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

Supporting Information

Synthesis of Enantiomerically Enriched Indolines and Tetrahydro-isoquinolines from (*S*)-Amino Acid-Derived Chiral Carbocations: An Easy Access to (3*S*,4*R*)-Demethoxy-3-isopropyl Diclofensine

Sudipta Kumar Manna[a] and Gautam Panda[a,b*]

[a]*Medicinal and Process Chemistry Division, CSIR-Central Drug Research Institute, BS 10/1, Jankipuram Extension, Sitapur Road, Lucknow 226031, India.*
[b]*Academy of Scientific and Innovative Research, New Delhi 110001, India.*
Fax: +91-522-2771941; Phone: +91-522-2772450, 2772550, Ext 4661, 4662
E-mail : gautam.panda@gmail.com; gautam_panda@cdri.res.in

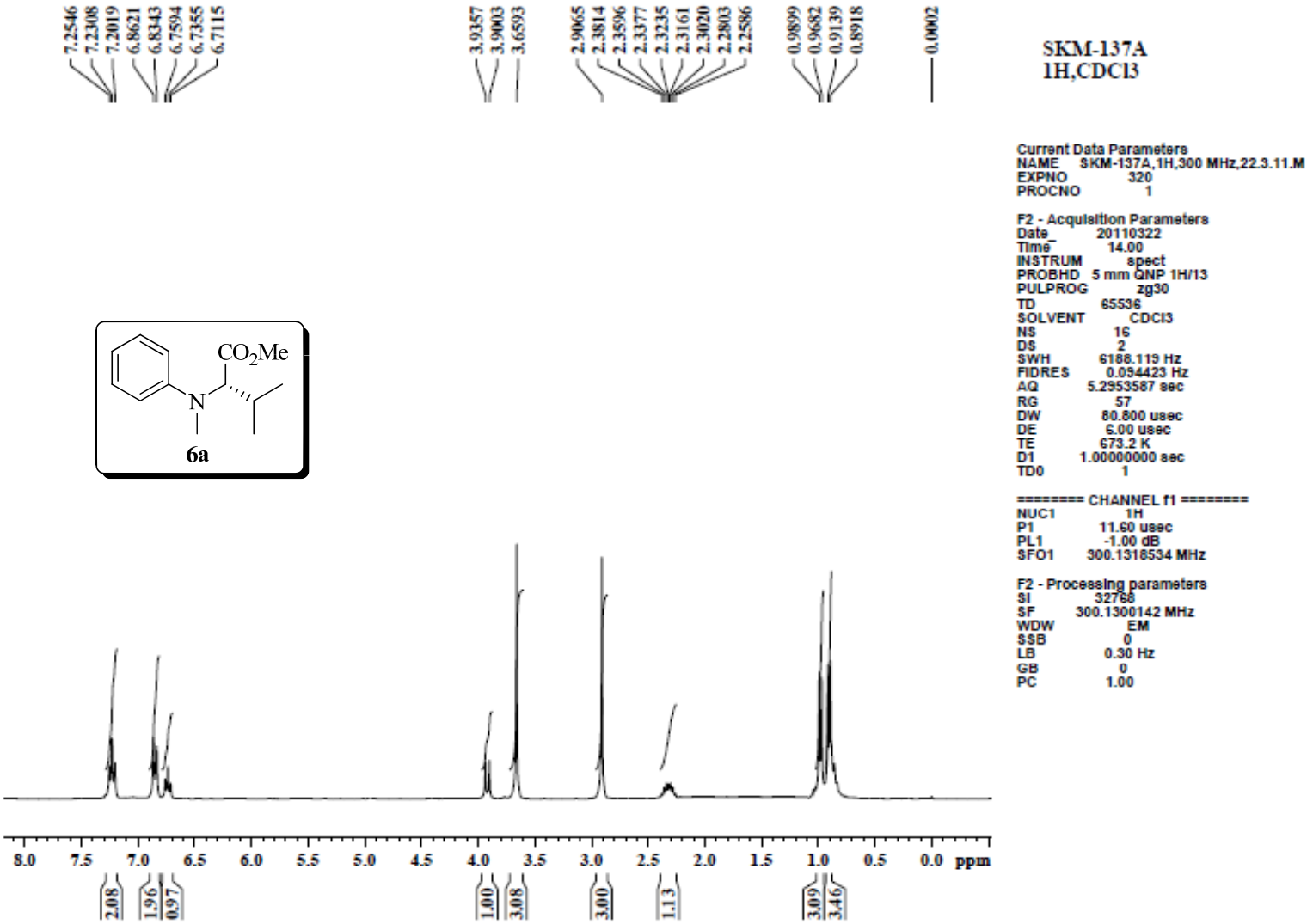


Figure 1: ^{1}H -NMR Spectrum of **6a.**

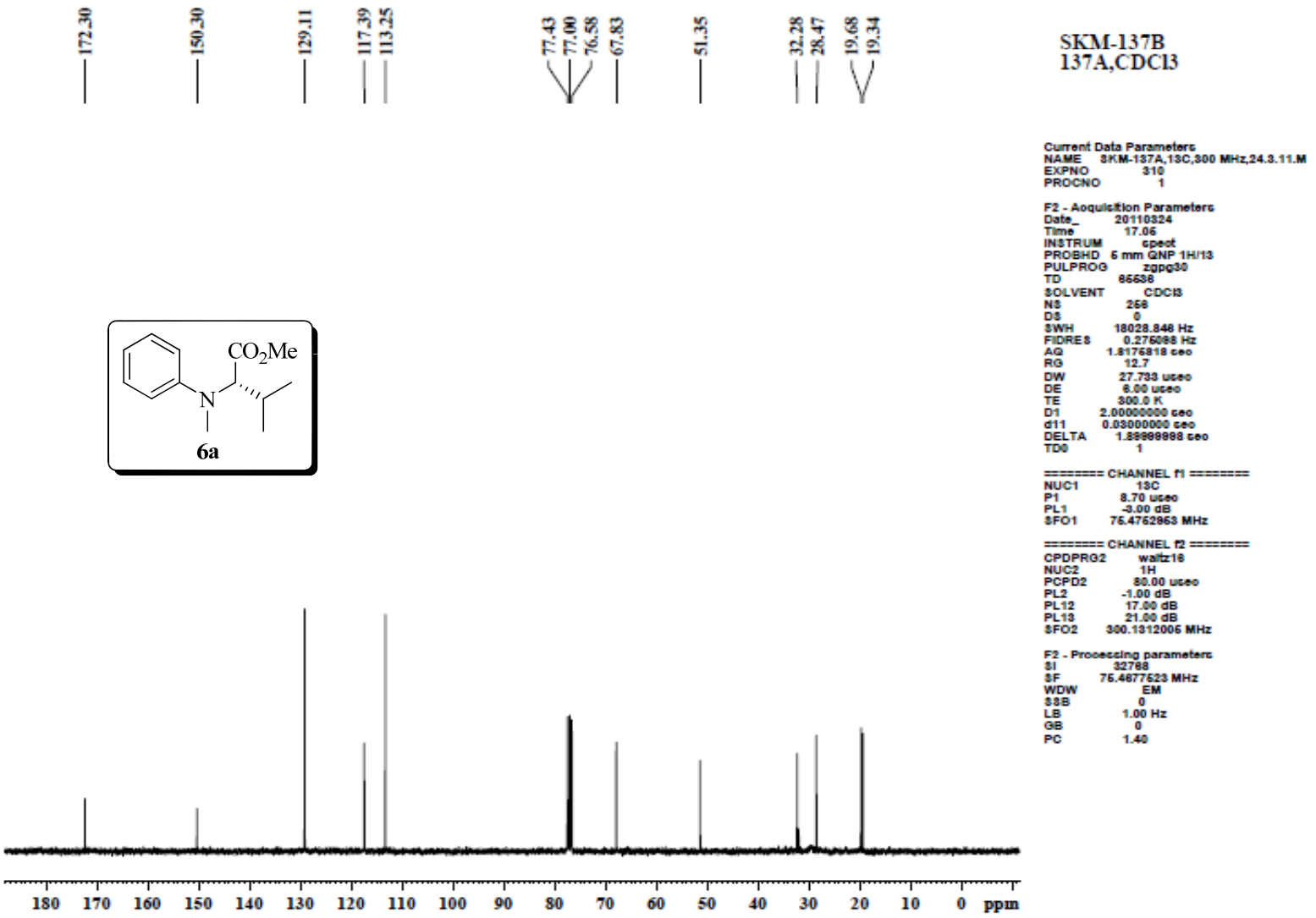


Figure 2: ^{13}C -NMR Spectrum of **6a.**

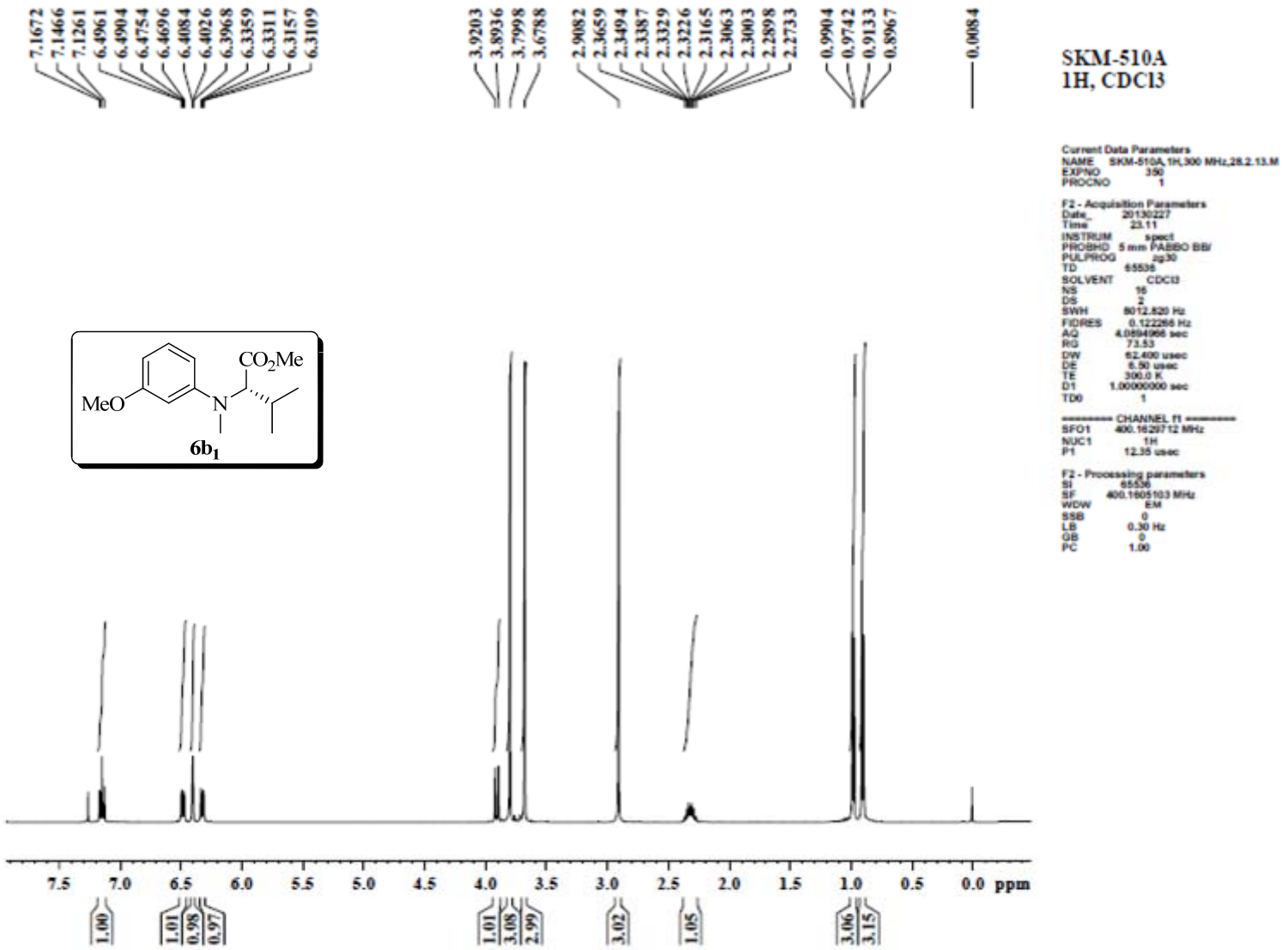


Figure 3: ^{1}H -NMR Spectrum of **$6b_1$.**

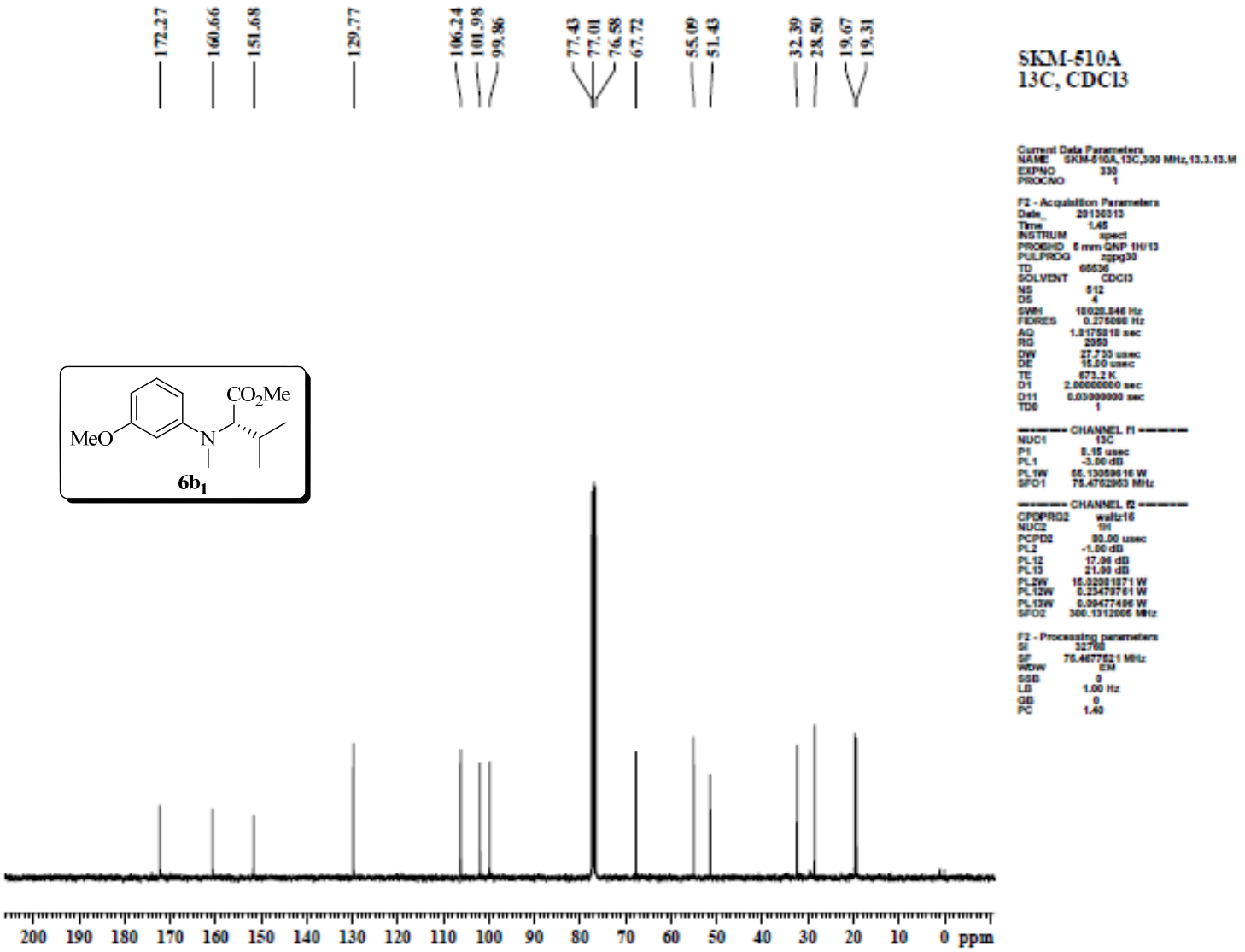


Figure 4: ^{13}C -NMR Spectrum of **$6b_1$.**

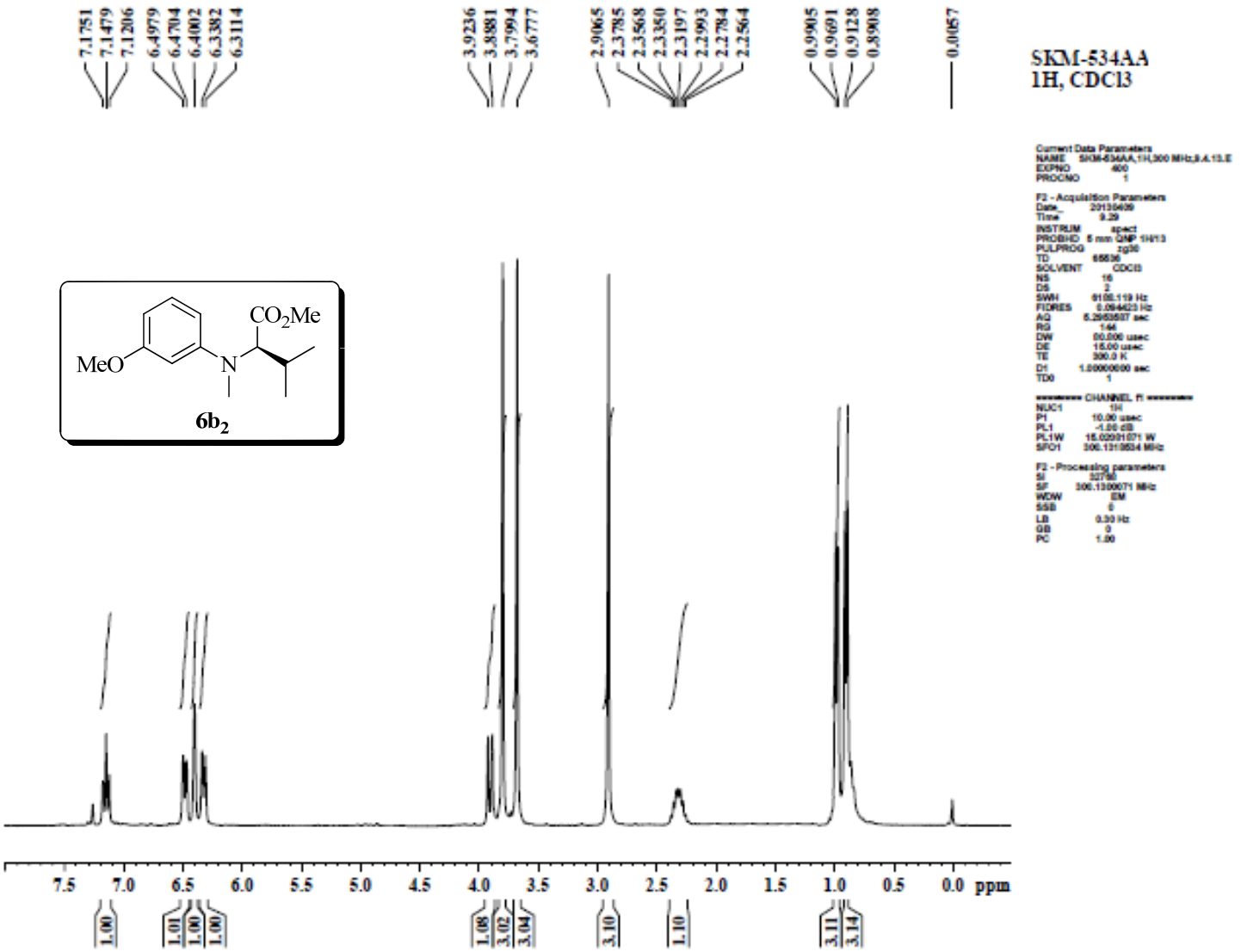


Figure 5: ^{1}H -NMR Spectrum of **$6b_2$.**

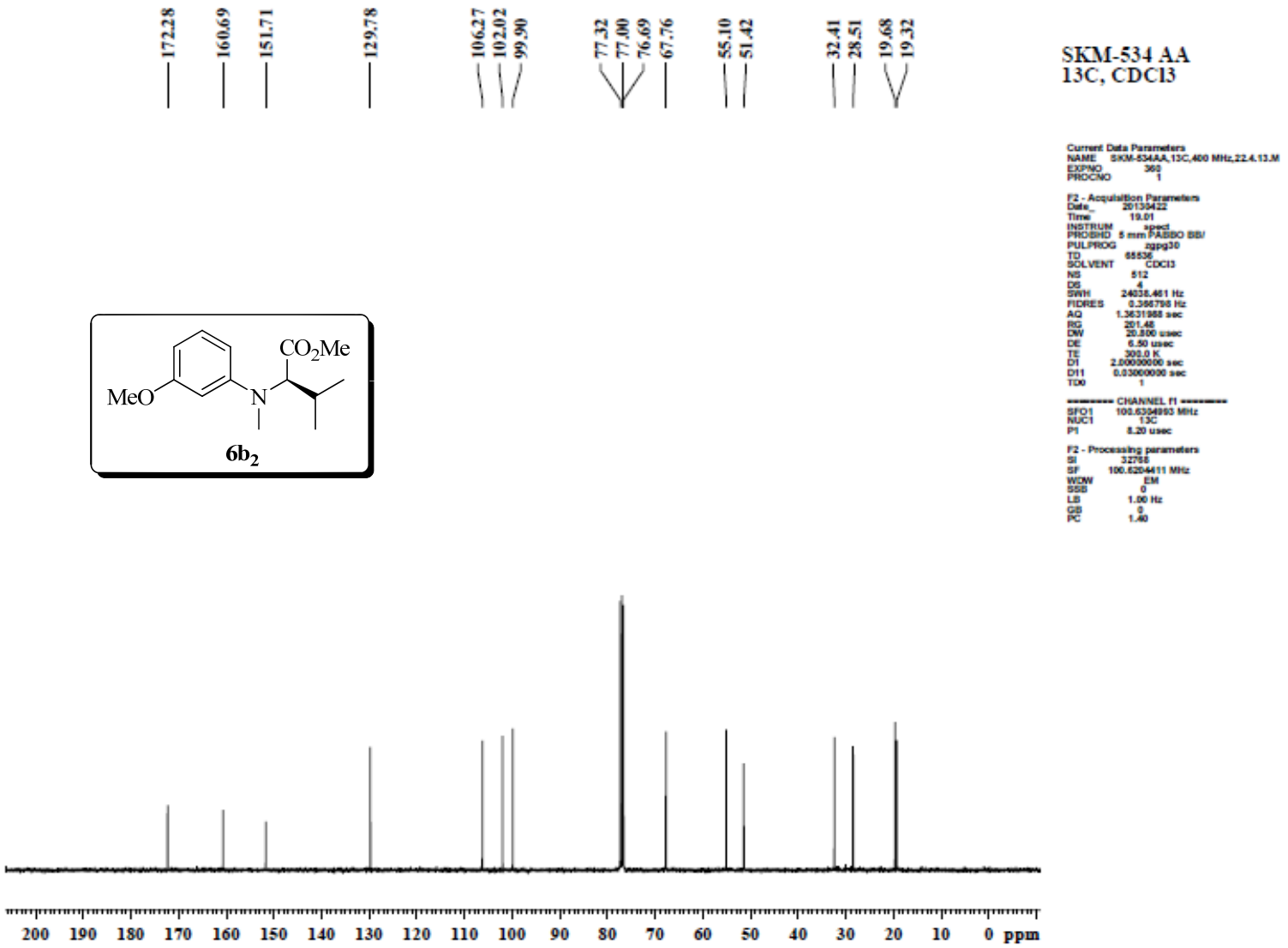


Figure 6: ^{13}C -NMR Spectrum of **$6b_2$.**

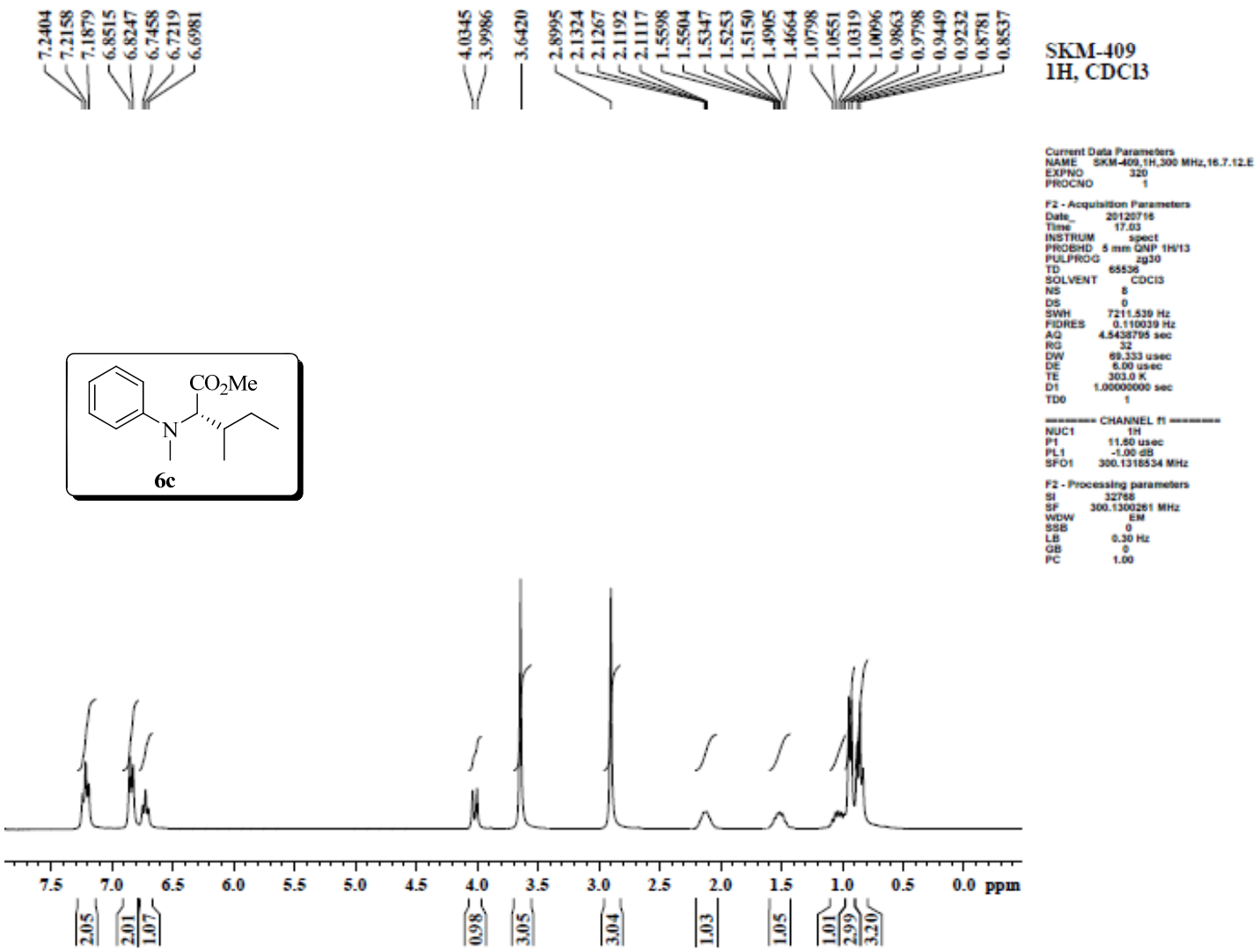
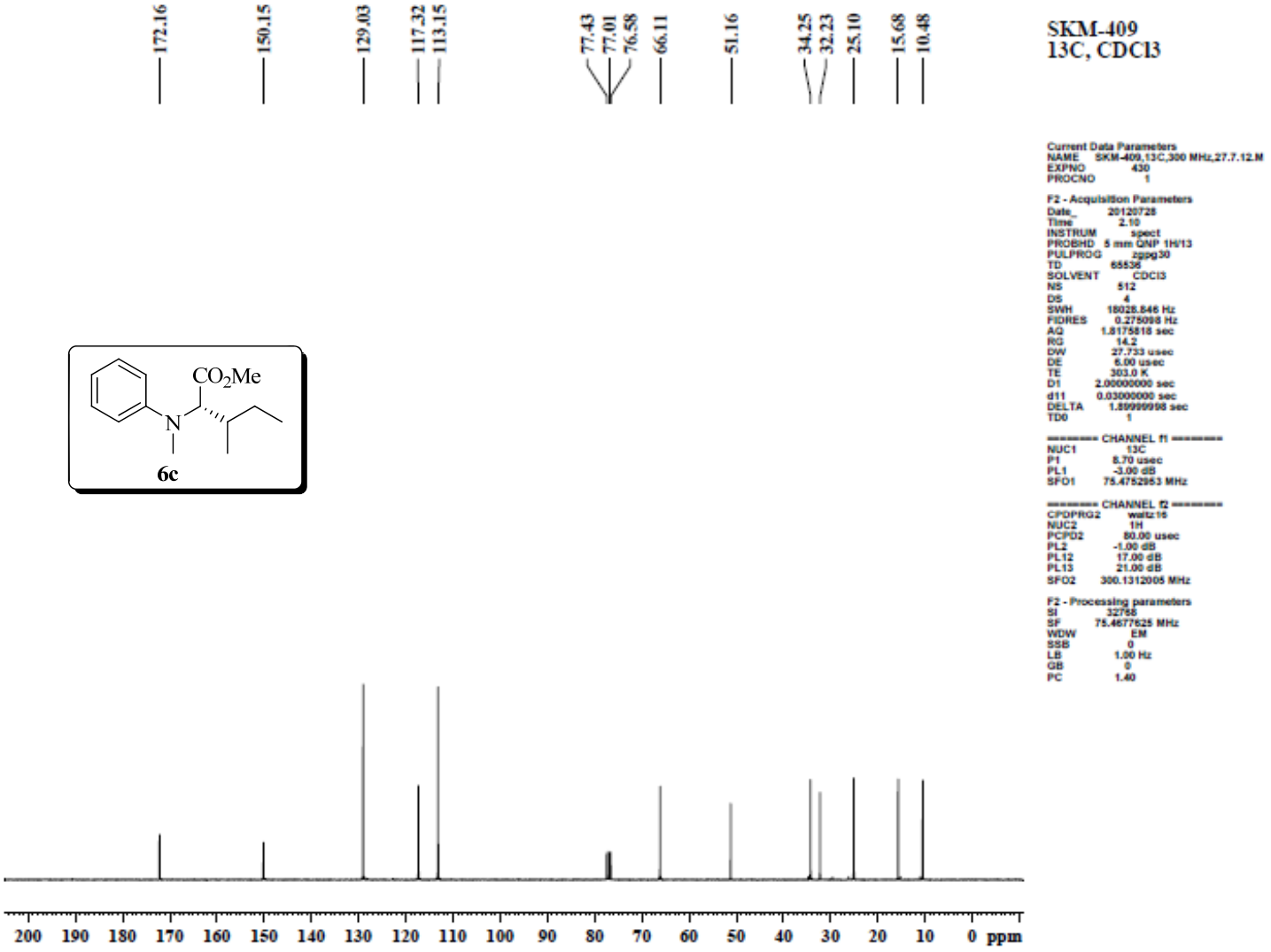


Figure 7: ^{1}H -NMR Spectrum of **6c.**



Current Data Parameters
NAME SKM-409.13C,300 MHz,27.7.12.M
EXPNO 430
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120728
Time 2.10
INSTRUM spect
PROBHD 5 mm DNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 14.2
DW 27.733 usec
DE 6.00 usec
TE 303.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 17.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677625 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure 8: ^{13}C -NMR Spectrum of **6c.**

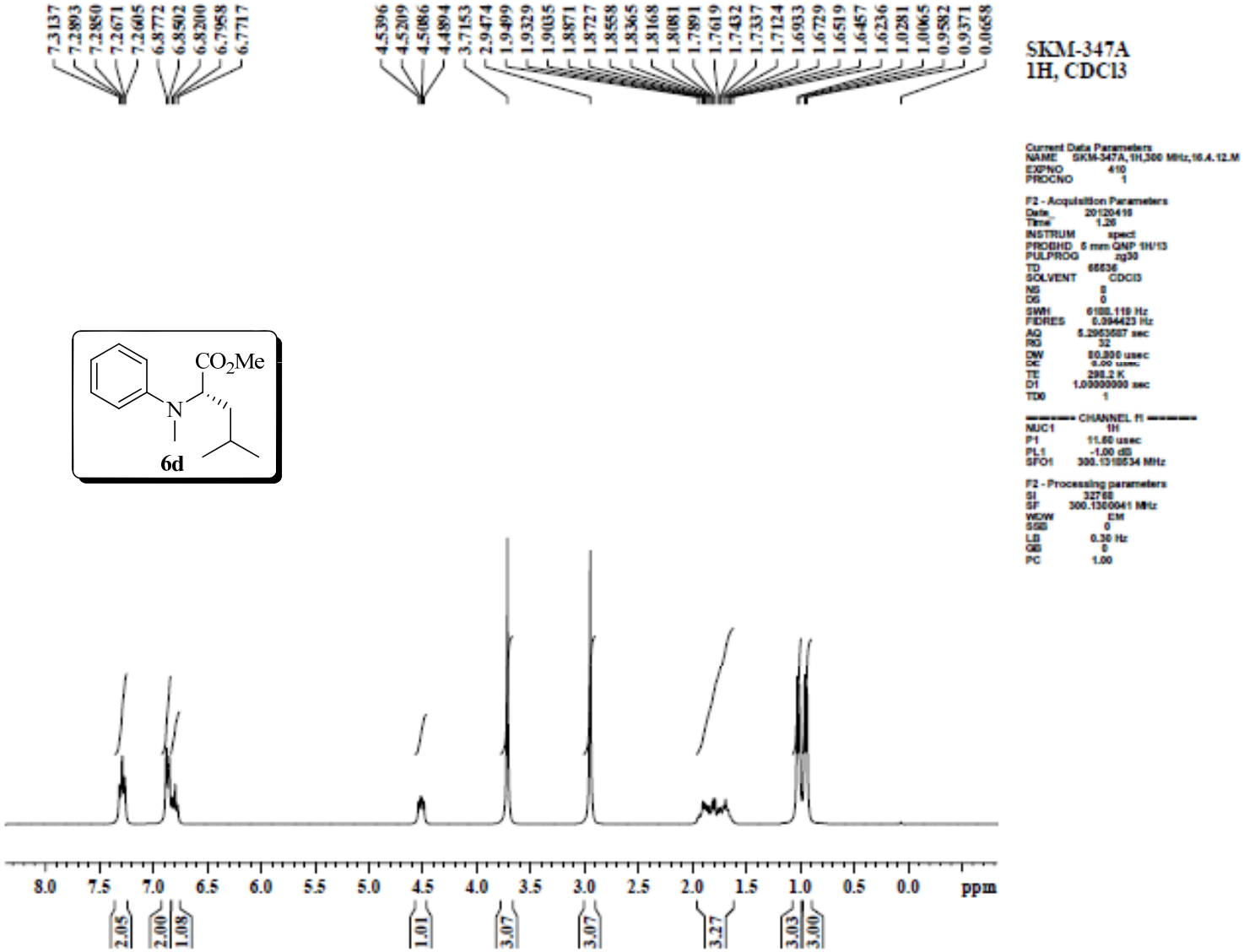


Figure 9: ^{1}H -NMR Spectrum of **6d.**

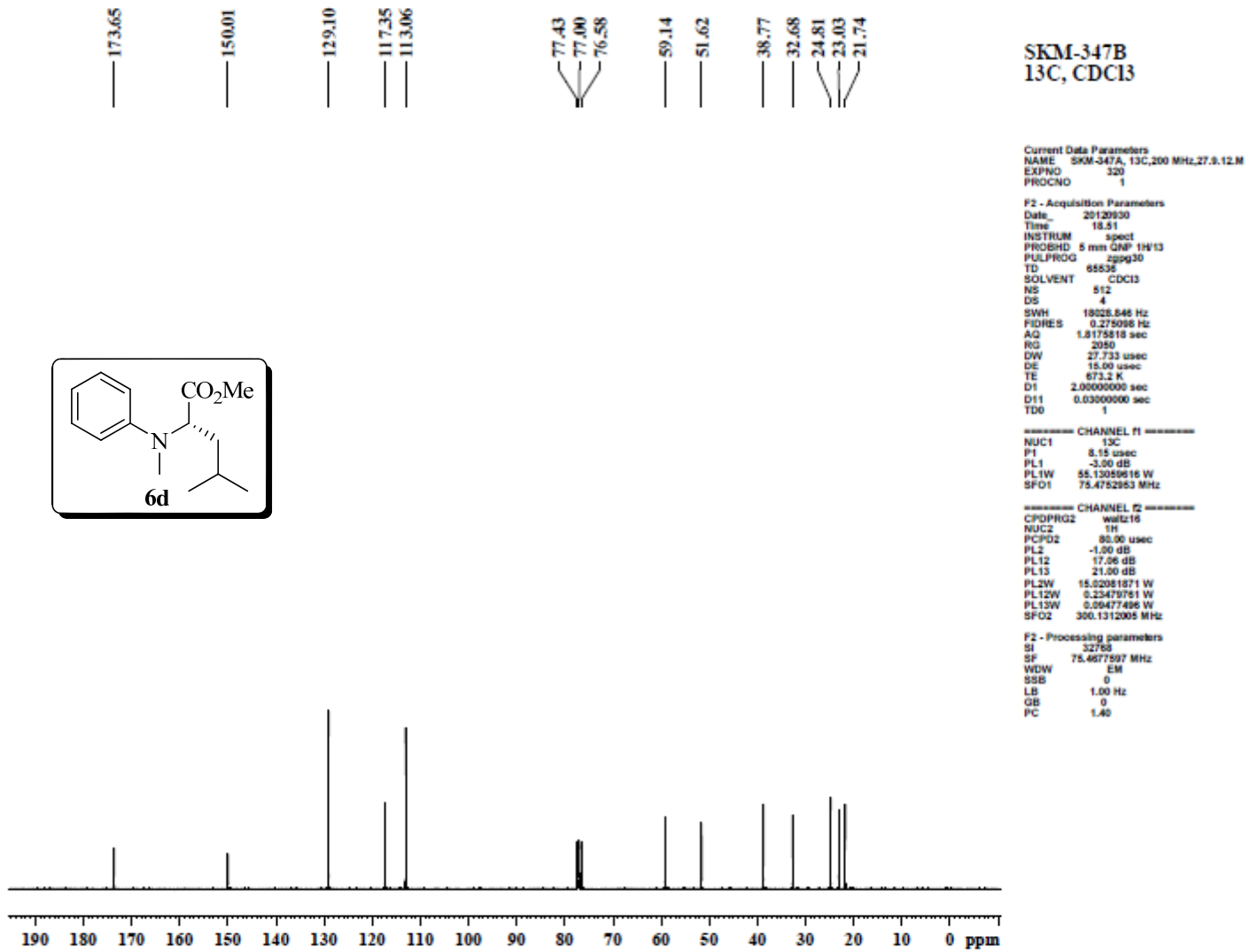


Figure 10: ^{13}C -NMR Spectrum of **6d.**

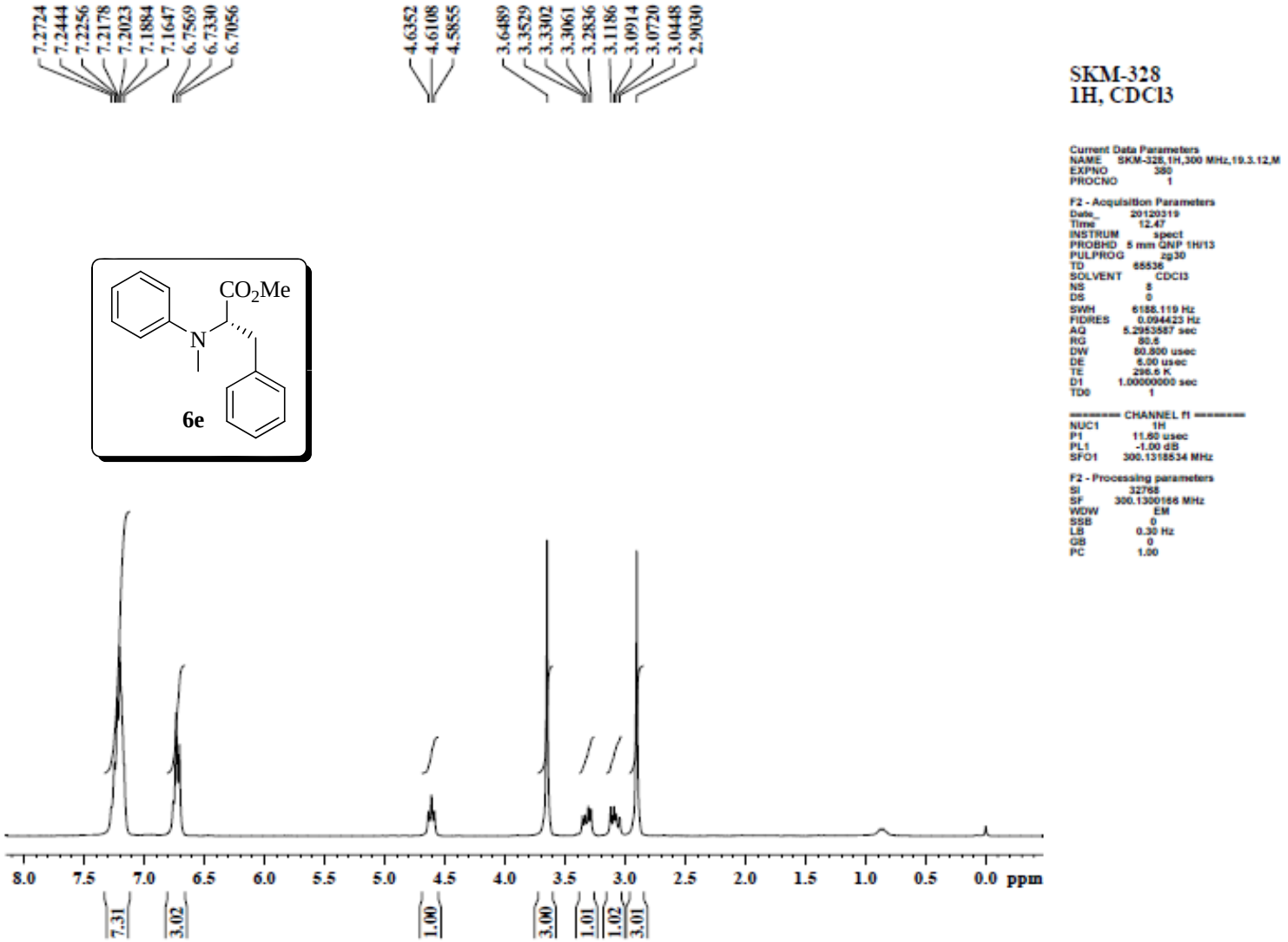


Figure 11: ^{1}H -NMR Spectrum of **6e.**

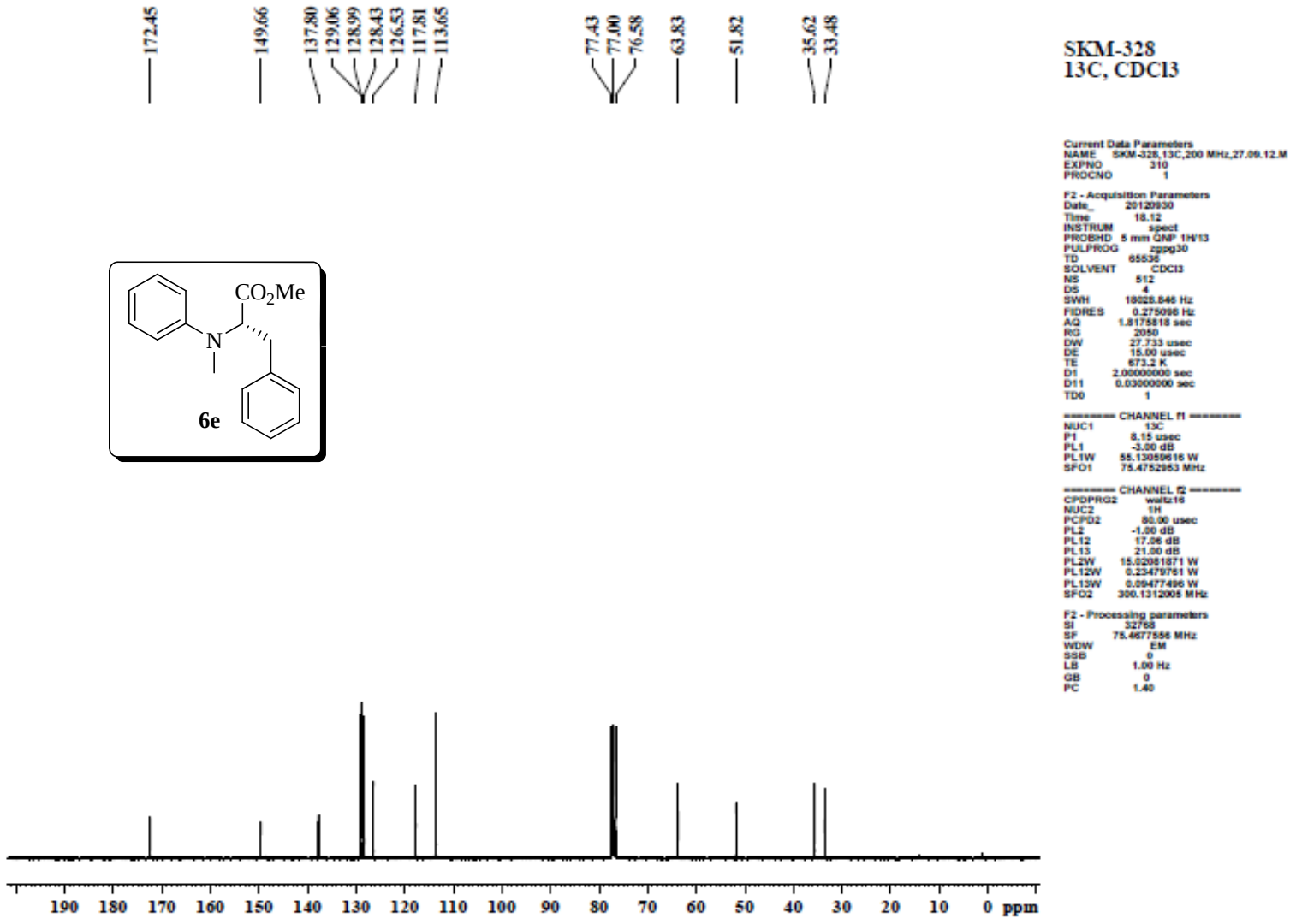


Figure 12: ^{13}C -NMR Spectrum of **6e.**

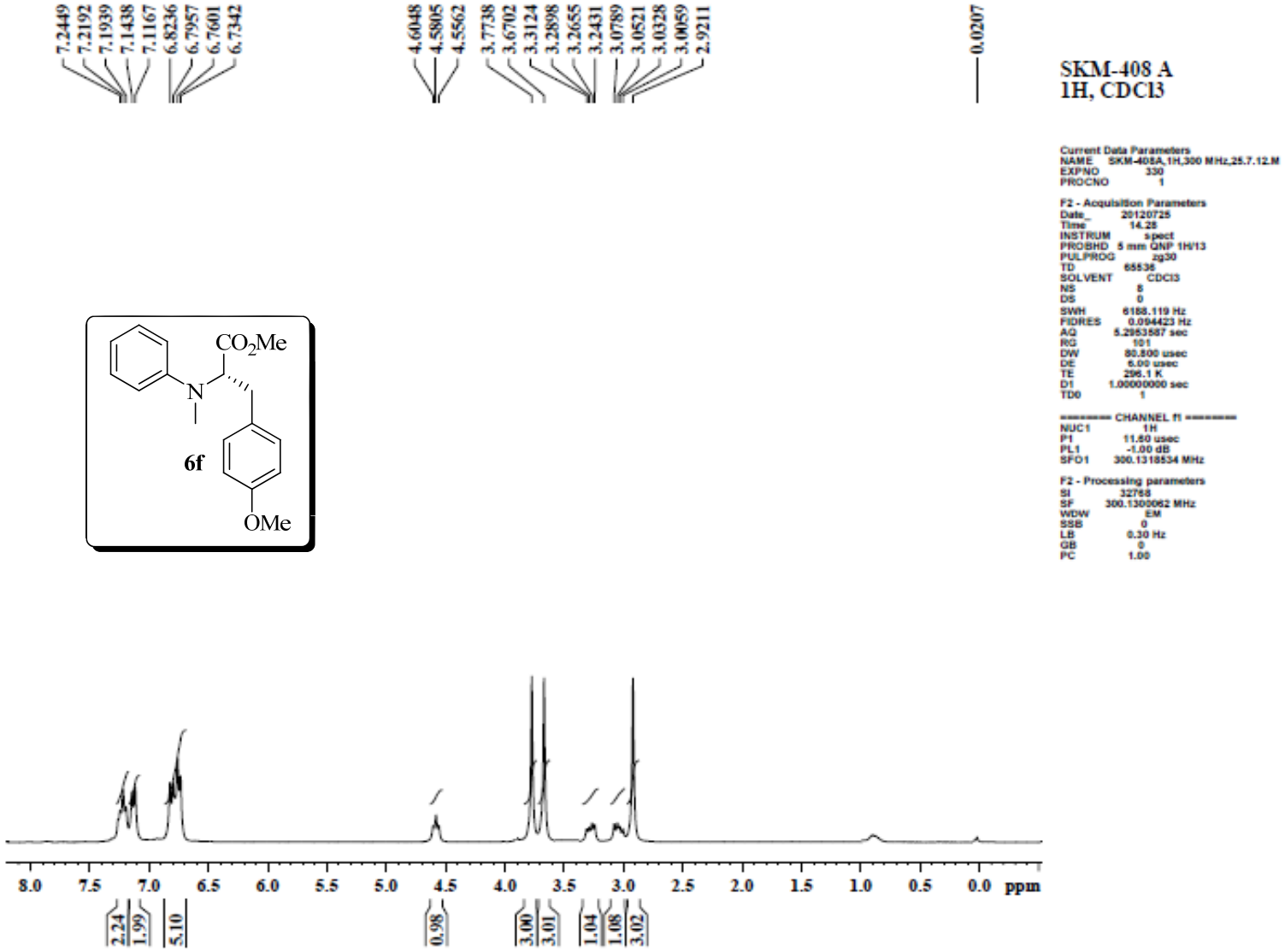


Figure 13: ^{1}H -NMR Spectrum of **6f.**

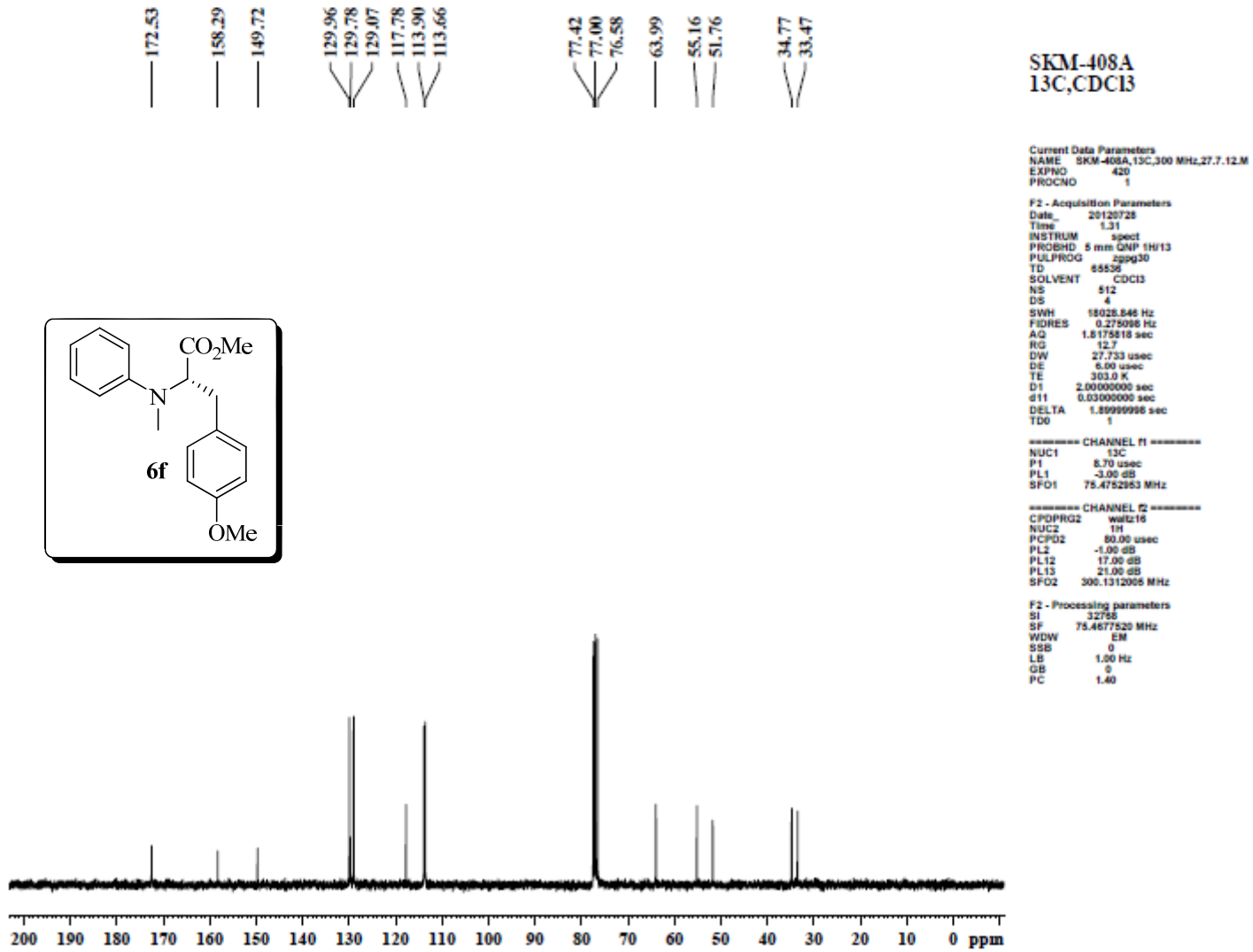


Figure 14: ^{13}C -NMR Spectrum of **6f.**

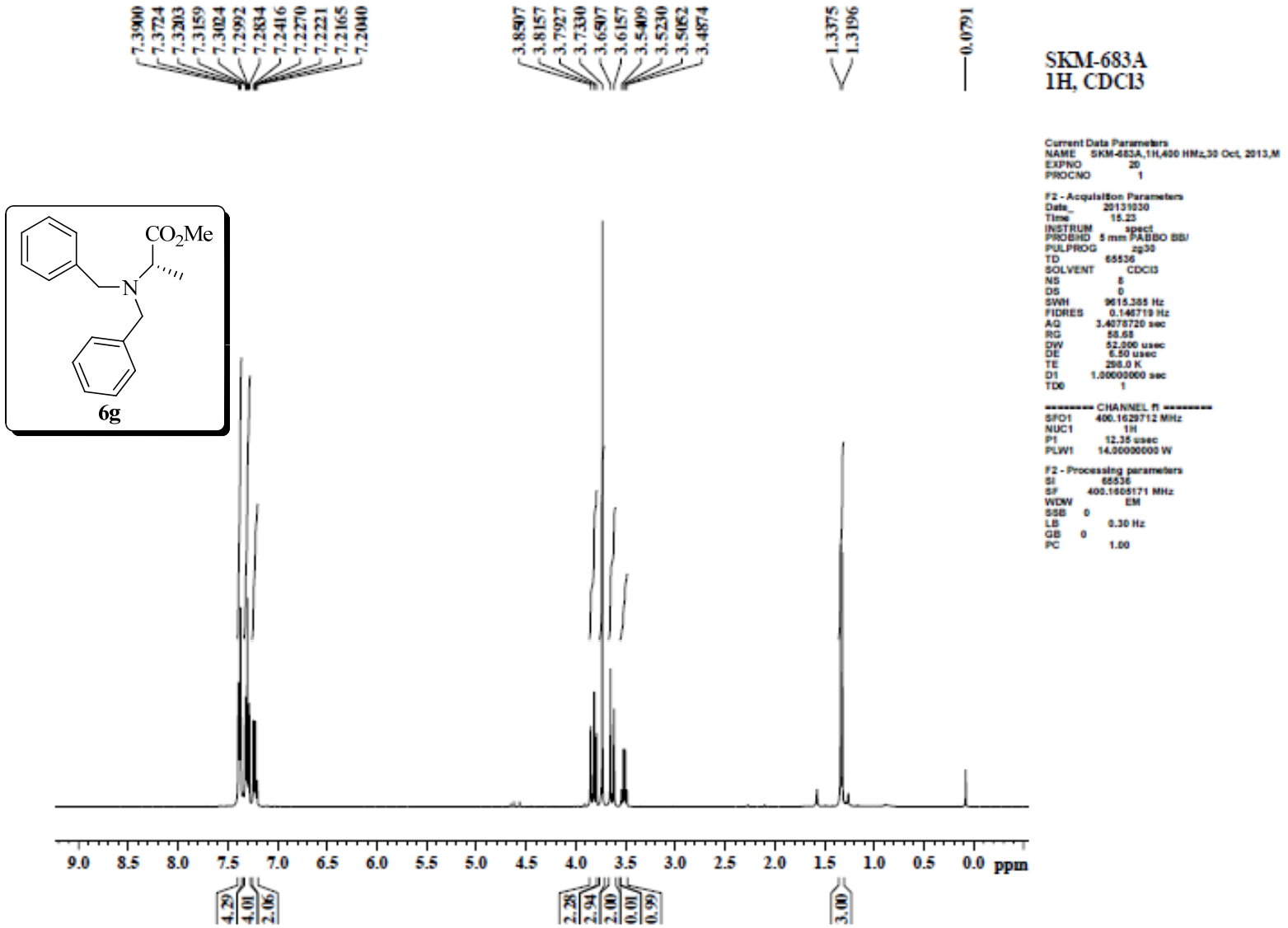


Figure 15: ^{1}H -NMR Spectrum of **6g.**

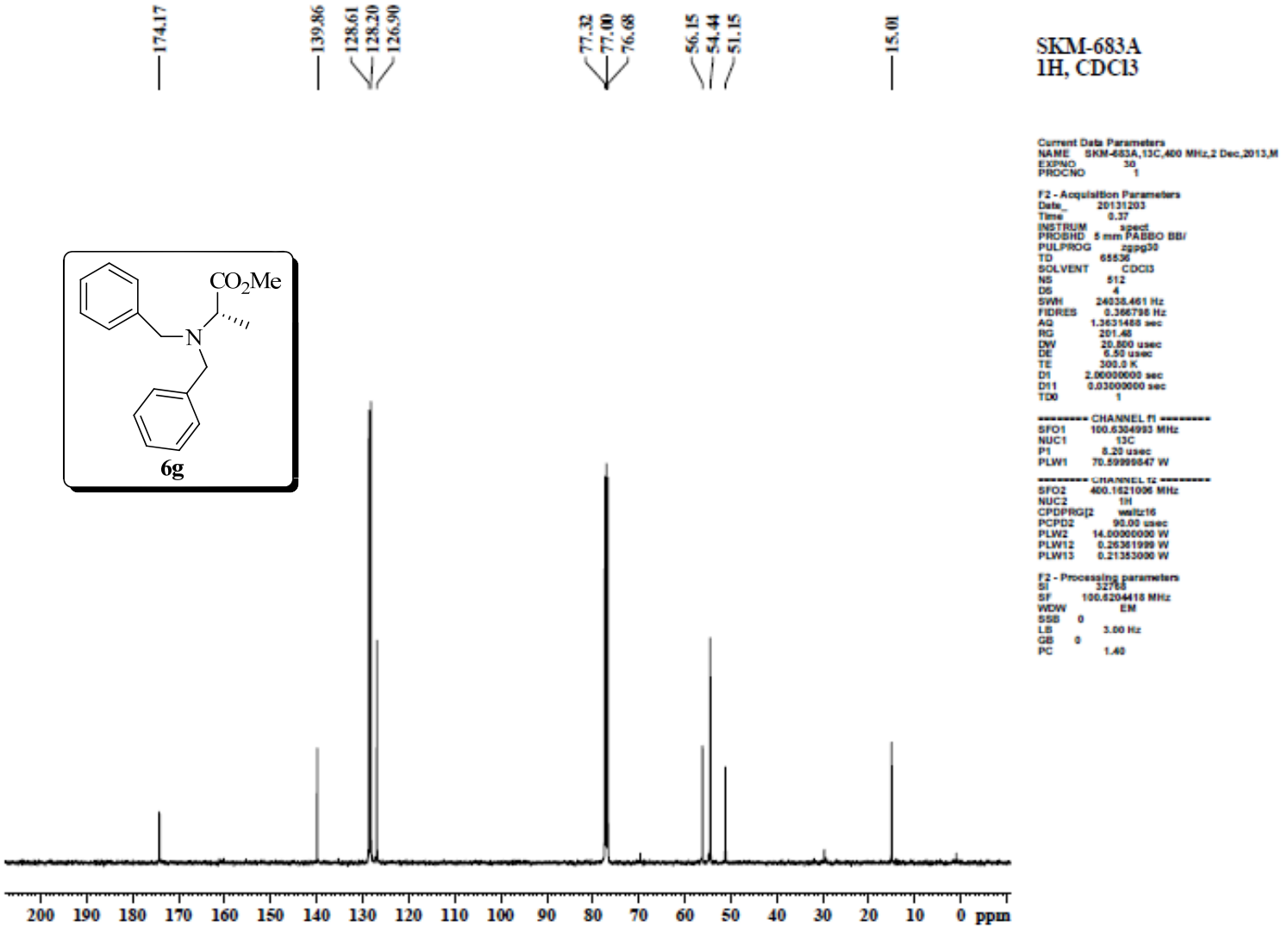


Figure 16: ^{13}C -NMR Spectrum of **6g.**

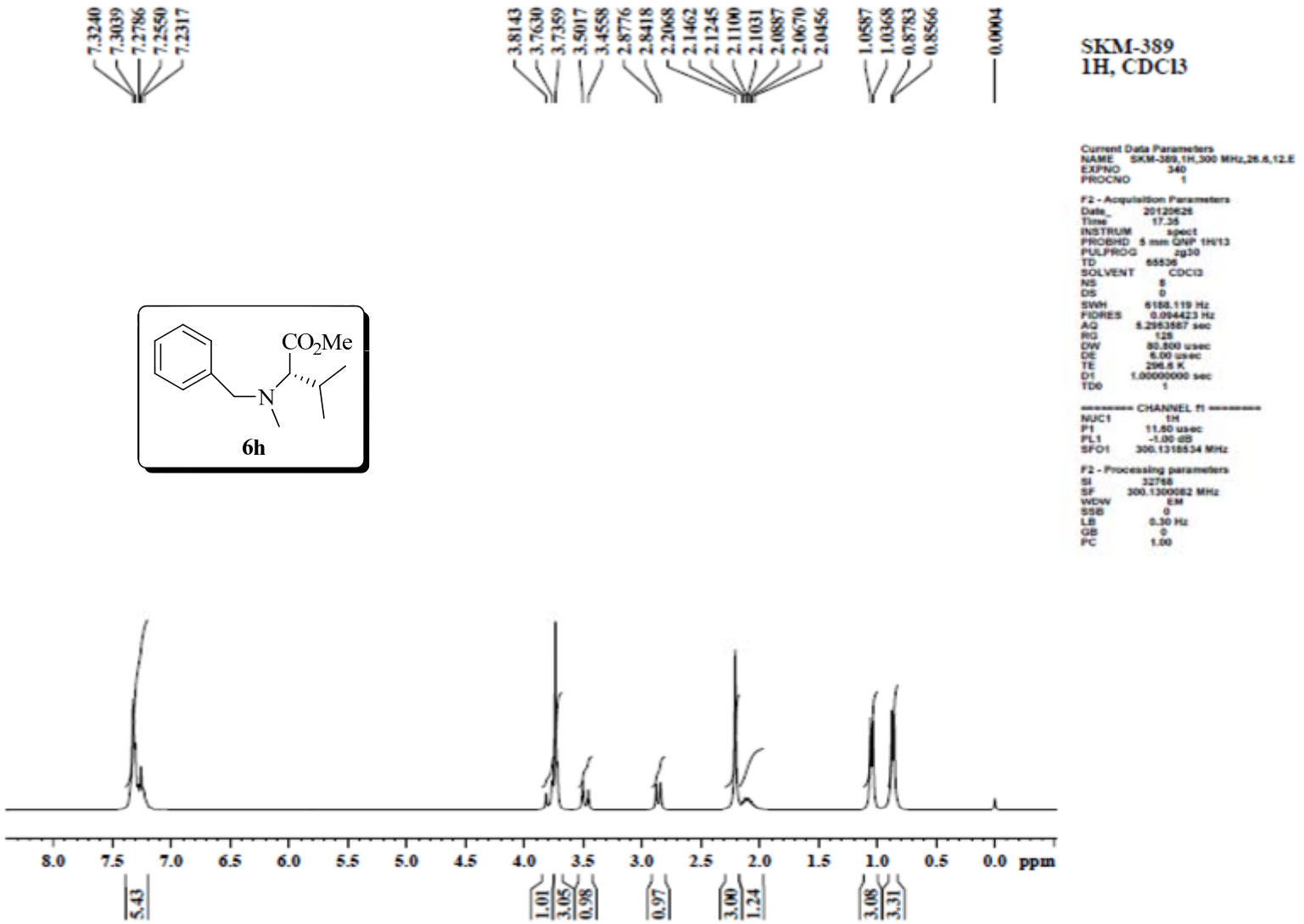


Figure 17: ^{1}H -NMR Spectrum of **6h.**

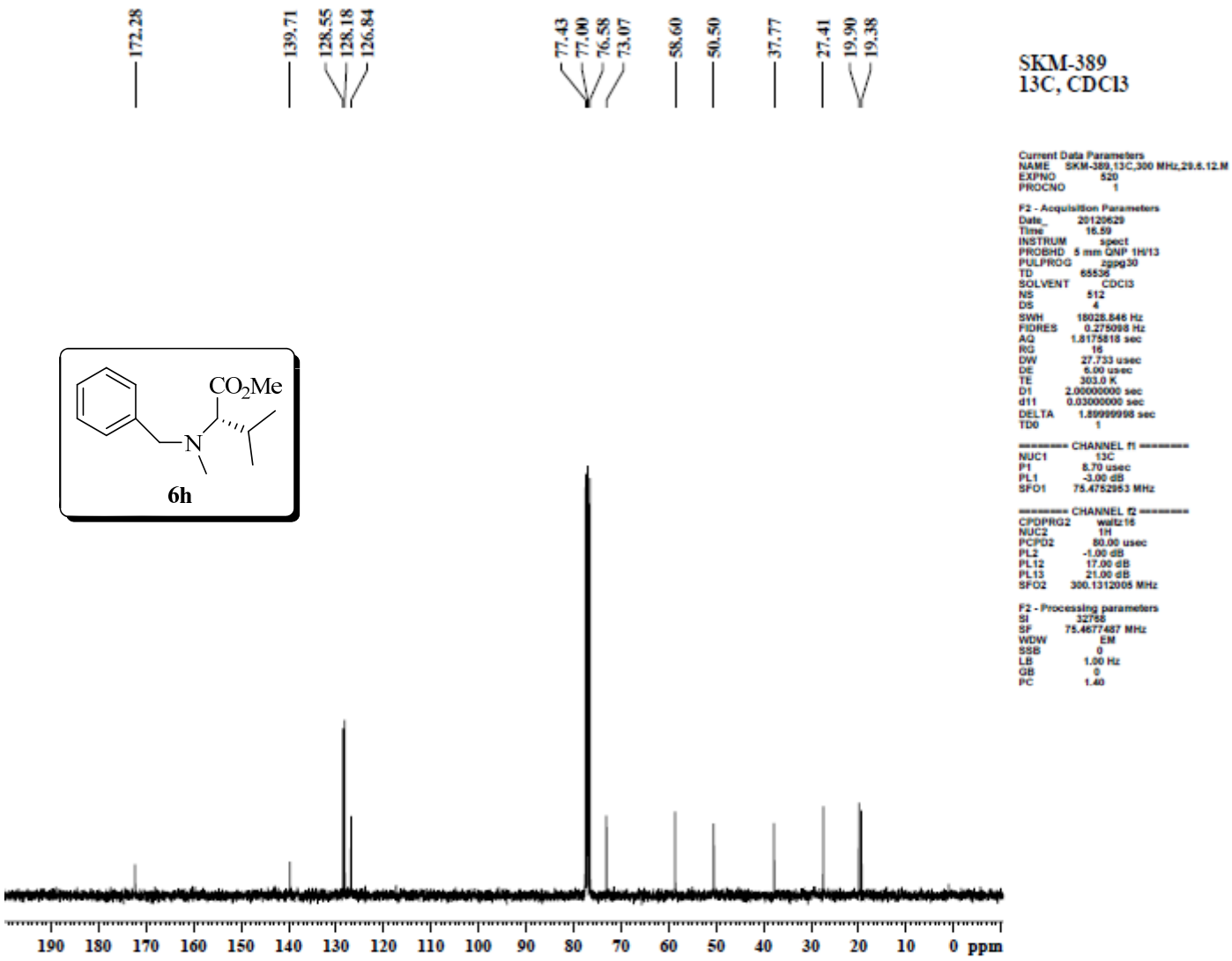


Figure 18: ^{13}C -NMR Spectrum of **6h.**

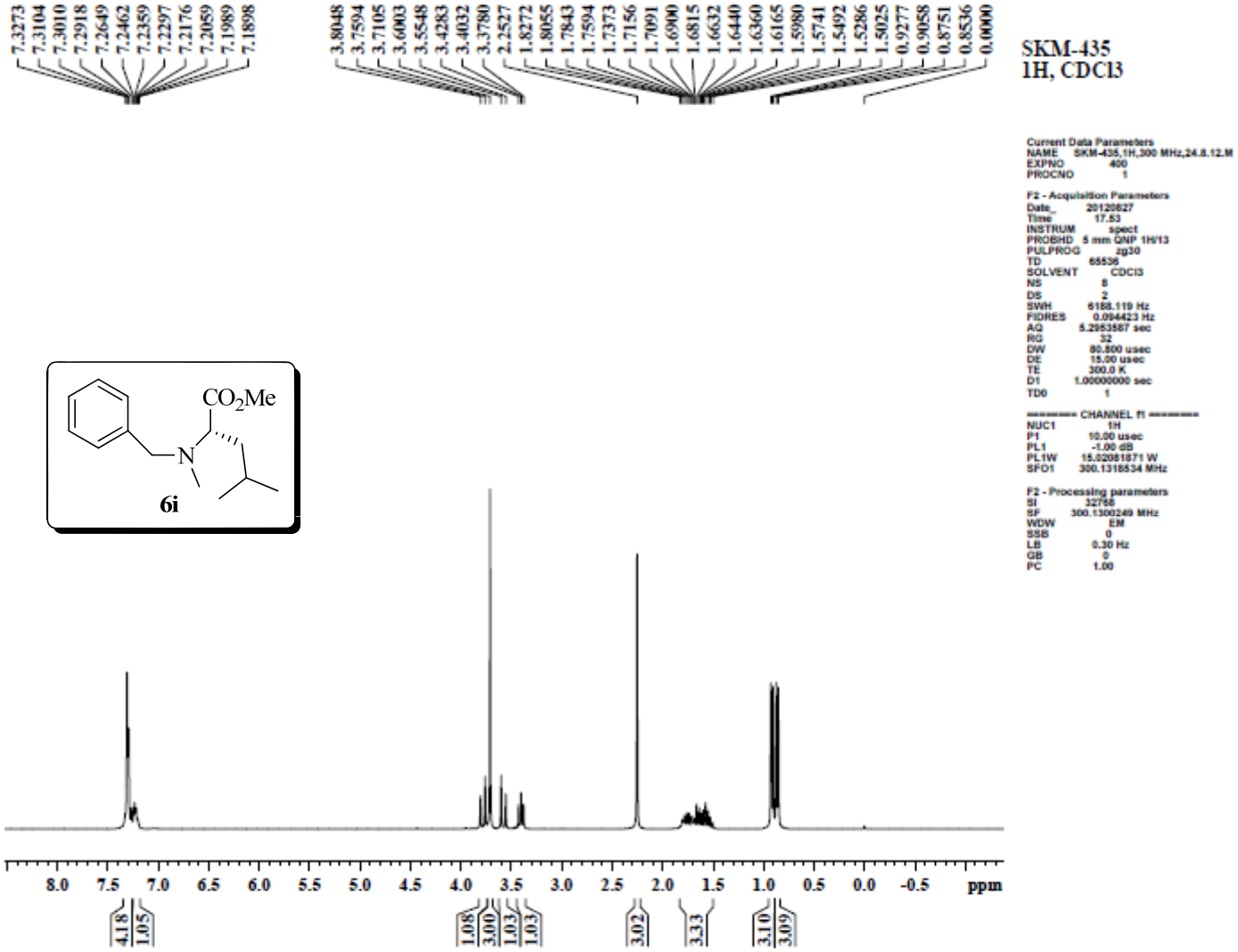


Figure 19: ^{1}H -NMR Spectrum of **6i.**

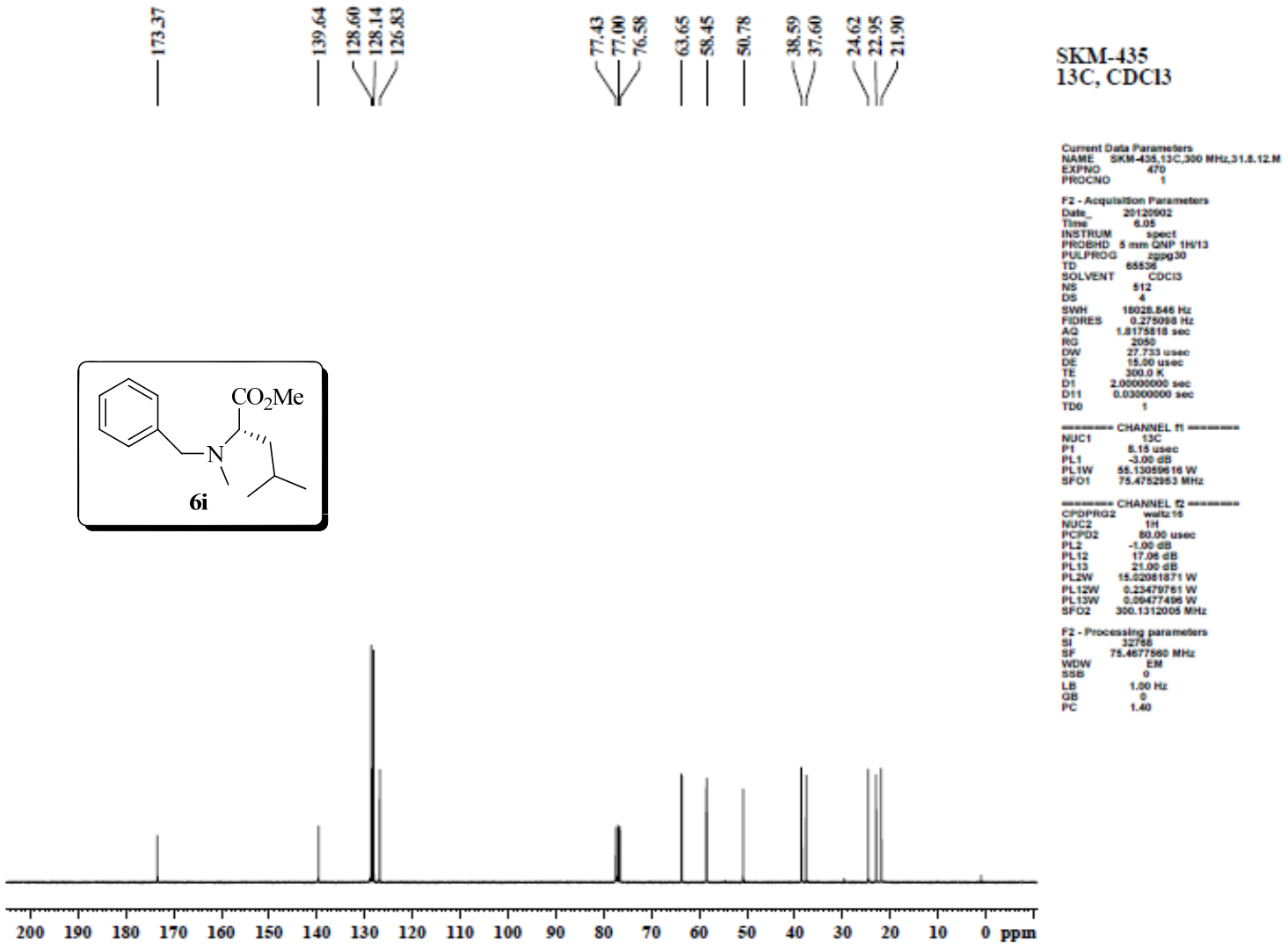


Figure 20: ^{13}C -NMR Spectrum of **6i.**

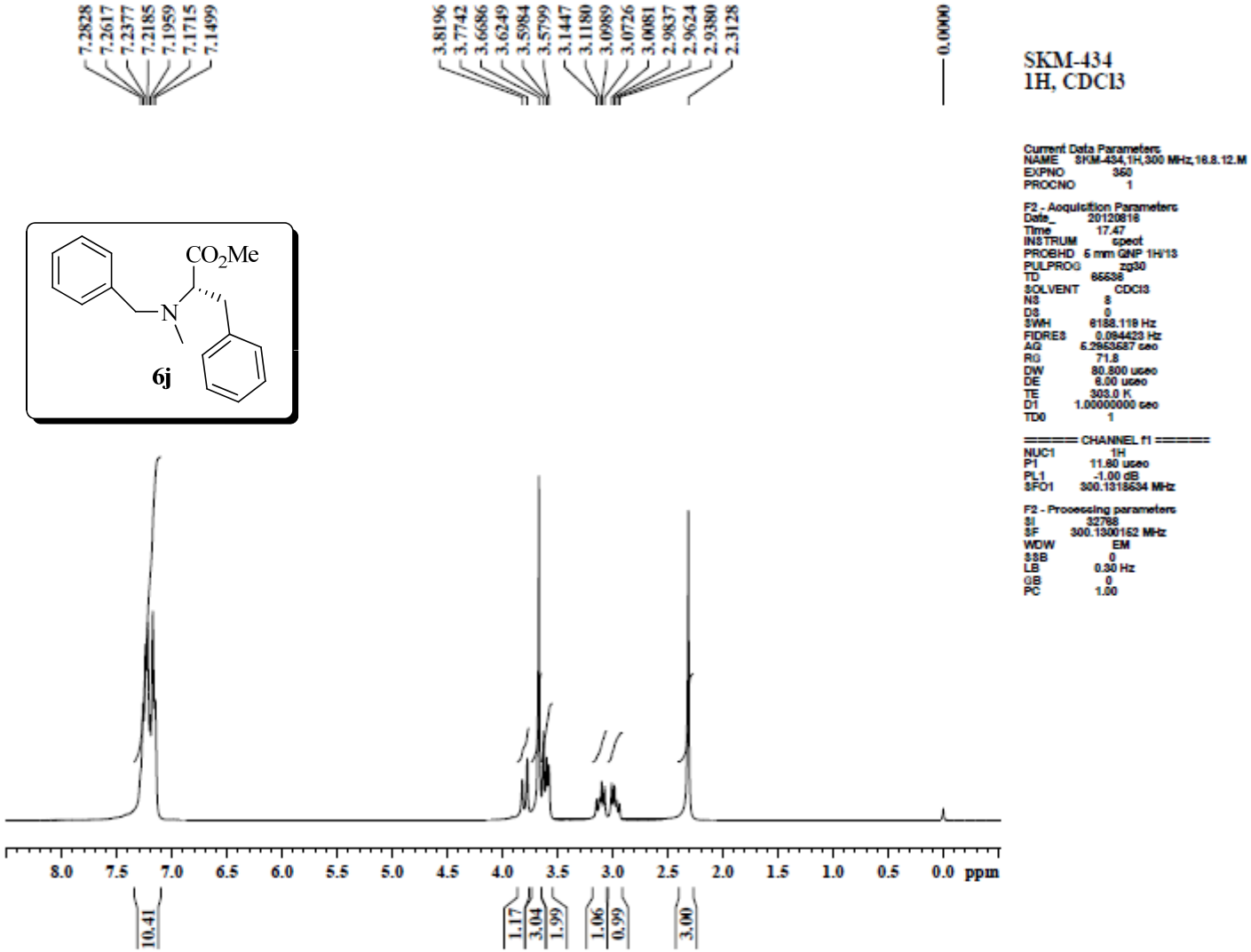


Figure 21: ^{1}H -NMR Spectrum of **6j.**

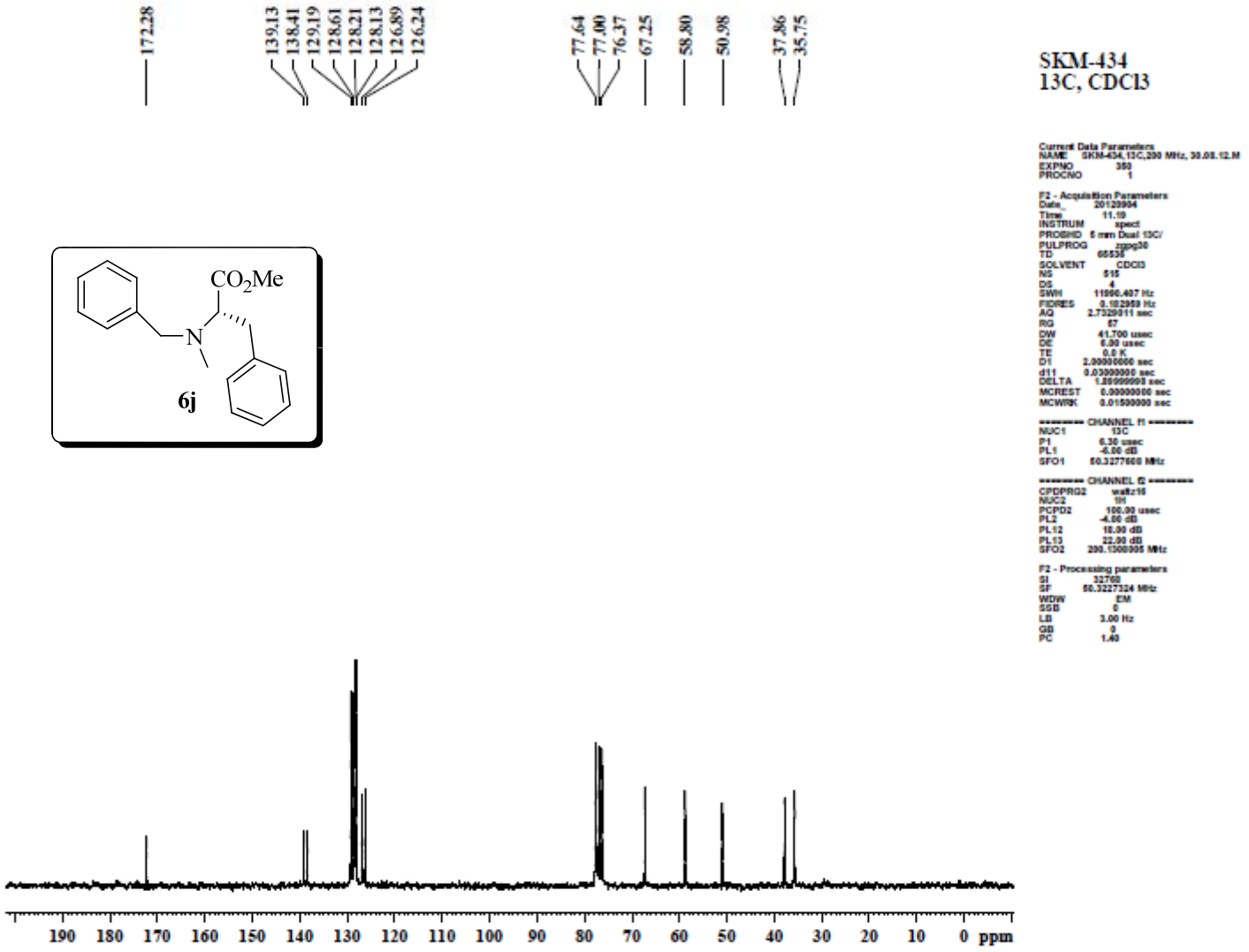


Figure 22: ^{13}C -NMR Spectrum of **6j.**

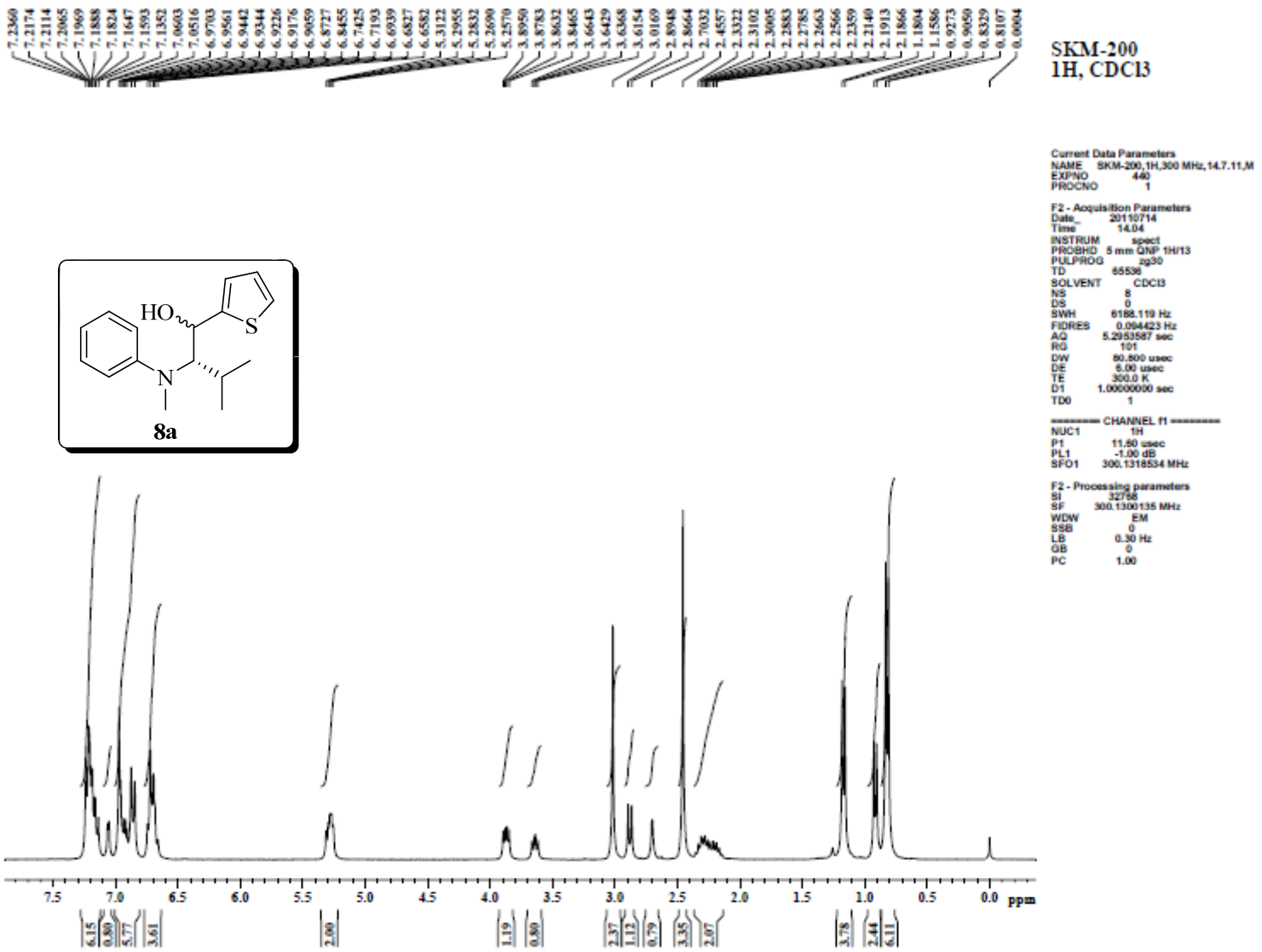


Figure 23: ^{1}H -NMR Spectrum of **8a.**

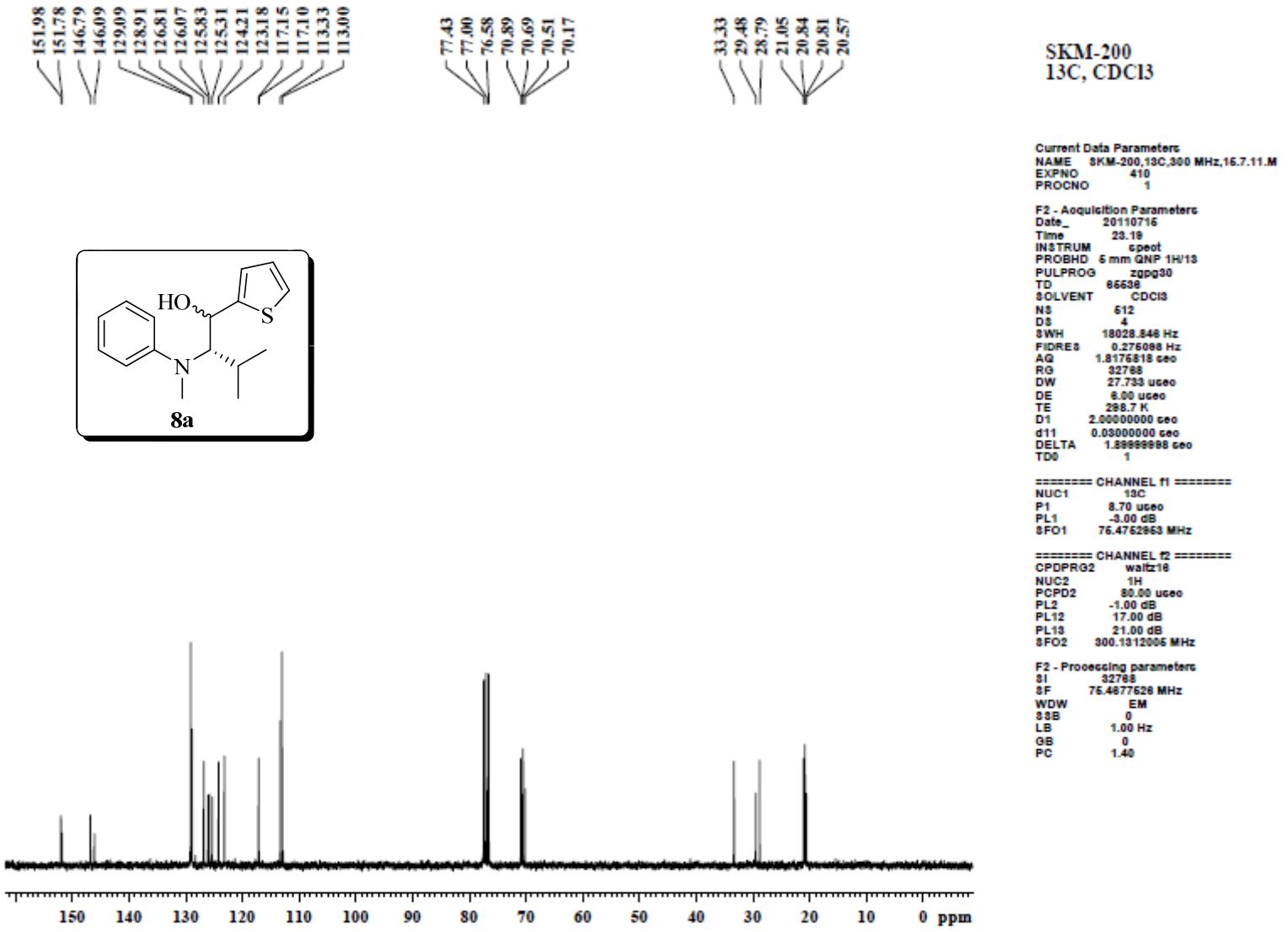


Figure 24: ^{13}C -NMR Spectrum of **8a.**

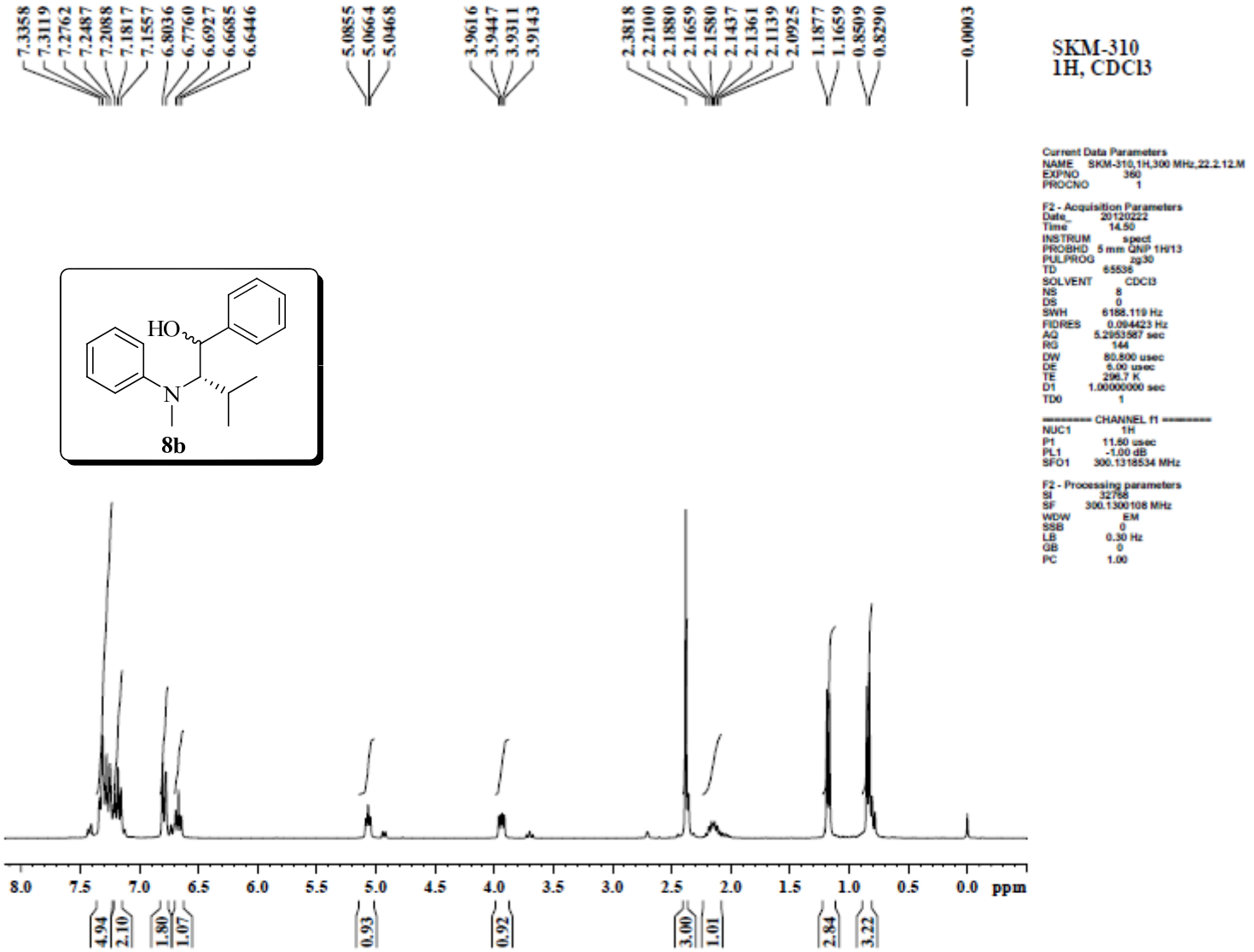


Figure 25: ^{1}H -NMR Spectrum of **8b.**

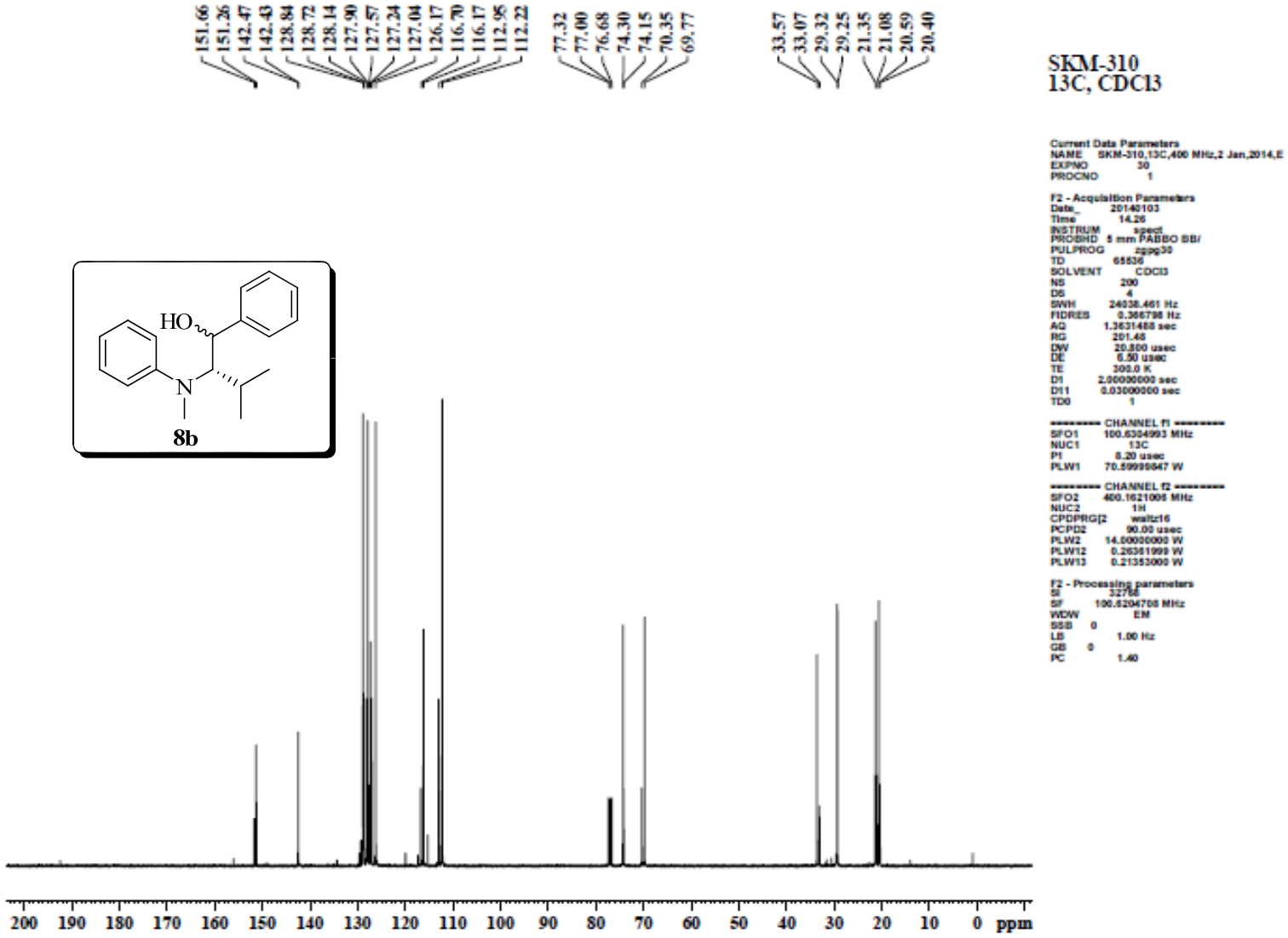


Figure 26: ^{13}C -NMR Spectrum of **8b.**

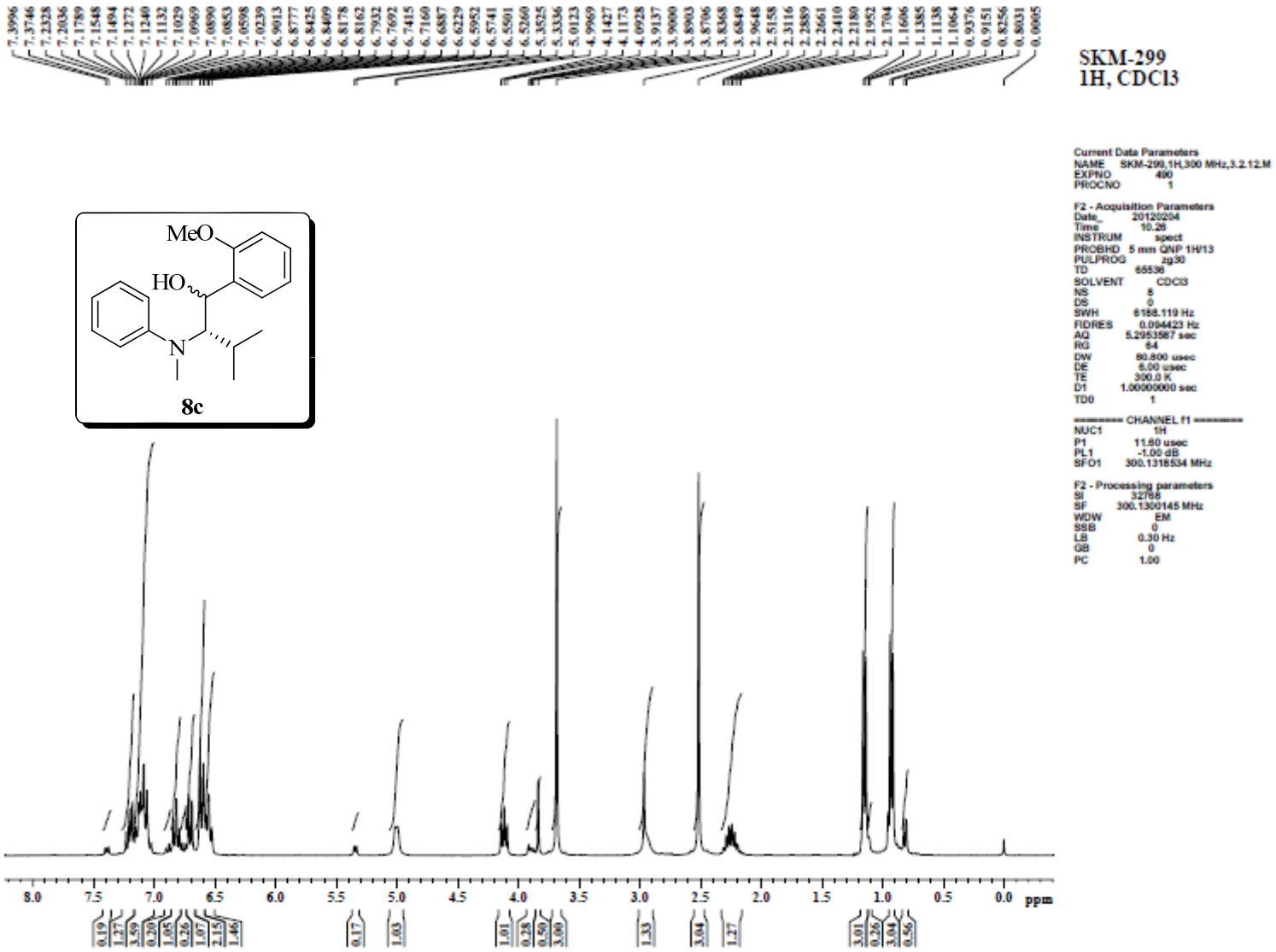


Figure 27: ^{1}H -NMR Spectrum of **8c.**

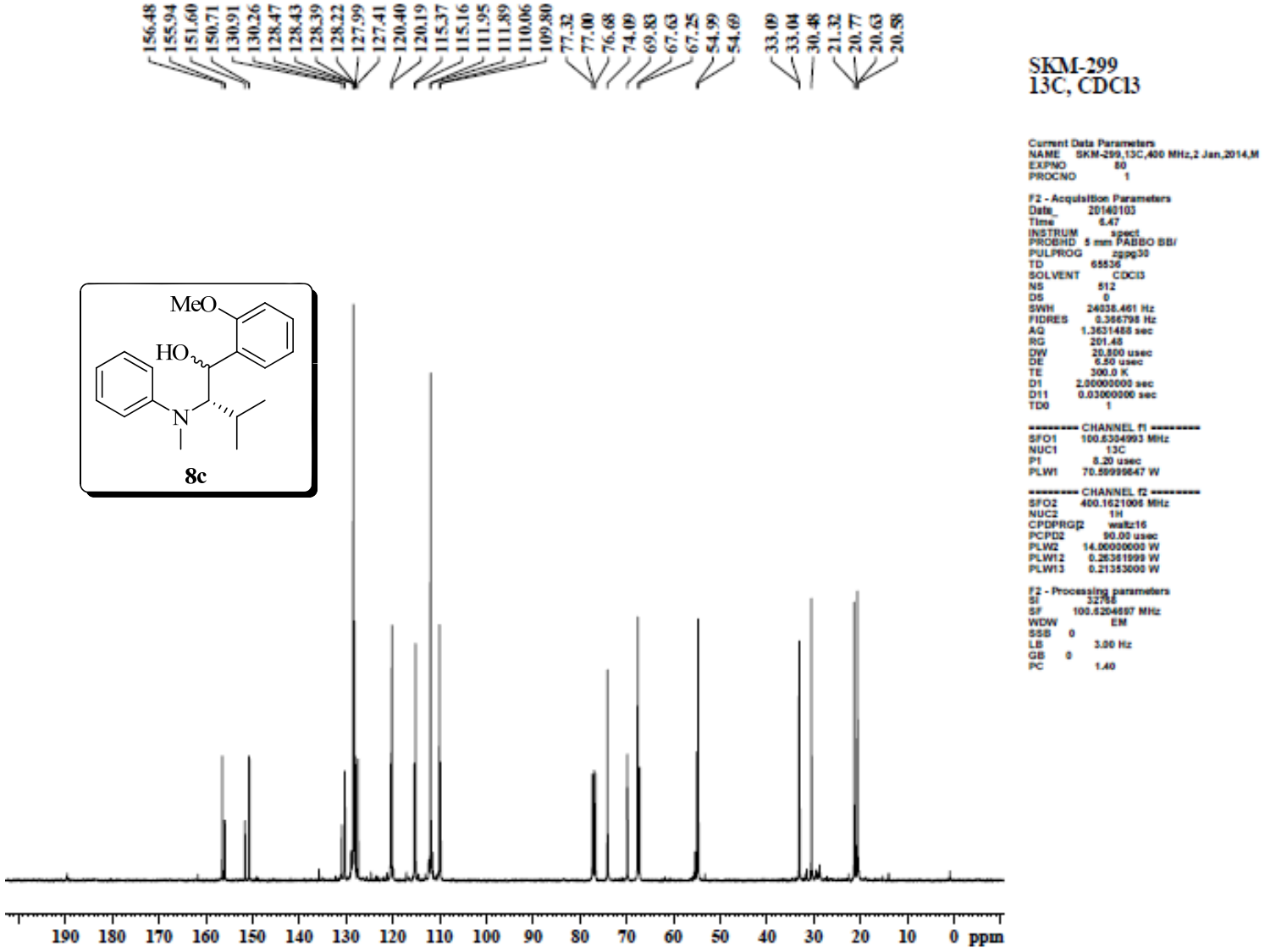


Figure 28: ^{13}C -NMR Spectrum of **8c.**

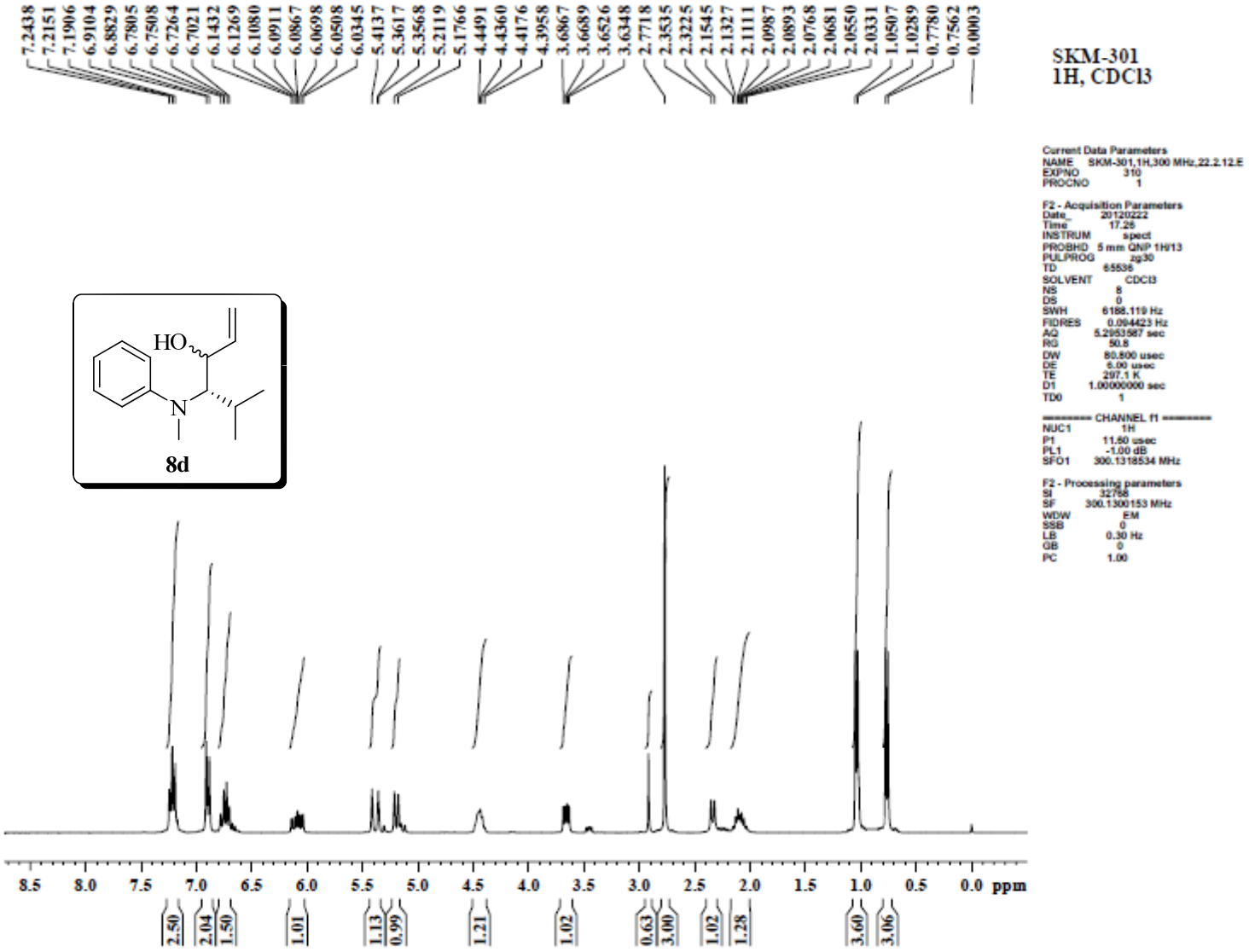


Figure 29: ^{1}H -NMR Spectrum of **8d.**

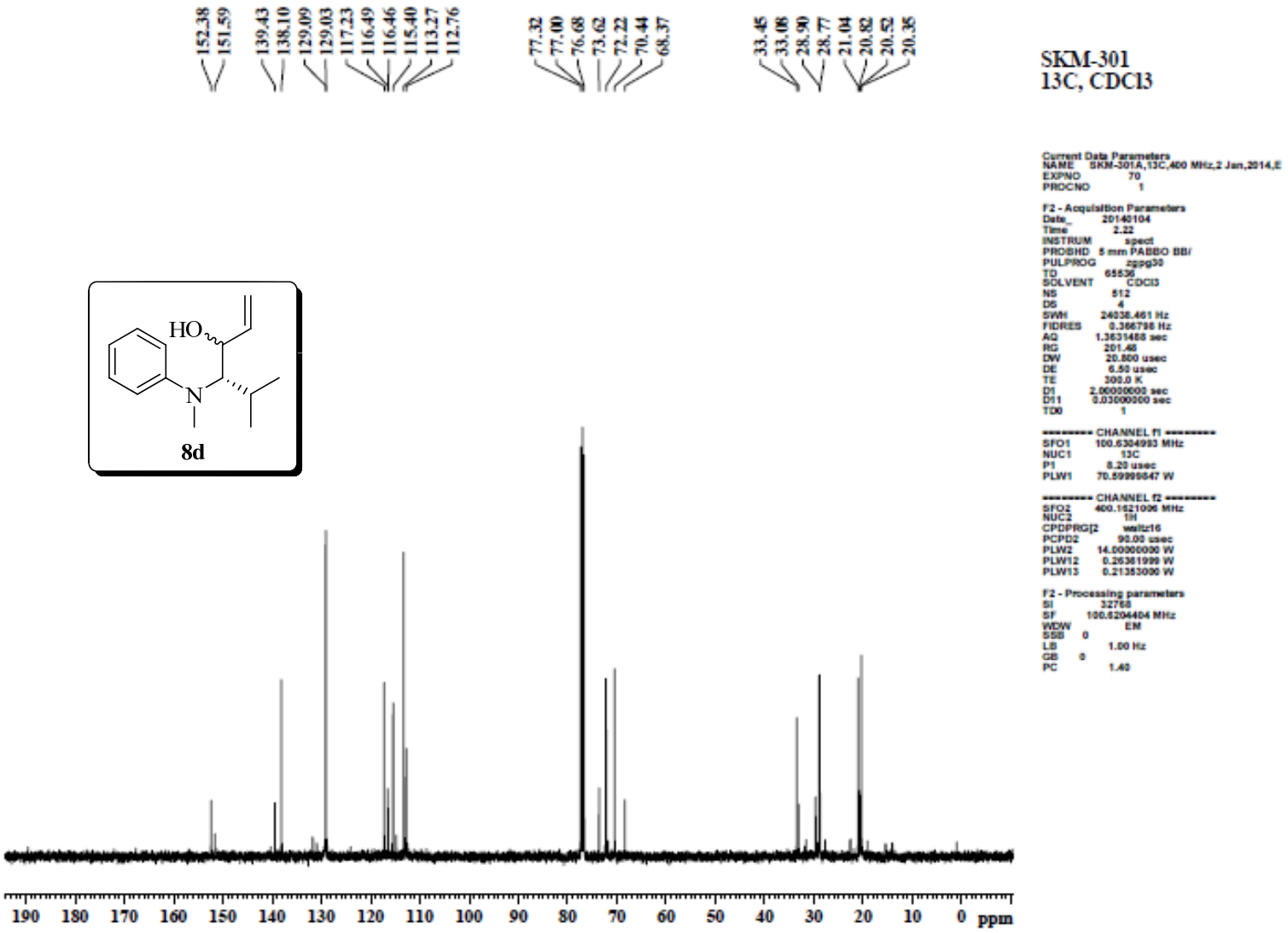


Figure 30: ^{13}C -NMR Spectrum of **8d.**

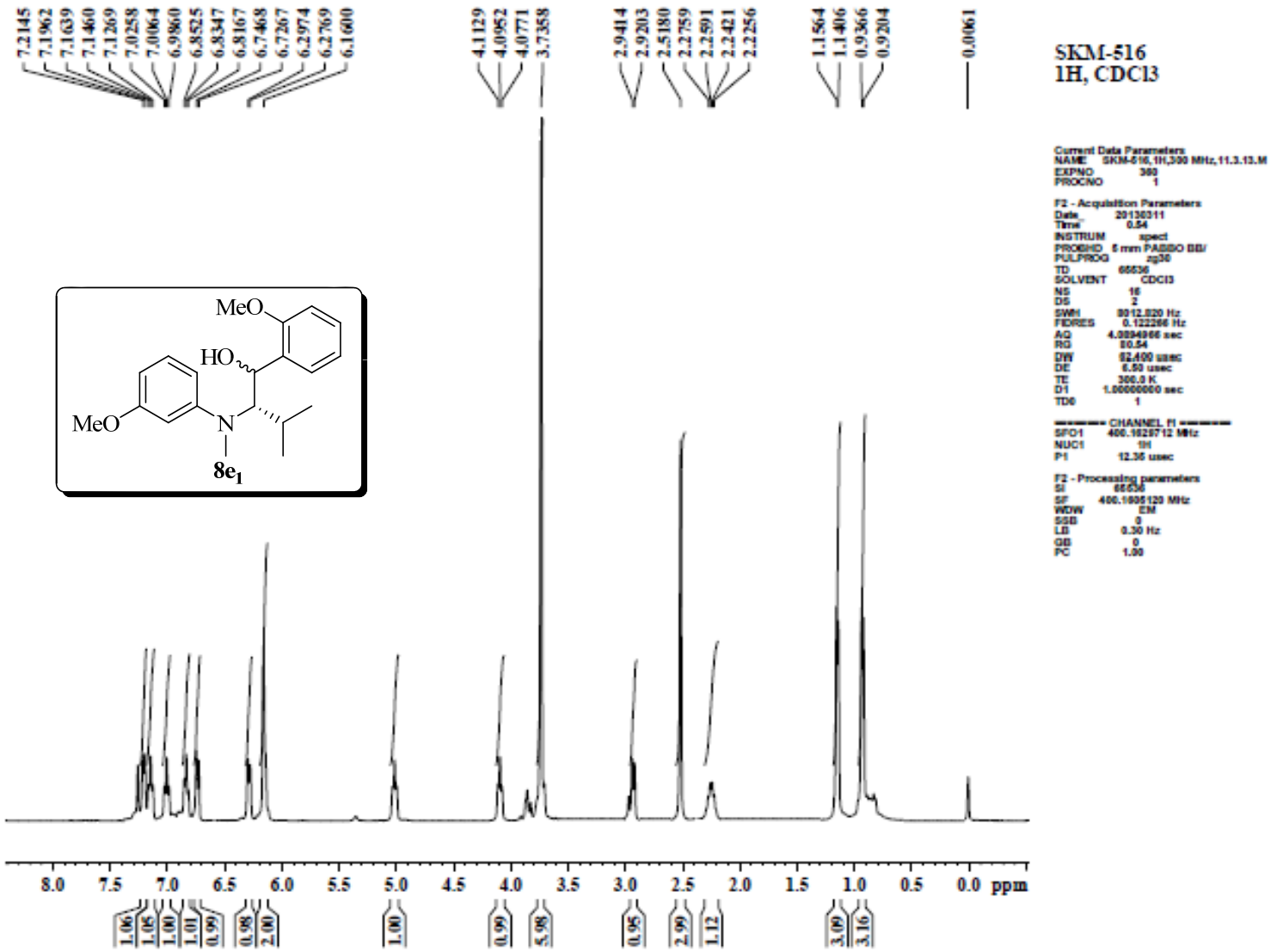


Figure 31: ^{1}H -NMR Spectrum of **$8e_1$.**

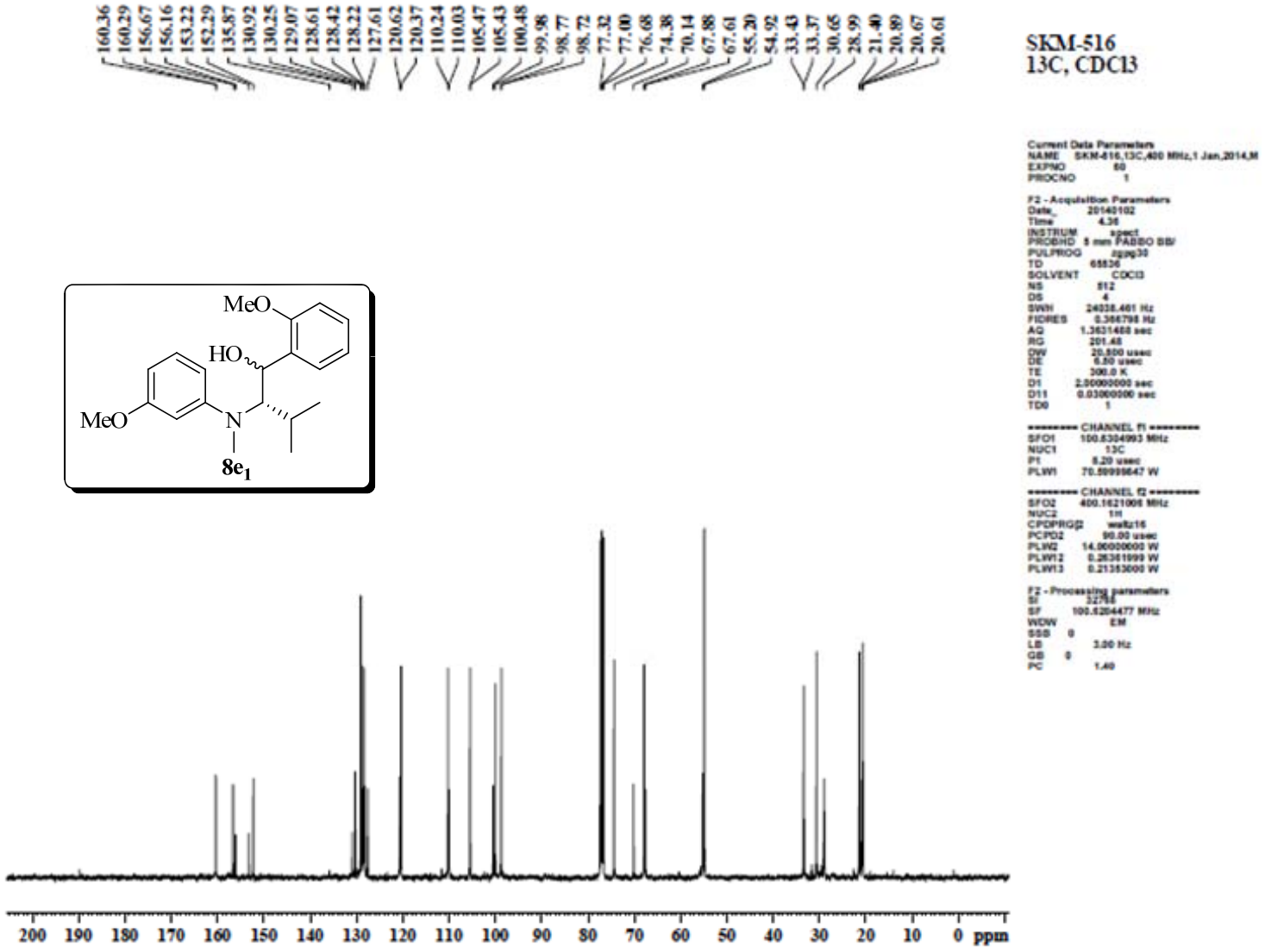


Figure 32: ^{13}C -NMR Spectrum of **8e$_1$.**

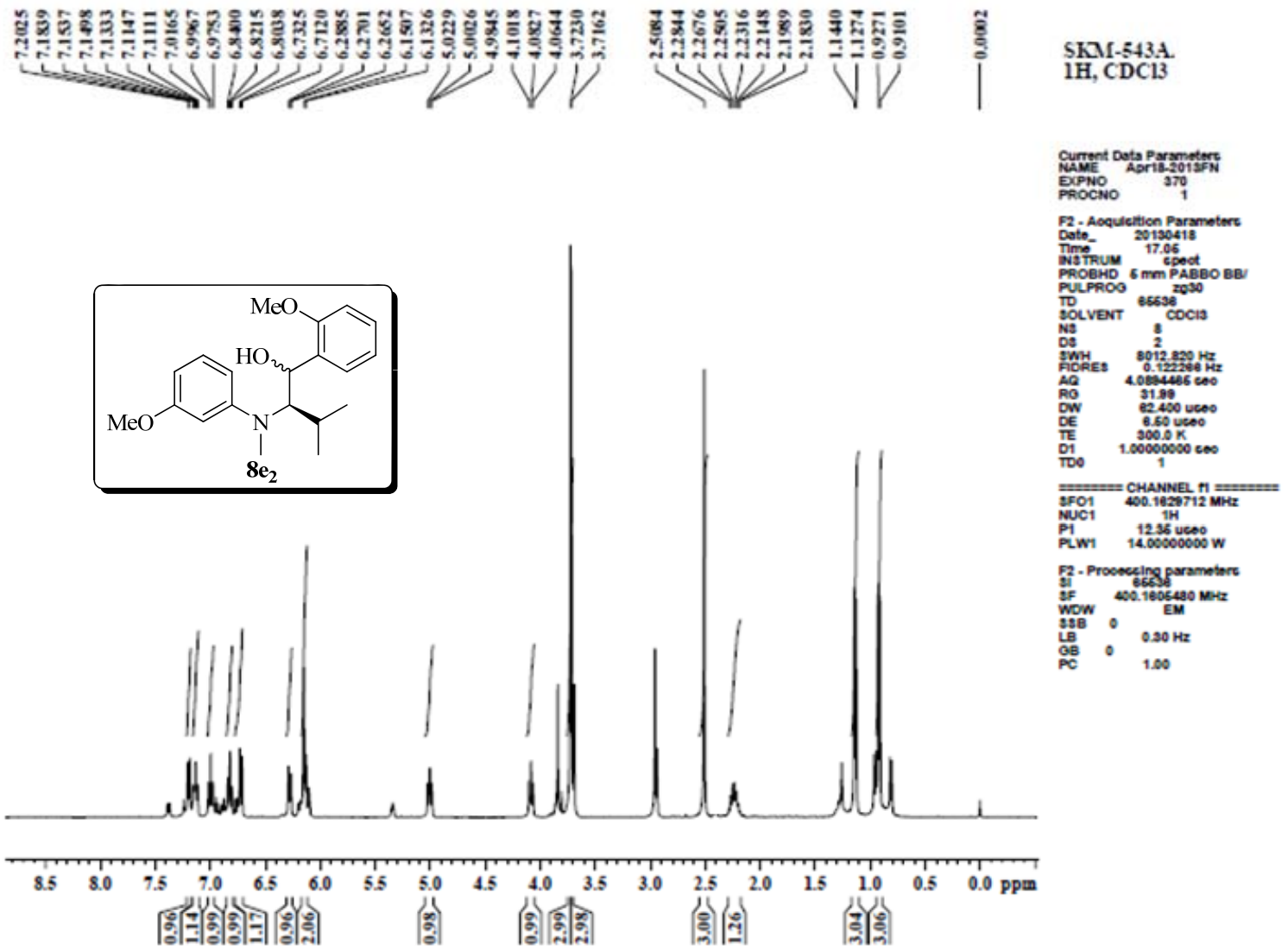


Figure 33: ^{1}H -NMR Spectrum of **$8e_2$.**

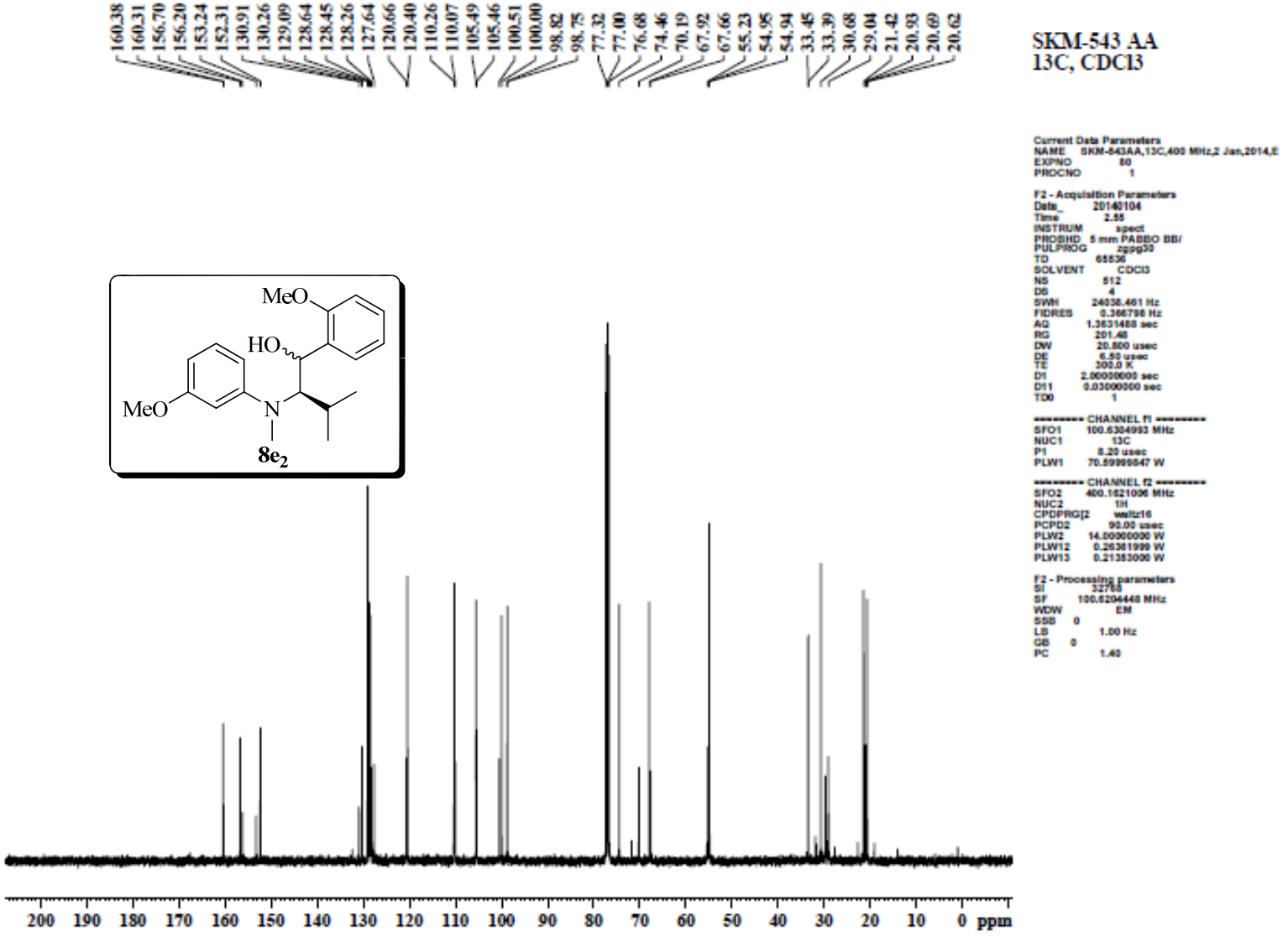


Figure 34: ^{13}C -NMR Spectrum of **8e$_2$.**

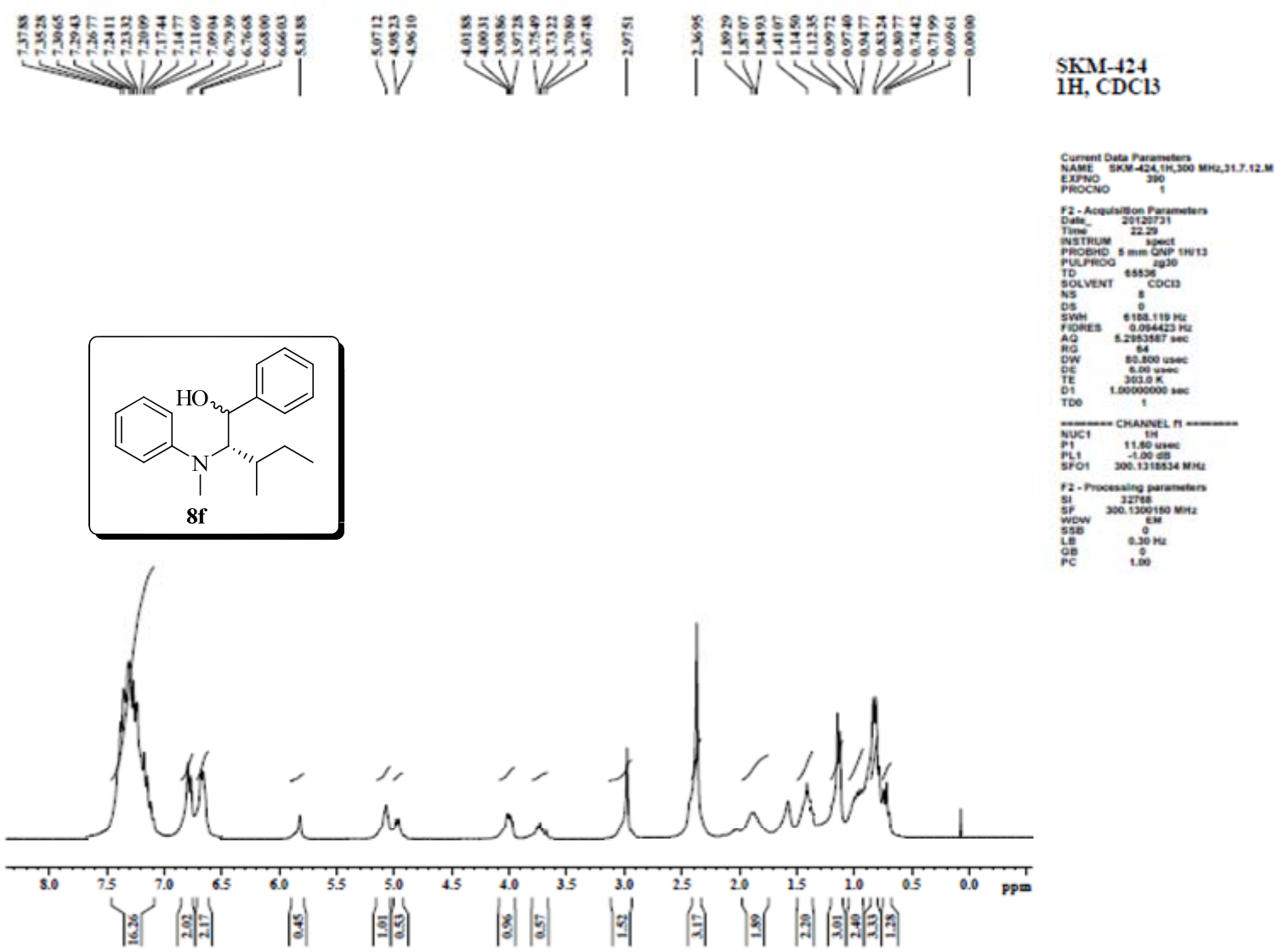


Figure 35: ^{1}H -NMR Spectrum of **8f.**

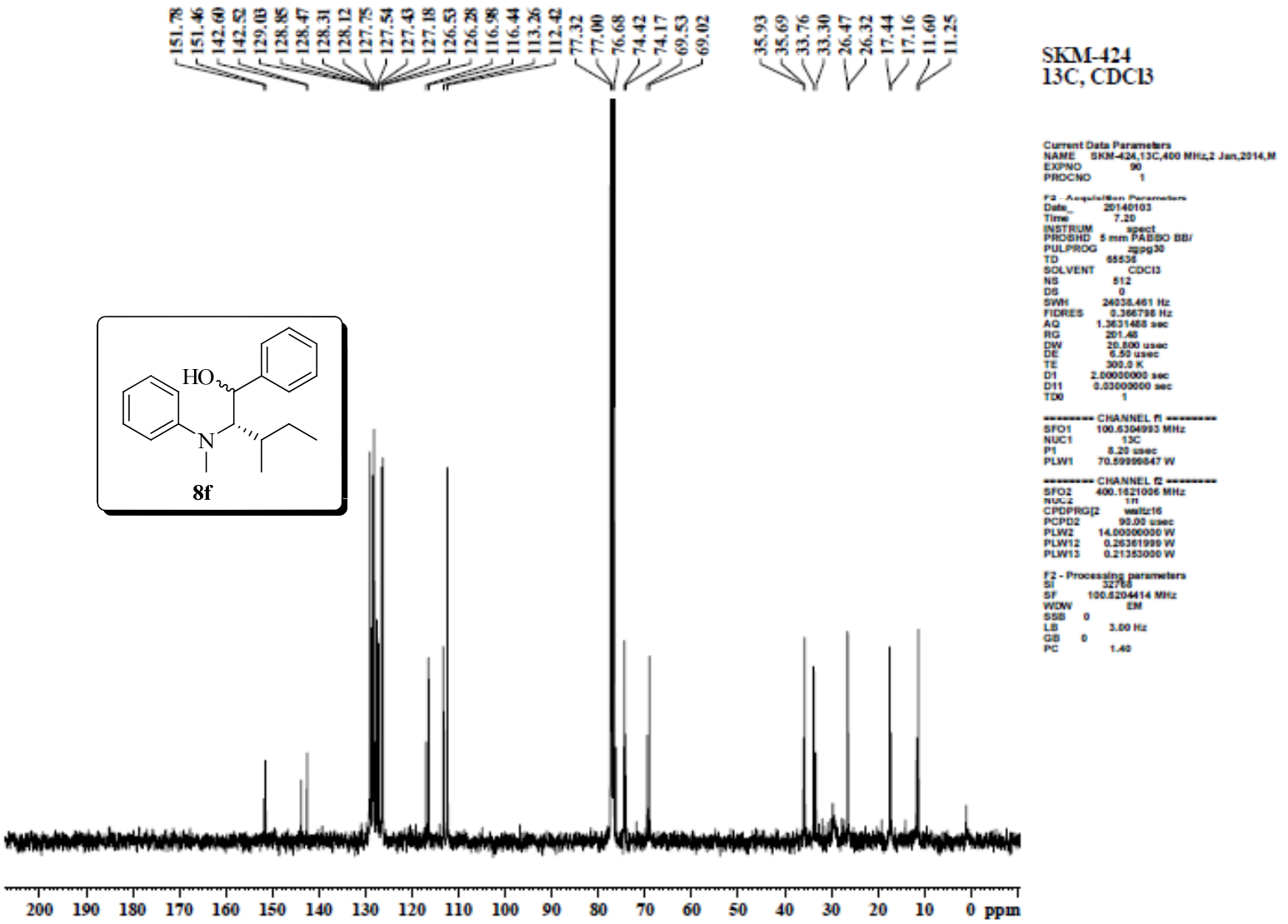


Figure 36: ^{13}C -NMR Spectrum of **8f.**

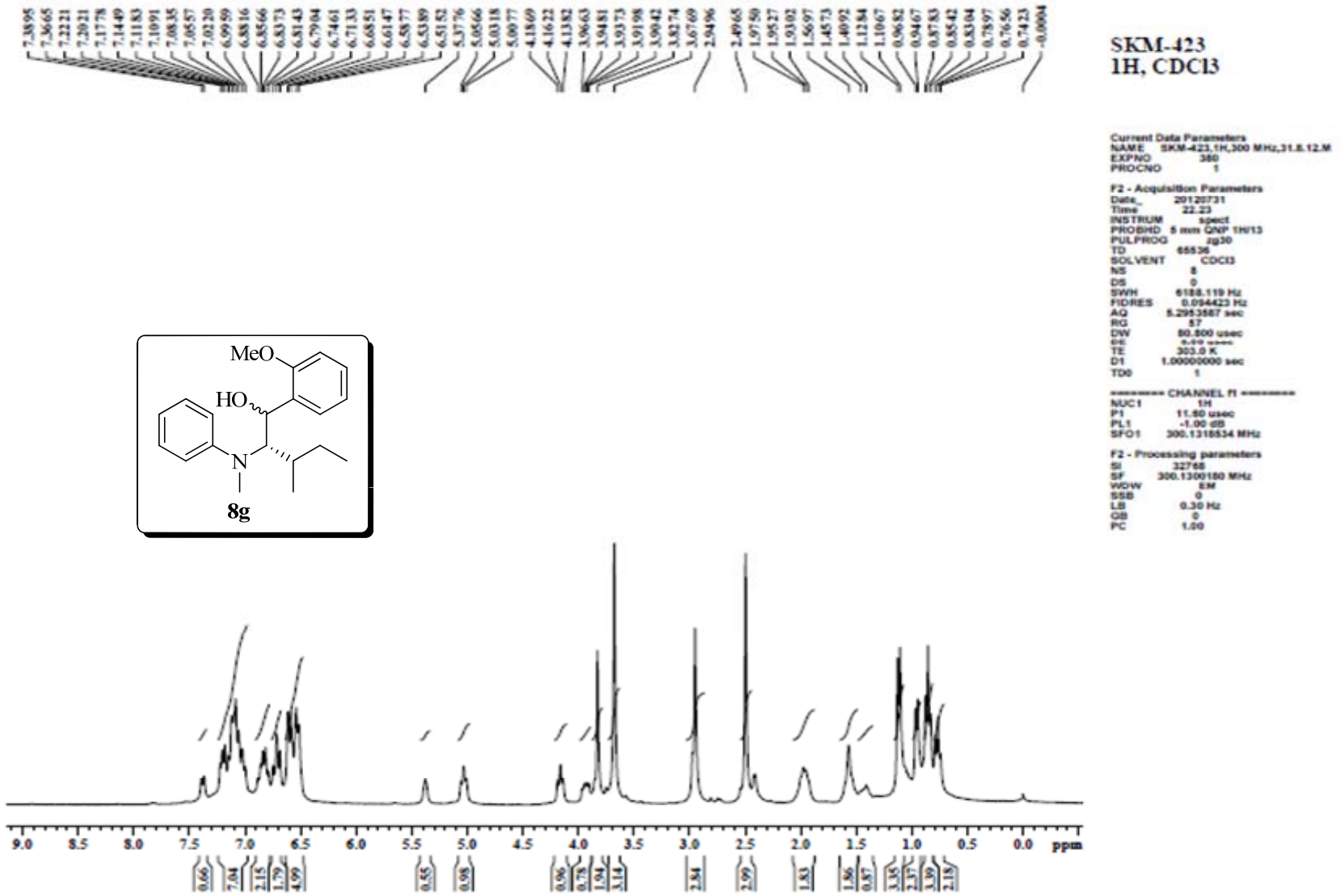


Figure 37: ^{1}H -NMR Spectrum of **8g.**

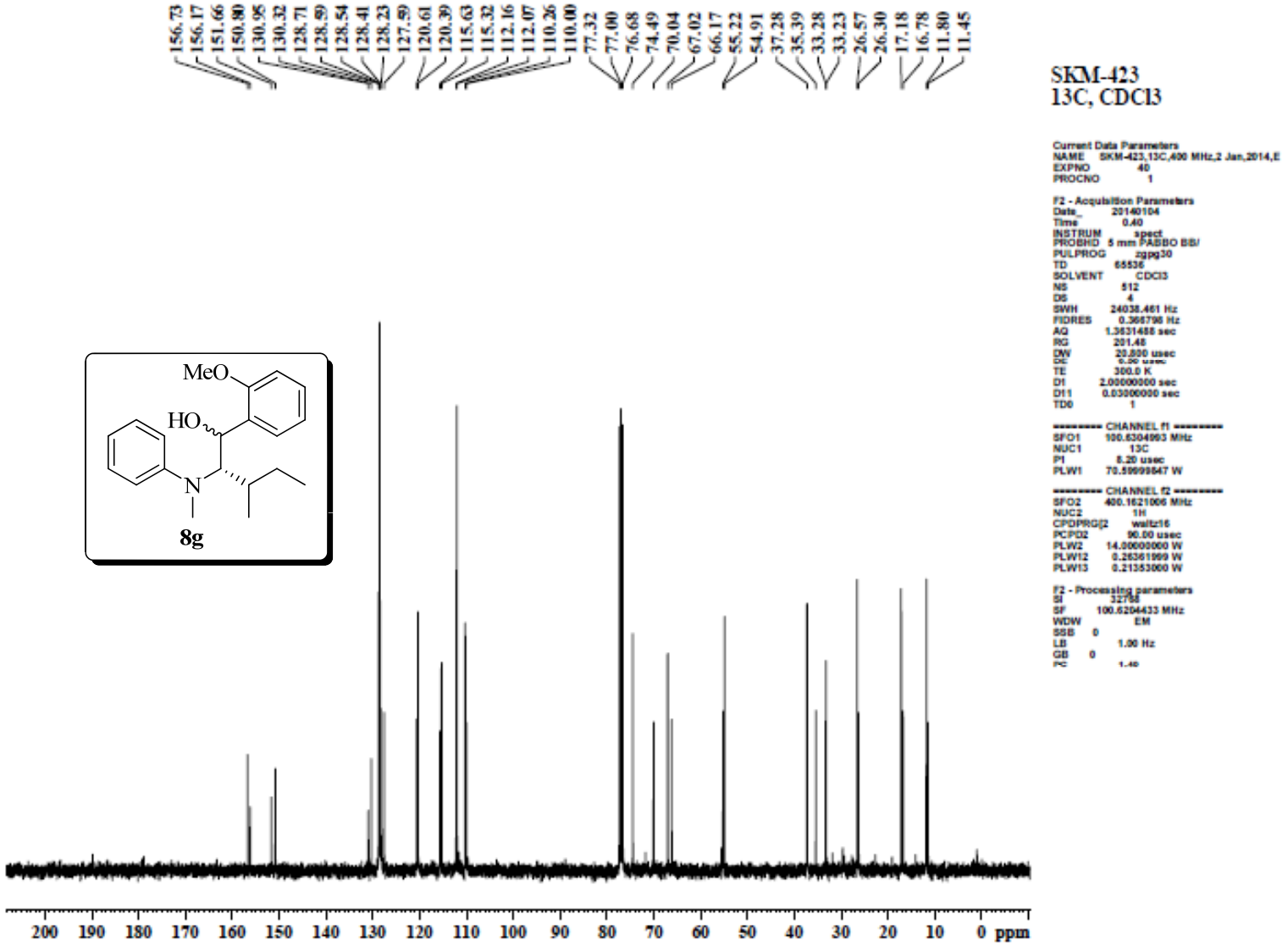


Figure 38: ^{13}C -NMR Spectrum of **8g.**

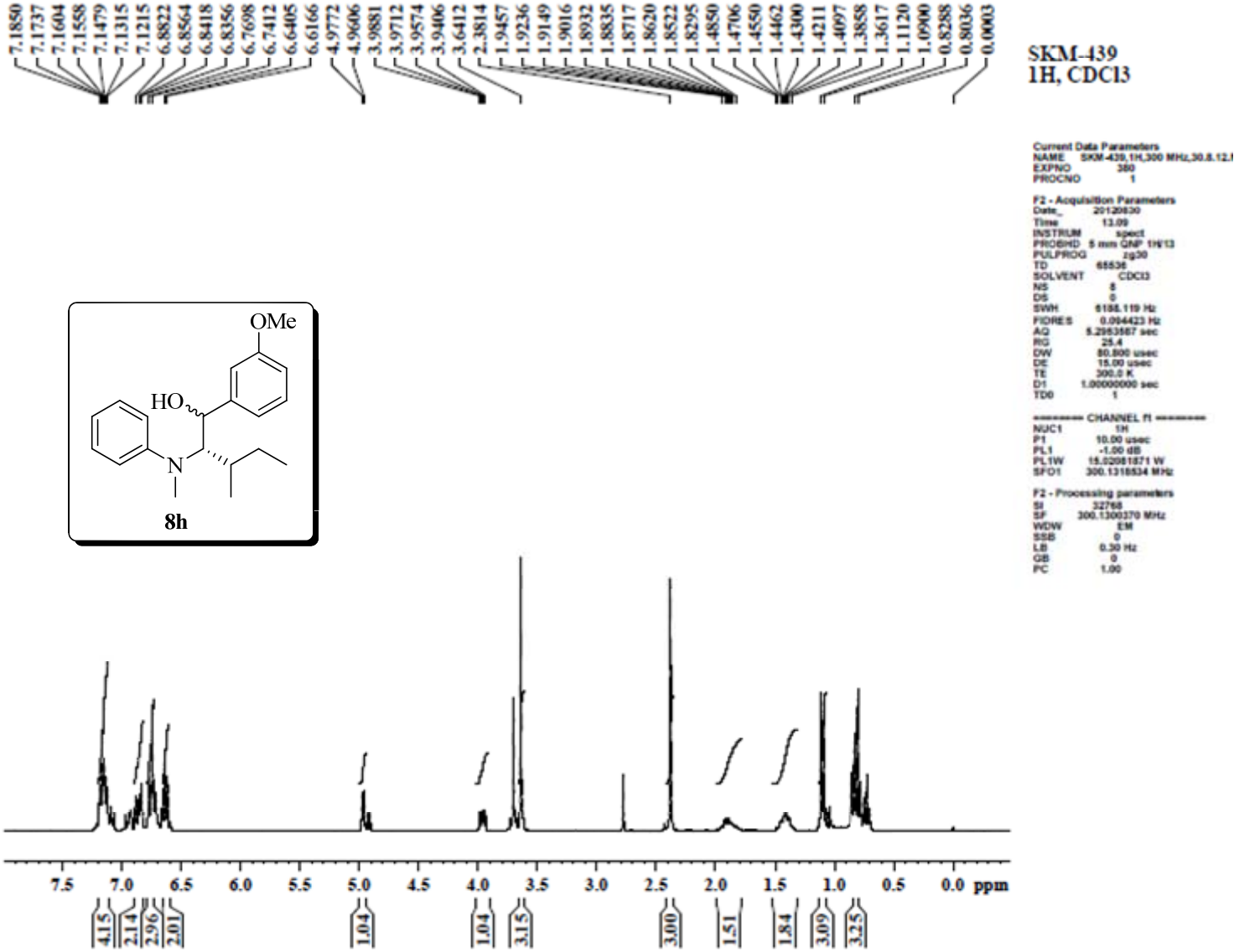


Figure 39: ^{1}H -NMR Spectrum of **8h.**

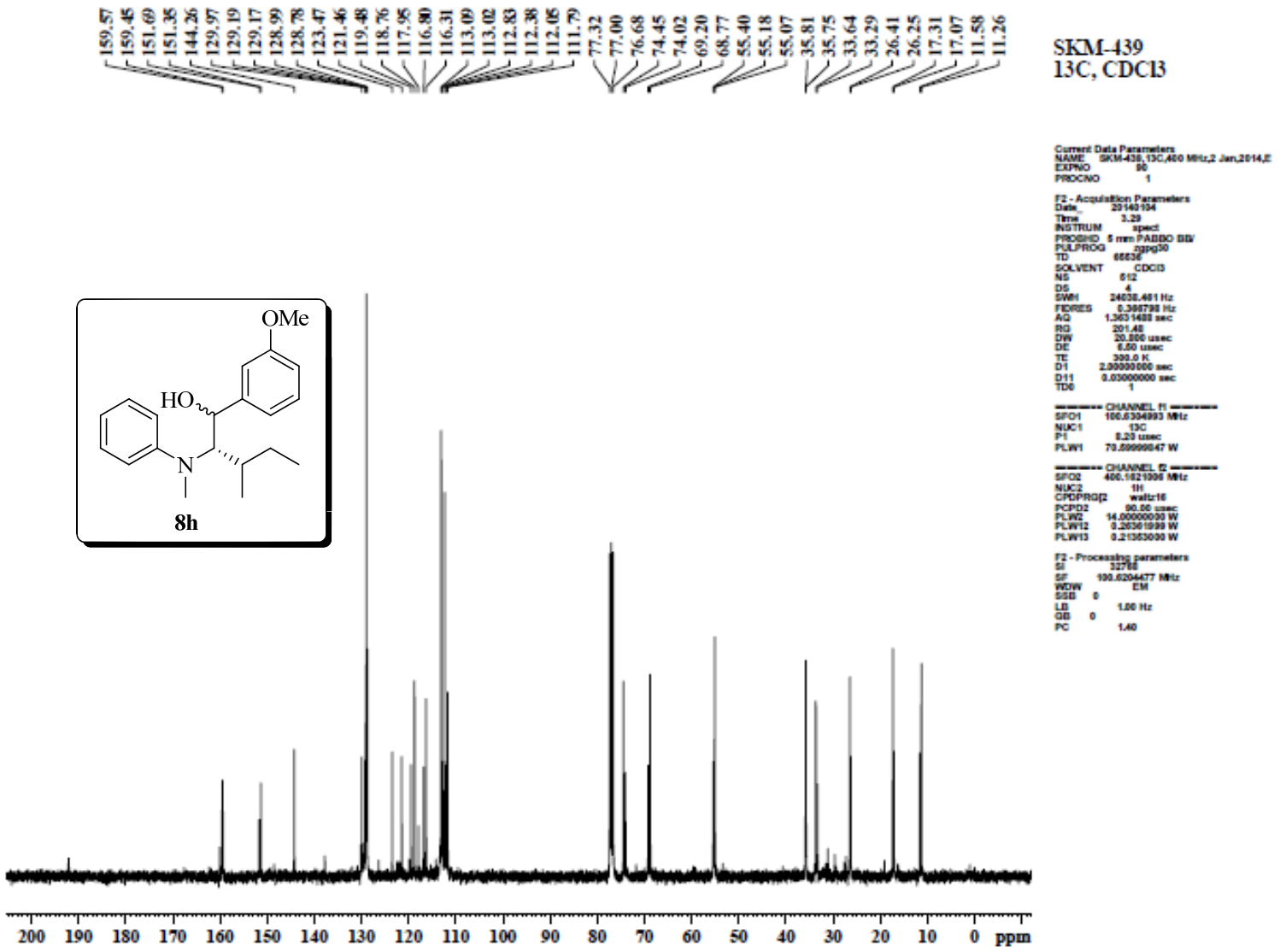


Figure 40: ^{13}C -NMR Spectrum of **8h.**

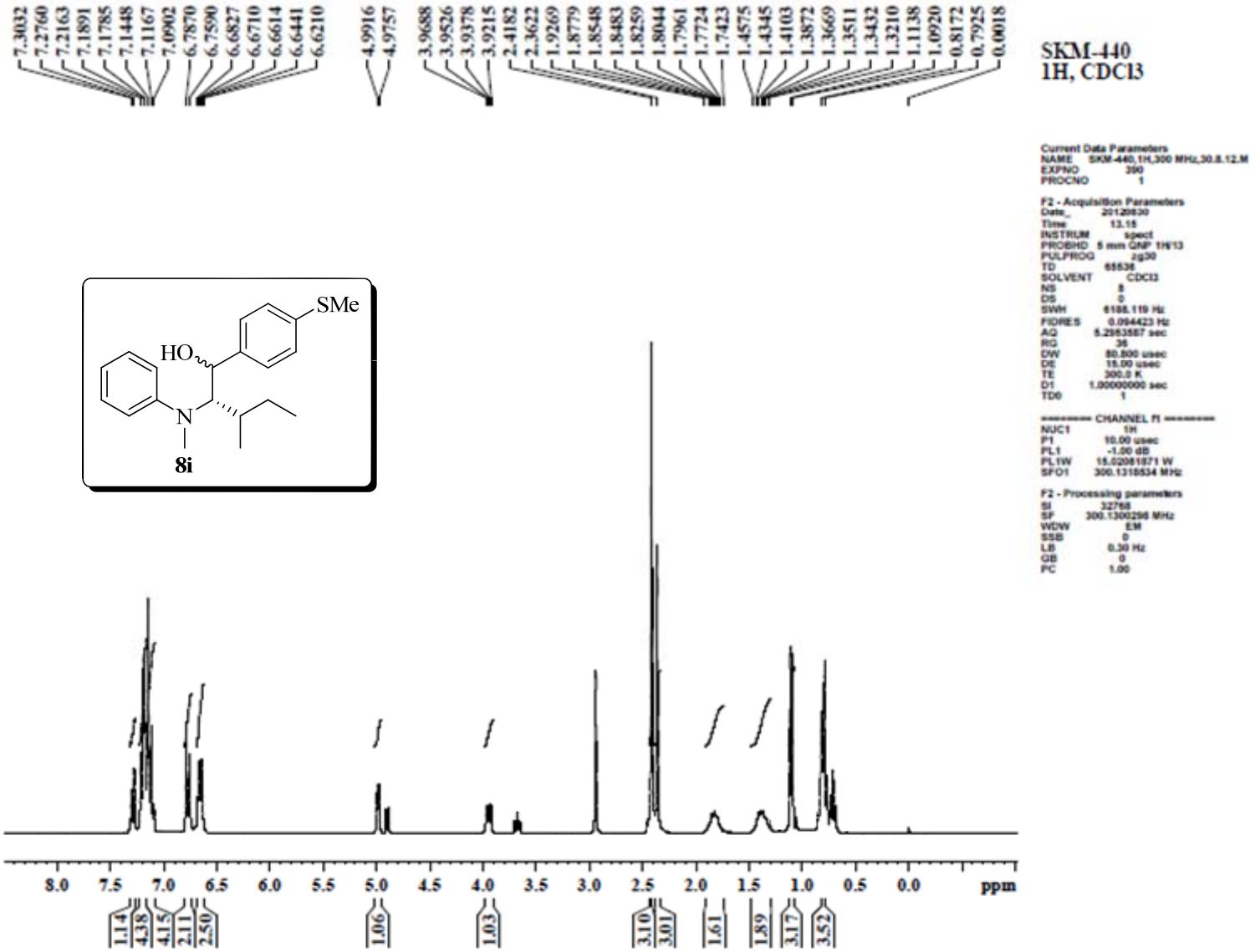


Figure 41: ^{1}H -NMR Spectrum of **8i.**

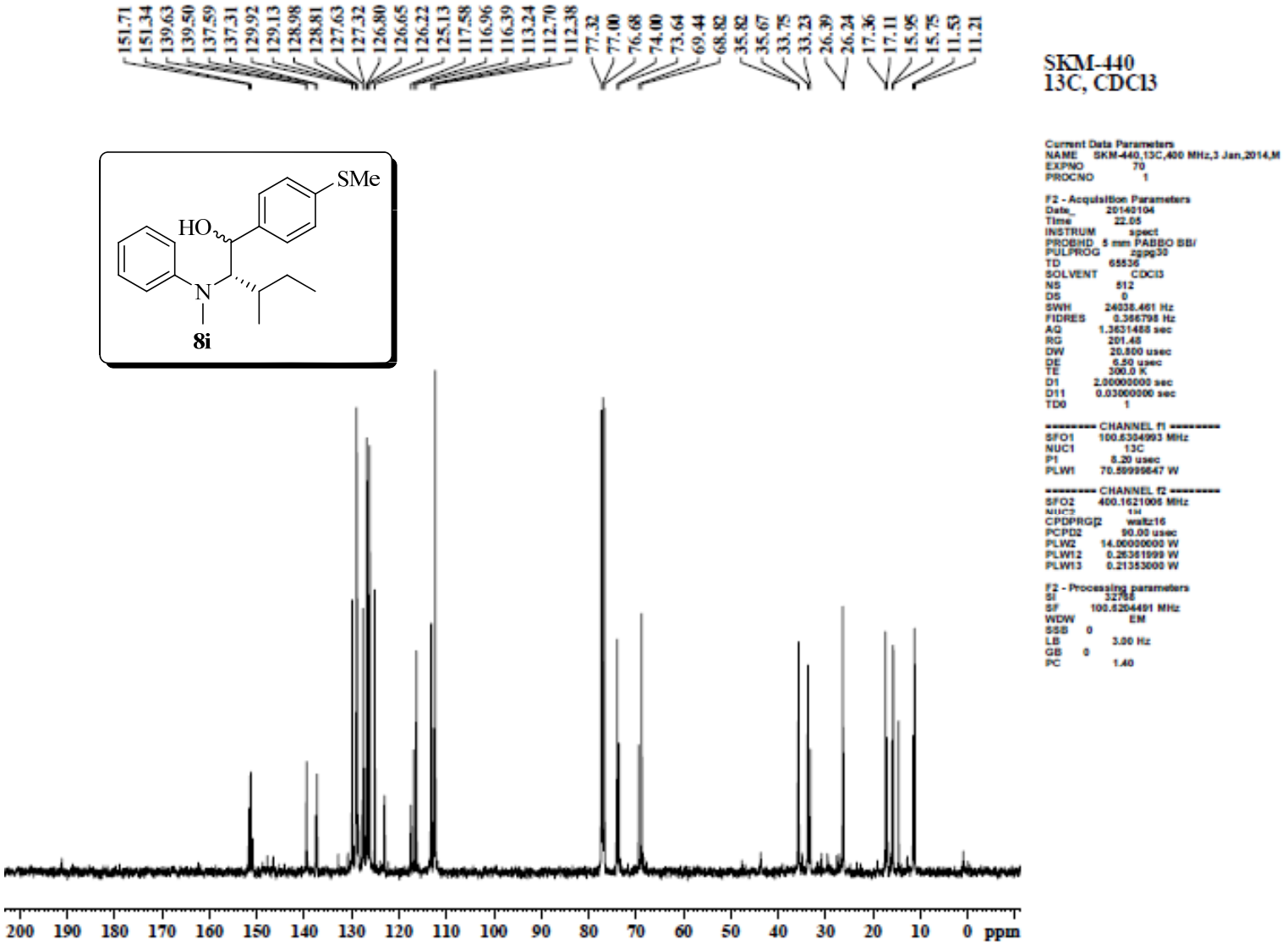


Figure 42: ^{13}C -NMR Spectrum of **8i.**

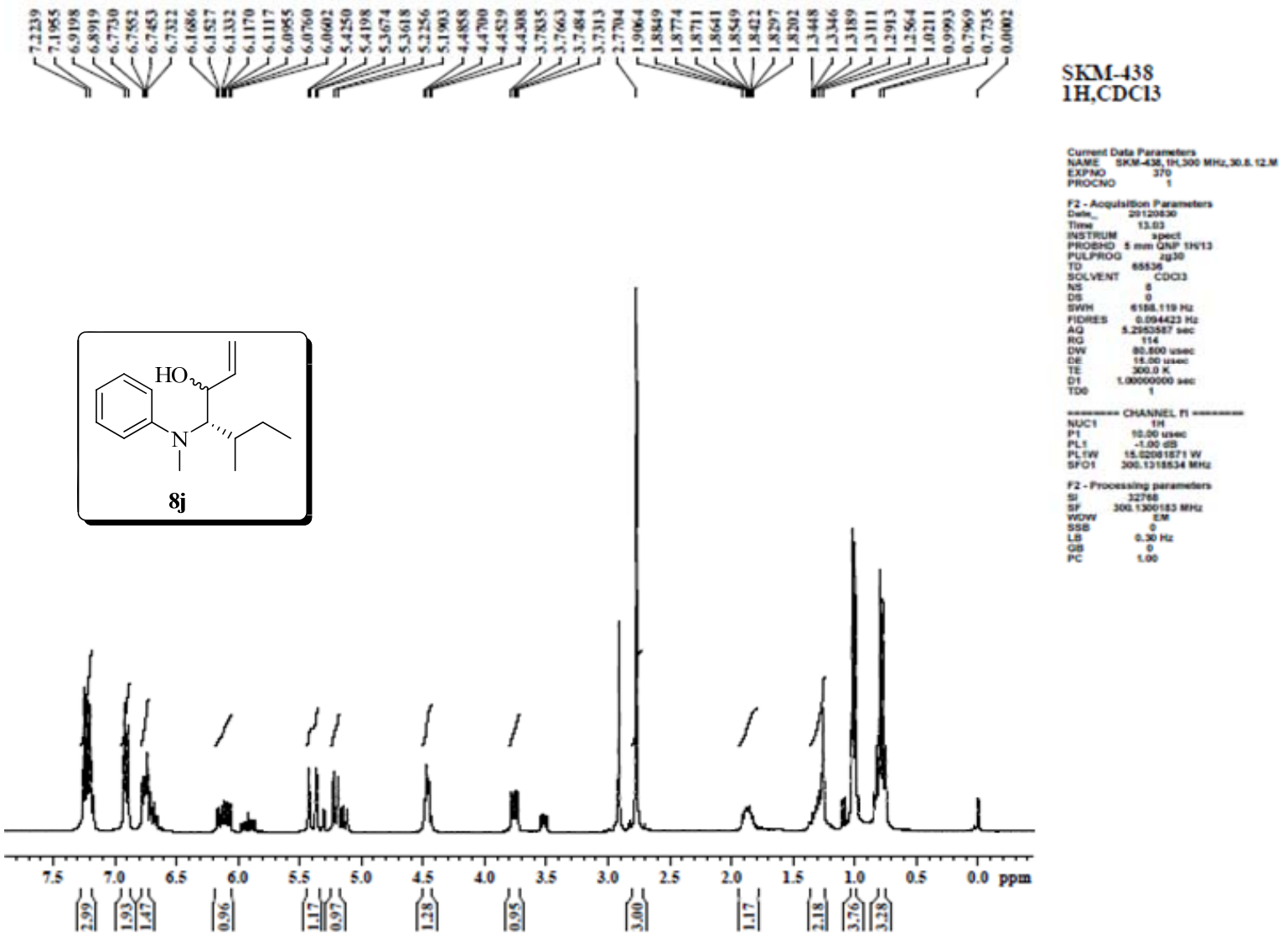


Figure 43: ^{1}H -NMR Spectrum of **8j.**

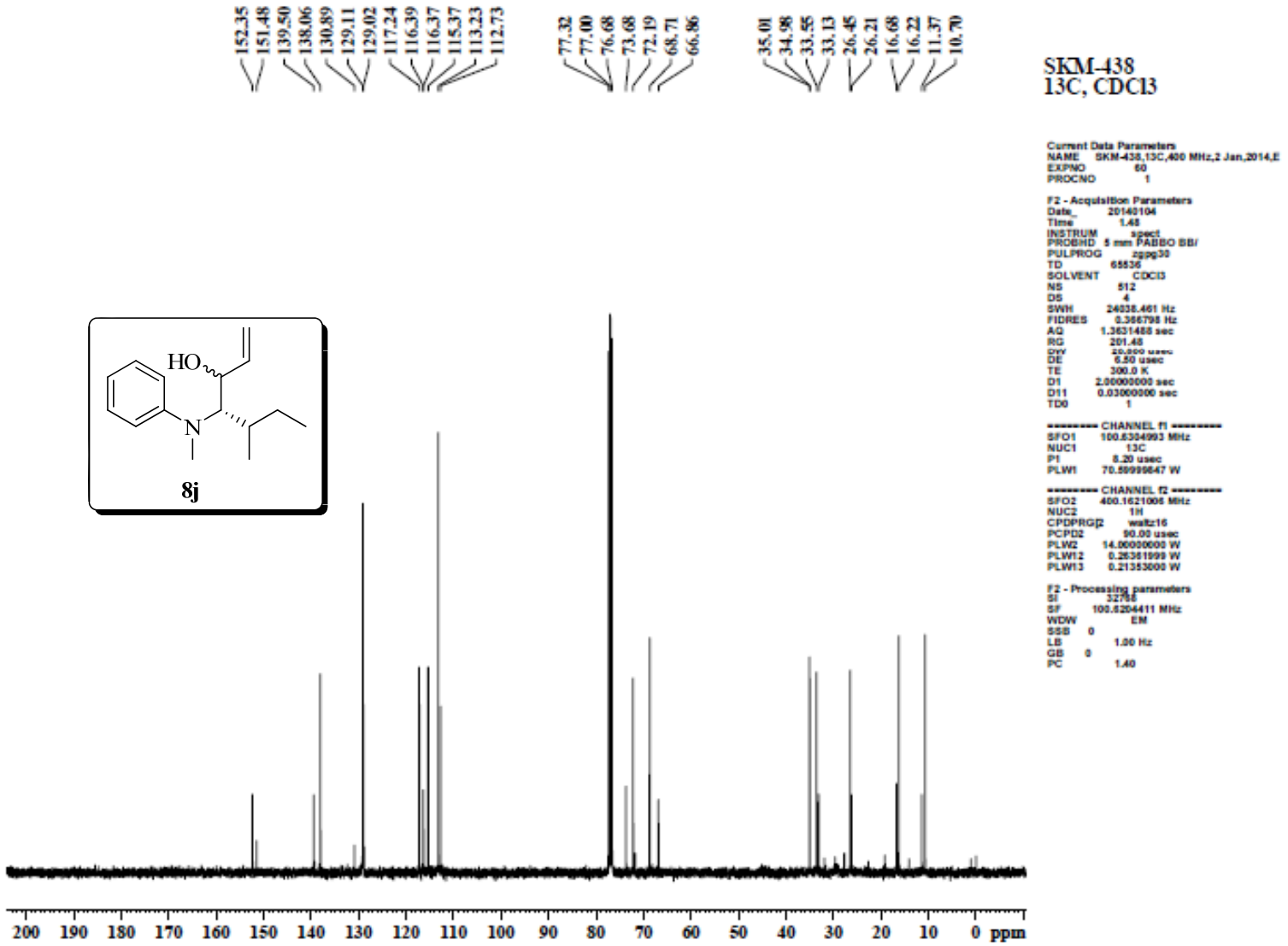


Figure 44: ^{13}C -NMR Spectrum of **8j.**

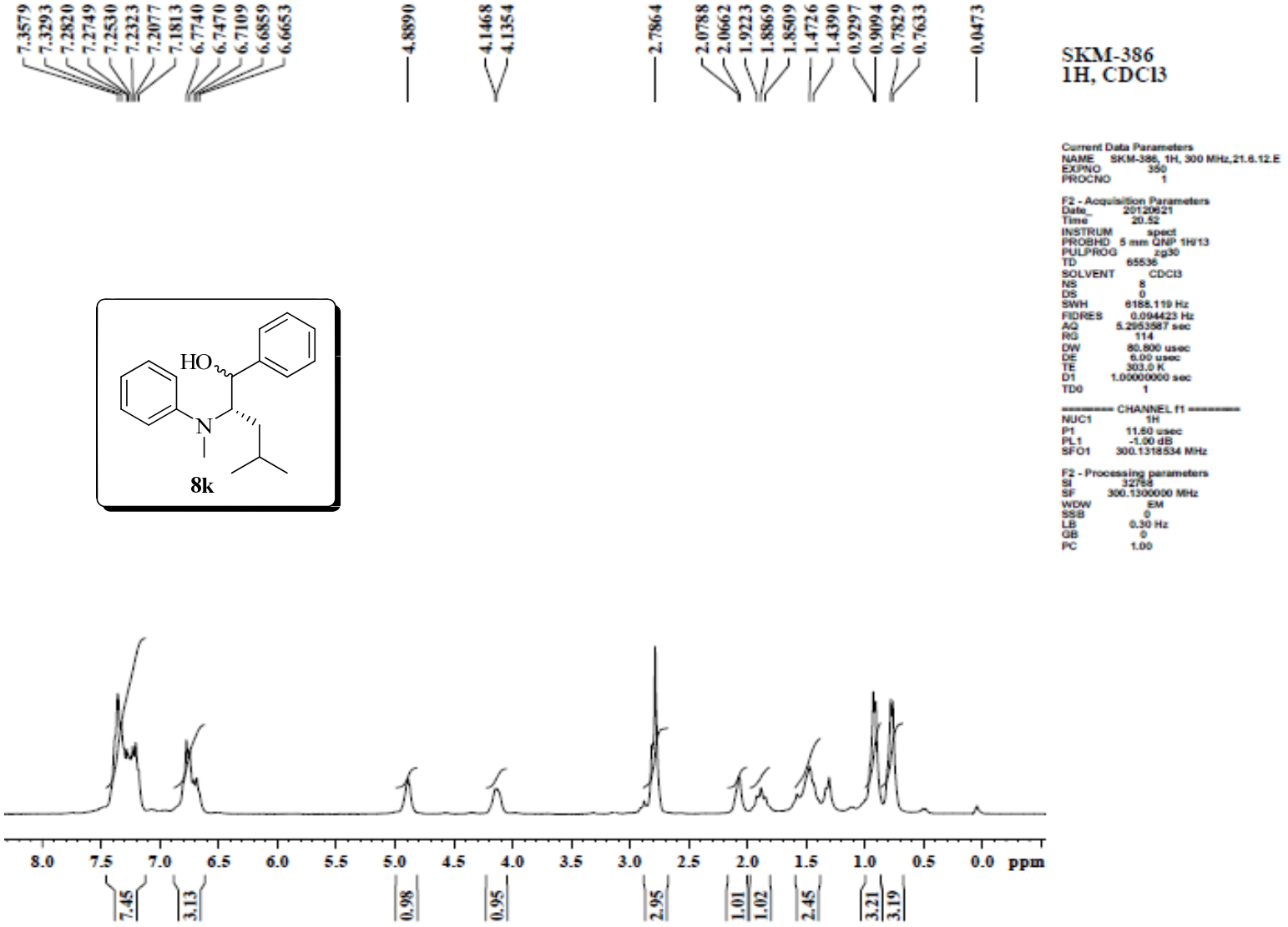


Figure 45: ^{1}H -NMR Spectrum of **8k.**

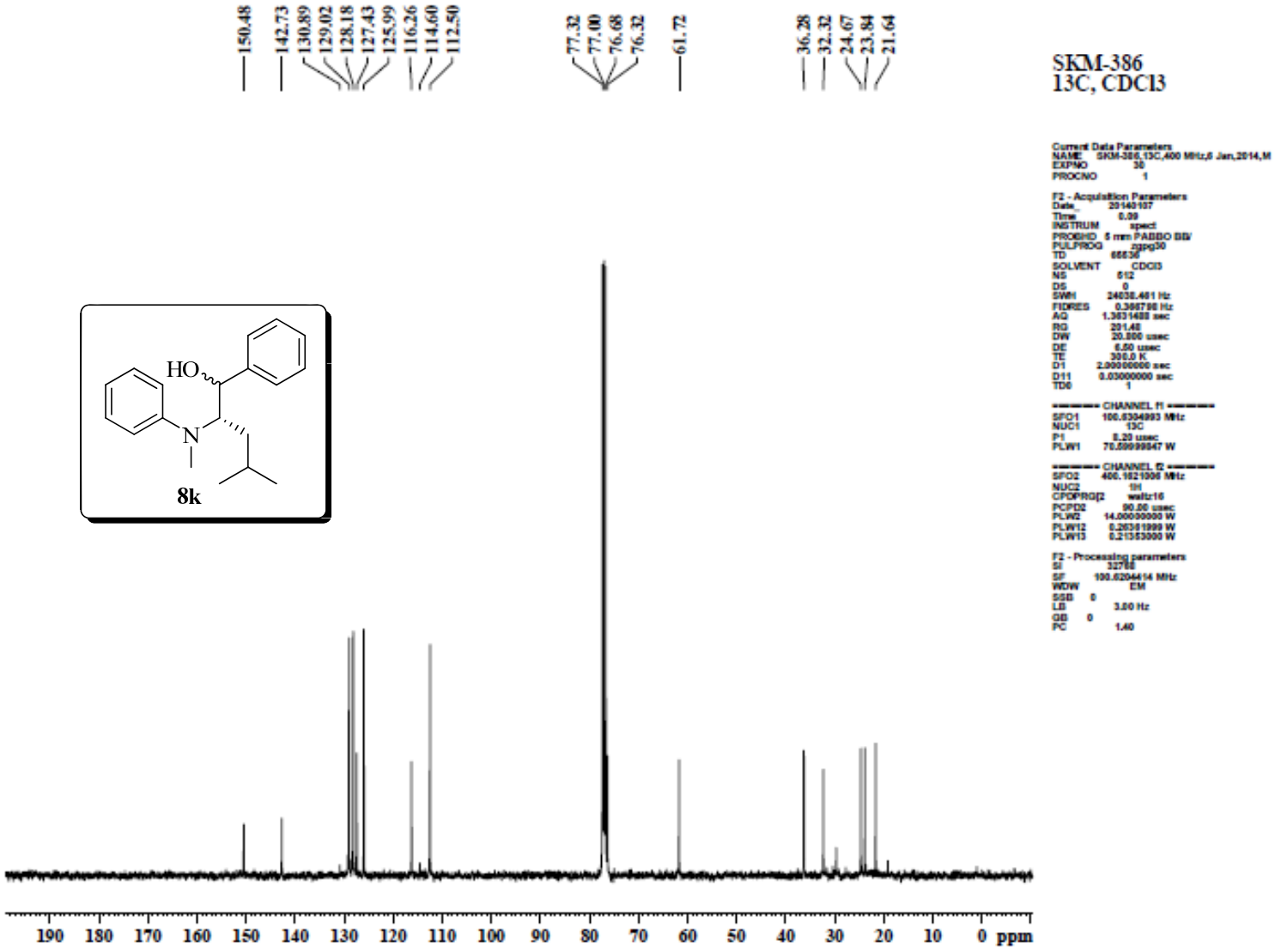


Figure 46: ^{13}C -NMR Spectrum of **8k.**

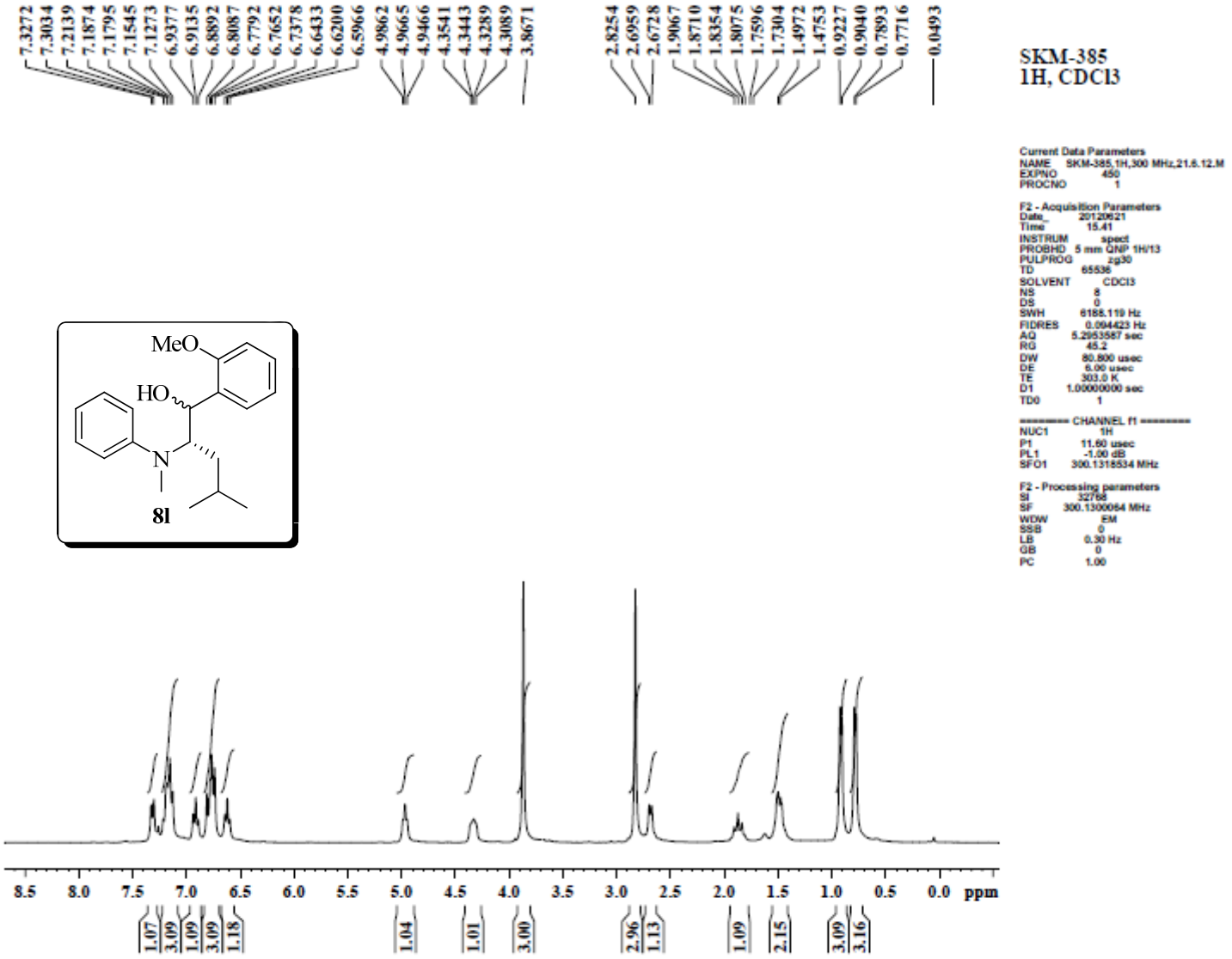


Figure 47: ^{1}H -NMR Spectrum of **8l.**

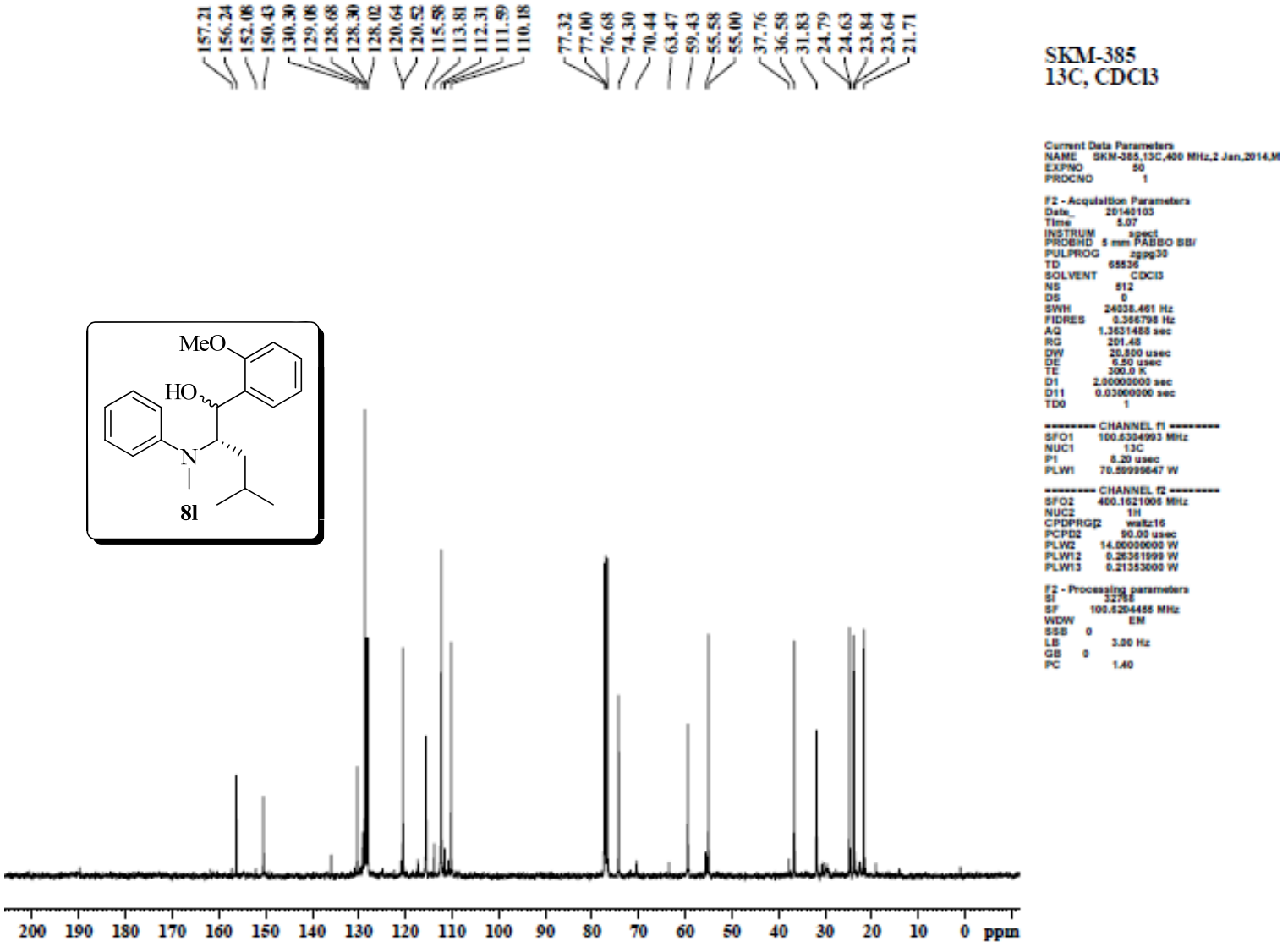


Figure 48: ^{13}C -NMR Spectrum of **8l.**

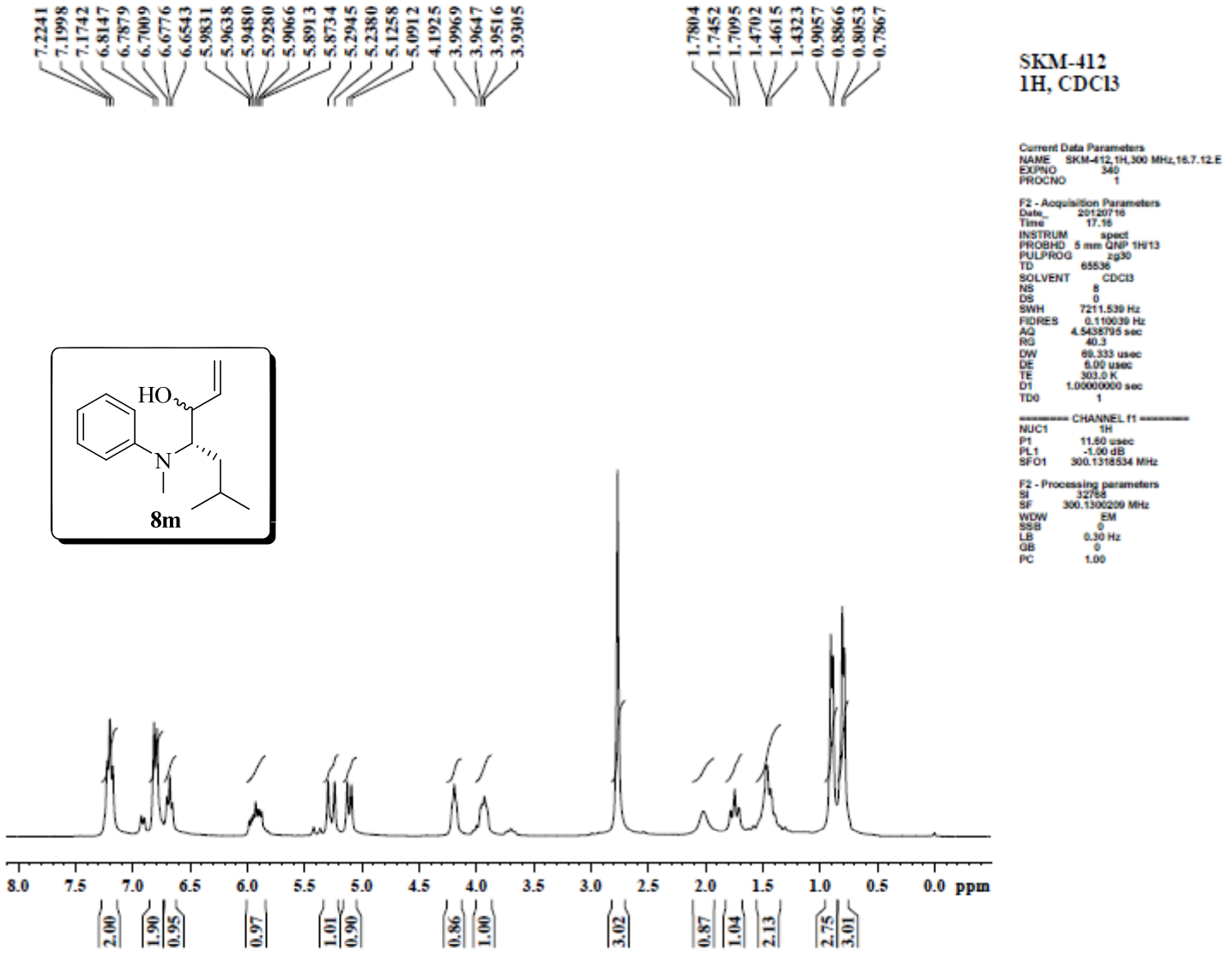


Figure 49: ^{1}H -NMR Spectrum of **8m.**

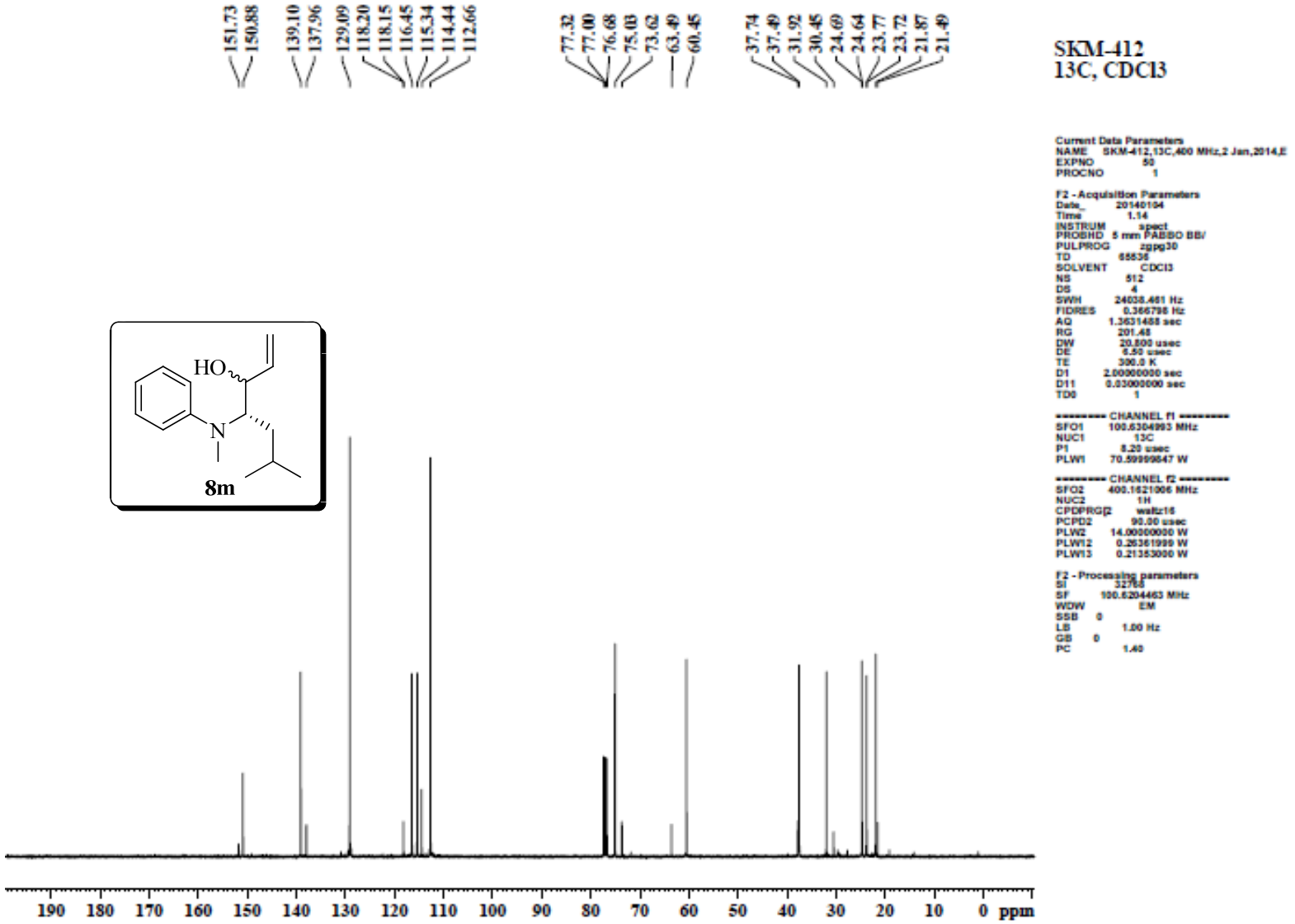


Figure 50: ^{13}C -NMR Spectrum of **8m.**

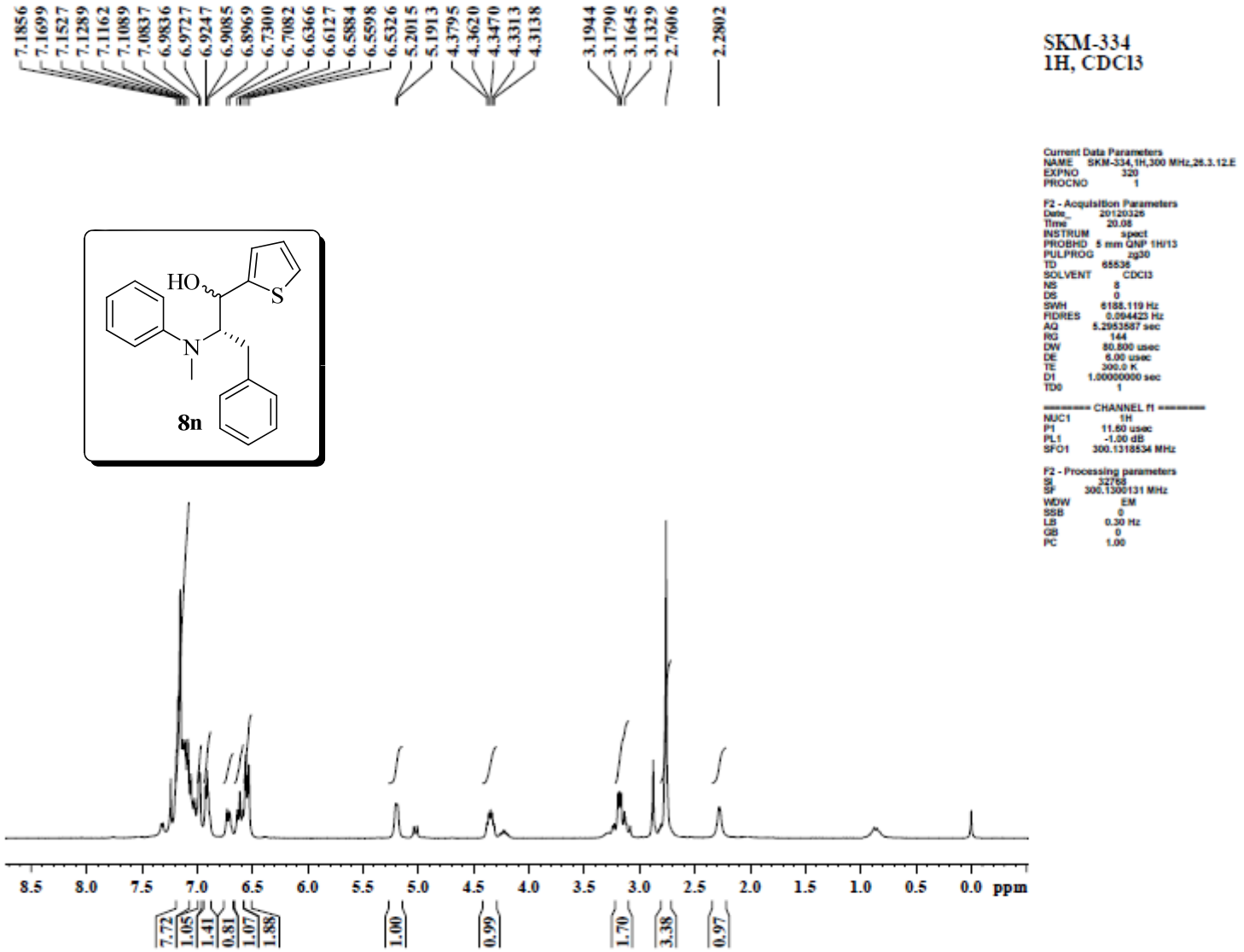


Figure 51: ^{1}H -NMR Spectrum of **8n.**

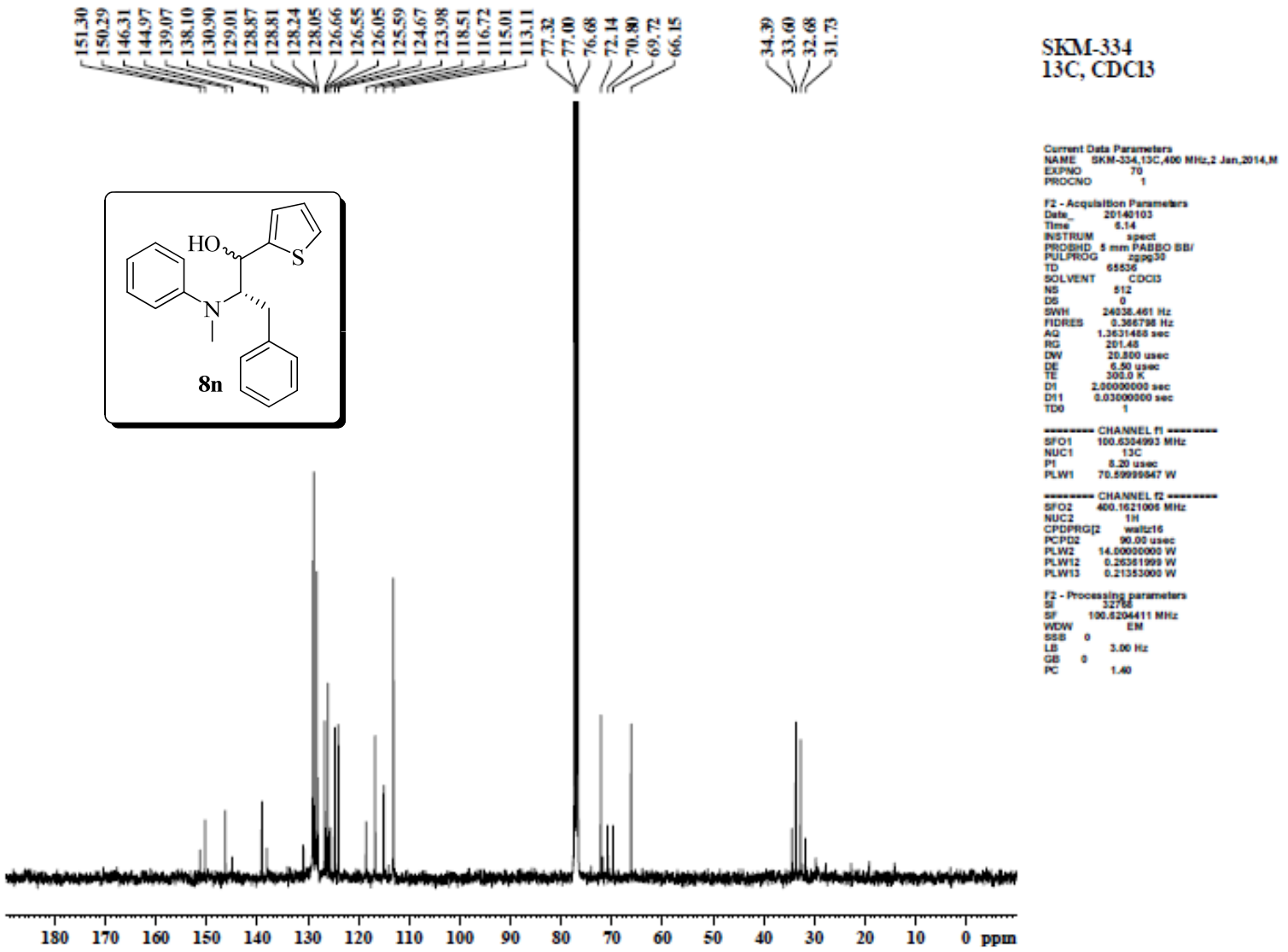


Figure 52: ^{13}C-NMR Spectrum of **8n.**

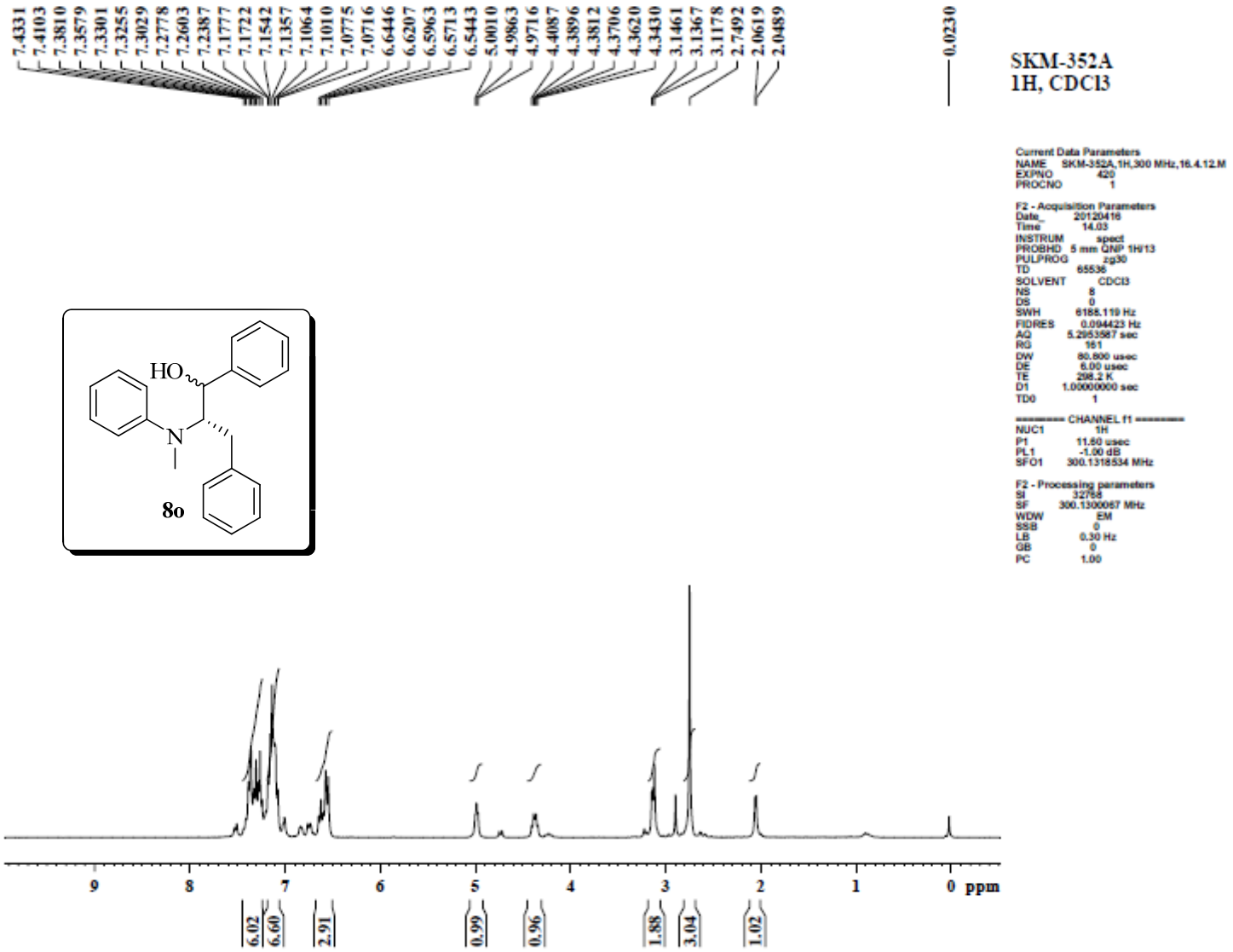


Figure 53: ^{1}H -NMR Spectrum of **8o.**

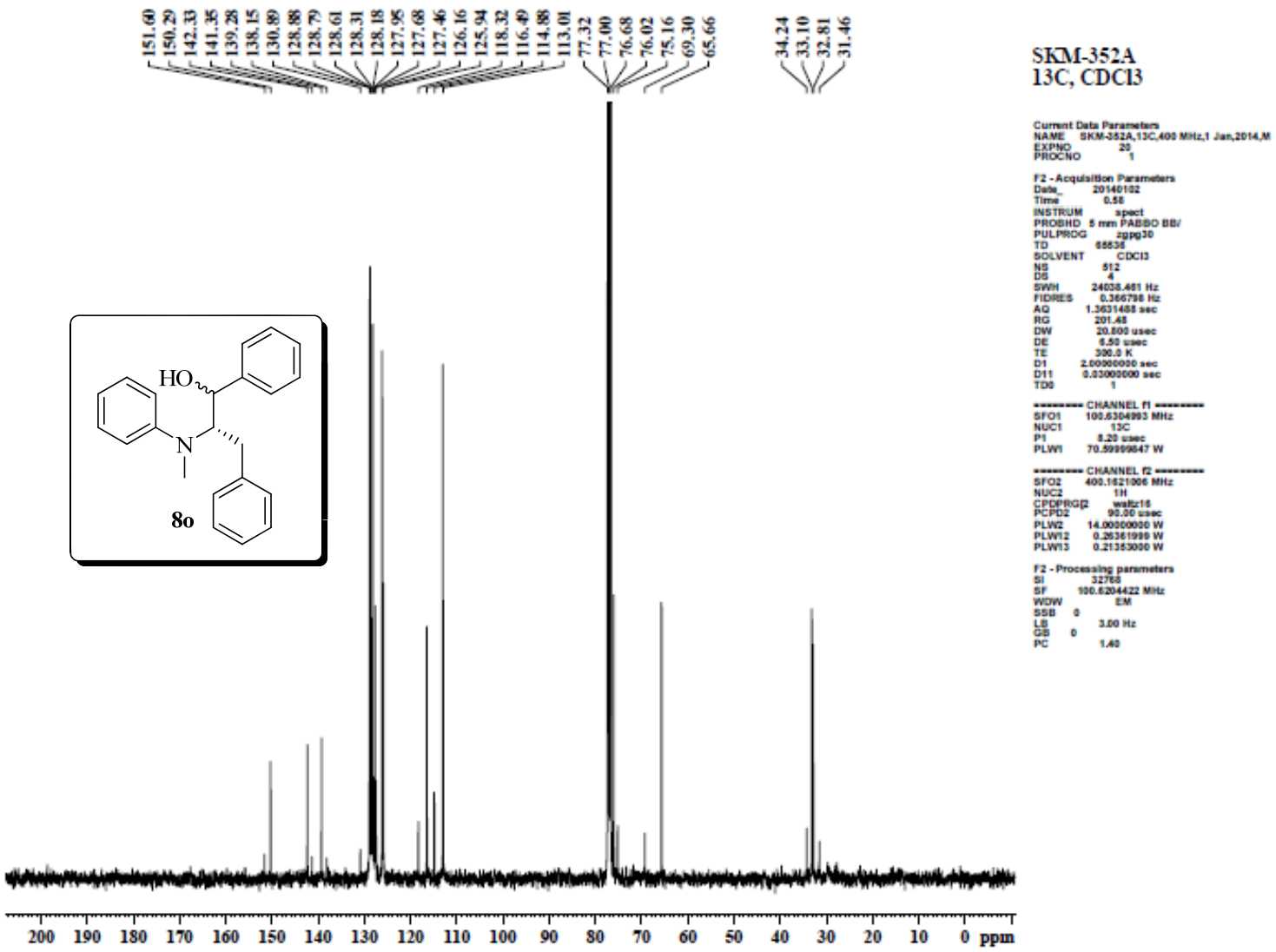


Figure 54: ^{13}C -NMR Spectrum of **8o.**

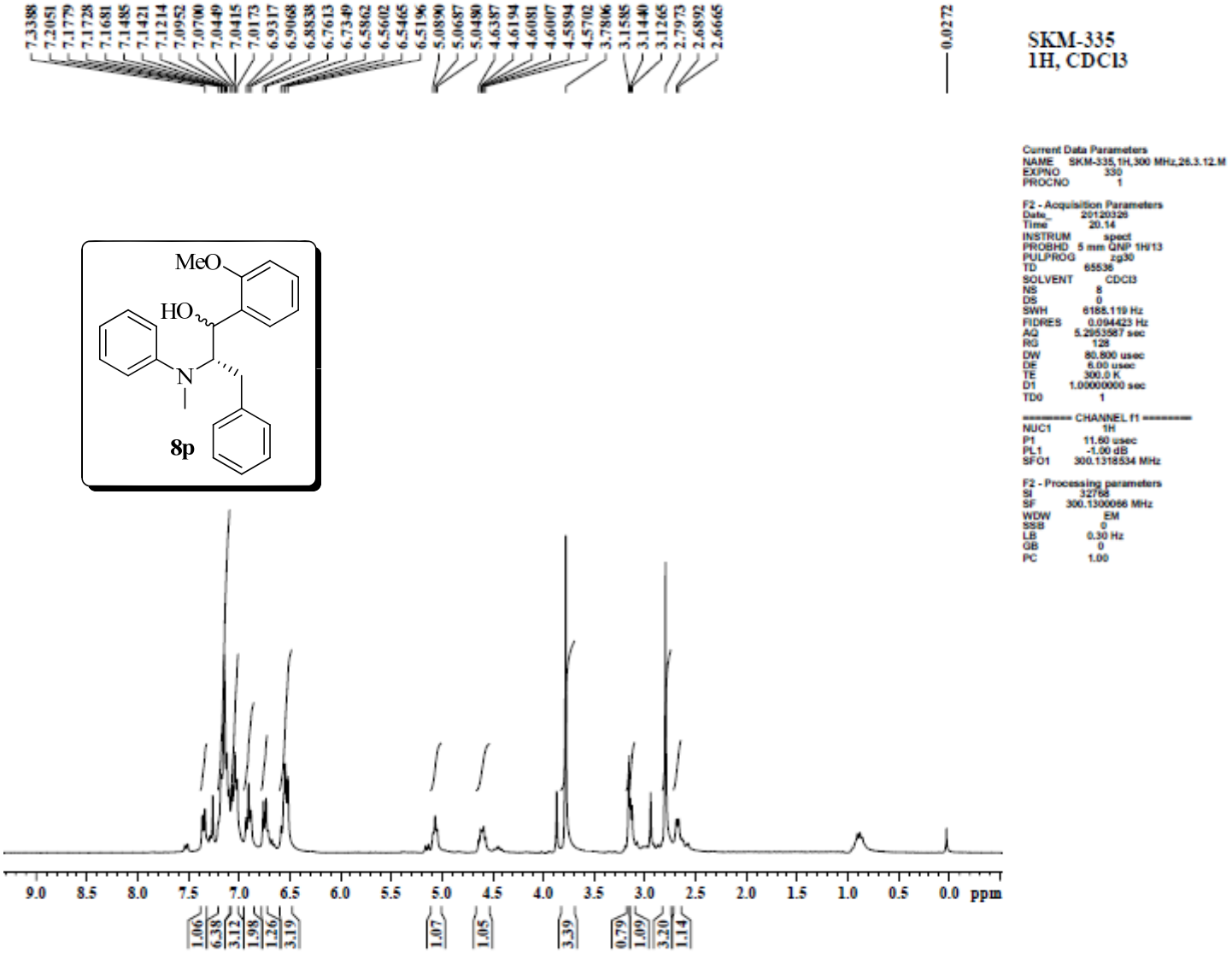


Figure 55: ^{1}H -NMR Spectrum of **8p.**

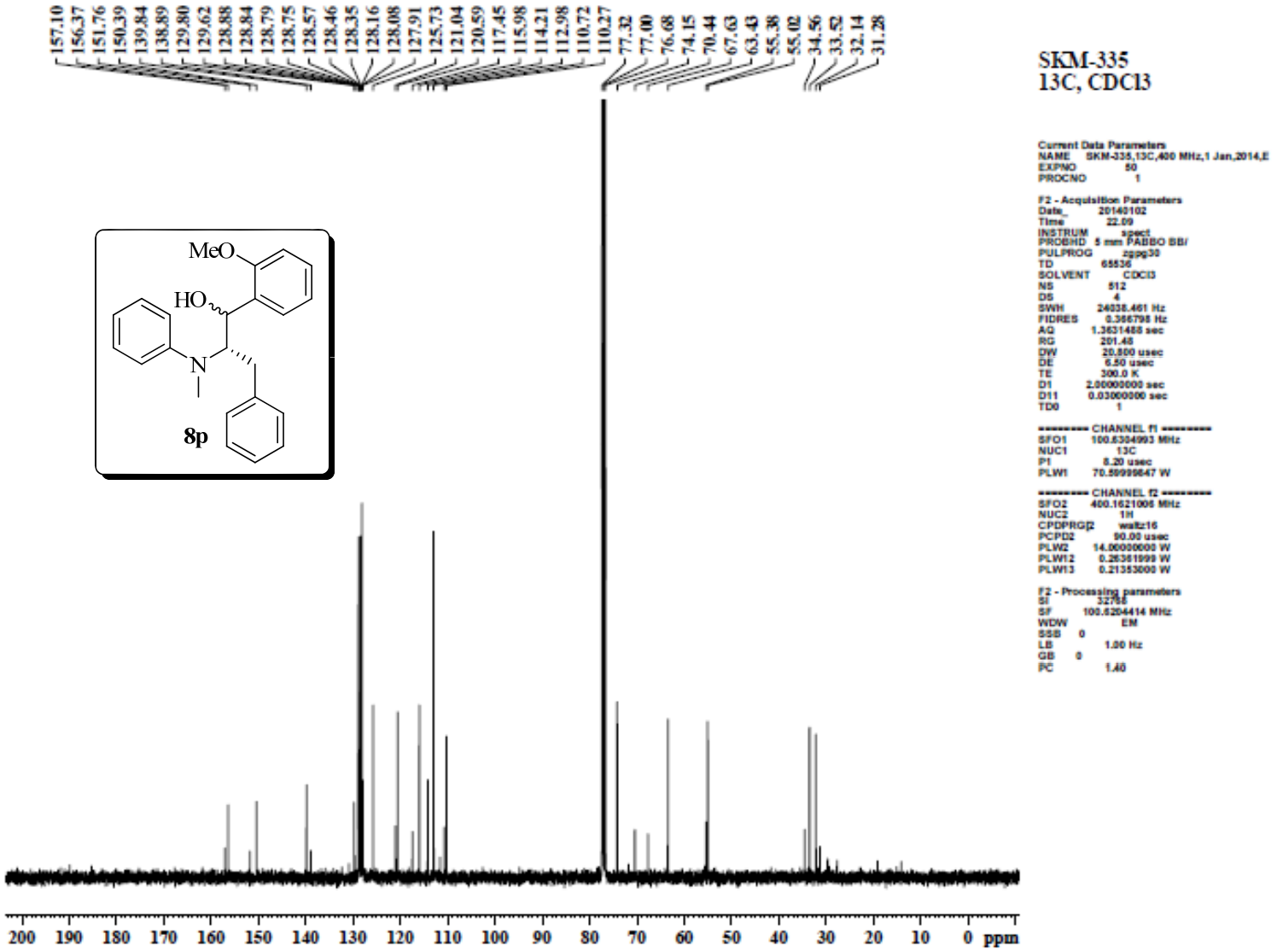


Figure 56: ^{13}C -NMR Spectrum of **8p.**

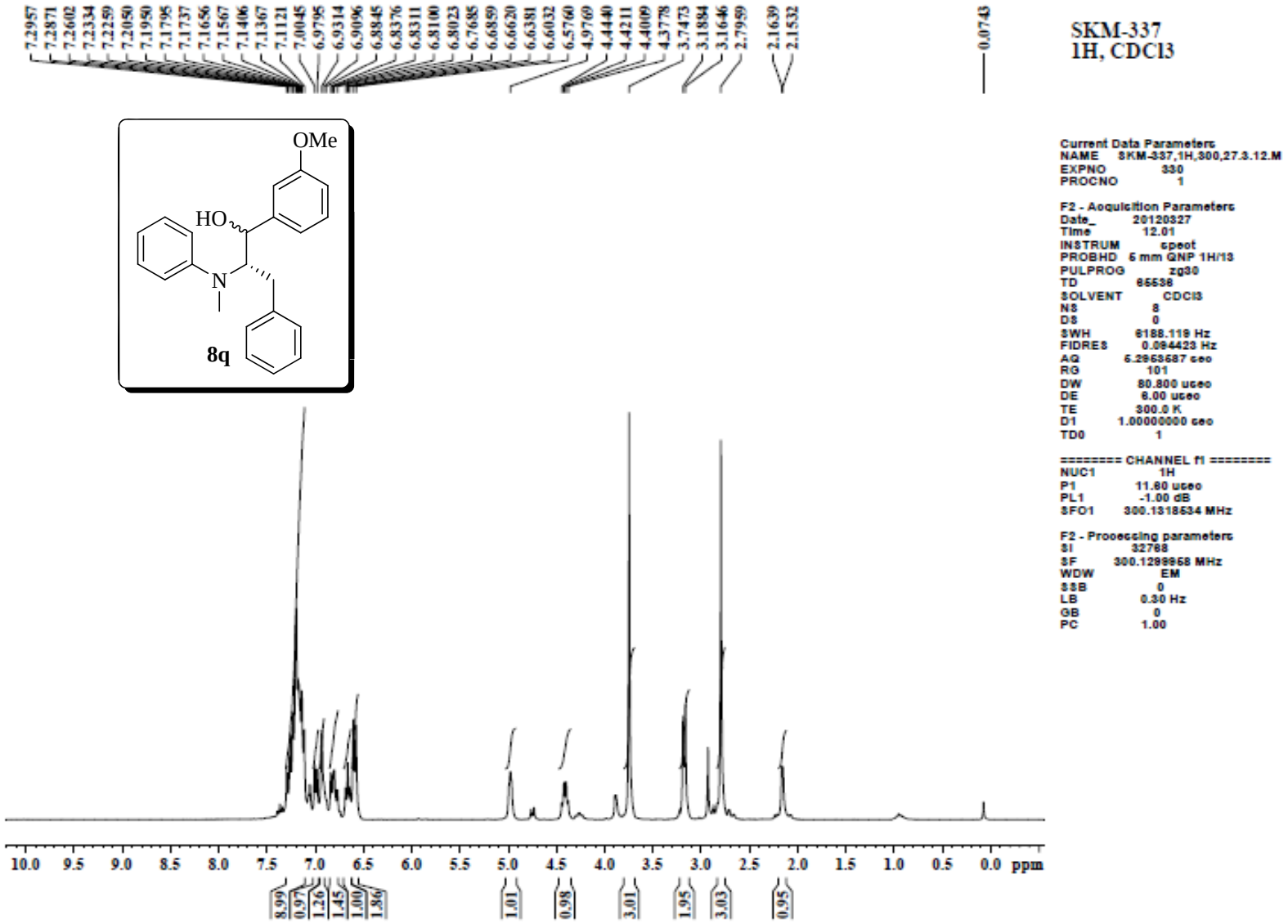


Figure 57: ^{1}H -NMR Spectrum of **8q.**

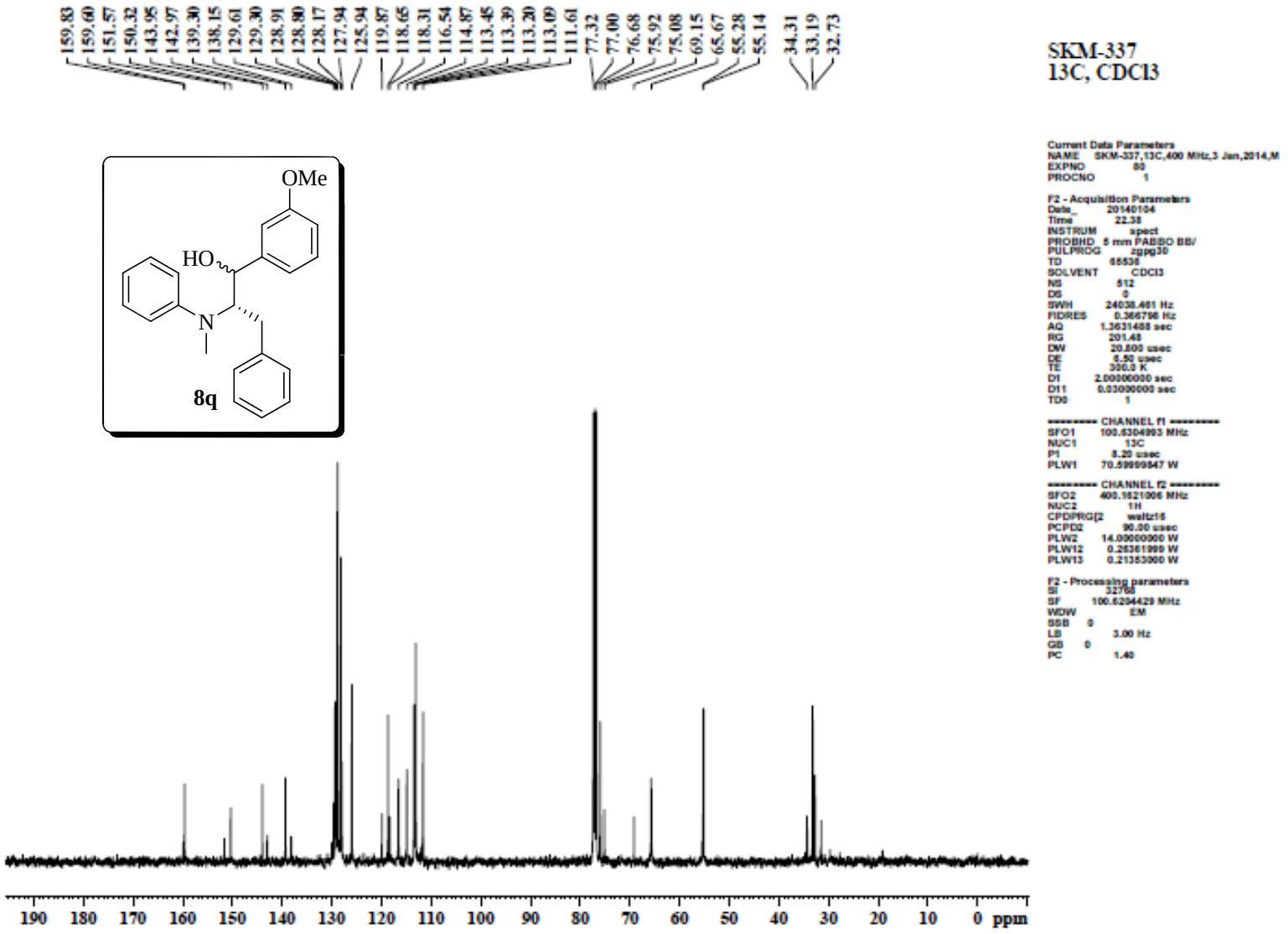


Figure 58: ^{13}C-NMR Spectrum of **8q.**

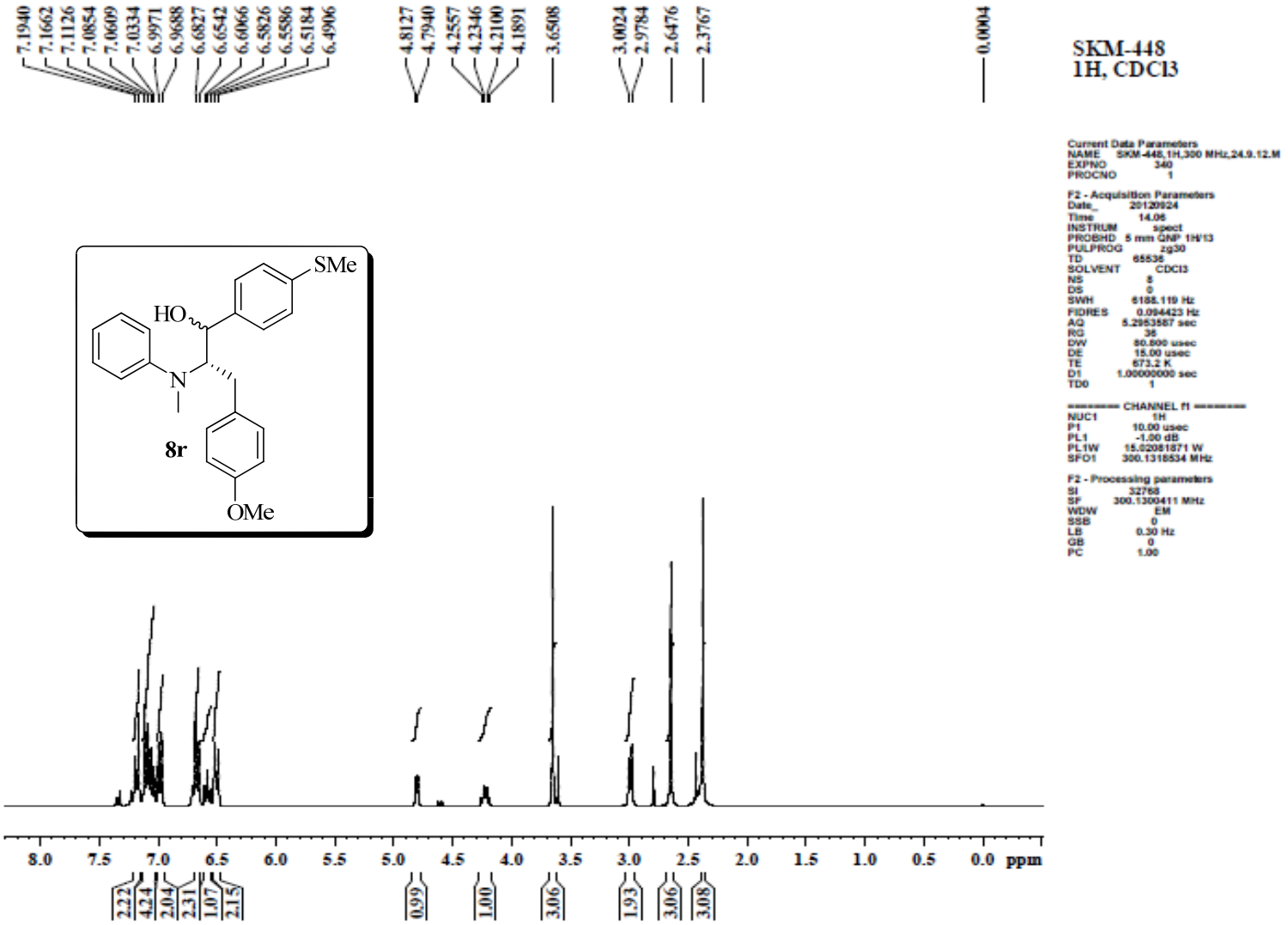


Figure 59: ^{1}H -NMR Spectrum of **8r.**

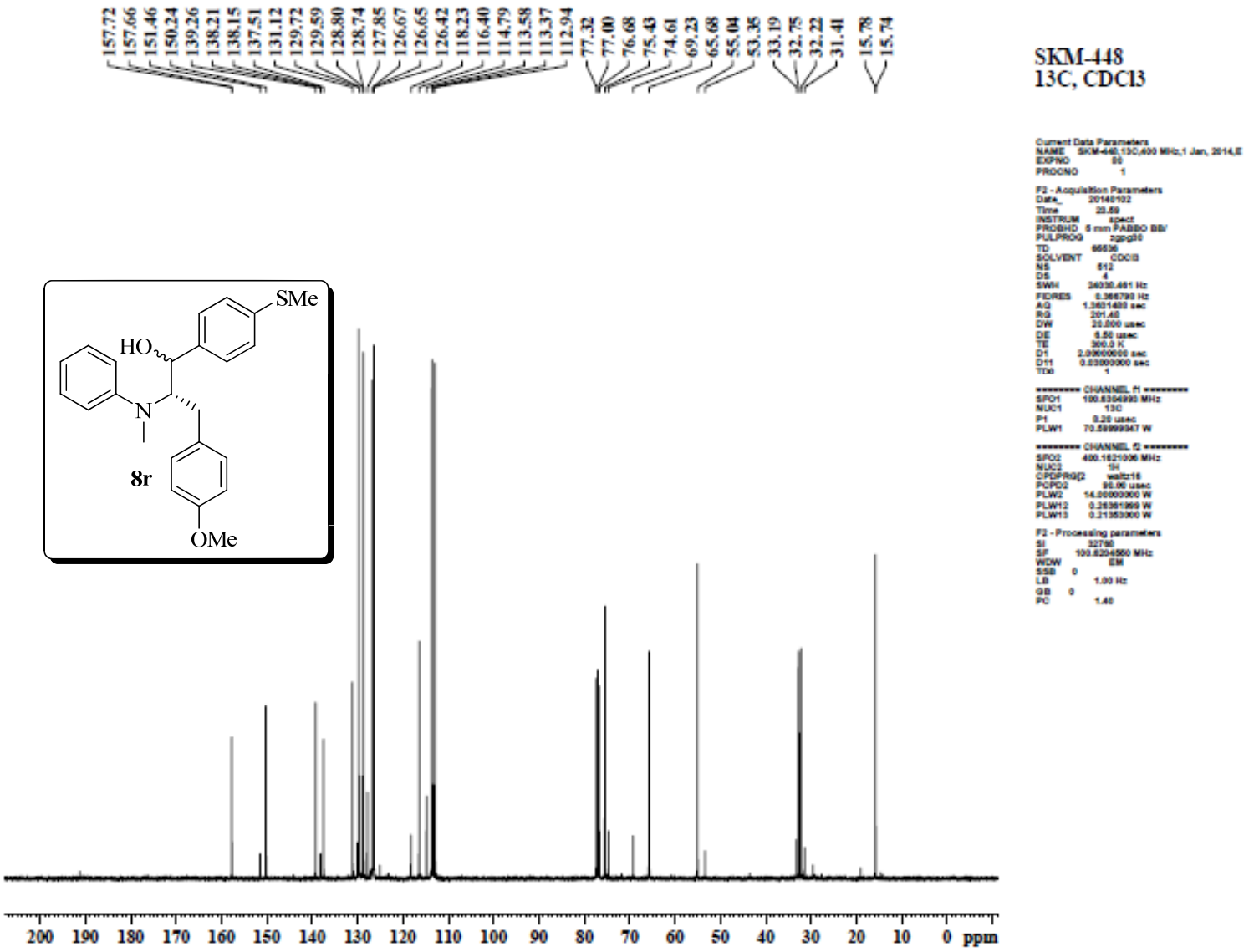


Figure 60: ^{13}C -NMR Spectrum of **8r.**

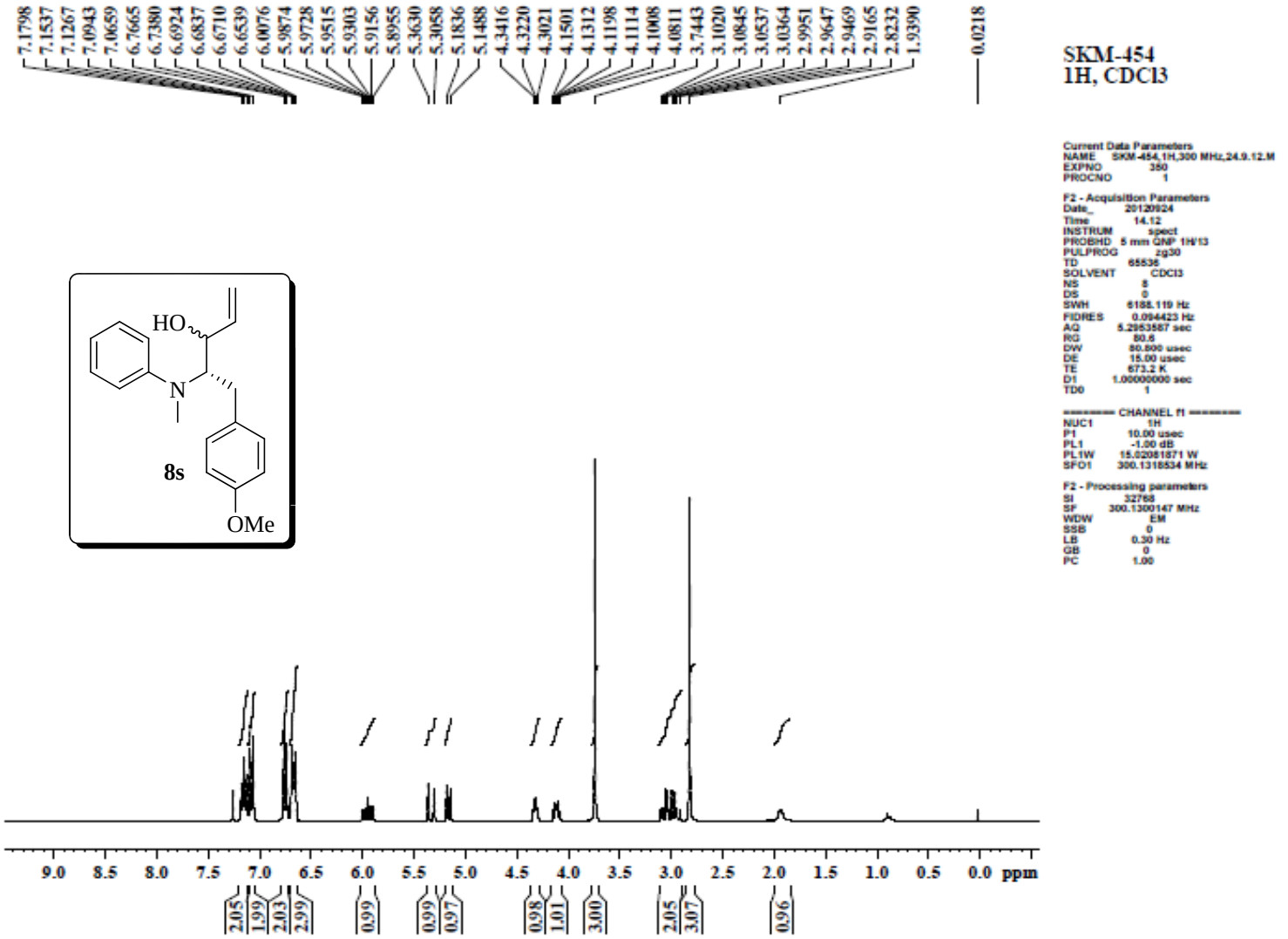


Figure 61: ^{1}H -NMR Spectrum of **8s.**

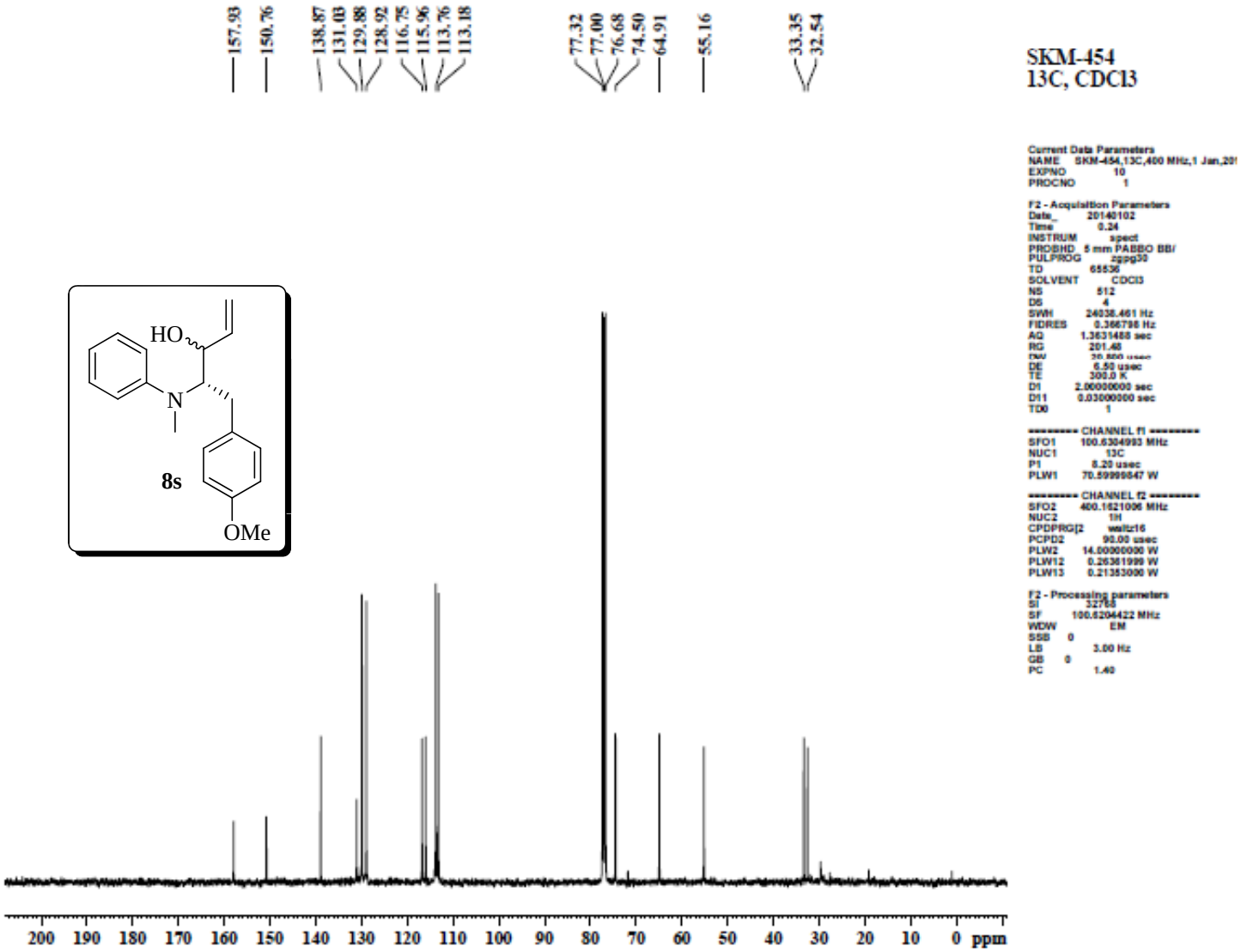


Figure 62: ^{13}C -NMR Spectrum of **8s.**

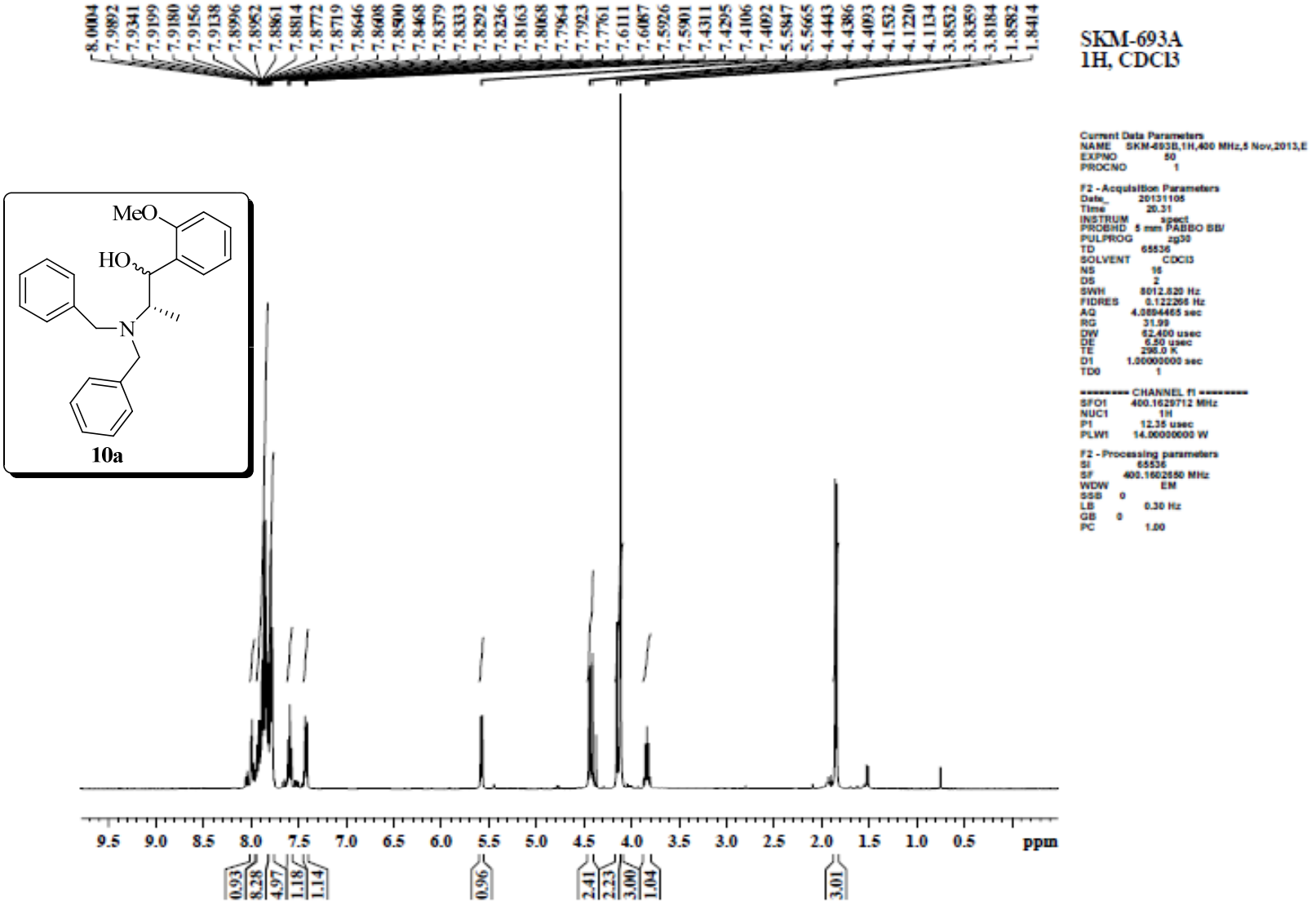


Figure 63: ^{1}H -NMR Spectrum of **10a.**

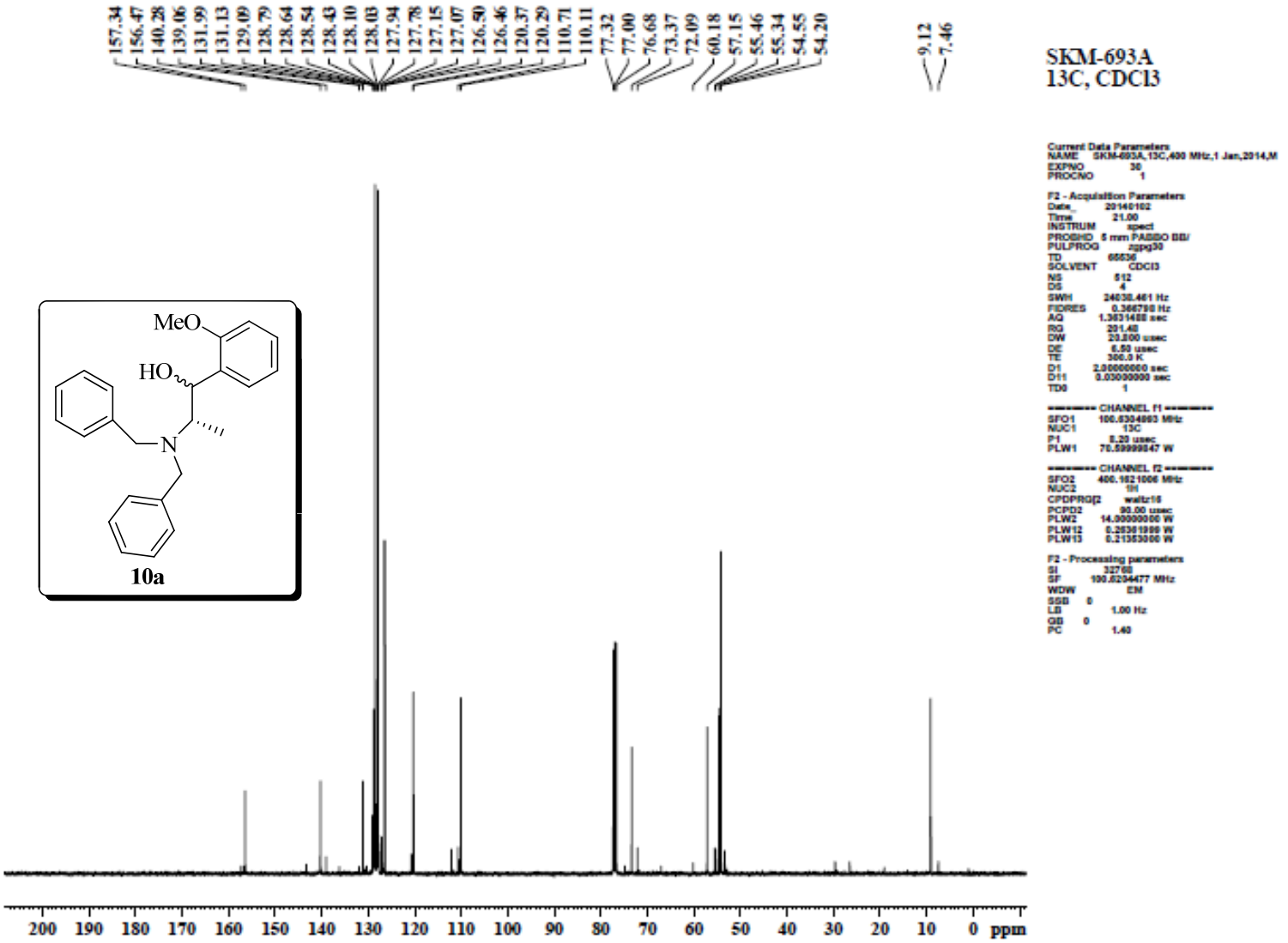


Figure 64: ^{13}C -NMR Spectrum of **10a.**

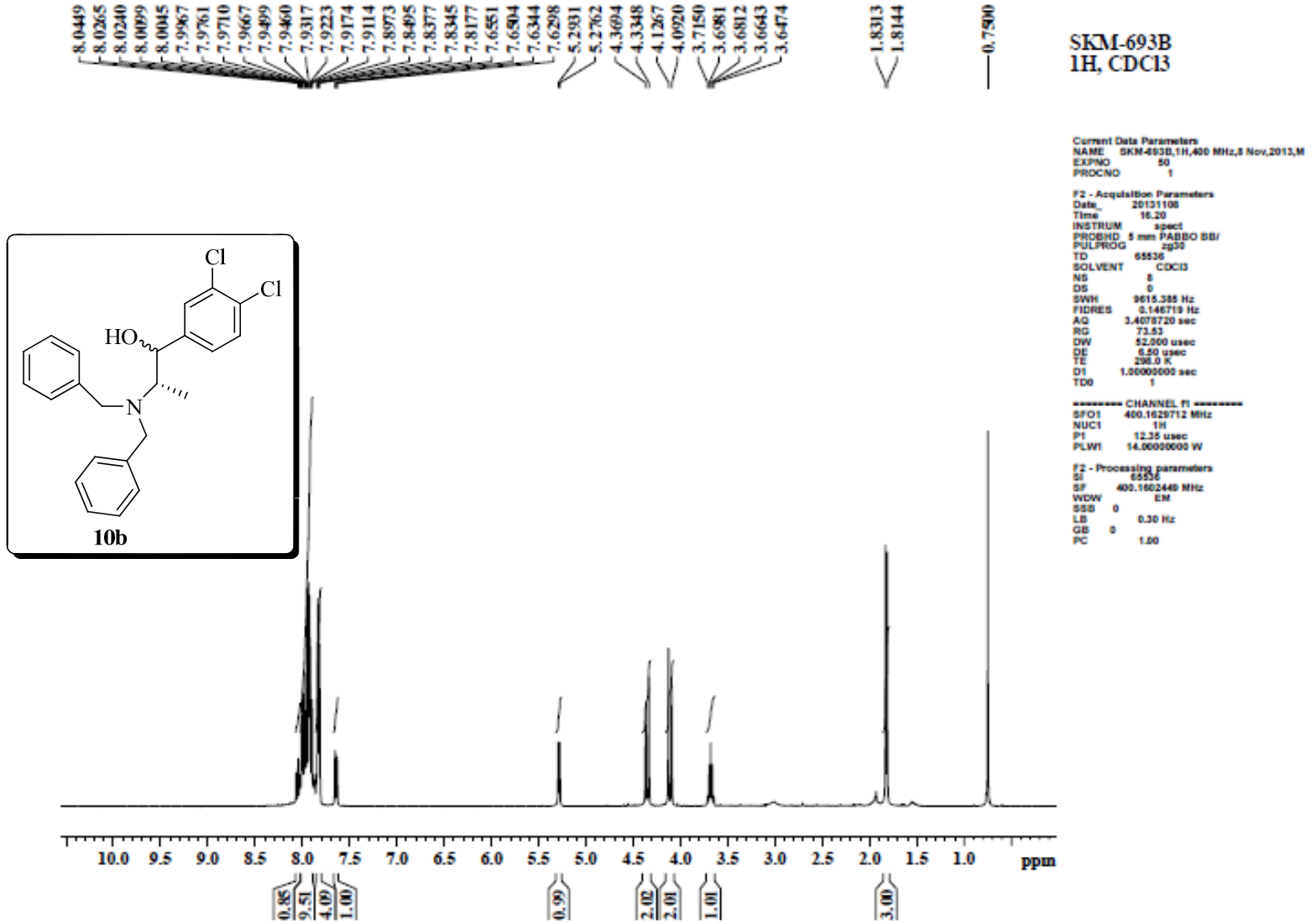


Figure 65: ^{1}H -NMR Spectrum of **10b.**

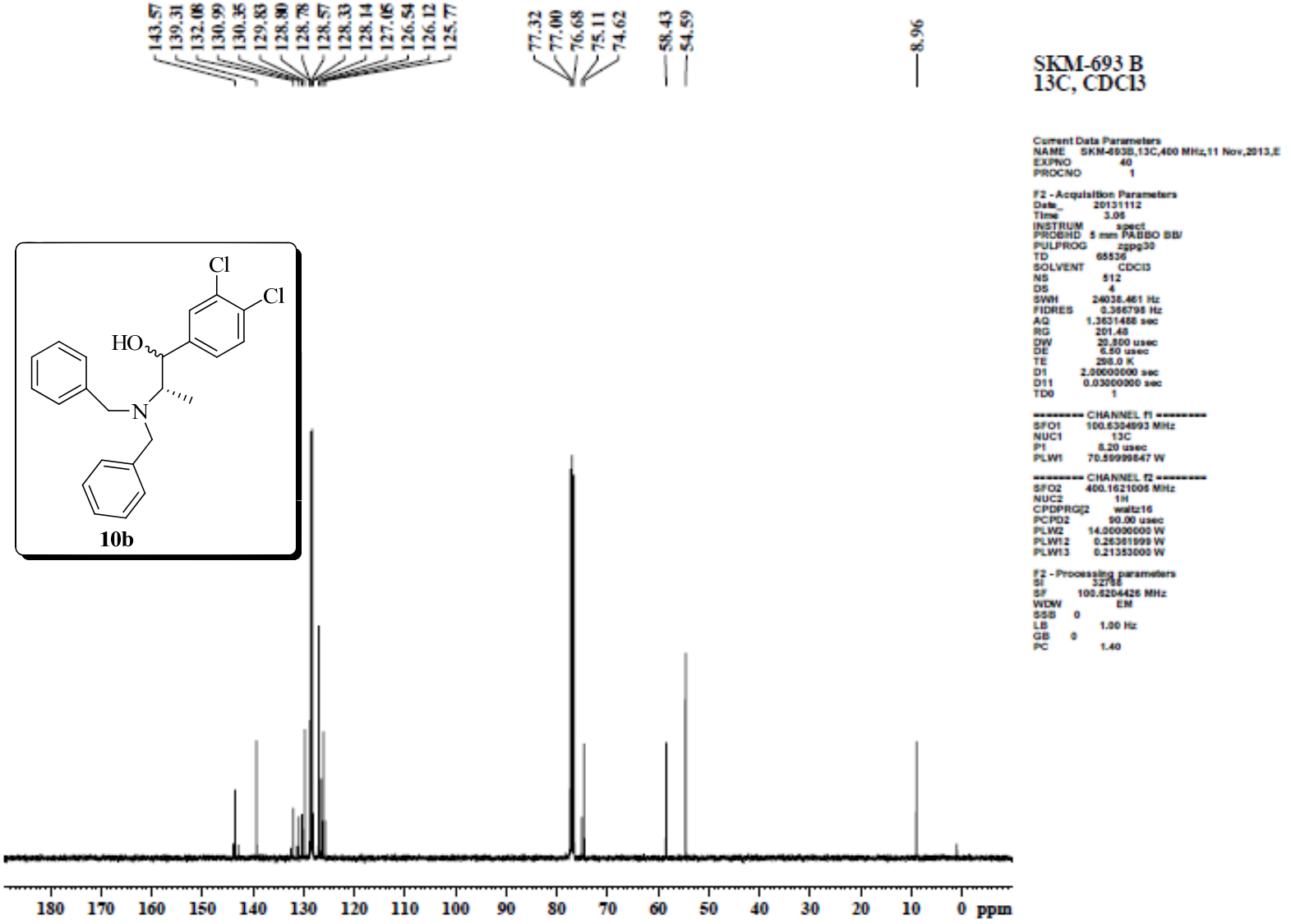


Figure 66: ^{13}C -NMR Spectrum of **10b.**

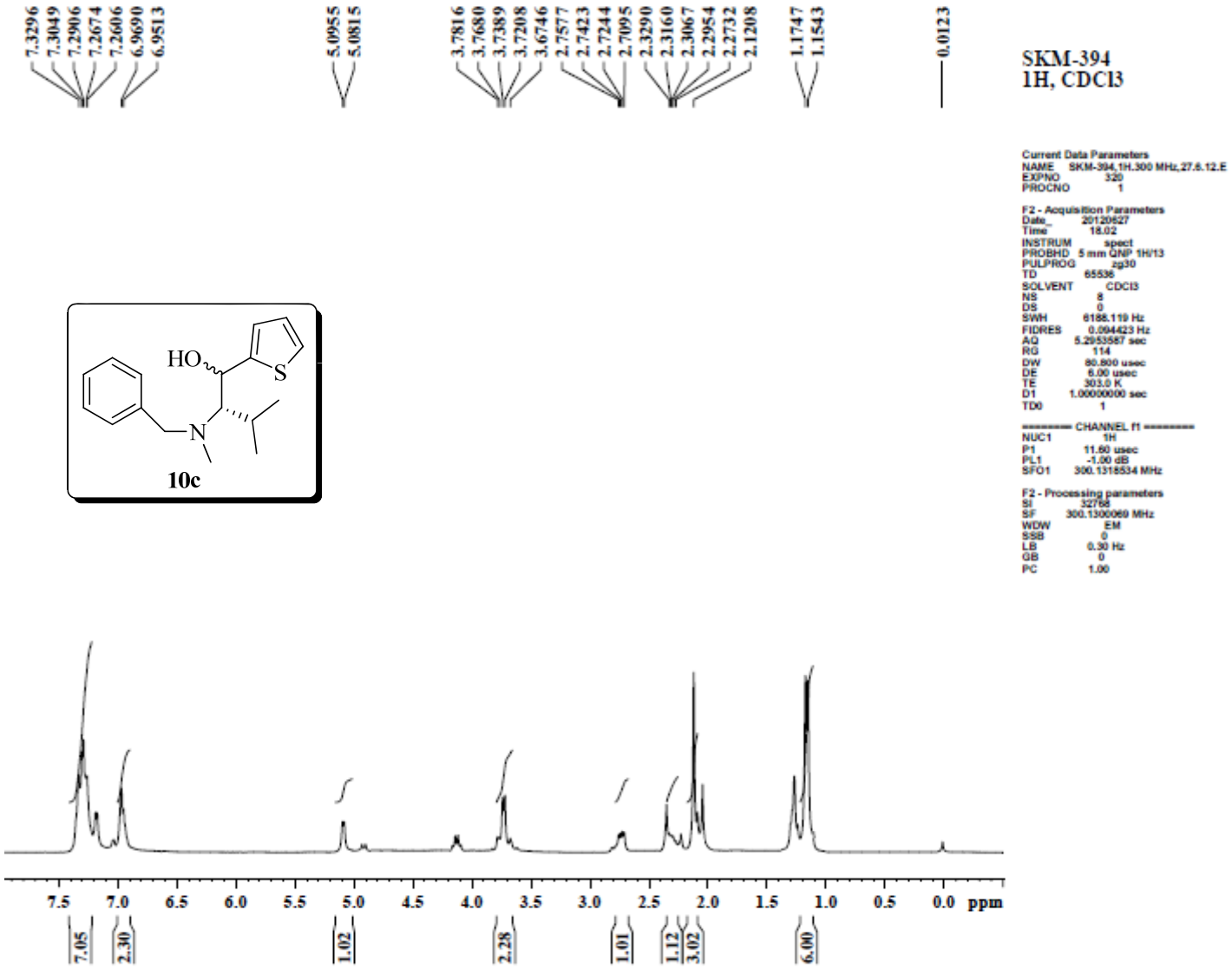


Figure 67: ^{1}H -NMR Spectrum of **10c.**

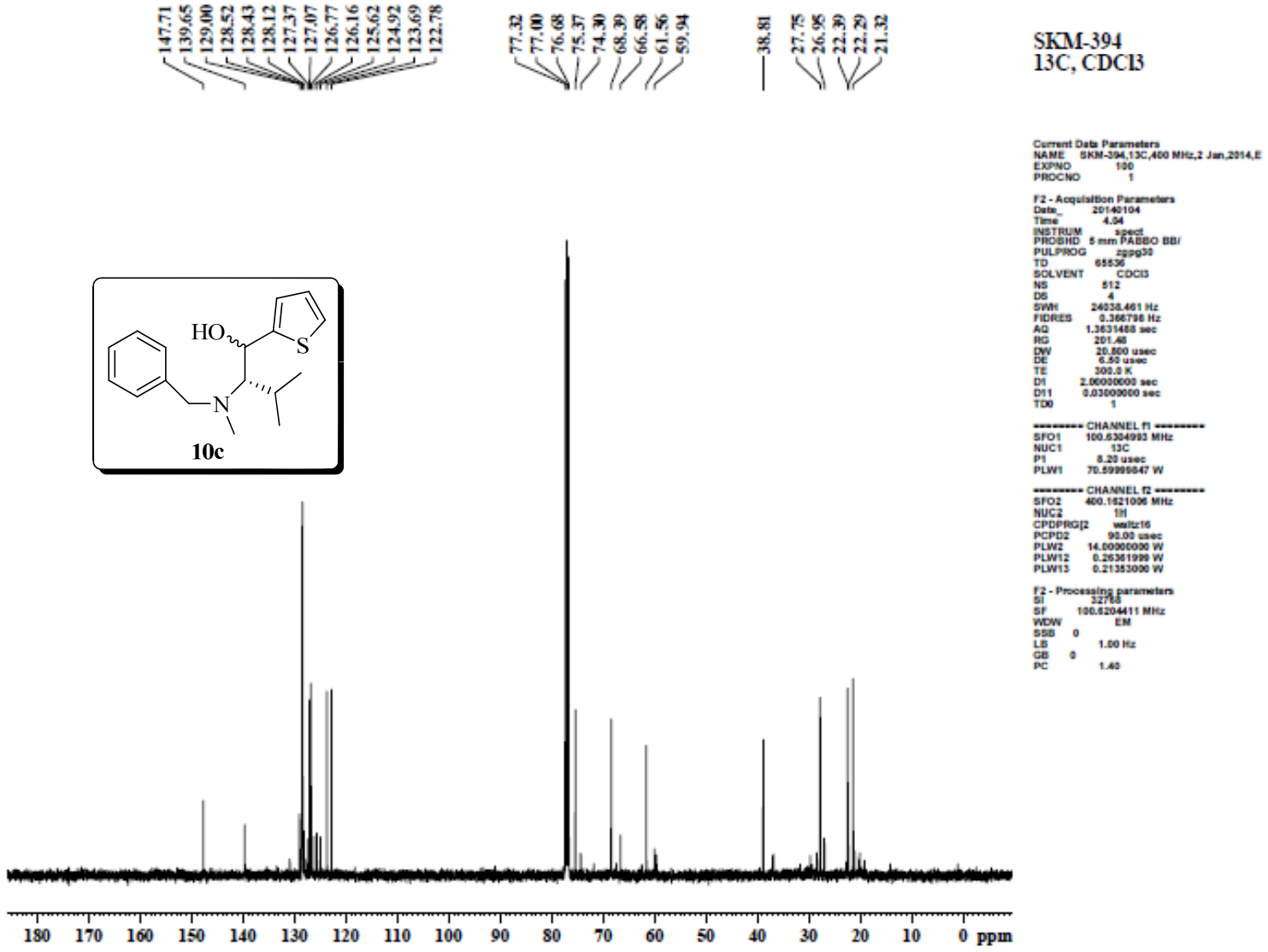


Figure 68: ^{13}C-NMR Spectrum of **10c.**

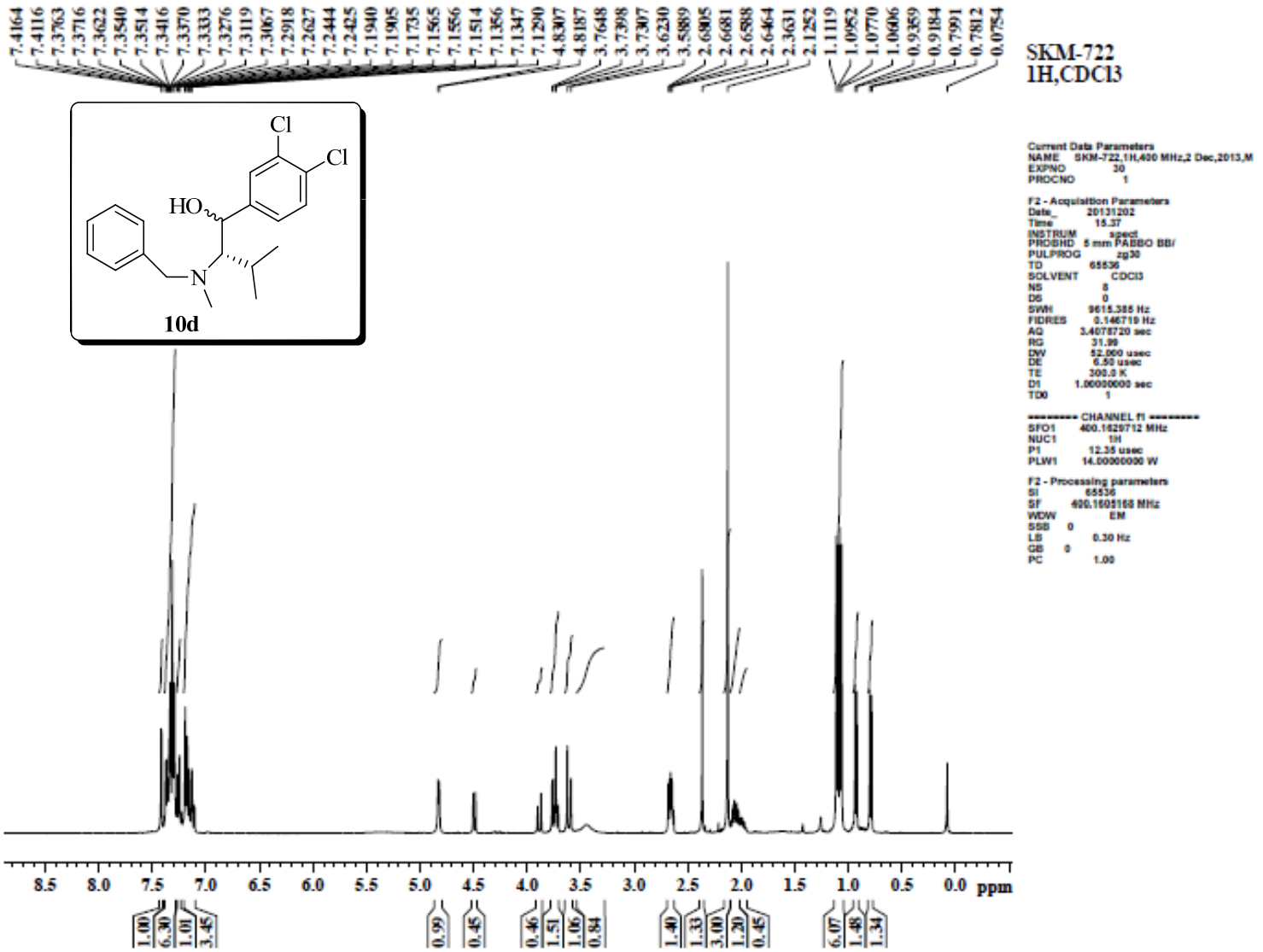


Figure 69: ^{1}H -NMR Spectrum of **10d.**

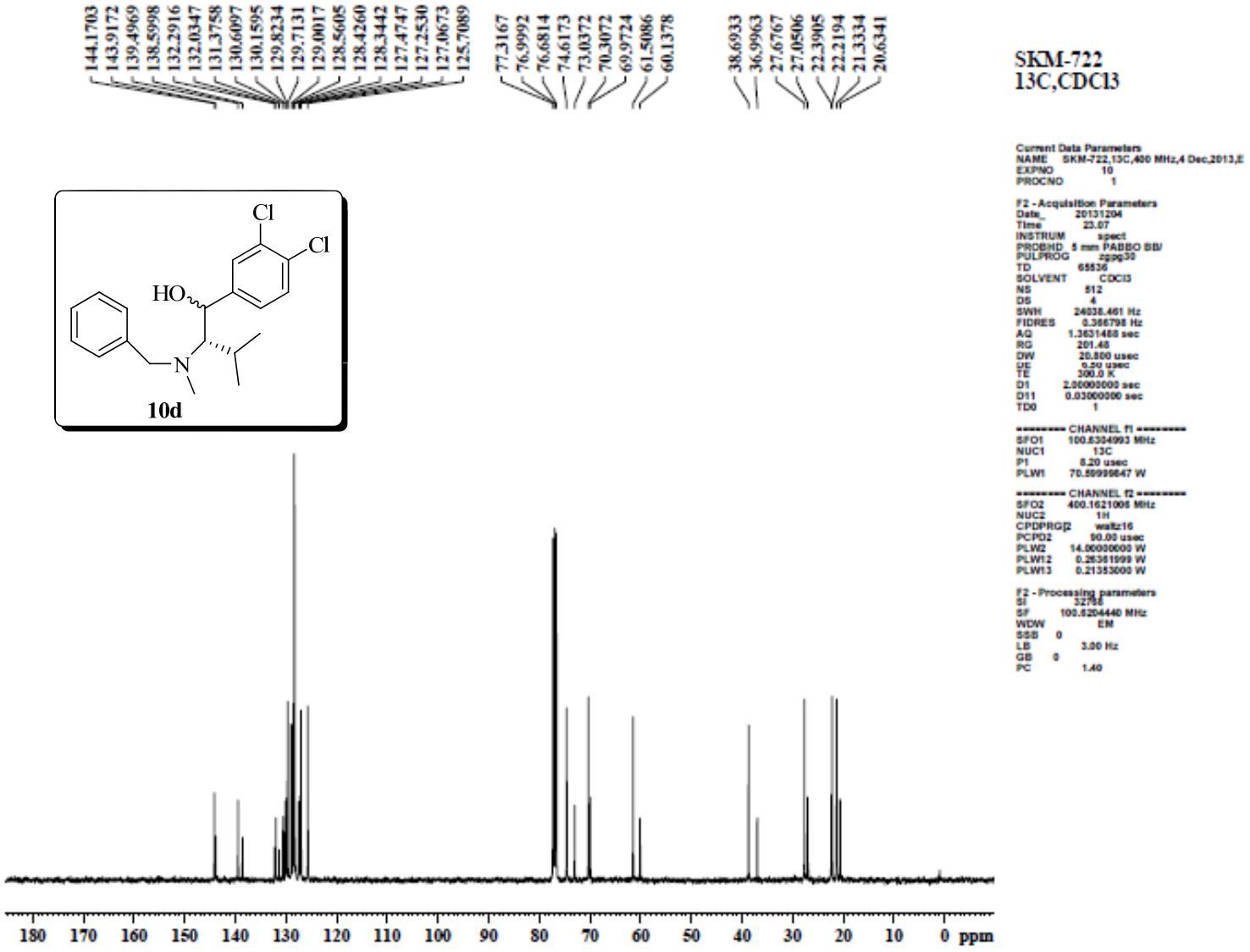


Figure 70: ^{13}C -NMR Spectrum of **10d.**

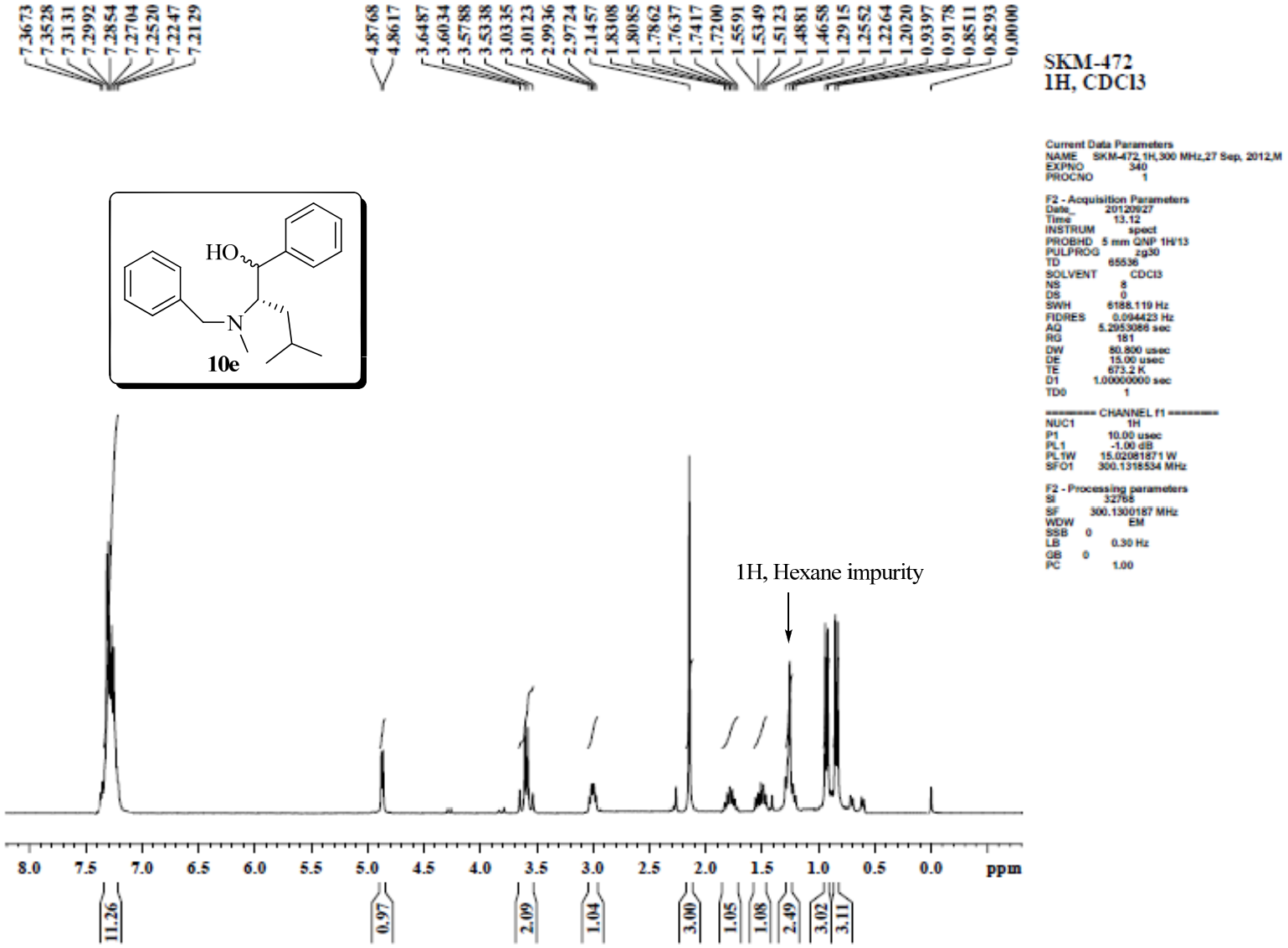


Figure 71: ^{1}H -NMR Spectrum of **10e.**

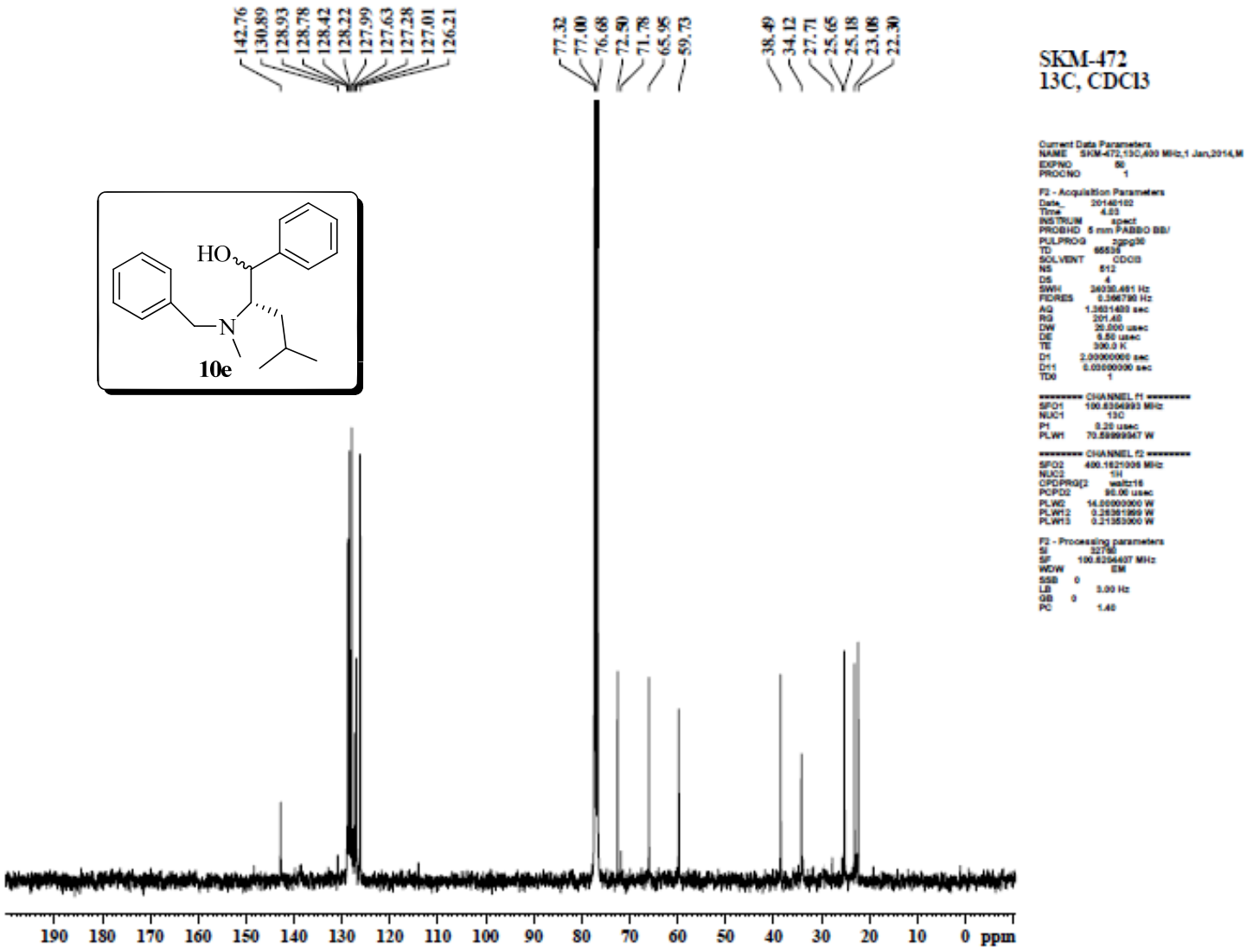


Figure 72: ^{13}C -NMR Spectrum of **10e.**

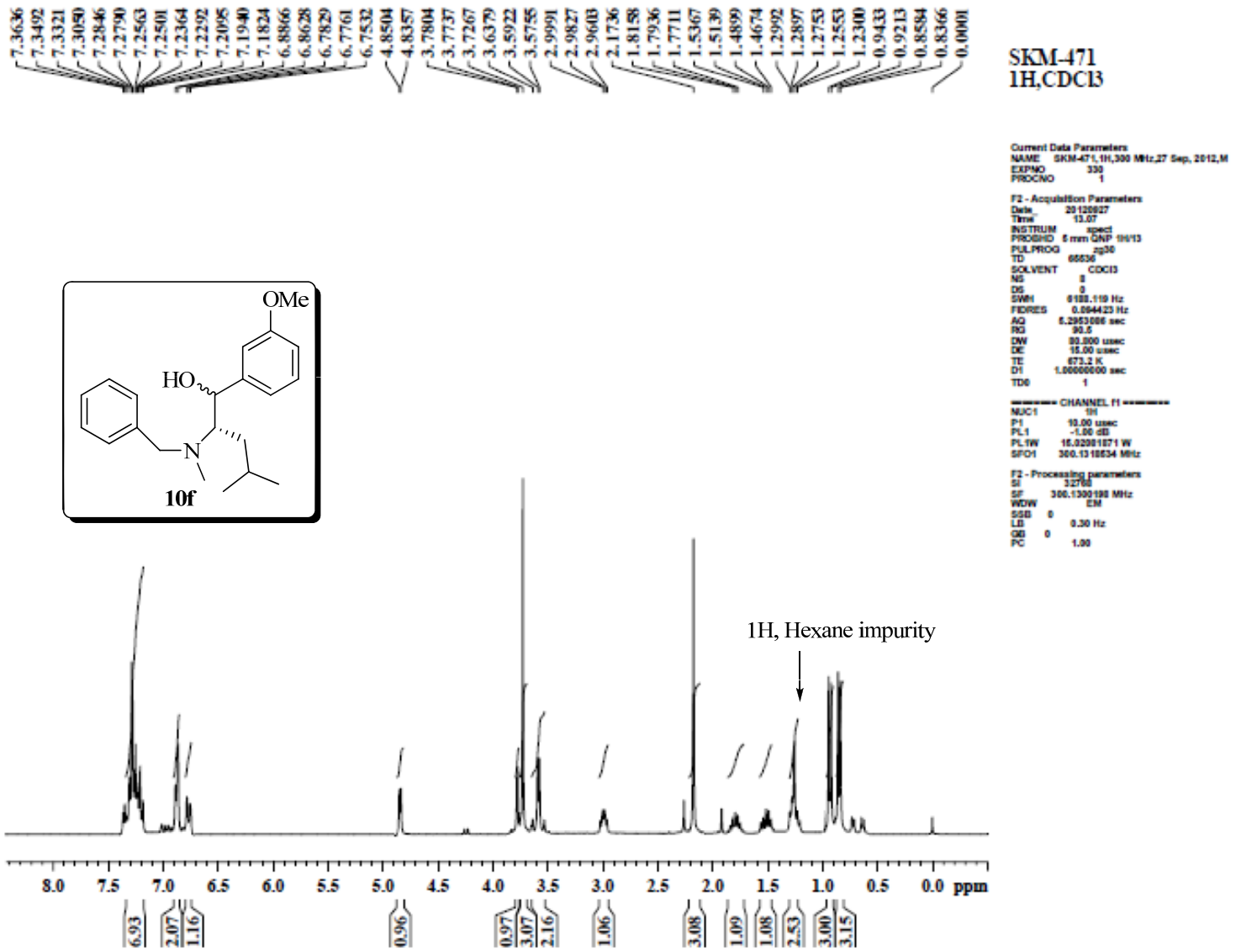


Figure 73: ^{1}H -NMR Spectrum of **10f.**

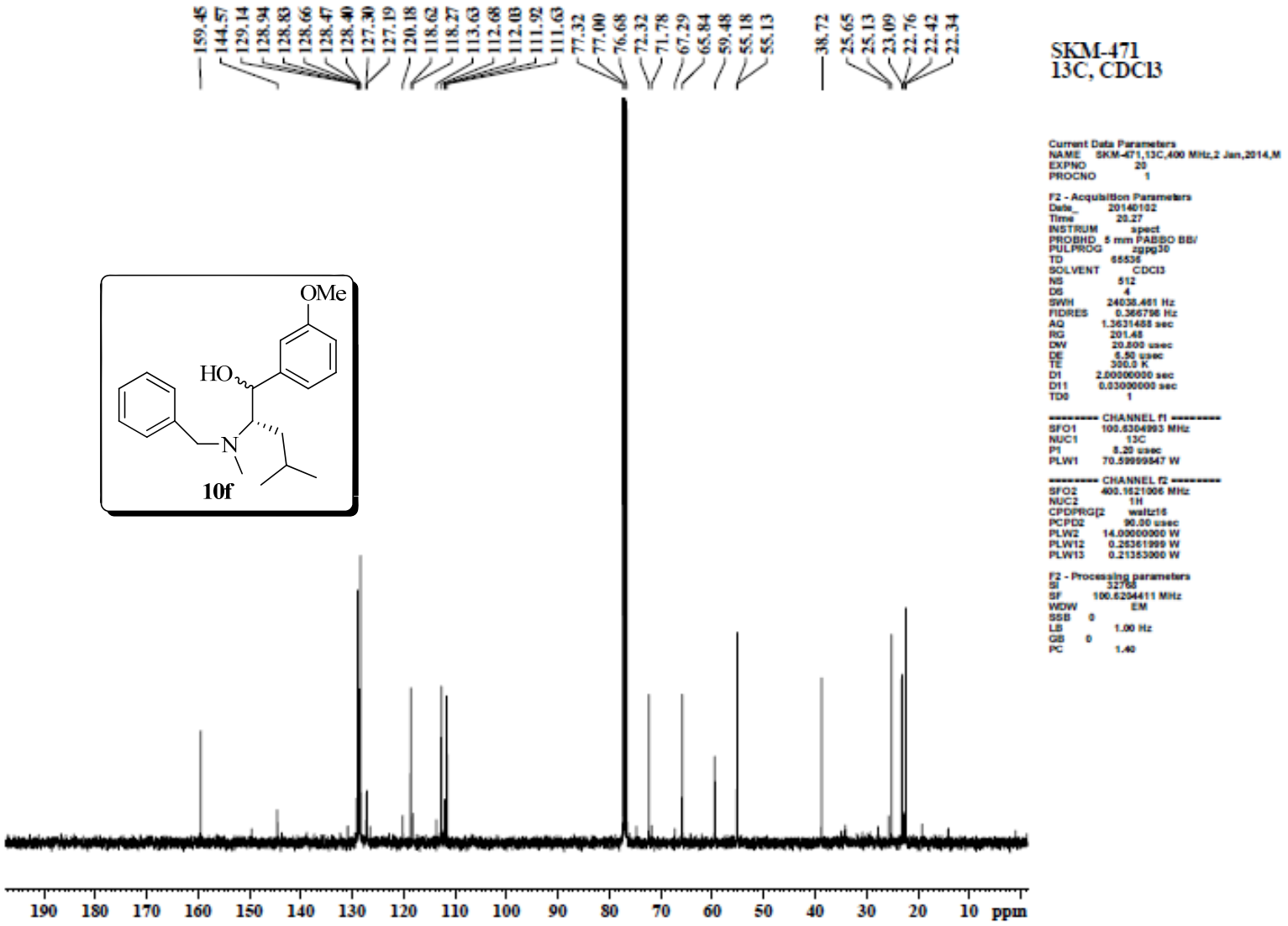


Figure 74: ^{13}C -NMR Spectrum of **10f.**

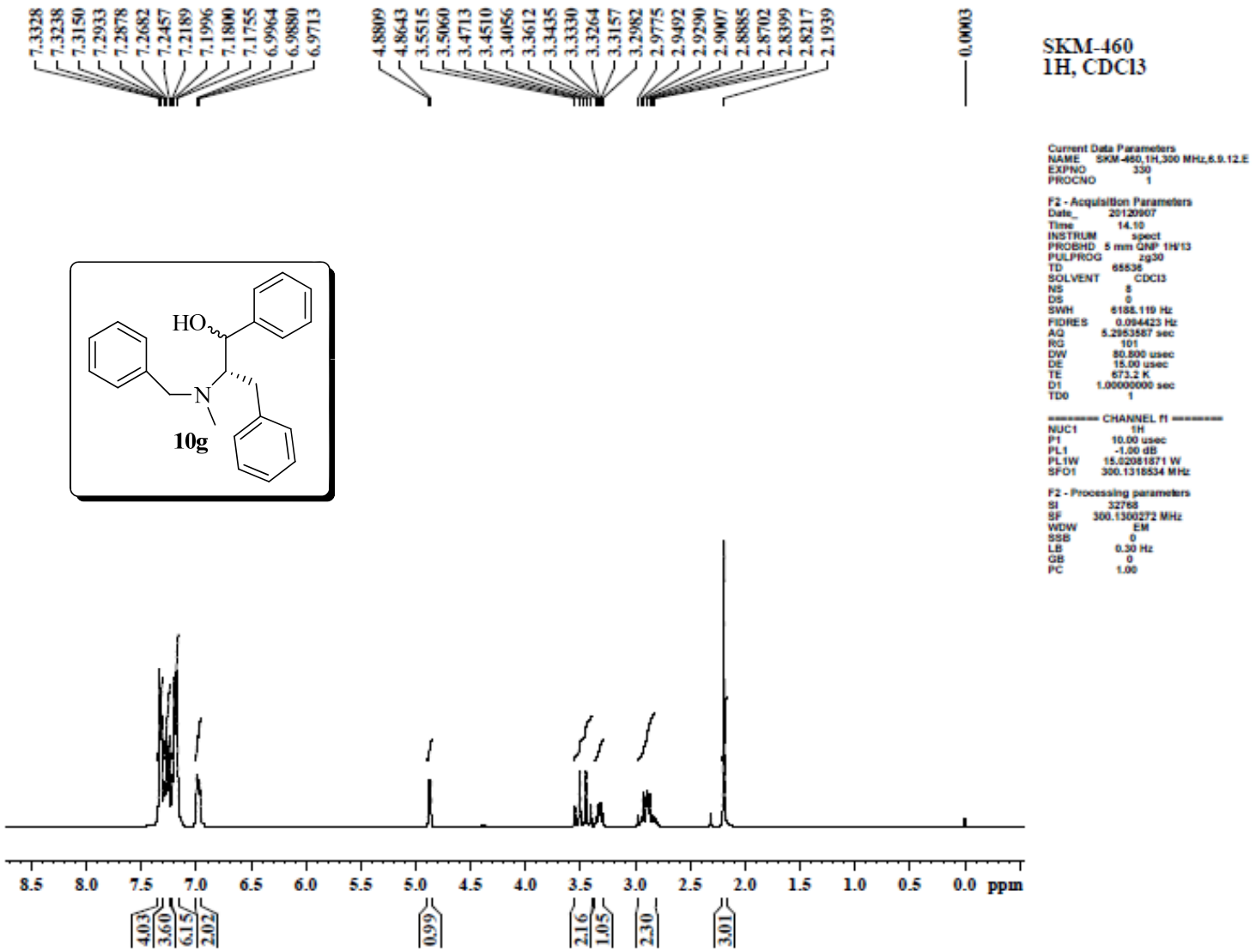


Figure 75: ^{1}H -NMR Spectrum of **10g.**

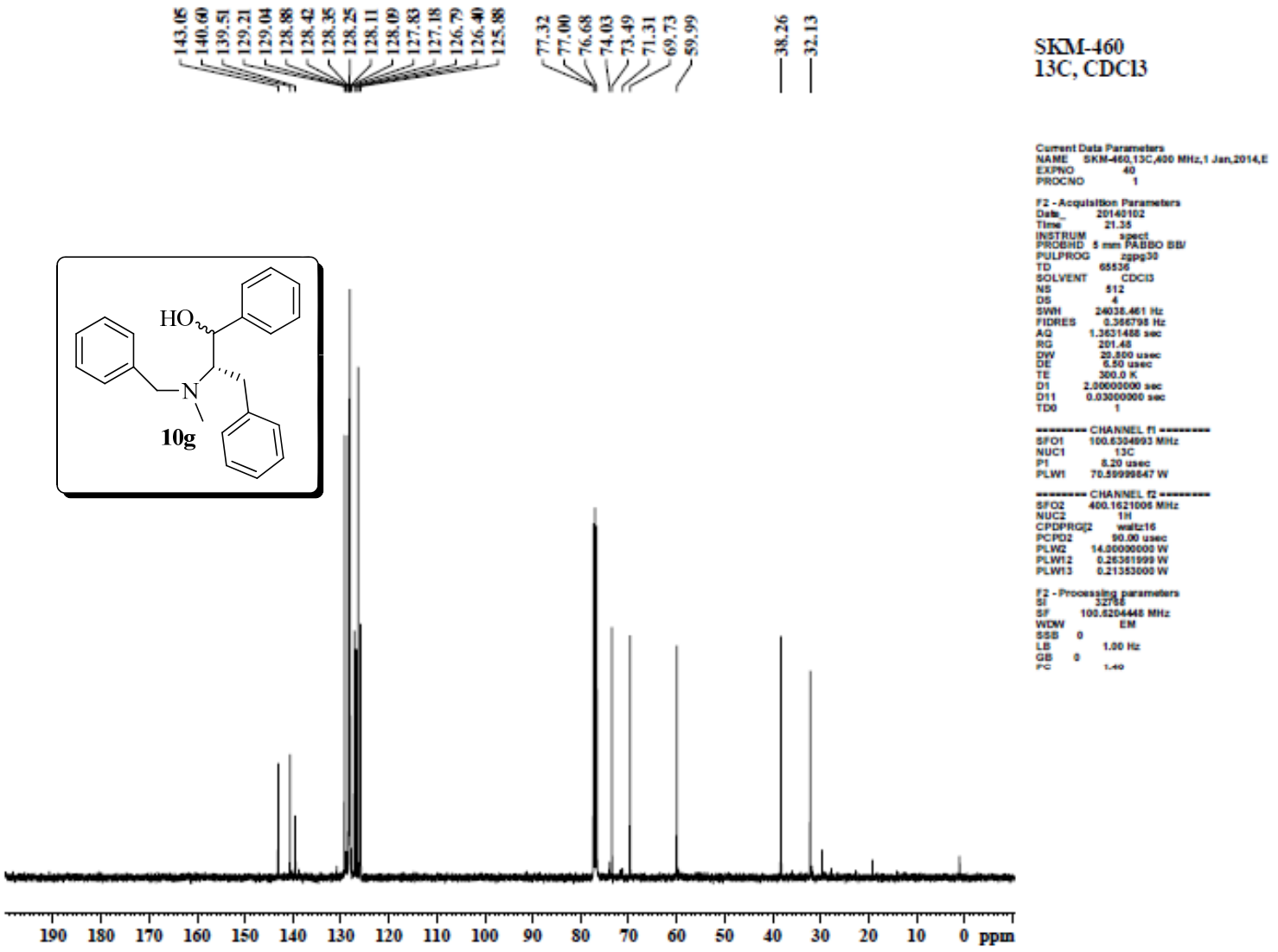


Figure 76: ^{13}C -NMR Spectrum of **10g.**

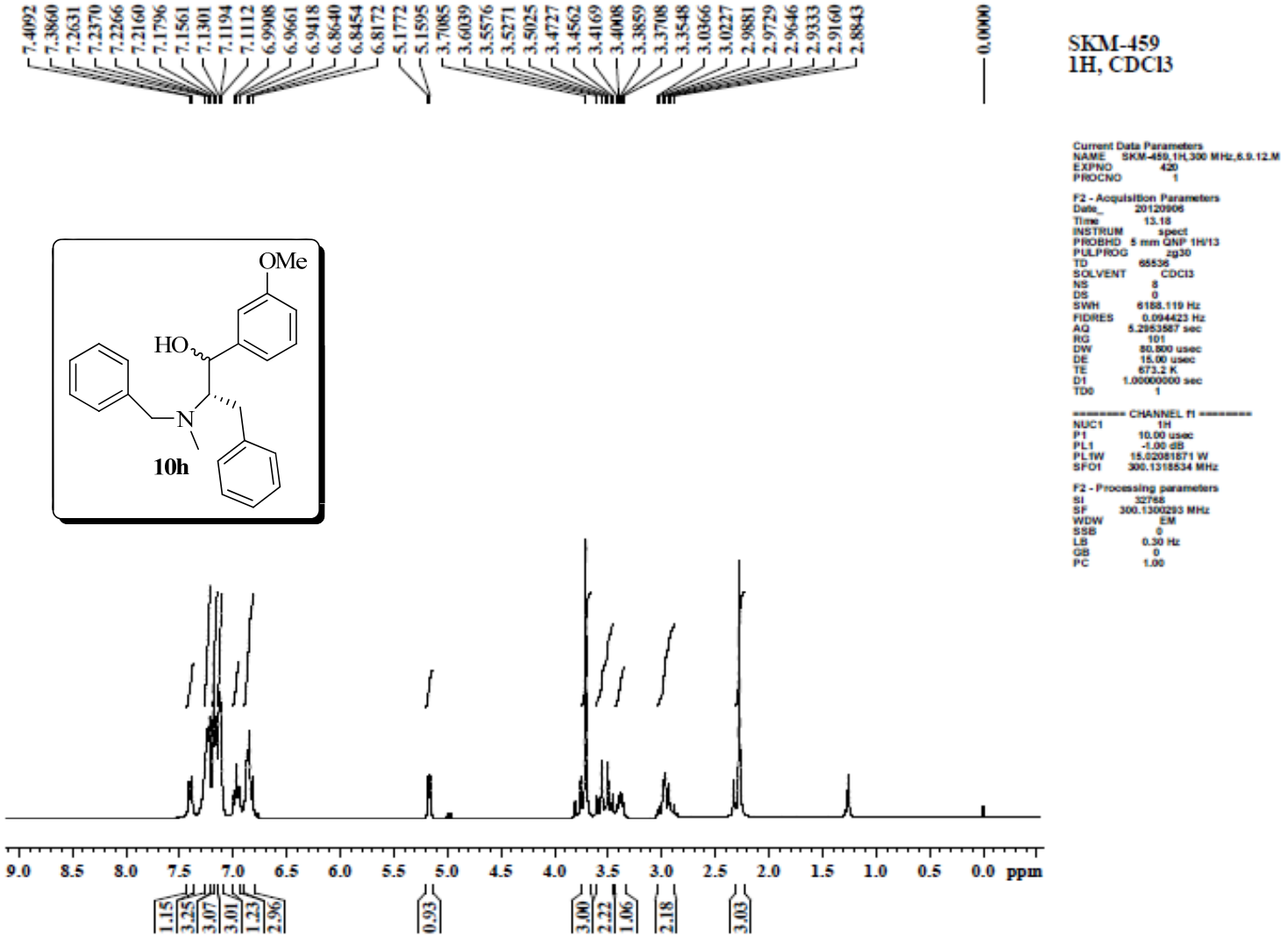


Figure 77: ^{1}H -NMR Spectrum of **10h.**

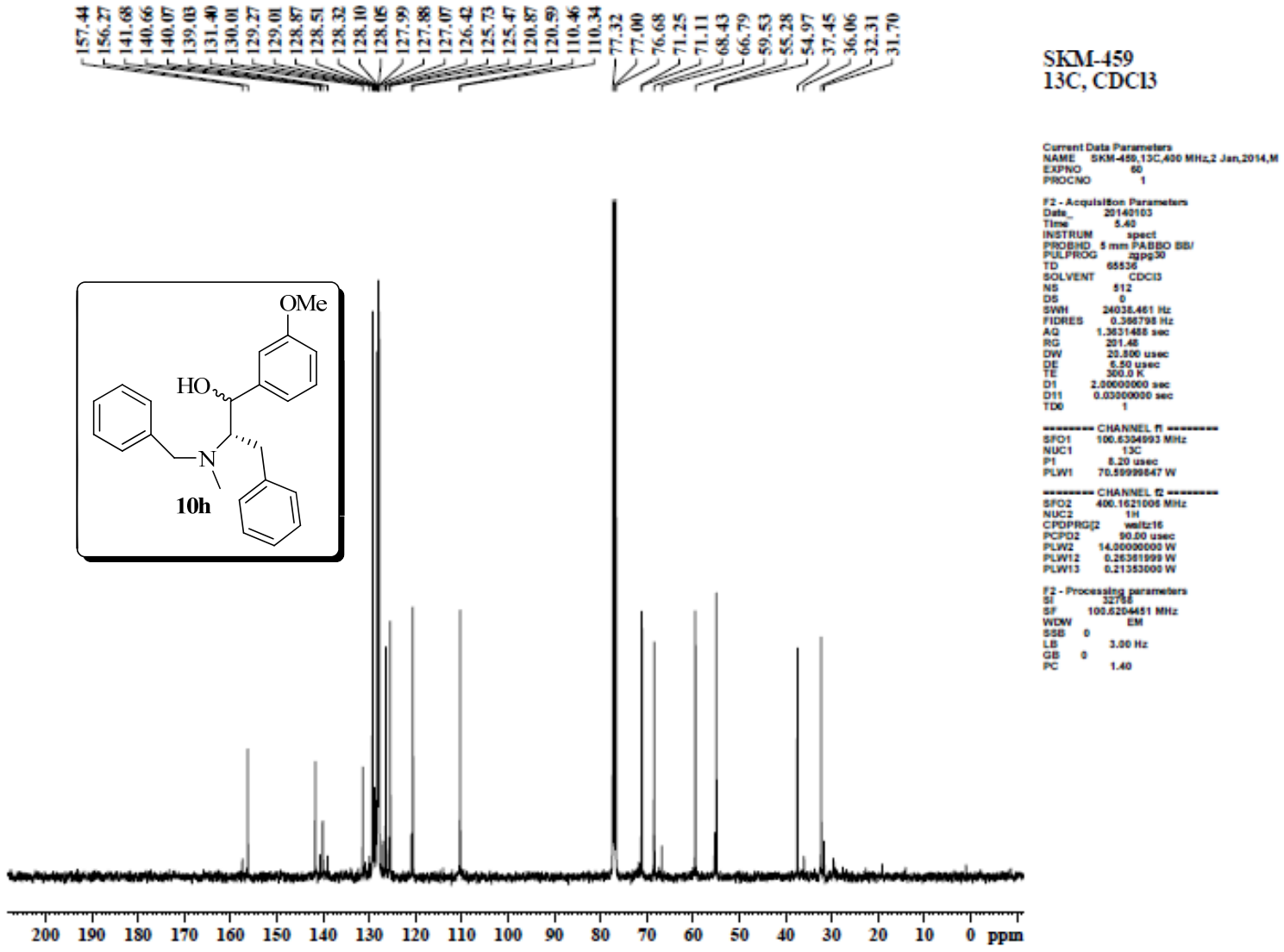


Figure 78: ^{13}C -NMR Spectrum of **10h.**

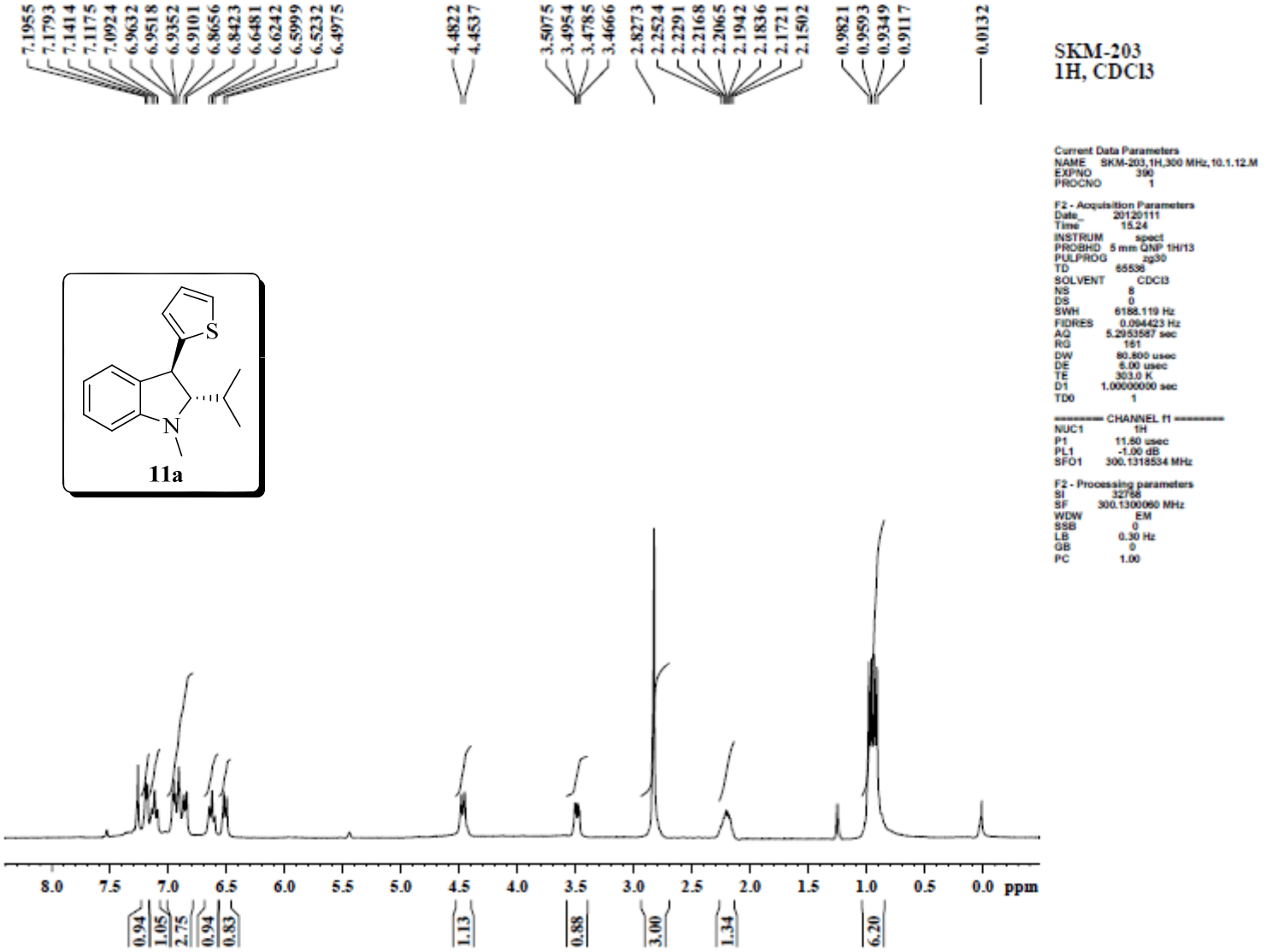


Figure 79: ^{1}H -NMR Spectrum of **11a.**

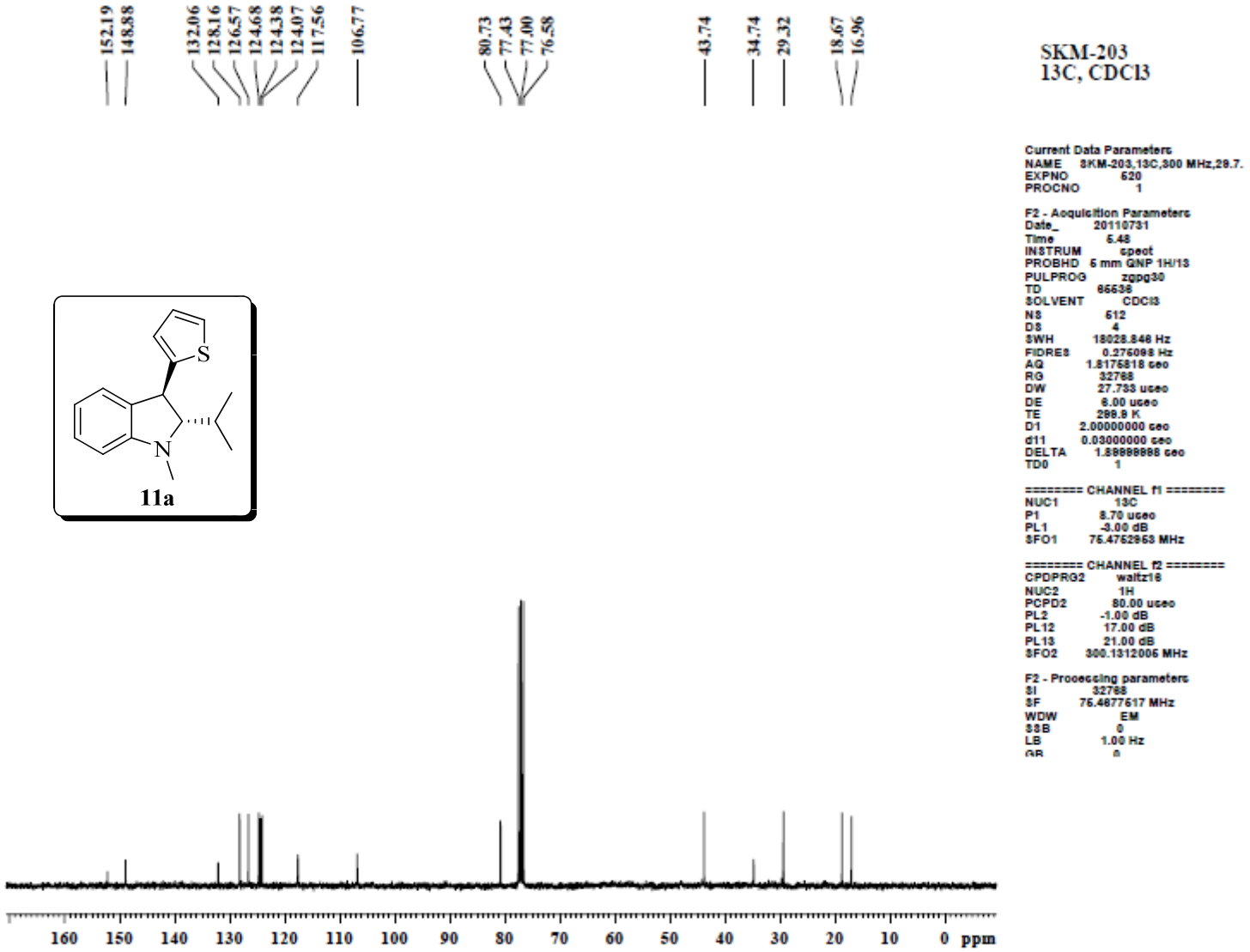


Figure 80: ^{13}C -NMR Spectrum of **11a.**

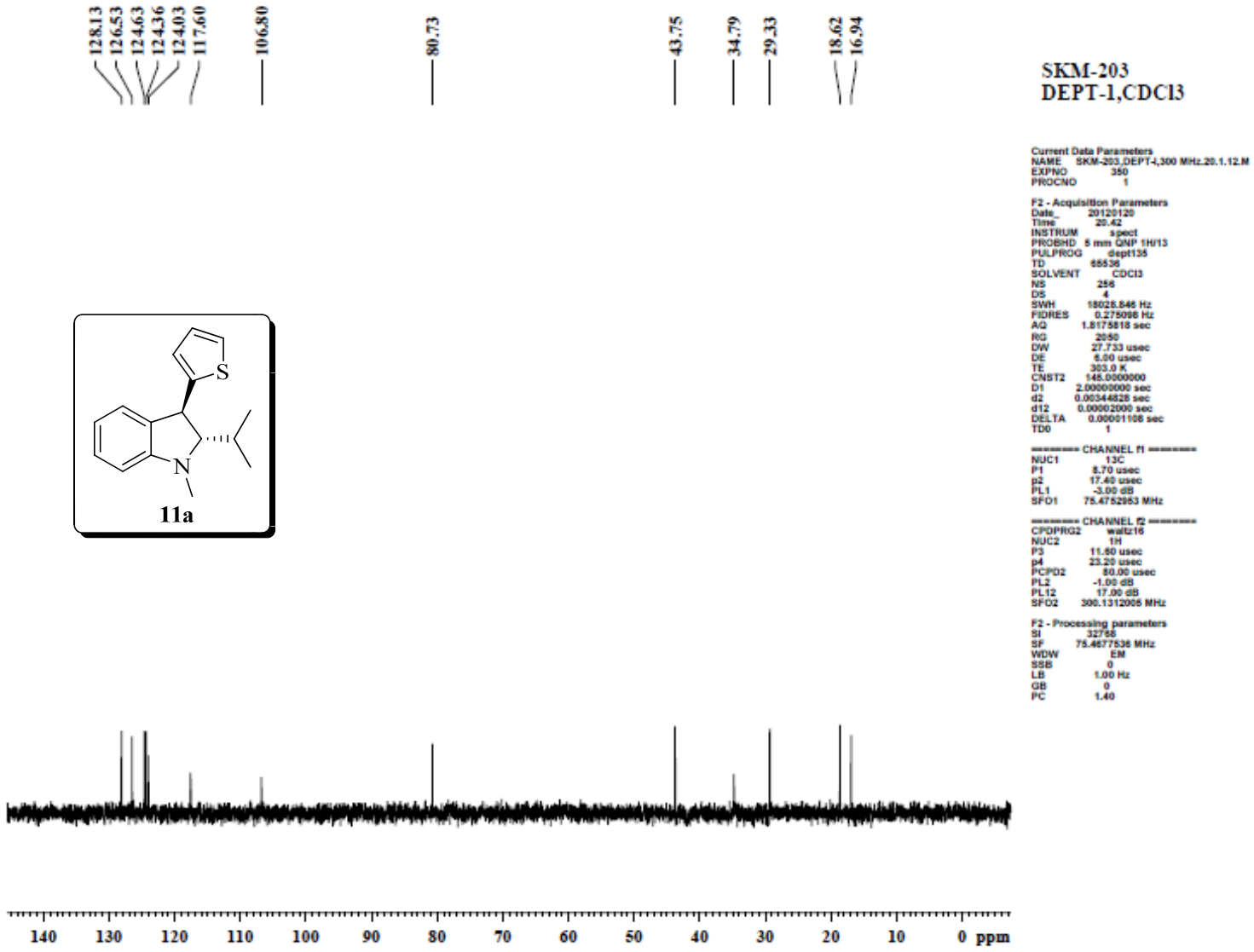


Figure 81: DEPT-I -Spectrum of **11a.**

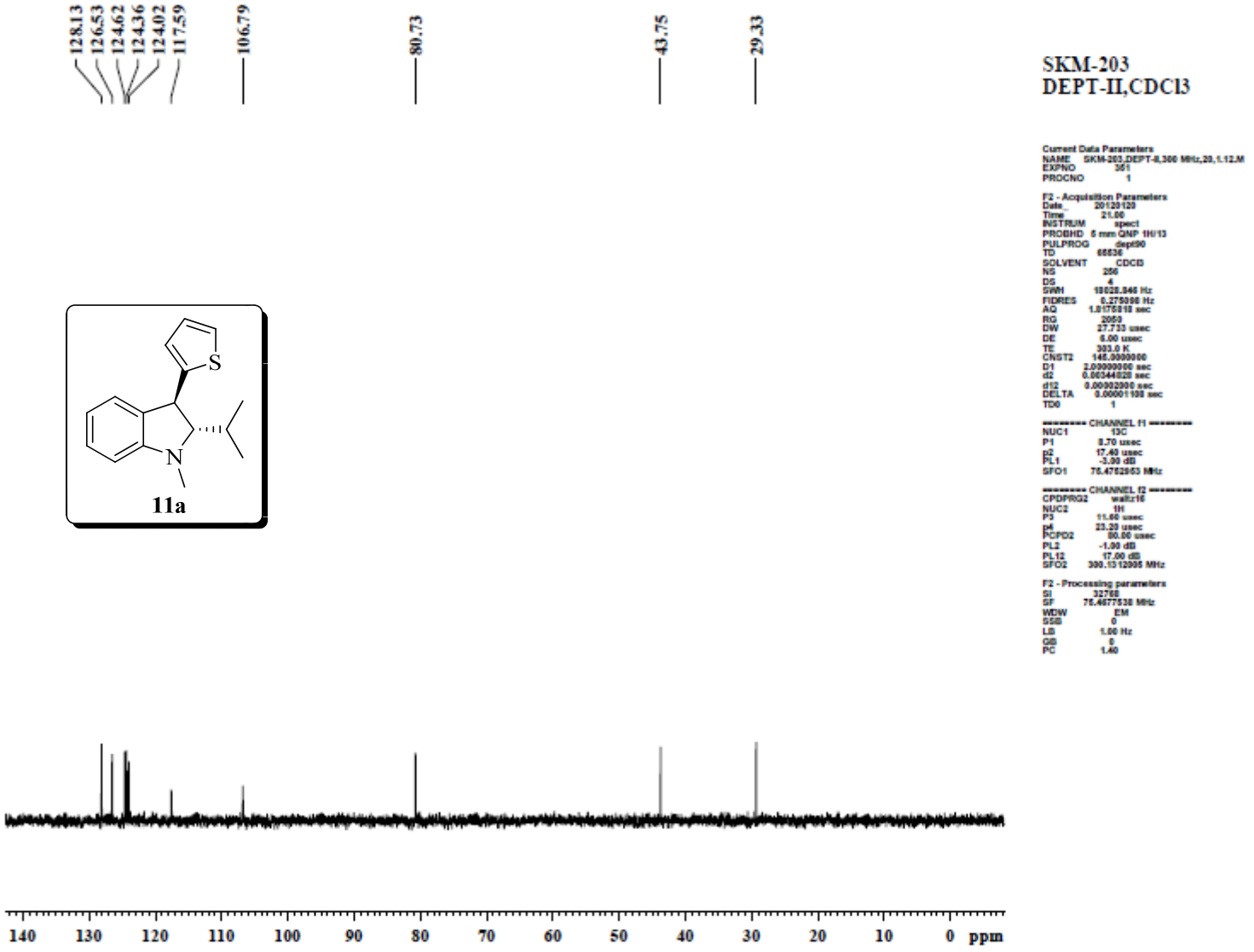


Figure 82: DEPT-II -Spectrum of **11a.**

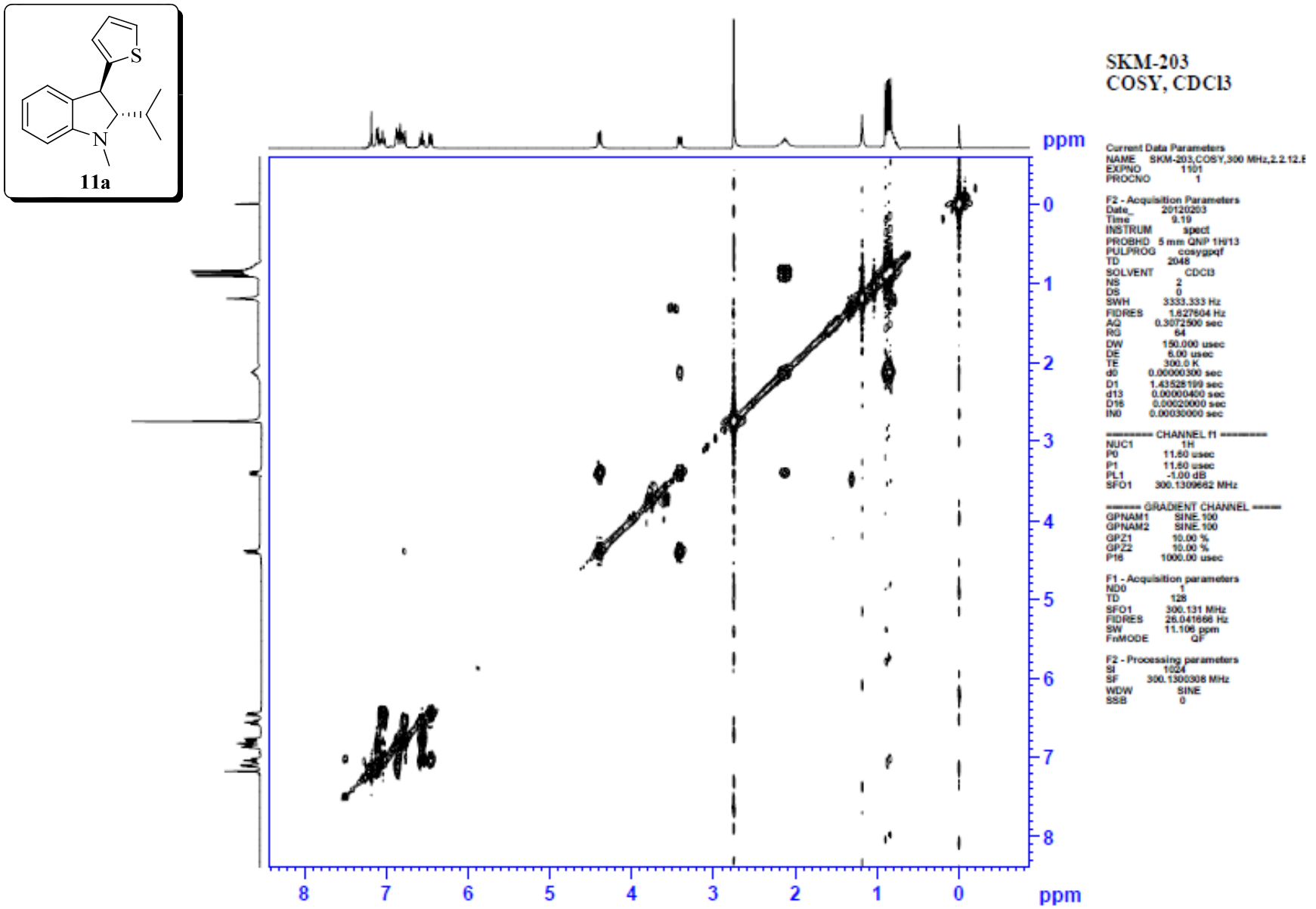


Figure 83: COSY -Spectrum of **11a.**

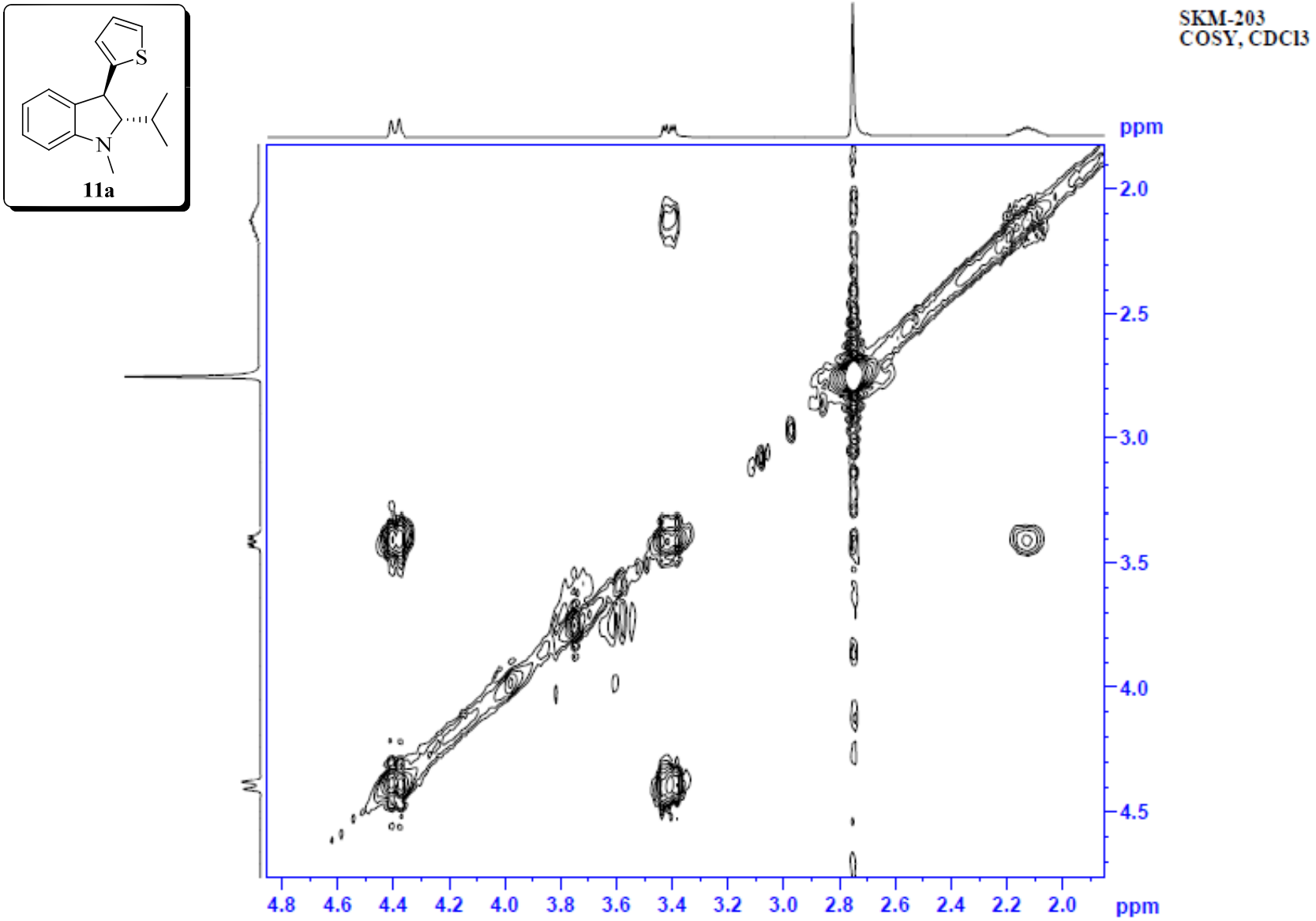


Figure 84: COSY -Spectrum of **11a.**

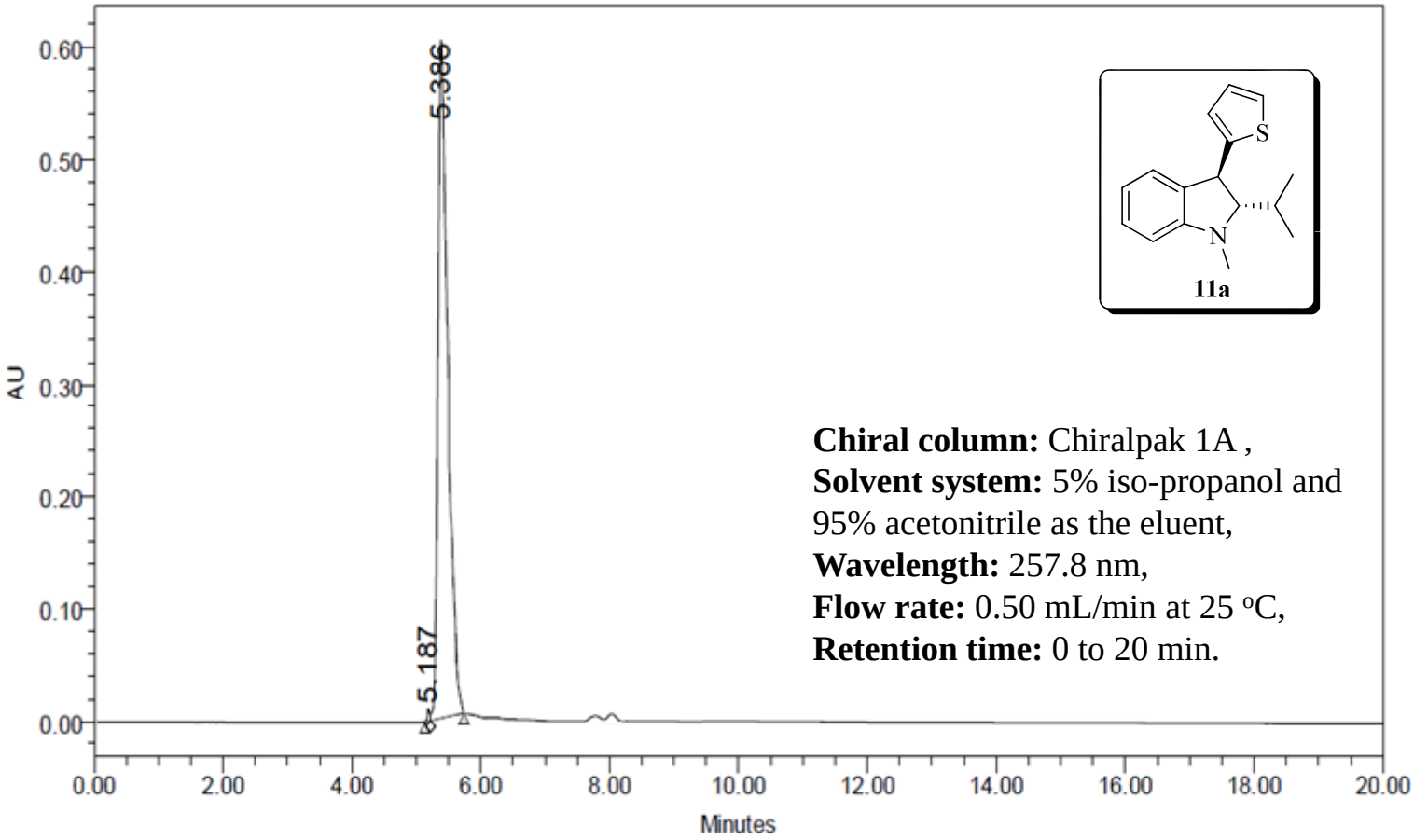


Figure 85: HPLC -Spectrum of **11a.**

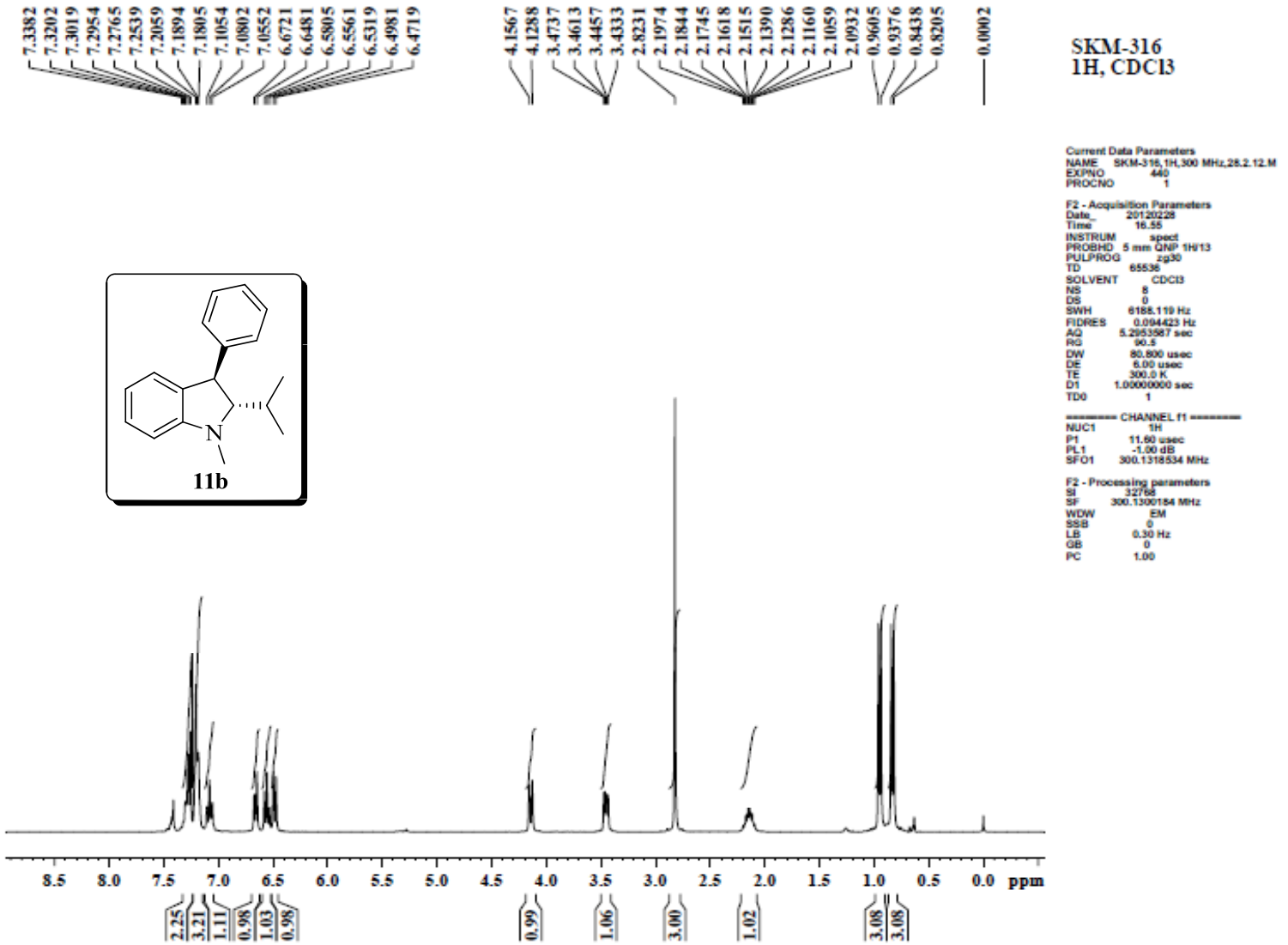


Figure 86: ^{1}H -NMR Spectrum of **11b.**

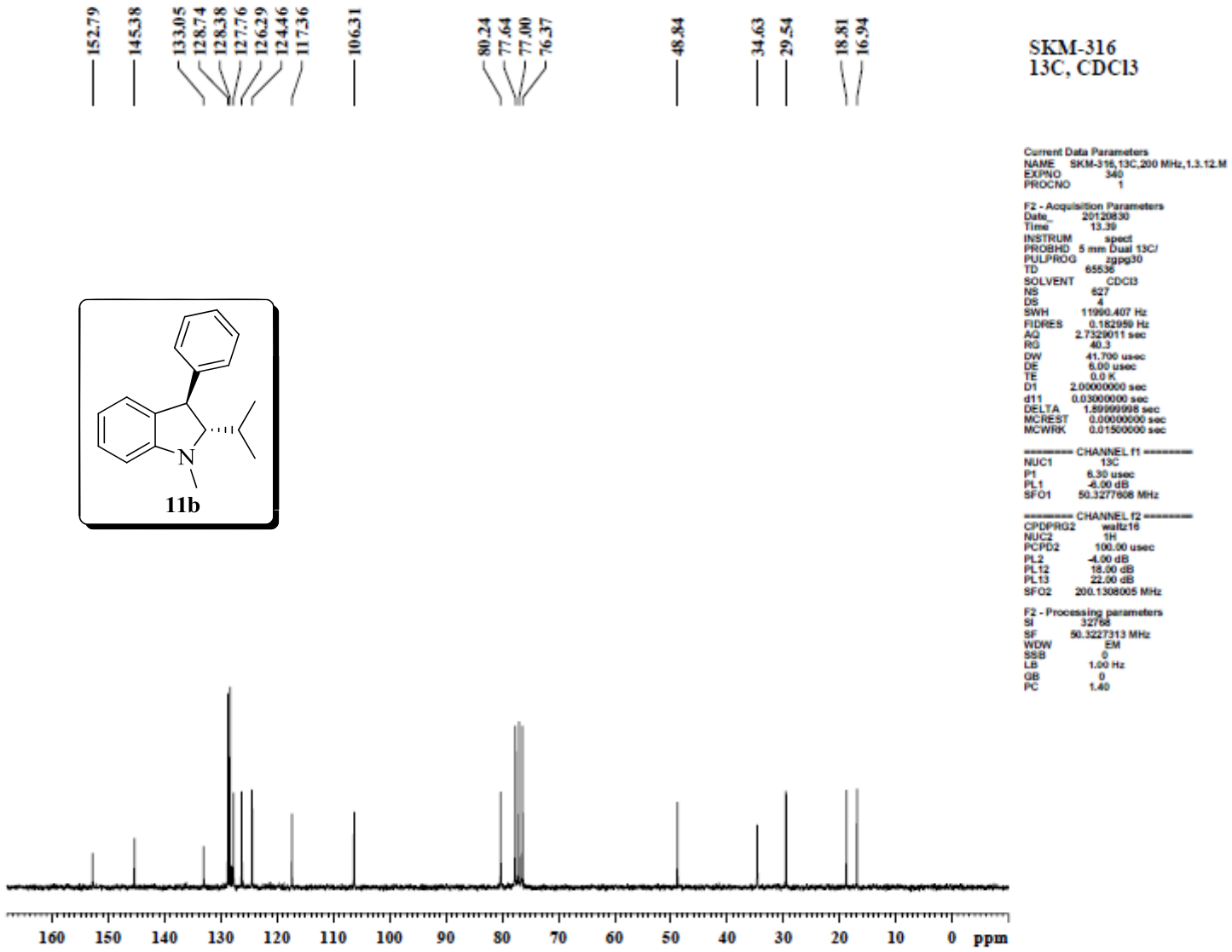


Figure 87: ^{13}C -NMR Spectrum of **11b.**

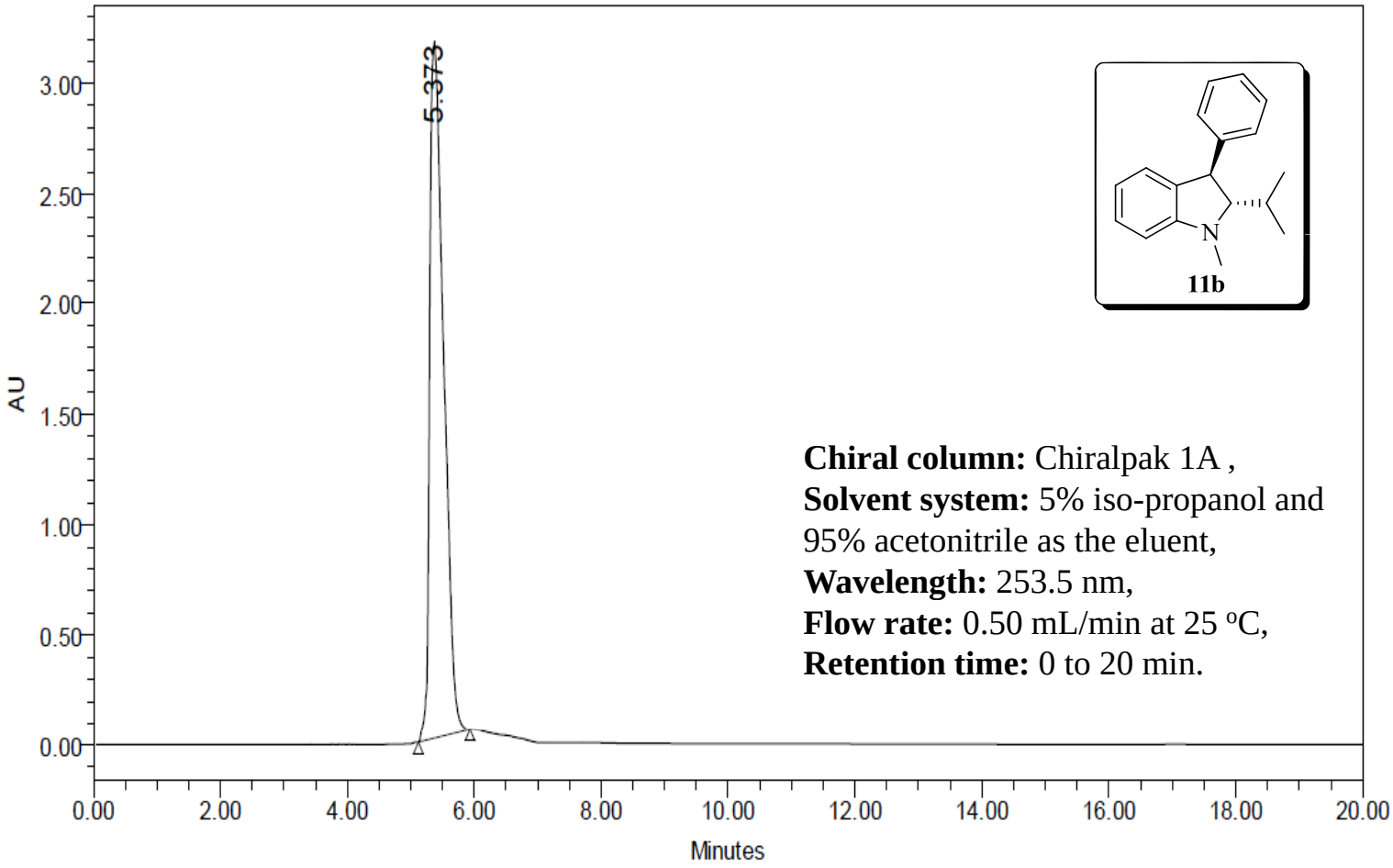


Figure 88: HPLC -Spectrum of **11b.**

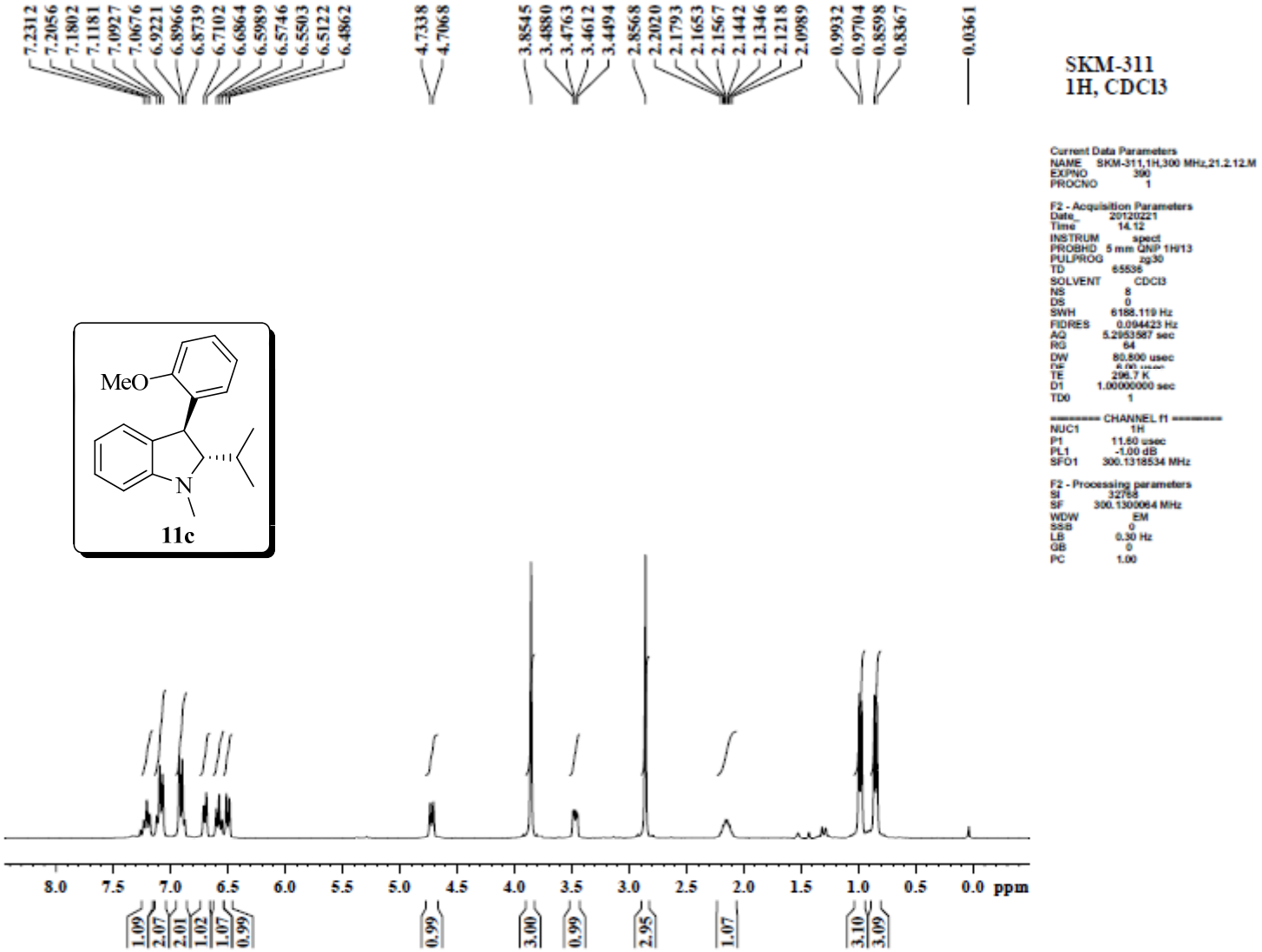


Figure 89: ^{1}H -NMR Spectrum of **11c.**

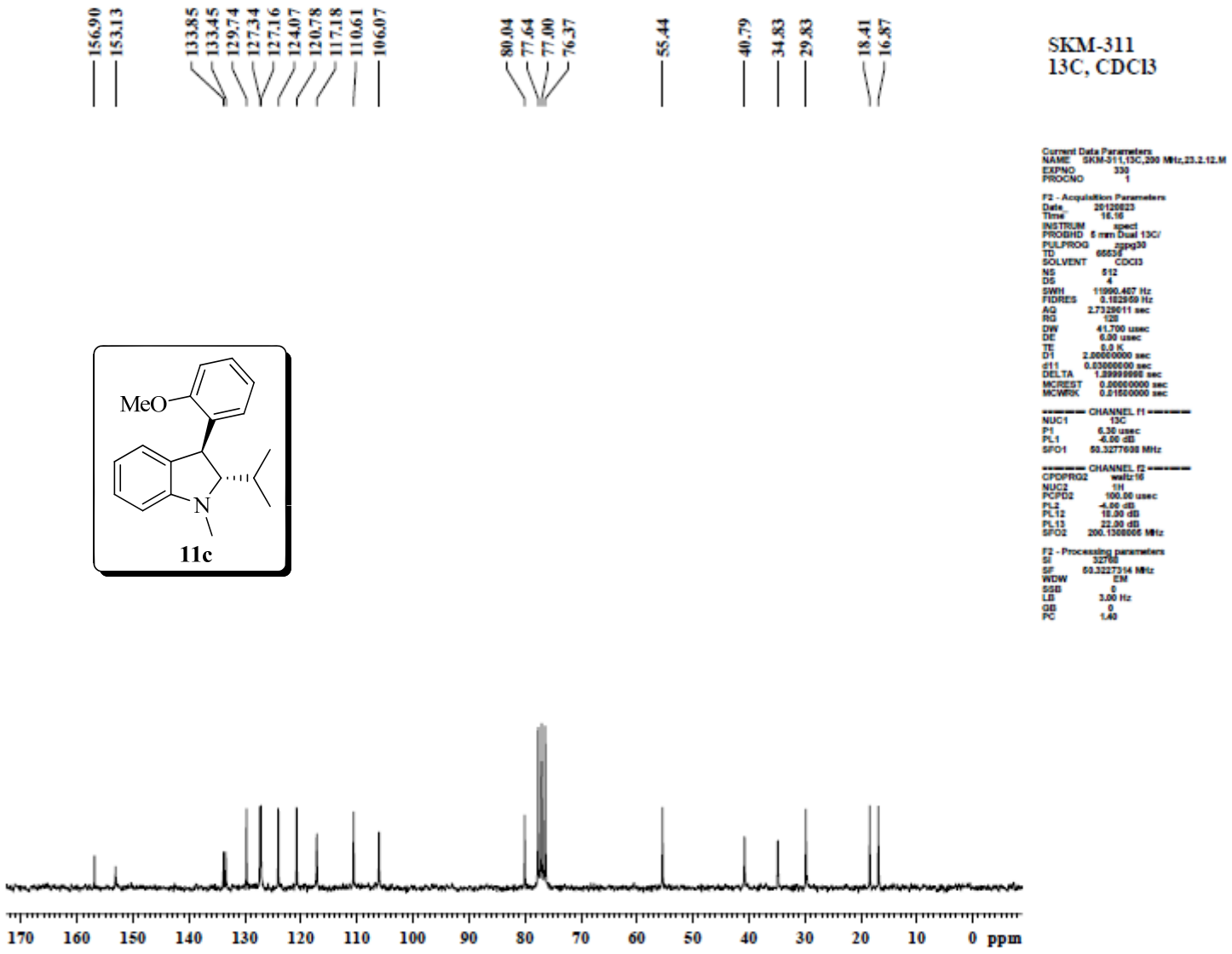


Figure 90: ^{13}C -NMR Spectrum of **11c.**

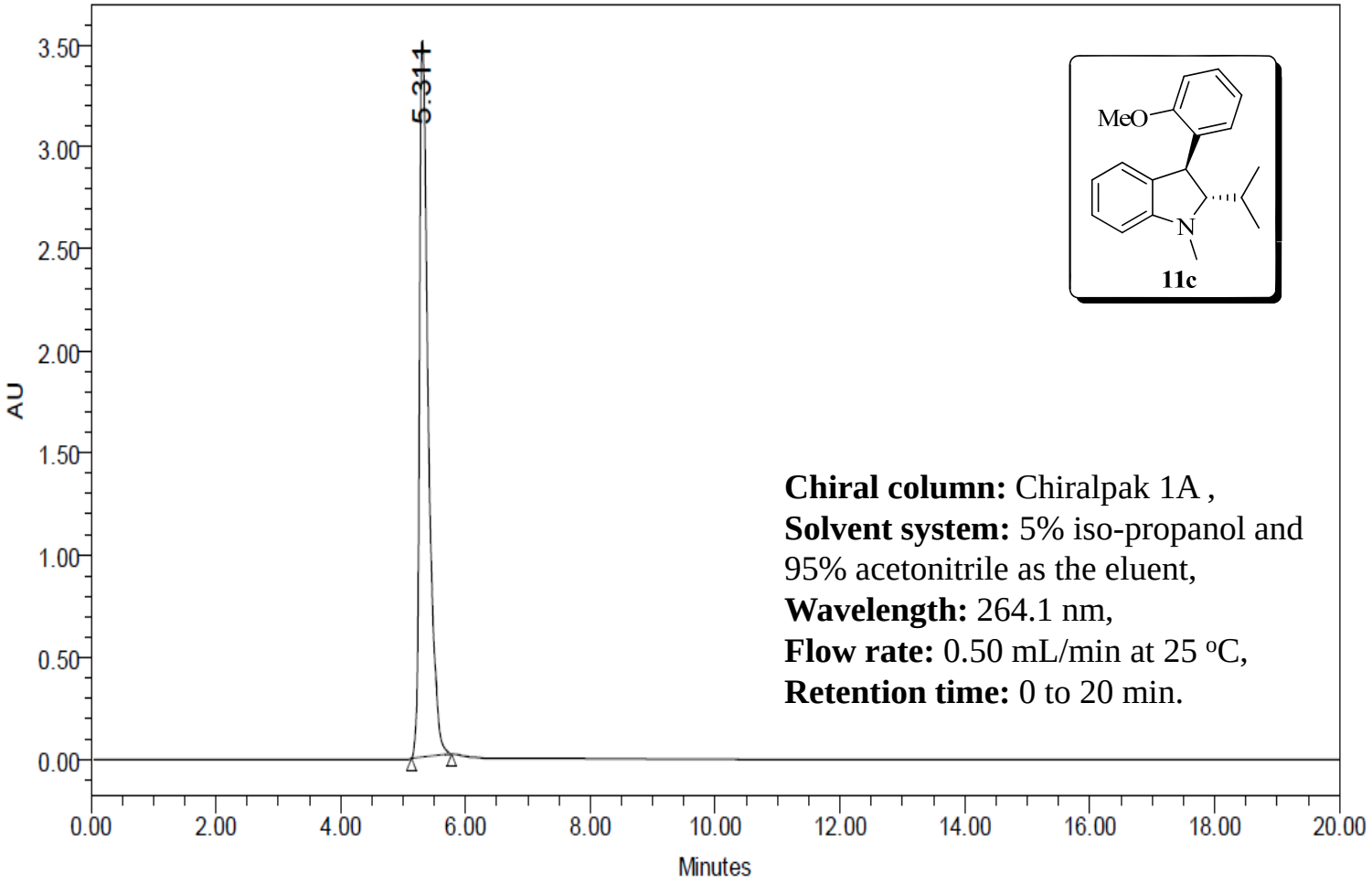


Figure 91: HPLC -Spectrum of **11c**

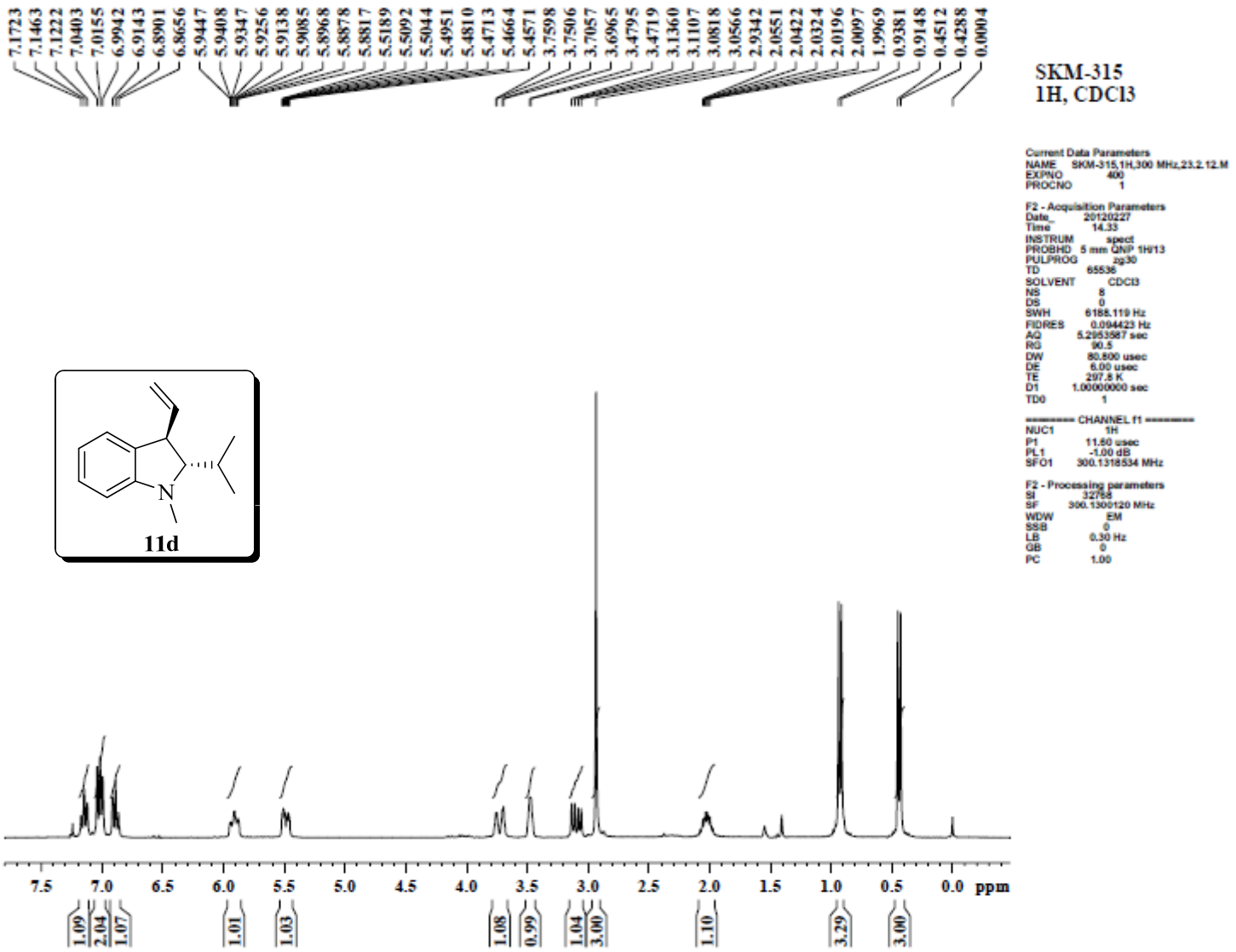


Figure 92: ^{1}H -NMR Spectrum of **11d.**

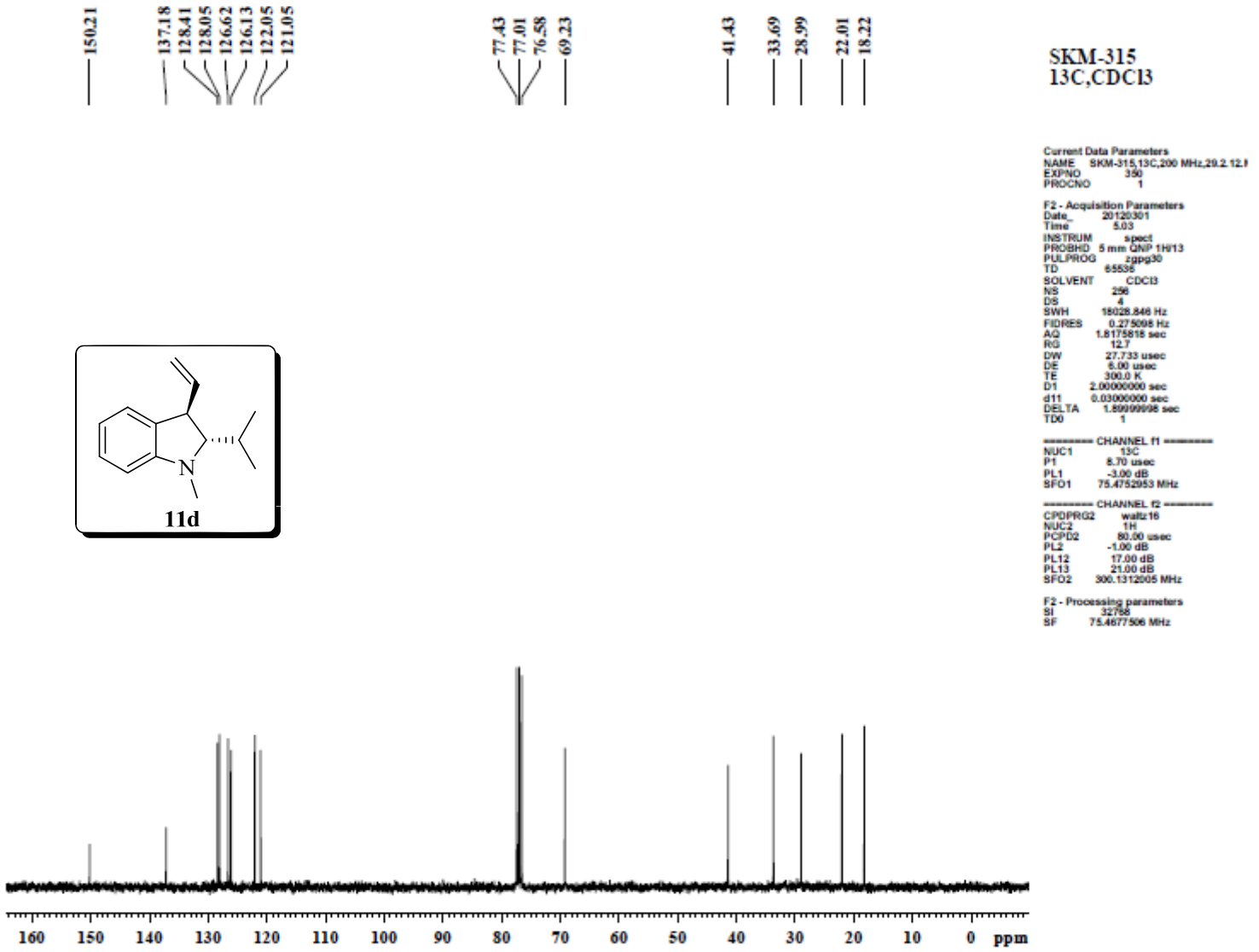


Figure 93: ^{13}C -NMR Spectrum of **11d.**

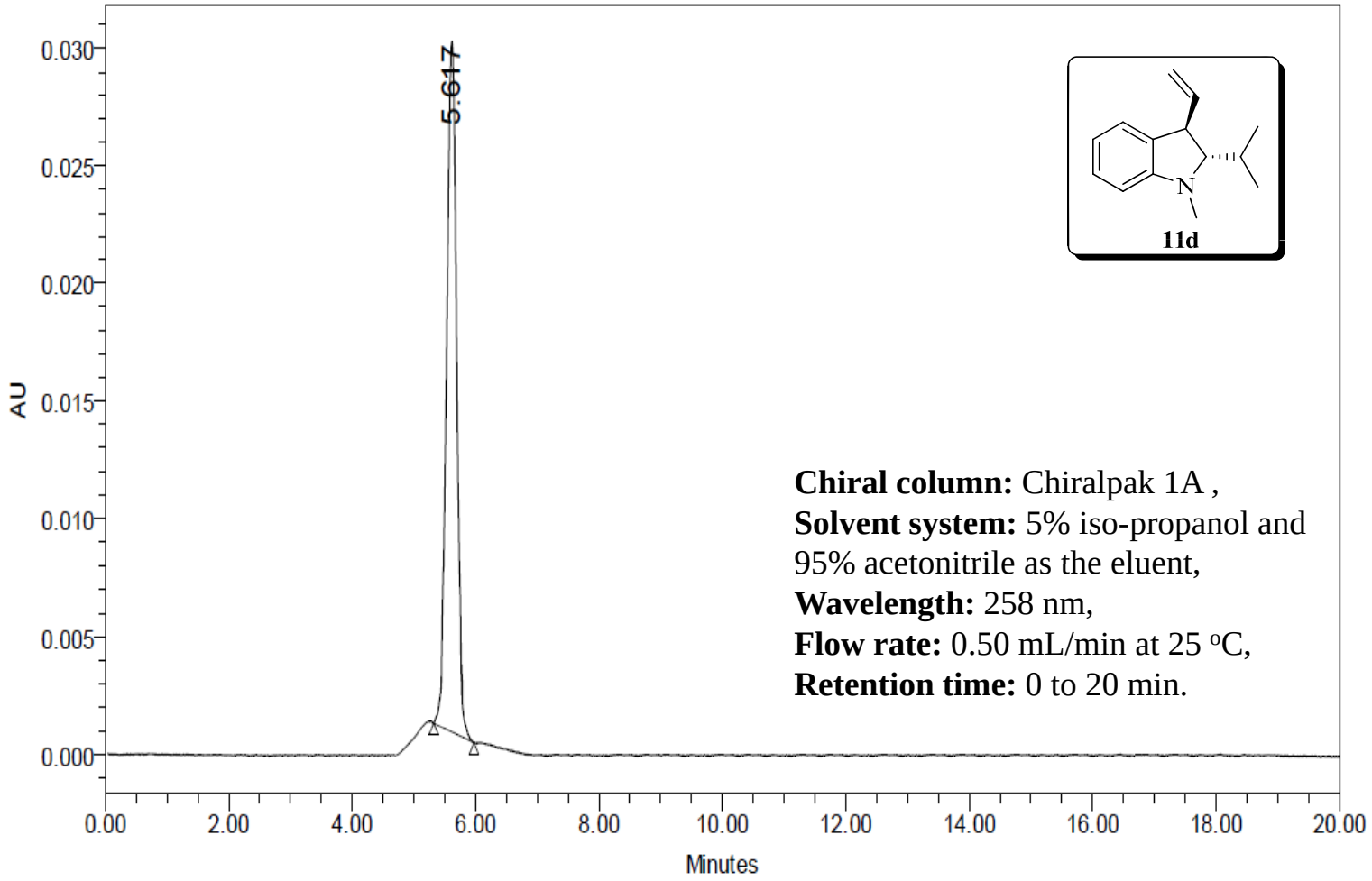


Figure 94: HPLC -Spectrum of **11d.**

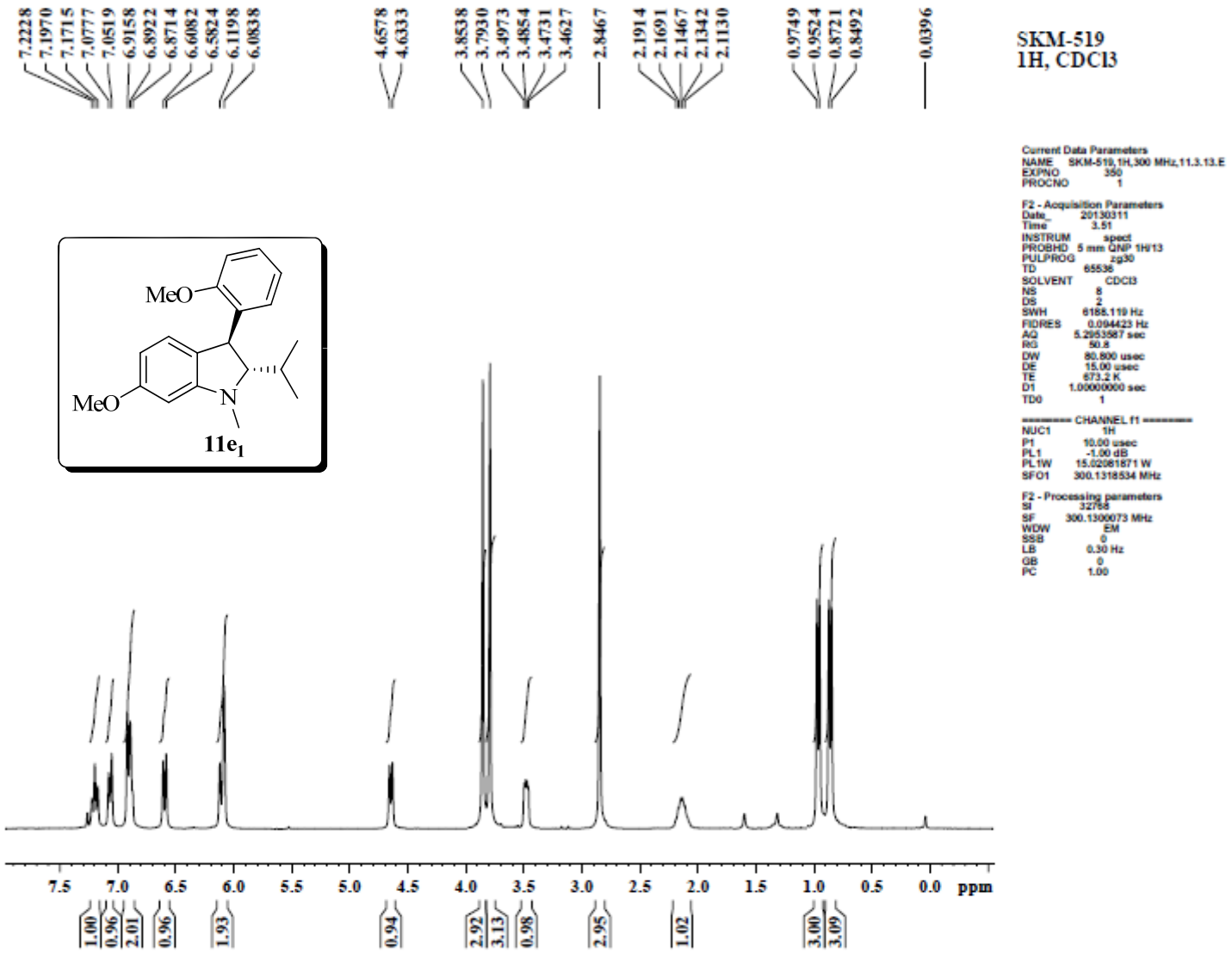


Figure 95: ^{1}H -NMR Spectrum of **$11e_1$.**

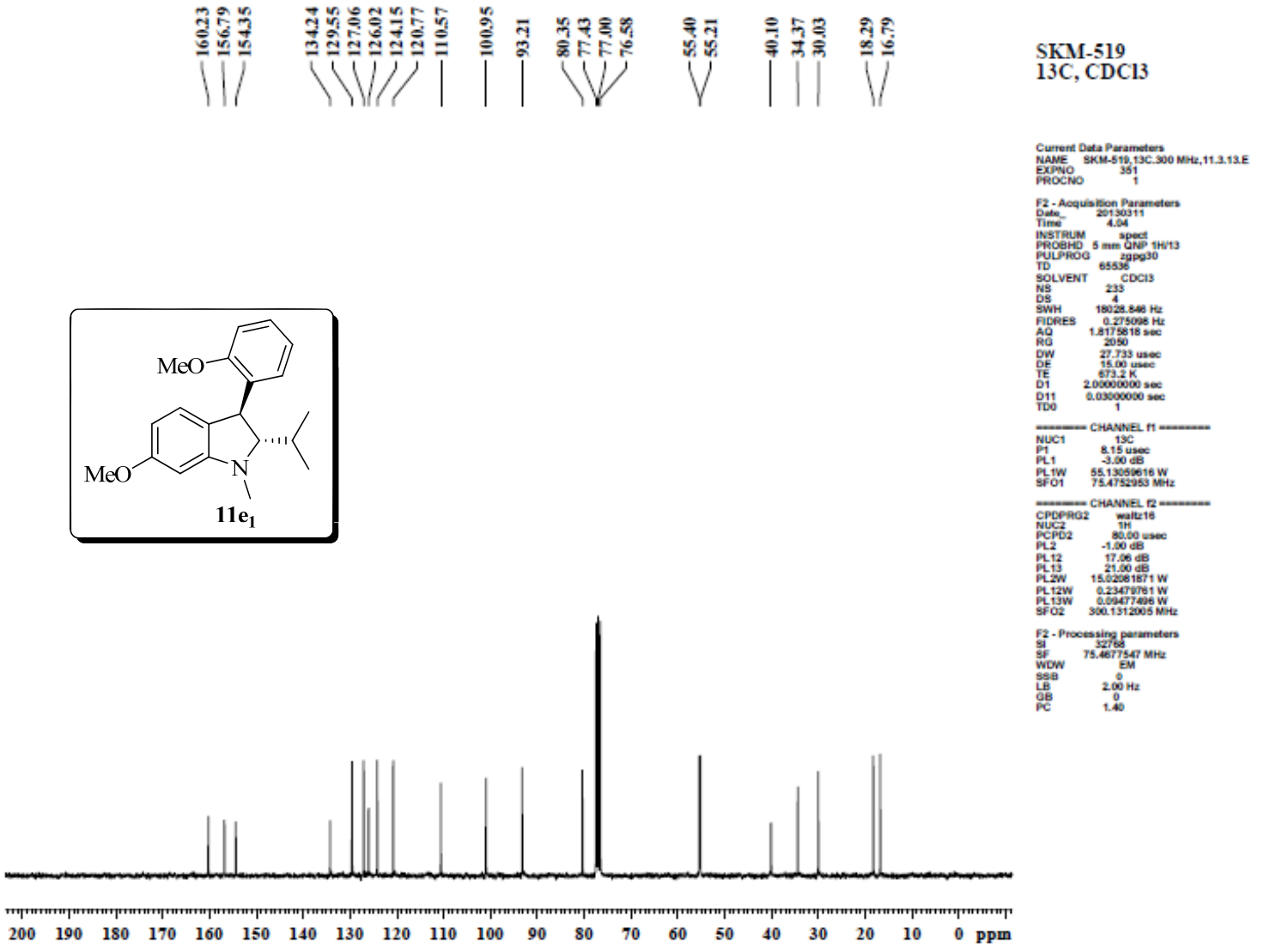


Figure 96: ^{13}C -NMR Spectrum of **11e$_1$.**

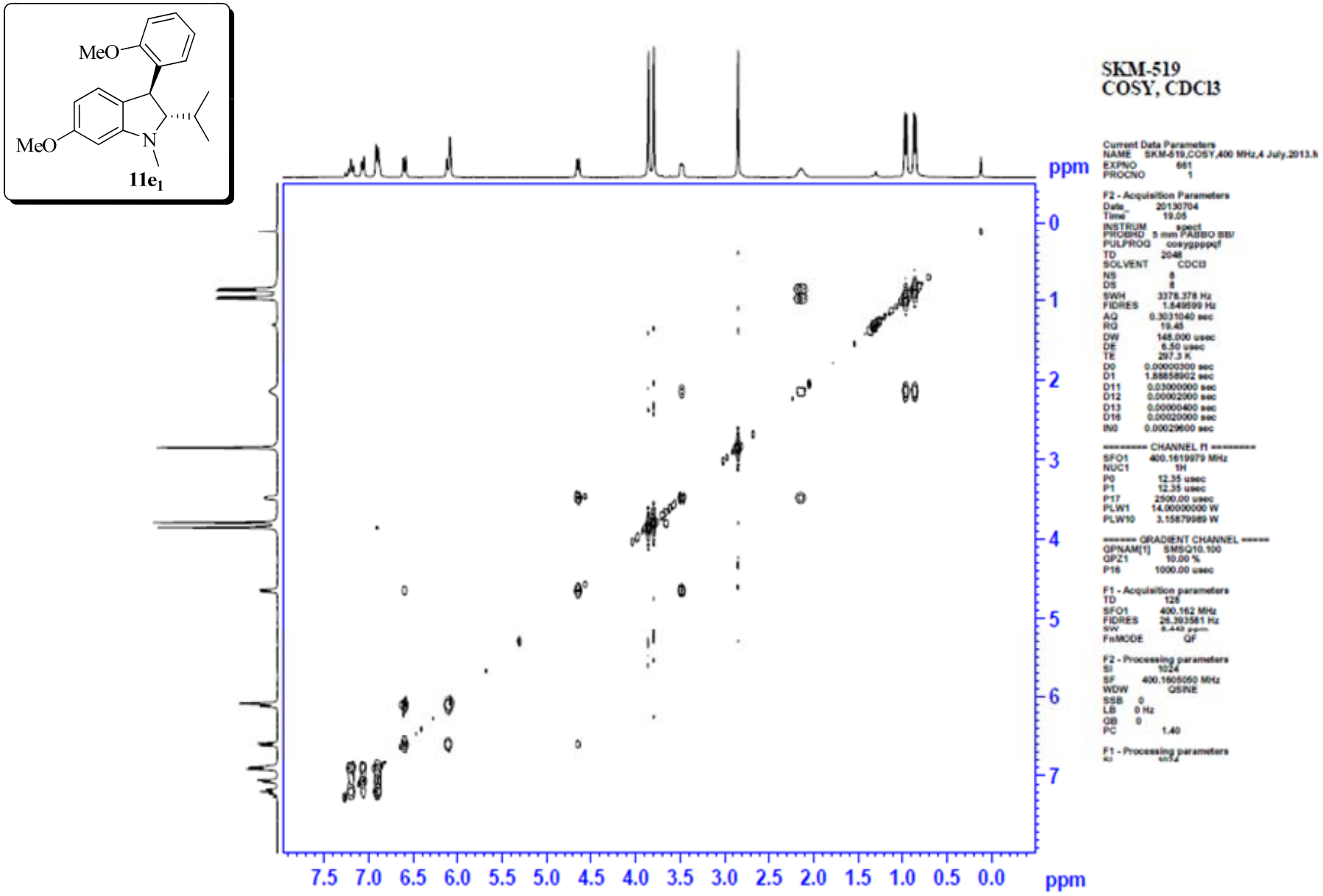


Figure 97: COSY -Spectrum of **$11e_1$.**

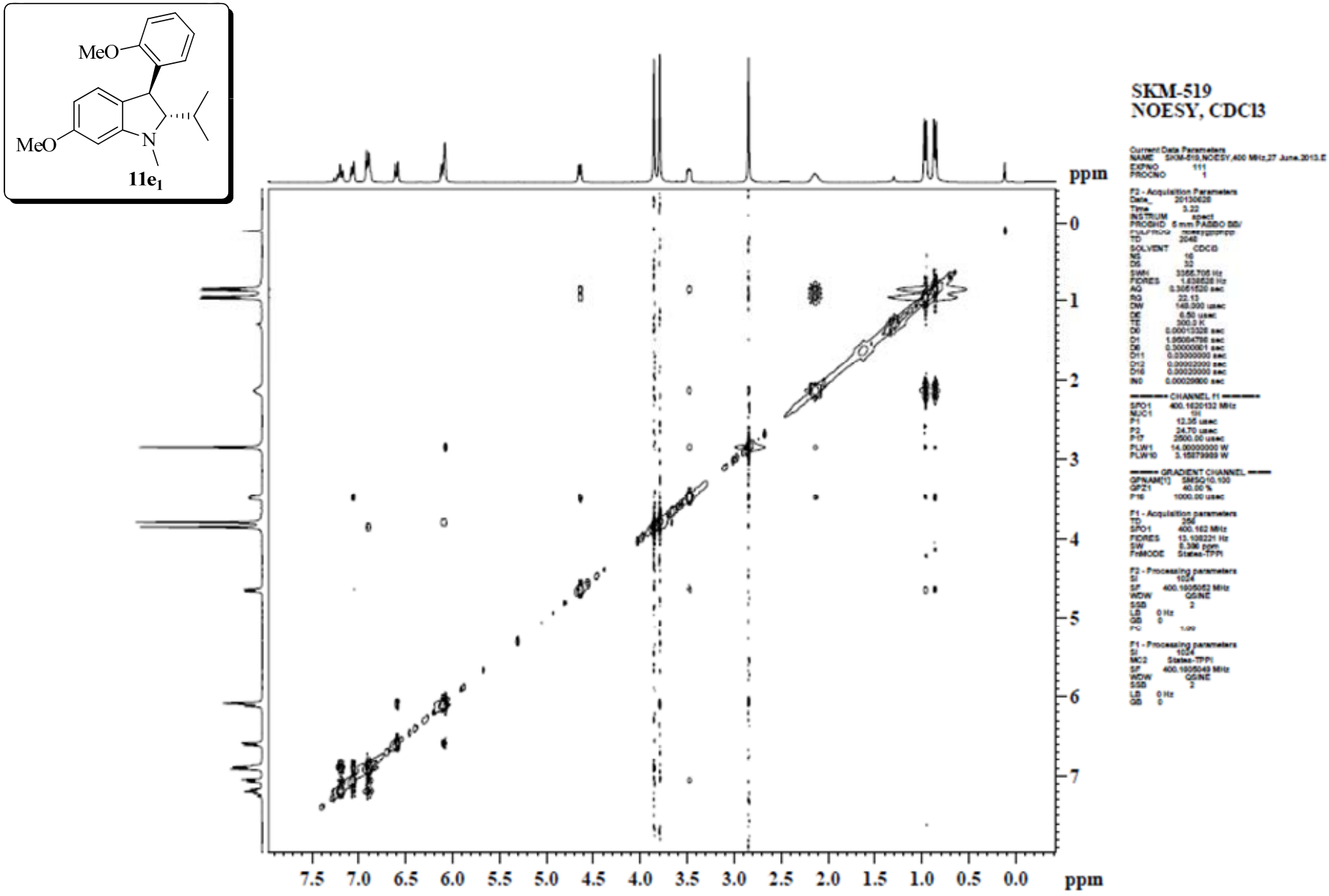


Figure 98: NOESY -Spectrum of **$11e_1$.**

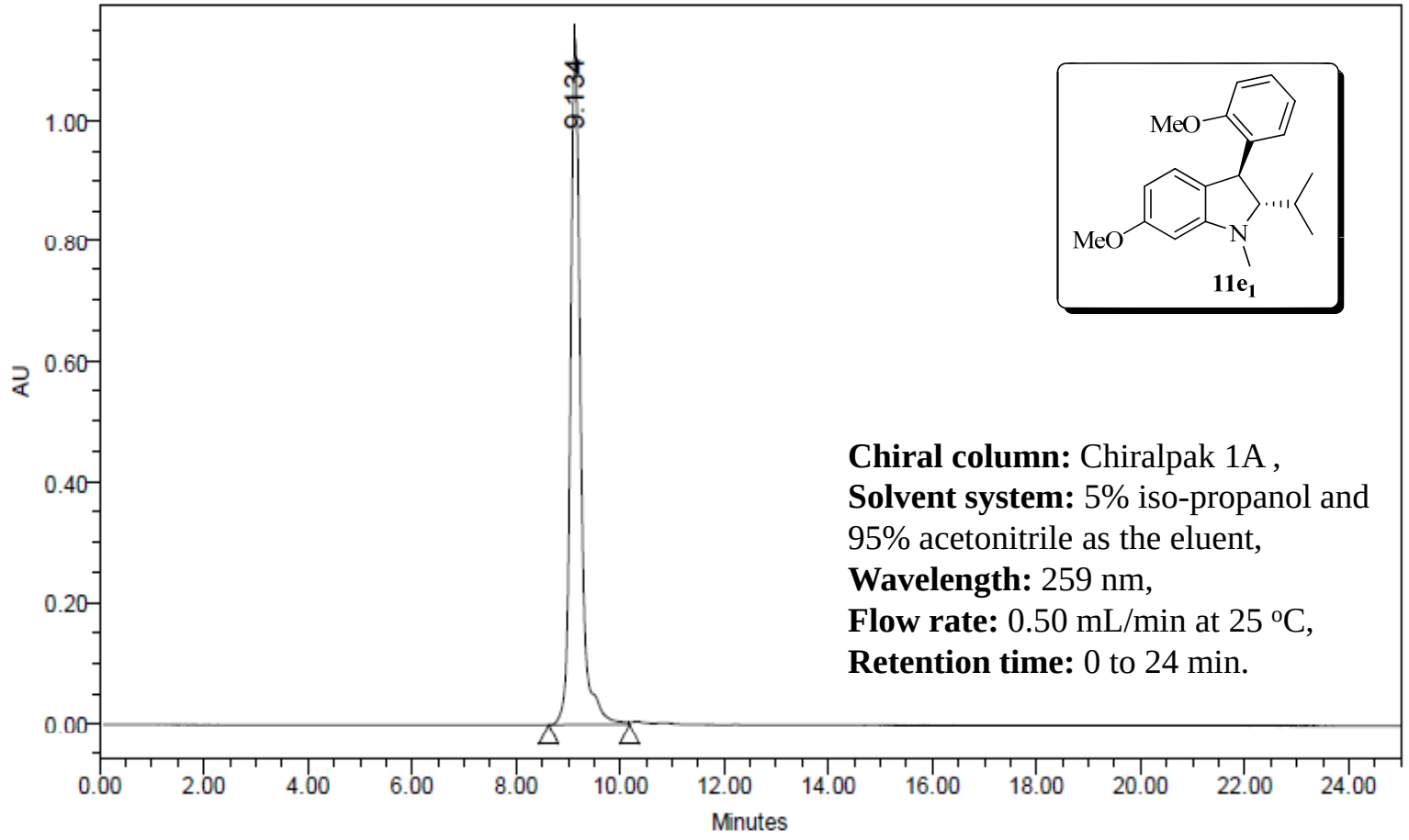


Figure 99: HPLC -Spectrum of **$11e_1$.**

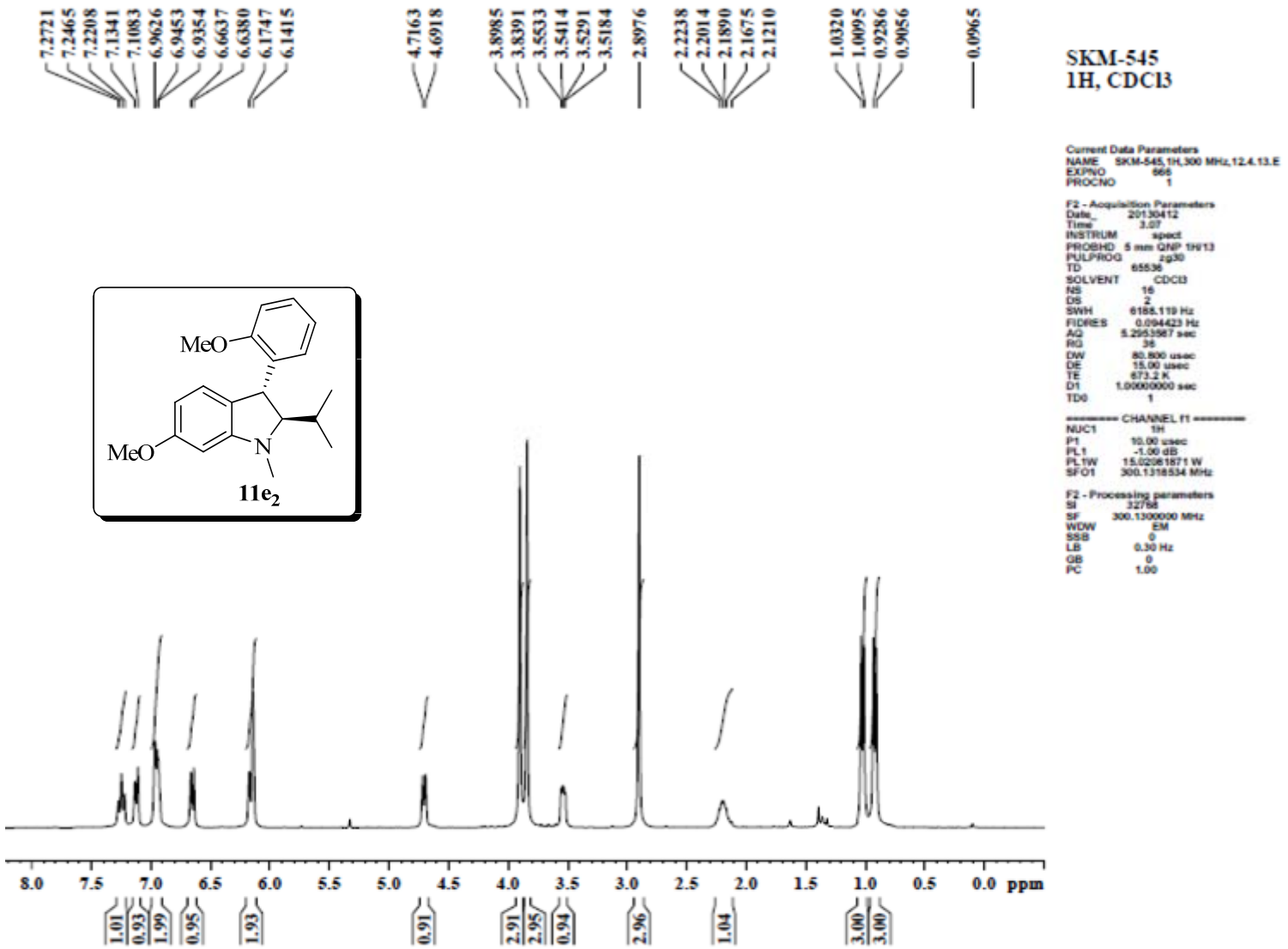


Figure 100: ^{1}H -NMR Spectrum of **11e$_2$.**

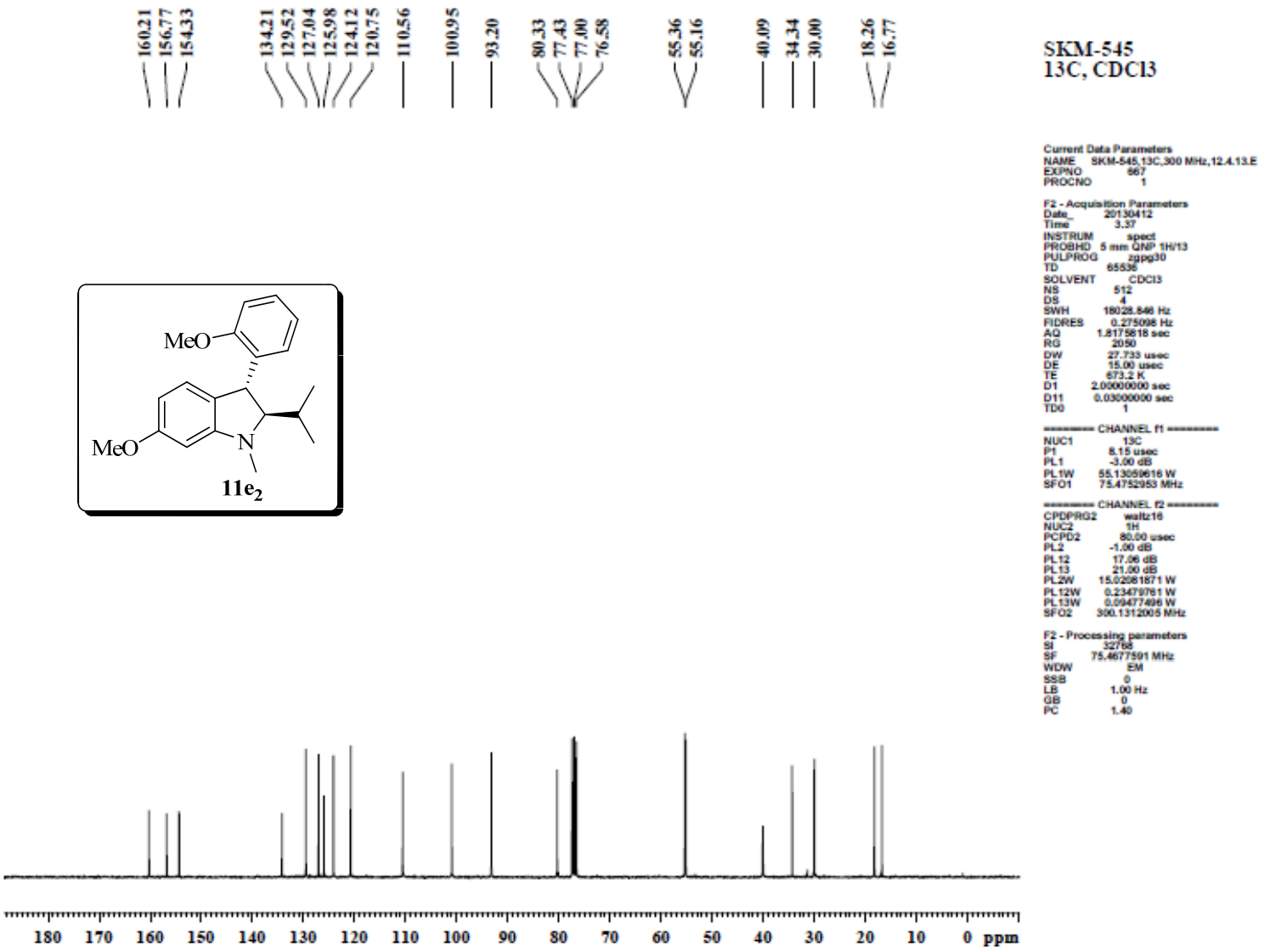


Figure 101: ^{13}C -NMR Spectrum of **11e$_2$.**

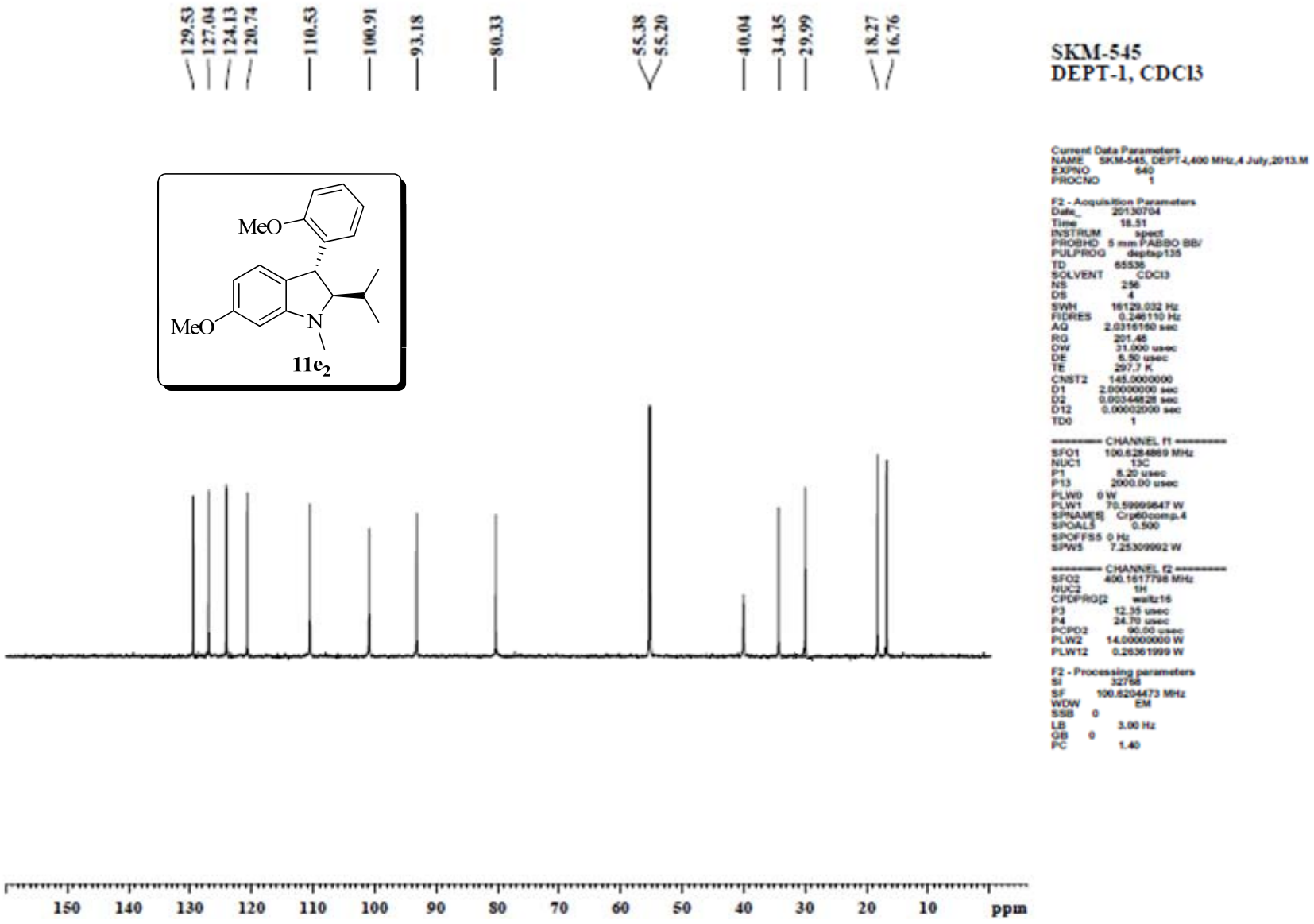


Figure 102: DEPT-I -Spectrum of **$11e_2$.**

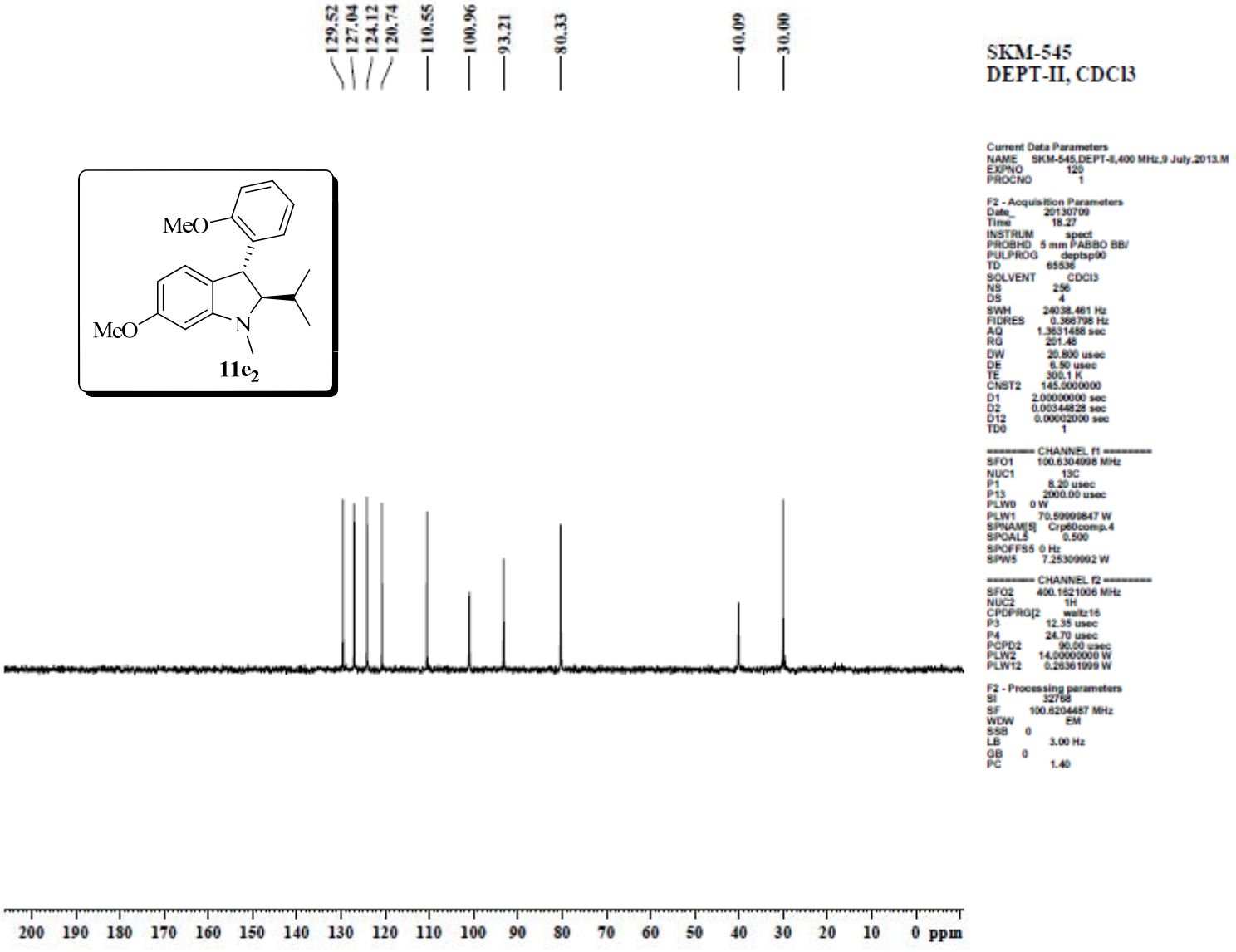


Figure 103: DEPT-II -Spectrum of **$11e_2$.**

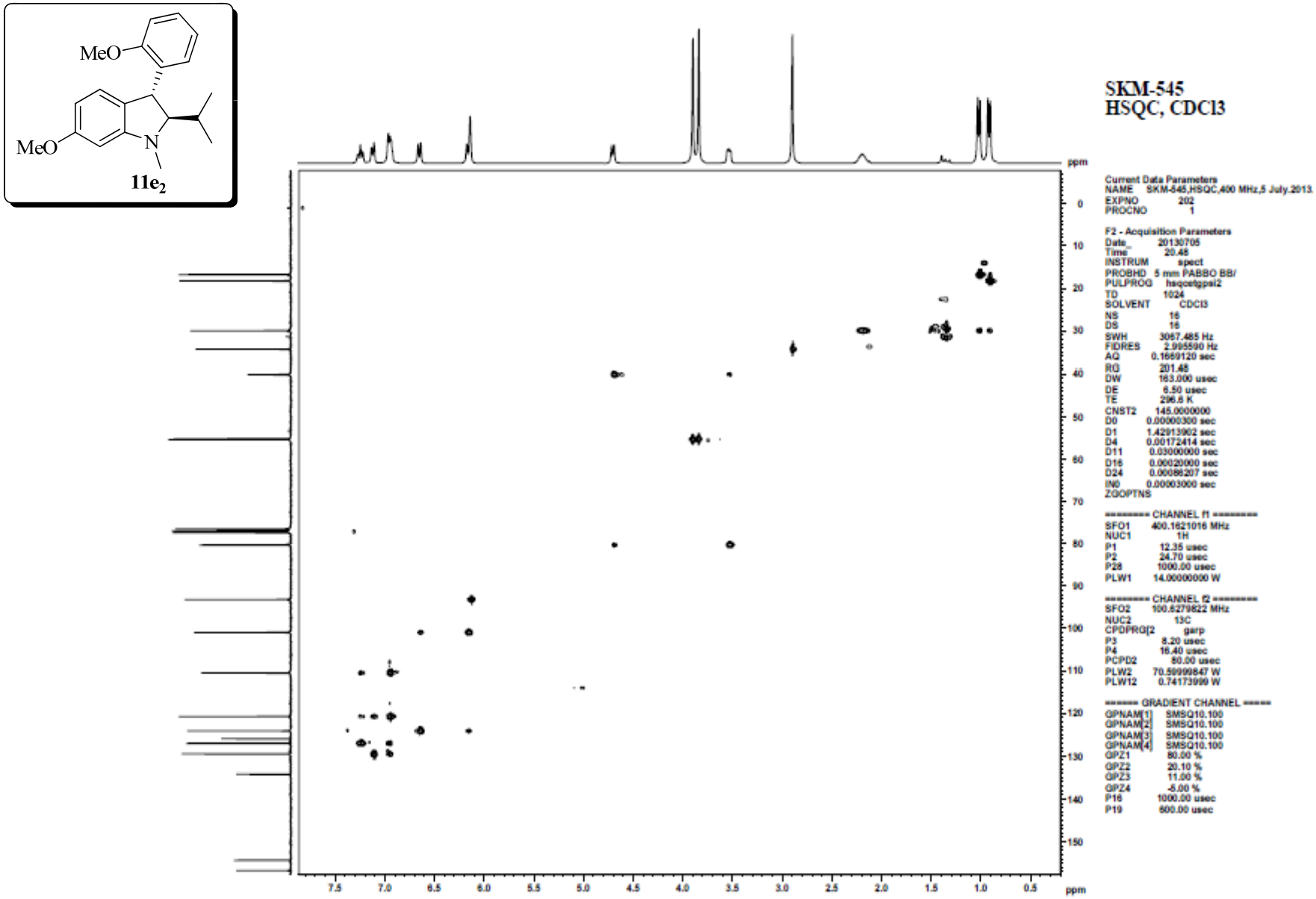


Figure 104: HSQC -Spectrum of **$11e_2$.**

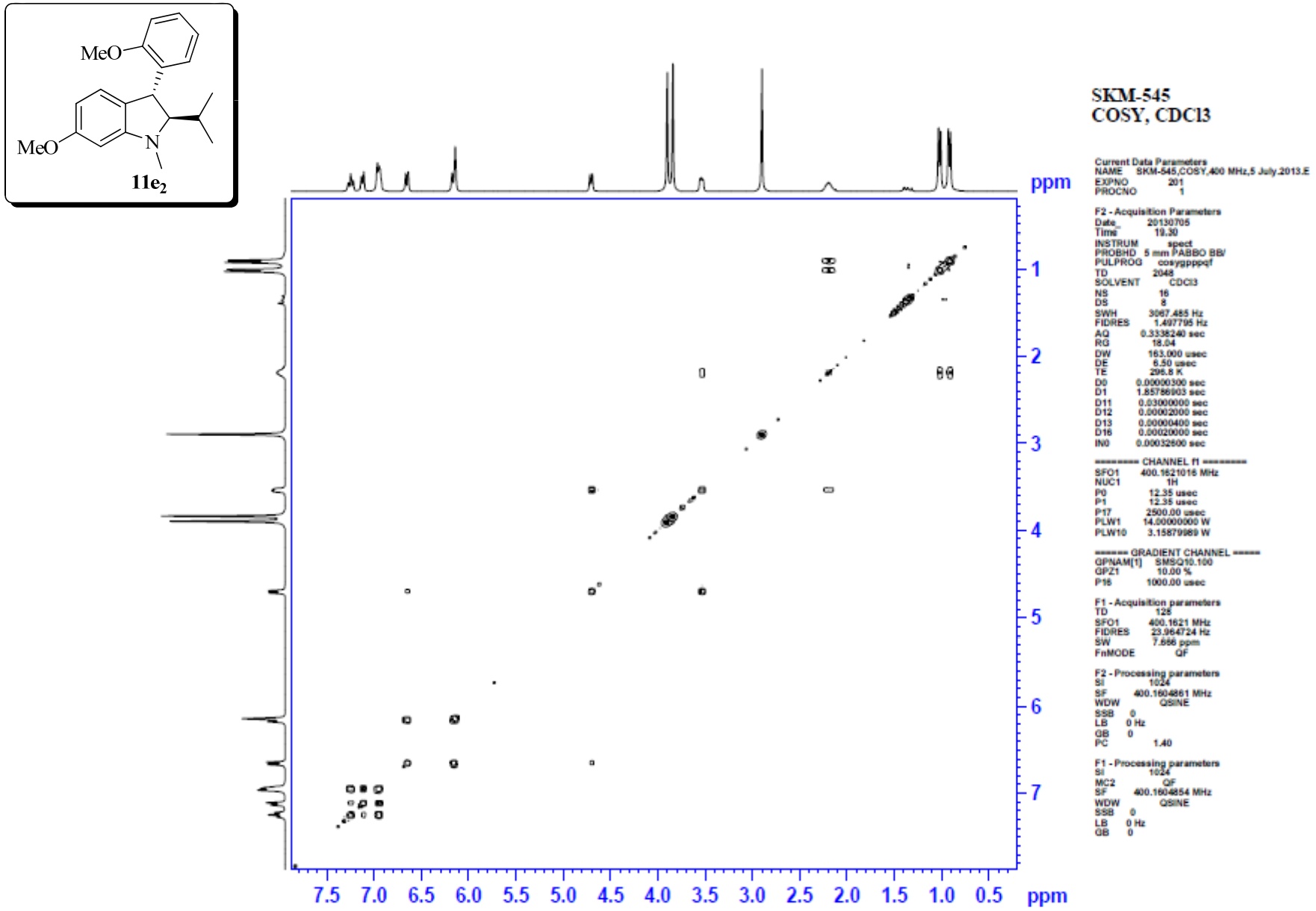


Figure 105: COSY -Spectrum of **$11e_2$.**

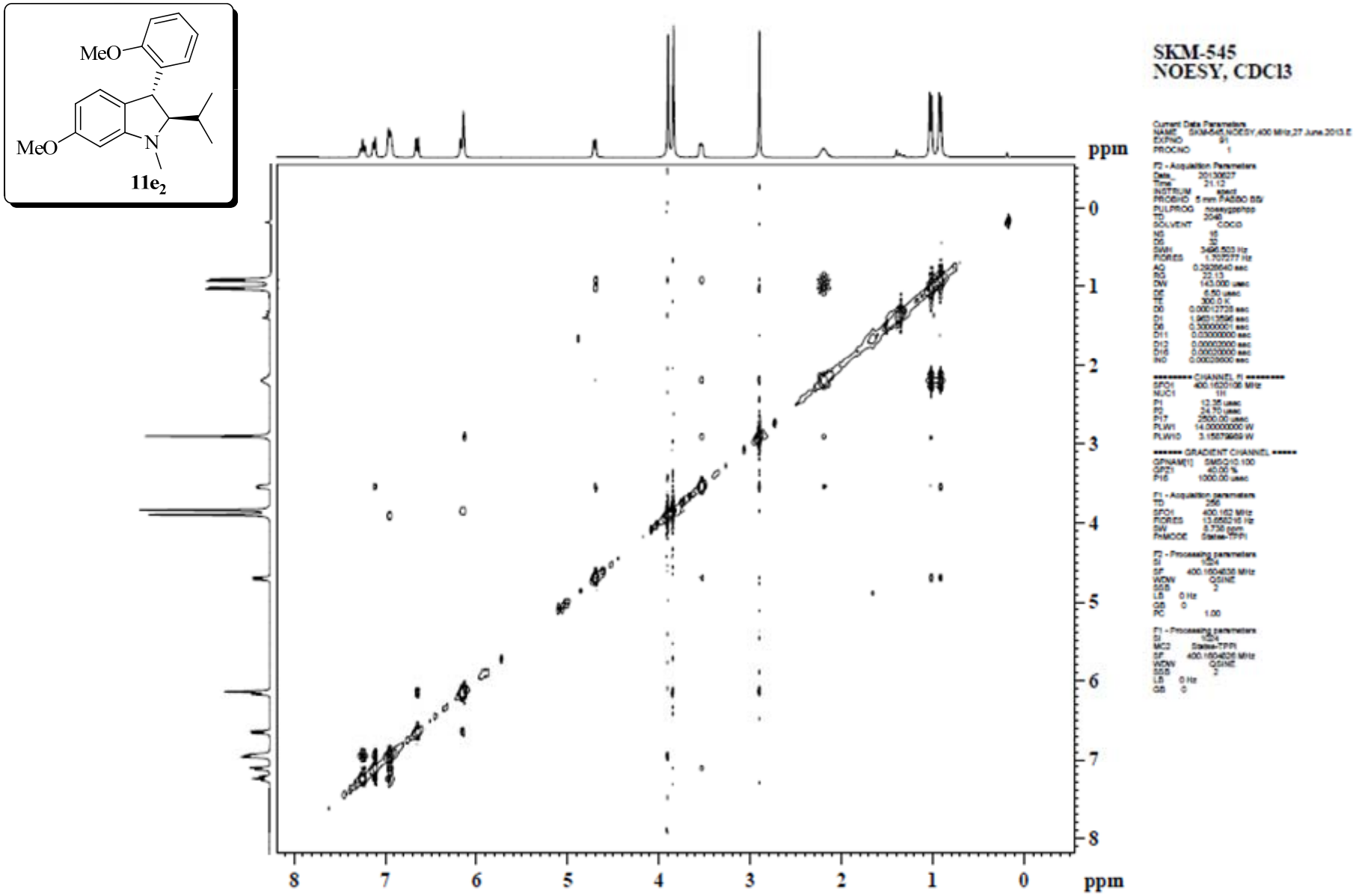


Figure 106: NOESY -Spectrum of **$11e_2$.**

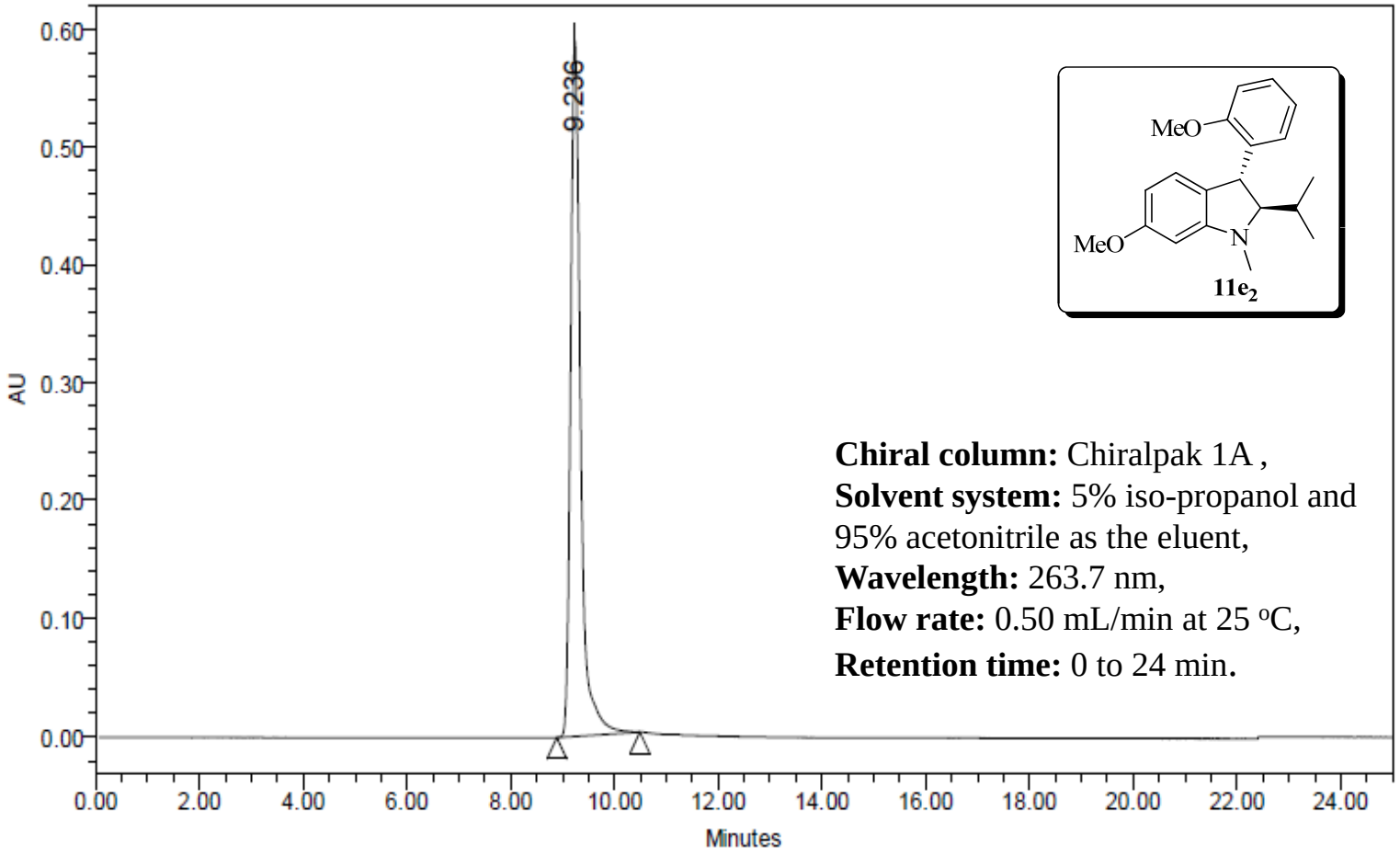


Figure 107: HPLC -Spectrum of **$11e_2$.**

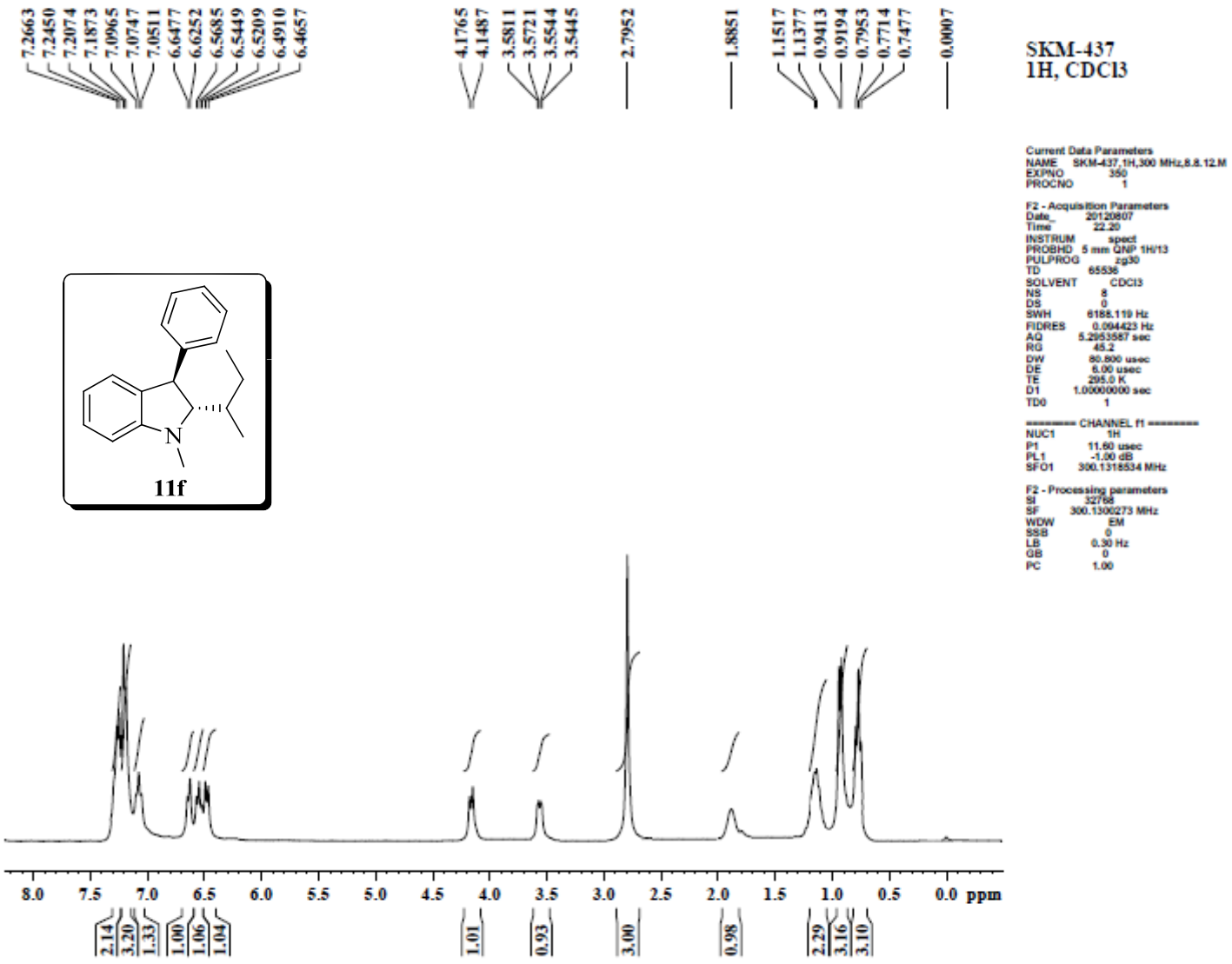


Figure 108: ^{1}H -NMR Spectrum of **11f.**

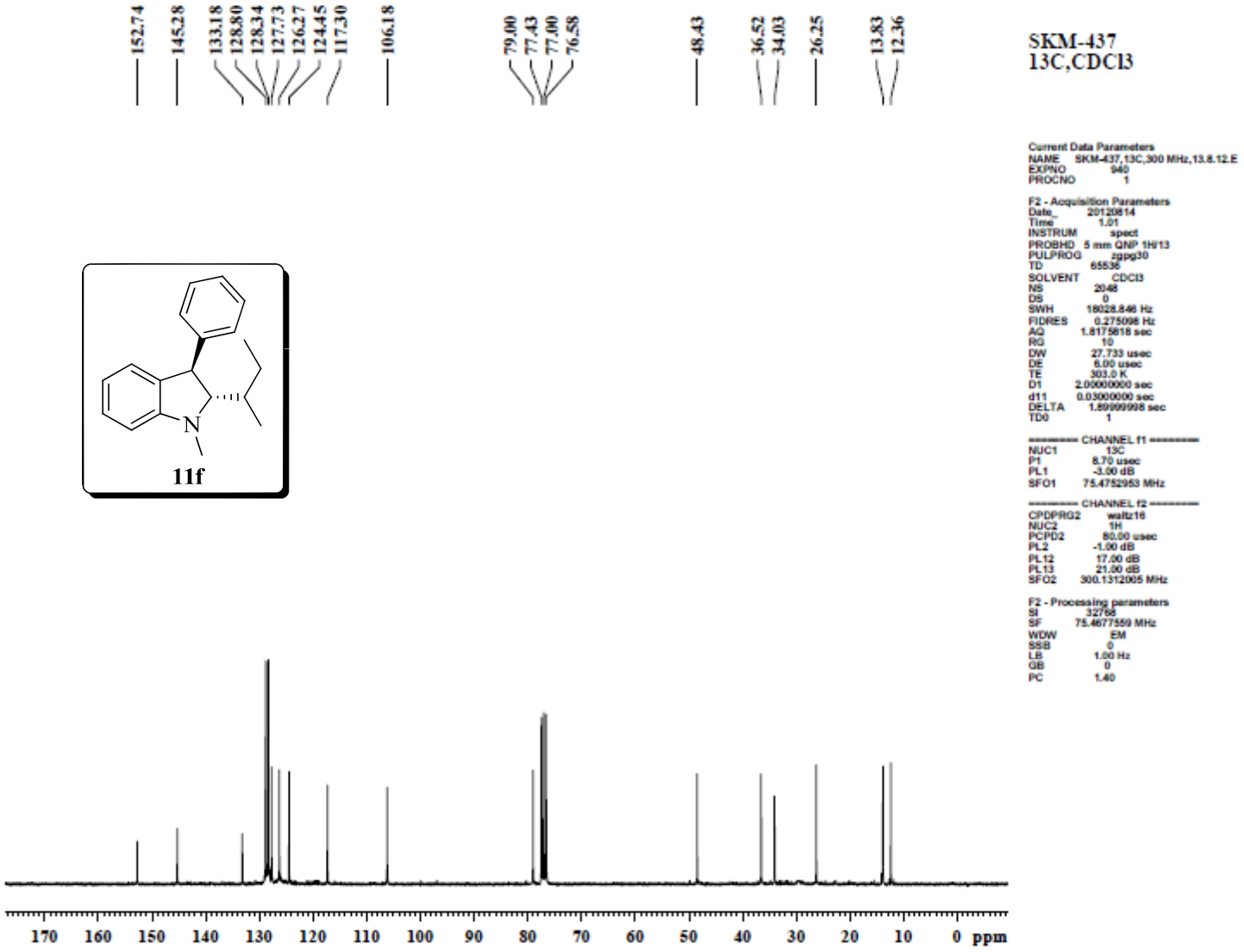


Figure 109: ^{13}C -NMR Spectrum of **11f.**

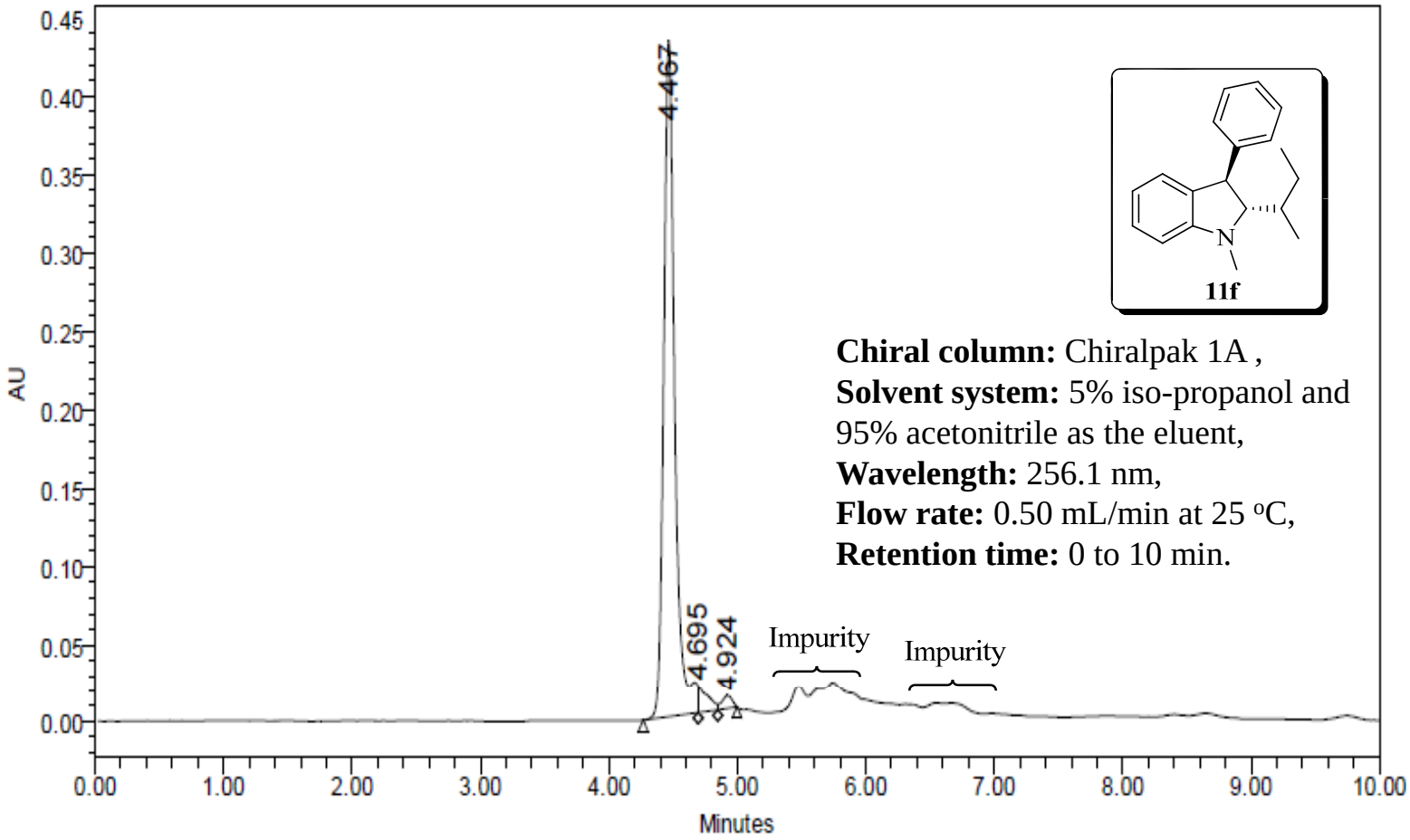


Figure 110: HPLC -Spectrum of **11f.**

Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **11f.**

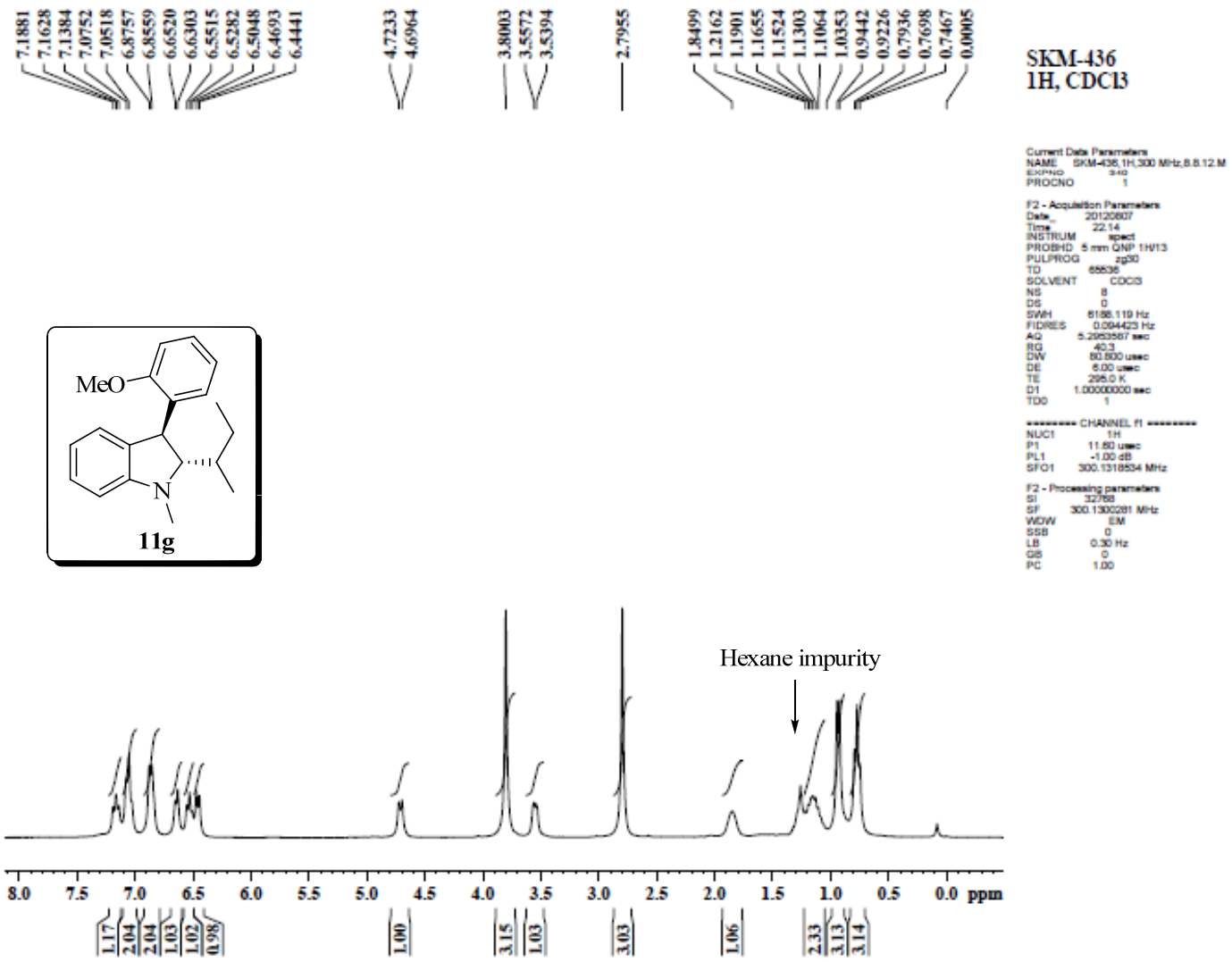


Figure 111: ^{1}H -NMR Spectrum of **11g.**

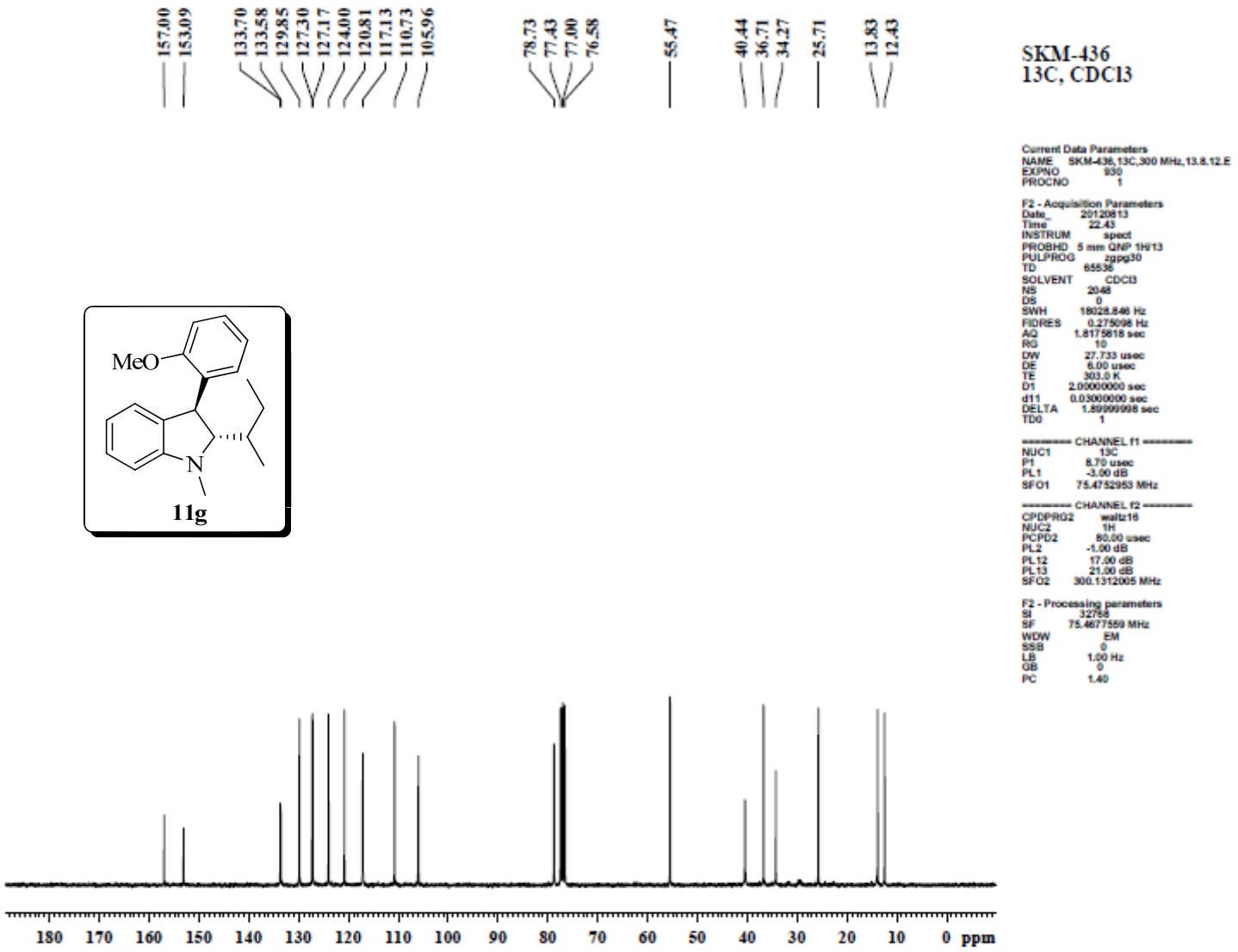


Figure 112: ^{13}C -NMR Spectrum of **11g.**

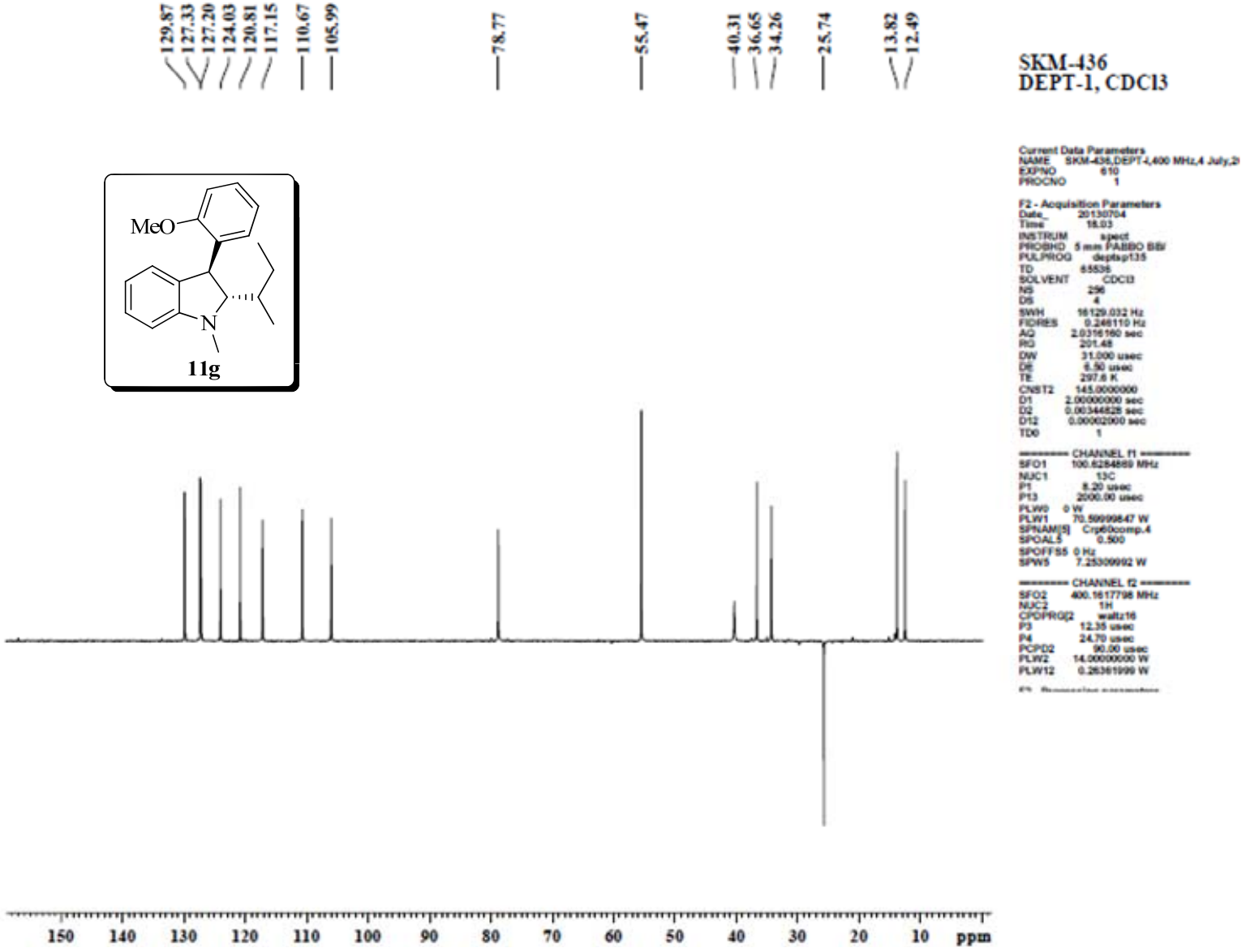


Figure 113: DEPT-I -Spectrum of **11g.**

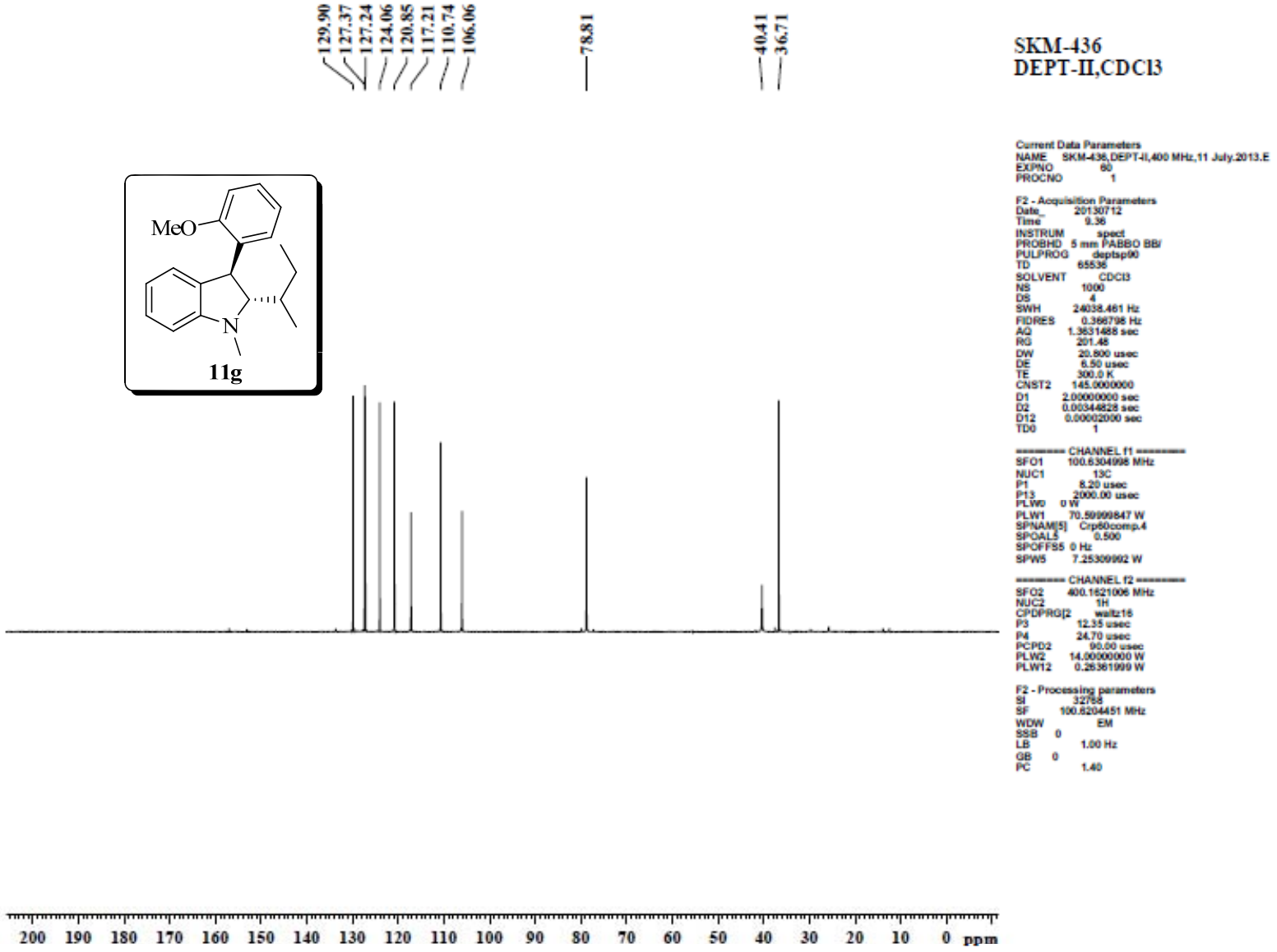


Figure 114: DEPT-II -Spectrum of **11g.**

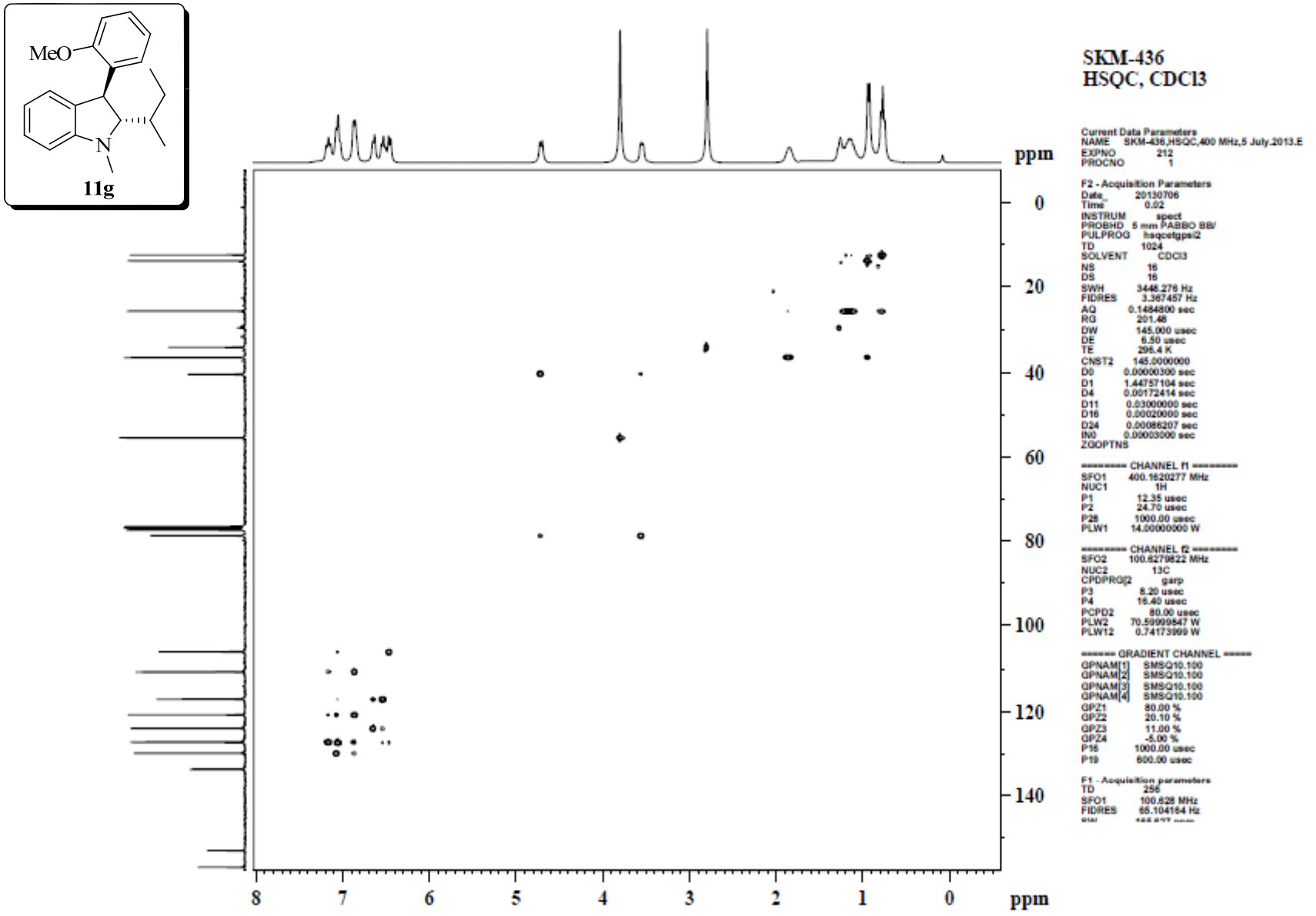


Figure 115: HSQC -Spectrum of **11g.**

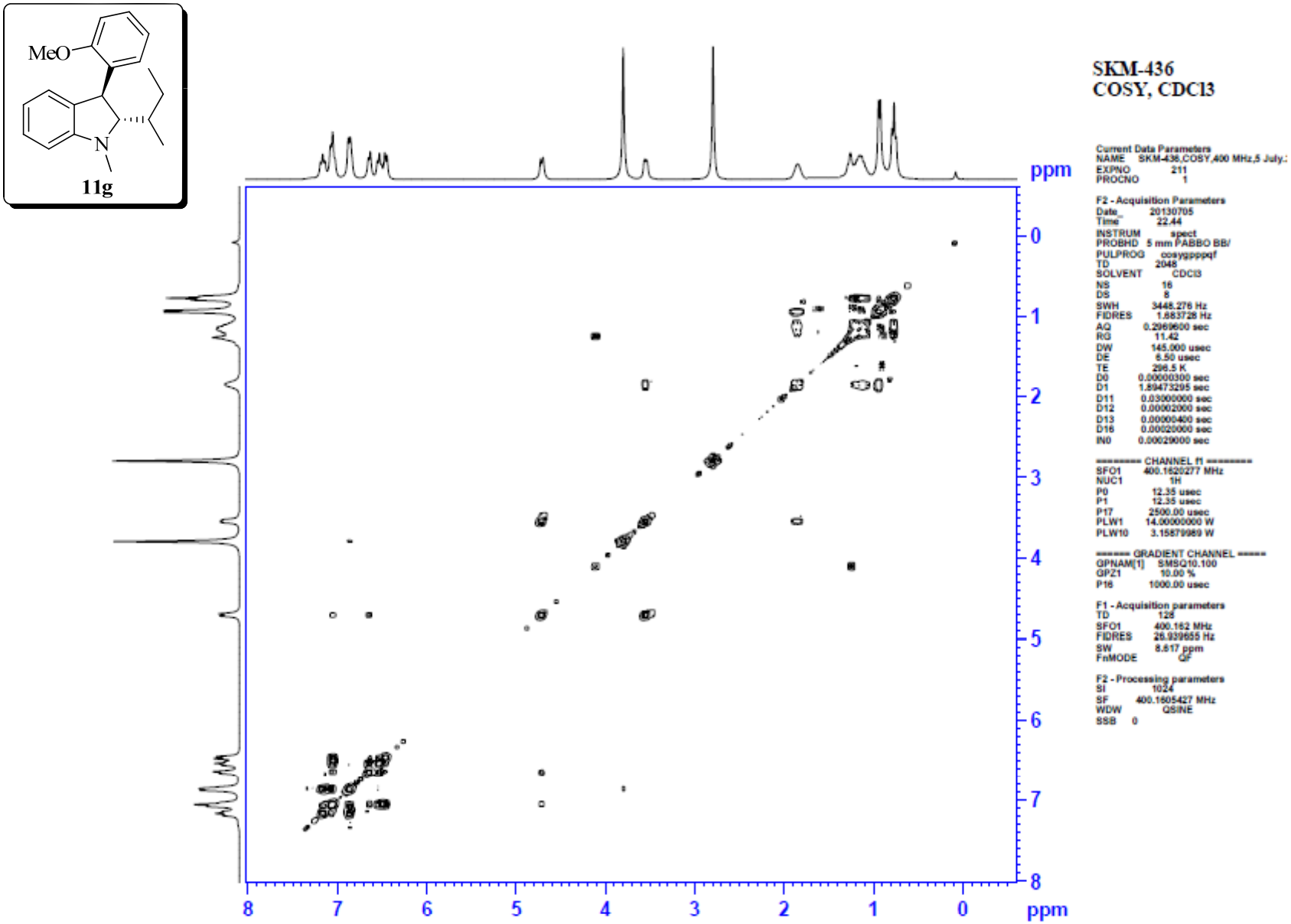


Figure 116: COSY -Spectrum of **11g.**

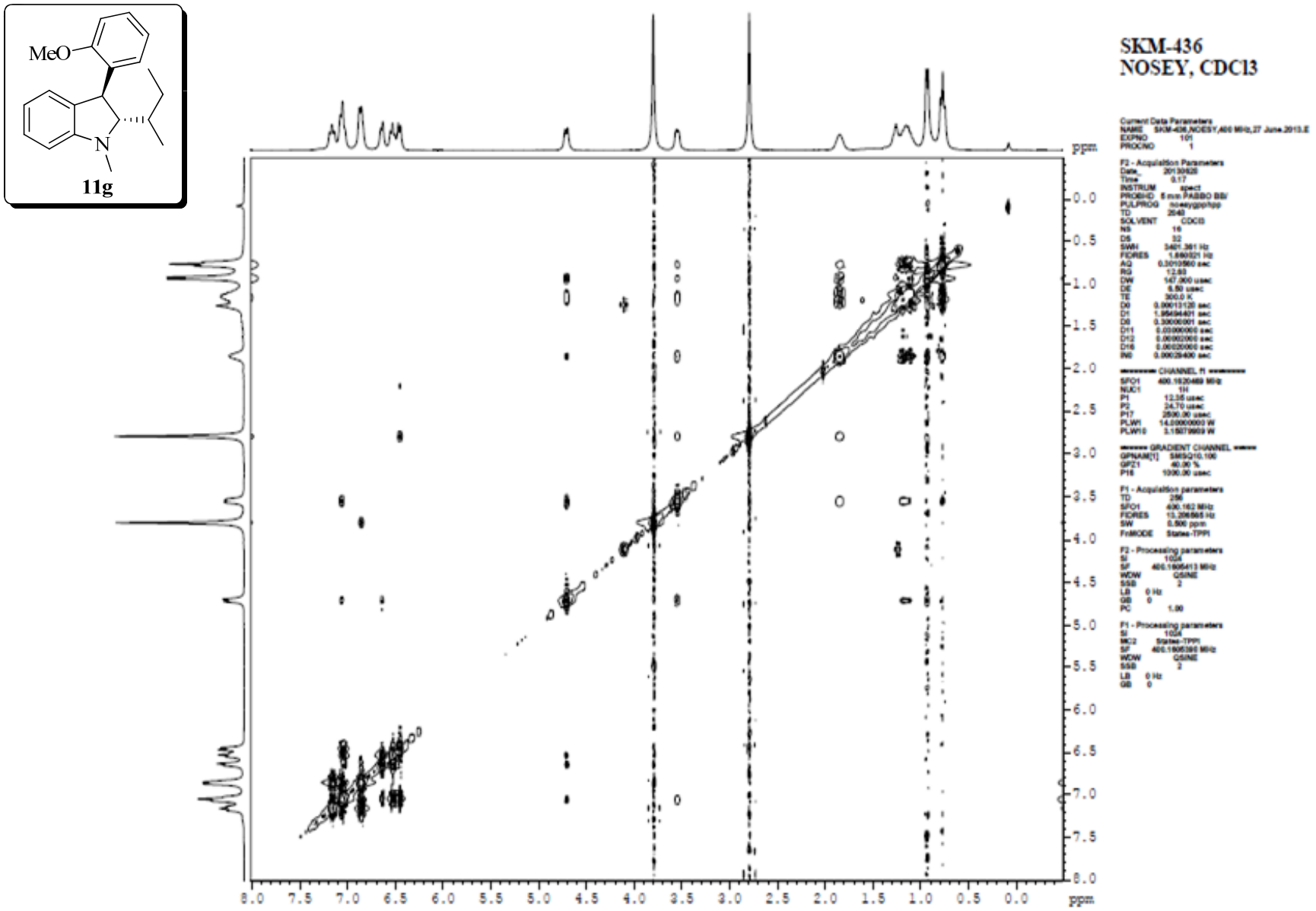


Figure 117: NOESY -Spectrum of **11g.**

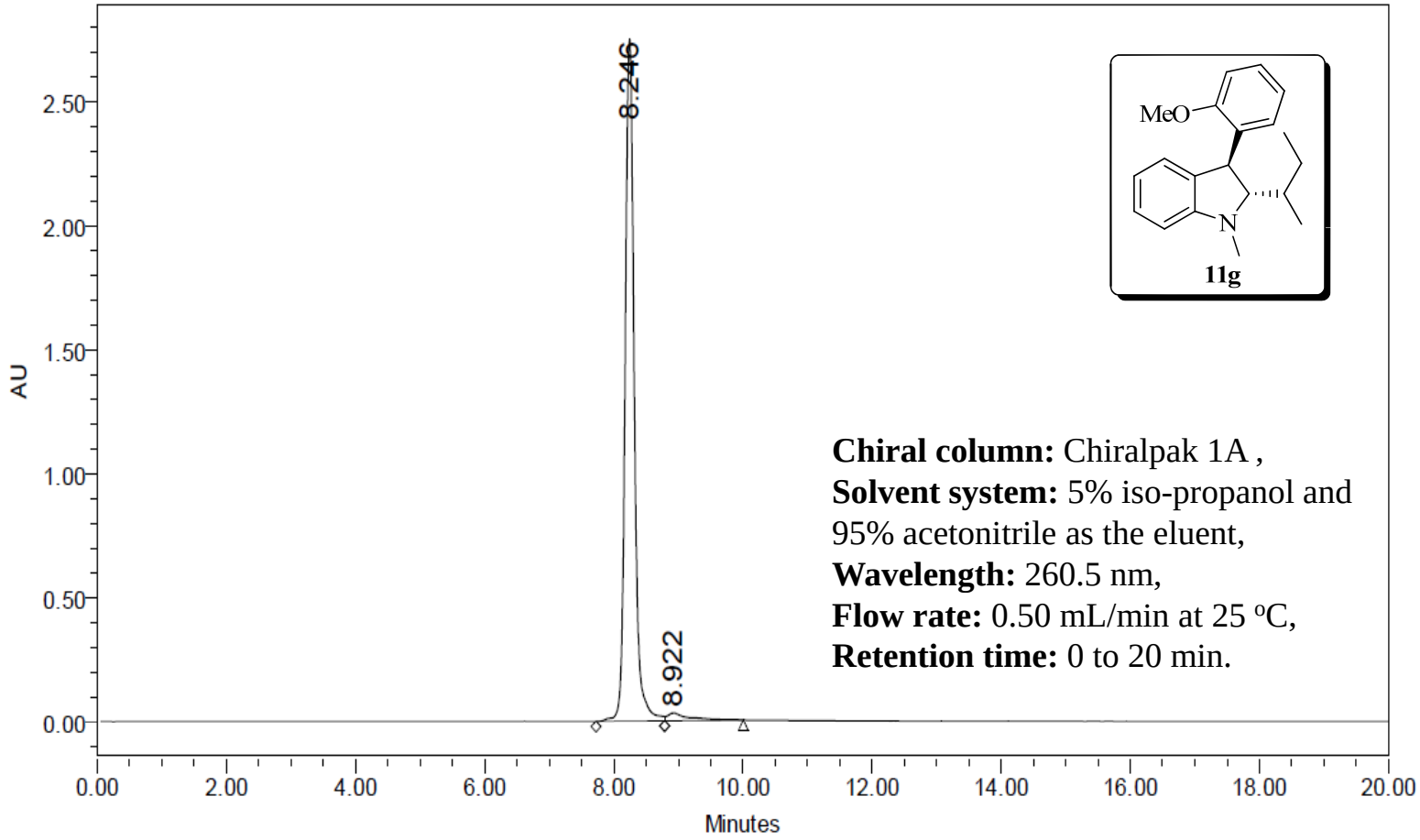


Figure 118: HPLC -Spectrum of **11g.**

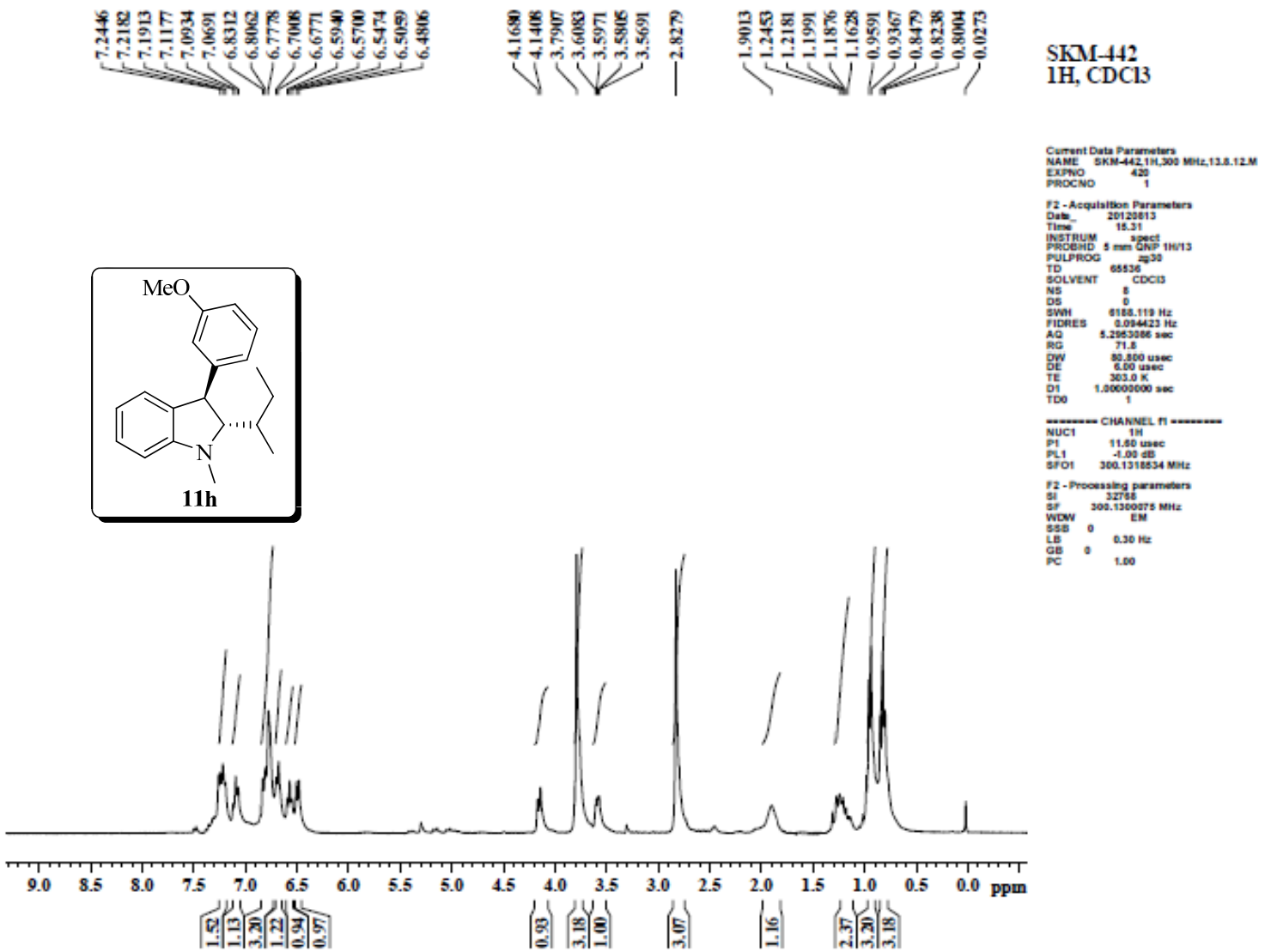


Figure 119: ^{1}H -NMR Spectrum of **11h.**

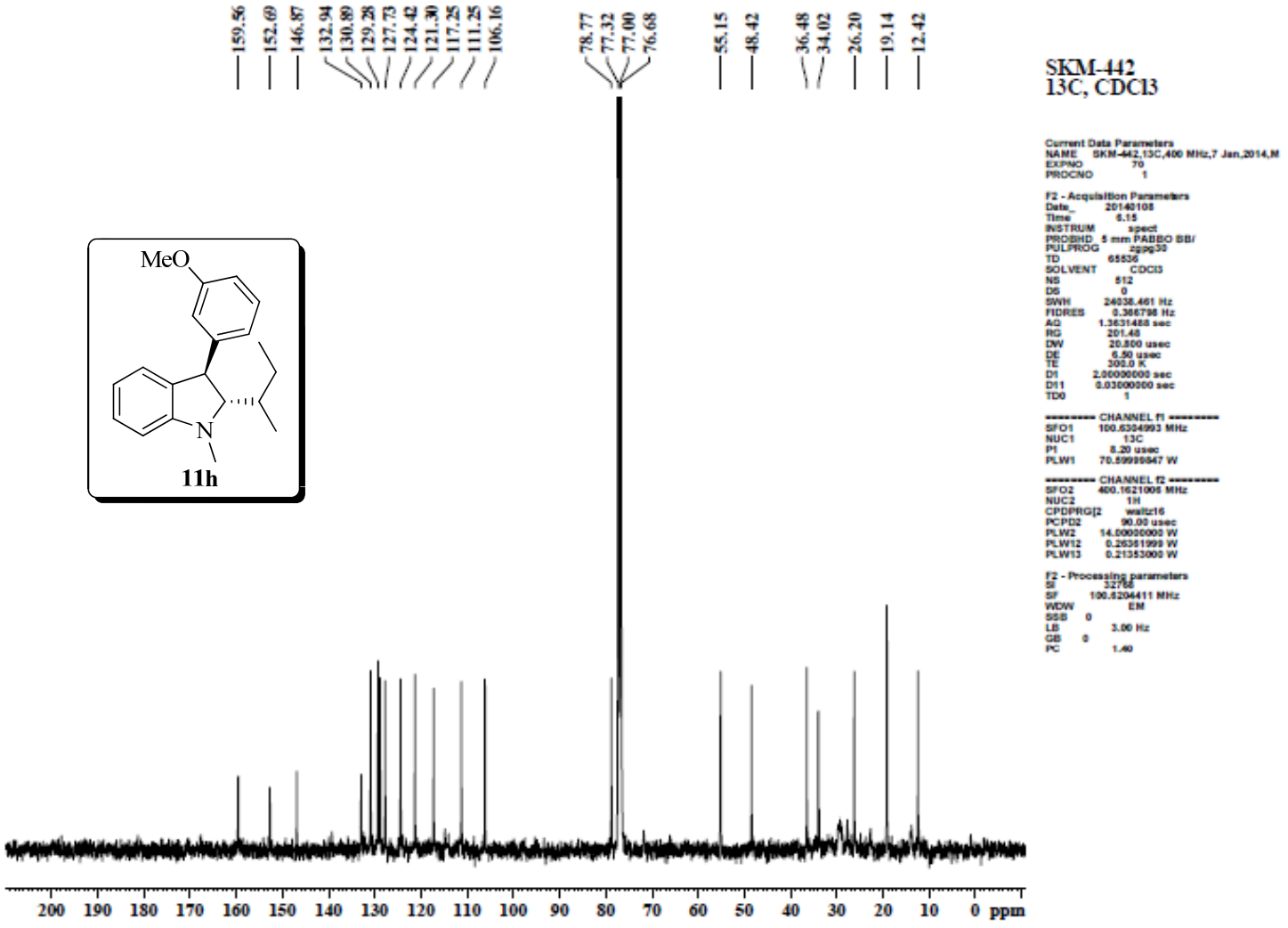


Figure 120: ^{13}C-NMR Spectrum of **11h.**

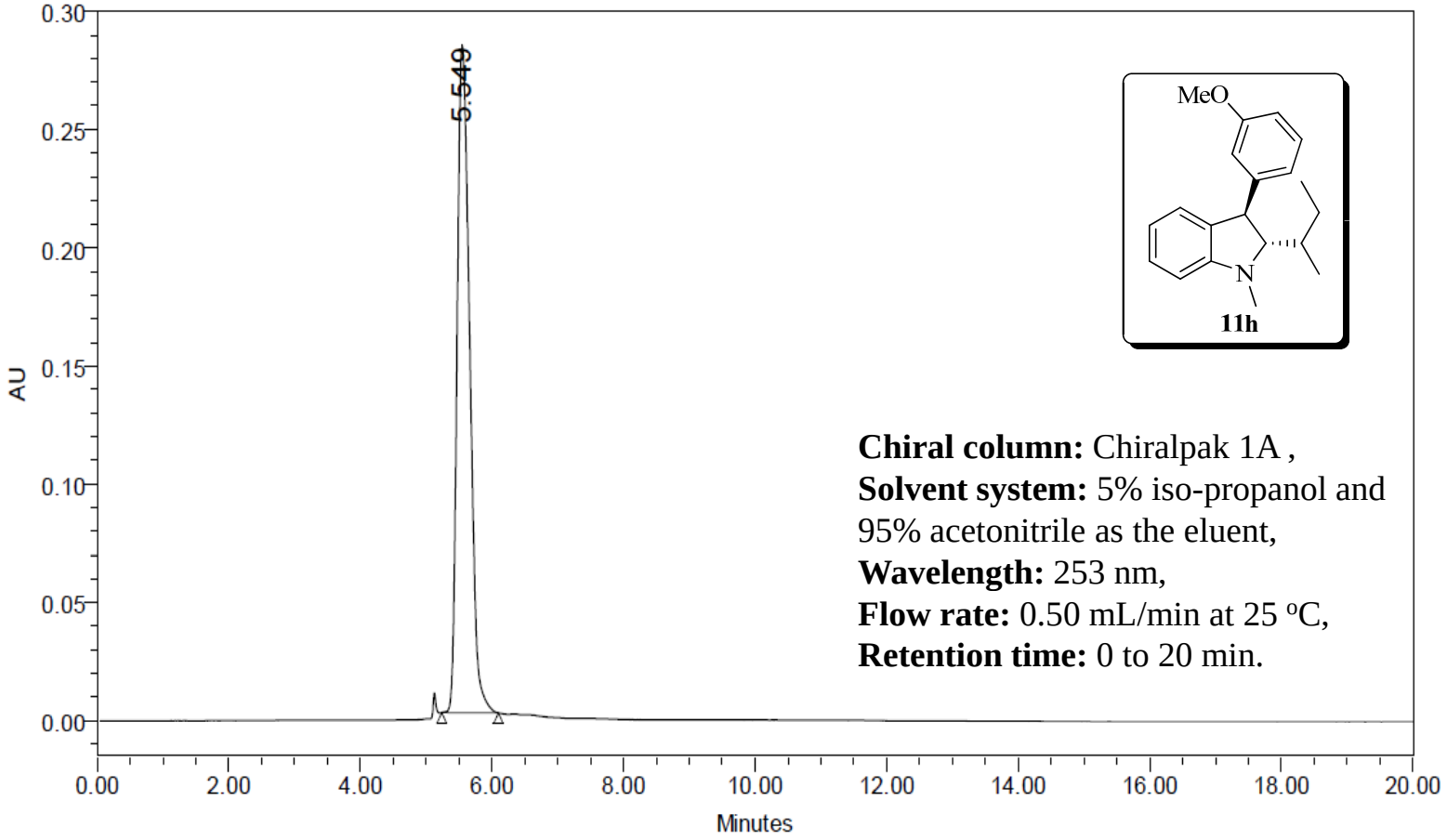


Figure 121: HPLC -Spectrum of **11h.**

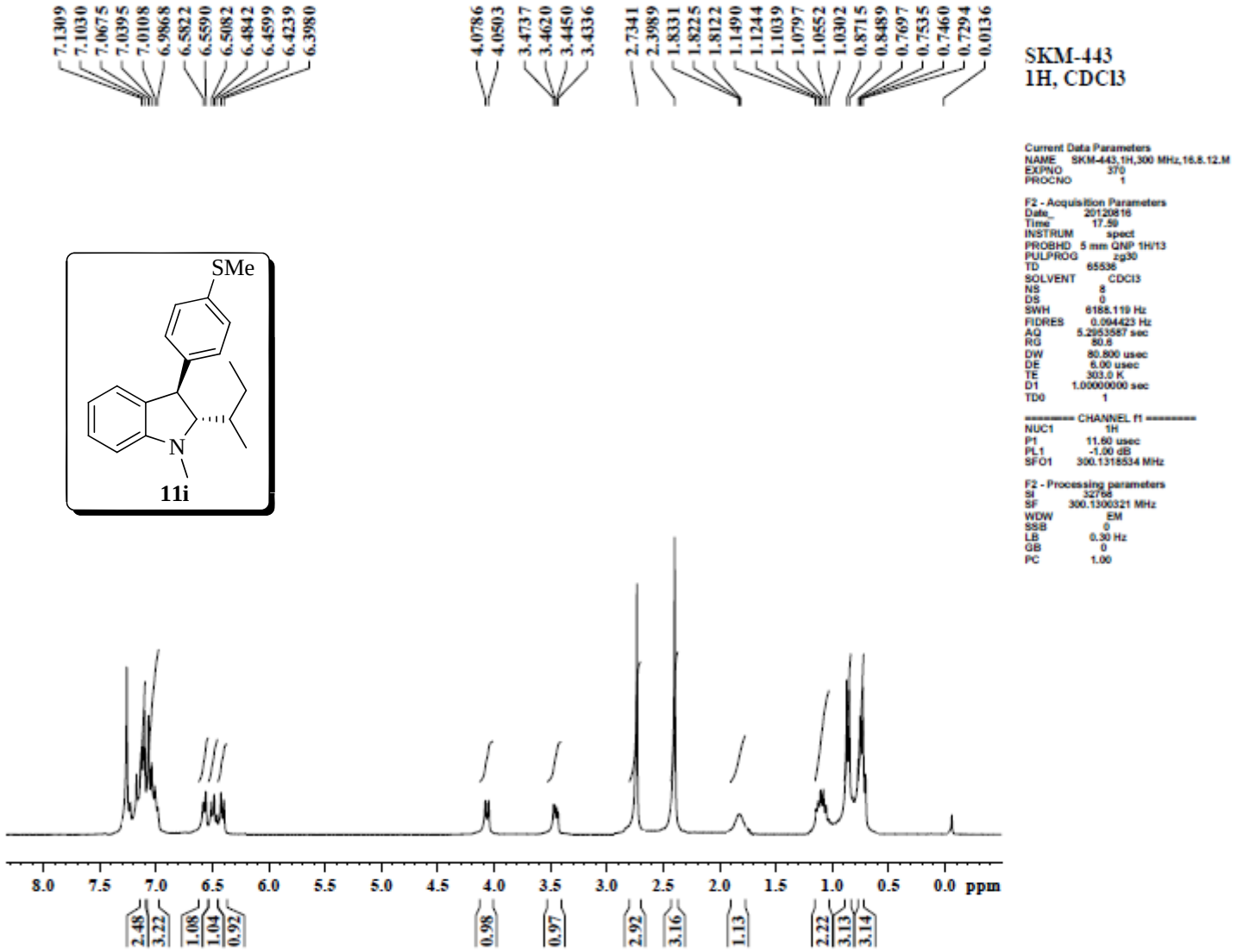


Figure 122: ^{1}H -NMR Spectrum of **11i.**

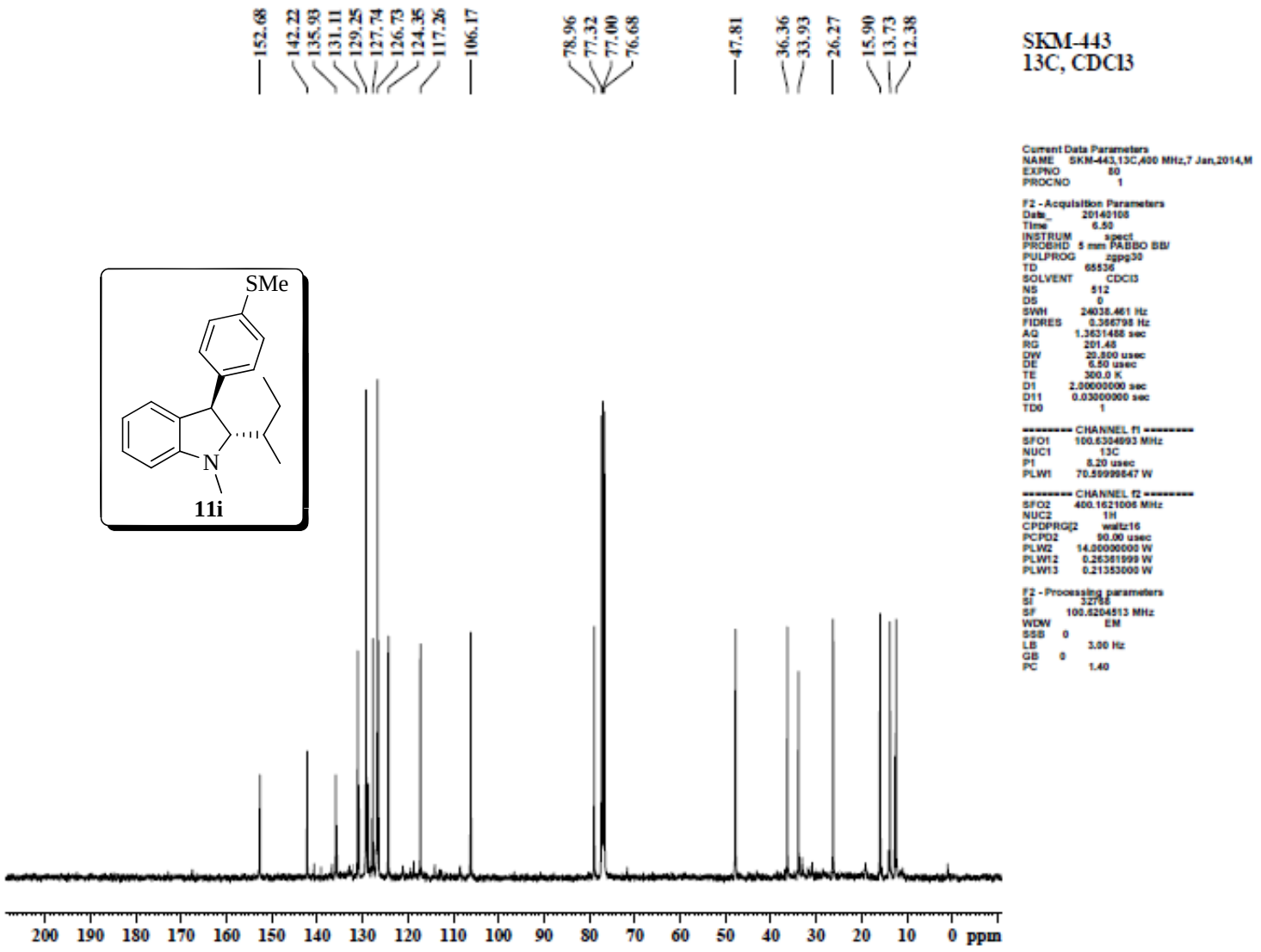


Figure 123: ^{13}C -NMR Spectrum of **11i.**

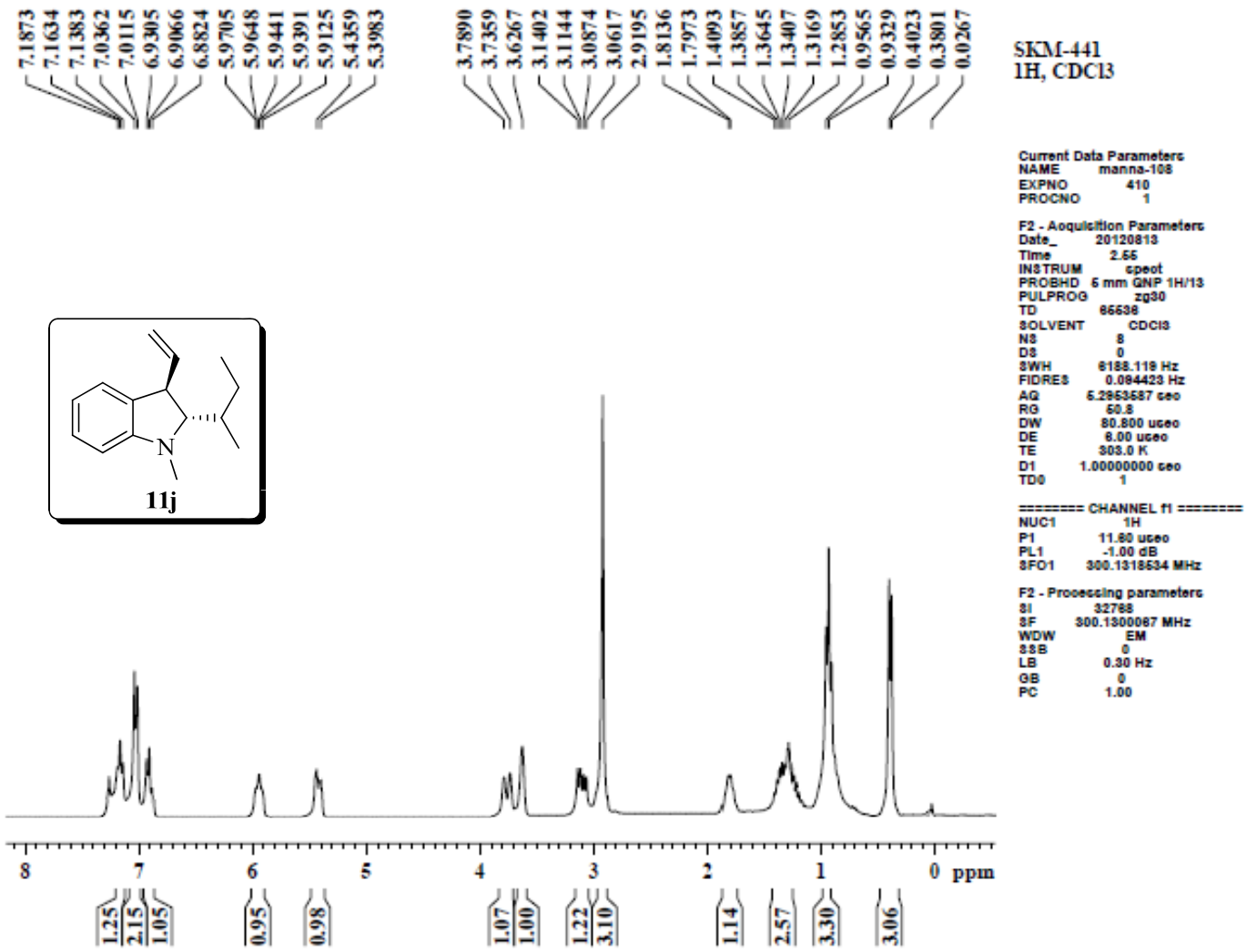


Figure 124: ^{1}H -NMR Spectrum of **11j.**

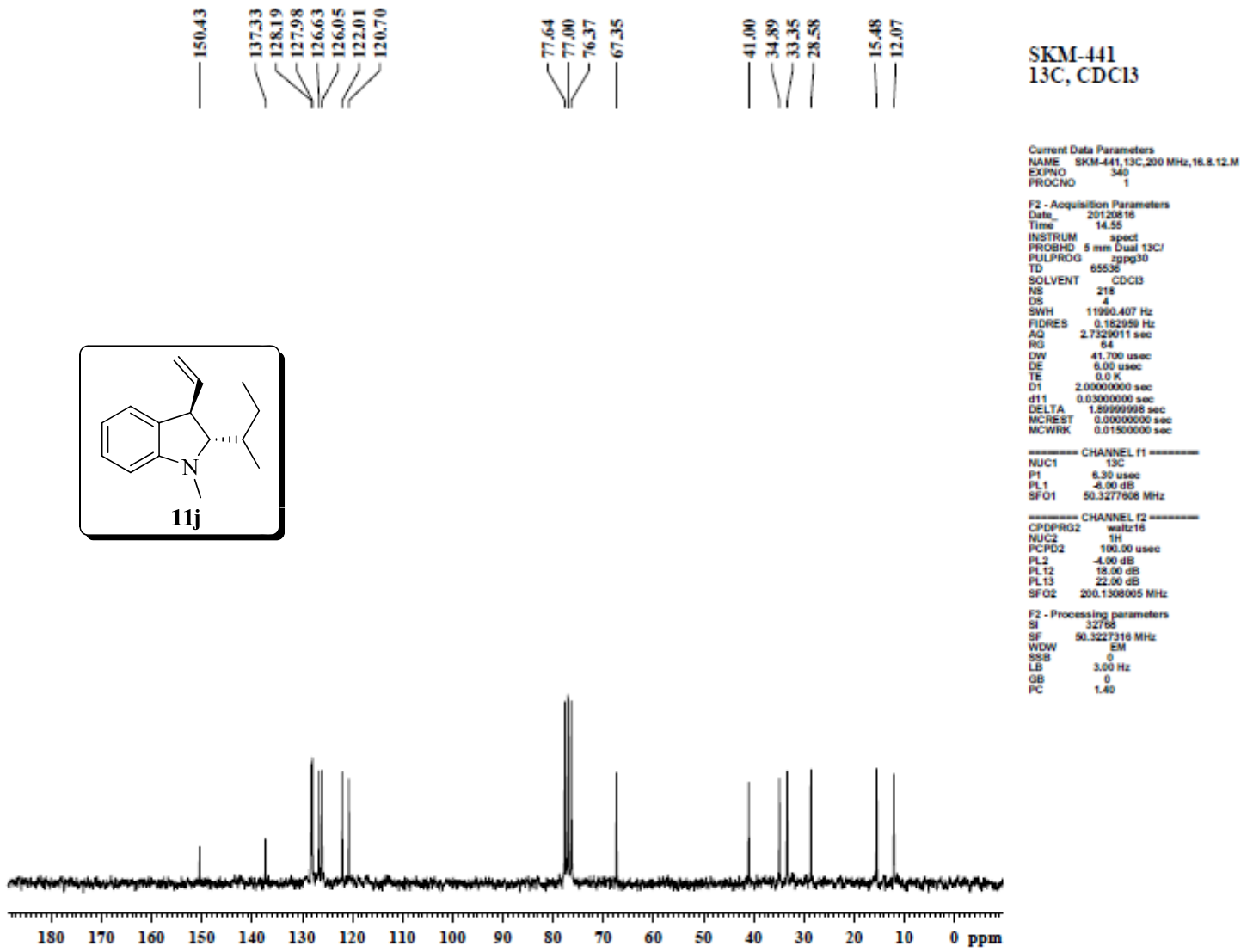


Figure 125: ^{13}C -NMR Spectrum of **11j.**

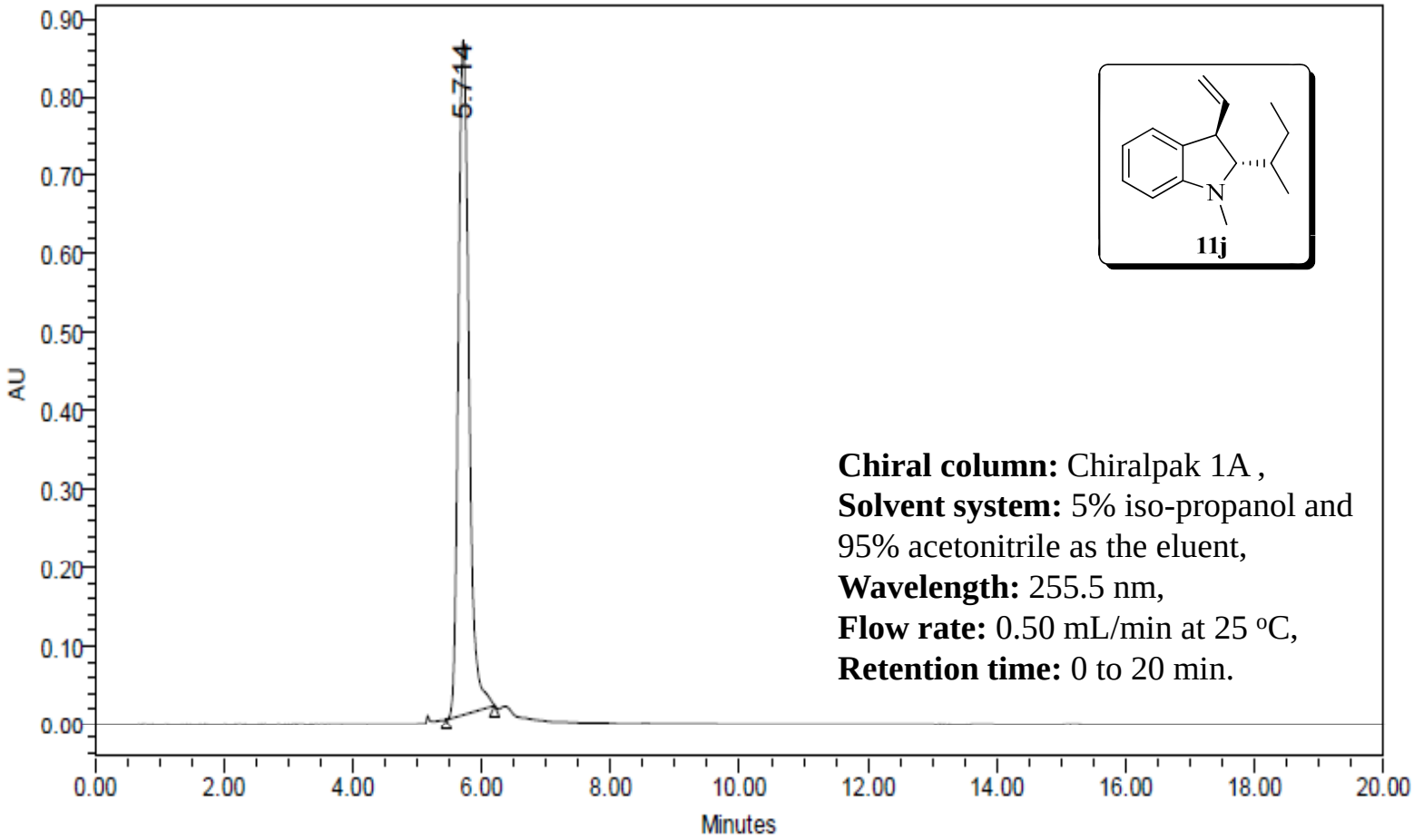


Figure 126: HPLC -Spectrum of **11j.**

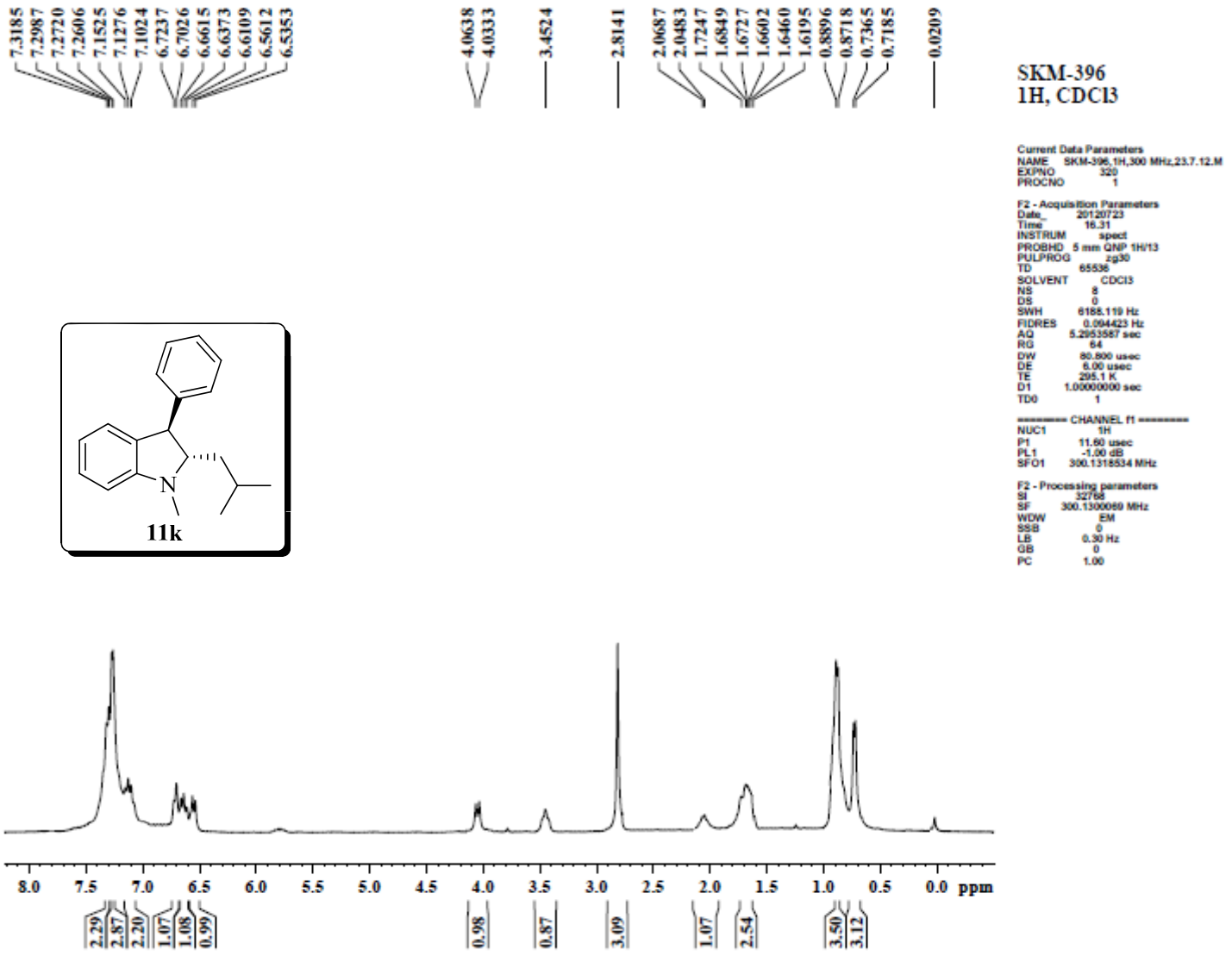


Figure 127: ^{1}H -NMR Spectrum of **11k.**

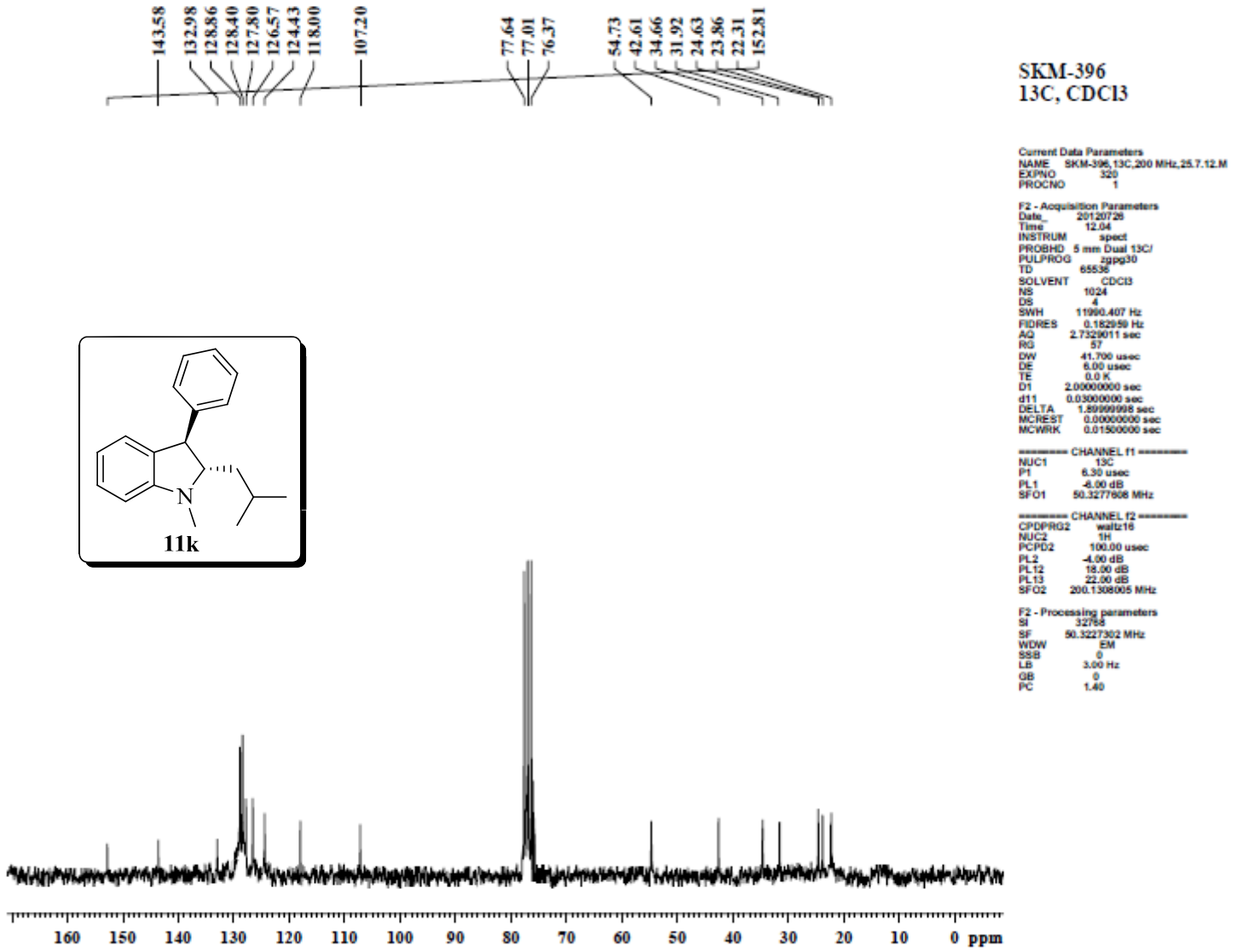


Figure 128: ^{13}C -NMR Spectrum of **11k.**

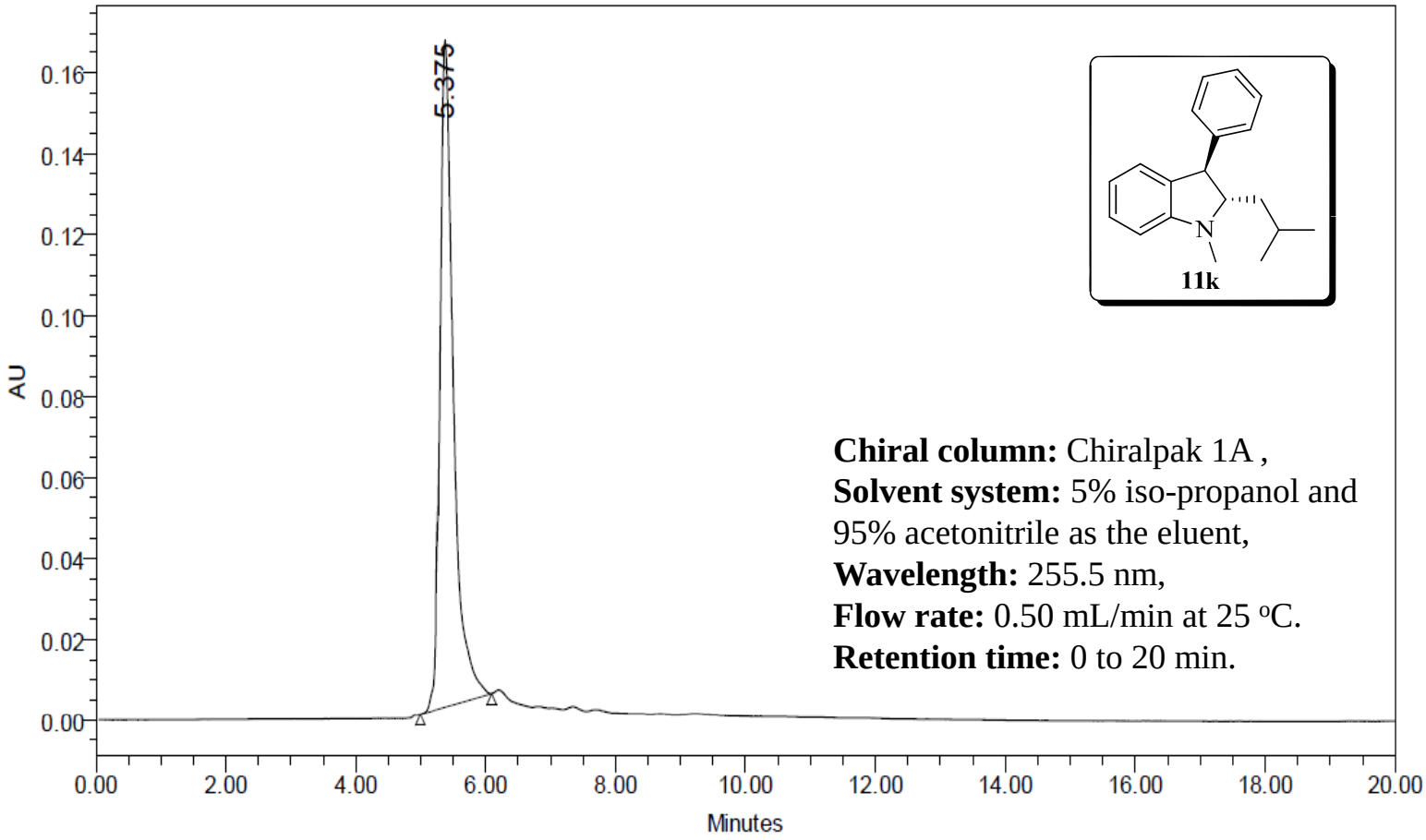


Figure 129: HPLC -Spectrum of **11k.**

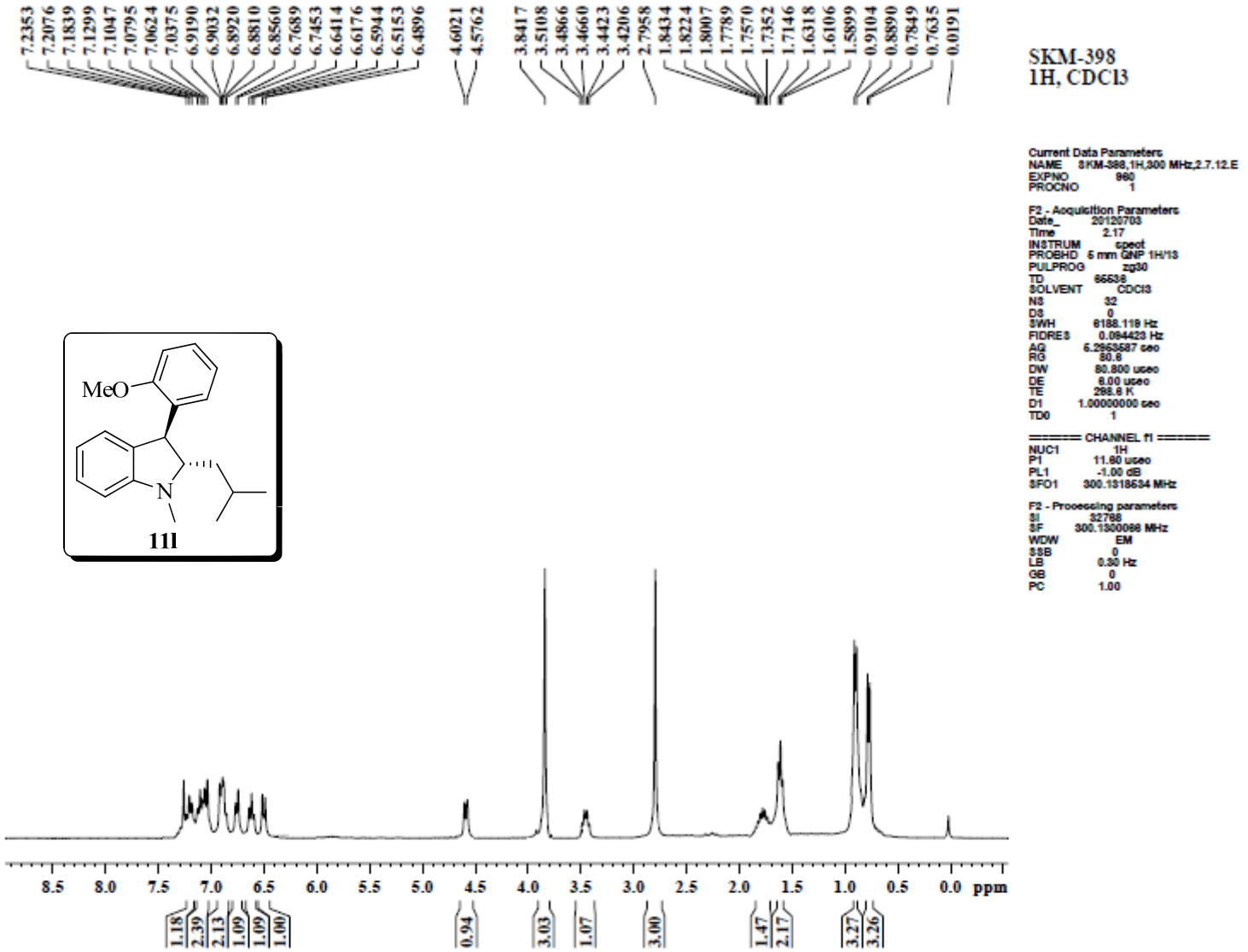


Figure 130: ^{1}H -NMR Spectrum of **11l.**

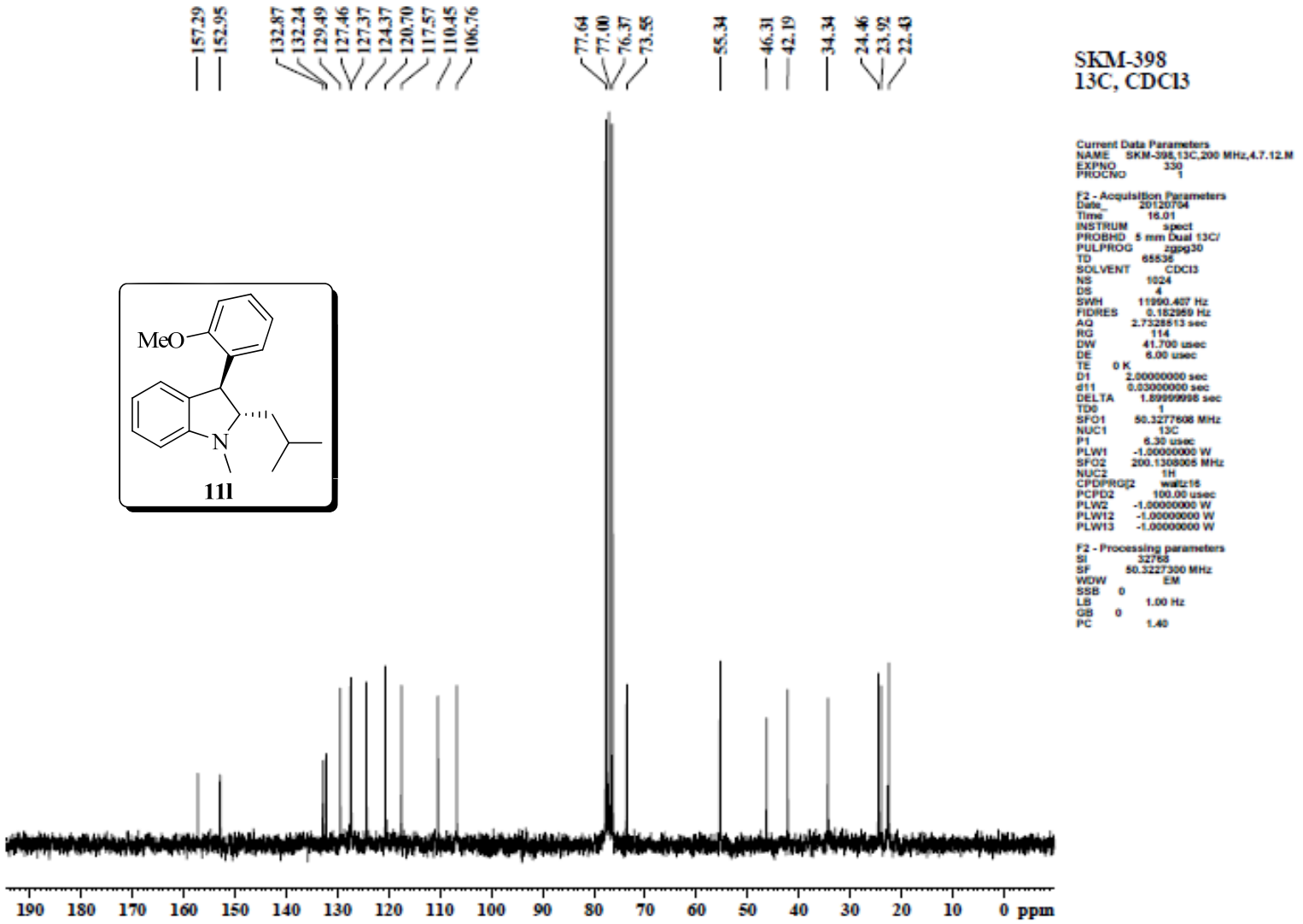


Figure 131: ^{13}C -NMR Spectrum of **11l.**

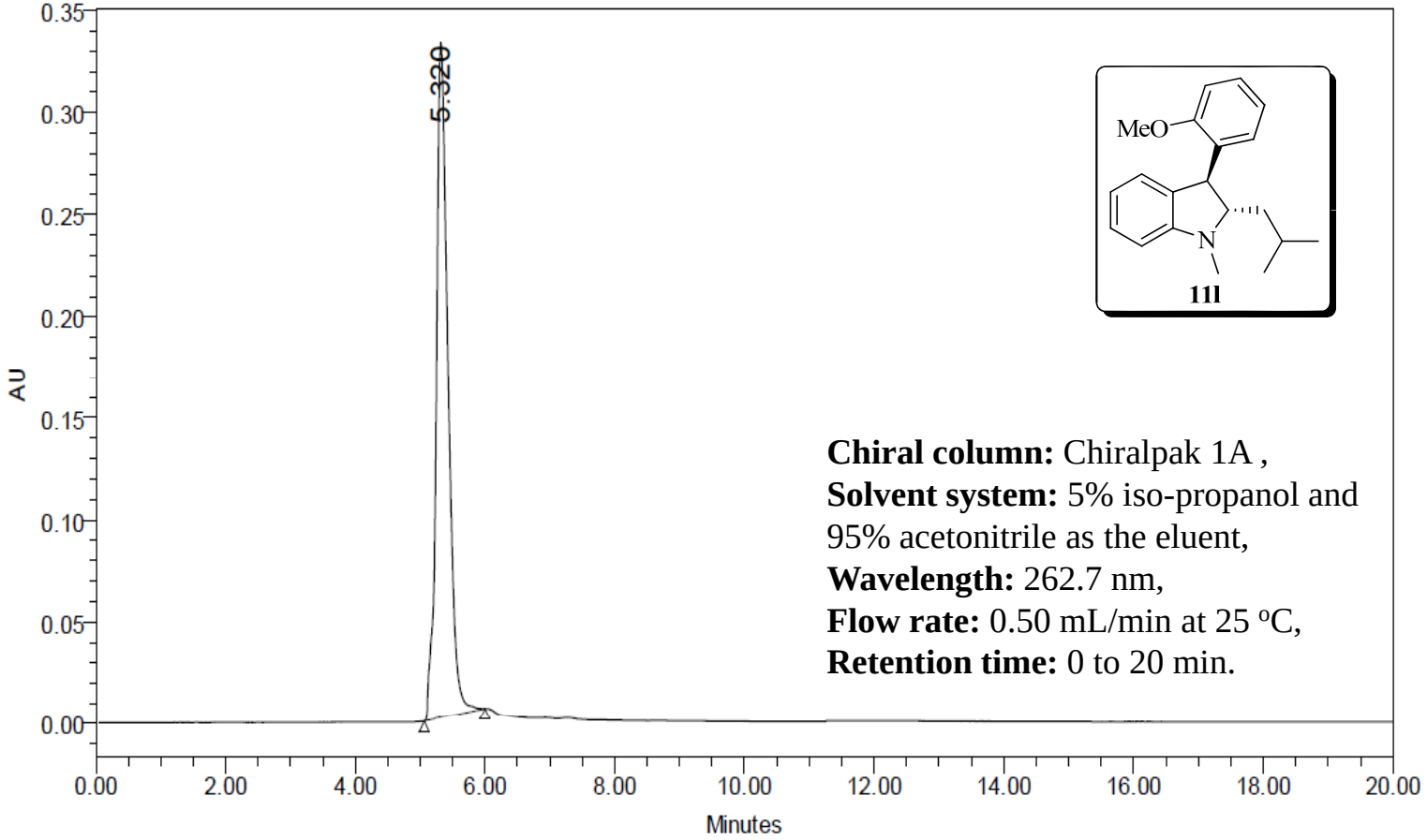


Figure 132: HPLC -Spectrum of **11l.**

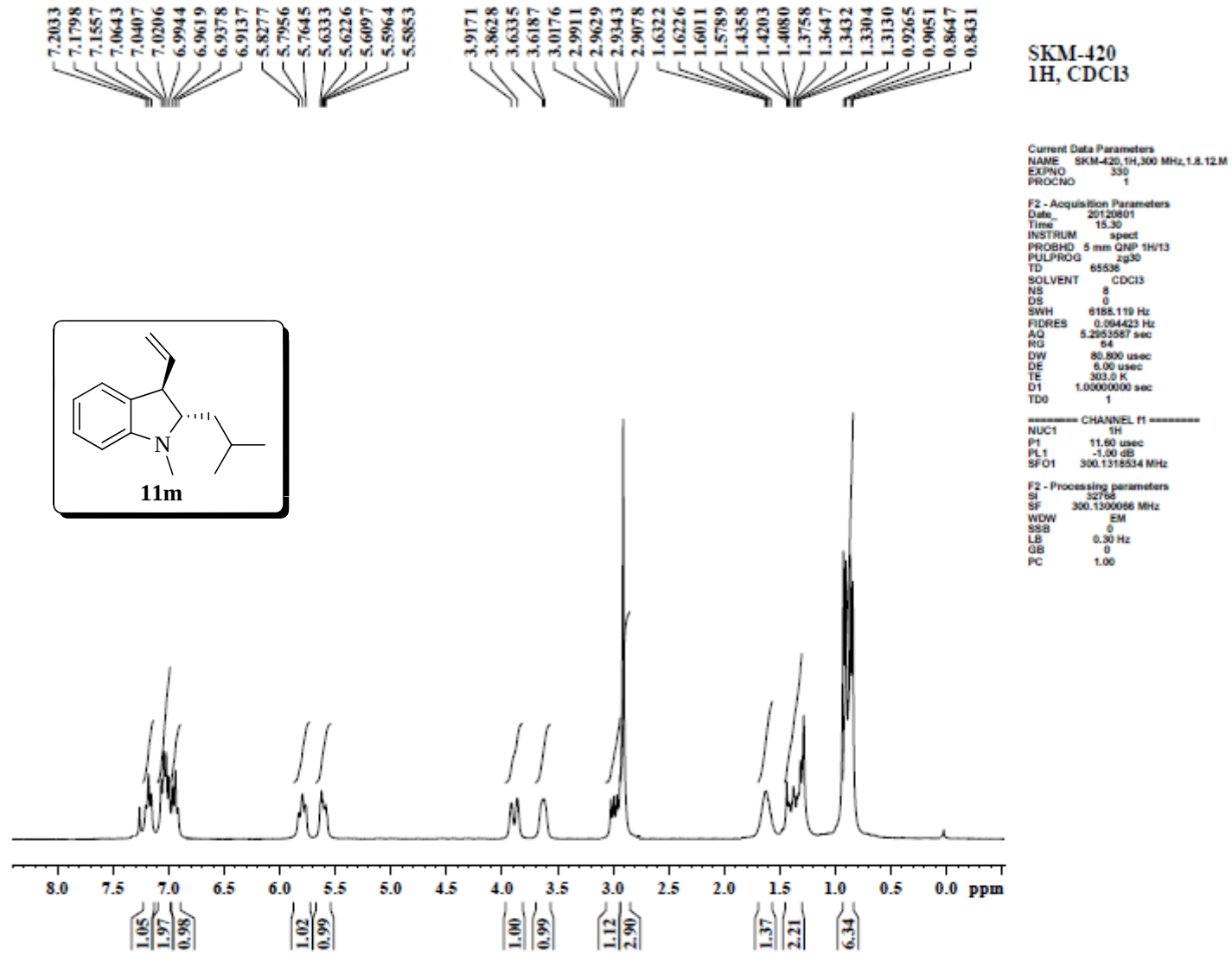


Figure 133: ^{1}H -NMR Spectrum of **11m.**

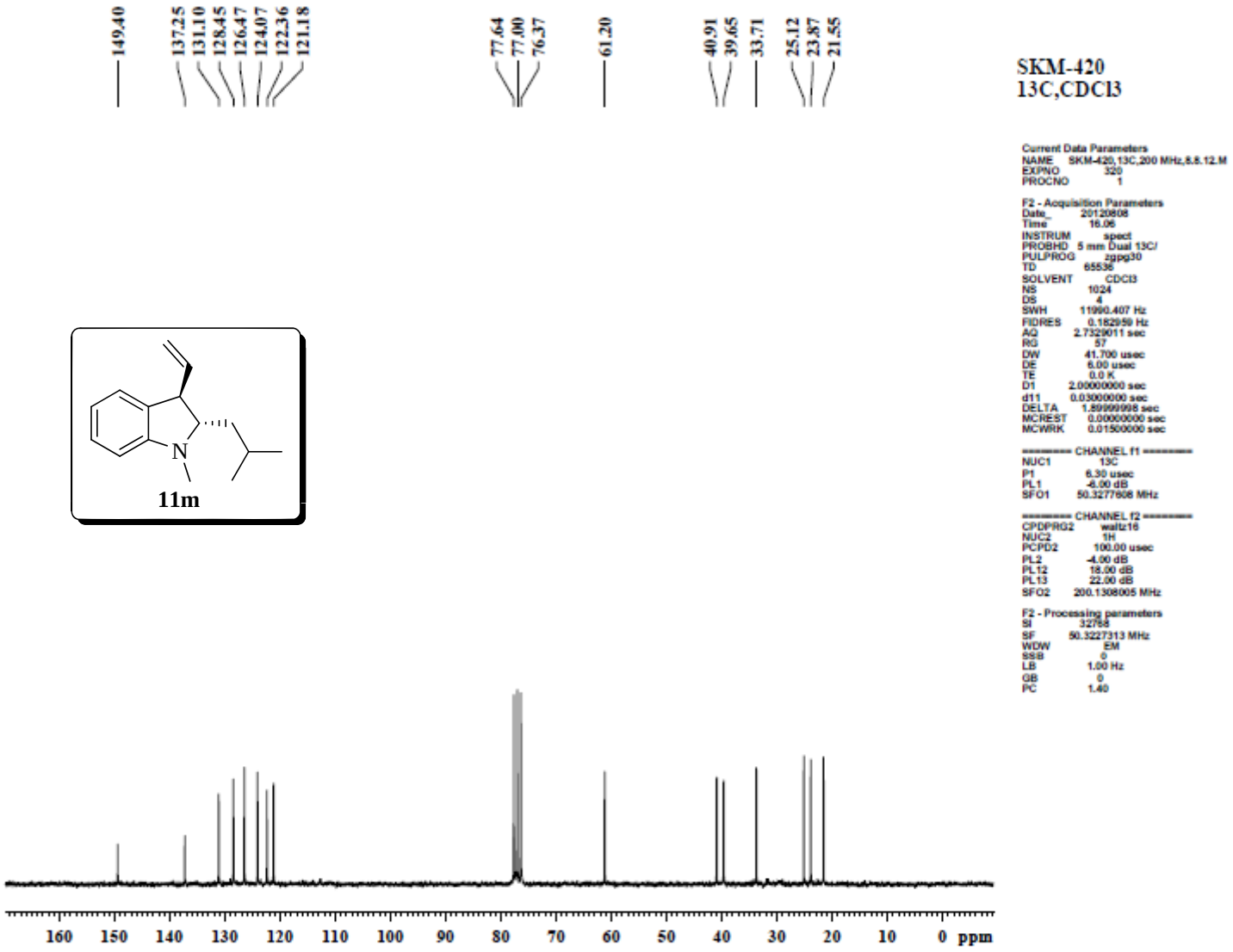


Figure 134: ^{13}C -NMR Spectrum of **11m.**

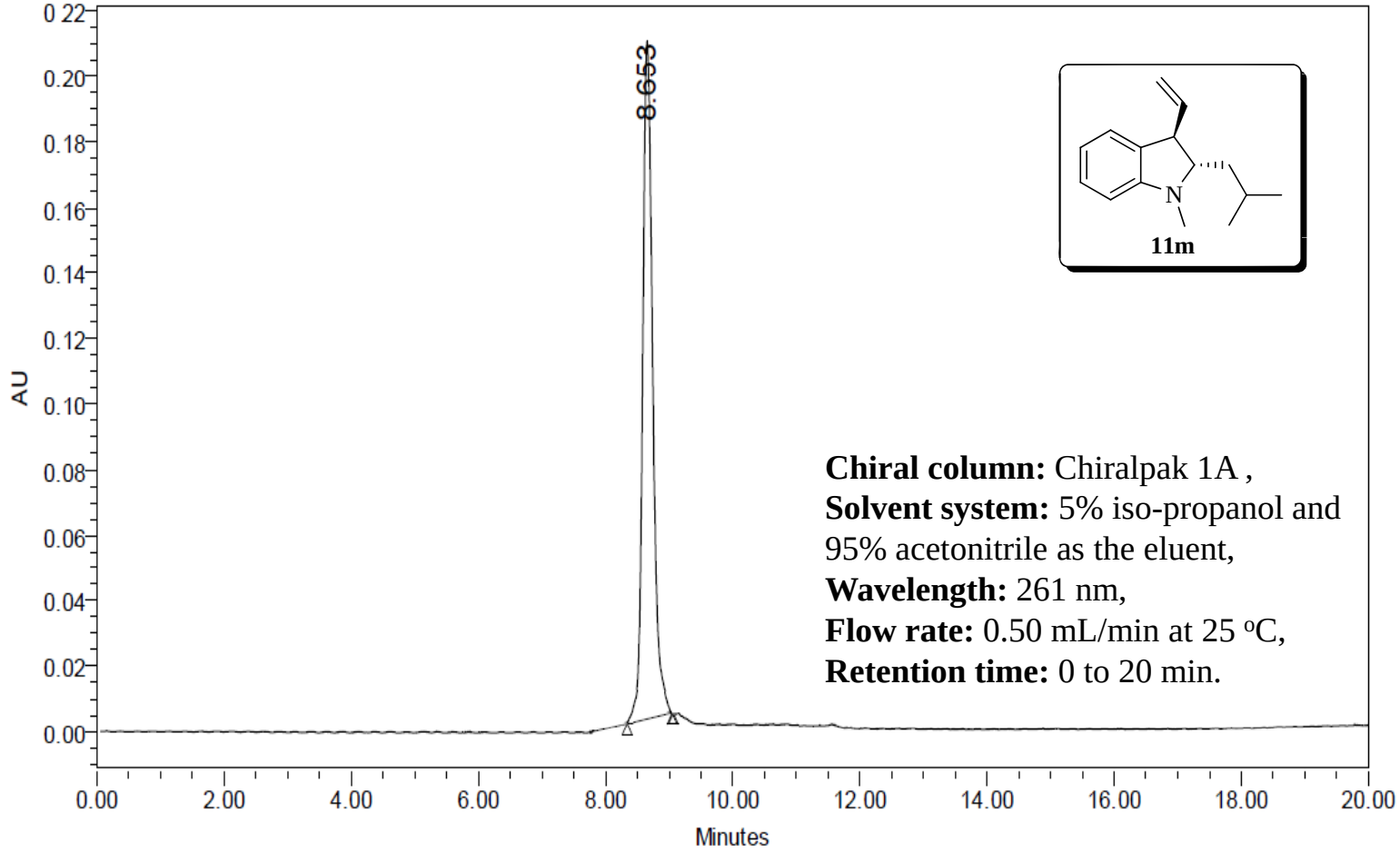


Figure 135: HPLC -Spectrum of **11m.**

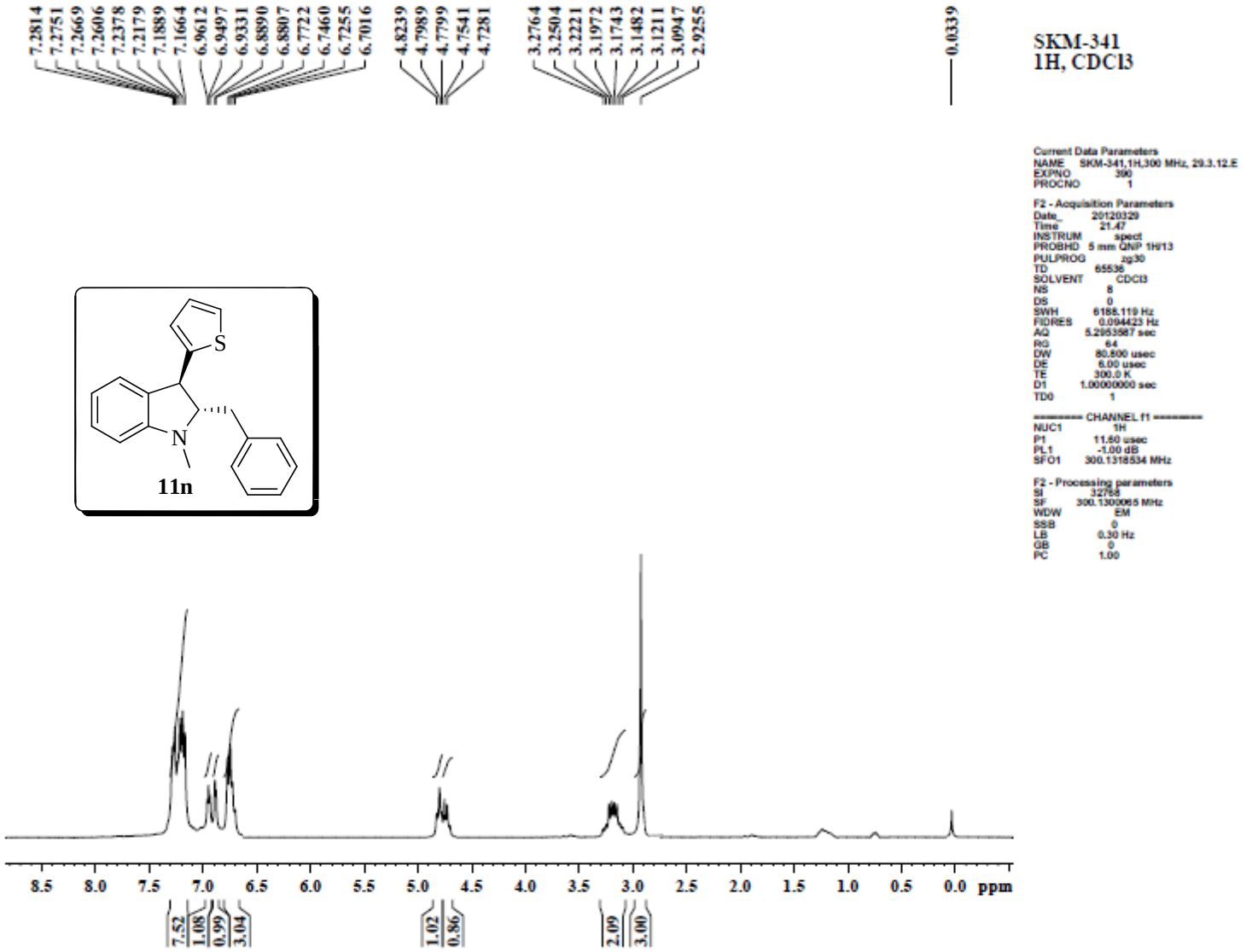


Figure 136: ^{1}H -NMR Spectrum of **11n.**

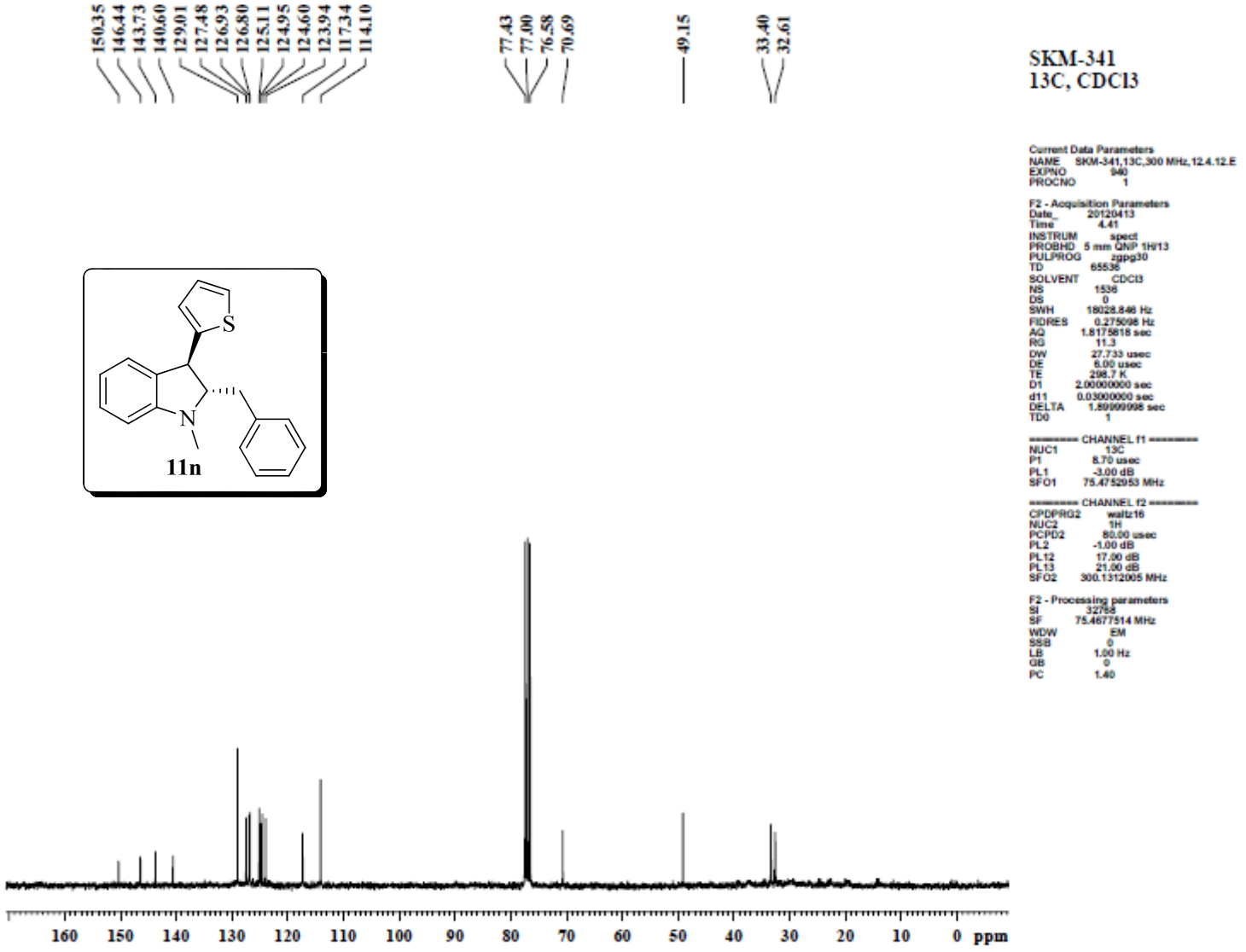


Figure 137: ^{13}C -NMR Spectrum of **11n.**

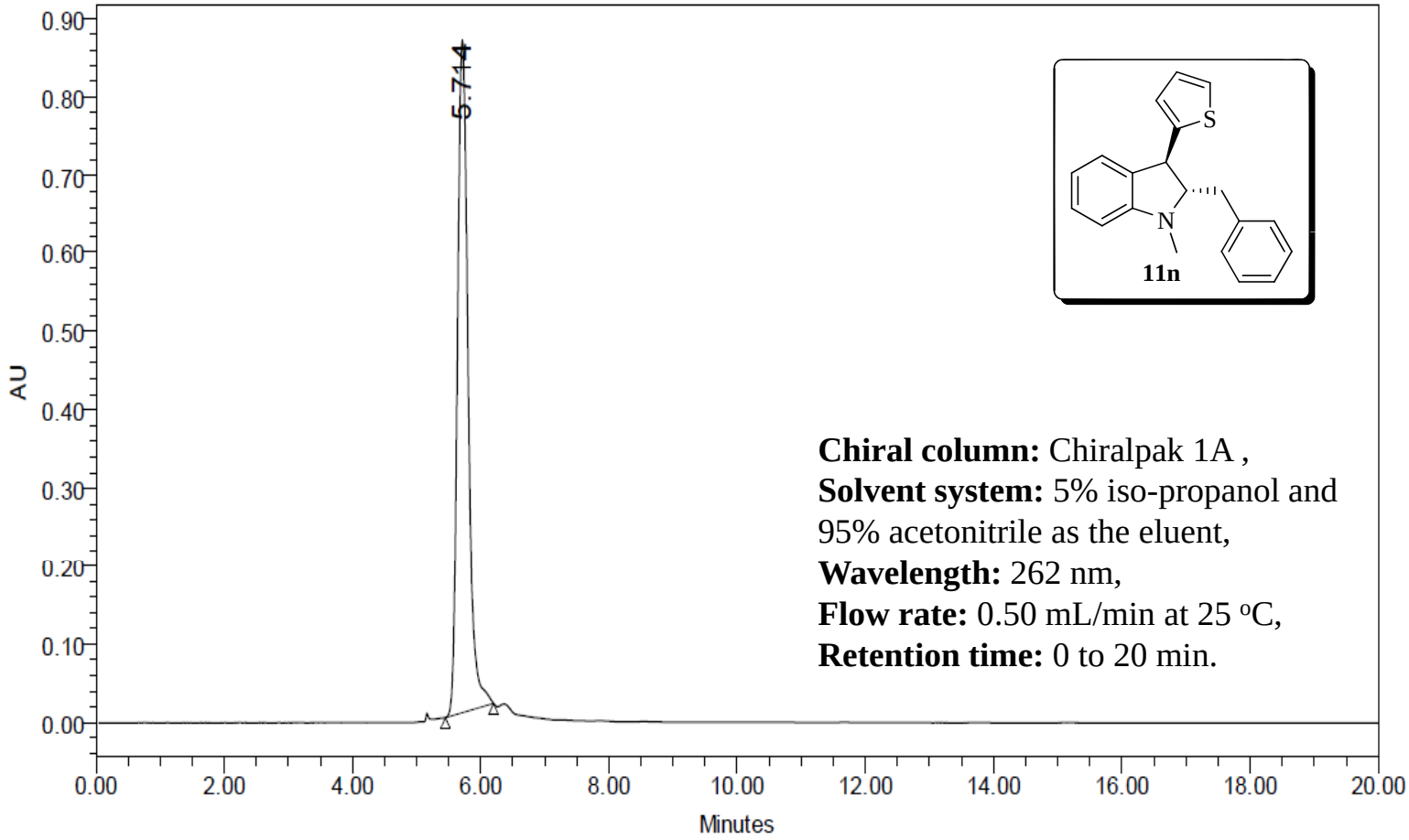


Figure 138: HPLC -Spectrum of **11n.**

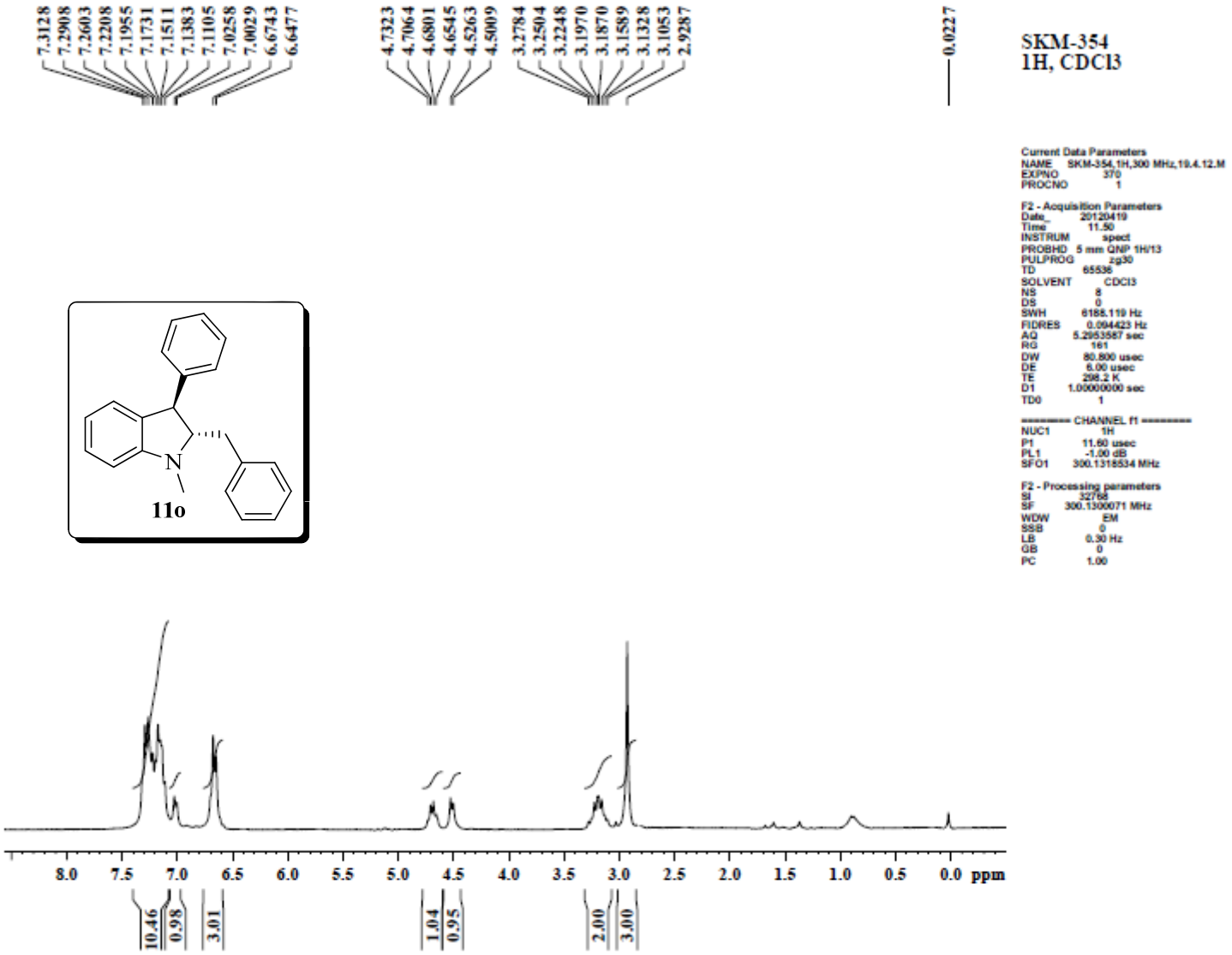


Figure 139: ^{1}H -NMR Spectrum of **11o.**

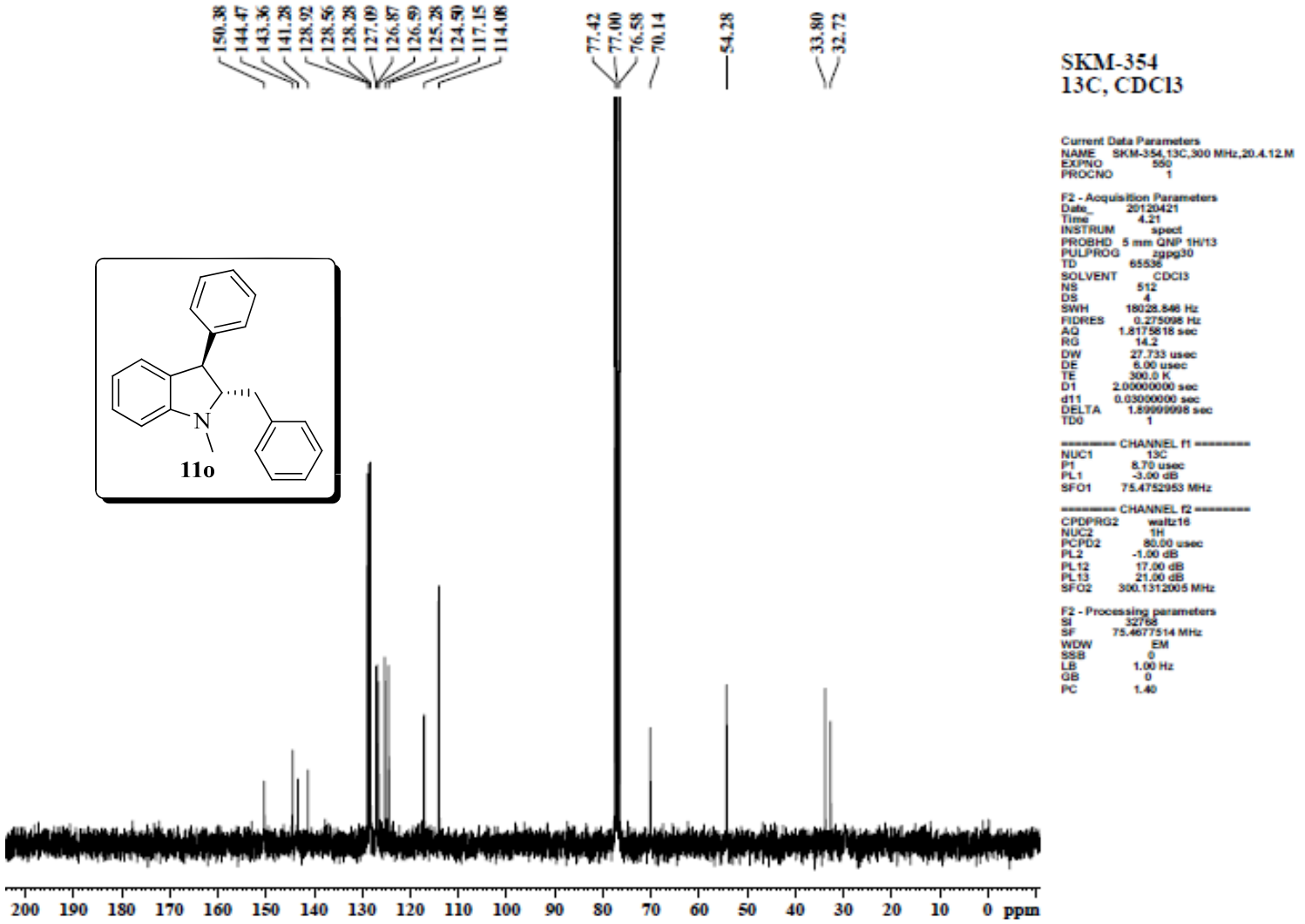
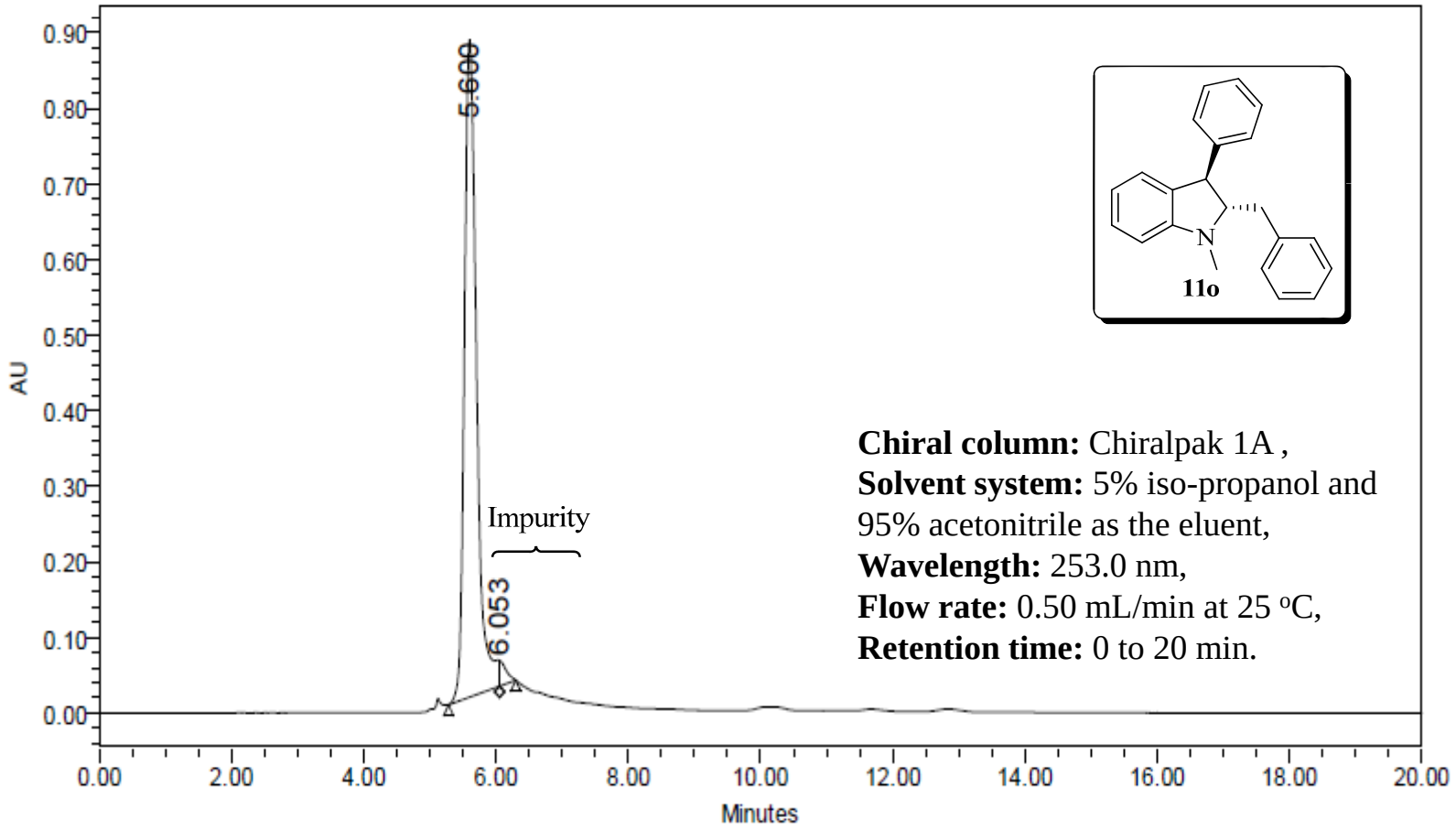


Figure 140: ^{13}C -NMR Spectrum of **11o.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **11o.**

Figure 141: HPLC -Spectrum of **11o.**

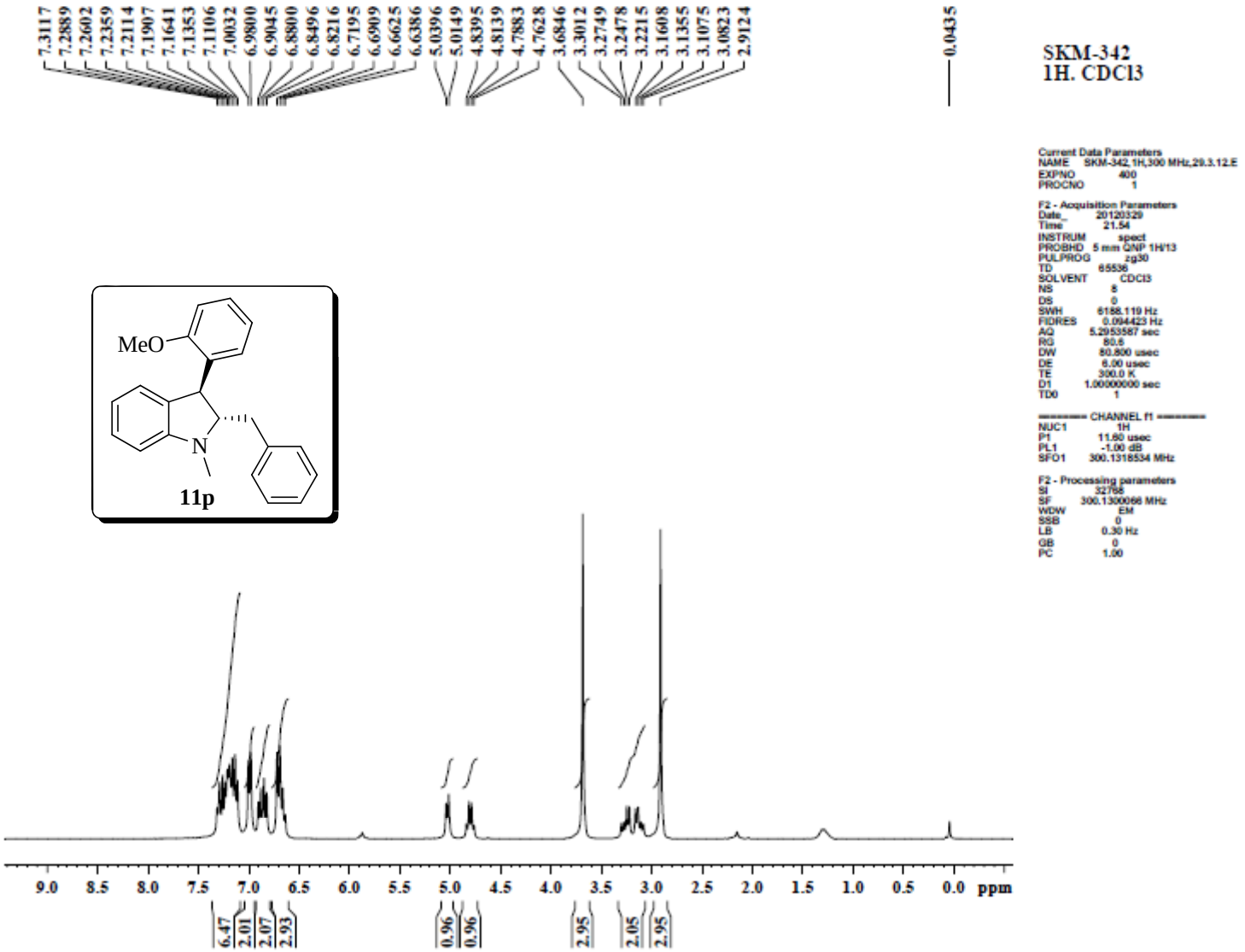


Figure 142: ^{1}H -NMR Spectrum of **11p.**

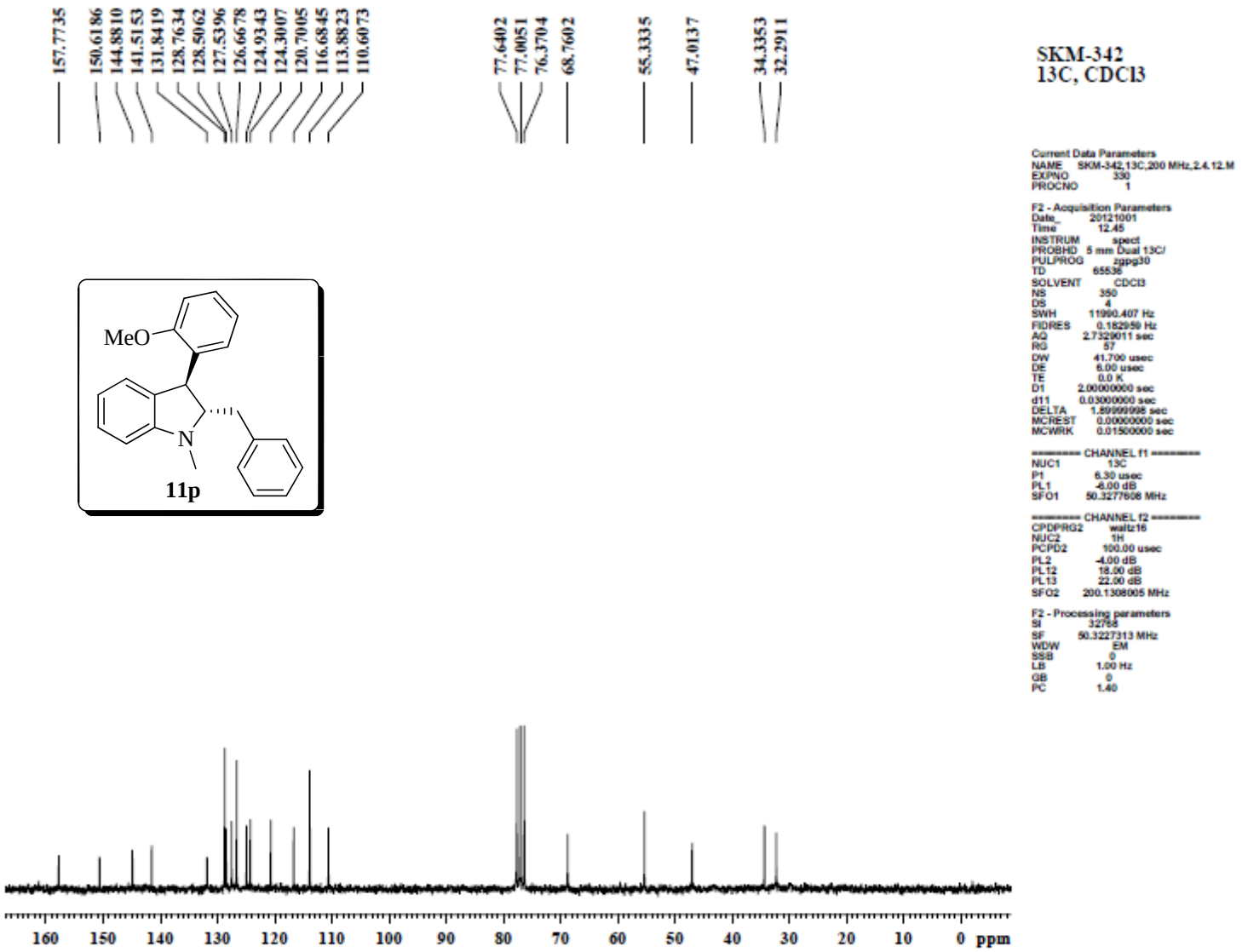


Figure 143: ^{13}C -NMR Spectrum of **11p.**

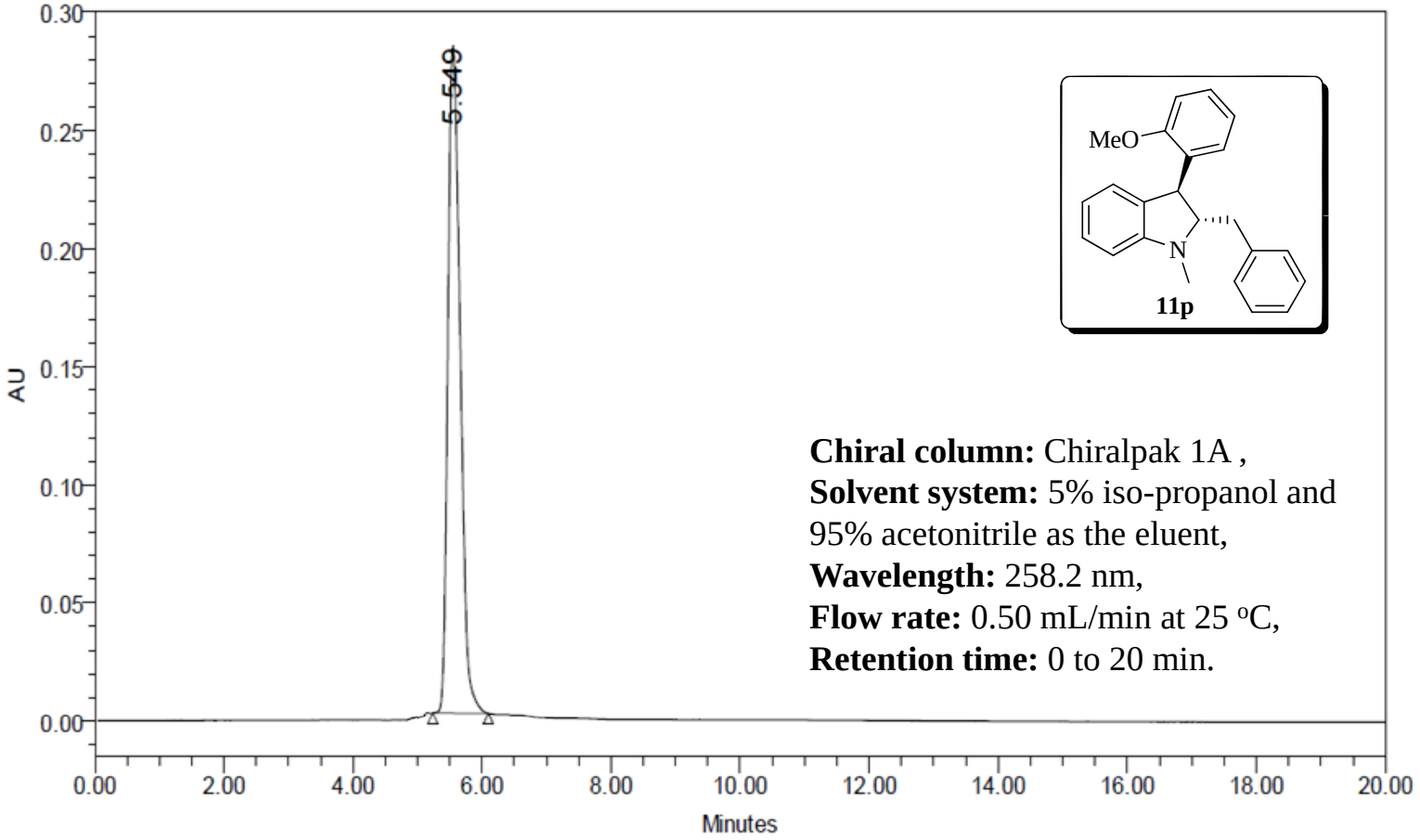


Figure 144: HPLC -Spectrum of **11p.**

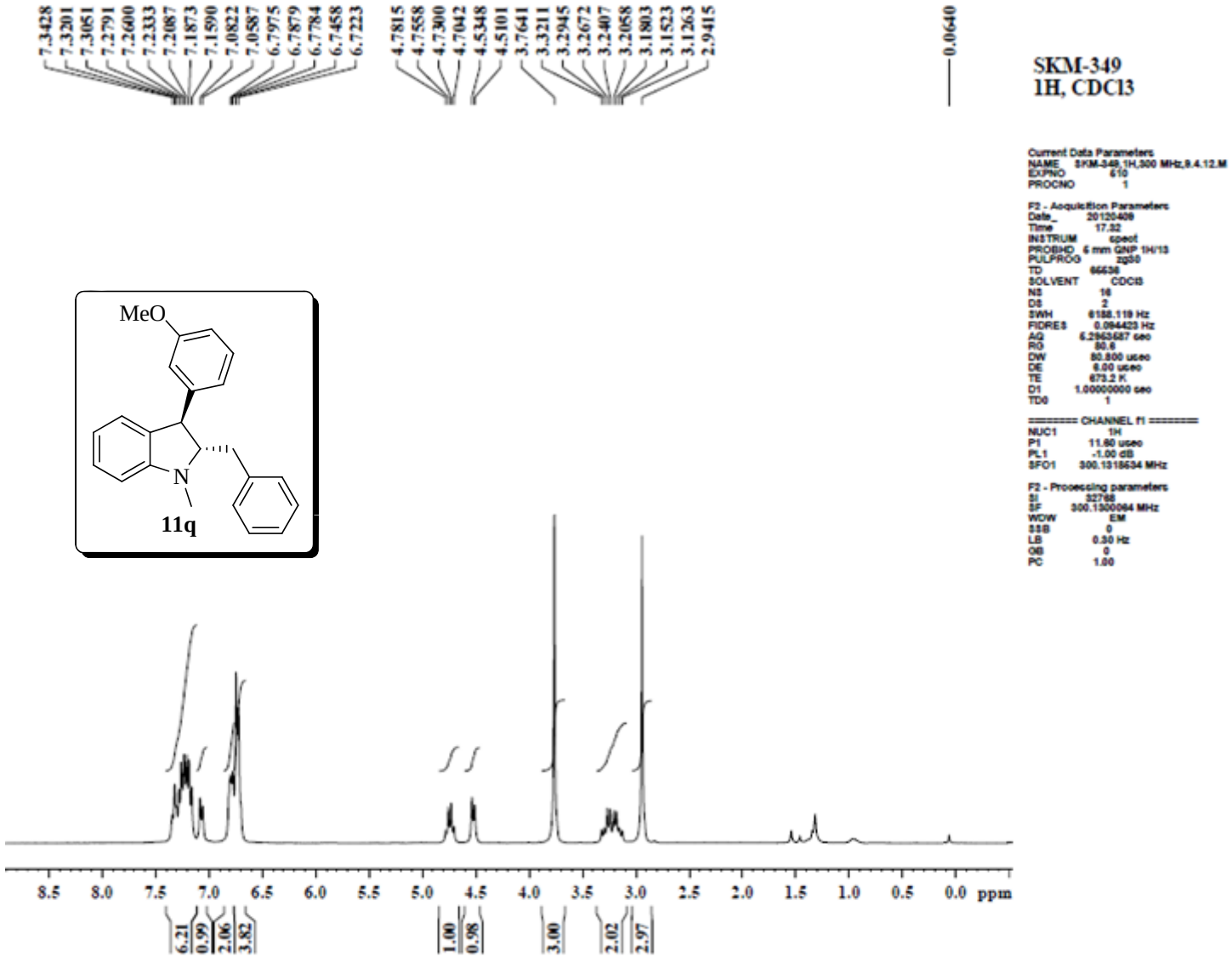


Figure 145: ^{1}H -NMR Spectrum of **11q.**

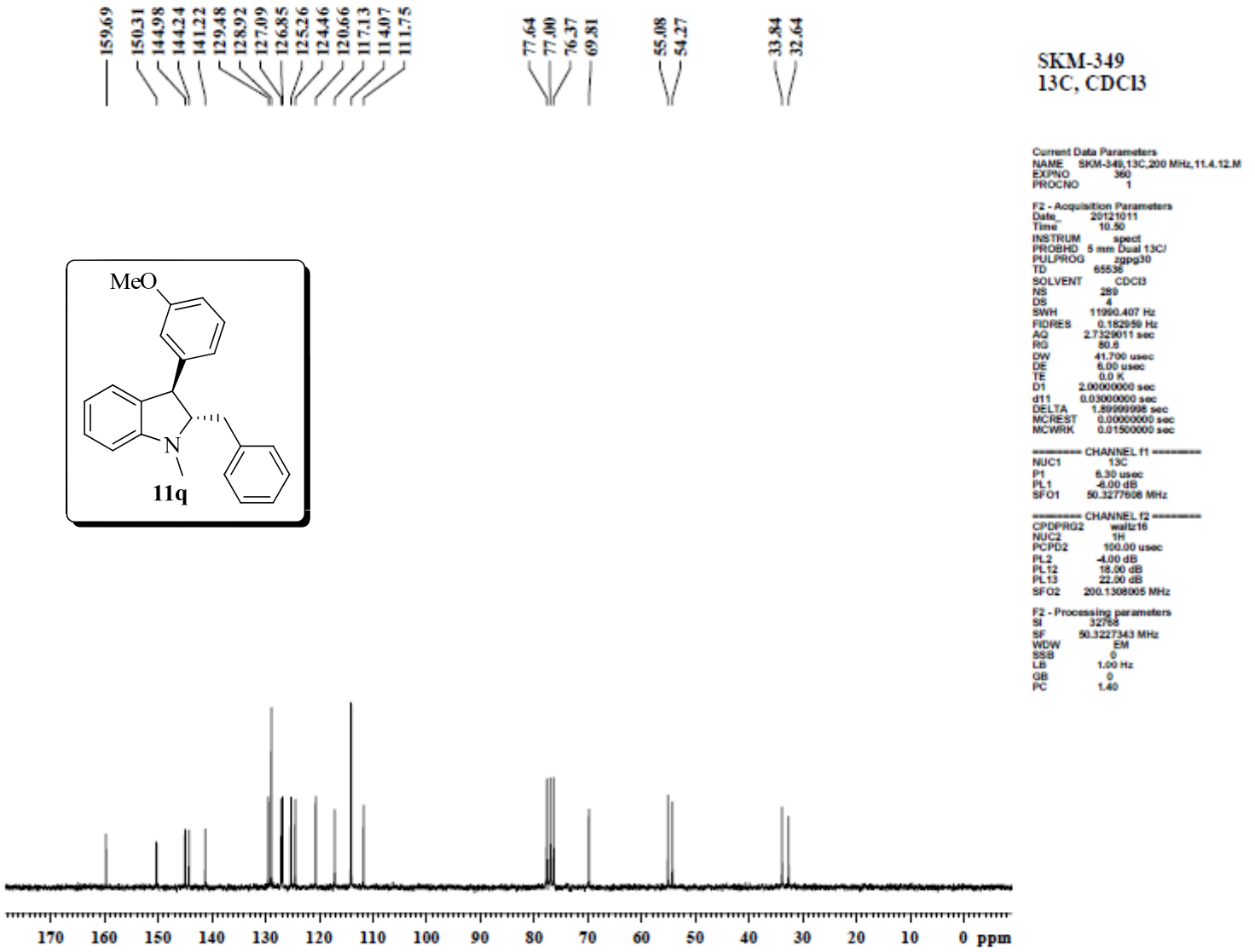


Figure 146: ^{13}C -NMR Spectrum of **11q.**

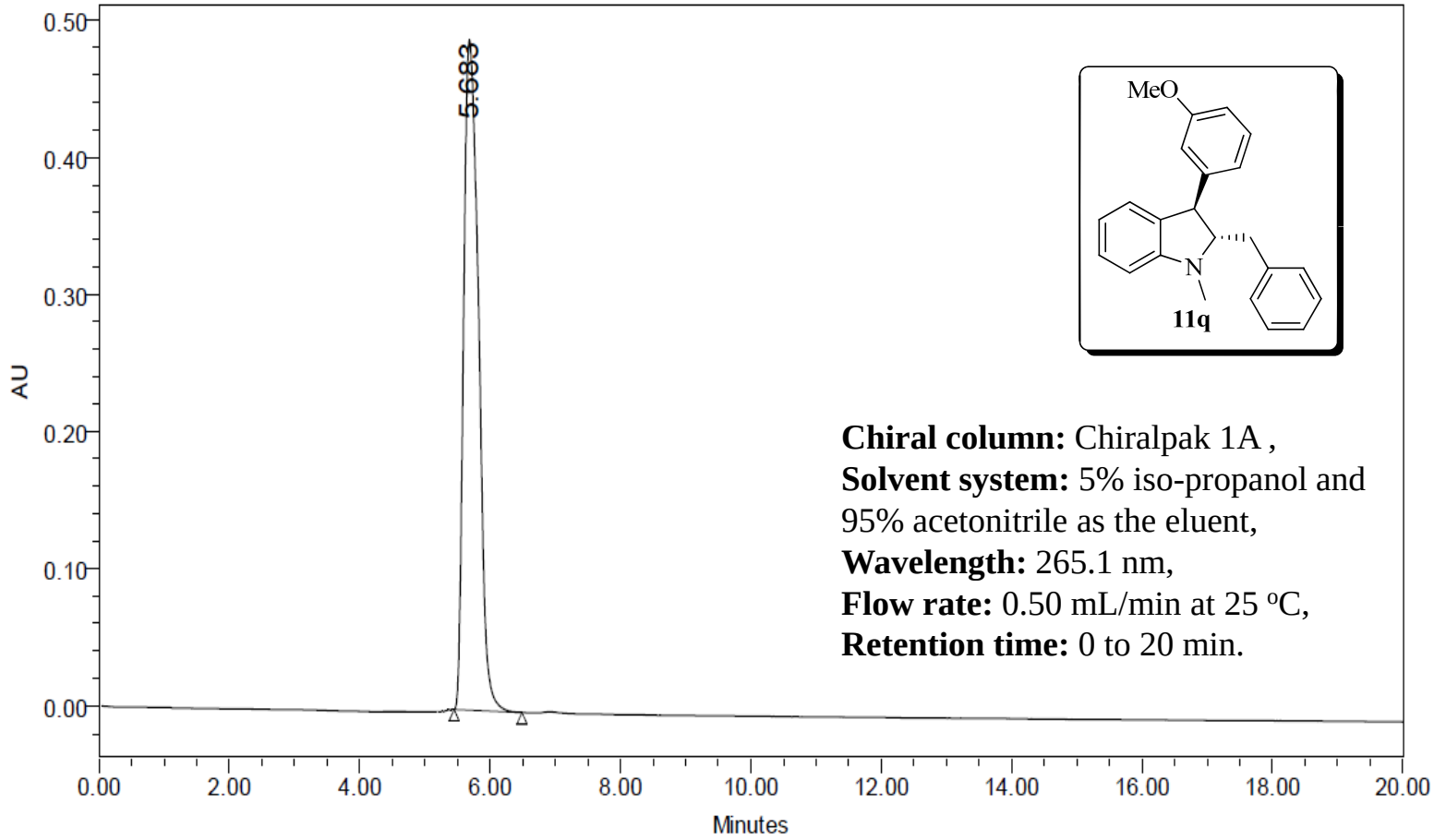


Figure 147: HPLC -Spectrum of **11q.**

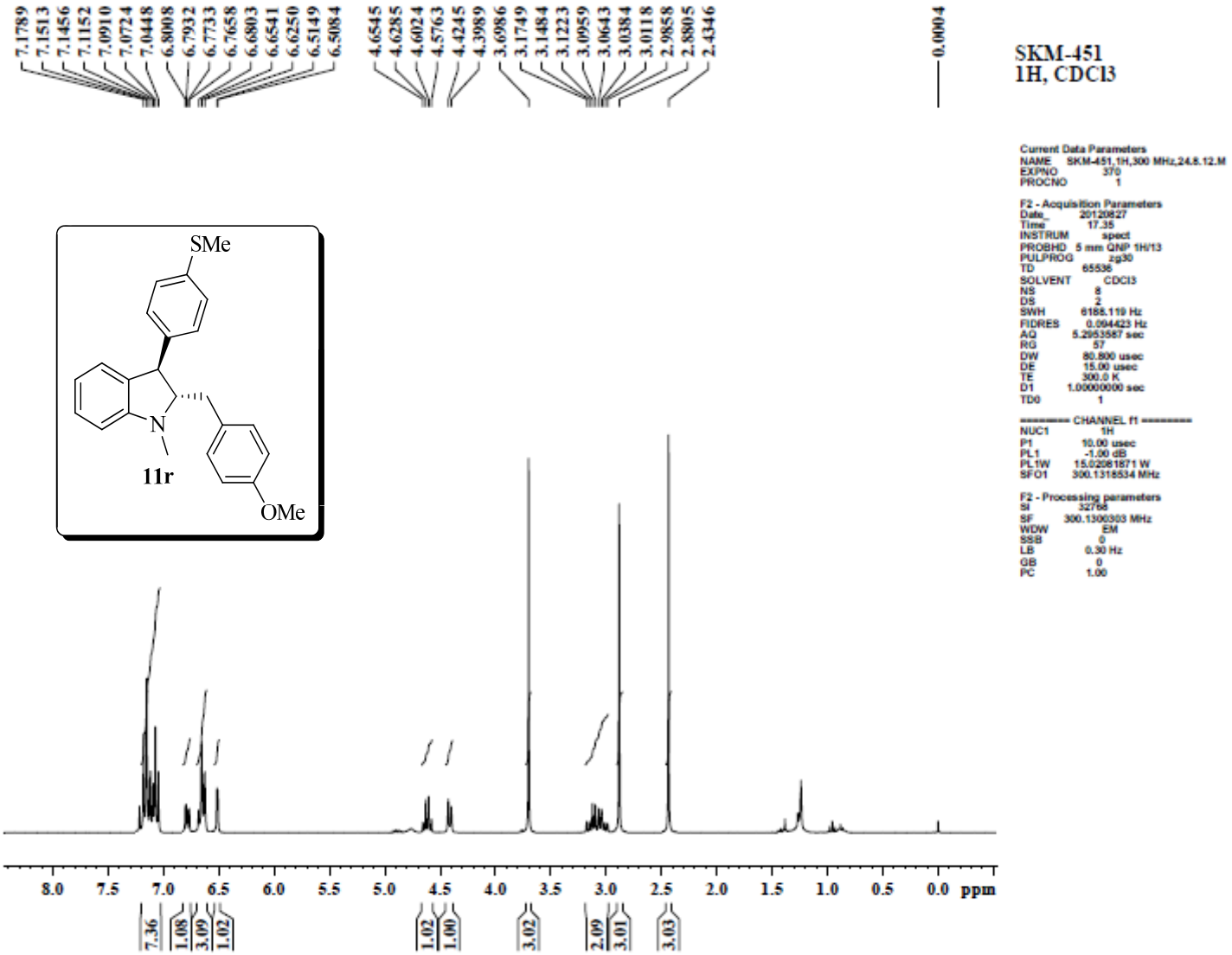


Figure 148: ^{1}H -NMR Spectrum of **11r.**

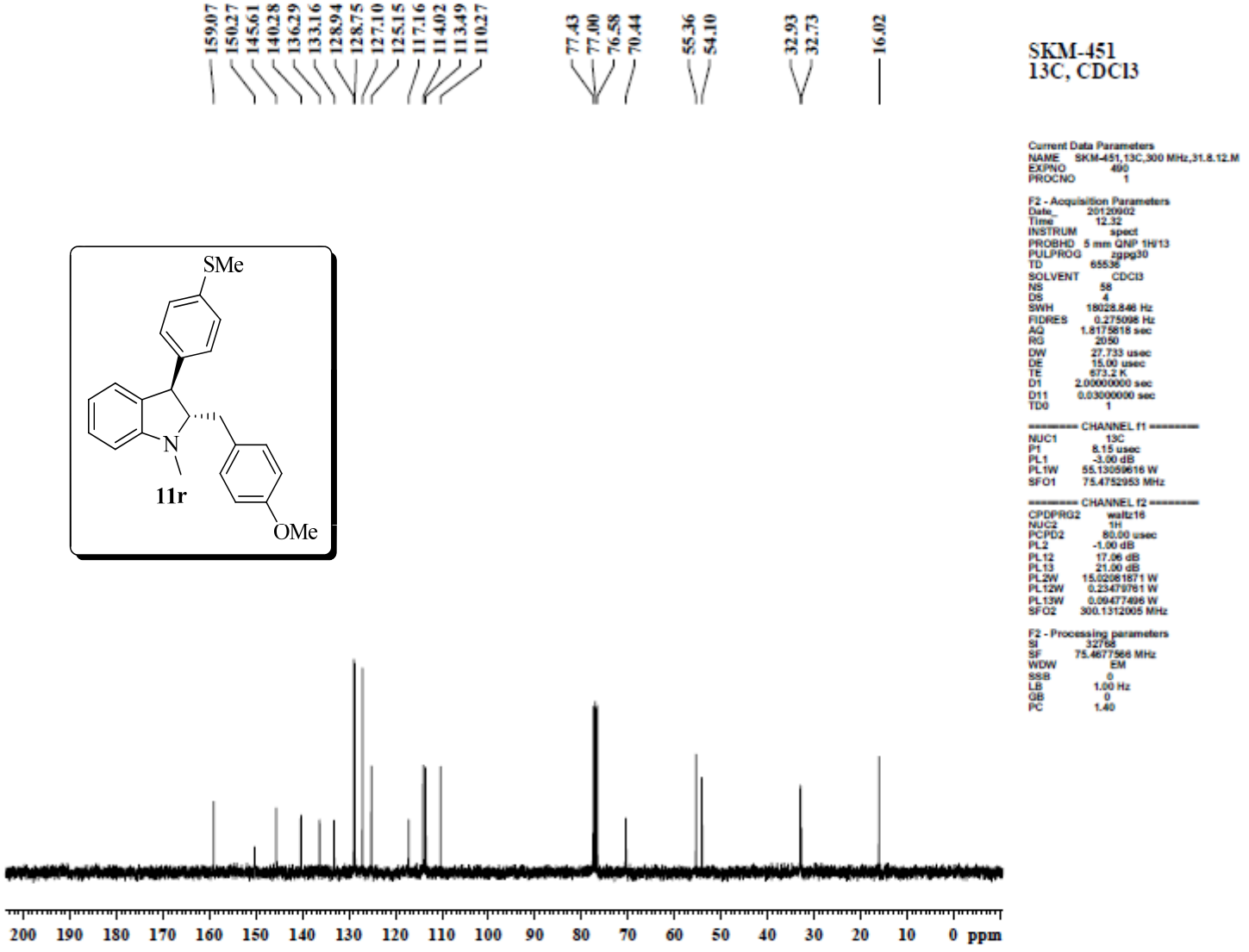


Figure 149: ^{13}C -NMR Spectrum of **11r.**

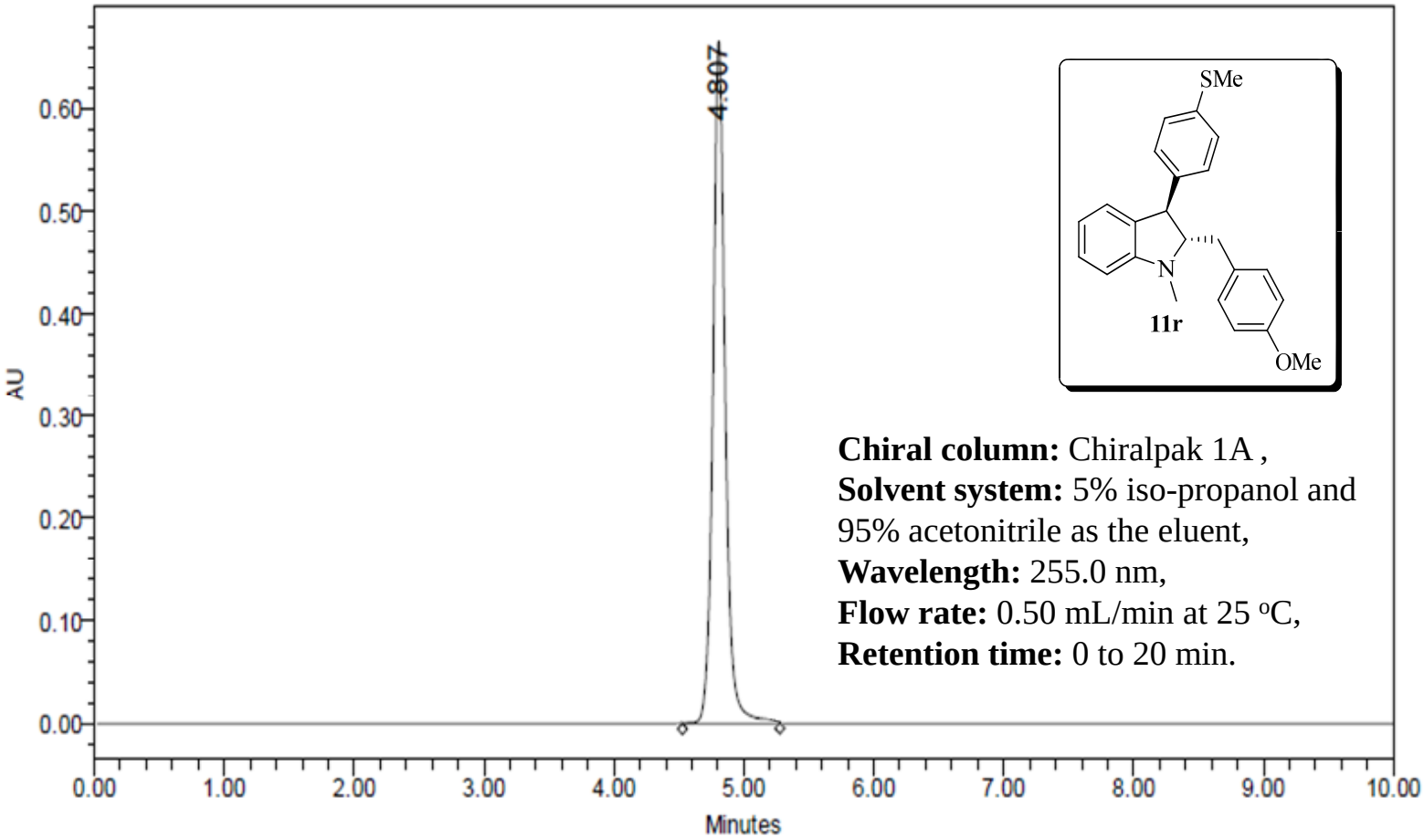
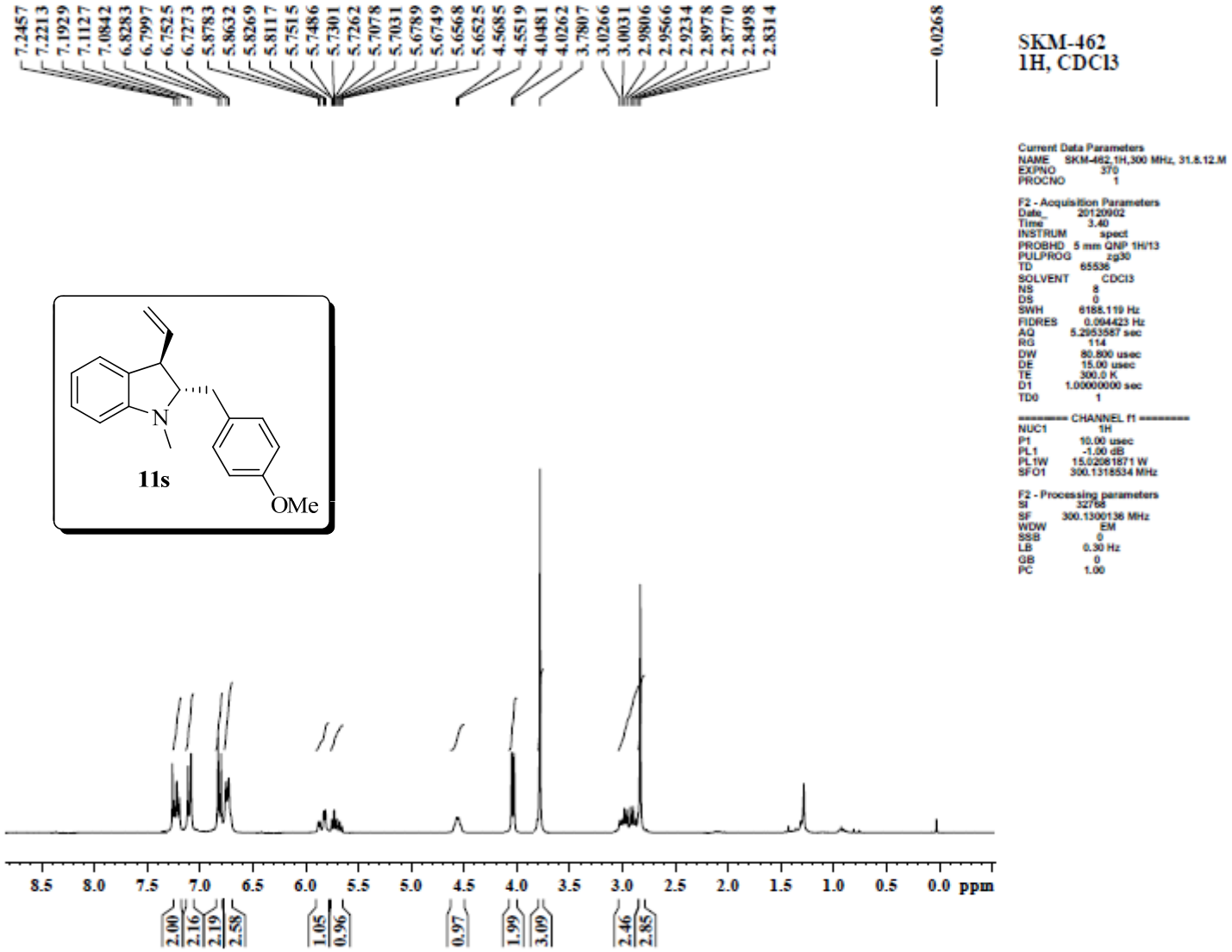


Figure 150: HPLC -Spectrum of **11r.**



Current Data Parameters
NAME SKM-462,1H,300 MHz, 31.8.12.M
EXPNO 370
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120902
Time 3.40
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 114
DW 80.800 usec
DE 15.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -1.00 dB
PL1W 15.02061871 W
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300136 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 151: ^{1}H -NMR Spectrum of **11s.**

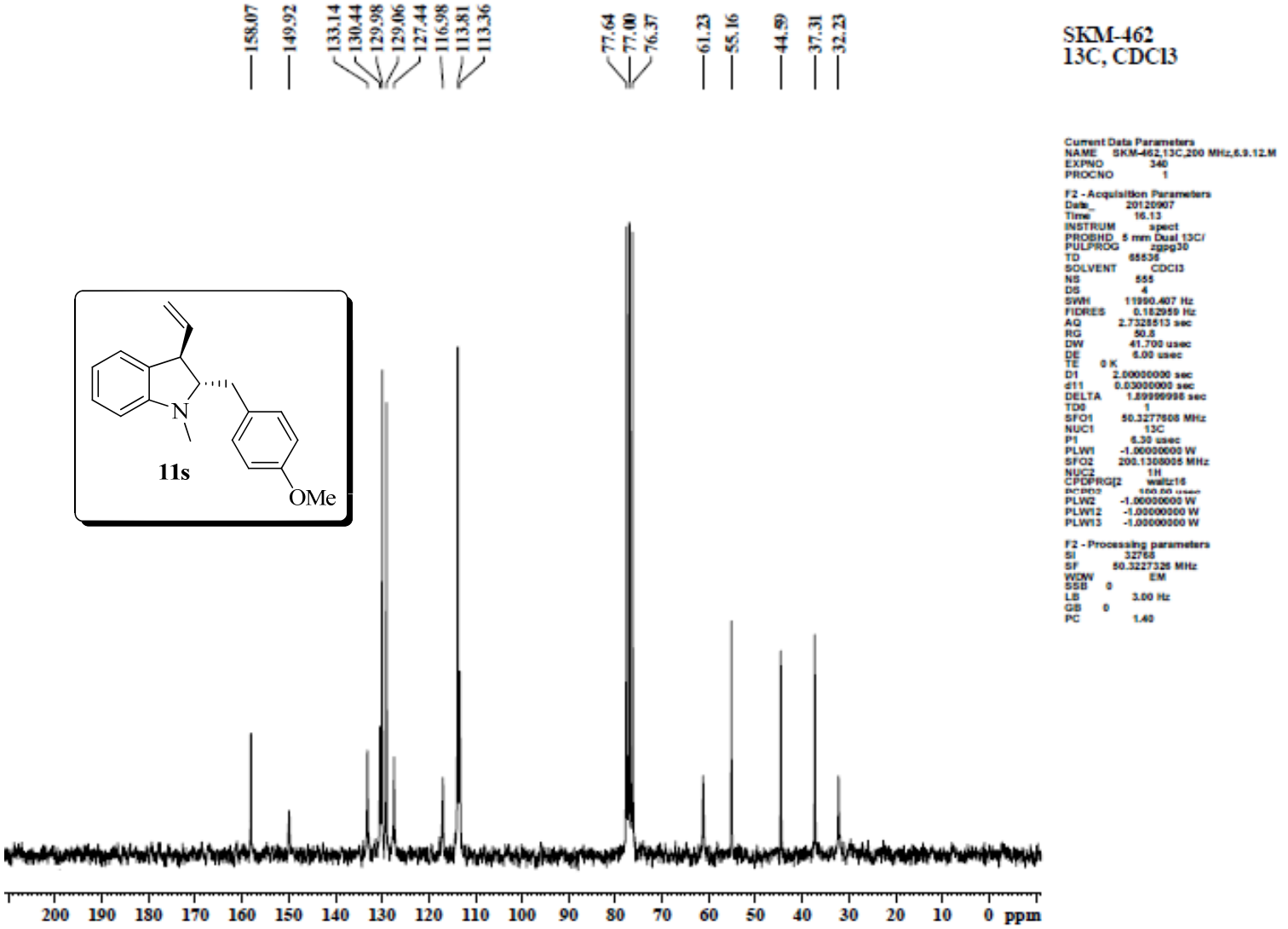
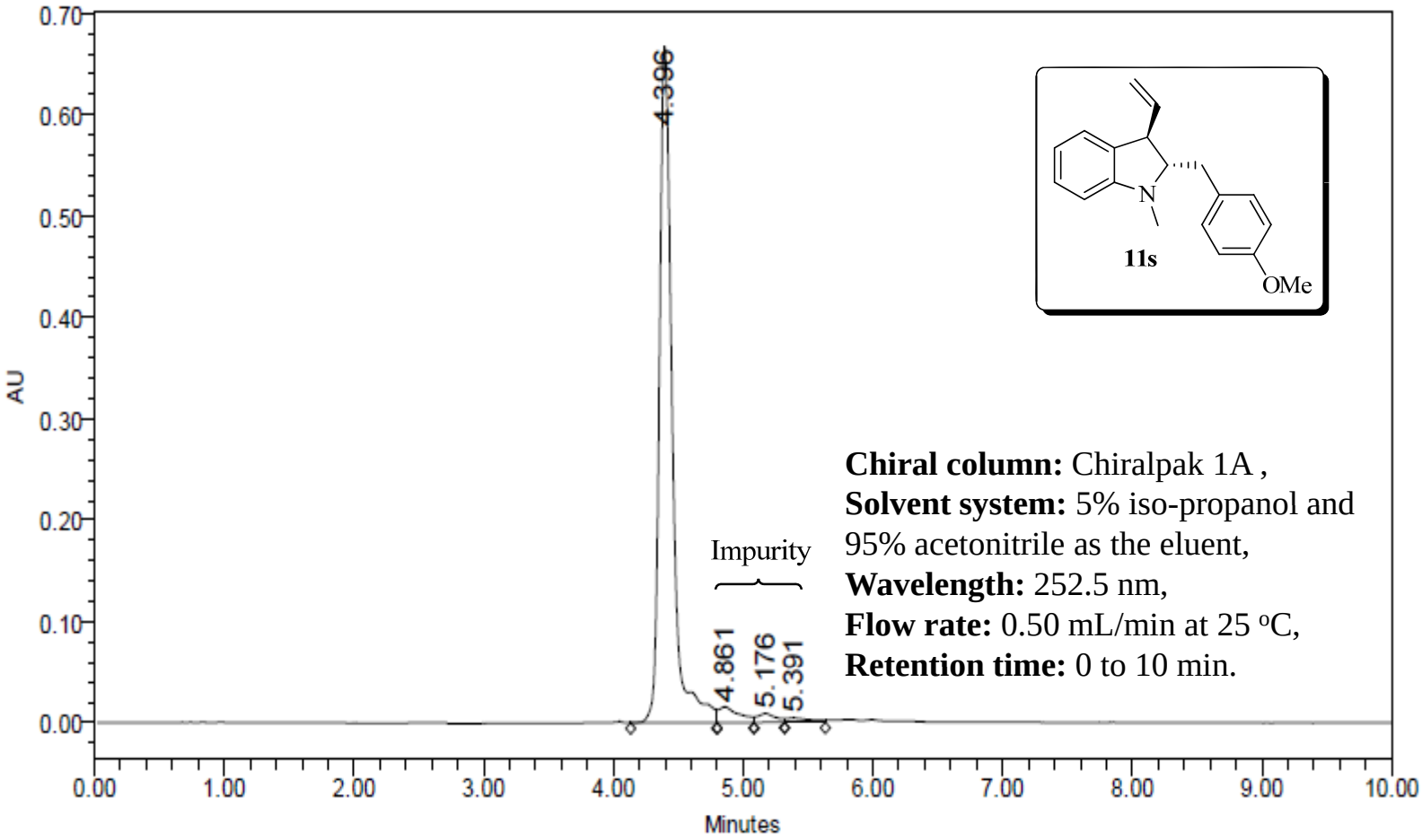


Figure 152: ^{13}C -NMR Spectrum of **11s.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **11s.**

Figure 153: HPLC -Spectrum of **11s.**

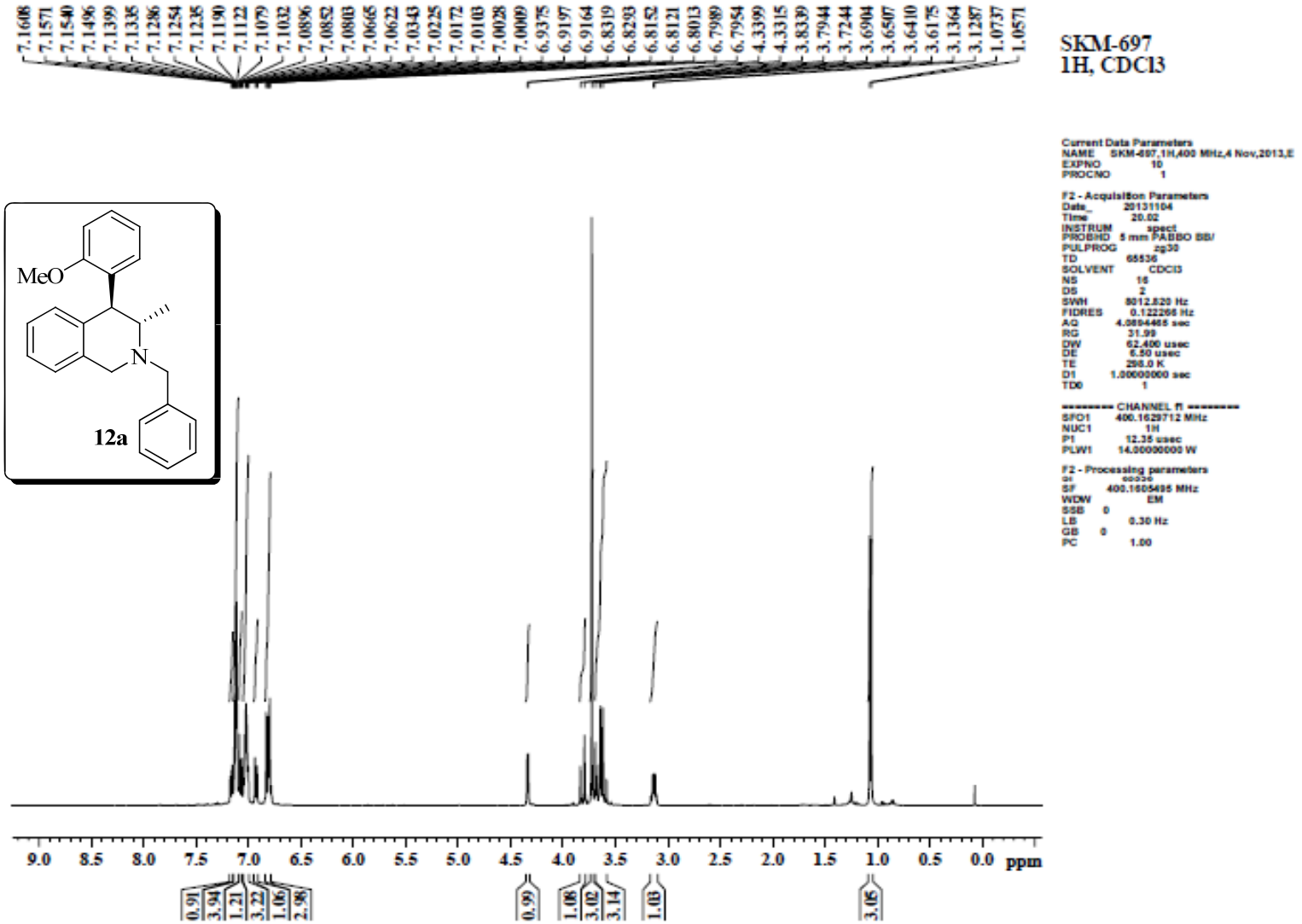


Figure 154: ^{1}H -NMR Spectrum of **12a.**

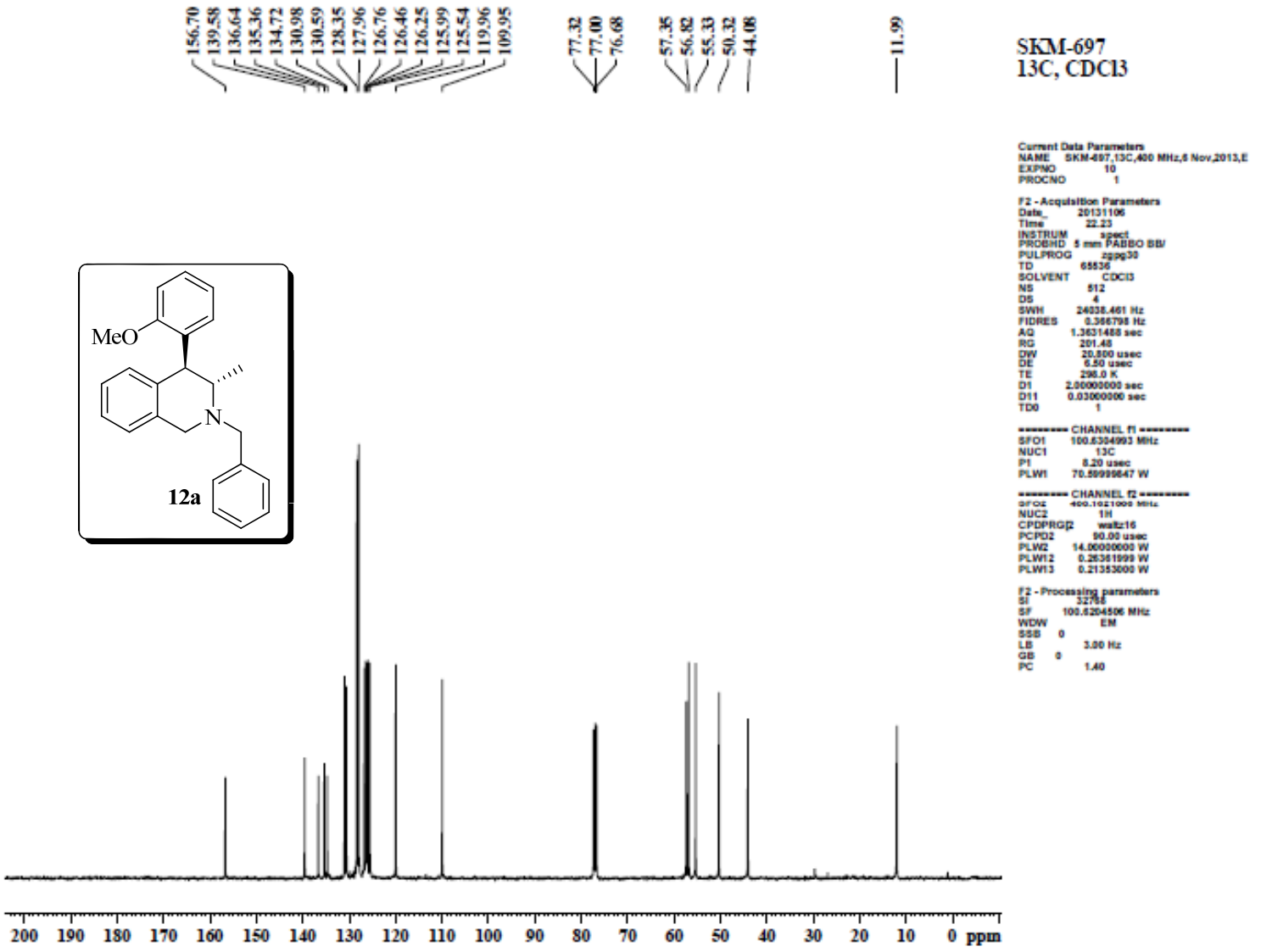


Figure 155: ^{13}C -NMR Spectrum of **12a.**

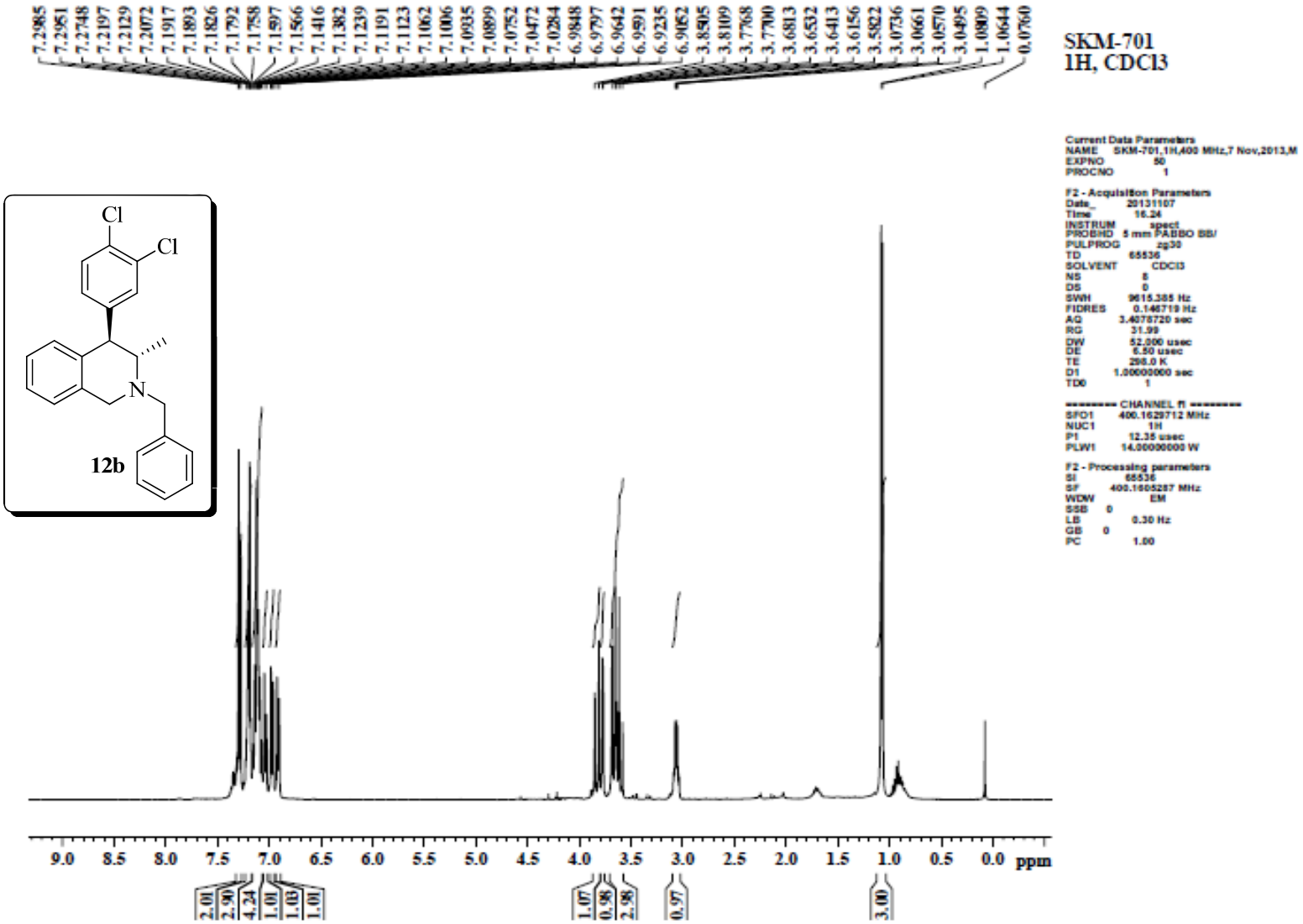


Figure 156: ^{1}H -NMR Spectrum of **12b.**

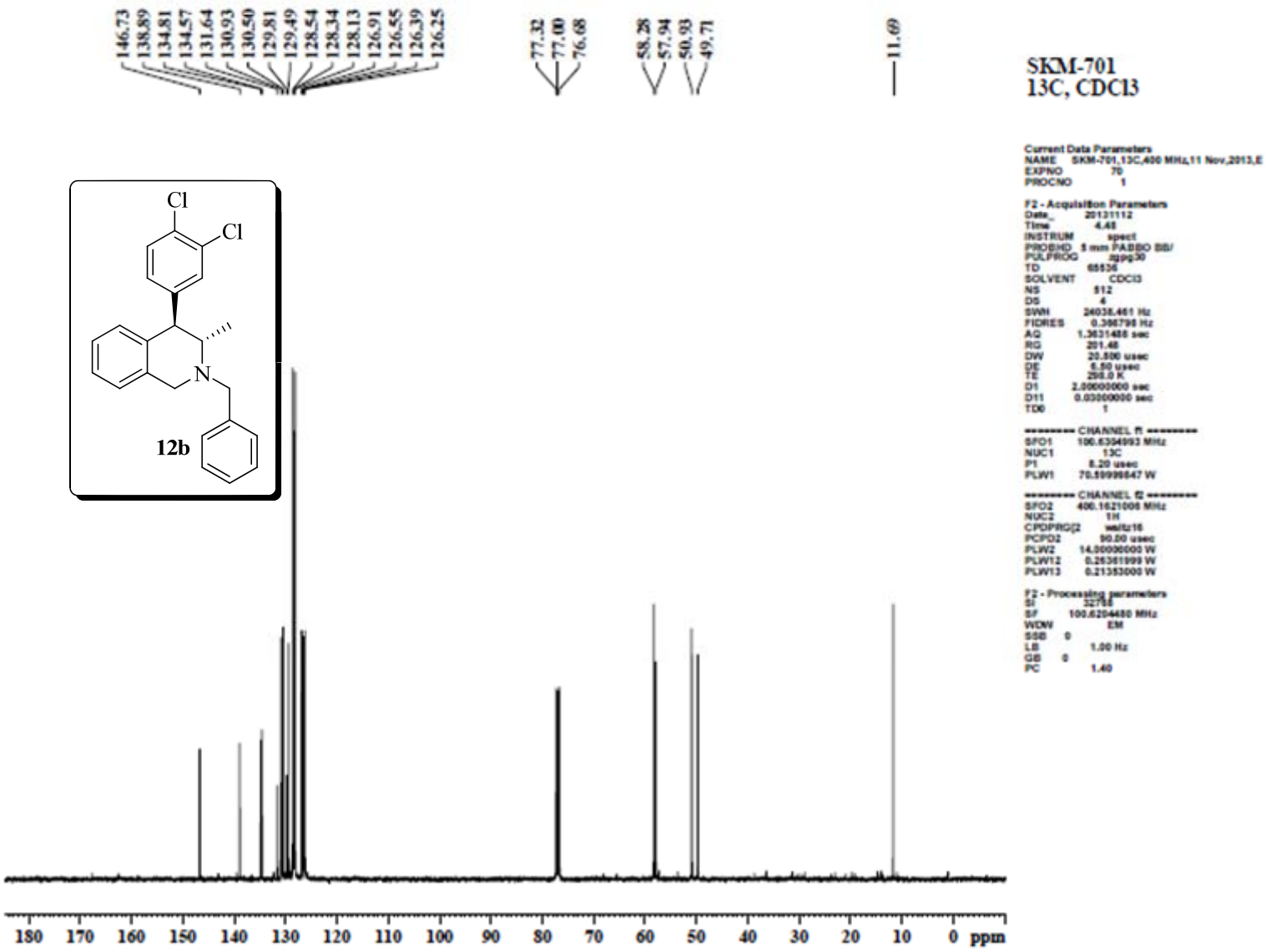
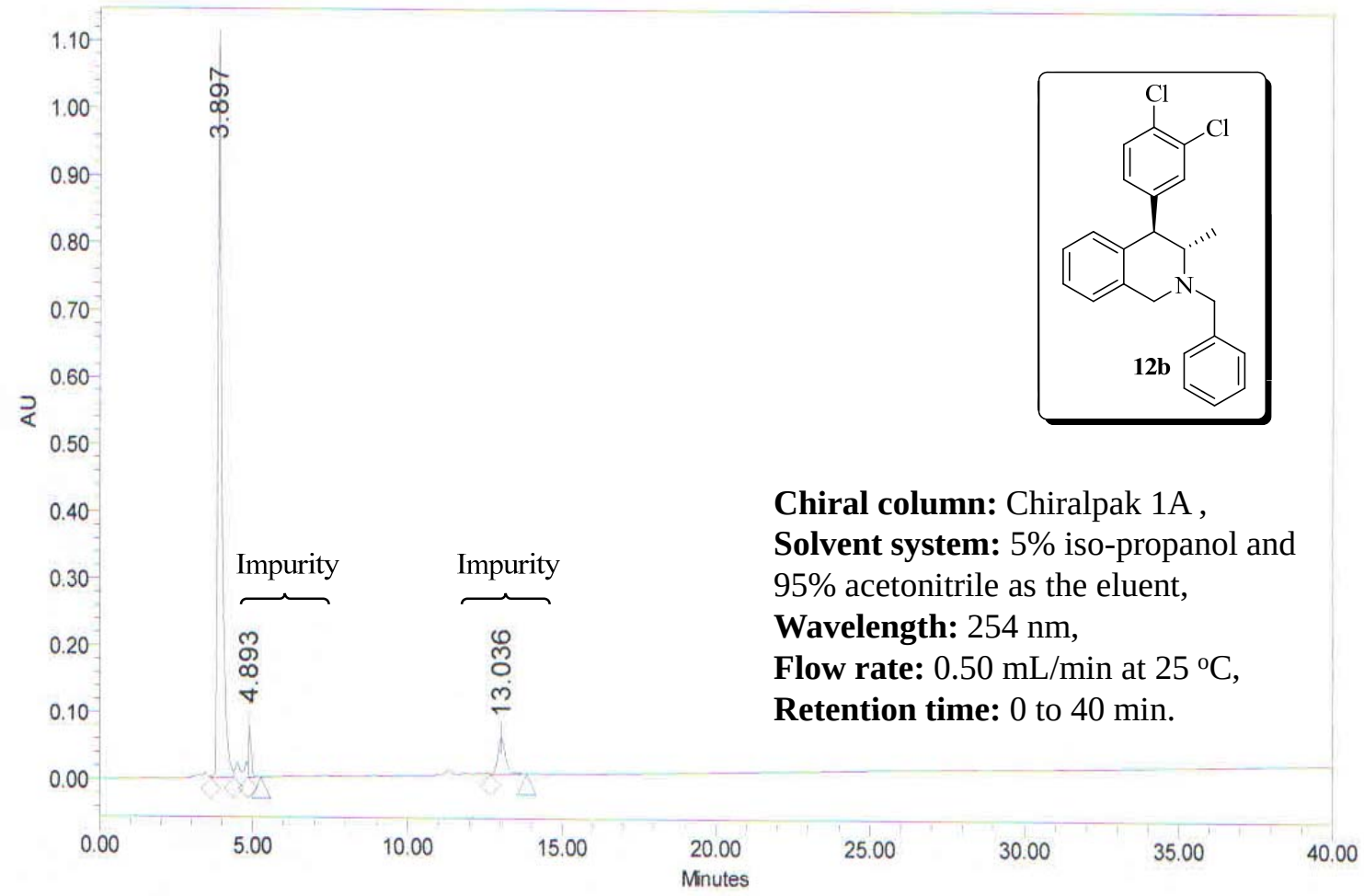


Figure 157: ^{13}C -NMR Spectrum of **12b.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **12b.**

Figure 158: HPLC -Spectrum of **12b.**

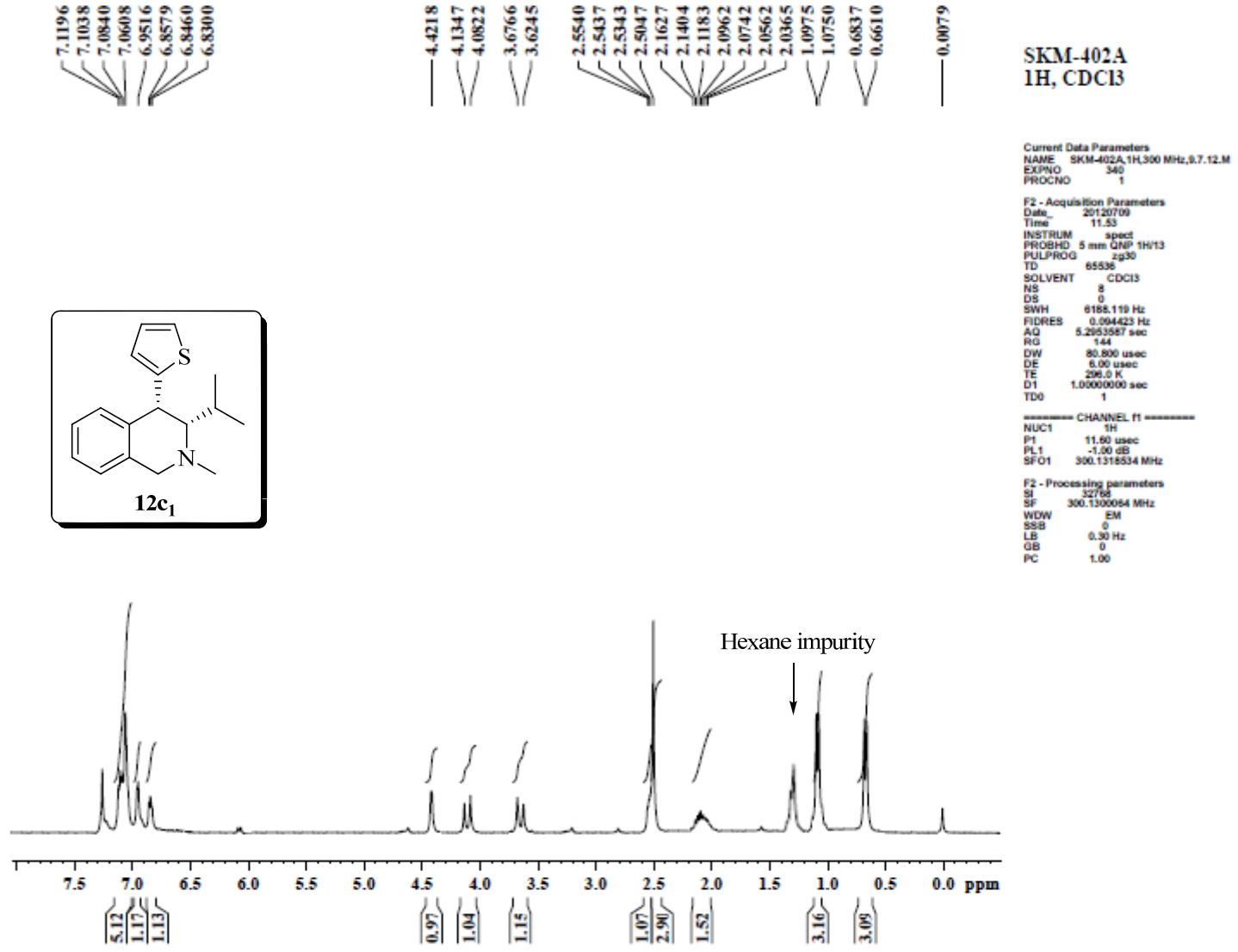


Figure 159: ^{1}H -NMR Spectrum of **$12c_1$.**

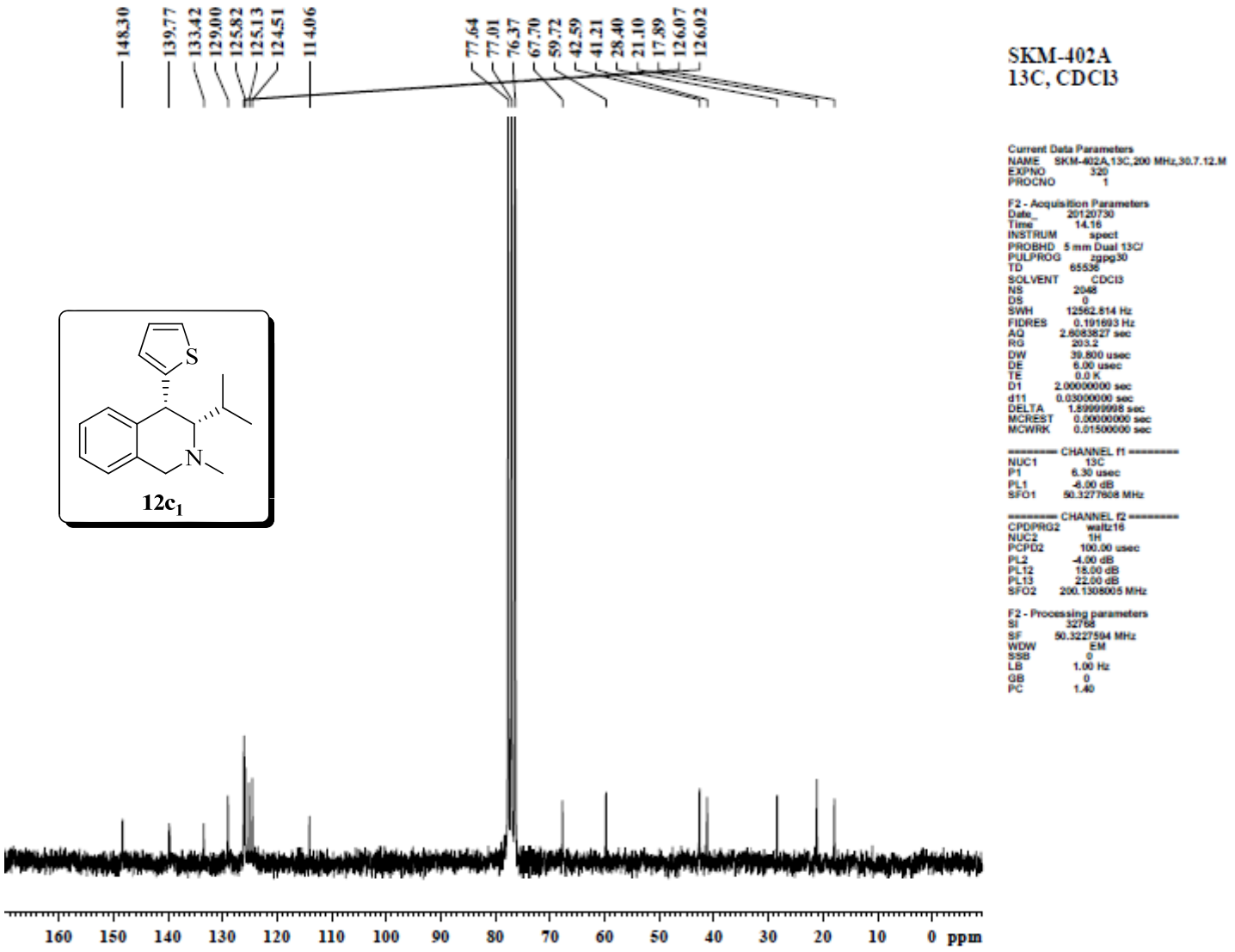


Figure 160: ^{13}C -NMR Spectrum of **12c$_1$.**

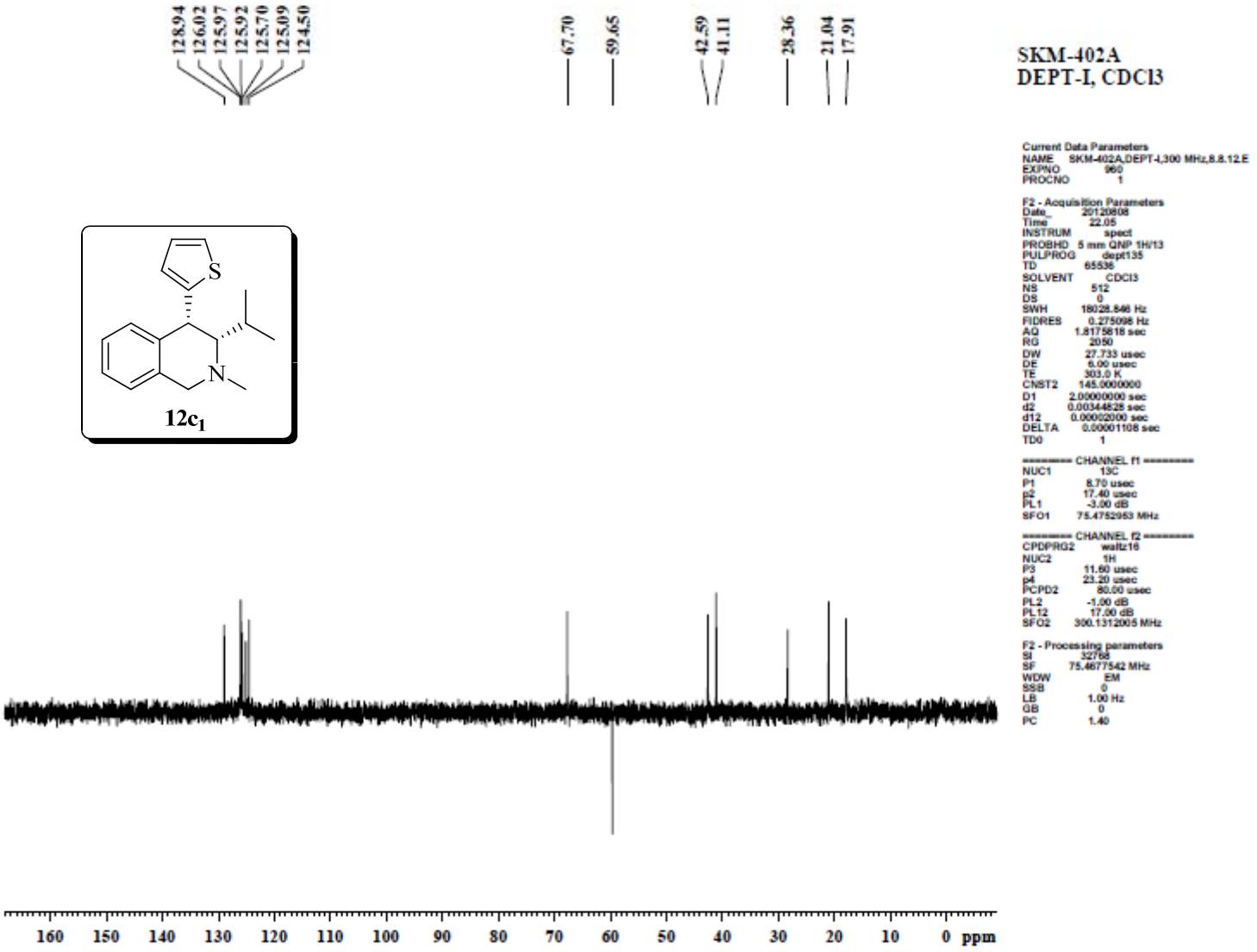


Figure 161: DEPT-I -Spectrum of **$12c_1$.**

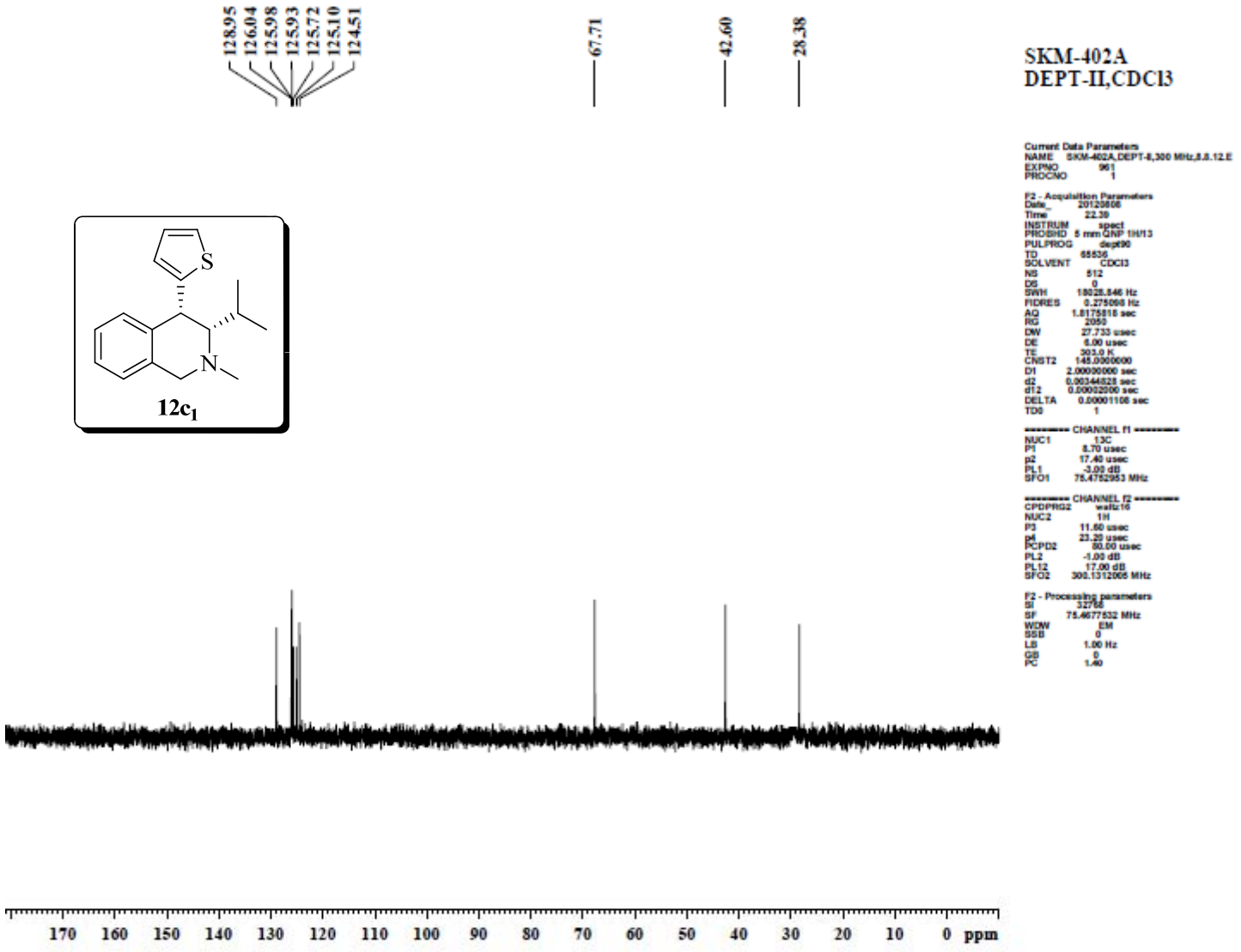
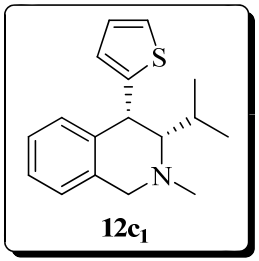
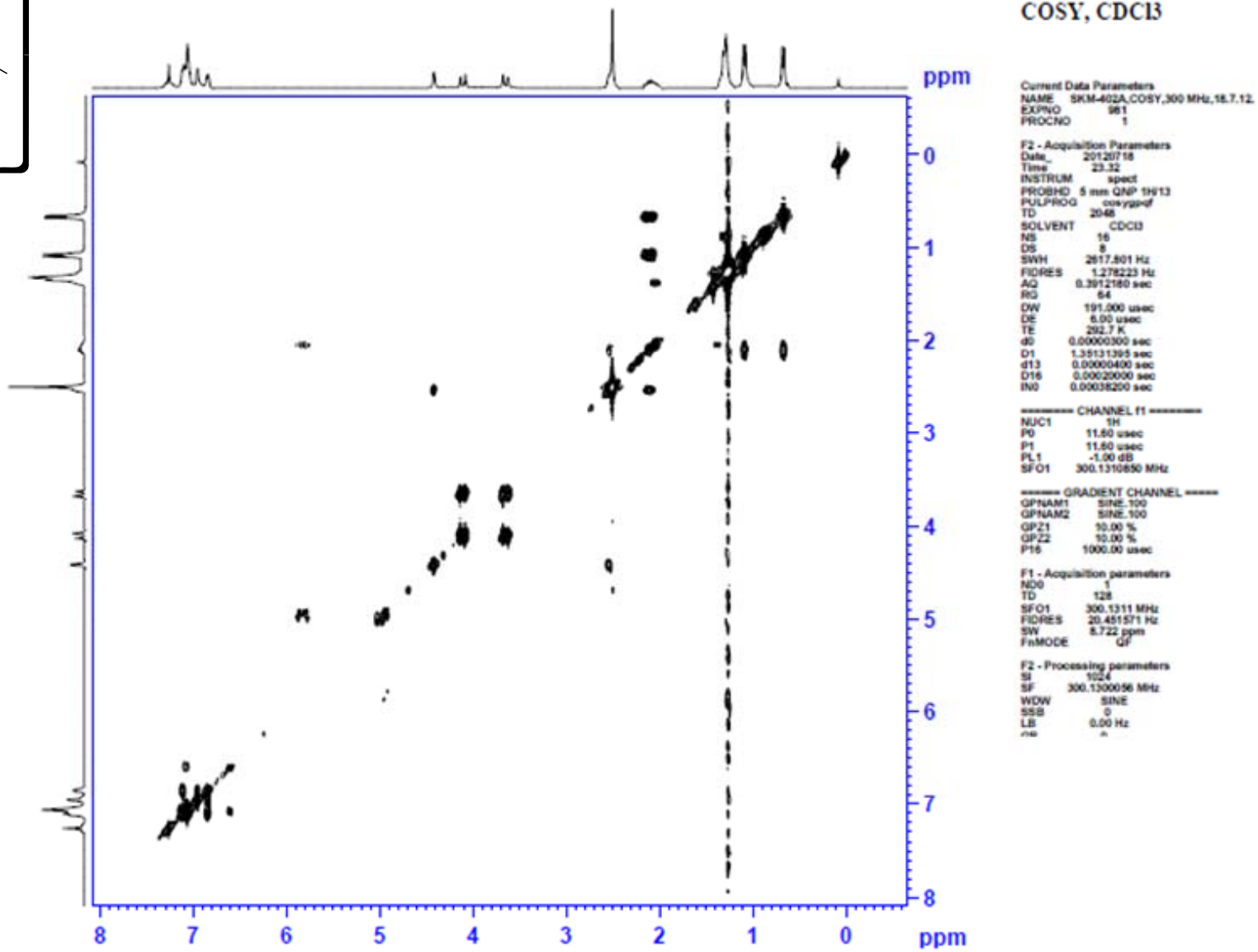


Figure 162: DEPT-II -Spectrum of **$12c_1$.**





SKM-402A
COSY, CDCl3

Current Data Parameters
NAME SKM-402A.COSY.300 MHz.18.7.12.
EXPNO 981
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120718
Time 23.32
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG cosygpqf
TD 2048
SOLVENT CDCl3
NS 16
DS 8
SWH 2617.801 Hz
FIDRES 1.278223 Hz
AQ 0.3912160 sec
RG 64
DW 191.000 usec
DE 6.00 usec
TE 292.7 K
d0 0.00000300 sec
D1 1.35131395 sec
d13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00038200 sec

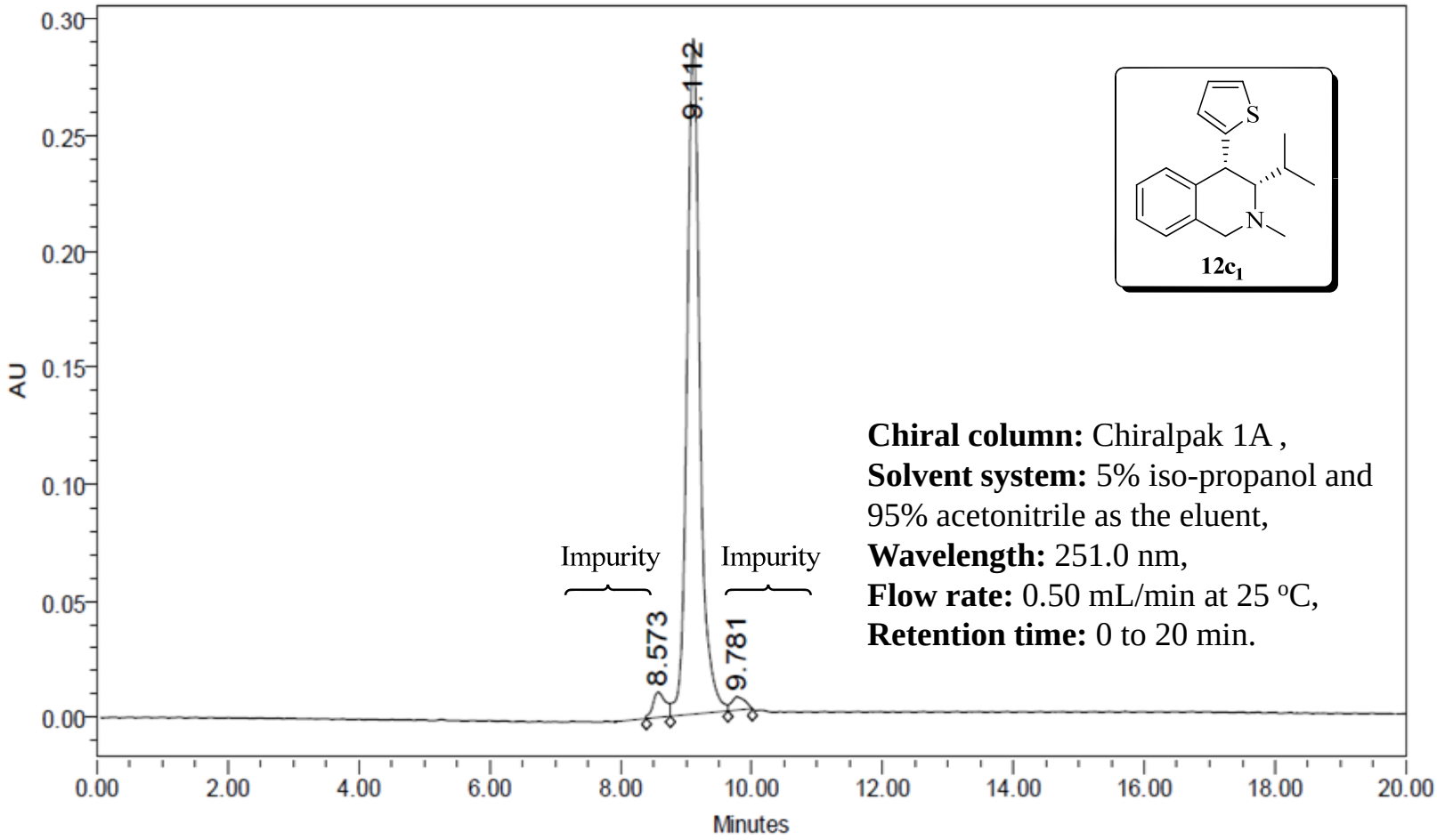
======== CHANNEL f1 ========
NUC1 1H
P0 11.60 usec
P1 11.60 usec
PL1 -1.00 dB
SFO1 300.1310850 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 10.00 %
GPZ2 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
ND0 1
TD 128
SFO1 300.1311 MHz
FIDRES 20.451571 Hz
SW 8.722 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 300.1300056 MHz
WDW SINE
SSB 0
LB 0.00 Hz

Figure 163: COSY - Spectrum of **$12c_1$.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **$12c_1$.**

Figure 164: HPLC -Spectrum of **$12c_1$.**

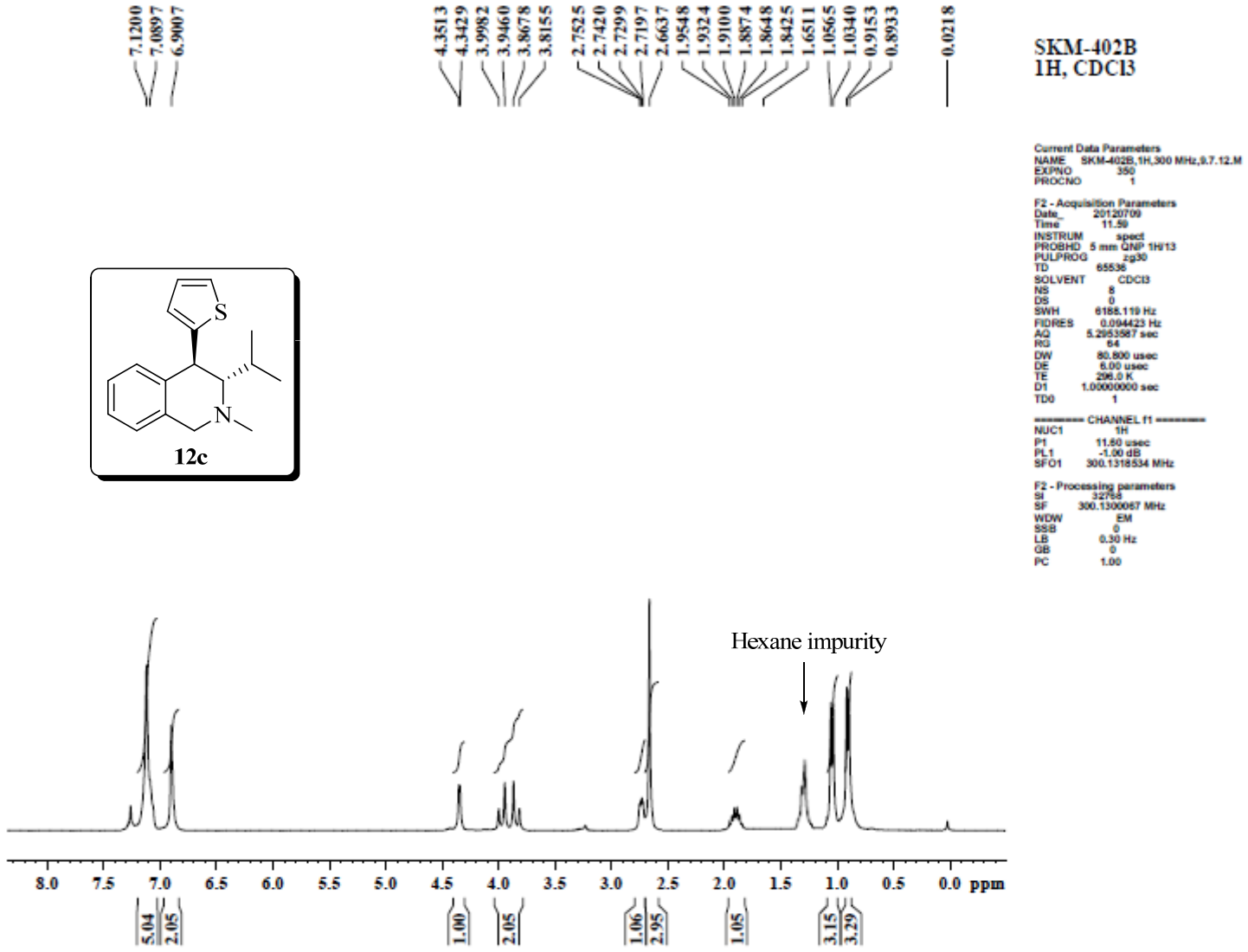


Figure 165: ^{1}H -NMR Spectrum of **12c.**

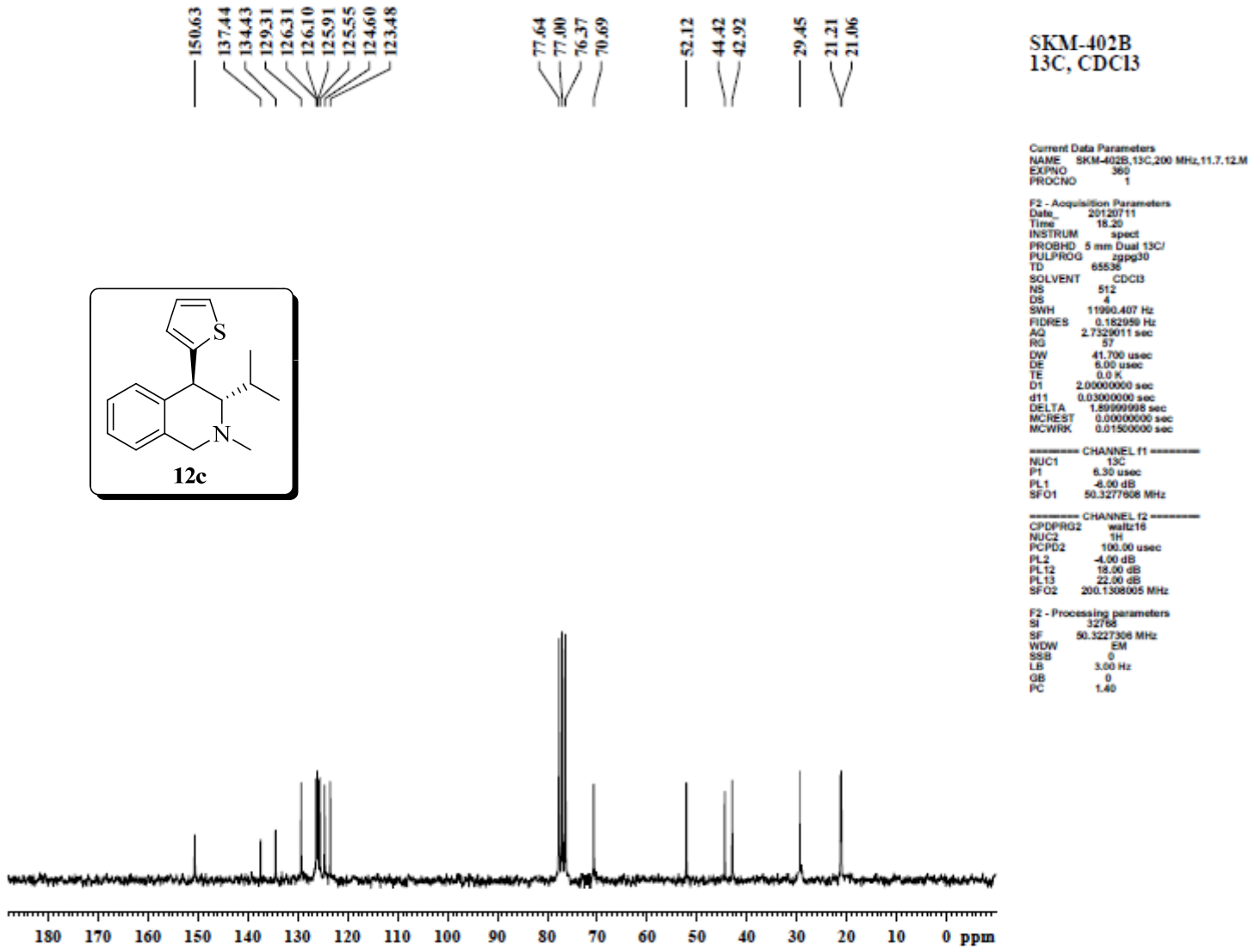


Figure 166: ^{13}C -NMR Spectrum of **12c.**

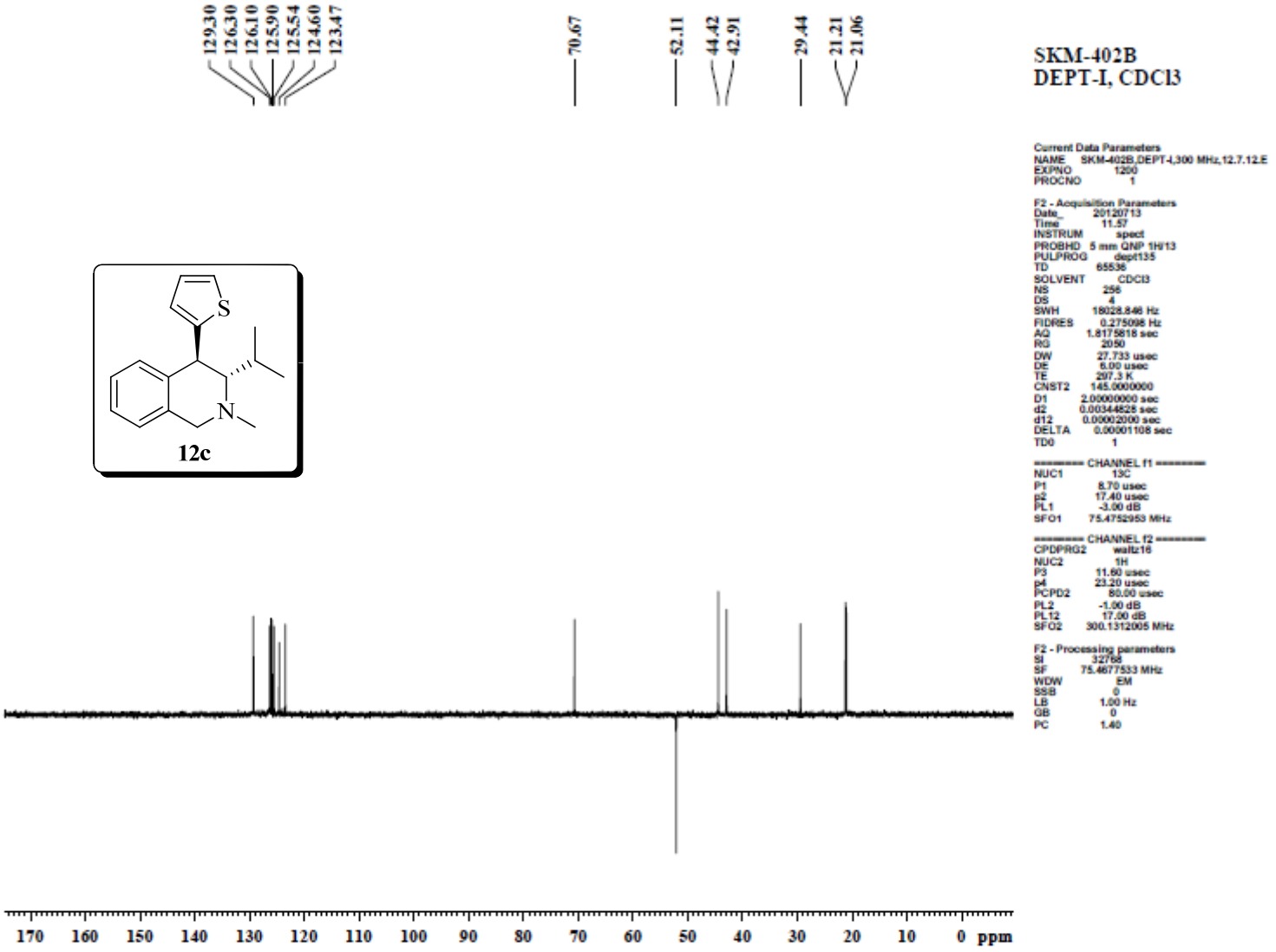


Figure 167: DEPT-I -Spectrum of **12c.**

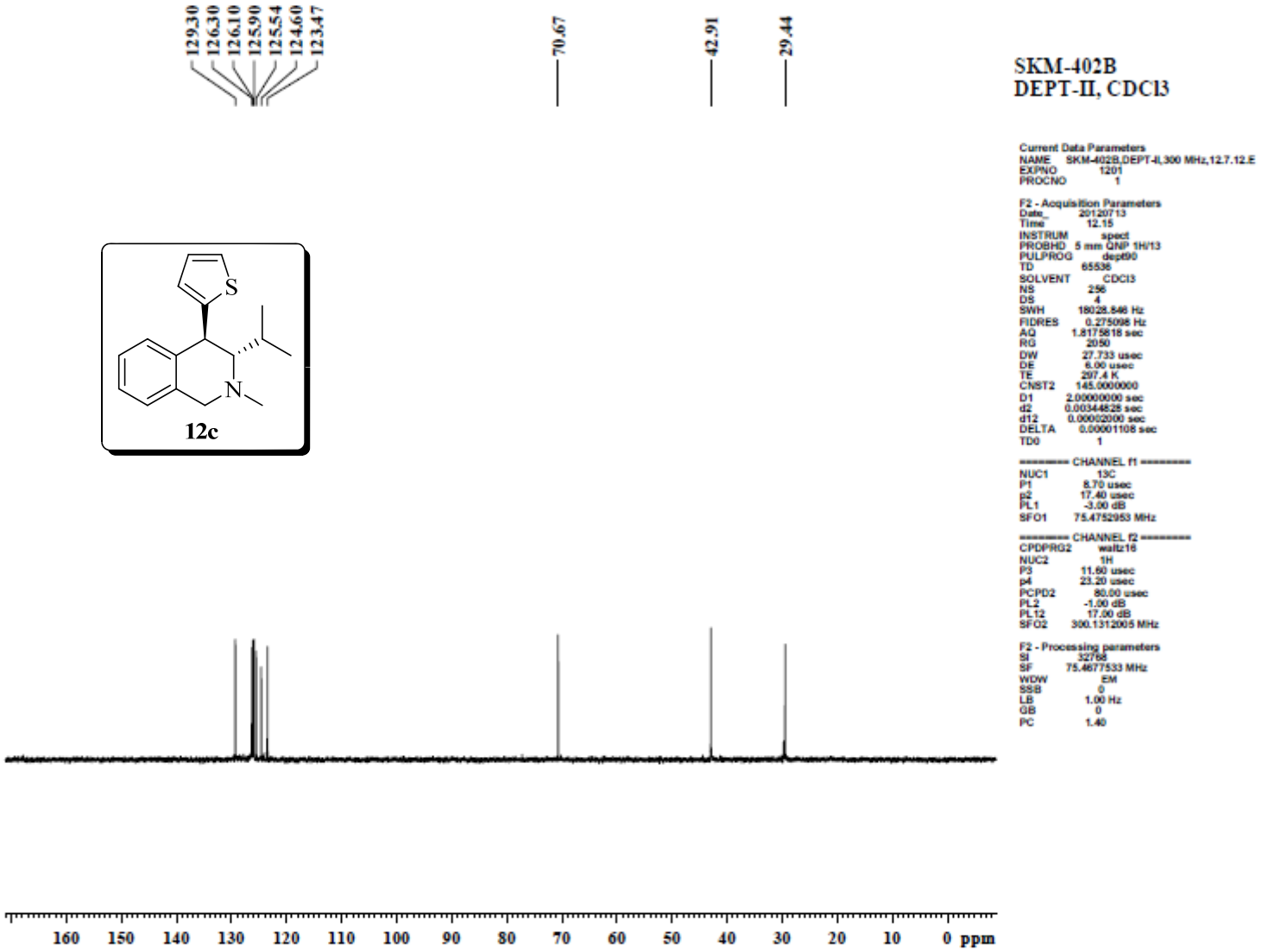


Figure 168: DEPT-II -Spectrum of **12c.**

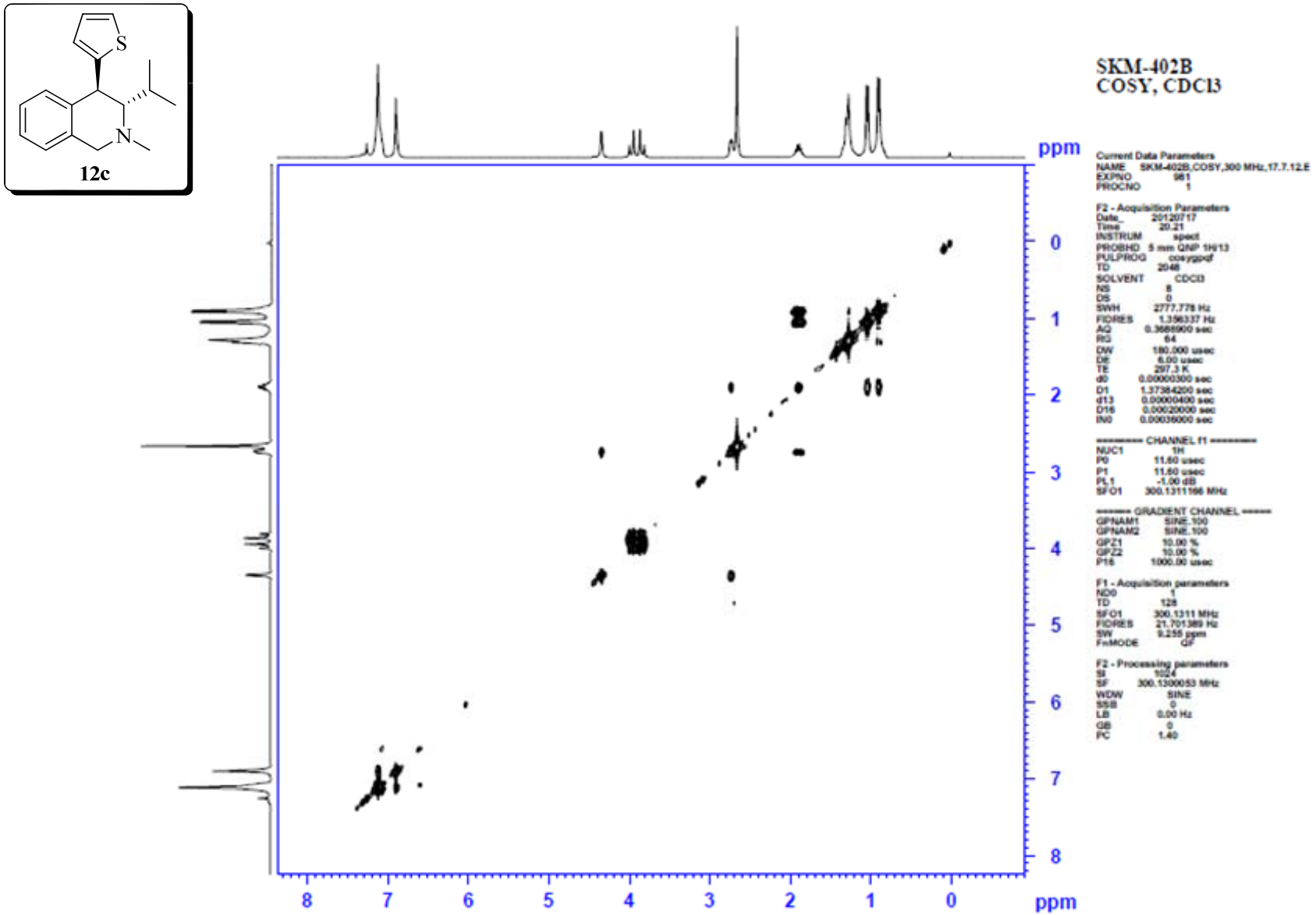


Figure 169: COSY -Spectrum of **12c.**

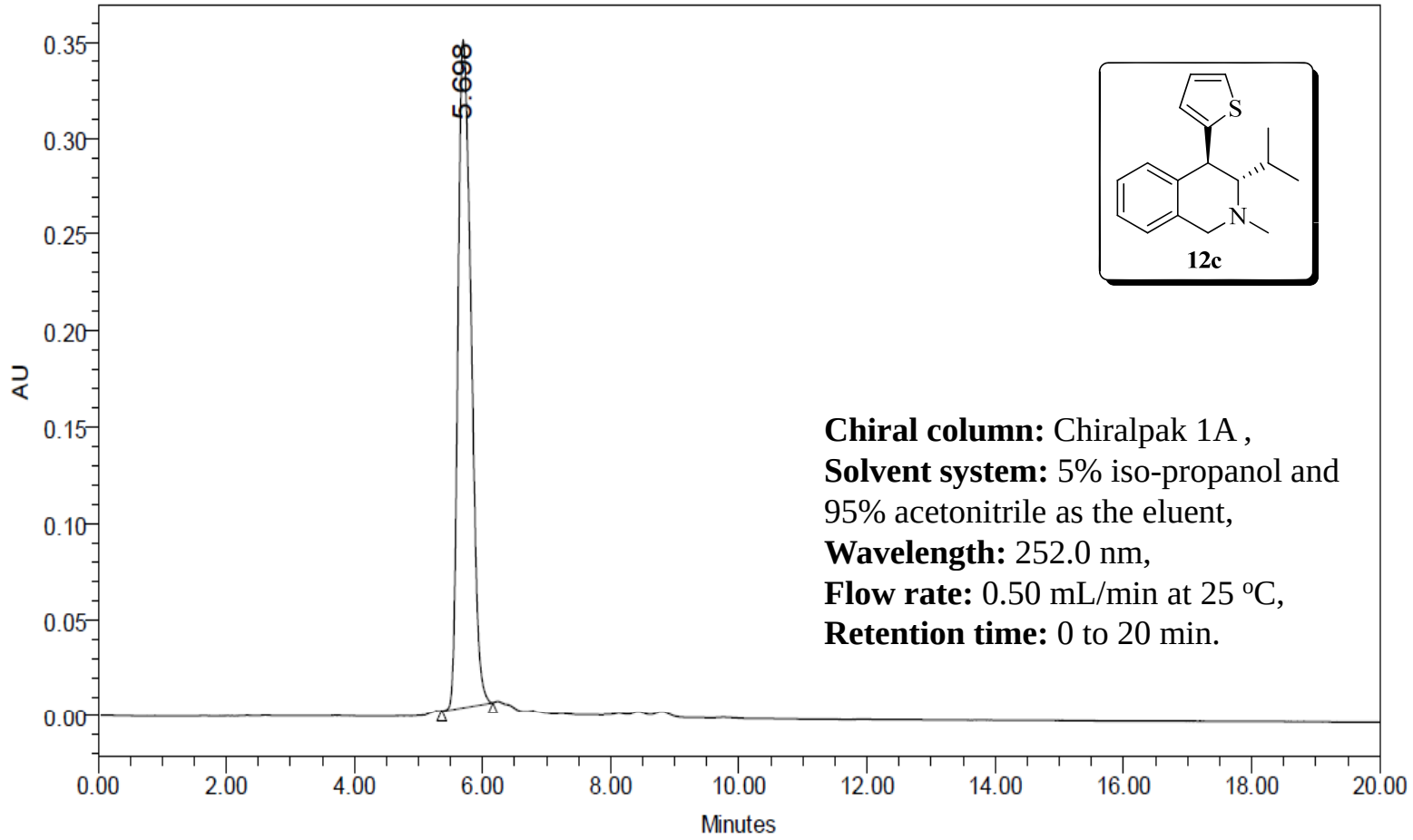


Figure 170: HPLC -Spectrum of **12c.**

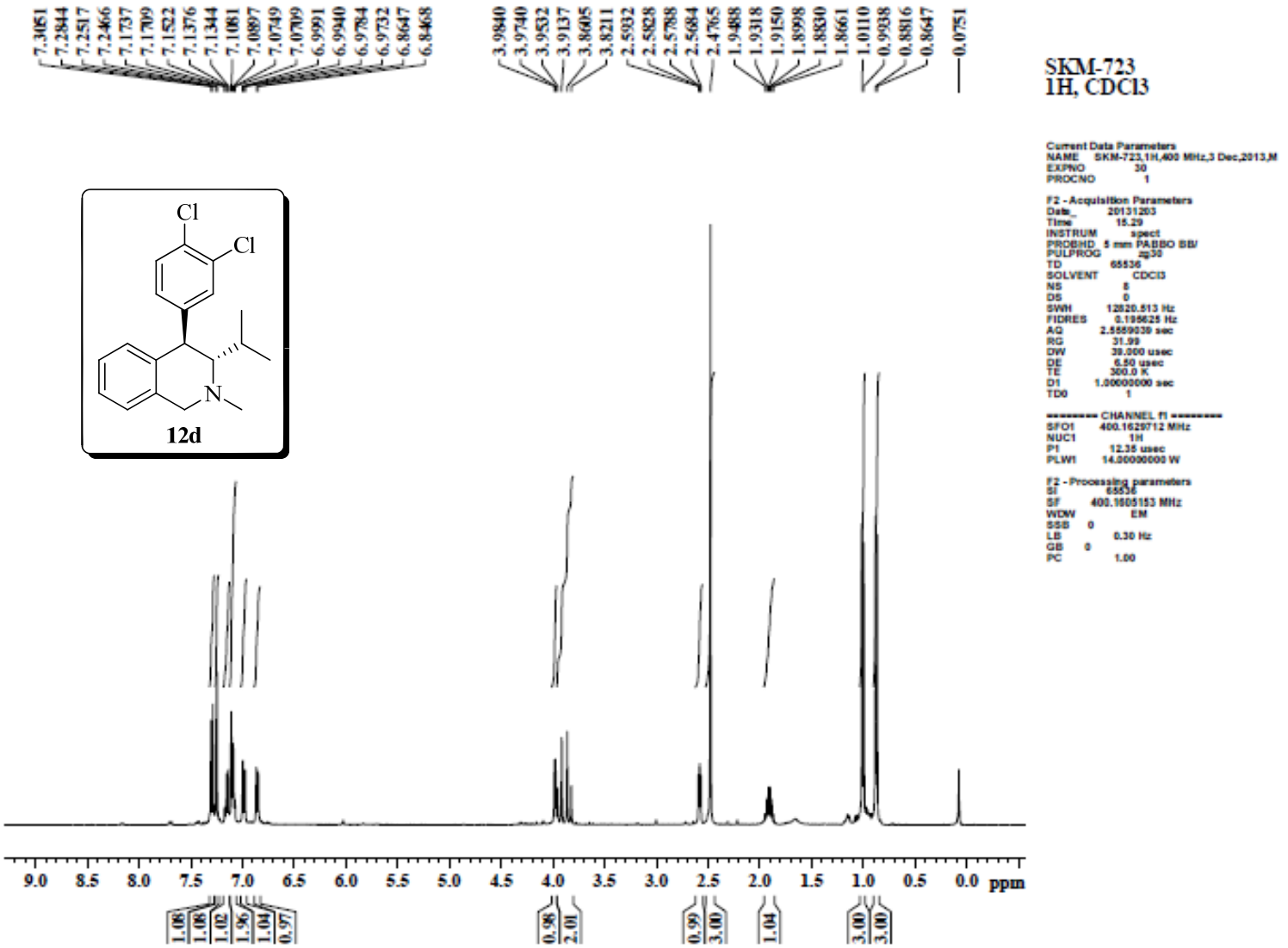


Figure 171: ^{1}H -NMR Spectrum of **12d.**

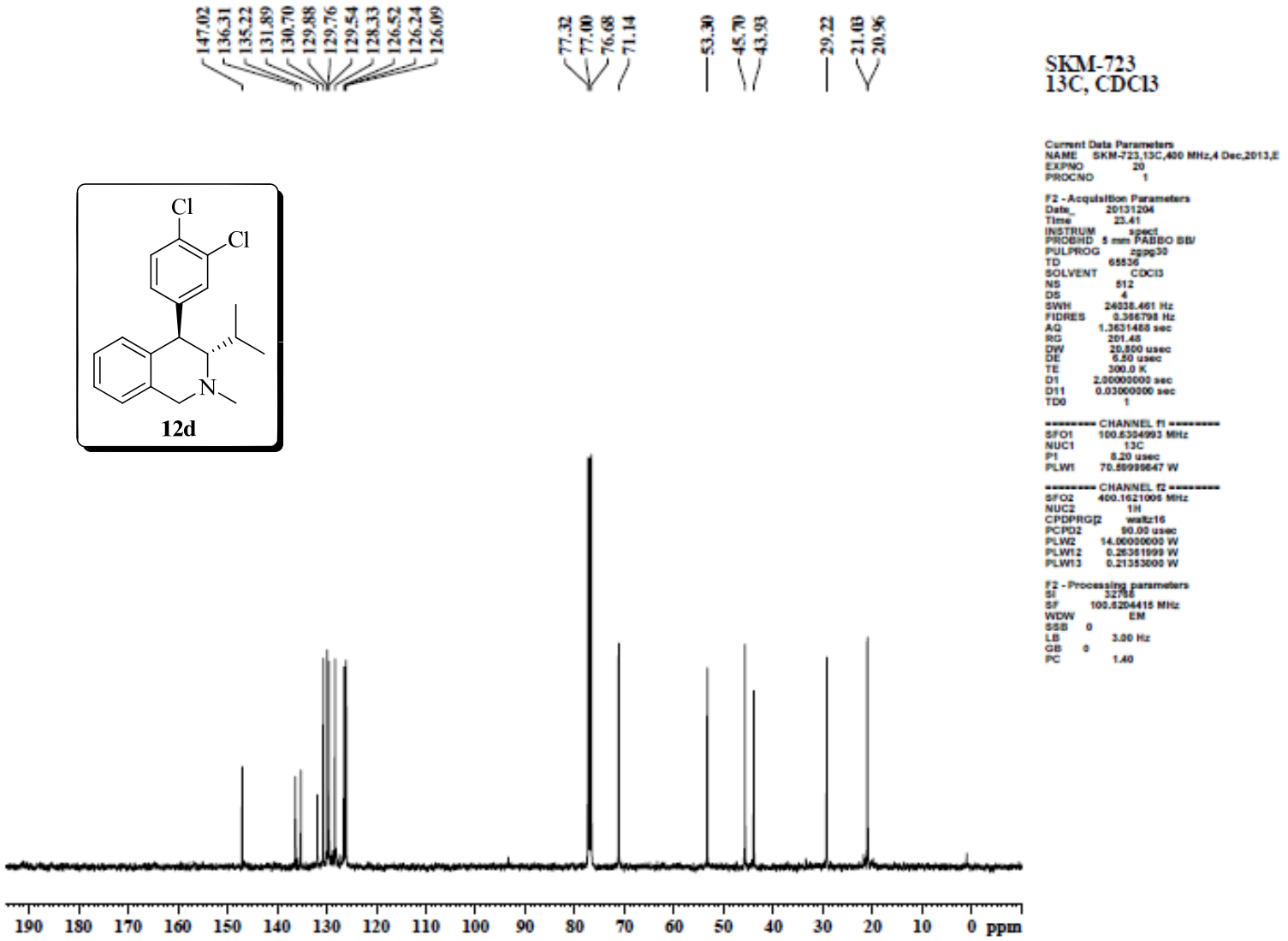


Figure 172: ^{13}C -NMR Spectrum of **12d.**

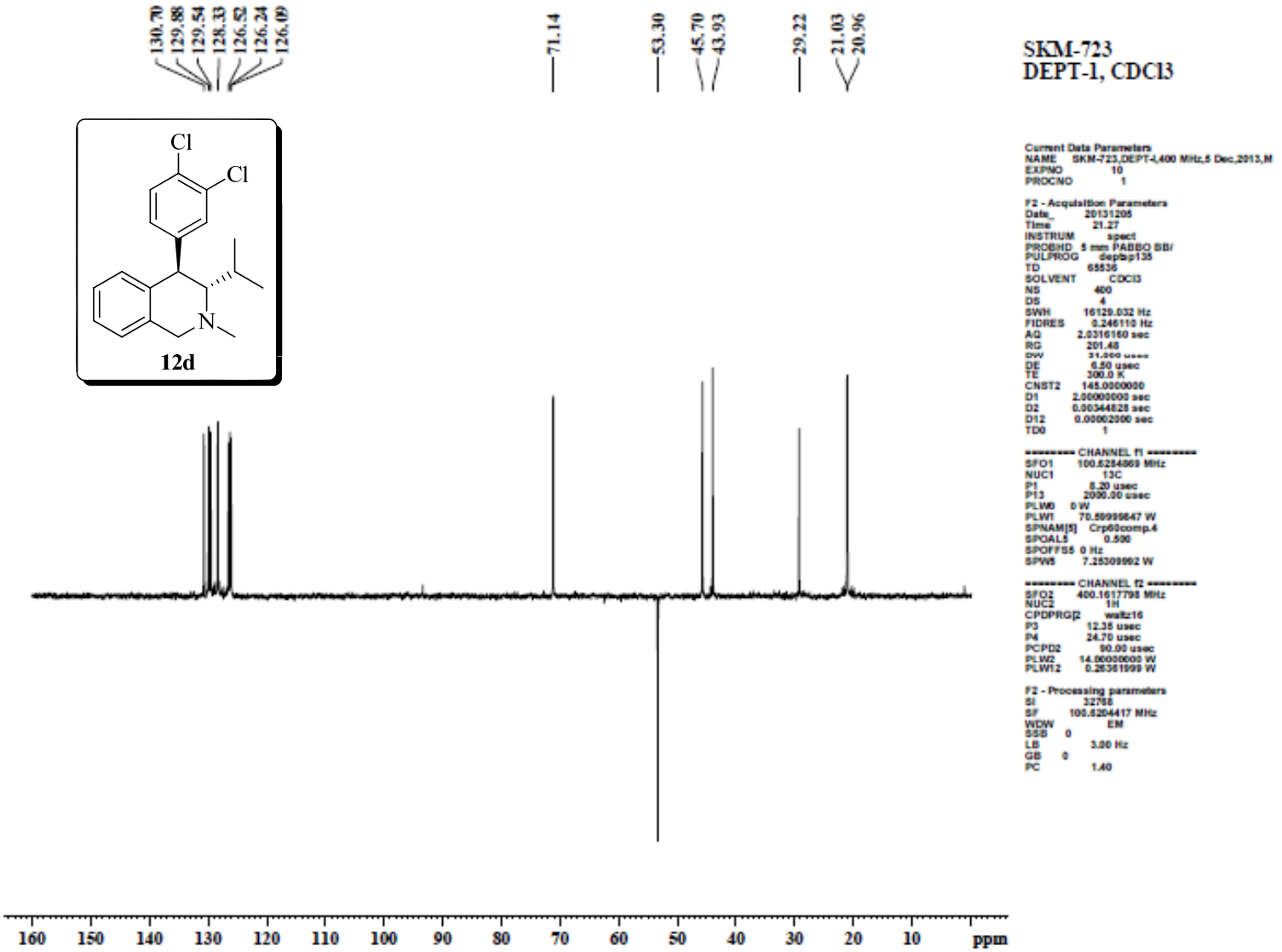


Figure 173: DEPT-I -Spectrum of **12d.**

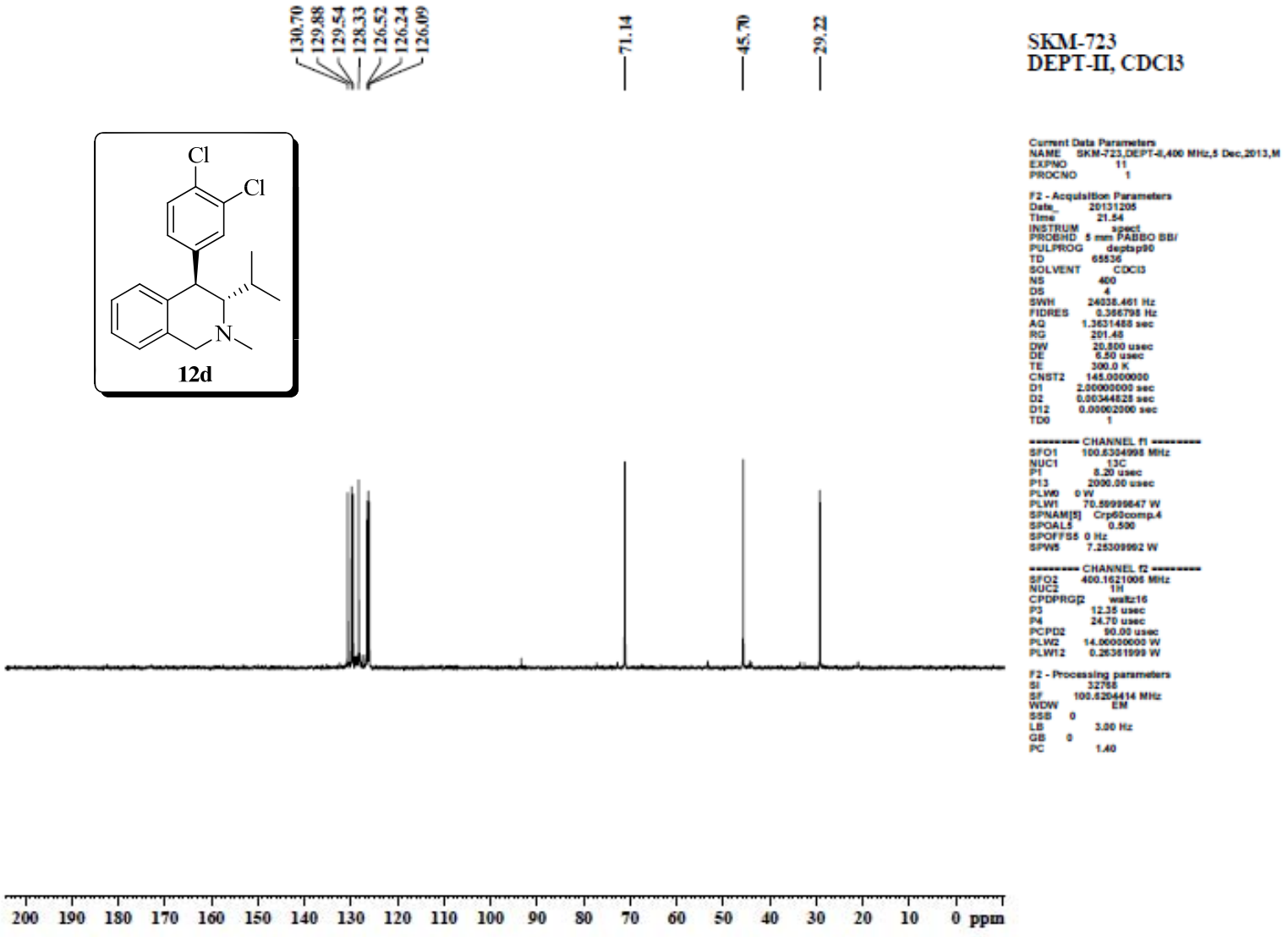


Figure 174: DEPT-II -Spectrum of **12d.**

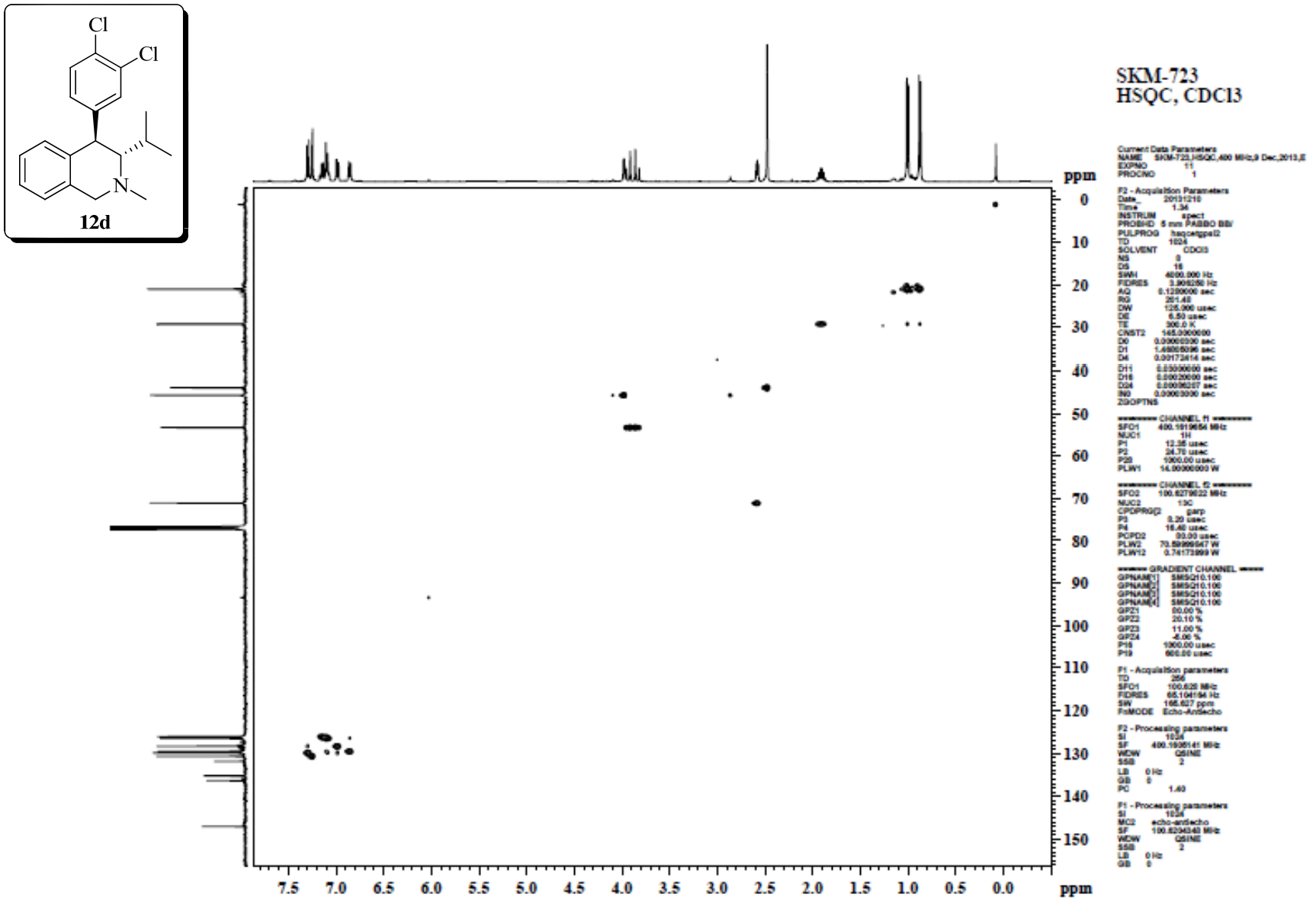


Figure 175: HSQC -Spectrum of **12d.**

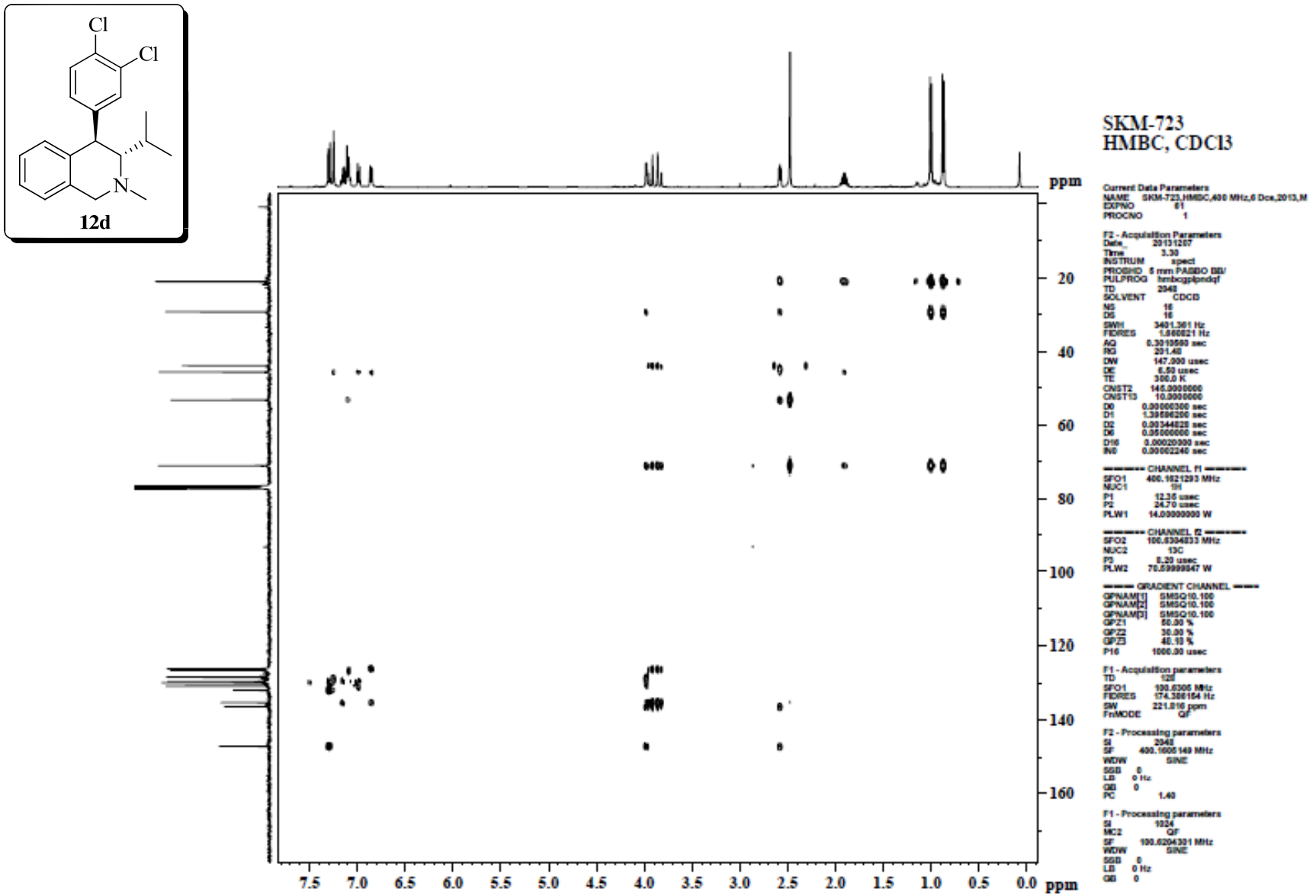


Figure 176: HMBC -Spectrum of **12d.**

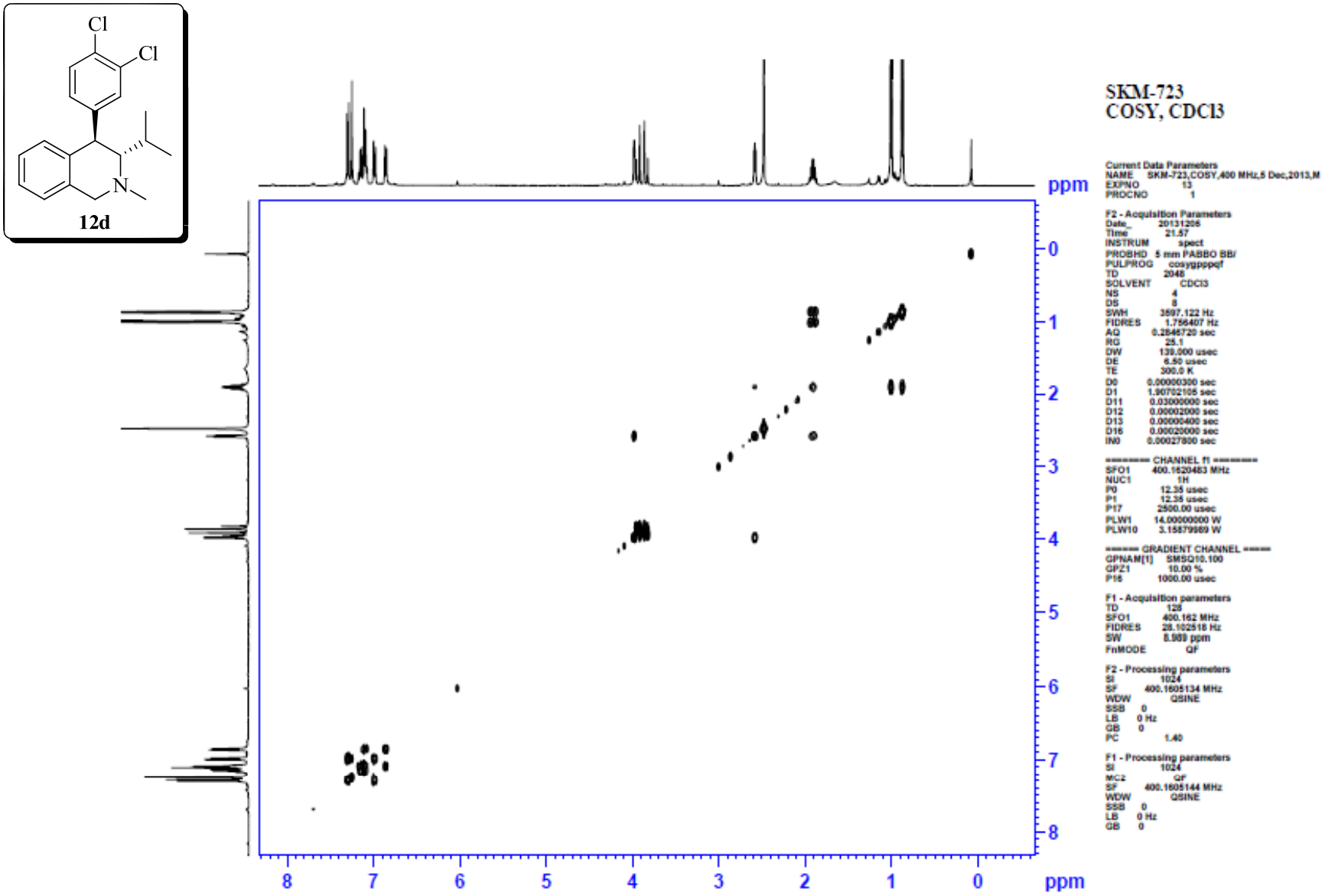


Figure 177: COSY -Spectrum of **12d.**

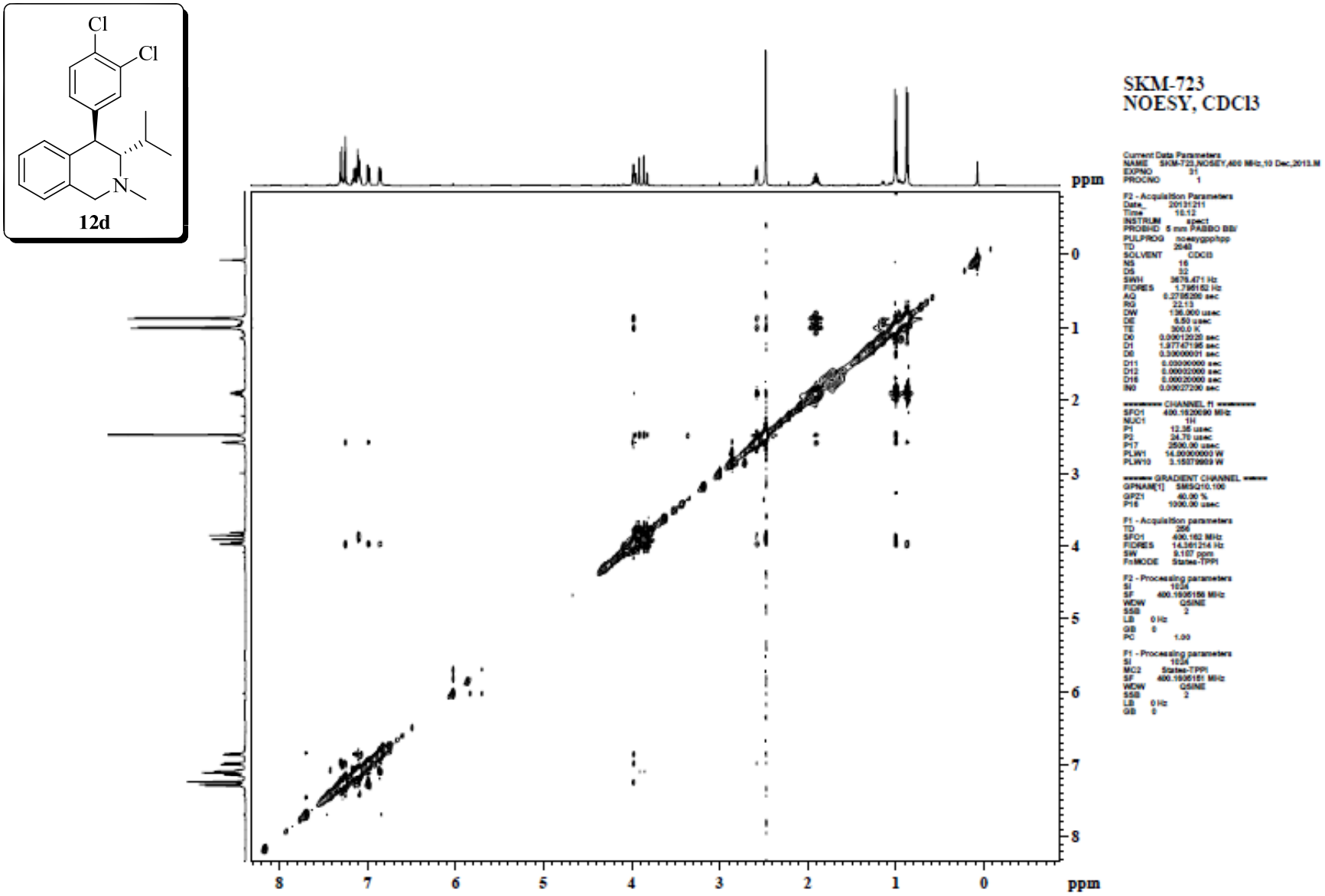
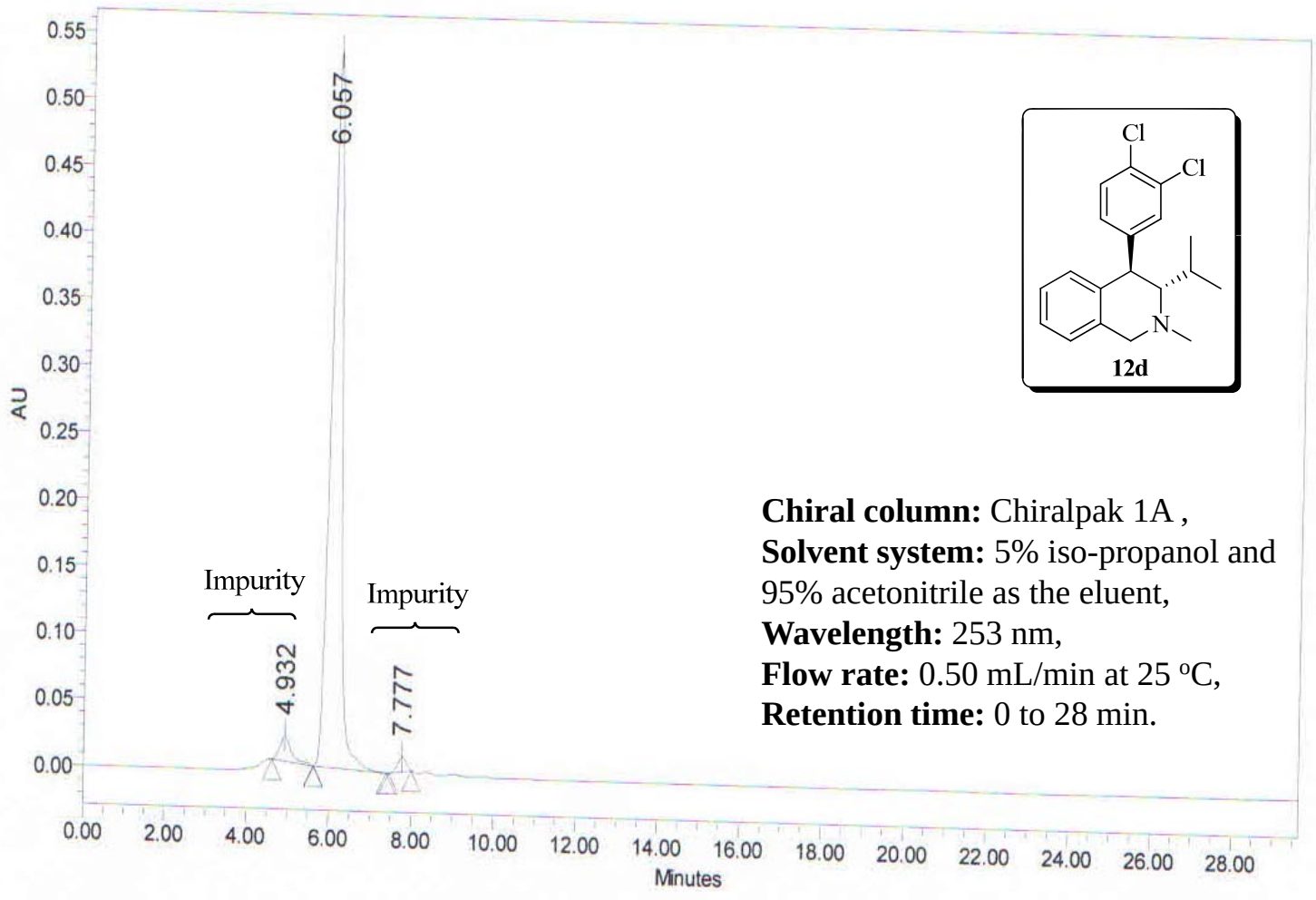


Figure 178: NOESY -Spectrum of **12d.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **12d.**

Figure 179: HPLC -Spectrum of **12d.**

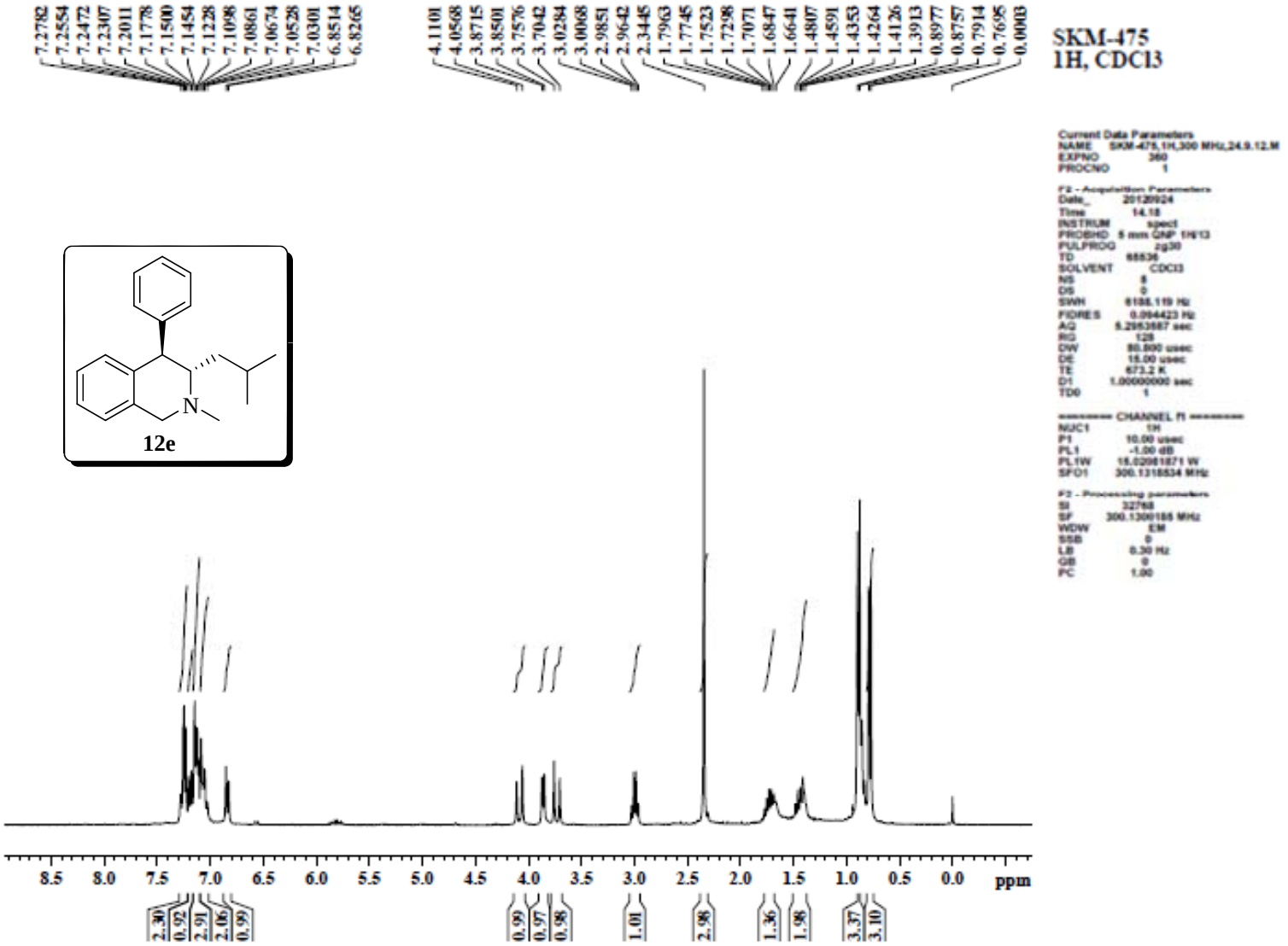


Figure 180: ^{1}H -NMR Spectrum of **12e.**

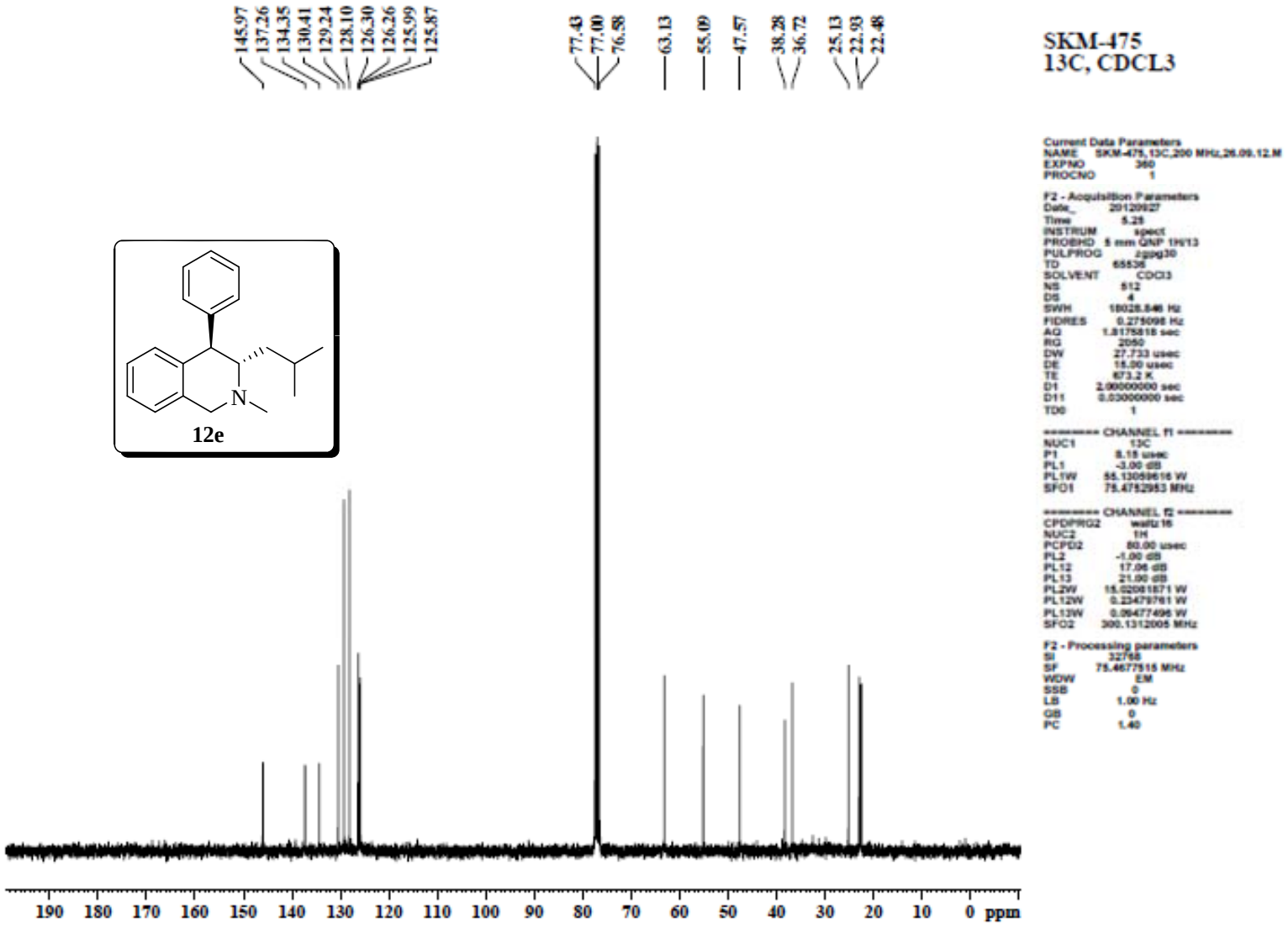
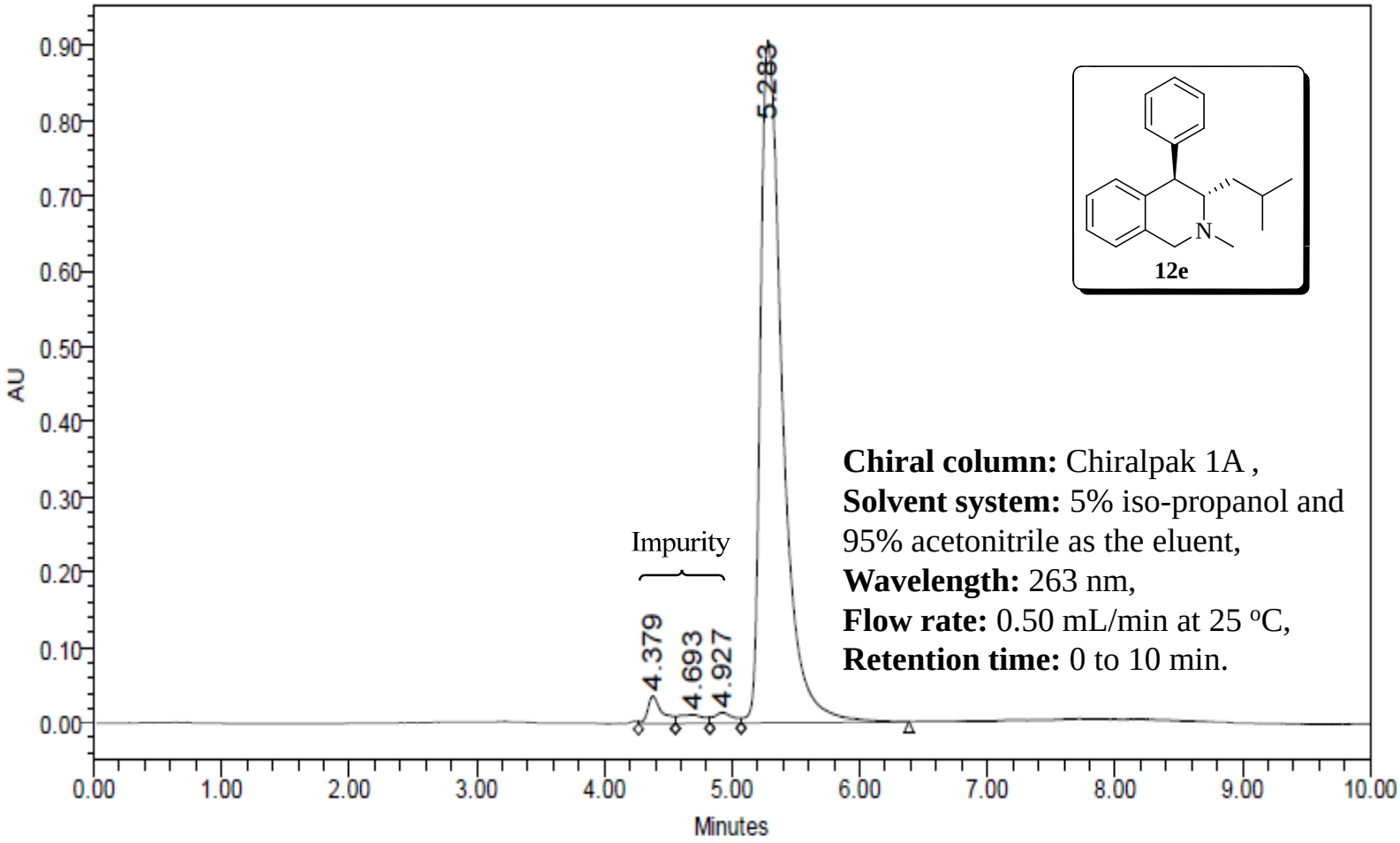


Figure 181: ^{13}C -NMR Spectrum of **12e.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **12e.**

Figure 182: HPLC -Spectrum of **12e.**

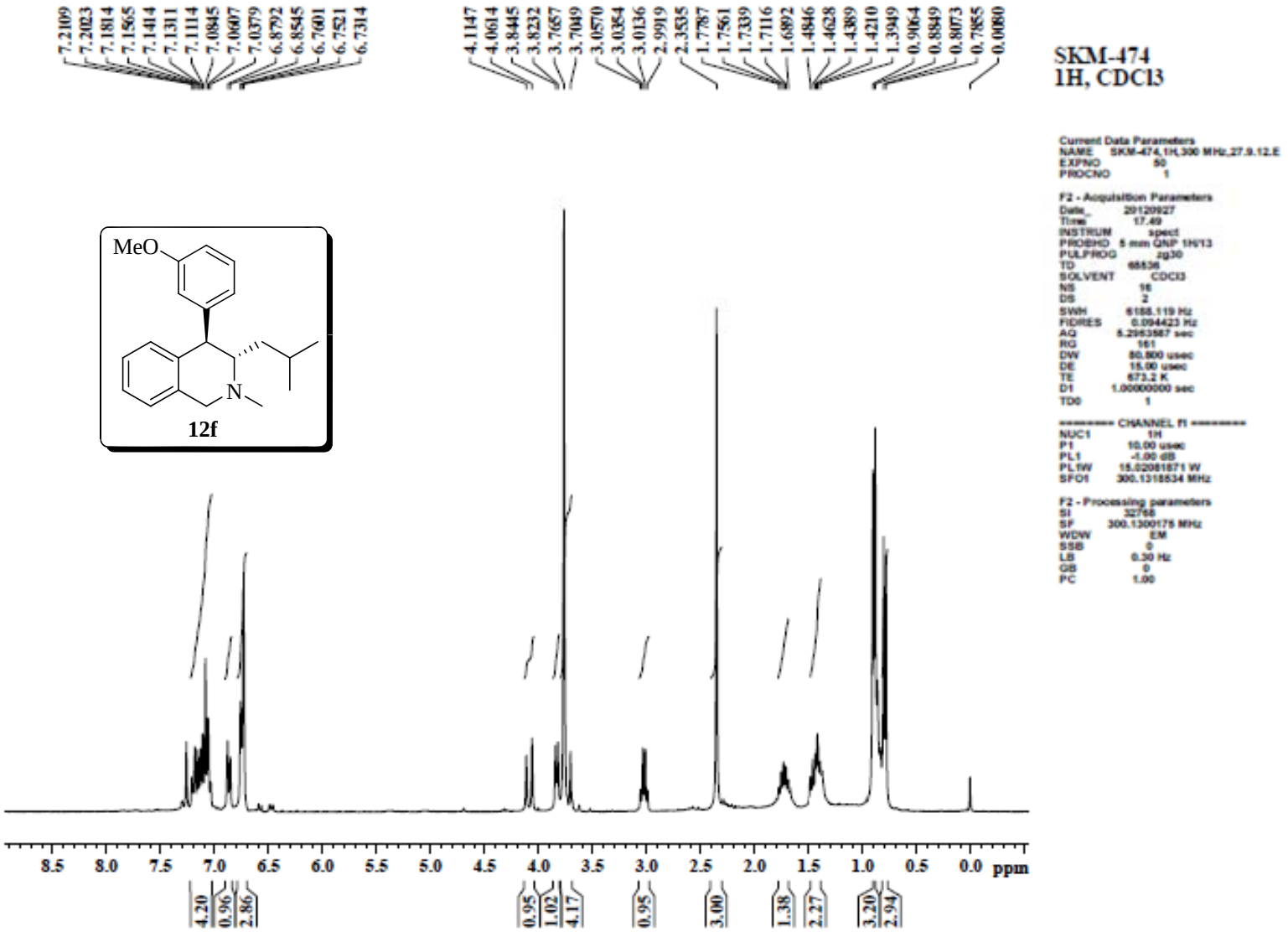


Figure 183: ^{1}H -NMR Spectrum of **12f.**

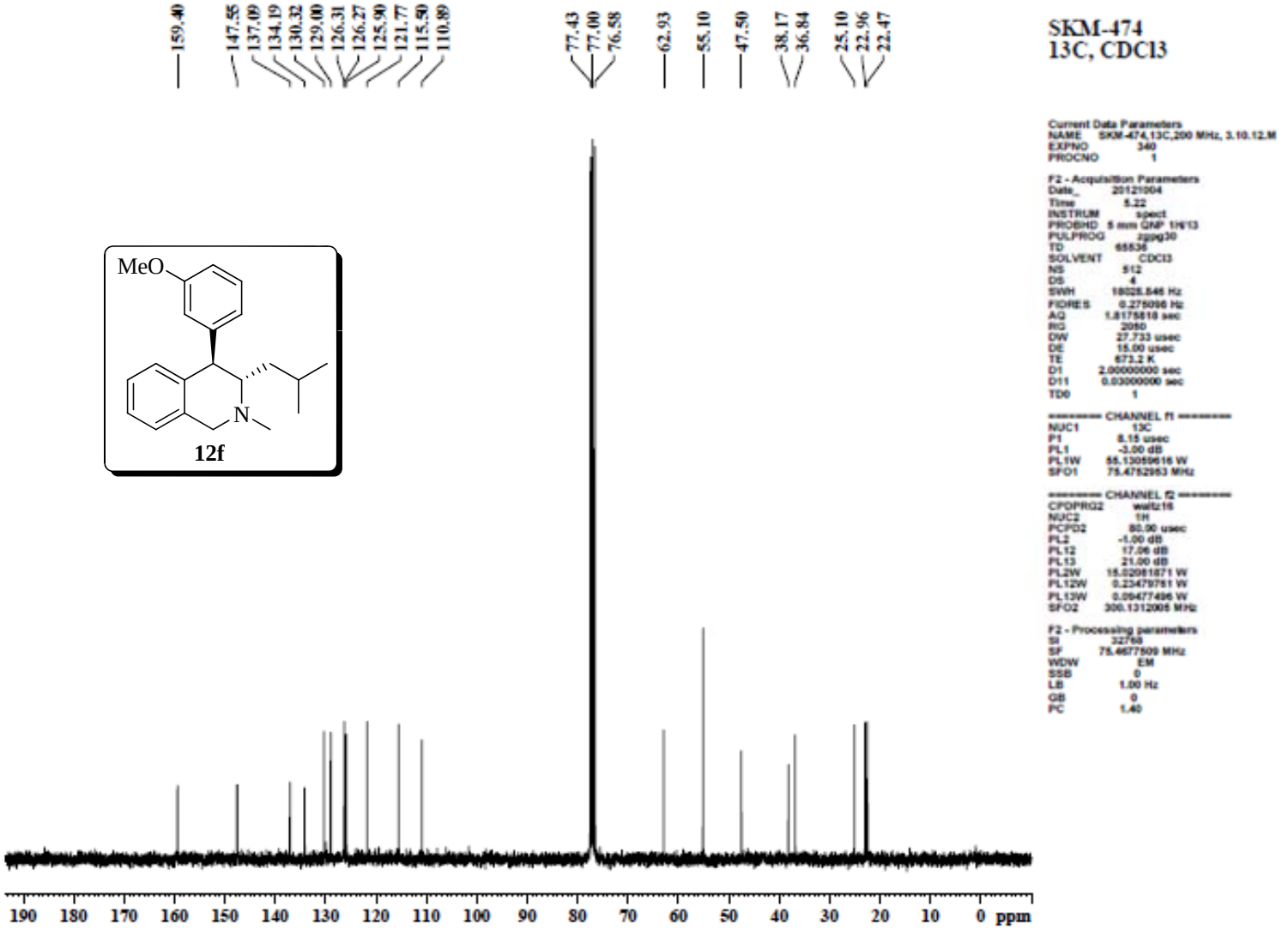
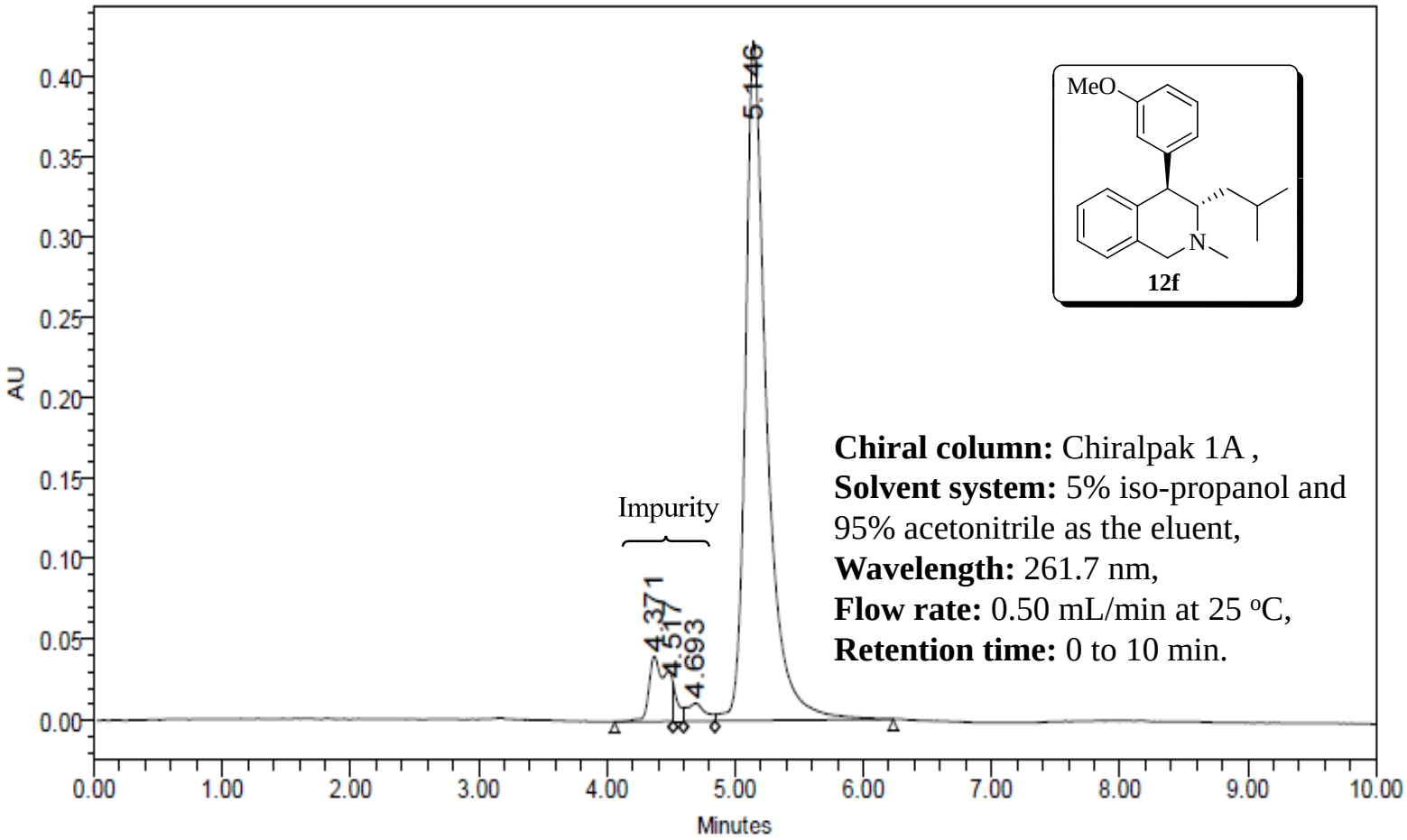


Figure 184: ^{13}C -NMR Spectrum of **12f.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **12f.**

Figure 185: HPLC -Spectrum of **12f.**

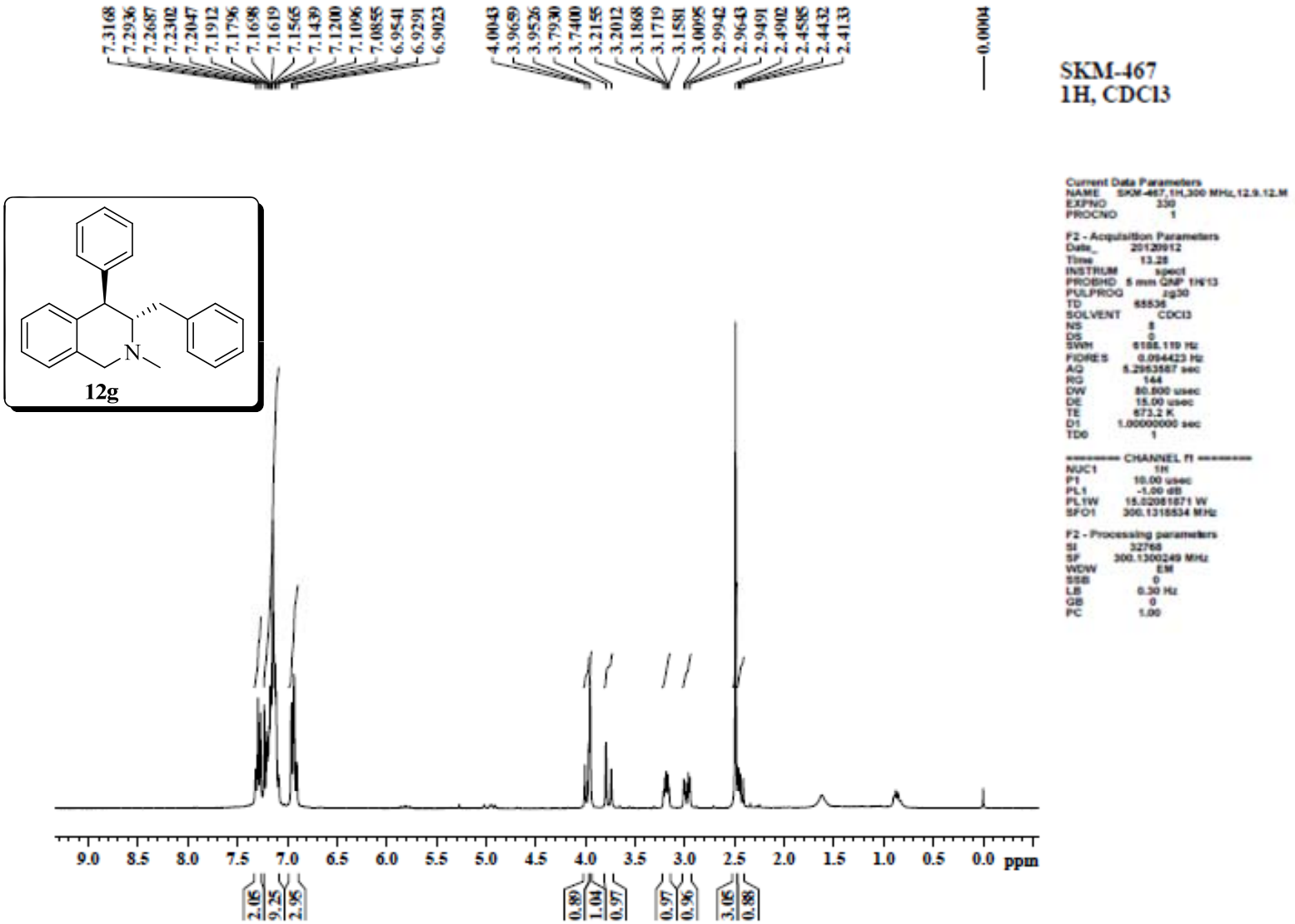


Figure 196: ^{1}H -NMR Spectrum of **12g.**

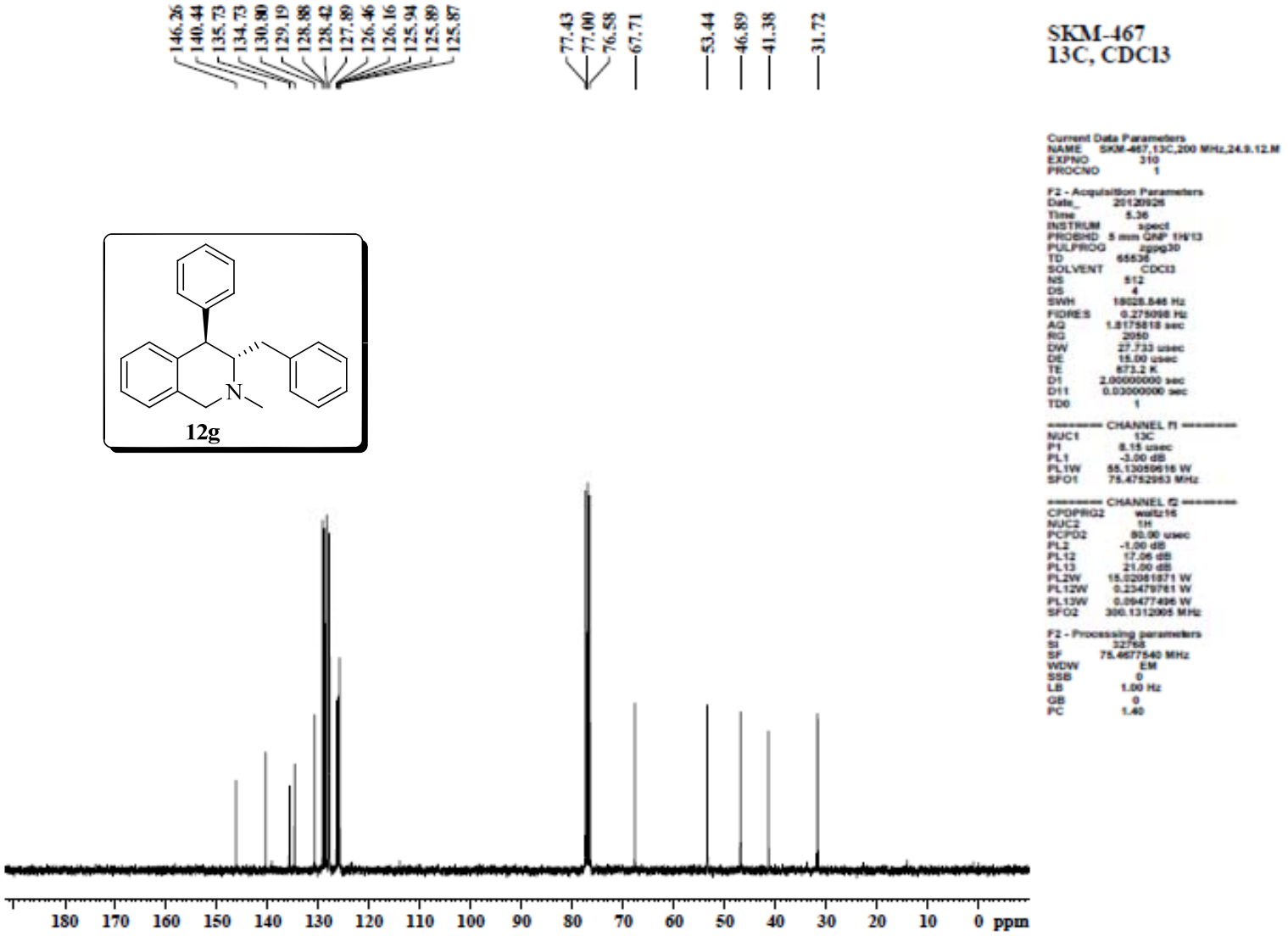
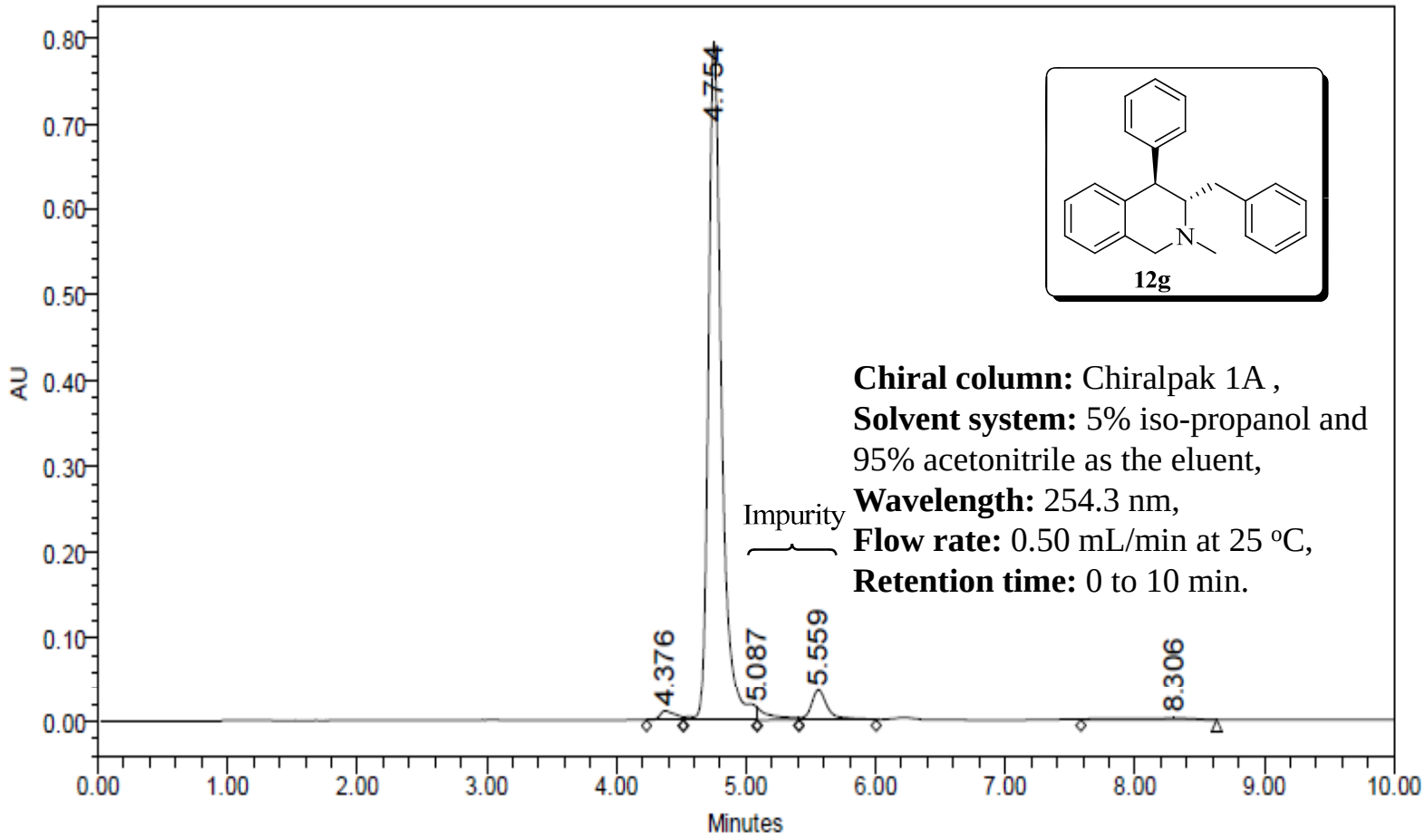


Figure 187: ^{13}C -NMR Spectrum of **12g.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **12g.**

Figure 188: HPLC -Spectrum of **12g.**

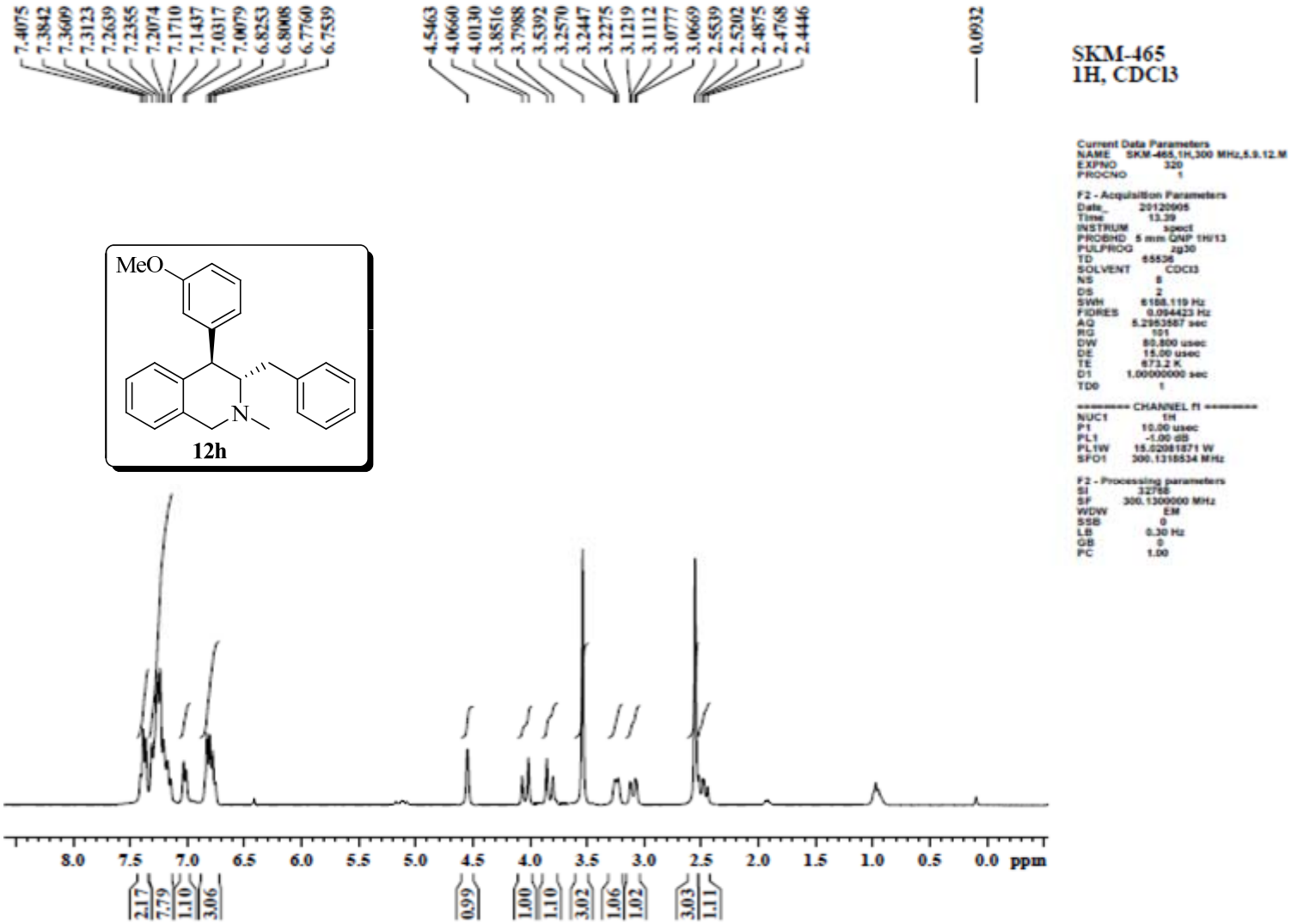


Figure 189: ^{1}H -NMR Spectrum of **12h.**

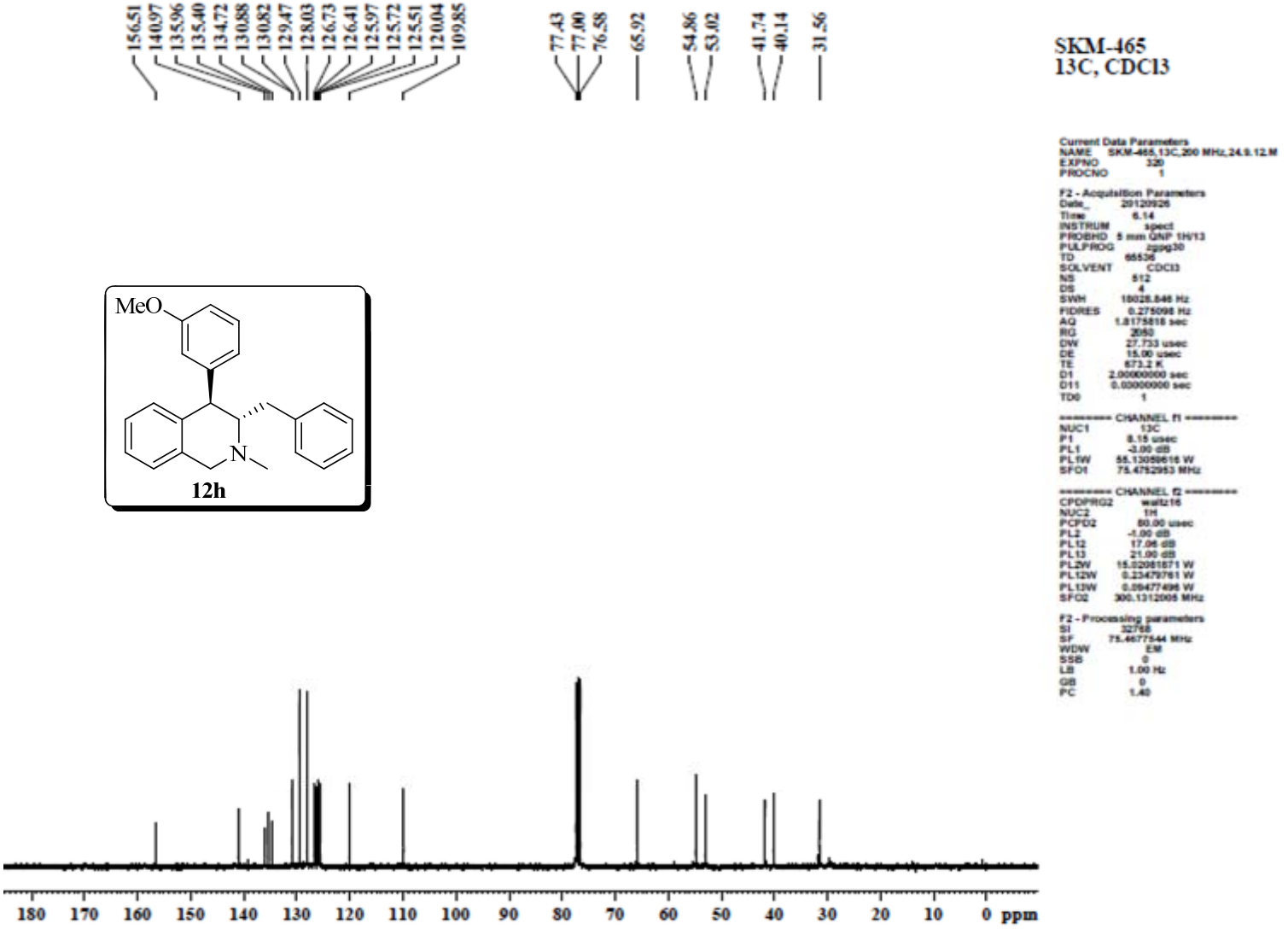
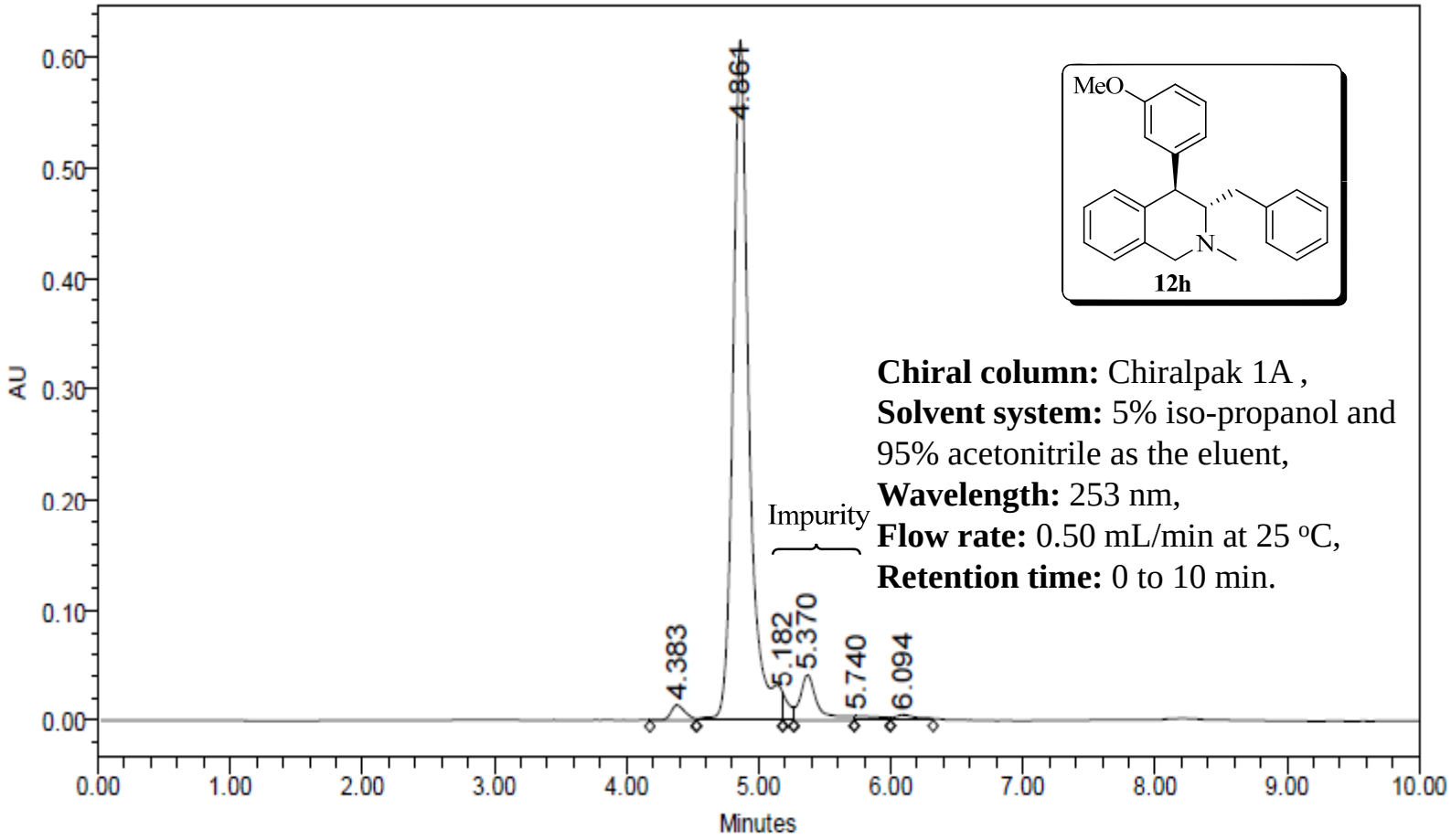


Figure 190: ^{13}C -NMR Spectrum of **12h.**



Note: The impurity species were collected and found by ^{1}H NMR not to contain any isomeric forms of compound **12h.**

Figure 191: HPLC -Spectrum of **12h.**

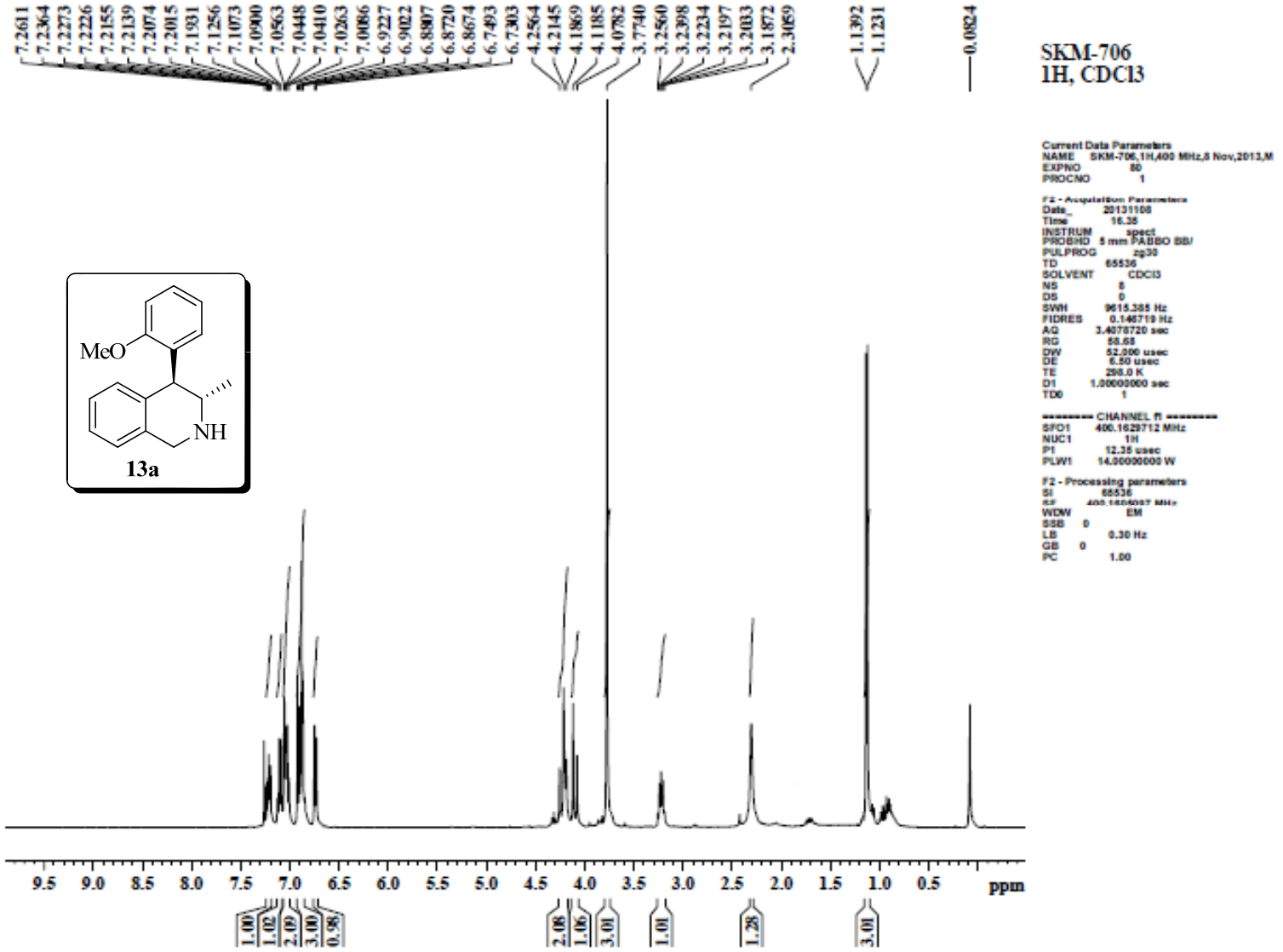


Figure 192: ^{1}H -NMR Spectrum of **13a.**

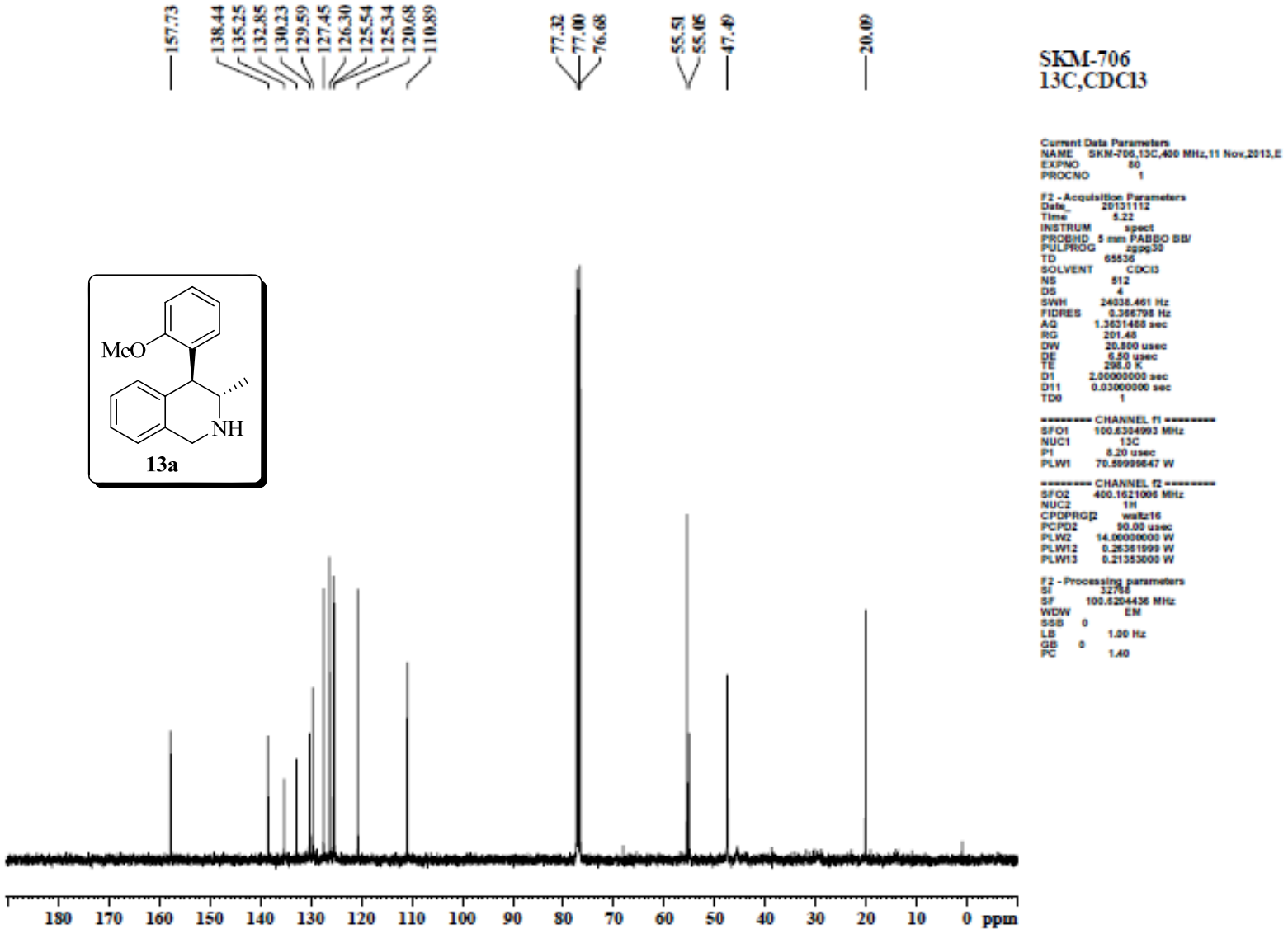


Figure 193: ^{13}C -NMR Spectrum of **13a.**