Rhodium(III)-Catalyzed Diastereoselective Ring-Opening of 7-Azabenzonorbornadienes with Aromatic Ketoximes: Synthesis of Benzophenanthridine Derivatives

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Supporting Information (SI)

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Crystallographic Data of Compound 3ba:

Suitable single crystals for X-ray diffraction studies were obtained from the compound synthesized in this study. Single crystals were grown in a NMR tube at room temperature using $CDCl_3$ over a period of 3-4 weeks by slow evaporation of solvent.

X-ray data was collected with a Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite monochromatic Mo (Kα) (λ = 0.7107 A) radiation source. The data were collected with 100% completeness for Θ up to 25º. ω and ϕ scans were employed to collect the data. The frame width for ω for was fixed to 0.5º for data collection. The crystal was solved by direct methods using Bruker SHELXS (Sheldrick, 1997). The Structure was refined using the Bruker SHELXTL (Version 6.12) software package. These data were deposited with Cambridge Crystallographic Data Center with the following numbers: **CCDC 1950036.**

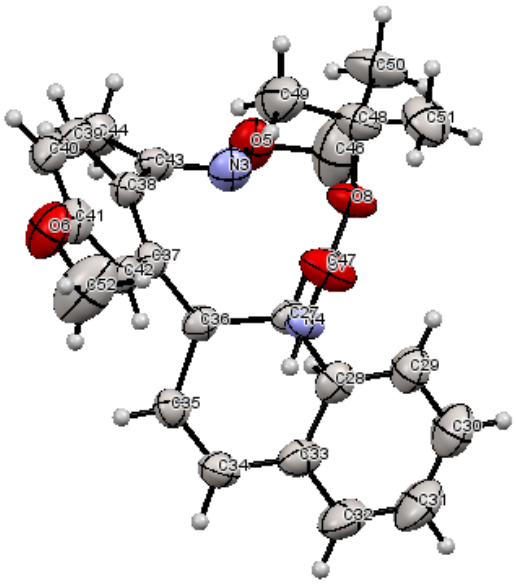
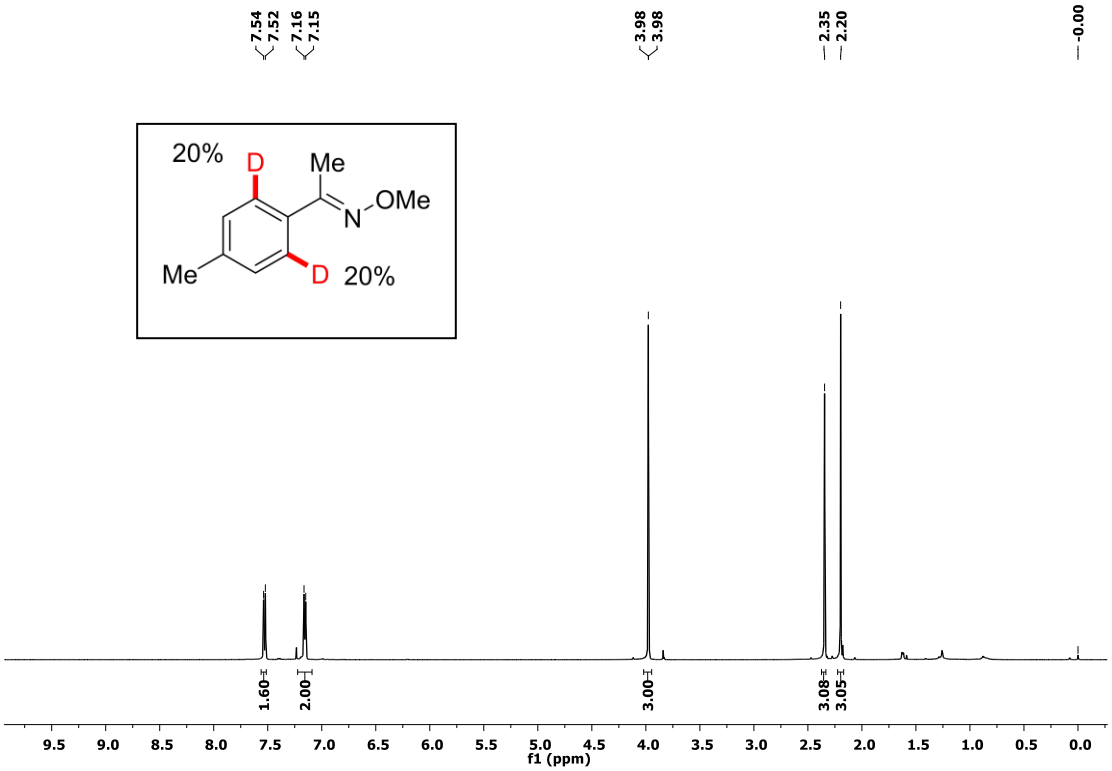


Figure S1: ORTEP representation of compound **3ba** displaying thermal elliposoid at 50% probability.

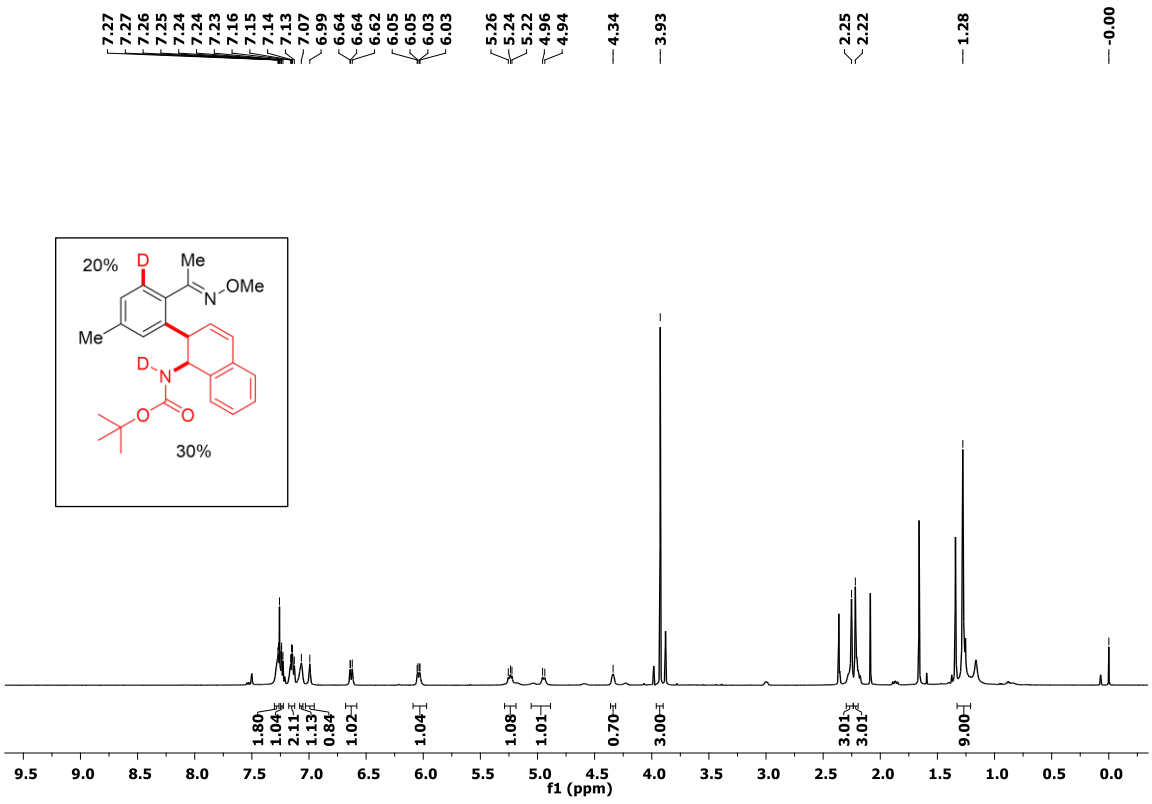
X-Ray Analysis of Compounds 3ba (the crystal is having dimeric compound).

Identification code	**3ba**	
Empirical formula	$C_{50}\ H_{61}\ N_4\ O_8$	
Formula weight	846.02	
Temperature	296(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 1114.05(16) pm	α= 89.364(5)°.
	b = 1469.54(16) pm	β= 79.407(4)°.
	c = 1523.2(2) pm	γ = 75.874(4)°.
Volume	2.3756(6) nm^3	
Z	2	
Density (calculated)	1.183 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	906	
Crystal size	0.250 x 0.220 x 0.150 mm^3	
Theta range for data collection	1.361 to 24.292°.	
Index ranges	-12<=h<=12, -16<=k<=16, -17<=l<=17	
Reflections collected	28630	
Independent reflections	7586 [R(int) = 0.0592]	
Completeness to theta = 24.292°	98.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7586 / 0 / 580	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0609, wR2 = 0.1617	
R indices (all data)	R1 = 0.1138, wR2 = 0.1996	
Extinction coefficient	0.0043(11)	
Largest diff. peak and hole	0.214 and -0.591 e.$Å^{-3}$	

^{1}H Spectra of Compound **D-1c** ($CDCl_3$ was used).

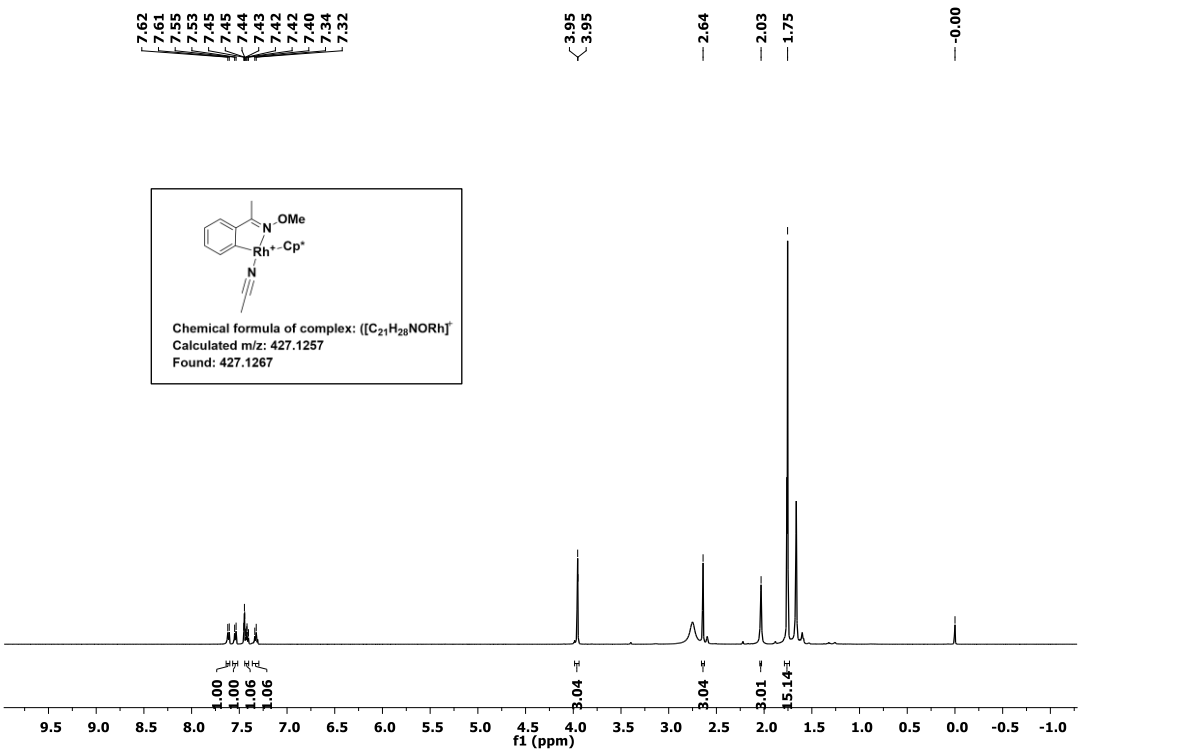


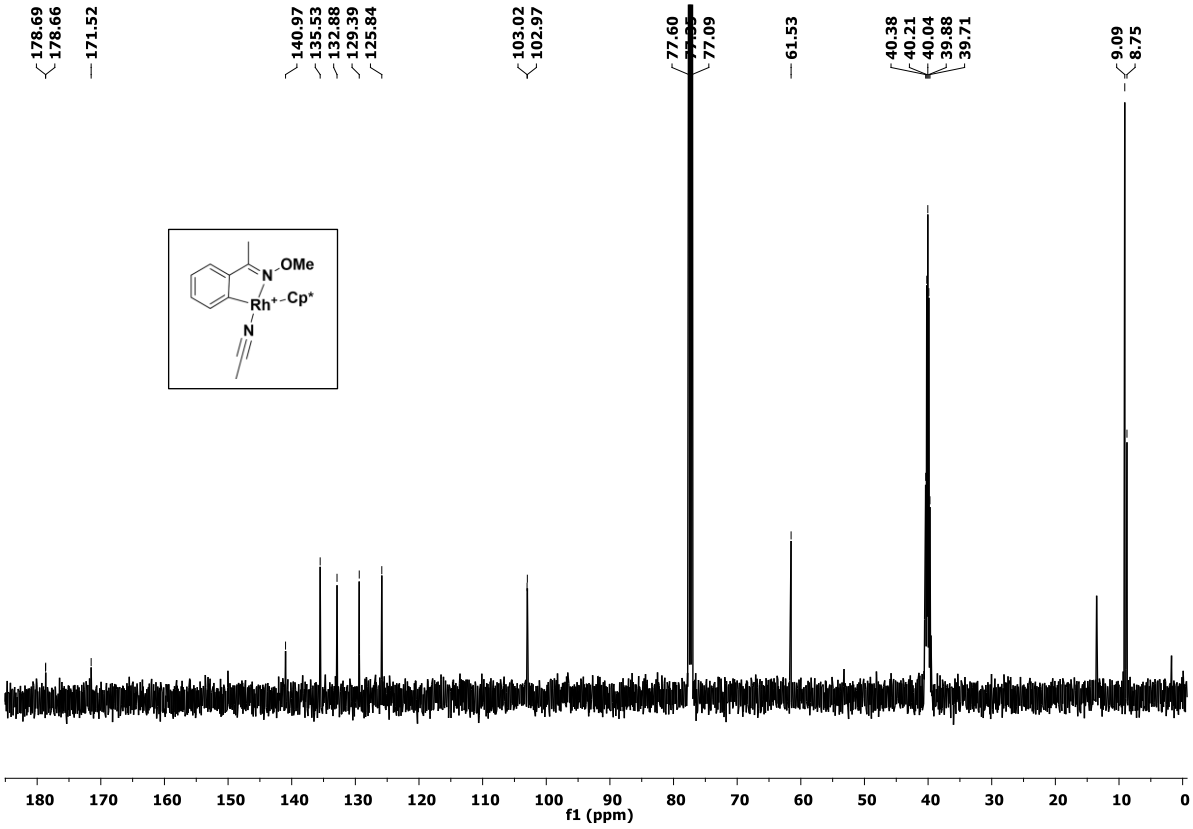
^{1}H Spectra of Compound **D-3ca** ($CDCl_3$ was used).



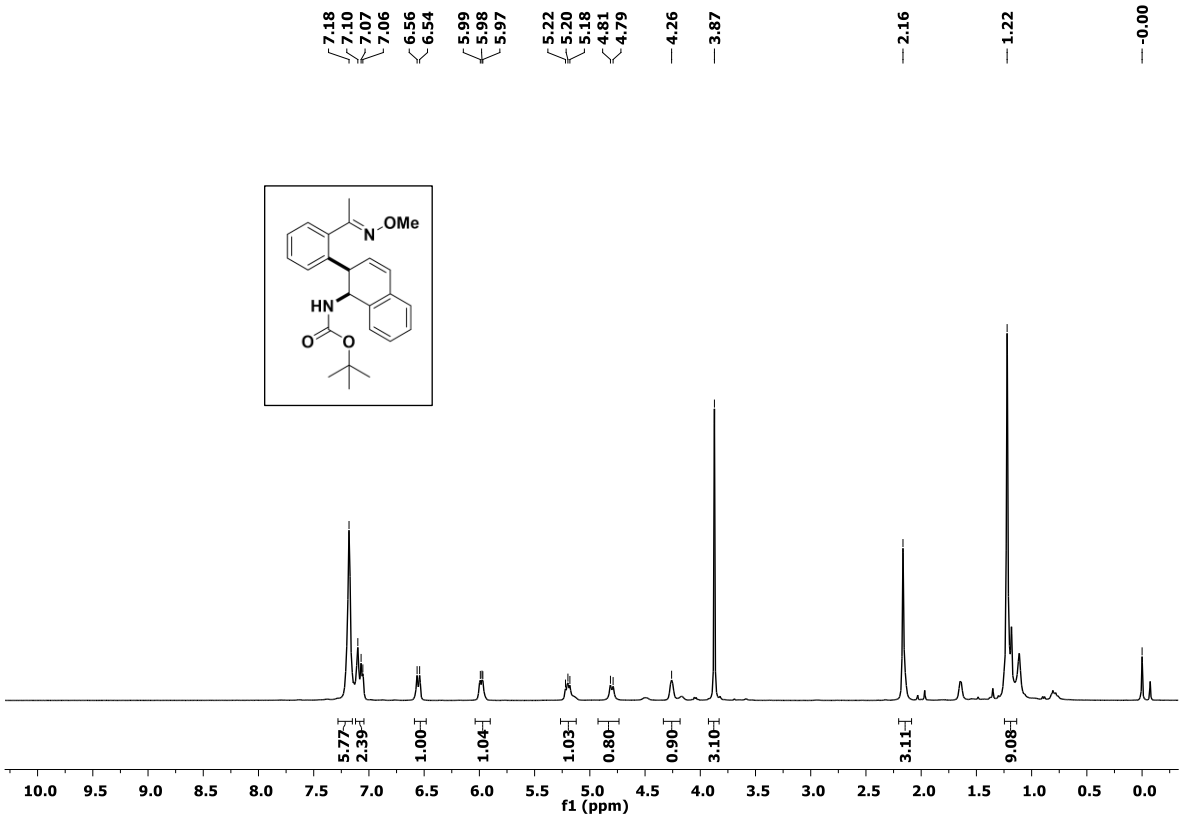
Isolation of intermediate B.

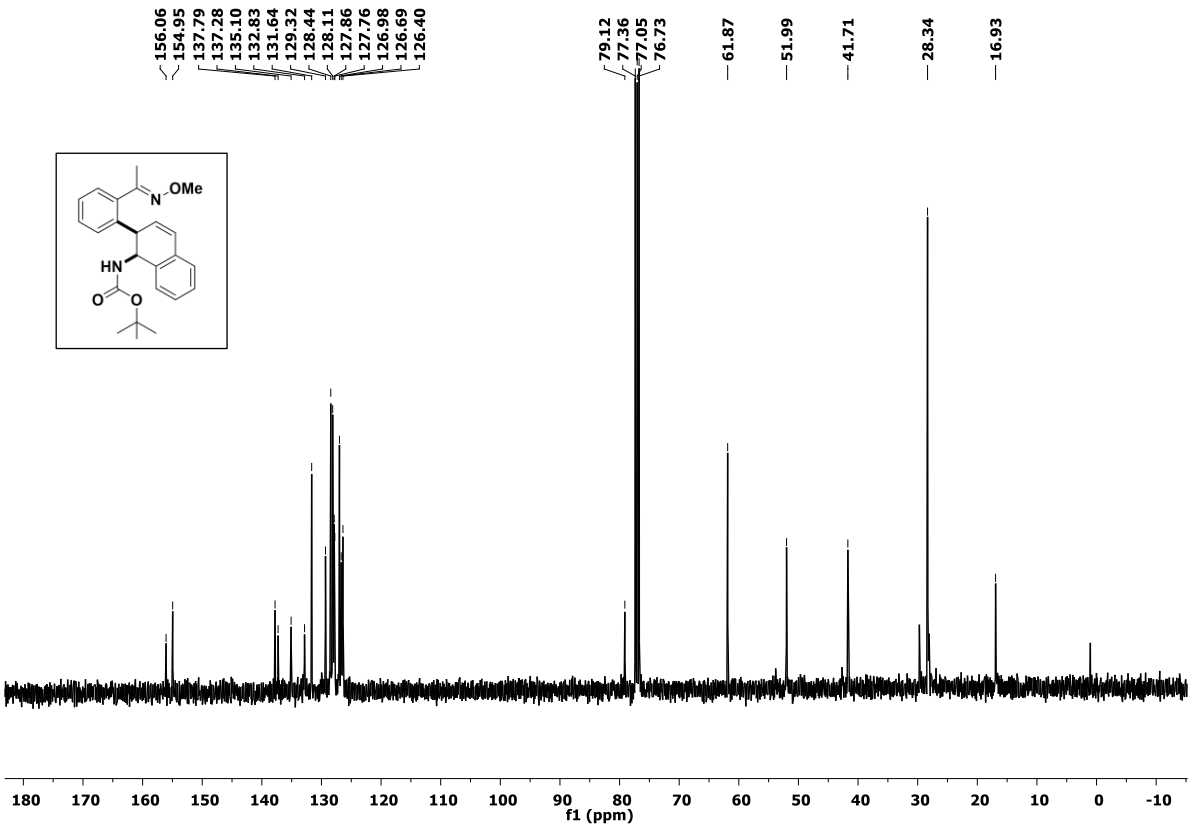
^{1}H and ^{13}C NMR Spectra of Compound **B**



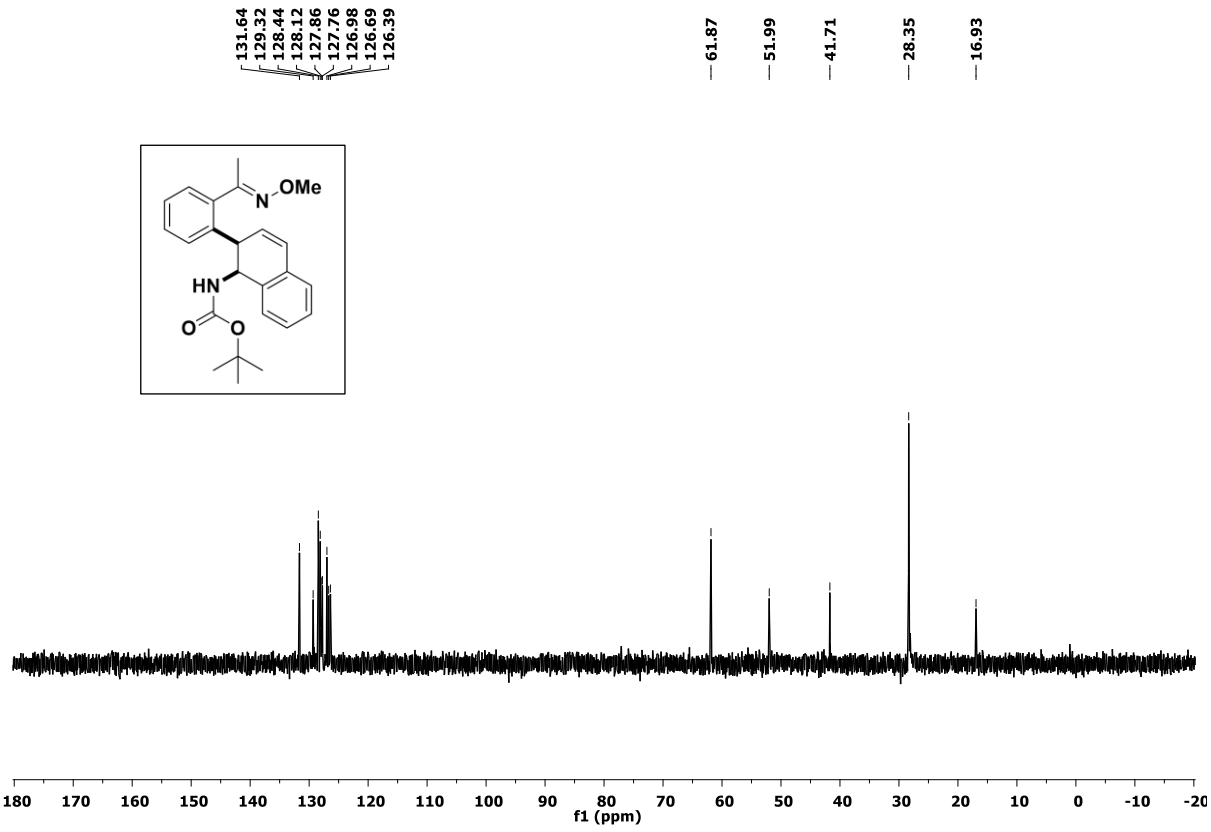


^{1}H and ^{13}C NMR Spectra of Compound **3aa.**

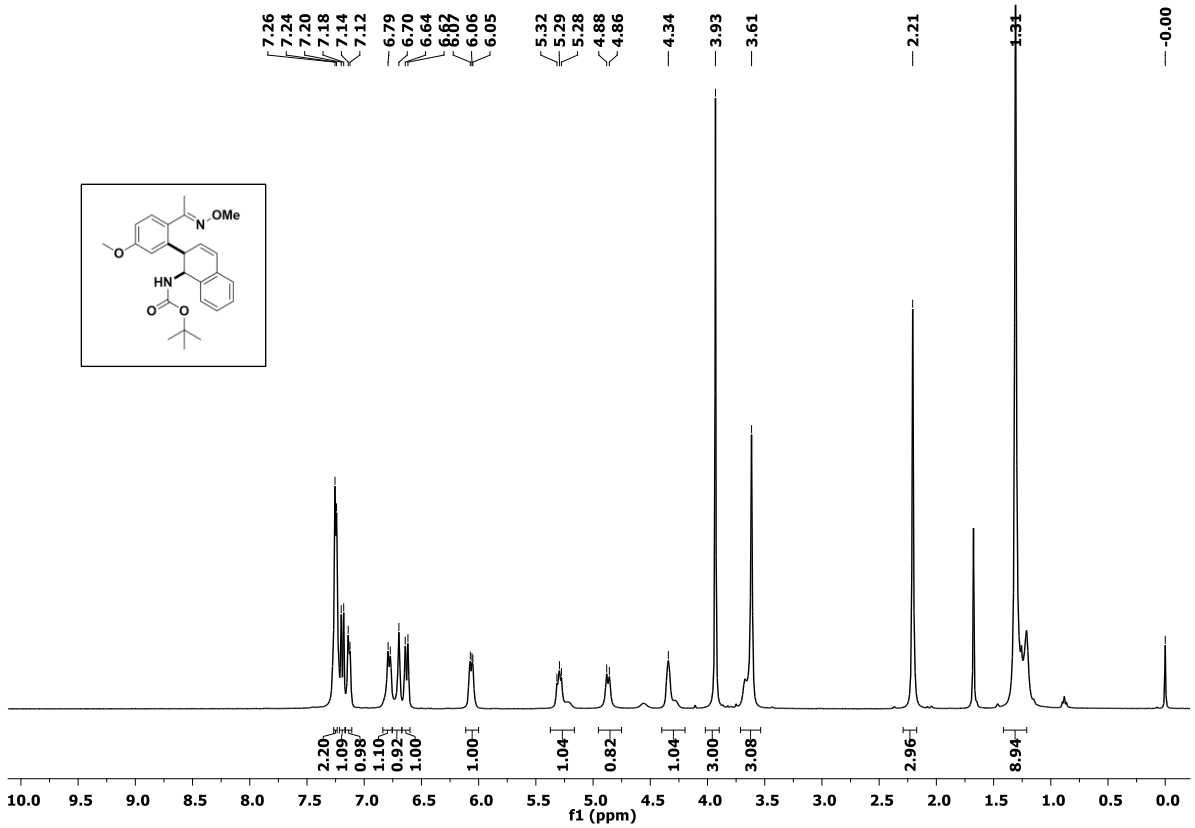


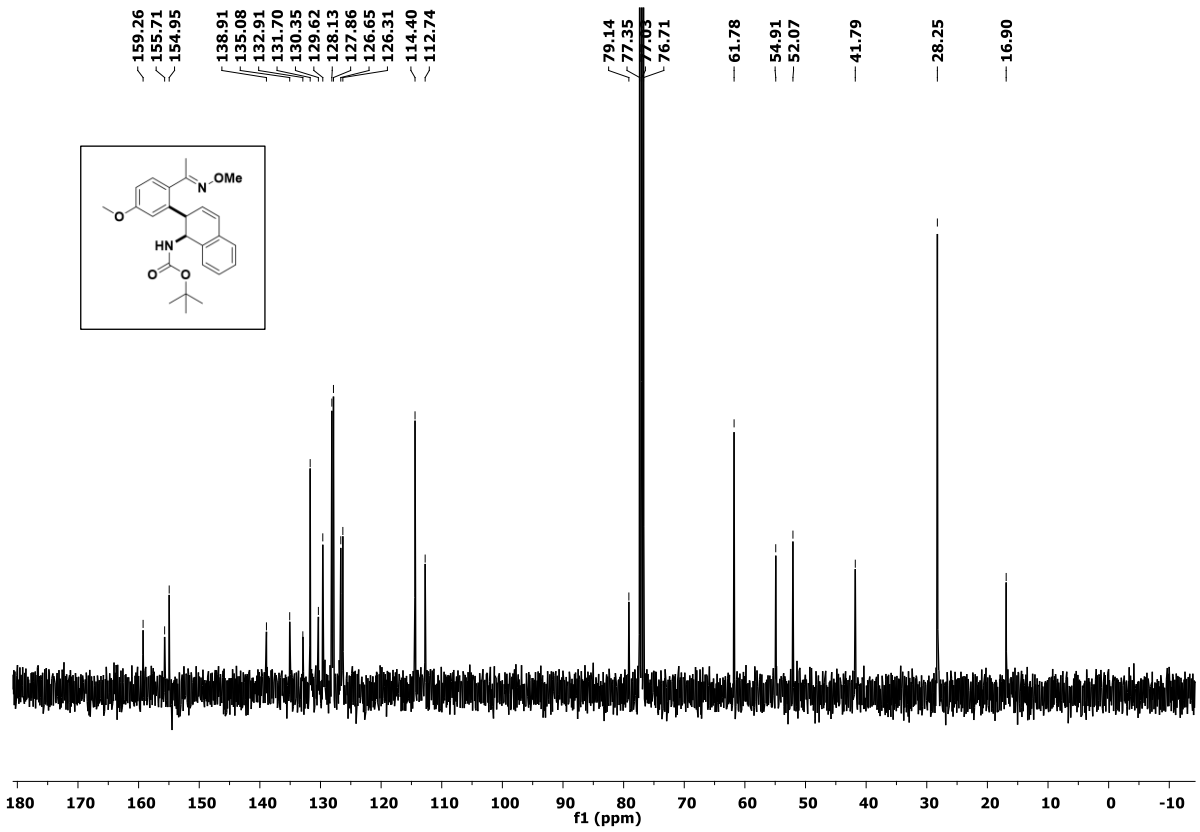


DEPT (135) NMR Spectrum of Compound **3aa.**

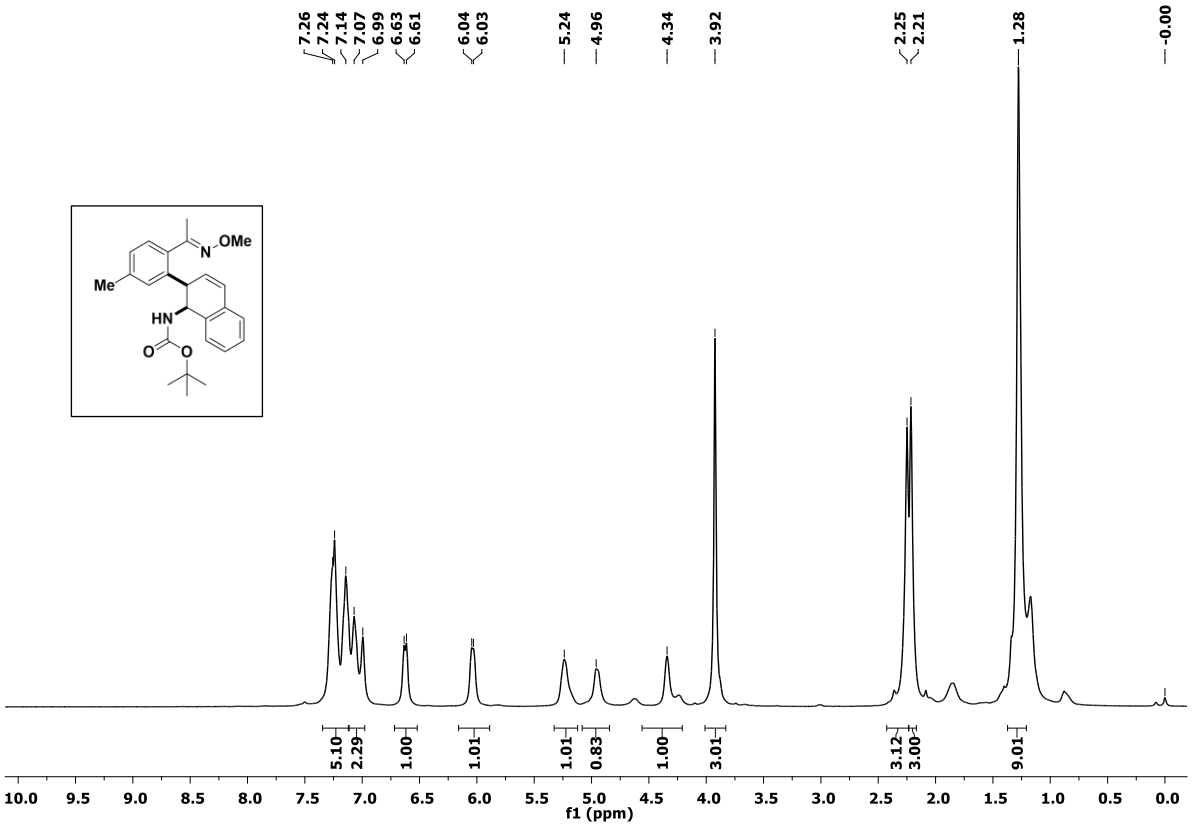


^{1}H and ^{13}C NMR Spectra of Compound **3ba.**

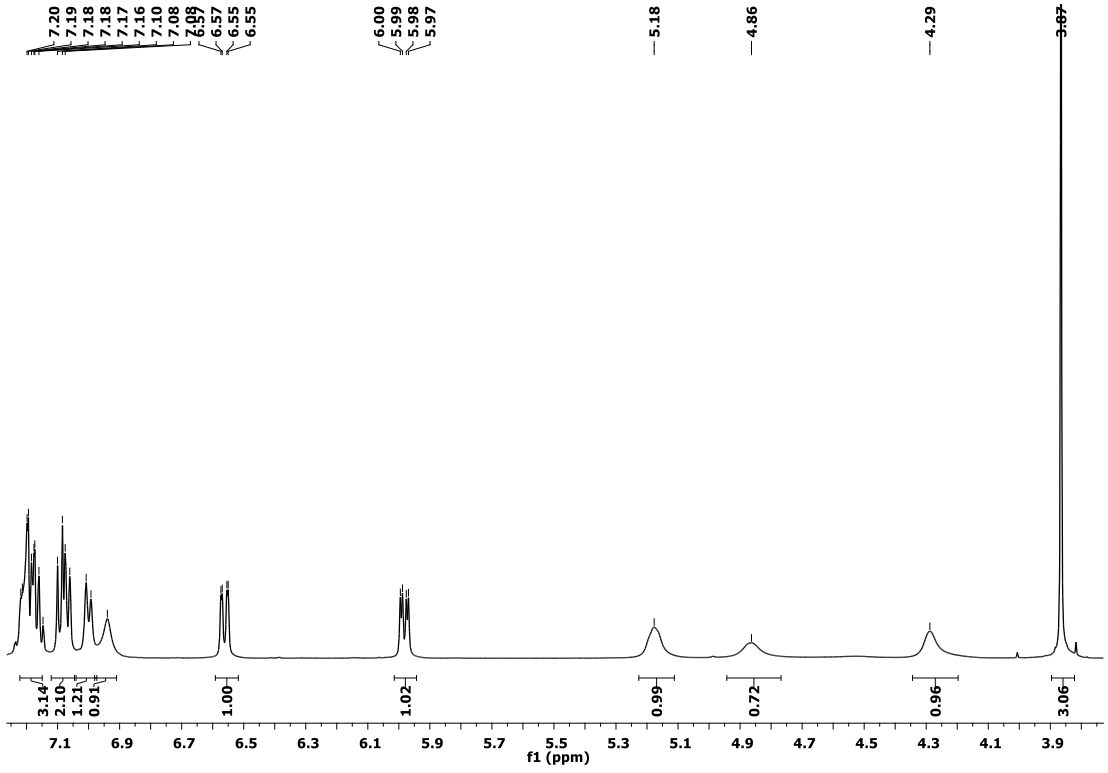


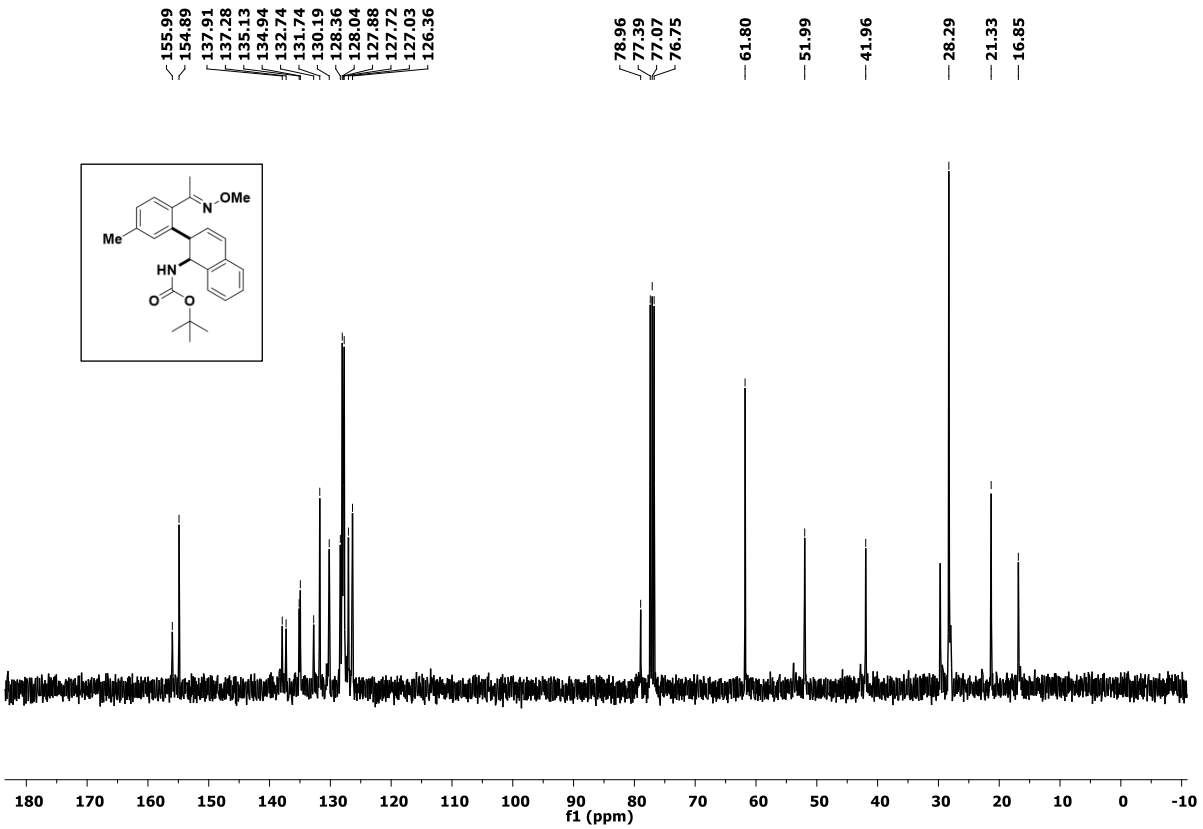


^{1}H and ^{13}C NMR Spectra of Compound **3ca.**

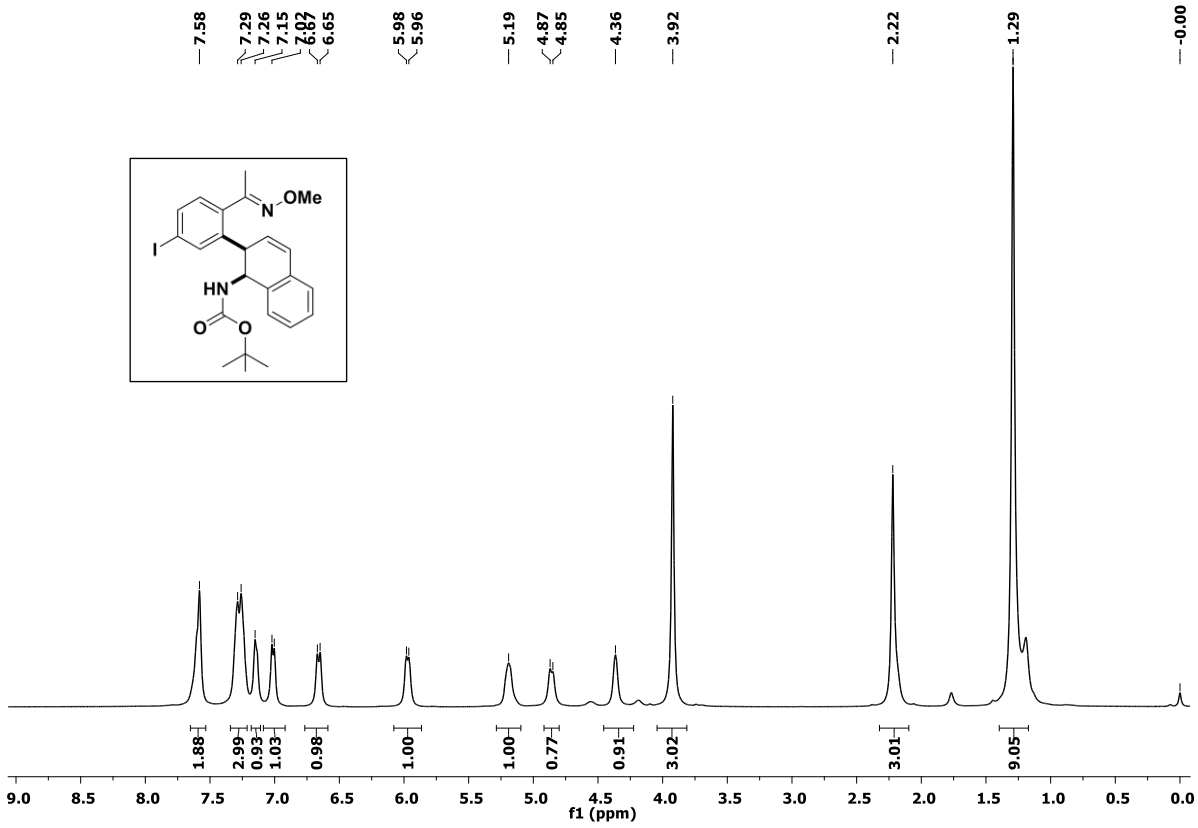


The NMR was taken at 50 ˚C. The bumps range 4.6 ppm and 4.2 ppm were disappeared

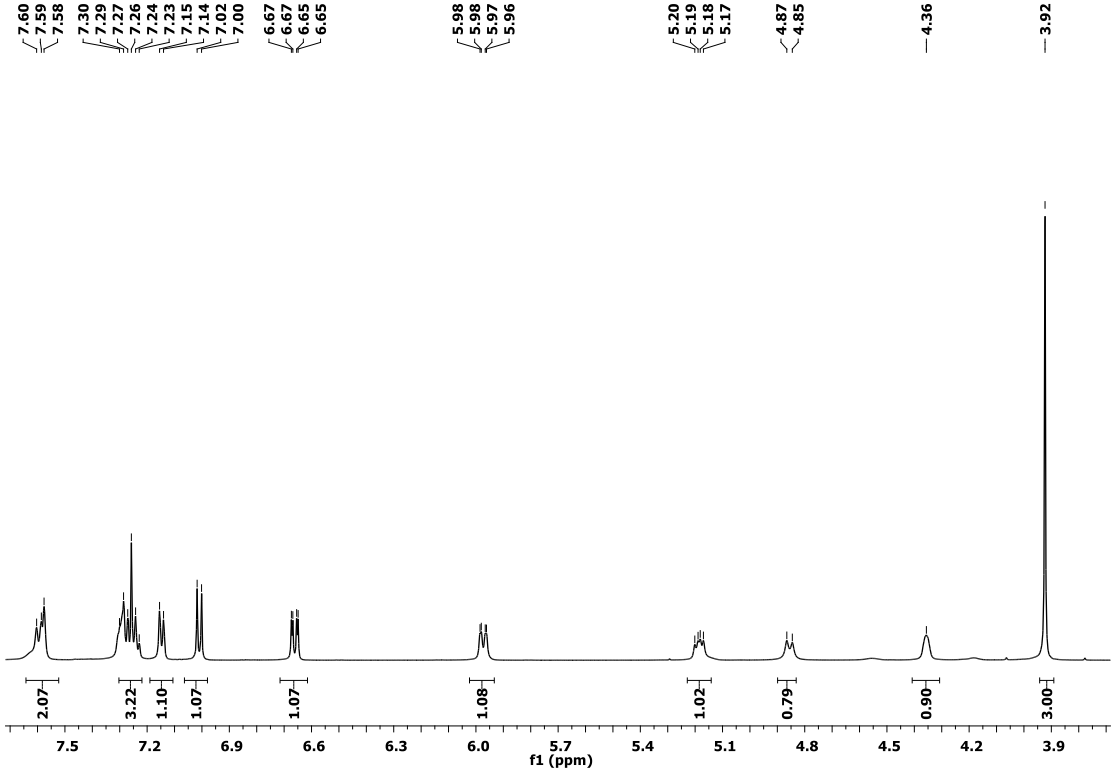


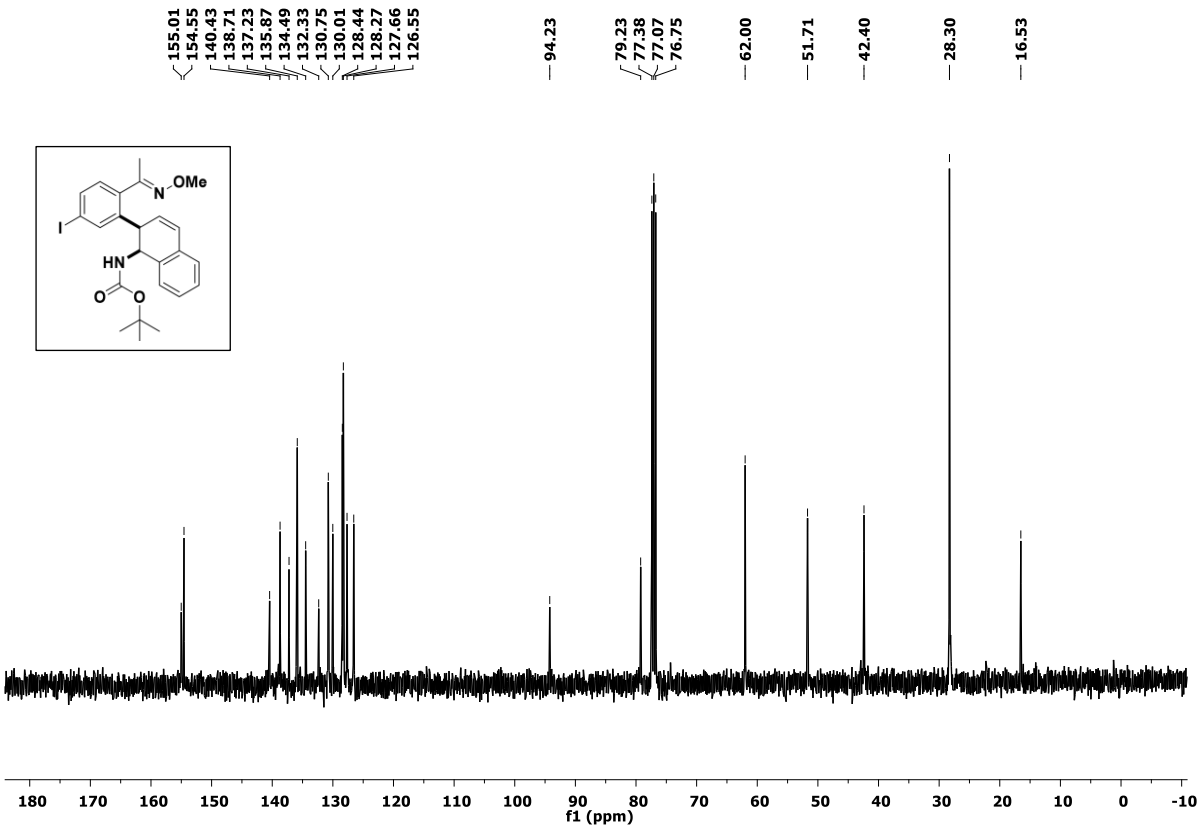

155.99
154.89
137.91
137.28
135.13
134.94
132.74
131.74
130.19
128.36
128.04
127.88
127.72
127.03
126.36
78.96
77.39
77.07
76.75
61.80
51.99
41.96
28.29
21.33
16.85
OMe
N
Me
HN
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H and ^{13}C NMR Spectra of Compound **3da.**

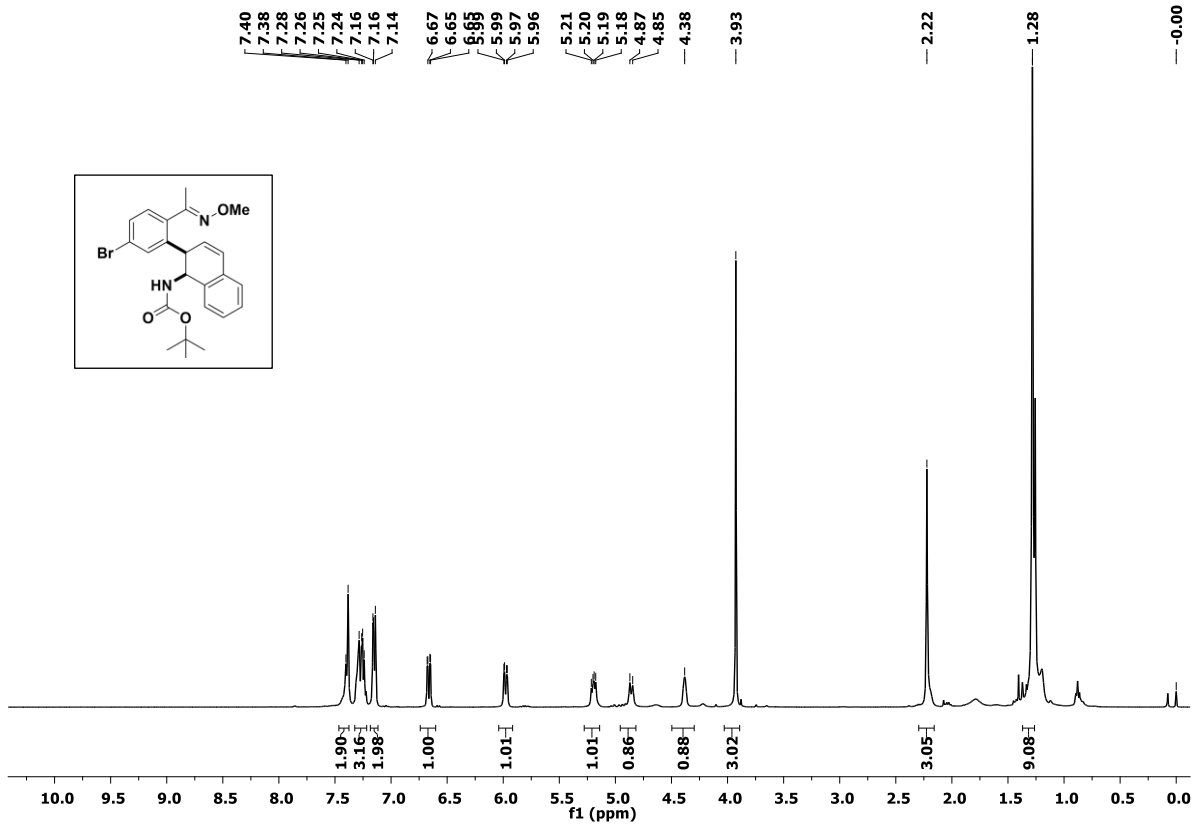


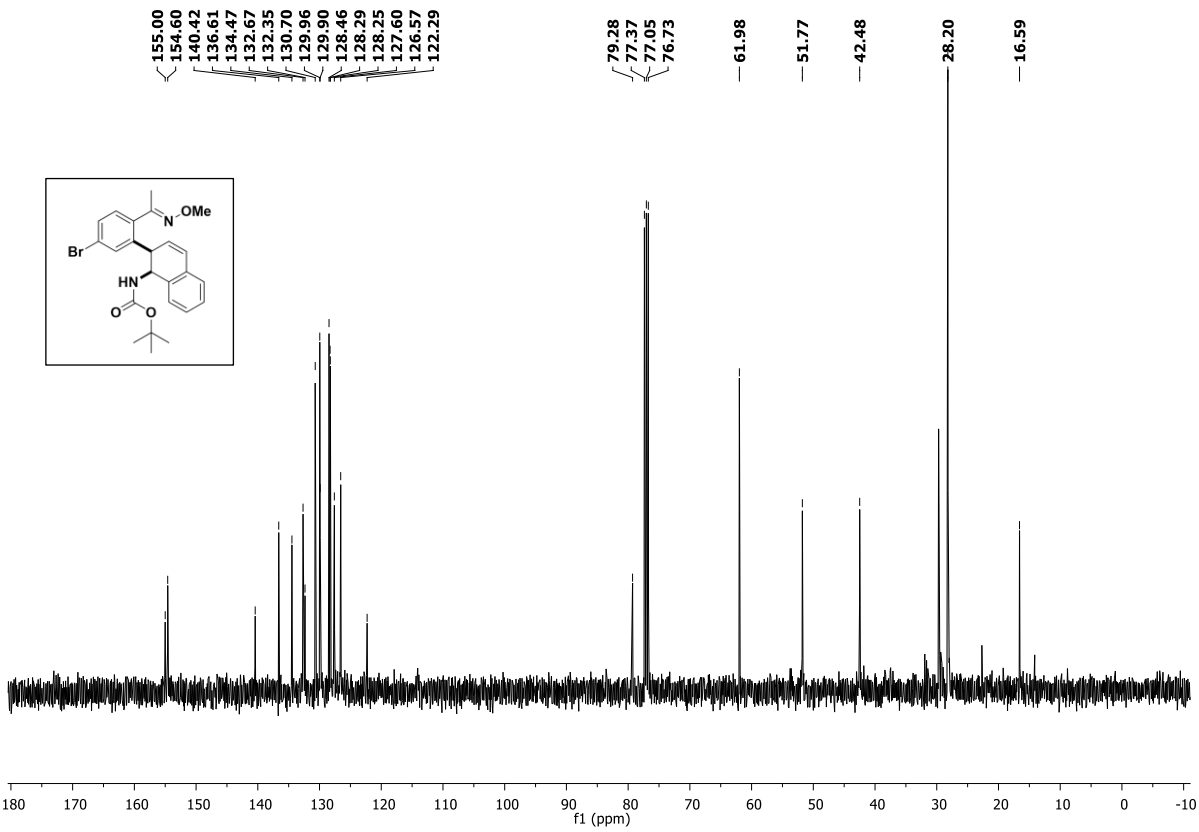
Fine shimming NMR: expended Chemical shift 7.60 ppm to 3.8 ppm for better splitting



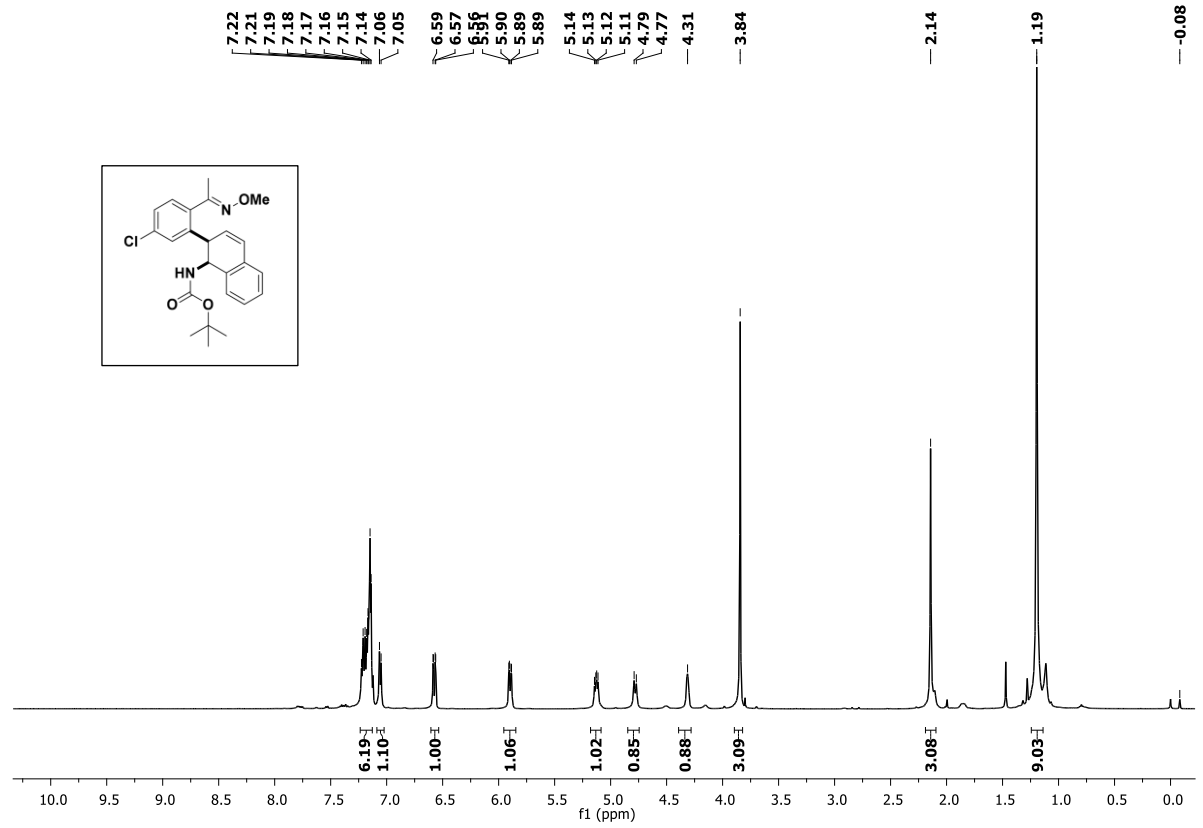

155.01
154.55
140.43
138.71
137.23
135.87
134.49
132.33
130.75
130.01
128.44
128.27
127.66
126.55
94.23
79.23
77.38
77.07
76.75
62.00
51.71
42.40
28.30
16.53
OMe
N
I
HN
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

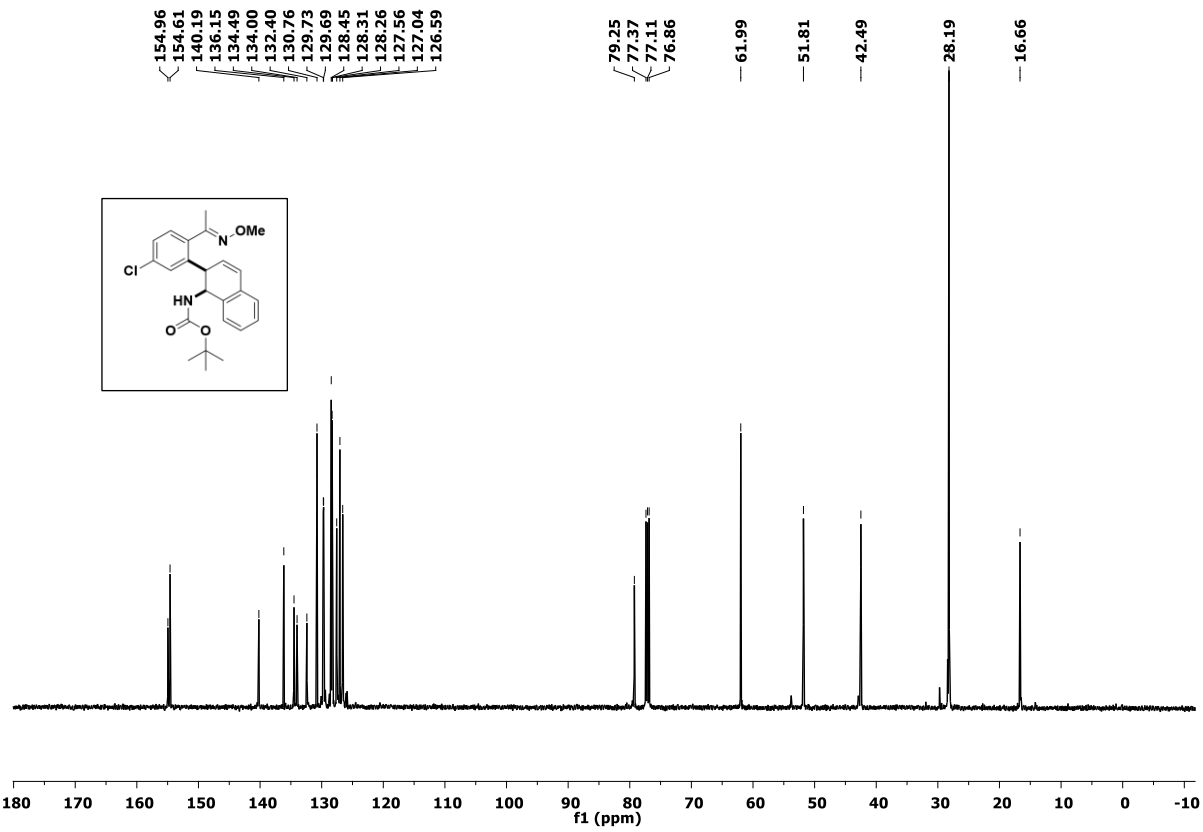
^{1}H and ^{13}C NMR Spectra of Compound **3ea.**



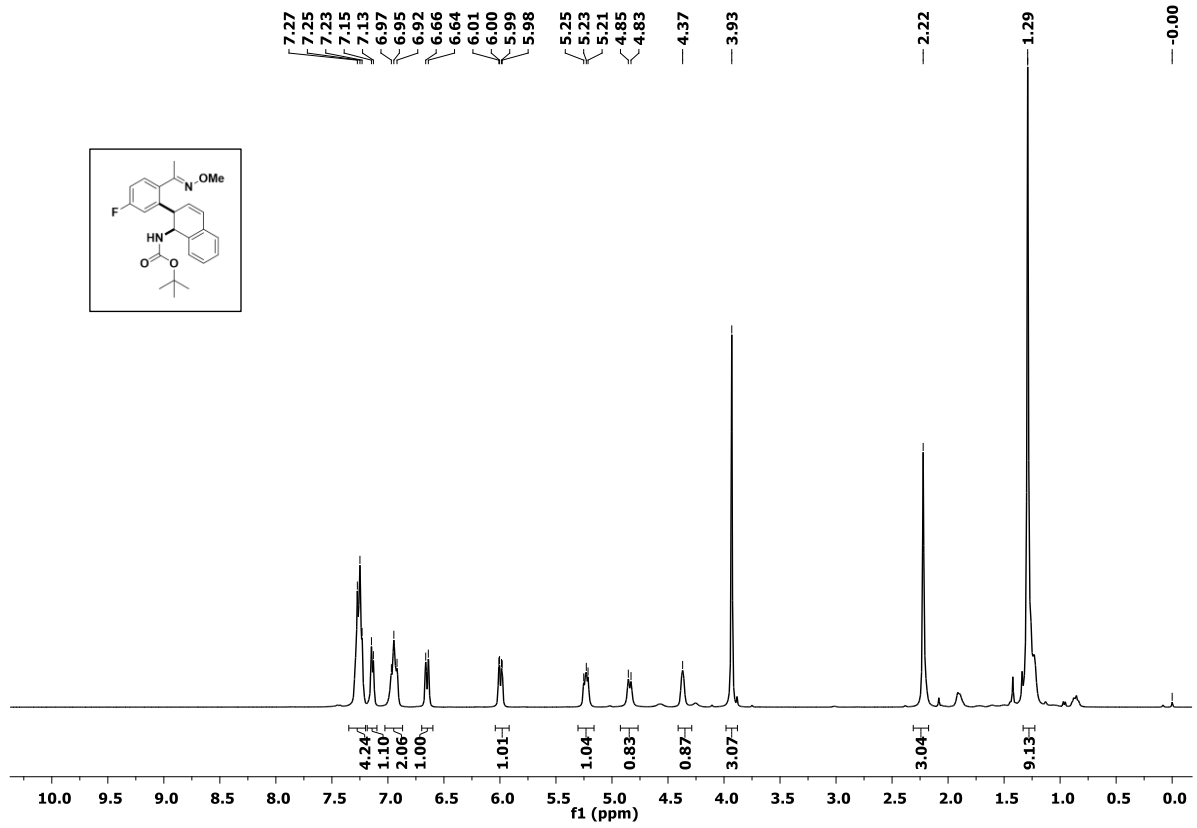


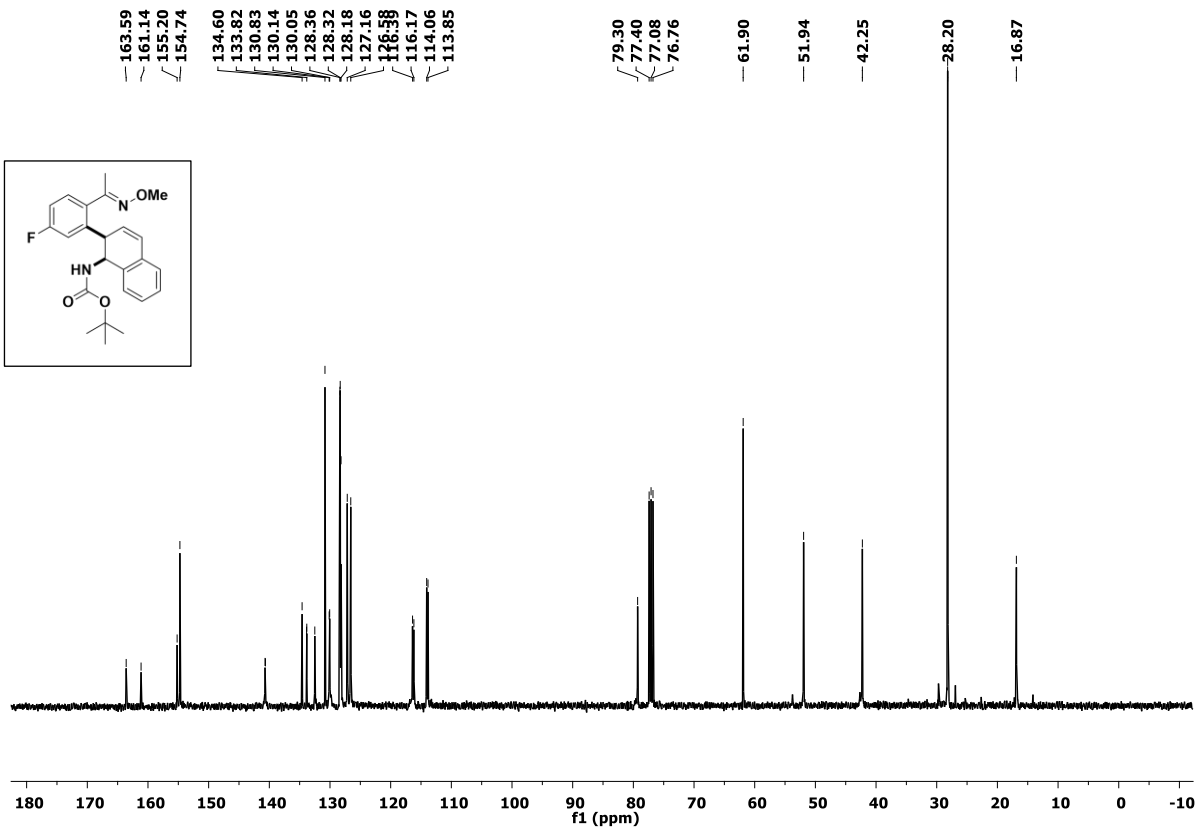
^{1}H and ^{13}C NMR Spectra of Compound **3fa.**



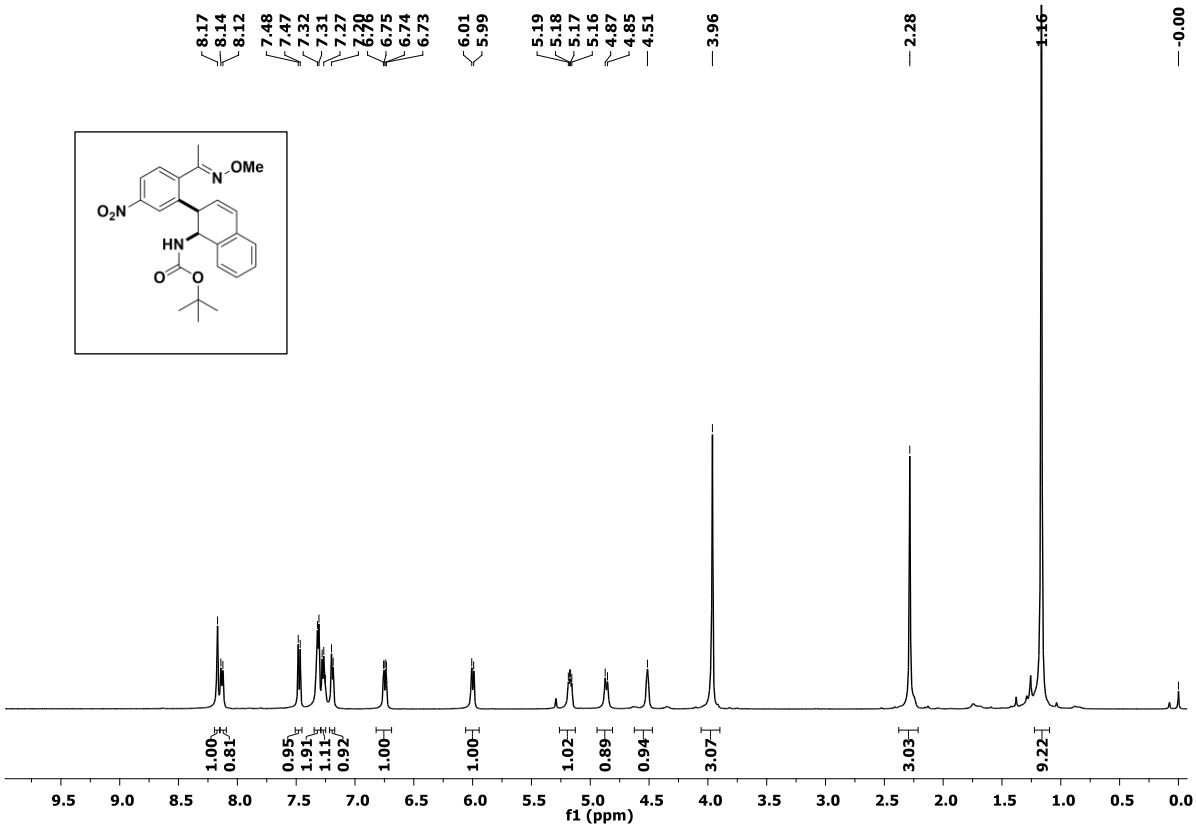


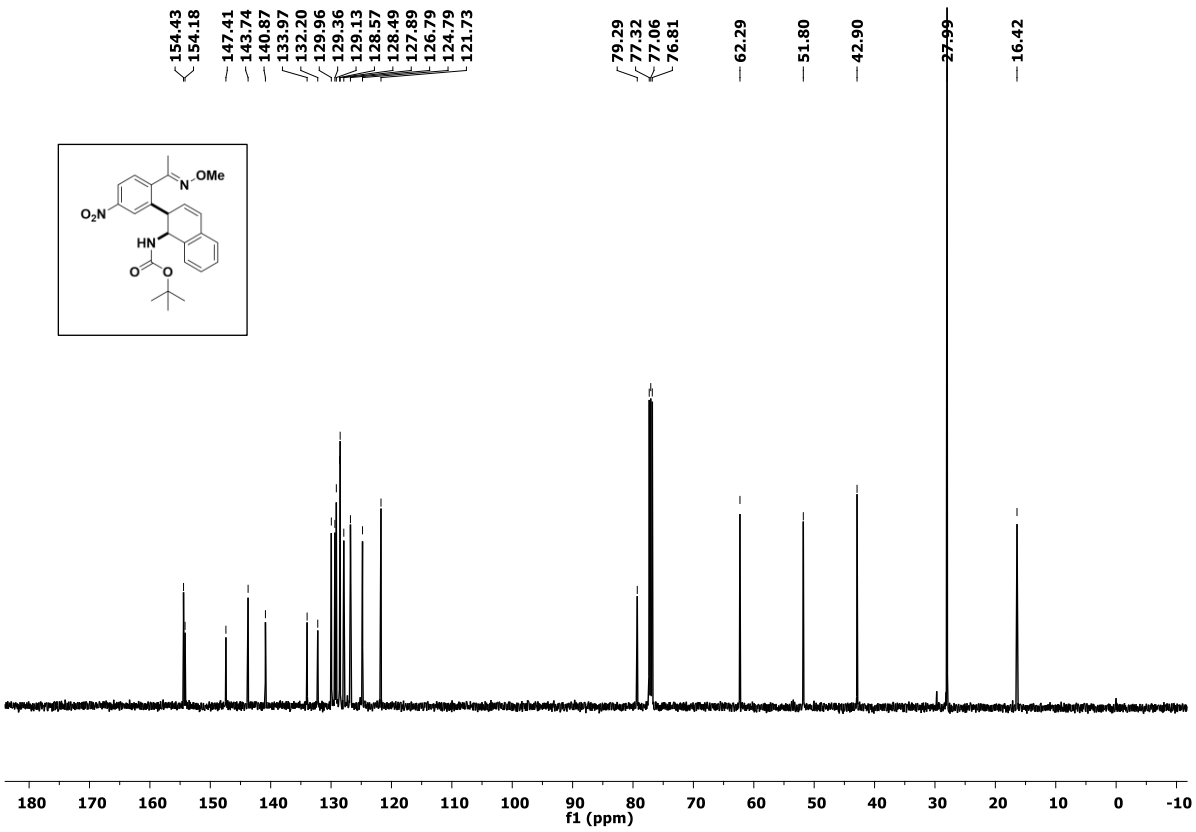
^{1}H and ^{13}C NMR Spectra of Compound **3ga.**



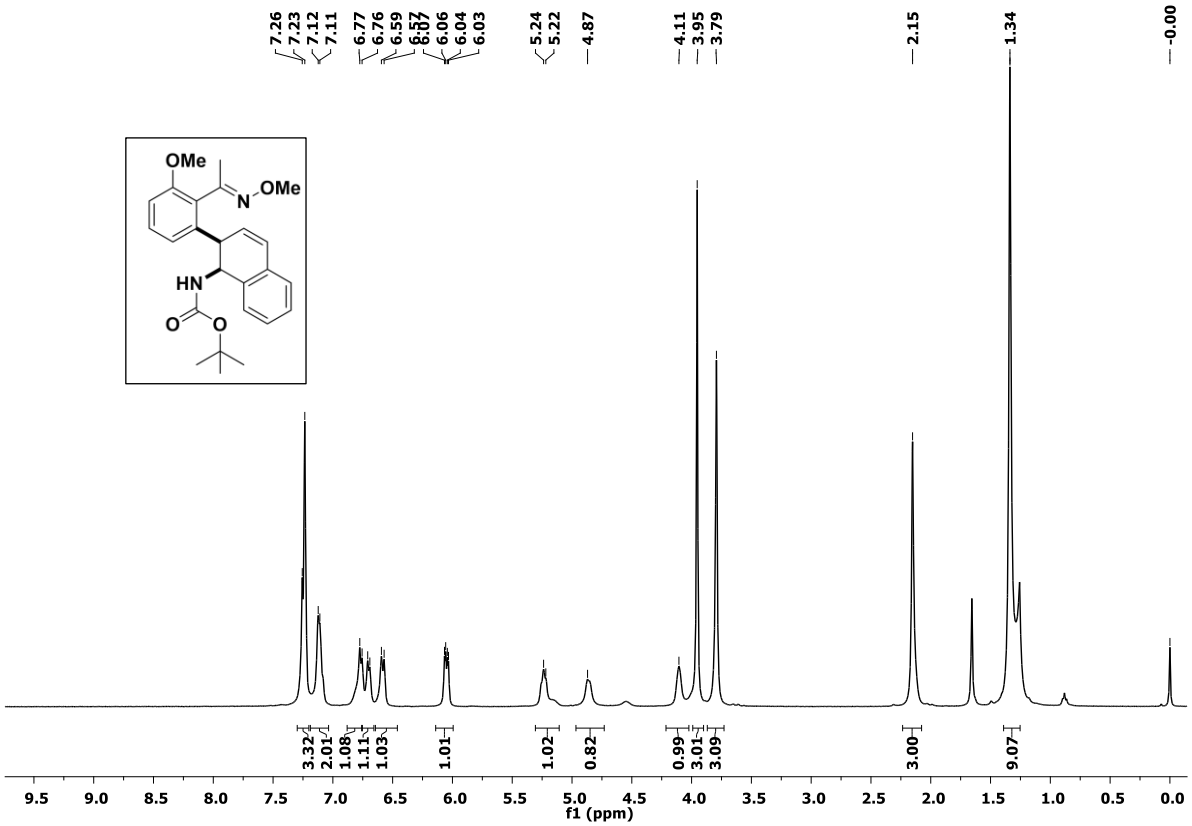


^{1}H and ^{13}C NMR Spectra of Compound **3ha.**

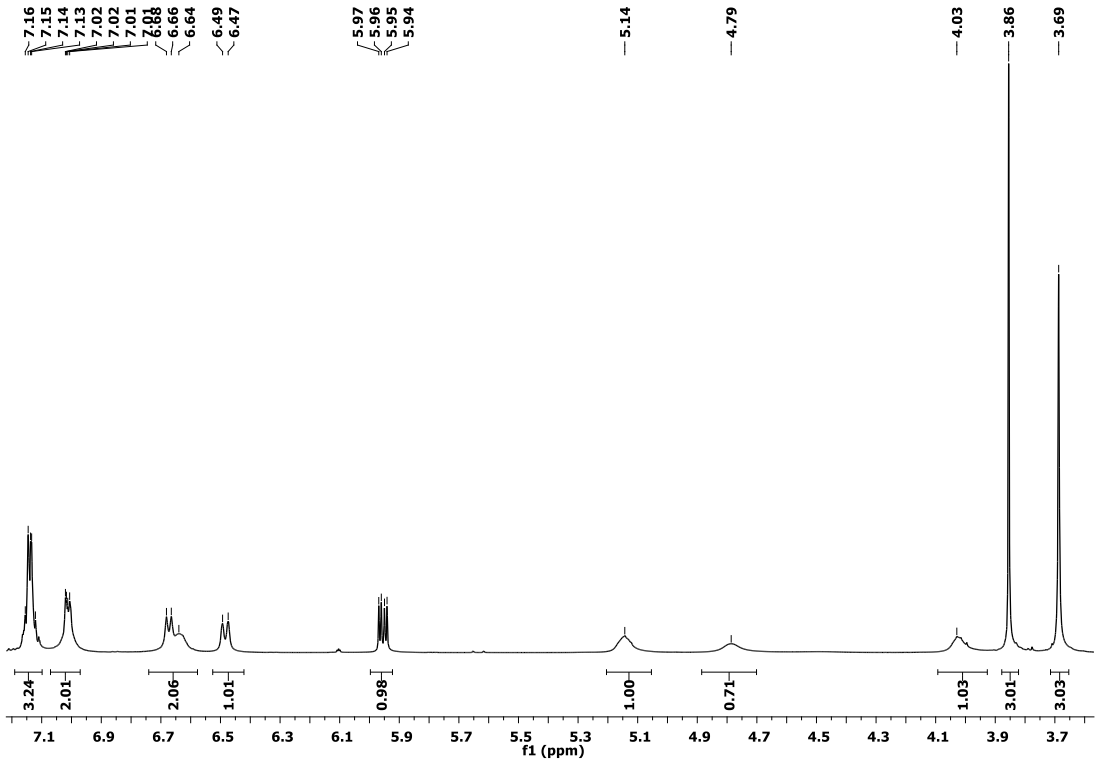


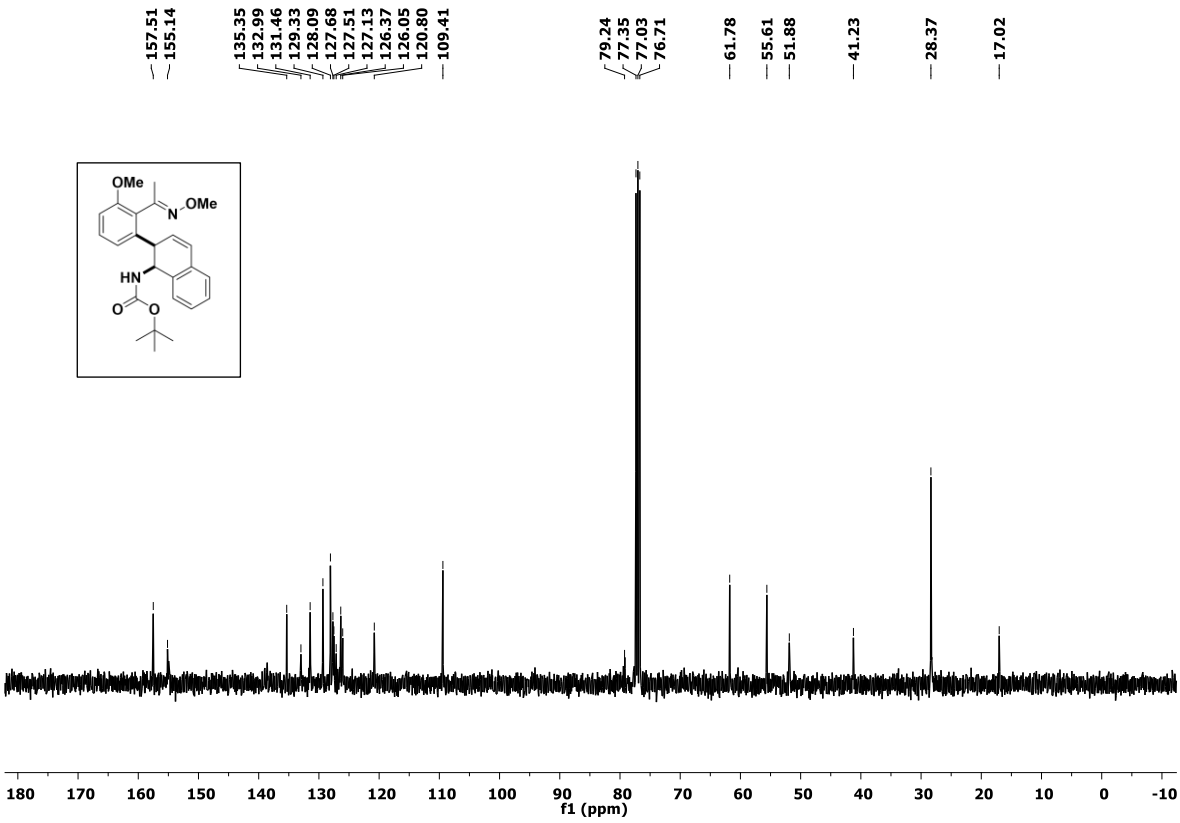


^{1}H and ^{13}C NMR Spectra of Compound **3ia.**

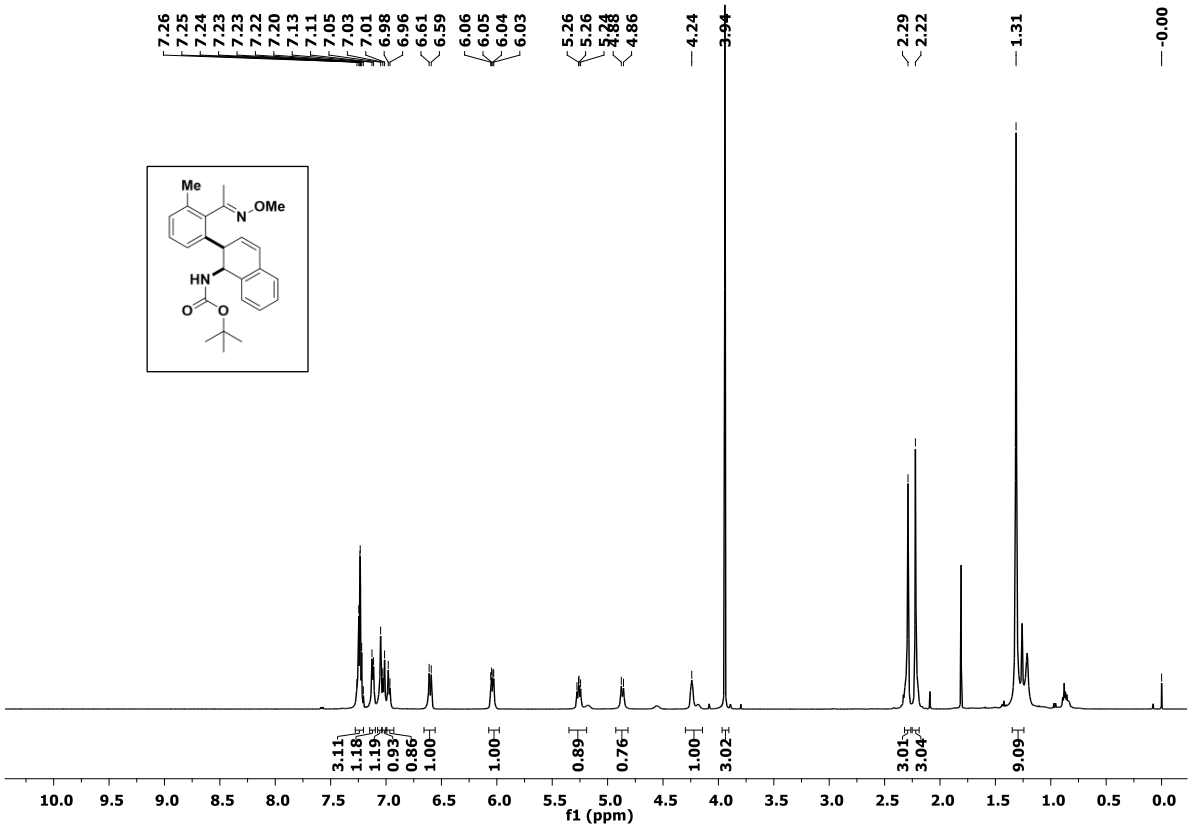


The NMR was taken at 50 ˚C. The bumps range 5.2 ppm and 4.5 ppm were disappeared

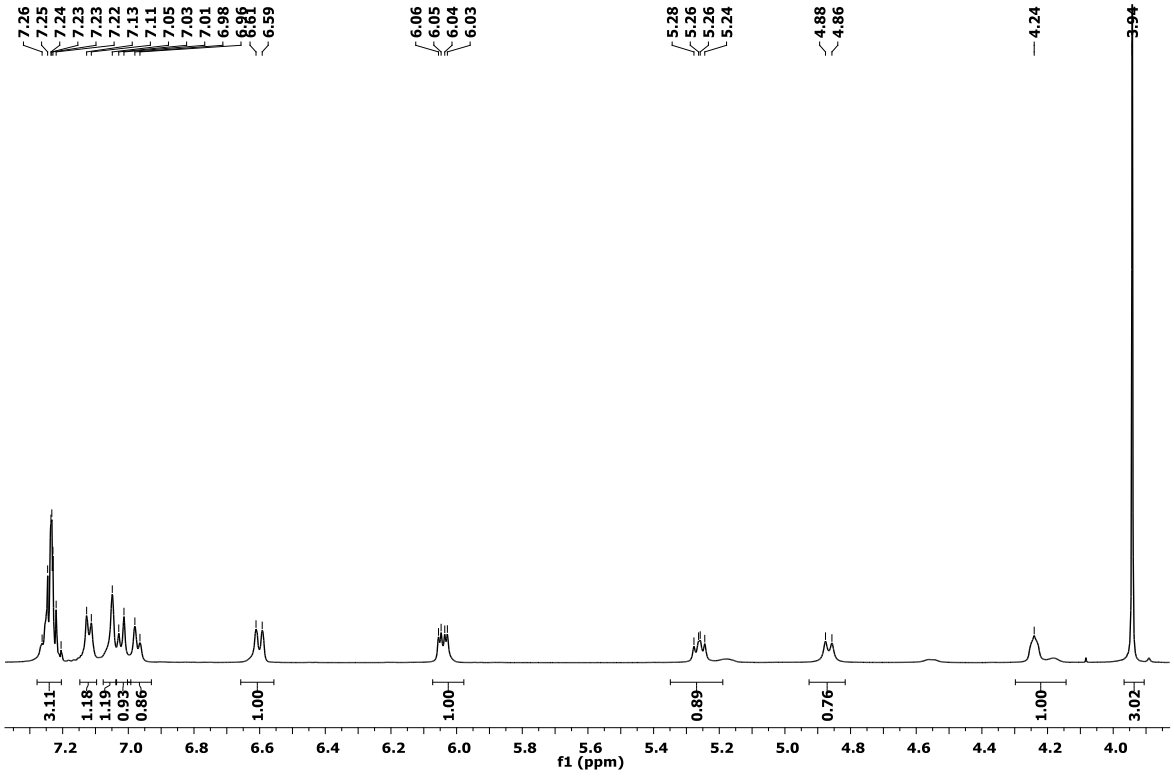


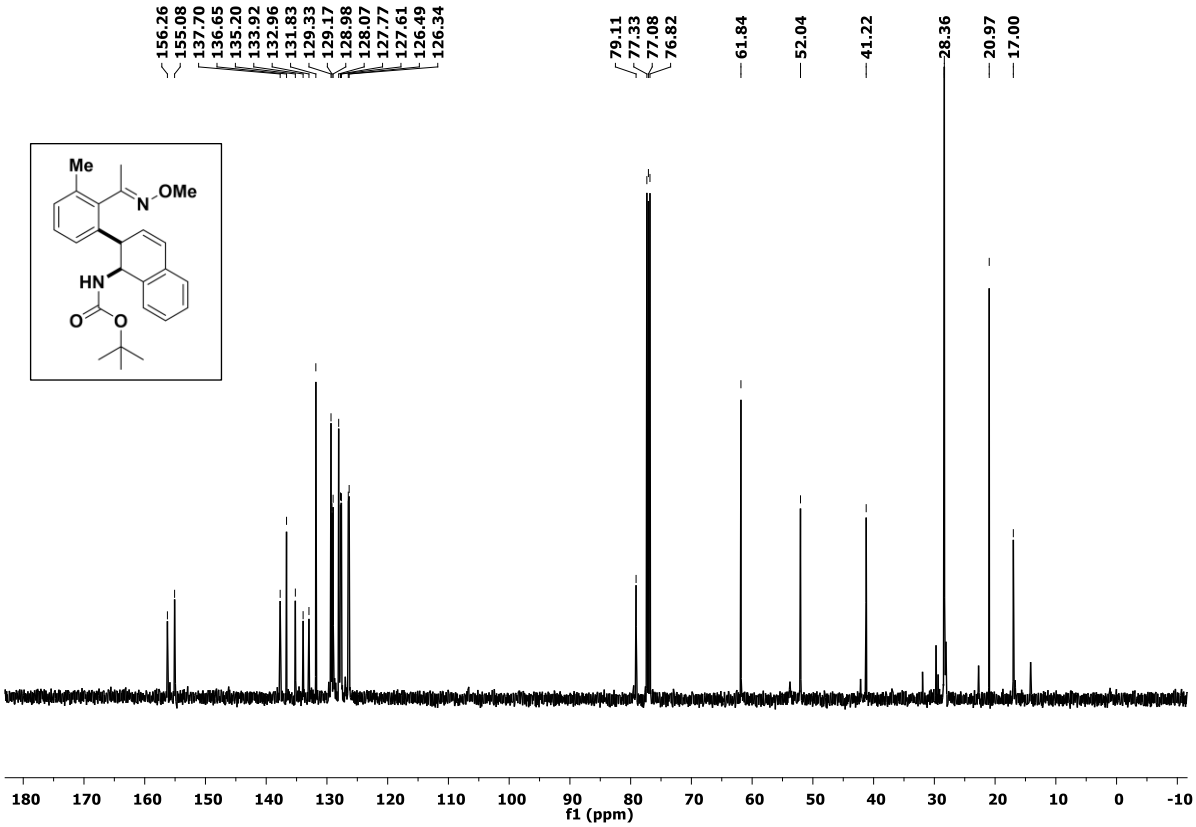

157.51
155.14
135.35
132.99
131.46
129.33
128.09
127.68
127.51
127.13
126.37
126.05
120.80
109.41
79.24
77.35
77.03
76.71
61.78
55.61
51.88
41.23
28.37
17.02
OMe
N
OMe
HN
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H and ^{13}C NMR Spectra of Compound **3ja.**

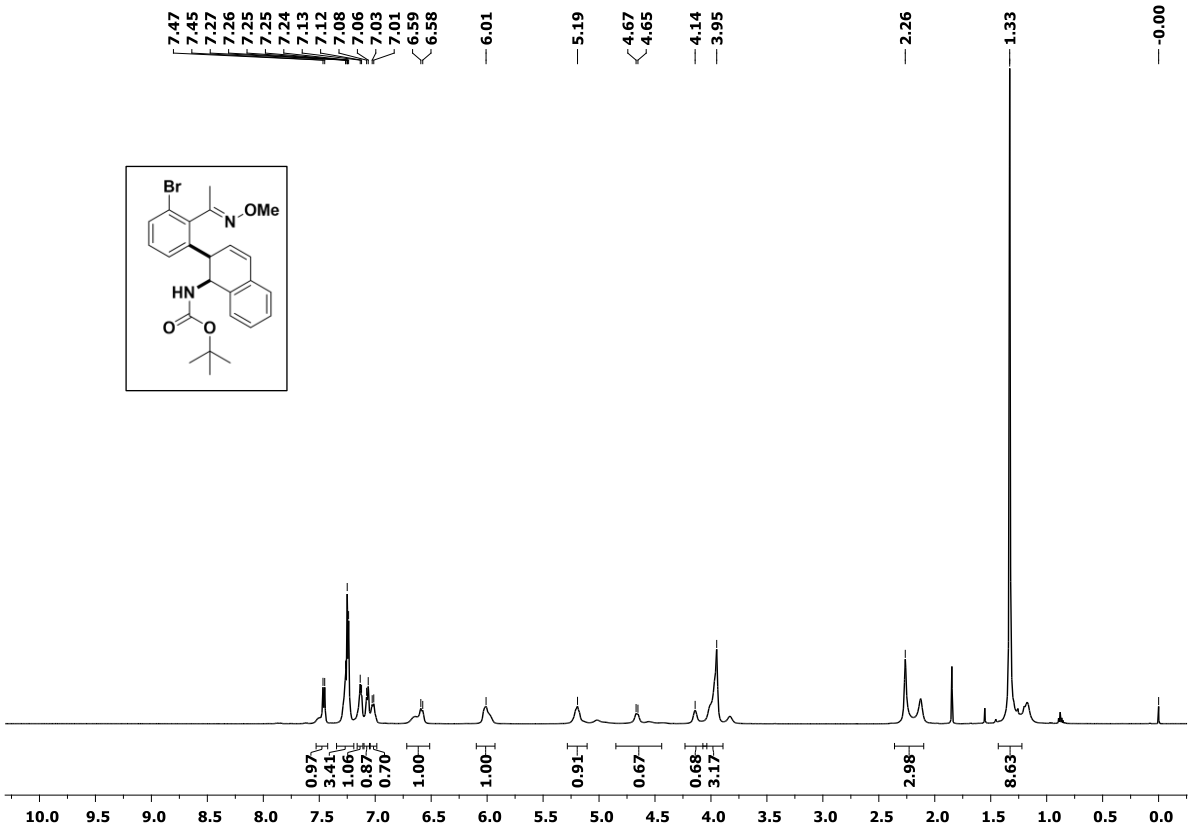


Fine shimming NMR: expended Chemical shift 7.30 ppm to 3.9 ppm for better splitting

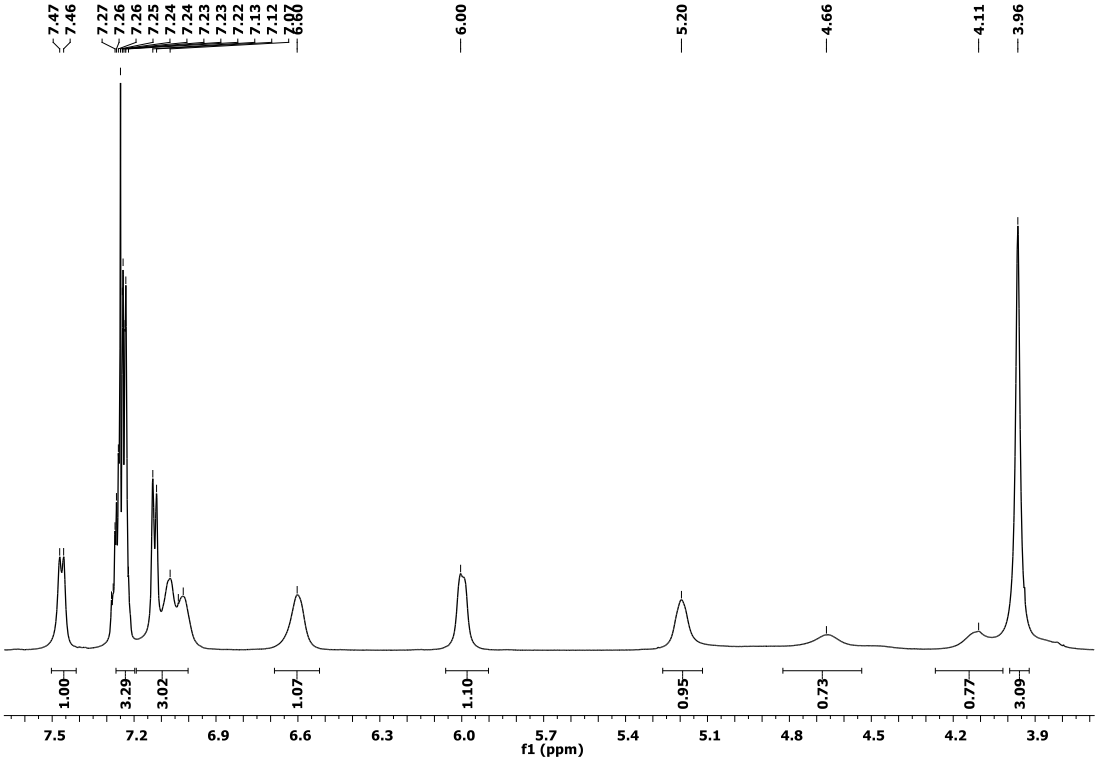


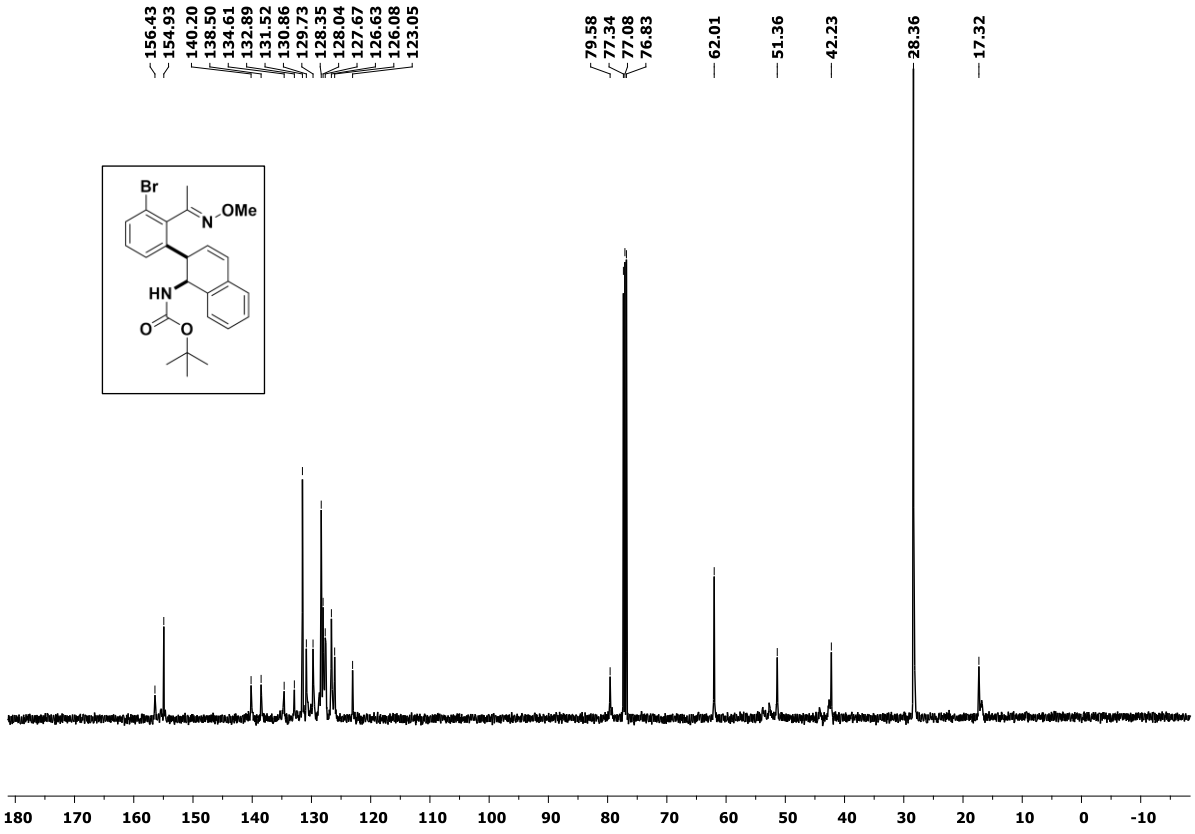

156.26
155.08
137.70
136.65
135.20
133.92
132.96
131.83
129.33
129.17
128.98
128.07
127.77
127.61
126.49
126.34
79.11
77.33
77.08
76.82
61.84
52.04
41.22
28.36
20.97
17.00
Me
N
OMe
HN
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H and ^{13}C NMR Spectra of Compound **3ka.**

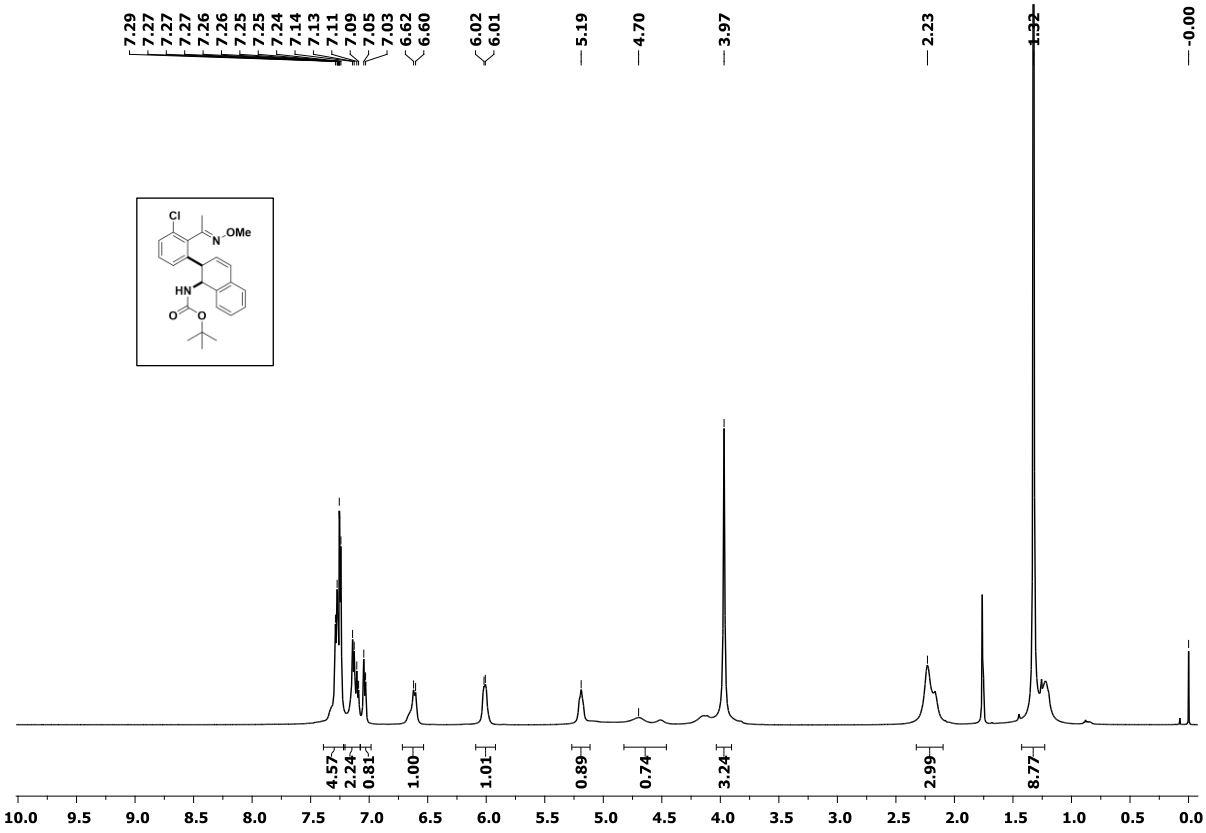


Fine shimming NMR expended: Chemical shift 7.60 ppm to 3.8 ppm for better splitting

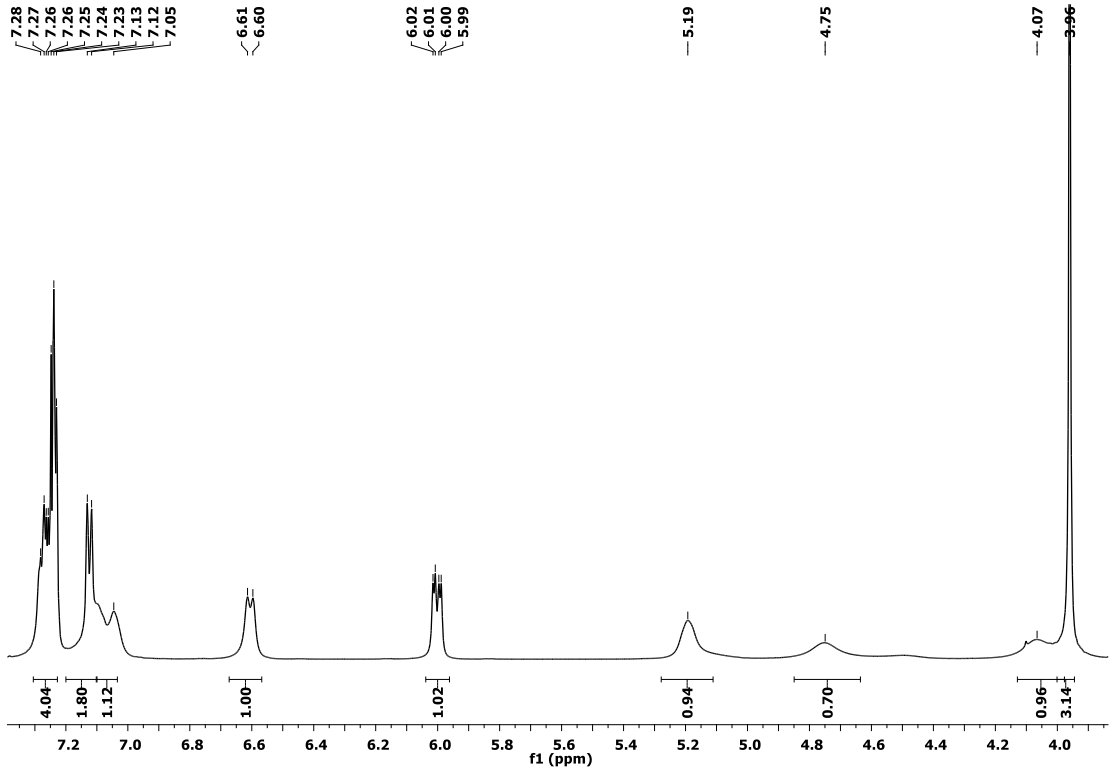


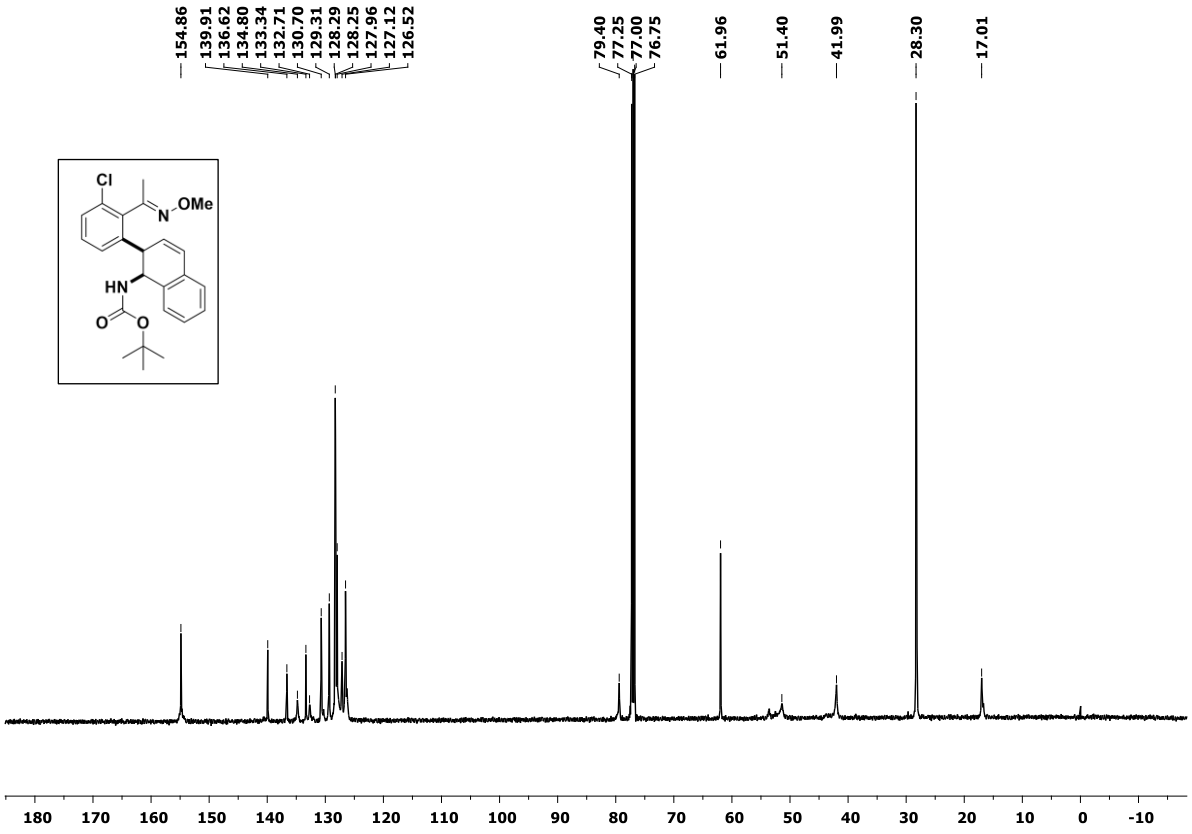

156.43
154.93
140.20
138.50
134.61
132.89
131.52
130.86
129.73
128.35
128.04
127.67
126.63
126.08
123.05
79.58
77.34
77.08
76.83
62.01
51.36
42.23
28.36
17.32
Br
N
OMe
HN
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{1}H and ^{13}C NMR Spectra of Compound **3la.**

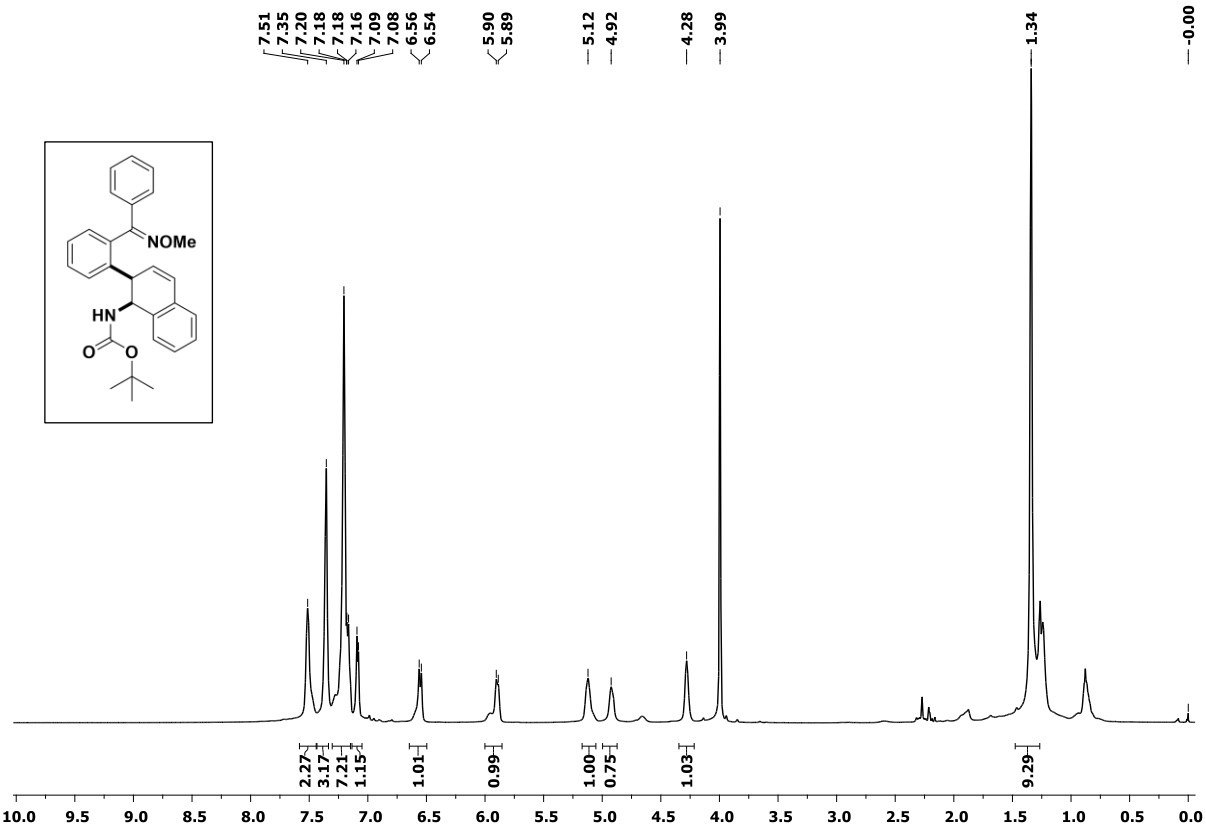


Fine shimming NMR expended: Chemical shift 7.30 ppm to 3.9 ppm for better splitting

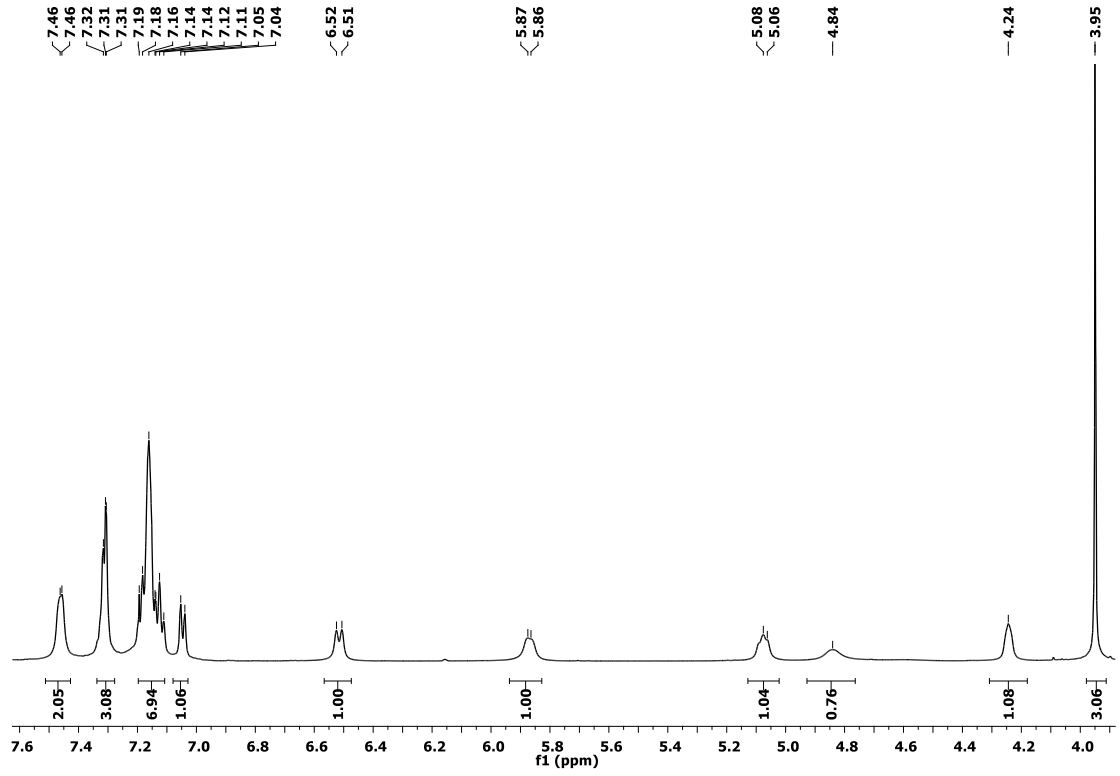


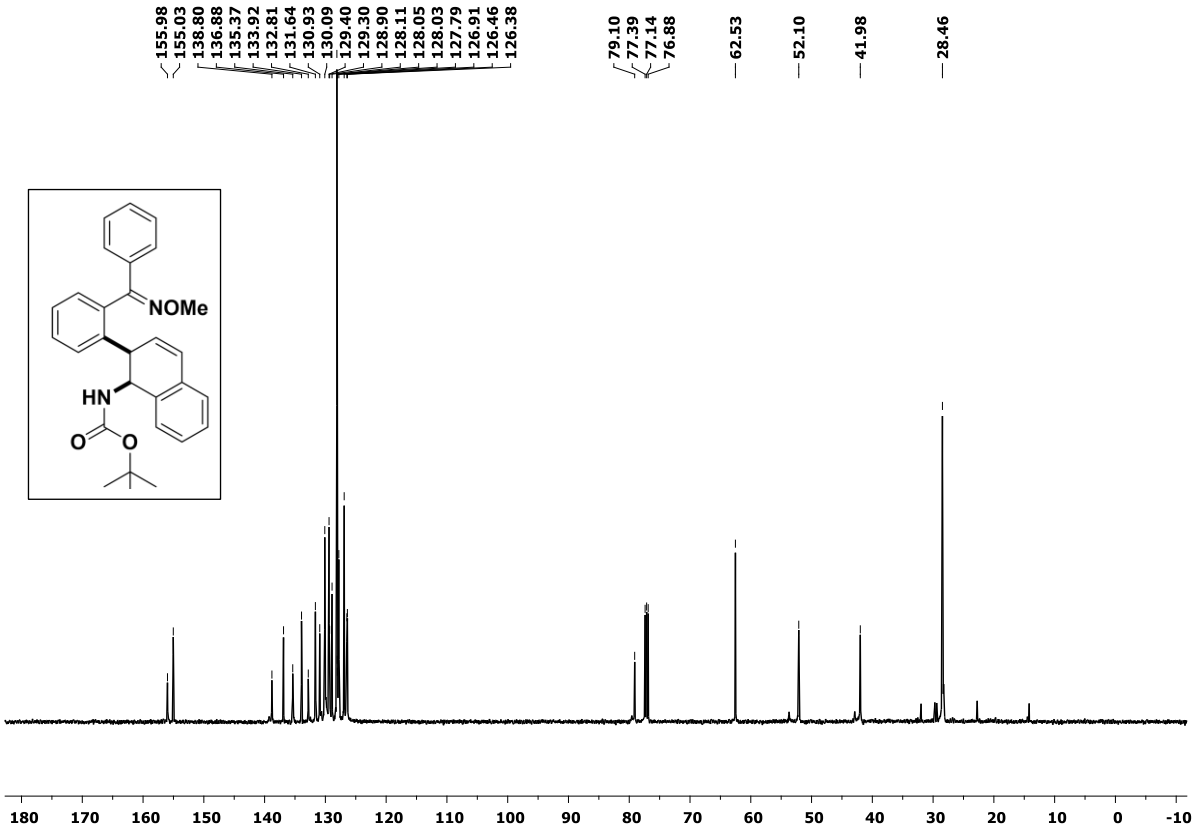

154.86
139.91
136.62
134.80
133.34
132.71
130.70
129.31
128.29
128.25
127.96
127.12
126.52
79.40
77.25
77.00
76.75
61.96
51.40
41.99
28.30
17.01
Cl
N
OMe
HN
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{1}H and ^{13}C NMR Spectra of Compound **3ma.**

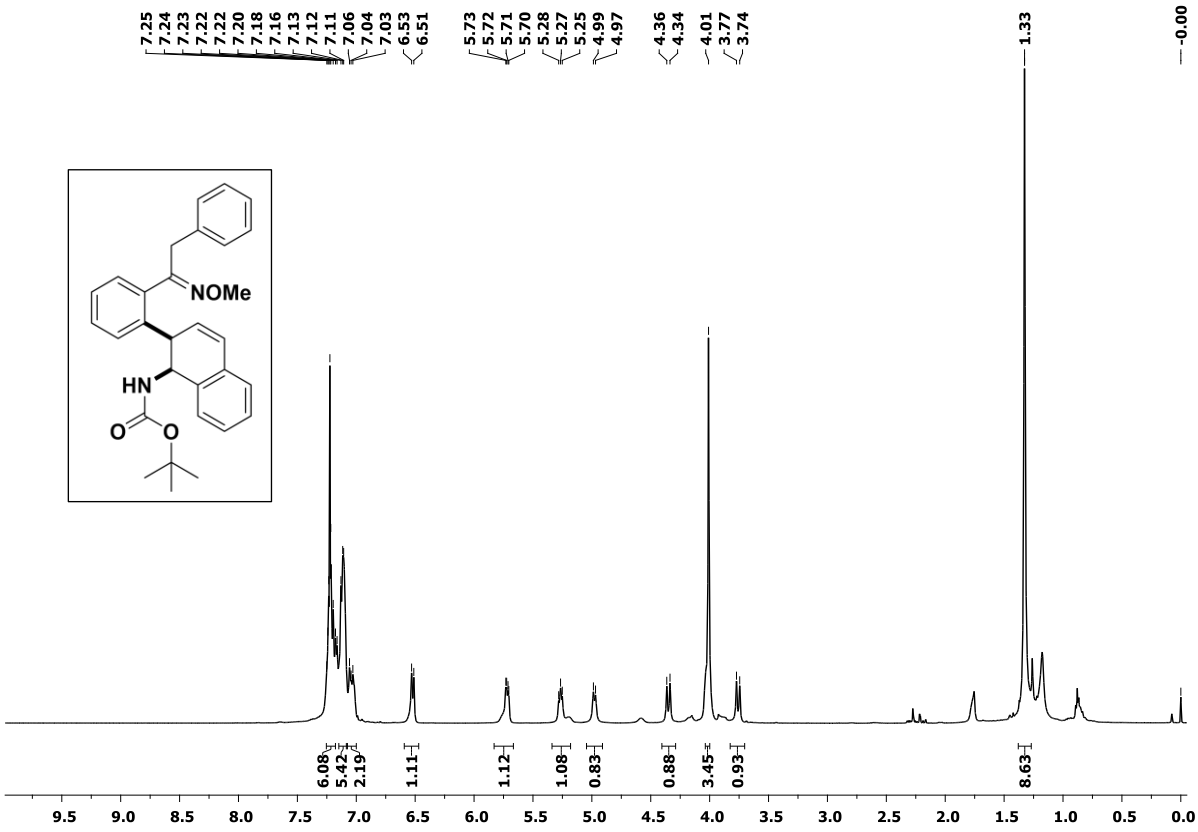


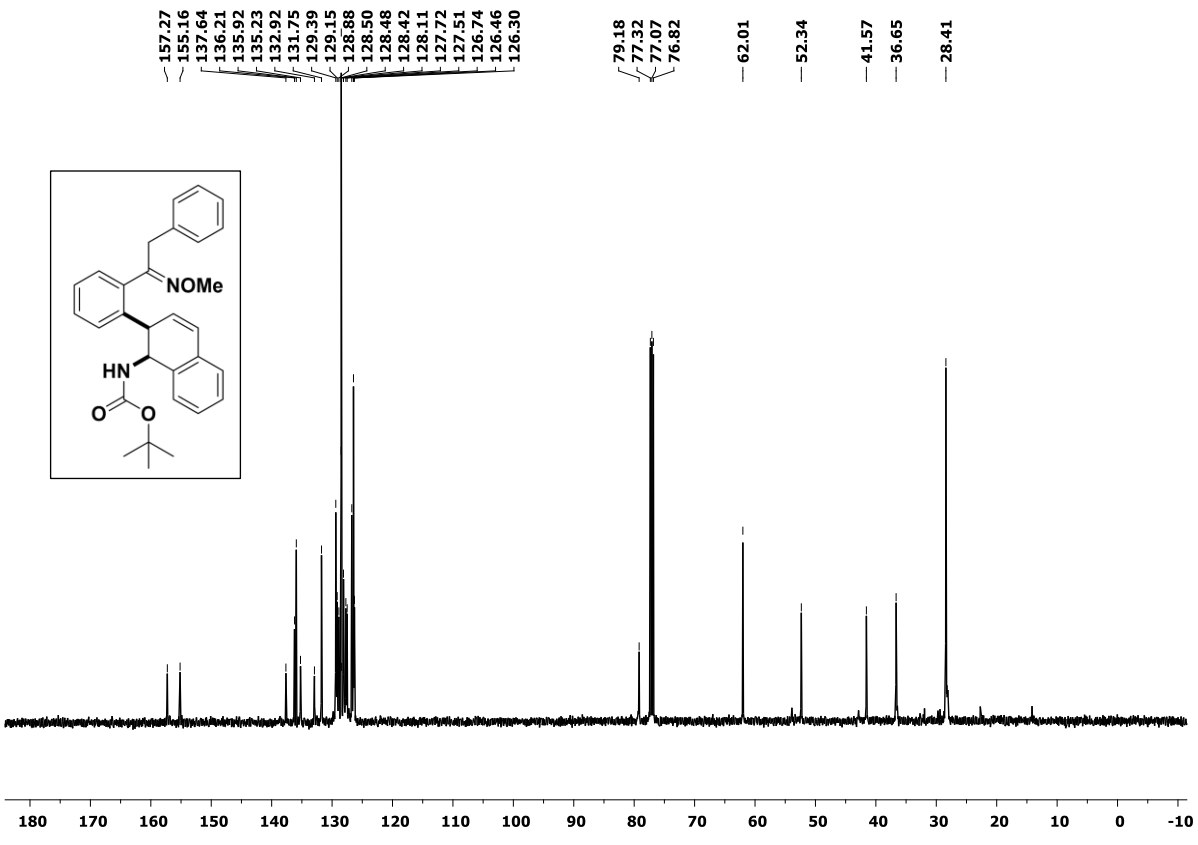
The NMR was taken at 50 ˚C. The bumps range 5.9 ppm and 4.6 ppm were disappeared



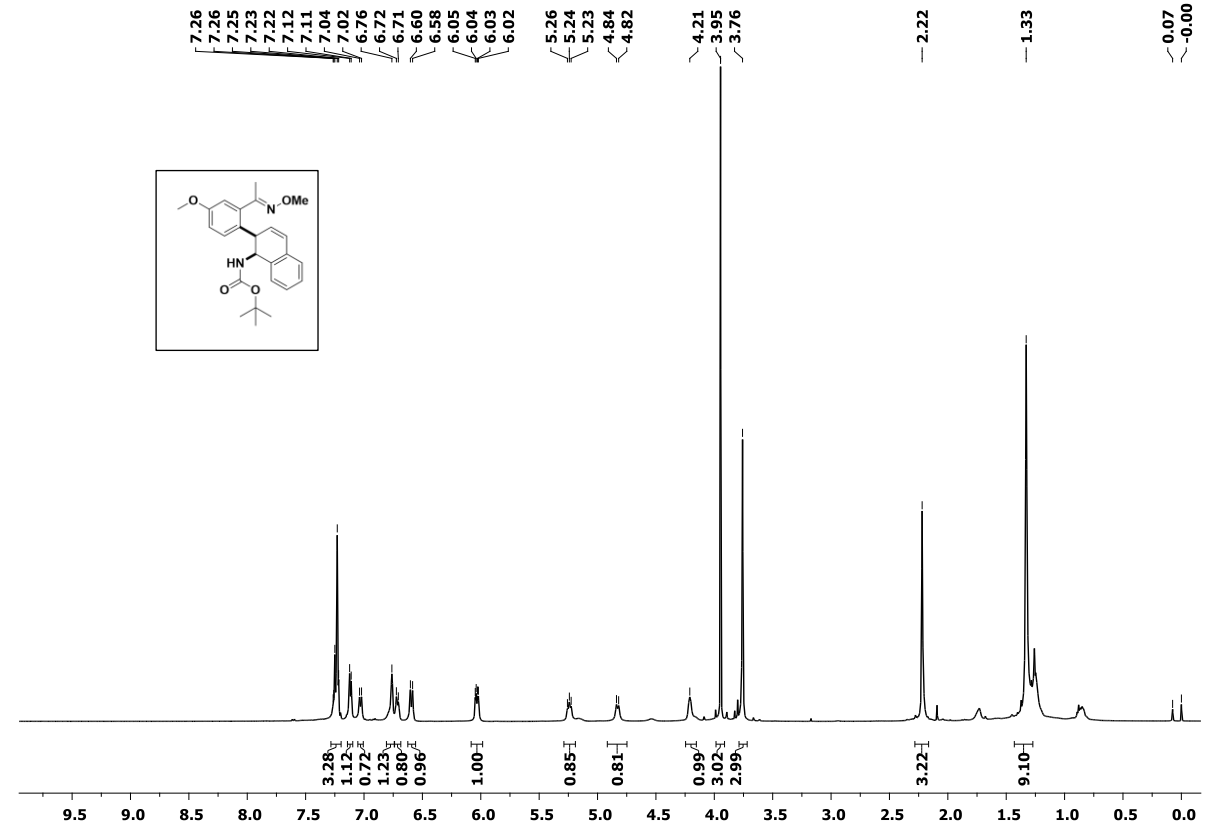

155.98
155.03
138.80
136.88
135.37
133.92
132.81
131.64
130.93
130.09
129.40
129.30
128.90
128.11
128.05
128.03
127.79
126.91
126.46
126.38
79.10
77.39
77.14
76.88
62.53
52.10
41.98
28.46
NOMe
HN
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

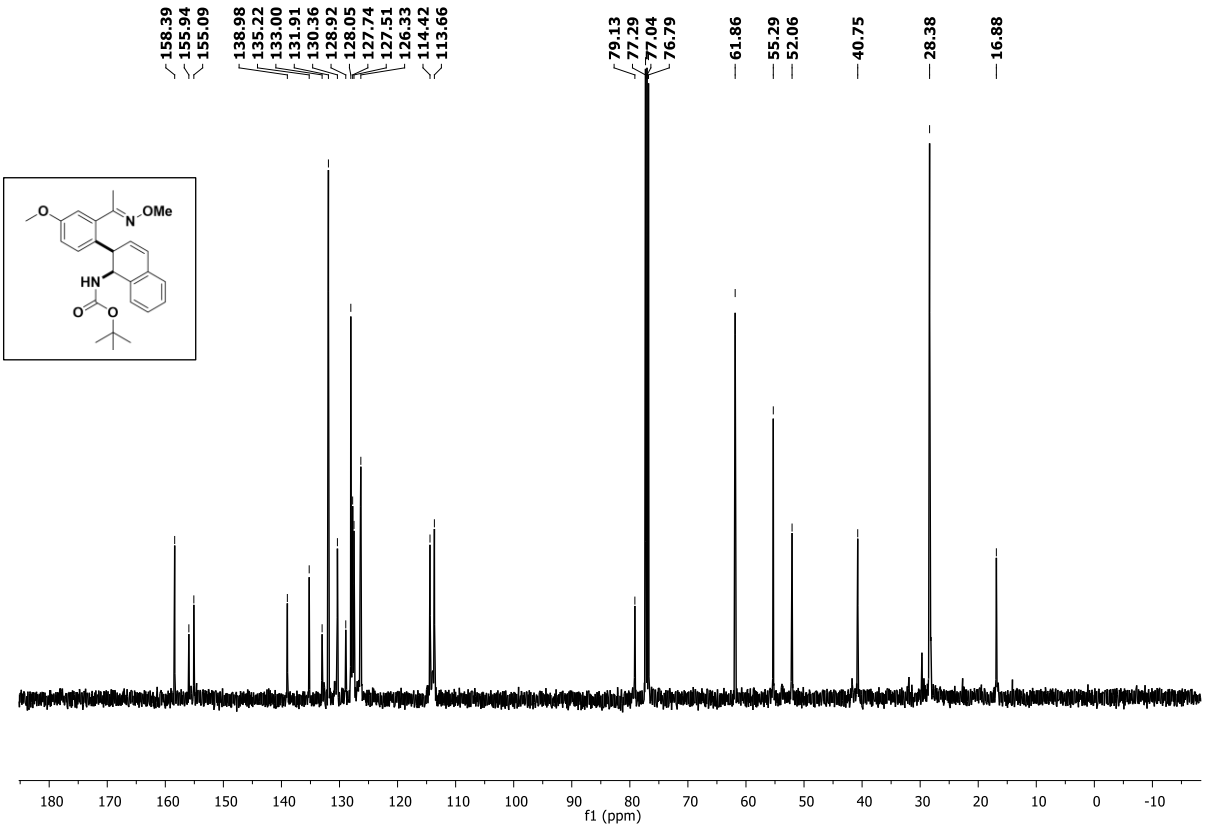
^{1}H and ^{13}C NMR Spectra of Compound **3na.**



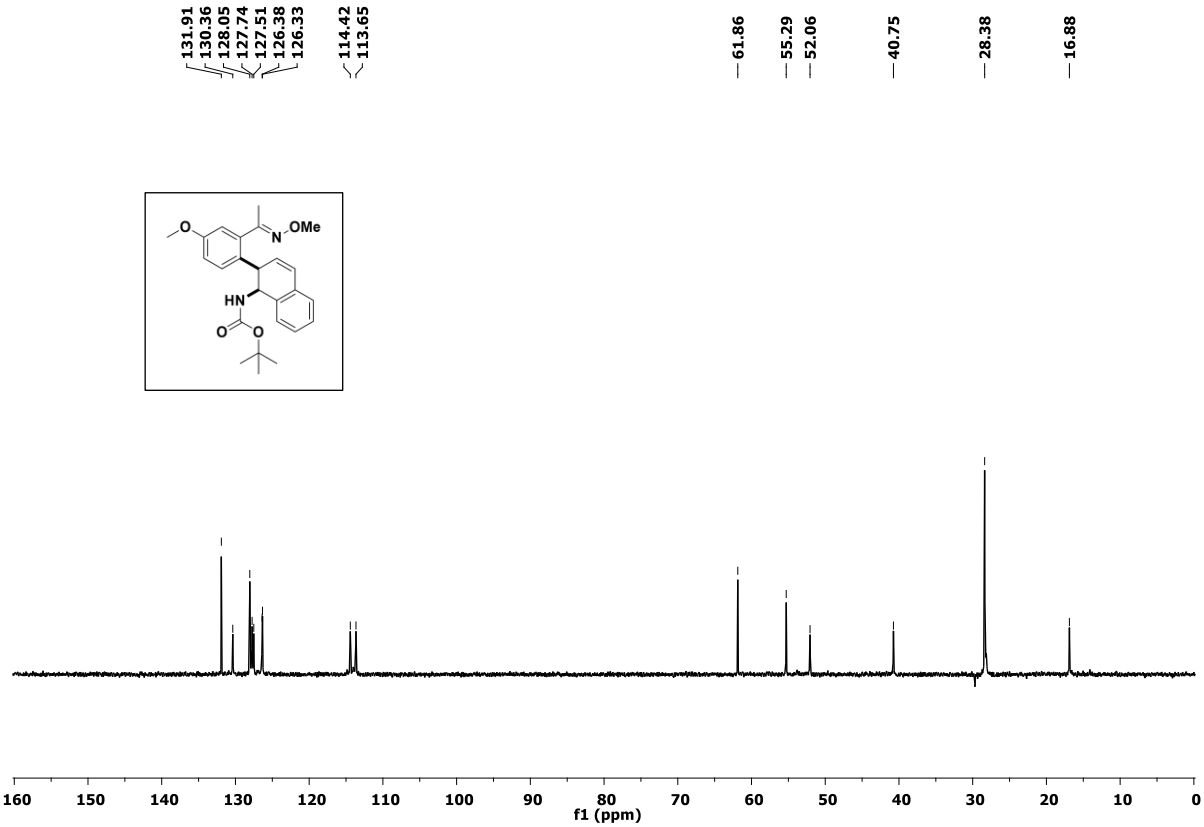


^{1}H and ^{13}C NMR Spectra of Compound **3oa.**

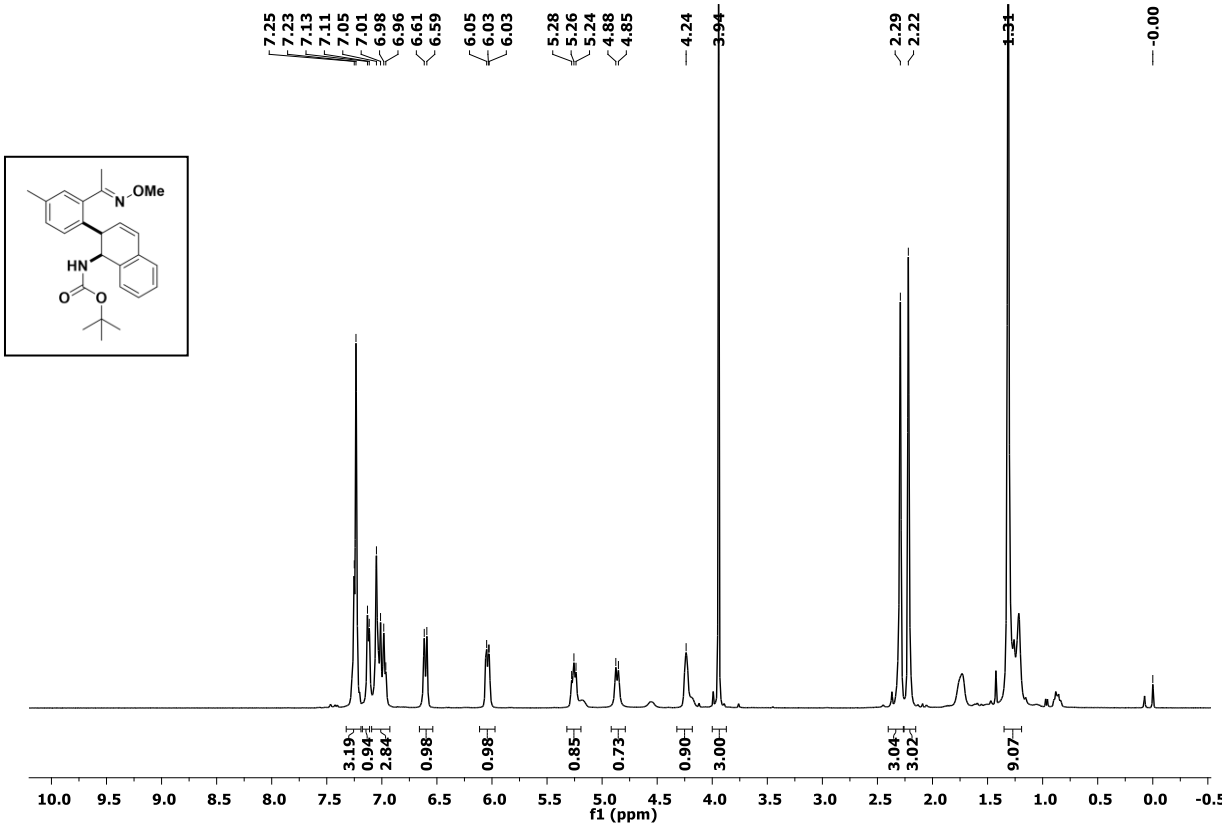


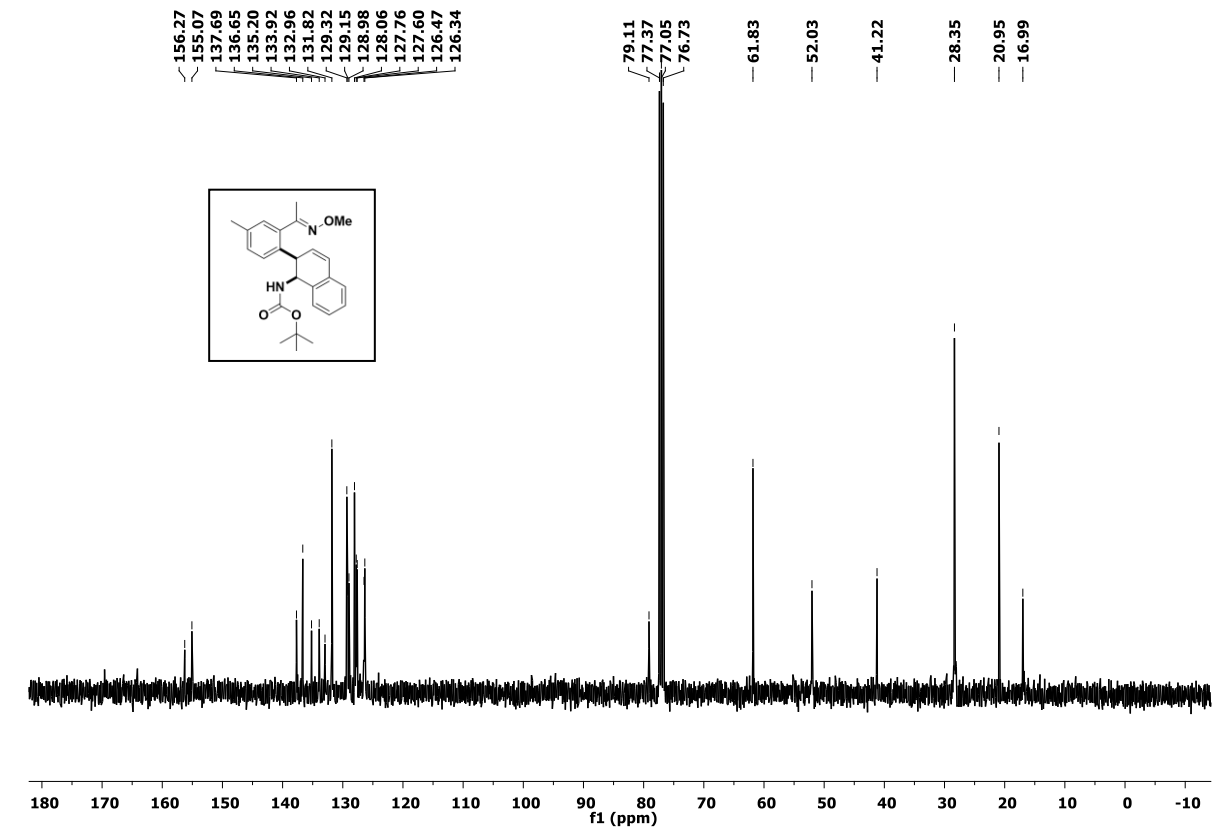


DEPT (135) NMR Spectrum of Compound **3oa.**

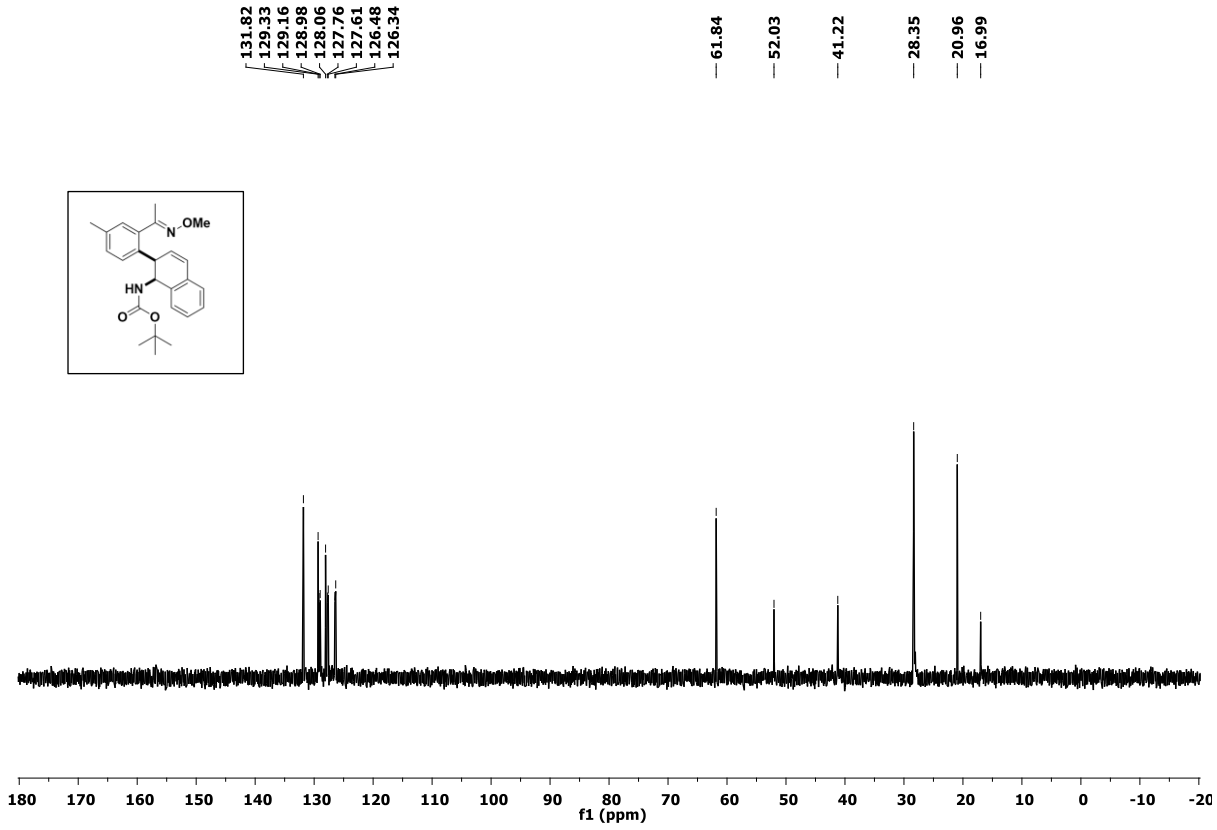


^{1}H and ^{13}C NMR Spectra of Compound **3pa.**

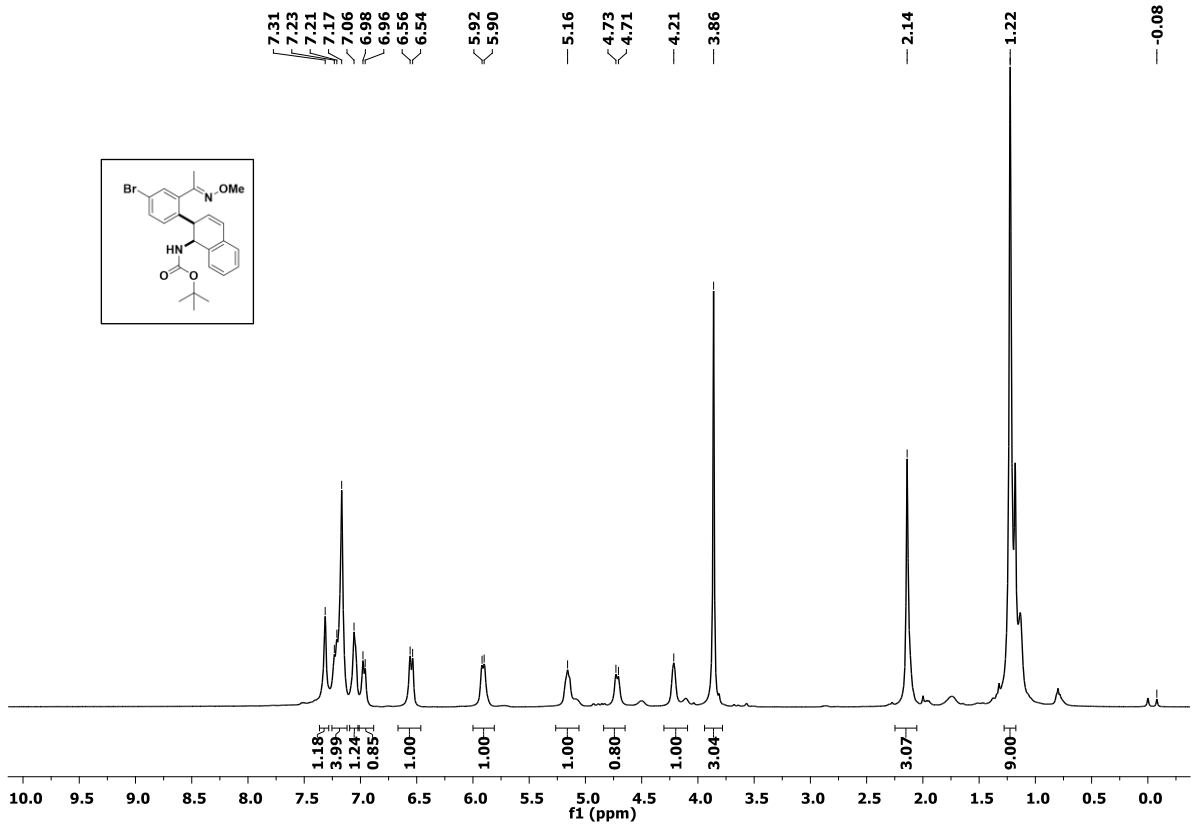




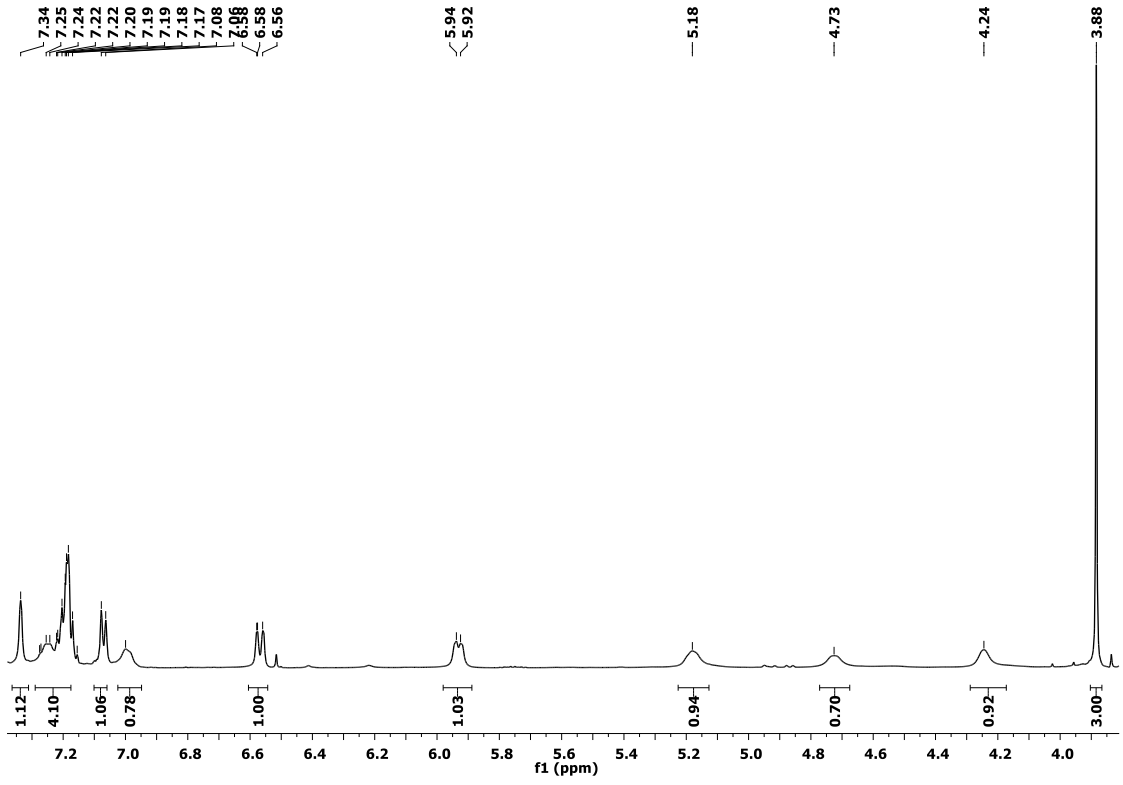
DEPT (135) NMR Spectrum of Compound **3pa.**

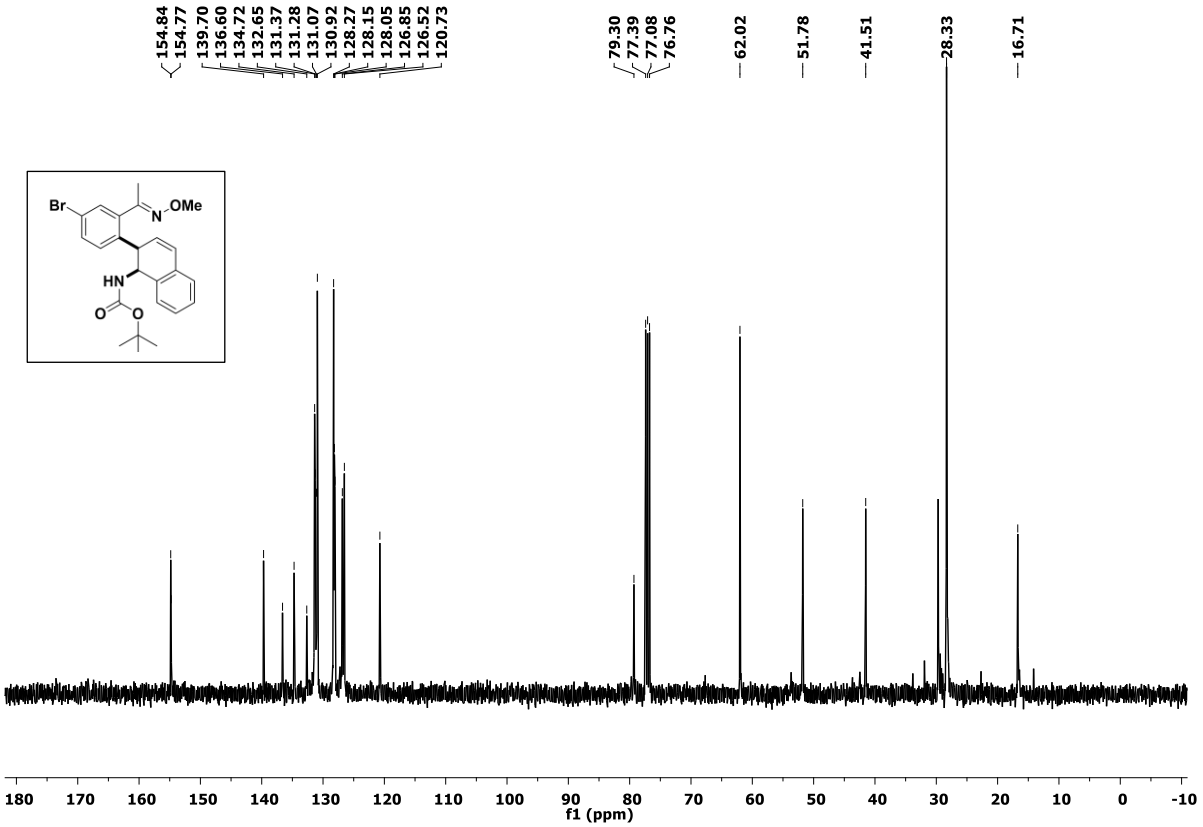


^{1}H and ^{13}C NMR Spectra of Compound **3qa.**

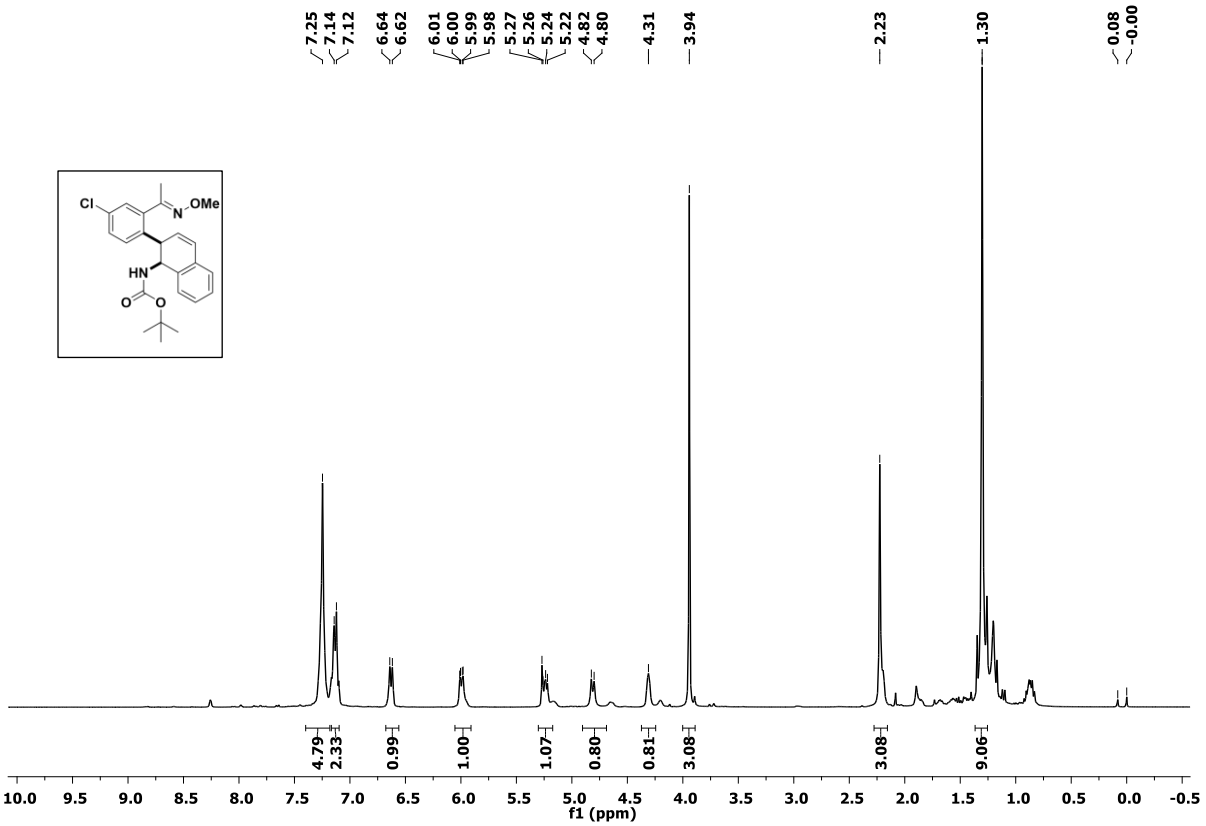


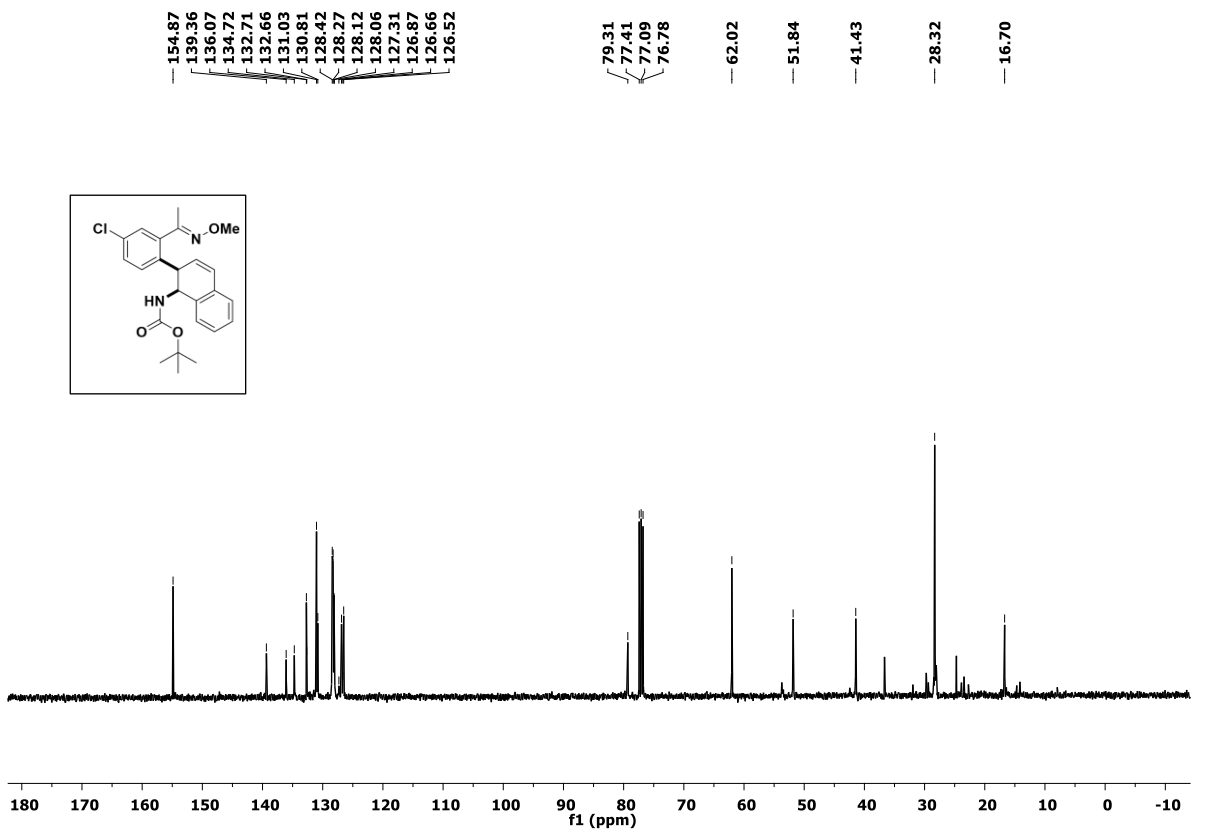
The NMR was taken at 50 ˚C. The bumps range 5.0 ppm and 4.4 ppm were disappeared



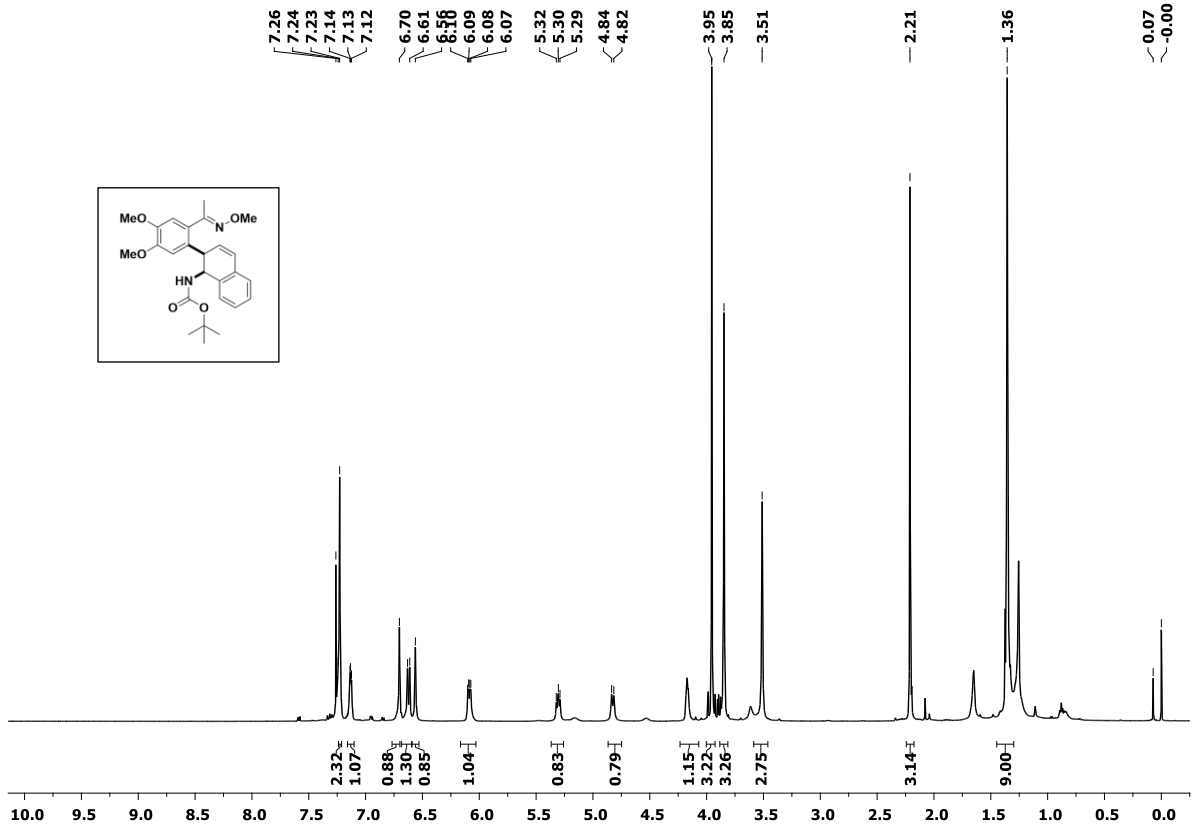

154.84
154.77
139.70
136.60
134.72
132.65
131.37
131.28
131.07
130.92
128.27
128.15
128.05
126.85
126.52
120.73
79.30
77.39
77.08
76.76
62.02
51.78
41.51
28.33
16.71
Br
N
OMe
HN
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

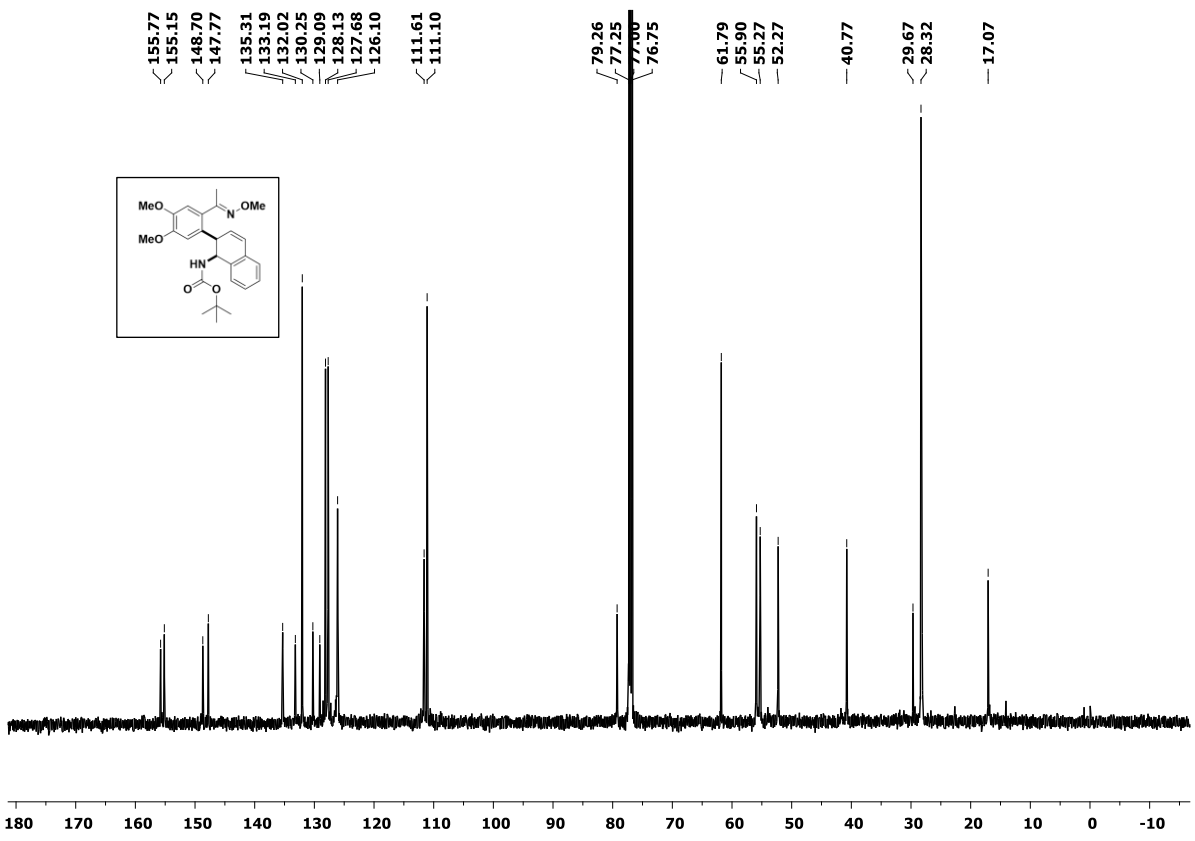
^{1}H and ^{13}C NMR Spectra of Compound **3ra.**



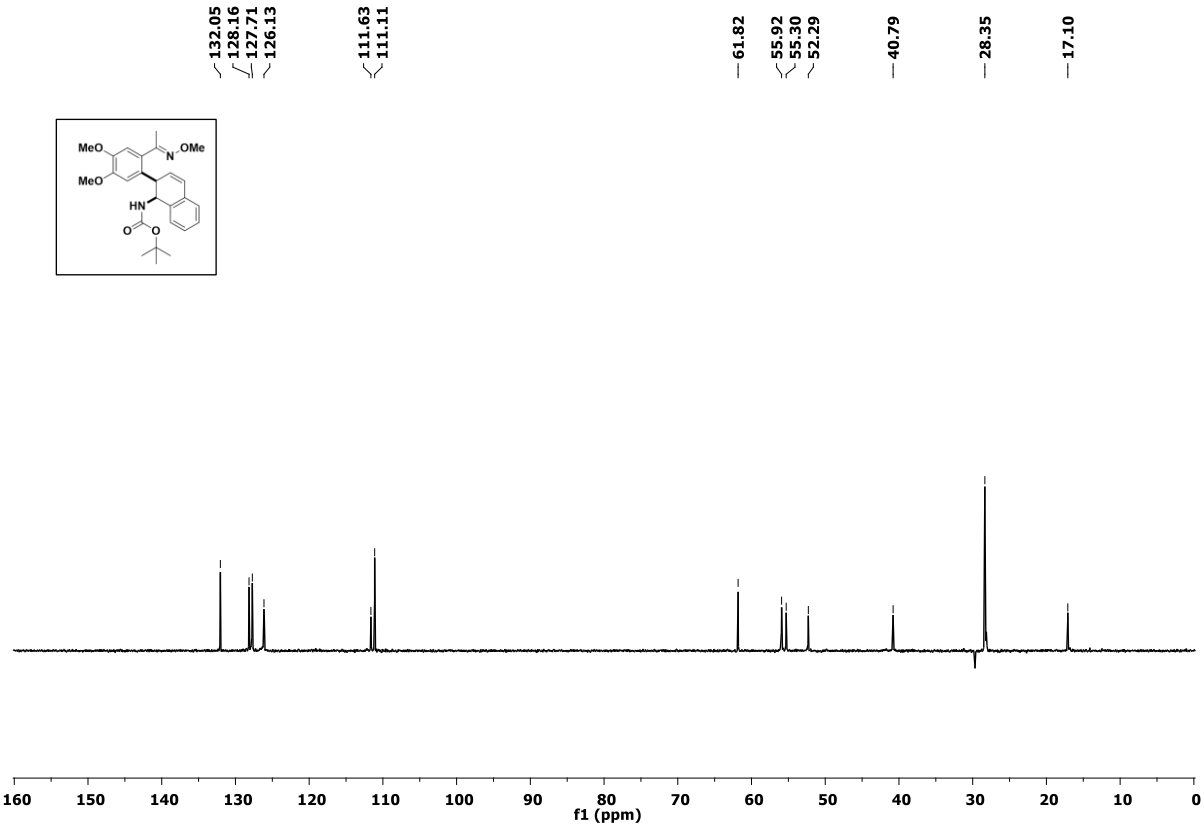


^{1}H and ^{13}C NMR Spectra of Compound **3sa.**

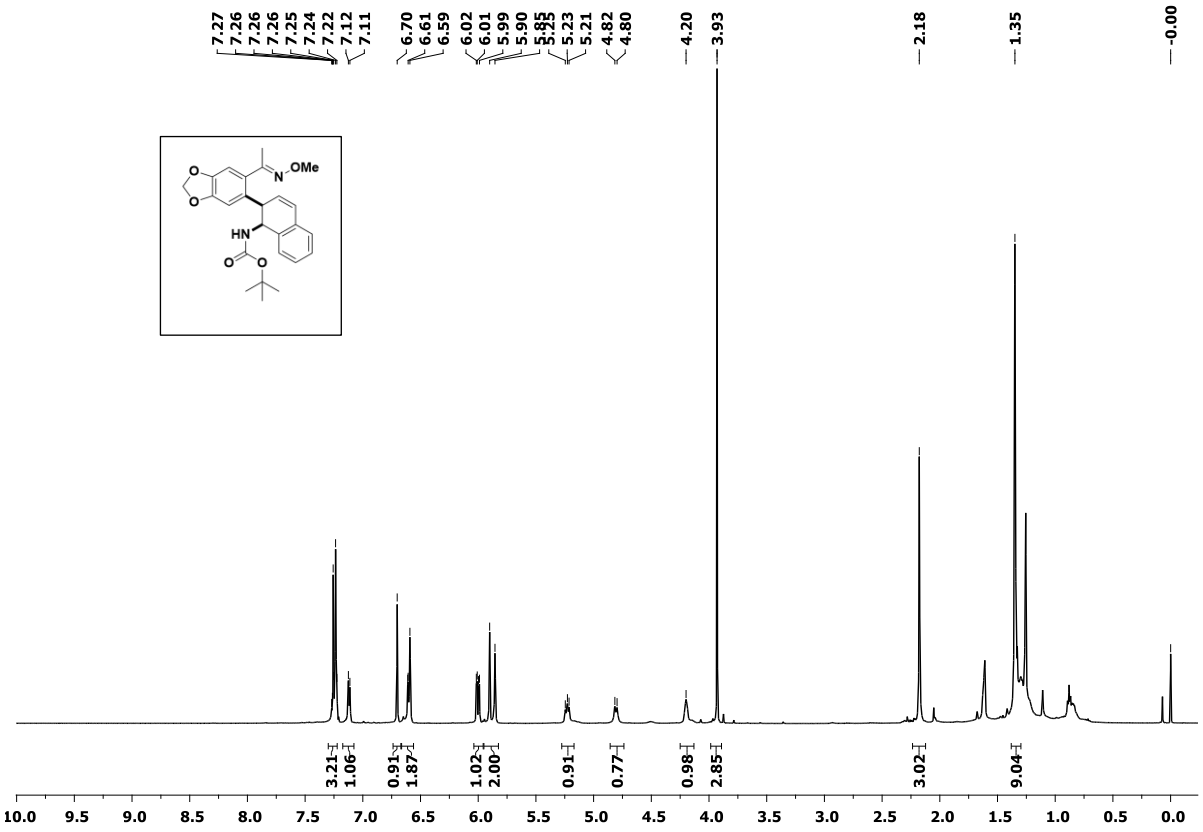


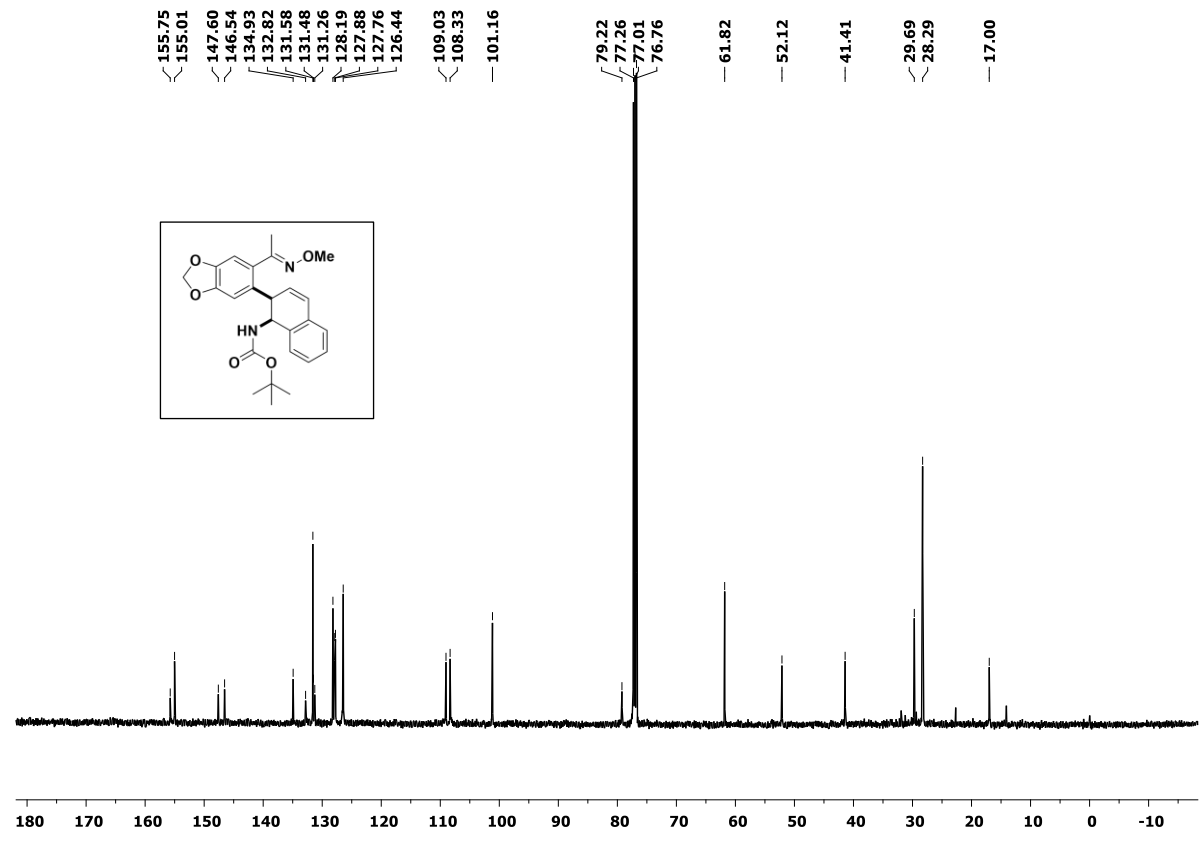


DEPT (135) NMR Spectrum of Compound **3sa.**

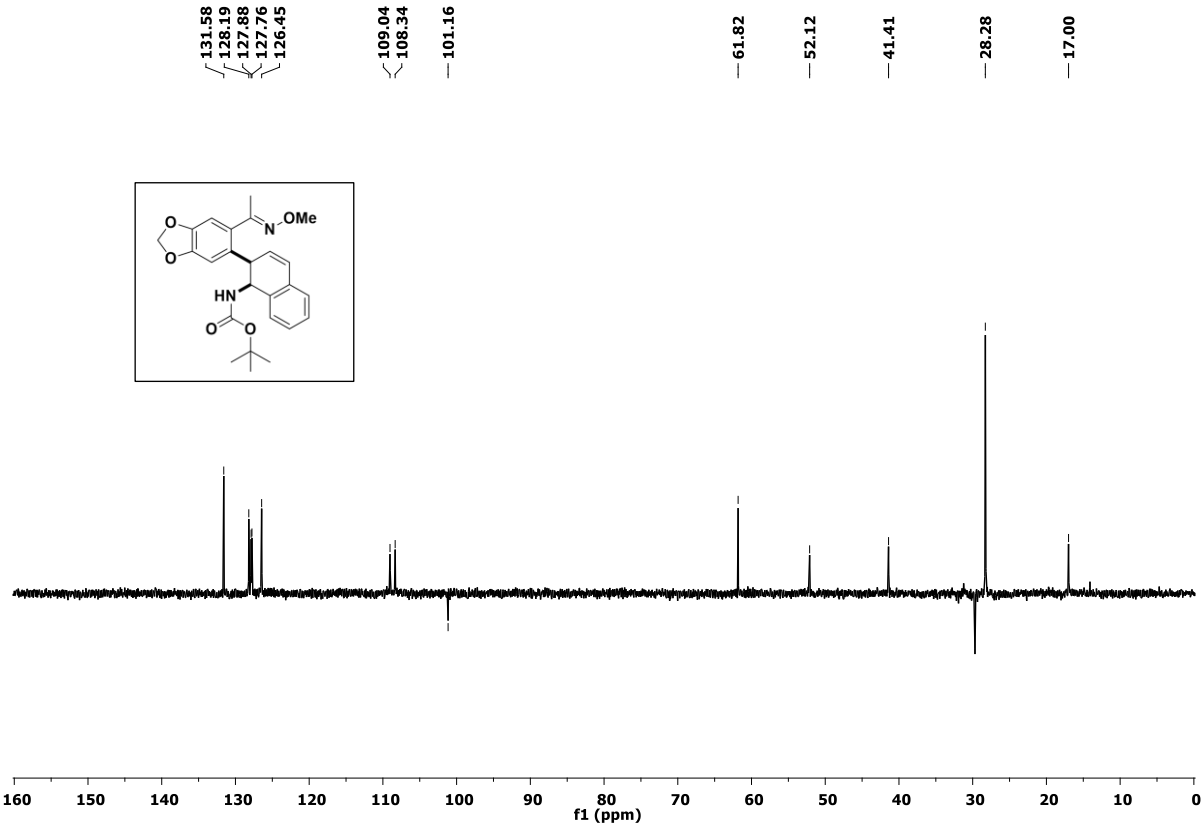


^{1}H and ^{13}C NMR Spectra of Compound **3ta.**

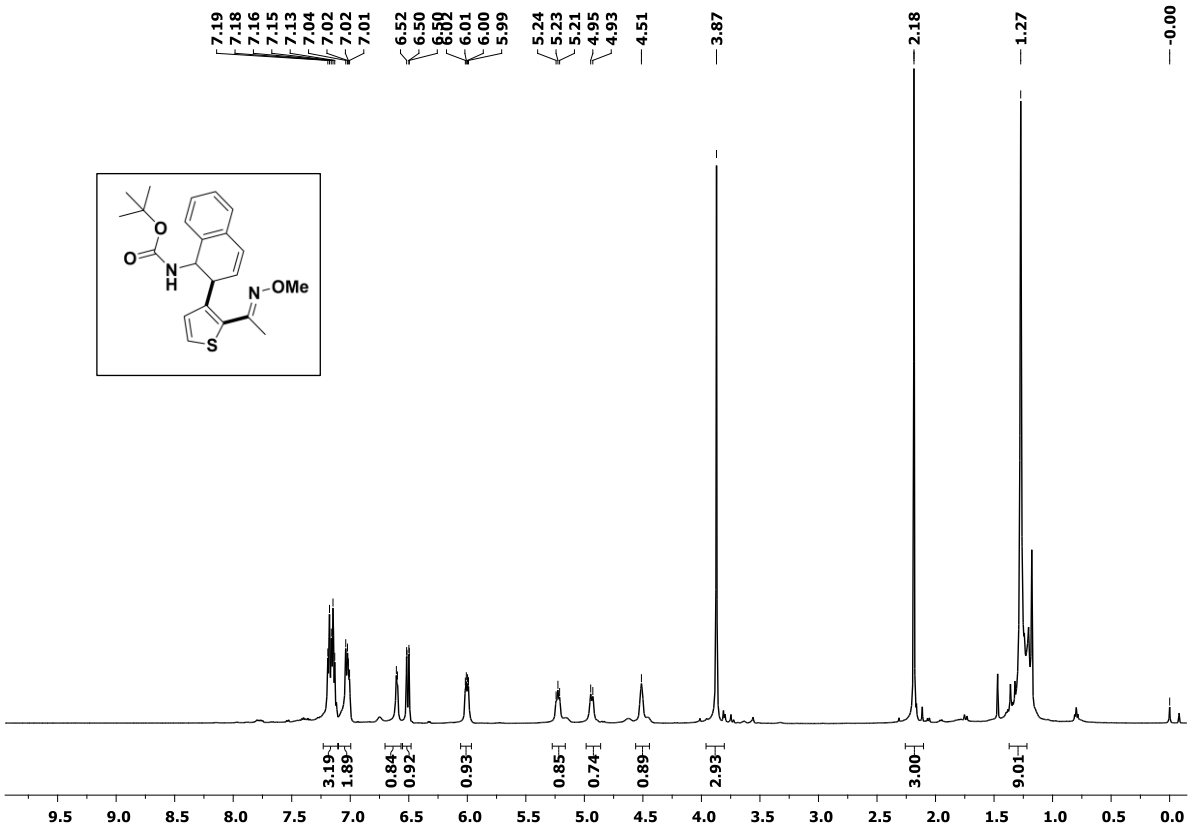


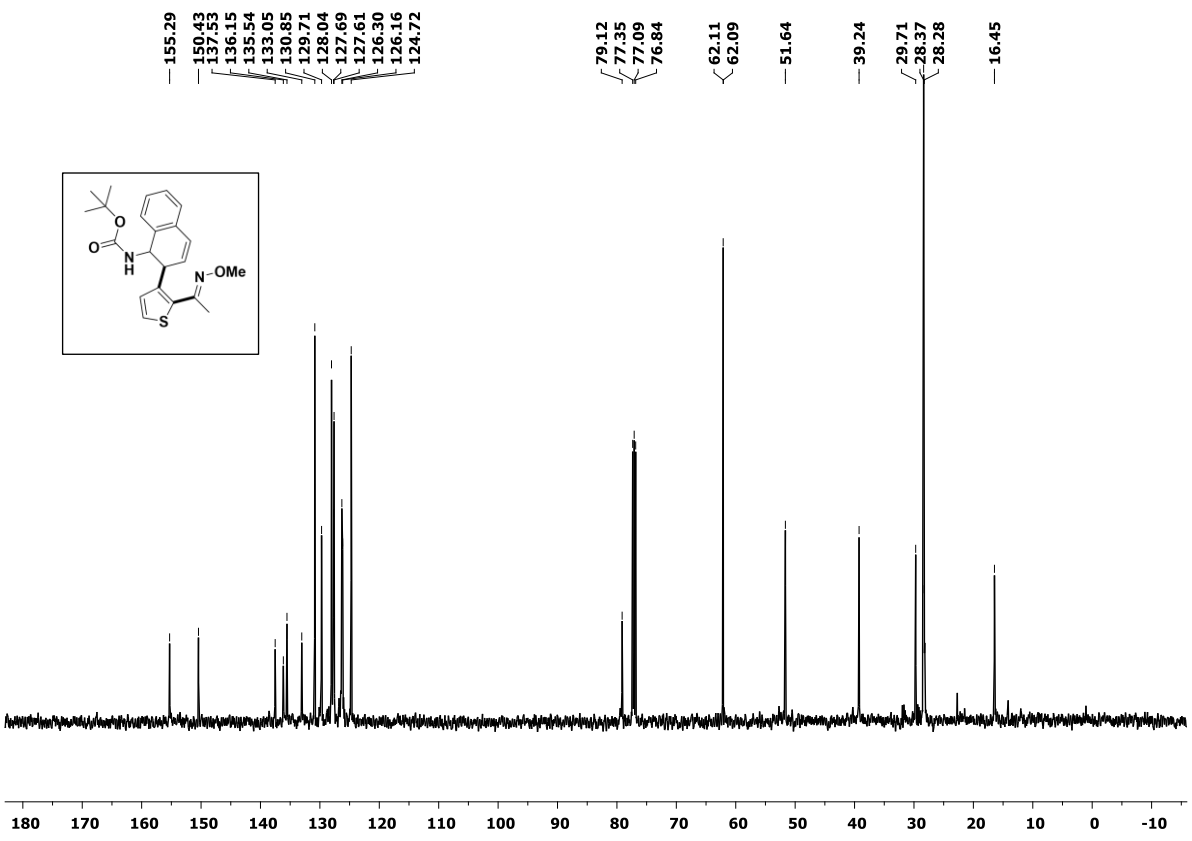


DEPT (135) NMR Spectrum of Compound **3ta.**

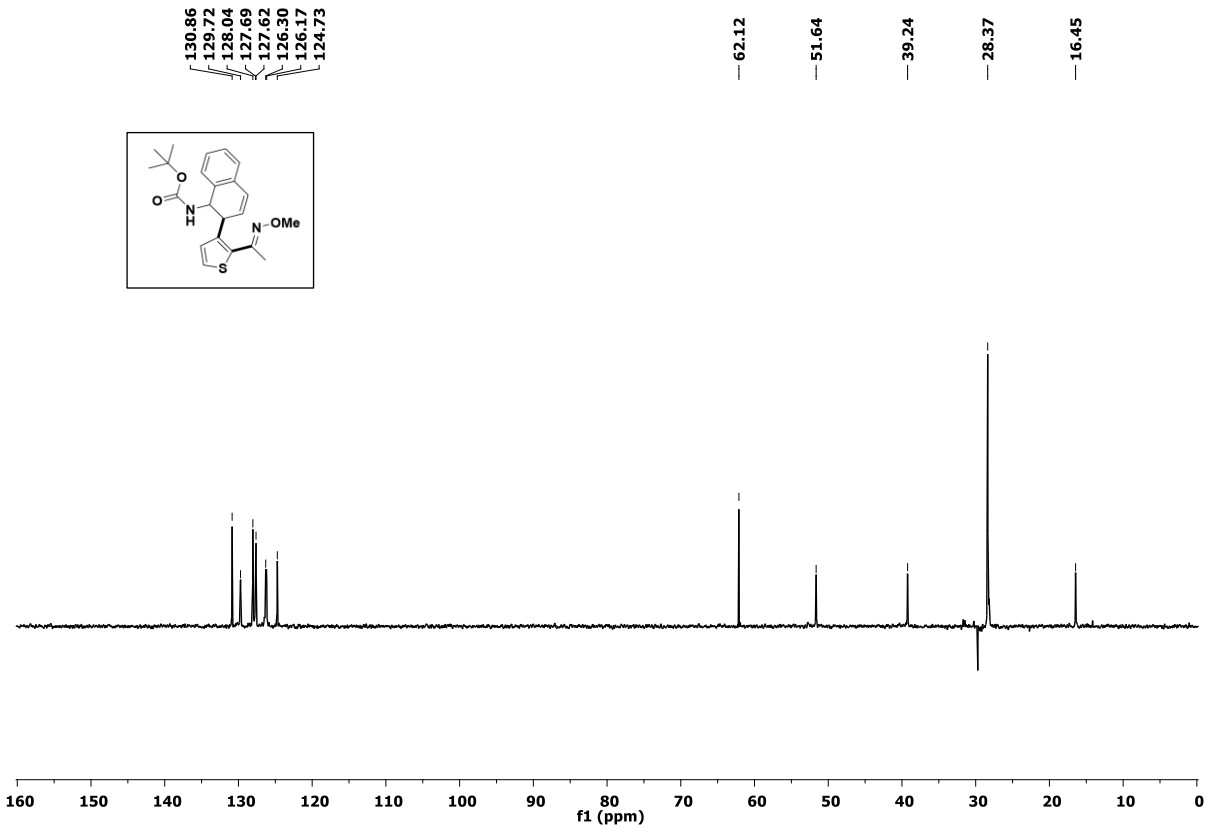


^{1}H and ^{13}C NMR Spectra of Compound **3ua.**

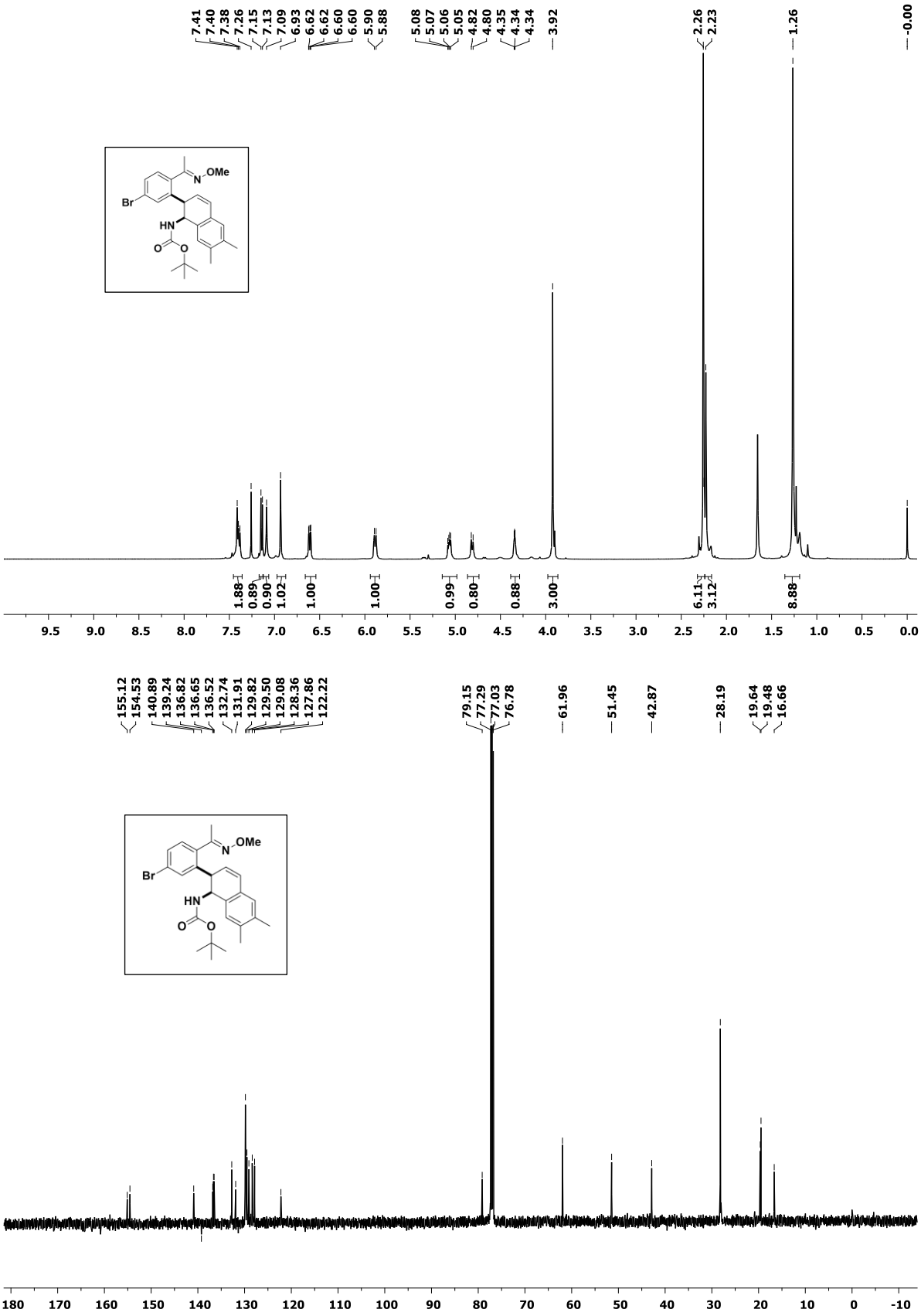




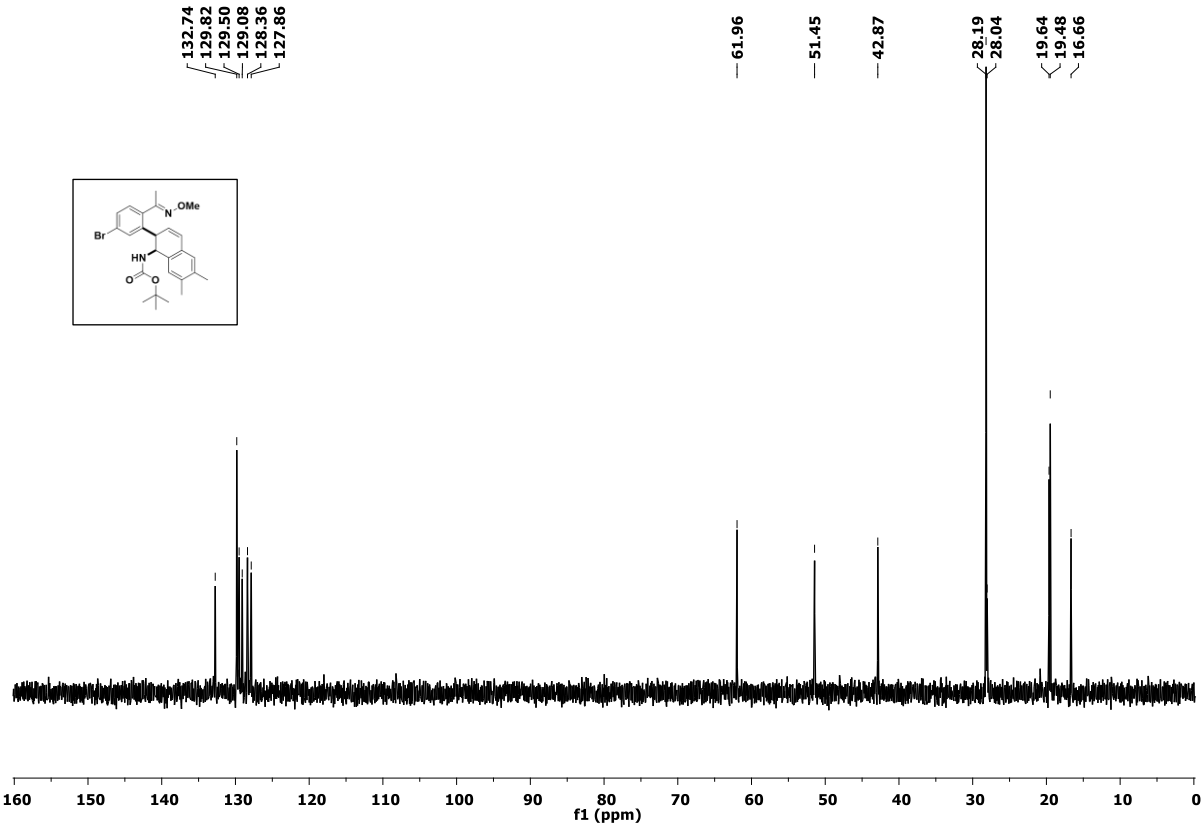
DEPT (135) NMR Spectrum of Compound **3ua.**



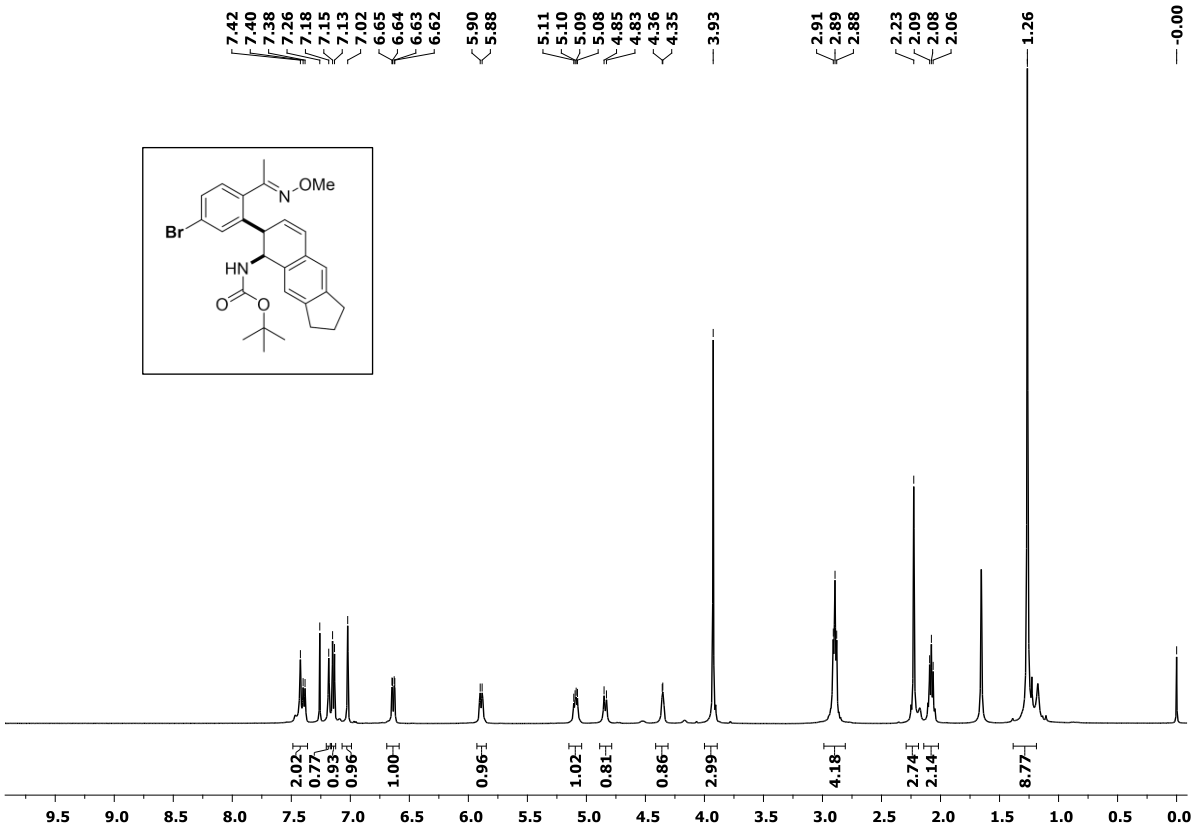
^{1}H and ^{13}C NMR Spectra of Compound **3eb.**

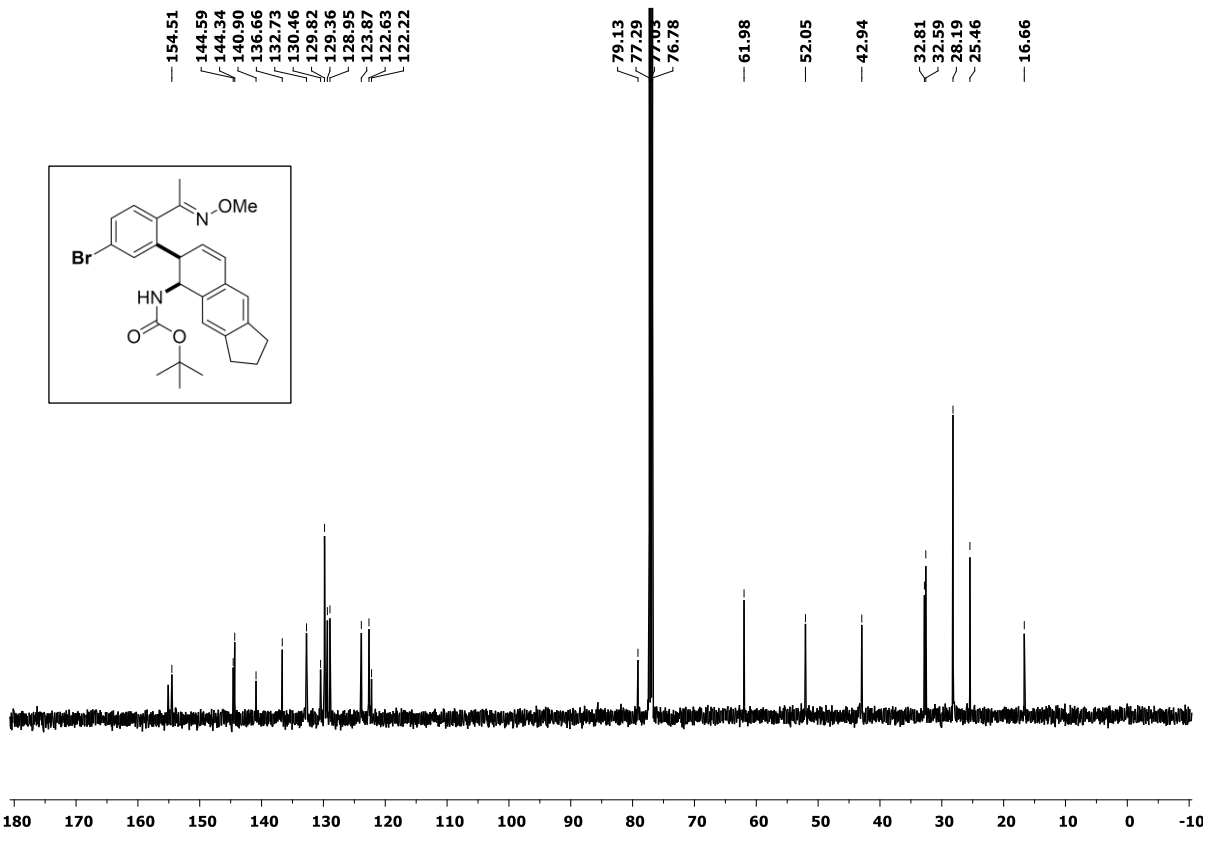


DEPT (135) NMR Spectrum of Compound **3eb.**

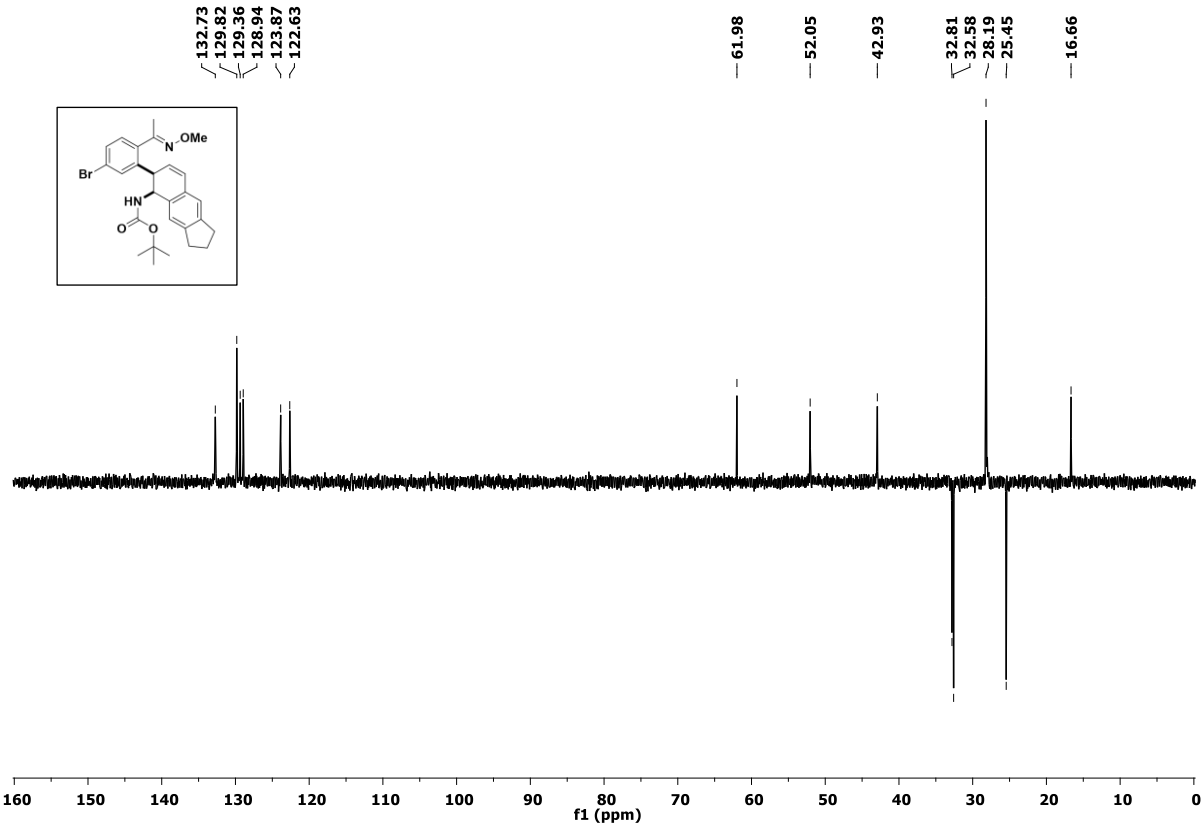


^{1}H and ^{13}C NMR Spectra of Compound **3cc.**

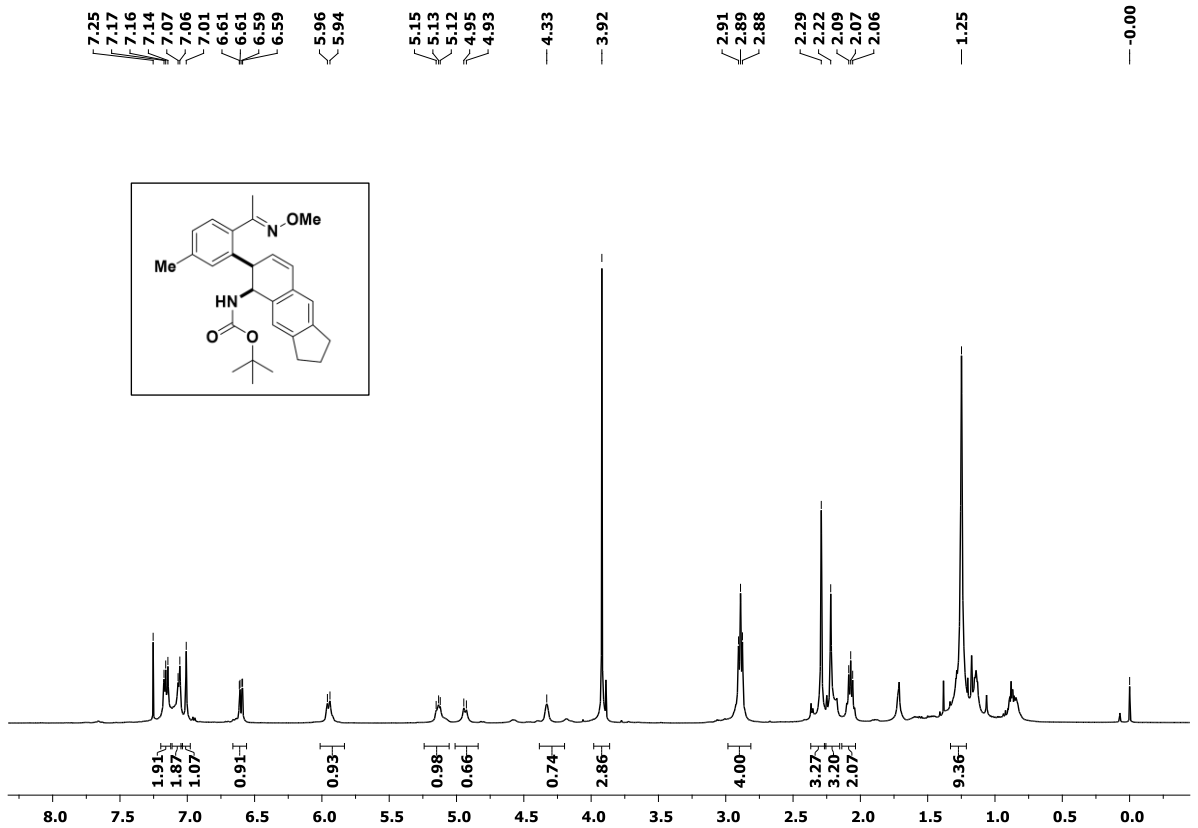


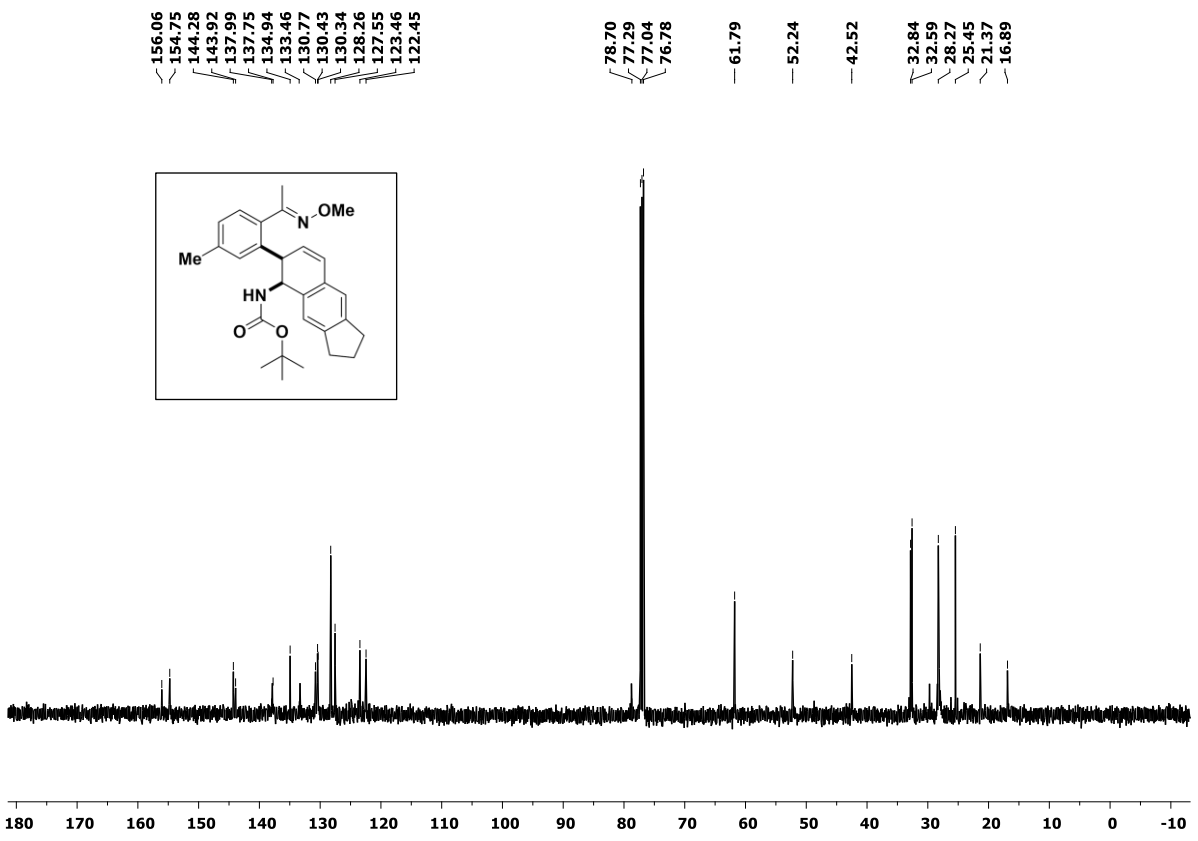


DEPT (135) NMR Spectrum of Compound **3cc.**

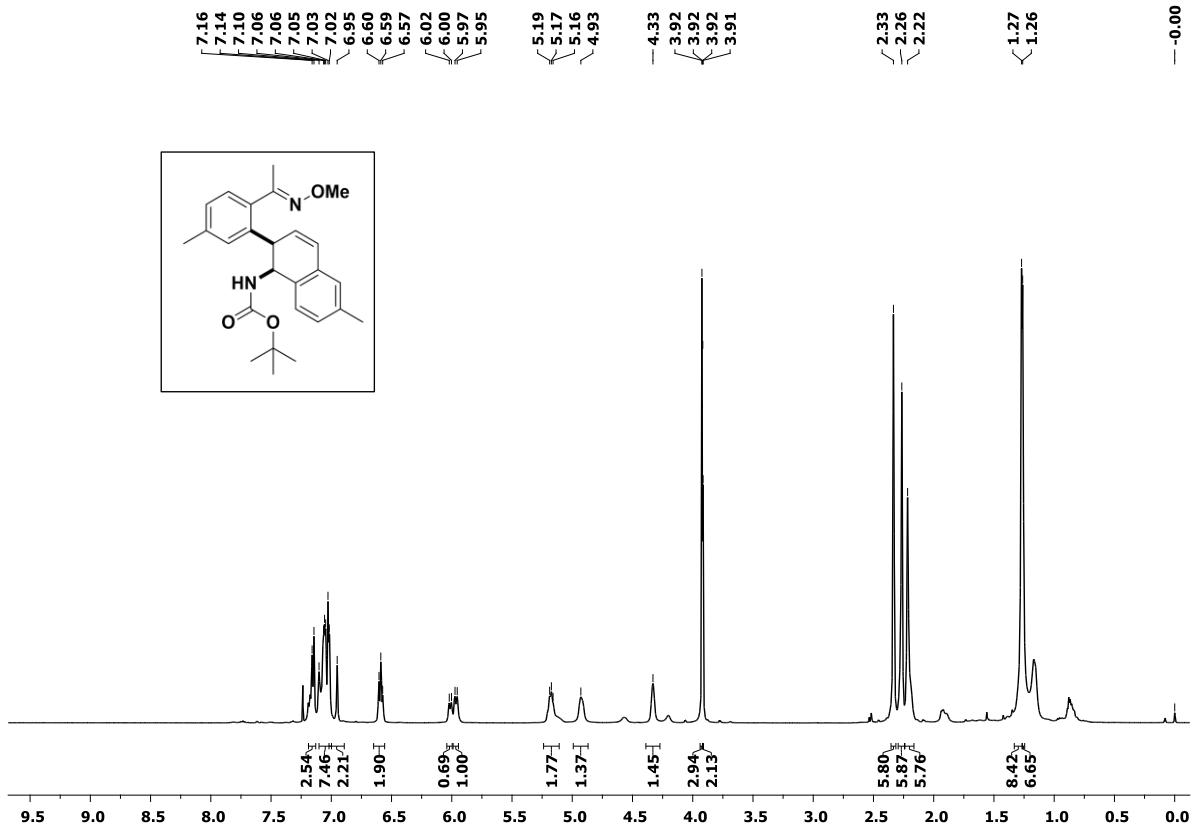


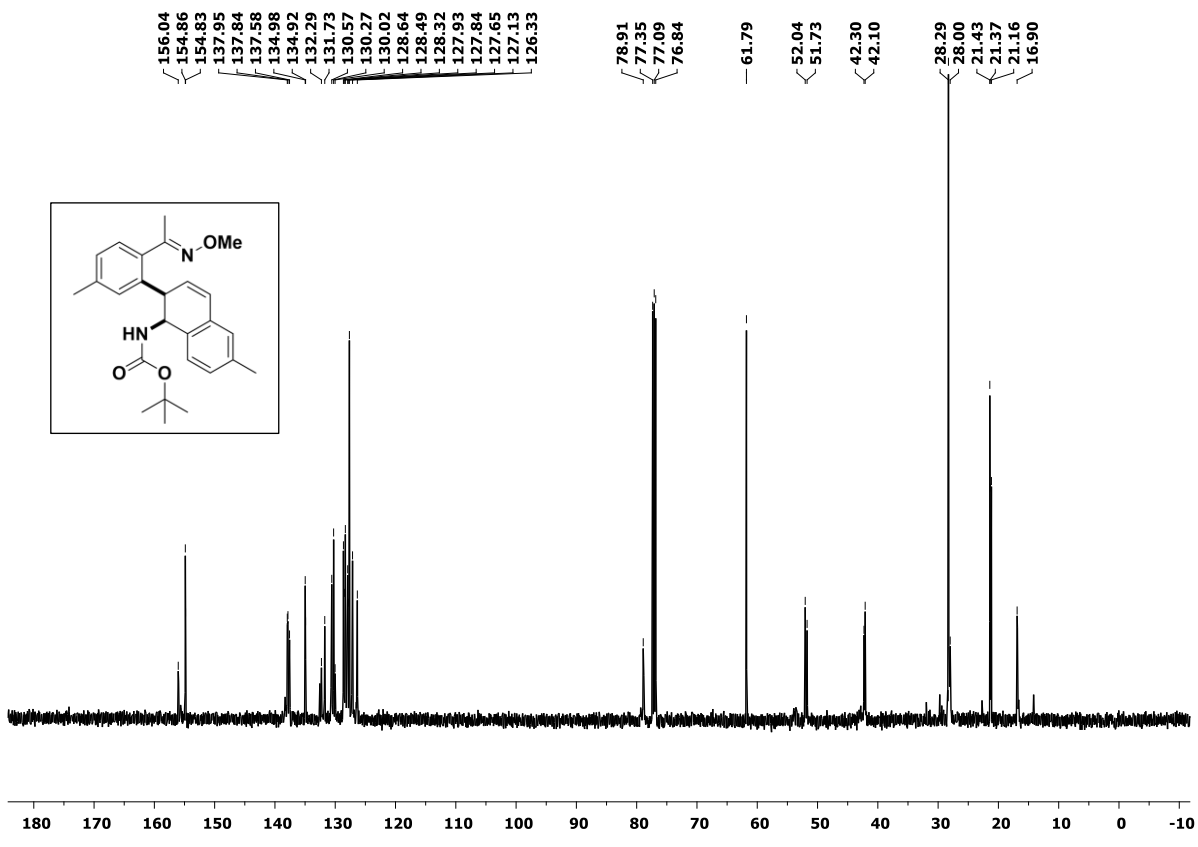
^{1}H and ^{13}C NMR Spectra of Compound **3ec.**



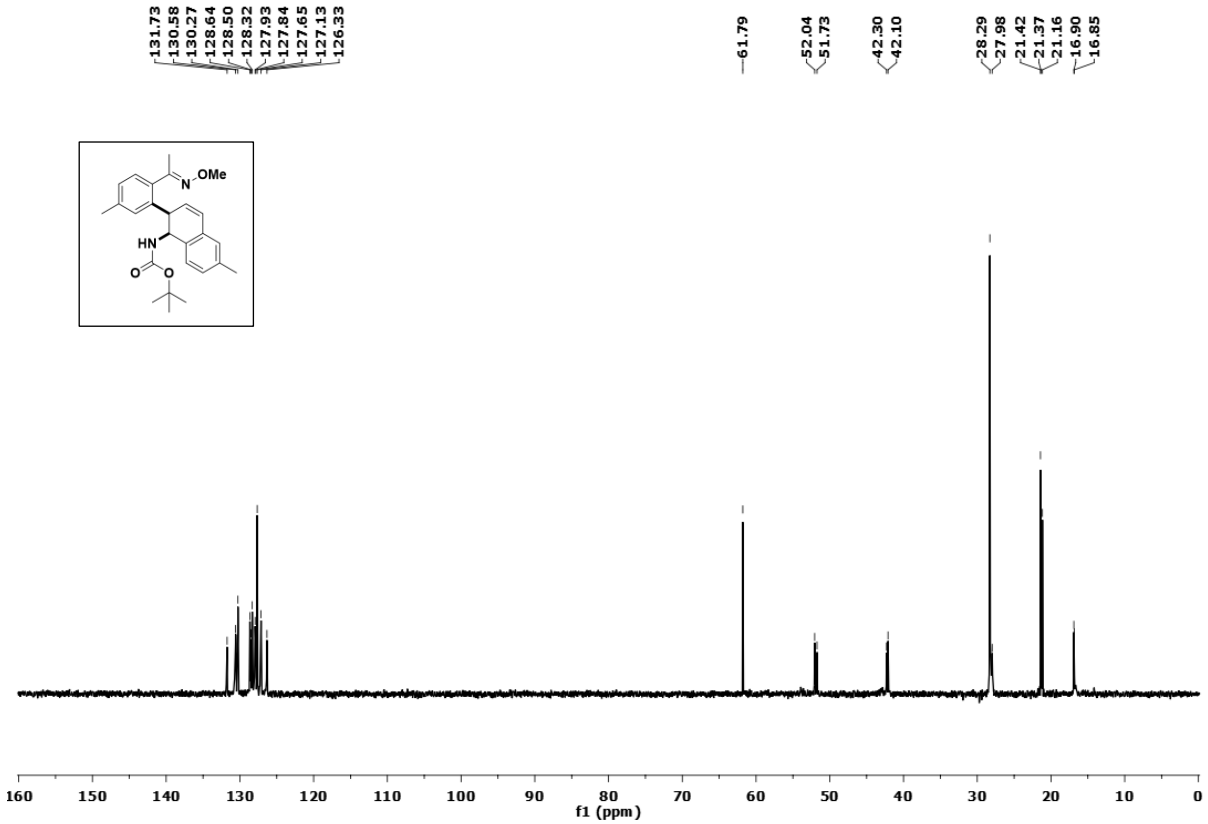


^{1}H and ^{13}C NMR Spectra of Compound **3cd.**

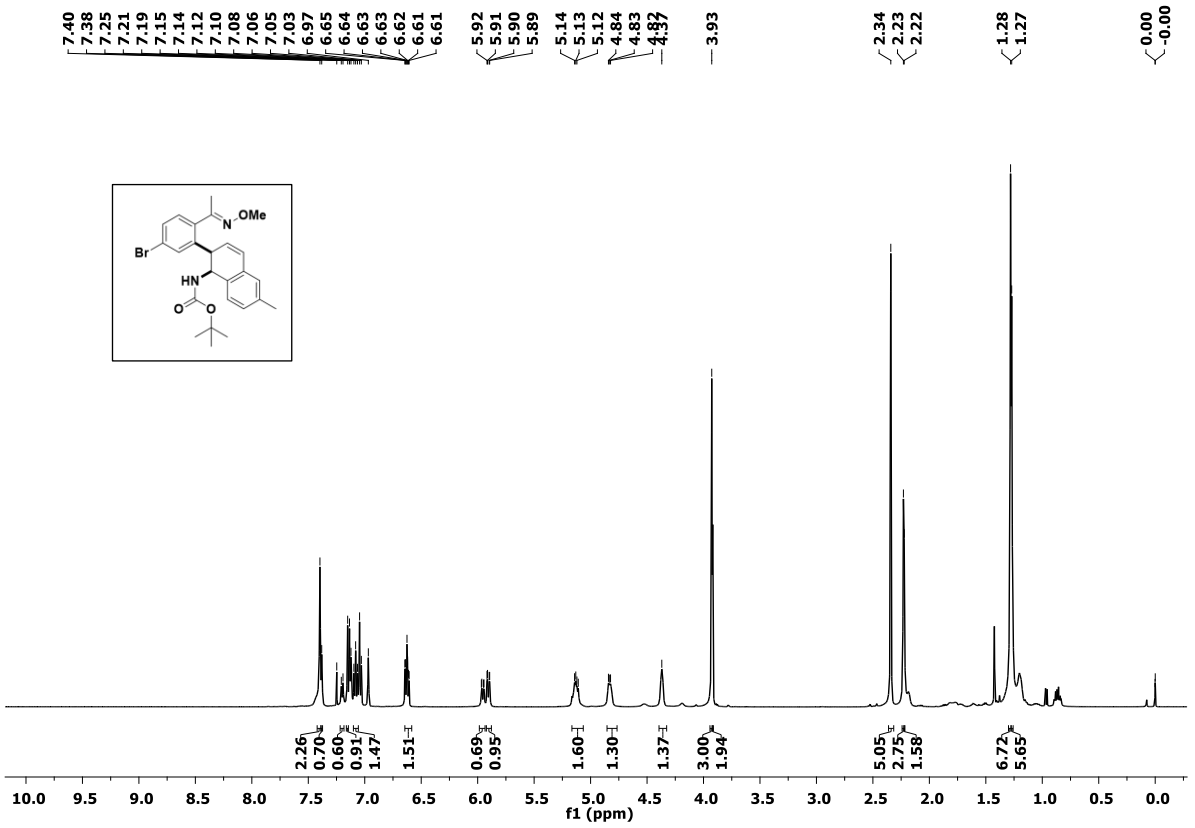


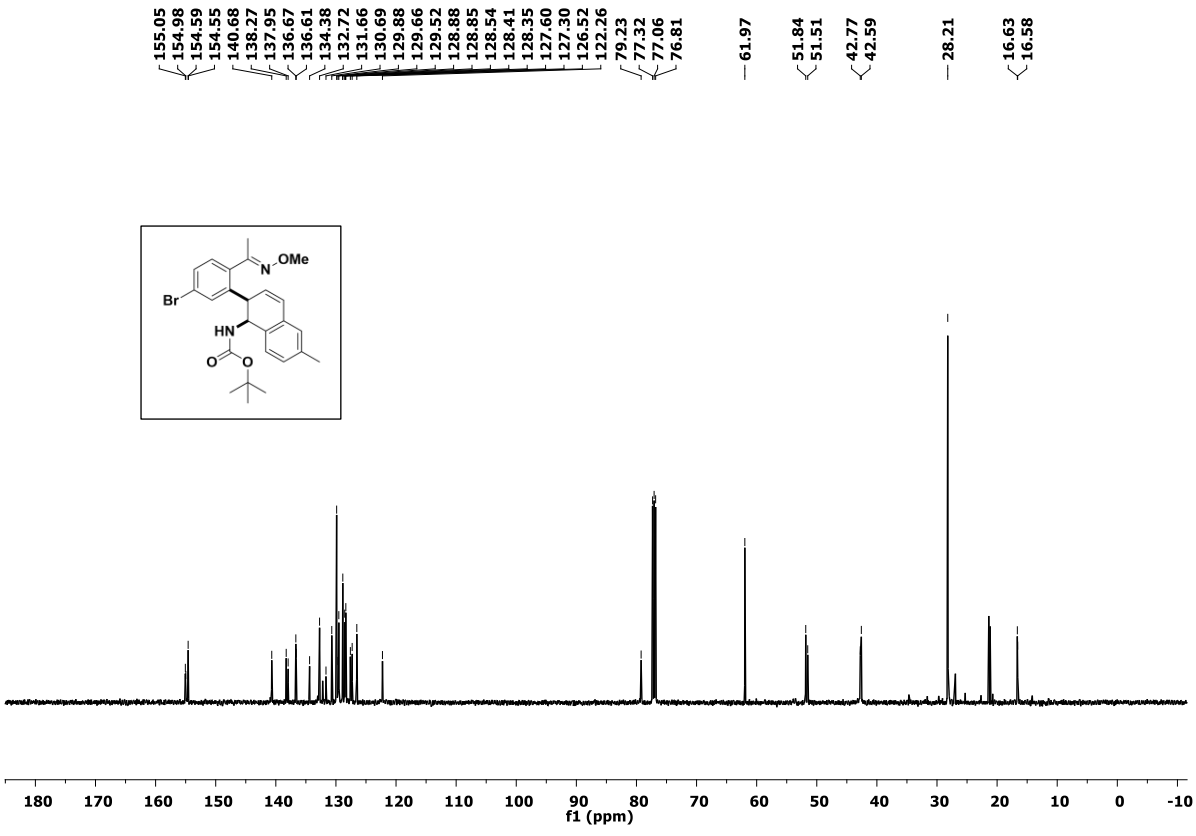


DEPT (135) NMR Spectrum of Compound **3cd.**

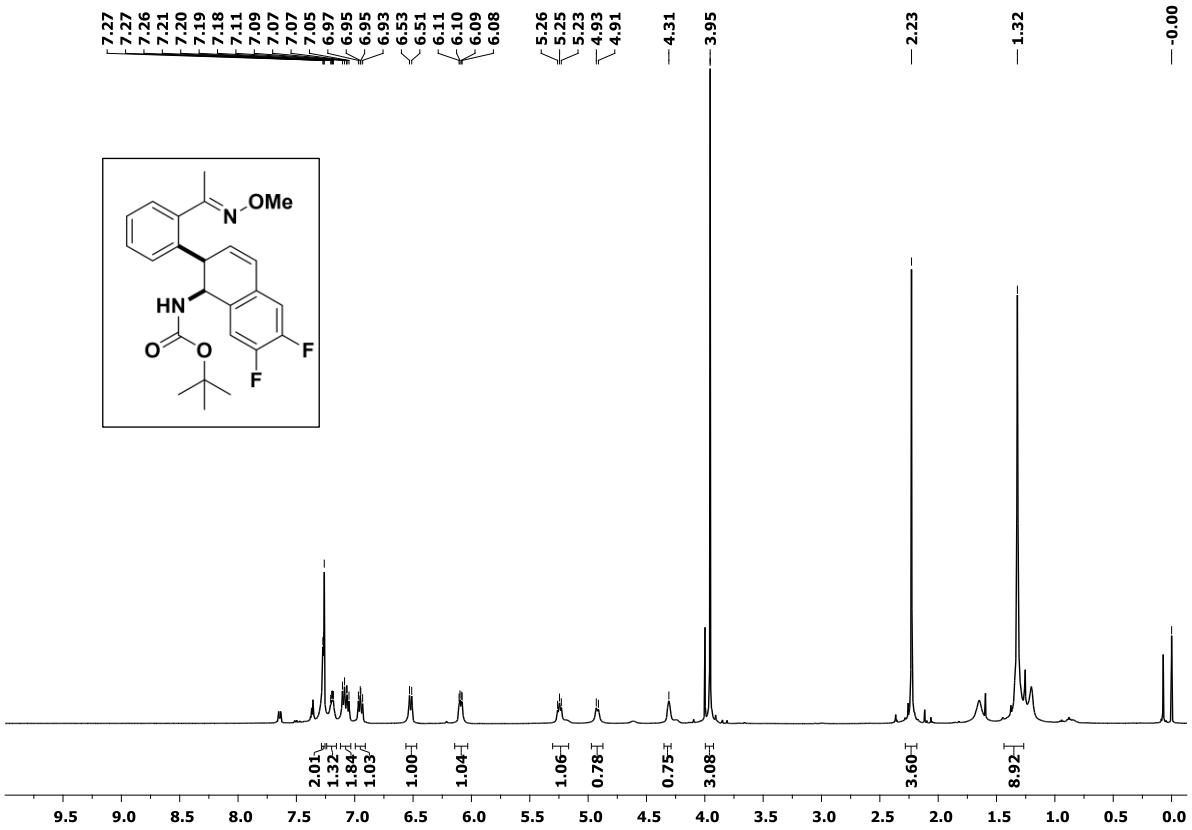


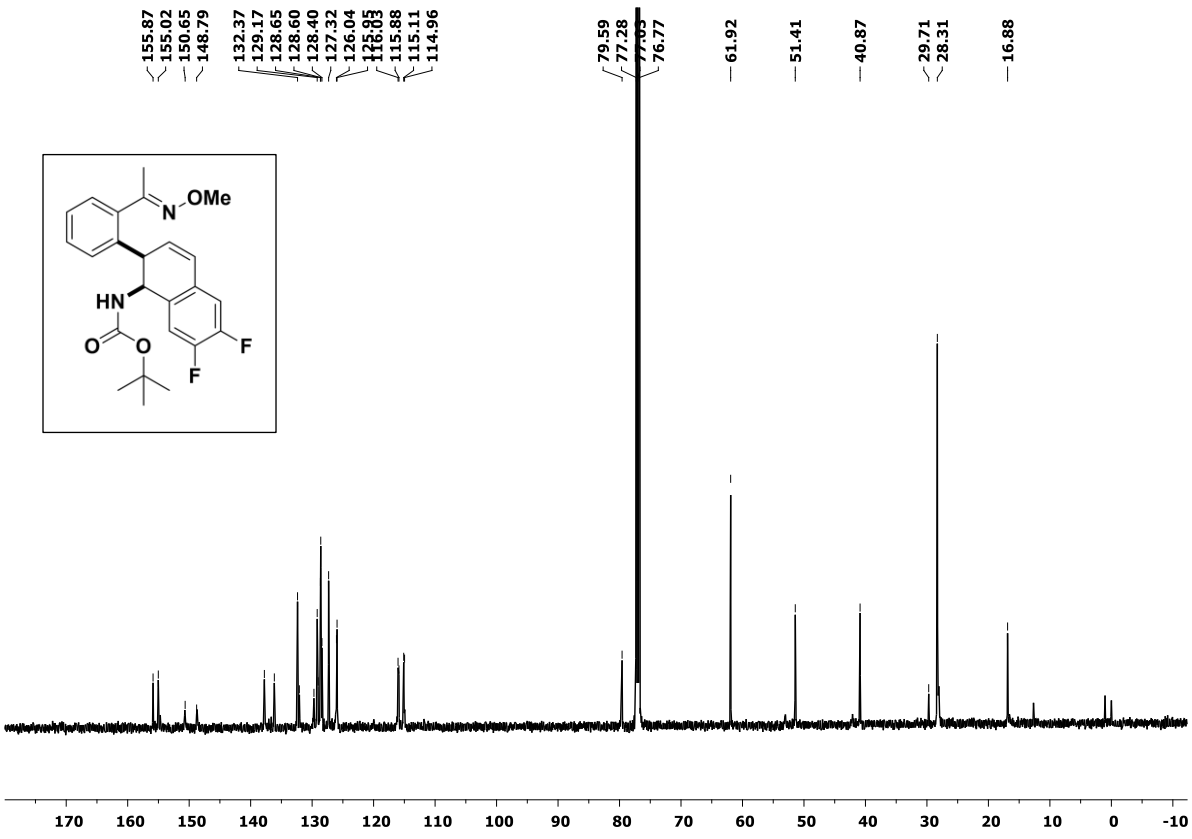
^{1}H and ^{13}C NMR Spectra of Compound **3ee.**



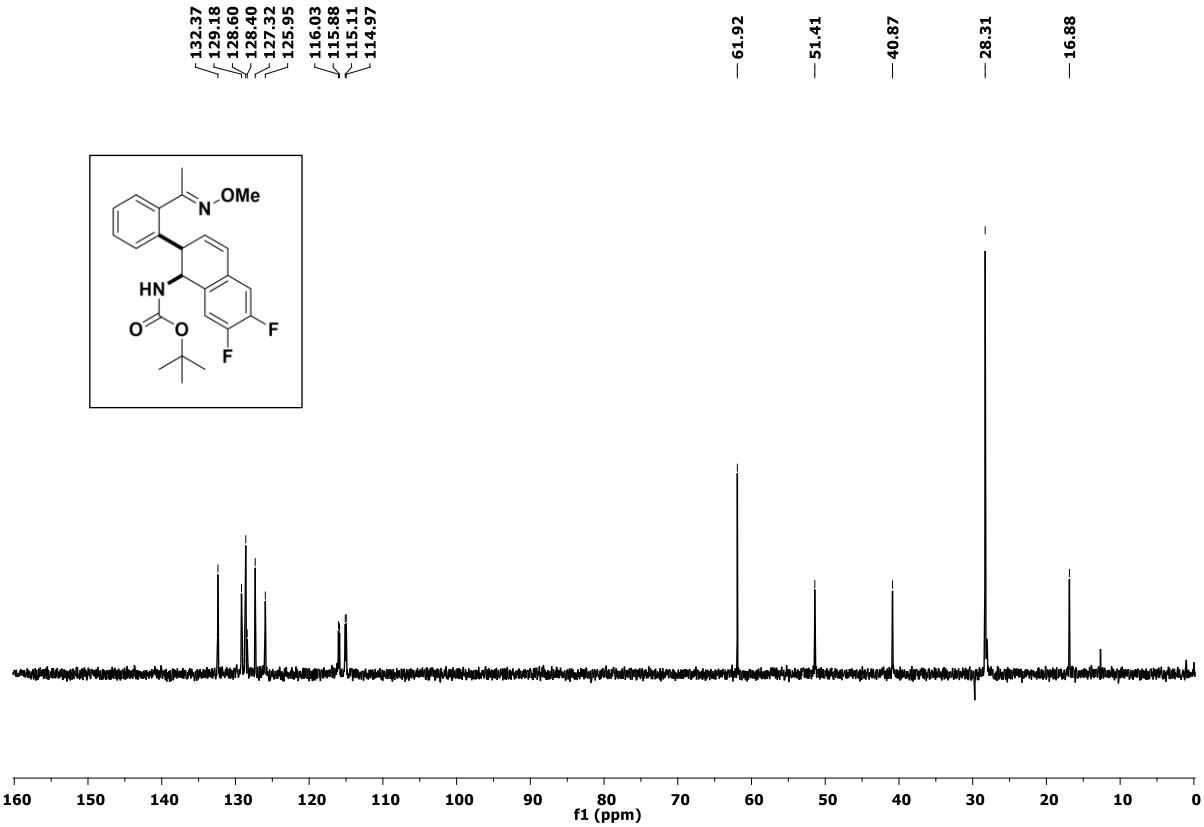


^{1}H and ^{13}C NMR Spectra of Compound **3ae.**

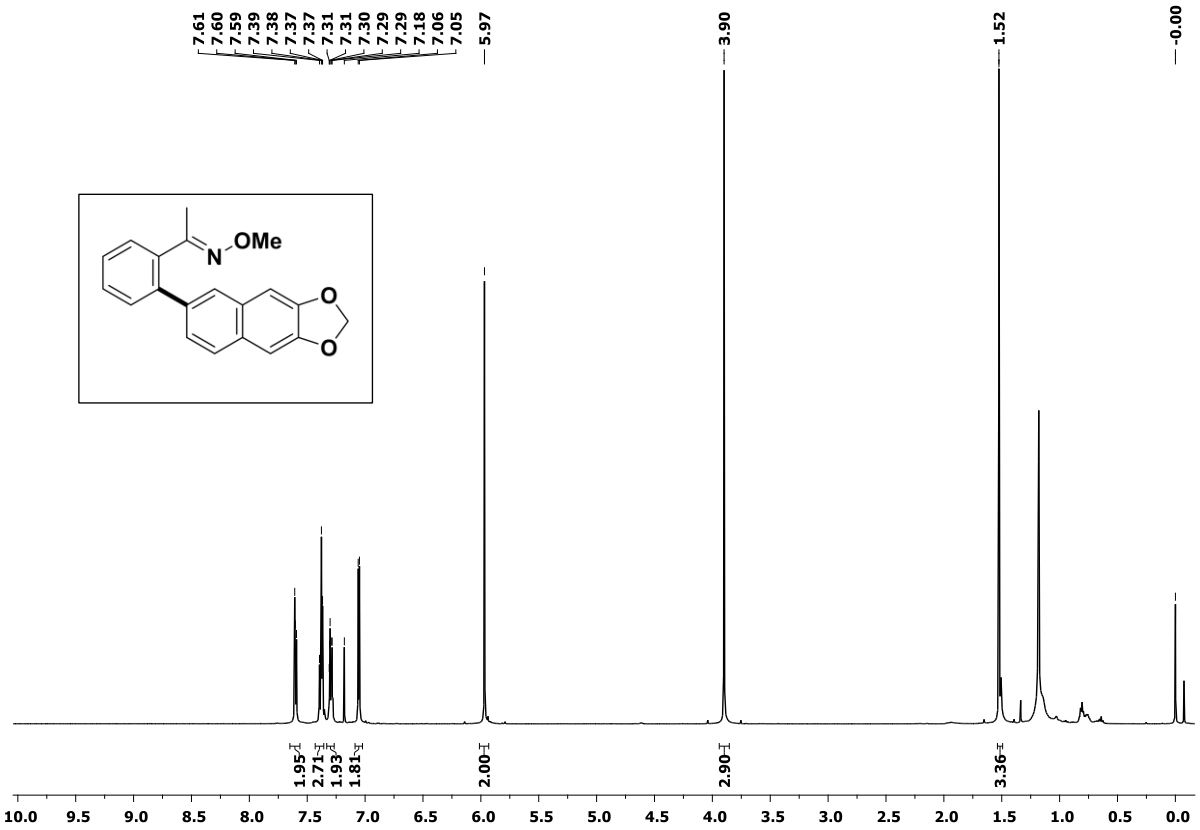


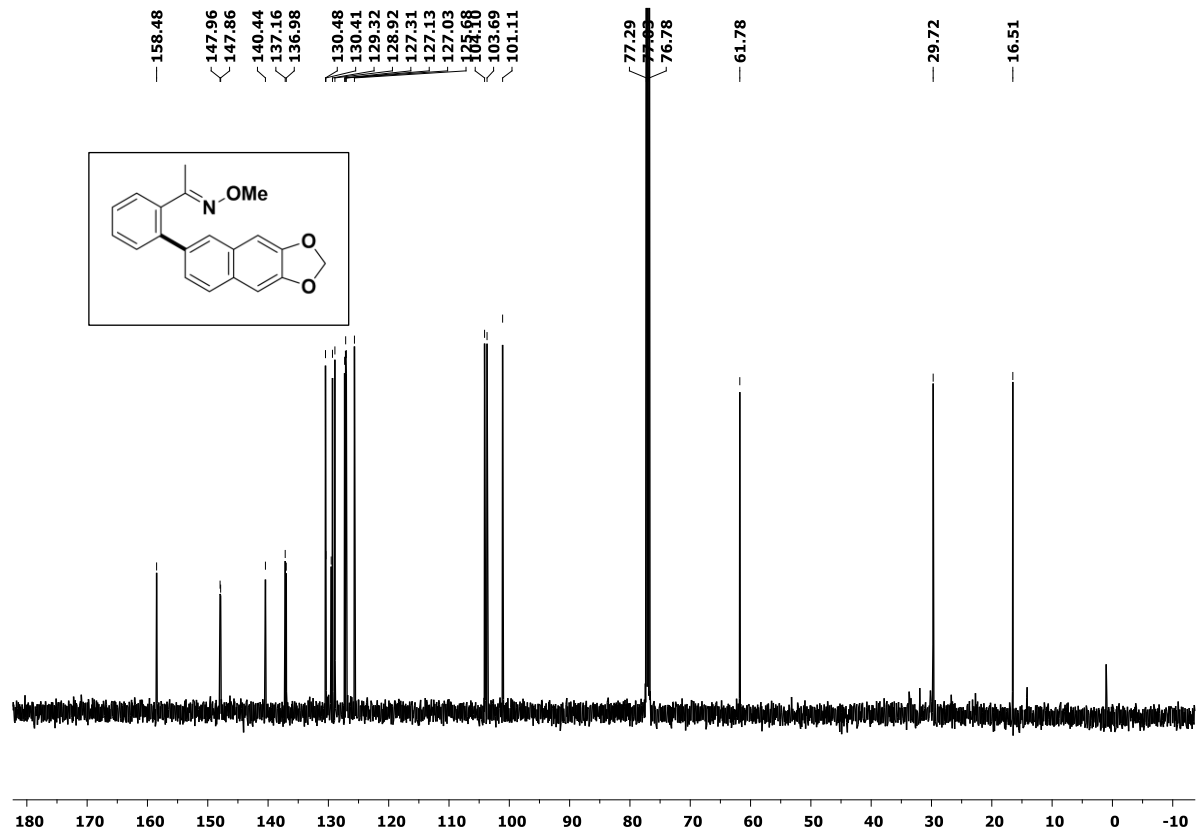


DEPT (135) NMR Spectrum of Compound **3ae.**

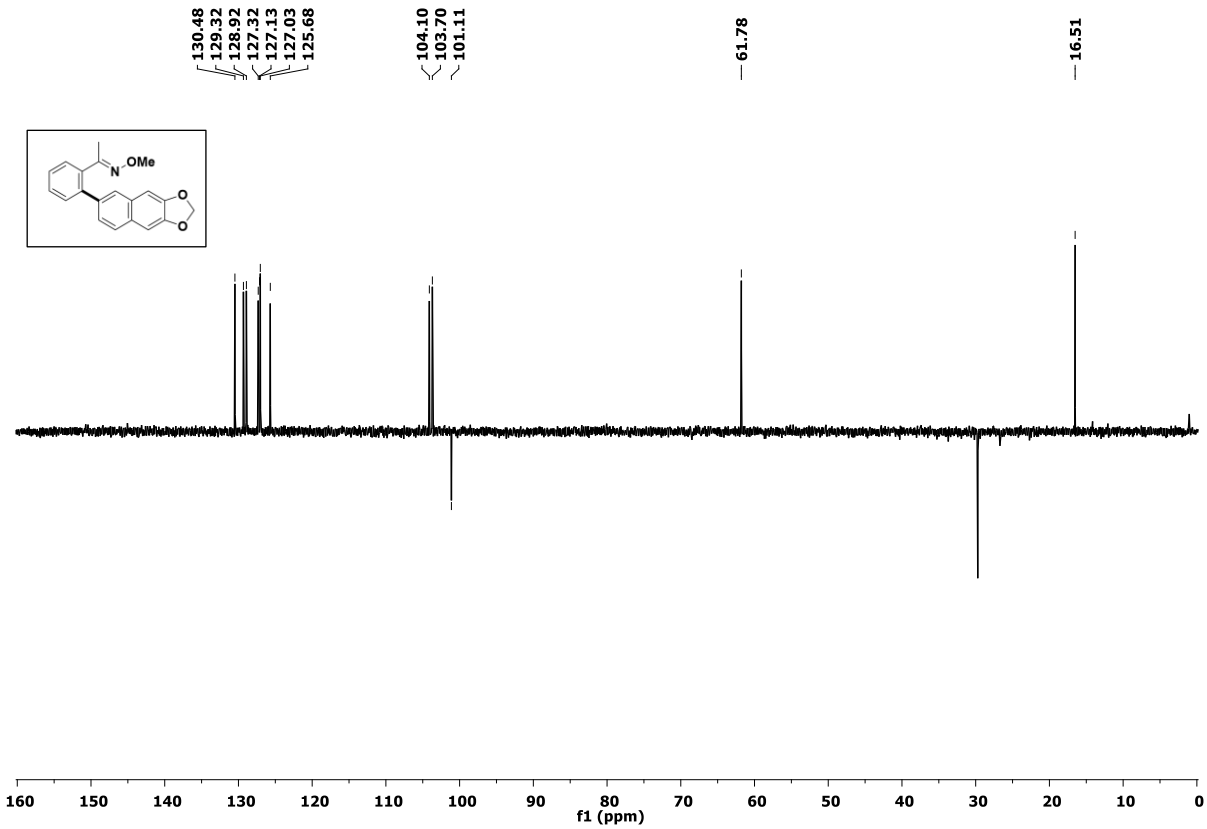


^{1}H and ^{13}C NMR Spectra of Compound **3ec.**

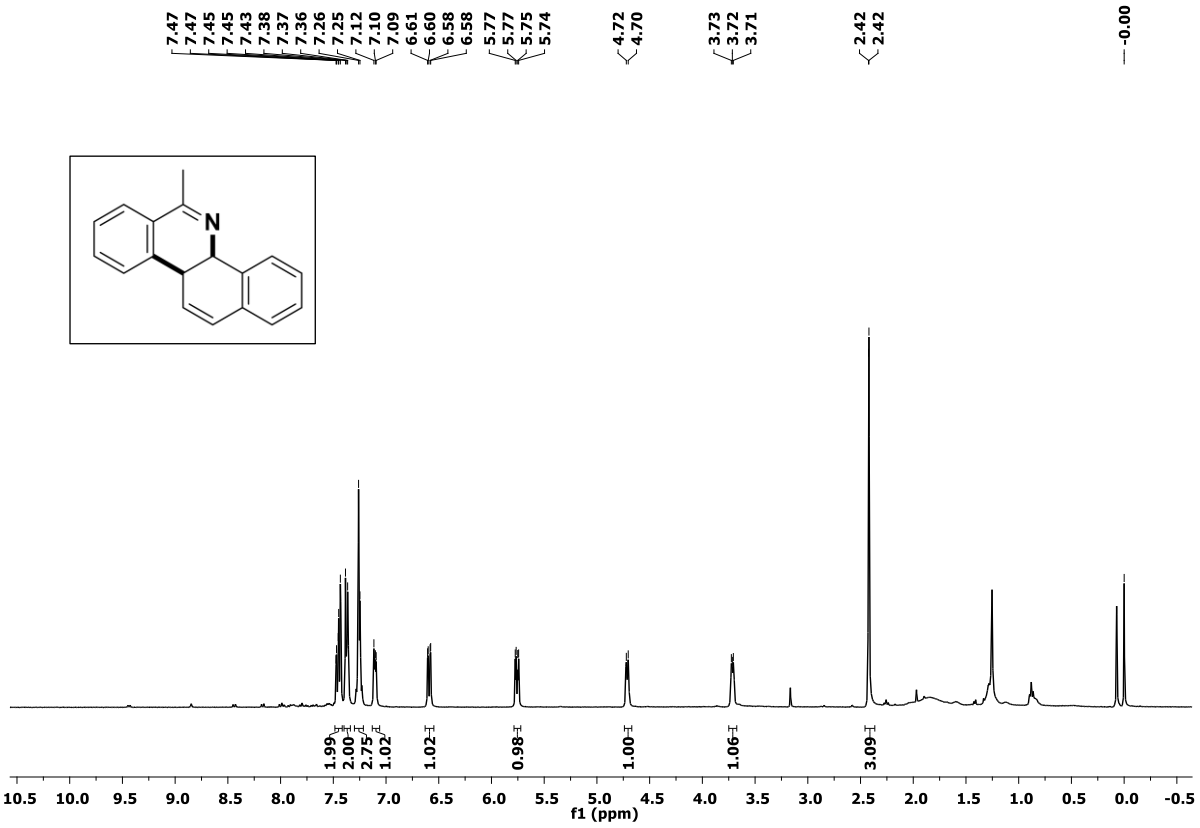


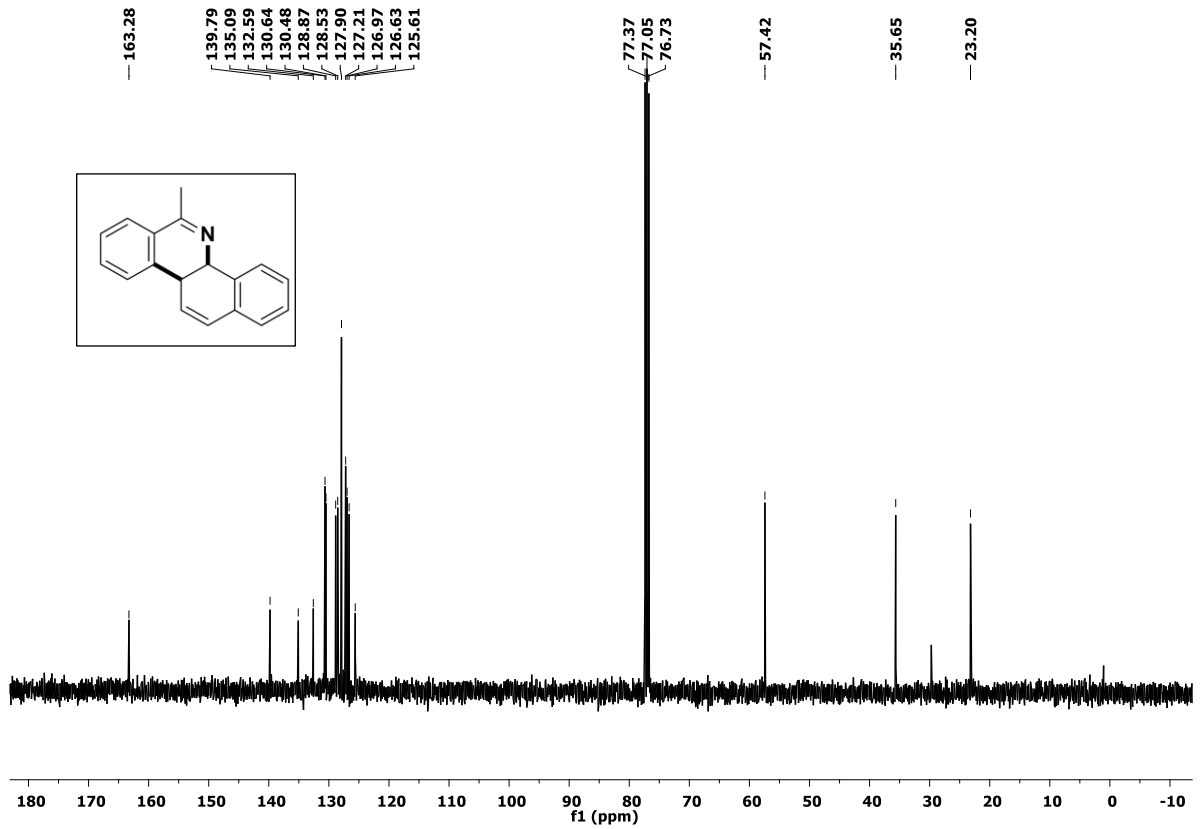


DEPT (135) NMR Spectrum of Compound **3ec.**

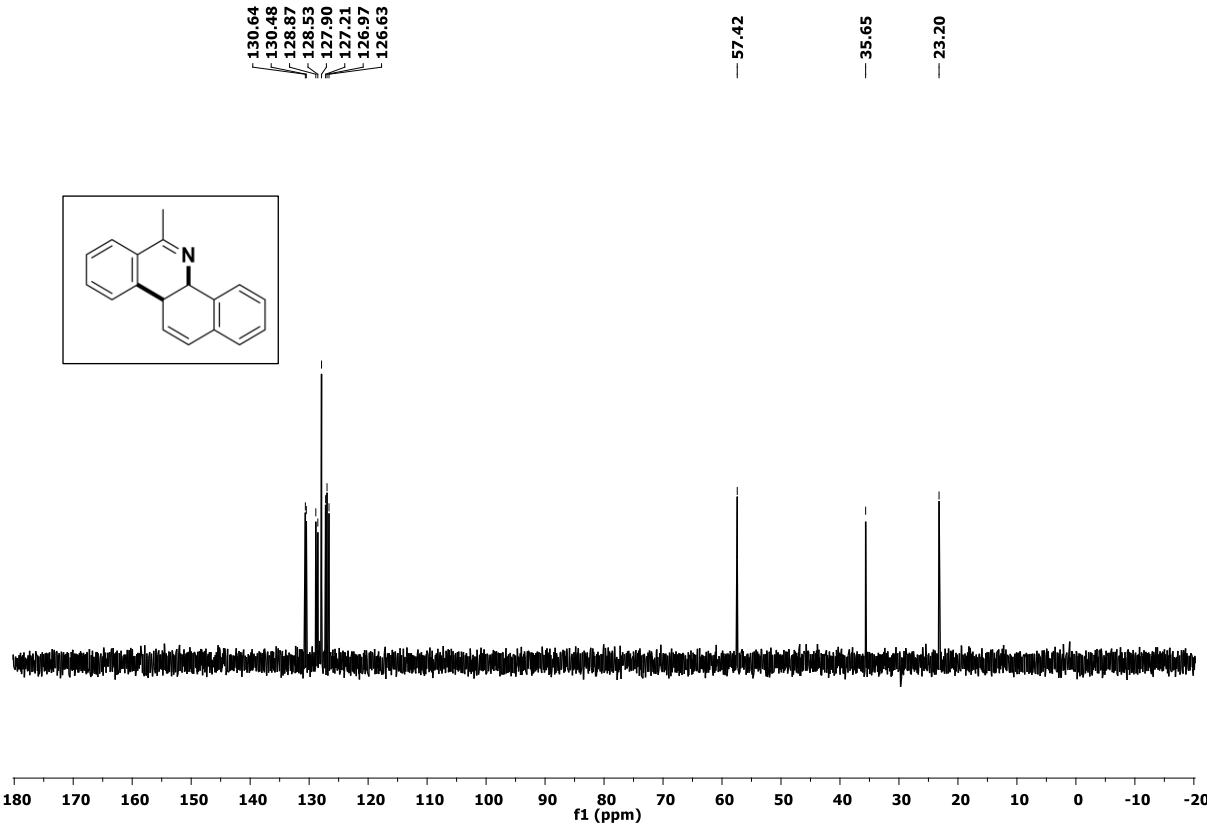


^{1}H and ^{13}C NMR Spectra of Compound **4a.**

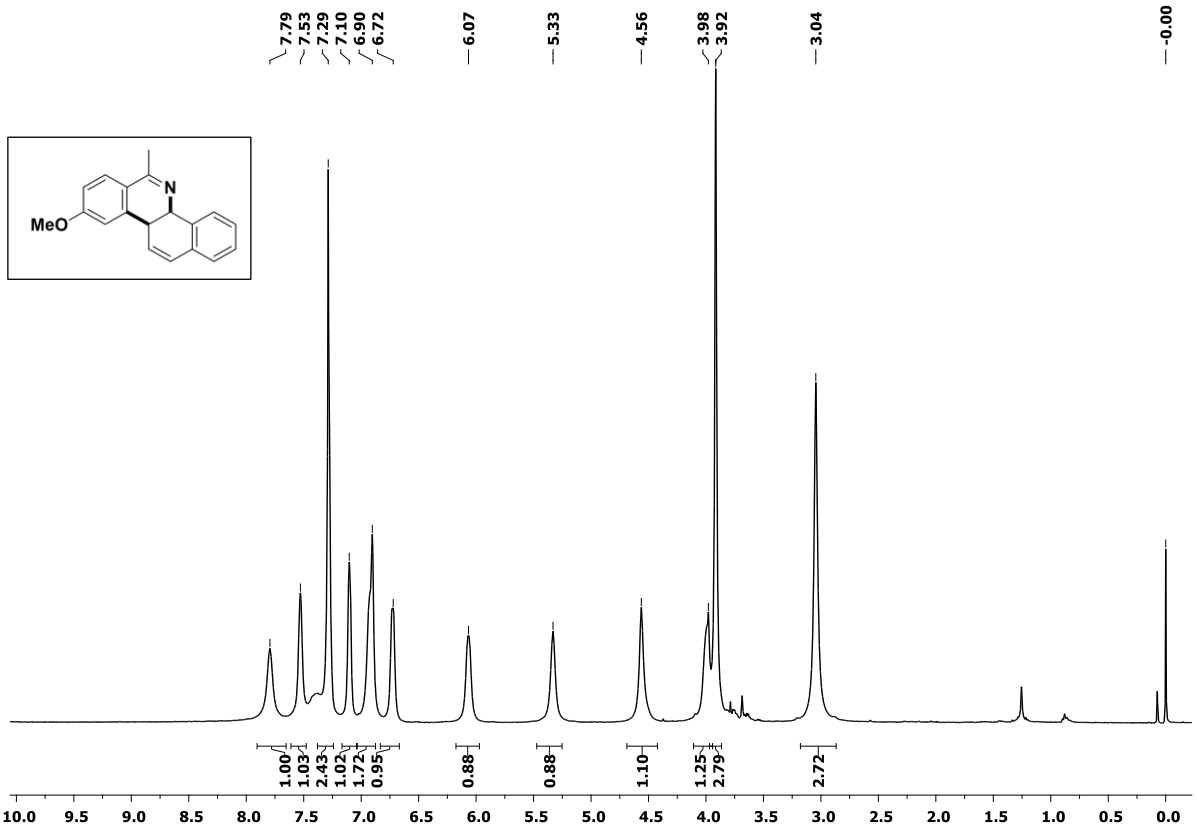




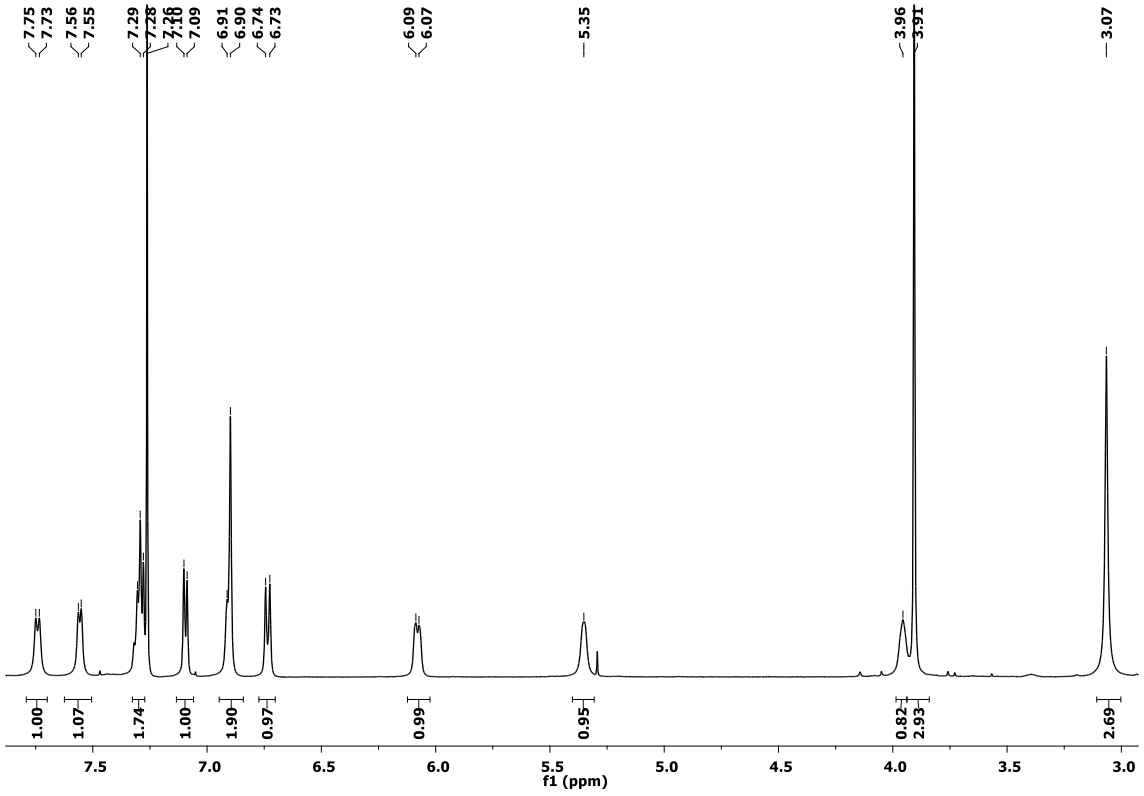
DEPT (135) NMR Spectrum of Compound **4a.**

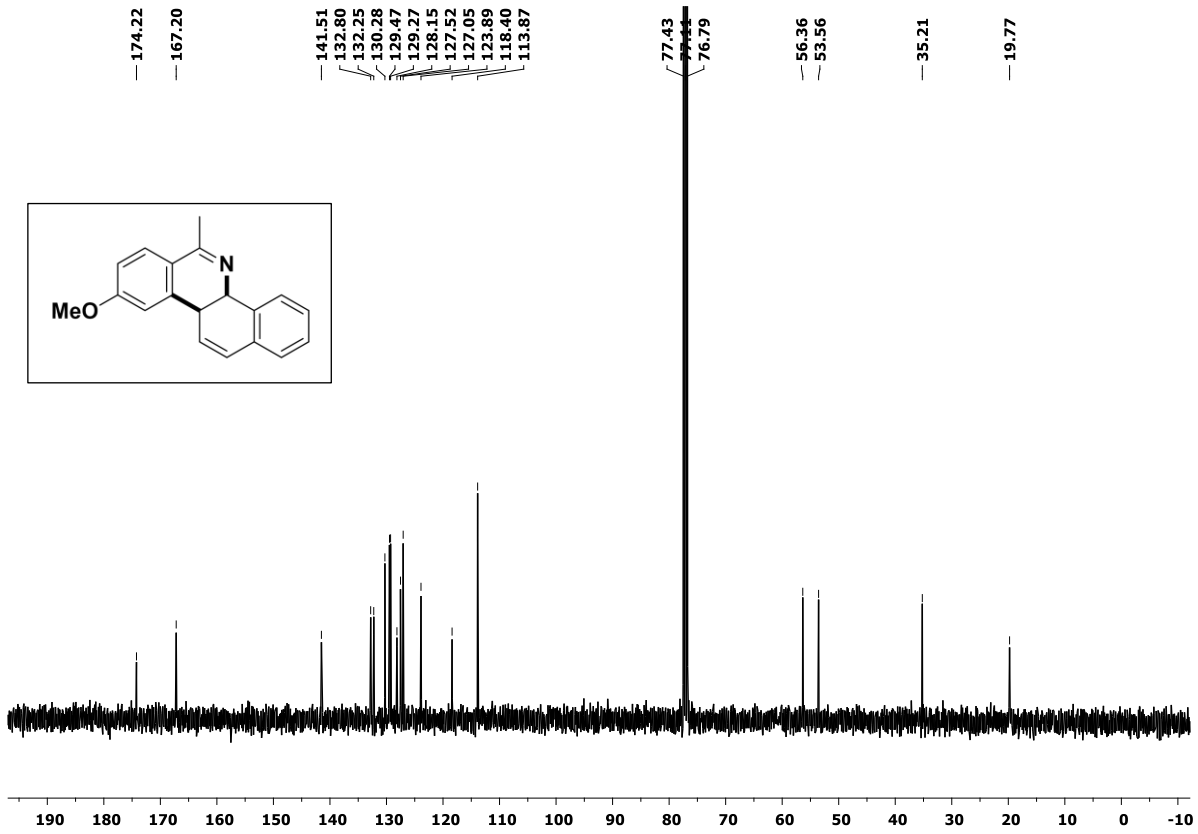


^{1}H and ^{13}C NMR Spectra of Compound **4b.**

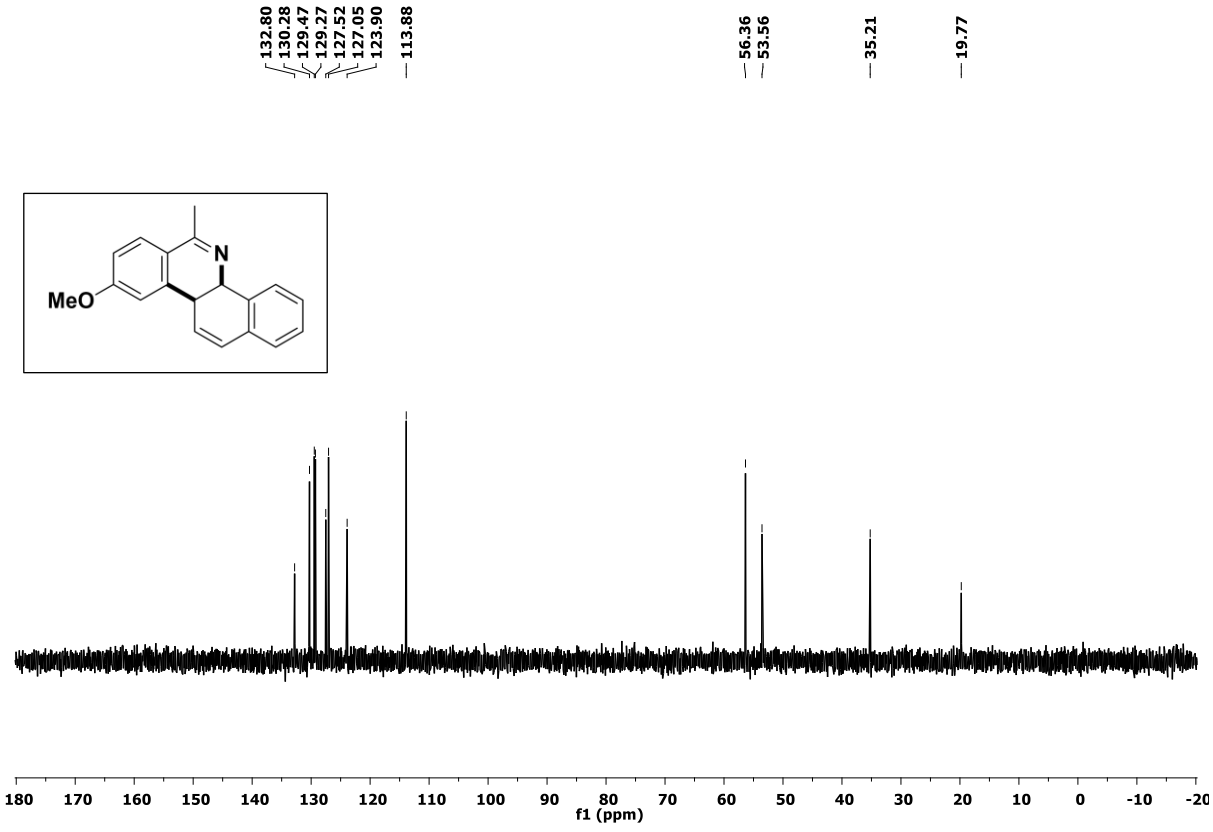


Fine shimming NMR expended Chemical shift 7.75 ppm to 3.0 ppm for better splitting

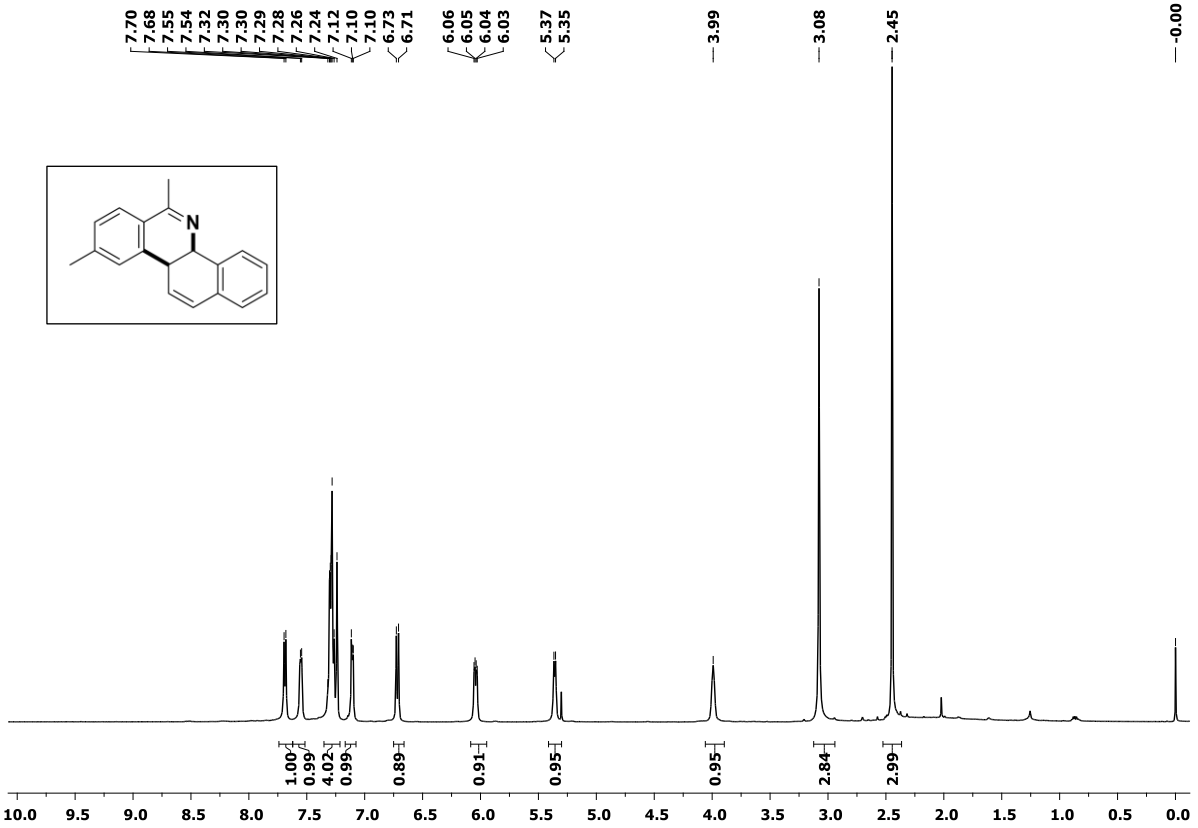


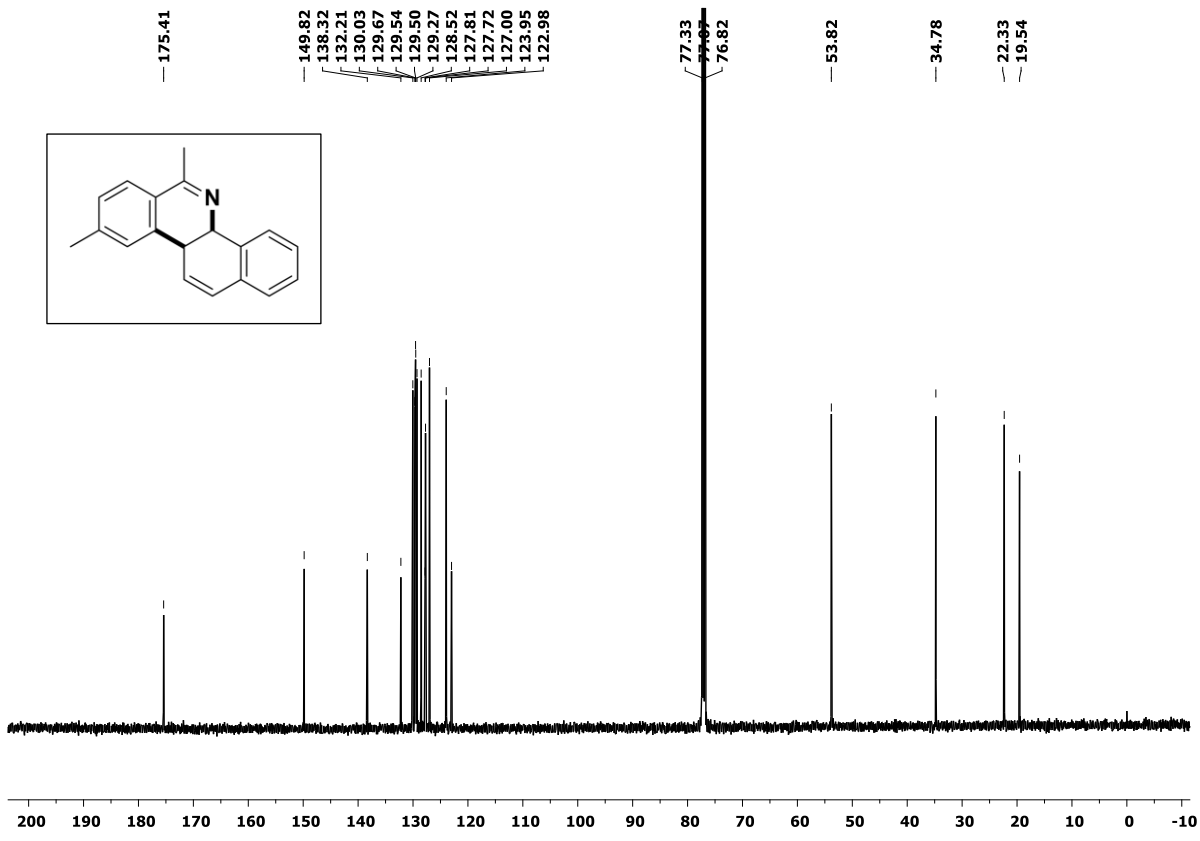


DEPT (135) NMR Spectrum of Compound **4b.**

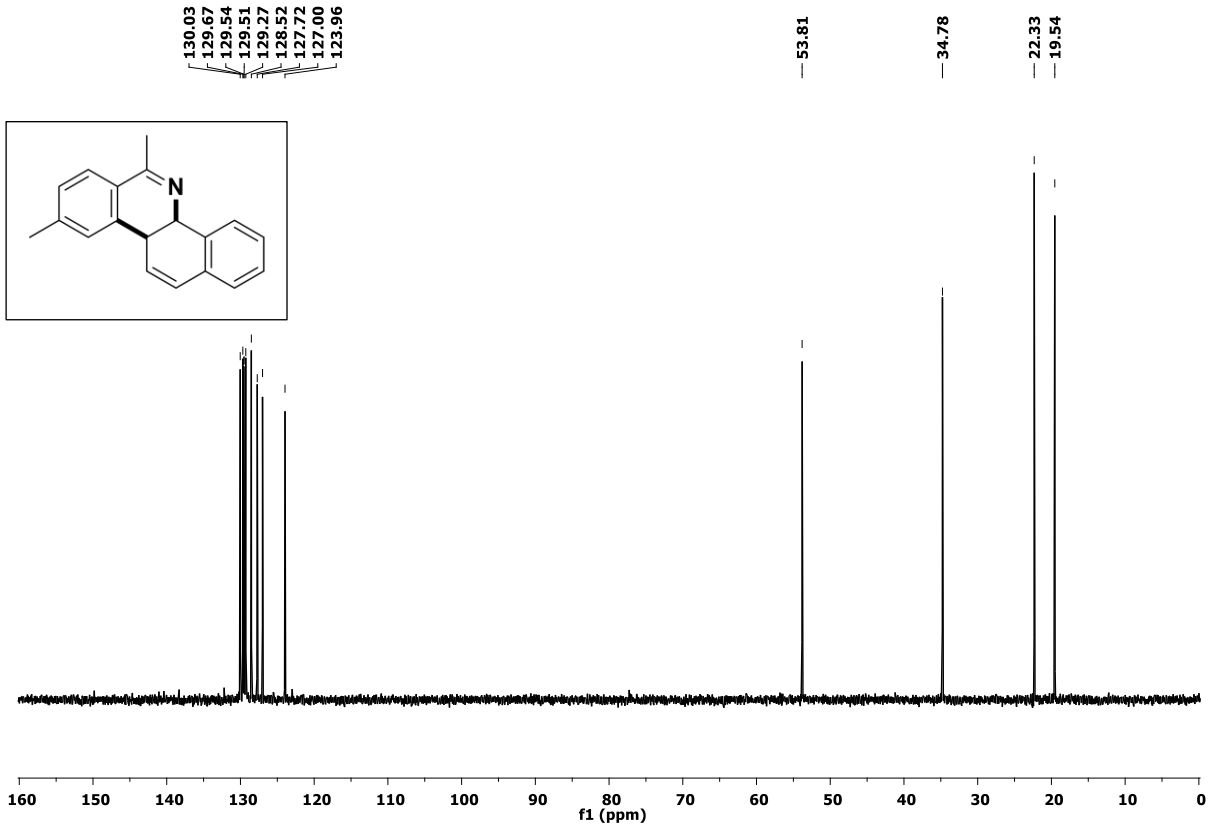


^{1}H and ^{13}C NMR Spectra of Compound **4c.**

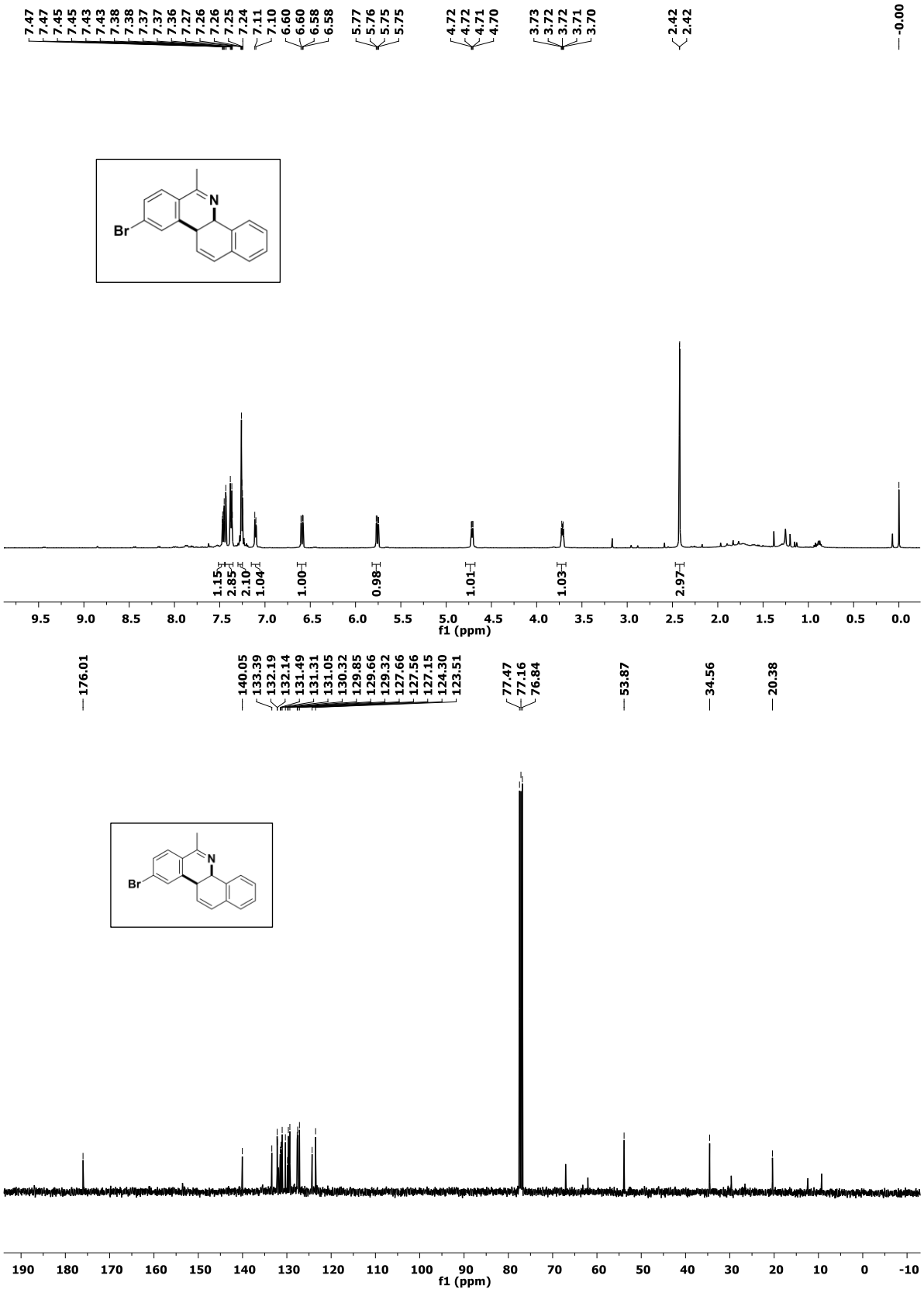




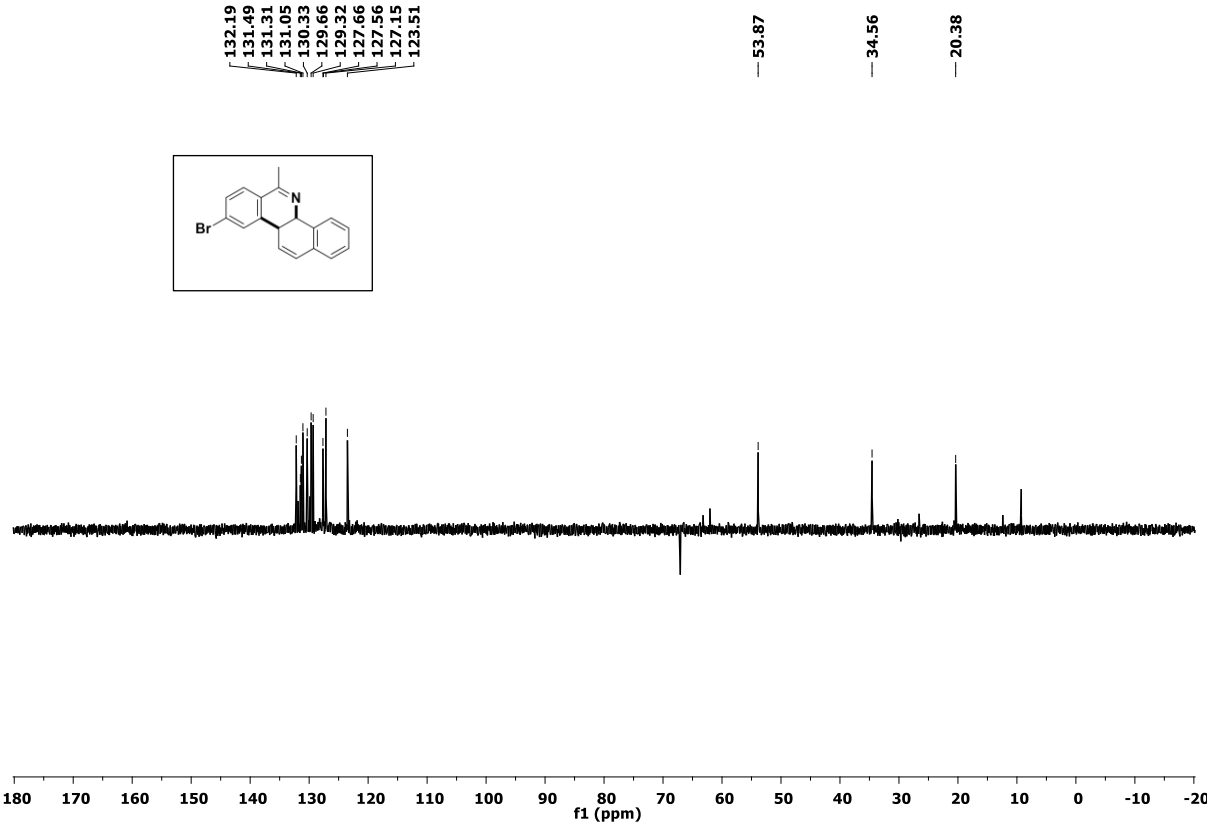
DEPT (135) NMR Spectrum of Compound **4c.**



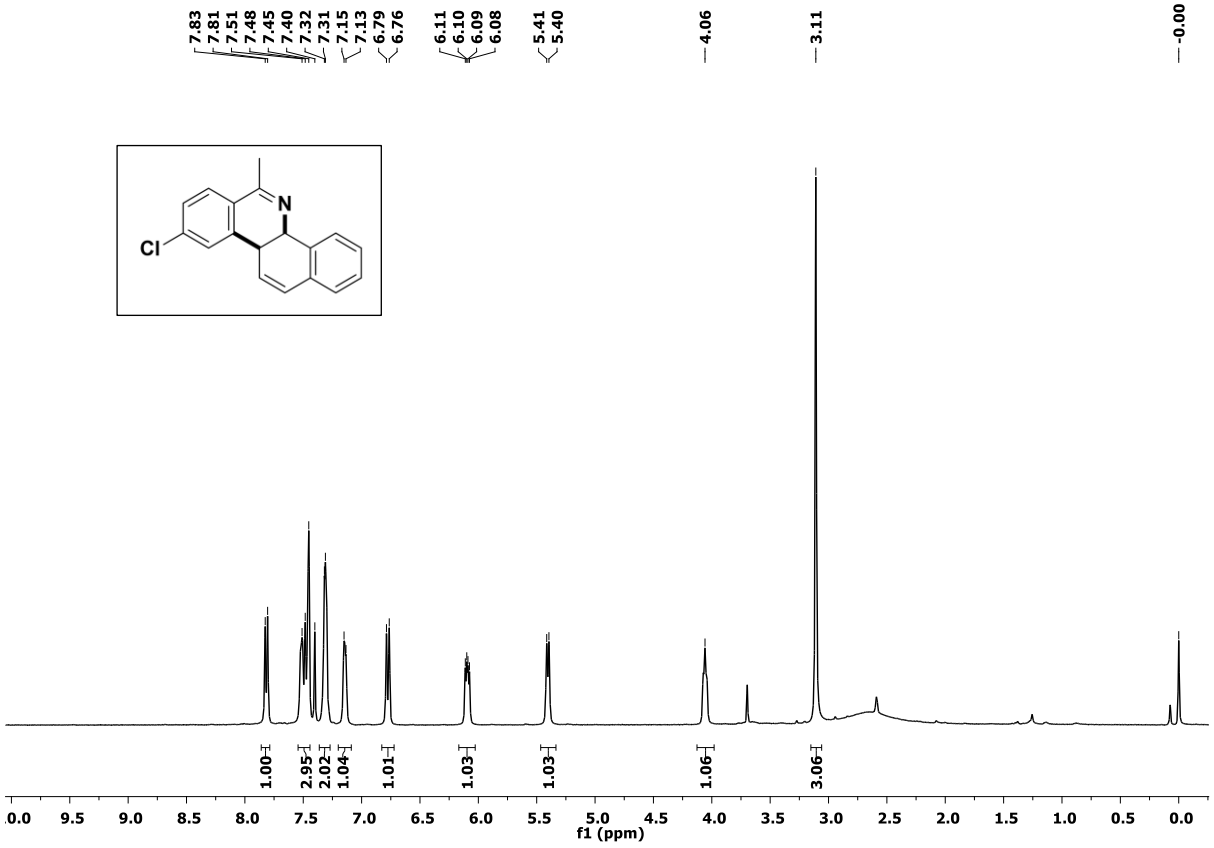
^{1}H and ^{13}C NMR Spectra of Compound **4d.**

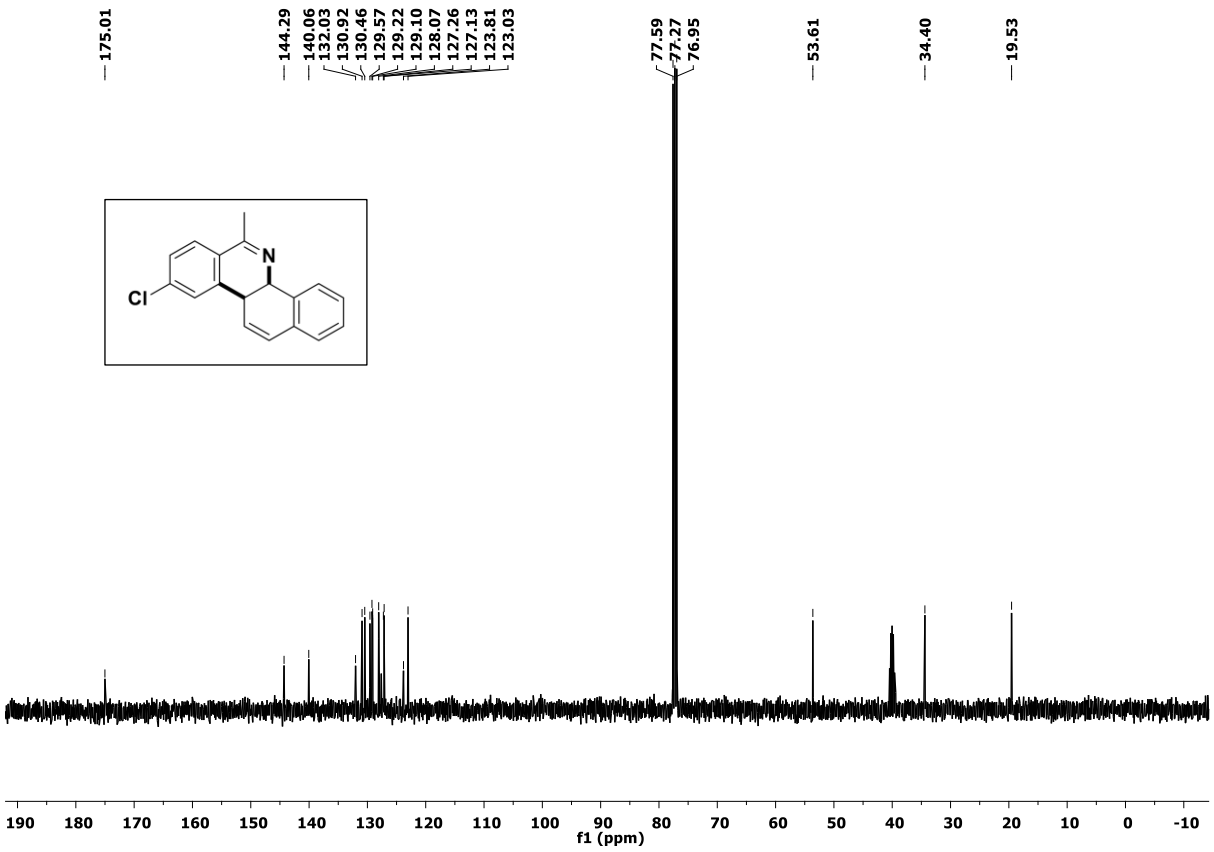


DEPT (135) NMR Spectrum of Compound **4d.**

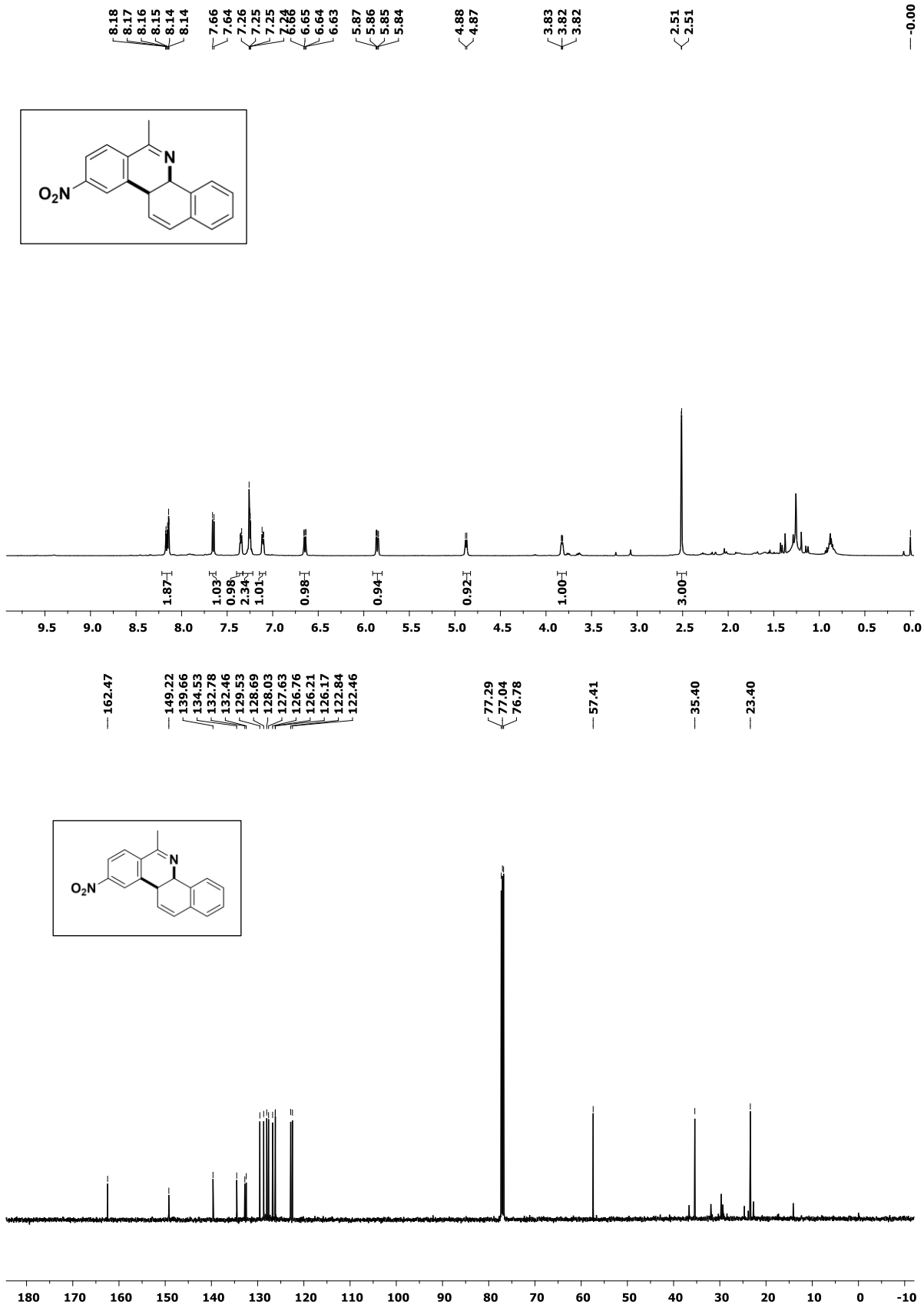


^{1}H and ^{13}C NMR Spectra of Compound **4e.**

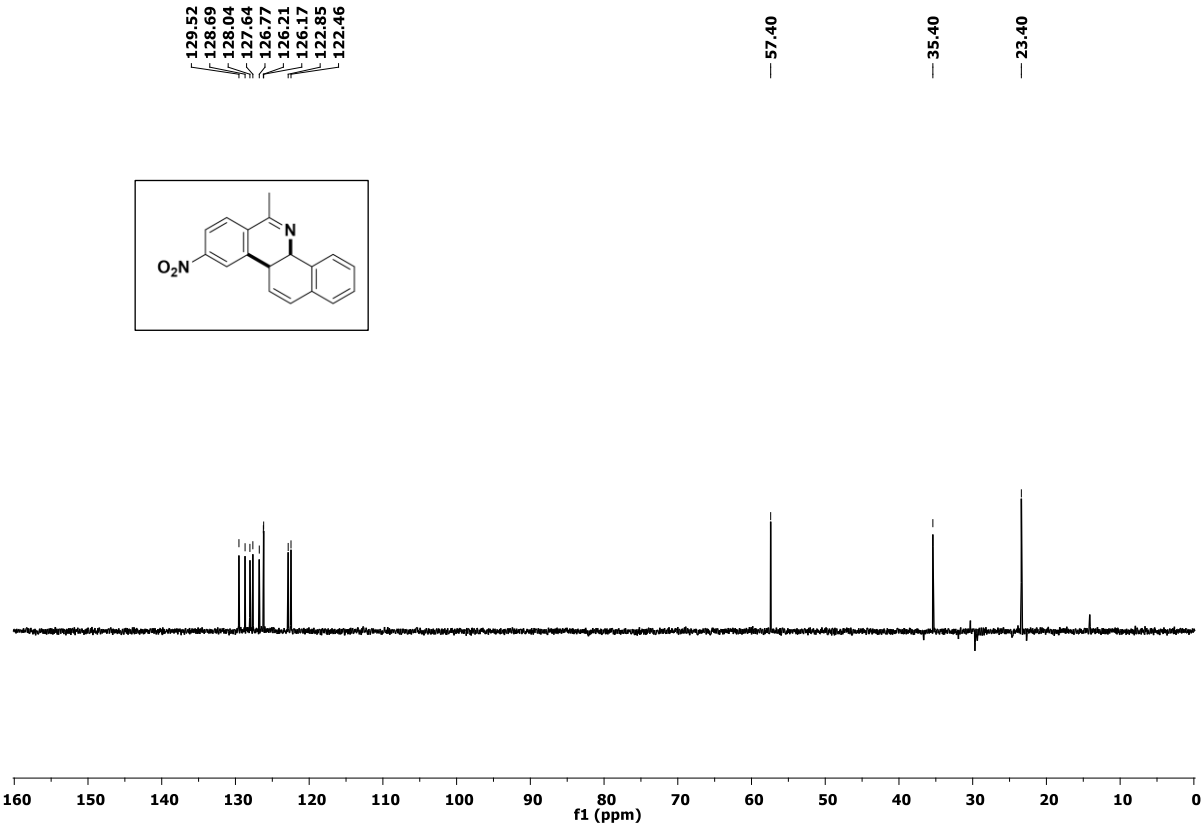




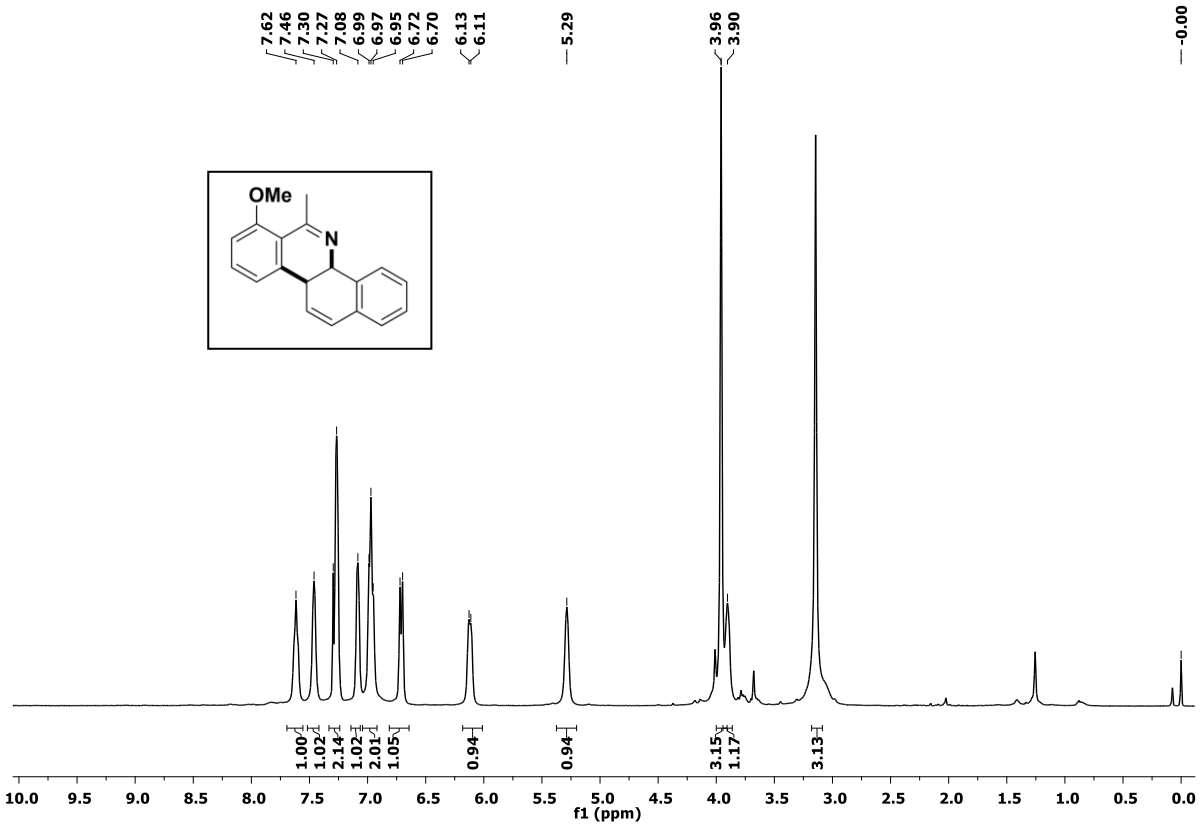
^{1}H and ^{13}C NMR Spectra of Compound **4f.**



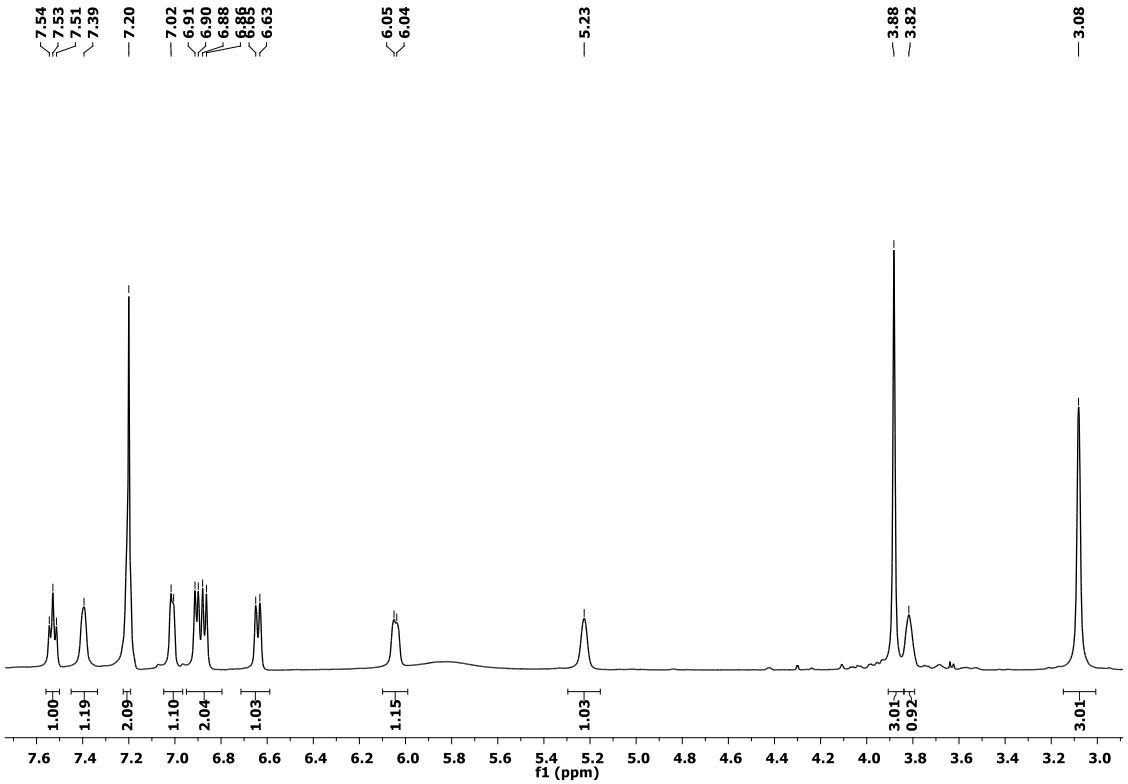
DEPT (135) NMR Spectrum of Compound **4f.**

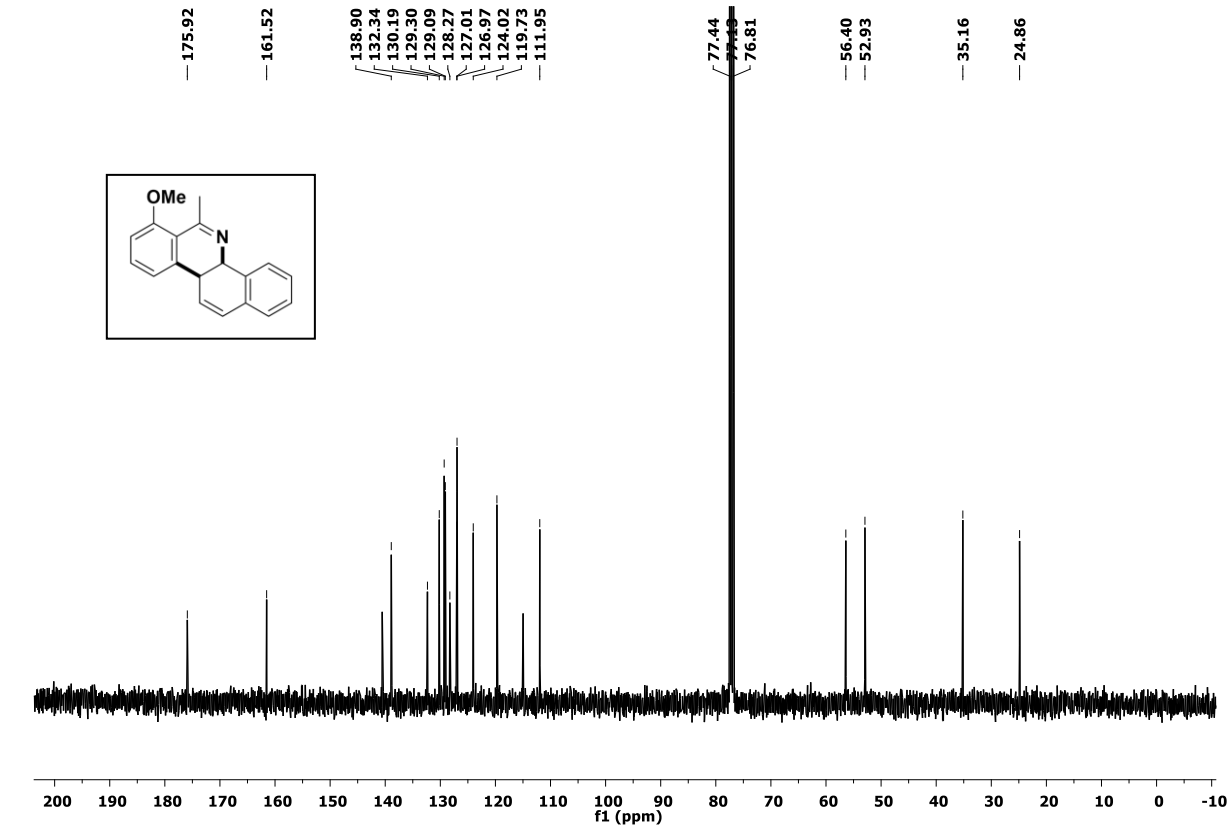


^{1}H and ^{13}C NMR Spectra of Compound **4g.**

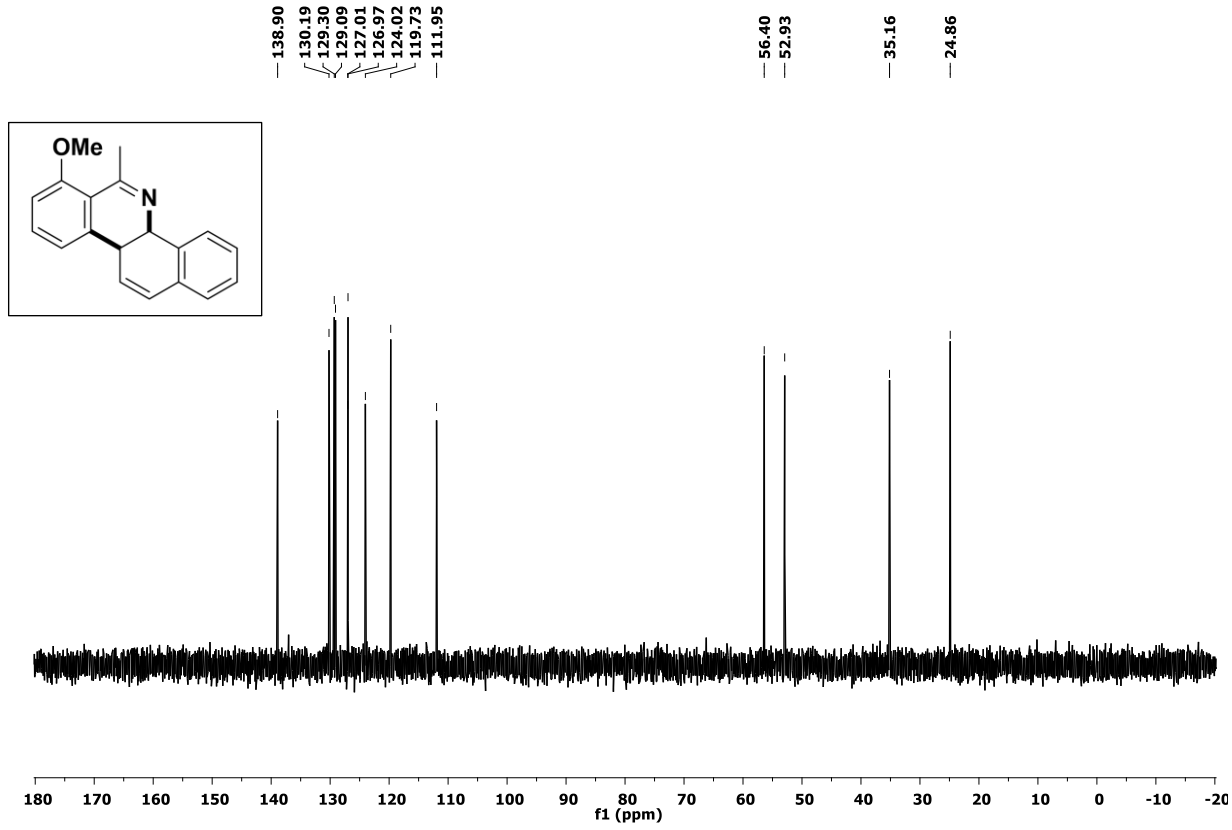


Fine shimming NMR expended Chemical shift 7.6 ppm to 3.0 ppm for better splitting

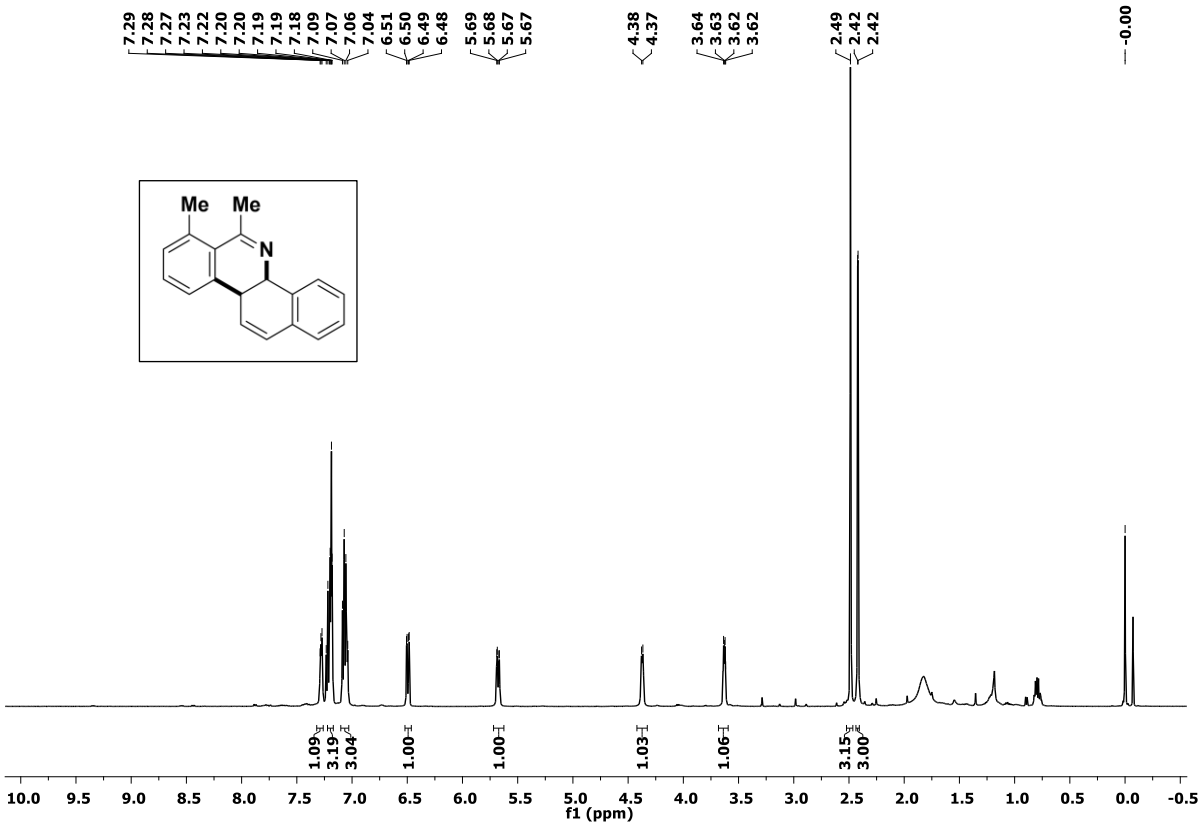


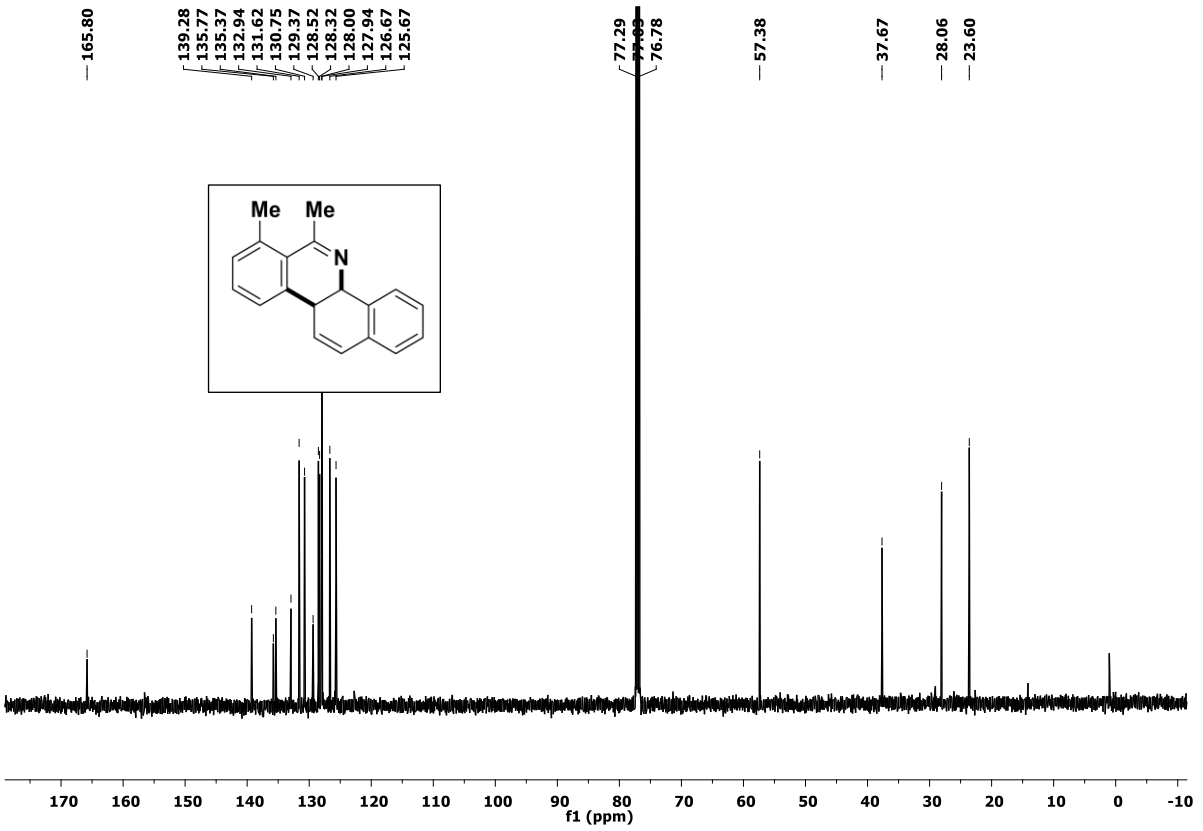


DEPT (135) NMR Spectrum of Compound **4g.**

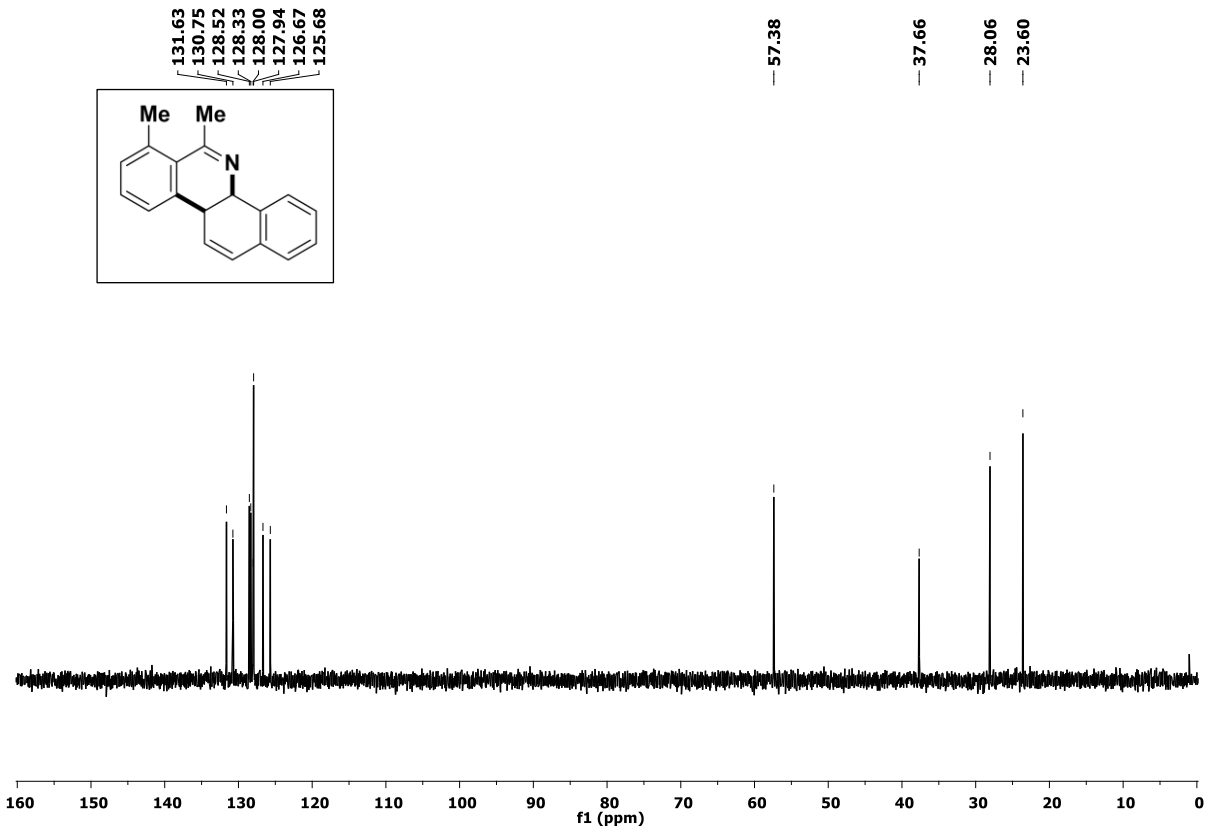


^{1}H and ^{13}C NMR Spectra of Compound **4h.**

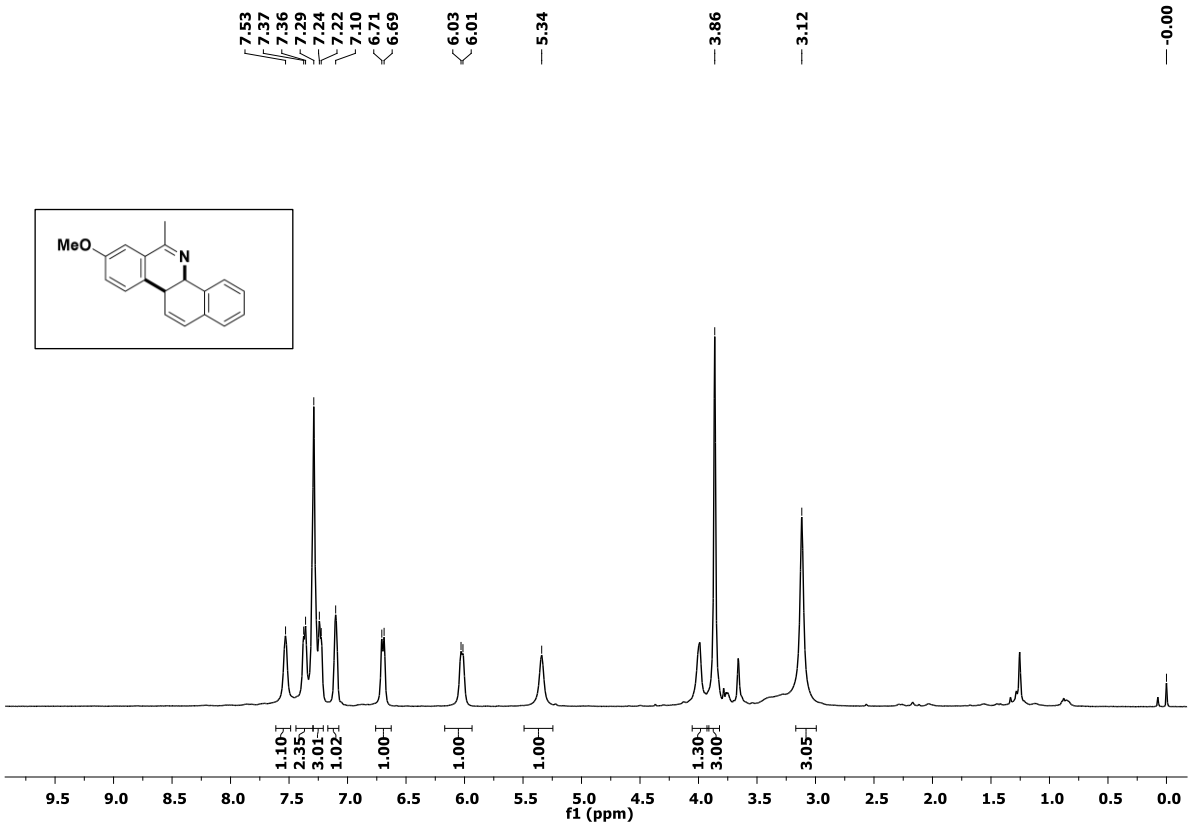




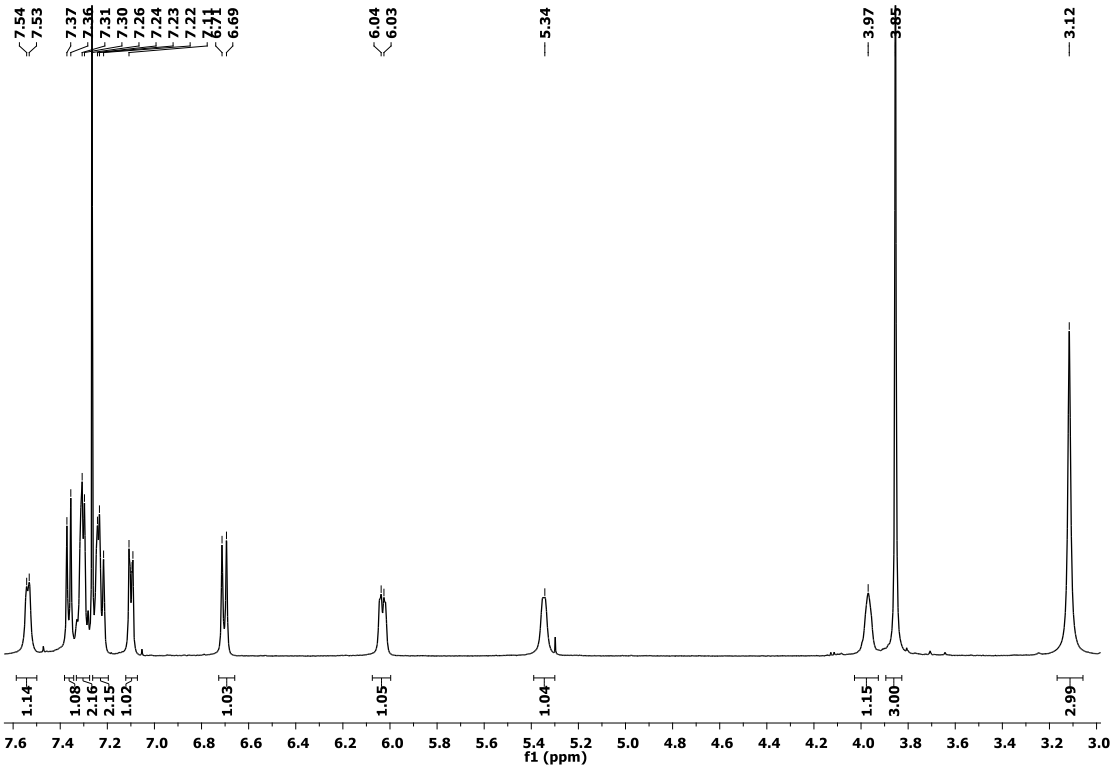
DEPT (135) NMR Spectrum of Compound **4h.**

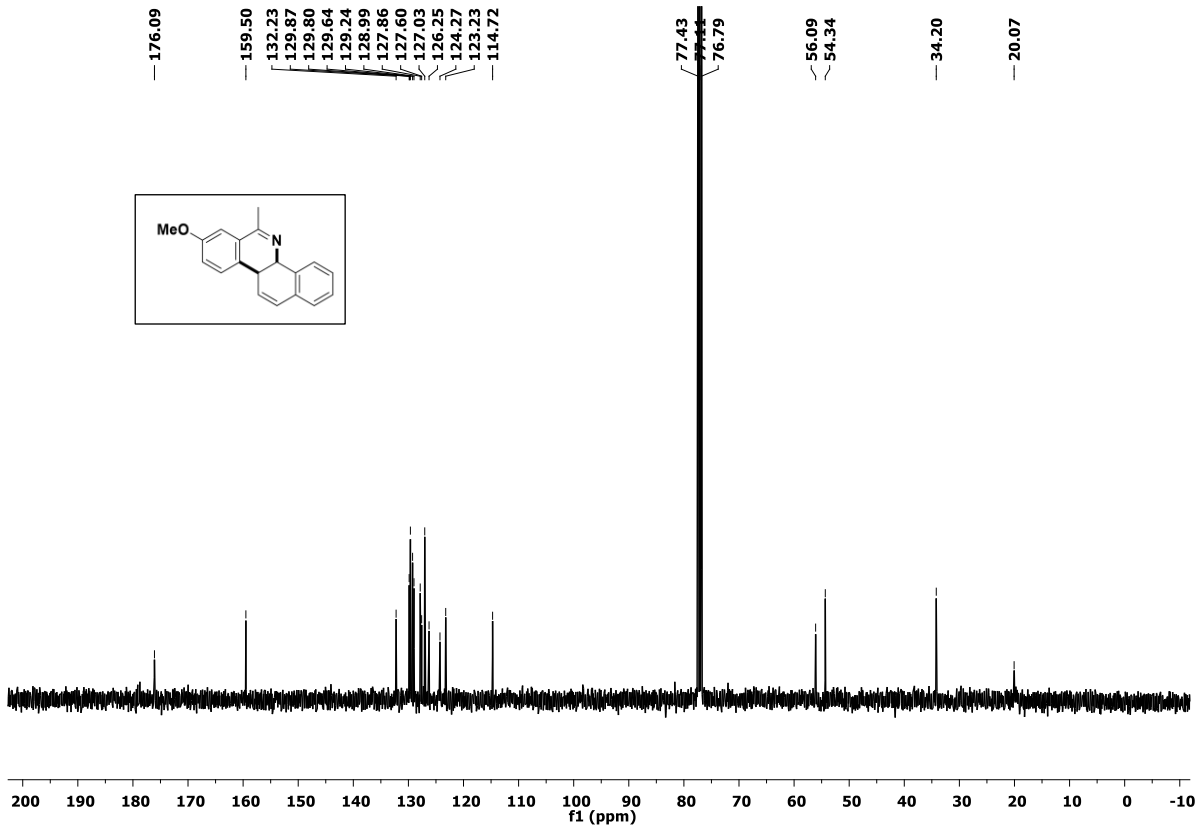


^{1}H and ^{13}C NMR Spectra of Compound **4i.**

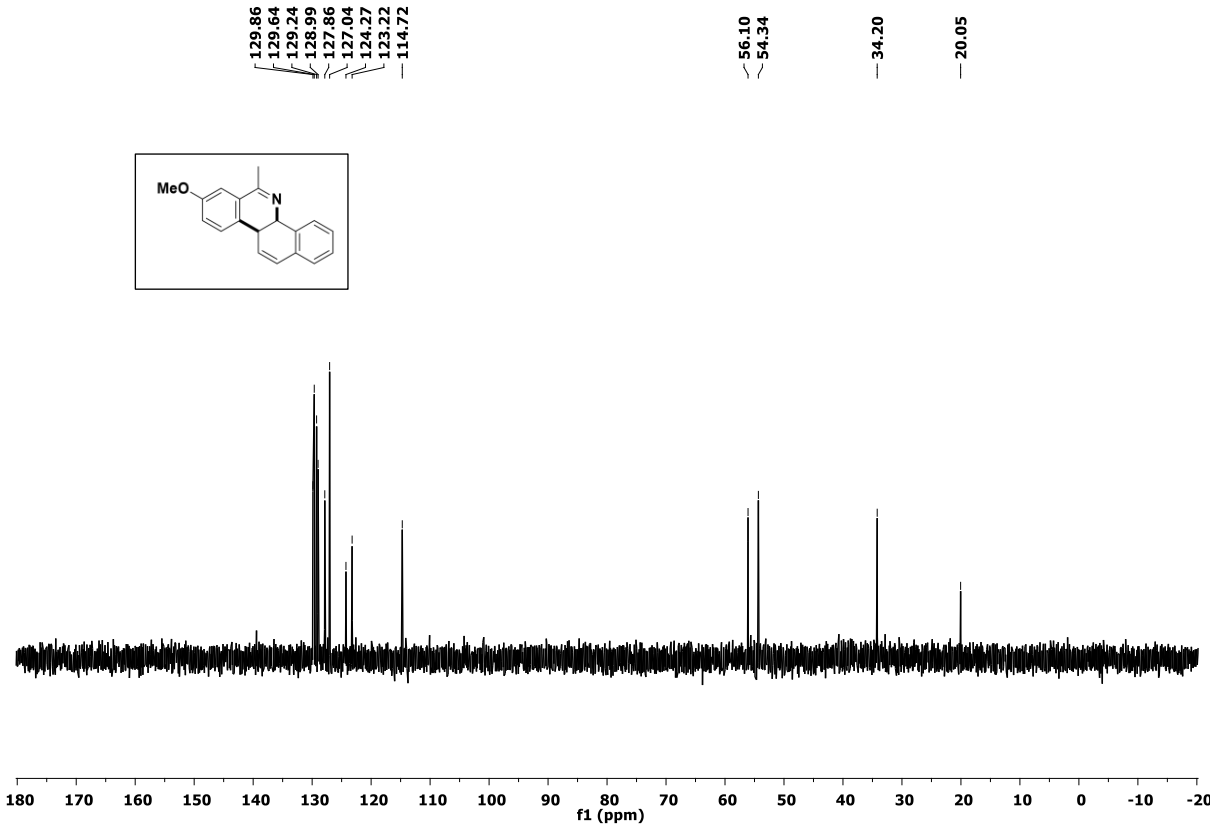


Fine shimming NMR expended: Chemical shift 7.54 ppm to 3.0 ppm for better splitting

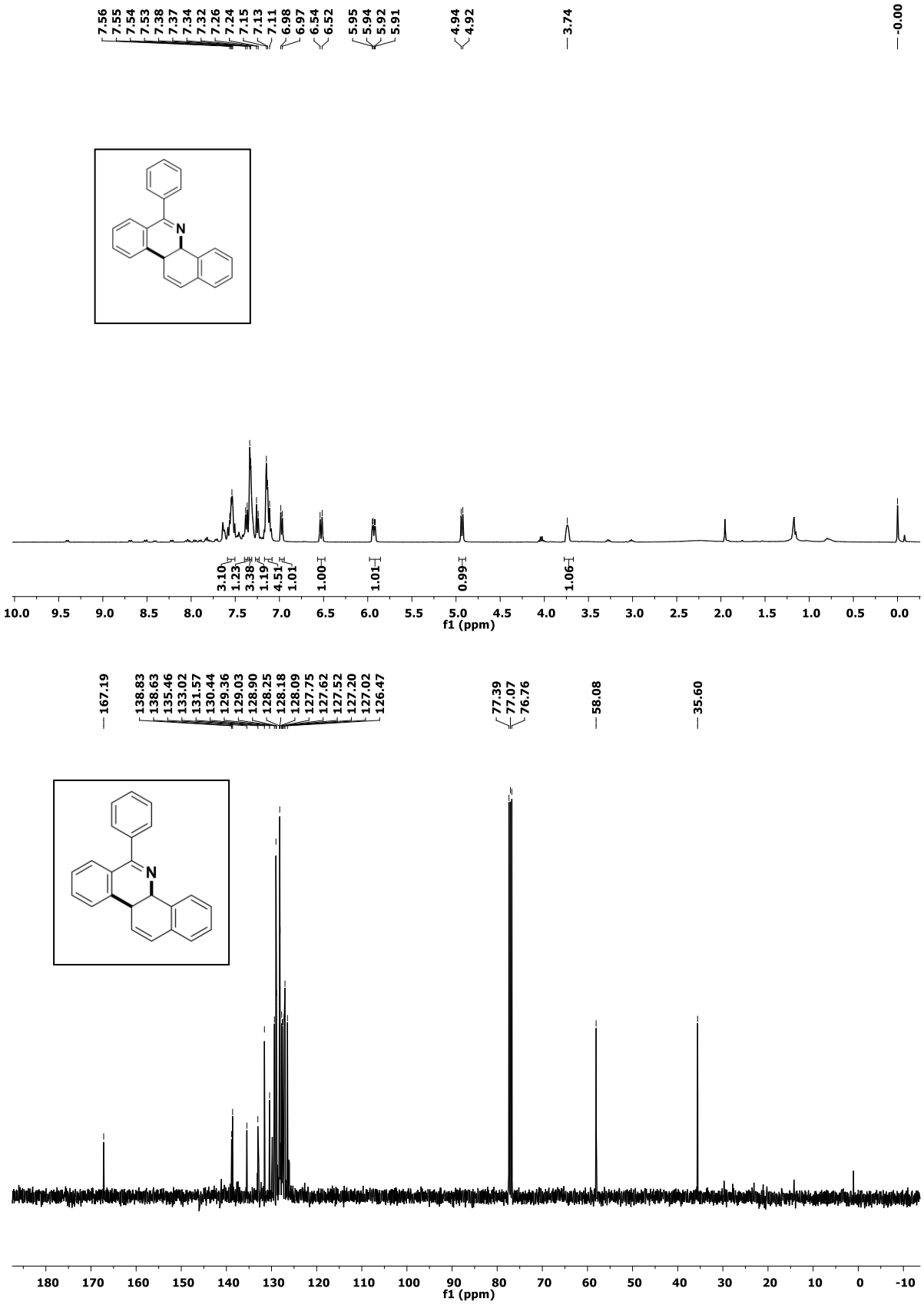




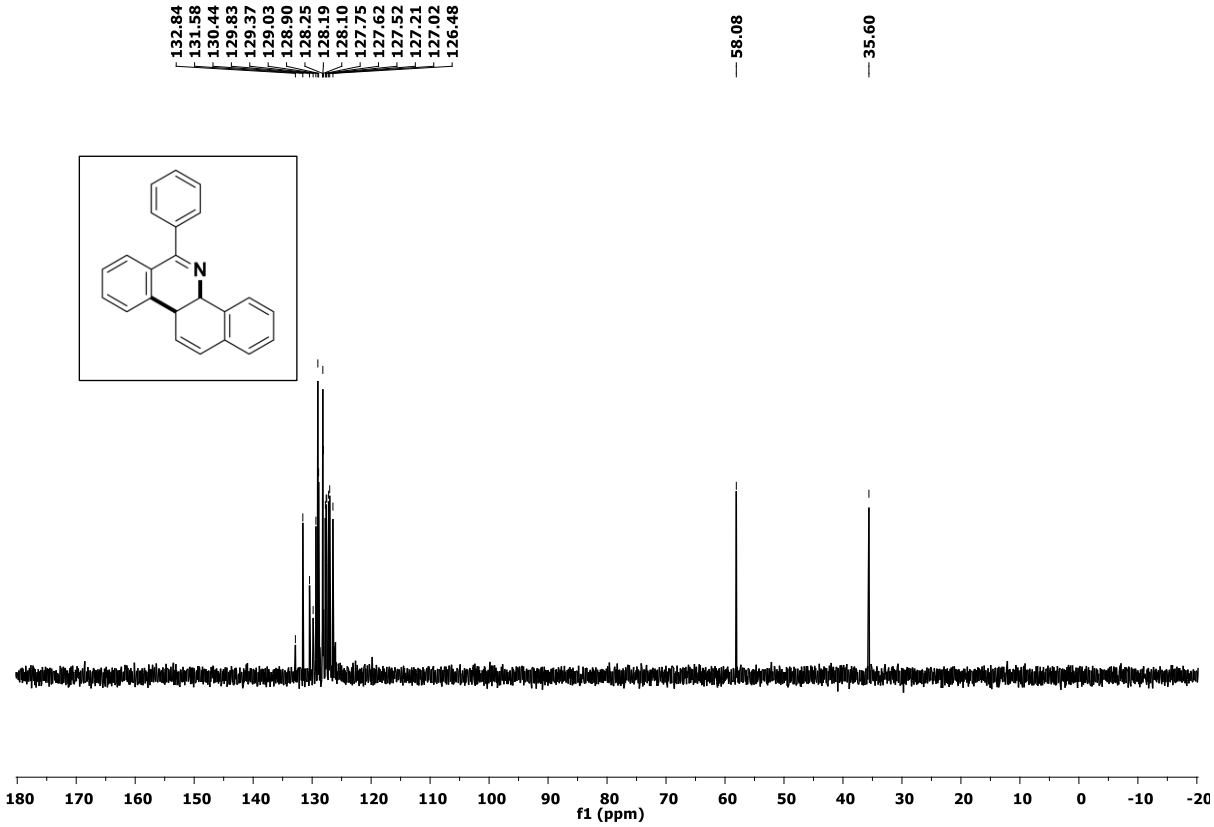
DEPT (135) NMR Spectrum of Compound **4i.**



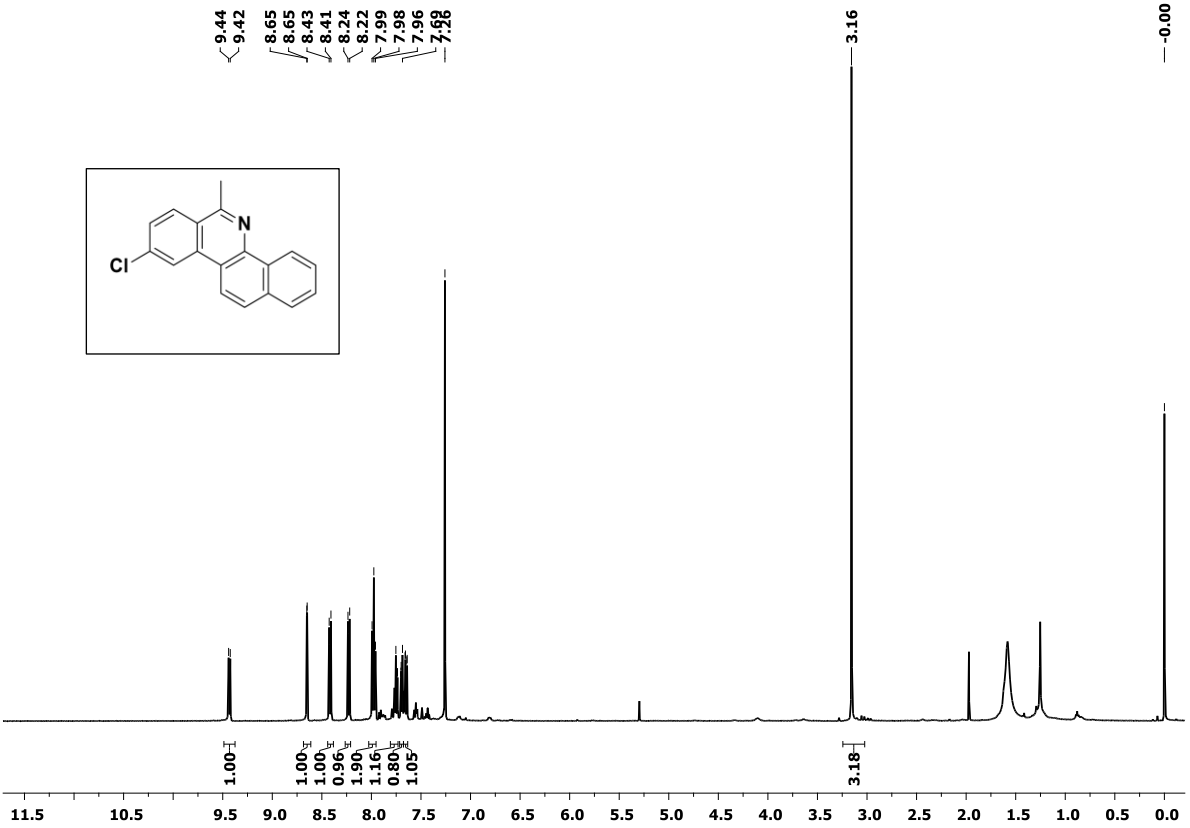
^{1}H and ^{13}C NMR Spectra of Compound **4j.**

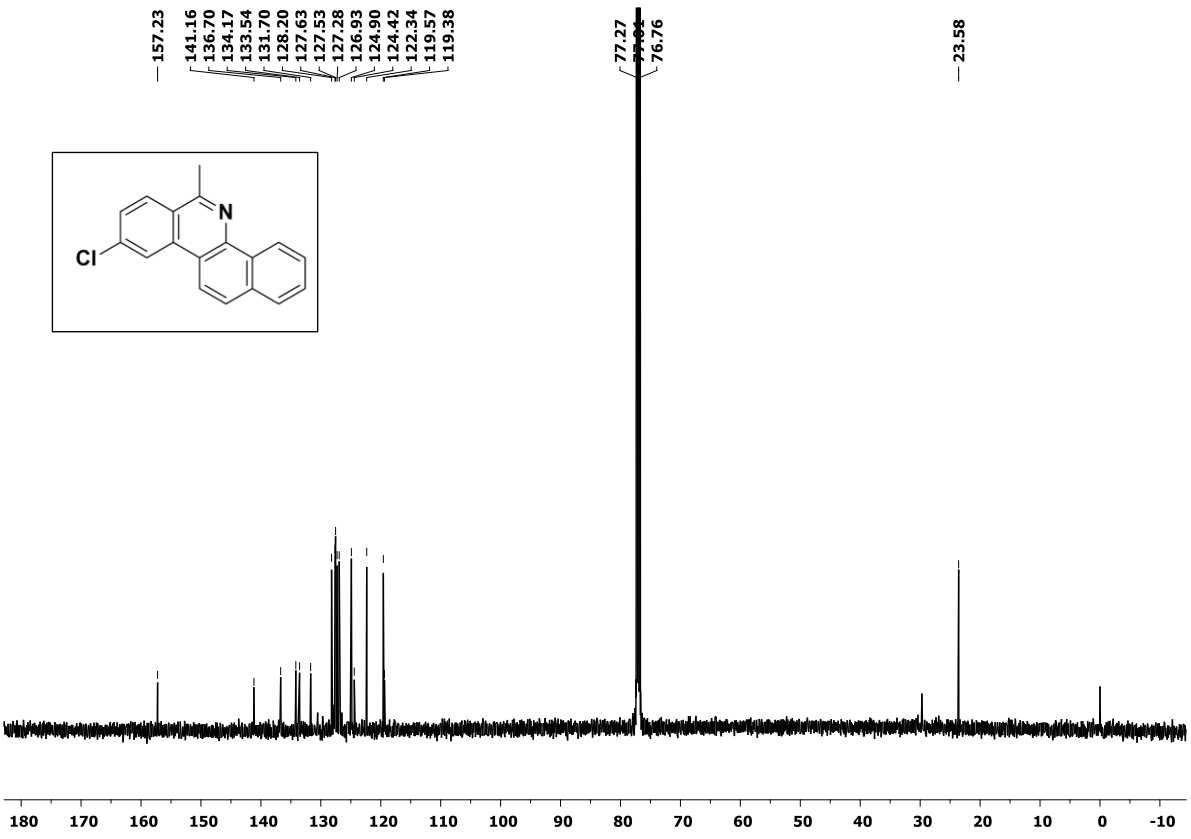


DEPT (135) NMR Spectrum of Compound **4j.**

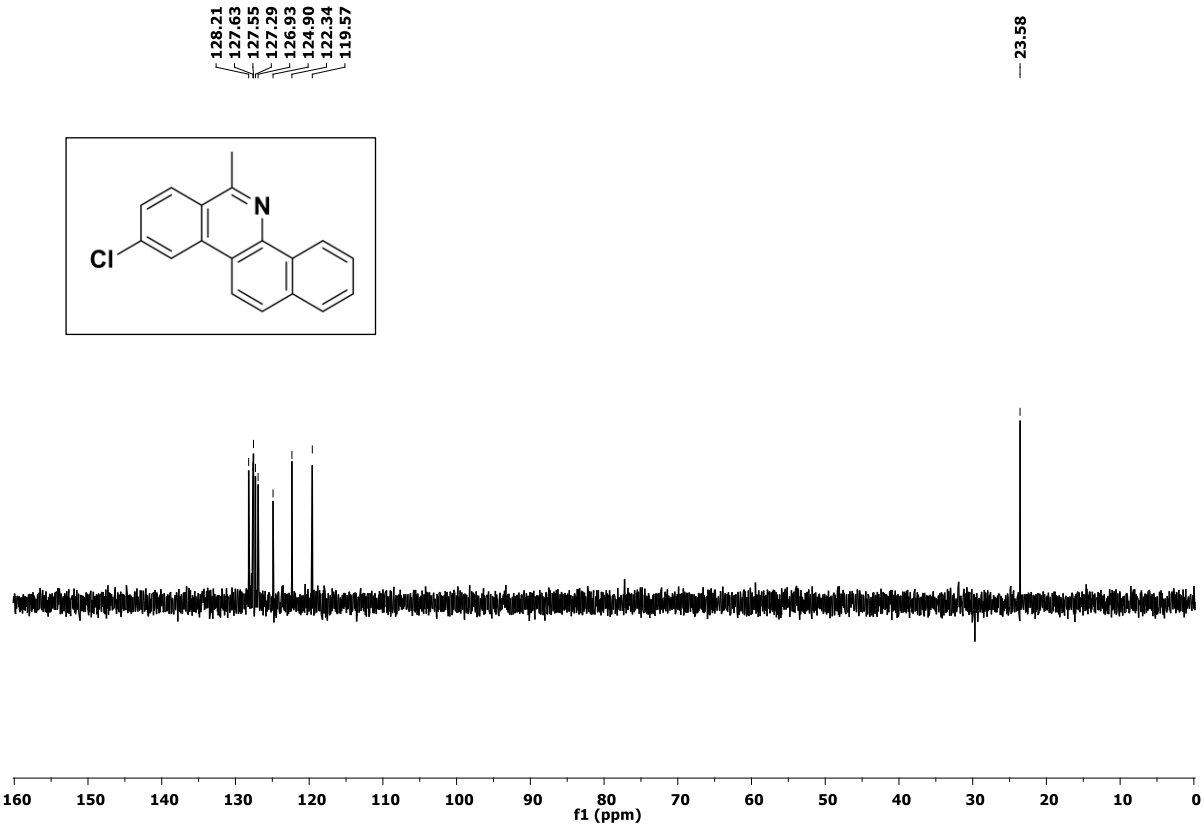


^{1}H and ^{13}C NMR Spectra of Compound **5a.**

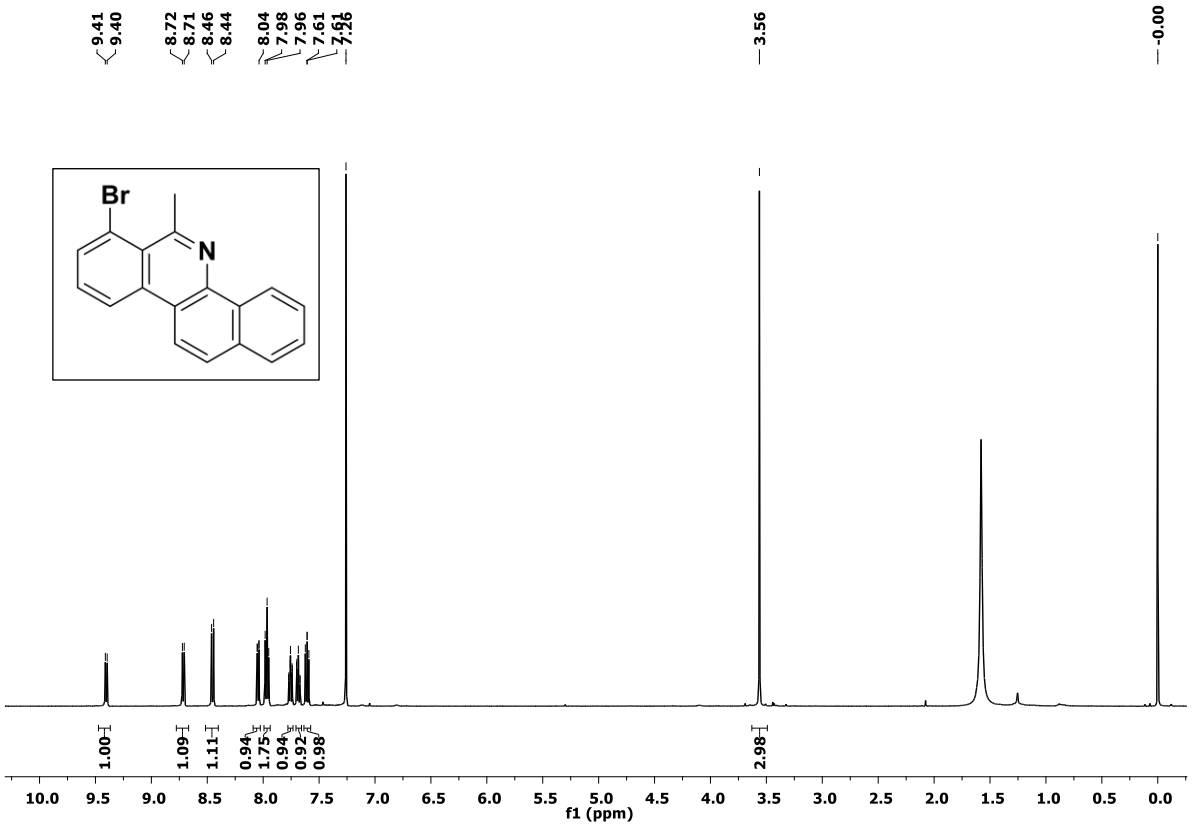


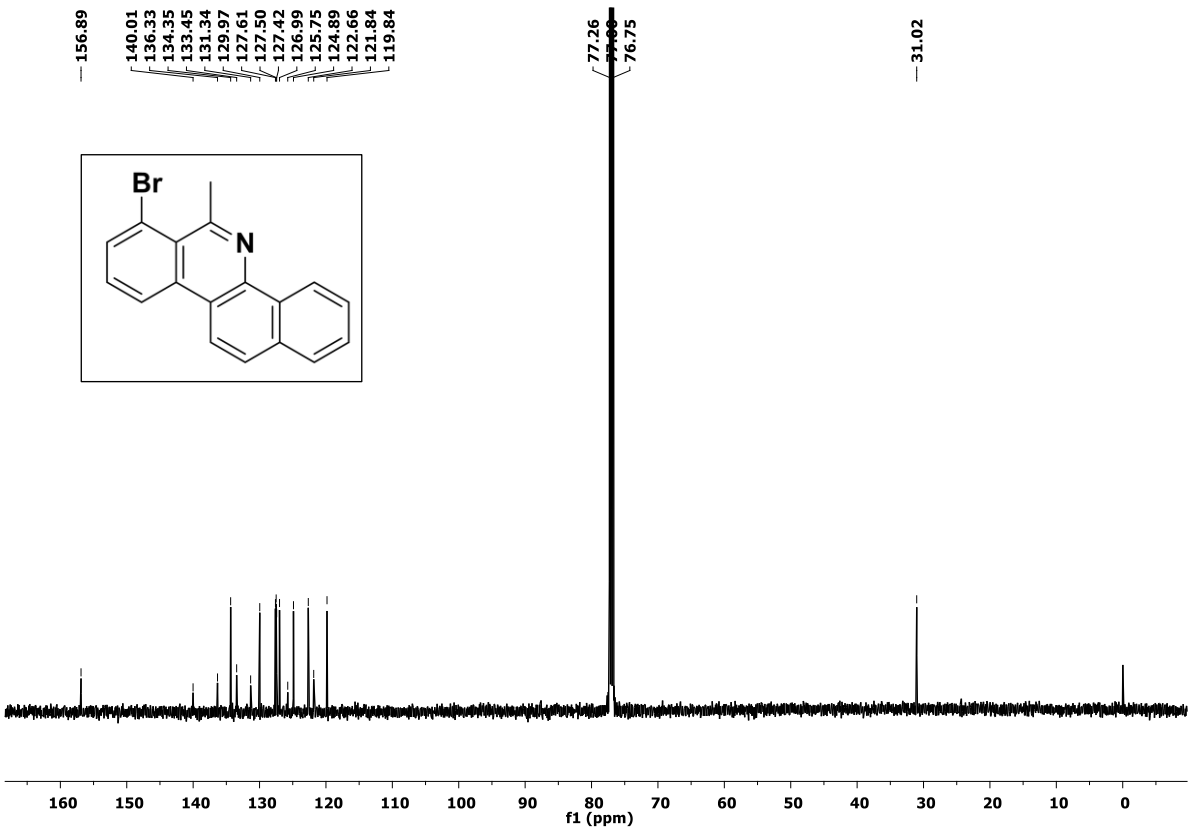


DEPT (135) NMR Spectrum of Compound **5a.**



^{1}H and ^{13}C NMR Spectra of Compound **5b.**





DEPT (135) NMR Spectrum of Compound **5b.**