Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Bioinspired Total Synthesis of Tetrahydrofuran Lignans by Tandem Nucleophilic Addition/Redox Isomerization/Oxidative Coupling and Cycloetherification Reactions as Keysteps

Pratap R. Jagtap,[a] Ivana Císařová,[b] Ullrich Jahn[a]*

[a] Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo náměstí 2, 16610 Prague 6, Czech Republic; e-mail: jahn@uochb.cas.cz

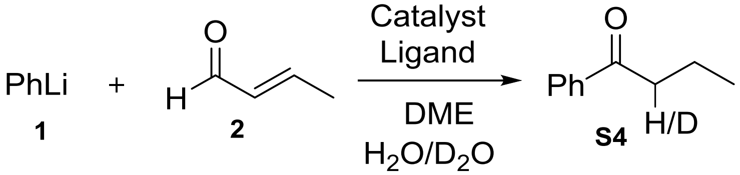
[b] Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Albertov 6, 12840 Prague 2, Czech Republic

Table of Contents: Page

1. Supplementary results and rationalization

1.1 Catalyst screening for isomerization of alkoxides

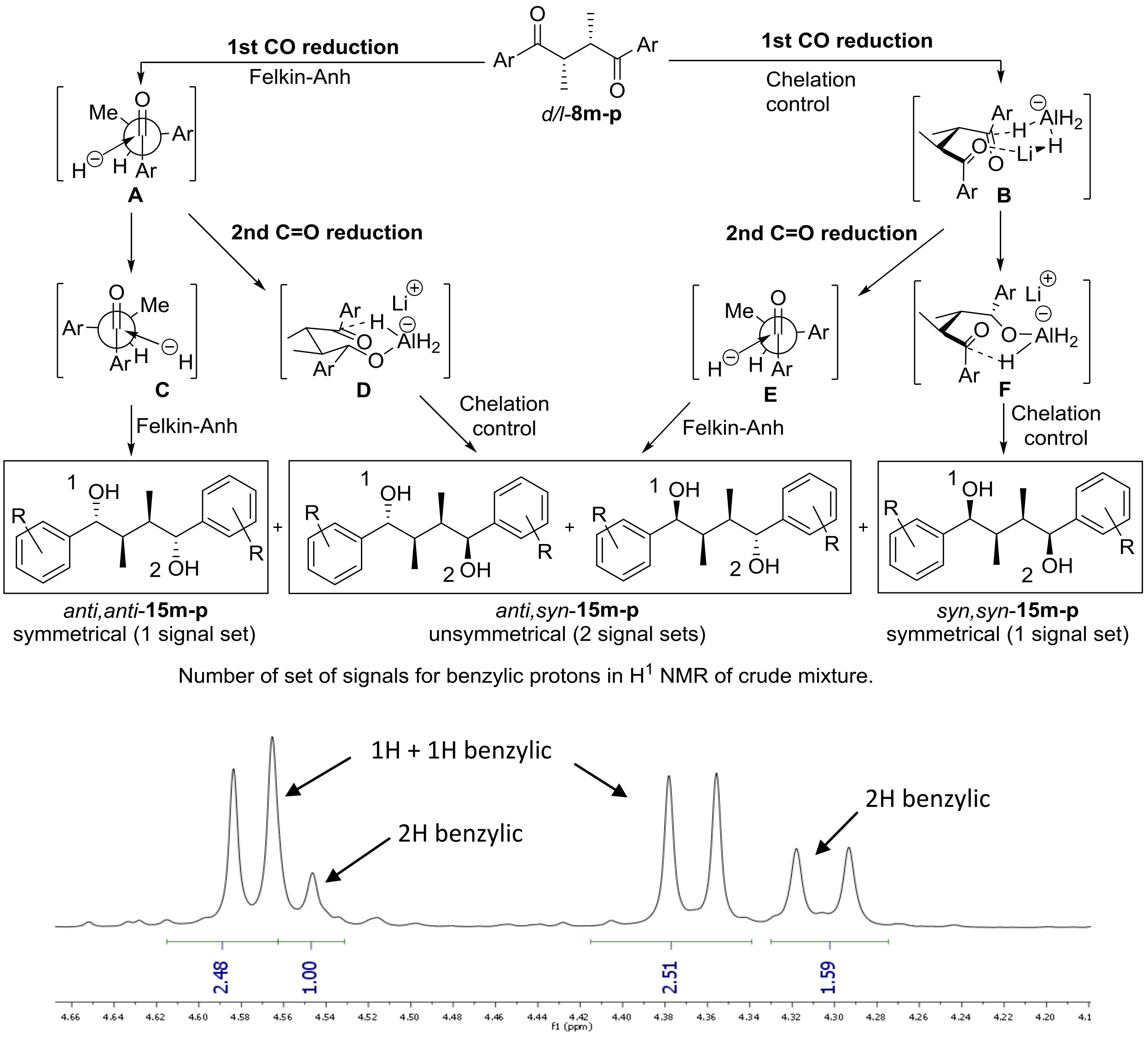
Table S1: Catalyst screening for isomerization of alkoxides.[a,b]



entry	Catalyst	Ligand (mol%)	T (°C)	t (h)	**S4** (%)
1	$Ni(PPh_3)_2Cl_2$	-	85	6	0
2	[Ru(*p*-cymene)$Cl_2]_2$	$P(OEt)_3$ (4)	55	4	71
3	[Ru(*p*-cymene)$Cl_2]_2$	$P(OEt)_3$ (4)	85	4	99
4	[Ru(*p*-cymene)$Cl_2]_2$	$P(OMe)_3$ (2)	85	0.25	99
5	[Ru(*p*-cymene)$Cl_2]_2$	1:1 $P(OMe)_3$ (5)[c]	25	3	60
6	RuCl(η^5-3-phenylindenyl)(PPh_3)]	-	25	48	0
7	[Ru(*p*-cymene)$Cl_2]_2$	(*S*)-Tol-BINAP (2)	85	0.5	90

[a] Phenyllithium **1** (0.72 mL, 1.3 mmol) was added to α,β-unsaturated aldehyde **2** (91 mg, 1.3 mmol) in DME (8 mL) at –5 °C. After 15 min, the respective catalyst (2 mol%) was added followed by the ligand. The mixture was subsequently heated with stirring for the specified time. After quenching, the crude mixture was analyzed by ^{1}H NMR spectroscopy. [b] Dodecane (20 mol%) used as internal standard to monitor the progress of reactions by GC. [c] 5 mol% of catalyst was used.

1.2 Reduction of 1,4-diketones 8 by $LiAlH_4$

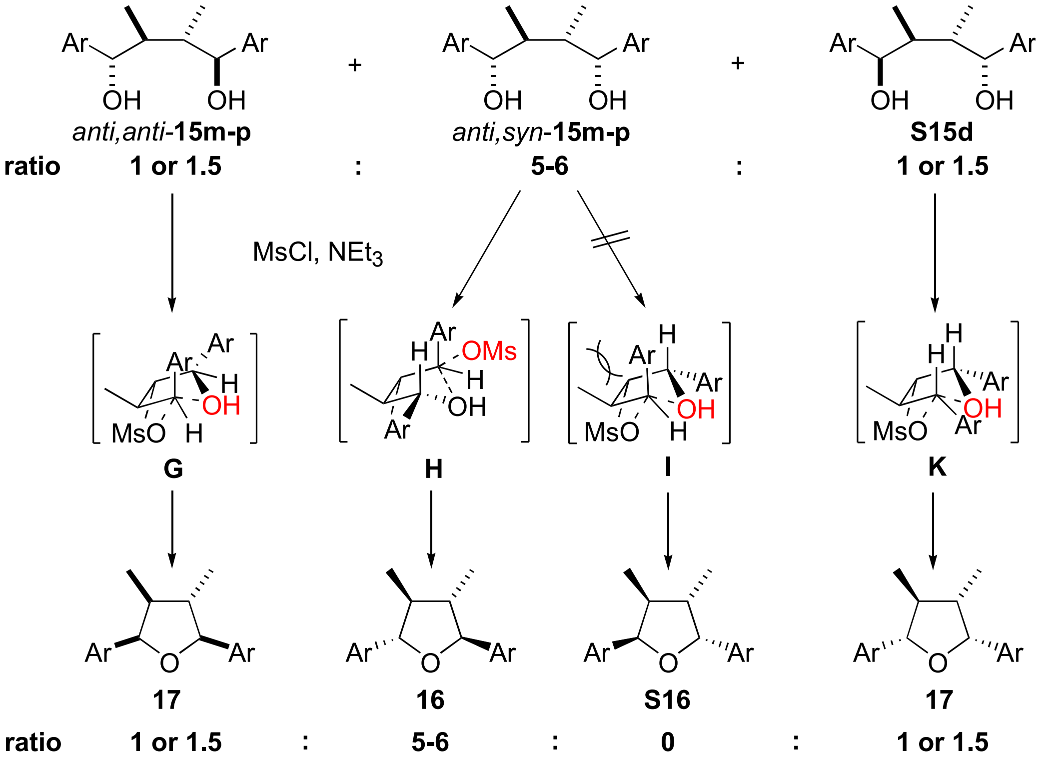


Scheme S1. $LiAlH_4$ reduction of 1,4-diketones **8m-p**.

Reduction of 1,4-diketones **8m-p** provided three diol diastereomers **15m-p** in similar 1 : 5-6 : 1.5 ratios (Scheme S1). The major isomer is clearly unsymmetrical *anti,syn*-**15m-p**. The configuration of minor anti,anti-**15m-p** and syn,syn-**15m-p** could not be established unequivocally, but since the proportion of both is similar, it is of negligible consequence for the rationalization of the results. The outcome can be explained by sequential reduction of the two carbonyl groups according to the Felkin-Anh and/or chelation control models. The minor symmetrical diols *anti,anti*-**15m-p** are most likely formed according to the Felkin-Ahn model via transition states **A** and **C**. Similarly, the formation of the other minor *syn,syn*-**15m-p** isomers can be explained by two consecutive chelation-controlled reduction steps via transition states **B** and **F**. Along the same lines the major unsymmetrical diol *anti-syn*-**15m-p** may form by consecutive reduction according to the Felkin-Anh via **A** and subsequent intramolecular chelation-controlled reduction via **D**. Alternatively the two reductive processes may also proceed initially via **B** and subsequently via **E**.

1.3 Formation of lignans from 1,4-diols

The diasteroemeric ratio of diols **15m-p** was not replicated in the formation of tetrahydrofurans **16** and **17** using $BF_3{\bullet}OEt_2$. Using the crude mixture of three diastereomers gave only two tetrahydrofuran lignans **16** and **17** with more than 8:1 selectivity. This can be explained by invoking cycloetherification via a largely stereoconvergent S_N1 mechanism (See Scheme 6).



Scheme S2. Rationalization of the formation of lignans **16** and **17** using mesyl chloride.

The diastereoselectivity of the cycloetherification is much lower using alcohol activation by mesylation and subsequent cyclization (See Scheme 4). The ratio of products is more in accord with an S_N2 mechanism (Scheme S2). Under these conditions, both *anti,anti*-**15m-p** and *syn,syn*-**15** should form the minor unsymmetrical tetrahydrofuran lignans **17a-e** via transition states **G** and **K**, respectively. Unsymmetrical *anti,syn*-**15m-p** can in principle cyclize via the diastereomeric transition states **H** and **I**. However, only formation of lignans *all-trans*-**16** were observed as the products and not a trace of the alternative lignan **S16** was detected. Similarly as in the BF_3•OEt_2-mediated cycloetherification, the *syn*-oriented hydroxy group is apparently faster mesylated than the *anti*-oriented and the subsequent cyclization can thus only proceed via transition state **H**. Moreover, transition state **I** is geometrically also much more unfavorable because of the *cis*-orientation of both of the aryl and methyl groups. Thus, only two diastereomers of tetrahydrofuran lignans **16** and **17** result with approximately 2:1 diastereoselectivity from the 1.5 : 5-6 : 1 diastereomeric mixtures of diols **15m-p** under S_N2 conditions.

2. Experimental part and analytical data

2.1 General Information

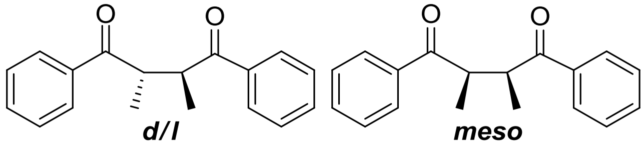
All reactions were conducted in flame or oven dried glassware under a nitrogen atmosphere. DME, THF and CH_2Cl_2 were dried following standard methods under an argon atmosphere. TLC plates POLYGRAM SIL G/UV254 (Macherey-Nagel) were used for monitoring reactions. Flash column chromatographic separations were performed at silica gel 60 (Fluka, 230-400 mesh). IR spectra were taken on a Bruker ALPHA FT-IR spectrometer as neat samples using an ATR device. ^1H and ^{13}C NMR spectra were recorded, unless otherwise noted, in $CDCl_3$ on Bruker Avance 500 and 400 at 500.0 and 400.1 MHz for ^1H NMR or 125.7 and 100.6 MHz for ^{13}C NMR, respectively. EI mass spectra were recorded on Waters GCT Premier spectrometer at 70 eV. ESI mass spectra were obtained on Thermo Fisher Scientific LCQ Fleet spectrometer, sample concentration approx. 1 μg/mL, spray voltage pos. mode: 3.3 kV. HRMS spectra were measured on Waters Q-Tof micro spectrometer, resolution: 100000. Combustion analyses were performed at the Microanalytical Laboratories of the IOCB ASCR Prague.

2.2 Tandem nucleophilic addition/redox isomerization/oxidative coupling

General procedure using PhLi: Phenyllithium **1a** (0.72 mL, 1.3 mmol, 1.8M in dibutyl ether) was added dropwise to α,β-unsaturated aldehyde **2** (1.3 mmol) in DME (8 mL) at –5 °C under an argon atmosphere. After stirring for 15 min, (*p*-cymene)ruthenium dichloride dimer (16 mg, 0.026 mmol, 2 mol%) was added. The flask was removed from the cooling bath, $P(OMe)_3$ (0.003 mL, 0.026 mmol, 2 mol%) was added dropwise and the mixture was stirred at room temperature for 5 min. The homogeneous solution was heated at a temperature of 86 °C in an oil bath until conversion of the allylic alkoxide **3** to ketone enolate **4** was complete as monitored by TLC or GC, typically 10-15 min. The reaction mixture was cooled to –78 °C and ferrocenium hexafluorophosphate **7** (331 mg, 1 mmol) was added in small portions with vigorous stirring. Further **7** (ca. 165 mg, 0.5 mmol) was added until the reaction mixture became blue-green. Stirring was continued for 20 min. The reaction was quenched by a few drops of water, filtered through a pad of silica gel, which was washed thoroughly with diethyl ether. The filtrate was evaporated in vacuum, the crude product was preadsorbed on silica gel and purified by flash column chromatography (hexane/EtOAc 100:1, gradient to 1:1). Ferrocene eluted first followed by some biphenyl, present in PhLi, phenones and products **8**, respectively.

General procedure using lithium-halogen exchange: *tert*-BuLi (1.53 mL, 2.6 mmol, 1.7M in pentane) was added to a stirred solution of the aryl halide (1.3 mmol) in DME (8 mL) at –78 °C under an argon atmosphere. After 35 min, the α,β-unsaturated aldehyde **2** (1.3 mmol) was added at once. After stirring at the same temperature for 15 min, (*p*-cymene)ruthenium dichloride dimer (16 mg, 0.026 mmol, 2 mol%) was added. The flask was removed from the cooling bath, $P(OMe)_3$ (0.003 mL, 0.026 mmol, 2 mol%) was added dropwise and the mixture was stirred at room temperature for 5 min. The homogeneous solution was heated at a temperature of 86 °C in an oil bath until conversion of the allylic alkoxide **3** to ketone enolate **4** was complete as monitored by TLC or GC, typically 10-20 min. The reaction mixture was cooled to –78 °C and ferrocenium hexafluorophosphate **7** (331 mg, 1 mmol) was added in small portions with vigorous stirring. Further **7** (ca. 165 mg, 0.5 mmol) was added until the reaction mixture became blue-green. Stirring was continued for 20 min. The reaction was quenched by a few drops of water, filtered through a pad of silica gel, which was washed thoroughly with diethyl ether. The filtrate was evaporated in vacuum, the crude product was preadsorbed on silica gel and purified by flash column chromatography (hexane/EtOAc 100:1, gradient to 1:1). Ferrocene eluted first followed by phenones and products **8**, respectively.

(2*S**,3*S**)-2,3-Dimethyl-1,4-diphenylbutane-1,4-dione and (2*R**,3*S**)-2,3-dimethyl-1,4-diphenylbutane-1,4-dione (8a):

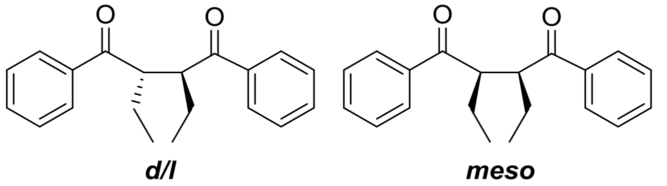


Separable 6.5:1 mixture of *d/l*:*meso* diastereomers as a colorless viscous liquid. Yield 108 mg (62%). - $R_f = 0.39$, hexane/EtOAc 9:1. - IR: ν = 3069 (w); 2983 (w); 2944 (w); 2887 (w); 1679 (s); 1601 (w); 1584 (w); 1452 (m); 1378 (w); 1334 (w); 1284 (w); 1211 (s); 1184 (w); 1163 (w); 1108 (w); 1004 (w); 970 (s); 849 (w); 795 (w); 774 (w); 738 (s); 702 (w); 660 (m); 632 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 289 ($M+Na^+$, 100), 267 ($M+H^+$, 39). - HRMS (+ESI) Calcd. for $C_{18}H_{19}O_2^+$: 267.1379; found: 267.1379.

***d/l*-8a:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 8.6, 1.6 Hz, 4H, *ortho*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$); 7.56-7.52 (m, 2H, *para*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$); 7.48-7.43 (m, 4H, *meta*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$); 4.02-3.93 (m, 2H, C$\underline{\mathrm{H}}CH_3$); 1.29 (d, *J* = 6.9 Hz, 6H, C$\underline{\mathrm{H}}_3$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.3 (s, Ar$\underline{\mathrm{C}}$=O); 136.2 (s, $\underline{\mathrm{C}}_{\mathrm{ArCO}}$); 133.0 (d, *para*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$); 128.7 (d, *ortho*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$); 128.5 (d, *meta*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$); 43.7 (d, $\underline{\mathrm{C}}$HCH$_3$); 15.6 (q, CH$\underline{\mathrm{C}}$H$_3$).

***meso*-8a:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 8.4, 1.3 Hz, 4H, *ortho*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$); 7.62-7.57 (m, 2H, *para*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$); 7.52-7.48 (m, 4H, *meta*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$); 4.09-4.01 (m, 2H, C$\underline{\mathrm{H}}CH_3$); 1.14 (d, *J* = 6.5 Hz, 6H, C$\underline{\mathrm{H}}_3$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.9 (s, Ar$\underline{\mathrm{C}}$=O); 137.0 (s, $\underline{\mathrm{C}}_{\mathrm{ArCO}}$); 133.5 (d, *para*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$); 128.9 (d, *ortho*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$); 128.6 (d, *meta*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$); 43.4 (d, $\underline{\mathrm{C}}$HCH$_3$); 17.6 (q, CH$\underline{\mathrm{C}}$H$_3$).

(2*S**,3*S**)-2,3-Diethyl-1,4-diphenylbutane-1,4-dione and (2*R**,3*S**)-2,3-diethyl-1,4-diphenylbutane-1,4-dione (8b):[1]

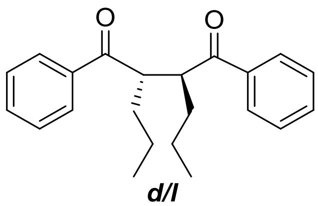


Inseparable 6:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 180 mg (94%). - $R_f = 0.46$, hexane/EtOAc 9:1. - IR: ν = 3070 (w); 2975 (w); 2944 (w); 2886 (w); 1677 (s); 1601 (w); 1584 (w); 1463 (w); 1451 (m); 1390 (w); 1355 (w); 1258 (w); 1233 (w); 1207 (m); 1183 (w); 1162 (w); 1118 (w); 1076 (w); 1005 (m); 985 (w); 933 (w); 832 (w); 778 (w); 701 (s); 659 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 611 (2M+Na$^+$, 24), 317 (M+Na$^+$, 100), 295 (M+H$^+$, 28). - HRMS (+ESI) Calcd. for $C_{20}H_{22}O_2Na^+$: 317.1512; found: 317.1512.

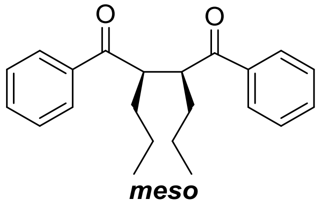
***d/l*- and *meso*-8b:** m.p. 72-73 °C (mixture). - ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 8.3, 1.2 Hz, 4H, *ortho*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}{}^{\#}$); 7.97 (dd, *J* = 8.3, 1.2 Hz, 4H, *ortho*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$); 7.63-7.58 (m, 2H, *para*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}{}^{\#}$); 7.56-7.48 (m, 6H, *para*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$, *meta*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}{}^{\#}$); 7.47-7.42 (m, 4H, *meta*-C$\underline{\mathrm{H}}_{\mathrm{ArCO}}$); 4.10-4.05 (m, 2H, C$\underline{\mathrm{H}}CH_2$); 4.05-4.00 (m, 2H, C$\underline{\mathrm{H}}CH_2{}^{\#}$); 1.90-1.77 (m, 4H, CHC$\underline{\mathrm{H}}_2CH_3$); 1.73-1.63 (m, 2H, CHC$\underline{\mathrm{H}}_2CH_3{}^{\#}$); 1.53-1.43 (m, 2H, CHC$\underline{\mathrm{H}}_2CH_3{}^{\#}$); 0.83 (t, *J* = 7.5 Hz, 6H, CH$_2$C$\underline{\mathrm{H}}_3$); 0.70 (t, *J* = 7.3 Hz, 6H, CH$_2$C$\underline{\mathrm{H}}_3{}^{\#}$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.5 (s, Ar$\underline{\mathrm{C}}$=O$^{\#}$); 204.4 (s, Ar$\underline{\mathrm{C}}$=O); 138.7 (s, $\underline{\mathrm{C}}_{\mathrm{ArCO}}{}^{\#}$); 137.7 (s, $\underline{\mathrm{C}}_{\mathrm{ArCO}}$); 133.5 (d, *para*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}{}^{\#}$); 132.9 (d, *para*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$); 128.9 (d, *ortho*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}{}^{\#}$); 128.6 (d, *ortho*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$); 128.5 (d, *meta*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}$, *meta*-$\underline{\mathrm{C}}H_{\mathrm{Ar}}{}^{\#}$);

49.2 (d, $\underline{C}HCH_2CH_3^{\#}$); 46.8 (d, $\underline{C}HCH_2CH_3$); 25.6 (t, $CH\underline{C}H_2CH_3^{\#}$); 22.3 (t, $CH\underline{C}H_2CH_3$); 11.9 (q, $CHCH_2\underline{C}H_3^{\#}$); 10.5 (q, $CHCH_2\underline{C}H_3$). $^{\#}$ Resonances of **_meso_-8b**.

(2S*,3S*)-1,4-Diphenyl-2,3-dipropylbutane-1,4-dione and (2R*,3S*)-1,4-diphenyl-2,3-dipropylbutane-1,4-dione (8c):



_d/l_



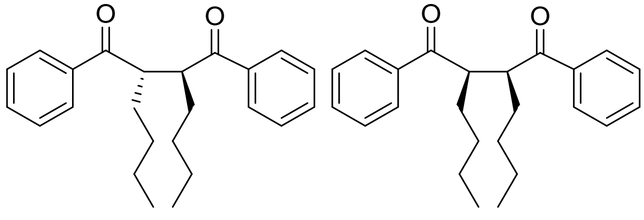
meso

Inseparable 7:1 mixture of *d/l*:*meso* diastereomers as a viscous liquid. Yield 145 mg (69%). - R_f = 0.35, hexane/EtOAc 19:1. - IR: ν = 2959 (w); 2932 (w); 2873 (w); 1672 (m); 1596 (w); 1579 (w); 1447 (w); 1379 (w); 1344 (w); 1243 (w); 1211 (w); 1179 (w); 1002 (w); 987 (w); 907 (m); 728 (s); 706 (s); 686 (w); 647 (m) cm^{-1}. - MS (+ESI) *m/z* (%): 667 (2M+Na$^+$, 30), 345 (M+Na$^+$, 100), 323 (M+H$^+$, 72). - HRMS (+ESI) Calcd. for $C_{22}H_{26}O_2Na^+$: 345.1825; found: 345.1825.

_d/l_- and _meso_-8c: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07 (dd, *J* = 8.5, 1.5 Hz, 4H, *ortho*-$C\underline{H}_{ArCO}{}^{\#}$); 7.95 (dd, *J* = 8.3, 1.5 Hz, 4H, *ortho*-$C\underline{H}_{ArCO}$); 7.62-7.58 (m, 2H, *para*-$C\underline{H}_{ArCO}{}^{\#}$); 7.55-7.51 (m, 2H, *para*-$C\underline{H}_{ArCO}$); 7.46-7.41 (m, 8H, *meta*-$C\underline{H}_{ArCO}$, *meta*-$C\underline{H}_{ArCO}{}^{\#}$); 4.08-4.01 (m, 4H, $C\underline{H}CH_2$, $C\underline{H}CH_2{}^{\#}$); 1.81-1.65 (m, 8H, $CHC\underline{H}_2$, $CHC\underline{H}_2{}^{\#}$); 1.34-1.21 (m, 4H, $CH_2C\underline{H}_2CH_3$, $CH_2C\underline{H}_2CH_3{}^{\#}$); 1.19-1.06 (m, 4H, $CH_2C\underline{H}_2CH_3$, $CH_2C\underline{H}_2CH_3{}^{\#}$); 0.84 (t, *J* = 7.3 Hz, 6H, $CH_2C\underline{H}_3$); 0.67 (t, *J* = 7.3 Hz, 6H, $CH_2C\underline{H}_3{}^{\#}$). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 204.64 (s, $Ar\underline{C}{=}O$); 204.61 (s, $Ar\underline{C}{=}O^{\#}$); 138.8 (s, $\underline{C}_{ArCO}{}^{\#}$); 137.9 (s, $\underline{C}_{ArCO}$); 133.4 (d, *para*-$\underline{C}H_{Ar}{}^{\#}$); 132.9 (d, *para*-$\underline{C}H_{Ar}$); 128.9 (d, *ortho*-$\underline{C}H_{Ar}{}^{\#}$); 128.6 (d, *ortho*-$\underline{C}H_{Ar}$); 128.5 (d, *meta*-$\underline{C}H_{Ar}$, *meta*-$\underline{C}H_{Ar}{}^{\#}$); 48.3 (d, $\underline{C}HCH_2CH_2{}^{\#}$); 47.1 (d, $\underline{C}HCH_2CH_2$); 34.9 (t, $CH\underline{C}H_2CH_2{}^{\#}$); 32.1 (t, $CH\underline{C}H_2CH_2$); 20.9 (t, $CH_2\underline{C}H_2CH_3{}^{\#}$); 19.9 (t, $CH_2\underline{C}H_2CH_3$); 14.5 (q, $CH_2CH_2\underline{C}H_3$); 14.2 (q, $CH_2CH_2\underline{C}H_3{}^{\#}$).

$^{\#}$ Resonances of **_meso_-8c**.

(2*S**,3*S**)-2,3-Dibutyl-1,4-diphenylbutane-1,4-dione and (2*R**,3*S**)-2,3-dibutyl-1,4-diphenylbutane-1,4-dione (8d):



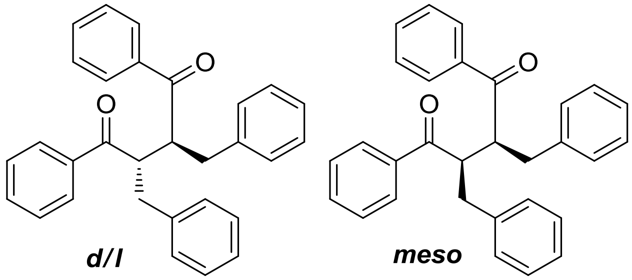
d/l ***meso***

Partially separable 7:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 139 mg (61%). - $R_f = 0.65$, hexane/EtOAc 5:1. - IR: ν = 2965 (w); 2940 (w); 2869 (w); 1679 (s); 1601 (w); 1584 (w); 1452 (m); 1382 (w); 1285 (w); 1210 (m); 1183 (w); 1162 (w); 1078 (w); 1027 (w); 1005 (w); 938 (w); 846 (w); 791 (w); 756 (w); 707 (s); 689 (s); 660 (w); 619 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 723 ($2M+Na^+$, 5), 373 ($M+Na^+$, 100), 351 ($M+H^+$, 47). - HRMS (+ESI) Calcd. for $C_{24}H_{30}O_2Na^+$: 373.2138; found: 373.2138.

***d/l*-8d:** ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.5 Hz, 4H, *ortho*-$C\underline{H}_{ArCO}$); 7.55-7.51 (m, 2H, *para*-$C\underline{H}_{ArCO}$); 7.45-7.42 (m, 4H, *meta*-$C\underline{H}_{ArCO}$); 4.07-4.01 (m, 2H, $C\underline{H}CH_2$); 1.83-1.72 (m, 4H, $CHC\underline{H_2}$); 1.29-1.18 (m, 6H, $CHCH_2C\underline{H_2}C\underline{H_2}CH_3$); 1.16-1.05 (m, 2H, $CHCH_2CH_2C\underline{H_2}CH_3$); 0.81 (t, *J* = 7.0 Hz, 6H, $CH_2C\underline{H_3}$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.6 (s, $Ar\underline{C}{=}O$); 137.6 (s, $\underline{C}_{ArCO}$); 132.9 (d, *para*-$\underline{C}H_{Ar}$); 128.6 (d, *ortho*-$\underline{C}H_{Ar}$); 128.50 (d, *meta*-$\underline{C}H_{Ar}$); 46.7 (d, $\underline{C}HCH_2CH_2$); 29.3 (t, $CH\underline{C}H_2CH_2$); 28.5 (t, $CHCH_2\underline{C}H_2$); 23.1 (t, $CH_2\underline{C}H_2CH_3$); 13.9 (q, $CH_2CH_2\underline{C}H_3$).

***meso*-8d:** m.p. 96-97 °C. - ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.5 Hz, 4H, *ortho*-$C\underline{H}_{ArCO}$); 7.62-7.59 (m, 2H, *para*-$C\underline{H}_{ArCO}$); 7.53-7.49 (m, 4H, *meta*-$C\underline{H}_{ArCO}$); 4.06-3.99 (m, 2H, $C\underline{H}CH_2$); 1.73-1.61 (m, 2H, $CHC\underline{H_2}$); 1.42-1.19 (m, 2H, $CHC\underline{H_2}$); 1.12-0.96 (m, 8H, $CHCH_2C\underline{H_2}C\underline{H_2}CH_3$); 0.65 (t, *J* = 7.0 Hz, 6H, $CH_2C\underline{H_3}$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.7 (s, $Ar\underline{C}{=}O$); 138.7 (s, $\underline{C}_{ArCO}$); 133.4 (d, *para*-$\underline{C}H_{Ar}$); 128.9 (d, *ortho*-$\underline{C}H_{Ar}$); 128.54 (d, *meta*-$\underline{C}H_{Ar}$); 48.4 (d, $\underline{C}HCH_2CH_2$); 32.4 (t, $CH\underline{C}H_2CH_2$); 29.7 (t, $CHCH_2\underline{C}H_2$); 22.8 (t, $CH_2\underline{C}H_2CH_3$); 13.8 (q, $CH_2CH_2\underline{C}H_3$).

(2*S,3*S**)-2,3-Dibenzyl-1,4-diphenylbutane-1,4-dione and (2*R**,3*S**)-2,3-dibenzyl-1,4-diphenylbutane-1,4-dione (8e):**[2]

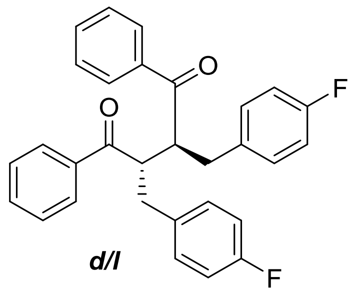


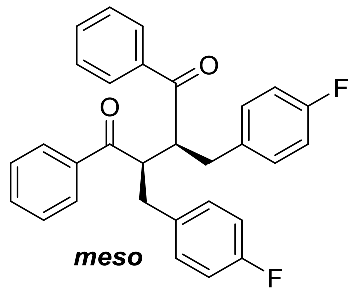
Separable 7:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 177 mg (65%). - $R_f = 0.31$, hexane/EtOAc 7:1. - IR: ν = 3071 (w); 3036 (w); 2934 (w); 1676 (s); 1601 (w); 1585 (w); 1499 (w); 1451 (m); 1339 (w); 1235 (m); 1208 (w); 1183 (w); 1079 (w); 1032 (w); 1006 (w); 972 (w); 939 (w); 749 (s); 698 (s); 687 (s); 635 (w); 600 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 859 ($2M+Na^+$, 32), 441 ($M+Na^+$, 100), 419 ($M+H^+$, 54). - HRMS (+ESI) Calcd. for $C_{30}H_{26}O_2Na^+$: 441.1825; found: 441.1824.

***d/l*-8e:** m.p. 124-126 °C. - ^1H NMR (400 MHz, $CDCl_3$): δ 7.66-7.62 (m, 4H, *ortho*-$C\underline{H}_{ArCO}$); 7.39-7.35 (m, 2H, *para*-$C\underline{H}_{ArCO}$); 7.26-7.22 (m, 4H, *meta*-$C\underline{H}_{ArCO}$); 7.17-7.12 (m, 4H, $C\underline{H}_{Ar}$); 7.10-7.05 (m, 6H, $C\underline{H}_{Ar}$); 4.23-4.19 (m, 2H, $PhCOC\underline{H}CH_2$); 3.23-3.12 (m, 4H, $PhCOCHC\underline{H_2}$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.3 (s, $Ph\underline{C}=O$); 138.6 (s, $\underline{C}_{ArCO}$); 137.5 (s, $\underline{C}_{Ar}$); 132.8 (d, *para*-$\underline{C}H_{ArCO}$); 129.1 (d, $\underline{C}H_{Ar}$); 128.38 (d, $\underline{C}H_{Ar}$); 128.3 (d, $2x\underline{C}H_{Ar}$); 126.4 (d, $\underline{C}H_{Ar}$); 50.1 (d, $PhCO\underline{C}HCH_2$); 35.7 (t, $PhCOCH\underline{C}H_2$).

***meso*-8e:** ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, J = 8.5, 1.3 Hz, 4H, *ortho*-$C\underline{H}_{ArCO}$); 7.48-7.44 (m, 2H, *para*-$C\underline{H}_{ArCO}$); 7.34-7.30 (m, 4H, *meta*-$C\underline{H}_{ArCO}$); 7.09-7.04 (m, 5H, $C\underline{H}_{Ar}$); 7.03-6.99 (m, 5H, $C\underline{H}_{Ar}$); 4.35-4.28 (m, 2H, $PhCOC\underline{H}CH_2$); 2.95 (dd, J = 13.2, 9.9 Hz, 2H, $PhCOCHC\underline{H_2}$); 2.81 (dd, J = 13.2, 3.3 Hz, 2H, $PhCOCHC\underline{H_2}$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.7 (s, $Ph\underline{C}=O$); 138.50 (s, $\underline{C}_{ArCO}$); 138.46 (s, $\underline{C}_{Ar}$); 133.2 (d, *para*-$\underline{C}H_{ArCO}$); 129.2 (d, $\underline{C}H_{Ar}$); 128.5 (d, $\underline{C}H_{Ar}$); 128.42 (d, $\underline{C}H_{Ar}$); 128.36 (d, $\underline{C}H_{Ar}$); 126.5 (d, $\underline{C}H_{Ar}$); 50.7 (d, $PhCO\underline{C}HCH_2$); 38.1 (t, $PhCOCH\underline{C}H_2$).

(2*S,3*S**)-2,3-Bis(4-fluorobenzyl)-1,4-diphenylbutane-1,4-dione and (2*R**,3*S**)-2,3-bis(4-fluorobenzyl)-1,4-diphenylbutane-1,4-dione (8f):**



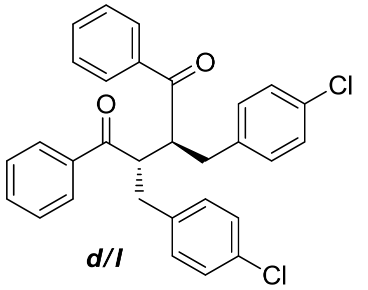


Separable 7:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 154 mg (52%). - R_f = 0.47, hexane/EtOAc 5:1. - IR: ν = 3073 (w); 2939 (w); 1679 (s); 1603 (m); 1585 (w); 1514 (s); 1452 (m); 1377 (w); 1359 (w); 1225 (s); 1162 (m); 1099 (w); 1017 (w); 1006 (w); 919 (w); 882 (m); 716 (m); 689 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 931 (2M+Na^+, 4), 477 (M+Na^+, 100), 455 (M+H^+, 7). - HRMS (+ESI) Calcd. for $C_{30}H_{24}F_2O_2Na^+$: 477.1636; found: 477.1636.

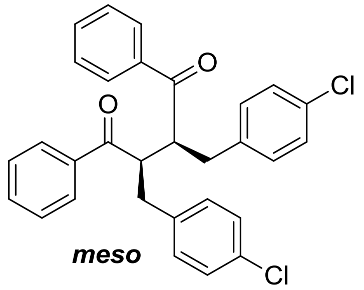
***d/l*-8f:** m.p. 135-136 °C. - ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.5 Hz, 4H, *ortho*-C$\underline{H}_{ArCO}$); 7.46 (t, *J* = 7.4 Hz, 2H, *para*-C$\underline{H}_{ArCO}$); 7.31 (t, *J* = 7.7 Hz, 4H, *meta*-C$\underline{H}_{ArCO}$); 7.00 (dd, *J* = 8.4, 5.5 Hz, 4H, *ortho*-C$\underline{H}_{Ar\text{-}F}$); 6.82 (t, *J* = 8.7 Hz, 4H, *meta*-C$\underline{H}_{Ar\text{-}F}$); 4.18-4.12 (m, 2H, PhCOC$\underline{H}$CH_2); 3.21-3.11 (m, 4H, PhCOCHC$\underline{H}_2$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.1 (s, Ph$\underline{C}$=O); 161.60 (s (d, J_{FC} = 244.6 Hz), *para*-$\underline{C}_{Ar\text{-}F}$); 137.4 (s, $\underline{C}_{ArCO}$); 134.2 (s (d, J_{FC} = 3.3 Hz), $\underline{C}_{Ar\text{-}F}$); 133.1 (d, *para*-C$\underline{H}_{ArCO}$); 130.6 (d (d, J_{FC} = 7.9 Hz), *ortho*-$\underline{C}H_{Ar\text{-}F}$); 128.5 (d, *ortho*-$CH_{ArCO}$); 128.3 (d, *meta*-$CH_{ArCO}$); 115.3 (d (d, J_{FC} = 21.3 Hz), *meta*-$\underline{C}H_{Ar\text{-}F}$); 50.0 (d, PhCO$\underline{C}HCH_2$); 34.7 (t, PhCOCH$\underline{C}H_2$).

***meso*-8f:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.5 Hz, 4H, *ortho*-C$\underline{H}_{ArCO}$); 7.49 (t, *J* = 7.4 Hz, 2H, *para*-C$\underline{H}_{ArCO}$); 7.35 (t, *J* = 7.7 Hz, 4H, *meta*-C$\underline{H}_{ArCO}$); 6.92 (dd, *J* = 8.4, 5.5 Hz, 4H, *ortho*-C$\underline{H}_{Ar\text{-}F}$); 6.74 (t, *J* = 8.7 Hz, 4H, *meta*-C$\underline{H}_{Ar\text{-}F}$); 4.38-4.18 (m, 2H, PhCOC$\underline{H}$CH_2); 2.90 (dd, *J* = 13.3, 9.8 Hz, 2H, PhCOCHC$\underline{H}_2$); 2.75 (dd, *J* = 13.3, 2.4 Hz, 2H, PhCOCHC$\underline{H}_2$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.6 (s, Ph$\underline{C}$=O); 161.58 (s (d, J_{FC} = 244.7 Hz), *para*-$\underline{C}_{Ar\text{-}F}$); 138.2 (s, $\underline{C}_{ArCO}$); 134.0 (s (d, J_{FC} = 3.2 Hz), $\underline{C}_{Ar\text{-}F}$); 133.5 (d, *para*-C$\underline{H}_{ArCO}$); 130.7 (d (d, J_{FC} = 7.9 Hz), *ortho*-$\underline{C}H_{Ar\text{-}F}$); 128.7 (d, *ortho*-C$\underline{H}_{ArCO}$); 128.4 (d, *meta*-C$\underline{H}_{ArCO}$); 115.2 (d (d, J_{FC} = 21.3 Hz), *meta*-$\underline{C}H_{Ar\text{-}F}$); 50.6 (d, PhCO$\underline{C}HCH_2$); 37.4 (t, PhCOCH$\underline{C}H_2$).

(2*S**,3*S**)-2,3-Bis(4-chlorobenzyl)-1,4-diphenylbutane-1,4-dione and (2*R**,3*S**)-2,3-bis(4-chlorobenzyl)-1,4-diphenylbutane-1,4-dione (8g):



d/l



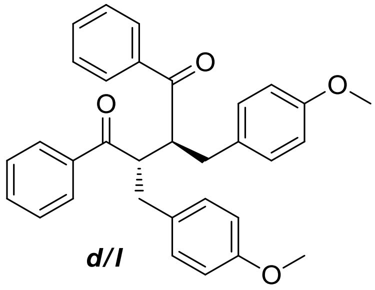
meso

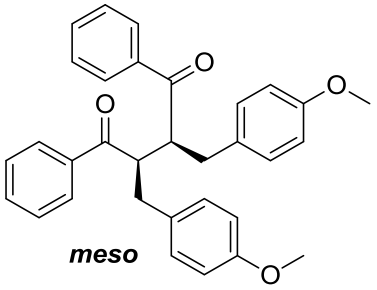
Partially separable 7:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 235 mg (74%). - $R_f = 0.54$, hexane/EtOAc 5:1. - IR: ν = 3071 (w); 2934 (w); 2860 (w); 1678 (s); 1601 (w); 1584 (w); 1514 (s); 1496 (s); 1451 (m); 1413 (w); 1357 (w); 1271 (w); 1235 (m); 1211 (m); 1183 (w); 1096 (m); 1018 (w); 973 (w); 914 (w); 835 (w); 801 (m); 733 (m); 707 (s); 688 (s); 669 (w) $\mathrm{cm^{-1}}$. - MS (+ESI) *m/z* (%): 513/511/509 ($\mathrm{M+Na^+}$, 13/68/100), 489/487 ($\mathrm{M+H^+}$, 20/28). - HRMS (+ESI) Calcd. for $\mathrm{C_{30}H_{25}{}^{35}Cl_2O_2{}^+}$: 487.1227; found: 487.1227.

***d/l*-8g:** m.p. 143-144 °C. - ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.65 (dd, *J* = 8.3, 1.1 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 7.50-7.46 (m, 2H, *para*-$\mathrm{C\underline{H}_{ArCO}}$); 7.35-7.31 (m, 4H, *meta*-$\mathrm{C\underline{H}_{ArCO}}$); 7.11 (d, *J* = 8.4 Hz, 4H, *meta*-$\mathrm{C\underline{H}_{Ar\text{-}Cl}}$); 6.97 (d, *J* = 8.4 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{Ar\text{-}Cl}}$); 4.16-4.10 (m, 2H, $\mathrm{PhCOC\underline{H}CH_2}$); 3.19-3.09 (m, 4H, $\mathrm{PhCOCHC\underline{H}_2}$). - ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 202.6 (s, $\mathrm{Ph\underline{C}{=}O}$); 137.2 (s, $\mathrm{\underline{C}_{ArCO}}$); 137.1 (s, $\mathrm{\underline{C}_{Ar\text{-}Cl}}$); 133.2 (d, *para*-$\mathrm{\underline{C}H_{ArCO}}$); 132.40 (s, *para*-$\mathrm{\underline{C}_{Ar\text{-}Cl}}$); 130.5 (d, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 128.6 (d, *meta*-$\mathrm{C\underline{H}_{ArCO}}$ and *ortho*-$\mathrm{C\underline{H}_{Ar\text{-}Cl}}$); 128.4 (d, *meta*-$\mathrm{C\underline{H}_{Ar\text{-}Cl}}$); 49.9 (d, $\mathrm{PhCO\underline{C}HCH_2}$); 34.4 (t, $\mathrm{PhCOCH\underline{C}H_2}$).

***meso*-8g:** ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.72 (dd, *J* = 8.3, 1.3 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 7.53-7.49 (t, *J* = 7.4 Hz, 2H, *para*-$\mathrm{C\underline{H}_{ArCO}}$); 7.39-7.33 (m, 4H, *meta*-$\mathrm{C\underline{H}_{ArCO}}$); 7.02 (d, *J* = 8.4 Hz, 4H, *meta*-$\mathrm{C\underline{H}_{Ar\text{-}Cl}}$); 6.89 (d, *J* = 8.4 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{Ar\text{-}Cl}}$); 4.30-4.23 (m, 2H, $\mathrm{PhCOC\underline{H}CH_2}$); 2.91 (dd, *J* = 13.3, 9.8 Hz, 2H, $\mathrm{PhCOCHC\underline{H}_2}$); 2.74 (dd, *J* = 13.3, 2.7 Hz, 2H, $\mathrm{PhCOCHC\underline{H}_2}$). - ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 203.3 (s, $\mathrm{Ph\underline{C}{=}O}$); 138.1 (s, $\mathrm{\underline{C}_{ArCO}}$); 136.8 (s, $\mathrm{\underline{C}_{Ar\text{-}Cl}}$); 133.6 (d, *para*-$\mathrm{\underline{C}H_{ArCO}}$); 132.41 (s, *para*-$\mathrm{\underline{C}_{Ar\text{-}Cl}}$); 130.6 (d, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 128.7 (d, *meta*-$\mathrm{C\underline{H}_{ArCO}}$); 128.5 (d, *ortho*-$\mathrm{C\underline{H}_{Ar\text{-}Cl}}$); 128.4 (d, *meta*-$\mathrm{C\underline{H}_{Ar\text{-}Cl}}$); 50.3 (d, $\mathrm{PhCO\underline{C}HCH_2}$); 37.5 (t, $\mathrm{PhCOCH\underline{C}H_2}$).

(2*S,3*S**)-2,3-Bis(4-methoxybenzyl)-1,4-diphenylbutane-1,4-dione and (2*R**,3*S**)-2,3-bis(4-methoxybenzyl)-1,4-diphenylbutane-1,4-dione (8h):**


d/l

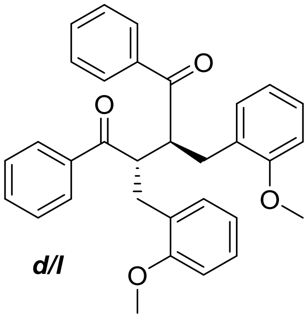

meso

Separable 4:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 193 mg (62%). - R_f = 0.28, hexane/EtOAc 5:1. - IR: ν = 3014 (w); 2942 (w); 2844 (w); 1676 (s); 1616 (w); 1601 (w); 1585 (w); 1515 (s); 1451 (m); 1355 (w); 1304 (w); 1249 (s); 1181 (s); 1111 (w); 1037 (w); 1006 (m); 943 (w); 919 (w); 824 (w); 757 (w); 711 (m); 689 (m); 635 (w) $\mathrm{cm^{-1}}$. - MS (+ESI) *m/z* (%): 979 ($\mathrm{2M+Na^+}$, 14), 501 ($\mathrm{M+Na^+}$, 100), 479 ($\mathrm{M+H^+}$, 24). - HRMS (+ESI) Calcd. for $\mathrm{C_{32}H_{31}O_4^+}$: 479.2217; found: 479.2219.

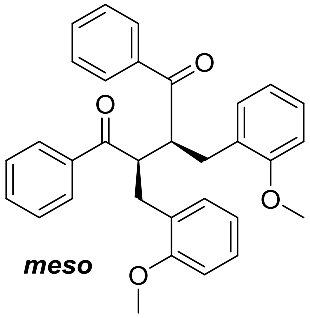
***d/l*-8h:** m.p. 97-98 °C. - ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.65 (dd, *J* = 8.3, 1.2 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 7.46-7.42 (m, 2H, *para*-$\mathrm{C\underline{H}_{ArCO}}$); 7.33-7.27 (m, 4H, *meta*-$\mathrm{C\underline{H}_{ArCO}}$); 6.96 (d, *J* = 8.6 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$); 6.68 (d, *J* = 8.6 Hz, 4H, *meta*-$\mathrm{C\underline{H}_{Ar}}$); 4.18-4.11 (m, 2H, $\mathrm{PhCOC\underline{H}CH_2}$); 3.70 (s, 6H, $\mathrm{OCH_3}$); 3.18 (m, 4H, $\mathrm{PhCOCHC\underline{H}_2}$). - ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 203.7 (s, $\mathrm{Ph\underline{C}{=}O}$); 158.3 (s, $\mathrm{\underline{C}_{ArOMe}}$); 137.7 (s, $\mathrm{\underline{C}_{ArCO}}$); 132.8 (d, *para*-$\mathrm{\underline{C}H_{ArCO}}$); 130.62 (s, $\mathrm{\underline{C}_{Ar}}$); 130.25 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 128.44 (d, *ortho*-$\mathrm{\underline{C}H_{ArCO}}$ and *meta*-$\mathrm{\underline{C}H_{ArCO}}$); 113.9 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}$); 55.4 (q, $\mathrm{O\underline{C}H_3}$); 50.2 (d, $\mathrm{PhCO\underline{C}HCH_2}$); 34.9 (t, $\mathrm{PhCOCH\underline{C}H_2}$).

***meso*-8h:** ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.71 (dd, *J* = 8.4, 1.3 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 7.49-7.45 (m, 2H, *para*-$\mathrm{C\underline{H}_{ArCO}}$); 7.35-7.32 (m, 4H, *meta*-$\mathrm{C\underline{H}_{ArCO}}$); 6.89 (d, *J* = 8.6 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$); 6.60 (d, *J* = 8.6 Hz, 4H, *meta*-$\mathrm{C\underline{H}_{Ar}}$); 4.30-4.23 (m, 2H, $\mathrm{PhCOC\underline{H}CH_2}$); 3.66 (s, 6H, $\mathrm{OCH_3}$); 2.89 (dd, *J* = 13.4, 9.8 Hz, 2H, $\mathrm{PhCOCHC\underline{H}_2}$); 2.74 (dd, *J* = 13.4, 3.2 Hz, 2H, $\mathrm{PhCOCHC\underline{H}_2}$). - ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 203.8 (s, $\mathrm{Ph\underline{C}{=}O}$); 158.2 (s, $\mathrm{\underline{C}_{ArOMe}}$); 138.5 (s, $\mathrm{\underline{C}_{ArCO}}$); 133.1 (d, *para*-$\mathrm{\underline{C}H_{ArCO}}$); 130.57 (s, $\mathrm{\underline{C}_{Ar}}$); 130.24 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 128.5 (d, *ortho*-$\mathrm{\underline{C}H_{ArCO}}$); 128.45 (d, *meta*-$\mathrm{\underline{C}H_{ArCO}}$); 113.8 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}$); 55.3 (q, $\mathrm{O\underline{C}H_3}$); 50.7 (d, $\mathrm{PhCO\underline{C}HCH_2}$); 37.2 (t, $\mathrm{PhCOCH\underline{C}H_2}$).

(2*S,3*S**)-2,3-Bis(2-methoxybenzyl)-1,4-diphenylbutane-1,4-dione and (2*R**,3*S**)-2,3-bis(2-methoxybenzyl)-1,4-diphenylbutane-1,4-dione (8i):**



d/l

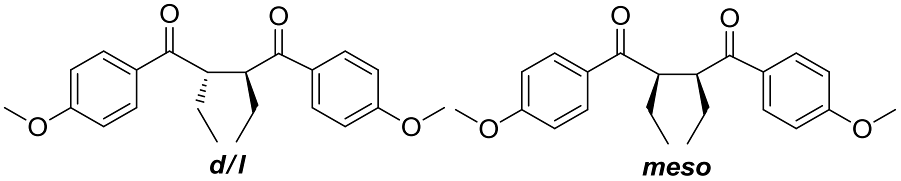


meso

Inseparable 2.7:1 mixture of *d/l*:*meso* diastereomers as a colorless viscous liquid. Yield 159 mg (51%). - R_f = 0.25, hexane/EtOAc 5:1. - IR: ν = 3072 (w); 2946 (w); 2844 (w); 1677 (w); 1603 (w); 1497 (s); 1468 (m); 1452 (m); 1340 (w); 1292 (w); 1245 (s); 1214 (m); 1182 (m); 1114 (m); 1054 (w); 1031 (w); 941 (w); 913 (w); 848 (w); 753 (s); 731 (s); 703 (s); 689 (m); 618 (w) $\mathrm{cm^{-1}}$. - MS (+ESI) *m/z* (%): 979 ($\mathrm{2M+Na^+}$, 13), 501 ($\mathrm{M+Na^+}$, 100), 479 ($\mathrm{M+H^+}$, 34). - HRMS (+ESI) Calcd. for $\mathrm{C_{32}H_{30}O_4Na^+}$: 501.2036; found: 501.2036.

***d/l*- and *meso*-8i:** ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.72 (dd, *J* = 8.4, 1.2 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}^{\#}$); 7.63 (dd, *J* = 8.4, 1.2 Hz, 4H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 7.46-7.42 (m, 2H, *para*-$\mathrm{C\underline{H}_{ArCO}}^{\#}$); 7.40-7.35 (m, 2H, *para*-$\mathrm{C\underline{H}_{ArCO}}$); 7.34-7.28 (m, 4H, *meta*-$\mathrm{C\underline{H}_{ArCO}}^{\#}$); 7.25-7.20 (m, 4H, *meta*-$\mathrm{C\underline{H}_{ArCO}}$); 7.19-7.14 (m, 2H, *ortho*-$\mathrm{C\underline{H}_{Ar}}^{\#}$); 7.05-7.01 (m, 6H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$, *para*-$\mathrm{C\underline{H}_{Ar}}$, *para*-$\mathrm{C\underline{H}_{Ar}}^{\#}$); 6.94-6.90 (m, 2H, *meta*-$\mathrm{C\underline{H}_{Ar}}^{\#}$); 6.89-6.85 (m, 2H, *meta*-$\mathrm{C\underline{H}_{Ar}}^{\#}$); 6.70 (dt, *J* = 7.4, 1.1 Hz, 2H, *meta*-$\mathrm{C\underline{H}_{Ar}}$); 6.64-6.59 (m, 2H, *meta*-$\mathrm{C\underline{H}_{Ar}}$); 4.47-4.38 (m, 4H, $\mathrm{PhCOC\underline{H}CH_2}$, $\mathrm{PhCOC\underline{H}CH_2}^{\#}$); 3.64 (s, 6H, $\mathrm{OCH_3}$); 3.62 (s, 6H, $\mathrm{OCH_3}^{\#}$); 3.30 (dd, *J* = 13.0, 3.2 Hz, 2H, $\mathrm{PhCOCHC\underline{H}_2}$); 2.74 (m, 6H, $\mathrm{PhCOCHC\underline{H}_2}$, $\mathrm{PhCOCHC\underline{H}_2}^{\#}$). - ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 204.5 (s, $\mathrm{Ph\underline{C}{=}O}$); 203.1 (s, $\mathrm{Ph\underline{C}{=}O}^{\#}$); 157.5 (s, $\mathrm{\underline{C}_{ArOMe}}$); 157.3 (s, $\mathrm{\underline{C}_{ArOMe}}^{\#}$); 138.6 (s, $\mathrm{\underline{C}_{ArCO}}^{\#}$); 138.1 (s, $\mathrm{\underline{C}_{ArCO}}$); 132.7 (d, *para*-$\mathrm{\underline{C}H_{ArCO}}^{\#}$); 132.4 (d, *para*-$\mathrm{\underline{C}H_{ArCO}}$); 131.4 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}^{\#}$); 131.3 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 128.3 (d, *meta*-$\mathrm{\underline{C}H_{ArCO}}$, *meta*-$\mathrm{\underline{C}H_{ArCO}}^{\#}$); 128.7 (d, *ortho*-$\mathrm{\underline{C}H_{ArCO}}^{\#}$); 128.0 (d, *ortho*-$\mathrm{\underline{C}H_{ArCO}}$); 127.83 (d, *para*-$\mathrm{\underline{C}H_{Ar}}$); 127.79 (d, *para*-$\mathrm{\underline{C}H_{Ar}}^{\#}$); 127.3 (s, $\mathrm{\underline{C}_{Ar}}$); 127.2 (s, $\mathrm{\underline{C}_{Ar}}^{\#}$); 120.31 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}$); 120.27 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}^{\#}$); 109.95 (d, *meta*-$\mathrm{\underline{C}H_{Ar(\mathit{o}\text{-}OMe)}}$); 109.92 (d, *meta*-$\mathrm{\underline{C}H_{Ar(\mathit{o}\text{-}OMe)}}^{\#}$); 55.0 (q, $\mathrm{O\underline{C}H_3}^{\#}$); 54.9 (q, $\mathrm{O\underline{C}H_3}$); 48.6 (d, $\mathrm{PhCO\underline{C}HCH_2}$); 48.3 (d, $\mathrm{PhCO\underline{C}HCH_2}^{\#}$); 32.8 (t, $\mathrm{PhCOCH\underline{C}H_2}^{\#}$); 31.9 (t, $\mathrm{PhCOCH\underline{C}H_2}$). $^{\#}$ Resonances of ***meso*-8i**.

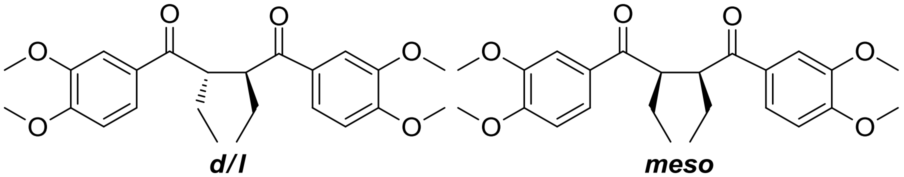
(2*S**,3*S**)-1,4-Bis(4-methoxyphenyl)-2,3-diethylbutane-1,4-dione and (2*R**,3*S**)-1,4-bis(4-methoxyphenyl)-2,3-diethylbutane-1,4-dione (8k):



Partially separable 5:1 mixture of *d/l*:*meso* diastereomers as a viscous liquid. Yield 143 mg (62%). - $R_f = 0.32$, hexane/EtOAc 5:1. - IR: ν = 2975 (w); 2943 (w); 2885 (w); 2850 (w); 1669 (m); 1602 (s); 1579 (w); 1514 (m); 1464 (w); 1424 (w); 1388 (w); 1356 (w); 1312 (w); 1260 (s); 1236 (m); 1213 (w); 1172 (s); 1121 (w); 1033 (m); 986 (w); 849 (w); 796 (w); 755 (w); 696 (w); 669 (w); 636 (w); 610 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 731 (2M+Na$^+$, 22), 377 (M+Na$^+$, 100), 355 (M+H$^+$, 33). - HRMS (+ESI) Calcd. for $C_{22}H_{26}O_4Na^+$: 377.1723; found: 377.1723.

***d/l*- and *meso*-8k:** ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06 (d, *J* = 9.0 Hz, 4H, *ortho*-$\text{C}\underline{\text{H}}_{\text{ArCO}}{}^{\#}$); 7.94 (d, *J* = 9.0 Hz, 4H, *ortho*-$\text{C}\underline{\text{H}}_{\text{ArCO}}$); 6.96 (d, *J* = 9.0 Hz, 4H, *meta*-$\text{C}\underline{\text{H}}_{\text{ArCO}}{}^{\#}$); 6.90 (d, *J* = 9.0 Hz, 4H, *meta*-$\text{C}\underline{\text{H}}_{\text{ArCO}}$); 4.00-3.95 (m, 2H, $\text{C}\underline{\text{H}}\text{CH}_2\text{CH}_3$); 3.95-3.90 (m, 2H, $\text{C}\underline{\text{H}}\text{CH}_2\text{CH}_3{}^{\#}$); 3.86 (s, 6H, $\text{OC}\underline{\text{H}}_3{}^{\#}$); 3.82 (s, 6H, $\text{OC}\underline{\text{H}}_3$); 1.86-1.74 (m, 4H, $\text{CHC}\underline{\text{H}}_2\text{CH}_3$); 1.73-1.69 (m, 2H, $\text{CHC}\underline{\text{H}}_2\text{CH}_3{}^{\#}$); 1.42-1.37 (m, 2H, $\text{CHC}\underline{\text{H}}_2\text{CH}_3{}^{\#}$); 0.81 (t, *J* = 7.5 Hz, 6H, $\text{CH}_2\text{C}\underline{\text{H}}_3$); 0.67 (t, *J* = 7.5 Hz, 6H, $\text{CH}_2\text{C}\underline{\text{H}}_3{}^{\#}$). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 203.0 (s, $\text{Ar}\underline{\text{C}}\text{=O}^{\#}$); 202.9 (s, $\text{Ar}\underline{\text{C}}\text{=O}$); 163.9 (s, *para*-$\underline{\text{C}}_{\text{Ar}}{}^{\#}$); 163.4 (s, *para*-$\underline{\text{C}}_{\text{Ar}}$); 132.0 (s, $\underline{\text{C}}_{\text{ArCO}}$, $\underline{\text{C}}_{\text{ArCO}}{}^{\#}$); 130.9 (d, *ortho*-$\underline{\text{C}}\text{H}_{\text{Ar}}{}^{\#}$); 130.8 (d, *ortho*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 114.0 (d, *meta*-$\underline{\text{C}}\text{H}_{\text{Ar}}{}^{\#}$); 113.9 (d, *meta*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 55.6 (q, $\text{C}_{\text{Ar}}\text{O}\underline{\text{C}}\text{H}_3{}^{\#}$); 55.5 (q, $\text{C}_{\text{Ar}}\text{O}\underline{\text{C}}\text{H}_3$); 49.1 (d, $\underline{\text{C}}\text{HCH}_2\text{CH}_3{}^{\#}$); 46.8 (d, $\underline{\text{C}}\text{HCH}_2\text{CH}_3$); 25.7 (t, $\text{CH}\underline{\text{C}}\text{H}_2\text{CH}_3{}^{\#}$); 22.7 (t, $\text{CH}\underline{\text{C}}\text{H}_2\text{CH}_3$); 12.0 (q, $\text{CHCH}_2\underline{\text{C}}\text{H}_3{}^{\#}$); 10.8 (q, $\text{CHCH}_2\underline{\text{C}}\text{H}_3$). $^{\#}$ Resonances of ***meso*-8k**.

(2*S**,3*S**)-1,4-Bis(3,4-dimethoxyphenyl)-2,3-diethylbutane-1,4-dione and (2*R**,3*S**)-1,4-bis(3,4-dimethoxyphenyl)-2,3-diethylbutane-1,4-dione (8l):

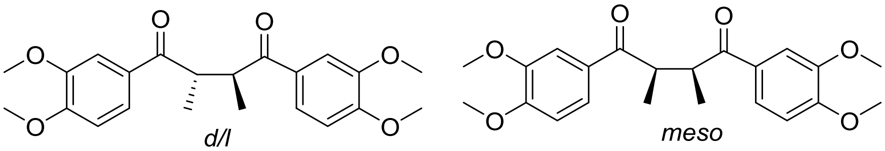


Partially separable 3:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 192 mg (71%). - $R_f = 0.45$, hexane/EtOAc 1:1. - IR: ν = 2973 (w); 2943 (w); 2884 (w); 2849 (w); 1663 (m); 1598 (m); 1588 (m); 1517 (s); 1464 (m); 1421 (m); 1387 (m); 1346 (w); 1263 (s); 1196 (w); 1155 (s); 1135 (m); 1025 (m); 889 (w); 805 (w); 759 (m); 669 (w); 623 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 851 (2M+Na$^+$, 19), 437 (M+Na$^+$, 100), 415 (M+H$^+$, 46). - HRMS (+EI) Calcd. for $\mathrm{C_{24}H_{31}O_6^+}$: 415.2115; found: 415.2115.

***d/l*-8l:** m.p. 109-110 °C. - ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.69 (dd, *J* = 8.4, 2.0 Hz, 2H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 7.44 (d, *J* = 2.0 Hz, 2H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 6.90 (d, *J* = 8.4 Hz, 2H, *meta*-$\mathrm{C\underline{H}_{ArCO}}$); 4.00-3.91 (m, 2H, $\mathrm{C\underline{H}CH_2CH_3}$); 3.93 (s, 6H, $\mathrm{OC\underline{H}_3}$); 3.88 (s, 6H, $\mathrm{OC\underline{H}_3}$); 1.90-1.74 (m, 4H, $\mathrm{CHC\underline{H}_2CH_3}$); 0.83 (t, *J* = 7.5 Hz, 6H, $\mathrm{CHCH_2C\underline{H}_3}$). - ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 209.9 (s, $\mathrm{Ar\underline{C}{=}O}$); 153.3 (s, *para*-$\mathrm{\underline{C}_{Ar}}$); 149.1 (s, *meta*-$\mathrm{\underline{C}_{Ar}}$); 131.0 (s, $\mathrm{\underline{C}_{ArCO}}$); 123.3 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 110.7 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 110.18 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}$); 56.17 (q, $\mathrm{C_{Ar}O\underline{C}H_3}$); 56.0 (q, $\mathrm{C_{Ar}O\underline{C}H_3}$); 49.0 (d, $\mathrm{\underline{C}HCH_2CH_3}$); 23.0 (t, $\mathrm{CH\underline{C}H_2CH_3}$); 11.0 (q, $\mathrm{CHCH_2\underline{C}H_3}$).

***meso*-8l:** ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.75 (dd, *J* = 8.5, 1.9 Hz, 2H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 7.60 (d, *J* = 1.9 Hz, 2H, *ortho*-$\mathrm{C\underline{H}_{ArCO}}$); 6.93 (d, *J* = 8.5 Hz, 2H, *meta*-$\mathrm{C\underline{H}_{ArCO}}$); 3.96 (s, 12H, $\mathrm{OC\underline{H}_3}$); 3.96-3.87 (m, 2H, $\mathrm{C\underline{H}CH_2CH_3}$); 1.71-1.59 (m, 2H, $\mathrm{CHC\underline{H}_2CH_3}$); 1.46-1.37 (m, 2H, $\mathrm{CHC\underline{H}_2CH_3}$); 0.68 (t, *J* = 7.4 Hz, 6H, $\mathrm{CHCH_2C\underline{H}_3}$). - ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 203.0 (s, $\mathrm{Ar\underline{C}{=}O}$); 153.8 (s, *para*-$\mathrm{\underline{C}_{Ar}}$); 149.3 (s, *meta*-$\mathrm{\underline{C}_{Ar}}$); 132.2 (s, $\mathrm{\underline{C}_{ArCO}}$); 123.6 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 110.3 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 110.22 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}$); 56.21 (q, $\mathrm{C_{Ar}O\underline{C}H_3}$); 56.1 (q, $\mathrm{C_{Ar}O\underline{C}H_3}$); 49.1 (d, $\mathrm{\underline{C}HCH_2CH_3}$); 25.8 (t, $\mathrm{CH\underline{C}H_2CH_3}$); 12.1 (q, $\mathrm{CHCH_2\underline{C}H_3}$).

(2*S,3*S**)-1,4-Bis(3,4-dimethoxyphenyl)-2,3-dimethylbutane-1,4-dione and (2*R**,3*S*-1,4-bis(3,4-dimethoxyphenyl)-2,3-dimethylbutane-1,4-dione (8m):**[3]

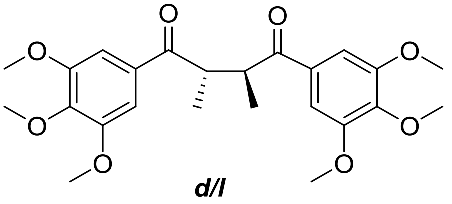


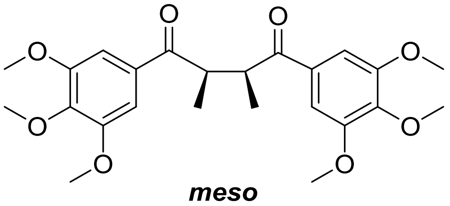
Partially separable 3:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 151 mg (60%). - $R_f = 0.25$, hexane/EtOAc 2:1. - IR: ν = 3086 (w); 3037 (w); 2972 (w); 2943 (w); 2882 (w); 2851 (w); 1662 (m); 1598 (m); 1587 (m); 1518 (m); 1466 (m); 1446 (w); 1420 (m); 1310 (m); 1262 (s); 1246 (s); 1224 (w); 1192 (w); 1154 (s); 1080 (w); 1024 (s); 996 (w); 891 (m); 863 (w); 817 (w); 809 (w); 760 (m); 751 (m); 730 (w); 670 (w); 621 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 795 (2M+Na$^+$, 37), 409 (M+Na$^+$, 100), 387 (M+H$^+$, 32). - HRMS (+EI) Calcd. for $\mathrm{C_{22}H_{27}O_6^+}$: 387.1802; found: 387.1803.

***d/l*-8m:** m.p. 190-191 °C. - ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (dd, *J* = 8.4, 2.0 Hz, 2H, *ortho*-C$\underline{H}_{ArCO}$); 7.48 (d, *J* = 2.0 Hz, 2H, *ortho*-C$\underline{H}_{ArCO}$); 6.90 (d, *J* = 8.4 Hz, 2H, *meta*-C$\underline{H}_{ArCO}$); 3.93 (s+m, 8H, OC$\underline{H}_3$, C$\underline{H}$CH$_3$); 3.88 (s, 6H, OC$\underline{H}_3$); 1.29 (d, *J* = 6.7 Hz, 6H, CHC$\underline{H}_3$). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 203.1 (s, Ar$\underline{C}$=O); 153.3 (s, *para*-$\underline{C}_{Ar}$); 149.1 (s, *meta*-$\underline{C}_{Ar}$); 129.3 (s, $\underline{C}_{Ar}$); 123.2 (d, *ortho*-$\underline{C}$H$_{Ar}$); 110.8 (d, *meta*-$\underline{C}$H$_{Ar}$); 110.2 (d, *ortho*-$\underline{C}$H$_{Ar}$); 56.17 (q, *para*-C$_{Ar}$O$\underline{C}$H$_3$); 56.0 (q, *meta*-C$_{Ar}$O$\underline{C}$H$_3$); 43.3 (d, $\underline{C}$HCH$_3$); 16.1 (q, CH$\underline{C}$H$_3$).

***meso*-8m:** ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.74 (dd, *J* = 8.5, 2.0 Hz, 2H, *ortho*-C$\underline{H}_{ArCO}$); 7.60 (d, *J* = 2.0 Hz, 2H, *ortho*-C$\underline{H}_{ArCO}$); 6.93 (d, *J* = 8.5 Hz, 2H, *meta*-C$\underline{H}_{ArCO}$); 3.97 (s+m, 14H, OC$\underline{H}_3$, C$\underline{H}$CH$_3$); 1.11 (d, *J* = 6.3 Hz, 6H, CHC$\underline{H}_3$). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 202.6 (s, Ar$\underline{C}$=O); 153.8 (s, *para*-$\underline{C}_{Ar}$); 149.4 (s, *meta*-$\underline{C}_{Ar}$); 130.3 (s, $\underline{C}_{Ar}$); 123.8 (d, *ortho*-$\underline{C}$H$_{Ar}$); 110.7 (d, *meta*-$\underline{C}$H$_{Ar}$); 110.3 (d, *ortho*-$\underline{C}$H$_{Ar}$); 56.3 (q, *para*-C$_{Ar}$O$\underline{C}$H$_3$); 56.19 (q, *meta*-C$_{Ar}$O$\underline{C}$H$_3$); 43.1 (d, $\underline{C}$HCH$_3$); 17.8 (q, CH$\underline{C}$H$_3$).

(2*S,3*S**)-1,4-Bis(3,4,5-trimethoxyphenyl)-2,3-dimethylbutane-1,4-dione and (2*R**,3*S**)-1,4-bis(3,4,5-trimethoxyphenyl)-2,3-dimethylbutane-1,4-dione (8n):**[4]


d/l


meso

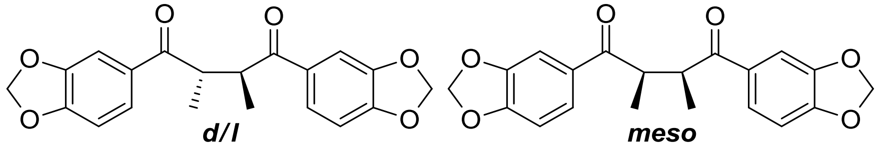
Partially separable 3:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 198 mg (68%). - R$_f$ = 0.46, hexane/EtOAc 7:3. - IR: ν = 2924 (w); 2853 (w); 1775 (w); 1708 (w); 1670 (m); 1581 (m); 1503 (w); 1457 (m); 1413 (m); 1339 (m); 1231 (w); 1183 (w); 1154 (m); 1125 (s); 998 (w); 865 (w); 759 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 915 (2M+Na$^+$, 6), 469 (M+Na$^+$, 100), 447 (M+H$^+$, 40). - HRMS (+ESI) Calcd. for $C_{24}H_{31}O_8^+$: 447.2013; found: 447.2013.

***d/l*- and *meso*-8n:** m.p. 172-173 °C (for *d/l*). - ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28 (s, 4H, *ortho*-C$\underline{H}_{ArCO}{}^{\#}$); 7.23 (s, 4H, *ortho*-C$\underline{H}_{ArCO}$); 3.92 (s+m, 14H, OC$\underline{H}_3{}^{\#}$, C$\underline{H}$CH$_3{}^{\#}$); 3.90 (s, 6H, OC$\underline{H}_3{}^{\#}$); 3.88 (s+m, 14H, OC$\underline{H}_3$, C$\underline{H}$CH$_3$); 3.87 (s, 6H, OC$\underline{H}_3$); 1.30 (d, *J* = 6.7 Hz, 6H, CHC$\underline{H}_3$); 1.12 (d, *J* = 6.3 Hz, 6H, CHC$\underline{H}_3{}^{\#}$). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 203.2 (s, Ar$\underline{C}$=O); 202.5 (s, Ar$\underline{C}$=O$^{\#}$); 153.3 (s, *meta*-$\underline{C}_{Ar}{}^{\#}$); 153.2 (s, *meta*-$\underline{C}_{Ar}$); 143.1 (s, *para*-$\underline{C}_{Ar}{}^{\#}$); 142.8 (s, *para*-$\underline{C}_{Ar}$);

132.1 (s, $\underline{\text{C}}_{\text{Ar}}{}^{\#}$); 131.3 (s, $\underline{\text{C}}_{\text{Ar}}$); 106.2 (d, *ortho*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 106.1 (d, *ortho*-$\underline{\text{C}}\text{H}_{\text{Ar}}{}^{\#}$); 61.0 (q, *para*-$\text{C}_{\text{Ar}}\text{O}\underline{\text{C}}\text{H}_3{}^{\#}$); 60.9 (q, *para*-$\text{C}_{\text{Ar}}\text{O}\underline{\text{C}}\text{H}_3$); 56.5 (q, *meta*-$\text{C}_{\text{Ar}}\text{O}\underline{\text{C}}\text{H}_3{}^{\#}$); 56.4 (q, *meta*-$\text{C}_{\text{Ar}}\text{O}\underline{\text{C}}\text{H}_3$); 43.6 (d, $\underline{\text{C}}\text{HCH}_3$); 43.2 (d, $\underline{\text{C}}\text{HCH}_3{}^{\#}$); 17.7 (q, $\text{CH}\underline{\text{C}}\text{H}_3{}^{\#}$); 15.9 (q, $\text{CH}\underline{\text{C}}\text{H}_3$).

$^{\#}$ Resonances of ***meso*-8n**.

(2*S,3*S**)-1,4-Bis(benzo[d][1,3]dioxol-5-yl)-2,3-dimethylbutane-1,4-dione and (2*R**,3*S**)-1,4-bis(benzo[d][1,3]dioxol-5-yl)-2,3-dimethylbutane-1,4-dione (8o):**[5]

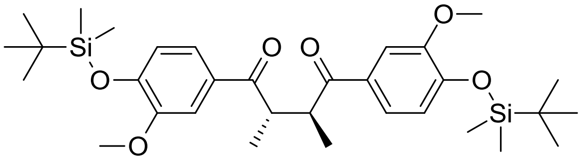


Separable 3:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 150 mg (65%). - R_f = 0.67, hexane/EtOAc 1:1. - IR: ν = 2978 (w); 2934 (w); 2864 (w); 1722 (s); 1674 (w); 1610 (w); 1509 (m); 1493 (m); 1445 (s); 1378 (w); 1358 (w); 1327 (w); 1250 (s); 1117 (w); 1093 (w); 1041 (s); 981 (w); 936 (w); 886 (w); 814 (w); 754 (w); 723 (w); 652 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 731 (2M+Na^+, 44), 377 (M+Na^+, 95), 355 (M+H^+, 100). - HRMS (+ESI) Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_6\text{Na}^+$: 377.0995; found: 377.0996.

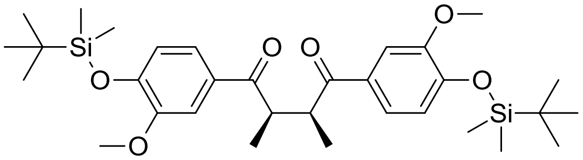
***d/l*-8o:** m.p. 193-194 °C. - ^{1}H NMR (400 MHz, CDCl_3): δ 7.63 (dd, *J* = 8.2, 1.4 Hz, 2H, *ortho*-$\text{C}\underline{\text{H}}_{\text{ArCO}}$); 7.44 (d, *J* = 1.4 Hz, 2H, *ortho*-$\text{C}\underline{\text{H}}_{\text{ArCO}}$); 6.90 (d, *J* = 8.2 Hz, 2H, *meta*-$\text{C}\underline{\text{H}}_{\text{ArCO}}$); 6.02 (s, 4H, $\text{OC}\underline{\text{H}_2}\text{O}$); 3.88-3.79 (m, 2H, $\text{C}\underline{\text{H}}\text{CH}_3$); 1.27 (d, *J* = 6.6 Hz, 6H, $\text{CHC}\underline{\text{H}_3}$). - ^{13}C NMR (100 MHz, CDCl_3): δ 202.5 (s, $\text{Ar}\underline{\text{C}}\text{=O}$); 151.8 (s, *para*-$\underline{\text{C}}_{\text{ArCO}}$); 148.3 (s, *meta*-$\underline{\text{C}}_{\text{ArCO}}$); 131.0 (s, $\underline{\text{C}}_{\text{ArCO}}$); 124.8 (d, *ortho*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 108.5 (d, *ortho*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 108.0 (d, *meta*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 101.9 (t, $\text{O}\underline{\text{C}}\text{H}_2\text{O}$); 43.7 (d, $\underline{\text{C}}\text{HCH}_3$); 16.0 (q, $\text{CH}\underline{\text{C}}\text{H}_3$).

***meso*-8o:** ^{1}H NMR (400 MHz, CDCl_3): δ 7.68 (dd, *J* = 8.2, 1.7 Hz, 2H, *ortho*-$\text{C}\underline{\text{H}}_{\text{ArCO}}$); 7.52 (d, *J* = 1.7 Hz, 2H, *ortho*-$\text{C}\underline{\text{H}}_{\text{ArCO}}$); 6.89 (d, *J* = 8.2 Hz, 2H, *meta*-$\text{C}\underline{\text{H}}_{\text{ArCO}}$); 6.06 (s, 4H, $\text{OC}\underline{\text{H}_2}\text{O}$); 3.95-3.86 (m, 2H, $\text{C}\underline{\text{H}}\text{CH}_3$); 1.08 (d, *J* = 6.4 Hz, 6H, $\text{CHC}\underline{\text{H}_3}$). - ^{13}C NMR (100 MHz, CDCl_3): δ 202.0 (s, $\text{Ar}\underline{\text{C}}\text{=O}$); 152.2 (s, *para*-$\underline{\text{C}}_{\text{ArCO}}$); 148.6 (s, *meta*-$\underline{\text{C}}_{\text{ArCO}}$); 131.9 (s, $\underline{\text{C}}_{\text{ArCO}}$); 125.0 (d, *ortho*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 108.3 (d, *ortho*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 108.1 (d, *meta*-$\underline{\text{C}}\text{H}_{\text{Ar}}$); 102.1 (t, $\text{O}\underline{\text{C}}\text{H}_2\text{O}$); 43.4 (d, $\underline{\text{C}}\text{HCH}_3$); 17.8 (q, $\text{CH}\underline{\text{C}}\text{H}_3$).

(2*S,3*S**)-1,4-Bis(4-((*tert*-butyldimethylsilyl)oxy)-3-(methoxy)phenyl)-2,3-dimethylbutane-1,4-dione and (2*R**,3*S**)-1,4-bis(4-((*tert*-butyldimethylsilyl)oxy)-3-(methoxy)phenyl)-2,3-dimethylbutane-1,4-dione (8p):**



d/l



meso

Separable 4.5:1 mixture of *d/l*:*meso* diastereomers as a colorless crystalline solid. Yield 157 mg (41%). - R_f = 0.70, hexane/EtOAc 5:1. - IR: ν = 2967 (w); 2940 (w); 2893 (w); 2867 (w); 1673 (m); 1596 (m); 1514 (s); 1468 (m); 1420 (m); 1396 (w); 1366 (w); 1288 (s); 1256 (s); 1200 (w); 1164 (s); 1137 (w); 1123 (w); 1041 (w); 919 (m); 861 (m); 842 (s); 826 (s); 808 (s); 785 (s); 706 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 1195 (2M+Na$^+$, 18), 609 (M+Na$^+$, 100), 587 (M+H$^+$, 48). - HRMS (+ESI) Calcd. for $C_{32}H_{51}O_6NaSi_2^+$: 609.3038; found: 609.3034.

***d/l*- and *meso*-8p:** m.p. 90-91 °C (for *d/l*). - ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.63 (dd, *J* = 8.2, 1.9 Hz, 2H, *ortho*-C$\underline{H}_{ArCO}{}^{\#}$); 7.58-755 (m, 4H, *ortho*-C$\underline{H}_{ArCO}$, *ortho*-C$\underline{H}_{ArCO}{}^{\#}$); 7.43 (d, *J* = 1.8 Hz, 2H, *ortho*-C$\underline{H}_{ArCO}$); 6.90 (d, *J* = 8.2 Hz, 2H, *meta*-C$\underline{H}_{ArCO}{}^{\#}$); 6.87 (d, *J* = 8.2 Hz, 2H, *meta*-C$\underline{H}_{ArCO}$); 4.02-3.94 (m, 2H, C$\underline{H}$CH$_3{}^{\#}$); 3.94-3.89 (m, 2H, C$\underline{H}$CH$_3$); 3.88 (s, 6H, OC$\underline{H}_3{}^{\#}$); 3.81 (s, 6H, OC$\underline{H}_3$); 1.28 (d, *J* = 6.2 Hz, 6H, CHC$\underline{H}_3$); 1.11 (d, *J* = 6.4 Hz, 6H, CHC$\underline{H}_3{}^{\#}$); 1.00 (s, 18H, SiC(C$\underline{H}_3$)$_3{}^{\#}$); 0.99 (s, 18H, SiC(C$\underline{H}_3$)$_3$); 0.19 (s, 12H, Si(C$\underline{H}_3$)$_2{}^{\#}$); 0.18 (s, 6H, Si(C$\underline{H}_3$)$_2$); 0.17 (s, 6H, Si(C$\underline{H}_3$)$_2$). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 203.2 (s, Ar$\underline{C}$=O); 202.8 (s, Ar$\underline{C}$=O$^{\#}$); 151.3 (s, *meta*-$\underline{C}_{ArCO}{}^{\#}$); 151.1 (s, *meta*-$\underline{C}_{ArCO}$); 150.5 (s, *para*-$\underline{C}_{ArCO}{}^{\#}$); 150.0 (s, *para*-$\underline{C}_{ArCO}$); 131.1 (s, $\underline{C}_{ArCO}{}^{\#}$); 130.2 (s, $\underline{C}_{ArCO}$); 123.0 (d, *ortho*-$\underline{C}$H$_{ArCO}{}^{\#}$); 122.9 (d, *ortho*-$\underline{C}$H$_{ArCO}$); 120.45 (d, *meta*-$\underline{C}$H$_{ArCO}{}^{\#}$); 120.41 (d, *meta*-$\underline{C}$H$_{ArCO}$); 111.8 (d, *ortho*-$\underline{C}$H$_{ArOMe}$); 111.5 (d, *ortho*-$\underline{C}$H$_{ArOMe}{}^{\#}$); 55.6 (q, C$_{Ar}$O$\underline{C}$H$_3{}^{\#}$); 55.5 (q, C$_{Ar}$O$\underline{C}$H$_3$); 43.4 (d, $\underline{C}$HCH$_3$); 43.1 (d, $\underline{C}$HCH$_3{}^{\#}$); 25.78 (q, SiC($\underline{C}$H$_3$)$_3$); 25.77 (q, SiC($\underline{C}$H$_3$)$_3{}^{\#}$); 18.6 (s, Si$\underline{C}$(CH$_3$)$_3$ and Si$\underline{C}$(CH$_3$)$_3{}^{\#}$); 17.9 (q, CH$\underline{C}$H$_3{}^{\#}$); 16.1 (q, CH$\underline{C}$H$_3$); –4.39 (q, Si($\underline{C}$H$_3$)$_2$); –4.43 (q, Si($\underline{C}$H$_3$)$_2{}^{\#}$). $^{\#}$ Resonances of ***meso*-8p**.

2.3 Total synthesis of tetrahydrofuran lignans

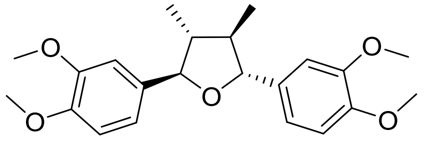
Method A: Lithium aluminum hydride (65 µL, 0.13 mmol, 2M in THF) was added to a stirred solution of **8m** (0.129 mmol) in THF (2 mL) at room temperature under an argon atmosphere. After 30 min, the reaction was quenched by a drop of water, diluted with ethyl acetate and filtered through a pad of celite, which was washed thoroughly with ethyl acetate. The filtrate was evaporated in vacuum to give crude diol. Boron trifluoride diethyl etherate (63 µL, 0.516 mmol) was added to a stirred solution of the crude diol in DCM (2 mL) at −78 °C under an argon atmosphere. After stirring at the same temperature for 20 min. the reaction mixture was quenched with water and diluted with CH_2Cl_2. The layers were separated and the aqueous was extracted with CH_2Cl_2. The combined organic fractions were dried over Na_2SO_4 and evaporated. The crude product was preadsorbed on silica gel and purified by flash column chromatography (hexane/EtOAc 100:1, gradient to 3:1).

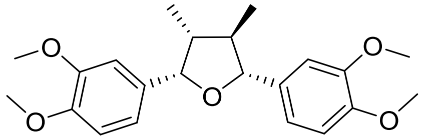
Note: For cyclization of **8m** and **8n** BF_3•OEt_2 (63 µL, 0.516 mmol); for **8o** and **8p**: BF_3•OEt_2 (24 µL, 0.193 mmol).

Method B: Lithium aluminum hydride (65 µL, 0.13 mmol, 2M in THF) was added to a stirred solution of **8m** (0.129 mmol) in THF (2 mL) at room temperature under an argon atmosphere. After 30 min, the reaction was quenched by a drop of water, diluted with ethyl acetate and filtered through a pad of celite, which was washed thoroughly with ethyl acetate. The filtrate was evaporated in vacuum to give crude diol. Triethylamine (38 µL, 0.28 mmol) was added to a stirred solution of the crude diol in DCM (2 mL) at 0 °C under an argon atmosphere. After stirring at the same temperature for 5 min, methanesulfonyl chloride (15 µL, 0.19 mmol) was added. After stirring at the same temperature for 1 h, the reaction mixture was quenched with water and diluted with CH_2Cl_2. The layers were separated and the aqueous was extracted with CH_2Cl_2. The combined organic fractions were dried over Na_2SO_4 and evaporated. The crude product was preadsorbed on silica gel and purified by flash column chromatography (hexane/EtOAc 100:1, gradient to 3:1).

Note: Methanesulfonyl chloride was added at −78 °C in the experiment performed to compare results with method A at low temperature.

(2R*,3R*,4R*,5R*)-2,5-Bis(3,4-dimethoxyphenyl)-3,4-dimethyltetrahydrofuran (16a) and (2R*,3R*,4R*,5S*)-2,5-bis(3,4-dimethoxyphenyl)-3,4-dimethyltetrahydrofuran (17a):[6]


(±)-Galbelgin

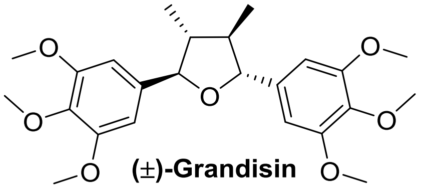

(±)-Veraguensin

Method A: Inseparable 10:1 mixture of two diastereomers as a viscous liquid. Yield 28 mg (57%). Method B: Inseparable 2:1 mixture of two diastereomers as a viscous liquid. Yield 38 mg (78%). - R_f = 0.80, hexane/EtOAc 1:1. - IR: ν = 3007 (w); 2965 (m); 2918 (w); 2844 (w); 1598 (w); 1563 (w); 1520 (s); 1462 (m); 1423 (w); 1379 (w); 1343 (w); 1267 (s); 1239 (s); 1165 (m); 1143 (m); 1110 (w); 1031 (s); 864 (w); 812 (w); 766 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 767 (2M+Na$^+$, 19), 395 (M+Na$^+$, 100), 373 (M+H$^+$, 10). - HRMS (+ESI) Calcd. for $C_{22}H_{29}O_5^+$: 373.2009; found: 373.2011.

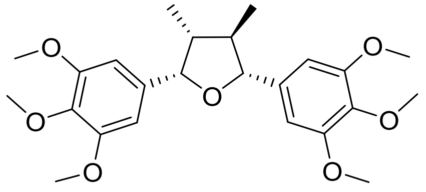
(2R*,3R*,4R*,5R*)-16a and (2R*,3R*,4R*,5S*)-17a: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.07 (d, *J* = 1.9 Hz, 1H, *ortho*-$\mathrm{C\underline{H}_{Ar}^{\#}}$); 7.04 (dd, *J* = 8.2, 1.9 Hz, 1H, *ortho*-$\mathrm{C\underline{H}_{Ar}^{\#}}$); 6.97 (d, *J* = 1.9 Hz, 2H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$); 6.92 (dd, *J* = 8.2, 1.9 Hz, 3H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$, *ortho*-$\mathrm{C\underline{H}_{Ar}^{\#}}$); 6.91-6.87 (m, 3H, *ortho*-$\mathrm{C\underline{H}_{Ar}^{\#}}$, *meta*-$\mathrm{C\underline{H}_{Ar}^{\#}}$, *meta*-$\mathrm{C\underline{H}_{Ar}^{\#}}$); 6.85 (d, *J* = 8.2 Hz, 2H, *meta*-$\mathrm{C\underline{H}_{Ar}}$); 5.14 (d, *J* = 8.6 Hz, 1H, $\mathrm{OC\underline{H}CHCH_3^{\#}}$); 4.66 (d, *J* = 9.2 Hz, 2H, $\mathrm{OC\underline{H}CHCH_3}$); 4.43 (d, *J* = 9.3 Hz, 1H, $\mathrm{OC\underline{H}CHCH_3^{\#}}$); 3.91 (s, 9H, $\mathrm{OC\underline{H_3}}$, $\mathrm{OC\underline{H_3}^{\#}}$); 3.89 (s, 3H, $\mathrm{OC\underline{H_3}^{\#}}$); 3.87 (s, 9H, $\mathrm{OC\underline{H_3}}$, $\mathrm{OC\underline{H_3}^{\#}}$); 3.86 (s, 3H, $\mathrm{OC\underline{H_3}^{\#}}$); 2.30-2.17 (m, 1H, $\mathrm{OCHC\underline{H}CH_3^{\#}}$); 1.85-1.74 (m, 3H, $\mathrm{OCHC\underline{H}CH_3}$, $\mathrm{OCHC\underline{H}CH_3^{\#}}$); 1.07 (d, *J* = 6.5 Hz, 3H, $\mathrm{CHC\underline{H_3}^{\#}}$); 1.05 (d, *J* = 6.1 Hz, 6H, $\mathrm{CHC\underline{H_3}}$); 0.66 (d, *J* = 7.0 Hz, 3H, $\mathrm{CHC\underline{H_3}^{\#}}$). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.1 (s, *meta*-$\mathrm{\underline{C}_{Ar}}$); 149.0 (s *meta*-$\mathrm{\underline{C}_{Ar}^{\#}}$); 148.59 (s, *meta*-$\mathrm{\underline{C}_{Ar}^{\#}}$); 148.57 (s, *para*-$\mathrm{\underline{C}_{Ar}^{\#}}$); 148.5 (s, *para*-$\mathrm{\underline{C}_{Ar}}$); 148.0 (s, *para*-$\mathrm{\underline{C}_{Ar}^{\#}}$); 134.9 (s, $\mathrm{\underline{C}_{Ar}}$); 133.8 (s, $\mathrm{\underline{C}_{Ar}^{\#}}$); 133.5 (s, $\mathrm{\underline{C}_{Ar}^{\#}}$); 119.2 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}^{\#}}$); 118.65 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}^{\#}}$); 118.62 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 111.1 (d, *meta*-$\mathrm{\underline{C}H_{Ar}^{\#}}$); 110.9 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}$); 110.7 (d, *meta*-$\mathrm{\underline{C}H_{Ar}^{\#}}$); 110.4 (d, *ortho*-$\mathrm{\underline{C}_{Ar}^{\#}}$); 110.0 (d, *ortho*-$\mathrm{\underline{C}_{Ar}^{\#}}$); 109.2 (d, *ortho*-$\mathrm{\underline{C}_{Ar}}$); 88.3 (d, $\mathrm{O\underline{C}HCHCH_3}$); 87.2 (d, $\mathrm{O\underline{C}HCHCH_3^{\#}}$); 83.0 (d, $\mathrm{O\underline{C}HCHCH_3^{\#}}$); 55.93 (q, $\mathrm{O\underline{C}H_3}$); 55.91 (q, $\mathrm{O\underline{C}H_3}$, $\mathrm{O\underline{C}H_3^{\#}}$); 55.88 (q, $\mathrm{O\underline{C}H_3^{\#}}$); 55.86 (q, $\mathrm{O\underline{C}H_3^{\#}}$); 55.81 (q, $\mathrm{O\underline{C}H_3^{\#}}$); 51.0 (d, $\mathrm{OCH\underline{C}HCH_3}$); 47.9 (d, $\mathrm{OCH\underline{C}HCH_3^{\#}}$); 46.0 (d, $\mathrm{OCH\underline{C}HCH_3^{\#}}$); 15.1 (q, $\mathrm{OCHCH\underline{C}H_3^{\#}}$); 15.0 (q, $\mathrm{OCHCH\underline{C}H_3^{\#}}$); 13.9 (q, $\mathrm{OCHCH\underline{C}H_3}$).

$^{\#}$ Resonances of **(2R*,3R*,4R*,5S*)-17a**.

(2*R,3*R**,4*R**,5*R**)-2,5-Bis(3,4,5-trimethoxyphenyl)-3,4-dimethyltetrahydrofuran (16b) and (2*R**,3*R**,4*R**,5*S**)-2,5-bis(3,4,5-trimethoxyphenyl)-3,4-dimethyltetrahydrofuran (17b):**[7]



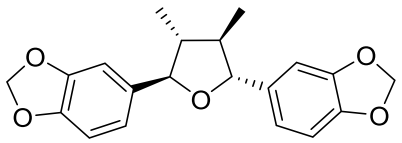
(±)-Grandisin



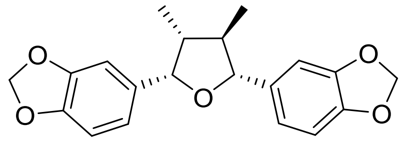
Method A: Inseparable 8:1 mixture of two diastereomers as a colorless viscous liquid. Yield 19.5 mg (40%). Method B: Inseparable 3:1 mixture of two diastereomers as a colorless viscous liquid. Yield 33.5 mg (69%). - R_f = 0.52, hexane/EtOAc 1:1. - IR: ν = 2966 (w); 2943 (w); 2848 (w); 1595 (m); 1510 (w); 1461 (m); 1422 (m); 1380 (w); 1356 (w); 1332 (m); 1235 (s); 1187 (w); 1125 (s); 1051 (w); 1010 (s); 915 (w); 861 (w); 827 (w); 788 (w); 731 (m); 671 (w); 648 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 887 (2M+Na$^+$, 5), 471 (M+K$^+$, 8), 455 (M+Na$^+$, 100). - HRMS (+ESI) Calcd. for $C_{24}H_{32}O_7Na^+$: 455.2040; found: 455.2039.

(2*R,3*R**,4*R**,5*R**)-16b and (2*R**,3*R**,4*R**,5*S**)-17b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (s, 2H, *ortho*-$C\underline{H}_{Ar}^{\#}$); 6.62 (s, 4H, *ortho*-$C\underline{H}_{Ar}$); 6.56 (s, 2H, *ortho*-$C\underline{H}_{Ar}^{\#}$); 5.12 (d, *J* = 8.5 Hz, 1H, $OC\underline{H}CHCH_3^{\#}$); 4.65 (d, *J* = 9.1 Hz, 2H, $OC\underline{H}CHCH_3$); 4.43 (d, *J* = 9.1 Hz, 1H, $OC\underline{H}CHCH_3^{\#}$); 3.89 (s, 12H, $OC\underline{H}_3$); 3.88 (s, 9H, $OC\underline{H}_3^{\#}$); 3.85 (s, 3H, $OC\underline{H}_3^{\#}$); 3.84 (s, 6H, $OC\underline{H}_3$); 3.83 (s, 6H, $OC\underline{H}_3^{\#}$); 2.31-2.21 (m, 1H, $OCHC\underline{H}CH_3^{\#}$); 1.85-1.73 (m, 3H, $OCHC\underline{H}CH_3$, $OCHC\underline{H}CH_3^{\#}$); 1.12 (d, *J* = 6.6 Hz, 3H, $CHC\underline{H}_3^{\#}$); 1.09 (d, *J* = 6.0 Hz, 6H, $CHC\underline{H}_3$); 0.70 (d, *J* = 7.0 Hz, 3H, $CHC\underline{H}_3^{\#}$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.40 (s, *meta*-$\underline{C}_{Ar}^{\#}$); 153.38 (s, *meta*-$\underline{C}_{Ar}$); 153.0 (s, *meta*-$\underline{C}_{Ar}^{\#}$); 138.1 (s, $\underline{C}_{Ar}$); 137.5 (s, *para*-$\underline{C}_{Ar}$ and *para*-$\underline{C}_{Ar}^{\#}$); 136.8 (s, *para*-$\underline{C}_{Ar}^{\#}$ and $\underline{C}_{Ar}^{\#}$); 136.7 (s, $\underline{C}_{Ar}^{\#}$); 104.2 (d, *ortho*-$\underline{C}H_{Ar}^{\#}$); 103.6 (d, *ortho*-$\underline{C}H_{Ar}^{\#}$); 103.1 (d, *ortho*-$\underline{C}H_{Ar}$); 88.6 (d, $O\underline{C}HCHCH_3$); 87.5 (d, $O\underline{C}HCHCH_3^{\#}$); 83.4 (d, $O\underline{C}HCHCH_3^{\#}$); 60.99 (q, $O\underline{C}H_3^{\#}$); 60.96 (q, $O\underline{C}H_3^{\#}$); 60.94 (q, $O\underline{C}H_3$); 56.3 (q, $O\underline{C}H_3$); 56.2 (q, $O\underline{C}H_3^{\#}$); 56.1 (q, $O\underline{C}H_3^{\#}$); 51.2 (d, $OCH\underline{C}HCH_3$); 47.9 (d, $OCH\underline{C}HCH_3^{\#}$); 46.2 (d, $OCH\underline{C}HCH_3^{\#}$); 15.5 (q, $OCHCH\underline{C}H_3^{\#}$); 15.0 (q, $OCHCH\underline{C}H_3^{\#}$); 14.1 (q, $OCHCH\underline{C}H_3$). $^{\#}$ Resonances of **(2*R**,3*R**,4*R**,5*S**)-17b**.

$(2R^*,3R^*,4R^*,5R^*)$-2,5-Bis(3,4-methylenedioxyphenyl)-3,4-dimethyltetrahydrofuran (16c) and $(2R^*,3R^*,4R^*,5S^*)$-2,5-bis(3,4-methylenedioxyphenyl)-3,4-dimethyltetrahydrofuran (17c):[8]



(±)-Galbacin



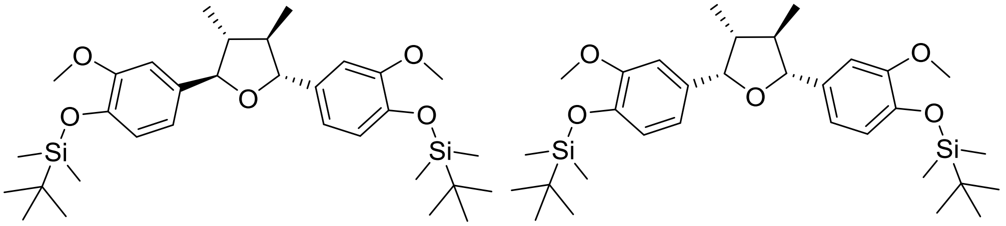
Method A: Partially separable 8:1 mixture of two diastereomers as a colorless viscous liquid. Yield 30 mg (62%). Method B: Partially separable 2:1 mixture of two diastereomers as a colorless viscous liquid. Yield 34 mg (70%). - $R_f = 0.34$, hexane/EtOAc 9:1. - IR: ν = 2967 (w); 2904 (w); 2784 (w); 1508 (m); 1492 (s); 1447 (s); 1384 (w); 1319 (w); 1248 (s); 1196 (w); 1130 (w); 1104 (w); 1040 (s); 937 (m); 895 (w); 868 (w); 811 (m); 720 (w); 666 (w); 620 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 703 ($2M+Na^+$, 7), 363 ($M+Na^+$, 100), 341 ($M+H^+$, 24). - HRMS (+ESI) Calcd. for $C_{20}H_{21}O_5^+$: 341.1383; found: 341.1384.

$(2R^*,3R^*,4R^*,5R^*)$-16c: ^1H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, J = 1.6 Hz, 2H, *ortho*-$C\underline{H}_{Ar}$); 6.83 (dd, J = 8.0, 1.6 Hz 2H, *ortho*-$C\underline{H}_{Ar}$); 6.77 (d, J = 8.0 Hz, 2H, *meta*-$C\underline{H}_{Ar}$); 5.94 (s, 4H, $OC\underline{H}_2O$); 4.59 (d, J = 9.2 Hz, 2H, $OC\underline{H}CHCH_3$); 1.80-1.69 (m, 2H, $OCHC\underline{H}CH_3$); 1.02 (d, J = 5.9 Hz, 6H, $CHC\underline{H}_3$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.93 (s, *meta*-$\underline{C}_{Ar}$); 147.1 (s, *para*-$\underline{C}_{Ar}$); 136.6 (s, $\underline{C}_{Ar}$); 119.9 (d, *ortho*-$\underline{C}H_{Ar}$); 108.1 (d, *meta*-$\underline{C}H_{Ar}$); 106.8 (d, *ortho*-$\underline{C}H_{Ar}$); 101.07 (t, $O\underline{C}H_2O$); 88.4 (d, $O\underline{C}HCHCH_3$); 51.2 (d, $OCH\underline{C}HCH_3$); 14.0 (q, $OCHCH\underline{C}H_3$).

$(2R^*,3R^*,4R^*,5S^*)$-17c: ^1H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, J = 1.7 Hz, 1H, *ortho*-$C\underline{H}_{Ar}$); 6.93-6.91 (m, 1H, *ortho*-$C\underline{H}_{Ar}$); 6.86-6.76 (m, 4H, *ortho*-$C\underline{H}_{Ar}$, *ortho*-$C\underline{H}_{Ar}$, *meta*-$C\underline{H}_{Ar}$, *meta*-$C\underline{H}_{Ar}$); 5.97 (s, 2H, $OC\underline{H}_2O$); 5.96 (s, 2H, $OC\underline{H}_2O$); 5.08 (d, J = 8.7 Hz, 1H, $OC\underline{H}CHCH_3$); 4.32 (d, J = 9.3 Hz, 1H, $OC\underline{H}CHCH_3$); 2.25-2.15 (m, 1H, $OCHC\underline{H}CH_3$); 1.80-1.65 (m, 1H, $OCHC\underline{H}CH_3$); 1.03 (d, J = 6.6 Hz, 3H, $CHC\underline{H}_3$); 0.66 (d, J = 7.0 Hz, 3H, $CHC\underline{H}_3$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.90 (s, *meta*-$\underline{C}_{Ar}$); 147.6 (s, *meta*-$\underline{C}_{Ar}$); 147.2 (s, *para*-$\underline{C}_{Ar}$); 146.7 (s, *para*-$\underline{C}_{Ar}$); 135.1 (s, $\underline{C}_{Ar}$); 134.7 (s, $\underline{C}_{Ar}$); 120.3 (d, *ortho*-$\underline{C}H_{Ar}$); 120.2 (d, *ortho*-$\underline{C}H_{Ar}$); 108.2 (d, *meta*-$\underline{C}H_{Ar}$); 107.9 (d, *meta*-$\underline{C}H_{Ar}$); 107.7 (d, *ortho*-$\underline{C}H_{Ar}$); 107.0 (d, *ortho*-$\underline{C}H_{Ar}$); 101.11 (t, $O\underline{C}H_2O$); 101.01 (t, $O\underline{C}H_2O$); 87.5 (d, $O\underline{C}HCHCH_3$); 83.0 (d, $O\underline{C}HCHCH_3$); 48.8 (d, OCH$\underline{C}$HCH$_3$); 46.1 (d, OCH$\underline{C}$HCH$_3$); 15.4 (q, OCHCH$\underline{C}$H$_3$); 15.1 (q, OCHCH$\underline{C}$H$_3$). - Minor **17c** was assigned from the mixture of **16c** and **17c**.

Method C: Lithium aluminum hydride (46 µL, 0.094 mmol, 2M in THF) was added to a stirred solution of **8p** (50 mg, 0.085 mmol) in THF (2 mL) at room temperature under an argon atmosphere. After 30 min, the reaction was quenched by a drop of water, diluted with ethyl acetate, filtered through a pad of celite, which was washed thoroughly with ethyl acetate. The filtrate was evaporated in vacuum to give crude diol. Diisopropyl azodicarboxylate (DIAD) (18.3 µL, 0.093 mmol) was added to a mixture of crude diols **15p** and triphenylphosphine (25 mg) in THF (2 mL) at 0 °C under an argon atmosphere and the reaction mixture was warmed to room temperature. After stirring for 1 h, the solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc 100:1, gradient to 5:1) to give 30.5 mg (62%) of **16d** and **17d** in 2:1 ratio.

(2*R,3*R**,4*R**,5*R**)-2,5-Bis(4-((*tert*-butyldimethylsilyl)oxy)-3-methoxyphenyl)-3,4-dimethyltetrahydrofuran (16d) and (2*R**,3*R**,4*R**,5*S**)-2,5-bis(4-((*tert*-butyldimethylsilyl)oxy)-3-methoxyphenyl)-3,4-dimethyl tetrahydrofuran (17d):**



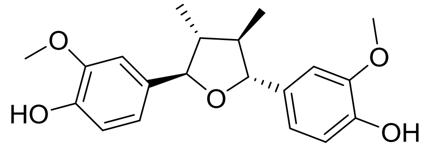
Method A: Separable 10:1 mixture of two diastereomers as a colorless viscous liquid. Yield 27 mg (55%). Method B: Separable 3:1 mixture of two diastereomers as a colorless viscous liquid. Yield 16 mg (32%). Method C: Separable 2:1 mixture of two diastereomers as a colorless viscous liquid. Yield 30.5 mg (62%). - R_f = 0.84, hexane/EtOAc 5:1. - IR: ν = 2965 (w); 2939 (w); 2902 (w); 2866 (w); 1611 (w); 1516 (s); 1468 (w); 1421 (w); 1380 (w); 1365 (w); 1283 (s); 1258 (m); 1237 (m); 1197 (w); 1165 (w); 1126 (w); 1042 (w); 918 (s); 881 (w); 842 (s); 822 (m); 807 (m); 784 (s); 708 (w); 668 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 1167 (2M+Na$^+$, 3), 595 (M+Na$^+$, 100), 573 (M+H$^+$, 7). - HRMS (+ESI) Calcd. for $C_{32}H_{52}O_5Si_2Na^+$: 595.3245; found: 595.3245.

(2R*,3R*,4R*,5R*)-16d: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93-6.92 (m, 2H, *ortho*-$C\underline{H}_{Ar}$); 6.82-6.81 (m, 4H, *ortho*-$C\underline{H}_{Ar}$, *meta*-$C\underline{H}_{Ar}$); 4.63 (d, *J* = 9.3 Hz, 2H, $OC\underline{H}CHCH_3$); 3.83 (s, 6H, $OC\underline{H}_3$); 1.86-1.73 (m, 2H, $OCHC\underline{H}CH_3$); 1.03 (d, *J* = 6.0 Hz, 6H, $CHC\underline{H}_3$); 0.99 (s, 18H, $SiC(C\underline{H}_3)_3$); 0.14 (s, 6H, $Si(C\underline{H}_3)_2$); 0.13 (s, 6H, $Si(C\underline{H}_3)_2$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1 (s, *meta*-$\underline{C}_{Ar}$); 144.6 (s, *para*-$\underline{C}_{Ar}$); 136.0 (s, $\underline{C}_{Ar}$); 120.7 (d, *meta*-$\underline{C}H_{Ar}$); 118.9 (d, *ortho*-$\underline{C}H_{Ar}$); 110.20 (d, *ortho*-$\underline{C}H_{Ar}$); 88.6 (d, $O\underline{C}HCHCH_3$); 55.65 (q, $O\underline{C}H_3$); 51.1 (d, $OCH\underline{C}HCH_3$); 25.9 (q, $SiC(\underline{C}H_3)_3$); 18.6 (s, $Si\underline{C}(CH_3)_3$); 14.0 (q, $OCHCH\underline{C}H_3$); –4.52 (q, $Si(C\underline{H}_3)_2$).

(2R*,3R*,4R*,5S*)-17d: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, *J* = 1.9 Hz, 1H, *ortho*-$C\underline{H}_{Ar}$); 6.94 (dd, *J* = 8.2, 1.9 Hz, 1H, *ortho*-$C\underline{H}_{Ar}$); 6.85 (d, *J* = 1.9 Hz, 1H, *ortho*-$C\underline{H}_{Ar}$); 6.84 (d, *J* = 8.2 Hz, 1H, *meta*-$C\underline{H}_{Ar}$); 6.81 (d, *J* = 8.2 Hz, 1H, *meta*-$C\underline{H}_{Ar}$); 6.77 (dd, *J* = 8.2, 1.8 Hz, 1H, *ortho*-$C\underline{H}_{Ar}$); 5.11 (d, *J* = 8.7 Hz, 1H, $OC\underline{H}CHCH_3$); 4.39 (d, *J* = 9.4 Hz, 1H, $OC\underline{H}CHCH_3$); 3.82 (s, 3H, $OC\underline{H}_3$); 3.77 (s, 3H, $OC\underline{H}_3$); 2.27-2.17 (m, 1H, $OCHC\underline{H}CH_3$); 1.83-1.73 (m, 1H, $OCHC\underline{H}CH_3$); 1.04 (d, *J* = 6.5 Hz, 3H, $CHC\underline{H}_3$); 1.00 (s, 9H, $SiC(C\underline{H}_3)_3$); 0.99 (s, 9H, $SiC(C\underline{H}_3)_3$); 0.63 (d, *J* = 7.0 Hz, 3H, $CHC\underline{H}_3$); 0.16 (s, 6H, $Si(C\underline{H}_3)_2$); 0.14 (s, 3H, $Si(C\underline{H}_3)_2$); 0.13 (s, 3H, $Si(C\underline{H}_3)_2$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0 (s, *meta*-$\underline{C}_{Ar}$); 150.7 (s, *meta*-$\underline{C}_{Ar}$); 144.7 (s, *para*-$\underline{C}_{Ar}$); 144.0 (s, *para*-$\underline{C}_{Ar}$); 135.0 (s, $\underline{C}_{Ar}$); 134.4 (s, $\underline{C}_{Ar}$); 120.8 (d, *meta*-$\underline{C}H_{Ar}$); 120.5 (d, *meta*-$\underline{C}H_{Ar}$); 119.5 (d, *ortho*-$\underline{C}H_{Ar}$); 119.0 (d, *ortho*-$\underline{C}H_{Ar}$); 111.3 (d, *ortho*-$\underline{C}H_{Ar}$); 111.0 (d, *ortho*-$\underline{C}H_{Ar}$); 87.5 (d, $O\underline{C}HCHCH_3$); 83.3 (d, $O\underline{C}HCHCH_3$); 55.64 (q, $O\underline{C}H_3$); 55.56 (q, $O\underline{C}H_3$); 47.8 (d, $OCH\underline{C}HCH_3$); 46.1 (d, $OCH\underline{C}HCH_3$); 25.9 (q, $SiC(\underline{C}H_3)_3$); 18.6 (s, $Si\underline{C}(CH_3)_3$); 15.1 (q, $OCHCH\underline{C}H_3$); 15.0 (q, $OCHCH\underline{C}H_3$); –4.46 (q, $Si(C\underline{H}_3)_2$); –4.47 (q, $Si(C\underline{H}_3)_2$); –4.52 (q, $Si(C\underline{H}_3)_2$); –4.55 (q, $Si(C\underline{H}_3)_2$).

Procedure for formation of 16e: Tetrabutylammonium fluoride (0.14 mL, 0.14 mmol, 1M in THF) was added to a stirred solution of **16d** (20 mg, 0.035 mmol) in THF (2 mL) at room temperature under an argon atmosphere. After 5 min, the reaction was quenched by saturated NH_4Cl solution, the layers were separated and the aqueous was extracted with EtOAc. The combined organic fractions were dried over Na_2SO_4 and evaporated to give the crude product, which was purified by flash column chromatography (hexane/EtOAc 100:1, gradient to 1:1).

(±)-Fragransin A_2 (16e):

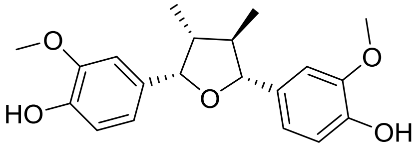


(±)-Fragransin A_2

Colorless viscous liquid. Yield 12 mg (98%). - $R_f = 0.45$, hexane/EtOAc 1:1. - IR: $\nu = 3436$ (w); 2967 (w); 2934 (m); 2863 (w); 1611 (w); 1519 (s); 1467 (m); 1437 (m); 1380 (w); 1333 (w); 1273 (s); 1240 (s); 1210 (m); 1162 (m); 1123 (m); 1102 (w); 1036 (s); 961 (w); 890 (w); 866 (w); 818 (m); 756 (s); 668 (w); 631 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 711 (2M+Na^+, 65), 367 (M+Na^+, 100), 345 (M+H^+, 25). - HRMS (+ESI) Calcd. for $C_{20}H_{25}O_5^+$: 345.1696; found: 345.1697.

(2*R,3*R**,4*R**,5*R**)-16e:** - ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, *J* = 1.6 Hz, 2H, *ortho*-C$\underline{H}_{Ar}$); 6.89 (d, *J* = 8.2 Hz, 2H, *meta*-C$\underline{H}_{Ar}$); 6.86 (d, *J* = 8.2, 1.6 Hz, 2H, *ortho*-C$\underline{H}_{Ar}$); 5.57 (s, 2H, ArO$\underline{H}$); 4.63 (d, *J* = 9.3 Hz, 2H, OC$\underline{H}$CHCH_3); 3.91 (s, 6H, OC$\underline{H}_3$); 1.81-1.72 (m, 2H, OCHC$\underline{H}$CH_3); 1.04 (d, *J* = 6.1 Hz, 6H, CHC$\underline{H}_3$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7 (s, *meta*-$\underline{C}_{Ar}$); 145.2 (s, *para*-$\underline{C}_{Ar}$); 134.5 (s, $\underline{C}_{Ar}$); 119.5 (d, *meta*-$\underline{C}H_{Ar}$); 114.1 (d, *ortho*-$\underline{C}H_{Ar}$); 108.6 (d, *ortho*-$\underline{C}H_{Ar}$); 88.5 (d, O$\underline{C}$HCHCH_3); 56.1 (q, O$\underline{C}H_3$); 51.2 (d, OCH$\underline{C}$HCH_3); 14.0 (q, OCHCH$\underline{C}H_3$).

(±)-Odoratisol C (17e):

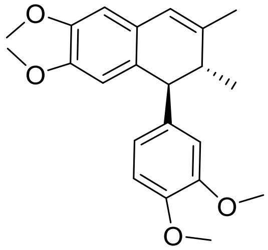


(±)-Odoratisol C

Colorless viscous liquid. Yield 6 mg (99%). - $R_f = 0.23$, hexane/EtOAc 7:3. - IR: $\nu = 3423$ (w); 3017 (w); 2968 (w); 2939 (w); 2881 (w); 1610 (w); 1519 (s); 1457 (m); 1436 (m); 1379 (w); 1349 (w); 1271 (s); 1239 (s); 1210 (s); 1163 (m); 1144 (m); 1123 (m); 1109 (w); 1035 (s); 945 (w); 860 (w); 821 (w); 787 (w); 752 (s); 688 (w); 668 (w); 633 (w); 615 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 711 (2M+Na$^+$, 83), 367 (M+Na$^+$, 100), 345 (M+H$^+$, 55). - HRMS (+ESI) Calcd. for $C_{20}H_{25}O_5^+$: 345.1696; found: 345.1697.

(2*R,3*R**,4*R**,5*S**)-17e:** - ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.04 (d, *J* = 1.8 Hz, 1H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$); 6.99 (dd, *J* = 8.2, 1.8 Hz, 1H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$); 6.93 (d, *J* = 8.2 Hz, 1H, *meta*-$\mathrm{C\underline{H}_{Ar}}$); 6.89 (d, *J* = 8.1 Hz, 1H, *meta*-$\mathrm{C\underline{H}_{Ar}}$); 6.85 (d, *J* = 1.7 Hz, 1H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$); 6.82 (dd, *J* = 8.1, 1.7 Hz, 1H, *ortho*-$\mathrm{C\underline{H}_{Ar}}$); 5.61 (s, 1H, $\mathrm{ArO\underline{H}}$); 5.55 (s, 1H, $\mathrm{ArO\underline{H}}$); 5.11 (d, *J* = 8.6 Hz, 1H, $\mathrm{OC\underline{H}CHCH_3}$); 4.40 (d, *J* = 9.3 Hz, 1H, $\mathrm{OC\underline{H}CHCH_3}$); 3.91 (s, 3H, $\mathrm{OC\underline{H}_3}$); 3.85 (s, 3H, $\mathrm{OC\underline{H}_3}$); 2.24 (ddq, *J* = 9.5, 8.8, 7.0 Hz, 1H, $\mathrm{OCHC\underline{H}CH_3}$); 1.78 (tq, *J* = 9.4, 6.5 Hz, 1H, $\mathrm{OCHC\underline{H}CH_3}$); 1.06 (d, *J* = 6.5 Hz, 3H, $\mathrm{CHC\underline{H}_3}$); 0.66 (d, *J* = 7.0 Hz, 3H, $\mathrm{CHC\underline{H}_3}$). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 146.6 (s, *meta*-$\mathrm{\underline{C}_{Ar}}$); 146.3 (s, *meta*-$\mathrm{\underline{C}_{Ar}}$); 145.3 (s, *para*-$\mathrm{\underline{C}_{Ar}}$); 144.7 (s, *para*-$\mathrm{\underline{C}_{Ar}}$); 133.3 (s, $\mathrm{\underline{C}_{Ar}}$); 132.9 (s, $\mathrm{\underline{C}_{Ar}}$); 120.0 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}$); 119.4 (d, *meta*-$\mathrm{\underline{C}H_{Ar}}$); 114.3 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 114.0 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 109.8 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 109.5 (d, *ortho*-$\mathrm{\underline{C}H_{Ar}}$); 87.5 (d, $\mathrm{O\underline{C}HCHCH_3}$); 83.3 (d, $\mathrm{O\underline{C}HCHCH_3}$); 56.01 (q, $\mathrm{O\underline{C}H_3}$); 55.98 (q, $\mathrm{O\underline{C}H_3}$); 47.9 (d, $\mathrm{OCH\underline{C}HCH_3}$); 46.1 (d, $\mathrm{OCH\underline{C}HCH_3}$); 15.14 (q, $\mathrm{OCHCH\underline{C}H_3}$); 15.10 (q, $\mathrm{OCHCH\underline{C}H_3}$).

(7'*S,8'*R**)-4,5,3',4'-Tetramethoxy-2,7'-cyclolignan-7-ene (18a):**

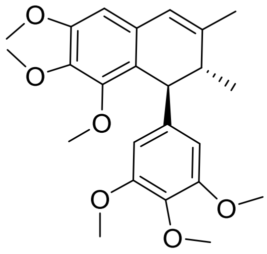


Method A: Inseparable 10:1 mixture of two diastereomers as a colorless viscous liquid. Yield 6 mg (14%). Method B: Inseparable >20:1 mixture of two diastereomers as a colorless viscous liquid. Yield 4.7 mg (11%). - R$_f$ = 0.66, hexane/EtOAc 5:1. - IR: ν = 2965 (w); 2933 (m); 2862 (w); 1515 (s); 1468 (m); 1421 (w); 1363 (w); 1343 (w); 1263 (s); 1236 (s); 1190 (w); 1144 (m); 1125 (w); 1099 (w); 1030 (m); 916 (w); 872 (w); 812 (w); 765 (w); 733 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 731 (2M+Na$^+$, 60), 377 (M+Na$^+$, 100), 355 (M+H$^+$, 10). - HRMS (+ESI) Calcd. for $C_{22}H_{26}O_4Na^+$: 377.1723; found: 377.1724.

(7'*S,8'*R**)-18a:** ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.71 (d, *J* = 8.3 Hz, 1H, H-5'); 6.66 (d, *J* = 2.0 Hz, 1H, H-2'); 6.62 (s, 1H, H-6); 6.552 (ddd, *J* = 8.3, 2.0, 0.5 Hz, 1H, H-6'); 6.550 (s, 1H, H-3);

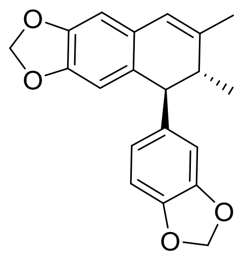
6.14 (q, *J* = 1.3 Hz, 1H, H-7); 3.91 (s, 6H, $\mathrm{OC\underline{H}_3}^{\#}$); 3.89 (s, 3H, $\mathrm{OC\underline{H}_3}$); 3.84 (s, 6H, $\mathrm{OC\underline{H}_3}^{\#}$); 3.82 (s, 3H, $\mathrm{OC\underline{H}_3}$); 3.79 (s, 3H, $\mathrm{OC\underline{H}_3}$); 3.78 (s, 3H, $\mathrm{OC\underline{H}_3}$); 3.68 (d, *J* = 3.3 Hz, 1H, H-7'); 2.39 (dq, *J* = 7.0, 3.3 Hz, 1H, H-8'); 1.80 (d, *J* = 1.3 Hz, 3H, H-9); 1.08 (d, *J* = 7.0 Hz, 3H, H-9'). - ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.8 (s, C-5); 148.7 (s, C-4); 147.7 (s, C-3'); 147.4 (s, C-4'); 138.9 (s, C-2); 138.2 (s, C-1'); 127.4 (s, C-1); 127.2 (s, C-8); 121.2 (d, C-7); 121.1 (d, C-7$^{\#}$); 119.7 (d, C-6'); 113.0 (d, C-3); 111.7 (d, C-2'$^{\#}$); 111.1 (d, C-2'); 111.0 (d, C-5'); 110.9 (d, C-5'$^{\#}$); 109.1 (d, C-6); 56.09 (q, $\mathrm{O\underline{C}H_3}^{\#}$); 56.07 (q, $\mathrm{O\underline{C}H_3}$); 56.05 (q, $\mathrm{O\underline{C}H_3}$); 56.03 (q, $\mathrm{O\underline{C}H_3}^{\#}$); 55.96 (q, $\mathrm{O\underline{C}H_3}^{\#}$); 55.94 (q, $\mathrm{O\underline{C}H_3}$); 55.92 (q, $\mathrm{O\underline{C}H_3}$); 55.90 (q, $\mathrm{O\underline{C}H_3}^{\#}$); 51.0 (d, C-7'); 42.1 (d, C-8'); 22.3 (q, C-9); 18.8 (q, C-9'). $^{\#}$Detectable resonances of minor diastereomer.

(7'*S**,8'*R**)-3,4,5,3',4',5'-Hexamethoxy-2,7'-cyclolignan-7-ene (18b):



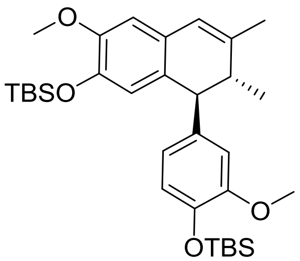
Method B: Inseparable 20:1 mixture of two diastereomers as a colorless viscous liquid. Yield 3.7 mg (8%). - R_f = 0.66, hexane/EtOAc 1:1. - IR: ν = 2965 (w); 2935 (m); 2862 (w); 1593 (w); 1495 (w); 1461 (m); 1412 (w); 1363 (w); 1348 (w); 1290 (w); 1236 (m); 1196 (w); 1129 (s); 1104 (m); 1039 (w); 1010 (w); 981 (w); 950 (w); 927 (w); 863 (w); 826 (w); 727 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 851 (2M+Na$^+$, 14), 437 (M+Na$^+$, 100), 415 (M+H$^+$, 21), 247 (M+H$^+$−$C_6H_3(OMe)_3$, 21). - HRMS (+ESI) Calcd. for $C_{24}H_{30}O_6Na^+$: 437.1934; found: 437.1936.
(7'*S,8'*R**)-18b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.44 (s, 1H, H-6); 6.34 (s, 2H, H-2', H-6'); 6.11 (dq, *J* = 1.5, 0.4 Hz, 1H, H-7); 4.07 (d, *J* = 1.3 Hz, 1H, H-7'); 3.87 (s, 3H, $\mathrm{OC\underline{H}_3}$); 3.84 (s, 3H, $\mathrm{OC\underline{H}_3}$); 3.78 (s, 3H, $\mathrm{OC\underline{H}_3}$); 3.74 (s, 6H, $\mathrm{OC\underline{H}_3}$); 3.61 (s, 3H, $\mathrm{OC\underline{H}_3}$); 2.38 (dq, *J* = 7.1, 1.3 Hz, 1H, H-8'); 1.81 (d, *J* = 1.5 Hz, 3H, H-9); 1.09 (d, *J* = 7.1 Hz, 3H, H-9'). - ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8 (s, C-3', C-5'); 152.2 (s, C-3); 152.1 (s, C-5); 141.5 (s, C-4); 141.1 (s, C-4' and C-1'); 136.2 (s, C-2); 130.1 (s, C-8); 121.1 (d, C-7); 120.5 (s, C-1); 105.1 (d, C-6); 104.5 (d, C-2', C-6'); 60.99 (q, $\mathrm{O\underline{C}H_3}$); 60.97 (q, $\mathrm{O\underline{C}H_3}$); 60.92 (q, $\mathrm{O\underline{C}H_3}$); 56.07 (q, $\mathrm{2xO\underline{C}H_3}$); 56.05 (q, $\mathrm{O\underline{C}H_3}$); 44.5 (d, C-7'); 41.9 (d, C-8'); 22.5 (q, C-9); 19.3 (q, C-9').

(7'S*,8'R*)-4,5:3',4'-Bis(methylenedioxy)-2,7'-cyclolignan-7-ene (18c):



Method A: Inseparable 20:1 mixture of two diastereomers as a colorless viscous liquid. Yield 6.5 mg (14%). Method B: Inseparable 11:1 mixture of two diastereomers as a colorless viscous liquid. Yield 6 mg (13%). - R_f = 0.50, hexane/EtOAc 10:1. - IR: ν = 2968 (w); 2906 (w); 1506 (m); 1486 (s); 1462 (w); 1443 (w); 1369 (w); 1288 (m); 1252 (s); 1219 (m); 1108 (w); 1041 (s); 940 (m); 874 (w); 796 (w); 733 (w); 642 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 323 (M+H$^+$, 100), 201 (M+H$^+$−C$_6$H$_4$(OCH$_2$O), 12). - HRMS (+ESI) Calcd. for $C_{20}H_{19}O_4^+$: 323.1277; found: 323.1276.
(7'S*,8'R*)-18c: ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.67 (dd, *J* = 7.8, 0.6 Hz, 1H, H-5’); 6.57 (s, 1H, H-6); 6.56 (d, *J* = 1.8 Hz, 1H, H-2’); 6.54 (ddd, *J* = 7.8, 1.8, 0.6 Hz, 1H, H-6’); 6.50 (s, 1H, H-3); 6.16 (dq, *J* = 1.4, 0.3 Hz, 1H, H-7$^{\#}$); 6.09 (q, *J* = 1.6 Hz, 1H, H-7); 5.89-5.87 (m, 4H, OC$\underline{\mathrm{H}}_2$O); 3.93 (bs, 1H, H-7’$^{\#}$); 3.63 (d, *J* = 3.2 Hz, 1H, H-7’); 2.34 (dq, *J* = 7.0, 3.2 Hz, 1H, H-8’); 1.80 (d, *J* = 1.4 Hz, 3H, H-9$^{\#}$); 1.79 (d, *J* = 1.6 Hz, 3H, H-9); 1.10 (d, *J* = 7.1 Hz, 3H, H-9’$^{\#}$); 1.06 (d, *J* = 7.0 Hz, 3H, H-9’). - ^{13}C NMR (100 MHz, CDCl$_3$): δ 147.6 (s, C-5); 146.4 (s, C-4); 146.1 (s, C-3’); 145.9 (s, C-4’); 139.5 (s, C-2); 138.8 (s, C-1’); 128.7 (s, C-1); 128.3 (s, C-8); 121.6 (d, C-7); 121.3 (d, C-7$^{\#}$); 120.6 (d, C-6’); 120.2 (d, C-6’$^{\#}$); 110.0 (d, C-3); 108.2 (d, C-2’); 108.1 (d, C-5’); 106.6 (d, C-6$^{\#}$); 106.2 (d, C-6); 100.9 (t, O$\underline{\mathrm{C}}$H$_2$O); 100.8 (t, O$\underline{\mathrm{C}}$H$_2$O); 51.4 (d, C-7’); 44.3 (d, C-7’$^{\#}$); 41.9 (d, C-8’); 41.6 (d, C-8’$^{\#}$); 22.7 (q, C-9$^{\#}$); 22.3 (q, C-9); 19.5 (q, C-9’$^{\#}$); 18.8 (q, C-9’). $^{\#}$Detectable resonances of the minor diastereomer.

(7'*S,8'*R**)-4,4'-Bis(*tert*-butyldimethylsilyloxy)-5,3'-dimethoxy-2,7'-cyclolignan-7-ene (18d):**



Method A: Inseparable >20:1 mixture of two diastereomers as a colorless viscous liquid. Yield 6.5 mg (14%). Method B: Inseparable >20:1 mixture of two diastereomers as a colorless viscous liquid. Yield 19 mg (40%). Method C: Inseparable 2:1 mixture of two diastereomers as a colorless viscous liquid. Yield 1 mg (2%). - R_f = 0.80, hexane/EtOAc 7:3. - IR: ν = 2964 (w); 2939 (w); 2906 (w); 2866 (w); 1609 (w); 1578 (w); 1511 (s); 1469 (w); 1410 (w); 1323 (w); 1287 (m); 1254 (s); 1230 (m); 1197 (w); 1156 (w); 1127 (w); 1099 (w); 1038 (w); 906 (s); 870 (w); 839 (s); 824 (m); 809 (m); 782 (s); 710 (w); 672 (w) cm^{-1}. - MS (+ESI) *m/z* (%): 1131 (2M+Na^+, 17), 577 (M+Na^+, 100), 555 (M+H^+, 10). - HRMS (+ESI) Calcd. for $C_{32}H_{50}O_4Si_2Na^+$: 577.3139; found: 577.3140.

(7'*S,8'*R**)-18d:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (d, *J* = 8.1 Hz, 1H, H-5'); 6.57 (d, *J* = 2.1 Hz, 1H, H-2'); 6.56 (s, 1H, H-6); 6.50 (dd, *J* = 8.1, 2.1 Hz, 1H, H-6'); 6.45 (s, 1H, H-3); 6.12 (s, 1H, H-7); 3.79 (s, 3H, $O\underline{CH_3}$); 3.69 (s, 3H, $OC\underline{H}_3$); 3.59 (d, *J* = 4.9 Hz, 1H, H-7'); 2.45-2.39 (m, 1H, H-8'); 1.80 (dd, *J* = 1.5, 0.6 Hz, 3H, H-9); 1.04 (d, *J* = 7.0 Hz, 3H, H-9'); 0.97 (s, 9H, $SiC(C\underline{H}_3)_3$); 0.93 (s, 9H, $SiC(C\underline{H}_3)_3$); 0.12 (s, 6H, $Si(C\underline{H}_3)_2$); 0.08 (s, 3H, $Si(C\underline{H}_3)_2$); 0.07 (s, 3H, $Si(C\underline{H}_3)_2$). - ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6 (s, C-5); 149.6 (s, C-3'); 143.4 (s, C-4'); 143.2 (s, C-4); 139.1 (s, C-1' and C-2); 128.3 (s, C-8); 128.2 (s, C-1); 122.2 (d, C-3); 121.6 (d, C-7); 120.5 (d, C-5'); 120.3 (d, C-6'); 112.0 (d, C-2'); 109.7 (d, C-6); 55.8 (q, $O\underline{C}H_3$); 55.5 (q, $O\underline{C}H_3$); 50.9 (d, C-7'); 41.5 (d, C-8'); 25.9 (q, $2xSiC(\underline{C}H_3)_3$); 22.2 (q, C-9); 18.6 (s, $2xSi\underline{C}(CH_3)_3$); 18.5 (q, C-9'); –4.44 (q, $Si(C\underline{H}_3)_2$); –4.48 (q, $2xSi(C\underline{H}_3)_2$); –4.50 (q, $Si(C\underline{H}_3)_2$).

2.4 X-Ray crystallographic data

Crystallographic data for all compounds were collected on a Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube CuKα 1.54178 Å at a temperature of 150(2) K. The structures were solved by direct methods (XP)[9] and refined by full matrix least squares based on F^2 (SHELXL2014).[10] The hydrogen atoms on carbons were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $Hiso(H) = 1.5\ U_{eq}$ for methyl moiety.

Table S2: X-Ray crystallographic data of ***meso*-8d**, *meso*-**8e**, and *meso*-**8f**.

Compound	*meso*-**8d**	*meso*-**8e**	*meso*-**8f**
CCDC	1538562	1538563	1538564
Formula	$C_{24}H_{30}O_2$	$C_{30}H_{26}O_2$	$C_{30}H_{24}F_2O_2$
M.w.	350.48	418.51	454.49
Crystal system	Monoclinic	Triclinic	Triclinic
Space group [No.]	$P\ 2_1/c$ (No 14)	$P\overline{1}$ (No 2)	$P\overline{1}$ (No 2)
a [Å]	14.8423 (4)	8.2432 (2)	8.2454 (2)
b [Å]	16.4382 (5)	10.4558 (3)	10.3667 (3)
c [Å]	12.5460 (4)	13.9905 (4)	14.2973 (4)
α [°]		89.460 (1)	90.201 (1)
β [°]	97.066 (1)	73.266 (1)	104.558 (1)
γ [°]		88.810 (1)	90.585 (1)
Z	6	2	2
V [Å^3]	3037.73 (16)	1154.51 (5)	1182.78 (6)
D_x [g cm^{-3}]	1.150	1.3204	1.276
Crystal colour	colorless	colorless	colorless
Crystal size [mm]	0.23 × 0.15× 0.15	0.25 × 0.23 × 0.12	0.36 × 0.23 × 0.21
Crystal shape	Prism	Prism	Prism
μ [mm^{-1}]	0.55	0.57	0.73
θ_{max} [°]	72.3	72.4	72.2
Measured reflections	37226	18313	20215
Independent diffractions (R_{int} [a])	5982 (0.054)	4541 (0.026)	4622 (0.025)
Observed diffract. [$I>2\sigma(I)$]	4778	3867	4131
T_{min}, T_{max}	0.83, 0.92	0.86, 0.93	0.77, 0.86
No. of parameters	356	290	307
R^c for $[F^2 > 2\sigma(F^2)]$	0.045	0.036	0.037
wR^c for all data	0.108	0.101	0.093
GOF [d]	1.03	1.03	1.04
Residual electron density [e/Å^3]	0.50, −0.22	0.24, −0.17	0.20, −0.18

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [c] $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$, Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = \_[\max(F_o^2,0) + 2F_c^2]/3$; [d] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

Table S2: X-Ray crystallographic data of *d/l*-**8g** and *meso*-**8g**.

Compound	*d/l*-**8g**	*meso*-**8g**
CCDC	1484494	1484493
Formula	$C_{30}H_{24}Cl_2O_2$	$C_{30}H_{24}Cl_2O_2$
M.w.	487.39	487.39
Crystal system	Triclinic	Monoclinic
Space group [No.]	$P\bar{1}$ (No 2)	$P\,2_1/c$ (No 14)
a [Å]	6.1640 (3)	15.2712 (5)
b [Å]	8.8470 (4)	11.6024 (4)
c [Å]	12.0067 (5)	14.6920 (5)
α [°]	106.131 (1)	
β [°]	92.963 (1)	107.143 (1)
γ [°]	101.467 (1)	
Z	1	4
V [Å^3]	612.44 (5)	2487.51 (15)
D_x [g cm^{-3}]	1.321	1.301
Crystal colour	colorless	colorless
Crystal size [mm]	0.15 × 0.12 × 0.12	0.19 × 0.07× 0.03
Crystal shape	Plate	Bar
μ [mm^{-1}]	2.58	2.54
θ_{max} [°]	72.2	72.3
Measured reflections	17890	31092
Independent diffractions (R_{int} [a])	2394 (0.023)	4889 (0.045)
Observed diffract. [I>2σ(I)]	2327	3984
T_{min}, T_{max}	0.695, 0.754	0.649, 0.923
No. of parameters	155	307
R^c for $[F^2 > 2\sigma(F^2)]$	0.030	0.037
wR^c for all data	0.078	0.091
GOF [d]	1.05	1.02
Residual electron density [e/Å^3]	0.21, −0.23	0.21, −0.53

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [c] $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$, Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where P = _$[\max(F_o^2,0) + 2F_c^2]/3$; [d] $\mathrm{GOF} = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$

3. References

---

[1] (a) E. Dinca, P. Hartmann, J. Smrček, I. Dix, P. G. Jones and U. Jahn, *Eur. J. Org. Chem.,* 2012, 4461-4482; (b) V. Amarnath and K. Amarnath, *J. Org. Chem*., 1995, **60**, 301-307; (c) A. J. Fry, M. Susla and M. Weltz, *J. Org. Chem*., 1987, **52**, 2496-2498; (d) G. A. Russell, B. Mudryk, F. Ros and M. Jawdosiuk, *Tetrahedron*, 1982, **38**, 1059-1067; (e) G. A. Russell, B. Mudryk, M. Jawdosiuk and Z. Wrobel, *J. Org. Chem*., 1982, **47**, 1879-1884; (f) G. A. Russell, B. Mudryk and M. Jawdosiuk, *J. Am. Chem. Soc*., 1981, **103**, 4610-4611; (g) H. Inoue; M. Sakata and E. Imoto, *Bull. Chem. Soc. Jpn*., 1973, **46**, 2211-2215; (h) H. Inoue; M. Sakata; E. Imoto, *Bull. Chem. Soc. Jpn*. 1971, **44**, 3490.

[2] (a) S. E. Drewes, C. J. Hogan, P. T. Kaye and G. H. P. Roos*, J. Chem. Soc., Perkin Trans. 1*, 1989, 1585-1591. (b) T. Amaya, T. Masuda, Y. Maegawa and T. Hirao, *Chem. Commun*., 2014, **50**, 2279-2281.

[3] (a) X. Li, J.-H. Jiang, Q. Chen, S.-X. Xiao, C.-H. Li, H.-W. Gu, H. Zhang, J.-L. Hu, F.-H. Yao and Q.-G. Li, *Eur. J. Med. Chem*., 2013, **62**, 605-613; (b) H. M. F. Allah, R. Soliman, *J. Heterocyclic Chem*., 1987, **24**, 1745-1748; (c) T. Biftu, N. F. Gamble, T. Doebber, S. B. Hwang, T. Y. Shen, J. Snyder, J. P. Springer and R. Stevenson, *J. Med. Chem*., 1986, **29**, 1917-1921; (d) K. V. Rao and F. M. Alvarez, *J. Nat. Prod*., 1985, **48**, 592-597; (e) C. Y.-C. Chan, M. A. Leaffer, R. M. Parkhurst, D. W. Thomas, L. M. Allen, R. T. Jordan and R. S. Pardini, *J. Labelled Comp. Radiopharm*., 1985, **22**, 79-87; (f) T. Biftu, B. G. Hazra, R. Stevenson and J. R. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1147-1150; (g) Y. Ito, T. Konoike, T. Harada and T. Saegusa, *J. Am. Chem. Soc.*, 1977, **99**, 1487-1493; (h) C. W. Perry, M. V. Kalnins and K. H. Deitcher, *J. Org. Chem*., 1972, **37**, 4371-4376; (i) S. B. Baker, T. H. Evans and H. Hibbert, *J. Am. Chem. Soc.*, 1948, **70**, 60-63; (j) J. R. Atkinson and R. D. Haworth, *J. Chem. Soc.*, 1938, 1681-1685.

[4] (a) A. de Melo Bezerra, A. C. da Silva Lins, P. Filgueiras de Athayde-Filho, M. S. da Silva, J. M. Barbosa-Filho, C. A. Camara, T. M. Sarmento Silva, V. da Silva Luna and C. Figueredo dos Santos, *Quim. Nova*, 2012, **35**, 2226-2228; (b) W. Qu, J. Xue, F. H. Wu and J. Y. Liang, *Chem. Nat. Comp*., 2014, **50**, 814-818; (c) J. M. Bárbosa-Filho, M. S. Da Silva, M. Yoshida and O. R. Gottlieb, *Phytochemistry*, 1989, **28**, 2209-2211; (d) T. Biftu, B. G. Hazra and R. Stevenson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2276-2281; (e) T. Biftu, B. G. Hazra and R. Stevenson, *J. Chem. Soc., Chem. Commun*., 1978, 491-492.

[5] (a) D. Enders, M. Milovanovic, E. Voloshina, G. Raabe and J. Fleischhauer, *Eur. J. Org. Chem*., 2005, 1984-1990; (b) K. R. Rezende and M. J. Kato, *Phytochemistry*, 2002, **61**, 427-432.

[6] (a) H. Kim, C. M. Wooten, Y. Park and J. Hong, *Org. Lett.*, 2007, **9**, 3965-3968; (b) K. V. Sarkanen and A. F. A Wallis, *J. Heterocyclic Chem.*, 1973, **6**, 1025-1027.

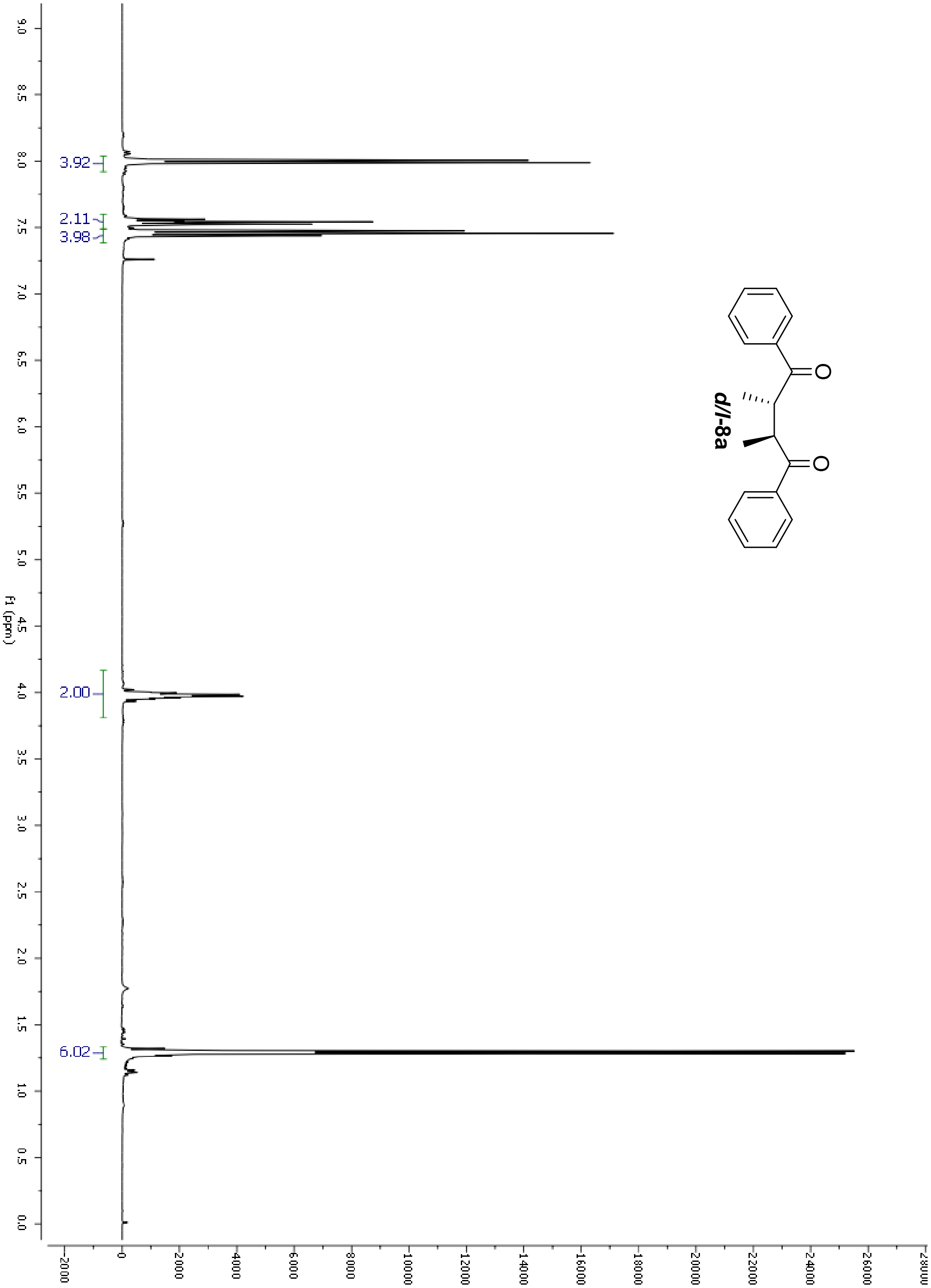
[7] J. M. Barbosa-Filho, E. V. L. da-Cunha and M. S. da Silva*, Magn. Reson. Chem.,* 1998, **36**, 929-935.

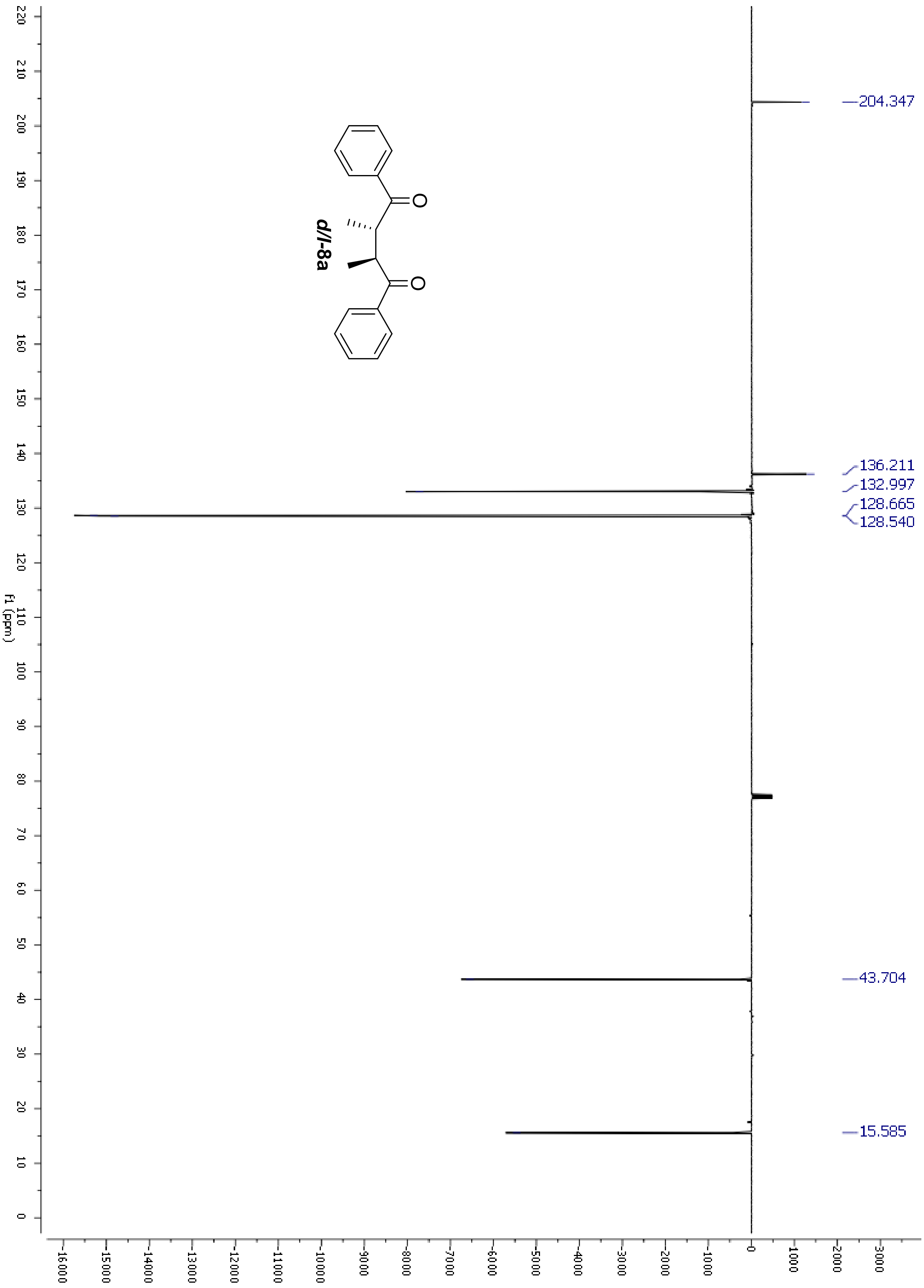
[8] (a) S. Hazra and S. Hajra, *RSC Adv.*, 2013, **3**, 22834-22836; (b) T. Biftu, B. G. Hazra, R. Stevenson and J. R. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1147-1150.

[9] G. M. Sheldrick, *Acta Cryst*., 2015, **A71**, 3-8.

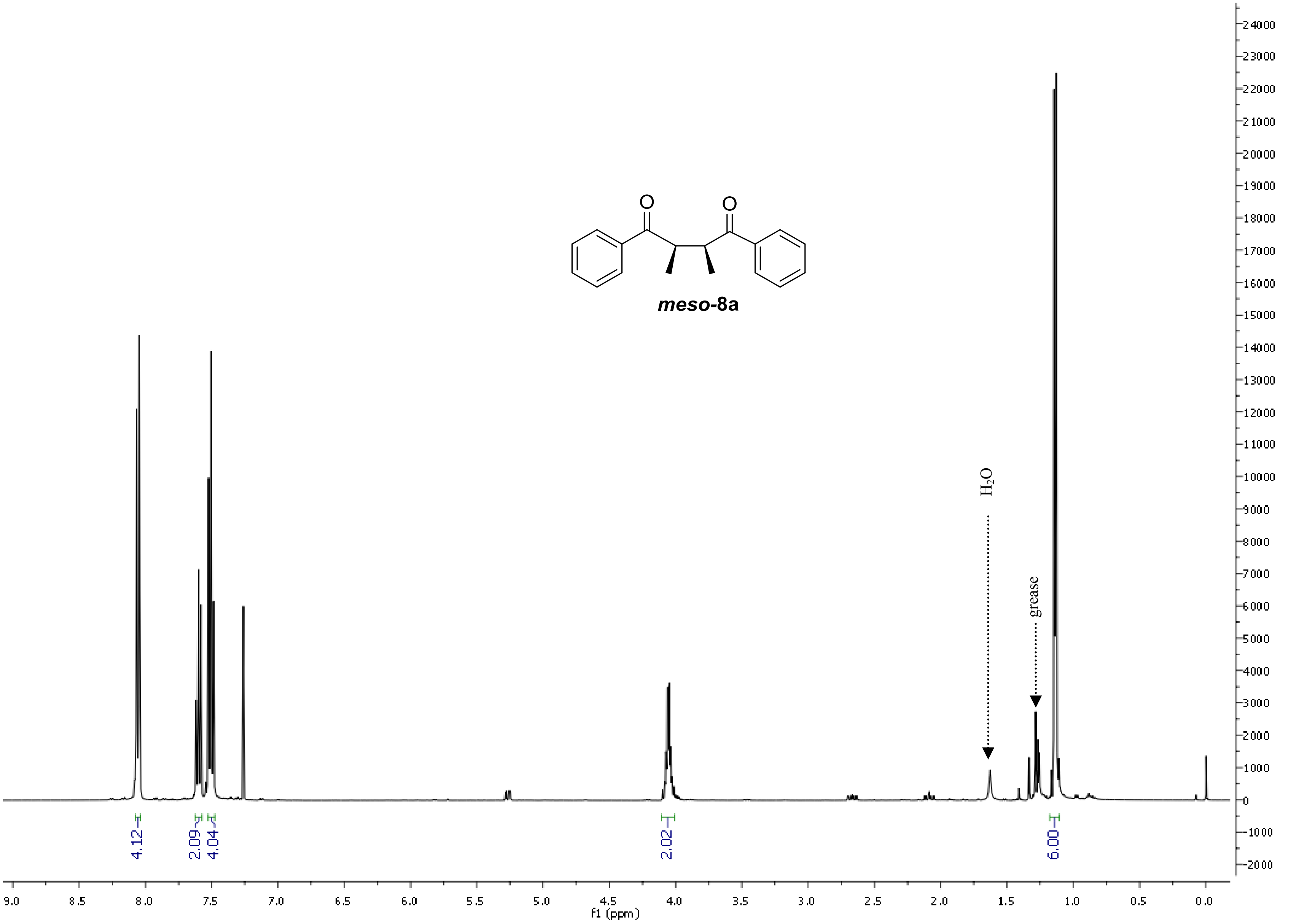
[10] G. M. Sheldrick, *Acta Cryst*., 2015, **C71**, 3-8.

4. ^{1}H and ^{13}C NMR spectra of all compounds

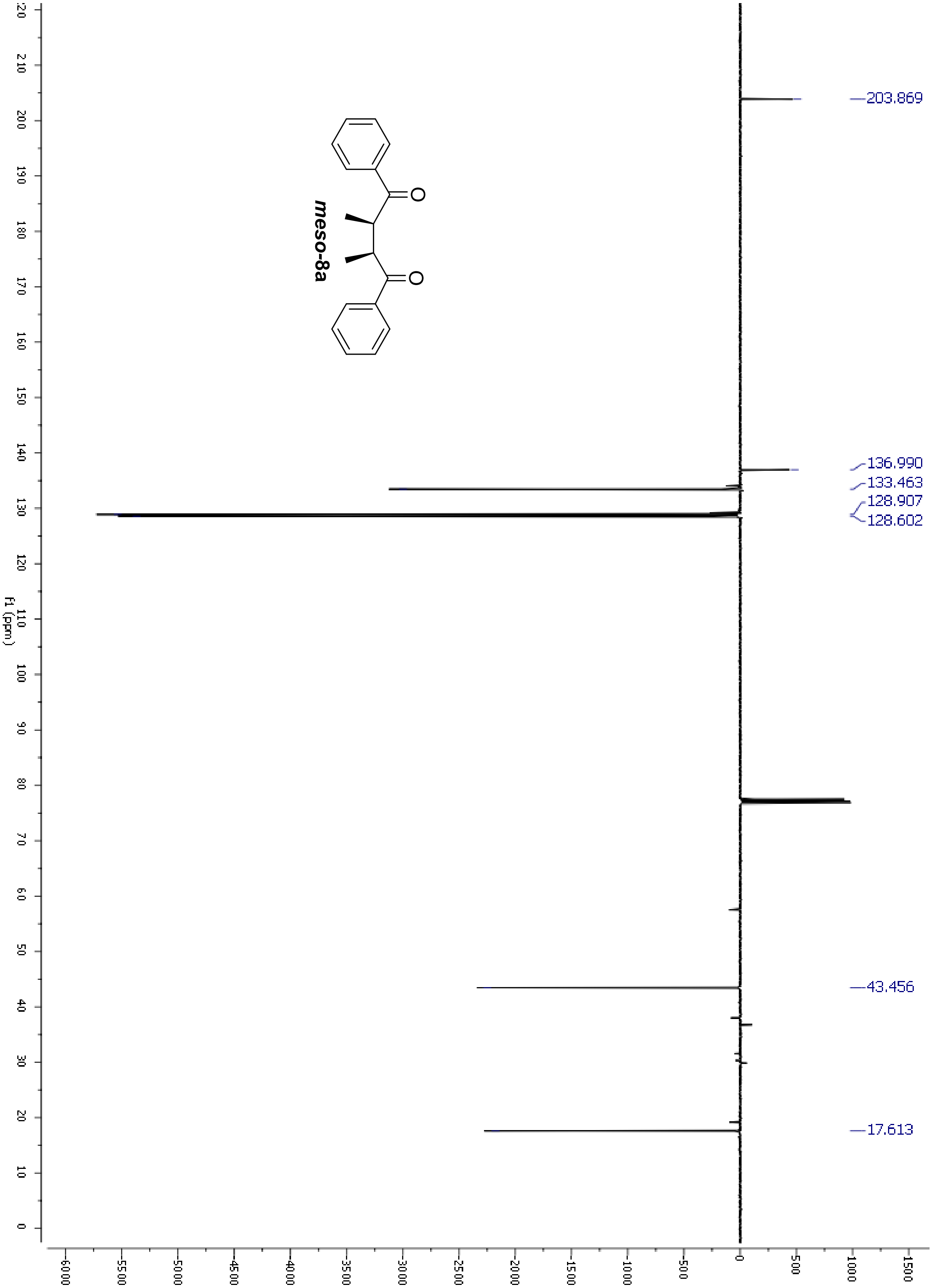

d/l-8a

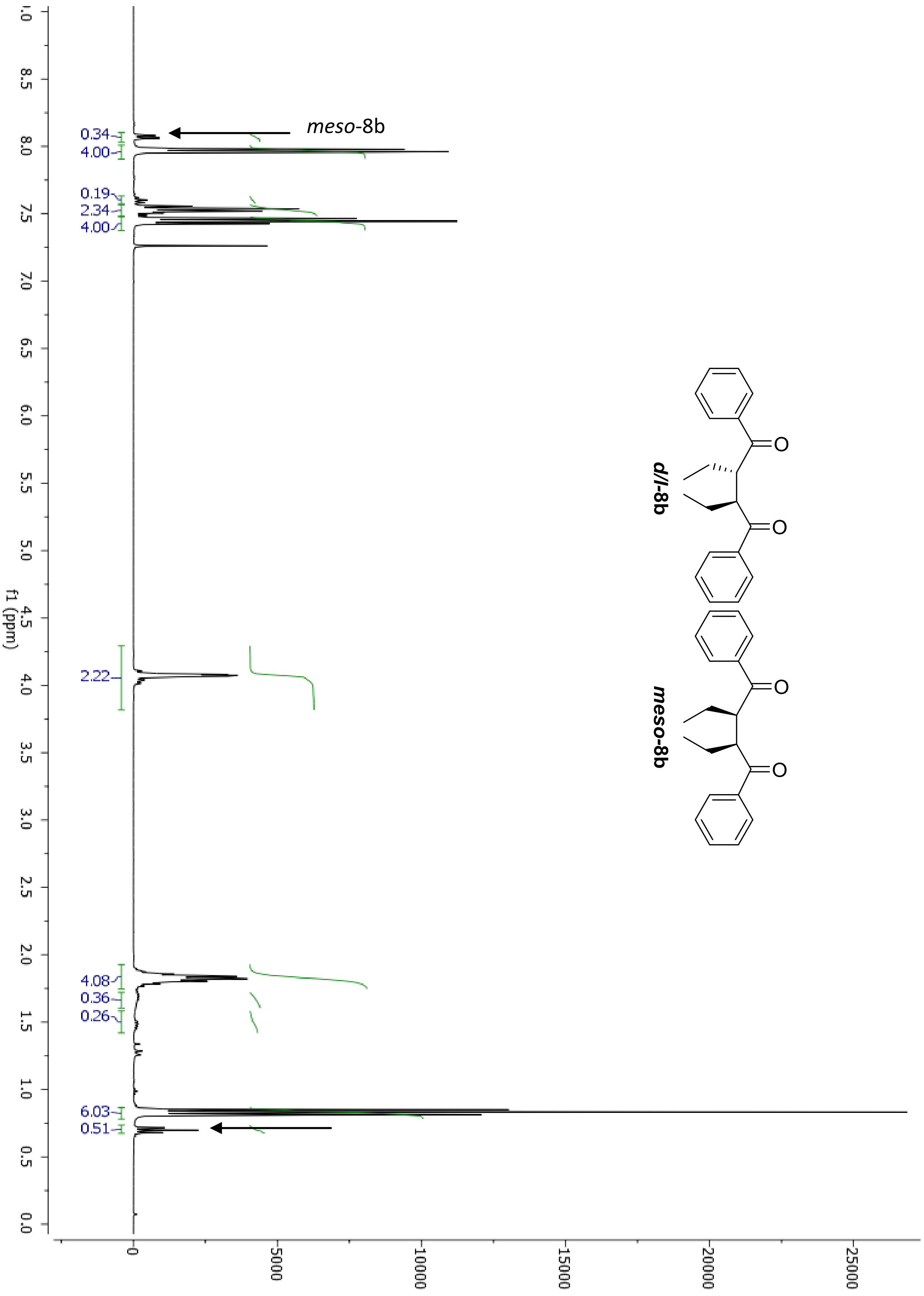

d/l-8a

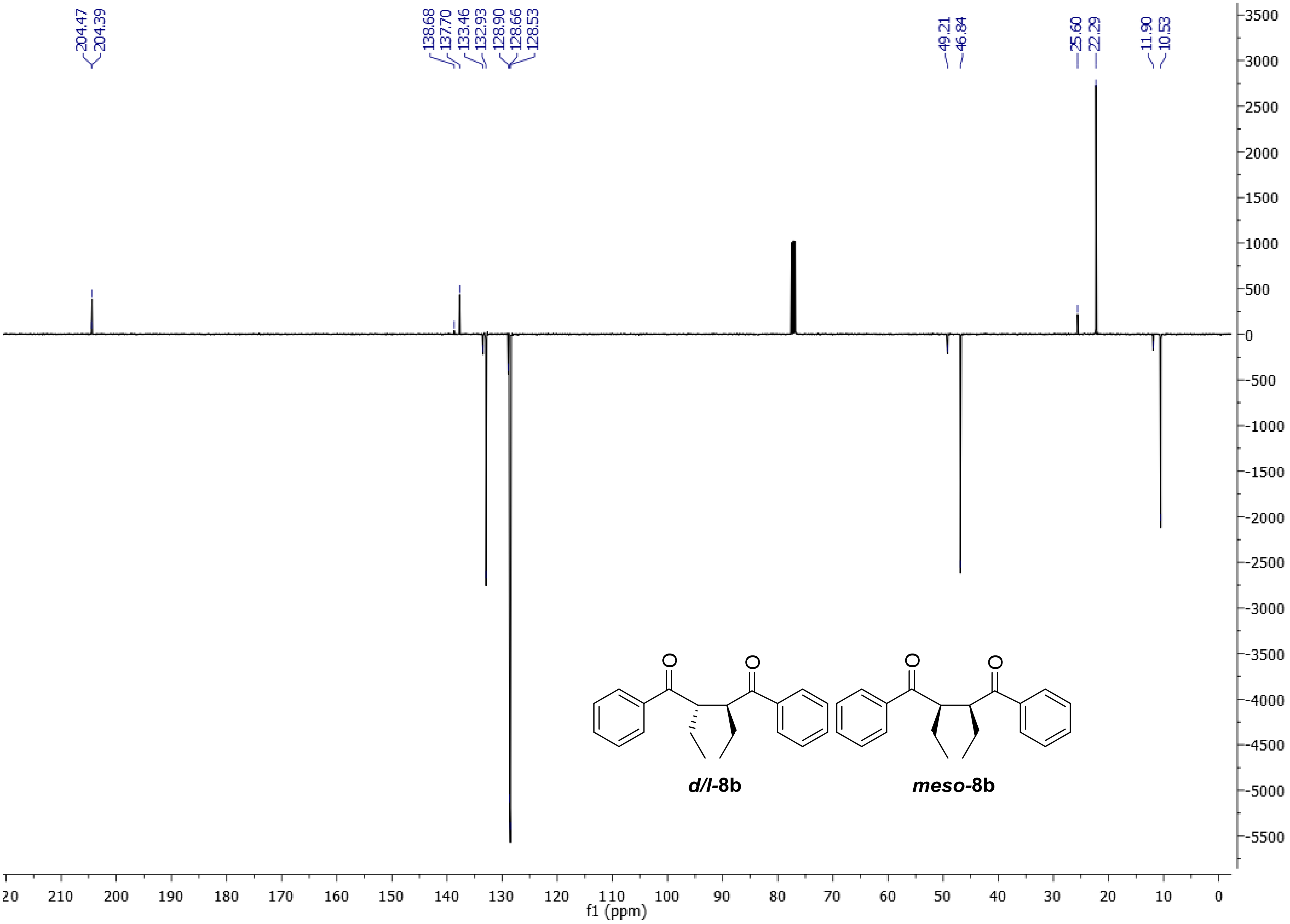
204.347
136.211
132.997
128.665
128.540
43.704
15.585
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
O
O

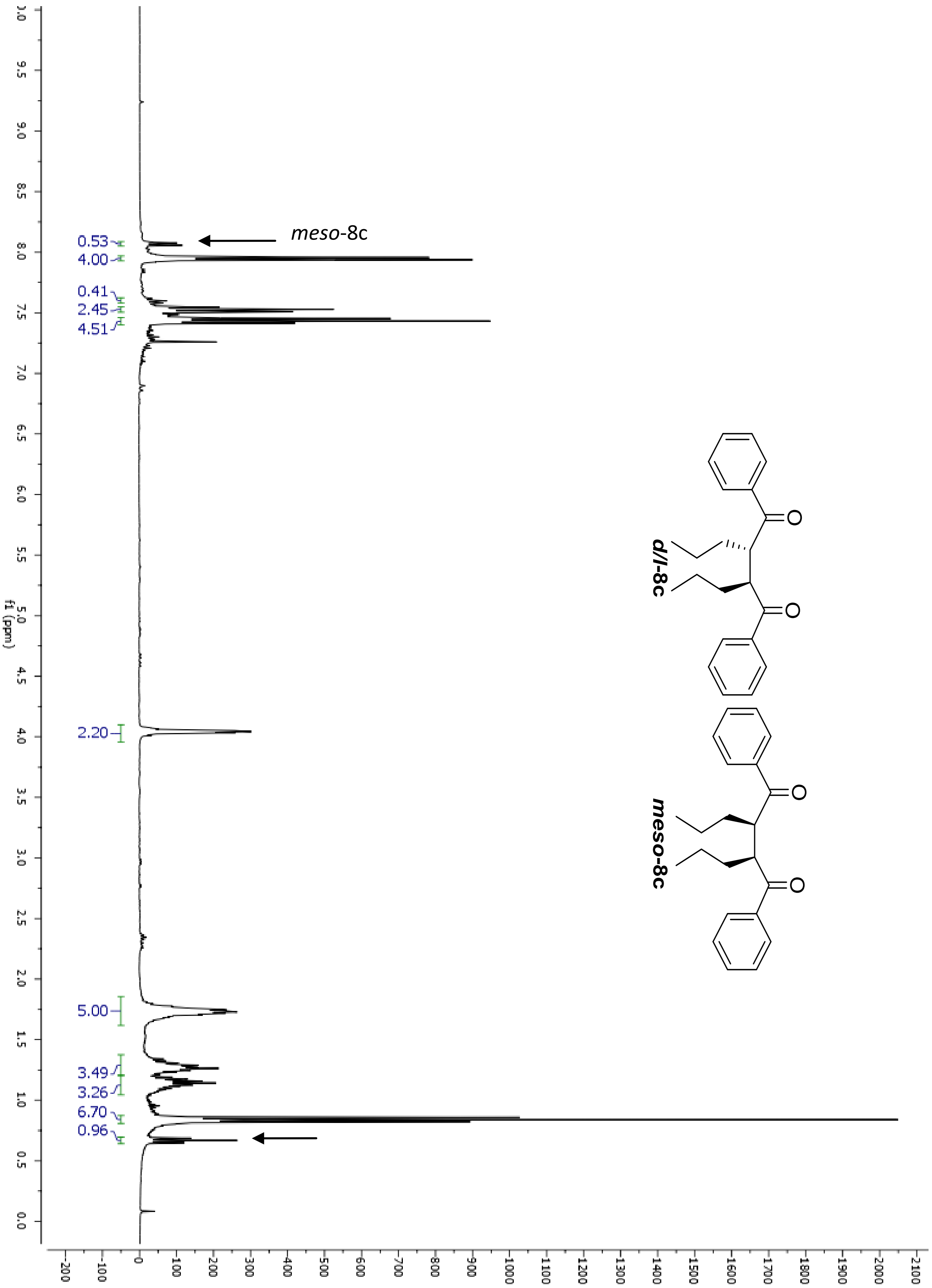


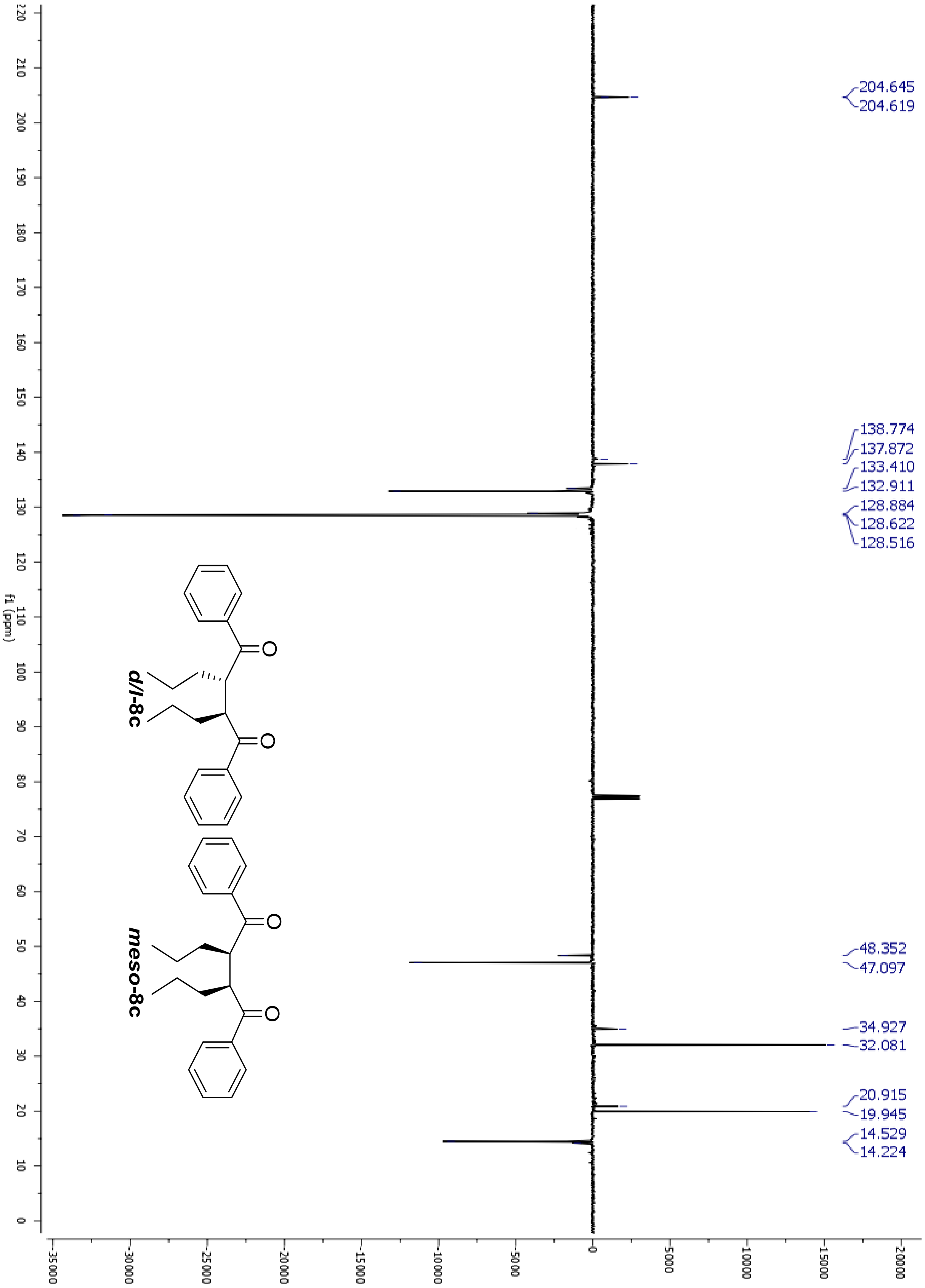
O
O
meso-8a
H2O
grease
4.12
2.09
4.04
2.02
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

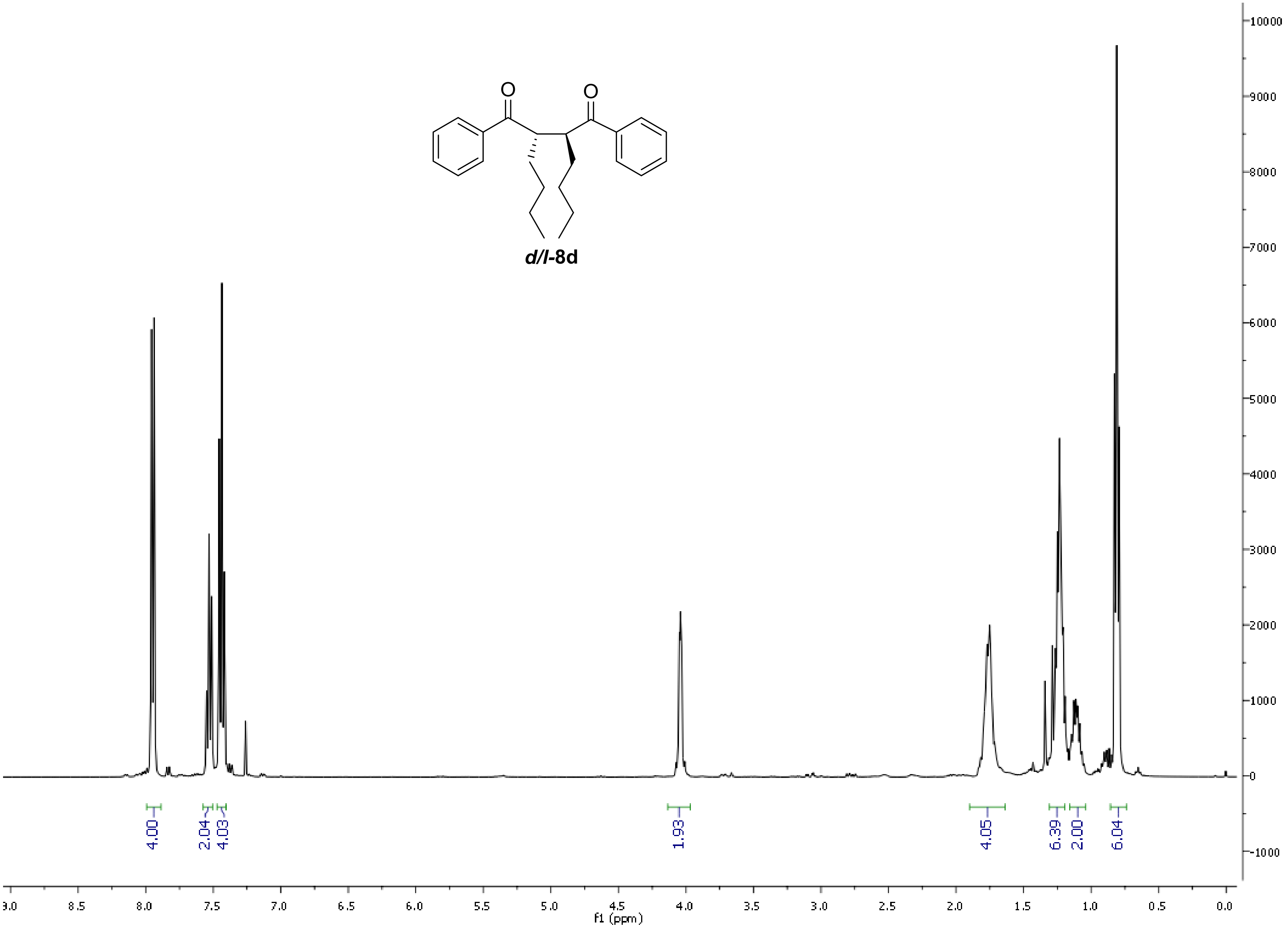

meso-8a
203.869
136.990
133.463
128.907
128.602
43.456
17.613
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-6000
-5500
-5000
-4500
-4000
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
500
1000
1500


meso-8b
d/l-8b
meso-8b
0.34
4.00
0.19
2.34
4.00
2.22
4.08
0.36
0.26
6.03
0.51
f1 (ppm)
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
0
5000
10000
15000
20000
25000
O
O
O
O


204.47
204.39
138.68
137.70
133.46
132.93
128.90
128.66
128.53
49.21
46.84
25.60
22.29
11.90
10.53
O
O
O
O
d/l-8b
meso-8b
f1 (ppm)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
-4000
-4500
-5000
-5500

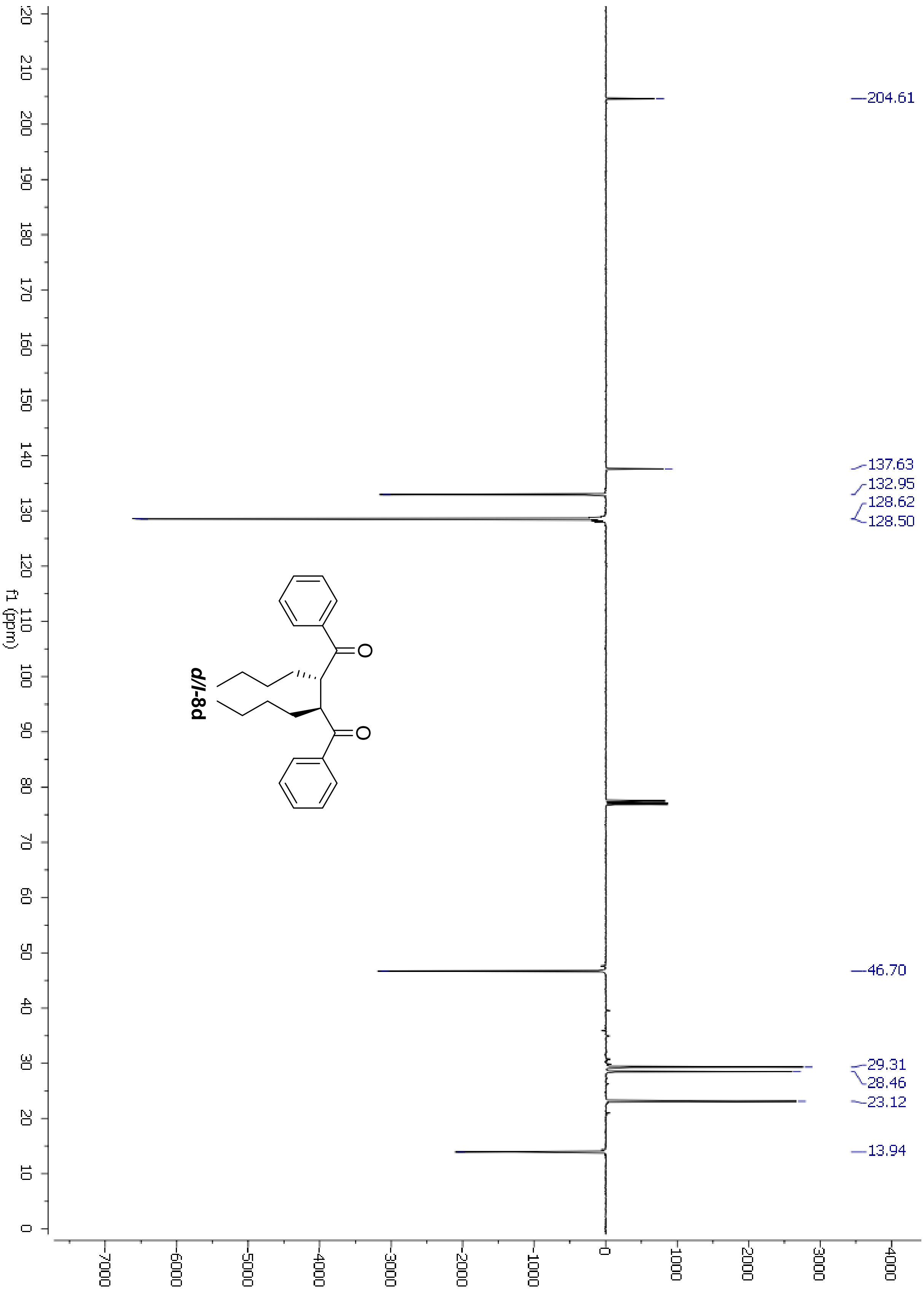

meso-8c
d/l-8c
meso-8c
f1 (ppm)
0.53
4.00
0.41
2.45
4.51
2.20
5.00
3.49
3.26
6.70
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-200
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100


204.645
204.619
138.774
137.872
133.410
132.911
128.884
128.622
128.516
48.352
47.097
34.927
32.081
20.915
19.945
14.529
14.224
f1 (ppm)
d/l-8c
meso-8c

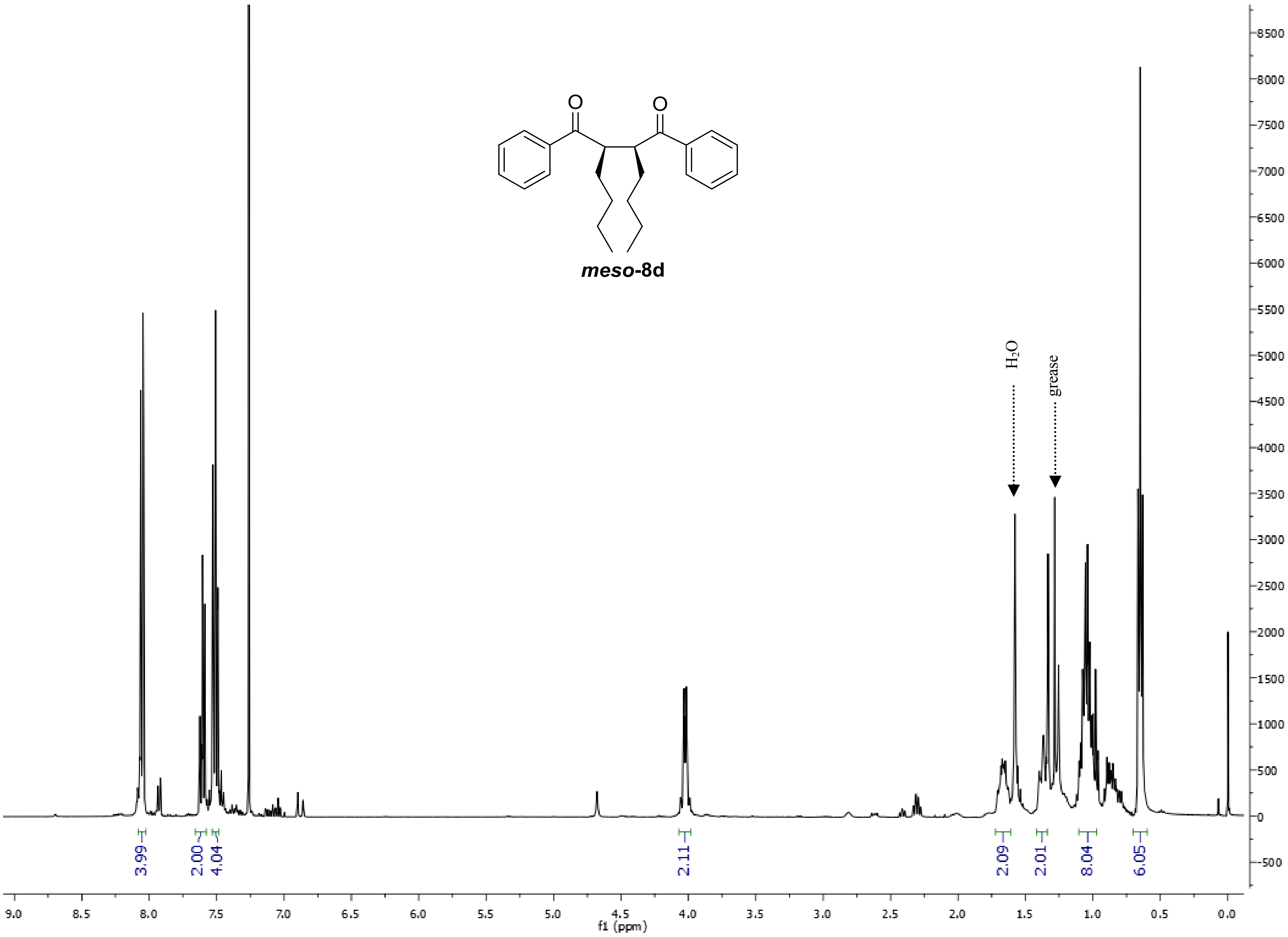


d/l-**8d**

O
O
4.00
2.04
4.03
1.93
4.05
6.39
2.00
6.04
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
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

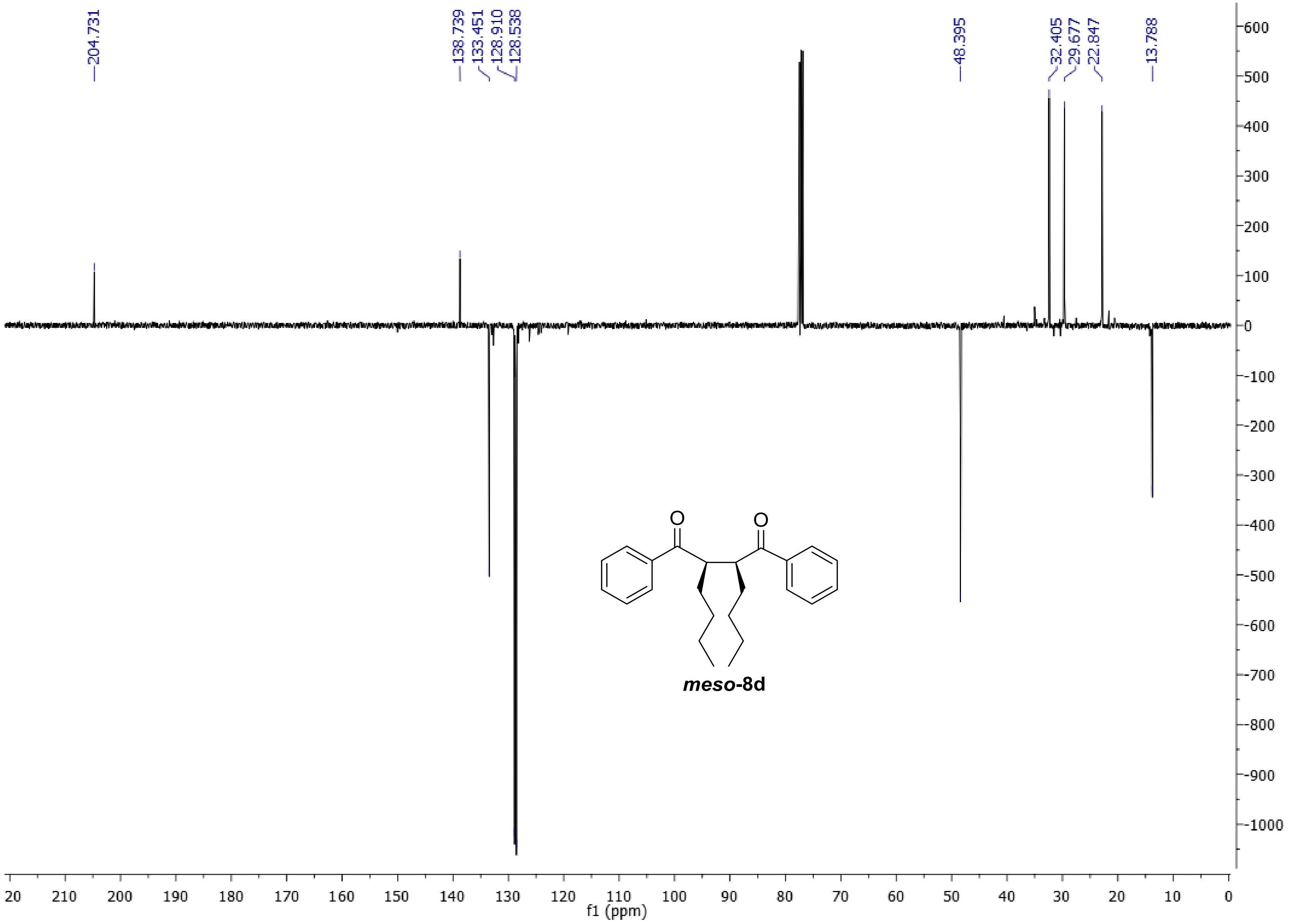


—204.61
137.63
132.95
128.62
128.50
—46.70
29.31
28.46
—23.12
—13.94
d/l-8d
O
O
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-7000
-6000
-5000
-4000
-3000
-2000
-1000
0
1000
2000
3000
4000

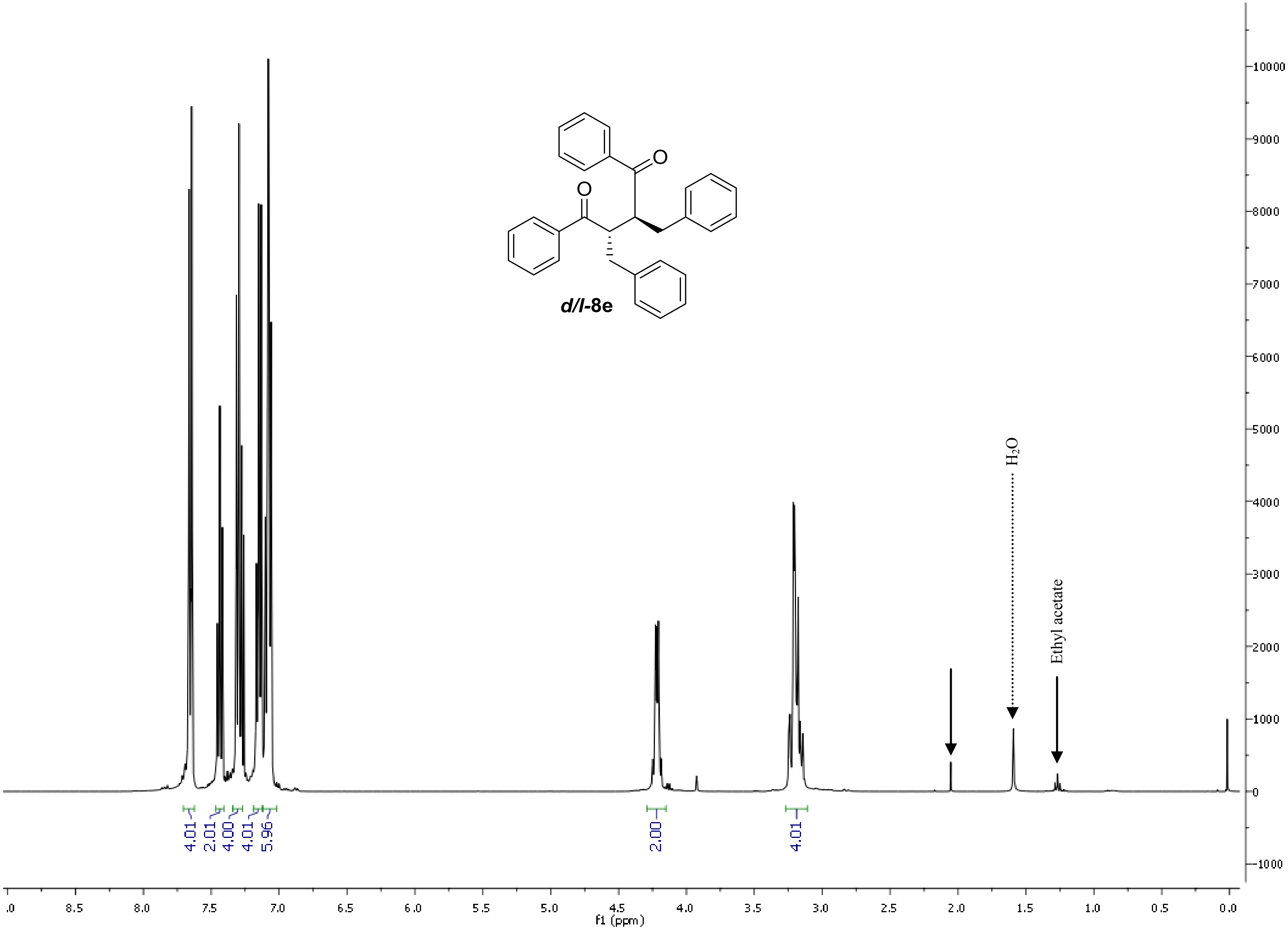


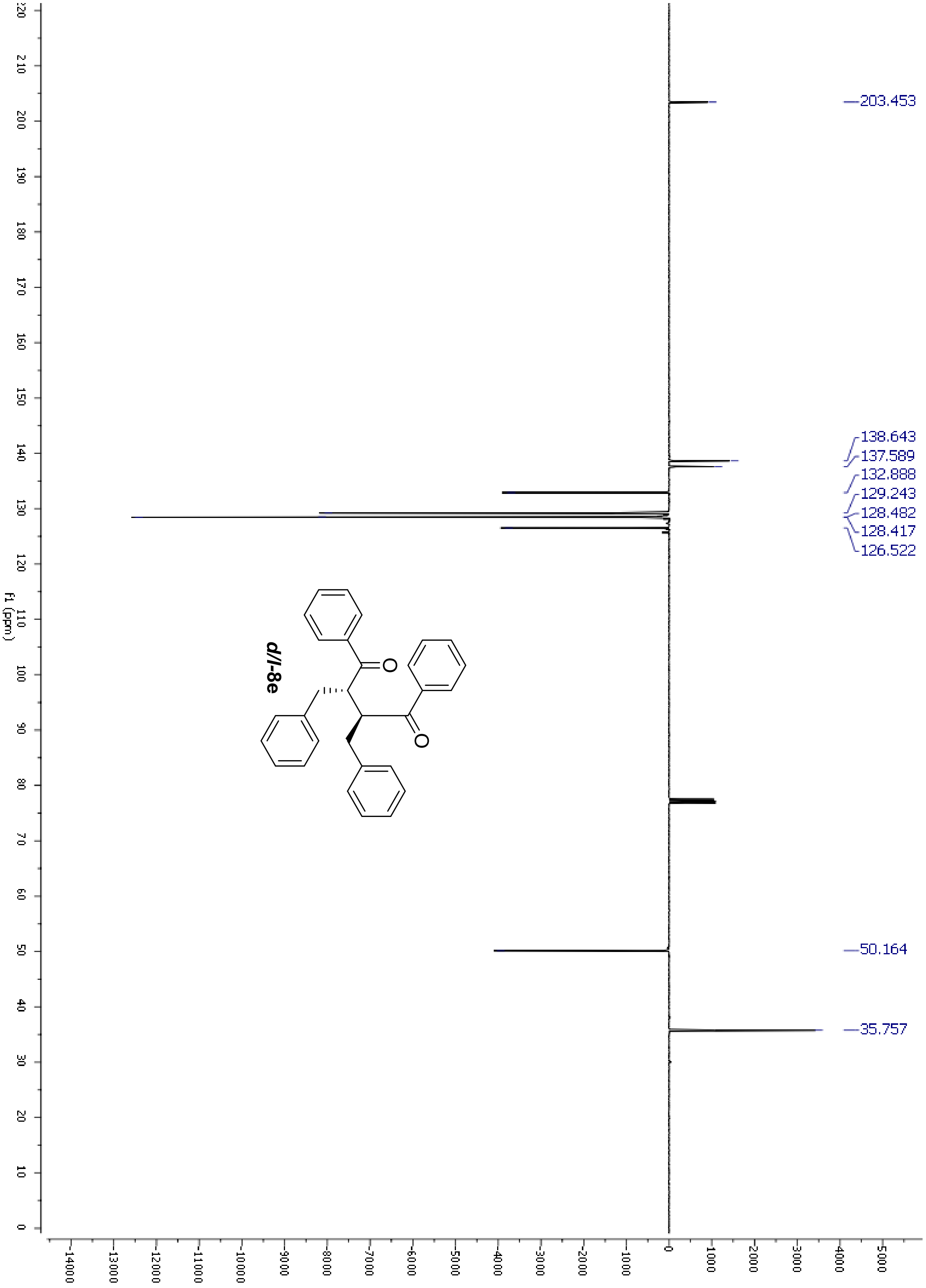
***meso*-8d**

O
O
H$_2$O
grease
3.99
2.00
4.04
2.11
2.09
2.01
8.04
6.05
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
f1 (ppm)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


204.731
138.739
133.451
128.910
128.538
48.395
32.405
29.677
22.847
13.788
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000

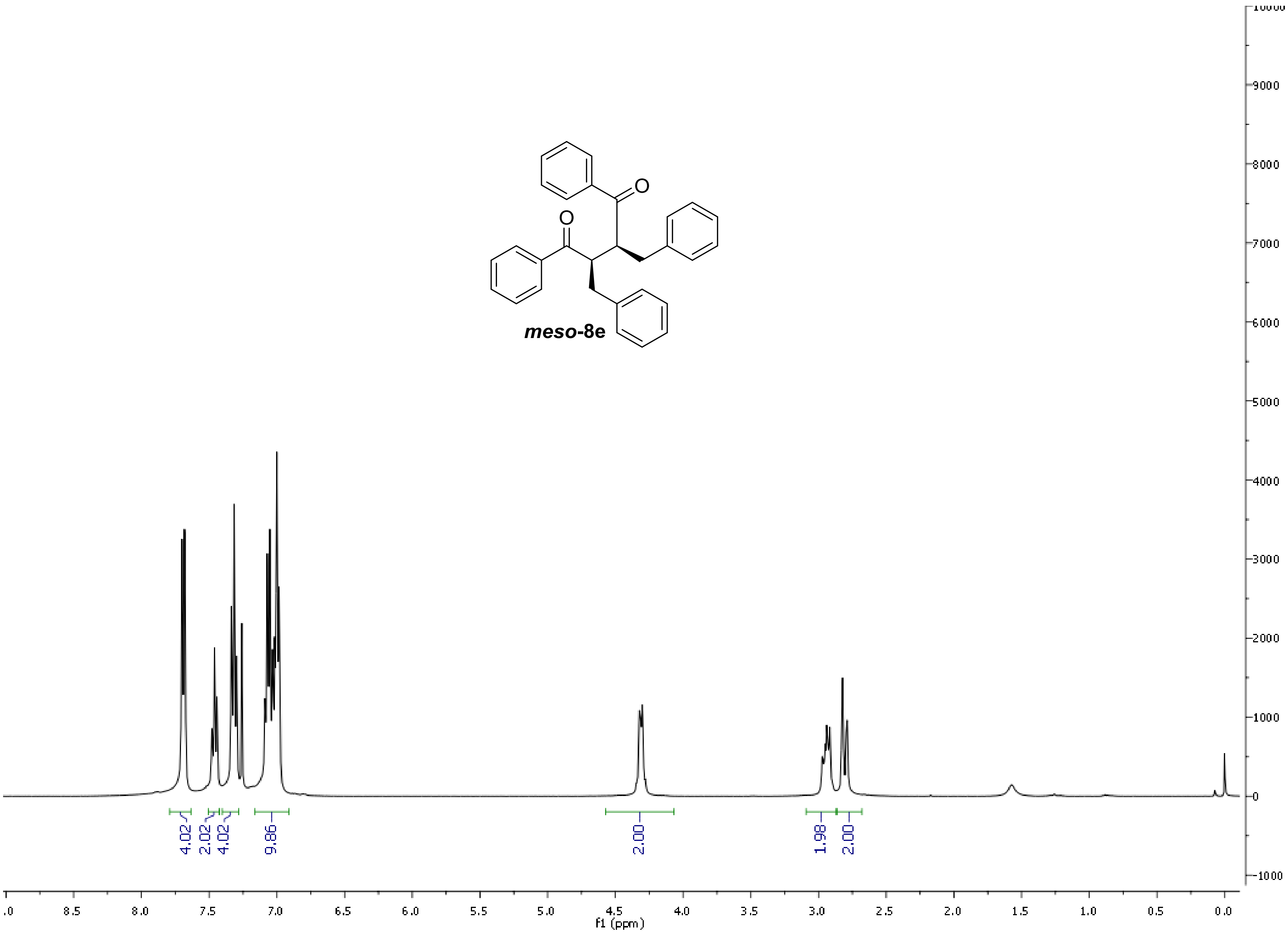
***meso*-8d**


d/l-8e
H2O
Ethyl acetate
4.01
2.01
4.00
4.01
5.96
2.00
4.01
f1 (ppm)
.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
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

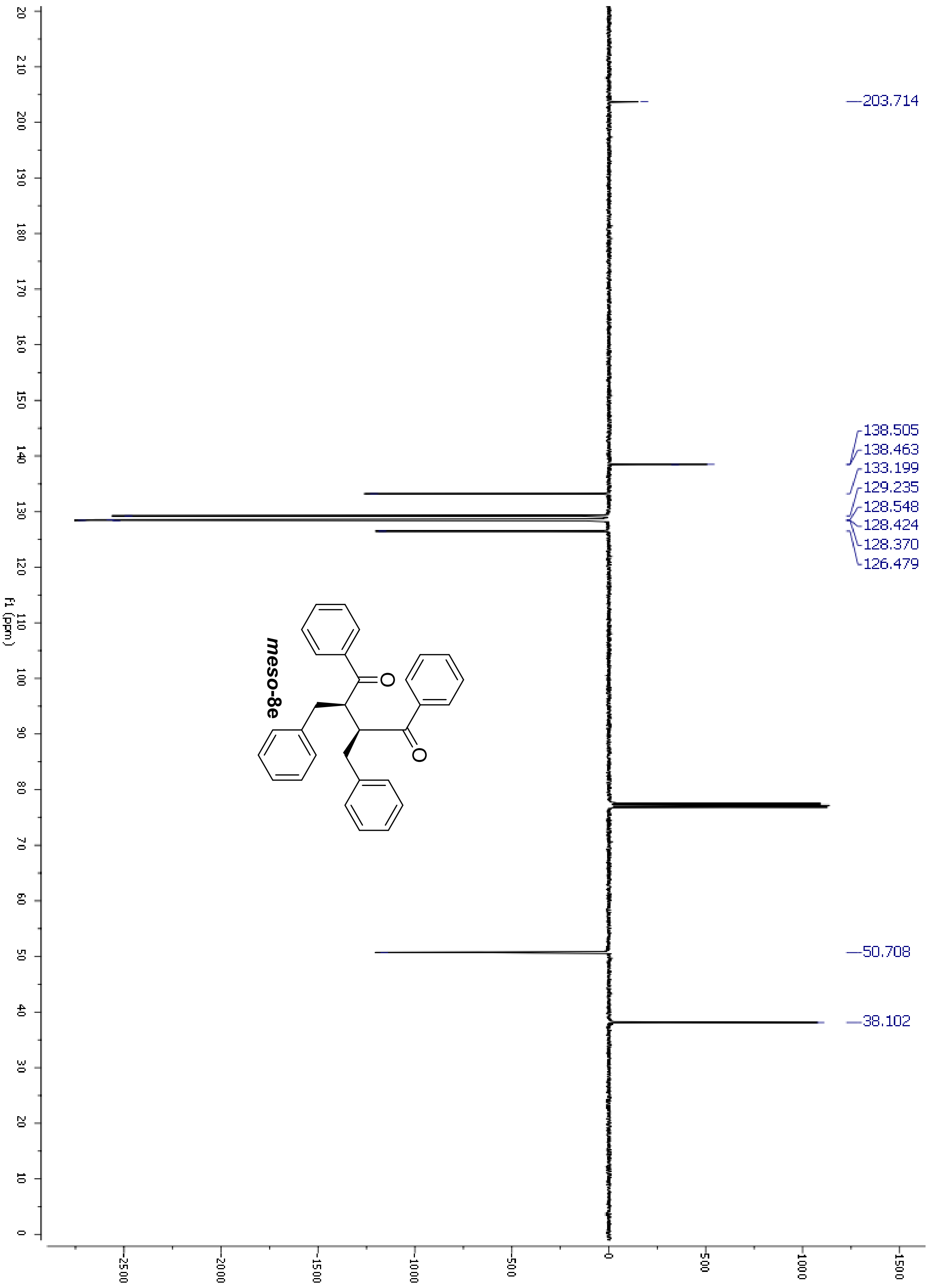


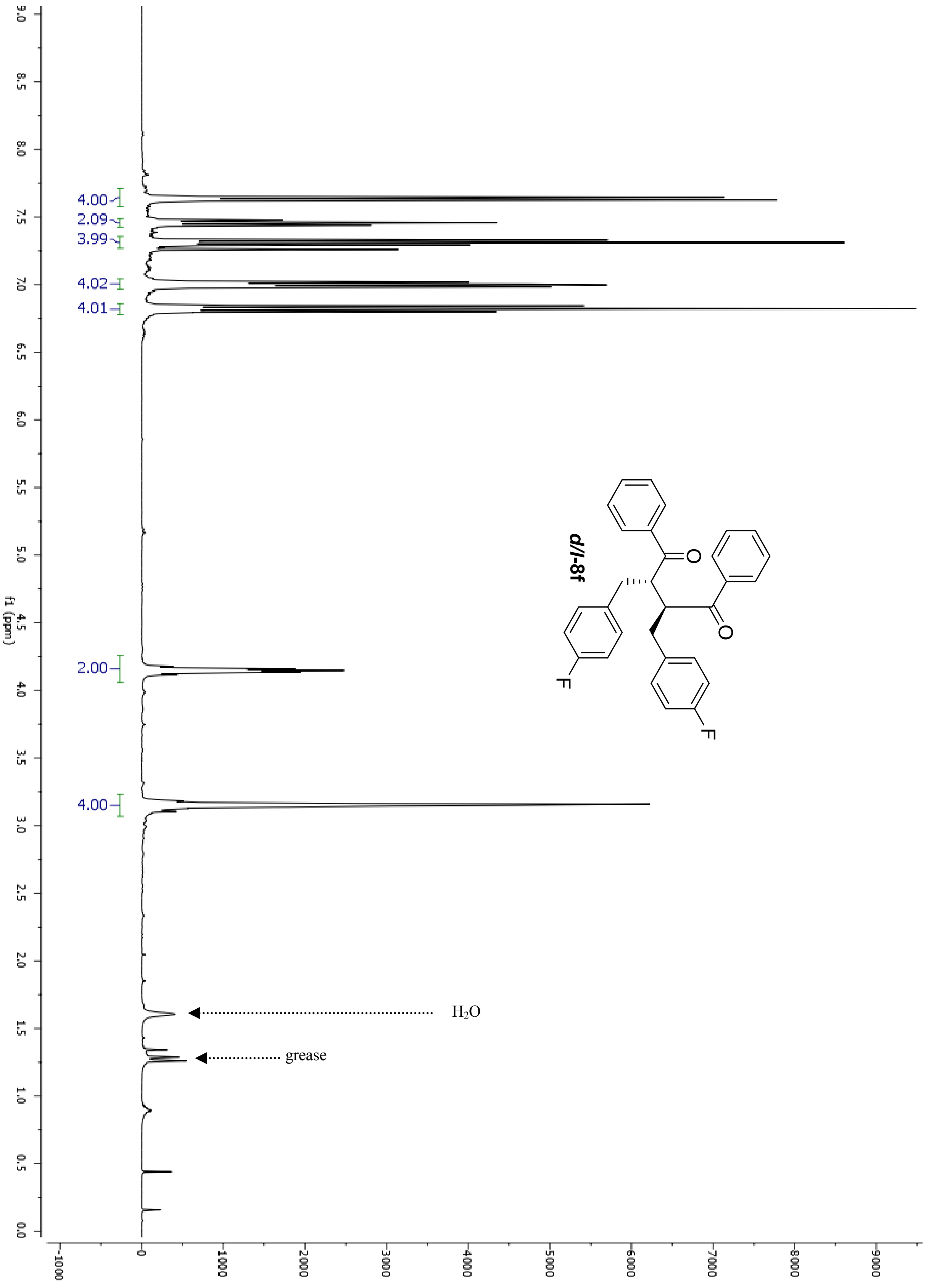
d/l-8e

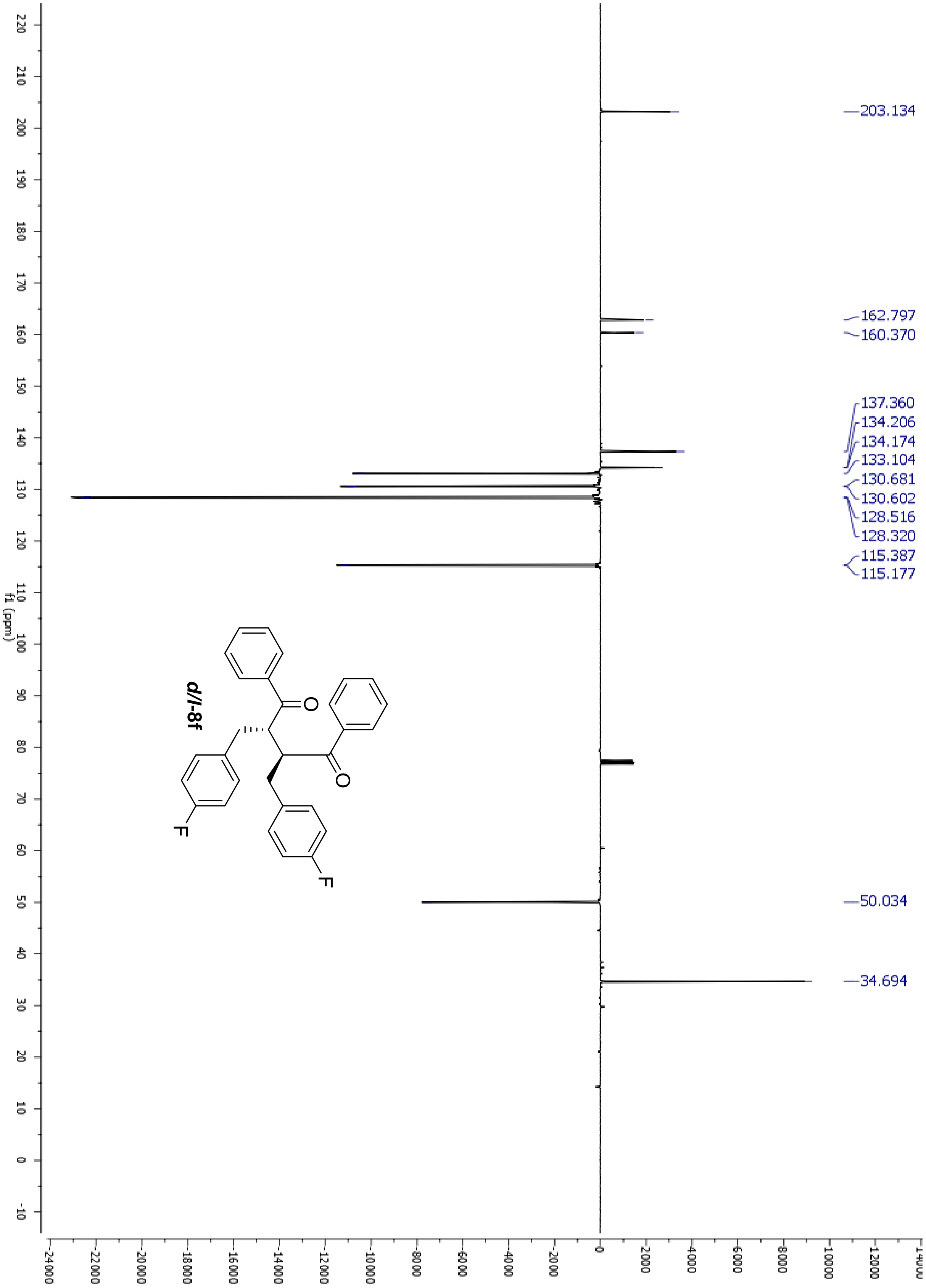
203.453
138.643
137.589
132.888
129.243
128.482
128.417
126.522
50.164
35.757
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-14000
-13000
-12000
-11000
-10000
-9000
-8000
-7000
-6000
-5000
-4000
-3000
-2000
-1000
0
1000
2000
3000
4000
5000
O
O

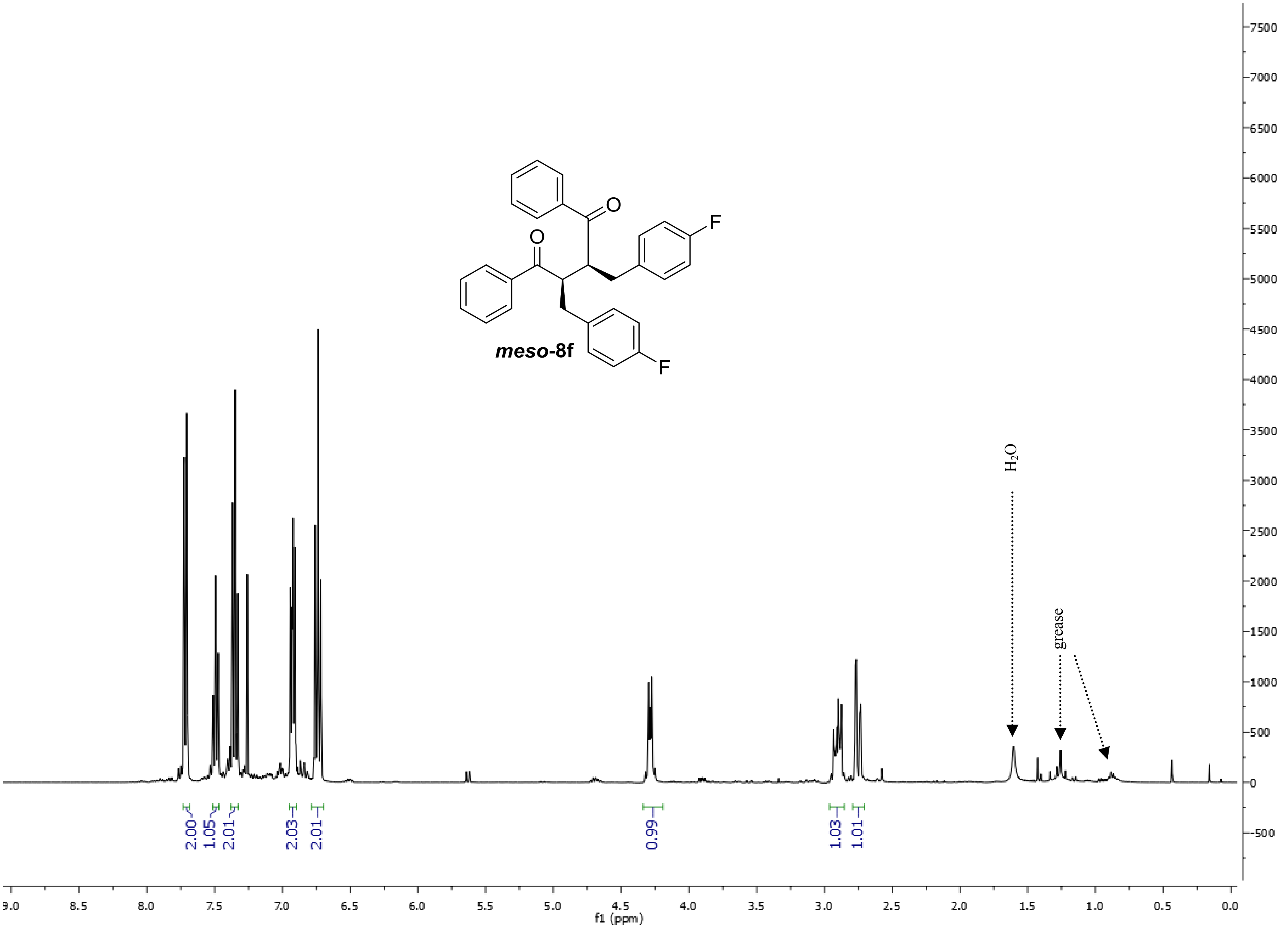

4.02
2.02
4.02
9.86
2.00
1.98
2.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
O
O

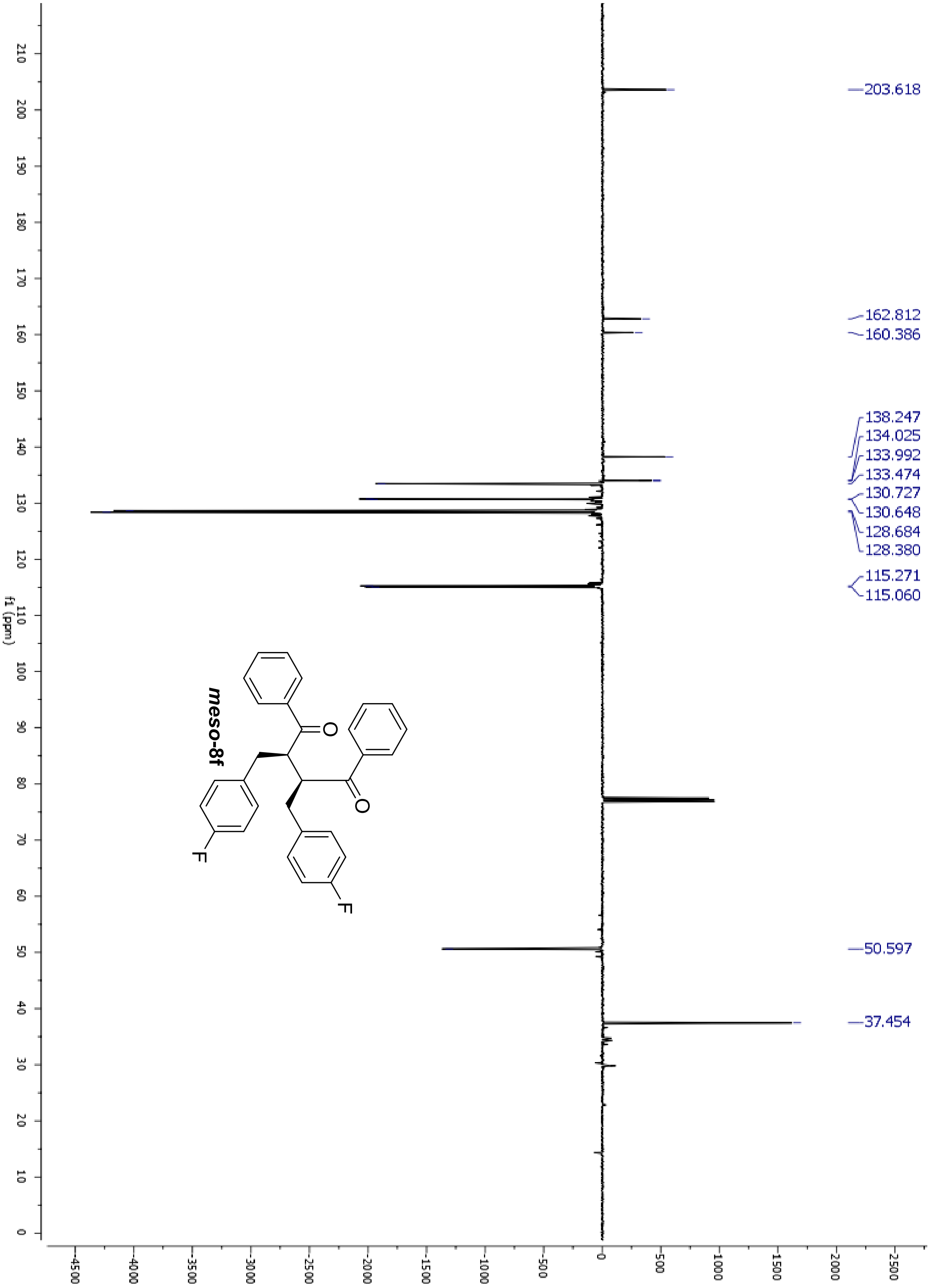
***meso*-8e**

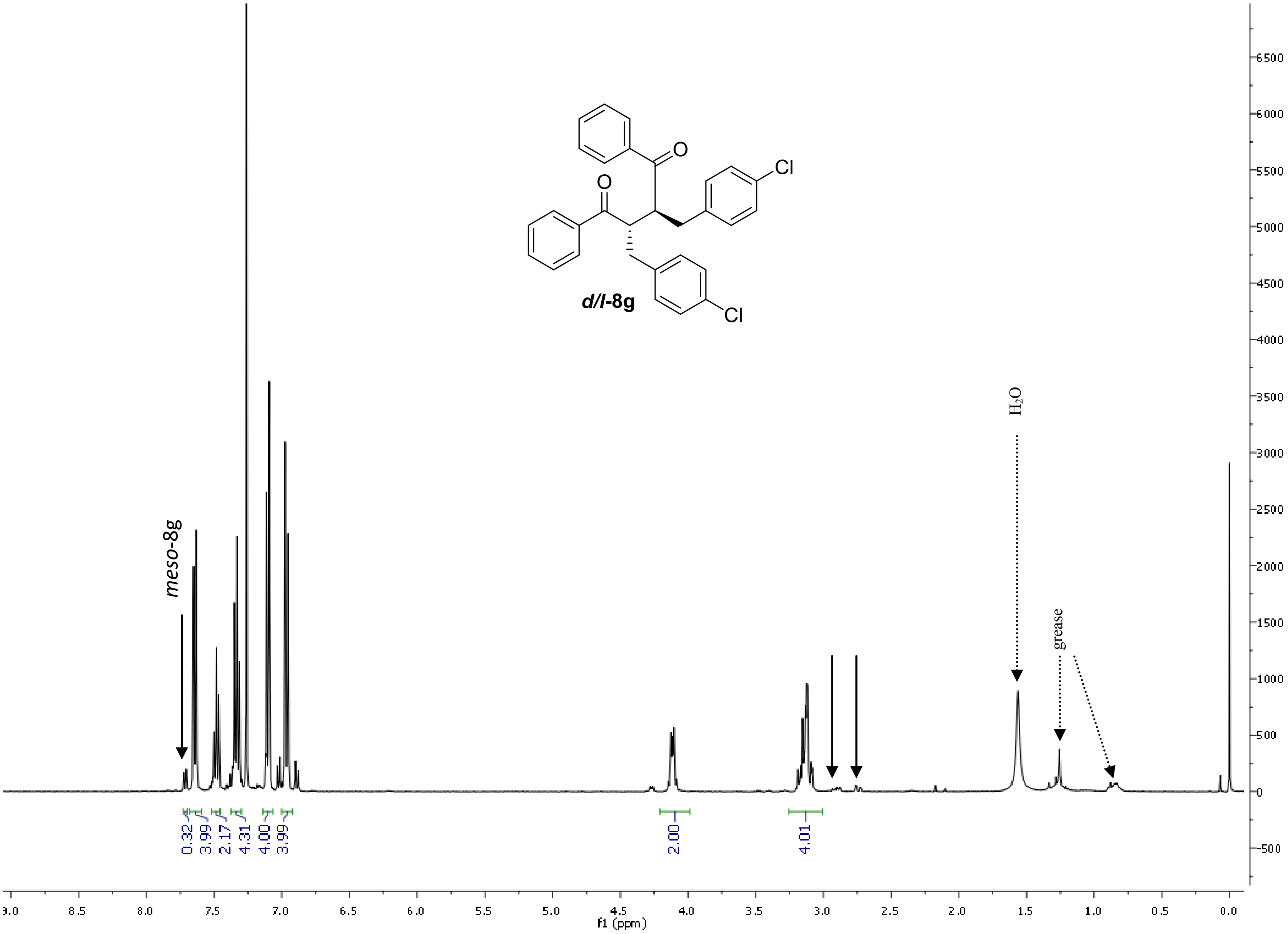

203.714
138.505
138.463
133.199
129.235
128.548
128.424
128.370
126.479
50.708
38.102
meso-8e
O
O
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
-2500
-2000
-1500
-1000
-500
0
500
1000
1500

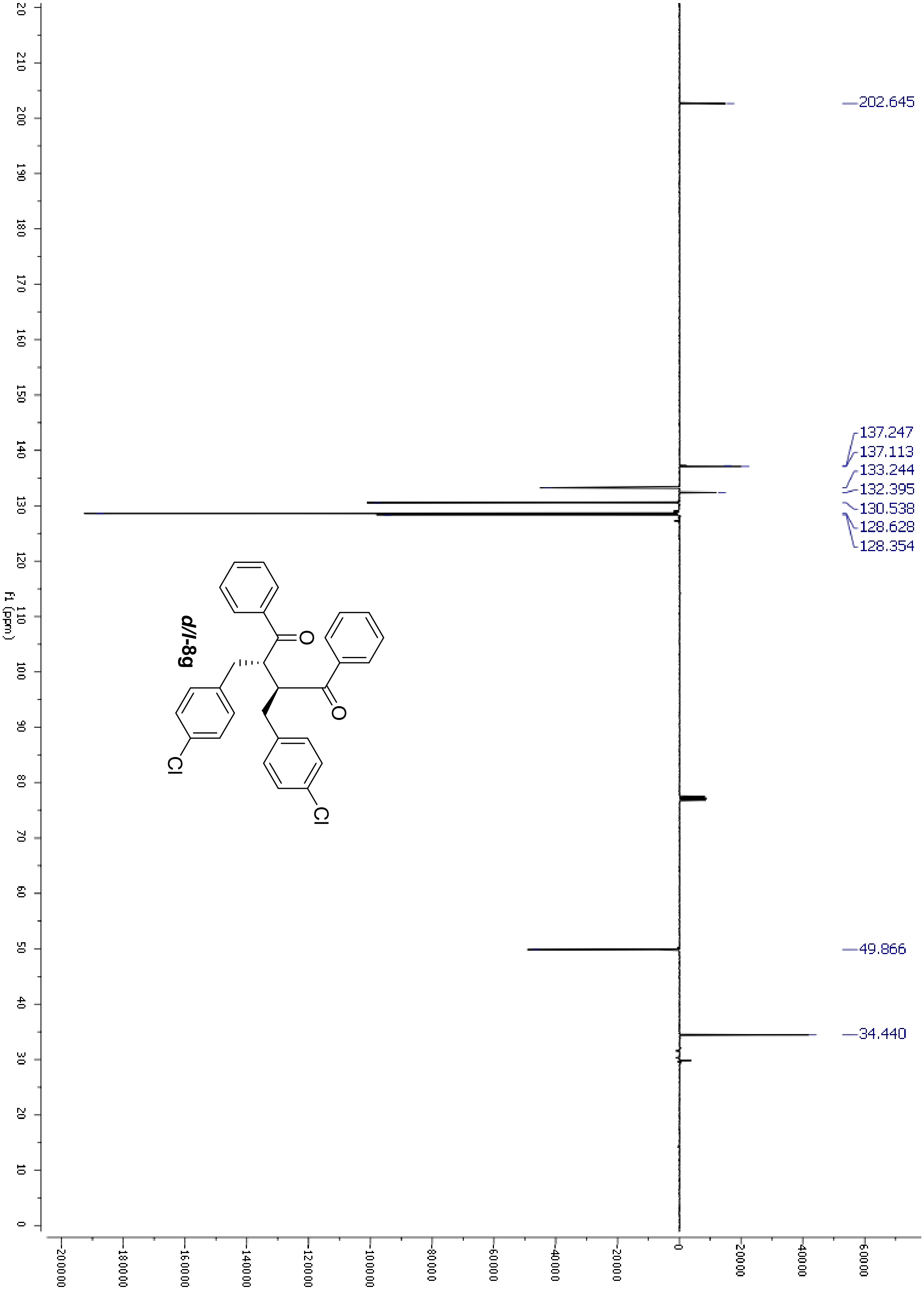

d/l-8f
O
O
F
F
4.00
2.09
3.99
4.02
4.01
2.00
4.00
H2O
grease
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000

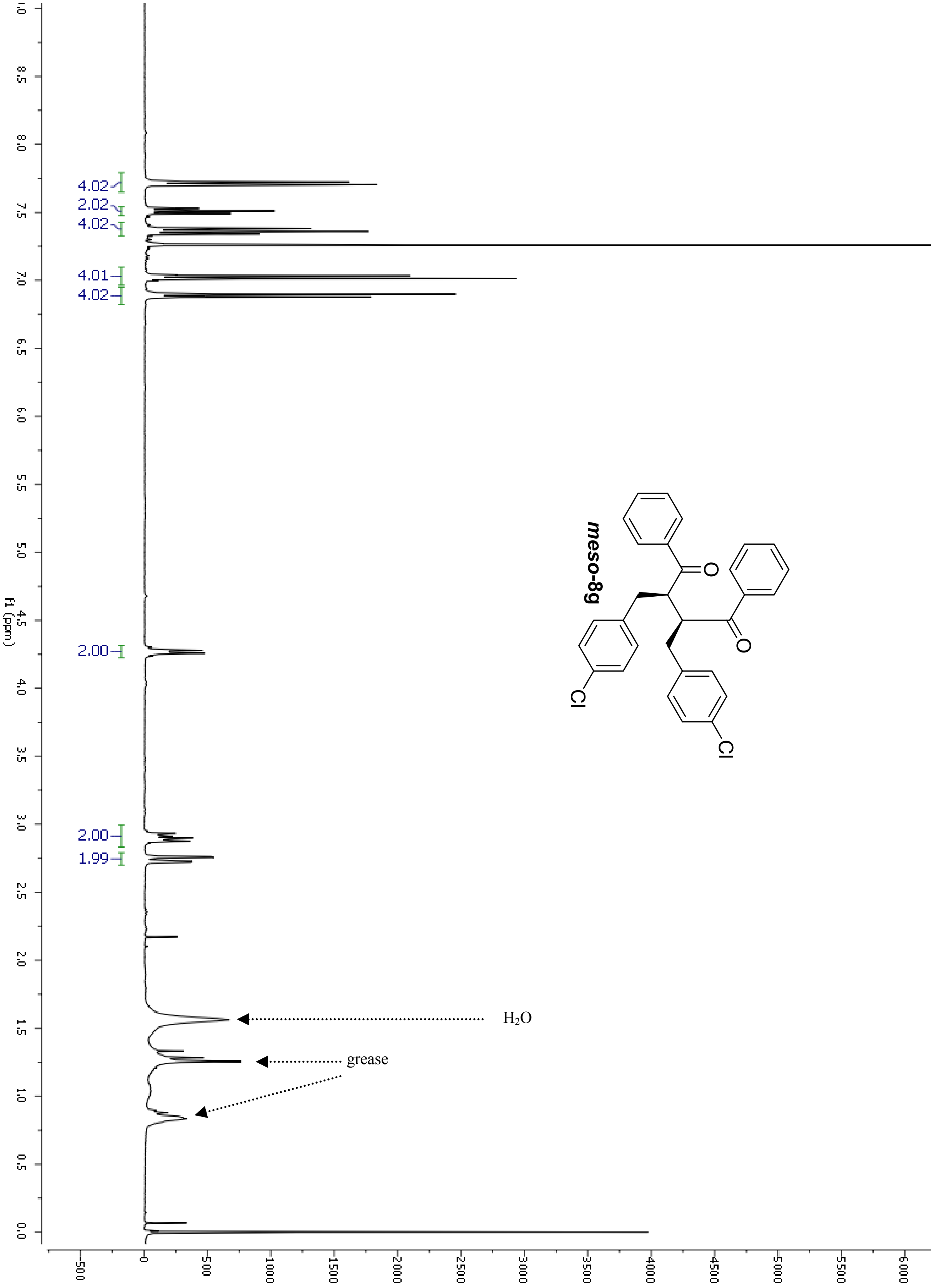

203.134
162.797
160.370
137.360
134.206
134.174
133.104
130.681
130.602
128.516
128.320
115.387
115.177
50.034
34.694
d/l-8f
O
O
F
F
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-24000
-22000
-20000
-18000
-16000
-14000
-12000
-10000
-8000
-6000
-4000
-2000
0
2000
4000
6000
8000
10000
12000
14000


meso-8f
F
F
O
O
H2O
grease
2.00
1.05
2.01
2.03
2.01
0.99
1.03
1.01
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
f1 (ppm)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


meso-8f
203.618
162.812
160.386
138.247
134.025
133.992
133.474
130.727
130.648
128.684
128.380
115.271
115.060
50.597
37.454
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-4500
-4000
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
500
1000
1500
2000
2500
O
O
F
F

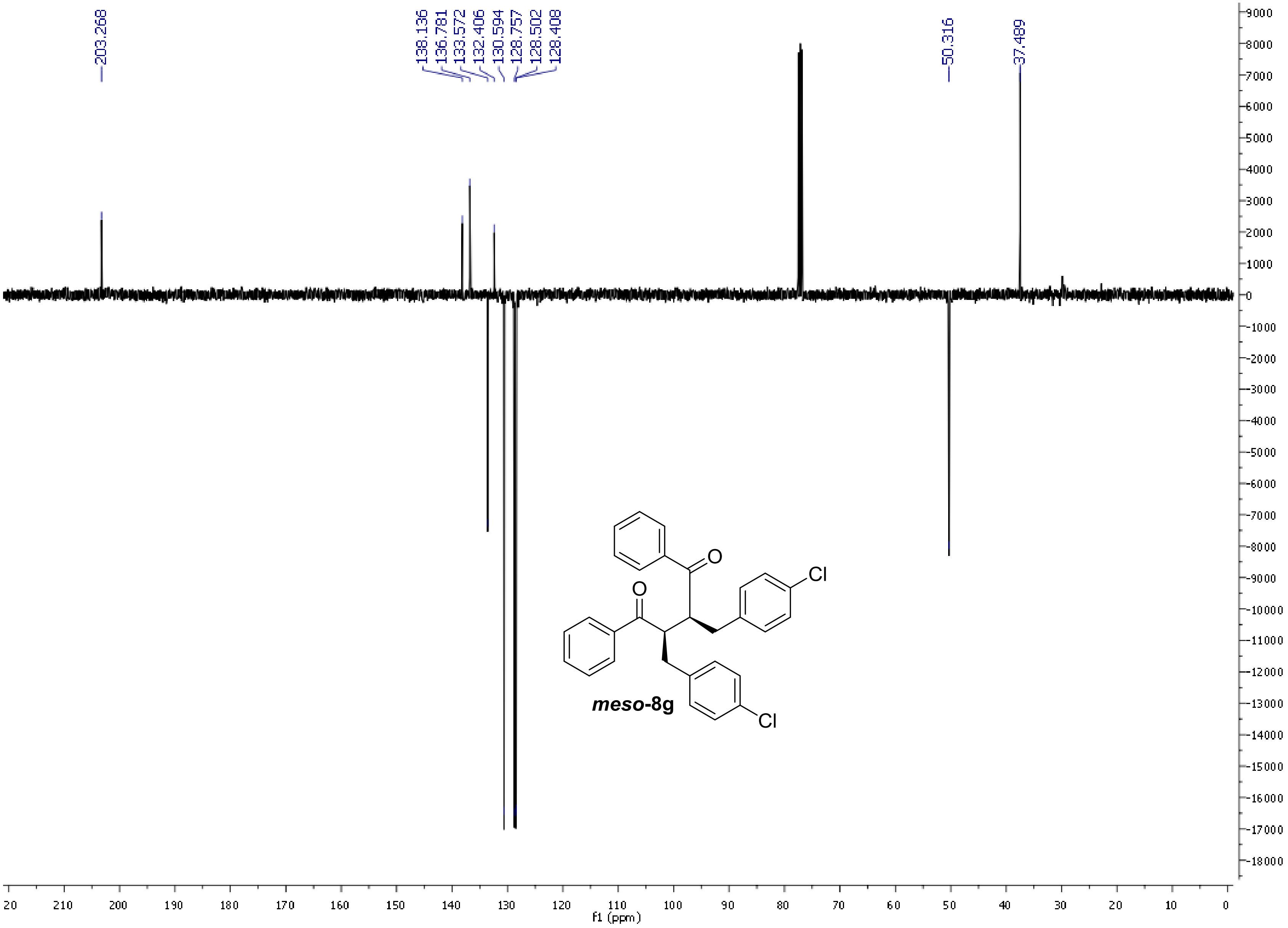

d/l-8g
O
O
Cl
Cl
meso-8g
H2O
grease
0.32
3.99
2.17
4.31
4.00
3.99
2.00
4.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


202.645
137.247
137.113
133.244
132.395
130.538
128.628
128.354
49.866
34.440
d/l-8g
O
O
Cl
Cl
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
-60000

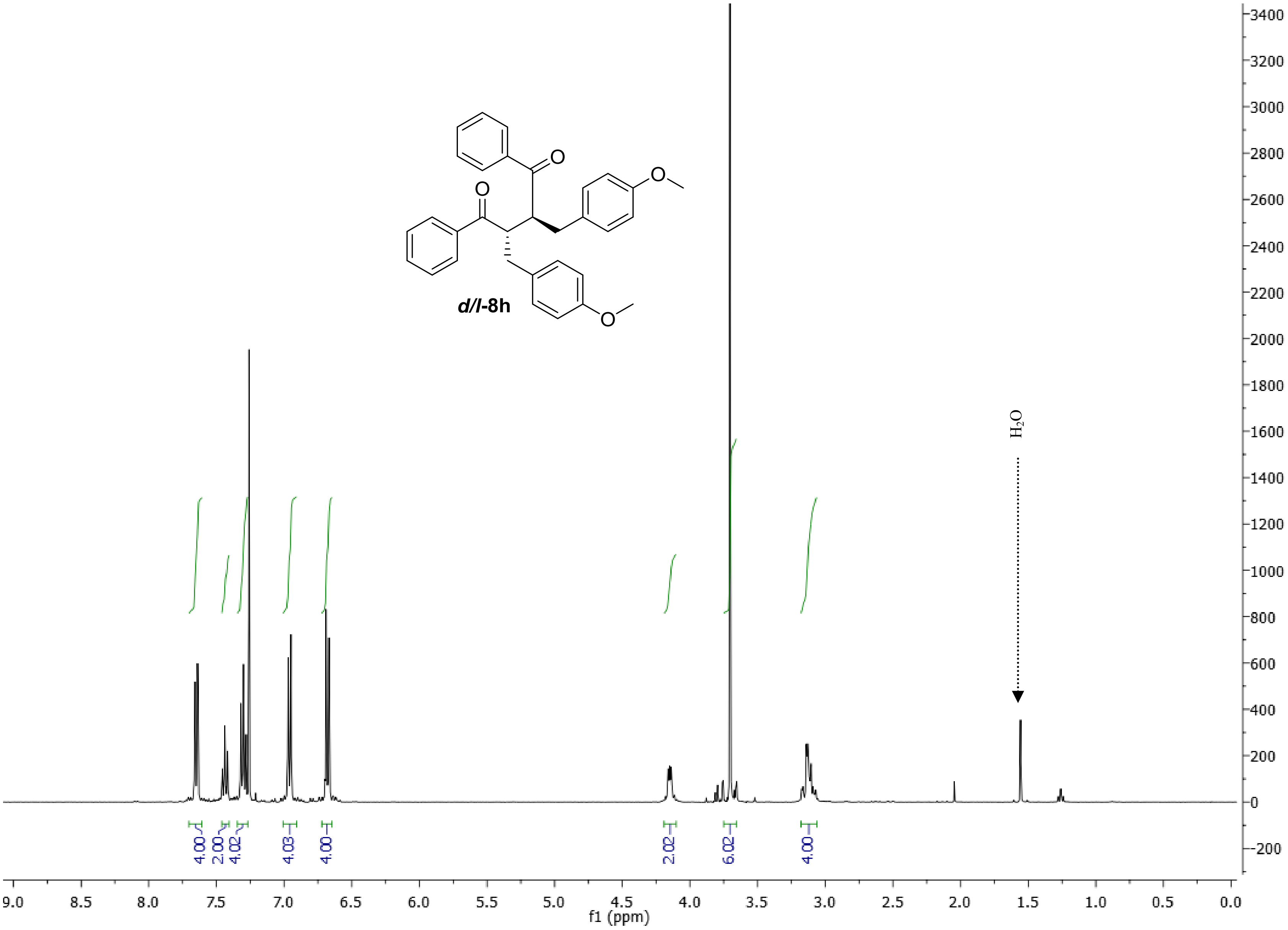


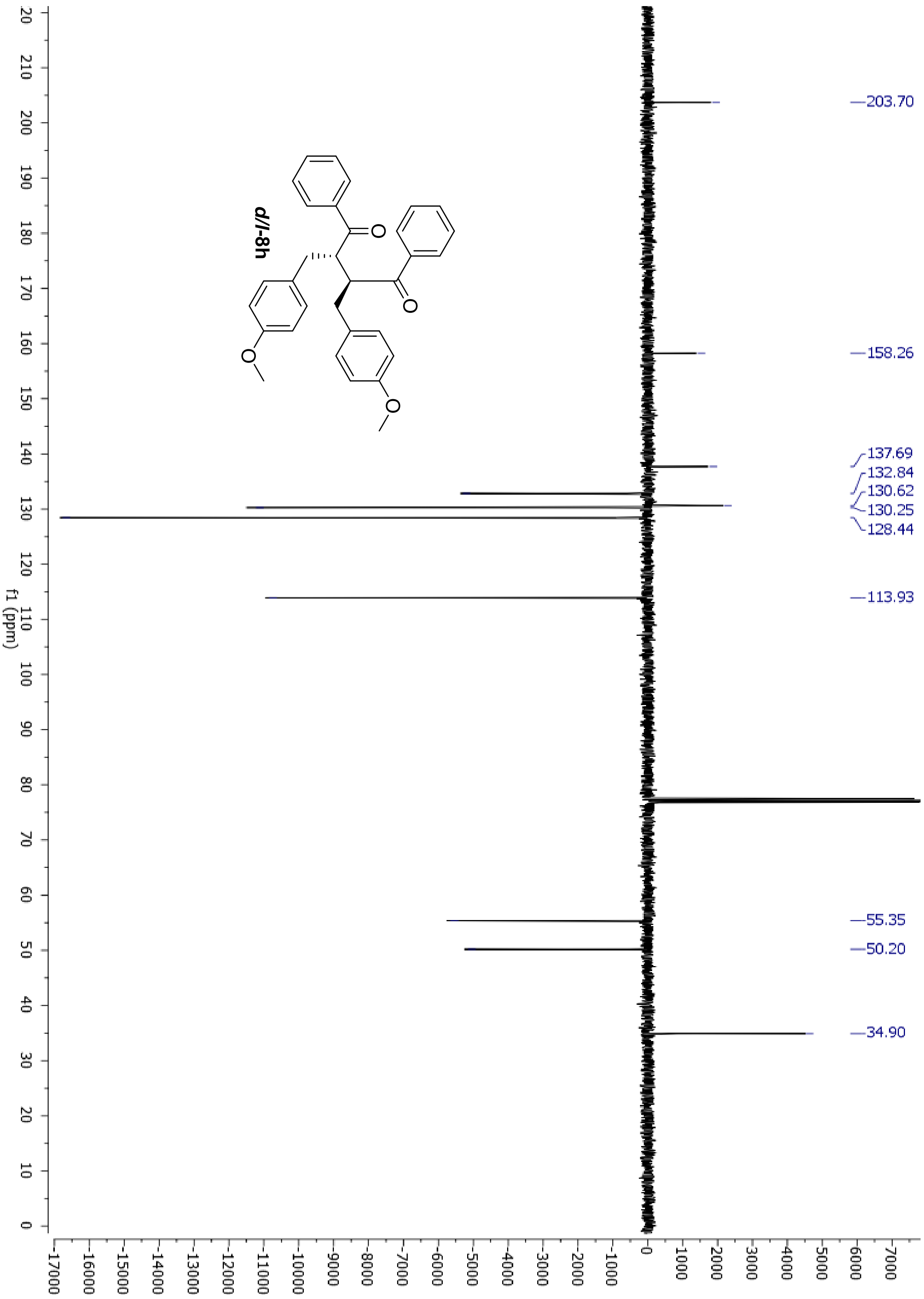
***meso*-8g**

4.02
2.02
4.02
4.01
4.02
2.00
2.00
1.99
H$_2$O
grease
O
O
Cl
Cl
f1 (ppm)
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
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000

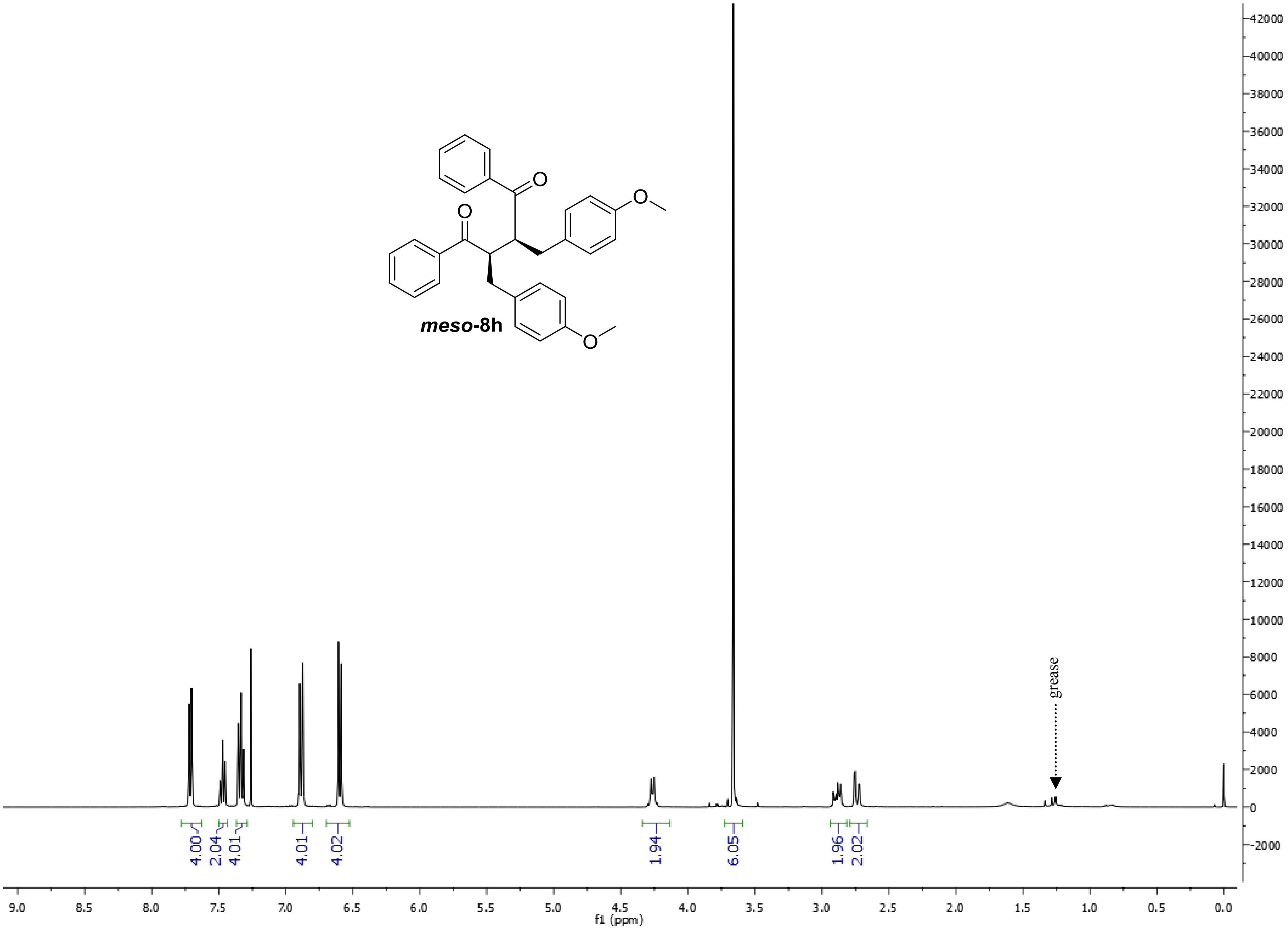

***meso*-8g**

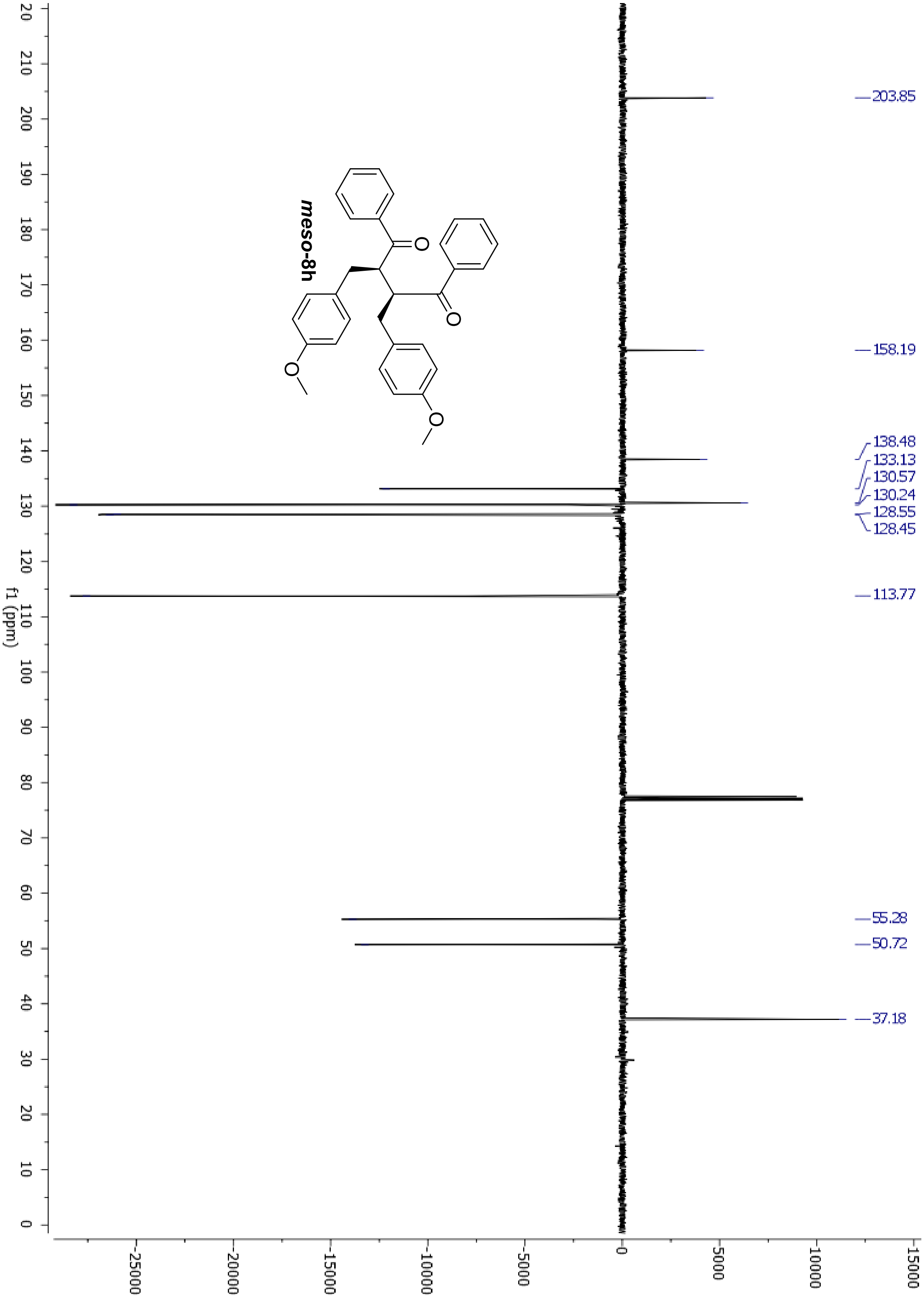
203.268
138.136
136.781
133.572
132.406
130.594
128.757
128.502
128.408
50.316
37.489
O
O
Cl
Cl
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
-7000
-8000
-9000
-10000
-11000
-12000
-13000
-14000
-15000
-16000
-17000
-18000
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

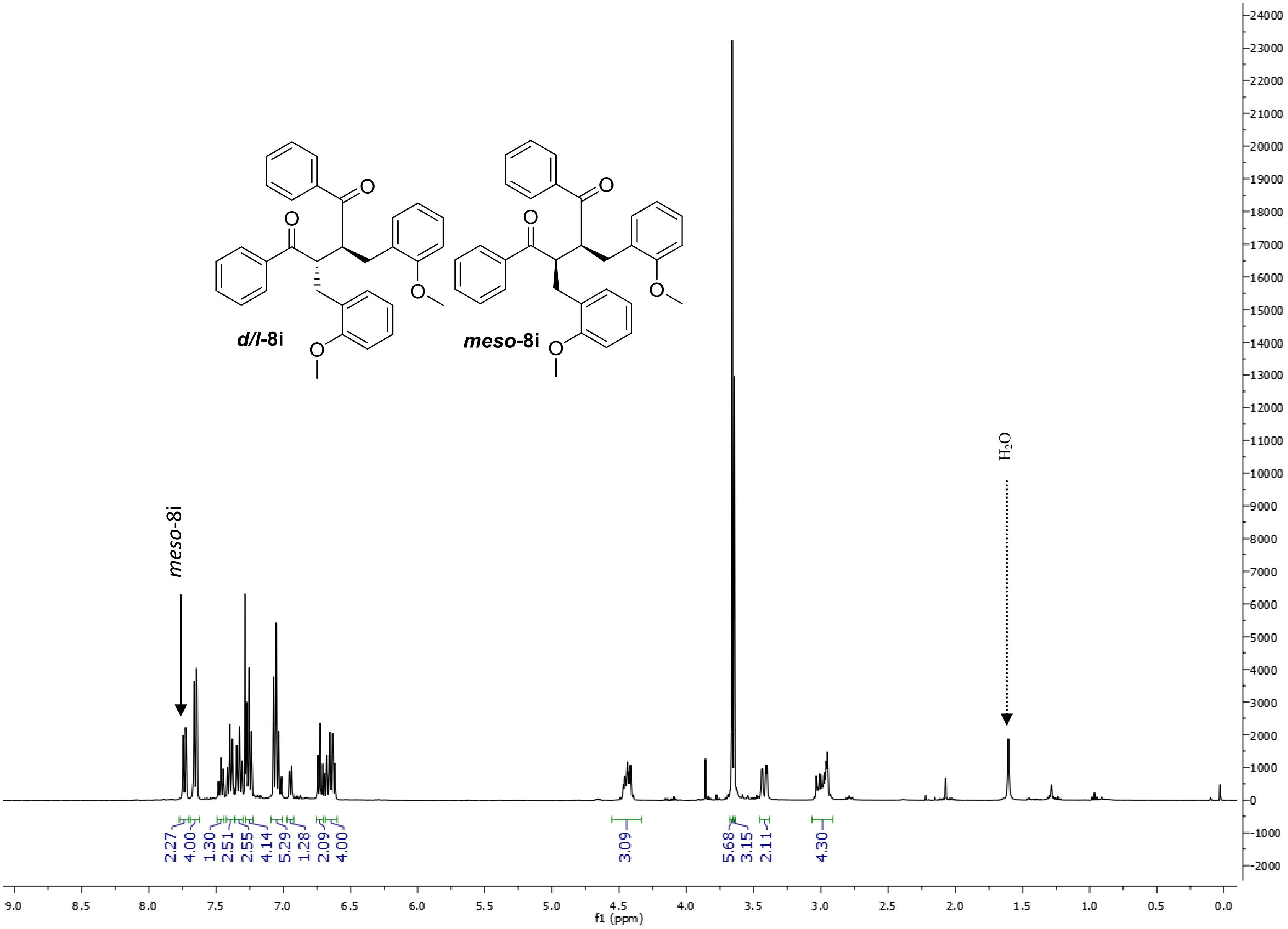

d/l-8h
H₂O
4.00
2.00
4.02
4.03
4.00
2.02
6.02
4.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

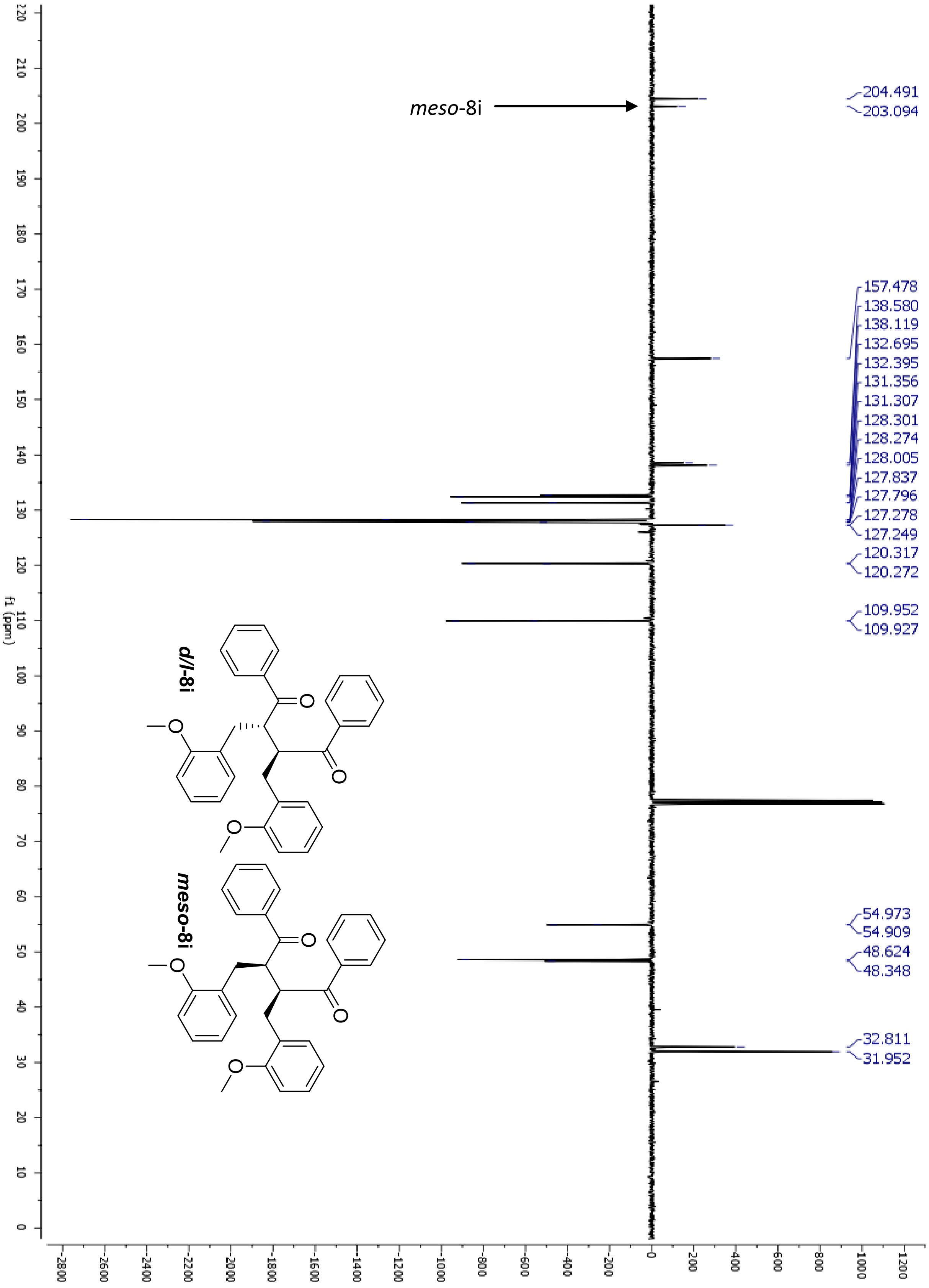


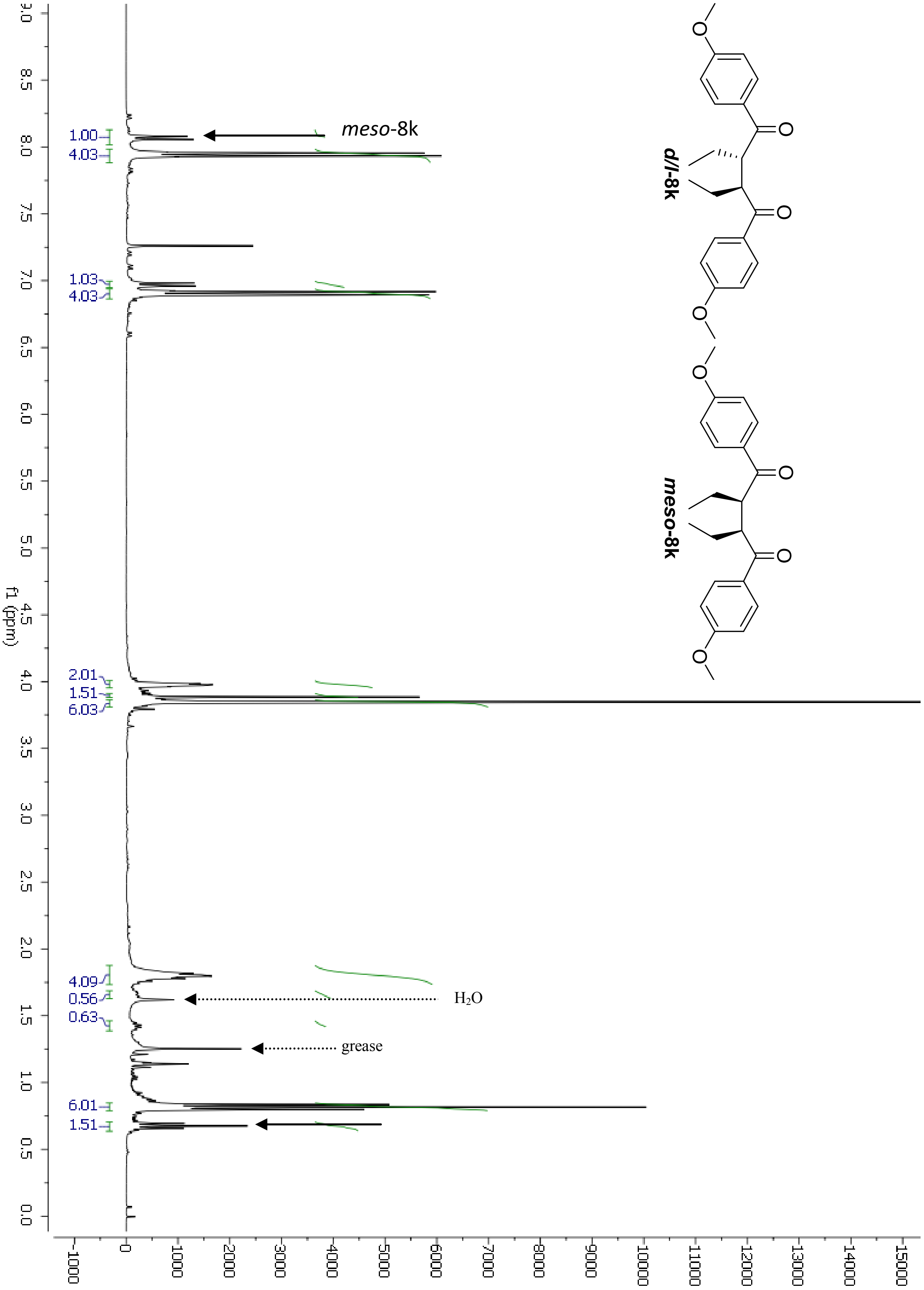
d/l-8h
203.70
158.26
137.69
132.84
130.62
130.25
128.44
113.93
55.35
50.20
34.90
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-17000
-16000
-15000
-14000
-13000
-12000
-11000
-10000
-9000
-8000
-7000
-6000
-5000
-4000
-3000
-2000
-1000
0
1000
2000
3000
4000
5000
6000
7000

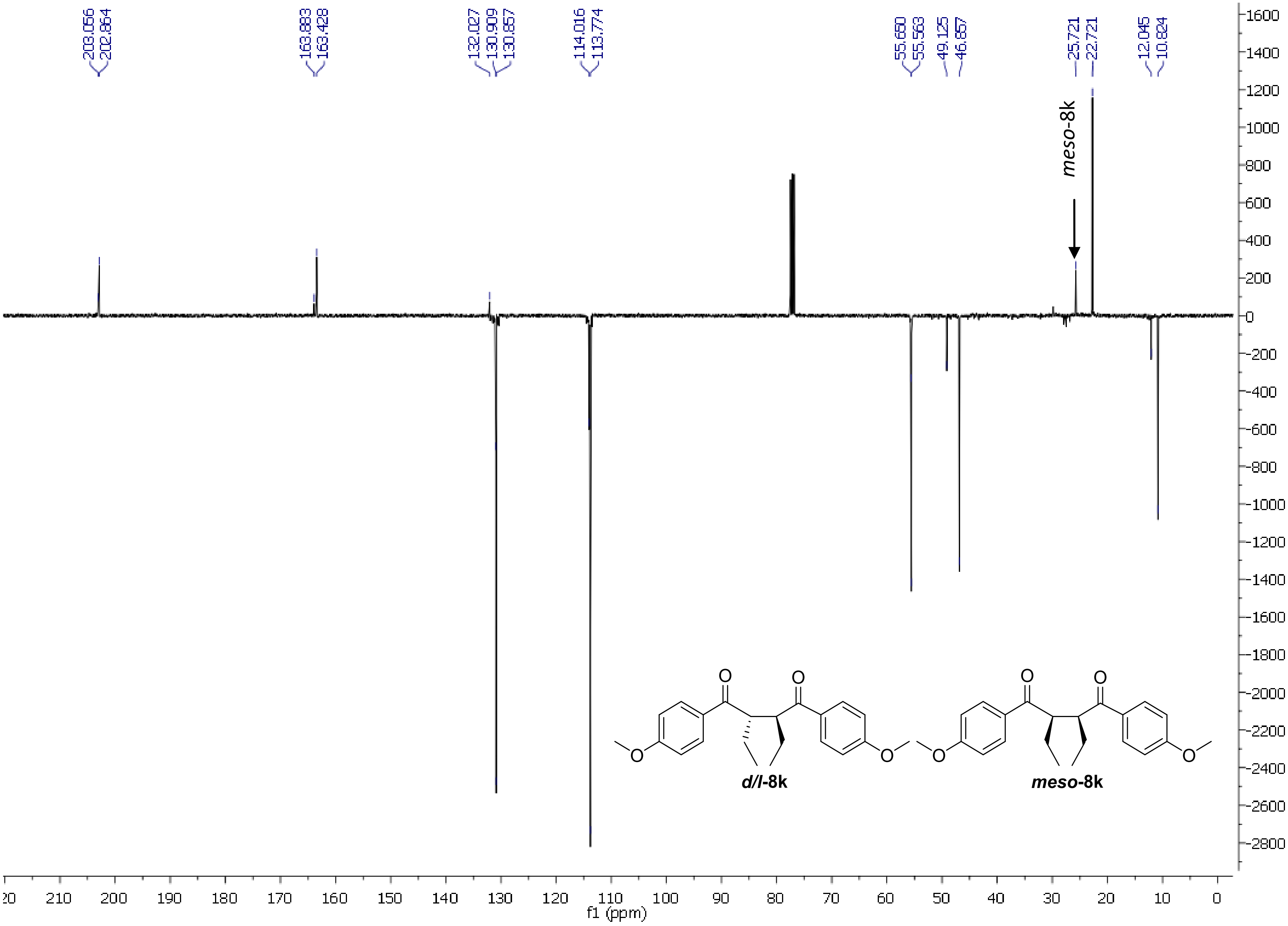

meso-8h
grease
4.00
2.04
4.01
4.01
4.02
1.94
6.05
1.96
2.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
42000
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

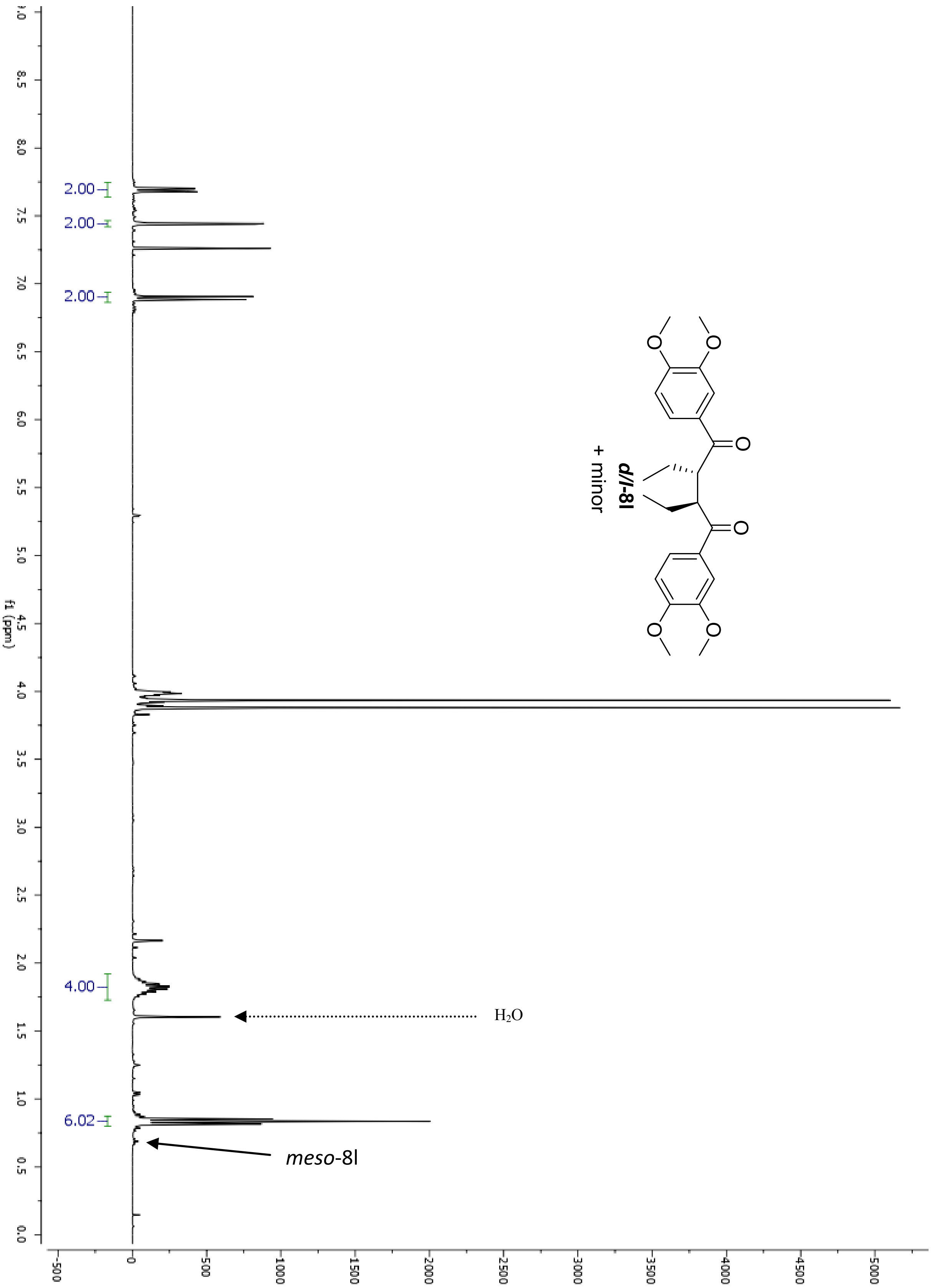

meso-8h
203.85
158.19
138.48
133.13
130.57
130.24
128.55
128.45
113.77
55.28
50.72
37.18
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-25000
-20000
-15000
-10000
-5000
0
5000
10000
15000

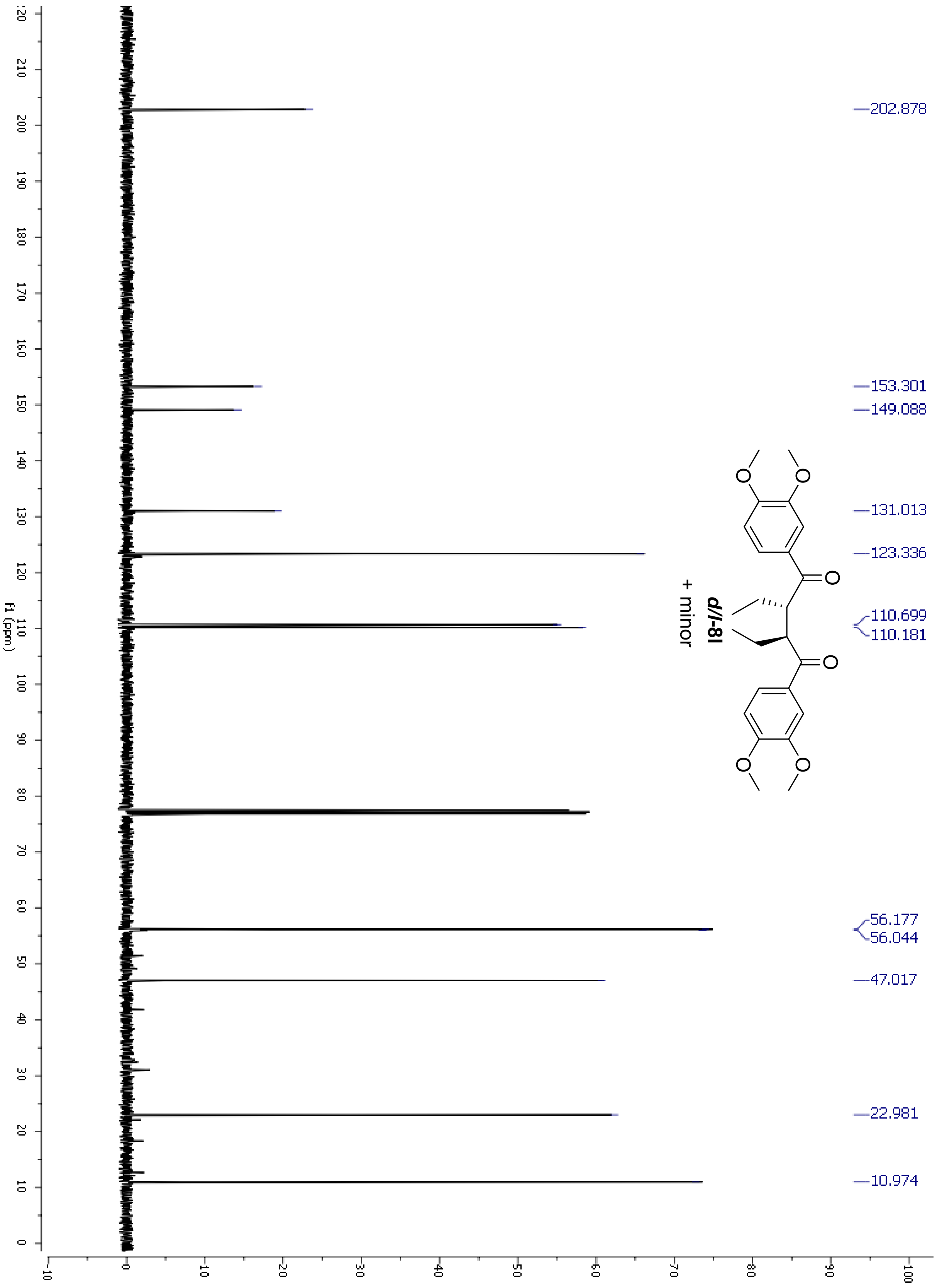

d/l-8i
meso-8i
meso-8i
H2O
2.27
4.00
1.30
2.51
2.55
4.14
5.29
1.28
2.09
4.00
3.09
5.68
3.15
2.11
4.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

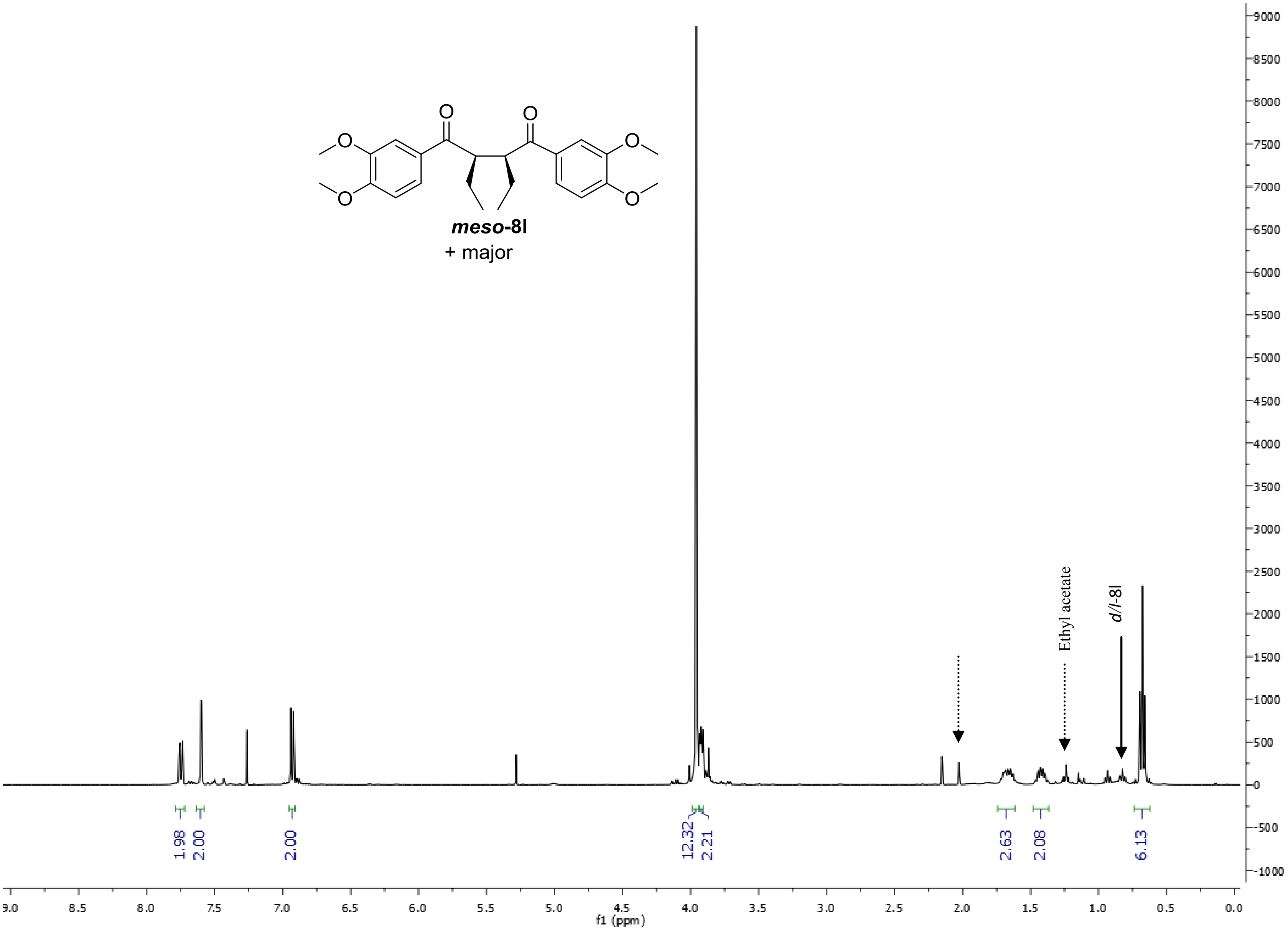

meso-8i
204.491
203.094
157.478
138.580
138.119
132.695
132.395
131.356
131.307
128.301
128.274
128.005
127.837
127.796
127.278
127.249
120.317
120.272
109.952
109.927
54.973
54.909
48.624
48.348
32.811
31.952
d/l-8i
meso-8i
O
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-2800
-2600
-2400
-2200
-2000
-1800
-1600
-1400
-1200
-1000
-800
-600
-400
-200
0
200
400
600
800
1000
1200


d/l-8k
meso-8k
meso-8k
H2O
grease
1.00
4.03
1.03
4.03
2.01
1.51
6.03
4.09
0.56
0.63
6.01
1.51
f1 (ppm)
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
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000

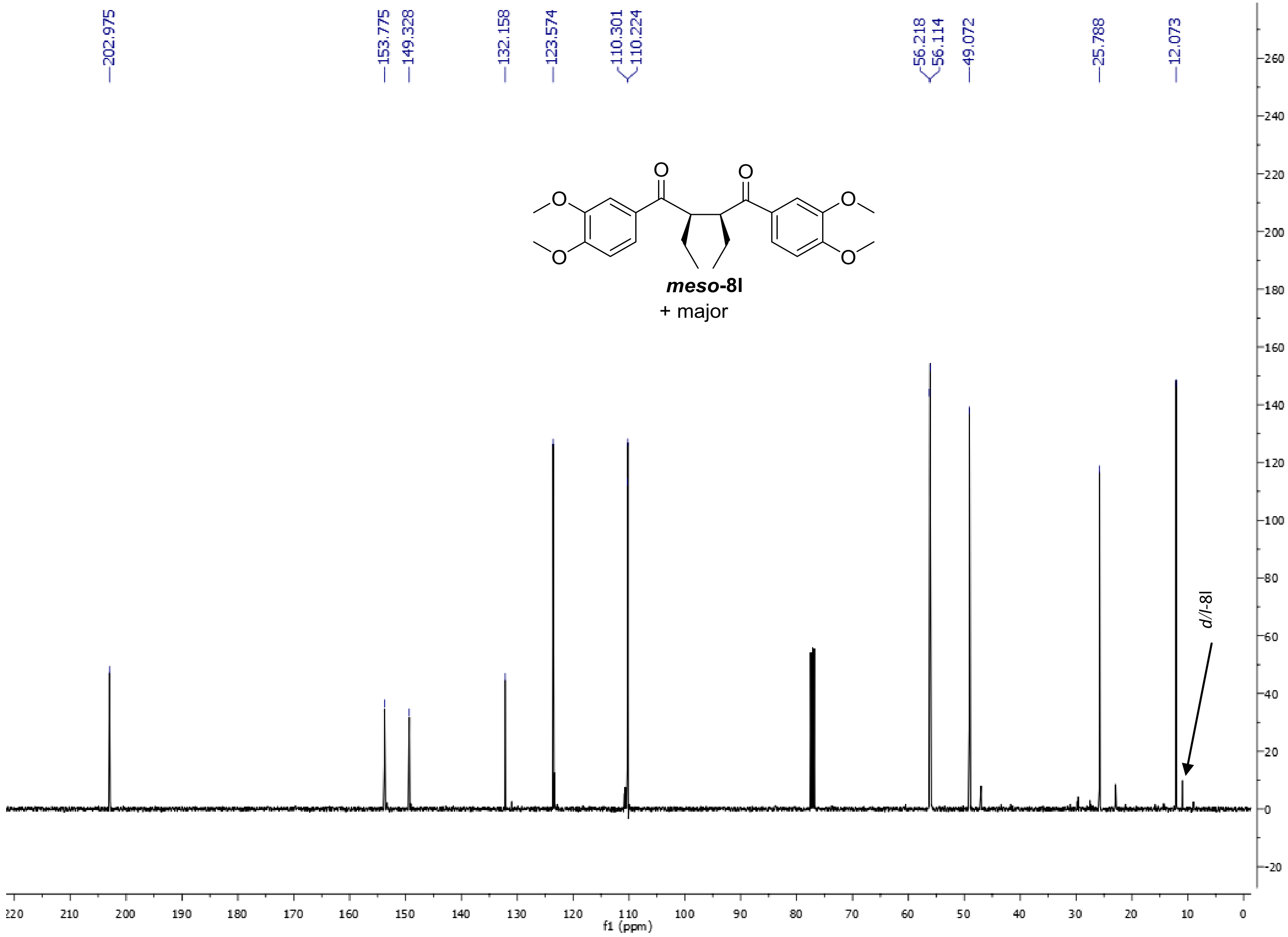

203.056
202.864
163.883
163.428
132.027
130.909
130.857
114.016
113.774
55.650
55.563
49.125
46.857
25.721
22.721
12.045
10.824
meso-8k
d/l-8k
meso-8k
O
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
-1200
-1400
-1600
-1800
-2000
-2200
-2400
-2600
-2800

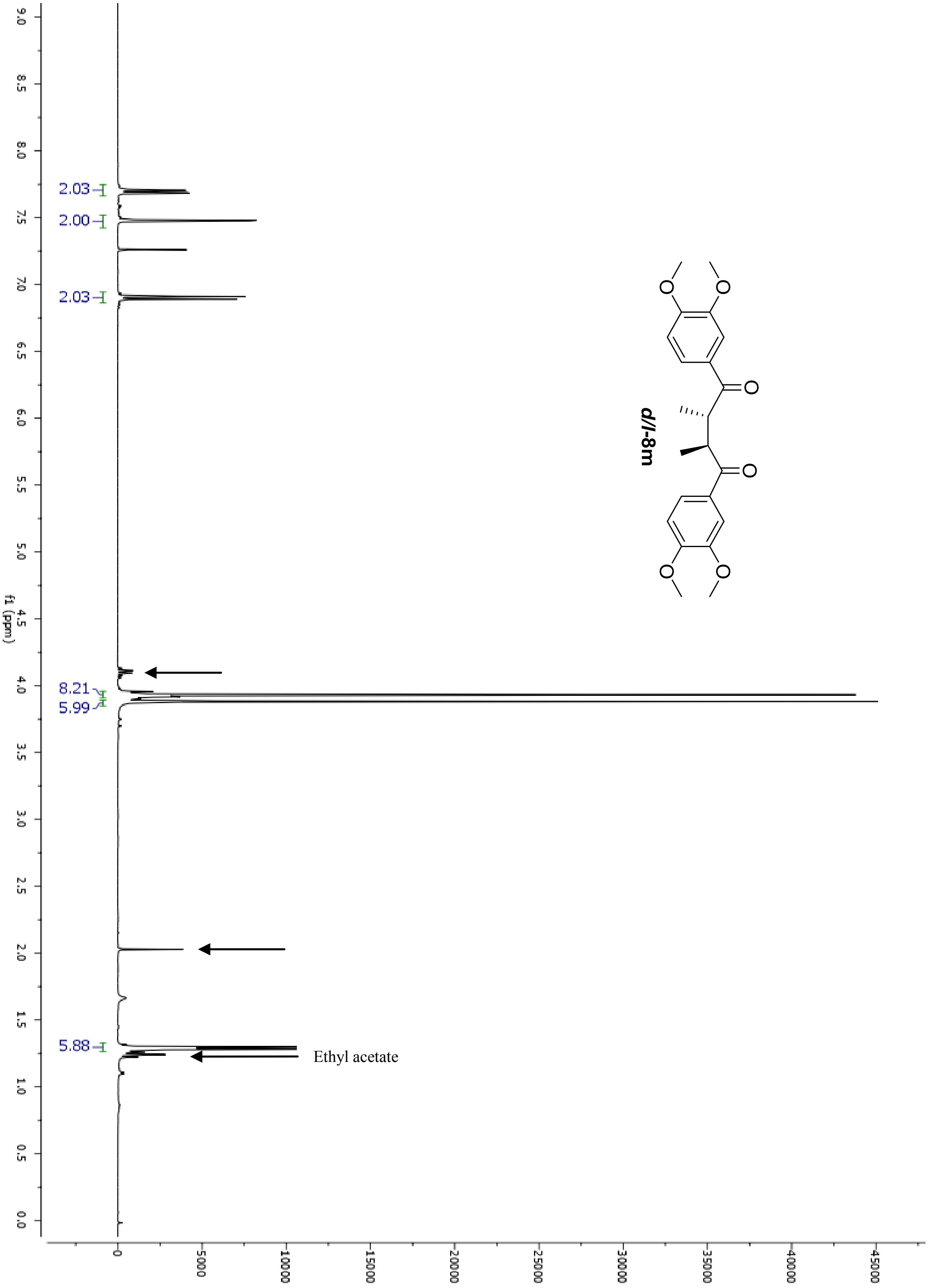

d/l-8l
+ minor
H2O
meso-8l
2.00
2.00
2.00
4.00
6.02
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000


202.878
153.301
149.088
131.013
123.336
110.699
110.181
56.177
56.044
47.017
22.981
10.974
d/l-8l
+ minor
O
O
O
O
O
O
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
0
10
20
30
40
50
60
70
80
90
100

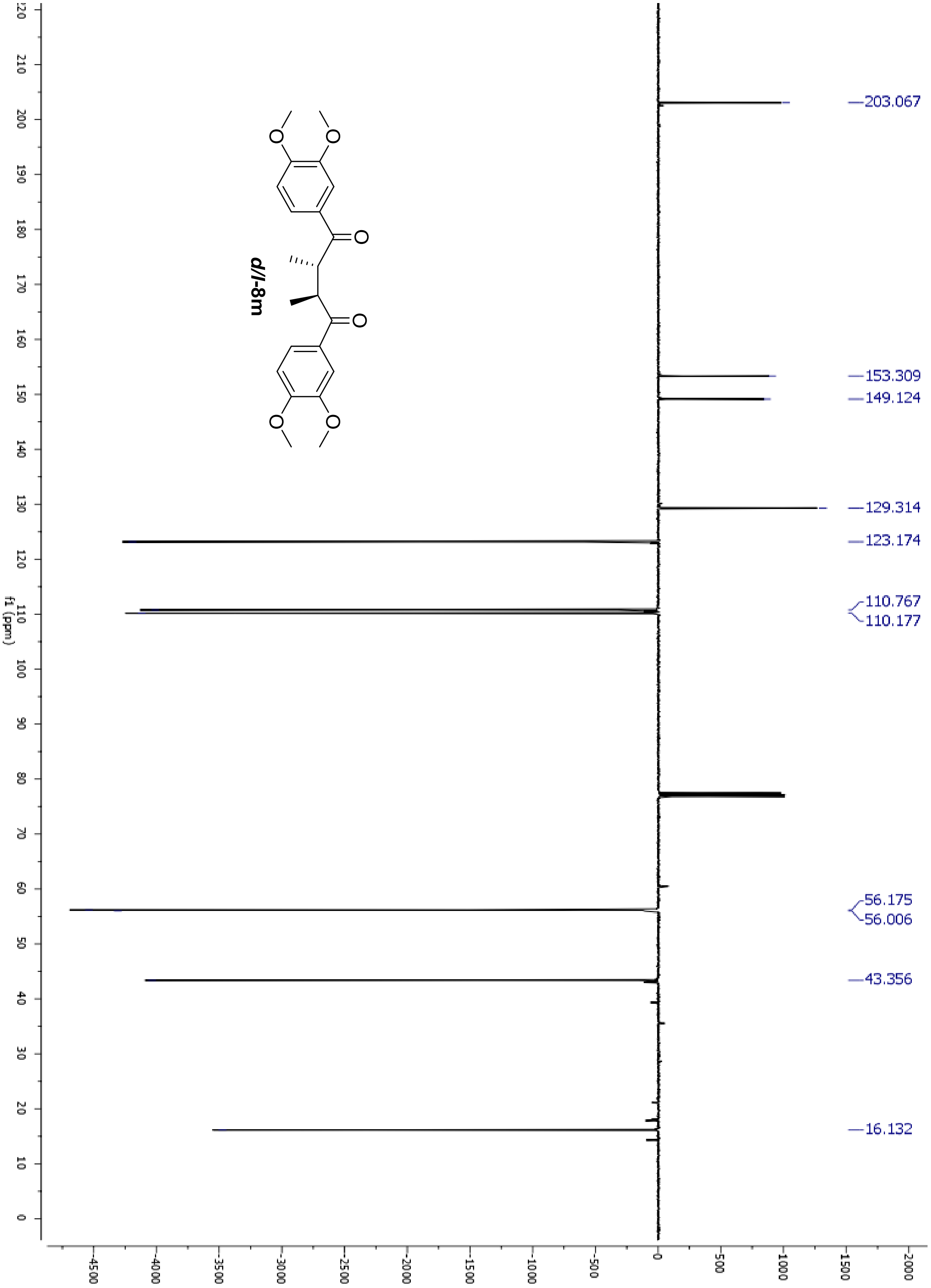


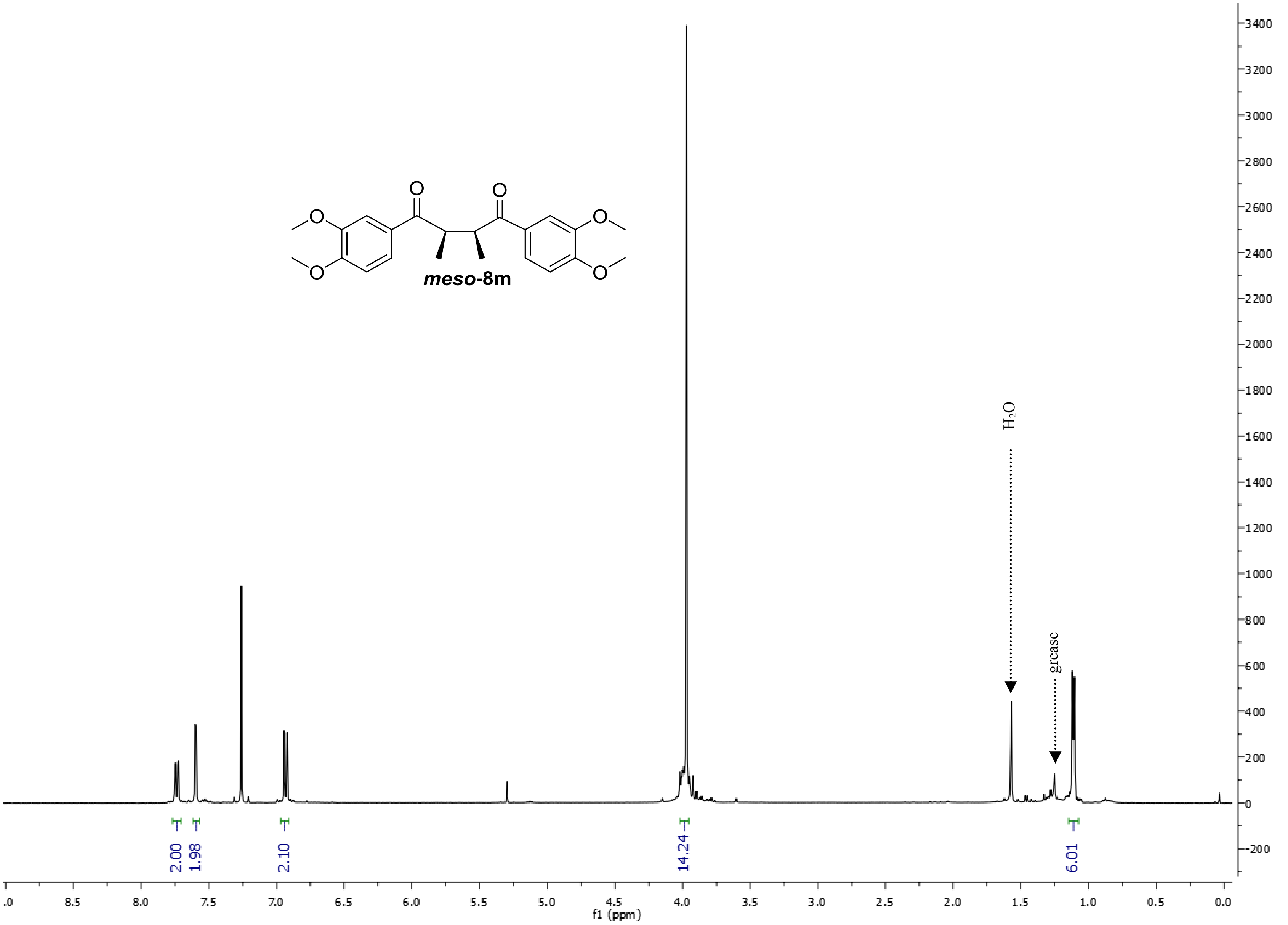
meso-8l
+ major
Ethyl acetate
d/*l*-8l
1.98
2.00
2.00
12.32
2.21
2.63
2.08
6.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000


202.975
153.775
149.328
132.158
123.574
110.301
110.224
56.218
56.114
49.072
25.788
12.073
meso-8l
+ major
d/l-8l
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20


2.03
2.00
2.03
8.21
5.99
5.88
Ethyl acetate
f1 (ppm)
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
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
O
O

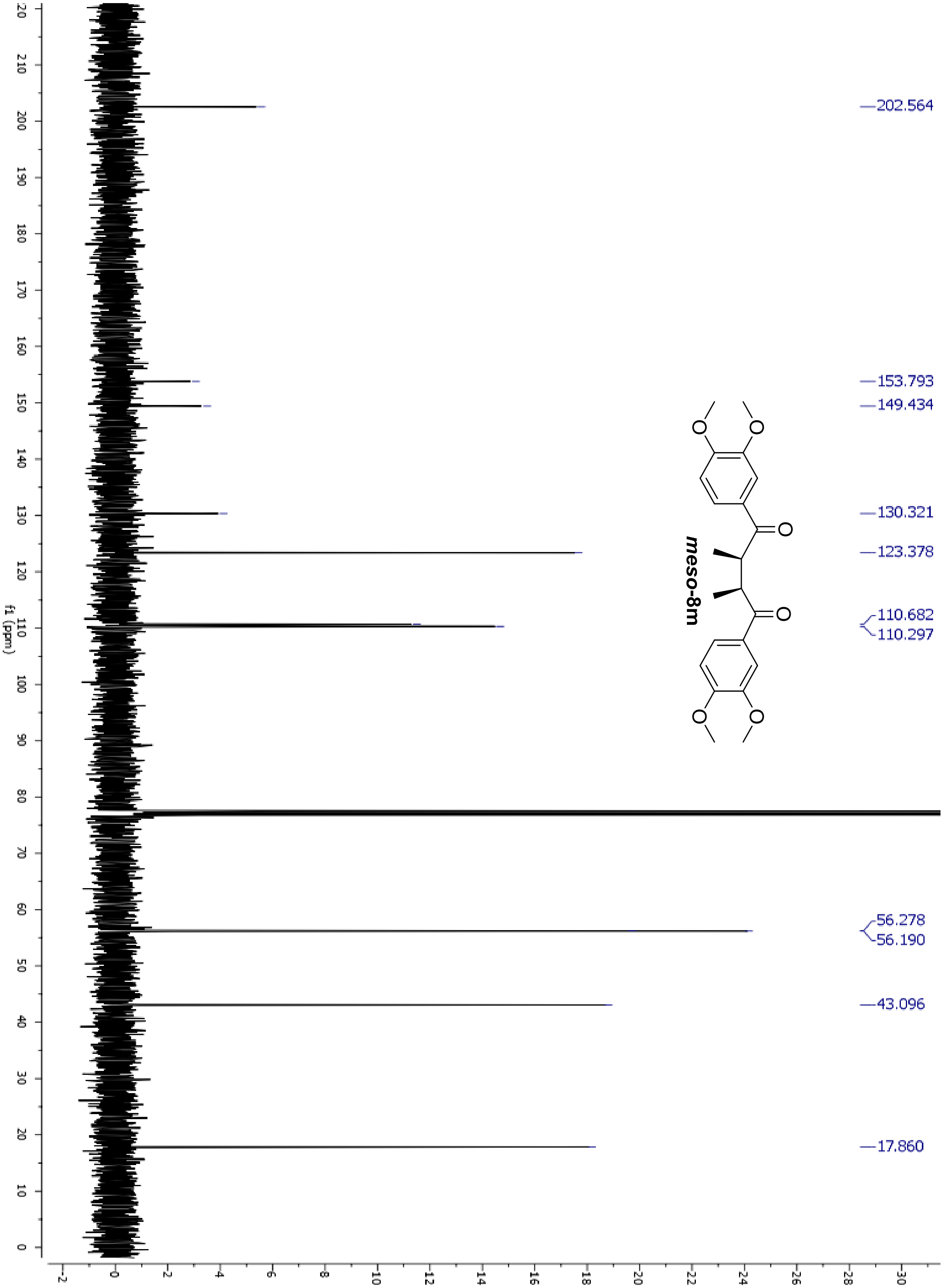
***d/l*-8m**


d/l-8m
203.067
153.309
149.124
129.314
123.174
110.767
110.177
56.175
56.006
43.356
16.132
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-4500
-4000
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
500
1000
1500
2000



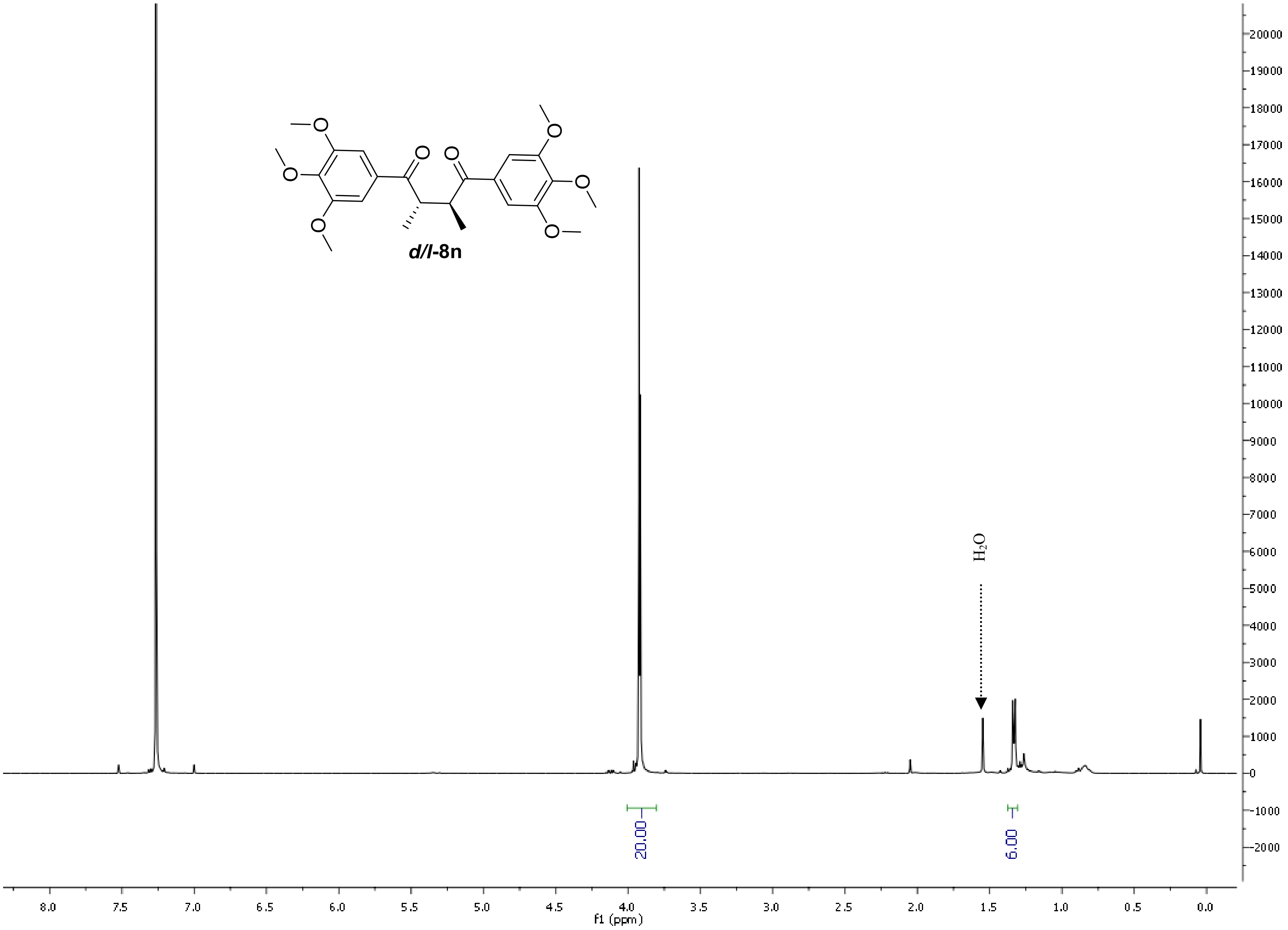
***meso*-8m**

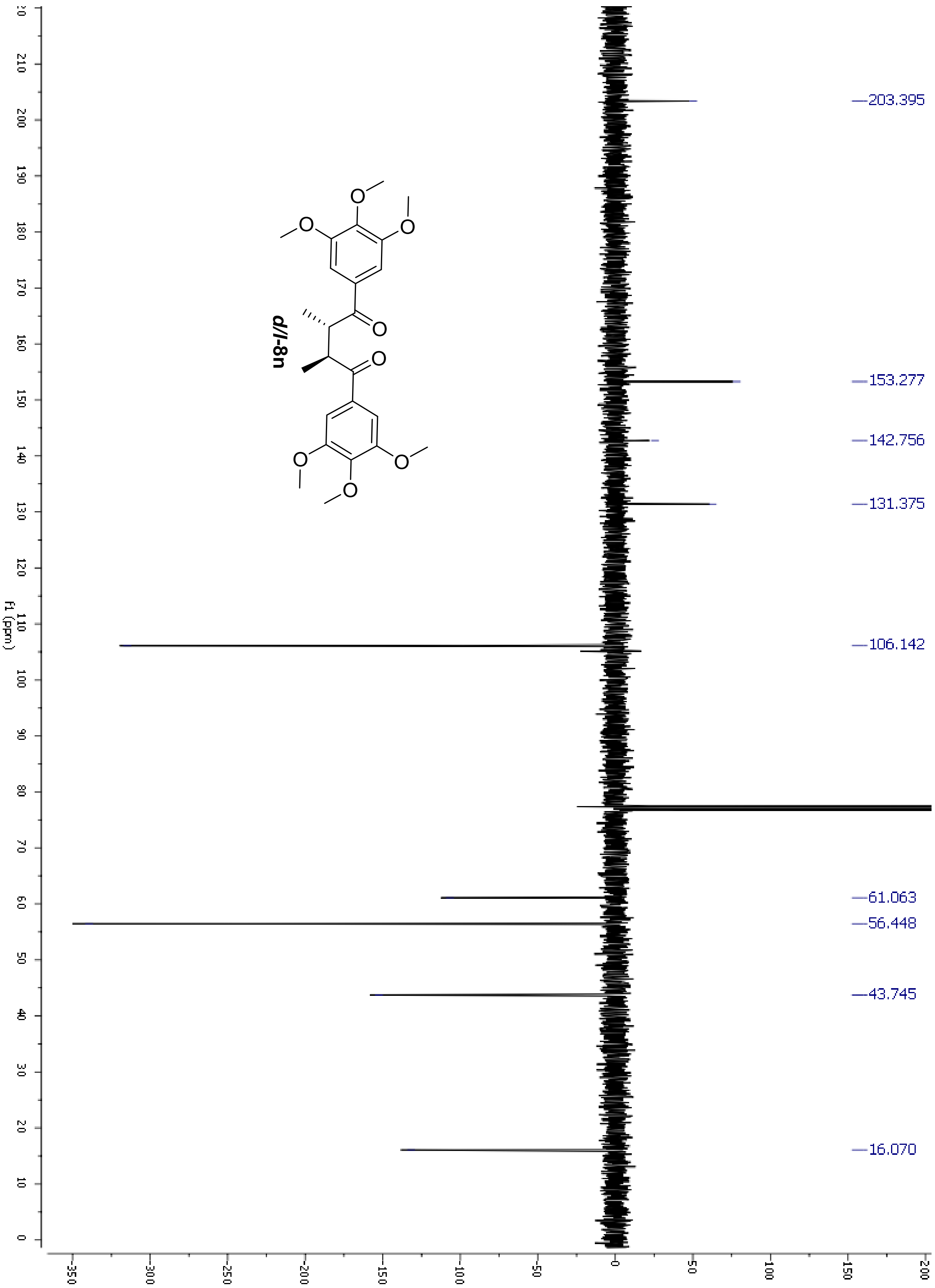
O
O
O
O
O
O
H2O
grease
2.00
1.98
2.10
14.24
6.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200



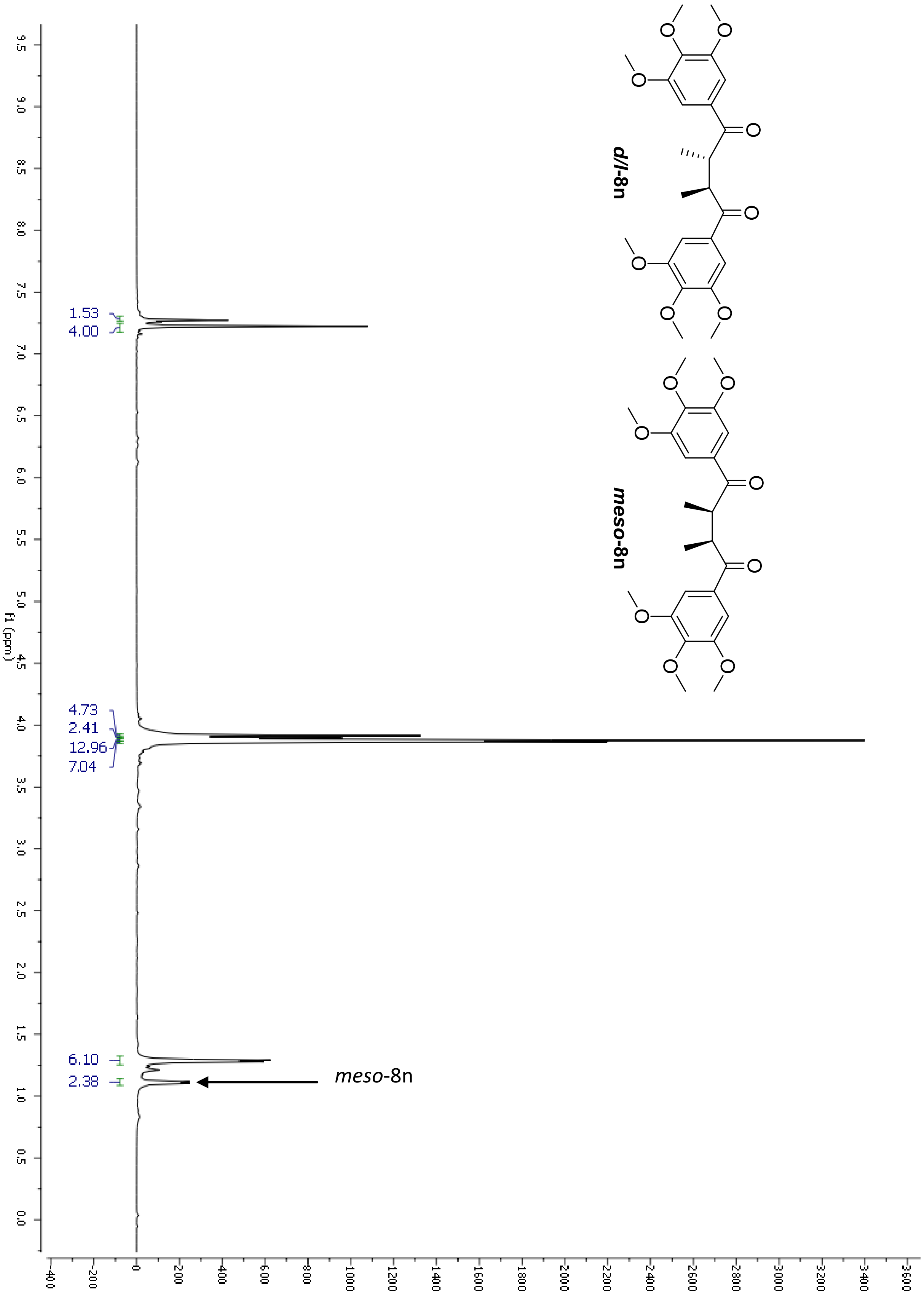
***meso*-8m**

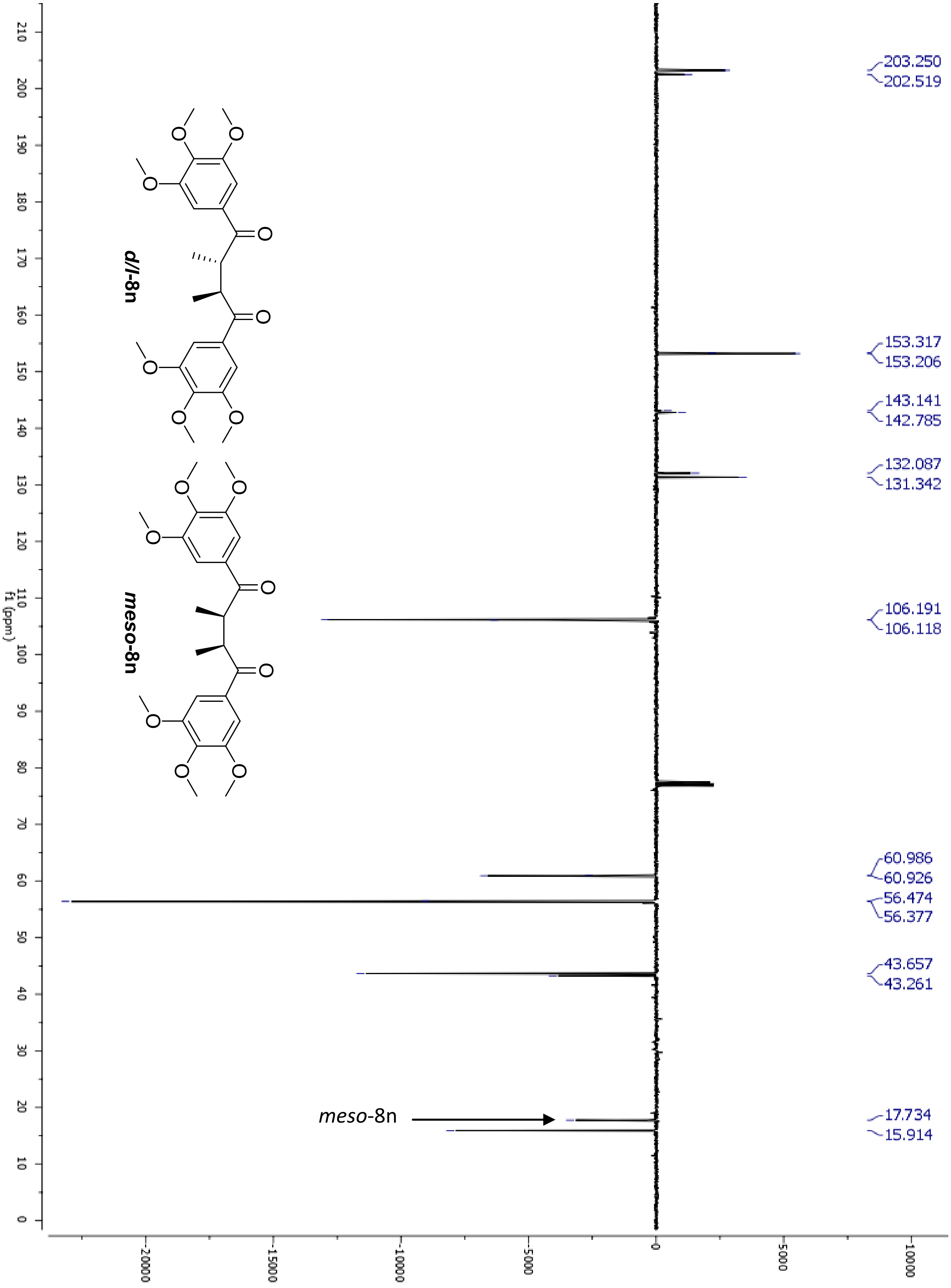
202.564
153.793
149.434
130.321
123.378
110.682
110.297
56.278
56.190
43.096
17.860
f1 (ppm)
O
O
O
O
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-2
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

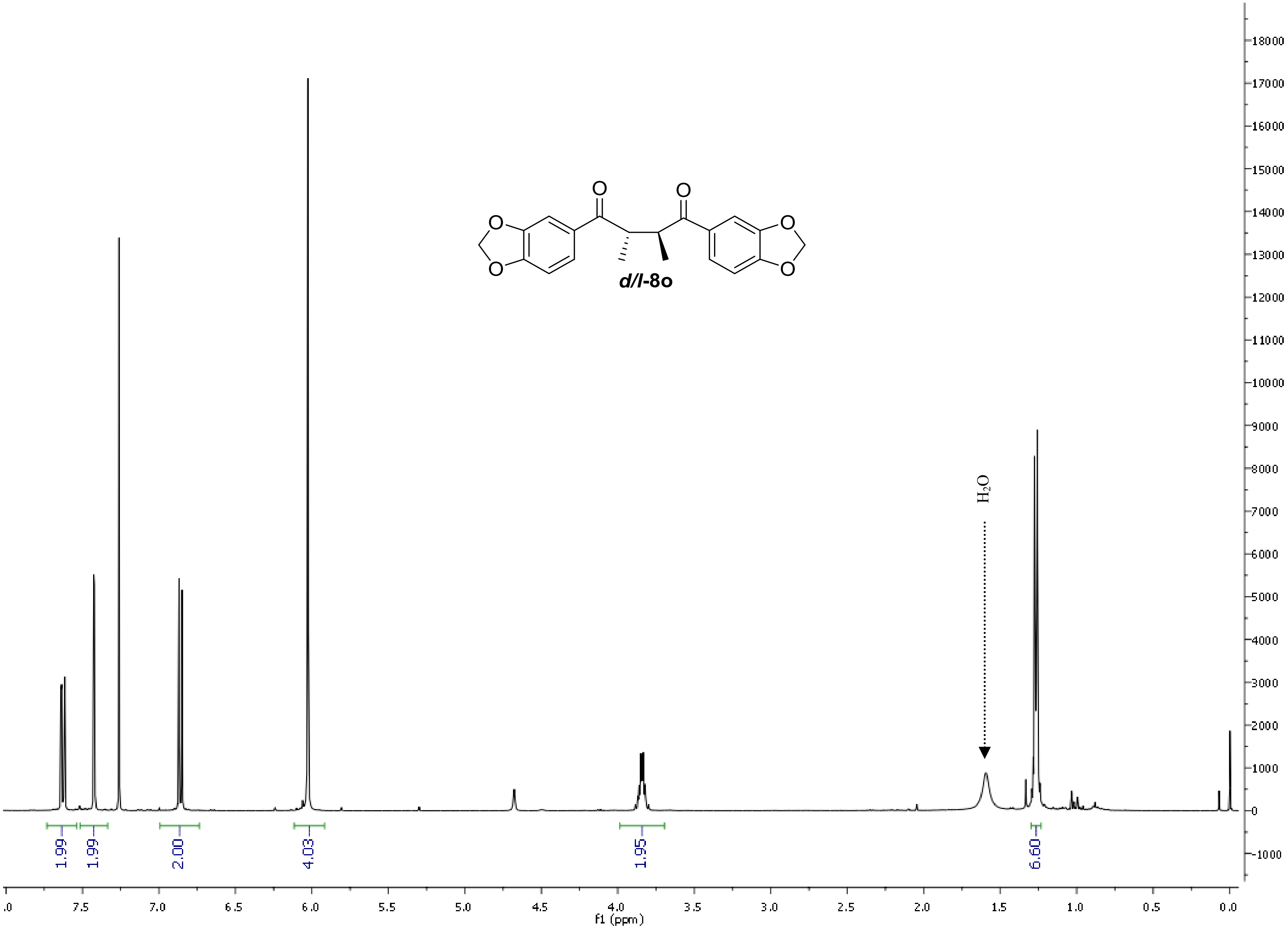

d/l-8n
H₂O
20.00
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

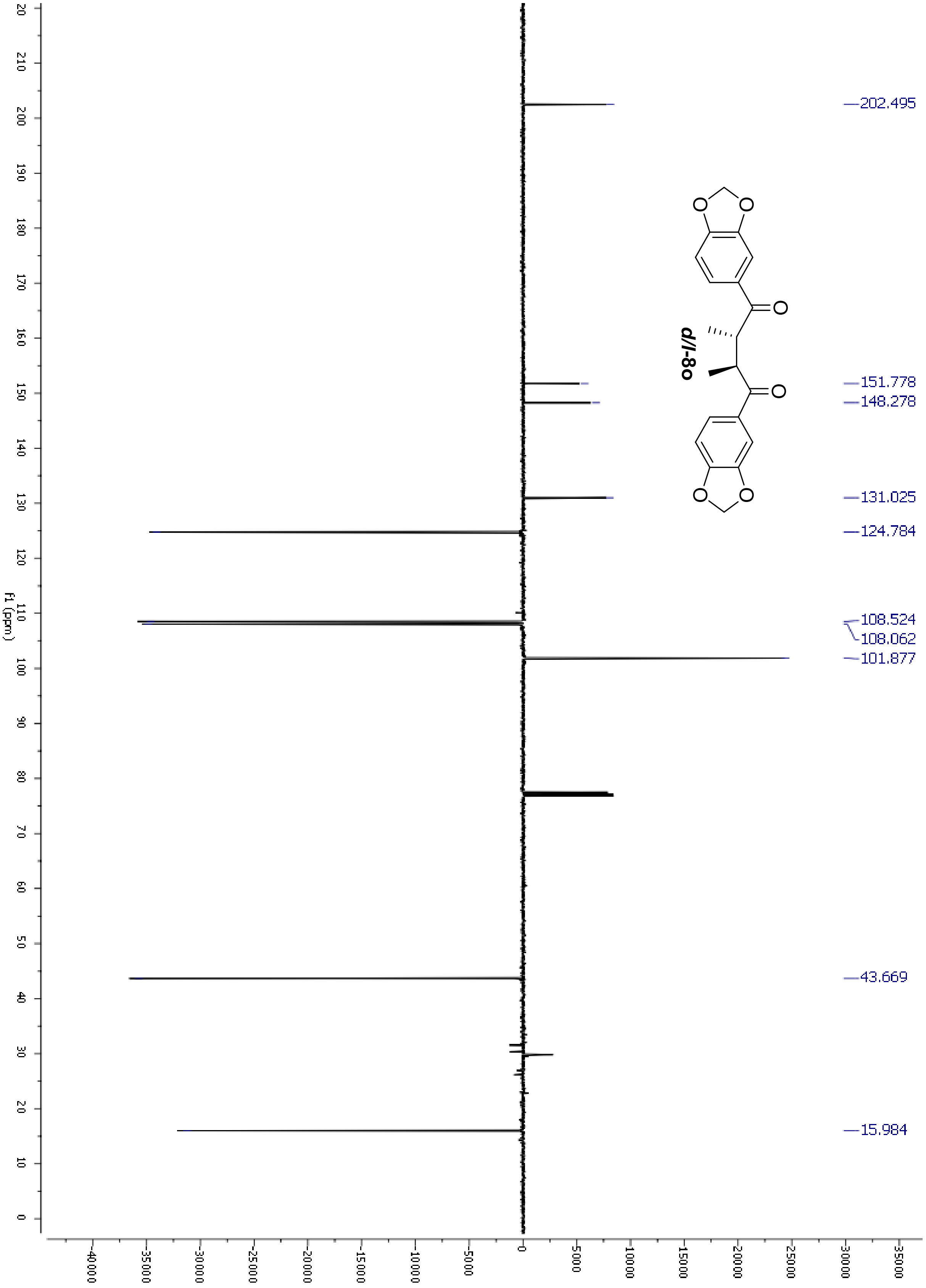


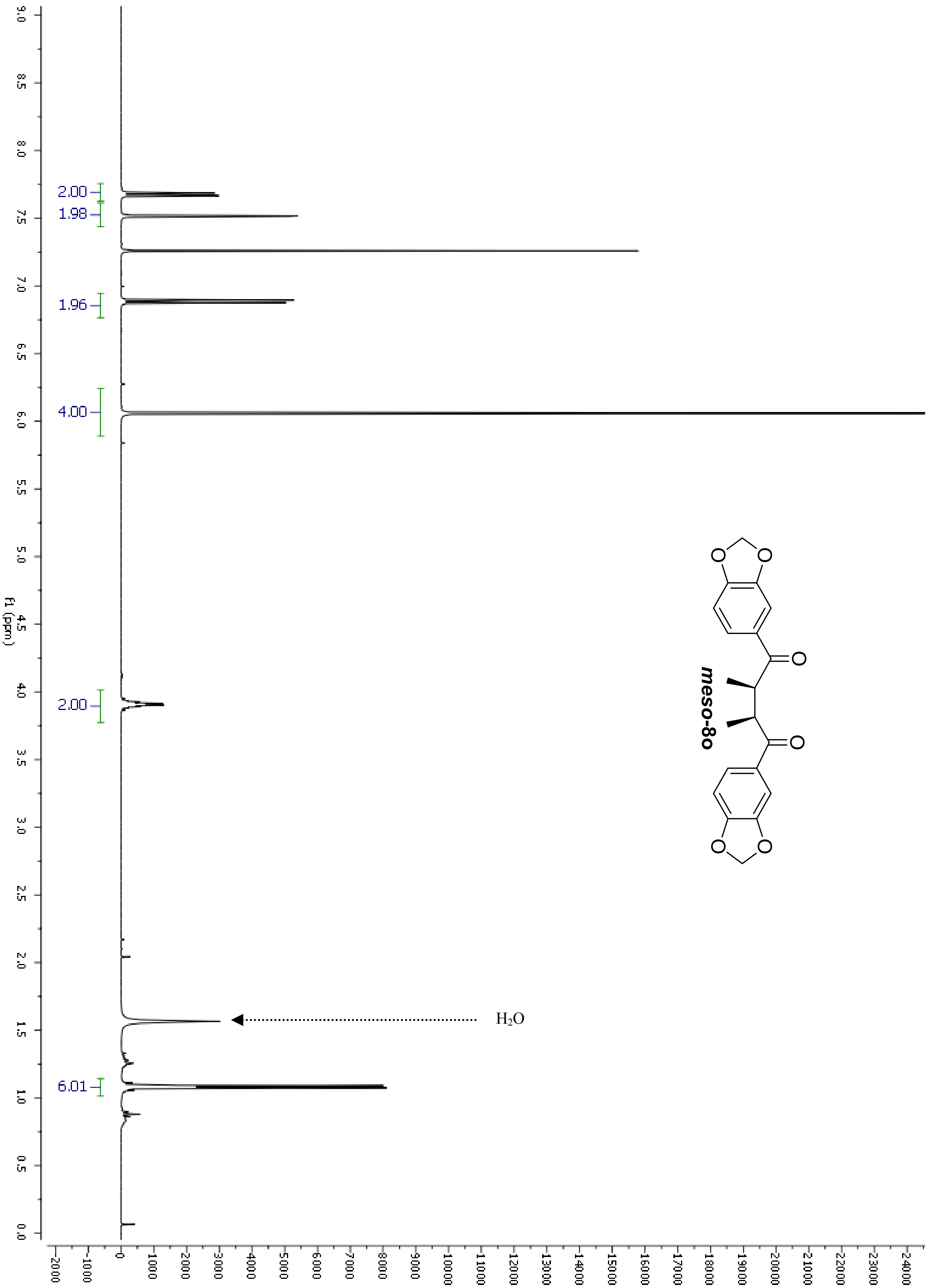
d/l-8n
O
O
O
O
O
O
O
O
—203.395
—153.277
—142.756
—131.375
—106.142
—61.063
—56.448
—43.745
—16.070
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-350
-300
-250
-200
-150
-100
-50
0
50
100
150
200


d/l-8n
meso-8n
meso-8n
1.53
4.00
4.73
2.41
12.96
7.04
6.10
2.38
f1 (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
-400
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600

203.250
202.519
153.317
153.206
143.141
142.785
132.087
131.342
106.191
106.118
60.986
60.926
56.474
56.377
43.657
43.261
17.734
15.914
d/l-8n
meso-8n
meso-8n
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-20000
-15000
-10000
-5000
0
5000
10000

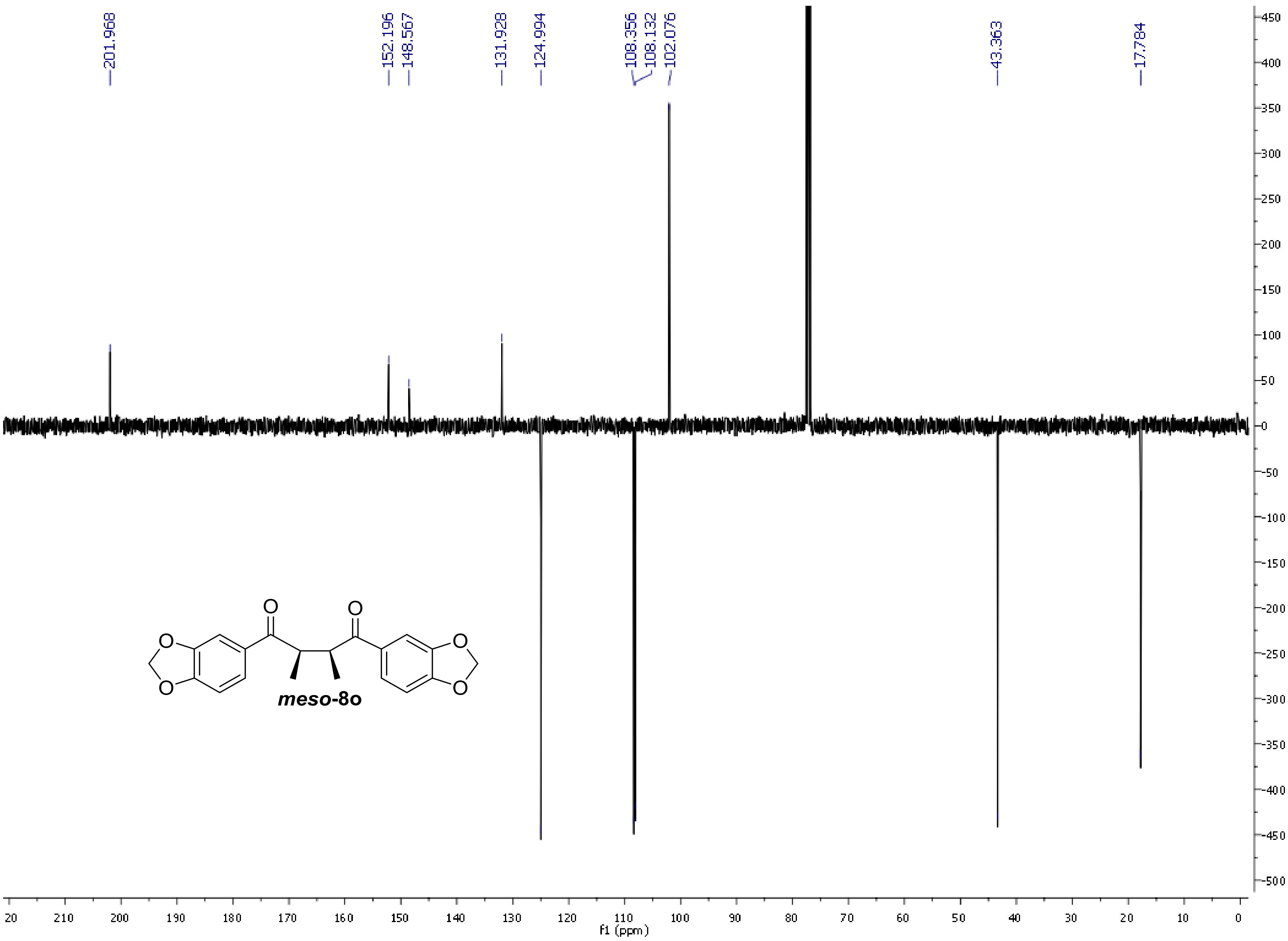

d/l-8o
H$_2$O
1.99
1.99
2.00
4.03
1.95
6.60
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


d/l-8o
—202.495
—151.778
—148.278
—131.025
—124.784
—108.524
—108.062
—101.877
—43.669
—15.984
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-40000
-35000
-30000
-25000
-20000
-15000
-10000
-5000
0
5000
10000
15000
20000
25000
30000
35000

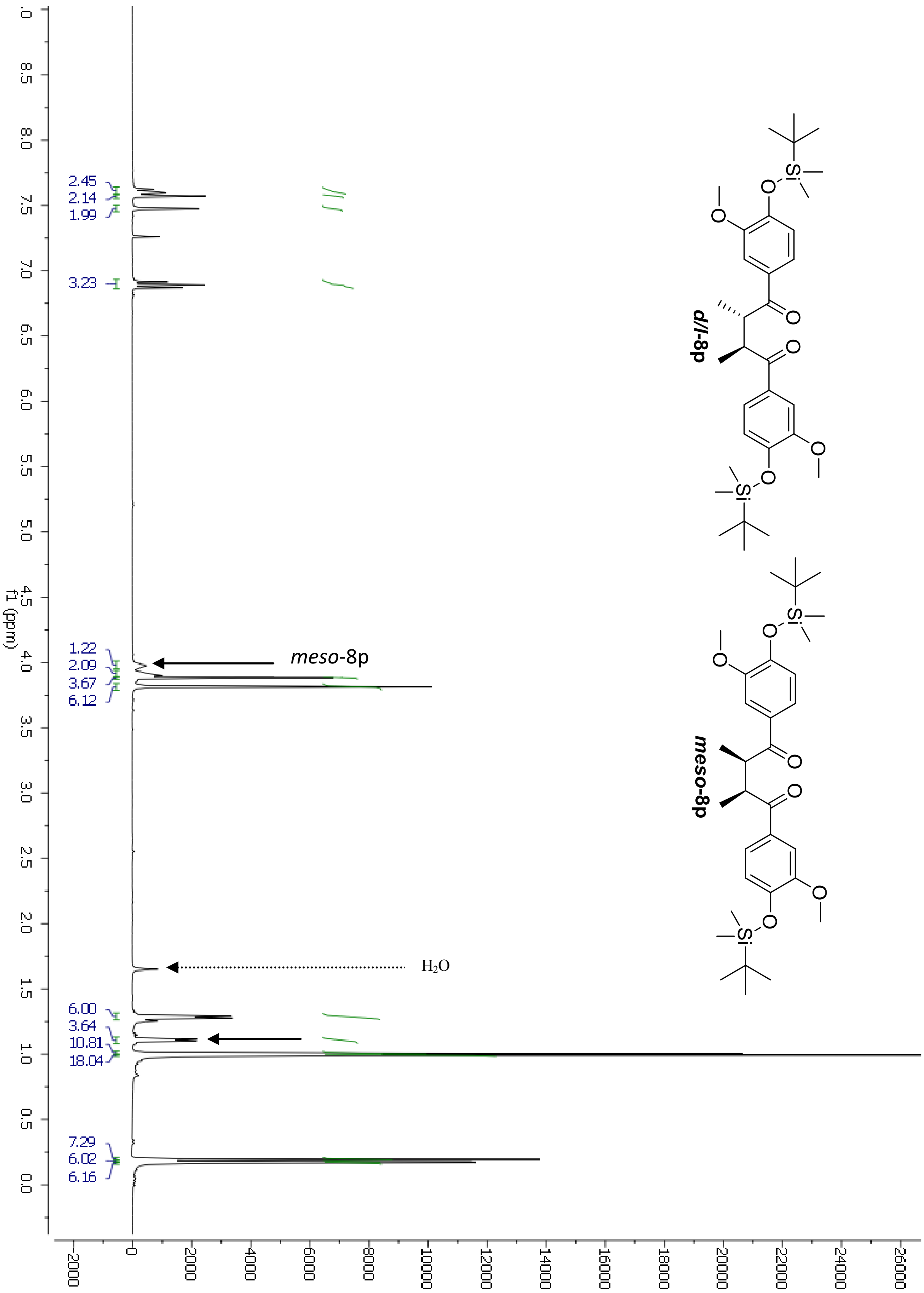


meso-8o

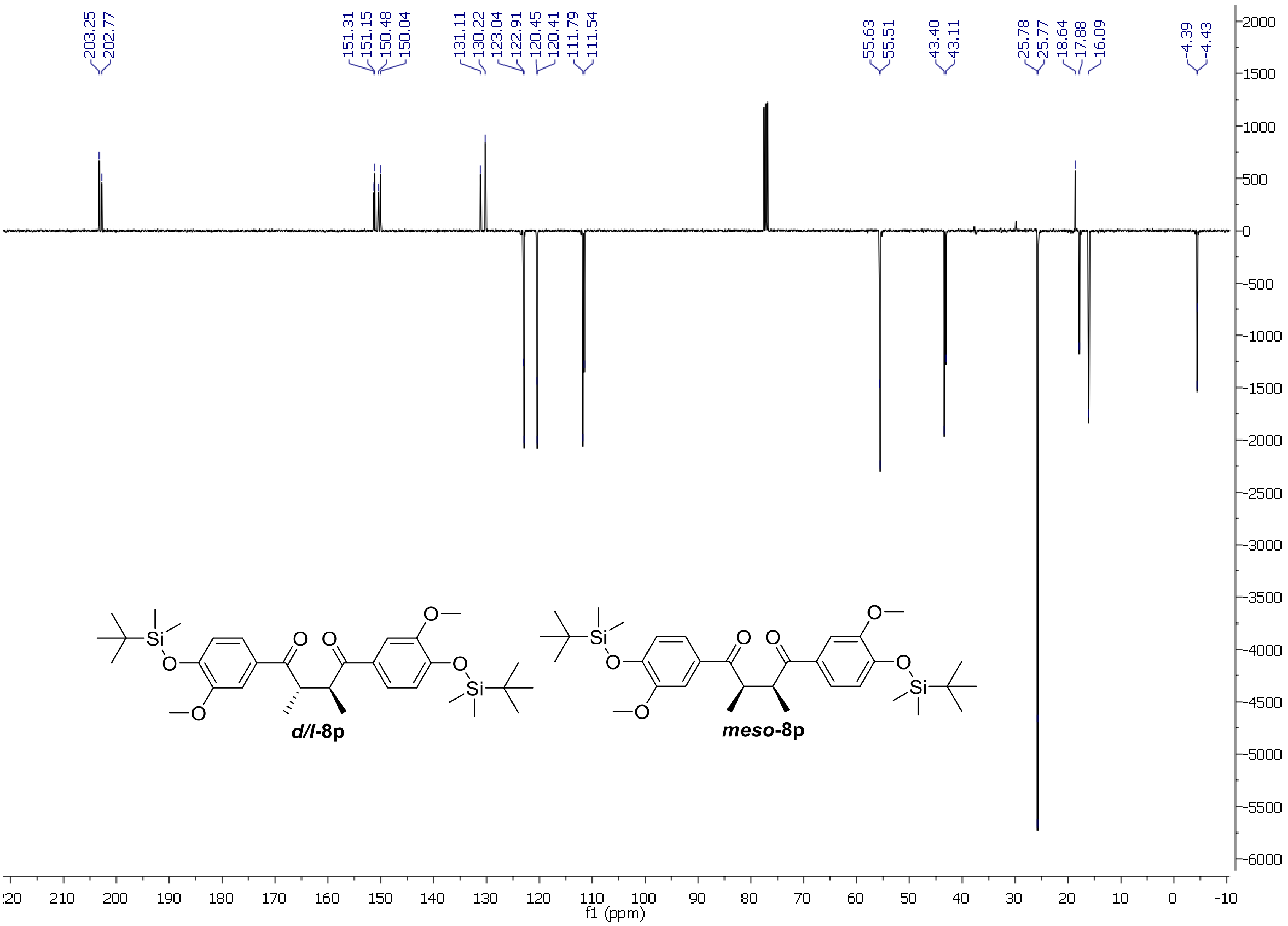
2.00
1.98
1.96
4.00
2.00
6.01
H2O
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2000
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
16000
17000
18000
19000
20000
21000
22000
23000
24000

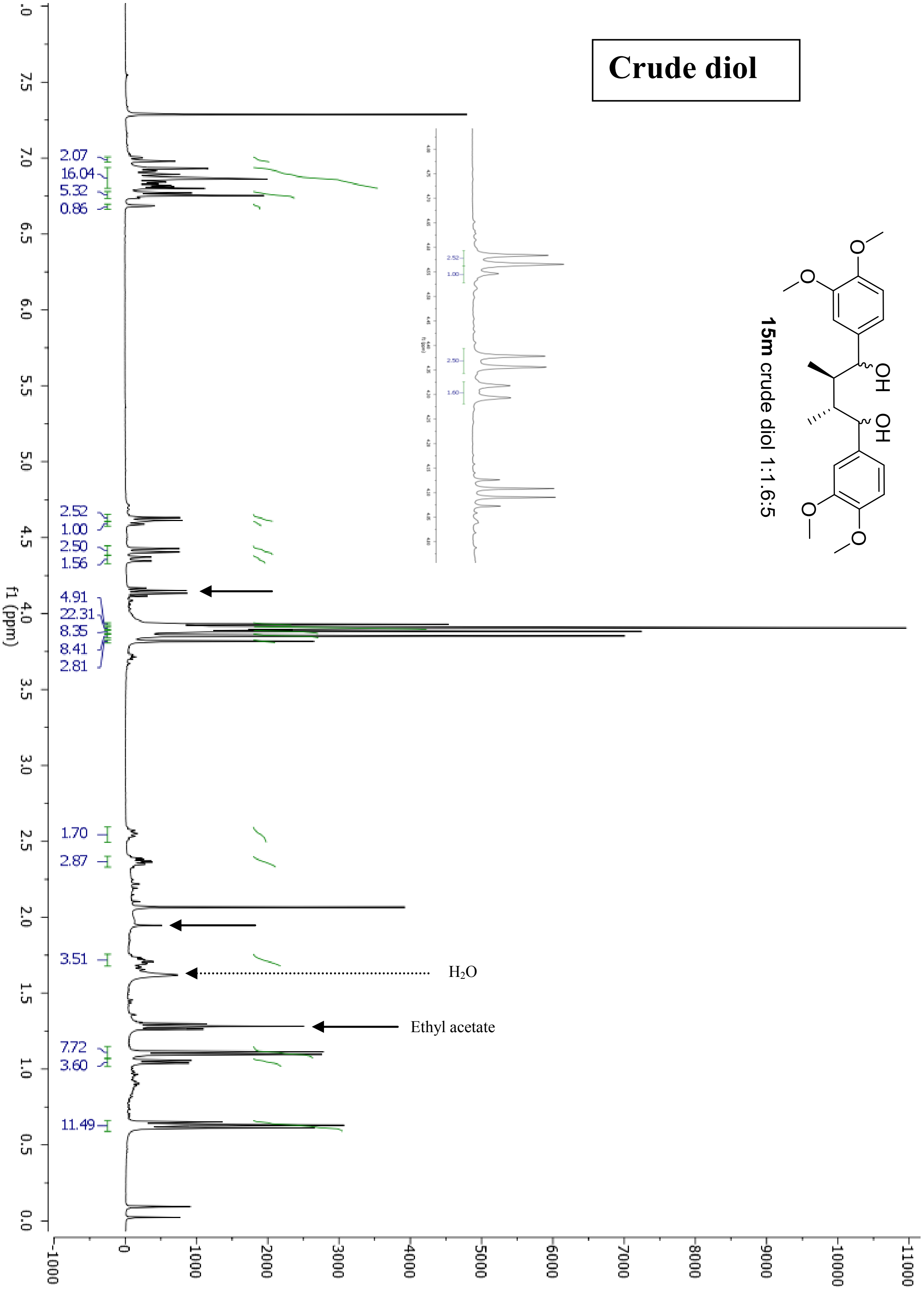


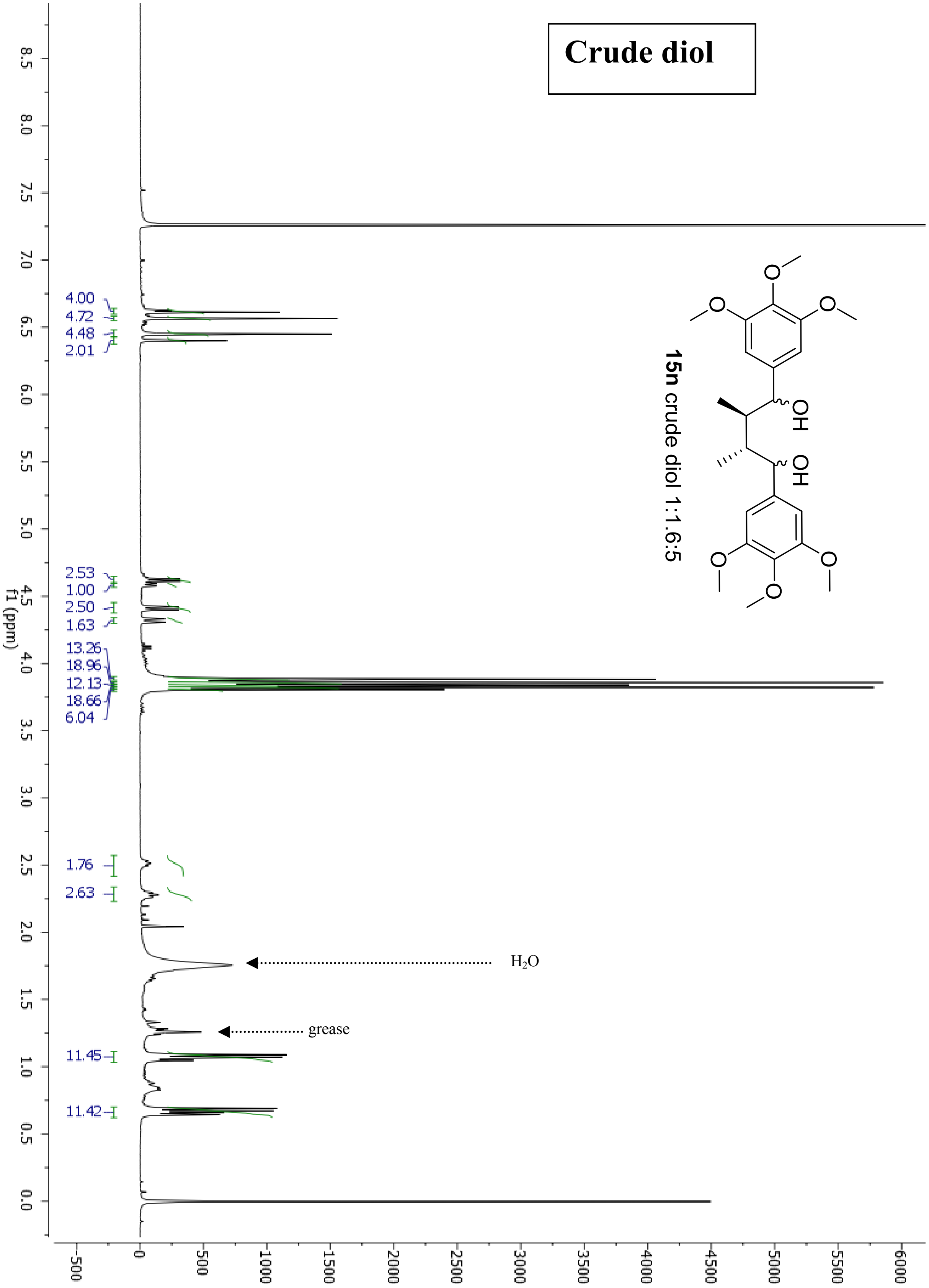
201.968
152.196
148.567
131.928
124.994
108.356
108.132
102.076
43.363
17.784
meso-8o
O
O
O
O
O
O
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-500

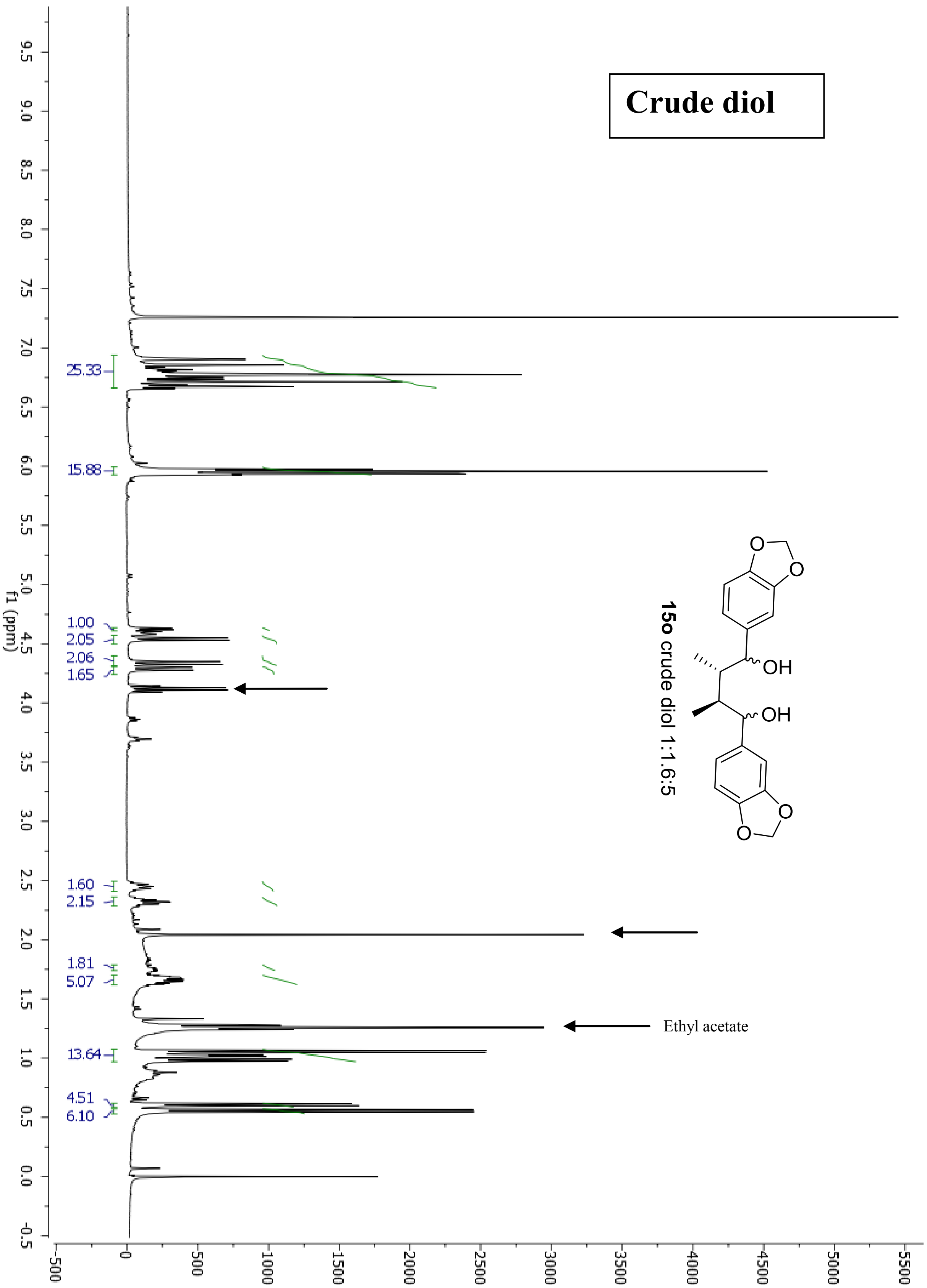


d/l-8p
meso-8p
Si
O
meso-8p
H2O
2.45
2.14
1.99
3.23
1.22
2.09
3.67
6.12
6.00
3.64
10.81
18.04
7.29
6.02
6.16
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2000
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
22000
24000
26000

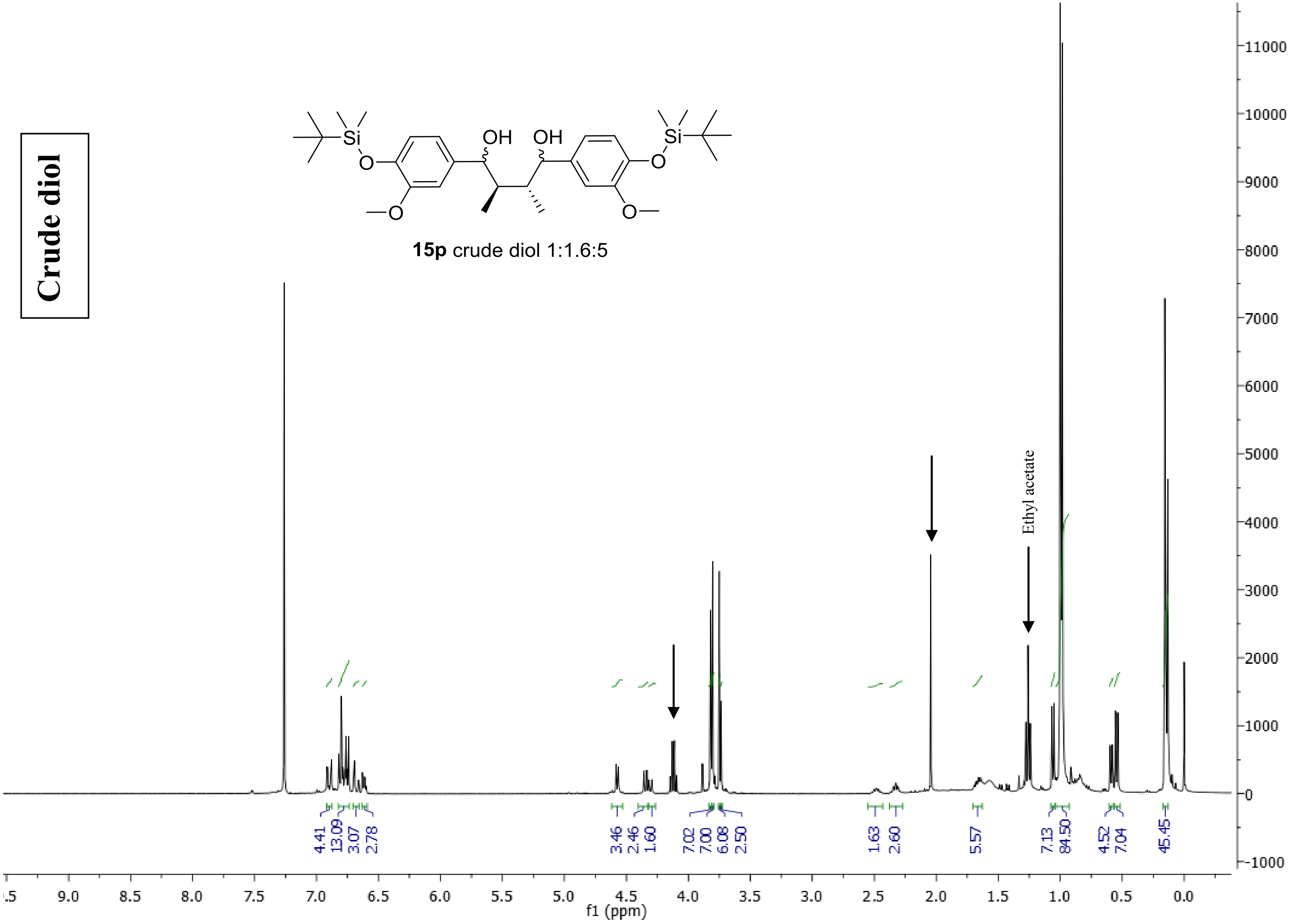

203.25
202.77
151.31
151.15
150.48
150.04
131.11
130.22
123.04
122.91
120.45
120.41
111.79
111.54
55.63
55.51
43.40
43.11
25.78
25.77
18.64
17.88
16.09
-4.39
-4.43
d/l-8p
meso-8p
Si
O
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
-4000
-4500
-5000
-5500
-6000


Crude diol
15m crude diol 1:1.6:5
OH
OH
H2O
Ethyl acetate
f1 (ppm)
2.07
16.04
5.32
0.86
2.52
1.00
2.50
1.56
4.91
22.31
8.35
8.41
2.81
1.70
2.87
3.51
7.72
3.60
11.49
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
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
2.52
1.00
2.50
1.60

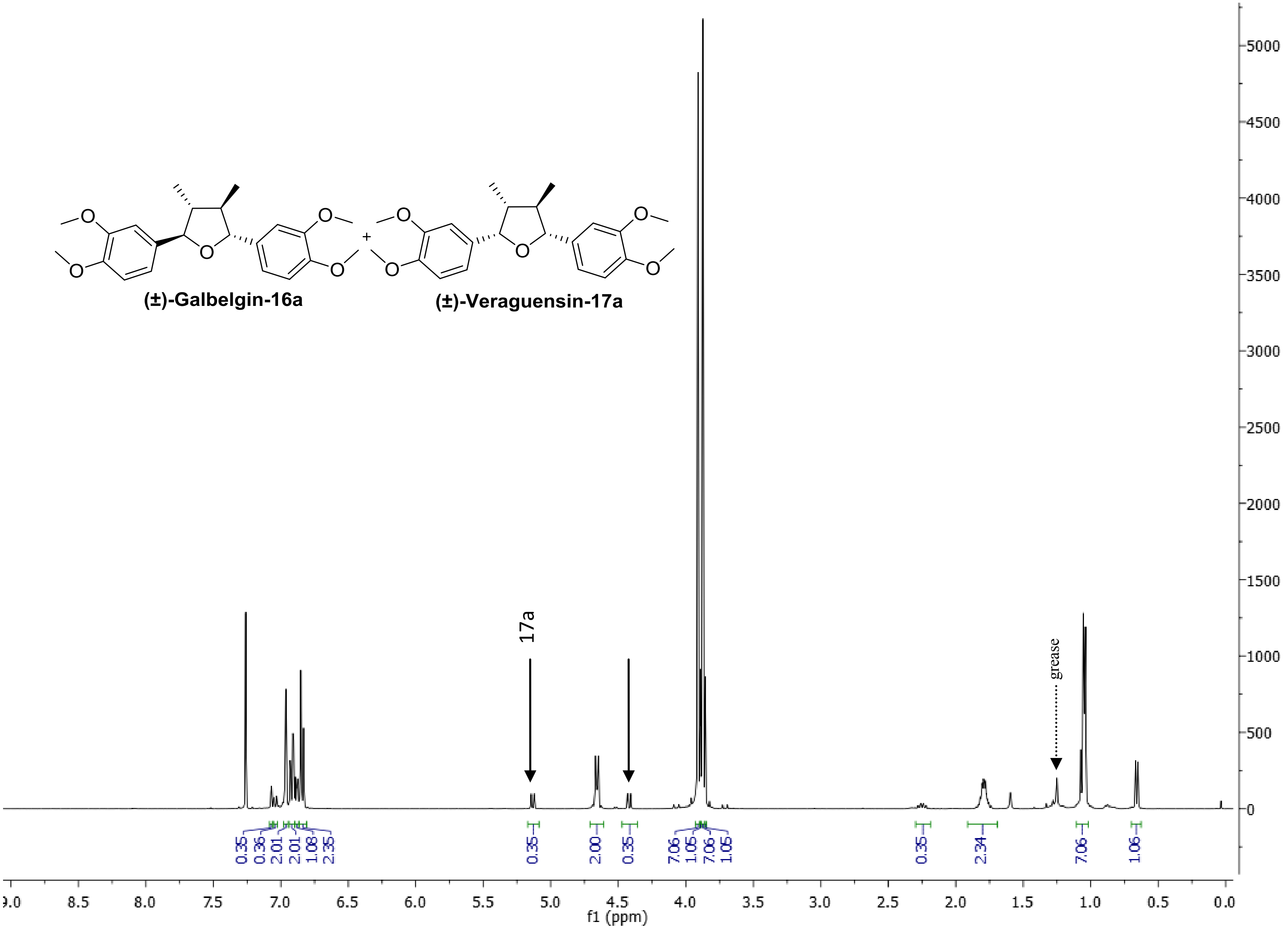

Crude diol
15n crude diol 1:1.6:5
OH
OH
O
H2O
grease
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4.00
4.72
4.48
2.01
2.53
1.00
2.50
1.63
13.26
18.96
12.13
18.66
6.04
1.76
2.63
11.45
11.42
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000

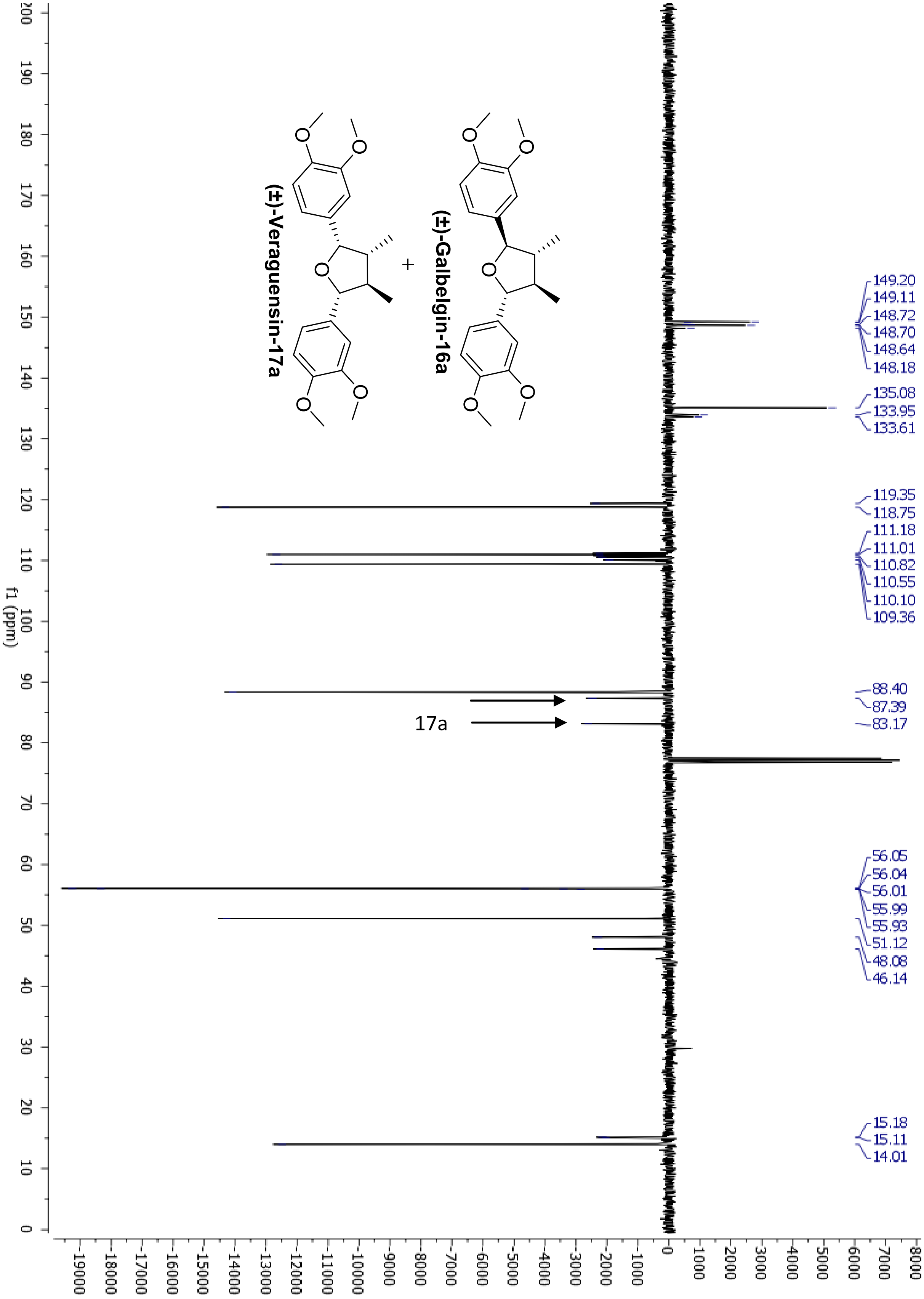

Crude diol
15o crude diol 1:1.6:5
OH
OH
O
O
O
O
Ethyl acetate
25.33
15.88
1.00
2.05
2.06
1.65
1.60
2.15
1.81
5.07
13.64
4.51
6.10
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500

Crude diol

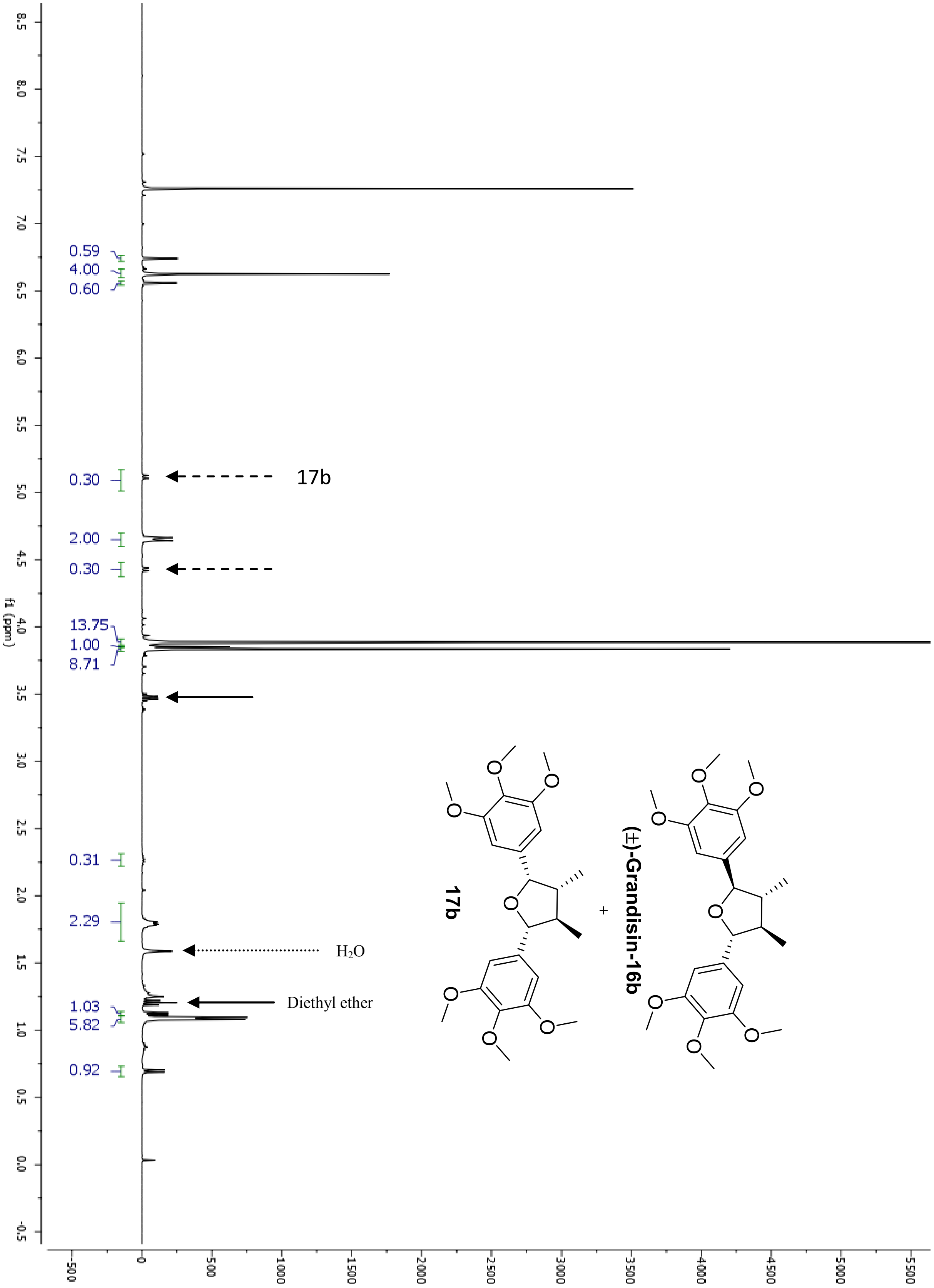


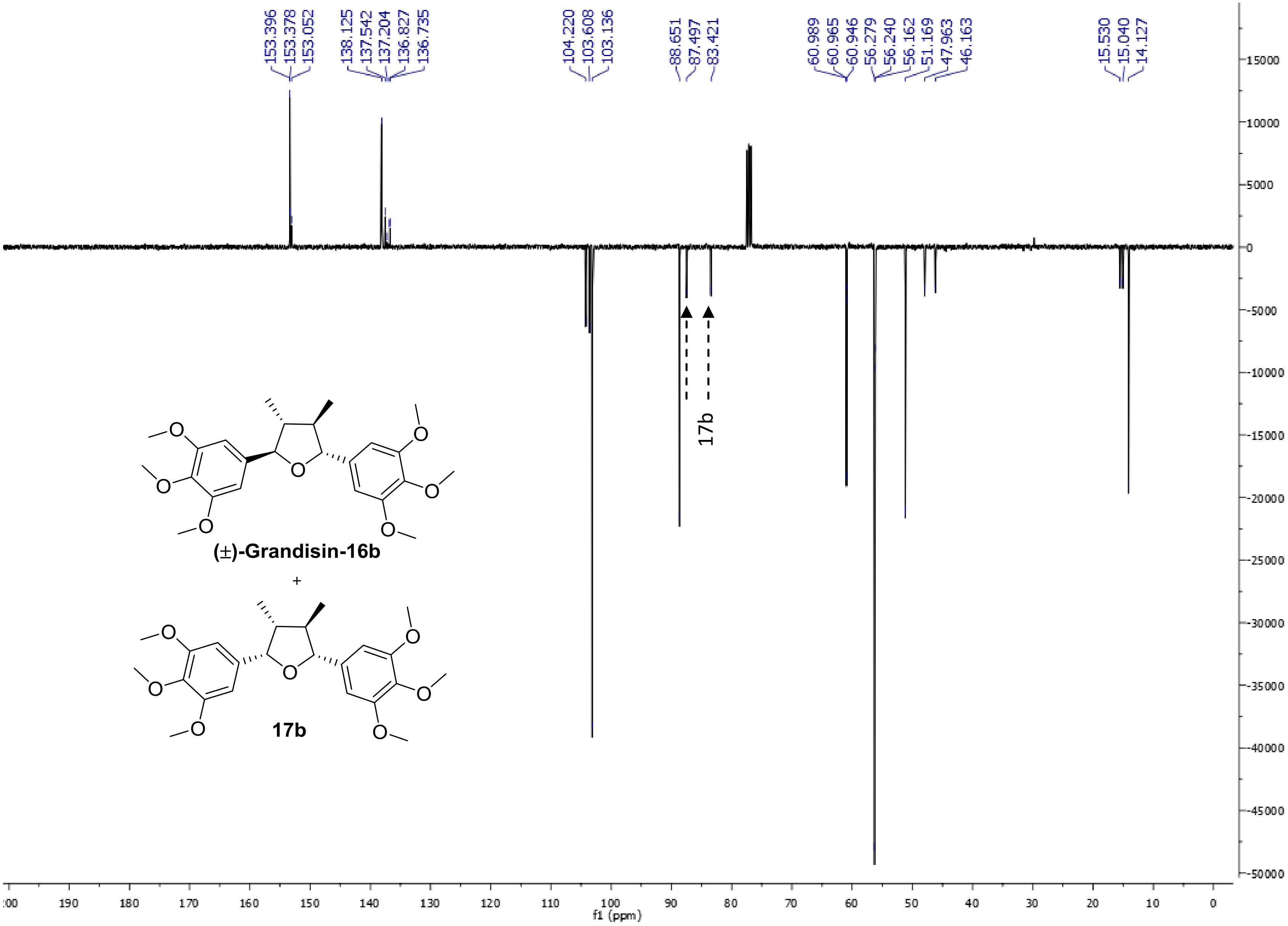
15p crude diol 1:1.6:5

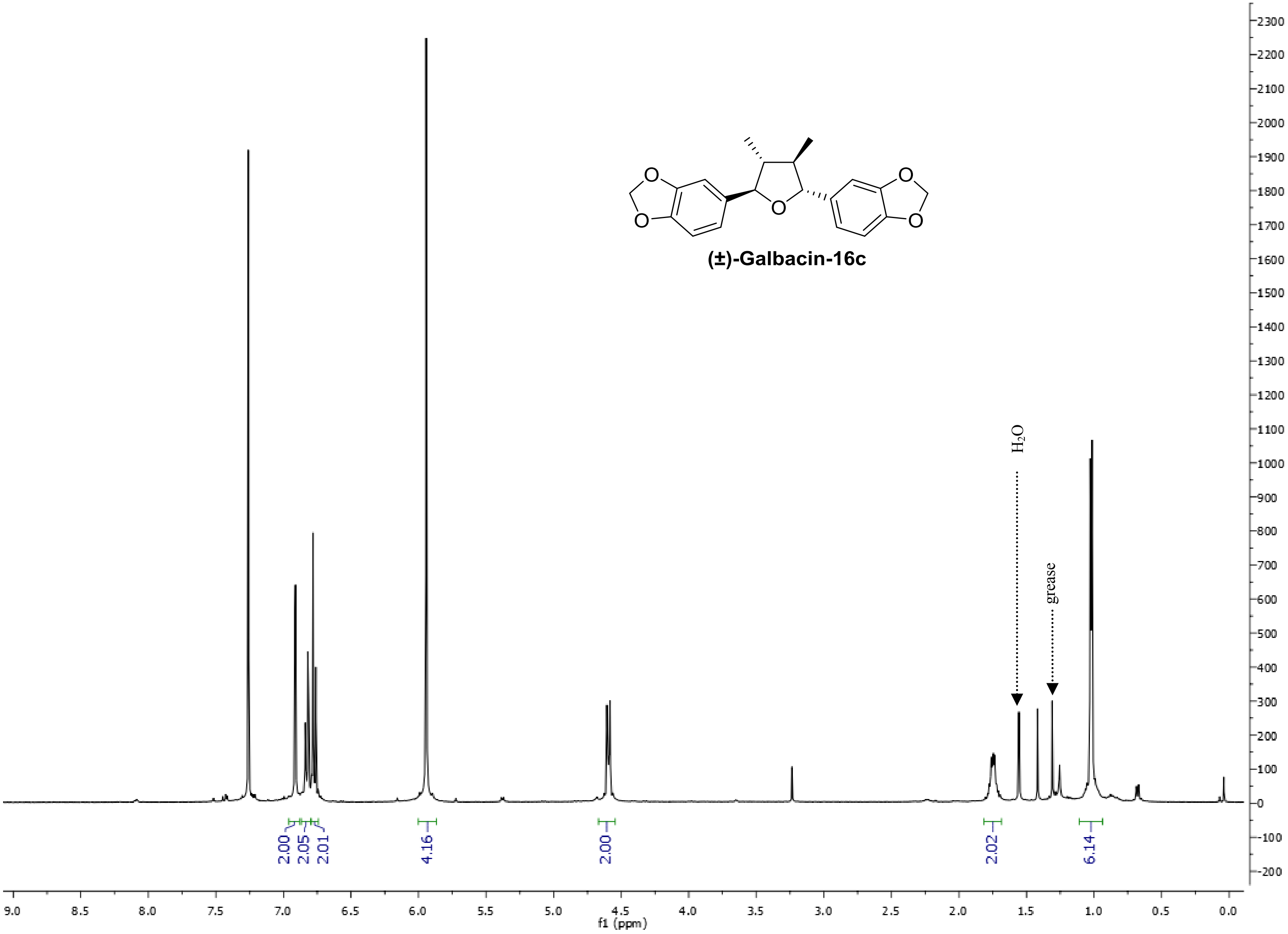

(±)-Galbelgin-16a
(±)-Veraguensin-17a
17a
grease
0.35
0.36
2.01
2.01
1.08
2.35
0.35
2.00
0.35
7.06
1.05
7.06
1.05
0.35
2.34
7.06
1.06
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0

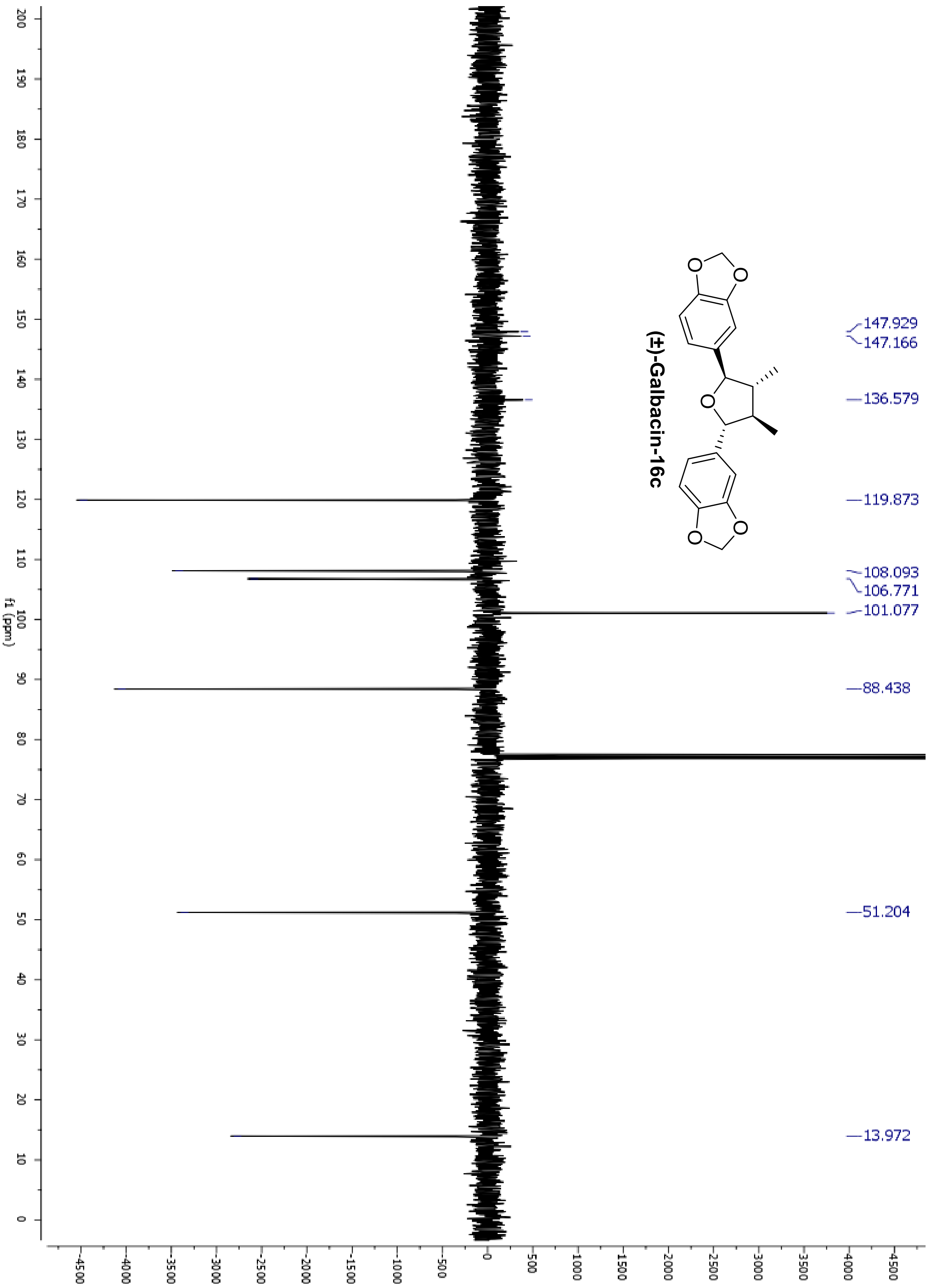


(±)-Galbelgin-16a
+
(±)-Veraguensin-17a
17a
149.20
149.11
148.72
148.70
148.64
148.18
135.08
133.95
133.61
119.35
118.75
111.18
111.01
110.82
110.55
110.10
109.36
88.40
87.39
83.17
56.05
56.04
56.01
55.99
55.93
51.12
48.08
46.14
15.18
15.11
14.01
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-19000
-18000
-17000
-16000
-15000
-14000
-13000
-12000
-11000
-10000
-9000
-8000
-7000
-6000
-5000
-4000
-3000
-2000
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000

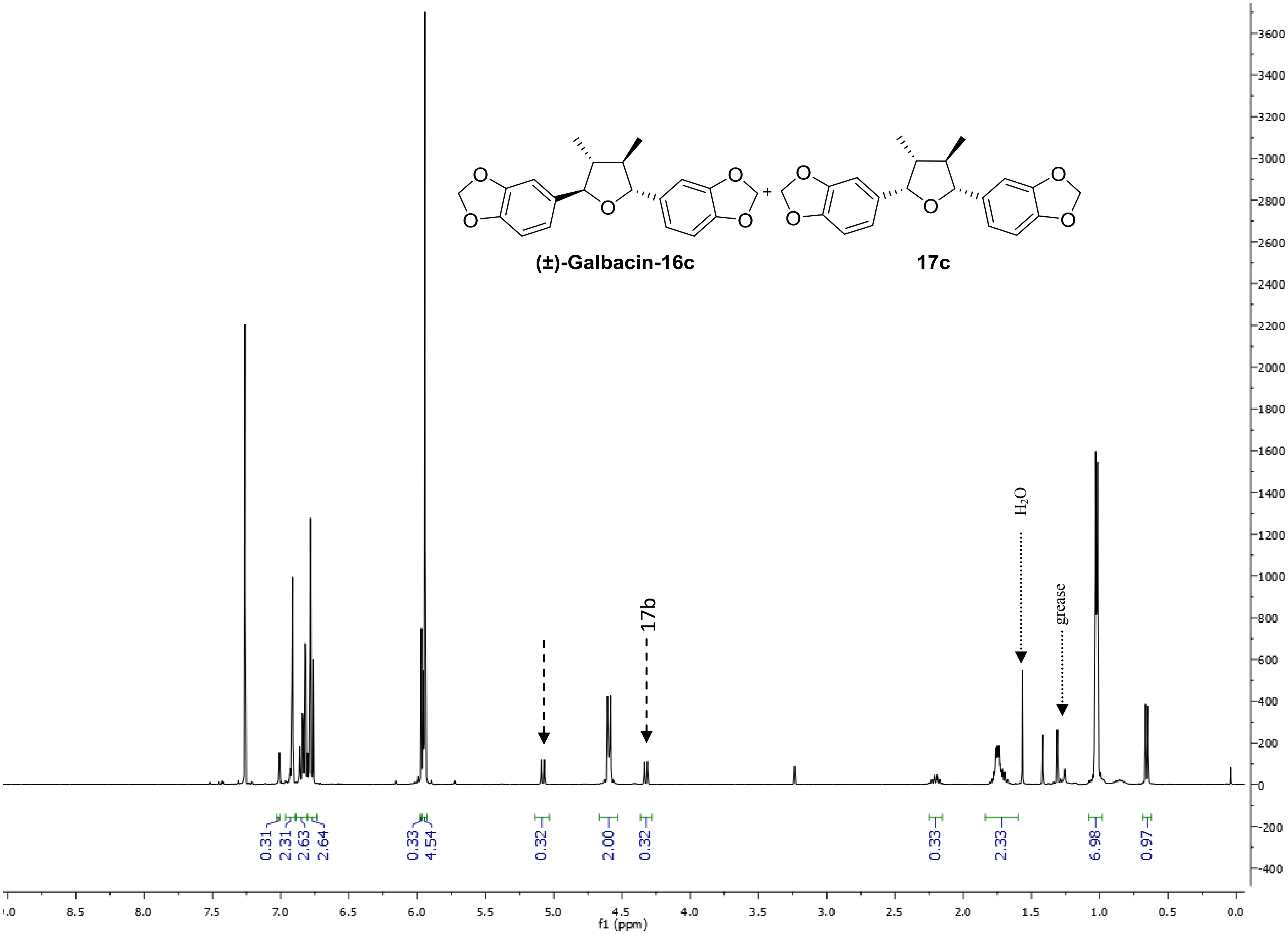

17b
H$_2$O
Diethyl ether
17b
+
(±)-Grandisin-16b
0.59
4.00
0.60
0.30
2.00
0.30
13.75
1.00
8.71
0.31
2.29
1.03
5.82
0.92
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500

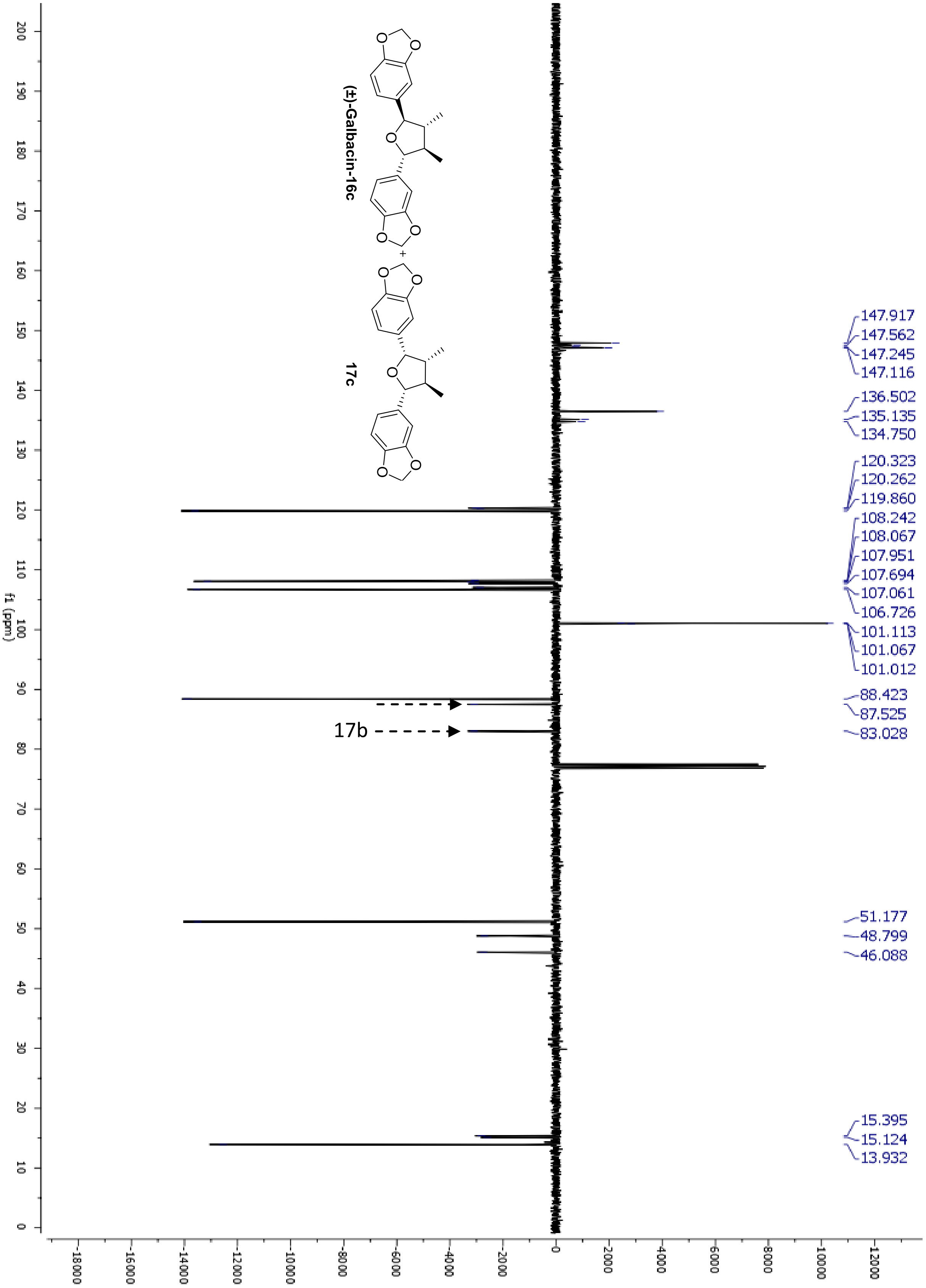

153.396
153.378
153.052
138.125
137.542
137.204
136.827
136.735
104.220
103.608
103.136
88.651
87.497
83.421
60.989
60.965
60.946
56.279
56.240
56.162
51.169
47.963
46.163
15.530
15.040
14.127
17b
(±)-Grandisin-16b
+
17b
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
-30000
-35000
-40000
-45000
-50000

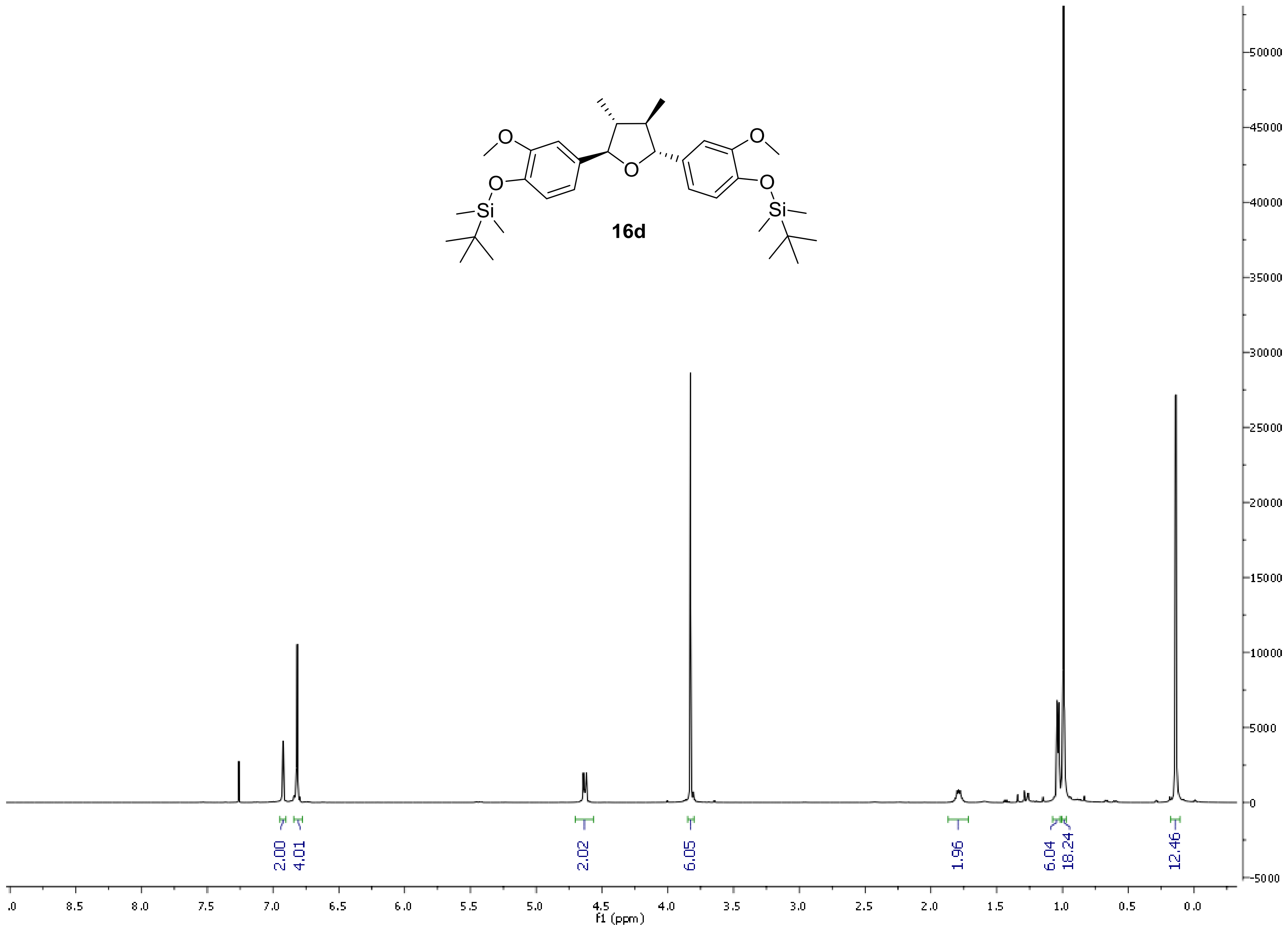

(±)-Galbacin-16c



(±)-Galbacin-16c

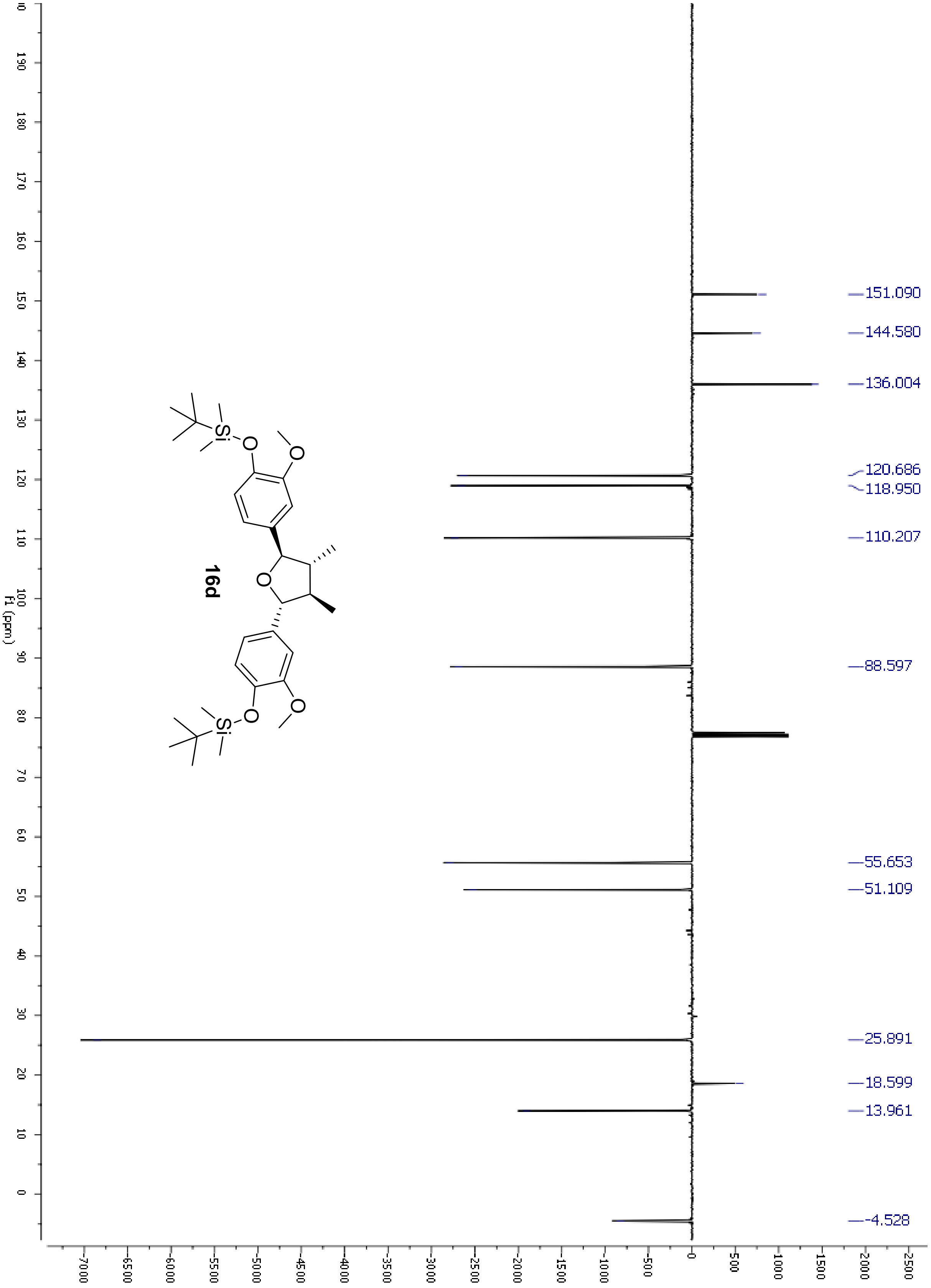

(±)-Galbacin-16c
+
17c
17b
H2O
grease
0.31
2.31
2.63
2.64
0.33
4.54
0.32
2.00
0.32
0.33
2.33
6.98
0.97
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400


(±)-Galbacin-16c
+
17c
17b
147.917
147.562
147.245
147.116
136.502
135.135
134.750
120.323
120.262
119.860
108.242
108.067
107.951
107.694
107.061
106.726
101.113
101.067
101.012
88.423
87.525
83.028
51.177
48.799
46.088
15.395
15.124
13.932
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-18000
-16000
-14000
-12000
-10000
-8000
-6000
-4000
-2000
0
2000
4000
6000
8000
10000
12000

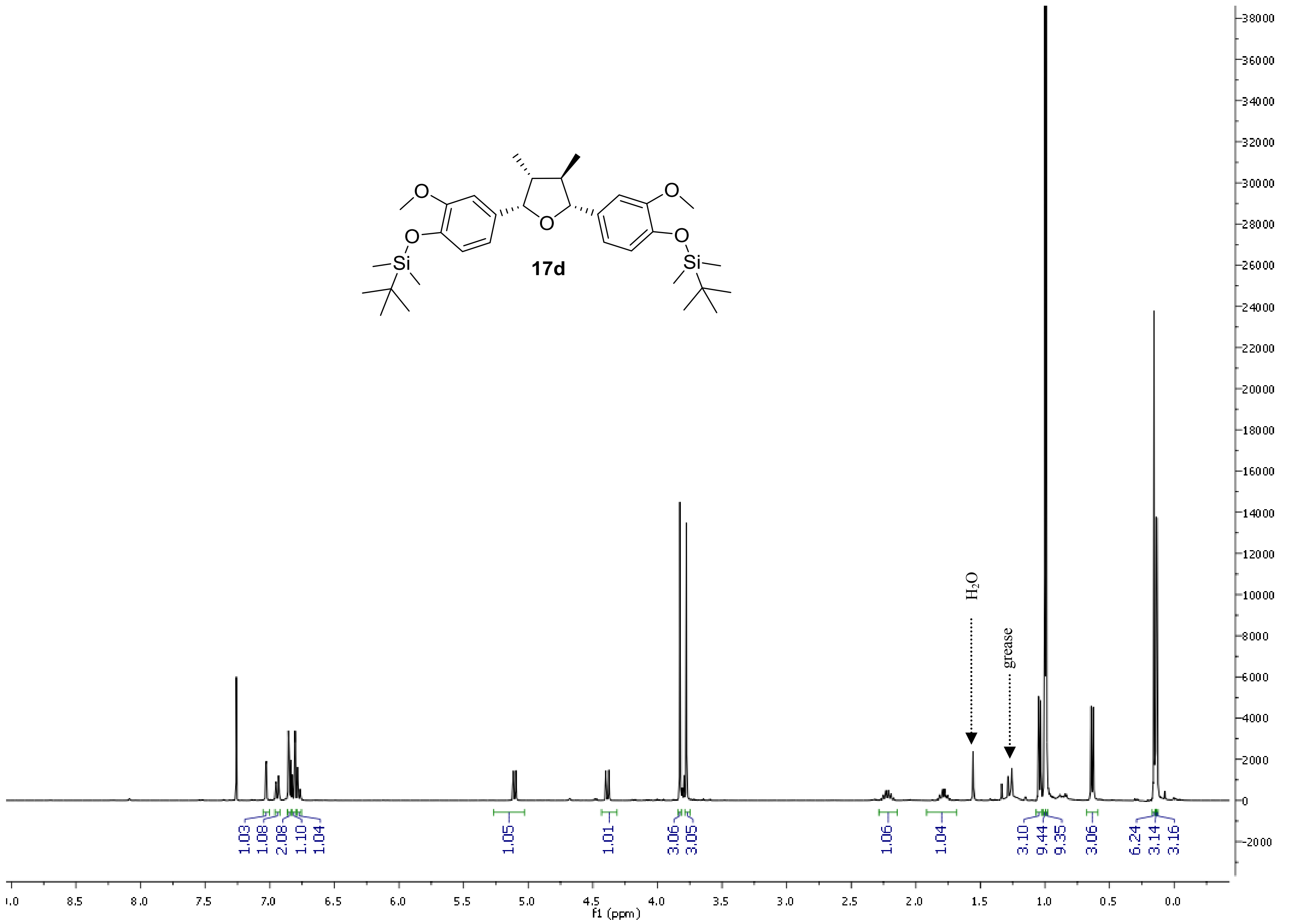


16d

2.00
4.01
2.02
6.05
1.96
6.04
18.24
12.46
.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
f1 (ppm)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
O
O
O
O
O
O
Si
Si

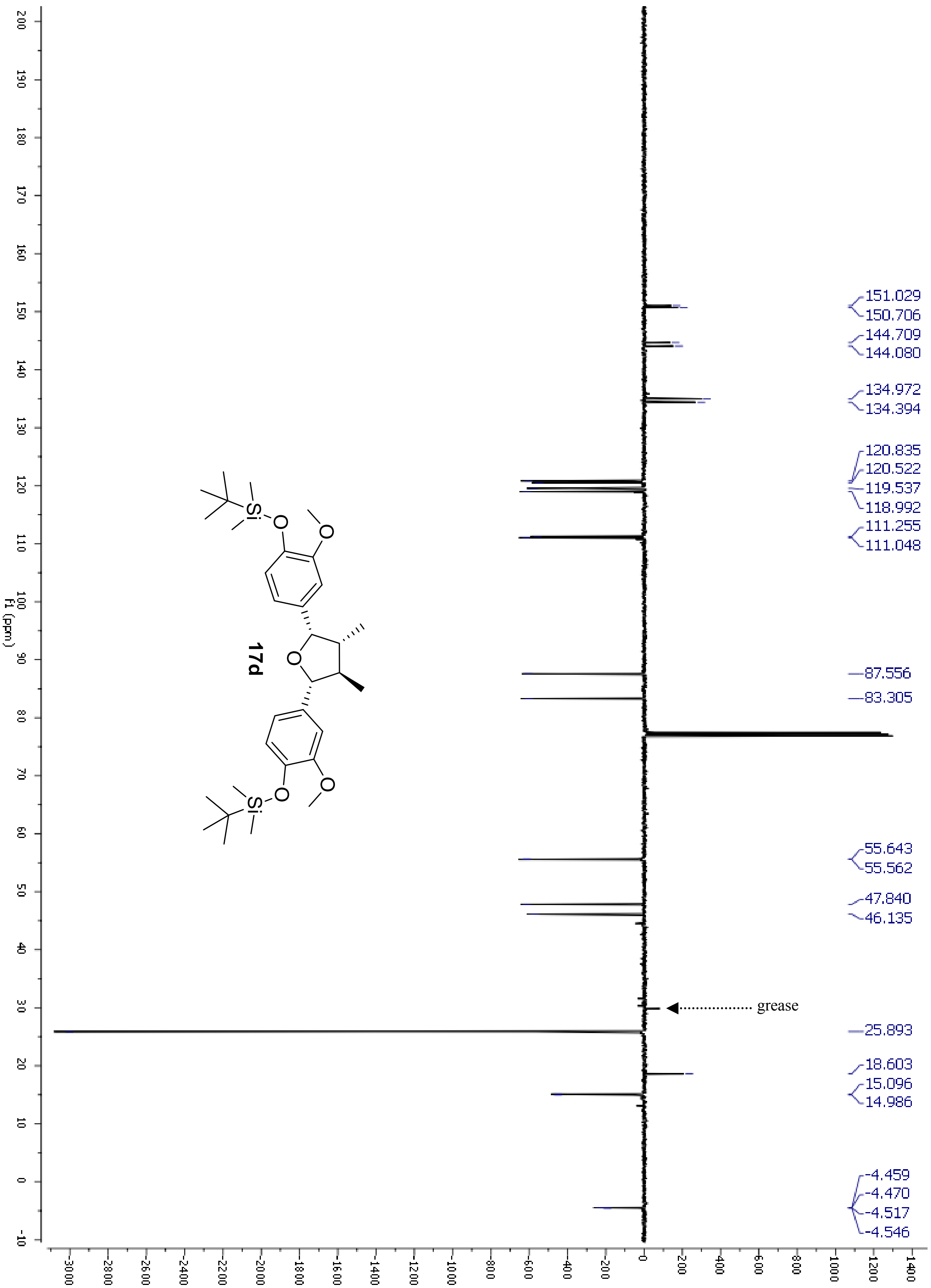

16d

151.090
144.580
136.004
120.686
118.950
110.207
88.597
55.653
51.109
25.891
18.599
13.961
-4.528
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-7000
-6500
-6000
-5500
-5000
-4500
-4000
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
500
1000
1500
2000
2500
Si
O
O
O
Si
O
O
O

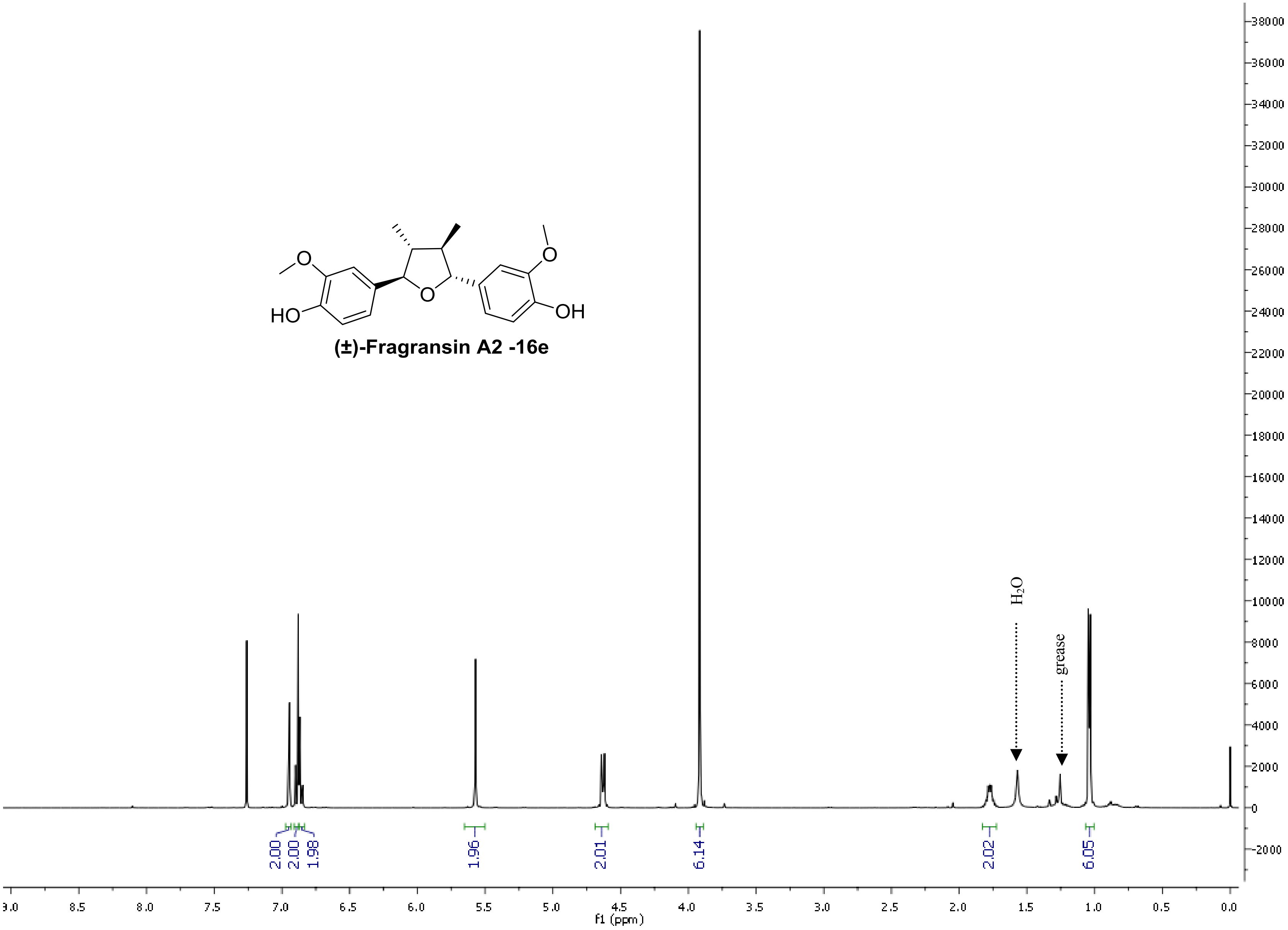


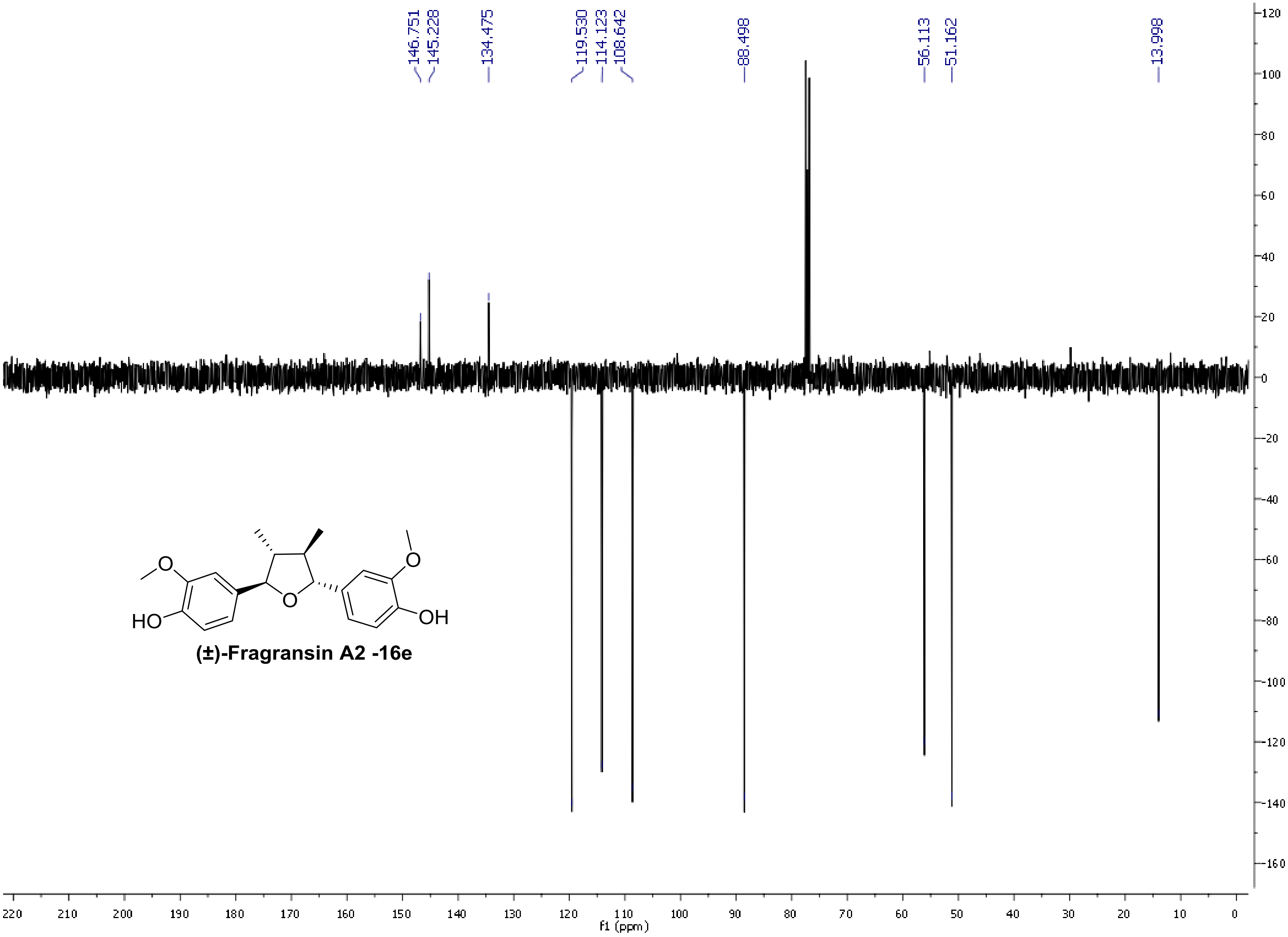
17d

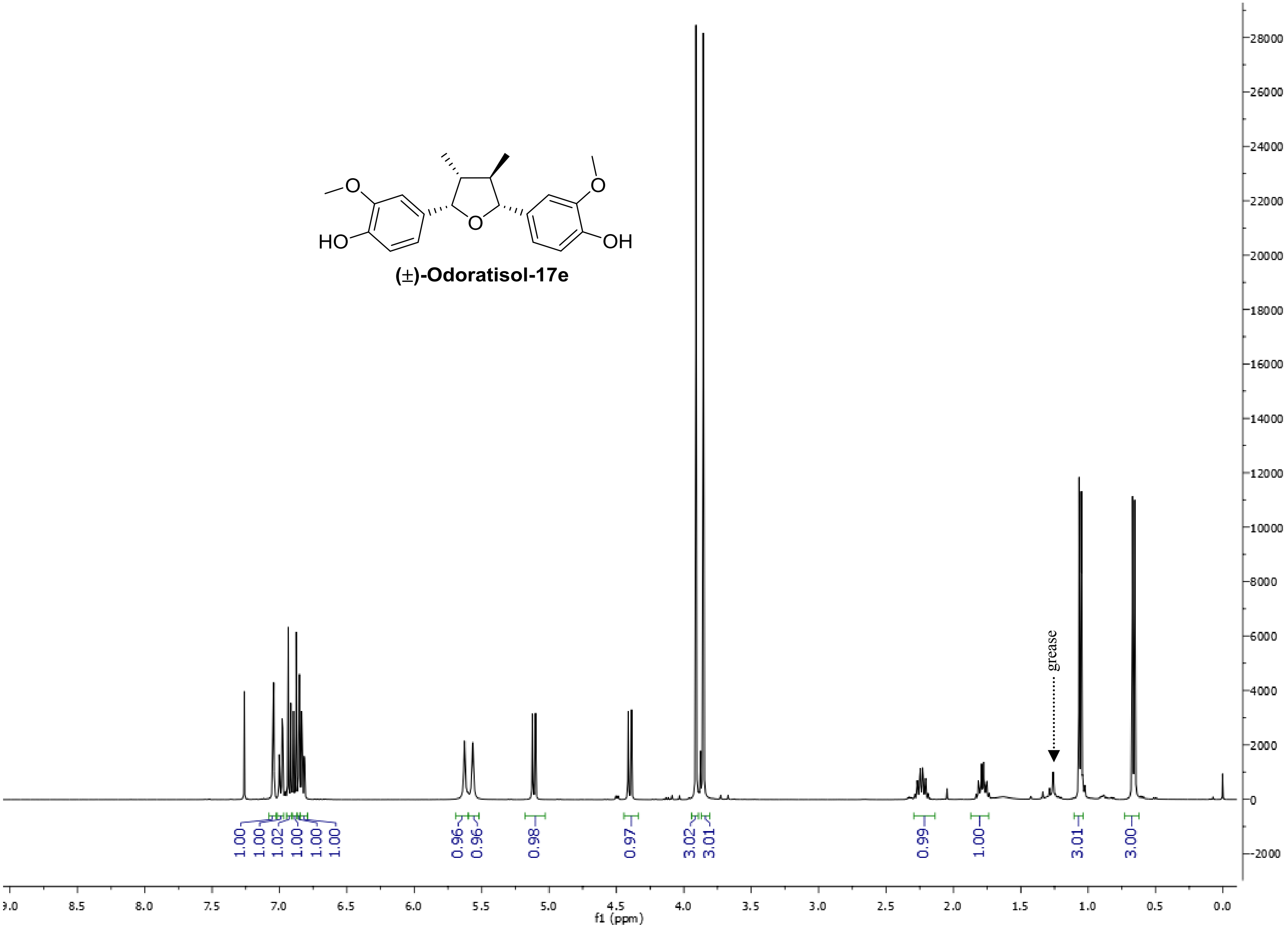
H₂O
grease
1.03
1.08
2.08
1.10
1.04
1.05
1.01
3.06
3.05
1.06
1.04
3.10
9.44
9.35
3.06
6.24
3.14
3.16
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
O
Si

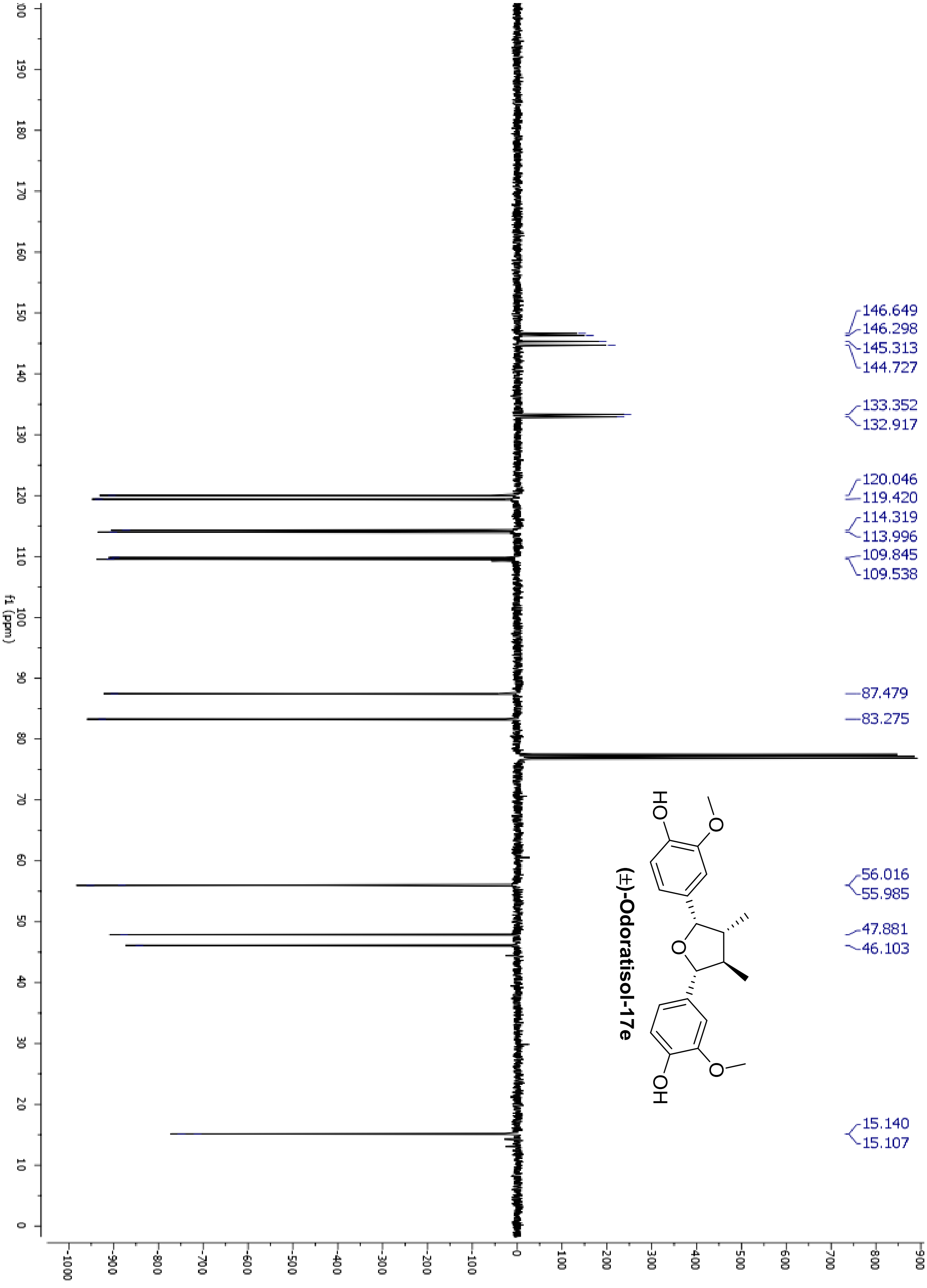


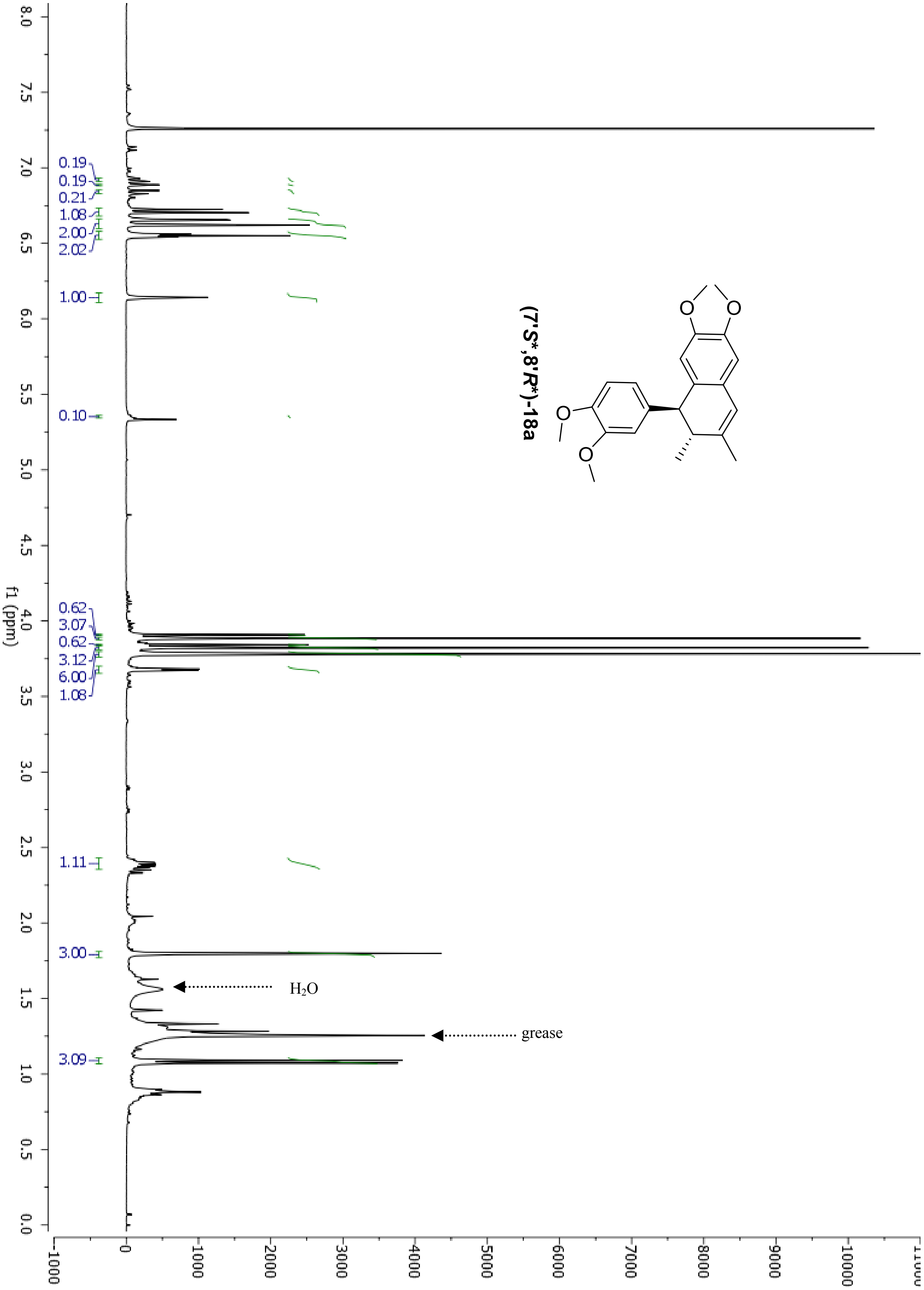
17d
grease
151.029
150.706
144.709
144.080
134.972
134.394
120.835
120.522
119.537
118.992
111.255
111.048
87.556
83.305
55.643
55.562
47.840
46.135
25.893
18.603
15.096
14.986
-4.459
-4.470
-4.517
-4.546
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
-1200
-1400


(±)-Fragransin A2 -16e


(±)-Fragransin A2 -16e

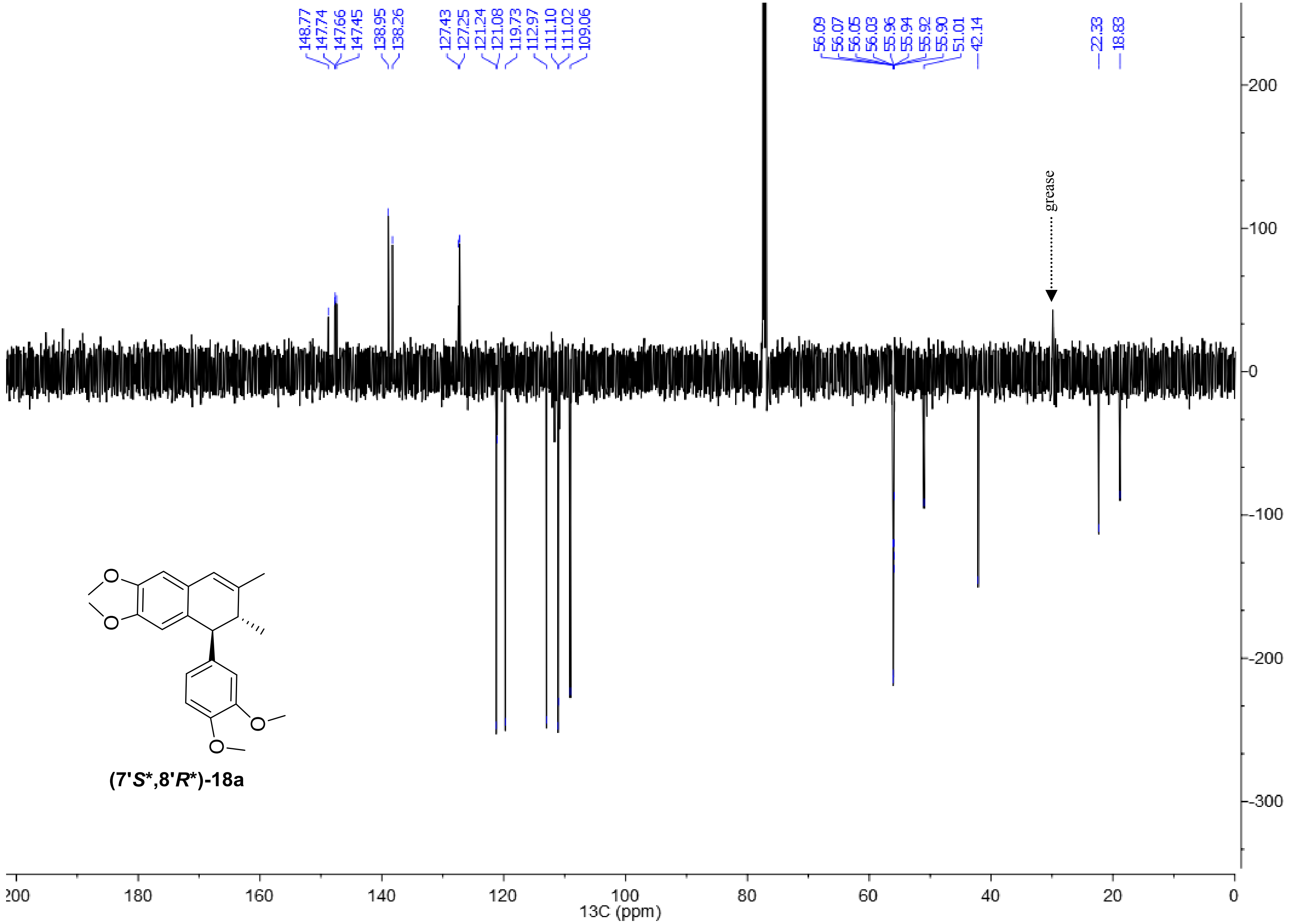

(±)-Odoratisol-17e

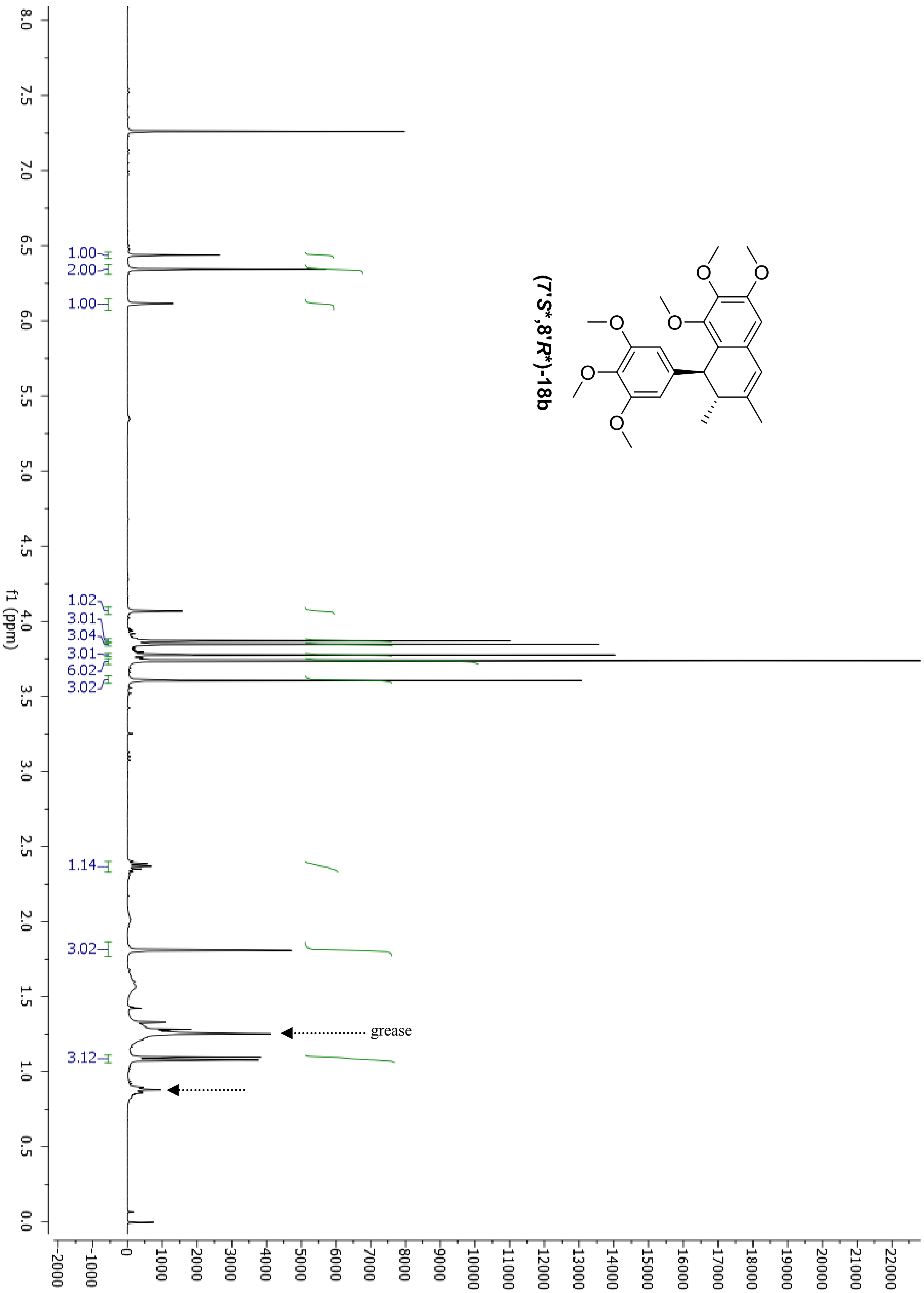

(±)-Odoratisol-17e



(7'S*,8'R*)-18a

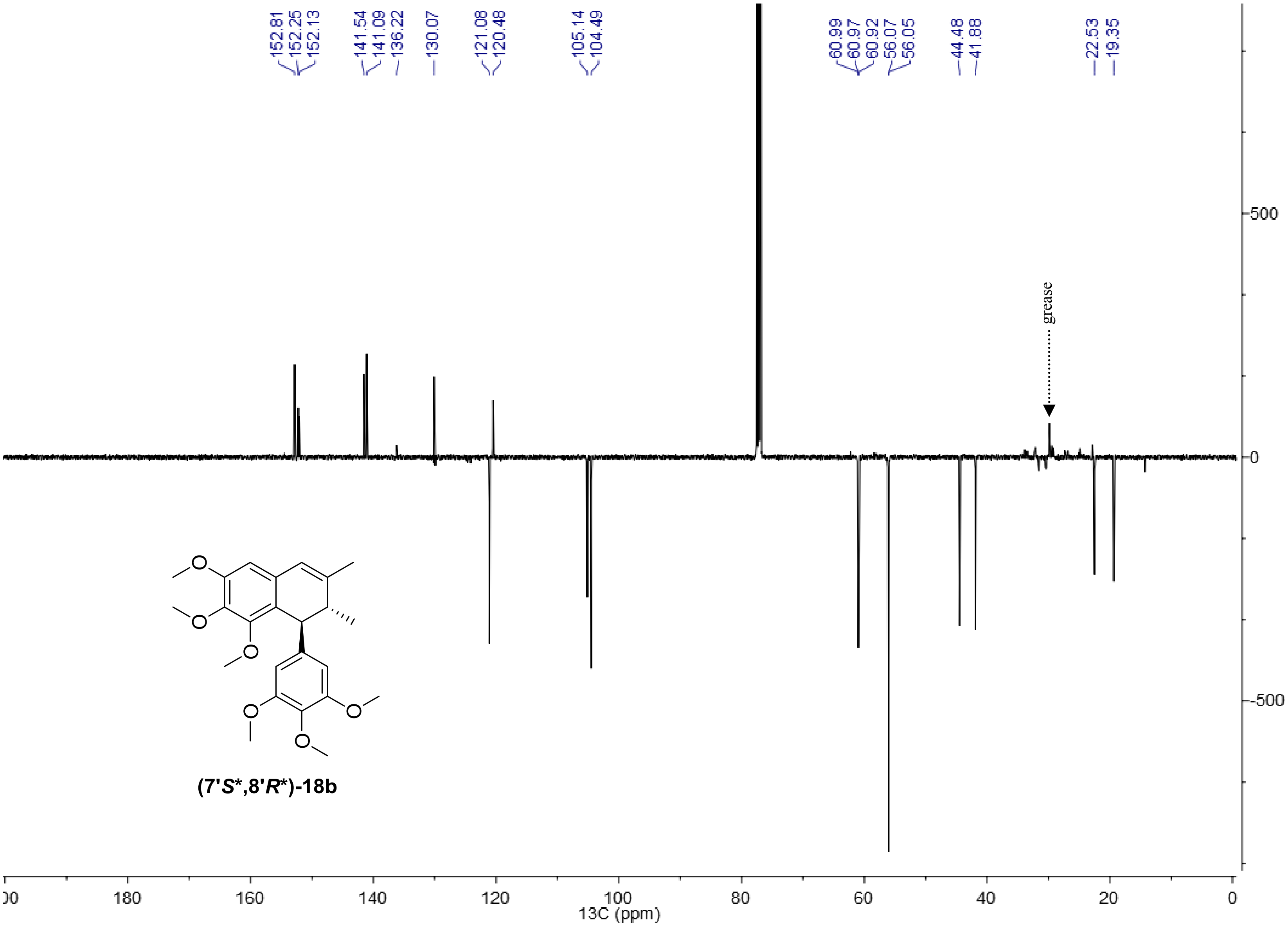
0.19
0.19
0.21
1.08
2.00
2.02
1.00
0.10
0.62
3.07
0.62
3.12
6.00
1.08
1.11
3.00
3.09
H₂O
grease
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000


148.77
147.74
147.66
147.45
138.95
138.26
127.43
127.25
121.24
121.08
119.73
112.97
111.10
111.02
109.06
56.09
56.07
56.05
56.03
55.96
55.94
55.92
55.90
51.01
42.14
22.33
18.83
grease
(7'*S**,8'*R**)-18a
200
100
0
-100
-200
-300
200
180
160
140
120
100
80
60
40
20
0
13C (ppm)

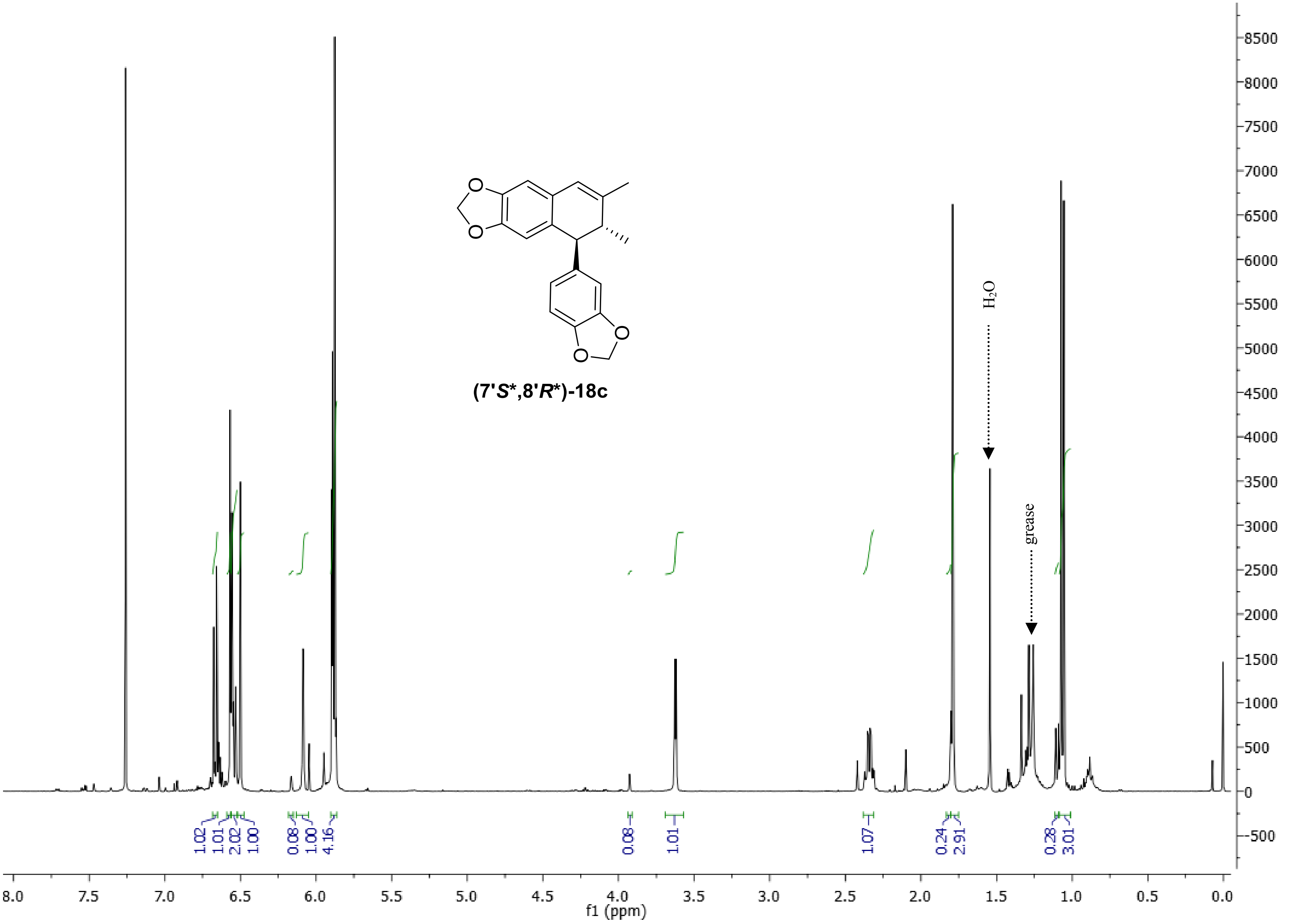


(7'S*,8'R*)-18b

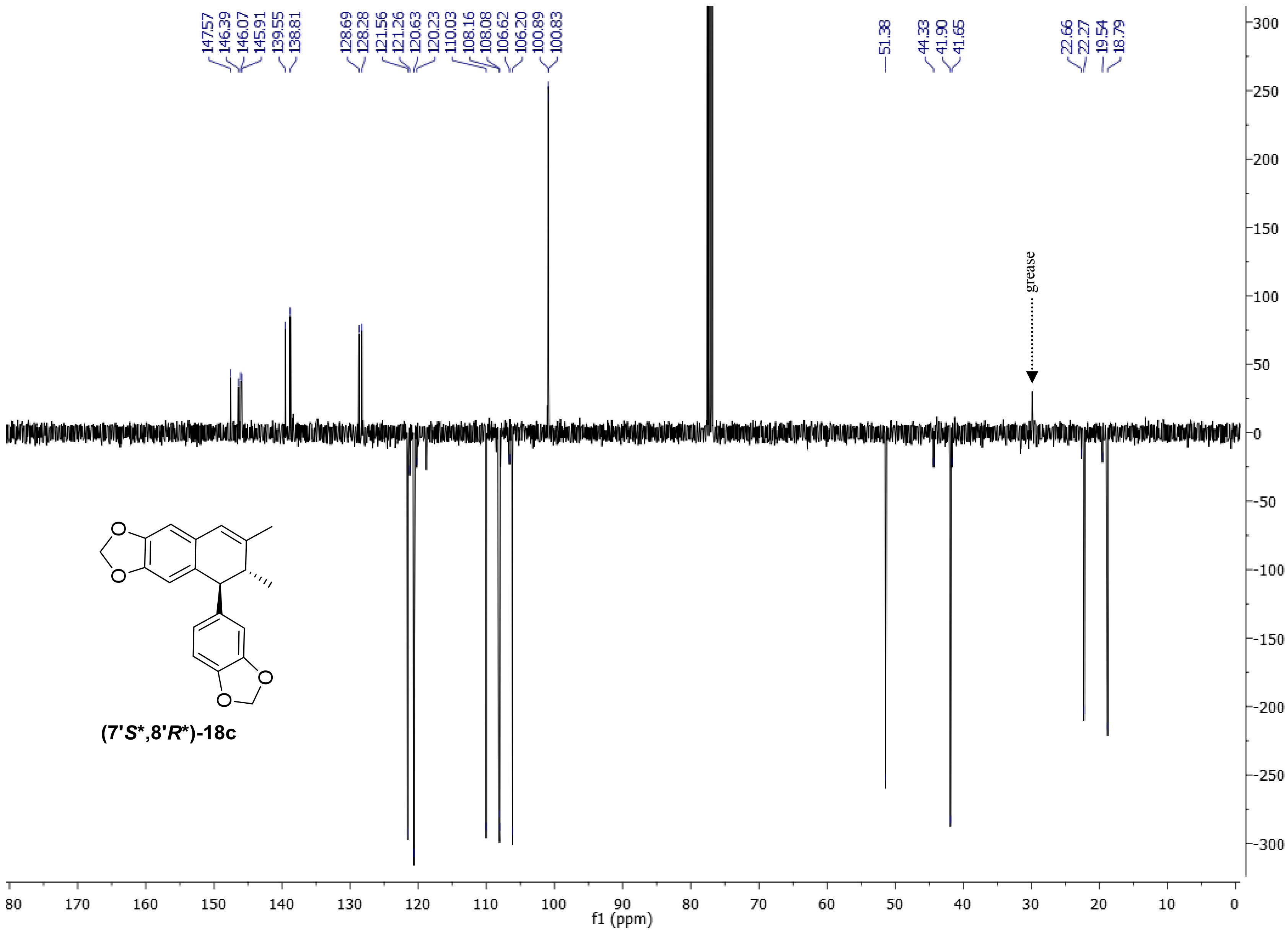
1.00
2.00
1.00
1.02
3.01
3.04
3.01
6.02
3.02
1.14
3.02
3.12
grease
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
-2000
-1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
16000
17000
18000
19000
20000
21000
22000
O
O
O
O
O
O


(7'*S**,8'*R**)-18b

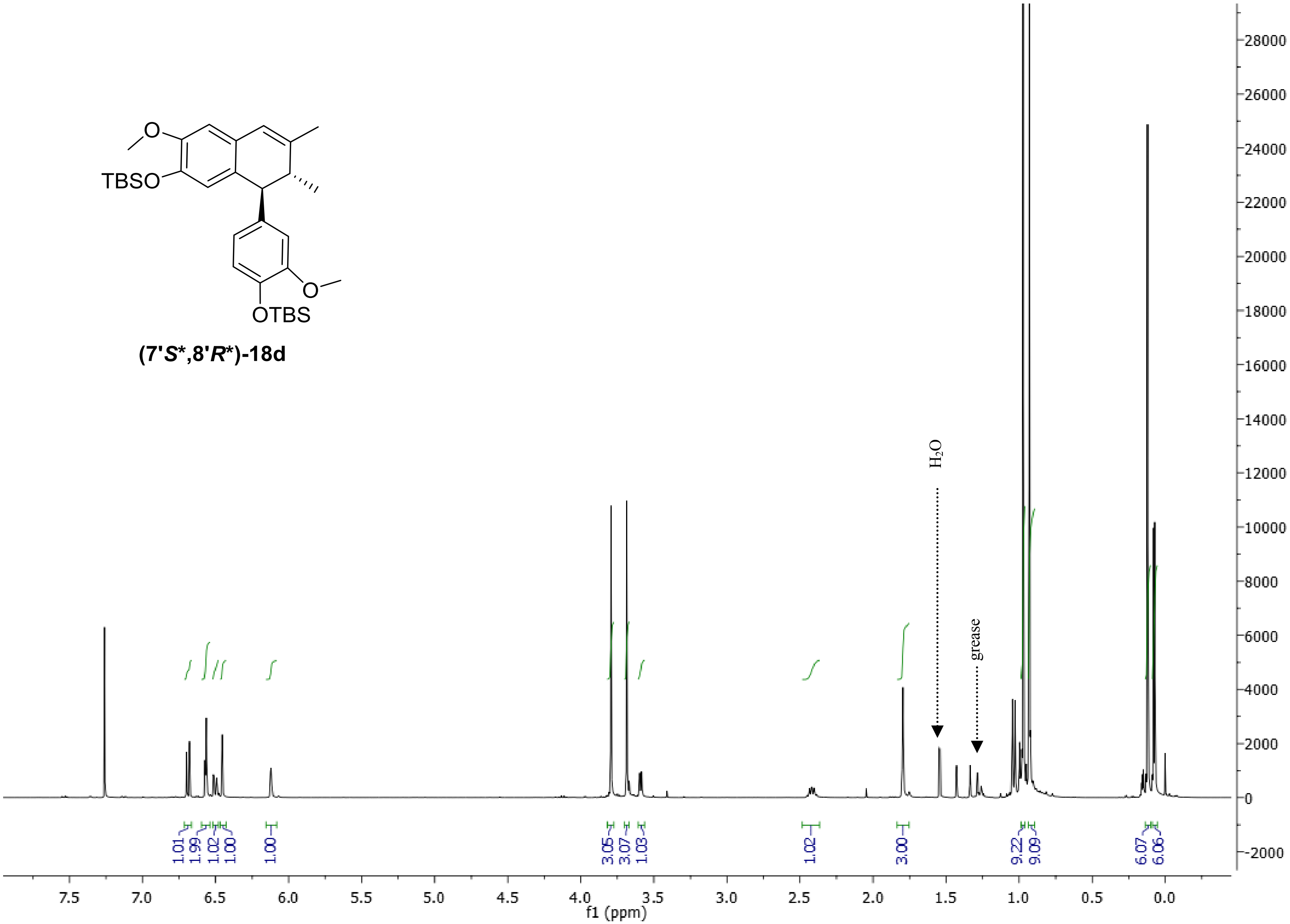
152.81
152.25
152.13
141.54
141.09
136.22
130.07
121.08
120.48
105.14
104.49
60.99
60.97
60.92
56.07
56.05
44.48
41.88
22.53
19.35
grease
500
0
-500
00
180
160
140
120
100
80
60
40
20
0
13C (ppm)


(7'*S**,8'*R**)-18c

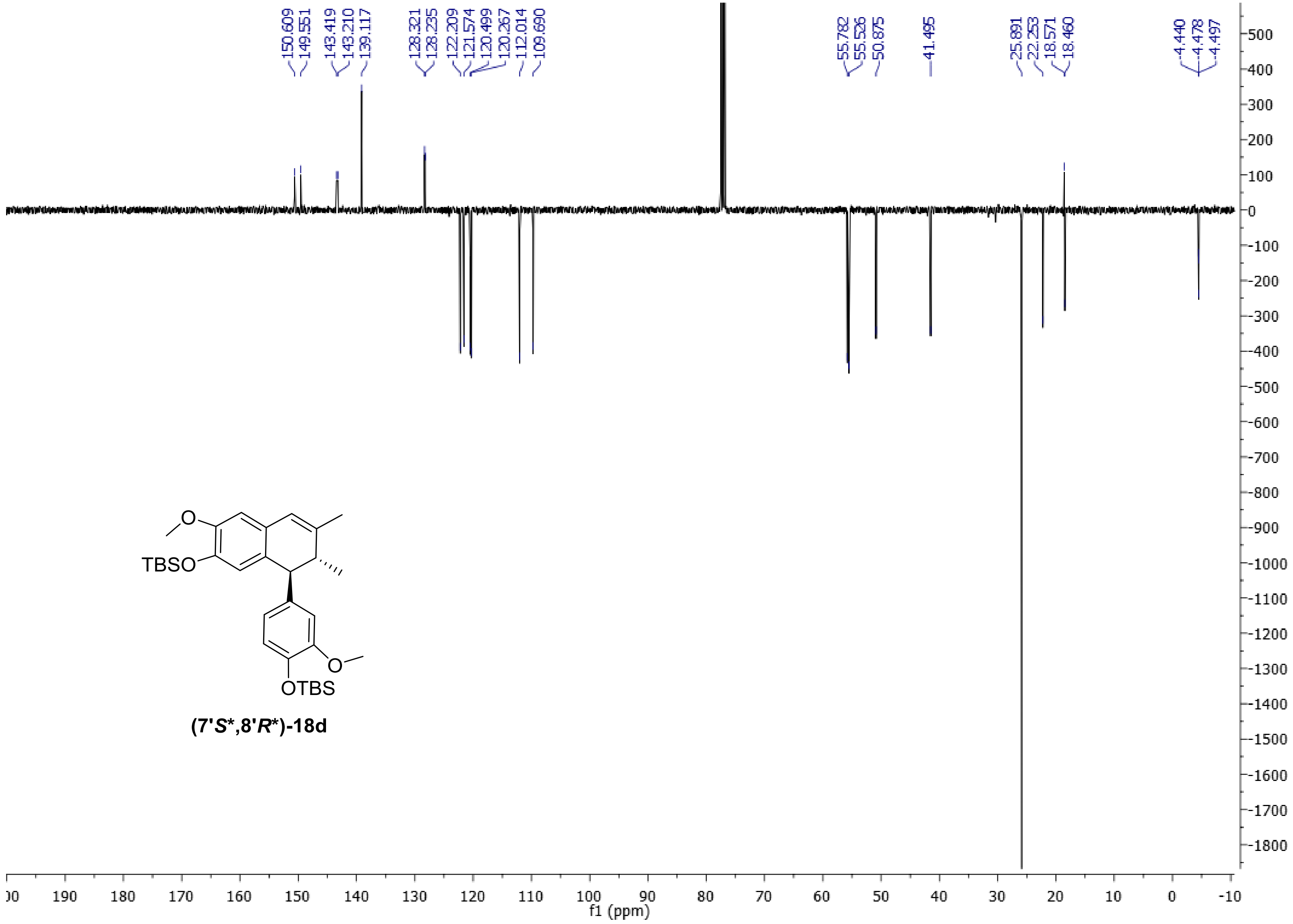
H₂O
grease
1.02
1.01
2.02
1.00
0.08
1.00
4.16
0.08
1.01
1.07
0.24
2.91
0.28
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


(7'*S**,8'*R**)-18c

147.57
146.39
146.07
145.91
139.55
138.81
128.69
128.28
121.56
121.26
120.63
120.23
110.03
108.16
108.08
106.62
106.20
100.89
100.83
51.38
44.33
41.90
41.65
22.66
22.27
19.54
18.79
grease
O
O
O
O
f1 (ppm)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300


(7'*S,8'*R**)-18d**

TBSO
O
O
OTBS
H2O
grease
1.01
1.99
1.02
1.00
1.00
3.05
3.07
1.03
1.02
3.00
9.22
9.09
6.07
6.06
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)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000


(7'*S**,8'*R**)-18d

TBSO
O
OTBS
O
150.609
149.551
143.419
143.210
139.117
128.321
128.235
122.209
121.574
120.499
120.267
112.014
109.690
55.782
55.526
50.875
41.495
25.891
22.253
18.571
18.460
-4.440
-4.478
-4.497
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
-1100
-1200
-1300
-1400
-1500
-1600
-1700
-1800