Electronic Supplementary Information

Facile synthesis of spirooxindole-pyrazolines and spirobenzofuranone-pyrazolines and their fungicidal activity

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E-mail*:* *zhourong@tyut.edu.cn*

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I. ORTEP Drawings for 3a and 3q.

Figure S1. ORTEP Drawing for **3a**.

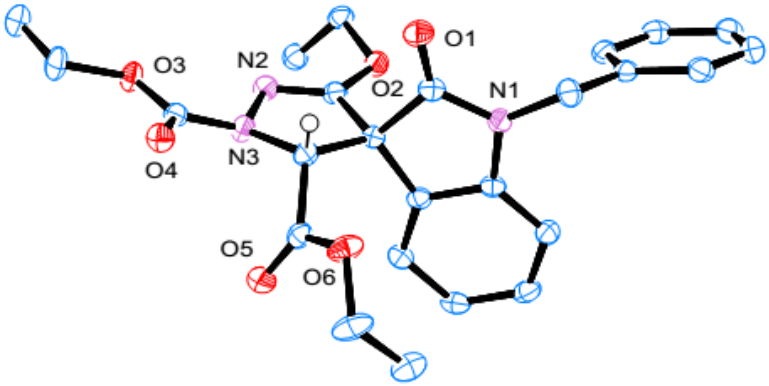


Table S1. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	$C_{25}H_{27}N_3O_6$
Formula weight	465.50
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.228(5) Å, α = 90° b = 9.602(3) Å, β = 97.418° c = 17.978(6) Å, γ = 90°
Volume,Z	2264.6(14) $Å^3$
Z , Calculated density	4, 1.365 Mg/m^3
Absorption coefficient	0.099 mm^{-1}
F(000)	984
Crystal size	0.20 x 0.18 x 0.12 mm^3
θ range for data collection	1.55 to 27.88°
Limiting indices	-17<=h<=17, -12<=k<=12, -23<=l<=19
Reflections collected / unique	12780/2378 [R(int) = 0.0753]
Completeness to θ = 27.88°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9883 and 0.9806
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5410 / 0 / 310
Goodness-of-fit on F^2	0.981
Final R indices [I>2σ(I)]	R_1 = 0.0380, wR_2 = 0.0781
R indices (all data)	R_1 = 0.0540, wR_2 = 0.0833
Largest diff. peak and hole	0.222 and -0.252 e. $Å^{-3}$

Figure S2. ORTEP Drawing for **3q**.

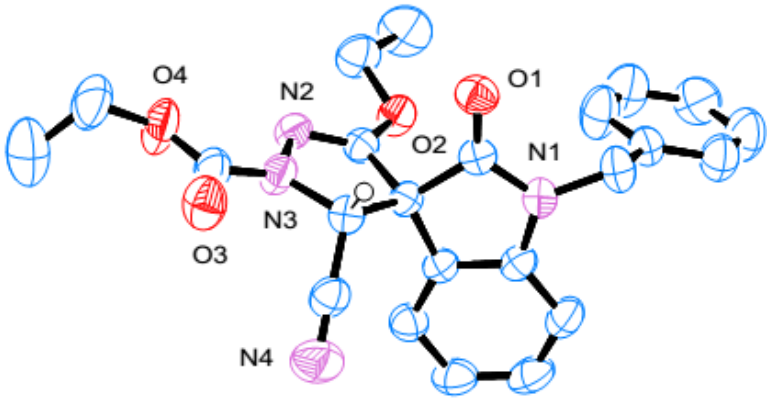
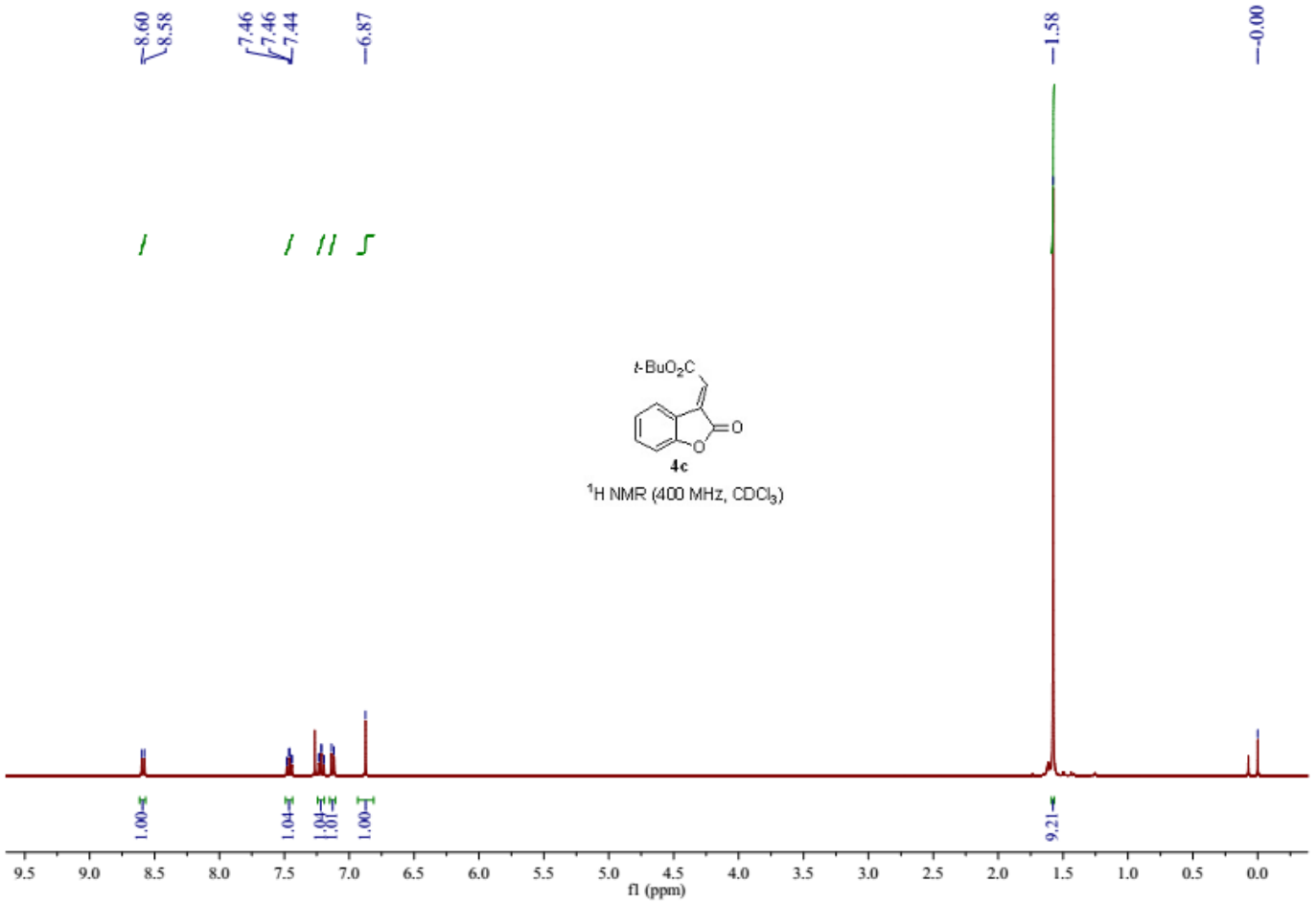
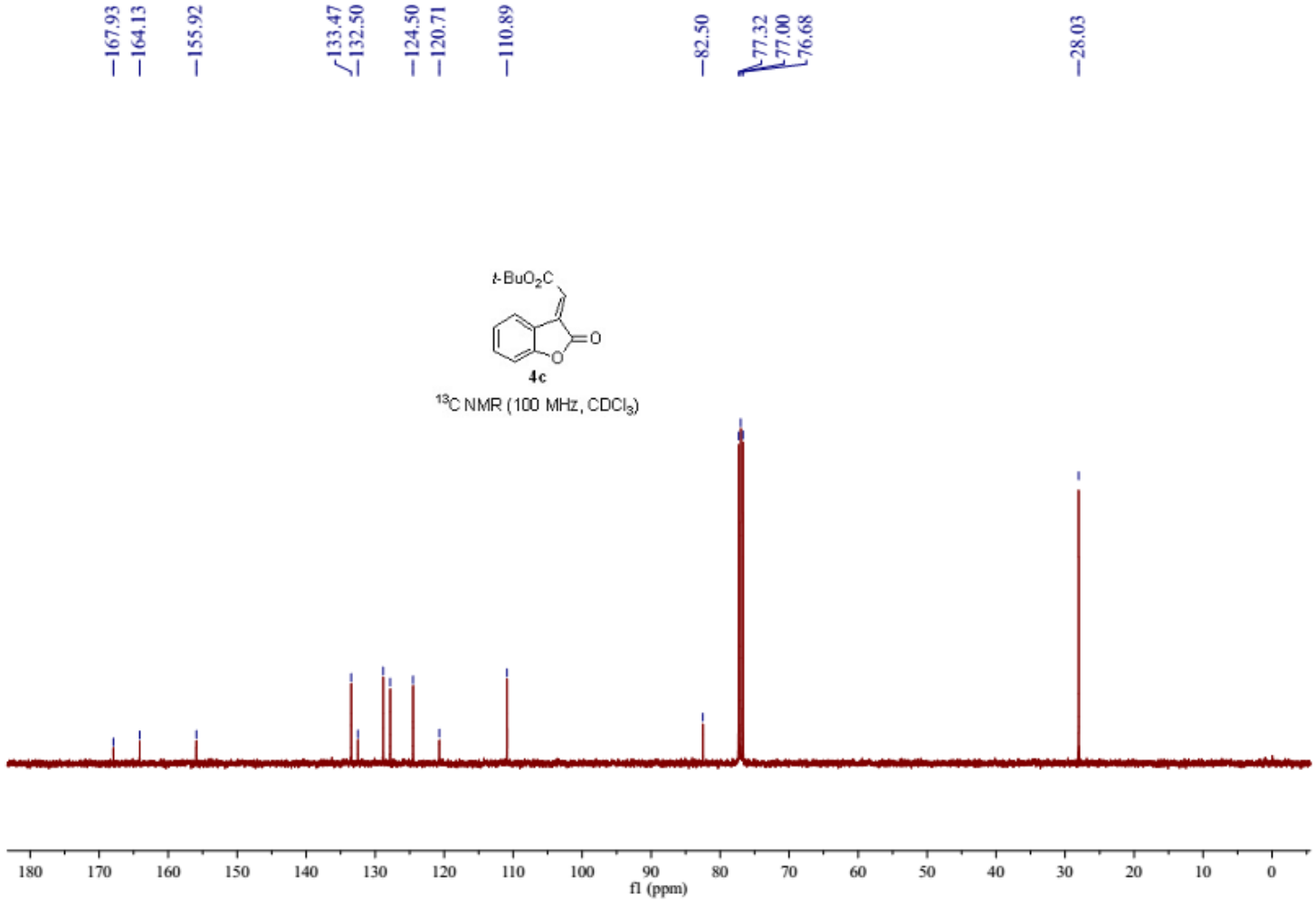


Table S2. Crystal data and structure refinement for **3q**.

Identification code	**3q**
Empirical formula	$C_{23}H_{22}N_4O_4$
Formula weight	418.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Triclinic, P-1
Unit cell dimensions	a = 8.8803(18) Å, α = 79.42(3)° b = 11.094(2) Å, β = 79.41(3)° c = 11.201(2) Å, γ = 77.65(3)°
Volume,Z	1047.6(3) $Å^3$
Z , Calculated density	2, 1.327 Mg/m^3
Absorption coefficient	0.093 mm^{-1}
F(000)	440
Crystal size	0.20 x 0.18 x 0.12 mm^3
θ range for data collection	1.90 to 27.86°
Limiting indices	-11<=h<=11, -14<=k<=14, -14<=l<=14
Reflections collected / unique	10830/4923 [R(int) = 0.0386]
Completeness to θ = 27.88°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9889 and 0.9817
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4923 / 64 / 300
Goodness-of-fit on F^2	0.997
Final R indices [I>2σ(I)]	R_1 = 0.0476, wR_2 = 0.1089
R indices (all data)	R_1 = 0.0889, wR_2 = 0.1270
Largest diff. peak and hole	0.230 and -0.239 e. $Å^{-3}$

II. NMR Spectra for 4c-4e, 3 and 5.

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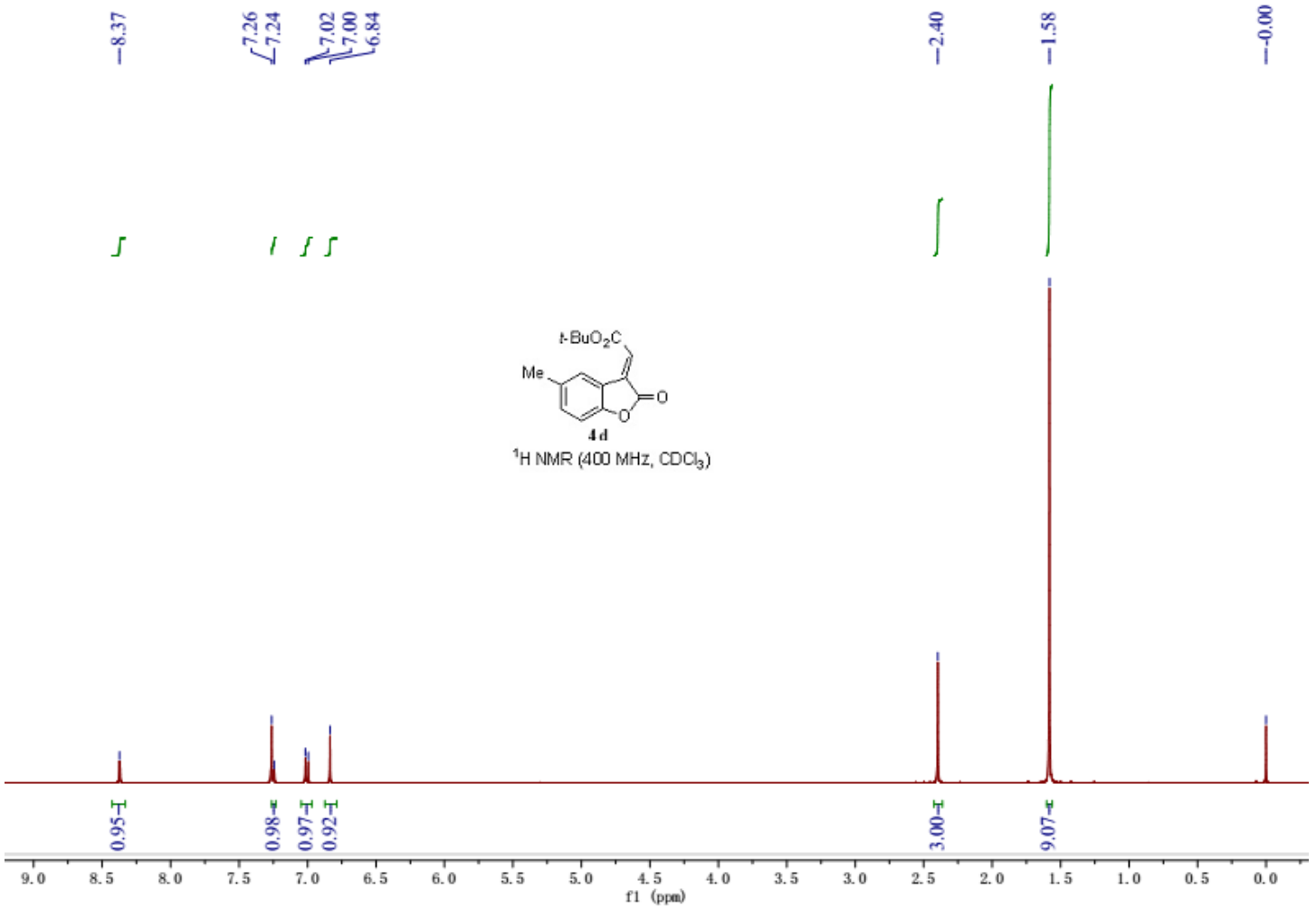
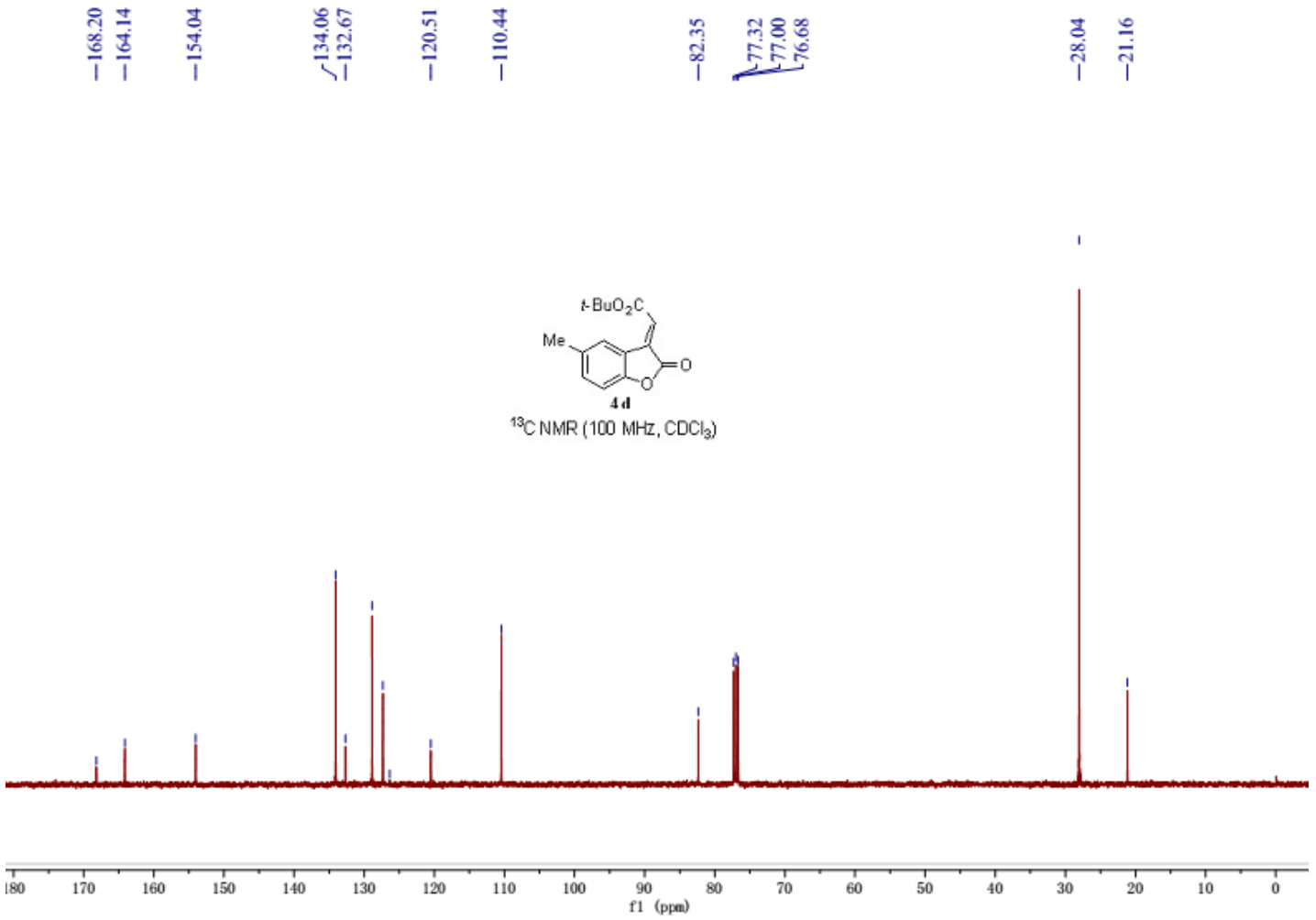
164.13
155.92
133.47
132.50
124.50
120.71
110.89
82.50
77.32
77.00
76.68
28.03
t-BuO2C
O
O
4c
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.37
7.26
7.24
7.02
7.00
6.84
2.40
1.58
0.00
t-BuO2C
Me
O
O
4d
1H NMR (400 MHz, CDCl3)
0.95
0.98
0.97
0.92
3.00
9.07
f1 (ppm)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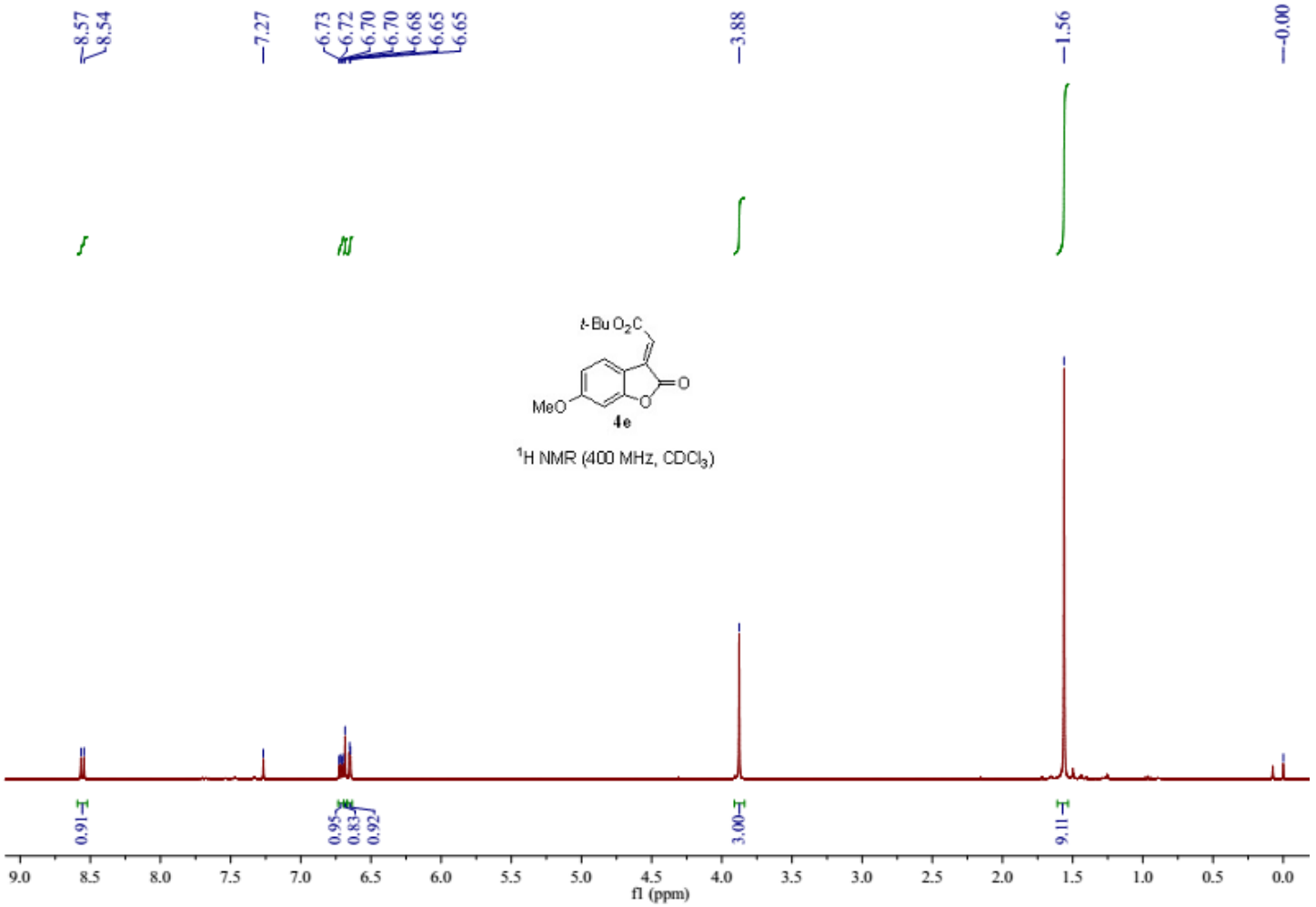
164.14
154.04
134.06
132.67
120.51
110.44
82.35
77.32
77.00
76.68
28.04
21.16
t-BuO2C
Me
O
O
4d
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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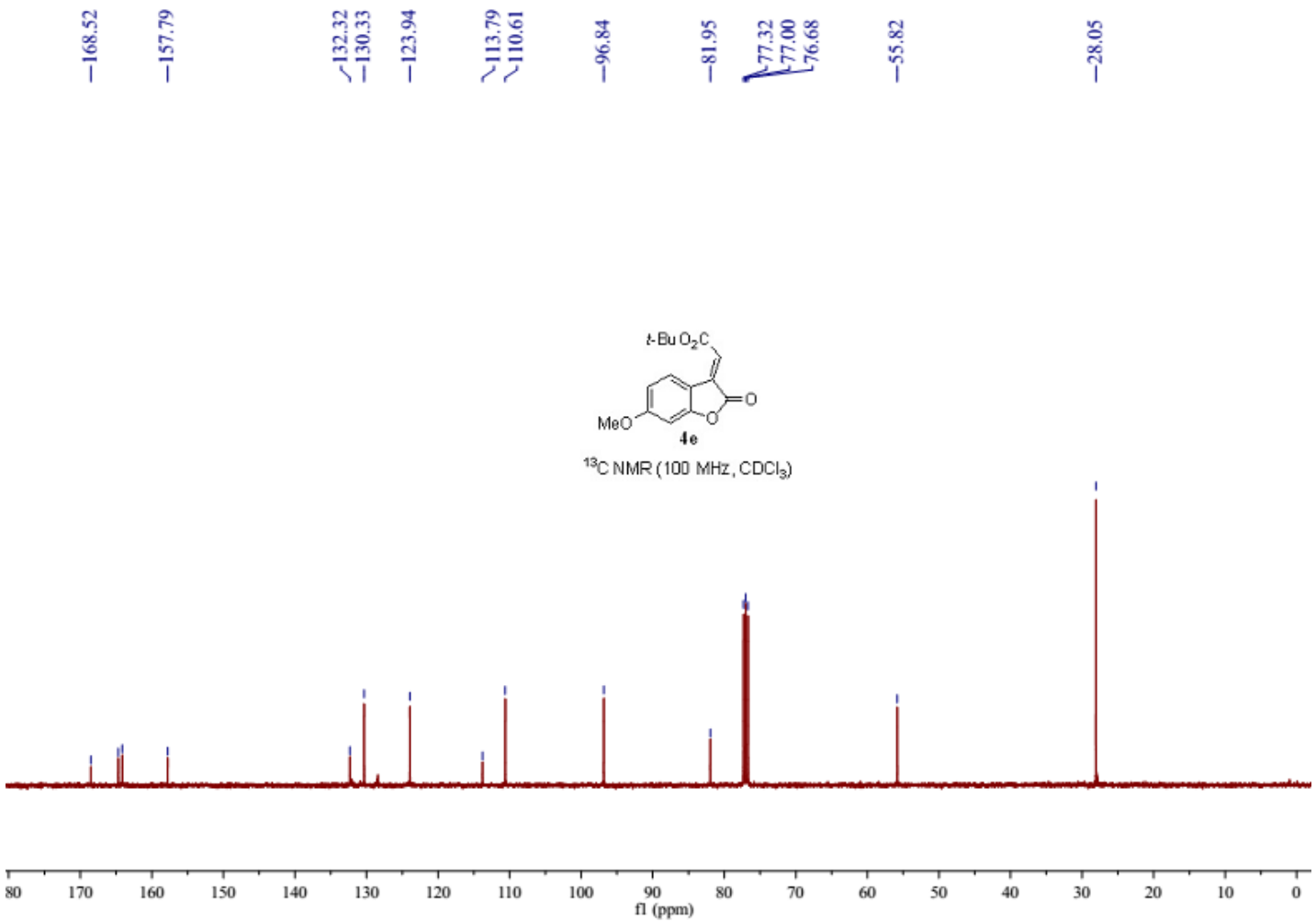
8.54
7.27
6.73
6.72
6.70
6.70
6.68
6.65
6.65
3.88
1.56
0.00
t-Bu O2C
MeO
O
O
4e
1H NMR (400 MHz, CDCl3)
0.91
0.95
0.83
0.92
3.00
9.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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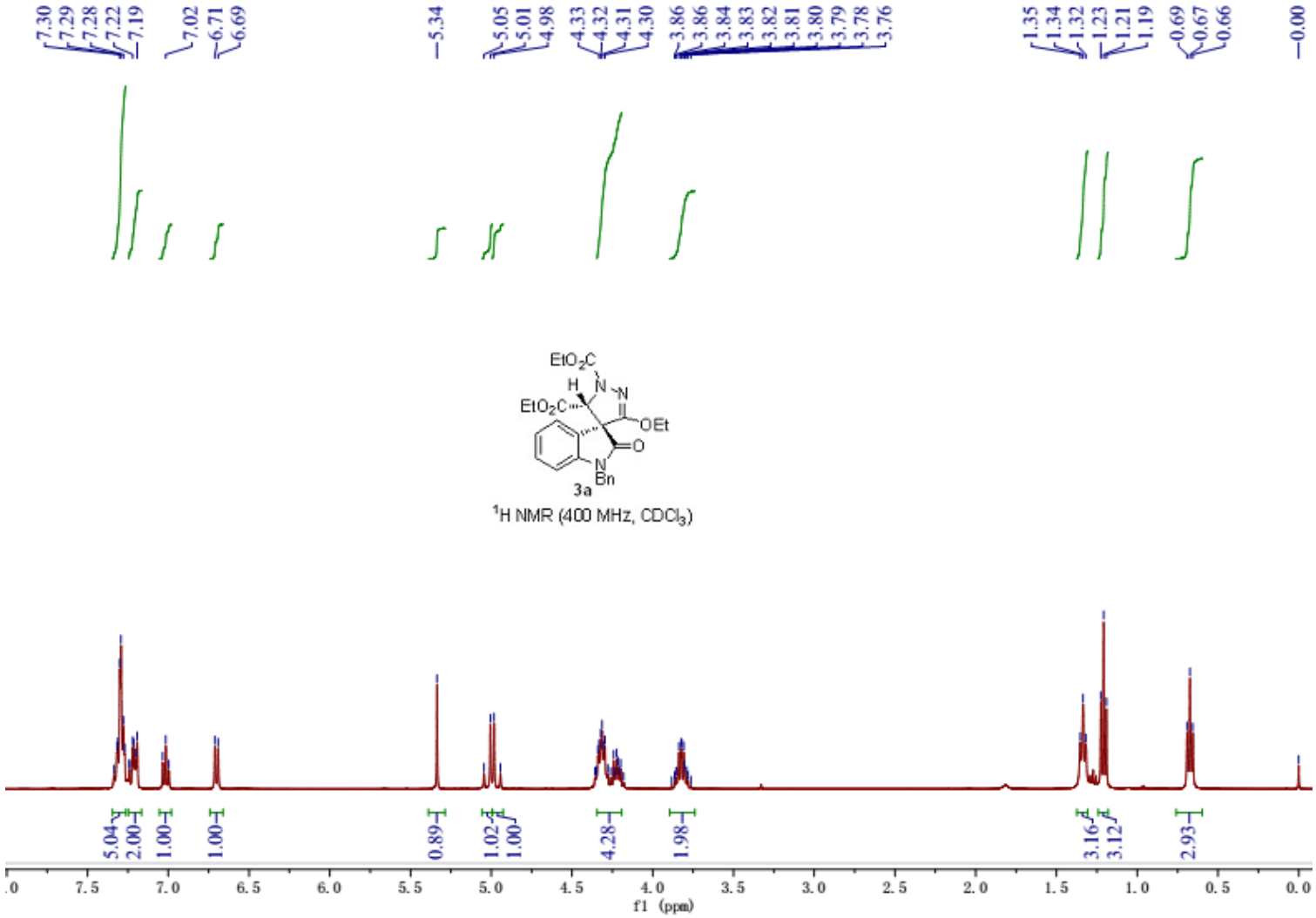
132.32
130.33
123.94
113.79
110.61
96.84
81.95
77.32
77.00
76.68
55.82
28.05
t-Bu O2C
MeO
O
O
4e
13C NMR (100 MHz, CDCl3)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.28
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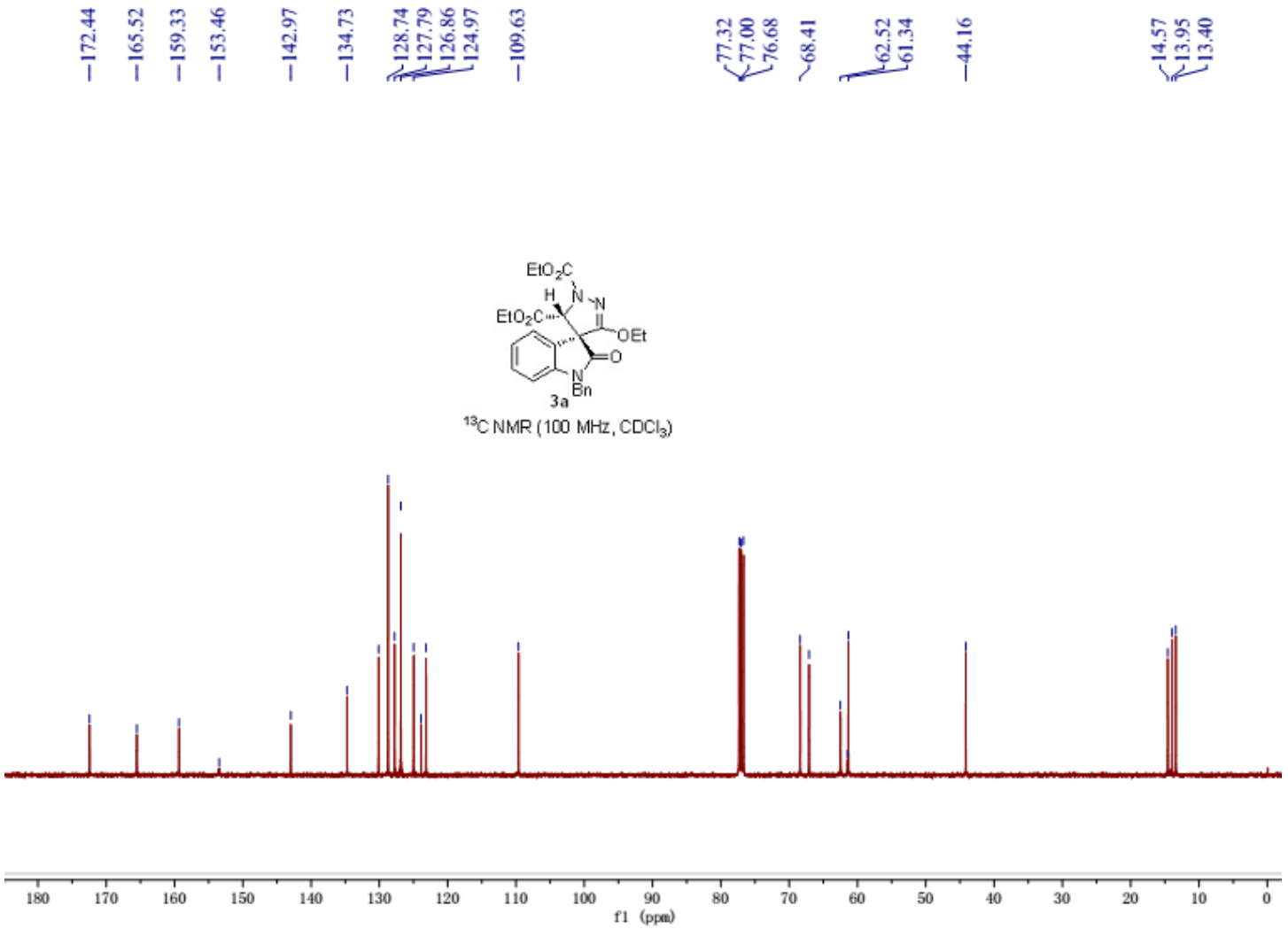
7.19
7.02
6.71
6.69
5.34
5.05
5.01
4.98
4.33
4.32
4.31
4.30
3.86
3.86
3.84
3.83
3.82
3.81
3.80
3.79
3.78
3.76
1.35
1.34
1.32
1.23
1.21
1.19
0.69
0.67
0.66
0.00
EtO2C
H
N
N
EtO2C
OEt
O
N
Bn
3a
1H NMR (400 MHz, CDCl3)
5.04
2.00
1.00
1.00
0.89
1.02
1.00
4.28
1.98
3.16
3.12
2.93
f1 (ppm)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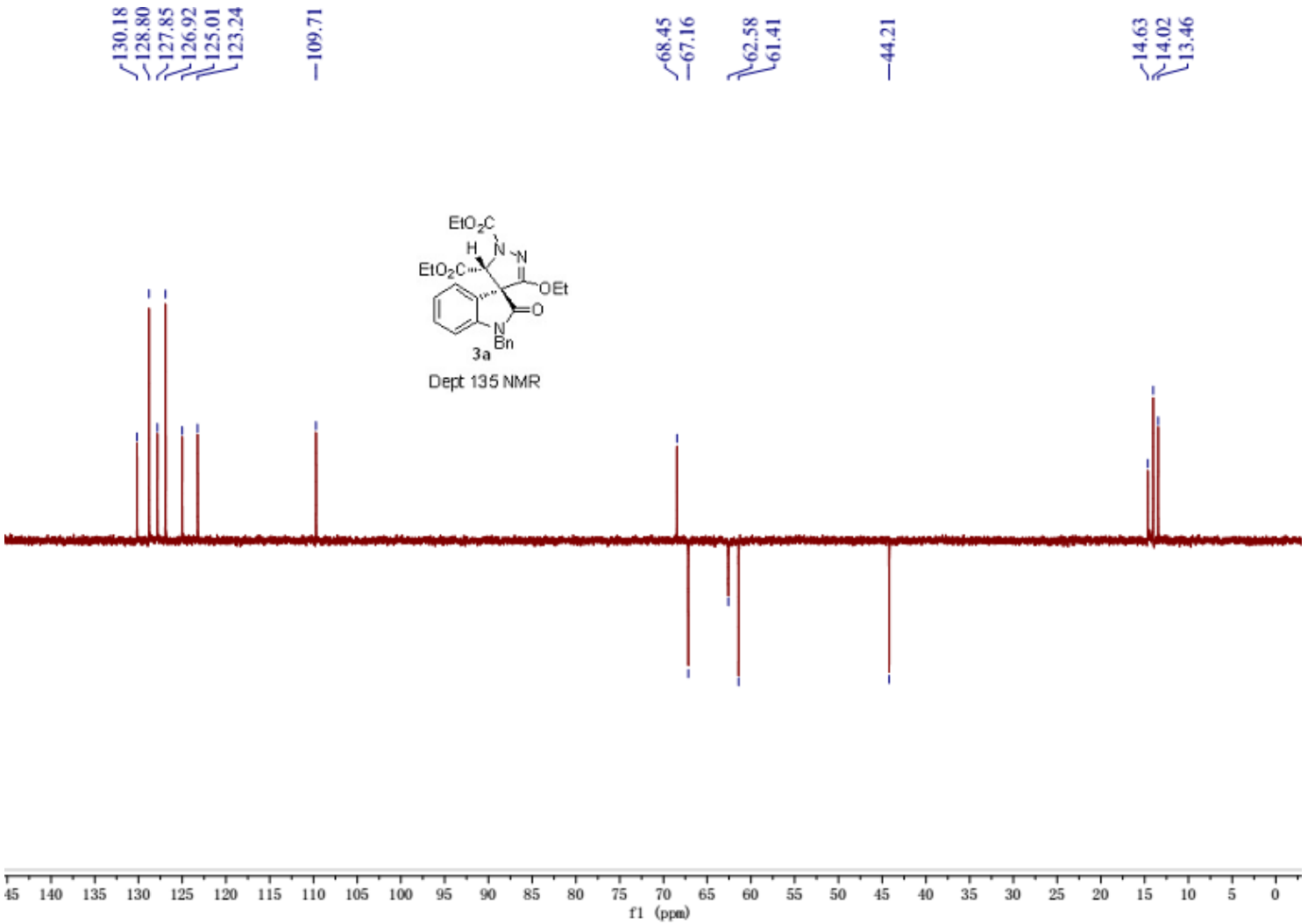
77.00
76.68
68.41
62.52
61.34
44.16
14.57
13.95
13.40
EtO2C
H
N
N
EtO2C
OEt
O
N
Bn
3a
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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125.01
123.24
109.71
68.45
67.16
62.58
61.41
44.21
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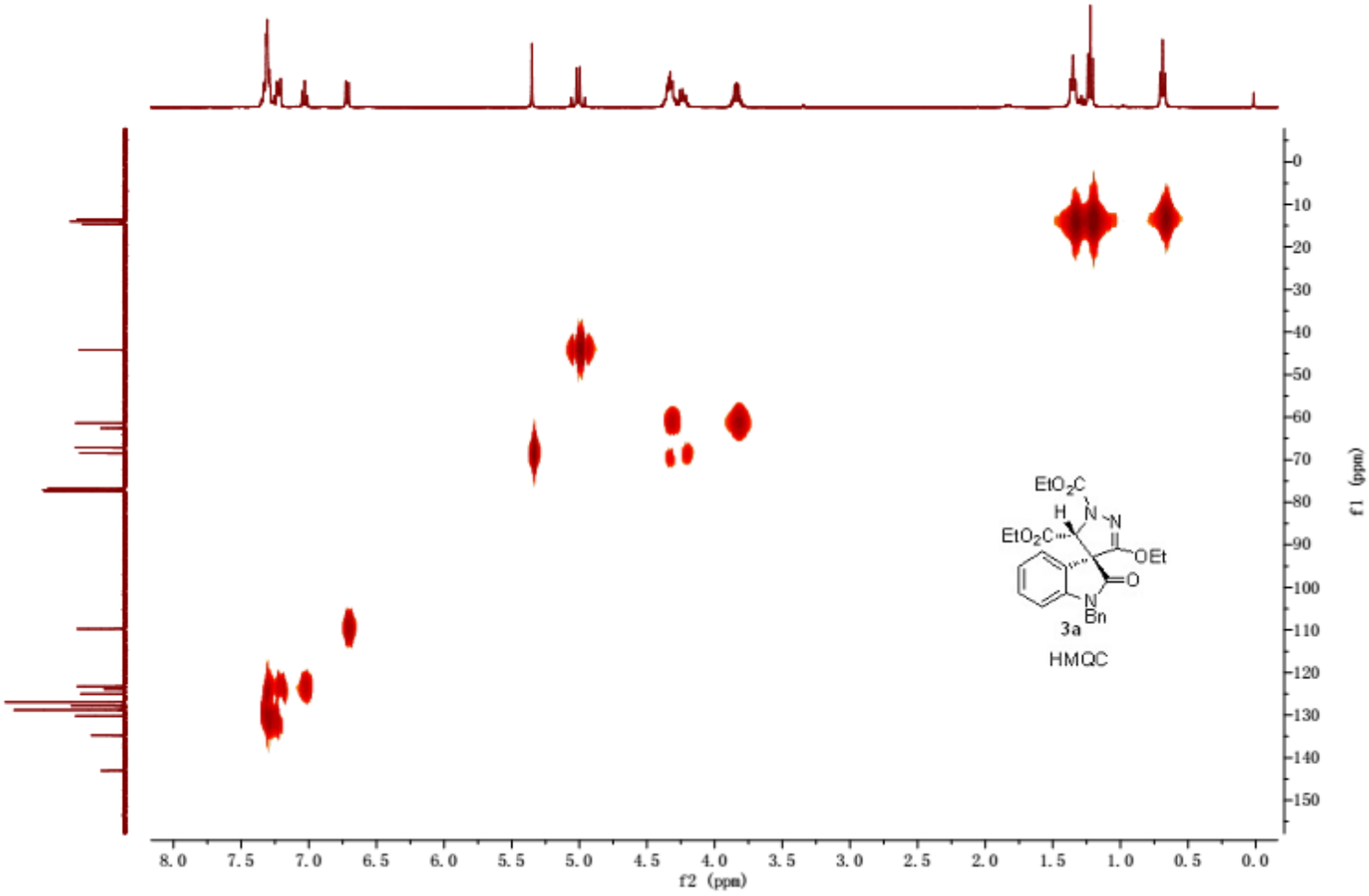
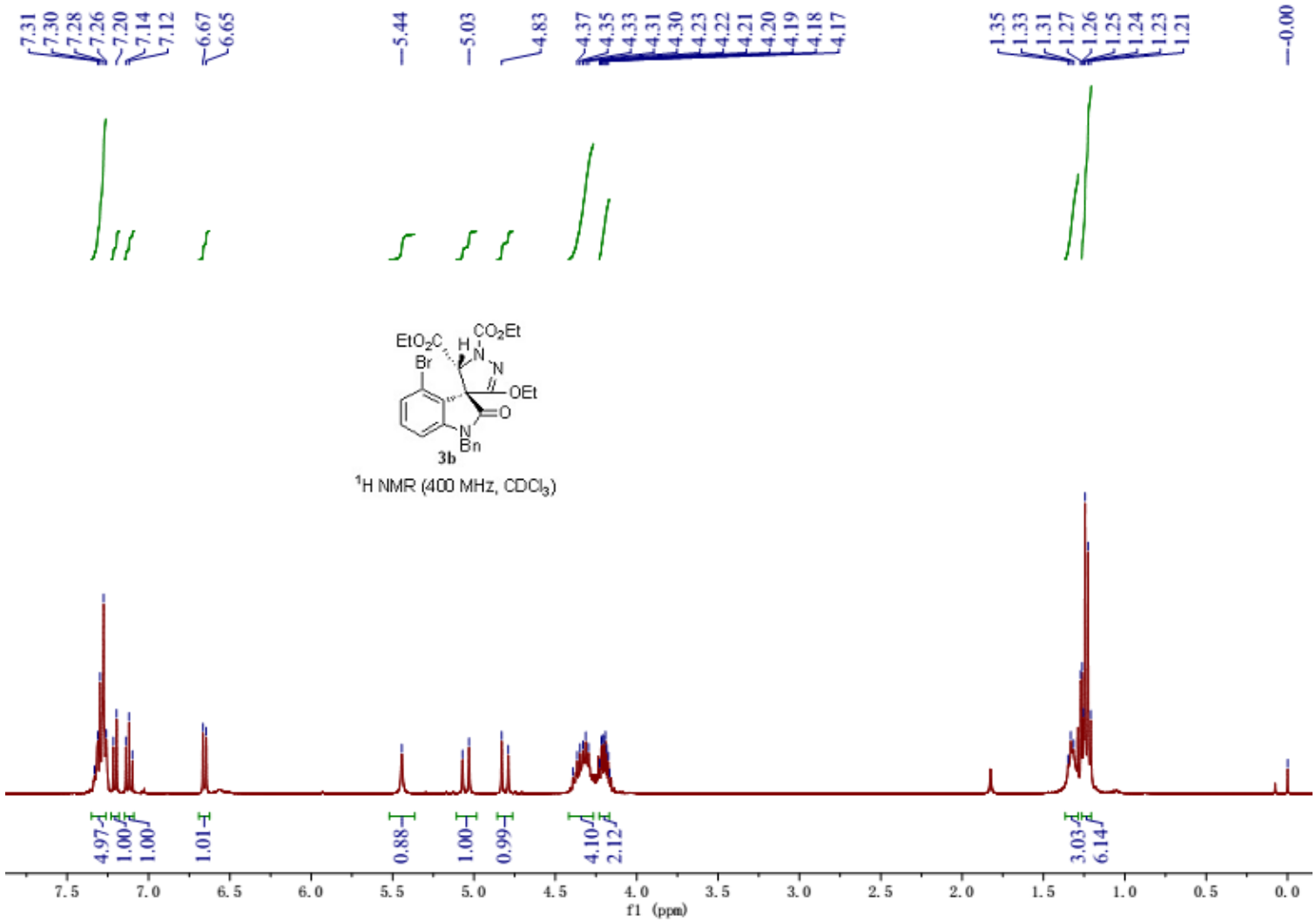
OEt
O
N
Bn
3a
Dept 135 NMR
f1 (ppm)


f2 (ppm)
f1 (ppm)
3a
HMQC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7.30
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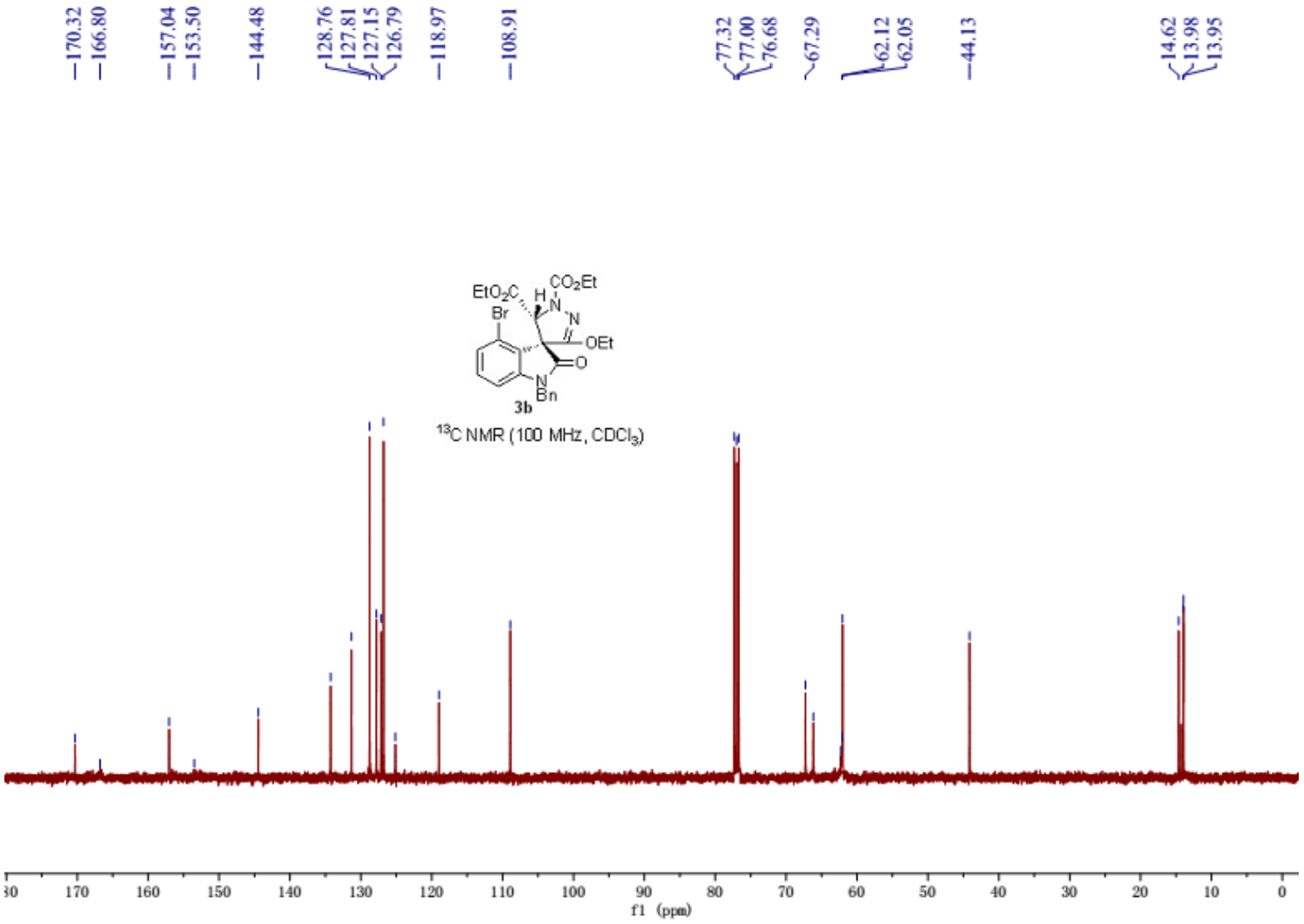
7.14
7.12
6.67
6.65
5.44
5.03
4.83
4.37
4.35
4.33
4.31
4.30
4.23
4.22
4.21
4.20
4.19
4.18
4.17
1.35
1.33
1.31
1.27
1.26
1.25
1.24
1.23
1.21
0.00
EtO2C
CO2Et
Br
OEt
O
N
Bn
3b
1H NMR (400 MHz, CDCl3)
4.97
1.00
1.00
1.01
0.88
1.00
0.99
4.10
2.12
3.03
6.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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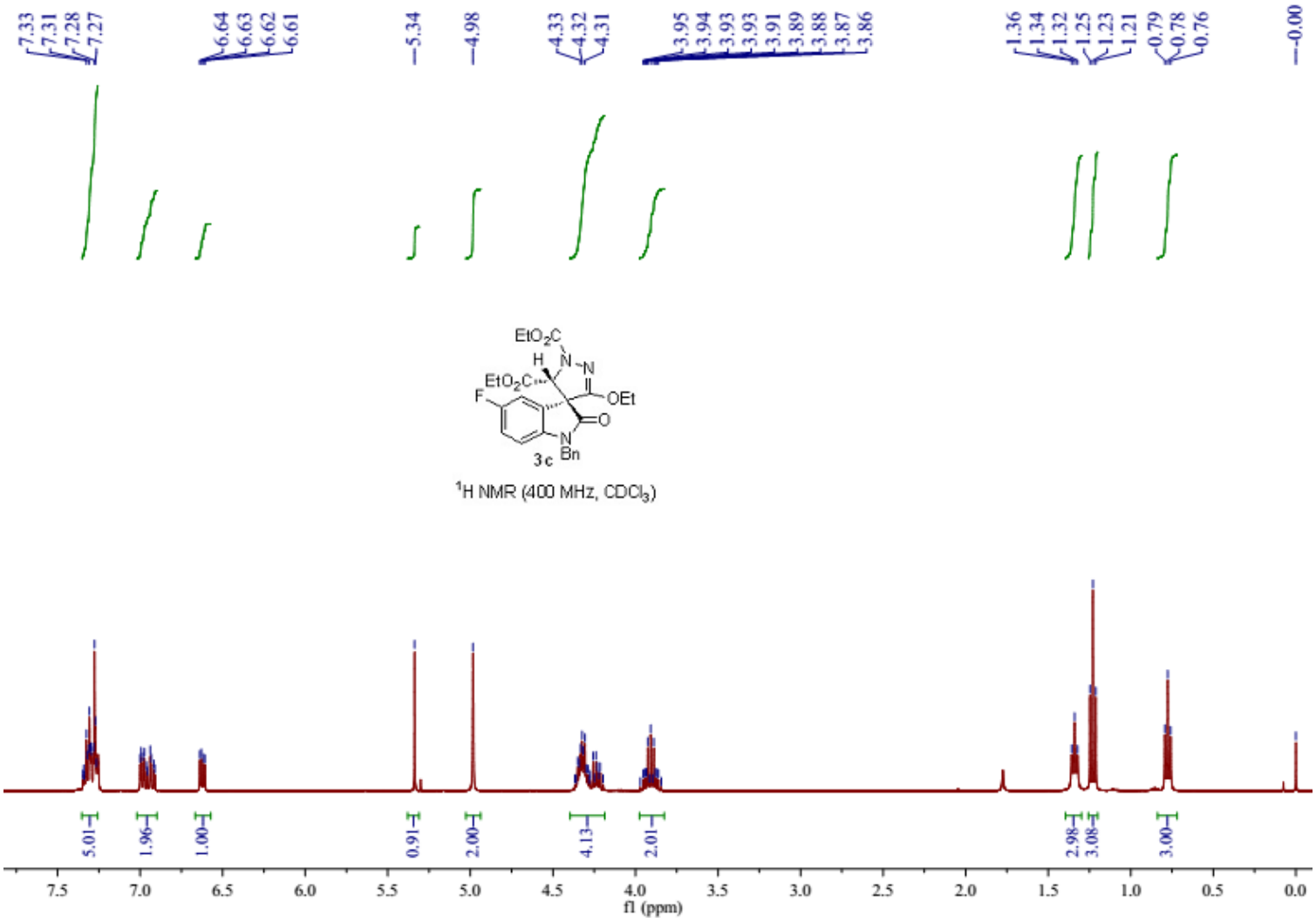
77.00
76.68
67.29
62.12
62.05
44.13
14.62
13.98
13.95
CO2Et
EtO2C
H
N
N
Br
OEt
O
N
Bn
3b
13C NMR (100 MHz, CDCl3)
f1 (ppm)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6.61
5.34
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4.33
4.32
4.31
3.95
3.94
3.93
3.93
3.91
3.89
3.88
3.87
3.86
1.36
1.34
1.32
1.25
1.23
1.21
0.79
0.78
0.76
0.00
EtO2C
H
N
N
EtO2C
F
OEt
O
N
Bn
3c
1H NMR (400 MHz, CDCl3)
5.01
1.96
1.00
0.91
2.00
4.13
2.01
2.98
3.08
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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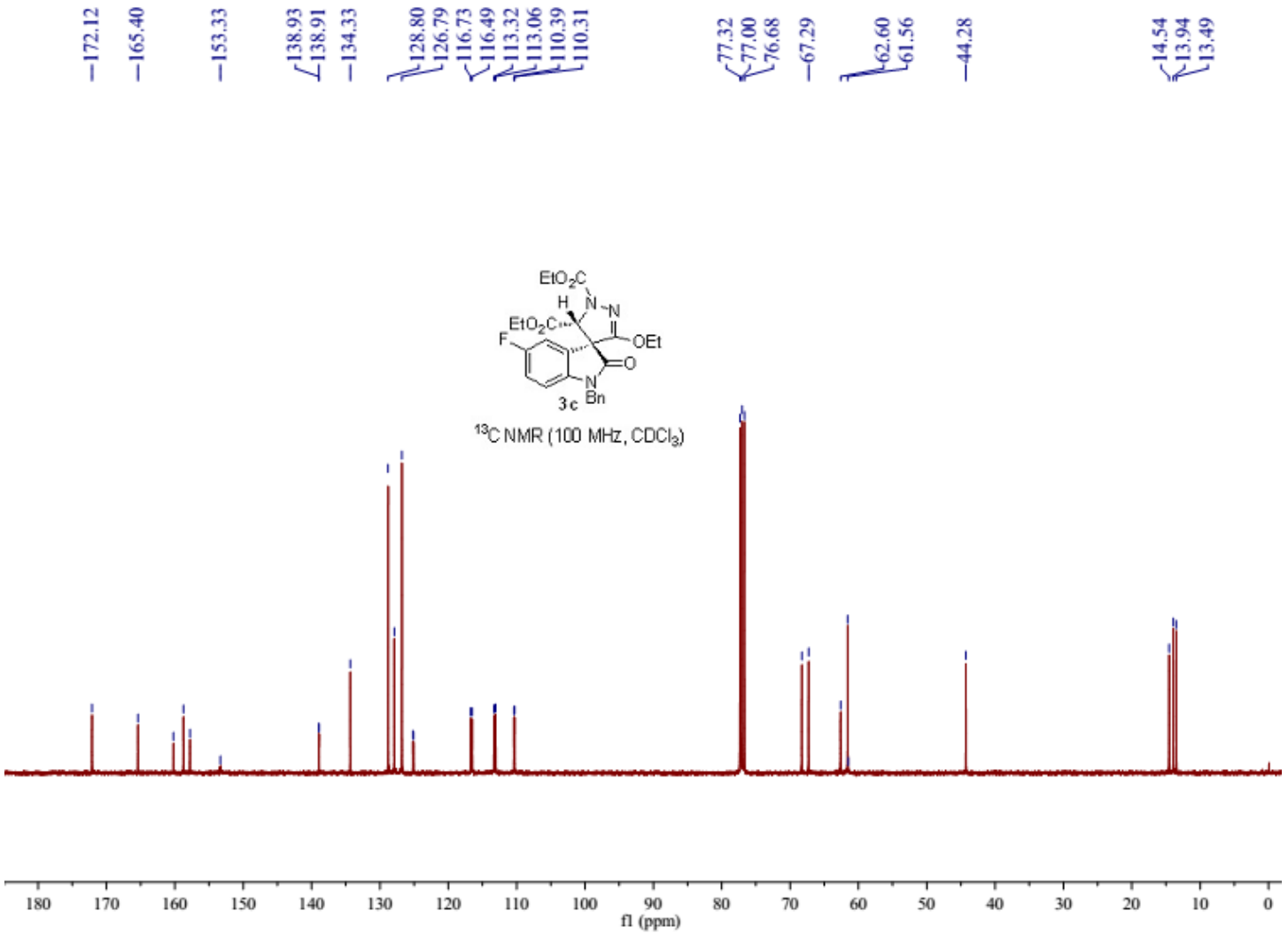
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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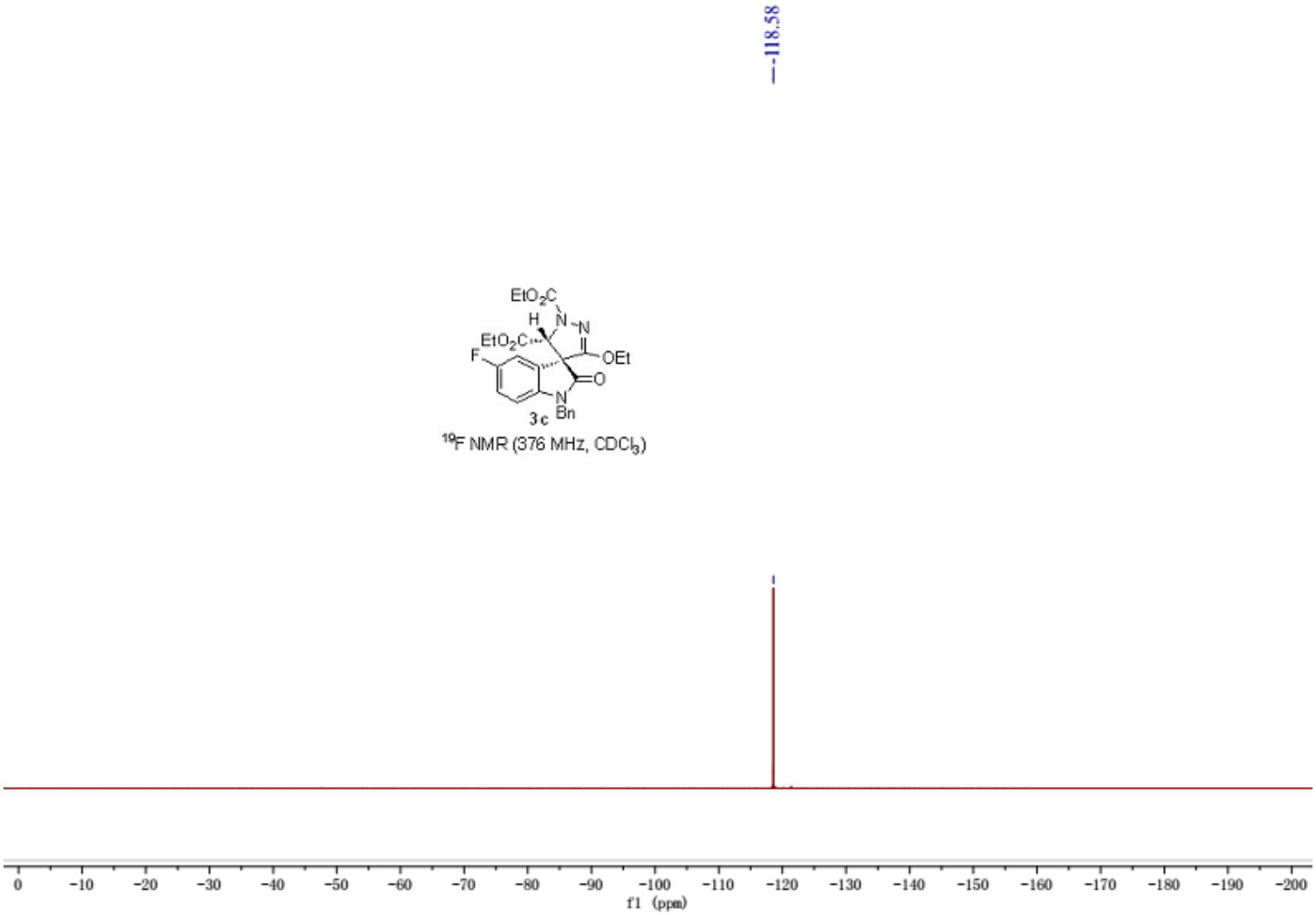
138.91
134.33
128.80
126.79
116.73
116.49
113.32
113.06
110.39
110.31
77.32
77.00
76.68
67.29
62.60
61.56
44.28
14.54
13.94
13.49
EtO2C
H
N
N
EtO2C
F
OEt
O
N
Bn
3c
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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H
N
N
EtO2C
F
OEt
O
N
Bn
3c
19F NMR (376 MHz, CDCl3)
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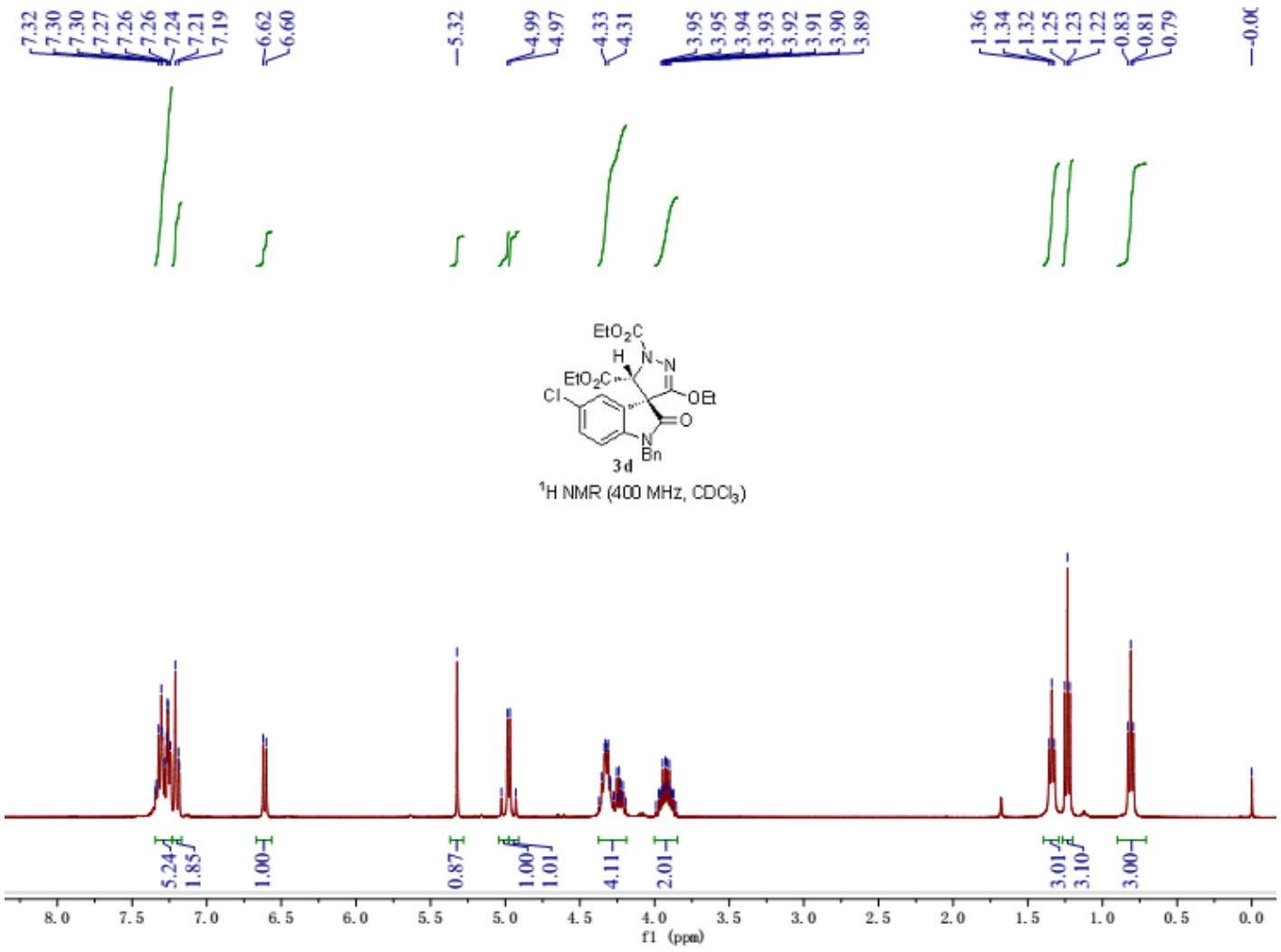
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)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7.19
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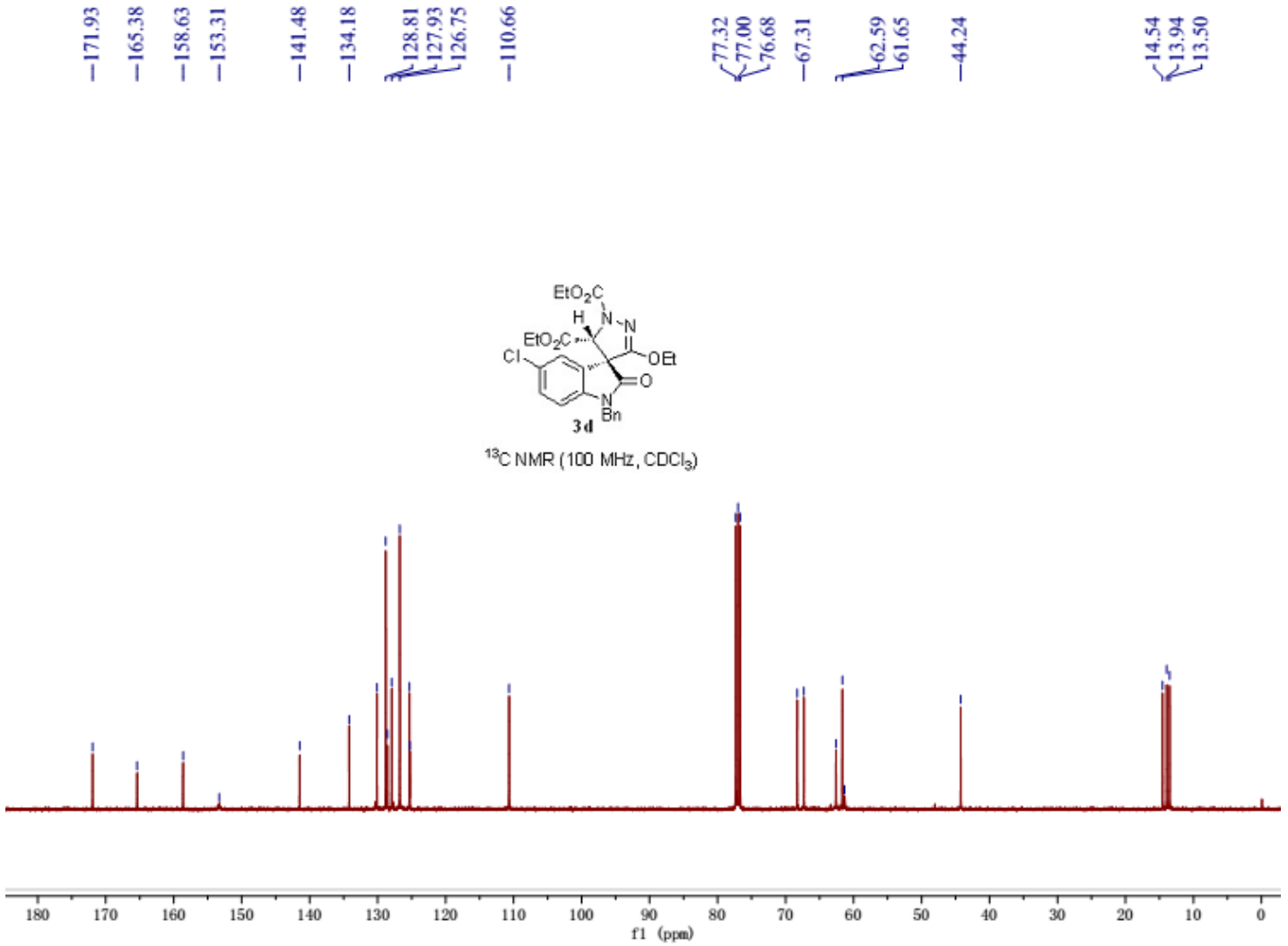
6.60
5.32
4.99
4.97
4.33
4.31
3.95
3.95
3.94
3.93
3.92
3.91
3.90
3.89
1.36
1.34
1.32
1.25
1.23
1.22
0.83
0.81
0.79
EtO2C
H
N
N
EtO2C
Cl
OEt
O
N
Bn
3d
1H NMR (400 MHz, CDCl3)
5.24
1.85
1.00
0.87
1.00
1.01
4.11
2.01
3.01
3.10
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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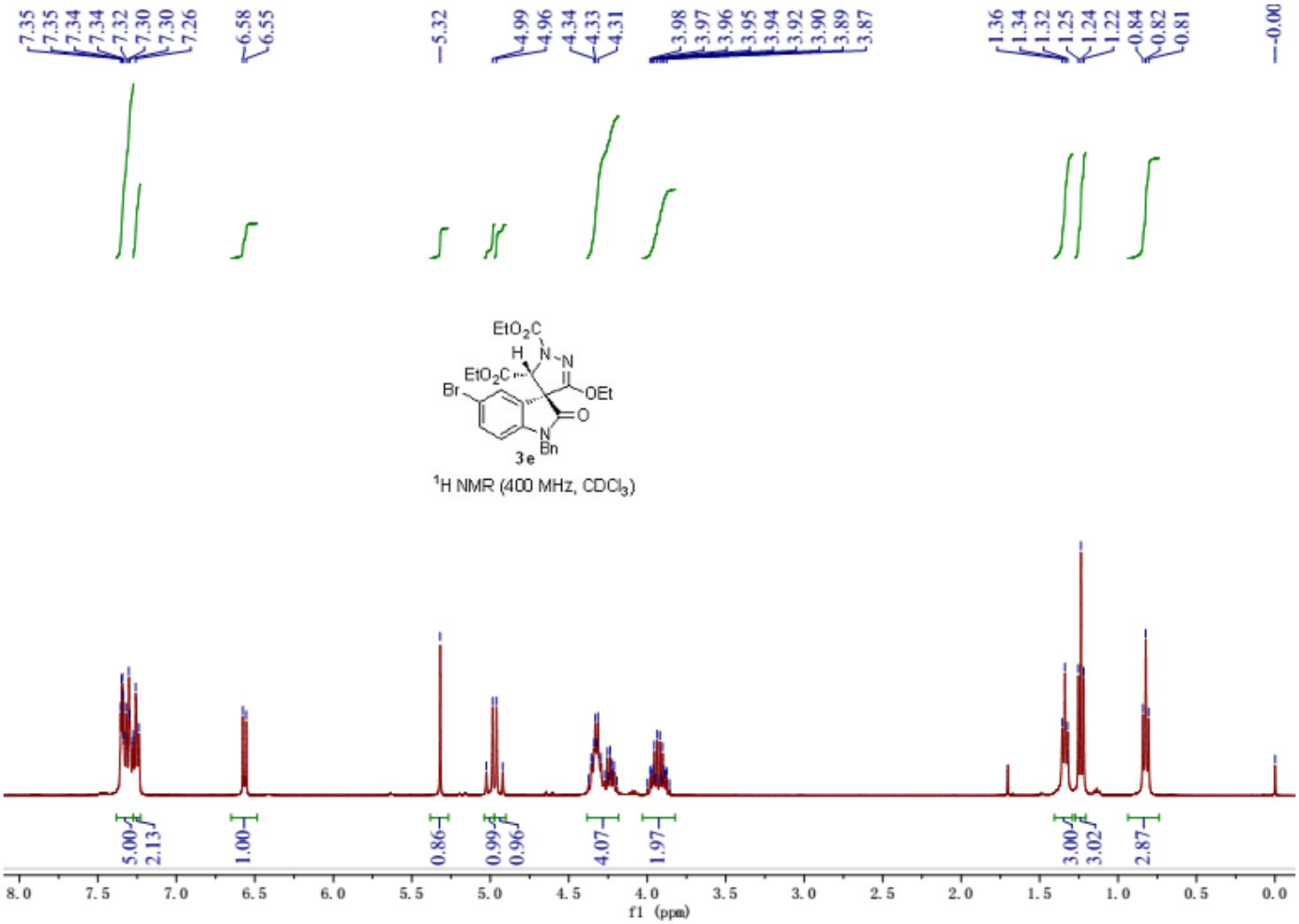
158.63
153.31
141.48
134.18
128.81
127.93
126.75
110.66
77.32
77.00
76.68
67.31
62.59
61.65
44.24
14.54
13.94
13.50
EtO2C
H
N
N
EtO2C
Cl
OEt
O
N
Bn
3d
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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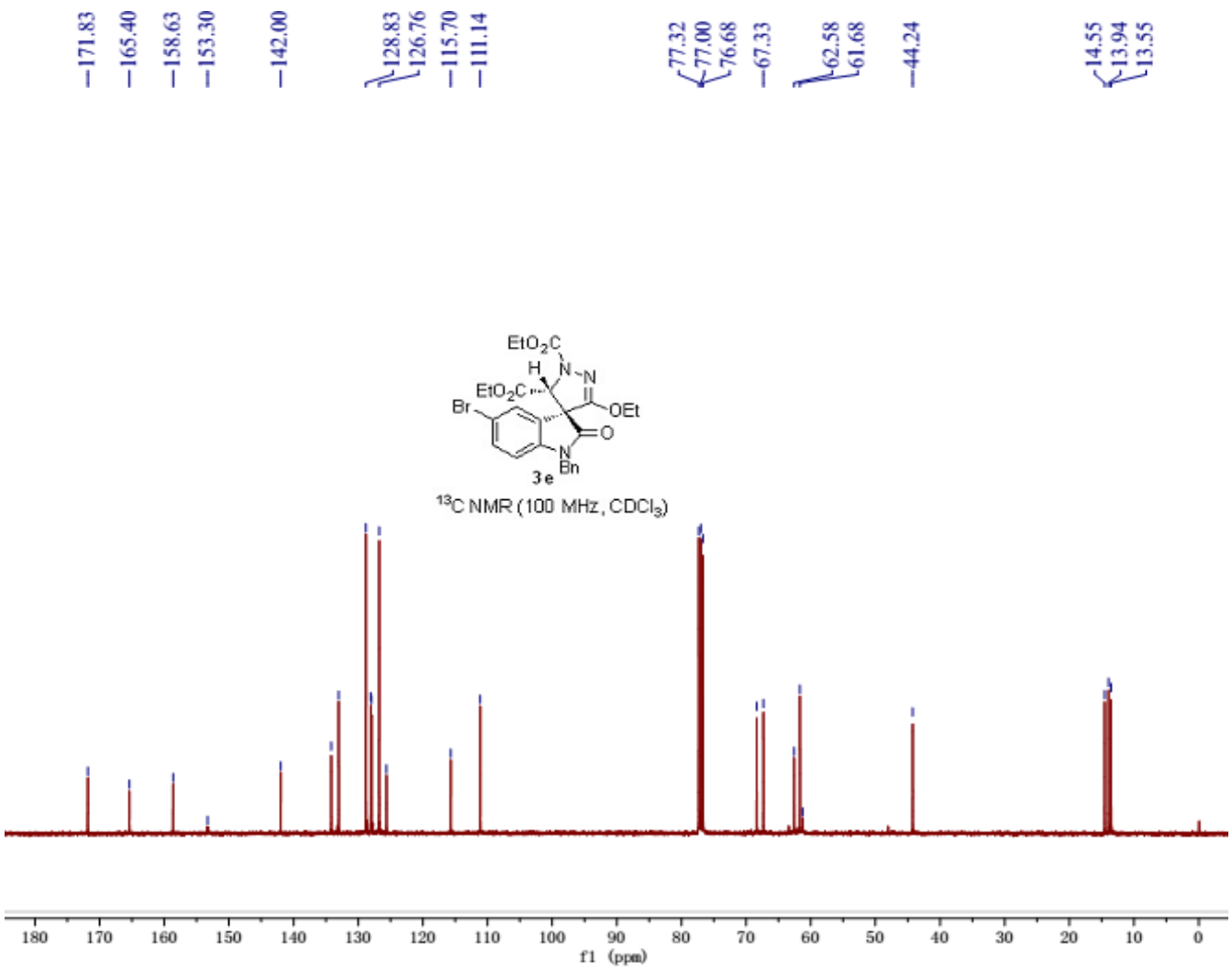
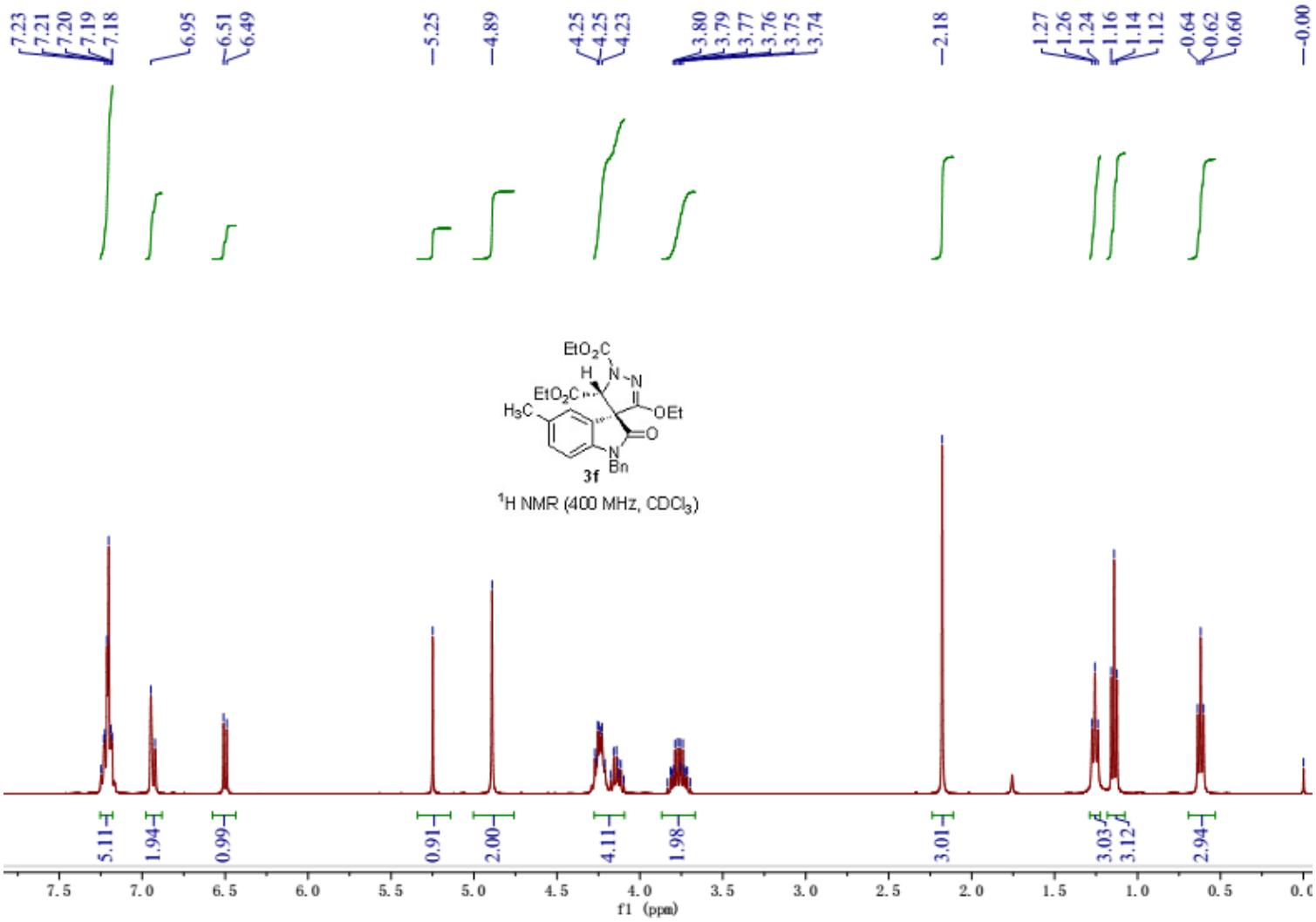
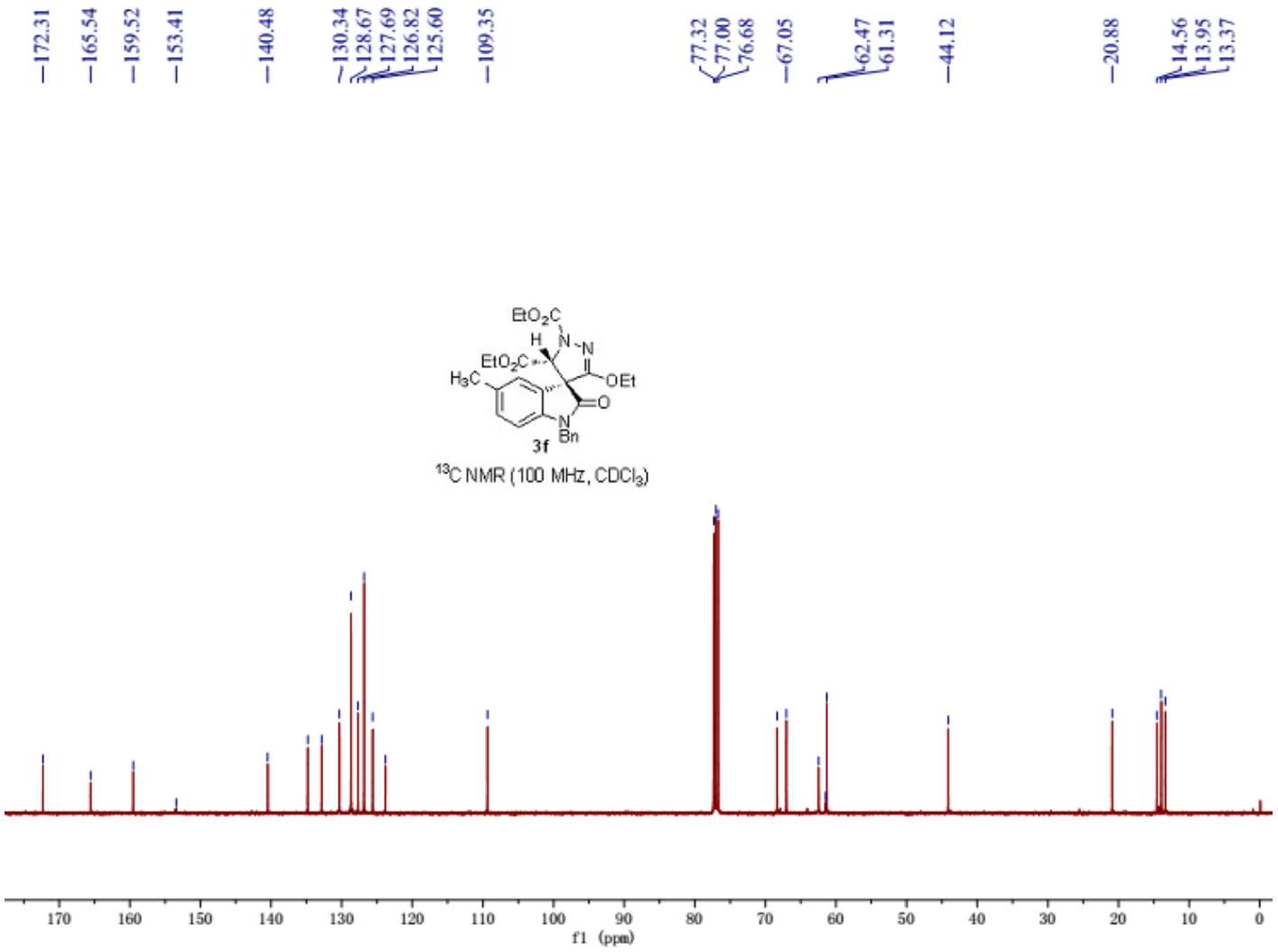
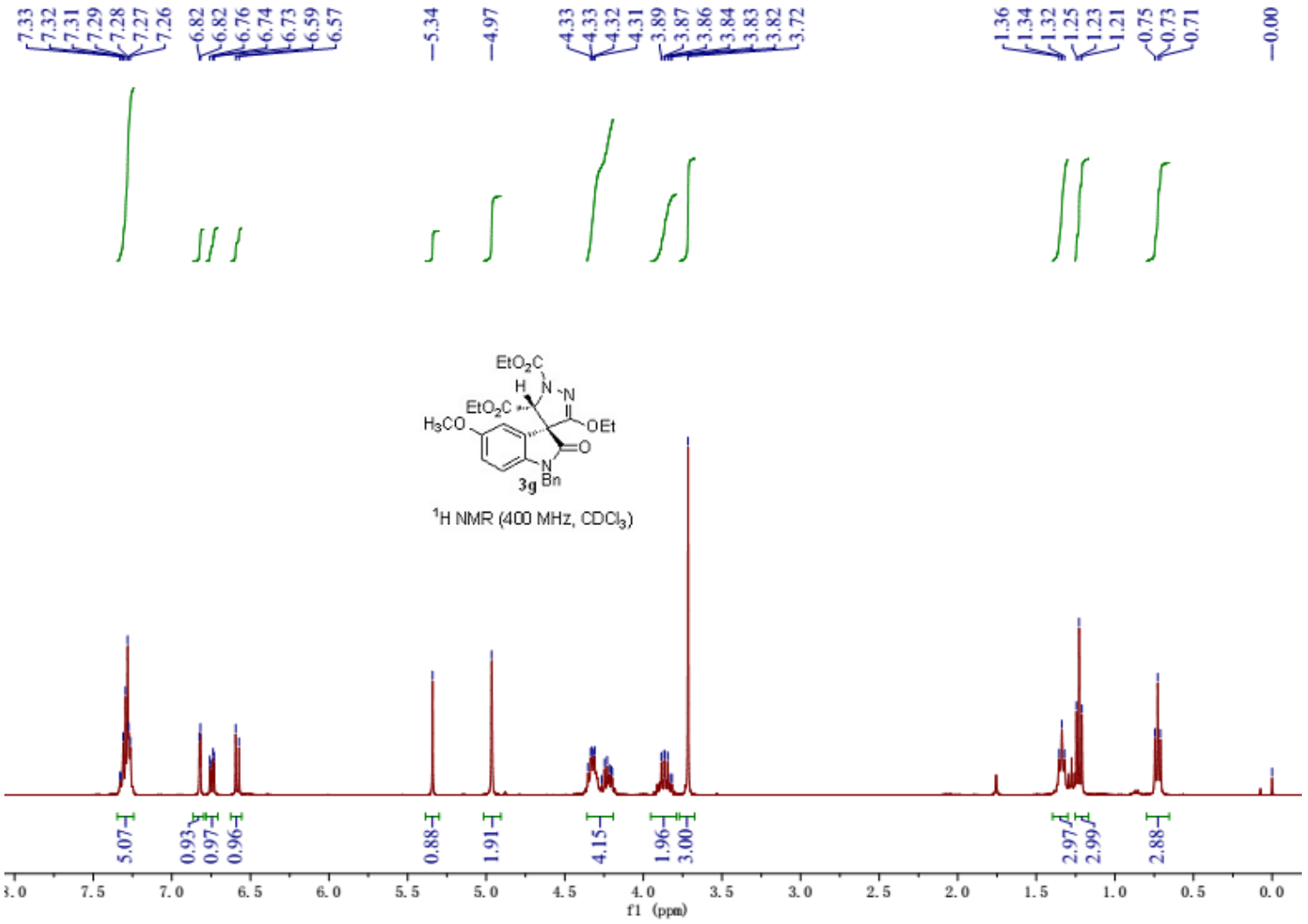
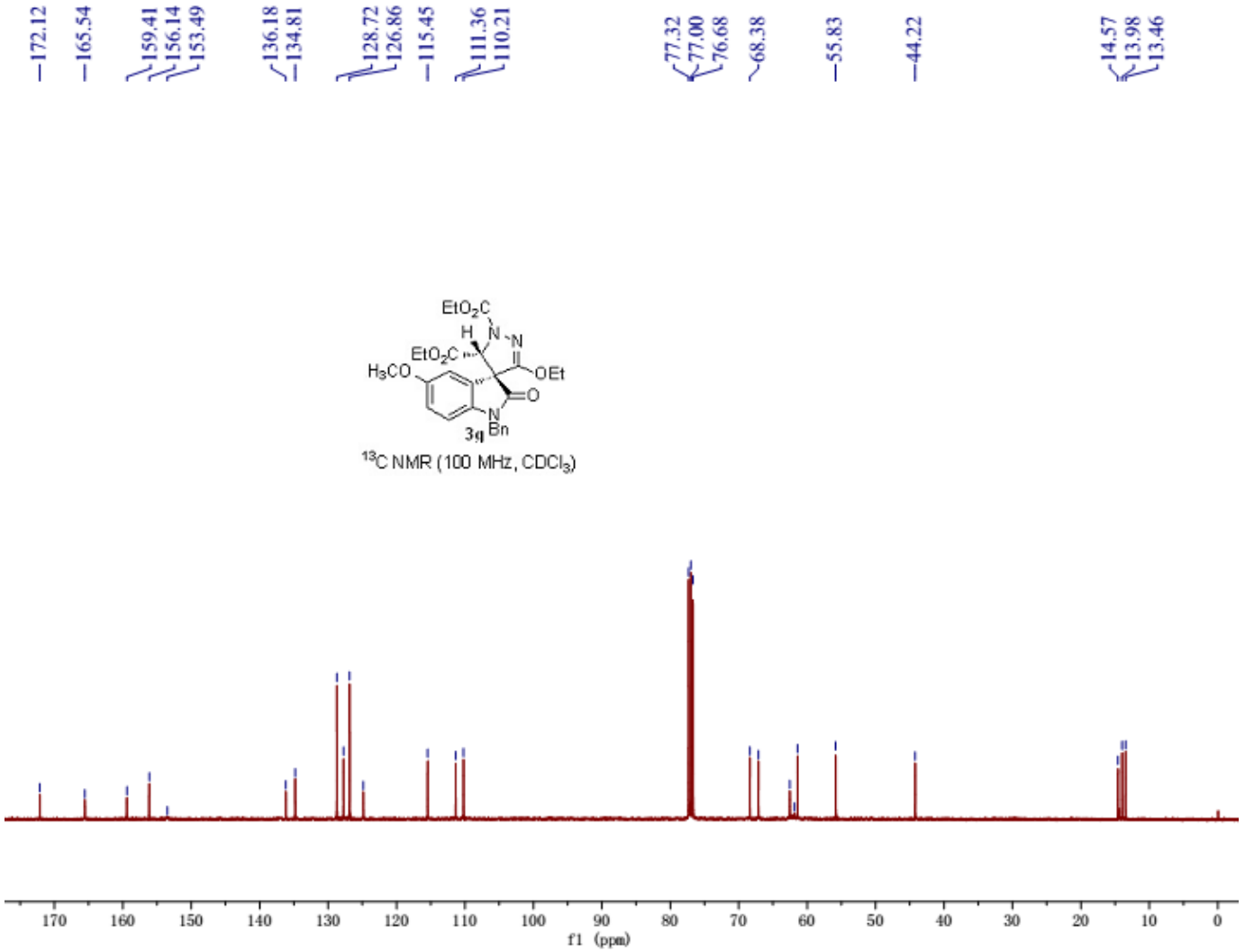
7.35
7.34
7.34
7.32
7.30
7.30
7.26
6.58
6.55
5.32
4.99
4.96
4.34
4.33
4.31
3.98
3.97
3.96
3.95
3.94
3.92
3.90
3.89
3.87
1.36
1.34
1.32
1.25
1.24
1.22
0.84
0.82
0.81
0.00
EtO2C
H
N
N
EtO2C
Br
OEt
O
N
Bn
3e
1H NMR (400 MHz, CDCl3)
5.00
2.13
1.00
0.86
0.99
0.96
4.07
1.97
3.00
3.02
2.87
8.0
7.5
7.0
6.5
6.0
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)

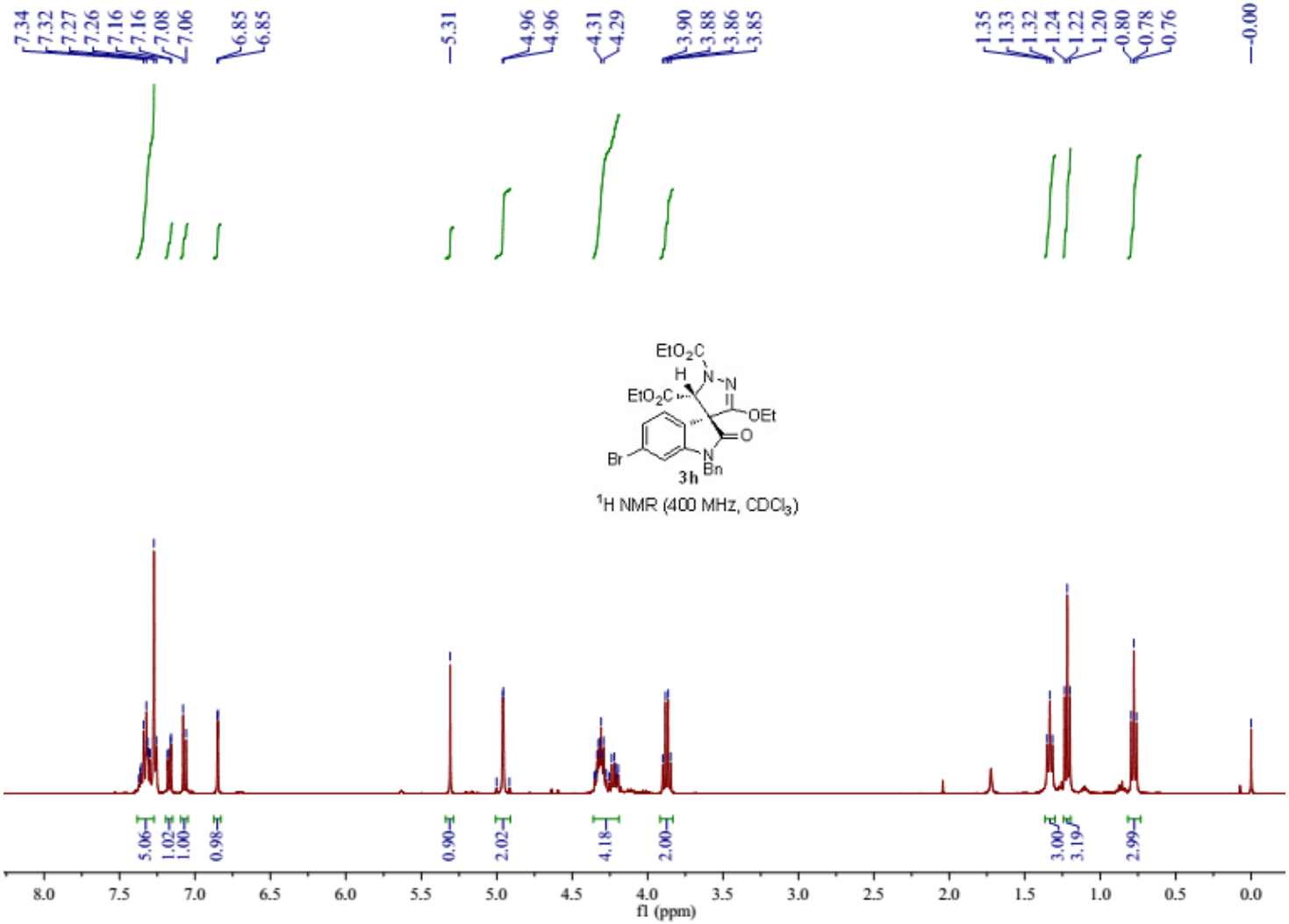

171.83
165.40
158.63
153.30
142.00
128.83
126.76
115.70
111.14
77.32
77.00
76.68
67.33
62.58
61.68
44.24
14.55
13.94
13.55
EtO2C
H
N
N
EtO2C
Br
OEt
O
N
Bn
3e
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

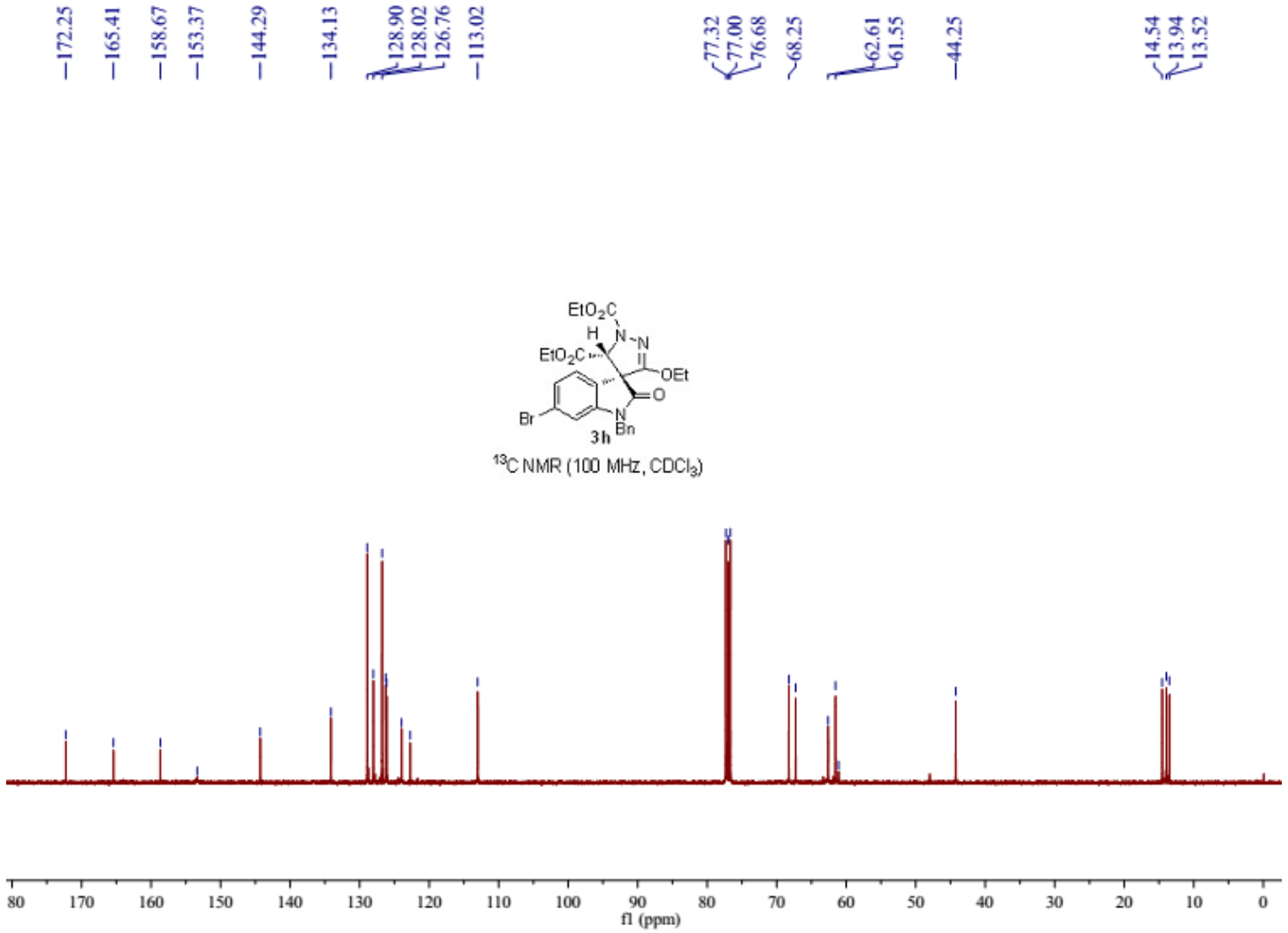

7.23
7.21
7.20
7.19
7.18
6.95
6.51
6.49
5.25
4.89
4.25
4.25
4.23
3.80
3.79
3.77
3.76
3.75
3.74
2.18
1.27
1.26
1.24
1.16
1.14
1.12
0.64
0.62
0.60
0.00
EtO2C
H
N
N
EtO2C
H3C
OEt
O
N
Bn
3f
1H NMR (400 MHz, CDCl3)
5.11
1.94
0.99
0.91
2.00
4.11
1.98
3.01
3.03
3.12
2.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

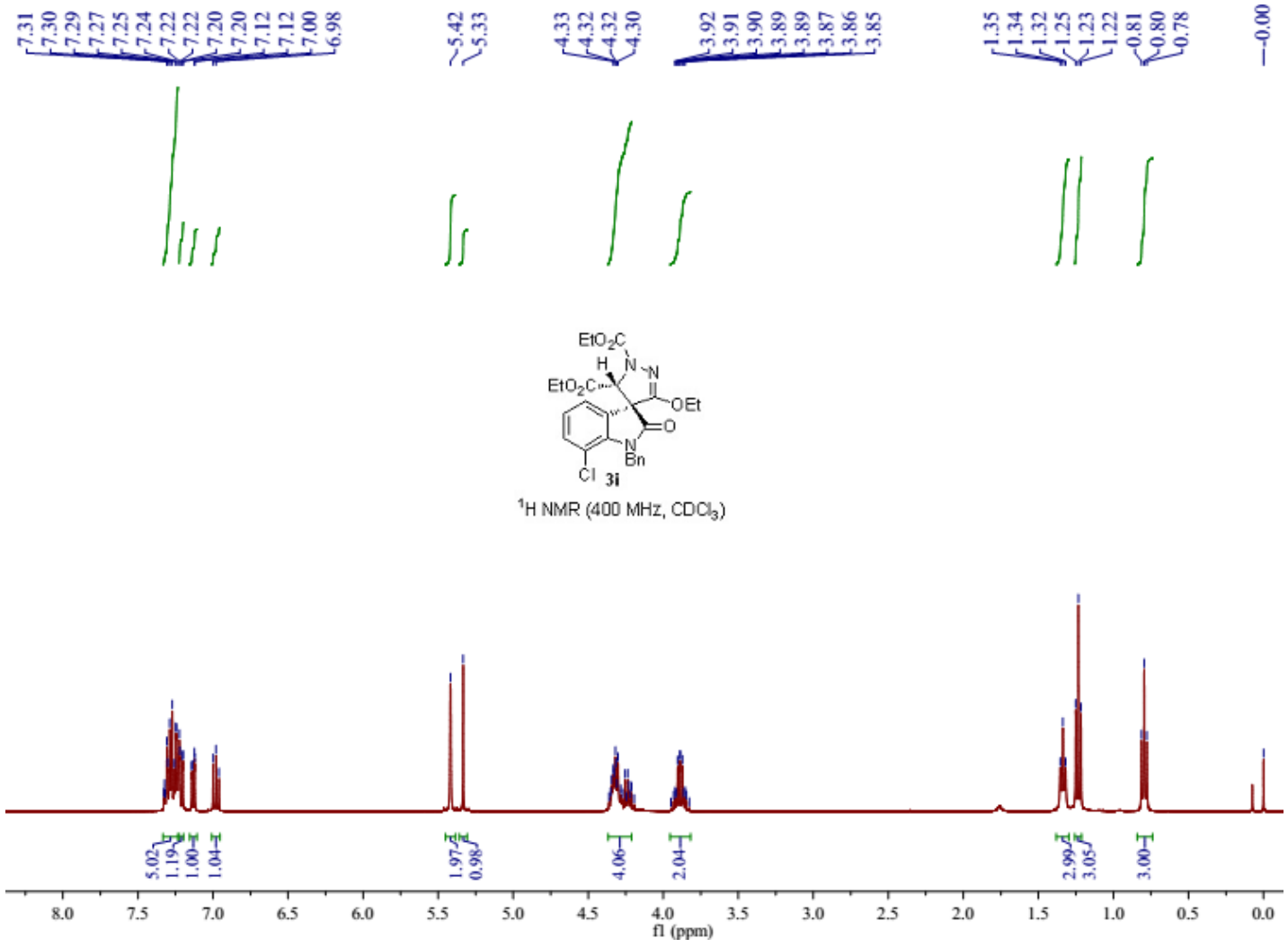

172.31
165.54
159.52
153.41
140.48
130.34
128.67
127.69
126.82
125.60
109.35
77.32
77.00
76.68
67.05
62.47
61.31
44.12
20.88
14.56
13.95
13.37
EtO2C
H
N
N
EtO2C
H3C
OEt
O
N
Bn
3f
13C NMR (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

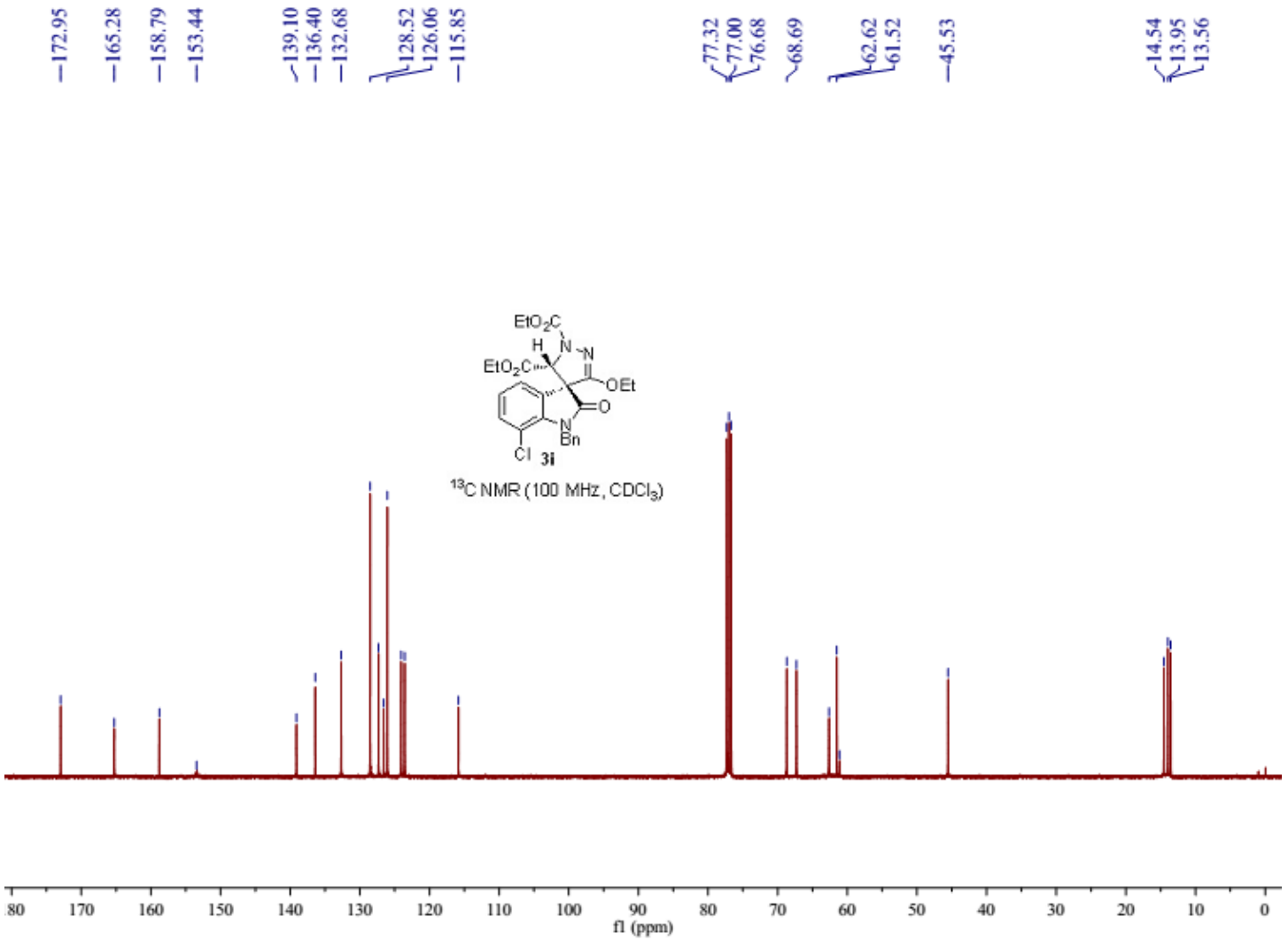

7.33
7.32
7.31
7.29
7.28
7.27
7.26
6.82
6.82
6.76
6.74
6.73
6.59
6.57
5.34
4.97
4.33
4.33
4.32
4.31
3.89
3.87
3.86
3.84
3.83
3.82
3.72
1.36
1.34
1.32
1.25
1.23
1.21
0.75
0.73
0.71
0.00
EtO2C
H
N
N
EtO2C
H3CO
OEt
O
N
Bn
3g
1H NMR (400 MHz, CDCl3)
5.07
0.93
0.97
0.96
0.88
1.91
4.15
1.96
3.00
2.97
2.99
2.88
f1 (ppm)

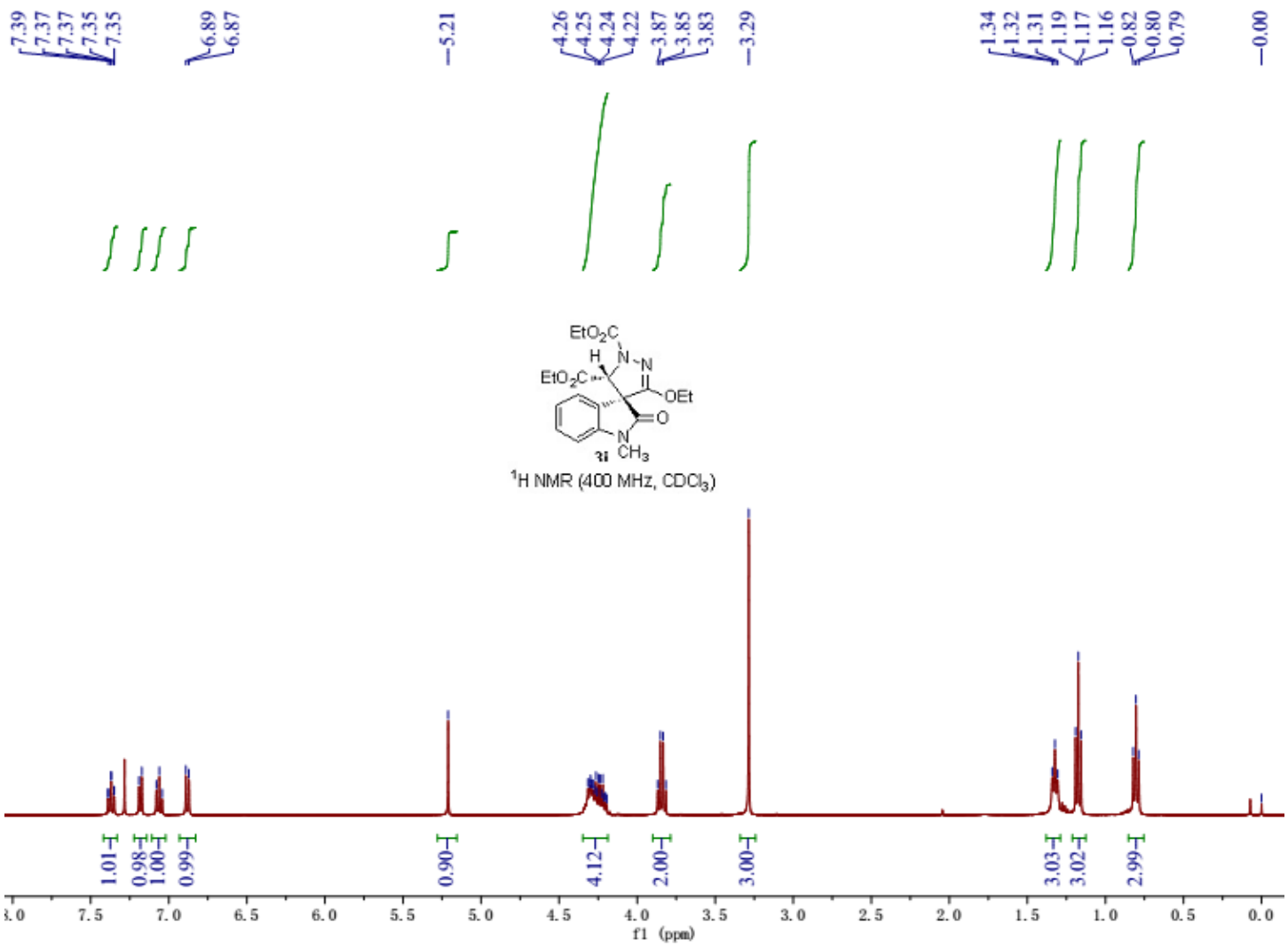

172.12
165.54
159.41
156.14
153.49
136.18
134.81
128.72
126.86
115.45
111.36
110.21
77.32
77.00
76.68
68.38
55.83
44.22
14.57
13.98
13.46
EtO2C
H
N
N
EtO2C
H3CO
OEt
O
N
Bn
3q
13C NMR (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

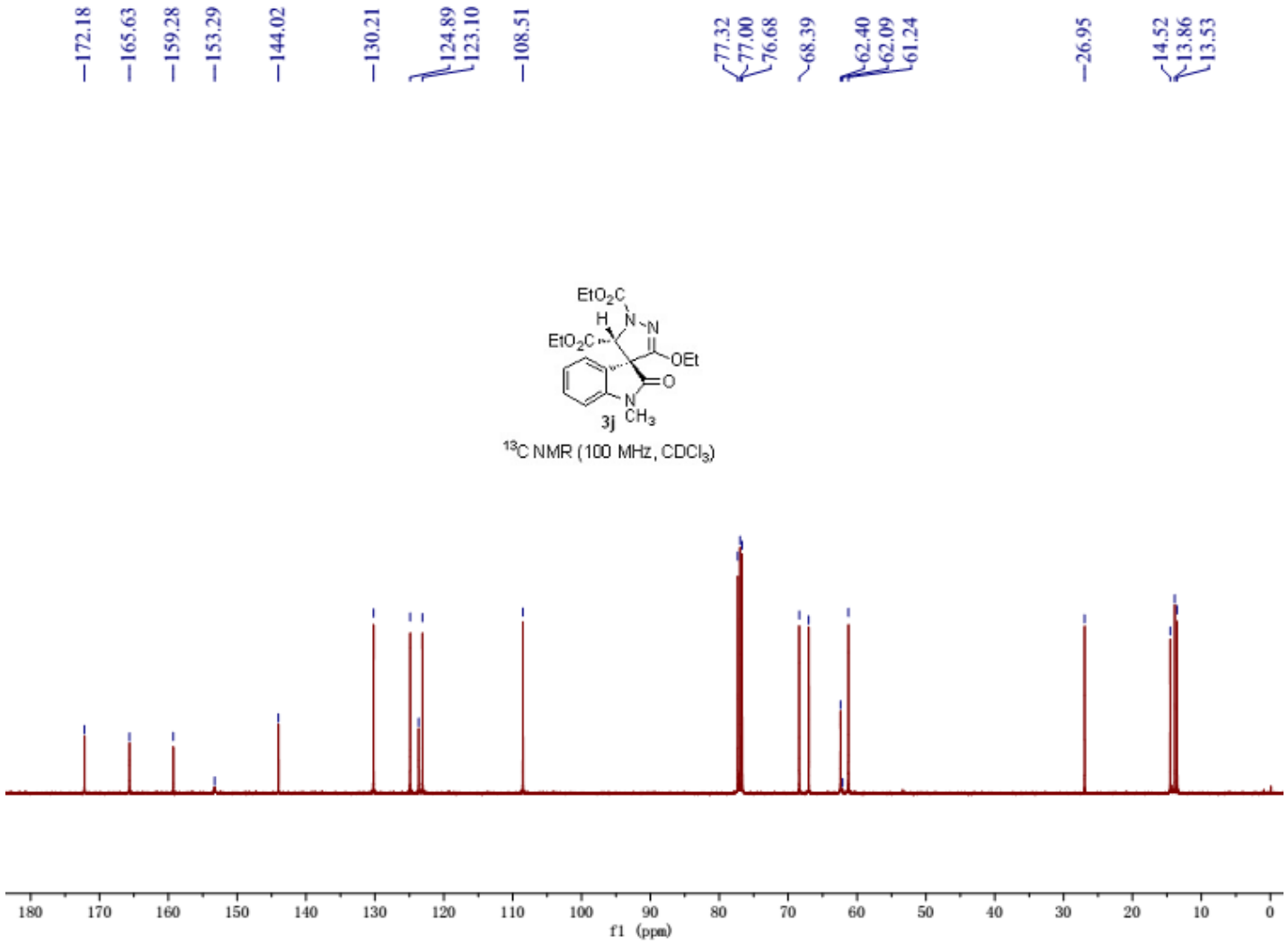

7.34
7.32
7.27
7.26
7.16
7.16
7.08
7.06
6.85
6.85
5.31
4.96
4.96
4.31
4.29
3.90
3.88
3.86
3.85
1.35
1.33
1.32
1.24
1.22
1.20
0.80
0.78
0.76
0.00
EtO2C
H
N
N
EtO2C
OEt
O
Br
N
Bn
3h
1H NMR (400 MHz, CDCl3)
5.06
1.02
1.00
0.98
0.90
2.02
4.18
2.00
3.00
3.19
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

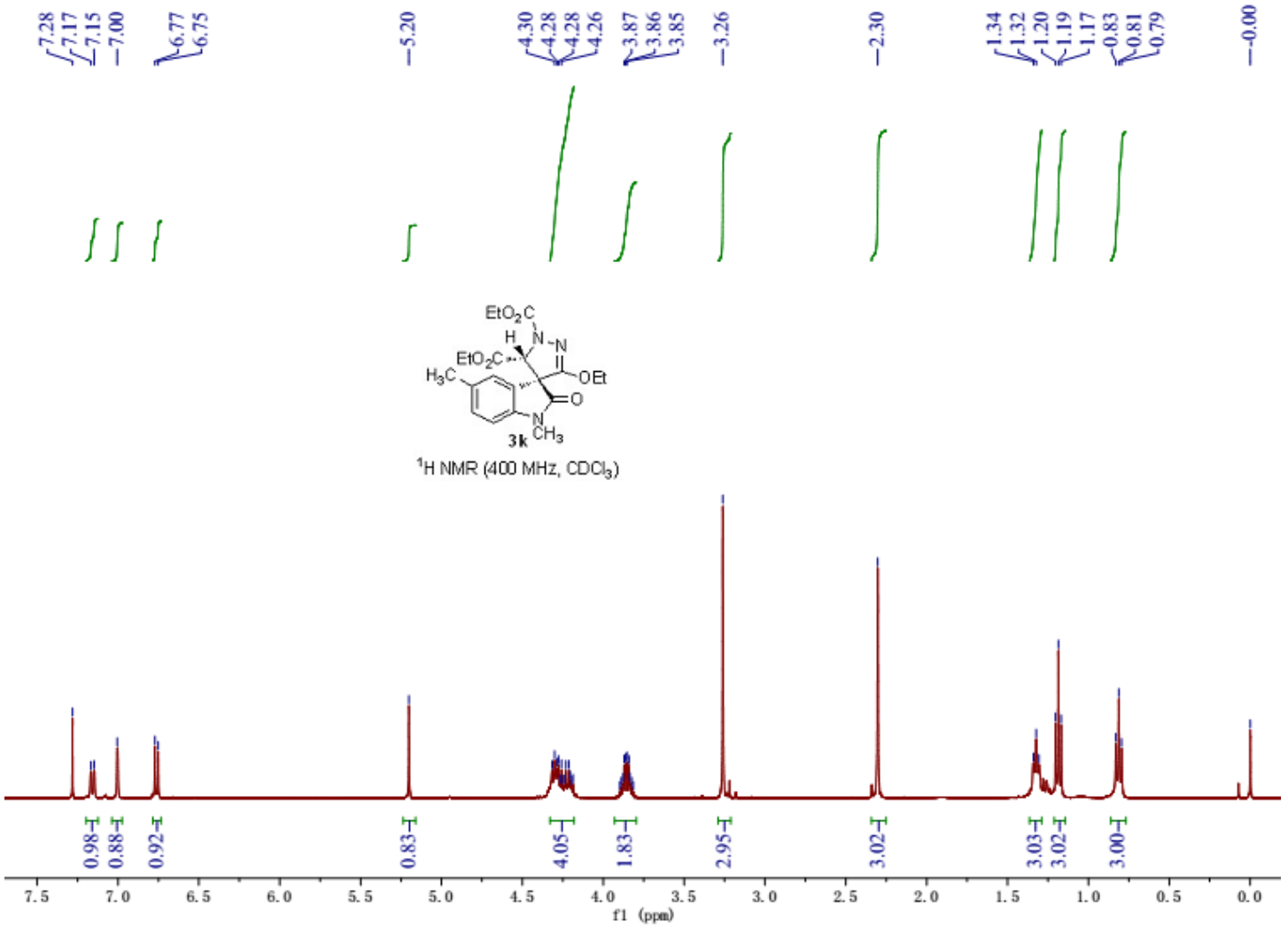

172.25
165.41
158.67
153.37
144.29
134.13
128.90
128.02
126.76
113.02
77.32
77.00
76.68
68.25
62.61
61.55
44.25
14.54
13.94
13.52
EtO2C
H
N
N
EtO2C
OEt
O
Br
N
Bn
3h
13C NMR (100 MHz, CDCl3)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

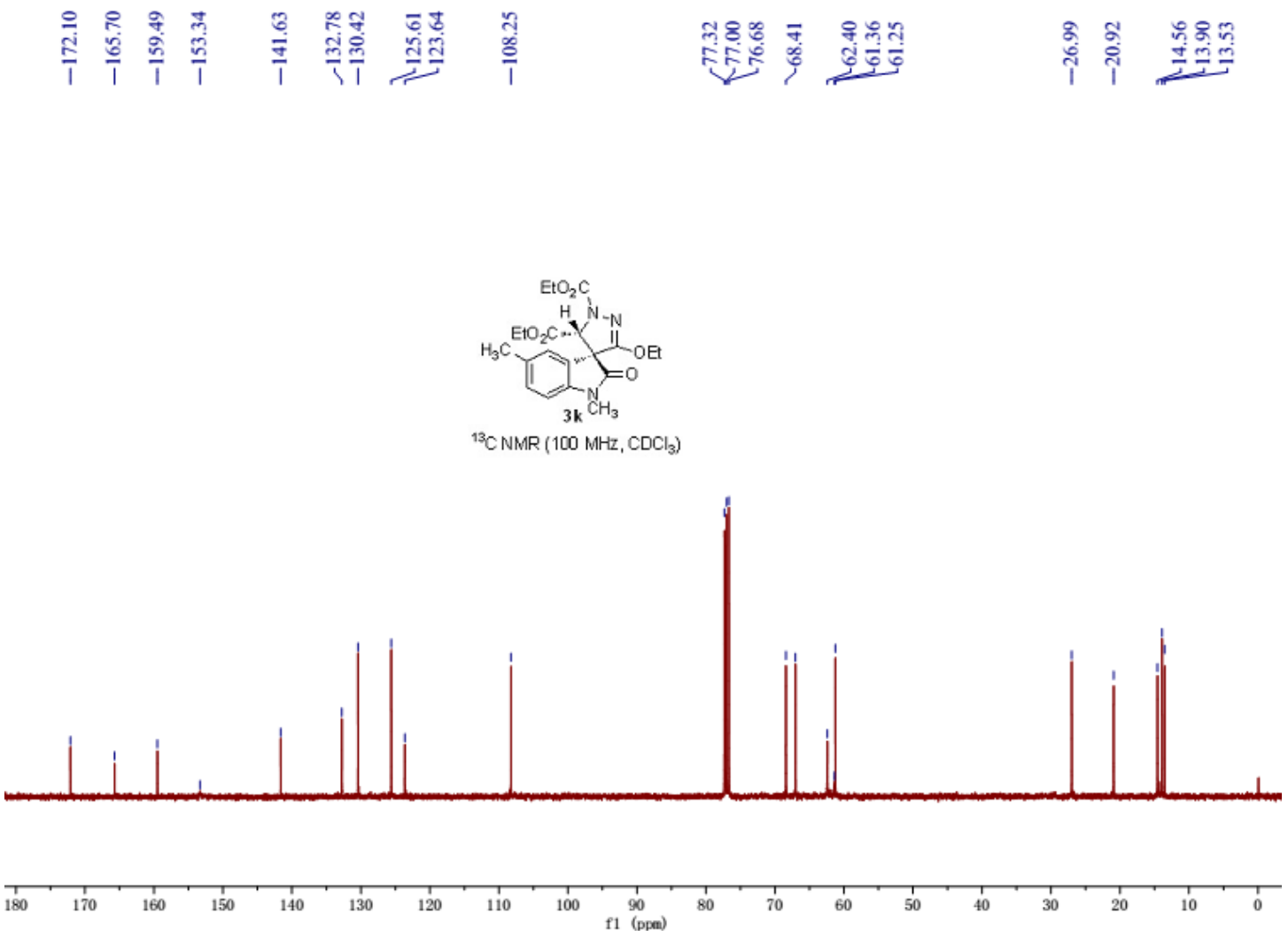

7.31
7.30
7.29
7.27
7.25
7.24
7.22
7.22
7.20
7.20
7.12
7.12
7.00
6.98
5.42
5.33
4.33
4.32
4.32
4.30
3.92
3.91
3.90
3.89
3.89
3.87
3.86
3.85
1.35
1.34
1.32
1.25
1.23
1.22
0.81
0.80
0.78
0.00
EtO2C
H
N
N
EtO2C
OEt
O
N
Bn
Cl
3i
1H NMR (400 MHz, CDCl3)
5.02
1.19
1.00
1.04
1.97
0.98
4.06
2.04
2.99
3.05
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

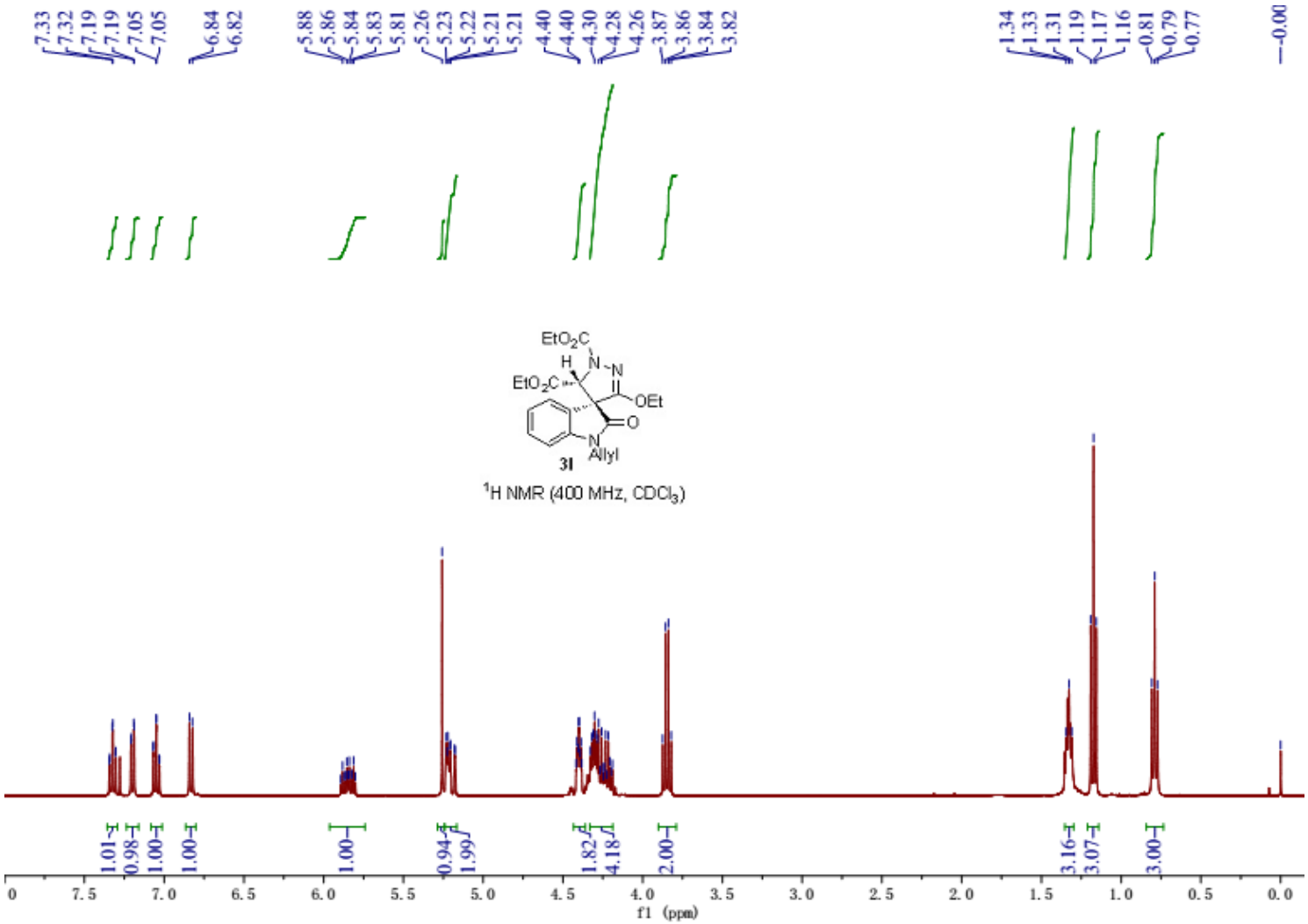

172.95
165.28
158.79
153.44
139.10
136.40
132.68
128.52
126.06
115.85
77.32
77.00
76.68
68.69
62.62
61.52
45.53
14.54
13.95
13.56
EtO2C
EtO2C
OEt
O
N
Bn
Cl
3i
13C NMR (100 MHz, CDCl3)
f1 (ppm)

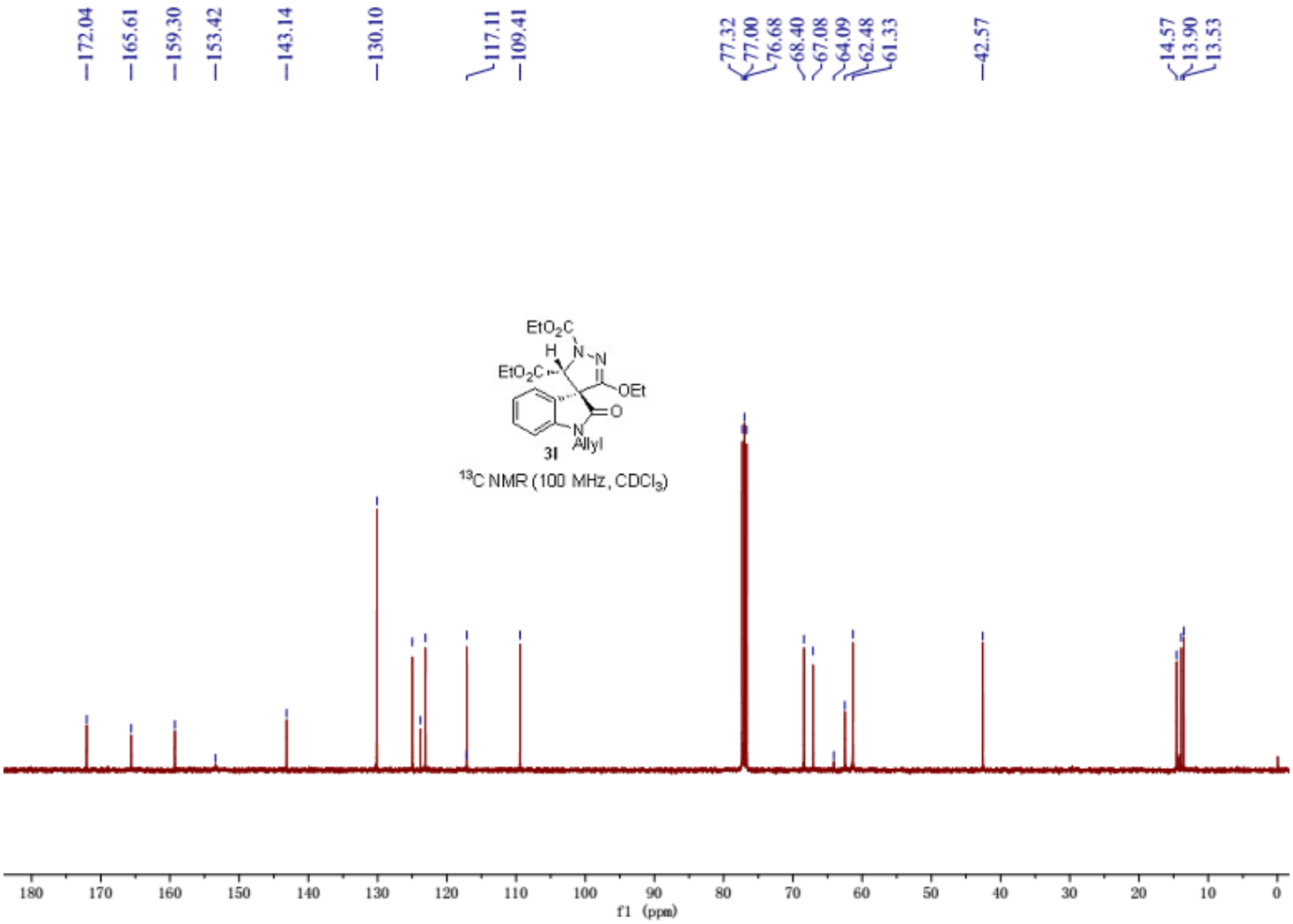

7.39
7.37
7.37
7.35
7.35
6.89
6.87
5.21
4.26
4.25
4.24
4.22
3.87
3.85
3.83
3.29
1.34
1.32
1.31
1.19
1.17
1.16
0.82
0.80
0.79
0.00
EtO2C
H
N
N
EtO2C
OEt
O
N
CH3
3i
1H NMR (400 MHz, CDCl3)
1.01
0.98
1.00
0.99
0.90
4.12
2.00
3.00
3.03
3.02
2.99
f1 (ppm)

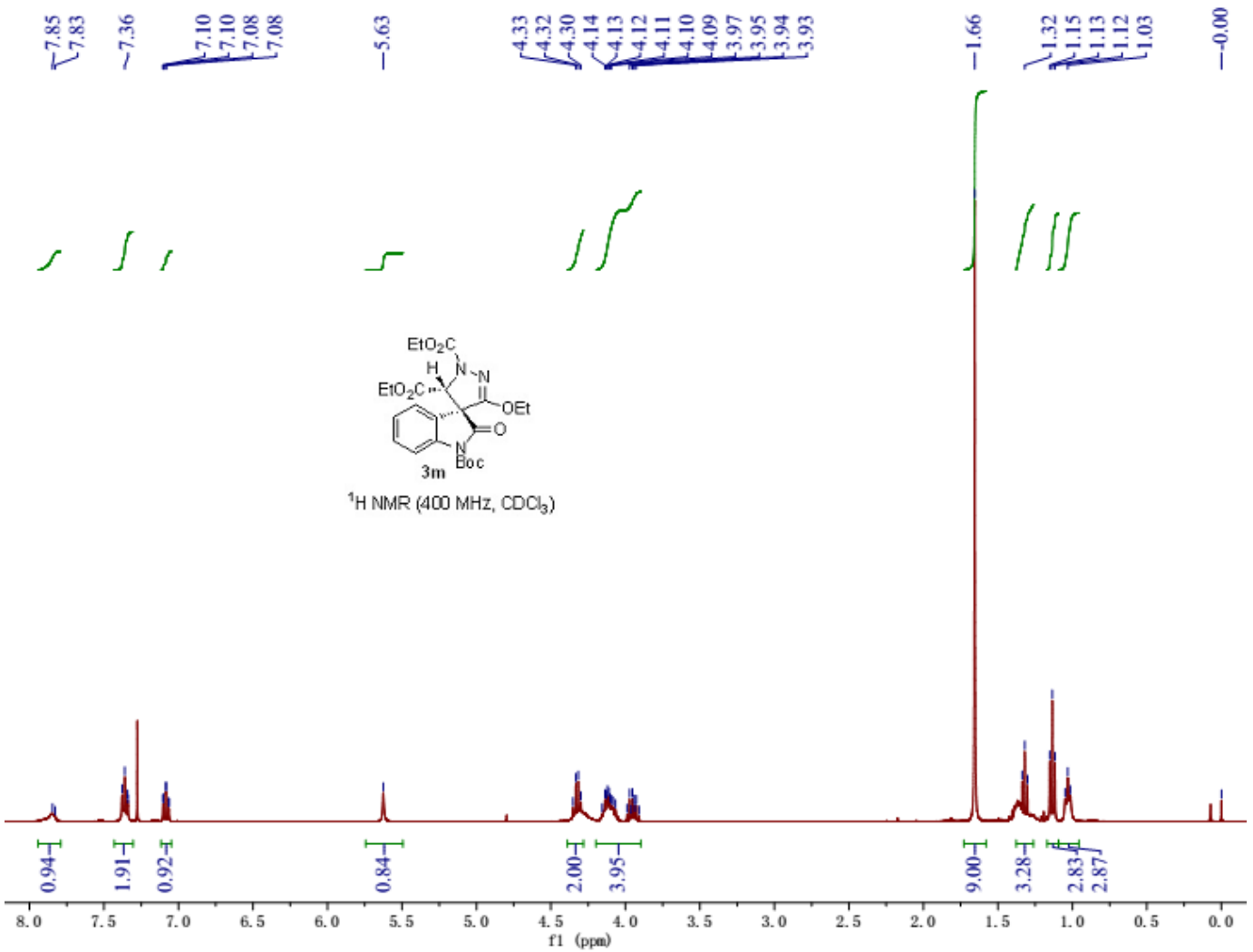

172.18
165.63
159.28
153.29
144.02
130.21
124.89
123.10
108.51
77.32
77.00
76.68
68.39
62.40
62.09
61.24
26.95
14.52
13.86
13.53
EtO2C
H
N
N
EtO2C
OEt
O
N
CH3
3j
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

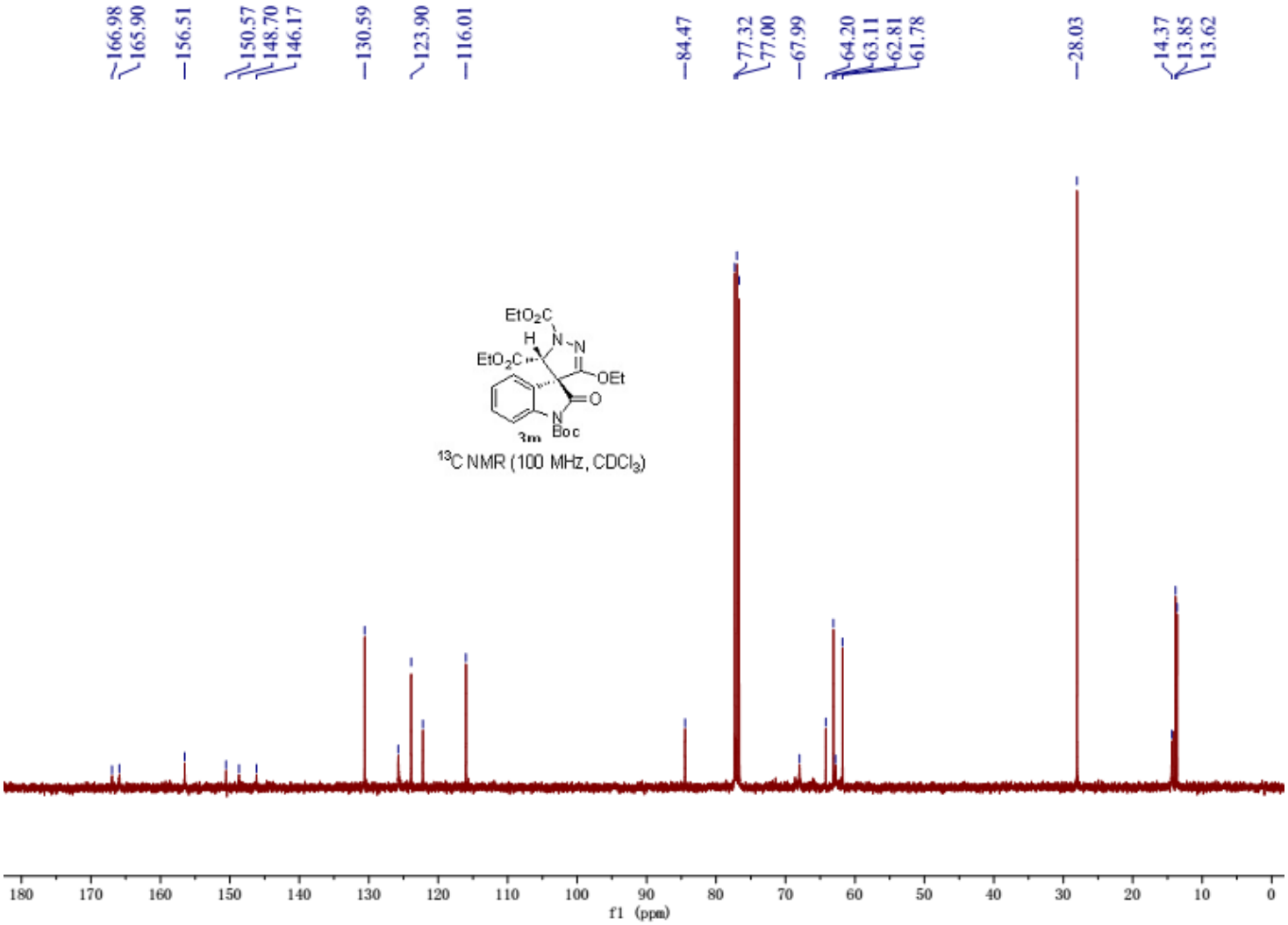

7.28
7.17
7.15
7.00
6.77
6.75
5.20
4.30
4.28
4.26
3.87
3.86
3.85
3.26
2.30
1.34
1.32
1.20
1.19
1.17
0.83
0.81
0.79
0.00
EtO2C
H
N
N
EtO2C
H3C
OEt
O
N
CH3
3k
1H NMR (400 MHz, CDCl3)
0.98
0.88
0.92
0.83
4.05
1.83
2.95
3.02
3.03
3.02
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

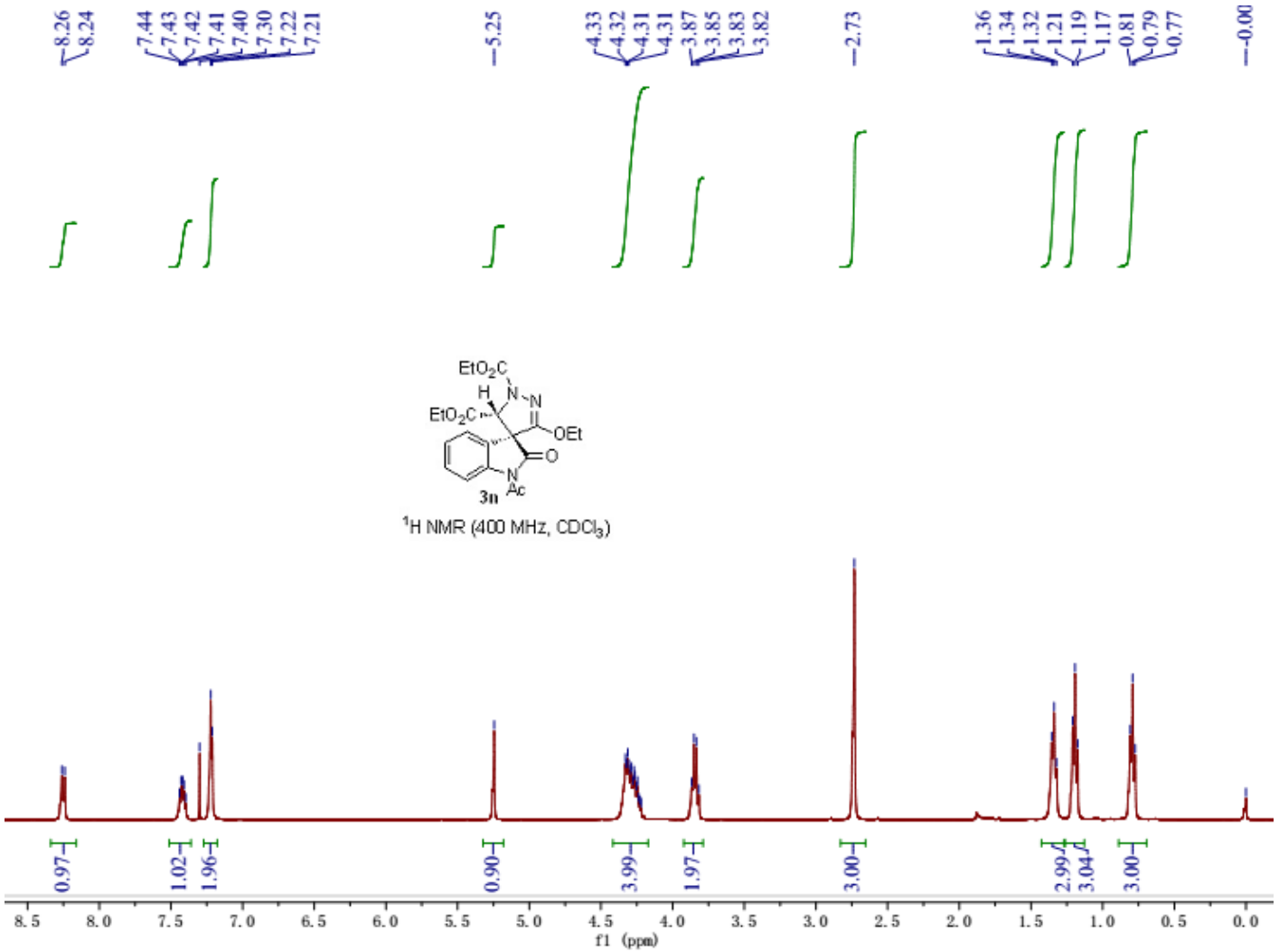

172.10
165.70
159.49
153.34
141.63
132.78
130.42
125.61
123.64
108.25
77.32
77.00
76.68
68.41
62.40
61.36
61.25
26.99
20.92
14.56
13.90
13.53
EtO2C
H
N
N
EtO2C
H3C
OEt
O
N
CH3
3k
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

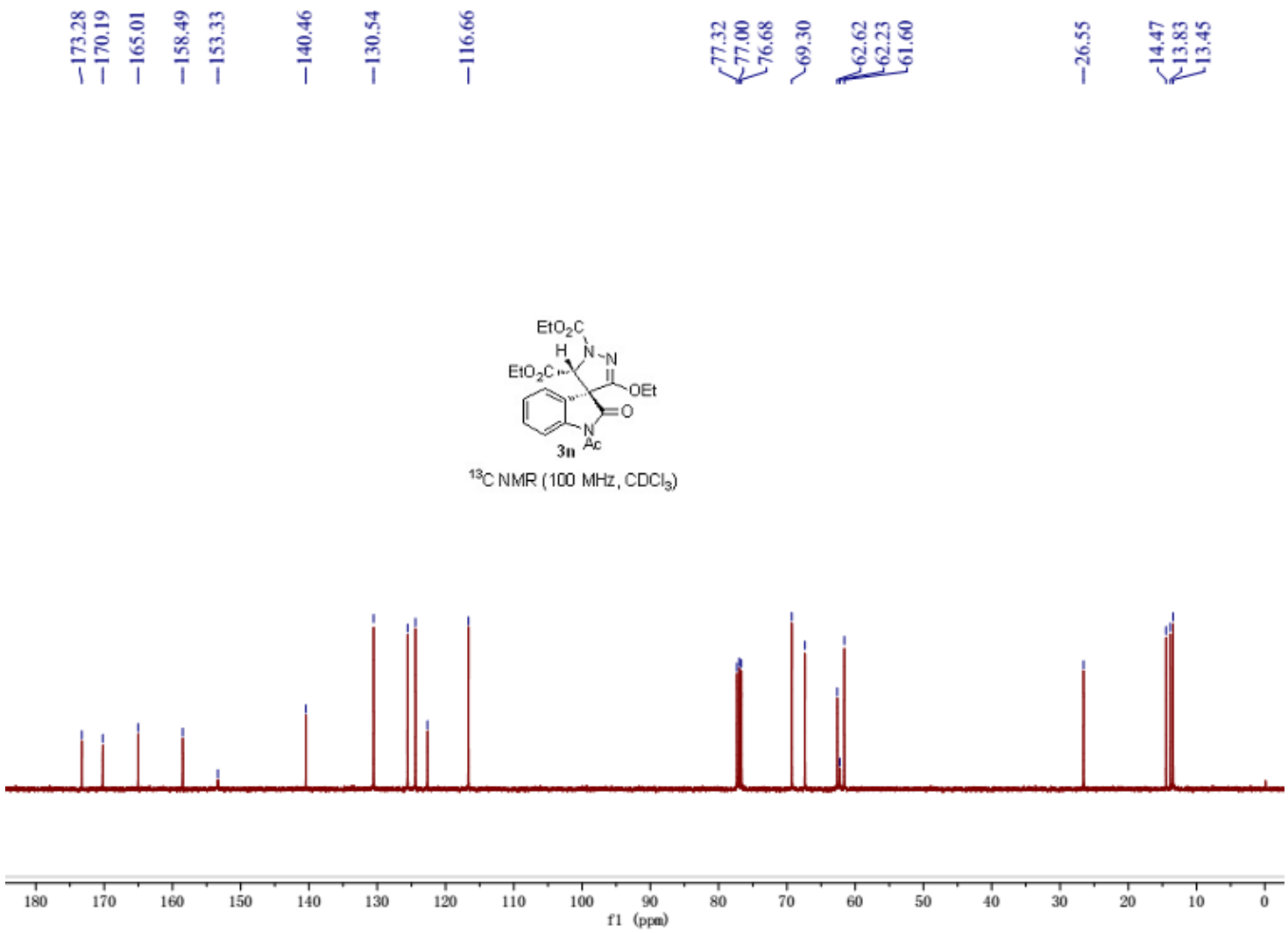

7.33
7.32
7.19
7.19
7.05
7.05
6.84
6.82
5.88
5.86
5.84
5.83
5.81
5.26
5.23
5.22
5.21
5.21
4.40
4.40
4.30
4.28
4.26
3.87
3.86
3.84
3.82
1.34
1.33
1.31
1.19
1.17
1.16
0.81
0.79
0.77
0.00
EtO2C
H
N
N
EtO2C
OEt
O
N
Allyl
3l
1H NMR (400 MHz, CDCl3)
1.01
0.98
1.00
1.00
1.00
0.94
1.99
1.82
4.18
2.00
3.16
3.07
3.00
f1 (ppm)

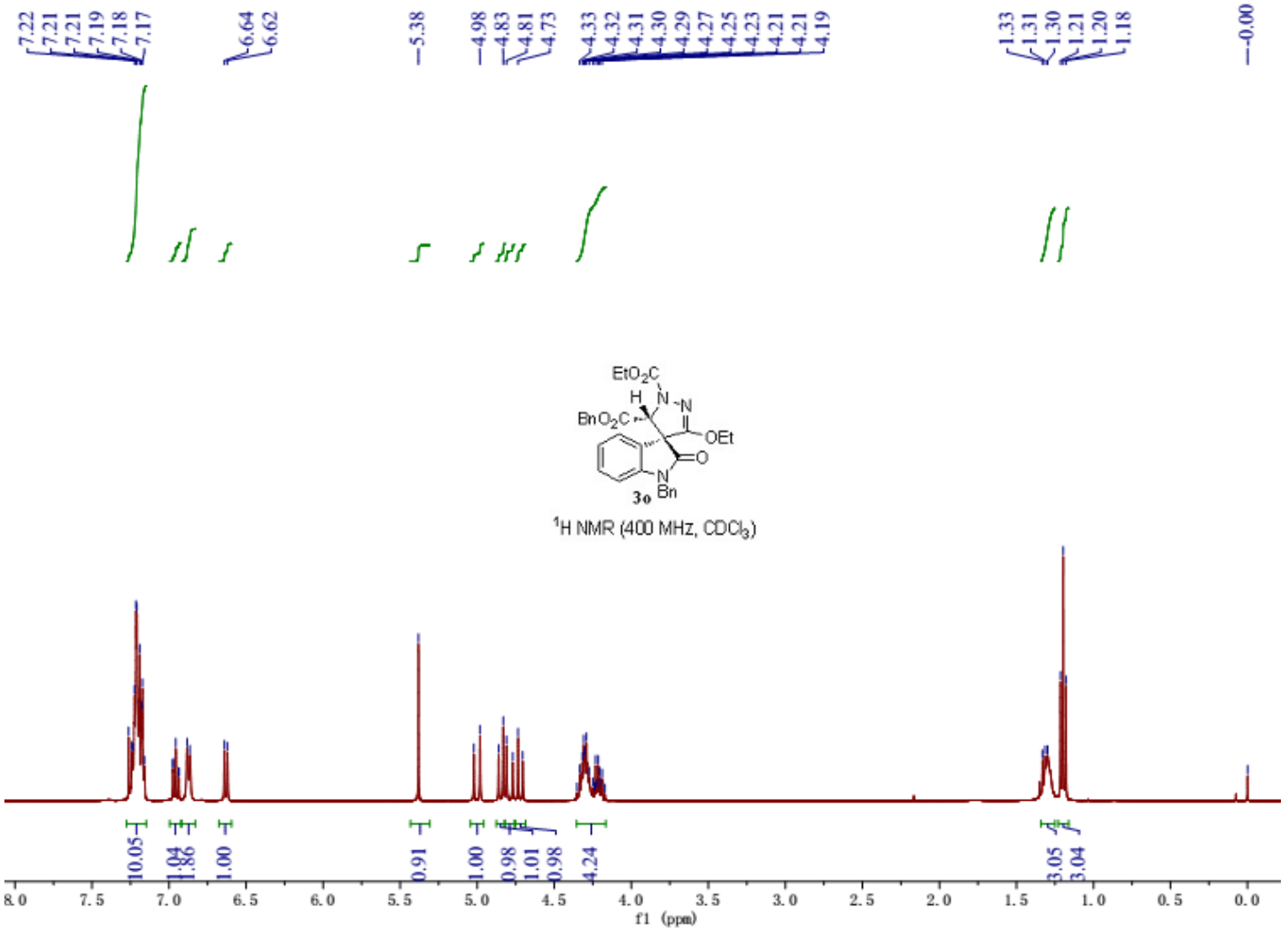

172.04
165.61
159.30
153.42
143.14
130.10
117.11
109.41
77.32
77.00
76.68
68.40
67.08
64.09
62.48
61.33
42.57
14.57
13.90
13.53
EtO2C
H
N
N
EtO2C
OEt
O
N
Allyl
3l
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

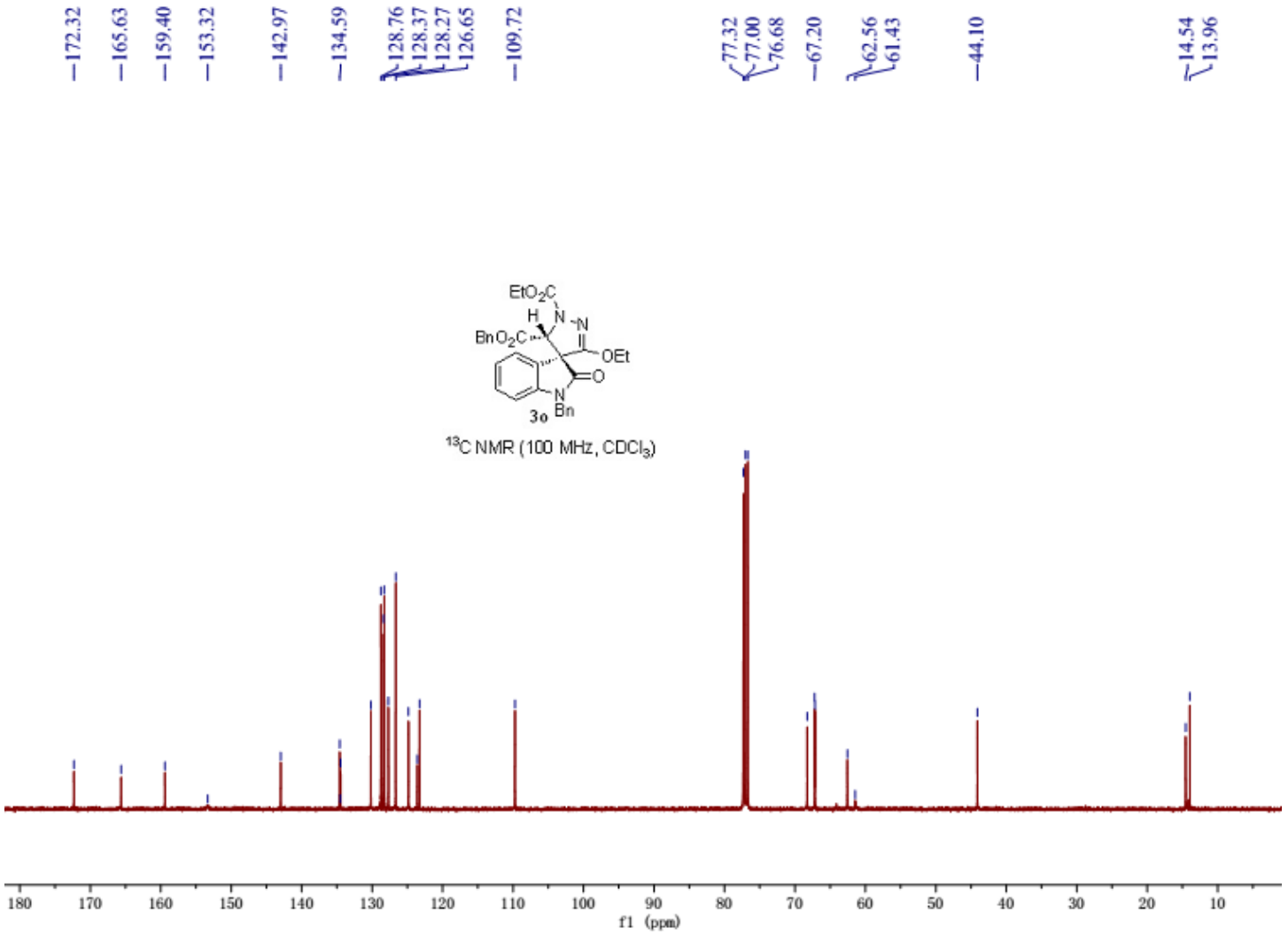

7.85
7.83
7.36
7.10
7.10
7.08
7.08
5.63
4.33
4.32
4.30
4.14
4.13
4.12
4.11
4.10
4.09
3.97
3.95
3.94
3.93
1.66
1.32
1.15
1.13
1.12
1.03
0.00
EtO2C
H
N
N
EtO2C
OEt
O
N
Boc
3m
1H NMR (400 MHz, CDCl3)
0.94
1.91
0.92
0.84
2.00
3.95
9.00
3.28
2.83
2.87
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

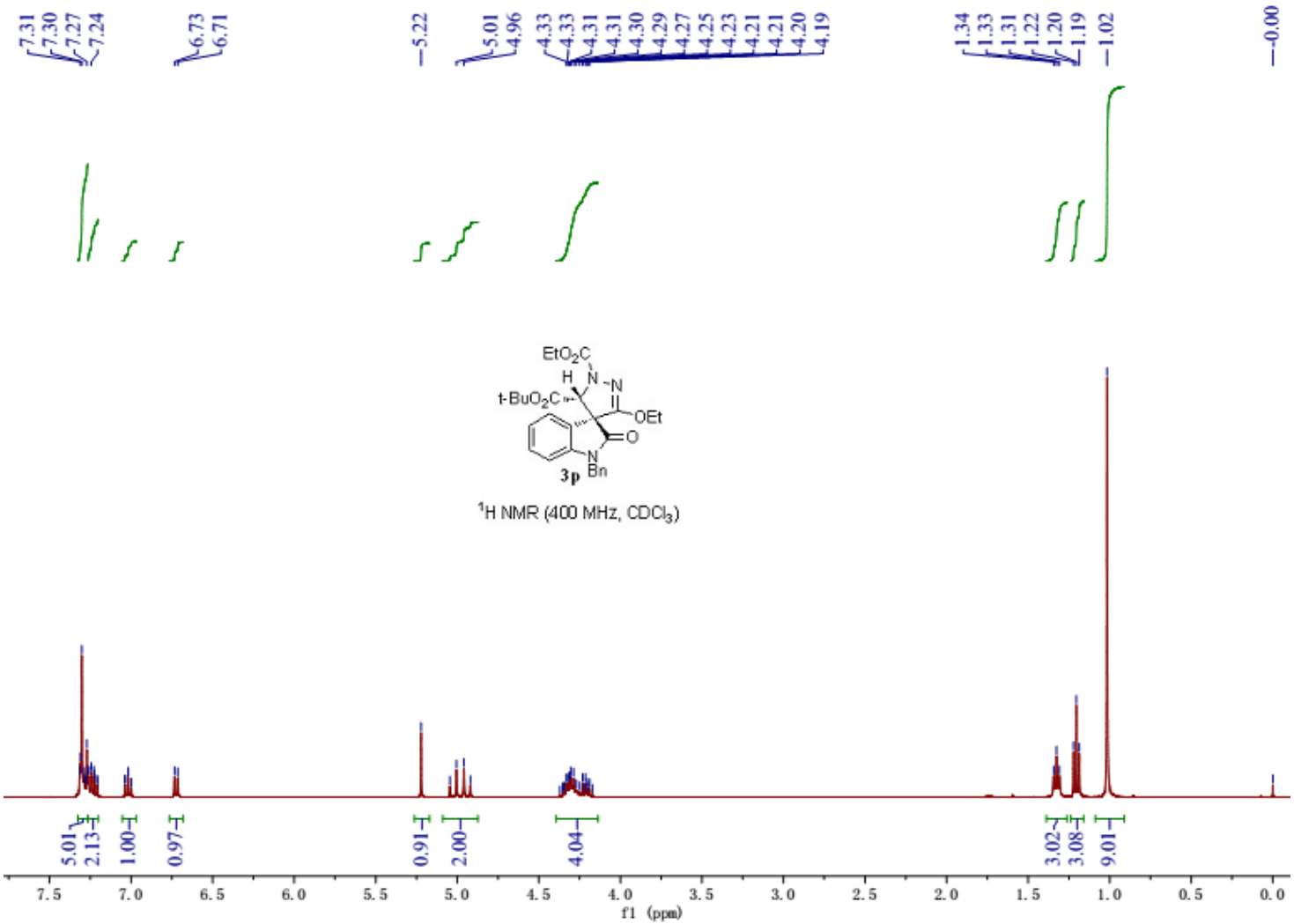

166.98
165.90
156.51
150.57
148.70
146.17
130.59
123.90
116.01
84.47
77.32
77.00
67.99
64.20
63.11
62.81
61.78
28.03
14.37
13.85
13.62
EtO2C
H
N
N
EtO2C
OEt
O
N
Boc
3m
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

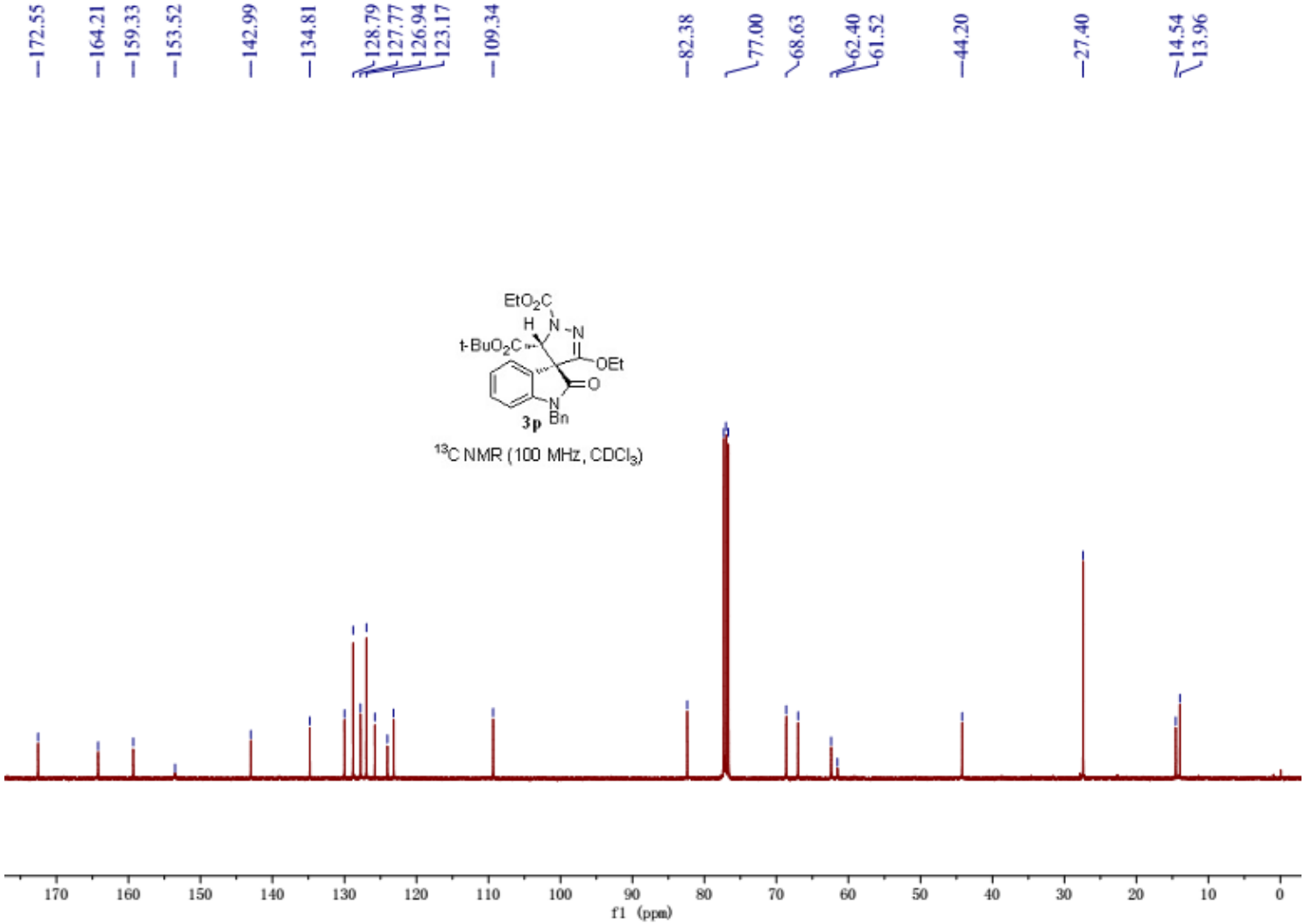

8.26
8.24
7.44
7.43
7.42
7.41
7.40
7.30
7.22
7.21
5.25
4.33
4.32
4.31
4.31
3.87
3.85
3.83
3.82
2.73
1.36
1.34
1.32
1.21
1.19
1.17
0.81
0.79
0.77
0.00
EtO2C
H
N
N
EtO2C
OEt
O
N
Ac
3n
1H NMR (400 MHz, CDCl3)
0.97
1.02
1.96
0.90
3.99
1.97
3.00
2.99
3.04
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

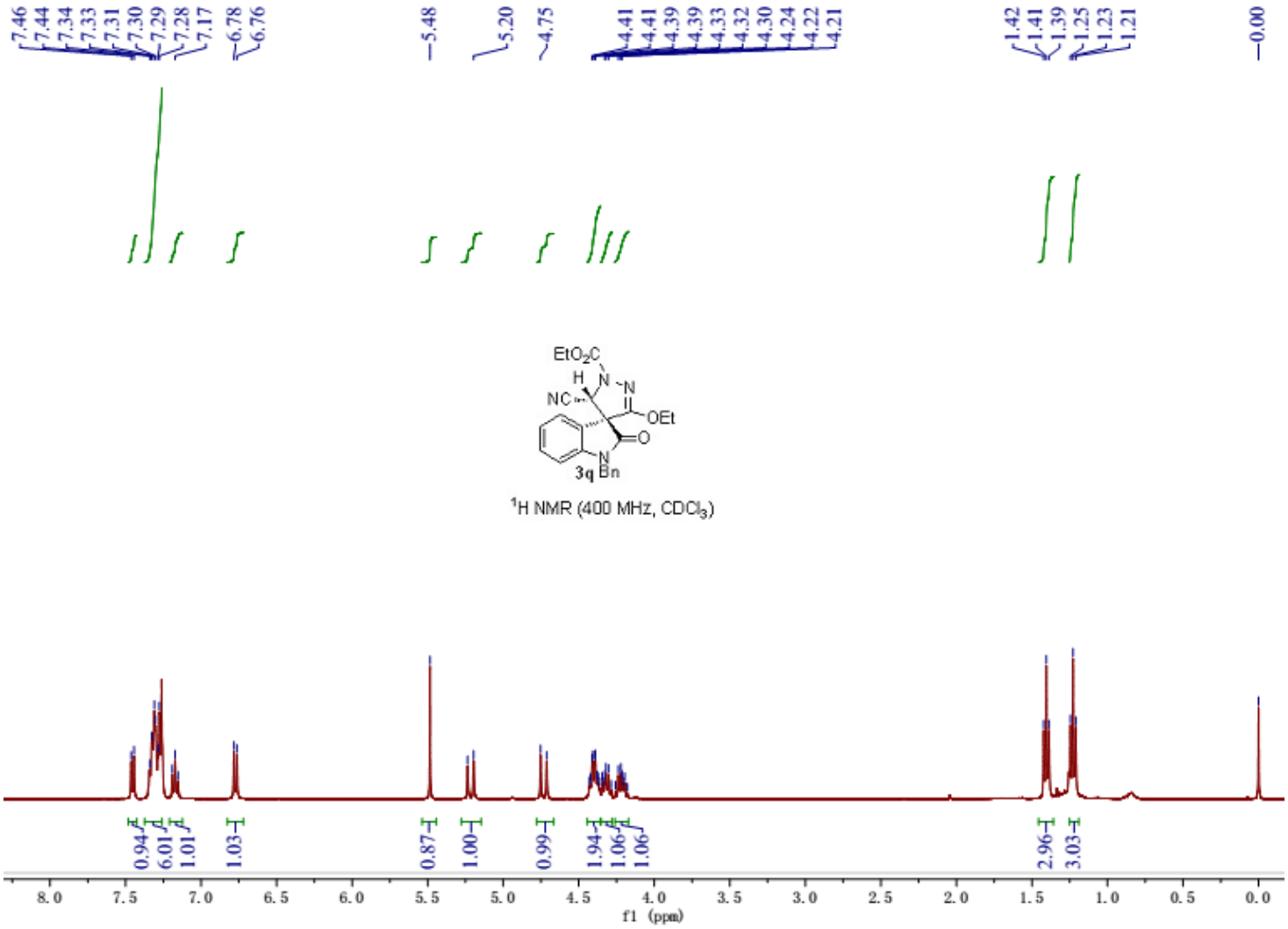

173.28
170.19
165.01
158.49
153.33
140.46
130.54
116.66
77.32
77.00
76.68
69.30
62.62
62.23
61.60
26.55
14.47
13.83
13.45
EtO2C
H
N
N
EtO2C
OEt
O
N
Ac
3n
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

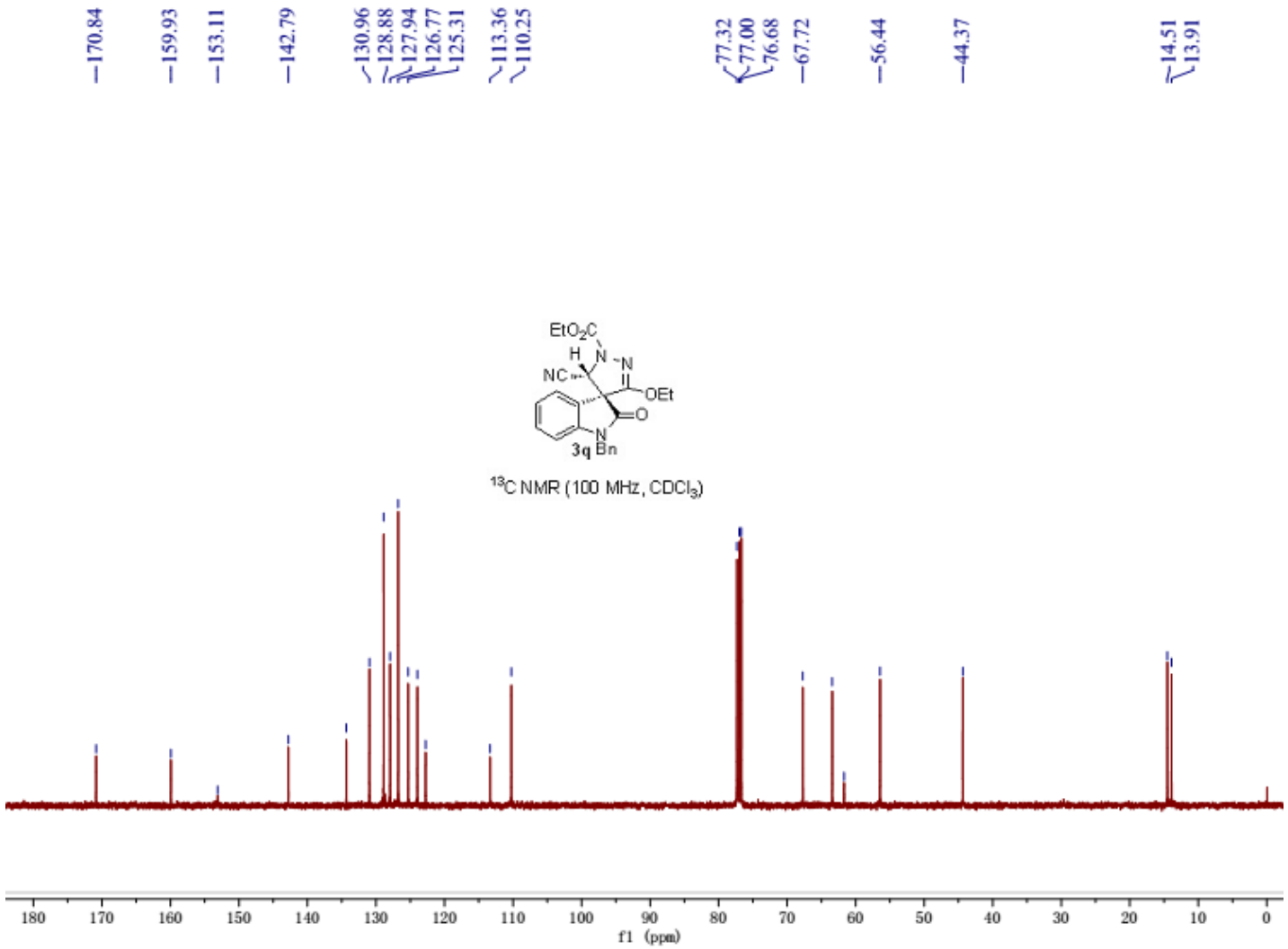

7.22
7.21
7.21
7.19
7.18
7.17
6.64
6.62
5.38
4.98
4.83
4.81
4.73
4.33
4.32
4.31
4.30
4.29
4.27
4.25
4.23
4.21
4.21
4.19
1.33
1.31
1.30
1.21
1.20
1.18
0.00
EtO2C
H
N
N
BnO2C
OEt
O
N
Bn
3o
1H NMR (400 MHz, CDCl3)
10.05
1.04
1.86
1.00
0.91
1.00
0.98
1.01
0.98
4.24
3.05
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

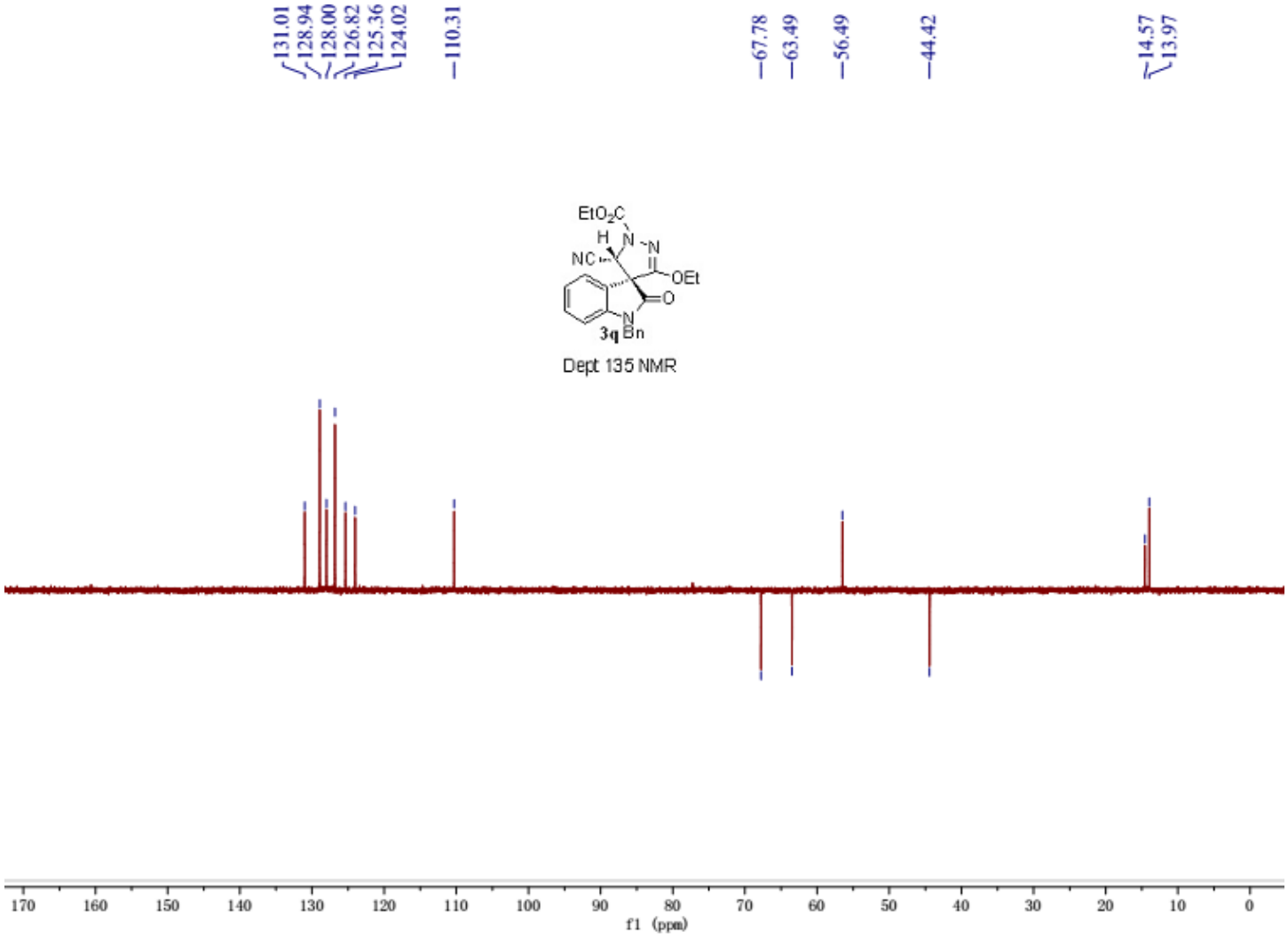

172.32
165.63
159.40
153.32
142.97
134.59
128.76
128.37
128.27
126.65
109.72
77.32
77.00
76.68
67.20
62.56
61.43
44.10
14.54
13.96
EtO2C
BnO2C
OEt
O
N
Bn
3o
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

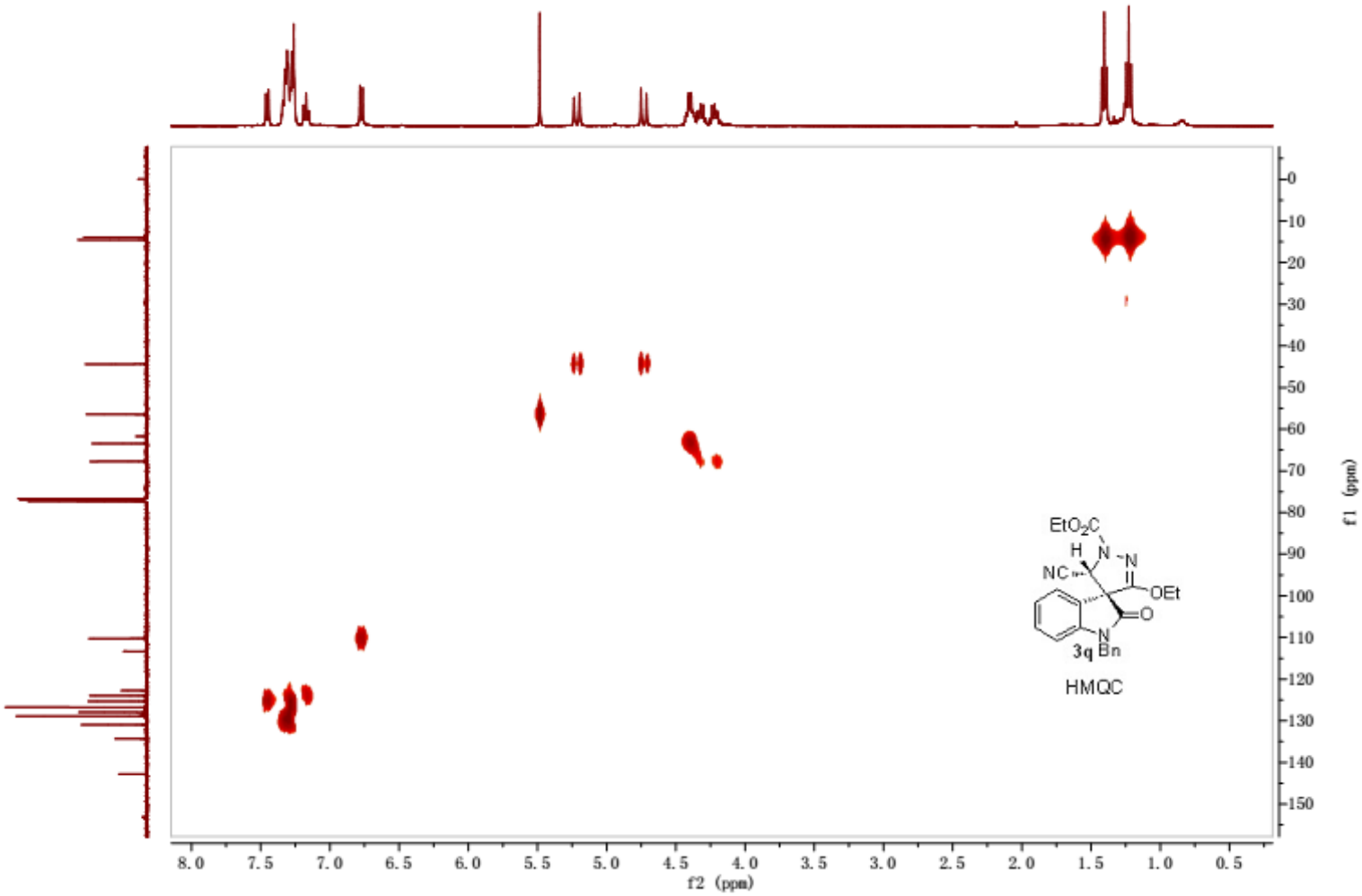

7.31
7.30
7.27
7.24
6.73
6.71
5.22
5.01
4.96
4.33
4.33
4.31
4.31
4.30
4.29
4.27
4.25
4.23
4.21
4.21
4.20
4.19
1.34
1.33
1.31
1.22
1.20
1.19
1.02
0.00
EtO2C
H
N
N
t-BuO2C
OEt
O
N
Bn
3p
1H NMR (400 MHz, CDCl3)
5.01
2.13
1.00
0.97
0.91
2.00
4.04
3.02
3.08
9.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

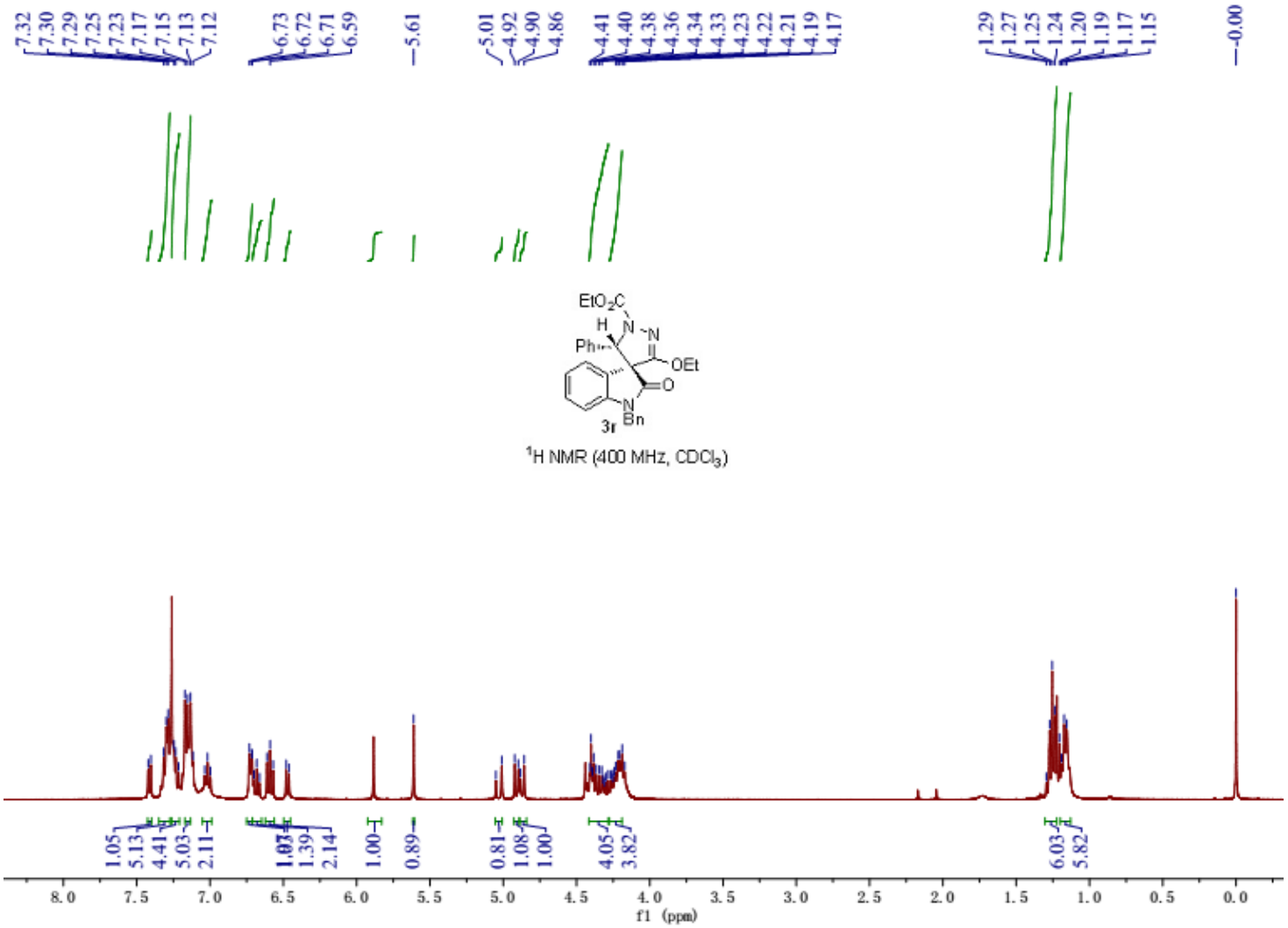

172.55
164.21
159.33
153.52
142.99
134.81
128.79
127.77
126.94
123.17
109.34
82.38
77.00
68.63
62.40
61.52
44.20
27.40
14.54
13.96
EtO2C
H
N
N
t-BuO2C
OEt
O
N
Bn
3p
13C NMR (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

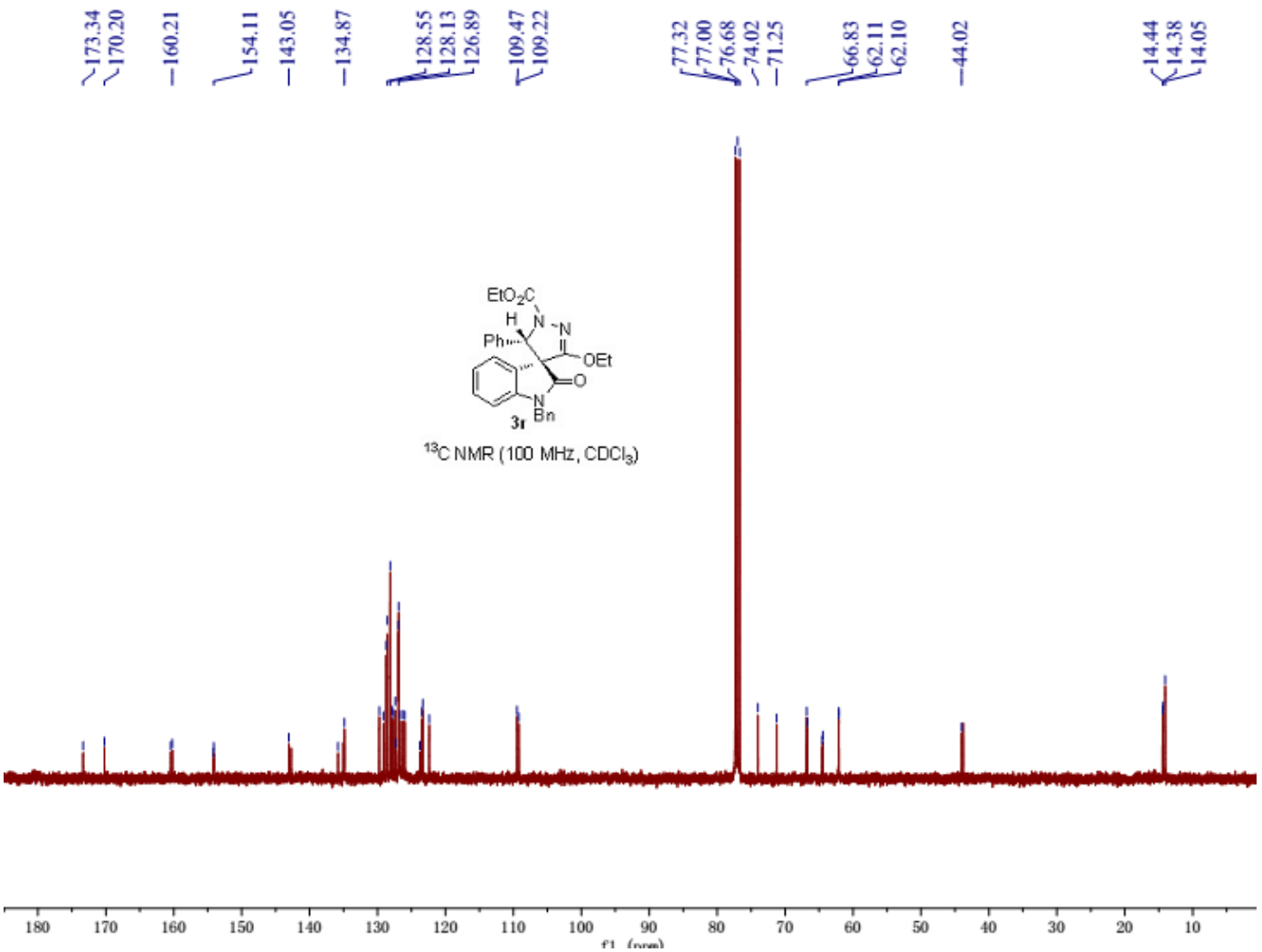

7.46
7.44
7.34
7.33
7.31
7.30
7.29
7.28
7.17
6.78
6.76
5.48
5.20
4.75
4.41
4.41
4.39
4.39
4.33
4.32
4.30
4.24
4.22
4.21
1.42
1.41
1.39
1.25
1.23
1.21
0.00
EtO2C
H
N
N
NC
OEt
O
N
Bn
3q
1H NMR (400 MHz, CDCl3)
0.94
6.01
1.01
1.03
0.87
1.00
0.99
1.94
1.06
1.06
2.96
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

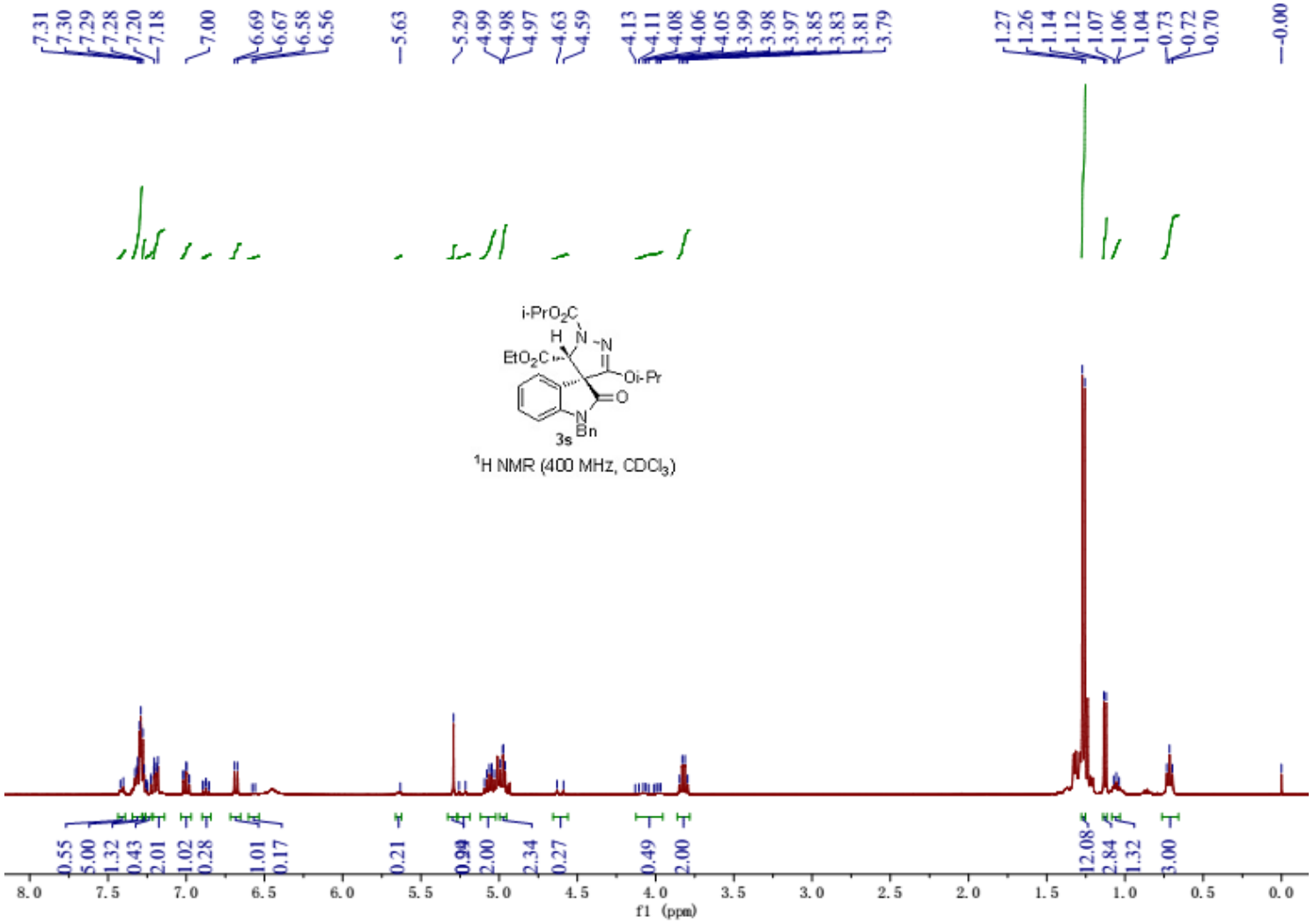

170.84
159.93
153.11
142.79
130.96
128.88
127.94
126.77
125.31
113.36
110.25
77.32
77.00
76.68
67.72
56.44
44.37
14.51
13.91
EtO2C
H
N
N
NC
OEt
O
N
Bn
3q
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

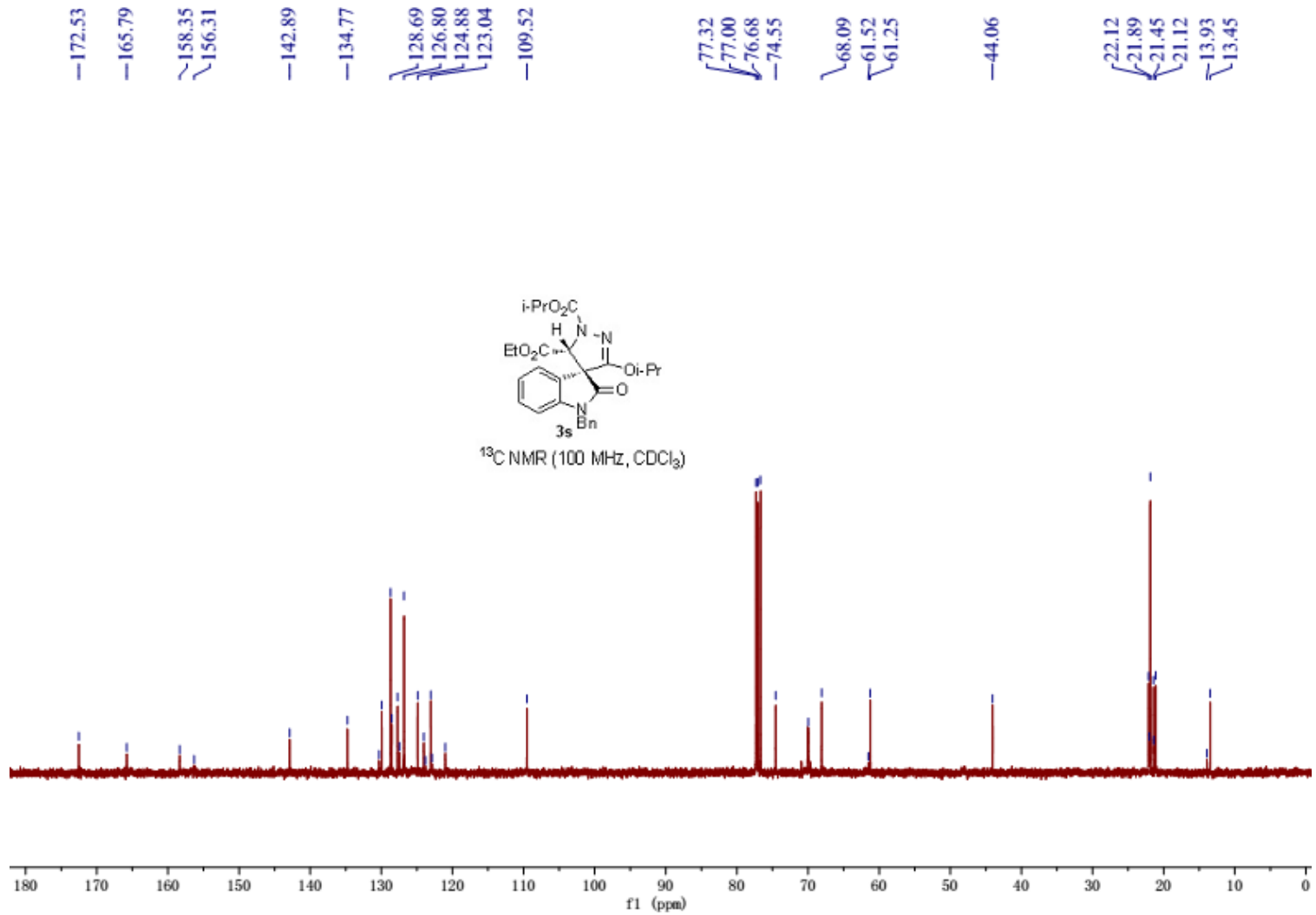

131.01
128.94
128.00
126.82
125.36
124.02
110.31
67.78
63.49
56.49
44.42
14.57
13.97
EtO2C
H
N
N
NC
OEt
O
N
Bn
3q
Dept 135 NMR
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

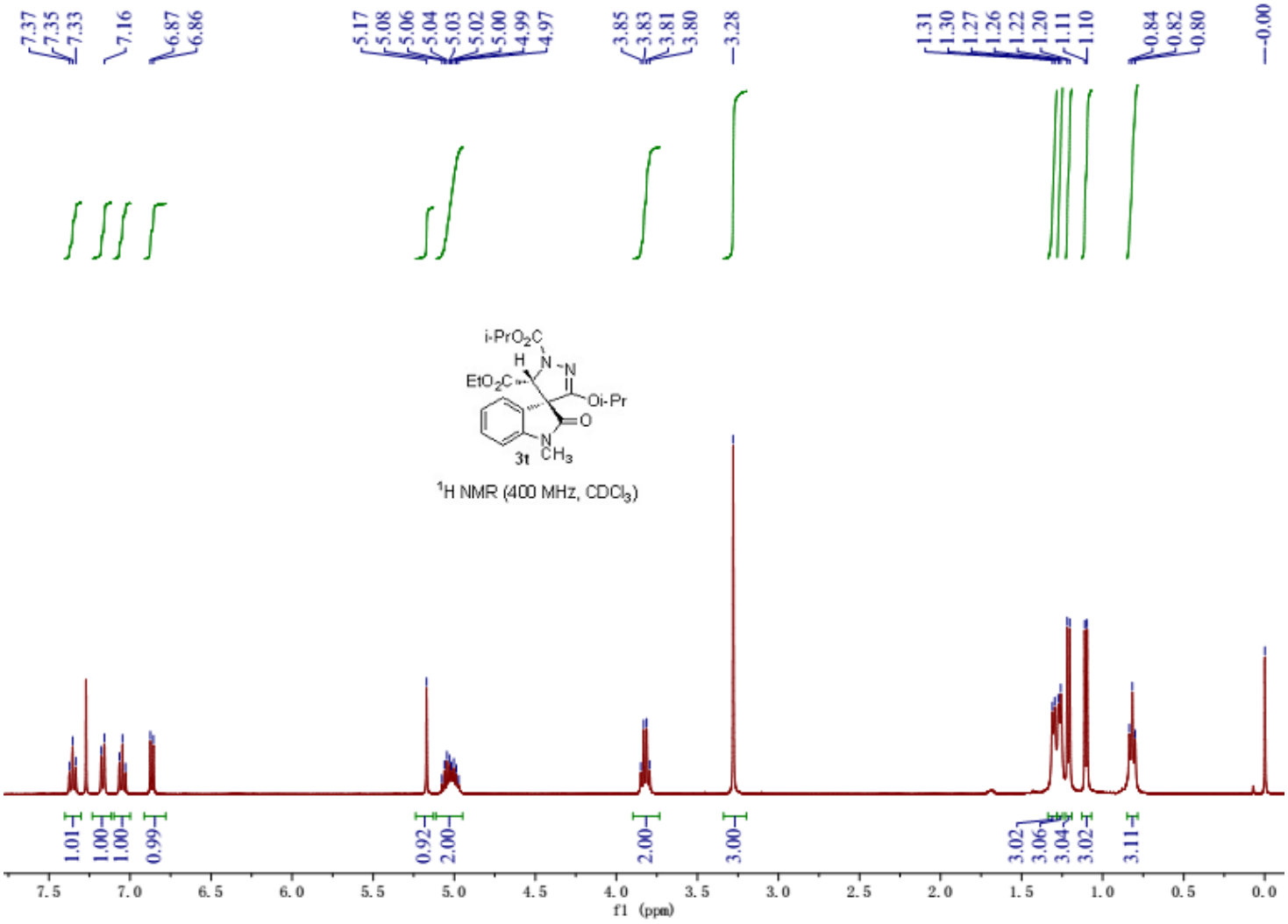

EtO2C
H
N
N
NC
OEt
O
N
3q Bn
HMQC
f2 (ppm)
f1 (ppm)

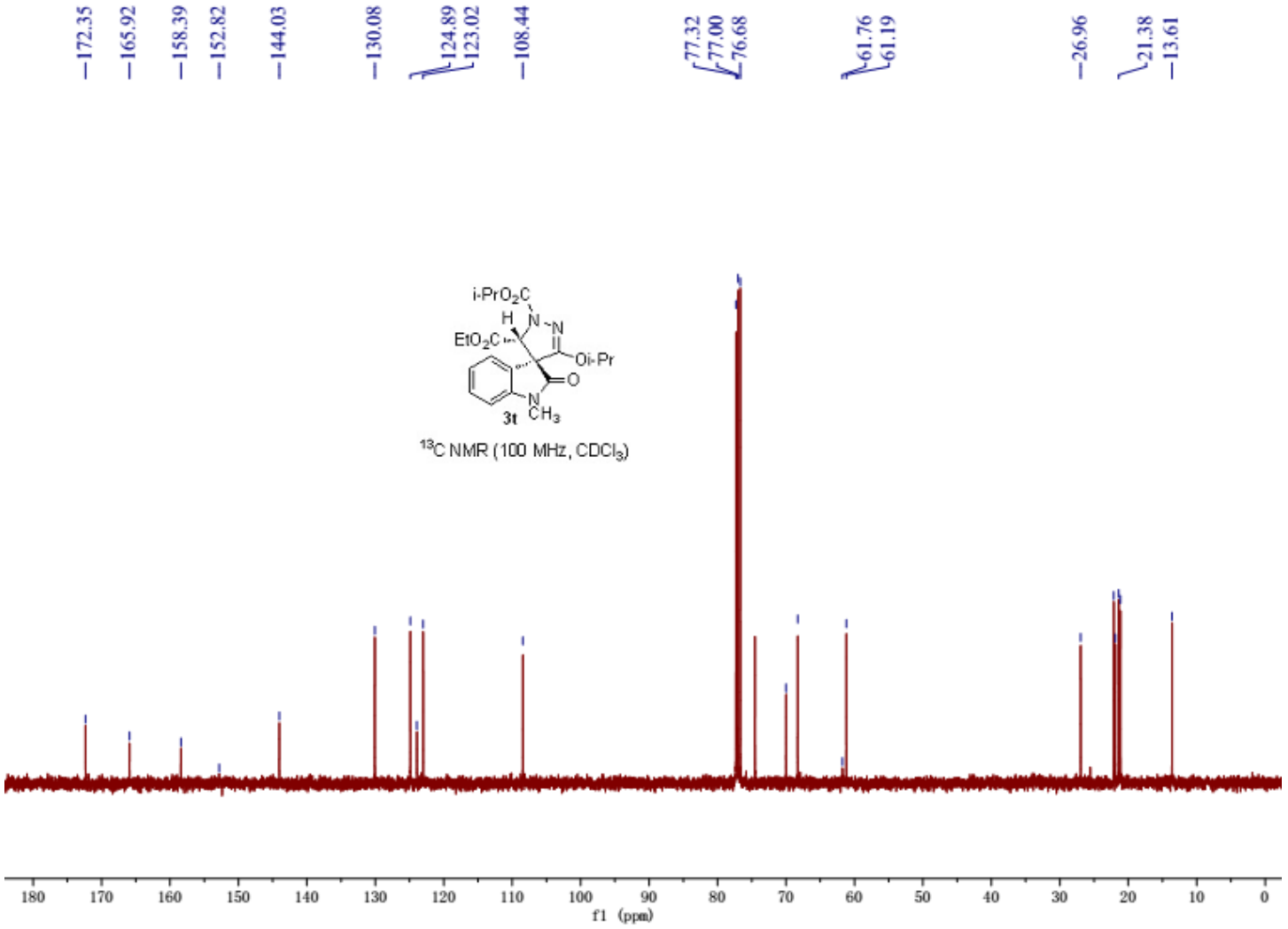

7.32
7.30
7.29
7.25
7.23
7.17
7.15
7.13
7.12
6.73
6.72
6.71
6.59
5.61
5.01
4.92
4.90
4.86
4.41
4.40
4.38
4.36
4.34
4.33
4.23
4.22
4.21
4.19
4.17
1.29
1.27
1.25
1.24
1.20
1.19
1.17
1.15
0.00
EtO2C
H
N
N
Ph
OEt
O
N
Bn
3r
1H NMR (400 MHz, CDCl3)
1.05
5.13
4.41
5.03
2.11
1.39
2.14
1.00
0.89
0.81
1.08
1.00
4.05
3.82
6.03
5.82
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)

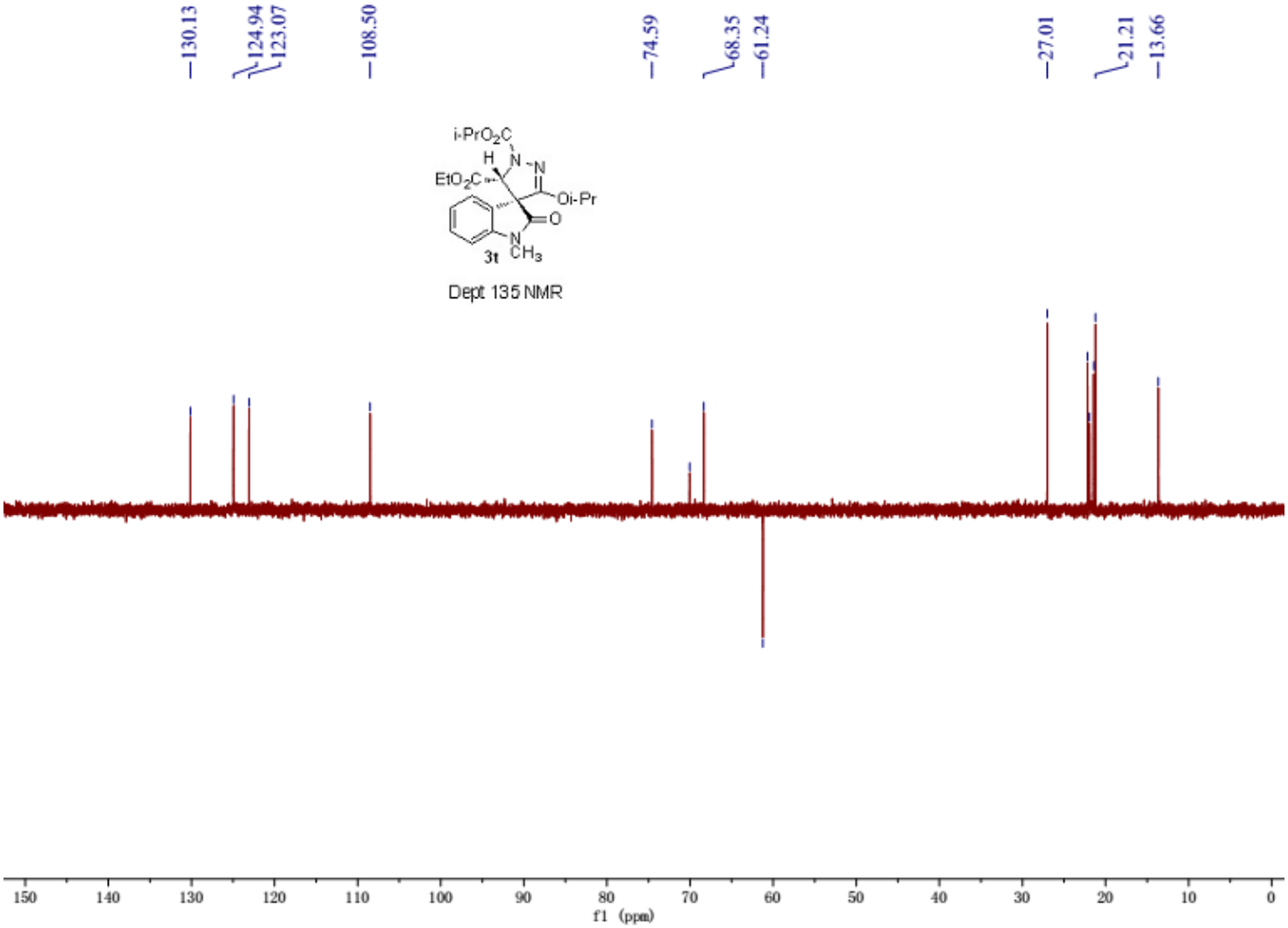

173.34
170.20
160.21
154.11
143.05
134.87
128.55
128.13
126.89
109.47
109.22
77.32
77.00
76.68
74.02
71.25
66.83
62.11
62.10
44.02
14.44
14.38
14.05
EtO2C
H
N
N
Ph
OEt
O
N
Bn
3t
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

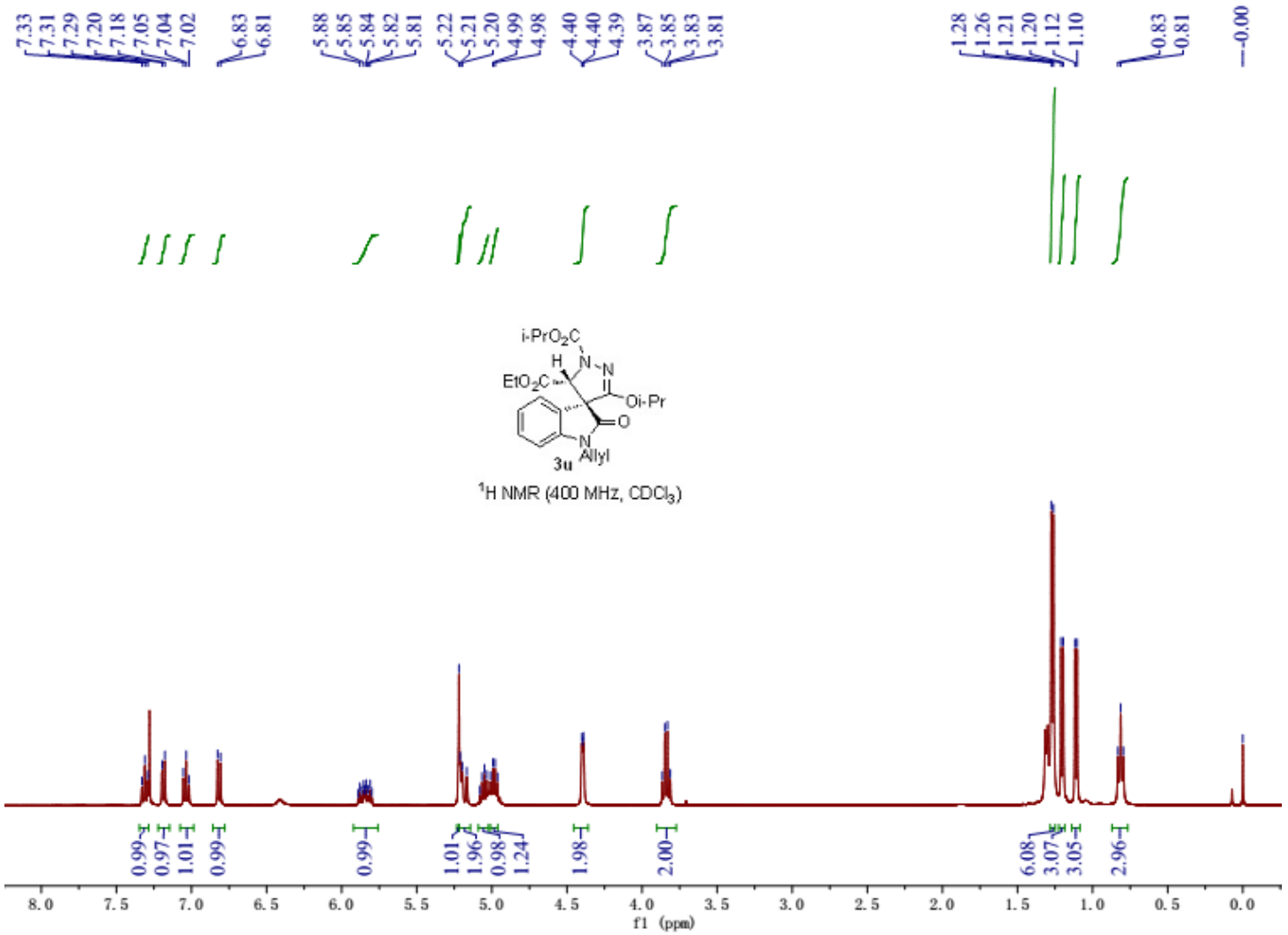

7.31
7.30
7.29
7.28
7.20
7.18
7.00
6.69
6.67
6.58
6.56
5.63
5.29
4.99
4.98
4.97
4.63
4.59
4.13
4.11
4.08
4.06
4.05
3.99
3.98
3.97
3.85
3.83
3.81
3.79
1.27
1.26
1.14
1.12
1.07
1.06
1.04
0.73
0.72
0.70
0.00
i-PrO2C
EtO2C
Oi-Pr
O
Bn
3s
1H NMR (400 MHz, CDCl3)
0.55
5.00
1.32
0.43
2.01
1.02
0.28
1.01
0.17
0.21
0.99
2.00
2.34
0.27
0.49
2.00
12.08
2.84
1.32
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

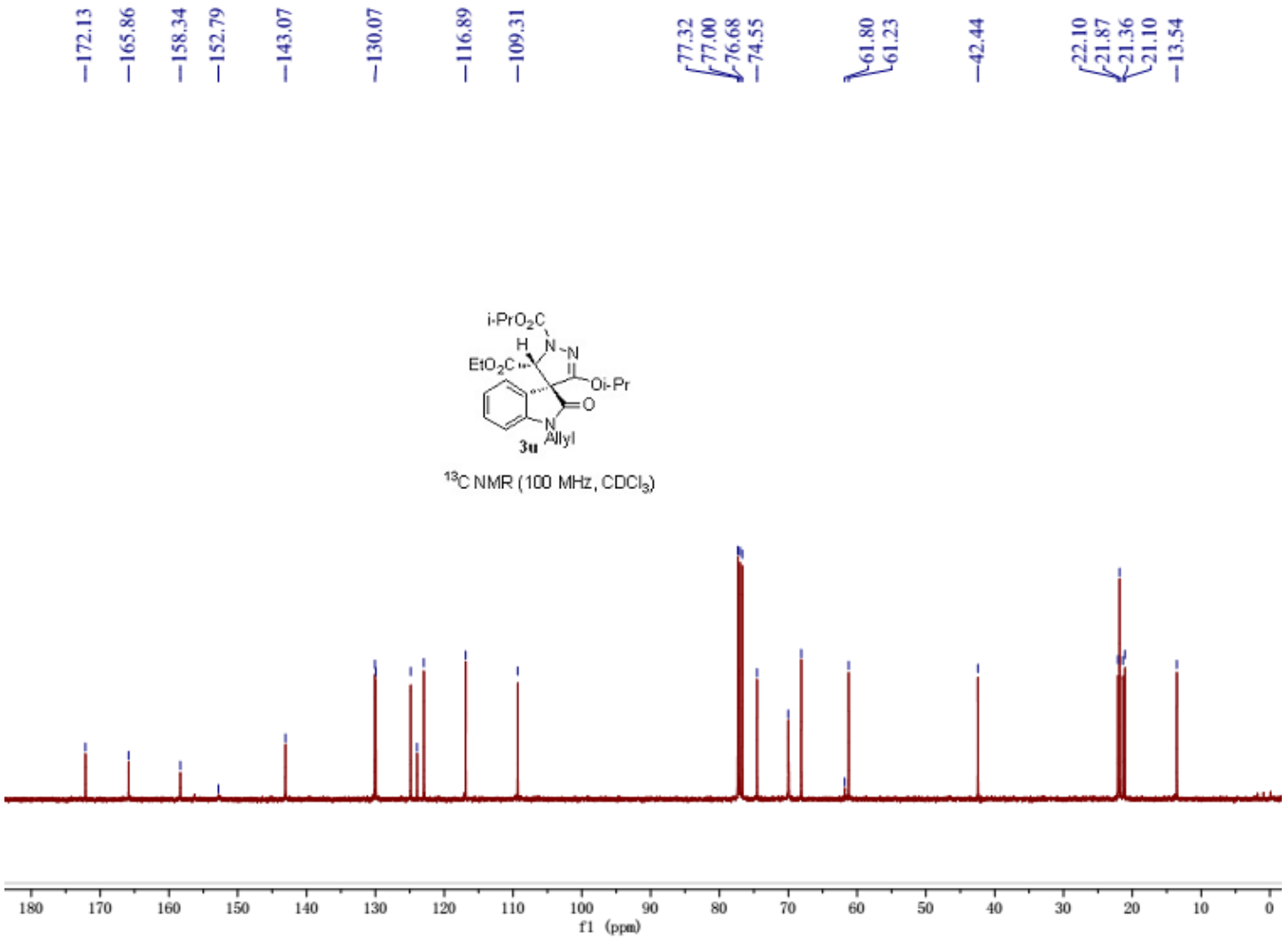

172.53
165.79
158.35
156.31
142.89
134.77
128.69
126.80
124.88
123.04
109.52
77.32
77.00
76.68
74.55
68.09
61.52
61.25
44.06
22.12
21.89
21.45
21.12
13.93
13.45
i-PrO2C
EtO2C
Oi-Pr
O
N
Bn
3s
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

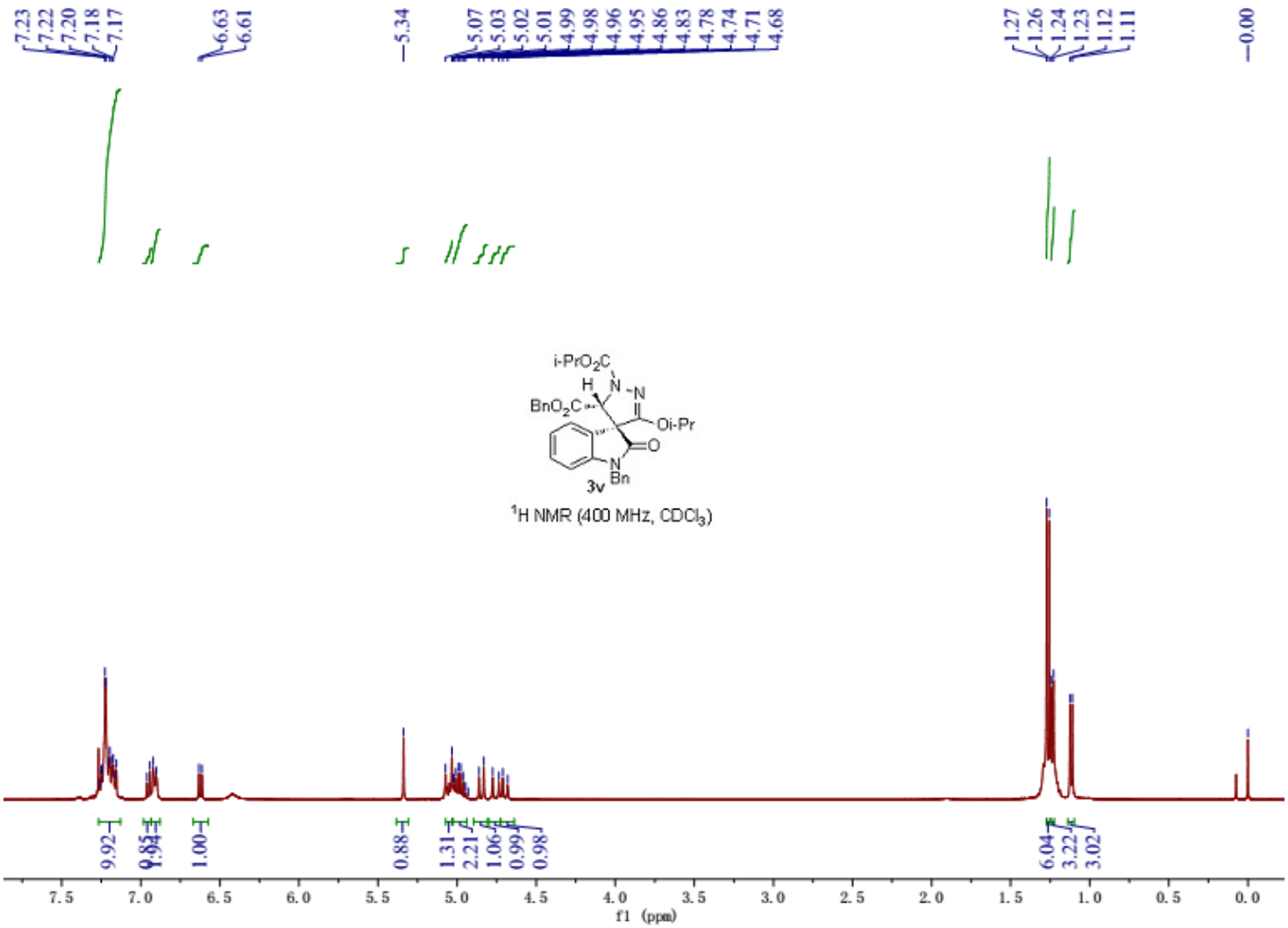

7.37
7.35
7.33
7.16
6.87
6.86
5.17
5.08
5.06
5.04
5.03
5.02
5.00
4.99
4.97
3.85
3.83
3.81
3.80
3.28
1.31
1.30
1.27
1.26
1.22
1.20
1.11
1.10
0.84
0.82
0.80
0.00
i-PrO2C
EtO2C
Oi-Pr
O
N
CH3
3t
1H NMR (400 MHz, CDCl3)
1.01
1.00
1.00
0.99
0.92
2.00
2.00
3.00
3.02
3.06
3.04
3.02
3.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

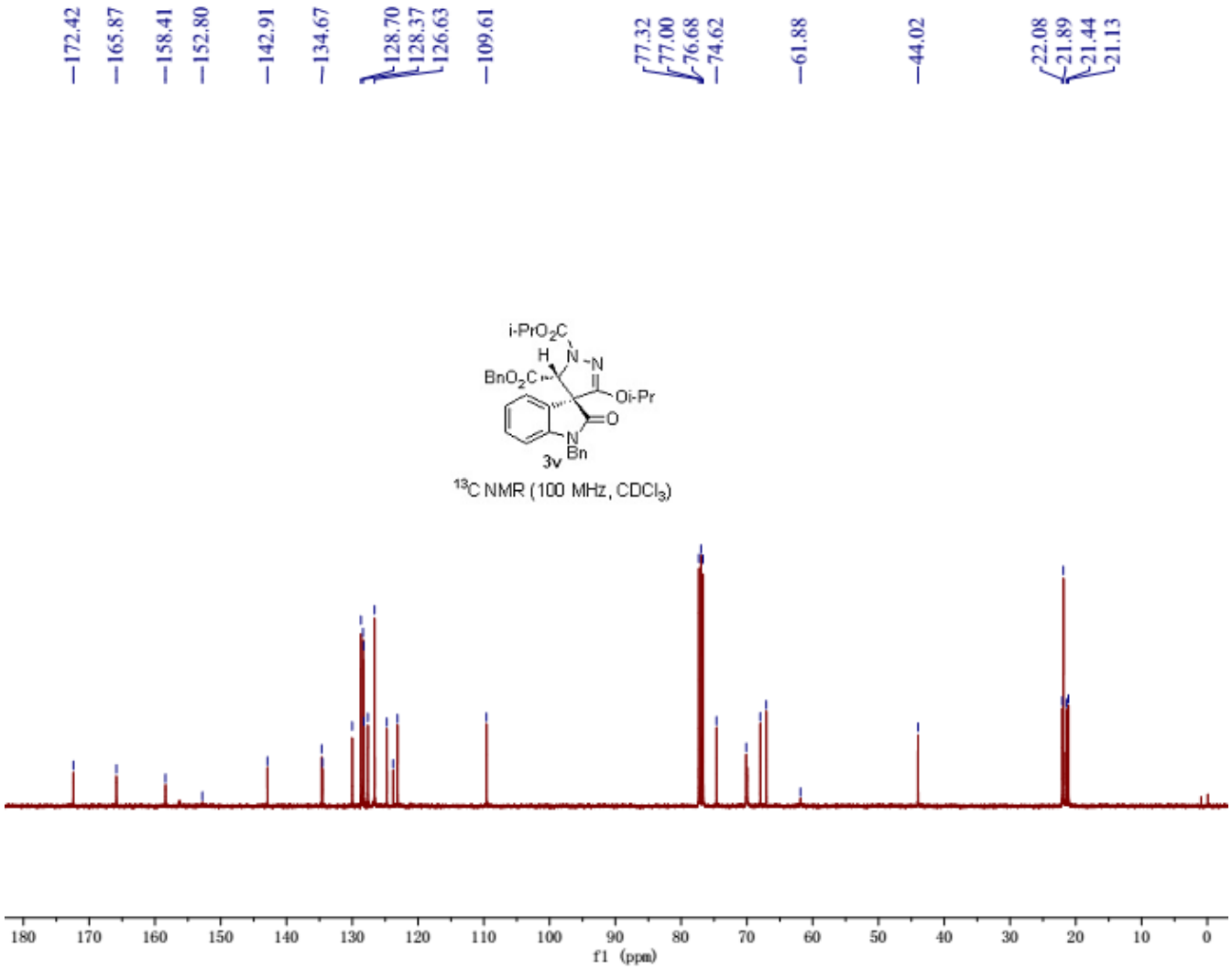

172.35
165.92
158.39
152.82
144.03
130.08
124.89
123.02
108.44
77.32
77.00
76.68
61.76
61.19
26.96
21.38
13.61
i-PrO2C
EtO2C
Oi-Pr
O
N
CH3
3t
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

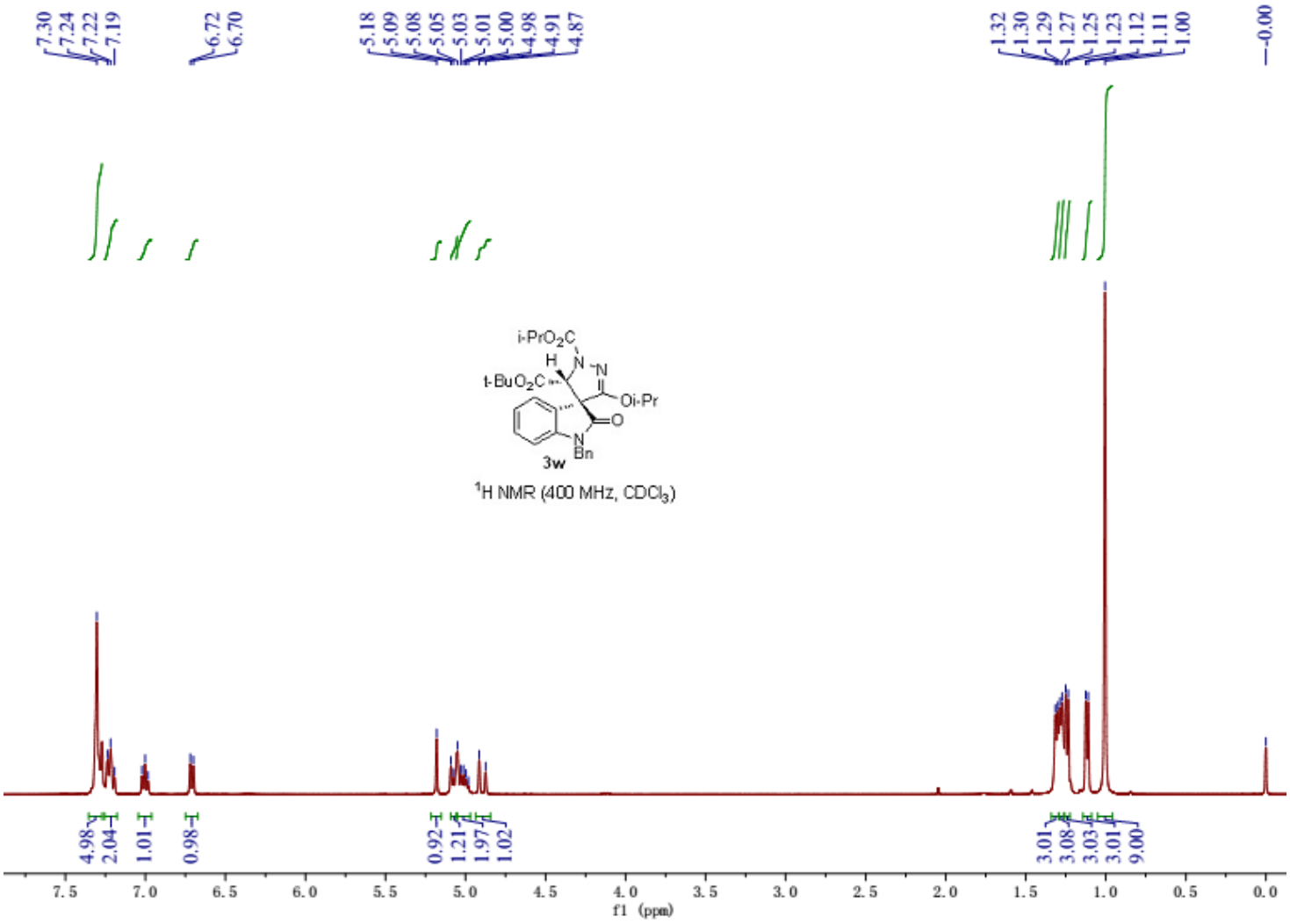

130.13
124.94
123.07
108.50
74.59
68.35
61.24
27.01
21.21
13.66
i-PrO2C
H
N
N
EtO2C
Oi-Pr
O
N
CH3
3t
Dept 135 NMR
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

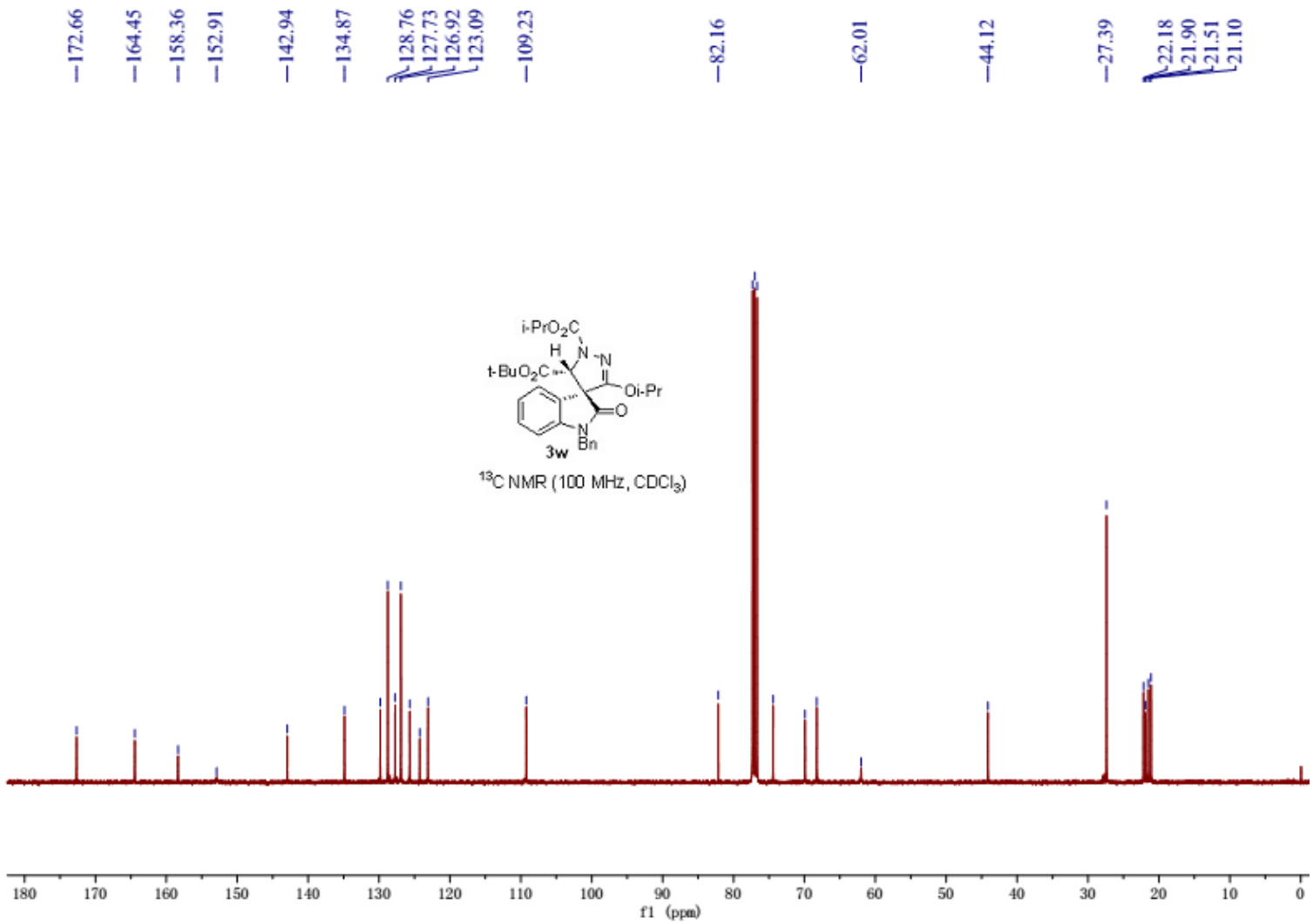

7.33
7.31
7.29
7.20
7.18
7.05
7.04
7.02
6.83
6.81
5.88
5.85
5.84
5.82
5.81
5.22
5.21
5.20
4.99
4.98
4.40
4.40
4.39
3.87
3.85
3.83
3.81
1.28
1.26
1.21
1.20
1.12
1.10
0.83
0.81
-0.00
i-PrO2C
EtO2C
Oi-Pr
O
N
Allyl
3u
1H NMR (400 MHz, CDCl3)
0.99
0.97
1.01
0.99
0.99
1.01
1.96
0.98
1.24
1.98
2.00
6.08
3.07
3.05
2.96
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)

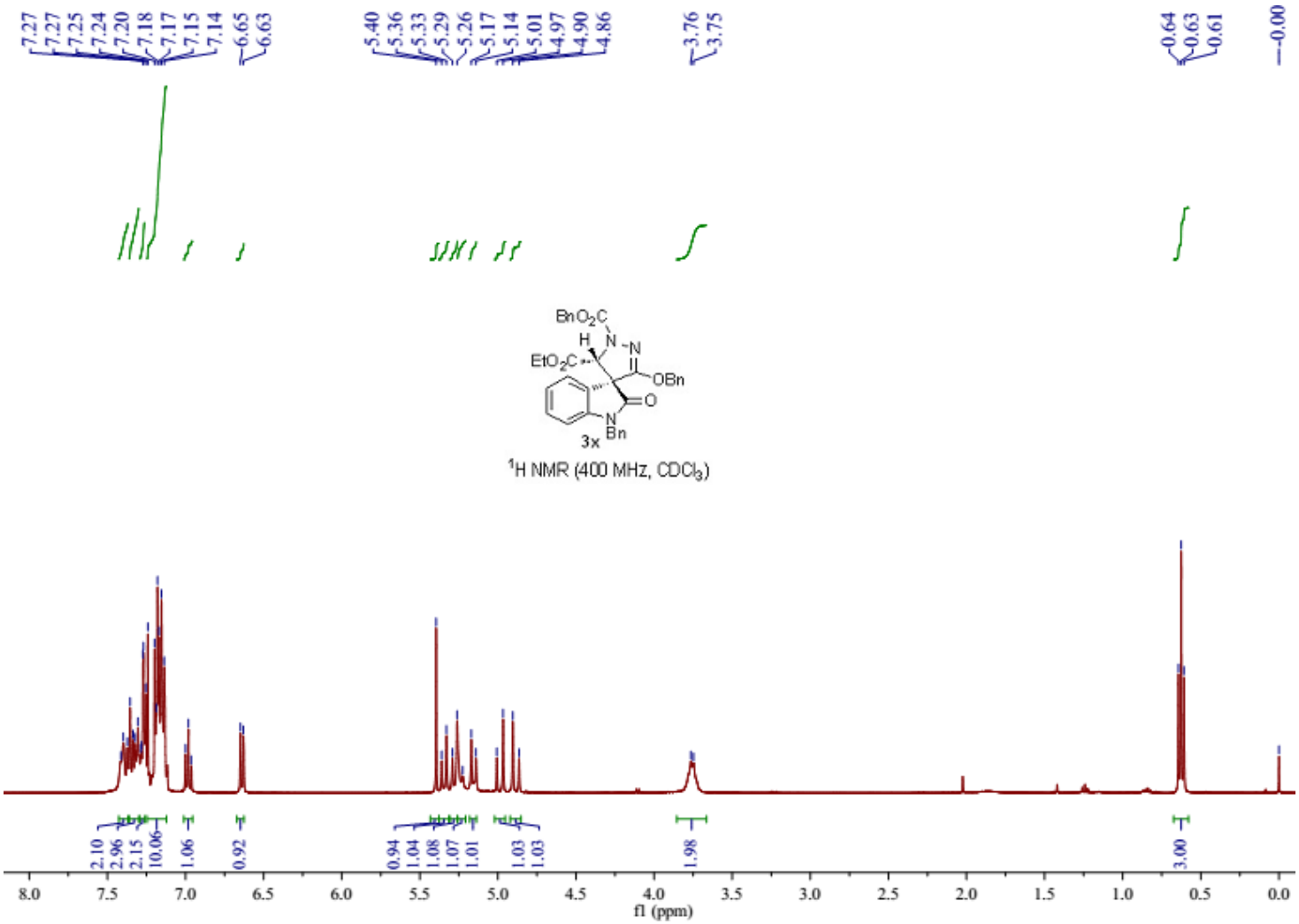

172.13
165.86
158.34
152.79
143.07
130.07
116.89
109.31
77.32
77.00
76.68
74.55
61.80
61.23
42.44
22.10
21.87
21.36
21.10
13.54
i-PrO2C
EtO2C
Oi-Pr
O
Allyl
3u
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

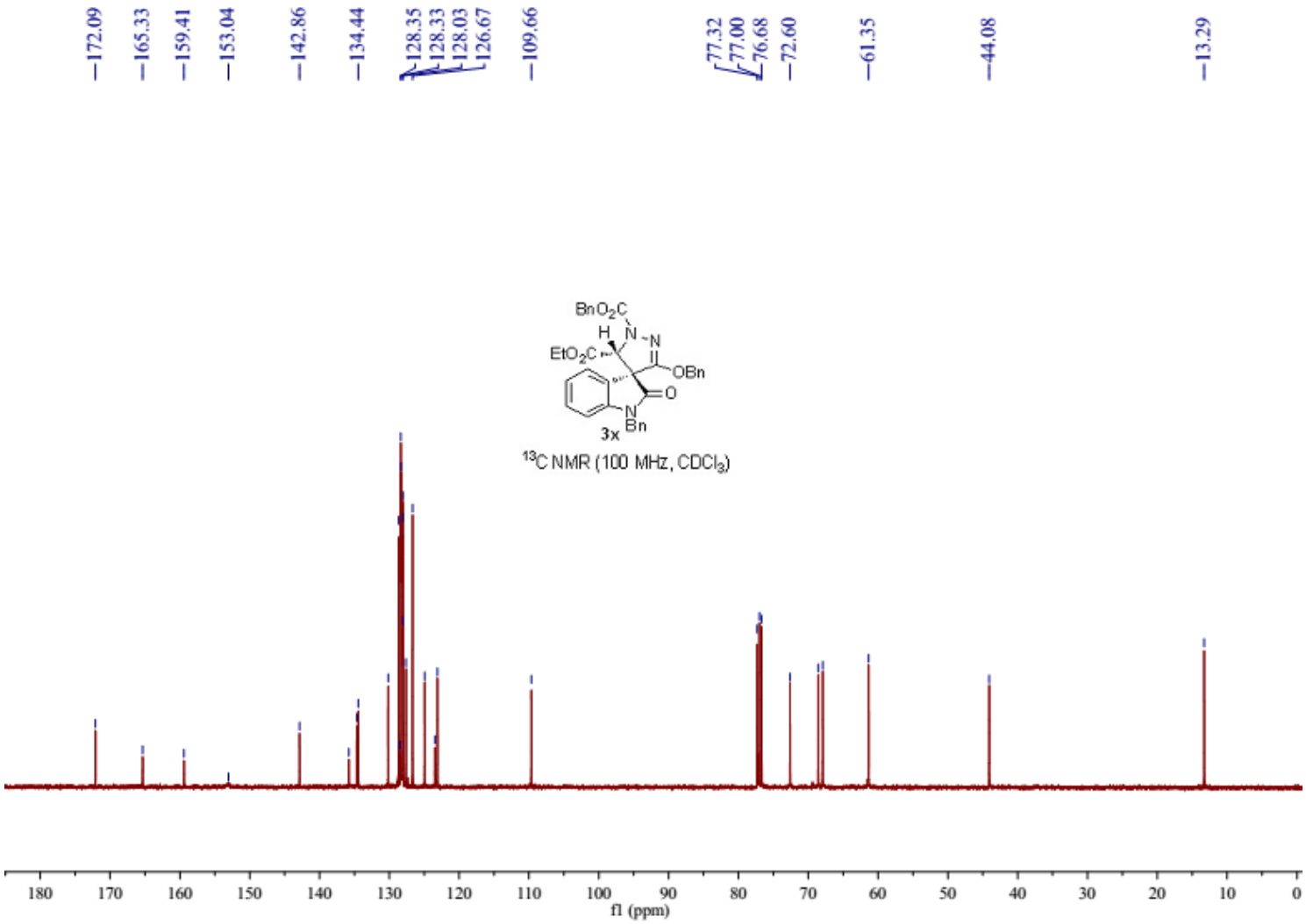

7.23
7.22
7.20
7.18
7.17
6.63
6.61
5.34
5.07
5.03
5.02
5.01
4.99
4.98
4.96
4.95
4.86
4.83
4.78
4.74
4.71
4.68
1.27
1.26
1.24
1.23
1.12
1.11
0.00
i-PrO2C
BnO2C
Oi-Pr
O
N
Bn
3v
1H NMR (400 MHz, CDCl3)
9.92
1.00
0.88
1.31
2.21
1.06
0.99
0.98
6.04
3.22
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

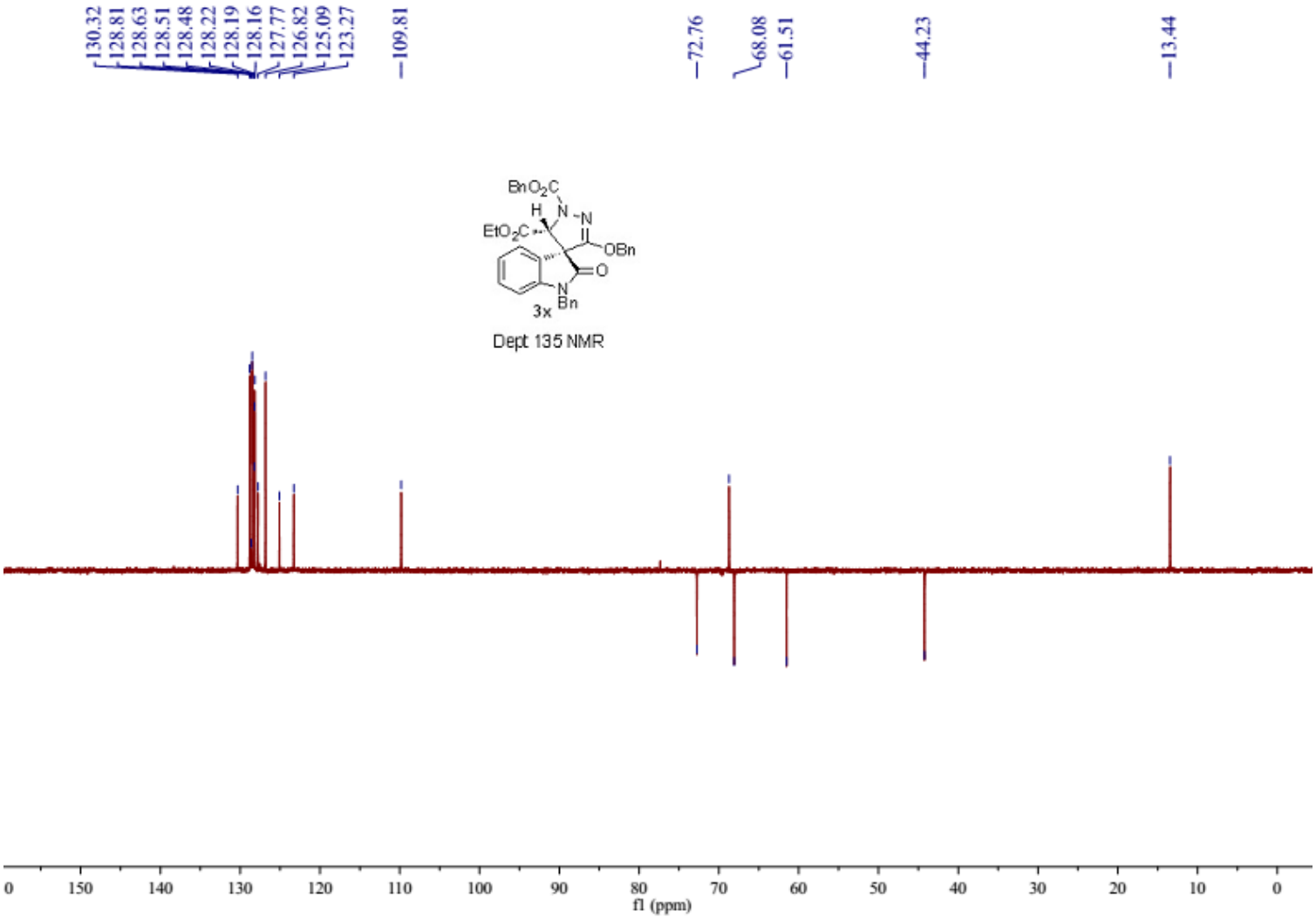

172.42
165.87
158.41
152.80
142.91
134.67
128.70
128.37
126.63
109.61
77.32
77.00
76.68
74.62
61.88
44.02
22.08
21.89
21.44
21.13
i-PrO2C
BnO2C
Oi-Pr
O
N
Bn
3v
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

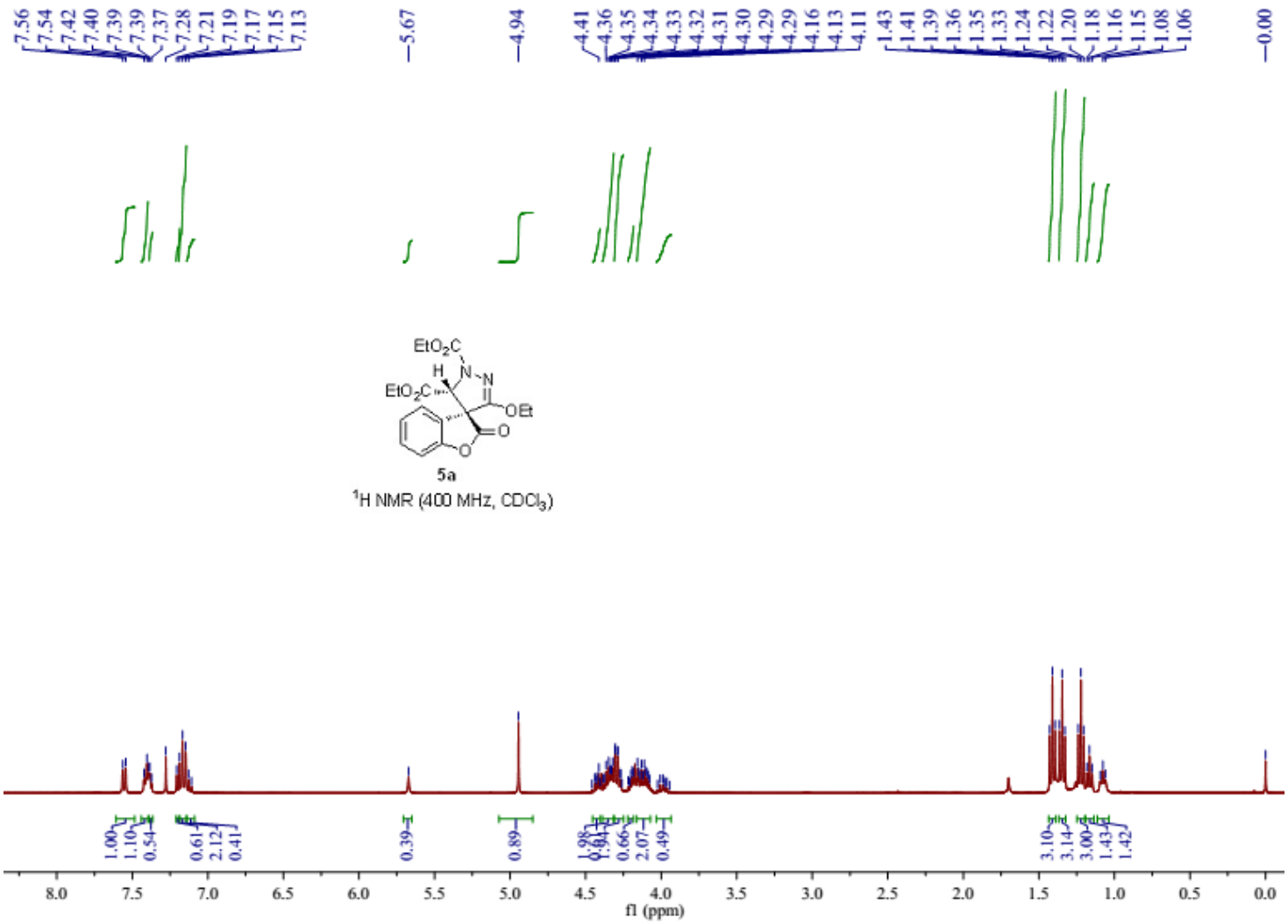

7.30
7.24
7.22
7.19
6.72
6.70
5.18
5.09
5.08
5.05
5.03
5.01
5.00
4.98
4.91
4.87
1.32
1.30
1.29
1.27
1.25
1.23
1.12
1.11
1.00
-0.00
i-PrO2C
H
N
N
t-BuO2C
Oi-Pr
O
N
Bn
3w
1H NMR (400 MHz, CDCl3)
4.98
2.04
1.01
0.98
0.92
1.21
1.97
1.02
3.01
3.08
3.03
3.01
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

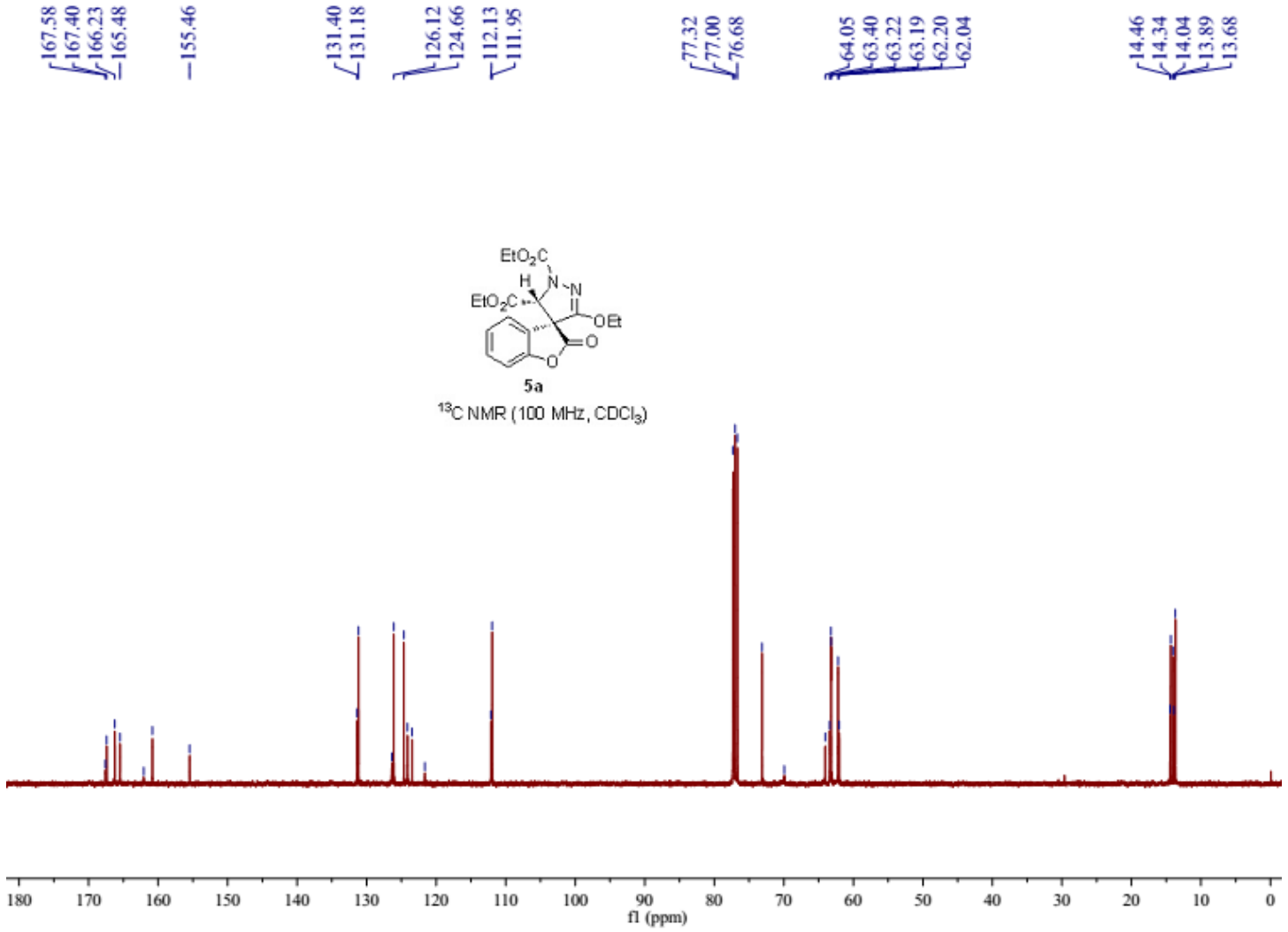

172.66
164.45
158.36
152.91
142.94
134.87
128.76
127.73
126.92
123.09
109.23
82.16
62.01
44.12
27.39
22.18
21.90
21.51
21.10
i-PrO2C
H
N
N
t-BuO2C
Oi-Pr
O
N
Bn
3w
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

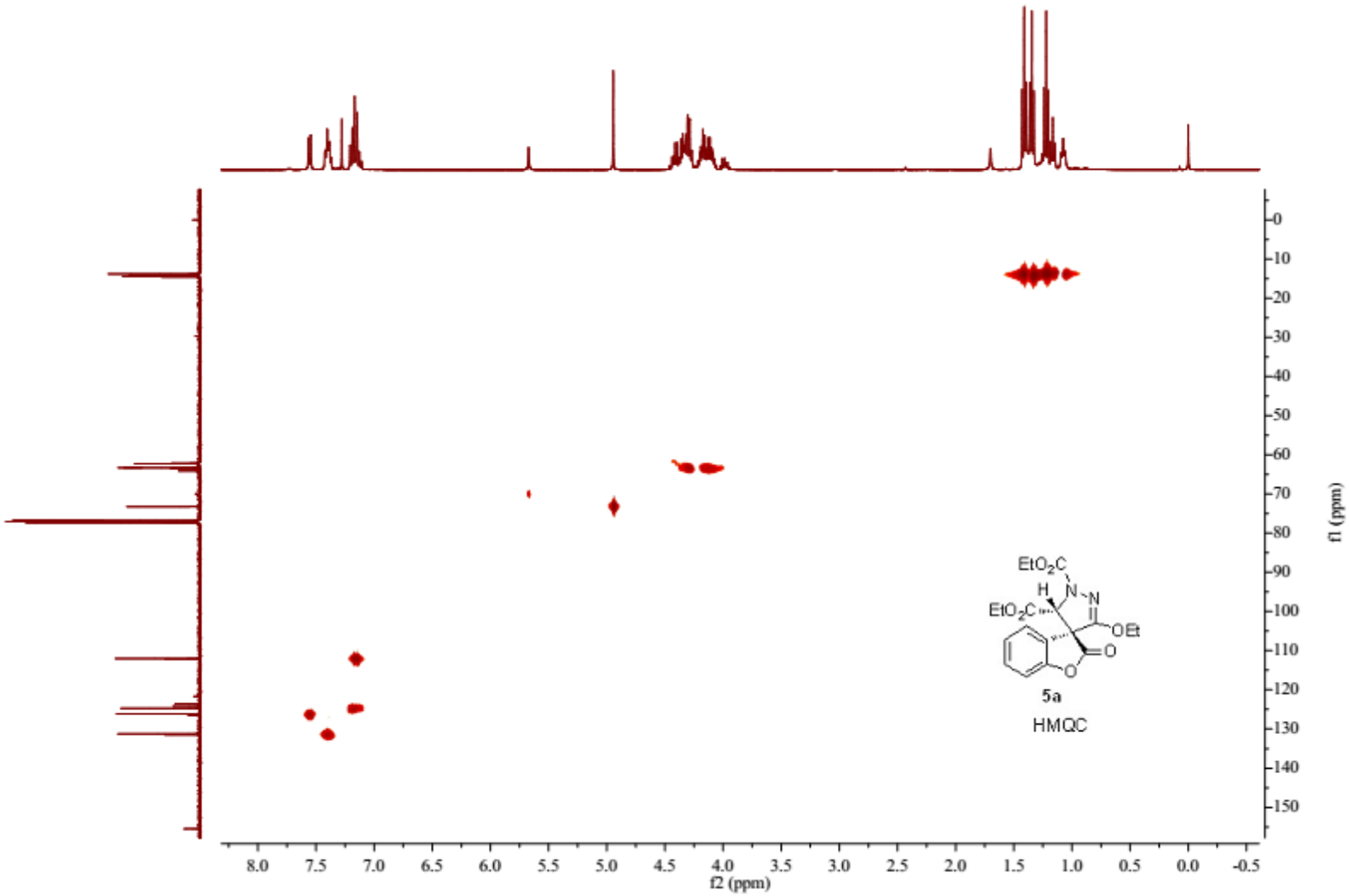

7.27
7.27
7.25
7.24
7.20
7.18
7.17
7.15
7.14
6.65
6.63
5.40
5.36
5.33
5.29
5.26
5.17
5.14
5.01
4.97
4.90
4.86
3.76
3.75
0.64
0.63
0.61
-0.00
BnO2C
H
N
N
EtO2C
OBn
O
N
Bn
3x
1H NMR (400 MHz, CDCl3)
2.10
2.96
2.15
10.06
1.06
0.92
0.94
1.04
1.08
1.07
1.01
1.03
1.03
1.98
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

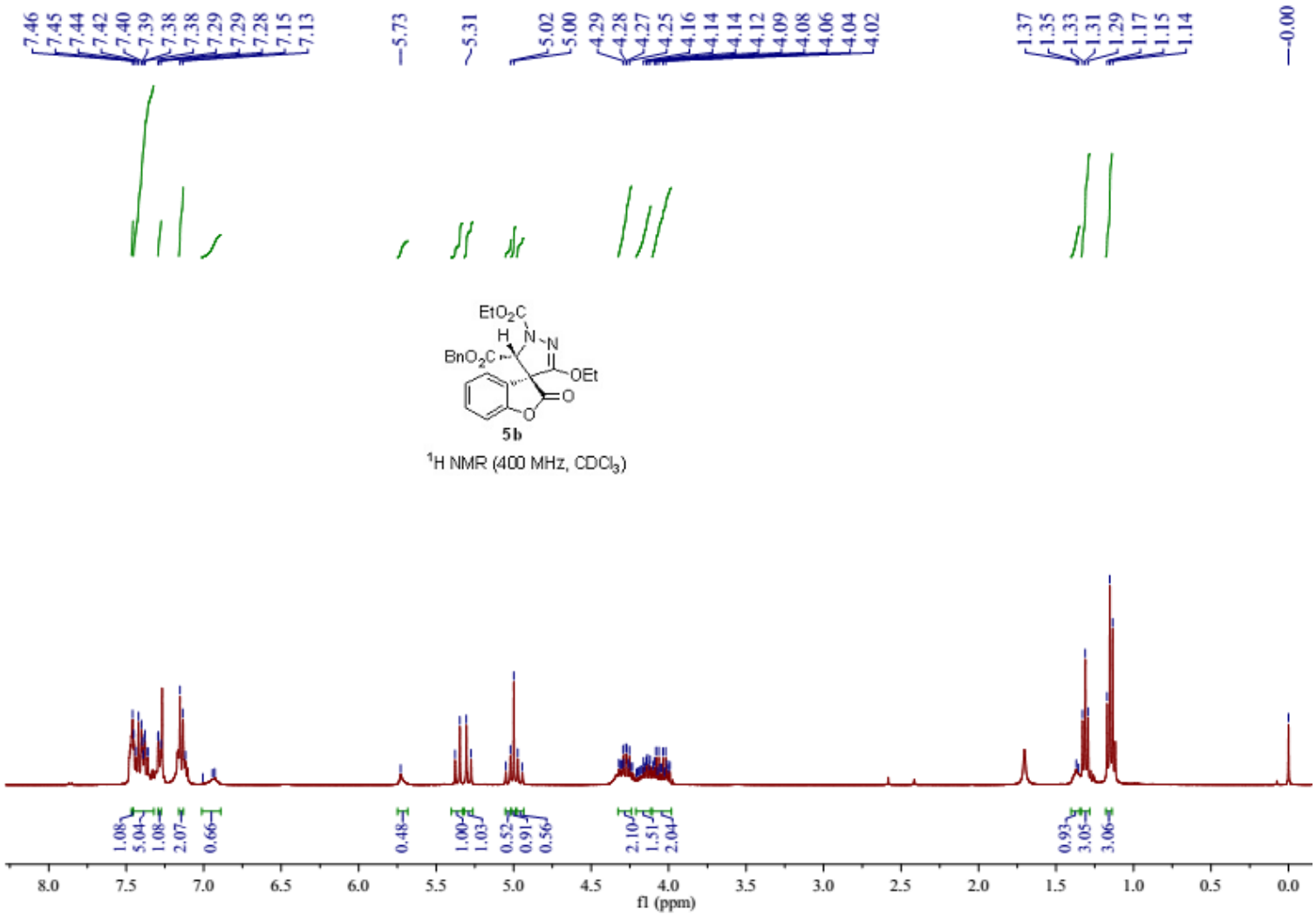

172.09
165.33
159.41
153.04
142.86
134.44
128.35
128.33
128.03
126.67
109.66
77.32
77.00
76.68
72.60
61.35
44.08
13.29
BnO2C
H
N
N
EtO2C
OBn
O
N
Bn
3x
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

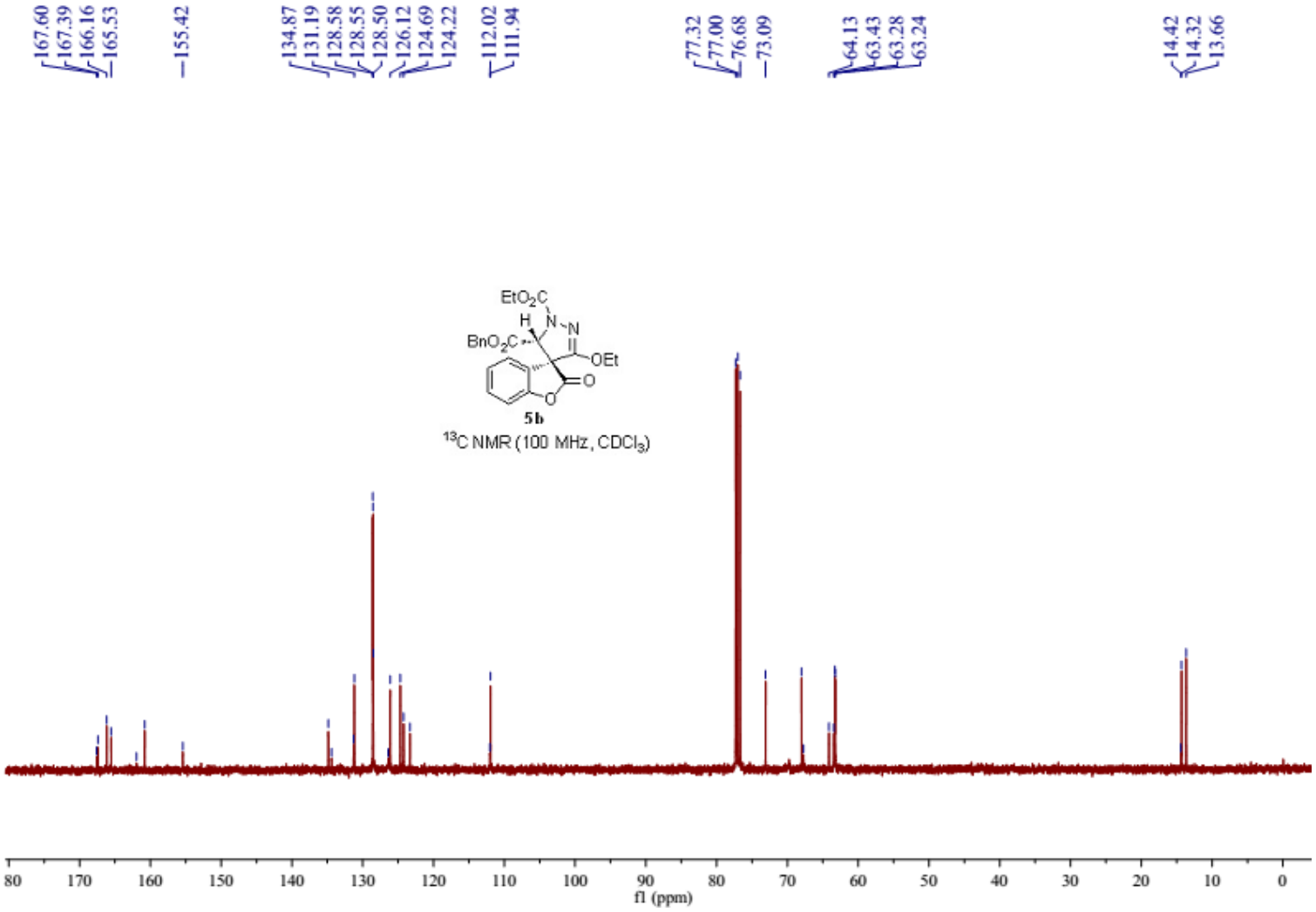

130.32
128.81
128.63
128.51
128.48
128.22
128.19
128.16
127.77
126.82
125.09
123.27
109.81
72.76
68.08
61.51
44.23
13.44
BnO2C
H
N
N
EtO2C
OBn
O
N
Bn
3x
Dept 135 NMR
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

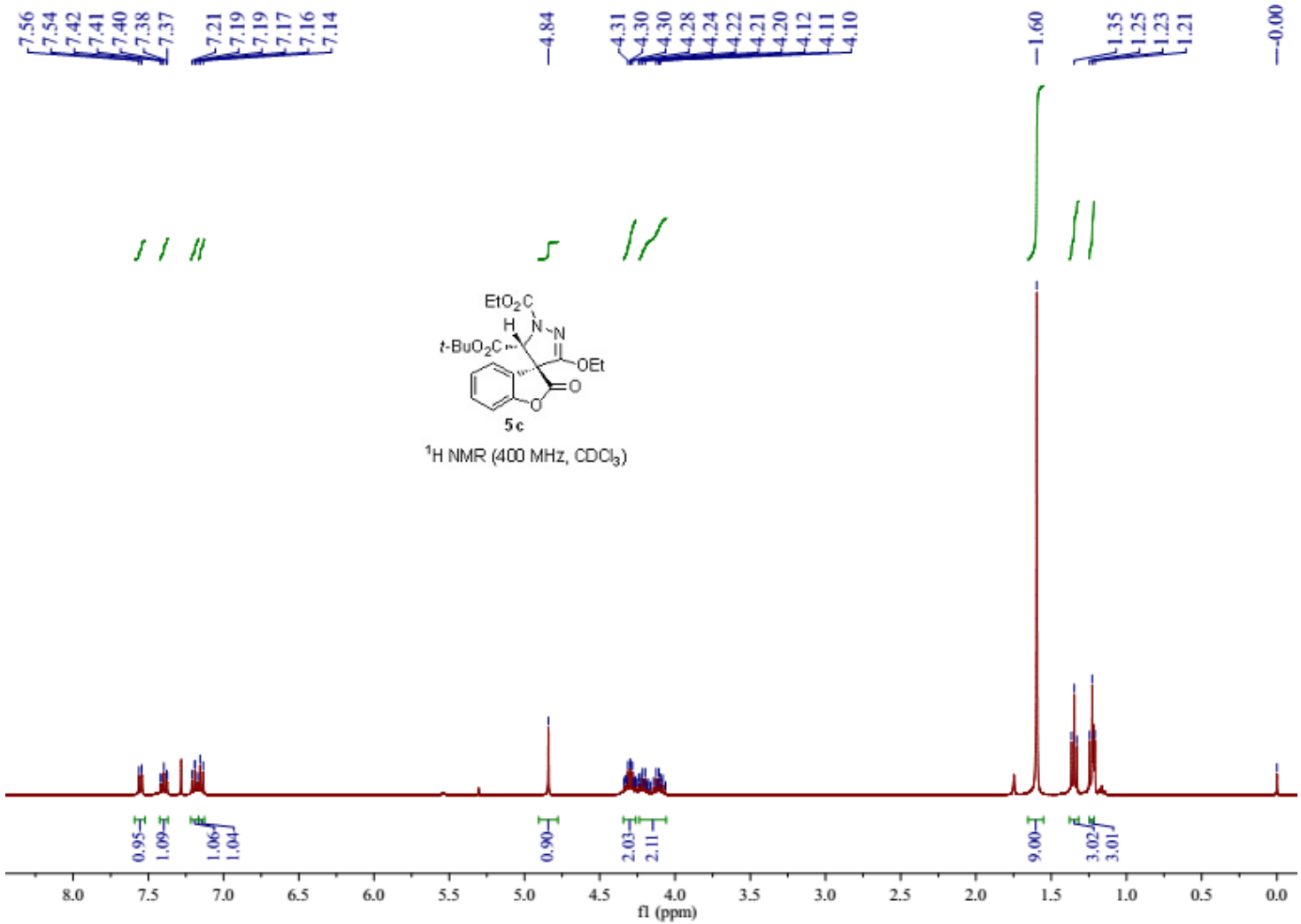

7.56
7.54
7.42
7.40
7.39
7.39
7.37
7.28
7.21
7.19
7.17
7.15
7.13
5.67
4.94
4.41
4.36
4.35
4.34
4.33
4.32
4.31
4.30
4.29
4.29
4.16
4.13
4.11
1.43
1.41
1.39
1.36
1.35
1.33
1.24
1.22
1.20
1.18
1.16
1.15
1.08
1.06
0.00
EtO2C
H
N
N
EtO2C
OEt
O
O
5a
1H NMR (400 MHz, CDCl3)
1.00
1.10
0.54
0.61
2.12
0.41
0.39
0.89
1.98
0.66
2.07
0.49
3.10
3.14
3.00
1.43
1.42
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)

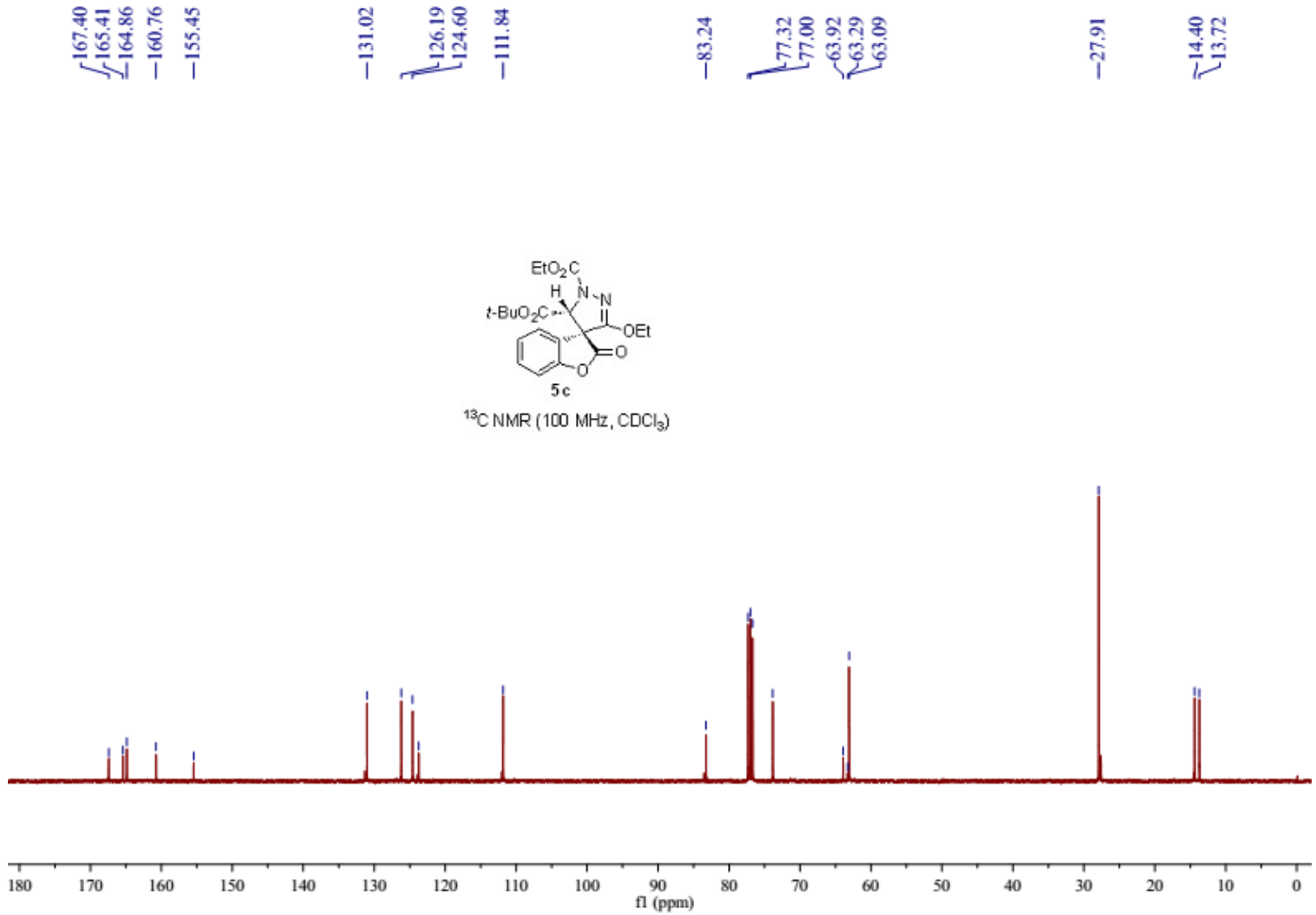

167.58
167.40
166.23
165.48
155.46
131.40
131.18
126.12
124.66
112.13
111.95
77.32
77.00
76.68
64.05
63.40
63.22
63.19
62.20
62.04
14.46
14.34
14.04
13.89
13.68
EtO2C
H
N
N
EtO2C
OEt
O
O
5a
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

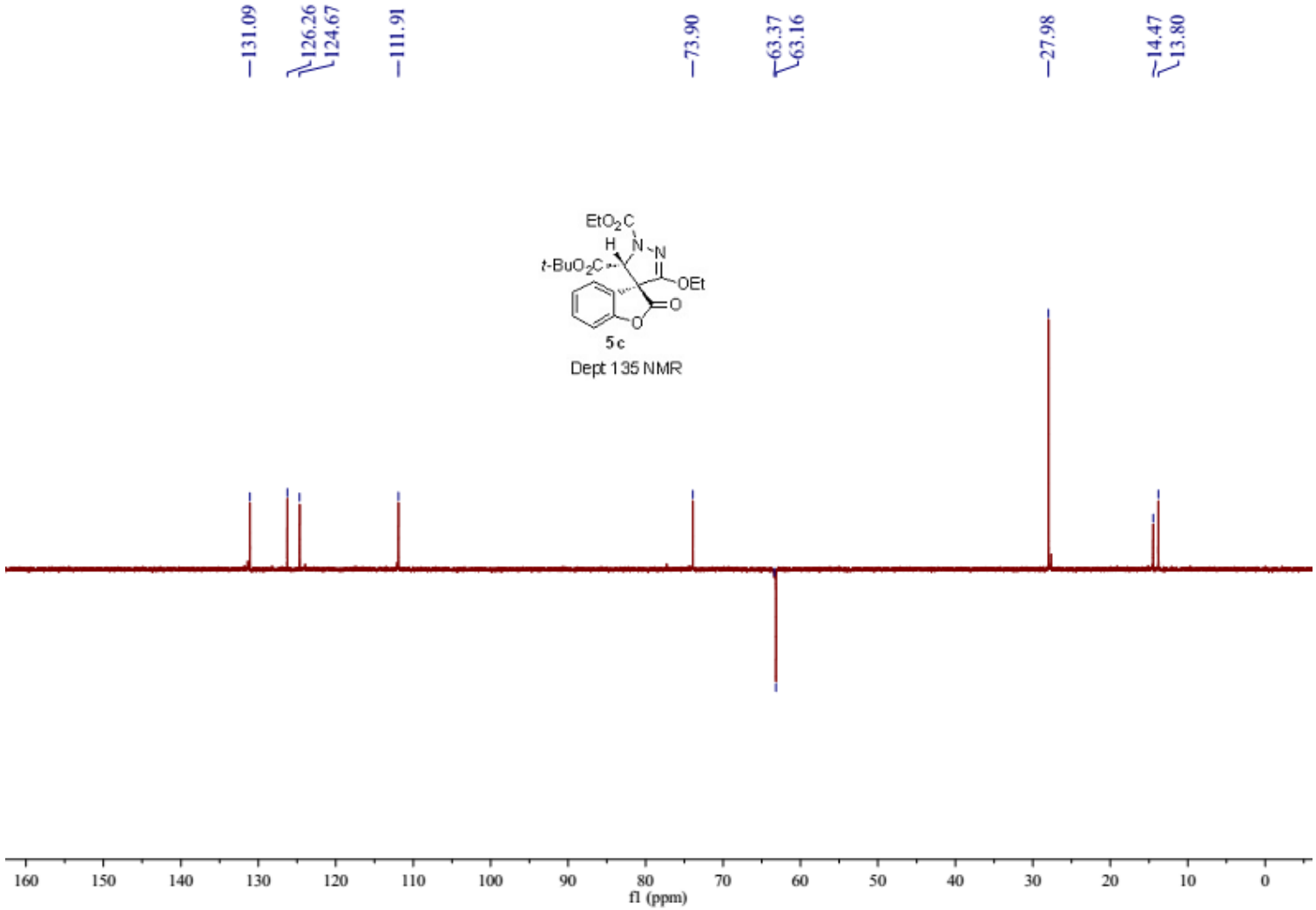

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
EtO2C
H
N
N
EtO2C
OEt
O
O
5a
HMQC

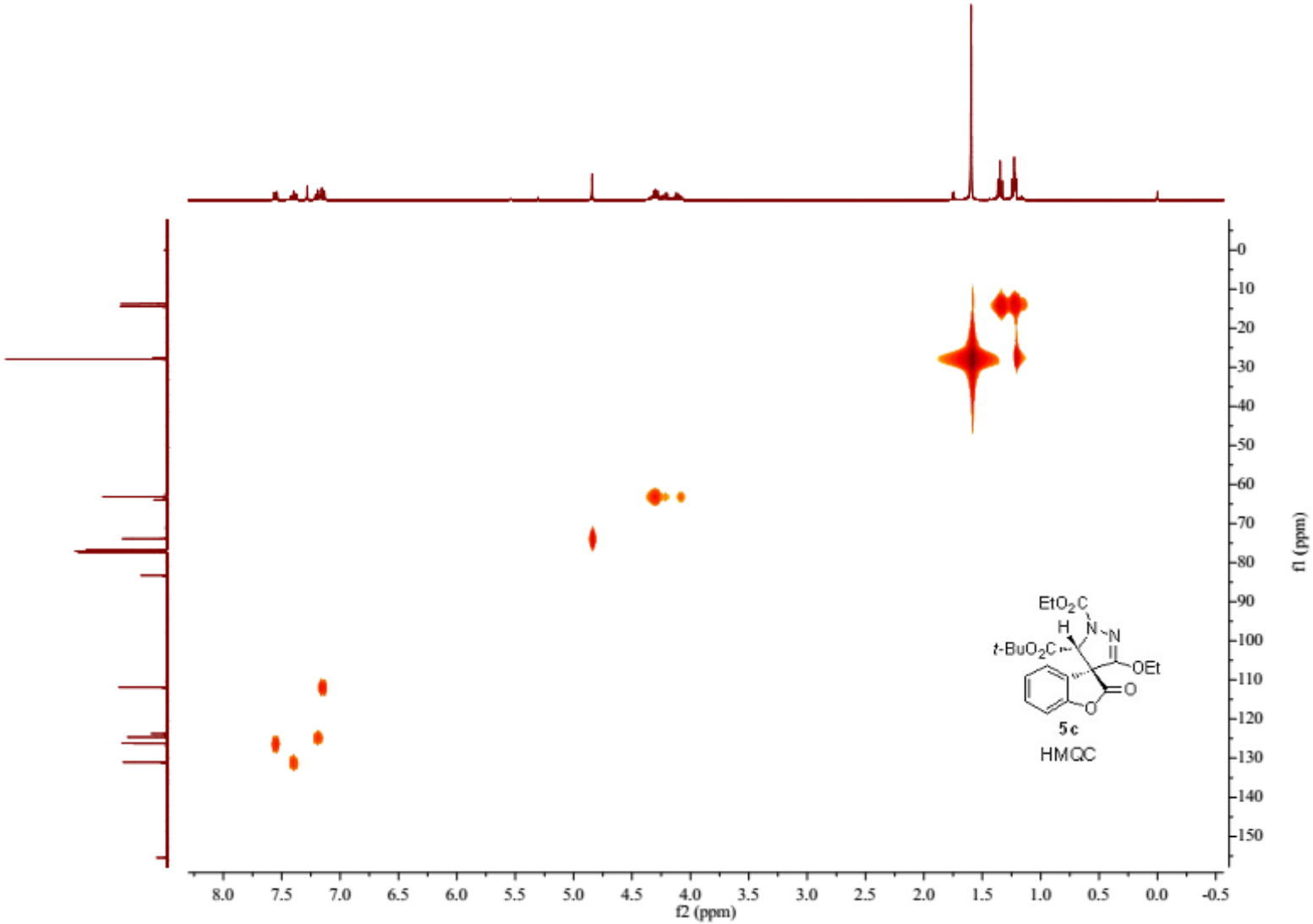

7.46
7.45
7.44
7.42
7.40
7.39
7.38
7.38
7.29
7.29
7.28
7.15
7.13
5.73
5.31
5.02
5.00
4.29
4.28
4.27
4.25
4.16
4.14
4.14
4.12
4.09
4.08
4.06
4.04
4.02
1.37
1.35
1.33
1.31
1.29
1.17
1.15
1.14
0.00
EtO2C
H
N
N
BnO2C
OEt
O
O
5b
1H NMR (400 MHz, CDCl3)
1.08
5.04
1.08
2.07
0.66
0.48
1.00
1.03
0.52
0.91
0.56
2.10
1.51
2.04
0.93
3.05
3.06
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)

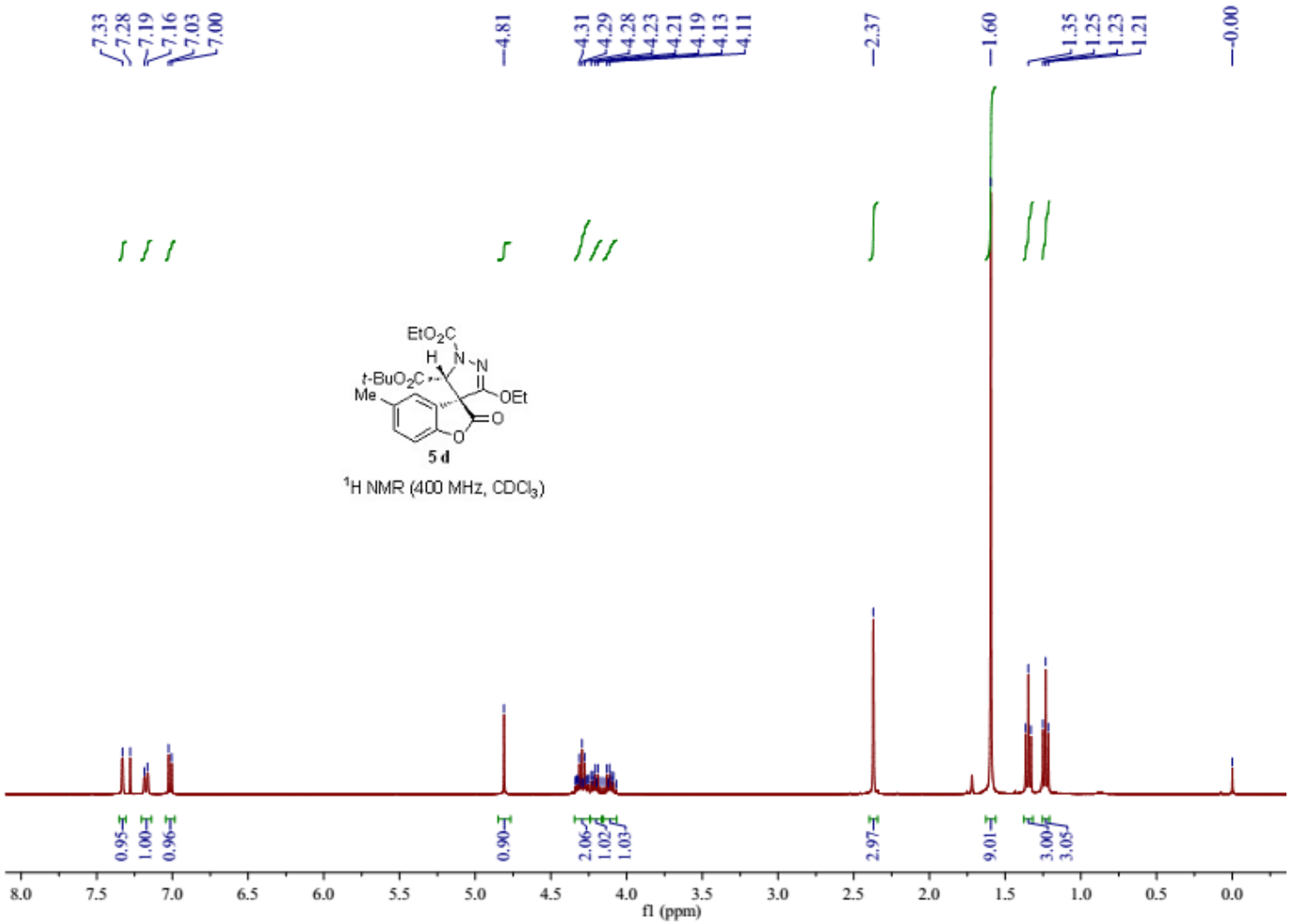

167.60
167.39
166.16
165.53
155.42
134.87
131.19
128.58
128.55
128.50
126.12
124.69
124.22
112.02
111.94
77.32
77.00
76.68
73.09
64.13
63.43
63.28
63.24
14.42
14.32
13.66
EtO2C
H
N
N
BnO2C
OEt
O
O
5b
13C NMR (100 MHz, CDCl3)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

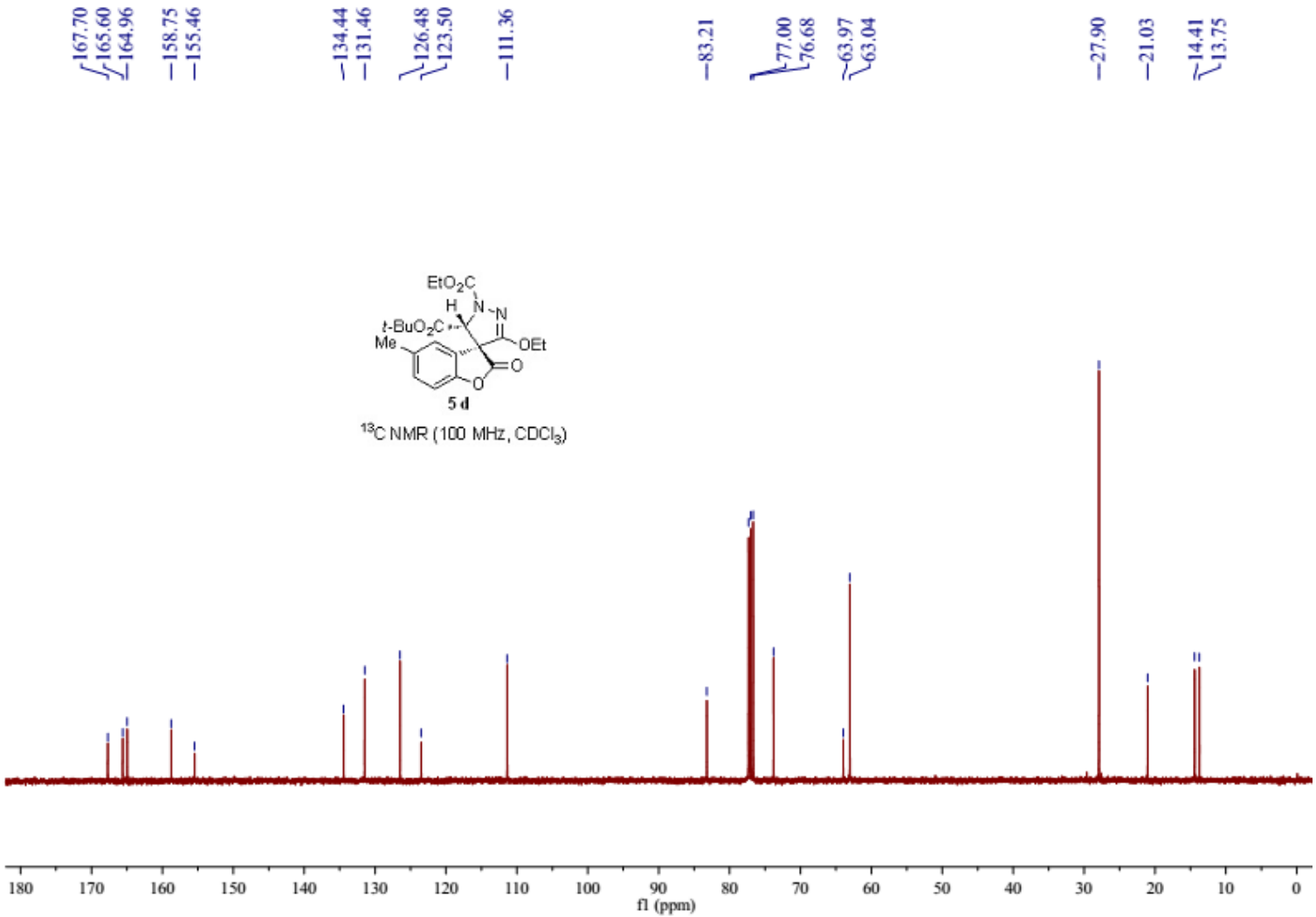

7.56
7.54
7.42
7.41
7.40
7.38
7.37
7.21
7.19
7.19
7.17
7.16
7.14
4.84
4.31
4.30
4.30
4.28
4.24
4.22
4.21
4.20
4.12
4.11
4.10
1.60
1.35
1.25
1.23
1.21
0.00
EtO2C
H
N
N
t-BuO2C
OEt
O
O
5c
1H NMR (400 MHz, CDCl3)
0.95
1.09
1.06
1.04
0.90
2.03
2.11
9.00
3.02
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

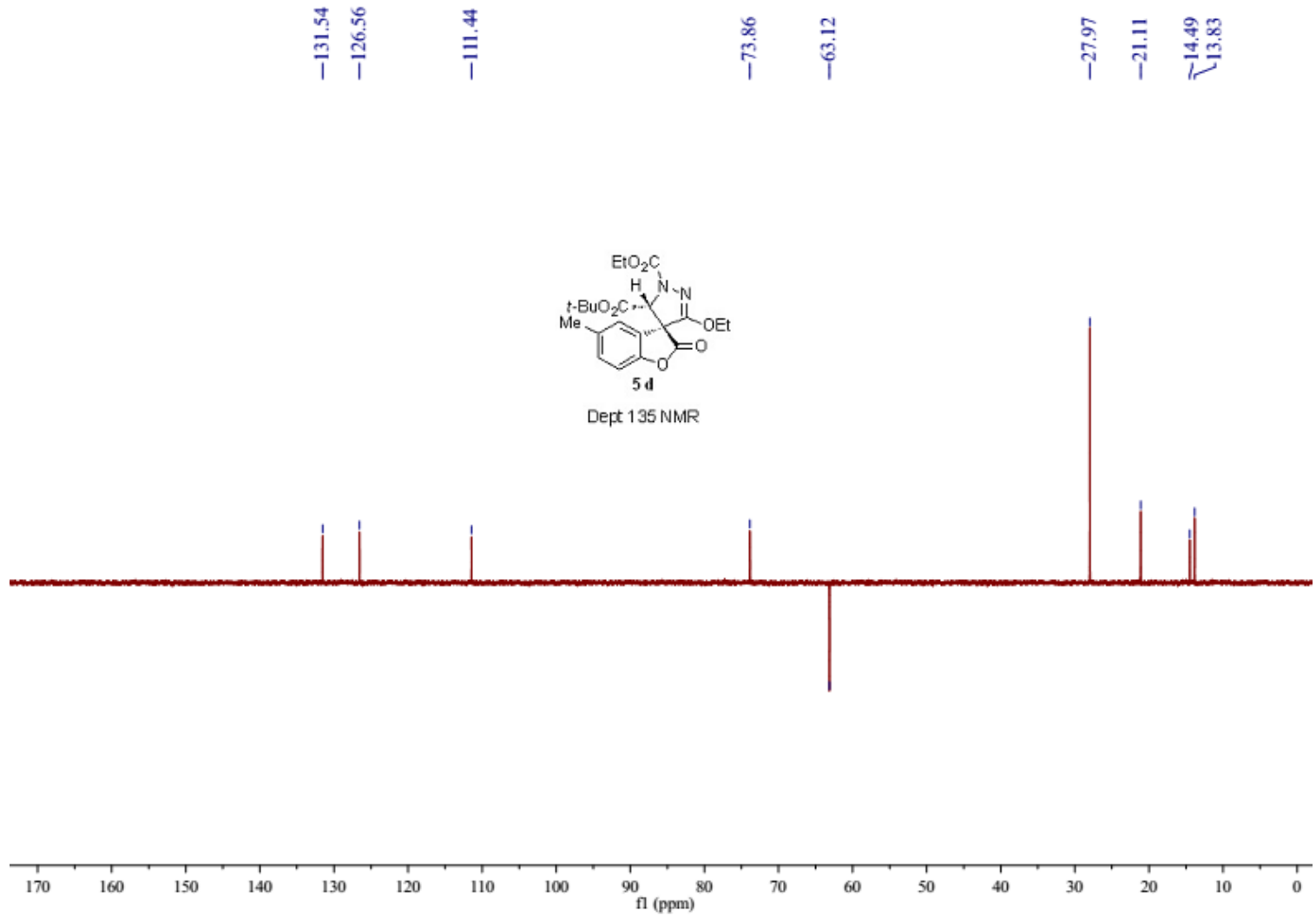

167.40
165.41
164.86
160.76
155.45
131.02
126.19
124.60
111.84
83.24
77.32
77.00
63.92
63.29
63.09
27.91
14.40
13.72
EtO2C
H
N
N
t-BuO2C
OEt
O
O
5c
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

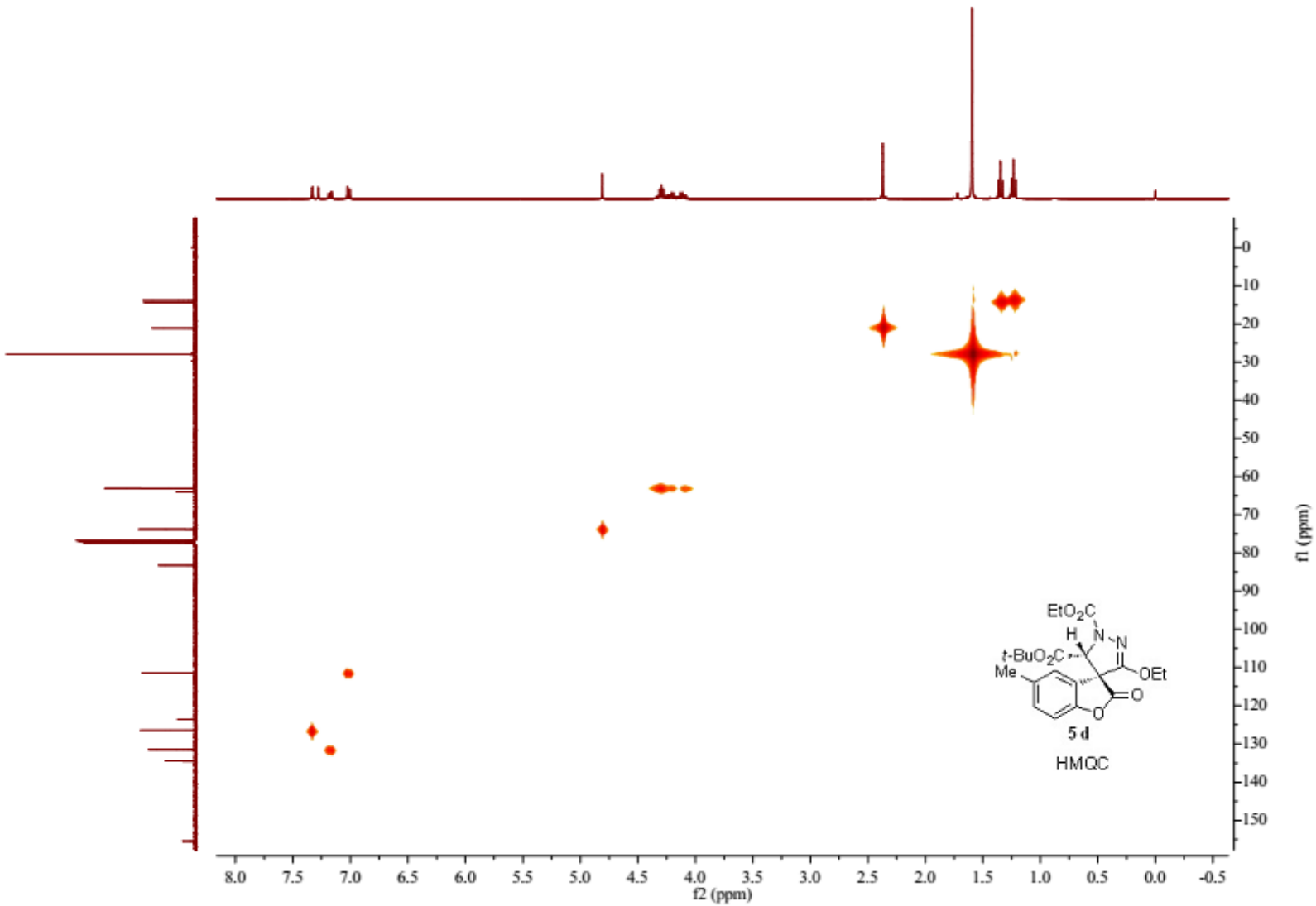

131.09
126.26
124.67
111.91
73.90
63.37
63.16
27.98
14.47
13.80
EtO2C
H
N
N
t-BuO2C
OEt
O
O
5c
Dept 135 NMR
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

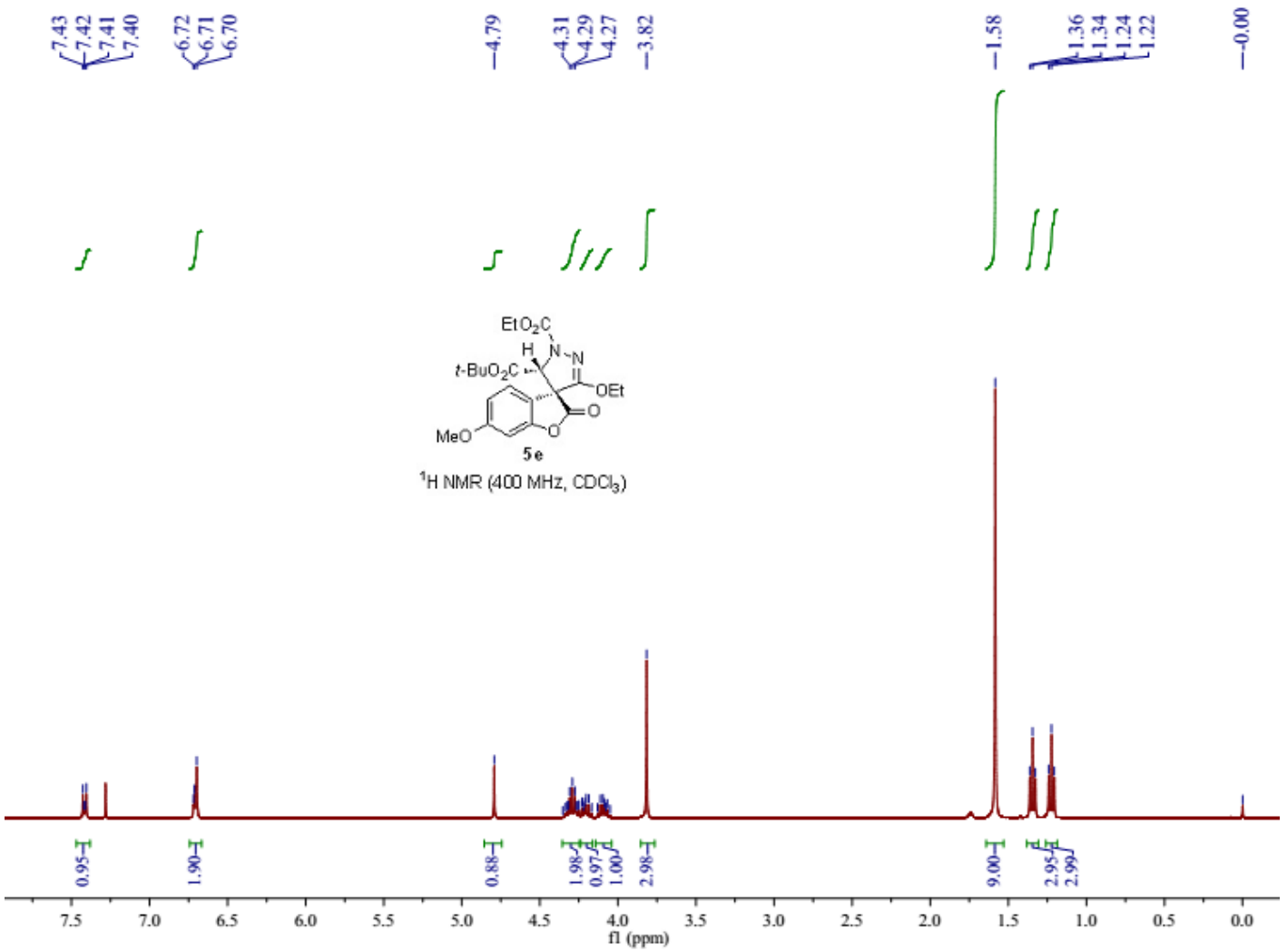

f2 (ppm)
f1 (ppm)
EtO2C
t-BuO2C
OEt
O
5c
HMQC

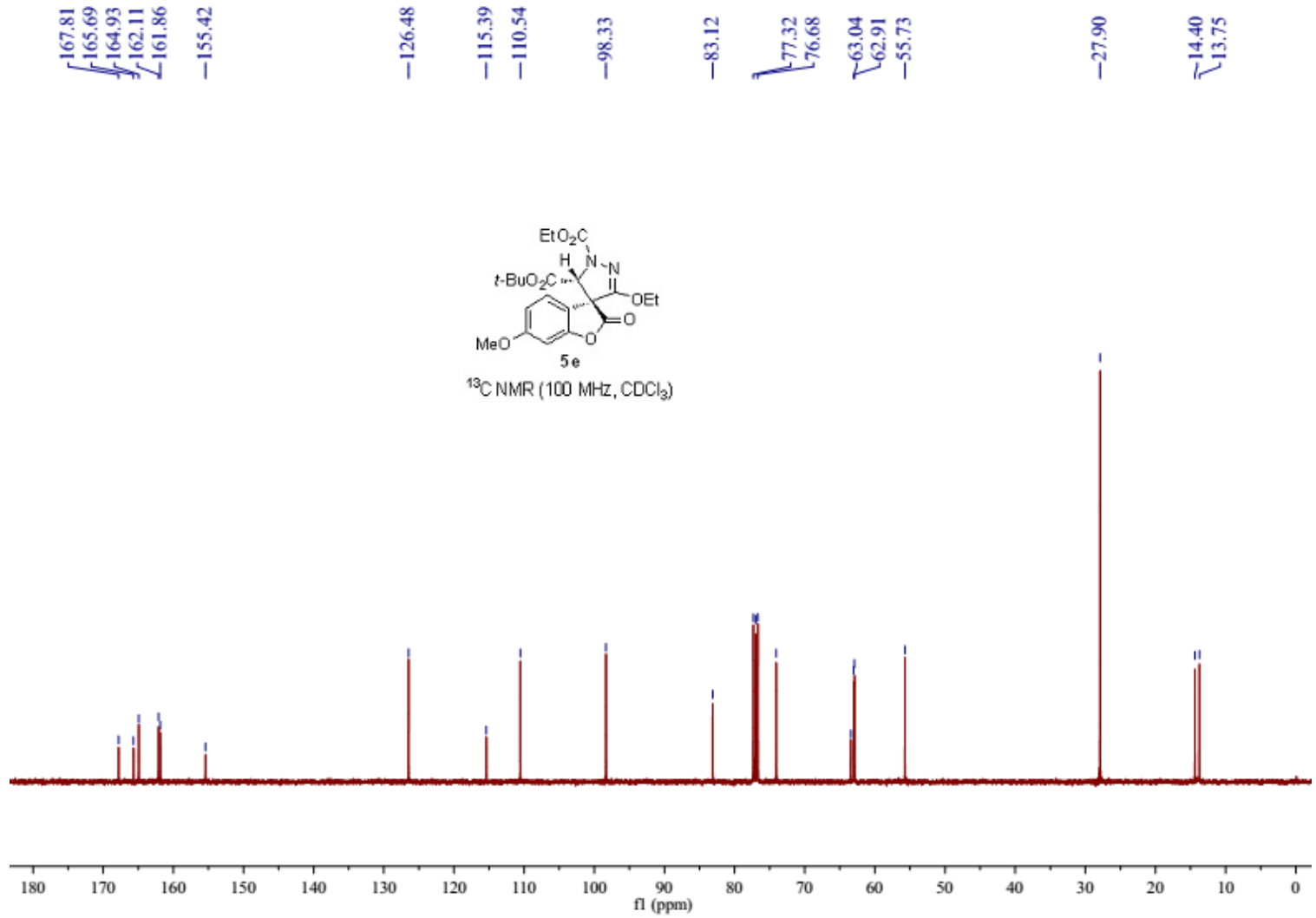

7.33
7.28
7.19
7.16
7.03
7.00
4.81
4.31
4.29
4.28
4.23
4.21
4.19
4.13
4.11
2.37
1.60
1.35
1.25
1.23
1.21
0.00
EtO2C
H
N
N
t-BuO2C
Me
OEt
O
O
5 d
1H NMR (400 MHz, CDCl3)
0.95
1.00
0.96
0.90
2.06
1.02
1.03
2.97
9.01
3.00
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

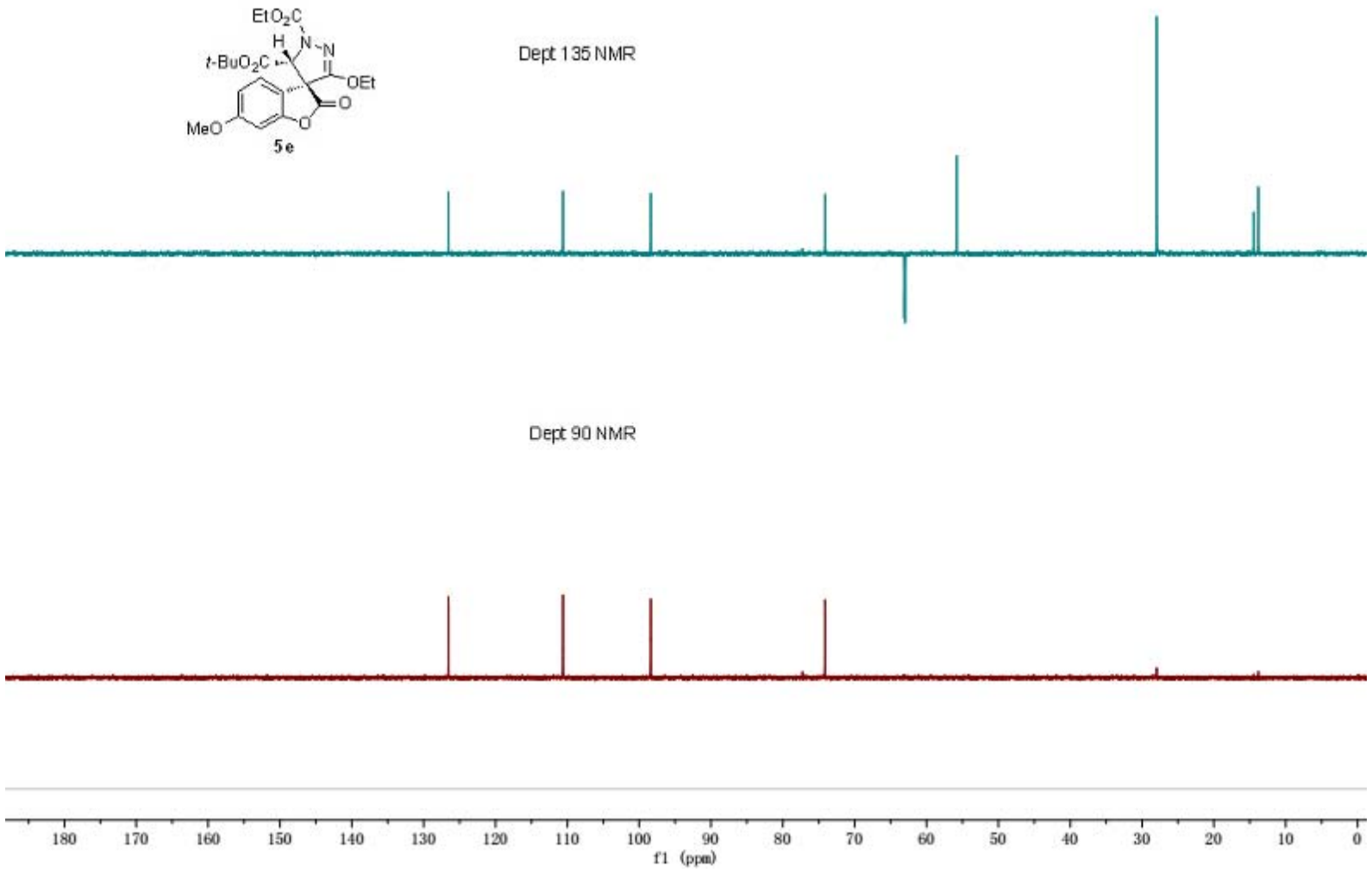

167.70
165.60
164.96
158.75
155.46
134.44
131.46
126.48
123.50
111.36
83.21
77.00
76.68
63.97
63.04
27.90
21.03
14.41
13.75
EtO2C
t-BuO2C
Me
OEt
5 d
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

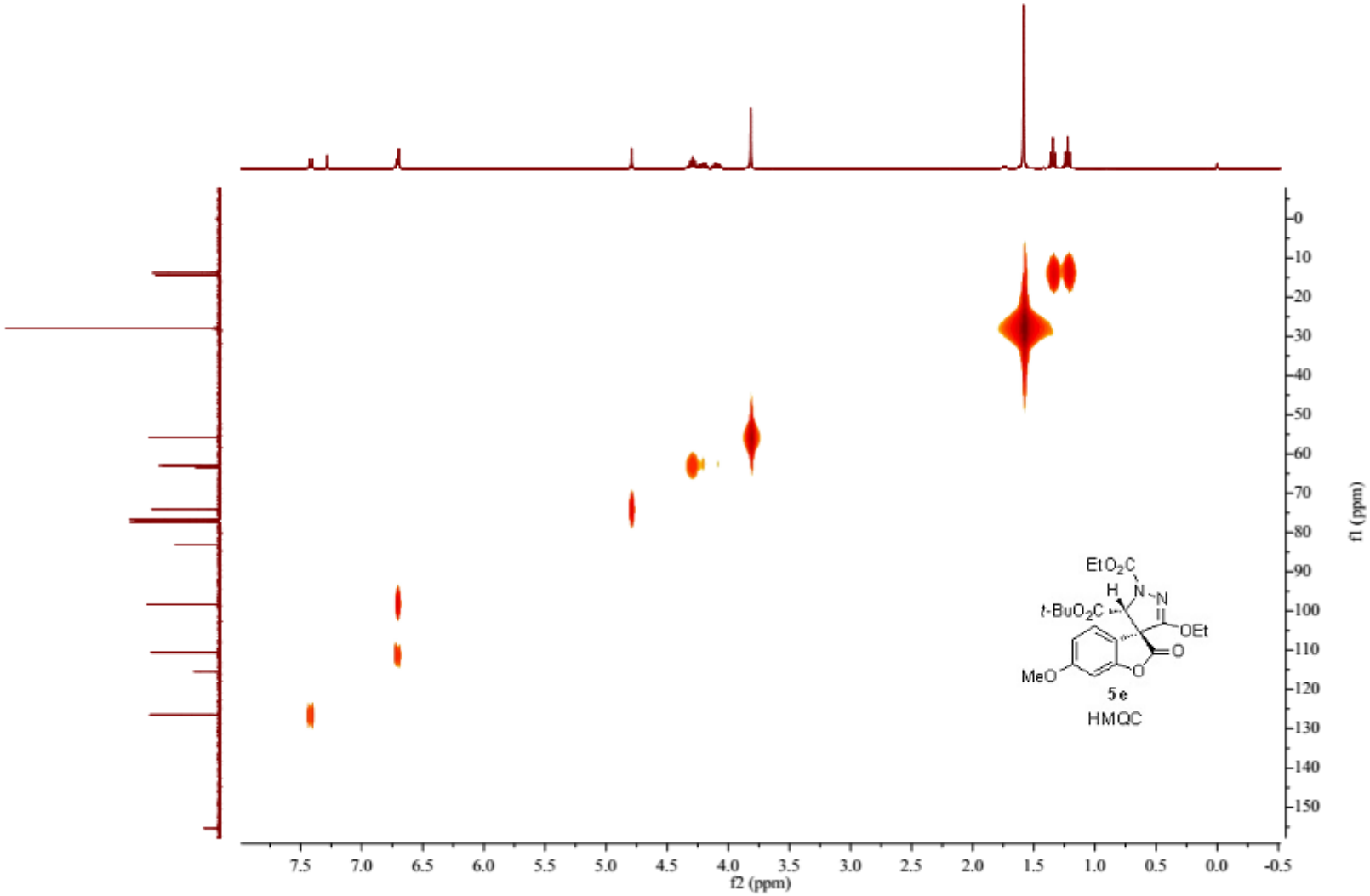

131.54
126.56
111.44
73.86
63.12
27.97
21.11
14.49
13.83
EtO2C
H
N
N
t-BuO2C
Me
OEt
O
O
5 d
Dept 135 NMR
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

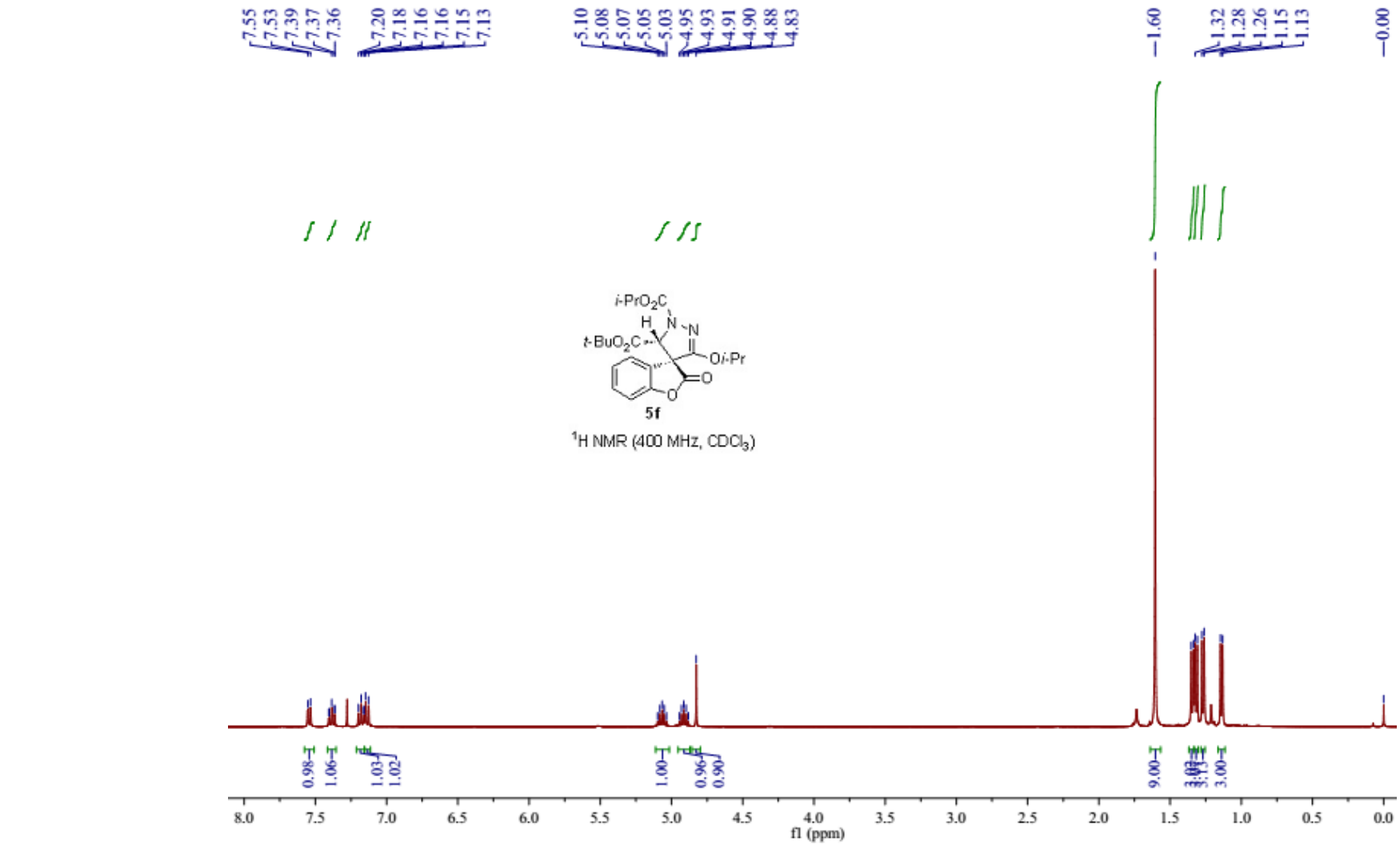

f2 (ppm)
f1 (ppm)
EtO2C
H
N
N
t-BuO2C
Me
OEt
O
O
5 d
HMQC

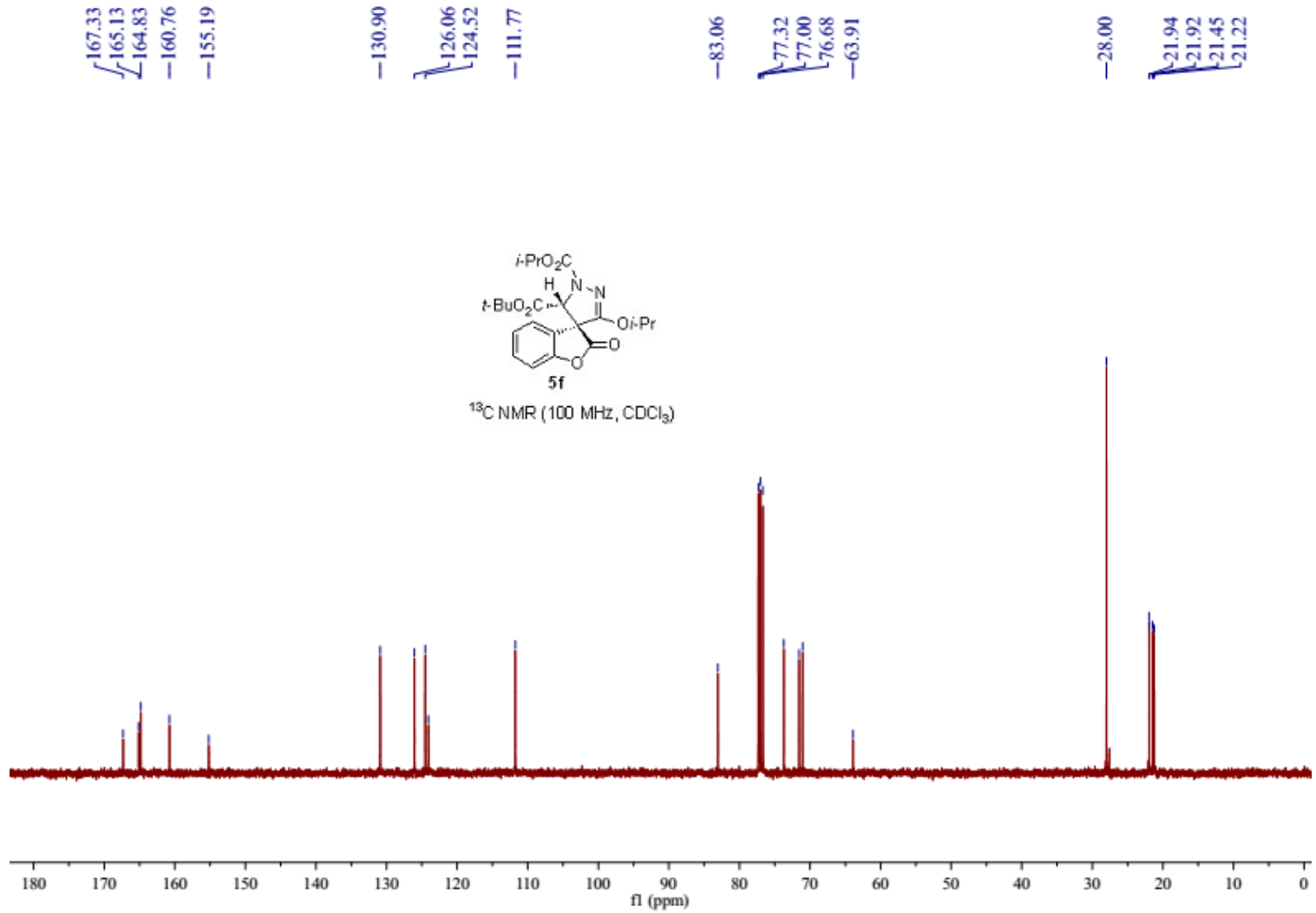

7.43
7.42
7.41
7.40
6.72
6.71
6.70
4.79
4.31
4.29
4.27
3.82
1.58
1.36
1.34
1.24
1.22
0.00
EtO2C
H
N
N
t-BuO2C
OEt
O
O
MeO
5e
1H NMR (400 MHz, CDCl3)
0.95
1.90
0.88
1.98
0.97
1.00
2.98
9.00
2.95
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

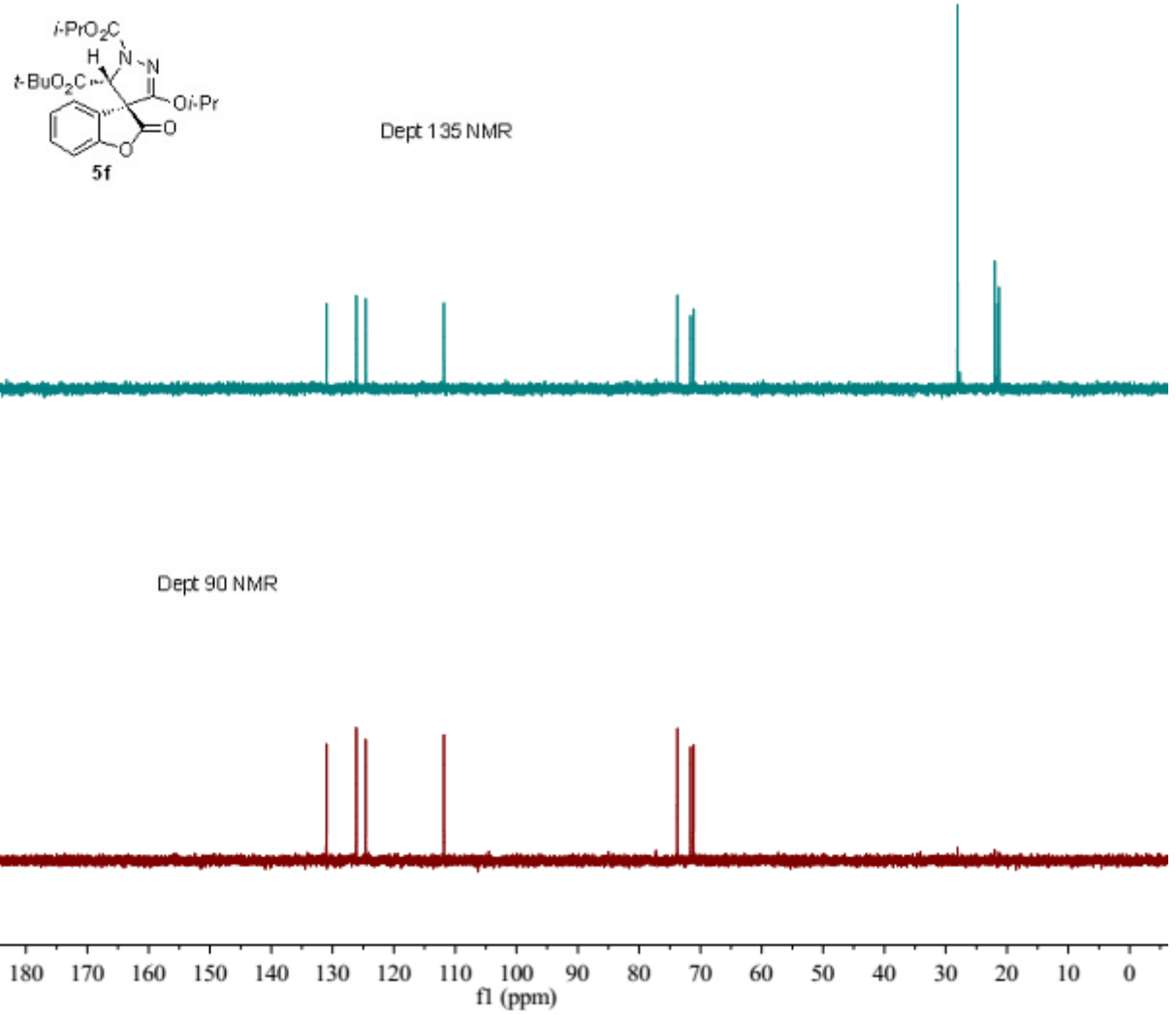

167.81
165.69
164.93
162.11
161.86
155.42
126.48
115.39
110.54
98.33
83.12
77.32
76.68
63.04
62.91
55.73
27.90
14.40
13.75
EtO2C
t-BuO2C
OEt
MeO
5e
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

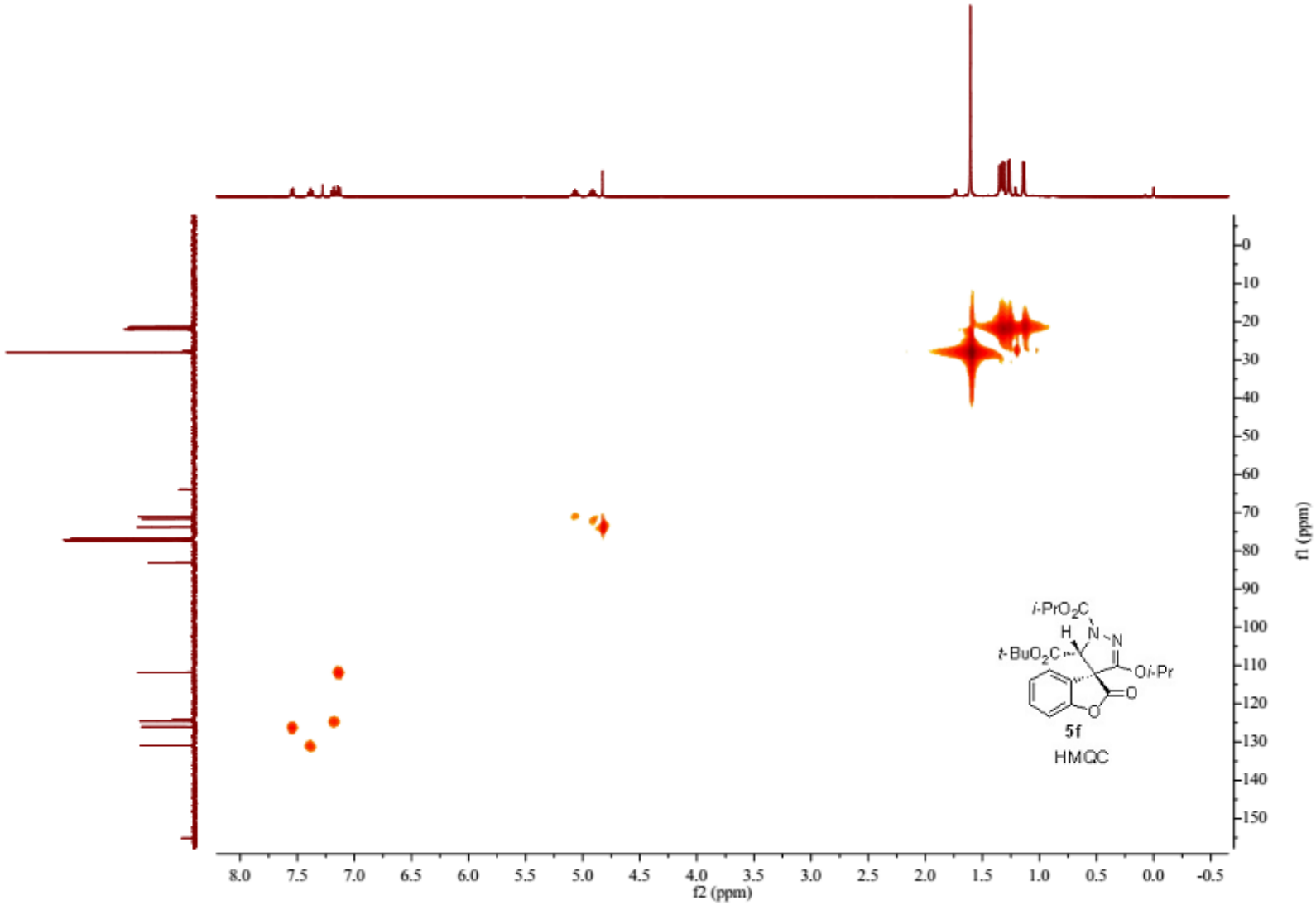

EtO2C
H
N
N
t-BuO2C
OEt
O
MeO
O
5e
Dept 135 NMR
Dept 90 NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

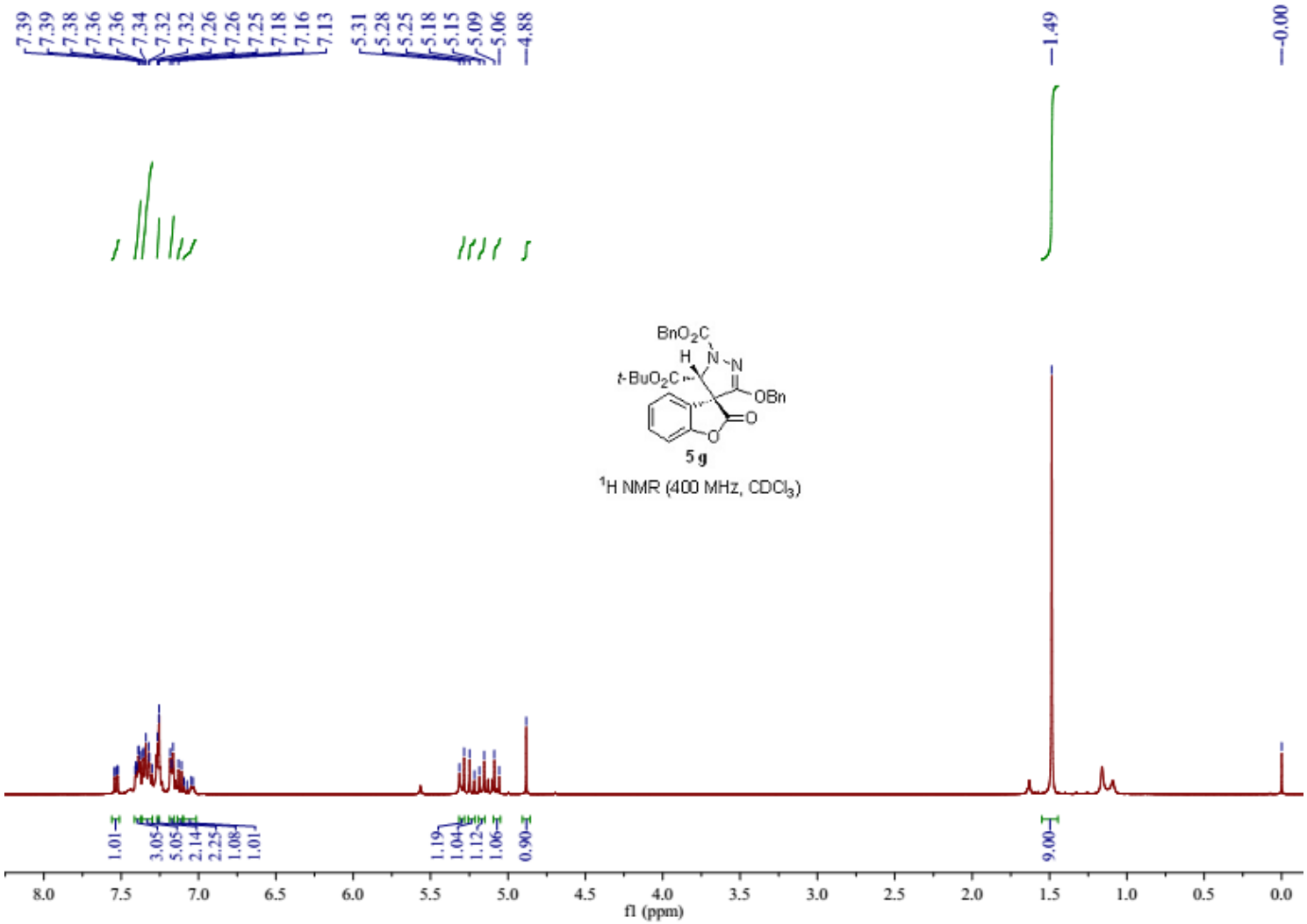

f2 (ppm)
f1 (ppm)
EtO2C
t-BuO2C
OEt
MeO
5e
HMQC

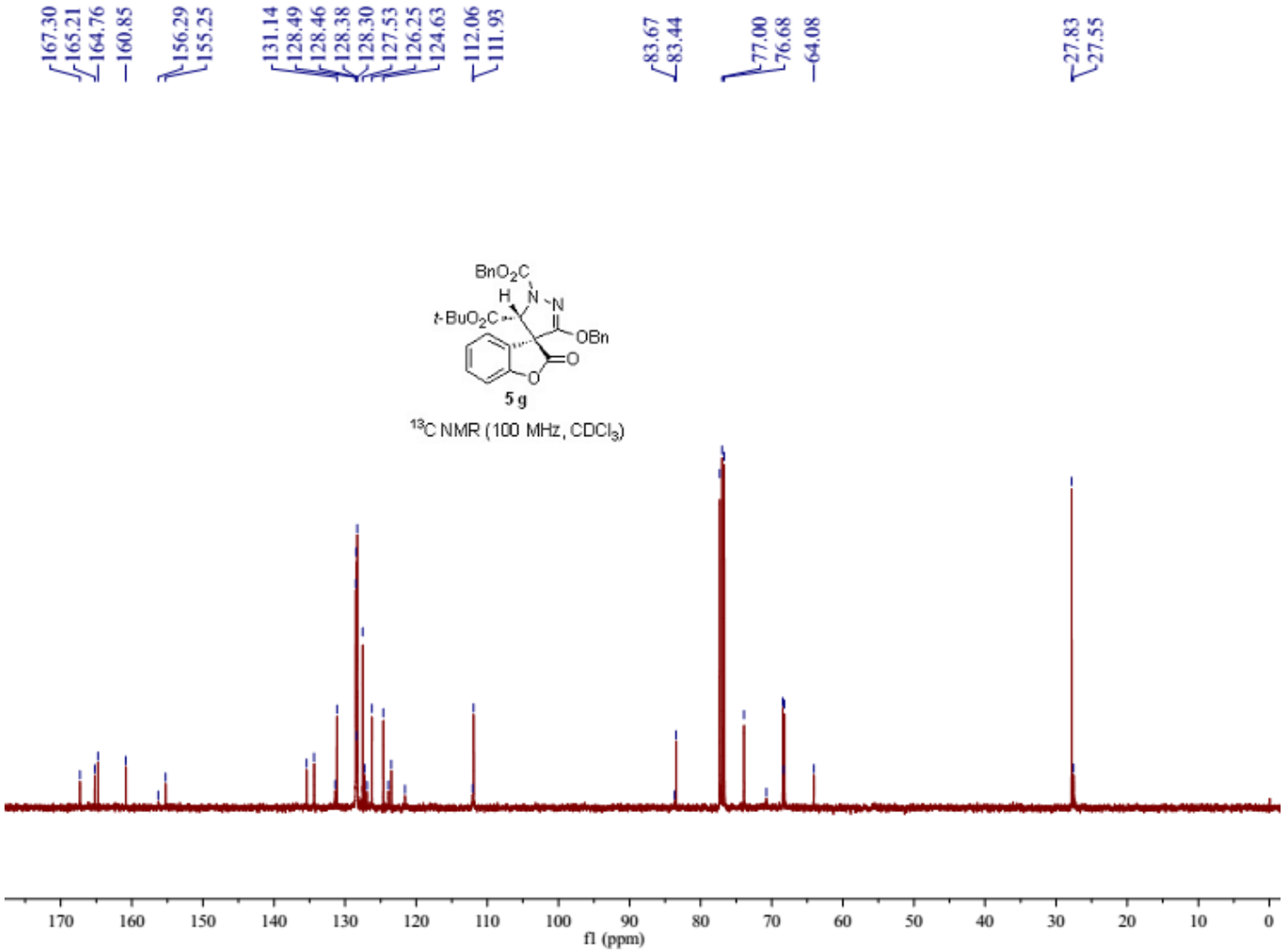

7.55
7.53
7.39
7.37
7.36
7.20
7.18
7.16
7.16
7.15
7.13
5.10
5.08
5.07
5.05
5.03
4.95
4.93
4.91
4.90
4.88
4.83
1.60
1.32
1.28
1.26
1.15
1.13
0.00
i-PrO2C
H
N
N
t-BuO2C
Oi-Pr
O
O
5f
1H NMR (400 MHz, CDCl3)
0.98
1.06
1.03
1.02
1.00
0.96
0.90
9.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.33
165.13
164.83
160.76
155.19
130.90
126.06
124.52
111.77
83.06
77.32
77.00
76.68
63.91
28.00
21.94
21.92
21.45
21.22
i-PrO2C
H
N
N
t-BuO2C
Oi-Pr
O
O
5f
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


i-PrO2C
H
N
N
t-BuO2C
Oi-Pr
O
O
5f
Dept 135 NMR
Dept 90 NMR
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


f2 (ppm)
f1 (ppm)
i-PrO2C
t-BuO2C
O i-Pr
5f
HMQC


7.39
7.39
7.38
7.36
7.36
7.34
7.32
7.32
7.26
7.26
7.25
7.18
7.16
7.13
5.31
5.28
5.25
5.18
5.15
5.09
5.06
4.88
1.49
0.00
BnO2C
H
N
N
t-BuO2C
OBn
O
O
5g
1H NMR (400 MHz, CDCl3)
1.01
3.05
5.05
2.14
2.25
1.08
1.01
1.19
1.04
1.12
1.06
0.90
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.30
165.21
164.76
160.85
156.29
155.25
131.14
128.49
128.46
128.38
128.30
127.53
126.25
124.63
112.06
111.93
83.67
83.44
77.00
76.68
64.08
27.83
27.55
BnO2C
H
N
N
t-BuO2C
OBn
O
O
5 g
13C NMR (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)