Supporting Information

Electrochemical Collective Synthesis of Labeled Pyrroloindoline Alkaloids with Freon-type Methanes as Functional C1 Synthons

Chao Chen, Ru-Xin Liu, Feng Xiong, Zi-Hao Li, Jun-Chen Kang, Tong-Mei Ding,* Shu-Yu Zhang*

Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs & School of Chemistry and Chemical Engineering, Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Shanghai Jiao Tong University, Shanghai 200240, P.R. China.
E-mail: zhangsy16@sjtu.edu.cn
E-mail: dtm@sjtu.edu.cn

Contents

1. General information

Reagents: All commercial materials were used as received from Energy Chemical or Adamas-beta, Alfa Aesar, Acros, Bidepharm and Leyan unless otherwise noted.

Reactions: All reactions were carried out in undivided electrochemical cells (10 mL) using pre-dried glassware, if not noted otherwise. The electrochemical cells were fitted with a rubber stopper with electrical feed-throughs. Electrocatalysis was conducted using an DC-power supplier HY3005ET in constant current mode, CV studies were performed using a CHI660E workstation.

Chromatography: Thin layer chromatography (TLC) was carried out on silica gel 60 F254 pre-coated glass plates. Visualization was detected by irradiation with UV light (254 nm), or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Flash chromatography was carried out on 200 – 300 mesh silica gel, eluting with a mixture of petroleum ether (b.p. 60 – 90 °C) and ethyl acetate.

NMR Spectroscope: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD 400, 500, 600 or 700 M spectrometer, operating at 400 (or 500 or 600 or 700) MHz and 100 (or 125 or 150 or 175) MHz respectively. Chemical shifts (δ) were given in parts per million (ppm), and referenced relative to residual solvent $CHCl_3$ (7.26 ppm) in $CDCl_3$, or tetramethylsilane (0.00 ppm) as an internal standard for ^{1}H NMR spectra and deuterated solvent $CDCl_3$ (77.0 ppm) for ^{13}C NMR spectra. Coupling constants (*J*) were reported in hertz (Hz). The following abbreviations are used to indicate the multiplicity of the signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and associated combinations, e.g. dd = doublet of doublets.

Mass Spectrometry: High-resolution mass spectra (HRMS) were obtained on a Bruker Buker impact II using the electrospray ionization (ESI) technique.

X-Ray: X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer.

Preparation of substrates: The acrylamides were prepared according to the related references. [1-6]

2. Cyclic voltammetry studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 20 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a saturated calomel electrode as reference electrode, and a platinum wire counter electrode. The solution of interest was sparged with nitrogen for 3-5 minutes before data collection. The diagrams were made using OriginLab 8.0.

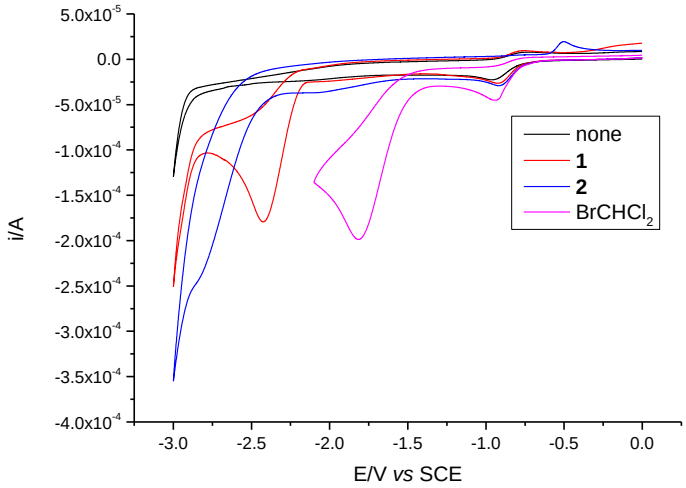


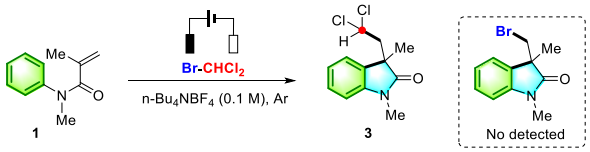
Fig. S1. Cyclic voltammogram of **1** (10 mM), **3** (10 mM), and $BrCHCl_2$ (10 mM) in DMF (10 mL) containing n-Bu_4NBF_4 (1 mmol). **Scan rate: 50 mV/s.**

3. Optimization table of reaction conditions

The desired chlorinated oxindoles could be obtained in 89% yield using a carbon felt as the anode and a foam Ni plate as the cathode, in an undivided cell containing DMF and n-Bu_4NBF_4 at 100 ℃ (**Table S1**, entry 1). Decrease of amounts of $BrCHCl_2$ to 5 equiv. resulted in 79% yield, while reaction temperature of 80 ℃ resulted in a sharp decrease in the yield (entry 2 and 3). A 66% yield was obtained when DMSO was used as the solvent (entry 4). Then various anodes and cathodes were screened, and Pt cathode, carbon felt cathode, Pt anode and even foam Ni anode can enable the reaction to proceed smoothly, although in lower yield (entries 5-8). A reaction process analysis was conducted to monitor the reaction (see SI), and we found that about 90% of acrylamide **1** was consumed and 81% of product was obtained when the reaction time

was 6 h (entry 9). However, when we conducted the reaction at a current of 10 mA, 3h instead of 5 mA, 6h to ensure the same quantity of electricity in the reaction, the yield decreased to 63%, which indicated that high current density may not be beneficial to the reaction probably because of overreduction of $BrCHCl_2$ and limited mass transfer rate to the electrode surface (entry 10). Exposure to air instead of Ar atmosphere resulted in a sharp decrease of yield (entry 11), while no products was obtained without electricity, confirming the indispensable role of electricity in the reaction (entry 12).

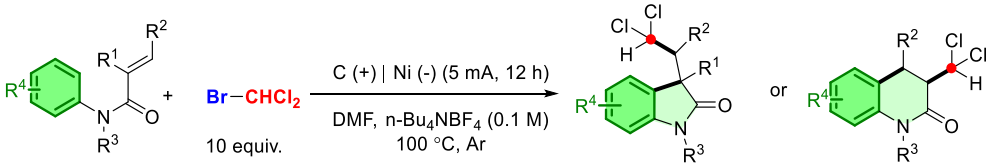
Table S1. Optimization.[a]



entry	(+)/(-)	Reagents (equiv.)	yield
1	C/Ni	$BrCHCl_2$ (10), 100 °C, DMF	89%
2	C/Ni	$BrCHCl_2$ (5), 100 °C, DMF	79%
3	C/Ni	$BrCHCl_2$ (10), 80 °C, DMF	13%
4	C/Ni	$BrCHCl_2$ (10), 100 °C, DMSO	66%
5	C/Pt	$BrCHCl_2$ (10), 100 °C, DMF	76%
6	C/C	$BrCHCl_2$ (10), 100 °C, DMF	88%
7	Pt/Ni	$BrCHCl_2$ (10), 100 °C, DMF	86%
8	Ni/Ni	$BrCHCl_2$ (10), 100 °C, DMF	79%
9[b]	C/Ni	$BrCHCl_2$ (10), 100 °C, DMF	81%
10[c]	C/Ni	$BrCHCl_2$ (10), 100 °C, DMF	63%
11[d]	C/Ni	$BrCHCl_2$ (10), 100 °C, DMF	22%
12[e]	C/Ni	$BrCHCl_2$ (10), 100 °C, DMF	<5%

[a]Reaction conditions: acrylamide (0.2 mmol), $BrCHCl_2$, solvent (4 mL), n-Bu_4NBF_4 (0.1 M), Ar, anode area (0.5 cm × 0.5 cm), cathode area (0.5 cm × 0.5 cm), constant current (5 mA, 12h), undivided cell. Isolated yield. [b]5 mA, 6h. [c]10 mA, 3h. [d]Air. [e]No current.

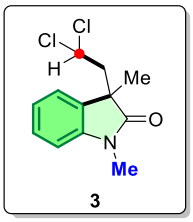
4. General procedure for electrochemical radical cyclization



General procedure 1: To an oven-dried Schlenk tube equipped with a magnetic stir bar, acrylamide (1 equiv., 0.2 mmol) and n-Bu_4NBF_4 (0.1 M, 0.4 mmol, 132 mg) were

added. The rubber plug equipped with a carbon felt anode (10 mm * 10 mm) and a foam Ni cathode (10 mm* mm) was used to keep the Schlenk tube sealed. The tube was evacuated and filled with Ar, repeating three times. $BrCHCl_2$ (10 equiv., 2 mmol, 165 μL) was dissolved in 4 mL DMF and then injected into the tube via syringe. The mixture was stirred for 5 min and put in the oil bath (100 ℃) with the electrolysis of 5 mA, 12h. After the reaction, the tube was cooled to room temperature and ethyl acetate (10 mL) and water (10 mL) was added. The aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

Fig. S2. The electrochemical reaction setup.

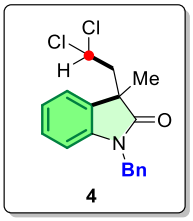


Purification of the crude product by flash column chromatography afforded the cyclization product **3** as colorless oil in 89% yield (46 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.7, 1.3 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.11 – 7.07 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.38 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.20 (s, 3H), 3.03 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.70 (dd, *J* = 14.8, 4.1 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 143.4, 131.0, 128.6, 122.6, 122.6, 108.6, 69.6, 50.1, 47.1, 26.4, 25.4.

HRMS (ESI) *m/z* calculated for $C_{12}H_{13}Cl_2NNaO$ [M+Na$^+$] 280.0266, found 280.0267.



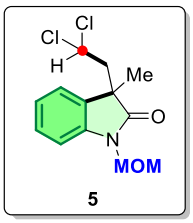
4

Purification of the crude product by flash column chromatography afforded the cyclization product **4** as pale yellow oil in 52% yield (35 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 5H), 7.23 – 7.19 (m, 2H), 7.09 – 7.05 (m, 1H), 6.80 – 6.78 (m, 1H), 5.45 (dd, *J* = 8.9, 4.4 Hz, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 3.10 (dd, *J* = 14.8, 9.0 Hz, 1H), 2.76 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 142.5, 135.7, 131.1, 128.7, 128.5, 127.7, 127.5, 122.7, 122.7, 109.6, 69.6, 49.9, 47.2, 44.1, 26.1.

HRMS (ESI) *m/z* calculated for $C_{18}H_{17}Cl_2NNaO$ [M+Na$^+$] 356.0579, found 356.0581.



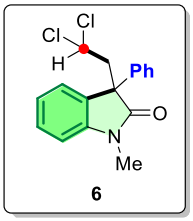
5

Purification of the crude product by flash column chromatography afforded the cyclization product **5** as colorless oil in 64% yield (37 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 7.7, 1.0 Hz, 1H), 7.22 (d, *J* = 6.9 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 5.44 (dd, *J* = 9.1, 4.3 Hz, 1H), 5.15 (d, *J* = 10.9 Hz, 1H), 5.08 (d, *J* = 10.9 Hz, 1H), 3.35 (s, 3H), 3.06 (dd, *J* = 14.9, 9.1 Hz, 1H), 2.74 (dd, *J* = 14.9, 4.3 Hz, 1H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 141.7, 130.6, 128.7, 123.2, 122.7, 1101, 71.8, 69.6, 56.5, 49.9, 47.5, 26.3.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}Cl_2NNaO_2$ [M+Na$^+$] 310.0372, found 310.0367.



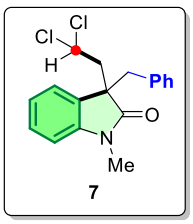
6

Purification of the crude product by flash column chromatography afforded the cyclization product **6** as white solid in 44% yield (28 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (td, *J* = 7.7, 0.9 Hz, 1H), 7.27 – 7.18 (m, 6H), 7.13 – 7.09 (m, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 5.38 (dd, *J* = 9.5, 3.8 Hz, 1H), 3.52 (dd, *J* = 14.7, 9.5 Hz, 1H), 3.11 (s, 3H), 3.02 (dd, *J* = 14.7, 3.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 144.4, 139.5, 129.2, 128.7, 128.6, 127.8, 126.4, 125.1, 122.7, 109.0, 69.8, 54.9, 50.1, 26.7.

HRMS (ESI) *m/z* calculated for $C_{17}H_{15}Cl_2NNaO$ [M+Na$^+$] 342.0423, found 342.0420.



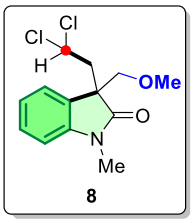
7

Purification of the crude product by flash column chromatography afforded the cyclization product **7** as white solid in 72% yield (48 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 1H), 7.14 – 7.02 (m, 5H), 6.79 – 6.76 (m, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 5.43 (dd, *J* = 9.3, 4.2 Hz, 1H), 3.18 (dd, *J* = 14.8, 9.3 Hz, 1H), 3.10 (d, *J* = 12.8 Hz, 1H), 2.99 (d, *J* = 12.8 Hz, 1H), 2.93 (s, 3H), 2.85 (dd, *J* = 14.8, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 144.0, 134.3, 130.0, 128.7, 128.1, 127.5, 126.8, 123.7, 122.1, 108.3, 69.7, 53.0, 48.6, 45.0, 26.0.

HRMS (ESI) *m/z* calculated for $C_{18}H_{17}Cl_2NNaO$ [M+Na$^+$] 356.0579, found 356.0580.



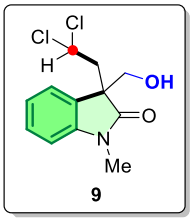
8

Purification of the crude product by flash column chromatography afforded the cyclization product **8** as pale yellow solid in 77% yield (44 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.11 – 7.07 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.40 (dd, *J* = 8.2, 5.3 Hz, 1H), 3.61 (d, *J* = 8.8 Hz, 1H), 3.40 (d, *J* = 8.8 Hz, 1H), 3.25 (s, 3H), 3.19 (s, 3H), 2.97 – 2.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 144.1, 128.8, 128.1, 124.0, 122.5, 108.4, 76.5, 69.7, 59.5, 52.4, 45.6, 26.5.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}Cl_2NNaO_2$ [M+Na$^+$] 310.0372, found 310.0375.



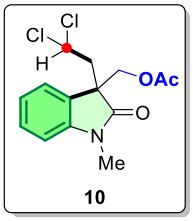
9

Purification of the crude product by flash column chromatography afforded the cyclization product **9** as pale gray sold in 83% yield (44 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (td, *J* = 7.7, 1.2 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.12 (td, *J* = 7.5, 0.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.43 (dd, *J* = 9.4, 4.3 Hz, 1H), 3.77 – 3.67 (m, 2H), 3.21 (s, 3H), 3.15 (dd, *J* = 14.9, 9.4 Hz, 1H), 2.85 (dd, *J* = 14.9, 4.2 Hz, 1H), 2.67 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 144.2, 129.2, 127.1, 123.3, 122.9, 108.8, 69.7, 67.7, 53.0, 45.5, 26.5.

HRMS (ESI) *m/z* calculated for $C_{12}H_{13}Cl_2NNaO_2$ [M+Na$^+$] 296.0216, found 296.0214.



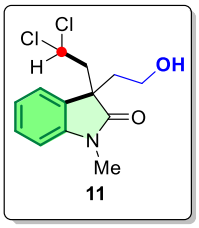
10

Purification of the crude product by flash column chromatography afforded the cyclization product **10** as colorless oil in 84% yield (53 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (td, *J* = 7.8, 1.2 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.10 (td, *J* = 7.5, 0.7 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.44 (dd, *J* = 9.2, 4.2 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 4.09 (d, *J* = 10.8 Hz, 1H), 3.22 (s, 3H), 3.03 (dd, *J* = 14.7, 9.3 Hz, 1H), 2.85 (dd, *J* = 14.7, 4.2 Hz, 1H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 170.1, 144.2, 129.4, 126.7, 123.8, 122.7, 108.7, 69.1, 67.2, 51.0, 45.5, 26.6, 20.5.

HRMS (ESI) *m/z* calculated for $C_{14}H_{15}Cl_2NNaO_3$ [M+Na$^+$] 338.0321, found 338.0320.



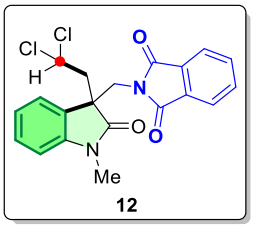
11

Purification of the crude product by flash column chromatography afforded the cyclization product **11** as colorless oil in 59% yield (34 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (td, J = 7.7, 1.2 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.14 – 7.10 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.36 (dd, *J* = 9.1, 4.1 Hz, 1H), 3.56 – 3.49 (m, 1H), 3.45 – 3.39 (m, 1H), 3.20 (s, 3H), 3.13 – 3.06 (m, 1H), 2.76 (dd, *J* = 14.8, 4.1 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.04 – 1.97 (m, 1H), 1.90 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 143.9, 129.0, 123.0, 122.9, 108.8, 69.3, 58.4, 49.9, 49.7, 41.2, 26.5.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}Cl_2NNaO_2$ [M+Na$^+$] 310.0372, found 310.0372.



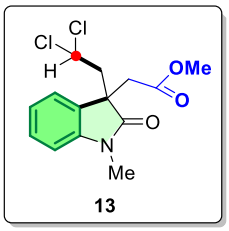
12

Purification of the crude product by flash column chromatography afforded the cyclization product **12** as white solid in 72% yield (58 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.29 (td, *J* = 7.8, 1.2 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.03 (td, *J* = 7.5, 0.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.41 (dd, *J* = 8.6, 4.9 Hz, 1H), 4.01 (d, *J* = 14.1 Hz, 1H), 3.94 (d, *J* = 14.1 Hz, 1H), 3.22 – 3.16 (m, 4H), 3.04 (dd, *J* = 14.9, 4.9Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 167.9, 144.0, 134.1, 131.6, 129.3, 126.8, 123.7, 123.5, 122.5, 108.7, 69.3, 51.4, 47.0, 44.1, 26.6.

HRMS (ESI) *m/z* calculated for $C_{20}H_{16}Cl_2N_2NaO_3$ [M+Na$^+$] 425.0430, found 425.0429.



13

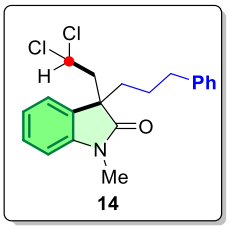
Purification of the crude product by flash column chromatography afforded the

cyclization product **13** as colorless oil in 87% yield (55 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (td, *J* = 7.7, 1.2 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.08 (td, *J* = 7.5, 0.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.42 (dd, *J* = 8.4, 4.6 Hz, 1H), 3.50 (s, 3H), 3.23 (s, 3H), 3.00 – 2.88 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 169.5, 144.3, 129.2, 128.3, 123.3, 122.6, 108.6, 68.9, 51.7, 49.0, 48.5, 41.4, 26.6.

HRMS (ESI) *m/z* calculated for $C_{14}H_{15}Cl_2NNaO_3$ [M+Na$^+$] 338.0321, found 338.0318.



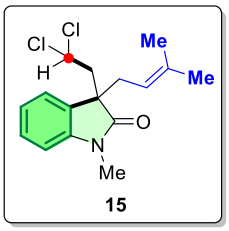
14

Purification of the crude product by flash column chromatography afforded the cyclization product **14** as colorless cream in 84% yield (61 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 1H), 7.23 – 7.19 (m, 2H), 7.15 – 7.06 (m, 3H), 7.01 (d, *J* = 7.0 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.34 (dd, *J* = 9.3, 4.0 Hz, 1H), 3.17 (s, 3H), 3.00 (dd, *J* = 14.8, 9.4 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.55 – 2.38 (m, 2H), 2.00 – 1.92 (m, 1H), 1.78 – 1.71 (m, 1H), 1.39 – 1.25 (m, 1H), 1.15 – 1.04 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 144.2, 141.4, 129.1, 128.6, 128.3, 128.2, 125.8, 122.8, 122.6, 108.4, 69.5, 51.4, 49.9, 38.7, 35.6, 26.3, 25.0.

HRMS (ESI) *m/z* calculated for $C_{20}H_{21}Cl_2NNaO$ [M+Na$^+$] 384.0892, found 384.0894.



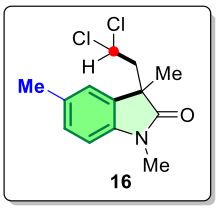
15

Purification of the crude product by flash column chromatography afforded the cyclization product **15** as colorless oil in 58% yield (36 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.7, 1.1 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 5.37 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.87 – 4.83 (m, 1H), 3.19 (s, 3H), 3.01 (dd, *J* = 14.8, 9.4 Hz, 1H), 2.76 (dd, *J* = 14.8, 4.2 Hz, 1H), 2.50 – 2.37 (m, 2H), 1.60 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 144.0, 136.7, 129.2, 128.5, 123.4, 122.3, 116.5, 108.3, 69.9, 51.6, 48.3, 37.3, 26.4, 25.9, 18.0.

HRMS (ESI) *m/z* calculated for $C_{16}H_{19}Cl_2NNaO$ [M+Na$^+$] 334.0736, found 334.0735.



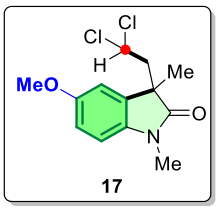
16

Purification of the crude product by flash column chromatography afforded the cyclization product **16** as colorless oil in 62% yield (34 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.10 (m, 1H), 7.00 – 6.99 (m, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.40 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.18 (s, 3H), 3.02 (dd, *J* = 14.8, 9.3 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.36 (s, 3H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 141.0, 132.2, 131.1, 128.9, 123.4, 108.3, 69.7, 50.2, 47.2, 26.4, 25.4, 21.1.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}Cl_2NNaO$ [M+Na$^+$] 294.0423, found 294.0424.



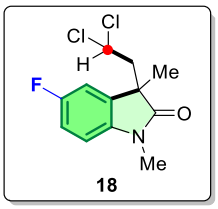
17

Purification of the crude product by flash column chromatography afforded the cyclization product **17** as pale yellow solid in 75% yield (43 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 – 6.75 (m, 3H), 5.41 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.80 (s, 3H), 3.17 (s, 3H), 3.01 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.66 (dd, *J* = 14.8, 4.2 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 156.1, 136.8, 132.4, 112.3, 110.5, 108.8, 69.6, 55.8, 50.1, 47.5, 26.5, 25.4.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}Cl_2NNaO_2$ [M+Na$^+$] 310.0372, found 310.0371.



18

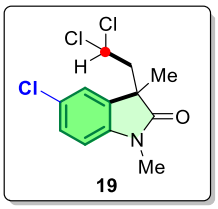
Purification of the crude product by flash column chromatography afforded the

cyclization product **18** as pale yellow solid in 89% yield (49 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (td, *J* = 8.7, 2.5 Hz, 1H), 6.95 (dd, *J* = 7.7, 2.5 Hz, 1H), 6.79 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.41 (dd, *J* = 8.8, 4.6 Hz, 1H), 3.18 (s, 3H), 3.01 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.68 (dd, *J* = 14.9, 4.6 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 159.2 (d, *J* = 241.4 Hz), 139.3 (d, *J* = 1.6 Hz), 132.8 (d, *J* = 7.8 Hz), 114.8 (d, *J* = 23.4 Hz), 110.9 (d, *J* = 24.7 Hz), 109.1 (d, *J* = 8.1 Hz), 69.3, 49.9, 47.6 (d, *J* = 1.7 Hz), 26.5, 25.4.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}Cl_2FNNaO$ [M+Na$^+$] 298.0172, found 298.0172.



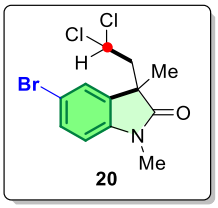
19

Purification of the crude product by flash column chromatography afforded the cyclization product **19** as white solid in 85% yield (50 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.18 (d, *J* = 2.0 Hz,1H), 6.79 (d, *J* = 8.3 Hz, 1H), 5.41 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.80 (s, 3H), 3.19 (s, 3H), 3.03 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.68 (dd, *J* = 14.9, 4.5 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 142.0, 132.9, 128.6, 128.1, 123.2, 109.5, 69.3, 49.9, 47.4, 26.6, 25.4.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}Cl_3NNaO$ [M+Na$^+$] 313.9877, found 313.9877.



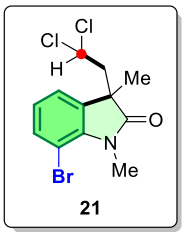
20

Purification of the crude product by flash column chromatography afforded the cyclization product **20** as pale yellow solid in 87% yield (58 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.31 (d, *J* = 1.7 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.40 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.18 (s, 3H), 3.01 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 142.2, 133.2, 131.5, 125.9, 115.3, 110.0, 69.3, 49.8, 47.3, 26.5, 25.4.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}BrCl_2NNaO$ [M+Na^+] 357.9372, found 357.9370.



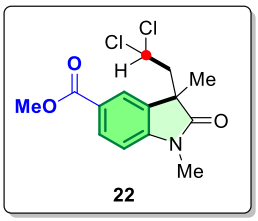
21

Purification of the crude product by flash column chromatography afforded the cyclization product **21** as colorless oil in 77% yield (52 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.10 (dd, *J* = 7.3, 1.0 Hz, 1H), 6.95 – 6.92 (m, 1H), 5.38 (dd, *J* = 9.0, 4.4 Hz, 1H), 3.58 (s, 3H), 3.02 (dd, *J* = 14.8, 9.0 Hz, 1H), 2.67 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 140.8, 134.3, 134.2, 123.8, 121.7, 103.0, 69.3, 50.2, 46.9, 30.0, 25.8.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}BrCl_2NNaO$ [M+Na^+] 357.9372, found 357.9371.



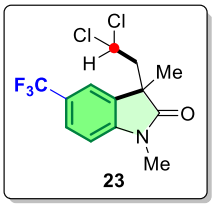
22

Purification of the crude product by flash column chromatography afforded the cyclization product **22** as pale yellow solid in 57% yield (36 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.87 (d, *J* = 1.5 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 5.37 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.92 (s, 3H), 3.23 (s, 3H), 3.05 (dd, *J* = 14.9, 9.3 Hz, 1H), 2.75 (dd, *J* = 14.9, 4.3 Hz, 1H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 166.6, 147.5, 131.3, 131.1, 124.6, 123.9, 108.1, 69.4, 52.1, 49.8, 47.0, 26.6, 25.4.

HRMS (ESI) *m/z* calculated for $C_{14}H_{15}Cl_2NNaO_3$ [M+Na^+] 338.0321, found 338.0318.



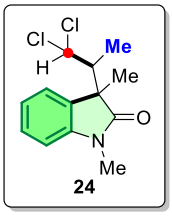
23

Purification of the crude product by flash column chromatography afforded the cyclization product **23** as colorless oil in 25% yield (16 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.43 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 5.39 (dd, *J* = 8.9, 4.6 Hz, 1H), 3.24 (s, 3H), 3.06 (dd, *J* = 14.9, 8.9 Hz, 1H), 2.75 (dd, *J* = 14.9, 4.6 Hz, 1H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 146.3, 131.8, 126.5 (q, *J* = 3.9 Hz, 1H), 125.0 (q, *J* = 32.8 Hz, 1H), 124.2 (q, *J* = 271.6 Hz, 1H), 119.7 (d, *J* = 3.5 Hz, 1H), 108.4, 69.2 (d, *J* = 5.6 Hz, 1H), 49.8, 47.1, 26.7, 25.4.

HRMS (ESI) *m/z* calculated for $C_{13}H_{12}Cl_2F_3NNaO$ [M+Na$^+$] 348.0140, found 348.0141.



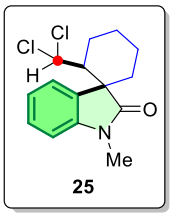
24

Purification of the crude product by flash column chromatography afforded the cyclization product **24** as colorless oil in 68% yield (37 mg, a mixture of diastereoisomers, d.r. ~ 4.1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 1H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.11 – 7.03 (m, 1H), 6.88 – 6.84 (m, 1H), 5.77 (d, *J* = 2.8 Hz, 0.19H), 5.65 (d, *J* = 1.6 Hz, 0.77H), 3.24 (s, 0.6H), 3.17 (s, 2.4H), 2.82 – 2.76 (m, 0.2H), 2.71 – 2.66 (m, 0.8H), 1.54 – 1.51 (m, 3H), 1.45 – 1.42 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 178.0, 143.2, 131.9, 131.0, 128.5, 128.2, 124.3, 122.8, 122.6, 122.5, 108.4, 108.3, 75.3, 75.0, 51.6, 50.6, 50.0, 49.5, 26.3, 26.2, 23.5, 22.8, 9.0, 7.5.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}Cl_2NNaO$ [M+Na$^+$] 294.0423, found 294.0421.



25

Purification of the crude product by flash column chromatography afforded the cyclization product **25** in 41% yield (25 mg, diastereoisomers can be isolated with d.r.

~ 1.2:1).

25-up (pale yellow solid):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 1H), 7.13 – 7.07 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.35 (s, 1H), 3.15 (s, 3H), 2.54 – 2.46 (m, 2H), 2.43 – 2.31 (m, 1H), 2.14 – 2.11 (m, 2H), 1.82 – 1.73 (m, 2H), 1.60 – 1.47 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 143.3, 131.8, 128.5, 122.7, 121.6, 108.1, 73.9, 55.8, 49.3, 36.6, 26.1, 25.5, 20.1, 19.3.

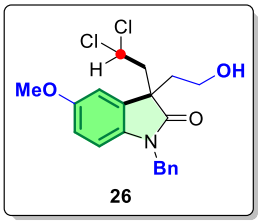
HRMS (ESI) *m/z* calculated for $C_{15}H_{17}Cl_2NNaO$ [M+Na$^+$] 320.0579, found 320.0580.

25-down (pale yellow solid):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.24 (d, *J* = 6.2 Hz, 1H), 3.23 (s, 3H), 2.83 – 2.77 (m, 1H), 2.41 – 2.36 (m, 1H), 2.11 – 2.08 (m, 1H), 1.95 – 1.88 (m, 1H), 1.85 – 1.65 (m, 4H), 1.48 – 1.42 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 143.4, 130.0, 128.2, 125.7, 121.8, 108.6, 75.1, 51.5, 51.5, 36.6, 26.6, 24.9, 24.6, 20.9.

HRMS (ESI) *m/z* calculated for $C_{15}H_{17}Cl_2NNaO$ [M+Na$^+$] 320.0579, found 320.0581.



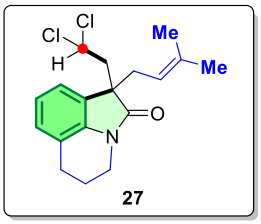
26

Purification of the crude product by flash column chromatography afforded the cyclization product **26** as pale yellow oil in 49% yield (38 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.75 – 6.72 (m, 1H), 6.69 – 6.67 (m, 1H), 5.44 (dd, *J* = 8.8, 4.4 Hz, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.72 (d, *J* = 15.6 Hz, 1H), 3.60 – 3.54 (m, 1H), 3.51 – 3.45 (m, 1H), 3.13 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.76 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.28 – 2.21 (m, 1H), 2.06 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 156.2, 136.6, 135.6, 130.6, 128.8, 127.7, 127.6, 112.6, 110.8, 110.2, 69.2, 58.5, 55.8, 50.3, 49.8, 44.5, 41.6

HRMS (ESI) *m/z* calculated for $C_{20}H_{21}Cl_2NNaO_3$ [M+Na$^+$] 416.0791, found 416.0785.



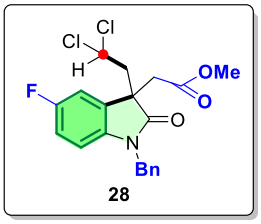
27

Purification of the crude product by flash column chromatography afforded the cyclization product **27** as colorless oil in 74% yield (50 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 – 7.04 (m, 1H), 7.01 – 7.00 (m, 1H), 6.97 – 6.93 (m, 1H), 5.37 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.93 – 4.89 (m, 1H), 3.73 – 3.62 (m, 2H), 2.99 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.79 – 2.73 (m, 3H), 2.48 (dd, *J* = 14.0, 7.7 Hz, 1H), 2.36 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.99 – 1.93 (m, 2H), 1.62 (s, 3H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 139.8, 136.6, 127.6, 127.3, 121.7, 121.3, 120.4, 116.8, 70.2, 52.8, 48.0, 39.0, 36.9, 25.9, 24.7, 21.1, 18.1.

HRMS (ESI) *m/z* calculated for $C_{18}H_{21}Cl_2NNaO$ [M+Na$^+$] 360.0892, found 360.0890.



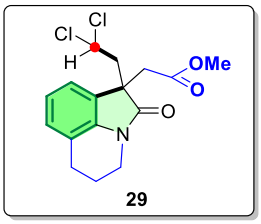
28

Purification of the crude product by flash column chromatography afforded the cyclization product **28** as pale yellow solid in 59% yield (48 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 7.07 (dd, *J* = 7.8, 2.6 Hz, 1H), 6.91 (td, *J* = 8.8, 2.6 Hz, 1H), 6.68 (dd, *J* = 8.6, 4.2 Hz, 1H), 5.51 (dd, *J* = 7.8, 5.2 Hz, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.7 Hz, 1H), 3.51 (s, 3H), 3.03 – 2.90 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 169.3, 159.1 (d, *J* = 241.9 Hz), 139.5 (d, *J* = 2.1 Hz), 135.2, 130.1 (d, *J* = 8.0 Hz), 128.8, 127.8, 127.5, 115.3 (d, *J* = 23.2 Hz), 111.8 (d, *J* = 25.0 Hz), 110.3 (d, *J* = 8.1 Hz), 68.6, 51.9, 49.0, 48.9 (d, J = 1.8 Hz), 44.6, 41.4.

HRMS (ESI) *m/z* calculated for $C_{20}H_{18}Cl_2FNNaO_3$ [M+Na$^+$] 432.0540, found 432.0539.



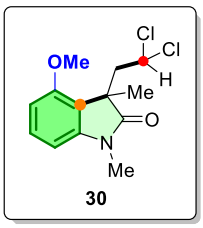
29

Purification of the crude product by flash column chromatography afforded the cyclization product **29** as pale yellow oil in 67% yield (46 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 7.06 (m, 2H), 6.97 – 6.93 (m, 1H), 5.42 (t, *J* = 6.5 Hz, 1H), 3.75 – 3.65 (m, 2H), 3.51 (s, 3H), 2.94 (d, *J* = 6.5 Hz, 2H), 2.91 – 2.81 (m, 2H), 2.77 (t, *J* = 6.1 Hz, 2H), 2.04 – 1.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 169.7, 140.0, 127.9, 126.6, 122.1, 121.3, 120.7, 69.3, 51.7, 49.6, 48.6, 41.1, 39.1, 24.6, 20.9.

HRMS (ESI) *m/z* calculated for $C_{16}H_{17}Cl_2NNaO_3$ [M+Na$^+$] 364.0478, found 364.0478.



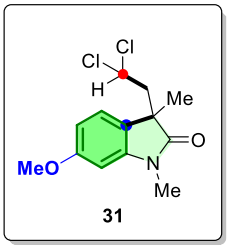
30

Purification of the crude product by flash column chromatography afforded the cyclization product **30** as pale yellow solid in 56% yield (32 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 5.33 (dd, *J* = 8.3, 5.3 Hz, 1H), 3.88 (s, 3H), 3.18 (s, 3H), 2.99 – 2.97 (m, 2H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 155.8, 144.7, 129.9, 116.3, 105.6, 101.9, 70.6, 55.5, 48.4, 47.5, 26.6, 23.1.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}Cl_2NNaO_2$ [M+Na$^+$] 310.0372, found 310.0373.



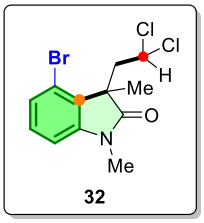
31

Purification of the crude product by flash column chromatography afforded the cyclization product **31** as colorless oil in 29% yield (17 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.2 Hz, 1H), 6.59 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.45 (d, *J* = 2.2 Hz, 1H), 5.37 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.84 (s, 3H), 3.18 (s, 3H), 3.00 (dd, *J* = 14.8, 9.4 Hz, 1H), 2.66 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 160.5, 144.7, 123.3, 122.8, 106.5, 96.6, 69.8, 55.5, 50.3, 46.7, 26.5, 25.5.

HRMS (ESI) *m/z* calculated for $C_{13}H_{15}Cl_2NNaO_2$ [M+Na$^+$] 310.0372, found 310.0374.



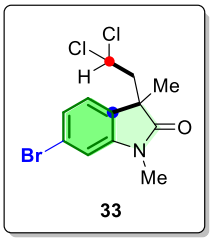
32

Purification of the crude product by flash column chromatography afforded the cyclization product **32** as white solid in 59% yield (40 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 6.82 (dd, *J* = 5.9, 2.9 Hz, 1H), 5.38 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.25 – 3.20 (m, 4H), 2.98 (dd, *J* = 14.8, 10.1 Hz, 1H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 145.6, 130.2, 128.9, 126.5, 118.9, 107.6, 70.0, 49.2, 47.6, 26.7, 22.5.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}BrCl_2NNaO$ [M+Na$^+$] 357.9372, found 357.9370.



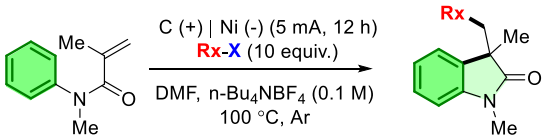
33

Purification of the crude product by flash column chromatography afforded the cyclization product **33** as colorless oil in 22% yield (15 mg).

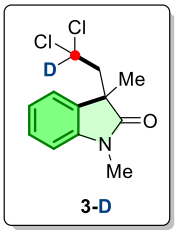
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 1.7 Hz, 1H), 5.38 (dd, *J* = 9.0, 4.4 Hz, 1H), 3.19 (s, 3H), 3.02 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.69 (dd, *J* = 14.9, 4.4 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 144.8, 130.0, 125.4, 124.0, 122.2, 112.2, 69.4, 49.9, 47.0, 26.6, 25.4.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}BrCl_2NNaO$ [M+Na^+] 357.9372, found 357.9367.



General procedure 2: To an oven-dried Schlenk tube equipped with a magnetic stir bar, acrylamide (1 equiv., 0.2 mmol, 35 mg) and n-Bu_4NBF_4 (0.1 M, 0.4 mmol, 132 mg) were added. The rubber plug equipped with a carbon felt anode (10 mm * 10 mm) and a foam Ni cathode (10 mm* mm) was used to keep the Schlenk tube sealed. The tube was evacuated and filled with Ar, repeating three times. halomethanes (10 equiv., 2 mmol) was dissolved in 4 mL DMF and then injected into the tube via syringe. The mixture was stirred for 5 min and put in the oil bath (100 ℃) with the electrolysis of 5 mA, 12h. After the reaction, the tube was cooled to room temperature and ethyl acetate (10 mL) and water (10 mL) was added. The aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

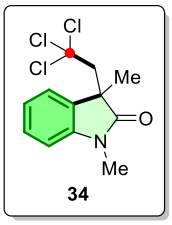


Purification of the crude product by flash column chromatography afforded the cyclization product **3-D** as colorless oil in 83% yield (43 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.7, 1.2 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.11 – 7.07 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.20 (s, 3H), 3.02 (d, *J* = 14.8 Hz, 1H), 2.69 (d, *J* = 14.8 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9 143.3, 131.0, 128.6, 122.6, 122.6, 108.6, 69.4 (*J* = 27.3 Hz), 49.9, 47.1, 26.4, 25.4.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}Cl_2DNNaO$ [M+Na^+] 281.0329, found 281.0327.



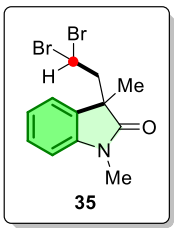
34

Purification of the crude product by flash column chromatography afforded the cyclization product **34** as pale yellow solid in 17% yield (10 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.69 (d, *J* = 15.2 Hz, 1H), 3.34 (d, *J* = 15.3 Hz, 1H), 3.23 (s, 3H), 1.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 143.2, 129.5, 128.5, 125.6, 122.0, 108.4, 96.1, 59.8, 48.0, 26.8, 26.6.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}Cl_3NNaO$ [M+Na$^+$] 313.9877, found 313.9875.



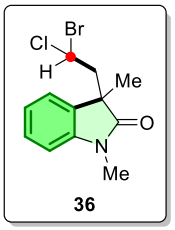
35

Purification of the crude product by flash column chromatography afforded the cyclization product **35** as colorless oil in 64% yield (44 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 7.7, 1.3 Hz, 1H), 7.19 – 7.17 (m, 1H), 7.12 – 7.08 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.30 (dd, *J* = 9.6, 4.3 Hz, 1H), 3.27 (dd, *J* = 15.1, 9.6 Hz, 1H), 3.20 (s, 3H), 2.99 (dd, *J* = 15.2, 4.3 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 143.5, 130.7, 128.6, 122.6, 108.6, 51.5, 48.5, 39.6, 26.5, 25.6.

HRMS (ESI) *m/z* calculated for $C_{12}H_{13}Br_2NNaO$ [M+Na$^+$] 367.9256, found 367.9254.



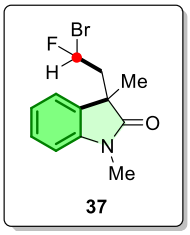
36

Purification of the crude product by flash column chromatography afforded the cyclization product **36** as colorless oil in 66% yield (40 mg, a mixture of diastereoisomers, d.r. ~ 1.2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (tdd, *J* = 7.7, 3.8, 1.1 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.12 – 7.08 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.43 – 5.36 (m, 1H), 3.21 – 3.09 (m, 4H), 2.87 – 2.81 (m, 1H), 1.39 (s, 1.3H), 1.38 (s, 1.5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 178.7, 143.5, 143.4, 131.1, 130.7, 128.6, 128.5, 122.7, 122.6, 122.6, 108.6, 108.6, 55.7, 55.6, 51.1, 50.8, 48.0, 47.8, 26.4, 25.6, 25.3.

HRMS (ESI) *m/z* calculated for $C_{12}H_{13}BrClNNaO$ [M+Na$^+$] 323.9761, found 323.9762.



37

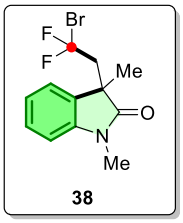
Purification of the crude product by flash column chromatography afforded the cyclization product **37** as colorless oil in 13% yield (8 mg, a mixture of diastereoisomers, d.r. ~ 1.5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 1H), 7.23 – 7.19 (m, 1H), 7.11 – 7.08 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.28 (dd, *J* = 7.4, 4.6 Hz, 0.2H), 6.25 (dd, *J* = 9.9, 2.0 Hz, 0.3H), 6.16 (dd, *J* = 7.4, 4.6 Hz, 0.2H), 6.12 (dd, *J* = 9.9, 2.0 Hz, 0.3H), 3.23 (s, 1.2H), 3.20 (s, 1.8H), 3.14 – 3.05 (m, 0.66H), 2.92 – 2.70 (m, 0.86H), 2.56 (dd, *J* = 14.9, 2.0 Hz, 0.32H), 2.46 (dd, *J* = 14.9, 2.0 Hz, 0.32H), 1.42 (s, 1.2H), 1.41 (s, 1.8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 178.7, 143.3, 142.9, 131.8, 131.3, 128.6, 128.4, 122.9, 122.8, 122.7, 122.7, 108.5, 108.5, 92.5 (d, *J* = 43.2 Hz), 90.0 (d, *J* = 43.2 Hz), 48.5 (d, *J* = 19.7 Hz), 47.6 (d, *J* = 19.4 Hz), 47.0, 46.9, 46.9, 26.4, 26.3, 24.7, 24.0.

^{19}F NMR (376 MHz, $CDCl_3$) -130.1 (s, 1F), -133.8 (s, 1.5F).

HRMS (ESI) *m/z* calculated for C12H13BrFNNaO [M+Na$^+$] 308.0057, found 308.0055.



38

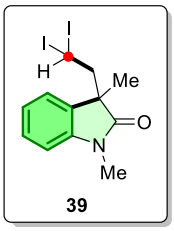
Purification of the crude product by flash column chromatography afforded the cyclization product **38** as colorless oil in 38% yield (23 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.7, 1.1 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.08 (td, *J* = 7.5, 0.7 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.34 – 3.22 (m, 4H), 3.10 – 2.98 (m, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 142.8, 130.8, 128.4, 123.8 (t, *J* = 1.7 Hz), 122.5, 119.5 (t, *J* = 307.5 Hz), 108.4, 50.9 (t, *J* = 21.0 Hz), 45.9, 26.4, 25.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ ppm −39.9 (d, *J* = 155.0 Hz, 1F), -43.9 (d, *J* = 154.9 Hz, 1F).

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}BrF_2NNaO$ [M+Na^+] 325.9963, found 325.9963.



39

Purification of the crude product by flash column chromatography afforded the cyclization product **39** as colorless cream in 29% yield (26 mg).

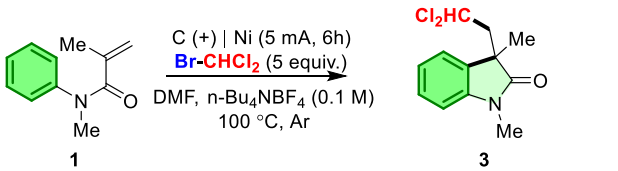
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (td, *J* = 7.7, 1.4 Hz, 1H), 7.17 – 7.15 (m, 1H), 7.12 – 7.08 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.68 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.35 (dd, J = 15.3, 9.7 Hz, 1H), 3.21 – 3.15 (m, 4H), 1.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 143.9, 130.3, 128.6, 122.7, 122.7, 108.7, 54.0, 50.8, 26.6, 25.9, -38.6.

HRMS (ESI) *m/z* calculated for $C_{12}H_{13}I_2NNaO$ [M+Na^+] 463.8979, found 463.8977.

5. Mechanistic studies

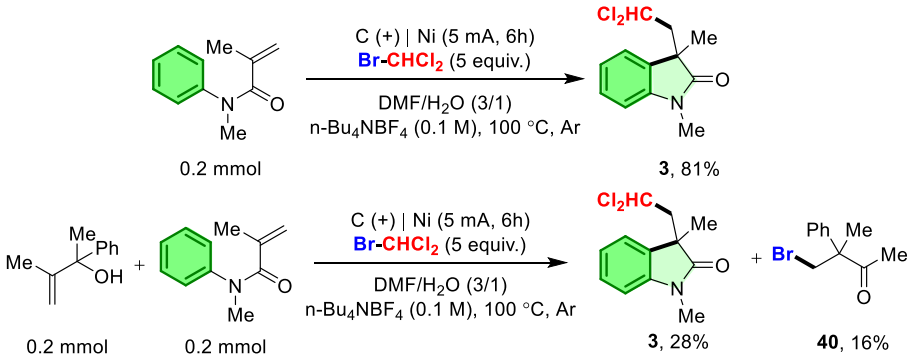
a) Radical scavenging experiments



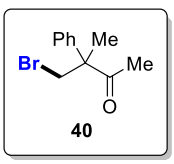
To an oven-dried Schlenk tube equipped with a magnetic stir bar, acrylamide (1 equiv., 0.2 mmol, 35 mg), n-Bu_4NBF_4 (0.1 M, 0.4 mmol, 132 mg) and radical scavenger (tempo, 5 equiv., 156 mg) were added. The rubber plug equipped with a carbon felt

anode (5 mm * 5 mm) and a foam Ni cathode (5 mm* 5 mm) was used to keep the Schlenk tube sealed. The tube was evacuated and filled with Ar, repeating three times. $BrCHCl_2$ (5 equiv., 2 mmol, 83 μL) was dissolved in 4 mL DMF and then injected into the tube via syringe. The mixture was stirred for 5 min and put in the oil bath (100 ℃) with the electrolysis of 5 mA, 6h. After the reaction, the tube was cooled to room temperature and trace **3** was detected by thin layer chromatography.

b) Detection of generated bromide ion



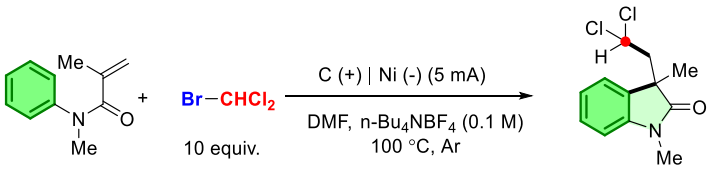
To an oven-dried Schlenk tube equipped with a magnetic stir bar, acrylamide (1 equiv., 0.2 mmol, 35 mg), n-Bu_4NBF_4 (0.1 M, 0.4 mmol, 132 mg) and allyl alcohol (1 equiv., 0.2 mmol, 33 mg) were added. The rubber plug equipped with a carbon felt anode (5 mm * 5 mm) and a foam Ni cathode (5 mm* 5 mm) was used to keep the Schlenk tube sealed. The tube was evacuated and filled with Ar, repeating three times. $BrCHCl_2$ (5 equiv., 2 mmol, 83 μL) was dissolved in DMF/H_2O (3/1 mL) and then injected into the tube via syringe. The mixture was stirred for 5 min and put in the oil bath (100 ℃) with the electrolysis of 5 mA, 6h. After the reaction, the tube was cooled to room temperature and ethyl acetate (10 mL) and water (10 mL) was added. The aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield **3** in 28% yield and **40** in 16% yield.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.33 – 7.30 (m, 1H), 7.26 – 7.24

(m, 2H), 3.95 (d, J = 10.4 Hz, 1H), 3.71 (d, J = 10.5 Hz, 1H), 2.00 (s, 3H), 1.72 (s, 3H). The ^{1}H NMR spectra is consistent with the literature.

c) Reaction process analysis



To an oven-dried Schlenk tube equipped with a magnetic stir bar, acrylamide (1 equiv., 0.2 mmol, 35 mg) and n-Bu_4NBF_4 (0.1 M, 0.4 mmol, 132 mg) were added. The rubber plug equipped with a carbon felt anode (5 mm * 5 mm) and a foam Ni cathode (5 mm * 5 mm) was used to keep the Schlenk tube sealed. The tube was evacuated and filled with Ar, repeating three times. $BrCHCl_2$ (10 equiv., 2 mmol, 165 μL) was dissolved in 4 mL DMF and then injected into the tube via syringe. The mixture was stirred for 5 min and put in the oil bath (100 ℃) with the electrolysis of 5 mA for different reaction time (1h, 2h, 3h, 6h, 12h). After the reaction, the tube was cooled to room temperature and ethyl acetate (10 mL) and water (10 mL) was added. The aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product and the acrylamide was recycled.

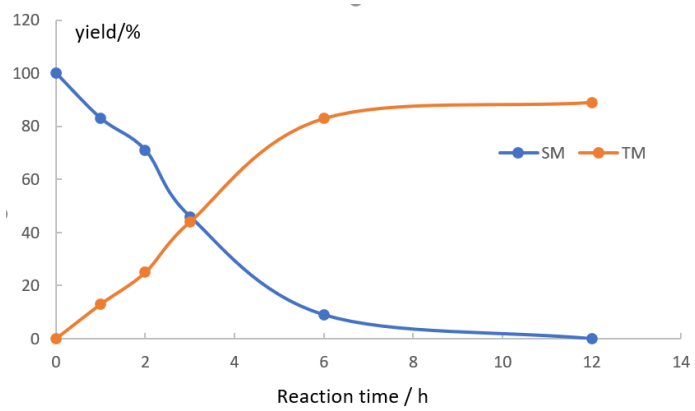
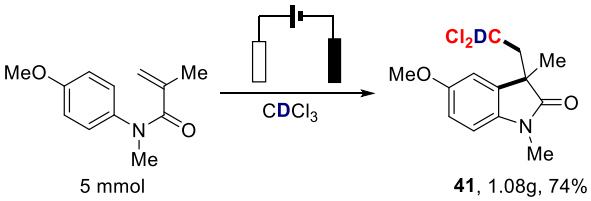


Fig. S3. Reaction process analysis.

6. Synthetic applications

(a) Gram-scale synthesis



To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar, acrylamide (1 equiv., 5 mmol, 1.025 g), $CDCl_3$ (10 equiv., 50 mmol, 4.05 mL), n-Bu_4NBF_4 (0.1 M, 5 mmol, 1.65 g) and dry DMF (50 mL) were added. The tube was flushed with Ar for 3 min to exclude the air. The rubber plug equipped with a carbon felt anode (25 mm * 20 mm) and a foam Ni cathode (25 mm * 20 mm) was used to keep the Schlenk tube sealed. The mixture was stirred for 5 min and put in the oil bath (100 ℃) with the electrolysis of 35 mA, 72 h. After the reaction, the tube was cooled to room temperature and ethyl acetate (50 mL) and water (200 mL) was added. The aqueous layer was separated and extracted with ethyl acetate (3×50 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **41** as white solid (1.08 g, 74%).

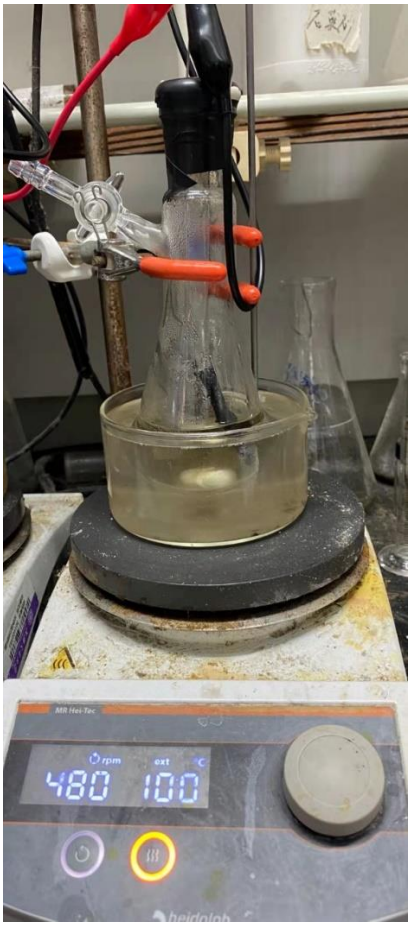
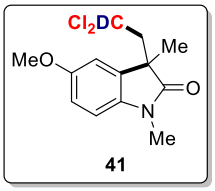


Fig. S4. The electrochemical reaction setup for gram-scale synthesis.

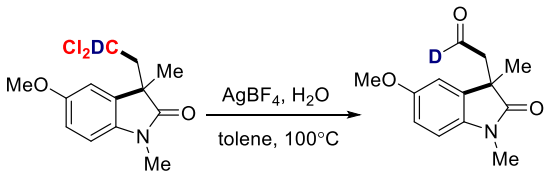


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.75 (m, 3H), 3.79 (s, 3H), 3.16 (s, 3H), 2.99 (d, *J* = 14.8 Hz, 1H), 2.65 (d, *J* = 14.8 Hz, 1H), 1.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 156.0, 136.8, 132.4, 112.3, 110.4, 108.8, 69.3 (t, *J* = 27.1 Hz), 55.7, 49.9, 47.5, 26.4, 25.4.

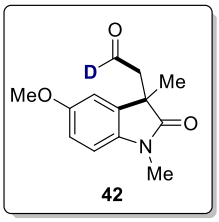
HRMS (ESI) *m/z* calculated for $C_{13}H_{14}Cl_2DNNaO_2$ [M+Na^+] 311.0435, found 311.0432.

(b) Synthesis of deuterated (±) -Physostigmine



41 **42**, 67%

To an oven-dried 10 mL reaction tube equipped with a magnetic stir bar, **41** (1 equiv., 0.2 mmol, 58 mg), $AgBF_4$ (4 equiv., 0.8 mmol, 160 mg), Celite (100 mg), H_2O (100 μL) and toluene (1 mL) were added. The tube was flushed with Ar for 1 min to exclude the air. The tube was sealed and put in the oil bath (100 ℃) with vigorous stirring. After the reaction, the tube was cooled to room temperature and the reaction mixture was subjected to flash column chromatography on silica gel directly to yield the desired product **42** as white solid (31 mg, 67%).

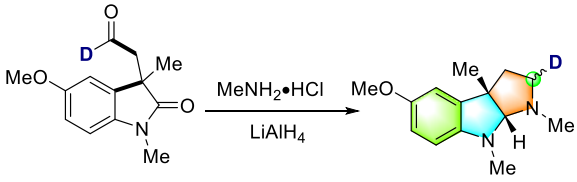


42

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 – 6.76 (m, 3H), 3.78 (s, 3H), 3.24 (s, 3H), 2.97 (d, *J* = 17.2 Hz, 1H), 2.90 (d, *J* = 17.2 Hz, 1H), 1.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3 (t, *J* = 26.8 Hz), 178.9, 155.8, 136.4, 133.9, 111.9, 110.1, 108.4, 55.5, 50.1 (t, *J* = 3.6 Hz), 45.1, 26.2, 23.7.

HRMS (ESI) *m/z* calculated for $C_{13}H_{14}DNNaO_3$ [M+Na$^+$] 257.1007, found 257.1006.

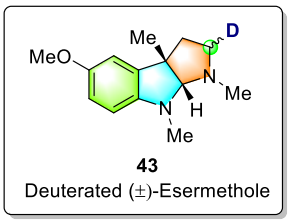


42

43, 83%
Deuterated (±)-Esermethole

To an oven-dried 100 mL flask equipped with a magnetic stir bar, **42** (1 equiv., 0.8 mmol, 180 mg), $MeNH_2 \cdot HCl$ (10 equiv., 8 mmol, 540 mg), Et_3N (10 equiv., 8 mmol, 1.115 mL), $MgSO_4$ (730 mg) and dry THF (45 mL) were added. The tube was flushed with Ar for 3 min to exclude the air. The tube was sealed and reacted for 16 h at room temperature. $LiAlH_4$ (10 equiv., 8 mmol, 306 mg) was then added and the mixture was refluxed at 80 ℃ for 1.5 h. After the reaction, the tube was cooled to room temperature

and ethyl acetate (30 mL) and saturated $NaHCO_3$ aq. solution (30 mL) were added. The aqueous layer was separated and extracted with ethyl acetate (3×20 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **43** as colorless oil (155 mg, 83%, a mixture of diastereoisomers, d.r. ~ 1.1:1).

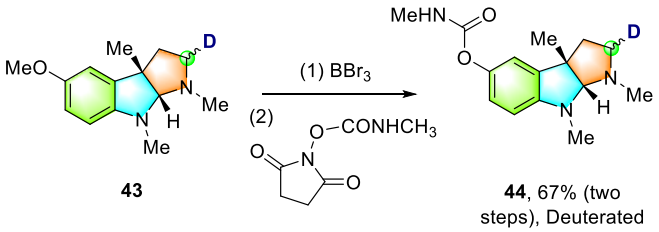


43
Deuterated (±)-Esermethole

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 – 6.63 (m, 2H), 6.35 (d, *J* = 8.1 Hz, 1H), 4.06 (s, 0.52H), 4.05 (s, 0.43H), 3.74 (s, 3H), 2.89 (s, 3H), 2.70 (t, *J* = 5.2 Hz, 0.51H), 2.61 (t, *J* = 7.5 Hz, 0.58H), 2.53 (s, 3H), 1.94 (d, *J* = 7.1 Hz, 2H), 1.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$; values in brackets were corresponding to the same carbon in diastereoisomers) δ 152.9, 146.5 (146.4), 138.2, 112.1, 109.7, 107.4, 98.3 (98.2), 55.9, 52.8 (td, *J* = 21.4, 3.1 Hz), 52.7, 40.7 (40.6), 38.1 (38.0), 37.9 (37.8), 27.4 (27.3).

HRMS (ESI) *m/z* calculated for $C_{14}H_{20}DN_2O$ $[M+H^+]$ 234.1711, found 234.1711.

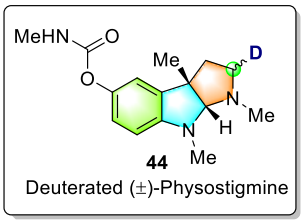


43

44, 67% (two steps), Deuterated (±)-Physostigmine

To an oven-dried 50 mL flask equipped with a magnetic stir bar, **43** (1 equiv., 0.5 mmol, 116 mg) was dissolved in dry DCM (10 mL). BBr_3 solution (1 M in DCM, 3 equiv., 1.5 mL) was slowly added at 0 °C and then reacted at rt for 5 h. After the reaction, the tube was cooled to 0 °C and quenched with H_2O (10 mL). The aqueous layer was separated and extracted with DCM (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was directly subjected to the next step of reaction. The resulting phenol was dissolved in dry THF (10 mL) and was added NaH (60% in mineral oil, 2.2 equiv., 1.1 mmol, 44 mg) slowly at 0 °C. After 10 min, N-succinimidyl-N-

methylcarbamate (1.1 equiv., 0.55 mmol, 95 mg) was added and reacted at room temperature for 2 h. Then the reaction was quenched with water and extracted with ethyl acetate. The organic layers were then combined, washed with brine, dried by Na_2SO_4, and concentrated. The residue was purified by using flashcolumn chromatography to give **44** as pale yellow oil (92 mg, 67% for two steps, a mixture of diastereoisomers, d.r. ~ 1.1:1).

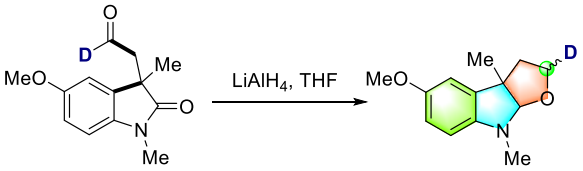


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.75 (d, *J* = 2.2 Hz, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 4.97 (d, *J* = 3.4 Hz, 1H), 4.16 (s, 0.50H), 4.15 (s, 0.49H), 2.91 (s, 3H), 2.86 (s, 1.29H), 2.85 (s, 1.50H), 2.73 (t, *J* = 4.9 Hz, 0.65H), 2.61 (t, *J* = 7.6 Hz, 0.63H), 2.53 (s, 3H), 1.95 (d, *J* = 7.2 Hz, 2H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$; values in brackets were corresponding to the same carbon in diastereoisomers) δ 156.1, 149.4 (149.3), 143.2, 137.3, 120.5, 116.1, 106.6, 97.8 (97.7), 52.7 (t, *J* =20.5 Hz), 52.6, 40.5 (40.4), 38.0 (37.9), 37.1 (37.0), 27.7, 27.2 (27.1).

HRMS (ESI) *m/z* calculated for $C_{15}H_{21}DN_3O_2$ [M+H$^+$] 277.1769, found 277.1767.

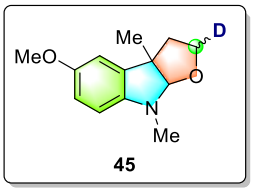
(c) Synthesis of furoindoline



42 **45**, 83%

To an oven-dried 10 mL reaction tube equipped with a magnetic stir bar, **42** (1 equiv., 0.3 mmol, 70 mg) was dissolved in dry THF (2 mL). $LiAlH_4$ solution (2.5 M in THF, 4 equiv., 0.48 mL) was slowly added at 0 ℃ with the atmosphere of Ar. After the reaction for 5 min, ethyl acetate and H_2O were added to quench the reaction. The aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was purified by using flashcolumn chromatography to give **45** as colorless oil (55 mg, 83%, a mixture of diastereoisomers,

d.r. ~ 1.5:1).

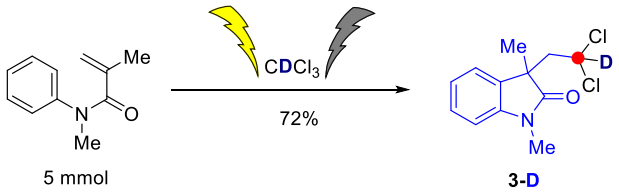


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, *J* = 2.2 Hz, 1H), 6.66 (d, *J* = 8.4, 2.3 Hz, 1H), 6.29 (d, *J* = 8.3 Hz, 1H), 5.03 (s, 1H), 3.93 (d, *J* = 7.1 Hz, 0.61H), 3.75 (s, 3H), 3.46 (dd, *J* = 10.9, 5.3 Hz, 0.43H), 2.88 (s, 3H), 2.14 – 2.01 (m, 2H), 1.45 (s, 3H).

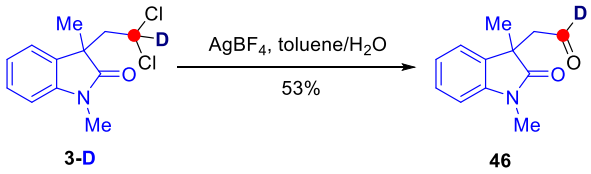
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 144.9, 136.0, 112.1, 110.4, 105.6, 105.2, 67.0 (t, *J* = 22.1 Hz), 56.0, 52.4, 41.3, 31.6, 24.4.

HRMS (ESI) *m/z* calculated for $C_{13}H_{17}DNO_2$ [M+H$^+$] 221.1395, found 221.1392.

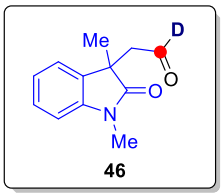
(d) Synthesis of deuterated (±)-Lansai B



To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar, acrylamide (1 equiv., 5 mmol, 857 mg), $CDCl_3$ (10 equiv., 50 mmol, 4.05 mL), n-Bu_4NBF_4 (0.1 M, 5 mmol, 1.65 g) and dry DMF (50 mL) were added. The tube was flushed with Ar for 3 min to exclude the air. The rubber plug equipped with a carbon felt anode (25 mm * 20 mm) and a foam Ni cathode (25 mm * 20 mm) was used to keep the Schlenk tube sealed. The mixture was stirred for 5 min and put in the oil bath (100 ℃) with the electrolysis of 35 mA, 72 h. After the reaction, the tube was cooled to room temperature and ethyl acetate (50 mL) and water (200 mL) was added. The aqueous layer was separated and extracted with ethyl acetate (3×50 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product **3-D**. Six parallel experiments (5 mmol×6) provided **3-D** in 72% yield (5.6g, 21.6 mmol).



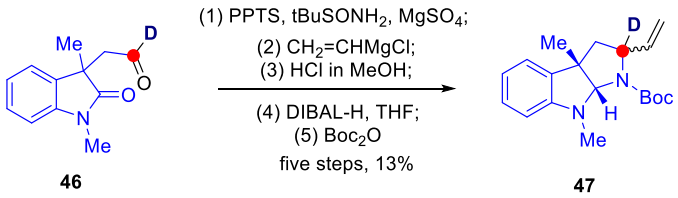
To an oven-dried 25 mL reaction tube equipped with a magnetic stir bar, **3-D** (1 equiv., 1 mmol, 259 mg), $AgBF_4$ (5 equiv., 5 mmol, 1 g), Celite (500 mg), H_2O (500 μL) and toluene (5 mL) were added. The tube was flushed with Ar for 3 min to exclude the air. The tube was sealed and put in the oil bath (100 ℃) with vigorous stirring for 2 h. After the reaction, the tube was cooled to room temperature and the reaction mixture was subjected to flash column chromatography on silica gel directly to yield the desired product **46** as colorless oil (109 mg, 53%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.18 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.04 (td, *J* = 7.6, 0.8 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 2.96 (d, *J* = 1.7 Hz, 2H), 1.41 (s, 3H).

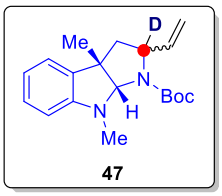
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4 (t, *J* = 26.9 Hz), 179.3, 143.0, 132.6, 128.1, 122.5, 122.2, 108.2, 50.2 (t, *J* = 3.7 Hz), 44.7, 26.2, 23.8.

HRMS (ESI) *m/z* calculated for $C_{12}H_{12}DNNaO_2$ [M+Na$^+$] 227.0901, found 227.0903.



To an oven-dried 50 mL reaction tube equipped with a magnetic stir bar, **46** (1 equiv., 7.5 mmol, 1.53 g), PPTS (5mol%, 0.38 mmol, 96 mg), $MgSO_4$ (5 equiv., 37.5 mmol, 4.52 g), ^{t}BuSONH$_2$ (2 equiv., 15 mmol, 1.82 g) and 20 mL dry DCM were added. The tube was sealed and reacted at room temperature overnight. After the reaction, the mixture was vacuum filtrated to remove salts firstly, and then filtrated through a short silica gel column quickly to remove PPTS and ^{t}BuSONH$_2$. The filtrate was concentrated, dried and used for the next step of reaction without further purification. The resulting

imine was dissolved in dry THF (15 mL) and cooled to – 65℃. Vinylmagnesium chloride (1 M in THF, 2 equiv., 15 mL) was added slowly to the reaction and the reaction proceeded at – 65℃ for 2 h. After the reaction, saturated aq. NH_4Cl solution was added to quench the reaction and ethyl acetate was added for extraction. The aqueous layer was separated and extracted with ethyl acetate (3×20 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to the further transformation. The resulting sulfinamide was dissolved in MeOH (20 mL) and then added aq. HCl (4 M, 2 equiv., 3.8 mL). The reaction proceeded at room temperature and monitored by TLC. After the reaction, the mixture was concentrated to remove solvent and then alkalized with aq $NaHCO_3$ solution followed by extraction with DCM. The combined organic layer was washed with 1N HCl aqueous solution until there was not amine in organic layer through TLC monitoring. Then aqueous layer was alkalized again with saturated aq. $NaHCO_3$ solution and extracted with DCM for three times. The combined organic phase was washed with brine, dried by anhydrous Na_2SO_4 and concentrated for the next step of reaction. The obtained amine was dissolved in dry THF (20 mL) and cooled to 0 ℃. DIBAL-H (1 M in hexane, 3 equiv., 22.5 mL) was added to the reaction and reacted at 0 ℃ for 1h, then at room temperature for 2h and at 80 ℃ for 15 h. After cooling to room temperature, a saturated aqueous solution of potassium sodium tartrate was added and ethyl acetate was used for extraction. The aqueous layer was separated and extracted with ethyl acetate (3×20 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to the further transformation. The resulting amine was dissolved in dry THF (10 mL) and Boc_2O (2 equiv., 3.5 mL) was added. The reaction proceeded at room temperature overnight and was then concentrated. The crude residue was subjected to flash column chromatography on silica gel to yield the **47** as colorless oil (307 mg, 13% for five steps, a mixture of diastereomers, d.r. ~ 4:1).

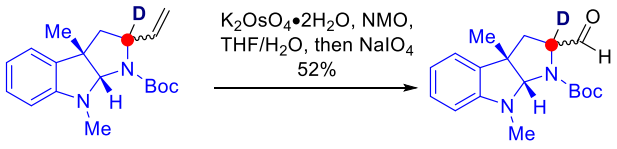


47

^{1}H NMR (400 MHz, $CDCl_3$; compound exists as a mixture of diastereomers, the major is denoted by *, minor denoted by §) δ 7.13 – 7.09 (m, 1H*§), 6.70 – 6.98 (m, 1H*§), 6.69 (t, *J* = 7.2 Hz, 0.87H*), 6.66 – 6.64 (m, 0.15H§), 6.43 (d, *J* = 7.8 Hz, 0.82H*), 6.38 (d, *J* = 7.8 Hz, 0.18H§), 5.88 (dd, *J* = 15.8, 10.5 Hz, 0.78H*), 5.48 (dd, *J* = 17.0, 10.0 Hz, 0.26H§), 5.23 (s, 1H*§), 5.07 – 5.01 (m, 1.91H*§), 4.84 (d, *J* = 10.0 Hz, 0.20H§), 3.01 (s, 2.55H*), 2.95 (s, 0.62H§), 2.30 (d, *J* = 12.7 Hz, 0.90H*), 2.18 (d, *J* = 12.8 Hz, 0.22H§), 2.01 (d, *J* = 12.8 Hz, 0.25H§), 1.85 (d, *J* = 12.8 Hz, 0.92H*),1.53 (s, 8.84H*§), 1.45 (s, 2.72H*§), 1.39 (s, 0.55H*§).

^{13}C NMR (101 MHz, $CDCl_3$; compound exists as a mixture of diastereomers, the major is denoted by *, minor denoted by §) δ 155.2§, 150.0*, 149.6§, 146.7*, 140.8*, 139.3§, 135.0*, 134.9§, 128.1*, 127.8§, 121.6§, 121.4*, 117.7*, 117.3§, 114.3§, 113.4*, 106.7*, 106.1§, 90.7*, 90.3§, 85.0*, 80.0§, 60.7* (t, *J* = 22.0 Hz), 50.0*, 46.3*, 45.1§, 35.2*, 32.7§, 28.2§, 27.3*, 24.5*, 24.1§.

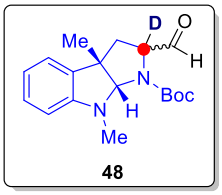
HRMS (ESI) *m/z* calculated for $C_{19}H_{26}DN_2O_2$ $[M+H^+]$ 316.2130, found 316.2128.



47 48

To an oven-dried 50 mL reaction tube equipped with a magnetic stir bar, **47** (1 equiv., 1.9 mmol, 595 mg), $K_2OsO_4 \cdot 2H_2O$ (0.2 equiv., 0.38 mmol, 140 mg), NMO (2 equiv., 3.8 mmol, 445 mg) and THF/H_2O (15/5 mL) were added. The tube was sealed and reacted at room temperature with stirring for 15 h. Then $NaIO_4$ (2 equiv., 3.8 mmol, 813 mg) was added and reacted for 2 h. $NaIO_4$ (2 equiv., 3.8 mmol, 813 mg) was added and reacted for 2 h again. After the reaction, a saturated aqueous solution of $Na_2S_2O_3$ (10 mL) was introduced. The mixture was then extracted with ethyl acetate (3 × 20 mL), and the combined organic phases were dried over anhydrous sodium sulfate. The filtrate was concentrated, and the residue was chromatographed on silica gel column to yield

48 as colorless oil (312 mg, 52%, a mixture of diastereomers, d.r. ~ 5:1, both diastereomers exist as a ~ 2:1 mixture of rotamers).

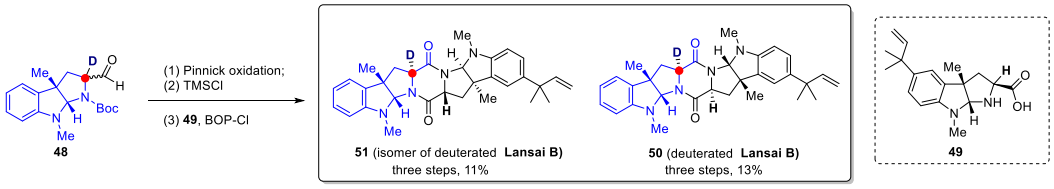


48

^{1}H NMR (400 MHz, $CDCl_3$; compound exists as a mixture of diastereomers, the major is denoted by *, minor denoted by §) δ 9.54 (s, 0.26H*), 9.51 (s, 0.50H*), 9.22 (s, 0.14H§), 7.16 – 7.10 (m, 1H*§), 7.01 – 6.94 (m, 1H*§), 6.73 – 6.67 (m, 1H*§), 6.46 – 6.43 (m, 1H*§), 5.30 (s, 0.51H*), 5.27 (s, 0.11H§), 5.14 (s, 0.06H§), 5.11 (s, 0.27H*), 3.05 (s, 1.51H*), 3.02 (s, 0.12H§), 3.01 (s, 0.29H§), 2.98 (s, 0.89H*), 2.36 (d, *J* = 13.2 Hz, 0.58H*), 2.31 – 2.25 (m, 0.44H*§), 2.18 (d, *J* = 12.8 Hz, 0.19H§), 2.03 (d, *J* = 13.5 Hz, 0.59H*), 1.98 (d, *J* = 13.3 Hz, 0.31H*), 1.55 (s, 3H*§), 1.45 (s, 5.45H*§), 1.42 (s, 1.59H*§), 1.40 (s, 1.81H*§).

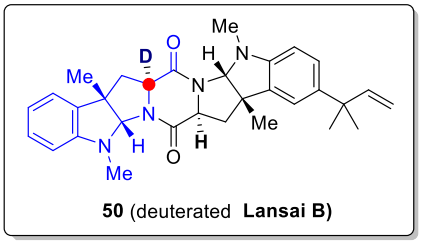
^{13}C NMR (101 MHz, $CDCl_3$; compound exists as a mixture of diastereomers, the major is denoted by *, minor denoted by §) δ 200.8§, 199.3*, 198.9*, 155.0§, 154.4*, 154.2*, 149.8*, 149.7*, 133.7*, 133.6*, 133.2§, 128.8*, 128.6*, 128.4§, 122.2§, 122.0§, 121.7*, 121.6*, 118.2*, 118.1*, 107.1*, 107.0*, 90.8*, 90.5§, 90.3*, 90.0§, 81.7*, 81.6*, 81.4§, 81.3§, 65.4* (t, *J* = 23.0 Hz), 65.2* (t, *J* = 23.0 Hz), 52.1*, 51.0§, 50.6*, 41.0*, 40.7§, 40.1*, 35.1*, 34.7*, 33.5§, 29.7§, 28.3*, 28.2§, 28.1*, 24.4*, 24.1*, 23.0§.

HRMS (ESI) *m/z* calculated for $C_{18}H_{23}DN_2NaO_3$ [M+Na$^+$] 340.1742, found 340.1741.



To an oven-dried flask equipped with a magnetic stir bar, **48** (1 equiv., 0.41 mmol, 130 mg) was dissolved in THF/H_2O/tBuOH (5/5/1.3 mL). 2-Methyl-2-butene (2.5 mL), $NaClO_2$ (2 equiv., 0.82 mmol, 80wt%, 93 mg), KH_2PO_4 (5 equiv., 2.05 mmol, 279 mg) were added and the reaction proceeded with stirring at room temperature for 3 h. After the reaction, a saturated aqueous solution of NH_4Cl (10 mL) was introduced. The mixture was then extracted with ethyl acetate (3 × 10 mL), and the combined organic

phases were dried over anhydrous sodium sulfate. The filtrate was concentrated, and the residue was subjected to the next step of the reaction without further purification. The resulting crude acid was dissolved in dry MeCN (5 mL) and TMSI (2 equiv., 0.82 mmol, 117 μL) was added at 0 ℃. The reaction proceeded at 0 ℃ for 1 h and then TMSI (2 equiv., 0.82 mmol, 117 μL) was added and reacted for one more hour. After the reaction, a saturated aqueous solution of $Na_2S_2O_3$ (2 mL) and H_2O (10 mL) was introduced. The mixture was then extracted with ethyl acetate (3 × 10 mL) and it is ensured that there was product in aqueous phase instead of organic phase. Organic phase was discarded and 1 M HCl aq. solution was added slowly to adjust the pH of aqueous phase to ~ 6. Then the aqueous phase was concentrated and dried on the rotary evaporator to remove moisture. The resulting mixture was then dissolved in DCM and turbid liquid was observed. The mixture was vacuum filtrated though filter paper and the filtrate was collected, concentrated and dried for the further transformation. The obtained amino acid and **49** (**49** was prepared according to the reference [7], 0.21 mmol, 63 mg) were dissolved in dry DCM (6 mL), followed by the addition of DIPEA (0.97 mmol, 167 μL) and BOP-Cl (0.84 mmol, 214 mg) at 0 ℃. The reaction was then conducted at ambient temperature for 13 h before it was quenched with a saturated aqueous solution of Na_2CO_3 (5 mL). The resulting mixture was extracted with ethyl acetate (3 × 5 mL). The organic phases were combined, dried over anhydrous sodium sulfate, and concentrated. The residue was purified by silica gel column chromatography (two times for silica gel column chromatography, eluent: PE/EA = 20:1; PE/acetone = 20:1) to afford **50** (target molecule, deuterated Lansai B, 13 mg, 13%) as pale yellow solid and **51** (isomers of deuterated Lansai B, 11 mg, 11%) as pale yellow solid.



50 (deuterated **Lansai B**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.06 (m, 2H), 7.04 (d, *J* = 7.0 Hz, 1H), 7.01 (d, *J* = 1.8 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 6.28 (d, *J* = 8.2 Hz,

1H), 5.97 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.44 (s, 1H), 5.42 (s, 1H), 5.02 (dd, *J* = 11.9, 1.3 Hz, 1H), 4.98 (dd, *J* = 5.1, 1.3 Hz, 1H), 4.17 (dd, *J* = 11.2, 6.1 Hz, 1H), 2.98 (s, 3H), 2.95 (s, 3H), 2.73 – 2.68 (m, 2H), 2.19 – 2.13 (m, 2H), 1.47 (s, 3H), 1.46 (s, 3H), 1.34 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 165.5, 150.1, 148.6, 148.2, 138.7, 132.9, 132.8, 128.7, 126.3, 122.3, 120.2, 118.1, 110.1, 105.8, 105.4, 86.9, 86.5, 60.1, 50.5, 50.3, 42.7, 42.6, 40.7, 33.1, 32.9, 28.5, 25.5, 25.4.

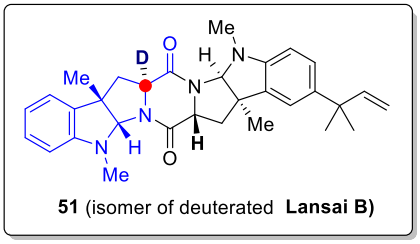
^{13}C NMR (176 MHz, $CDCl_3$) δ 165.8, 165.7, 149.9, 148.4, 147.5, 139.6, 133.2, 133.0, 128.8, 126.5, 122.4, 120.3, 118.3, 110.3, 106.3, 106.1, 87.1, 86.7, 60.2, 59.8 (t, *J* = 21.9 Hz), 50.5, 50.3, 42.7, 42.6, 40.7, 33.8, 33.1, 28.5, 25.6, 25.5.

HRMS (ESI) *m/z* calculated for $C_{31}H_{35}DN_4NaO_2$ [M+Na^+] 520.2793, found 520.2793.

Tuntiwachwuttikul et al. Report,[1] Natural (–)-lansai B ^{1}H NMR, 300 MHz, $CDCl_3$	Reisman et al. Report[2] Synthetic (–)-lansai B ^{1}H NMR, 500 MHz, $CDCl_3$	This Work, Synthetic Deuterated (±)-lansai B ^{1}H NMR, 400 MHz, $CDCl_3$
δ 7.11 (dt, *J* = 7.8, 1.5 Hz, 1H)	δ 7.13 – 7.05 (m, 1H)	δ 7.11 – 7.06 (m, 2H)
7.08 (dd, *J* = 8.1, 1.5 Hz, 1H)	7.07 (dd, *J* = 8.1, 1.8 Hz, 1H)	
7.06 (dd, *J* = 7.8, 1.5 Hz, 1H)	7.04 (dd, *J* = 7.3, 1.2 Hz, 1H)	7.04 (d, *J* = 7.0 Hz, 1H)
7.02 (d, *J* = 1.5 Hz, 1H)	7.01 (d, *J* = 1.9 Hz, 1H)	7.01 (d, *J* = 1.8 Hz, 1H)
6.71 (dt, *J* = 7.8, 1.5 Hz, 1H)	6.70 (td, *J* = 7.4, 0.9 Hz, 1H)	6.70 (t, *J* = 7.4 Hz, 1H)
6.36 (dd, *J* = 7.8, 1.5 Hz, 1H)	6.34 (d, *J* = 7.8 Hz, 1H)	6.34 (d, *J* = 7.8 Hz, 1H)
6.29 (d, *J* = 8.1 Hz, 1H)	6.28 (d, *J* = 8.1 Hz, 1H)	6.28 (d, *J* = 8.2 Hz, 1H)
5.99 (dd, *J* = 17.5, 10.6 Hz, 1H)	5.97 (dd, *J* = 17.4, 10.6 Hz, 1H)	5.97 (dd, *J* = 17.4, 10.6 Hz, 1H)
5.46 (s, 1H)	5.44 (s, 1H)	5.44 (s, 1H)
5.44 (s, 1H)	5.42 (s, 1H)	5.42 (s, 1H)
5.03 (d, *J* = 10.6 Hz, 1H)	5.01 (dd, *J* = 14.0, 1.4 Hz, 1H)	5.02 (dd, *J* = 11.9, 1.3 Hz, 1H)
5.01 (d, *J* = 17.5 Hz, 1H)	4.99 (dd, *J* = 7.2, 1.4 Hz, 1H)	4.98 (dd, *J* = 5.1, 1.3 Hz, 1H)
4.16 (m, 1H)	4.15 (app dddd, *J* = 13.5, 11.1, 6.1, 2.1 Hz, 2H)	4.17 (dd, *J* = 11.2, 6.1 Hz, 1H)
4.16 (m, 1H)	–	–
2.99 (s, 3H)	2.97 (s, 3H)	2.98 (s, 3H)
2.97 (s, 3H)	2.95 (s, 3H)	2.95 (s, 3H)
2.72 (dd, *J* = 12.3, 5.9 Hz, 1H)	2.71 (dd, *J* = 12.7, 3.0 Hz, 1H)	2.73 – 2.68 (m, 2H)
2.72 (dd, *J* = 12.3, 5.9 Hz, 1H)	2.69 (dd, *J* = 12.7, 3.0 Hz, 1H)	
2.18 (dd, *J* = 12.3, 11.3 Hz, 1H)	2.18 (dd, *J* = 12.6, 6.3 Hz, 1H)	2.19 – 2.13 (m, 2H)
2.17 (dd, J = 12.3, 11.3 Hz, 1H)	2.15 (dd, J = 12.7, 6.4 Hz, 1H)	
1.49 (s, 3H)	1.47 (s, 3H)	1.47 (s, 3H)
1.48 (s, 3H)	1.46 (s, 3H)	1.46 (s, 3H)
1.36 (s, 6H)	1.34 (s, 6H)	1.34 (s, 6H)

Tuntiwachwuttikul et al. Report,[1] Natural (–)-lansai B ^{13}C NMR, 75 MHz, $CDCl_3$	Reisman et al. Report[2] Synthetic (–)-lansai B ^{13}C NMR, 126 MHz, $CDCl_3$	This Work, Synthetic Deuterated (±)-lansai B ^{13}C NMR, 101 MHz, $CDCl_3$	Chemical Shift Difference, Δδ
δ 165.8	δ 165.7	165.8	0.1
165.6	165.5	165.5	0
150.1	150.1	150.1	0
148.6	148.6	148.6	0
148.3	148.2	148.2	0
138.7	138.7	138.7	0
132.9	132.9	132.9	0
132.8	132.8	132.8	0
128.8	128.7	128.7	0
126.3	126.3	126.3	0
122.3	122.3	122.3	0
120.2	120.2	120.2	0
118.1	118.1	118.1	0
110.2	110.1	110.1	0
105.8	105.8	105.8	0
105.4	105.4	105.4	0
86.9	86.9	86.9	0
86.6	86.5	86.5	0
60.1	60.1	60.1	0
60.1	60.1	\	\
50.5	50.5	50.5	0
50.3	50.3	50.3	0
42.7	42.7	42.7	0
42.7	42.7	42.6	0.1
40.7	40.7	40.7	0
33.1	33.1	33.1	0
32.9	32.9	32.9	0
28.5	28.5	28.5	0
28.5	28.5	–	–
25.5	25.5	25.5	0
25.4	25.4	25.4	0

Tuntiwachwuttikul et al. Report,[8] Natural (–)-lansai B ^{13}C NMR, 75 MHz, $CDCl_3$	Reisman et al. Report[7] Synthetic (–)-lansai B ^{13}C NMR, 126 MHz, $CDCl_3$	This Work, Synthetic Deuterated (±)-lansai B ^{13}C NMR, 175 MHz, $CDCl_3$	Chemical Shift Difference, Δδ
δ 165.8	δ 165.7	165.8	0.1
165.6	165.5	165.7	0.2
150.1	150.1	149.9	0.2
148.6	148.6	148.4	0.2
148.3	148.2	147.5	0.7
138.7	138.7	139.6	0.9
132.9	132.9	133.2	0.3
132.8	132.8	133.0	0.2
128.8	128.7	128.8	0.1
126.3	126.3	126.5	0.2
122.3	122.3	122.4	0.1
120.2	120.2	120.3	0.1
118.1	118.1	118.3	0.2
110.2	110.1	110.3	0.2
105.8	105.8	106.3	0.5
105.4	105.4	106.1	0.7
86.9	86.9	87.1	0.2
86.6	86.5	86.7	0.2
60.1	60.1	60.2	0.1
60.1	60.1	59.8 (t, J = 21.9 Hz)	0.3
50.5	50.5	50.5	0
50.3	50.3	50.3	0
42.7	42.7	42.7	0
42.7	42.7	42.6	0.1
40.7	40.7	40.7	0
33.1	33.1	33.8	0.7
32.9	32.9	33.1	0.2
28.5	28.5	28.5	0
28.5	28.5	–	–
25.5	25.5	25.6	0.1
25.4	25.4	25.5	0.1



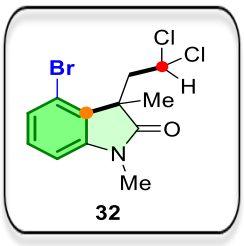
51 (isomer of deuterated **Lansai B)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.08 (m, 2H), 7.05 (d, *J* = 7.0 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 6.31 (d, *J* = 8.2 Hz, 1H), 5.99 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.48 (s, 1H), 5.47 (s, 1H), 5.03 (dd, *J* = 14.4, 1.2 Hz, 1H), 4.99 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.04 (dd, *J* = 12.3, 5.2 Hz, 1H), 2.98 (s, 3H), 2.96 (s, 3H), 2.69 – 2.65 (m, 2H), 2.03 – 1.97 (m, 2H), 1.47 (s, 3H), 1.46 (s, 3H), 1.36 (s, 6H).

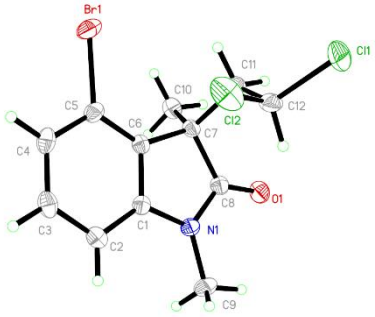
^{13}C NMR (176 MHz, $CDCl_3$) δ 164.8, 164.5, 150.7, 148.7, 148.6, 138.7, 132.4, 132.3, 128.8, 126.4, 122.9, 120.7, 118.0, 110.1, 105.4, 105.1, 87.4, 87.0, 59.7, 59.4 (t, *J* = 22.0 Hz), 50.9, 50.7, 45.2, 45.0, 40.7, 32.3, 31.9, 28.5, 26.0, 25.8.

HRMS (ESI) *m/z* calculated for $C_{31}H_{36}DN_4O_2$ [M+H$^+$] 498.2974, found 498.2969.

7. X-ray structure of compound 32, 51

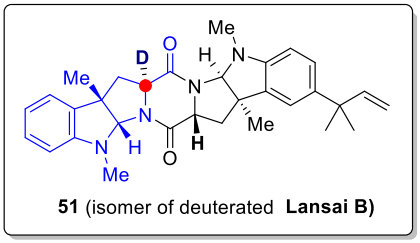


32

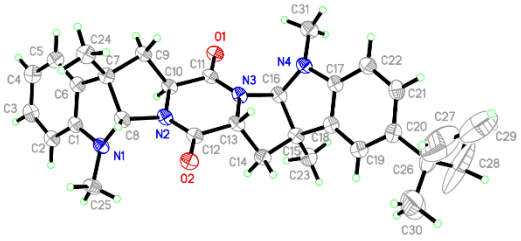


A colorless block shaped crystal of **32** ($C_{12}H_{12}BrCl_2NO$) was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 173(2) K, on a Bruker D8 VENTURE CMOS photon 100 diffractometer with helios mx multilayer monochrmator Cu-Kα radiation (λ = 1.54178 Å). The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers **CCDC 2128341** for **32**. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax:

+44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).



51 (isomer of deuterated **Lansai B)**



A colorless block shaped crystal of **51** ($C_{31}H_{35}DN_4O_2$) was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 173(2) K, on a Bruker D8 VENTURE CMOS photon 100 diffractometer with helios mx multilayer monochrmator Cu-Kα radiation (λ = 1.54178 Å). The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers **CCDC 2128343** for **51**. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

8. Reference

[1] M.-Z. Lu, T.-P. Loh, *Org. Lett.* **2014**, *16*, 4698.

[2] Y. Tian, Z.-Q. Liu, *RSC Adv.* **2014**, *4*, 64855.

[3] B. V. S. Reddy, V. Swathi, M. Swain, M. P. Bhadra, B. Sridhar, D. Satyanarayana, B. Jagadeesh, *Org. Lett.* **2014**, *16*, 6267.

[4] D. C. Fabry, M. Stodulski, S. Hoerner, T. Gulder, *Chem. Eur. J.* **2012**, *18*, 10834.

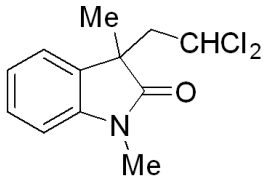
[5] Z. Cui, D.-M. Du, *Adv. Synth. Catal.* **2018**, 360, *93*.

[6] W. Ou, G. Zhang, J. Wu, C. Su, *ACS Catal.* **2019**, *9*, 5178.

[7] H. Wang, S. E. Reisman, *Angew. Chem. Int. Ed.* **2014**, *53*, 6206.

[8] P. Tuntiwachwuttikul, T. Taechowisan, A. Wanbanjob, S. Thadaniti, W. C. Taylor, *Tetrahedron* **2008**, *64*, 7583.

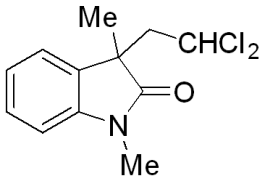
NAME cc-i94-5
SOLVENT CDCl3
SF 400.1500096 MHz



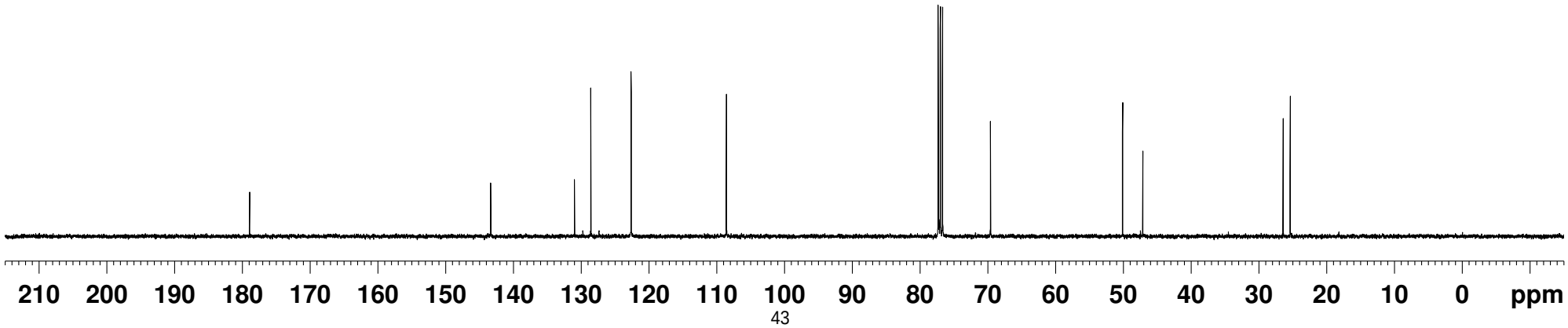
3

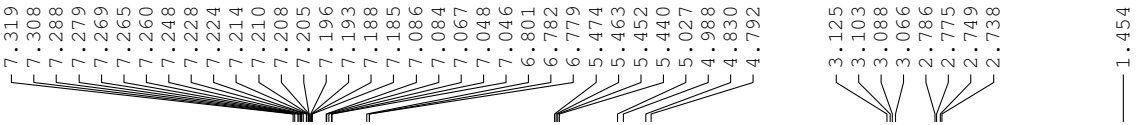
178.95
143.37
131.00
128.59
122.64
122.62
108.57
77.32
77.00
76.68
69.61
50.11
47.12
26.41
25.37

NAME cc-i94-5
SOLVENT CDCl3
SF 100.6178037 MHz

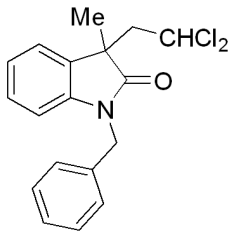


3

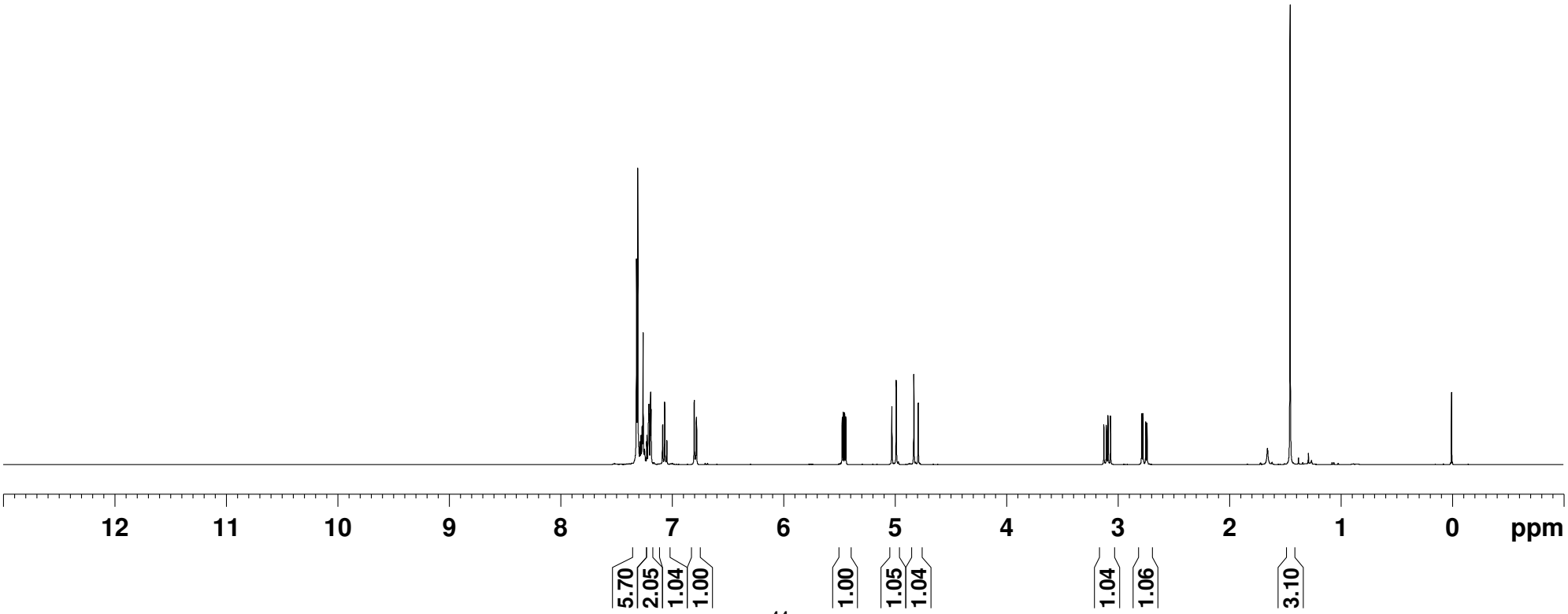




NAME cc-g110-5
SOLVENT CDCl3
SF 400.1500096 MHz

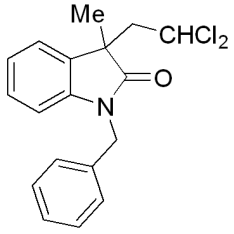


4

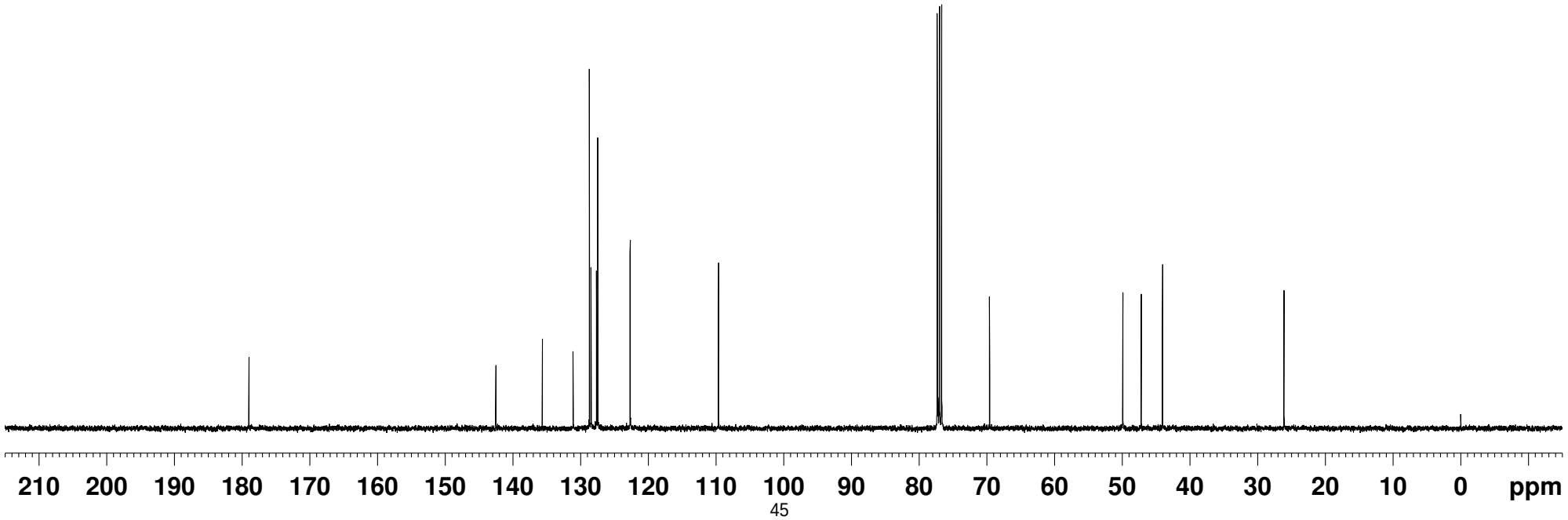


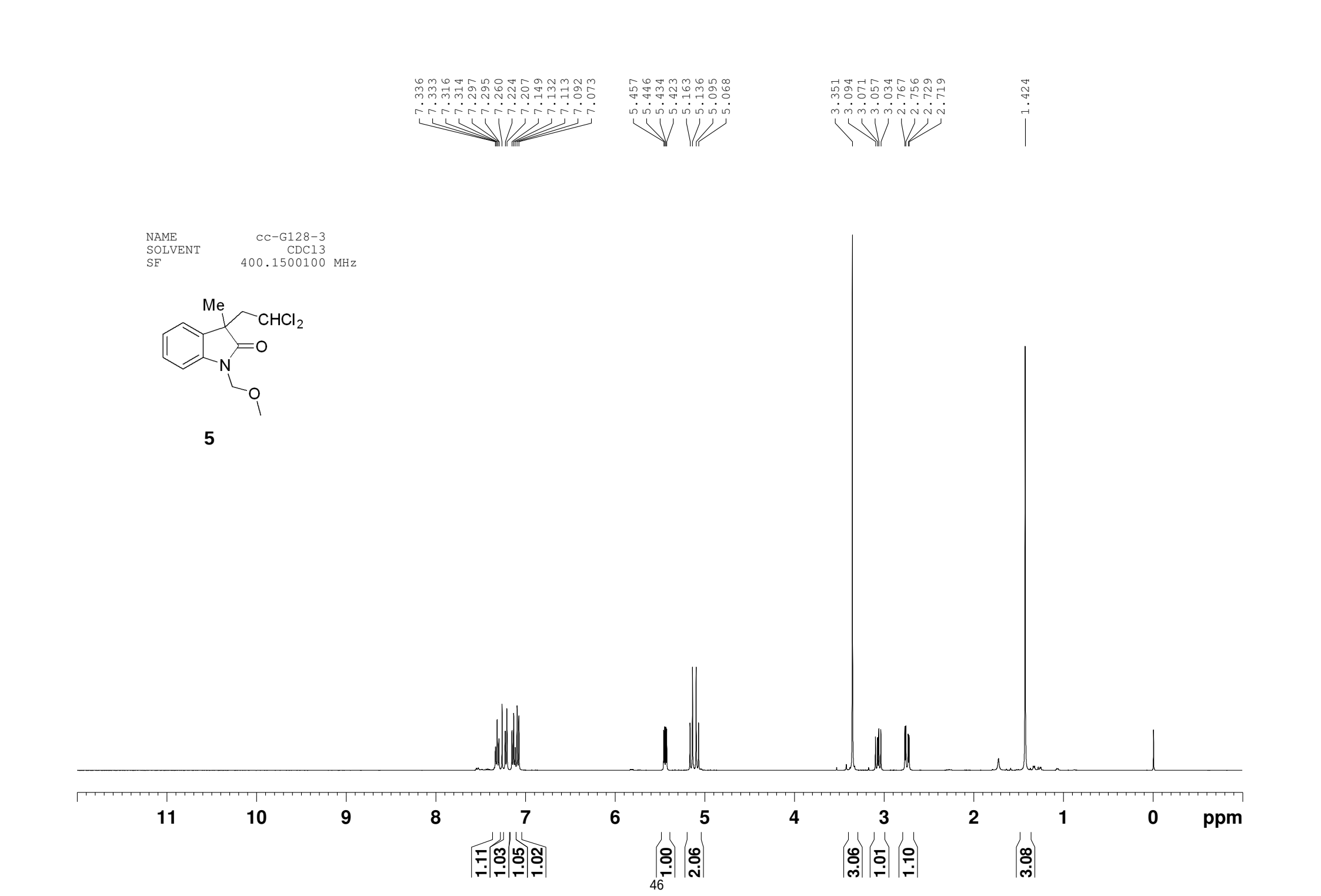
179.01
142.53
135.65
131.11
128.71
128.46
127.65
127.48
122.70
122.67
109.64
77.32
77.00
76.68
69.59
49.90
47.18
44.05
26.08

NAME cc-g110-5
SOLVENT CDCl3
SF 100.6178030 MHz



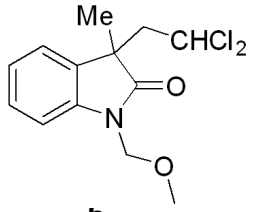
4



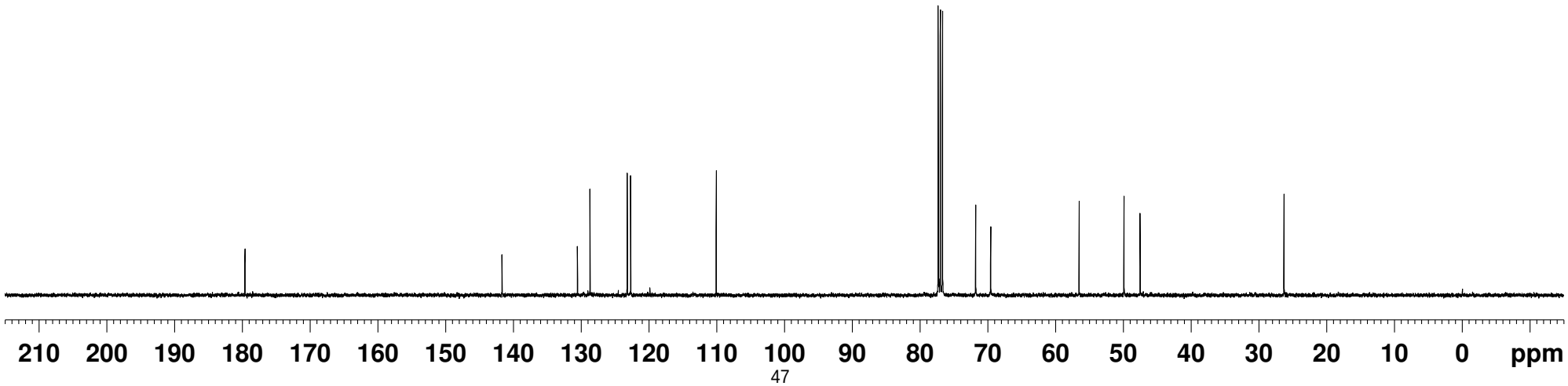

7.336
7.333
7.316
7.314
7.297
7.295
7.260
7.224
7.207
7.149
7.132
7.113
7.092
7.073
5.457
5.446
5.434
5.423
5.163
5.136
5.095
5.068
3.351
3.094
3.071
3.057
3.034
2.767
2.756
2.729
2.719
1.424
NAME cc-G128-3
SOLVENT CDCl3
SF 400.1500100 MHz
Me
CHCl2
O
N
O
5
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.11
1.03
1.05
1.02
1.00
2.06
3.06
1.01
1.10
3.08

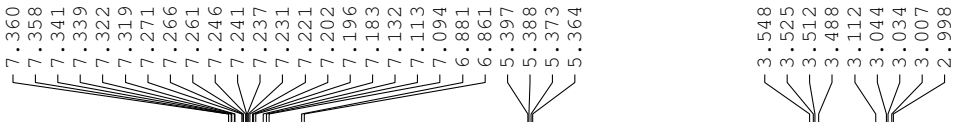
179.63
141.69
130.55
128.71
123.21
122.71
110.08
77.32
77.00
76.68
71.78
69.57
56.52
49.90
47.51
26.28

NAME cc-g128-3-1127
SOLVENT CDCl3
SF 100.6178033 MHz

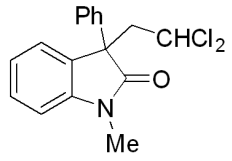


5

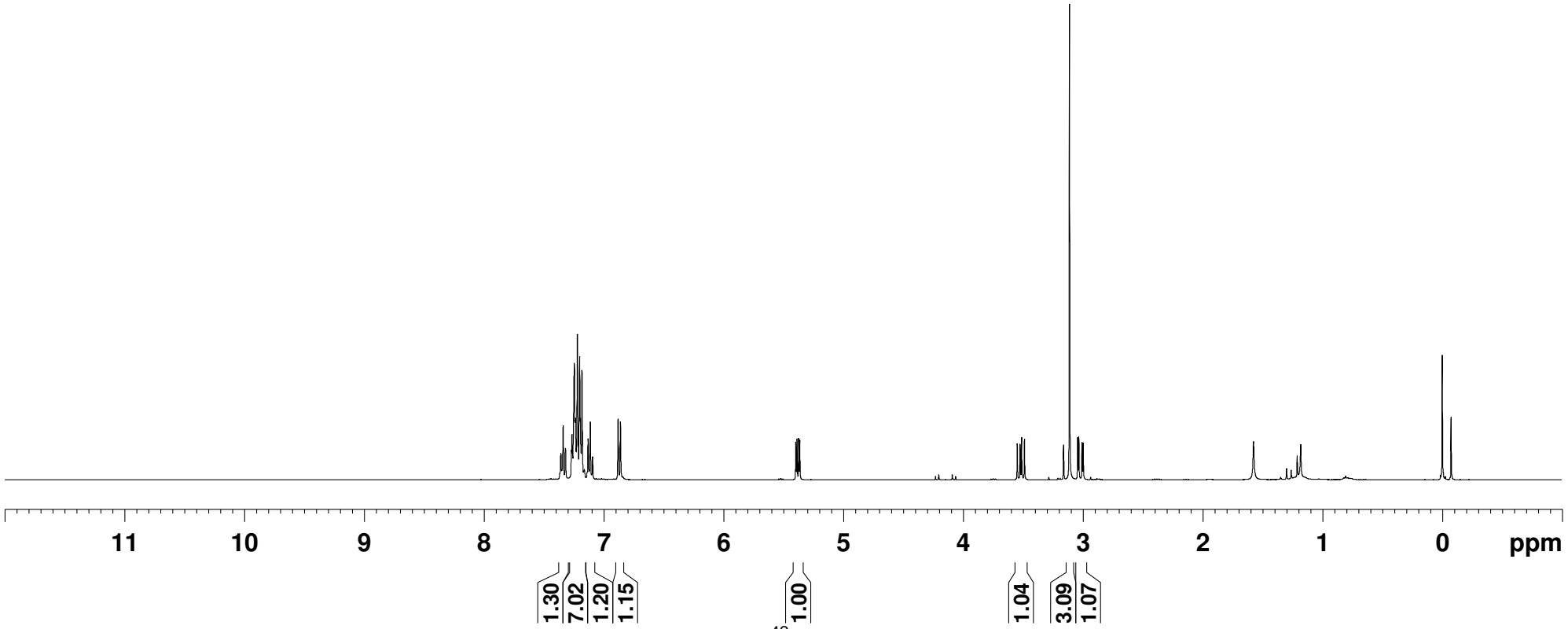




NAME CC-G110-11-down-0717
SOLVENT CDCl3
SF 400.1500401 MHz

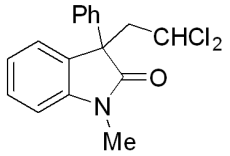


6

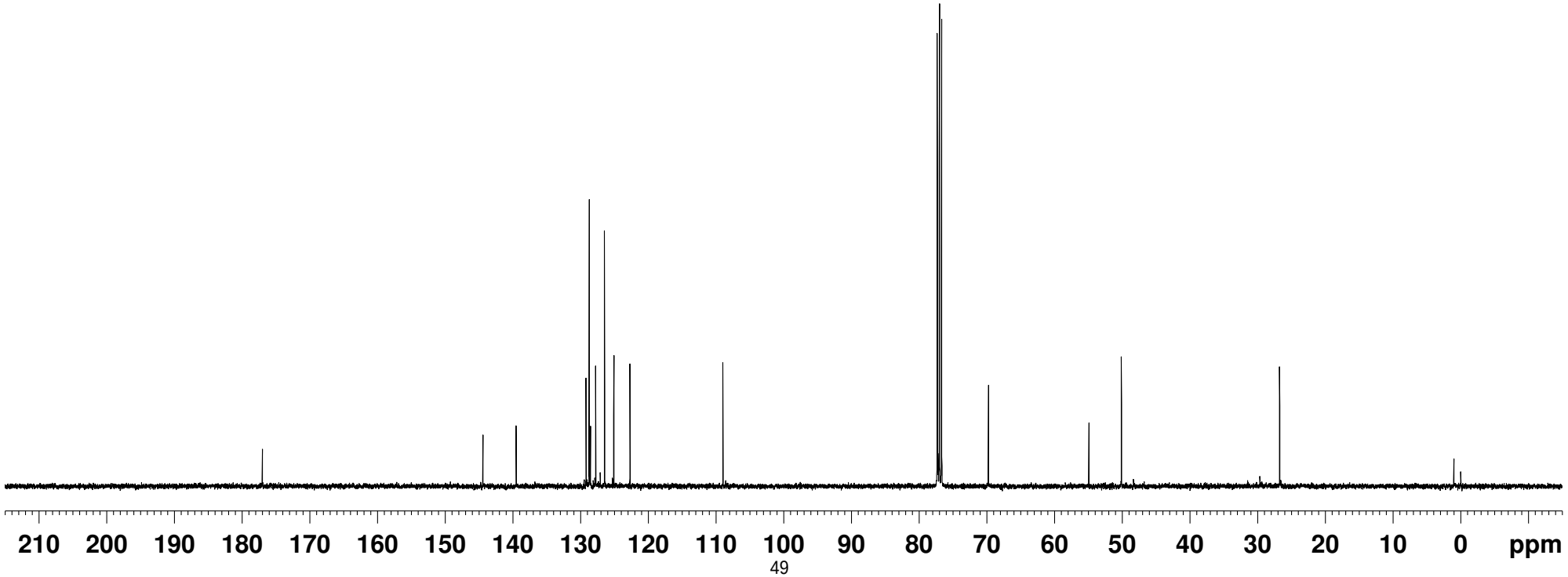


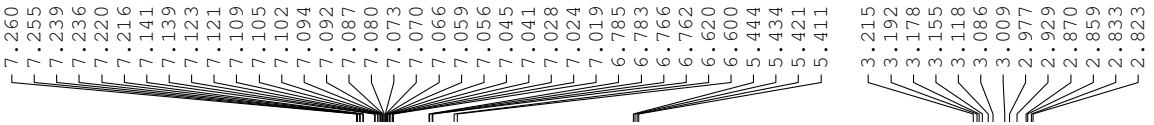
177.03
144.43
139.54
129.22
128.74
128.55
127.79
126.47
125.11
122.71
108.98
77.32
77.00
76.68
69.76
54.91
50.11
26.74

NAME CC-G110-11-down-0717
SOLVENT CDCl3
SF 100.6178030 MHz

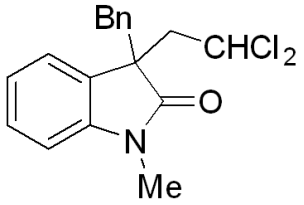


6





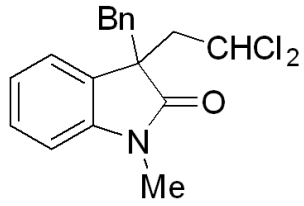
NAME cc-g116-1
SOLVENT CDCl3
SF 400.1500096 MHz



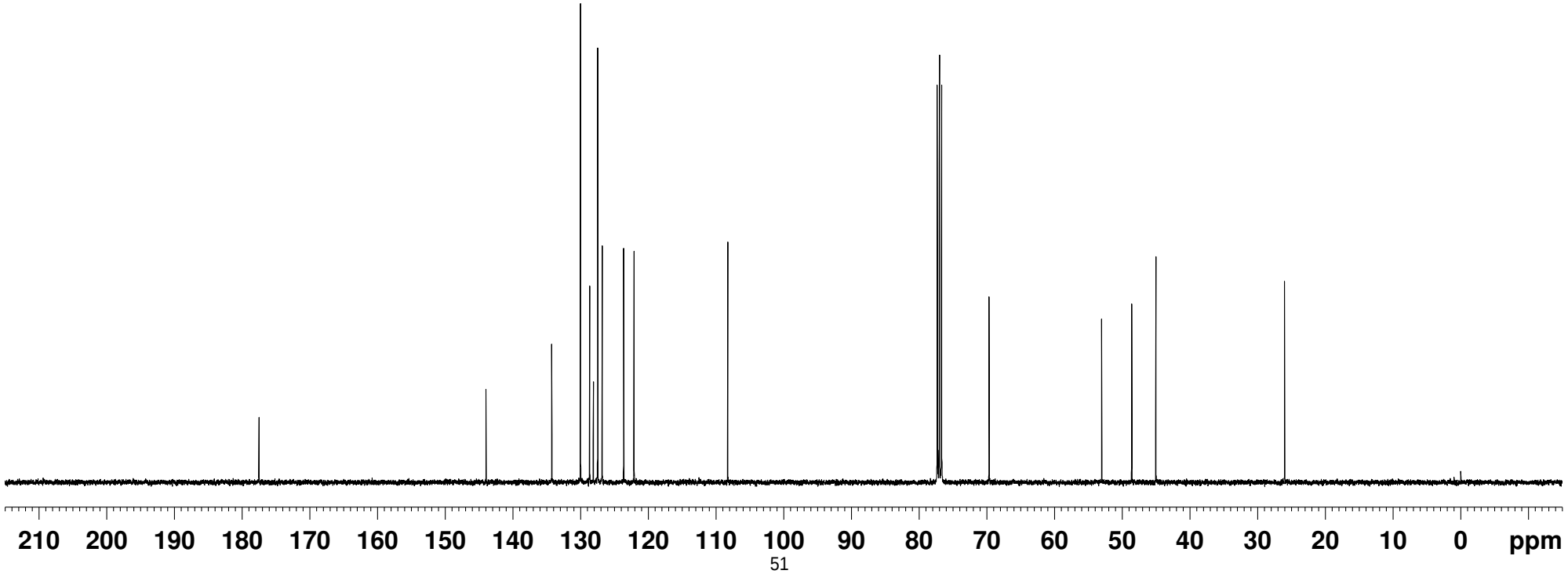
7

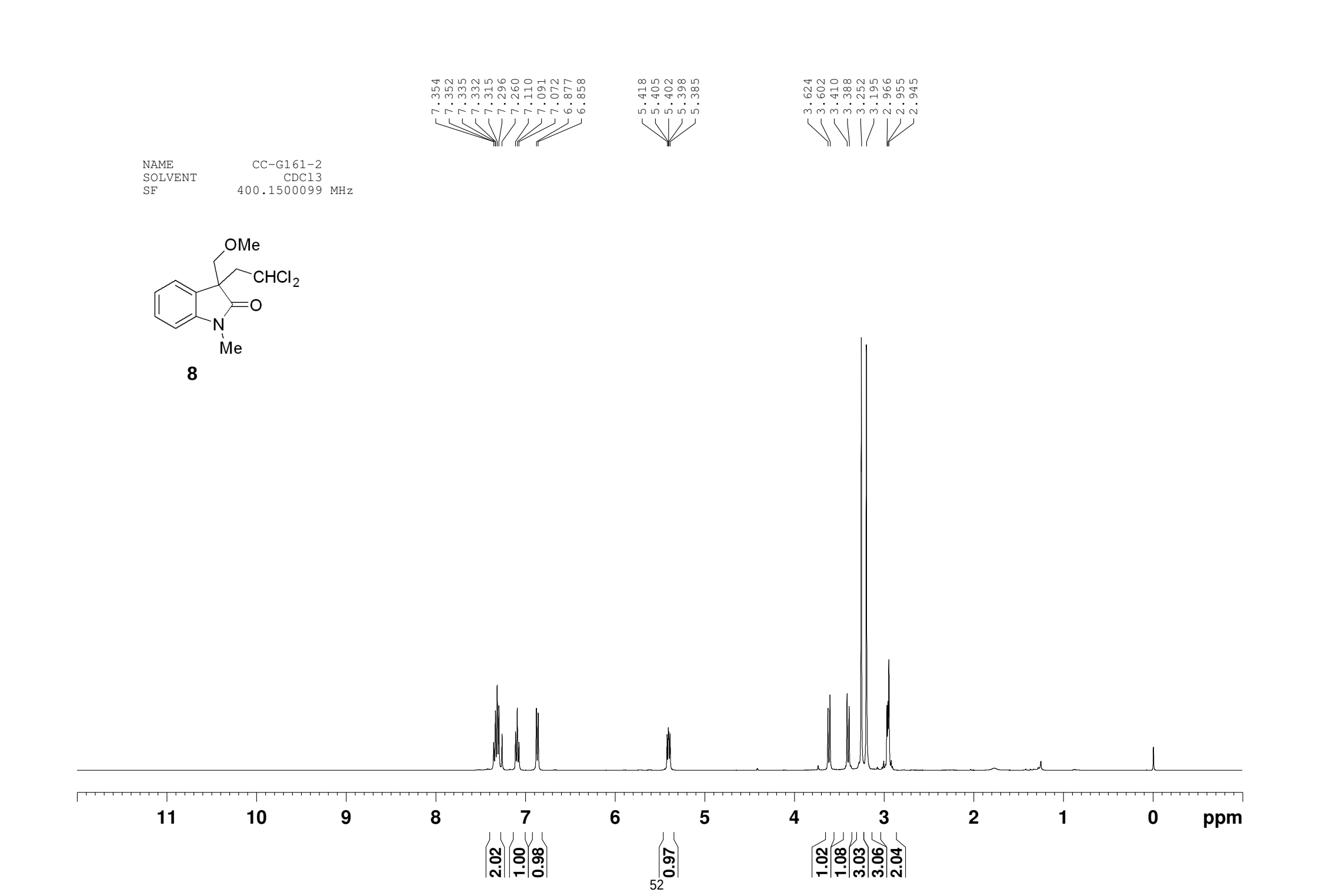
177.51
144.00
134.26
130.02
128.67
128.13
127.48
126.82
123.65
122.11
108.27
77.32
77.00
76.68
69.66
53.02
48.59
45.02
26.01

NAME cc-g116-1
SOLVENT CDCl3
SF 100.6178038 MHz



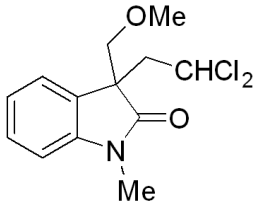
7



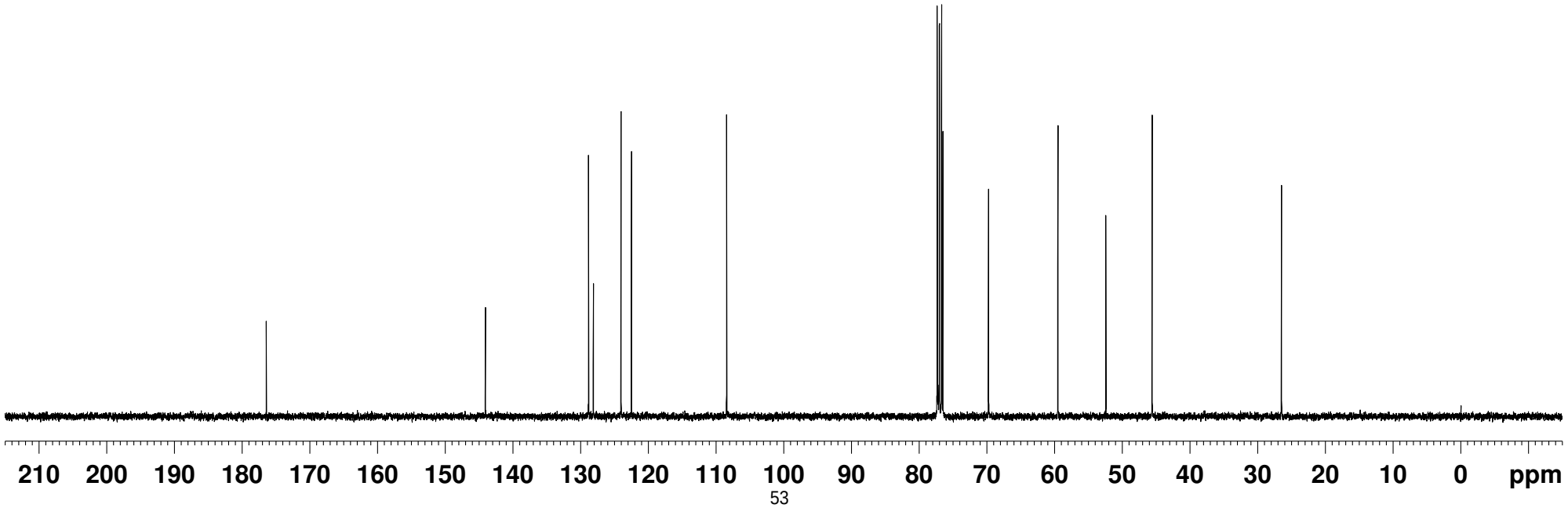

7.354
7.352
7.335
7.332
7.315
7.296
7.260
7.110
7.091
7.072
6.877
6.858
5.418
5.405
5.402
5.398
5.385
3.624
3.602
3.410
3.388
3.252
3.195
2.966
2.955
2.945
NAME CC-G161-2
SOLVENT CDCl3
SF 400.1500099 MHz
OMe
CHCl2
O
N
Me
8
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
1.00
0.98
0.97
1.02
1.08
3.03
3.06
2.04

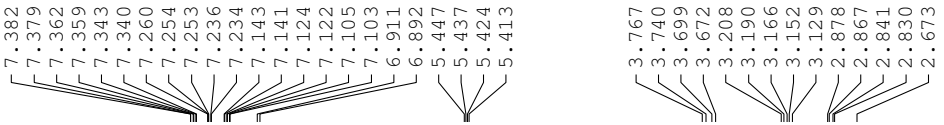
176.45
144.07
128.83
128.13
124.03
122.50
108.43
77.32
77.00
76.68
76.49
69.74
59.50
52.41
45.56
26.45

NAME CC-G161-2
SOLVENT CDCl3
SF 100.6178048 MHz

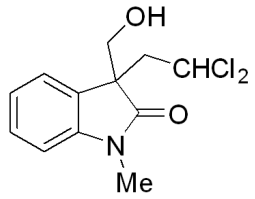


8





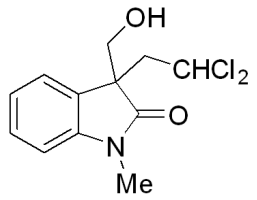
NAME cc-G141-10-H
SOLVENT CDCl3
SF 400.1500095 MHz



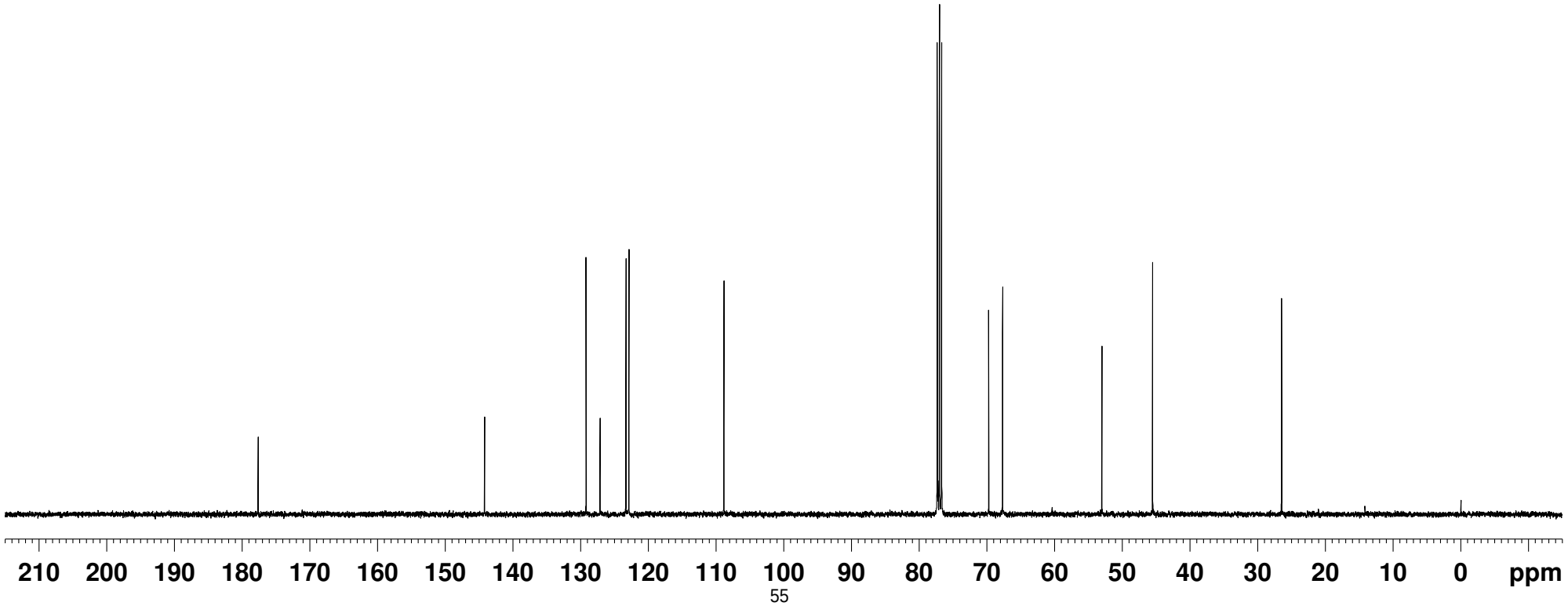
9

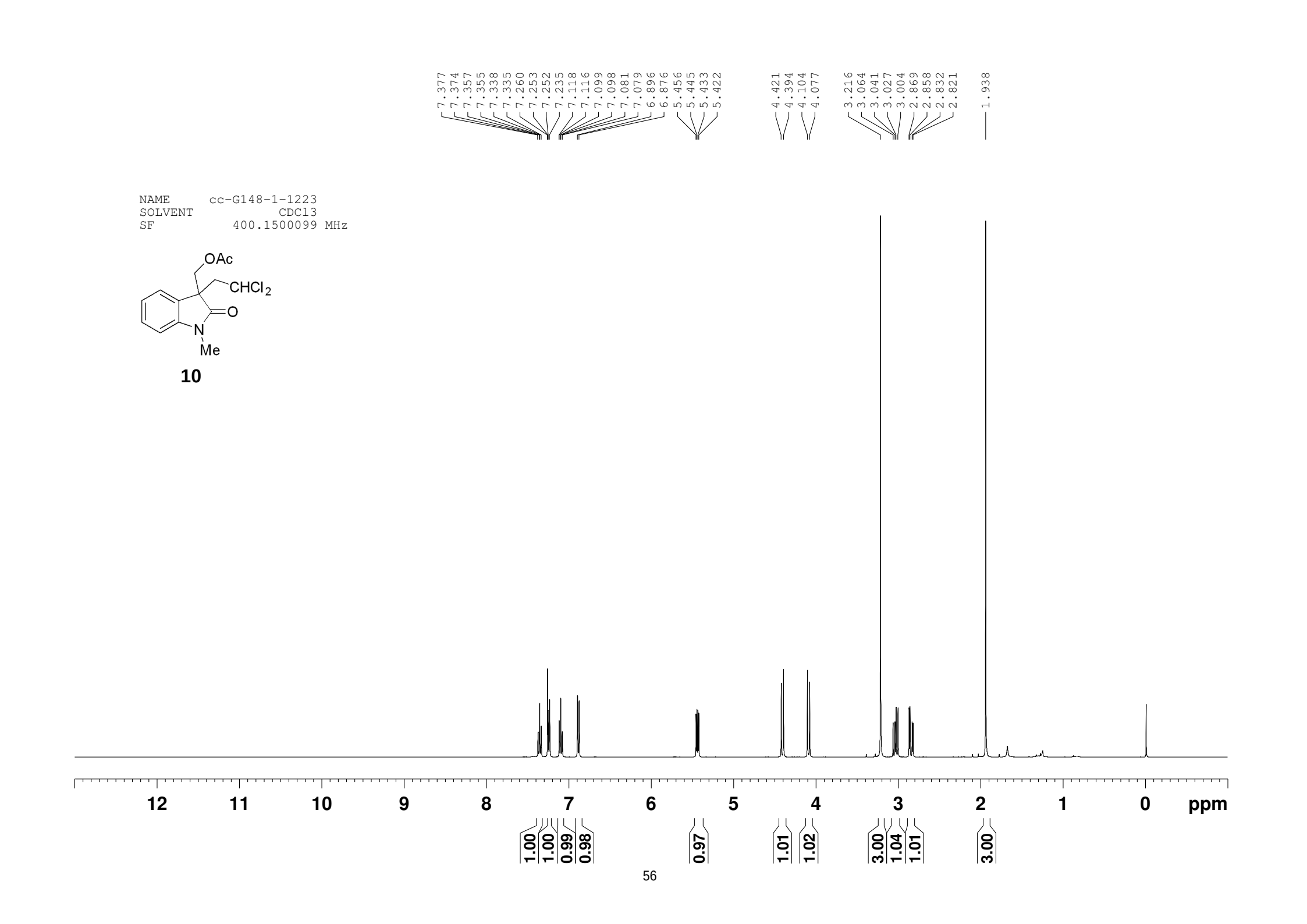
177.65
144.19
129.20
127.14
123.31
122.87
108.84
77.32
77.00
76.68
69.72
67.66
52.99
45.51
26.45

NAME cc-g141-10
SOLVENT CDCl3
SF 100.6178037 MHz



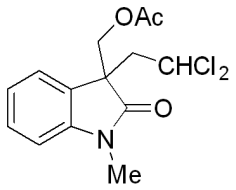
9



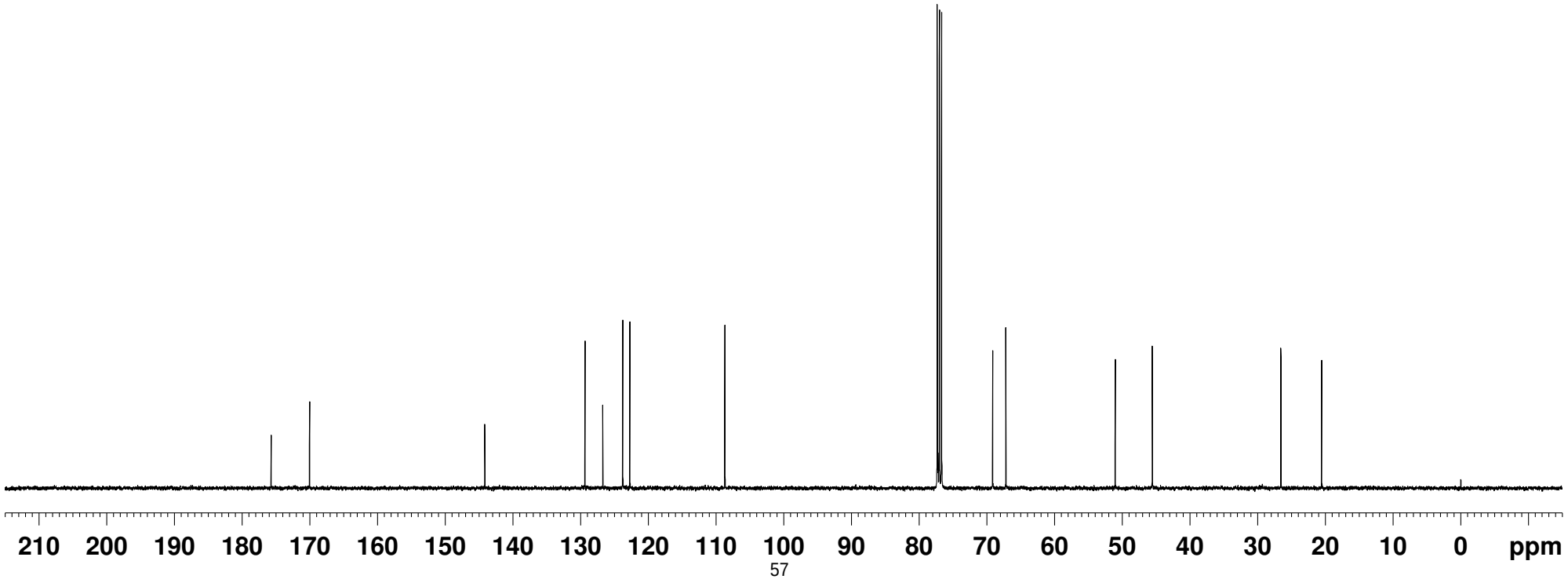

7.377
7.374
7.357
7.355
7.338
7.335
7.260
7.253
7.252
7.235
7.118
7.116
7.099
7.098
7.081
7.079
6.896
6.876
5.456
5.445
5.433
5.422
4.421
4.394
4.104
4.077
3.216
3.064
3.041
3.027
3.004
2.869
2.858
2.832
2.821
1.938
NAME cc-G148-1-1223
SOLVENT CDCl3
SF 400.1500099 MHz
OAc
CHCl2
O
N
Me
10
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
0.99
0.98
0.97
1.01
1.02
3.00
1.04
1.01
3.00

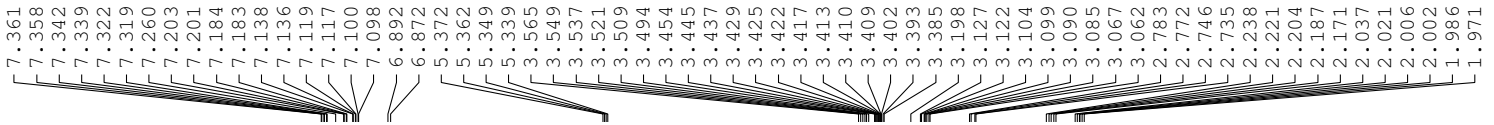
175.72
170.05
144.16
129.36
126.73
123.78
122.74
108.69
77.32
77.00
76.68
69.13
67.19
51.03
45.54
26.55
20.53

NAME cc-G148-1-1223
SOLVENT CDCl3
SF 100.6178023 MHz

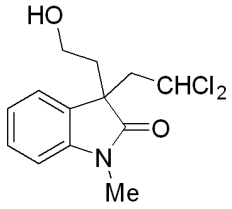


10





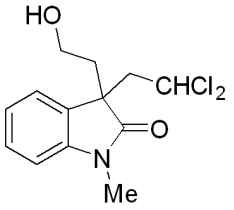
NAME cc-h80-0419
SOLVENT CDCl3
SF 400.1500099 MHz



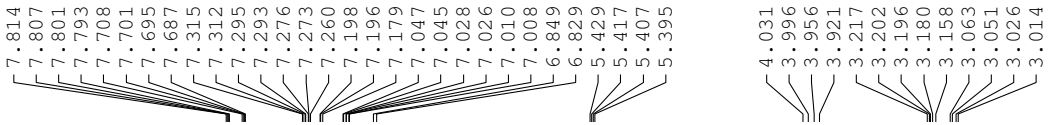
11

178.86
143.86
128.95
122.98
122.87
108.77
77.32
77.00
76.68
69.30
58.40
49.90
49.69
41.18
26.52

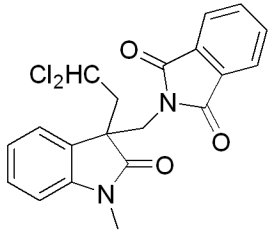
NAME CC-H80-0416
SOLVENT CDCl3
SF 100.6178037 MHz



11



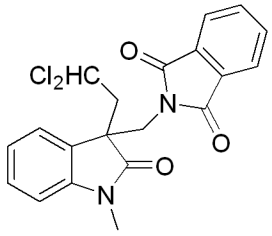
NAME cc-G148-2-1225
SOLVENT CDCl3
SF 400.1500099 MHz



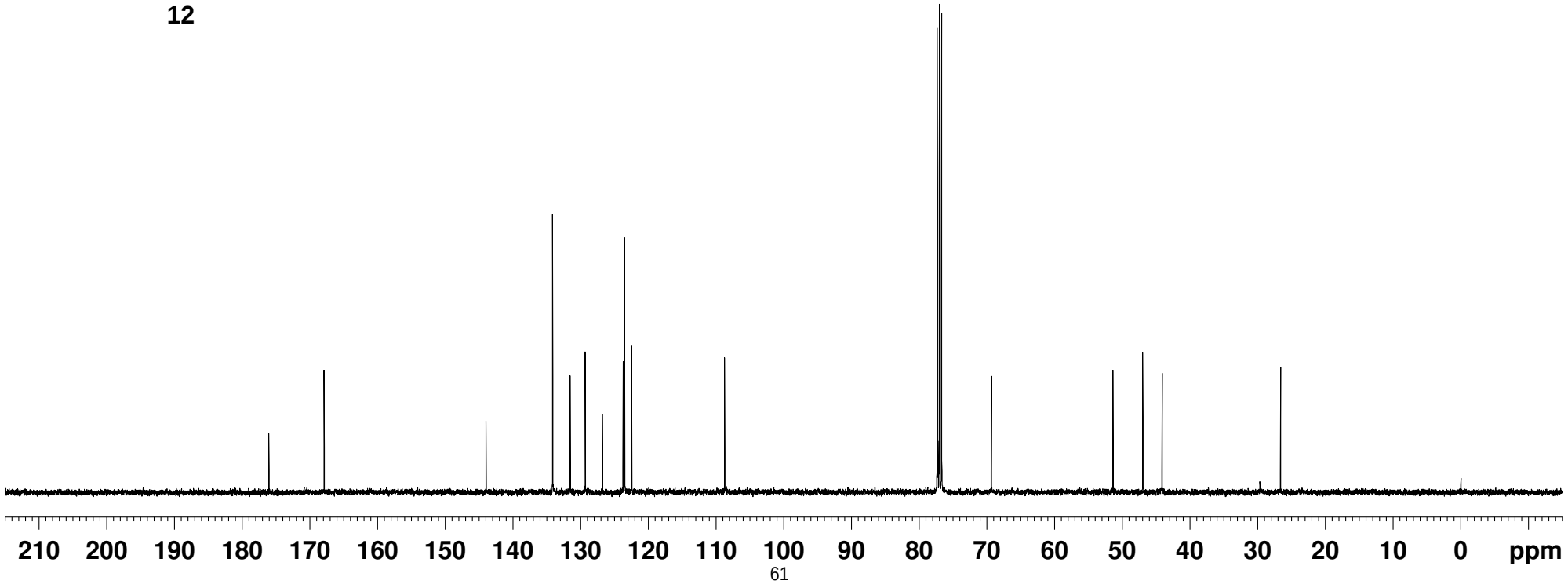
12

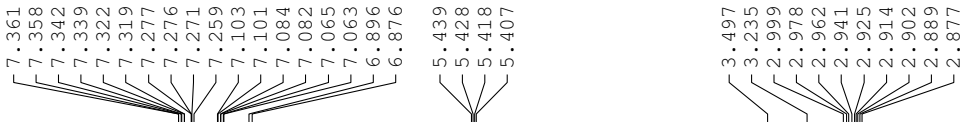
176.06
167.90
143.98
134.14
131.55
129.33
126.79
123.73
123.52
122.47
108.73
77.32
77.00
76.68
69.32
51.35
46.95
44.09
26.59

NAME cc-G148-2-1225
SOLVENT CDCl3
SF 100.6178030 MHz

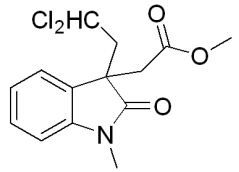


12

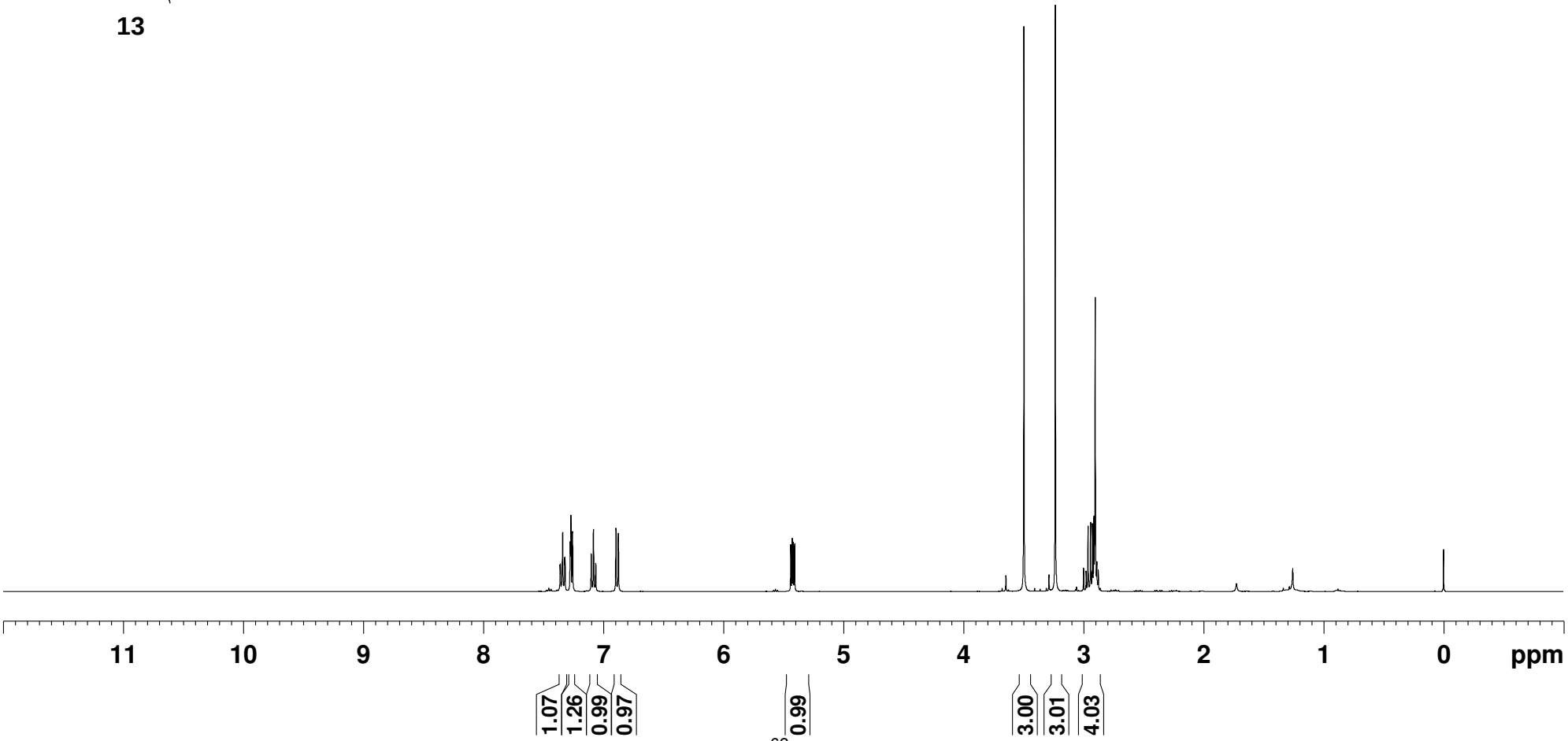




NAME cc-G148-4-1225
SOLVENT CDCl3
SF 400.1500057 MHz

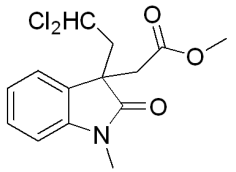


13

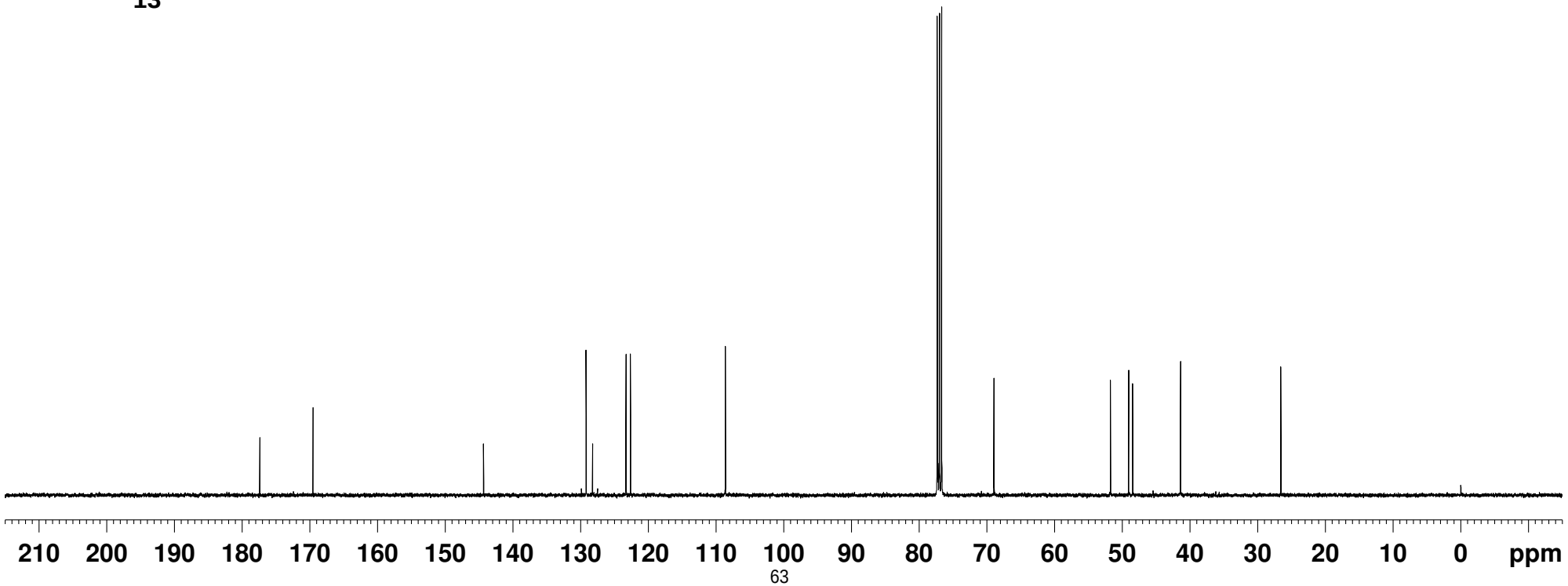


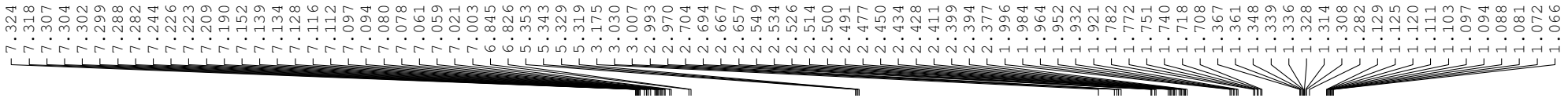
177.40
169.54
144.34
129.19
128.25
123.31
122.63
108.62
77.32
77.00
76.68
68.94
51.73
49.04
48.45
41.38
26.56

NAME cc-G148-4-1223
SOLVENT CDCl3
SF 100.6178023 MHz

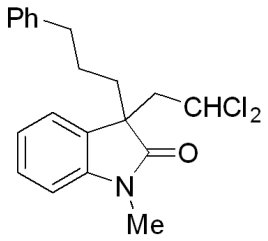


13





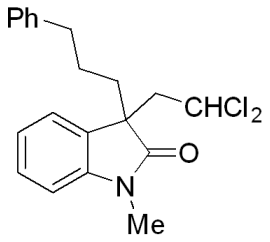
NAME cc-g161-8
SOLVENT CDCl3
SF 400.1500165 MHz



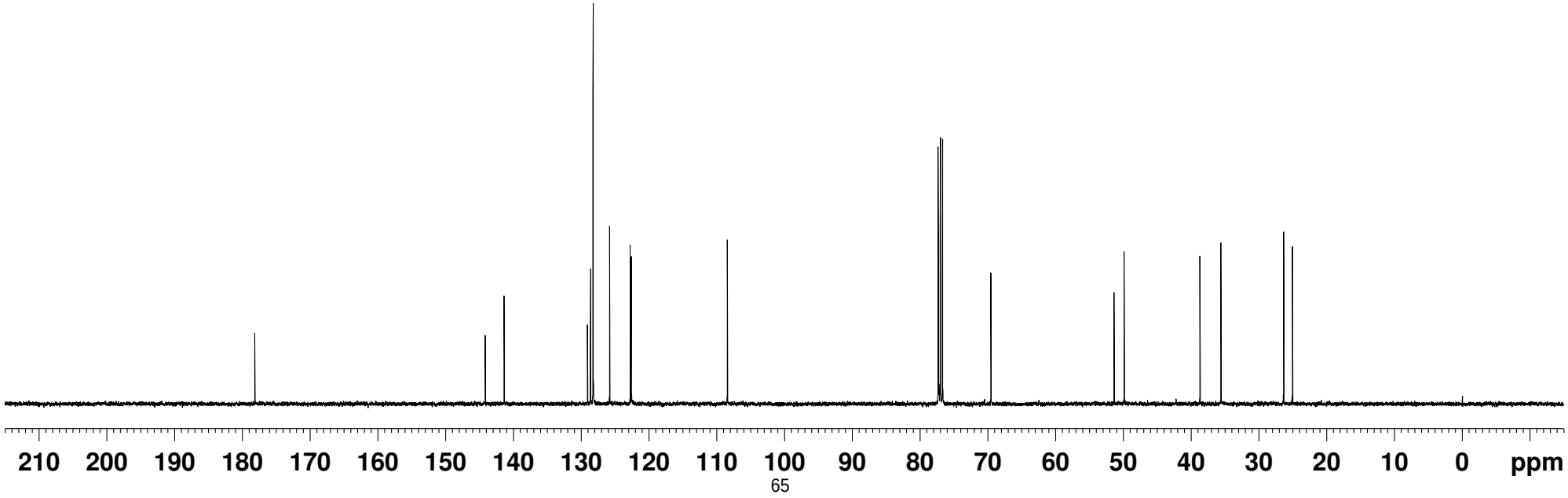
14

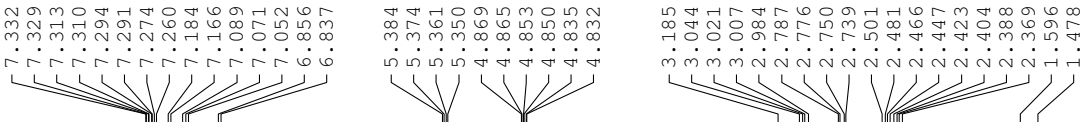
178.18
144.16
141.37
129.07
128.62
128.26
128.23
125.81
122.77
122.60
108.43
77.32
77.00
76.68
69.54
51.35
49.87
38.69
35.59
26.33
25.03

NAME cc-G161-8-c
SOLVENT CDCl3
SF 100.6178074 MHz

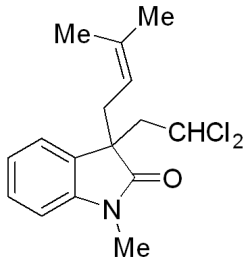


14

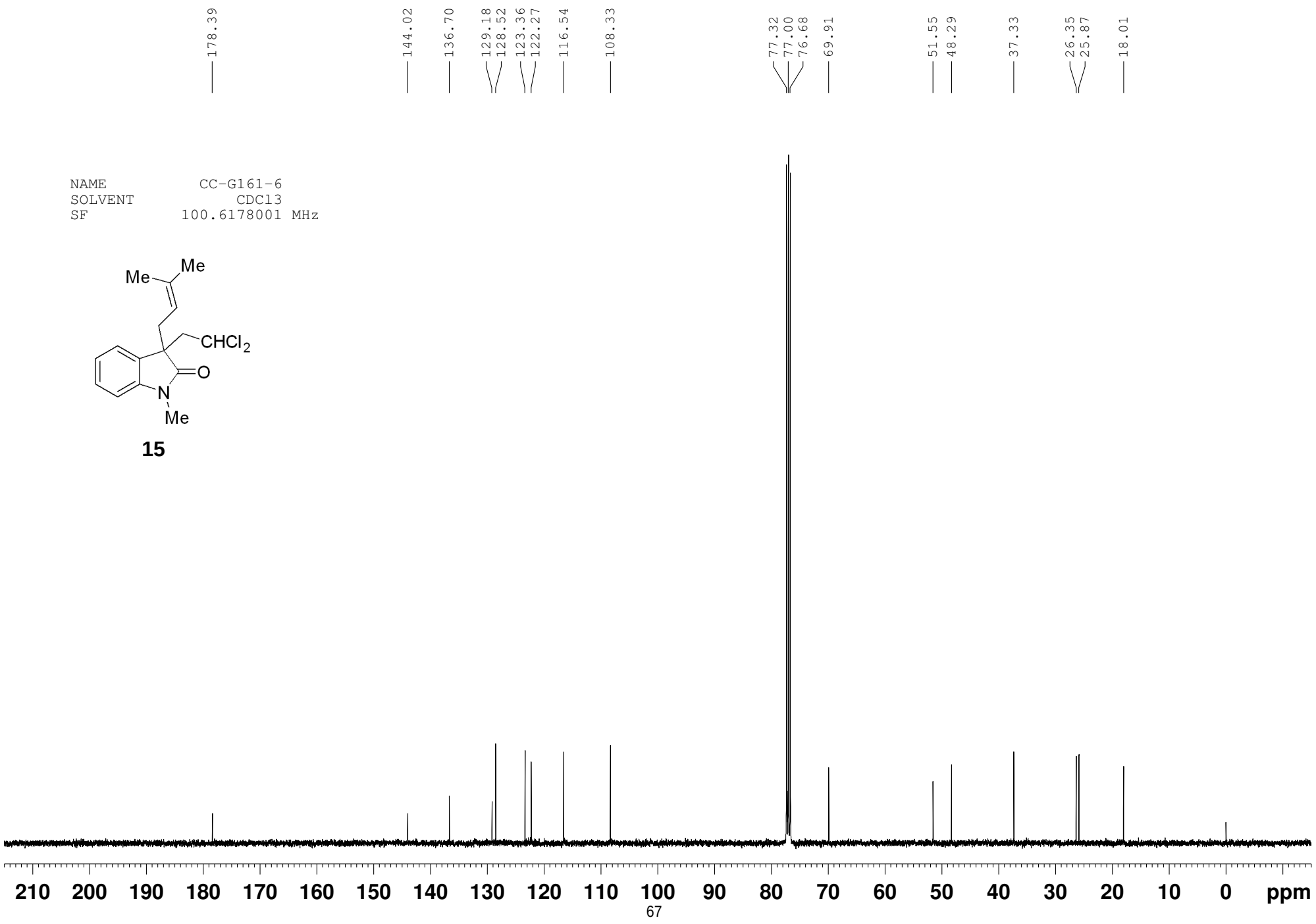




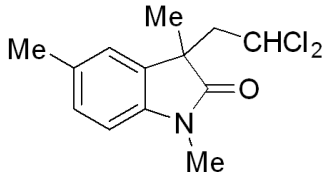
NAME CC-G161-6
SOLVENT CDCl3
SF 400.1500097 MHz



15


178.39
144.02
136.70
129.18
128.52
123.36
122.27
116.54
108.33
77.32
77.00
76.68
69.91
51.55
48.29
37.33
26.35
25.87
18.01
NAME CC-G161-6
SOLVENT CDCl3
SF 100.6178001 MHz
Me
Me
CHCl2
O
N
Me
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

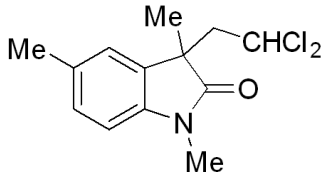
NAME cc-g116-2
SOLVENT CDCl3
SF 400.1500096 MHz



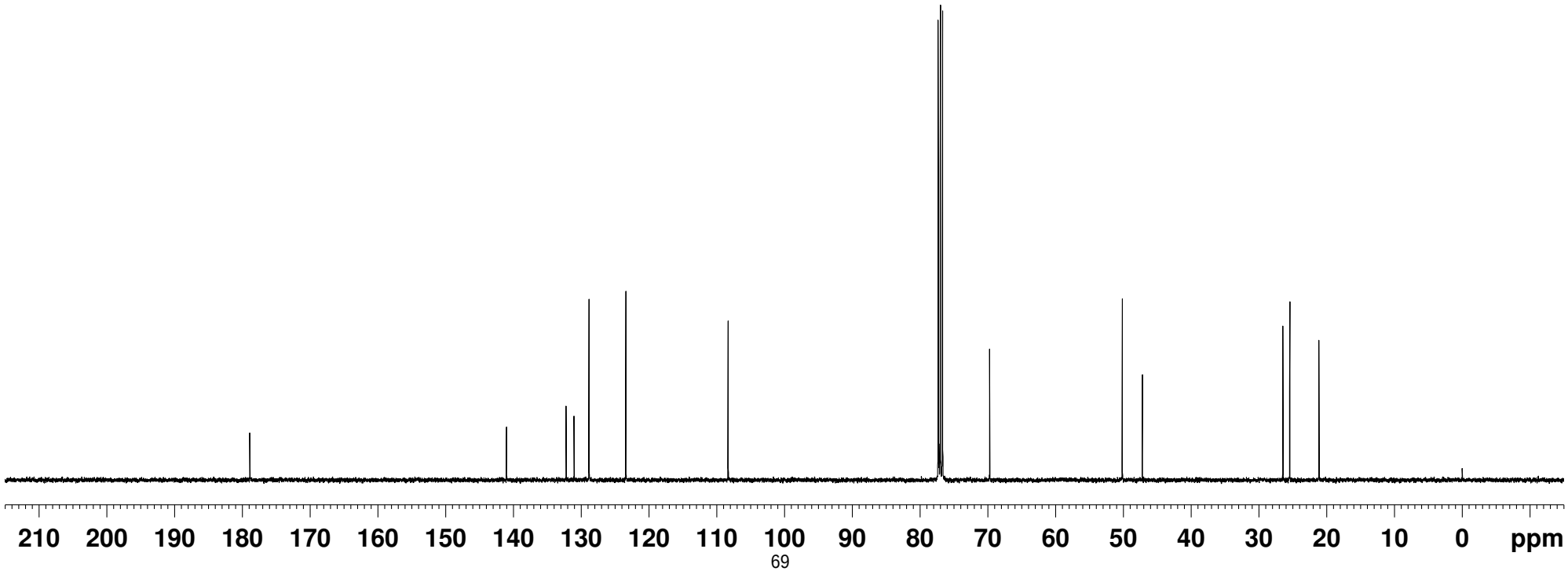
16

178.92
141.03
132.24
131.07
128.85
123.42
108.32
77.32
77.00
76.68
69.73
50.15
47.19
26.44
25.43
21.12

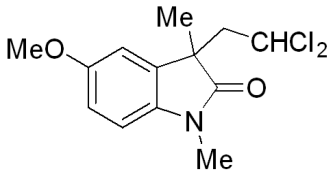
NAME cc-g116-2
SOLVENT CDCl3
SF 100.6178015 MHz



16



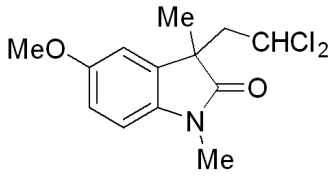
NAME cc-g110-6
SOLVENT CDCl3
SF 400.1500096 MHz



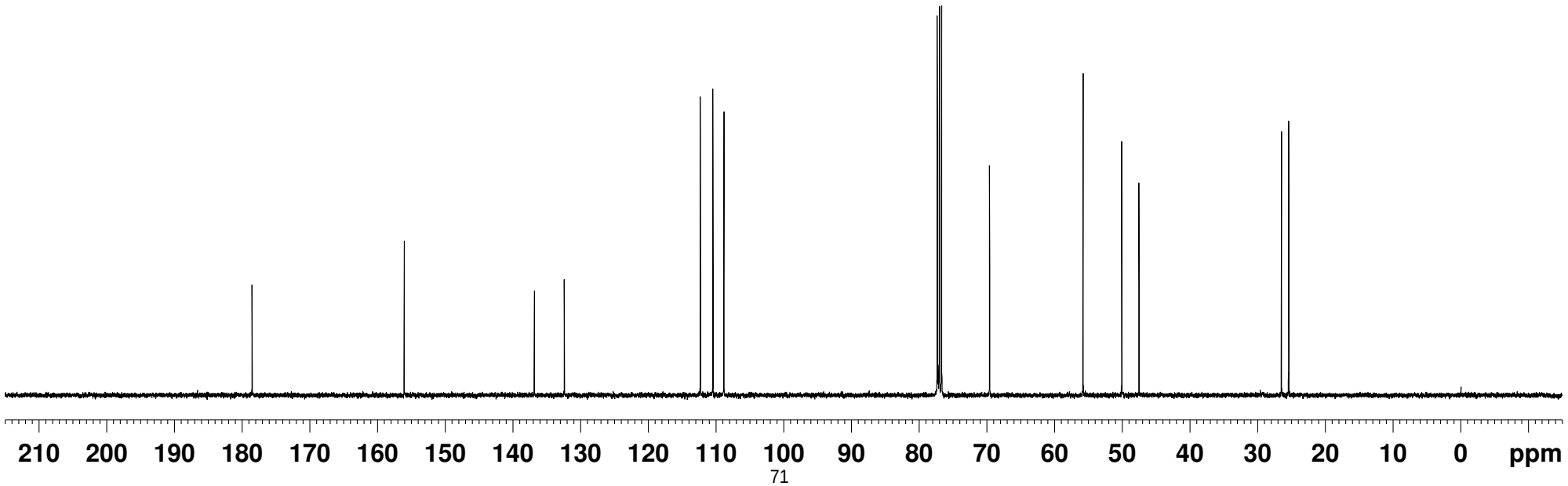
17

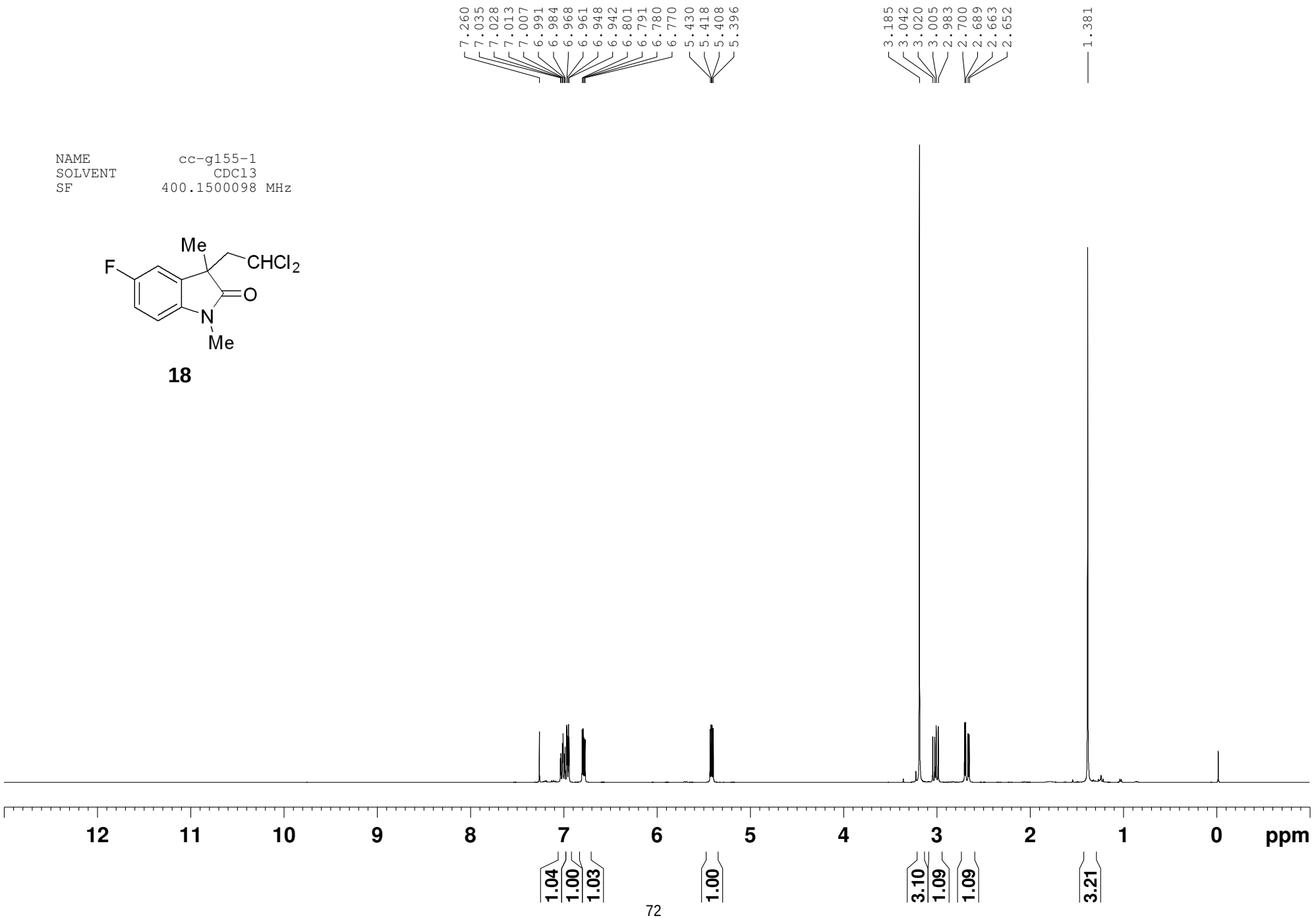
178.56
156.06
136.84
132.42
112.32
110.46
108.84
77.32
77.00
76.68
69.59
55.78
50.06
47.52
26.47
25.40

NAME cc-g110-6
SOLVENT CDCl3
SF 100.6178045 MHz



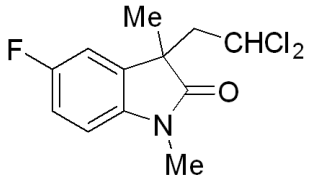
17



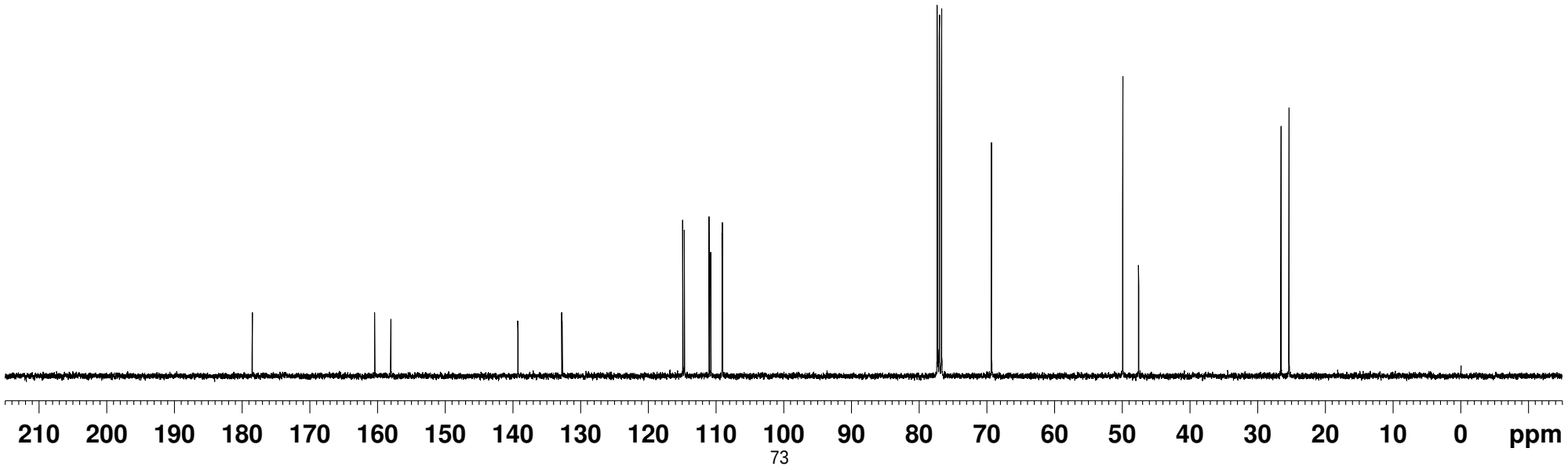

7.260
7.035
7.028
7.013
7.007
6.991
6.984
6.968
6.961
6.948
6.942
6.801
6.791
6.780
6.770
5.430
5.418
5.408
5.396
3.185
3.042
3.020
3.005
2.983
2.700
2.689
2.663
2.652
1.381
NAME cc-g155-1
SOLVENT CDCl3
SF 400.1500098 MHz
Me
CHCl2
F
O
N
Me
18
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.00
1.03
1.00
3.10
1.09
1.09
3.21

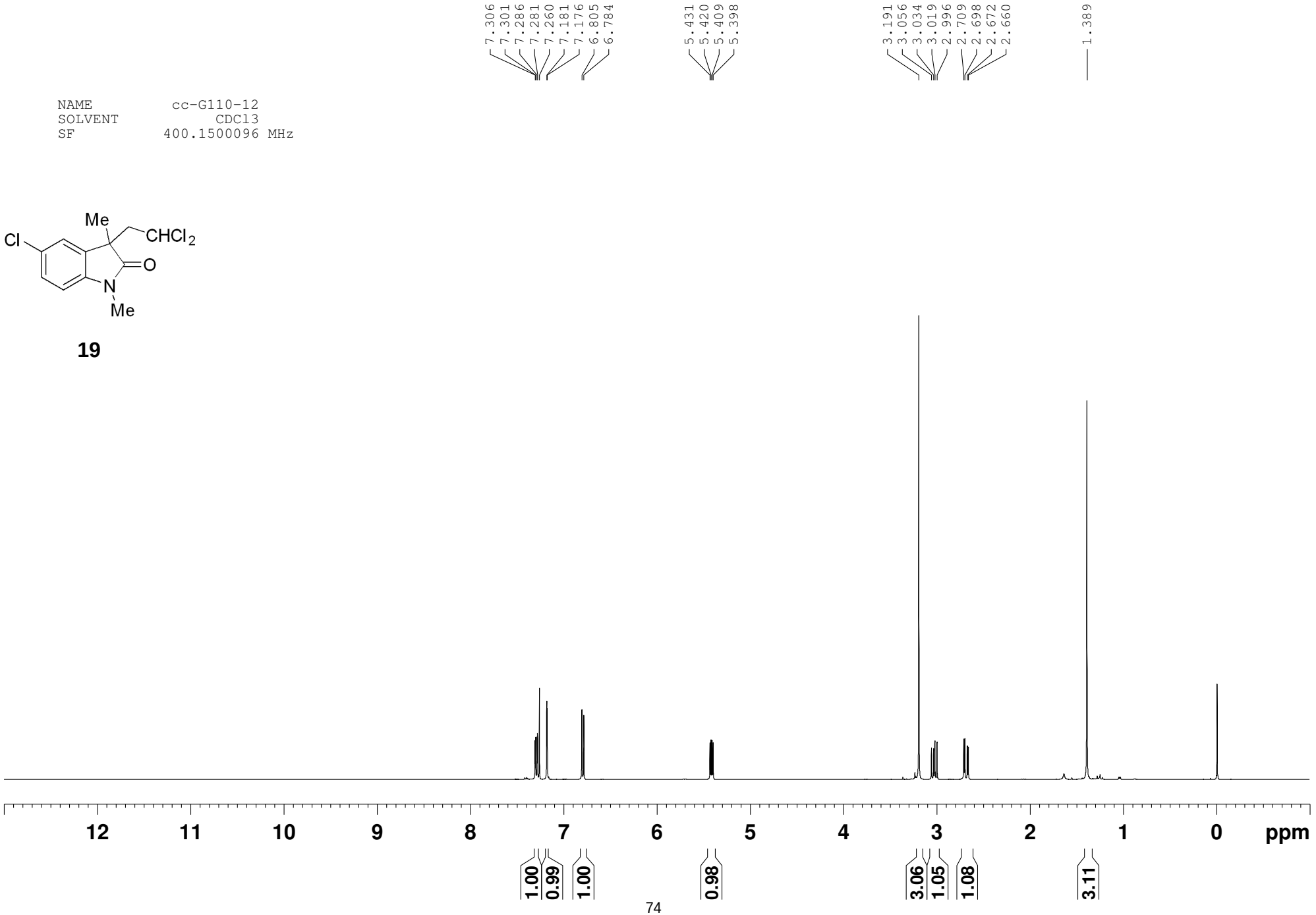
178.51
160.44
158.04
139.28
139.27
132.80
132.72
114.92
114.69
111.03
110.78
109.12
109.04
77.32
77.00
76.68
69.31
49.91
47.59
47.57
26.54
25.35

NAME cc-g155-1
SOLVENT CDCl3



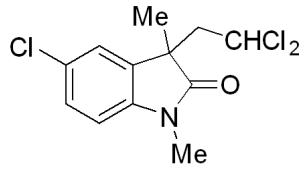
18



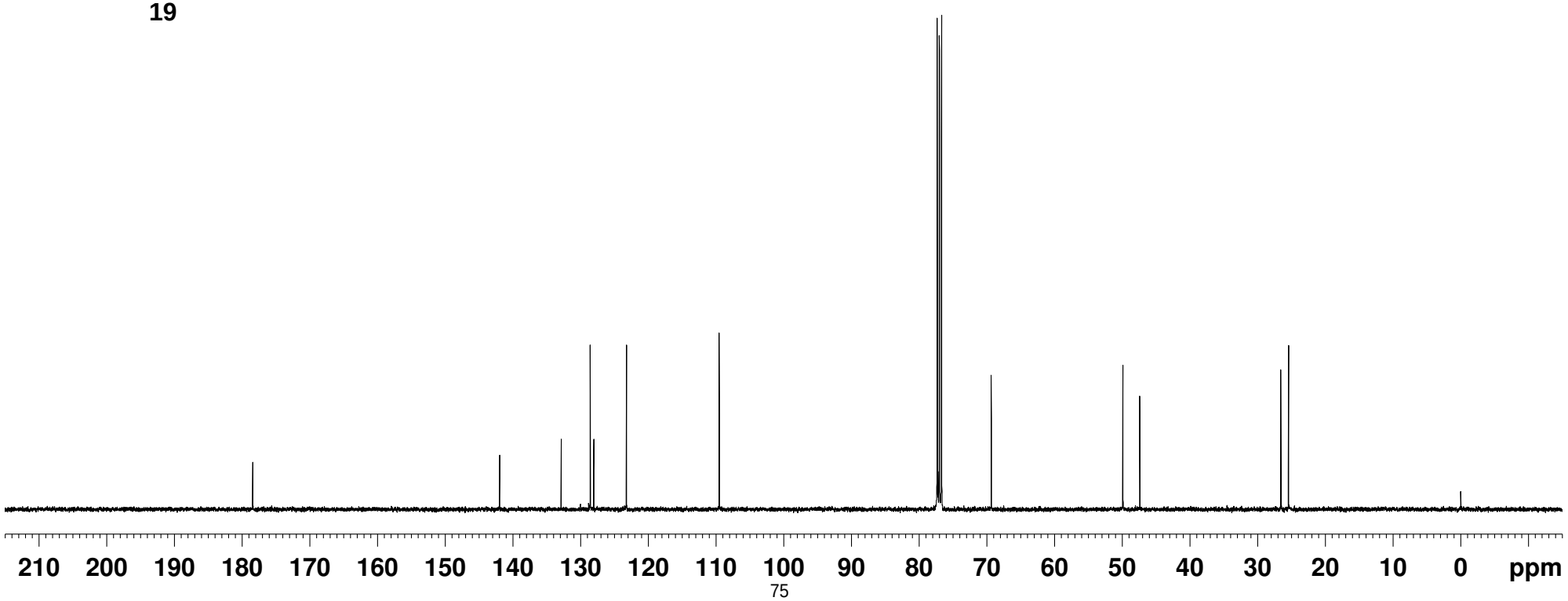

7.306
7.301
7.286
7.281
7.260
7.181
7.176
6.805
6.784
5.431
5.420
5.409
5.398
3.191
3.056
3.034
3.019
2.996
2.709
2.698
2.672
2.660
1.389
NAME cc-G110-12
SOLVENT CDCl3
SF 400.1500096 MHz
Me
CHCl2
Cl
O
N
Me
19
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.00
0.98
3.06
1.05
1.08
3.11

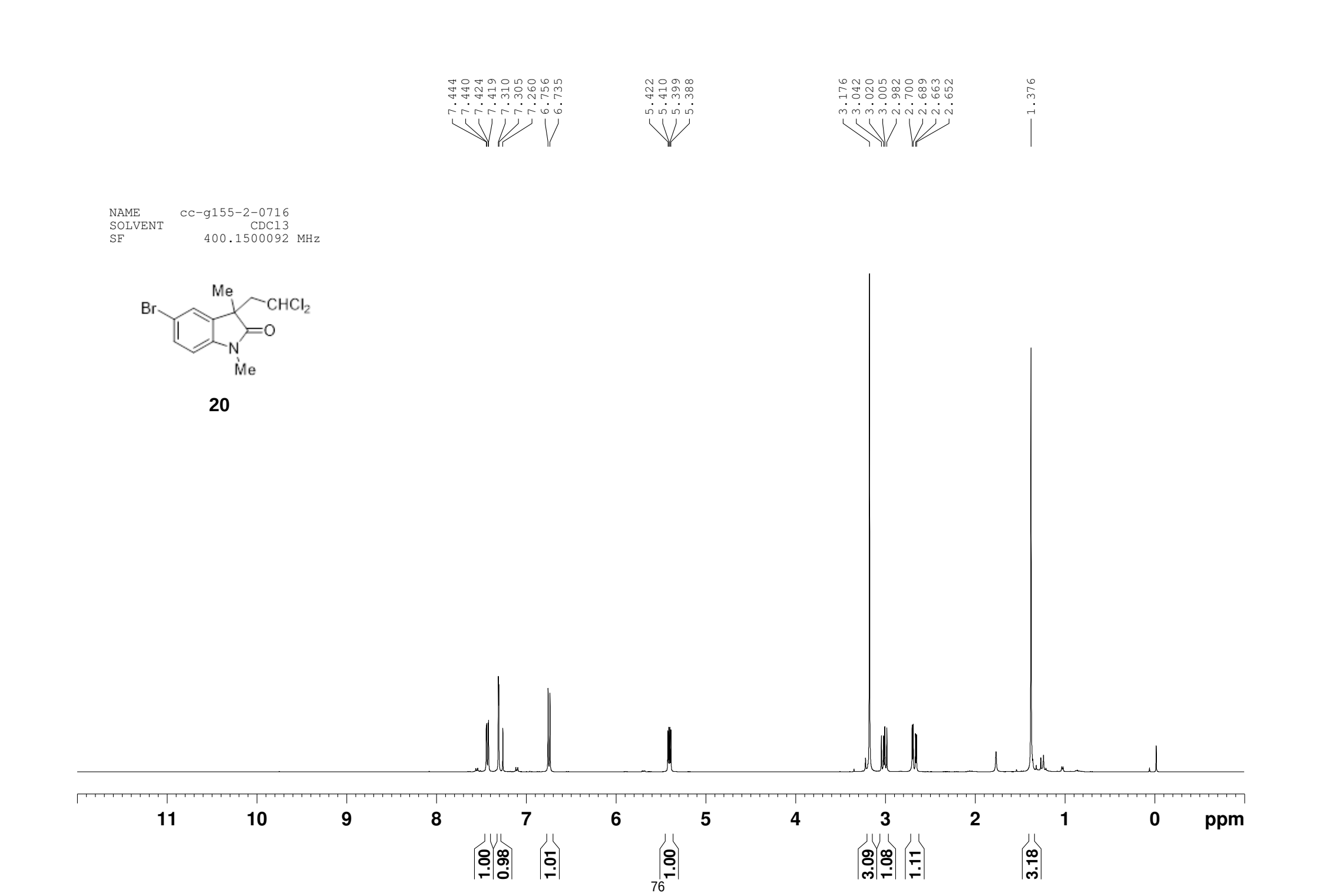
178.43
141.97
132.87
128.58
128.07
123.23
109.52
77.32
77.00
76.68
69.33
49.89
47.40
26.56
25.42

NAME cc-G110-12
SOLVENT CDCl3
SF 100.6178012 MHz



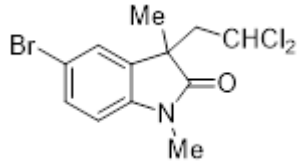
19



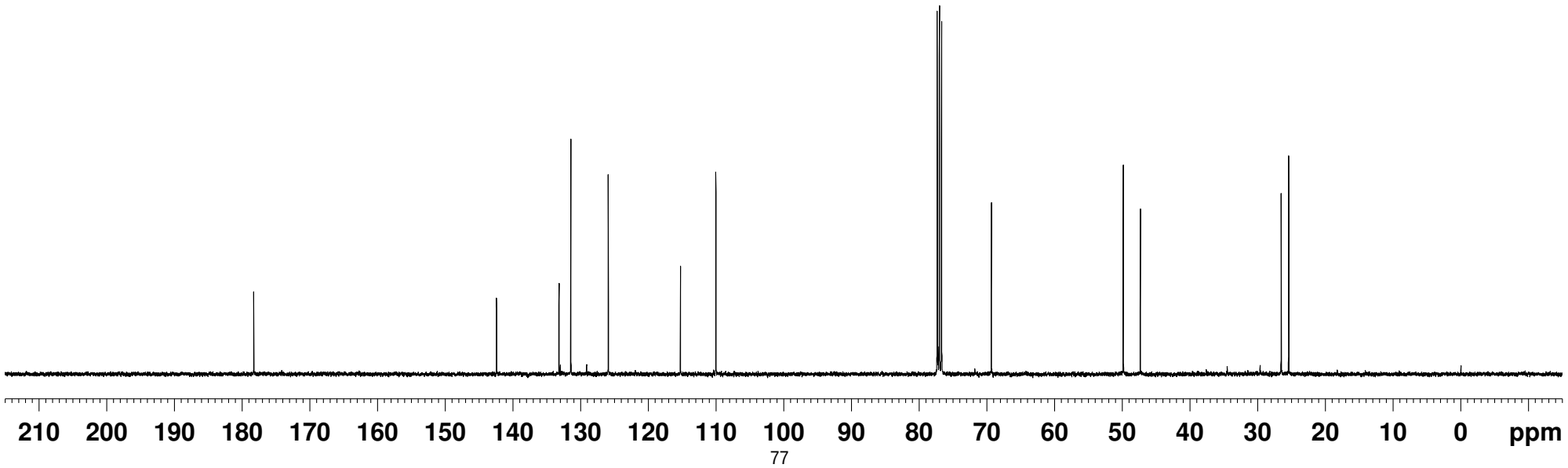

7.444
7.440
7.424
7.419
7.310
7.305
7.260
6.756
6.735
5.422
5.410
5.399
5.388
3.176
3.042
3.020
3.005
2.982
2.700
2.689
2.663
2.652
1.376
NAME cc-g155-2-0716
SOLVENT CDCl3
SF 400.1500092 MHz
Me
CHCl2
Br
O
N
Me
20
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
1.01
1.00
3.09
1.08
1.11
3.18

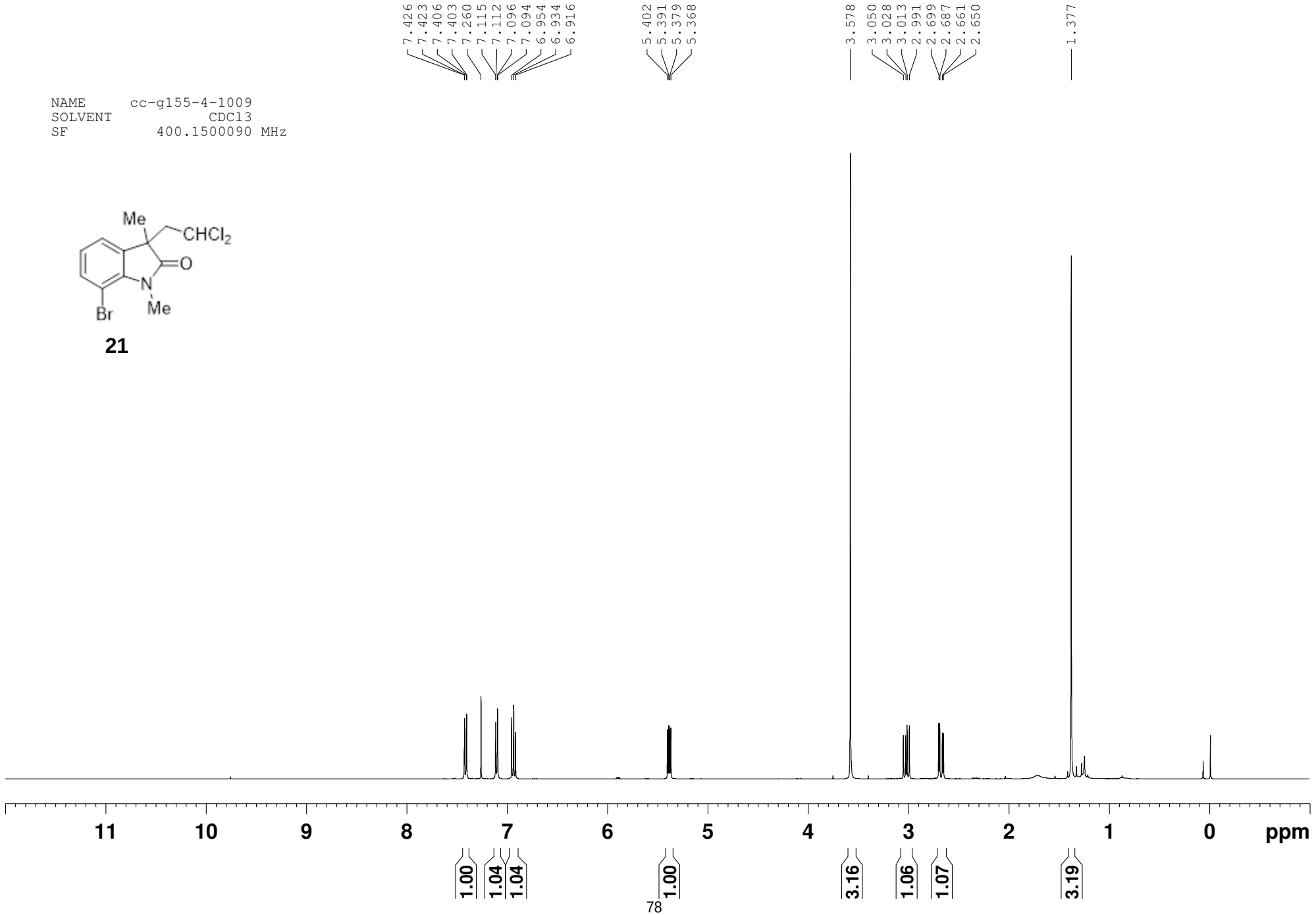
178.30
142.42
133.20
131.46
125.92
115.26
110.02
77.32
77.00
76.68
69.33
49.83
47.32
26.51
25.40

NAME cc-g155-2-0716
SOLVENT CDCl3
SF 100.6178045 MHz



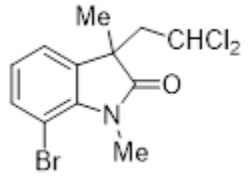
20



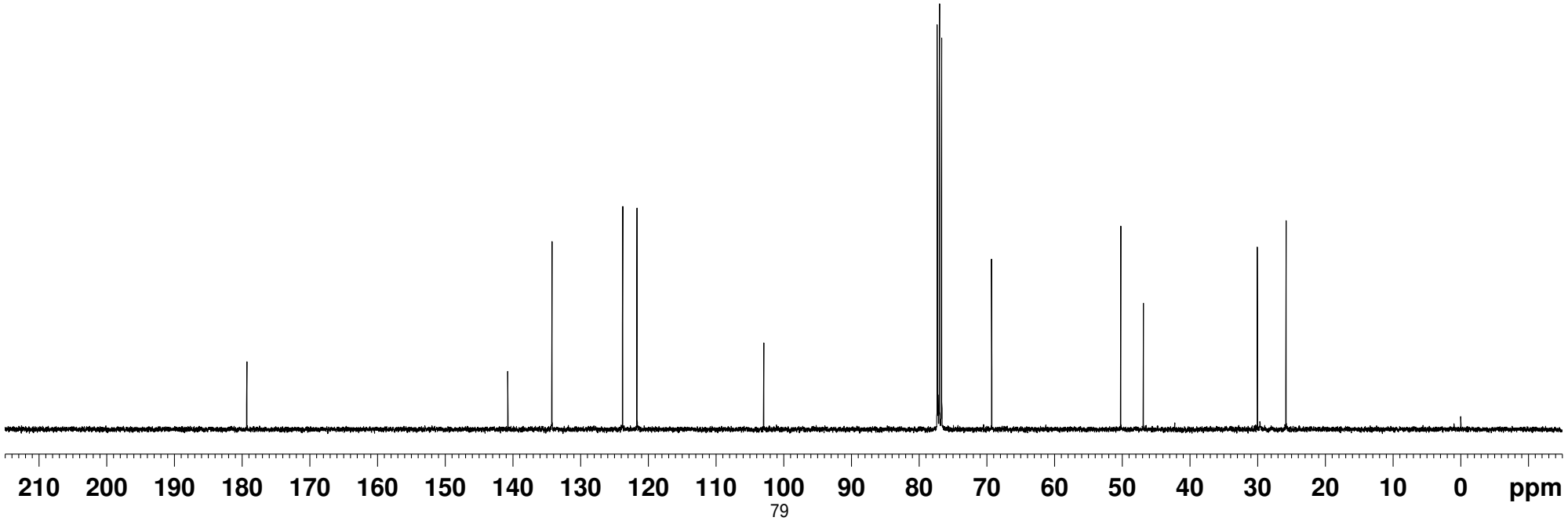

7.426
7.423
7.406
7.403
7.260
7.115
7.112
7.096
7.094
6.954
6.934
6.916
5.402
5.391
5.379
5.368
3.578
3.050
3.028
3.013
2.991
2.699
2.687
2.661
2.650
1.377
NAME cc-g155-4-1009
SOLVENT CDCl3
SF 400.1500090 MHz
Me
CHCl2
O
N
Me
Br
21
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.04
1.00
3.16
1.06
1.07
3.19

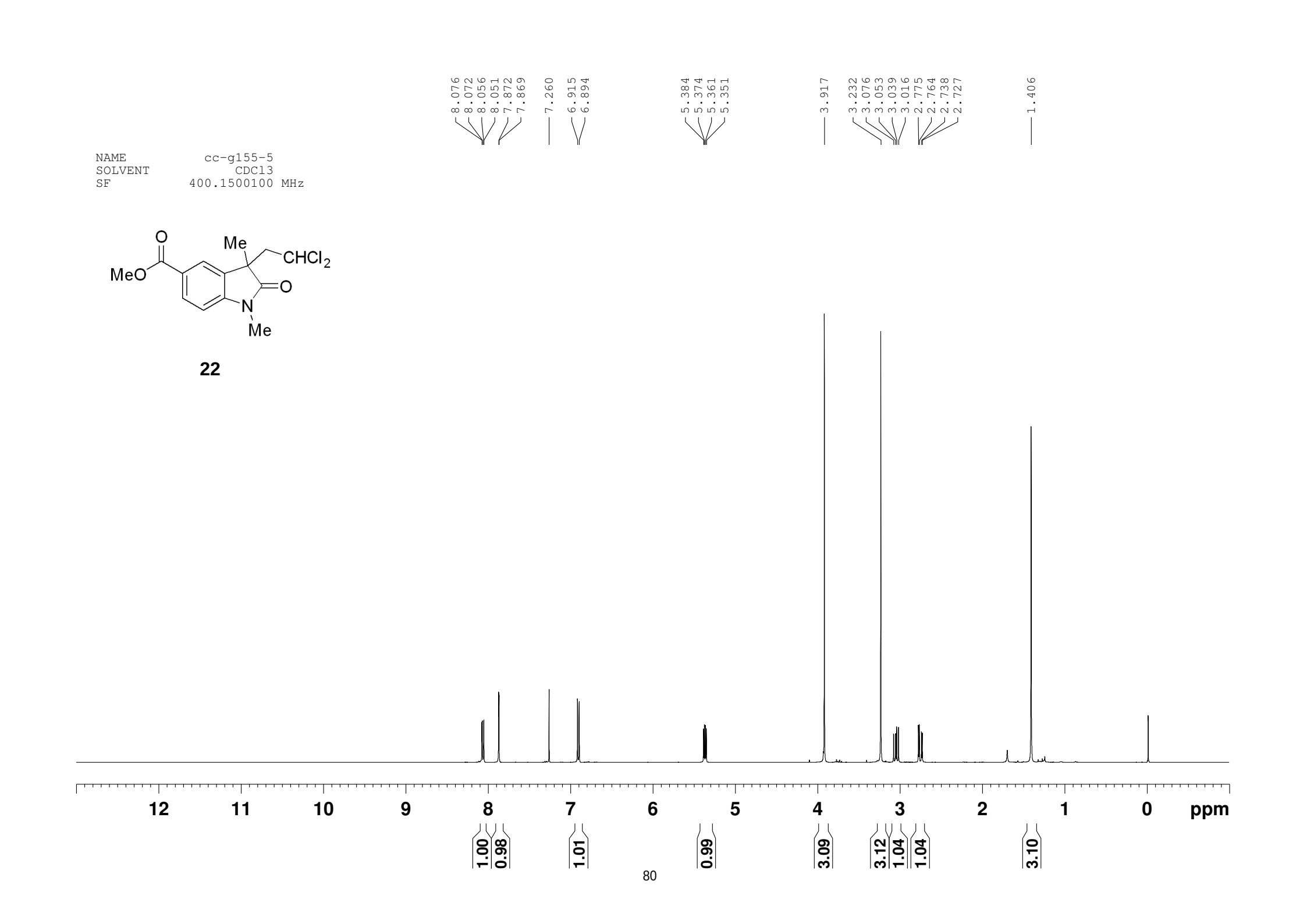
179.33
140.76
134.25
134.23
123.80
121.68
102.96
77.32
77.00
76.68
69.29
50.21
46.86
30.03
25.80

NAME cc-g155-4-1009
SOLVENT CDCl3
SF 100.6178023 MHz



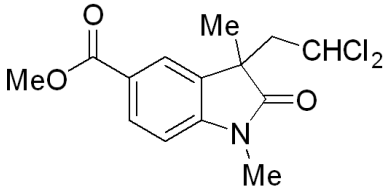
21




8.076
8.072
8.056
8.051
7.872
7.869
7.260
6.915
6.894
5.384
5.374
5.361
5.351
3.917
3.232
3.076
3.053
3.039
3.016
2.775
2.764
2.738
2.727
1.406
NAME cc-g155-5
SOLVENT CDCl3
SF 400.1500100 MHz
O
Me
CHCl2
MeO
O
N
Me
22
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
1.01
0.99
3.09
3.12
1.04
1.04
3.10

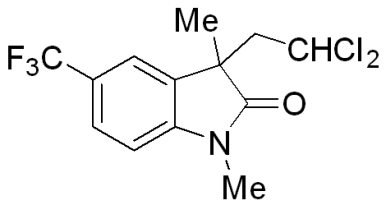
179.25
166.64
147.50
131.32
131.06
124.62
123.94
108.10
77.32
77.00
76.68
69.40
52.12
49.82
46.98
26.64
25.43

NAME cc-g155-5
SOLVENT CDCl3
SF 100.6178023 MHz

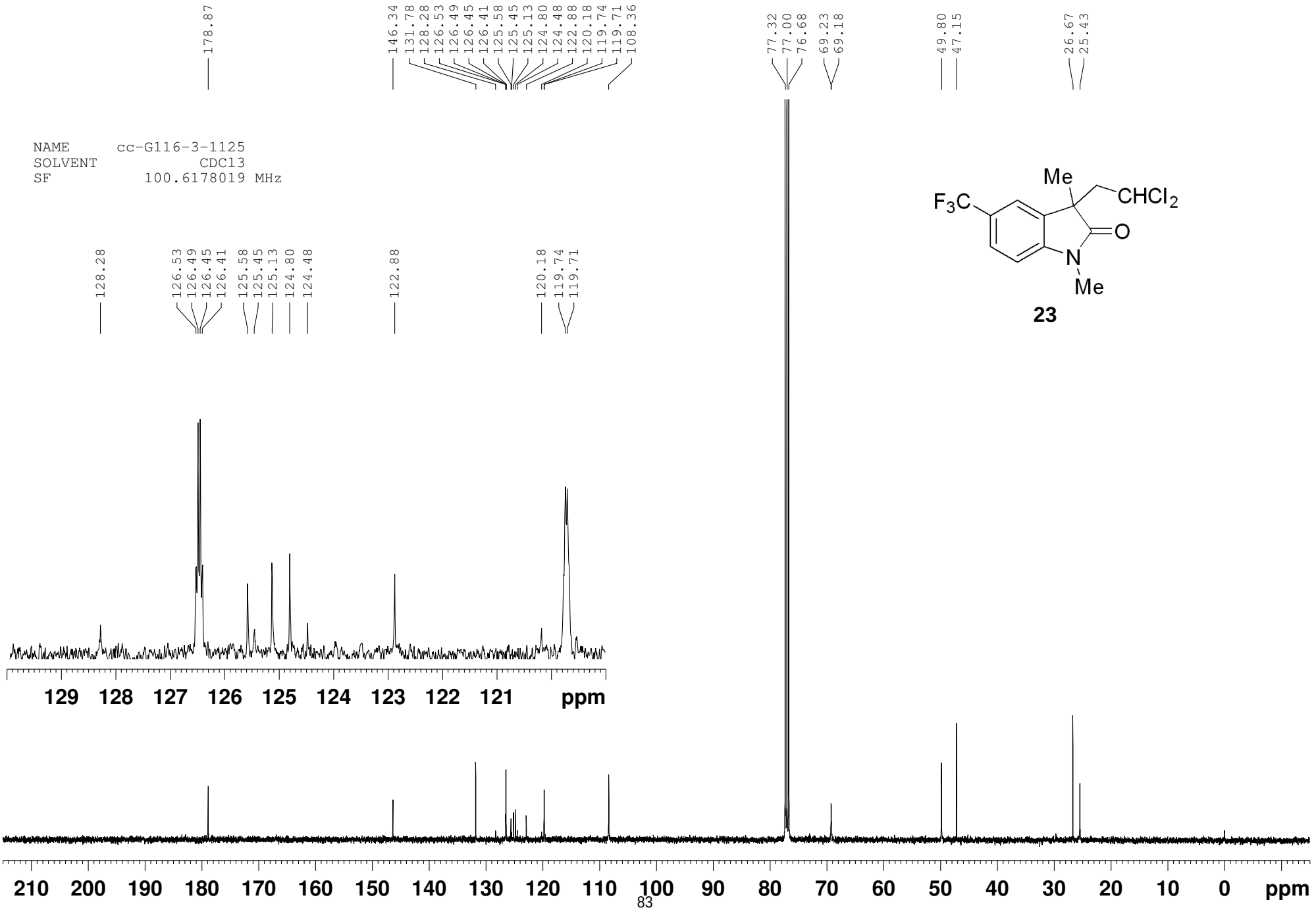


22

NAME cc-G116-3-1125
SOLVENT CDCl3
SF 400.1500101 MHz

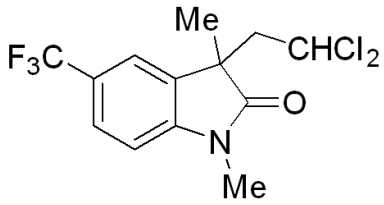


23

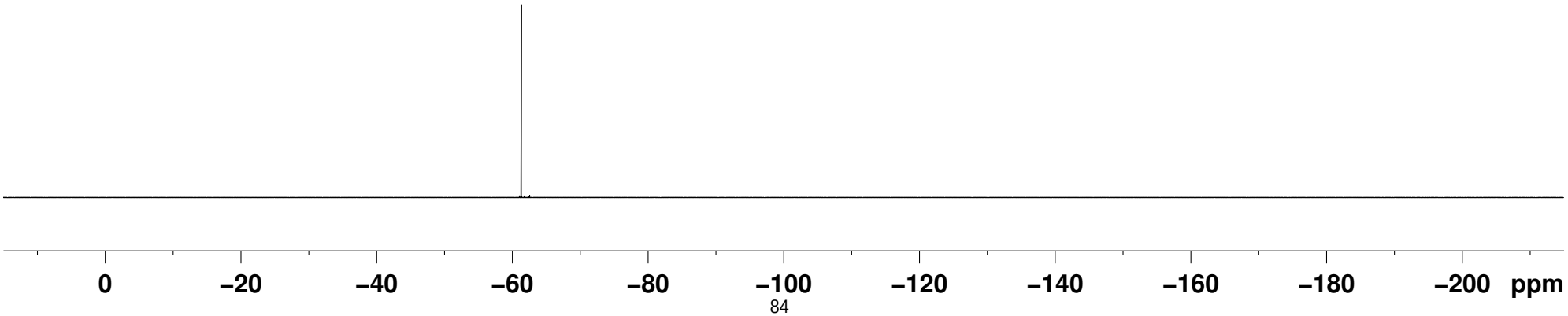

178.87
146.34
131.78
128.28
126.53
126.49
126.45
126.41
125.58
125.45
125.13
124.80
124.48
122.88
120.18
119.74
119.71
108.36
77.32
77.00
76.68
69.23
69.18
49.80
47.15
26.67
25.43
NAME cc-G116-3-1125
SOLVENT CDCl3
SF 100.6178019 MHz
Me
CHCl2
F3C
O
N
Me
23
129 128 127 126 125 124 123 122 121 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

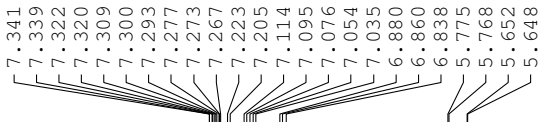
-61.324

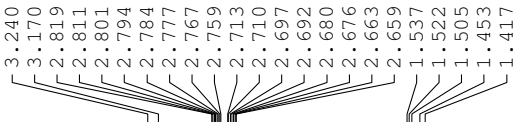
NAME cc-G116-3-1125
SOLVENT CDCl3
SF 376.5171850 MHz



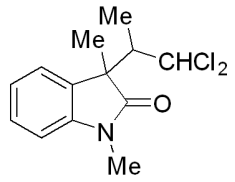
23



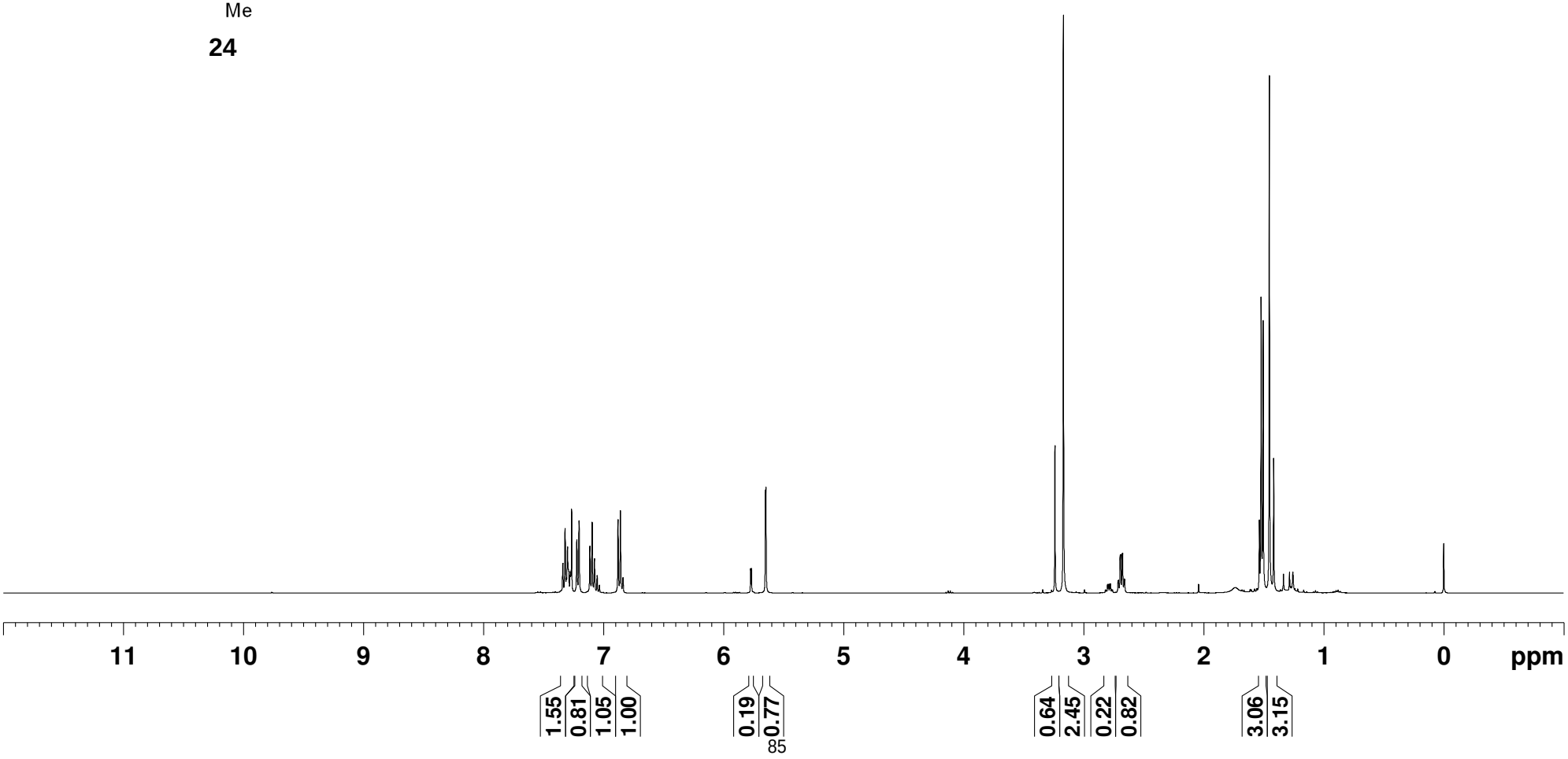




NAME cc-h129-3-0608
SOLVENT CDCl3
SF 400.1500070 MHz

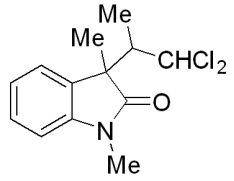


24

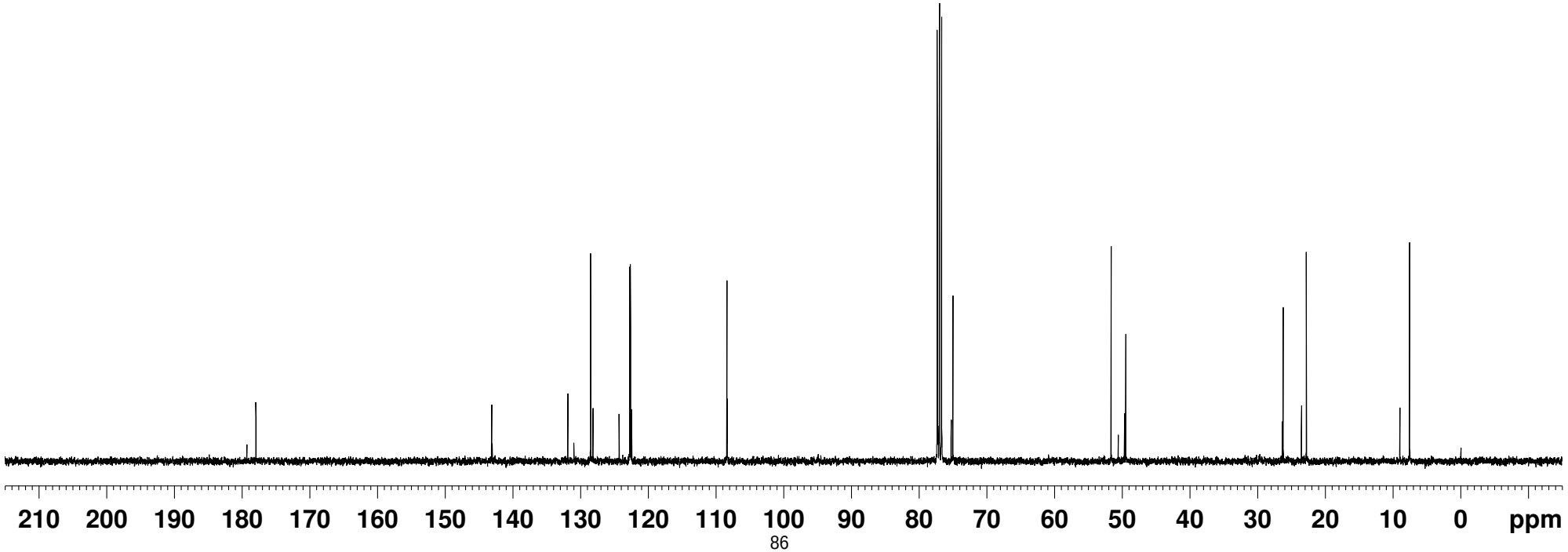


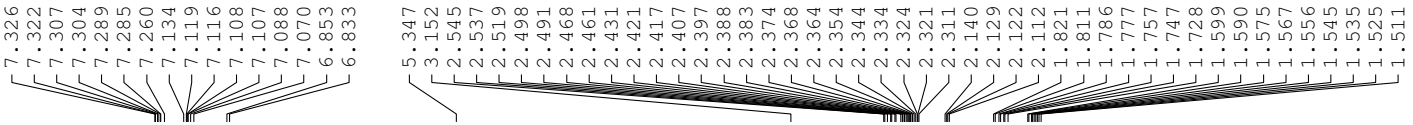
179.31
177.97
143.15
131.89
131.02
128.53
128.18
124.32
122.76
122.63
122.47
108.39
108.34
77.32
77.00
76.68
75.26
75.00
51.64
50.58
49.65
49.46
26.33
26.21
23.51
22.80
8.96
7.54

NAME cc-h129-3-0608
SOLVENT CDCl3
SF 100.6178030 MHz

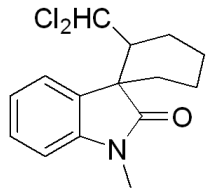


24

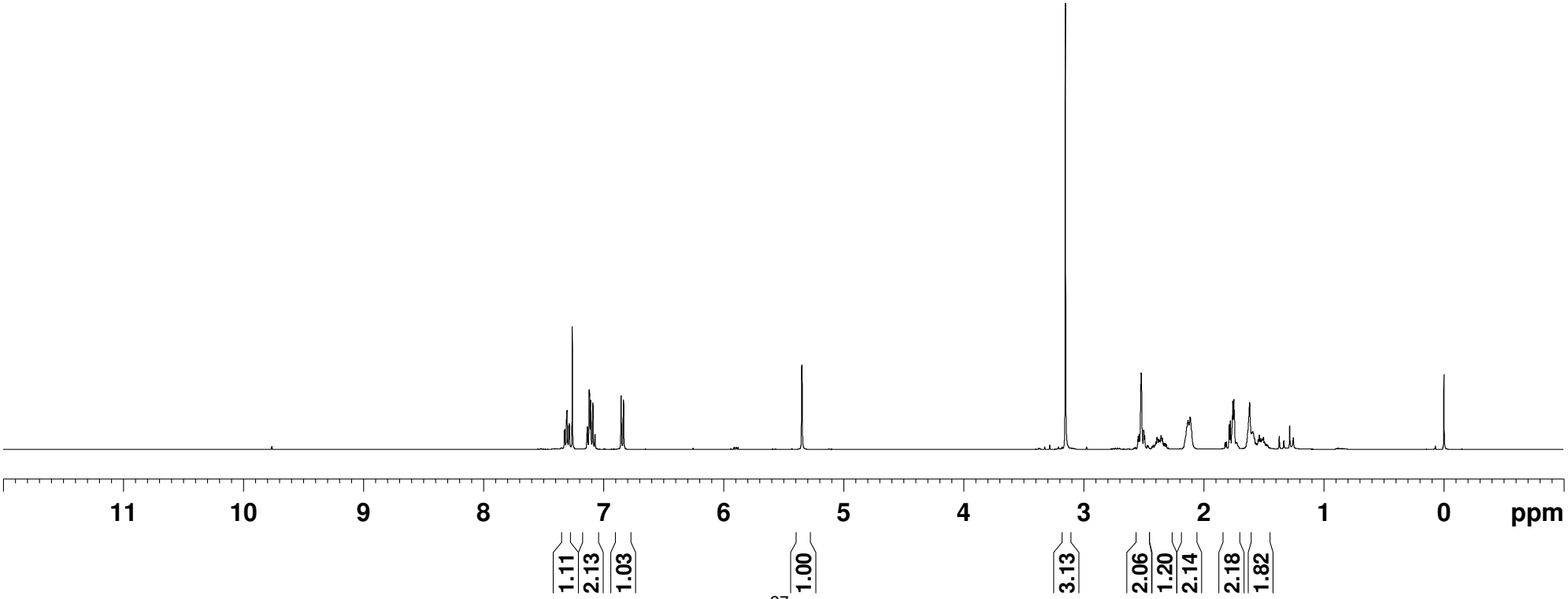




NAME cc-h163-up
SOLVENT CDCl3
SF 400.1500096 MHz

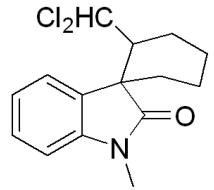


25-up

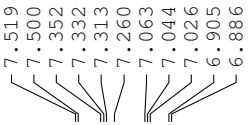


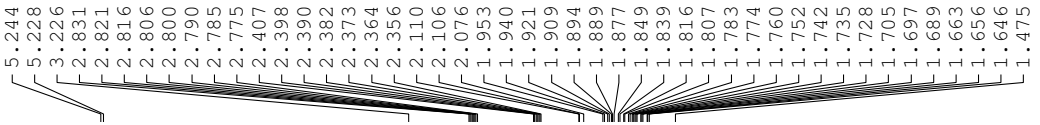
177.05
143.28
131.81
128.46
122.65
121.60
108.13
77.32
77.00
76.68
73.85
55.80
49.31
36.57
26.06
25.50
20.08
19.25

NAME cc-h163-up
SOLVENT CDCl3
SF 100.6178008 MHz

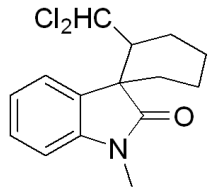


25-up

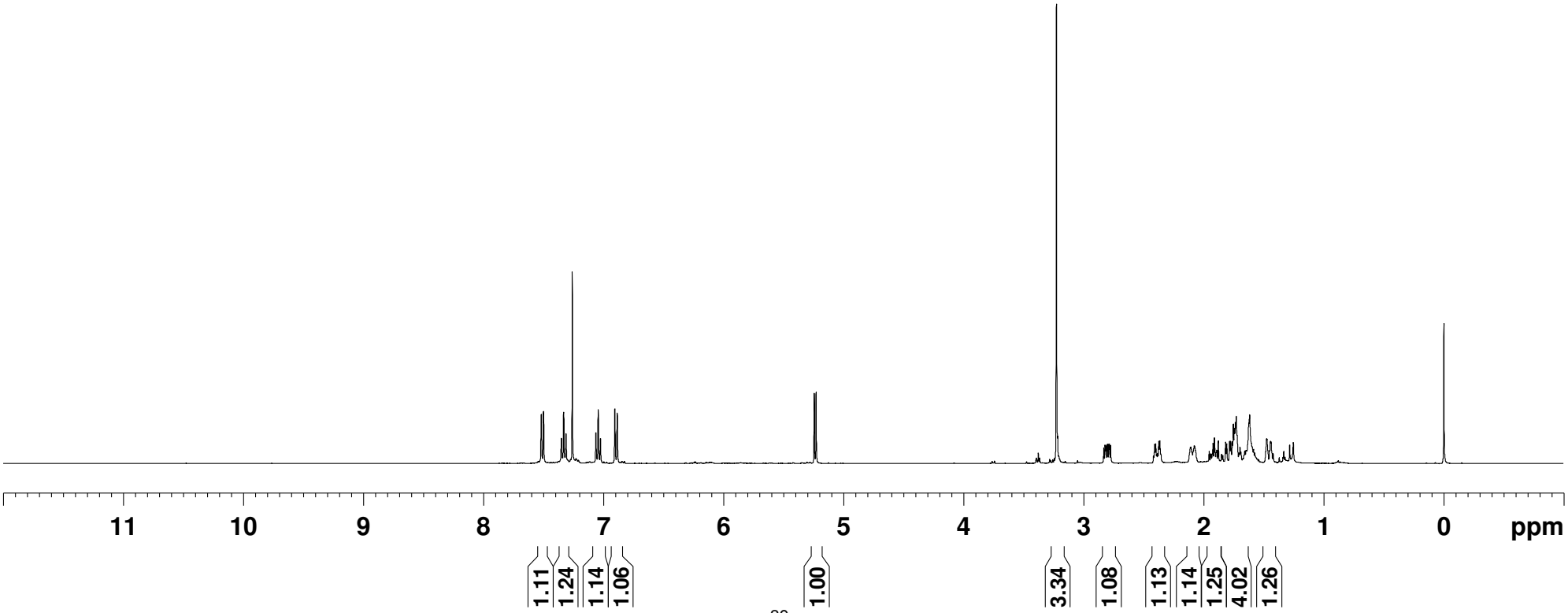




NAME cc-h163-down
SOLVENT CDCl3
SF 400.1500096 MHz

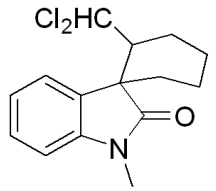


25-down

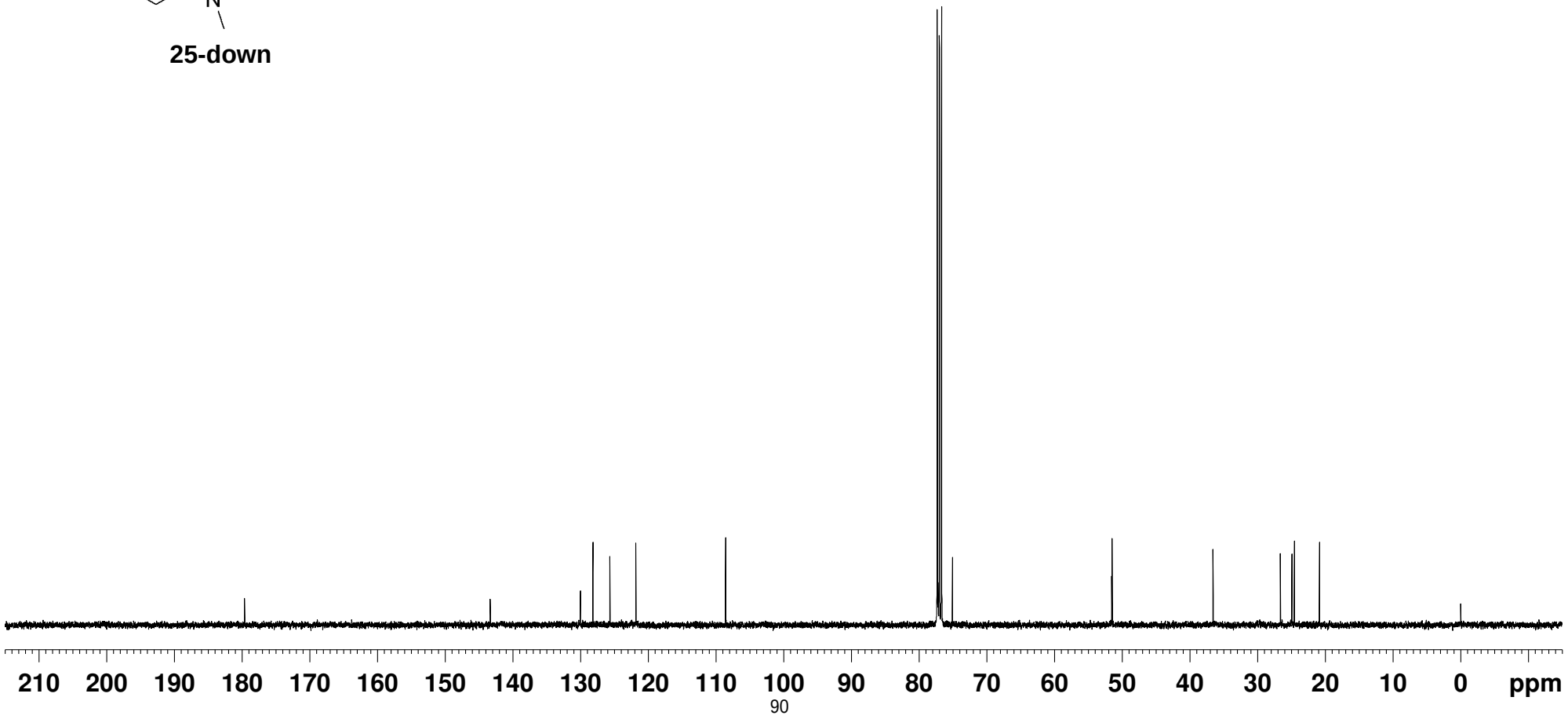


179.64
143.35
130.03
128.19
125.67
121.84
108.59
77.32
77.00
76.68
75.07
51.53
51.47
36.57
26.63
24.91
24.55
20.85

NAME cc-h163-down
SOLVENT CDCl3
SF 100.6178004 MHz

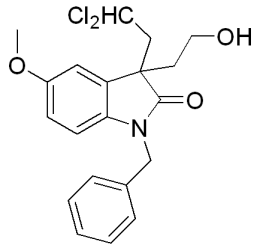


25-down

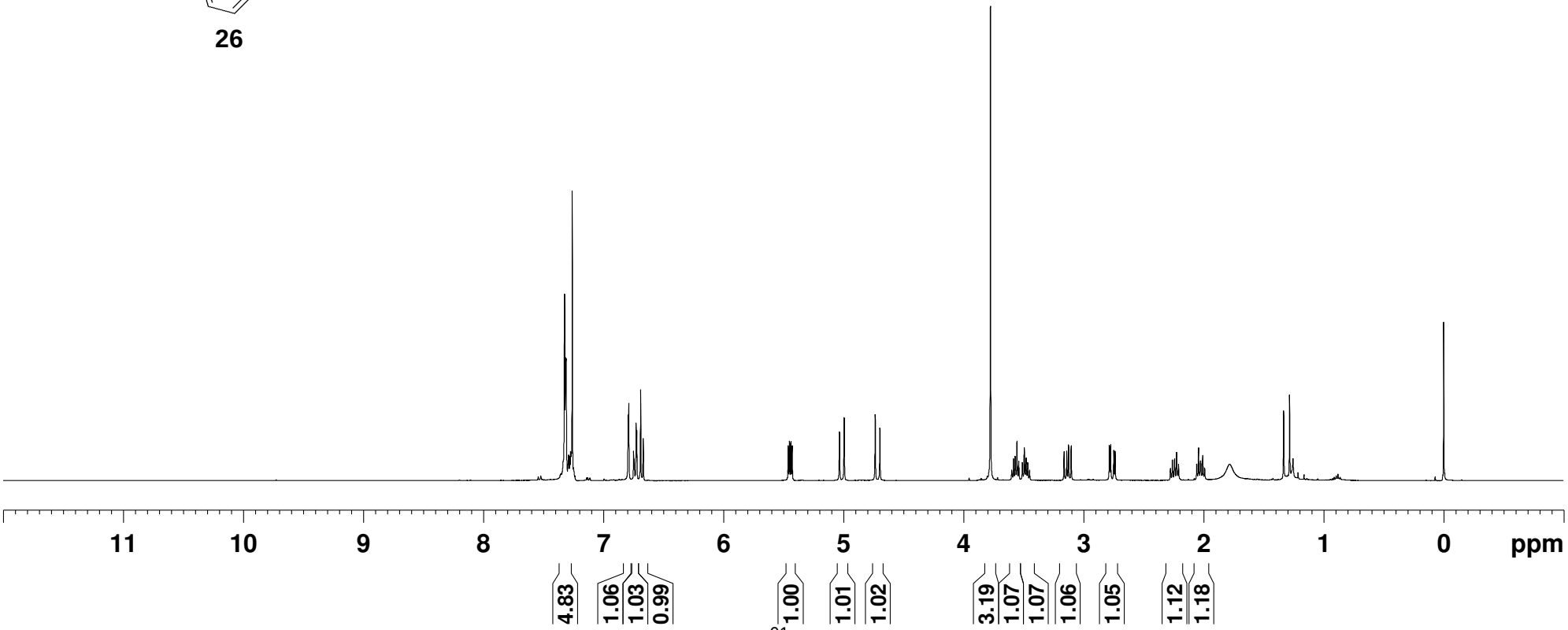


7.337
7.324
7.317
7.311
7.296
7.292
7.290
7.281
7.274
7.268
6.795
6.789
6.749
6.743
6.728
6.722
6.690
6.669
5.461
5.450
5.439
5.428
5.033
4.994
4.736
4.697
3.776
3.599
3.583
3.570
3.555
3.539
3.510
3.494
3.478
3.466
3.449
3.162
3.140
3.125
3.103
2.785
2.774
2.748
2.737
2.276
2.259
2.241
2.224
2.209
2.057
2.041
2.026
2.022
2.006
1.991

NAME CC-I120
SOLVENT CDCl3
SF 400.1500095 MHz

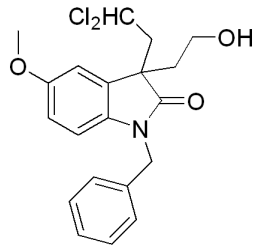


26

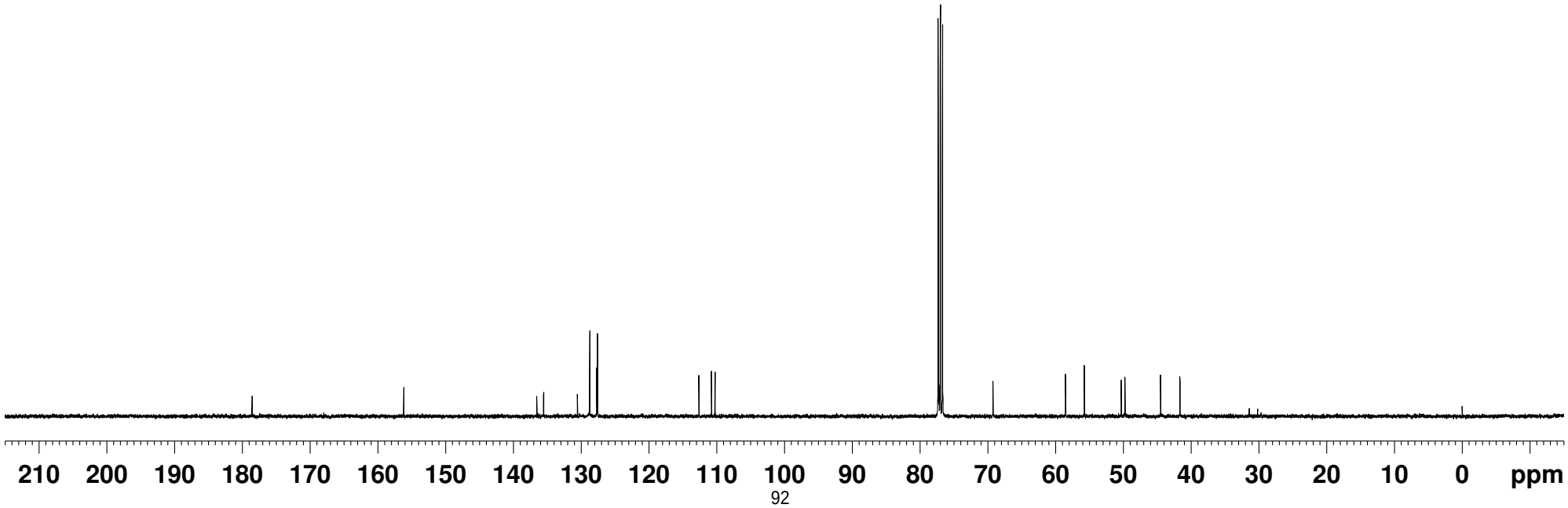


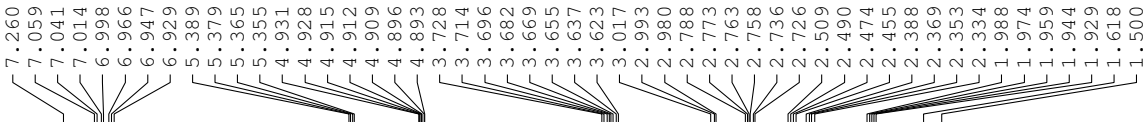
178.57
156.18
136.55
135.56
130.57
128.75
127.72
127.59
112.64
110.79
110.23
77.32
77.00
76.68
69.24
58.52
55.76
50.29
49.76
44.51
41.64

NAME CC-I120
SOLVENT CDCl3
SF 100.6178001 MHz

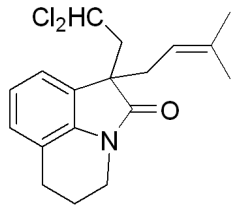


26

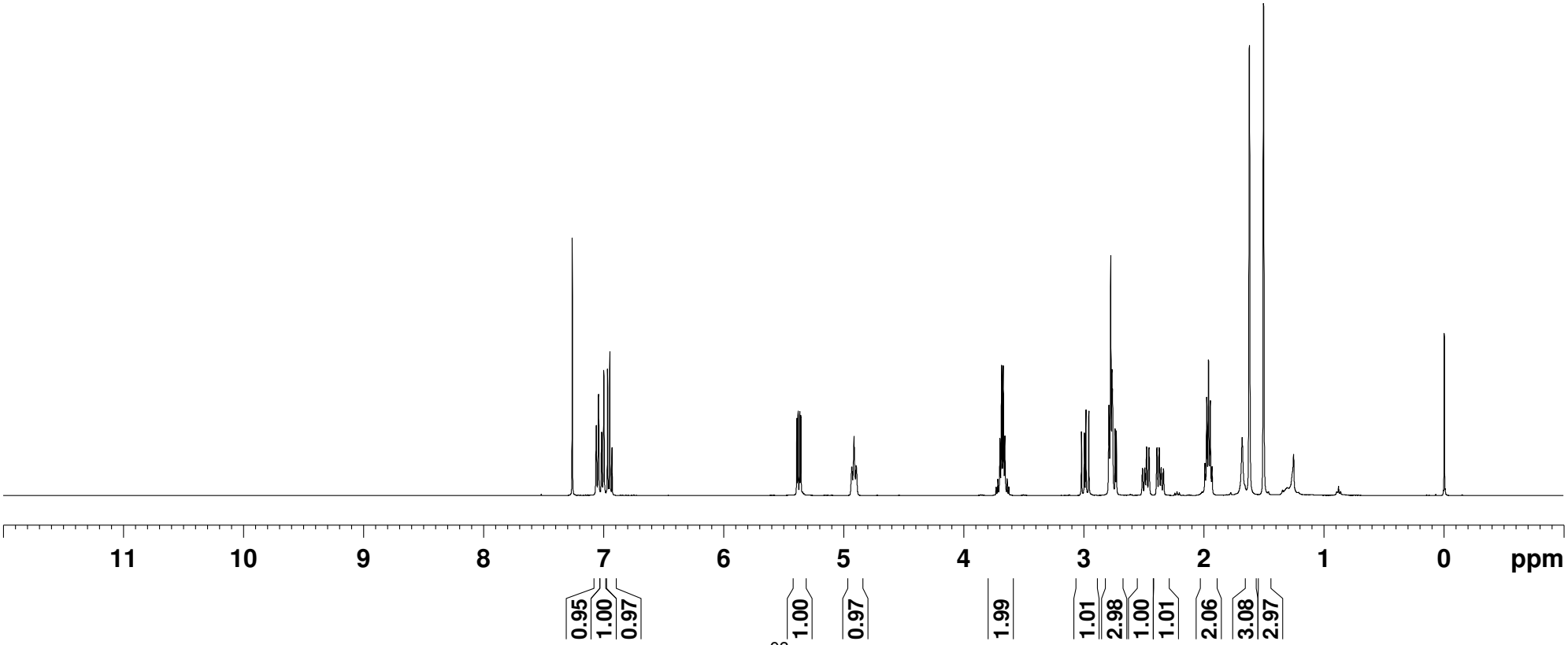




NAME cc-I27-0709
SOLVENT CDCl3
SF 400.1500091 MHz

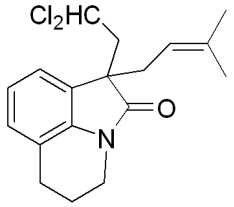


27

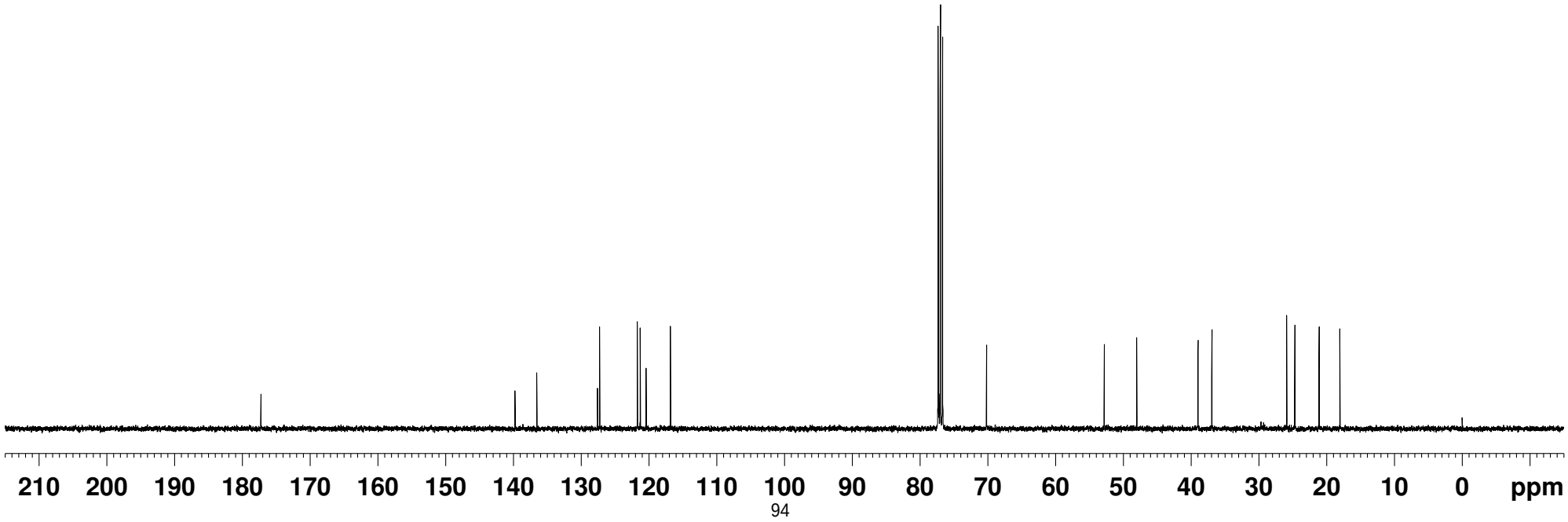


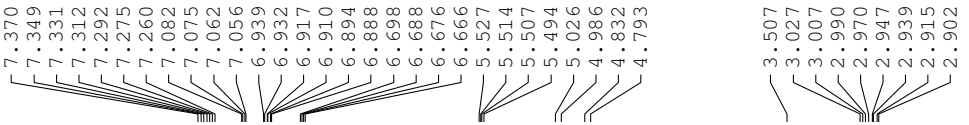
177.27
139.77
136.55
127.61
127.28
121.73
121.30
120.44
116.84
77.32
77.00
76.68
70.18
52.82
48.03
38.97
36.94
25.89
24.68
21.11
18.05

NAME cc-I27-0709
SOLVENT CDCl3
SF 100.6178008 MHz

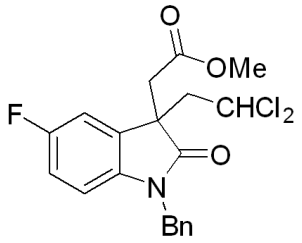


27





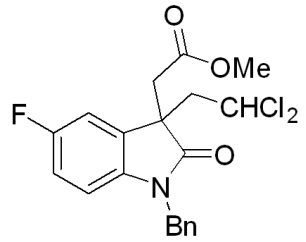
NAME cc-h6-3-0608
SOLVENT CDCl3
SF 400.1500098 MHz



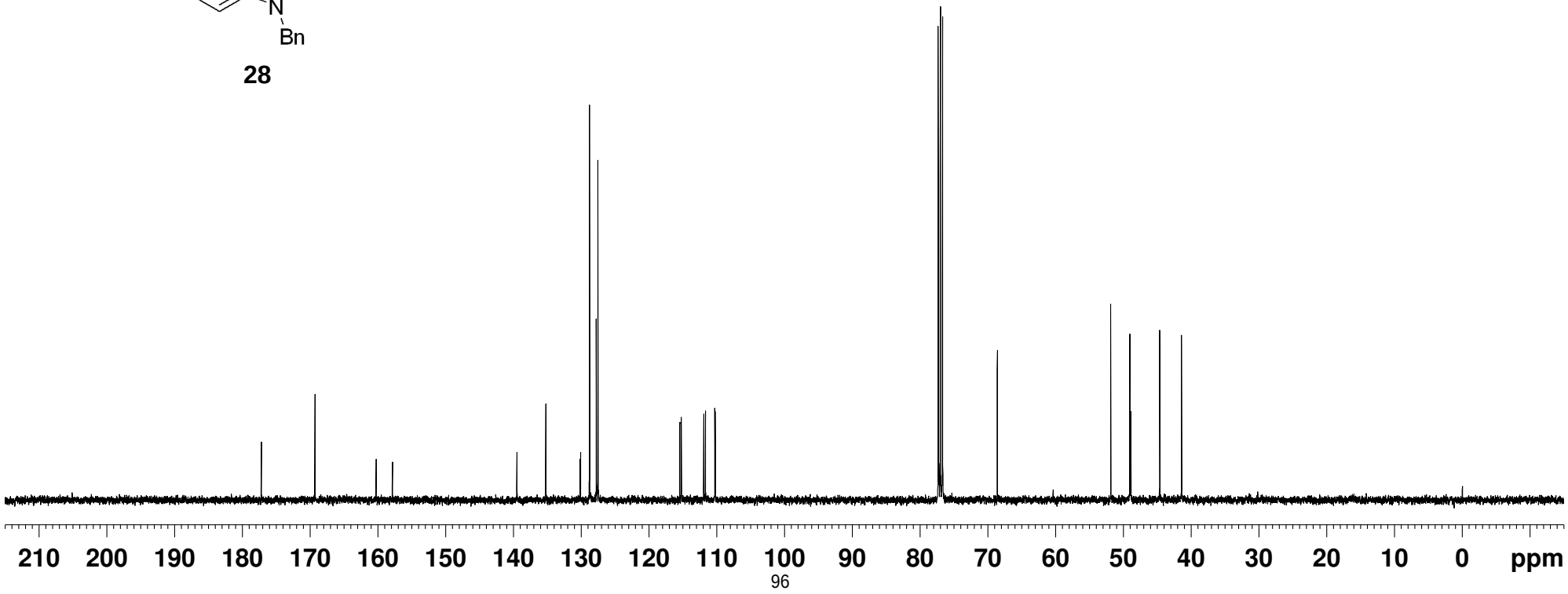
28

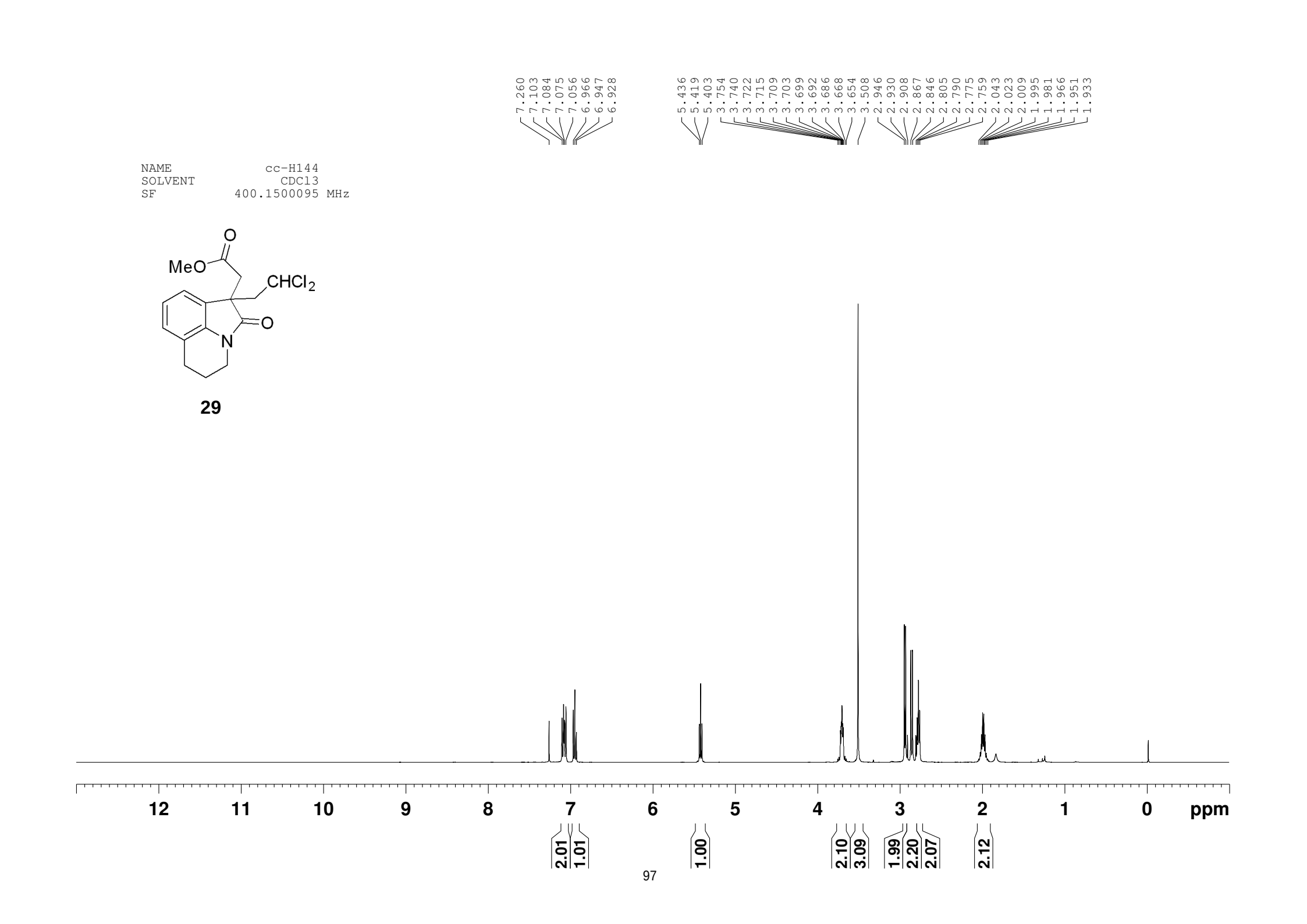
177.20
169.29
160.27
157.87
139.50
139.48
135.22
130.19
130.11
128.78
127.79
127.54
115.46
115.23
111.92
111.67
110.30
110.22
77.32
77.00
76.68
68.59
51.85
49.04
48.91
48.89
44.63
41.41

NAME cc-h6-3-0609
SOLVENT CDCl3
SF 100.6178030 MHz



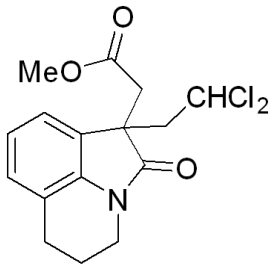
28



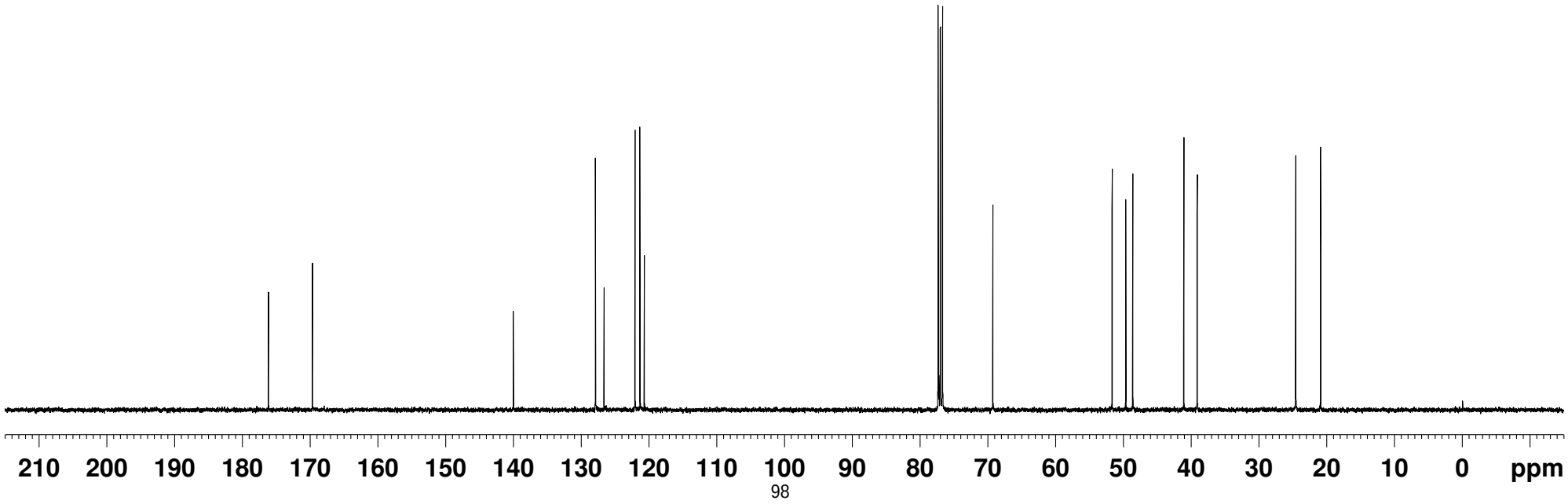

7.260
7.103
7.084
7.075
7.056
6.966
6.947
6.928
5.436
5.419
5.403
3.754
3.740
3.722
3.715
3.709
3.703
3.699
3.692
3.686
3.668
3.654
3.508
2.946
2.930
2.908
2.867
2.846
2.805
2.790
2.775
2.759
2.043
2.023
2.009
1.995
1.981
1.966
1.951
1.933
NAME cc-H144
SOLVENT CDCl3
SF 400.1500095 MHz
MeO
O
CHCl2
O
N
29
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.01
1.00
2.10
3.09
1.99
2.20
2.07
2.12

176.16
169.67
140.04
127.91
126.63
122.06
121.34
120.68
77.32
77.00
76.68
69.26
51.65
49.63
48.59
41.07
39.09
24.55
20.86

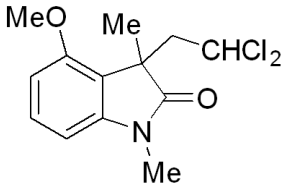
NAME cc-H144
SOLVENT CDCl3
SF 100.6178063 MHz



29



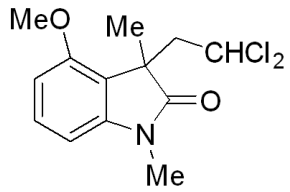
NAME cc-g161-1-up-0710
SOLVENT CDCl3
SF 400.1500061 MHz



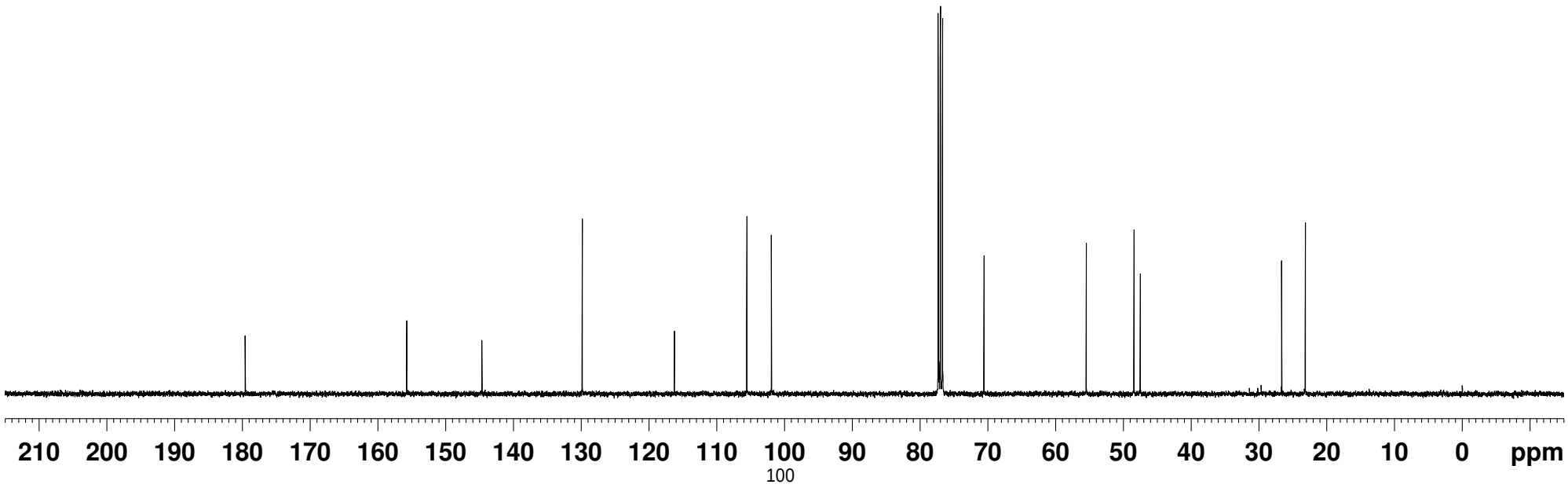
30

179.61
155.76
144.67
129.86
116.25
105.57
101.94
77.32
77.00
76.68
70.55
55.47
48.42
47.49
26.64
23.13

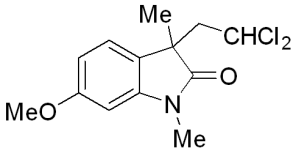
NAME cc-g161-up
SOLVENT CDCl3
SF 100.6178023 MHz



30



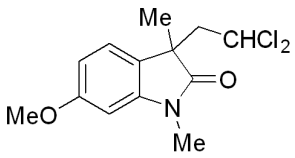
NAME cc-g161-1-down-0710
SOLVENT CDCl3
SF 400.1500090 MHz



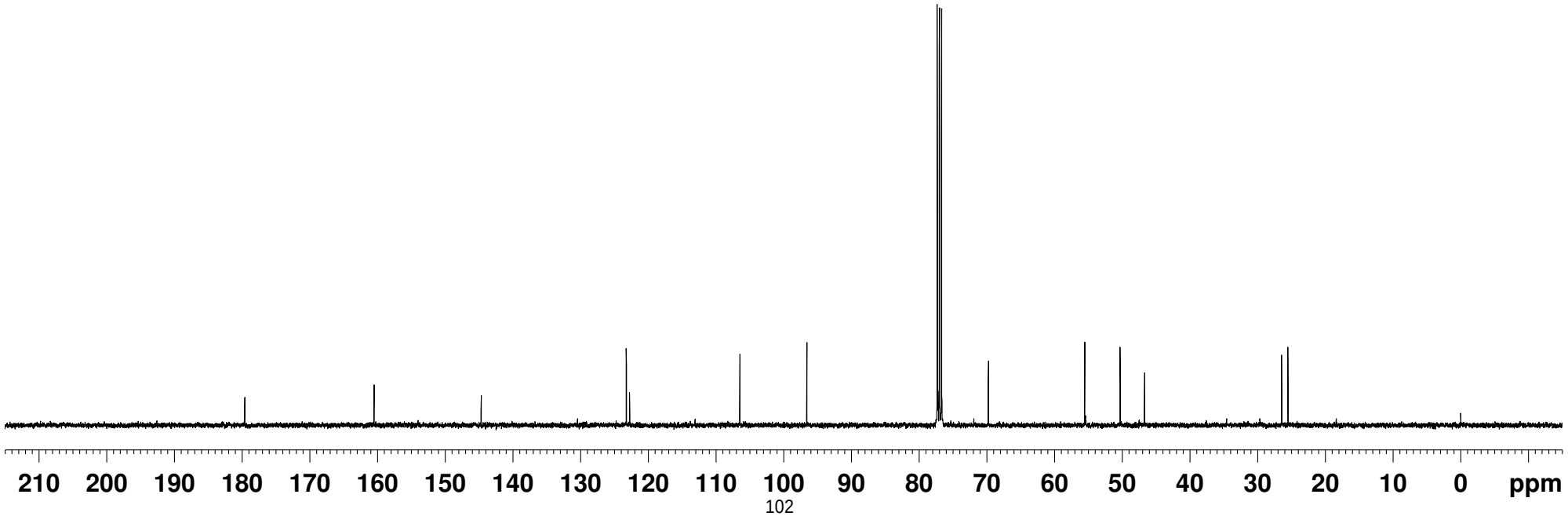
31

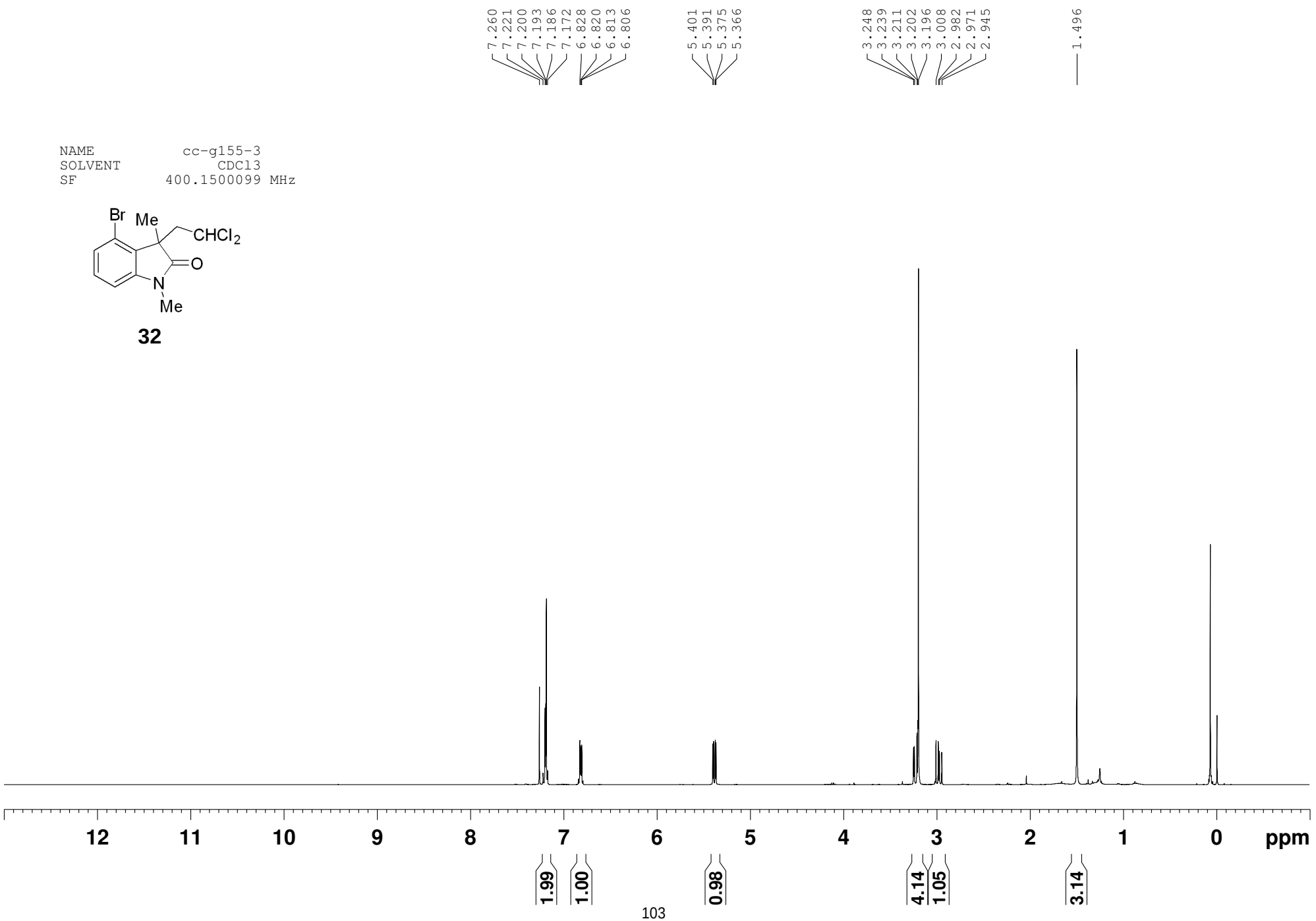
179.61
160.51
144.70
123.25
122.76
106.47
96.58
77.32
77.00
76.69
69.77
55.53
50.29
46.69
26.45
25.52

NAME cc-g161-1-down
SOLVENT CDCl3
SF 100.6178008 MHz



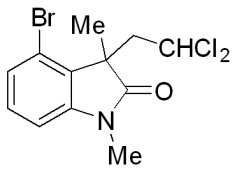
31



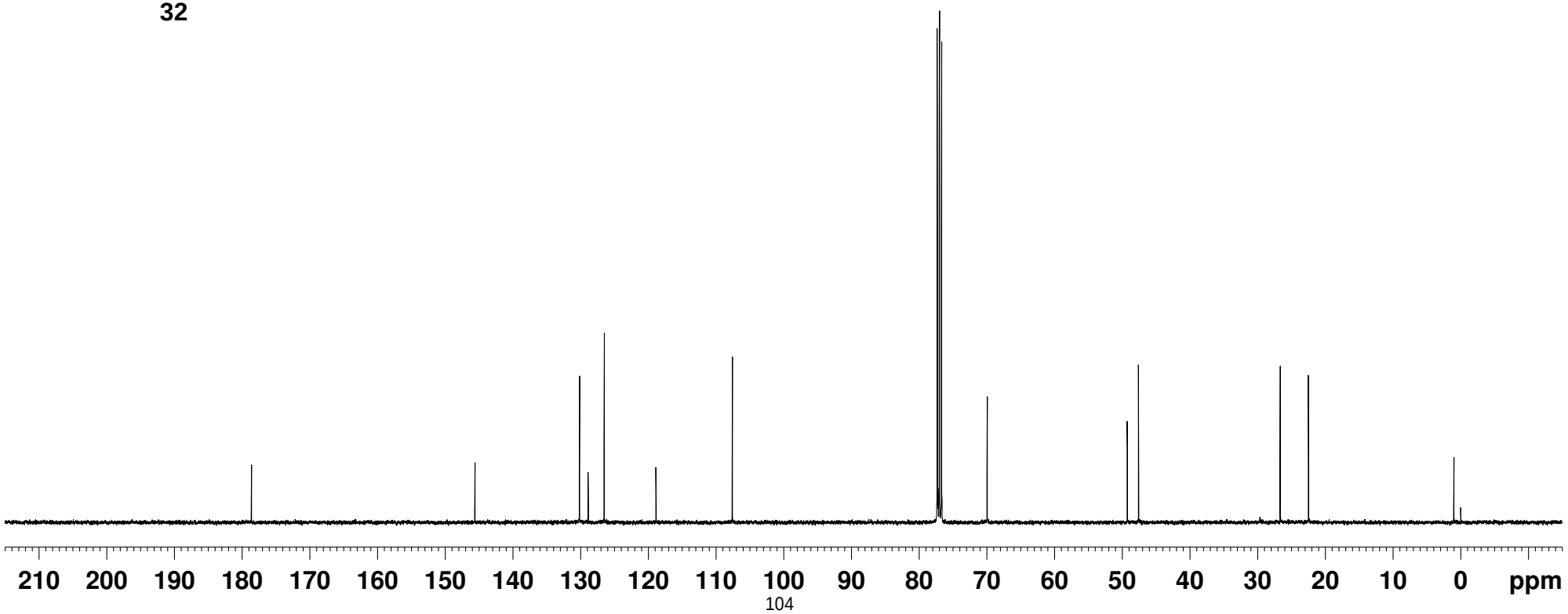

7.260
7.221
7.200
7.193
7.186
7.172
6.828
6.820
6.813
6.806
5.401
5.391
5.375
5.366
3.248
3.239
3.211
3.202
3.196
3.008
2.982
2.971
2.945
1.496
NAME cc-g155-3
SOLVENT CDCl3
SF 400.1500099 MHz
Br
Me
CHCl2
O
N
Me
32
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.00
0.98
4.14
1.05
3.14

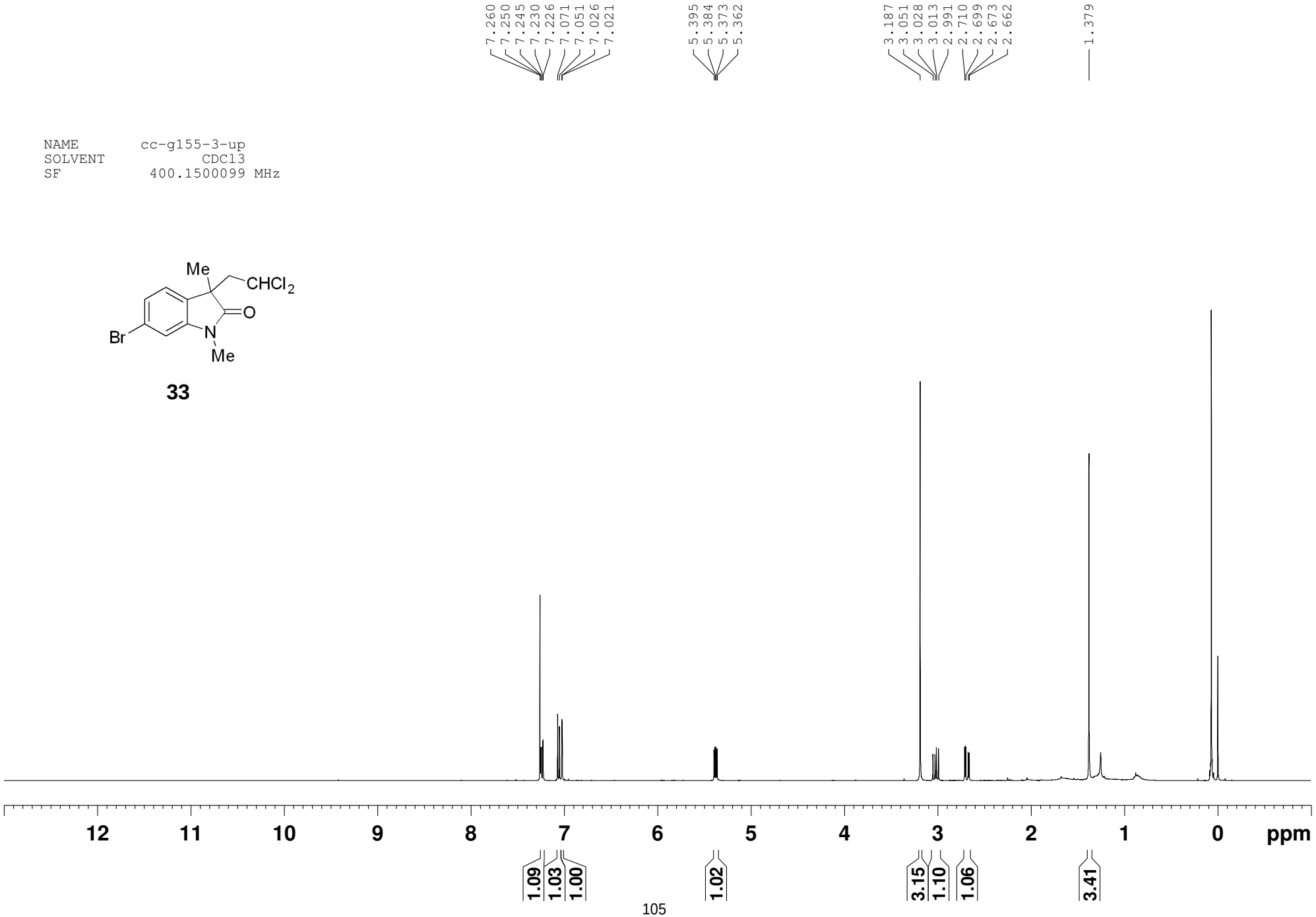
178.63
145.62
130.17
128.89
126.53
118.87
107.58
77.32
77.00
76.68
69.95
49.24
47.59
26.65
22.47

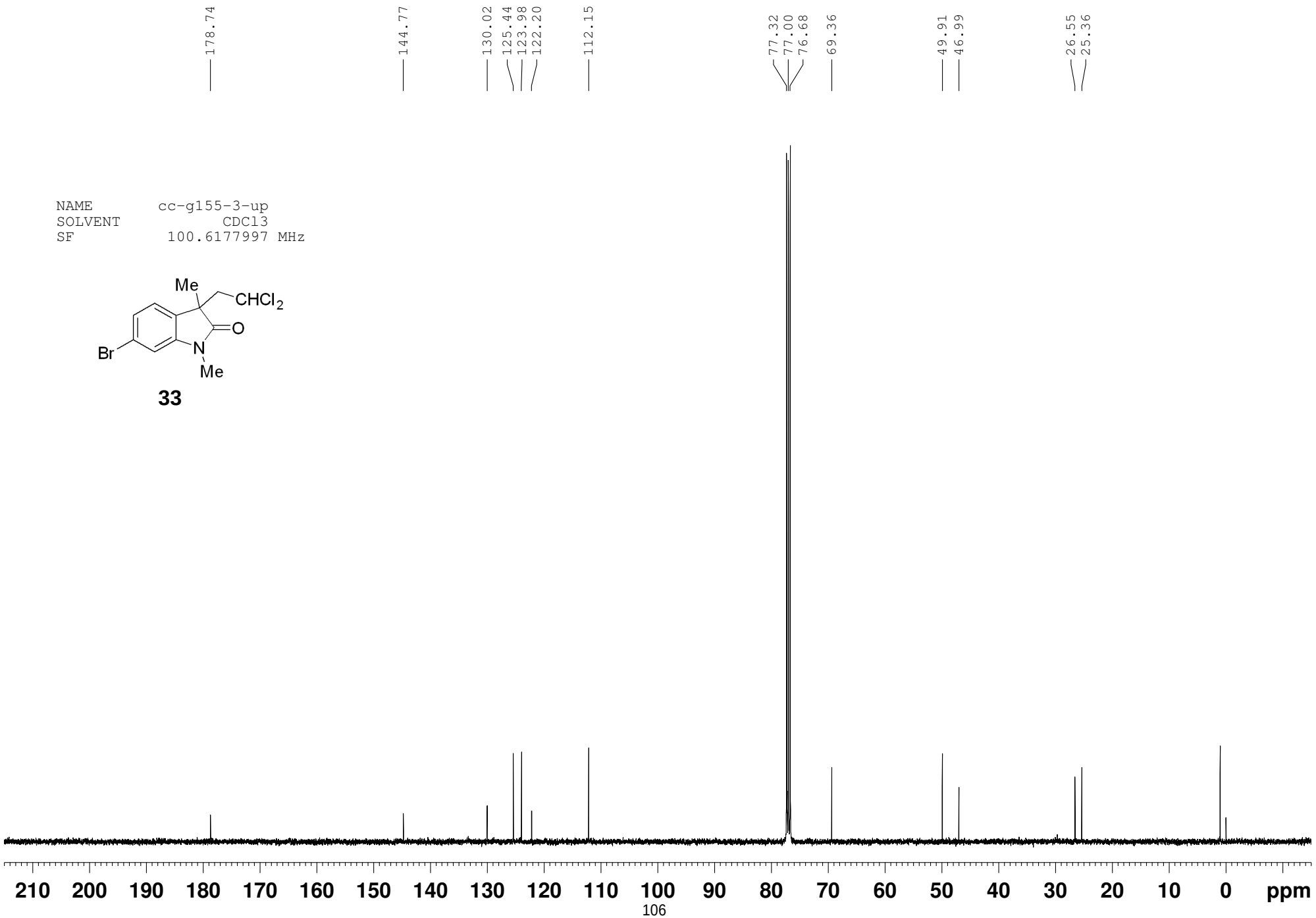
NAME cc-g155-3
SOLVENT CDCl3
SF 100.6178016 MHz

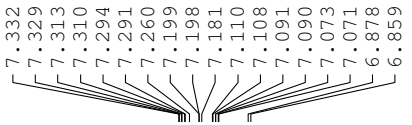


32

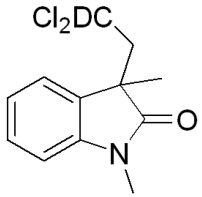



7.260
7.250
7.245
7.230
7.226
7.071
7.051
7.026
7.021
5.395
5.384
5.373
5.362
3.187
3.051
3.028
3.013
2.991
2.710
2.699
2.673
2.662
1.379
NAME cc-g155-3-up
SOLVENT CDCl3
SF 400.1500099 MHz
Me
CHCl2
O
N
Me
Br
33
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.09
1.03
1.00
1.02
3.15
1.10
1.06
3.41

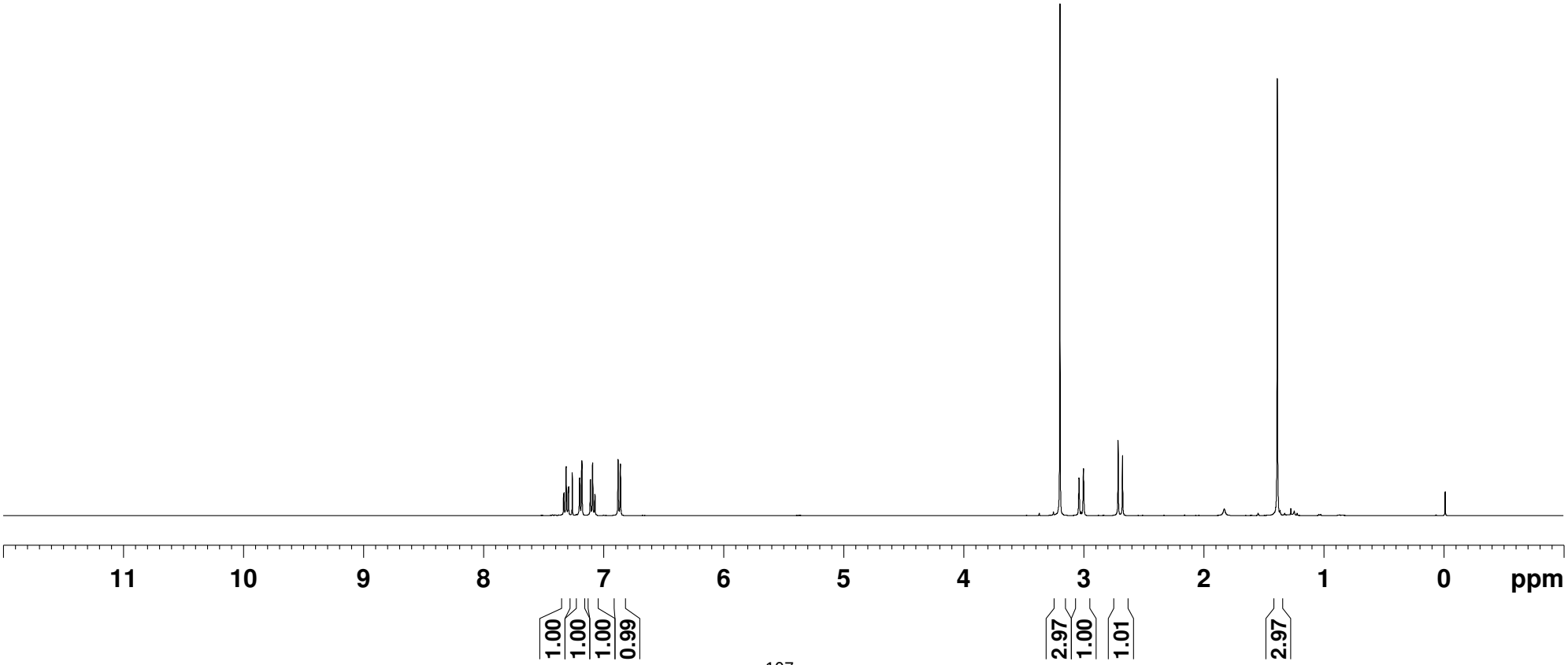

178.74
144.77
130.02
125.44
123.98
122.20
112.15
77.32
77.00
76.68
69.36
49.91
46.99
26.55
25.36
NAME cc-g155-3-up
SOLVENT CDCl3
SF 100.6177997 MHz
Me
CHCl2
O
Br
N
Me
33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



NAME cc-g104-2
SOLVENT CDCl3
SF 400.1500096 MHz

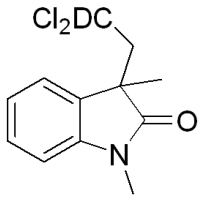


3-D

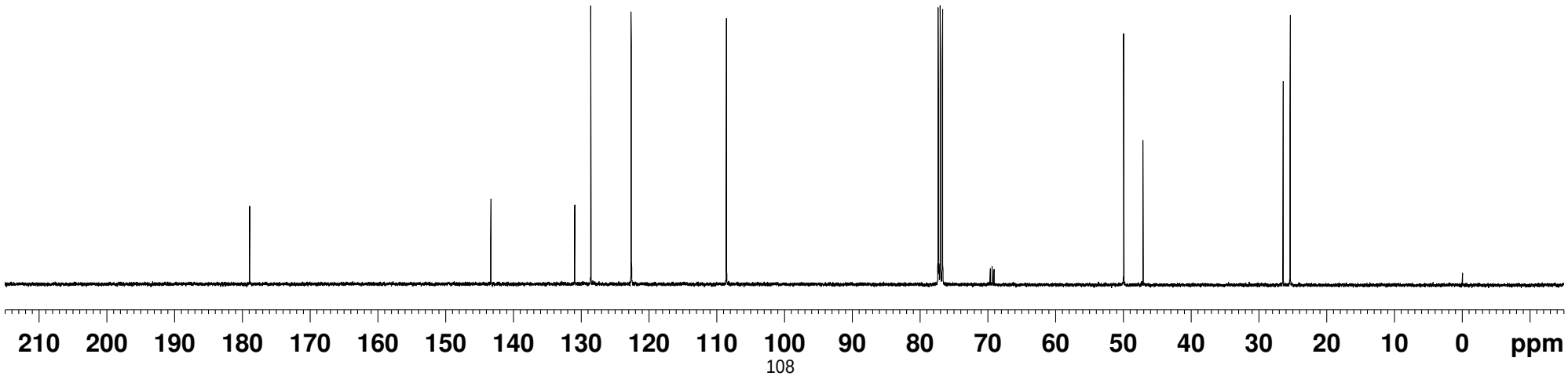


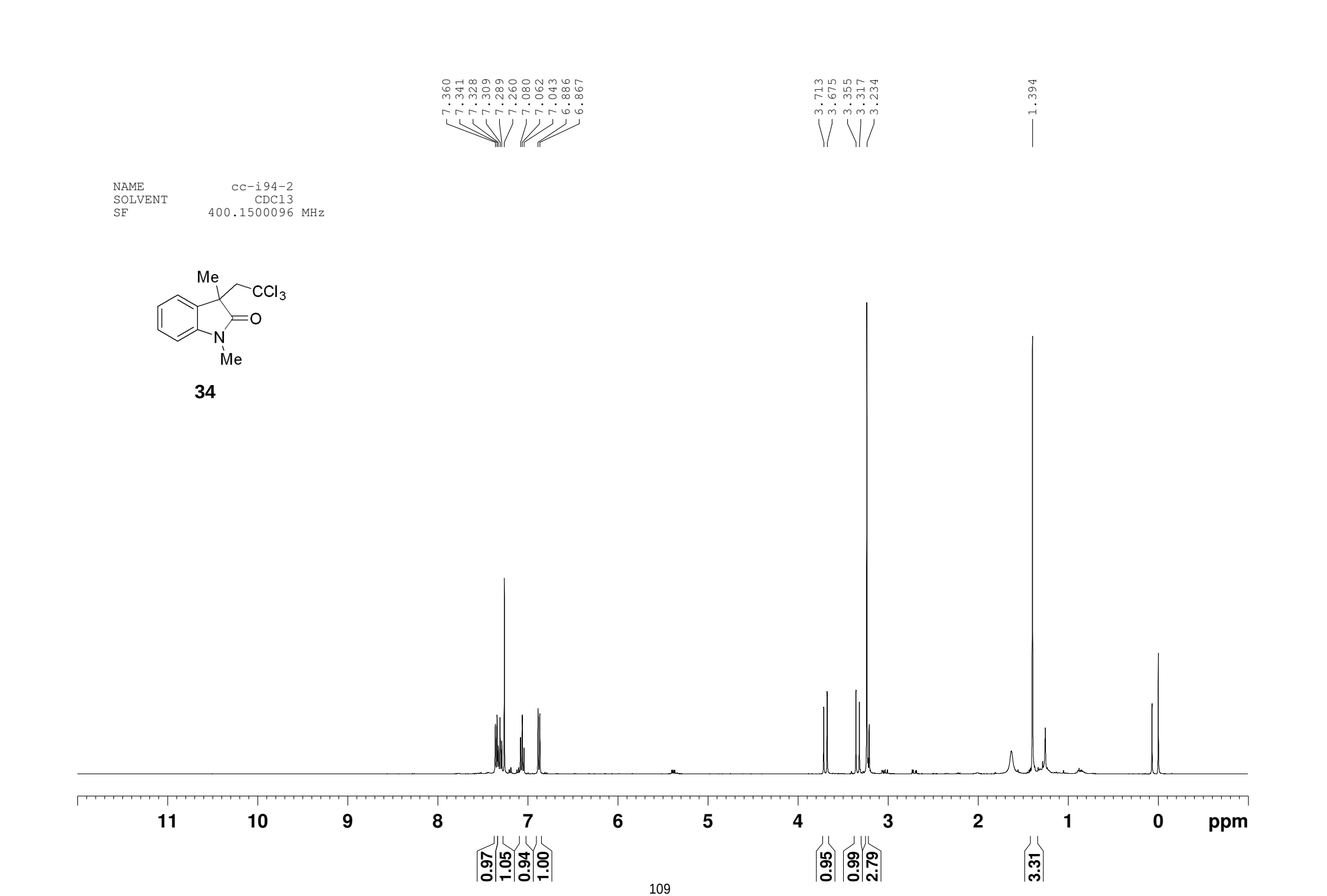
178.94
143.34
130.97
128.58
122.64
122.60
108.57
77.32
77.00
76.68
69.62
69.35
69.08
49.94
47.09
26.40
25.37

NAME cc-G104-2-C
SOLVENT CDCl3
SFO1 100.6228293 MHz



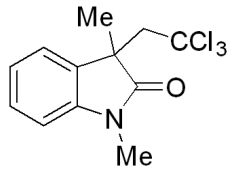
3-D



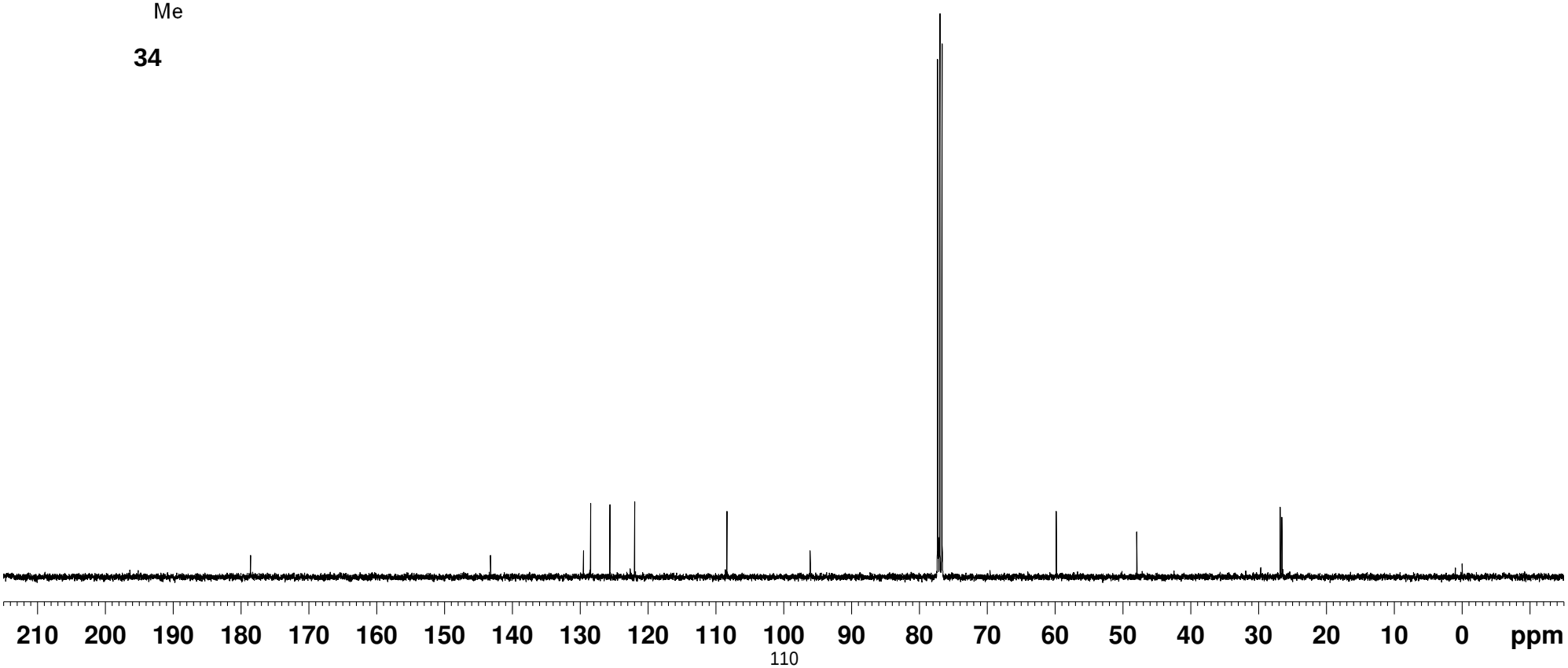

7.360
7.341
7.328
7.309
7.289
7.260
7.080
7.062
7.043
6.886
6.867
3.713
3.675
3.355
3.317
3.234
1.394
NAME cc-i94-2
SOLVENT CDCl3
SF 400.1500096 MHz
Me
CCl3
O
N
Me
34
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
1.05
0.94
1.00
0.95
0.99
2.79
3.31

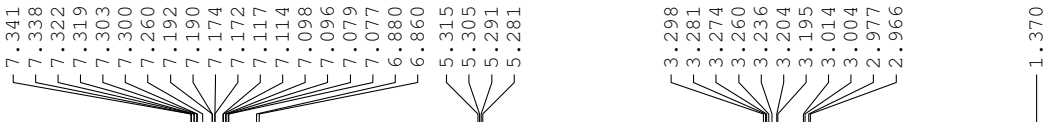
178.62
143.24
129.53
128.48
125.63
122.00
108.38
96.11
77.32
77.00
76.68
59.83
47.95
26.82
26.56

NAME cc-i94-2
SOLVENT CDCl3
SF 100.6178001 MHz

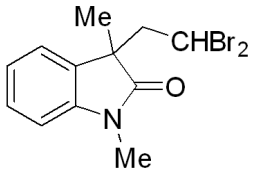


34

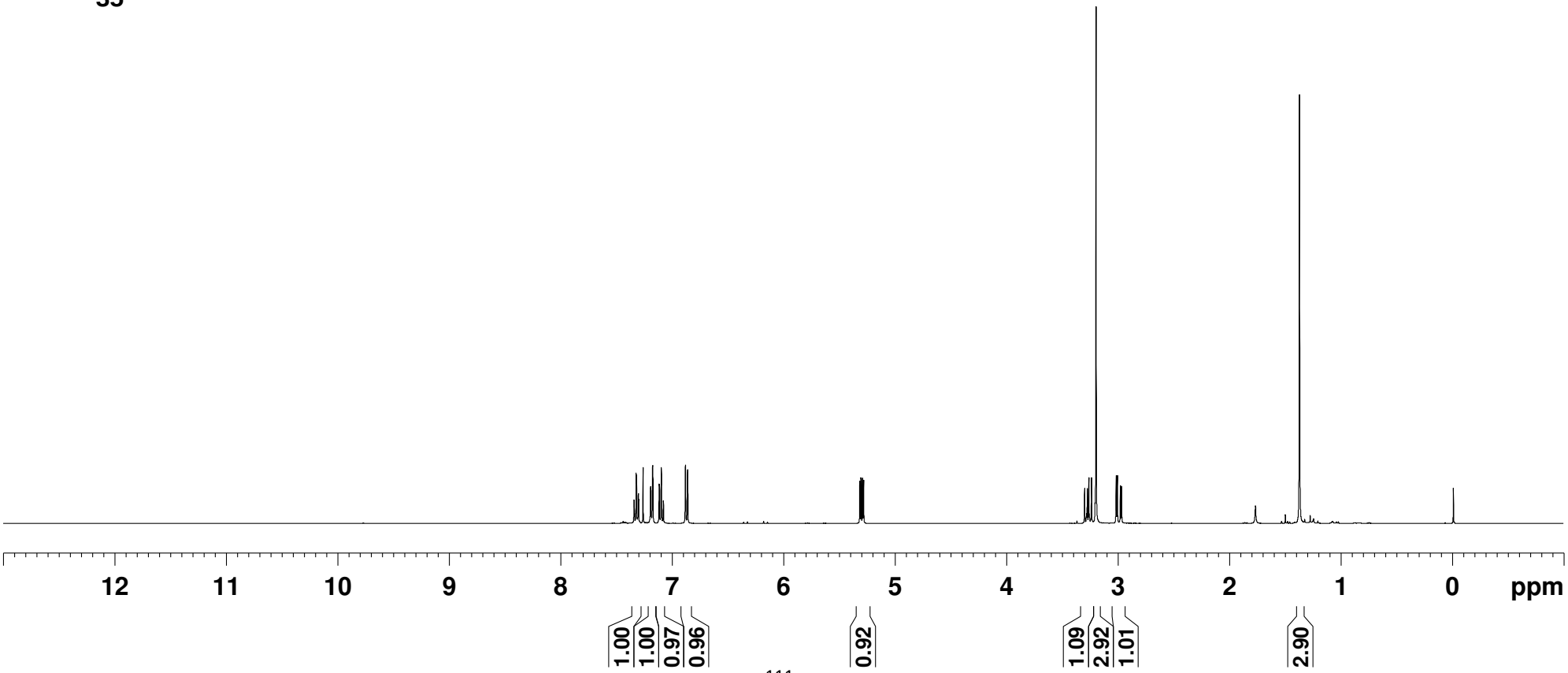




NAME cc-G104-5
SOLVENT CDCl3
SF 400.1500096 MHz

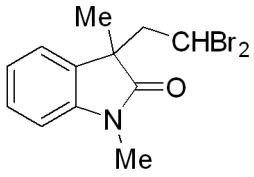


35

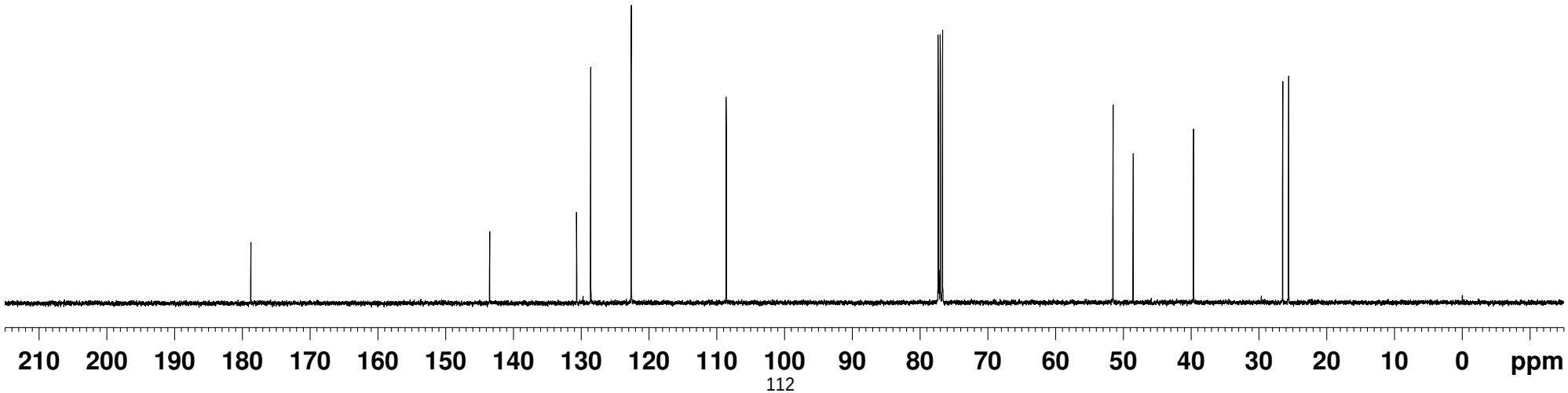


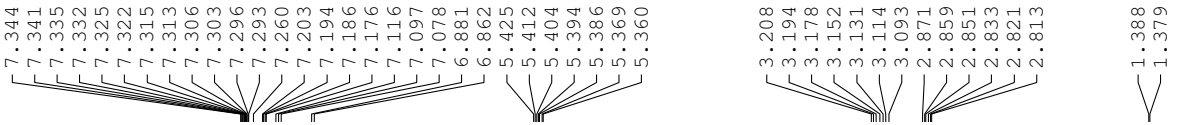
178.77
143.52
130.68
128.60
122.62
108.60
77.32
77.00
76.68
51.52
48.54
39.64
26.48
25.60

NAME cc-I94-1-C
SOLVENT CDCl3
SF 100.6127761 MHz

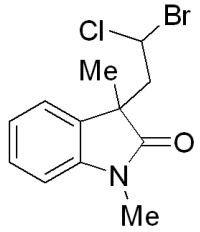


35

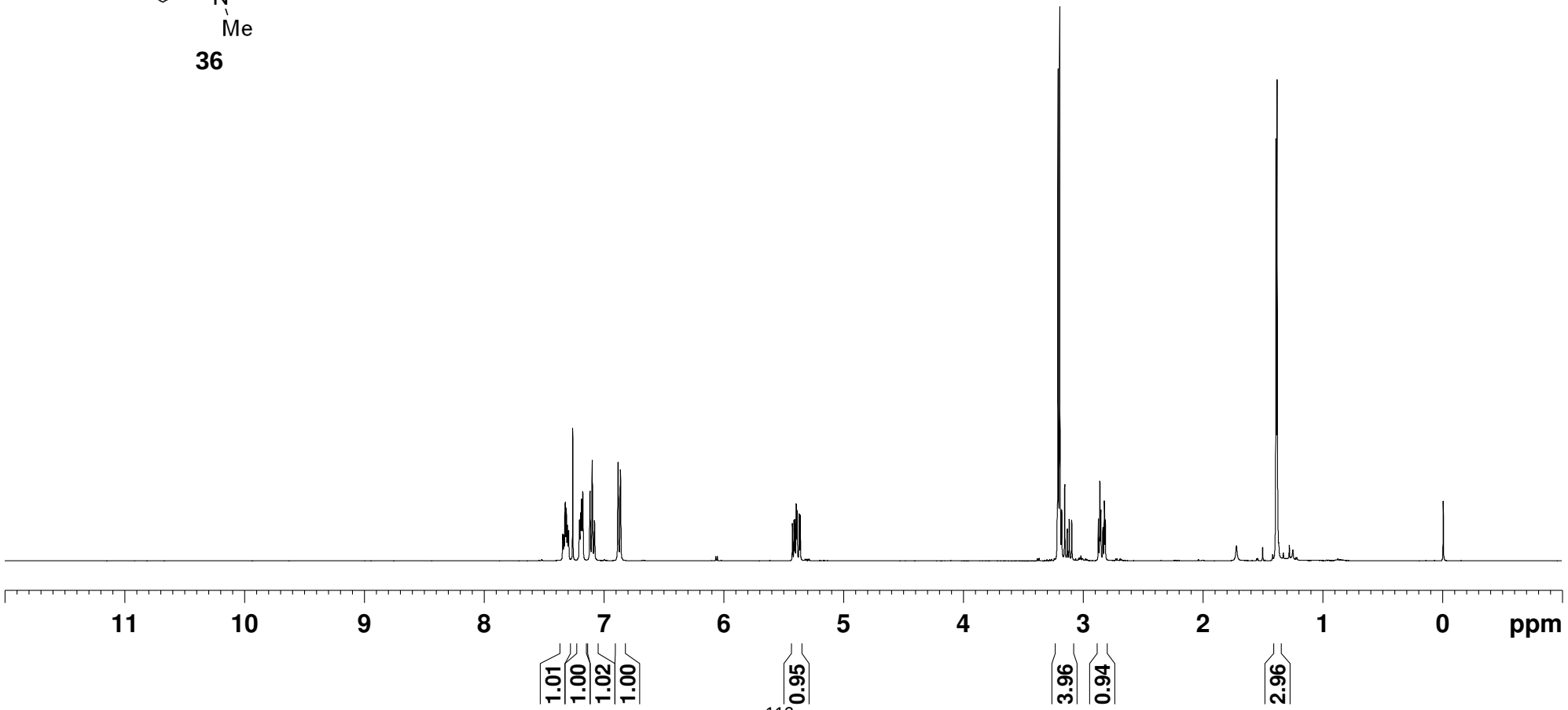




NAME cc-g104-12
SOLVENT CDCl3
SFO1 400.1524711 MHz

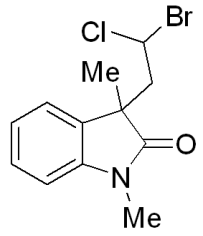


36

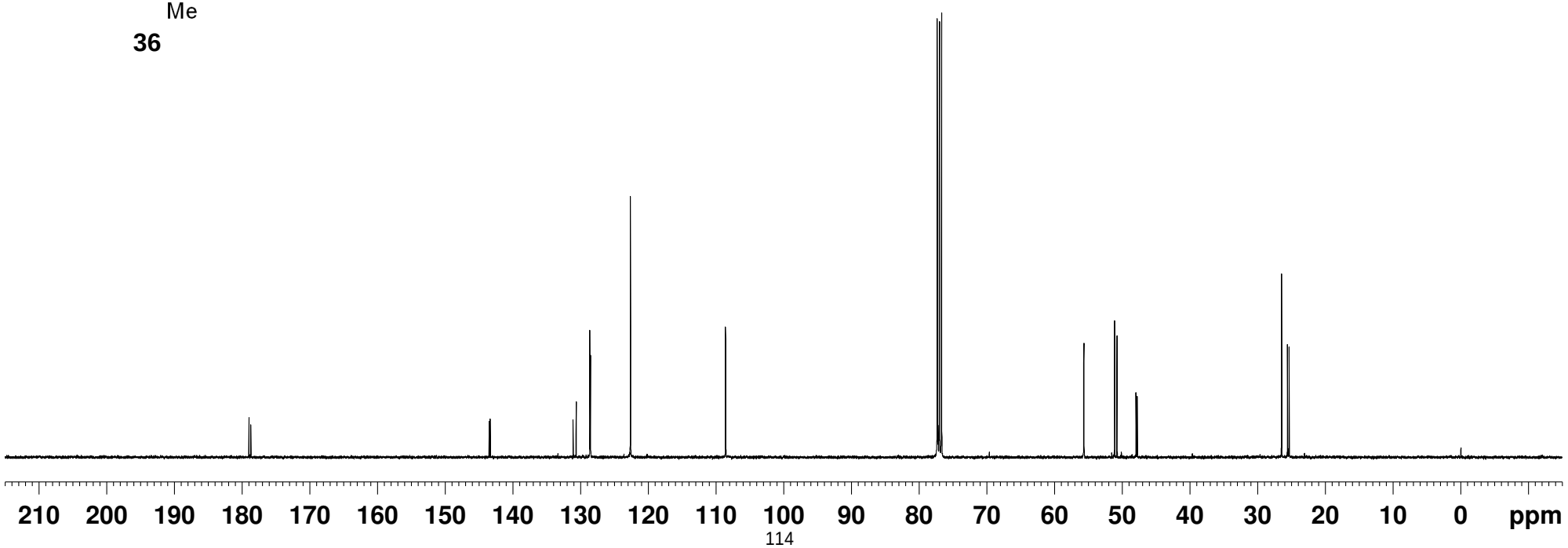


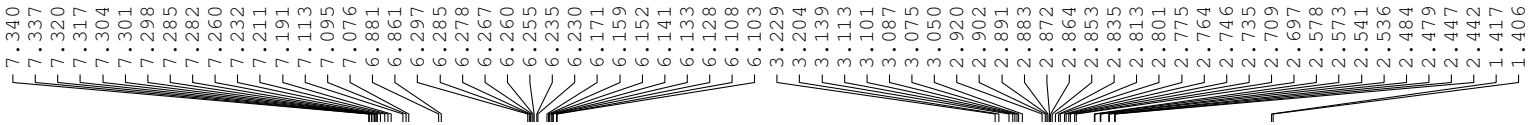
178.99
178.74
143.50
143.36
131.11
130.67
128.64
128.54
122.66
122.64
122.61
108.60
108.56
77.31
77.00
76.68
55.70
55.64
51.13
50.76
47.95
47.78
26.44
25.59
25.33

NAME cc-g104-12
SOLVENT CDCl3
SF 100.6178037 MHz

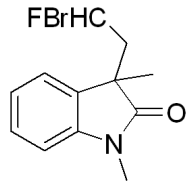


36

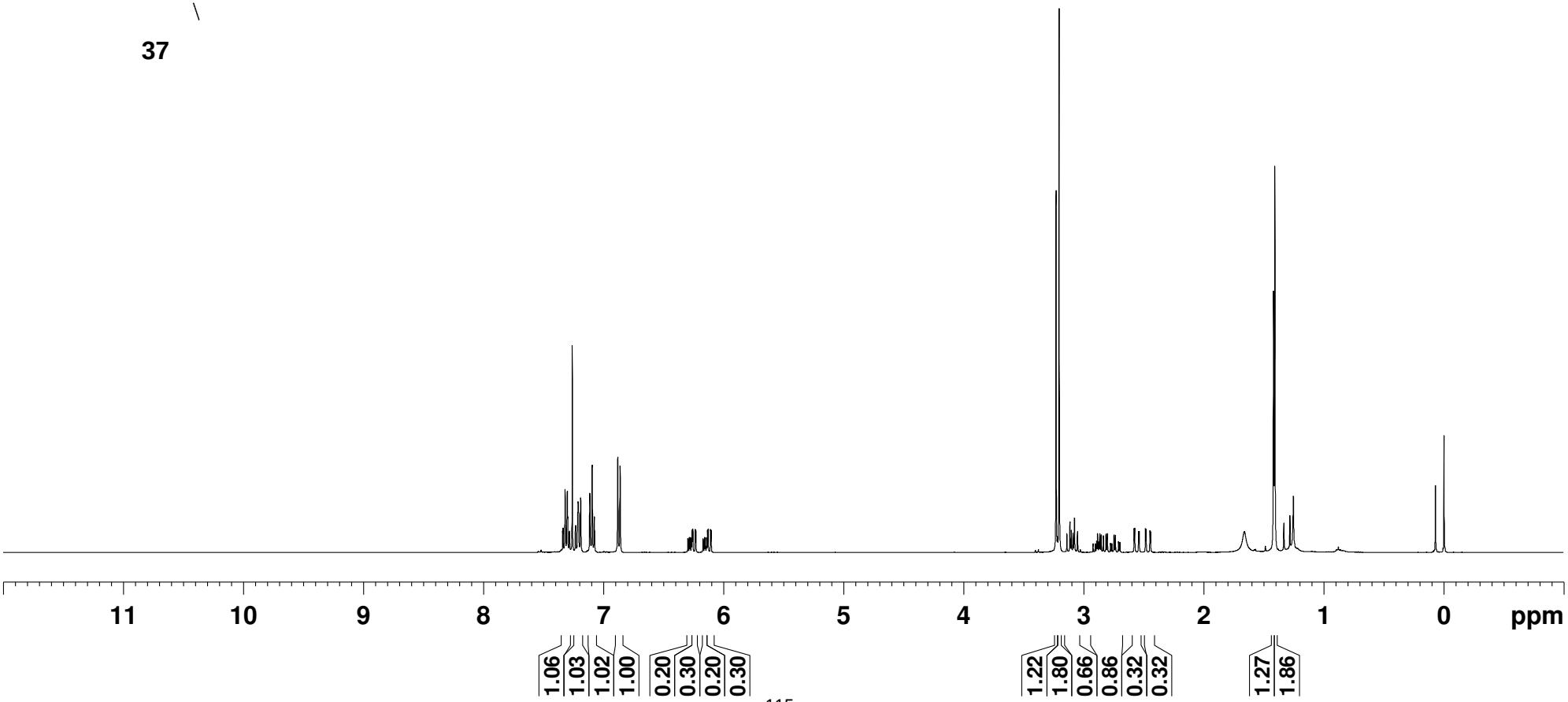




NAME cc-i94-4-H
SOLVENT CDCl3
SF 400.1500090 MHz



37



179.00
178.70

143.26
142.85

131.77
131.25
128.64
128.42
122.89
122.77
122.72
122.70

108.52
108.48

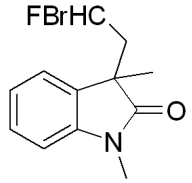
92.75
92.32
90.23
89.80

77.32
77.00
76.68

48.57
48.38
47.69
47.50
47.02
46.91
46.88

26.38
26.33
24.74
24.04

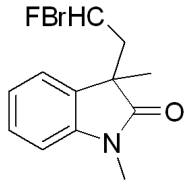
NAME cc-i94-4
SOLVENT CDCl3
SF 100.6178006 MHz



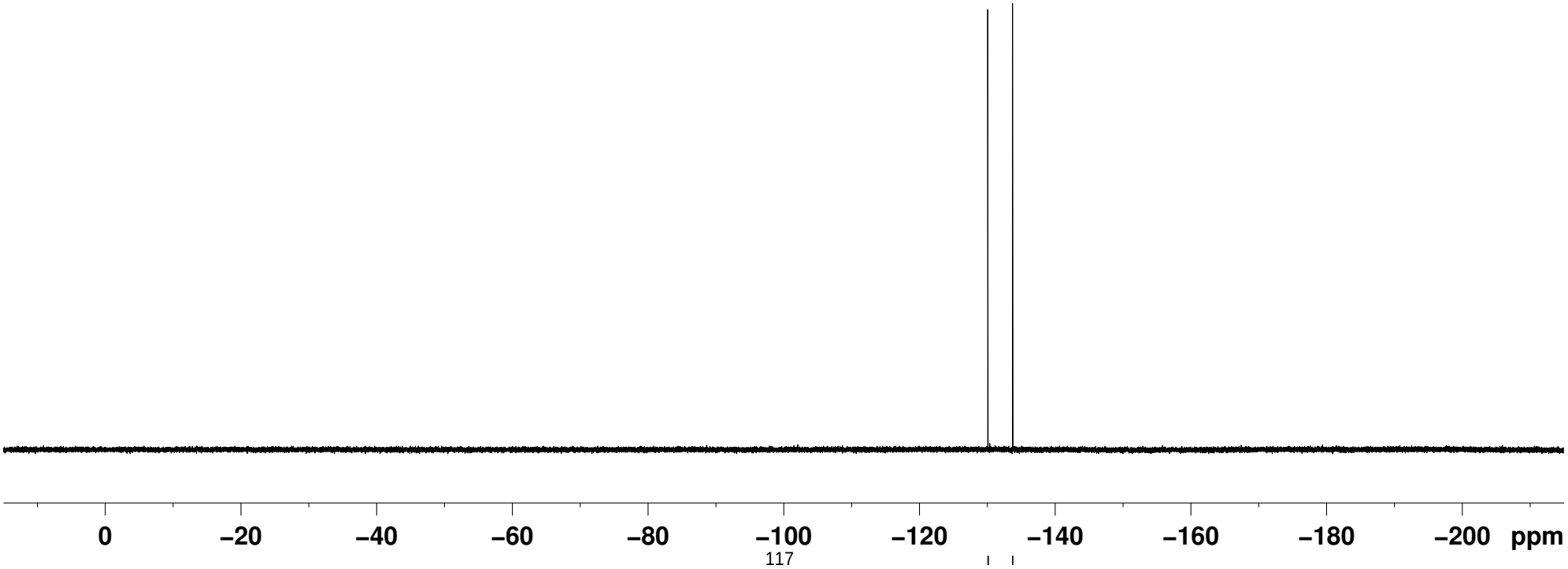
37

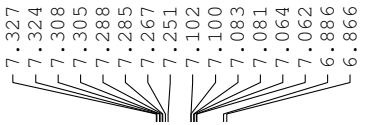
NAME cc-i94-4
SOLVENT CDCl3
SF 376.5171850 MHz

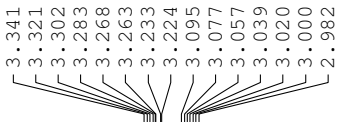
-130.128
-133.763



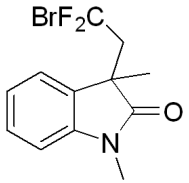
38



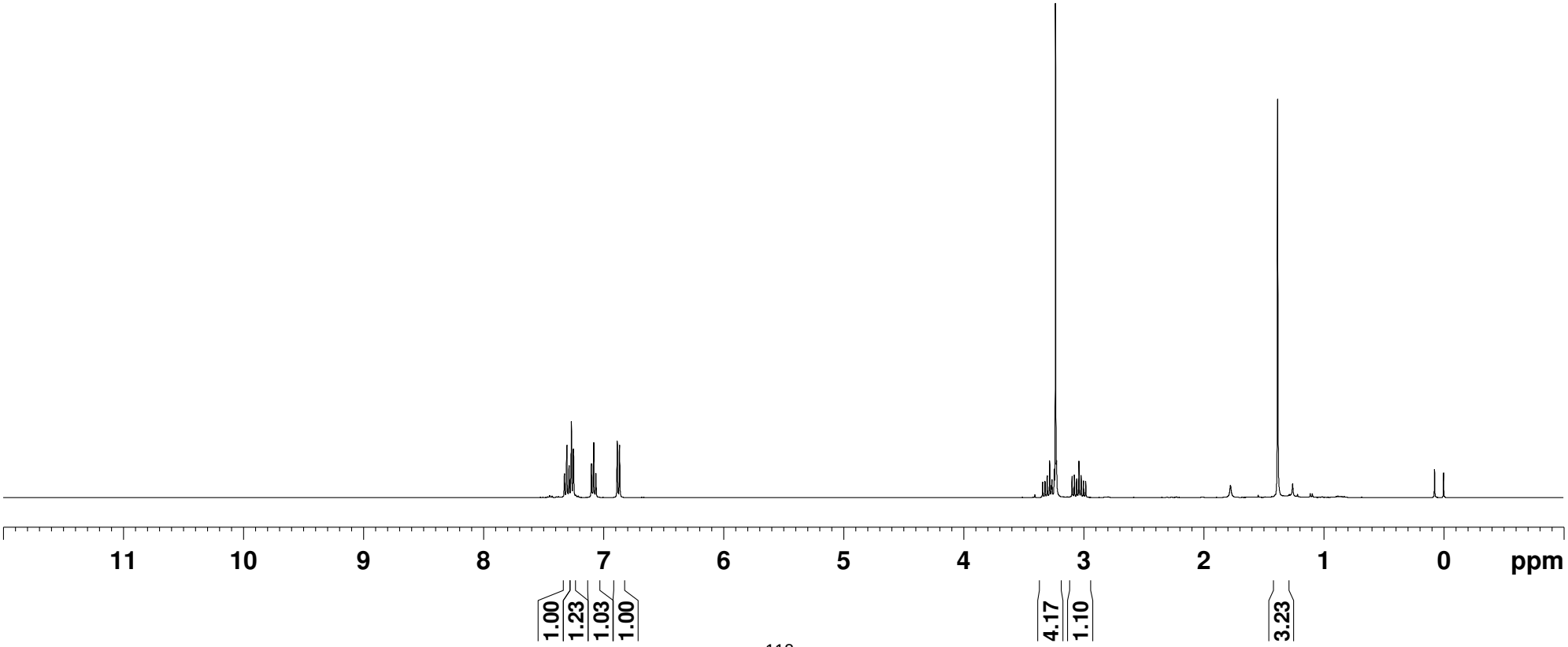




NAME cc-i94-3
SOLVENT CDCl3
SF 400.1500069 MHz

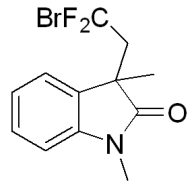


38

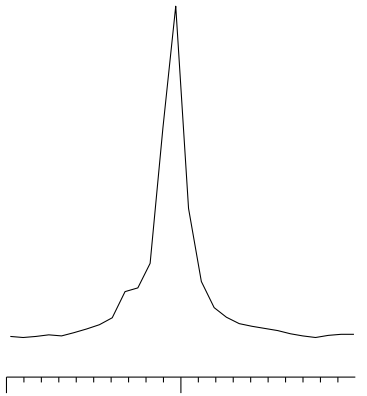


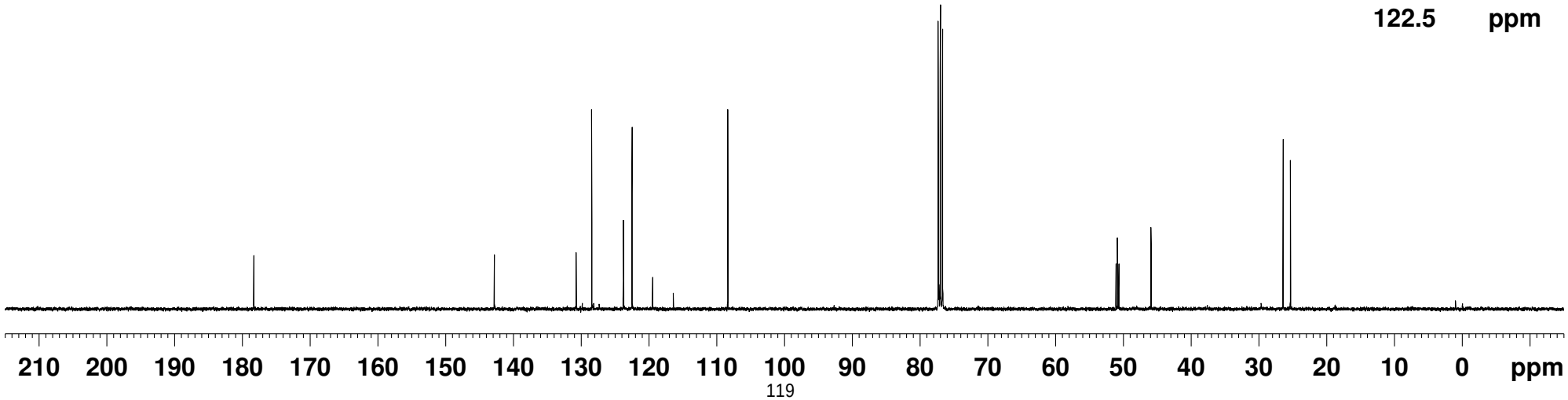
178.32
142.82
130.77
128.44
123.79
123.77
123.76
122.50
119.47
116.41
108.38
77.32
77.00
76.68
122.53
51.07
50.87
50.66
45.90
26.42
25.33
122.50
122.53

NAME cc-i94-3
SOLVENT CDCl3
SF 100.6178030 MHz



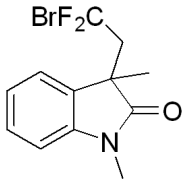
39



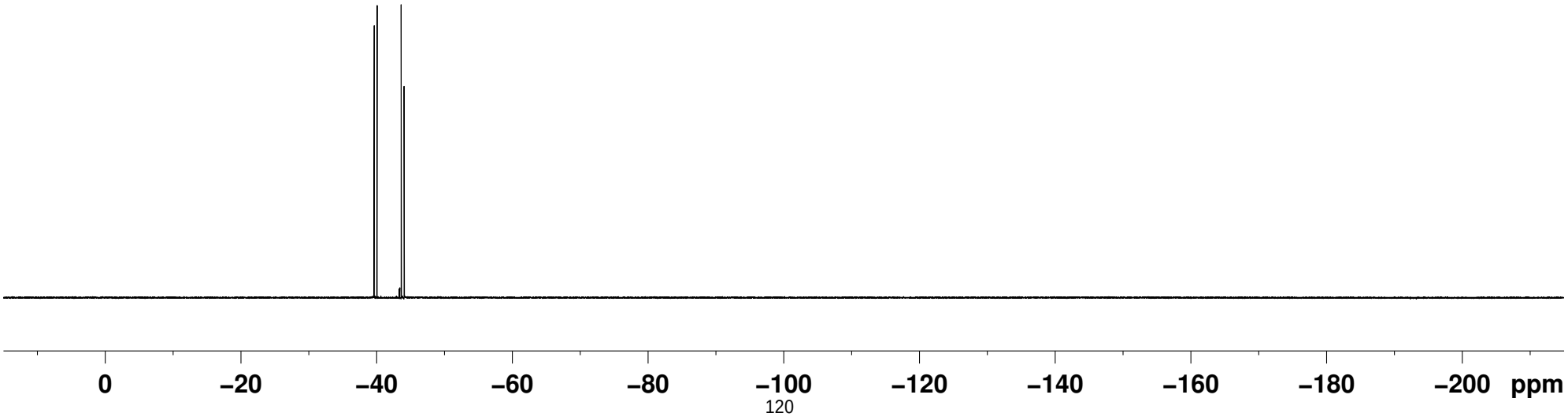


-39.669
-40.080
-43.649
-44.060

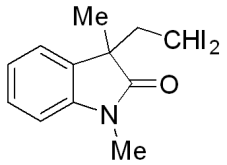
NAME cc-i94-3-0930
SOLVENT CDCl3
SF 376.5171850 MHz



38



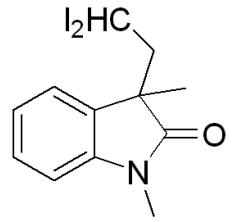
NAME cc-i94-6
SOLVENT CDCl3
SF 400.1500095 MHz



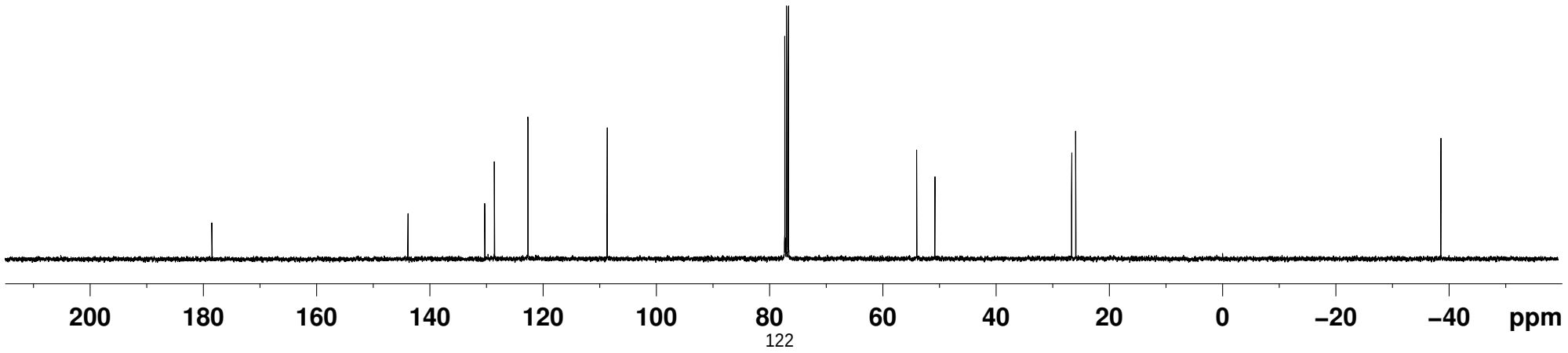
39

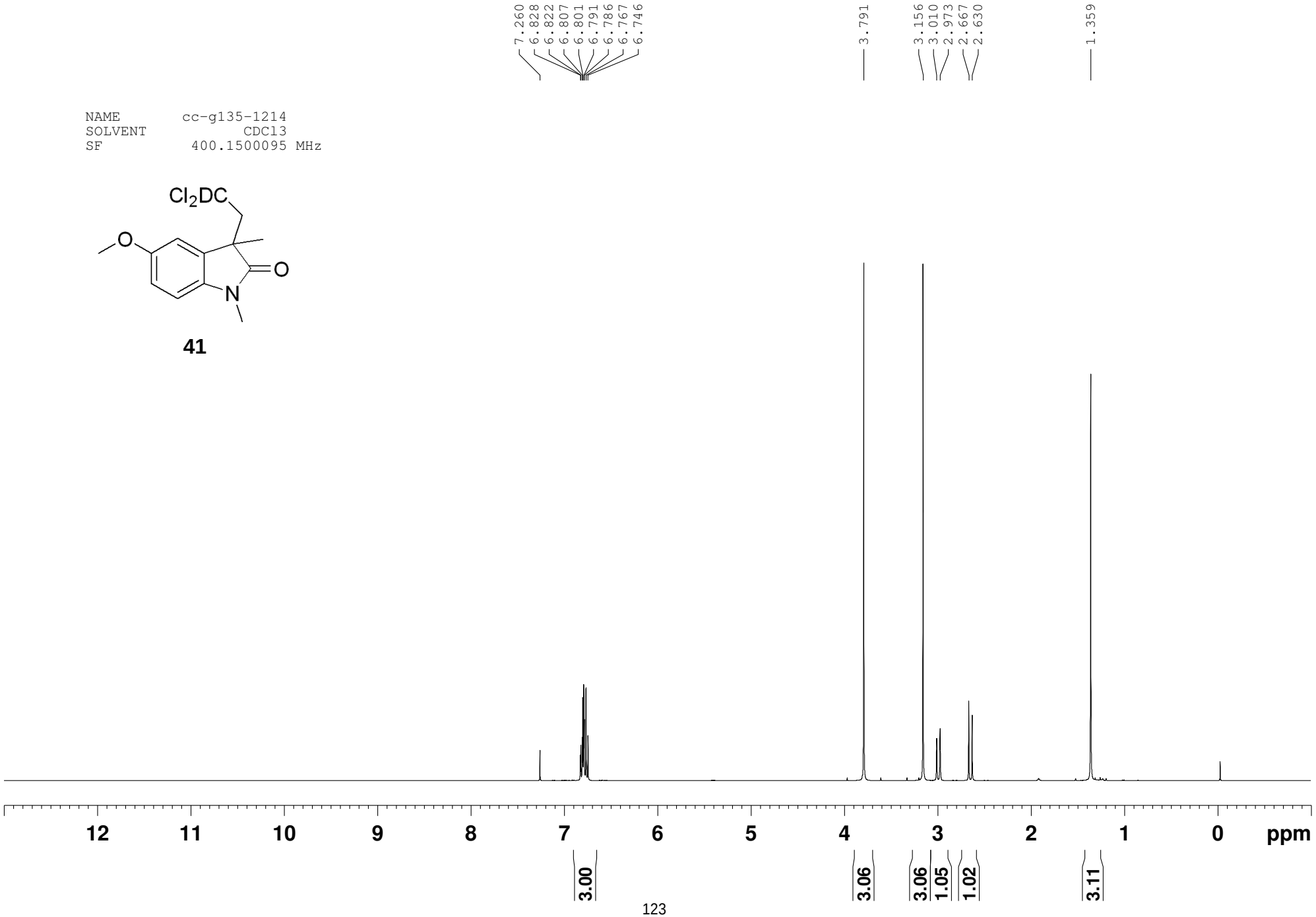
178.49
143.87
130.31
128.61
122.69
122.66
108.67
77.32
77.00
76.68
54.00
50.77
26.64
25.92
-38.60

NAME cc-i94-6-0930
SOLVENT CDCl3
SF 100.6178033 MHz



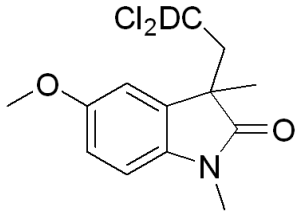
39



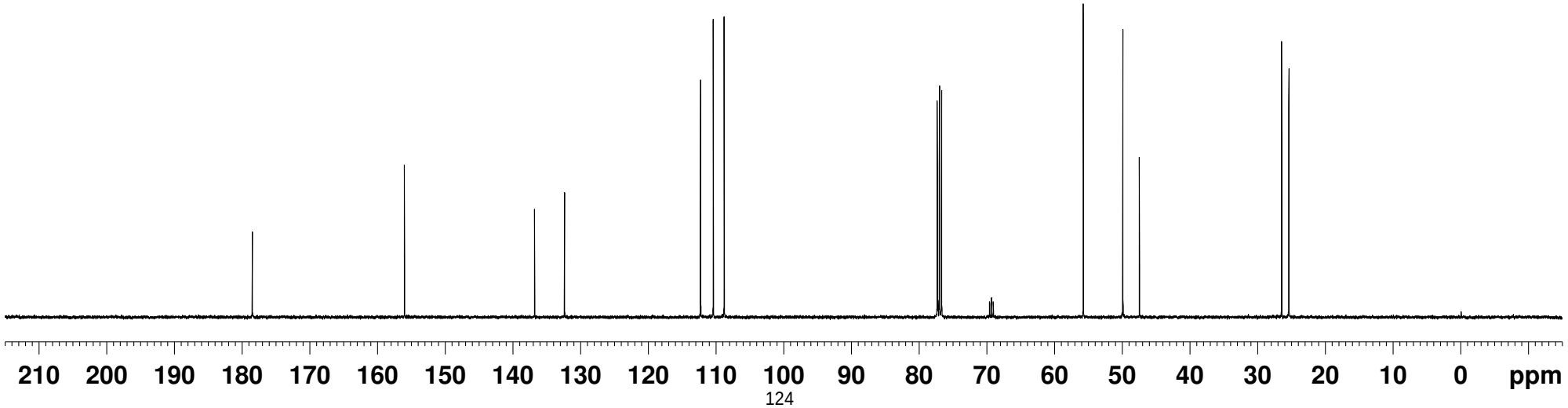

7.260
6.828
6.822
6.807
6.801
6.791
6.786
6.767
6.746
3.791
3.156
3.010
2.973
2.667
2.630
1.359
NAME cc-g135-1214
SOLVENT CDCl3
SF 400.1500095 MHz
Cl2DC
O
O
N
41
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.00
3.06
3.06
1.05
1.02
3.11

178.50
156.03
136.80
132.38
112.28
110.41
108.80
77.32
77.00
76.68
69.59
69.32
69.05
55.74
49.89
47.45
26.43
25.38

NAME cc-g135-1214
SOLVENT CDCl3
SF 100.6178074 MHz



41



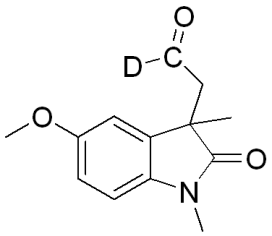
7.260
6.810
6.805
6.800
6.793
6.787
6.784
6.761

3.781

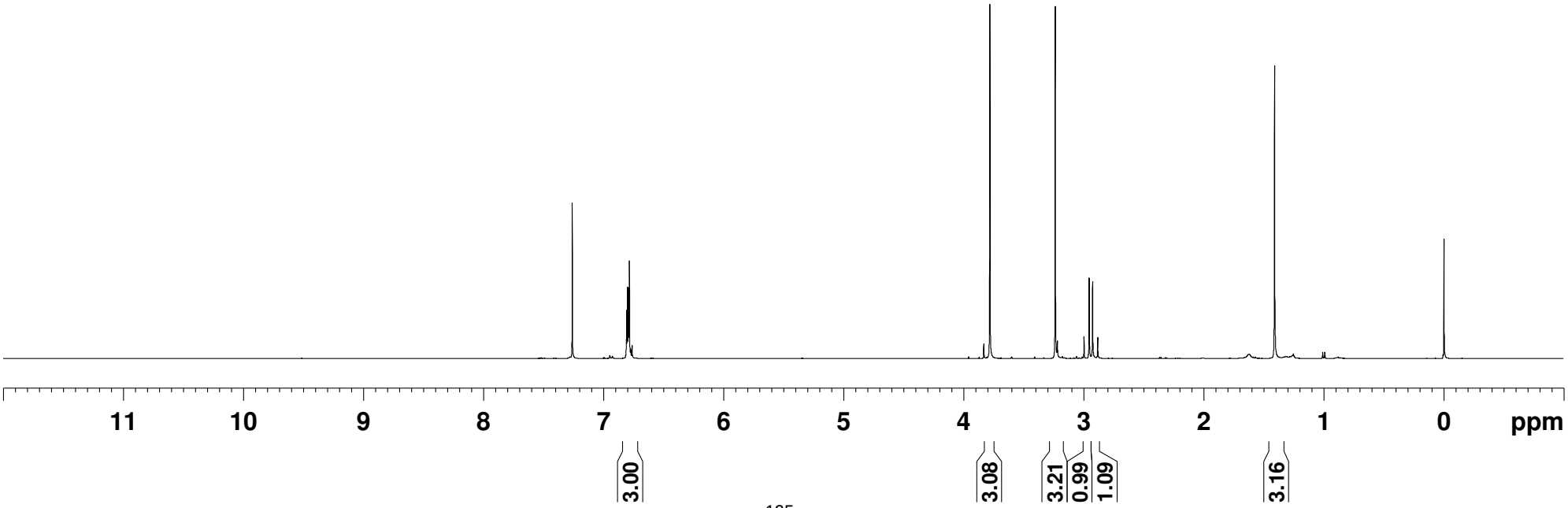
3.236
2.996
2.953
2.924
2.881

1.408

NAME cc-G156
SOLVENT CDCl3
SF 400.1500099 MHz

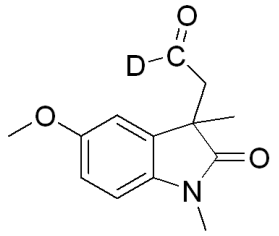


42

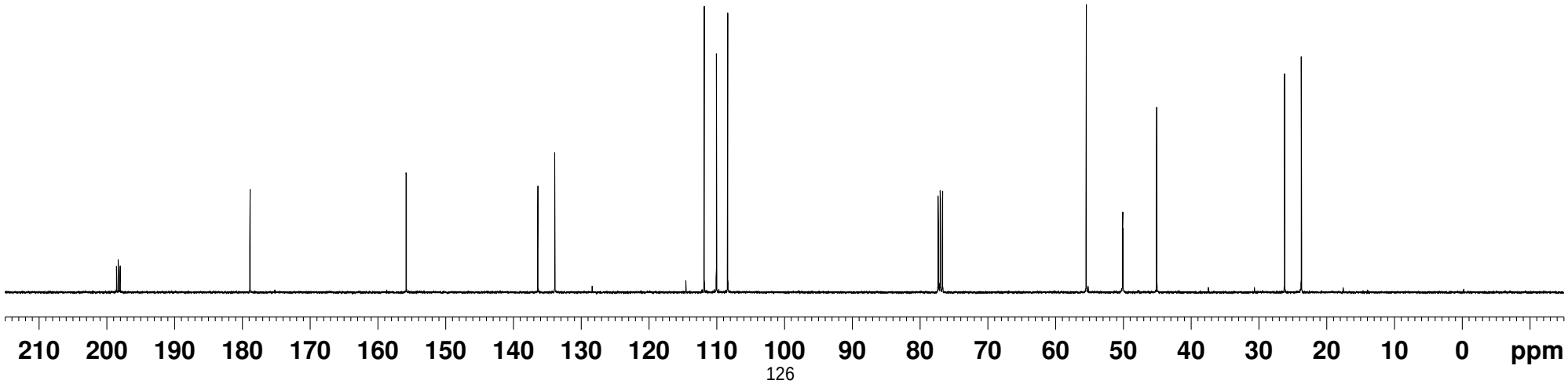


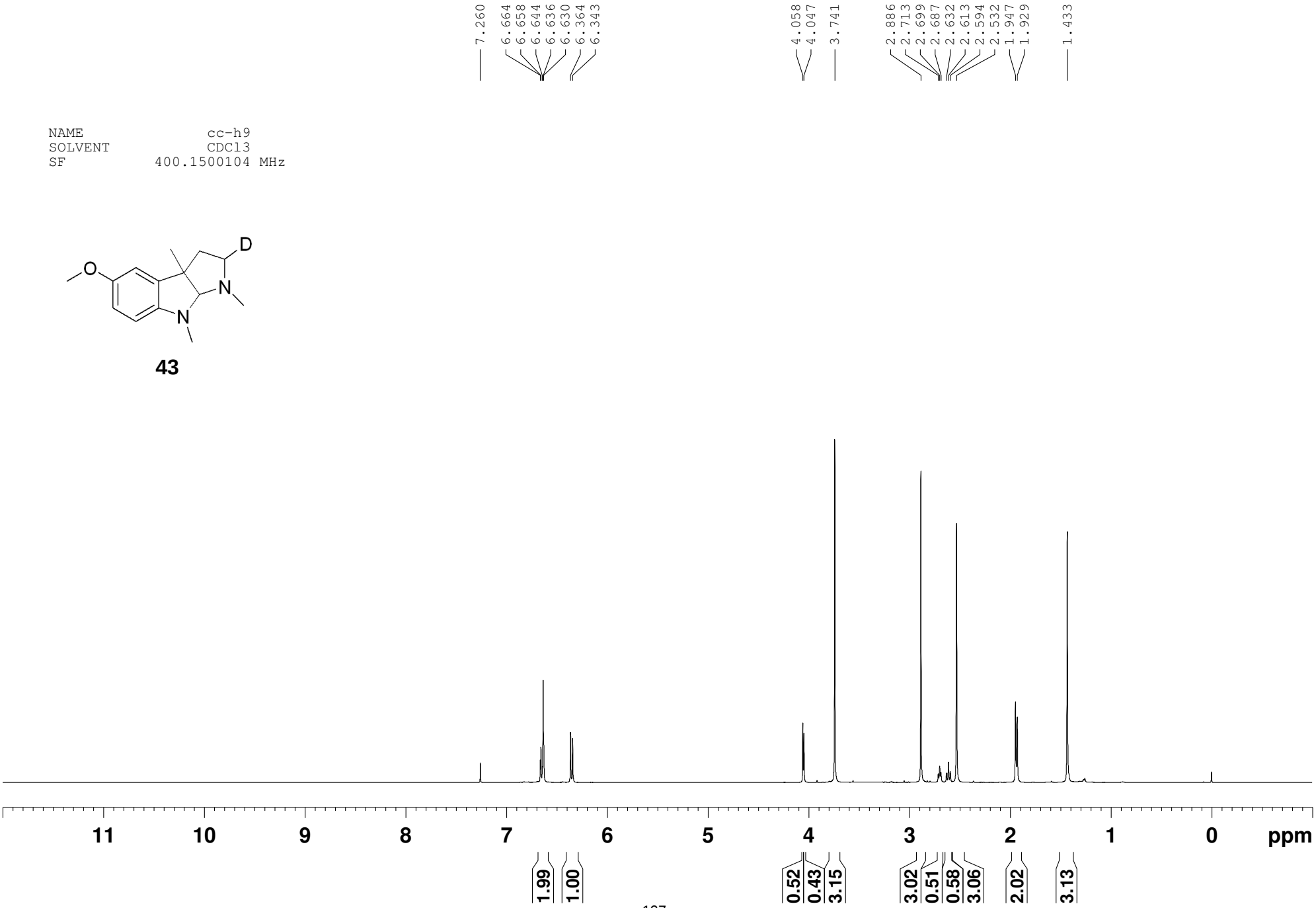
198.52
198.26
197.99
178.89
155.83
136.41
133.91
111.85
110.05
108.39
77.32
77.00
76.68
55.47
50.11
50.07
50.04
45.07
26.19
23.72

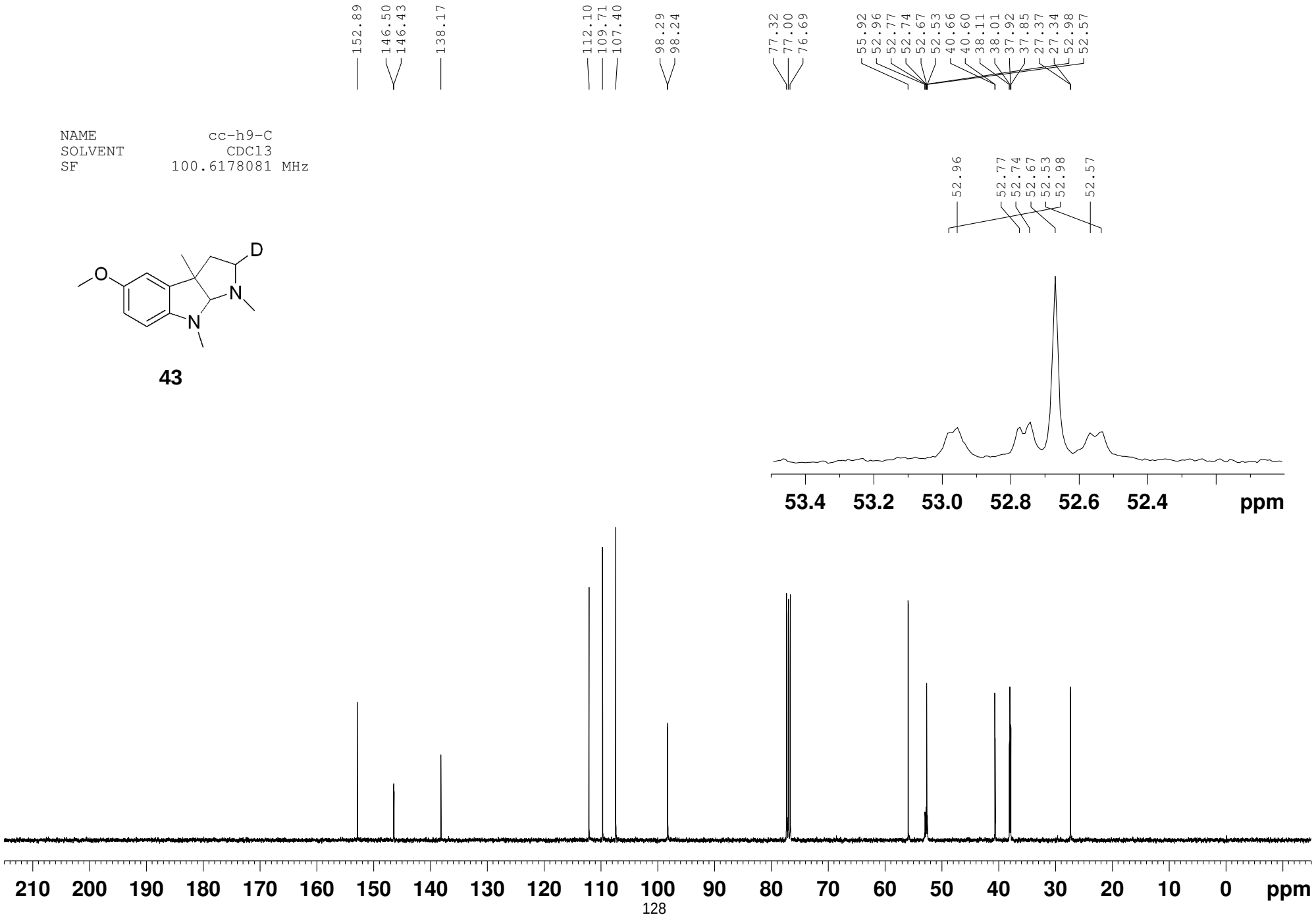
NAME CC-G156-0107
SOLVENT CDCl3
SF 100.6178213 MHz

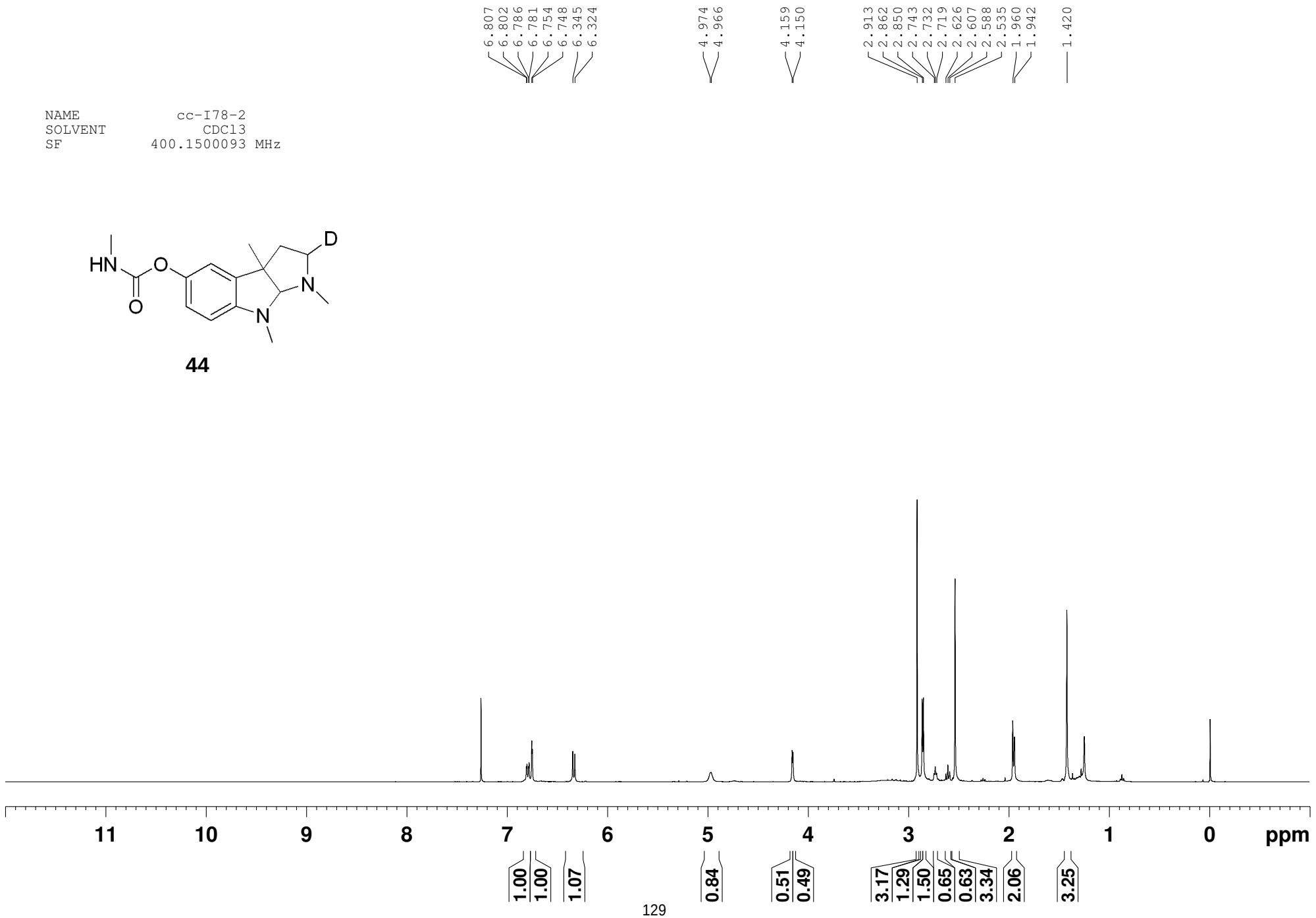


42

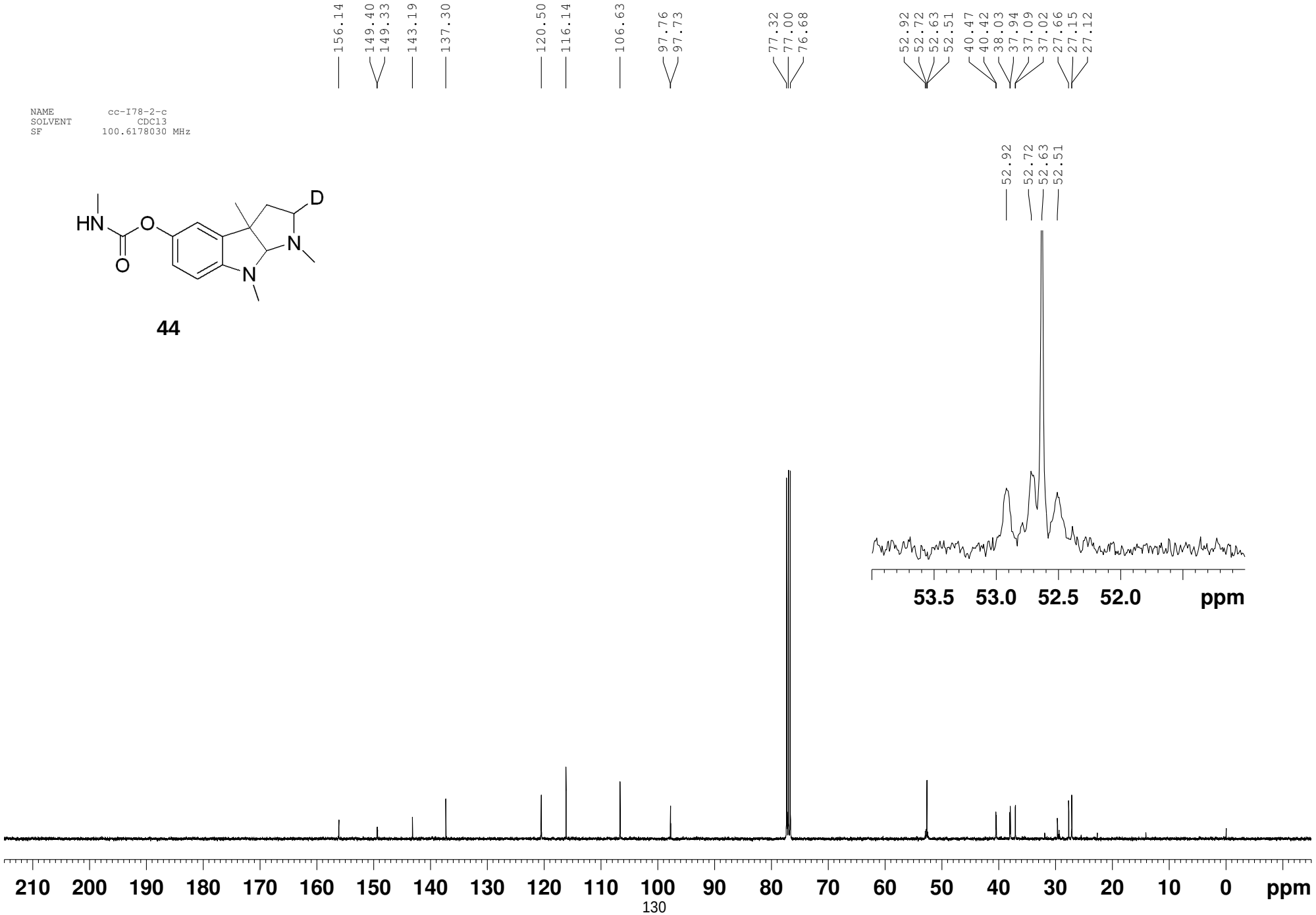


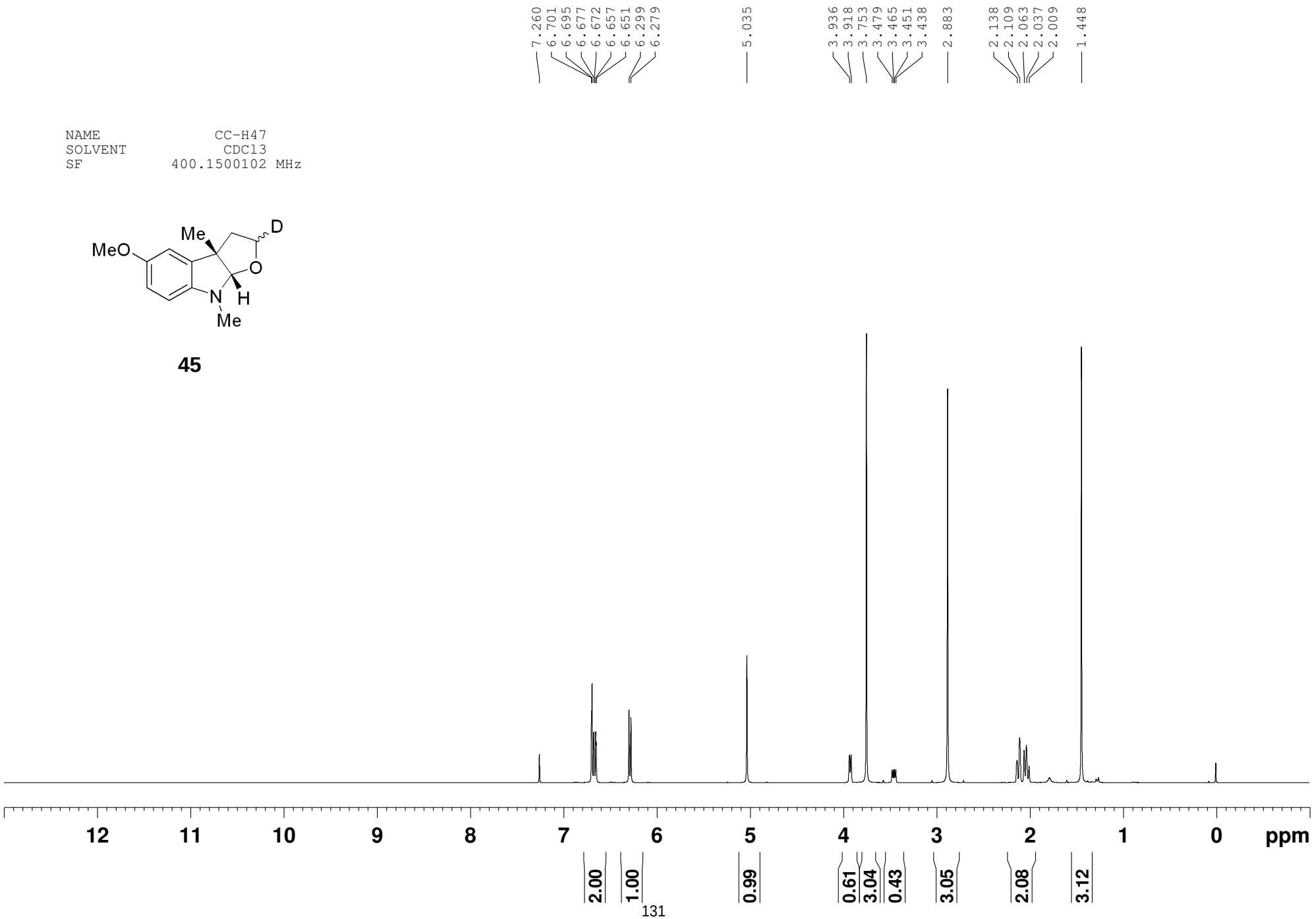

7.260
6.664
6.658
6.644
6.636
6.630
6.364
6.343
4.058
4.047
3.741
2.886
2.713
2.699
2.687
2.632
2.613
2.594
2.532
1.947
1.929
1.433
NAME cc-h9
SOLVENT CDCl3
SF 400.1500104 MHz
O
D
N
N
43
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.00
0.52
0.43
3.15
3.02
0.51
0.58
3.06
2.02
3.13


152.89
146.50
146.43
138.17
112.10
109.71
107.40
98.29
98.24
77.32
77.00
76.69
55.92
52.96
52.77
52.74
52.67
52.53
40.66
40.60
38.11
38.01
37.92
37.85
27.37
27.34
52.98
52.57
NAME cc-h9-C
SOLVENT CDCl3
SF 100.6178081 MHz
O
N
N
D
43
52.96
52.77
52.74
52.67
52.53
52.98
52.57
53.4
53.2
53.0
52.8
52.6
52.4
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


6.807
6.802
6.786
6.781
6.754
6.748
6.345
6.324
4.974
4.966
4.159
4.150
2.913
2.862
2.850
2.743
2.732
2.719
2.626
2.607
2.588
2.535
1.960
1.942
1.420
NAME cc-I78-2
SOLVENT CDCl3
SF 400.1500093 MHz
HN
O
O
N
N
D
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.07
0.84
0.51
0.49
3.17
1.29
1.50
0.65
0.63
3.34
2.06
3.25

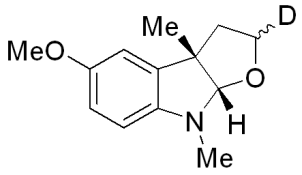
44


156.14
149.40
149.33
143.19
137.30
120.50
116.14
106.63
97.76
97.73
77.32
77.00
76.68
52.92
52.72
52.63
52.51
40.47
40.42
38.03
37.94
37.09
37.02
27.66
27.15
27.12
NAME cc-I78-2-c
SOLVENT CDCl3
SF 100.6178030 MHz
HN
O
O
O
N
N
D
44
53.5 53.0 52.5 52.0 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

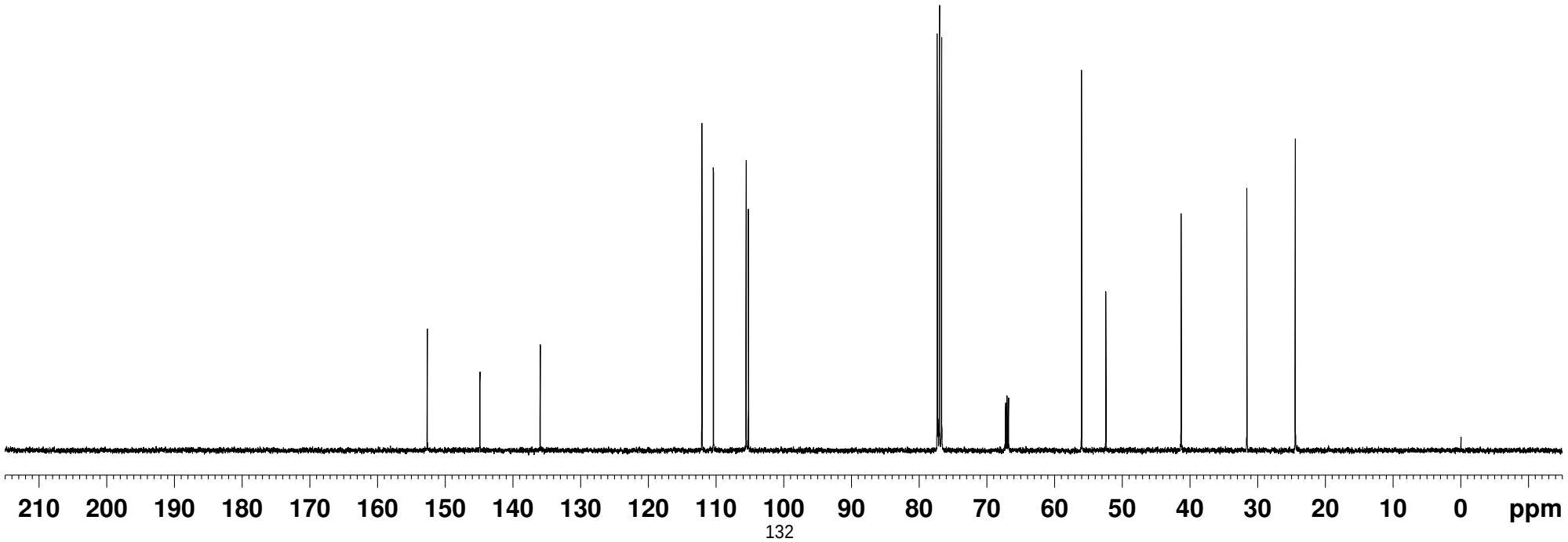

7.260
6.701
6.695
6.677
6.672
6.657
6.651
6.299
6.279
5.035
3.936
3.918
3.753
3.479
3.465
3.451
3.438
2.883
2.138
2.109
2.063
2.037
2.009
1.448
NAME CC-H47
SOLVENT CDCl3
SF 400.1500102 MHz
Me
D
MeO
O
N
H
Me
45
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
0.99
0.61
3.04
0.43
3.05
2.08
3.12

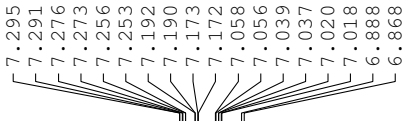
152.66
144.89
135.97
112.09
110.39
105.56
105.23
77.32
77.00
76.68
67.22
67.00
66.78
56.00
52.41
41.29
31.58
24.43

NAME CC-H47
SOLVENT CDCl3
SF 100.6178052 MHz

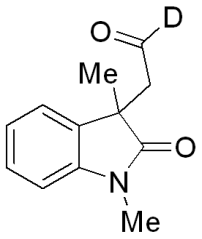


45

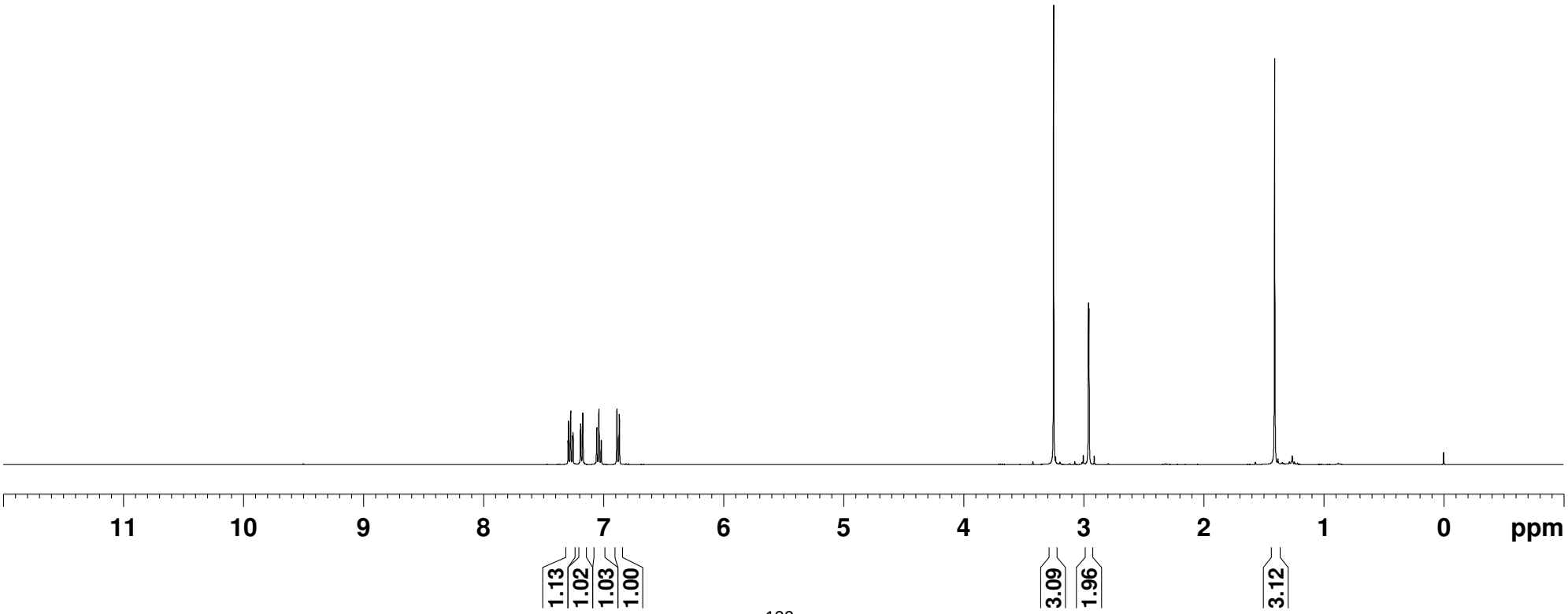




NAME CC-I119
SOLVENT CDCl3
SF 400.1499969 MHz

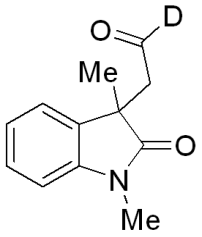


46

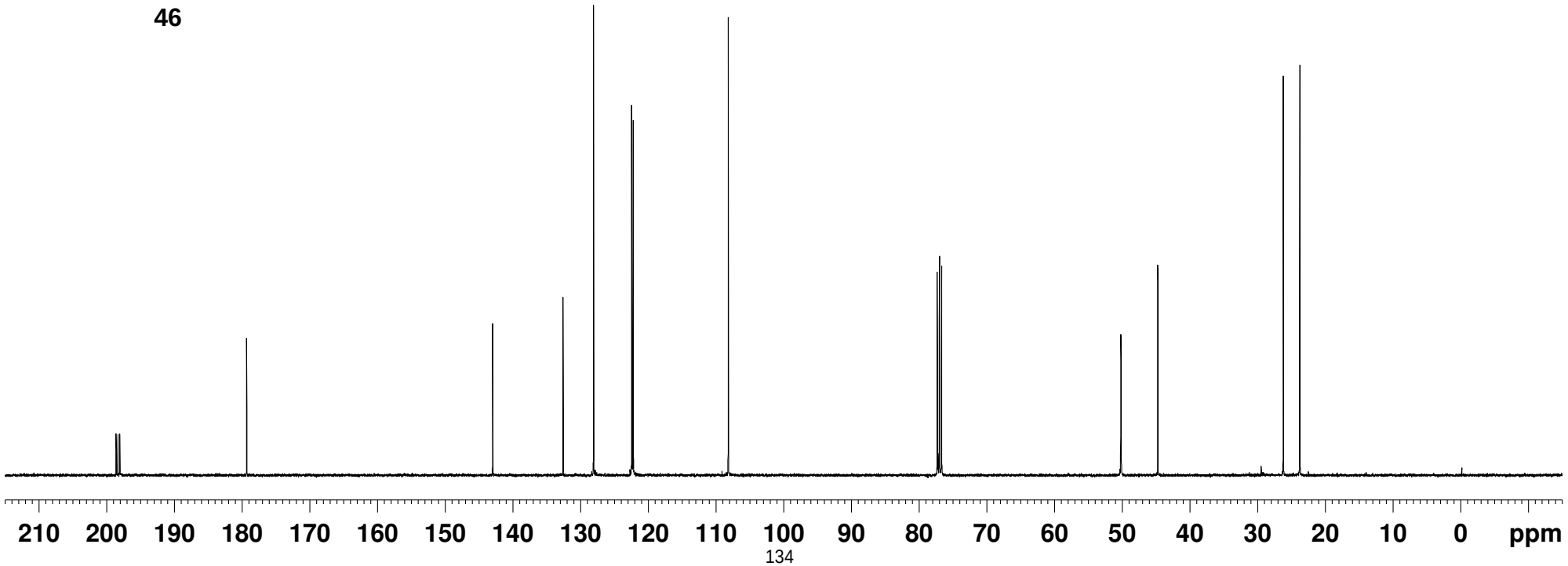


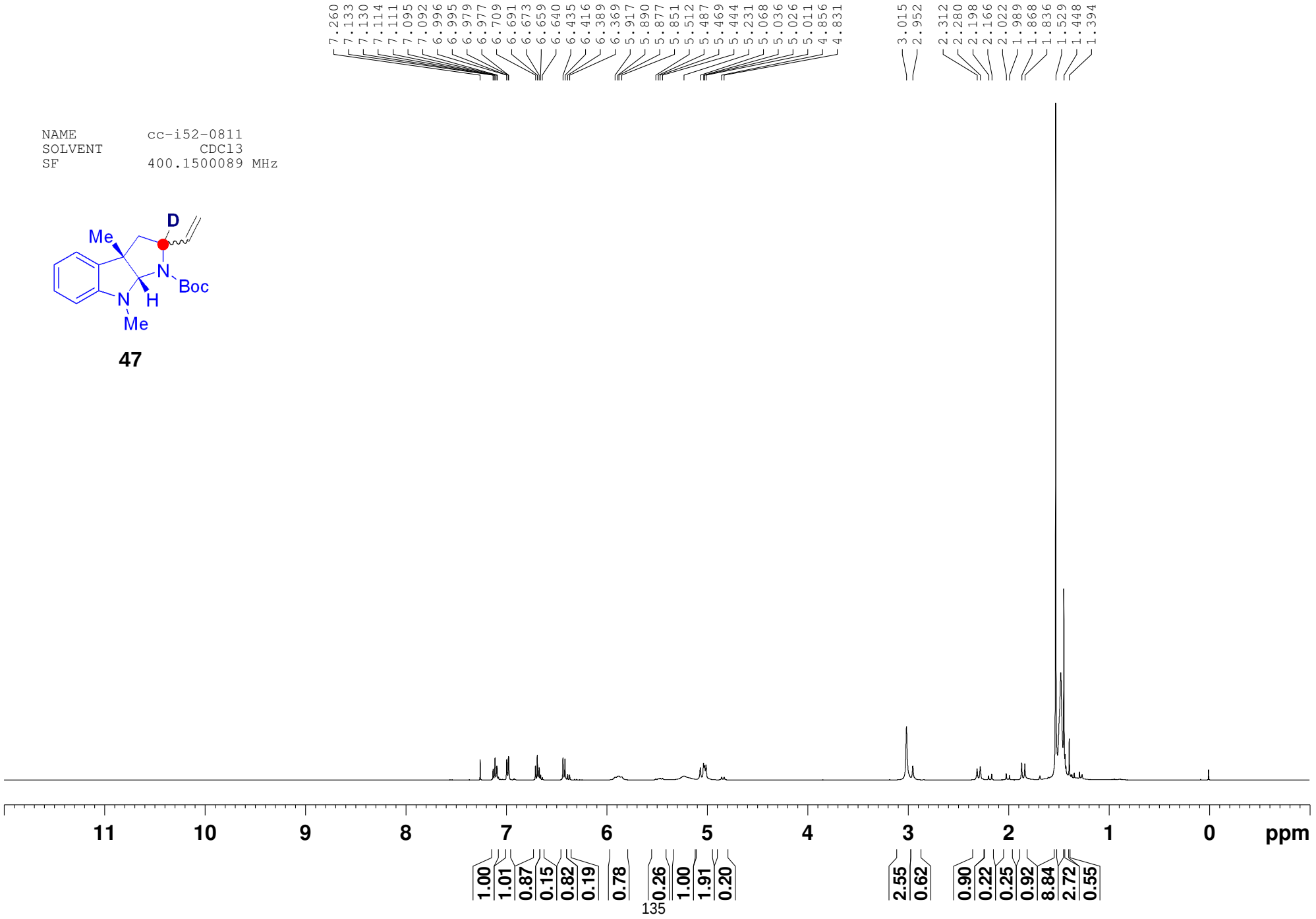
198.56
198.30
198.03
179.34
143.00
132.59
128.09
122.46
122.24
108.19
77.32
77.00
76.68
50.21
50.18
50.14
44.73
26.20
23.76

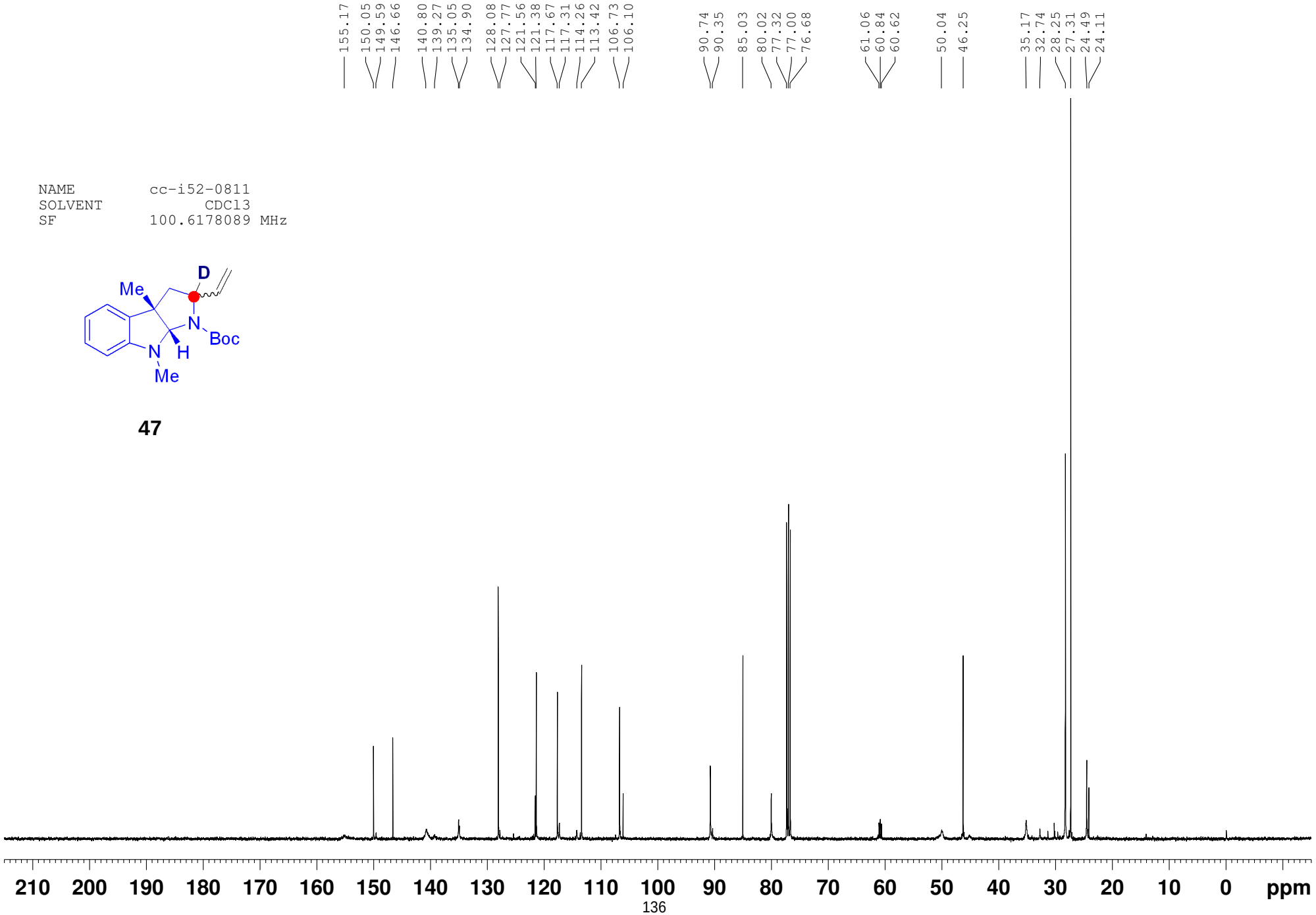
NAME CC-I119
SOLVENT CDCl3
SF 100.6178169 MHz



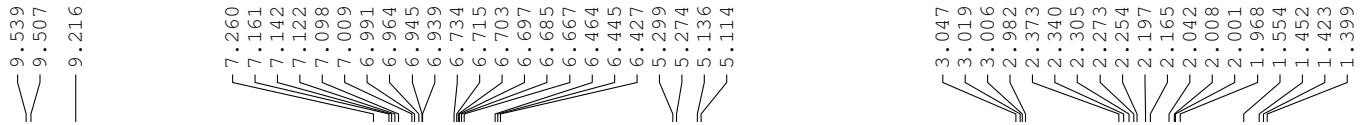
46



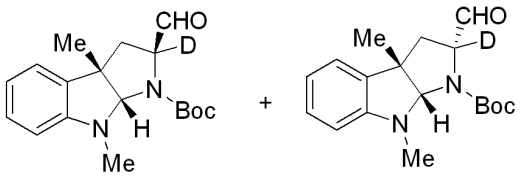

7.260
7.133
7.130
7.114
7.111
7.095
7.092
6.996
6.995
6.979
6.977
6.709
6.691
6.673
6.659
6.640
6.435
6.416
6.389
6.369
5.917
5.890
5.877
5.851
5.512
5.487
5.469
5.444
5.231
5.068
5.036
5.026
5.011
4.856
4.831
3.015
2.952
2.312
2.280
2.198
2.166
2.022
1.989
1.868
1.836
1.529
1.448
1.394
NAME cc-i52-0811
SOLVENT CDCl3
SF 400.1500089 MHz
Me
D
N
Boc
N
H
Me
47
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
0.87
0.15
0.82
0.19
0.78
0.26
1.00
1.91
0.20
2.55
0.62
0.90
0.22
0.25
0.92
8.84
2.72
0.55


155.17
150.05
149.59
146.66
140.80
139.27
135.05
134.90
128.08
127.77
121.56
121.38
117.67
117.31
114.26
113.42
106.73
106.10
90.74
90.35
85.03
80.02
77.32
77.00
76.68
61.06
60.84
60.62
50.04
46.25
35.17
32.74
28.25
27.31
24.49
24.11
NAME cc-i52-0811
SOLVENT CDCl3
SF 100.6178089 MHz
D
Me
N
Boc
N
H
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

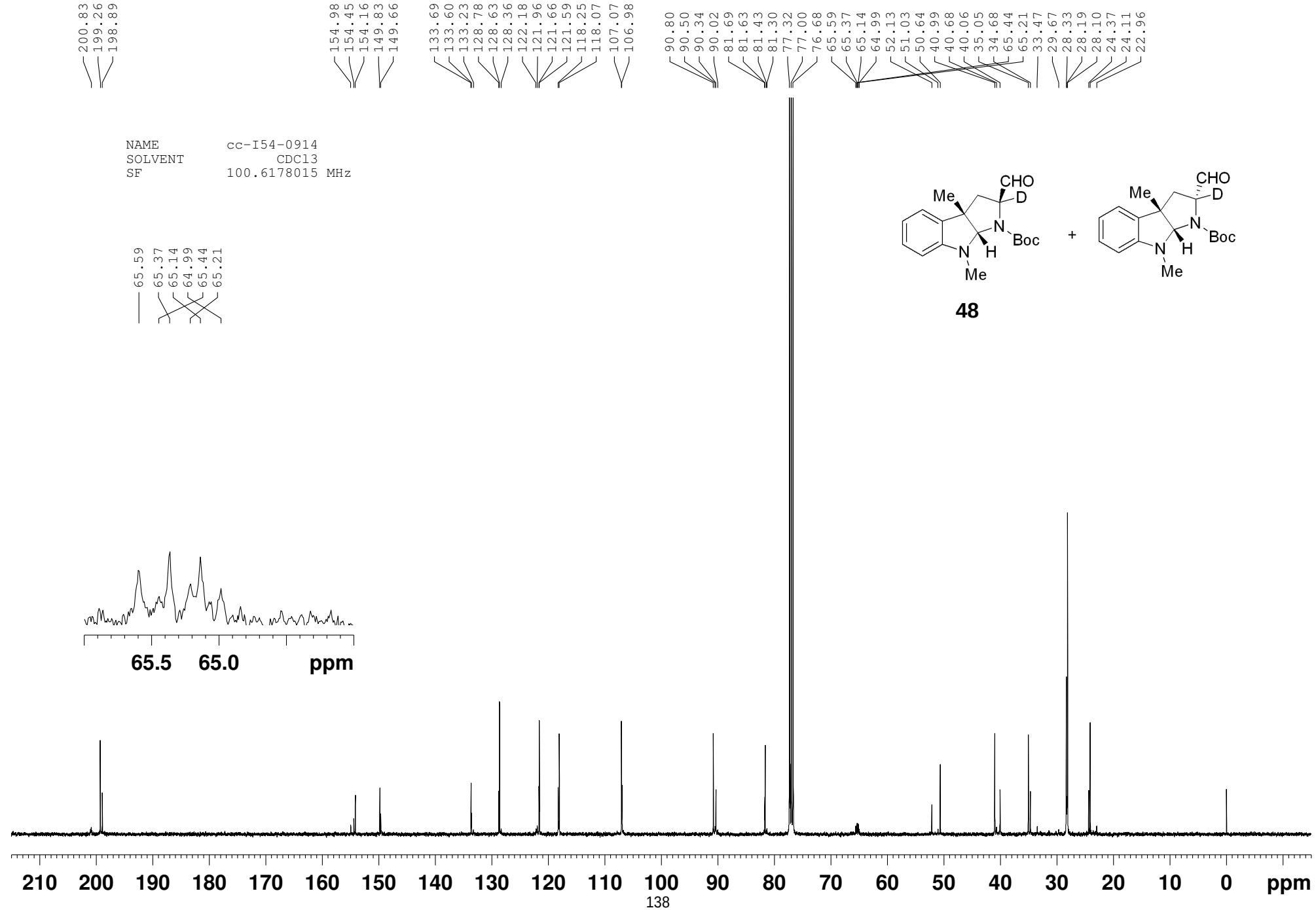
47

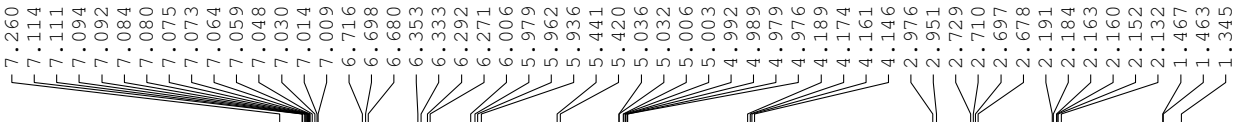


NAME cc-i54
SOLVENT CDCl3
SF 400.1500092 MHz

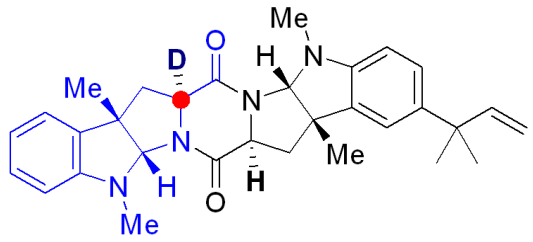


48

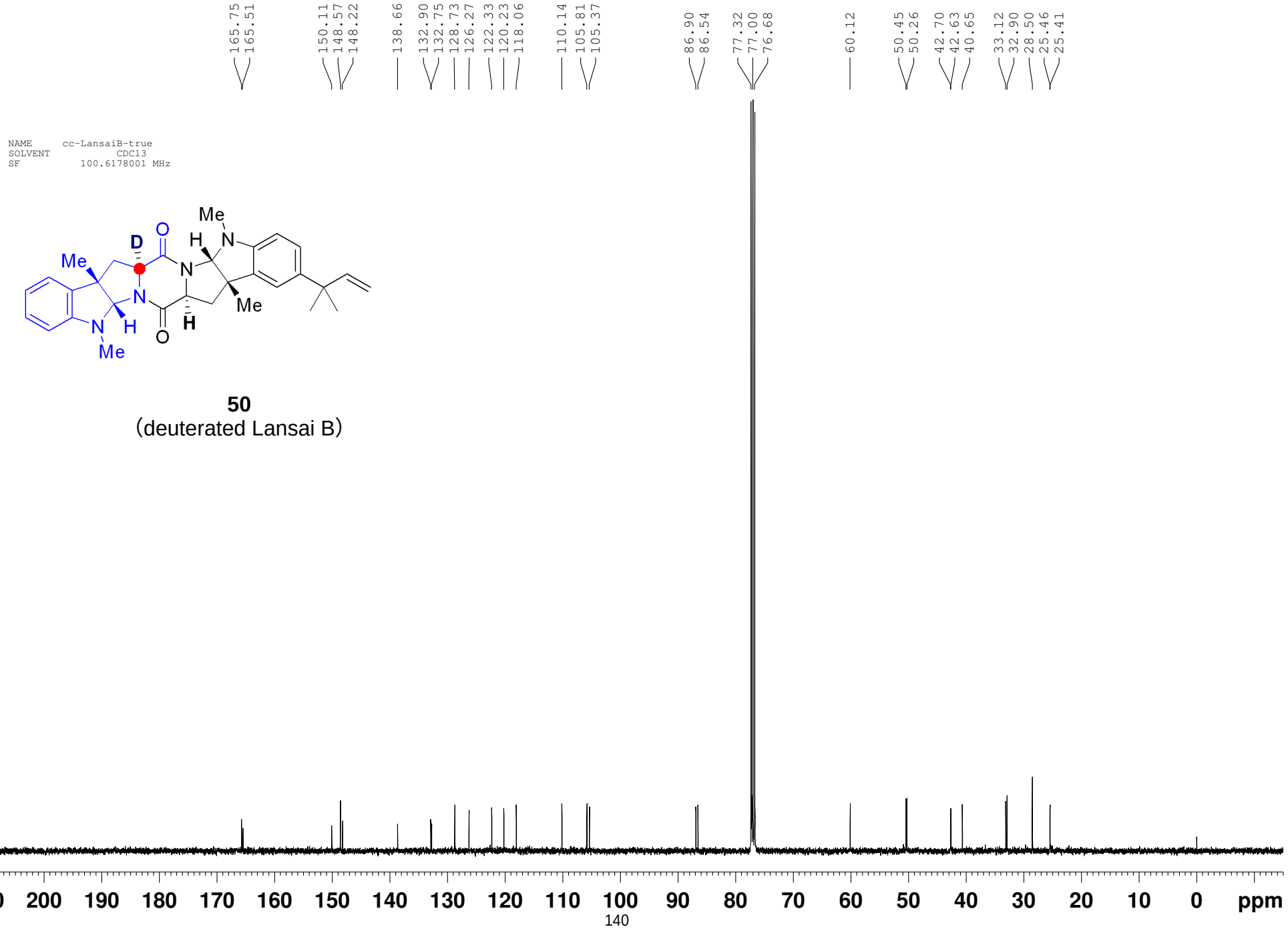

200.83
199.26
198.89
154.98
154.45
154.16
149.83
149.66
133.69
133.60
133.23
128.78
128.63
128.36
122.18
121.96
121.66
121.59
118.25
118.07
107.07
106.98
90.80
90.50
90.34
90.02
81.69
81.63
81.43
81.30
77.32
77.00
76.68
65.59
65.37
65.14
64.99
52.13
51.03
50.64
40.99
40.68
40.06
35.05
34.68
65.44
65.21
33.47
29.67
28.33
28.19
28.10
24.37
24.11
22.96
NAME cc-I54-0914
SOLVENT CDC13
SF 100.6178015 MHz
65.59
65.37
65.14
64.99
65.44
65.21
65.5
65.0
ppm
Me
CHO
D
N
Boc
N
H
Me
+
48
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



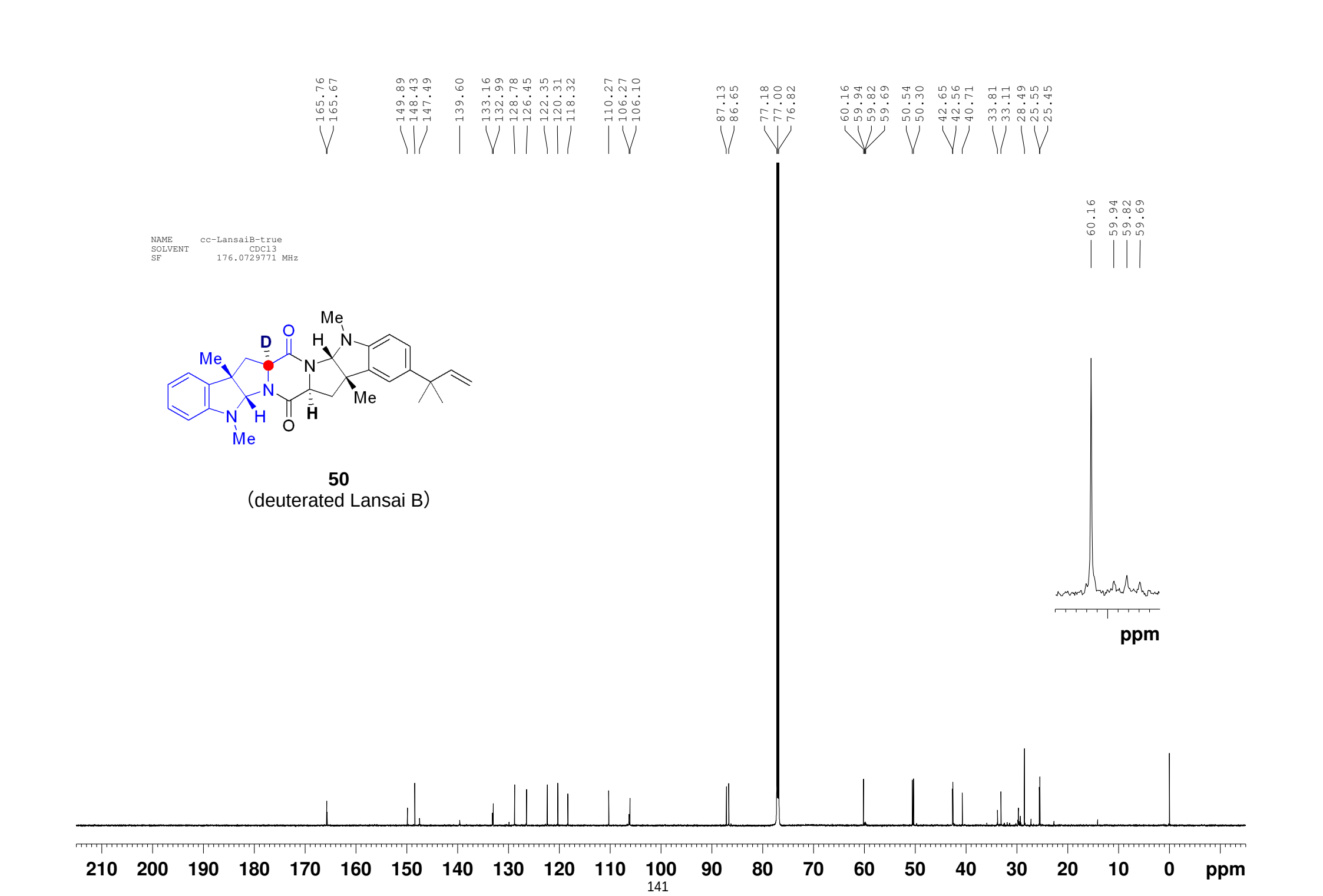
NAME cc-LansaiB-true
SOLVENT CDCl3
SF 400.1300097 MHz



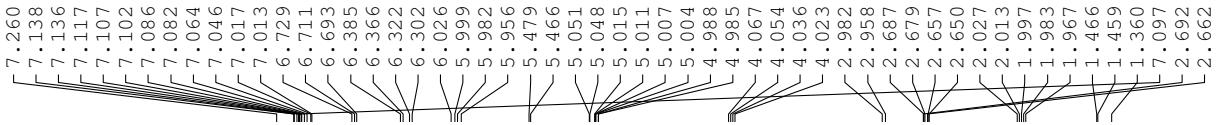
50
(deuterated Lansai B)



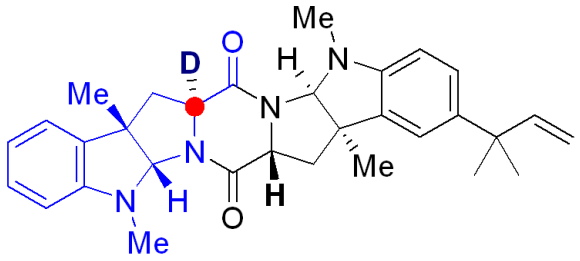
50
(deuterated Lansai B)



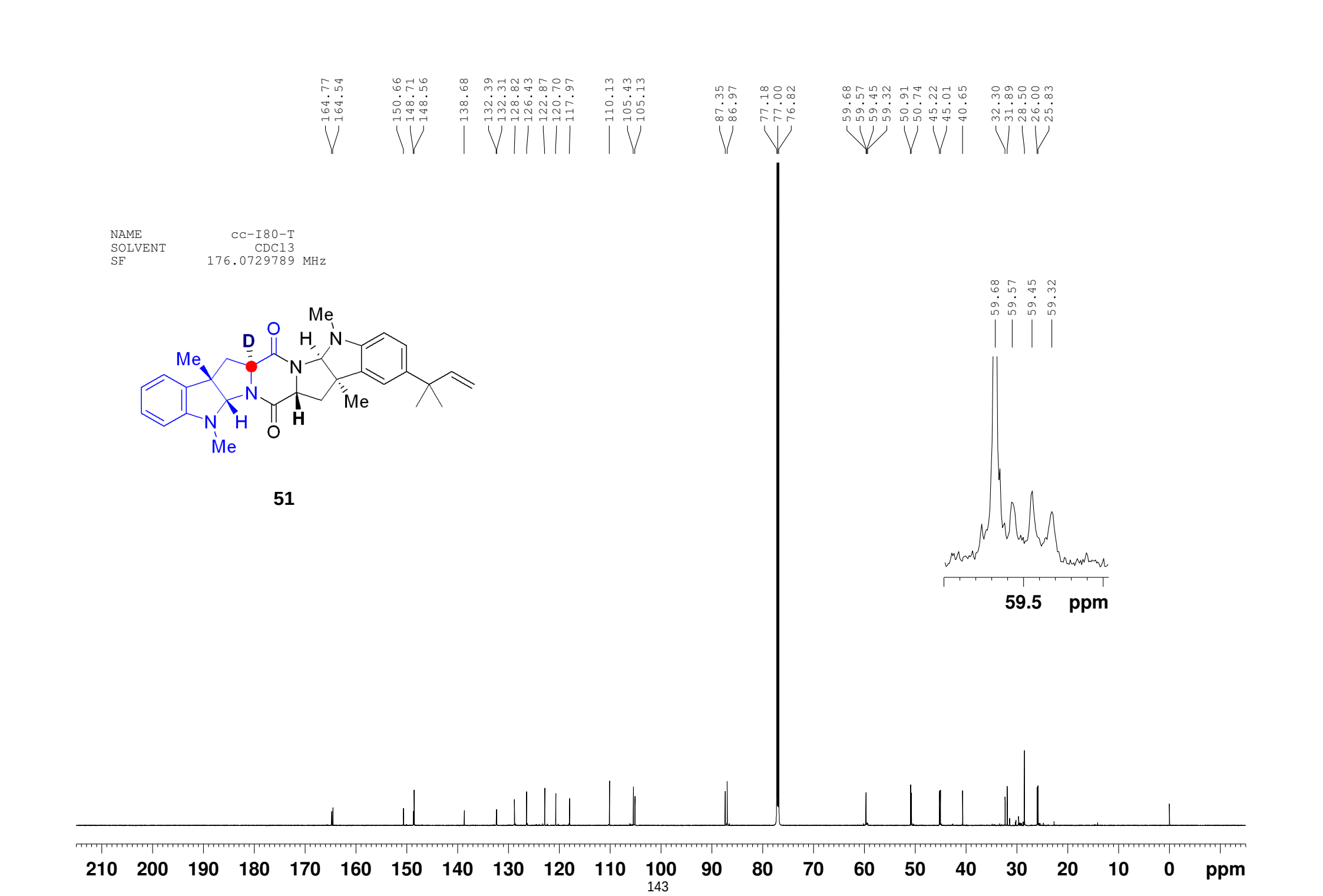
50
(deuterated Lansai B)



NAME cc-I80-T
SOLVENT CDCl3
SF 400.1500092 MHz



51


164.77
164.54
150.66
148.71
148.56
138.68
132.39
132.31
128.82
126.43
122.87
120.70
117.97
110.13
105.43
105.13
87.35
86.97
77.18
77.00
76.82
59.68
59.57
59.45
59.32
50.91
50.74
45.22
45.01
40.65
32.30
31.89
28.50
26.00
25.83
NAME cc-I80-T
SOLVENT CDCl3
SF 176.0729789 MHz
Me
H
N
O
D
Me
N
N
H
Me
O
H
Me
59.68
59.57
59.45
59.32
59.5 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

51