SUPPORTING INFORMATION

New Synthetic Routes towards Enantiopure Nitrogen Donor Ligands

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EXPERIMENTAL SECTION

General procedures. Unless otherwise specified, materials were obtained from commercial suppliers and were used without further purification. All reactions requiring anhydrous conditions were conducted in oven-dried glassware under a dry nitrogen atmosphere. All solvents were distilled under nitrogen over appropriate drying agents (sodium or calcium hydride).

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 200 MHz NMR spectrometer. DEPT experiments were used to establish the structures and to assign the signals. Chemical Shifts (δ) for ^{1}H and ^{13}C were referred to internal solvent resonances. The IR spectra were recorded using an ATR system. Optical rotations were recorded in $CHCl_3$ at 25 ºC unless otherwise indicated with an error of less than ±0.1. The $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Yields are given for isolated products showing one spot on a TLC plate and no impurities detectable in the NMR spectrum.

X-ray crystal structure determination: Crystals of **(-)-20** were obtained by slow evaporation of a solution of the compound in acetonitrile at room temperature. Crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data Collection: Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = -173 °C). Full-sphere data collection was used with ω and φ scans.

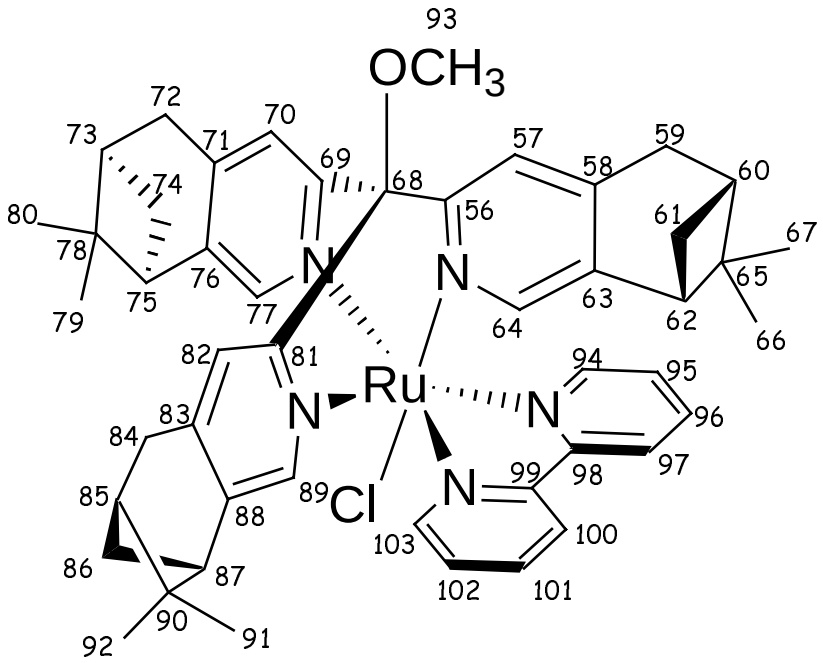
Programs used: Data collection Apex2 V. 1.0-22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001) and absorption correction SADABS V. 2.10 (2003).

Structure Solution and Refinement: SHELXTL Version 6.10 (Sheldrick, 2000) was used.[1] **(-)-20** refined in a monoclinic cell ($P2_1$) with a beta angle of approximately 90º applying a twin law (1 0 0 0 -1 0 0 0 -1; BASF: 0.154). The asymmetric unit contains two independent molecules (A and B) of **(-)-20** with similar conformations and two independent molecules of acetonitrile. Refinement in an orthorhombic cell ($P2_12_12_1$) leaded to R_1-values over 12 %.

*Crystal data for **(-)-20***: $C_{30}H_{40}Br_2Mn_1N_4$, 671.42 g mol^{-1}, monoclinic, $P2_1$, a = 9.8452(11) Å, b = 24.338(3) Å, c = 12.7573(14) Å, β = 90.164(3)°, V = 3056.8(6) $Å^3$, Z = 4, ρ_{calcd} = 1.459 Mg/m^3, R_1 = 0.0484 (0.548), wR2 = 0.01197 (0.1239), for 19283 reflections with I>2σ(I) (for 21282 reflections [R_{int}: 0.0547] with a total measured of 47950 reflections), Flack -0.006(6), goodness-of-fit on F^2 = 1.044, largest diff. peak (hole) = 1.782 (-1.360) e $Å^{-3}$.

[1] G. M. Sheldrick (2000) *SHELXTL Crystallographic System Ver. 6.10*, Bruker AXS, Inc.: Madison, Wisconsin.

Numbering scheme for **[Ru^{II}Cl((-)-10)(bpy)](BF$_4$)**



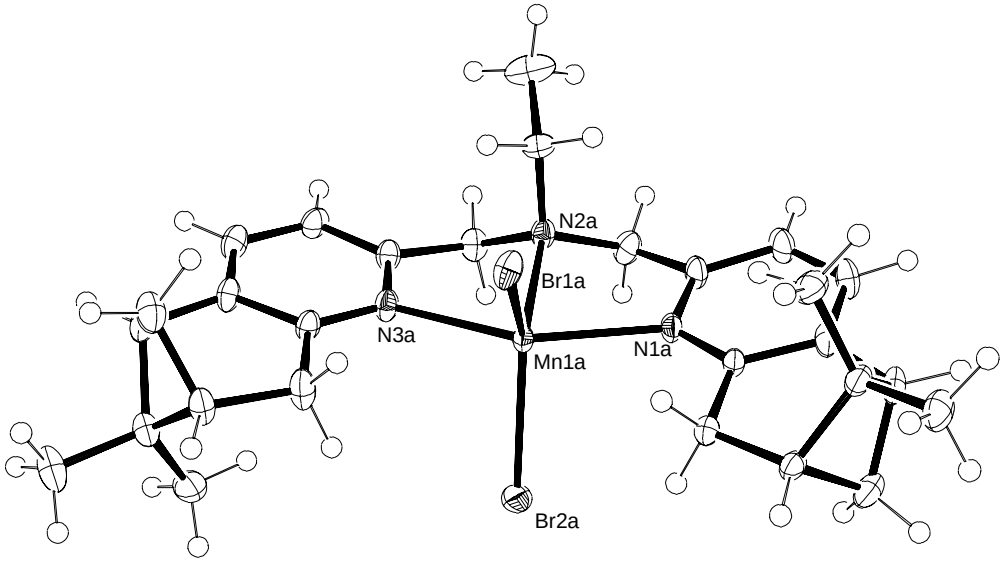
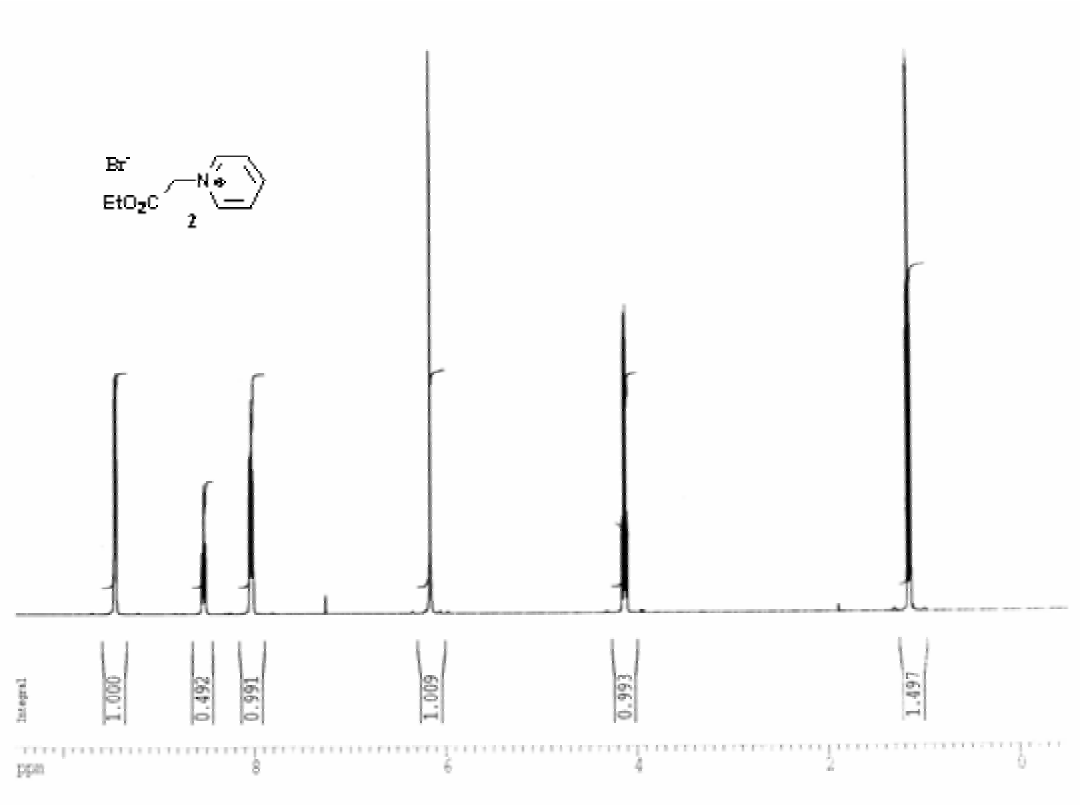
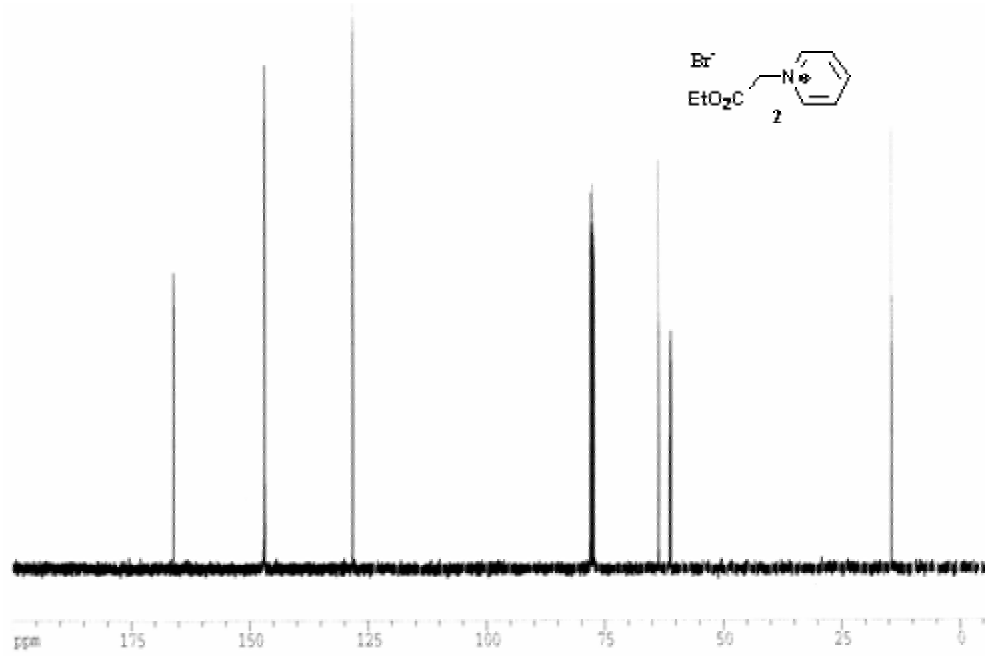


Figure 1. An ORTEP view (ellipsoids are drawn at 50% probability level) of the molecular structure of **(-)-20** (molecule A), including the atom numbering scheme.

^{1}H NMR (360 MHz, $CDCl_3$)



^{13}C NMR (90 MHz, $CDCl_3$)



ppm
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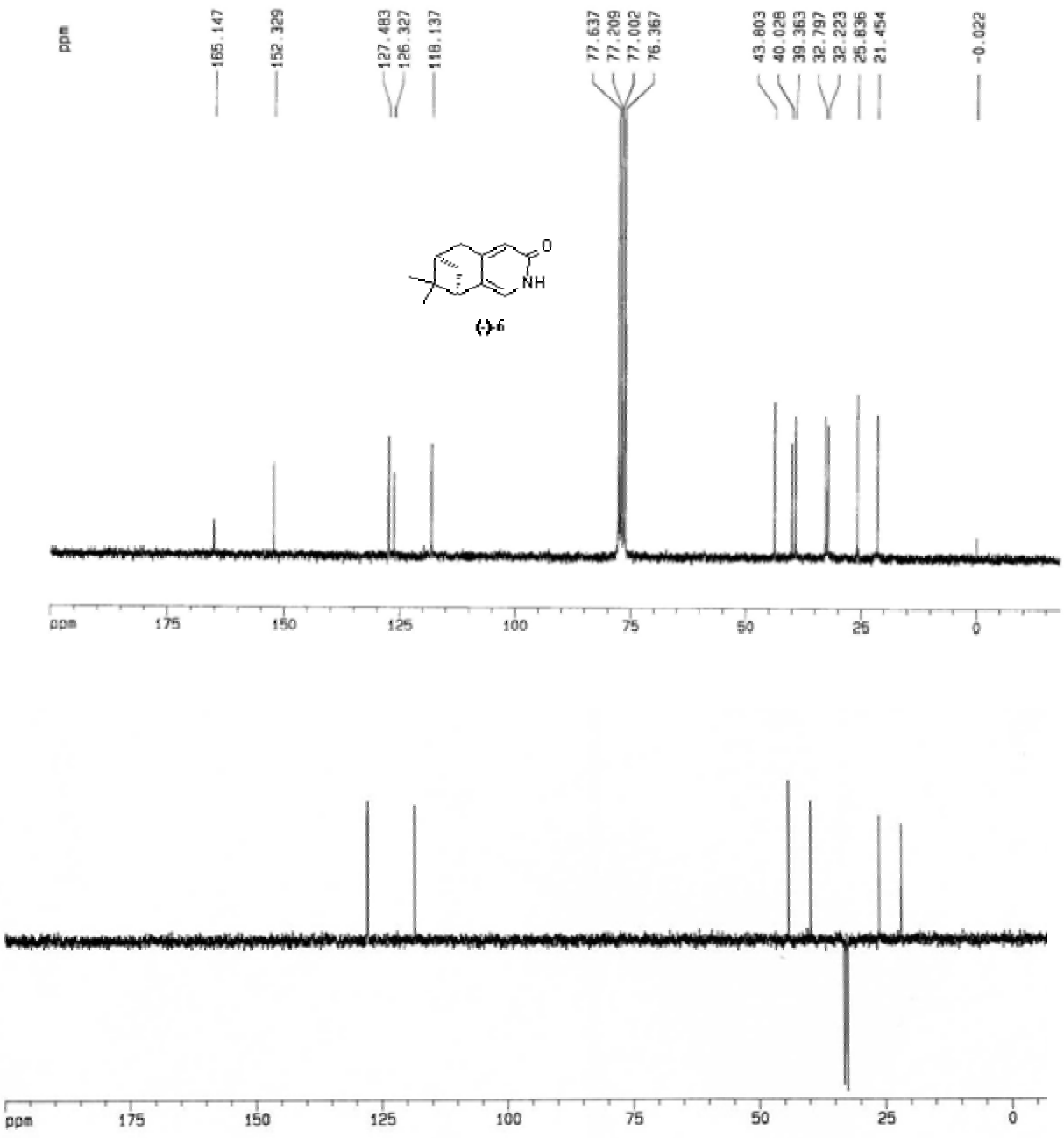
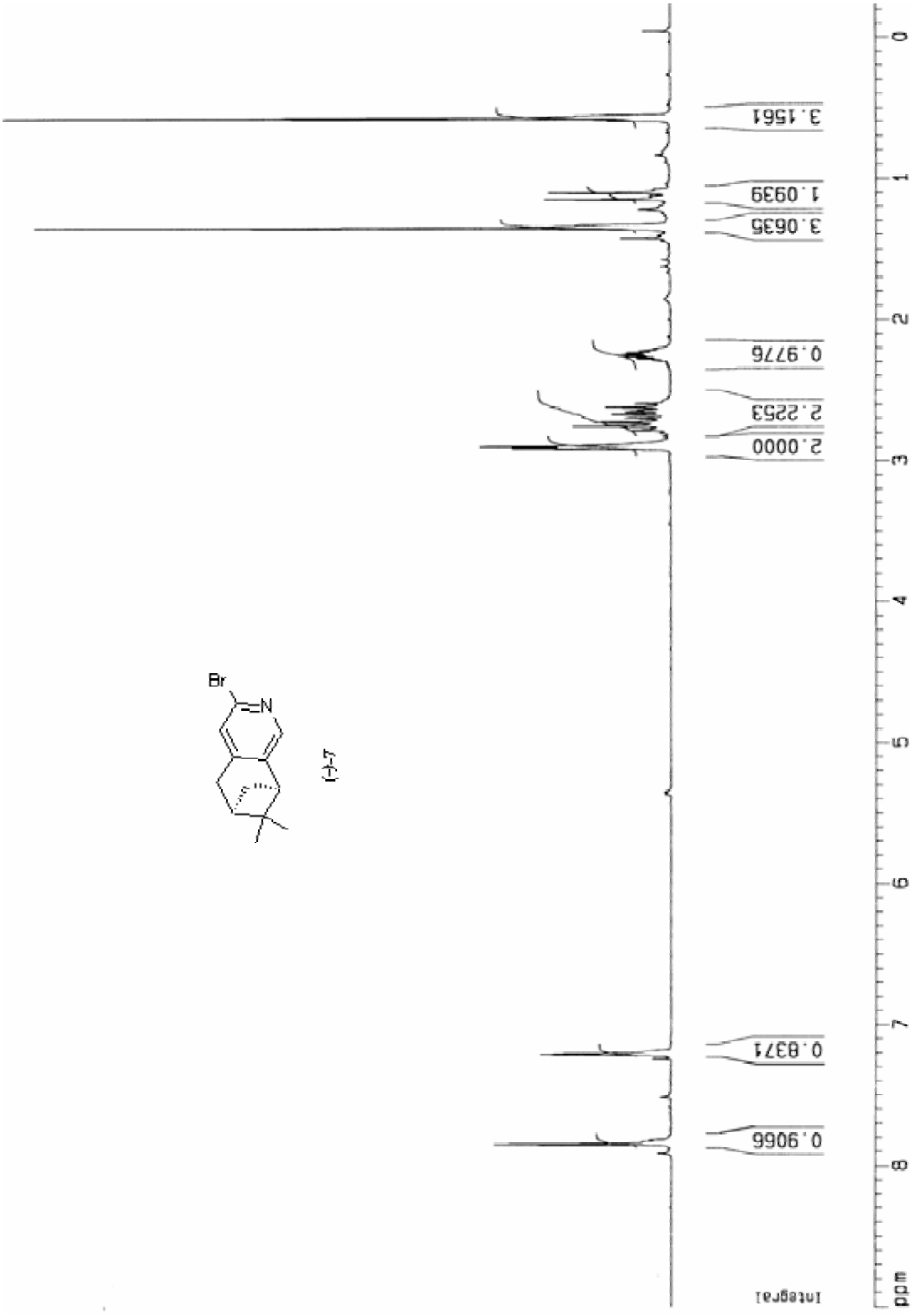
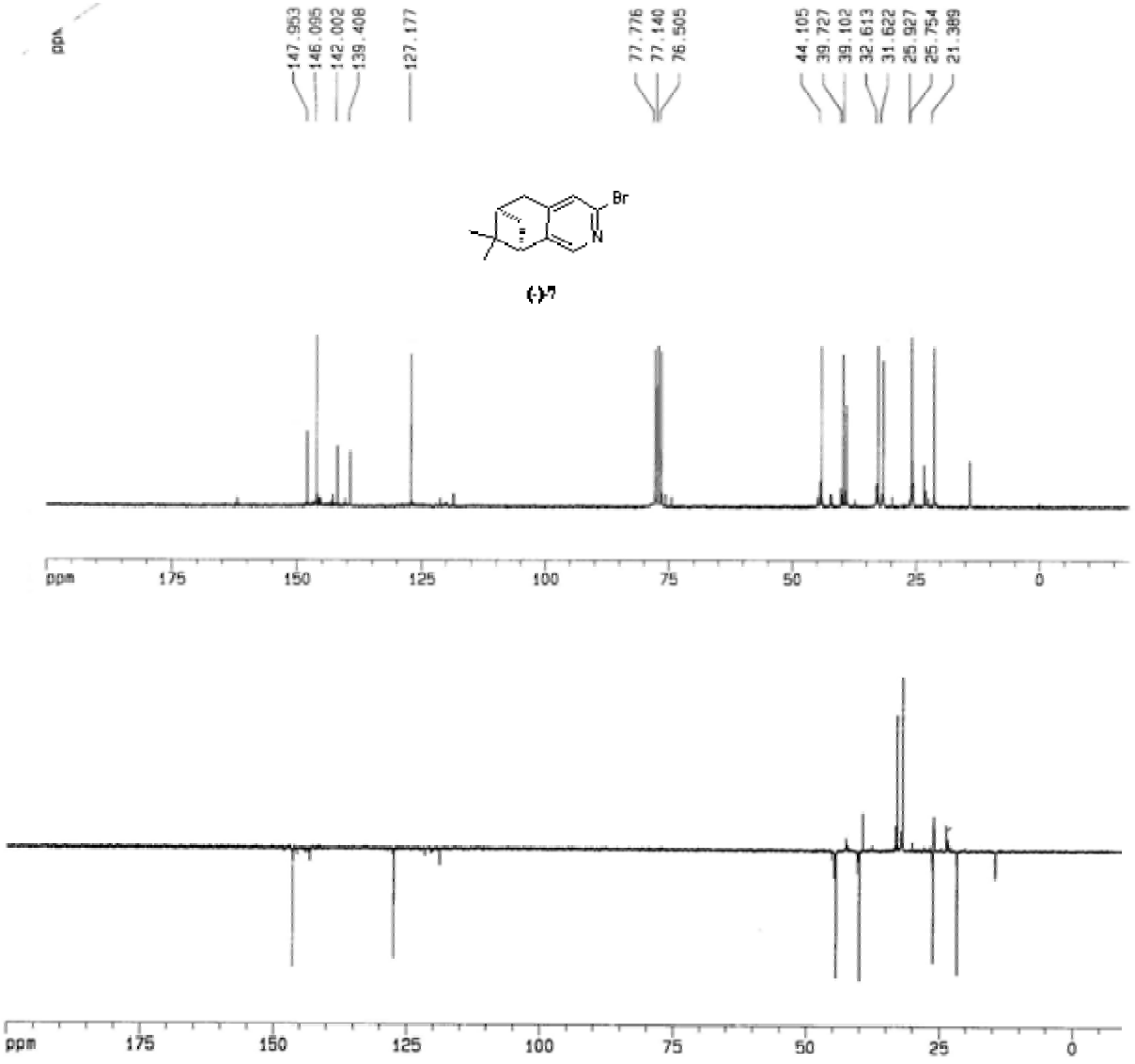
6.87
6.39
2.89
2.88
2.87
2.65
2.60
2.57
2.17
2.16
1.33
1.18
1.14
0.66
-0.02
Integral
1.0000
1.0033
1.9850
2.1513
1.4372
3.0705
1.0503
3.0052
9-(-)

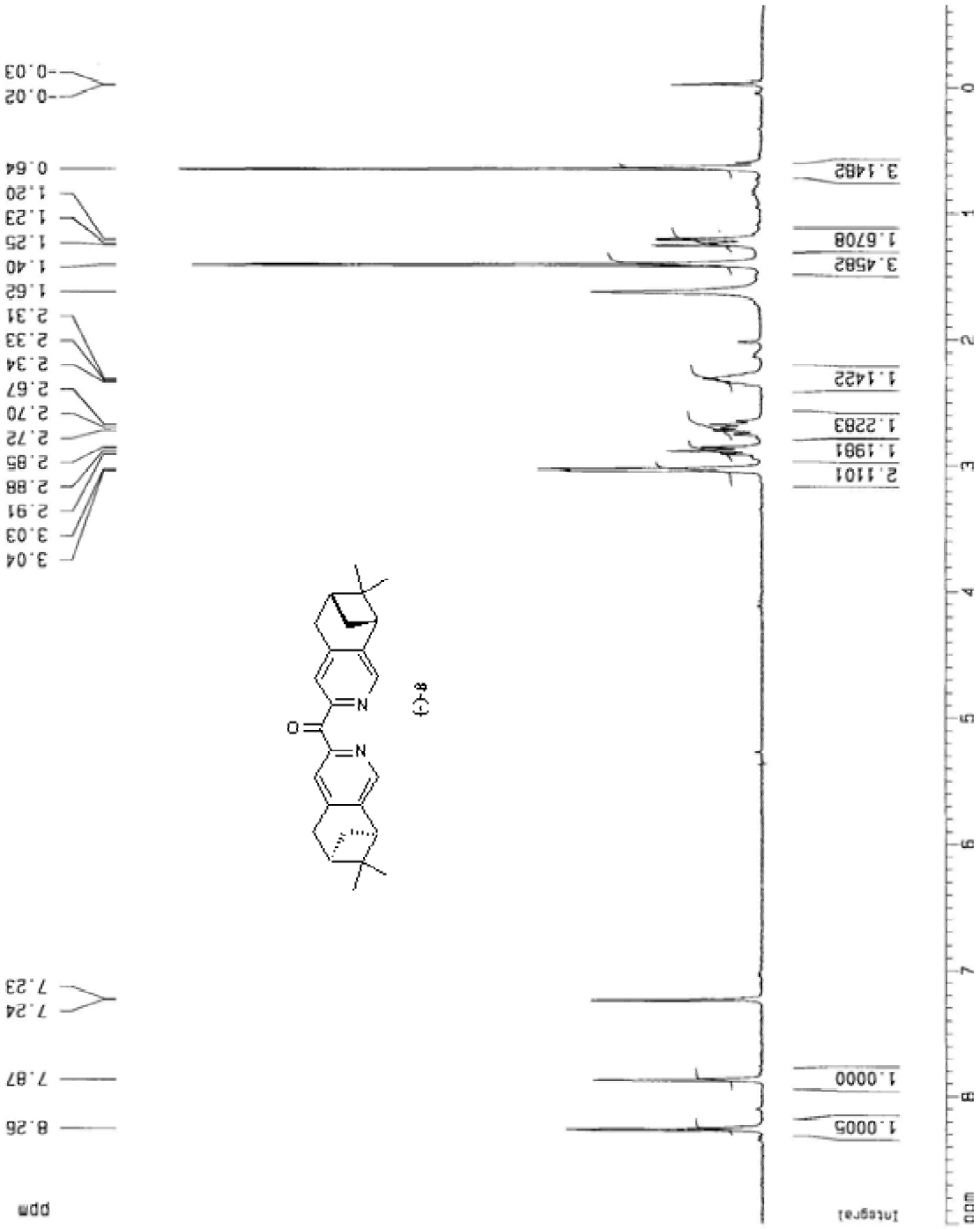
^{13}C NMR (50 MHz, $CDCl_3$)



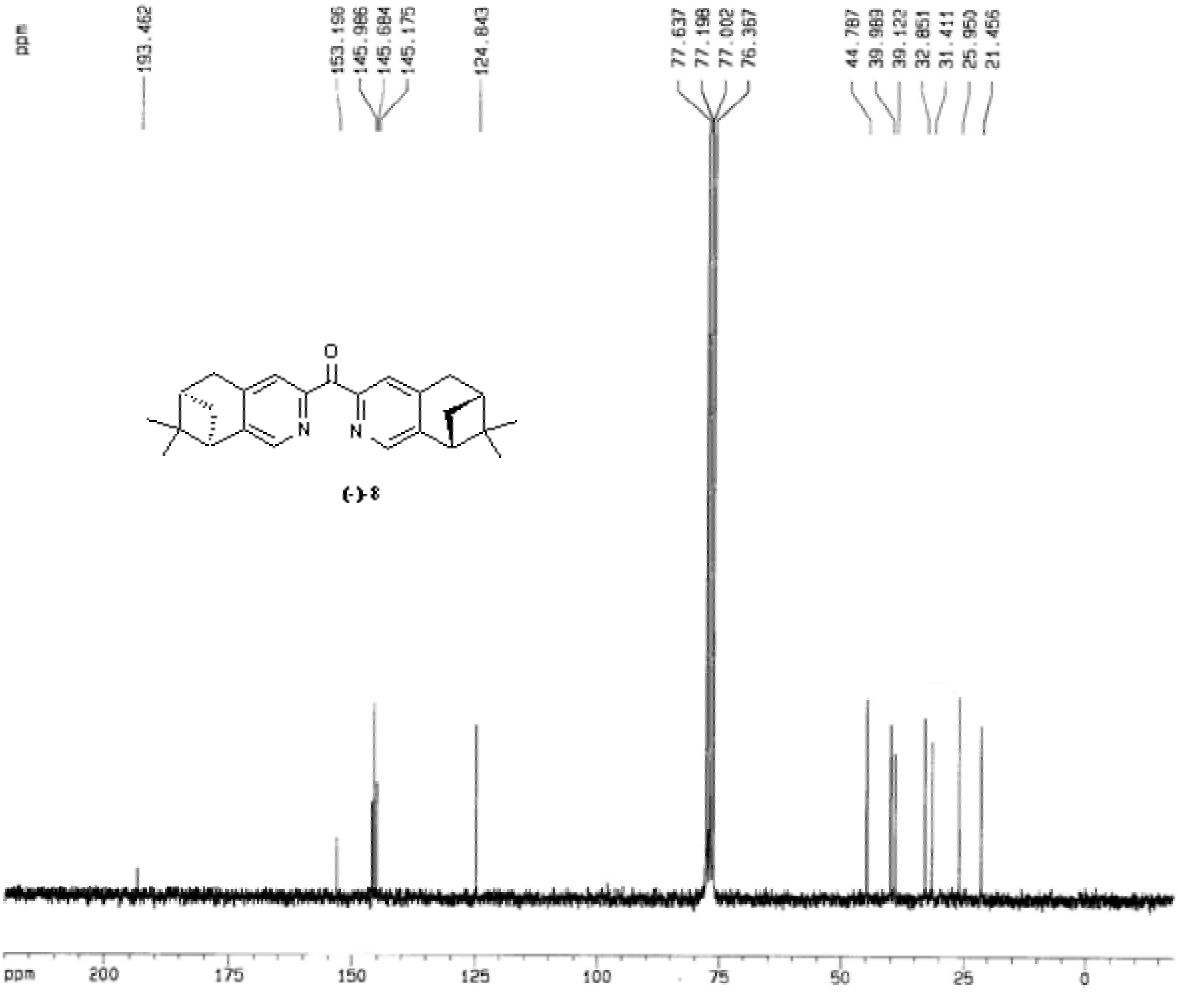

Br
N
(-)-7
3.1561
1.0939
3.0635
0.9776
2.2253
2.0000
0.8371
0.9066
Integral
ppm

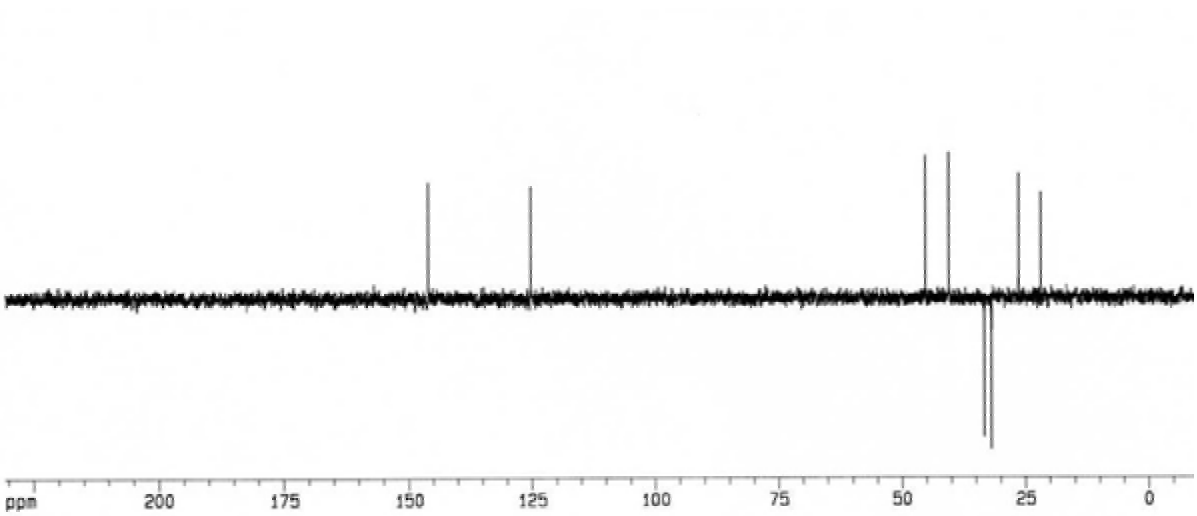
^{13}C NMR (50 MHz, $CDCl_3$)




8-(-)
ppm
8.26
7.87
7.24
7.23
3.04
3.03
2.91
2.88
2.85
2.72
2.70
2.67
2.34
2.33
2.31
1.62
1.40
1.25
1.23
1.20
0.64
-0.02
-0.03
Integral
1.0005
1.0000
2.1101
1.1981
1.2283
1.1422
3.4582
1.6708
3.1482

^{13}C NMR (50 MHz, $CDCl_3$)





ppm
integral
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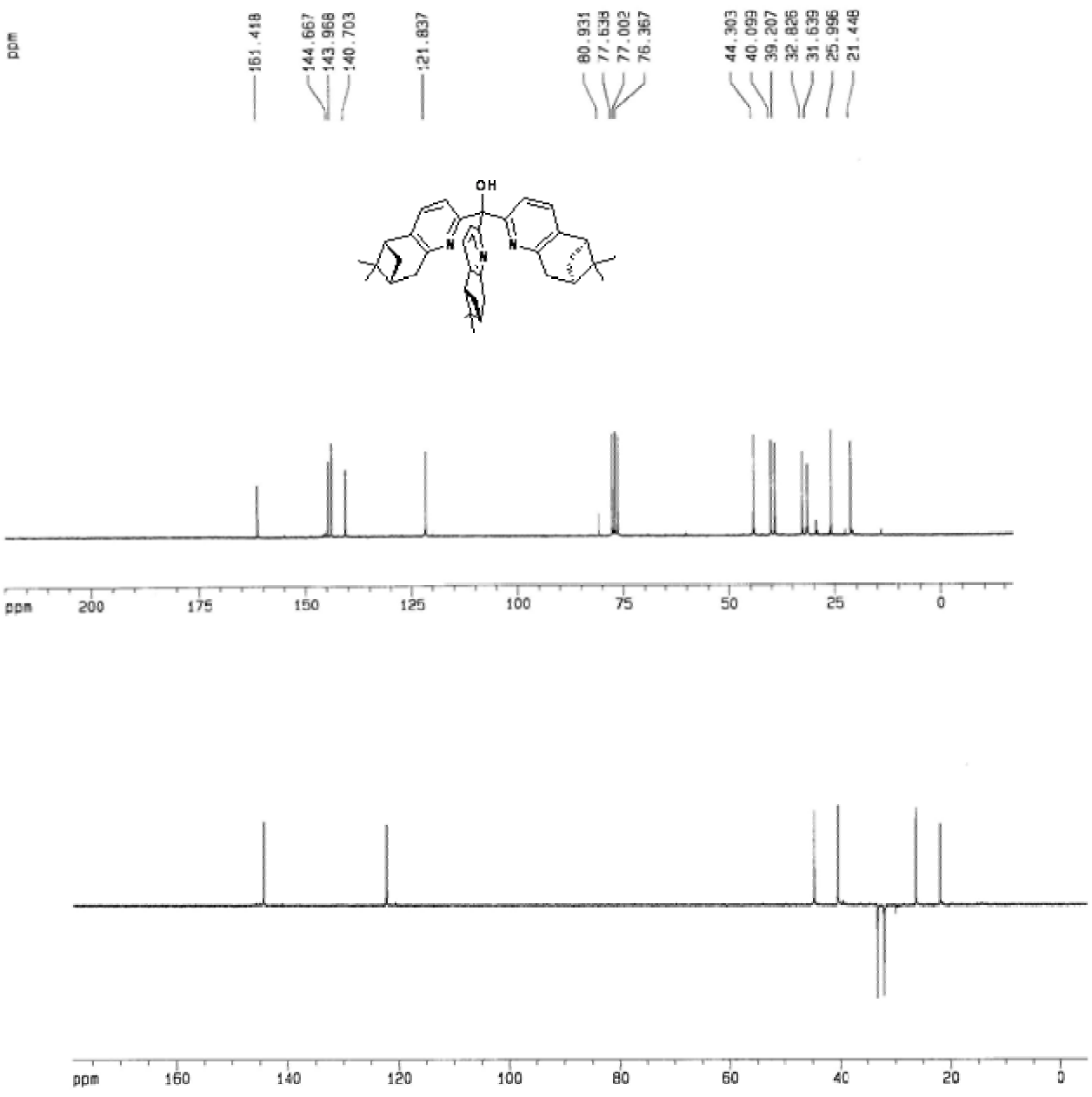
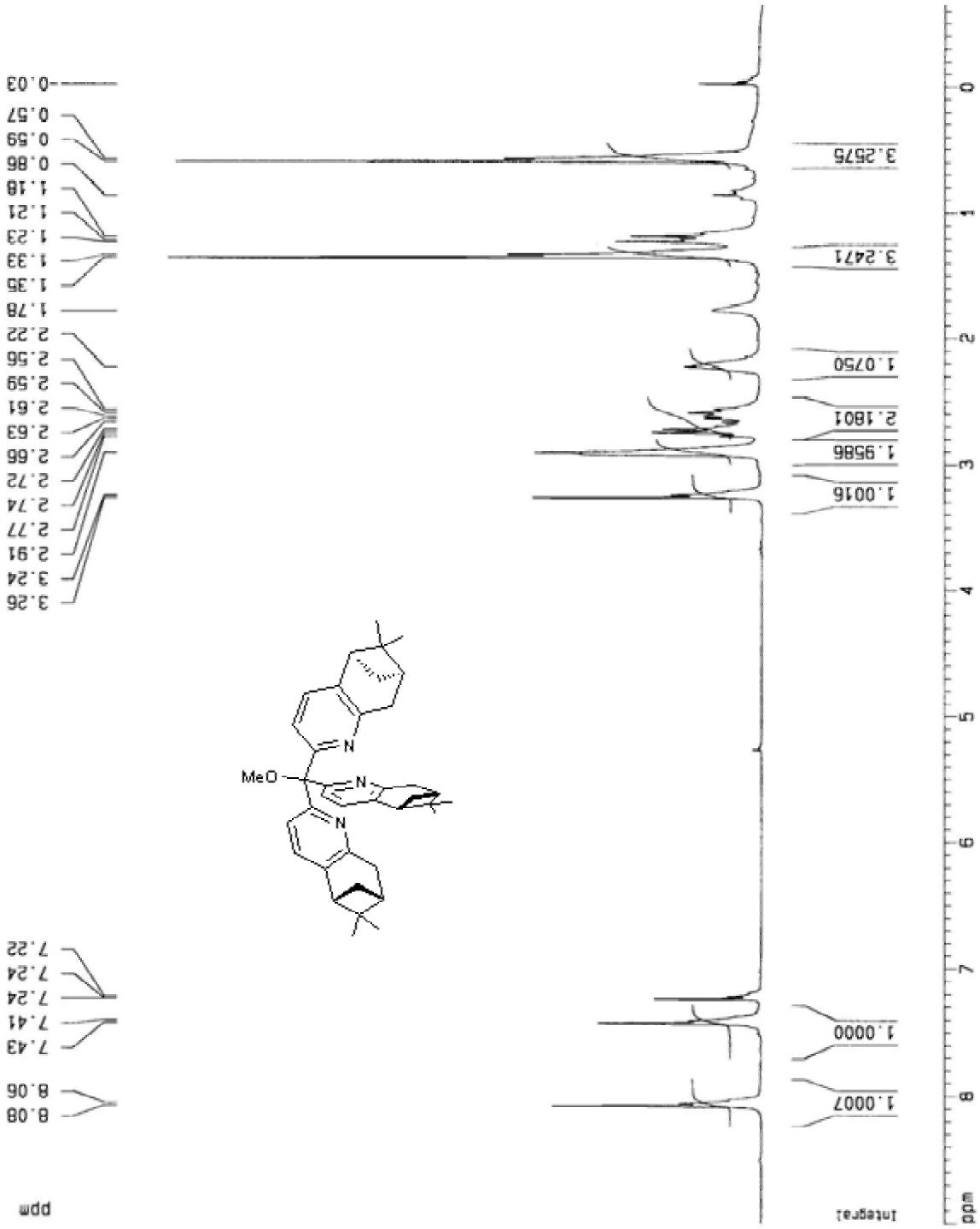
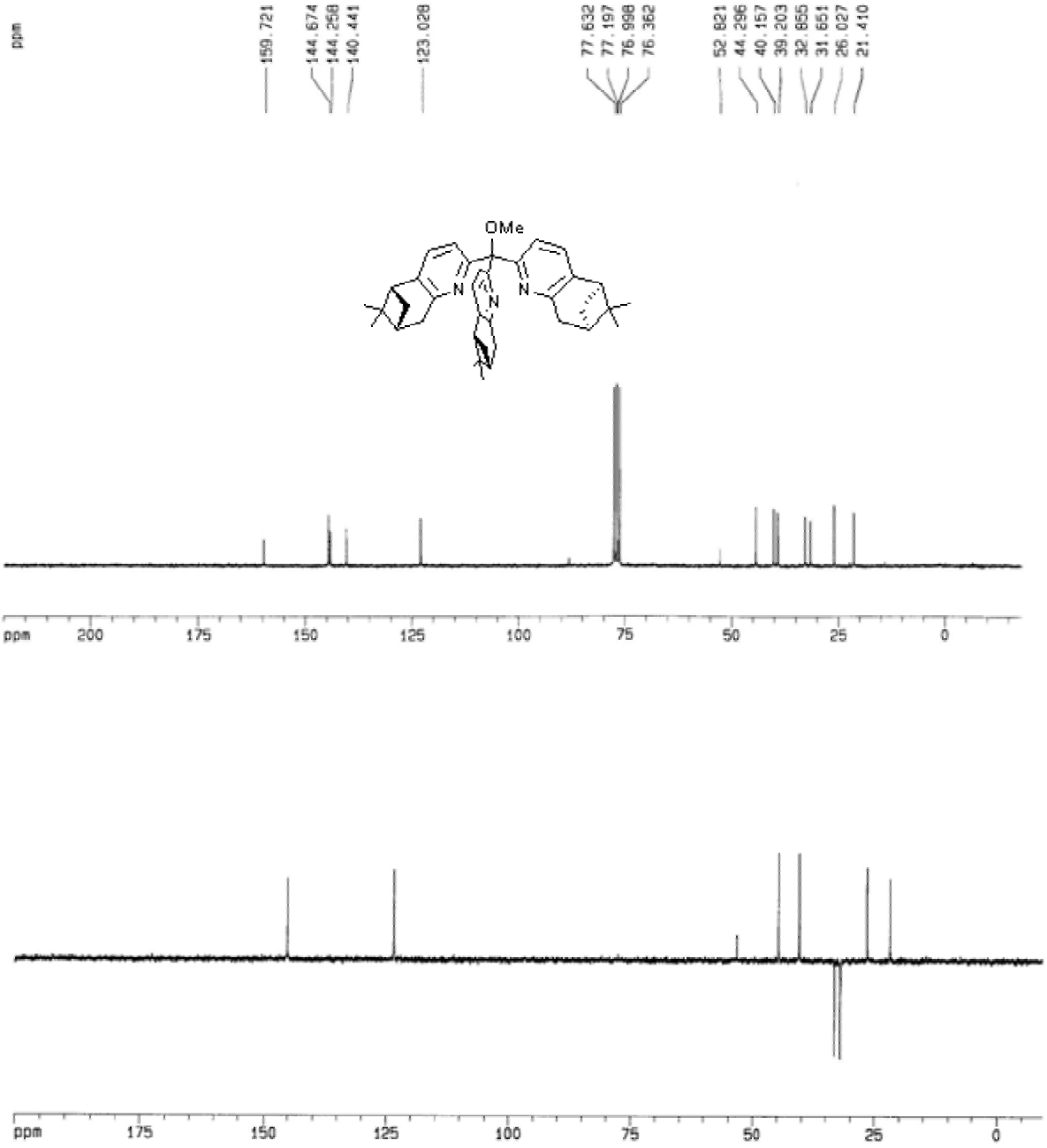
7.445
2.906
2.896
2.751
2.724
2.630
2.612
2.584
2.230
2.217
2.008
1.348
1.260
1.230
1.204
1.157
0.586
2.1539
1.1532
1.1943
1.1893
3.2660
1.9089
3.3123
1.0000
1.0222
HO
N
N
N

^{13}C NMR (50 MHz, $CDCl_3$)




MeO
N
N
N
ppm
integral
8.08
8.06
7.43
7.41
7.24
7.24
7.22
3.26
3.24
2.91
2.77
2.74
2.72
2.66
2.63
2.61
2.59
2.56
2.22
1.78
1.35
1.33
1.23
1.21
1.18
0.86
0.59
0.57
0.03
1.0007
1.0000
1.0016
1.9586
2.1801
1.0750
3.2471
3.2575

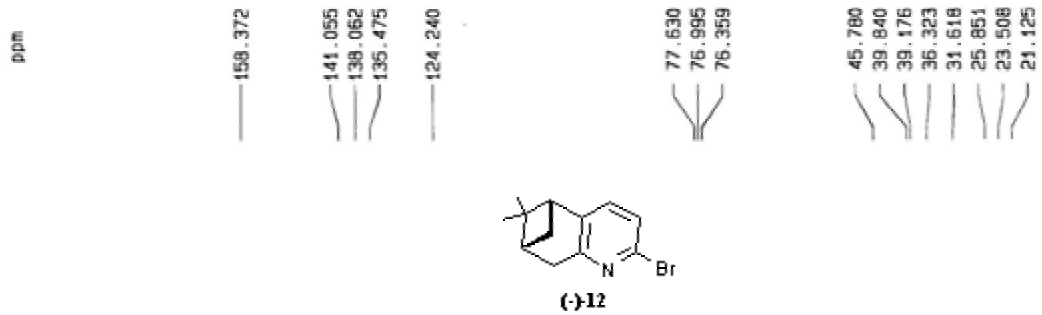
^{13}C NMR (50 MHz, $CDCl_3$)



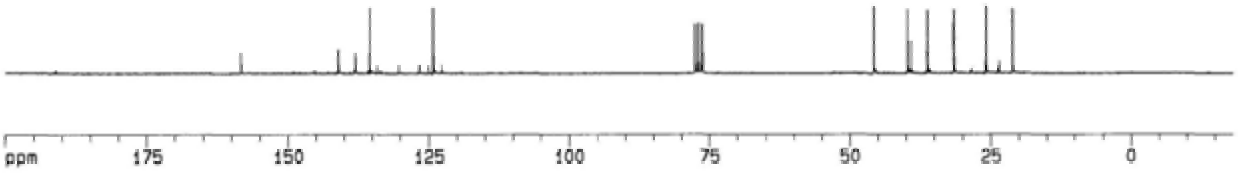
ppm
Integral
7.13
7.08
6.32
6.27
2.92
2.63
2.60
2.58
2.56
2.53
2.50
2.25
1.34
1.29
1.24
1.19
0.67
-0.04
1.0000
0.9934
1.9363
2.1443
1.1024
3.0744
1.1783
3.1095
(-)-11
NH
O

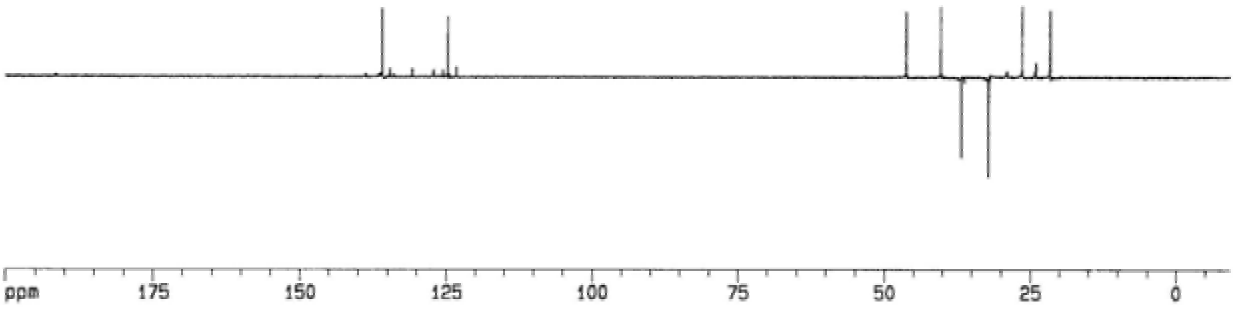
ppm
Integral
7.140
7.136
7.100
7.098
7.043
7.004
3.054
3.040
2.697
2.678
2.669
2.649
2.603
2.304
1.377
1.352
1.327
1.323
1.213
1.167
0.598
1.0000
1.0156
2.1731
2.3943
1.1244
4.1525
1.2510
3.4695
Br
N
(+)-13

^{13}C NMR (50 MHz, $CDCl_3$)



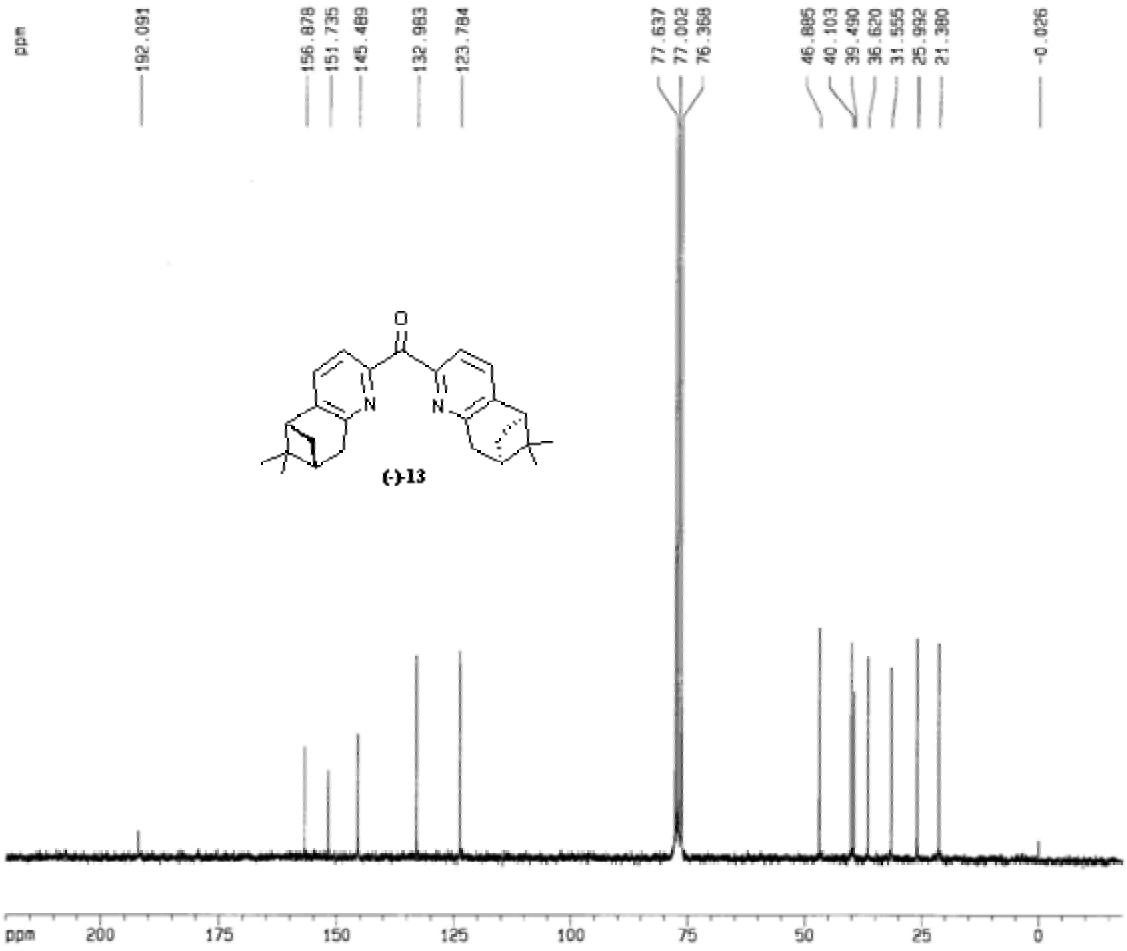
(-)-12

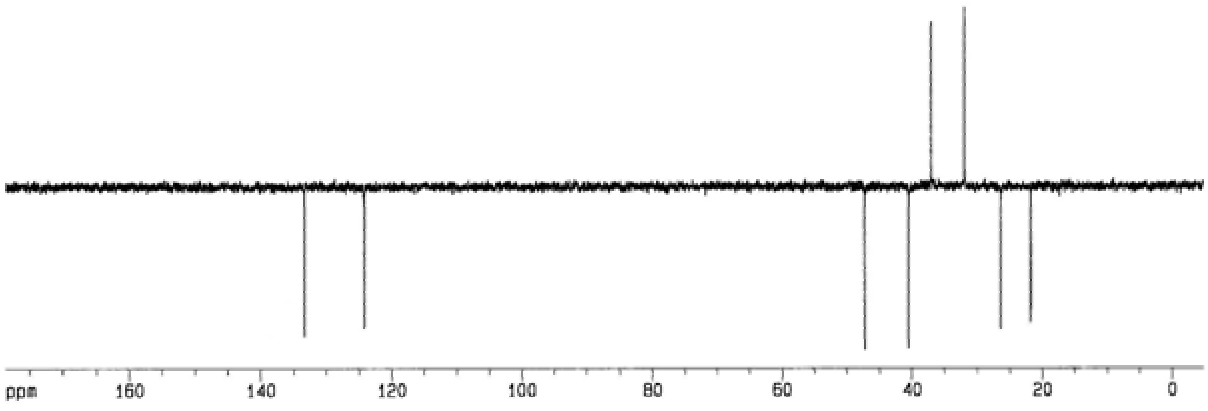




ppm
Integral
7.88
7.84
7.35
7.31
7.25
7.25
3.20
3.19
2.85
2.82
2.73
2.68
2.40
2.39
1.42
1.33
1.29
0.67
-0.01
-0.02
0.9552
1.0000
2.0250
1.0510
1.1119
1.0745
3.1412
1.1152
2.9976
(-)-13
O
N
N

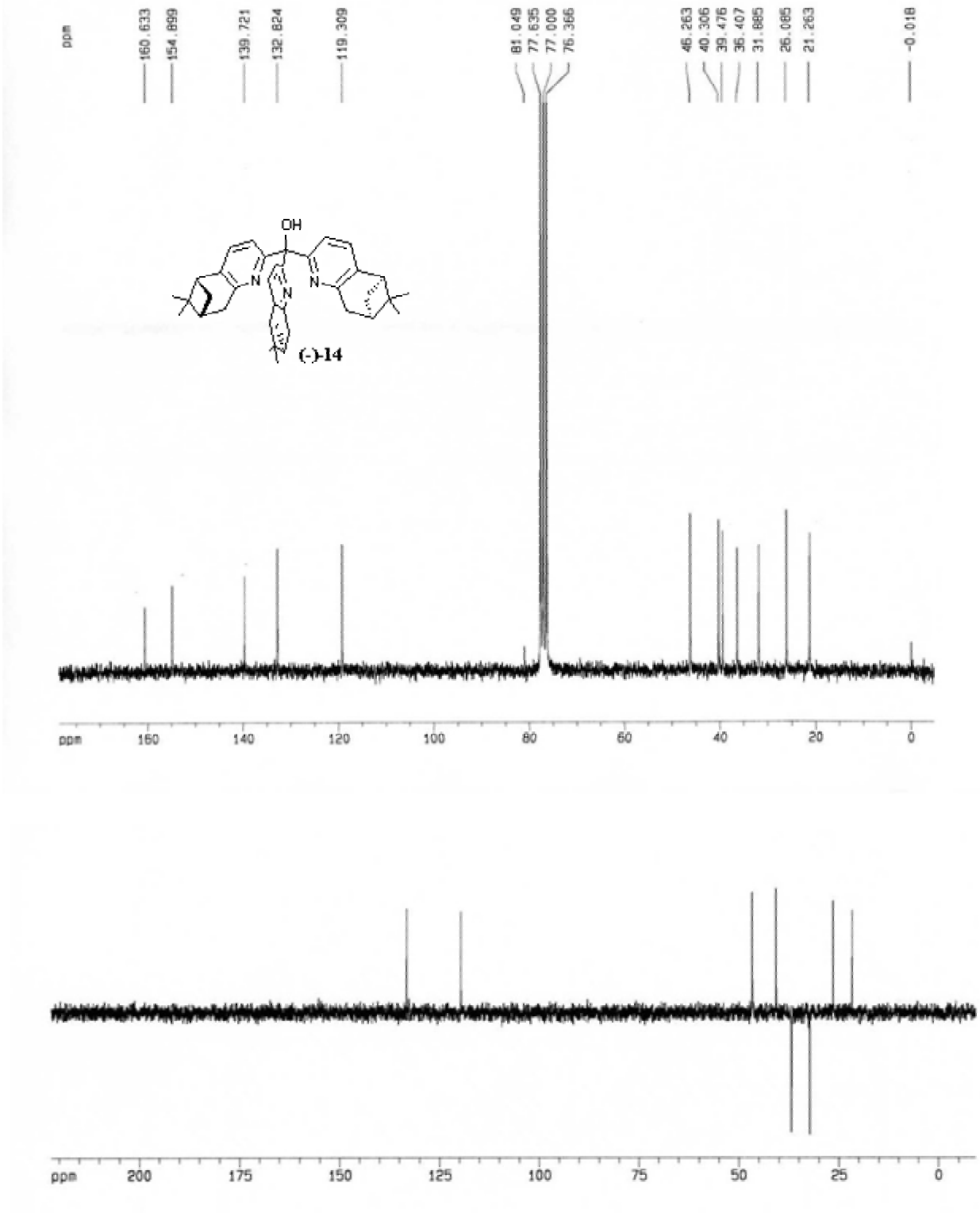
^{13}C NMR (50 MHz, $CDCl_3$)

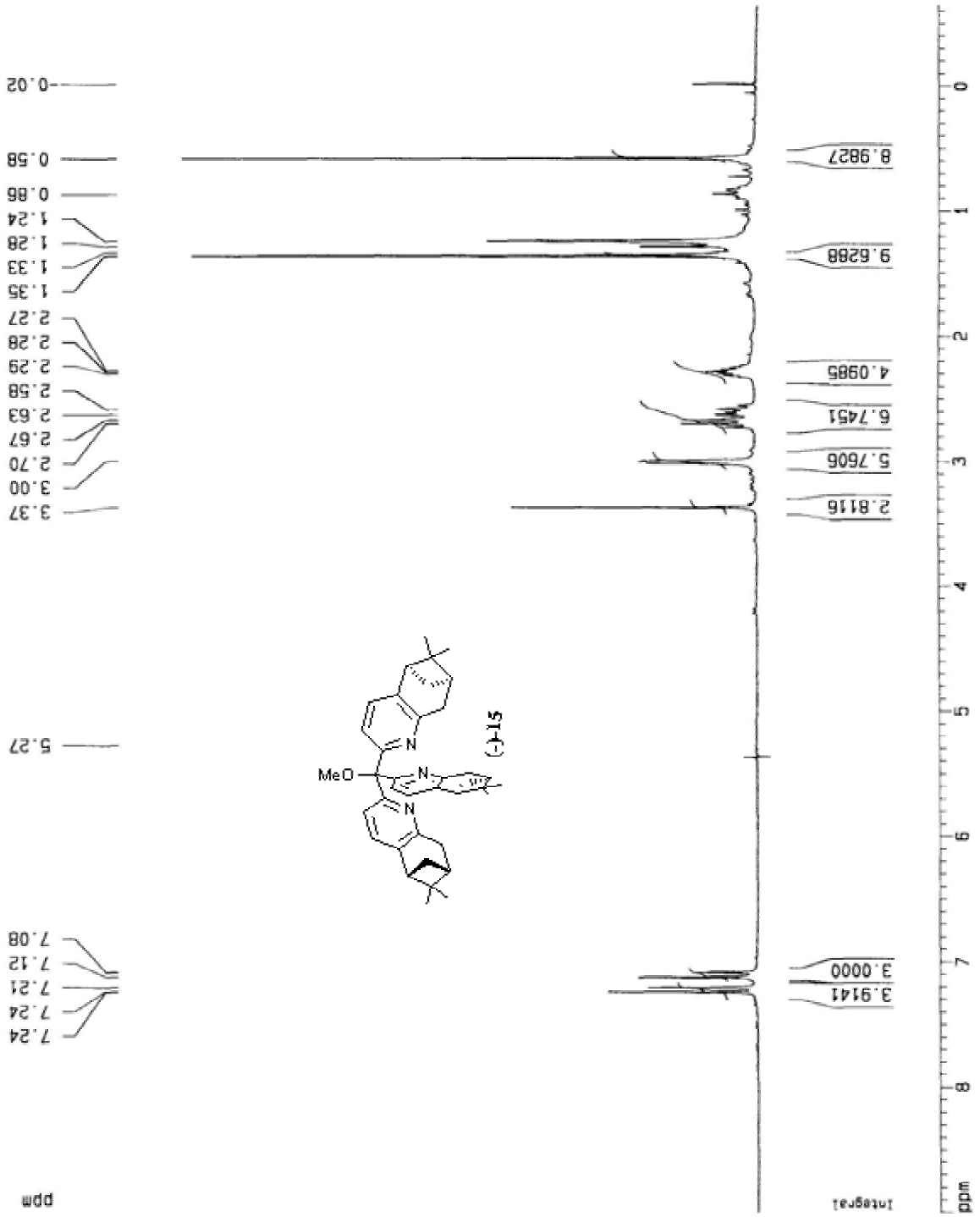




ppm
integral
7.24
7.24
7.20
7.12
7.08
3.01
3.00
2.70
2.67
1.36
1.26
1.22
0.60
-0.02
1.0000
0.5489
1.8790
2.1843
1.1248
3.0917
1.2851
2.8031
HO
N
N
N
(+)-14

^{13}C NMR (50 MHz, $CDCl_3$)




ppm
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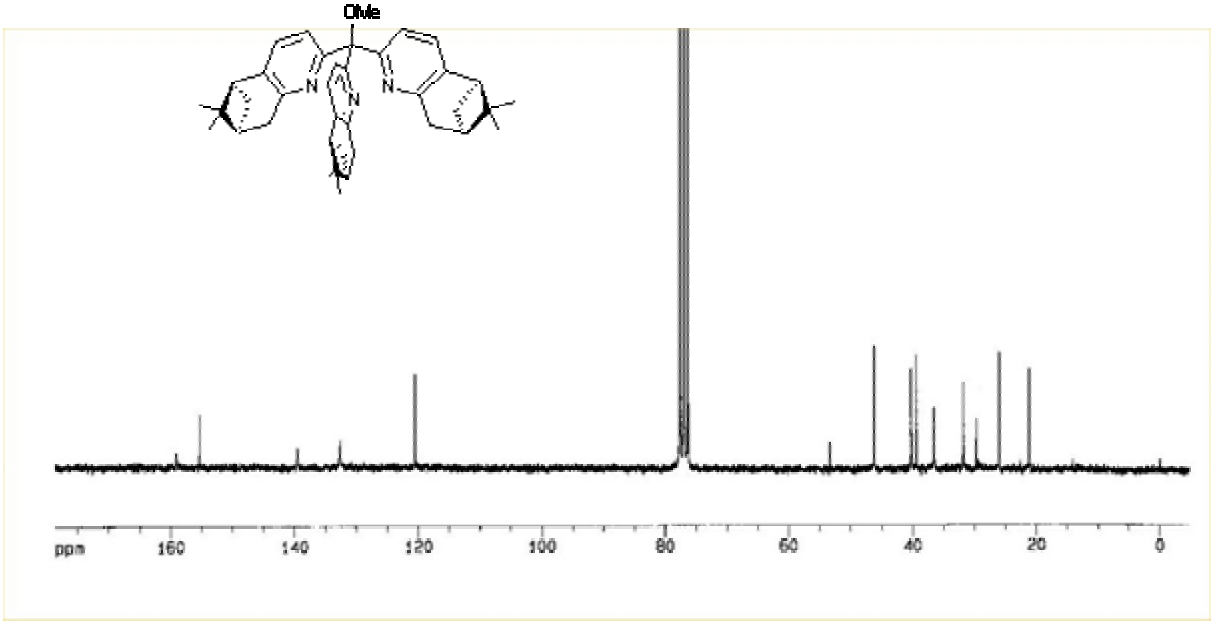
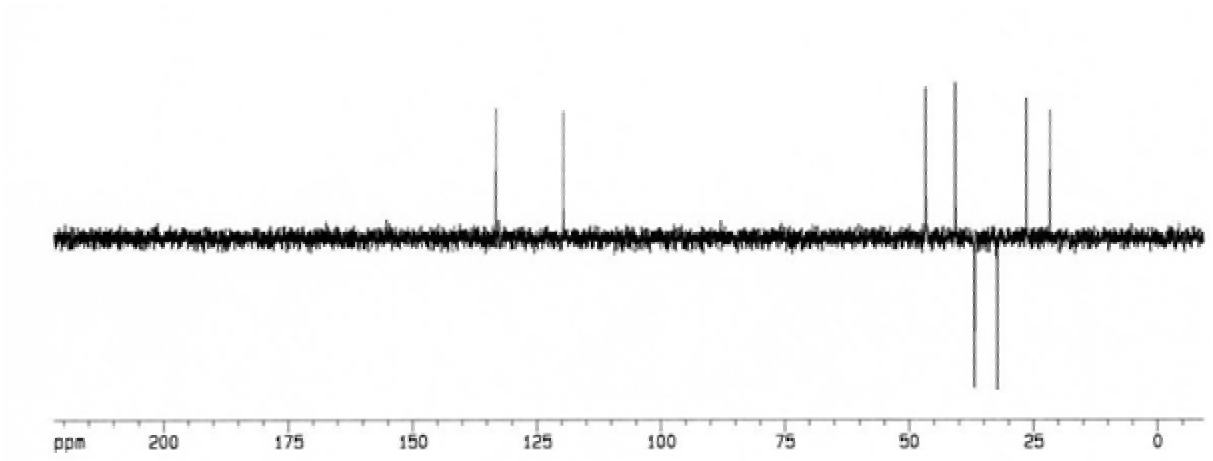
6.7451
5.7606
2.8116
5.27
7.08
7.12
7.21
7.24
7.24
3.37
3.00
2.70
2.67
2.63
2.58
2.29
2.28
2.27
1.35
1.33
1.28
1.24
0.86
0.58
-0.02
MeO
N
N
N
(-)-1S

^{13}C NMR (50 MHz, $CDCl_3$)





ppm
10.04
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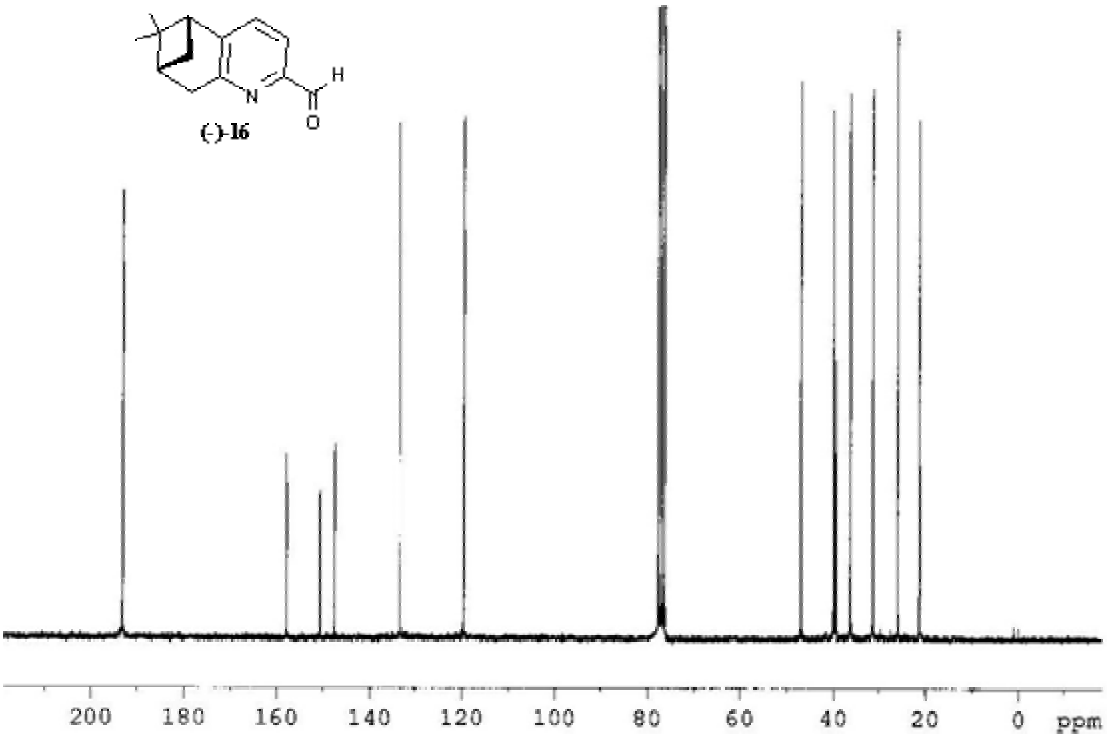
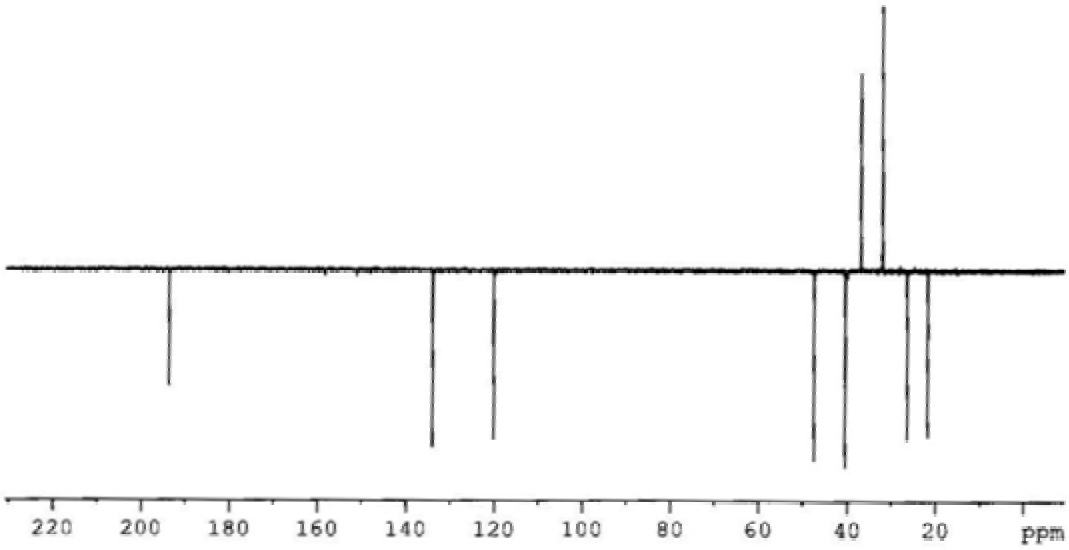
7.68
7.39
7.36
3.22
3.20
2.91
2.88
2.85
2.77
2.72
2.45
2.44
2.42
1.44
1.33
1.28
1.26
0.88
0.85
0.66
Integral
1.0000
1.1236
1.1164
2.3377
1.1757
1.2563
1.1874
4.0099
1.3034
4.5573
3.5688
ppm
0
2
4
6
8
10
9f-(-)
H
O
N

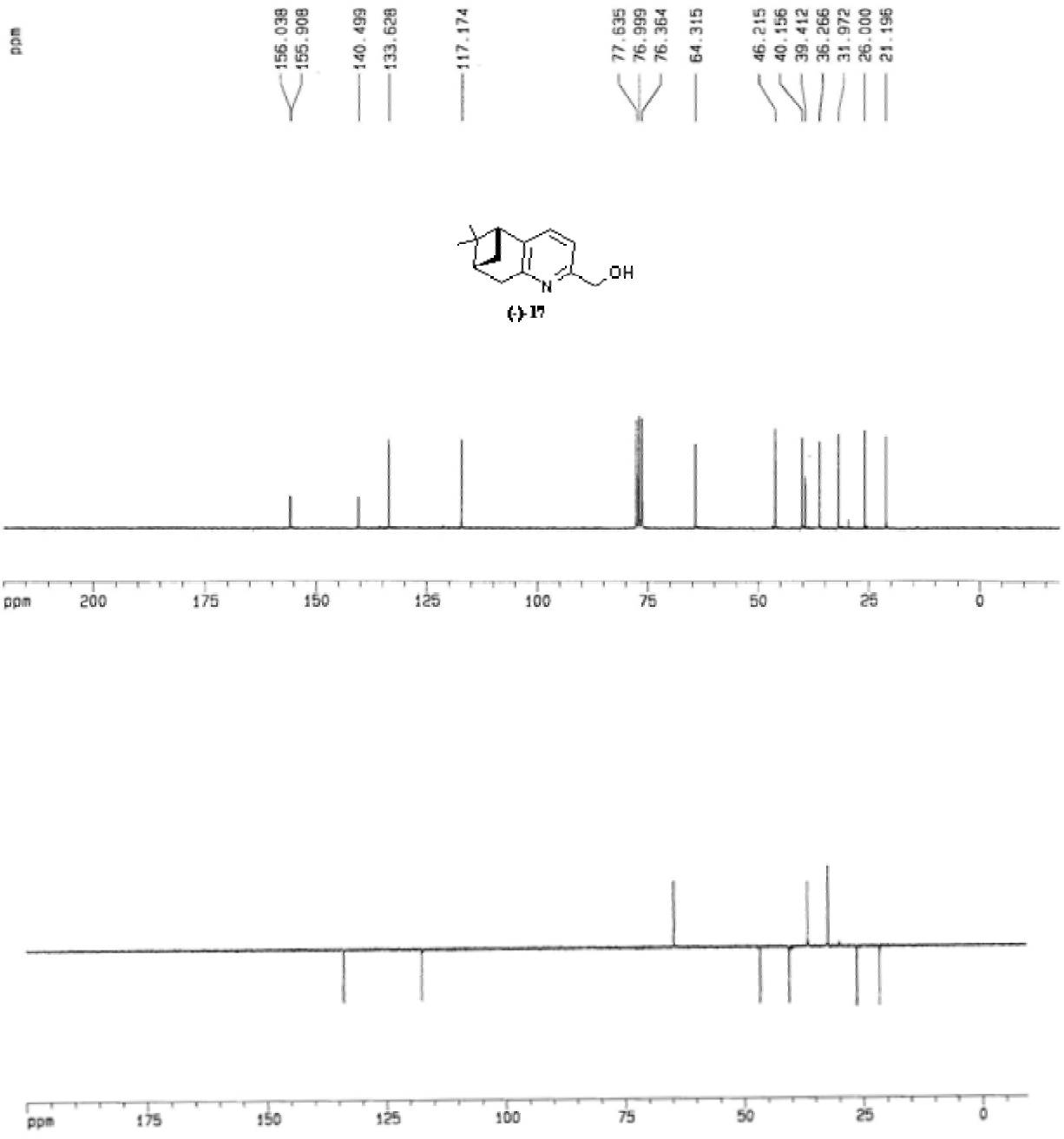
^{13}C NMR (50 MHz, $CDCl_3$)





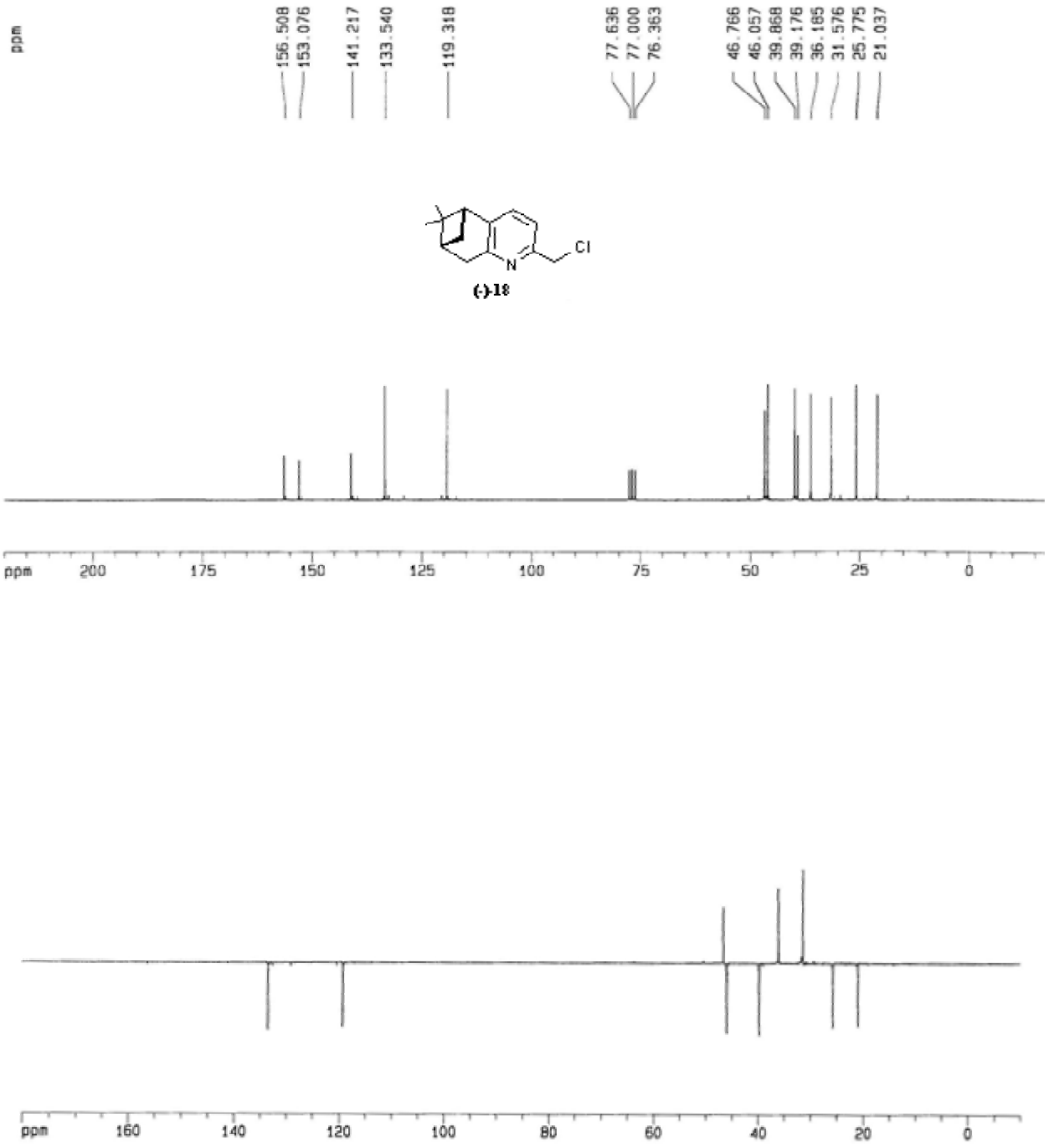
0.596
1.194
1.240
1.370
2.314
2.328
2.343
2.358
2.618
2.648
2.663
2.692
2.720
2.749
3.044
3.056
4.674
6.895
6.932
7.137
7.175
ppm
integral
3.2144
1.9431
3.3963
1.1549
2.2193
2.1059
0.9647
2.0984
1.0000
0.9956
(+)-17
HO
N

^{13}C NMR (50 MHz, $CDCl_3$)



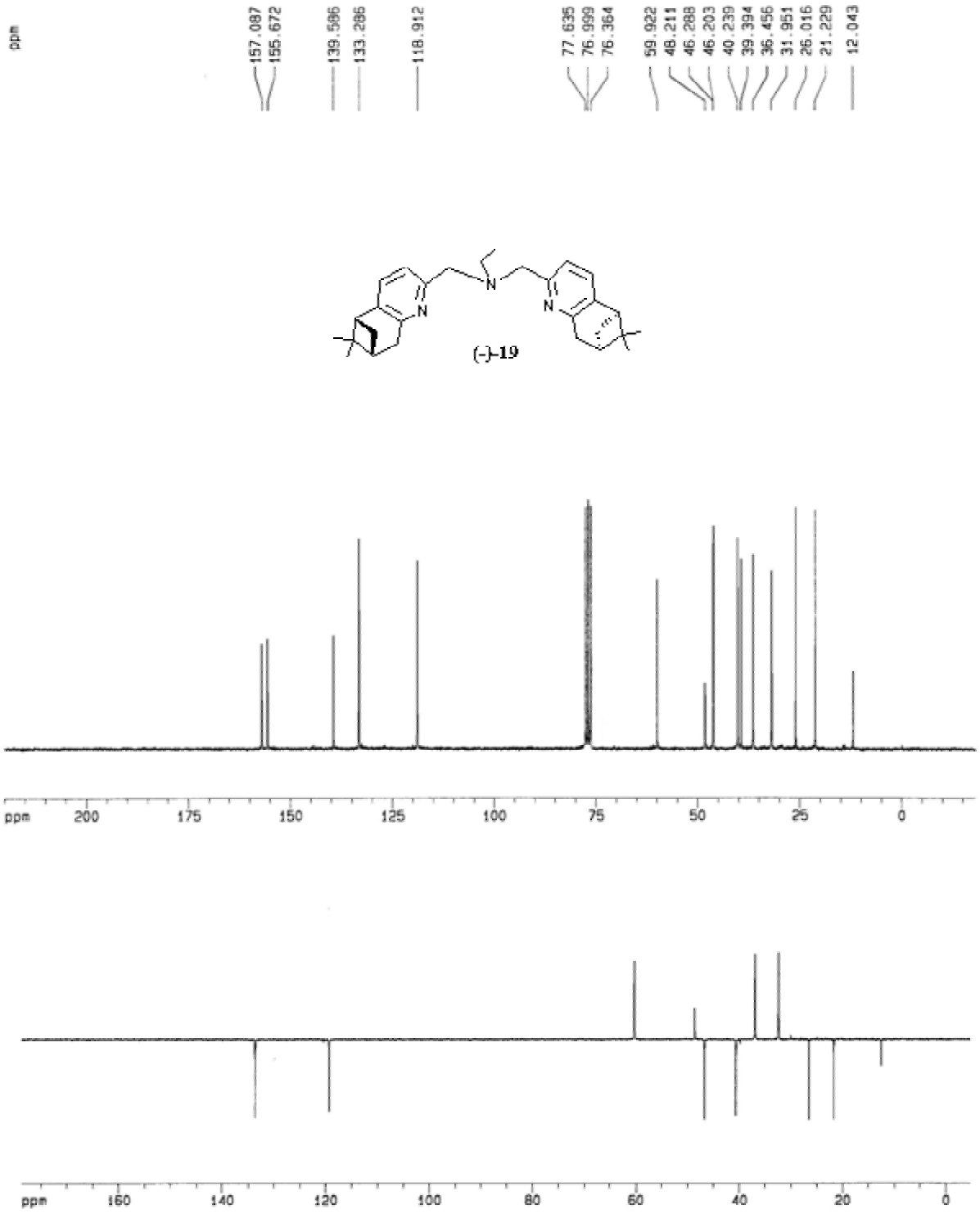
0.530
1.127
1.174
1.297
2.262
2.277
2.546
2.592
2.636
2.665
2.995
3.007
4.532
7.010
7.048
7.095
7.133
ppm
3.3314
1.4759
3.4929
1.1124
2.3325
2.1752
2.0000
1.0199
1.0375
integral
0
1
2
3
4
5
6
7
8
ppm
Cl
N
8t (-)

^{13}C NMR (50 MHz, $CDCl_3$)



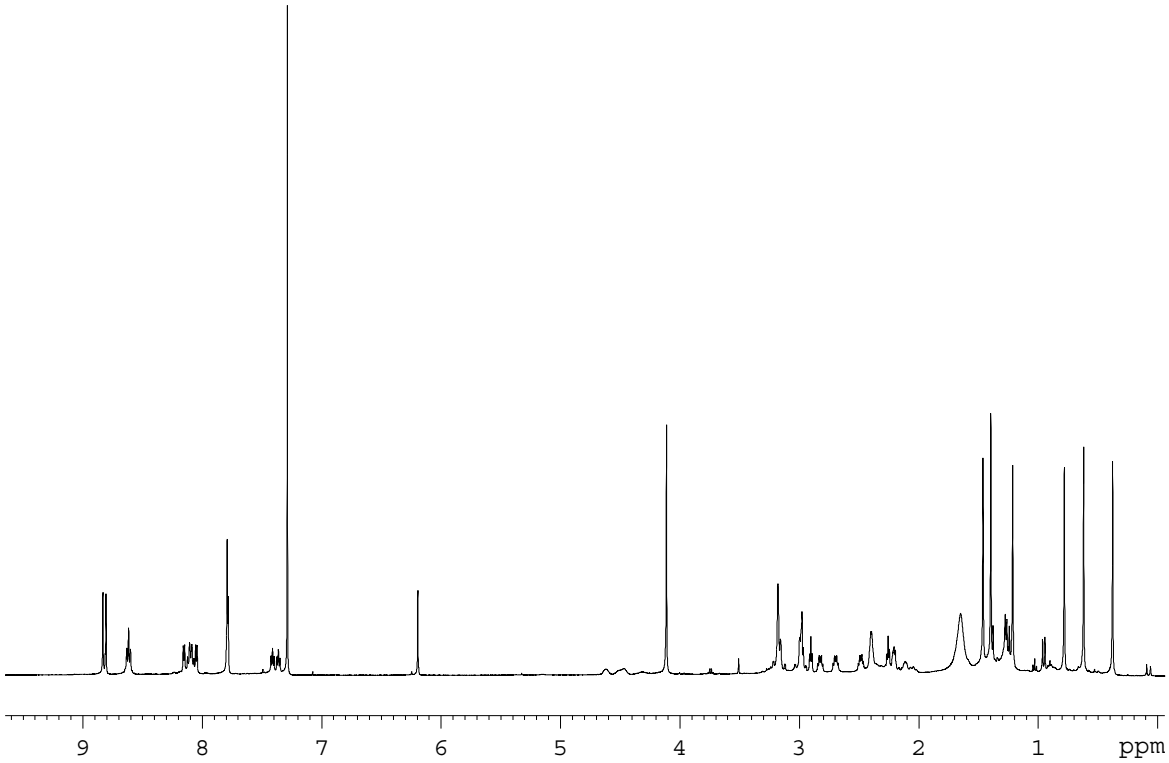
ppm
integral
7.284
7.248
7.163
7.125
3.826
3.801
3.081
3.067
2.712
2.699
2.682
2.672
2.654
2.638
2.625
2.601
2.375
2.360
2.345
2.331
1.387
1.271
1.227
1.138
1.102
1.067
0.618
1.9924
2.0182
4.0000
4.2112
6.1069
2.1369
6.4518
3.1439
6.2522
(-)-19
N
N
N

^{13}C NMR (50 MHz, $CDCl_3$)

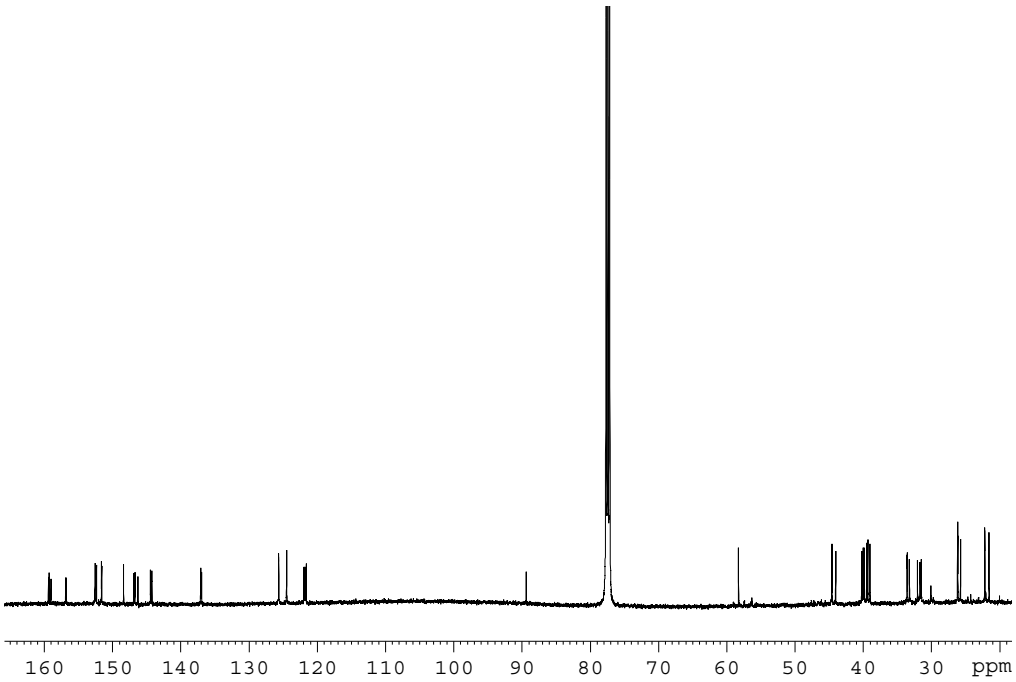


NMR of complex **(-)-21**:

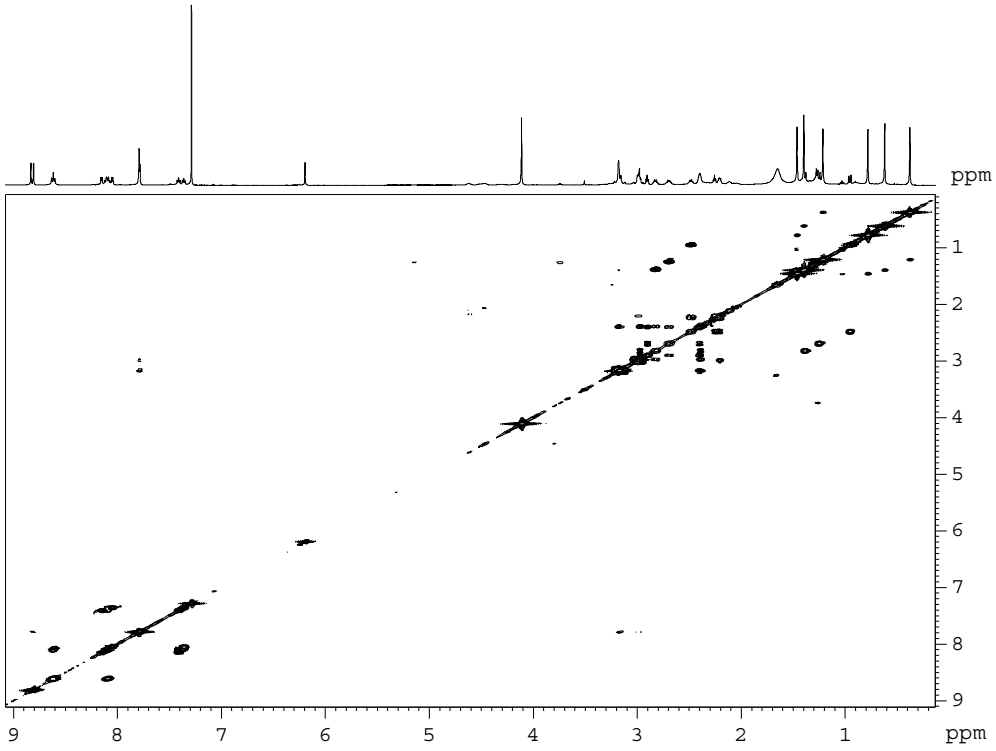
^{1}H NMR (500.13 MHz, $CDCl_3$)



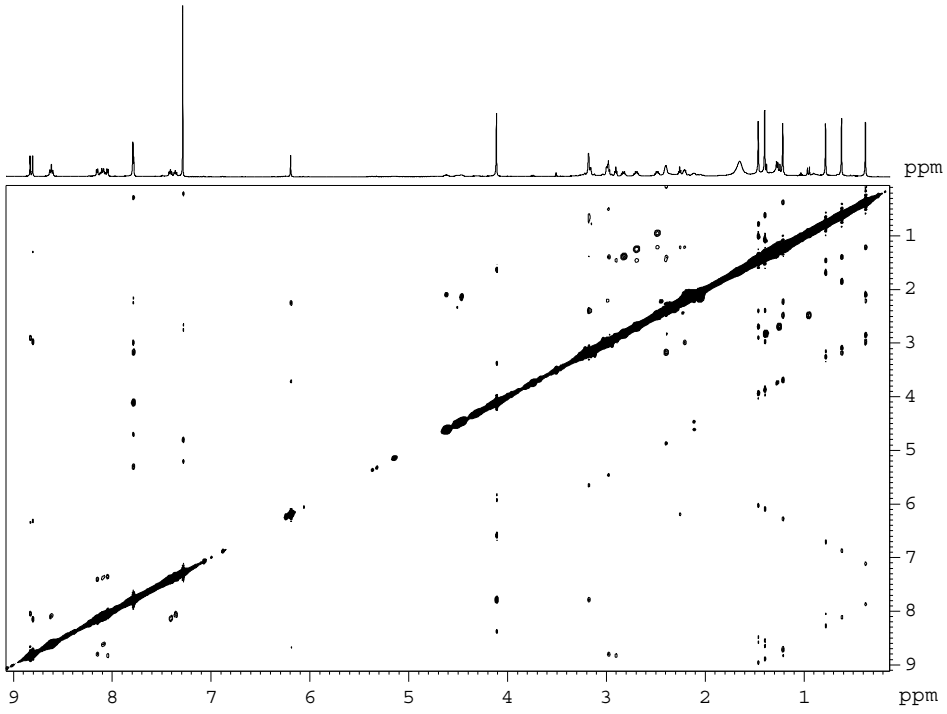
^{13}C NMR (100.25 MHz, $CDCl_3$)



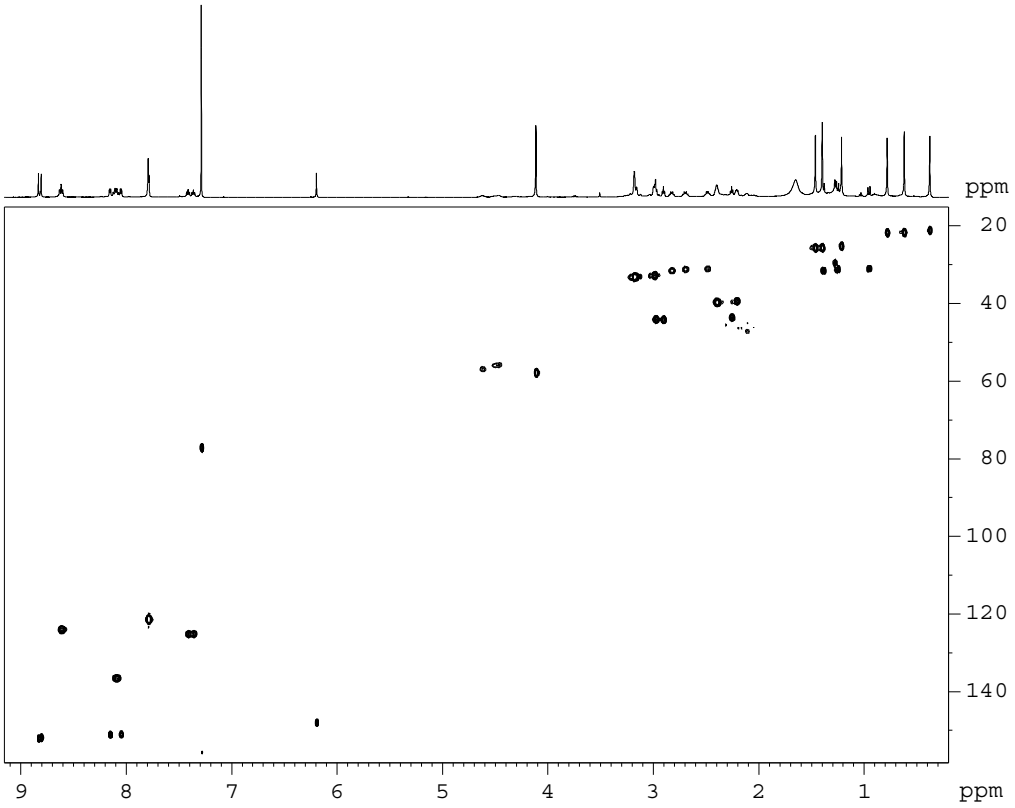
2D ^{1}H-^{1}H COSY

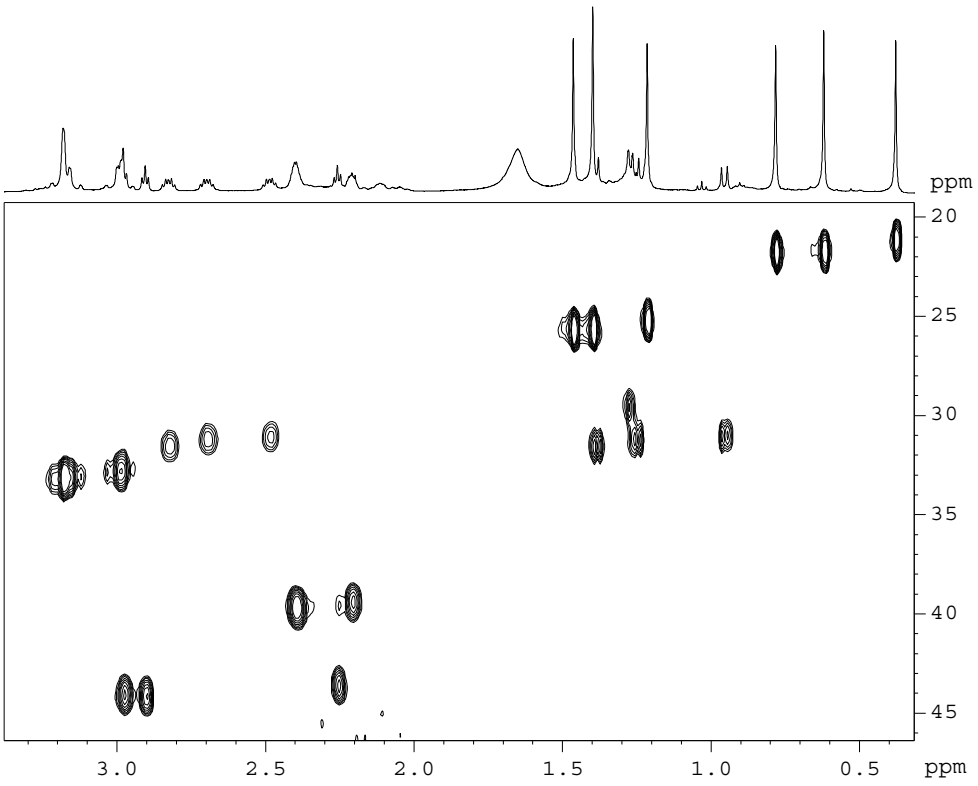


2D ^{1}H-^{1}H NOESY



2D ^{1}H-^{13}C HSQC





2D ^{1}H-^{13}C HMBC