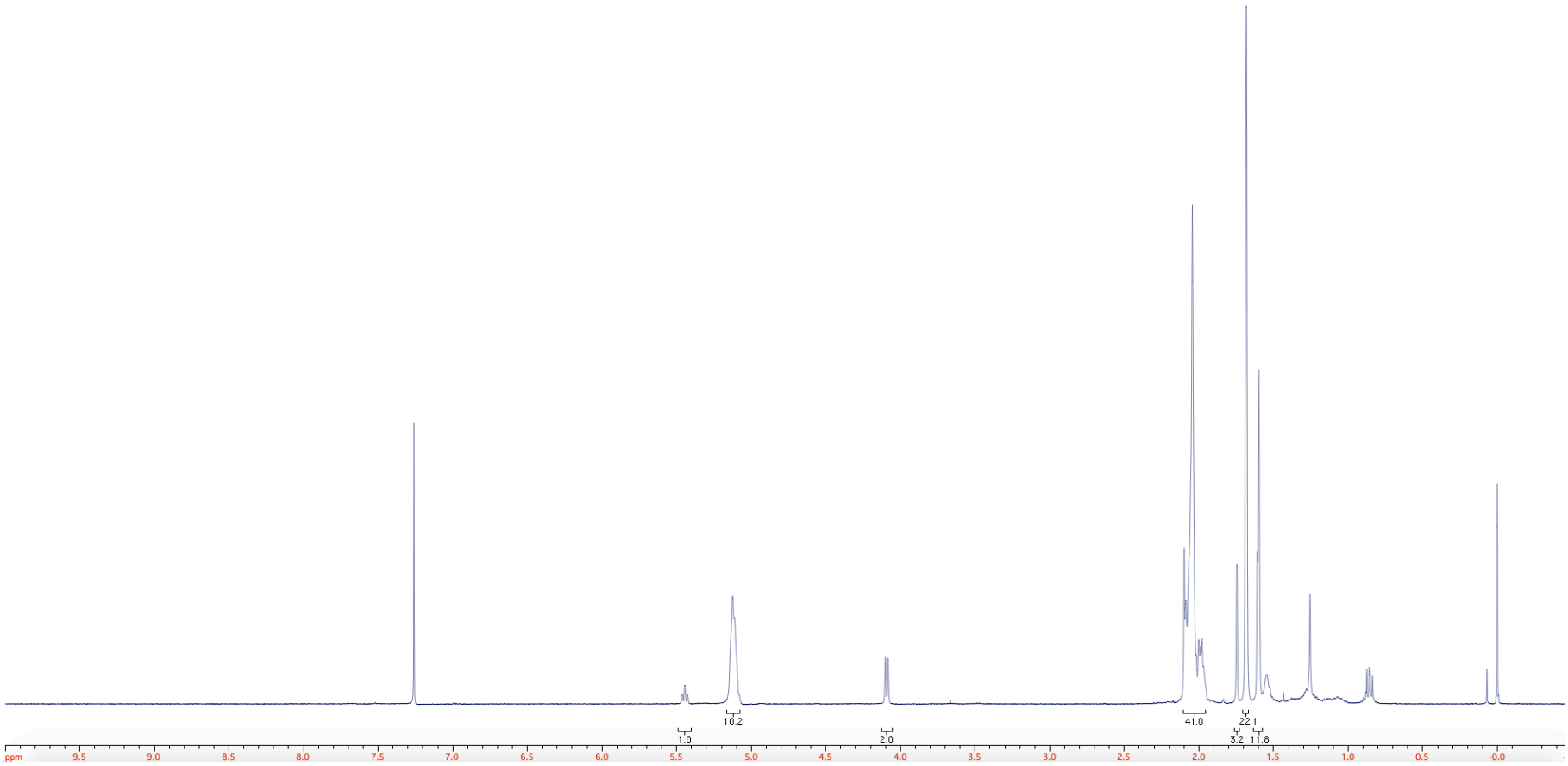

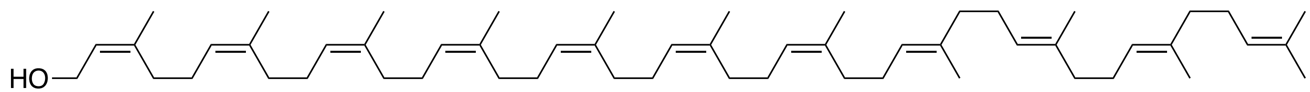
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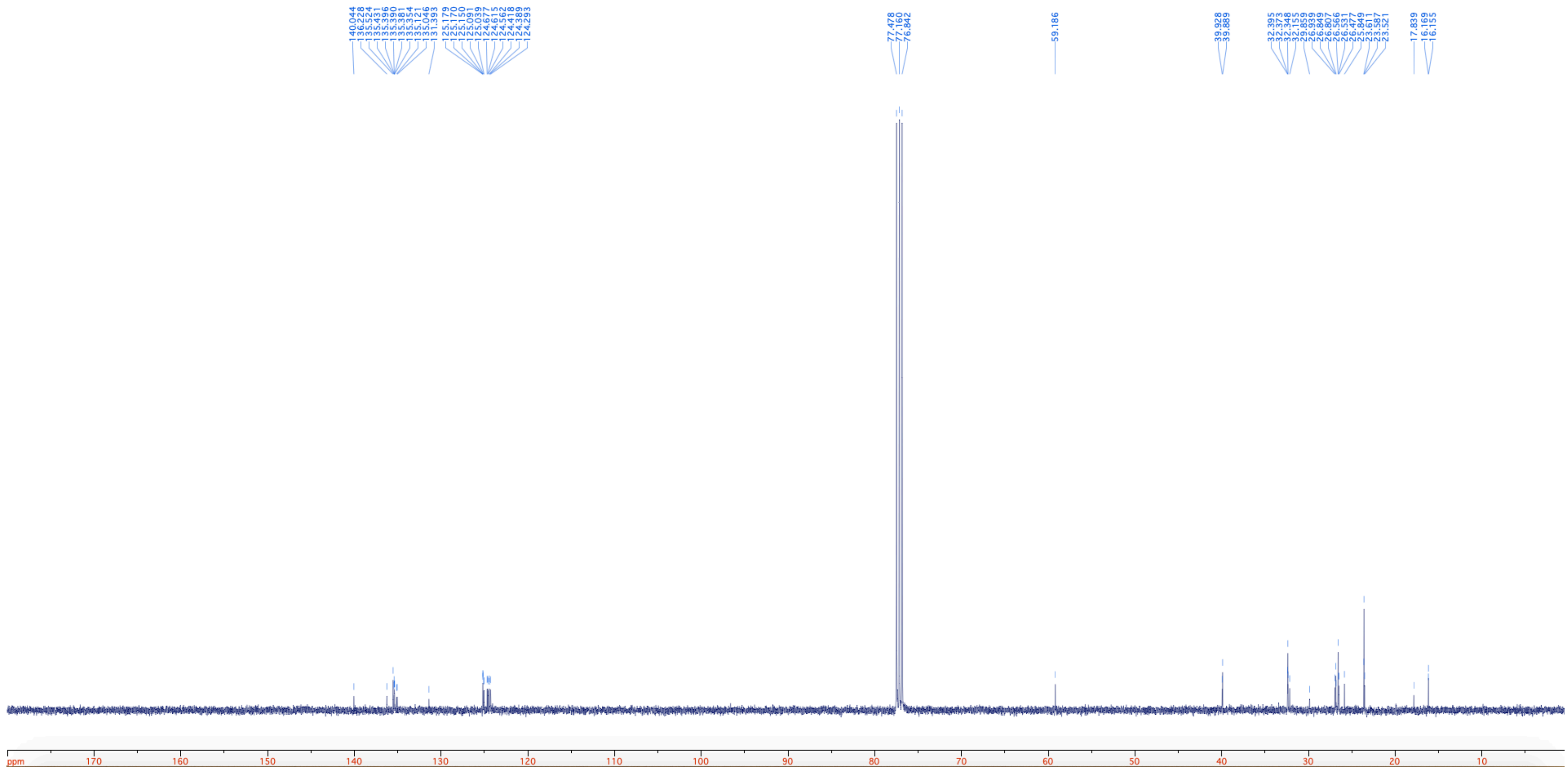
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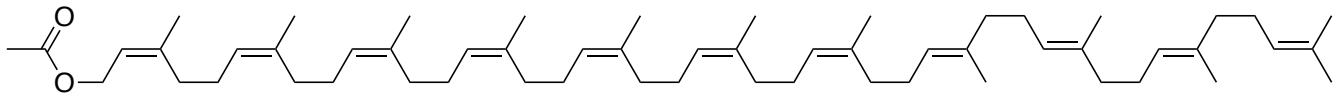

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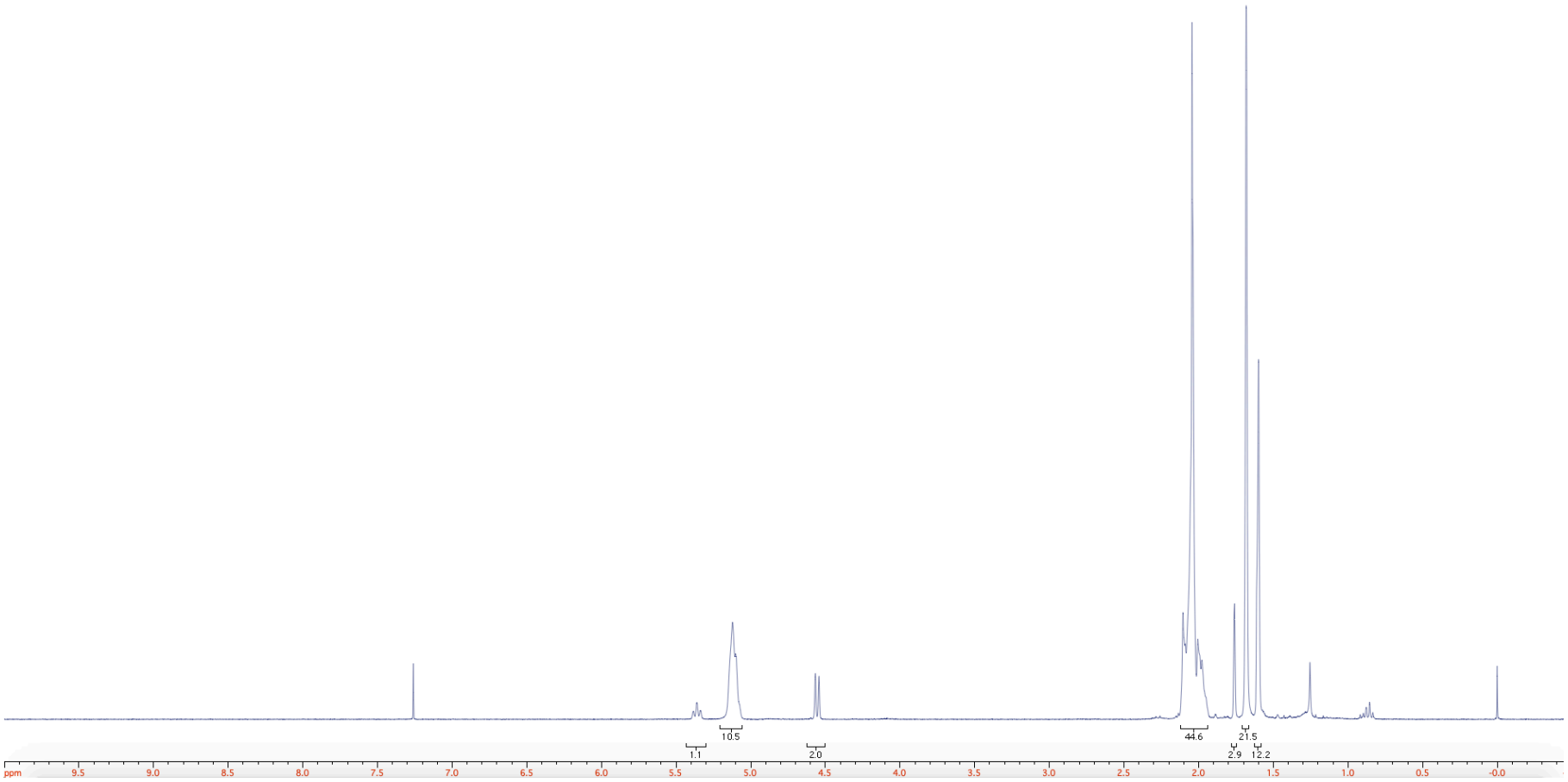
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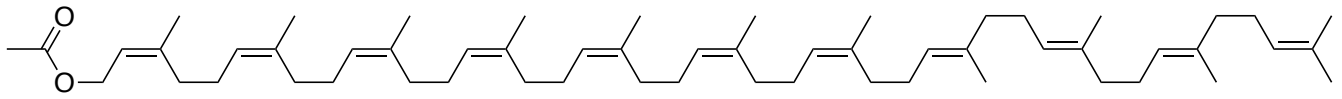

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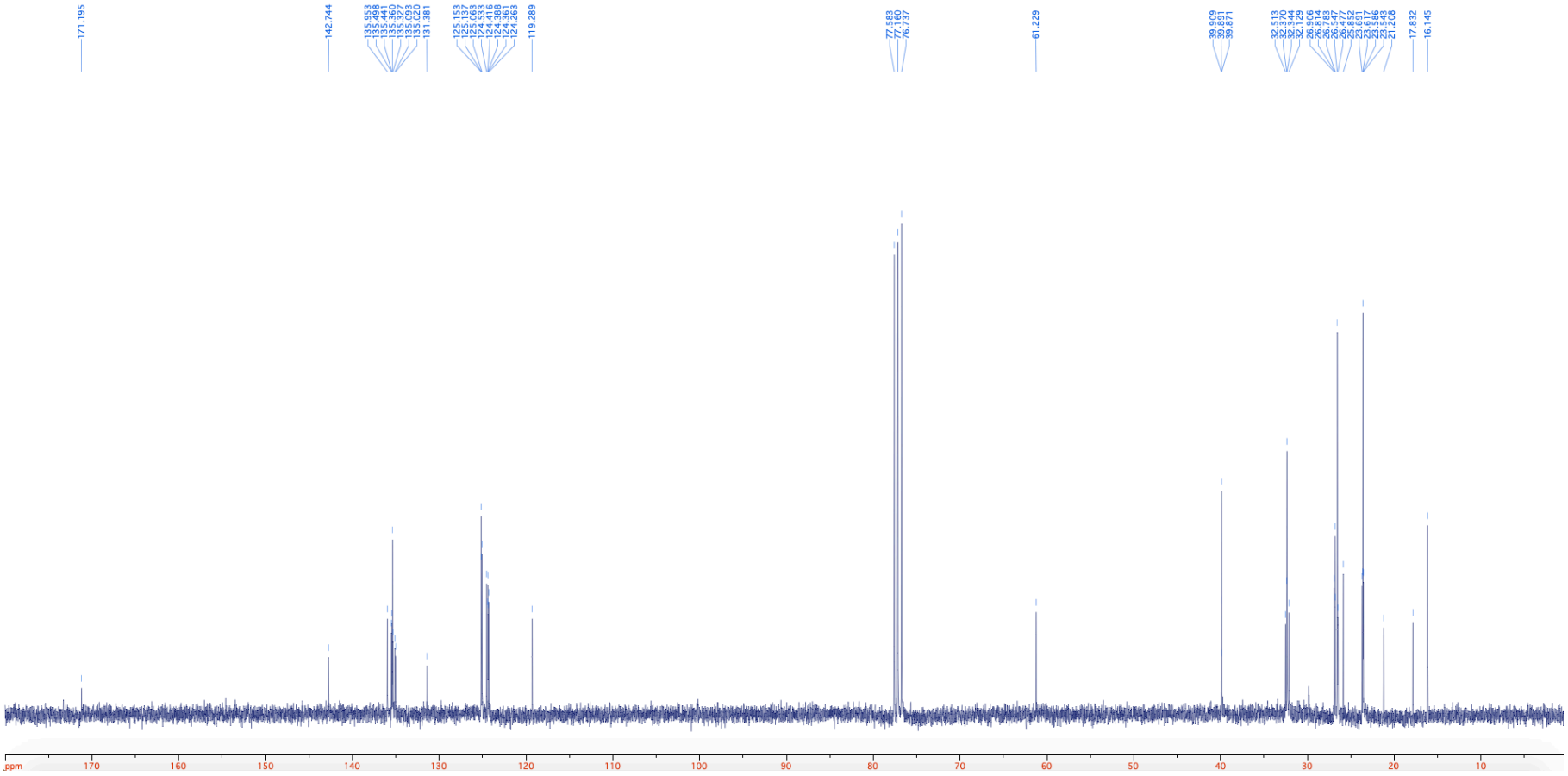
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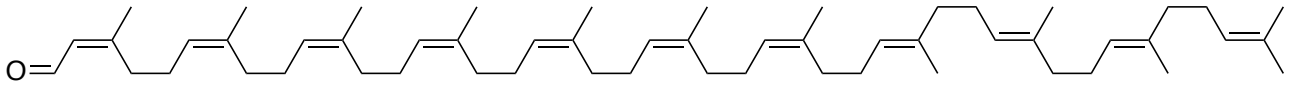
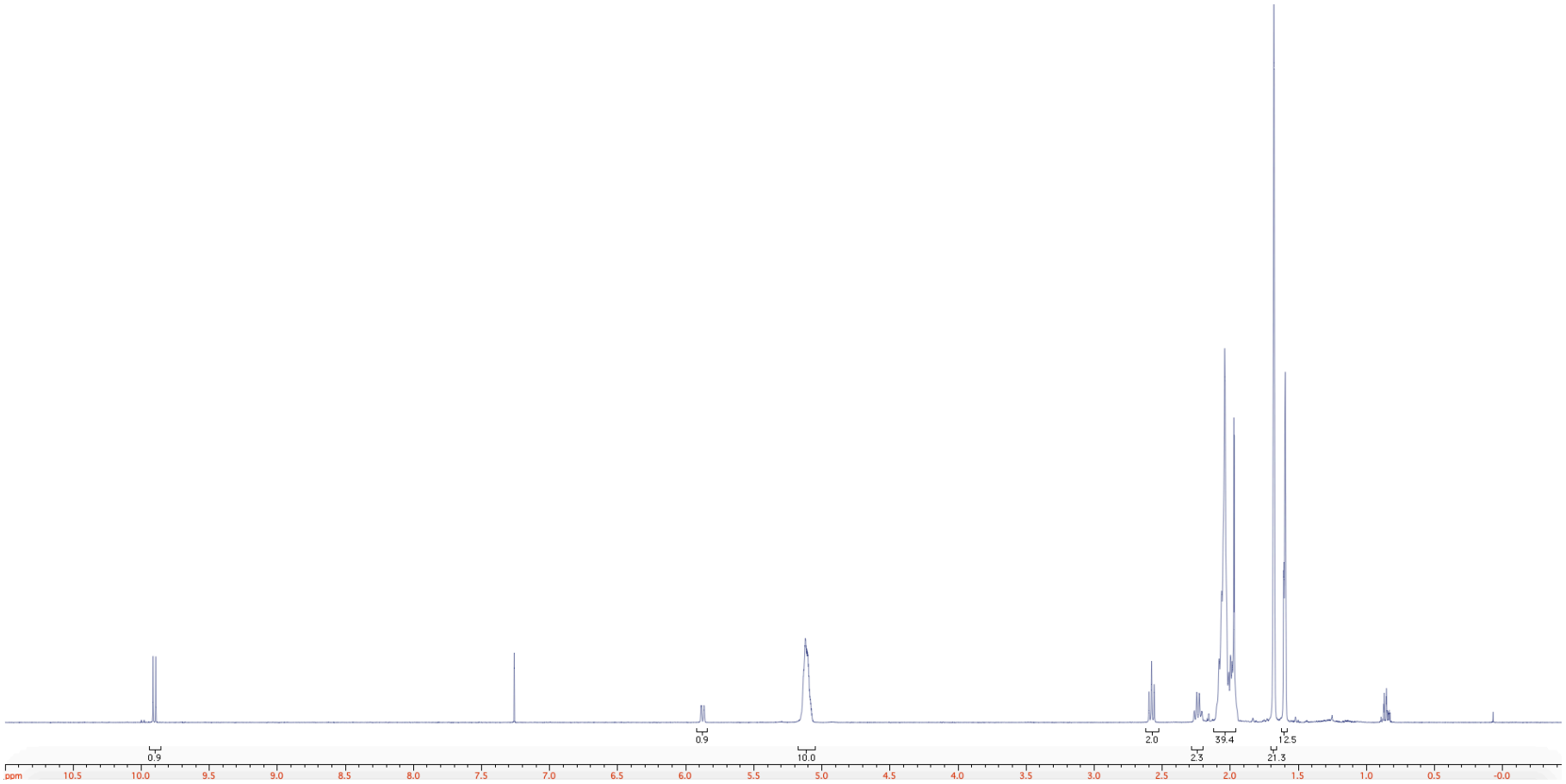
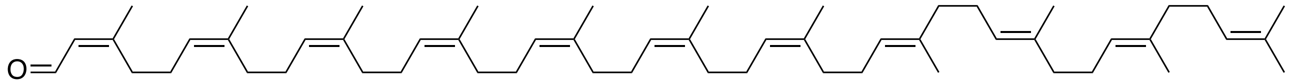


3

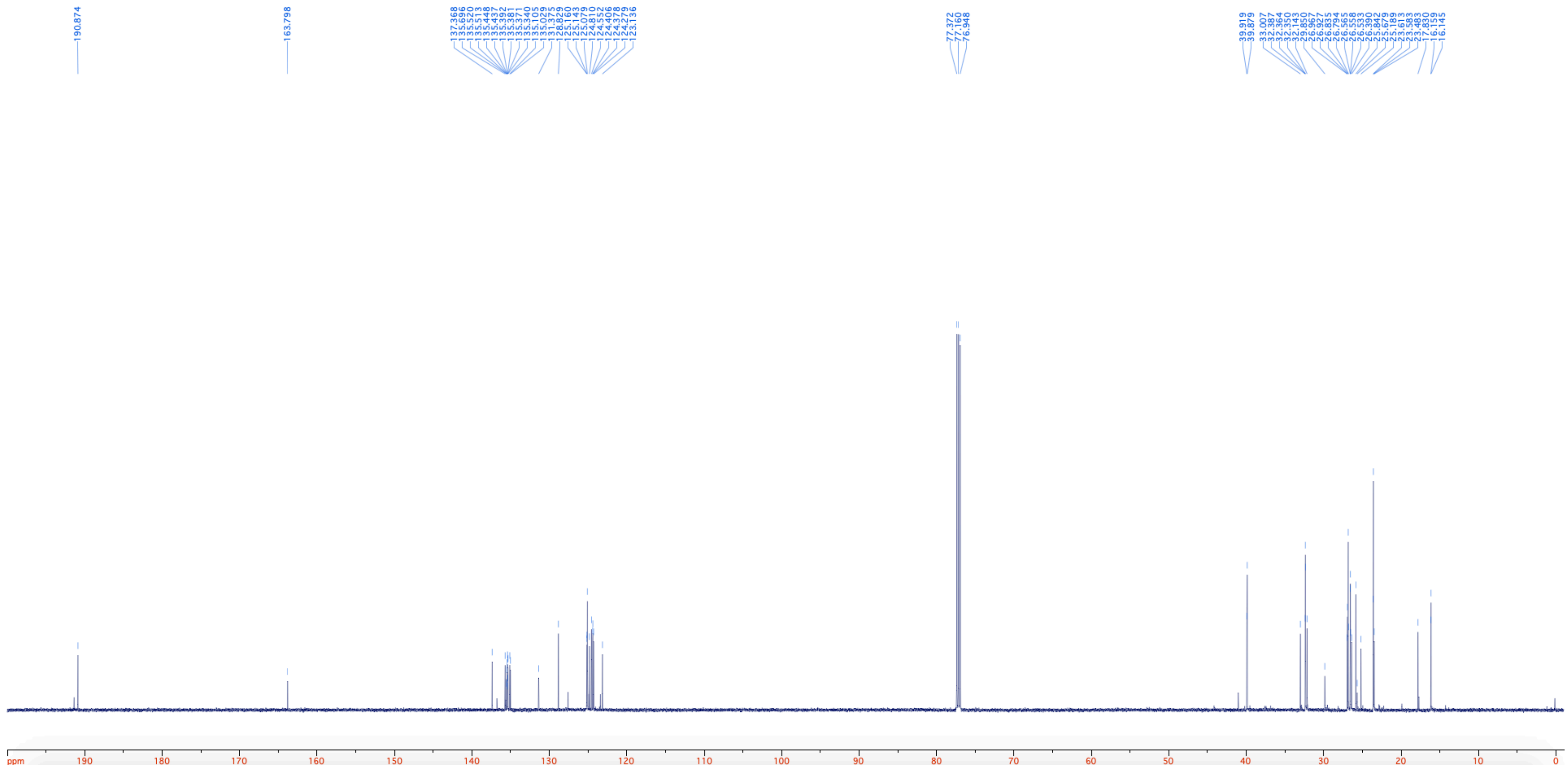
^{1}H-NMR:

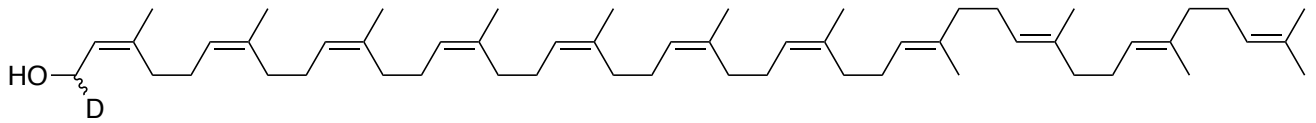

0.9
0.9
10.0
2.0
2.3
39.4
12.5
21.3
ppm
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


O

3

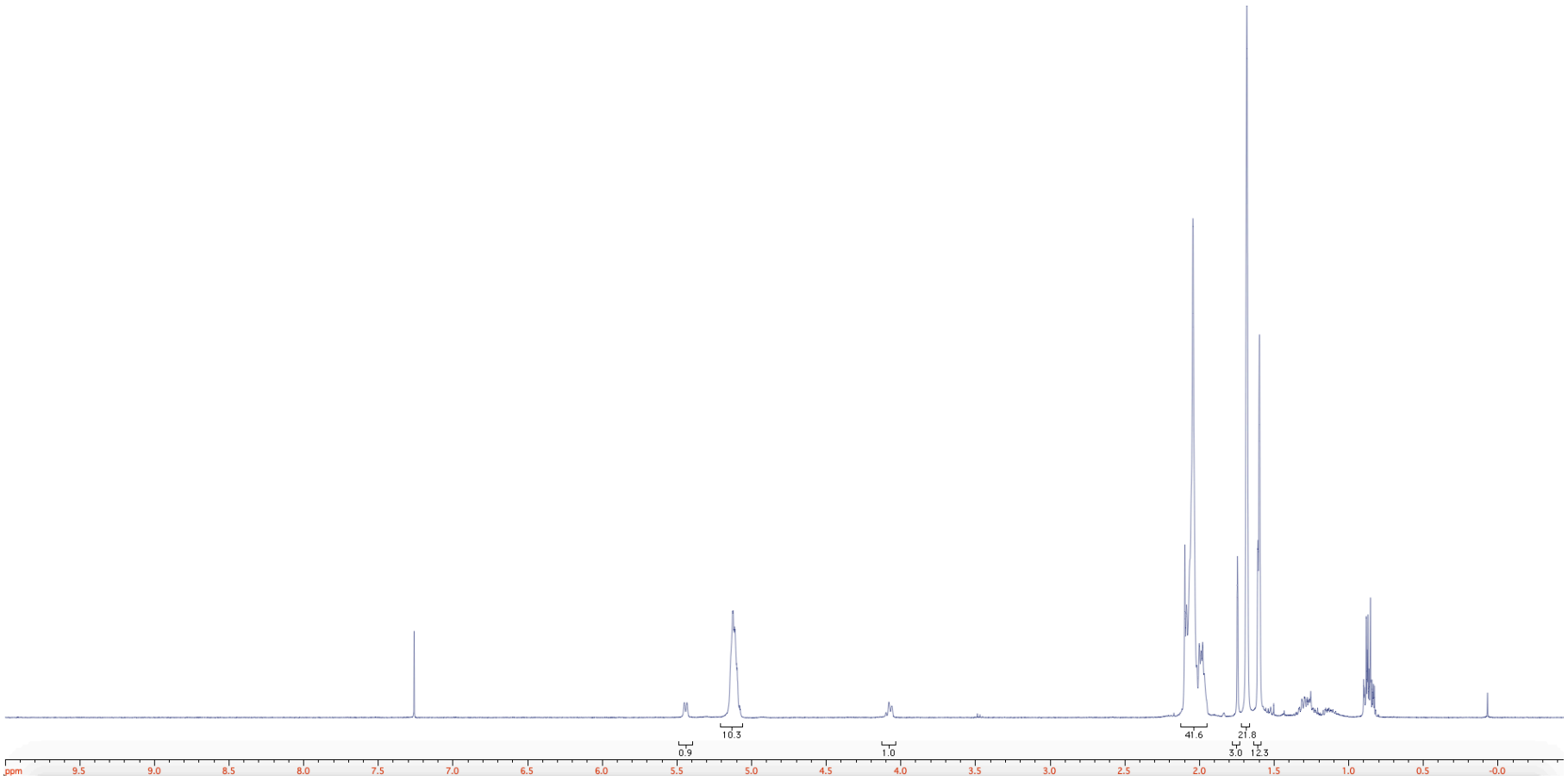
[13]C-NMR:

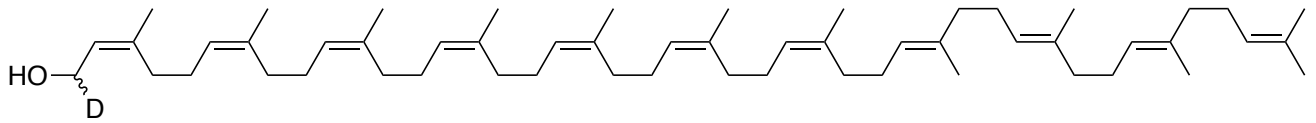

190.874
163.798
137.368
135.696
135.520
135.513
135.448
135.437
135.392
135.381
135.371
135.340
135.105
135.029
131.375
128.829
125.160
125.143
125.079
124.810
124.452
124.406
124.378
124.279
123.136
77.372
77.160
76.948
39.919
39.879
33.007
32.387
32.364
32.350
32.143
29.850
26.967
26.927
26.835
26.794
26.565
26.558
26.530
26.390
25.842
25.679
25.189
23.613
23.583
23.483
17.830
16.159
16.145
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


HO
D

4

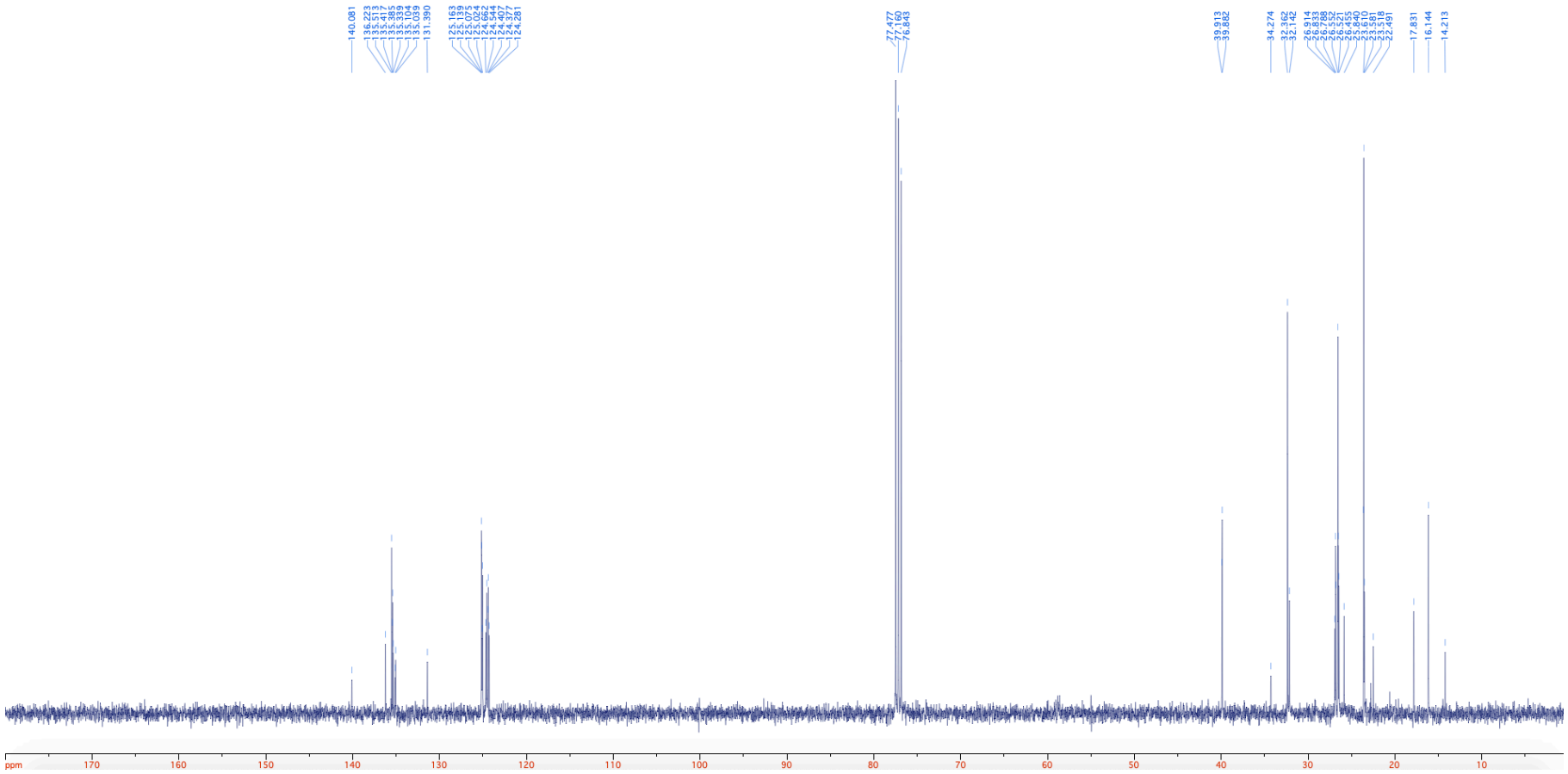
^{1}H-NMR:

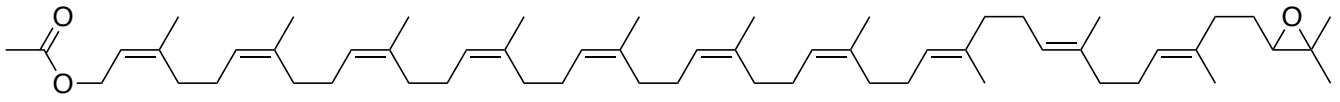

10.3
0.9
1.0
41.6
21.8
3.0
12.3
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


HO
D

4

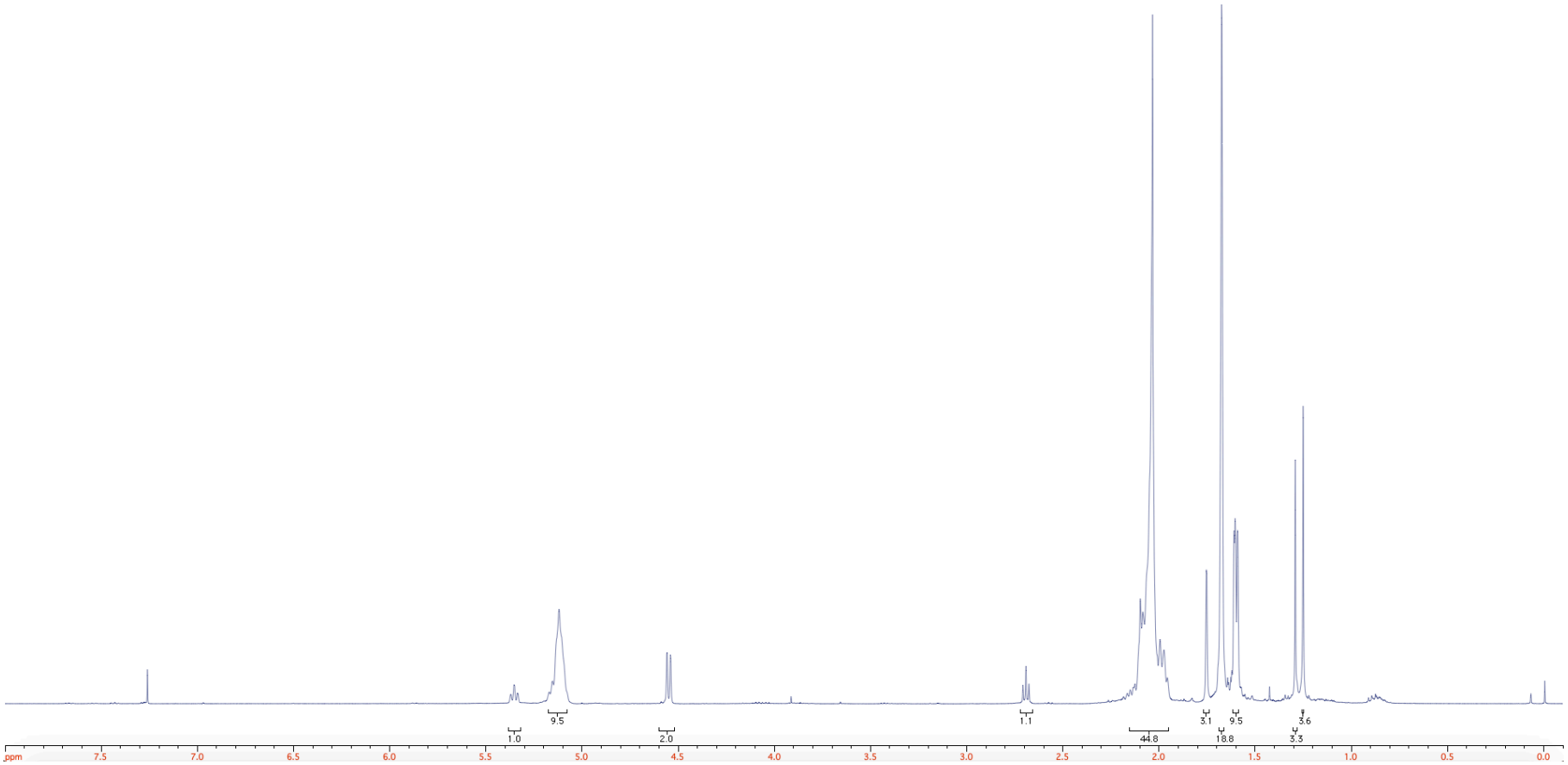
^{13}C-NMR:

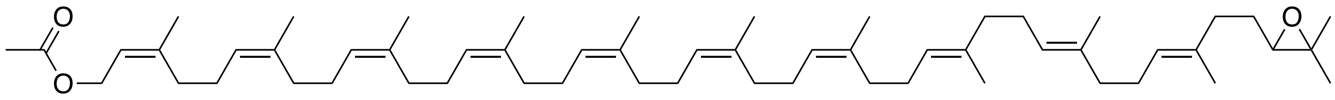

140.081
136.223
135.513
135.417
135.385
135.339
135.104
135.039
131.390
125.163
125.139
125.075
125.024
124.662
124.544
124.407
124.377
124.281
77.477
77.160
76.843
39.913
39.882
34.274
32.362
32.142
26.914
26.833
26.788
26.732
26.521
26.455
26.440
23.610
23.581
23.518
22.491
17.831
16.144
14.213
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



5

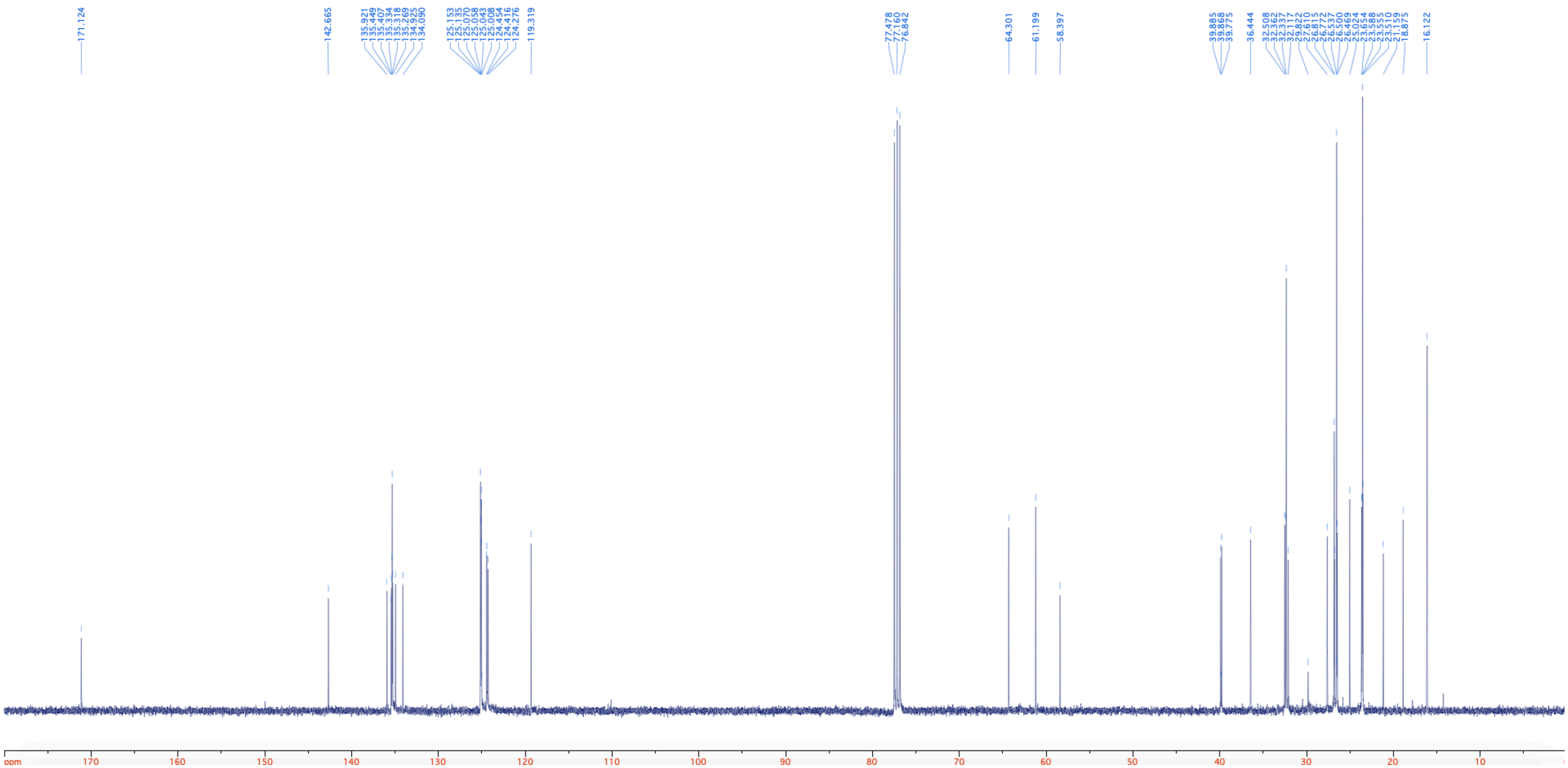
^{1}H-NMR:

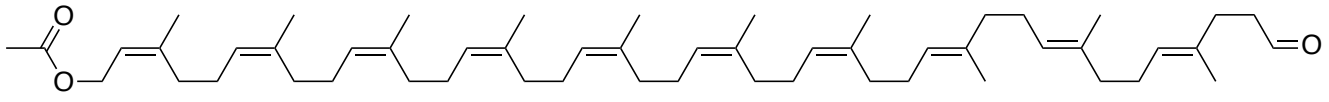

9.5
1.0
2.0
1.1
44.8
3.1
18.8
9.5
3.3
3.6
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



5

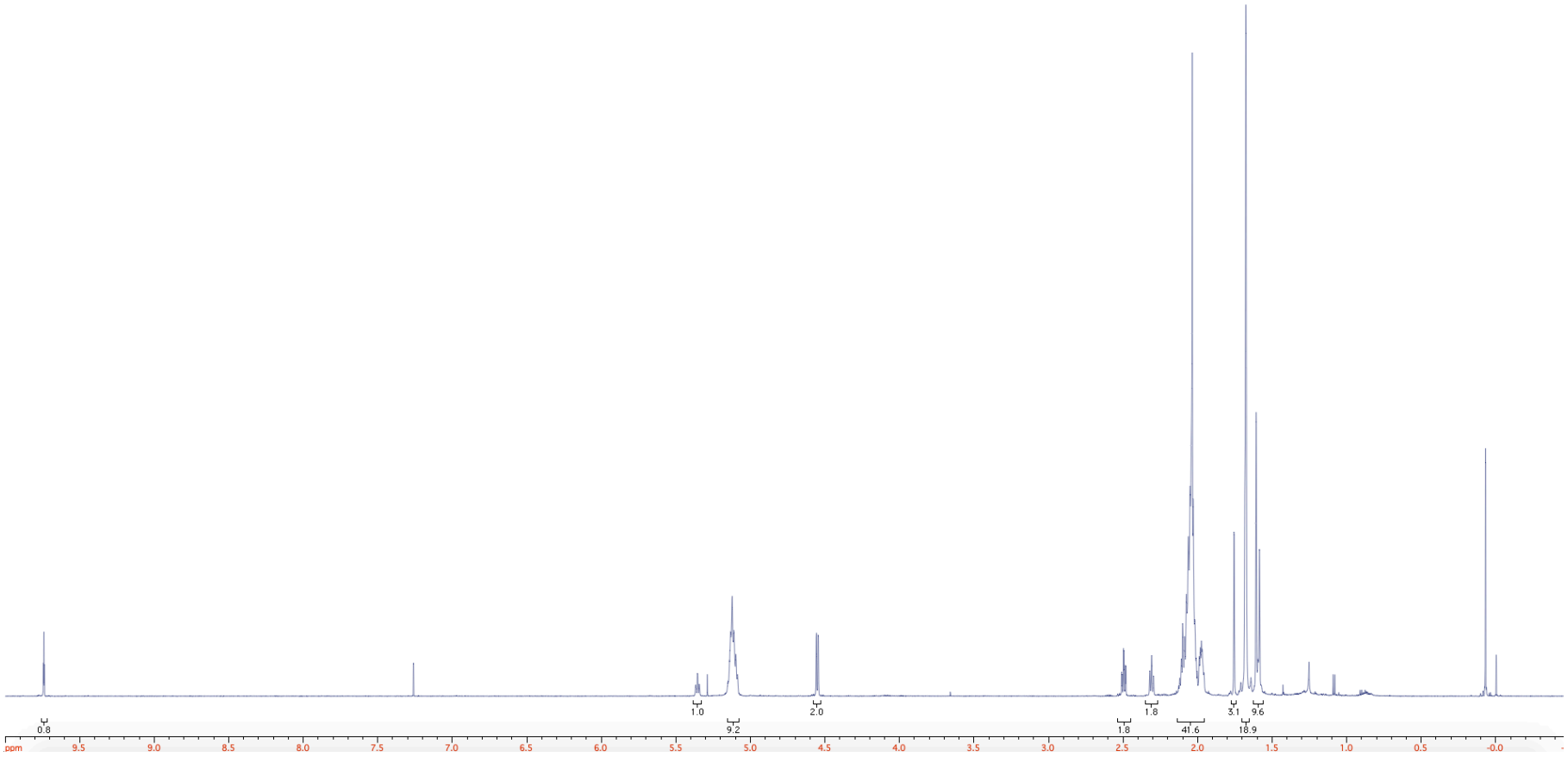
^{13}C-NMR:

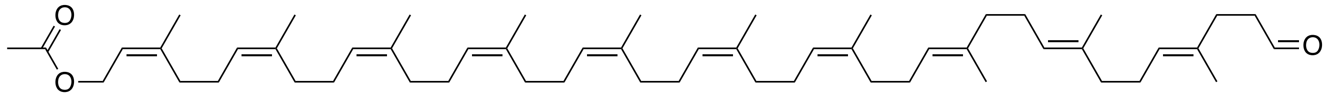




6

^{1}H-NMR:

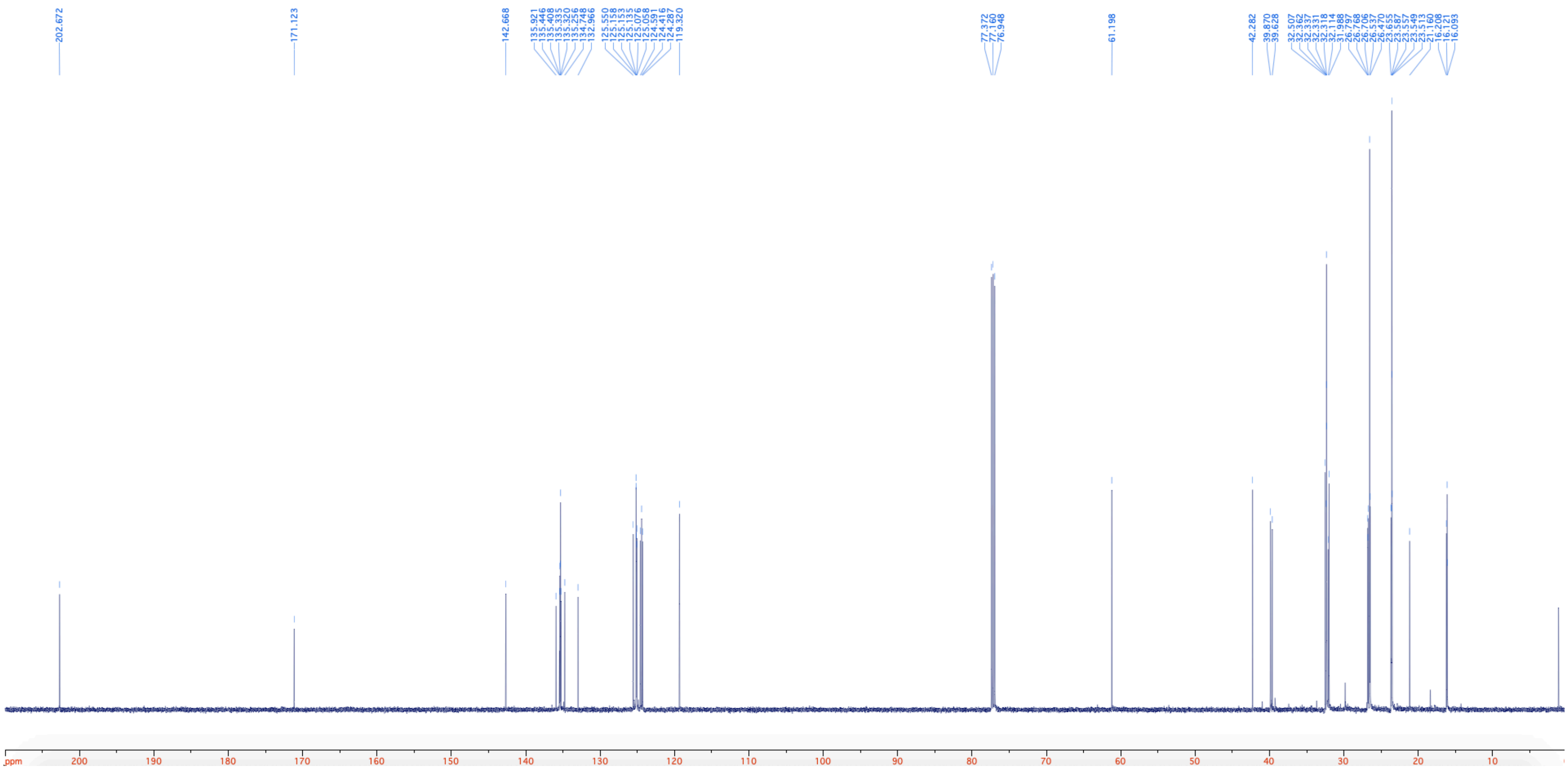

1.0
2.0
1.8
3.1
9.6
0.8
9.2
1.8
41.6
18.9
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0



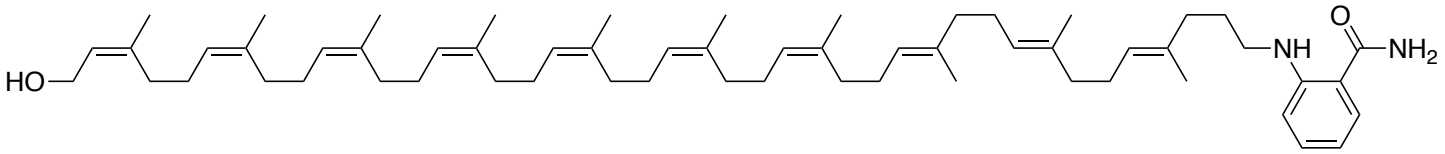
O
O
O

6

^{13}C-NMR:

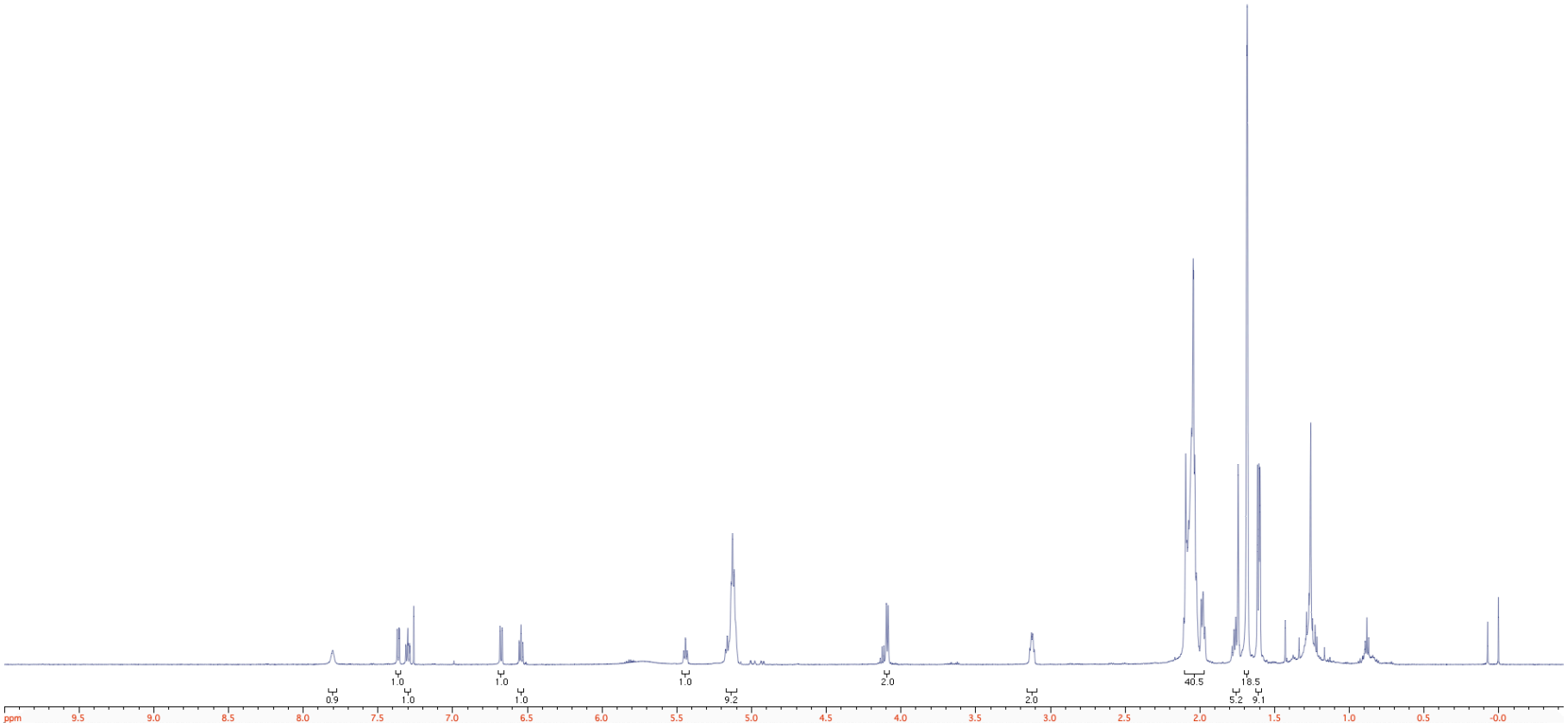


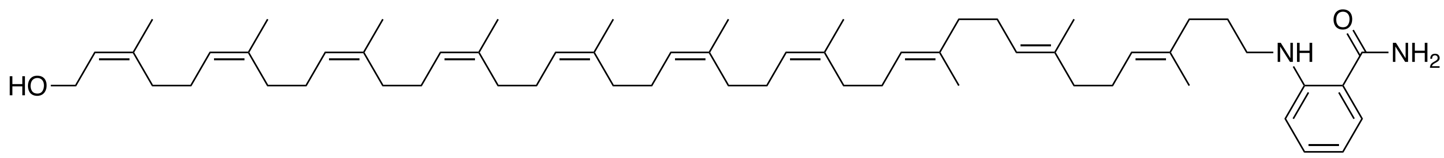
202.672
171.123
142.668
135.921
135.446
135.408
135.335
135.320
135.256
134.748
132.966
125.550
125.158
125.153
125.135
125.076
125.058
124.591
124.416
124.287
119.320
77.372
77.160
76.948
61.198
42.282
39.870
39.628
32.507
32.362
32.337
32.331
32.318
32.114
31.988
26.797
26.768
26.706
26.537
26.470
23.655
23.587
23.557
23.549
23.513
21.160
16.208
16.121
16.093
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HO
NH
O
NH2

7

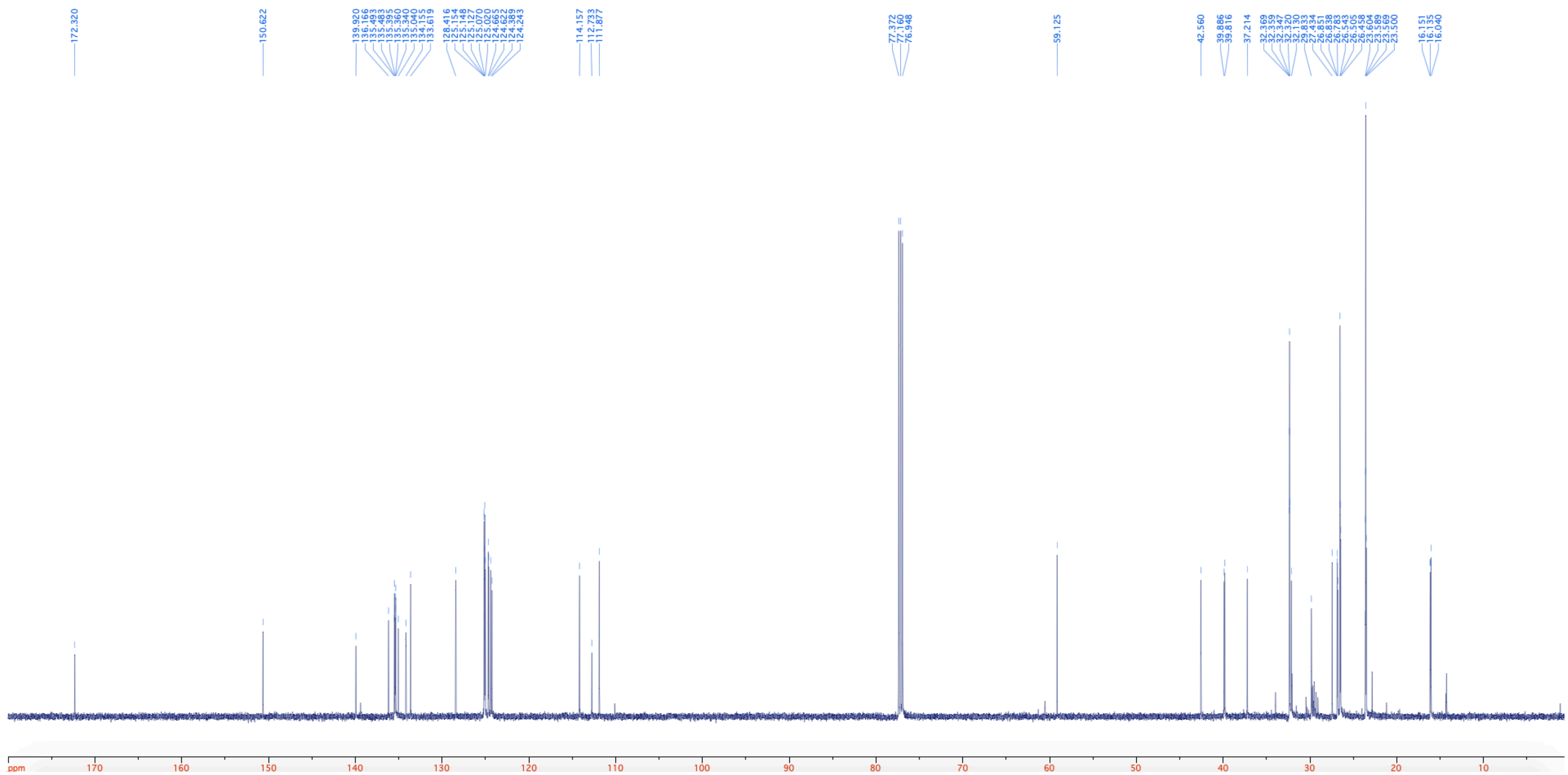
^{1}H-NMR:

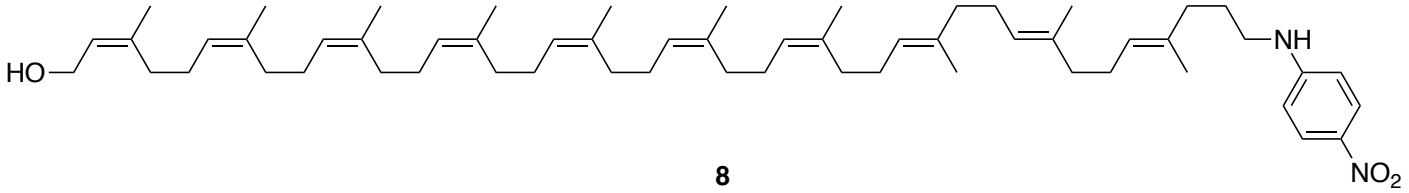

1.0
1.0
1.0
1.0
1.0
2.0
40.5
18.5
0.9
1.0
1.0
9.2
2.0
5.2
9.1
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0



7

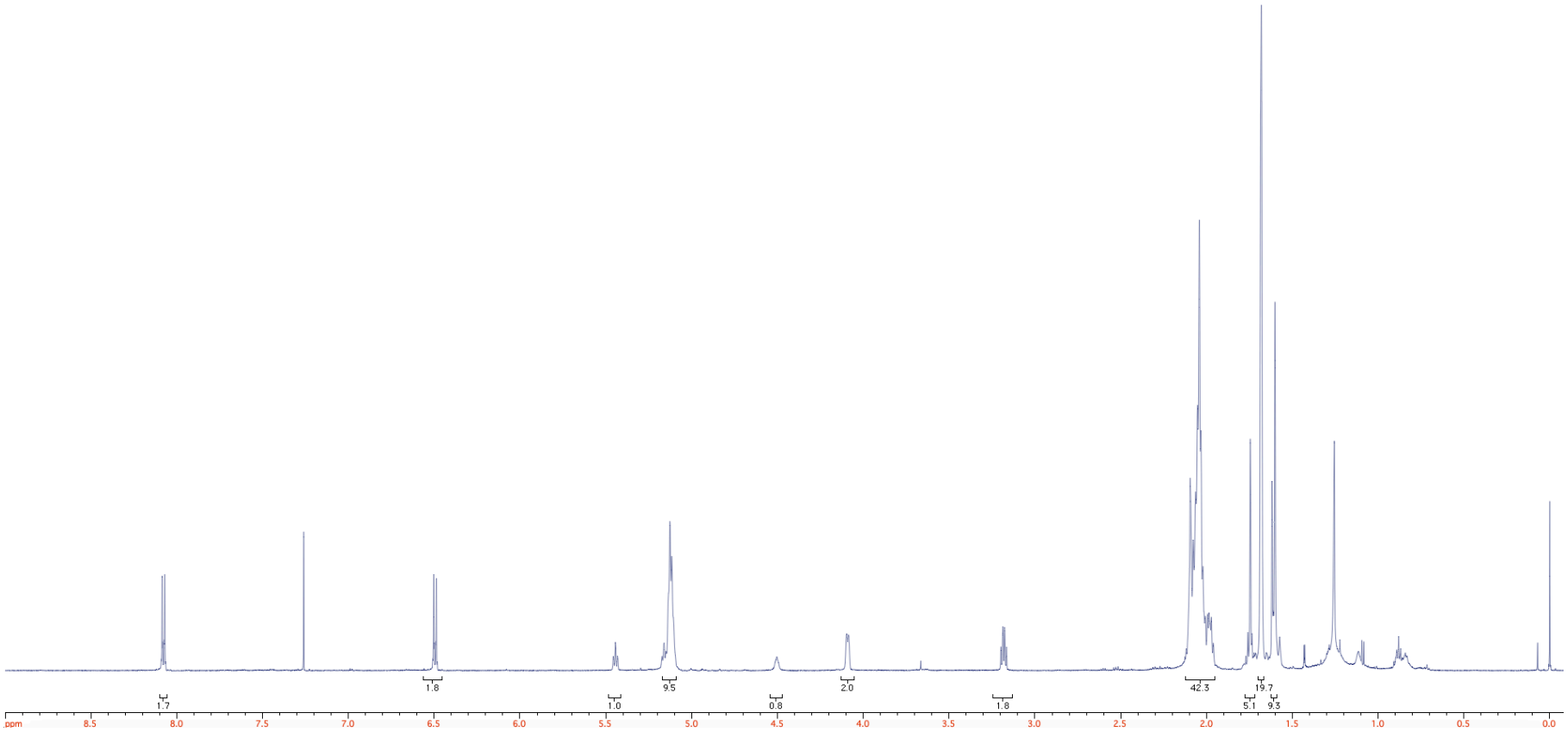
^{13}C-NMR:

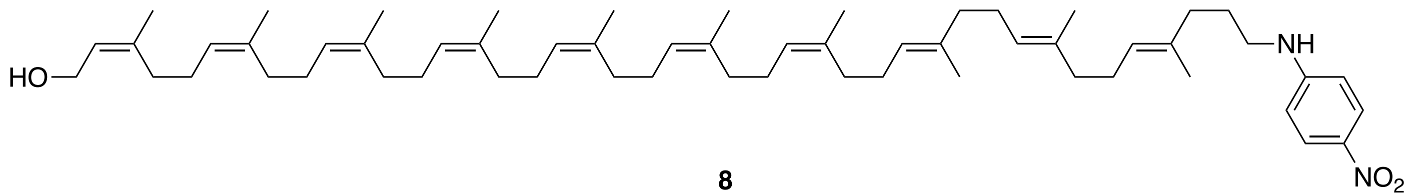



HO
NH
NO_2

8

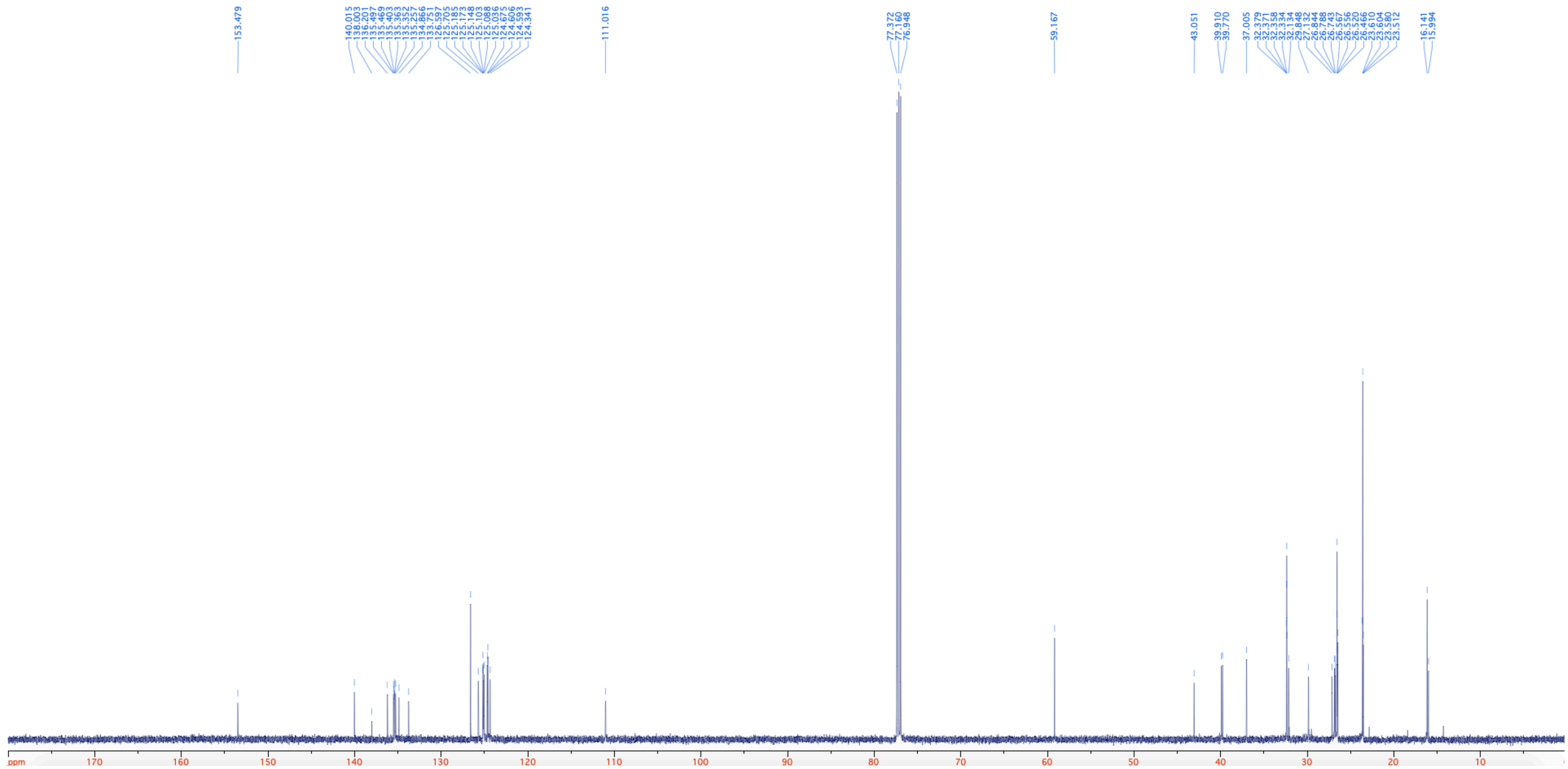
^{1}H-NMR:

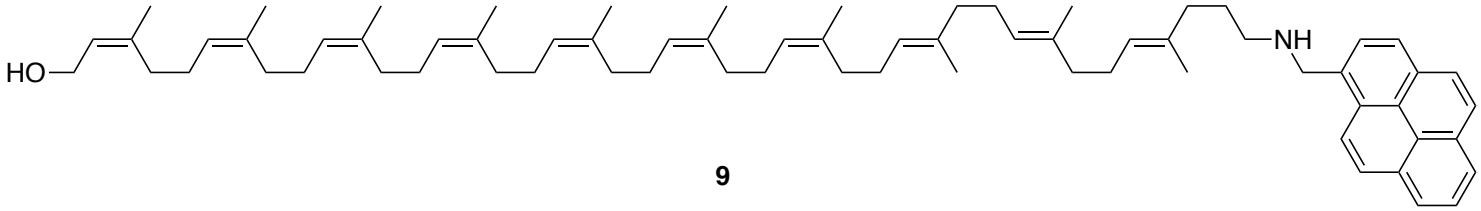

1.7
1.8
1.0
9.5
0.8
2.0
1.8
42.3
5.1
19.7
9.3
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



8

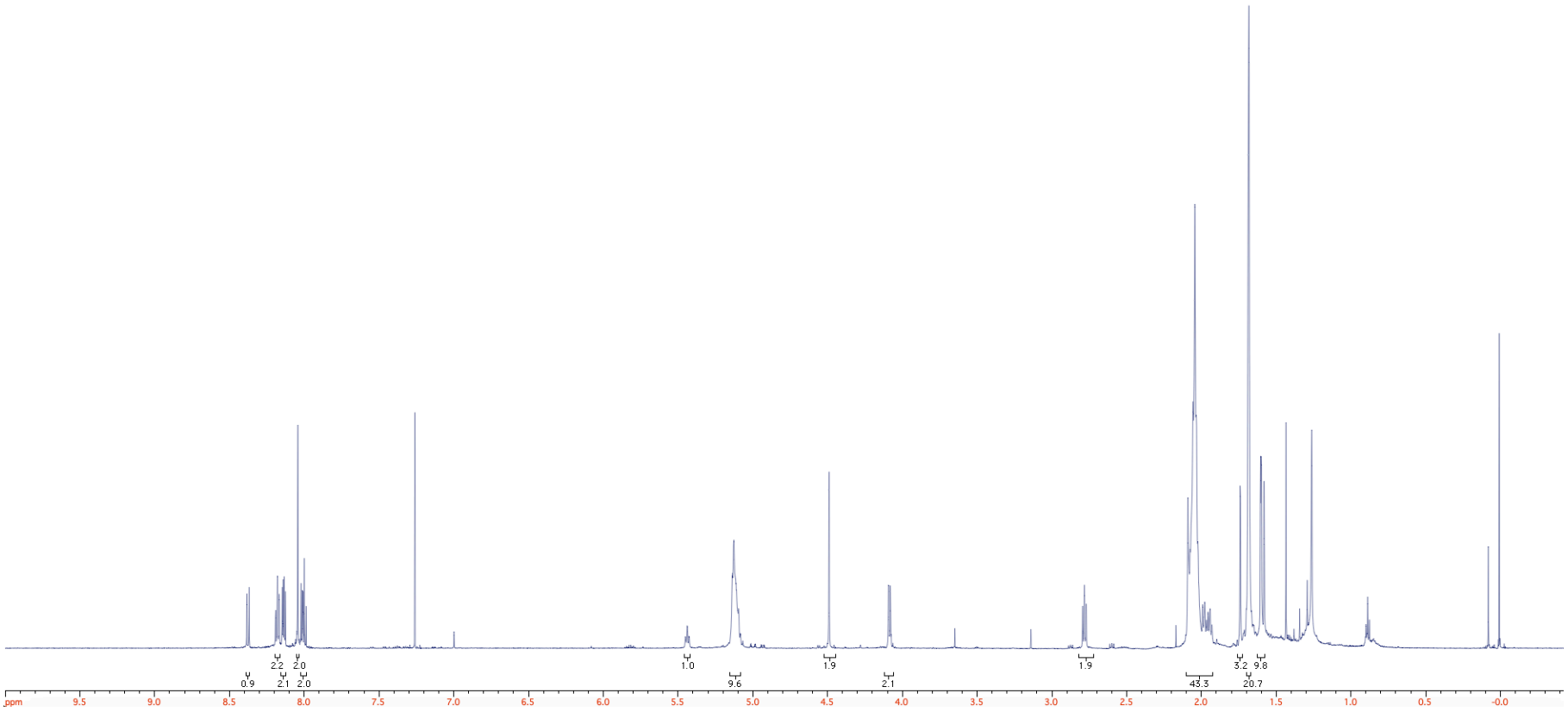
^{13}C-NMR:

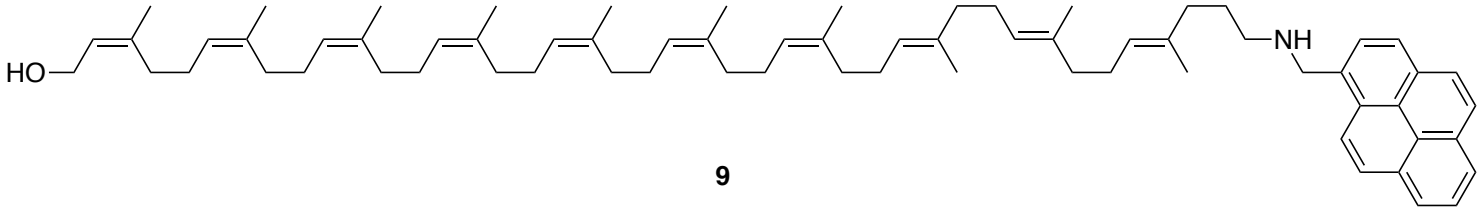



HO
NH

9

^{1}H-NMR:

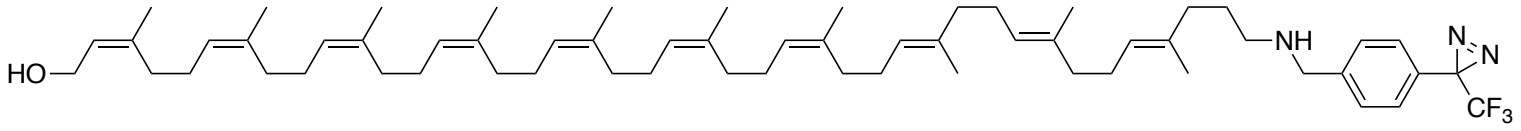

0.9
2.2
2.1
2.0
2.0
1.0
9.6
1.9
2.1
1.9
43.3
3.2
9.8
20.7
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


HO
NH

9

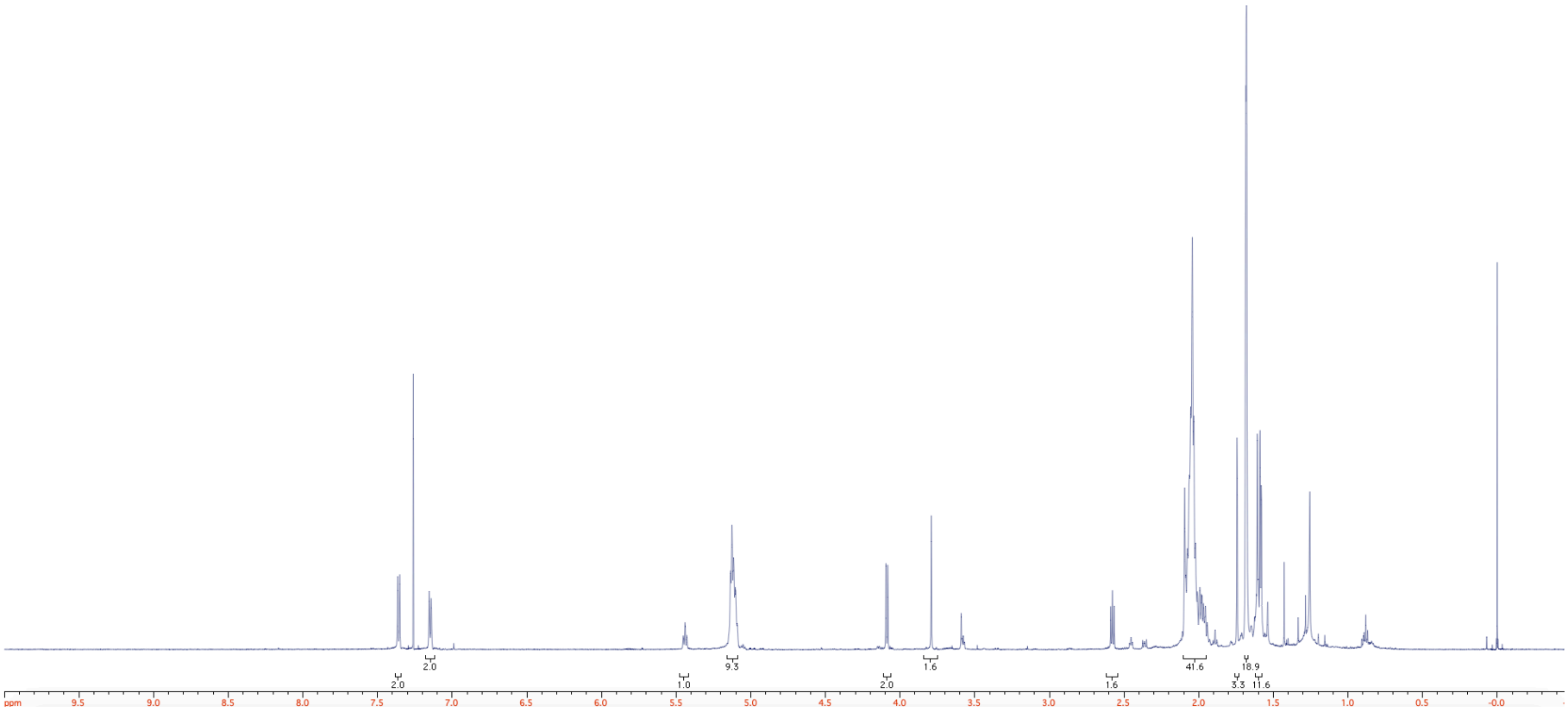
^{13}C-NMR:

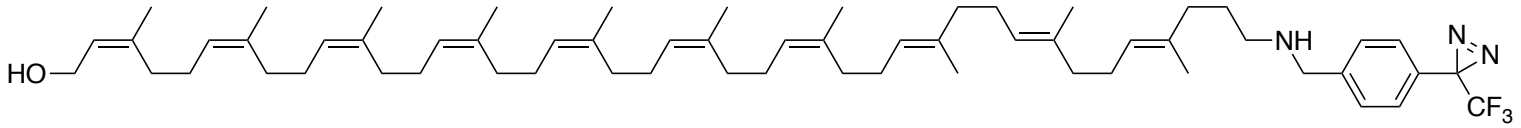

77.372
77.160
76.948
59.143
51.998
49.781
39.817
39.826
37.536
16.154
16.028
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HO
NH
N
N
CF3

10

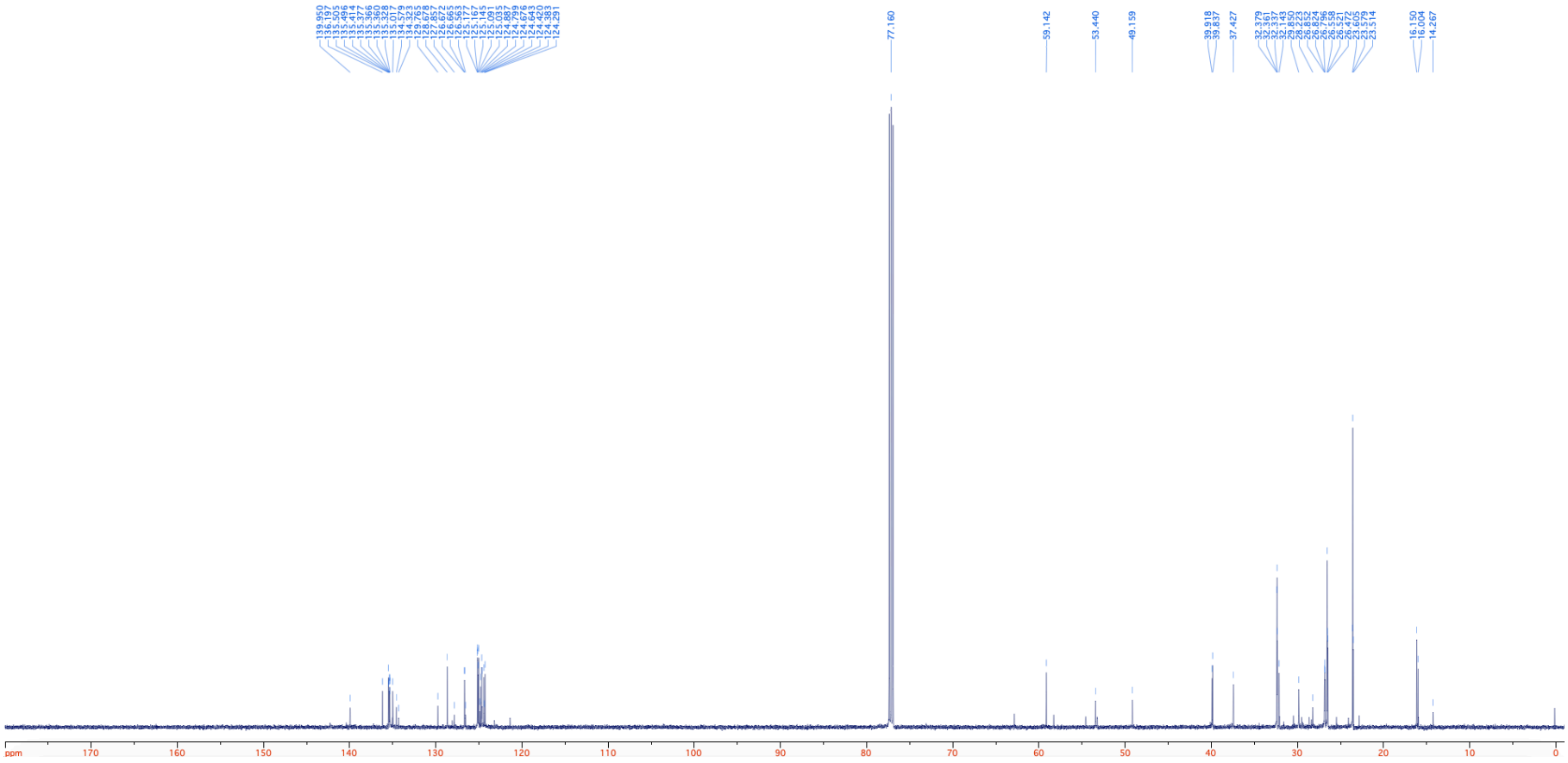
^{1}H-NMR:

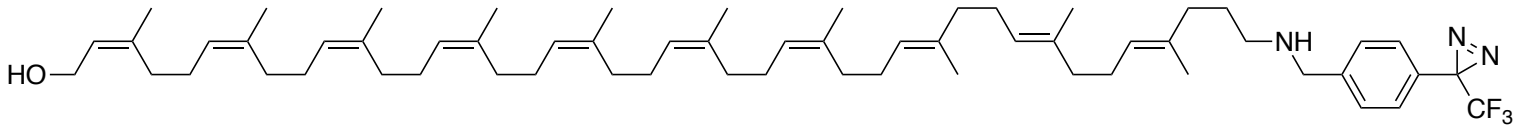

2.0
2.0
1.0
9.3
2.0
1.6
1.6
41.6
18.9
3.3
11.6
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


HO
NH
N
N
CF3

10

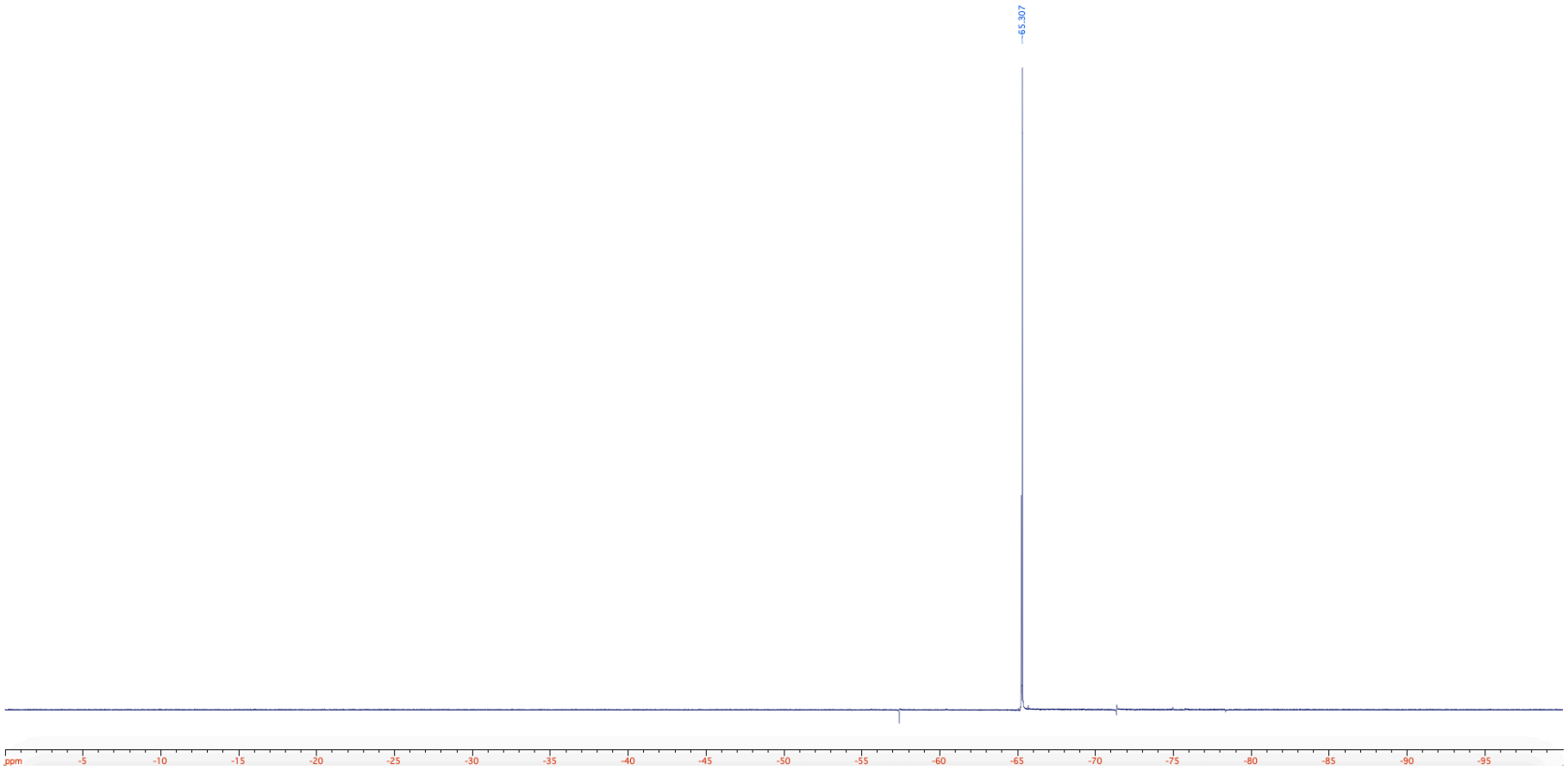
^{13}C-NMR:

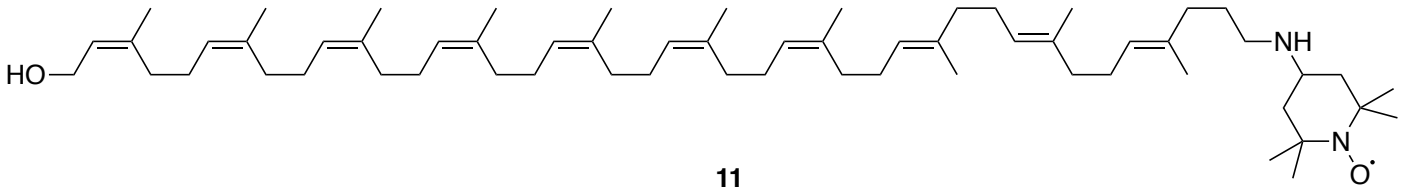

77.160
59.142
53.440
49.159
39.918
39.837
37.427
16.150
16.004
14.267
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


HO
NH
N
N
CF3

10

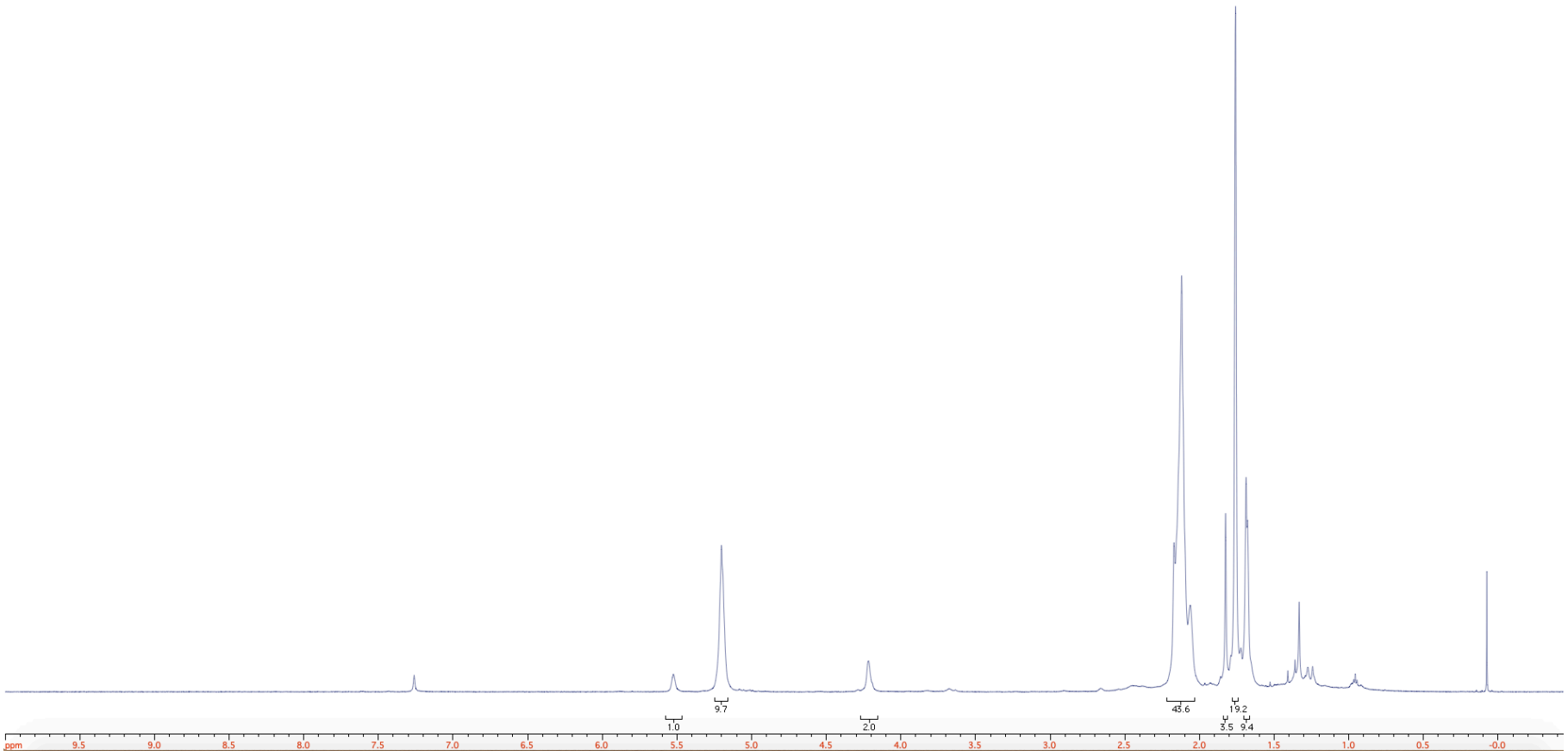
^{19}F-NMR:

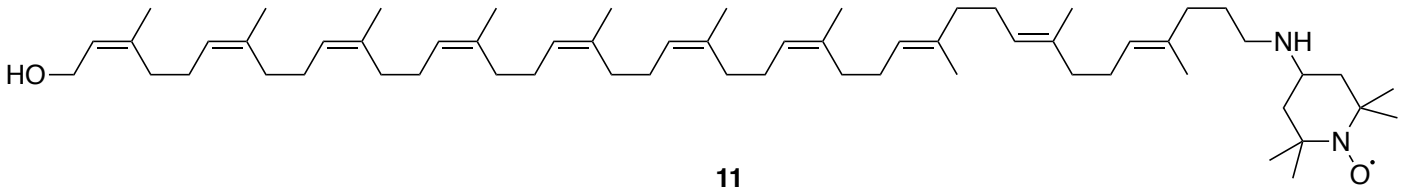

-65.307
ppm
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95


HO
NH
N
O

11

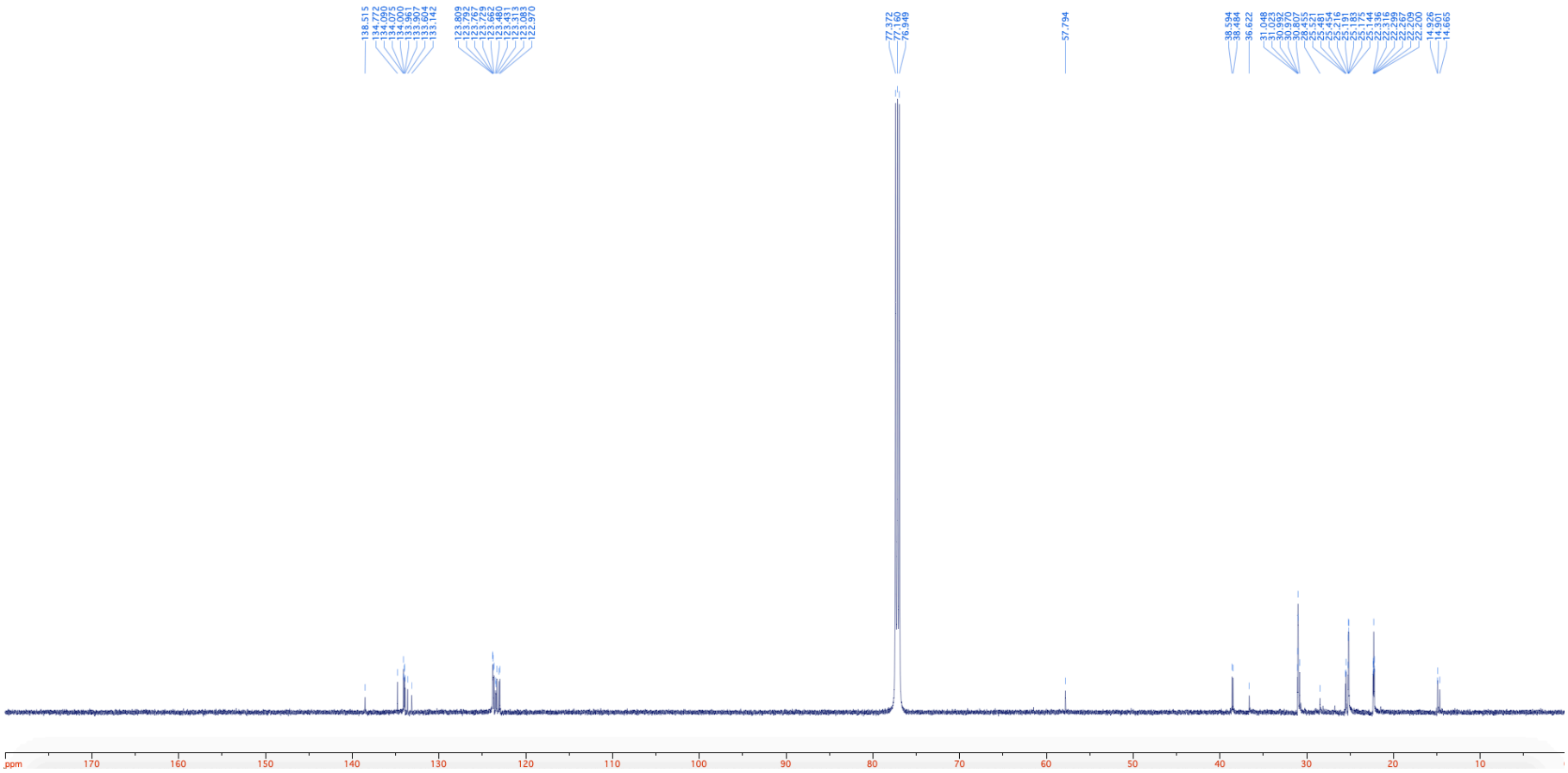
^{1}H-NMR:

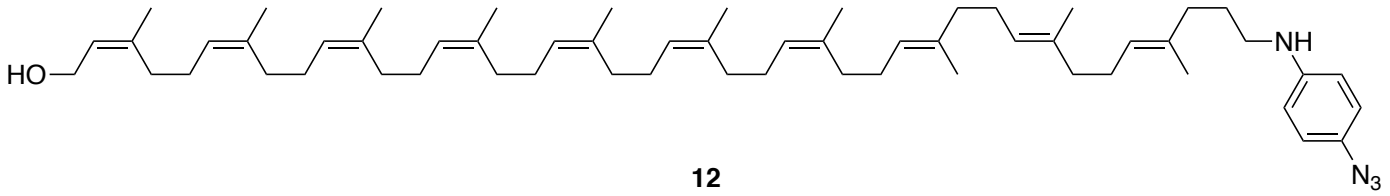

1.0
9.7
2.0
45.6
19.2
3.5
9.4
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


HO
NH
N
O

11

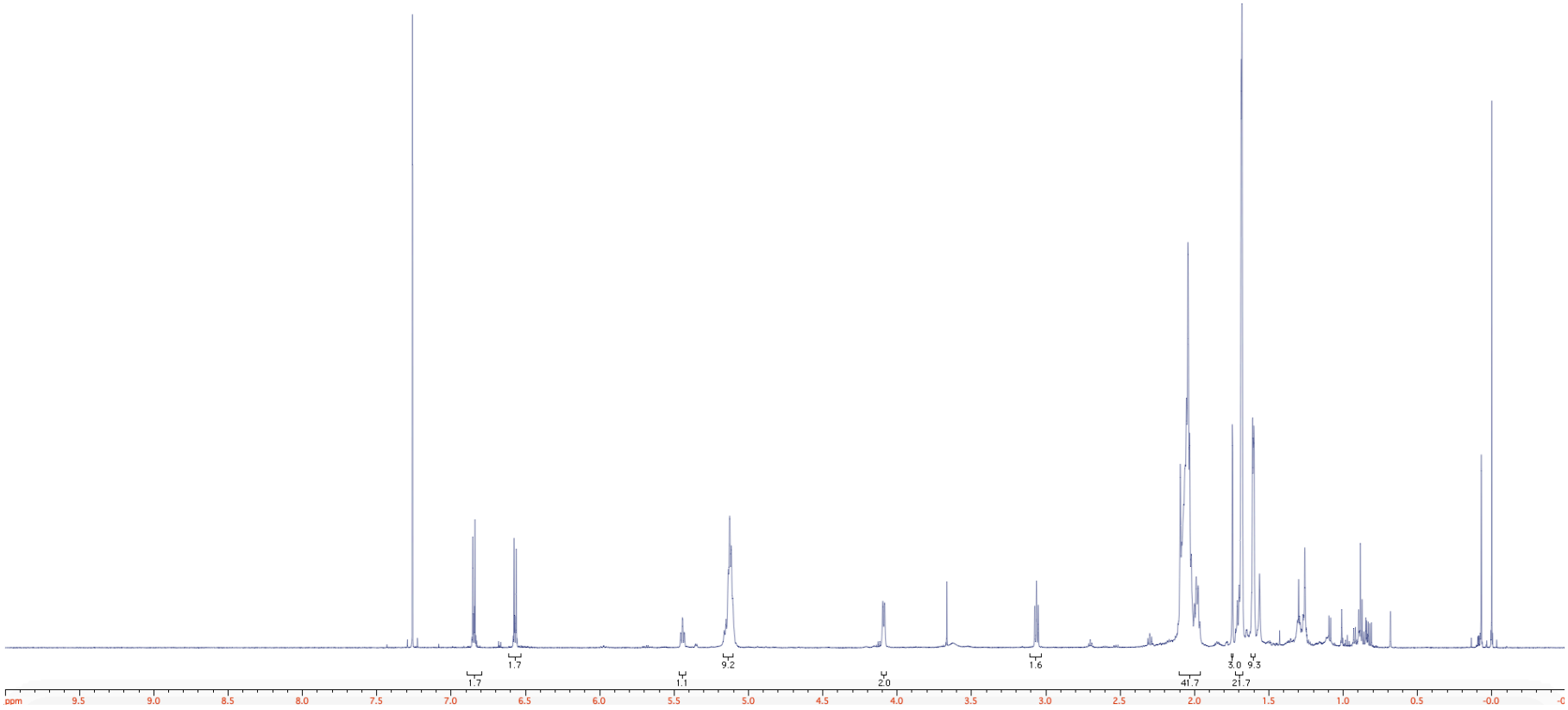
^{13}C-NMR:

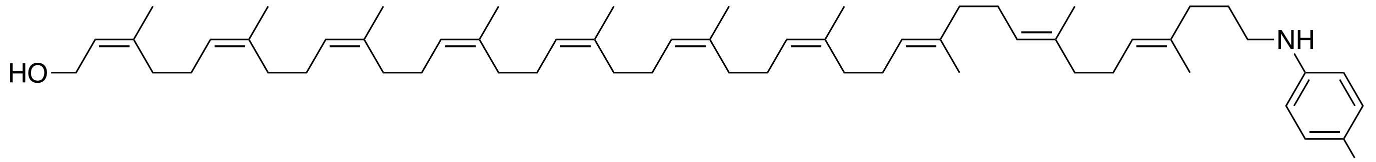

138.515
134.772
134.090
134.055
134.000
133.961
133.907
133.804
133.142
123.809
123.792
123.767
123.729
123.462
123.460
123.431
123.313
123.163
122.970
77.372
77.160
76.949
57.794
38.584
38.464
36.622
31.048
31.042
30.992
30.970
30.957
28.455
25.521
25.454
25.216
25.181
25.175
25.144
22.336
22.316
22.289
22.267
22.209
22.200
14.926
14.901
14.665
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HO
NH
N3

12

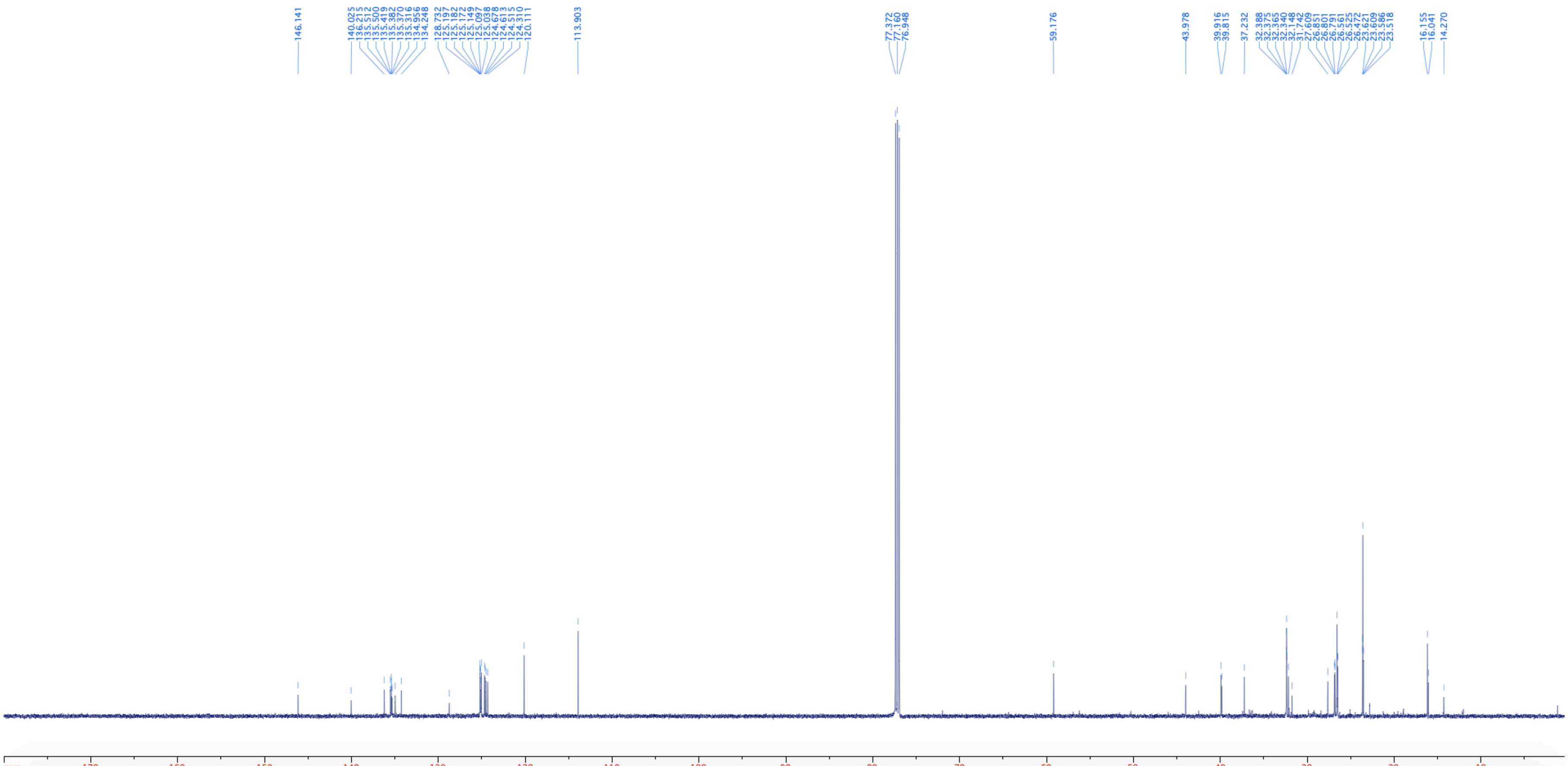
^{1}H-NMR:

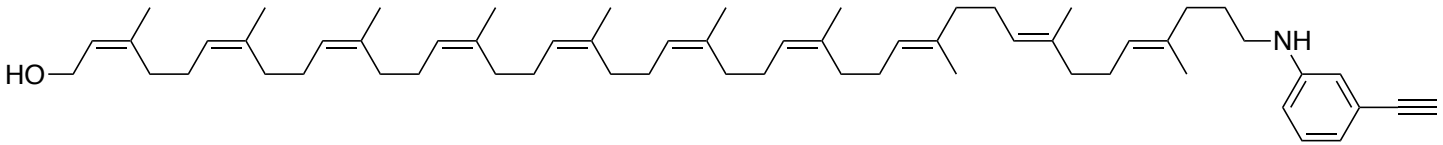

1.7
1.7
1.1
9.2
2.0
1.6
41.7
3.0
21.7
9.3
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


HO
NH
N3

12

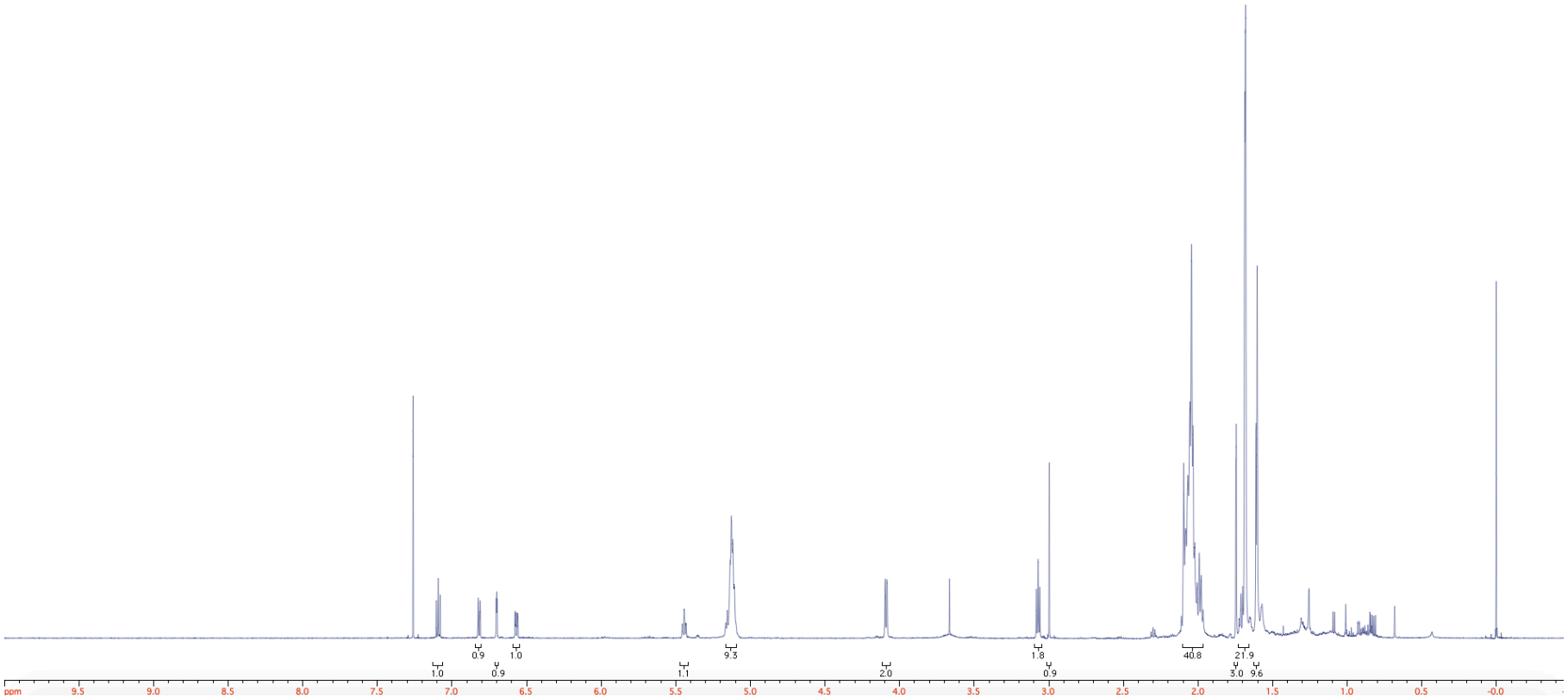
^{13}C-NMR:

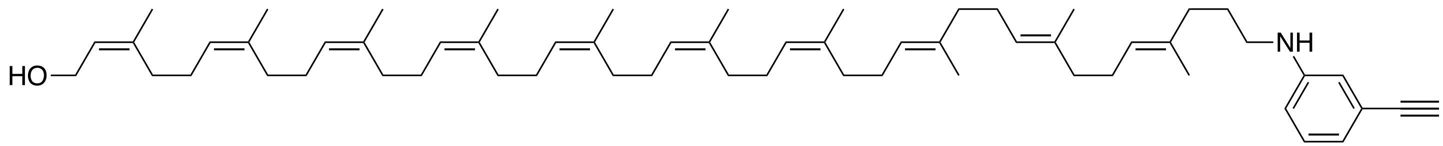

146.141
140.025
136.215
135.512
135.500
135.419
135.382
135.370
135.316
134.956
134.248
128.732
125.197
125.182
125.172
125.149
125.097
125.038
124.678
124.613
124.515
124.310
120.111
113.903
77.372
77.160
76.948
59.176
43.978
39.916
39.815
37.232
32.388
32.375
32.365
32.340
32.148
31.742
27.609
26.851
26.801
26.791
26.561
26.525
26.472
23.621
23.609
23.586
23.518
16.155
16.041
14.270
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HO
NH

13

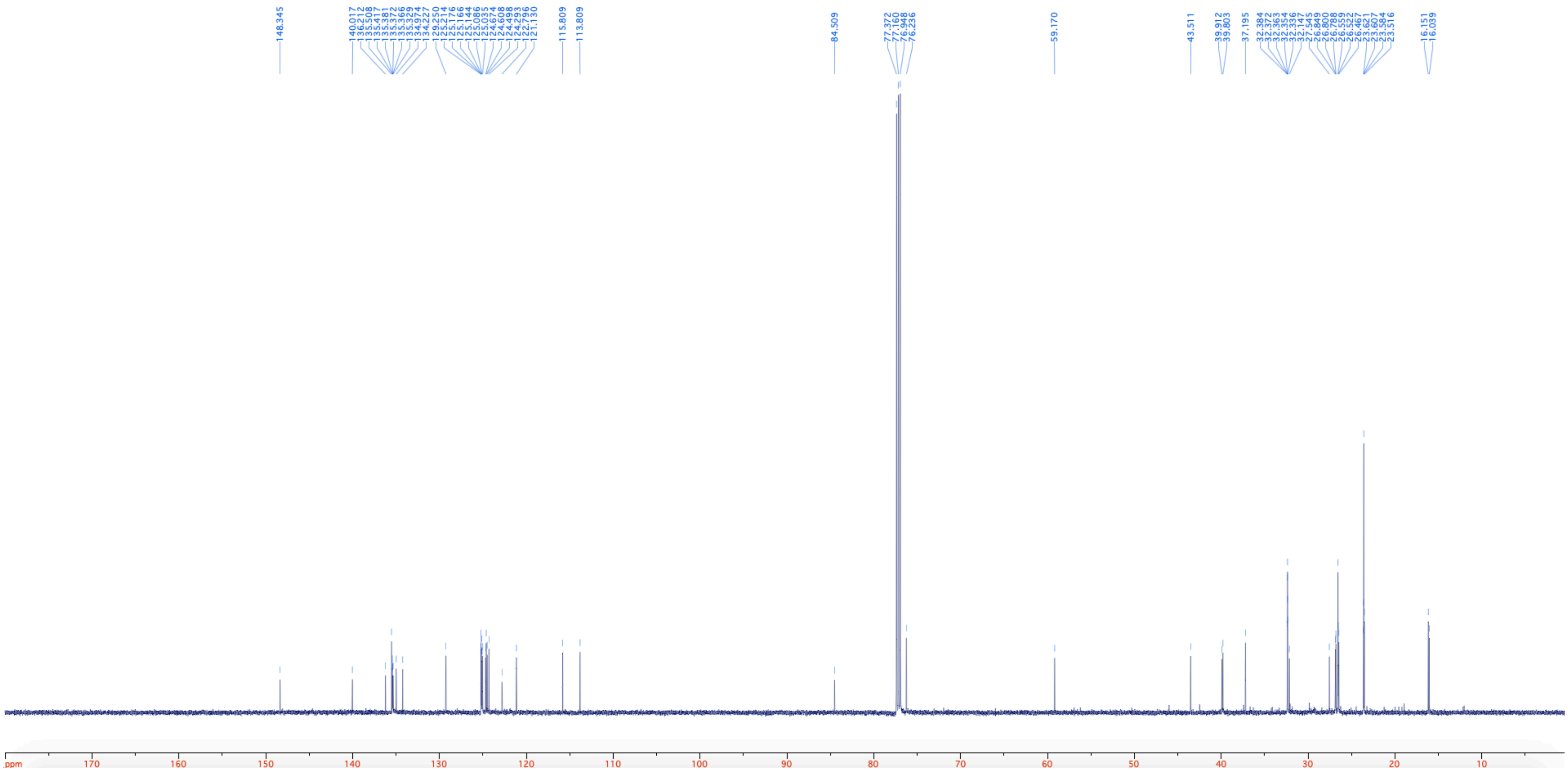
^{1}H-NMR:

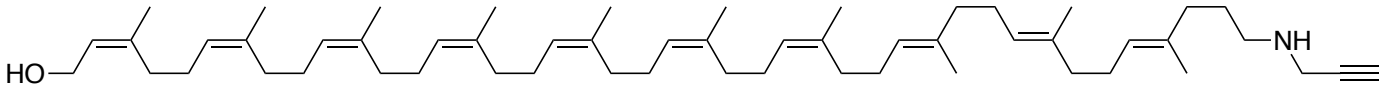

1.0
0.9
0.9
1.0
1.1
9.3
2.0
1.8
0.9
40.8
21.9
3.0
9.6
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


HO
NH

13

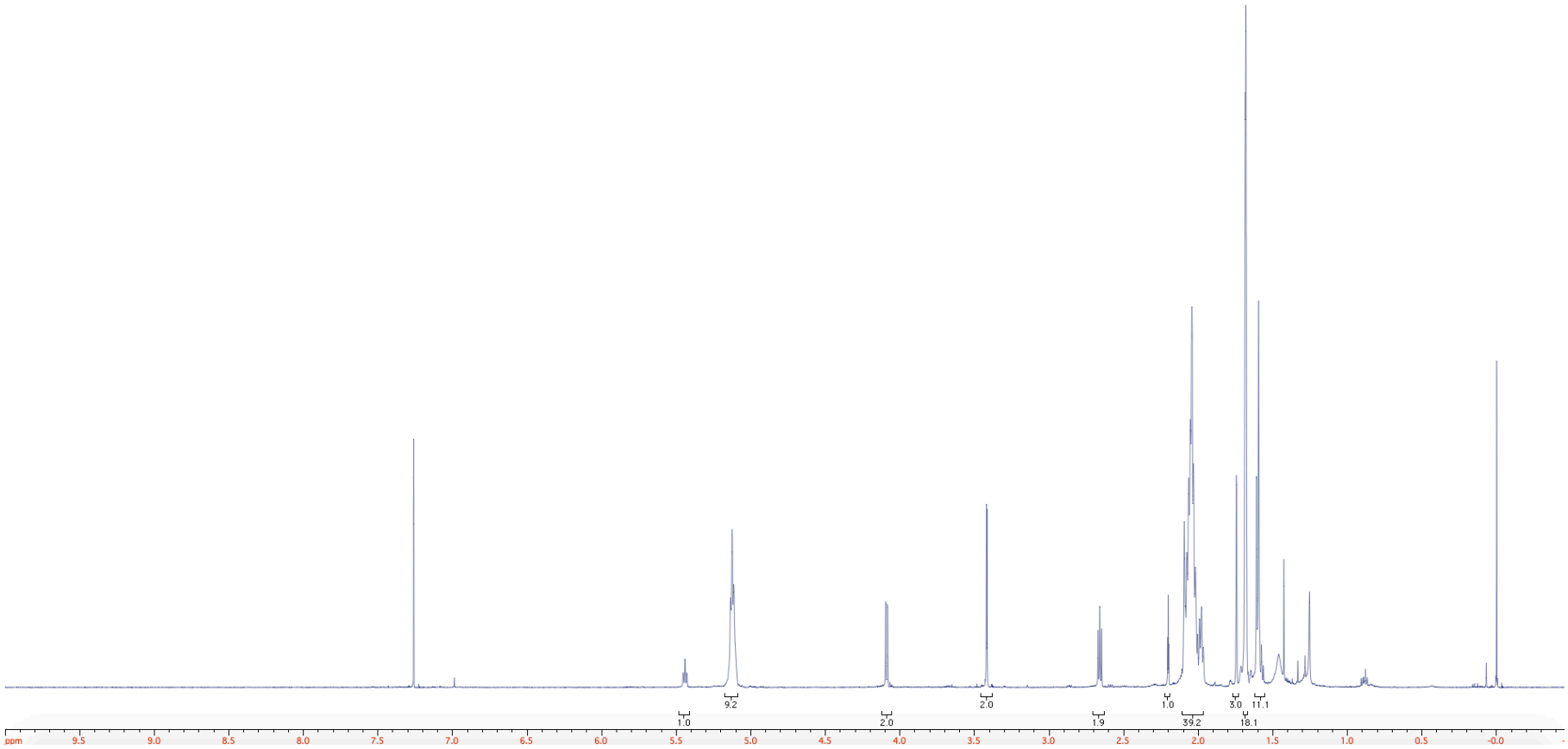
[13]C-NMR:

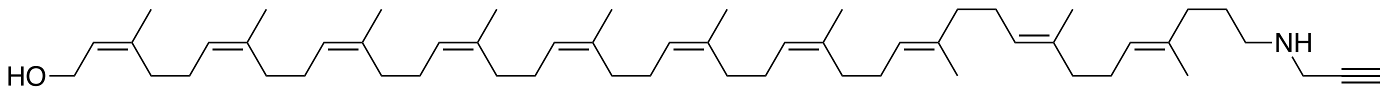

148.345
140.017
136.212
135.508
135.417
135.381
135.372
135.366
135.329
134.974
134.227
129.250
125.214
125.176
125.166
125.144
125.086
125.035
124.674
124.608
124.498
124.293
122.796
121.130
115.809
113.809
84.509
77.372
77.160
76.948
76.236
59.170
43.511
39.912
39.803
37.195
32.384
32.372
32.363
32.354
32.336
32.147
27.545
26.849
26.800
26.788
26.559
26.522
26.467
23.621
23.607
23.584
23.516
16.151
16.039
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HO
NH

14

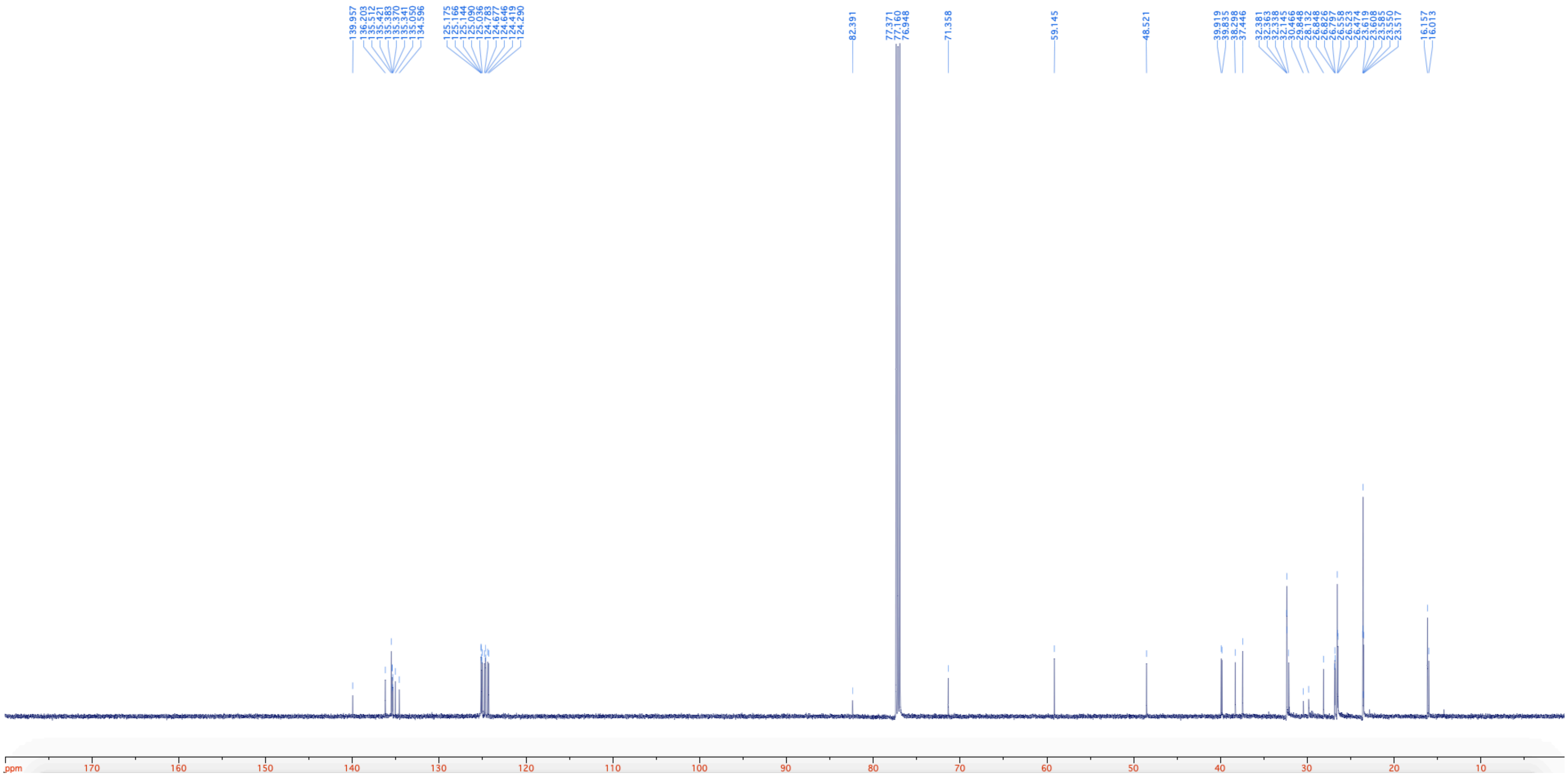
^{1}H-NMR:

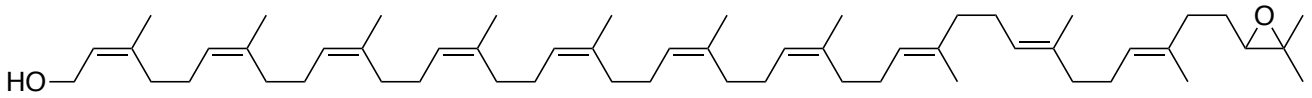

9.2
2.0
2.0
1.0
3.0
11.1
1.0
2.0
1.9
39.2
18.1
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0



14

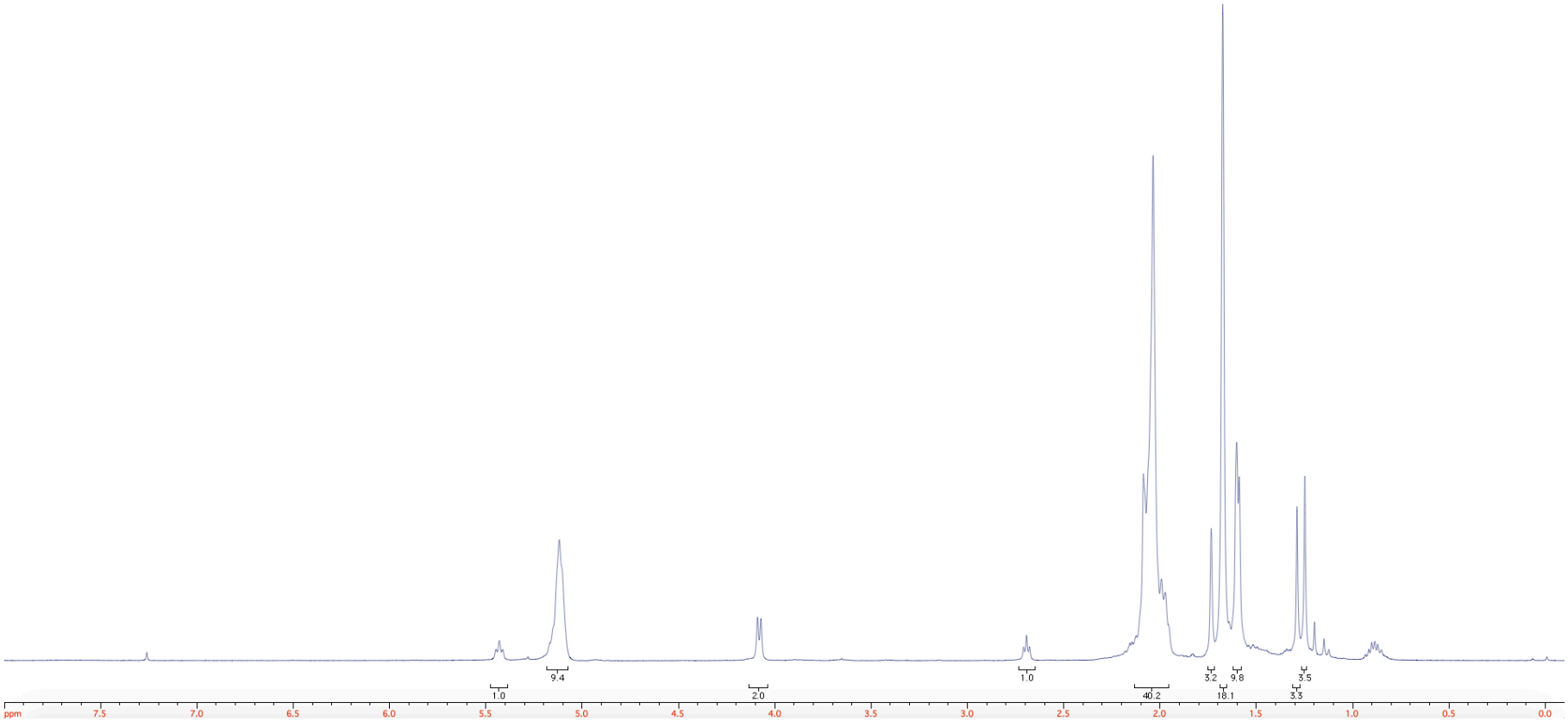
^{13}C-NMR:

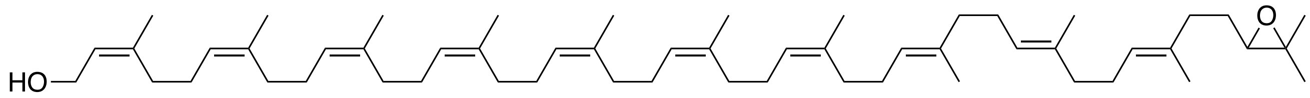



HO
O

15

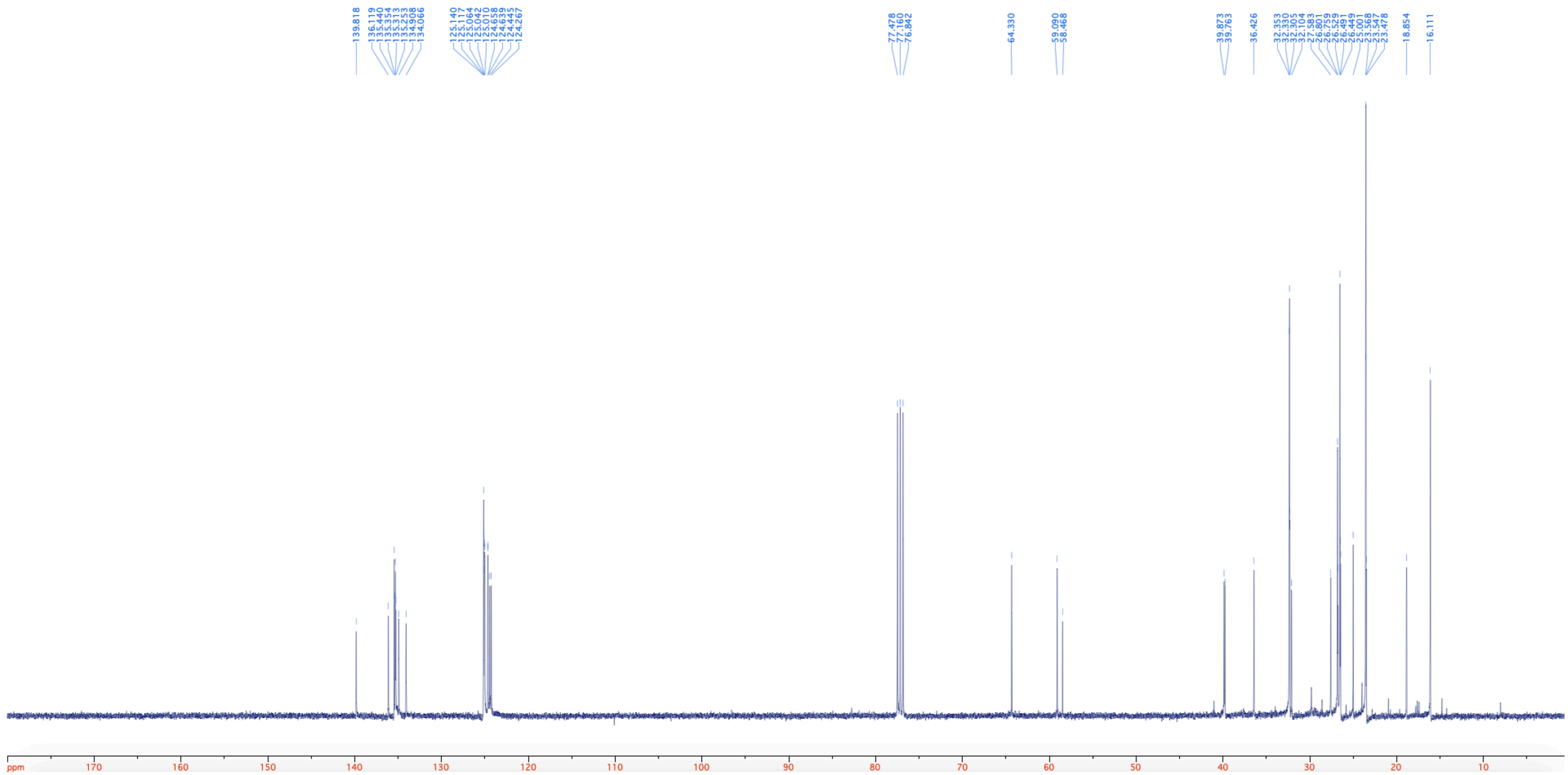
^{1}H-NMR:

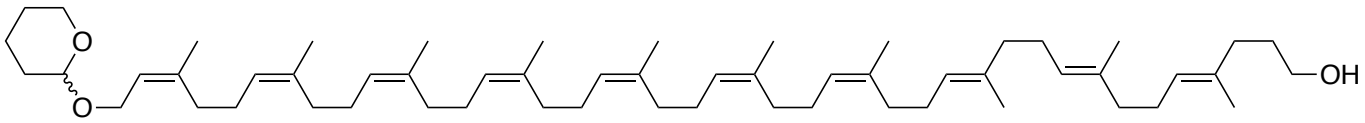

1.0
9.4
2.0
1.0
40.2
3.2
16.1
9.8
3.5
3.3
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


HO
O

15

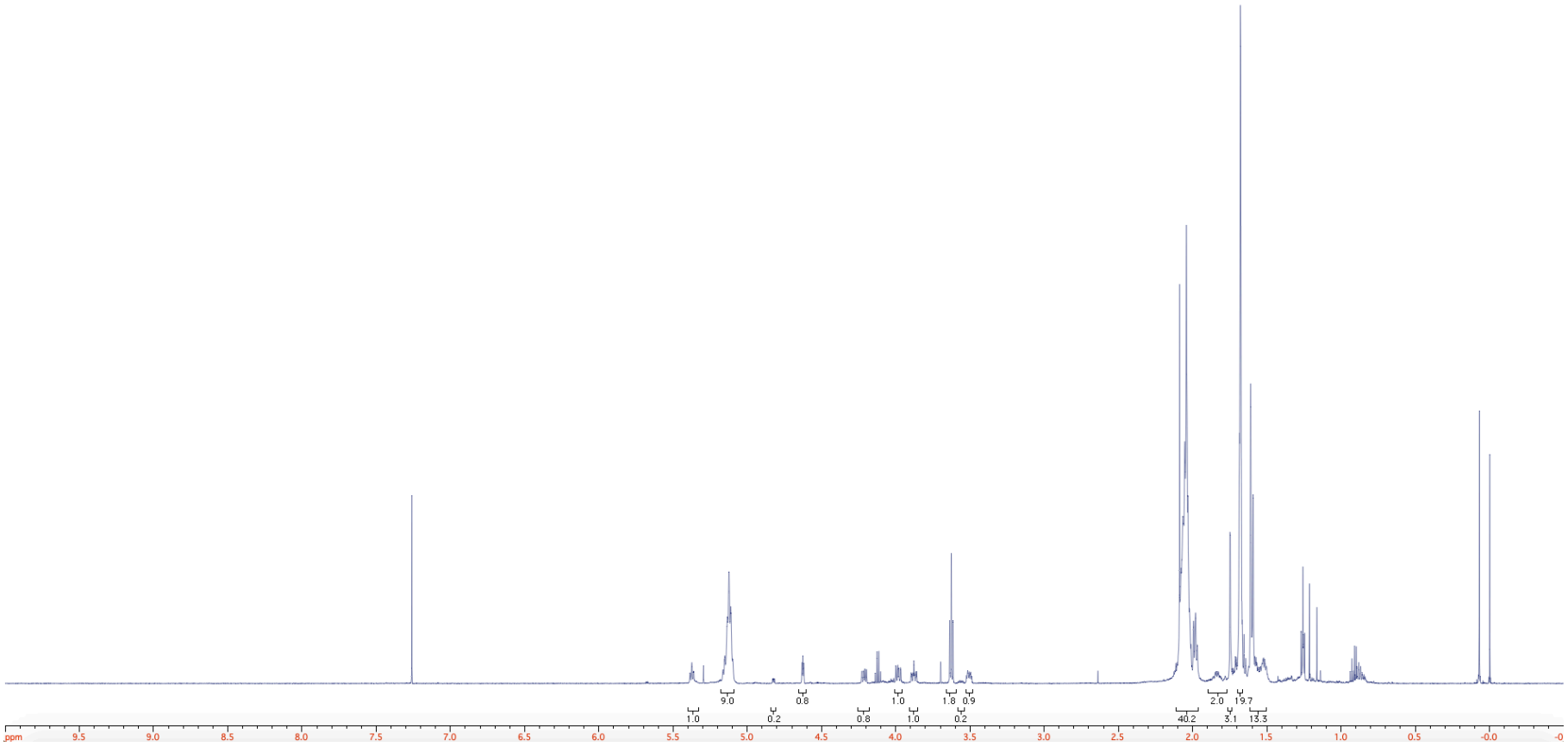
[13]C-NMR:

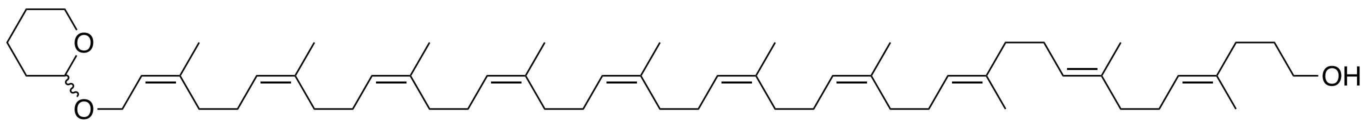

139.818
136.119
135.440
135.354
135.313
135.253
134.908
134.066
125.140
125.117
125.064
125.042
125.010
124.658
124.639
124.445
124.267
77.478
77.160
76.842
64.330
59.090
58.468
39.873
39.763
36.426
32.353
32.330
32.305
32.104
27.583
26.801
26.759
26.529
26.481
26.449
25.001
23.568
23.547
23.478
18.854
16.111
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


O
O
OH

16

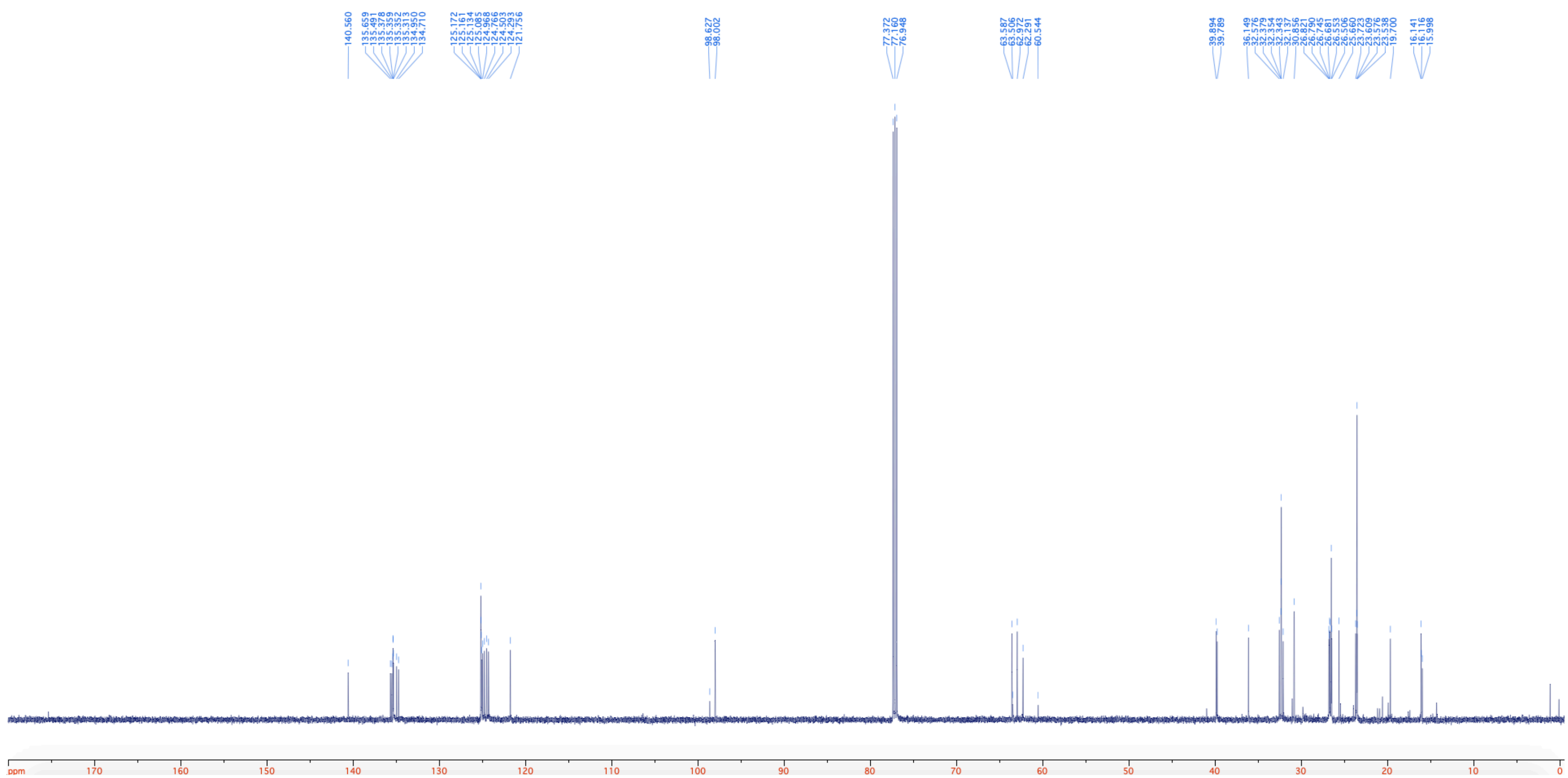
^{1}H-NMR:

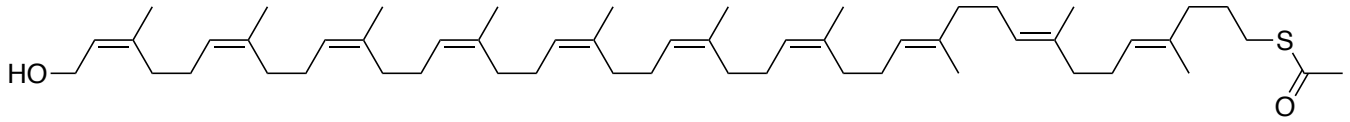

9.0
0.8
1.0
1.8
0.9
2.0
19.7
1.0
0.2
0.8
1.0
0.2
40.2
3.1
13.3
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


O
O
OH

16

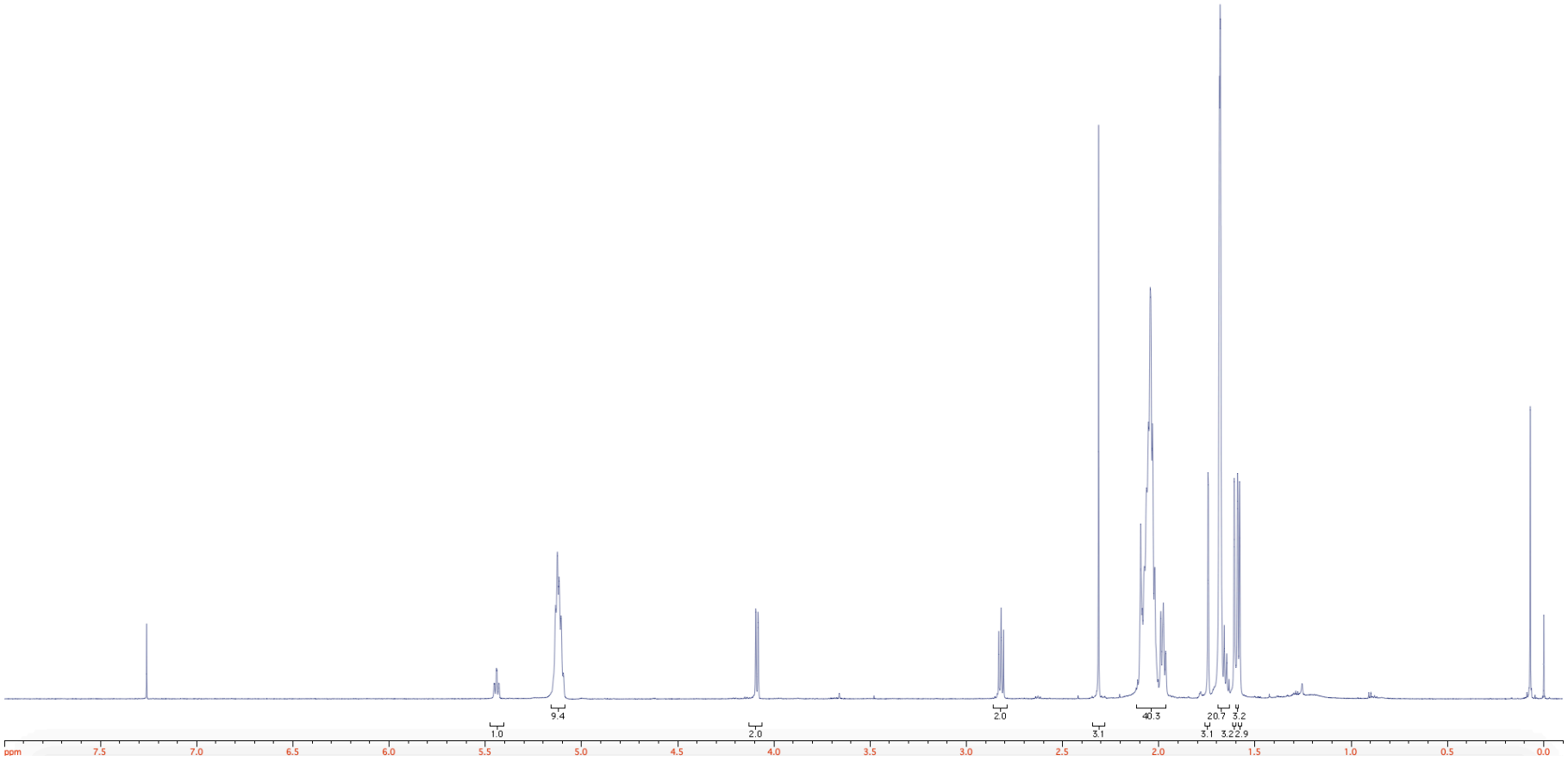
[13]C-NMR:

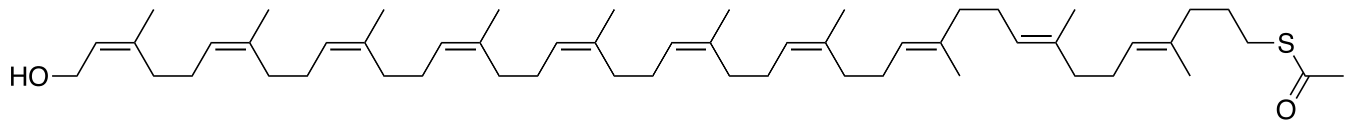

140.560
135.659
135.491
135.378
135.359
135.352
135.313
134.950
134.710
125.172
125.161
125.134
125.085
124.968
124.766
124.503
124.293
121.756
98.627
98.002
77.372
77.160
76.948
63.587
63.506
62.972
62.291
60.544
39.894
39.789
36.149
32.576
32.379
32.354
32.343
32.137
30.856
26.821
26.790
26.745
26.681
26.553
26.523
25.660
25.506
23.723
23.609
23.576
23.538
19.700
16.141
16.116
15.998
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


HO
S
O

17

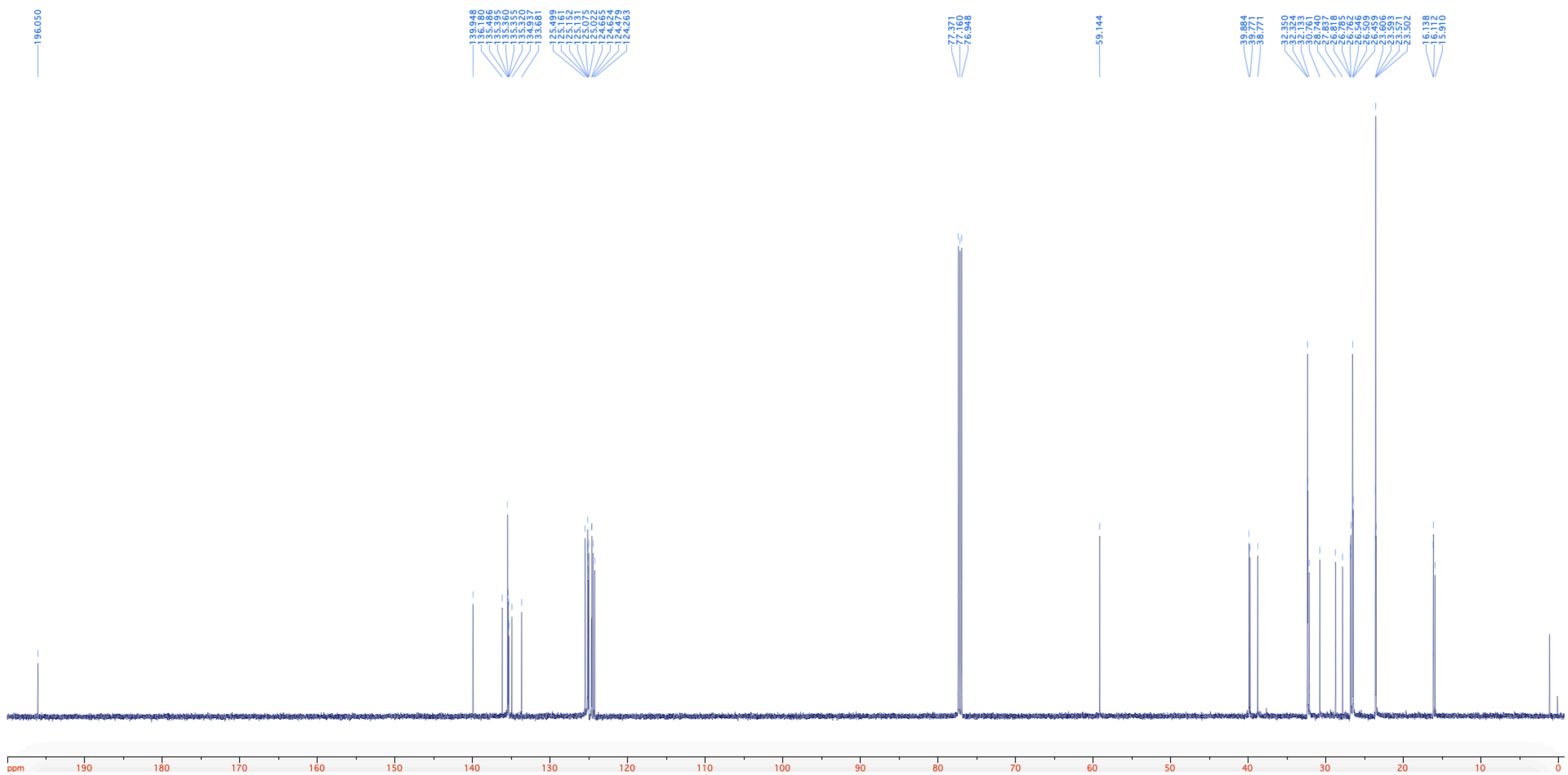
^{1}H-NMR:

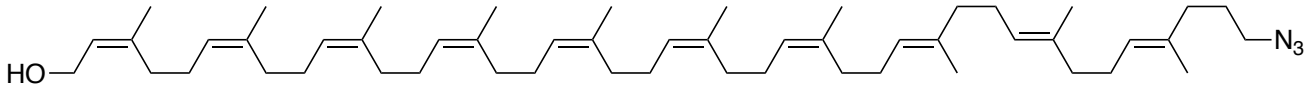

9.4
2.0
2.0
3.1
40.3
2.0.7
3.2
3.1
3.2
2.9
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



17

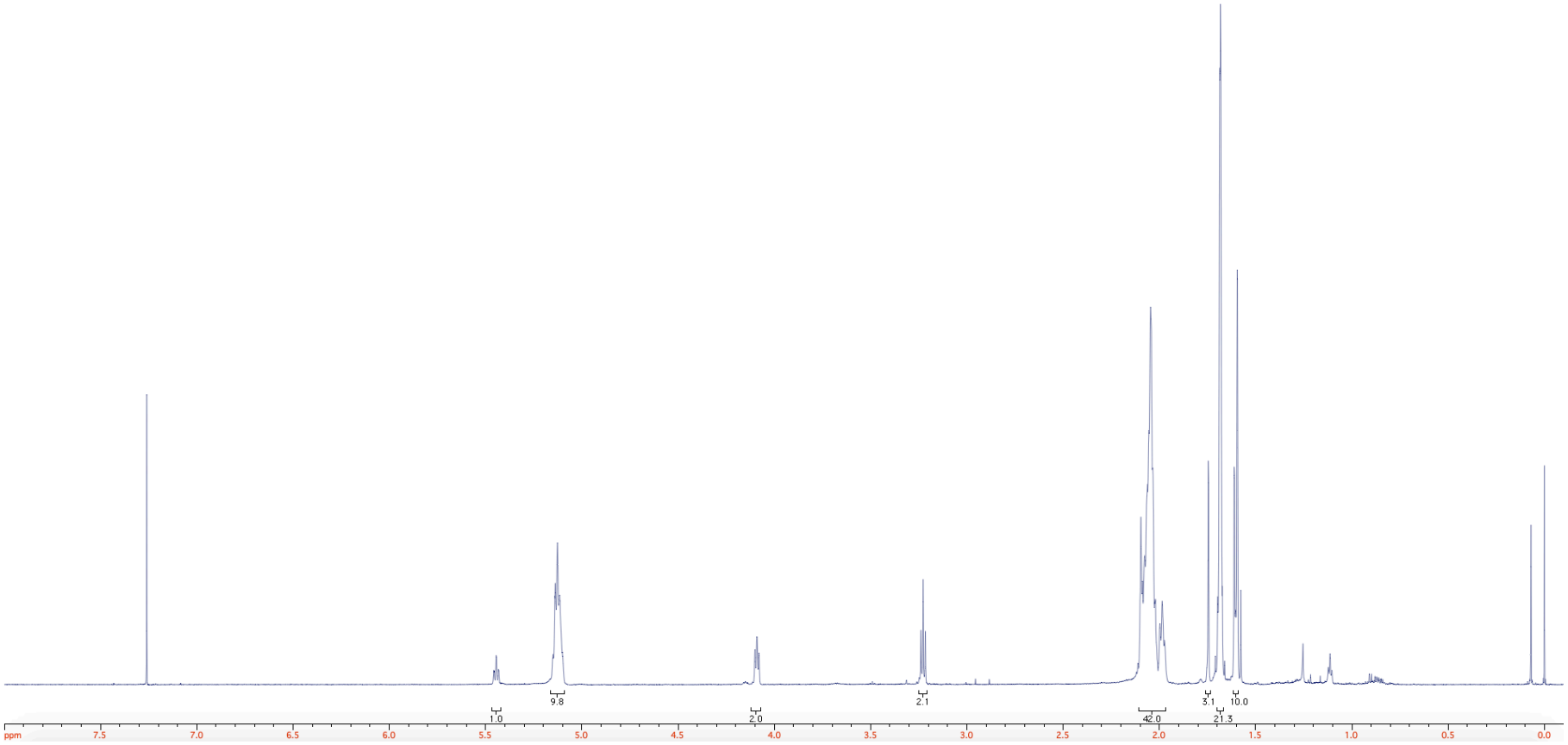
^{13}C-NMR:

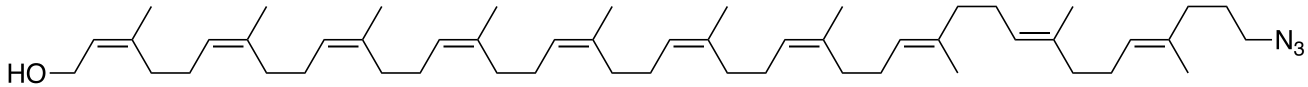



HO
N3

18

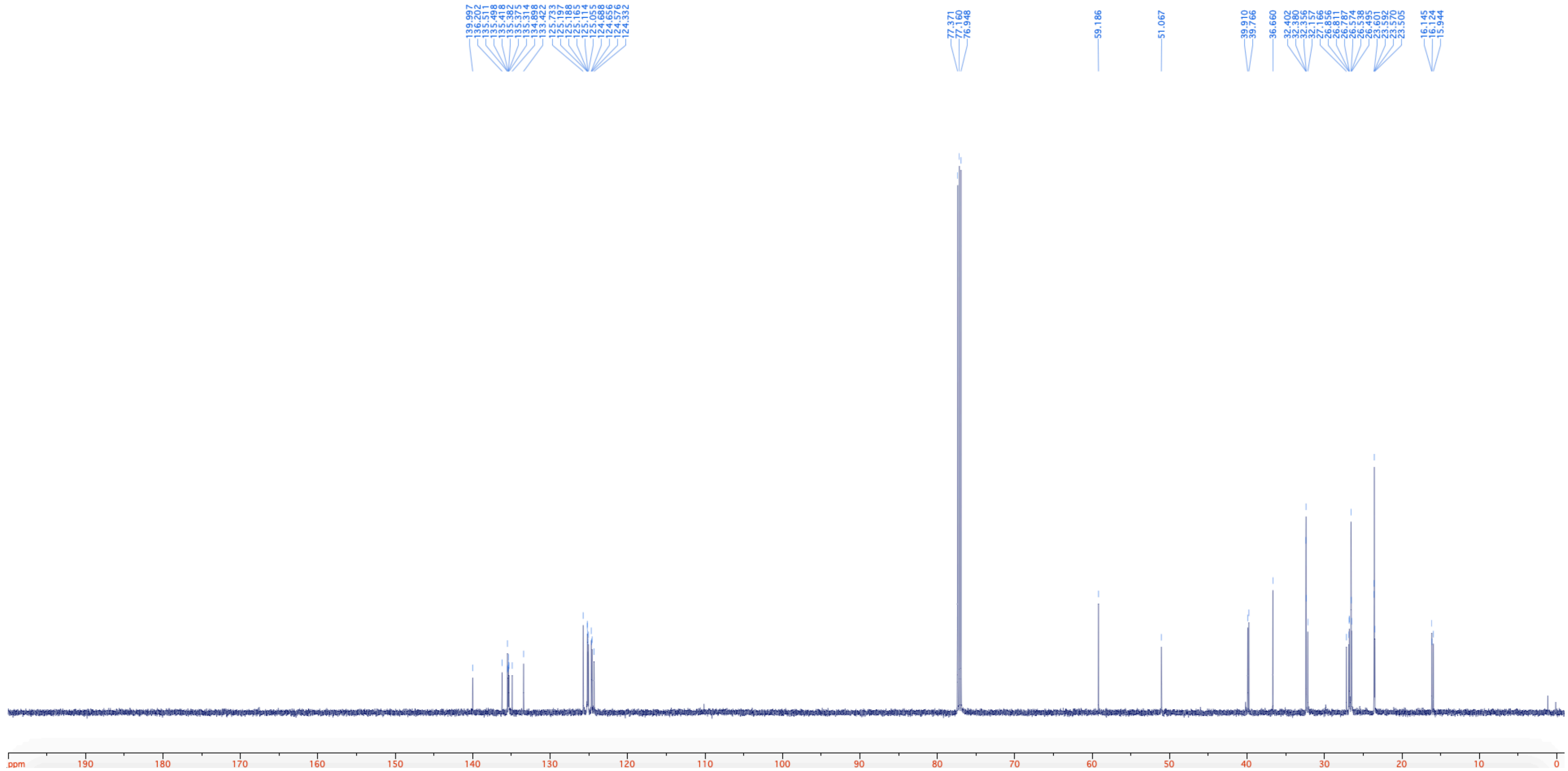
^{1}H-NMR:

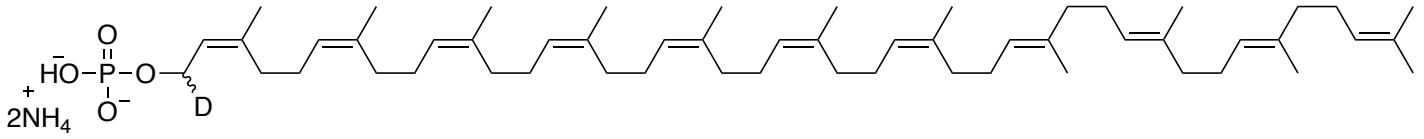

1.0
9.8
2.0
2.1
42.0
3.1
10.0
21.3
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


HO
N_3

18

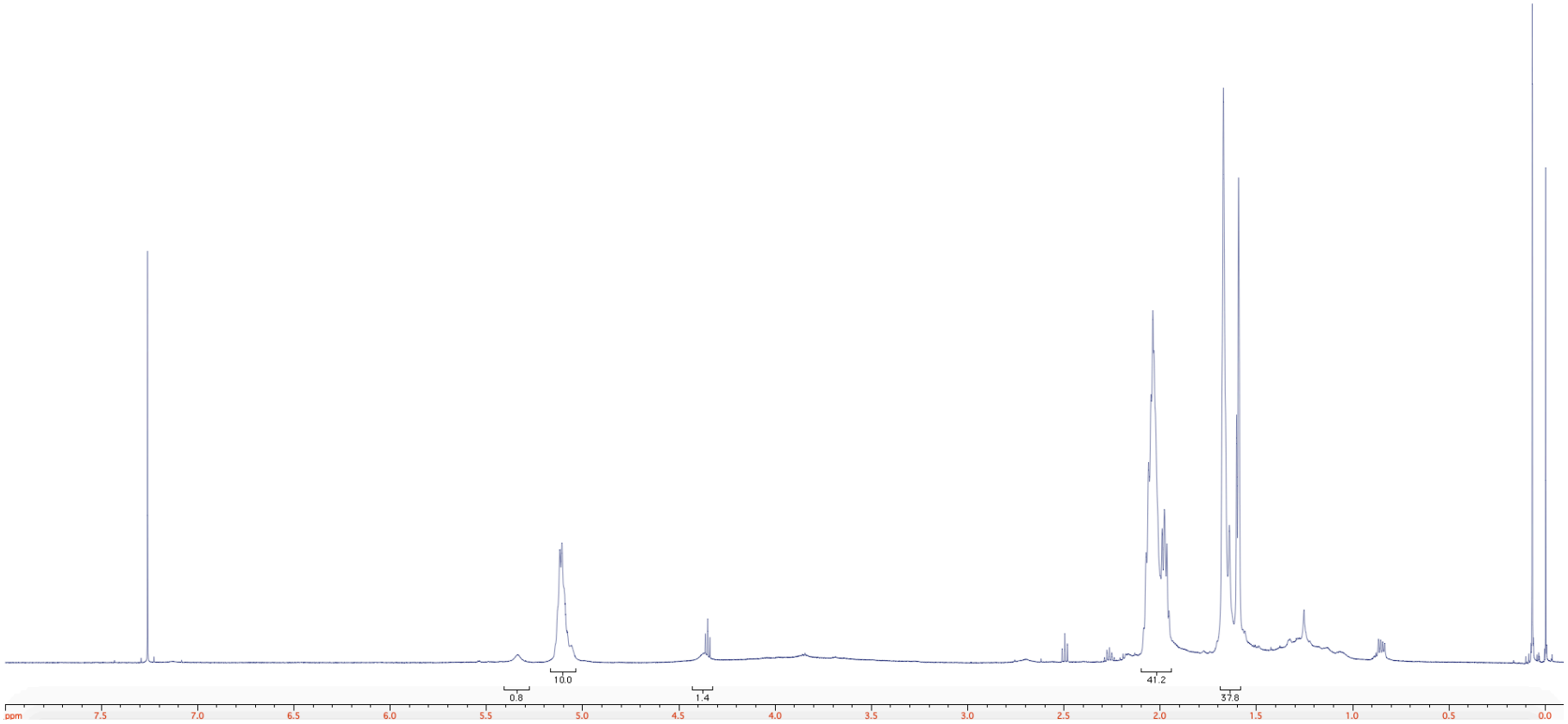
[13]C-NMR:

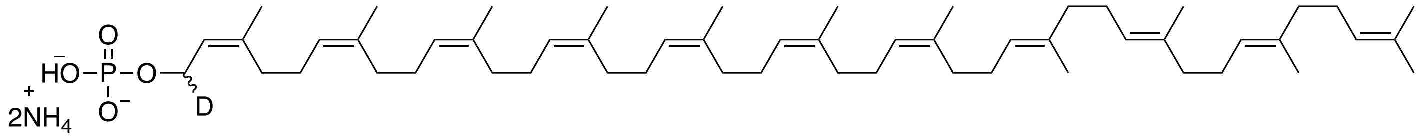

139.997
136.202
135.511
135.498
135.418
135.382
135.375
135.314
134.898
133.422
125.733
125.197
125.188
125.165
125.114
125.055
124.688
124.656
124.576
124.332
77.371
77.160
76.948
59.186
51.067
39.910
39.766
36.660
32.402
32.380
32.356
32.157
27.166
26.856
26.811
26.787
26.574
26.538
26.495
23.601
23.592
23.570
23.505
16.145
16.124
15.944
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



20

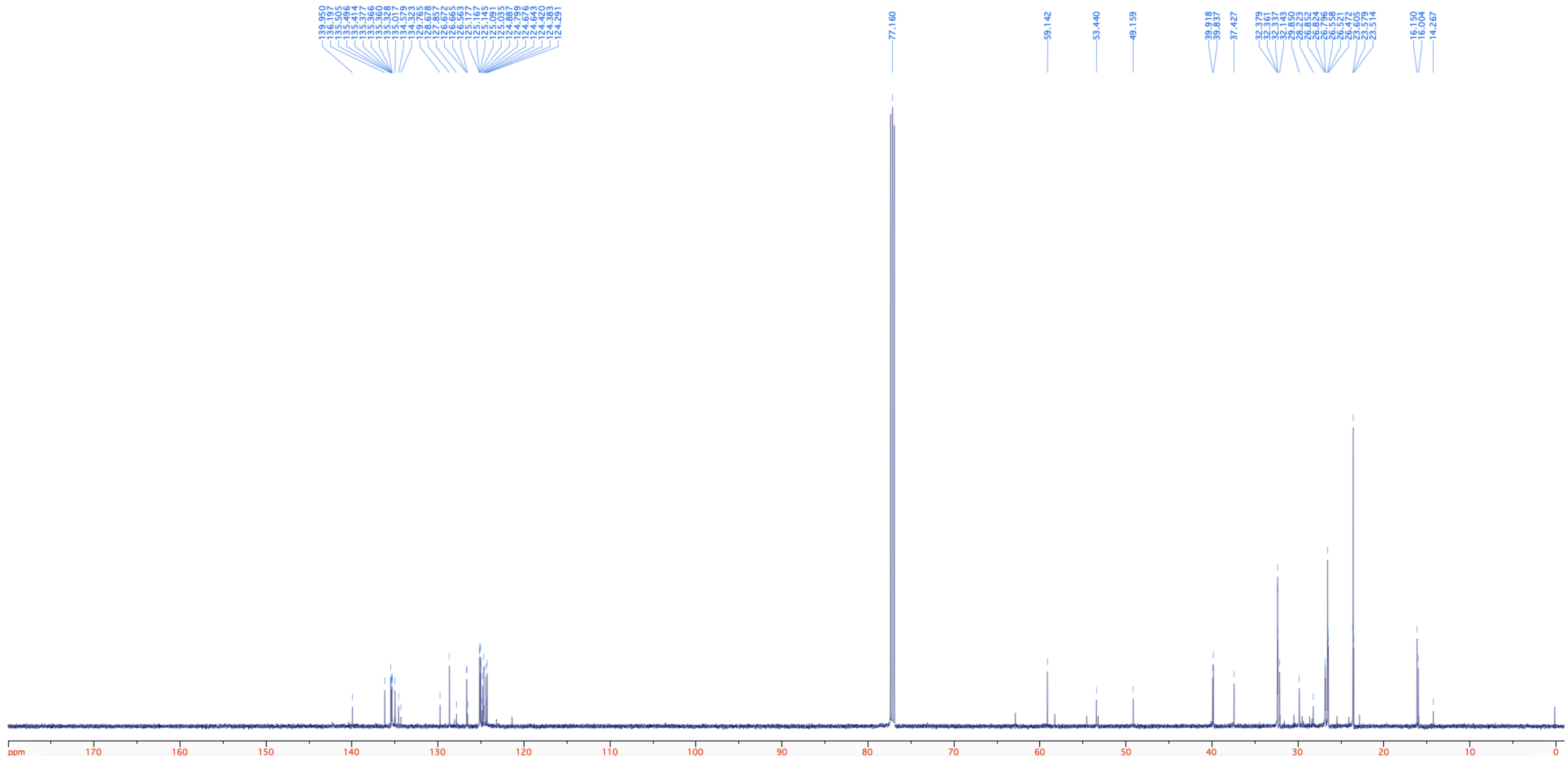
^{1}H-NMR:

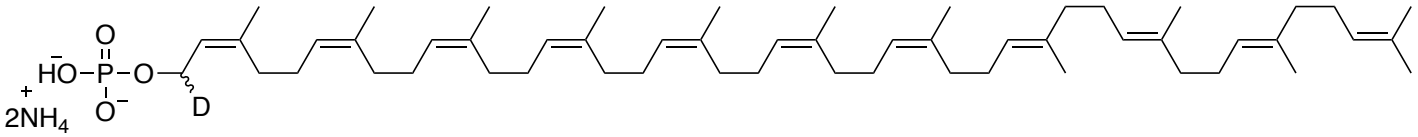




20

[13]C-NMR:





20

^{31}P-NMR: