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Supporting Information

for

Nostochopcerol, a new antibacterial monoacylglycerol from the edible cyanobacterium *Nostochopsis lobatus*

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Experimental details, characterization data and copies of spectra

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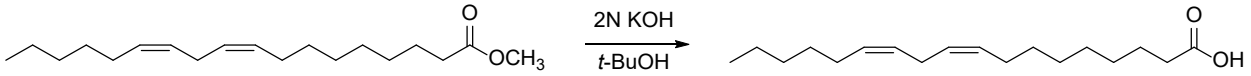
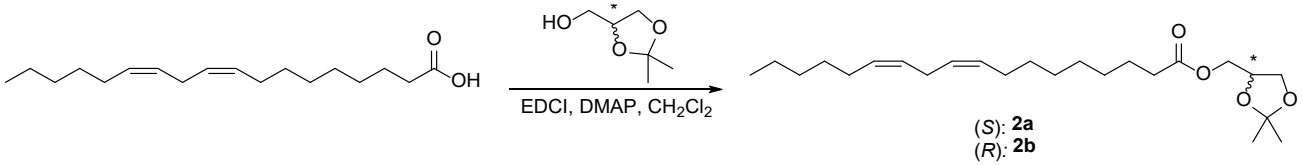
Preparation of linoleic acid from methyl linoleate



Methyl linoleate (1.00 g), purchased from Tokyo Chemical Industry Co., Ltd. (product code S0325), was dissolved in a 1:1 mixture of *t*-BuOH (5 mL) and 2 N KOH (3 mL) and the solution was stirred for 3 h at an ambient temperature. After removing *t*-BuOH under reduced pressure, the resulting residue was partitioned between EtOAc (20 mL) and 2 N HCl (20 mL). The EtOAc layer was successively washed with water and brine and then slowly passed through anhydrous Na_2SO_4 to give linoleic acid (1.04 g), which was used for the next step without further purification.

Chiral α-linoleyl-α',β-*O*-isopropylidene glycerols 2a and 2b

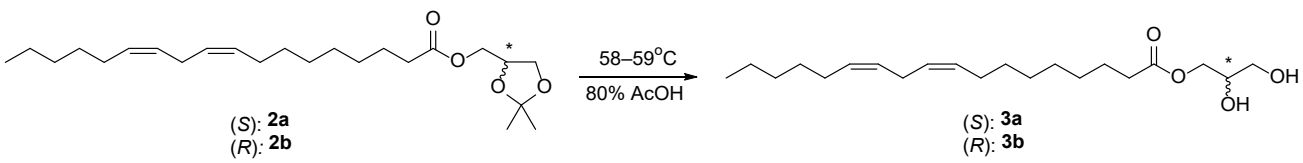


To the solution of linoleic acid (112.8 mg, 0.402 mmol for **2a**; 122.2 mg, 0.436 mmol for **2b**) in CH_2Cl_2 (3 mL) was added (*R*)- or (*S*)-solketal (2,2-dimethyl-1,3-dioxolane-4-methanol, Tokyo Chemical Industry, product codes D1705 and D1691, respectively: 59 mg, 0.45 mmol; 1.1 equiv), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (86.9 mg, 0.45 mmol: 1.1 equiv), and one crystal of *N*,*N*-dimethyl-4-aminopyridine (DMAP, ≈ 5 mg), and the reaction mixture was stirred for 2.5 h at ambient temperature. After removing the solvent under reduced pressure, the resulting concentrate was passed through a short column of silica gel to remove DMAP and 1-(3-(dimethylamino)propyl)-3-ethylurea. The eluate was concentrated and purified by ODS-HPLC (solvent: 95%MeCN) to give 1-linoleoyl-2,3-*O*-isopropylidene-*sn*-glycerol (**2a**, 90.6 mg, 57.5%) and 3-linoleoyl-1,2-*O*-isopropylidene-*sn*-glycerol (**2b**, 125.0 mg, 72.7%), respectively [34].

1-Linoleoyl-2,3-*O*-isopropylidene-*sn*-glycerol (**2a**): $[\alpha]^{23.7}_D$ 0.69 (*c* 1.0, MeOH); HRESIMS: *m/z* 417.2969 $[M + Na]^+$ (calcd for $C_{24}H_{42}NaO_4$, 417.2975). IR (ATR) ν_{max} 3010, 2987, 2929, 2856, 1743, 1458, 1381, 1372, 1254 sh, 1215, 1161, 1087, 1059, 976, 844, 726 cm^{-1}. ^1H and ^{13}C NMR data are essentially the same as **2b**.

3-Linoleoyl-1,2-*O*-isopropylidene-*sn*-glycerol (**2b**): $[\alpha]^{23.7}_D$ −0.64 (*c* 1.0, MeOH); HRESIMS: *m/z* 417.2961 $[M + Na]^+$ (calcd for $C_{24}H_{42}NaO_4$, 417.2975). IR (ATR) ν_{max} 3010, 2987, 2929, 2857, 1743, 1458, 1381, 1372, 1254 sh, 1215, 1161, 1085, 1058, 977, 844, 727 cm^{-1}; ^1H and ^{13}C NMR, see Table S1.

Chiral α-linoleoylglycerols 3a and 3b



Compound **2a** (5.9 mg, 15.0 μmol) or **2b** (6.2 mg, 15.7 μmol) was dissolved in 80% aqueous acetic acid (2 mL) and the solution was stirred occasionally in a sealed 6-mL screw-capped vial at 58–59 °C for 30 min. After removing the solvents by a stream of N_2 gas, the resulting concentrate was purified by silica gel-HPLC (Cosmosil SL-II Ø 1 × 25 cm) eluted with *n*-hexane/EtOAc 1:1 (4 mL/min) monitored at 210 nm to give 1-linoleoyl-*sn*-glycerol (**3a**, 4.3 mg, 81.1%) or 3-

linoleoyl-*sn*-glycerol (**3b**, 5.1 mg, 91.6%), respectively [1-4].

1-Linoleoyl-*sn*-glycerol (**3a**): $[\alpha]^{22.2}_{D}$ +5.5 (*c* 0.30, MeOH); HRESIMS: *m/z* 377.2652 $[M + Na]^+$ (calcd for $C_{21}H_{38}NaO_4$, 377.2662). IR (ATR) ν_{max} 3404, 3010, 2927, 2856, 1740, 1458, 1378, 1243, 1177, 1118, 1052, 726 cm^{-1}; ^1H and ^{13}C NMR, see Table S1.

3-Linoleoyl-*sn*-glycerol (**3b**): $[\alpha]^{22.7}_{D}$ −5.5 (*c* 0.30, MeOH); HRESIMS: *m/z* 377.2642 $[M + Na]^+$ (calcd for $C_{21}H_{38}NaO_4$, 417.2662). IR (ATR) ν_{max} 3407, 3010, 2926, 2856, 1739, 1458, 1379, 1242, 1177, 1120, 1053, 723 cm^{-1}. ^1H and ^{13}C NMR data are essentially the same as for **3a**.

References

1. Zhang, G.-L.; Xing, Q.-Y.; Zhang, M.-Z. *Phytochemistry*, **1997,** *45,* 1213–1215.
2. Kim, C.; Ha, H.; Kim, J. S.; Kim, Y. T.; Kwon, S.-C.; Park, W.-W. *Arch. Pharm. Res.* **2003,** *26,* 34–39.
3. Fraser, B. H.; Perlmutter, P.; Wijesundera, C. *J. Am. Oil Chem. Soc.* **2007,** *84,* 11–21.
4. Degenhardt, A. G.; Hofmann, T.; *J. Agric. Food Chem.* **2010,** *58,* 12906–12915.

Table S1: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for compounds **2b** and **3a** in $CDCl_3$.

	2b		**3a**	
Position	δ_C	δ_H[a]	δ_C	δ_H[a]
1	173.6		173.4	
2	34.1	2.34, t (7.6), 2H	34.1	2.35, t (7.6), 2H
3	24.9	1.62, brqui (7.3), 2H	24.9	1.63, brqui (7.2), 2H
4	29.081[b]	1.30, ovl	29.12	1.3068, ovl
5	29.087[b]	1.30, ovl	29.06	1.3076, ovl
6	29.1	1.30, ovl	29.06	1.3076, ovl
7	29.3[c]	1.32, ovl, 2H	29.3[i]	1.31, ovl, 2H
8	27.19[d]	2.05, ovl, 2H	27.18[j]	2.05, ovl, 2H
9	130.2[e]	5.38[f], m, 1H	130.2[k]	5.38[l], m, 1H
10	128.1[g]	5.323[h], m, 1H	128.1[m]	5.348[n], m, 1H
11	25.6	2.77, brt (6.6), 2H	25.6	2.77, brt (6.6), 2H
12	127.9[g]	5.316[h], m, 1H	127.9[m]	5.32[n], m, 1H
13	130.0[e]	5.36[f], ovl, 1H	130.0[k]	5.355[l], ovl, 1H
14	27.18[d]	2.05, ovl, 2H	27.15[j]	2.05, ovl, 2H
15	29.6[c]	1.33, ovl, 2H	29.6[i]	1.34, ovl, 2H
16	31.5	1.29, ovl, 2H	31.5	1.29, ovl, 2H
17	22.6	1.30, ovl, 2H	22.5	1.302, ovl, 2H
18	14.1	0.89, t (7.0), 3H	14.0	0.89, t (6.9), 3H
sn-1	66.4	3.74, dd (6.2, 8.4), 1H	63.3	3.60, dd (5.8, 11.4), 1H
		4.07, dd (6.4, 8.6), 1H		3.70, dd (4.0, 11.5), 1H
sn-2	73.7	4.31, m, 1H	70.3	3.93, m, 1H
sn-3	64.5	4.09, dd (6.0, 11.5), 1H	65.2	4.15, dd (6.2, 11.7), 1H
		4.16, dd (4.7, 11.5), 1H		4.21, dd (4.7, 11.7), 1H
acetonide-O*C*O	109.8			
acetonide-CH_3-1	26.7	1.43, s, 3H		
acetonide-CH_3-2	25.4	1.37, s, 3H		

[a]Chemical shift in ppm, multiplicity (*J* in Hz), integral. [b-u]Interchangeable.

Mass Spectrum Molecular Formula Report

Analysis Info

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Sample Name	42A-22-2 pos-2	Instrument / Ser#	micrOTOF 210
Comment			

Acquisition Parameter

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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

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Formula, max.	C20H36O5Na						
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Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	no	Electron Configuration	both				
Filter H/C Ratio	no	Minimum	0		Maximum	3	
Estimate Carbon	yes						

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
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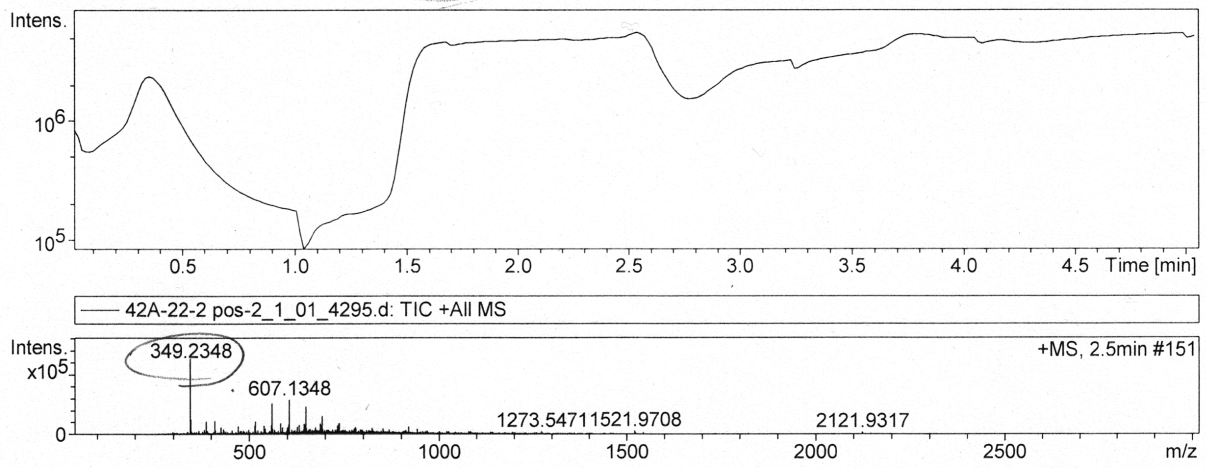
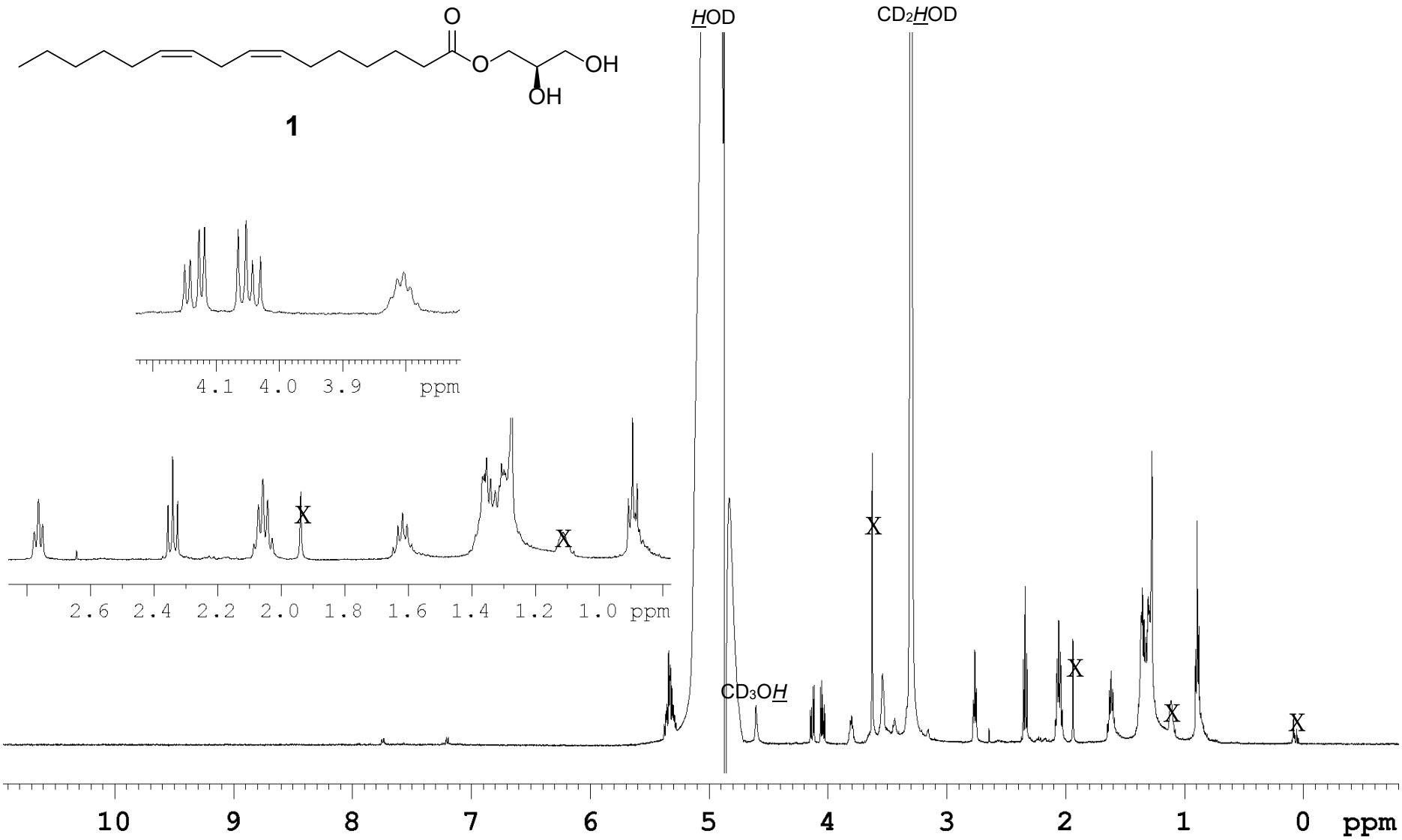
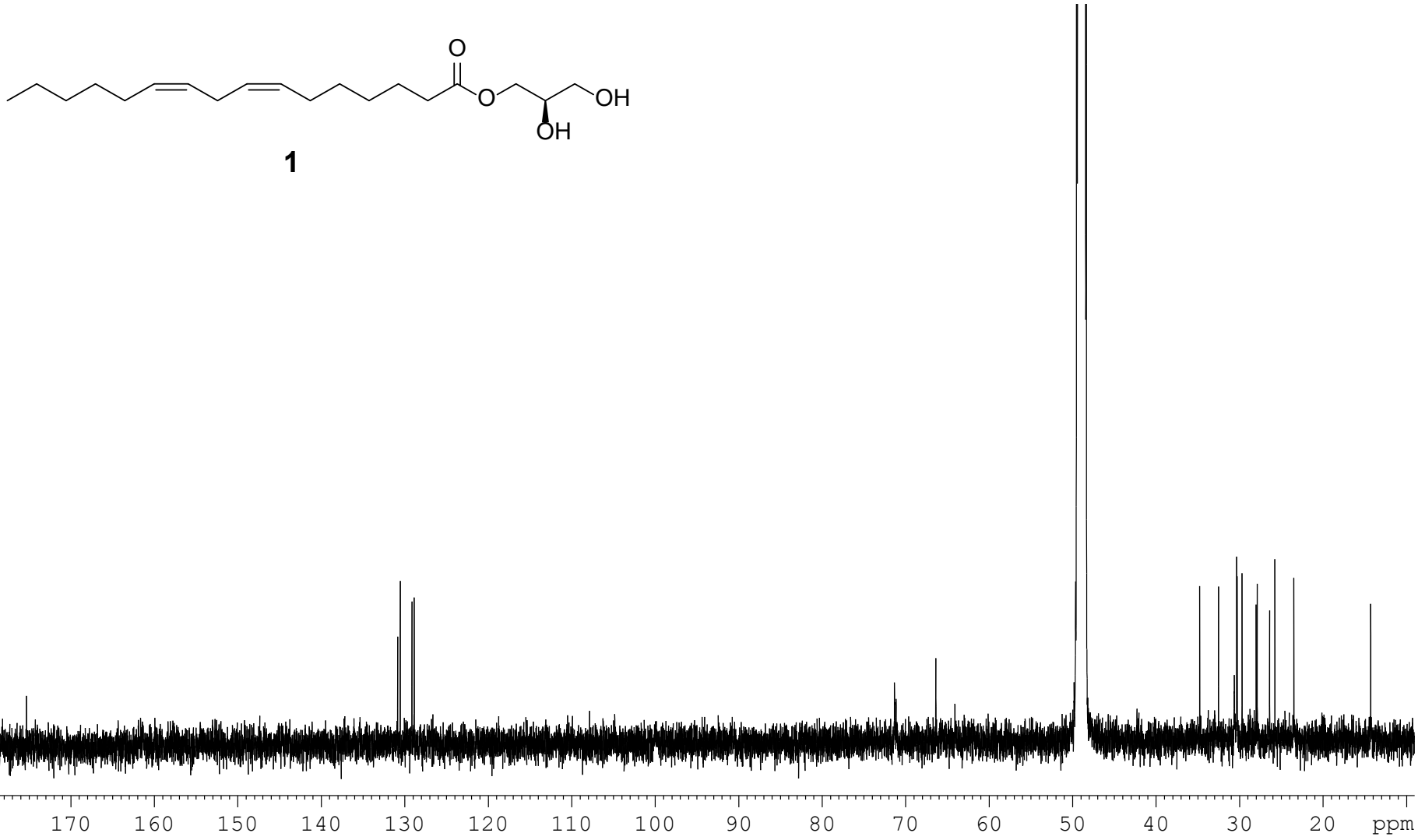


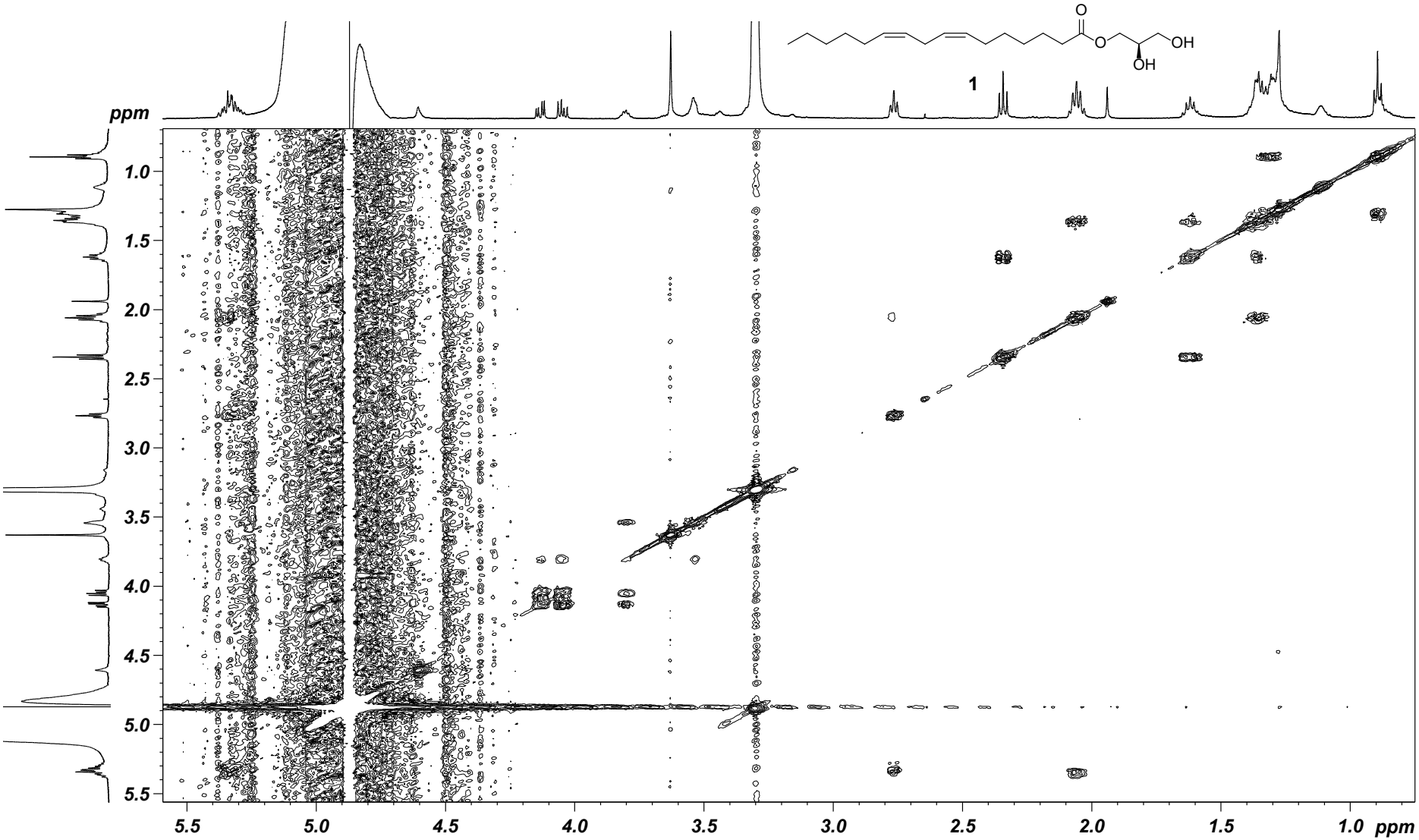
Positive ion HRESITOFMS spectrum of nostochopcerol (**1**)



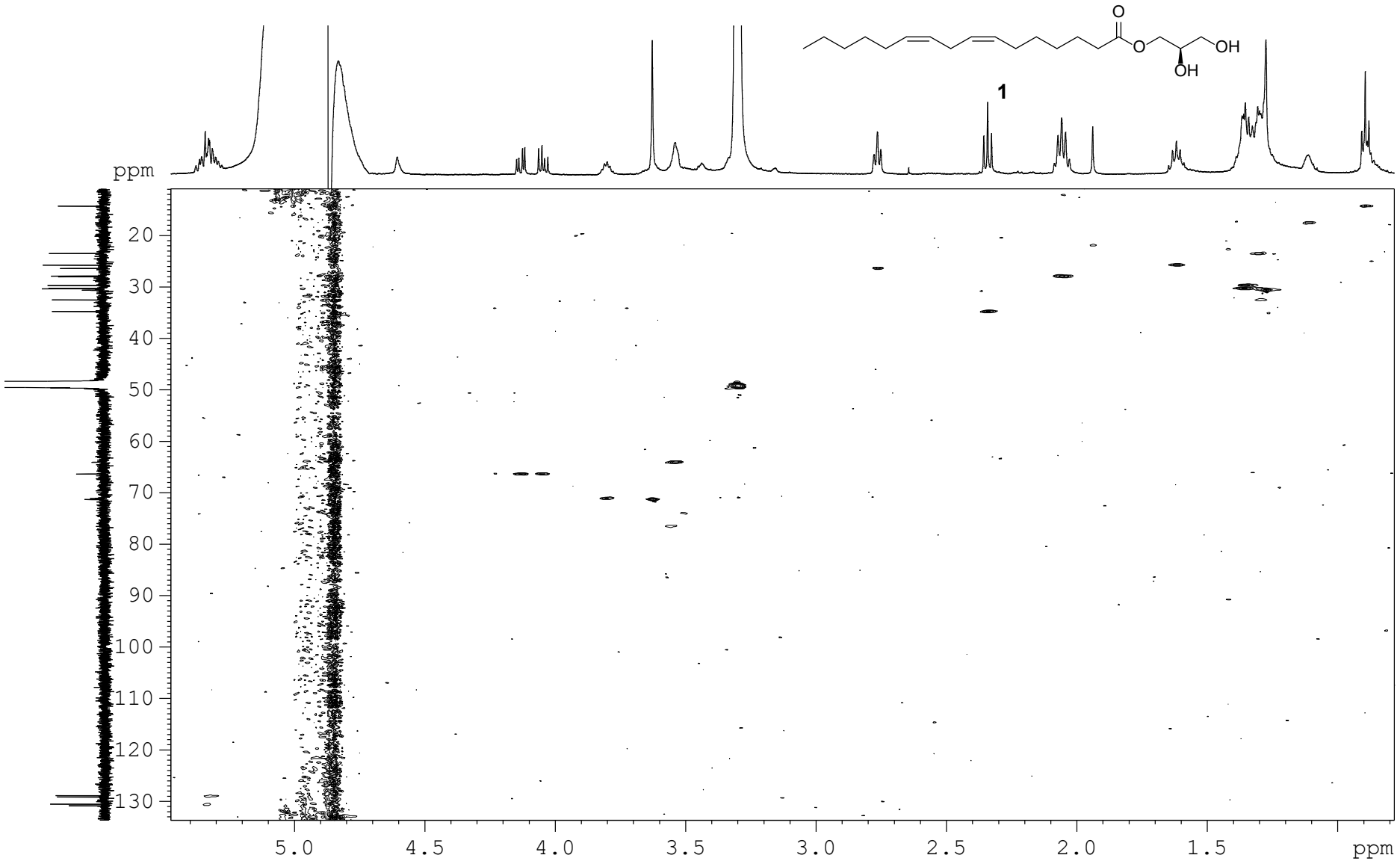
^{1}H NMR spectrum of nostochopcerol (**1**) (500 MHz, CD_3OH)



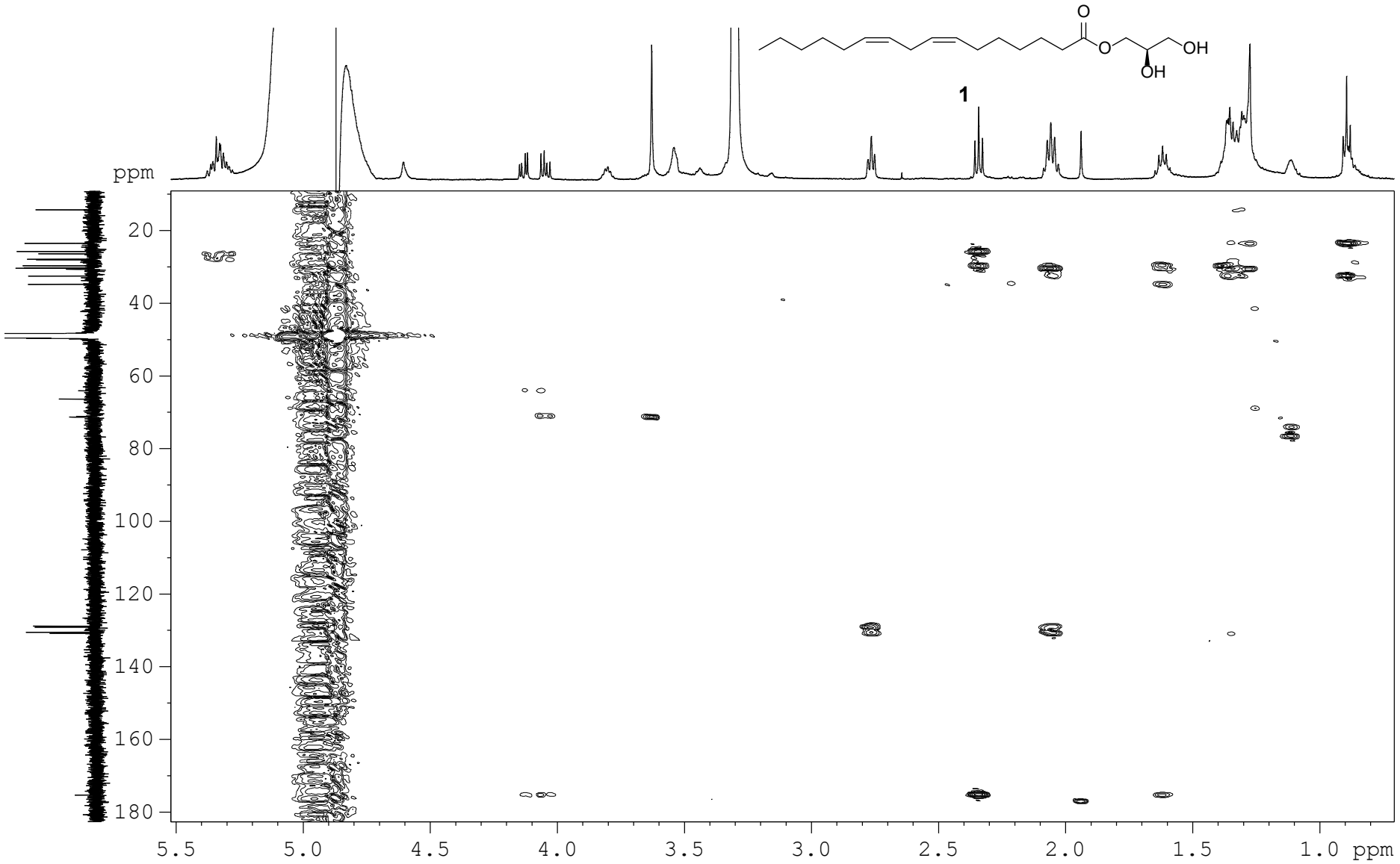
^{13}C NMR spectrum of nostochopcerol (**1**) (125 MHz, CD_3OH)



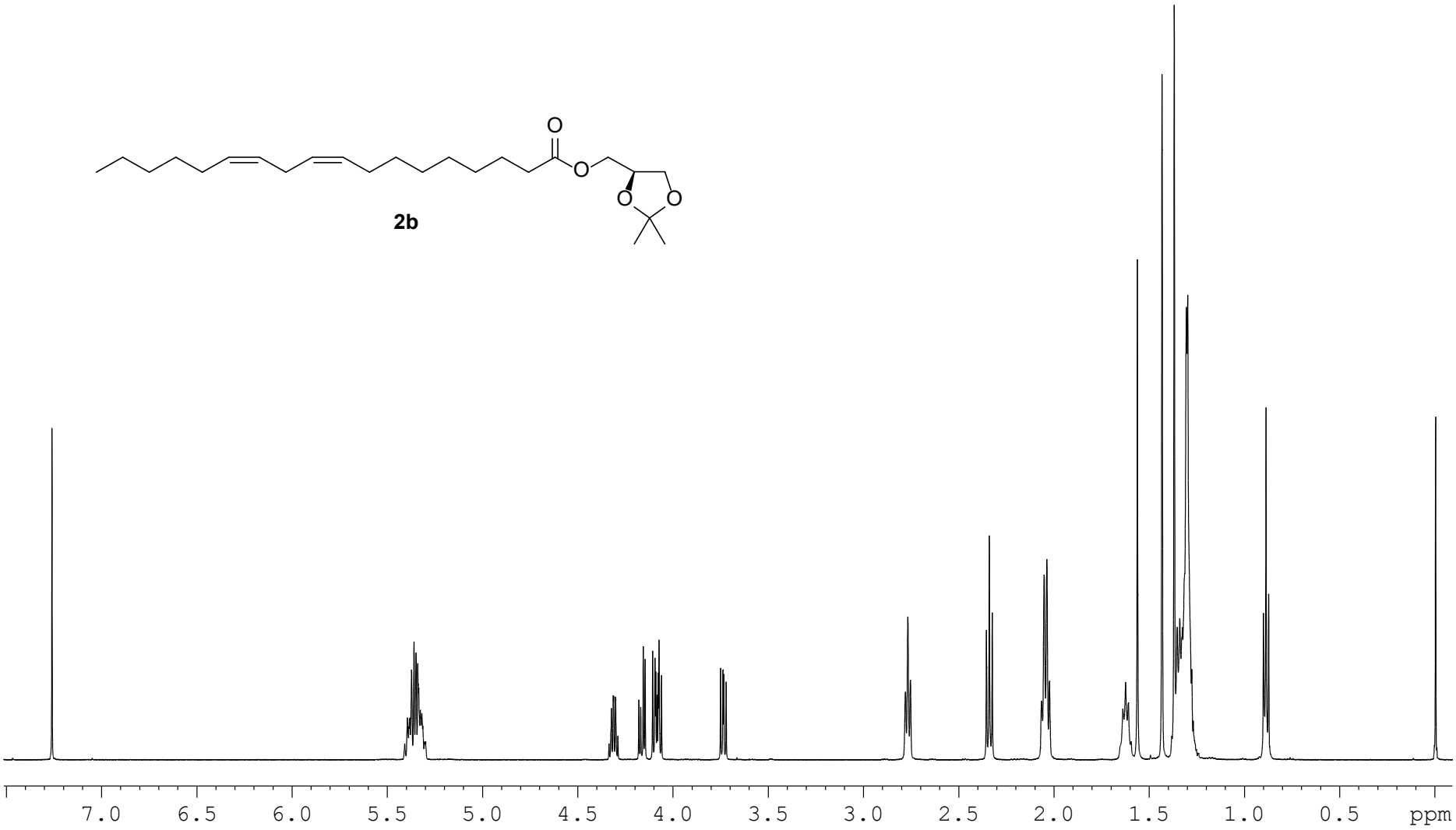
COSY spectrum of nostochopcerol (**1**) (500 MHz, CD_3OH)



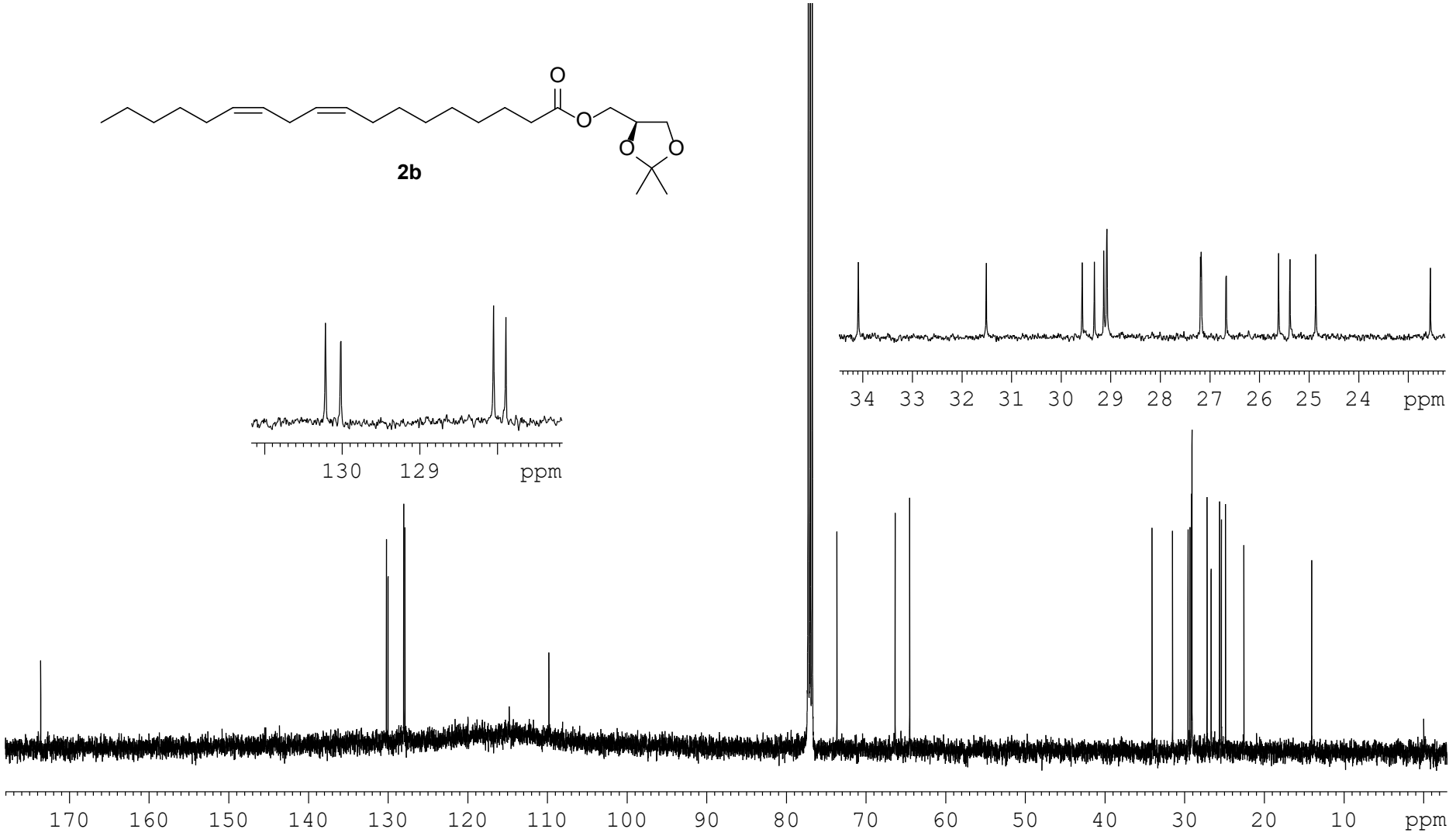
HSQC spectrum of nostochopcerol (**1**) (500 MHz, CD_3OH)



HMBC spectrum of nostochopcerol (**1**) (500 MHz, CD_3OH)



^{1}H NMR spectrum of 3-linoleoyl-1,2-*O*-isopropylidene-*sn*-glycerol (**2b**) (500 MHz, $CDCl_3$)



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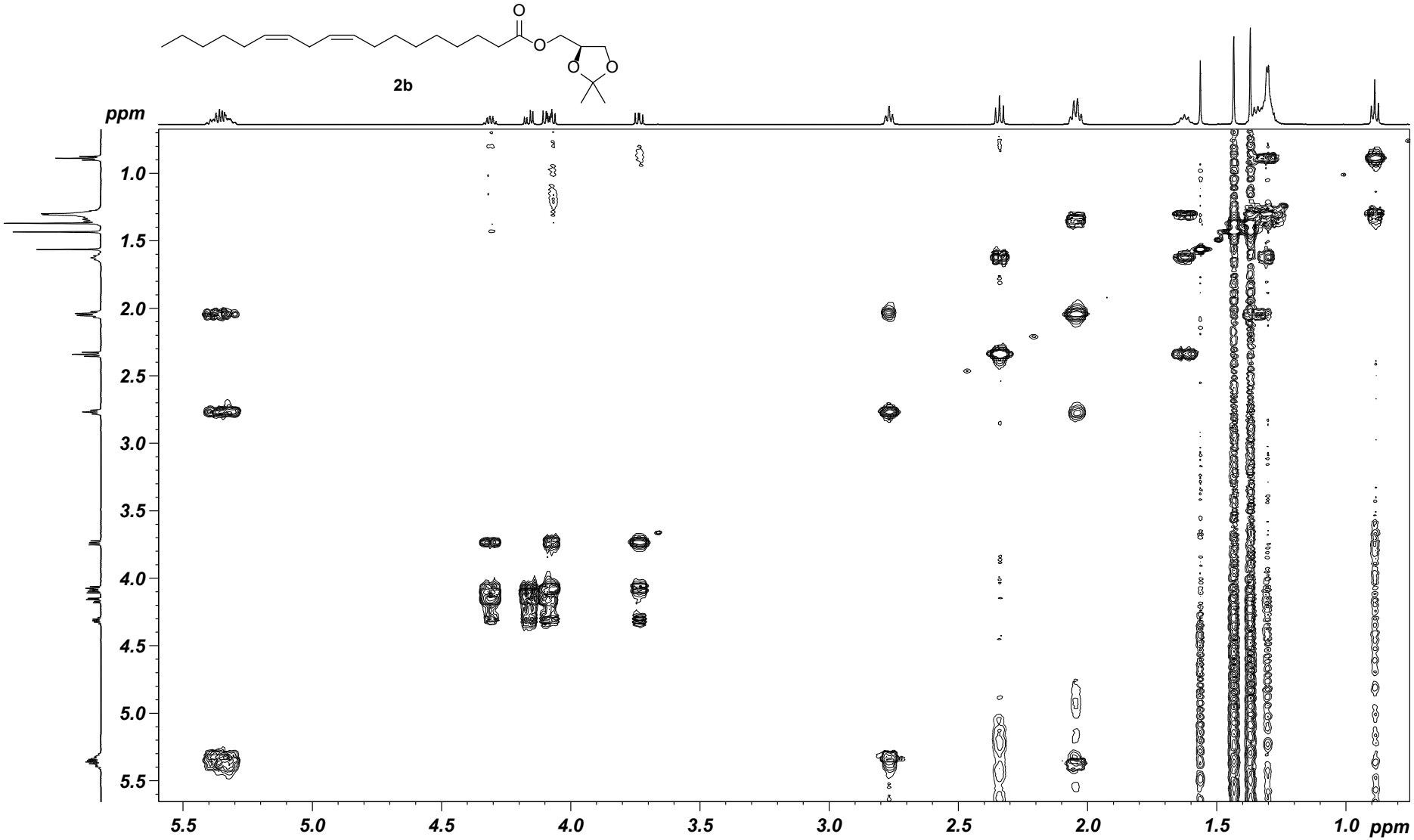
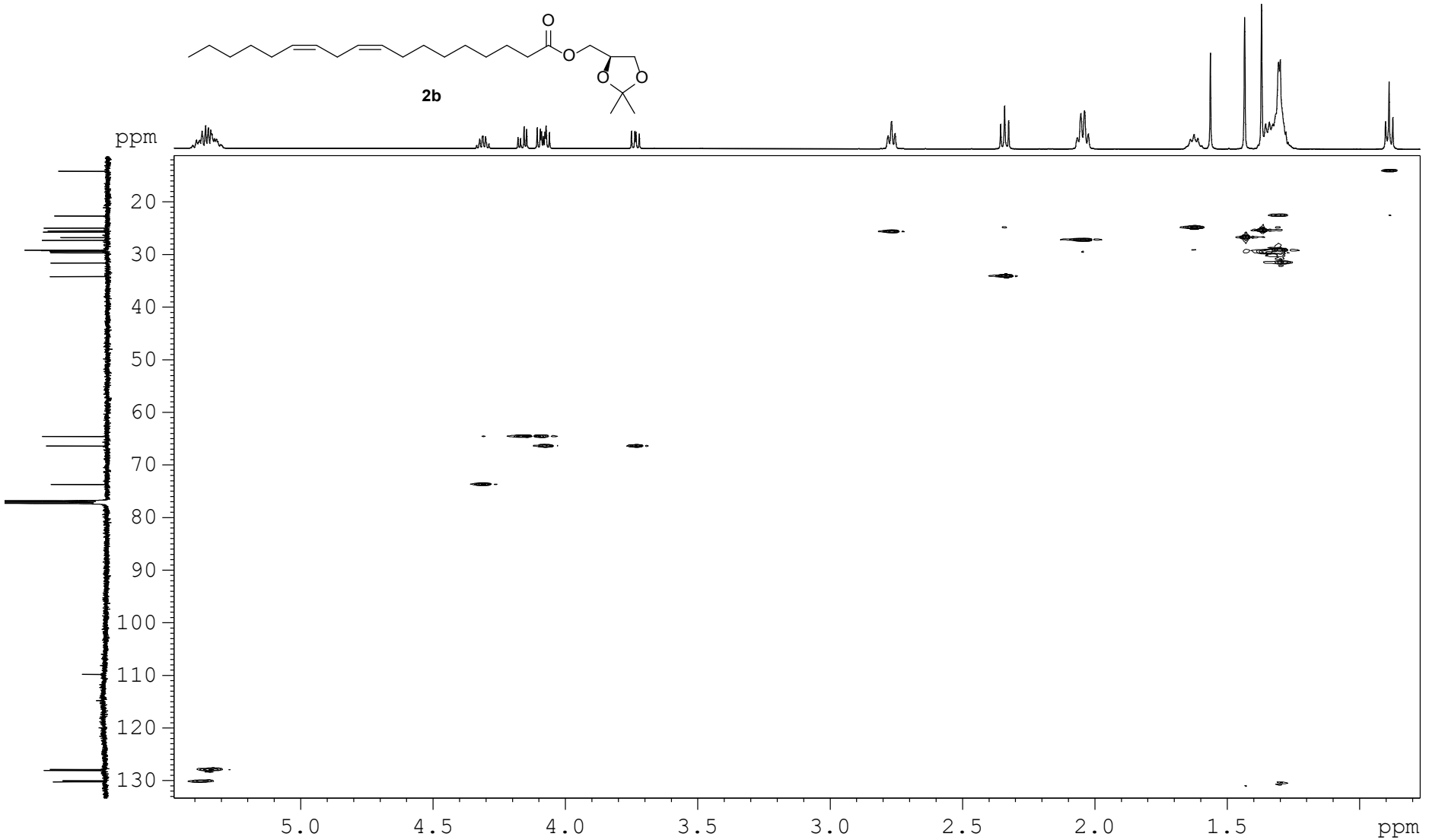


COSY45 spectrum of 3-linoleoyl-1,2-*O*-isopropylidene-*sn*-glycerol (**2b**) (500 MHz, $CDCl_3$)



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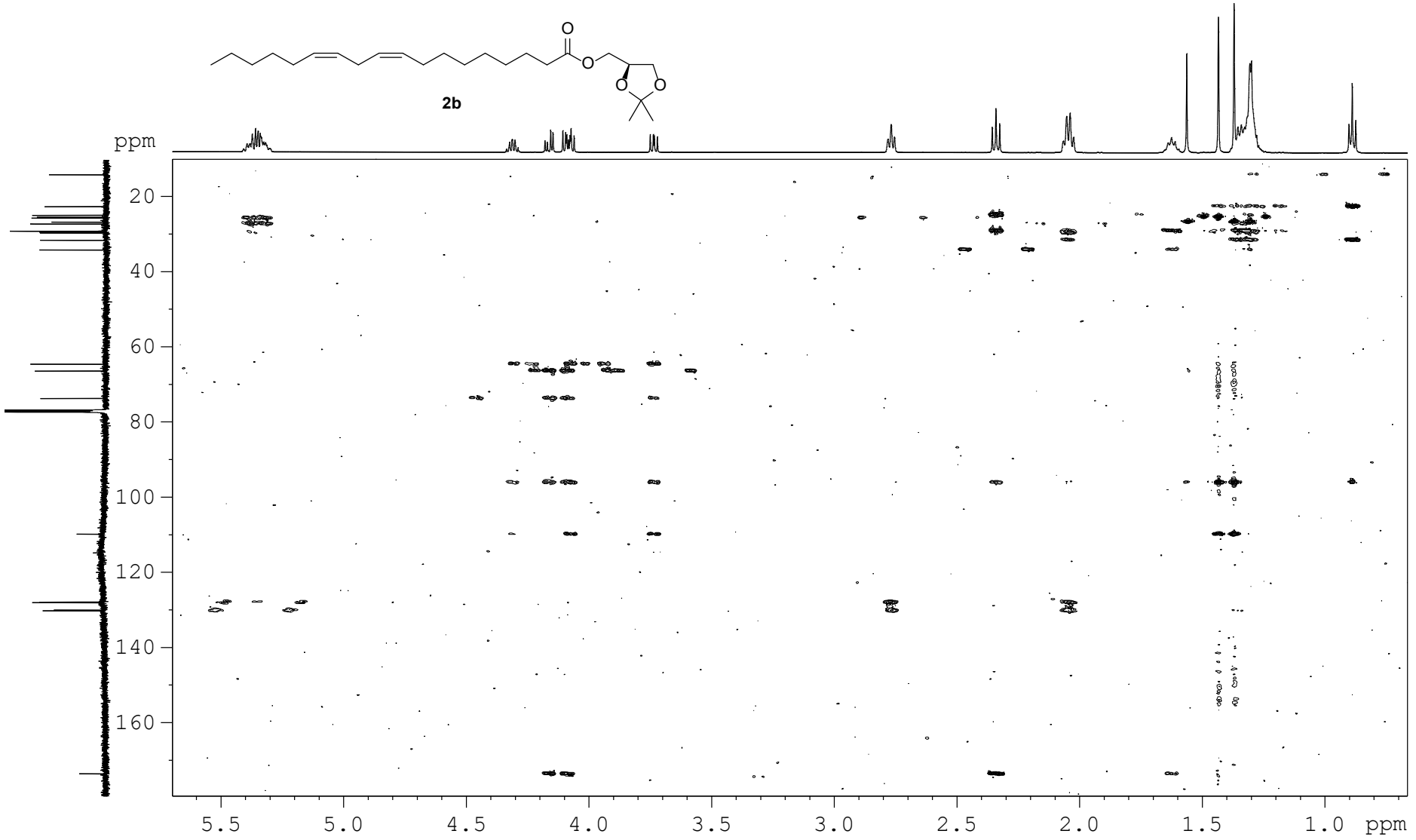

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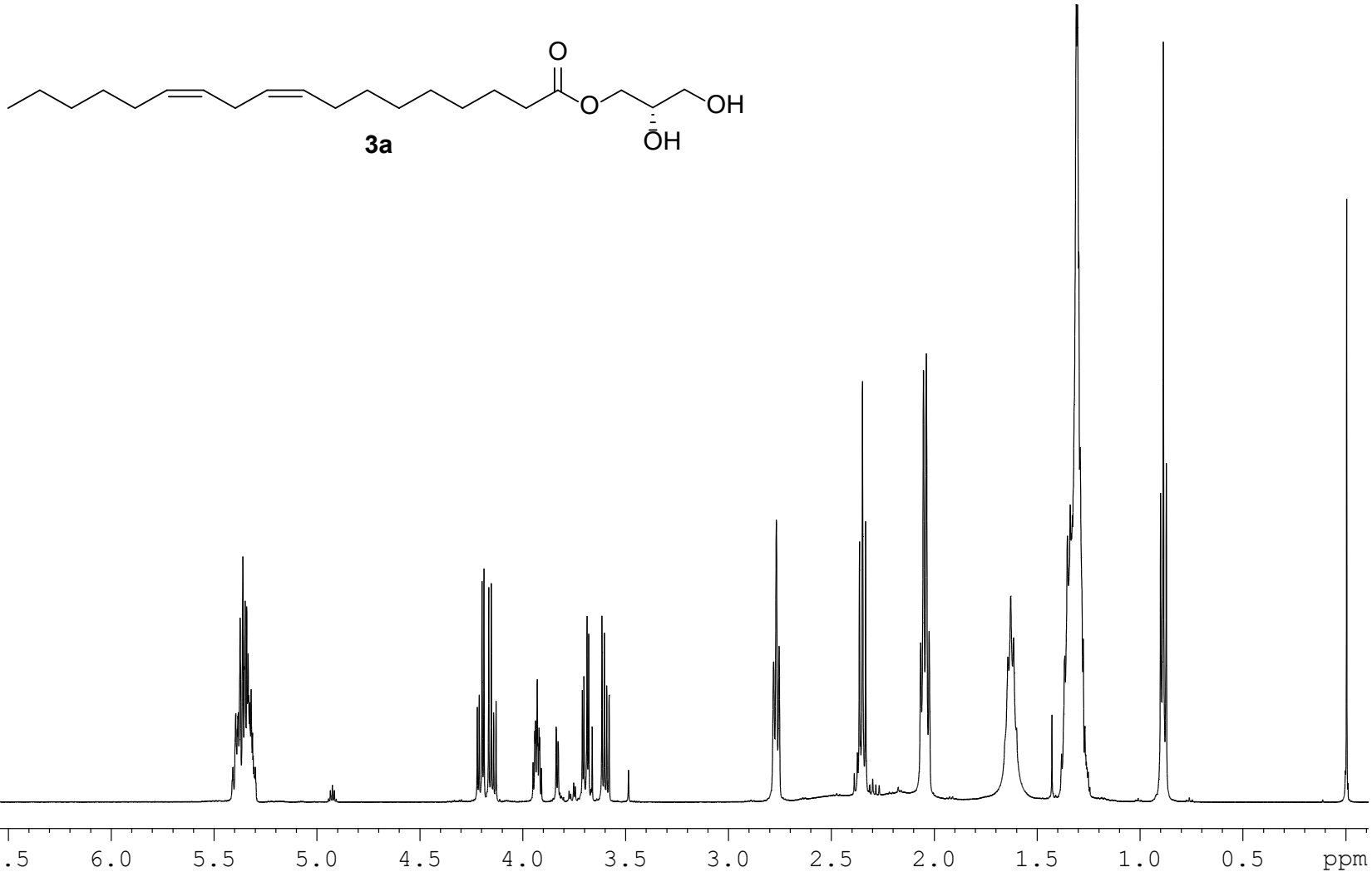
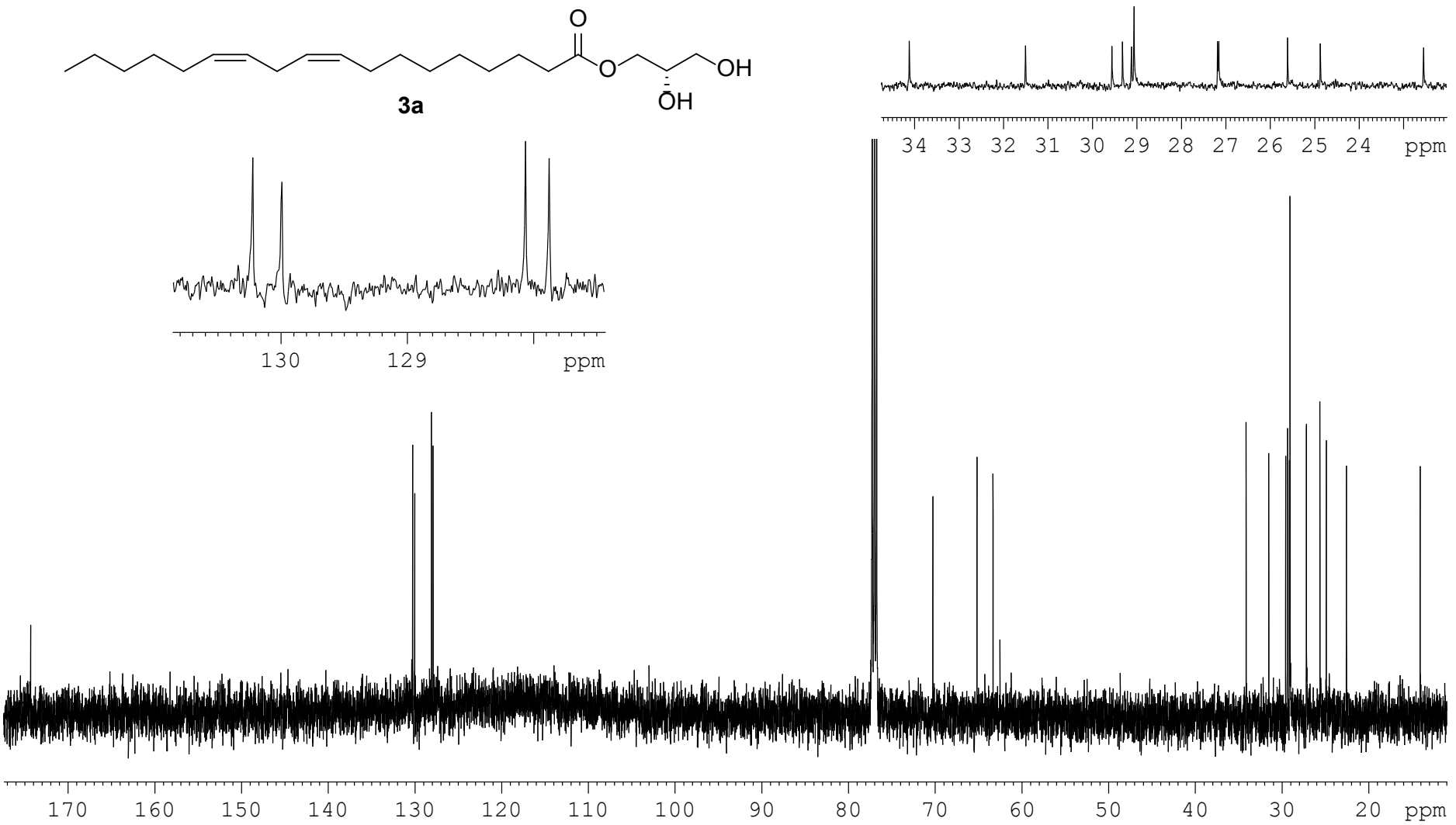


^{1}H NMR spectrum of 1-linoleoyl-*sn*-glycerol (**3a**) (500 MHz, $CDCl_3$)



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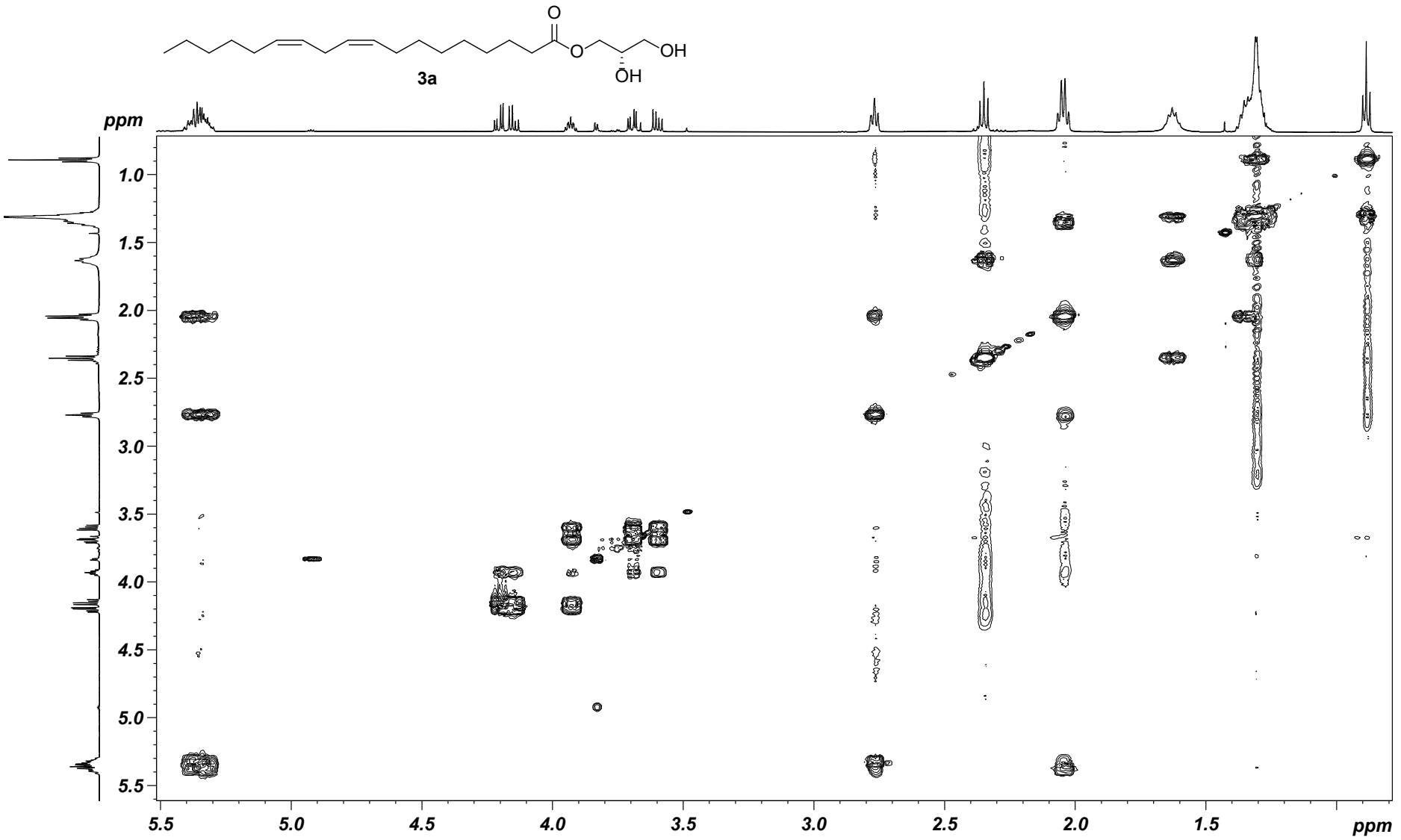
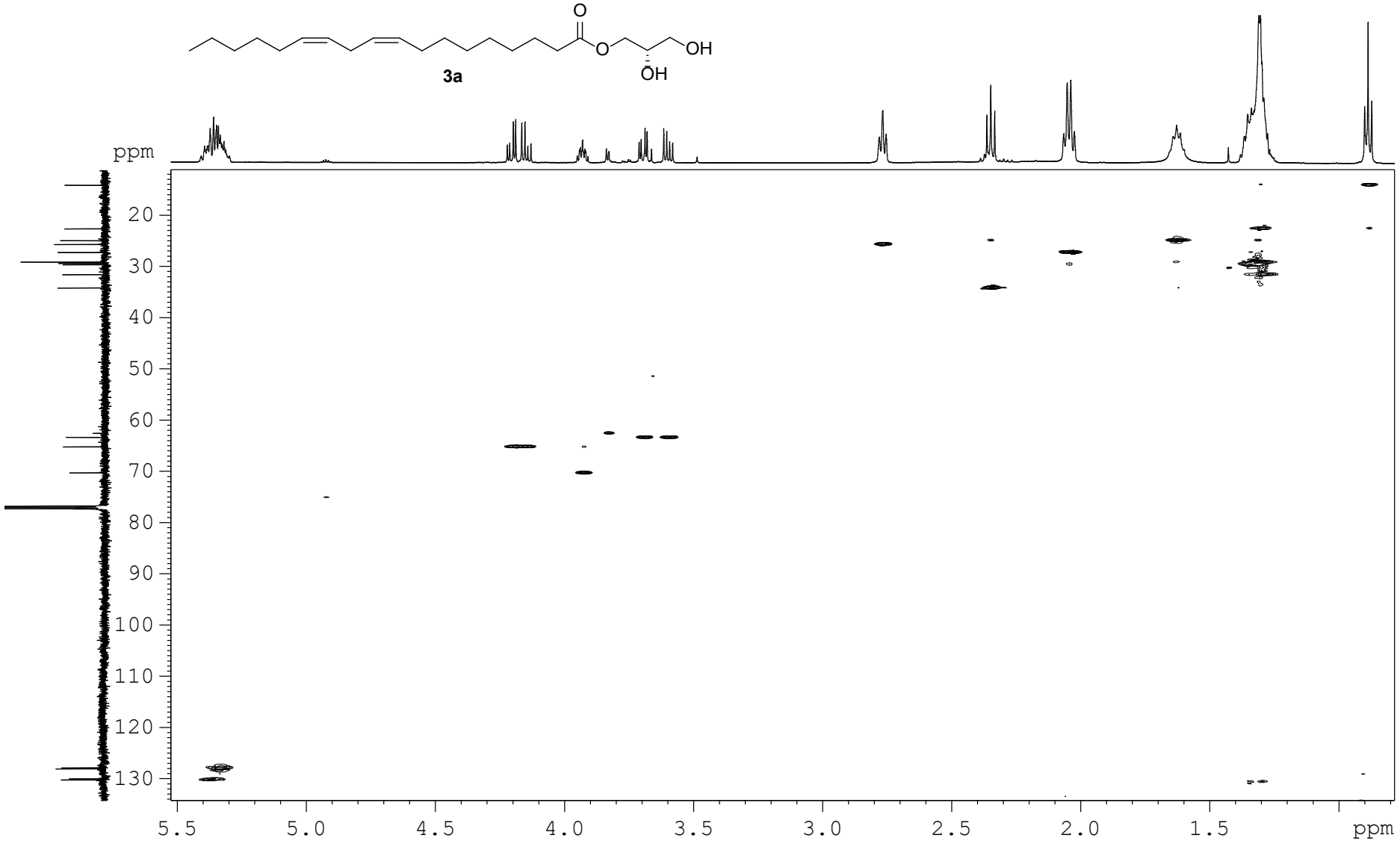
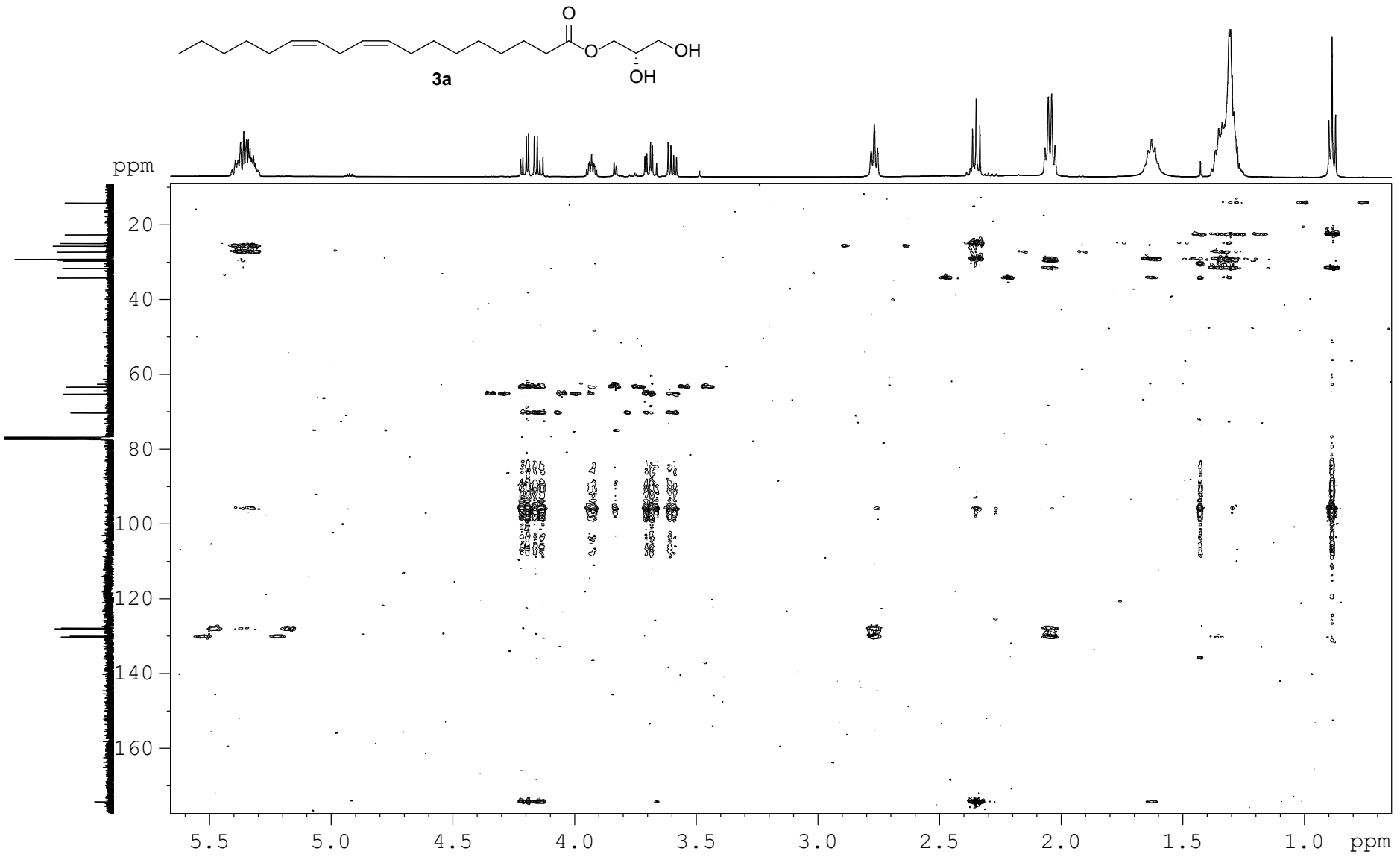


COSY45 spectrum of 1-linoleoyl-*sn*-glycerol (**3a**) (500 MHz, $CDCl_3$)



HSQC spectrum of 1-linoleoyl-*sn*-glycerol (**3a**) (500 MHz, $CDCl_3$)



HMBC spectrum of 1-linoleoyl-*sn*-glycerol (**3a**) (500 MHz, $CDCl_3$)