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

Directed Nucleophilic Addition of Phenoxides to Cyclopropenes

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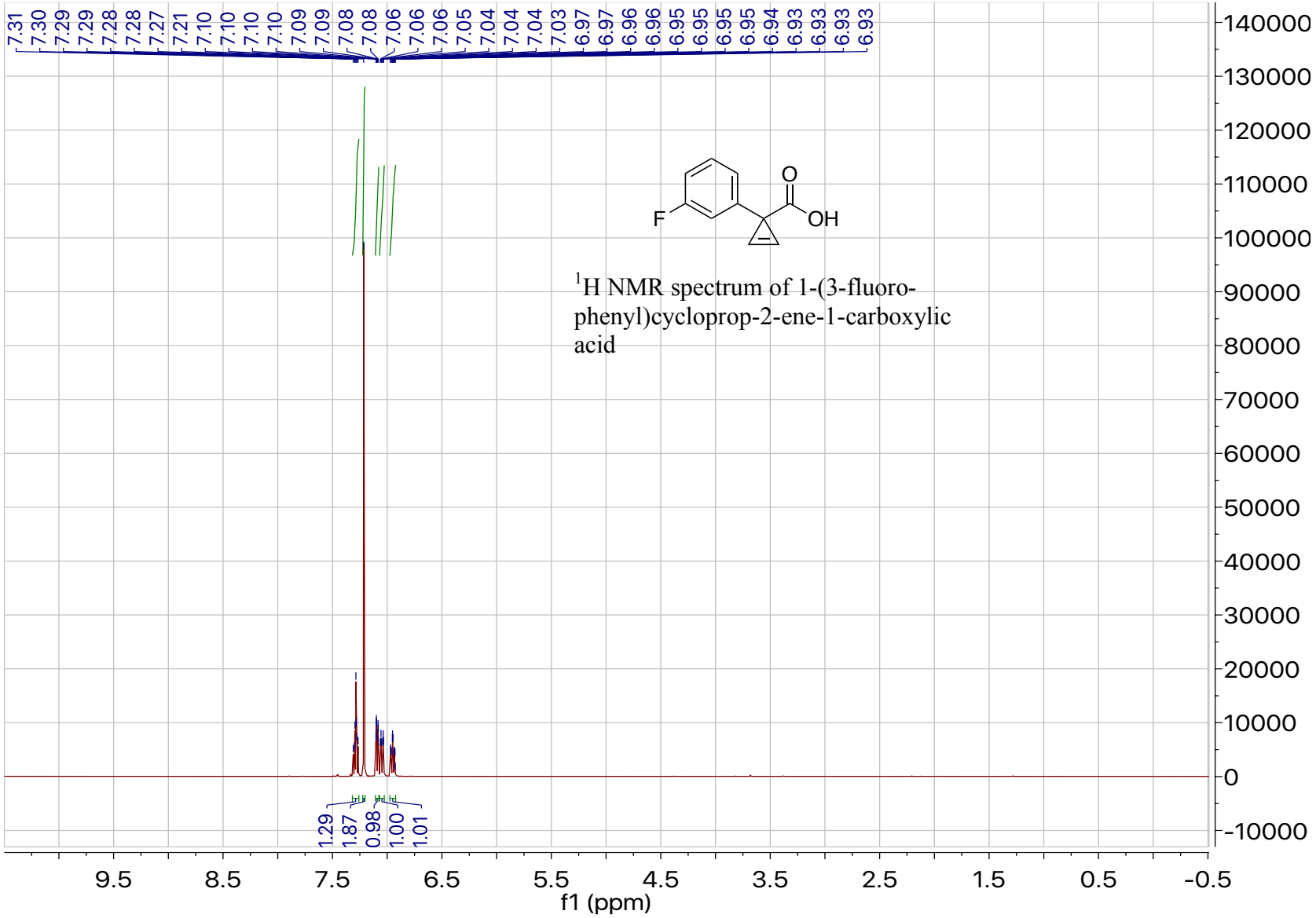
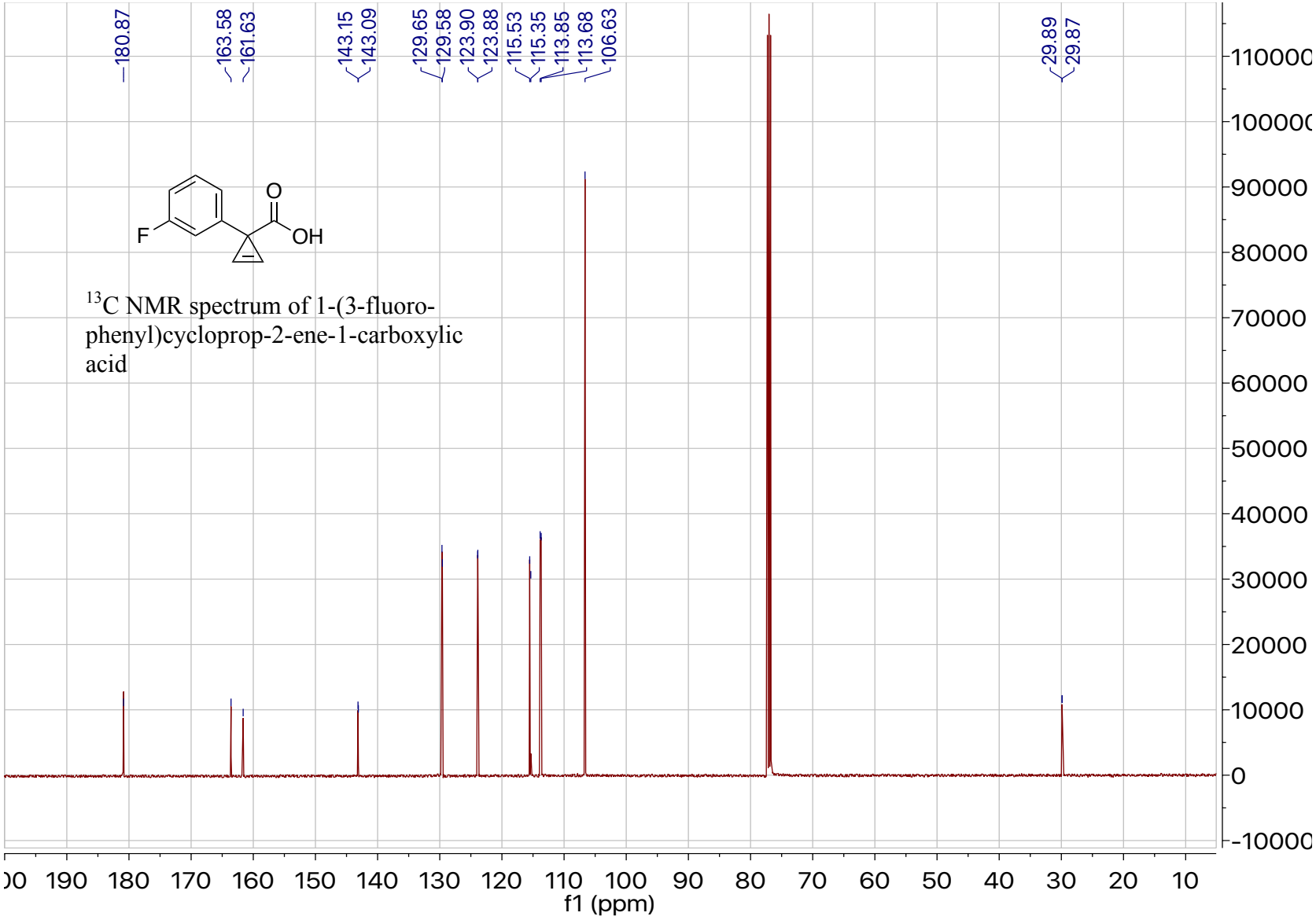
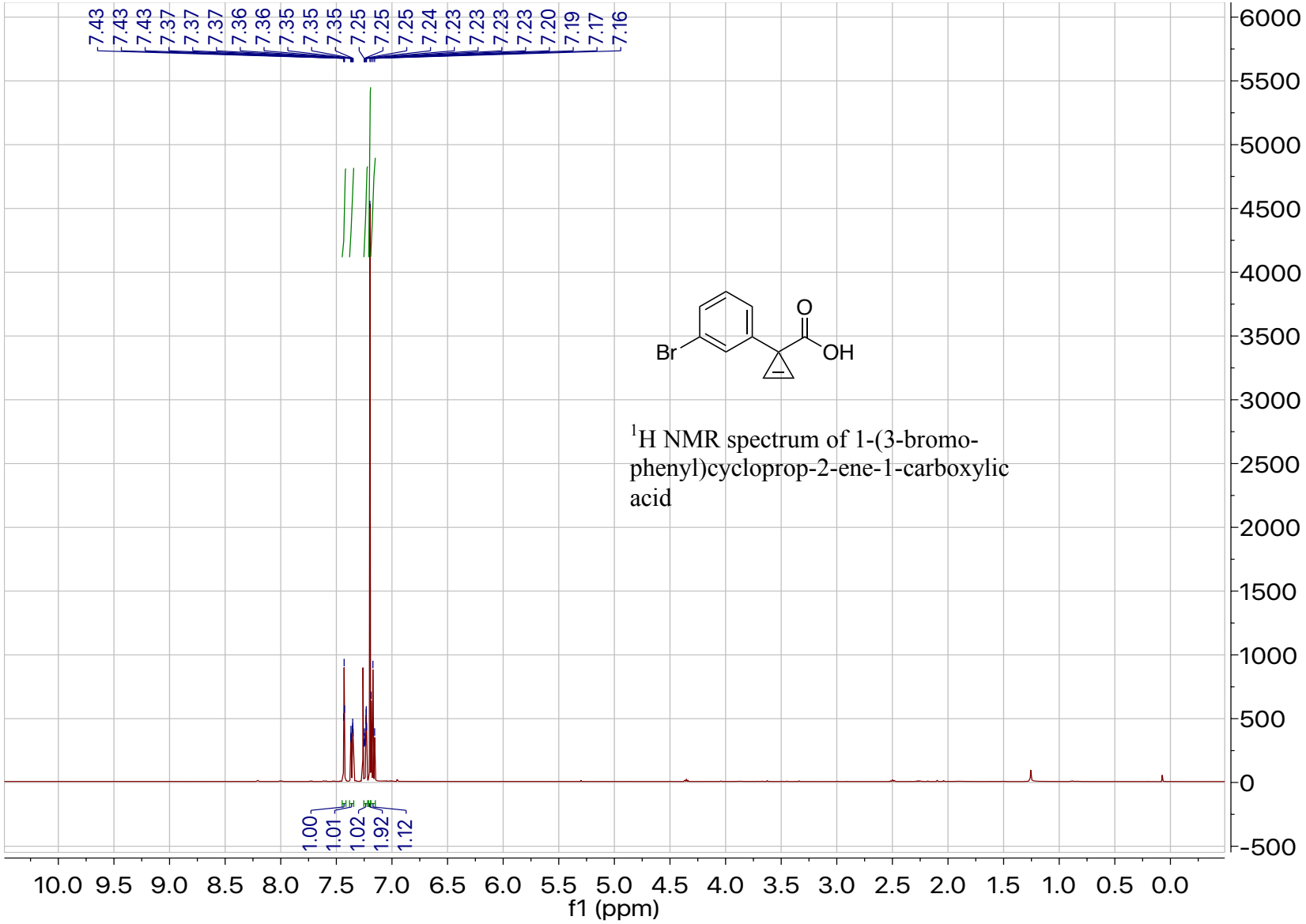
Supporting Information



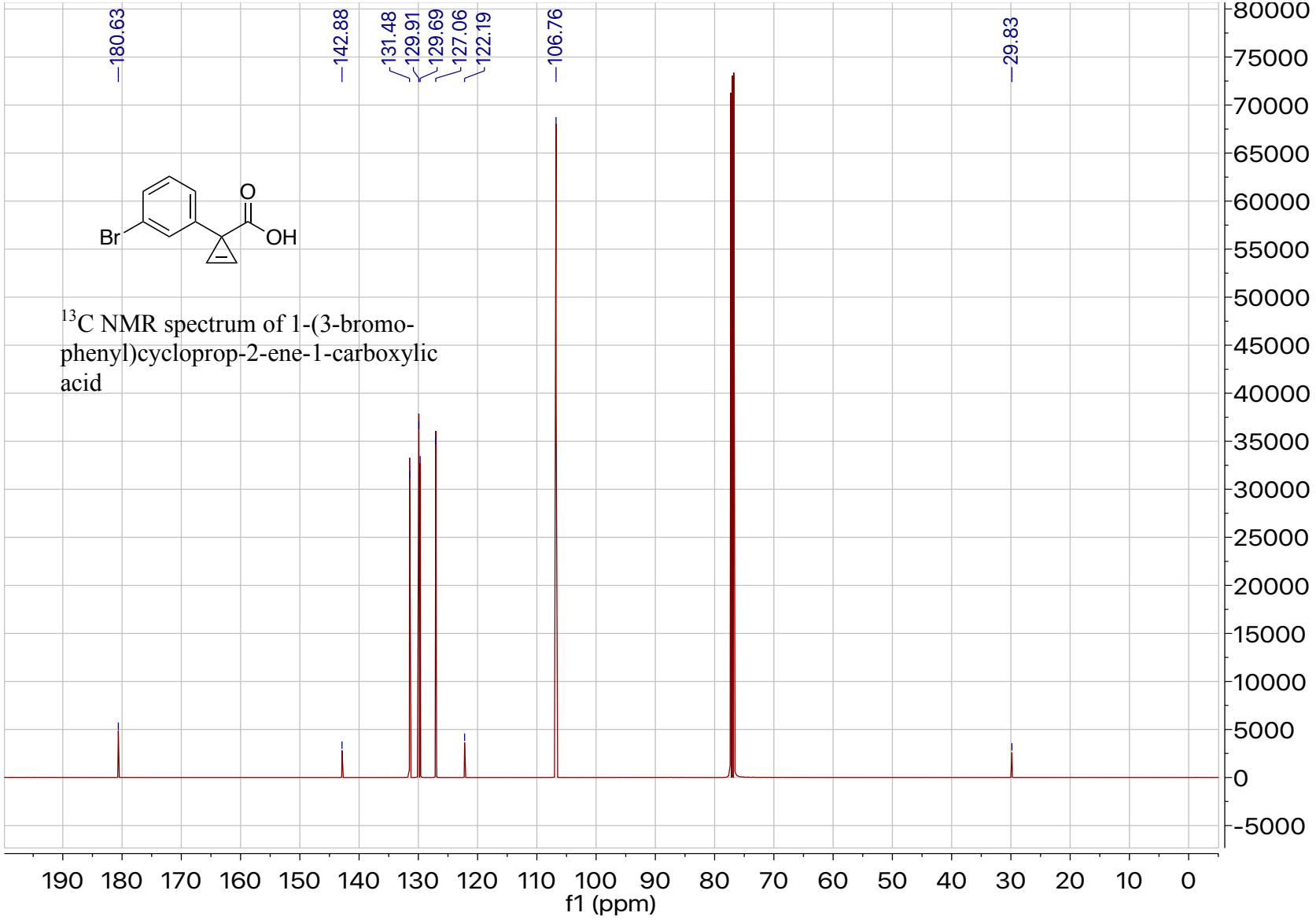
^{1}H NMR spectrum of 1-(3-fluoro-phenyl)cycloprop-2-ene-1-carboxylic acid

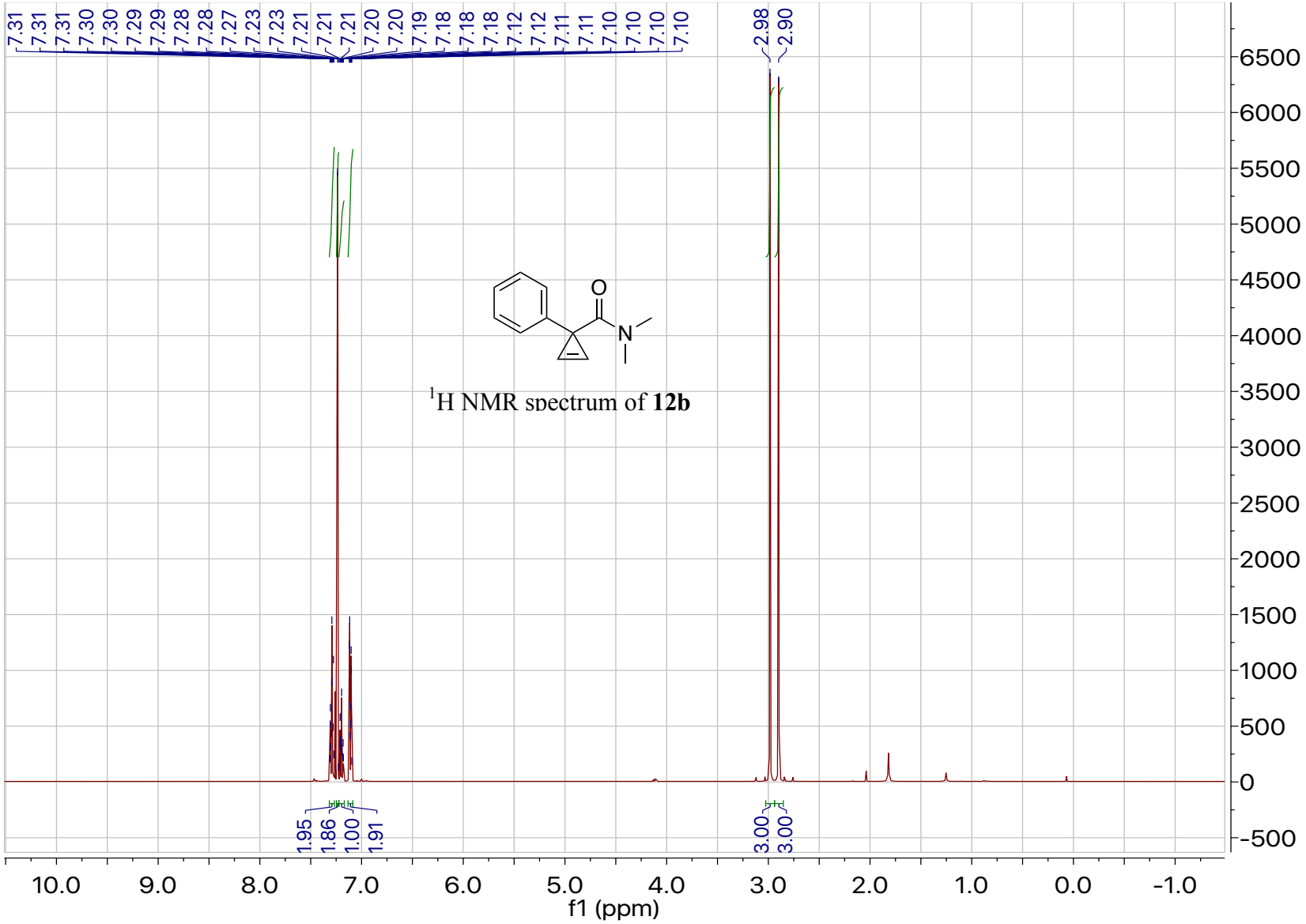


^{13}C NMR spectrum of 1-(3-fluoro-phenyl)cycloprop-2-ene-1-carboxylic acid

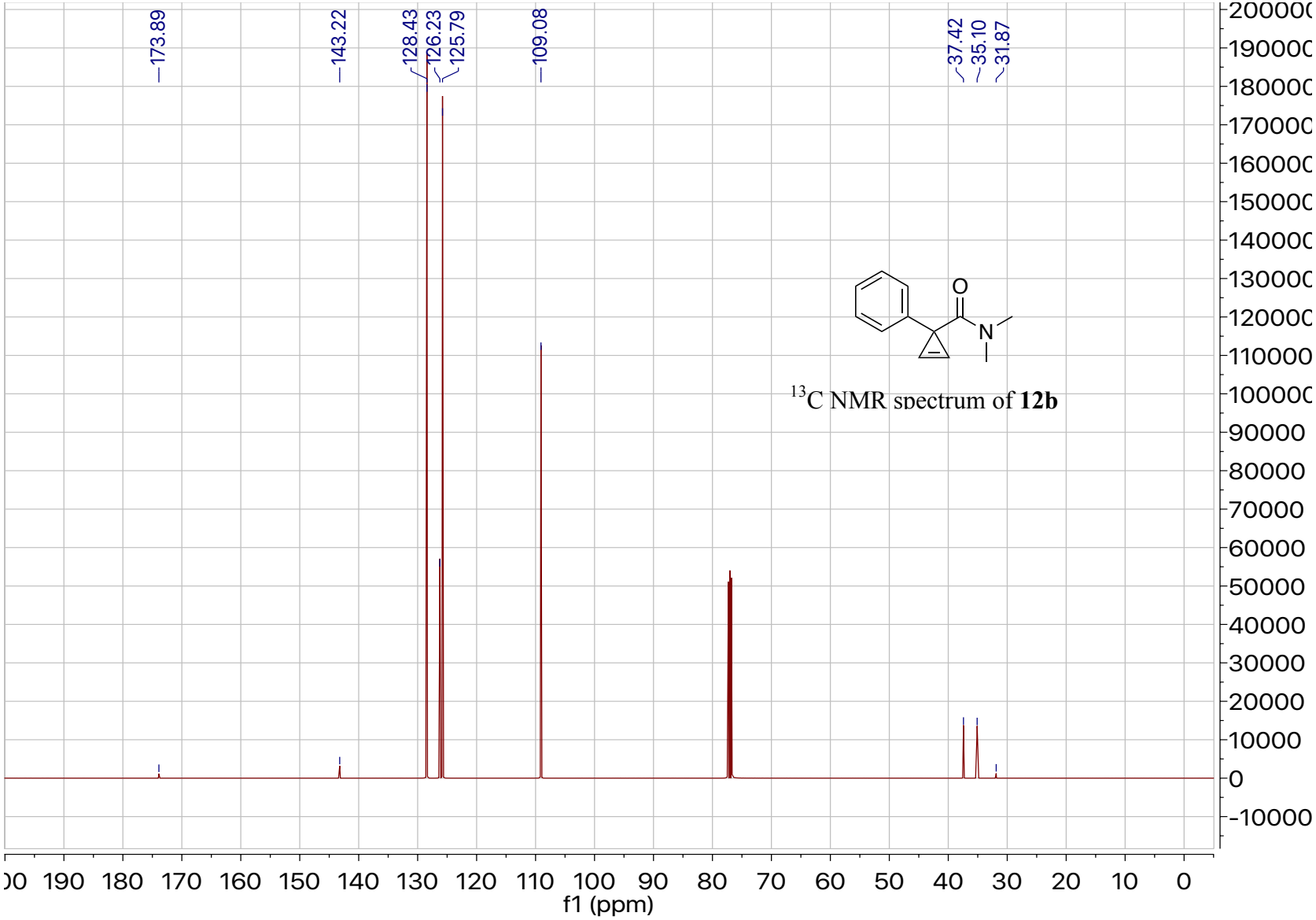


^{1}H NMR spectrum of 1-(3-bromo-phenyl)cycloprop-2-ene-1-carboxylic acid

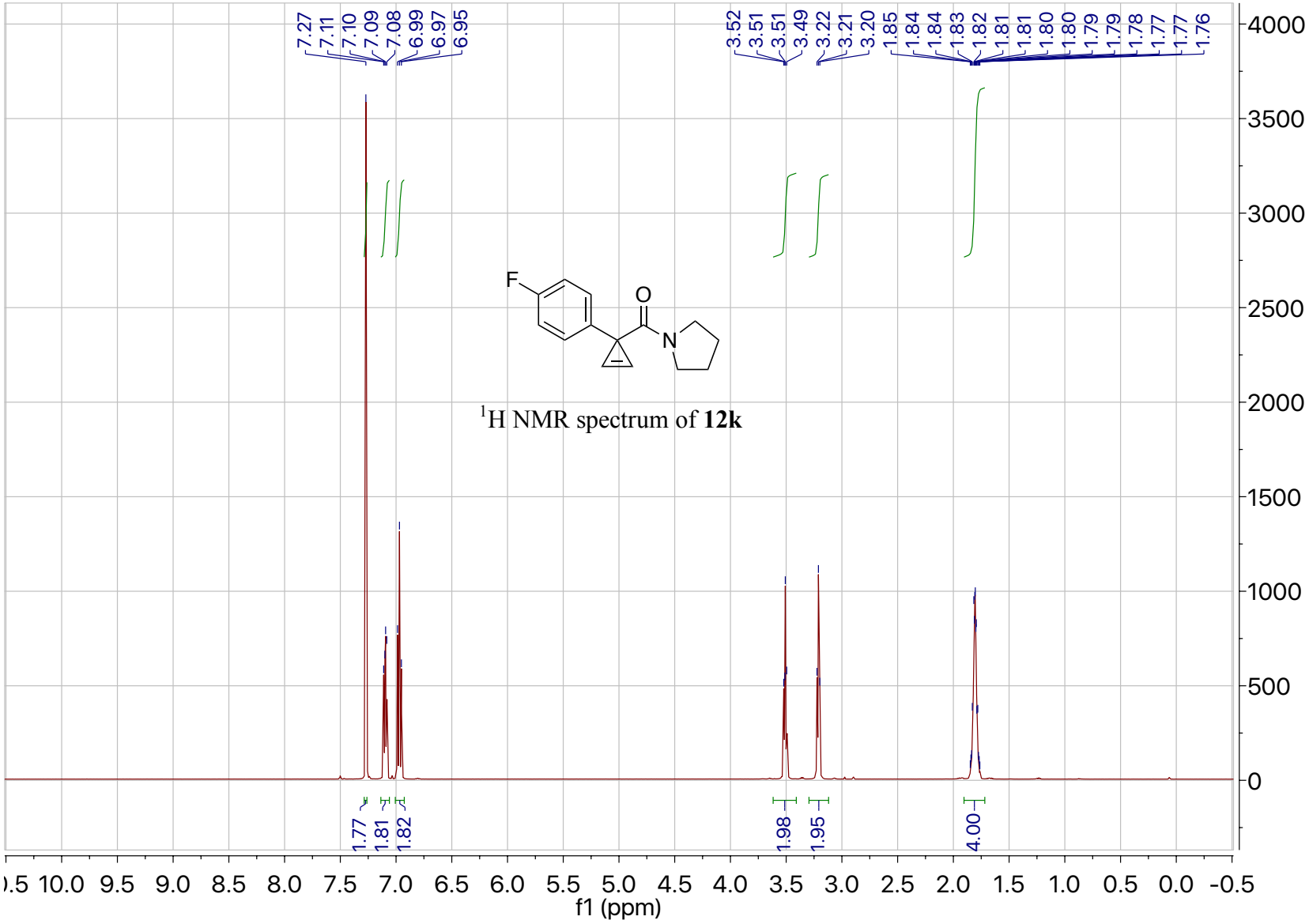

180.63
142.88
131.48
129.91
129.69
127.06
122.19
106.76
29.83
Br
O
OH
13C NMR spectrum of 1-(3-bromo-phenyl)cycloprop-2-ene-1-carboxylic acid
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



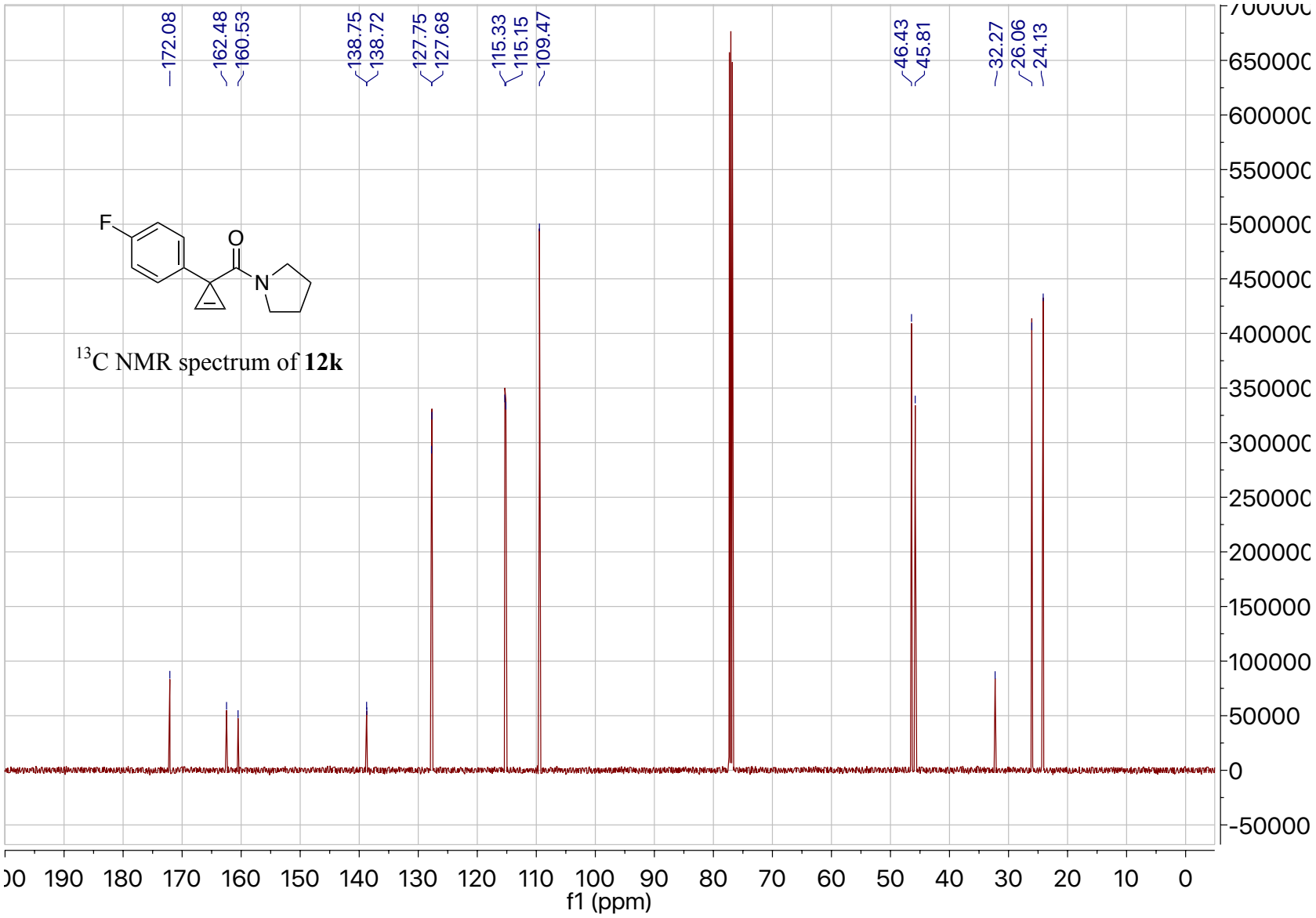
^{1}H NMR spectrum of **12b**



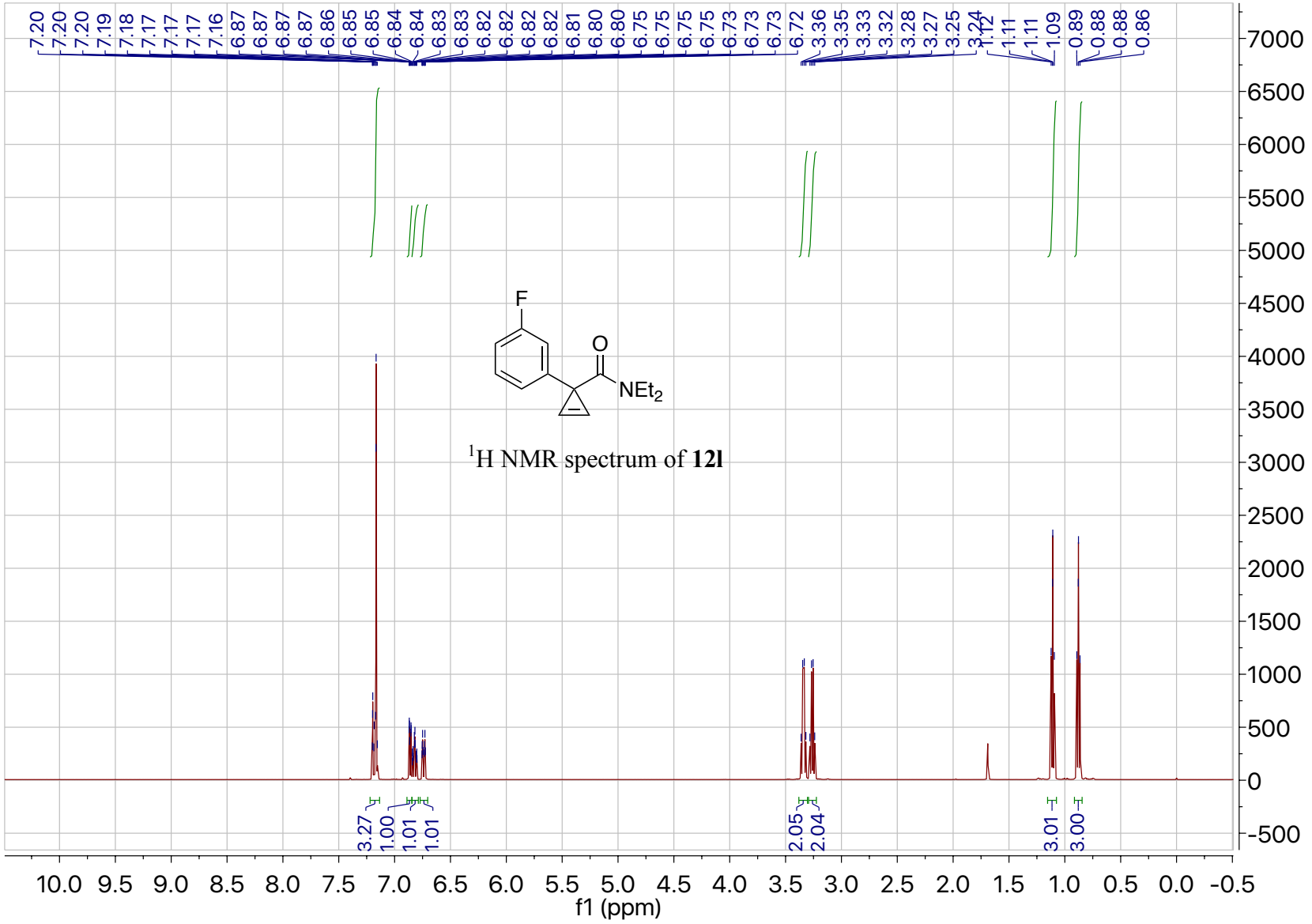
^{13}C NMR spectrum of **12b**



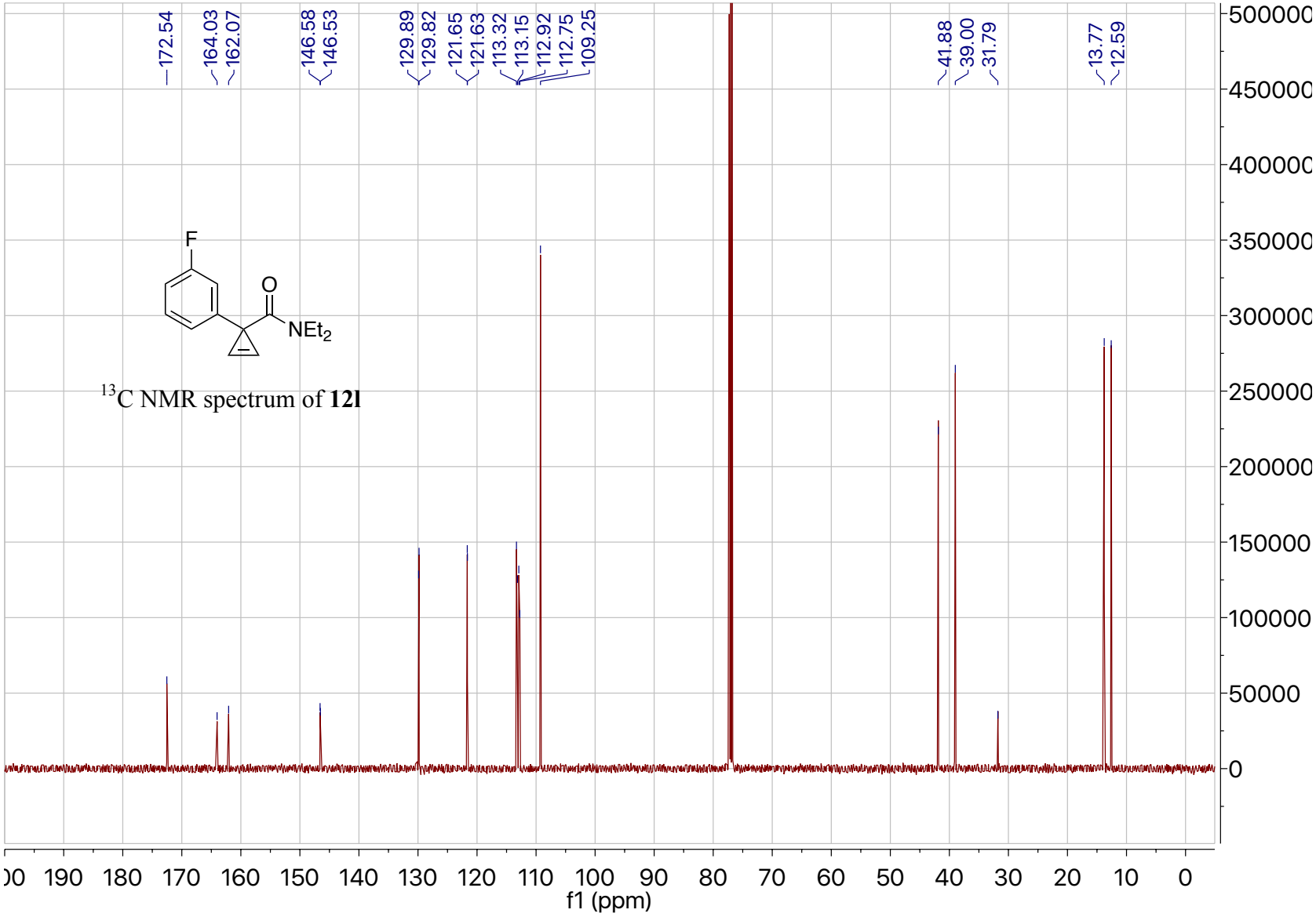
^{1}H NMR spectrum of **12k**



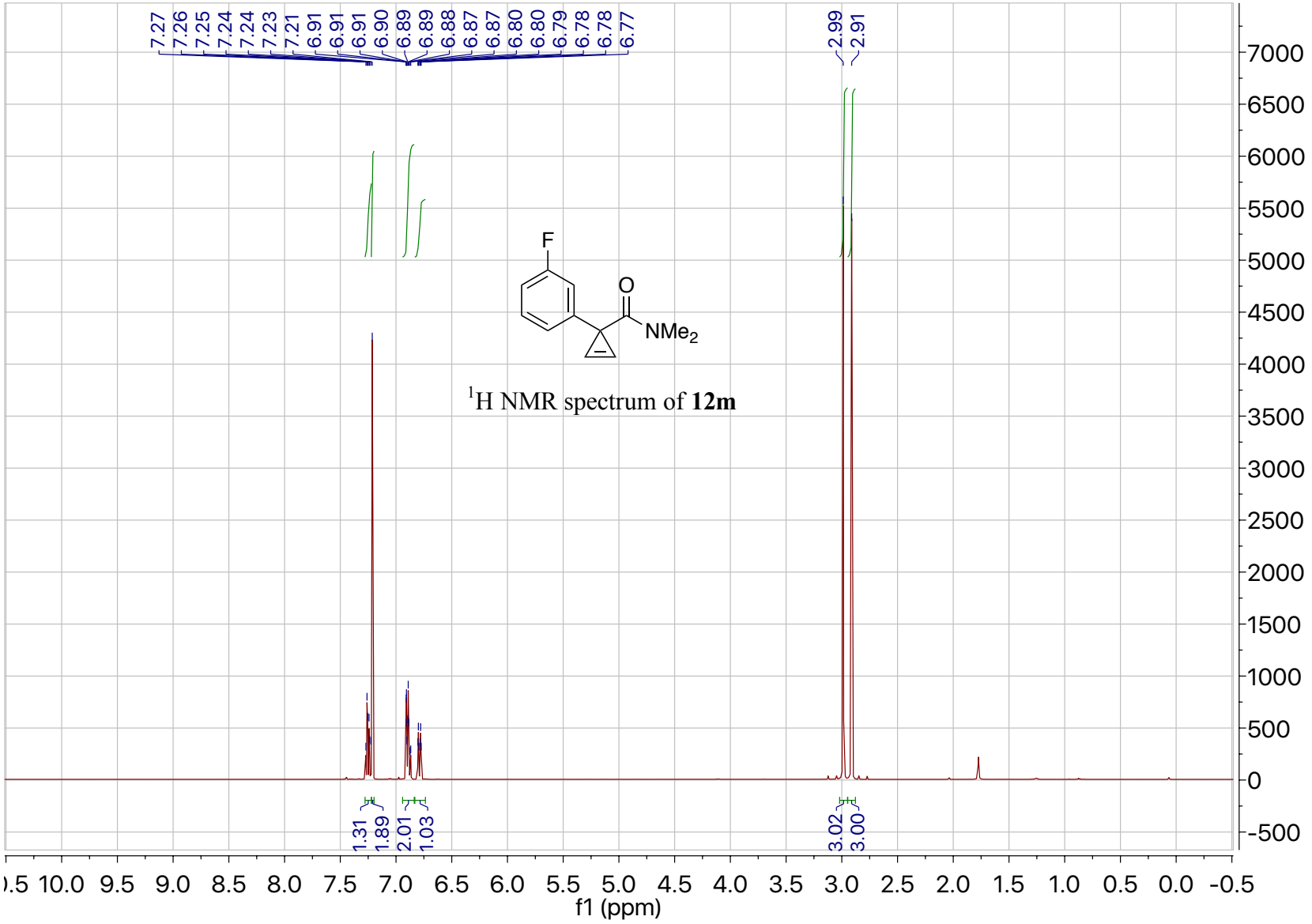
^{13}C NMR spectrum of **12k**



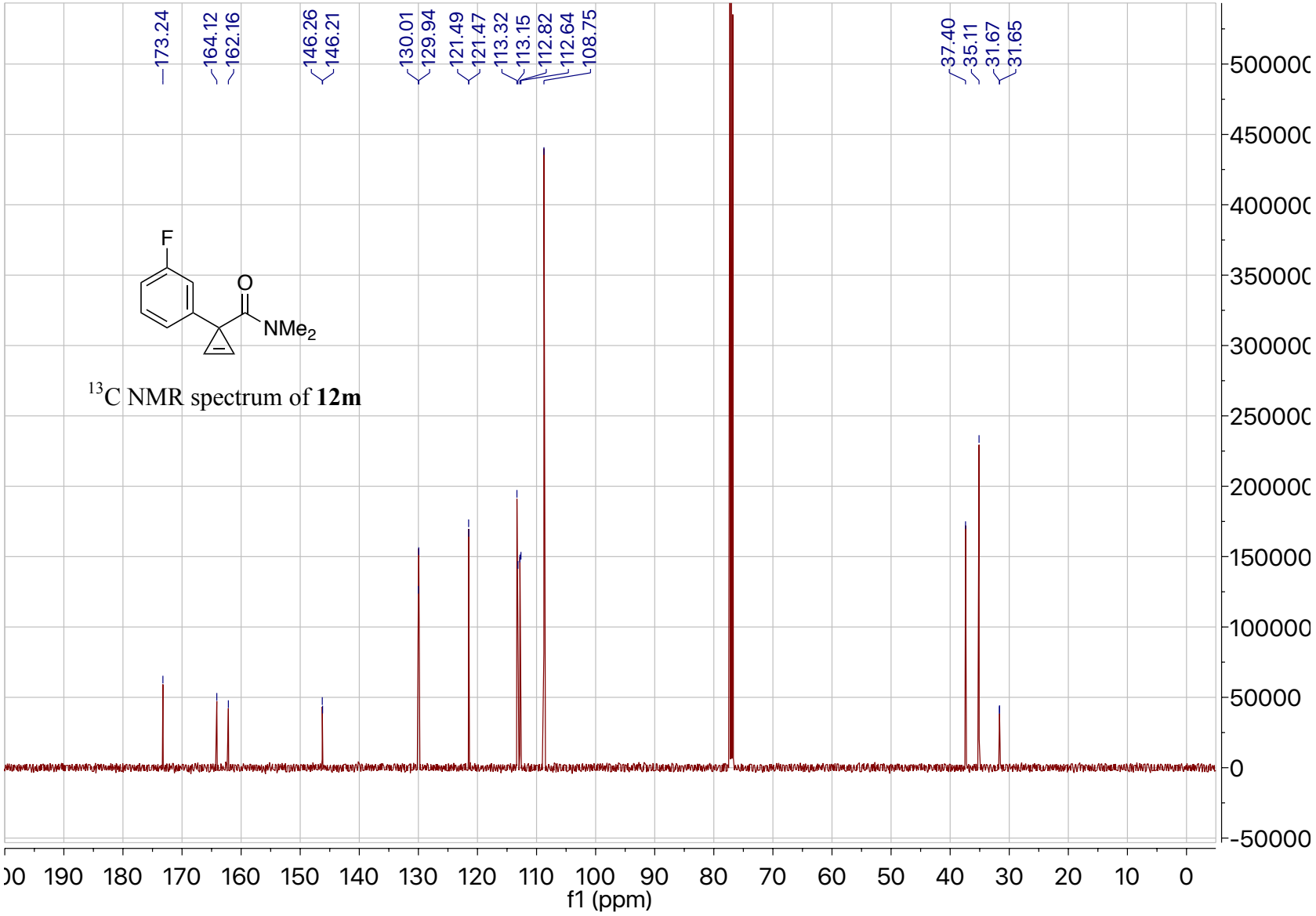
^{1}H NMR spectrum of **12l**



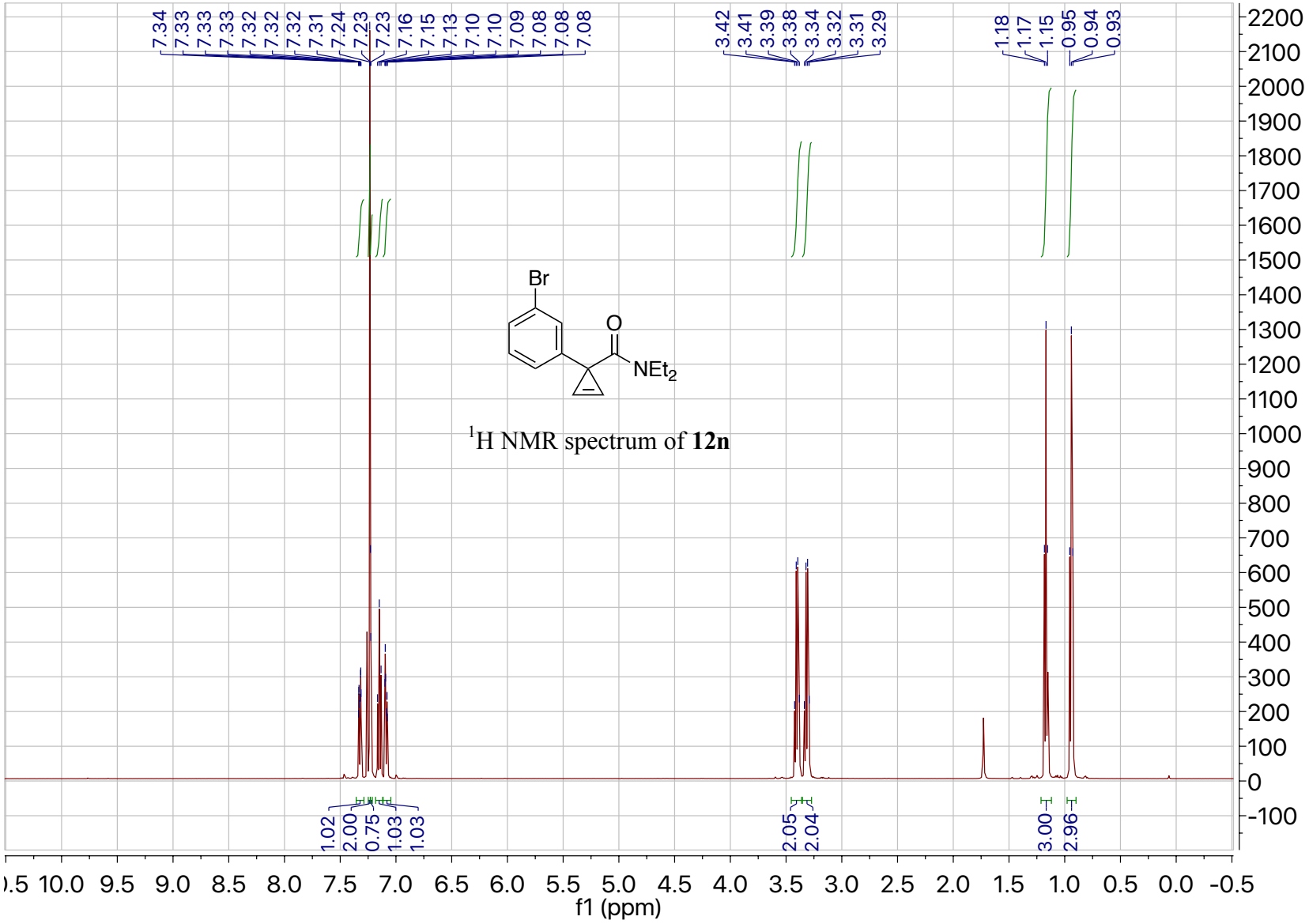
^{13}C NMR spectrum of **12l**



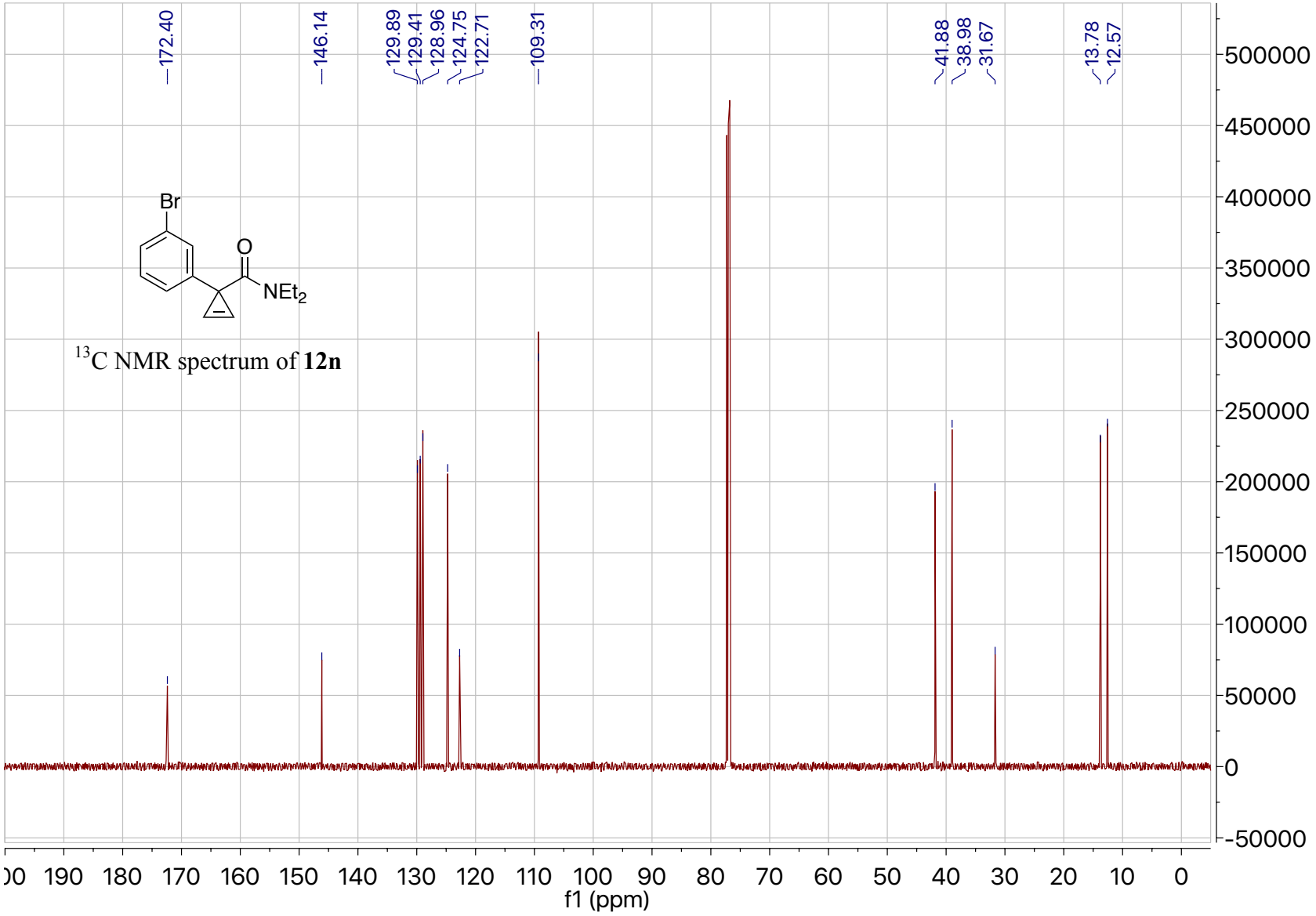
^{1}H NMR spectrum of **12m**



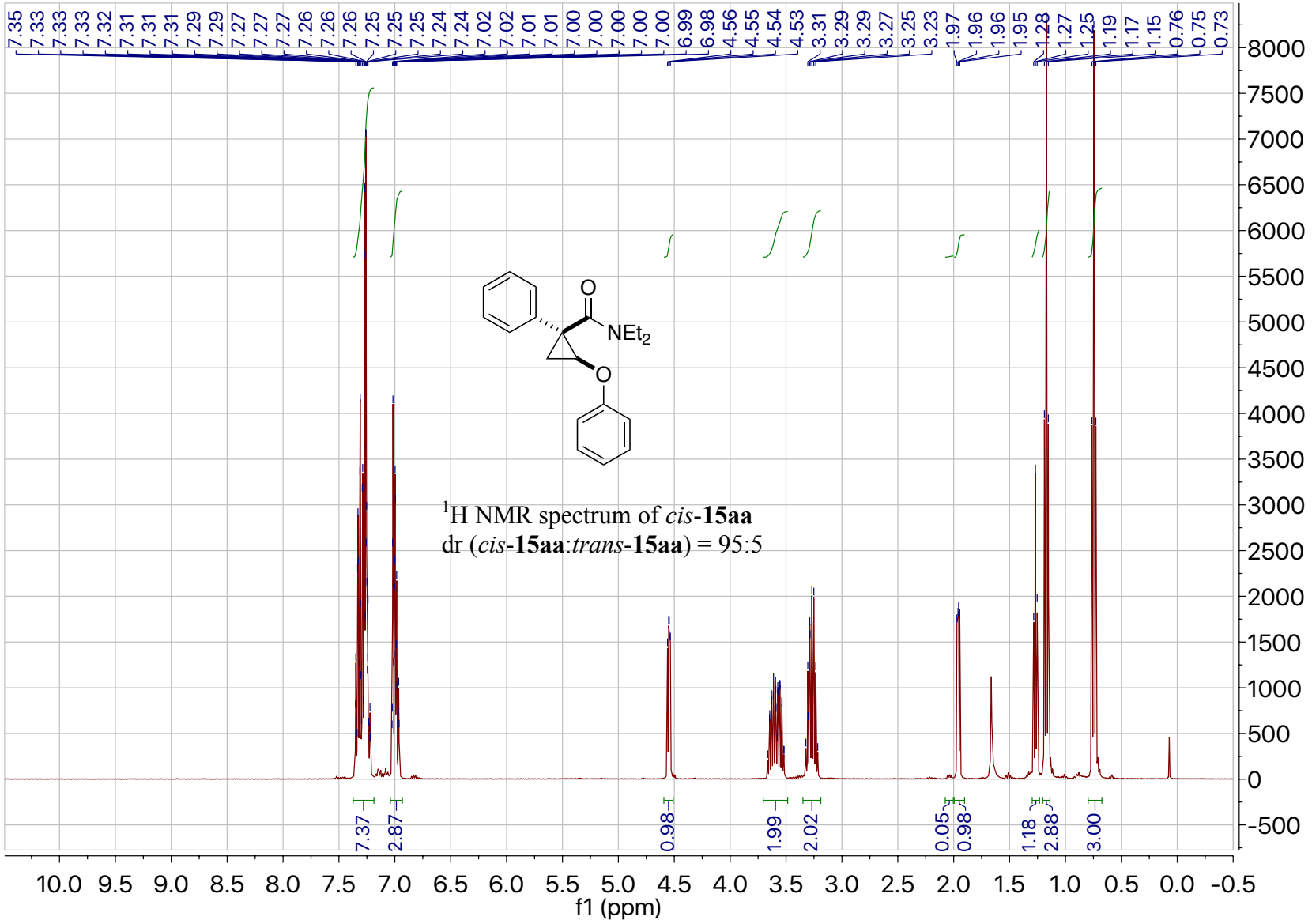
^{13}C NMR spectrum of **12m**

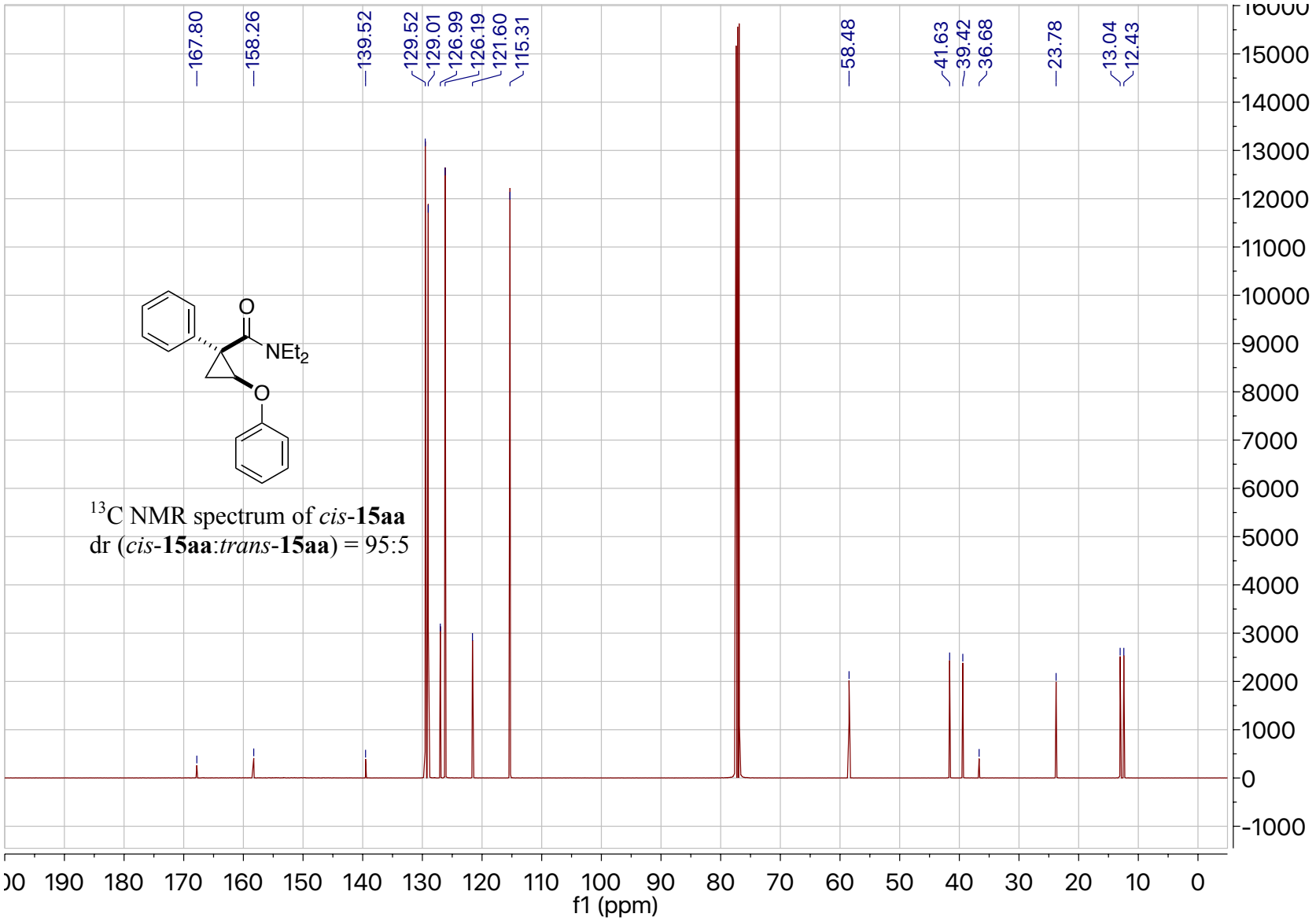


^{1}H NMR spectrum of **12n**

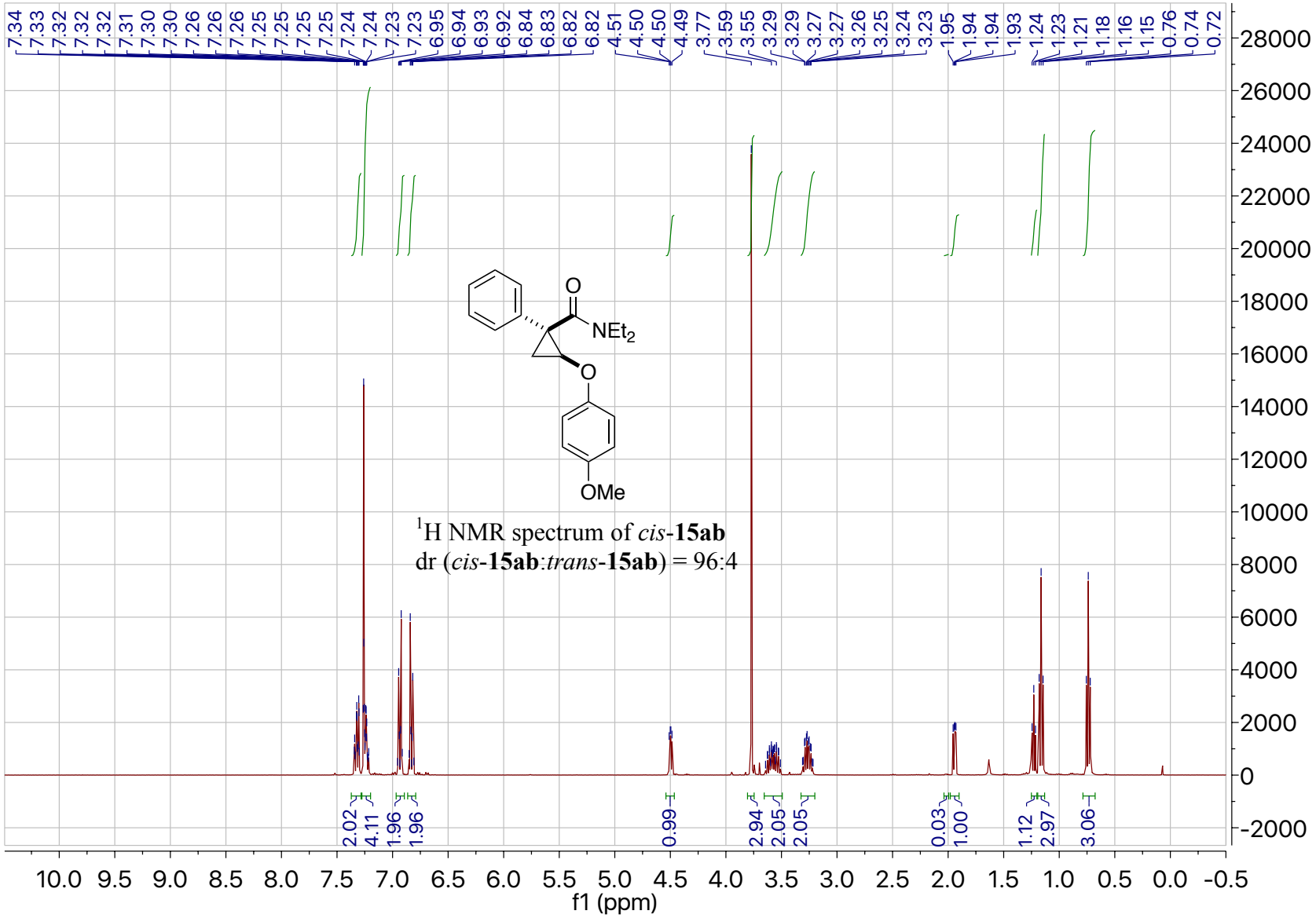


^{13}C NMR spectrum of **12n**

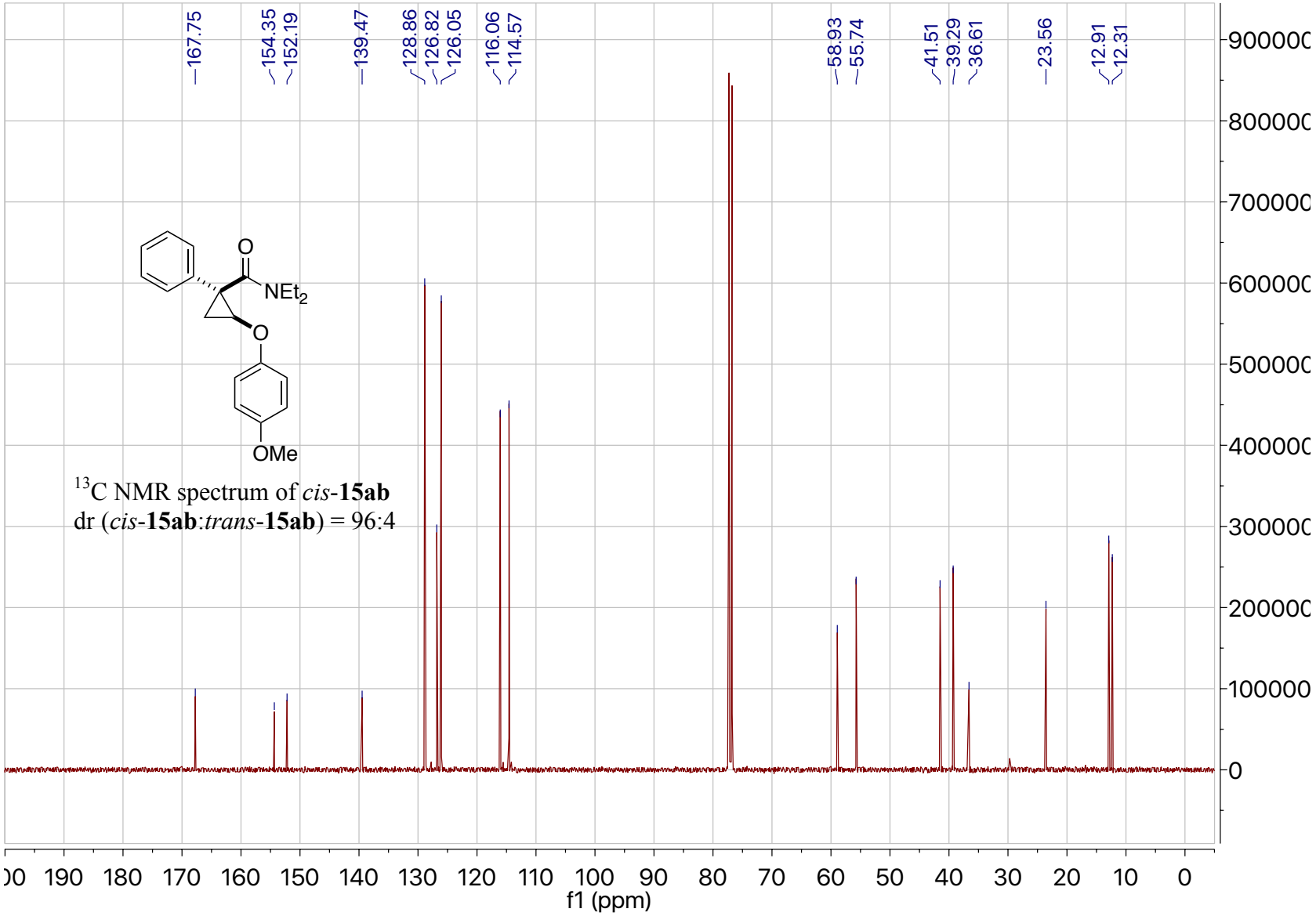

O
NEt2
O
1H NMR spectrum of cis-15aa
dr (cis-15aa:trans-15aa) = 95:5
f1 (ppm)



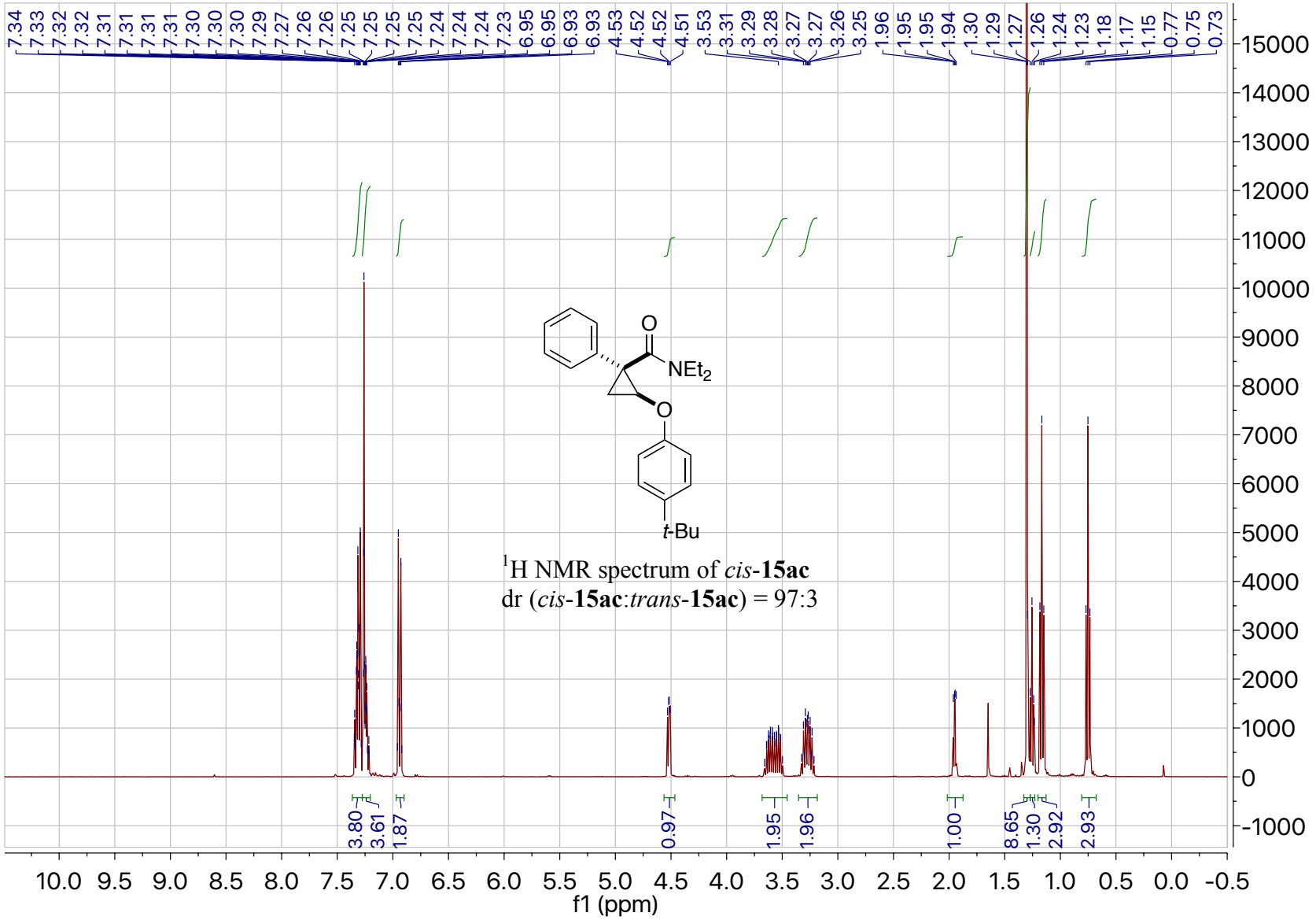
^{13}C NMR spectrum of *cis*-**15aa**
dr (*cis*-**15aa**:*trans*-**15aa**) = 95:5

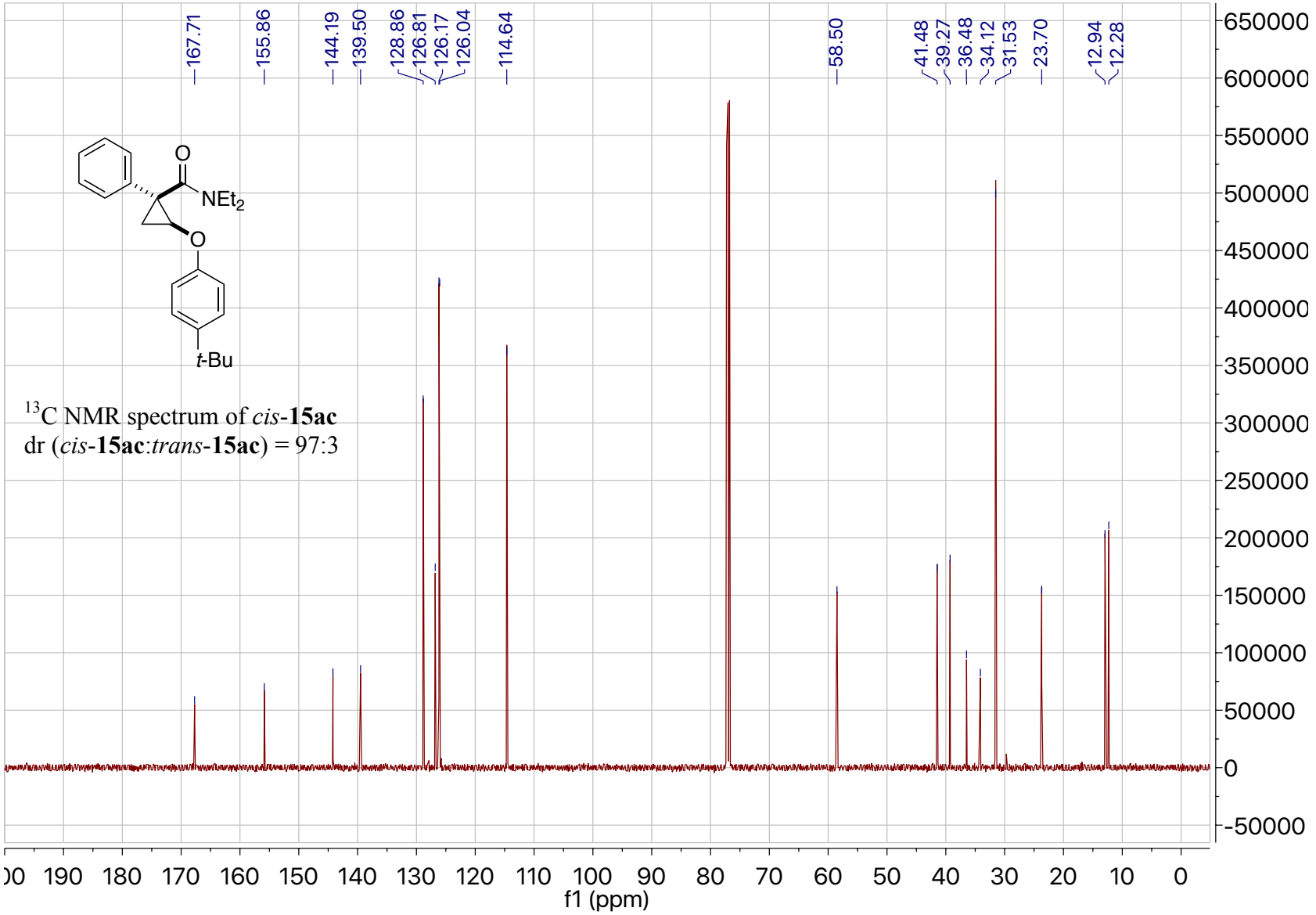


^{1}H NMR spectrum of *cis*-**15ab**
dr (*cis*-**15ab**:*trans*-**15ab**) = 96:4

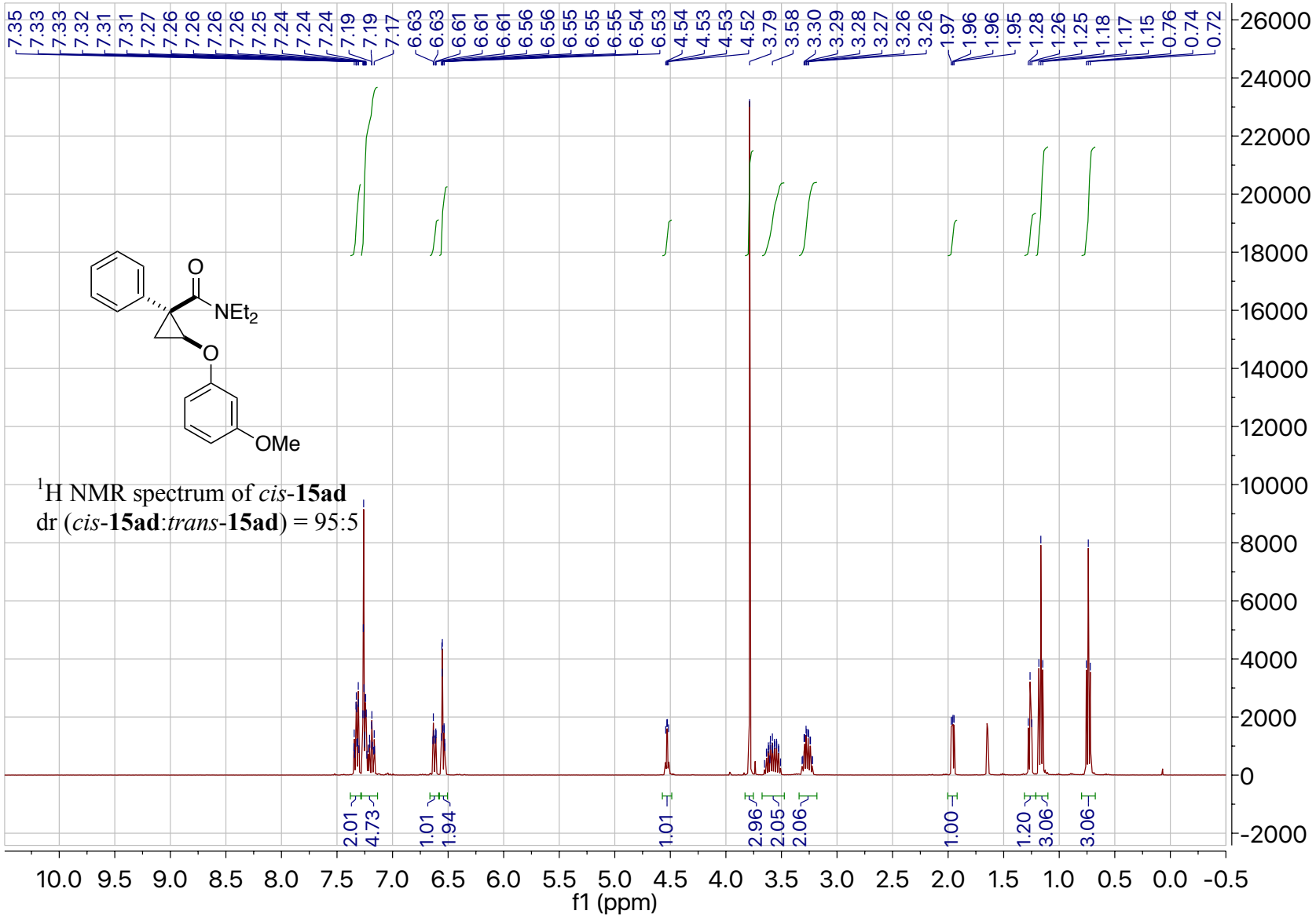


^{13}C NMR spectrum of *cis*-**15ab**
dr (*cis*-**15ab**:*trans*-**15ab**) = 96:4

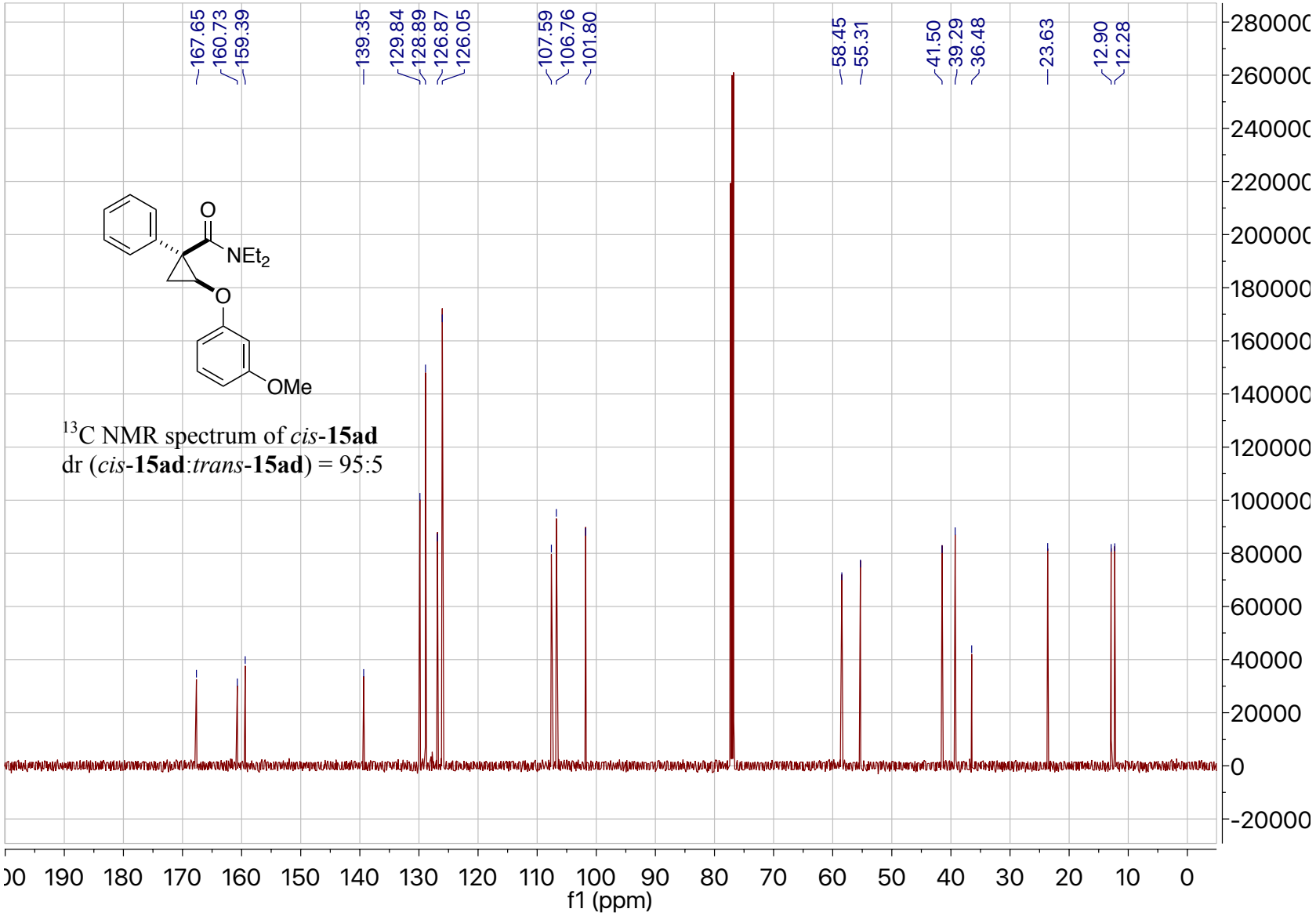

7.34 7.33 7.32 7.32 7.31 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.27 7.26 7.26 7.25 7.25 7.25 7.25 7.24 7.24 7.24 7.23 6.95 6.95 6.93 6.93
4.53 4.52 4.52 4.51
3.53 3.31 3.29 3.28 3.27 3.27 3.26 3.25
1.96 1.95 1.95 1.94 1.30 1.29 1.27 1.26 1.24 1.23 1.18 1.17 1.15 0.77 0.75 0.73
O
NEt2
O
t-Bu
1H NMR spectrum of cis-15ac
dr (cis-15ac:trans-15ac) = 97:3
3.80
3.61
1.87
0.97
1.95
1.96
1.00
8.65
1.30
2.92
2.93
15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
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 -0.5
f1 (ppm)



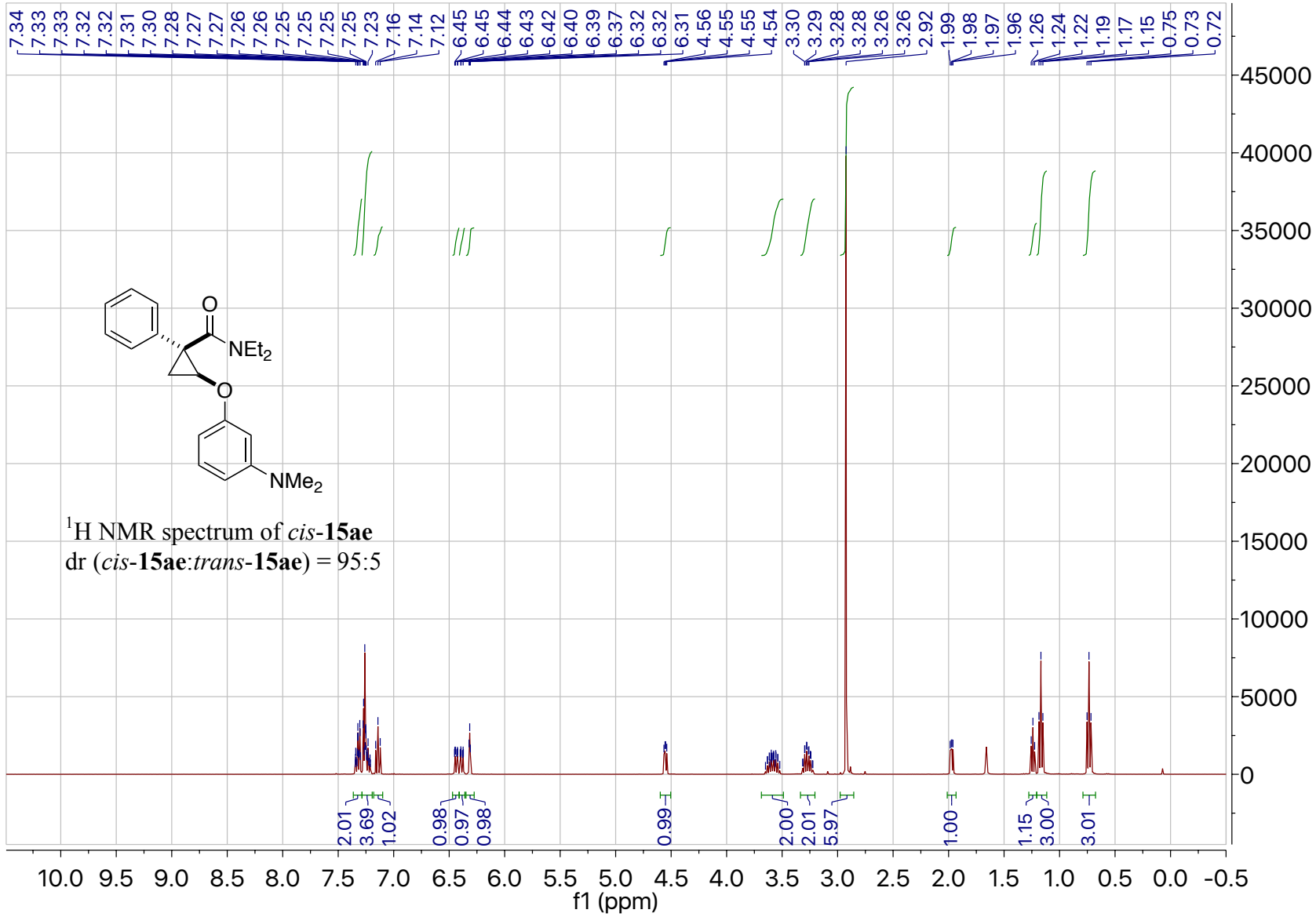
^{13}C NMR spectrum of *cis*-**15ac**
dr (*cis*-**15ac**:*trans*-**15ac**) = 97:3



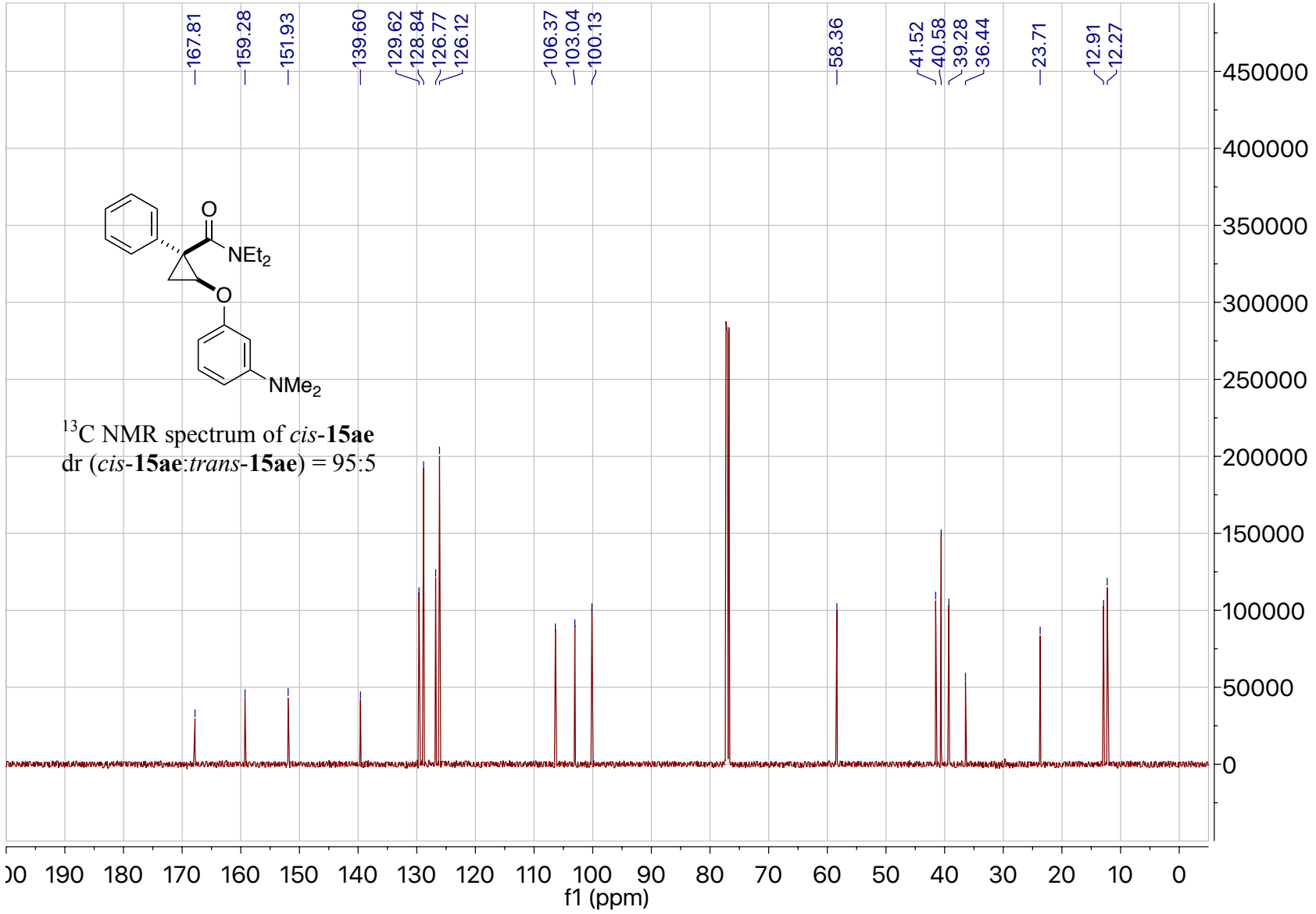
^{1}H NMR spectrum of *cis*-**15ad**
dr (*cis*-**15ad**:*trans*-**15ad**) = 95:5



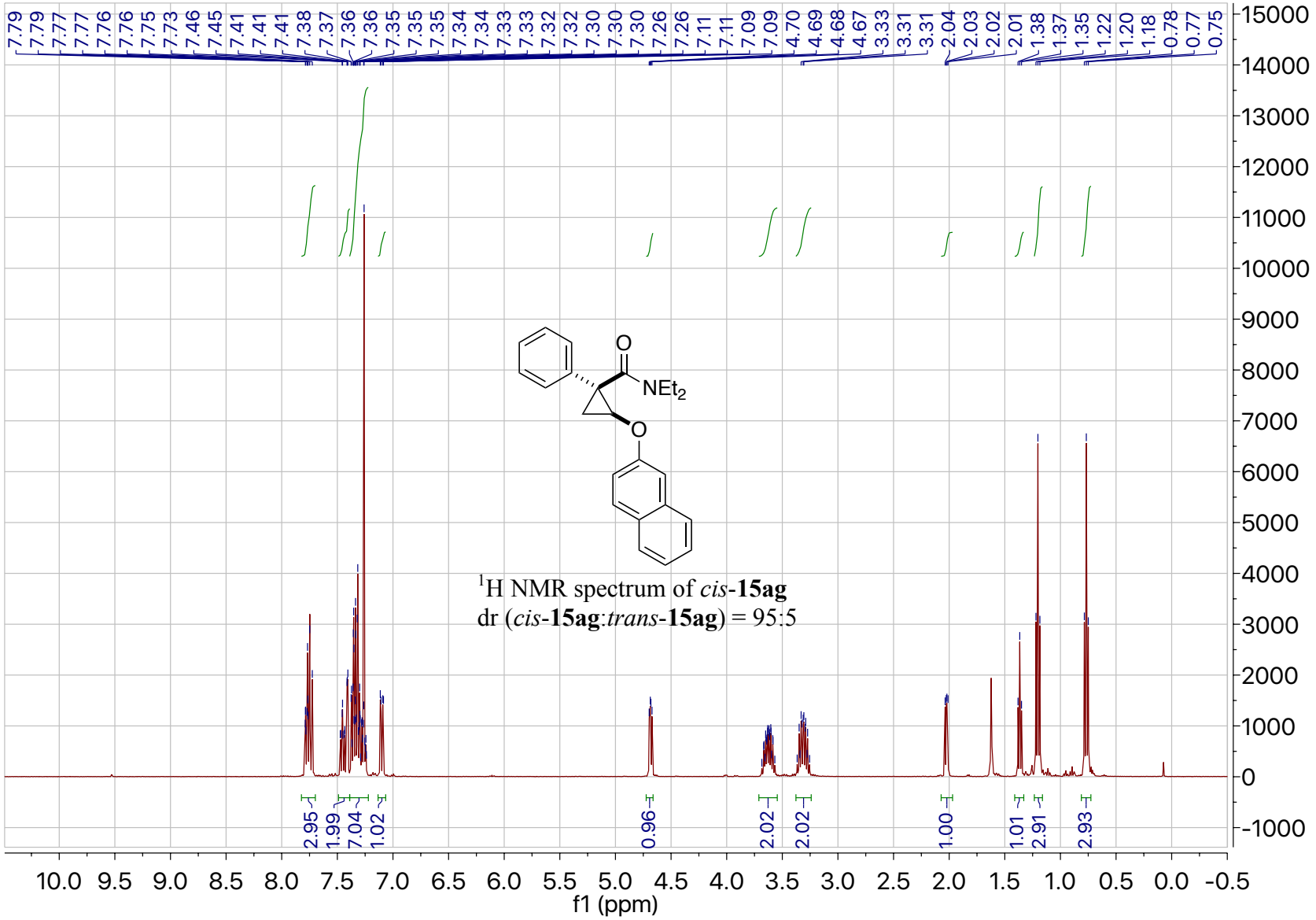
^{13}C NMR spectrum of *cis*-**15ad**
dr (*cis*-**15ad**:*trans*-**15ad**) = 95:5



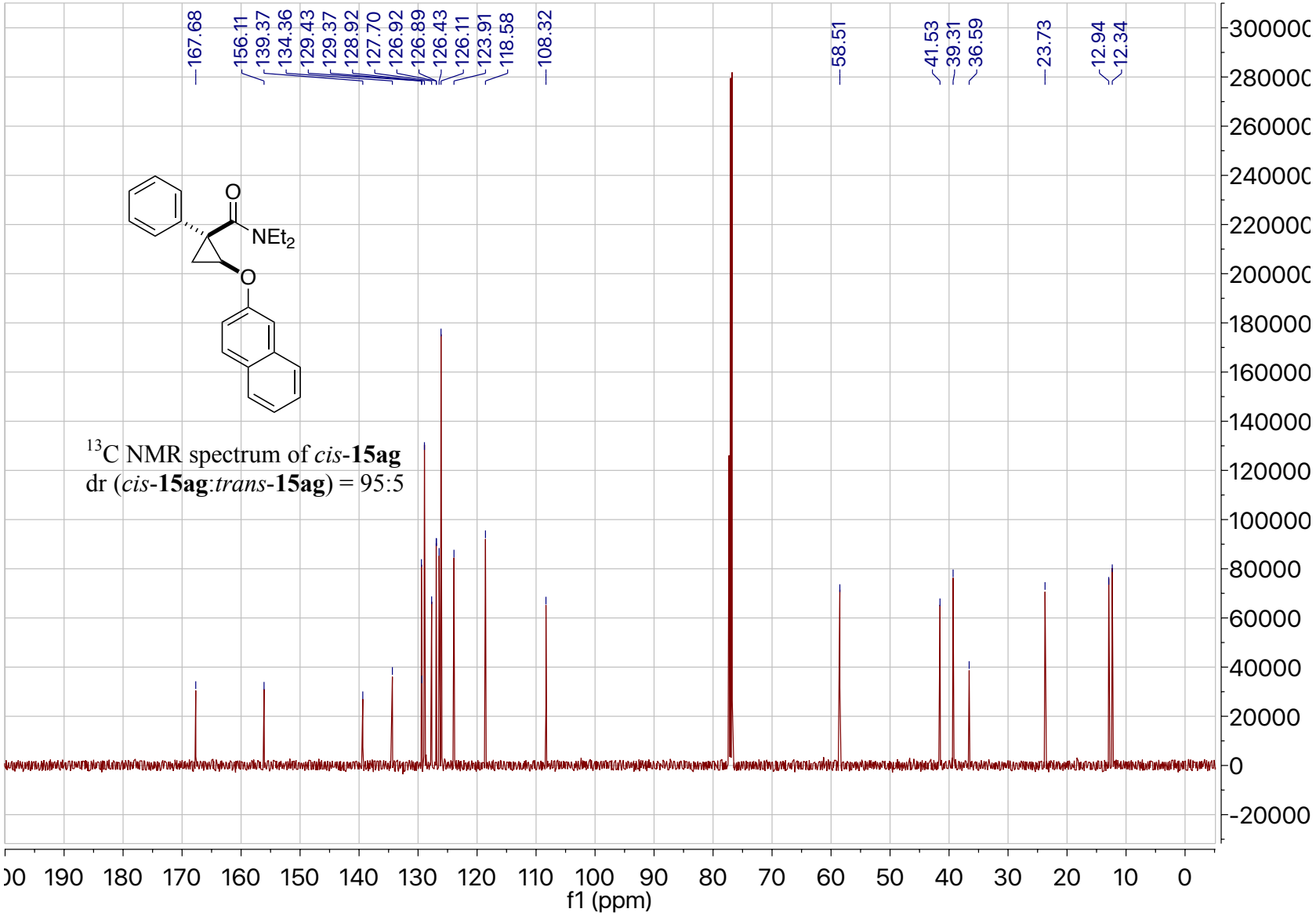
^{1}H NMR spectrum of *cis*-**15ae**
dr (*cis*-**15ae**:*trans*-**15ae**) = 95:5

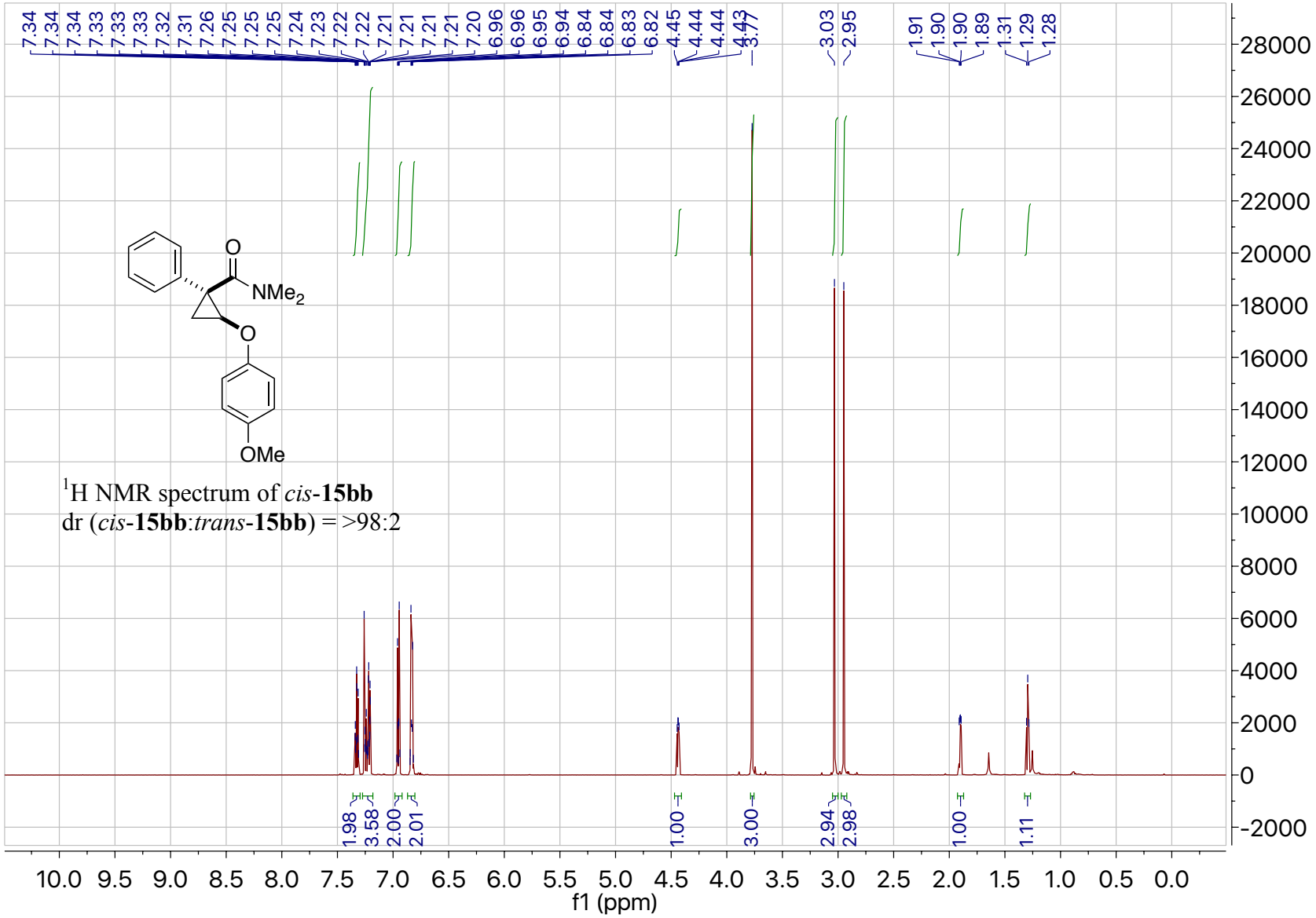


^{13}C NMR spectrum of *cis*-**15ae**
dr (*cis*-**15ae**:*trans*-**15ae**) = 95:5

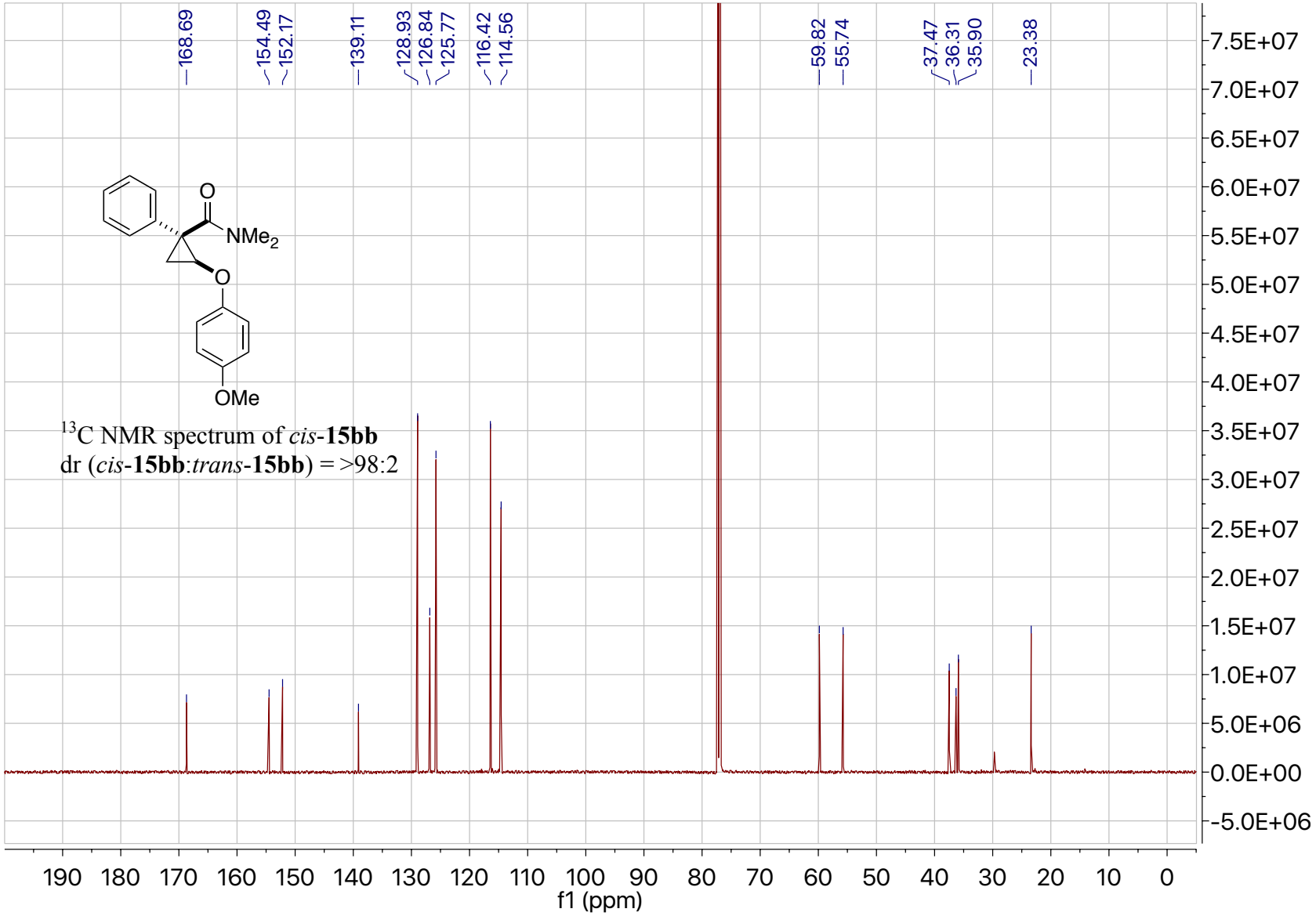


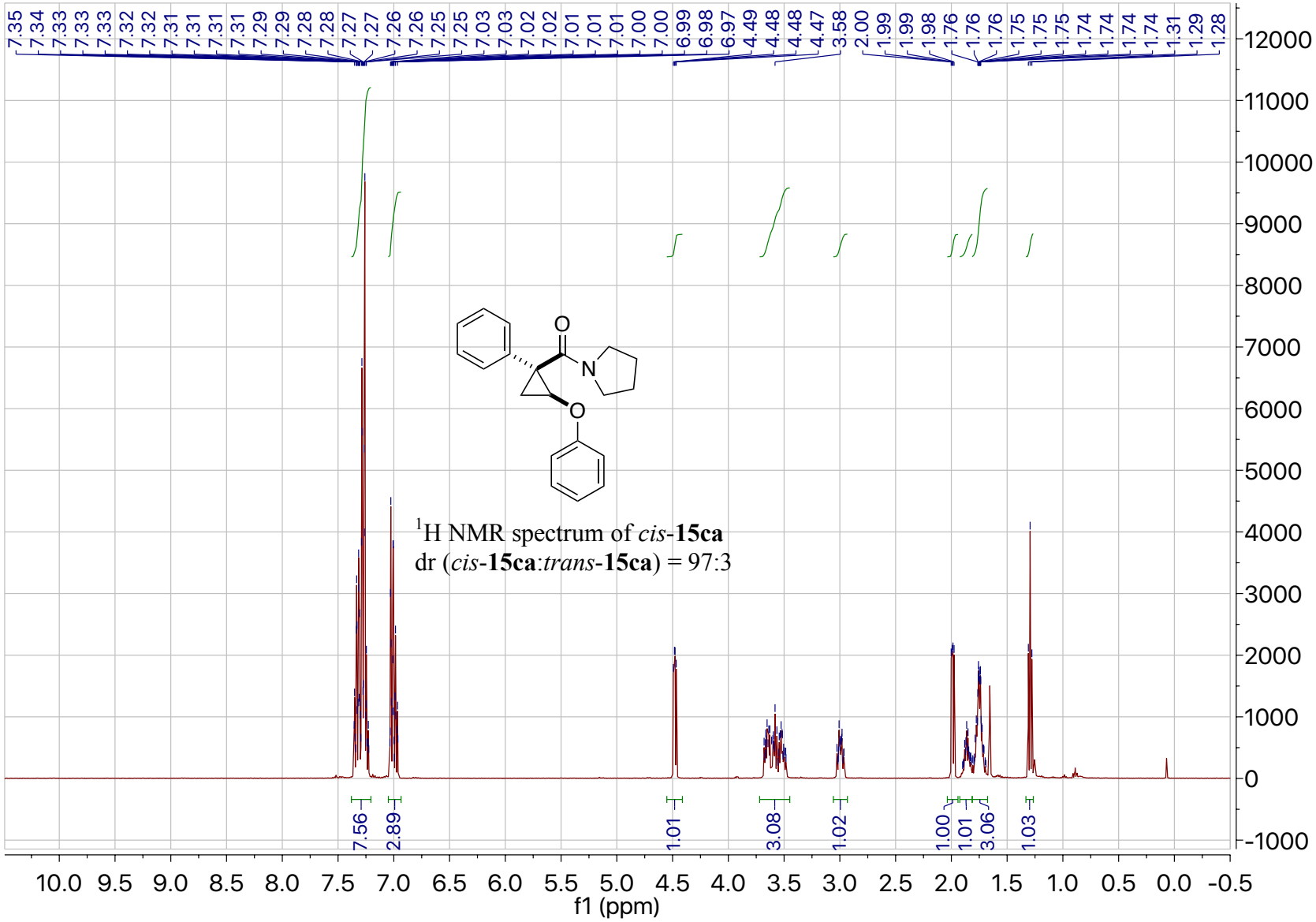
^{1}H NMR spectrum of *cis*-**15ag**
dr (*cis*-**15ag**:*trans*-**15ag**) = 95:5

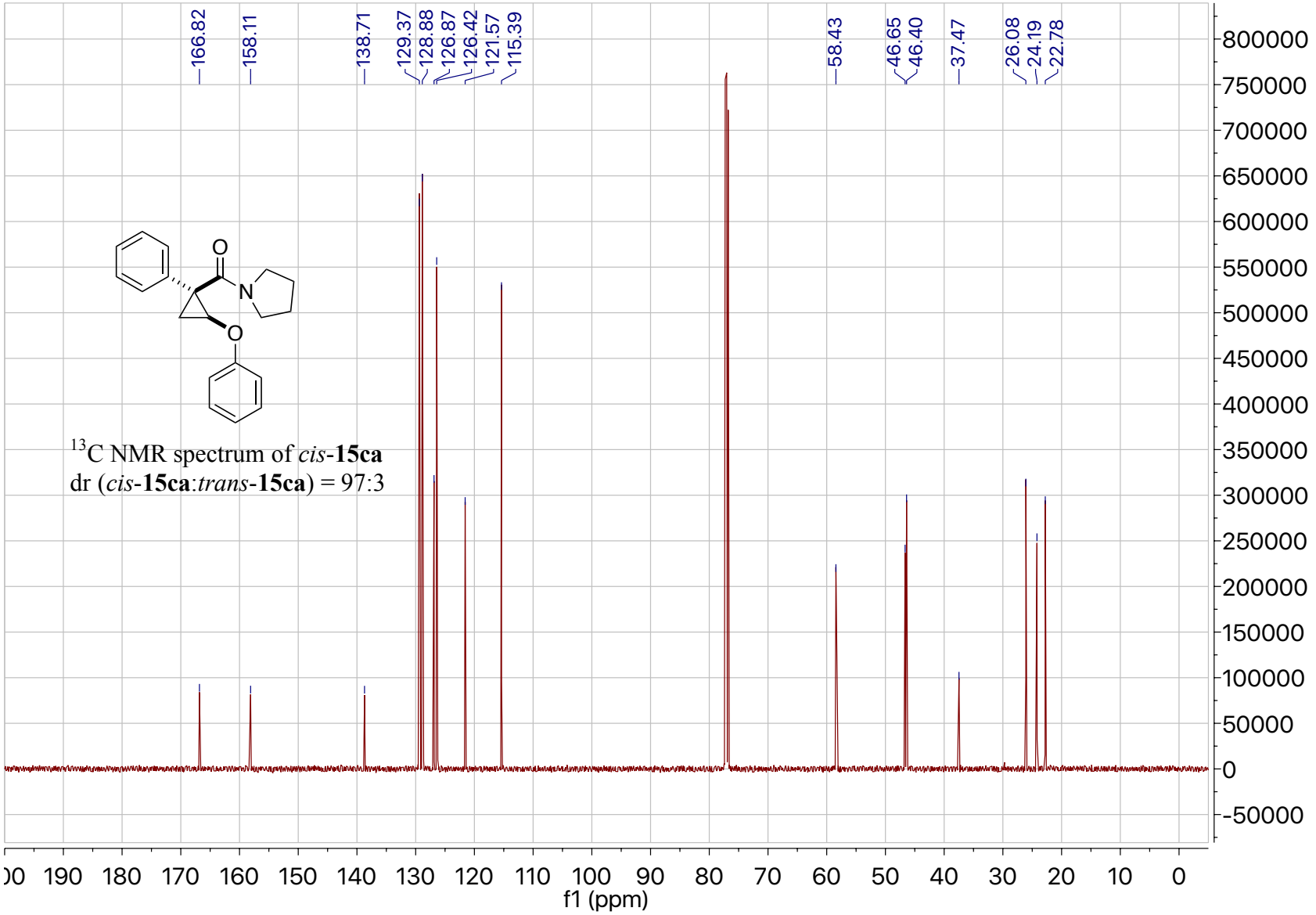

167.68
156.11
139.37
134.36
129.43
129.37
128.92
127.70
126.92
126.89
126.43
126.11
123.91
118.58
108.32
58.51
41.53
39.31
36.59
23.73
12.94
12.34
O
NEt2
O
13C NMR spectrum of cis-15ag
dr (cis-15ag:trans-15ag) = 95:5
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

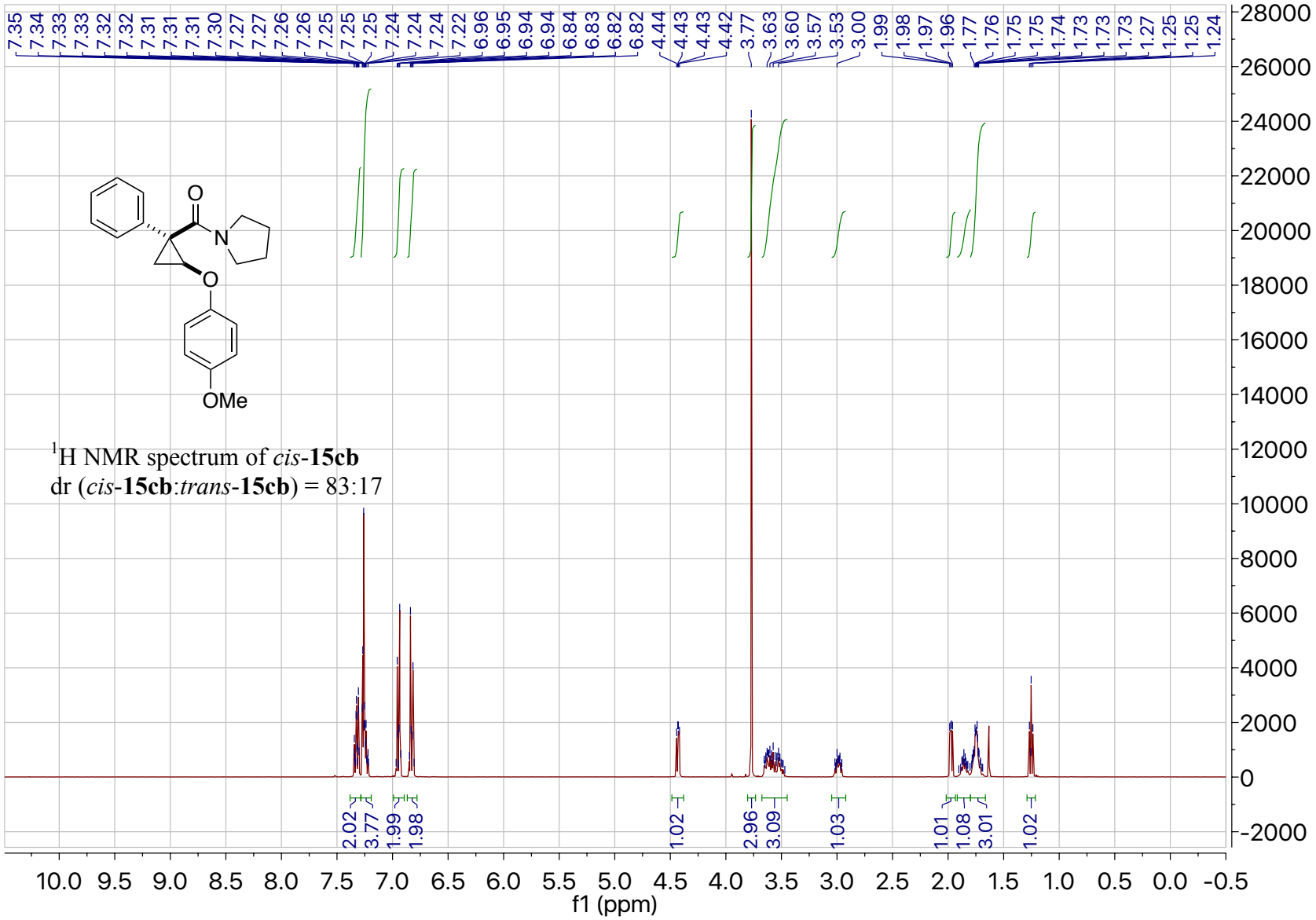


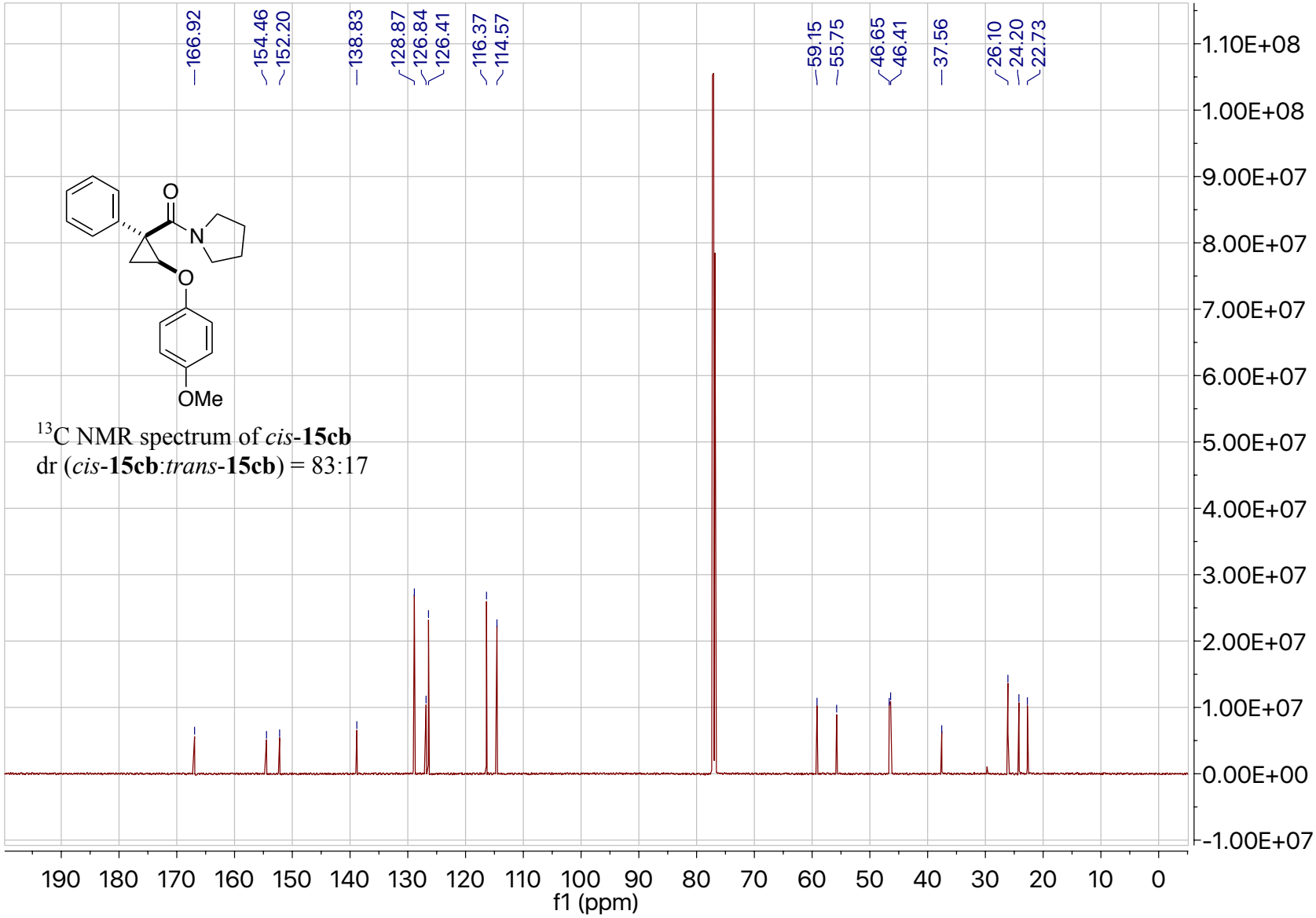
^{1}H NMR spectrum of *cis*-**15bb**
dr (*cis*-**15bb**:*trans*-**15bb**) = >98:2


168.69
154.49
152.17
139.11
128.93
126.84
125.77
116.42
114.56
59.82
55.74
37.47
36.31
35.90
23.38
O
NMe2
O
OMe
13C NMR spectrum of cis-15bb
dr (cis-15bb:trans-15bb) = >98:2
7.5E+07
7.0E+07
6.5E+07
6.0E+07
5.5E+07
5.0E+07
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
-5.0E+06
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

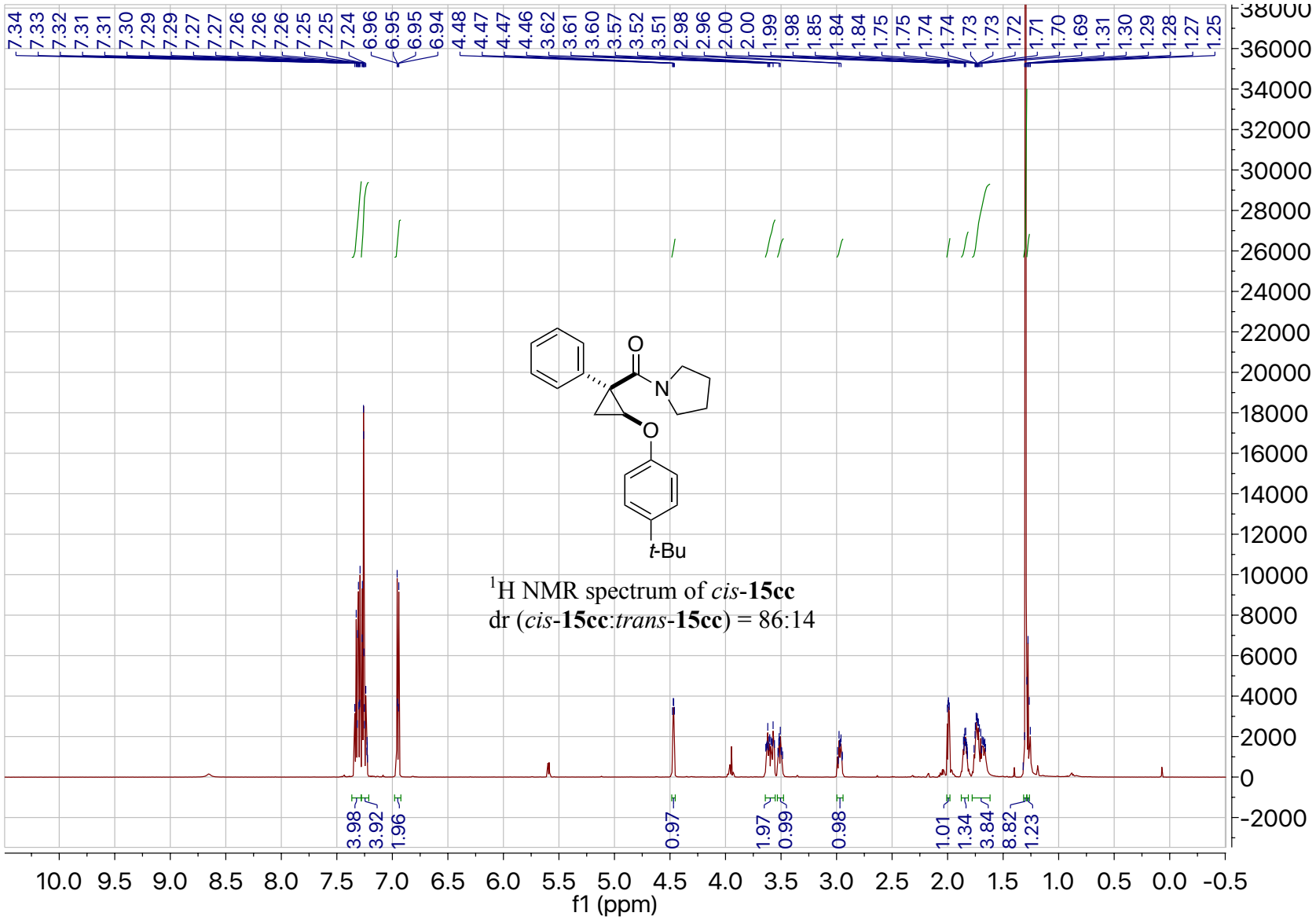

7.35 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.31 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.03 7.03 7.02 7.02 7.01 7.01 7.01 7.00 7.00 6.99 6.98 6.97 4.49 4.48 4.48 4.47 3.58 2.00 1.99 1.99 1.98 1.76 1.76 1.76 1.75 1.75 1.75 1.74 1.74 1.74 1.74 1.31 1.29 1.28
O
N
O
[1]H NMR spectrum of *cis*-**15ca**
dr (*cis*-**15ca**:*trans*-**15ca**) = 97:3
7.56
2.89
1.01
3.08
1.02
1.00
1.01
3.06
1.03
12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
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 -0.5
f1 (ppm)


166.82
158.11
138.71
129.37
128.88
126.87
126.42
121.57
115.39
58.43
46.65
46.40
37.47
26.08
24.19
22.78
O
N
O
^{13}C NMR spectrum of *cis*-**15ca**
dr (*cis*-**15ca**:*trans*-**15ca**) = 97:3
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

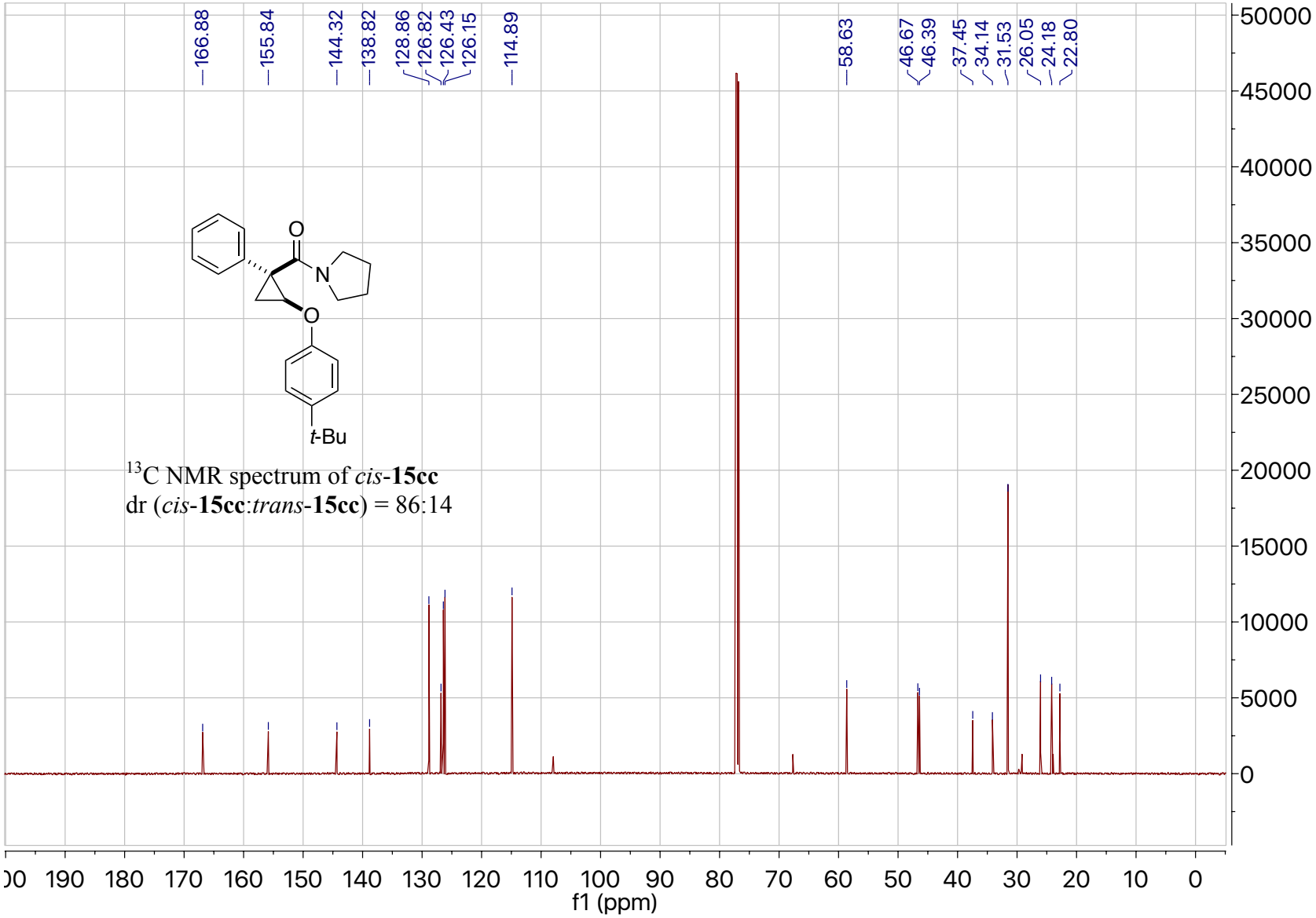

7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.27 7.27 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.24 7.22 6.96 6.95 6.94 6.94 6.84 6.83 6.82 6.82 4.44 4.43 4.43 4.42 3.77 3.63 3.60 3.57 3.53 3.00 1.99 1.98 1.97 1.96 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.73 1.27 1.25 1.25 1.24
O
N
O
OMe
^{1}H NMR spectrum of *cis*-**15cb**
dr (*cis*-**15cb**:*trans*-**15cb**) = 83:17
2.02 3.77 1.99 1.98 1.02 2.96 3.09 1.03 1.01 1.08 3.01 1.02
28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000
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 -0.5
f1 (ppm)



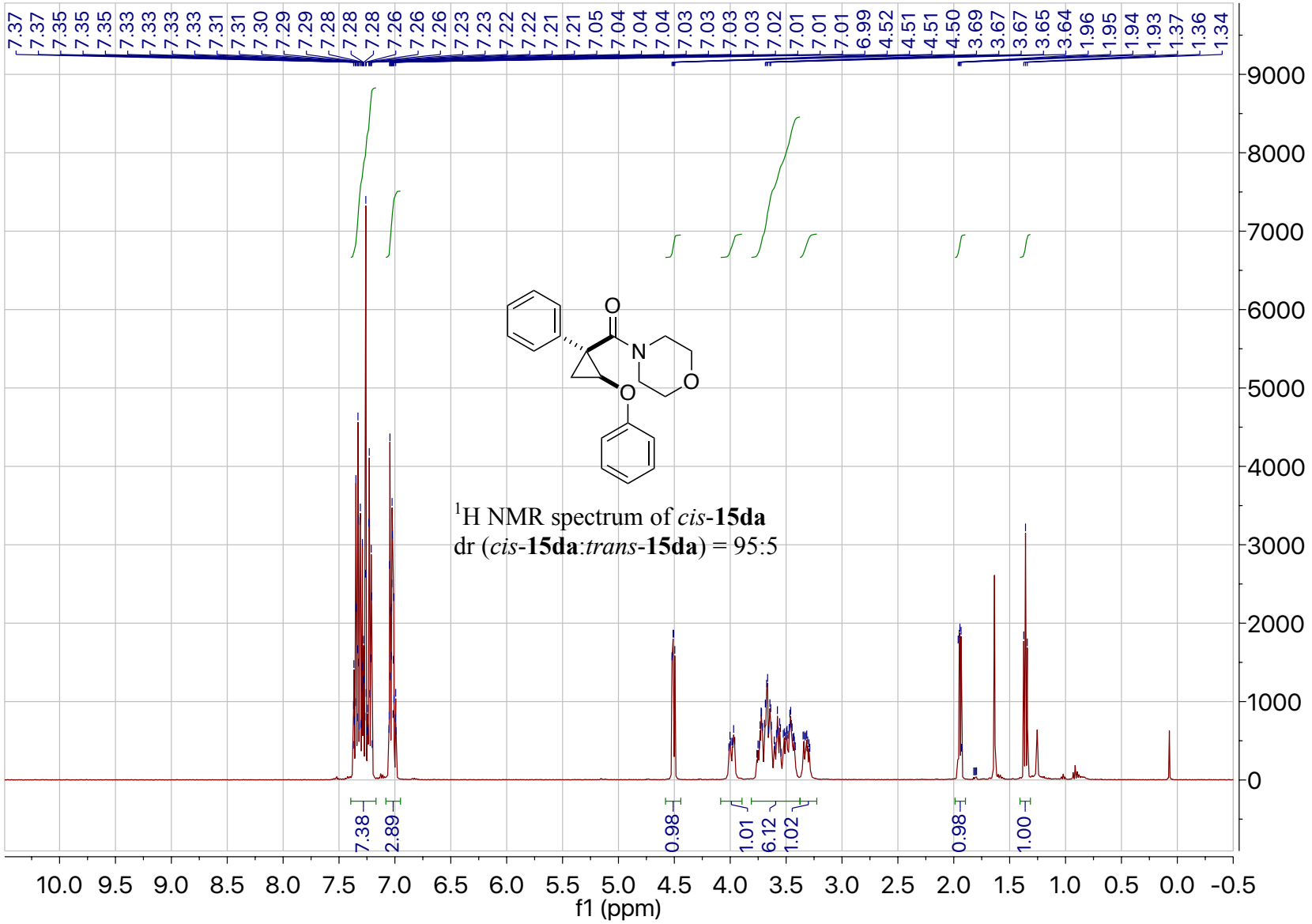
^{13}C NMR spectrum of *cis*-**15cb**
dr (*cis*-**15cb**:*trans*-**15cb**) = 83:17

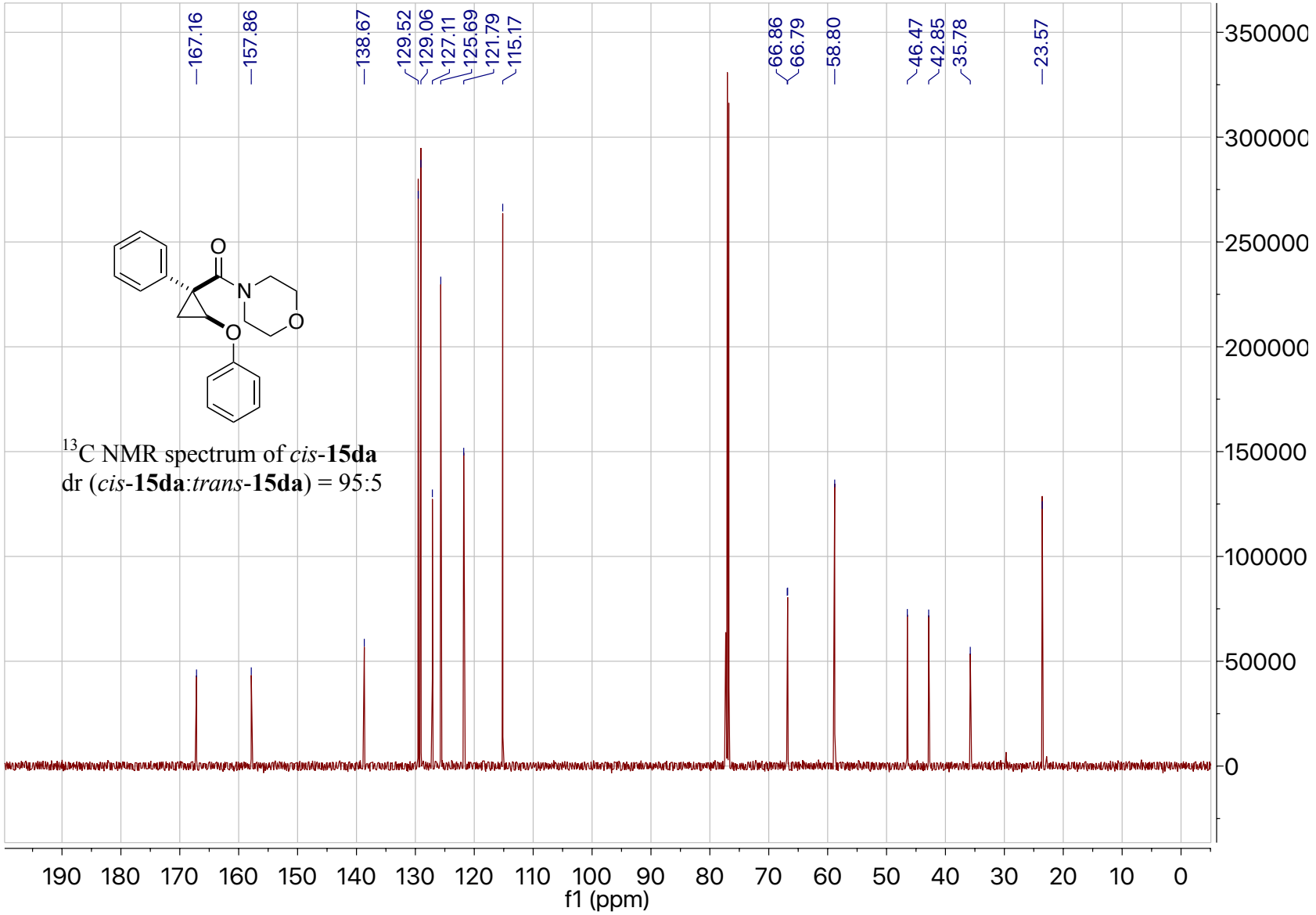


^{1}H NMR spectrum of *cis*-**15cc**
dr (*cis*-**15cc**:*trans*-**15cc**) = 86:14

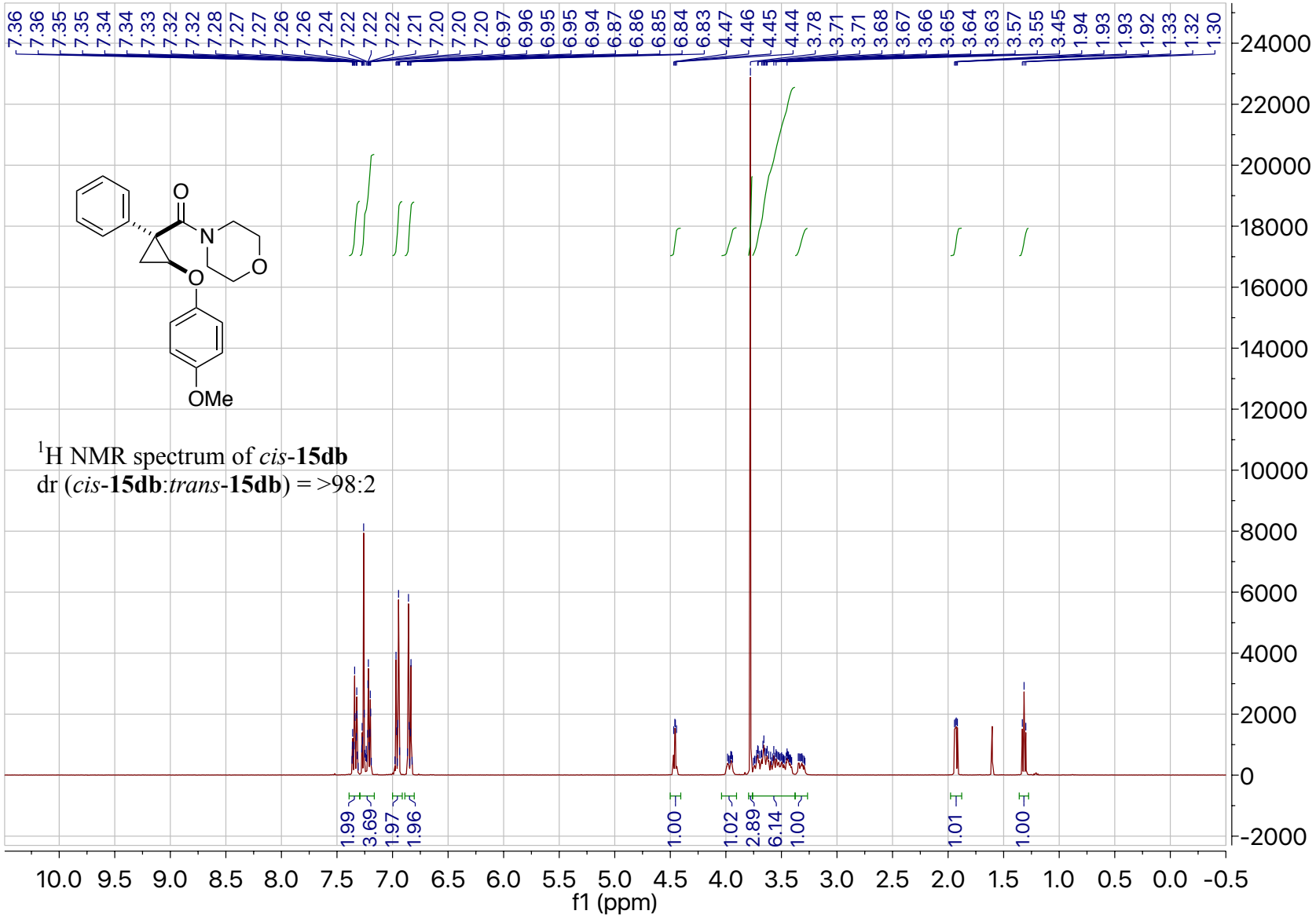


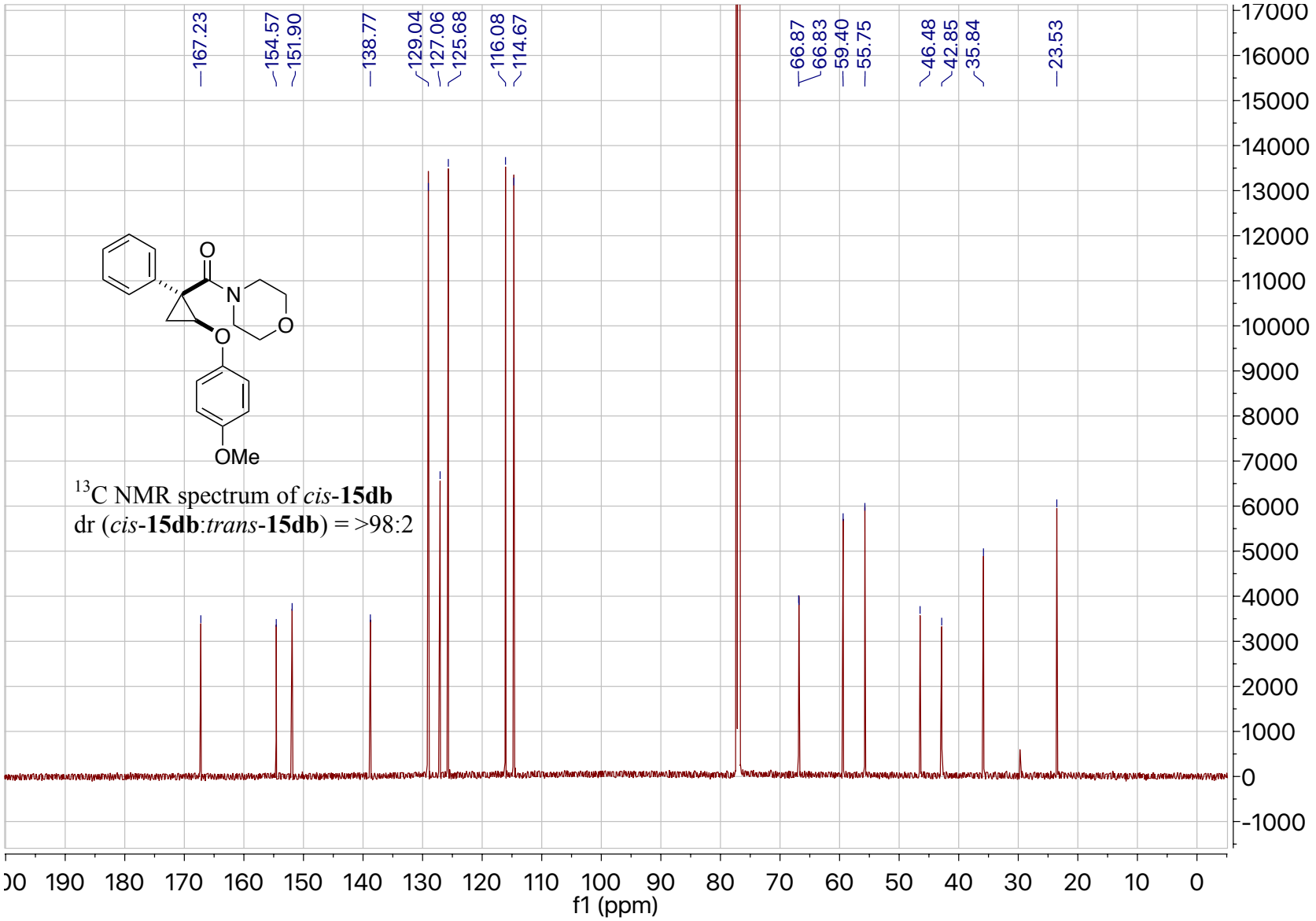
^{13}C NMR spectrum of *cis*-**15cc**
dr (*cis*-**15cc**:*trans*-**15cc**) = 86:14


7.37 7.37 7.35 7.35 7.35 7.33 7.33 7.33 7.33 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.28 7.26 7.26 7.26 7.23 7.23 7.22 7.22 7.21 7.21 7.05 7.04 7.04 7.04 7.03 7.03 7.03 7.03 7.02 7.01 7.01 7.01 6.99 4.52 4.51 4.51 4.50 3.69 3.67 3.67 3.65 3.64 1.96 1.95 1.94 1.93 1.37 1.36 1.34
O
N
O
O
^{1}H NMR spectrum of *cis*-**15da**
dr (*cis*-**15da**:*trans*-**15da**) = 95:5
7.38
2.89
0.98
1.01
6.12
1.02
0.98
1.00
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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 -0.5
f1 (ppm)

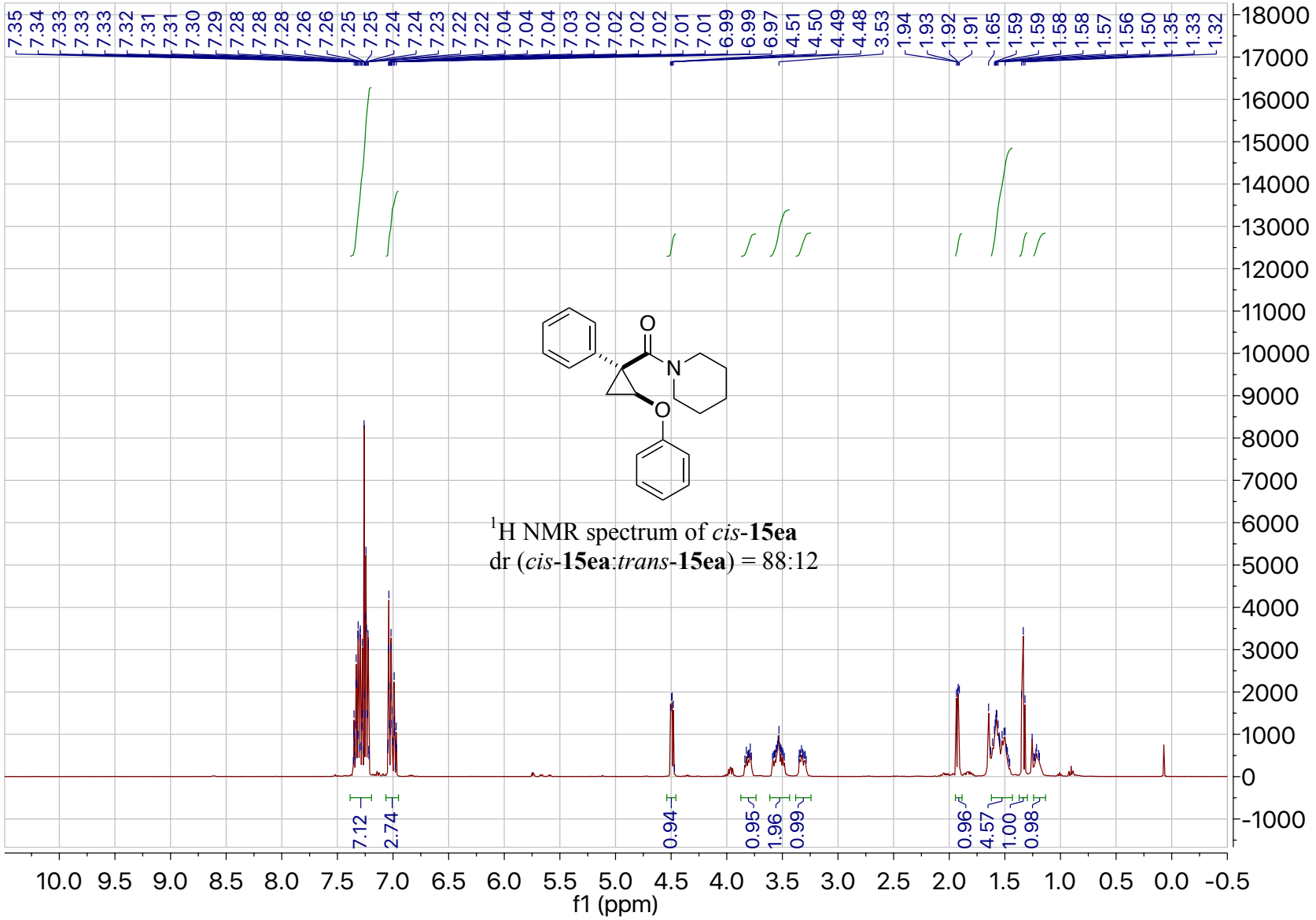


^{13}C NMR spectrum of *cis*-**15da**
dr (*cis*-**15da**:*trans*-**15da**) = 95:5

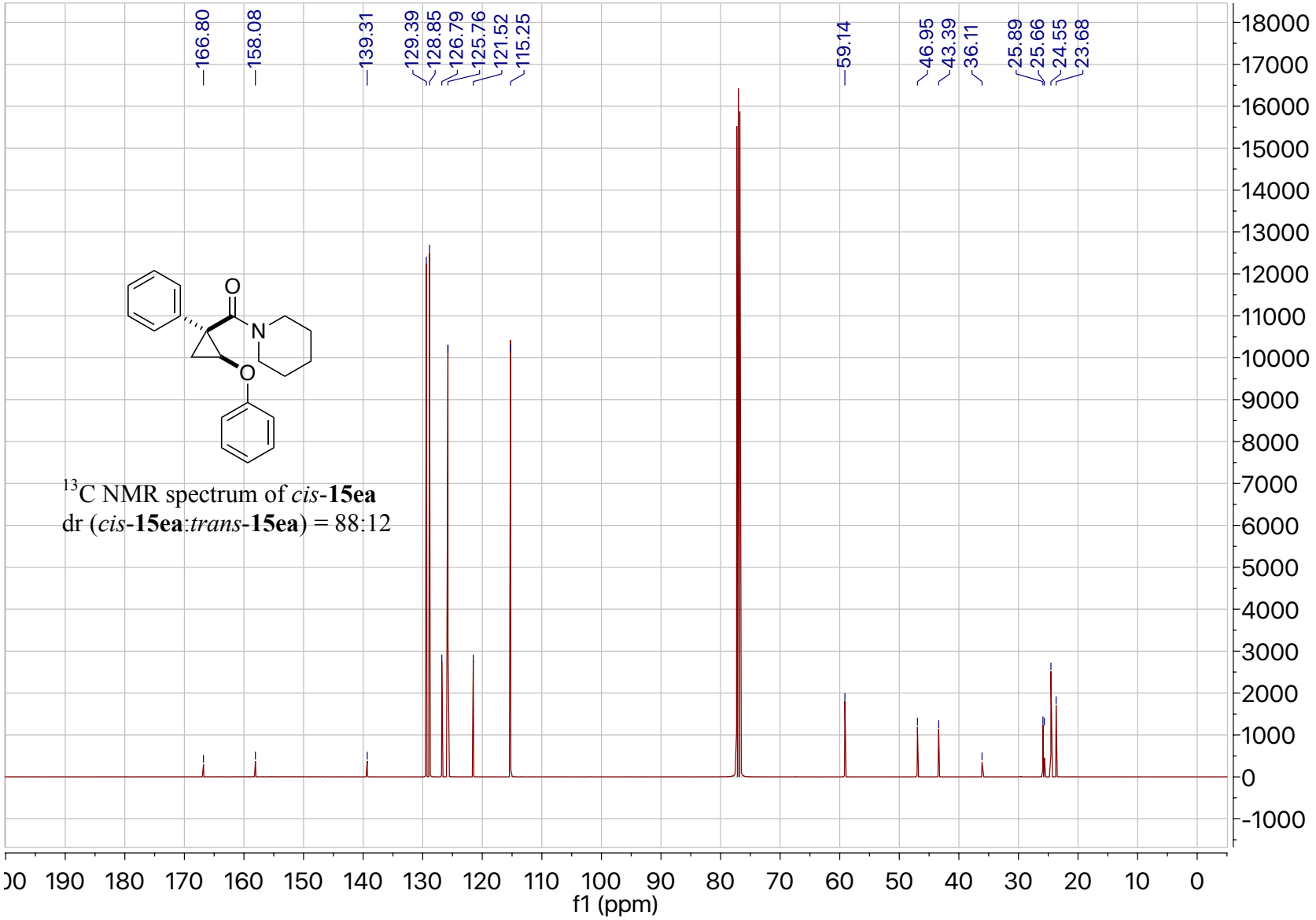

O
N
O
O
OMe
[1]H NMR spectrum of *cis*-**15db**
dr (*cis*-**15db**:*trans*-**15db**) = >98:2
f1 (ppm)



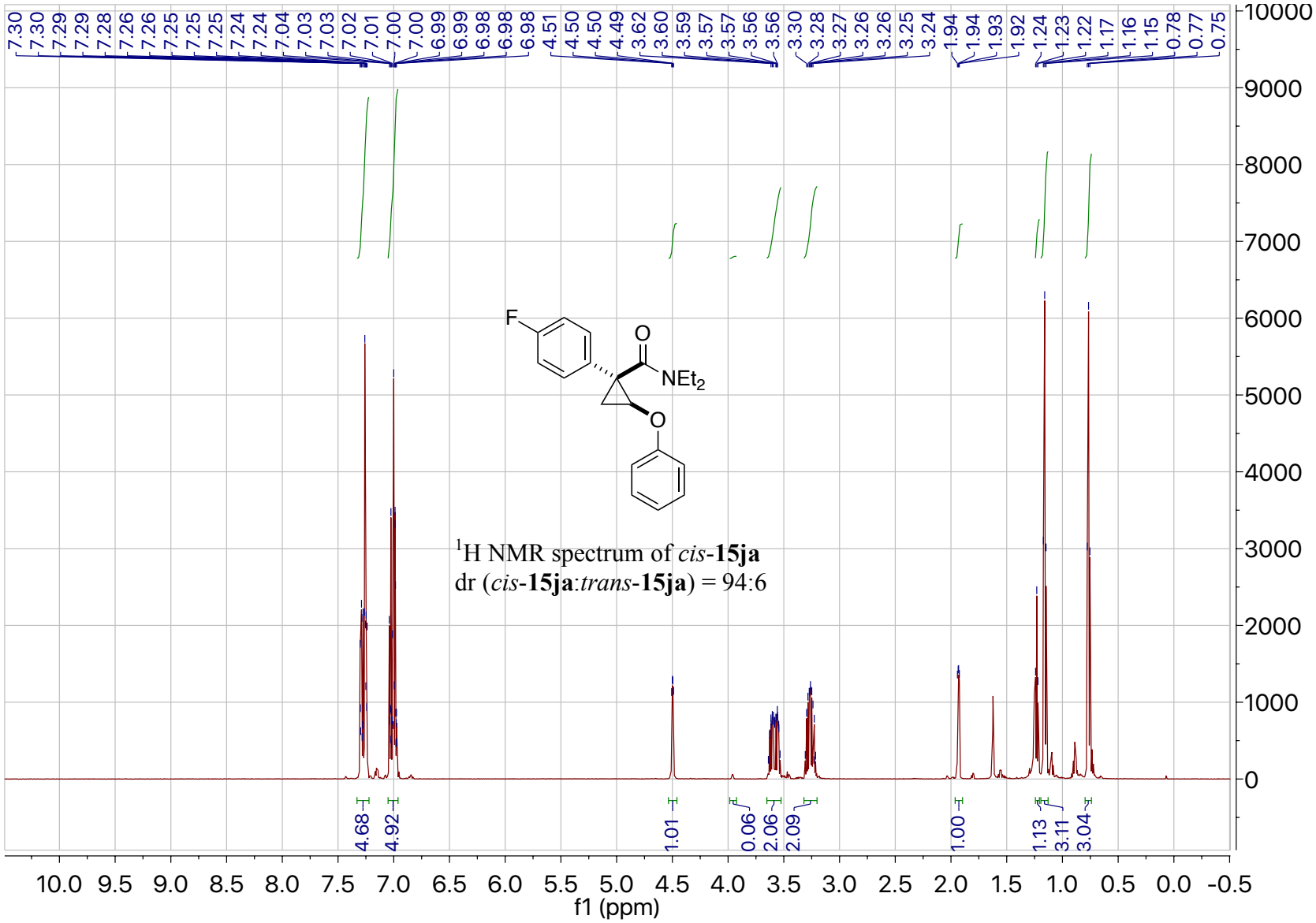
^{13}C NMR spectrum of *cis*-**15db**
dr (*cis*-**15db**:*trans*-**15db**) = >98:2

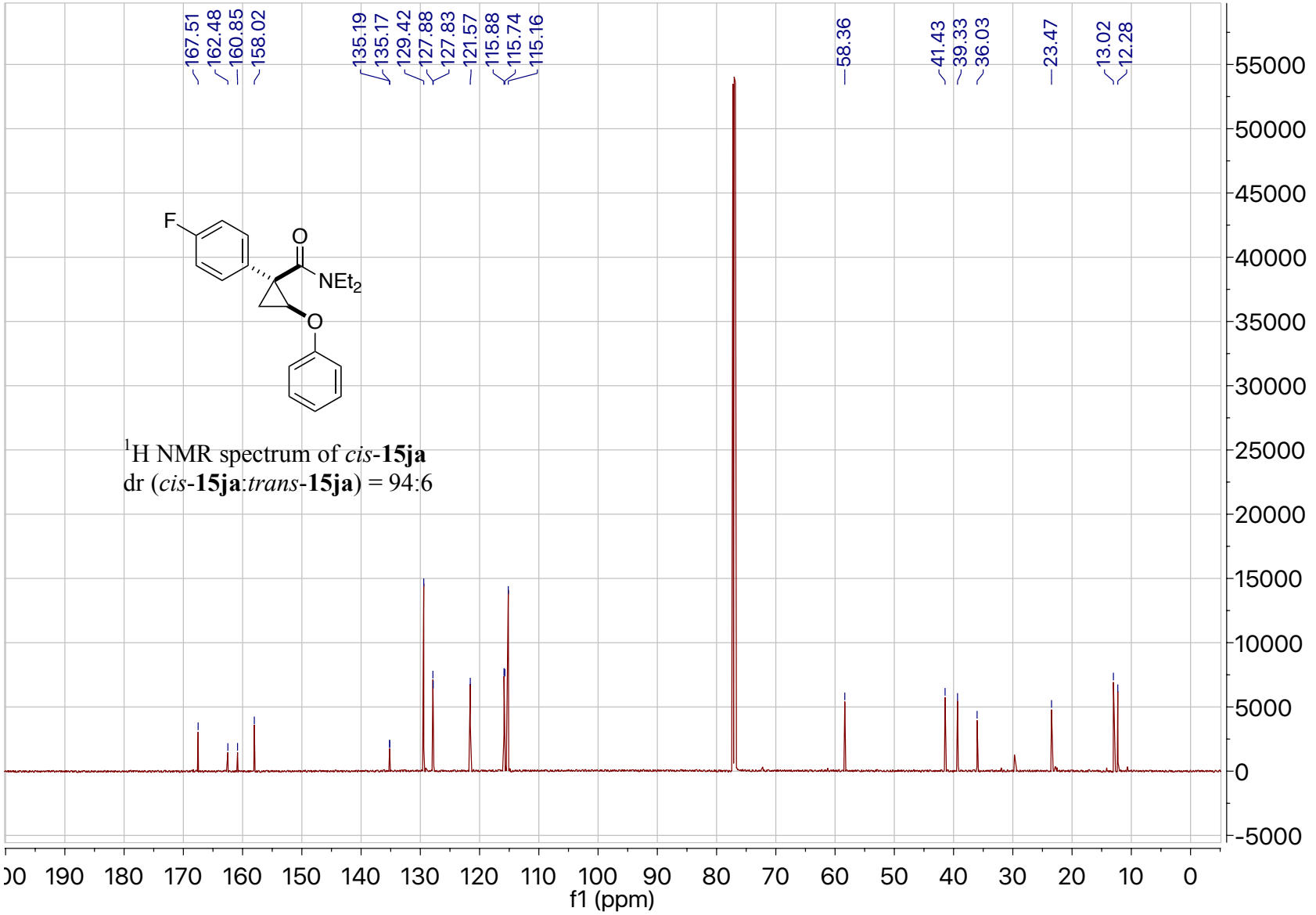


^{1}H NMR spectrum of *cis*-**15ea**
dr (*cis*-**15ea**:*trans*-**15ea**) = 88:12

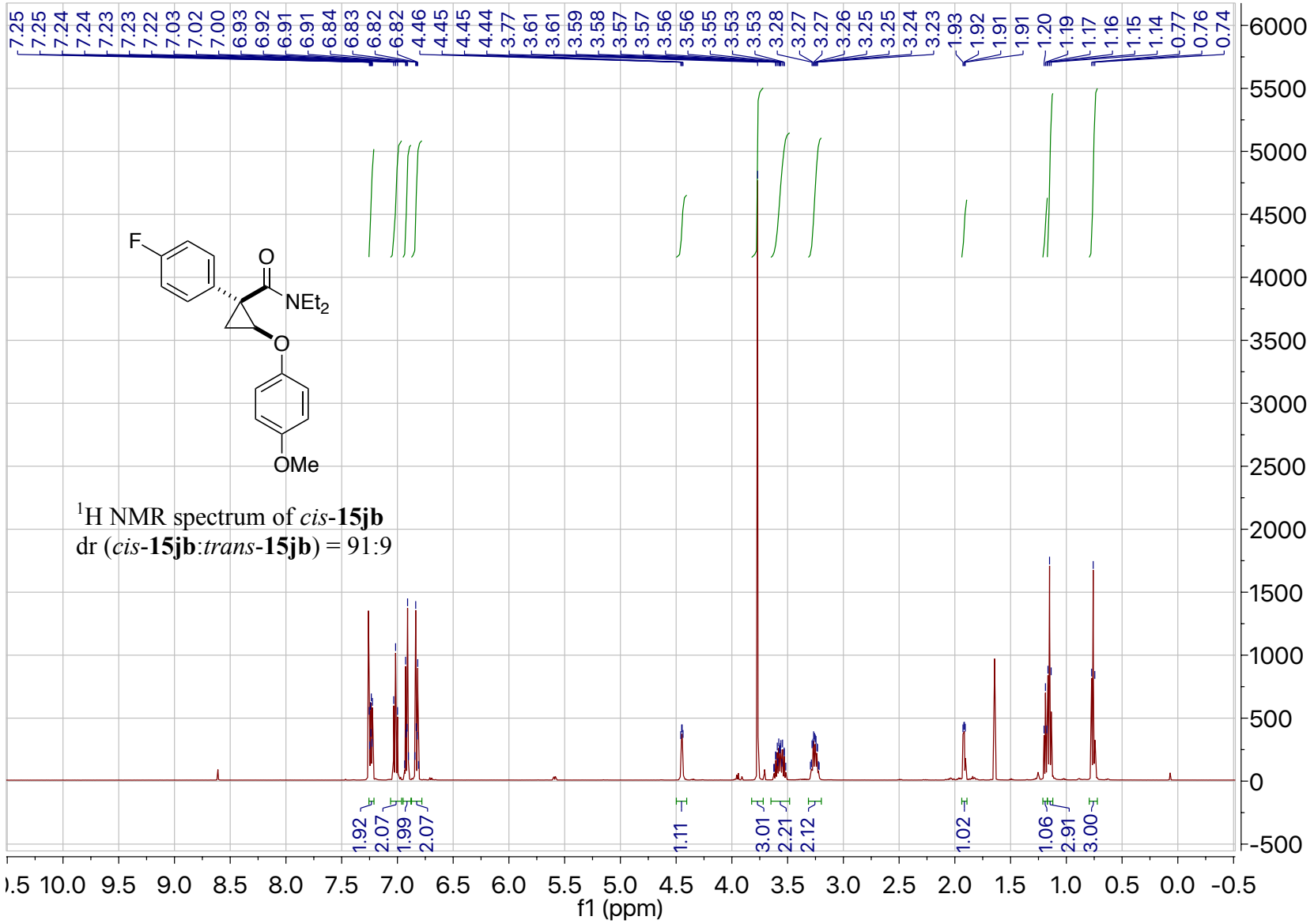


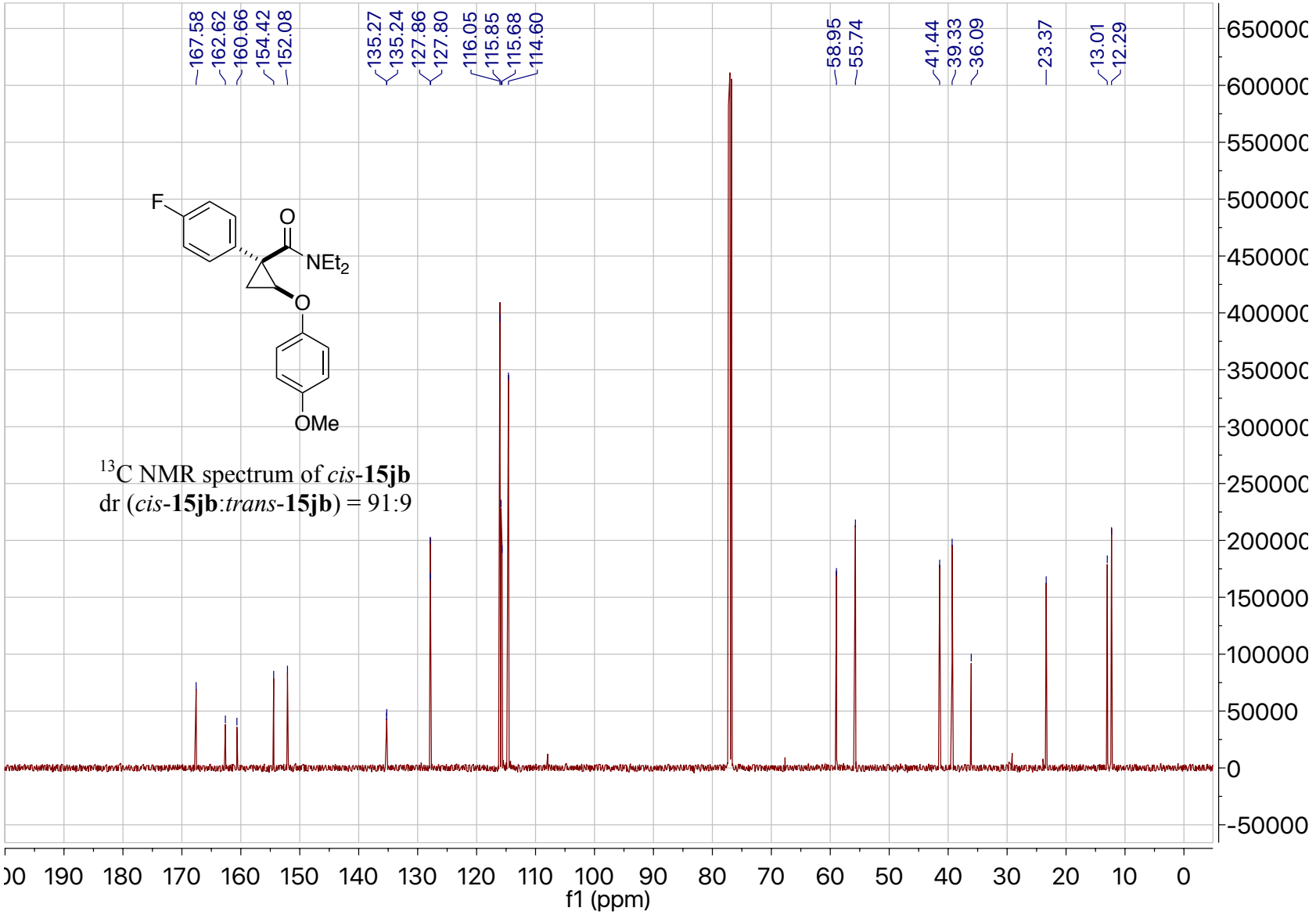
^{13}C NMR spectrum of *cis*-**15ea**
dr (*cis*-**15ea**:*trans*-**15ea**) = 88:12


7.30 7.30 7.29 7.29 7.28 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.04 7.03 7.03 7.02 7.01 7.00 7.00 6.99 6.99 6.98 6.98 6.98 4.51 4.50 4.50 4.49 3.62 3.60 3.59 3.57 3.57 3.56 3.56 3.30 3.28 3.27 3.26 3.26 3.25 3.24 1.94 1.94 1.93 1.92 1.24 1.23 1.22 1.17 1.16 1.15 0.78 0.77 0.75
F
O
NEt2
O
1H NMR spectrum of cis-15ja
dr (cis-15ja:trans-15ja) = 94:6
4.68 4.92 1.01 0.06 2.06 2.09 1.00 1.13 3.11 3.04
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0
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 -0.5
f1 (ppm)

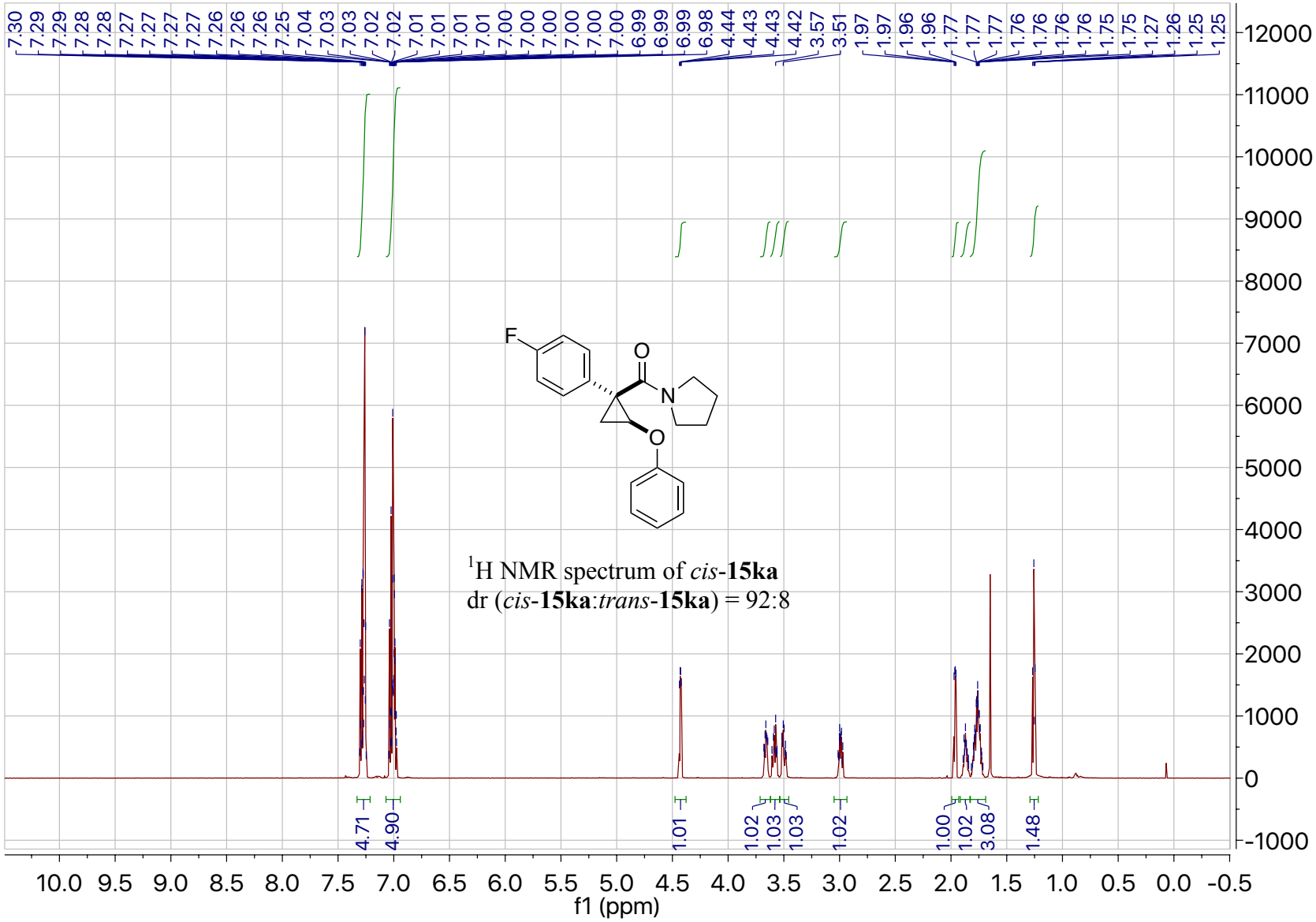


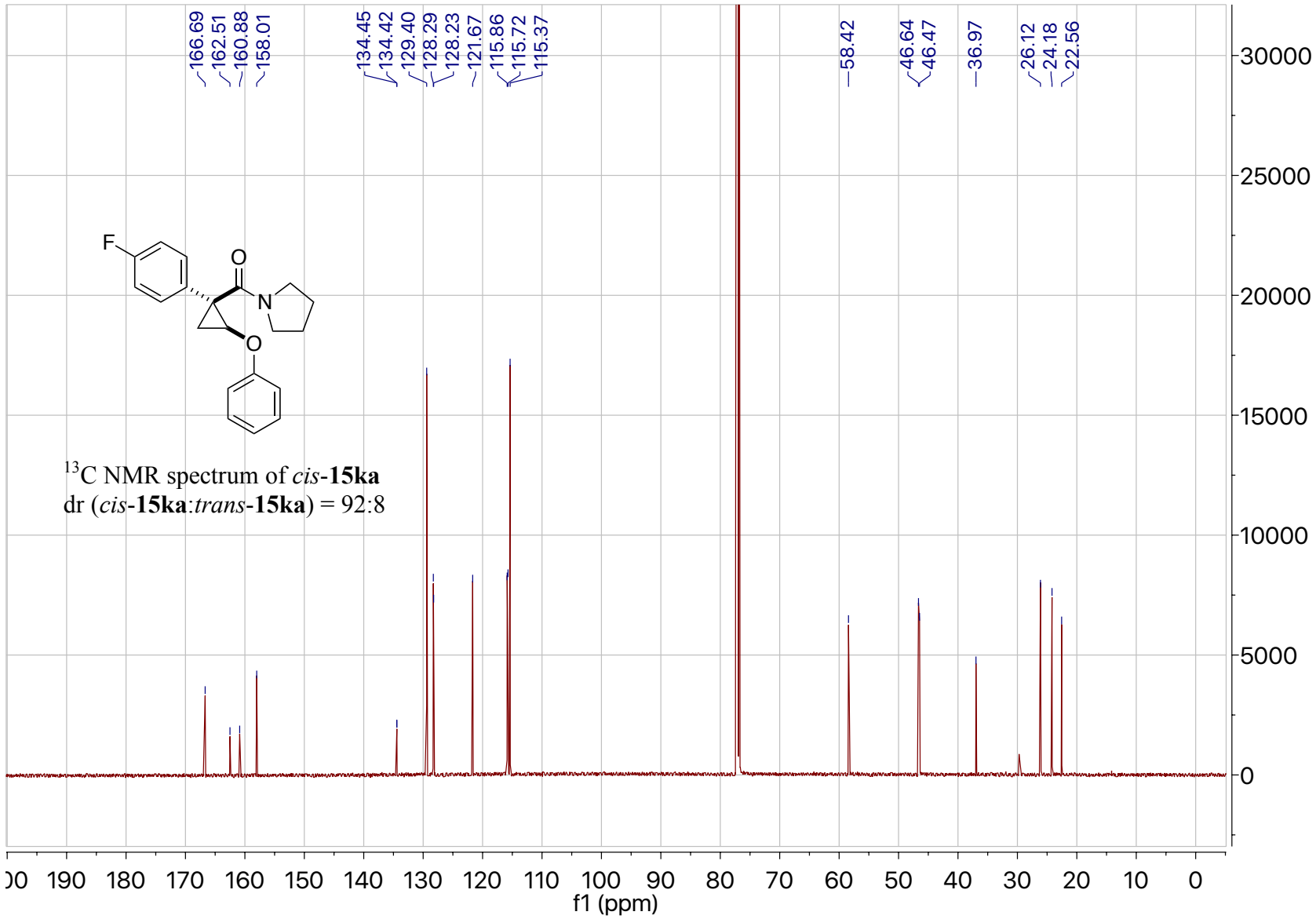
^{1}H NMR spectrum of *cis*-**15ja**
dr (*cis*-**15ja**:*trans*-**15ja**) = 94:6


F
O
NEt2
O
OMe
1H NMR spectrum of cis-15jb
dr (cis-15jb:trans-15jb) = 91:9
f1 (ppm)

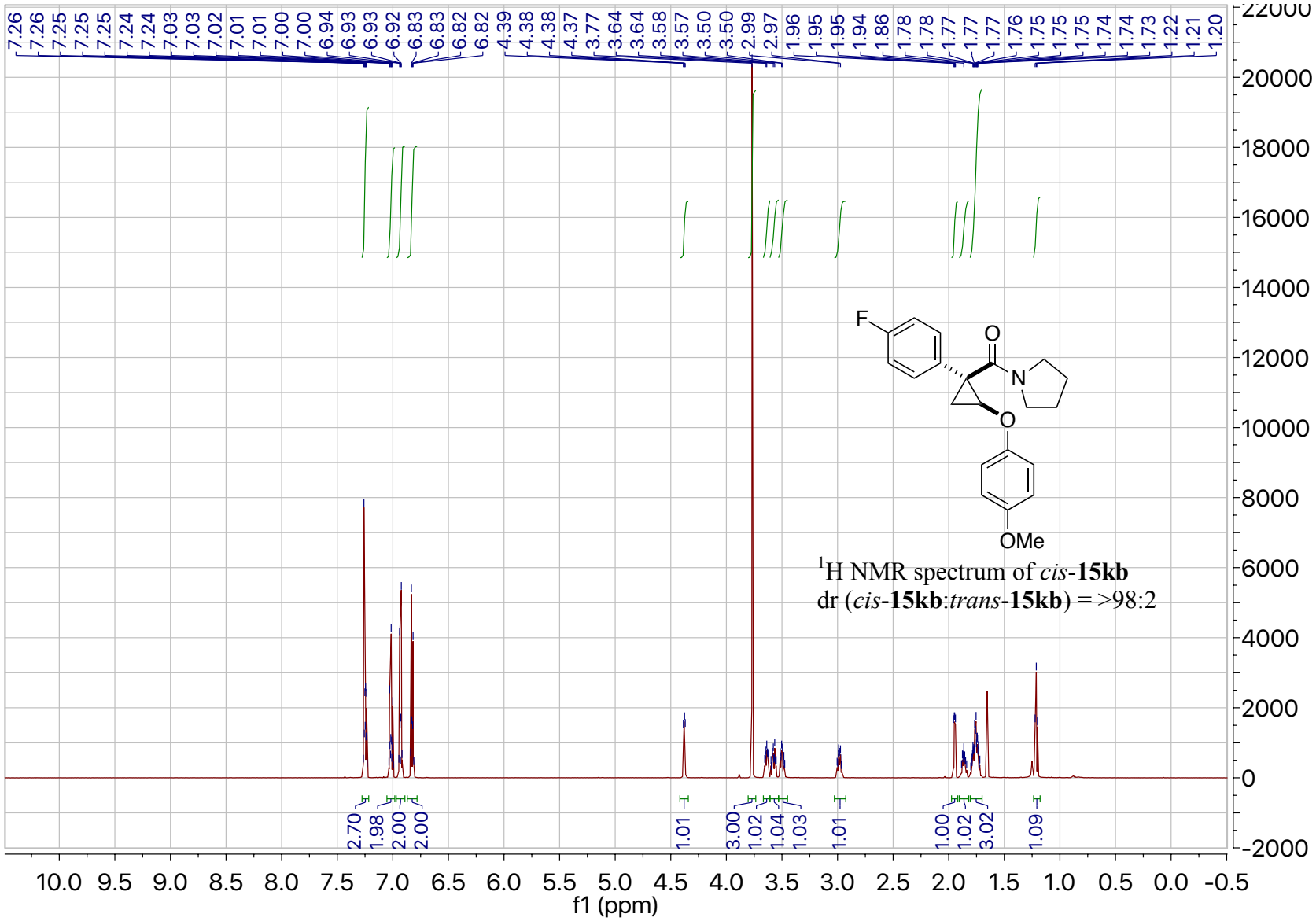


^{13}C NMR spectrum of *cis*-**15jb**
dr (*cis*-**15jb**:*trans*-**15jb**) = 91:9

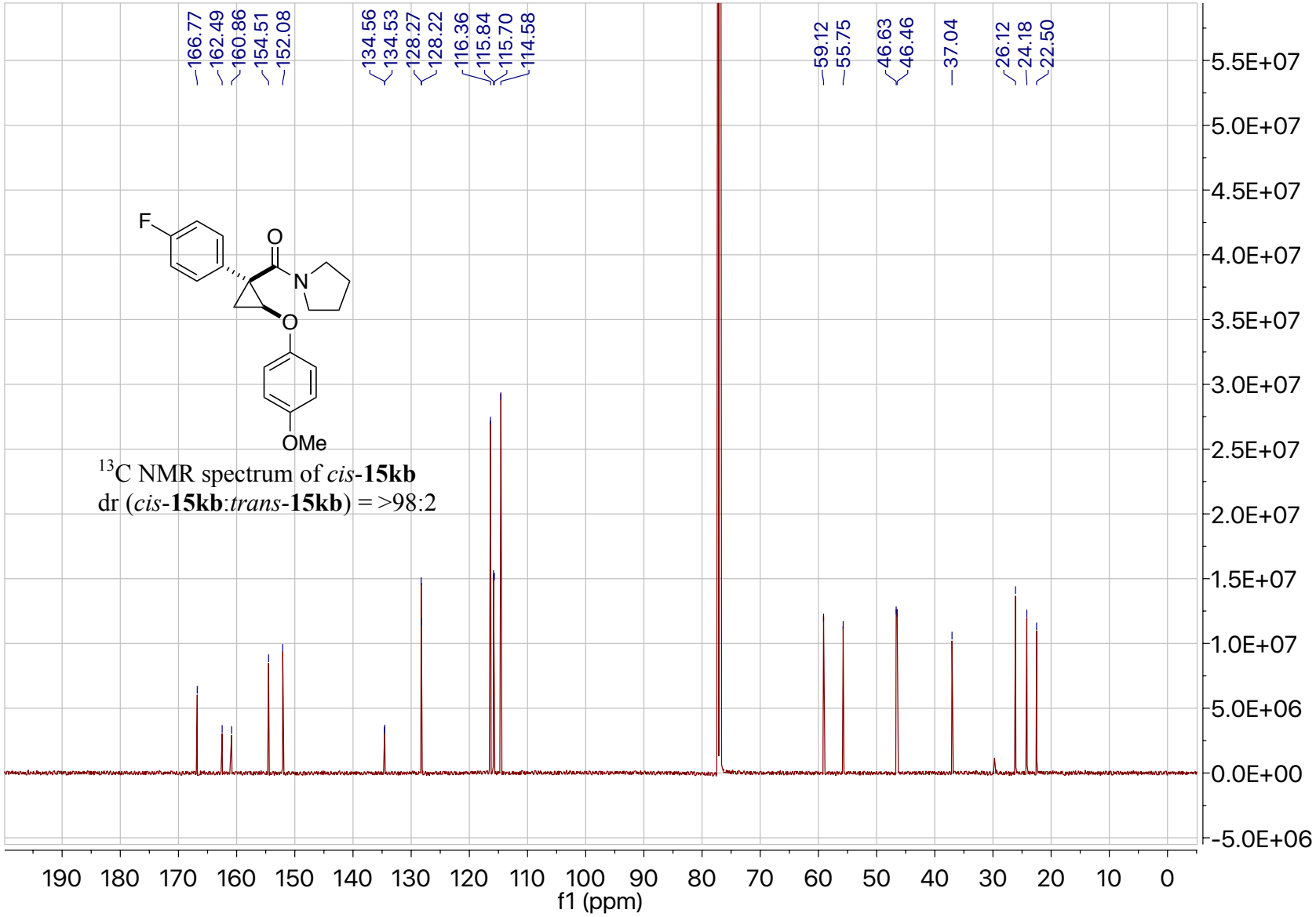

F
O
N
O
^{1}H NMR spectrum of *cis*-**15ka**
dr (*cis*-**15ka**:*trans*-**15ka**) = 92:8
f1 (ppm)



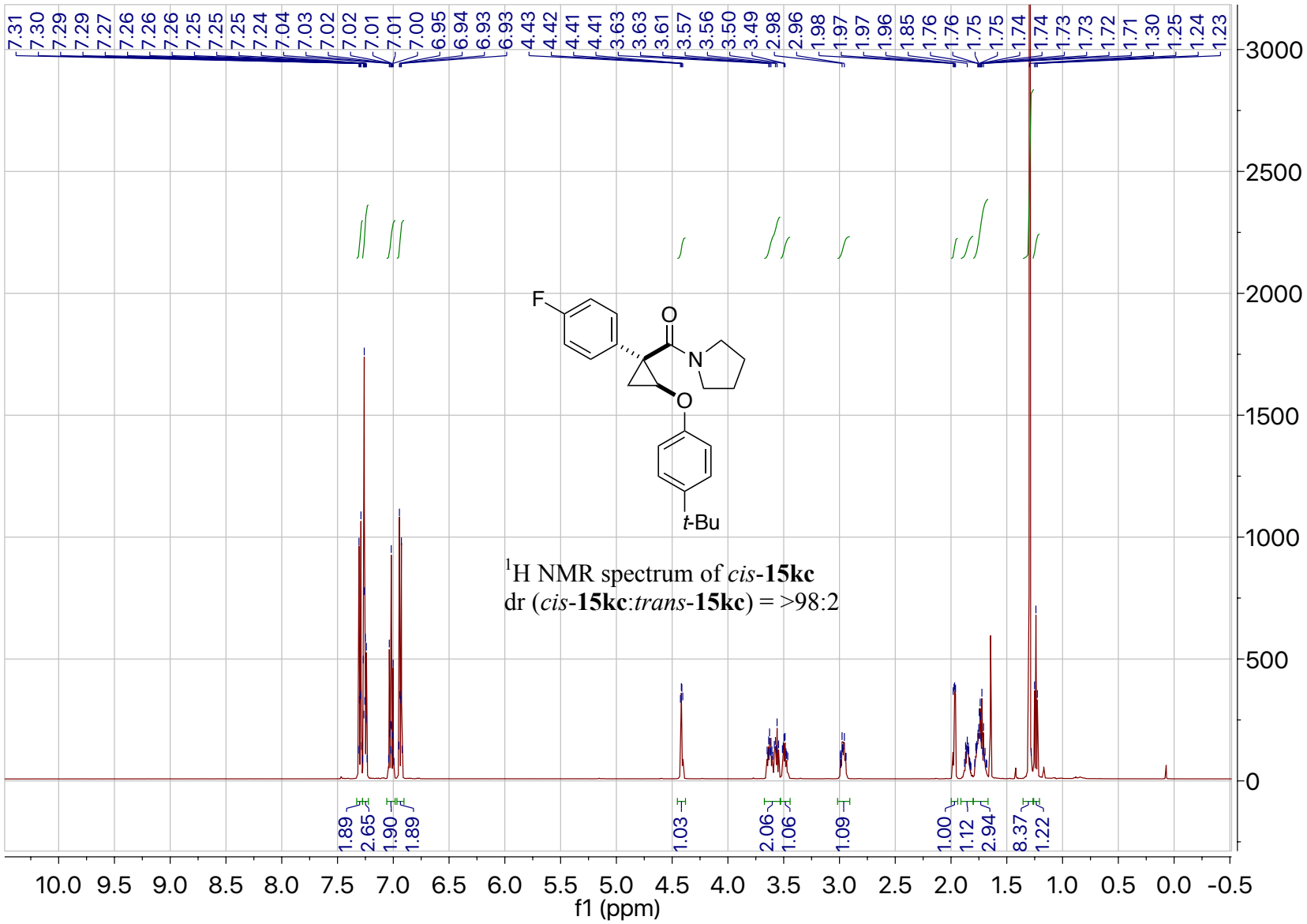
^{13}C NMR spectrum of *cis*-**15ka**
dr (*cis*-**15ka**:*trans*-**15ka**) = 92:8

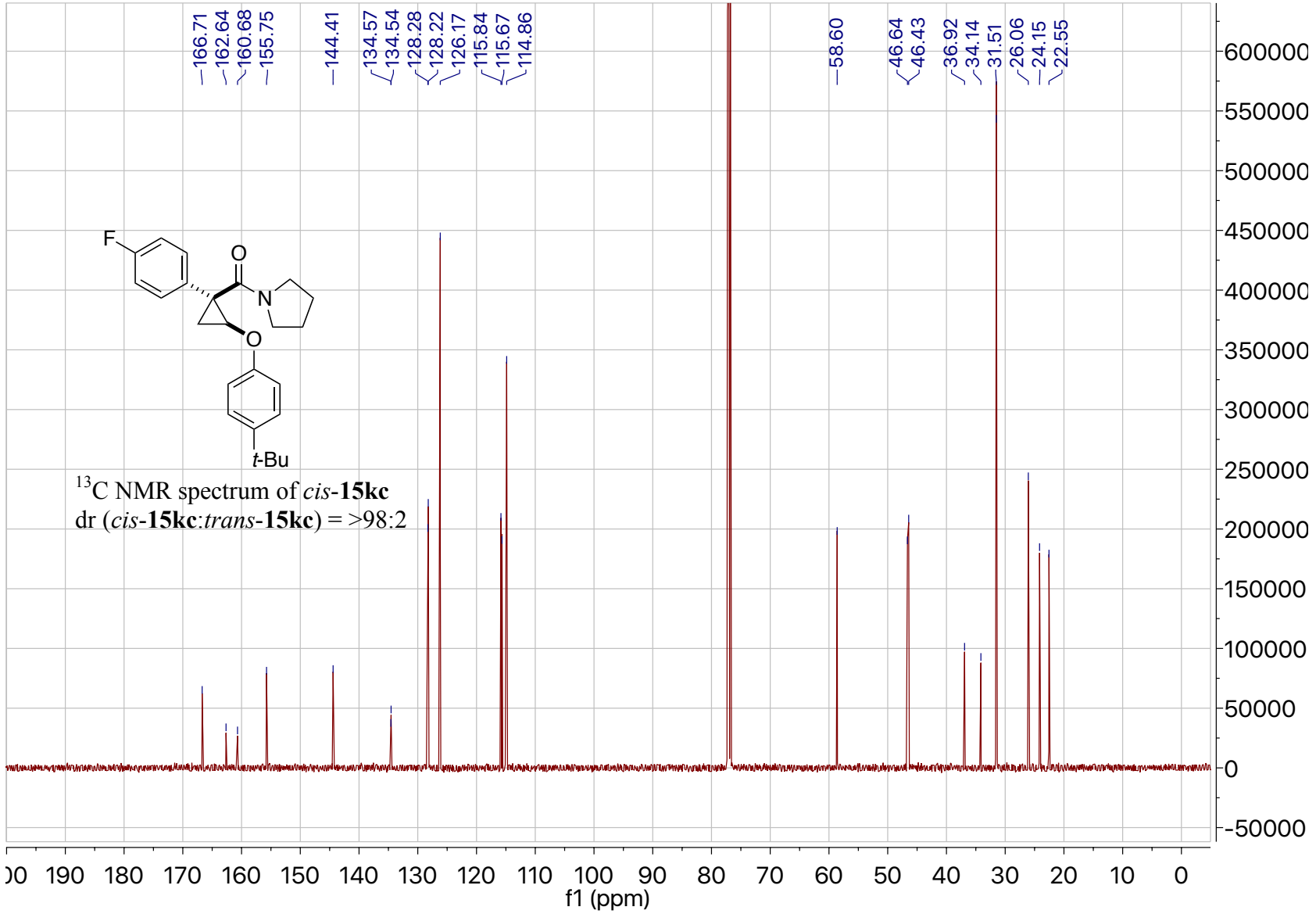


^{1}H NMR spectrum of *cis*-**15kb**
dr (*cis*-**15kb**:*trans*-**15kb**) = >98:2

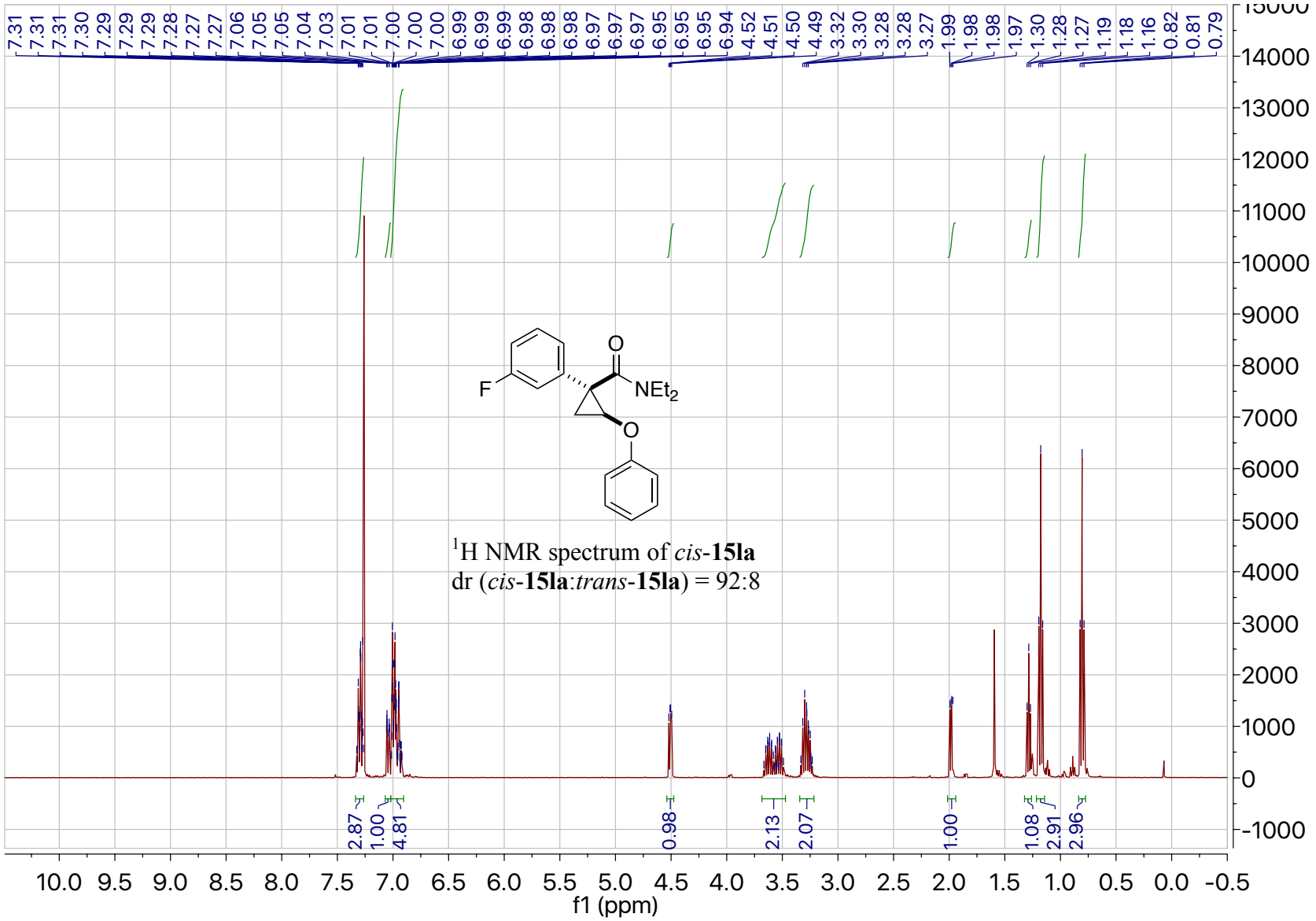


^{13}C NMR spectrum of *cis*-**15kb**
dr (*cis*-**15kb**:*trans*-**15kb**) = >98:2

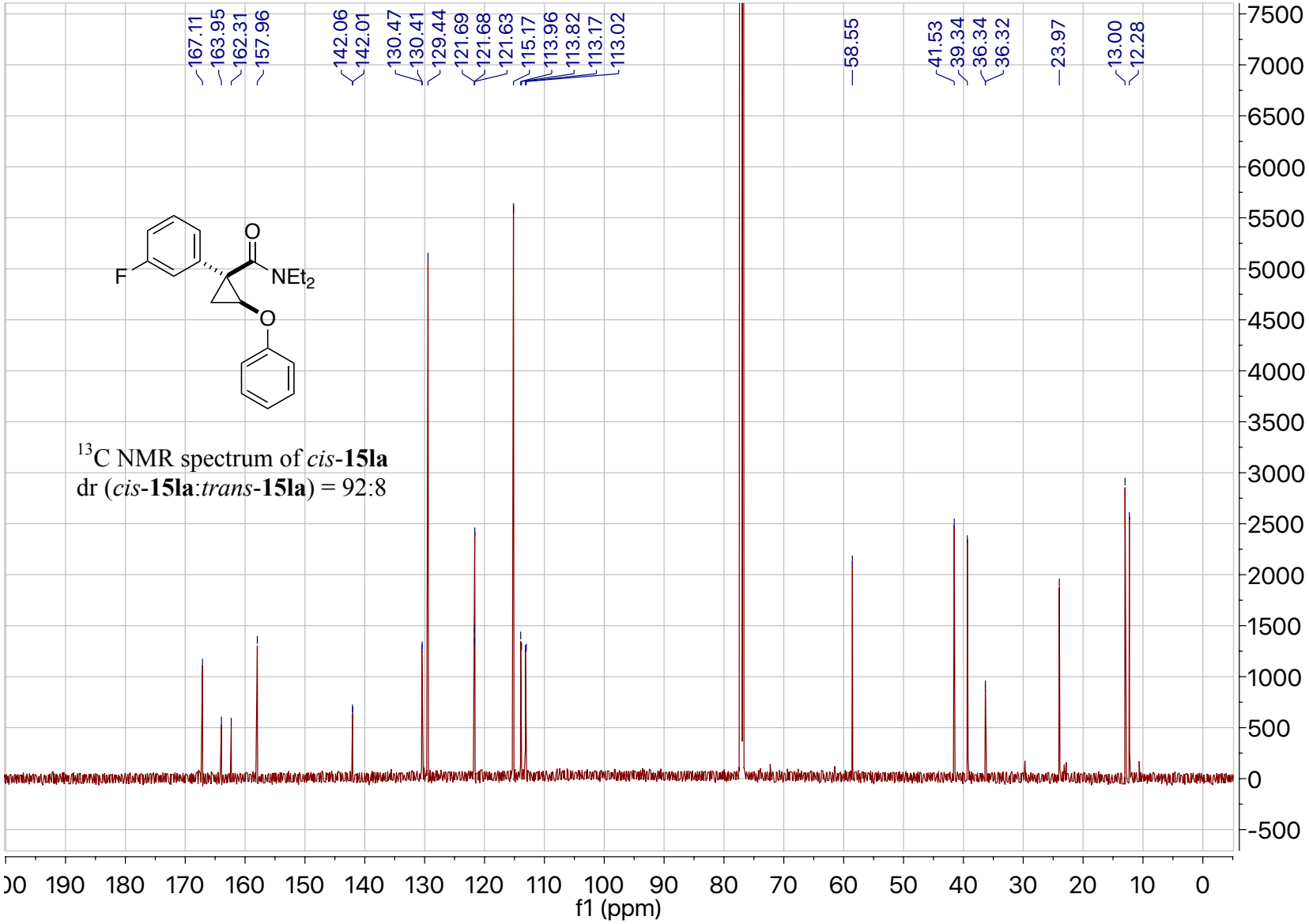

F
O
N
O
t-Bu
[1]H NMR spectrum of cis-15kc
dr (cis-15kc:trans-15kc) = >98:2
f1 (ppm)

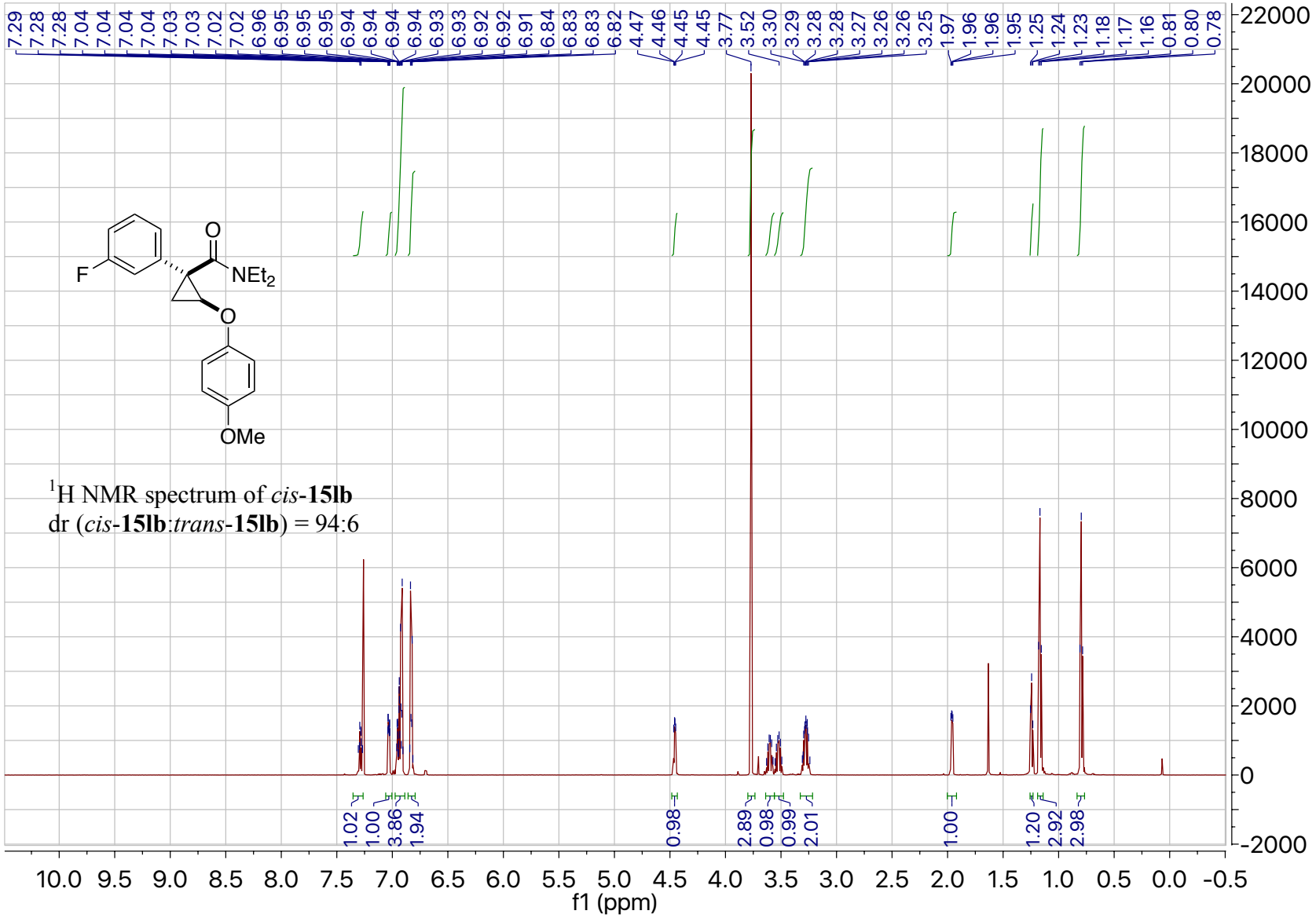


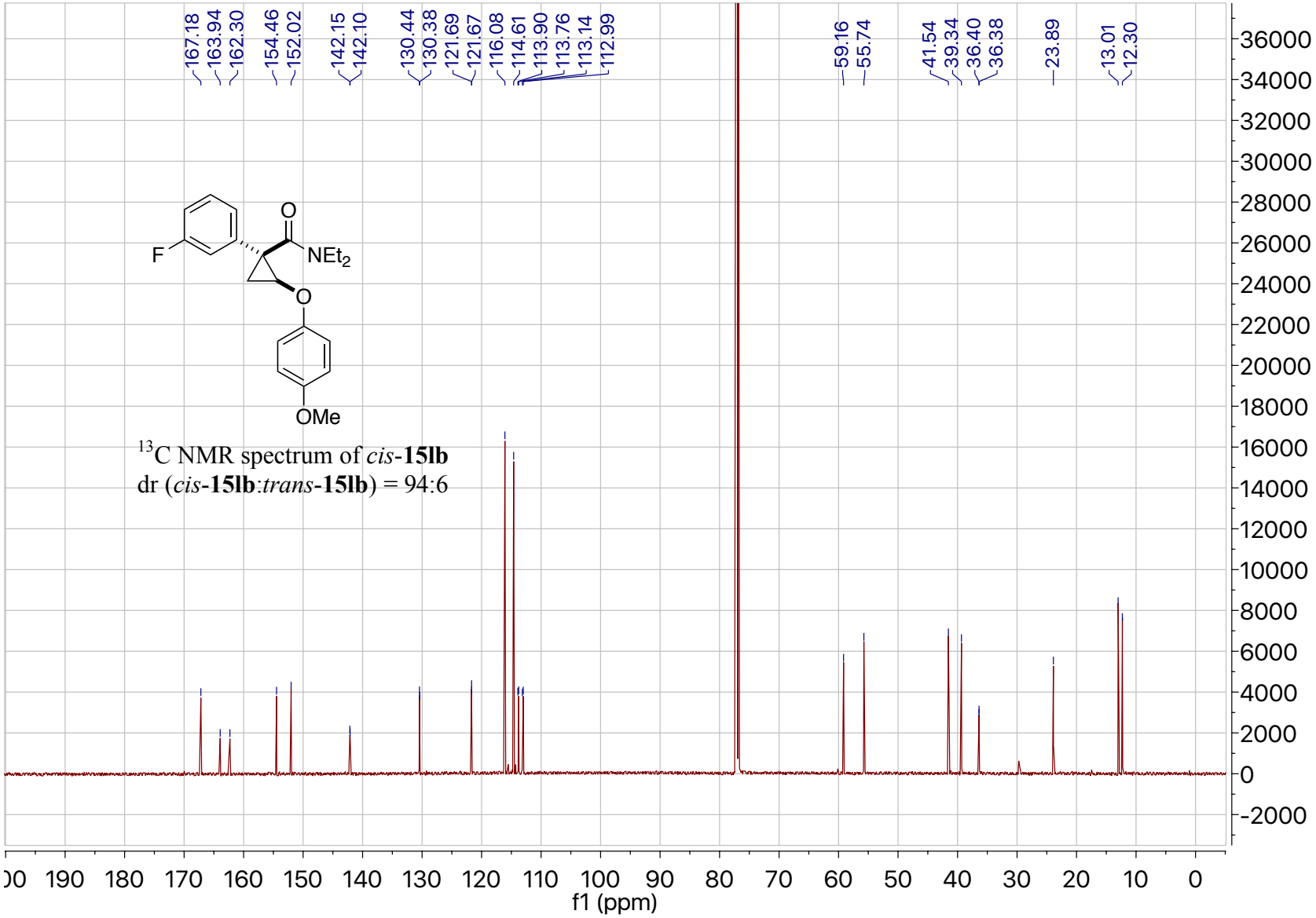
^{13}C NMR spectrum of *cis*-**15kc**
dr (*cis*-**15kc**:*trans*-**15kc**) = >98:2

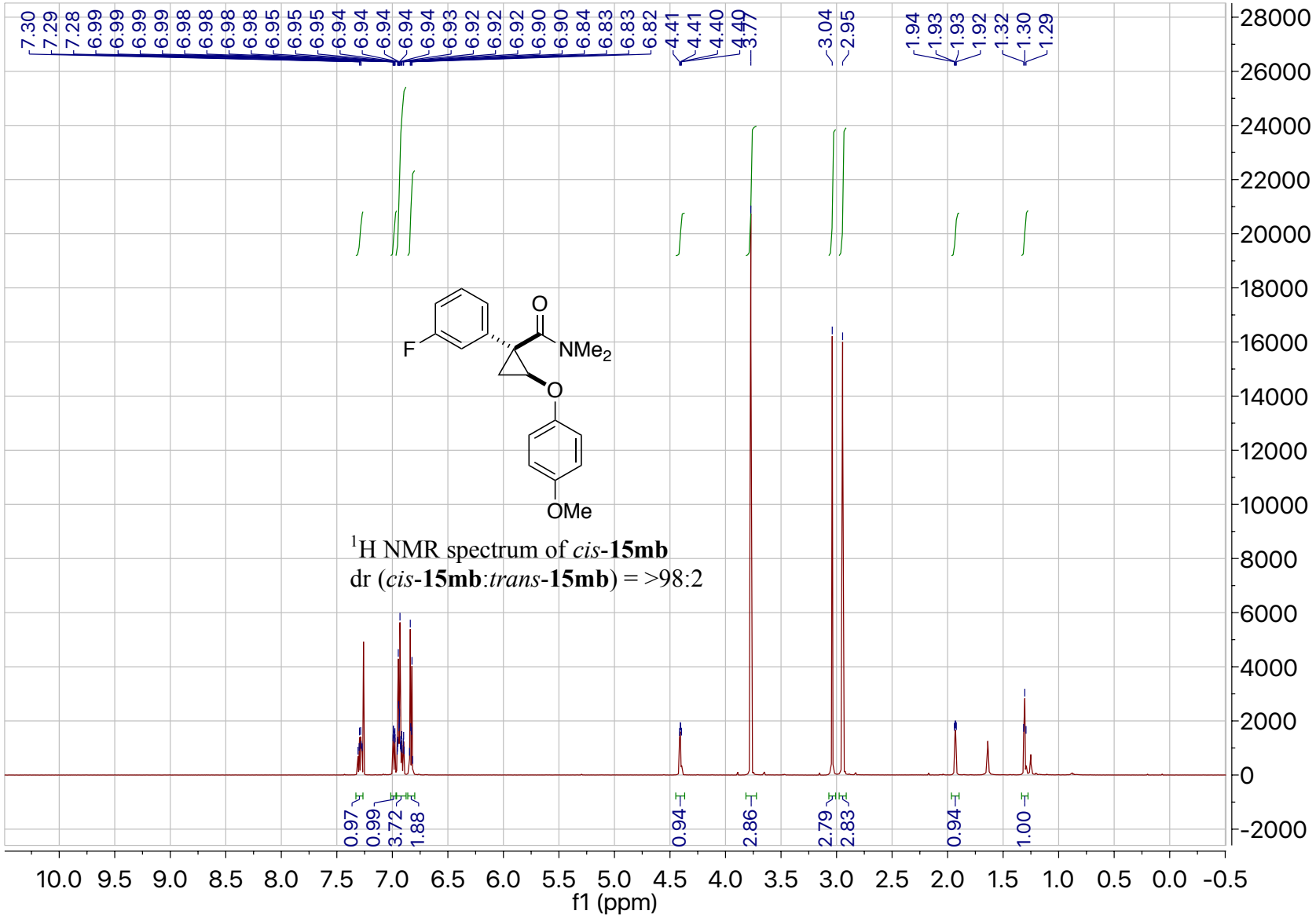


^{1}H NMR spectrum of *cis*-**15la**
dr (*cis*-**15la**:*trans*-**15la**) = 92:8

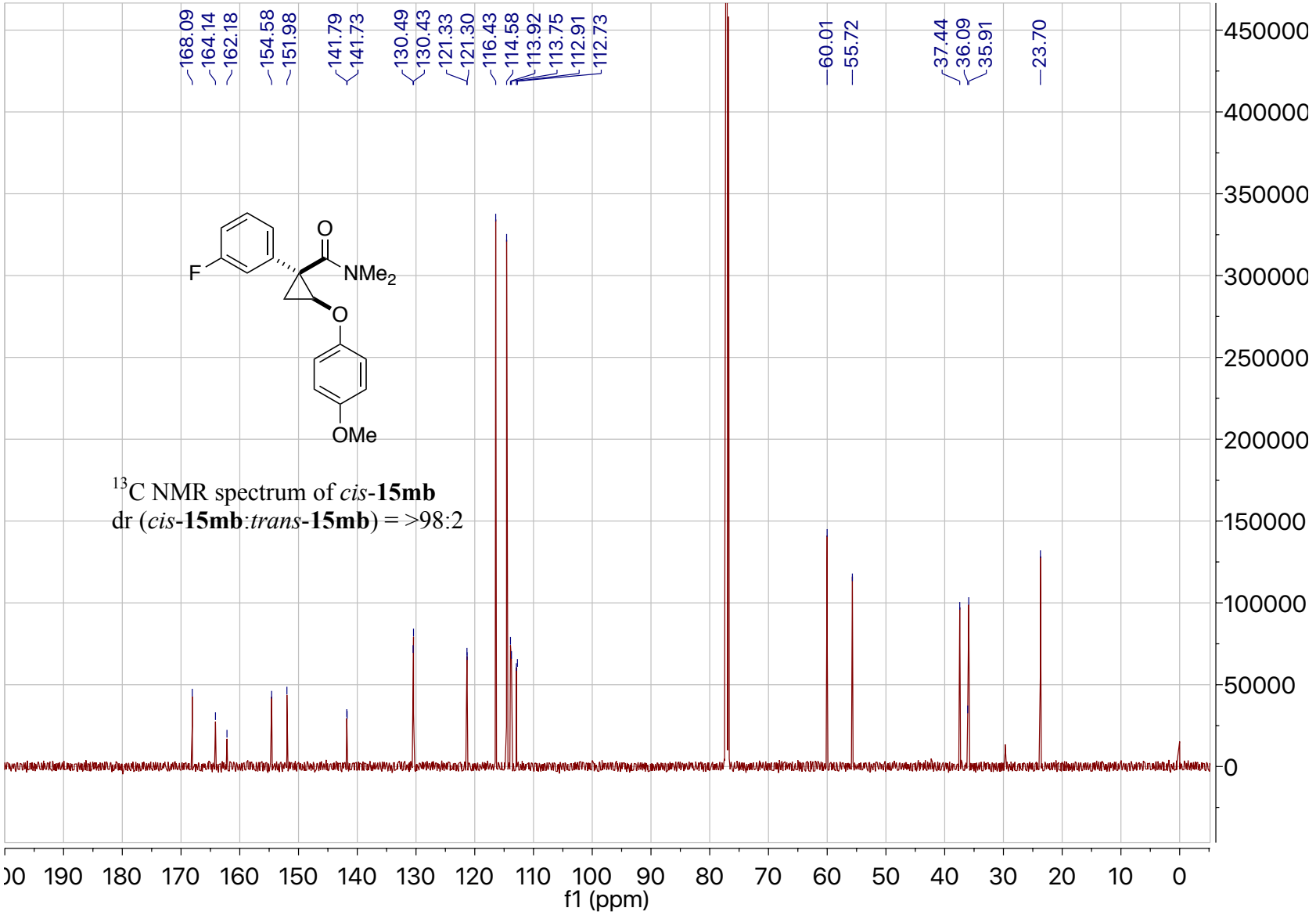

167.11
163.95
162.31
157.96
142.06
142.01
130.47
130.41
129.44
121.69
121.68
121.63
115.17
113.96
113.82
113.17
113.02
58.55
41.53
39.34
36.34
36.32
23.97
13.00
12.28
F
O
NEt2
O
13C NMR spectrum of cis-15la
dr (cis-15la:trans-15la) = 92:8
f1 (ppm)


F
O
NEt2
O
OMe
1H NMR spectrum of cis-15lb
dr (cis-15lb:trans-15lb) = 94:6
f1 (ppm)

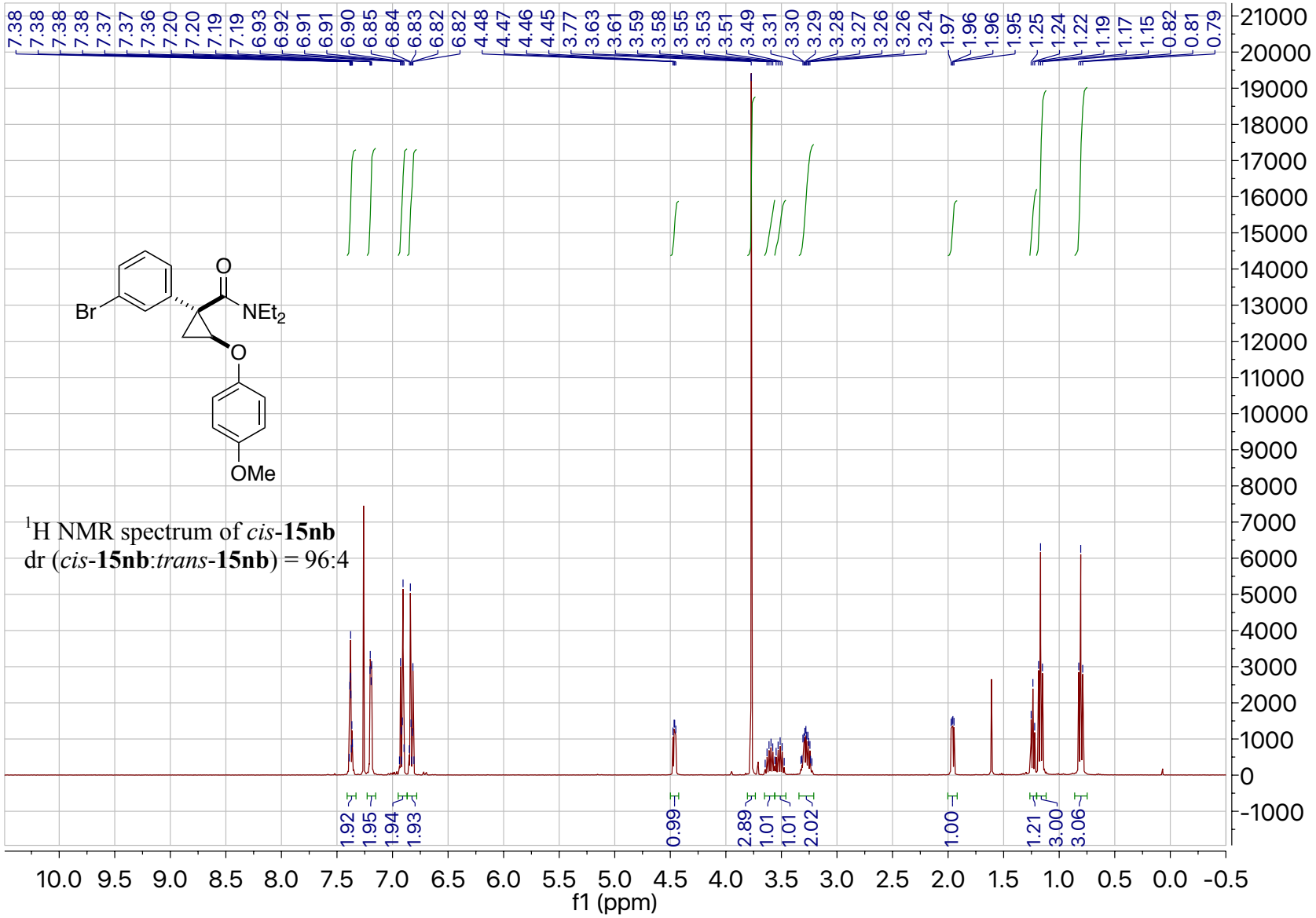

167.18
163.94
162.30
154.46
152.02
142.15
142.10
130.44
130.38
121.69
121.67
116.08
114.61
113.90
113.76
113.14
112.99
59.16
55.74
41.54
39.34
36.40
36.38
23.89
13.01
12.30
F
O
NEt2
O
OMe
13C NMR spectrum of cis-15lb
dr (cis-15lb:trans-15lb) = 94:6
f1 (ppm)

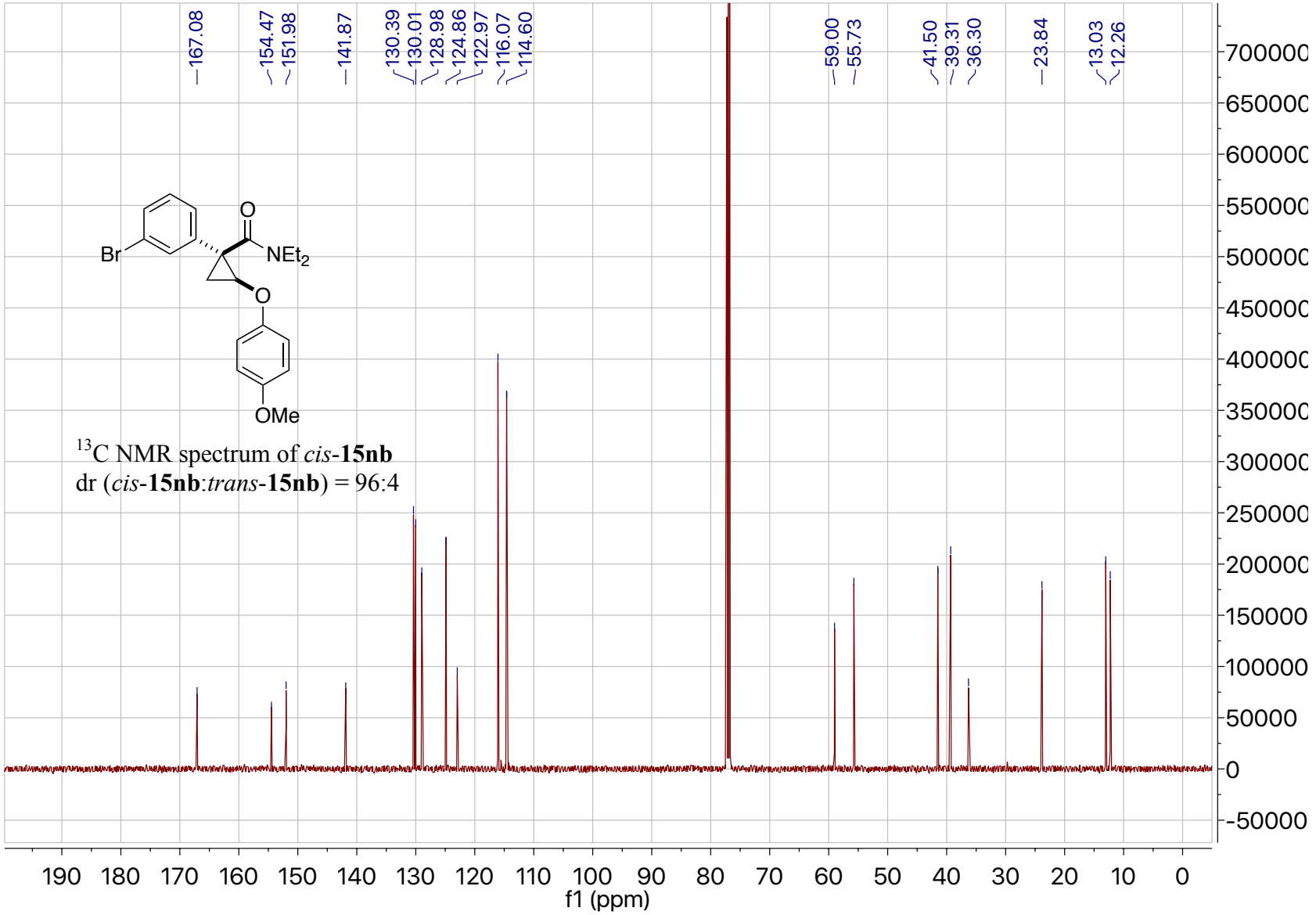


^{1}H NMR spectrum of *cis*-**15mb**
dr (*cis*-**15mb**:*trans*-**15mb**) = >98:2

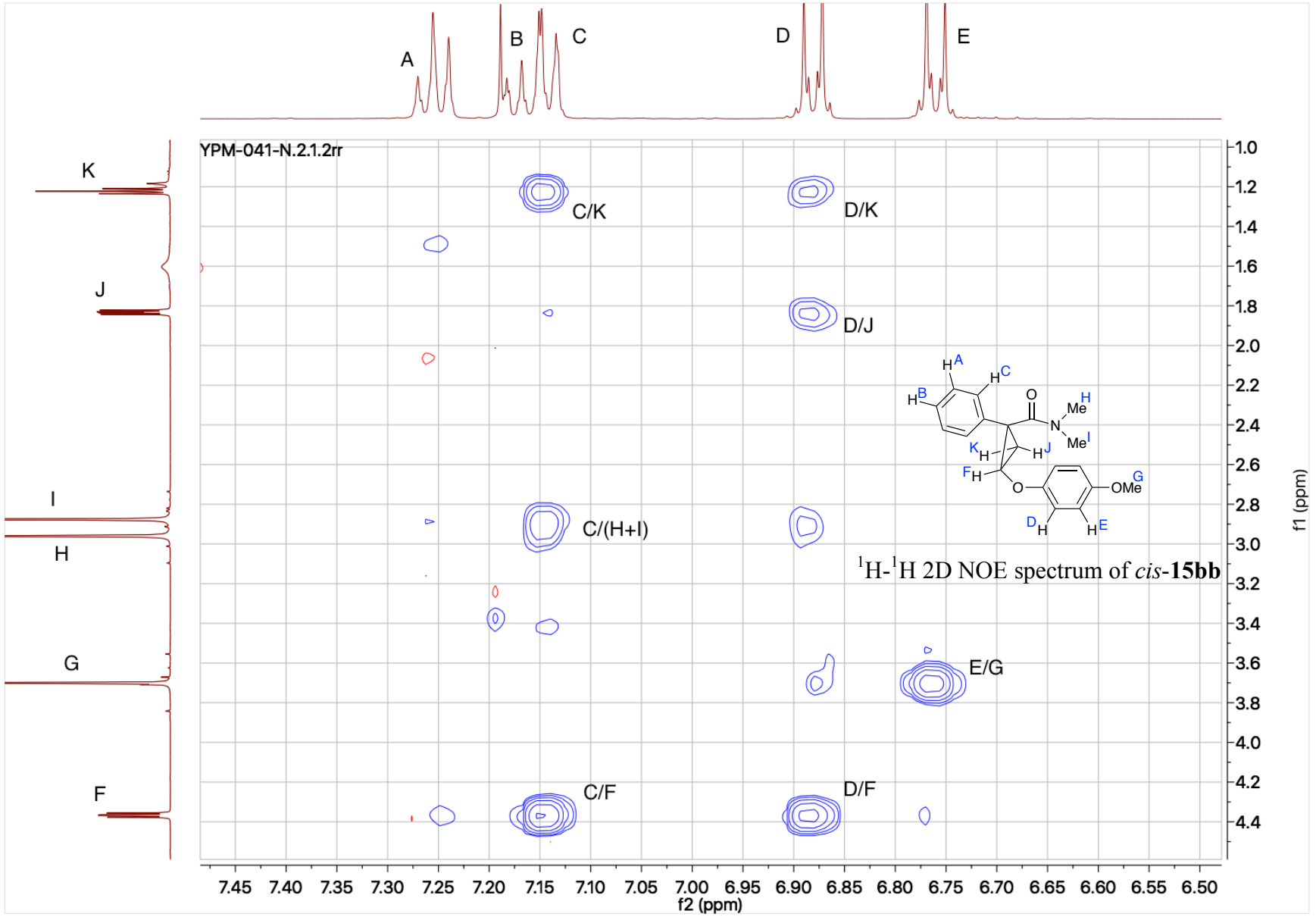


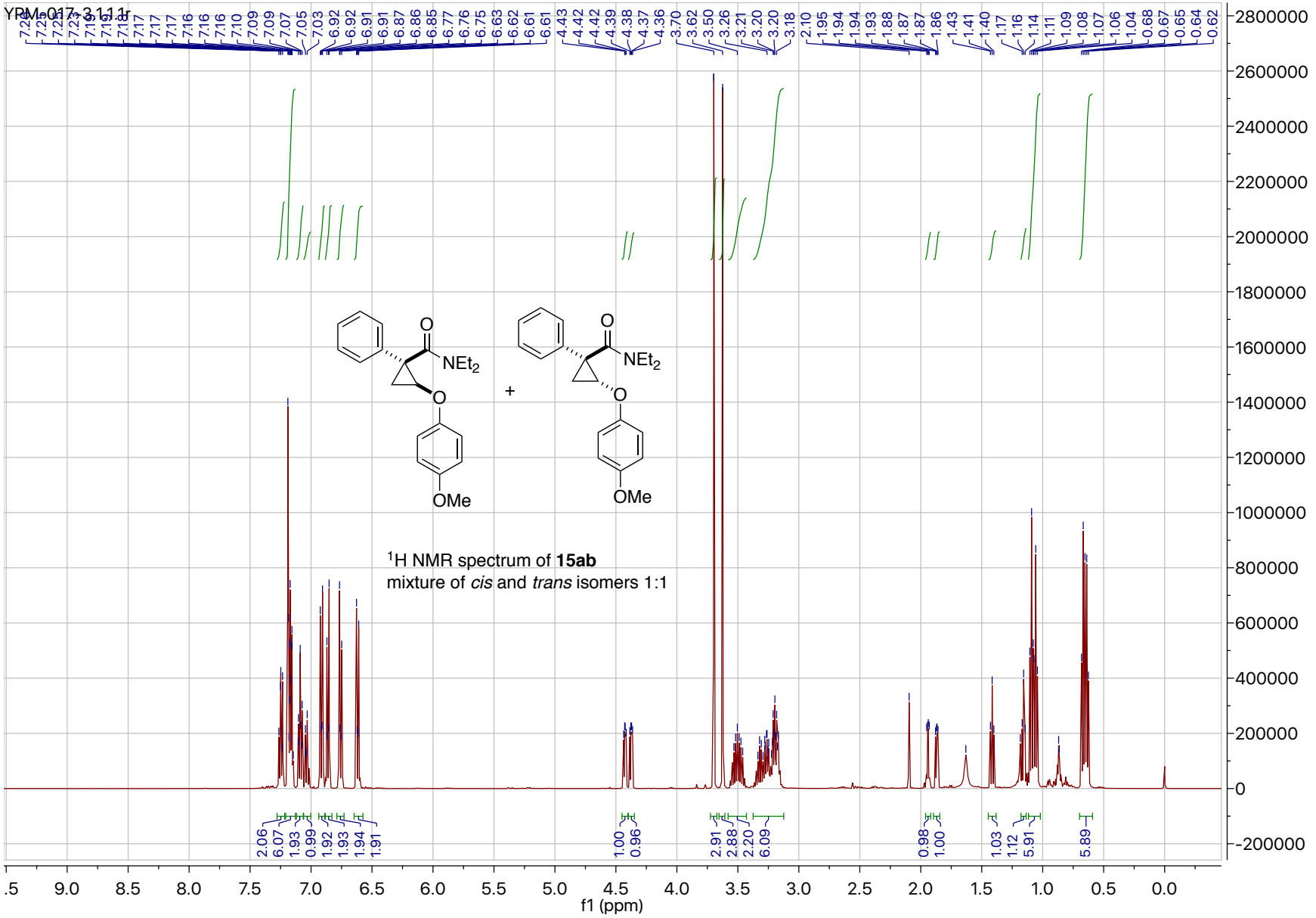
^{13}C NMR spectrum of *cis*-**15mb**
dr (*cis*-**15mb**:*trans*-**15mb**) = >98:2

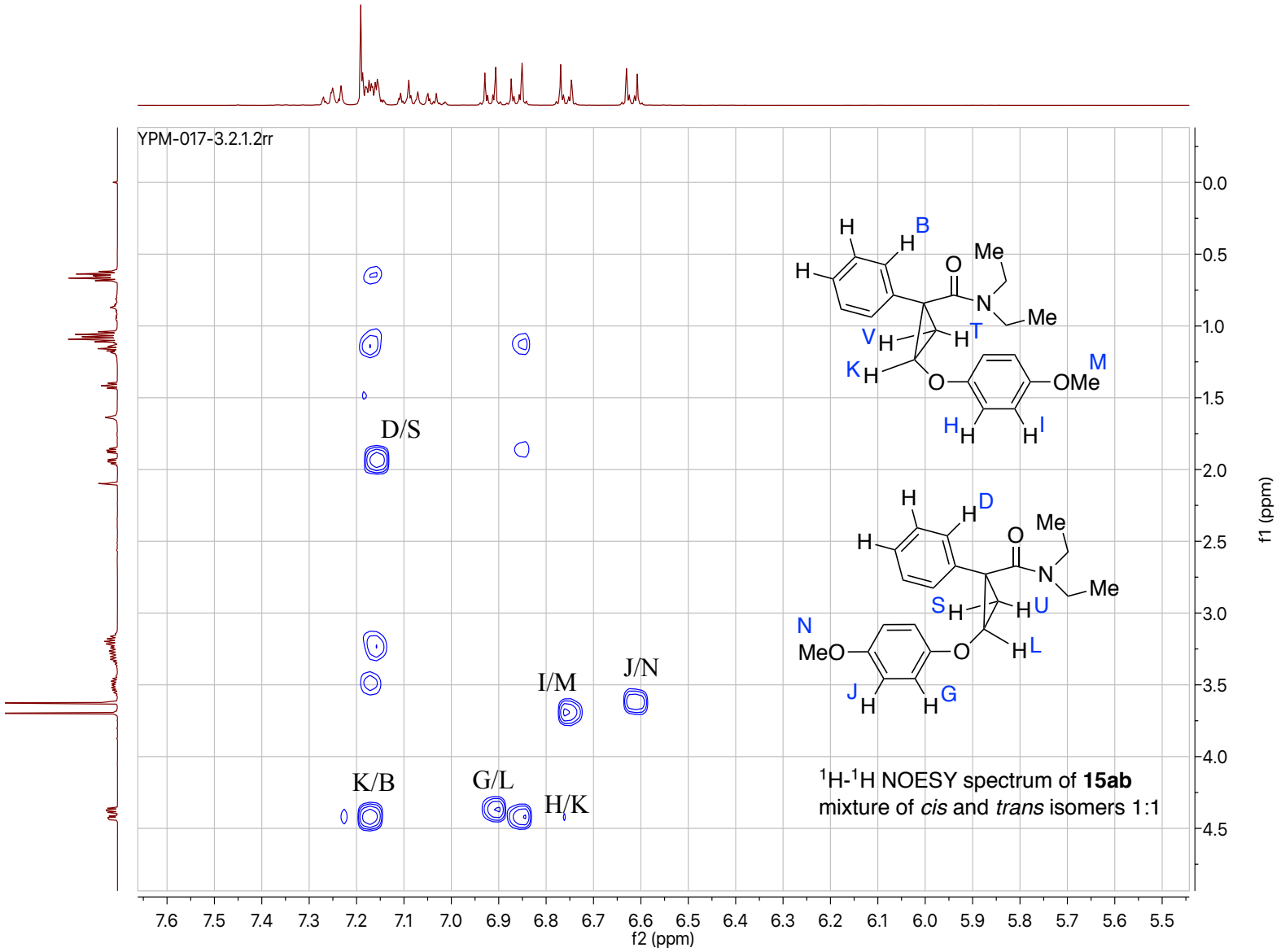

Br
O
NEt2
O
OMe
1H NMR spectrum of cis-15nb
dr (cis-15nb:trans-15nb) = 96:4
f1 (ppm)

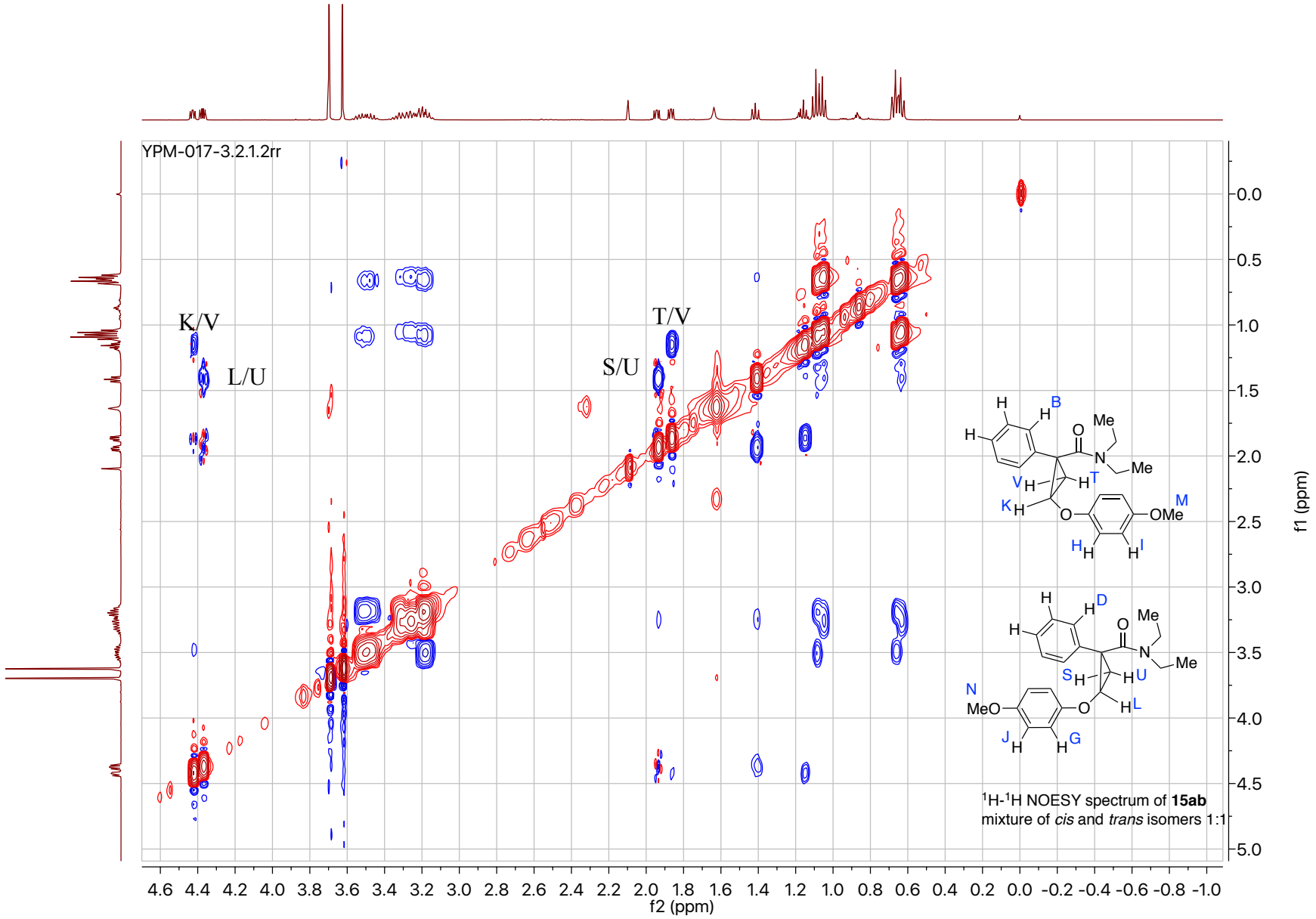


^{13}C NMR spectrum of *cis*-**15nb**
dr (*cis*-**15nb**:*trans*-**15nb**) = 96:4


A
B
C
D
E
K
J
I
H
G
F
YPM-041-N.2.1.2rr
C/K
D/K
D/J
C/(H+I)
E/G
C/F
D/F
^{1}H-^{1}H 2D NOE spectrum of *cis*-**15bb**
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60 6.55 6.50
f2 (ppm)
1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4
f1 (ppm)


YPM-017-3.1.11.fr
NEt2
O
OMe
+
1H NMR spectrum of 15ab
mixture of cis and trans isomers 1:1
f1 (ppm)


YPM-017-3.2.1.2rr
D/S
I/M
J/N
K/B
G/L
H/K
f2 (ppm)
f1 (ppm)
^{1}H-^{1}H NOESY spectrum of **15ab**
mixture of *cis* and *trans* isomers 1:1


YPM-017-3.2.1.2rr
K/V
L/U
S/U
T/V
f2 (ppm)
f1 (ppm)
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4 -0.6 -0.8 -1.0
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
Me
O
N
Me
OMe
MeO
B
D
M
N
^{1}H-^{1}H NOESY spectrum of **15ab**
mixture of *cis* and *trans* isomers 1:1

Preparation of 15ab as a mixture of *cis*- and *trans*-isomers (1:1) used in ^{1}H-^{1}H 2D NOESY studies (see pages S61-S63).

An oven dried round bottom flask was flushed with nitrogen and charged with *N*,*N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (50 mg, 0.232 mmol) , 4-methoxyphenol (37 mg, 0.301 mmol), potassium hydroxide (19 mg, 0.348 mmol) and freshly distilled DMSO (1.0 mL). Reaction mixture was stirred overnight (c.a. 15 h) at 90 ^{o}C under nitrogen atmosphere. When the reaction was complete (controlled by GC) reaction mixture was poured on ice and extracted with EtOAc, organic layer was washed with water three times and then with 3M KOH solution another three times, dried over $MgSO_4$ and concentrated under reduced pressure. Resulted brown oil was fractioned on silica gel to afford 24.1 mg (31% yield) diastereomeric mixture of desired compound.

X-Ray studies of 15db

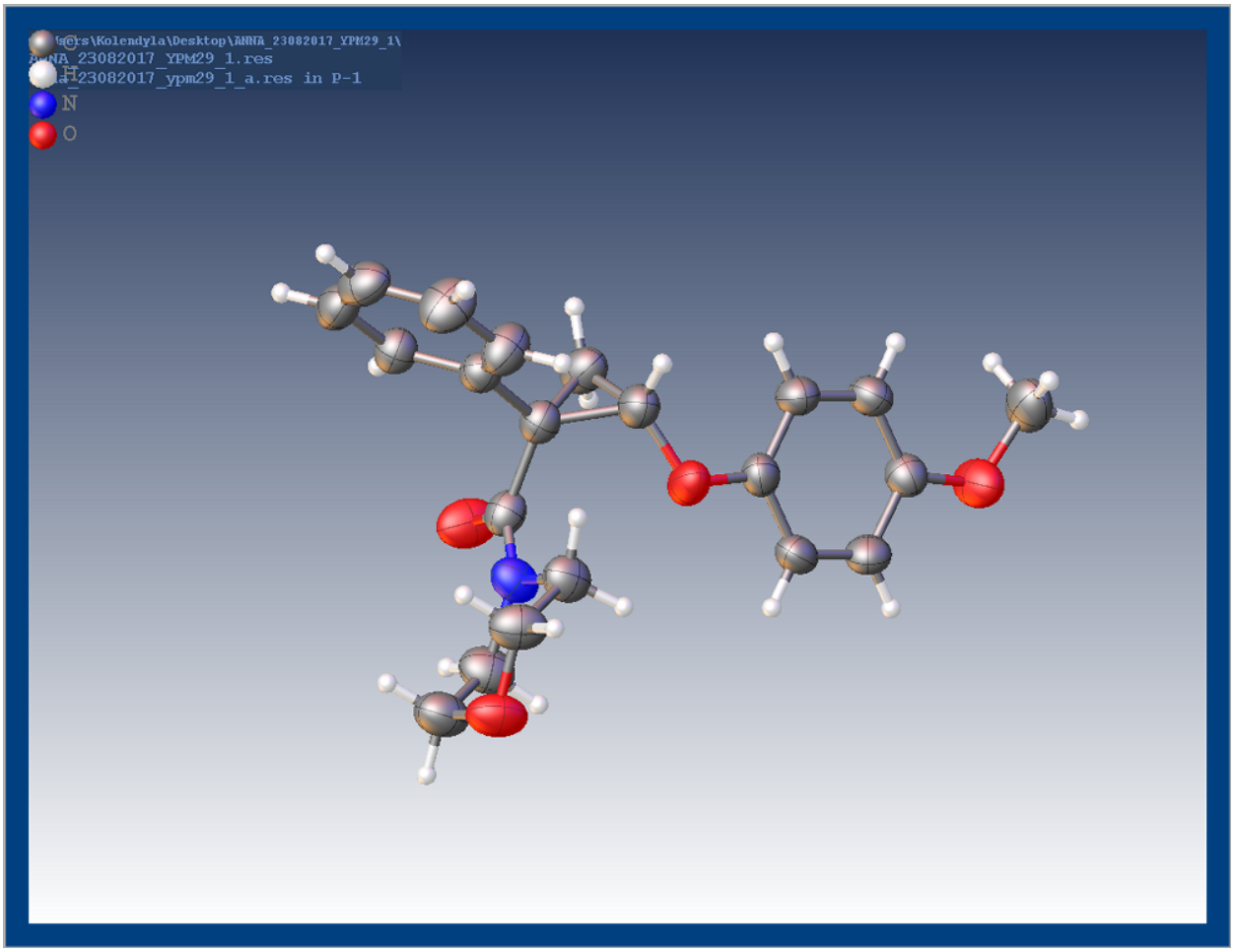


Table 1 Crystal data and structure refinement for *cis*-15db.

Identification code	ANNA_23082017_YPM29_1
Empirical formula	$C_{21}H_{23}NO_4$
Formula weight	353.40
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.4667(5)
b/Å	10.5554(6)
c/Å	10.6002(6)
α/°	62.334(6)
β/°	83.248(5)
γ/°	79.062(5)
Volume/Å^3	920.55(10)
Z	2
ρ_{calc}g/cm^3	1.275
μ/mm^{-1}	0.715
F(000)	376.0
Crystal size/mm^3	0.562 × 0.3 × 0.247
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.426 to 136.45
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -12 ≤ l ≤ 9
Reflections collected	8033
Independent reflections	3369 [R_{int} = 0.0172, R_{sigma} = 0.0176]
Data/restraints/parameters	3369/0/237
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1119
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.1163
Largest diff. peak/hole / e Å^{-3}	0.26/-0.16

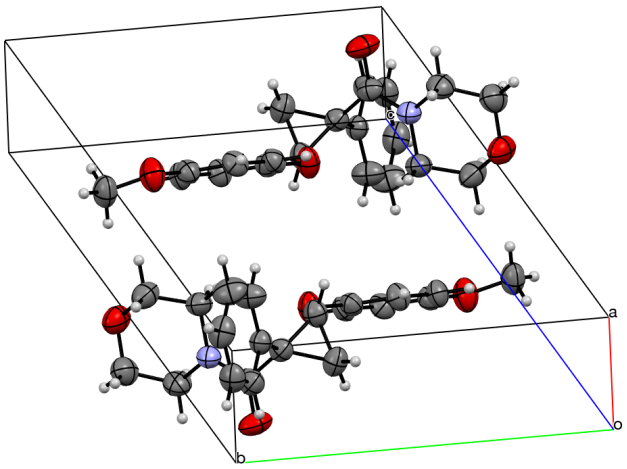


Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for *cis*-15db. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	5071.9(11)	3706.6(11)	7169.7(13)	57.0(3)
O3	5981.5(14)	-1147.9(13)	6711.2(12)	66.9(3)
O4	618.9(12)	6952.8(13)	8734.5(14)	65.8(3)
O1	7352.6(14)	683.0(14)	9756.8(11)	67.8(4)
N1	6605.9(15)	596.5(13)	7871.7(12)	50.1(3)
C4	7161.9(15)	1257.4(16)	8475.0(14)	45.0(3)
C9	4042.1(15)	4605.0(14)	7542.2(15)	44.6(3)
C10	2757.2(16)	4083.3(15)	8095.8(15)	47.9(3)
C16	9051.9(15)	2634.6(15)	6726.5(15)	43.9(3)
C12	1801.1(16)	6233.5(15)	8329.8(15)	46.8(3)
C2	7629.8(15)	2722.3(15)	7506.8(15)	44.4(3)
C17	10272.3(16)	1908.6(16)	7520.9(16)	50.1(4)
C13	3079.9(16)	6759.3(15)	7777.2(16)	49.5(4)
C11	1650.6(16)	4882.2(16)	8495.8(16)	50.5(4)
C14	4207.0(16)	5943.0(15)	7382.2(16)	49.7(4)
C1	6486.2(16)	4027.6(16)	6888.6(17)	51.1(4)
C8	6181.5(19)	1234.3(17)	6395.1(15)	54.4(4)
C21	9190.3(18)	3218(2)	5263.0(17)	62.3(4)
C18	11600.4(17)	1775.4(18)	6861.7(19)	57.2(4)
C3	7307.9(17)	3796.9(18)	8113.1(18)	55.9(4)
C19	11725.3(18)	2367.8(19)	5400.4(19)	61.8(4)
C7	6590(2)	134.1(19)	5844.4(17)	62.8(4)
C5	6064(2)	-776.5(18)	8770.2(17)	62.6(4)
C15	628(2)	8432.4(19)	8357(2)	67.7(5)
C6	6481(2)	-1789.4(19)	8121.2(19)	66.5(5)
C20	10525(2)	3082(2)	4605.1(19)	71.1(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *cis*-15db. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	41.4(5)	53.9(6)	85.7(8)	-41.3(6)	-3.7(5)	-2.5(4)
O3	85.4(9)	65.5(7)	59.5(7)	-28.7(6)	-1.3(6)	-33.5(6)
O4	56.7(7)	60.0(7)	84.2(8)	-39.8(6)	17.7(6)	-9.7(5)
O1	79.7(8)	85.4(8)	37.9(6)	-19.9(5)	-2.7(5)	-33.1(7)
N1	65.4(8)	44.0(6)	38.8(6)	-16.0(5)	-3.6(5)	-9.9(6)
C4	38.9(7)	54.5(8)	39.6(7)	-20.7(6)	-0.1(5)	-4.9(6)

C9	42.7(7)	40.5(7)	48.2(7)	-18.9(6)	-6.9(6)	-1.1(6)
C10	51.4(8)	35.8(7)	52.9(8)	-15.2(6)	-5.8(6)	-9.4(6)
C16	43.2(7)	43.8(7)	47.3(7)	-22.5(6)	-0.7(6)	-8.2(6)
C12	47.8(8)	44.6(7)	44.8(7)	-18.7(6)	2.1(6)	-6.2(6)
C2	40.7(7)	48.8(8)	45.5(7)	-23.3(6)	-2.5(6)	-4.9(6)
C17	47.2(8)	53.5(8)	51.3(8)	-25.9(7)	-3.2(6)	-5.1(6)
C13	52.1(8)	40.1(7)	57.2(8)	-22.2(6)	1.2(7)	-10.4(6)
C11	47.8(8)	46.4(8)	51.6(8)	-15.9(6)	4.4(6)	-15.1(6)
C14	44.2(8)	45.2(7)	59.3(9)	-22.5(7)	2.7(6)	-12.4(6)
C1	44.4(8)	48.2(8)	61.8(9)	-26.5(7)	-1.3(6)	-5.3(6)
C8	64.1(10)	52.7(8)	43.7(8)	-17.6(7)	-8.3(7)	-10.5(7)
C21	50.9(9)	78.1(11)	48.2(8)	-20.7(8)	-2.2(7)	-9.0(8)
C18	42.6(8)	60.8(9)	73.7(10)	-36.1(8)	-3.3(7)	-4.8(7)
C3	48.3(8)	63.6(9)	68.9(10)	-41.5(8)	0.6(7)	-8.6(7)
C19	48.1(9)	71.8(10)	76.7(11)	-43.6(9)	13.8(8)	-17.5(8)
C7	77.9(11)	68.3(10)	50.6(9)	-29.2(8)	3.5(8)	-27.9(9)
C5	79.4(12)	56.9(9)	46.0(8)	-15.9(7)	3.0(8)	-21.2(8)
C15	61.2(10)	62.9(10)	91.2(13)	-48.5(10)	-7.1(9)	2.5(8)
C6	78.6(12)	53.8(9)	65.9(10)	-21.3(8)	-7.0(9)	-20.9(8)
C20	63.2(11)	94.4(14)	51.6(9)	-29.9(9)	12.0(8)	-20.4(10)

Table 4 Bond Lengths for *cis*-15db.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C9	1.3827(17)	C16	C17	1.387(2)
O2	C1	1.4073(18)	C16	C21	1.378(2)
O3	C7	1.4227(19)	C12	C13	1.380(2)
O3	C6	1.422(2)	C12	C11	1.387(2)
O4	C12	1.3712(18)	C2	C1	1.504(2)
O4	C15	1.422(2)	C2	C3	1.514(2)
O1	C4	1.2238(17)	C17	C18	1.381(2)
N1	C4	1.3436(19)	C13	C14	1.392(2)
N1	C8	1.4599(18)	C1	C3	1.490(2)
N1	C5	1.468(2)	C8	C7	1.498(2)
C4	C2	1.523(2)	C21	C20	1.385(2)
C9	C10	1.383(2)	C18	C19	1.375(2)
C9	C14	1.379(2)	C19	C20	1.371(3)
C10	C11	1.371(2)	C5	C6	1.494(2)
C16	C2	1.5056(19)			

Table 5 Bond Angles for *cis*-15db.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O2	C1	117.42(11)	C1	C2	C4	118.44(12)
C6	O3	C7	110.00(12)	C1	C2	C16	121.15(12)
C12	O4	C15	117.38(13)	C1	C2	C3	59.18(10)
C4	N1	C8	126.36(12)	C3	C2	C4	114.50(12)
C4	N1	C5	119.98(12)	C18	C17	C16	120.82(14)
C8	N1	C5	112.35(13)	C12	C13	C14	120.22(13)
O1	C4	N1	121.62(14)	C10	C11	C12	120.27(13)
O1	C4	C2	120.16(13)	C9	C14	C13	119.81(13)
N1	C4	C2	118.14(12)	O2	C1	C2	114.15(12)
O2	C9	C10	115.13(12)	O2	C1	C3	117.71(14)
C14	C9	O2	125.14(13)	C3	C1	C2	60.74(10)
C14	C9	C10	119.73(13)	N1	C8	C7	109.56(13)
C11	C10	C9	120.47(13)	C16	C21	C20	120.39(16)
C17	C16	C2	118.38(12)	C19	C18	C17	119.99(15)
C21	C16	C2	122.98(13)	C1	C3	C2	60.07(10)
C21	C16	C17	118.63(14)	C20	C19	C18	119.67(15)
O4	C12	C13	125.04(13)	O3	C7	C8	111.83(13)
O4	C12	C11	115.47(13)	N1	C5	C6	110.37(13)
C13	C12	C11	119.48(13)	O3	C6	C5	110.94(14)
C16	C2	C4	114.04(12)	C19	C20	C21	120.50(16)
C16	C2	C3	118.38(12)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *cis*-15db.

Atom	*x*	*y*	*z*	U(eq)
H10	2642.9	3184.41	8197.44	57
H17	10194.92	1506.54	8509.79	60
H13	3189.3	7662.29	7668.18	59
H11	795.68	4516.45	8879.96	61
H14	5068.86	6298.63	7011.35	60
H1	6698.57	4808.52	5952.89	61
H8A	6657.62	2069.58	5814.8	65
H8B	5149.96	1553.7	6340.59	65
H21	8383.21	3705.45	4713.57	75
H18	12410.3	1284.9	7406.14	69
H3A	6810.24	3499.29	9036.47	67
H3B	8009.9	4429.18	7926.55	67
H19	12619.58	2284.92	4953.39	74

H7A	6262.93	547.09	4879.72	75
H7B	7630.22	-109.05	5814.51	75
H5A	5024.03	-594.48	8873.09	75
H5B	6458.32	-1214.77	9710.74	75
H15A	756.08	8964.75	7341.66	102
H15B	1403.64	8506.62	8814.17	102
H15C	-269.74	8824.42	8658.62	102
H6A	7520.44	-2042.82	8102.84	80
H6B	6074.87	-2671.5	8700.04	80
H20	10606.75	3477.48	3616.78	85

Experimental

Single crystals of $C_{21}H_{23}NO_4$ (**15db**) were obtained via crystallization of the material purified by column chromatography. This material was dissolved in a mixture of hexane and diethyl ether, and ether was allowed to evaporate slowly at room temperature. A suitable crystal was selected and analyzed on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 293(2) K during data collection. The structure was solved with the ShelXT [1] structure solution program under Olex2 interface [2], using Intrinsic Phasing and refined with the ShelXL [1] refinement package using Least Squares minimization.

1. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

Crystal structure determination of *cis*-15db

Crystal Data for $C_{21}H_{23}NO_4$ (M =353.40 g/mol): triclinic, space group P-1 (no. 2), a = 9.4667(5) Å, b = 10.5554(6) Å, c = 10.6002(6) Å, α = 62.334(6)°, β = 83.248(5)°, γ = 79.062(5)°, V = 920.55(10) Å^3, Z = 2, T = 293(2) K, μ(CuKα) = 0.715 mm^{-1}, *Dcalc* = 1.275 g/cm^3, 8033 reflections measured (9.426° ≤ 2Θ ≤ 136.45°), 3369 unique (R_{int} = 0.0172, R_{sigma} = 0.0176) which were used in all calculations. The final R_1 was 0.0401 (I > 2σ(I)) and wR_2 was 0.1163 (all data).

Refinement model description

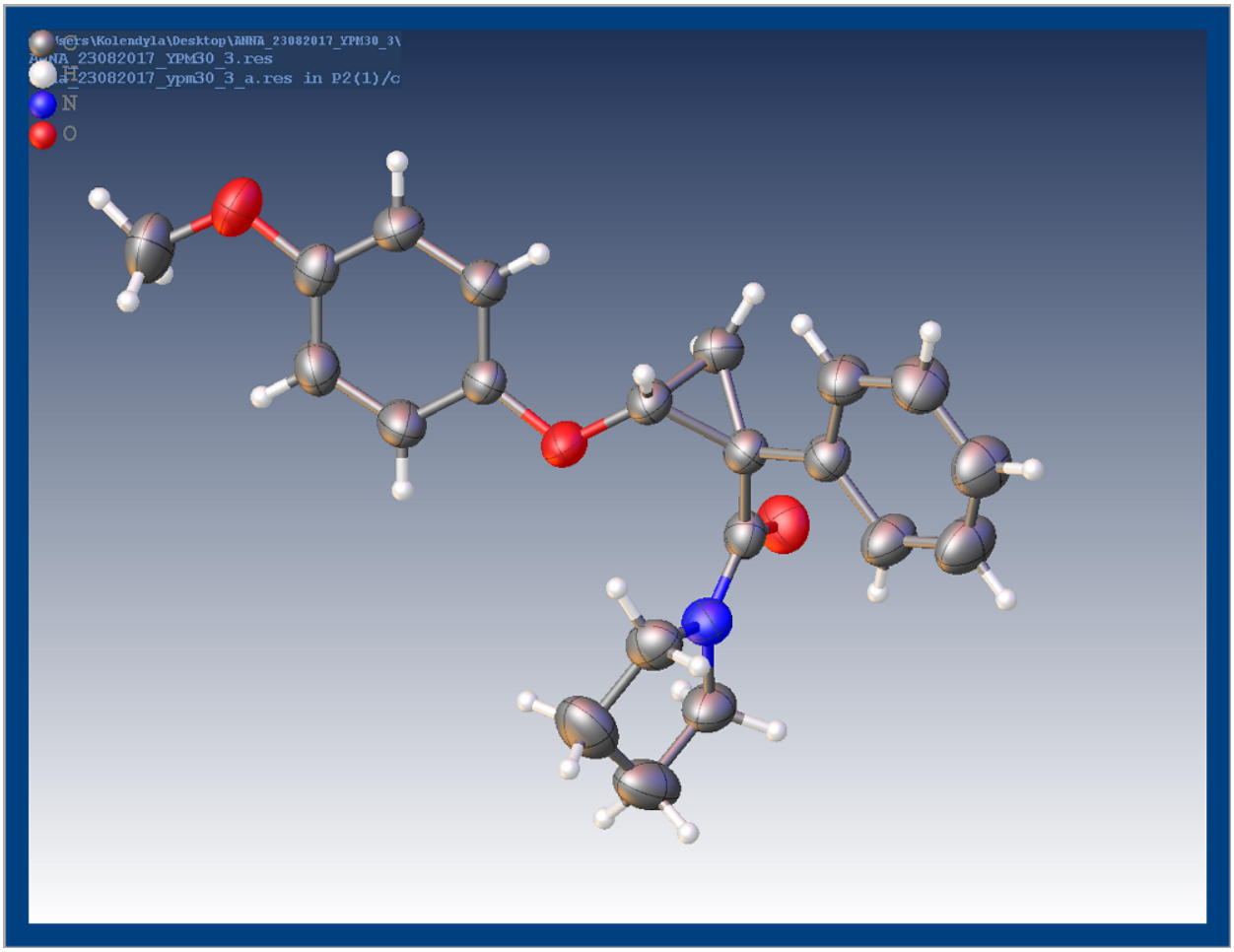
Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C1(H1)
2.b Secondary CH2 refined with riding coordinates:
 C8(H8A,H8B), C3(H3A,H3B), C7(H7A,H7B), C5(H5A,H5B), C6(H6A,H6B)
2.c Aromatic/amide H refined with riding coordinates:
 C10(H10), C17(H17), C13(H13), C11(H11), C14(H14), C21(H21), C18(H18),
 C19(H19), C20(H20)
2.d Idealised Me refined as rotating group:
 C15(H15A,H15B,H15C)
```

This report has been created with Olex2, compiled on 2017.03.28 svn.r3405 for OlexSys.

X-Ray studies of 15cb



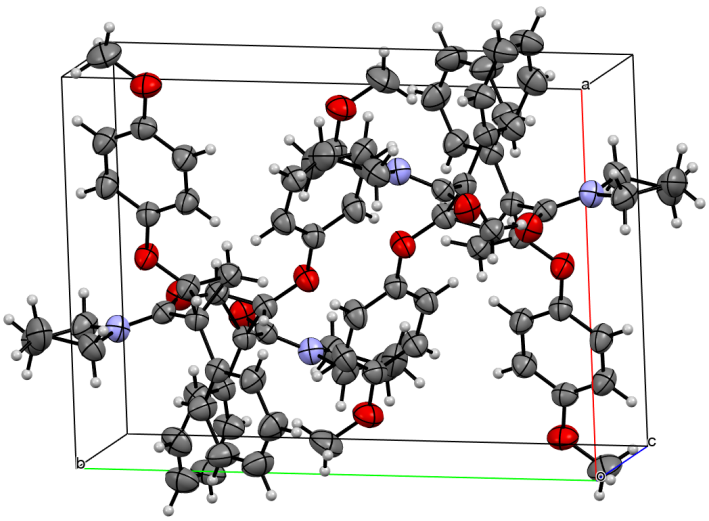


Table 7. Crystal data and structure refinement for 15cb.

Identification code	ANNA_23082017_YPM30_3
Empirical formula	$C_{21}H_{23}NO_3$
Formula weight	337.40
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.9367(4)
b/Å	14.2449(4)
c/Å	11.4918(3)
α/°	90
β/°	112.287(4)
γ/°	90
Volume/Å^3	1808.07(10)
Z	4
ρ_{calc}g/cm^3	1.239
μ/mm^{-1}	0.661
F(000)	720.0
Crystal size/mm^3	0.44 × 0.32 × 0.23
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.004 to 136.496
Index ranges	$-14 \leq h \leq 13$, $-17 \leq k \leq 17$, $-13 \leq l \leq 11$
Reflections collected	11506
Independent reflections	3304 [R_{int} = 0.0411, R_{sigma} = 0.0263]
Data/restraints/parameters	3304/0/215
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0592, wR_2 = 0.1653
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1717
Largest diff. peak/hole / e Å^{-3}	0.30/-0.32

Table 8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 15cb. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	5261.1(11)	4281.3(9)	7193.1(10)	54.1(3)
O1	5933.0(12)	3340.0(9)	10384.0(12)	57.8(3)
O3	1294.6(12)	4619.5(11)	2721.2(13)	66.1(4)
N1	6863.1(13)	4606(1)	10022.8(12)	49.1(4)
C4	6440.8(13)	3728.2(11)	9764.9(13)	42.5(4)
C3	6680.3(14)	3202.1(11)	8733.9(14)	42.6(4)
C9	4283.8(14)	4332.5(11)	6050.8(14)	44.8(4)
C15	7950.9(8)	2802.9(8)	9124(1)	45.2(4)
C16	8237.1(9)	2213.1(9)	8313.2(8)	56.8(4)
C17	9386.9(11)	1821.5(10)	8687.5(11)	67.0(5)
C18	10250.5(9)	2019.6(11)	9872.5(12)	71.1(6)
C19	9964.3(9)	2609.3(12)	10683.4(10)	72.7(6)
C20	8814.5(10)	3000.9(9)	10309.1(9)	59.8(5)
C1	5990.1(15)	3482.1(12)	7379.2(14)	46.3(4)
C12	2280.8(14)	4577.0(12)	3849.7(16)	49.2(4)
C14	4017.5(16)	3667.9(12)	5109.7(16)	51.7(4)
C2	5623.5(15)	2624.5(12)	7866.6(16)	51.3(4)
C5	6722.5(18)	5134.5(14)	11056.9(17)	60.1(5)
C11	2552.2(17)	5239.9(13)	4784.0(18)	57.8(5)
C13	3015.0(17)	3800.7(13)	4007.3(17)	55.7(4)
C8	7413.7(18)	5186.0(14)	9327.8(18)	58.7(5)
C10	3557.7(18)	5113.1(13)	5888.9(17)	57.2(5)
C6	7133(2)	6120.7(16)	10911(3)	78.0(7)
C7	7081(2)	6163.0(16)	9582(3)	83.2(7)
C21	558(2)	5425(2)	2498(3)	86.8(8)

Table 9. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 15cb. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	63.4(7)	48.6(7)	39.4(6)	-4.7(5)	7.4(5)	9.6(5)
O1	69.6(8)	60.5(8)	52.4(7)	8.8(5)	33.5(6)	1.1(6)
O3	54.4(7)	76.3(9)	53.6(7)	5.4(6)	4.8(6)	5.9(6)
N1	57.5(8)	50.2(8)	41.2(7)	-3.0(6)	20.5(6)	0.8(6)
C4	44.7(7)	45.5(8)	36.3(7)	5.7(6)	14.2(6)	5.3(6)
C3	46.5(8)	43.3(8)	36.9(7)	0.9(6)	14.5(6)	0.9(6)

C9	51.7(8)	43.1(8)	37.1(8)	2.2(6)	14.0(6)	1.8(6)
C15	48.5(8)	47.0(8)	40.3(8)	1.2(6)	17.0(6)	1.2(6)
C16	62.1(10)	59.4(10)	47.1(9)	-5.8(8)	18.5(8)	8.7(8)
C17	69.4(11)	73.0(13)	62.7(11)	-6.9(9)	29.7(9)	17.1(10)
C18	52.3(10)	87.1(15)	72.4(13)	-7.0(11)	22.0(9)	14(1)
C19	50.2(10)	95.3(16)	62.1(11)	-12.8(11)	9.5(8)	11.9(10)
C20	53.0(9)	74.7(12)	47.5(9)	-10.5(8)	14.3(7)	9.0(8)
C1	53.4(8)	46.8(8)	36.0(7)	-1.7(6)	13.7(6)	5.8(7)
C12	46.6(8)	54.6(9)	44.3(8)	9.0(7)	14.9(7)	0.6(7)
C14	57.7(9)	45.9(9)	46.6(9)	-3.0(7)	14.0(7)	7.8(7)
C2	51.2(8)	47.6(9)	50.1(9)	-5.1(7)	13.5(7)	-1.8(7)
C5	64.8(10)	63.2(11)	48.1(9)	-11.9(8)	16.9(8)	12.0(8)
C11	62.9(10)	50.9(9)	56.4(10)	6.5(8)	19.0(8)	14.0(8)
C13	60.7(10)	53.7(10)	45.5(9)	-6.0(7)	11.8(7)	2.8(8)
C8	63.3(10)	57.4(10)	54.9(10)	-1.2(8)	21.9(8)	-12.5(8)
C10	73.3(11)	45.9(9)	47.1(9)	-4.0(7)	16.9(8)	9.4(8)
C6	68.5(12)	62.1(12)	97.1(17)	-26.6(12)	24.1(11)	2.3(9)
C7	86.5(15)	53.3(12)	108.2(19)	4.5(12)	35.2(14)	-6.4(10)
C21	65.3(12)	90.6(17)	81.0(15)	15.9(13)	1.3(11)	19.9(12)

Table 10. Bond Lengths for 15cb.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C9	1.3884(19)	C15	C16	1.3900
O2	C1	1.399(2)	C15	C20	1.3900
O1	C4	1.2273(19)	C16	C17	1.3900
O3	C12	1.383(2)	C17	C18	1.3900
O3	C21	1.409(3)	C18	C19	1.3900
N1	C4	1.339(2)	C19	C20	1.3900
N1	C5	1.469(2)	C1	C2	1.478(2)
N1	C8	1.466(2)	C12	C11	1.373(3)
C4	C3	1.518(2)	C12	C13	1.380(3)
C3	C15	1.5196(16)	C14	C13	1.387(2)
C3	C1	1.513(2)	C5	C6	1.518(3)
C3	C2	1.519(2)	C11	C10	1.389(3)
C9	C14	1.381(2)	C8	C7	1.506(3)
C9	C10	1.378(2)	C6	C7	1.506(4)

Table 11. Bond Angles for 15cb.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O2	C1	115.98(12)	C17	C16	C15	120.0
C12	O3	C21	117.18(17)	C16	C17	C18	120.0
C4	N1	C5	120.58(15)	C17	C18	C19	120.0
C4	N1	C8	127.93(14)	C20	C19	C18	120.0
C8	N1	C5	111.35(15)	C19	C20	C15	120.0
O1	C4	N1	121.32(15)	O2	C1	C3	115.86(13)
O1	C4	C3	120.70(14)	O2	C1	C2	118.30(15)
N1	C4	C3	117.86(13)	C2	C1	C3	61.05(10)
C4	C3	C15	114.64(11)	C11	C12	O3	124.58(16)
C4	C3	C2	115.10(13)	C11	C12	C13	119.92(16)
C1	C3	C4	118.87(13)	C13	C12	O3	115.51(16)
C1	C3	C15	119.69(12)	C9	C14	C13	118.99(16)
C1	C3	C2	58.33(11)	C1	C2	C3	60.62(10)
C2	C3	C15	118.58(13)	N1	C5	C6	104.12(17)
C14	C9	O2	124.46(14)	C12	C11	C10	119.42(16)
C10	C9	O2	115.46(14)	C12	C13	C14	120.96(16)
C10	C9	C14	120.09(15)	N1	C8	C7	102.10(17)
C16	C15	C3	120.00(8)	C9	C10	C11	120.62(16)
C16	C15	C20	120.0	C7	C6	C5	104.96(17)
C20	C15	C3	119.96(8)	C8	C7	C6	104.29(19)

Table 12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 15cb.

Atom	*x*	*y*	*z*	U(eq)
H16	7659.37	2080.6	7520.31	68
H17	9578.39	1426.92	8144.95	80
H18	11019.73	1757.51	10122.93	85
H19	10542.07	2741.8	11476.27	87
H20	8623.05	3395.49	10851.65	72
H1	6404.91	3391.48	6797.13	56
H14	4503.17	3139.27	5213.48	62
H2A	5803.39	2023.73	7579.71	62
H2B	4872.4	2644.03	8007.55	62
H5A	7223.82	4870.18	11865.04	72
H5B	5885.32	5133.15	10982.14	72
H11	2067.07	5769.01	4678	69
H13	2834.89	3360.01	3364.95	67
H8A	7075.47	5042.98	8436.05	70

H8B	8284.93	5102.82	9645.56	70
H10	3742.81	5559.15	6525.42	69
H6A	6598.69	6584.94	11042.63	94
H6B	7951.1	6232.47	11507.73	94
H7A	6274.03	6328.02	9000.3	100
H7B	7652.39	6619.78	9506.64	100
H21A	-71.1	5386.13	1675.93	130
H21B	1040.27	5973.82	2548.83	130
H21C	201.49	5463.22	3118.67	130

Experimental

Single crystals of $C_{21}H_{23}NO_3$ (**15cb**) were were obtained via crystallization of the material purified by column chromatography. This material was dissolved in a mixture of hexane and diethyl ether, and ether was allowed to evaporate slowly at room temperature. A suitable crystal was selected and **mounted on the glass stick with acrylic glue,** and the reflections were registered on a **SuperNova, Dual, Cu at zero, AtlasS2** diffractometer. The crystal was kept at 293(2) K during data collection. The structure was solved with the ShelXT [1] structure solution program under Olex2 interface [2], using Intrinsic Phasing and refined with the ShelXL [1] refinement package using Least Squares minimization.

1. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

Crystal structure determination of 15cb

Crystal Data for $C_{21}H_{23}NO_3$ (M =337.40 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 11.9367(4) Å, b = 14.2449(4) Å, c = 11.4918(3) Å, β = 112.287(4)°, V = 1808.07(10) Å^3, Z = 4, T = 293(2) K, μ(CuKα) = 0.661 mm^{-1}, *Dcalc* = 1.239 g/cm^3, 11506 reflections measured (8.004° ≤ 2Θ ≤ 136.496°), 3304 unique (R_{int} = 0.0411, R_{sigma} = 0.0263) which were used in all calculations. The final R_1 was 0.0592 (I > 2σ(I)) and wR_2 was 0.1717 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C1(H1)
2.b Secondary CH2 refined with riding coordinates:
 C2(H2A,H2B), C5(H5A,H5B), C8(H8A,H8B), C6(H6A,H6B), C7(H7A,H7B)
2.c Aromatic/amide H refined with riding coordinates:
 C16(H16), C17(H17), C18(H18), C19(H19), C20(H20), C14(H14), C11(H11),
 C13(H13), C10(H10)
2.d Fitted hexagon refined as free rotating group:
 C15(C16,C17,C18,C19,C20)
2.e Idealised Me refined as rotating group:
 C21(H21A,H21B,H21C)
```

This report has been created with Olex2, compiled on 2017.03.28 svn.r3405 for OlexSys.