Supporting Information

Effect of lipid length and branching of monoacylglycerides on Mincle agonist activity.

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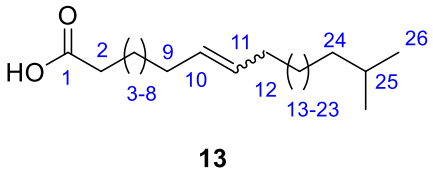
Chemistry Experimental

General Chemicals:

Prior to use, toluene (ROMIL) was dried and stored over Na wire, and the following solvents were distilled: acetone (Fisher Scientific), ethyl acetate (Fisher Scientific) and petroleum ether (Merck), DMSO (Merck). Behenic acid (BDH Biochem), $MgSO_4$ (Pure Science), NaCl (Chem Solute), Et_2O (LabServ), DMAP (Lab Supply), EDCI (Chem Impex), TFA (Pancreac), THF (ROMIL), $NaHCO_3$ (Pure Science), HCl (Chem Solute), isopropanol (Fischer Scientific), $KMnO_4$ (AnalR), 11-methyldodecanoic acid (Larodan AB), 13-methyltetradecanoic acid (Larodan AB), 15-methylhexadecanoic acid (Larodan AB), 17-methyloctadecanoic acid (Larodan AB), 18-methylnonadecanoic acid (Larodan AB), 21-methyldocosanoic acid (Larodan AB), Palmitic Acid (Fulka), Oleic acid (Sigma Aldich), Stearic acid (Fisher Scientific), Hexacosanoic acid (Merck), $CDCl_3$ (Aldrich), Diisopropylamine (Sigma Aldich), Sodium Hydride (Sigma Aldrich), Triphenylphosphene (Acros Organics), Methyl iodide (Sigma Aldrich), Boron trifluoride diethyl etherate (Janssen Chimica), Triethylsilane (Sigma Aldrich), Pyridinium Chlorochromate (Sigma Aldirch), and 10-bromodecanoic acid (Sigma Aldrich) were used as received. Reactions were monitored by TLC analysis by dipping in 10% H_2SO_4 in EtOH followed by charring or dipping in a solution of $KMnO_4$ (0.05 M), K_2CO_3 (0.4 M), and NaOH (0.06%) in water. Column chromatography was performed using Pure Science silica gel (40-63 μm). All solvents were removed by evaporation under reduced pressure. High resolution mass spectra were recorded on an Agilent 6530 Q-TOF mass spectrometer utilising a JetStream^{TM} electro-spray ionisation (ESI) source in positive or negative mode. Optical rotations were recorded on a Autopol II (Rudolph Research Analytical) at 589 nm (sodium D-line). Infrared (IR) spectra were recorded as thin films using either a Bruker Platinum-ATR spectrometer and are reported in wave numbers (cm^{-1}).

Nuclear magnetic resonance spectra were obtained at 20 °C in $CDCl_3$ or C_5D_5N using a Varian INOVA operating at 500 MHz. Chemical shifts are given in ppm (δ) relative to the solvent residual peak. NMR peak assignments were made using COSY, HSQC, and HMBC 2D experiments.

25-Methylhexacos-10-enoic acid (13). 10-bromodecanoic acid (225 mg, 1 mmol) and triphenyl phosphine (262 mg, 1 mmol) were combined and heated at 80 ºC for 30 mins under Ar atmosphere. The resulting red oil was suspended in 8 mL of dry DMSO and subjected to further heating for 20 mins. The mixture was then cooled to 0 ºC, and butyl lithium (2.0 M in cyclohexane, 1.25 mL, 2.5 mmol) was added drop wise. The reaction was stirred for one hour before aldehyde **12** (500 mg, 2 mmol) was added. The reaction mixture was warmed to r.t. and further stirred for 3 hr. The suspension was then diluted with EtOAc, washed with 1M HCl and brine, dried with anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* to give a red oil. The crude product was purified by silica gel flash chromatography (PE) to yield **13** as a white solid (172 mg, 0.84 mmol, 21%). R_f = 0.8 (PE); IR (film) = 2998, 2923, 2853, 1708, 1462, 1411, 932, 739; ^{1}H NMR (500 MHz, $CDCl_3$) 5.47–5.41 (m, 2H, H-10, H-11), 2.37–2.29 (m, 2H, H-2), 2.08–1.94 (m, 4H, H-9, H-1), 1.6–1.58 (m, 2H, H-3), 1.55–1.46 (m, 1H, H-25), 1.32–1.21 (m, 32H, H-4–8, H-13–23), 1.17–1.10 (m, 2H, H-24), 0.86 (d, $J_{25,26a+b}$ = 7.1 Hz, 6H, H-26); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.97 (C-10), 129.78 (C-11), 39.05 (C-24), 35.58 (C-2), 33.98 (C-12), 32.13 (C-10), 29.94, 29.76, 29.73, 29.69, 29.68, 29.66, 29.65, 29.63, 29.60, 29.58, 29.56, 29.42, 29.32, 29.28, 29.23, 29.22, 29.21, 29.17, 29.05, 29.04, 28.99 (C-4–8, C-13–22), 27.96 (C-25), 27.41 (C-23), 24.67 (C-3), 22.65 (C-26); HRMS (ESI) *m/z* calculated for $[C_{27}H_{53}O_2]^+$: 409.4040, found 409.4029.



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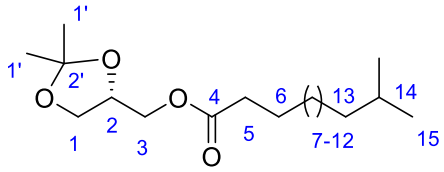
General procedure for esterification:

MAGs of different chain lengths were synthesised according to a procedure by Khan *et al.*[1] (*S*)-(*R*)-1,2-*O*-Isopropylideneglycerol (1 mmol, 1 equiv.) and the carboxylic acid (2 mmol, 2 equiv.) were co-evaporated together with dry toluene (5 mL), then suspended in dry toluene. To the reaction mixture, EDCI (3.3 mmol, 3.3 equiv.) and DMAP (1 mmol, 1 equiv.) were added and the resulting suspension was heated to 70 ºC for 48 h. The reaction mixture was then cooled to r.t. and diluted with of EtOAc (5 mL). The organic layer was washed with water (5 mL), sat. aq. $NaHCO_3$

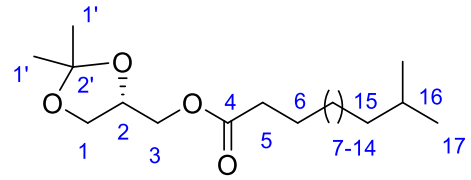
(5 mL), and brine (5 mL). The combined aqueous phases were re-extracted with of EtOAc (5 mL) and the combined organic phases were dried with anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified using gradient silica-gel column chromatography (PE to PE/EtOAc, 4:1, *v/v*).

1,2-*O*-Isopropylidene-1-*O*-(11-methyldodecanoyl)-*sn*-glycerol (16a). By subjecting diol **14** (30 mg, 0.22 mmol), 11-methyldodecanoic acid **15a** (97 mg, 0.45 mmol), EDCI (139 mg, 0.726 mmol) and DMAP (27 mg, 0.34 mmol) to the general procedure for esterification (8 h), the title compound **16a** was obtained as a colourless oil (46.2 mg, 0.140 mmol, 64%). R_f = 0.4 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{23.1}$ = +4.8 (c = 1 $CHCl_3$); IR (film) = 2924, 2854, 1740, 1459, 1380, 1251, 1212, 1157, 1083, 1056, 1042, 964, 861, 841, 737, 681 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.31 (p, $J_{2,3}$ = $J_{2,1}$ = 6.2 Hz, 1H, H-2), 4.16 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.11–4.09 (m, 2H, H-3b, H1a), 3.75–3.71 (m, 1H, H-1b), 2.34 (t, $J_{5,6}$ = 7.5 Hz, 2H, H-5), 1.62 (p, $J_{6,5}$ = $J_{6,7}$ = 7.3 Hz, 2H, H-6), 1.53–1.48 (m, 1H, H-14), 1.44 (s, 3H, H-1′), 1.37 (s, 3H, H-1′), 1.31–1.23 (m, 12H, H-7–12), 1.18–1.11 (m, 2H, H-13), 0.85 (d, $J_{14,15a+b}$ = 6.6 Hz, 6H, H-15); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.55 (C-4), 109.70 (C-2′), 73.54 (C-2), 66.23 (C-1), 64.40 (C-3), 38.92 (C-13), 34.00 (C-5), 29.77, 29.58, 29.50, 29.34, 29.13, 29.00 (C-7–11), 27.84 (C-14), 27.27 (C-12), 26.56 (C-1′), 25.28 (C-1′), 24.78 (C-6), 22.54 (C-15); HRMS (ESI) *m/z* calculated for $[C_{19}H_{36}NaO_4]^+$: 351.2506, found 351.2523.



16a

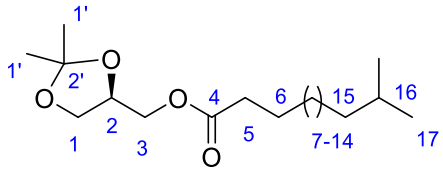
1,2-*O*-Isopropylidene-1-*O*-(13-methyltetradecanoyl)-*sn*-glycerol (16b). By subjecting diol **14** (22 mg, 0.16 mmol), 13-methyltetradecanoic acid **15b** (82 mg, 0.33 mmol), EDCI (105 mg, 0.549 mmol) and DMAP (20 mg, 0.1664 mmol) to the general procedure for esterification (8 h), the title compound **16b** was obtained as a colourless oil (45 mg, 0.125 mmol, 78%). R_f = 0.3 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{18.1}$ = +7.6 (c = 1, $CHCl_3$); IR (film) = 2923, 2851, 1741, 1465, 1370, 1250, 1159, 1056, 1009, 871, 841, 743, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.31 (p, $J_{2,3}$ = 6.2 Hz, $J_{2,1}$ = 4.69 Hz, 1H, H-2), 4.16 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.09 (t, $J_{3b,2}$ = 5.8 Hz, 1H, H-3b), 4.07–4.05 (m, 1H, H-1a), 3.74 (dd, $J_{1b,1a}$ = 8.5 Hz, $J_{1b,2}$ = 6.2 Hz, 1H, H-1b), 2.34 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 1.66–1.58 (m, 2H, H-6), 1.54–1.46 (m, 1H, H-16), 1.43 (s, 3H, H-



16b

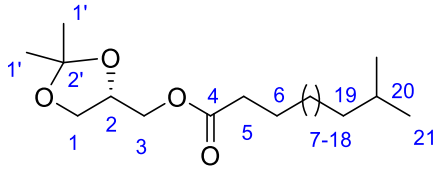
1′), 1.37 (s, 3H, H-1′), 1.32–1.21 (m, 16H, H-7–14), 1.18–1.11 (m, 2H, H-15), 0.86 (d, $J_{16,17a+b}$ = 6.6 Hz, 6H, H-17); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.64 (C-4), 109.79 (C-2′), 73.66 (C-2), 66.33 (C-1), 64.49 (C-3), 39.03 (C-15), 34.25 (C-5), 29.92, 29.68, 29.63, 29.58, 29.43, 29.23, 29.10 (C-7–13), 27.95 (C-16), 27.40 (C-14), 26.65 (C-1′), 25.35 (C-1′), 24.87 (C-6), 22.70 (C-17). HRMS (ESI) *m/z* calculated for $[C_{21}H_{40}NaO_4]^+$: 379.2819, found 379.2835.

1,2-*O*-Isopropylidene-3-*O*-(13-methyltetradecanoyl)-*sn*-glycerol (16c). By subjecting diol **14** (25 mg, 0.18 mmol), 13-methyltetradecanoic acid **15b** (87 mg, 0.36 mmol), EDCI (113 mg, 0.594 mmol) and DMAP (22 mg, 0.18 mmol) to the general procedure for esterification (8 h), the title compound **16c** was obtained as a colourless oil (50 mg, 0.14 mmol, 77%). R_f = 0.3 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{21.1}$ = -4.2 (c = 2, $CHCl_3$); IR (film) = 2921, 2851, 1743, 1464, 1370, 1250, 1173, 1056, 1089, 871, 841, 756, 653 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.31 (p, $J_{2,3}$ = $J_{2,1}$ = 6.2 Hz, 1H, H-2), 4.16 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.09 (t, $J_{3b,2}$ = 5.8 Hz, 1H, H-3b), 4.07–4.05 (m, 1H, H-1a), 3.74 (dd, $J_{1b,1a}$ = 8.5 Hz, $J_{1b,2}$ = 6.2 Hz, 1H, H-1b), 2.34 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 1.66–1.58 (m, 2H, H-6), 1.54–1.46 (m, 1H, H-16), 1.43 (s, 3H, H-1′), 1.37 (s, 3H, H-1′), 1.32–1.21 (m, 16H, H-7–14), 1.18–1.11 (m, 2H, H-15), 0.86 (d, $J_{16,17a+b}$ = 6.6 Hz, 6H, H-17); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.51 (C-4), 109.67 (C-2′), 73.52 (C-2), 66.18 (C-1), 64.37 (C-3), 38.92 (C-15), 33.98 (C-5), 29.80, 29.57, 29.51, 29.47, 29.32, 29.12, 29.99 (C-7–13), 27.84 (C-16), 27.29 (C-14), 26.54 (C-1′), 25.27 (C-1′), 24.76 (C-6), 22.48 (C-17); HRMS (ESI) *m/z* calculated for $[C_{21}H_{41}O_4]^+$: 357.2999, found 357.2991.



16c

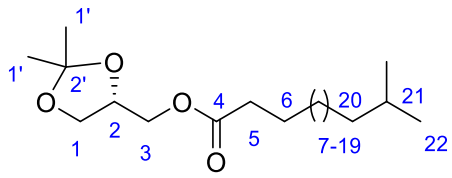
1,2-*O*-Isopropylidene-1-*O*-(17-methyloctadecanoyl)-*sn*-glycerol (16d). By subjecting diol **14** (33.5 mg, 0.25 mmol), 17-methyloctadecanoic acid **15c** (150 mg, 0.50 mmol), EDCI (160 mg, 0.83 mmol) and DMAP (31 mg, 0.25 mmol) to the general procedure for esterification (8 h), the title compound **16d** was obtained as a white solid (75 mg, 0.18 mmol, 73%). R_f = 0.3 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{22.1}$ = +5.1 (c = 2, $CHCl_3$); IR (film) = 2916, 2848, 1733, 1469, 1212, 1153, 1049, 1048, 871, 846, 747, 683 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.31 (p, $J_{2,3}$ = $J_{2,1}$ = 5.1 Hz, 1H, H-2), 4.16 (dd, $J_{3a,3b}$ = 11.6 Hz, $J_{3a,2}$ = 4.8 Hz, 1H, H-3a), 4.12–4.03 (m, H, H-3b, H-1a), 3.73 (dd, $J_{1b,1a}$ = 8.9 Hz, $J_{1b,2}$ =



16d

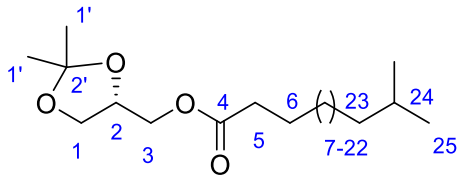
5.8 Hz, 1H, H-1b), 2.33 (t, $J_{5,6}$ = 7.3 Hz, 2H, H-5), 1.61 (p, $J_{6,5}$ = $J_{6,7}$ = 7.3 Hz, 2H, H-6), 1.50 (m, 1H, H-20), 1.43 (s, 3H, H-1′), 1.36 (s, 3H, H-1′), 1.33–1.21 (m, 24H, H-7–18), 1.16–1.10 (m, 2H, H-19), 0.85 (d, $J_{20,21a+b}$ = 6.6 Hz, 6H, H-21); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.63 (C-4), 109.80 (C-2′), 73.65 (C-2), 66.33 (C-1), 64.49 (C-3), 39.05 (C-19), 34.10 (C-5), 29.94, 29.72, 29.68, 29.67, 29.66, 29.63, 29.58, 29.44, 29.24, 29.11 (C-7–17), 27.95 (C-20), 27.41 (C-18), 26.67 (C-1′), 25.38 (C-1 ′), 24.88 (C-6), 22.65 (C-21); HRMS (ESI) *m/z* calculated for $[C_{25}H_{48}NaO_4]^+$: 435.3445, found 435.3449.

1,2-*O*-Isopropylidene-1-*O*-(18-methylnonadecanoyl)-*sn*-glycerol (16e). By subjecting diol **14** (32 mg, 0.24 mmol), 18-methylnonadecanoic acid **15d** (150 mg, 0.48 mmol), EDCI (153 mg, 0.79 mmol) and DMAP (29 mg, 0.24 mmol) to the general procedure for esterification (48 h), the title compound **16e** was obtained as a white solid (77 mg, 0.18 mmol, 75%). R_f = 0.4 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{19.5}$ = +3.7 (c = 2, $CHCl_3$); IR (film) = 2916, 2849, 1731, 1453, 1253, 1158, 1110, 1055, 931, 874, 791, 582 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30 (p, $J_{2,3}$ = $J_{2,1}$ = 6.2 Hz, 1H, H-2), 4.15 (dd, $J_{3a,3b}$ = 11.6 Hz, $J_{3a,2}$ = 4.9 Hz, 1H, H-3a), 4.11–4.02 (m, H, H-3b, H-1a), 3.72 (dd, $J_{1b,1a}$ = 8.0 Hz, $J_{1b,2}$ = 6.7 Hz, 1H, H-1b), 2.33 (t, $J_{5,6}$ = 7.4 Hz, 2H, H-5), 1.64–1.57 (m, 2H, H-6), 1.53–1.46 (m, 1H, H-21), 1.42 (s, 3H, H-1′), 1.35 (s, 3H, H-1′), 1.32–1.19 (m, 26H, H-7–19), 1.17–1.10 (m, 2H, H-20), 0.85 (d, $J_{21,22a+b}$ = 6.6 Hz, 6H, H-22); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.64 (C-4), 109.81 (C-2′), 73.66 (C-2), 66.35 (C-1), 64.50 (C-3), 39.05 (C-20), 34.11 (C-5), 29.94, 29.71, 29.68, 29.67, 29.66, 29.63, 29.58, 29.44, 29.23, 29.11 (C-7–18), 27.95 (C-21), 27.41 (C-19), 26.67 (C-1′), 25.39 (C-1′), 24.88 (C-6), 22.65 (C-22); HRMS (ESI) *m/z* calculated for $[C_{26}H_{50}NaO_4]^+$: 449.3601, found 449.3616.



16e

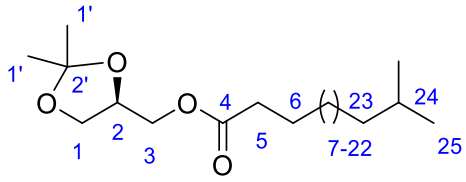
1,2-*O*-Isopropylidene-1-*O*-(21-methyldoconoyl)-*sn*-glycerol (16f). By subjecting diol **14** (20 mg, 0.15 mmol), 21-methyldoconoic acid **15e** (107 mg, 0.30 mmol), EDCI (88 mg, 0.46 mmol) and DMAP (18 mg, 0.15 mmol) to the general procedure for esterification (8 h), the title compound **16f** was obtained as a white solid (51.5 mg, 0.11 mmol, 73%). R_f = 0.4 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{19.0}$ = +4.9 (c = 2, $CHCl_3$); IR (film) = 2987, 2917, 2849, 1733, 1471, 1372, 1239, 1158, 1114, 1051,



16f

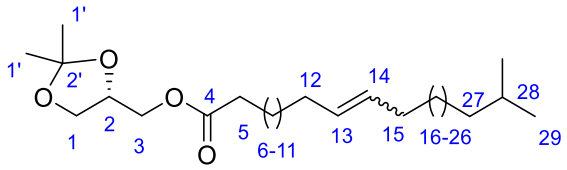
996, 890, 771, 583, 463 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (p, $J_{2,3} = J_{2,1}$ = 5.9 Hz, 1H, H-2), 4.18 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.14–4.05 (m, 2H, H-3b, H-1a), 3.76 (dd, $J_{1b,1a}$ = 8.5 Hz, $J_{1b,2}$ = 6.2 Hz, 1H, H-1b), 2.36 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 1.66–1.60 (m, 2H, H-6), 1.56–1.48 (s, 1H, H-24), 1.45 (s, 3H, H-1′), 1.38 (s, 3H, H-1′), 1.34–1.21 (m, 38H, H-7–22), 1.18–1.11 (m, 2H, H-23), 0.85 (d, $J_{24,25a+b}$ = 6.6 Hz, 6H, H-25); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.67 (C-4), 109.83 (C-2′), 73.67 (C-2), 66.36 (C-1), 64.53 (C-3), 39.07 (C-23), 34.13 (C-5), 29.97, 29.75, 29.72, 29.69, 29.67, 29.62, 29.47, 29.27, 29.14 (C-7–21), 27.98 (C-24), 27.44 (C-22), 26.70 (C-1′), 25.41 (C-1′), 24.91 (C-6), 22.68 (C-25); HRMS (ESI) *m/z* calculated for $[C_{29}H_{56}NaO_4]^+$: 491.4071, found 491.4098.

1,2-*O*-Isopropylidene-3-*O*-(21-methyldoconoyl)-*sn*-glycerol (16g). By subjecting diol **14** (20 mg, 0.15 mmol), 21-methyldoconoic acid **15e** (107 mg, 0.30 mmol), EDCI (88 mg, 0.46 mmol) and DMAP (18 mg, 0.15 mmol) to the general procedure for esterification (8 h), the title compound **16g** was obtained as a white solid (52 mg, 0.11 mmol, 74%). R_f = 0.4 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{17.5}$ = -1.6 (c = 2, $CHCl_3$); IR (film) = 2986, 2927, 2846, 1732, 1414, 1301, 1222, 1188, 1028, 983, 846, 718, 550, 449 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30 (p, $J_{2,3} = J_{2,1}$ = 5.8 Hz, 1H, H-2), 4.18 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.14–4.06 (m, 2H, H-3b, H-1a), 3.76 (dd, $J_{1b,1a}$ = 8.5 Hz, $J_{1b,2}$ = 6.2 Hz, 1H, H-1b), 2.36 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 1.67–1.59 (m, 2H, H-6), 1.55–1.48 (m, 1H, H-24), 1.45 (s, 3H, H-1′), 1.39 (s, 3H, H-1′), 1.34–1.22 (m, 32H, H-7–22), 1.18–1.13 (m, 2H, H-23), 0.86 (d, $J_{24,25a+b}$ = 6.6 Hz, 6H, H-25); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.69 (C-4), 109.83 (C-2′), 73.66 (C-2), 66.35 (C-1), 64.52 (C-3), 39.07 (C-23), 34.16 (C-5), 234.13, 29.96, 29.75, 29.72, 29.69, 29.66, 29.61, 29.47, 29.14 (C-7–21), 27.98 (C-24), 27.44 (C-22), 26.69 (C-1′), 25.41 (C-1′), 24.90 (C-6), 22.68 (C-25); HRMS (ESI) *m/z* calculated for $[C_{29}H_{56}NaO_4]^+$: 491.4071, found 491.4074.



16g

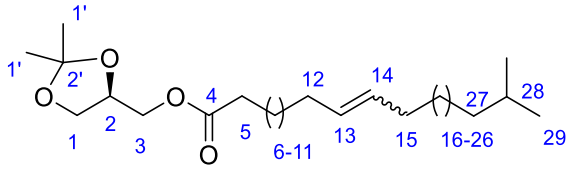
1,2-*O*-Isopropylidene-1-*O*-(25-methylhexacos-10-enoyl)-*sn*-glycerol (16h). By subjecting diol



16h

14 (7.5 mg, 0.056 mmol), (*E*/*Z*)-25-methylhexacos-10-enoic acid **13** (45 mg, 0.112 mmol), EDCI (36 mg, 1.84 mmol) and DMAP (7 mg, 0.056 mmol) to the general procedure for esterification (8 h), the title compound **16h** was obtained as a white solid (21 mg, 0.039 mmol, 71%). R_f = 0.5 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{17.1}$ = +8.6 (c = 2, $CHCl_3$); IR (film) = 2922, 2852, 1741, 1644, 1465, 1380, 1251, 1158, 1085, 1056, 975, 841, 871, 720, 582, 489 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.37–5.30 (m, 2H, H-13, H-14), 4.29 (p, $J_{2,3}$ = $J_{2,1}$ = 5.8 Hz, 1H, H-2), 4.16 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.10–4.15 (m, 2H, H-3b, H-1a), 3.73 (dd, $J_{1b,1a}$ = 8.0 Hz, $J_{1b,2}$ = 6.7 Hz, 1H, H-1b), 2.33 (t, $J_{5,6}$ = 7.4 Hz, 2H, H-5), 2.02–1.95 (m, 2H, H12), 1.64–1.60 (m, 2H, H-6), 1.54–1.47 (m, 1H, H-28), 1.42 (s, 3H, H-1′), 1.36 (s, 3H-H-1′), 1.33–1.20 (m, 32H, H-7–11, H-15–25), 1.17–1.07 (m, 4H, H-26–27), 0.85 (d, $J_{28,29a+b}$ = 6.6 Hz, 6H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.50 (C-4), 129.83 (C13), 129.65 (C-14), 109.68 (C-2′), 73.54 (C-2), 66.22 (C-1), 64.38 (C-3), 38.94 (C-27), 33.98 (C-5), 29.82, 29.65, 29.60, 29.58, 29.56, 29.55, 29.52, 29.47, 29.45, 29.33, 29.23, 29.12, 29.10, 28.99 (C-7–12, C15–25), 27.84 (C-28), 27.09 (C-26), 26.55 (C-1′), 25.27 (C-1′), 24.77 (C-6), 22.53 (C-29); HRMS (ESI) *m/z* calculated for $[C_{33}H_{62}NaO_4]^+$: 545.4540, found 545.4541.

1,2-*O*-Isopropylidene-3-*O*-(25-methylhexacos-10-enoyl)-*sn*-glycerol (16i). By subjecting diol

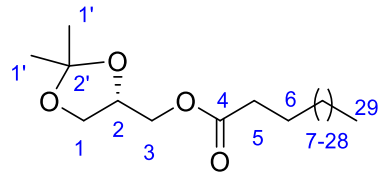


16i

14 (12.5 mg, 0.095 mmol), (*E*/*Z*)-25-methylhexacos-10-enoic acid **13** (78 mg, 0.191 mmol), EDCI (60 mg, 0.313 mmol) and DMAP (12 mg, 0.095 mmol) to the general procedure for esterification (8 h), the title compound **16i** was obtained as a white solid (37 mg, 0.071 mmol, 75%). R_f = 0.5 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{22.1}$ = -7.4 (c = 1 $CHCl_3$); IR (film) = 2921, 2852, 1741, 1645, 1465, 1369, 1213, 1158, 1063, 1056, 917, 843, 720, 657, 515, 463 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.35–5.37 (m, 2H, H-13, H-14), 4.29 (p, $J_{2,3}$ = $J_{2,1}$ = 5.8 Hz, 1H, H-2), 4.16 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.10–4.15 (m, 2H, H-3b, H-1a), 3.73 (dd, $J_{1b,1a}$ = 8.0 Hz, $J_{1b,2}$ = 6.7 Hz, 1H, H-1b), 2.32 (t, $J_{5,6}$ = 7.4 Hz, 2H, H-5), 2.02–1.95 (m, 2H, H12), 1.64–1.60 (m, 2H, H-6), 1.54–1.49 (m, 1H, H-28), 1.42 (s, 3H, H-1′), 1.36 (s, 3H, H-1′), 1.33–1.19 (m, 34H, H-7–11, H-15–26), 1.17–1.07 (m, 2H, H-27), 0.85 (d, $J_{28,29a+b}$ = 6.6 Hz, 6H, H-29); ^{13}C NMR (125 MHz,

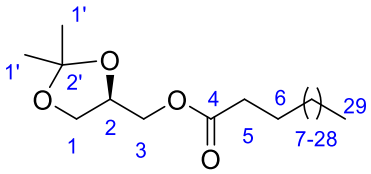
$CDCl_3$) δ 173.60 (C-4), 129.94 (C13), 129.76 (C-14), 109.79 (C-2′), 73.64 (C-2), 66.33 (C-1), 64.49 (C-3), 39.04 (C-27), 34.09 (C-5), 29.93, 29.72, 29.70, 29.68, 29.67, 29.65, 29.64, 29.62, 29.58, 29.55, 29.43, 29.31, 29.23, 29.21, 29.10 (C-7–12, C15–25), 27.95 (C-28), 27.41 (C-26), 26.66 (C-1′), 25.37 (C-1′), 24.87 (C-6), 22.64 (C-29); HRMS (ESI) *m/z* calculated for $[C_{33}H_{63}O_4]^+$: 523.4721, found 523.7442.

1,2-*O*-Isopropylidene-1-*O*-(hexacosanoyl)-*sn*-glycerol (19f). By subjecting diol **14** (30 mg, 0.23 mmol), hexacosanoic acid **17e** (182.5 mg, 0.46 mmol), EDCI (145.5 mg, 0.759 mmol) and DMAP (28 mg, 0.23 mmol) to the general procedure for esterification (8 h), the title compound **19f** was obtained as a white solid (86 mg, 0.17 mmol, 73%). R_f = 0.5 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{16.9}$ = +9.4 (c = 4, $CHCl_3$); IR (film) = 2945, 2914, 2837, 1731, 1463, 1267, 1192, 1054, 1041, 919, 896, 753, 681 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.33 (p, $J_{2,3}$ = $J_{2,1}$ = 5.4 Hz, 1H, H-2), 4.16 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.11–4.03 (m, 2H, H-3b, H-1a), 3.75 (dd, $J_{1b,1a}$ = 8.5 Hz, $J_{1b,2}$ = 6.2 Hz, 1H, H-1b), 2.34 (t, $J_{5,6}$ = 7.4 Hz, 2H, H-5), 1.63 (p, $J_{6,7}$ = $J_{6,5}$ = 7.5 Hz, 2H, H6), 1.43 (s, 3H, H-1′), 1.36 (s, 3H, H-1′), 1.33–1.20 (m, 44H, H-7–28), 0.87 (t, $J_{29,28}$ = 6.9Hz, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.67 (C-4), 109.83 (C-2′), 73.67 (C-2), 66.35 (C-1), 64.52 (C-3), 34.12 (C-5), 31.93, 29.72, 29.69, 29.67, 29.61, 29.47, 29.38, 29.27, 29.13 (C-7–27), 26.69 (C-1′), 25.41 (C-1′), 24.90 (C-6), 22.71 (C-28), 14.14 (C-29); HRMS (ESI) *m/z* calculated for$[C_{32}H_{62}NaO_4]^+$: 533.4540, found 533.4551.



19f

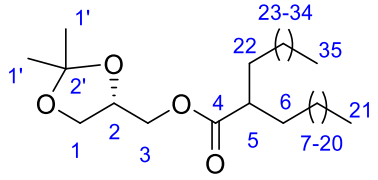
1,2-*O*-Isopropylidene-3-*O*-(hexacosanoyl)-*sn*-glycerol (19g). By subjecting diol **14** (30 mg, 0.23 mmol), hexacosanoic acid **17e** (182.5 mg, 0.46 mmol), EDCI (145.5 mg, 0.759 mmol) and DMAP (28 mg, 0.23 mmol) to the general procedure for esterification (8 h), the title compound **19g** was obtained as a white solid (83.5 mg, 0.16 mmol, 71%). R_f = 0.5 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{22.3}$ = -8.9 (c = 4 $CHCl_3$); IR (film) = 2931, 2852, 1714, 1439, 1251, 1146, 1109, 1084, 1047, 951, 863, 843, 746, 681, 547 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.33 (p, $J_{2,3}$ = $J_{2,1}$ = 5.3 Hz, 1H, H-2), 4.16 (dd, $J_{3a,3b}$ = 11.5 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.11–4.03 (m, 2H, H-3b, H-1a), 3.73 (t, $J_{1b,2}$ = 7.3, 1H, H-1b), 2.34 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 1.63 (p, $J_{6,7}$ = $J_{6,5}$ = 7.5 Hz, 2H, H6), 1.43 (s, 3H, H-1′), 1.36 (s, 3H, H-1′), 1.33–



19g

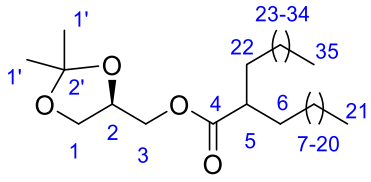
1.20 (m, 44H, H-7–28), 0.87 (t, $J_{29,28}$ = 6.8 Hz, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.60 (C-4), 109.79 (C-2′), 73.66 (C-2), 66.34 (C-1), 64.50 (C-3), 34.10 (C-5), 31.94, 29.72, 29.67, 29.66, 29.61, 29.47, 29.38, 29.26, 29.13 (C-7–27), 26.67 (C-1′), 25.38 (C-1′), 24.89 (C-6), 22.69 (C-28), 14.12 (C-29); HRMS (ESI) *m/z* calculated for $[C_{32}H_{62}NaO_4]^+$: 533.4540, found 533.4553.

1,2-*O*-Isopropylidene-1-*O*-(2-tetradecyloctadecanoyl)-*sn*-glycerol (20a). By subjecting diol **14** (25 mg, 0.19 mmol), 2-tetradecyloctadecanoic acid **18** (183 mg, 0.38 mmol), EDCI (120 mg, 0.62 mmol) and DMAP (23 mg, 0.19 mmol) to the general procedure for esterification (8 h), the title compound **20a** was obtained as a white solid (89 mg, 0.15 mmol, 77%). R_f = 0.6 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{21.1}$ = +9.4 (c = 4 $CHCl_3$); IR (film) = 2943, 2914, 2865, 1754, 1417, 1345, 1234, 1160, 1114, 1097, 1009, 952, 826, 715, 621, 519 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30 (p, $J_{2,3}$ = $J_{2,1}$ = 5.8 Hz, 1H, H-2), 4.16 (d, $J_{3a,2}$ = 5.4 Hz, 1H, H-3a), 4.07 (dd, $J_{1a,1b}$ = 8.4 Hz, $J_{1a,2}$ = 6.4 Hz, 2H, H-3b, H-1a), 3.74 (dd, $J_{1b,1a}$ = 8.4, $J_{1b,2}$ = 6.1 Hz, 1H, H-1b), 2.39–2.33 (m, 1H, H-5), 1.61–1.55 (m, 4H, H-6, H-22), 1.43 (s, 3H, H-1′), 1.36 (s, 3H, H-1′), 1.31–1.16 (m, 52H, H-7–20, H-23–34), 0.87 (t, $J_{21,20}$ = $J_{35,34}$ = 6.9Hz, 6H, H-21, H-35); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.40 (C-4), 109.71 (C-2′), 73.62 (C-2), 66.46 (C-1), 64.17 (C-3), 46.66 (C-5), 32.44, 32.39, 31.92, 29.67, 29.36, 27.44, (C-6–19, C-22–33), 26.72 (C-1′), 25.42 (C-1′), 22.69 (C-20, C-34), 14.10 (C-21, C-35); HRMS (ESI) *m/z* calculated for $[C_{38}H_{74}NaO_4]^+$: 617.5479, found 617.5483.



20a

1,2-*O*-Isopropylidene-3-*O*-(2-tetradecyloctadecanoyl)-*sn*-glycerol (20b). By subjecting diol **14** (25 mg, 0.19 mmol), 2-tetradecyloctadecanoic acid **18** (183 mg, 0.38 mmol), EDCI (120 mg, 0.62 mmol) and DMAP (23 mg, 0.19 mmol) to the general procedure for esterification (8 h), the title compound **20b** was obtained as a white solid (80 mg, 0.13 mmol, 78%). R_f = 0.6 (PE/EtOAc, 9:1, v/v); $[\alpha]_D^{18.8}$ = -8.2 (c = 3, $CHCl_3$); IR (film) = 2924, 2914, 2818, 1732, 1409, 1312, 1214, 1187, 1110, 1031, 953, 825, 742, 534 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30 (p, $J_{2,3}$ = $J_{2,1}$ = 5.9 Hz, 1H, H-2), 4.16 (d, $J_{3a,2}$ = 5.4 Hz, 1H, H-3a), 4.07 (dd, $J_{1a,1b}$ = 8.4 Hz, $J_{1a,2}$ = 6.4 Hz, 2H, H-3b, H-1a), 3.74 (dd, $J_{1b,1a}$ = 8.4, $J_{1b,2}$ = 6.3 Hz, 1H, H-1b), 2.39–2.31 (m, 1H, H-5), 1.60–1.54 (m, 4H, H-6, H-22), 1.43 (s, 3H, H-1′), 1.36 (s, 3H, H-1′), 1.31–1.16 (m, 52H, H-7–20, H-23–34), 0.88 (t, $J_{21,20}$ = $J_{35,34}$ = 6.9Hz,



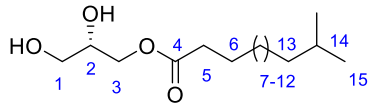
20b

6H, H-21, H-35); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.48 (C-4), 109.80 (C-2′), 73.72 (C-2), 66.57 (C-1), 64.27 (C-3), 46.71 (C-5), 32.53, 32.48, 32.01, 29.78, 29.74, 29.69, 29.64, 29.58, 29.45, 27.53 (C-6–19, C-22–33), 26.81 (C-1′), 25.50 (C-1′), 22.78 (C-20, C-34), 14.21 (C-21, C-35); HRMS (ESI) *m/z* calculated for $[C_{38}H_{74}NaO_4]^+$: 617.5479, found 617.5485.

General procedure for isopropylidene deprotection:

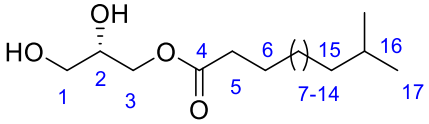
A solution of isopropylidene protected *iso*-branched, linear, or α-branched MAGs in TFA:THF:H_2O mixture (5 mL, 3:8:1, v/v/v) was added and the reaction was stirred at room temperature on rotary evaporator.[2] After 20-30 min, the reaction mixture was concentrated *in vacuo* and the resulting residue was purified using silica-gel column chromatography (PE/EtOAc, 10:1-2:1, v/v).

1-*O*-(11-methyldodecanoyl)-*sn*-glycerol (6a). By subjecting **16a** (46 mg, 0.140 mmol), to the general procedure for isopropylidene deprotection (20 mins), the title compound **6a** was obtained as a colourless oil (34 mg, 0.11 mmol, 85%). R_f = 0.3 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{21.3}$ = +5.4 (c = 1, $CHCl_3$); IR (film) = 3435, 3004, 2923, 2851, 1711, 1424, 1372, 1221, 1091, 532 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.6 Hz, 1H, H-3a), 4.15 (dd, $J_{3b,3a}$ = 11.7 Hz, $J_{3b,2}$ = 6.2 Hz, 1H, H-3b), 3.93 (p, $J_{2,3}$ = $J_{2,1}$ = 5.5 Hz, 1H, H-2), 3.70 (dd, $J_{1a,1b}$ = 11.4 Hz, $J_{1a,2}$ = 3.8 Hz, 1H, H-1a), 3.60 (dd, $J_{1b,1a}$ = 11.4 Hz, $J_{1b,2}$ = 5.8 Hz, 1H, H-1b), 2.54 (br s, 1H, OH), 2.35 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 2.11 (br s, 1H, OH), 1.66–1.59 (m, 2H, H-6), 1.54–1.46 (m, 1H, H-14), 1.33–1.23 (m, 12H, H-7–12), 1.18–1.11 (m, 2H, H-13), 0.86 (d, $J_{14,15a+b}$ = 6.6 Hz, 6H, H-15); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.37 (C-4), 70.26 (C-2), 65.16 (C-3), 63.31 (C-1), 39.03 (13), 34.15 (C-5), 29.88, 29.61, 29.44, 29.24, 29.11 (C-7–11), 27.95 (C-14), 27.38 (C-12), 24.90 (C-6), 22.65 (C-15); HRMS (ESI) *m/z* calculated for $[C_{16}H_{32}NaO_4]^+$: 311.2193, found 311.2191.



6a

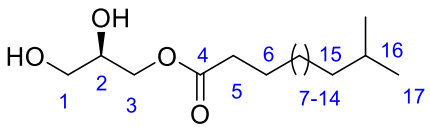
1-*O*-(13-methyltetradecanoyl)-*sn*-glycerol (6b). By subjecting **16b** (45 mg, 0.125 mmol), to the general procedure for isopropylidene deprotection (25 mins), the title compound **6b** was obtained as a white solid (36 mg, 0.11 mmol, 91%). R_f = 0.3 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{22.3}$ = +6.5 (c = 1, $CHCl_3$); IR (film) = 3434, 3004, 2917, 2849, 1732,



6b

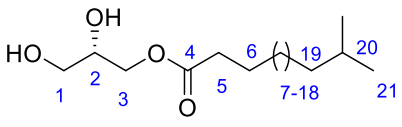
1467, 1372, 1171, 1045, 720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.21 (dd, $J_{3a,3b}$ = 11.6 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.14 (dd, $J_{3b,3a}$ = 11.6 Hz, $J_{3b,2}$ = 6.1 Hz, 1H, H-3b), 3.93 (p, $J_{2,3}$ = $J_{2,1}$ = 5.1 1H, H-2), 3.71 (dd, $J_{1a,1b}$ = 11.3 Hz, $J_{1a,2}$ = 4.1 Hz, 1H, H-1a), 3.60 (dd, $J_{1a,1b}$ = 11.3 Hz, $J_{1b,2}$ = 5.6 Hz, 1H, H-1b), 2.36 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 1.67–1.59 (m, 2H, H-6), 1.55–1.48 (m, 1H, H-16), 1.35–1.22 (m, 16H, H-7–16), 1.18–1.12 (m, 2H, H-15), 0.86 (d, $J_{16,17a+b}$ = 7.2 Hz, 6H, H-17); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.40 (C-4), 70.27 (C-2), 65.16 (C-3), 63.33 (C-1), 39.05 (15), 34.16 (C-5), 29.94, 29.71, 29.65, 29.60, 29.45, 29.25, 29.13 (C-7–13), 27.42 (C-16), 27.42 (C-14), 24.92 (C-6), 22.67 (C-17); HRMS (ESI) *m/z* calculated for $[C_{18}H_{36}NaO_4]^+$: 339.2506, found 339.2514.

3-*O*-(13-methyltetradecanoyl)-*sn*-glycerol (6c). By subjecting **16c** (50 mg, 0.14 mmol), to the general procedure for isopropylidene deprotection (30 mins), the title compound **6c** was obtained as a white solid (41 mg, 0.13 mmol, 92%). R_f = 0.3 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{17.1}$ = -5.3 (c = 1, $CHCl_3$); IR (film) = 3435, 3014, 2927, 2843, 1722, 1462, 1376, 1156, 1045, 987, 856, 719 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.19 (dd, $J_{3a,3b}$ = 11.6 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.14 (dd, $J_{3b,3a}$ = 11.6 Hz, $J_{3b,2}$ = 6.1 Hz, 1H, H-3b), 3.96–3.92 (m, 1H, H-2), 3.68 (d, $J_{1b,2}$ = 3.9 Hz, 1H, H-1a), 3.62–3.56 (m, 1H, H-1b), 2.77 (br s, 1H, OH), 2.34 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 1.62 (p, $J_{6,7}$ = $J_{6,5}$ = 7.6 Hz, 2H, H-6), 1.55–1.45 (m, 1H, H-16), 1.34–1.99 (m, 16H, H-7–14), 1.17–1.11 (m, 2H, H-15), 0.86 (d, $J_{16,17a+b}$ = 7.2 Hz, 6H, H-17); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.41 (C-4), 70.25 (C-2), 65.13 (C-3), 63.33 (C-1), 39.04 (15), 34.15 (C-5), 29.93, 29.70, 29.68, 29.67, 29.64, 29.60, 29.44, 29.24, 29.12 (C-7–13), 27.96 (C-16), 27.41 (C-14), 24.90 (C-6), 22.66 (C-17); HRMS (ESI) *m/z* calculated for $[C_{18}H_{36}NaO_4]^+$: 339.2506, found 339.2511.



6c

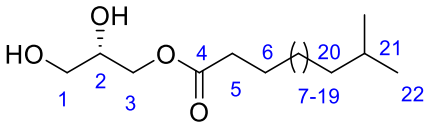
1-*O*-(17-methyloctadecanoyl)-*sn*-glycerol (6d). By subjecting **16d** (75 mg, 0.18 mmol), to the general procedure for isopropylidene deprotection (20 mins), the title compound **6d** was obtained as a white solid (59.6 mg, 0.16 mmol, 89%). R_f = 0.3 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{17.0}$ = +2.8 (c = 1, $CHCl_3$); IR (film) = 3425, 3114, 2926, 2849, 1734, 1467, 1363, 1171, 1152, 1008, 907, 887, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.19 (dd, $J_{3a,3b}$ = 11.6 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.14 (dd, $J_{3b,3a}$ = 11.6 Hz, $J_{3b,2}$ = 6.1 Hz, 1H, H-3b), 3.95–3.90 (m, 1H, H-2), 3.68 (d, $J_{1a,2}$ = 3.9 Hz, 1H, H-1a), 3.62–3.56 (m, 1H, H-1b), 2.61 (br s, 1H, OH), 2.34



6d

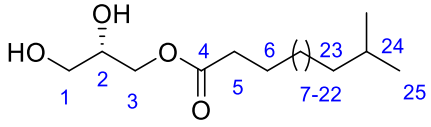
(t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 2.17 (br s, 1H, OH), 1.62 (p, $J_{6,5}$ = $J_{6,7}$ = 7.6 Hz, 2H, H-6), 1.55–1.47 (m, 1H, H-20), 1.34–1.22 (m, 24H, H-7–18), 1.17–1.11 (m, 2H, H-19), 0.86 (d, $J_{20,21a+b}$ = 7.2 Hz, 6H, H-21); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.39 (C-4), 70.26 (C-2), 65.15 (C-3), 63.31 (C-1), 39.05 (19), 34.15 (C-5), 29.94, 29.72, 29.69, 29.68, 29.67, 29.64, 29.59, 29.45, 29.24, 29.12, 29.10 (C-7–17), 27.96 (C-20), 27.42 (C-18), 24.90 (C-6), 22.66 (C-21); HRMS (ESI) *m/z* calculated for $[C_{22}H_{45}O_4]^+$: 373.3312, found 373.3318.

1-*O*-(18-methylnonadecanoyl)-*sn*-glycerol (6e). By subjecting **16e** (77 mg, 0.18 mmol), to the general procedure for isopropylidene deprotection (30 mins), the title compound **6e** was obtained as a white solid (65 mg, 0.167 mmol, 93%). R_f = 0.2 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{21.4}$ = +2.2 (c = 1.2, $CHCl_3$); IR (film) = 3411, 3304, 2916, 2849, 1724, 1463, 1351, 1172, 1018, 906, 867, 729 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.15 (dd, $J_{3b,2}$ = 11.7 Hz, $J_{3b,2}$ = 4.7 Hz, 1H, H-3b), 3.93 (p, $J_{2,3}$ = $J_{2,1}$ = 5.2 Hz, 1H, H-2), 3.69 (dd, $J_{1a,1b}$ = 11.5 Hz, $J_{1a,2}$ = 3.9 Hz, 1H, H-1a), 3.59 (dd, $J_{1b,1a}$ = 11.5 Hz, $J_{1b,2}$ = 5.9 Hz, H-1b), 2.35 (t, $J_{5,6}$ = 7.5 Hz, 2H, H-5), 1.62 (p, $J_{6,7}$ = $J_{6,5}$ = 7.4 Hz, 2H, H-6), 1.55–1.48 (m, 1H, H-21), 1.34–1.19 (m, 26H, H-7–19), 1.18–1.12 (m, 2H, H-20), 0.86 (d, $J_{21,22a+b}$ = 7.1 Hz, 6H, H-22); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.38 (C-4), 70.26 (C-2), 65.14 (C-3), 63.32 (C-1), 39.05 (20), 34.15 (C-5), 29.94, 29.72, 29.69, 29.67, 29.64, 29.60, 29.45, 29.24, 29.12 (C-7–18), 27.96 (C-21), 27.42 (C-19), 24.90 (C-6), 22.66 (C-22); HRMS (ESI) *m/z* calculated for $[C_{23}H_{47}O_4]^+$: 387.3469, found 387.3474.



6e

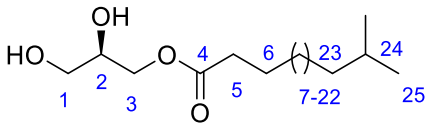
1-*O*-(21-methyldoconoyl)-*sn*-glycerol (6f). By subjecting **16f** (51.5 mg, 0.11 mmol), to the general procedure for isopropylidene deprotection (30 mins), the title compound **6f** was obtained as a white solid (43 mg, 0.10 mmol, 91%). R_f = 0.3 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{18.8}$ = +2.4 (c = 1, $CHCl_3$); IR (film) = 3384, 2922, 2852, 1737, 1457, 1341, 1172, 1012, 916, 854, 769, 543 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.6 Hz, 1H, H-3a), 4.14 (dd, $J_{3b,3a}$ = 11.7 Hz, $J_{3b,2}$ = 6.2 Hz, 1H, H-3b), 3.94 (p, $J_{2,3}$ = $J_{2,1}$ = 5.3 Hz, 1H, H-2, 3.68 (d, $J_{1a,2}$ = 3.9 Hz, 1H, H-1a), 3.62–3.56 (d, $J_{1b,2}$ = 3.8 Hz, 1H, H-1b), 2.61 (br s, 1H, OH), 2.35 (t, $J_{5,6}$ = 7.6 Hz, 2H, H-5), 2.18 (br s, 1H, OH), 1.62 (p, $J_{6,7}$ = $J_{6,5}$ = 7.6 Hz, 2H, H-6), 1.54–1.45 (m, 1H, H-24), 1.31–1.25 (m, 30H, H-7–22), 1.17–1.14 (m, 2H, H-



6f

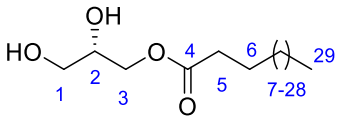
23), 0.86 (d, $J_{24,25a+b}$ = 7.2 Hz, 6H, H-25); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.38 (C-4), 70.27 (C-2), 65.16 (C-3), 63.32 (C-1), 39.05 (23), 34.15 (C-5), 29.93, 29.70, 29.64, 29.59, 29.44, 29.24, 29.12, 29.10 (C-7–21), 27.96 (C-24), 27.41 (C-22), 24.91 (C-6), 22.66 (C-25); HRMS (ESI) *m/z* calculated for $[C_{26}H_{52}NaO_4]^+$: 451.3758, found 451.3762.

3-*O*-(21-methyldoconoyl)-*sn*-glycerol (6g). By subjecting diol **16g** (52 mg, 0.11 mmol), to the general procedure for isopropylidene deprotection (30 mins), the title compound **6g** was obtained as a white solid (43.5 mg, 0.101 mmol, 92%). R_f = 0.3 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{21.8}$ = -1.8 (c = 2, $CHCl_3$); IR (film) = 3384, 2922, 2852, 1737, 1457, 1341, 1172, 1012, 916, 854, 769, 543 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 4.21 (dd, $J_{3a,3b}$ = 11.6 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.16 (dd, $J_{3b,3b}$ = 11.6 Hz, $J_{3b,2}$ = 4.7 Hz, 1H, H-3b), 3.96 (p, $J_{2,3}$ = $J_{2,1}$ = 5.1 Hz, 1H, H-2), 3.70 (dd, $J_{1a,1b}$ = 11.6 Hz, $J_{1a,2}$ = 3.9 Hz, 1H, H-1a), 3.64 (dd, $J_{1b,1a}$ = 11.6 Hz, $J_{1b,2}$ = 5.9 Hz, H-1b), 2.64 (br s, 1H, OH), 2.39 (t, $J_{5,6}$ = 7.4 Hz, 2H, H-5), 1.66–1.61 (m, 2H, H-6), 1.55–1.47 (m, 1H, H-24), 1.30–1.18 (m, 32H, H-7–22), 1.15–1.12 (m, 2H, H-23), 0.86 (d, $J_{24,25a+b}$ = 7.1 Hz, 6H, H-25);^{13}C NMR (125 MHz, $CDCl_3$) δ 174.28 (C-4), 70.15 (C-2), 65.03 (C-3), 63.22 (C-1), 38.95 (23), 34.04 (C-5), 28.84, 29.62, 29.64, 29.59, 29.58, 29.56, 29.49, 29.34, 29.14, 29.12, 29.02, 29.00 (C-7–21), 27.85 (C-24), 27.31 (C-22), 24.80 (C-6), 22.55 (C-25); HRMS (ESI) *m/z* calculated for $[C_{26}H_{53}O_4]^+$: 429.3938, found 429.3924.



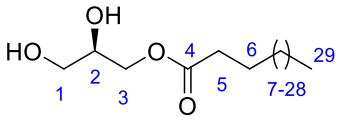
6g

1-*O*-(hexacosanoyl)-*sn*-glycerol (7f). By subjecting **19f** (86 mg, 0.17 mmol), to the general procedure for isopropylidene deprotection (30 mins), the title compound **7f** was obtained as a white solid (63 mg, 0.16 mmol, 93%). R_f = 0.3 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{20.5}$ = +8.4 (c = 2, $CHCl_3$); IR (film) = 3361, 2924, 2852, 1731, 1452, 1332, 1187, 1007, 957, 823, 791, 673 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 4.20 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.6 Hz, 1H, H-3a), 4.15 (dd, $J_{3b,3b}$ = 11.6 Hz, $J_{3b,2}$ = 6.2 Hz, 1H, H-3b), 3.93 (p, $J_{2,3}$ = $J_{2,1}$ = 5.2 Hz, 1H, H-2), 3.69 (dd, $J_{1a,1b}$ = 11.4 Hz, $J_{1a,2}$ = 4 Hz, 1H, H-1a), 3.59 (dd, $J_{1b,1a}$ = 11.4 Hz, $J_{1b,2}$ = 5.8 Hz, H-1b), 2.36 (t, $J_{5,6}$ = 8.0 Hz, 2H, H-5), 1.67–1.61 (m, 2H, H-6), 1.31–1.27 (m, 44H, H-7–28), 0.88 (t, $J_{28,29}$ = 7.0 Hz, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.62 (C-4), 73.66 (C-2), 66.34 (C-3), 64.51 (C-1), 34.11 (C-5), 31.94, 29.71, 29.69, 29.67, 29.47, 29.38, 29.26, 29.13 (C-7–27), 24.90 (C-6), 22.71 (C-28), 14.13 (C-29); HRMS (ESI) *m/z* calculated for $[C_{29}H_{59}O_4]^+$: 471.4408, found 471.4422.



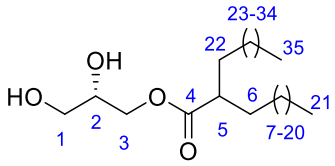
7f

3-*O*-(hexacosanoyl)-*sn*-glycerol (7g). By subjecting **19g** (83 mg, 0.16 mmol), to the general procedure for isopropylidene deprotection (25 mins), the title compound **7g** was obtained as a white solid (58 mg, 0.145 mmol, 91%). R_f = 0.3 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{19.6}$ = -8.8 (c = 2, $CHCl_3$); IR (film) = 3341, 2921, 2851, 1724, 1487, 1331, 1165, 1009, 967, 823, 761, 656 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 4.23 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.5 Hz, 1H, H-3a), 4.15 (dd, $J_{3b,3b}$ = 11.7 Hz, $J_{3b,2}$ = 6.2 Hz, 1H, H-3b), 3.95 (p, $J_{2,3}$ = $J_{2,1}$ = 5.2 Hz, 1H, H-2), 3.69 (dd, $J_{1a,1b}$ = 11.5 Hz, $J_{1a,2}$ = 4.0 Hz, 1H, H-1a), 3.59 (dd, $J_{1b,1a}$ = 11.5 Hz, $J_{1b,2}$ = 5.8 Hz, H-1b), 2.36 (t, $J_{5,6}$ = 7.4 Hz, 2H, H-5), 1.67–1.61 (m, 2H, H-6), 1.31–1.27 (m, 44H, H-7–28), 0.89 (t, $J_{28,29}$ = 7.0 Hz, 3H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.66 (C-4), 73.66 (C-2), 66.34 (C-3), 64.52 (C-1), 34.12 (C-5), 31.94, 29.71, 29.69, 29.67, 29.66, 29.61, 29.47, 29.38, 29.26, 29.13 (C-7–27), 24.90 (C-6), 22.70 (C-28), 14.14 (C-29); HRMS (ESI) *m/z* calculated for $[C_{29}H_{59}O_4]^+$: 471.4408, found 471.4413.



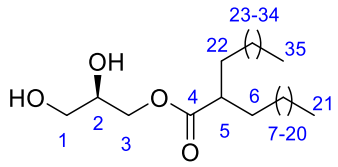
7g

1-*O*-2-tetradecyloctadecanoyl-*sn*-glycerol (8a). By subjecting **20a** (89 mg, 0.15 mmol), to the general procedure for isopropylidene deprotection (20 mins), the title compound **8a** was obtained as a white solid (66 mg, 0.137 mmol, 91%). R_f = 0.4 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{18.6}$ = +7.6 (c = 2, $CHCl_3$); IR (film) = 3381, 2924, 2862, 1727, 1476, 1345, 1174, 1008, 926, 853, 787, 5490 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 4.21 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.15 (dd, $J_{3b,3b}$ = 11.7 Hz, $J_{3b,2}$ = 6.1 Hz, 1H, H-3b), 3.92 (p, $J_{2,3}$ = $J_{2,1}$ = 5.2 Hz, 1H, H-2), 3.69 (dd, $J_{1a,1b}$ = 11.5 Hz, $J_{1a,2}$ = 3.9 Hz, 1H, H-1a), 3.59 (dd, $J_{1b,1a}$ = 11.5 Hz, $J_{1b,2}$ = 5.7 Hz, H-1b), 2.39–2.34 (m, 1H, H-5), 2.28 (br s, 1H, OH), 1.62–1.57 (m, 2H, H-6), 1.49–1.39 (m, 2H, H-22), 1.32–1.05 (m, 54H, H-7–20, H-23–35), 0.86 (t, $J_{21,20}$ = $J_{35,34}$ = 7.0 Hz, 6H, H-21, H-35); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.27 (C-4), 70.3 (C-2), 65.00 (C-3), 63.34 (C-1), 46.70 (C-5), 32.48, 32.40, 31.92, 29.69, 29.67, 29.60, 29.54, 29.47, 29.36, 27.46, 27.43, 22.69 (C-6–20, C22–33), 14.12 (C-21, C-35); HRMS (ESI) *m/z* calculated for $[C_{35}H_{71}O_4]^+$: 555.5347, found 555.5349.



8a

3-*O*-2-tetradecyloctadecanoyl-*sn*-glycerol (8b). By subjecting diol **20b** (80 mg, 0.13 mmol), to the general procedure for isopropylidene deprotection (30 mins), the title compound **8b** was obtained as a white solid (53 mg, 0.11 mmol, 89%). R_f = 0.4 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{20.4}$ = -7.8 (c = 2, $CHCl_3$); IR (film) = 3381, 2924, 2835, 1714, 1443, 1328, 1179, 1013, 906, 854, 761, 541 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 4.21 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.8 Hz, 1H, H-3a), 4.15 (dd, $J_{3b,3b}$ = 11.7 Hz, $J_{3b,2}$ = 6.0 Hz, 1H, H-3b), 3.92 (p, $J_{2,3}$ = $J_{2,1}$ = 5.2 Hz, 1H, H-2), 3.69 (dd, $J_{1a,1b}$ = 11.5 Hz, $J_{1a,2}$ = 3.9 Hz, 1H, H-1a), 3.59 (dd, $J_{1b,1a}$ = 11.5 Hz, $J_{1b,2}$ = 5.8 Hz, H-1b), 2.39–2.33 (m, 1H, H-5), 2.28 (br s, 1H, OH), 1.61–1.57 (m, 2H, H-6), 1.48–1.41 (m, 2H, H-22), 1.31–1.24 (m, 54H, H-7–20, H-23–35), 0.86 (t, $J_{21,20}$ = $J_{35,34}$ = 7.0 Hz, 6H, H-21, H-35); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.26 (C-4), 70.36 (C-2), 64.99 (C-3), 63.35 (C-1), 46.70 (C-5), 32.40, 31.92, 29.70, 29.64, 29.60, 29.54, 29.47, 29.36, 27.45, 27.43, 22.69 (C-6–20, C22-34), 14.12 (C-21, C-34); HRMS (ESI) *m/z* calculated for $[C_{35}H_{70}NaO_4]^+$: 577.5166, found 577.5172.

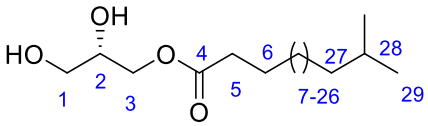


8b

General procedure for hydrogenation:

A solution of isopropylidene protected MAGs dissolved in DCM (5 mL) was added $Pd(OH)_2/C$. H_2-gas was allowed to bubble through the reaction mixture for 12 hours. The suspension was then diluted with CH_2Cl_2, filtered through celite and concentrated *in vacuo*. The resulting residue was purified using silica-gel column chromatography (PE/EtOAc, 10:1-2:1, v/v).

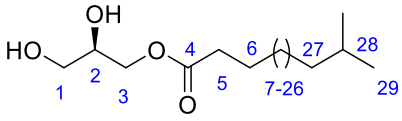
1-*O*-(25-methylhexacosanoyl)-*sn*-glycerol (6h). By subjecting **16h** (21 mg, 0.039 mmol) and $Pd(OH)_2/C$ (40 mg) to the general procedure for hydrogenation, the title compound **6h** was obtained as a white solid (17 mg, 0.034 mmol, 89%). R_f = 0.4 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{21.5}$ = +6.4 (c = 1, $CHCl_3$); IR (film) = 3374, 2932, 2851, 1734, 1453, 1346, 1189, 1012, 918, 857, 799, 673, 576 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 4.20 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.15 (dd, $J_{3b,3a}$ = 11.7 Hz, $J_{3b,2}$ = 4.7 Hz, 1H, H-3b), 3.93 (p, $J_{2,3}$ = $J_{2,1}$ = 5.2 Hz, 1H, H-2), 3.69 (dd, $J_{1a,1b}$ = 11.7 Hz, $J_{1a,2}$ = 3.9 Hz, 1H, H-1a), 3.60 (dd, $J_{1b,1a}$ = 11.7 Hz, $J_{1b,2}$ = 5.9 Hz, H-1b), 2.39–2.33 (m, 2H, H-5), 1.65–1.61 (m, 2H, H-6), 1.55–1.48 (m, 1H, H-28), 1.32–1.21 (m, 40H, H-7–26), 1.1–1.12 (m, 2H, H-27), 0.86 (d, $J_{28,29a+b}$ = 7.1 Hz, 6H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.28 (C-4), 70.16 (C-2), 65.06 (C-3), 63.21 (C-



6h

1), 38.95 (27), 34.05 (C-5), 29.84, 29.62, 29.60, 29.58, 29.57, 29.54, 29.53, 29.49, 29.34, 29.14, 29.02 (C-7–25), 27.86 (C-28), 27.32 (C-26), 24.80 (C-6), 22.56 (C-29); HRMS (ESI) *m/z* calculated for $[C_{30}H_{60}NaO_4]^+$: 507.4401, found 507.4402

3-*O*-(25-methylhexacosanoyl)-*sn*-glycerol (6i). By subjecting **16i** (37 mg, 0.071 mmol) and $Pd(OH)_2/C$ (53 mg) to the general procedure for hydrogenation, the title compound **6i** was obtained as a white solid (30 mg, 0.062 mmol, 87%). R_f = 0.4 (PE/EtOAc, 2:1, v/v); $[\alpha]_D^{21.6}$ = -4.8 (c = 1, $CHCl_3$); IR (film) = 3314, 2912, 2841, 1715, 1452, 1347, 1189, 1009, 927, 853, 712, 576 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 4.20 (dd, $J_{3a,3b}$ = 11.7 Hz, $J_{3a,2}$ = 4.7 Hz, 1H, H-3a), 4.15 (dd, $J_{3b,3b}$ = 11.6 Hz, $J_{3b,2}$ = 4.7 Hz, 1H, H-3b), 3.93 (p, $J_{2,3}$ = $J_{2,1}$ = 5.2 Hz, 1H, H-2), 3.69 (dd, $J_{1a,1b}$ = 11.6 Hz, $J_{1a,2}$ = 3.9 Hz, 1H, H-1a), 3.59 (dd, $J_{1b,1a}$ = 11.6 Hz, $J_{1b,2}$ = 5.9 Hz, H-1b), 2.39–2.33 (m, 2H, H-5), 1.6 –1.61 (m, 2H, H-6), 1.55–1.48 (m, 1H, H-28), 1.32–1.21 (m, 40H, H-7–26), 1.15–1.12 (m, 2H, H-27), 0.86 (d, $J_{28,29a+b}$ = 7.1 Hz, 6H, H-29); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.38 (C-4), 70.26 (C-2), 65.16 (C-3), 63.31 (C-1), 39.05 (27), 34.15 (C-5), 29.94, 29.72, 29.69, 29.68, 29.67, 29.64, 29.59, 29.44, 29.24, 29.12 (C-7–25), 27.96 (C-28), 27.41 (C-26), 24.90 (C-6), 22.66 (C-29); HRMS (ESI) *m/z* calculated for $[C_{30}H_{61}O_4]^+$: 485.4564, found 485.4571.



6i

Biological Methods:

2B4-NFAT-GFP reporter cells assay:

Purified lipids (1 mg/mL) in chloroform/methanol (2:1, *v*/*v*) were serially diluted with isopropanol and added to the wells of 96-well plates, followed by evaporation of the solvent. The concentration of 2B4-NFAT-GFP reporter cells expressing hMincle + FcRγ, mMincle + FcRγ, or FcRγ was adjusted to 4×10^5 cells/mL and 100 uL/well were added to MAG-coated plates (0.1, or 1 nmol/well) for 18 h.[3] The reporter cells were harvested, stained with DAPI, and analysed for NFAT-GFP expression using flow cytometry.

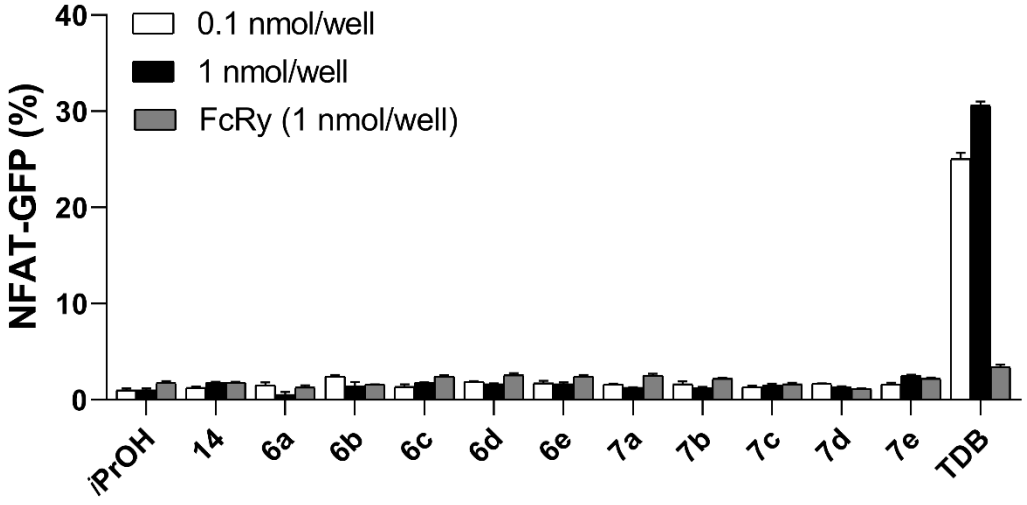


Figure 1: NFAT-GFP 2B4 reporter cells expressing mMincle + FcRγ, or FcRγ-only were stimulated using MAG-coated plates (0.1 or 1 nmol/well) for 18 h. The cells were then harvested and examined for NFAT-GFP expression. Data reported is a representative of two independent experiments performed in duplicate (mean ± SEM).

Human Monocyte Assay:

The use of human leukocyte from 20 healthy donors with written informed consent was approved by New Zealand Northern A Health and Disability Ethics Committee (approval number 15/NTA/178). Human monocytes were purified from whole blood by negative selection[4] using RosettaSep Human Monocyte Enrichment Cocktail (StemCell) according to the manufacturer's instructions. The density centrifugation was carried out using Ficoll-Paque (1.078 g/L, GE

Healthcare Life Sciences) and stained with CellTrace™ CFSE Cell Proliferation Kit (Thermo Fisher). The cell concentration was adjusted to 1 x 10^6 cell/mL in complete RMPI (10% FCS, 1% PenStrep) and 100 µL were added to individual well, with plate-coated MAGs or TDB (0.1, or 1 nmol/well). Supernatant was collected after 24 h incubation at 37 °C (5% CO_2).

Cytokine Analysis: hIL-8 (BD Biosciences) levels were determined via sandwich ELISA according to the manufacturer's instructions.

MMT Assay:

A standard MTT assay was performed using HL-60 cell line.[5] Cells suspended in cRPMI media (1×10^6 cells/mL) were added to a 96 well plate (100 µL/well) coated with **6b**, **7d**, **7f**, **8a** or cyclohexamide (positive control) at concentrations of 0.001, 0.01, 0.1, 1, 10, or 100 nmol/well, and incubated at 37 °C (5% CO_2) for 22 h. Untreated cells served as a negative control. The supernatant was then removed, and the cells were treated with 100 µL of 1mg/mL MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] solution and incubated for a further 3 h. After this time, 150 µL of MTT solvent (4 mM HCl, 0.1% NP40 in isopropanol) was added into each well. The solution was pipetted to fully dissolve the MTT formazan and optical density was measured at 590 nm.

Endotoxin Testing:

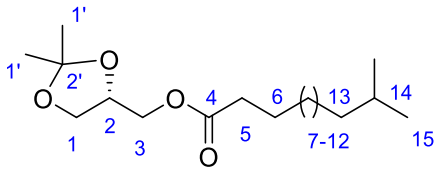
All synthesised MAGs were confirmed to be endotoxin free at a sensitivity of ≤0.1 EU/mL by using the Pierce Limulus amebocyte lysate (LAL) chromogenic endotoxin quantitation kit (Thermo Scientific).

References:

1. A. A. Khan, B. L. Stocker and M. S. M. Timmer, *Carbohydr. Res.*, 2012, **356**, 25-36.
2. P. L. van der Peet, C. Gunawan, S. Torigoe, S. Yamasaki and S. J. Williams, *Chem. Commun.*, 2015, **51**, 5100-5103.
3. S. Yamasaki, E. Ishikawa, M. Sakuma, H. Hara, K. Ogata and T. Saito, *Nat Immunol*, 2008, **9**, 1179-1188.
4. L. Ziegler-Heitbrock, *Front. Immunol*, 2015, **6**.
5. M. V. Berridge, P. M. Herst and A. S. Tan, in *Biotechnol. Ann. Rev.*, Elsevier, 2005, vol. 11, 127-152.

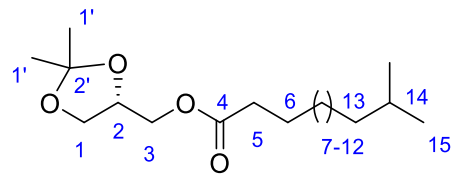
NMR Spectra

^{1}H NMR, $CDCl_3$, 500 MHz

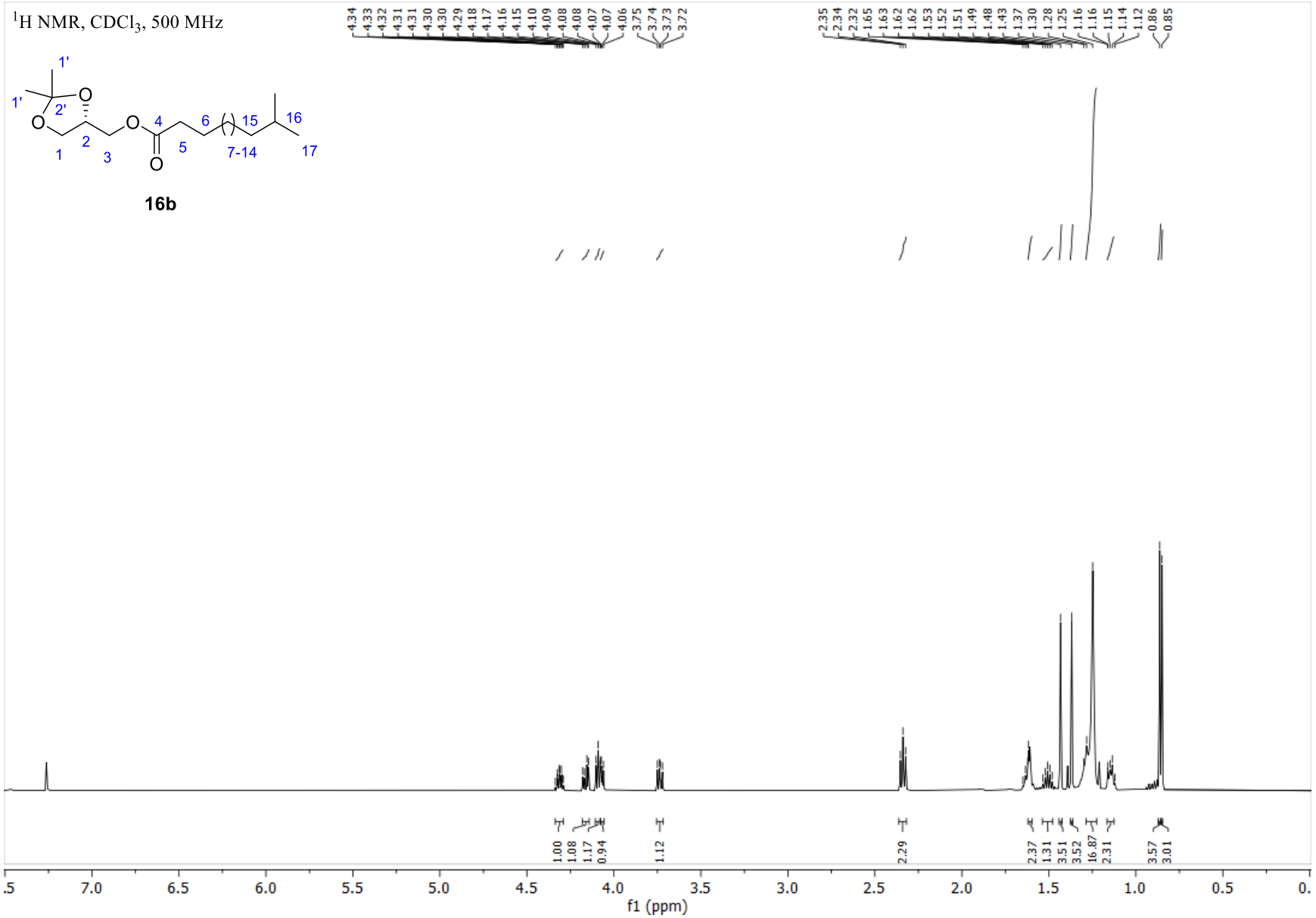


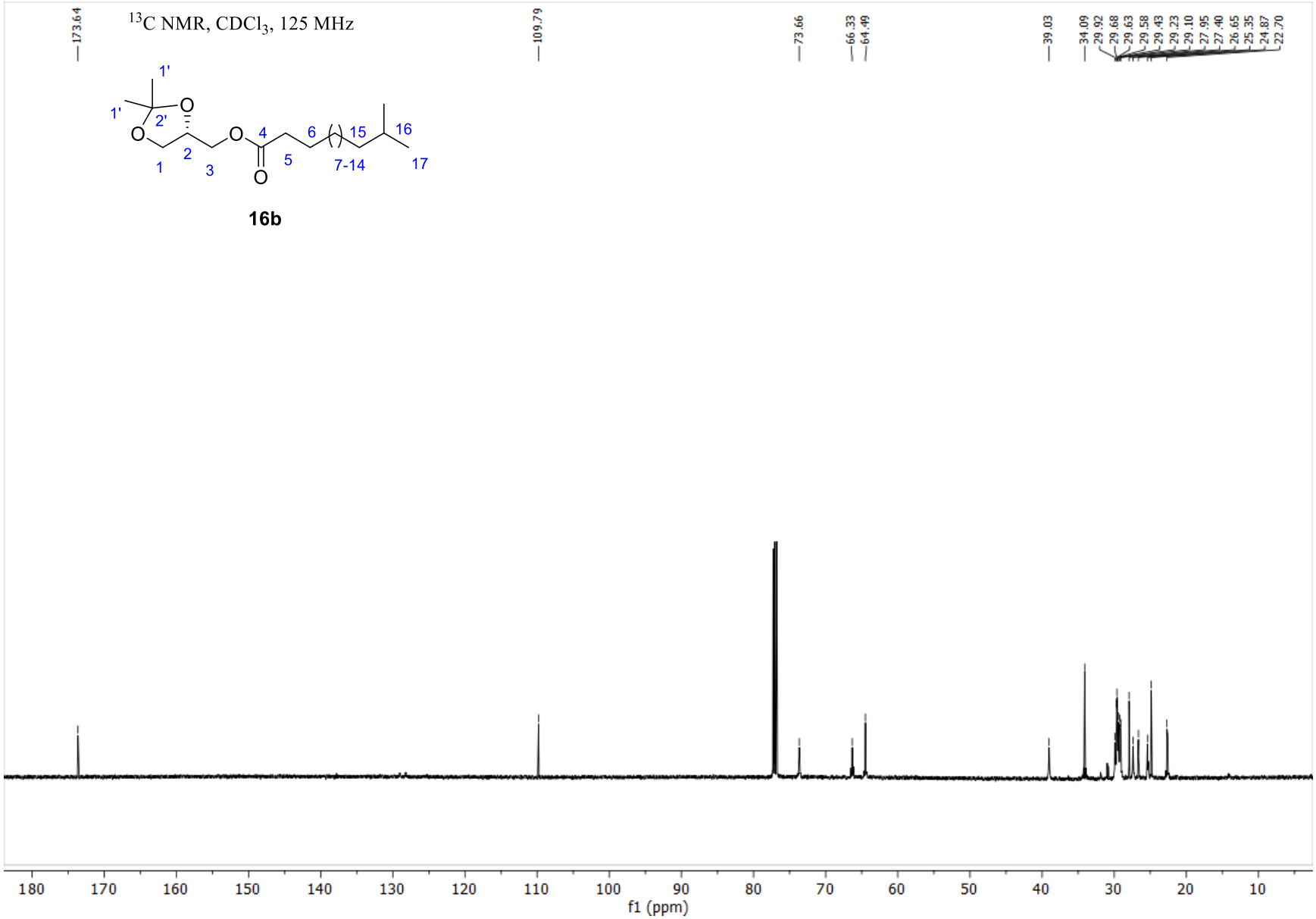
16a

^{13}C NMR, $CDCl_3$, 125 MHz



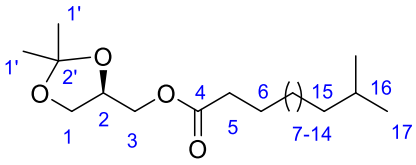
16a


^{1}H NMR, $CDCl_3$, 500 MHz
1'
1'
2'
O
O
O
1
2
3
4
5
6
7-14
15
16
17
O
16b
4.34
4.33
4.32
4.31
4.31
4.30
4.30
4.29
4.18
4.17
4.16
4.15
4.10
4.09
4.08
4.08
4.07
4.07
4.06
3.75
3.74
3.73
3.72
2.35
2.34
2.32
1.65
1.63
1.62
1.62
1.53
1.52
1.51
1.49
1.48
1.43
1.37
1.30
1.28
1.25
1.16
1.16
1.15
1.14
1.12
0.86
0.85
1.00
1.08
1.17
0.94
1.12
2.29
2.37
1.31
3.51
3.52
16.87
2.31
3.57
3.01
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
f1 (ppm)

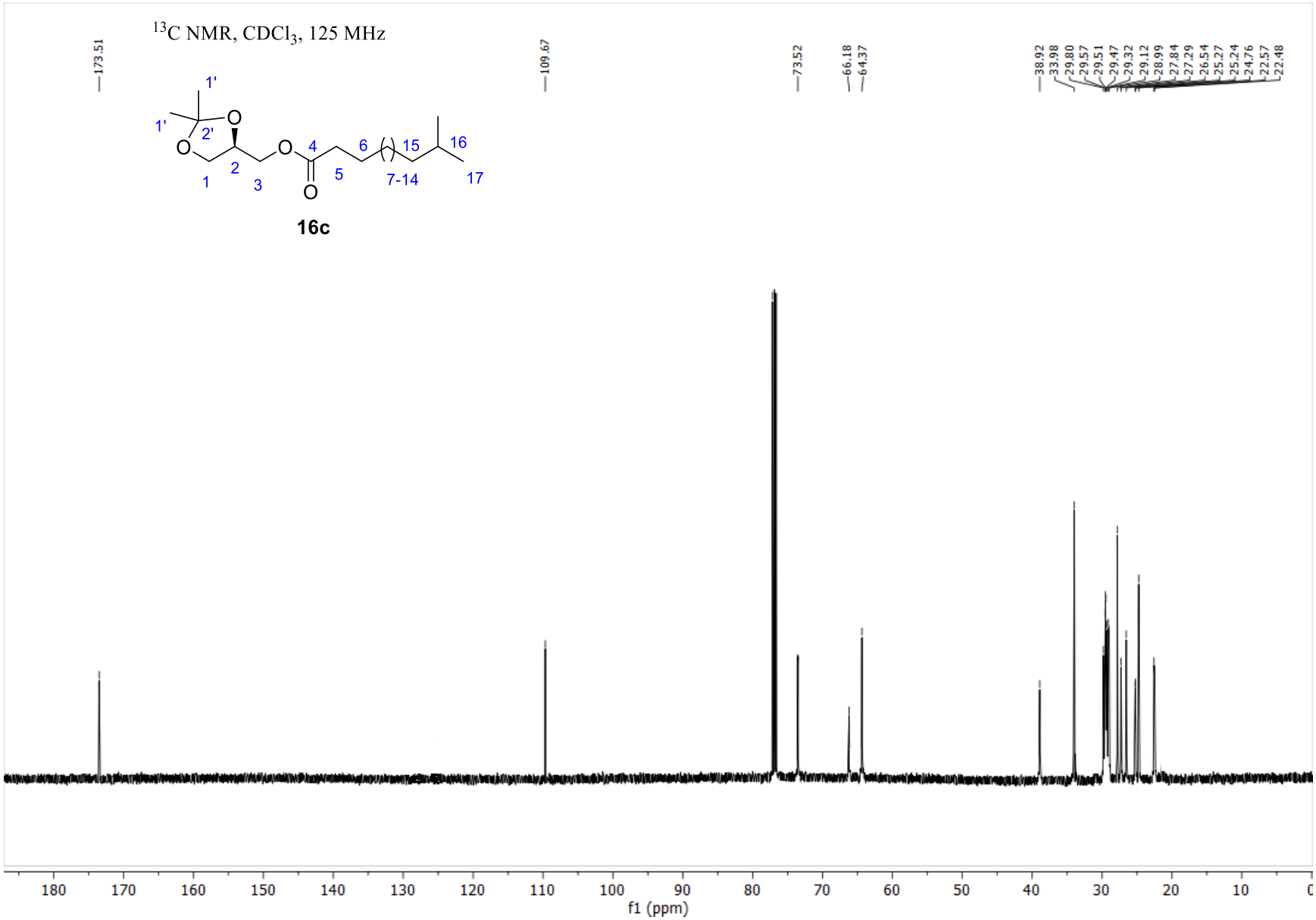

^{13}C NMR, $CDCl_3$, 125 MHz
173.64
109.79
73.66
66.33
64.49
39.03
34.09
29.92
29.68
29.63
29.58
29.43
29.23
29.10
27.95
27.40
26.65
25.35
24.87
22.70
1'
1'
2'
O
O
O
1
2
3
4
5
6
7-14
15
16
17
O
f1 (ppm)

16b

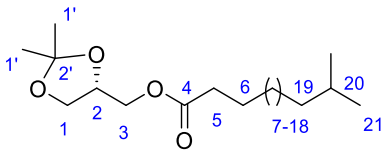
^{1}H NMR, $CDCl_3$, 500 MHz



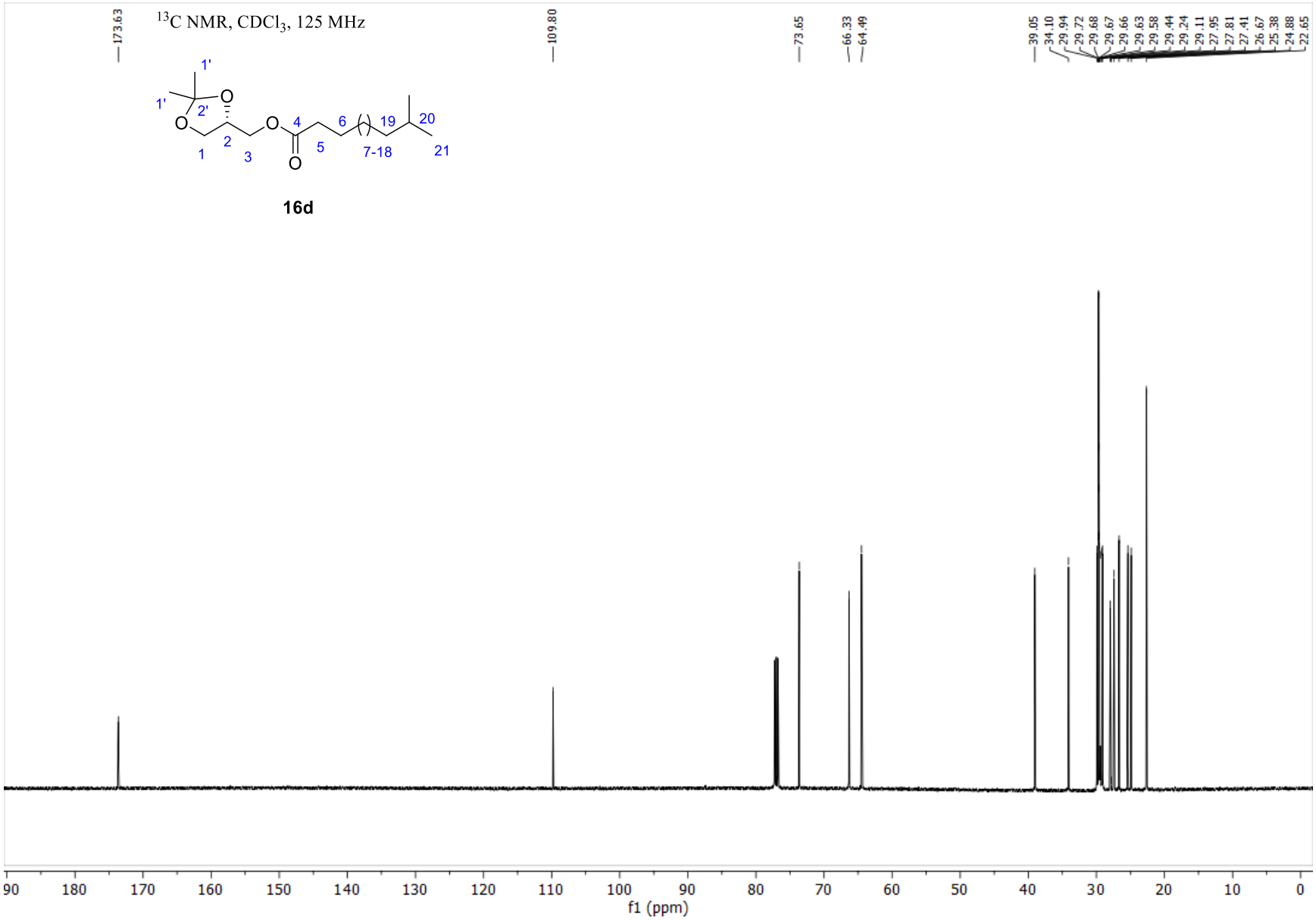
16c

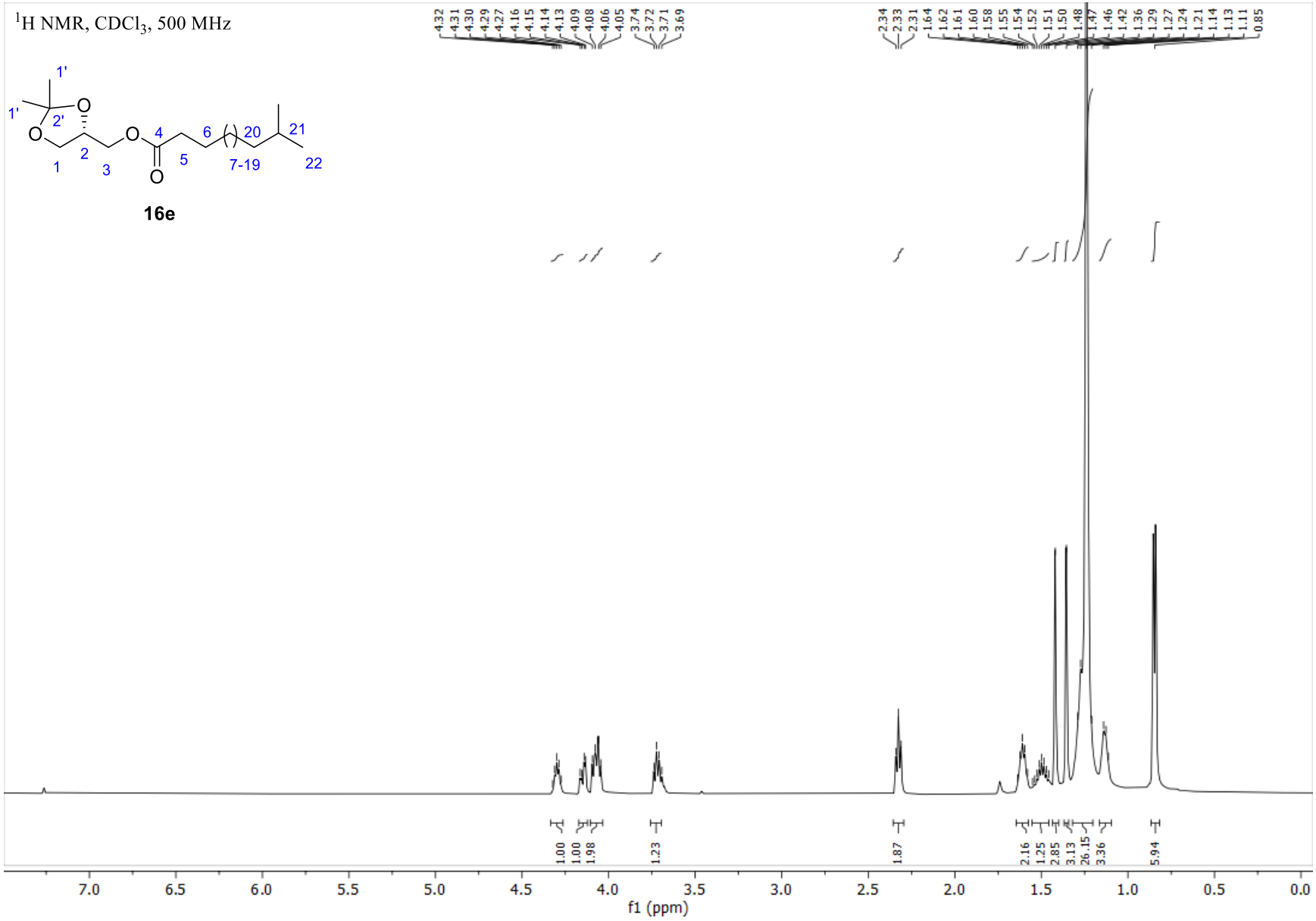

^{13}C NMR, $CDCl_3$, 125 MHz
173.51
109.67
73.52
66.18
64.37
38.92
33.98
29.80
29.57
29.51
29.47
29.32
29.12
28.99
27.84
27.29
26.54
25.27
25.24
24.76
22.57
22.48
1'
1'
2'
O
O
O
1
2
3
4
5
6
7-14
15
16
17
O
16c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

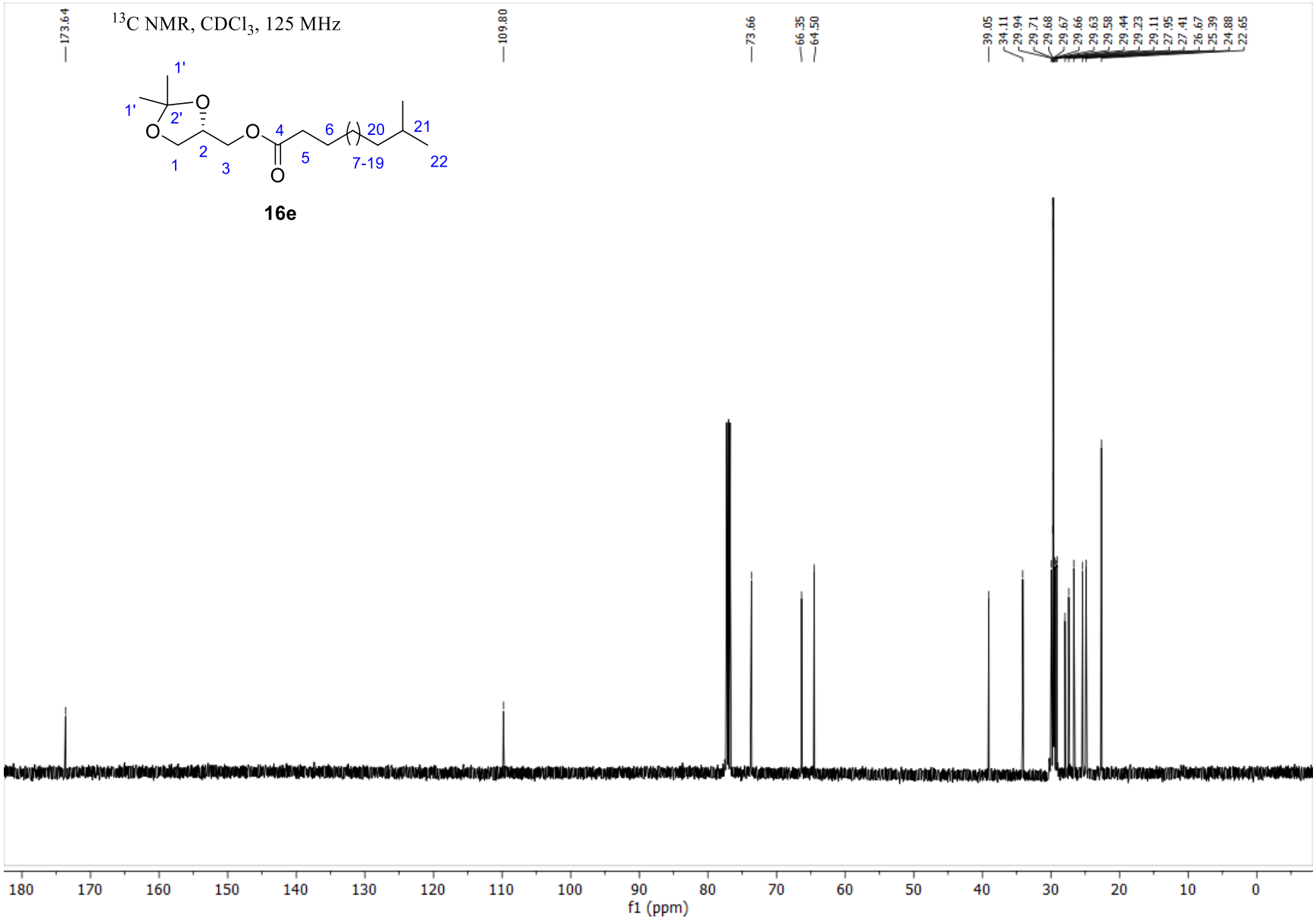
^{1}H NMR, $CDCl_3$, 500 MHz

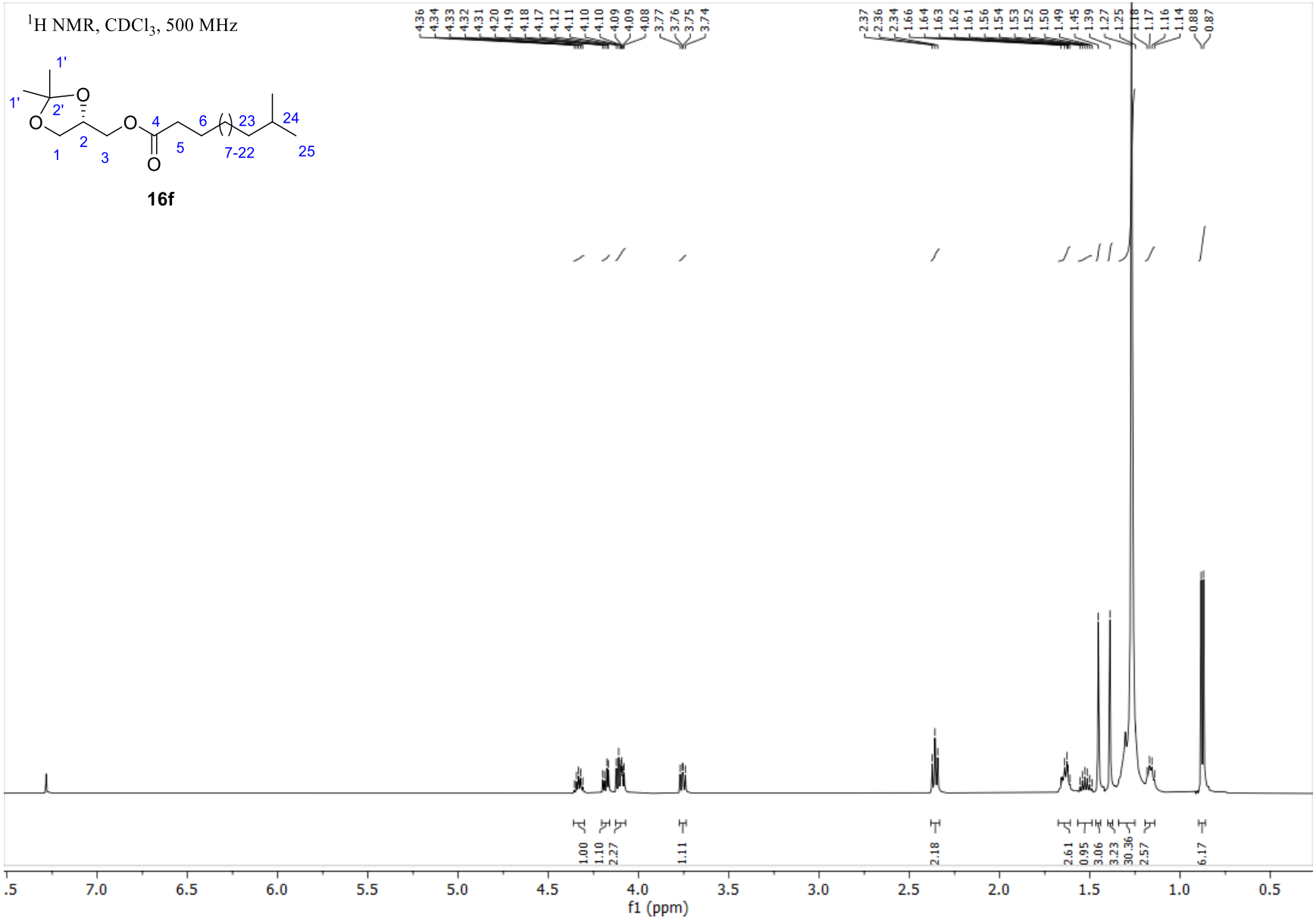


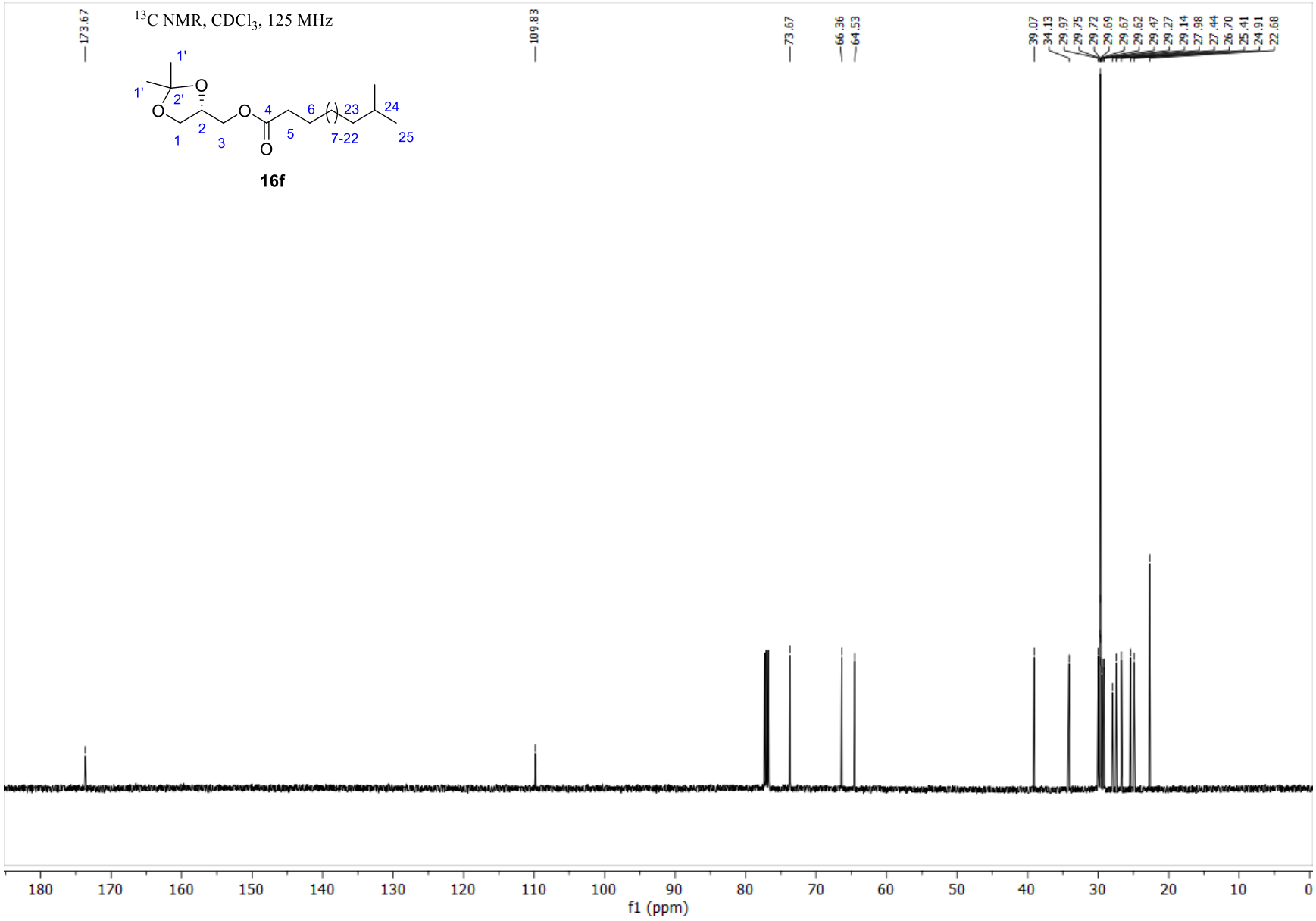
16d


^{13}C NMR, $CDCl_3$, 125 MHz
173.63
109.80
73.65
66.33
64.49
39.05
34.10
29.94
29.72
29.68
29.67
29.66
29.63
29.58
29.44
29.24
29.11
27.95
27.81
27.41
26.67
25.38
24.88
22.65
1'
1'
2'
O
O
O
O
1
2
3
4
5
6
7-18
19
20
21
16d
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

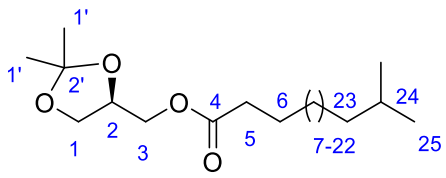

^{1}H NMR, $CDCl_3$, 500 MHz
1'
1'
2'
O
O
O
1
2
3
4
5
6
20
21
7-19
22
O
16e
4.32
4.31
4.30
4.29
4.27
4.16
4.15
4.14
4.13
4.09
4.08
4.06
4.05
3.74
3.72
3.71
3.69
2.34
2.33
2.31
1.64
1.62
1.61
1.60
1.58
1.55
1.54
1.52
1.51
1.50
1.48
1.47
1.46
1.42
1.36
1.29
1.27
1.24
1.21
1.14
1.13
1.11
0.85
1.00
1.00
1.98
1.23
1.87
2.16
1.25
2.85
3.13
26.15
3.36
5.94
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
f1 (ppm)


^{13}C NMR, $CDCl_3$, 125 MHz
16e
173.64
109.80
73.66
66.35
64.50
39.05
34.11
29.94
29.71
29.68
29.67
29.66
29.63
29.58
29.44
29.23
29.11
27.95
27.41
26.67
25.39
24.88
22.65
f1 (ppm)

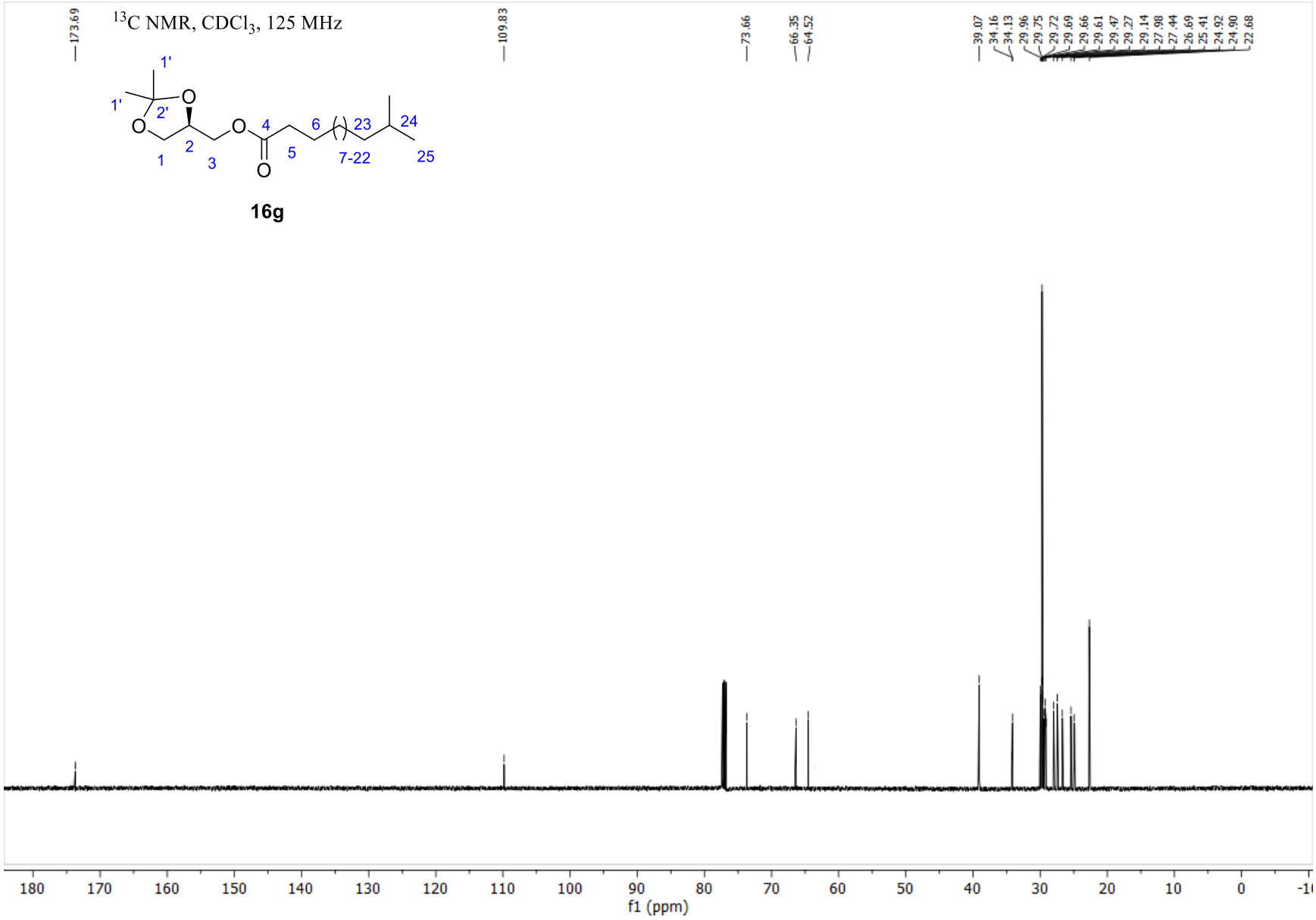

^{1}H NMR, $CDCl_3$, 500 MHz
1'
2'
1'
O
O
4
6
23
24
1
2
3
O
5
7-22
25
O
16f
4.36
4.34
4.33
4.32
4.31
4.20
4.19
4.18
4.17
4.12
4.11
4.10
4.10
4.09
4.09
4.08
3.77
3.76
3.75
3.74
2.37
2.36
2.34
1.66
1.64
1.63
1.62
1.61
1.56
1.54
1.53
1.52
1.50
1.49
1.45
1.39
1.27
1.25
1.18
1.17
1.16
1.14
0.88
0.87
1.00
1.10
2.27
1.11
2.18
2.61
0.95
3.06
3.23
30.36
2.57
6.17
.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
f1 (ppm)


^{13}C NMR, $CDCl_3$, 125 MHz
16f
173.67
109.83
73.67
66.36
64.53
39.07
34.13
29.97
29.75
29.72
29.69
29.67
29.62
29.47
29.27
29.14
27.98
27.44
26.70
25.41
24.91
22.68
f1 (ppm)

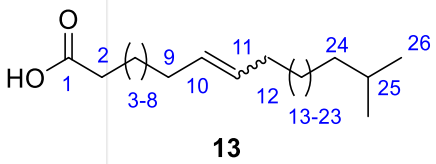
^{1}H NMR, $CDCl_3$, 500 MHz



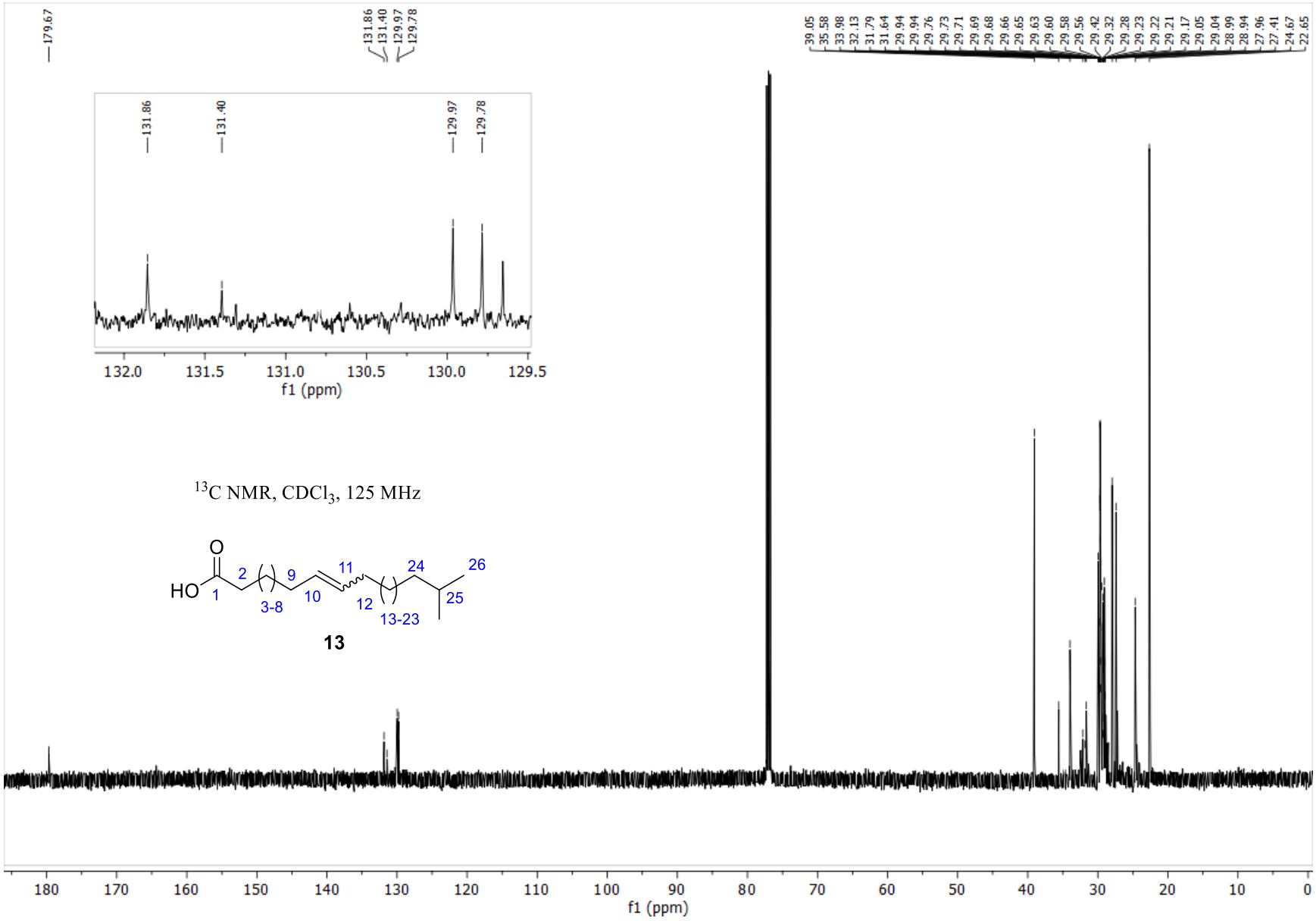
16g


^{13}C NMR, $CDCl_3$, 125 MHz
173.69
109.83
73.66
66.35
64.52
39.07
34.16
34.13
29.96
29.75
29.72
29.69
29.66
29.61
29.47
29.27
29.14
27.98
27.44
26.69
25.41
24.92
24.90
22.68
1'
1'
2'
O
O
O
O
1
2
3
4
5
6
7-22
23
24
25
16g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR, $CDCl_3$, 500 MHz



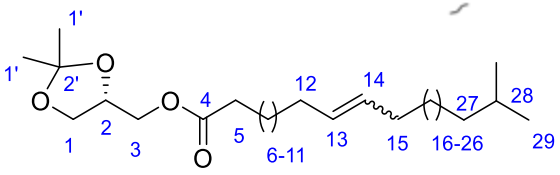
13



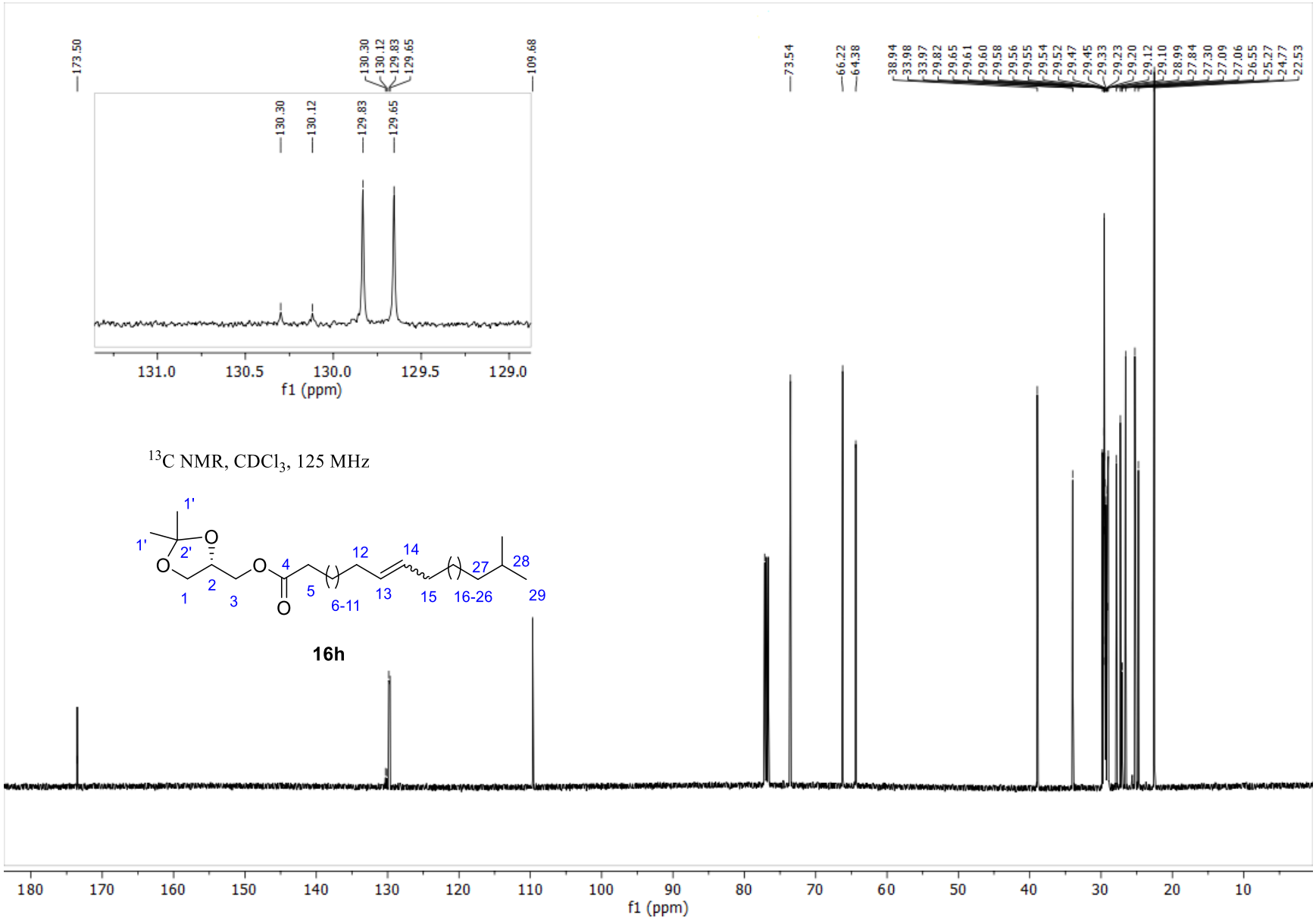
^{13}C NMR, $CDCl_3$, 125 MHz

13

^{1}H NMR, $CDCl_3$, 500 MHz

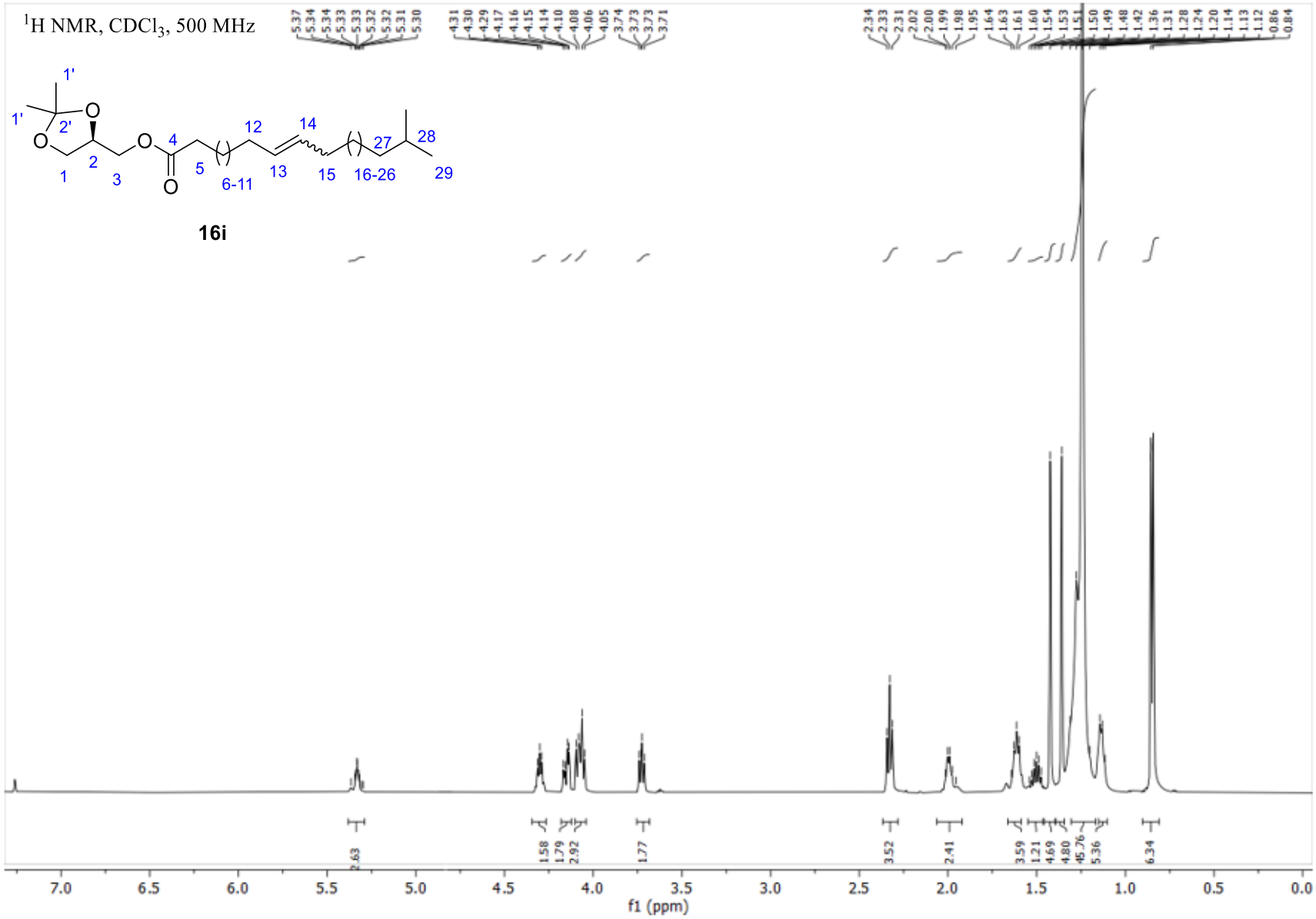


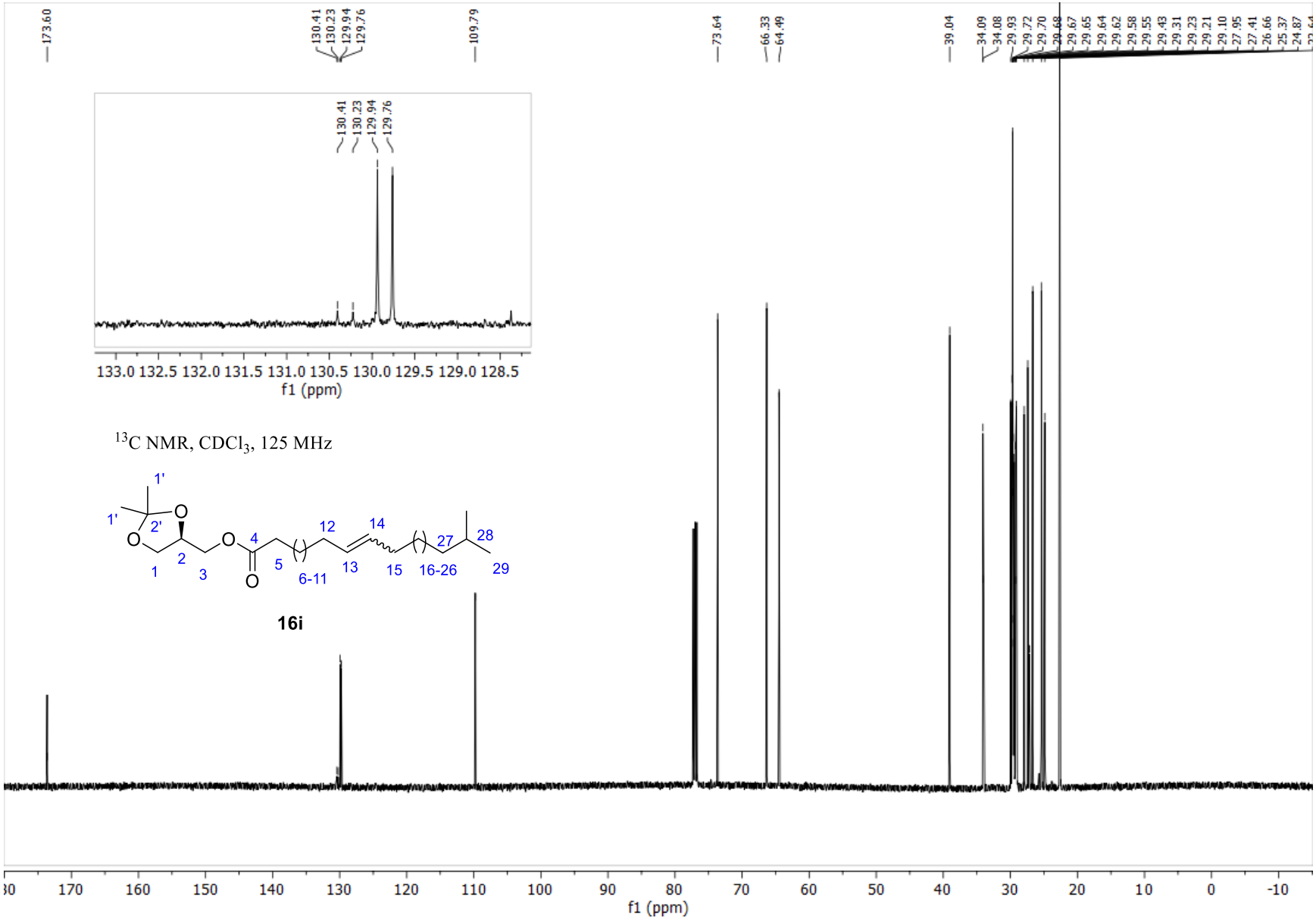
16h



^{13}C NMR, $CDCl_3$, 125 MHz

16h

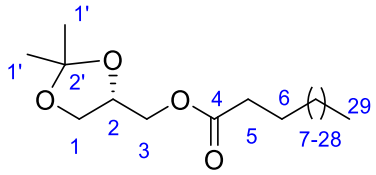

1H NMR, CDCl3, 500 MHz
1'
1'
2'
O
O
O
O
4
12
14
27
28
1
2
3
5
6-11
13
15
16-26
29
16i
f1 (ppm)



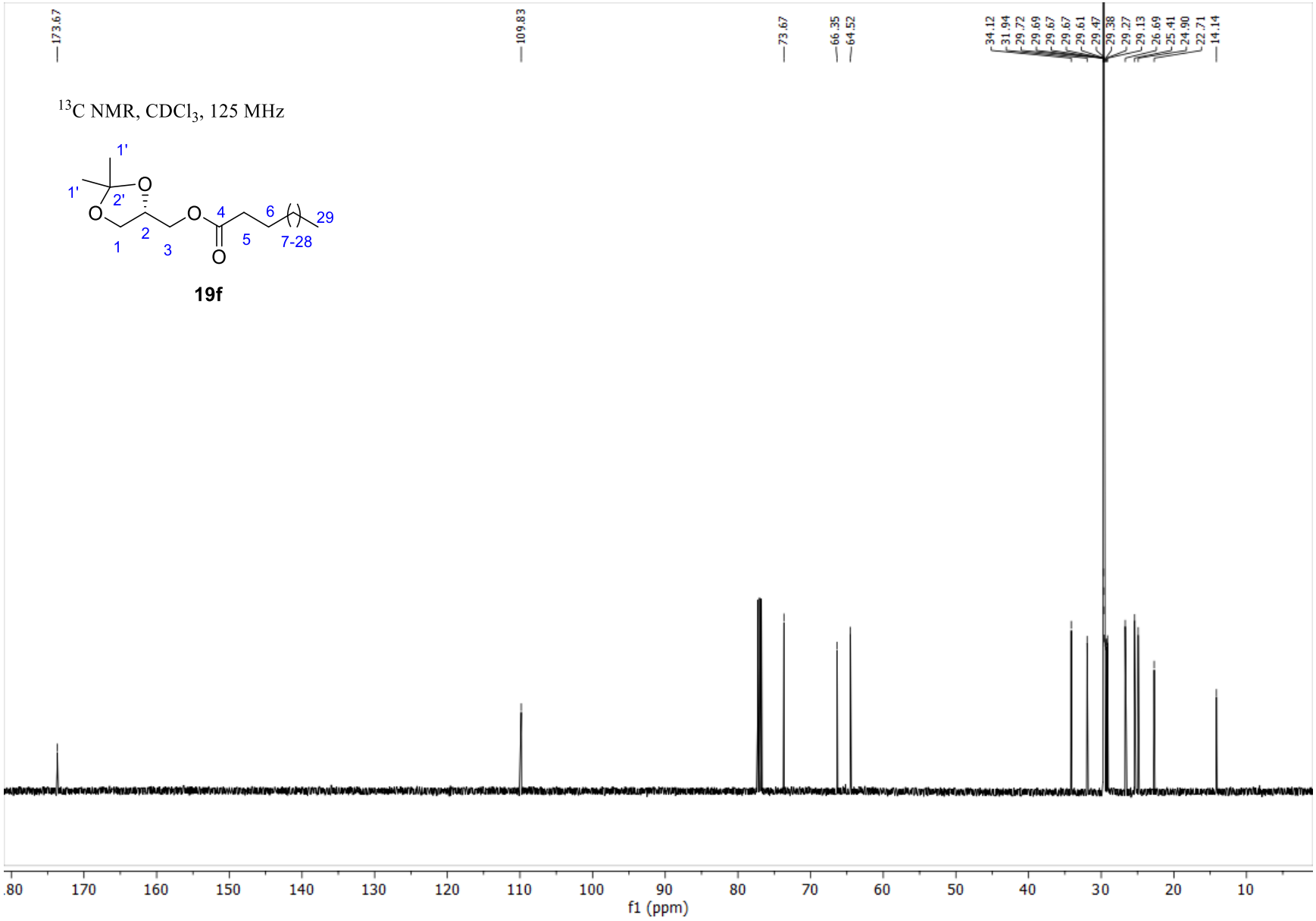
^{13}C NMR, $CDCl_3$, 125 MHz

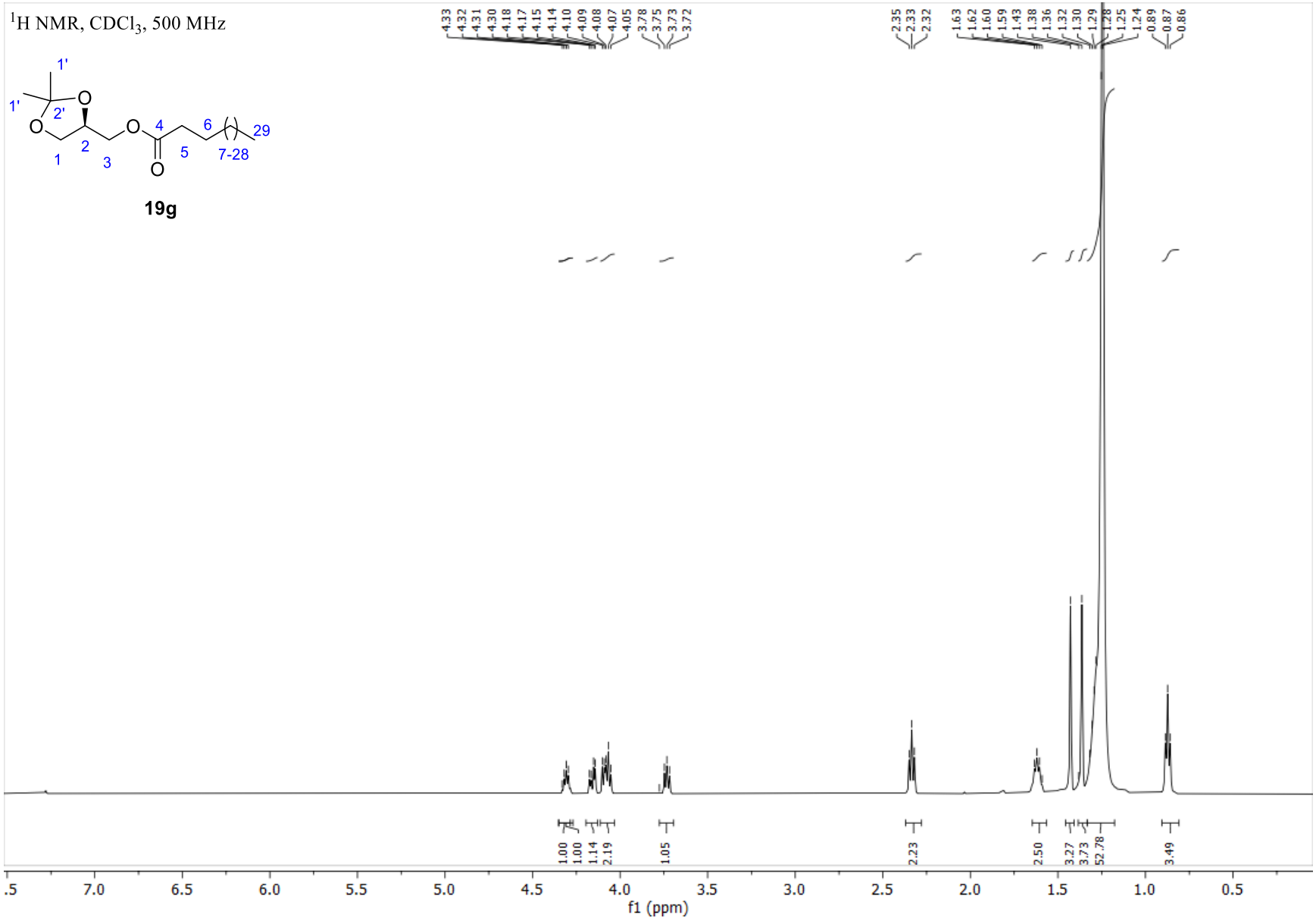
16i

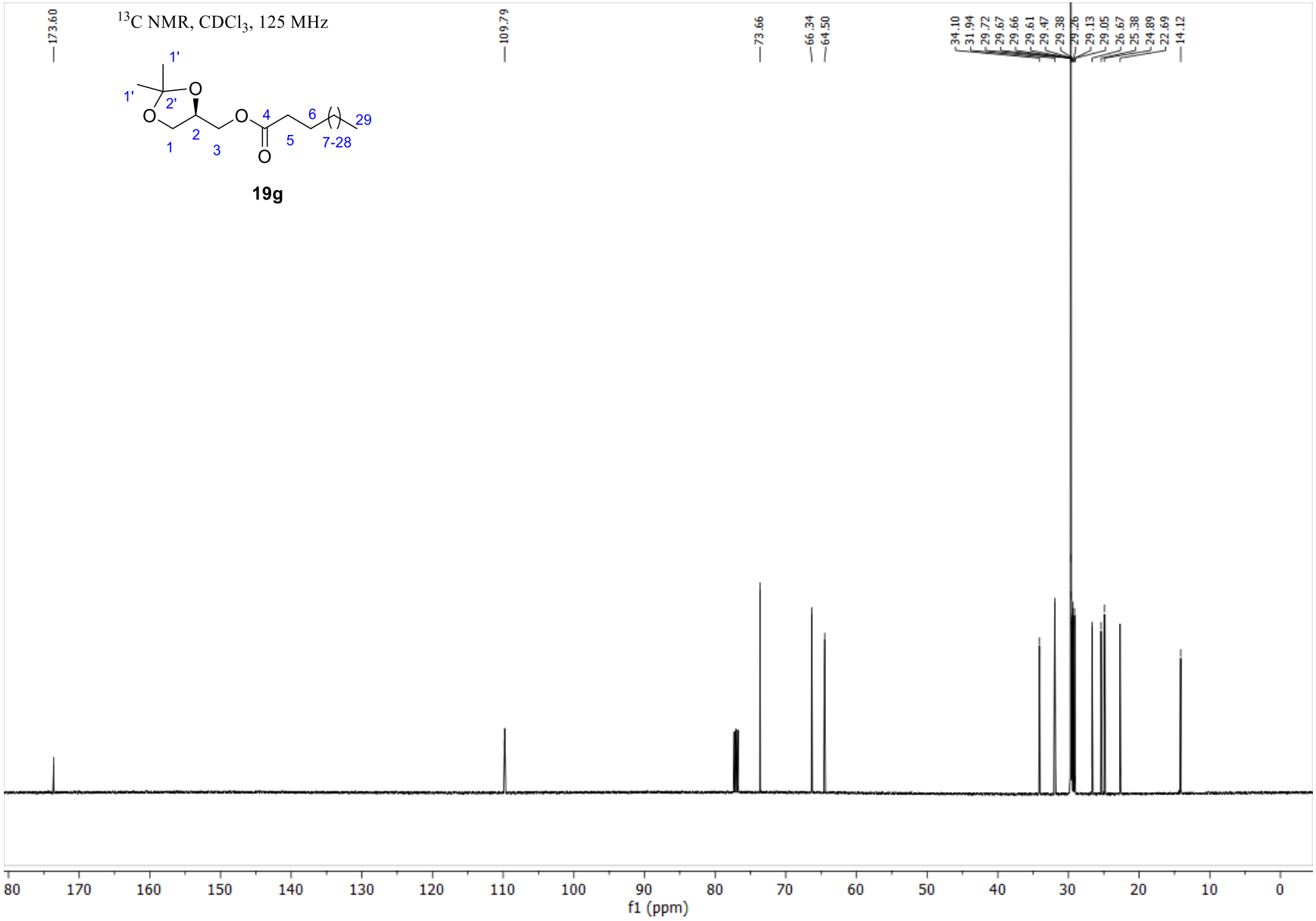
^{1}H NMR, $CDCl_3$, 500 MHz



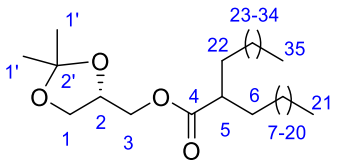
19f


173.67
109.83
73.67
66.35
64.52
34.12
31.94
29.72
29.69
29.67
29.67
29.61
29.47
29.38
29.27
29.13
26.69
25.41
24.90
22.71
14.14
13C NMR, CDCl3, 125 MHz
1'
1'
2'
O
O
O
1
2
3
4
5
6
7-28
29
O
19f
f1 (ppm)

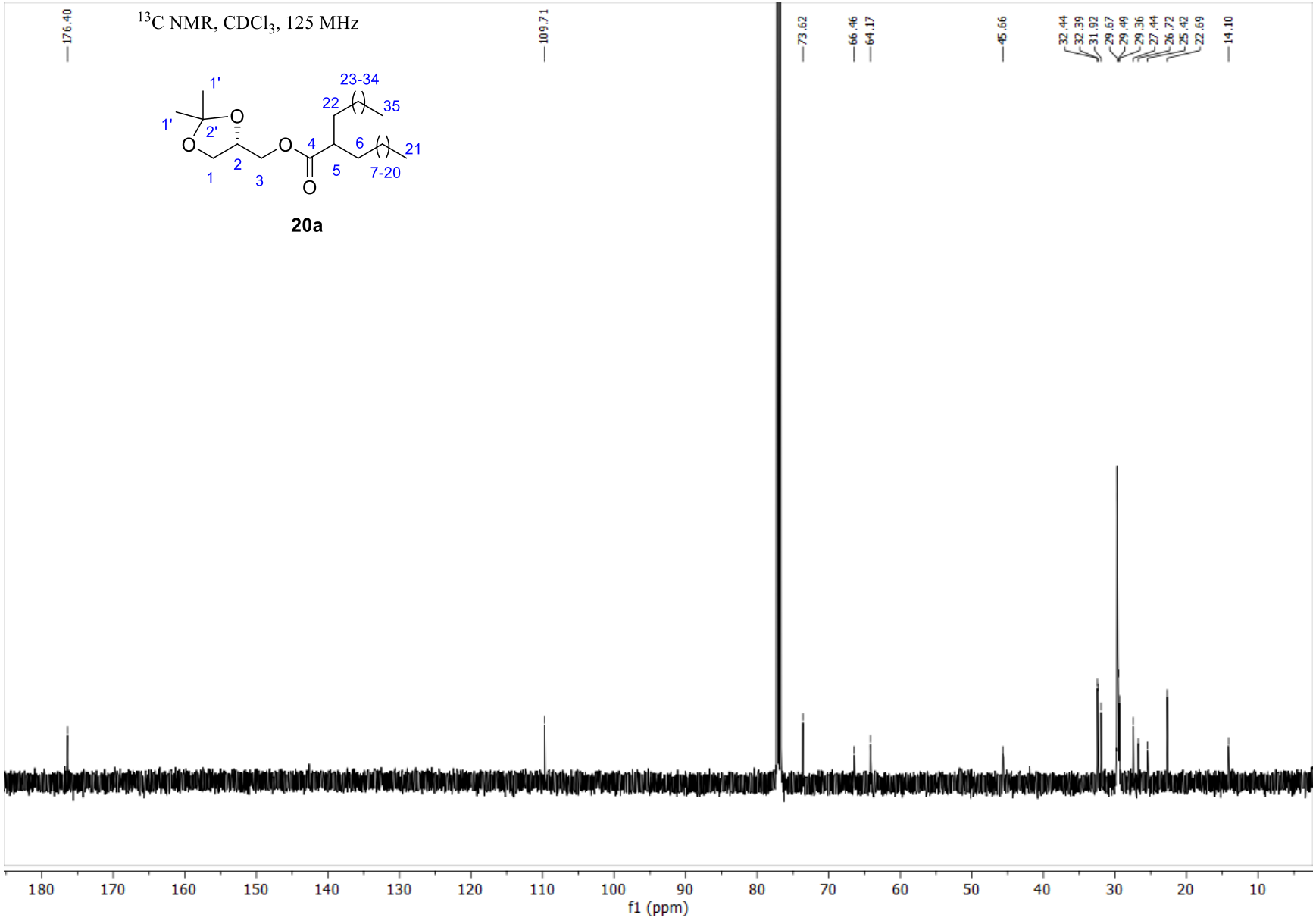

^{1}H NMR, $CDCl_3$, 500 MHz
1'
1'
2'
O
O
O
1
2
3
4
5
6
7-28
29
O
19g
4.33
4.32
4.31
4.30
4.18
4.17
4.15
4.14
4.10
4.09
4.08
4.07
4.05
3.78
3.75
3.73
3.72
2.35
2.33
2.32
1.63
1.62
1.60
1.59
1.43
1.38
1.36
1.32
1.30
1.29
1.28
1.25
1.24
0.89
0.87
0.86
1.00
1.00
1.14
2.19
1.05
2.23
2.50
3.27
3.73
52.78
3.49
.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
f1 (ppm)


^{13}C NMR, $CDCl_3$, 125 MHz
19g
173.60
109.79
73.66
66.34
64.50
34.10
31.94
29.72
29.67
29.66
29.61
29.47
29.38
29.26
29.13
29.05
26.67
25.38
24.89
22.69
14.12
f1 (ppm)

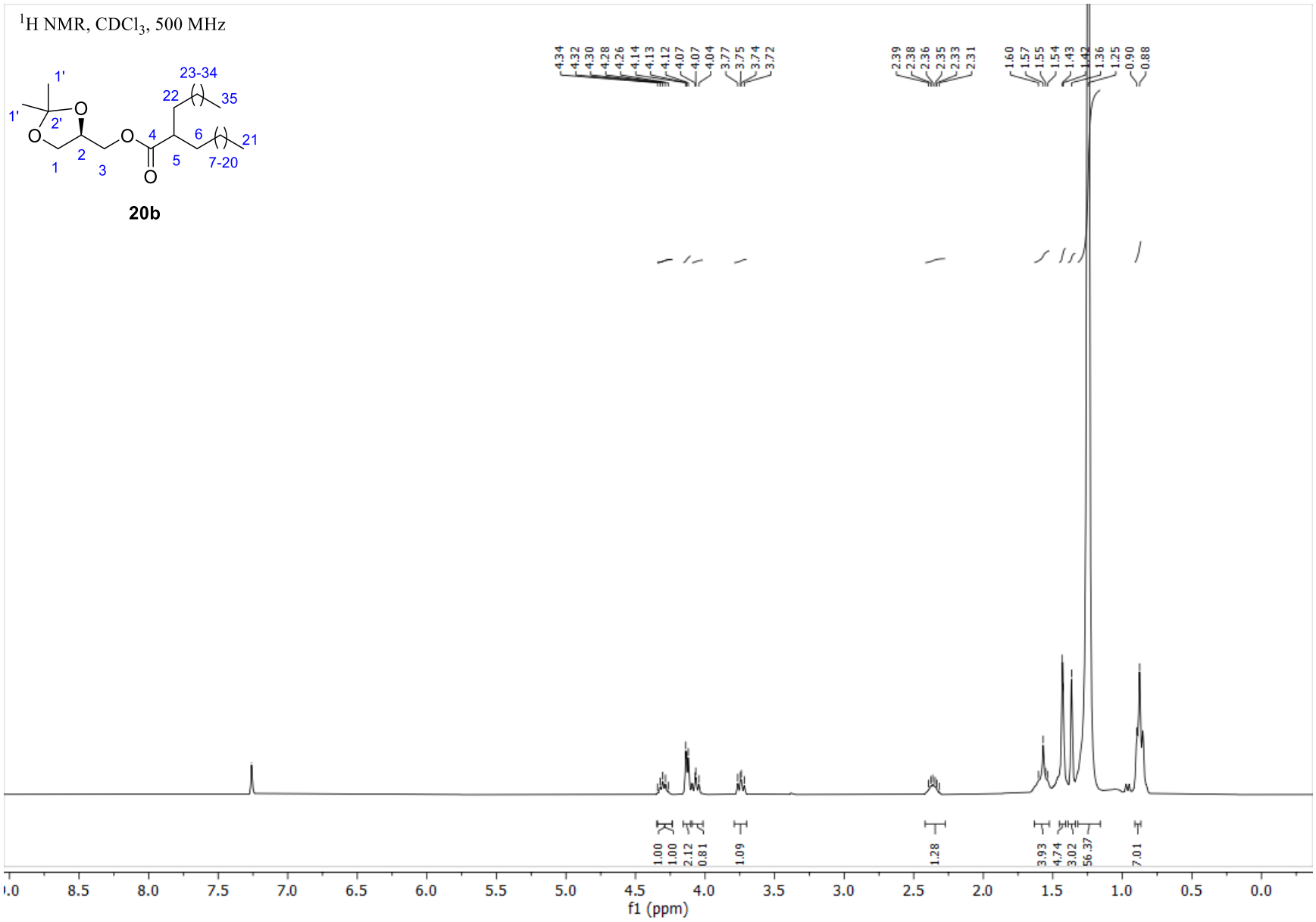
^{1}H NMR, $CDCl_3$, 500 MHz

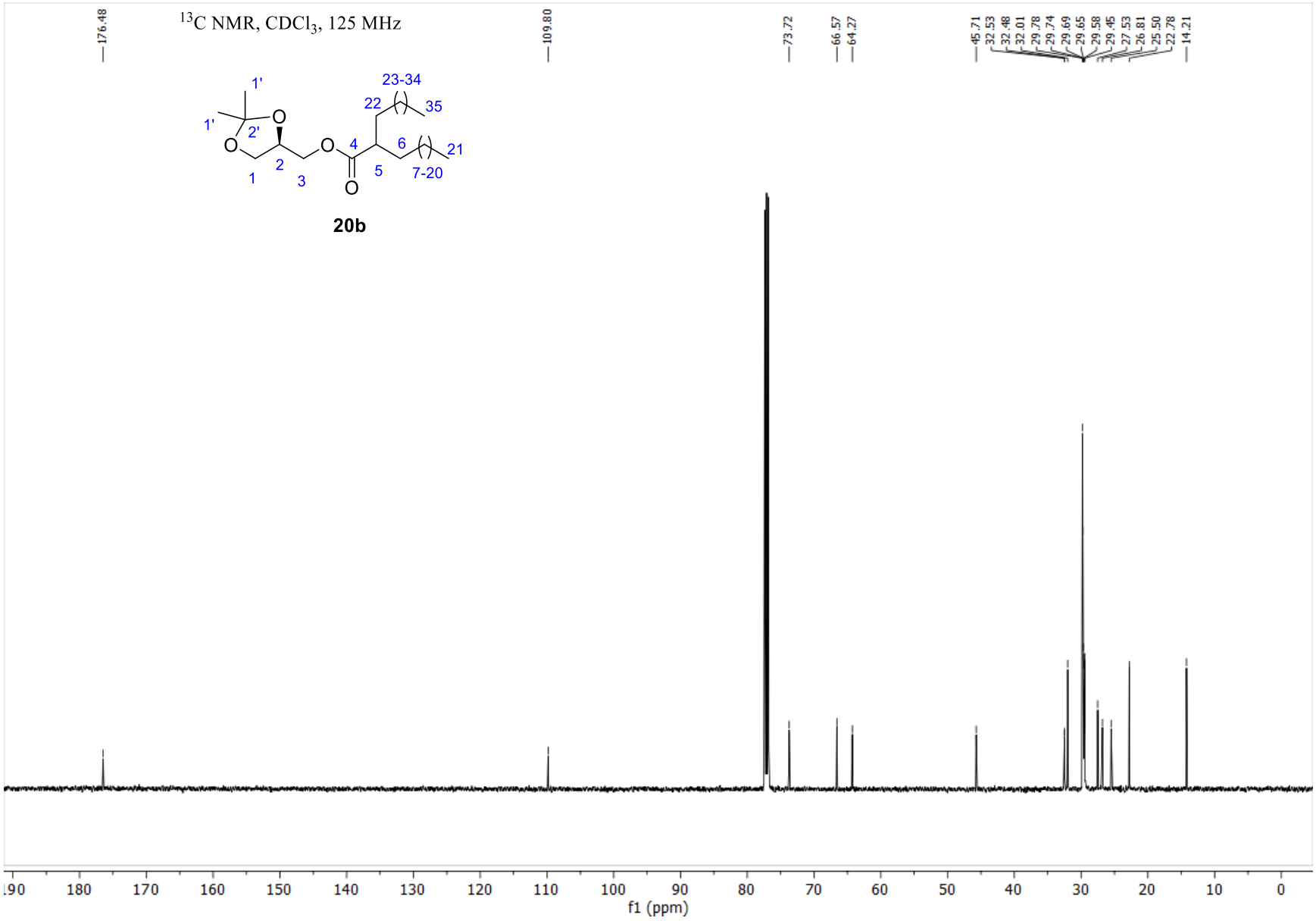


20a

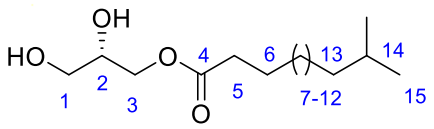

^{13}C NMR, $CDCl_3$, 125 MHz
176.40
109.71
73.62
66.46
64.17
45.66
32.44
32.39
31.92
29.67
29.49
29.36
27.44
26.72
25.42
22.69
14.10
1'
2'
1
2
3
4
5
6
7-20
21
22
23-34
35
O
f1 (ppm)

20a

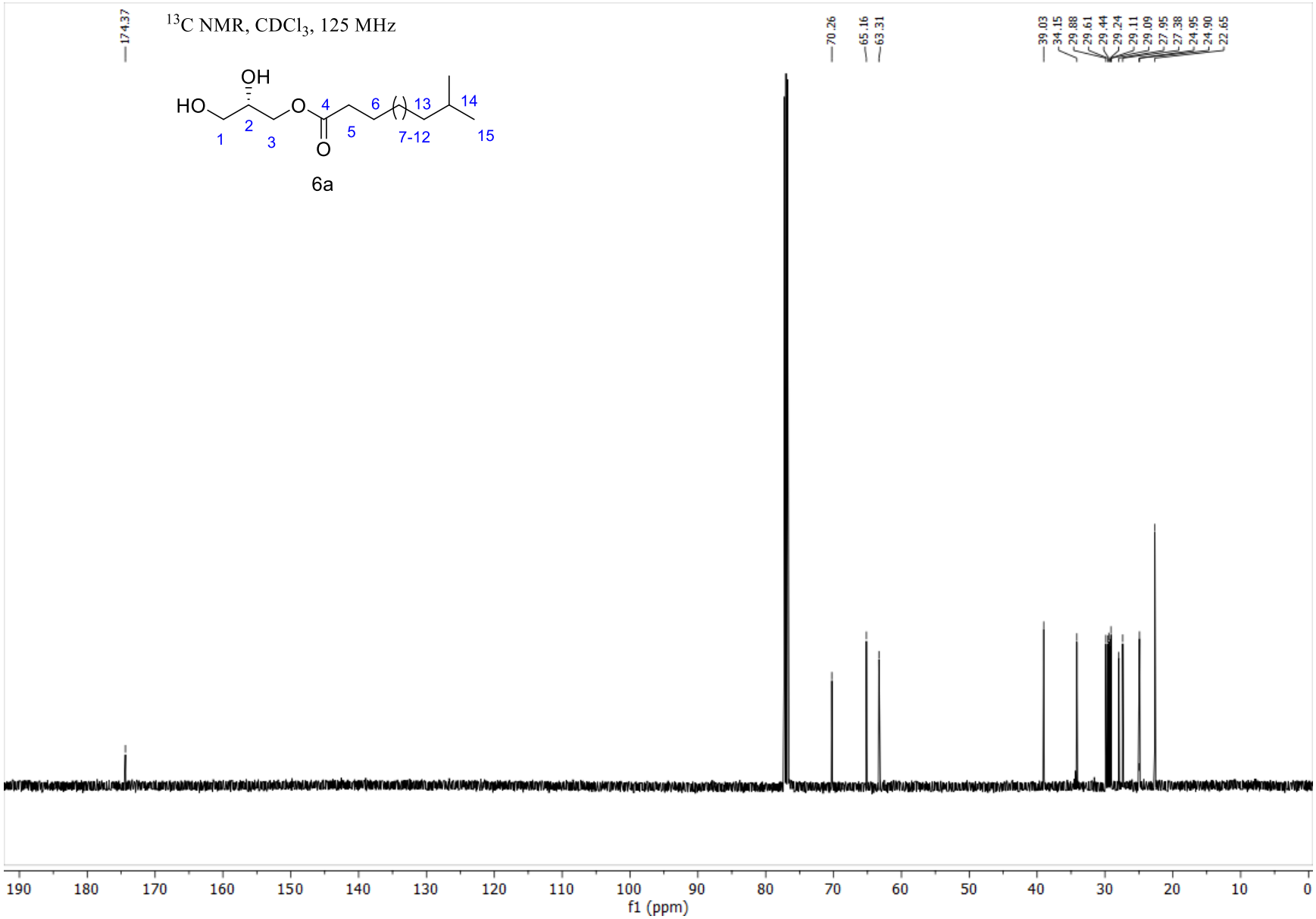

^{1}H NMR, $CDCl_3$, 500 MHz
1'
23-34
22
35
1'
2'
O
O
4
6
21
1
2
3
5
7-20
O
20b
4.34
4.32
4.30
4.28
4.26
4.14
4.13
4.12
4.07
4.07
4.04
3.77
3.75
3.74
3.72
2.39
2.38
2.36
2.35
2.33
2.31
1.60
1.57
1.55
1.54
1.43
1.42
1.36
1.25
0.90
0.88
1.00
1.00
2.12
0.81
1.09
1.28
3.93
4.74
3.02
56.37
7.01
8.5
8.0
7.5
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
f1 (ppm)

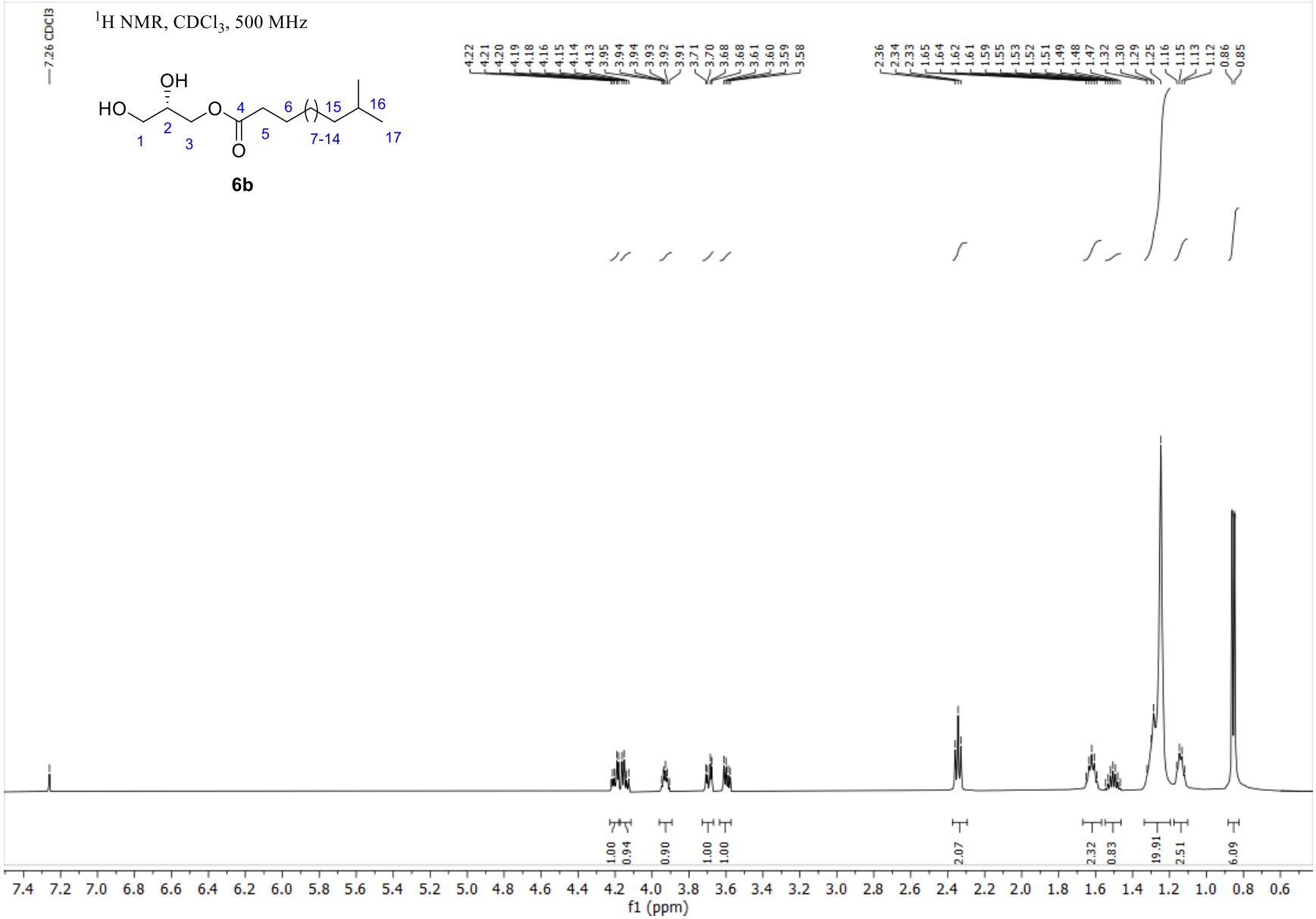

^{13}C NMR, $CDCl_3$, 125 MHz
176.48
109.80
73.72
66.57
64.27
45.71
32.53
32.48
32.01
29.78
29.74
29.69
29.65
29.58
29.45
27.53
26.81
25.50
22.78
14.21
1'
2'
1
2
3
4
5
6
7-20
21
22
23-34
35
O
20b
f1 (ppm)

^{1}H NMR, $CDCl_3$, 500 MHz

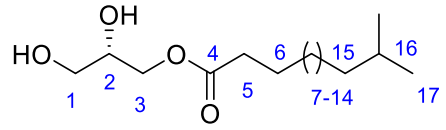


6a


174.37
^{13}C NMR, $CDCl_3$, 125 MHz
70.26
65.16
63.31
39.03
34.15
29.88
29.61
29.44
29.24
29.11
29.09
27.95
27.38
24.95
24.90
22.65
OH
HO
O
O
1
2
3
4
5
6
7-12
13
14
15
6a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

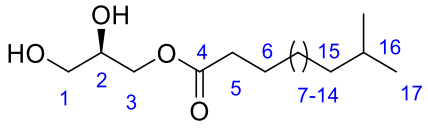

7.26 CDCl3
^{1}H NMR, $CDCl_3$, 500 MHz
OH
HO
O
4
6
15
16
1
2
3
5
7-14
17
O
6b
4.22 4.21 4.20 4.19 4.18 4.16 4.15 4.14 4.13 3.95 3.94 3.94 3.93 3.92 3.91 3.71 3.70 3.68 3.68 3.61 3.60 3.59 3.58
2.36 2.34 2.33 1.65 1.64 1.62 1.61 1.59 1.55 1.53 1.52 1.51 1.49 1.48 1.47 1.32 1.30 1.29 1.25 1.16 1.15 1.13 1.12 0.86 0.85
1.00 0.94 0.90 1.00 1.00 2.07 2.32 0.83 19.91 2.51 6.09
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f1 (ppm)

^{13}C NMR, $CDCl_3$, 125 MHz

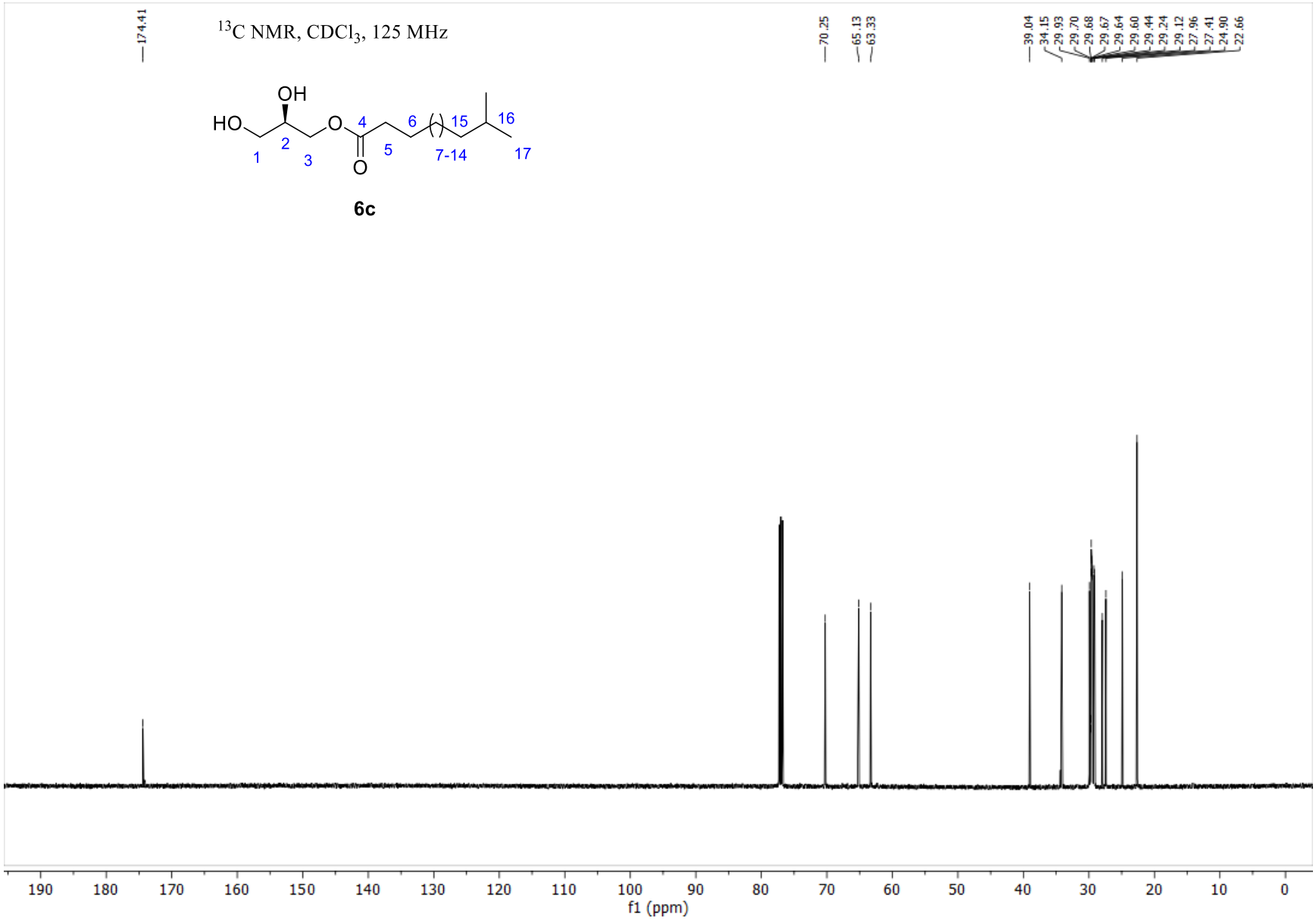


6b

^{1}H NMR, $CDCl_3$, 500 MHz



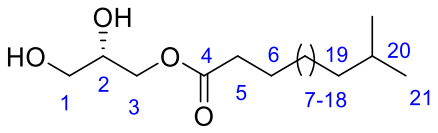
6c



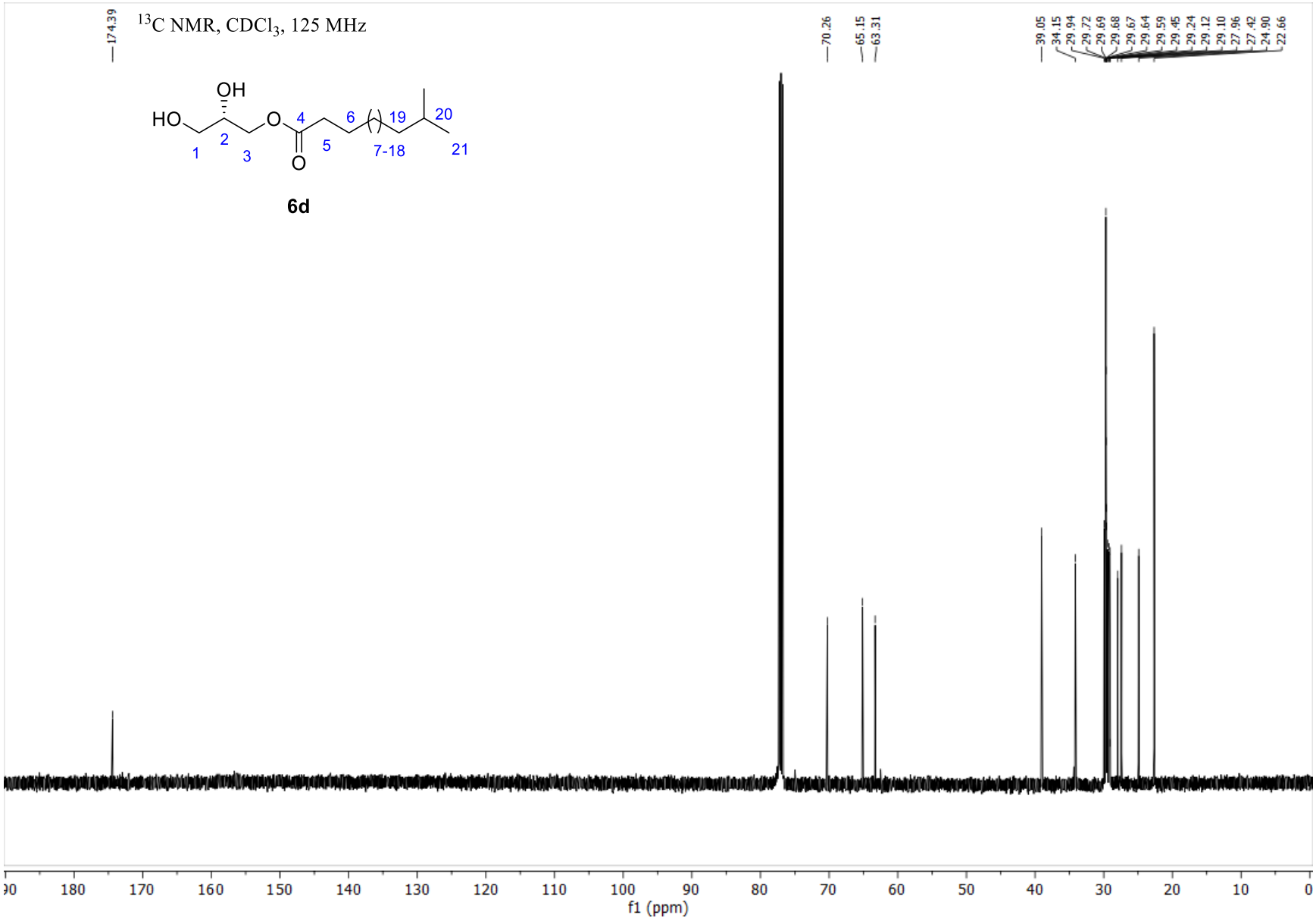
^{13}C NMR, $CDCl_3$, 125 MHz

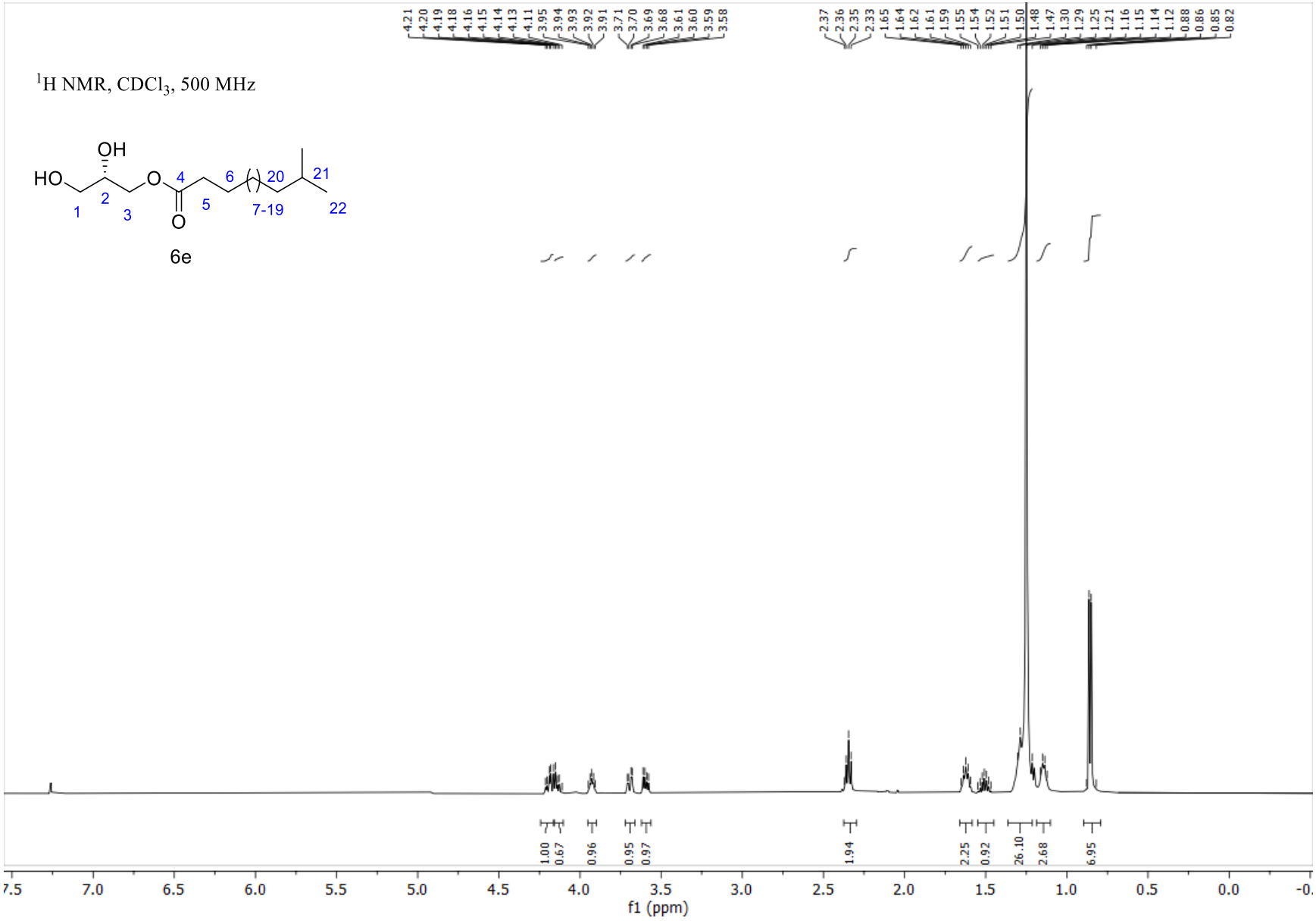
6c

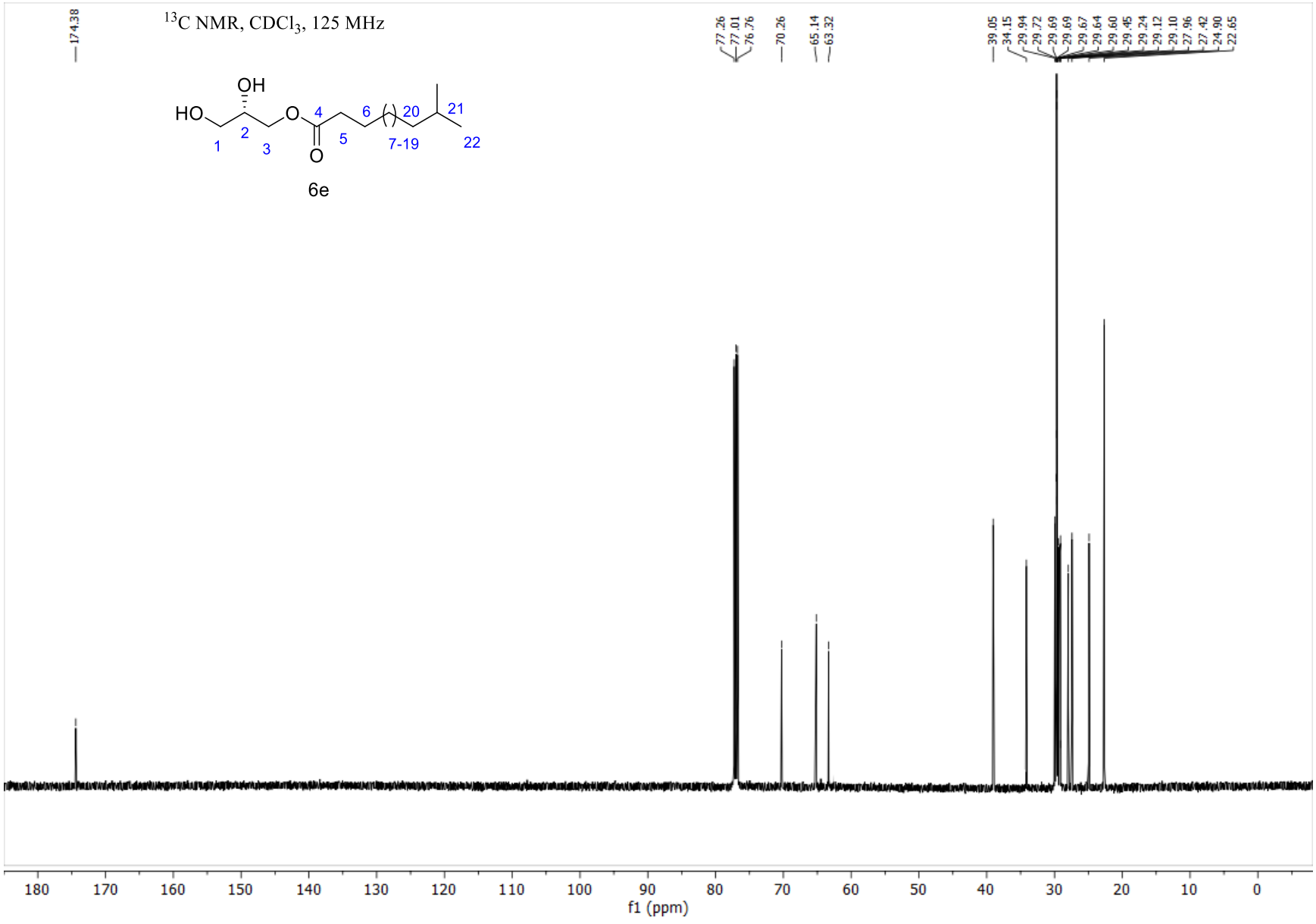
^{1}H NMR, $CDCl_3$, 500 MHz



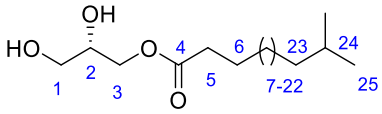
6d


^{13}C NMR, $CDCl_3$, 125 MHz
174.39
70.26
65.15
63.31
39.05
34.15
29.94
29.72
29.69
29.68
29.67
29.64
29.59
29.45
29.24
29.12
29.10
27.96
27.42
24.90
22.66
OH
HO
O
O
1
2
3
4
5
6
7-18
19
20
21
6d
f1 (ppm)

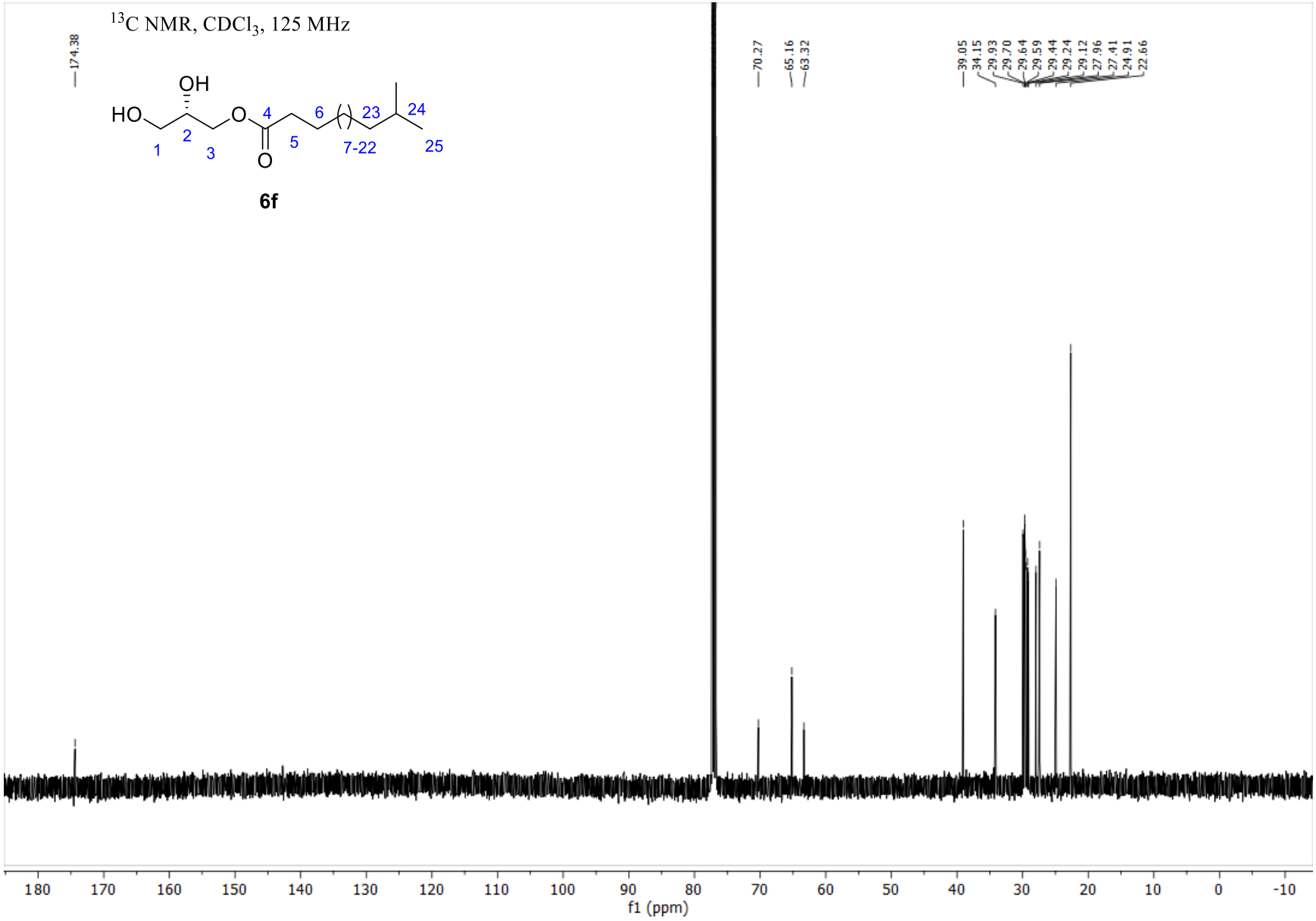

^{1}H NMR, $CDCl_3$, 500 MHz
OH
HO
O
1
2
3
4
5
6
7-19
20
21
22
O
6e
f1 (ppm)

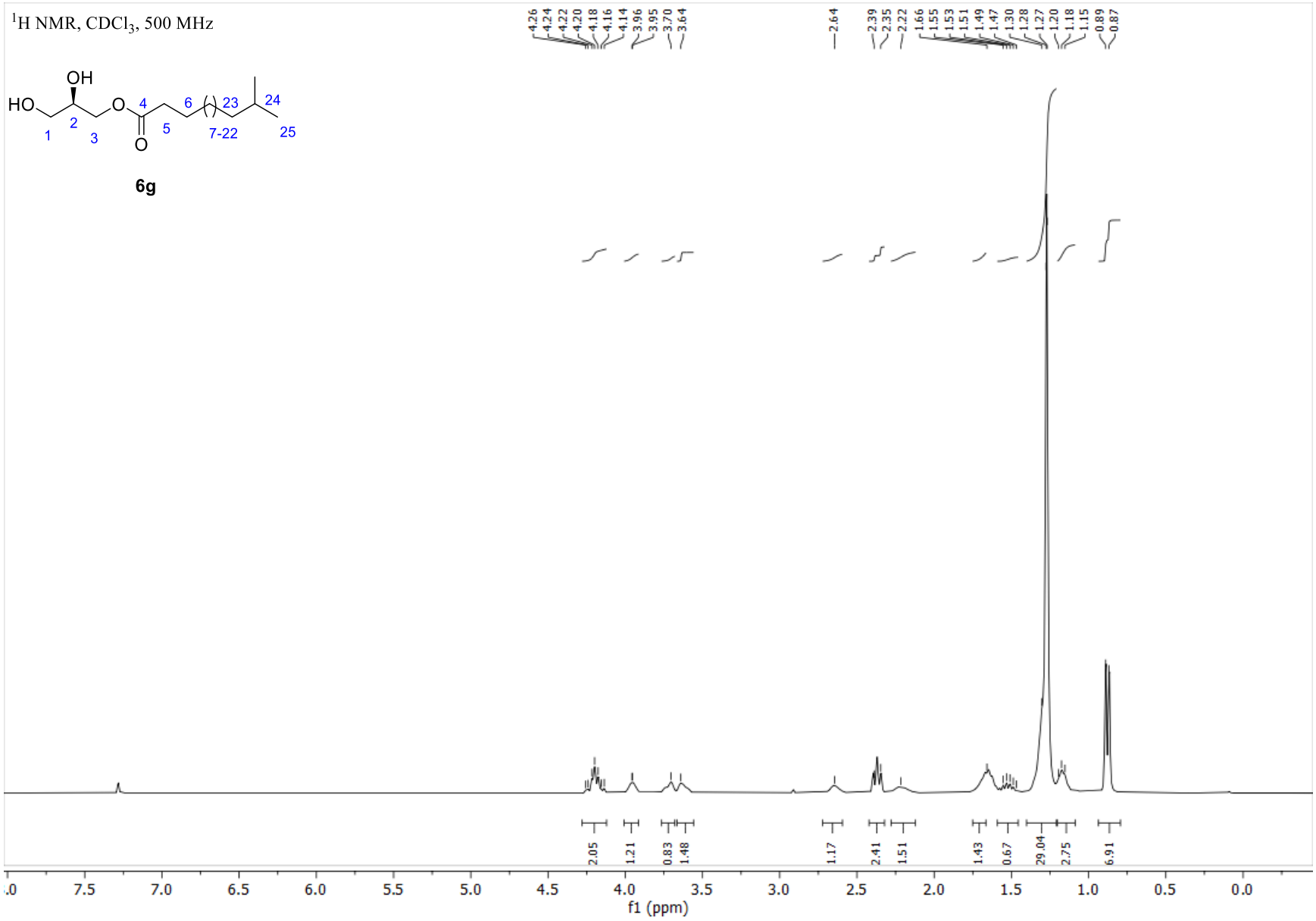

^{13}C NMR, $CDCl_3$, 125 MHz
174.38
77.26
77.01
76.76
70.26
65.14
63.32
39.05
34.15
29.94
29.72
29.69
29.69
29.67
29.64
29.60
29.45
29.24
29.12
29.10
27.96
27.42
24.90
22.65
OH
HO
O
O
1
2
3
4
5
6
7-19
20
21
22
6e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR, $CDCl_3$, 500 MHz

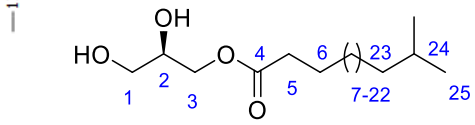


6f

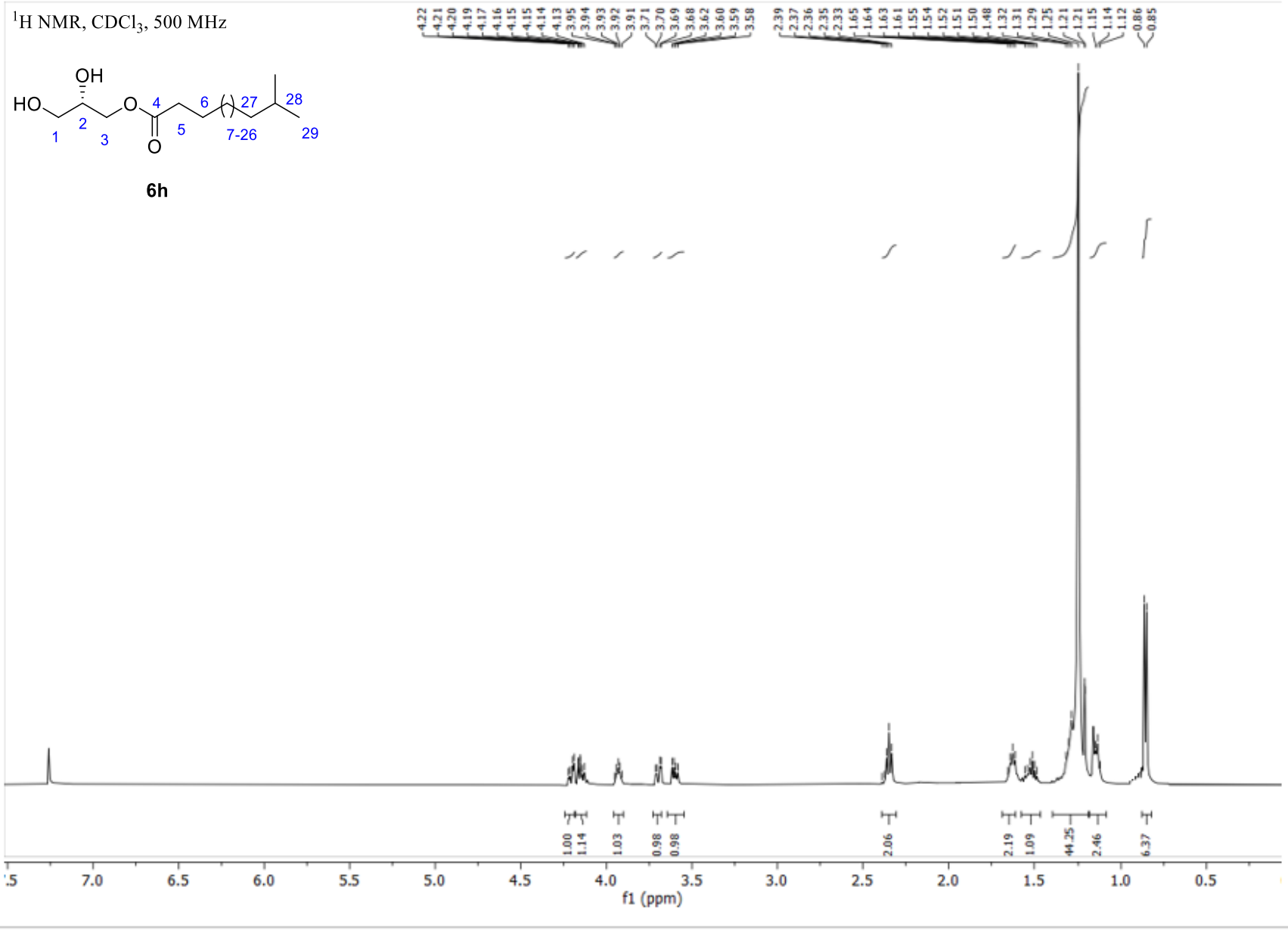

^{13}C NMR, $CDCl_3$, 125 MHz
174.38
70.27
65.16
63.32
39.05
34.15
29.93
29.70
29.64
29.59
29.44
29.24
29.12
27.96
27.41
24.91
22.66
OH
HO
O
O
1
2
3
4
5
6
7-22
23
24
25
6f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

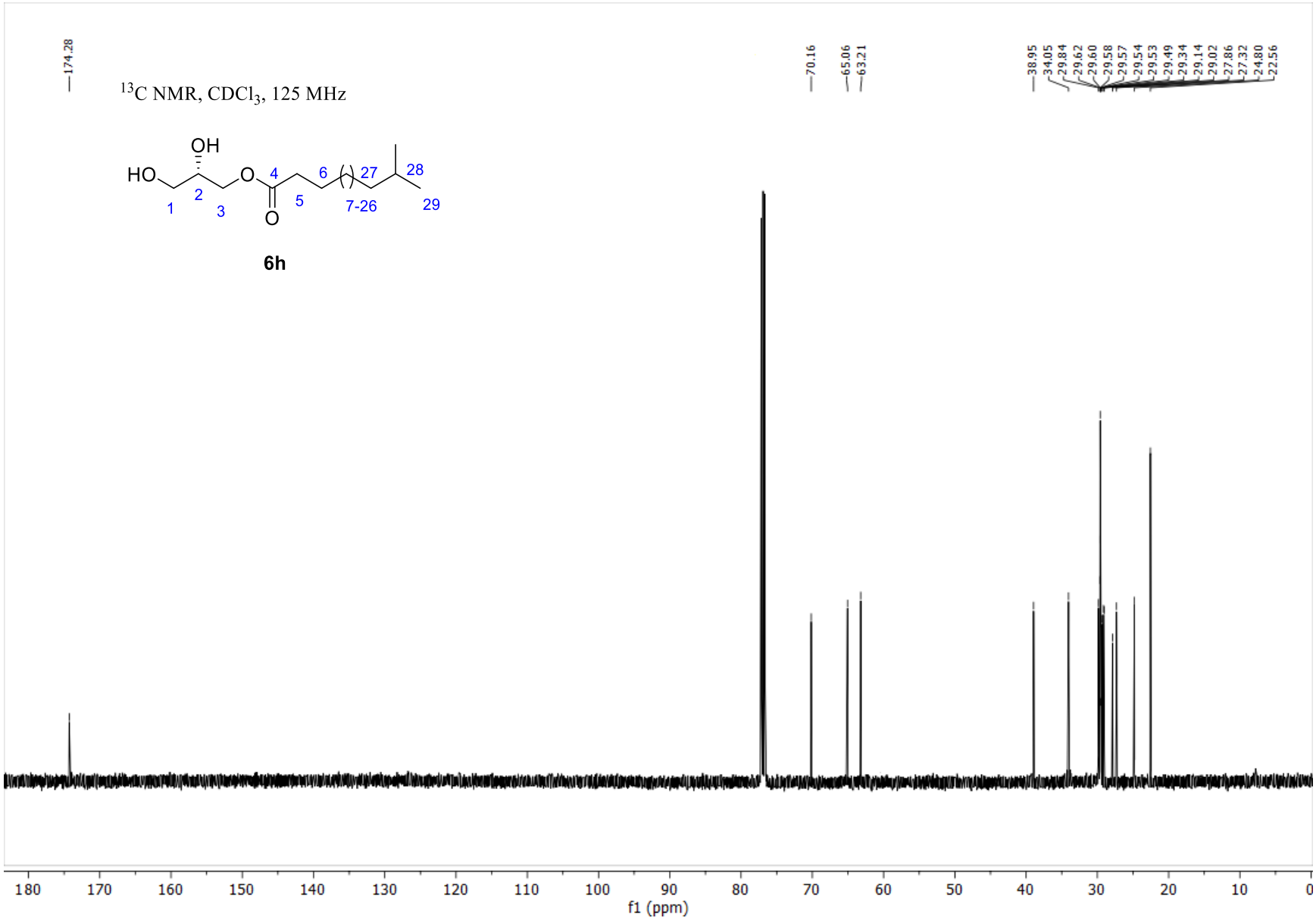

^{1}H NMR, $CDCl_3$, 500 MHz
OH
HO
O
4
6
23
24
1
2
3
5
7-22
25
O
6g
4.26
4.24
4.22
4.20
4.18
4.16
4.14
3.96
3.95
3.70
3.64
2.64
2.39
2.35
2.22
1.66
1.55
1.53
1.51
1.49
1.47
1.30
1.28
1.27
1.20
1.18
1.15
0.89
0.87
2.05
1.21
0.83
1.48
1.17
2.41
1.51
1.43
0.67
29.04
2.75
6.91
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

^{13}C NMR, $CDCl_3$, 125 MHz

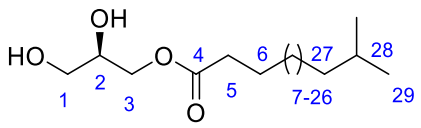


6g

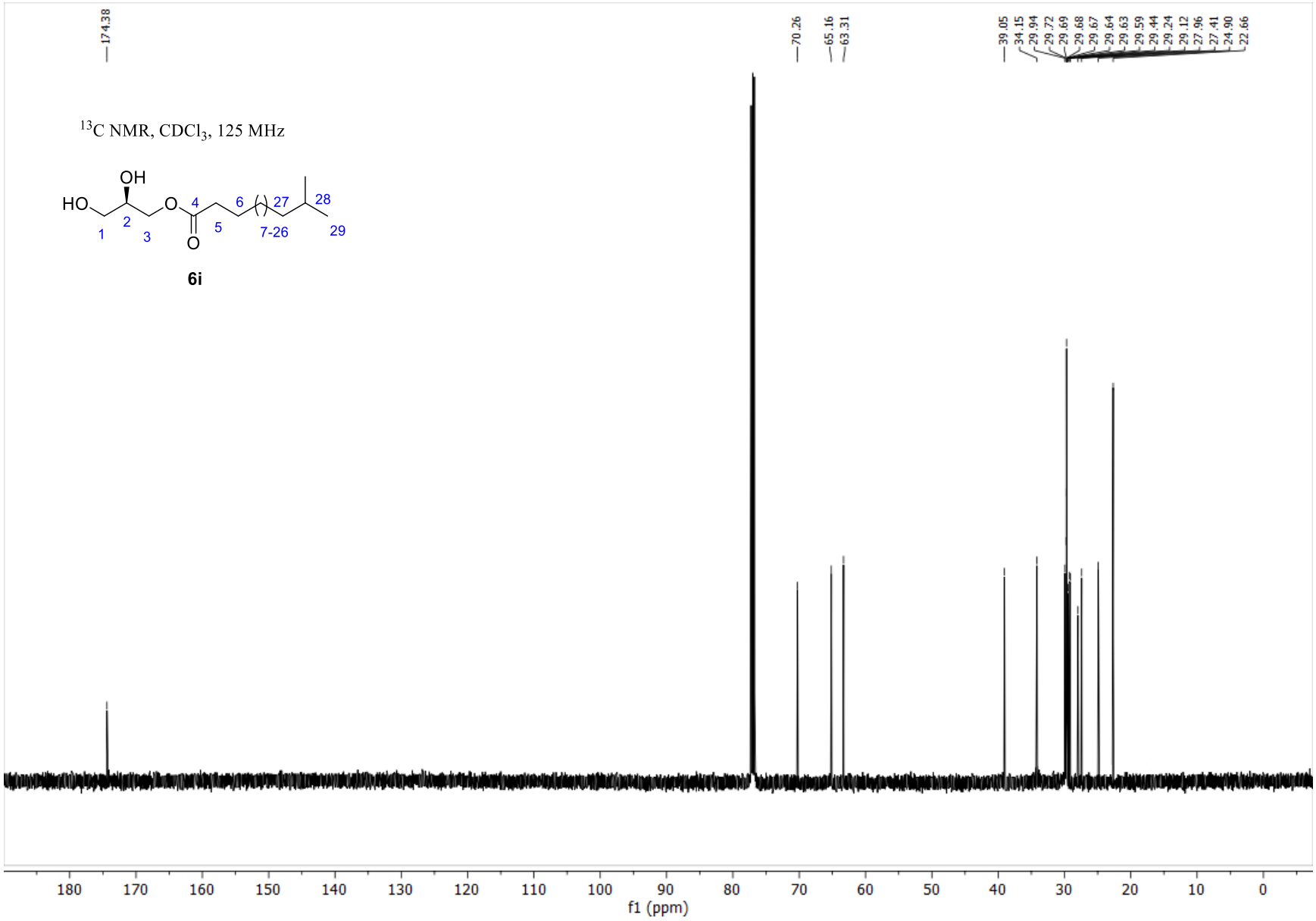

^{1}H NMR, $CDCl_3$, 500 MHz
OH
HO
O
1
2
3
4
5
6
7-26
27
28
29
O
6h
f1 (ppm)


174.28
70.16
65.06
63.21
38.95
34.05
29.84
29.62
29.60
29.58
29.57
29.54
29.53
29.49
29.34
29.14
29.02
27.86
27.32
24.80
22.56
13C NMR, CDCl3, 125 MHz
OH
HO
O
O
1
2
3
4
5
6
7-26
27
28
29
6h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

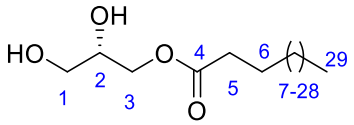
^{1}H NMR, $CDCl_3$, 500 MHz



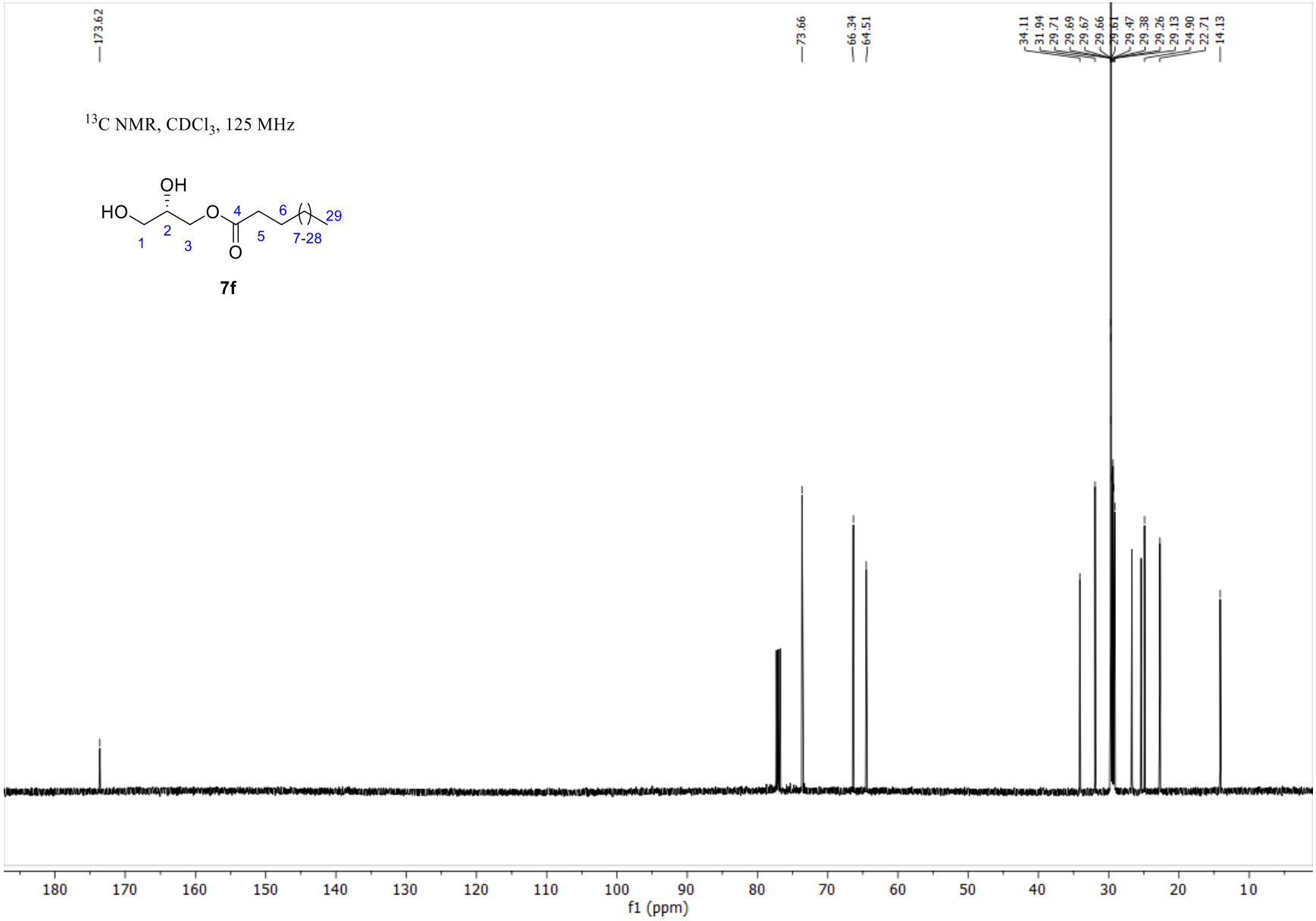
6i


174.38
70.26
65.16
63.31
39.05
34.15
29.94
29.72
29.69
29.68
29.67
29.64
29.63
29.59
29.44
29.24
29.12
27.96
27.41
24.90
22.66
13C NMR, CDCl3, 125 MHz
OH
HO
O
O
1
2
3
4
5
6
7-26
27
28
29
6i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

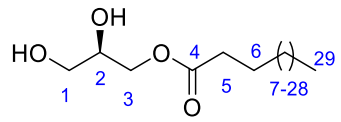
^{1}H NMR, $CDCl_3$, 500 MHz



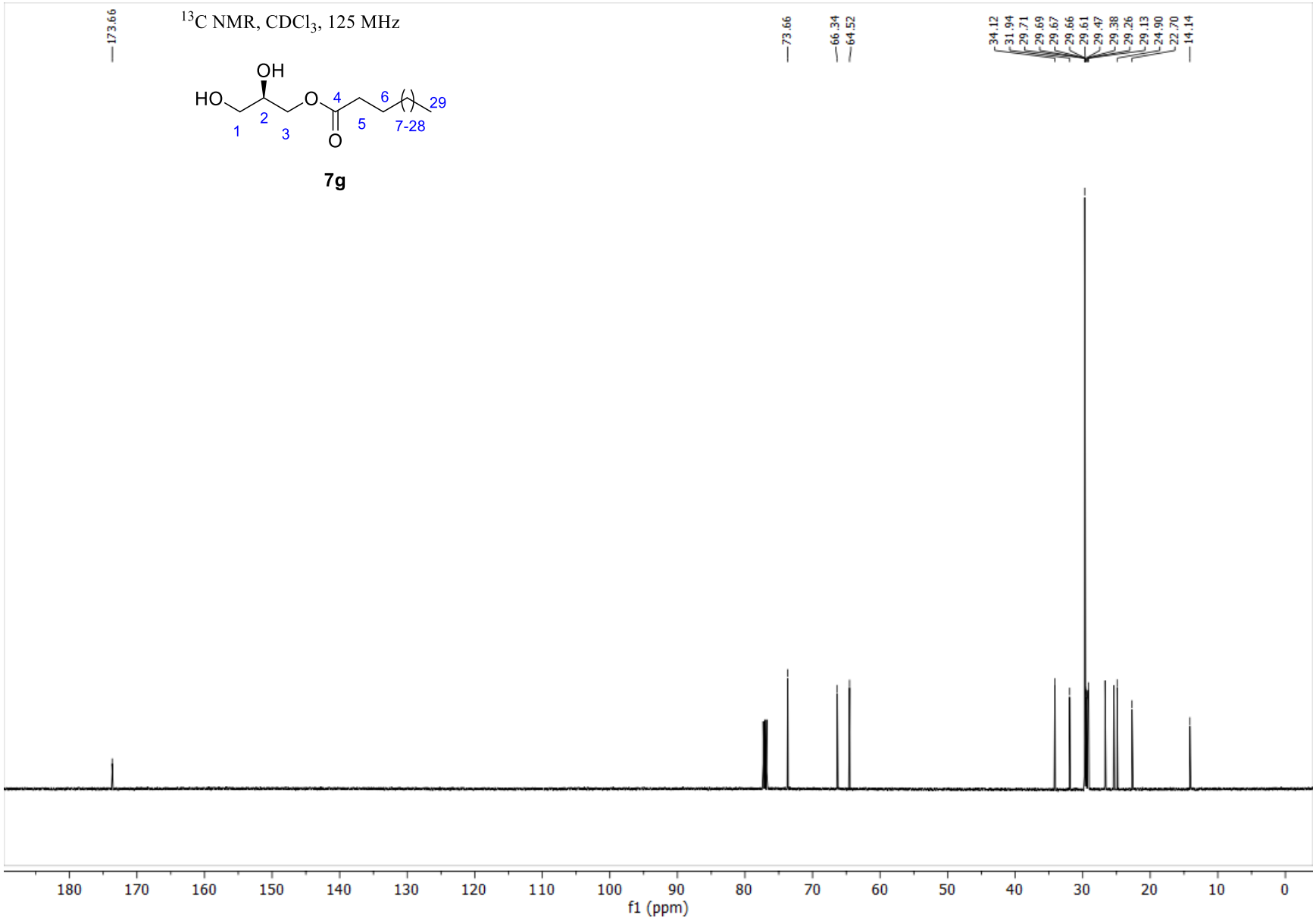
7f

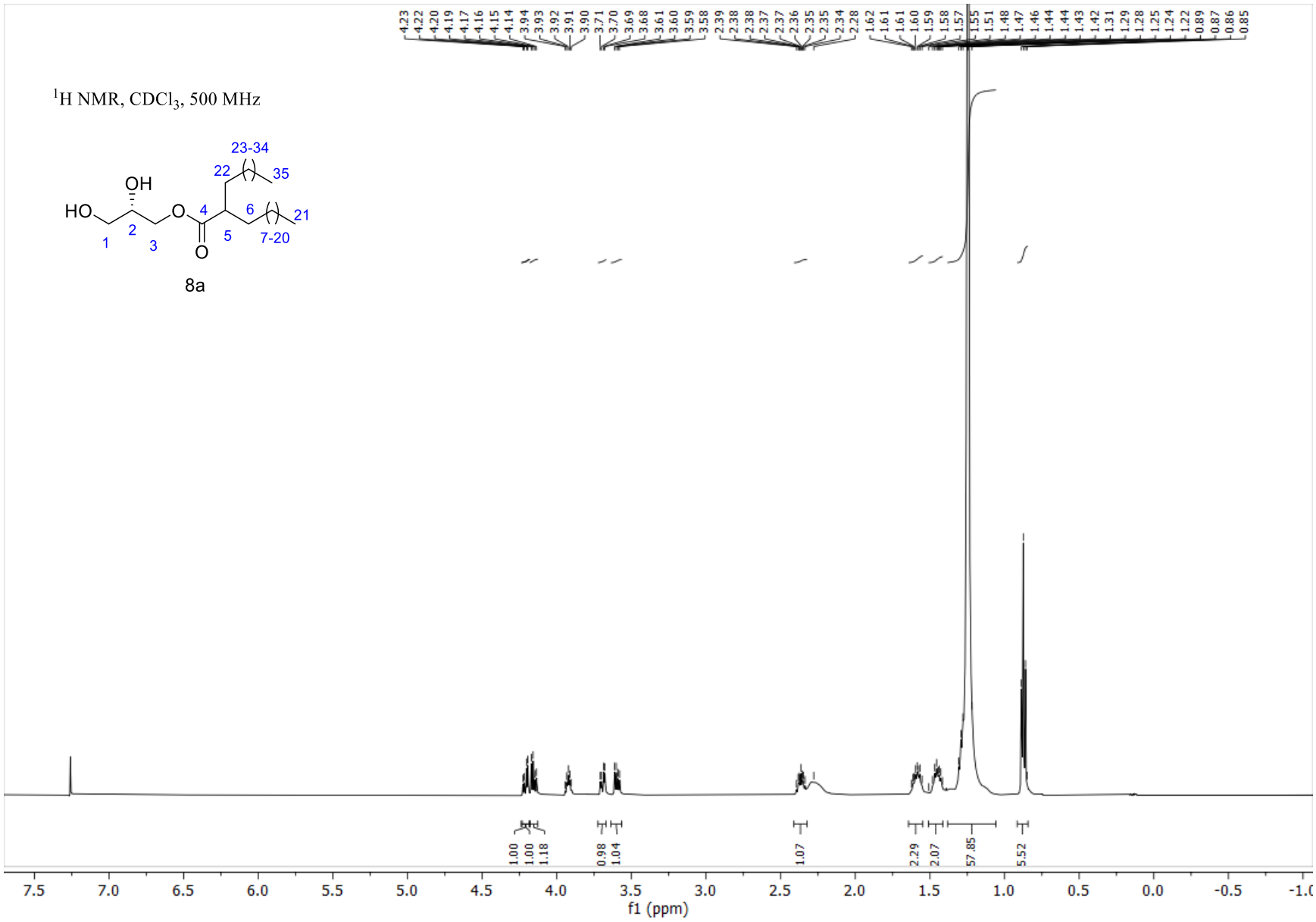

173.62
73.66
66.34
64.51
34.11
31.94
29.71
29.69
29.67
29.66
29.61
29.47
29.38
29.26
29.13
24.90
22.71
14.13
13C NMR, CDCl3, 125 MHz
OH
HO
O
O
1
2
3
4
5
6
7-28
29
7f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

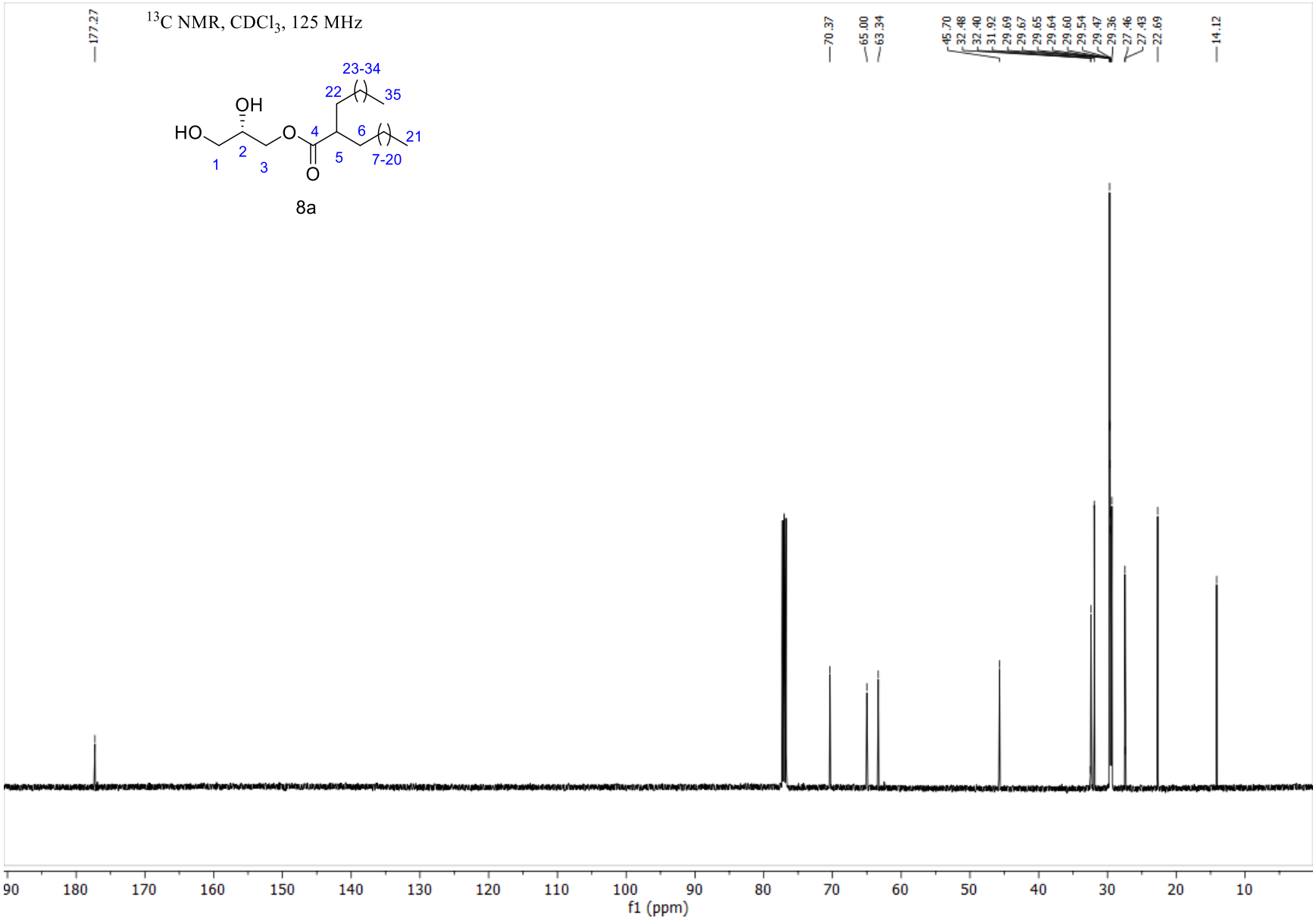
^{1}H NMR, $CDCl_3$, 500 MHz



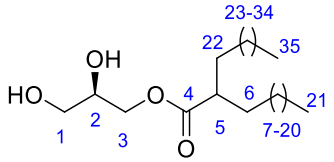
7g


^{13}C NMR, $CDCl_3$, 125 MHz
173.66
73.66
66.34
64.52
34.12
31.94
29.71
29.69
29.67
29.66
29.61
29.47
29.38
29.26
29.13
24.90
22.70
14.14
HO
OH
O
O
1
2
3
4
5
6
7-28
29
7g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

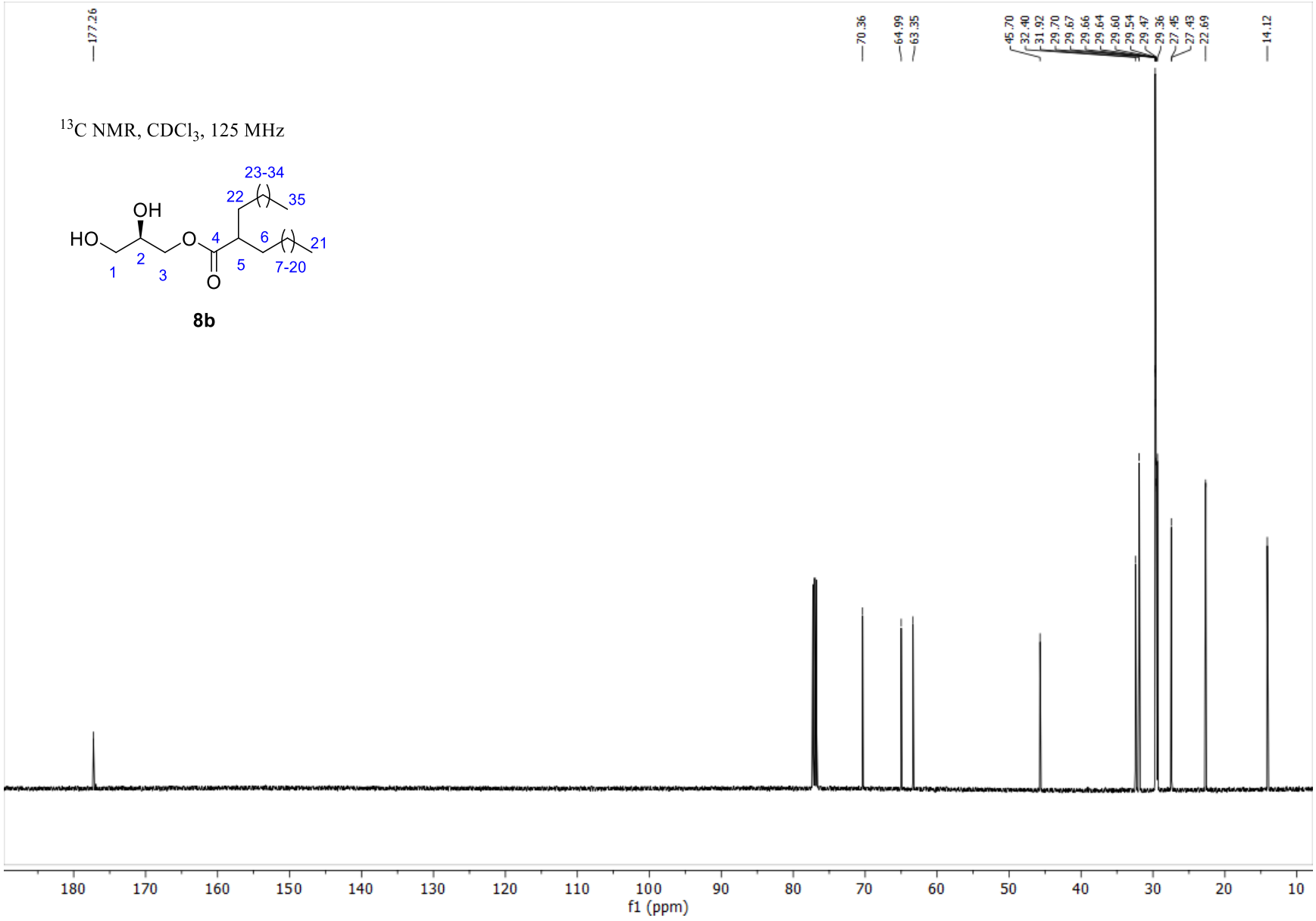

^{1}H NMR, $CDCl_3$, 500 MHz
HO
OH
O
O
1
2
3
4
5
6
7-20
21
22
23-34
35
8a
f1 (ppm)


^{13}C NMR, $CDCl_3$, 125 MHz
177.27
70.37
65.00
63.34
45.70
32.48
32.40
31.92
29.69
29.67
29.65
29.64
29.60
29.54
29.47
29.36
27.46
27.43
22.69
14.12
23-34
22
35
OH
HO
O
4
6
21
1
2
3
5
7-20
O
8a
f1 (ppm)

^{1}H NMR, $CDCl_3$, 500 MHz



8b


177.26
70.36
64.99
63.35
45.70
32.40
31.92
29.70
29.67
29.66
29.64
29.60
29.54
29.47
29.36
27.45
27.43
22.69
14.12
^{13}C NMR, $CDCl_3$, 125 MHz
23-34
22
35
OH
HO
O
4
6
21
1
2
3
5
7-20
O
8b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)