Supporting Information

A Chiral LC-MS Strategy for Stereochemical Assignment of Natural Products Sharing a 3-Methylpent-4-en-2-ol Moiety in Their Terminal Structures

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1. Experimental Section

General Experimental Procedures

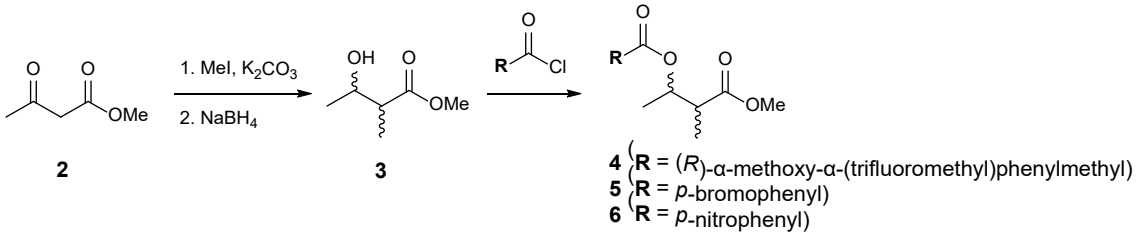
Optical rotations were measured on a JASCO P-2300 polarimeter. UV spectra were measured on a JASCO V-730 spectrophotometer. IR spectra were recorded on a JASCO FT/IR-400 spectrometer. NMR spectra were measured on a JEOL alpha 500 spectrometer or a Bruker AVANCE III HD 400 spectrometer using residual solvent signals (δ_H 3.30; δ_C 49.0 ppm of CD_3OD and δ_H 7.24; δ_C 77.0 ppm of $CDCl_3$) as internal standards. LC-MS experiments were performed on a Shimadzu LC-20AD solvent delivery system interfaced with a SCIEX X500R Q-TOF mass spectrometer (ESI source), or a Thermo Scientific UltiMate 3000 basic automated system interfaced with a Thermo Fisher Scientific Q Exactive Focus mass spectrometer (ESI source). Analytical or preparative thin-layer chromatography (TLC) was performed using a Merck silica gel 60 F254 plate (0.25 or 0.50 mm thickness). Flash column chromatography was carried out using Kanto chemical silica gel 60N (40–50 mesh) or Yamazen silica gel HiFlash (SiOH-30 μ Premium, 30 μm, 60 Å) with automated flash column system EPCLC-Wprep2XY-10VW (Yamazen Corporation). All reactions susceptible to moisture and air were carried out in an atmosphere of argon gas, using the glassware oven-dried over 3 h. CH_2Cl_2 and THF were purified by Glass Contour Solvent Dispensing System (Nikko Hansen). All other reagents were purchased at the highest commercial grade and used directly.

Fermentation, Extraction and Isolation of Capsulactone (1)

Fusarium sp. was grown on rice solid medium (to 70 g Japanese commercially available rice was added 70 mL of sterile sea water and 70 mL of distilled water) at room temperature. After 25 days, the whole culture was extracted with MeOH and EtOAc. The extracts were combined, concentrated *in vacuo*, and partitioned between EtOAc and H_2O. The dried EtOAc extracts was subjected to ODS flash column chromatography with stepwise elution of 5% MeOH, 50% MeOH, 90% MeOH, 100% MeOH and $CHCl_3$/MeOH (1:1). The 90% MeOH fraction was first purified by RP-HPLC on a Cosmosil 5C_{18}-AR-II column with gradient elution from 60% MeOH to 90% MeOH in the presence of 0.5% AcOH to afford several fractions. Each fraction was further purified by RP-HPLC on a Cosmosil 5C_{18}-AR-II column with gradient elution from 36% MeCN to 52% MeCN in the presence of 0.5% AcOH to give capsulactone (**1**, 1.2 mg).

Capsulactone (**1**); colorless gum; $[\alpha]_D^{26}$ +12 (*c* 0.1, MeOH); UV (MeOH) λ_{max} (log ε) 308 (3.6), 250 (3.6); ^1H and ^{13}C NMR data, see Table 1; HRMS (ESI, positive) calcd for $C_{17}H_{24}O_4$ $[(M+H)^+]$ 293.1747, found 293.1741.

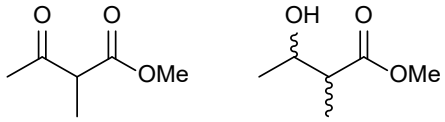
Synthetic Procedures for Esters 4–6, Each as a Mixture of Four Stereoisomers



2 **3**

4 (**R** = (*R*)-α-methoxy-α-(trifluoromethyl)phenylmethyl)
5 (**R** = *p*-bromophenyl)
6 (**R** = *p*-nitrophenyl)

Methyl 2-methyl-3-oxobutanoate (S1), and methyl-3-hydroxy-2-methylbutanoate (3)

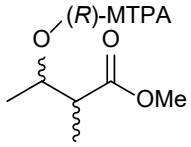


S1 **3**

To a stirred mixture of methyl acetoacetate (**2**, 0.500 mL, 4.65 mmol) and iodomethane (0.290 mL, 4.65 mmol) at 0 °C was added K_2CO_3 (965.2 mg, 6.98 mmol) portionwise over 5 min. After stirring at 0 °C for 1.5 h, the mixture was allowed to warm to rt. After 19 h, to the mixture was added Et_2O (5 mL), and the resulting suspension was filtrated. The filtrate was washed with brine (5 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (SiOH-30μ Premium, 14 g, EtOAc/hexane = 1:4) to give racemic **S1** (377.3 mg, 62%) as a colorless syrup: ^{1}H NMR (selected for the keto tautomer, 400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.50 (q, *J* = 7.2 Hz, 1H), 2.22 (s, 3H), 1.33 (d, *J* = 7.1 Hz, 3H). Other spectroscopic data for **S1** were in good agreement with those reported.[1]

To a stirred suspension of $NaBH_4$ (9.3 mg, 0.25 mmol) in EtOH (3.0 mL) at 0 °C was added a solution of ketone **S1** (100.2 mg, 0.770 mmol), thus obtained above, in EtOH (2.0 mL) in a dropwise manner over 3 min. After stirring at 0 °C for 1.5 h, to the mixture was added saturated aqueous NH_4Cl (0.5 mL). The mixture was partitioned between EtOAc and H_2O (5 mL each). Aqueous layer was separated and extracted with EtOAc (2 × 5 mL). Combined extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (SiOH-30μ Premium, 7 g, EtOAc/hexane = 2:3) to give alcohol **3** (a mixture of four stereoisomers, 65.3 mg, 64%) as a colorless syrup: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 and 3.86 (two multiplets, 1H total), 3.70 and 3.69 (two singlets, 3H total), 2.59 and 2.49 (two multiplets, 1H total), 2.49 and 2.44 (multiplet and doublequartet, *J* = 7.2, 7.2 Hz, 1H total), 1.20 and 1,16 (two doublets, *J* = 6.4 Hz each, 3H total), 1.17 and 1.17 (two doublets, *J* = 7.2 Hz each, 3H total). Other spectroscopic data for **3** were in good agreement with those reported.[2]

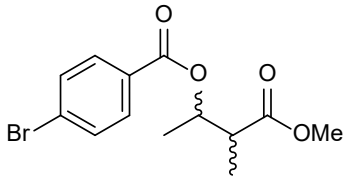
Methyl 2-methyl-3-(((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl)oxy)butanoate (4)



4

To a stirred solution of alcohol **3** (5.0 mg, 0.038 mmol) in pyridine (150 µL) at rt was added (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride ((*S*)-(+)-MTPACl, 10 µL, 0.053 mmol). After 16 h, the reaction mixture was diluted with water (0.7 mL) and extracted with $CHCl_3$ (2 × 0.5 mL). Combined extracts were concentrated *in vacuo* to afford crude (*R*)-MTPA ester **4** (9.2 mg) as a colorless solid: HRMS (ESI, positive) calcd for $C_{16}H_{19}F_3O_5$ [(M+Na)$^+$] 371.1077, found 371.1082.

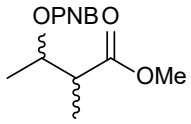
4-Methoxy-3-methyl-4-oxobutan-2-yl 4-bromobenzoate (5)



5

To a stirred solution of alcohol **3** (5.0 mg, 0.038 mmol) in pyridine (180 µL) at rt were added *p*-bromobenzoyl chloride (20.9 mg, 0.0952 mmol) and DMAP (1.7 mg, 0.014 mmol). After 16 h, the reaction mixture was diluted with water (0.8 mL) and extracted with $CHCl_3$ (2 × 0.5 mL). Combined extracts were concentrated *in vacuo* to afford crude ester **5** (12.9 mg) as a white solid: HRMS (ESI, positive) calcd for $C_{13}H_{15}BrNaO_4$ [(M+Na)$^+$] 337.0046, found 337.0058.

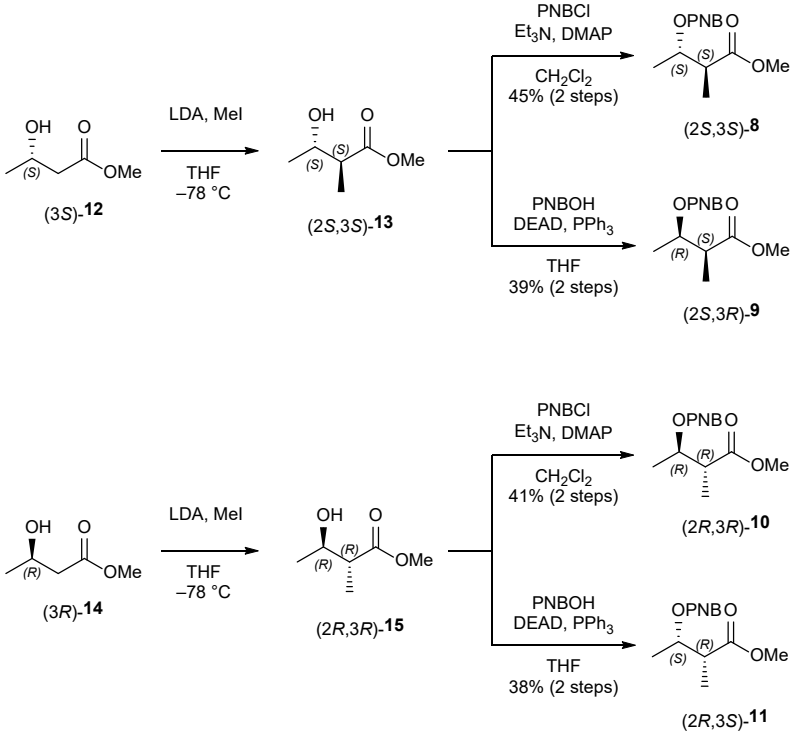
4-Methoxy-3-methyl-4-oxobutan-2-yl 4-nitrobenzoate (6)



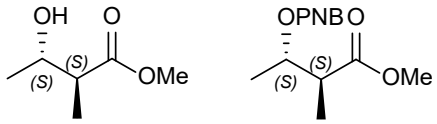
6

To a stirred solution of alcohol **3** (5.0 mg, 0.038 mmol) in CH_2Cl_2 (300 µL) at rt were added Et_3N (21 µL, 0.151 mmol), DMAP (1.45 mg, 0.012 mmol) and *p*-nitrobenzoyl chloride (21.6 mg, 0.117 mmol). After 5 h, the reaction mixture was concentrated *in vacuo* to afford crude ester **6** (14.9 mg) as a yellow solid: HRMS (ESI, positive) calcd for $C_{13}H_{15}NO_6$ [(M+Na)$^+$] 304.0792, found 304.0796.

Synthetic Procedures for PNB esters 8–11



Methyl (2*S*,3*S*)-3-hydroxy-2-methylbutanoate (13), and (2*S*,3*S*)-4-methoxy-3-methyl-4-oxobutan-2-yl 4-nitrobenzoate (8)



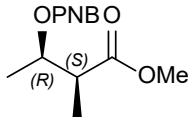
(2*S*,3*S*)-**13** (2*S*,3*S*)-**8**

To a stirred solution of LDA (1.0 M in THF/hexanes, 25 mL, 25 mmol) at –78 °C was added methyl (*S*)-(+)-3-hydroxybutyrate (**12**, 0.928 mL, 8.33 mmol) in THF (8.0 mL) in a dropwise manner for 3 min. After stirring at –78 °C for 30 min, to the solution was added iodomethane (3.11 mL, 49.5 mmol) in a dropwise manner over 3 min. After stirring at –78 °C for additional 2 h, the mixture was then allowed to warm to 0 °C and quenched with hydrochloric acid (1 M, 32 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 30 mL). Combined extracts were washed with brine (2 × 60 mL), dried over Na_2SO_4, and concentrated *in vacuo* to a volume of ca. 5 mL to afford a yellow solution of crude **13** (6.54 g), which was used for the next reaction without purification.

A part of the residual solution of crude **13** (129.8 mg), thus obtained above, was diluted with CH_2Cl_2 (1.0 mL). To the stirred solution at rt were added Et_3N (69.0 μL, 0.495 mmol), DMAP

(2.7 mg, 0.022 mmol) and *p*-nitrobenzoyl chloride (PNBCl, 46.3 mg, 0.250 mmol). After 1 h, the mixture was poured into saturated aqueous NH_4Cl (1 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 1 mL). Combined extracts were washed with brine (2 × 1 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative TLC (0.50 mm thickness, 20 × 20 cm, EtOAc/hexane = 1:4) to give PNB ester **8** (21.2 mg, 45% for 2 steps) as a colorless oil: $[\alpha]_D^{26}$ +49 (*c* 1.0, MeOH); IR (ATR) 2987, 2952, 1726, 1726, 1528, 1274, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (m, 2H), 8.15 (m, 2H), 5.35 (dq, *J* = 6.5, 6.5 Hz, 1H), 3.65 (s, 3H), 2.86 (dq, *J* = 7.2, 7.2 Hz, 1H), 1.37 (d, *J* = 6.4 Hz, 3H), 1.23 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 163.7, 150.6, 135.7, 130.7 (×2), 123.5 (×2), 73.4, 51.9, 44.6, 17.1, 12.8; HRMS (ESI, positive) calcd for $C_{13}H_{15}NO_6$ [$(M+Na)^+$] 304.0792, found 304.0796.

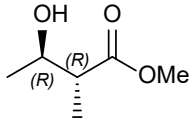
(2*S*,3*R*)-4-Methoxy-3-methyl-4-oxobutan-2-yl 4-nitrobenzoate (9)



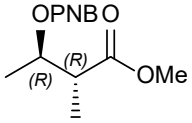
(2*S*,3*R*)-**9**

A part of the residual solution of crude **13** (125.1 mg), thus obtained above, was diluted with THF (1.0 mL). To the stirred solution at 0 °C were added *p*-nitrobenzoic acid (PNBOH, 54.6 mg, 0.327 mmol), PPh_3 (86.5 mg, 0.330 mmol), and a solution of diethyl azodicarboxylate in toluene (2.2 M, 0.148 mL, 0.326 mmol). After stirring at rt for 2 h, the mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (SiOH-30μ Premium, 7 g, EtOAc/hexane = 23:77) to give PNB ester **9** (18.3 mg, 39% for 2 steps) as a colorless oil: $[\alpha]_D^{26}$ –14 (*c* 1.0, MeOH); IR (ATR) 2990, 2952, 1728, 1728, 1529, 1275, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (m, 2H), 8.16 (m, 2H), 5.43 (m, 1H), 3.67 (s, 3H), 2.79 (qd, *J* = 7.1, 5.5 Hz, 1H), 1.39 (d, *J* = 6.4 Hz, 3H), 1.27 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 163.9, 150.6, 135.7, 130.7, 123.5, 72.8, 51.9, 44.3, 17.5, 12.2; HRMS (ESI, positive) calcd for $C_{13}H_{15}NO_6$ [$(M+Na)^+$] 304.0792, found 304.0795.

Methyl (2*R*,3*R*)-3-hydroxy-2-methylbutanoate (15), and
(2*R*,3*R*)-4-methoxy-3-methyl-4-oxobutan-2-yl 4-nitrobenzoate (10)



(2*R*,3*R*)-**15**



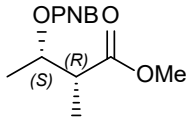
(2*R*,3*R*)-**10**

To a stirred solution of LDA (1.0 M in THF/hexanes, 25 mL, 25 mmol) at –78 °C was added

methyl (*R*)-(–)-3-hydroxybutyrate (**14**, 0.928 mL, 8.33 mmol) in THF (8 mL) in a dropwise manner for 3 min. After stirring at –78 °C for 30 min, to the solution was added iodomethane (3.11 mL, 49.5 mmol) in a dropwise manner for 3 min. After stirring at –78 °C for additional 2 h, the mixture was then allowed to warm to 0 °C, poured into hydrochloric acid (1 M, 30 mL), and extracted with CH_2Cl_2 (60 mL, 20 mL, 100 mL). The combined extracts were washed with brine (70 mL), dried over Na_2SO_4, and concentrated *in vacuo* to a volume of ca. 5 mL to afford a yellow solution of crude **15** (6.36 g), which was used for the next reaction without purification.

A part of the residual solution of crude alcohol **15** (121.5 mg), thus obtained above, was diluted with CH_2Cl_2 (1.0 mL). To the stirred solution at rt were added Et_3N (69.7 μL, 0.500 mmol), DMAP (2.6 mg, 0.021 mmol), and *p*-nitrobenzoyl chloride (PNBCl, 50.0 mg, 0.269 mmol). After 1 h, the mixture was poured into saturated aqueous NH_4Cl (1 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 1 mL). Combined extracts were washed with brine (2 × 1 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative TLC (0.50 mm thickness, 20 × 20 cm, EtOAc/hexane = 1:4) to give PNB ester **10** (19.0 mg, 41% for 2 steps) as a colorless oil: $[\alpha]_D^{26}$ –49 (*c* 1.0, MeOH); IR (ATR) 2987, 2952, 1726, 1726, 1528, 1273, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (m, 2H), 8.15 (m, 2H), 5.35 (m, 1H), 3.65 (s, 3H), 2.85 (dq, *J* = 7.1, 7.1 Hz, 1H), 1.37 (d, *J* = 6.4 Hz, 3H), 1.23 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 163.7, 150.5, 135.7, 130.7, 123.5, 73.4, 51.9, 44.6, 17.1, 12.8; HRMS (ESI, positive) calcd for $C_{13}H_{15}NO_6$ [$(M+Na)^+$] 304.0792, found 304.0797.

(2*R*,3*S*)-4-Methoxy-3-methyl-4-oxobutan-2-yl 4-nitrobenzoate (11)

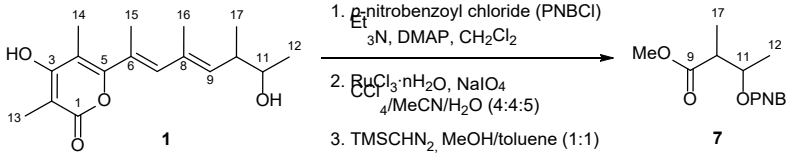


(2*R*,3*S*)-**11**

A part of the residual solution of crude alcohol **15** (113.1 mg), thus obtained above, was diluted with THF (1.0 mL). To the stirred solution at 0 °C were added *p*-nitrobenzoic acid (PNBOH, 56.7 mg, 0.339 mmol), PPh_3 (88.9 mg, 0.339 mmol), and a solution of diethyl azodicarboxylate in toluene (2.2 M, 154 μL, 0.339 mmol). After stirring at rt for 1.5 h, the mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (60N, 6.9 g, EtOAc/hexane = 3:17) to give PNB ester **11** (18.3 mg, 39% for 2 steps) as a colorless oil: $[\alpha]_D^{26}$ +14 (*c* 1.0, MeOH); IR (ATR) 2989, 2951, 1725, 1725, 1528, 1275, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (m, 2H), 8.16 (m, 2H), 5.43 (m, 1H), 3.67

(s, 3H), 2.79 (qd, *J* = 7.1, 5.5 Hz, 1H), 1.39 (d, *J* = 6.4 Hz, 3H), 1.27 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 163.9, 150.6, 135.7, 130.7, 123.5, 72.8, 51.9, 44.3, 17.5, 12.2; HRMS (ESI, positive) calcd for $C_{13}H_{15}NO_6Na^+$ [(M+Na)$^+$] 304.0792, found 304.0795.

Degradation to Detect the C9–C12 Fragment (7) from Capsulactone (1)



To a solution of capsulactone (**1**, 100 μg, 0.342 μmol) in CH_2Cl_2 (100 μL) at rt were added Et_3N (10.0 μL, 0.072 mmol), *p*-nitrobenzoyl chloride (PNBCl, 2.0 mg, 0.072 mmol) and DMAP (2.0 mg, 0.016 mmol). After stirring overnight, the mixture was concentrated *in vacuo* to afford crude 4-nitrobenzoyl ester, which was used in the next reaction without purification: ESIMS *m/z* 464.2 [(M+Na)$^+$], *m/z* 613.2 [(M+Na)$^+$].

To a solution of crude nitrobenzoyl ester, thus obtained above, in CCl_4/MeCN/H_2O (4:4:5, 104 μL) at rt were added aqueous $RuCl_3$•nH_2O (25 mM, 10 μL, 0.25 μmol) and $NaIO_4$ (2.0 mg, 0.0093 mmol). After 1 h, the mixture was diluted with hydrochloric acid (0.5 M, 100 μL) and extracted with EtOAc (2 × 0.5 mL). Combined extracts were concentrated *in vacuo* to give crude carboxylic acid, which was used for the next reaction without purification.

To a solution of crude carboxylic acid, thus obtained above, in MeOH and toluene (1:1, 2.0 mL) at rt was added a solution of $TMSCHN_2$ (1.0 M in hexane) until the color of the solution became yellow. After stirring for 30 min, a few drops of AcOH were added until the yellow color of the solution disappeared and then the mixture was concentrated *in vacuo* to afford crude C9–C12 fragment **7**: HRMS (ESI, positive) calcd for $C_{13}H_{15}NO_6$ [(M+Na)$^+$] 304.0792, found 304.0784.

References

(1) Trotta, A. H. *Org. Lett.* **2015**, *17*, 3358–3361.

(2) Kalaitzakis, D.; Smonou, I. A. *J. Org. Chem.* **2008**, *73*, 3919–3921.

2. LC-MS chromatograms

LC-MS separation of esters 4–6

Aliquots (1 μL) of each sample were injected into an CHIRALPAK® IC (4.6 × 250 mm, 5 μm), CHIRALPAK® IF (4.6 × 250 mm, 5 μm), CHIRALPAK® ID-3 (4.6 × 250 mm, 3 μm) at flow late of 0.6 mL/min at 40 °C, with gradient elution from 50% MeOH to 100% MeOH, respectively. Gradient elution was performed using solvent A (H_2O) and solvent B (MeOH) with the following linear gradient combination: 50% (B) kept for 3 min, increased to 100% (B) over 20 min, and kept for 15 min. Gradient elution was also performed using MeCN, but each combination was unsuccessful. The LC-MS chromatograms performed using CHIRALPAK® IC, IF, ID-3 in MeOH condition was shown as below.

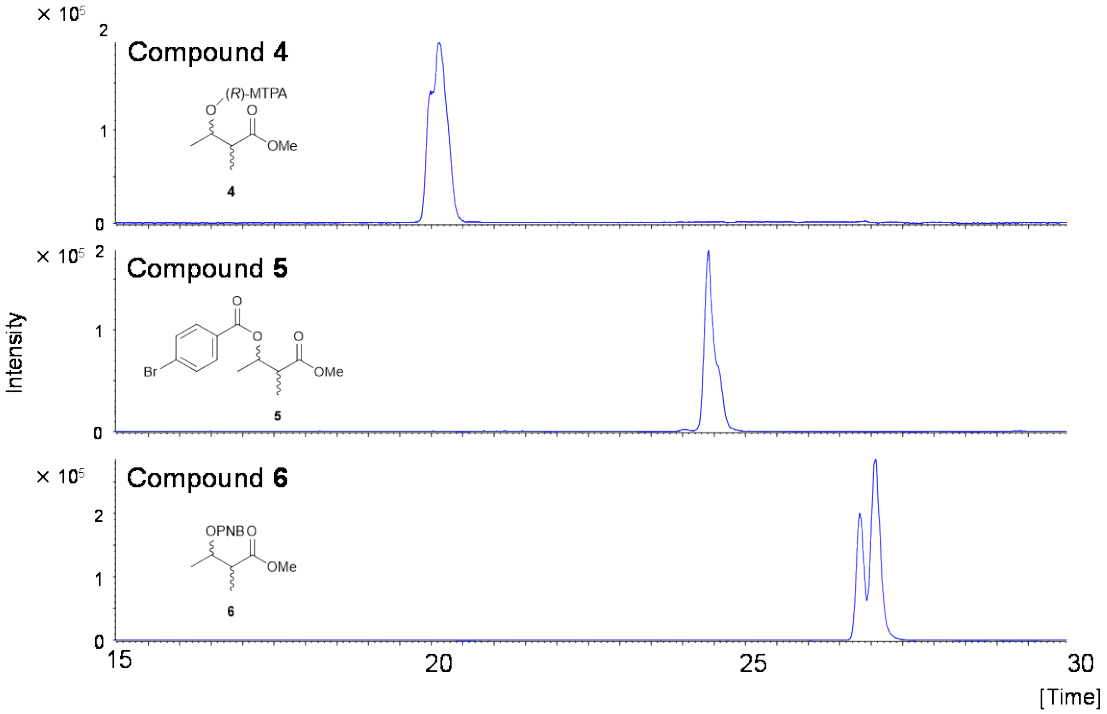


Figure S1. LC-MS chromatograms of esters **4**–**6** using CHIRALPAK® IC (MeOH condition)

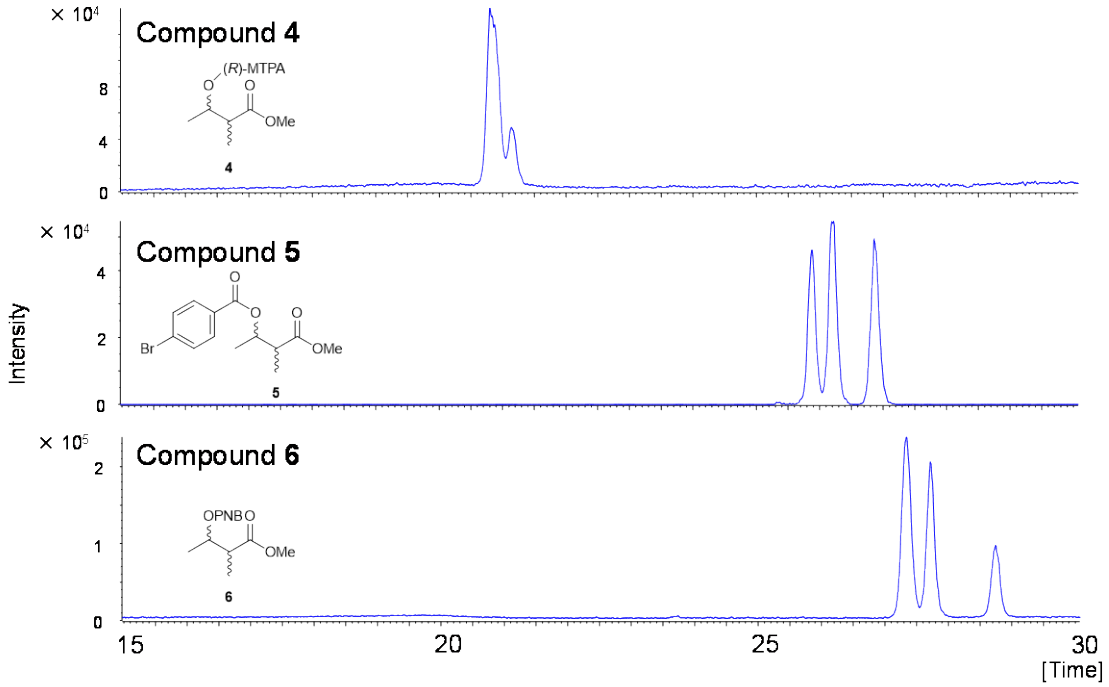


Figure S2. LC-MS chromatograms of esters **4**–**6** using CHIRALPAK® IF (MeOH condition)

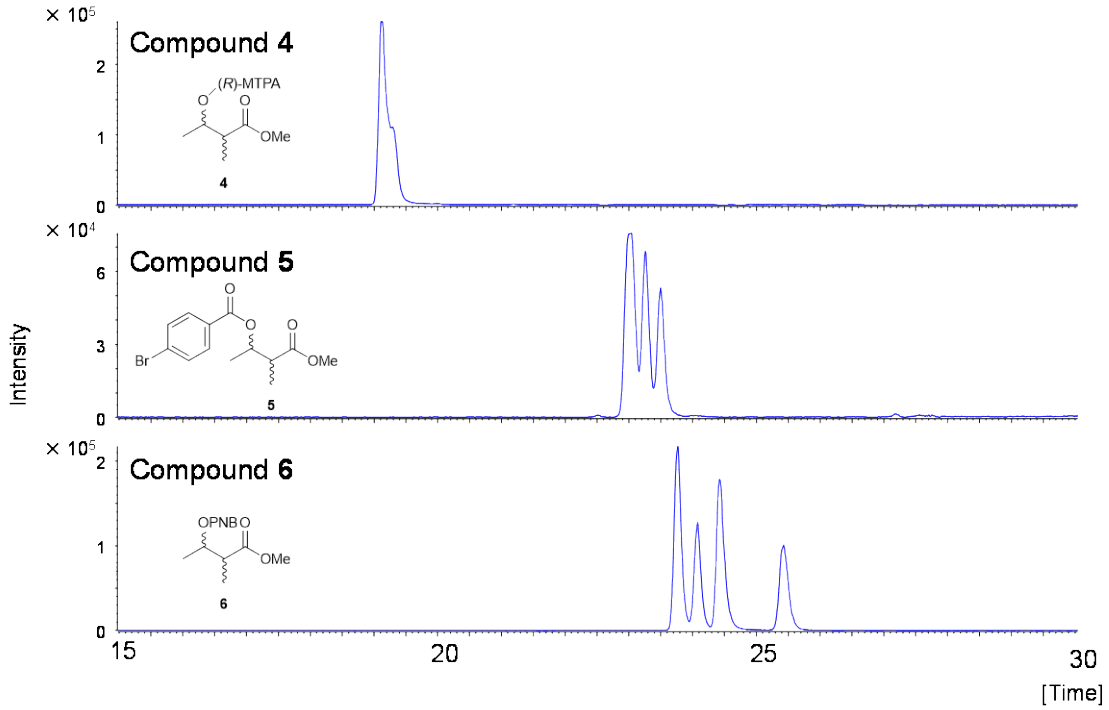
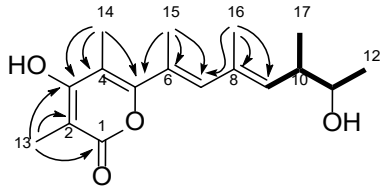


Figure S3. LC-MS chromatograms of ester **4**–**6** using CHIRALPAK® ID-3 (MeOH condition)

3. NMR spectra

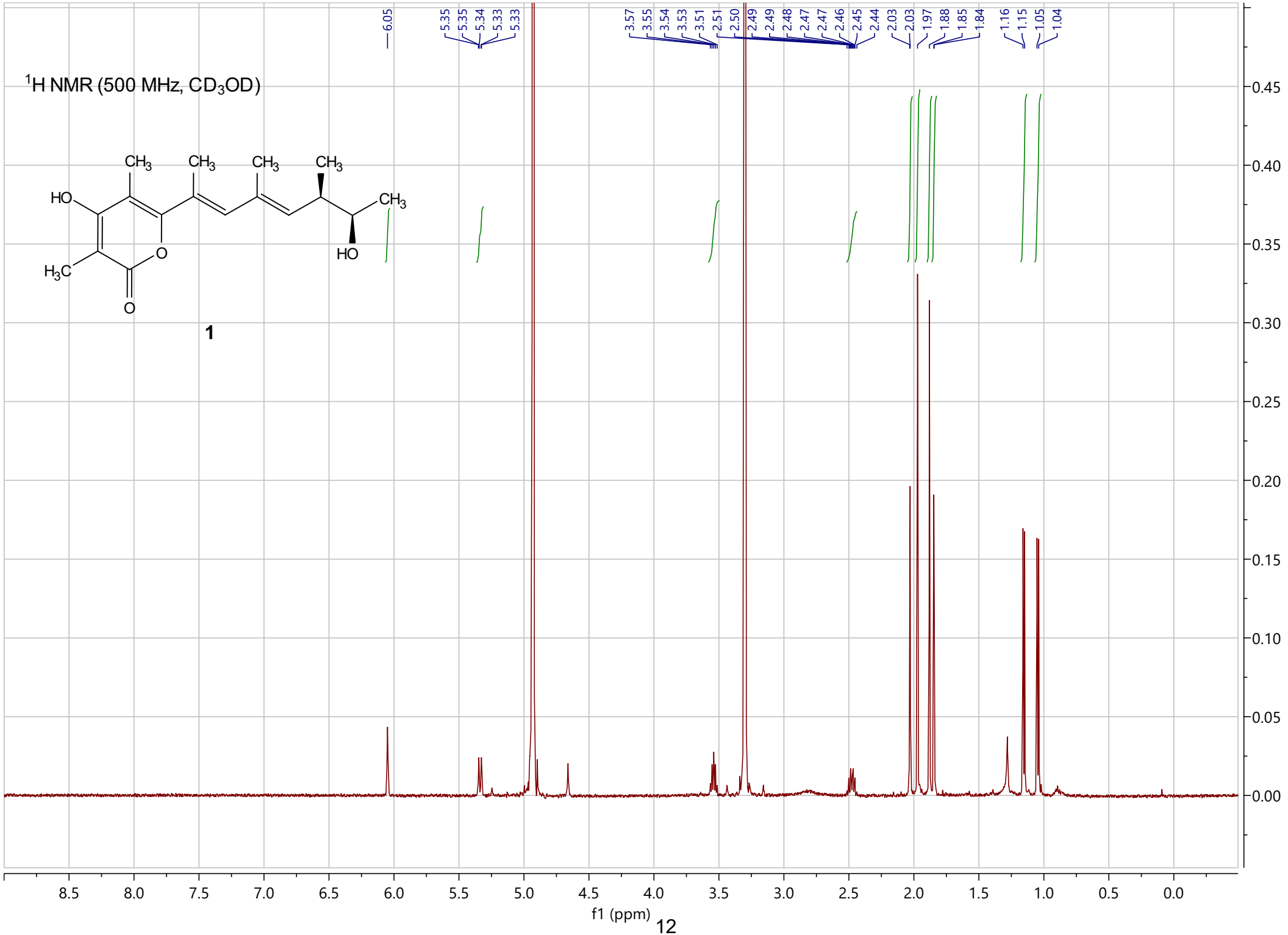
Table S1. ^{1}H NMR data (500 MHz) of capsulactone (1) in CD_3OD.

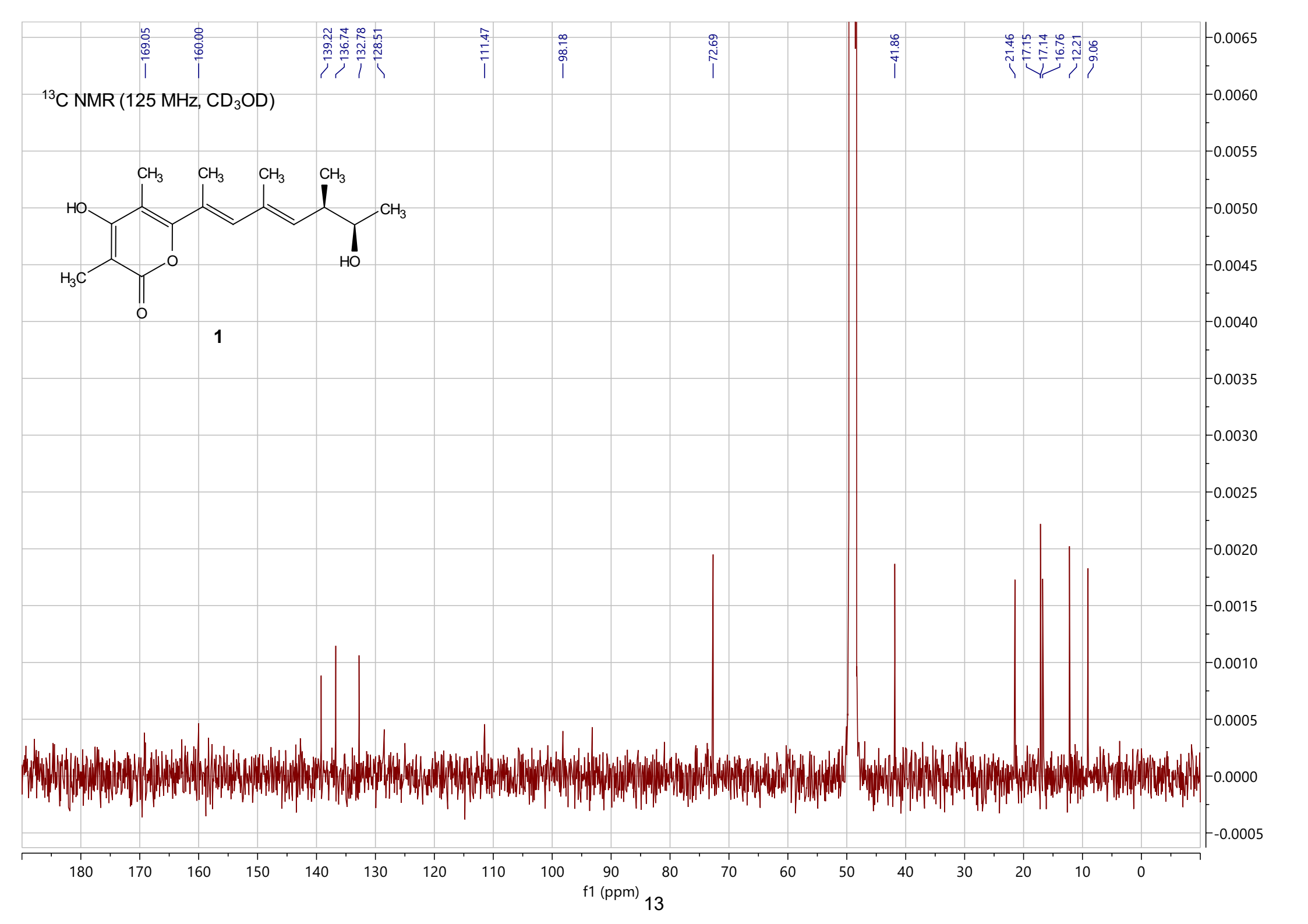
COSY correlations (boldline) and key HMBC correlations (arrow).

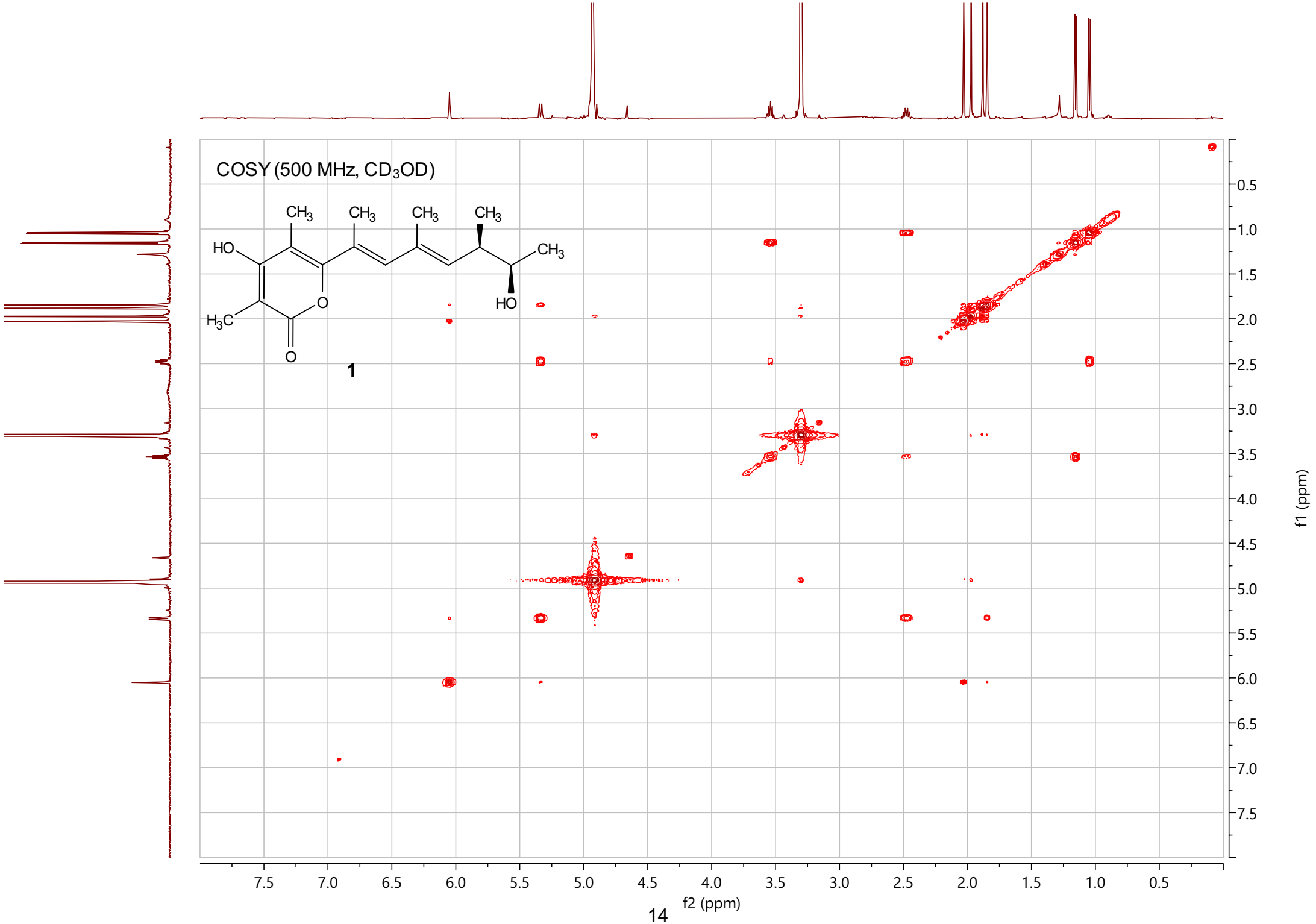


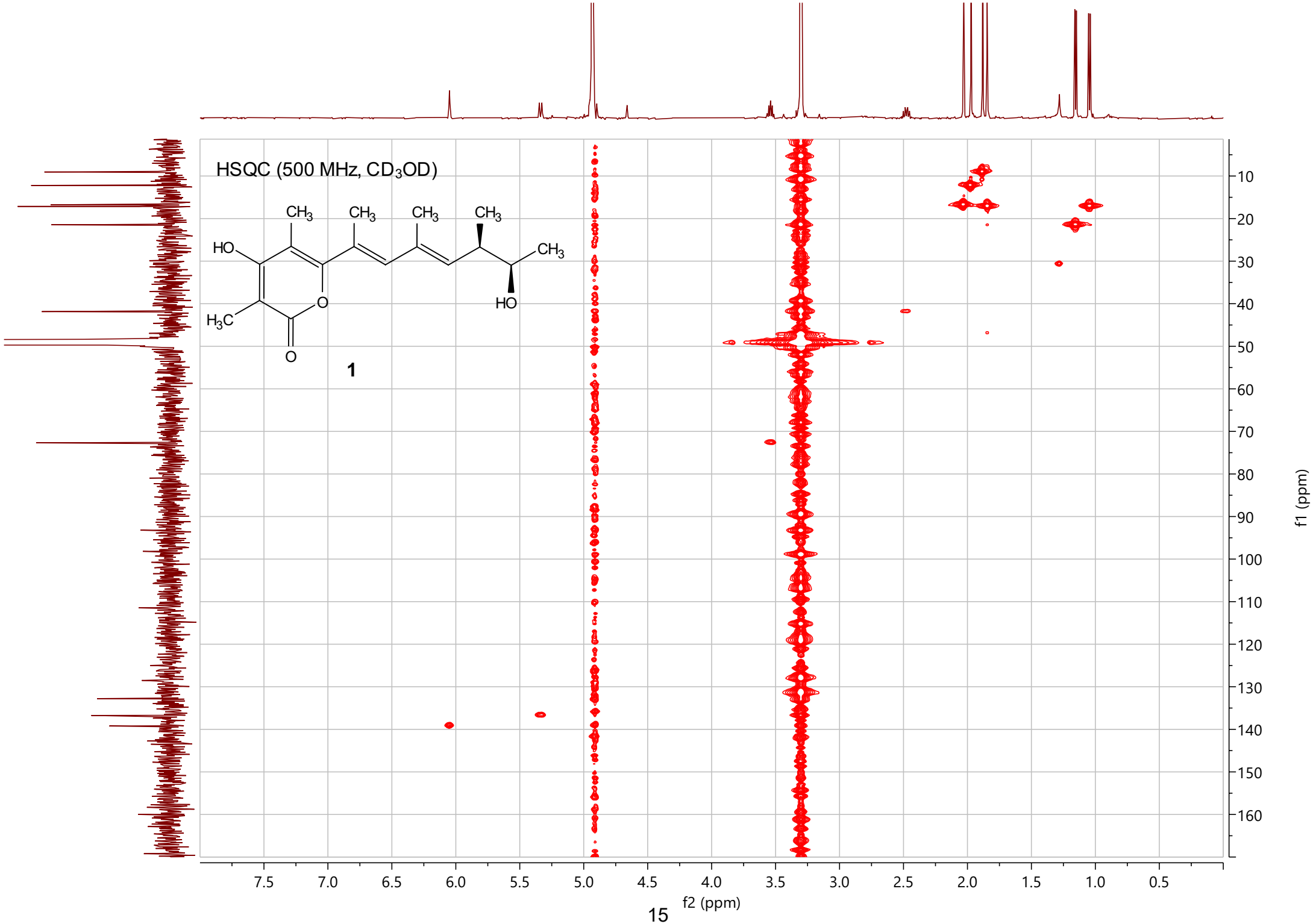
Position	δ_H, mult (*J* in Hz)	δ_C	COSY	HMBC
1		169.0		
2		98.2		
3		174.1[a]		
4		111.5		
5		160.0		
6		128.5		
7	6.05 (1H, brs)	139.2	H9, H15, H16	C5, C9, C15
8		132.8		
9	5.34 (1H, brd, *J* = 10.0 Hz)	136.7	H7, H10, H16	C7, C17
10	2.48 (1H, m)	41.9	H9, H11, H17	C11
11	3.54 (1H, dq, *J* = 6.4, 6,4 Hz)	72.7	H10, H12	
12	1.15 (3H, d, *J* = 6.4 Hz)	21.5	H11	C10, C11
13	1.88 (3H, s)	9.1		C1, C2, C3
14	1.97 (3H, s)	12.2		C3, C4, C5
15	2.03 (3H, d, *J* = 1.5 Hz)	16.8	H7	C5, C6, C7
16	1.85 (3H, d, *J* = 1.4 Hz)	17.1	H7, H9	C7, C8, C9
17	1.05 (3H, d, *J* = 6.7 Hz)	17.2	H10	C9, C10, C11

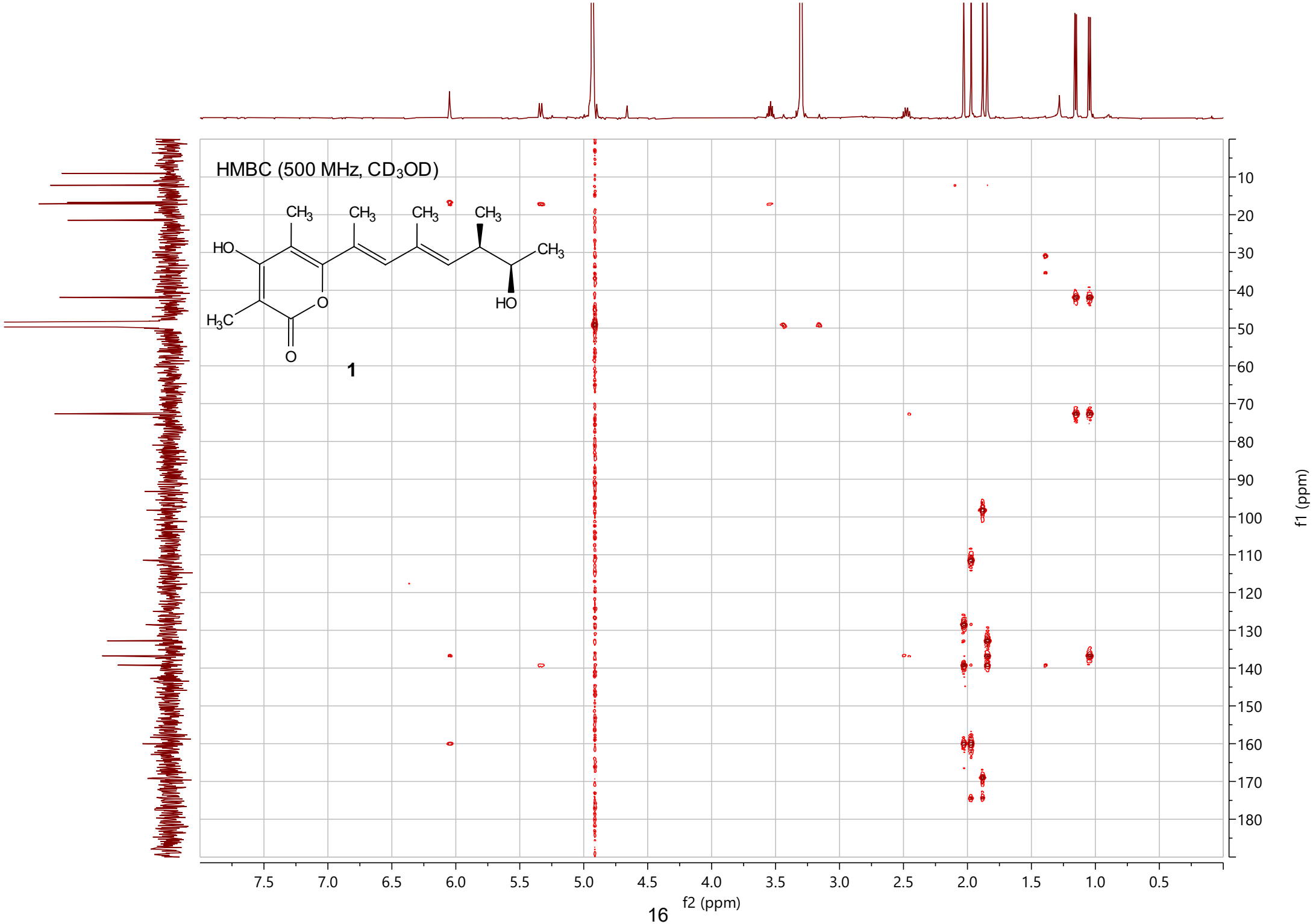
[a] assigned by HMBC data.


^{1}H NMR (500 MHz, CD_3OD)
HO
CH_3
CH_3
CH_3
CH_3
CH_3
H_3C
O
O
HO
1
6.05
5.35
5.35
5.34
5.33
5.33
3.57
3.55
3.54
3.53
3.51
2.51
2.50
2.49
2.49
2.48
2.47
2.47
2.46
2.45
2.44
2.03
2.03
1.97
1.88
1.85
1.84
1.16
1.15
1.05
1.04
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
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)

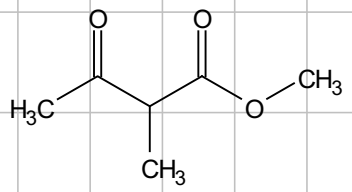

169.05
160.00
139.22
136.74
132.78
128.51
111.47
98.18
72.69
41.86
21.46
17.15
17.14
16.76
12.21
9.06
^{13}C NMR (125 MHz, CD_3OD)
HO
CH_3
CH_3
CH_3
CH_3
CH_3
HO
O
H_3C
O
1
0.0065
0.0060
0.0055
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
-0.0005
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


COSY (500 MHz, CD3OD)
CH3
CH3
CH3
CH3
CH3
HO
HO
O
H3C
O
1
f2 (ppm)
f1 (ppm)

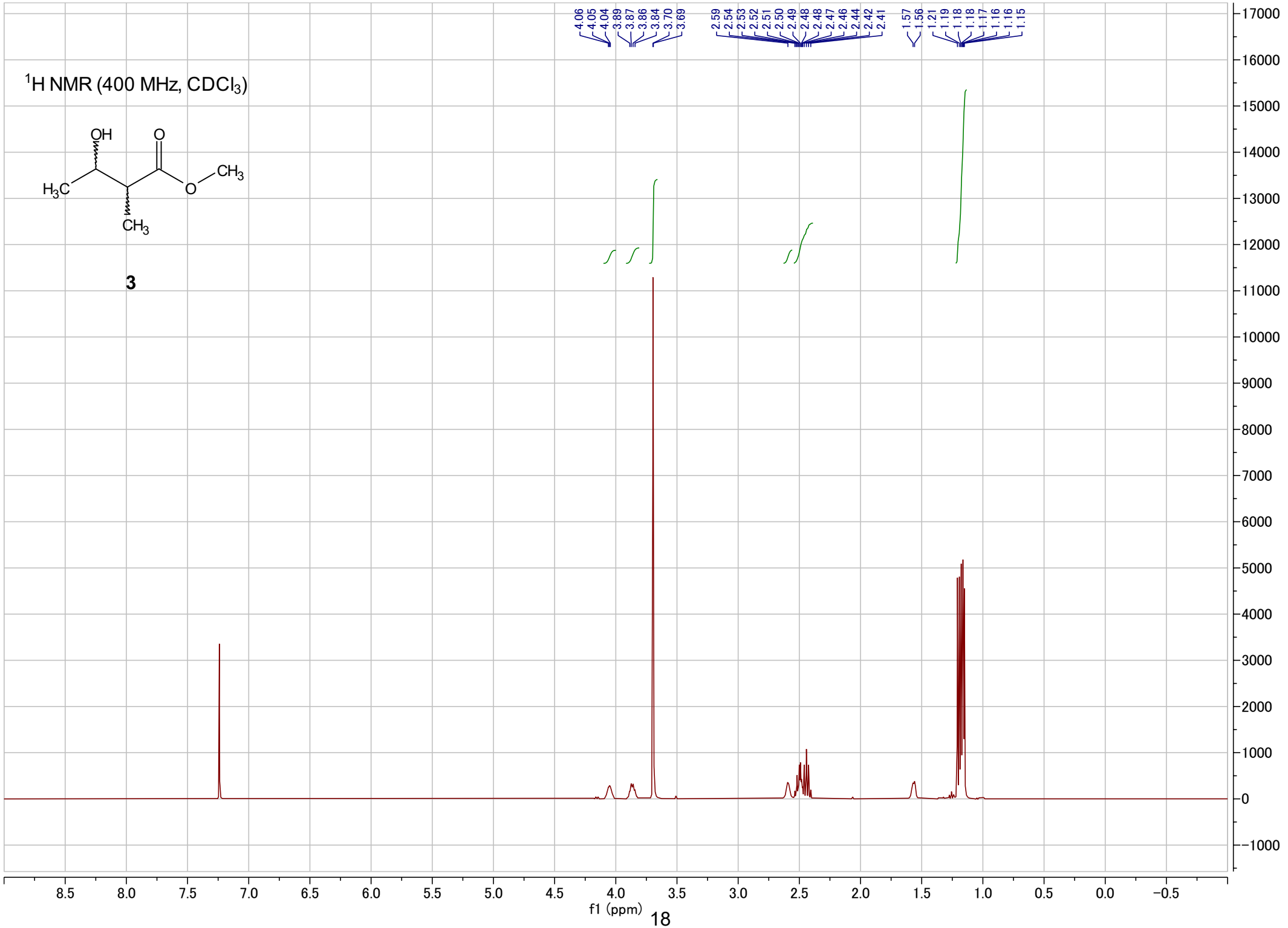

HSQC (500 MHz, CD3OD)
CH3
CH3
CH3
CH3
HO
CH3
H3C
O
HO
O
1
f2 (ppm)
f1 (ppm)

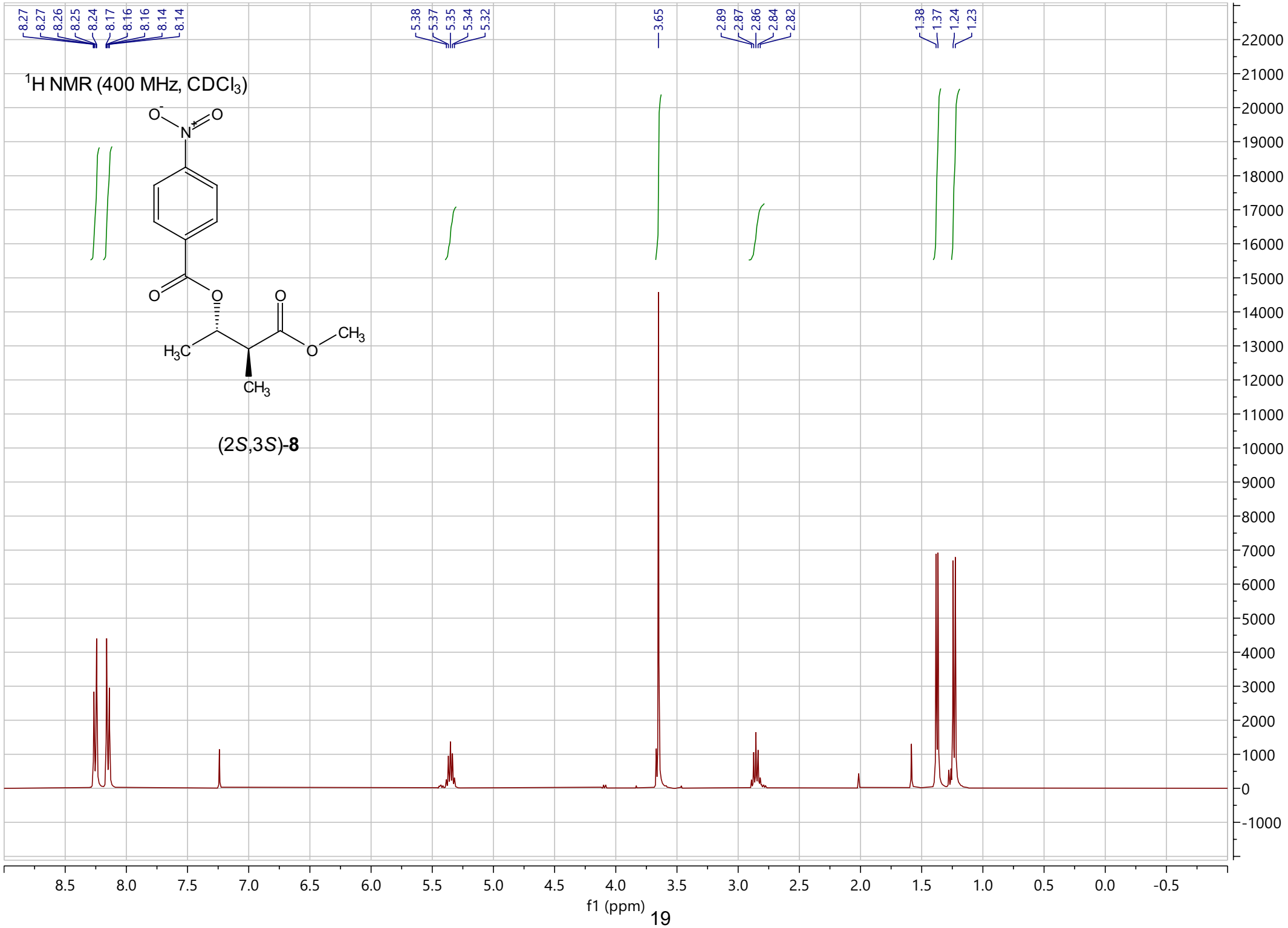

HMBC (500 MHz, CD3OD)
CH3
CH3
CH3
CH3
HO
CH3
O
H3C
HO
O
1
f2 (ppm)
f1 (ppm)

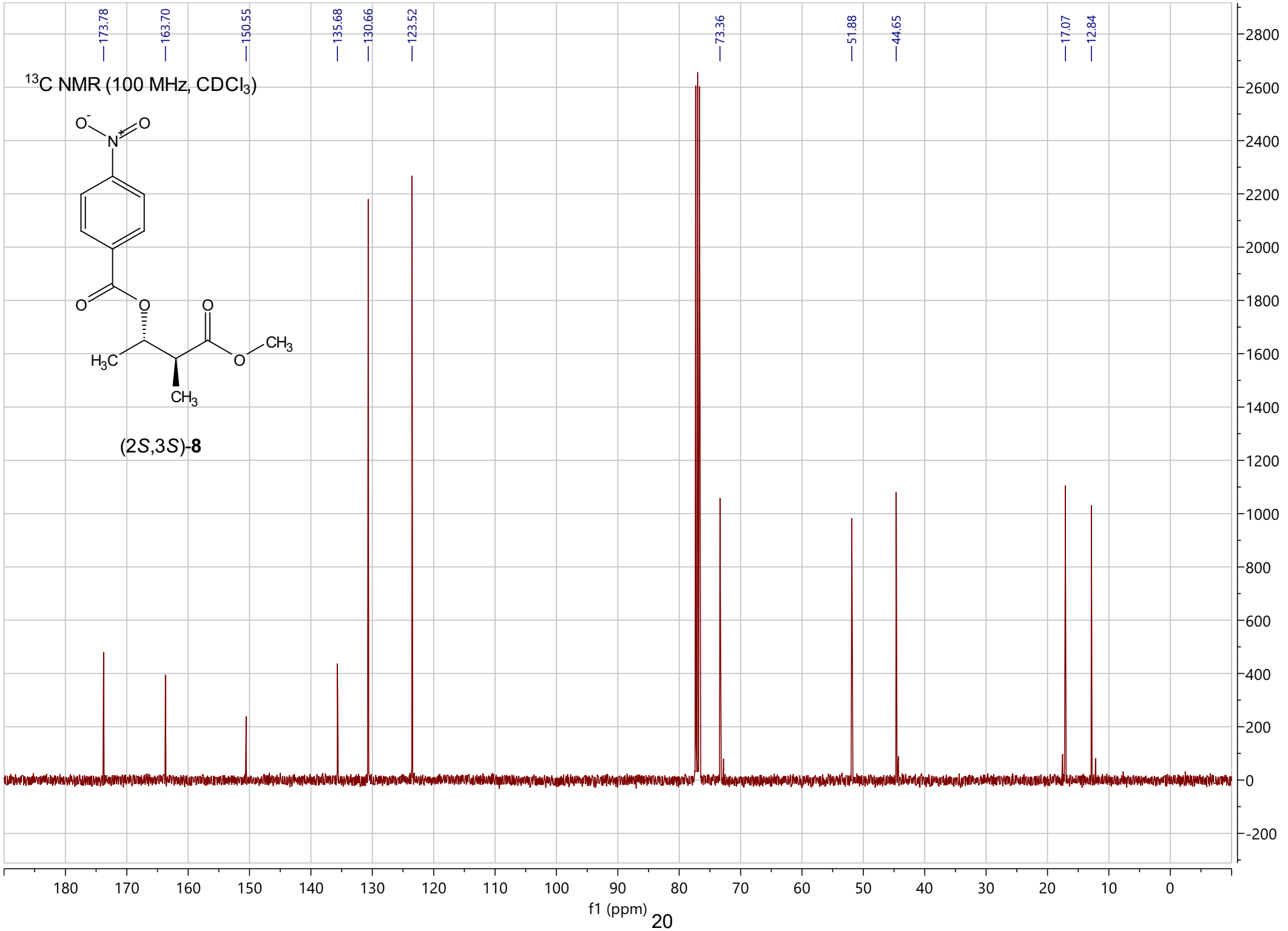
^{1}H NMR (400 MHz, $CDCl_3$)

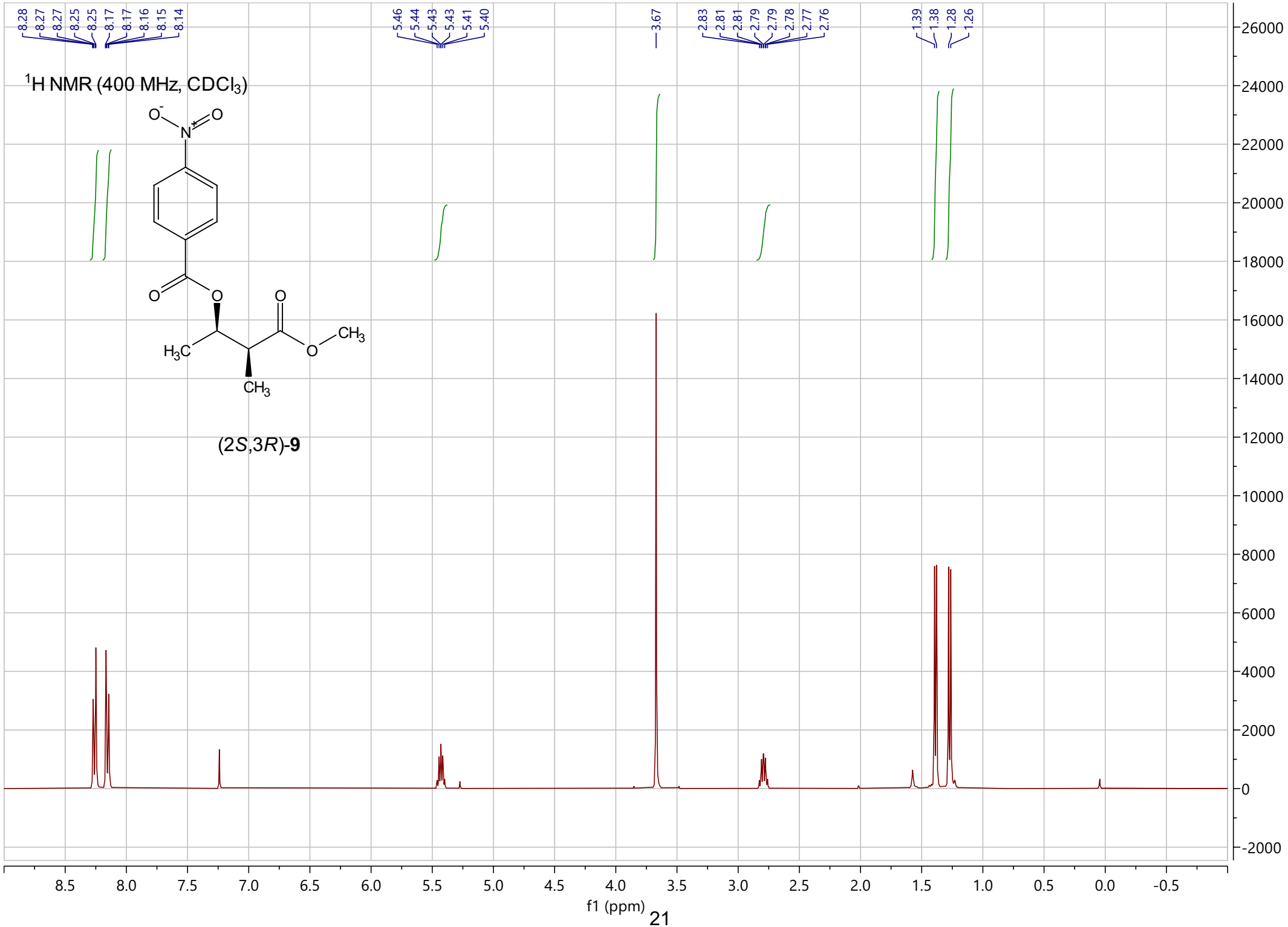


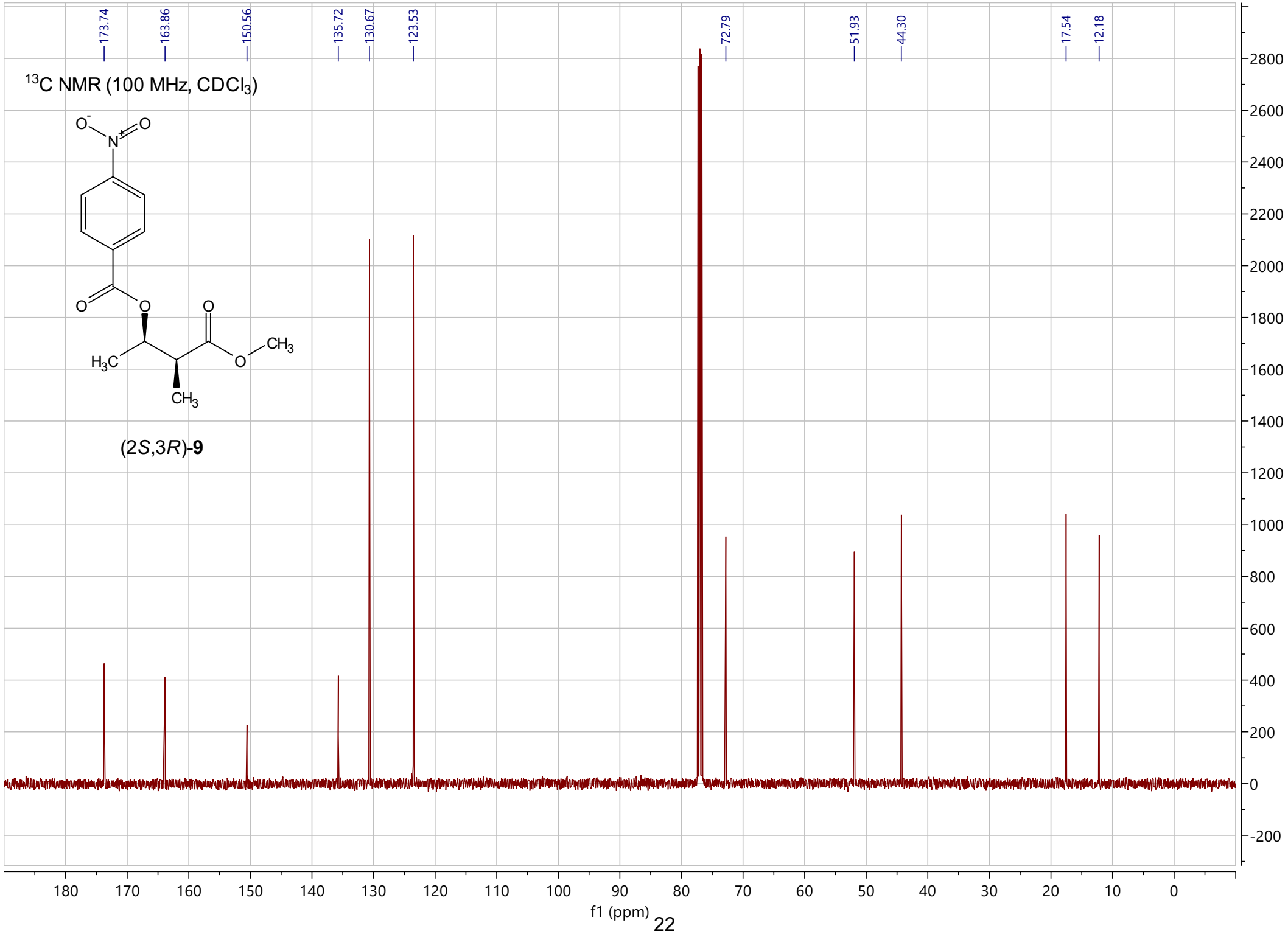
S1

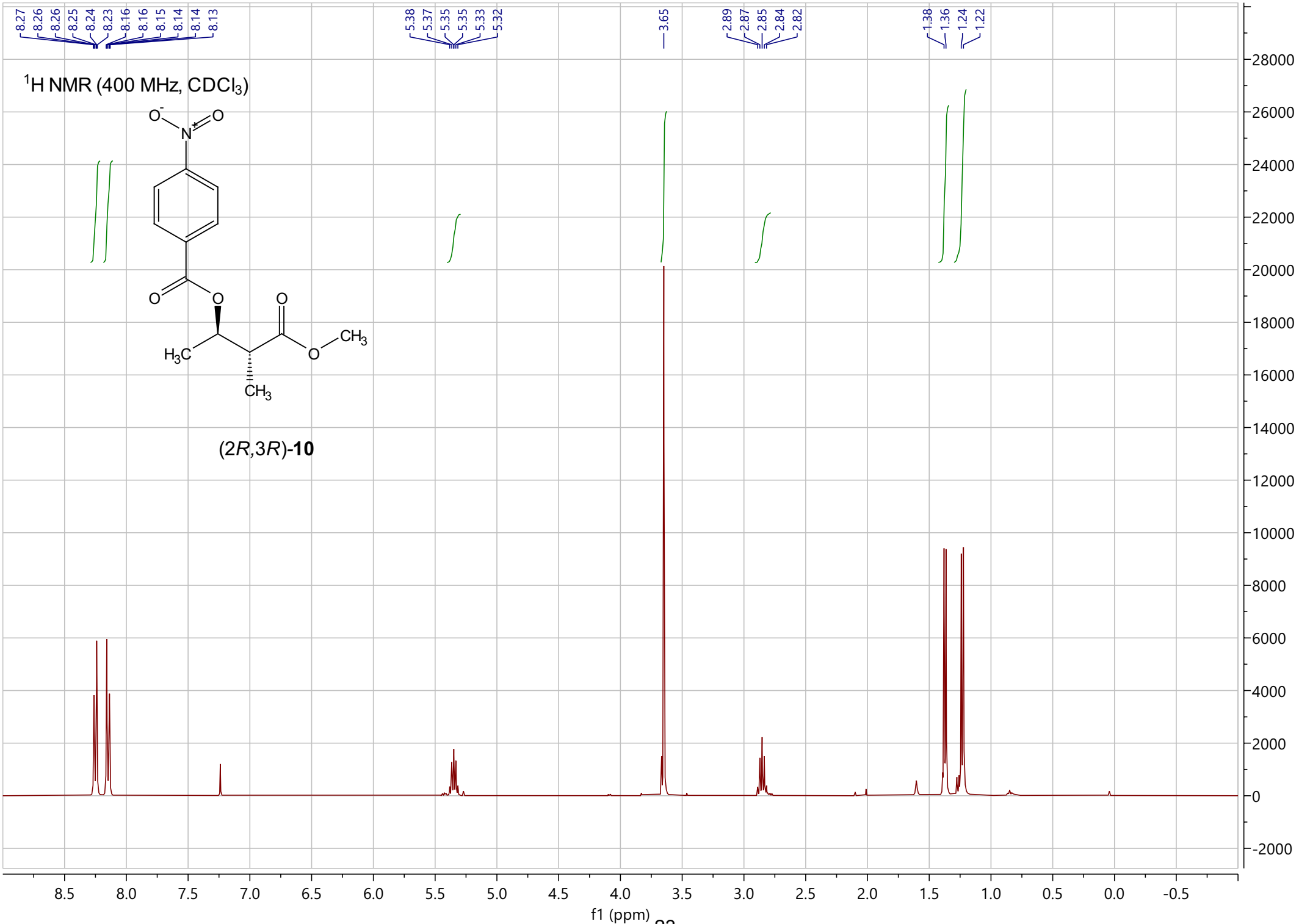

^{1}H NMR (400 MHz, $CDCl_3$)
OH
O
H_3C
O
CH_3
CH_3
3
4.06 4.05 4.04 3.89 3.87 3.86 3.84 3.70 3.69
2.59 2.54 2.53 2.52 2.51 2.50 2.49 2.48 2.48 2.47 2.46 2.44 2.42 2.41
1.57 1.56
1.21 1.19 1.18 1.18 1.17 1.16 1.16 1.15
f1 (ppm)

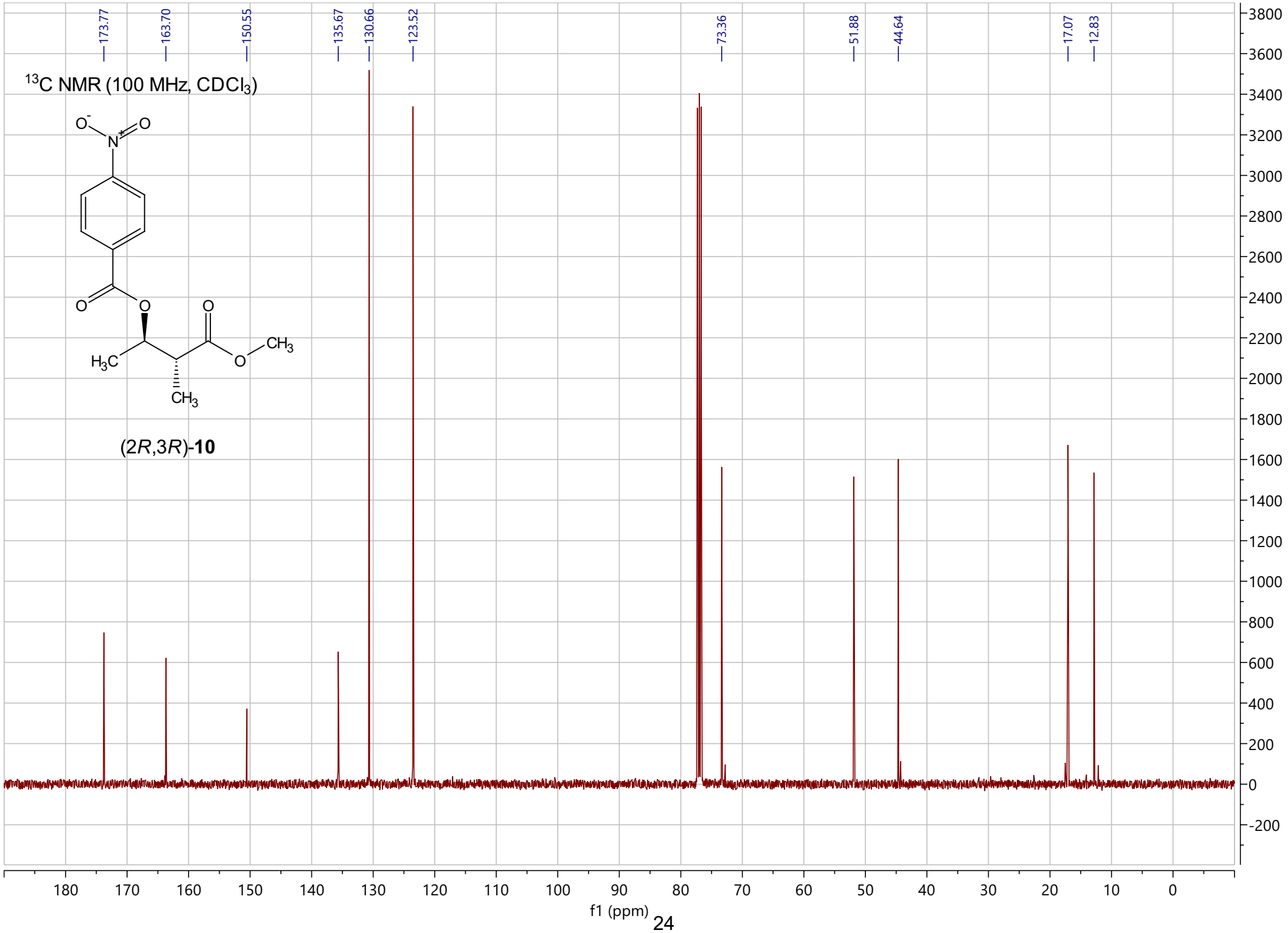

8.27
8.27
8.26
8.25
8.24
8.17
8.16
8.16
8.14
8.14
5.38
5.37
5.35
5.34
5.32
3.65
2.89
2.87
2.86
2.84
2.82
1.38
1.37
1.24
1.23
^{1}H NMR (400 MHz, CDCl$_3$)
(2S,3S)-8
f1 (ppm)

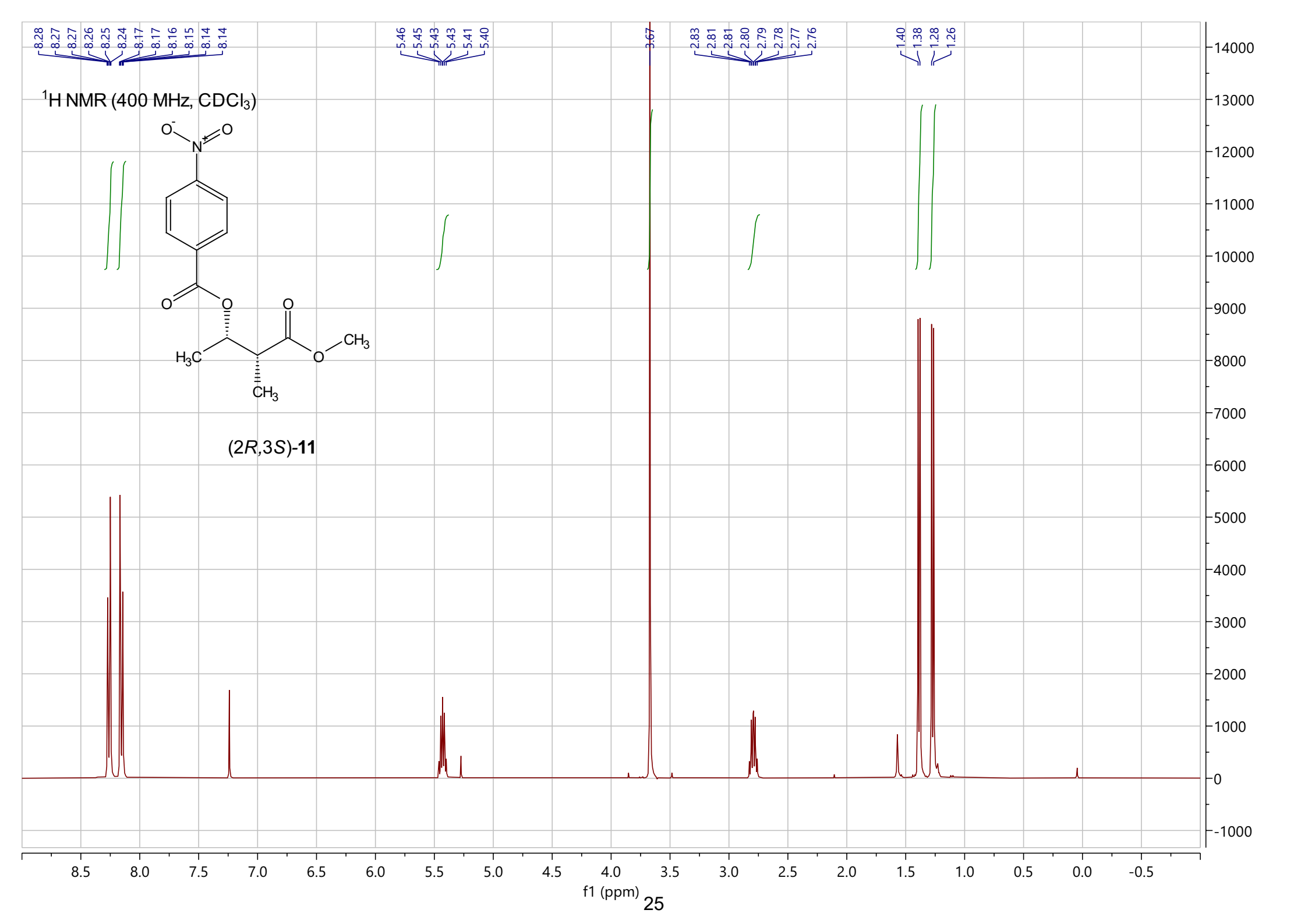

173.78
163.70
150.55
135.68
130.66
123.52
73.36
51.88
44.65
17.07
12.84
^{13}C NMR (100 MHz, $CDCl_3$)
(2*S*,3*S*)-**8**
f1 (ppm)

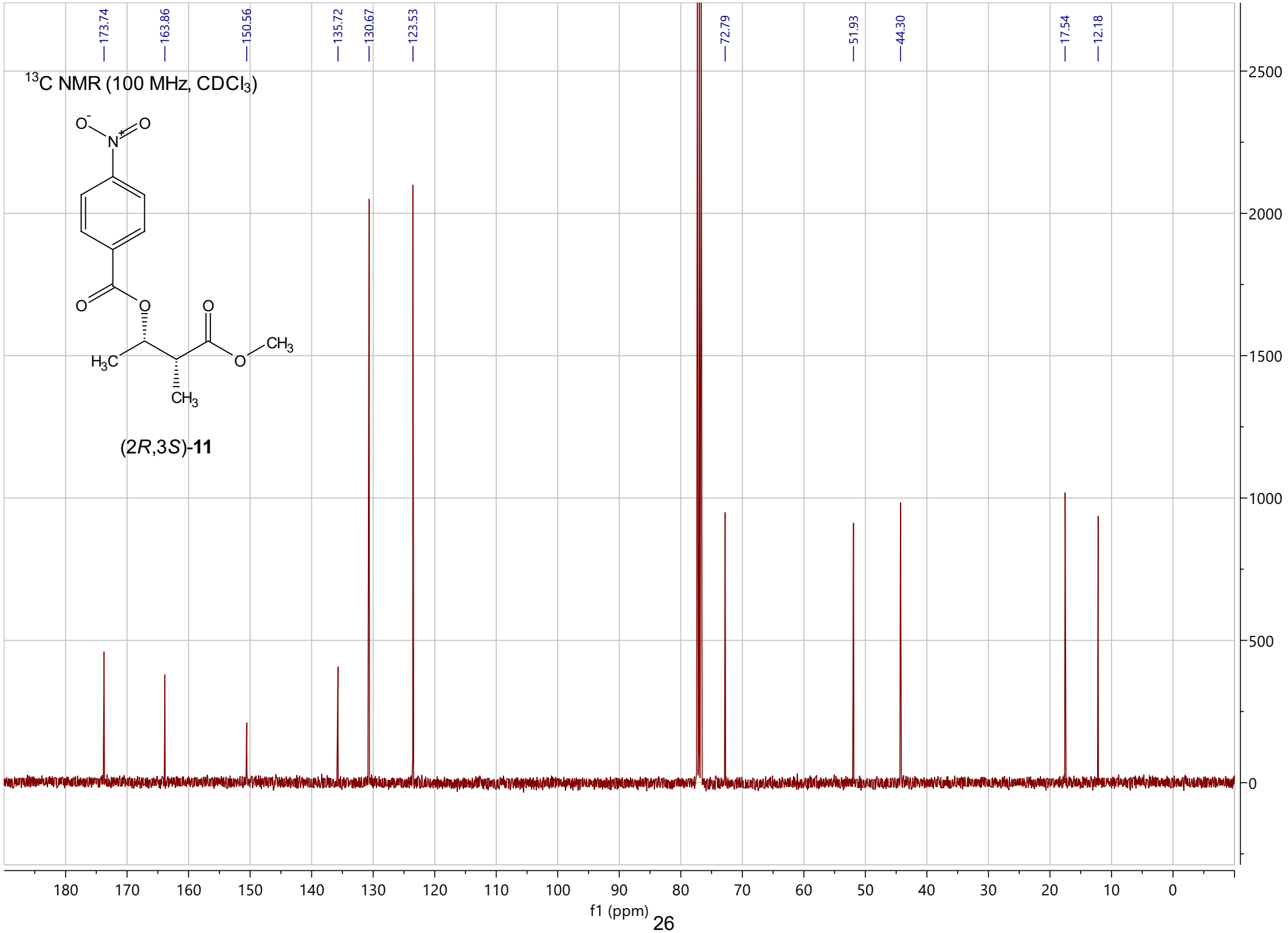

8.28
8.27
8.27
8.25
8.25
8.17
8.17
8.16
8.15
8.14
5.46
5.44
5.43
5.43
5.41
5.40
3.67
2.83
2.81
2.81
2.79
2.79
2.78
2.77
2.76
1.39
1.38
1.28
1.26
^{1}H NMR (400 MHz, CDCl$_3$)
(2*S*,3*R*)-**9**
f1 (ppm)


173.74
163.86
150.56
135.72
130.67
123.53
72.79
51.93
44.30
17.54
12.18
^{13}C NMR (100 MHz, $CDCl_3$)
(2*S*,3*R*)-**9**
f1 (ppm)


8.27
8.26
8.26
8.25
8.24
8.23
8.16
8.16
8.15
8.14
8.14
8.13
5.38
5.37
5.35
5.35
5.33
5.32
3.65
2.89
2.87
2.85
2.84
2.82
1.38
1.36
1.24
1.22
^{1}H NMR (400 MHz, $CDCl_3$)
(2*R*,3*R*)-**10**
f1 (ppm)


173.77
163.70
150.55
135.67
130.66
123.52
73.36
51.88
44.64
17.07
12.83
^{13}C NMR (100 MHz, $CDCl_3$)
(2*R*,3*R*)-**10**
f1 (ppm)


8.28
8.27
8.27
8.26
8.25
8.24
8.17
8.17
8.16
8.15
8.14
8.14
5.46
5.45
5.43
5.43
5.41
5.40
3.67
2.83
2.81
2.81
2.80
2.79
2.78
2.77
2.76
1.40
1.38
1.28
1.26
^{1}H NMR (400 MHz, $CDCl_3$)
(2*R*,3*S*)-**11**
f1 (ppm)


173.74
163.86
150.56
135.72
130.67
123.53
72.79
51.93
44.30
17.54
12.18
^{13}C NMR (100 MHz, CDCl$_3$)
(2*R*,3*S*)-**11**
2500
2000
1500
1000
500
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)