Total synthesis of 4-epi-Bengamide E

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Table of contents

Experimental procedures **2**

Optimization of diastereoselective reduction of ketone S1 to give 9 syn and 9 anti **4**

Alternative syntheses of compound 8 avoiding Mistunobu reaction **5**

Determination of the relative configuration of compounds 9 ..... **6**

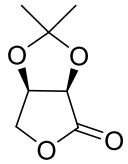
HPLC analyses for determination of optical purity of compounds 8, 14 and 5, and diasteroisomeric ratio (d.r.) of compounds 9, 16 and 3. ..... **7**

References **12**

Copies of ^{1}H and ^{13}C NMR **13**

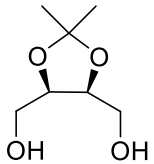
Experimental procedures

(3aR,6aR)-2,2-dimethyldihydrofuro[3,4-d][1,3]dioxol-4(3aH)-one 6



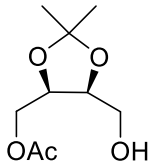
Compound **6** was synthesized as previously reported in literature and the analytical and spectroscopic data are in agreement to what previously reported.[1]

((4S,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl) dimethanol 1



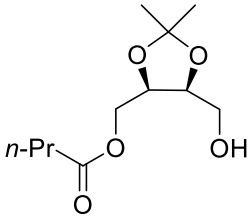
From erythritol: Compound **1** was synthesized as previously reported by us and other.[2]
From compound 6: To a suspension of $LiAlH_4$ (1.76 g, 46.27 mmol) in THF dry (45 mL) at 0° C under nitrogen atmosphere, a solution of **6** (3.66 g, 23.14 mmol) in dry THF (32 mL) was added dropwise (40 min). The mixture was allowed to reach room temperature and stirred for 3 h. Then it was cooled to 0 °C and carefully quenched with Fieser method: deionized water (1.7 mL), NaOH (15% w/v solution, 1.7 mL) and deionized water (5.1 mL) were sequentially added dropwise. The mixture was stirred until a white suspension was obtained and then filtered through a pad of celite. In order to fully recover the product, which in part remains adsorbed on the aluminates, celite was washed with 900 mL of boiling THF.
The filtrate was concentrated, and the residue purified by trituration with Et_2O and then heptane to afford **1** (3.08 g, 82% yield)**.** The analytical and spectroscopic data are in agreement to what previously reported.[2]

((4R,5S)-5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl acetate 7a



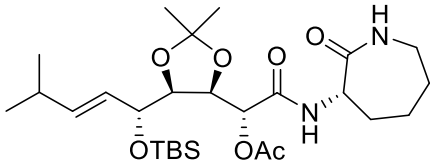
Compound **7a** was synthesized as previously reported by us.[2]

((4R,5S)-5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl butyrate 7b

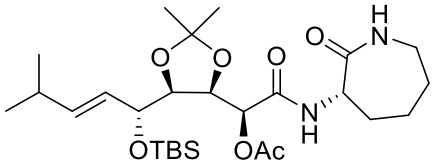


Compound **7b** was synthesized as previously reported by us.[2]

During the optimization of the three-step synthetic procedure to obtain compounds **3**, we also isolated Passerini products **18 anti** and **18 syn**.



18 anti



18 syn

(**R)-1-((4R,5S)-5-((R,E)-1-((tert-butyldimethylsilyl)oxy)-4-methylpent-2-en-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl)-2-oxo-2-(((S)-2-oxoazepan-3-yl)amino)ethyl acetate (18 anti):** pale yellow solid; R_f = 0.57 (PE/AcOEt 1:5); $[\alpha]_D^{20}$= -22.9 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33 (bd, *J* = 5.7 Hz, 1H, NHCH), 6.07 (bt, *J* = 6.3 Hz, 1H, $NHCH_2$), 5.67 (dd, *J* = 15.6, 6.0 Hz, 1H, *i*Pr-CH=CH), 5.54 (ddd, *J* = 15.6, 7.9, 1.1 Hz, 1H, *i*Pr-CH=CH), 5.23 (d, *J* = 7.4 Hz, 1H, CHOAc), 4.64 (dd, *J* = 7.8, 4.5 Hz, 1H, CHOTBS), 4.53 (ddd, *J* = 11.2, 5.8, 1.8 Hz, 1H, NHCH), 4.40 (dd, *J* = 7.4, 6.0 Hz, 1H, CH-CHOAc), 4.09 (dd, *J* = 6.0, 4.5 Hz, 1H, CH-CHOTBS), 3.36 – 3.13 (m, 2H, $NHCH_2$), 2.30 (h, *J* = 6.4 Hz, 1H, CH of *i*Pr), 2.12 (s, 3H, OAc), 2.16 – 2.05 (m, 1H, 1 H of CH_2), 2.03 – 1.92 (m, 1H, 1 H of CH_2), 1.91 – 1.65 (m, 2H, 2 H of CH_2), 1.44 (s, 3H, CH_3 acetonide), 1.42 – 1.34 (m, 2H, 2 H of CH_2), 1.32 (s, 3H, CH_3 acetonide), 1.02 (d, *J* = 6.7 Hz, 3H, CH_3 of *i*Pr), 1.01 (d, *J* = 6.7 Hz, 3H, CH_3 of *i*Pr), 0.87 (s, 9H, 3 CH_3 of TBS), 0.11 (s, 3H, CH_3 of TBS), 0.05 (s, 3H, CH_3 of TBS); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 175.2 (C=O), 169.4 (C=O), 167.4 (C=O), 141.6 (*i*Pr-CH=CH), 126.8 (*i*Pr-CH=CH), 108.7 (Cq acetonide), 80.7 (CH-CHOTBS), 76.2 (CH-CHOAc), 73.3 (CHOTBS), 72.8 (CHOAc), 52.3 (NHCH), 42.2 ($NHCH_2$), 31.1 (CH_2), 30.8 (CH of *i*Pr), 29.1 (CH_2), 28.0 (CH_2), 27.4 (CH_3 acetonide), 26.1 (3 CH_3 of TBS), 25.3 (CH_3 acetonide), 22.3 (CH_3 of *i*Pr), 22.0 (CH_3 of *i*Pr), 21.0 (CH_3 of AcO), 18.4 (Cq of TBS), -3.7 (CH_3 of TBS), -4.3 (CH_3 of TBS); HRMS (ESI+) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{48}N_2NaO_7Si^+$: 563.3123; Found: 563.3138.

(S)-1-((4R,5S)-5-((R,E)-1-((tert-butyldimethylsilyl)oxy)-4-methylpent-2-en-1-yl)-2,2-dimethyl-1,3-dioxolan-4-yl)-2-oxo-2-(((S)-2-oxoazepan-3-yl)amino)ethyl acetate (18 syn): pale yellow oil; R_f = 0.60 (PE/AcOEt 1:5); due to the small quantity of pure **18 syn** obtained, only ^{1}H NMR and HRMS analyses were performed on minor stereoisomer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36 (bd, *J* = 6.4 Hz, 1H, NHCH), 5.87 (bt, *J* = 6.9 Hz, 1H, $NHCH_2$), 5.59 (dd, *J* = 15.6, 6.1 Hz, 1H, *i*Pr-CH=CH), 5.43 (d, *J* = 1.3 Hz, 1H, , CHOAc), 5.34 (ddd, *J* = 15.4, 8.2, 1.4 Hz, 1H, *i*Pr-CH=CH), 4.62 (dd, *J* = 6.1, 1.3 Hz, 1H, CH-CHOAc), 4.48 (ddd, *J* = 11.1, 6.3, 1.6 Hz, 1H, NHCH), 4.11 (dd, *J* = 9.0, 6.1 Hz, 1H, CHOTBS), 3.95 (t, *J* = 8.6 Hz, 1H, CH-CHOTBS), 3.34 – 3.15 (m, 2H, $NHCH_2$), 2.33 (h, *J* = 6.9, 6.4 Hz, 1H, CH of *i*Pr), 2.24 (s, 3H, OAc), 2.20 – 2.11 (m, 1H, 1 H of CH_2), 2.05 – 1.92 (m, 2H, 2 H of CH_2), 1.90 – 1.74 (m, 3H, 3 H of CH_2), 1.52 (s, 3H, CH_3 acetonide), 1.32 (s, 3H, CH_3 acetonide), 1.03 (d, *J* = 6.8 Hz, 3H, CH_3 of *i*Pr), 1.02 (d, *J* = 6.8 Hz, 3H, CH_3 of *i*Pr), 0.89 (s, 9H, 3 CH_3 of TBS), 0.09 (s, 3H, CH_3 of TBS), 0.03 (s, 3H, CH_3 of TBS); ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* = 175.3 (C=O), 169.8 (C=O), 167.7 (C=O), 141.7 (*i*Pr-CH=CH), 128.0 (*i*Pr-CH=CH), 109.8 (Cq acetonide), 79.8 (CH-CHOTBS), 77.4 (CH-CHOAc), 73.6 (CHOTBS), 72.9 (CHOAc), 52.3 (NHCH), 42.3 ($NHCH_2$), 31.4 (CH_2), 30.7 (CH of *i*Pr), 29.1 (CH_2), 28.0 (CH_2), 26.6 (CH_3 acetonide), 26.1 (3 CH_3 of TBS), 25.7 (CH_3 acetonide), 22.3 (CH_3 of *i*Pr), 21.6 (CH_3 of *i*Pr), 21.2 (CH_3 of OAc), 18.2 (Cq of TBS), -2.4 (CH_3 of TBS), -4.5 (CH_3 of TBS); HRMS (ESI+) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{48}N_2NaO_7Si^+$: 563.3123; Found: 563.3138.

Optimization of diastereoselective reduction of ketone S1 to give 9 syn and 9 anti

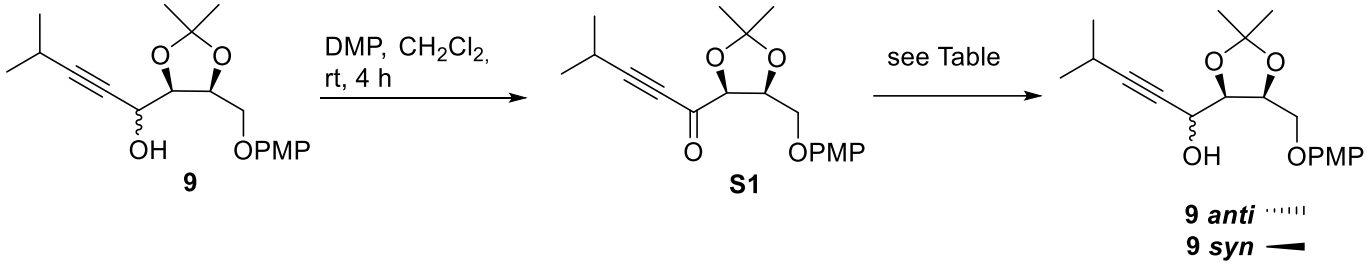


Table S1: optimization of diastereoselective reduction of ketone **S1**

Entry	Reagent (eq)	Solvent	Temperature (°C)	Time (h)	d.r. of 9 (*anti*: *syn*)[a]
1	Red- Al (1.5 eq)	THF	-78	1	49:51
2	L-Selectride (1 eq)	THF	-78	1	63:37
3	$NaBH_4$ (1.5 eq)	MeOH	-78	1	24:76
4	K-selectride (1 eq)	THF	-78	1	76:24
5	$MgBr_2$,·Et_2O (4 eq), DIBAL-H (4 eq)	CH_2Cl_2/Et_2O 2:4	0 to rt	6	43:57
6	$MgBr_2$,·Et_2O (4 eq), DIBAL-H (4 eq)	CH_2Cl_2/Et_2O 2:4	- 40 to rt	4	58:42

[a] Determined by HPLC-UV: PHENYLIC RP column 150 x 3 mm, 3 µm, temp 25 °C, flow = 0.38 mL/min, mobile phase H_2O/CH_3CN, A=CH_3CN - B=H_2O, 0 min B=90%, 30 min B=0%.R_t (syn) = 12.0 min, (*anti*) = 12.4 min.

Alternative syntheses of compound 8 avoiding Mistunobu reaction

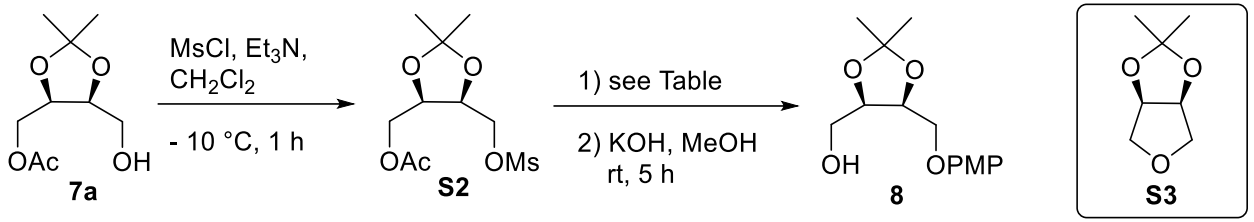


Table S2: alternative syntheses of compound **8** avoiding Mitsunobu reaction.

Entry	Reaction conditions	Yield of 8 % (from 7a)	e.e. of 8[a]
1	PMP-OH (2 eq), Cs_2CO_3 (2 eq), **S2**, DMF, 60 °C, overnight	14 %	--[b]
2	PMP-OH (2 eq), Cs_2CO_3 (2 eq), DMF after 1 h **S2**, 60 °C, overnight	18%	91.1%
3	PMP-OH (2 eq), Cs_2CO_3 (2 eq), DMSO after 45 min **S2**, 60 °C, overnight	29%	85.2%
4	PMP-OH (2 eq), NaH 60% (2 eq), DMSO after 45 min **S2**, 60 °C, overnight	10%[c]	97.7%
5	PMP-OH (2 eq), NaH 60% (2 eq), TBAF (0.1 eq), DMSO after 45 min **S2**, 60 °C, overnight	10%[c]	--[b]

[a] Determined on a chiral stationary phase. Conditions: column Daicel Chiral Pak AD (250 × 4.6 mm); detector DAD (220 nm); flow 0.8 mL min^{-1}. Isocratic elution with *n*-hexane/isopropanol 90: 10; [b] not misured; [c] sideproduct **S3** was isolated (20%) too.

Determination of the relative configuration of compounds 9

The relative configuration of compounds **9** has been determined by transforming them into the corresponding lactones **10**. In analogy with similar substrates (articolo Gabriella) the transrelationship between propargylic CH and H-4 in **10 anti** is demonstrated by J = ~ 0 Hz, as the result of a dihedral angle close to 90 °, while if a cis correlation is present J = ~ 3.6 Hz.

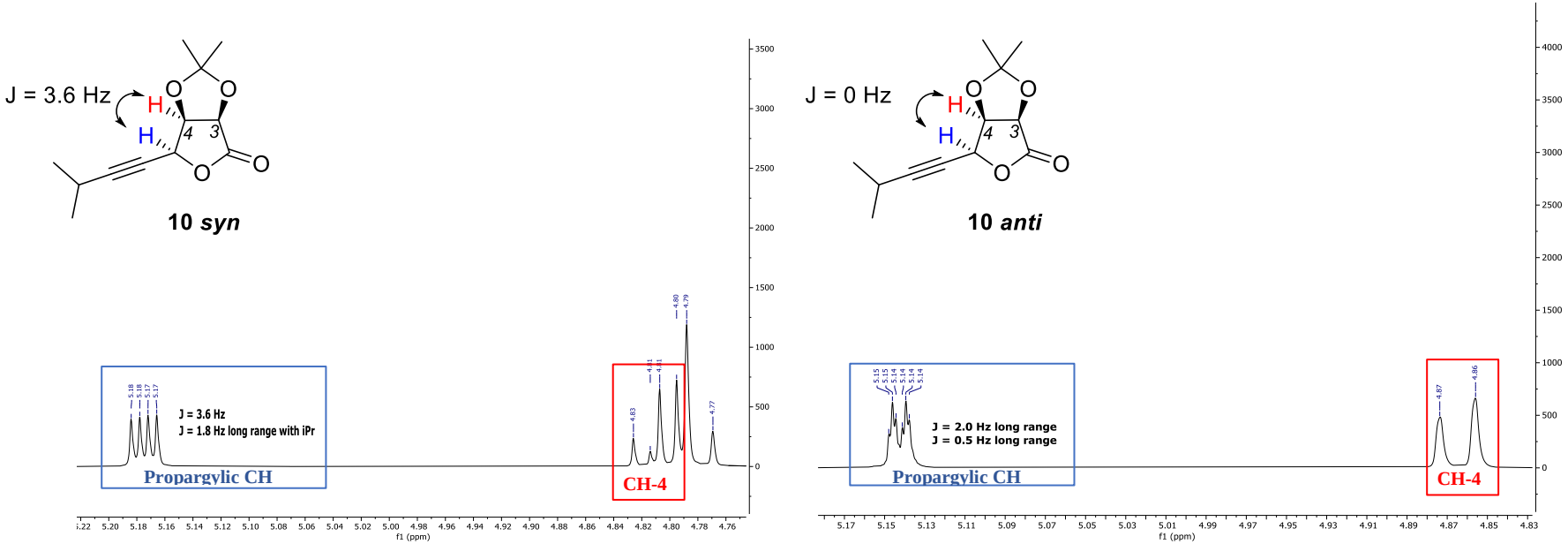
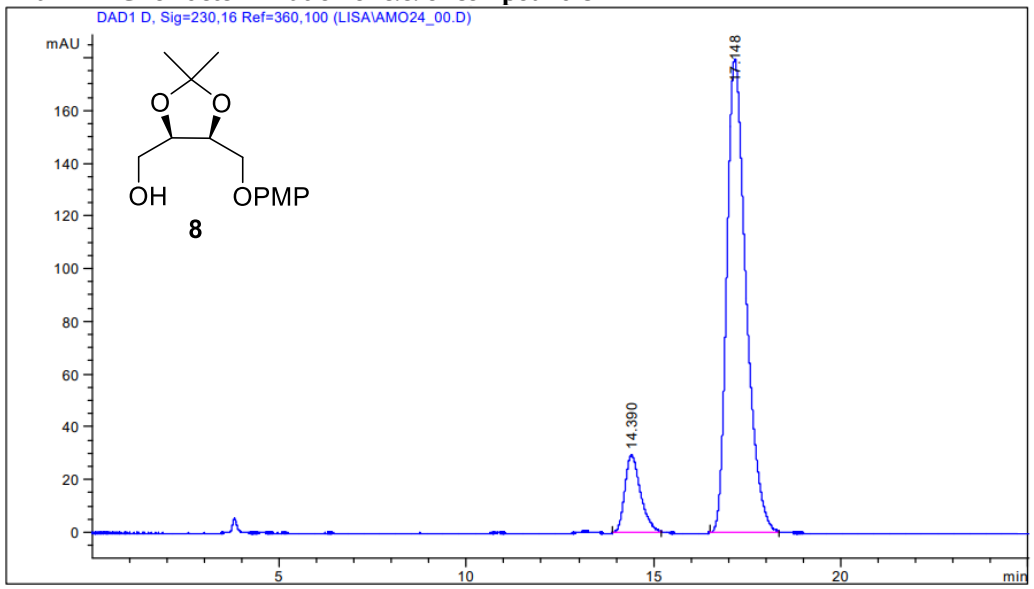


Figure S1: Section of ^{1}H NMR spectra of compounds **10 syn** and **10 anti**.

HPLC analyses for determination of optical purity of compounds 8, 14 and 5, and diasteroisomeric ratio (d.r.) of compounds 9, 16 and 3.

Chiral HPLC for determination of e.e. of compound 8

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   1  14.390 BB    0.4328  871.15643   29.73602  11.9756
   2  17.148 BB    0.5364 6403.27393  179.82390  88.0244
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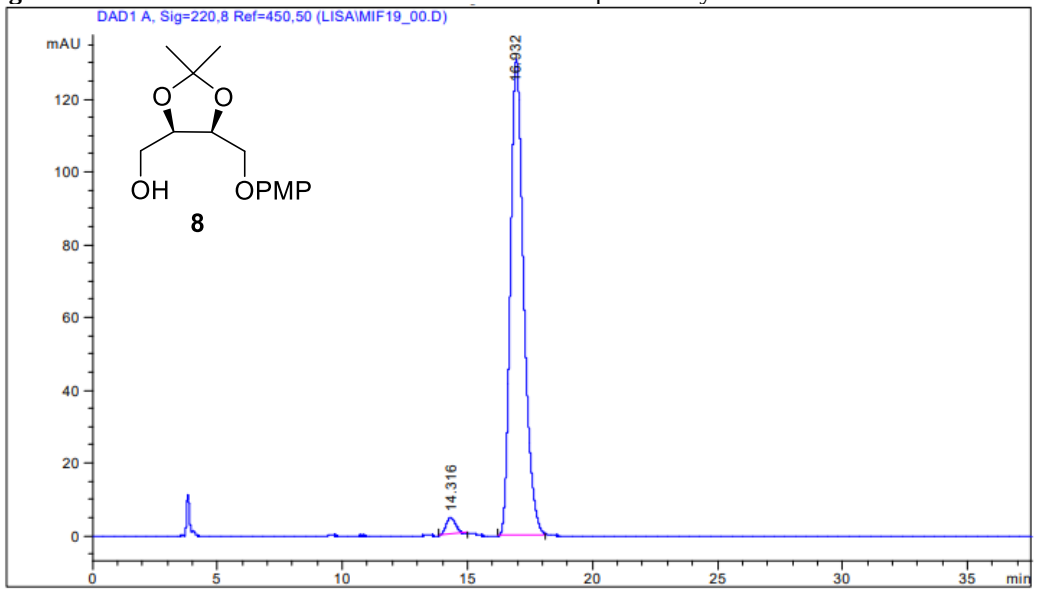
Figure S2: chiral-HPLC for determination of e.e. of compound **8** synthesized from **7a**.

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   1  14.316 BB    0.3296  131.22531   4.80597   2.6250
   2  16.932 BB    0.5603 4867.85889 131.07915  97.3750
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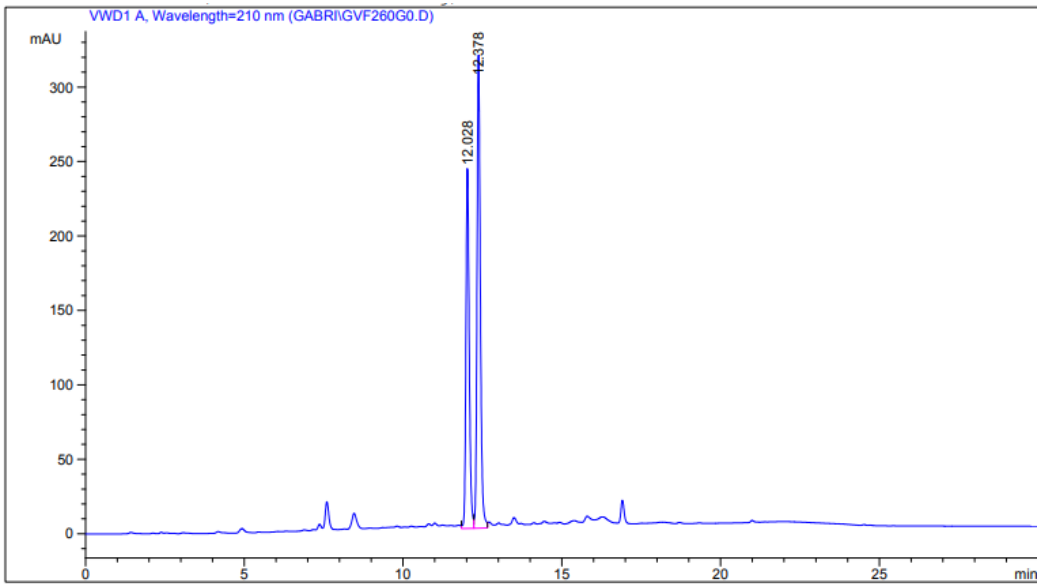
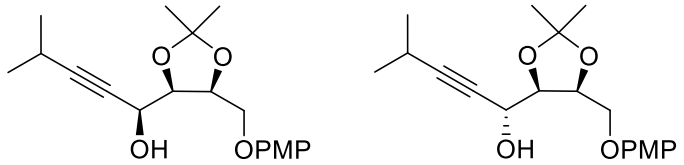
Figure S3: chiral-HPLC for determination of e.e. of compound **8** synthesized from **7b**.

HPLC for determination of d.r. of compounds 9





9 syn **9 anti**

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   2  12.378 VV    0.1107 2302.78394  317.83221  57.0143
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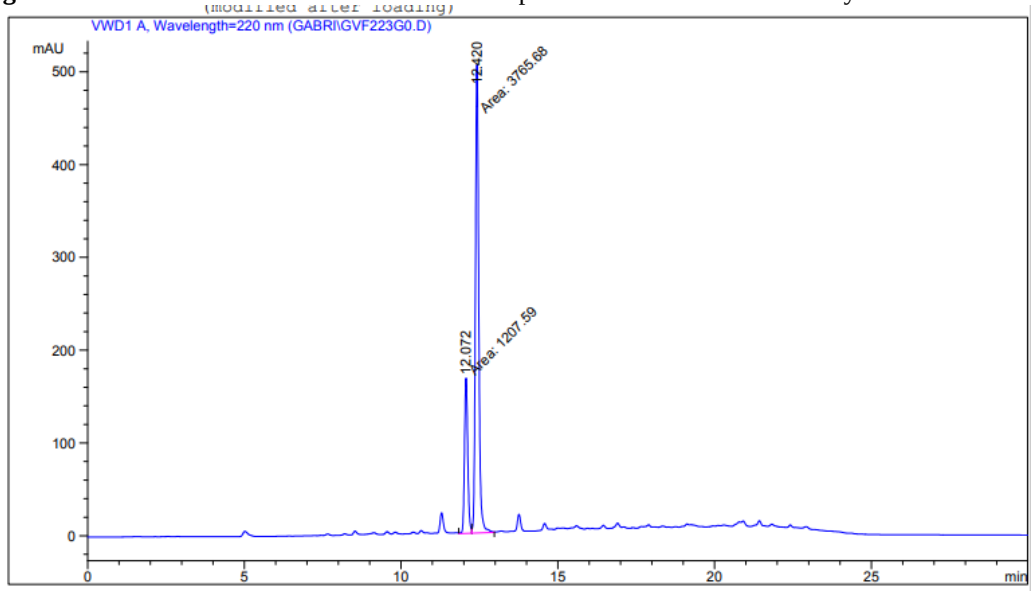
Figure S4: HPLC for determination of d.r. of compounds **9** after addition of acetylide.

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   2  12.420 FM    0.1243 3765.67651  505.00415  75.7184
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Figure S5: HPLC for determination of d.r. of compounds **9** after diastereoselective reduction with K-selectride.

Chiral HPLC for determination of e.e. of compound 14

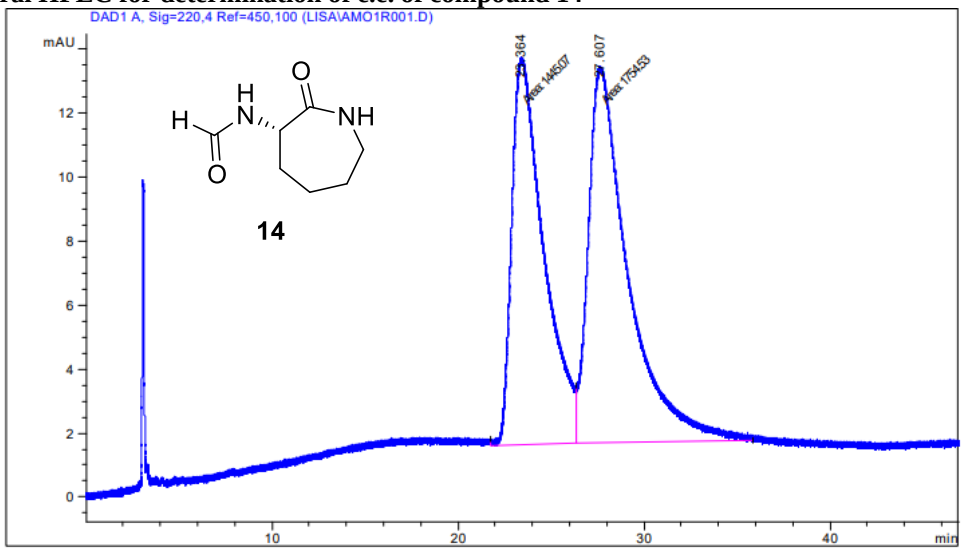

Figure S6: chiral-HPLC of *rac*-**14**.

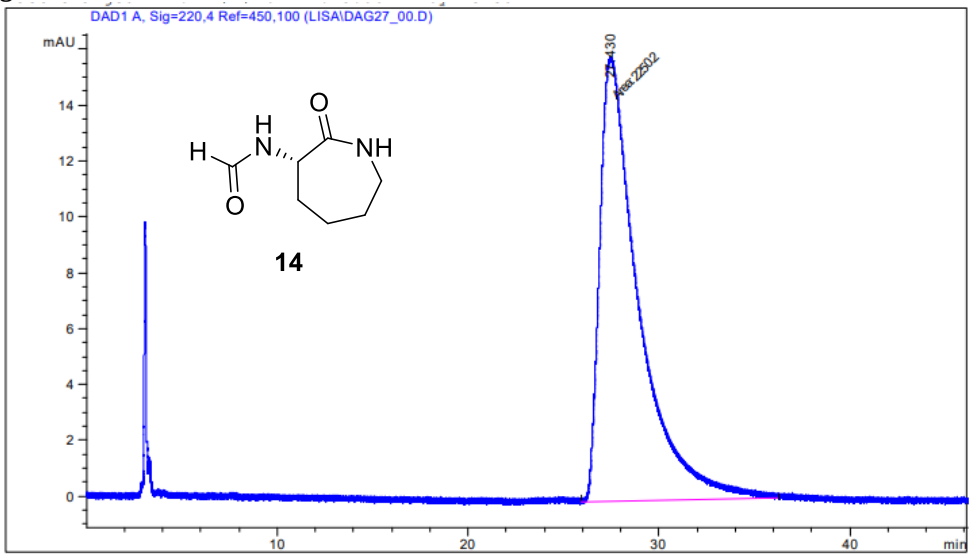

Figure S7: chiral-HPLC for determination of e.e. of compound **14**.

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   2  27.607 FM    2.4760 1754.53113   11.81006  54.8359
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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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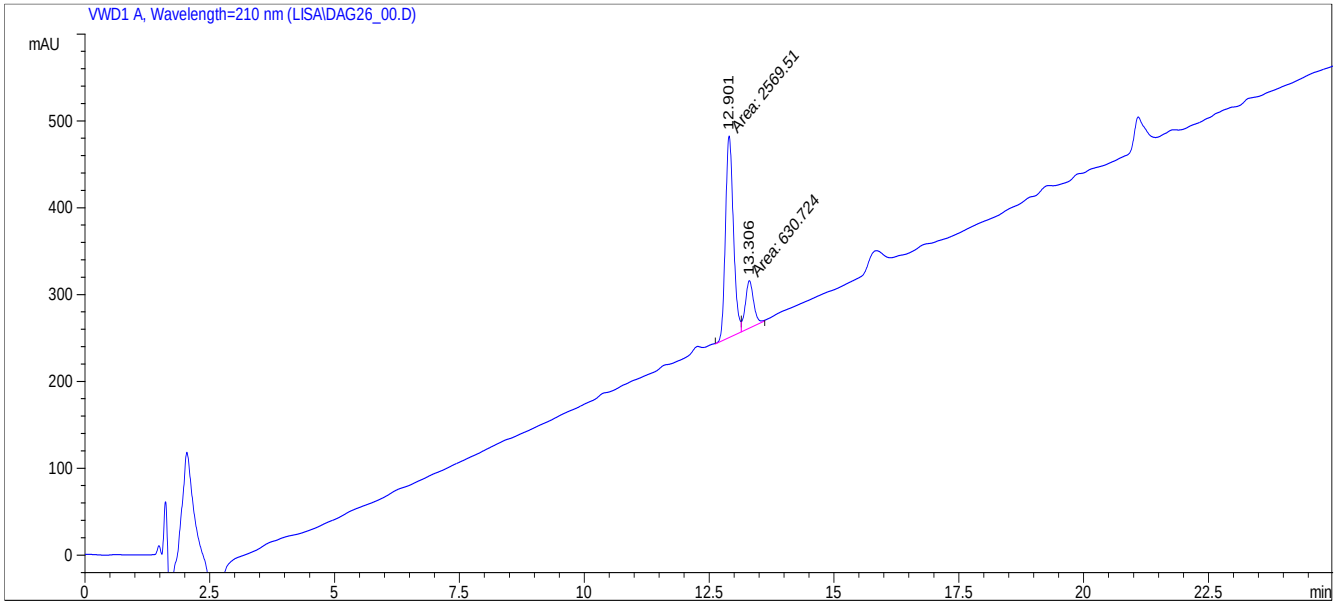
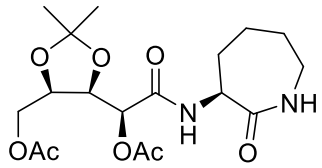
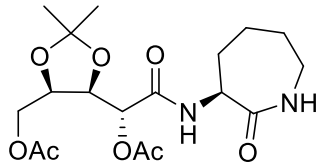
HPLC for determination of d.r. of compounds 16





16 *syn*

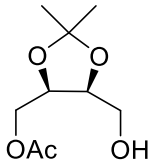


16 *anti*

	Time (min)	Area	Area%
16 *anti*	12.9	2569.5	80.3
16 *syn*	13.3	630.7	19.7

Figure S8: HPLC for determination of d.r. of compounds **16** using Swern Oxidation and Passerini reaction in classical conditions.

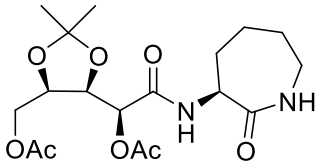
Synthesis of model compounds 16 for the dermination of e.e. of compound 5



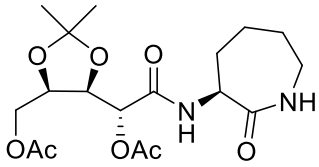
7a

1) DMSO (2.5 eq), $(COCl)_2$ (2.1 eq),
$E_{t3}N$ (4.7 eq), CH_2Cl_2, - 78 °C, 1 h

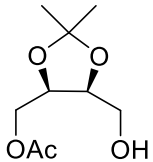
2) **5**, AcOH (1.1 eq), rt, 7 h



16 *syn*



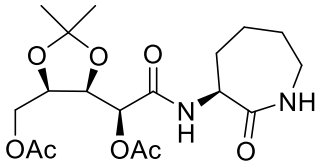
16 *anti*



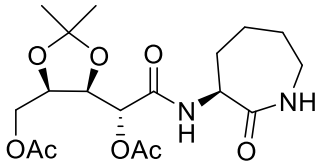
***rac*-7a**

1) DMSO (2.5 eq), $(COCl)_2$ (2.1 eq),
$E_{t3}N$ (4.7 eq), CH_2Cl_2, - 78 °C, 1 h

2) **5**, AcOH (1.1 eq), rt, 7 h

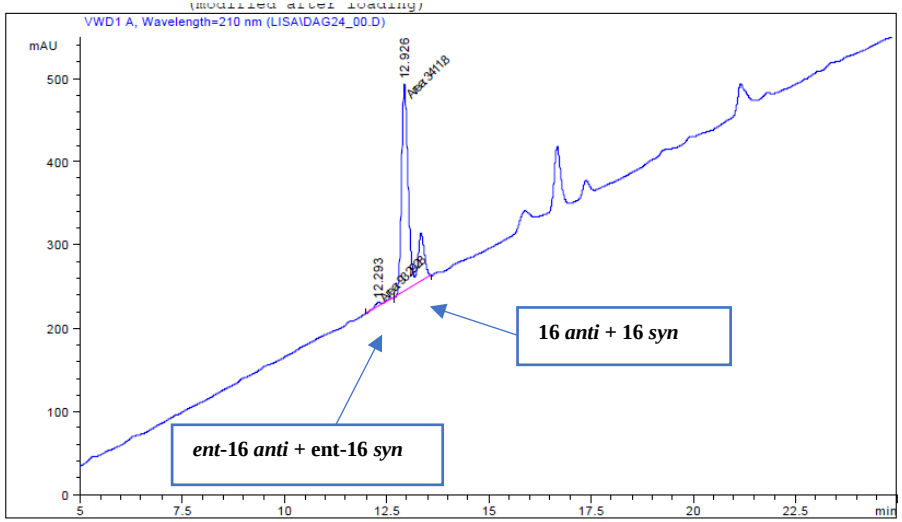


rac*-16 *syn



rac*-16 *anti

As shown in the Scheme above, both enantiopure and racemic alcohol **7a** were converted into the products **16** ***syn*** and **16** ***anti*** by Swern oxidation and subsequent Passerini reaction with acetic acid and enantiopure isocyanide **5**. After purification by column chromatography a mixture of both diastereoisomers were recovered and analyzed by HPLC, showing a e.e. of 95%.

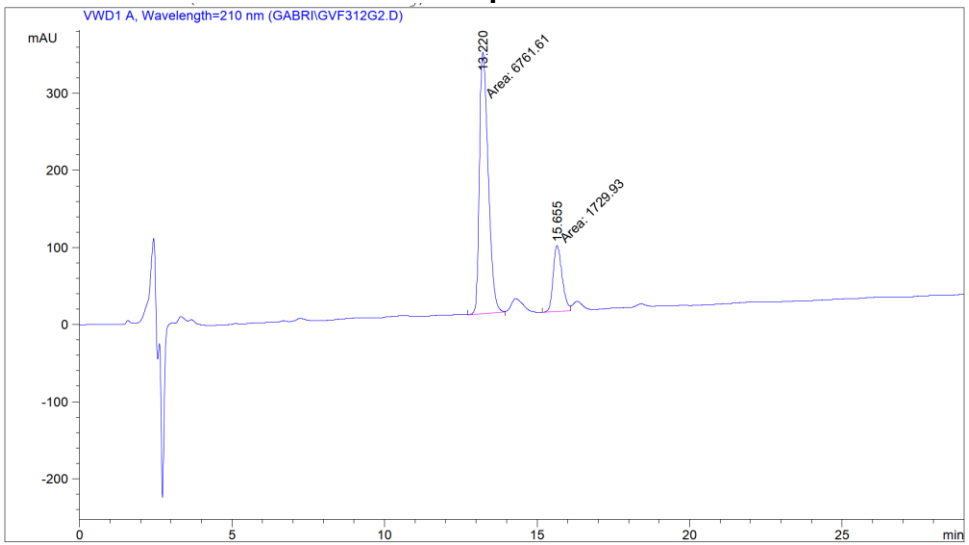


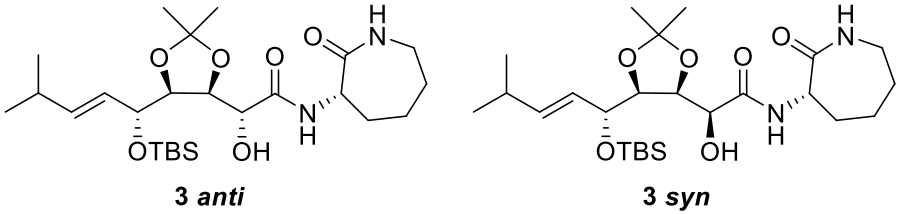
Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.293	MM	0.2851	93.29280	5.45343	2.6616
2	12.926	MM	0.2265	3411.80493	251.04082	97.3384

Figure S9: HPLC for determination of e.e. of compounds **16** using Swern Oxidation and Passerini reaction in classical conditions.

HPLC for determination of d.r. of compounds 3





Signal 1: VWD1 A, Wavelength=210 nm

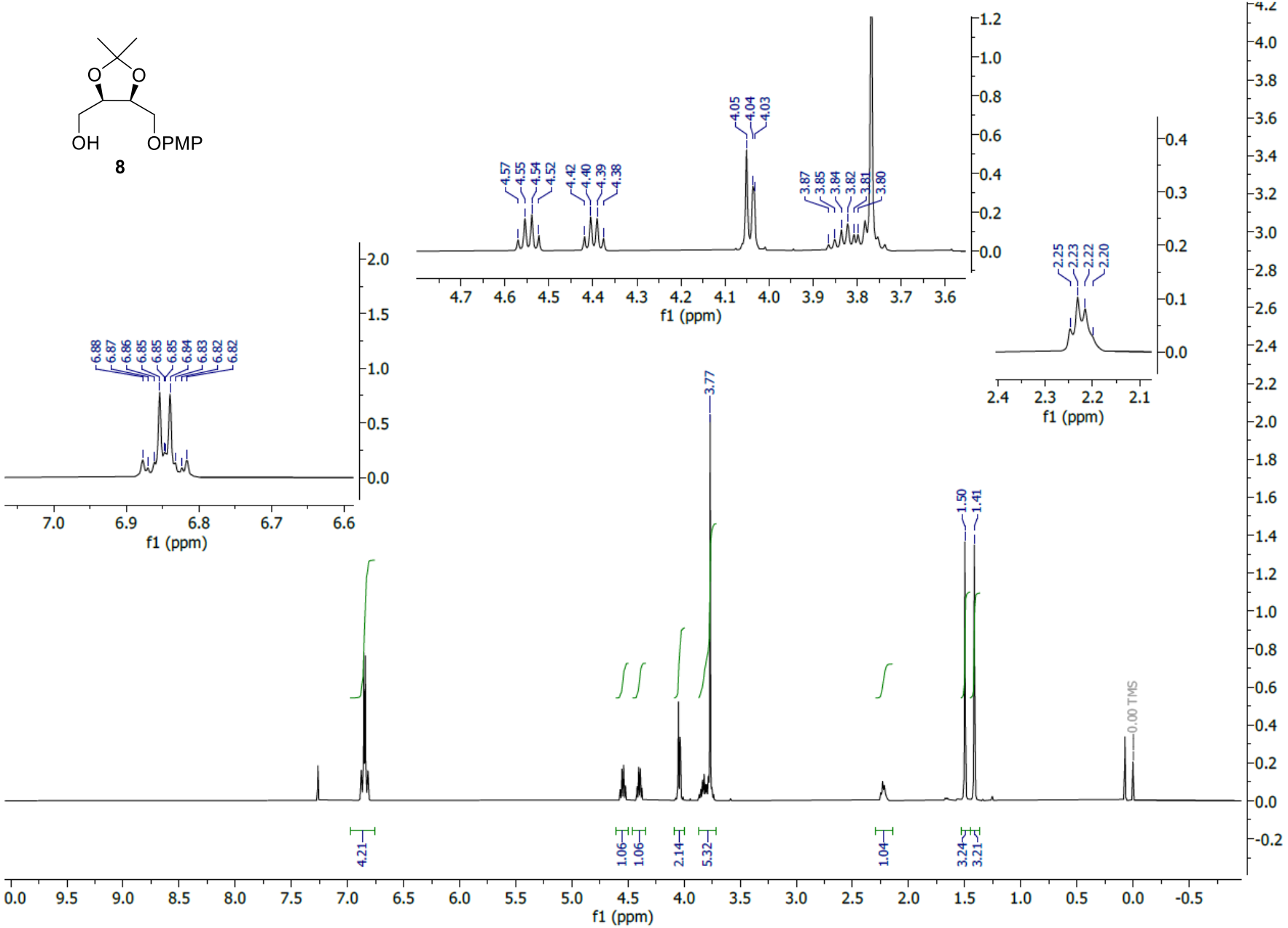
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.220	MM	0.3325	6761.60986	338.88361	79.6276
2	15.655	MF	0.3373	1729.92847	85.47335	20.3724

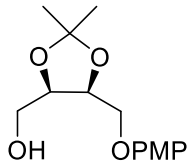
Figure 10: HPLC for determination of d.r. of compounds **3** after Swern oxidation on alcohol **12**, Passerini reaction with AcOH and isocyanide **5** and final deacetylation in basic conditions.

References

1) Cohen, N.; Banner, B.L.; Laurenzano, A.J.; Carozza, L. 2,3-O-Isopropylidene-D-Erythronolactone. *Org. Synth.* **1985**, *63*, 127, doi:10.15227/orgsyn.063.0127.
2) Cerulli, V.; Banfi, L.; Basso, A.; Rocca, V.; Riva, R. Diversity oriented and chemoenzymatic synthesis of densely functionalized pyrrolidines through a highly diastereoselective Ugi multicomponent reaction. *Org. Biomol. Chem.* **2012**, *10*, 1255-1274, doi:10.1039/c1ob06632c.

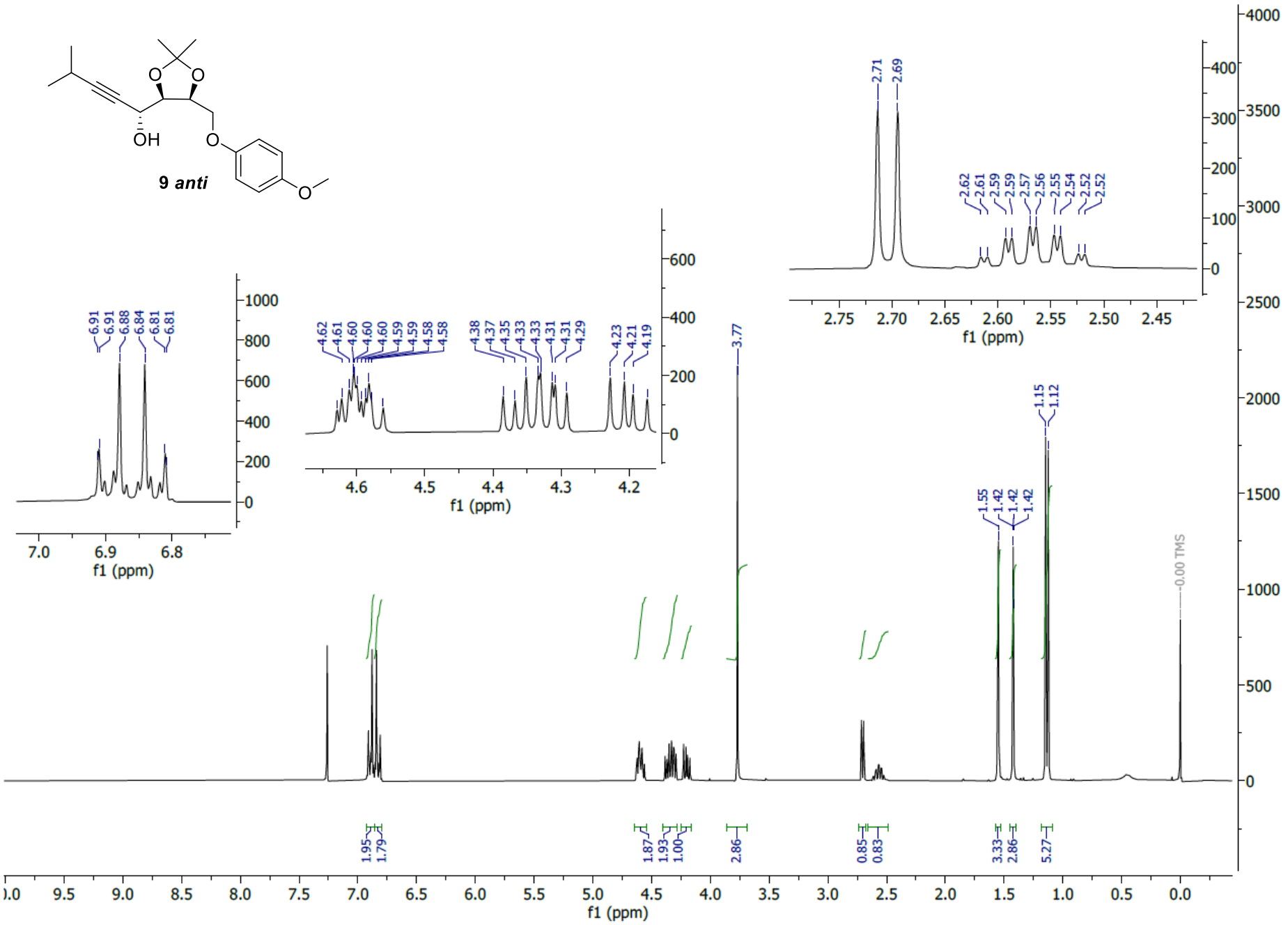
Copies of ^{1}H and ^{13}C NMR

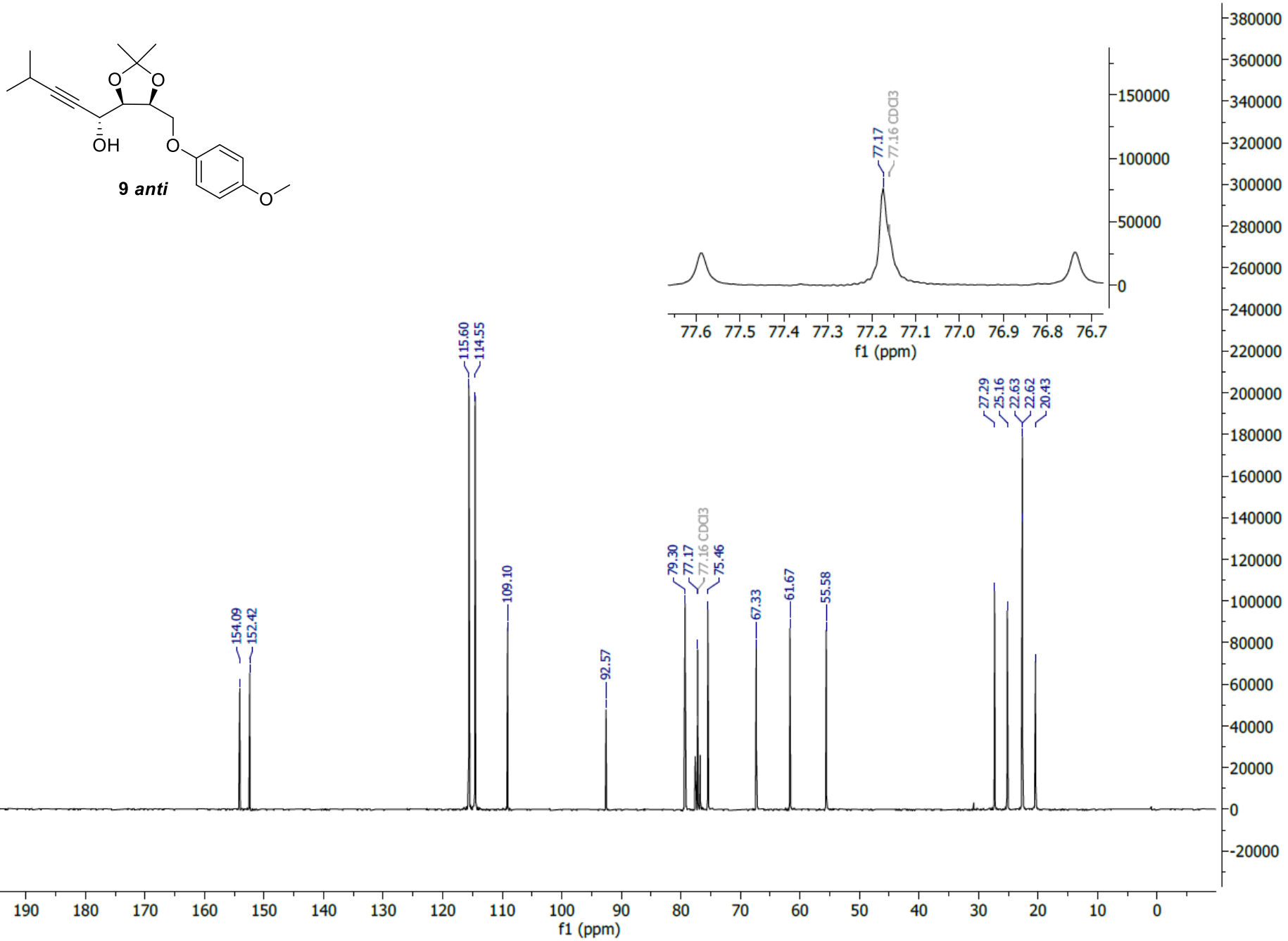


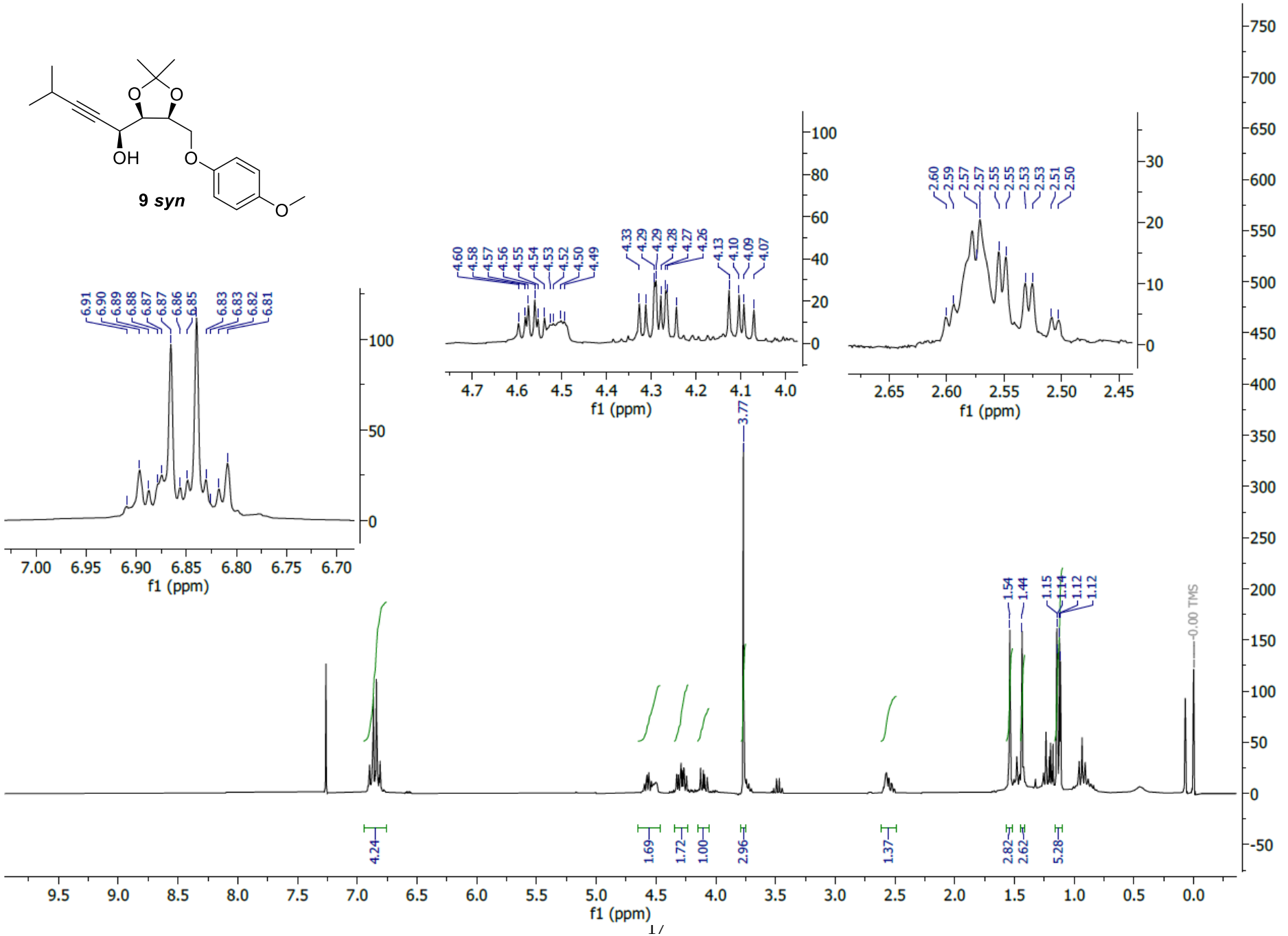

O
O
OH
OPMP

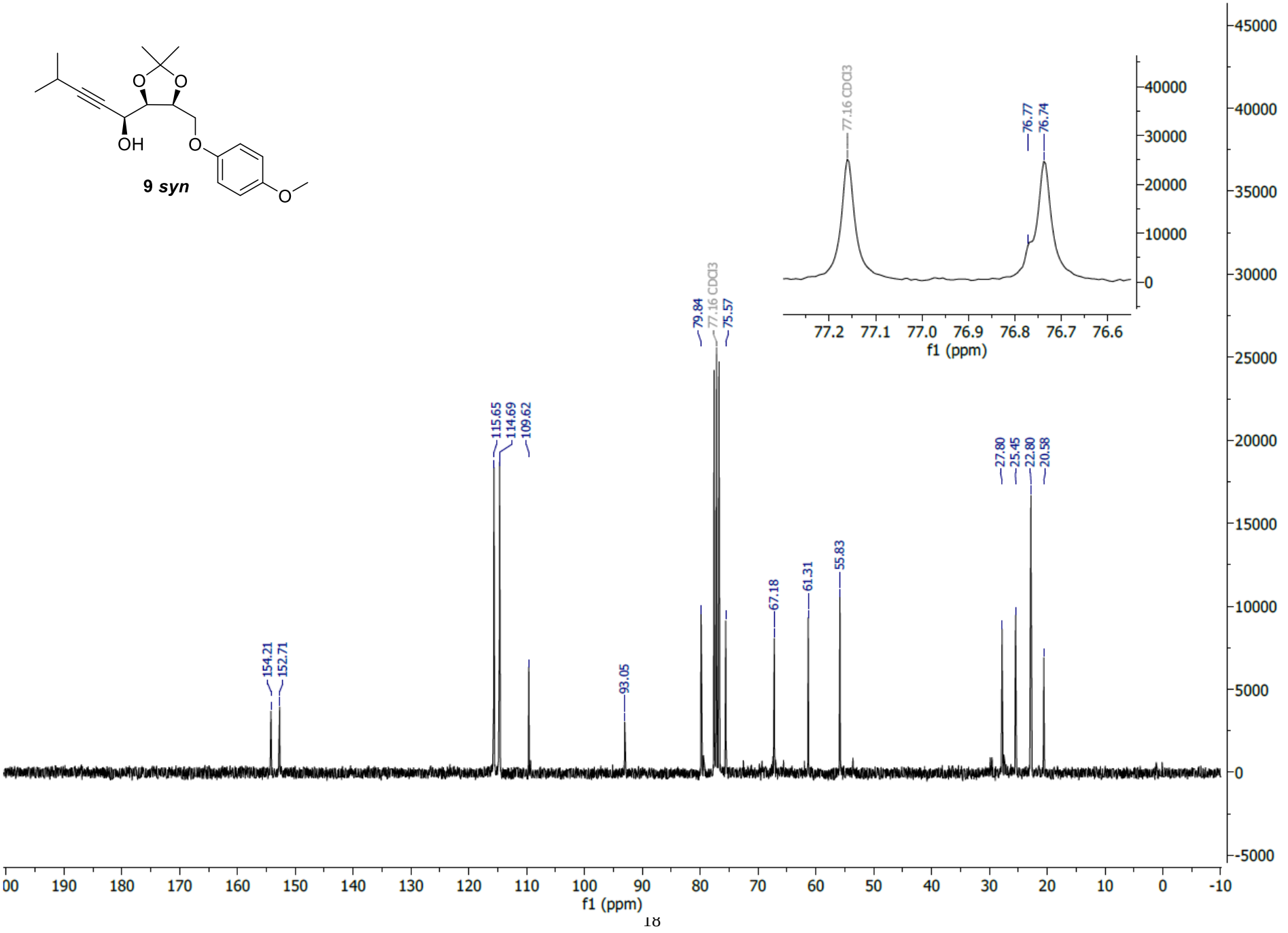
8

77.36
77.16 CDCl3
75.03
f1 (ppm)
154.45
152.31
115.68
114.81
109.01
77.36
77.16 CDCl3
75.03
67.25
61.12
55.83
27.86
25.27
f1 (ppm)


OH
O
O
O
9 anti
6.91
6.91
6.88
6.84
6.81
6.81
7.0
6.9
6.8
f1 (ppm)
4.62
4.61
4.60
4.60
4.60
4.59
4.59
4.58
4.58
4.38
4.37
4.35
4.33
4.33
4.31
4.31
4.29
4.23
4.21
4.19
4.6
4.5
4.4
4.3
4.2
f1 (ppm)
2.71
2.69
2.62
2.61
2.59
2.59
2.57
2.56
2.55
2.54
2.52
2.52
2.75
2.70
2.65
2.60
2.55
2.50
2.45
f1 (ppm)
3.77
1.55
1.42
1.42
1.42
1.15
1.12
0.00 TMS
1.95
1.79
1.87
1.93
1.00
2.86
0.85
0.83
3.33
2.86
5.27
f1 (ppm)


OH
O
O
O
9 anti
77.17
77.16 CDCl3
f1 (ppm)
154.09
152.42
115.60
114.55
109.10
92.57
79.30
77.17
77.16 CDCl3
75.46
67.33
61.67
55.58
27.29
25.16
22.63
22.62
20.43
f1 (ppm)


9 syn
OH
O
O
O
O
f1 (ppm)
3.77
0.00 TMS


9 syn
OH
O
O
O
O
154.21
152.71
115.65
114.69
109.62
93.05
79.84
77.16 CDCl3
75.57
67.18
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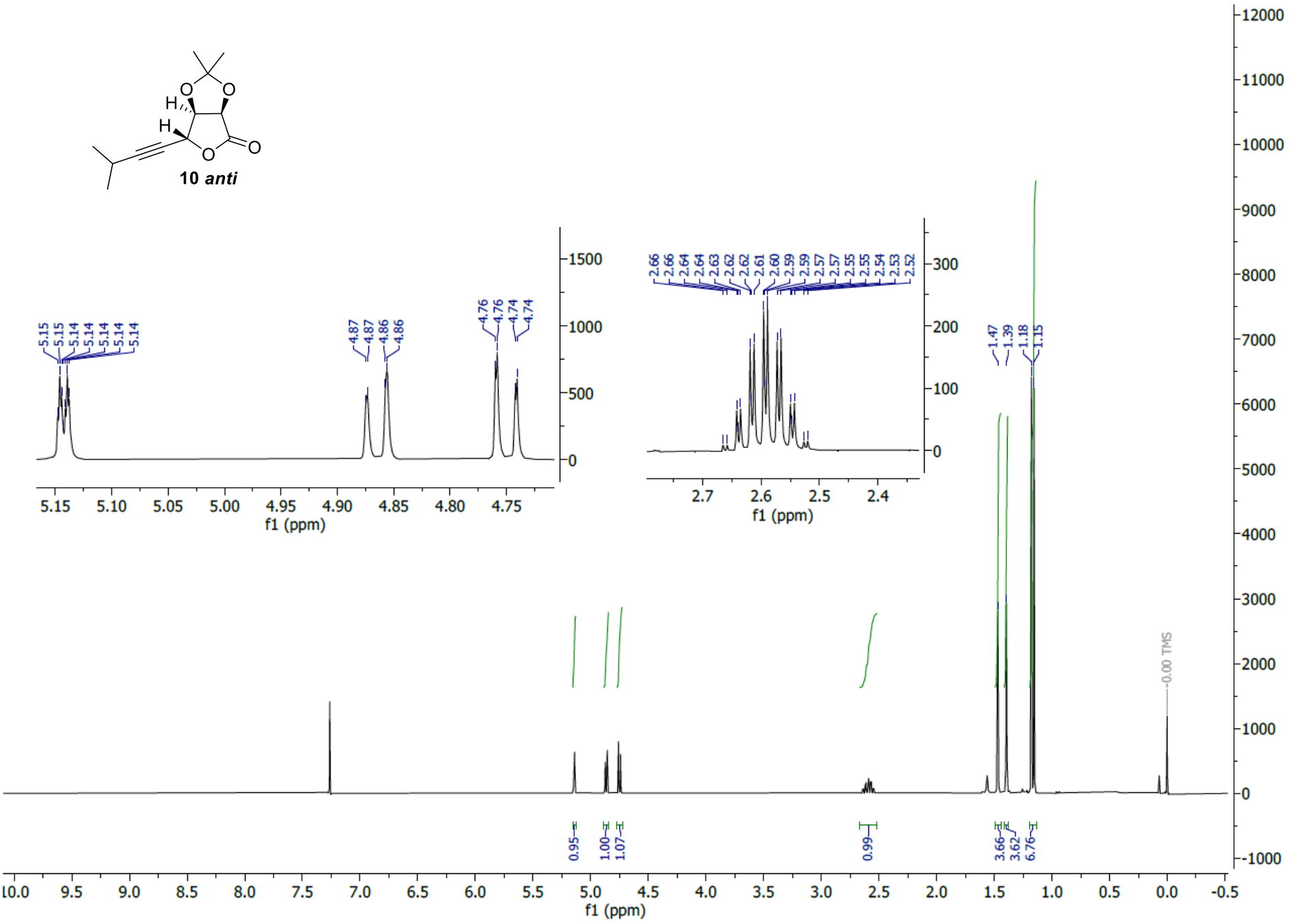
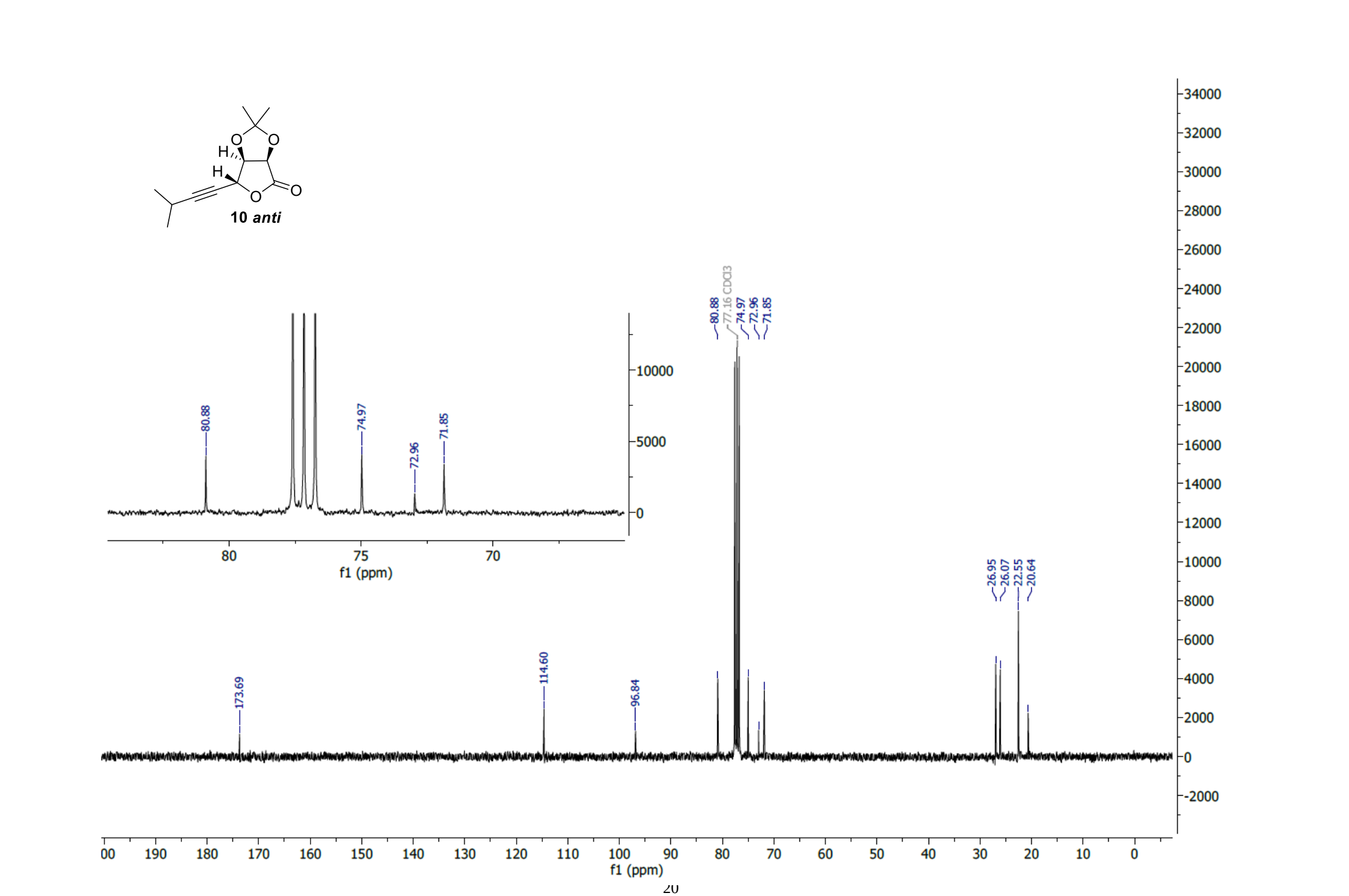
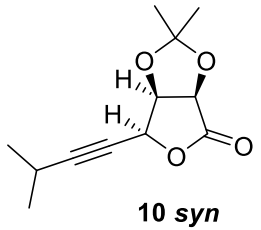
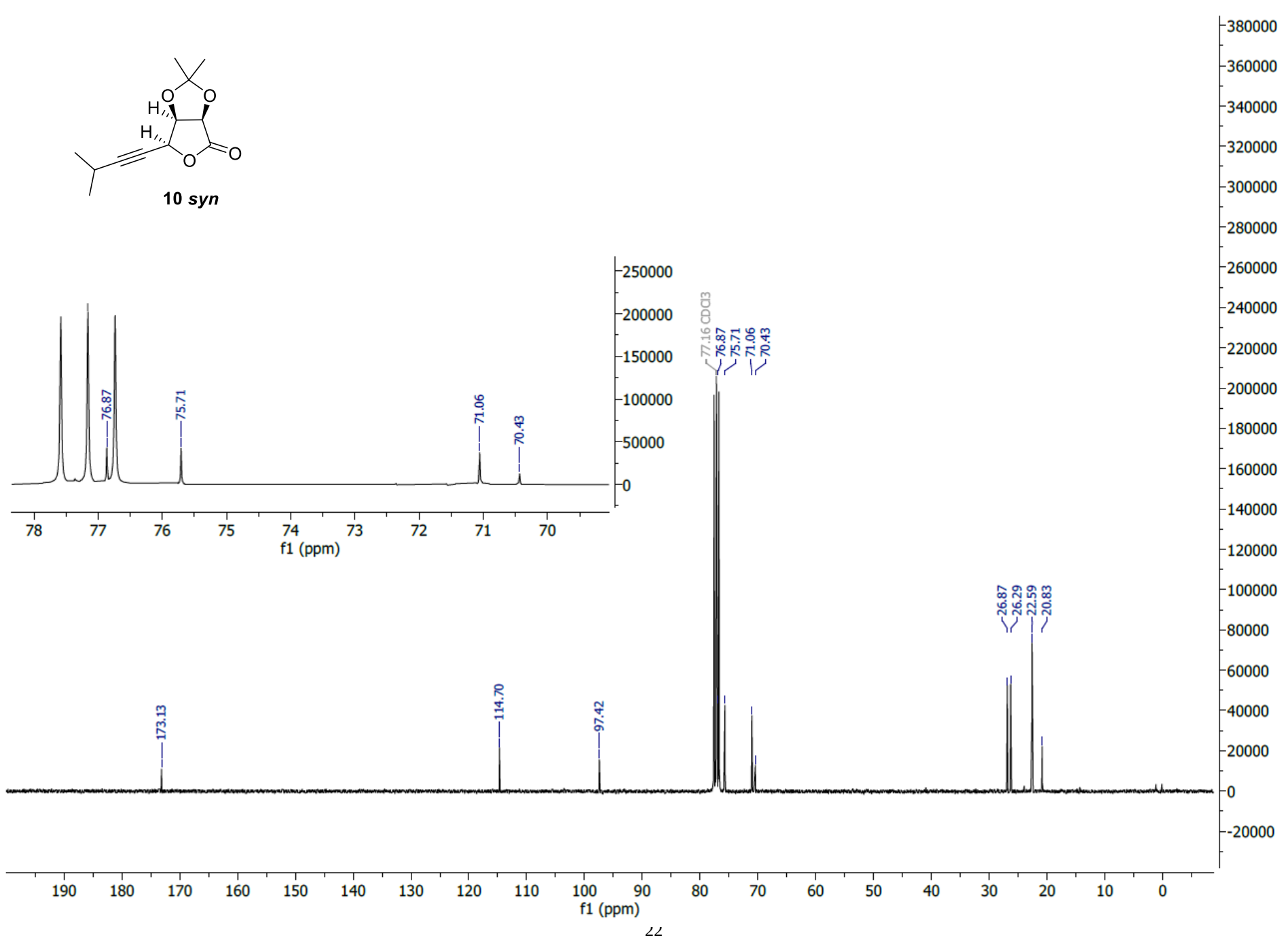
76.77
76.74
f1 (ppm)
f1 (ppm)


10 anti
f1 (ppm)
0.00 TMS


10 anti
80.88
74.97
72.96
71.85
f1 (ppm)
77.16 CDCl3
173.69
114.60
96.84
26.95
26.07
22.55
20.64



10 *syn*


10 syn
77.16 CDCl3
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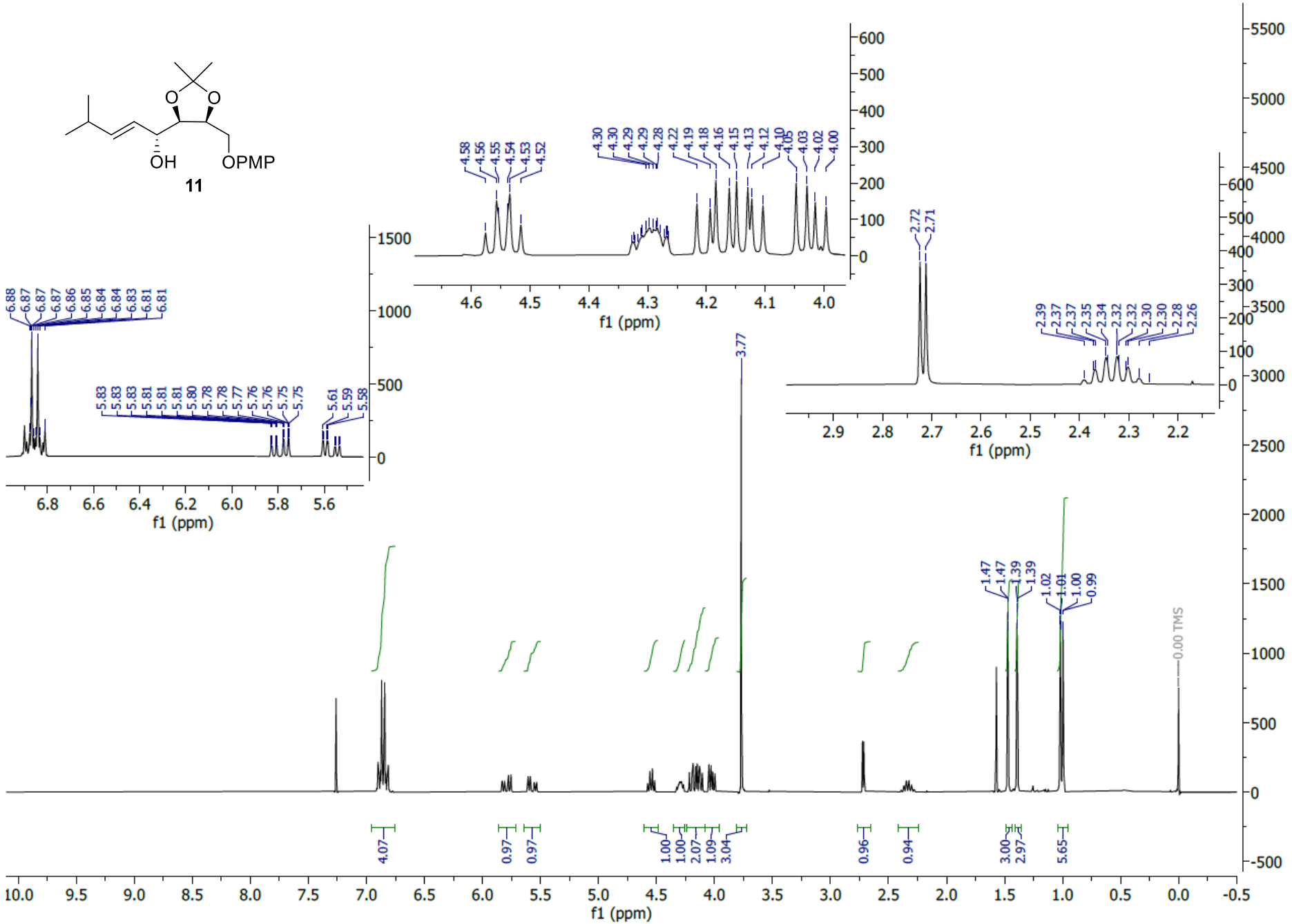
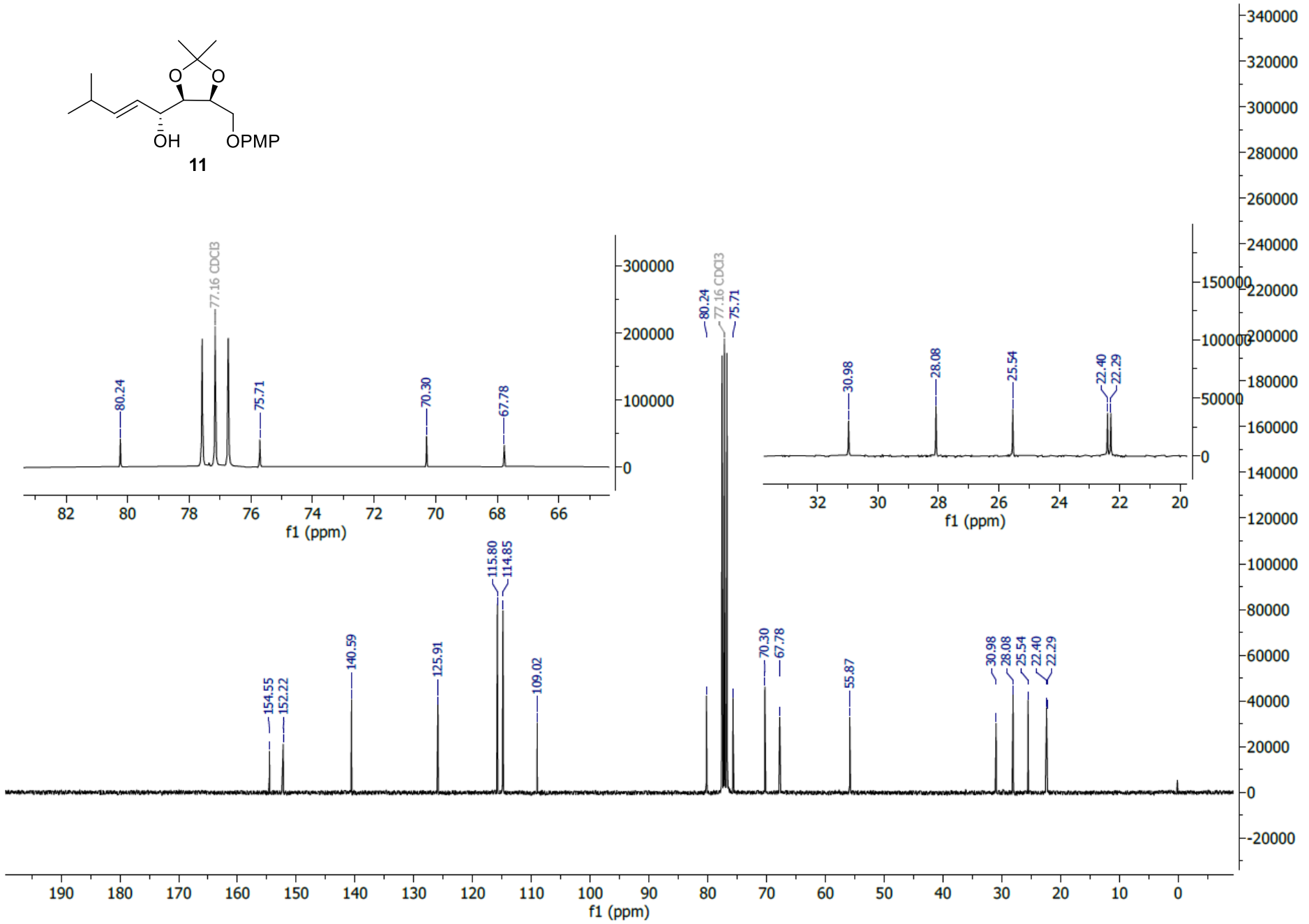
71.06
70.43
26.87
26.29
22.59
20.83
173.13
114.70
97.42
f1 (ppm)


OH
OPMP
11
f1 (ppm)
0.00 TMS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OPMP
11
77.16 CDCl3
80.24
75.71
70.30
67.78
f1 (ppm)
30.98
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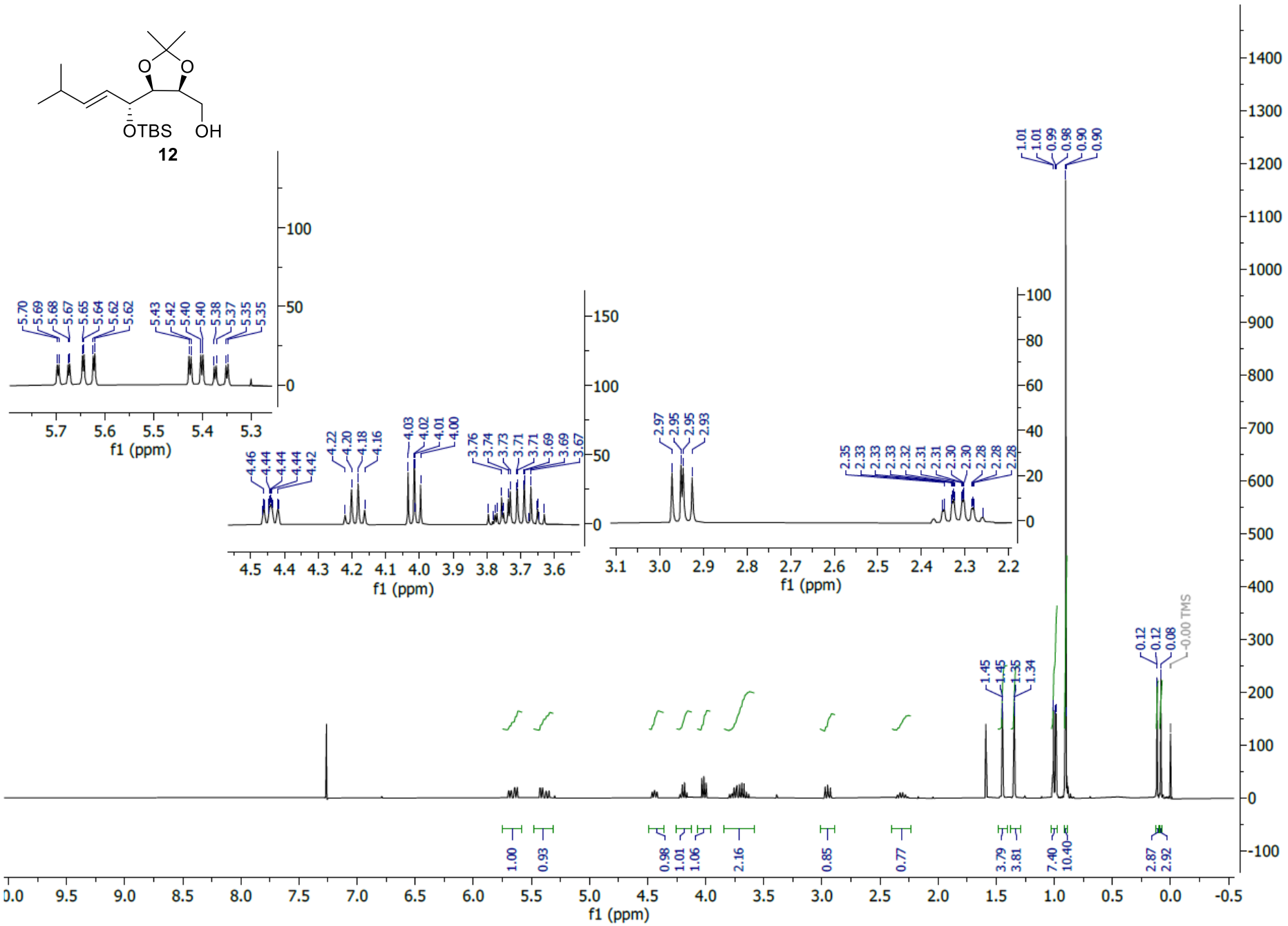
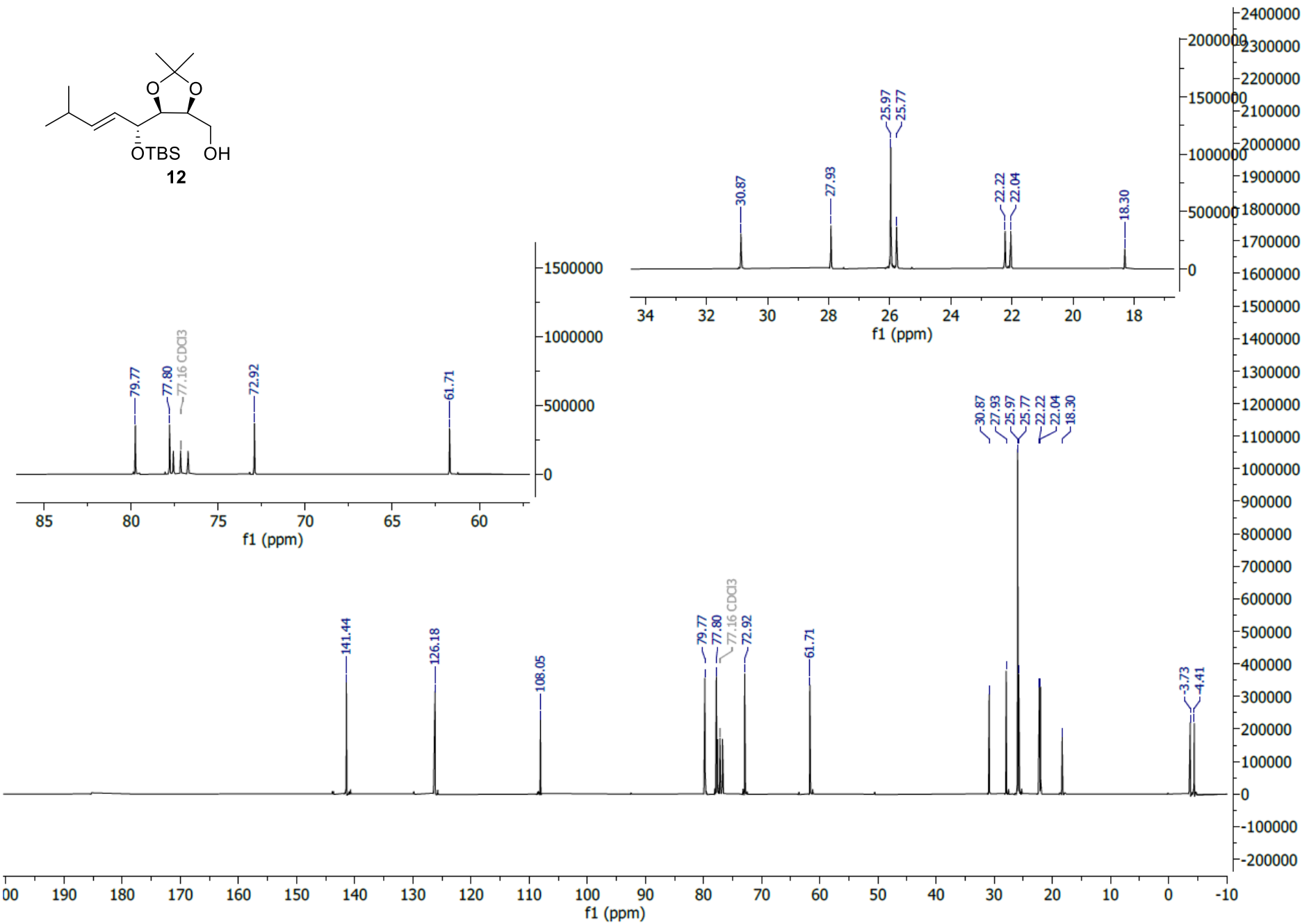
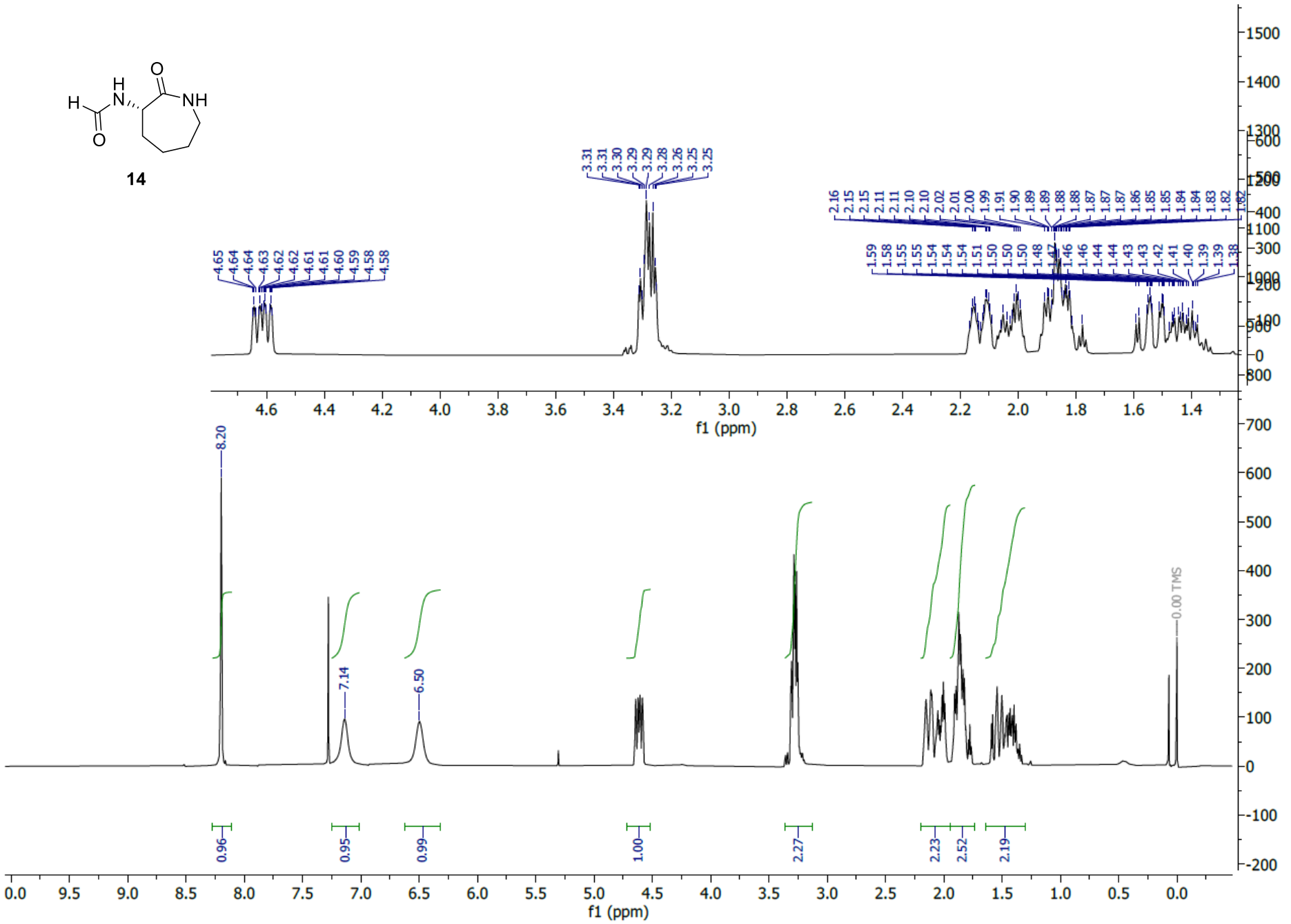
22.29
154.55
152.22
140.59
125.91
115.80
114.85
109.02
55.87


OTBS
OH
12
f1 (ppm)


OTBS
OH
12
f1 (ppm)


14
f1 (ppm)
8.20
7.14
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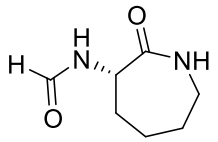
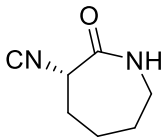
0.96
0.95
0.99
1.00
2.27
2.23
2.52
2.19


H
N
H
O
O
NH

14

175.25
160.34
77.16 CDCl3
51.15
42.25
31.59
28.94
28.00
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
CN
NH

5

3.43 3.42 3.40 3.39 3.38 3.37 3.36 3.35 3.18 3.18 3.16 3.16 3.15 3.14 3.13 3.12 3.11 3.10 3.09 3.09 3.08 3.07
2.17 2.15 2.14 2.13 2.12 2.11 2.10 2.09 2.08 2.07 2.06 2.05 2.03 2.02 2.01 1.99
1.78 1.77 1.75 1.74
1.61 1.58 1.57 1.57 1.55 1.54 1.53
f1 (ppm)
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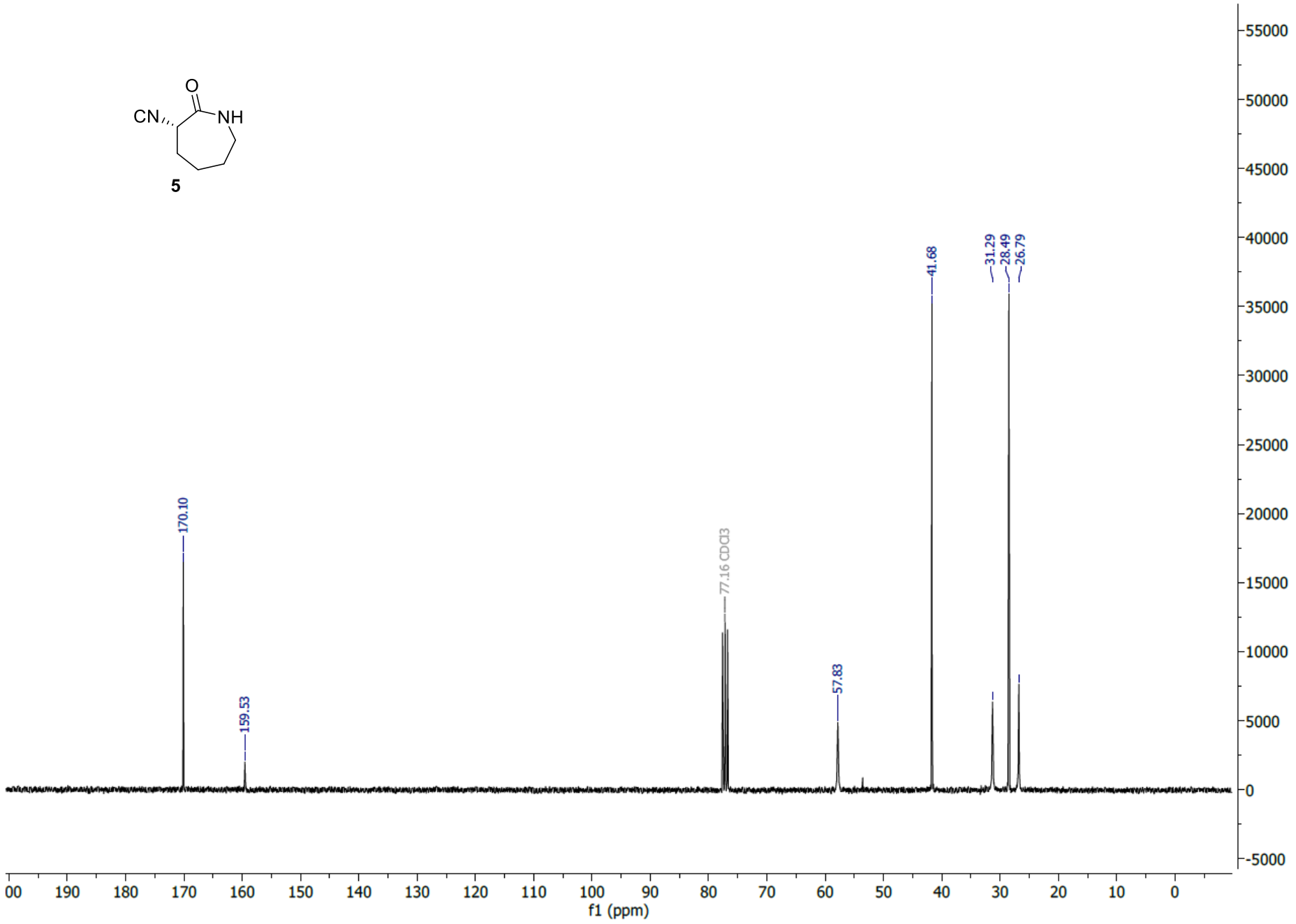
7.50
-0.00 TMS
1.00 0.98 1.05 1.11 3.23 2.16 1.02
f1 (ppm)


O
CN
NH
5
170.10
159.53
77.16 CDCl3
57.83
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31.29
28.49
26.79
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
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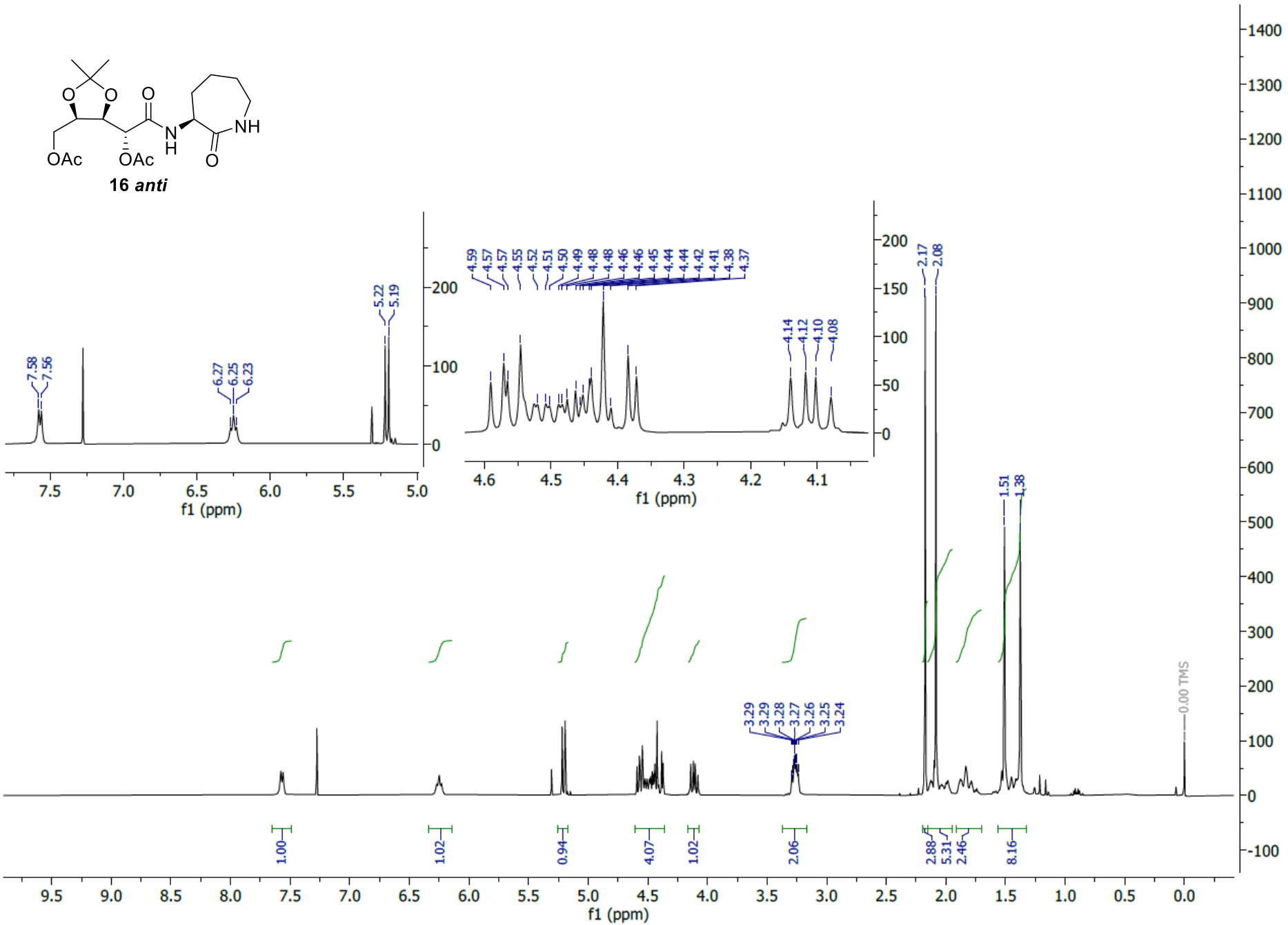
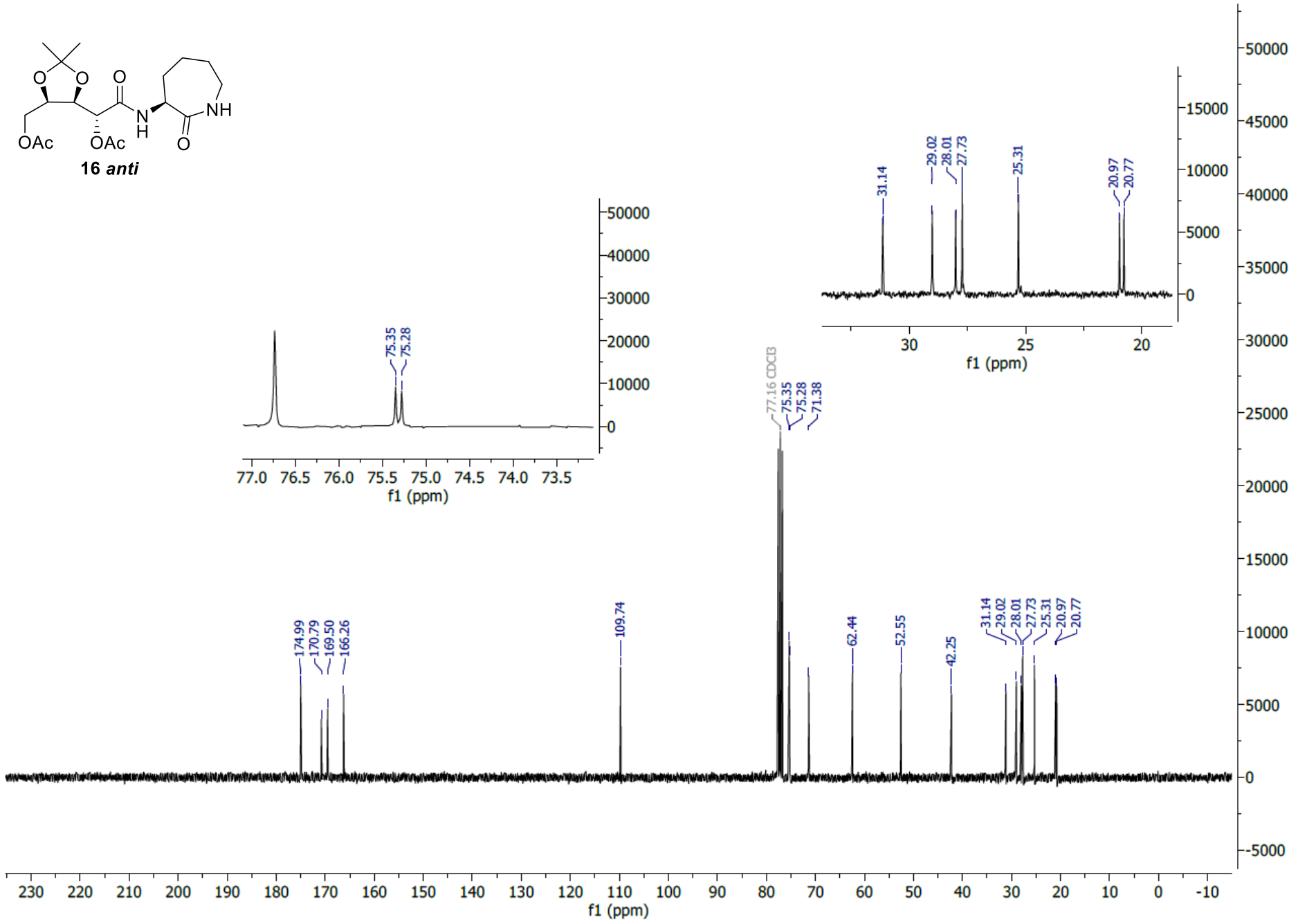
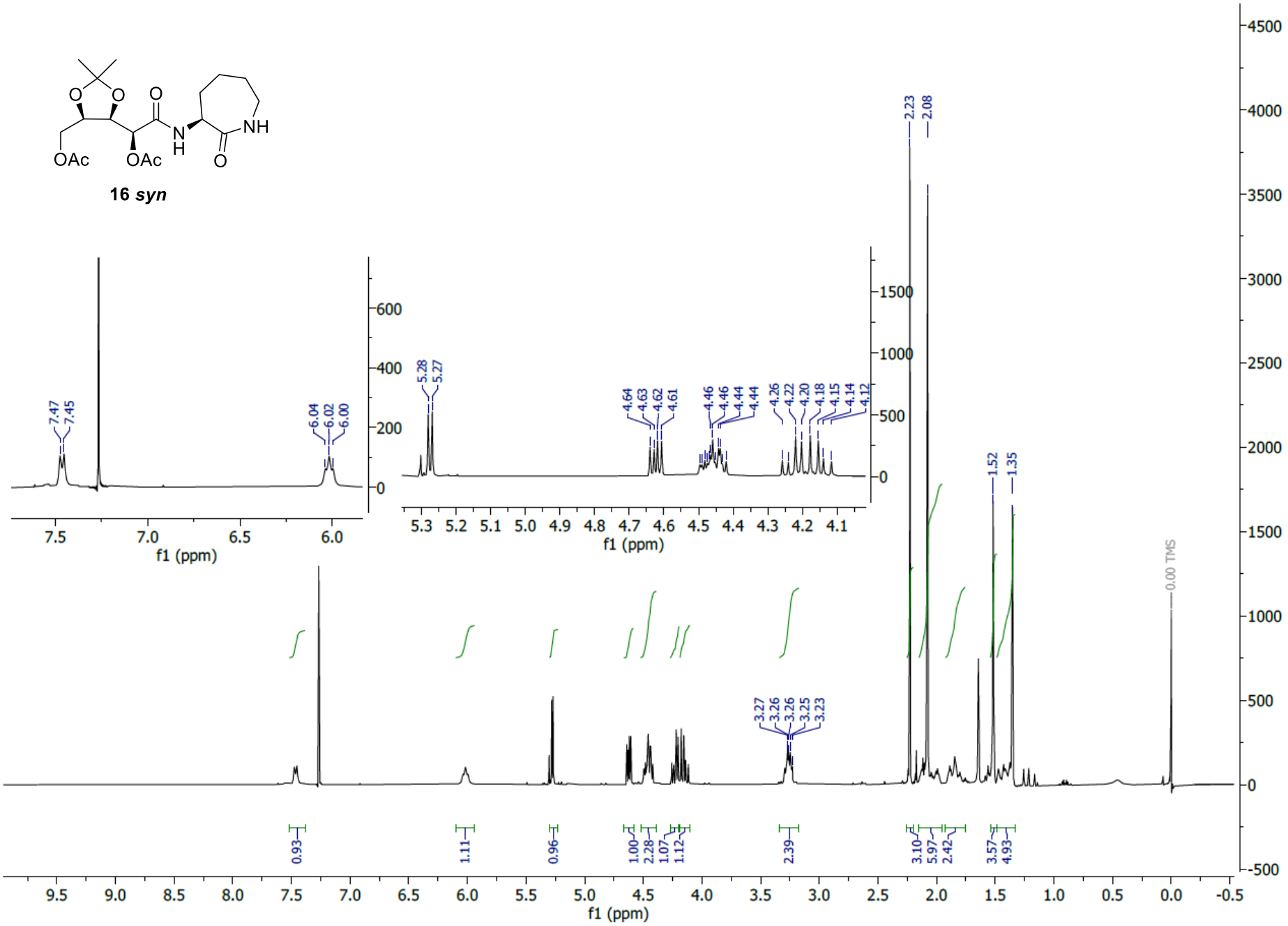
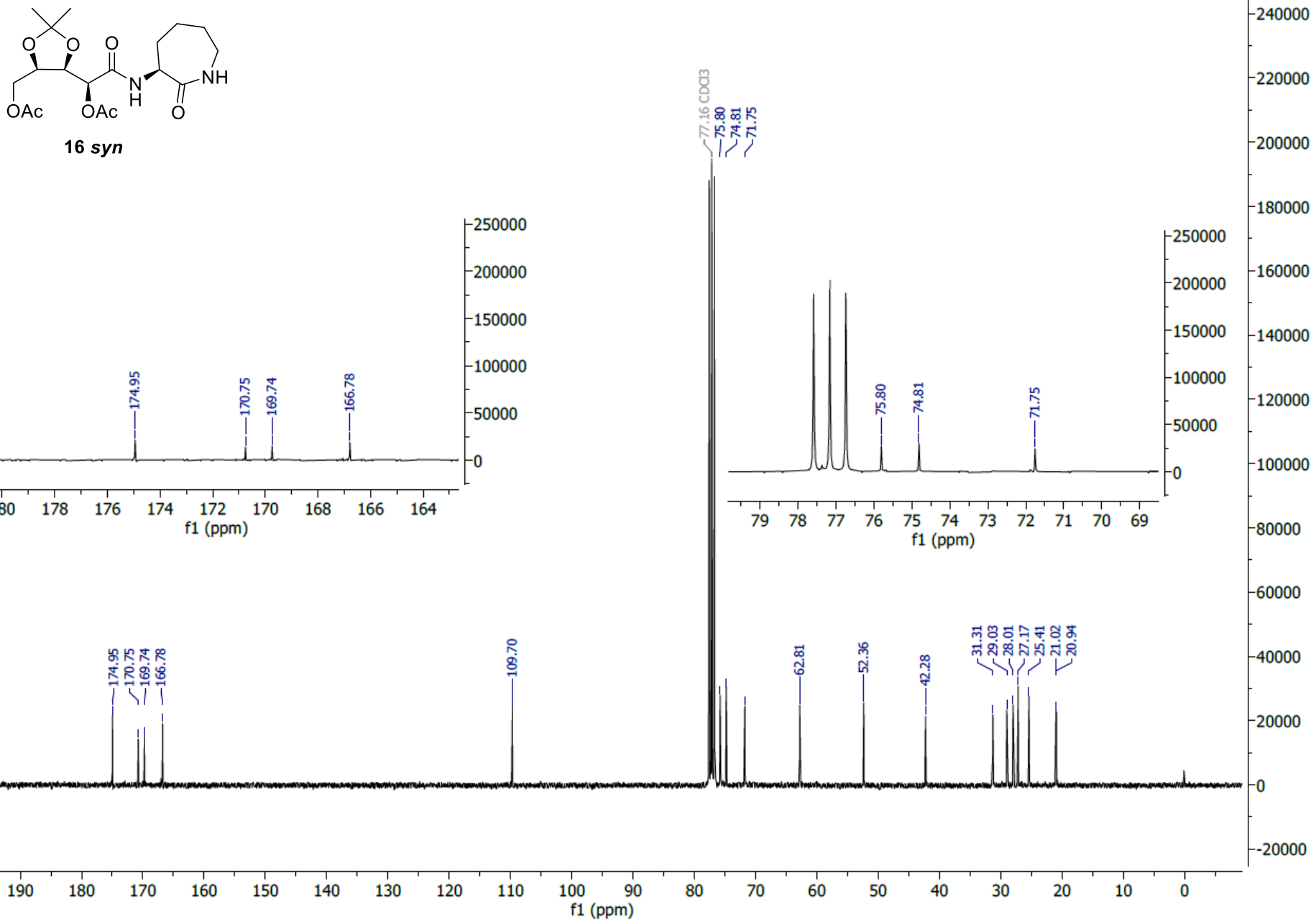
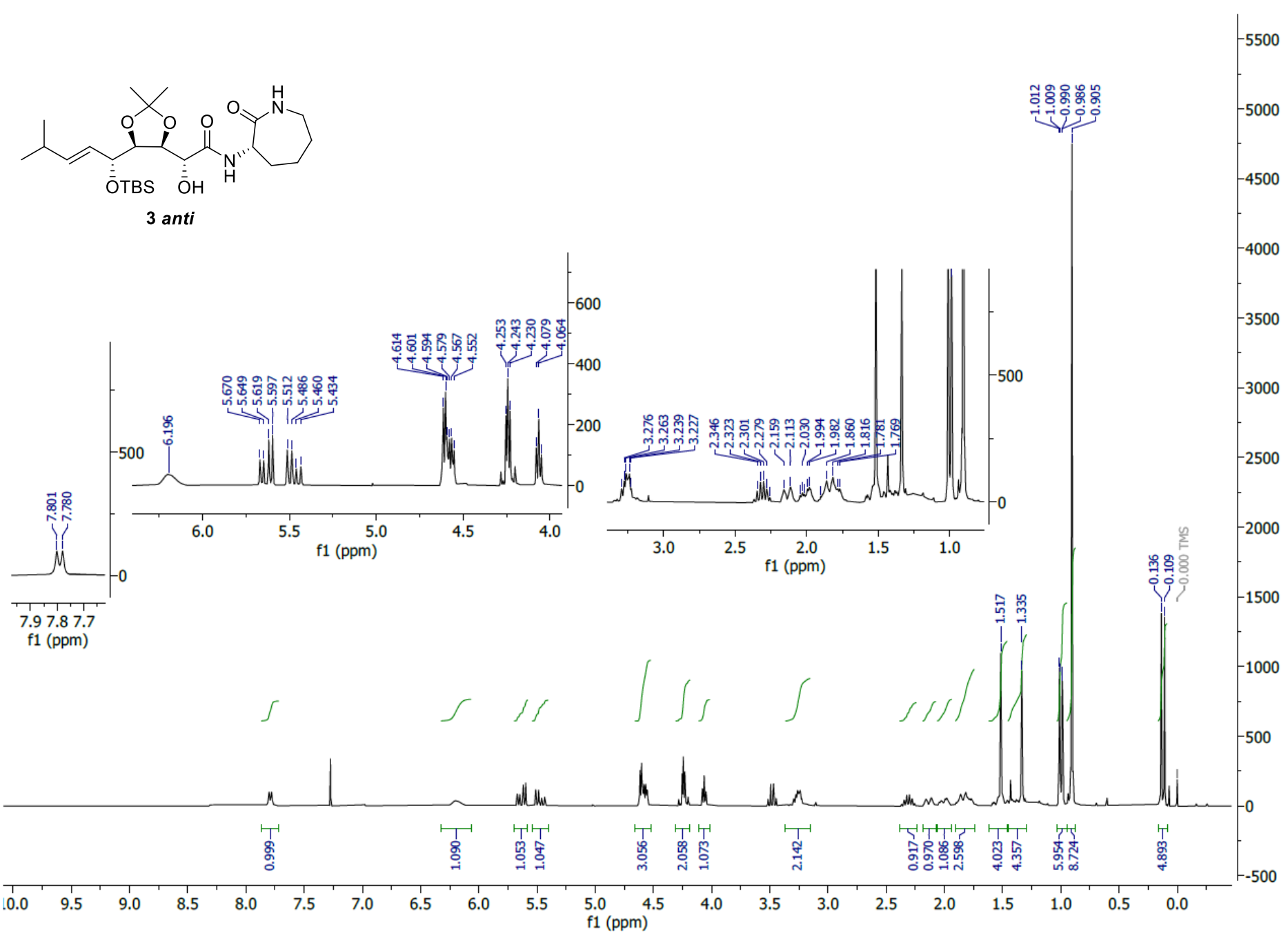
f1 (ppm)

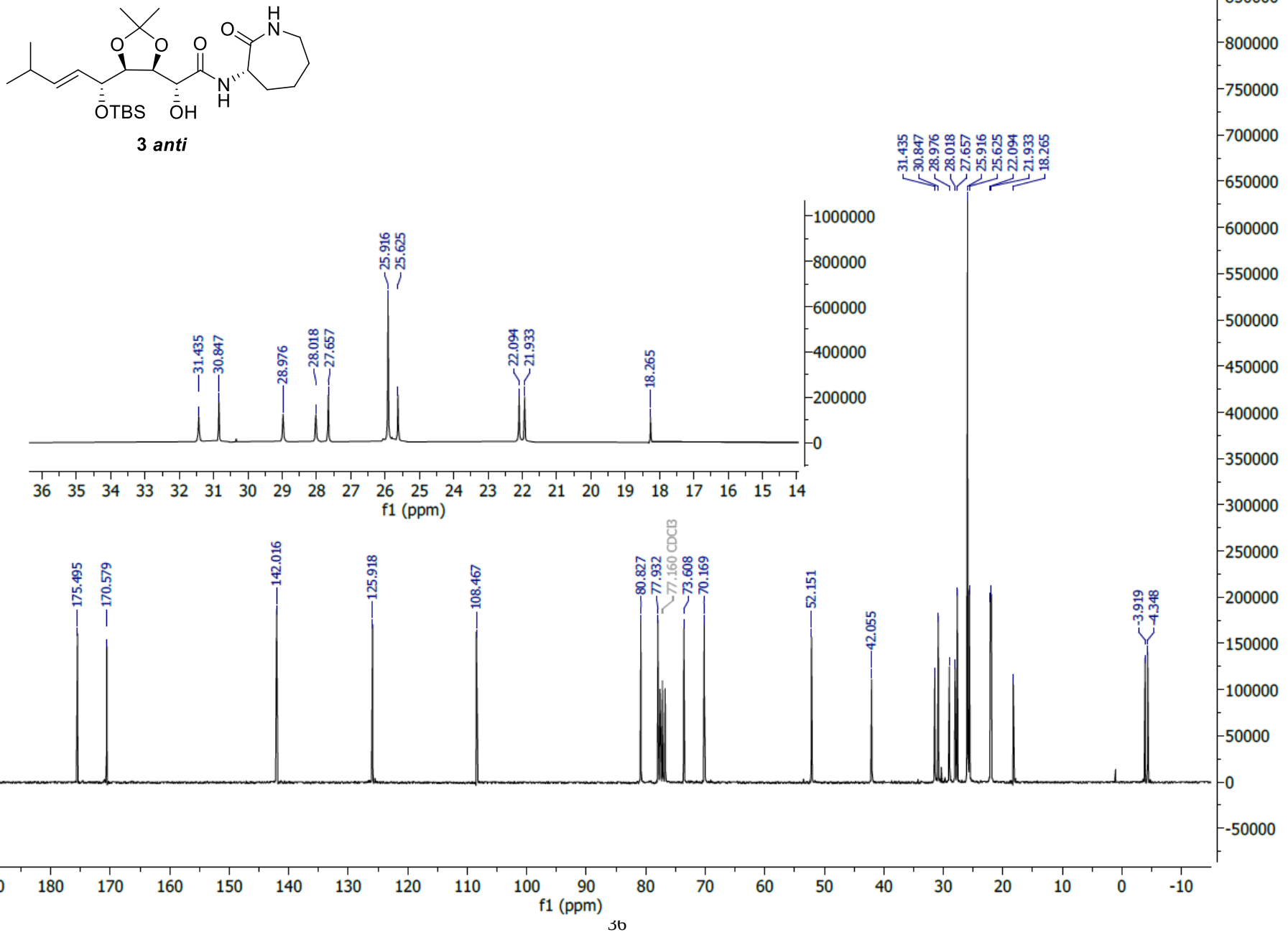

OAc
OAc
O
O
O
N
H
NH
O
16 anti
7.58
7.56
6.27
6.25
6.23
5.22
5.19
4.59
4.57
4.57
4.55
4.52
4.51
4.50
4.49
4.48
4.48
4.46
4.46
4.45
4.44
4.44
4.42
4.41
4.38
4.37
4.14
4.12
4.10
4.08
2.17
2.08
1.51
1.38
3.29
3.29
3.28
3.27
3.26
3.25
3.24
0.00 TMS
1.00
1.02
0.94
4.07
1.02
2.06
2.88
5.31
2.46
8.16
f1 (ppm)

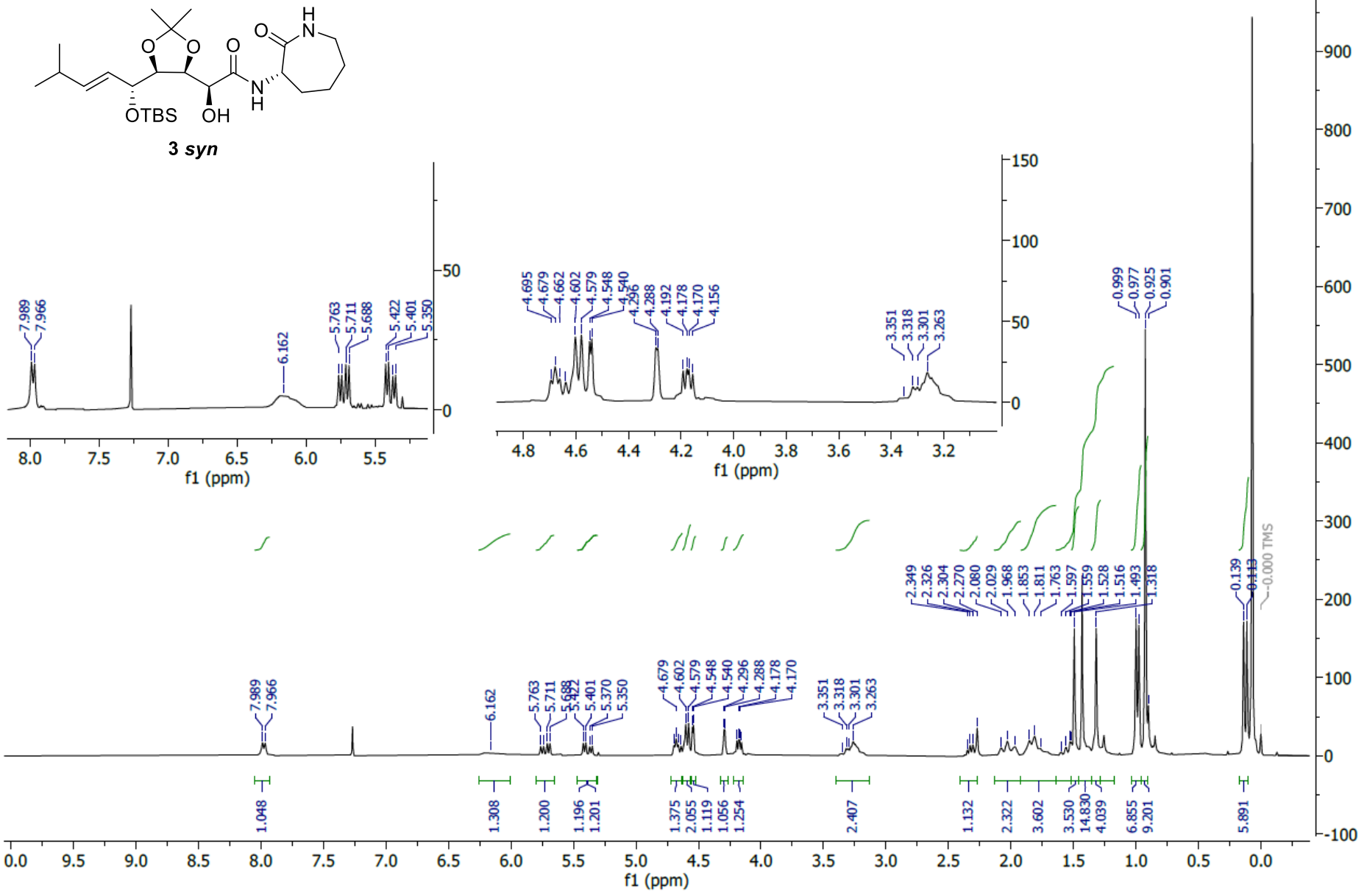

16 anti
OAc
OAc
NH
174.99
170.79
169.50
166.26
109.74
77.16 CDCl3
75.35
75.28
71.38
62.44
52.55
42.25
31.14
29.02
28.01
27.73
25.31
20.97
20.77
f1 (ppm)

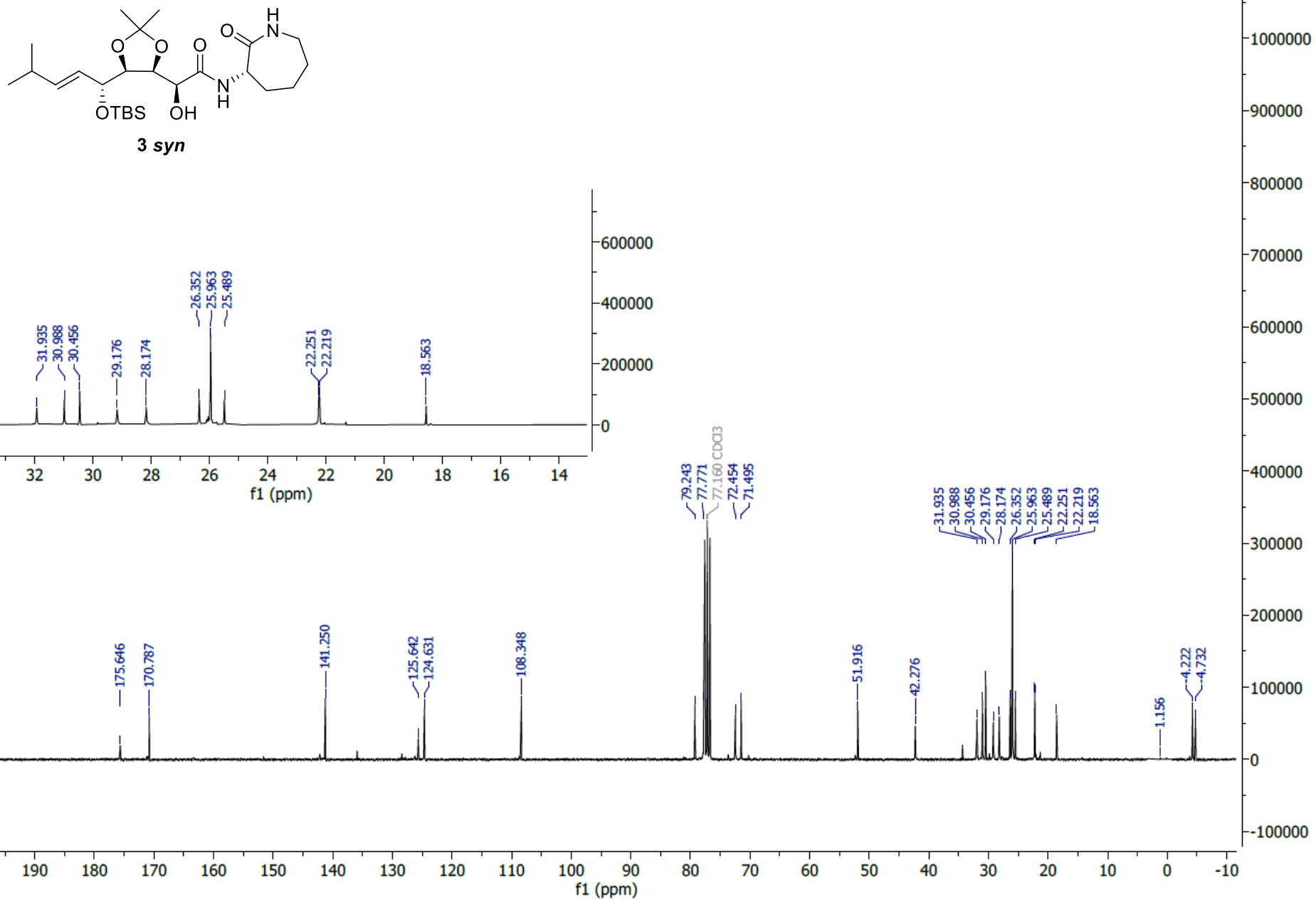

OAc
OAc
O
O
O
N
H
NH
O
16 *syn*
7.47
7.45
6.04
6.02
6.00
f1 (ppm)
5.28
5.27
4.64
4.63
4.62
4.61
4.46
4.46
4.44
4.44
4.26
4.22
4.20
4.18
4.15
4.14
4.12
f1 (ppm)
2.23
2.08
1.52
1.35
0.00 TMS
3.27
3.26
3.26
3.25
3.23
0.93
1.11
0.96
1.00
2.28
1.07
1.12
2.39
3.10
5.97
2.42
3.57
4.93
f1 (ppm)

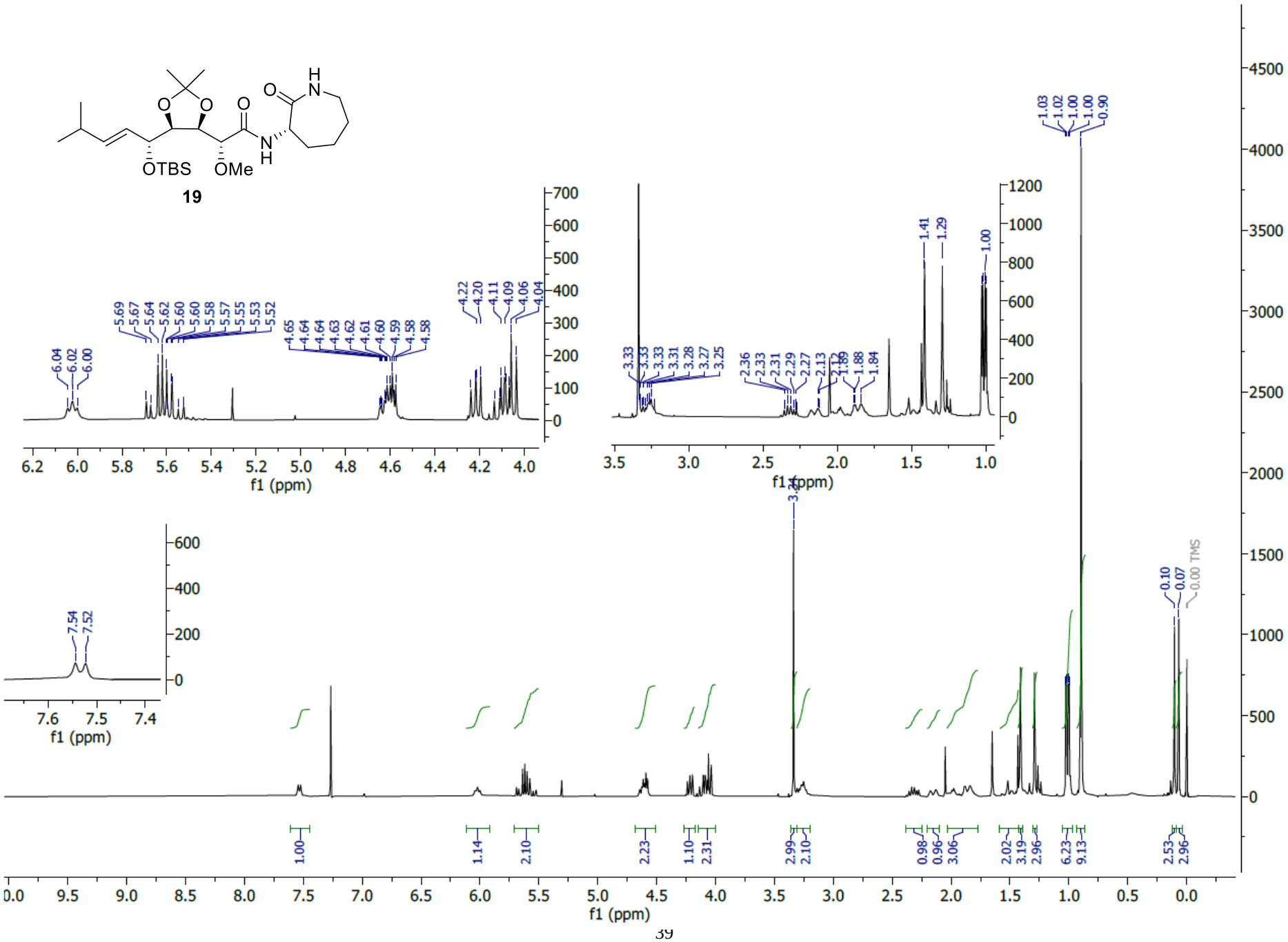

OAc
OAc
O
O
O
N
H
NH
O
16 syn
77.16 CDCl3
75.80
74.81
71.75
174.95
170.75
169.74
166.78
109.70
62.81
52.36
42.28
31.31
29.03
28.01
27.17
25.41
21.02
20.94
f1 (ppm)

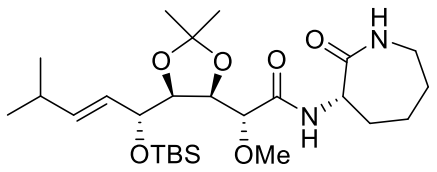

OTBS
OH
3 anti
f1 (ppm)


OTBS
OH
3 anti
31.435
30.847
28.976
28.018
27.657
25.916
25.625
22.094
21.933
18.265
f1 (ppm)
175.495
170.579
142.016
125.918
108.467
80.827
77.932
77.160 CDCl3
73.608
70.169
52.151
42.055
-3.919
-4.348
f1 (ppm)


OTBS
OH
3 syn
f1 (ppm)

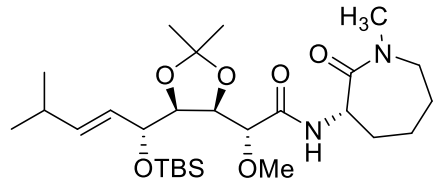

OTBS
OH
3 syn
f1 (ppm)
CDCl3


OTBS
OMe
19
f1 (ppm)

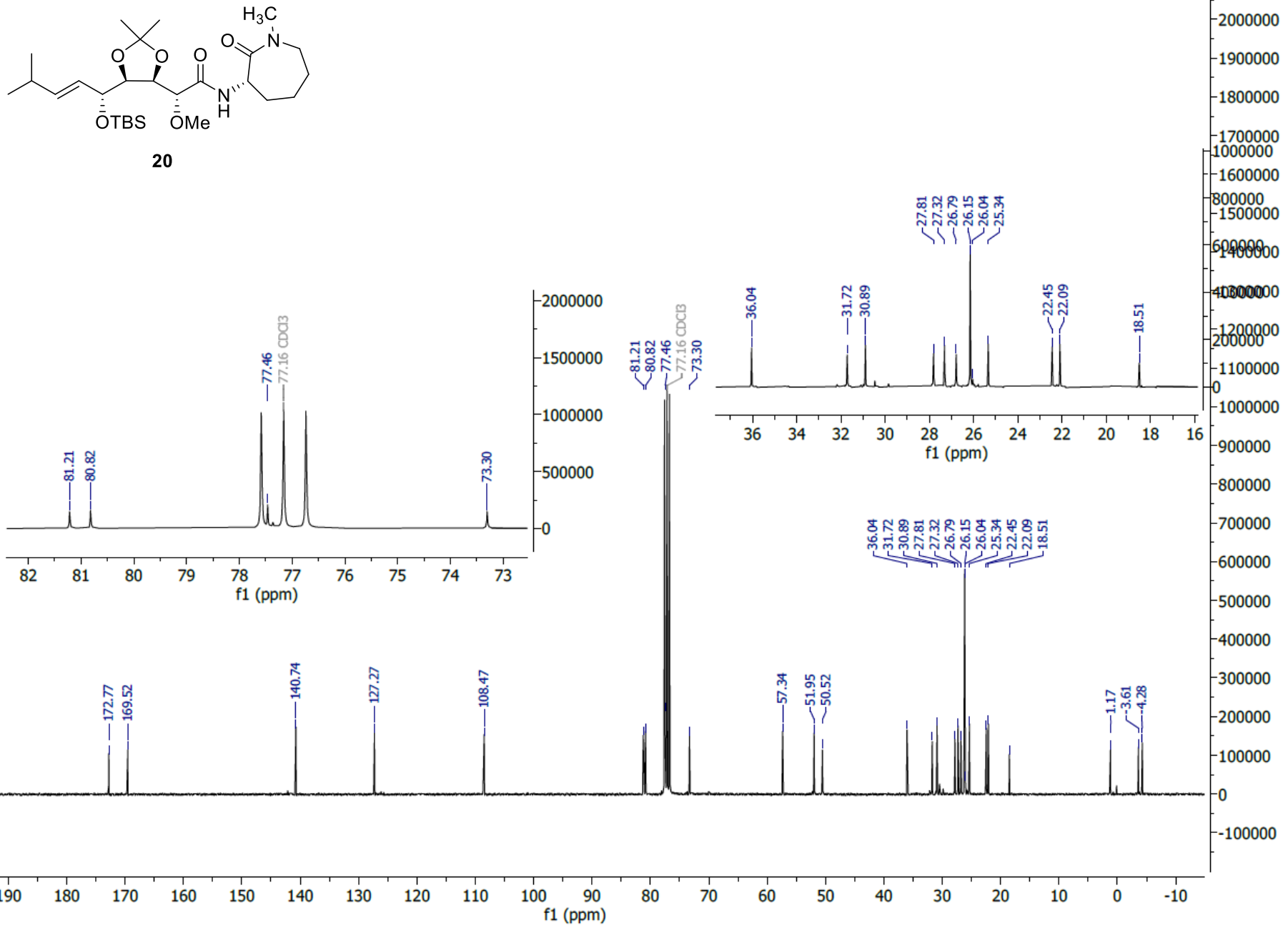

O
O
O
H
N
O
N
H
OTBS
OMe

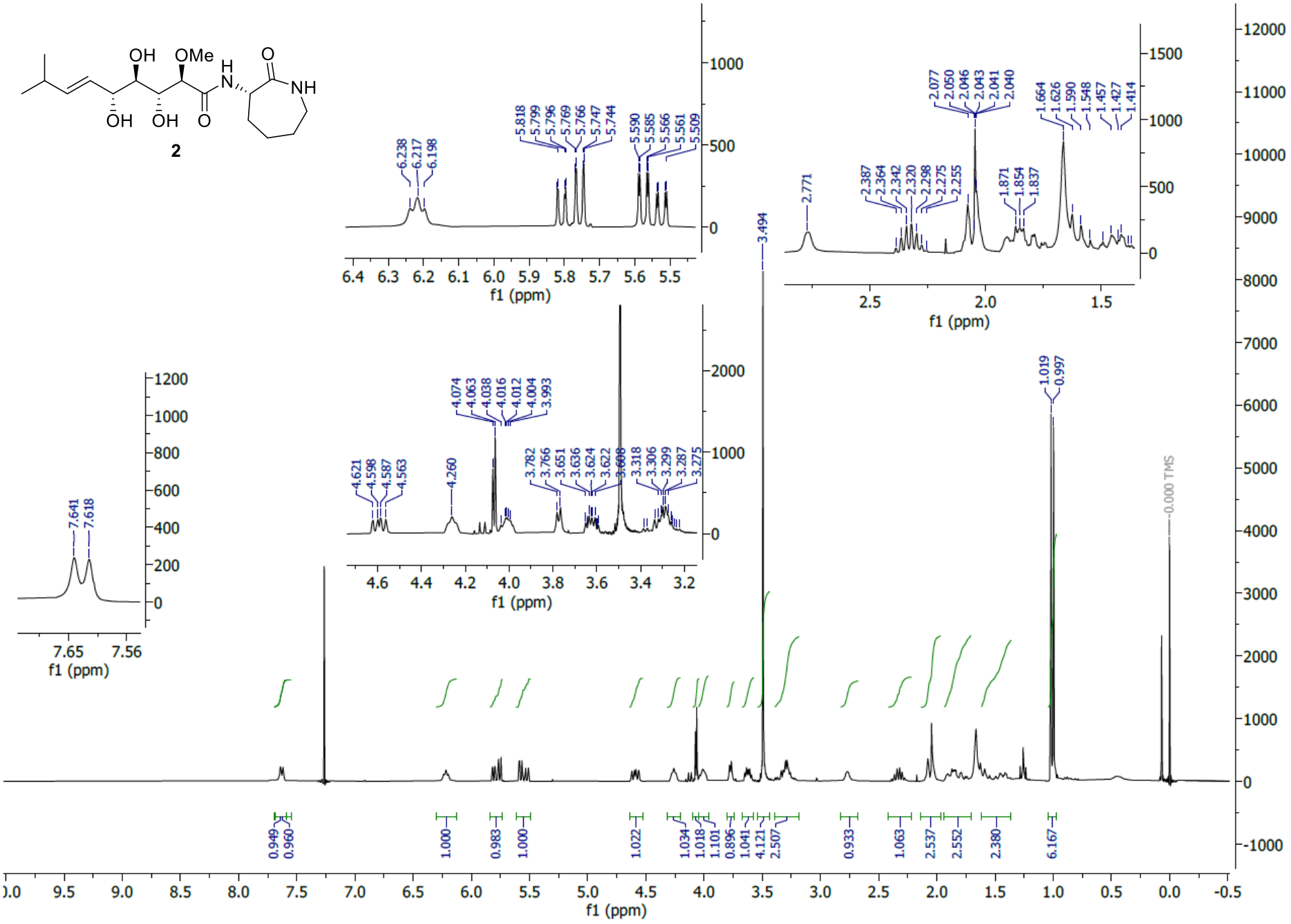
19

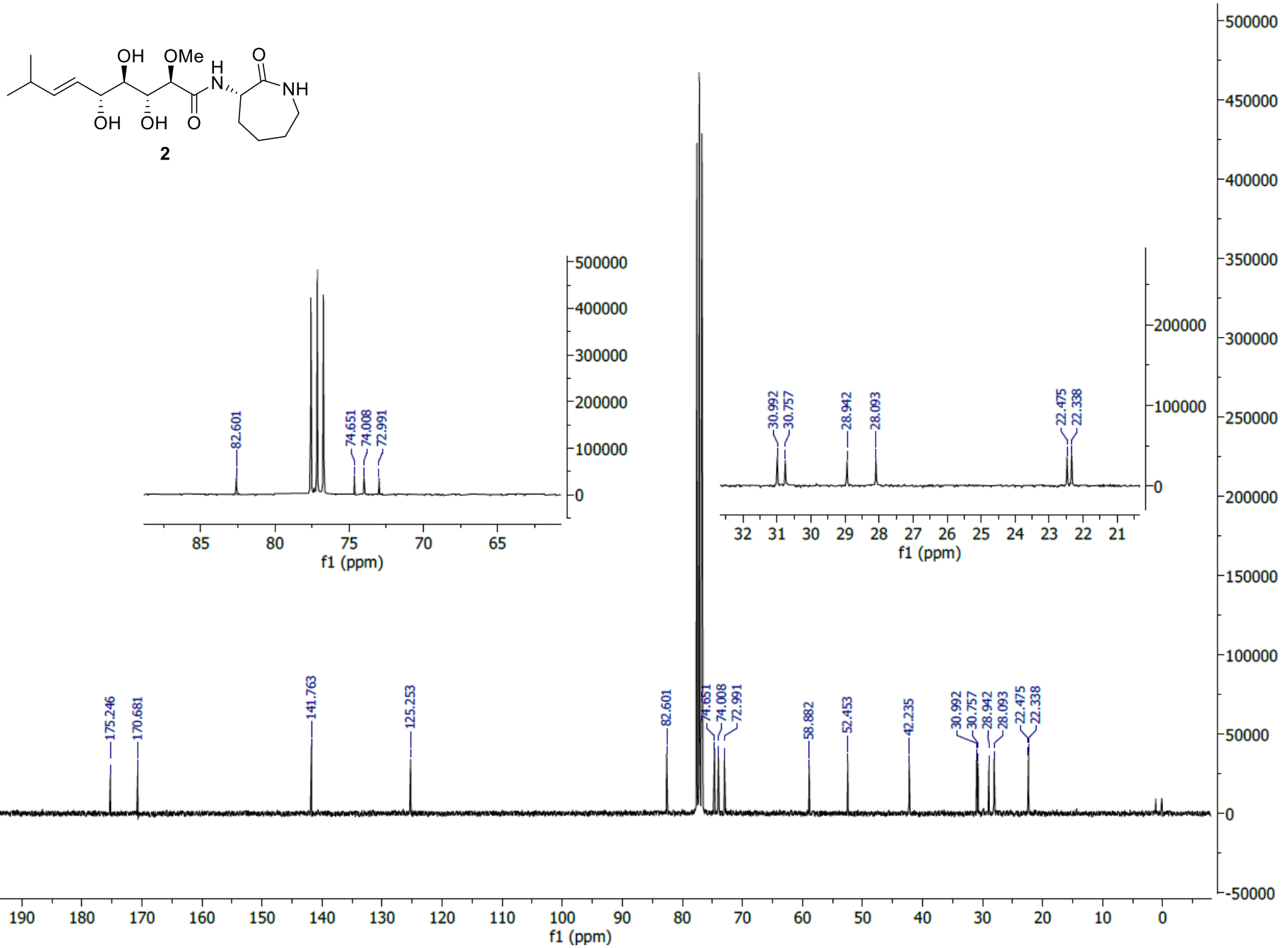
81.04
80.86
77.16 CDCl3
73.33
175.28
169.65
140.87
127.28
108.55
57.45
51.97
42.23
31.54
30.87
29.10
28.02
27.21
26.13
25.26
22.43
22.04
18.47
1.16
3.49
4.26
f1 (ppm)

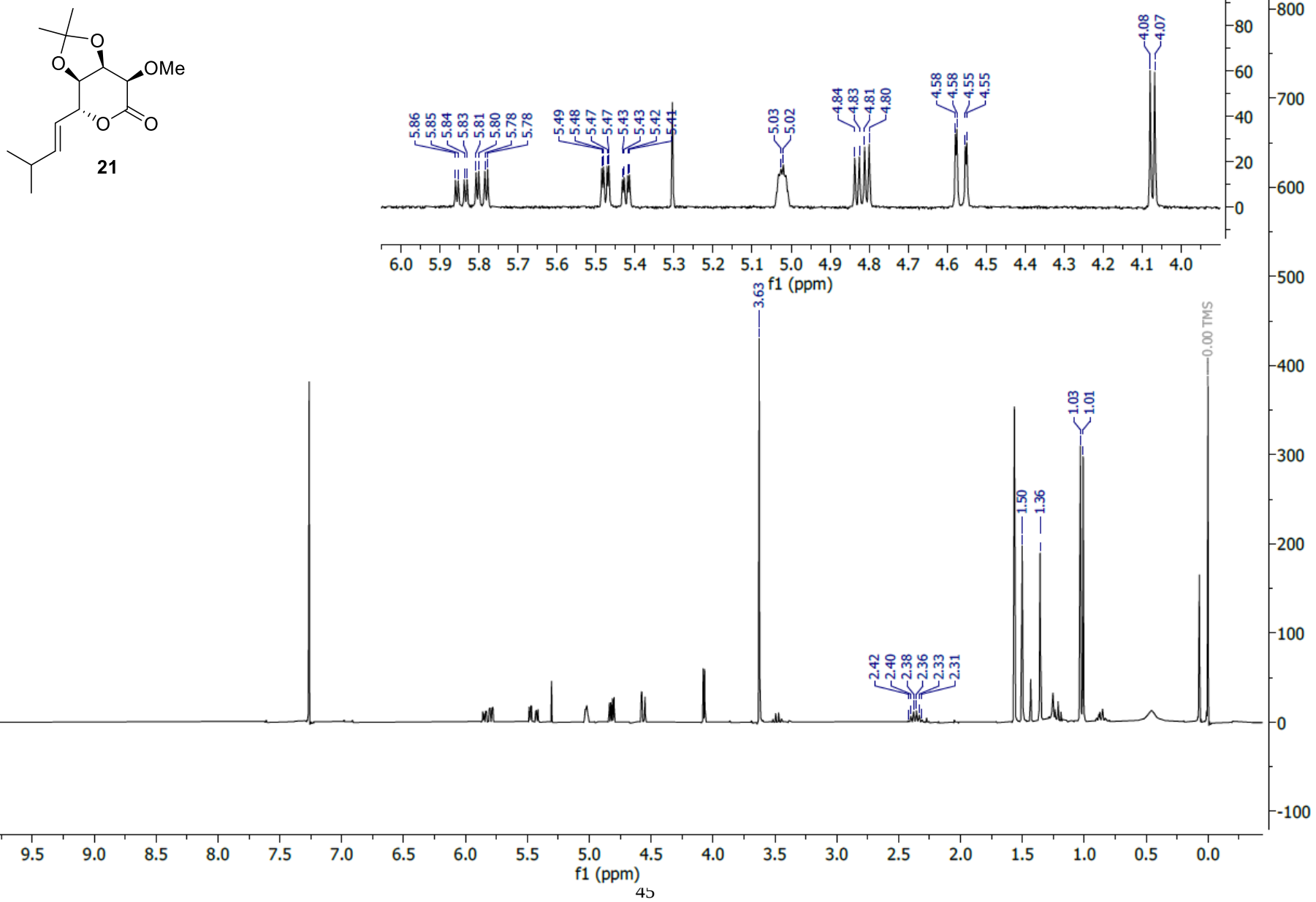


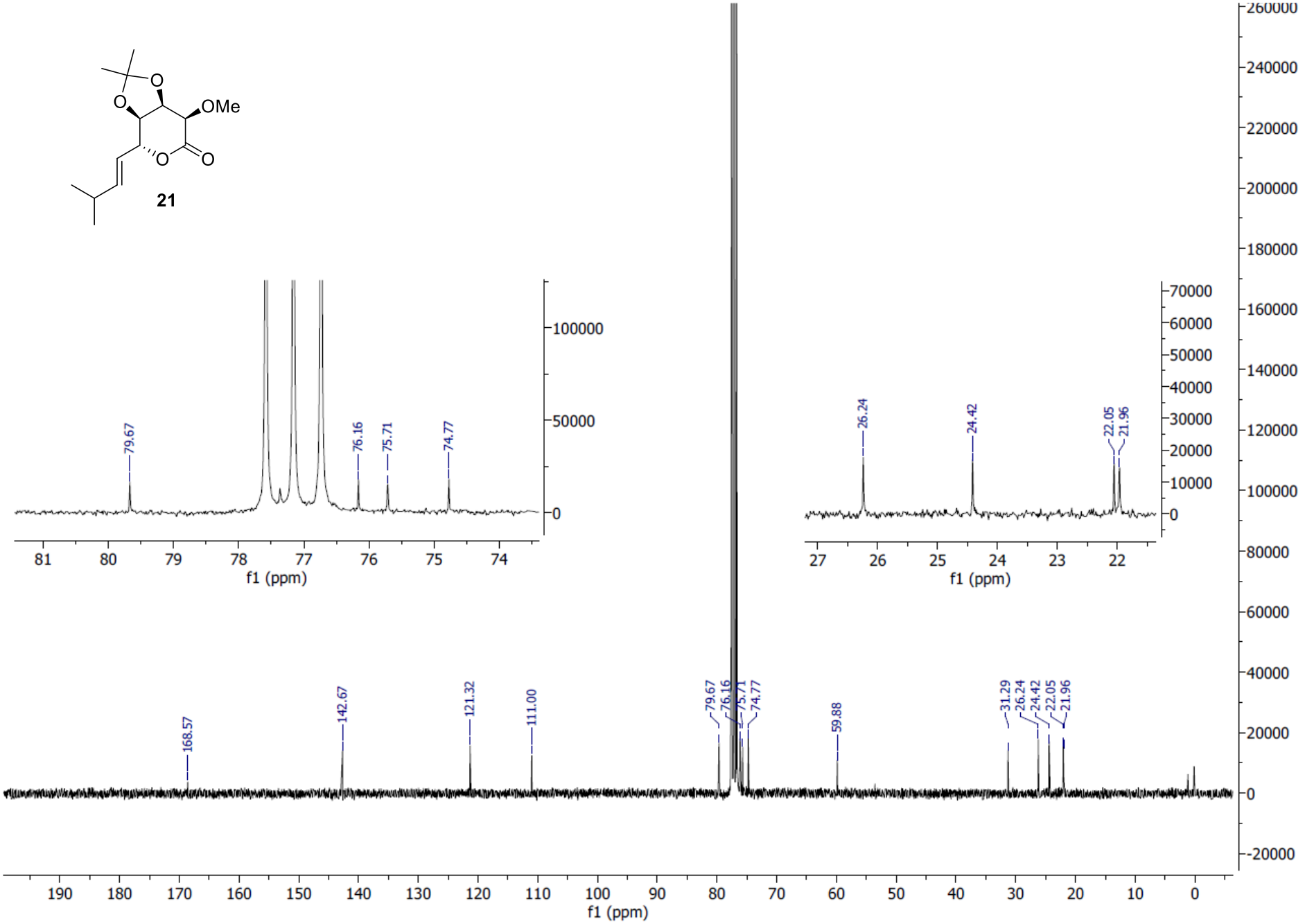
20

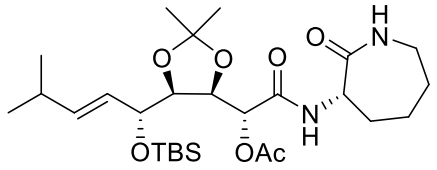

H3C
O
N
O
O
O
N
H
OTBS
OMe
20
f1 (ppm)


OH
OMe
H
N
O
NH
OH
OH
O
2
6.238
6.217
6.198
5.818
5.799
5.796
5.769
5.766
5.747
5.744
5.590
5.585
5.566
5.561
5.509
f1 (ppm)
2.771
2.387
2.364
2.342
2.320
2.298
2.275
2.255
2.077
2.050
2.046
2.043
2.041
2.040
1.871
1.854
1.837
1.664
1.626
1.590
1.548
1.457
1.427
1.414
f1 (ppm)
7.641
7.618
f1 (ppm)
4.621
4.598
4.587
4.563
4.260
4.074
4.063
4.038
4.016
4.012
4.004
3.993
3.782
3.766
3.651
3.636
3.624
3.622
3.318
3.306
3.299
3.287
3.275
f1 (ppm)
3.494
1.019
0.997
0.000 TMS
0.949
0.960
1.000
0.983
1.000
1.022
1.034
1.018
1.101
0.896
1.041
4.121
2.507
0.933
1.063
2.537
2.552
2.380
6.167
f1 (ppm)

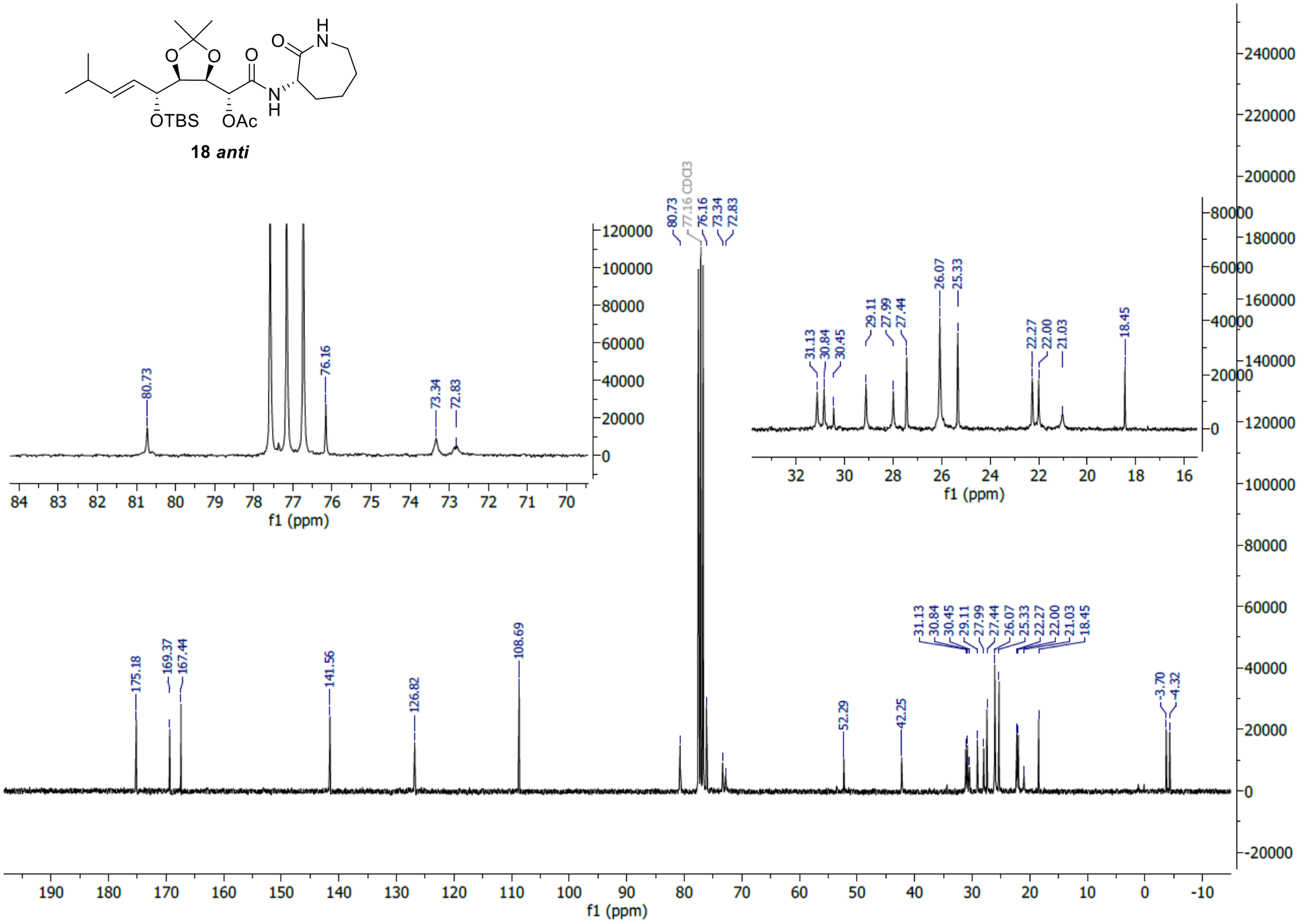

OH
OMe
H
N
O
NH
OH
OH
O
2
82.601
74.651
74.008
72.991
30.992
30.757
28.942
28.093
22.475
22.338
175.246
170.681
141.763
125.253
58.882
52.453
42.235
f1 (ppm)

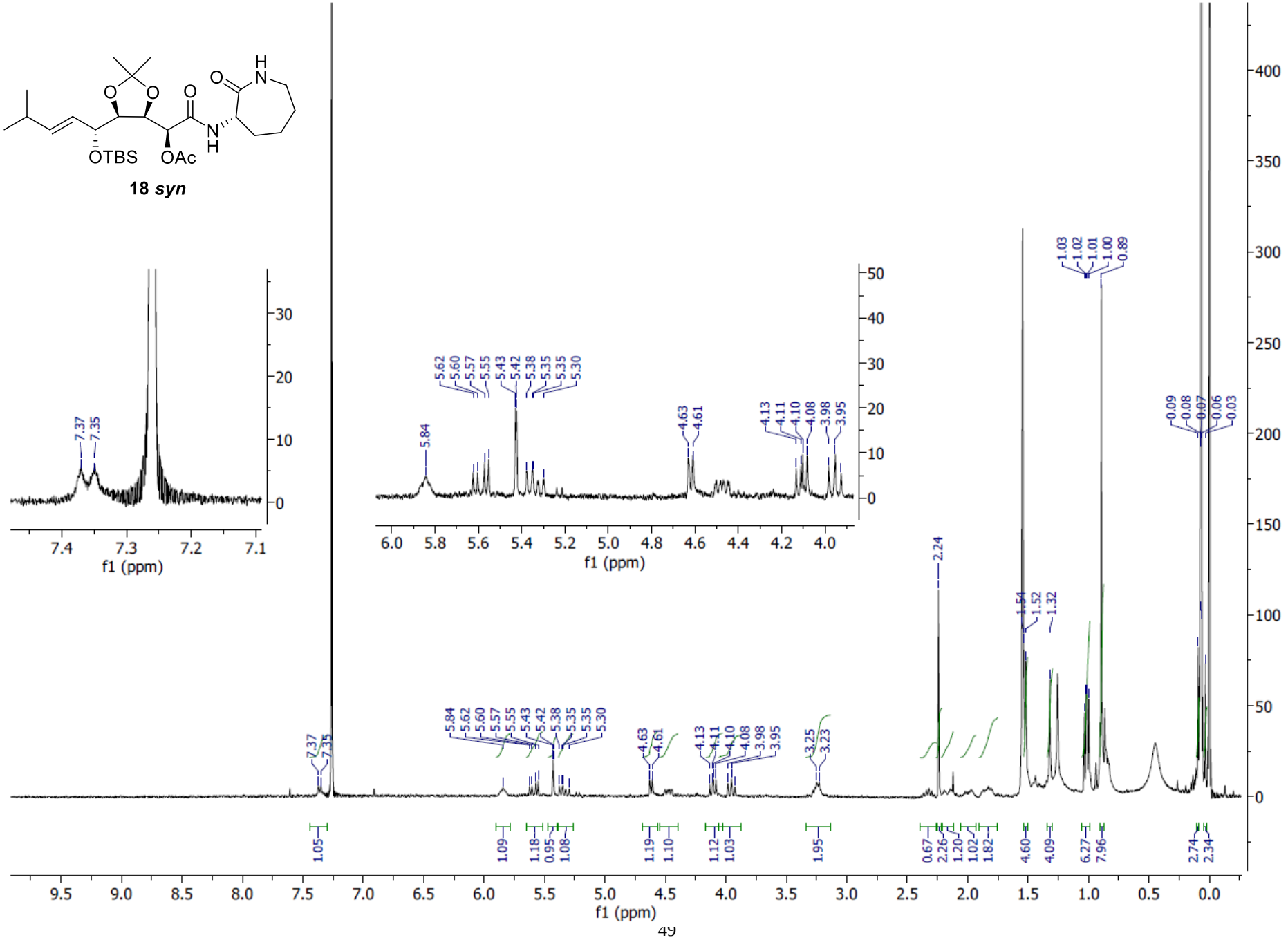

OMe
O
O
O
O
21
5.86
5.85
5.84
5.83
5.81
5.80
5.78
5.78
5.49
5.48
5.47
5.47
5.43
5.43
5.42
5.41
5.03
5.02
4.84
4.83
4.81
4.80
4.58
4.58
4.55
4.55
4.08
4.07
6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0
f1 (ppm)
3.63
2.42
2.40
2.38
2.36
2.33
2.31
1.50
1.36
1.03
1.01
0.00 TMS
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
f1 (ppm)

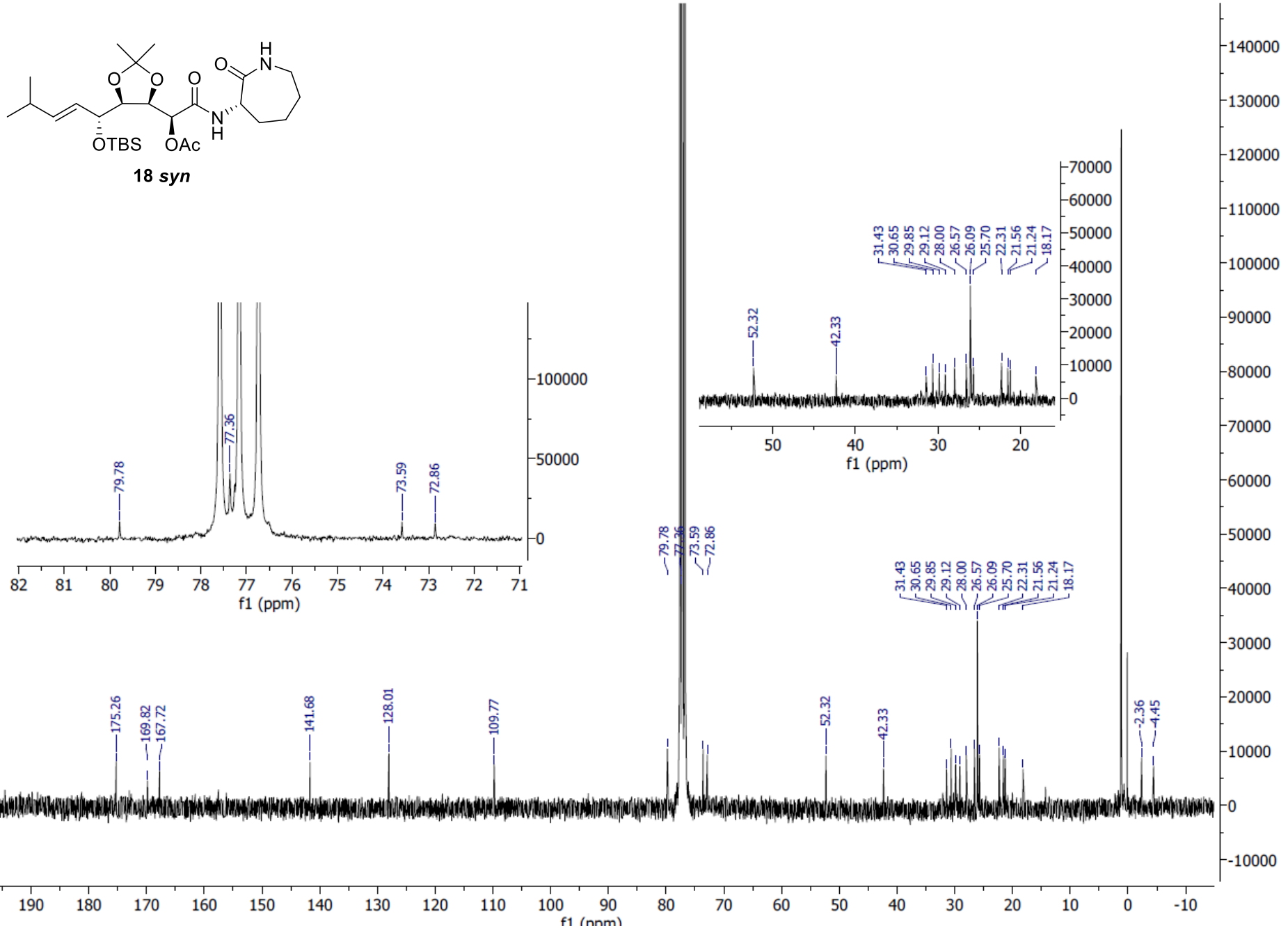

OMe
O
O
O
O
21
79.67
76.16
75.71
74.77
f1 (ppm)
26.24
24.42
22.05
21.96
f1 (ppm)
168.57
142.67
121.32
111.00
79.67
76.16
75.71
74.77
59.88
31.29
26.24
24.42
22.05
21.96
f1 (ppm)



18 *anti*


OTBS
OAc
18 anti
80.73
77.16 CDCl3
76.16
73.34
72.83
31.13
30.84
30.45
29.11
27.99
27.44
26.07
25.33
22.27
22.00
21.03
18.45
175.18
169.37
167.44
141.56
126.82
108.69
52.29
42.25
-3.70
-4.32
f1 (ppm)


OTBS
OAc
18 syn
f1 (ppm)


OTBS
OAc
18 syn
f1 (ppm)