Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

A Lewis acid initiated intramolecular cyclization of benzylidene acetal with azide functional group: Novel synthesis of oxazolines and oxazines.

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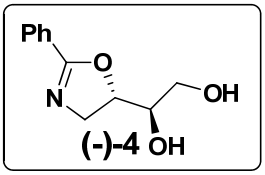
General Information:

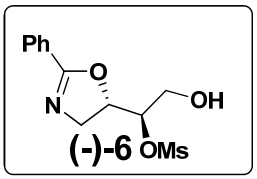
All reactions were carried out under nitrogen or argon atmosphere with dry solvent. Solvent is dried over CaH_2 under nitrogen atmosphere. Solvent for Column chromatography was distilled at atmosphere pressure prior to use. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV lamp for visualization. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Column chromatography was performed using silica gel (particle size 100-200 mesh). ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker AV-400 instrument and calibrated using tetramethylsilane as an internal reference. Chemical shift (δ) are given in ppm relative to TMS (0 ppm). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). Coupling constants J are reported in Hz. Mass spectra (MS) were obtained by EI (70 eV) or ESI and High resolution mass spectra (HRMS) by Electrospray Ionisation (ESI) or by electron impact (EI). IR spectra were recorded on a Nicolet-4700 Spectrum One FTIR spectrometer with diamond ATR accessory.

General experimental procedure for the Lewis acid initiated intramolecular Schmidt type cyclization of benzylidene acetal with azide functional group:

To a stirred solution of benzylidene acetal (-)-**3** (235 mg, 1 mmol) in dry DCM (10 mL) at 0 °C was added $BF_3.OEt_2$ (0.51 mL) and stirred for 30 min. Temperature was then slowly raised to room temperature and stirred for 3.5 h. After completion of the reaction as indicated by TLC, reaction mixture was diluted with water and extracted with EtOAc. Organic layers were collected, dried and concentrated under reduced pressure to give the crude compound. Purification of the crude compound over silica gel using column chromatography (gradient elution with 20-30% EtOAc in hexane) furnished the pure title compound (-)-**4** (182 mg, 88%) as a white solid.

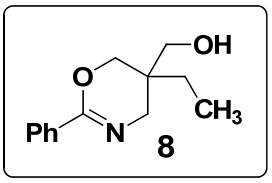


Compound (-)-4 : $[\alpha]^{27}_D$ -1.6 (*c* 0.16, $CHCl_3$); **IR(Neat)**: 3350.7, 2925.3, 1715.9, 1645.7, 1450.7, 1350.6, 1262.7, 1068.1, 968.6, 692.7 cm^{-1}; **^{1}H NMR** [300 MHz, $CDCl_3$] δ 7.86-7.84 (d, *J* = 7.3 Hz, 2 H), 7.43-7.40 (m, 1 H), 7.36-7.31 (m, 2 H), 4.63-4.60 (m, 2 H), 4.04-4.00 (m, 2 H), 3.82-3.76 (m, 2 H), 3.67-3.64 (m, 1 H); **^{13}C [100 MHz, $CDCl_3$]** δ 163.7, 131.5, 128.4, 128.1, 127.3, 79.1, 72.5, 63.2, 56.4; **HRMS** Calculated for $C_{11}H_{14}NO_3$ $(M+H)^+$ is 208.0974; found 208.0971.

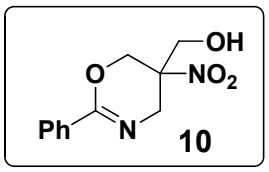


Compound (-)-6: $[\alpha]^{28}_D$ -12.4 (*c* 1, $CHCl_3$); **IR(Neat)**: 2921.1, 2850.6, 1651.9, 1450.3, 1345.7, 1262.3, 916.2, 696.1 cm^{-1}; **^{1}H NMR** [300 MHz, $CDCl_3$] δ 7.87-7.84 (m, 2 H), 7.45-7.42 (m, 1 H), 7.38-7.34 (m, 2 H), 4.89-4.84 (m, 2 H), 4.16-4.05 (m, 2 H), 3.92 (dd, *J* = 12.8, 3.6 Hz, 1H), 3.84 (dd, *J* = 12.4, 5.6 Hz, 1H), 2.94 (s, 3 H); **^{13}C [100 MHz,**

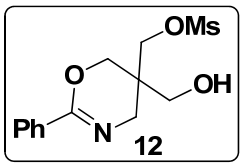
$CDCl_3$] δ 163.5, 131.8, 128.6, 128.2, 126.8, 82.2, 76.7, 61.6, 56.2, 38.5; **HRMS** Calculated for $C_{12}H_{16}NO_5SNa$ $(M+H)^+$ is 286.0749; found 286.0753.



Compound 8 : IR(Neat): 3255.5,2964.3,2880, 1650.8, 1448.4, 1354.4, 1270.6, 1175.7, 1052.7, 780.3, 731.0, 693.5 cm^{-1}; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.87- 7.85 (m, 2 H), 7.40- 7.38 (m,1 H), 7.36-7.32 (m, 2 H), 4.21 (dd, *J* = 10.8, 2 Hz, 1 H), 3.93 (d, *J* = 10.8 Hz, 1 H), 3.41 (dd, *J* = 16.8, 2 Hz, 1 H), 3.29 (d, *J* = 16.8, 1 H), 1.07 (m, 2 H), .90 (t, *J* = 7.6 Hz, 3 H) ; **^{13}C NMR(100 MHz, $CDCl_3$)** δ 155.6,133.3, 130.5,128.0, 127.0, 69.2, 62.4, 49.0, 35.0, 24.6, 7.1; **HRMS** Calculated for $C_{13}H_{18}NO_2(M^+Na^+)$ is 220.1338, found 220.1333.

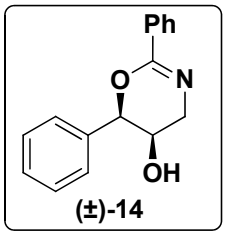


Compound 10 : IR(Neat): 3204.9**,** 2936.0, 1657.7, 1544.7,1348.4, 1277.9, 1157.0, 1071.2, 696.5 cm^{-1}; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.90-7.88 (m, 2 H), 7.45- 7.43 (m, 1 H), 7.39-7.36 (m, 2 H), 4.8 (dd, *J* = 11.6, 2 Hz, 1 H), 4.53 (dd, *J* = 13.6, 2 Hz, 1H), 4.22 (dd, *J* = 10, 2 Hz, 1 H), 4.12 (d, *J* = 12.4 Hz, 1 H), 3.94 (d, *J* = 12.4 Hz, 1 H), 3.84 (dd, *J* = 17.8, 2 Hz, 1 H) ; **^{13}C NMR(100 MHz, $CDCl_3$)** δ 155.2, 131.9, 131.2, 128.2, 127.3, 127.2, 84.9, 64.4, 63.7, 47.5; **HRMS** calculated for $C_{11}H_{13}N_2O_4$ (M^+H^+) is 237.0875, found 237.0875.



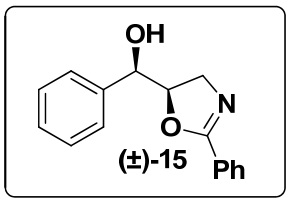
Compound 12 :IR(Neat):: 3205.5, 2935.4, 1655.6, 1352.9, 1174.5, 1068.4, 1028.9, 697.5cm^{-1} ; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.88-7.86 (m, 2 H), 7.44- 7.42, (m, 1H), 7.39-7.35 (m, 2 H), 4.25 (s, 2H), 4.21- 4.16 (m, 2H), 3.61- 3.60 (d, 2H)3.49 (s, 2H), 3.03 (s,

3H) ; **^{13}C NMR(100 MHz, $CDCl_3$)** δ 155.6, 132.7, 131.1, 128.4, 127.2, 68.7, 66.4, 61.6, 46.2, 37.2, 37.0; **HRMS** Calculated for C13H18NO5S (M^+H^+) is 300.0906, found 300.0910



(±)-14

Compound (±)-14 :IR(Neat): 3205.0, 2936.5, 1657.2, 1272.0, 1131.0,1156.0, 696.0, cm^{-1}; **^{1}H NMR (400MHz, $CDCl_3$)** δ 8.05- 8.02 (m, 2 H), 7.50- 7.38 (m, 8 H), 5.35 (s, 1 H), 4.24- 4.22 (m, 1 H), 3.96–3.91 (dd, *J* =3.6, 17.2 Hz, 1 H), 3.84–3.79 (d, *J* = 17.2 Hz, 1 H) ; **^{13}C NMR(100 MHz, $CDCl_3$)** δ 155.4, 130.9, 129.0, 128.6, 128.3, 127.4, 126.2, 76.9, 65.3, 50.2 ; **HRMS** Calculated for $C_{16}H_{16}NO_2$ (M^+H^+) is 254.1181, found 254.1177



(±)-15

.**Compound (±)-15 :IR(Neat):** 3205.8, 2935.5, 1655.0, 1352.8, 1170.5, 1155.5, 696.5cm^{-1}; **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.96-7.94(m, 2H), 7.51-7.47 (m, 1H), 7.43-7.34(m, 8H), 4.88-4.84 (M, 1H), 4.69-4.68(d, *J= 7.2*), 3.89-3.83(dd, *J* =11.8, 9.6, 1H), 3.78-3.73(dd, *J* =7.2, 7.6) ; **^{13}C NMR(100 MHz, $CDCl_3$)** δ 163.9, 138.8, 131.7, 128.9, 128.8, 128.5, 128.3, 127.3, 83.4, 76.3, 57.0 ; **HRMS** Calculated for $C_{16}H_{16}NO_2$ (M^+H^+) is 254.1181, found 254.1176

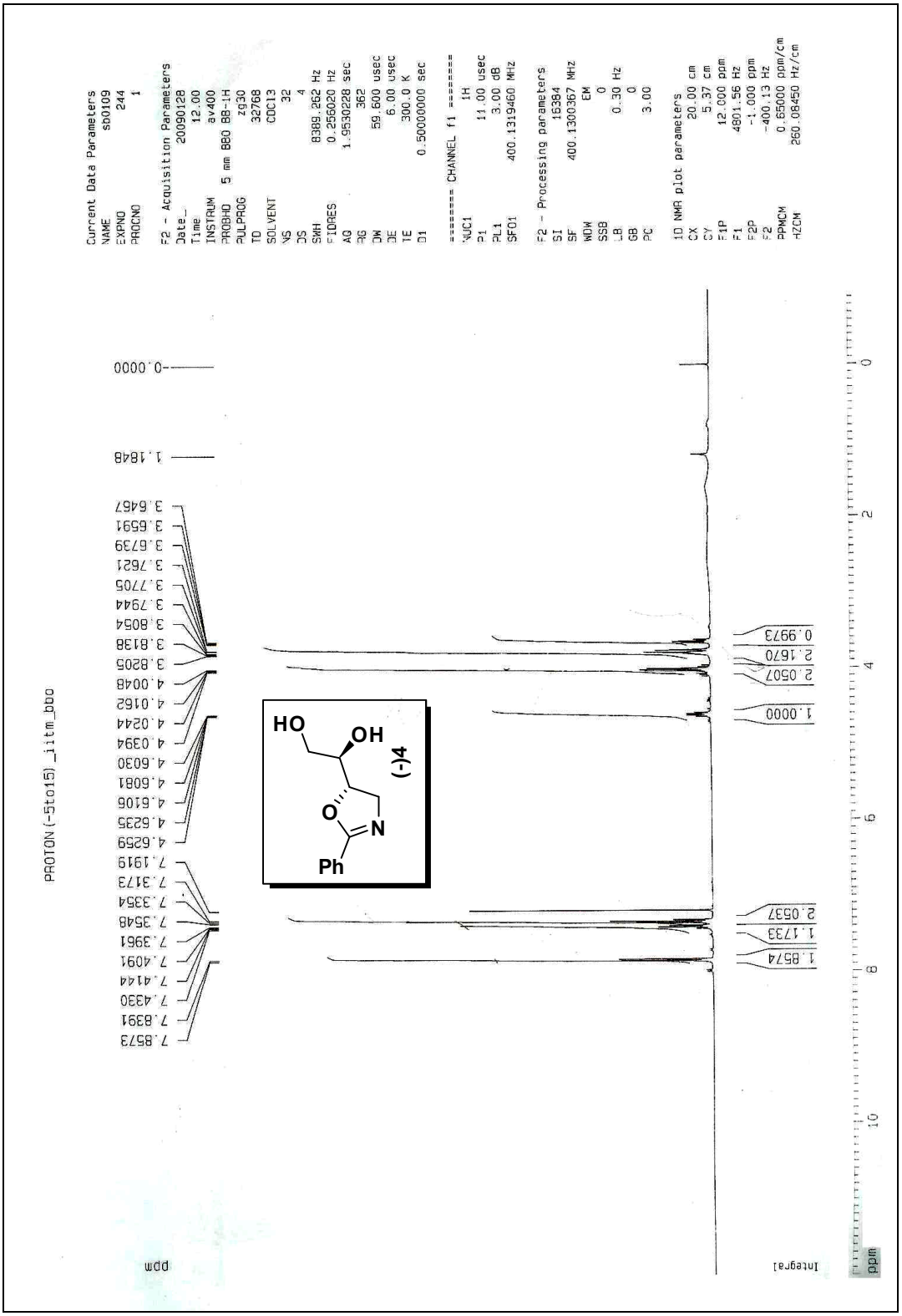


Figure 1. ^{1}H NMR spectrum of compound(-)- **4**

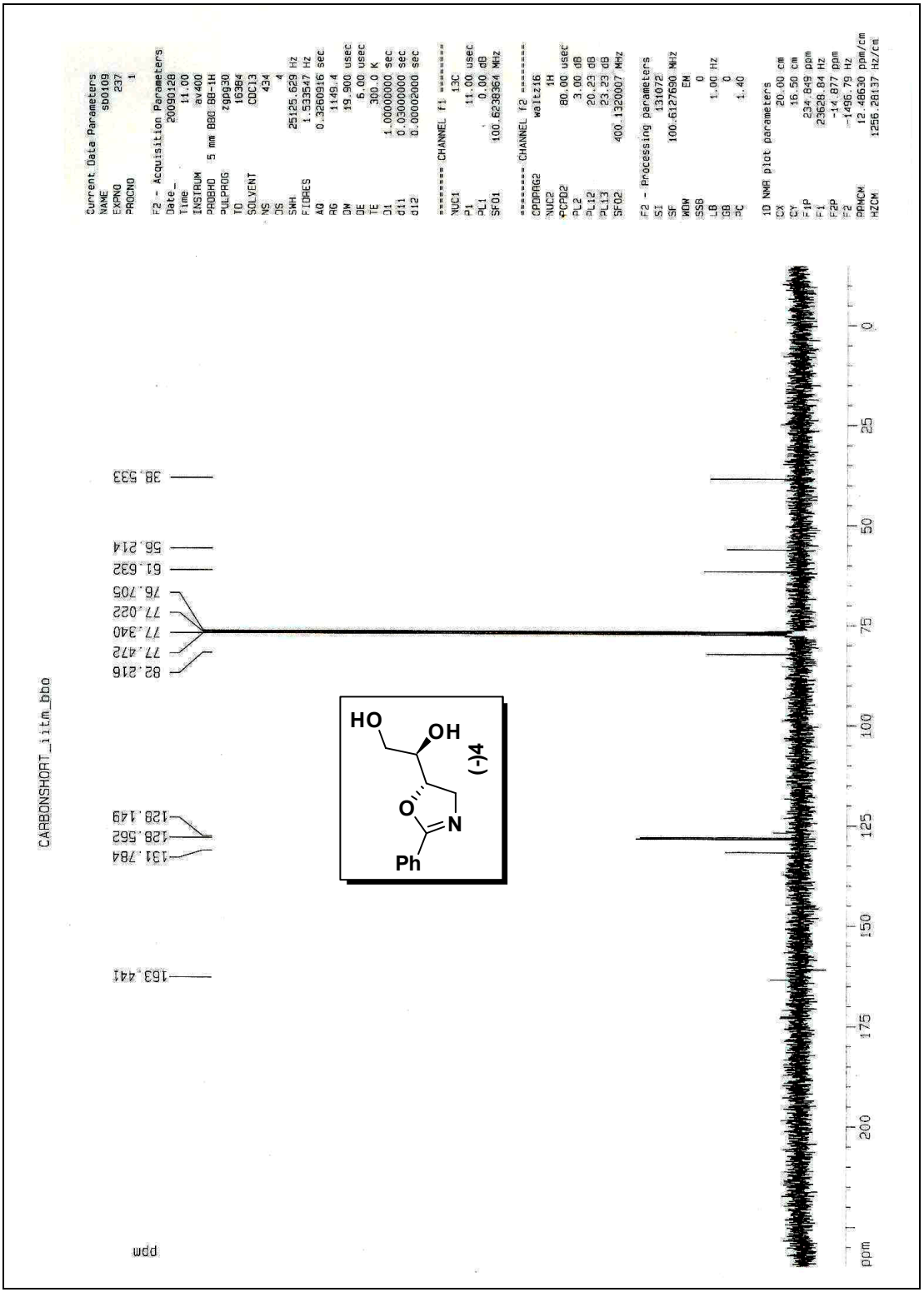


Figure 2. ^{13}C NMR spectrum of compound(-)- **4**

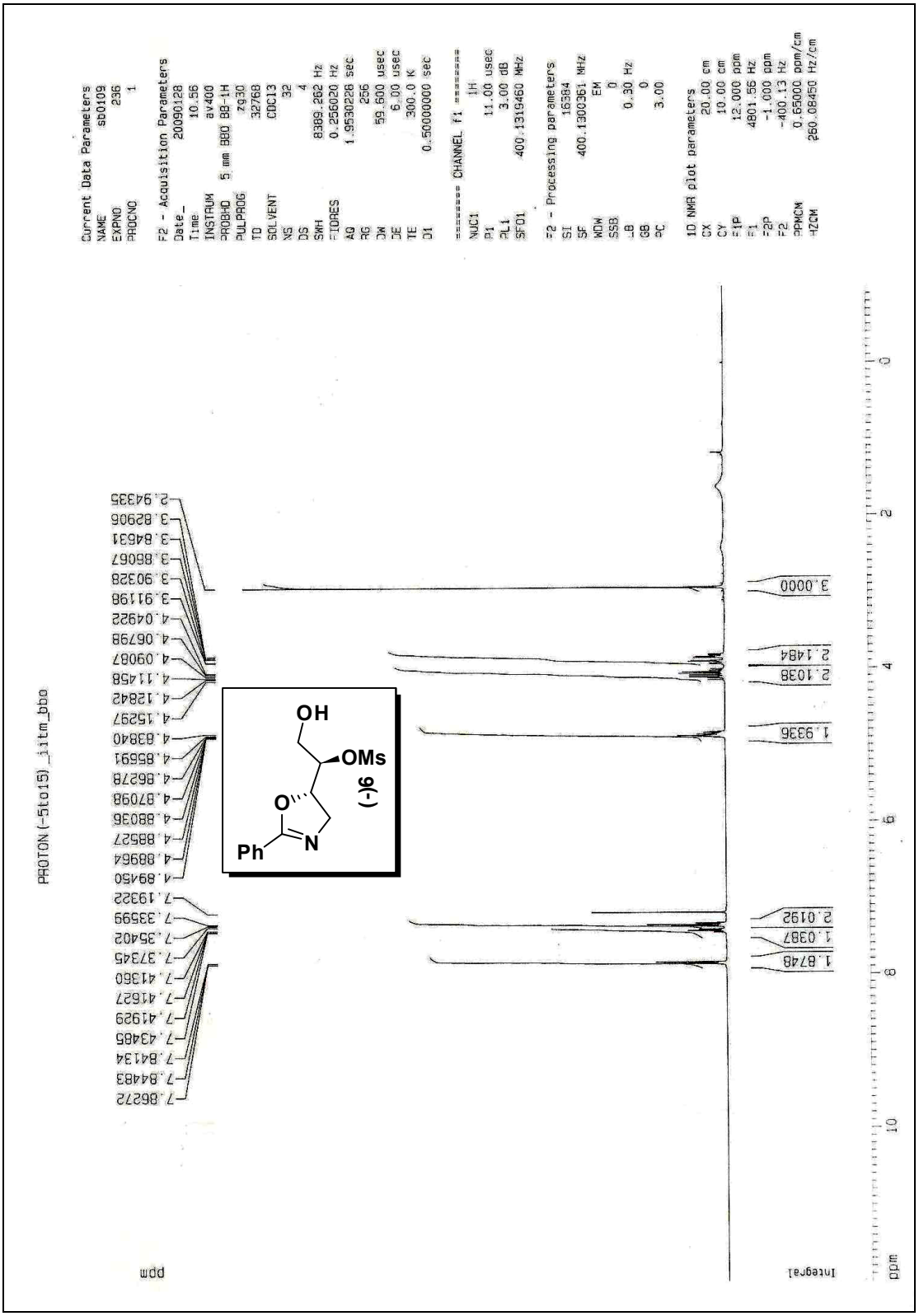


Figure 3. ^{1}H NMR spectrum of compound (-)-**6**

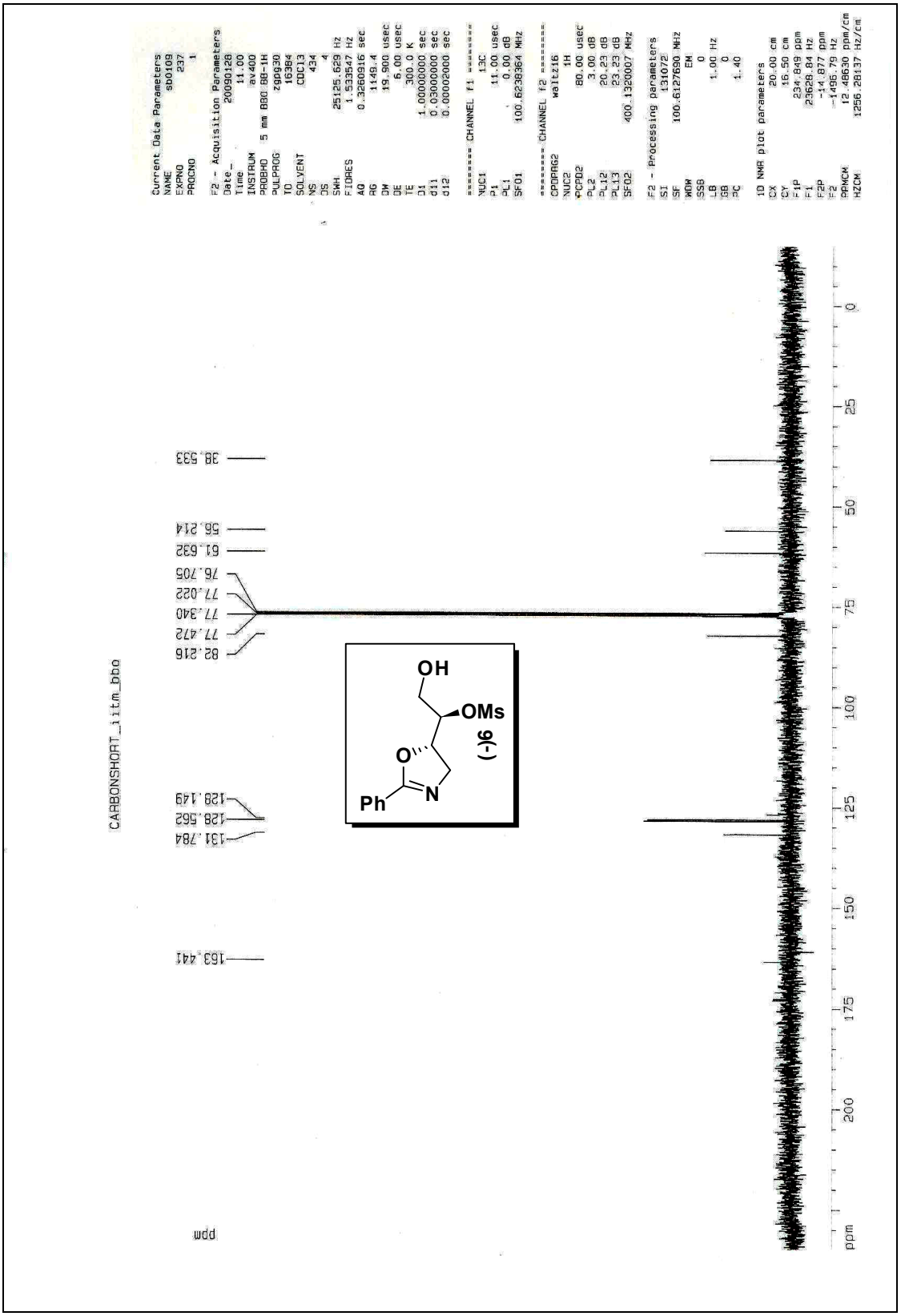


Figure 4. ^{13}C NMR spectrum of compound (-)-**6**

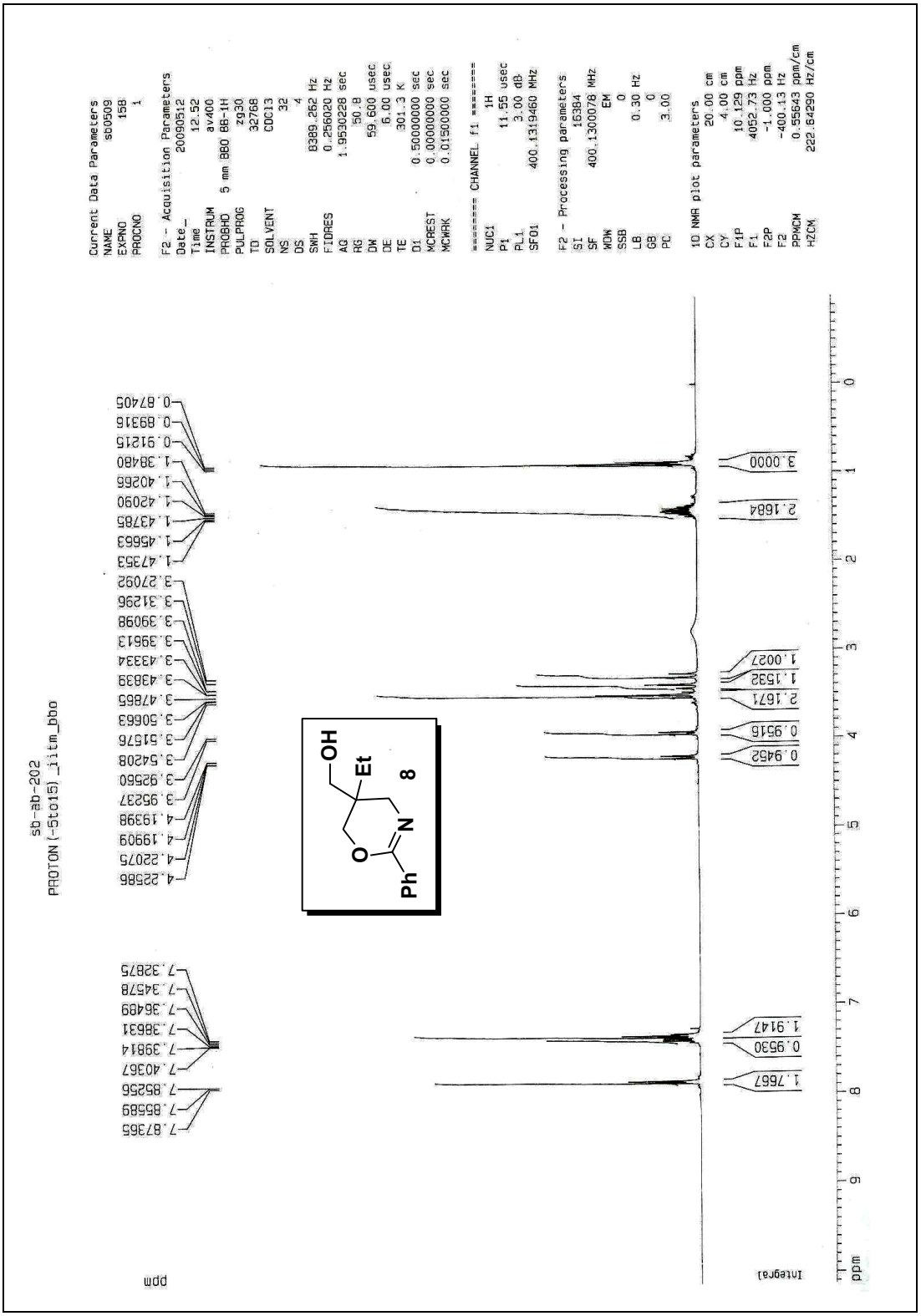


Figure 5. ^{1}H NMR spectrum of compound **8**

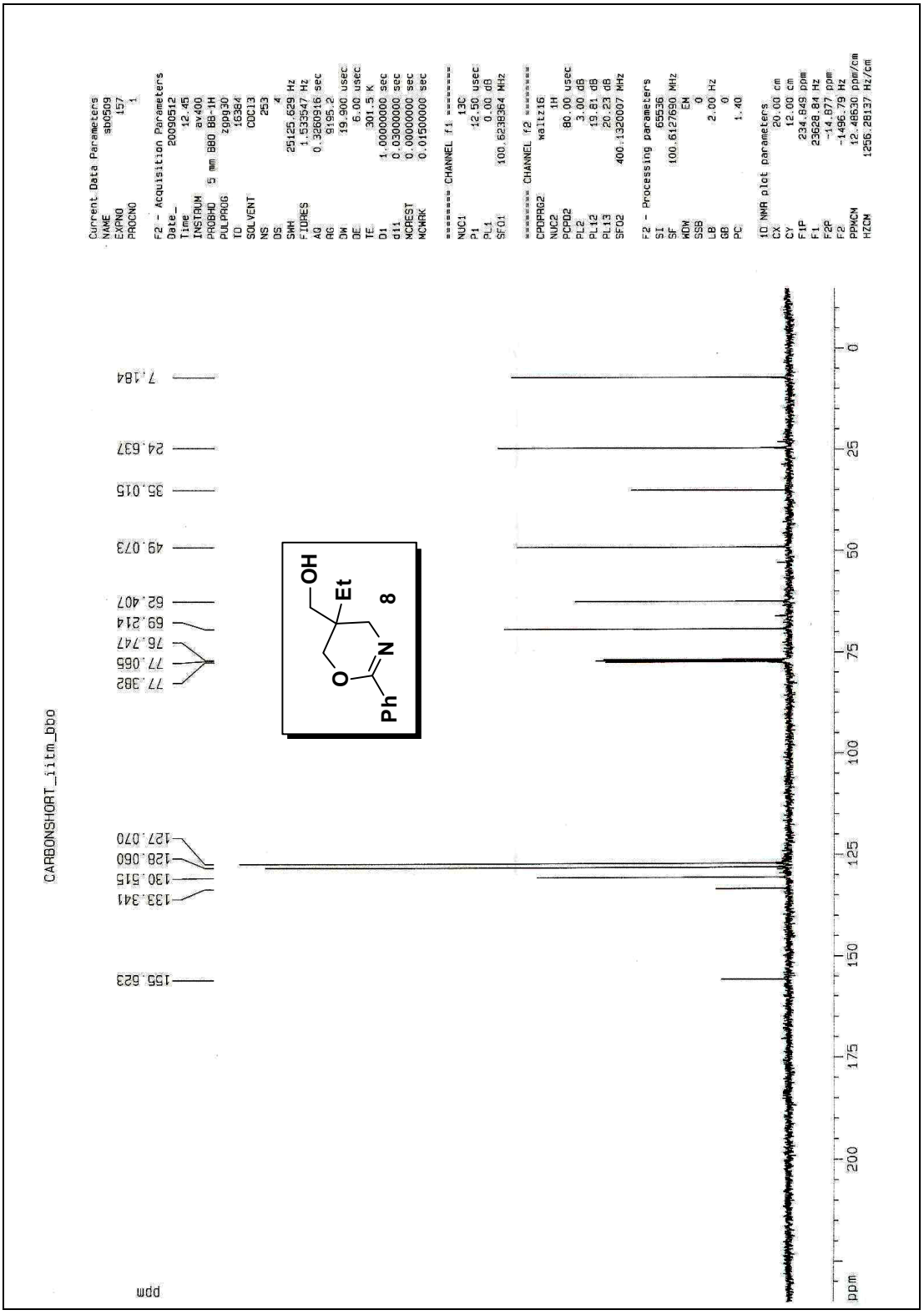


Figure 6. ^{13}C NMR spectrum of compound **8**

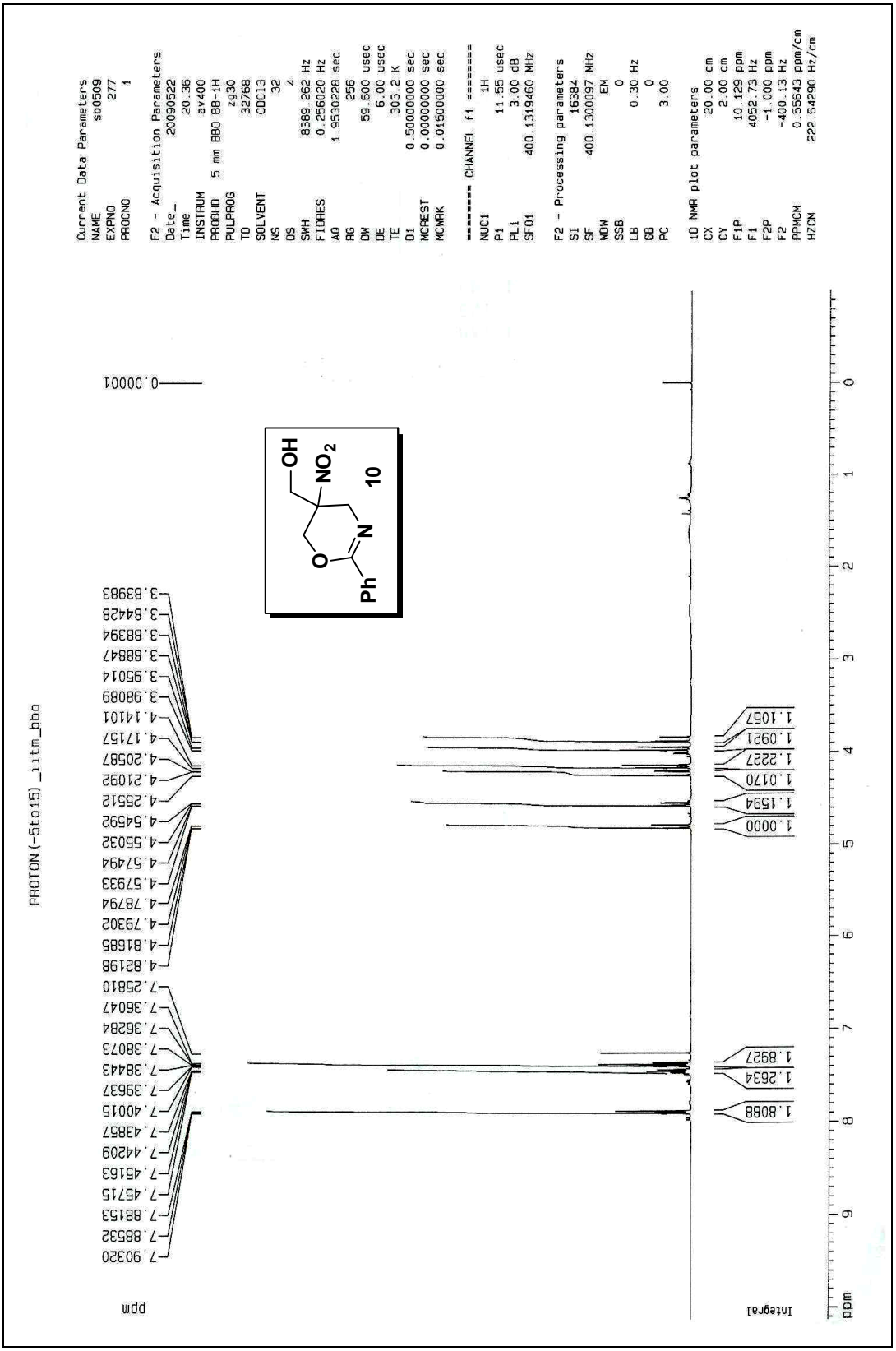


Figure 7. ^{1}H NMR spectrum of compound **10**

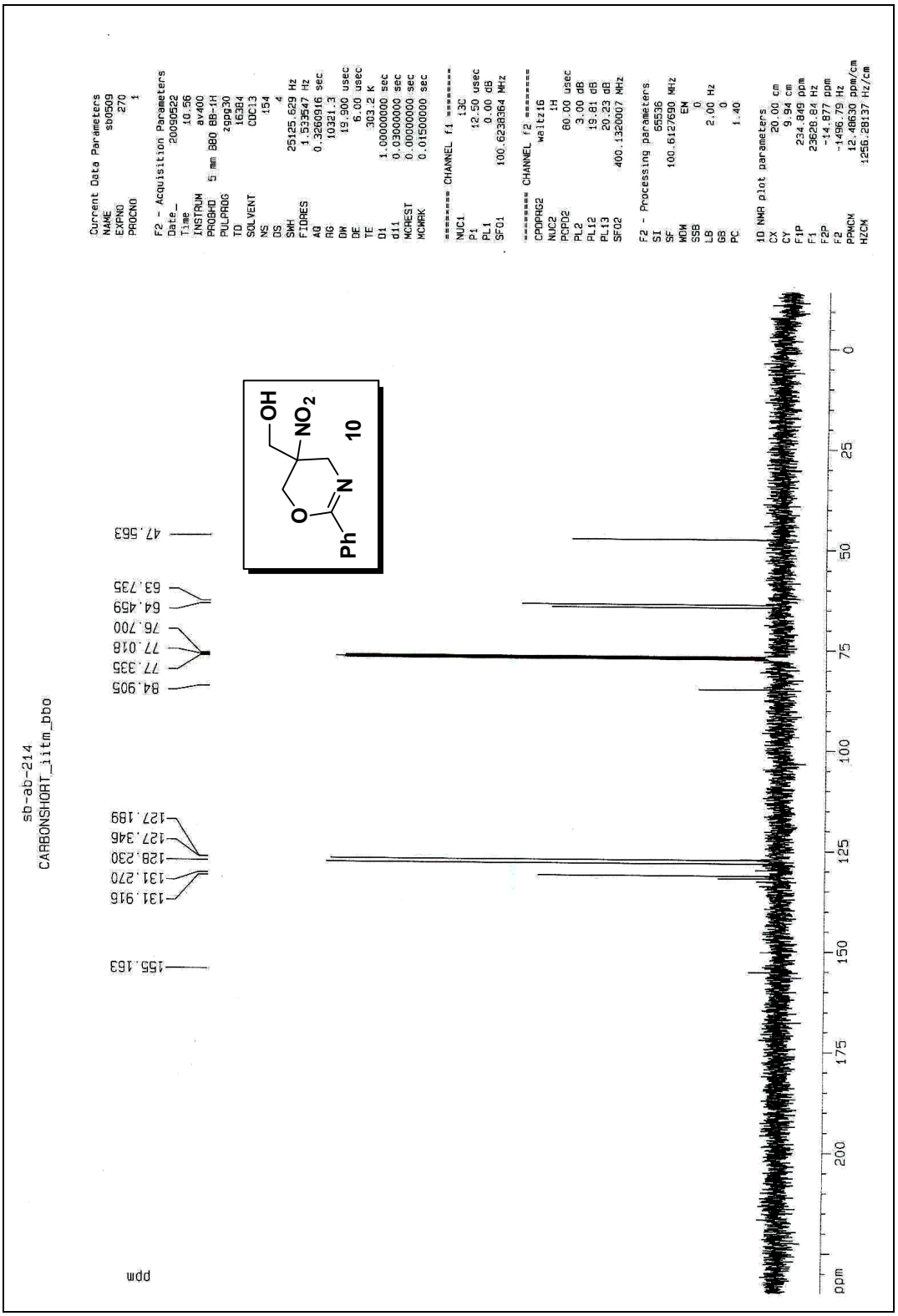


Figure 8. ^{13}C NMR spectrum of compound **10**

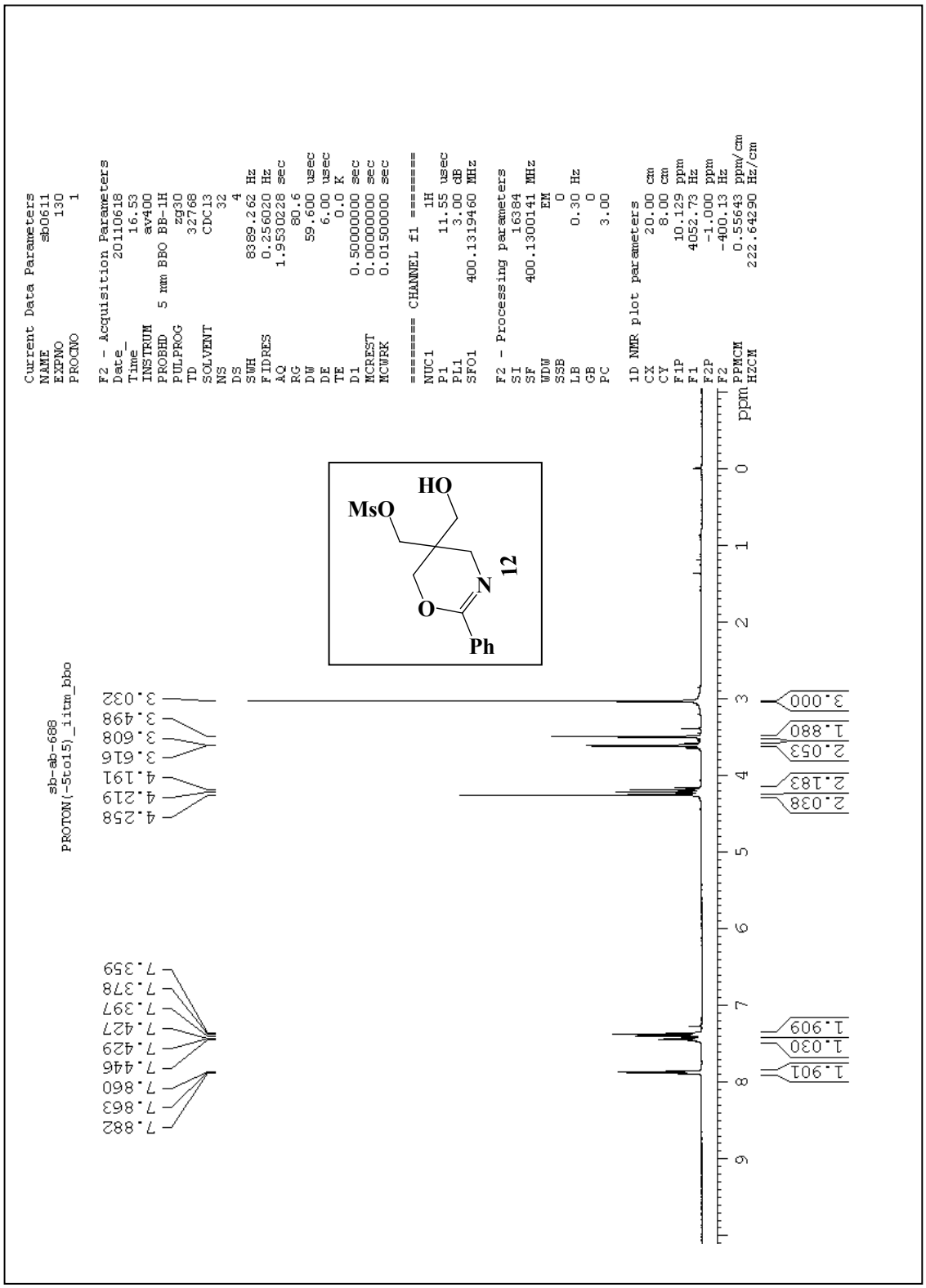


Figure 9. ^{1}H NMR spectrum of compound **12**

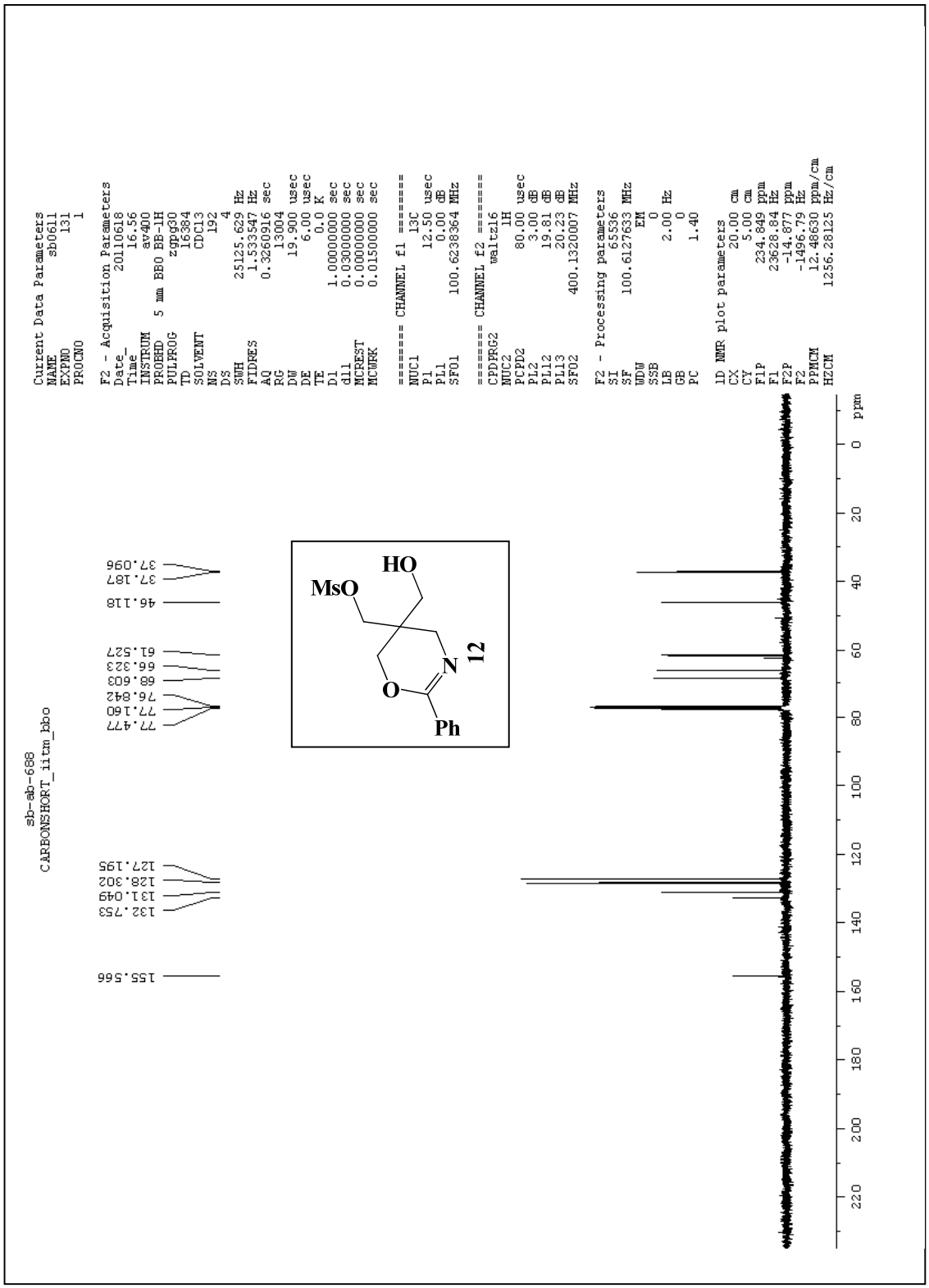


Figure 10. ^{13}C NMR spectrum of compound **12**

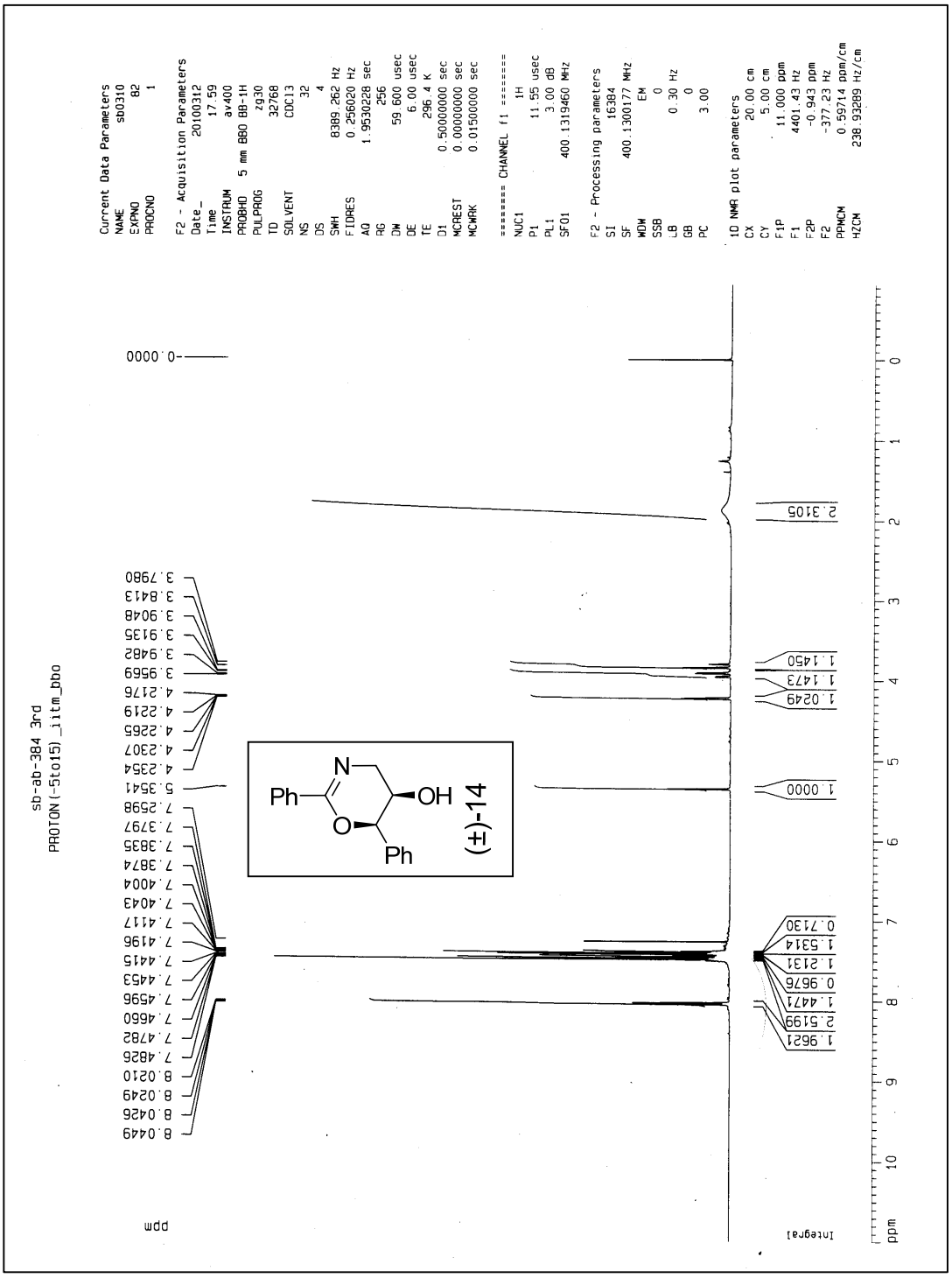


Figure 11. ^{1}H NMR spectrum of compound **(±)-14**

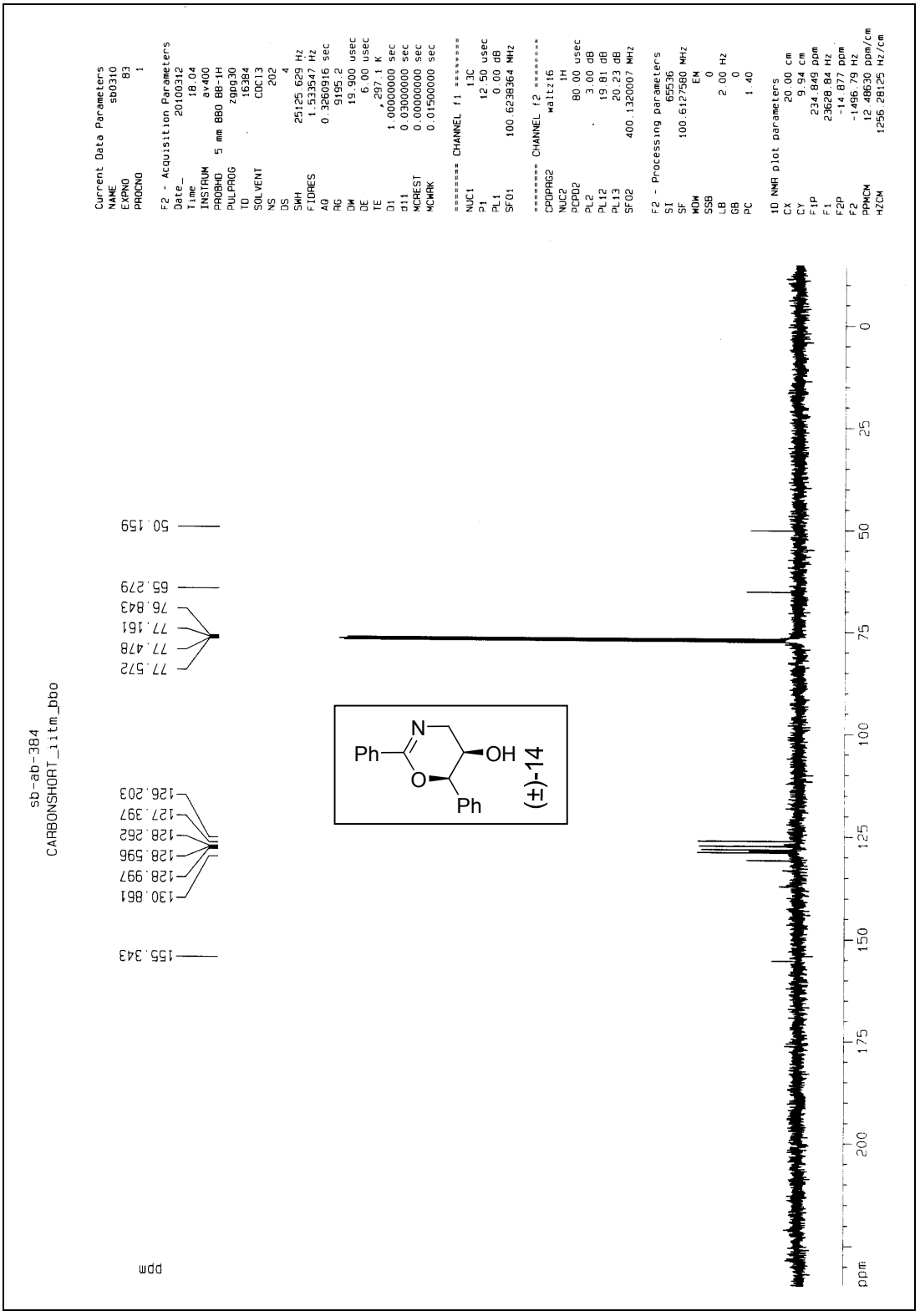


Figure 12. ^{13}C NMR spectrum of compound (±)-**14**

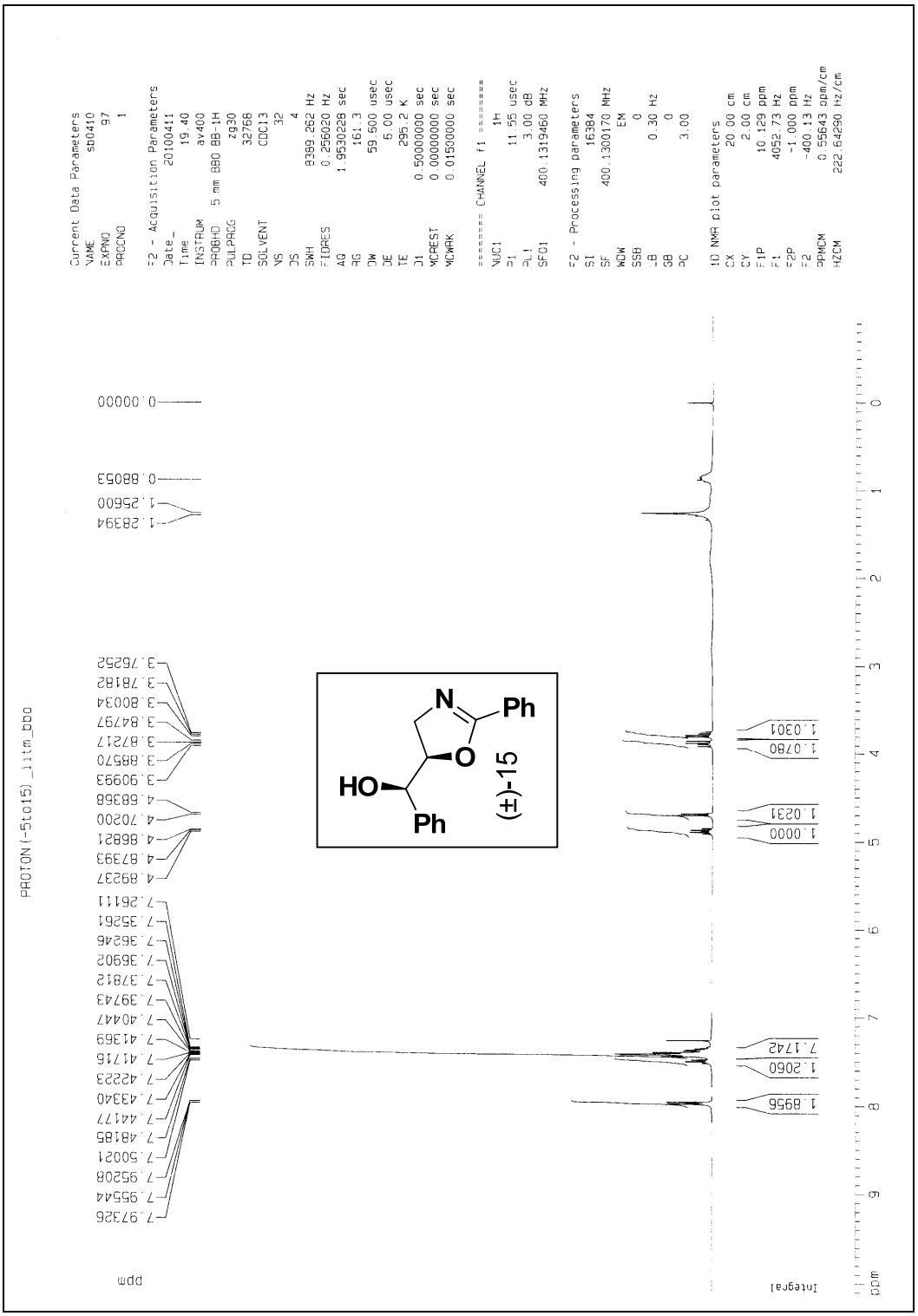


Figure 13. ^{1}H NMR spectrum of compound **(±)-15**

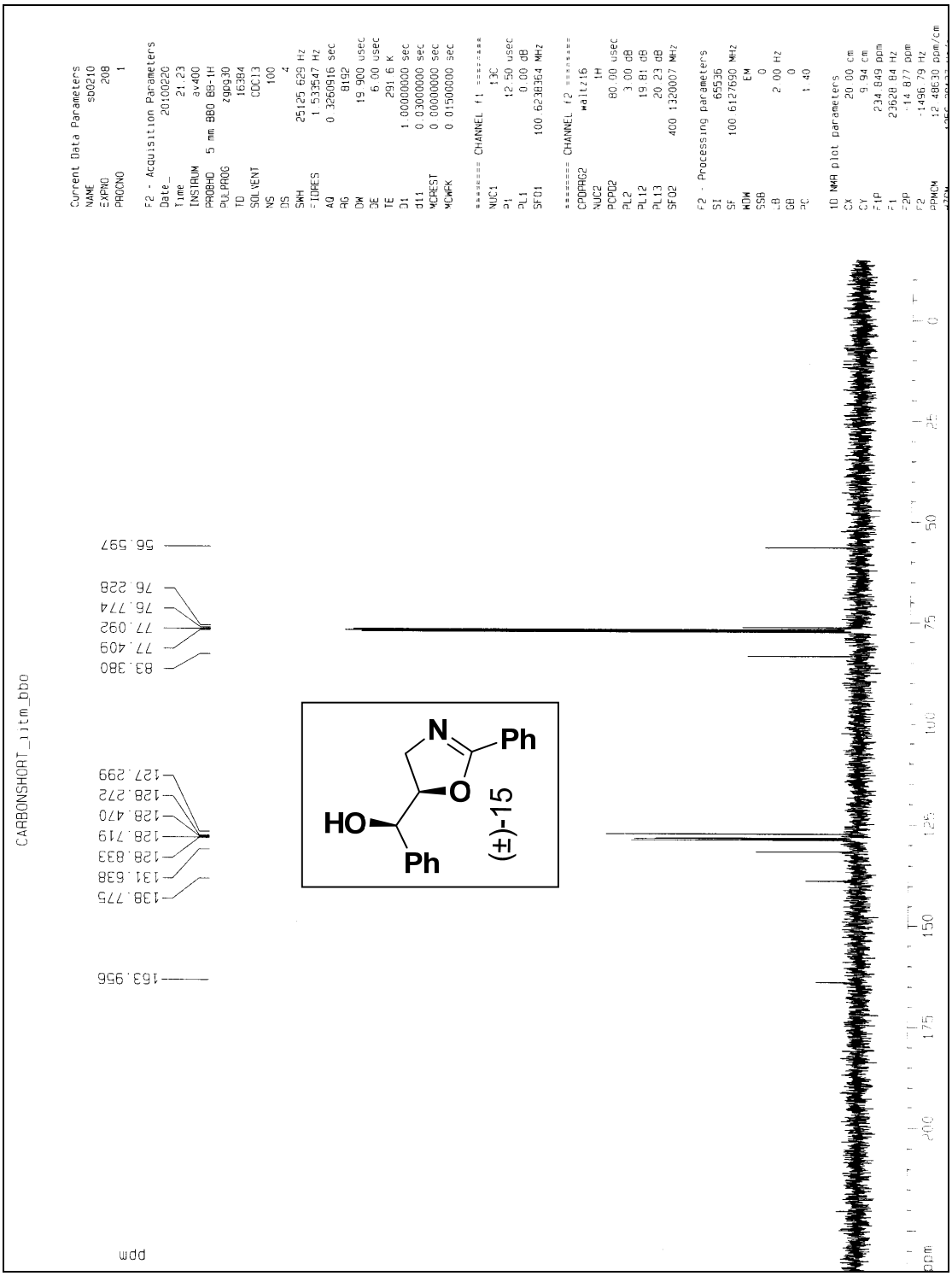


Figure 14. ^{13}C NMR spectrum of compound (±)-**15**