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Supporting Information

N-Tosyloxycarbamates as Reagents in Rhodium-Catalyzed C-H Amination Reaction

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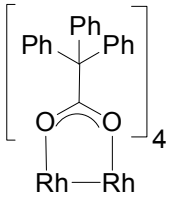
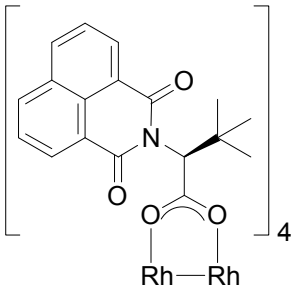
Scheme 1. Structure of Dirhodium Tetracarboxylate Catalysts



$Rh_2(TPA)_4$



$Rh_2[(S)\text{-NTTL}]_4$

General Information: Rhodium(II) triphenylacetate[1] and $Rh_2[(S)\text{-nttl}]_4$,[2] were prepared according to the literature and recrystallyzed from methanol/dichloromethane prior to use. Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, or aqueous potassium permanganate. Flash chromatography was performed using EM Silica Gel 60 (230-400 mesh) with the indicated solvent system. Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter at 589 nm. Data are reported as follows: $[\alpha]_l^{temp.}$, concentration (*c* g/100mL), and solvent. Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer equipped with a Golden Gate Diamond ATR and are reported in reciprocal centimeters (cm^{-1}). Only the most important and relevant frequencies are reported. ^1H NMR spectra were recorded in $CDCl_3$, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively). Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of $CDCl_3$ (76.9 ppm) on the δ scale. Mass spectra were obtained on a LC-MSD TOF (ESI) Agilent Technologies high resolution from the Centre régional de spectrométrie de masse de l'Université de Montréal. The elementary analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal. Analytical gas chromatography with a mass spectroscopy (GC-MS) was carried out on a Hewlett Packard 6890 series gas chromatograph equipped with a split mode capillary injector and electron impact mass detector. Unless otherwise noted, injector and detector temperatures were 250°C and the carrier gas was hydrogen (2 mL/min) with a HP-5MS column. Data are reported as follows: column type, oven temperature, and retention time (t_r). High performance liquid chromatography (HPLC) analyses were performed on a Hewlett Packard 1100 Series quaternary gradient pump with diode-array detector interfaced with HP Chemstation software. Values for enantiomeric excess were determined using a chiral column. Data are reported as follows: column type, flow, solvent used, and retention time (t_r).

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[1] (a) Hashimoto, S.; Watanabe, N.; Ikegami, S., *Tetrahedron Lett.* **1992**, *33*, 2709-2712. (b) Espino, C. G.; Du Bois, J., *Angew. Chem. Int. Ed.* **2001**, *40*, 598-600.
[2] Müller, P.; Ghanem, A. *Org. Lett.* **2004**, *6*, 4347-4350.

General Procedure A: Intramolecular C-H Bond Insertion. To a solution of the *N*-tosyloxycarbamate (0.500 mmol) in dichloromethane (5.0 mL), were added tetrakis(triphenylacetate)dirhodium (0.040 g, 0.030 mmol) and potassium carbonate (0.210 g, 1.50 mmol). The resulting green suspension was stirred at room temperature for 6 h. The mixture was then diluted with DCM, filtered through a celite pad, rinsed with DCM and the solvent was removed under vacuum. The corresponding oxazolidinone was purified by flash chromatography on silica gel using EtOAc/DCM as eluent.

General Procedure B: Intramolecular C-H Bond Insertion for Reactions of ≥1 mmol. To a solution of the *N*-tosyloxycarbamate (1.00 mmol) in dichloromethane (10.0 mL), was added tetrakis(triphenylacetate)dirhodium (0.080 g, 0.060 mmol). Potassium carbonate (0.280 g, 2.00 mmol) dissolved in water (0.50 mL) was added dropwise and the resulting green suspension was stirred at room temperature for 6 h. The mixture was then filtered through a celite pad, rinsed with DCM and the solvent was removed under vacuum. The corresponding oxazolidinone was purified by flash chromatography on silica gel using EtOAc/DCM as eluent.

General Procedure C: Intermolecular C-H Bond Insertion with Aliphatic Alkanes. To a solution of 2,2,2-trichloroethyl-*N*-tosyloxycarbamate (0.500 mmol) and the alkane (2.50 mmol) in the required solvent (TCE or DCM) (1 mL), were added the catalyst ($Rh_2(TPA)_4$ or $Rh_2[(S)\text{-NTTL}]_4$) and potassium carbonate (0.210 g, 1.50 mmol). The resulting green suspension was stirred overnight at room temperature. The mixture was then diluted with DCM, filtered through a celite pad, rinsed with DCM and the solvent was removed under vacuum. The corresponding Troc-protected amine was purified by flash chromatography on silica gel.

General Procedure D: Intermolecular C-H Bond Insertion with Aromatic Alkanes. To a solution of 2,2,2-trichloroethyl-*N*-tosyloxycarbamate (0.500 mmol) and the aromatic substrate (2.50 or 7.50 mmol), were added tetrakis(triphenylacetate)dirhodium (0.040 g, 0.030 mmol) and potassium carbonate (0.210 g, 1.50 mmol). The resulting green suspension was stirred overnight at room temperature. The mixture was then filtered through a celite pad, rinsed with DCM and the solvent was removed under vacuum. The corresponding Troc-protected amine was purified by flash chromatography on silica gel.

General Procedure E: Intermolecular C-H Bond Insertion Reaction with Substituted Diphenylmethanes or for Intermolecular Reactions of ≥1 mmol. To the substituted diphenylmethane (2.5 mmol) was added 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.181 g, 0.500 mmol) and $Rh_2(TPA)_4$ (0.041 g, 0.030 mmol). Potassium carbonate (0.183 g, 1.00 mmol) dissolved in water (0.2 mL) was added dropwise over a 15 min period. The heterogeneous mixture was stirred overnight at room temperature. It was then diluted with dichloromethane, filtered through a celite pad and rinsed with dichloromethane. Pyridine[3] (0.10 mL) was added and the solvent was removed under vacuum. The corresponding Troc-protected amine was purified by flash chromatography on silica gel using EtOAc/hexanes as eluent.

Preparation and characterization of the *N*-tosyloxycarbamates

for the intramolecular reaction, see supporting information of previous paper[4]

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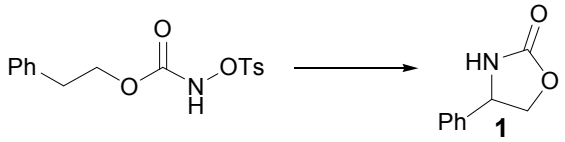
[3] Pyridine is added to liberate completely the product from the catalyst.

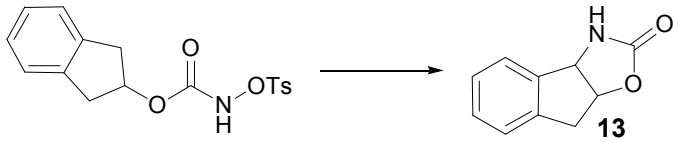
[4] Lebel, H.; Huard, K.; Lectard, S. *J. Am. Chem. Soc.* **2005**, *127*, 14198-14199.

for the intermolecular reaction, see supporting information of previous paper[5]

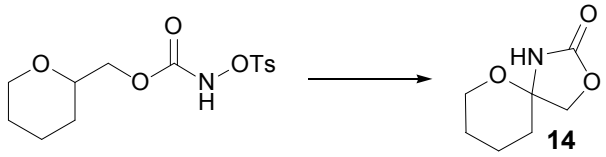
Characterization of oxazolidinones



4-Phenyloxazolidin-2-one (1).[6] The title compound was prepared from phenethyl tosyloxycarbamate (0.170 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **1** (0.075 g, 92%) was obtained as a white solid after flash chromatography (25% EtOAc/DCM): R_f 0.51 (30% EtOAc/DCM); m.p. 135-136°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.43-7.26 (m, 5H, CH), 5.91 (s (br), 1H, NH), 4.96 (t, J = 8 Hz, 1H, CH_2), 4.74 (t, J = 7 Hz, 1H, CH_2), 4.20 ppm (dd, J = 8, 7 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 159.7 (CO), 139.2 (*C*CH), 128.8 (CH), 128.4 (CH), 125.7 (CH), 72.2 (CH_2), 56.0 ppm (CH).



3,3a,8,8a-Tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one (13).[6] The title compound was prepared from 2,3-dihydro-1*H*-inden-2-yl tosyloxycarbamate (0.170 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **13** (0.074 g, 84%) was obtained as a white solid after flash chromatography (25% EtOAc/DCM): R_f 0.33 (30% EtOAc/DCM); m.p. 160-162°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.32-7.24 (m, 4H, CH), 6.84 (s (br), 1H, NH), 5.43-5.39 (m, 1H, CH), 5.15 (d, J = 7 Hz, 1H, CH), 3.44-3.32 ppm (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 159.8 (CO), 140.1 (*C*CH), 139.3 (*C*CH_2), 128.9 (CH), 127.5 (CH), 125.1 (CH), 124.6 (CH), 80.3 (CH), 61.0 (CH), 38.4 ppm (CH_2).



3,6-Dioxa-1-azaspiro[4.5]decan-2-one (14).[6] The title compound was prepared from tetrahydropyran-2-methyl tosyloxycarbamate (0.160 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **14** (0.067 g, 87%) was obtained as a white solid after flash chromatography (30% EtOAc/DCM): R_f 0.27 (30% EtOAc/DCM); m.p. 98°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.52 (s (br), 1H, NH), 4.30 (d, J = 9 Hz, 1H, CH_2), 4.10 (d, J = 9 Hz, 1H, CH_2), 3.79-3.74 (m, 2H, CH_2), 1.84-1.72 (m, 4H, CH_2CH_2), 1.60-1.56 ppm (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 159.3 (CO), 86.7 (CH_2), 75.8 (CNH), 62.7 (CH_2), 33.2 (CH_2), 24.2 (CH_2), 19.6 ppm (CH_2).

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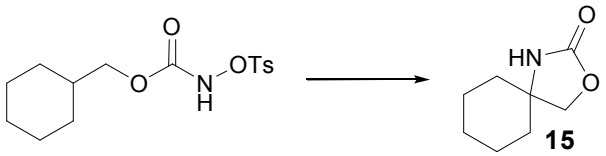
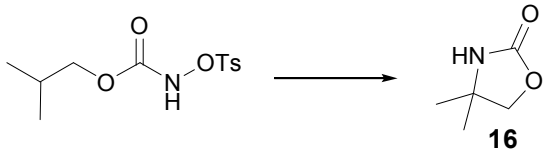
[5] Lebel, H.; Huard, K. *Org. Lett.* **2007**, *9*, 639-642.
[6] Espino, C. G.; Du Bois, J. *Angew. Chem. Int. Ed.* **2001**, *40*, 598-600.



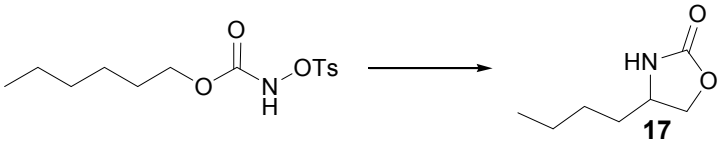
15

3-Oxa-1-azaspiro[4.5]decan-2-one (15).[6] The title compound was prepared from cyclohexylmethyl tosyloxycarbamate (0.160 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **15** (0.064 g, 84%) was obtained as a white solid after flash chromatography (25% EtOAc/DCM): R_f 0.53 (30% EtOAc/DCM); m.p. 75°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 6.79 (s (br), 1H, NH), 4.06 (s, 2H, CH_2), 1.72-1.35 ppm (m, 10H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 160.2 (CO), 76.1 (CH_2), 58.3 (CNH), 37.5 (CH_2), 25.2 (CH_2), 23.0 ppm (CH_2).



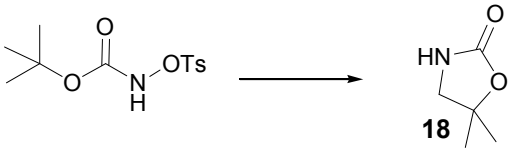
16

4,4-Dimethyloxazolidin-2-one (16).[6] The title compound was prepared from 2-methylpropyl tosyloxycarbamate (0.130 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **16** (0.037 g, 71%) was obtained as a colorless liquid after flash chromatography (25% EtOAc/DCM): R_f 0.40 (30% EtOAc/DCM); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 6.22 (s (br), 1H, NH), 4.06 (s, 2H, CH_2), 1.35 ppm (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 158.9 (CO), 76.6 (CNH), 54.9 (CH_2), 27.2 ppm (CH_3).



17

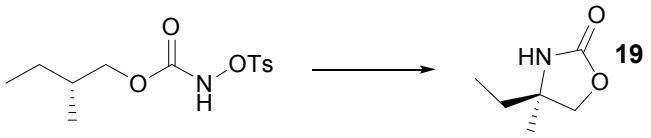
4-Butyloxazolidin-2-one (17).[7] The title compound was prepared from *n*hexyl tosyloxycarbamate (0.160 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **17** (0.046 g, 64%) was obtained as a colorless oil after flash chromatography (25% EtOAc/DCM): R_f 0.43 (30% EtOAc/DCM); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 6.13-5.89 (m (br), 1H, NH), 4.50 (t, J = 8 Hz, 1H, CH_2), 4.04 (t, J = 8 Hz, 1H, CH_2), 3.88 (qn, J = 7 Hz, 1H, CH), 1.67-1.26 (m, 2H, CH_2), 1.40-1.26 (m, 4H, CH_2), 0.93 ppm (t, J = 7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 160.0 (CO), 70.2 (CH_2), 52.5 (CH), 34.9 (CH_2), 27.1 (CH_2), 22.3 (CH_2), 13.7 ppm (CH_3); IR (neat): ν bar = 3270, 2955, 2930, 2860, 1740 (C=O), 1405, 1240, 1025 cm^{-1}; HRMS (ESI) calcd for $C_7H_{13}NO_2Na$ [M+Na]$^+$: 166.08385; found: 166.08417.



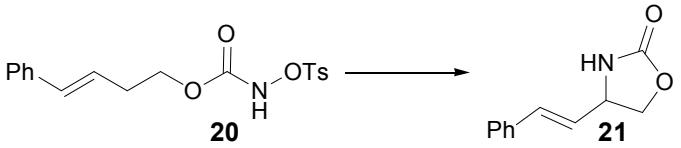
18

[7] Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Org. Chem.* **1989**, *54*, 4398-4404.

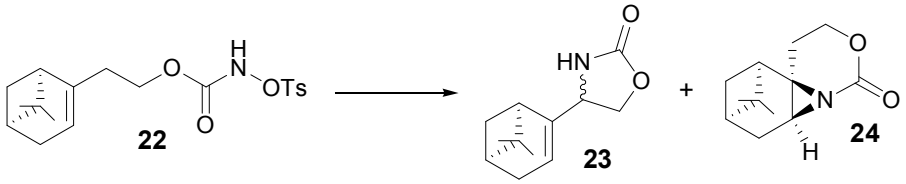
5,5-Dimethyloxazolidin-2-one (18).[8] The title compound was prepared from *t*butyl *N*-tosyloxycarbamate (0.144 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **18** (0.024 g, 41% yield) was obtained as a white solid after flash chromatography (30% EtOAc/DCM): R_f 0.17 (30% EtOAc/DCM); m.p. 78°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 5.75 (s, 1H, NH), 3.23 (s, 2H, CH_2), 1.36 ppm (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 159.3 (CO), 80.9 (*C*CH_2), 52.5 (CH_2), 27.1 ppm (CH_3).



(*R*)-4-Ethyl-4-methyloxazolidin-2-one (19).[6] The title compound was prepared from (*S*)-2-methylbutyl tosyloxycarbamate (0.150 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **19** (0.045 g, 73%) was obtained as a colorless oil after flash chromatography (25% EtOAc/DCM): R_f 0.62 (30% EtOAc/DCM); $[\alpha]_D^{25}$ = +1.7 (*c* = 0.50 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 5.21 (s (br), 1H, NH), 4.15 (d, *J* = 8 Hz, 1H, CH_2), 4.05 (d, *J* = 8 Hz, 1H, CH_2), 1.62 (q, *J* = 7 Hz, 2H, CH_2), 1.34 (s, 3H, CH_3), 0.96 ppm (t, *J* = 7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ = 159.4 (CO), 75.2 (CH_2), 57.9 (CNH), 33.0 (CH_2), 25.3 (CH_3), 7.9 ppm (CH_3). The enantiomeric excess was determined to be ≥99% (≥200:1) by chiral GC analysis (Cyclodex B, 40 °C for 1 min. and then, a ramp of 2 °C/min., t_R 58.23 (major), 58.42 (minor)).



(*E*)-4-Styryloxazolidin-2-one (21).[9] The title compound was prepared from (*E*)-4-phenylbut-3-enyl tosyloxycarbamate (0.180 g, 0.500 mmol) according to the general procedure **A**. The desired oxazolidinone **21** (0.056 g, 60%) was obtained as a white solid after flash chromatography (15% EtOAc/DCM): R_f 0.44 (20% EtOAc/DCM); m.p. 97-100°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.39-7.28 (m, 5H, CH), 6.62 (d, *J* = 16 Hz, 1H, CH), 6.14 (dd, *J* = 16, 8 Hz, 1H, CH), 5.53 (s (br), 1H, NH), 4.63-4.54 (m, 2H, CH_2), 4.18-4.14 ppm (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 159.2 (CO), 135.2 (*C*CH), 133.8 (CH), 128.6 (CH), 128.4 (CH), 126.5 (CH), 126.2 (CH), 70.1 (CH_2), 55.0 ppm (CH); IR (neat): ν bar = 3280, 1745 (C=O), 1400, 1230, 1020, 750, 695 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{12}NO_2$ [*M*+H]$^+$: 190.08626; found: 190.08624.



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[8] Kirby, G. W.; McGuigan, H.; Mackinnon, J. W. M.; McLean, D.; Sharma, R. P. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1437-1442.

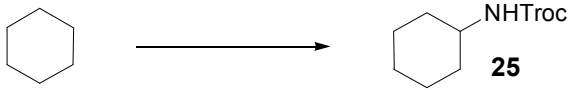
[9] Park, C. S.; Kim, M. S.; Sim, T. B.; Pyun, D. K.; Lee, C. H.; Choi, D.; Lee, W. K.; Chang, J. W.; Ha, H. J. *J. Org. Chem.* **2003**, *68*, 43-49.

4-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)oxazolidin-2-one (23). The title compound was prepared from 2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl tosyloxycarbamate (0.190 g, 0.500 mmol) according to the general procedure **A**. A mixture of oxazolidinone **23** and aziridine **24** was obtained and were separated by flash chromatography (10% EtOAc/DCM).

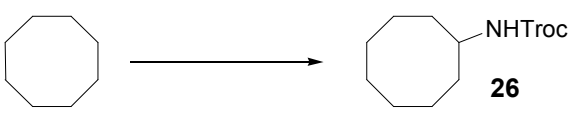
Oxazolidinone **23** (0.048 g, 45%) was obtained as a inseparable racemic mixture of diastereomers and as white solid: R_f 0.59 (30% EtOAc/DCM); m.p. 74-76°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ = 5.55 (s, 2H, NH), 5.29 (d, J = 20 Hz, 2H, CH), 4.43 (dd, J = 17, 8 Hz, 2H, CH_2), 4.39-4.33 (m, 2H, CH_2), 4.00 (dd, J = 8, 6 Hz, 1H, CH), 3.95 (dd, J = 8, 6 Hz, 1H, CH), 2.51-2.40 (m, 2H, cycle), 2.33-2.17 (m, 6H, cycle), 2.16-2.09 (m, 2H, cycle), 1.31 (s, 6H, CH_3), 1.16 (s, 1H, cycle), 1.13 (d, J = 9 Hz, 1H, cycle), 0.82 (s, 3H, CH_3), 0.80 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 159.2 (2CO), 144.4 (*C*CH), 144.2 (*C*CH), 121.6 (CH), 121.3 (CH), 68.0 (CH_2), 67.7 (CH_2), 56.2(CH), 56.0 (CH), 40.7 (2CH), 40.5 (2CH), 40.3 (2*C*CH_3), 37.6(CH_2), 31.9 (CH_2), 31.3 (CH_2), 30.8 (2CH_2), 25.6 (CH_3), 25.6 (CH_3), 20.9 ppm (2CH_3); IR (neat): ν bar = 3260, 2915, 2830, 1750 (C=O), 1400, 1230, 1030 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{18}NO_2$ [*M*+H]$^+$: 208.13321; found: 208.13283.

Aziridine **24** (0.044 g, 40%) was obtained as a single diastereomer and as a white solid: R_f 0.71 (30% EtOAc/DCM); m.p. 144-147°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.35-4.24 (m, 2H, CH_2), 2.61 (d, J = 6 Hz, 1H, CH), 2.20 (d, J = 15 Hz, 1H, CH_2), 2.12-2.03 (m, 4H, cycle), 1.83-1.78 (m, 1H, cycle), 1.77 (d, J = 10 Hz, 1H, cycle), 1.69-1.60 (m, 1H, CH_2), 1.34 (s, 3H, CH_3), 1.01 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 161.0 (CO), 66.3 (CH_2), 46.2 (CN), 45.1 (CH), 44.1 (*C*CH_3), 39.9 (CH_2), 39.6 (CH), 30.9 (CH_2), 26.0 (CH_2), 25.8 (CH_3), 24.8 (CH_3), 19.9 ppm (CH_2); IR (neat): ν bar = 2980, 2940, 2875, 1710 (C=O), 1390, 1250, 1200, 1105, 905, 730 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{18}NO_2$ [*M*+H]$^+$: 208.13321; found: 208.13292.

Characterization of Troc-protected aliphatic amines

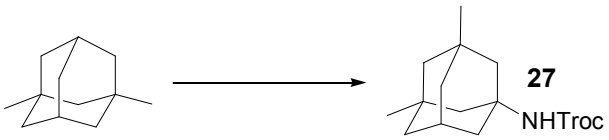


2,2,2-Trichloroethyl-*N*-cyclohexylcarbamate (25). The title compound was prepared from 2,2,2-trichloroethyl-*N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and cyclohexane (0.27 mL, 2.50 mmol or 0.54 mL, 5.00 mmol) according to the general procedure **C**. The desired protected amine **25** was obtained as a white solid after flash chromatography (10% EtOAc/hexane). R_f 0.37 (10% EtOAc/hexane); m.p. 74-76°C; ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): δ = 4.92 (s (br), 1H, NH), 4.68 (s, 2H, CH_2), 3.55-3.42 (m, 1H, CH), 2.01-1.84 (m, 2H, CH_2), 1.75-1.64 (m, 2H, CH_2), 1.63-1.52 (m, 1H, CH_2), 1.41-1.25 (m, 2H, CH_2), 1.24-1.08 ppm (m, 3H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.6 (CO), 95.7 (CCl_3), 74.2 (CH_2), 50.2 (CH), 33.0 (CH_2), 25.3 (CH_2), 24.7 ppm (CH_2); IR (neat): ν bar = 3300, 2935, 2855, 1705 (C=O), 1545, 1275, 1235, 1150, 1085, 1045, 730 cm^{-1}; HRMS (ESI): calcd for $C_9H_{15}NO_2Cl_3$ [*M*+H]$^+$: 274.0185; found: 274.0173.

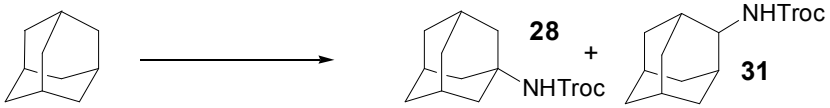


2,2,2-Trichloroethyl cyclooctylcarbamate (26). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and cyclooctane (0.34 mL, 2.50 mmol or

0.68 mL, 5.00 mmol) according to the general procedure **C**. The desired protected amine **26** was obtained as a colorless oil after flash chromatography (10% EtOAc/hexane): R_f 0.44 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): δ = 5.08 (s, 1H, NH), 4.65 (s, 2H, CH_2), 3.71-3.67 (m, 1H, CH), 2.00-1.77 (m, 2H, CH_2), 1.80-1.31 ppm (m, 12H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C): δ = 153.4 (CO), 95.6 (CCl_3), 74.2 (CH_2), 51.4 (CH), 32.0 (CH_2), 27.0 (CH_2), 25.2 (CH_2), 23.3 ppm (CH_2); IR (neat): ν bar = 3330, 2920, 2855, 1710 (C=O), 1505, 1230, 1115, 1085, 1045, 730 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{19}Cl_3NO_2$ [*M*+H]$^+$: 302.0476; found: 302.0476.



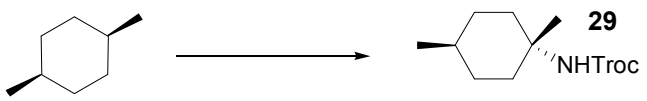
2,2,2-Trichloroethyl 3,5-Dimethyladamantylcarbamate (27). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and 1,3-dimethyladamantane (2.5 or 5.00 mmol) according to the general procedure **C**. The desired protected amine **27** was obtained as a white solid after flash chromatography (5% EtOAc/Hexane): R_f 0.42 (10% EtOAc/hexanes); m.p. 62-65°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.88 (s, 1H, NH), 4.66 (s, 2H, CH_2), 2.31-2.05 (m, 1H, CH), 1.80 (d, *J* = 3 Hz, 2H, CH_2), 1.68-1.54 (m, 4H, CH_2), 1.47-1.23 (m, 4H, CH_2), 1.16 (s, 2H, CH_2), 0.87 ppm (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 151.9 (CO), 95.6 (CCl_3), 73.5 (CH_2), 52.5 (CNH), 50.1 (CH_2), 47.2 (CH_2), 42.2 (CH_2), 39.8 (CH_2), 32.1 (*C*CH_3), 32.1 (CH), 29.7 ppm (CH_3); IR (neat): ν bar = 3430, 3335, 2945, 2900, 2845, 1725 (C=O), 1505, 1455, 1215, 1125, 730 cm^{-1}; HRMS (ESI$^+$): calcd for $C_{15}H_{22}NO_2Cl_3Na$ [*M*+Na]$^+$: 376.0608; found: 376.0609.



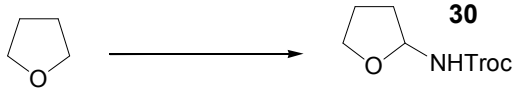
2,2,2-Trichloroethyl adamantylcarbamates (28 and 31). The title compounds were prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and adamantane (0.340 g, 2.50 mmol or 0.681 g, 5.00 mmol) according to the general procedure **C**. The desired protected amines **28** and **31** were obtained as white solids after flash chromatography (5% EtOAc/hexane).

2,2,2-Trichloroethyl 1-adamantylcarbamate (**28**): R_f 0.43 (10% EtOAc/hexane); m.p. 111-113°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.83 (s (br), 1H, NH), 4.65 (s, 2H, CH_2), 2.09 (m, 3H, CH), 1.95 (m, 6H, CH_2), 1.67 ppm (m, 6H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 152.1 (CO), 95.9 (CCl_3), 73.8 (CH_2), 51.2 (CNH), 41.5 (CH_2), 36.2 (CH_2), 29.4 ppm (CH); IR (neat): ν bar = 3430, 3340, 2905, 2850, 1720 (C=O), 1505, 1215, 1105, 1085, 1050, 730 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{19}Cl_3NO_2$ [*M*+H]$^+$: 326.0476; found: 326.0478.

2,2,2-Trichloroethyl 2-adamantylcarbamate (**31**): R_f 0.37 (10% EtOAc/hexane); m.p. 83-86°C; ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ = 5.25 (s, 1H, NH), 4.73 (s, 2H, CH_2), 3.84 (d, *J* = 8 Hz, 1H, CH), 2.00 (s, 2H, CH), 1.94-1.74 (m, 11H, CH_2), 1.72-1.61 ppm (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.4 (CO), 95.4 (CCl_3), 74.1 (CH_2), 55.0 (CHN), 37.1 (CH), 36.7 (CH_2), 31.6 (CH_2), 31.3 (CH_2), 26.8 (CH), 26.7 ppm (CH); IR (neat): ν bar = 3450, 3340, 2905, 2855, 1720 (C=O), 1505, 1225, 1100, 1045, 730 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{19}Cl_3NO_2$ [*M*+H]$^+$: 326.0476; found: 326.0476.

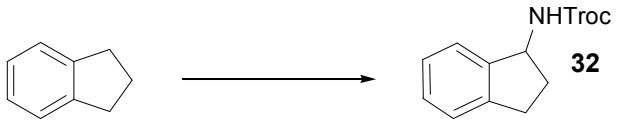


2,2,2-Trichloroethyl 1,4-*cis*-dimethylcyclohex-1-ylcarbamate (29). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and 1,4-*cis*-dimethylcyclohexane (0.36 mL, 2.50 mmol or 0.72 mL, 5.00 mmol) according to the general procedure **C**. The desired protected amine **29** was obtained as a colorless liquid after flash chromatography (5% EtOAc/hexane): R_f 0.43 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 50°C): δ = 4.89 (s (br), 1H, NH), 4.66 (s, 2H, CH_2), 1.89-1.85 (m, 2H, CH_2), 1.67-1.53 (m, 4H, CH_2), 1.50-1.38 (m, 1H, CH), 1.35 (s, 3H, CH_3), 1.16-1.05 (m, 2H, CH_2), 0.91 ppm (d, J = 7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 152.4 (CO), 95.9 (CCl_3), 73.9 (CH_2), 53.1 (CNH), 36.2 (CH_2), 31.5 (CH), 30.7 (CH_3), 22.5 (CH_2), 21.5 ppm (CH_3); IR (neat): ν bar = 3435, 3345, 2925, 2860, 1725 (C=O), 1505, 1220, 1105, 1065, 820, 730 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{19}Cl_3NO_2$ [M+H]$^+$: 302.0476; found: 302.0475.

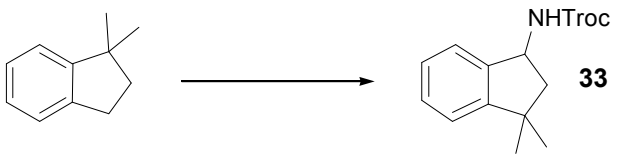


2,2,2-Trichloroethyl tetrahydrofuran-2-ylcarbamate (30). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and tetrahydrofuran (0.20 mL, 2.50 mmol or 0.40 mL, 5.00 mmol) according to the general procedure **C**. The desired protected amine **30** was obtained as a white solid after flash chromatography (5% EtOAc/DCM): R_f 0.39 (5% EtOAc/DCM); m.p. 80-82°C; ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ = 5.65-5.50 (m, 1H, CH), 5.33 (s (br), 1H, NH), 4.74 (s (br), 2H, CH_2), 3.98-3.92 (m, 1H, CH_2), 3.87-3,81 (m, 1H, CH_2), 2.28-2.19 (m, 1H, CH_2), 2.05-1.88 (m, 2H, CH_2), 1.85-1.72 ppm (m, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.5 (CO), 95.1 (CCl_3), 82.8 (CH), 74.4 (CH_2), 67.3 (CH_2), 31.7 (CH_2), 24.4 ppm (CH_2); IR (neat): ν bar = 3305, 2955, 2880, 1720 (CO), 1525, 1230, 1115, 1040, 815, 720 cm^{-1}; HRMS (ESI): calcd for $C_7H_{10}Cl_3NO_3Na$ [M+Na]$^+$: 283.9618; found: 283.9621.

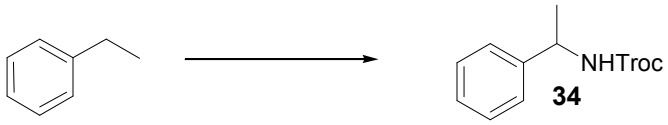
Characterization of Troc-protected benzylic amines



2,2,2-Trichloroethyl 1-indanylcarbamate (32). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and indane (0.31 mL, 2.50 mmol or 0.92 mL, 7.50 mmol) according to the general procedure **D**. The desired protected amine **32** was obtained as a white solid after flash chromatography (5% EtOAc/hexane): R_f 0.64 (30% EtOAc/hexane); m.p. 52-53°C; ^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ = 7.35 (d, J = 6 Hz, 1H, CH), 7.29-7.19 (m, 3H, CH), 5.27 (q, J = 8 Hz, 1H, CH), 5.15 (s (br), 1H, NH), 4.82-4.75 (m, 2H, CH_2), 3.02 (ddd, J = 16, 8, 4 Hz, 1H, CH_2), 2.88 (td, J = 16, 8 Hz, 1H, CH_2), 2.71-2.54 (m, 1H, CH_2), 1.94-1.85 ppm (m, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 40 °C): δ = 154.3 (CO), 143.2 (*C*CH), 142.4 (*C*CH_2), 128.2 (CH), 126.8 (CH), 124.9 (CH), 124.0 (CH), 95.6 (CCl_3), 74.5 (CH_2), 56.7 (CH), 34.0 (CH_2), 30.0 ppm (CH_2); IR (neat): ν bar = 3320, 2950, 1710 (C=O), 1525, 1235, 1140, 720 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{13}Cl_3NO_2$ [M+H]$^+$: 308.0006; found: 308.0013. Enantiomer separation by HPLC (Chiralcel OD column, 25 x 0.46 cm, isopropanol/hexane 1:9; 1 mL/min. τ_1 = 5.80, τ_2= 7.35 min).

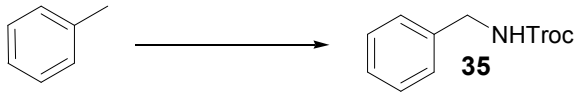


2,2,2-Trichloroethyl 1,1-dimethylindan-3-ylcarbamate (33). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and 1,1-dimethylindane (0.365 g, 2.50 mmol or 1.095 g, 7.50 mmol) according to the general procedure **D**. The desired protected amine **33** was obtained as a white solid after flash chromatography (2% EtOAc/hexane): R_f 0.58 (20% EtOAc/hexane); m.p. 66-68°C; ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): δ = 7.40-7.12 (m, 4H, CH), 5.32 (q, J = 8 Hz, 1H, CH), 5.18 (s (br)), 1H, NH), 4.83 (d, J = 12 Hz, 1H, CH_2), 4.77 (d, J = 12 Hz, 1H, CH_2), 2.50 (dd, J = 13, 7 Hz, 1H, CH_2), 1.75 (dd, J = 13, 8 Hz, 1H, CH_2), 1.39 (s, 3H, CH_3), 1.23 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C): δ = 151.9 (CO), 149.3 (*C*CH), 138.6 (*C*CH_2), 126.0 (CH), 124.5 (CH), 121.3 (CH), 119.7 (CH), 93.2 (CCl_3), 72.1 (CH_2), 52.1 (CH), 47.3 (CH_2), 39.6 (*C*CH_3), 26.9 (CH_3), 26.6 ppm (CH_3); IR (neat): ν bar = 3320, 2955, 2865, 1715 (C=O), 1510, 1230, 1110, 715 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{16}Cl_3NO_2Na$ [*M*+Na]$^+$: 358.01388; found: 358.01396.



34

2,2,2-Trichloroethyl 1-phenylethylcarbamate (34).[10] The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and ethylbenzene (0.31 mL, 2.50 mmol or 0.92 mL, 7.50 mmol) according to the general procedure **D**. The desired protected amine **34** was obtained as a colorless oil after flash chromatography (5% EtOAc/hexane): R_f 0.36 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ = 7.43-7.18 (m, 5H, CH), 5.29 (s (br), 1H, NH), 4.89 (qn, J = 7 Hz, 1H, CH), 4.77-4.69 (m, 2H, CH_2), 1.54 ppm (d, J = 7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6 (CO), 142.7 (*C*CH), 128.7 (CH), 127.6 (CH), 125.9 (CH), 95.5 (CCl_3), 74.4 (CH_2), 51.0 (CH), 22.2 ppm (CH_3); IR (neat): ν bar = 3325, 3030, 2975, 1715 (C=O), 1525, 1450, 1240, 1115, 700 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{13}Cl_3NO_2$ [*M*+H]$^+$: 296.0006; found: 296.0010.



35

2,2,2-Trichloroethyl benzylcarbamate (35).[11] The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and toluene (0.27 mL, 2.50 mmol or 0.80 mL, 7.50 mmol) according to the general procedure **D**. The desired protected amine **35** was obtained as a white solid after flash chromatography (10% EtOAc/hexane): R_f 0.56 (30% EtOAc/hexane); m.p. 65-67°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.40-7.27 (m, 5H, CH), 5.29 (s (br), 1H, NH), 4.77 (s, 2H, CH_2), 4.43 ppm (d, J = 6 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 154.5 (CO), 137.6 (*C*CH_2), 128.6 (CH), 127.6 (CH), 127.4 (CH), 95.4 (CCl_3), 74.5 (CH_2), 45.2 ppm (CH_2); IR (neat): ν bar = 3355, 3310, 3030, 2960, 1700 (C=O), 1535, 1245, 1145, 725, 695 cm^{-1}; HRMS (ESI): calcd for $C_{10}H_{11}Cl_3NO_2$ [*M*+H]$^+$: 281.9850; found: 281.9840.

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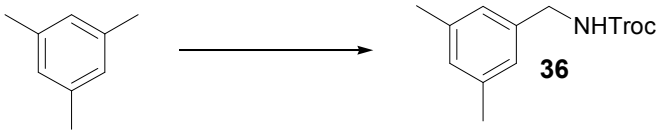
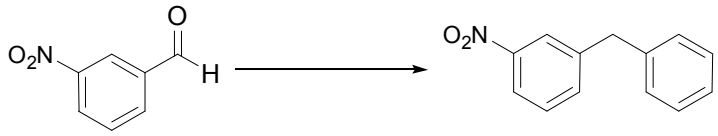
[10] Shimizu, M.; Sodeoka, M. *Org. Lett.* **2007**, *9*, 5231-5234.

[11] Kazuyoshi, T.; Tsuboyama, K.; Hoshino, M.; Kishino, M.; Ogura, H. *Synthesis* **1987**, 557-560.



2,2,2-Trichloroethyl 3,5-dimethylbenzylcarbamate (36). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and mesitylene (0.35 mL, 2.50 mmol or 1.04 mL, 7.50 mmol) according to the general procedure **D**. The desired protected amine **36** was obtained as a colorless oil after flash chromatography (5% EtOAc/hexane): R_f 0.63 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): δ = 6.94-6.92 (m, 3H, CH), 5.27 (s (br), 1H, NH), 4.78 (s, 2H, CH_2), 4.35 (d, J = 6 Hz, 2H, CH_2), 2.32 ppm (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C): δ = 154.6 (CO), 138.4 ($C$$CH_2$), 137.7 ($C$$CH_3$), 129.3 (CH), 125.4 (CH), 95.7 (CCl_3), 74.8 (CH_2), 45.4 (CH_2), 21.1 ppm (CH_3); IR (neat): ν bar = 3325, 2920, 1715 (C=O), 1515, 1235, 1140, 1035, 725 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{14}Cl_3NO_2Na$ [M+Na]$^+$: 331.9982; found: 331.9978.

Synthesis of 3-nitrodiphenylmethane.



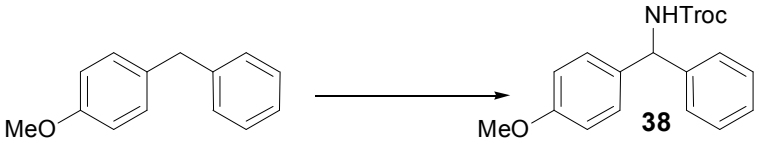
To a solution of the 3-nitrobenzaldehyde (7.56 g, 50.0 mmol) in ether (500 mL) at 0 °C was added an ether solution of phenyl Grignard 1M (55.0 mL, 55.0 mmol) dropwise. The resulting mixture was stirred for 3 hrs and HCl 10% was carefully added. The two layers were separated and the aqueous phase was extracted with ether. The combined organic layers were washed with brine and then dried over $MgSO_4$. The solvent was removed under reduced pressure.

Sodium borohydride (3.78 g, 100 mmol) was added to trifluoroacetic acid (165 mL) over 30 min at 0°C. The alcohol obtained from the first step was dissolved in DCM (15 mL) and was added to the solution dropwise. The reaction mixture was stirred at room temperature for 24 hrs and then water was added. The solution was cooled in an ice bath and was made alkaline with NaOH pellets. The layers were separated and the aqueous phase was extracted twice with ether. The combined organic phases were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the desired 3-nitrodiphenylmethane[12] was obtained as a yellowish liquid (4.14 g, 55%) after flash chromatography (5% EtOAc/hexanes) followed by a distillation: R_f 0.38 (5% EtOAc/hexanes); b.p. 164-166°C at 3 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C):□ δ = 8.17-7.95 (m, 2H, CH), 7.54 (d, J = 8 Hz, 1H, CH), 7.47 (d, J = 16 Hz, 1H, CH), 7.35 (d, J = 15 Hz, 2H, CH), 7.30-7.25 (m, 1H, CH), 7.22 (d, J = 7 Hz, 2H, CH), 4.11 ppm (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 148.1 (CNO_2), 142.8 ($C$$CH_2$), 139.0 ($C$$CH_2$), 134.7 (CH), 129.0 (CH), 128.5 (CH), 128.5 (CH), 126.4 (CH), 123.3 (CH), 121.0 (CH), 41.2 ppm (CH_2); IR (neat): n bar = 3065, 3030, 2920, 1525, 1495, 1455, 1345, 815, 730, 700 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{12}NO_2$ [M+H]$^+$: 214.08626; found: 214.08694.

[12] L'Hermite, N.; Giraud, A.; Provot, O.; Peyrat, J.-F.; Alami, M.; Brion, J.-D. *Tetrahedron* **2006**, *62*, 11994-12002.

Characterization of Troc-protected benzhydrylamines

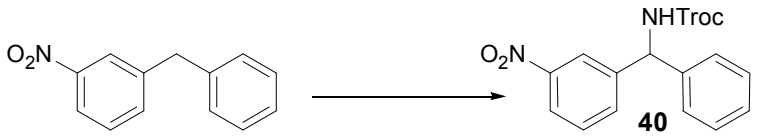
2,2,2-Trichloroethyl benzhydrylcarbamate (37). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and diphenylmethane (0.421 g, 2.50 mmol) according to the general procedure **E**. The desired protected amine was obtained as a white solid (0.115 g, 60%) after flash chromatography (10% EtOAc/hexanes): R_f 0.26 (10% EtOAc/hexanes); m.p. 110-113°C; ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ = 7.53-7.00 (m, 10H, CH), 6.01 (d, J = 8 Hz, 1H, CH), 5.58 (s, 1H, NH), 4.76 pm (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.7 (CO), 140.9 (*C*CH), 128.6 (CH), 127.6 (CH), 127.1 (CH), 95.4 (CCl_3), 74.5 (CH_2), 59.0 ppm (CH); IR (neat): ν bar = 3300, 3030, 2950, 1710 (C=O), 1525, 1495, 1235, 1135, 1025, 700 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{14}NO_2Cl_3Na$ [M+Na]$^+$: 379.9982; found: 379.9999.



2,2,2-Trichloroethyl 4-methoxybenzhydrylcarbamate (38). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and 4-methoxydiphenylmethane (0.496 g, 2.50 mmol) according to the general procedure **E**. The desired protected amine was obtained as a white solid (0.128 g, 61%) after flash chromatography (5% EtOAc/hexanes): R_f 0.29 (20% EtOAc/hexanes); m.p. 100-102°C; ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ = 7.40-7.31 (m, 2H, CH), 7.31-7.24 (m, 3H, CH), 7.17 (d, J = 8 Hz, 2H, CH), 6.87 (d, J = 9 Hz, 2H, CH), 5.96 (d, J = 8 Hz, 1H, CH), 5.54 (s, 1H, NH), 4.75 (s, 2H, CH_2), 3.80 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 158.7 (CO), 153.4 (*C*OCH_3), 140.9 (*C*CH), 132.8 (*C*CH), 128.4 (CH), 128.2 (CH), 127.3 (CH), 126.8 (CH), 113.8 (CH), 95.2 (CCl_3), 74.3 (CH_2), 58.3 (CH), 55.0 ppm (CH_3); IR (neat): ν bar = 3330, 2955, 2835, 1720 (C=O), 1510, 1245, 1135, 725, 700 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{16}NO_3Cl_3Na$ [M+Na]$^+$: 410.0088; found: 410.0083.

2,2,2-Trichloroethyl 4-fluorobenzhydrylcarbamate (39). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and 4-fluorodiphenylmethane (0.466 g, 2.50 mmol) according to the general procedure **E**. The desired protected amine was obtained as a white solid (0.134 g, 71%) after flash chromatography (10% EtOAc/hexanes): R_f 0.49 (20% EtOAc/hexanes); m.p. 102-104°C; ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ = 7.44-7.18 (m, 7H, CH), 7.03 (t, J = 9 Hz, 2H, CH), 5.99 (d, J = 8 Hz, 1H, CH), 5.55 (s, 1H, NH), 4.75 ppm (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 162.0 (d, J = 247 Hz, CF), 153.6 (CO), 140.6 (*C*CH), 136.7 (d, J = 3 Hz, *C*CH), 128.8 (d, J = 8 Hz, CH), 128.7 (CH), 127.8 (CH), 127.1 (CH), 115.5 (d, J = 22 Hz, CH), 95.3 (CCl_3), 74.5 (CH_2),

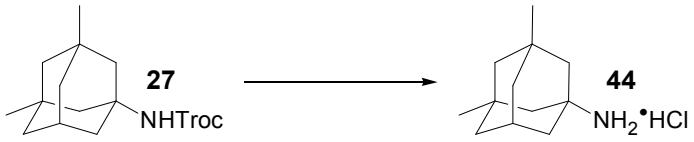
58.4 ppm (CH); IR (neat): ν bar = 3320, 3030, 2950, 1710 (C=O), 1505, 1225, 1135, 725, 700 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{13}NO_2Cl_3FNa$ $[M+Na]^+$: 397.9882; found: 397.9888.



2,2,2-Trichloroethyl 3-nitrobenzhydrylcarbamate (40). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and 3-nitrodiphenylmethane (0.533 g, 2.50 mmol) according to the general procedure **E**. The desired protected amine was obtained as a white solid (0.151 g, 75%) after flash chromatography (10% EtOAc/hexanes): R_f 0.38 (20% EtOAc/hexanes); m.p. 86-88°C; ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ = 8.20 (s, 1H, CH), 8.16 (d, J = 9 Hz, 1H, CH), 7.63 (d, J = 8 Hz, 1H, CH), 7.53 (t, J = 8 Hz, 1H, CH), 7.44-7.30 (m, 3H, CH), 7.29-7.21 (m, 2H, CH), 6.07 (d, J = 7 Hz, 1H, CH), 5.66 (s, 1H, NH), 5.23-4.38 ppm (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.7 (CO), 148.4 (CNO_2), 143.2 (*C*CH), 139.4 (*C*CH), 133.1 (CH), 129.6 (CH), 129.1 (CH), 128.4 (CH), 127.4 (CH), 122.6 (CH), 121.6 (CH), 95.1 (CCl_3), 74.6 (CH_2), 58.7 ppm (CH); IR (neat): ν bar = 3320, 3065, 1715 (C=O), 1530, 1350, 1230, 700 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{13}N_2O_4Cl_3Na$ $[M+Na]^+$: 424.9831; found: 424.9833.

2,2,2-Trichloroethyl 2-chlorobenzhydrylcarbamate (41). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and 2-chlorodiphenylmethane (0.507 g, 2.50 mmol) according to the general procedure **E**. The desired protected amine was obtained as a white solid (0.069 g, 37%) after flash chromatography (5-10% EtOAc/hexanes): R_f 0.24 (10% EtOAc/hexanes); m.p. 103-105°C; ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ = 7.55-6.98 (m, 9H, CH), 6.35 (d, J = 8 Hz, 1H, CH), 5.64 (s, 1H, NH), 4.76 ppm (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.5 (CO), 139.3 (*C*CH), 138.1 (*C*CH), 133.5 (*C*Cl), 130.1 (CH), 129.0 (CH), 128.6 (CH), 128.4 (CH), 127.7 (CH), 127.1 (CH), 127.0 (CH), 95.3 (CCl_3), 74.5 (CH_2), 56.6 ppm (CH); IR (neat): ν bar = 3320, 1720 (C=O), 1500, 1230, 1030, 700 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{14}NO_2Cl_4$ $[M+H]^+$: 391.9769; found: 391.9773.

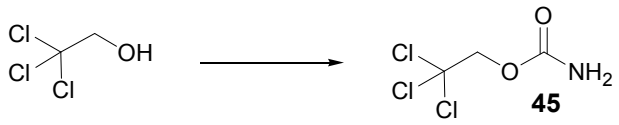
Synthesis of memantine hydrochloride (44).



Troc-protected 3,5-dimethyladamantanamine **27** (0.071 g, 0.20 mmol) was dissolved in AcOH (1.0 mL) and zinc dust (0.13 g, 2.0 mmol) was added. The mixture was stirred at room temperature for 2 hrs and was then filtered through a celite pad, rinsed with MeOH and the solvent was removed under vacuum. The white solid was dissolved in MeOH (7.0 mL) and acetyl chloride (0.57 mL, 8.0 mmol) was added.

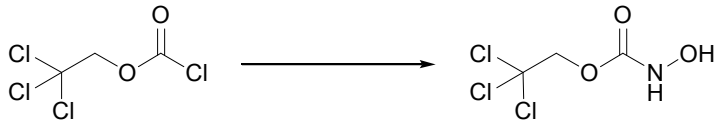
The reaction mixture was stirred at 40°C for 16 hrs and the volatiles were removed under reduced pressure. The memantine hydrochloride[13] **44** was obtained as a white solid in a quantitative yield: ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25°C): δ = 7.82 (s, 3H, NH$_3$), 2.16 (m, 1H, CH), 1.60 (s, 2H, CH$_2$), 1.43 (d, J = 11 Hz, 2H, CH$_2$), 1.37 (d, J = 11 Hz, 2H, CH$_2$), 1.29 (s, 4H, CH$_2$), 1.16 (d, J = 13 Hz, 1H, CH$_2$), 1.09 (d, J = 13 Hz, 1H, CH$_2$), 0.85 ppm (s, 6H, CH$_3$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25°C): δ = 52.5 (CH$_2$), 49.4 (CNH$_3$), 46.1 (CH$_2$), 41.5 (CH$_2$), 38.7 (CH$_2$), 32.1 (CH$_3$), 29.6 (CH$_3$), 29.2 ppm (*C*CH$_3$); IR (neat): ν bar = 3230, 3065, 2925, 2900, 2865, 2850, 2835, 1595, 1570, 1490, 1450, 1350, 1170. 1020, 960 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{21}N$ [*M*+H]$^+$: 180.17468; found: 180.17438.

Synthesis of 2,2,2-trichloroethylcarbamate (45).



To a solution of 2,2,2-trichloroethanol (0.48 mL, 5.0 mmol) in toluene (10 mL), chlorosulfonyl isocyanate (0.45 mL, 5.2 mmol) was added at 0°C and the resulting solution was stirred for 2 h. After evaporation of the solvent under reduced pressure, water was added to the residue which was extracted with Et$_2$O, dried over MgSO$_4$, filtered and the solvent was removed under vacuum. The desired 2,2,2-trichloroethylcarbamate[14] was isolated as a white solid (0.62 g, 64%) after recrystallisation from hexane/CHCl$_3$: R$_f$ 0.54 (40% EtOAc/hexanes); m.p. 63-64°C; ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): δ = 5.37 (s (br), 2H, NH$_2$), 4.71 ppm (s, 2H, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): δ = 155.2 (CO), 95.1 (CCl$_3$), 74.4 ppm (CH$_2$); IR (neat): ν bar = 3465, 3335, 3270, 3195, 2957, 1710 (C=O), 1600, 1390, 1325, 1100, 1050, 900, 810, 770, 720 cm^{-1}; HRMS (ESI): calcd for $C_3H_5NO_2Cl_3$ [*M*+H]$^+$: 191.9380; found: 191.9390.

Synthesis of 2,2,2-trichloroethyl *N*-hydroxycarbamate.[8]



Hydroxylamine hydrochloride (34.7 g, 500 mmol) was added to a 1.5M aqueous solution of sodium hydroxide (400 mL, 600 mmol). The solution was cooled to 0°C and 2,2,2-trichloroethyl chloroformate (13.8 mL, 100 mmol) was added slowly. The reaction mixture was stirred at room temperature for 1 hr and then, it was acidified to pH 5 with concentrated HCl. The resulting mixture was extracted with ether (4 x 200 mL), the combined organic layers were washed with brine (100 mL), then dried over MgSO$_4$. Removal of the solvent under reduced pressure provided a colorless oily product which slowly solidified to give a white solid. After recrystallisation from CHCl$_3$/Hexane, the desired 2,2,2-trichloroethyl *N*-hydroxycarbamate was isolated as a white solid (13.3 g, 64% yield): R$_f$ 0.78 (10% EtOAc/DCM); m.p.

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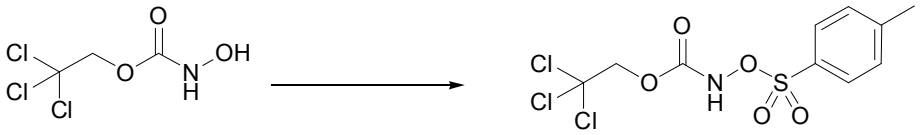
[13] (a) Reddy, J. M.; Prasad, G.; Raju, V.; Ravikumar, M.; Himabindu, V.; Reddy, G. M. *Org. Process Res. Dev.* **2007**, *11*, 268-269. (b) Madhra, M. K.; Sharma, M.; Khanduri, C. H. *Org. Process Res. Dev.* **2007**, *11*, 922-923.

[14] Bachand, C.; Driguez, H.; Paton, J. M.; Touchard, D.; Lessard, J. *J. Org. Chem.* **1974**, *39*, 3136-3138.

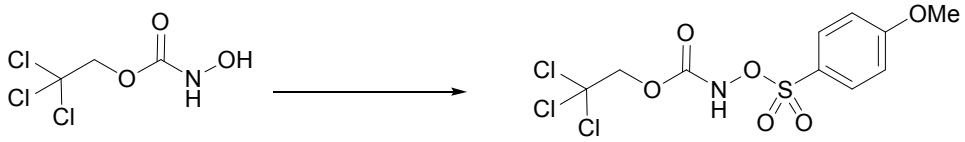
86-88°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.62 (s, 1H, NH), 6.92 (s, 1H, OH), 4.81 ppm (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 156.8 (CO), 94.3 (CCl_3), 74.6 ppm (CH_2).

General Procedure F: Preparation of 2,2,2-Trichloroethyl *N*-(Substituted benzenesulfonyloxy)carbamates. To a solution of 2,2,2-trichloroethyl *N*-hydroxycarbamate (3.13 g, 15.0 mmol) in Et_2O (150 mL) at 0°C was added the corresponding sulfonyl chloride (16.5 mmol). Triethylamine (2.10 mL, 15.0 mmol) was then added dropwise to the solution. The resulting white suspension was stirred at room temperature for 5 hours. Water (25 mL) was added to the solution and the two layers were separated. The aqueous phase was extracted with ether (2 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford the desired *N*-sulfonyloxycarbamate.

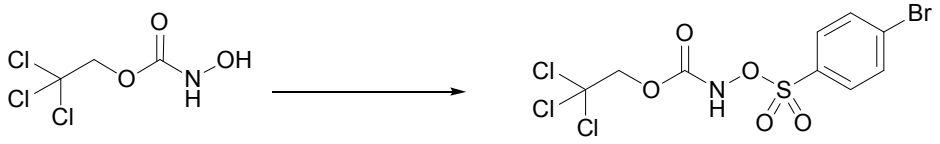
Characterization of 2,2,2-trichloroethyl *N*-(substituted benzenesulfonyloxy)carbamates



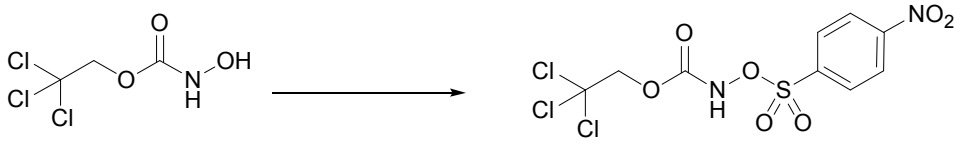
2,2,2-Trichloroethyl *N*-4-tosyloxycarbamate (12). The title compound was prepared from 2,2,2-trichloroethyl *N*-hydroxycarbamate and *p*-toluenesulfonyl chloride (3.15 g) according to the general procedure **F**. The desired product was obtained as a white solid (4.13 g, 76%) after recrystallisation from hexanes and chloroform: R_f 0.45 (30% EtOAc/hexanes); m.p. 123°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.14 (s, 1H, NH), 7.90 (d, J = 8 Hz, 2H, CH), 7.36 (d, J = 8 Hz, 2H, CH), 4.65 (s, 2H, CH_2), 2.46 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.6 (CO), 146.5 (CSO_2), 130.0 (CCH_3), 129.9 (CH), 129.7 (CH), 94.1 (CCl_3), 75.1 (CH_2), 21.8 ppm (CH_3); IR (neat): ν bar = 3265, 3010, 2960, 1765 (C=O), 1600, 1445, 1380, 1190, 1185, 1115, 735 cm^{-1}; HRMS (ESI): calcd for $C_{10}H_{11}NO_5SCl_3$ $[M+H]^+$: 361.9418; found: 361.9419.



2,2,2-Trichloroethyl *N*-4-methoxybenzenesulfonyloxycarbamate. The title compound was prepared from 2,2,2-trichloroethyl *N*-hydroxycarbamate and *p*-methoxybenzenesulfonyl chloride (3.41 g) according to the general procedure **F**. The desired product was obtained as a white solid (4.08 g, 72%) after a flash chromatography (2-5% EtOAc/DCM): R_f 0.68 (5% EtOAc/DCM); m.p. 78°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.29 (s, 1H, NH), 7.96 (d, J = 9 Hz, 2H, CH), 7.03 (d, J = 9 Hz, 2H, CH), 4.68 (s, 2H, CH_2), 3.91 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 164.8 (CO), 153.5 ($COCH_3$), 131.9 (CH), 123.7 (CSO_2), 114.4 (CH), 94.0 (CCl_3), 74.9 (CH_2), 55.7 ppm (CH_3); IR (film): ν bar = 3270, 2950, 2845, 1785 (C=O), 1595, 1380, 1265, 1190, 1170, 730 cm^{-1}; HRMS (ESI): calcd for $C_{10}H_{11}NO_6SCl_3$ $[M+H]^+$: 377.9367; found: 377.9368.

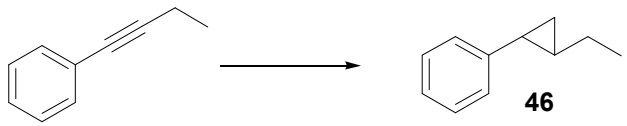


2,2,2-Trichloroethyl *N*-4-bromobenzenesulfonyloxycarbamate. The title compound was prepared from 2,2,2-trichloroethyl *N*-hydroxycarbamate and *p*-bromobenzenesulfonyl chloride (4.22 g) according to the general procedure **F**. The desired product was obtained as a white solid (4.87 g, 76%) after recrystallisation from hexanes and chloroform: R_f 0.53 (5 % EtOAc/DCM); m.p. 99-102°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.30 (s, 1H, NH), 7.88 (d, J = 9 Hz, 2H, CH), 7.72 (d, J = 9 Hz, 2H, CH), 4.67 ppm (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.4 (CO), 132.5 (CH), 131.7 (CSO_2), 130.9 (CH), 130.7 (CBr), 93.9 (CCl_3), 75.0 ppm (CH_2); IR (neat): ν bar = 3280, 1760 (C=O), 1575, 1395, 1190, 750 cm^{-1}; HRMS (ESI): calcd for $C_9H_7BrCl_3NO_5S$ [M+H]$^+$: 425.8367; found: 425.8368.



2,2,2-Trichloroethyl *N*-4-nosyloxycarbamate. The title compound was prepared from 2,2,2-trichloroethyl *N*-hydroxycarbamate and *p*-nitrobenzenesulfonyl chloride (3.66 g) according to the general procedure **F**. The desired product was obtained as a white solid (4.92 g, 84%) after recrystallisation from hexanes and chloroform: R_f 0.45 (5 % EtOAc/DCM); m.p. 107-109°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.41 (d, J = 9 Hz, 2H, CH), 8.32 (s, 1H, NH), 8.24 (d, J = 9 Hz, 2H, CH), 4.66 ppm (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.3 (CO), 151.4 (CSO_2), 138.6 (CNO_2), 131.0 (CH), 124.2 (CH), 93.7 (CCl_3), 75.2 ppm (CH_2); IR (neat): ν bar = 3290, 3110, 1785 (C=O), 1535, 1390, 1350, 1190, 745 cm^{-1}; HRMS (ESI): calcd for $C_9H_7Cl_3N_2O_7SNa$ [M+Na]$^+$: 414.8932; found: 414.8933.

Synthesis of *trans*-1-ethyl-2-phenylcyclopropane (46).

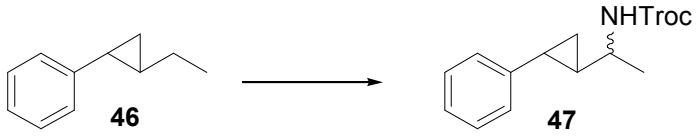


$LiAlH_4$ (4.75 g, 125 mmol) was added portionwise to a solution of 1-phenylbut-1-yne (7.10 mL, 50.0 mmol) in THF (100 mL) at 0°C. The mixture was stirred under reflux for 36 hrs and cooled to 0°C. H_2O was then added dropwise and the mixture was filtered on a pad of celite. The aqueous layer was washed with Et_2O (3 x 100 mL), the combined ethereal phase was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The desired alkene (5.82 g, 88%) was obtained as a colorless oil and was used without further purification.

Et_2Zn (18.2 mL, 220 mmol) in hexane (200 mL) was added to a solution of 1-phenylbut-1-ene (5.82 g, 44.0 mmol) in DCM (500 mL) at -30°C. The resulting mixture was stirred for 5 min., CH_2I_2 was then added dropwise and the mixture was stirred for 16 hrs with slow warm up. The solution was poured on NH_4Cl, the aqueous layer was washed with DCM (2 x 200 mL), the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The *trans*-1-ethyl-2-phenylcyclopropane[14] was obtained as a colorless oil (1.94 g, 68%) after distillation : R_f 0.72 (100% pentane); b.p. 75°C at 3 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.33-7.24 (m, 2H, CH), 7.17 (t,

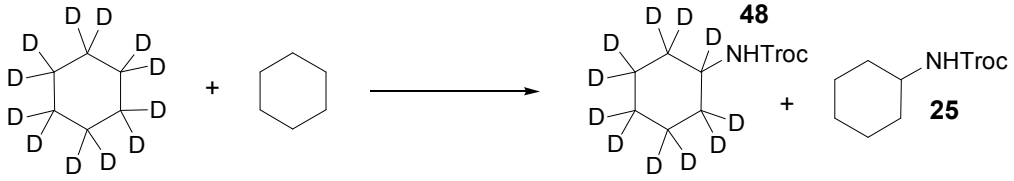
[14] Du Bois, J.; Fiori, K. W. *J. Am. Chem. Soc.* **2007**, *129*, 562-568.

J = 7 Hz, 1H, CH), 7.09 (d, J = 7 Hz, 2H, CH), 1.72-1.57 (m, 1H, CH), 1.51-1.38 (m, 2H, CH_2), 1.10-1.01 (m, 4H, C*H*CH_2C*H*$_3$), 0.95-0.87 (m, 1H, CH_2), 0.85-0.75 ppm (m, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 143.8 (*C*CH), 127.9 (CH), 125.2 (CH), 124.8 (CH), 27.2 (CH_2), 25.3 (CH), 22.9 (CH), 15.7 (CH_2), 13.2 ppm (CH_3); IR (neat): ν bar = 3065, 3030, 3000, 2960, 2925, 2875, 1605, 1495, 1460, 910, 730, 695 cm^{-1}.



2,2,2-Trichloroethyl 1-(2-phenylcyclopropyl)ethylcarbamate (47). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and *trans*-1-ethyl-2-phenylcyclopropane **46** (0.366 g, 2.50 mmol) according to the general procedure **C**. The desired protected amine **47** was obtained as a white solid (0.086 g, 51%, 4:1 inseparable diastereomeric mixture) after flash chromatography (10% EtOAc/hexane): R_f 0.26 (10% EtOAc/hexane); m.p. 60-64°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.35-7.23 (m, 2H, CH), 7.19 (t, J = 7 Hz, 1H, CH), 7.13-7.00 (m, 2H, CH), 5.03 (s, 1H, NH), 4.77 (s, 2H, CH_2), 3.56-3.33 (m, 1H, CH), 2.18-1.98 (m, 1H, single diastereomer, CH), 1.95-1.75 (m, 1H, single diastereomer, CH), 1.35 (d, J = 7 Hz, 3H, CH_3), 1.26-1.16 (m, 1H, CH), 1.16-1.07 (m, 1H, CH_2), 1.01-0.90 ppm (m, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.7 (CO), 141.8 (*C*CH), 128.0 (single diastereomer, CH), 128.0 (single diastereomer, CH), 125.6 (CH), 125.4 (CH), 95.4 (CCl_3), 74.1 (CH_2), 51.0 (CH), 28.7 (CH), 21.3 (CH), 20.3 (CH_3), 13.6 (single diastereomer, CH_2), 13.4 ppm (single diastereomer, CH_2); IR (neat): ν bar = 3330, 2970, 1715 (C=O), 1500, 1450, 1230, 1115, 1095, 730, 695 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{17}NO_2Cl_3$ [M+H]$^+$: 336.0319; found: 336.0309.

Experimental procedure for the isotopic effect determination.

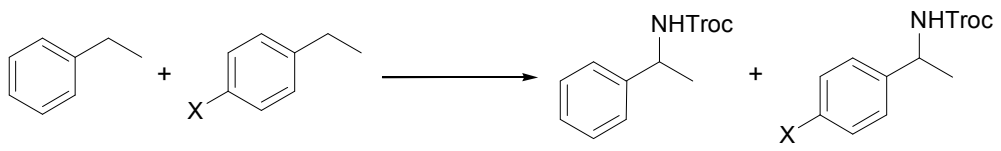


To a solution of 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.073 g, 0.20 mmol), cyclohexane (0.22 mL, 2.0 mmol) and deuterated cyclohexane (0.22 mL, 2.0 mmol) in DCM (0.4 mL) was added $Rh_2(TPA)_4$ (0.014 g, 0.010 mmol). Potassium carbonate (0.055 g, 0.40 mmol) dissolved in water (0.1 mL) was then added dropwise over a 15 minutes period. The resulting green suspension was stirred overnight at room temperature. The mixture was diluted with DCM, filtered through a celite pad and the solvent was removed under vacuum. The corrected product ratio (5:1) was determined by GC/MS analysis of the unpurified reaction mixture. The reaction was performed in triplicate.

Characterization of 2,2,2-trichloroethyl [D_{11}]cyclohexylcarbamate (48). The title compound was prepared from 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.183 g, 0.500 mmol) and deuterated cyclohexane (0.27 mL, 2.50 mmol) according to the general procedure **C**. The desired protected amine **48** was obtained as a white solid after flash chromatography (10% EtOAc/hexane): R_f 0.34 (10% EtOAc/hexane); m.p. 71-73°C; ^{1}H NMR (400 MHz, $CDCl_3$, 45 °C): δ = 4.85 (s, 1H, NH), 4.73 (s, 2H, CH_2); ^{2}H NMR (77 MHz, $CDCl_3$) δ 3.49 (1D, CD), 1.92 (2D, CD_2), 1.67 (2D, CD_2), 1.56 (1D, CD_2),

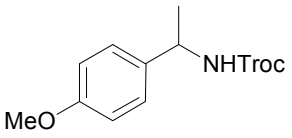
1.30 (2D, CD_2), 1.14 (3D, CD_2); IR (neat): ν bar = 3300, 2950, 2205, 2105, 1705 (C=O), 1530, 1250, 1235, 1140, 1095, 730 cm^{-1}; HRMS (ESI): calcd for $C_9H_4D_{11}NO_2Cl_3$ $[M+H]^+$: 285.0872; found: 285.0861.

Experimental procedure for electronic analysis.

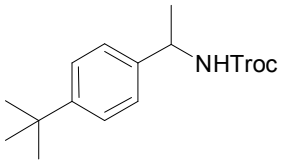


To a mixture of 2,2,2-trichloroethyl *N*-tosyloxycarbamate (0.073 g, 0.20 mmol), 4-ethylbenzene (0.25 mL, 2.0 mmol) and 4-substituted ehtylbenzene (2.0 mmol) in DCM (0.2 mL) was added $Rh_2(TPA)_4$ (0.014 g, 0.010 mmol). Potassium carbonate (0.055 g, 0.40 mmol) dissolved in water (0.1 mL) was then added dropwise over a 15 minutes period. The resulting green suspension was stirred overnight at room temperature. The mixture was filtered through a celite pad and the solvent was removed under vacuum. The corrected product ratios were determined by GC/MS analysis of the unpurified reaction mixture. The reactions were performed in triplicate and the average product ratio used to generate the graph.

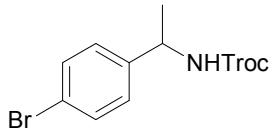
Characterization of substituted Troc-protected benzylamines.



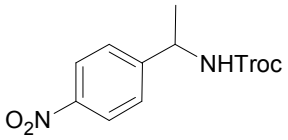
2,2,2-Trichloroethyl 1-(4-methoxyphenyl)ethylcarbamate. The title compound was isolated as a white solid after a flash chromatography (10-20% EtOAc/Hexanes): R_f 0.47 (20% EtOAc/hexanes); m.p. 43-45°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.27 (d, J = 7 Hz, 2H, CH), 6.90 (d, J = 8 Hz, 2H, CH), 5.20 (s (br), 1H, NH), 4.86 (m, 1H, CH), 4.78-4.69 (m, 2H, CH_2), 3.82 (s, 3H, CH_3), 1.54 ppm (d, J = 7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 158.7 (CO), 153.3 ($COCH_3$), 134.5 (CCH), 126.8 (CH), 113.7 (CH), 95.3 (CCl_3), 74.2 (CH_2), 54.9 (CH_3), 50.1 (CH), 21.7 ppm (CH_3); IR (neat): ν bar = 3335, 2975, 1720 (C=O), 1515, 1245, 830, 725 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{14}Cl_3NO_3Na$ $[M+Na]^+$: 347.9932; found: 347.9920.



2,2,2-Trichloroethyl 1-(4-*t*-butylphenyl)ethylcarbamate. The title compound was isolated as a white solid after a flash chromatography (10% EtOAc/Hexanes): R_f 0.55 (20% EtOAc/hexanes); m.p. 64-65°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.38 (d, J = 8 Hz, 2H, CH), 7.27 (d, J = 8 Hz, 2H, CH), 5.22 (s, 1H, NH), 4.98-4.81 (m, 1H, CH), 4.77-4.68 (m, 2H, CH_2), 1.54 (d, J = 7 Hz, 3H, CH_3), 1.32 ppm (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.5 (CO), 150.4 (C*t*Bu), 139.5 (*C*CH), 125.6 (CH), 125.5 (CH), 95.5 (CCl_3), 74.4 (CH_2), 50.5 (CH), 34.4 (CCH_3), 31.2 (CH_3), 21.9 ppm (CH_3); IR (neat): ν bar = 3330, 2965, 1720 (C=O), 1515, 1240, 1115, 830, 730 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{20}Cl_3NO_2Na$ $[M+Na]^+$: 374.0452; found: 374.0447.



2,2,2-Trichloroethyl 1-(4-bromophenyl)ethylcarbamate. The title compound was isolated as a white solid after a flash chromatography (10% EtOAc/Hexanes): R_f 0.40 (20% EtOAc/hexanes); m.p. 80-82°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.47 (d, J = 8 Hz, 2H, CH), 7.21 (d, J = 8 Hz, 2H, CH), 5.25 (s, 1H, NH), 4.94-4.78 (m, 1H, CH), 4.76-4.67 (m, 2H, CH_2), 1.51 ppm (d, J = 7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.5 (CO), 141.8 (*C*CH), 131.7 (CH), 127.5 (CH), 121.2 (CBr), 95.3 (CCl_3), 74.4 (CH_2), 50.4 (CH), 22.1 ppm (CH_3); IR (neat): ν bar = 3325, 2975, 1715 (C=O), 1530, 1490, 1240, 1120, 1100, 820, 735 cm^{-1}; HRMS (ESI$^+$): calcd for $C_{11}H_{12}BrCl_3NO_2$ [*M*+H]$^+$: 373.91115; found: 373.91025.



2,2,2-Trichloroethyl 1-(4-nitrophenyl)ethylcarbamate. The title compound was isolated as a yellowish solid after a flash chromatography (10-20% EtOAc/Hexanes): R_f 0.28 (20% EtOAc/hexanes); m.p. 80-82°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.24 (d, J = 9 Hz, 2H, CH), 7.52 (d, J = 9 Hz, 2H, CH), 5.35 (s, 1H, NH), 5.09-4.87 (m, 1H, CH), 4.85-4.59 (m, 2H, CH_2), 1.58 ppm (d, J = 8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.3 (CO), 150.1 (*C*CH), 147.0 (CNO_2), 126.4 (CH), 123.7 (CH), 95.0 (CCl_3), 74.3 (CH_2), 50.4 (CH), 21.9 ppm (CH_3); IR (neat): ν bar = 3325, 2980, 1720 (C=O), 1520, 1345, 1240, 1120, 820, 735 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{12}Cl_3N_2O_4$ [*M*+H]$^+$: 340.9852; found: 340.9857.

CDCl3, 400 MHz
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.97
0.90
0.96
1.03
1.00
Ph
HN
O
O
1
7.405
7.384
7.374
7.360
7.354
7.346
7.329
7.323
7.307
7.302
7.297
7.237
5.980
4.961
4.935
4.909
4.739
4.710
4.681
4.186
4.163
4.158
4.135

CDCl3, 100 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Ph
1
HN
O
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139.399
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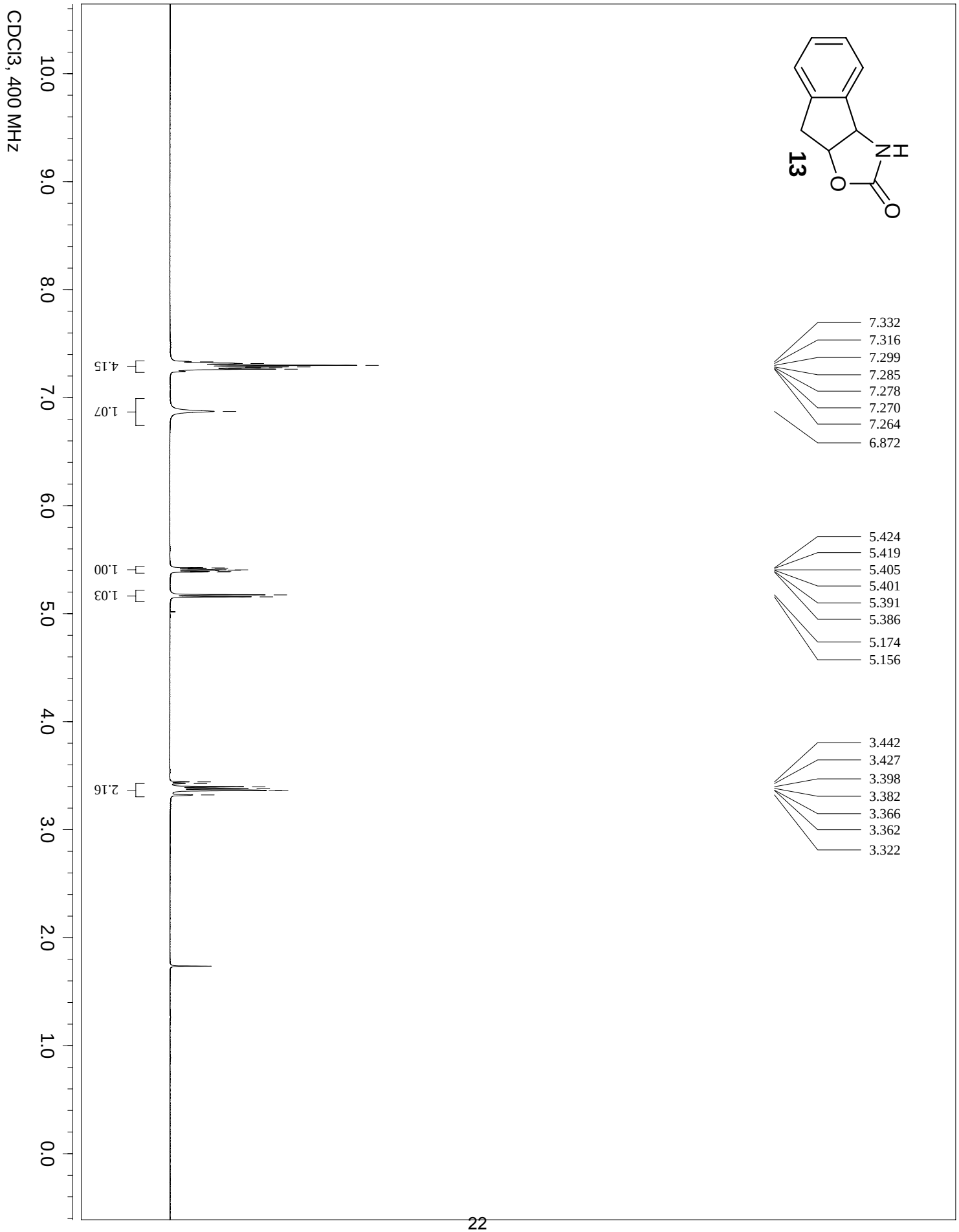
128.816
126.010
77.423
77.000
76.576
72.515
56.349


CDCl3, 400 MHz
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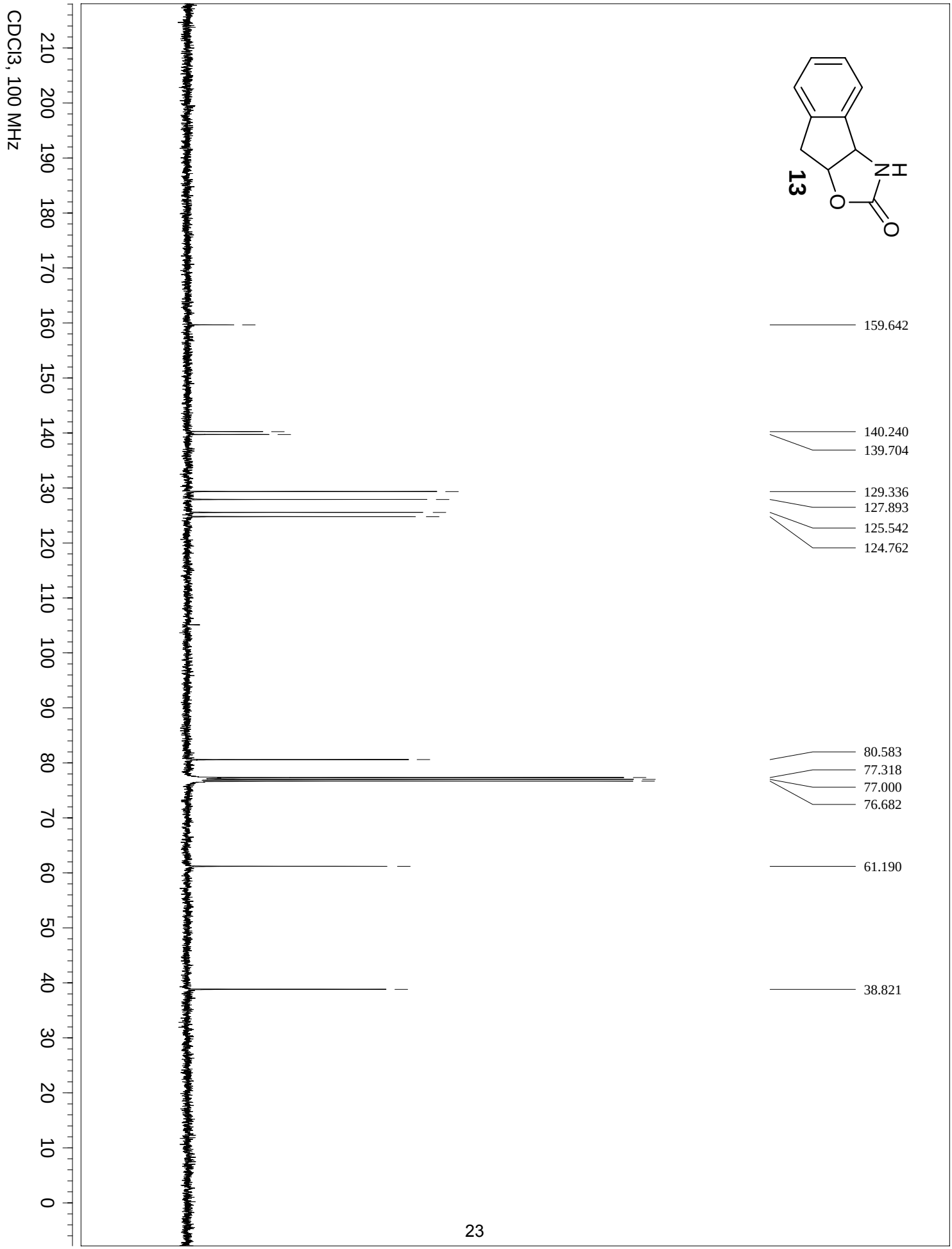
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.15
1.07
1.00
1.03
2.16
13
H
N
O
O
7.332
7.316
7.299
7.285
7.278
7.270
7.264
6.872
5.424
5.419
5.405
5.401
5.391
5.386
5.174
5.156
3.442
3.427
3.398
3.382
3.366
3.362
3.322


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13
N
H
O
O
159.642
140.240
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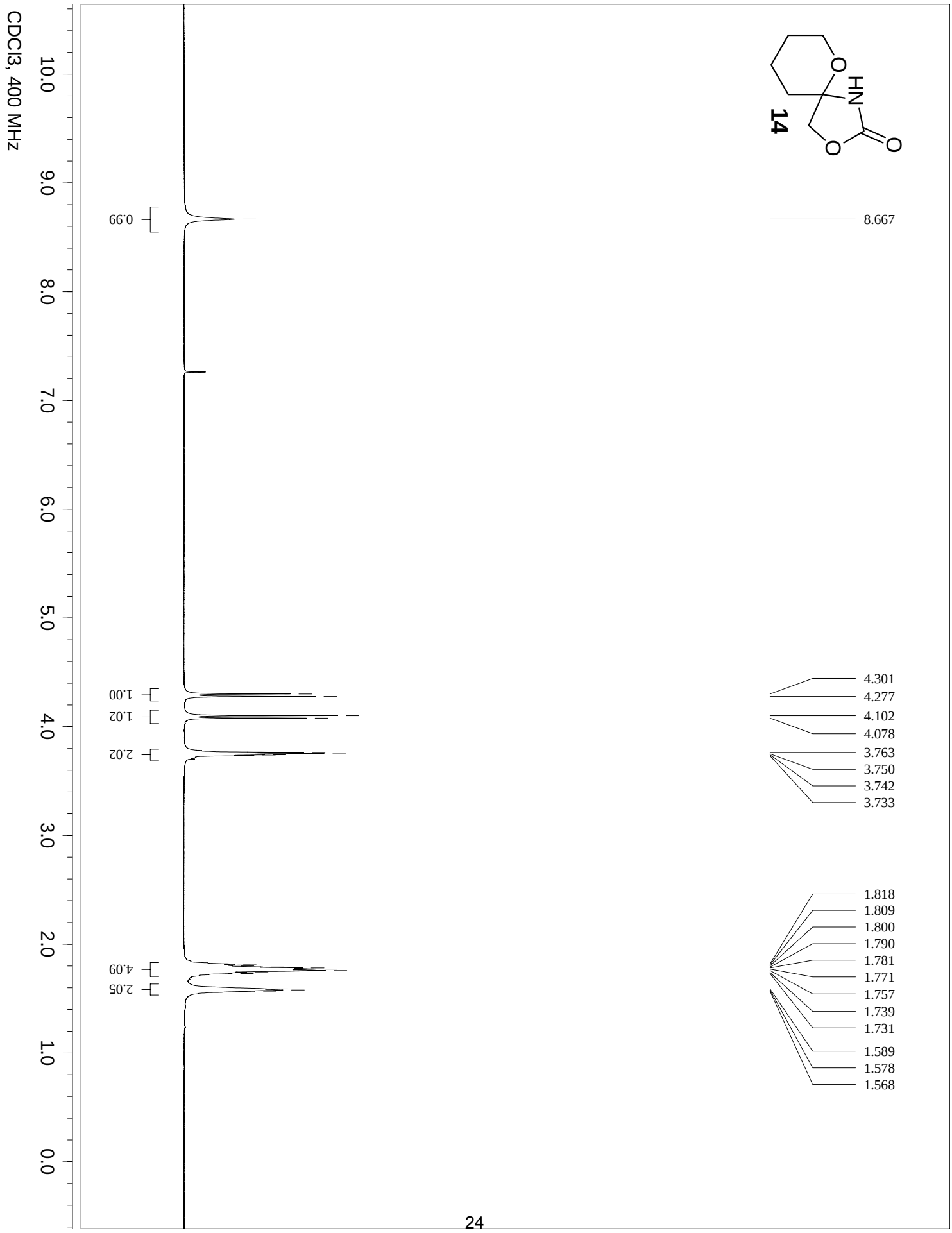
129.336
127.893
125.542
124.762
80.583
77.318
77.000
76.682
61.190
38.821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7.0
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3.0
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0.0
0.99
1.00
1.02
2.02
4.09
2.05
14
O
HN
O
O
8.667
4.301
4.277
4.102
4.078
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3.750
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3.733
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1.731
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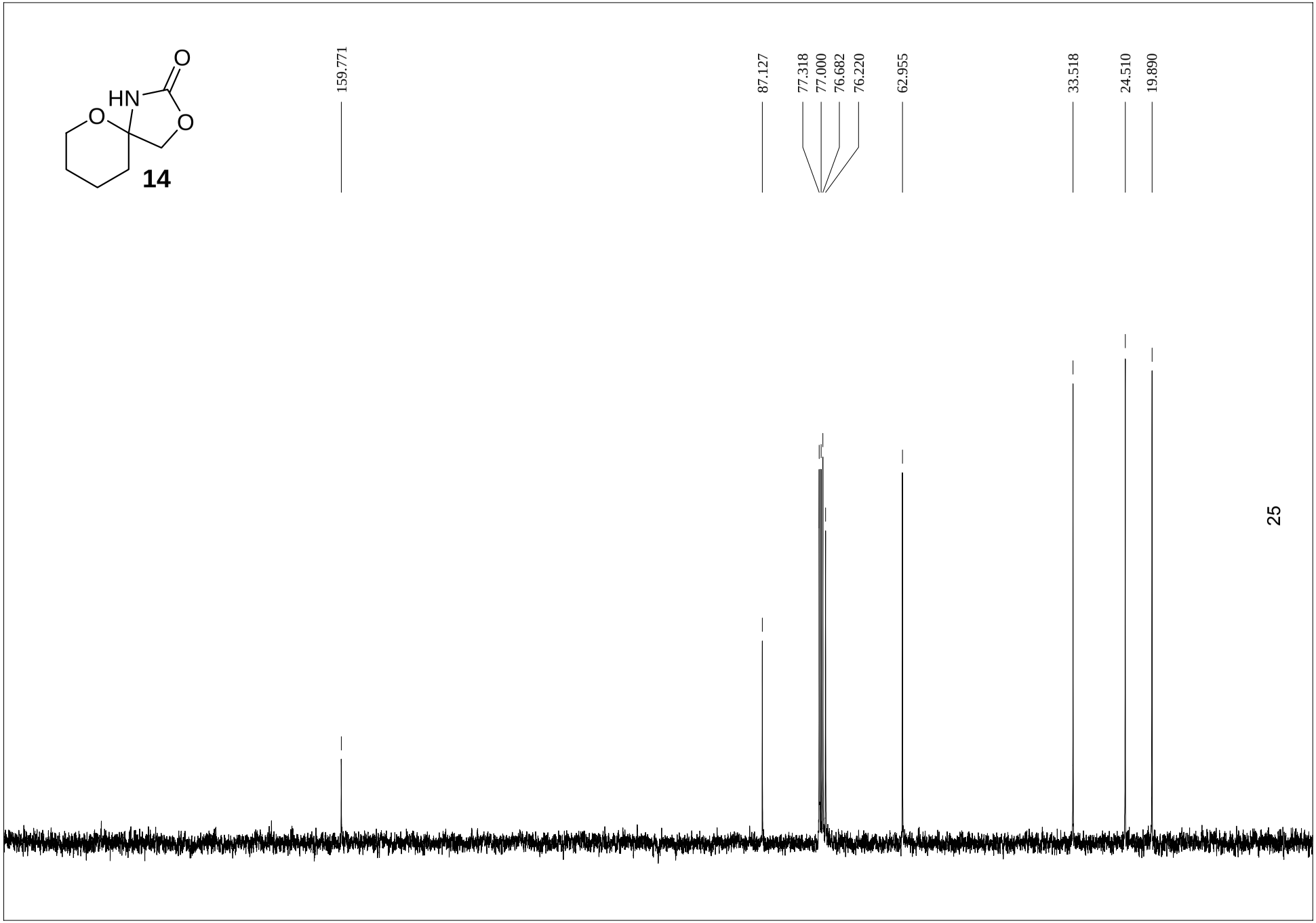
1.578
1.568


O
HN
O
O
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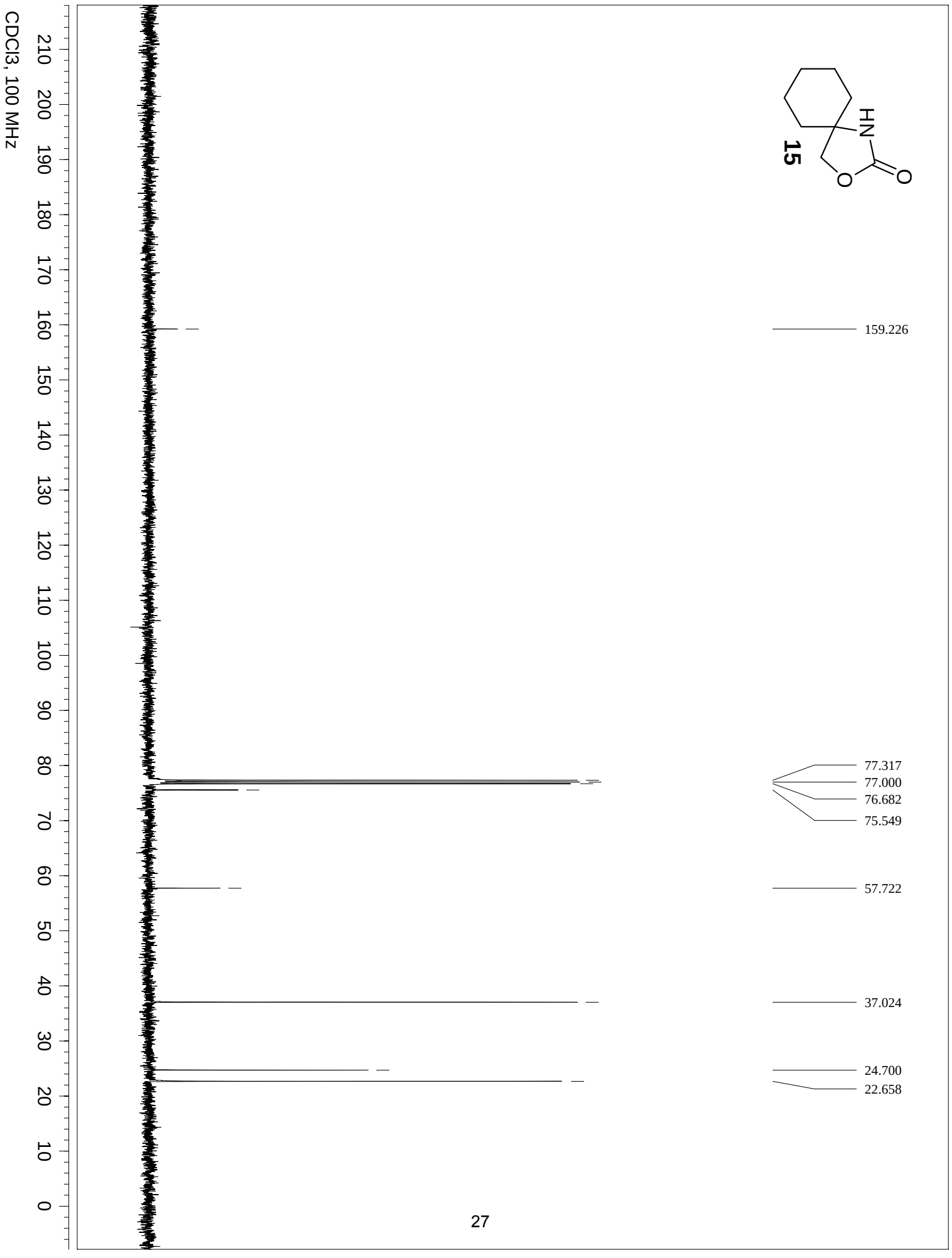
77.318
77.000
76.682
76.220
62.955
33.518
24.510
19.890
25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
CDCl3, 100 MHz

CDCl3, 400 MHz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.98
2.00
10.26
7.344
4.051
1.686
1.668
1.645
1.620
1.614
1.572
1.553
1.530
1.467
1.446
1.352
1.348
1.346
1.334
1.326
HN
O
O
15


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
HN
O
O
15
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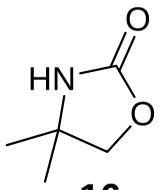
77.317
77.000
76.682
75.549
57.722
37.024
24.700
22.658

CDCl3, 400 MHz



16

158.911

76.599

54.858

27.166

76.599

77.00

76.50

76.00

29

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

CDCl3, 100 MHz

CDCl3, 400 MHz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.92
1.00
1.02
0.96
2.09
4.23
3.05
17
HN
O
O
6.256
4.494
4.473
4.452
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1.493
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1.334
1.317
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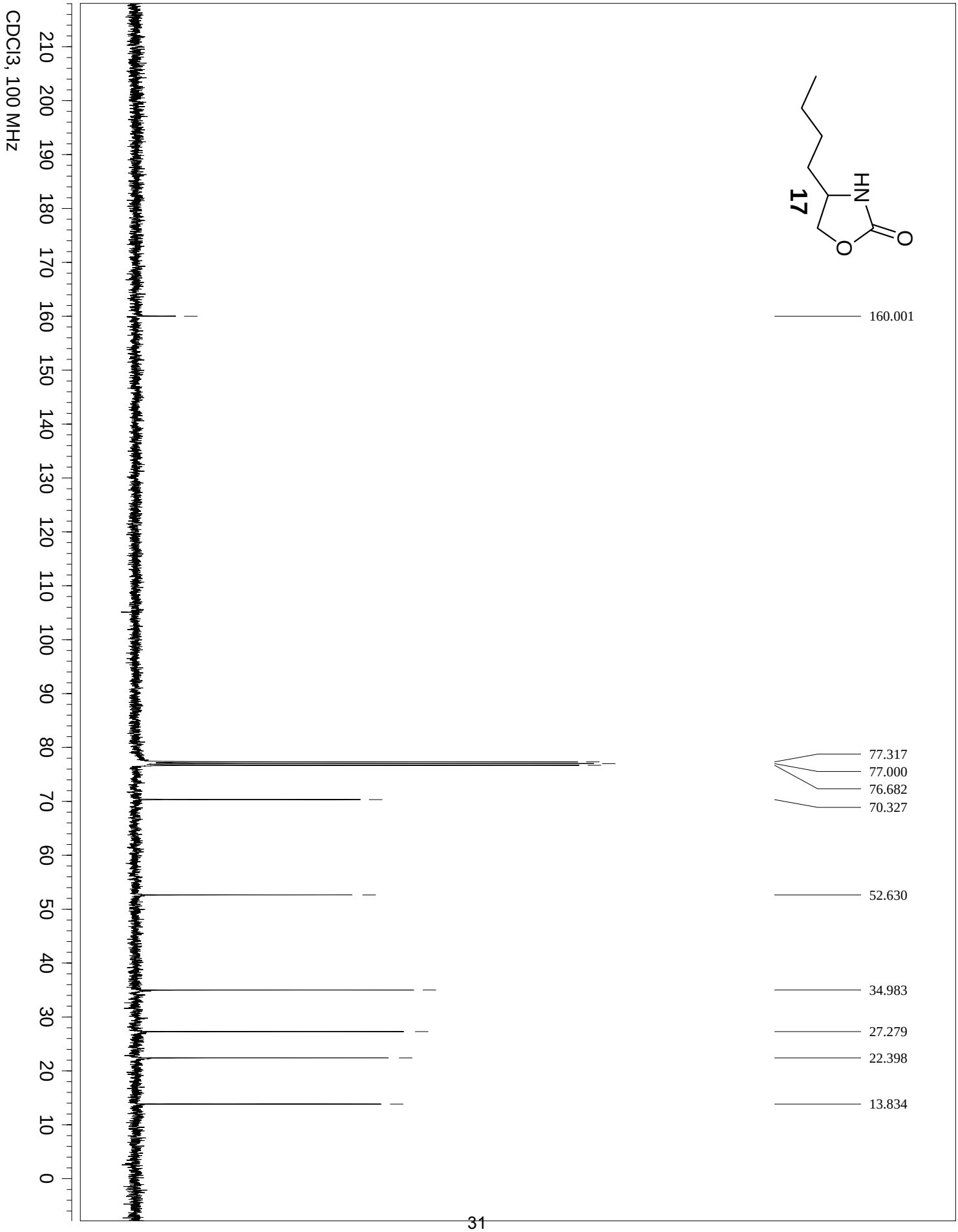
0.904
0.887


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
17
HN
O
O
160.001
77.317
77.000
76.682
70.327
52.630
34.983
27.279
22.398
13.834

CDCl3, 400 MHz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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0.0
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O
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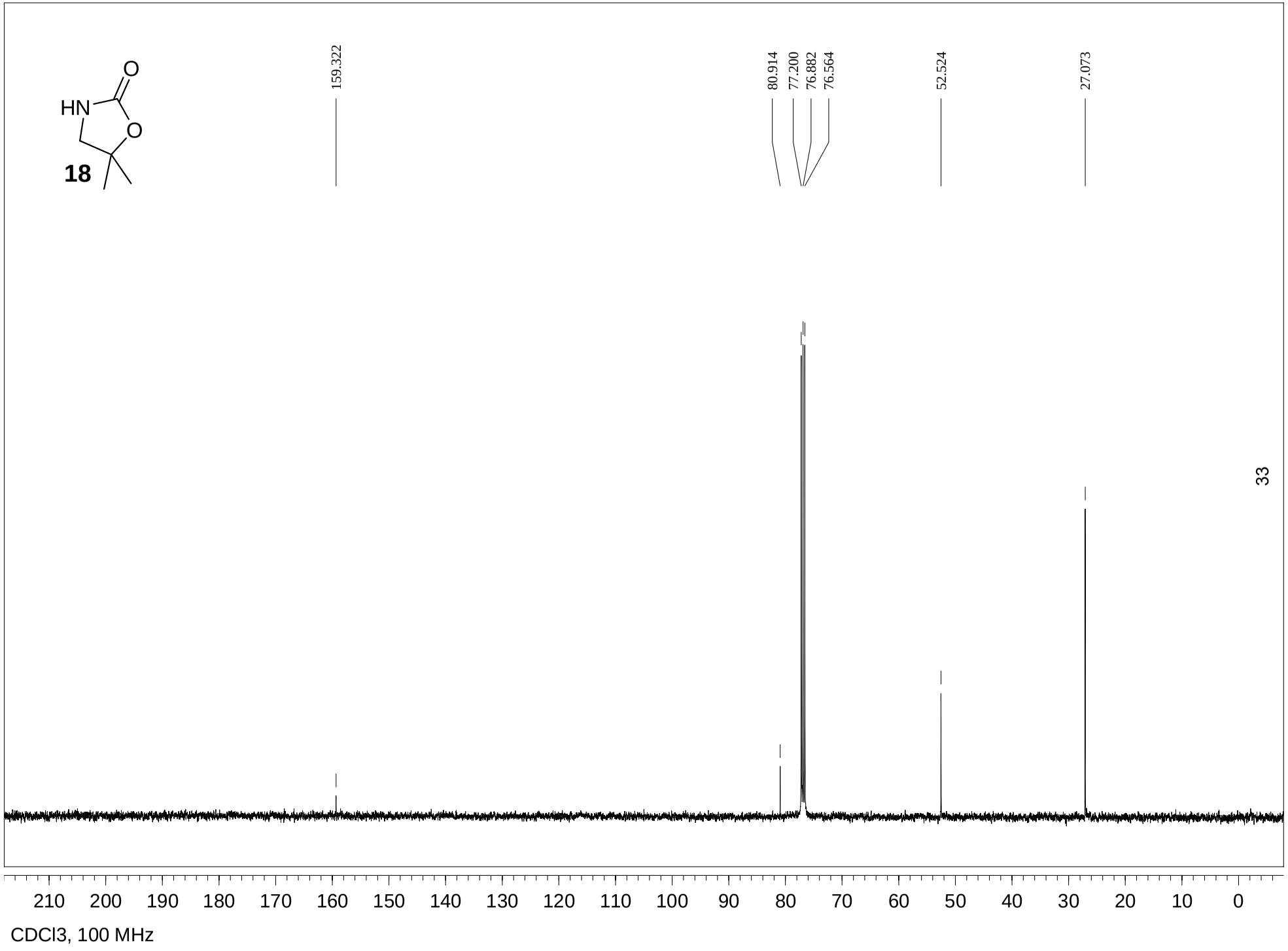
2.00
6.10
5.752
3.234
1.362


O
HN
O
18
159.322
80.914
77.200
76.882
76.564
52.524
27.073
33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
CDCl3, 100 MHz

CDCl3, 400 MHz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.52
0.93
0.93
2.20
3.00
3.00
5.695
4.151
4.130
4.049
4.028
1.642
1.629
1.623
1.604
1.586
1.326
0.969
0.950
0.932
HN
O
O
19

CDCl3, 100 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
HN
O
O
19
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77.000
76.682
75.329
58.041
33.100
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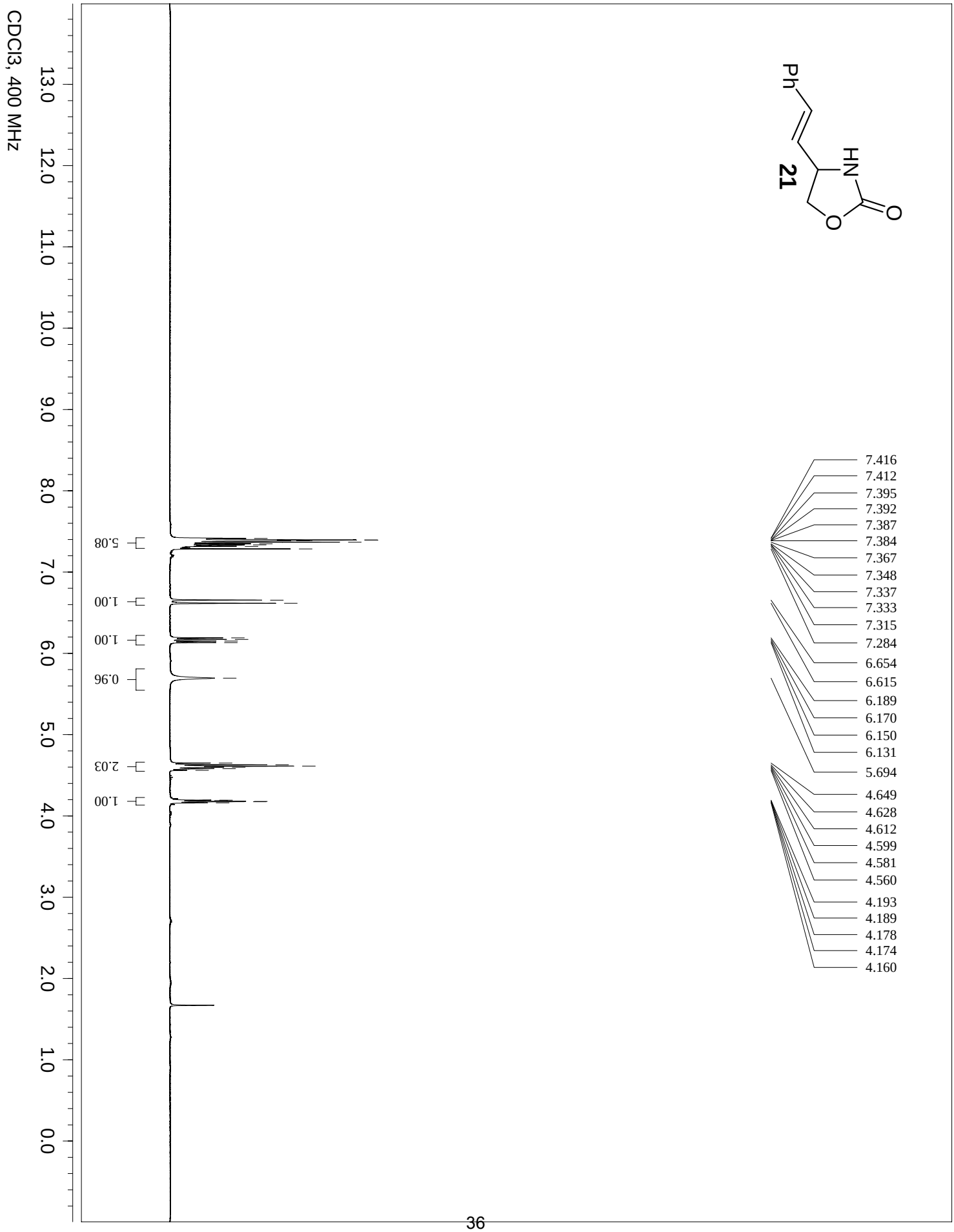
8.006


CDCl3, 400 MHz
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10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
5.08
1.00
1.00
0.96
2.03
1.00
Ph
HN
O
O
21
7.416
7.412
7.395
7.392
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7.384
7.367
7.348
7.337
7.333
7.315
7.284
6.654
6.615
6.189
6.170
6.150
6.131
5.694
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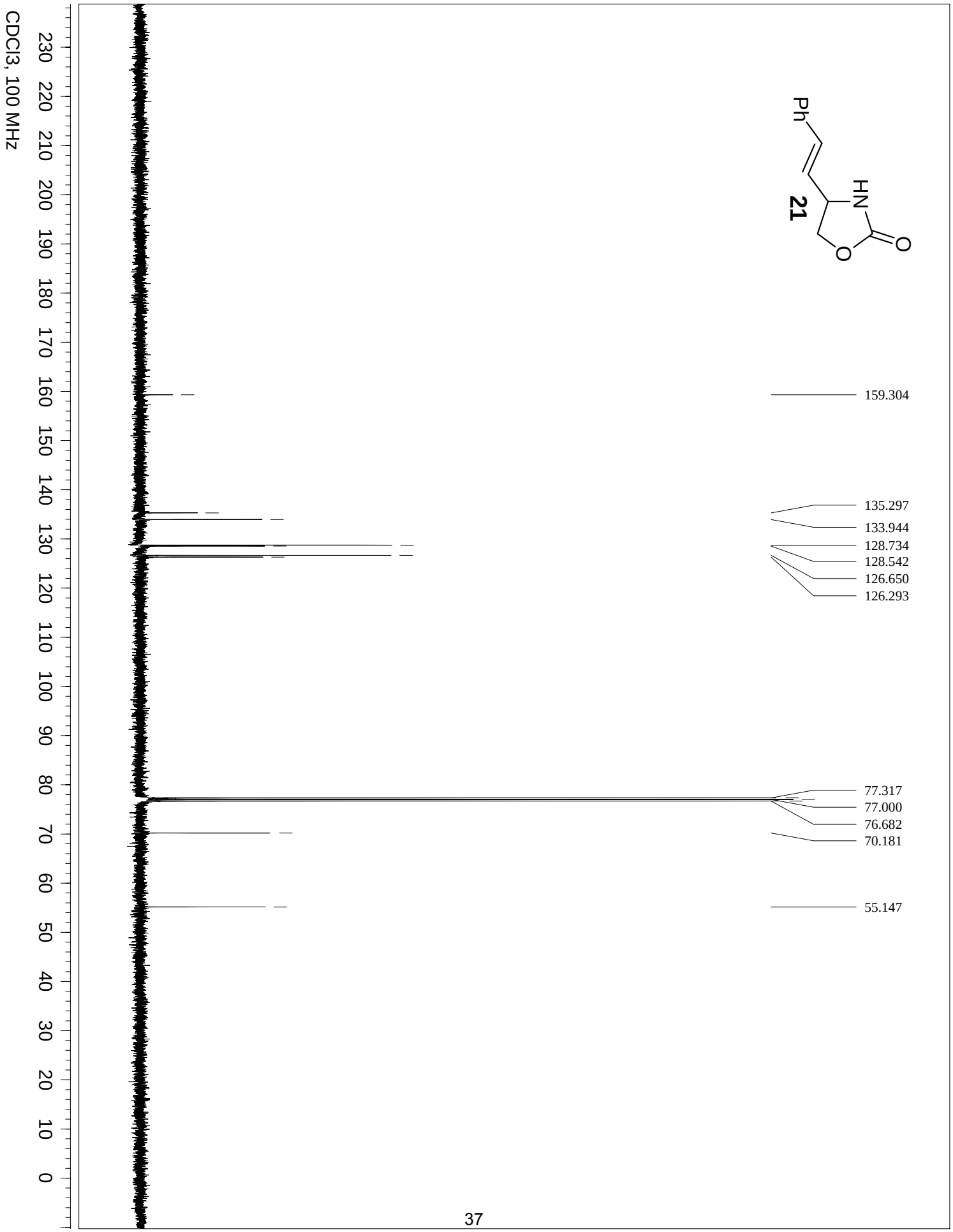
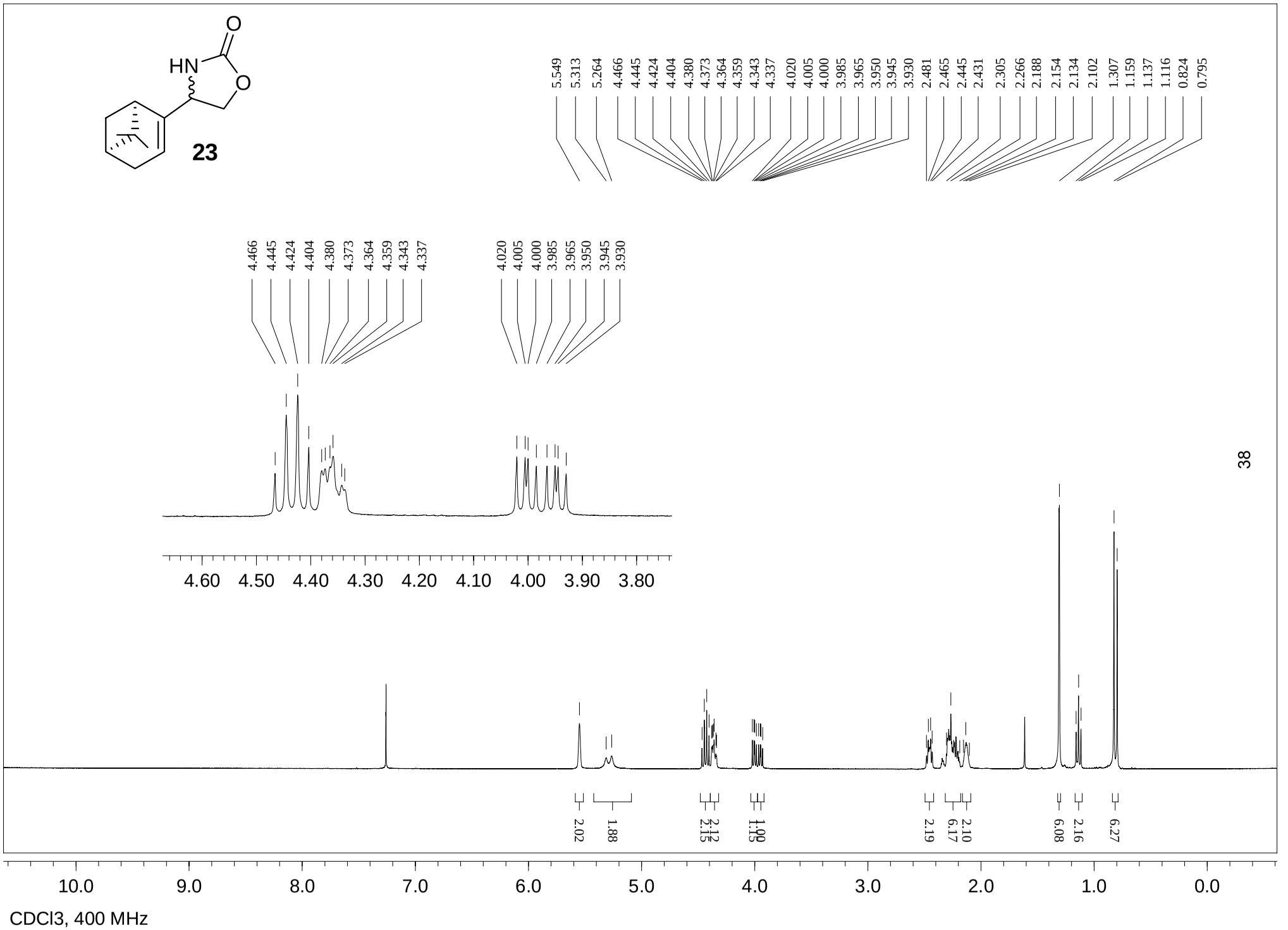
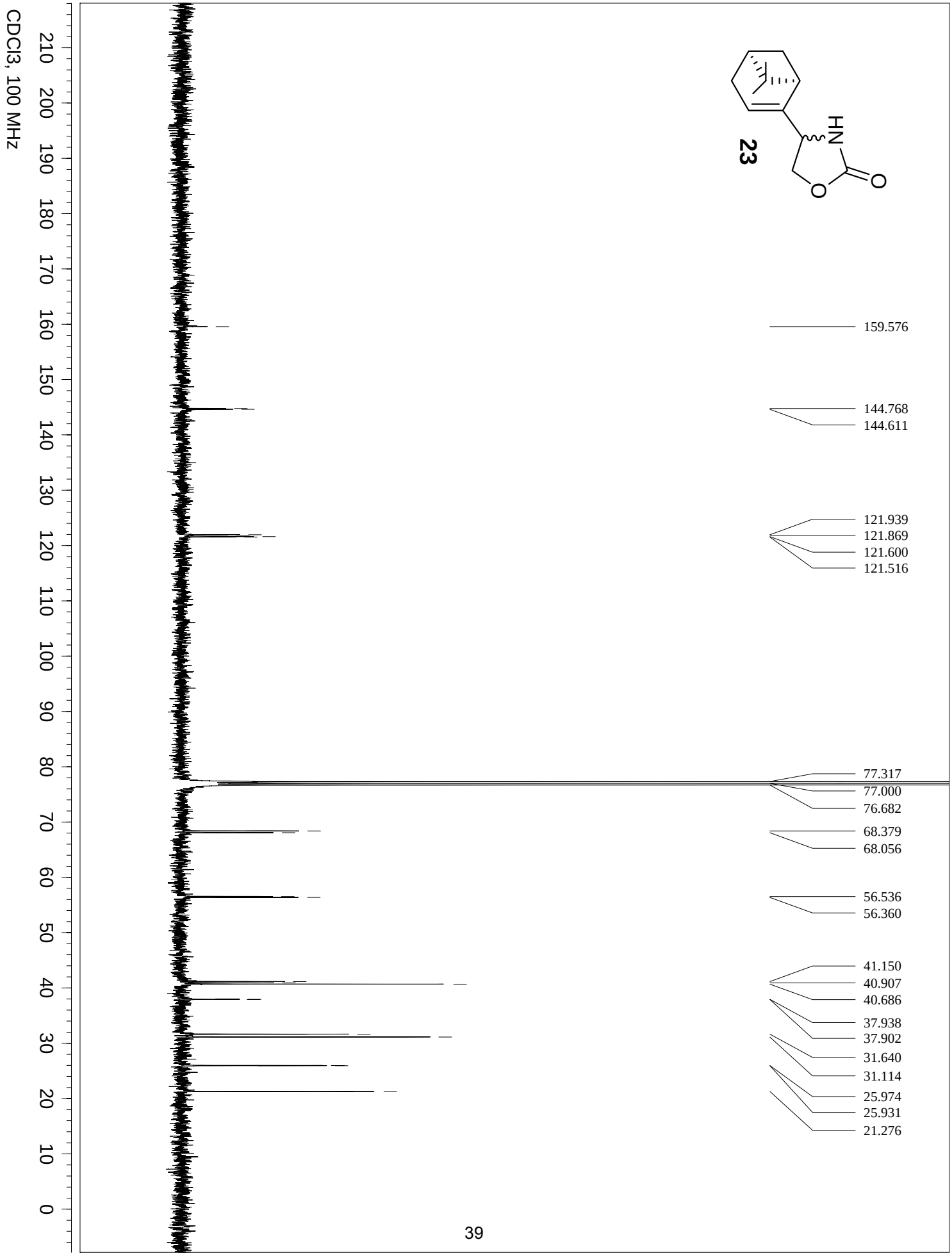
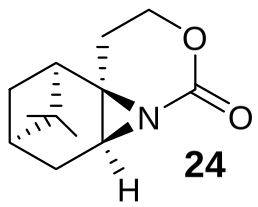
4.581
4.560
4.193
4.189
4.178
4.174
4.160


CDCl3, 100 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Ph
HN
O
O
21
159.304
135.297
133.944
128.734
128.542
126.650
126.293
77.317
77.000
76.682
70.181
55.147

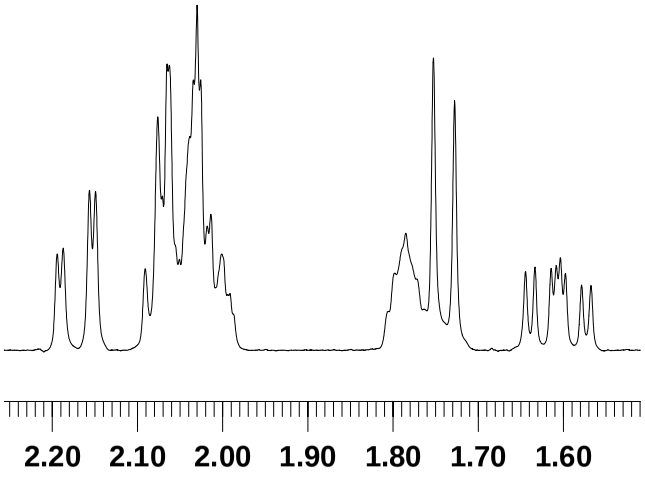

HN
O
O
O
23
5.549
5.313
5.264
4.466
4.445
4.424
4.404
4.380
4.373
4.364
4.359
4.343
4.337
4.020
4.005
4.000
3.985
3.965
3.950
3.945
3.930
2.481
2.465
2.445
2.431
2.305
2.266
2.188
2.154
2.134
2.102
1.307
1.159
1.137
1.116
0.824
0.795
4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90
3.80
2.02
1.88
2.12
2.15
1.09
1.09
2.19
6.17
2.10
6.08
2.16
6.27
38
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CDCl3, 400 MHz


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
23
HN
O
O
159.576
144.768
144.611
121.939
121.869
121.600
121.516
77.317
77.000
76.682
68.379
68.056
56.536
56.360
41.150
40.907
40.686
37.938
37.902
31.640
31.114
25.974
25.931
21.276

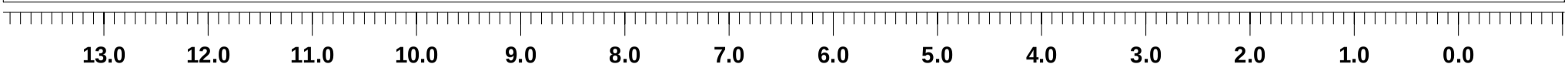


24

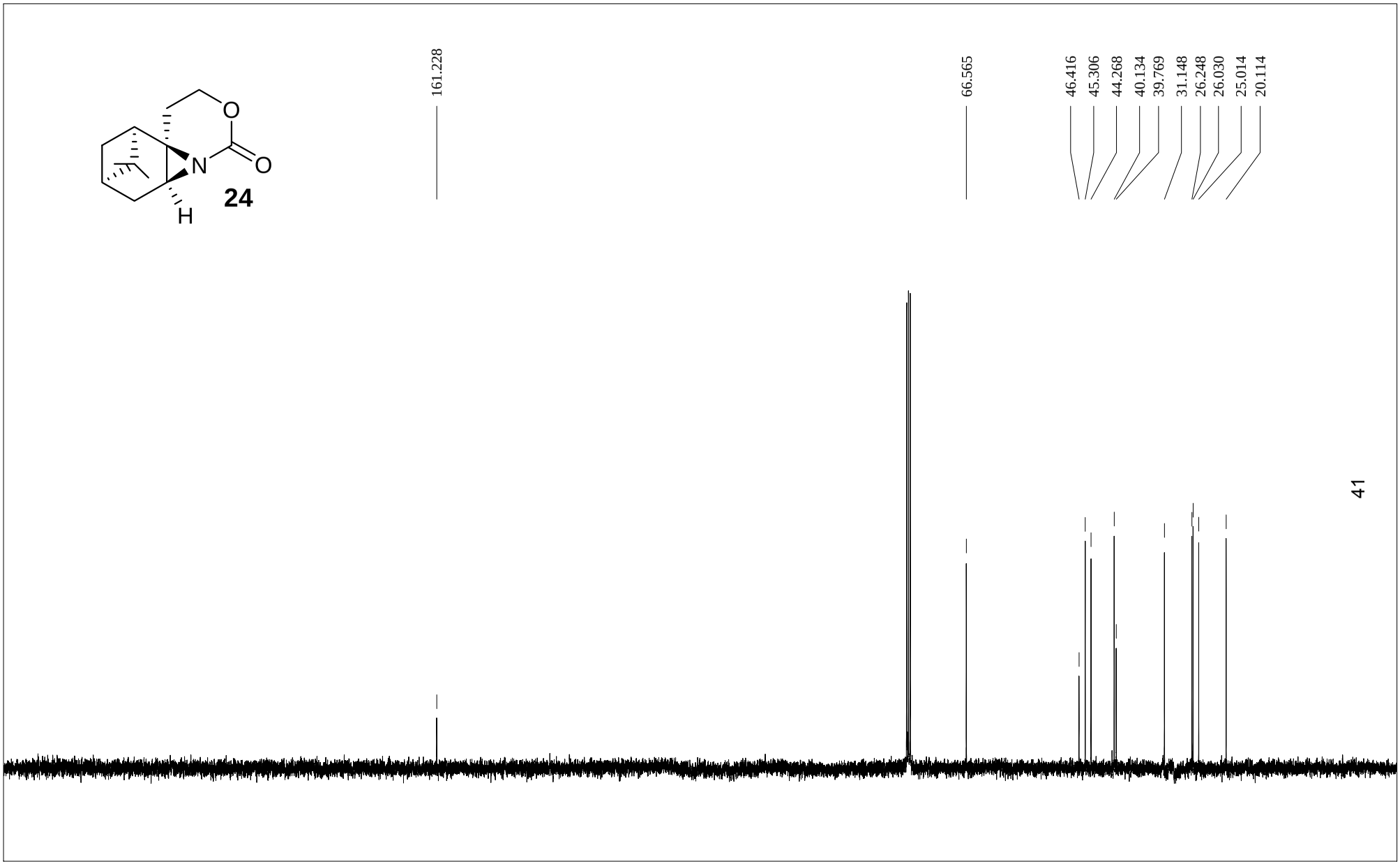
4.32 4.31 4.29 4.29 4.26 4.26 4.25 4.25 4.24 4.23 4.22 4.22 4.21 4.21 2.59 2.58 2.19 2.19 2.16 2.15 1.75 1.73 1.64 1.63 1.61 1.61 1.60 1.60 1.58 1.57 1.31 0.98



40



CDCl3, 400 MHz

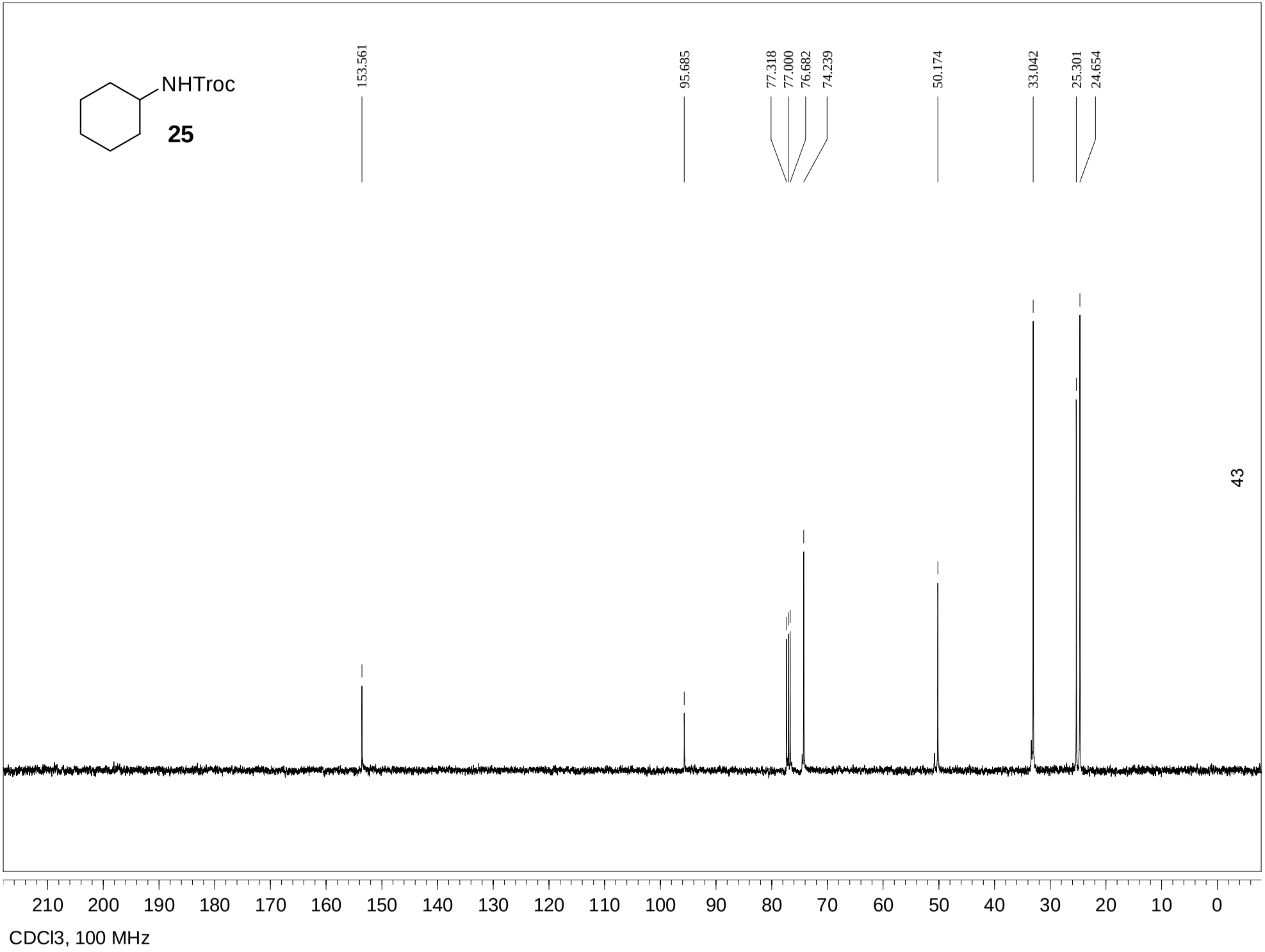

161.228
66.565
46.416
45.306
44.268
40.134
39.769
31.148
26.248
26.030
25.014
20.114
O
N
O
H
24
41
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
CDCl3, 100 MHz

CDCl3, 400 MHz, 50 °C

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

0.98
2.00
0.94
2.13
2.14
1.08
2.15
3.18

4.922
4.679
3.536
3.464
3.444
1.958
1.938
1.917
1.731
1.713
1.689
1.669
1.608
1.599
1.567
1.548
1.386
1.348
1.318
1.277
1.221
1.184
1.157
1.103

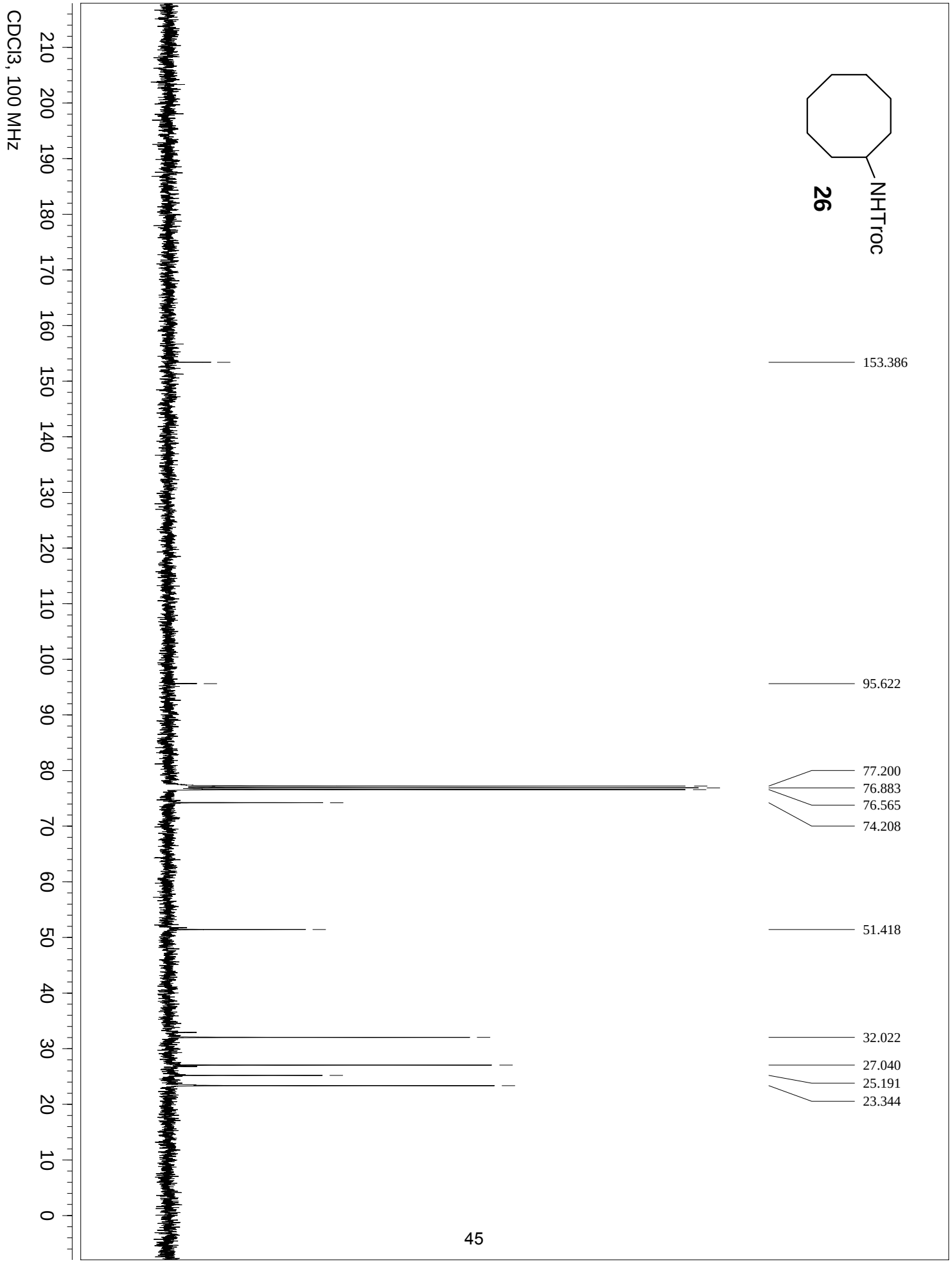

NHTroc
25
153.561
95.685
77.318
77.000
76.682
74.239
50.174
33.042
25.301
24.654
43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
CDCl3, 100 MHz

CDCl3, 400 MHz, 50 °C

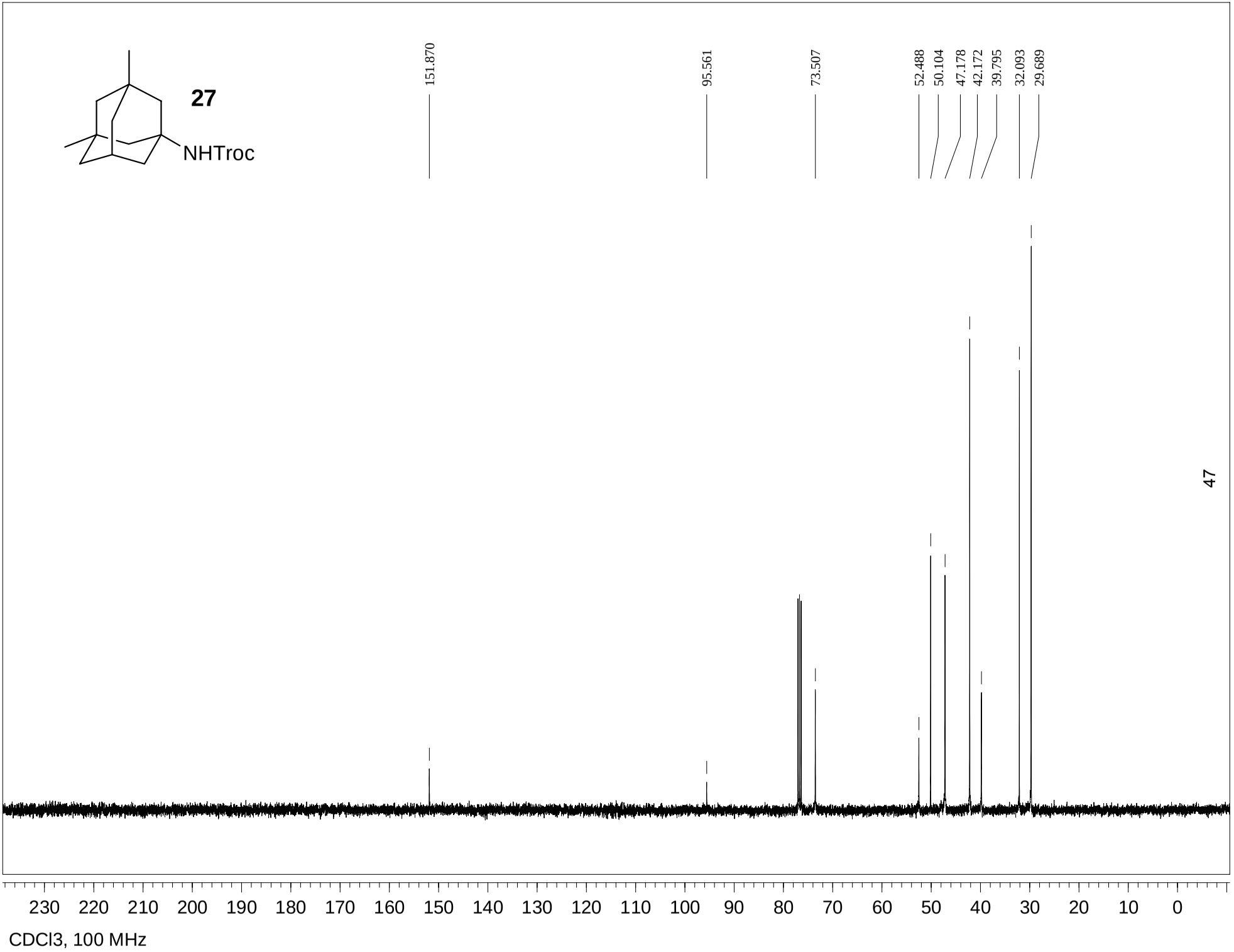
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

0.98
2.00
0.96
2.08
12.80

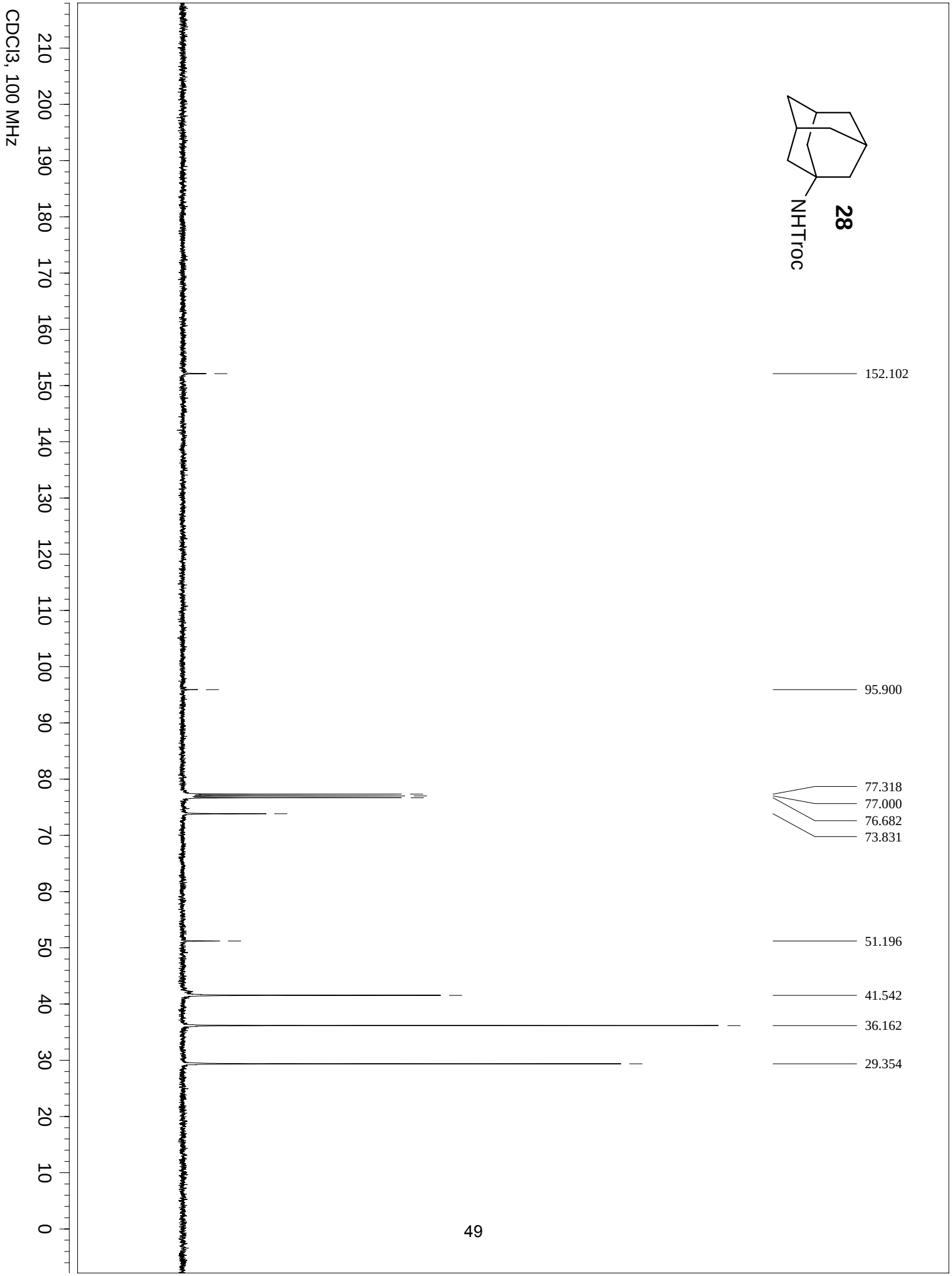
5.080
4.646
3.708
3.699
3.688
1.850
1.842
1.829
1.818
1.807
1.794
1.646
1.622
1.606
1.582
1.562
1.540
1.527
1.522
1.504
1.481
1.457


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
NHTroc
26
153.386
95.622
77.200
76.883
76.565
74.208
51.418
32.022
27.040
25.191
23.344

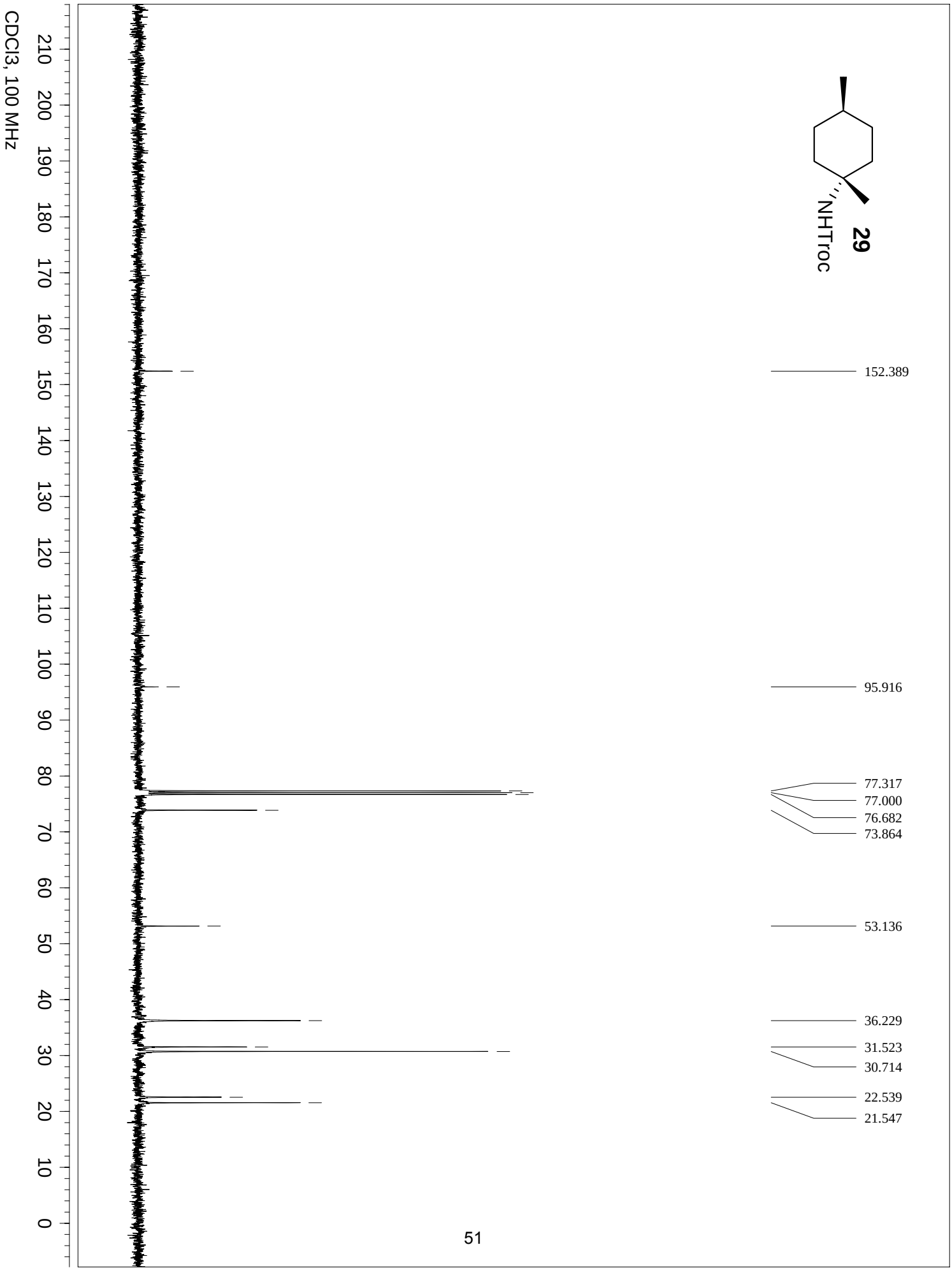
CDCl3, 400 MHz
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
NHTroc
27
0.95
1.84
0.98
2.00
4.07
4.06
2.02
6.04
4.884
4.658
2.186
2.179
2.171
2.163
2.155
1.807
1.800
1.647
1.617
1.581
1.397
1.366
1.322
1.291
1.164
0.867

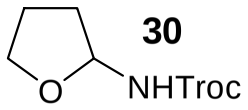

27
NHTroc
151.870
95.561
73.507
52.488
50.104
47.178
42.172
39.795
32.093
29.689
47
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
CDCl3, 100 MHz

CDCl3, 400 MHz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
28
NHTroc
1.04
2.00
3.12
6.26
6.42
4.826
4.652
2.092
1.958
1.952
1.670


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
NHTroc
28
152.102
95.900
77.318
77.000
76.682
73.831
51.196
41.542
36.162
29.354

CDCl3, 400 MHz, 50 °C

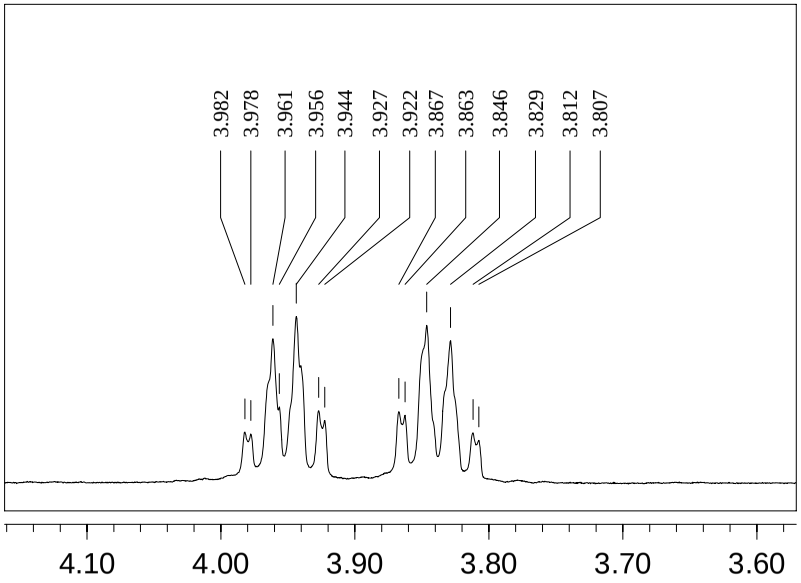

CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
NHTroc
29
152.389
95.916
77.317
77.000
76.682
73.864
53.136
36.229
31.523
30.714
22.539
21.547



30

NHTroc

5.608 5.604 5.597 5.592 5.587 5.582 5.576 5.571 5.566 5.559 5.555 5.334 4.776 4.750 4.728 4.727 4.723 3.982 3.978 3.961 3.956 3.944 3.927 3.922 3.867 3.863 3.846 3.829 3.812 3.807 2.278 2.257 2.241 2.224 2.208 2.203 2.191 2.019 1.999 1.972 1.923 1.824 1.808 1.792 1.740

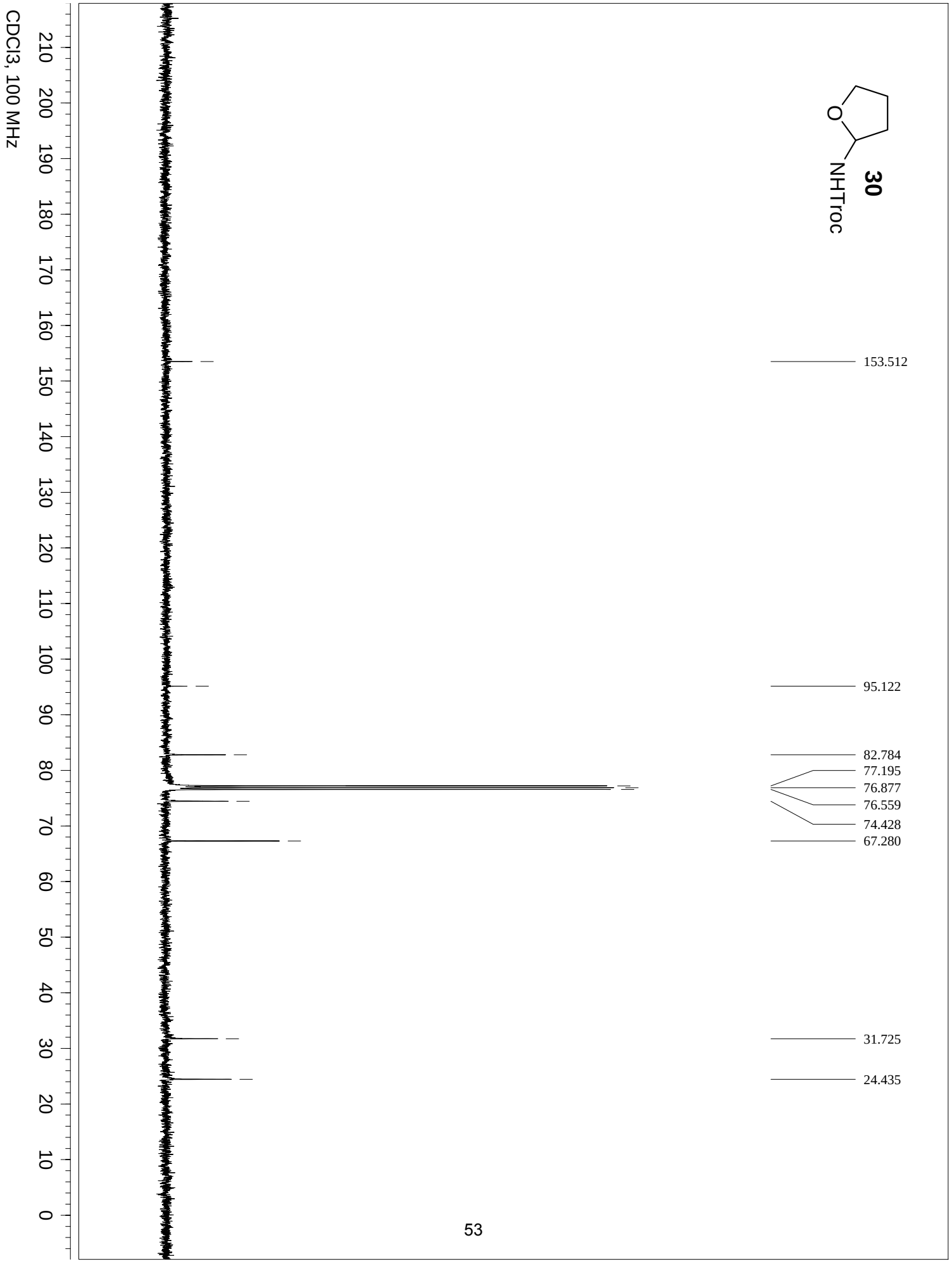


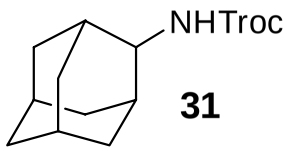
52

1.00 0.81 2.03 1.07 1.08 1.15 2.08 1.11

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

CDCl3, 400 MHz, 45 °C


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
NHTroc
30
153.512
95.122
82.784
77.195
76.877
76.559
74.428
67.280
31.725
24.435



31

153.363
95.437
74.059
55.046
37.106
36.712
31.637
31.298
26.767
26.673

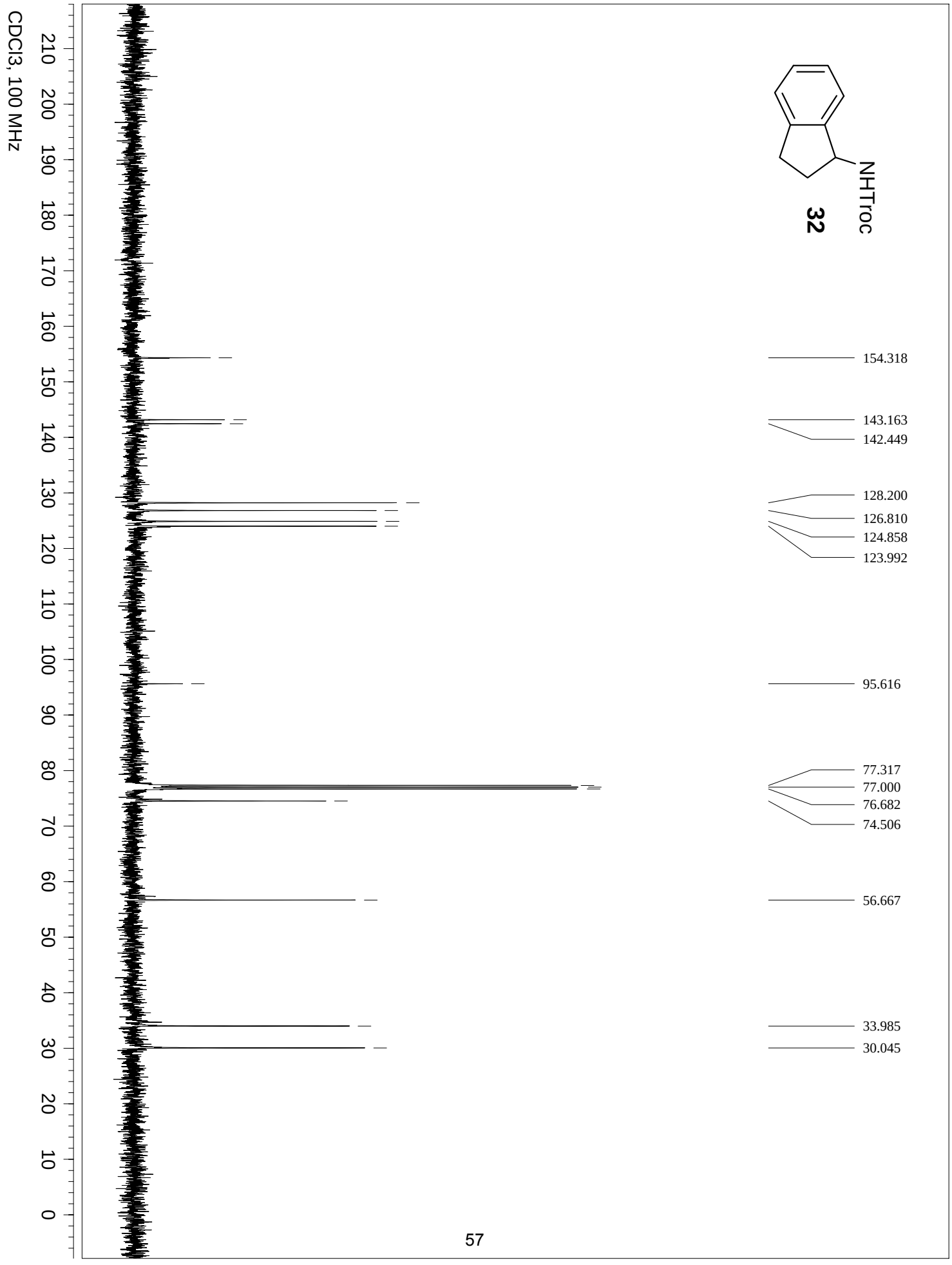
54

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

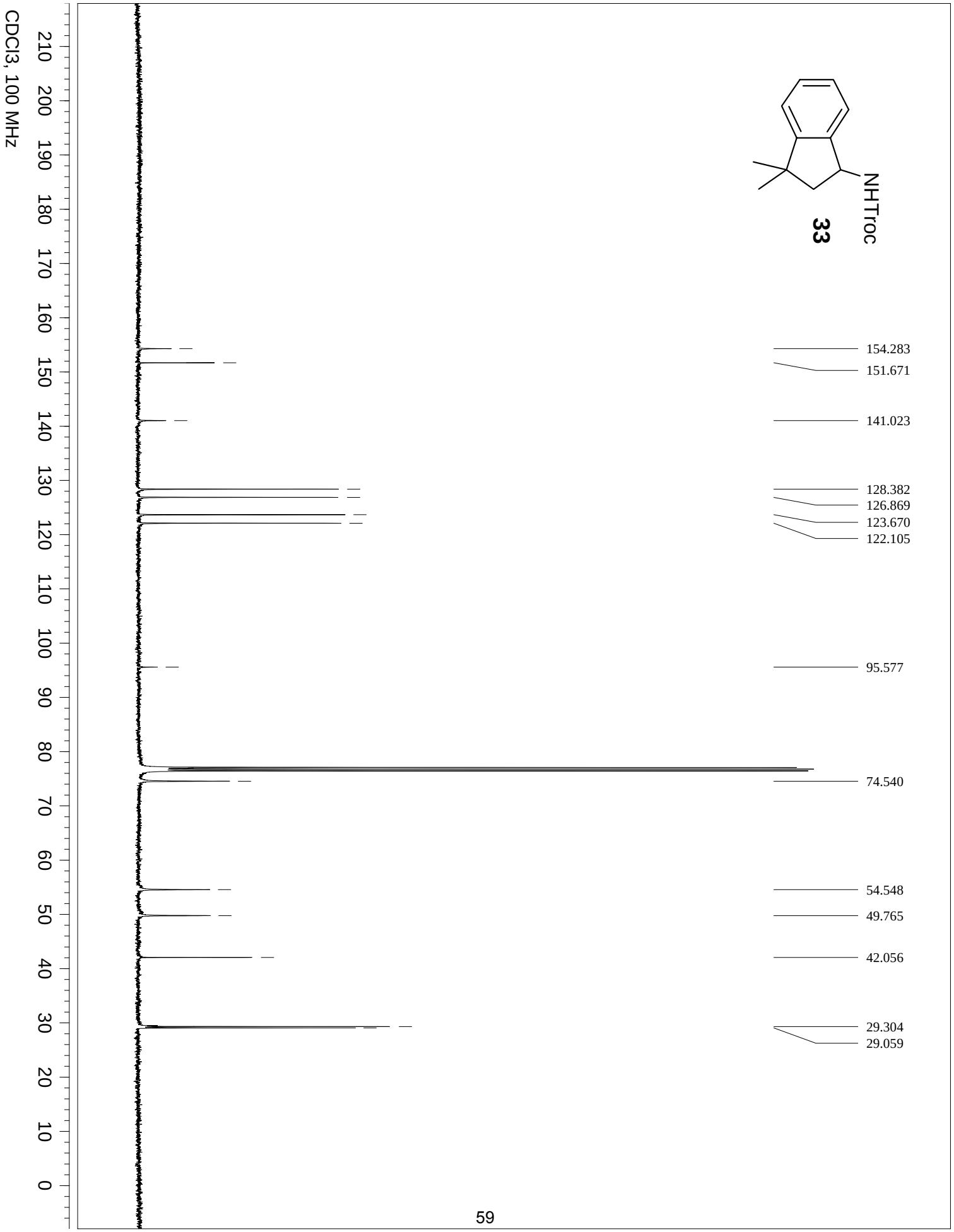
CDCl3, 100 MHz

CDCl3, 400 MHz, 45 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.78
2.03
1.00
2.17
11.77
2.15
5.251
4.733
3.849
3.829
1.997
1.867
1.846
1.808
1.762
1.676
1.643
NHTroc
31

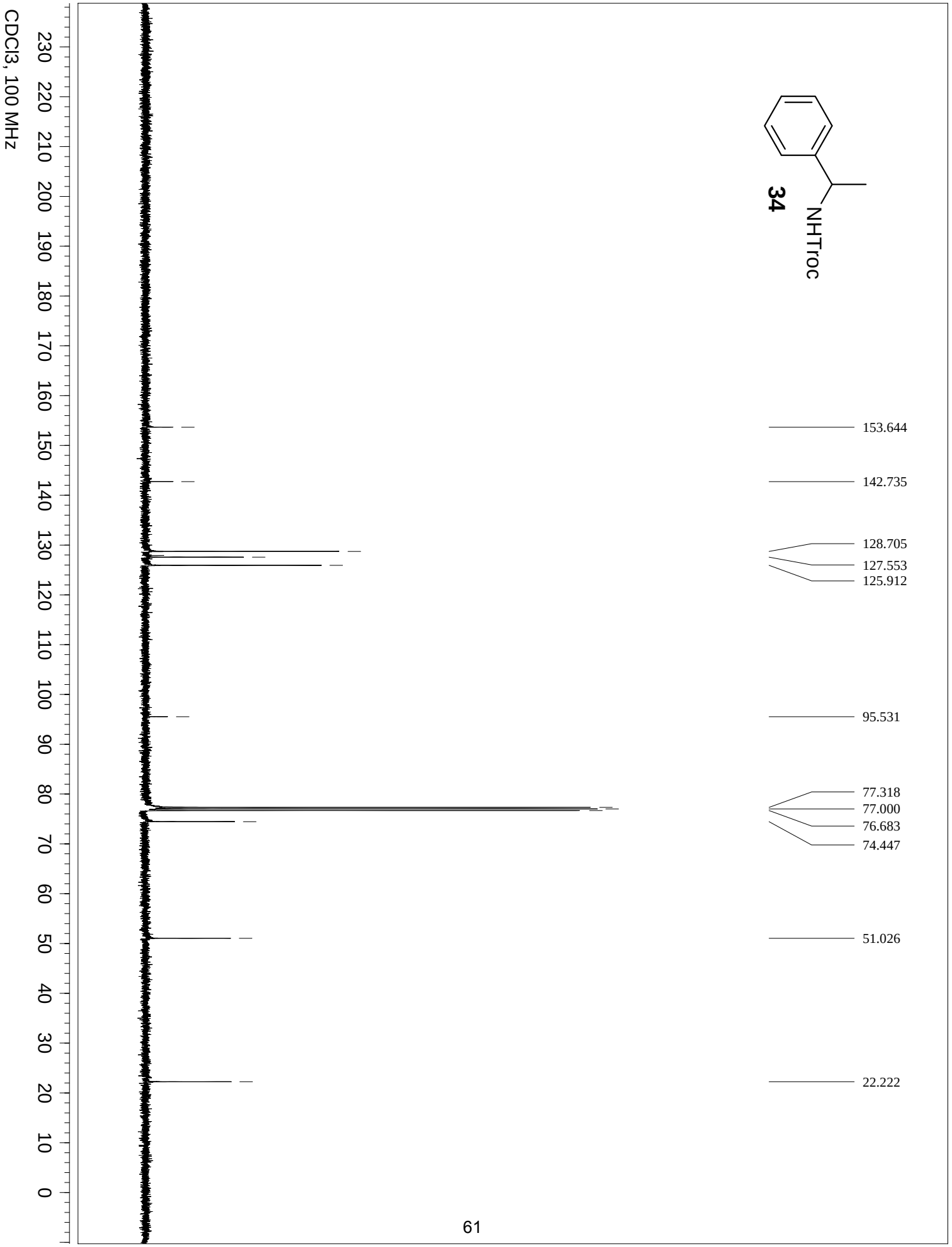
CDCl3, 400 MHz, 40 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
3.20
1.02
0.75
2.00
1.18
1.18
1.16
1.16
NHTroc
32
7.355
7.339
7.263
7.252
7.230
7.219
5.300
5.280
5.261
5.242
5.151
4.828
4.797
4.786
4.755
3.053
3.042
3.031
3.021
3.013
3.003
2.991
2.981
2.923
2.903
2.883
2.863
2.843
2.674
2.664
2.655
2.643
2.633
2.623
2.613
2.603
2.592
1.944
1.924
1.905
1.892
1.873
1.853
5.50
5.00
4.50


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
NHTroc
32
154.318
143.163
142.449
128.200
126.810
124.858
123.992
95.616
77.317
77.000
76.682
74.506
56.667
33.985
30.045

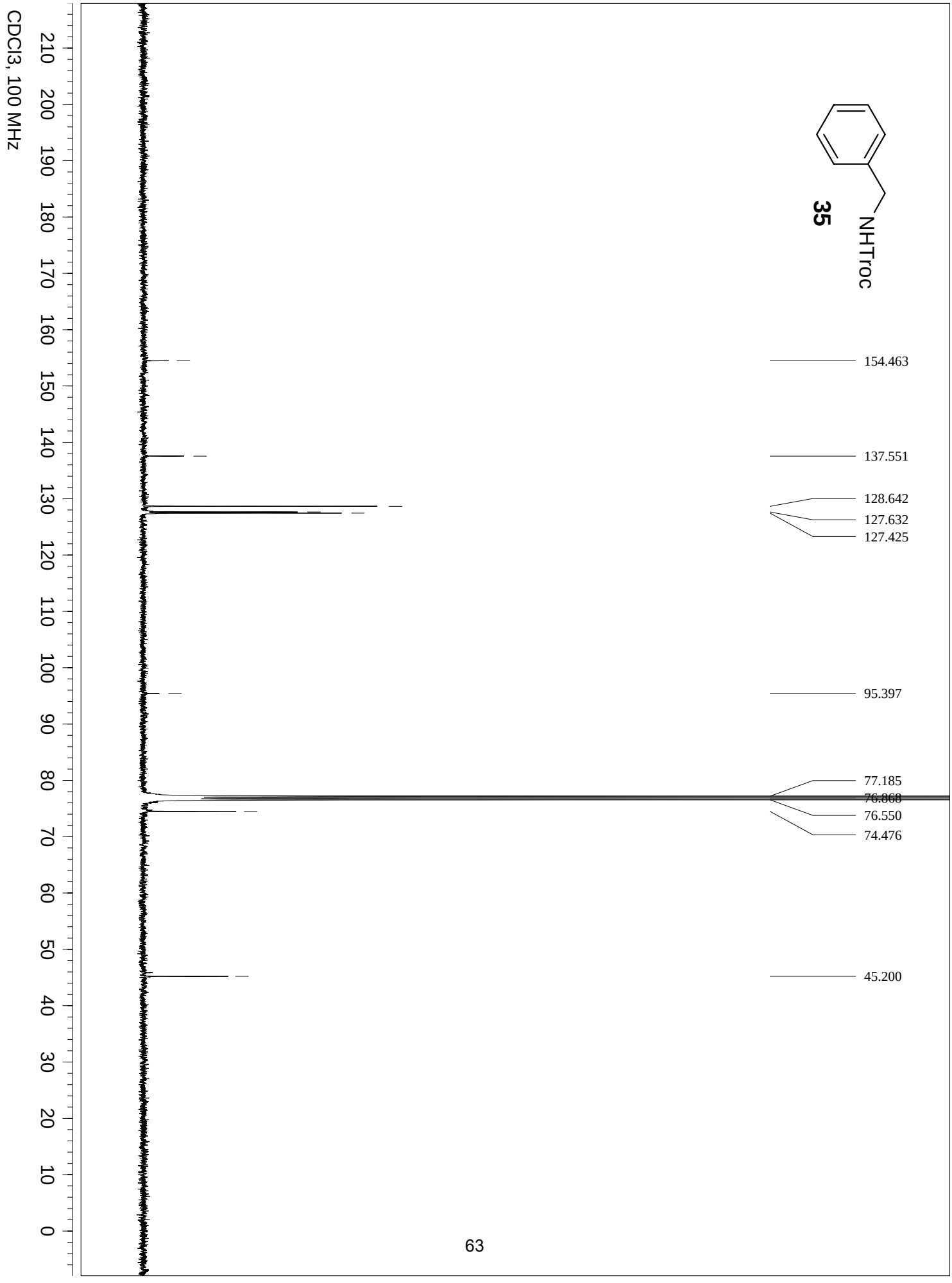
CDCl3, 400 MHz, 50 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.29
1.00
0.86
2.02
1.07
0.99
3.00
3.05
NHTroc
33
7.316
7.299
7.288
7.287
7.264
7.254
7.238
7.217
7.209
7.199
7.191
5.352
5.332
5.311
5.291
5.179
4.843
4.813
4.787
4.757
2.525
2.507
2.494
2.475
1.780
1.759
1.748
1.728
1.393
1.232


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
NHTroc
33
154.283
151.671
141.023
128.382
126.869
123.670
122.105
95.577
74.540
54.548
49.765
42.056
29.304
29.059

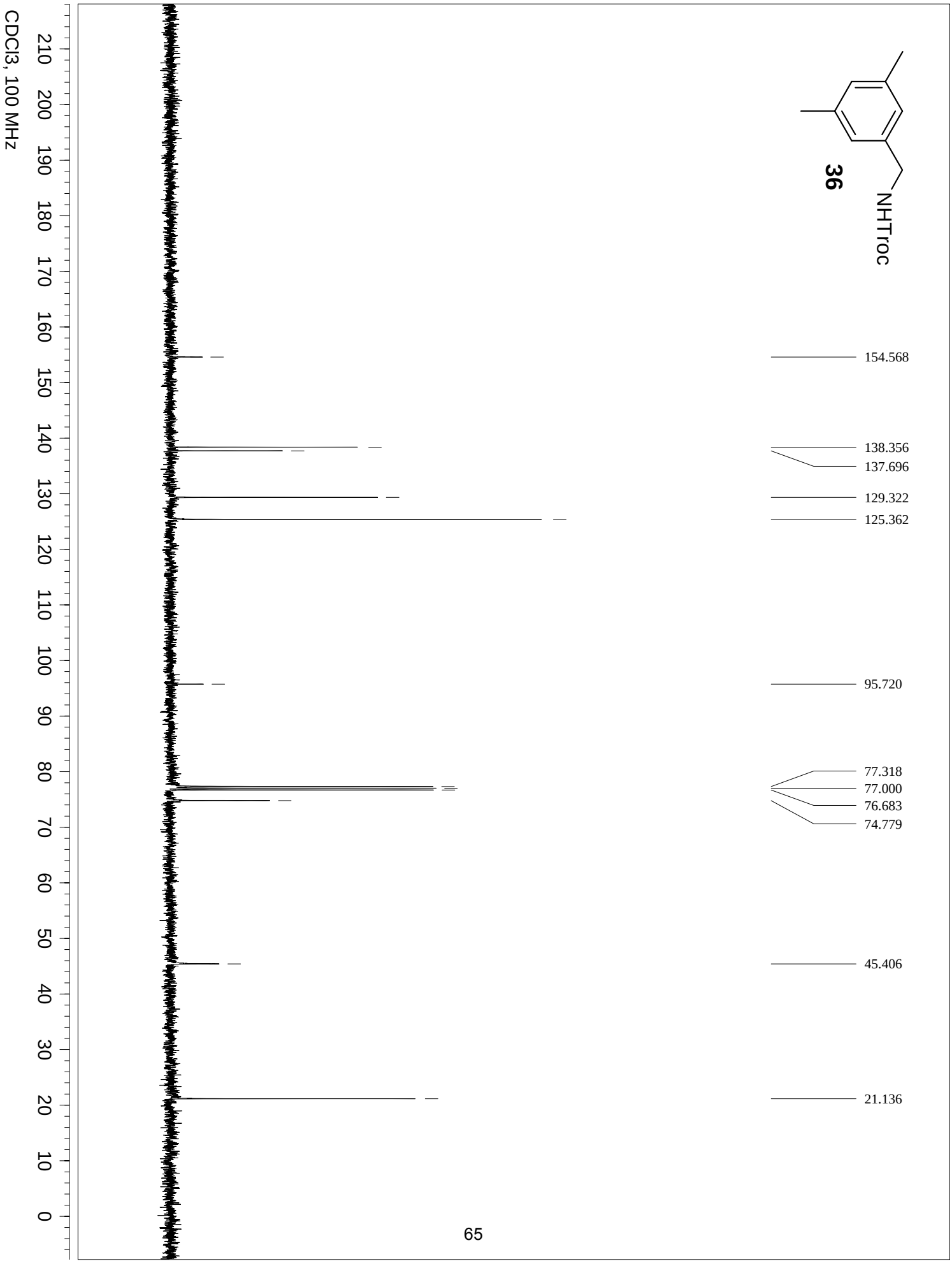
CDCl3, 400 MHz, 40 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.97
0.96
1.00
2.13
3.15
34
NHTroc
7.379
7.376
7.372
7.362
7.357
7.355
7.341
7.337
7.325
7.321
7.301
7.296
7.287
7.284
7.279
7.271
7.262
7.258
5.288
4.927
4.909
4.891
4.873
4.855
4.766
4.736
4.717
4.688
1.550
1.533

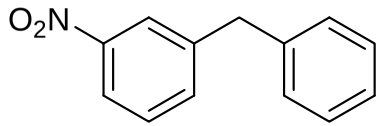

CDCl3, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
34
NHTroc
153.644
142.735
128.705
127.553
125.912
95.531
77.318
77.000
76.683
74.447
51.026
22.222

CDCl3, 400 MHz


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
35
NHTroc
154.463
137.551
128.642
127.632
127.425
95.397
77.185
76.868
76.550
74.476
45.200

CDCl3, 400 MHz, 50 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.76
0.62
2.00
2.20
6.10
6.935
6.922
6.920
5.265
4.775
4.359
4.345
2.321
36
NHTroc


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
36
NHTroc
154.568
138.356
137.696
129.322
125.362
95.720
77.318
77.000
76.683
74.779
45.406
21.136



148.125
142.847
139.001
134.689
128.971
128.542
128.465
126.379
123.345
120.977

41.168

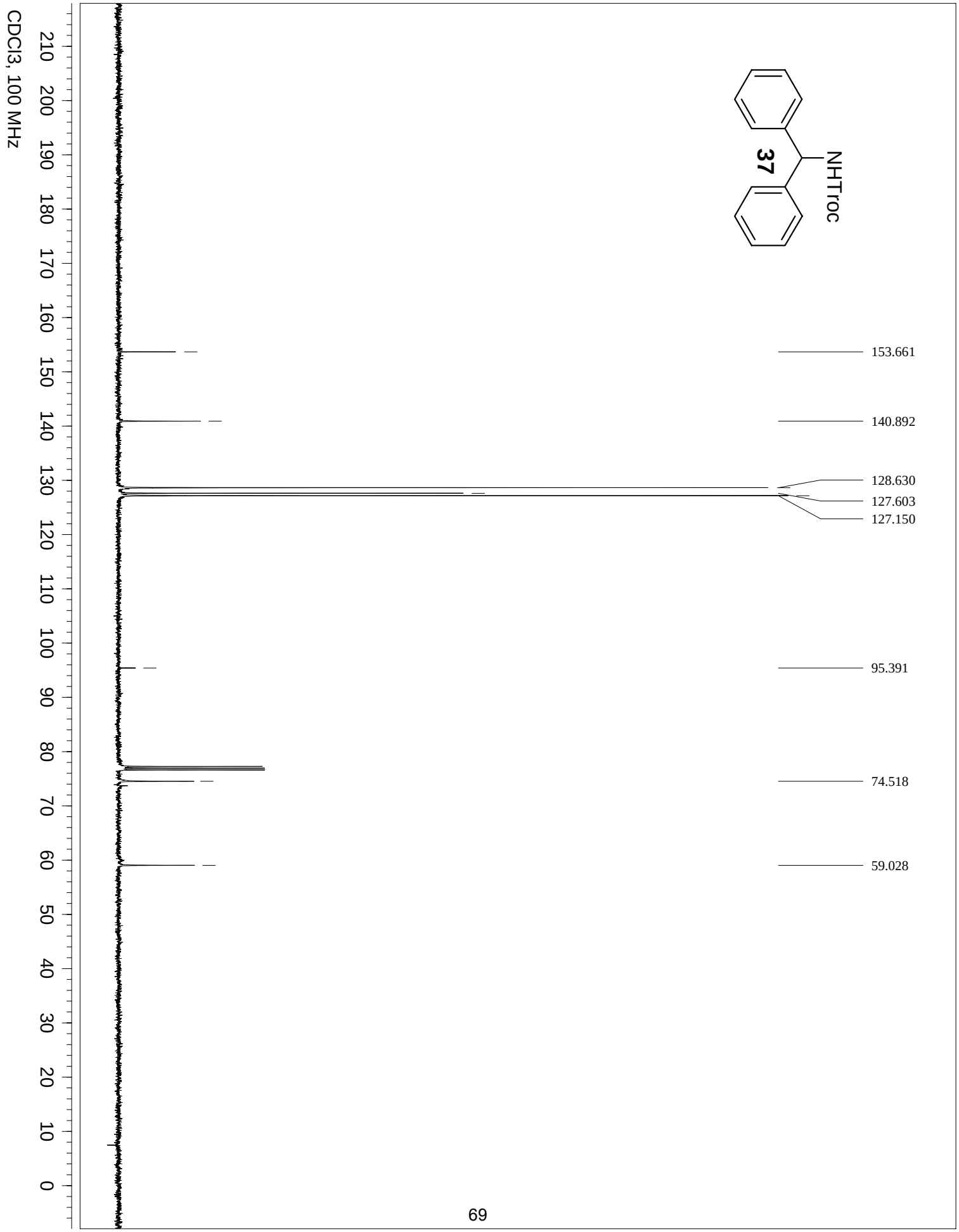
66

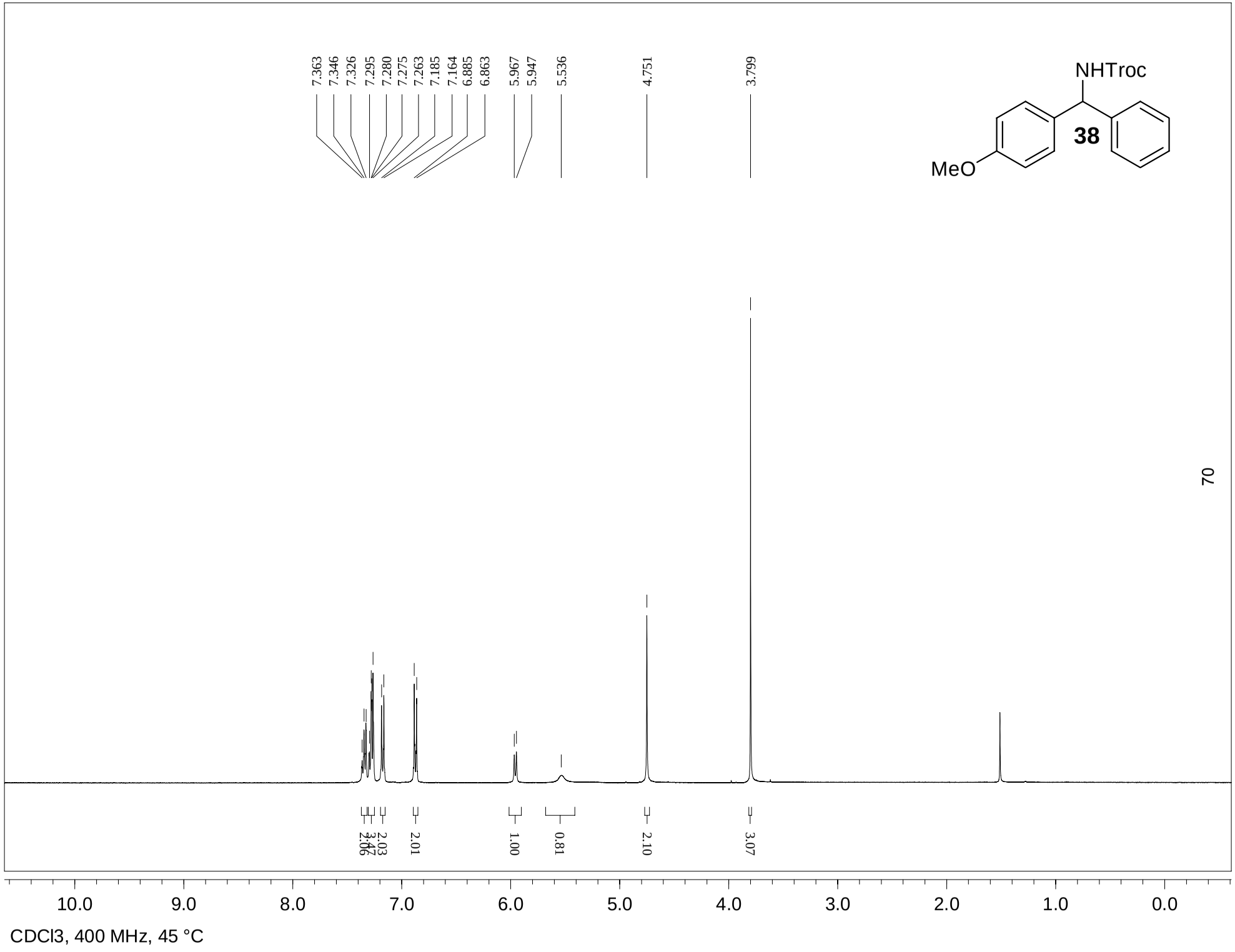
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

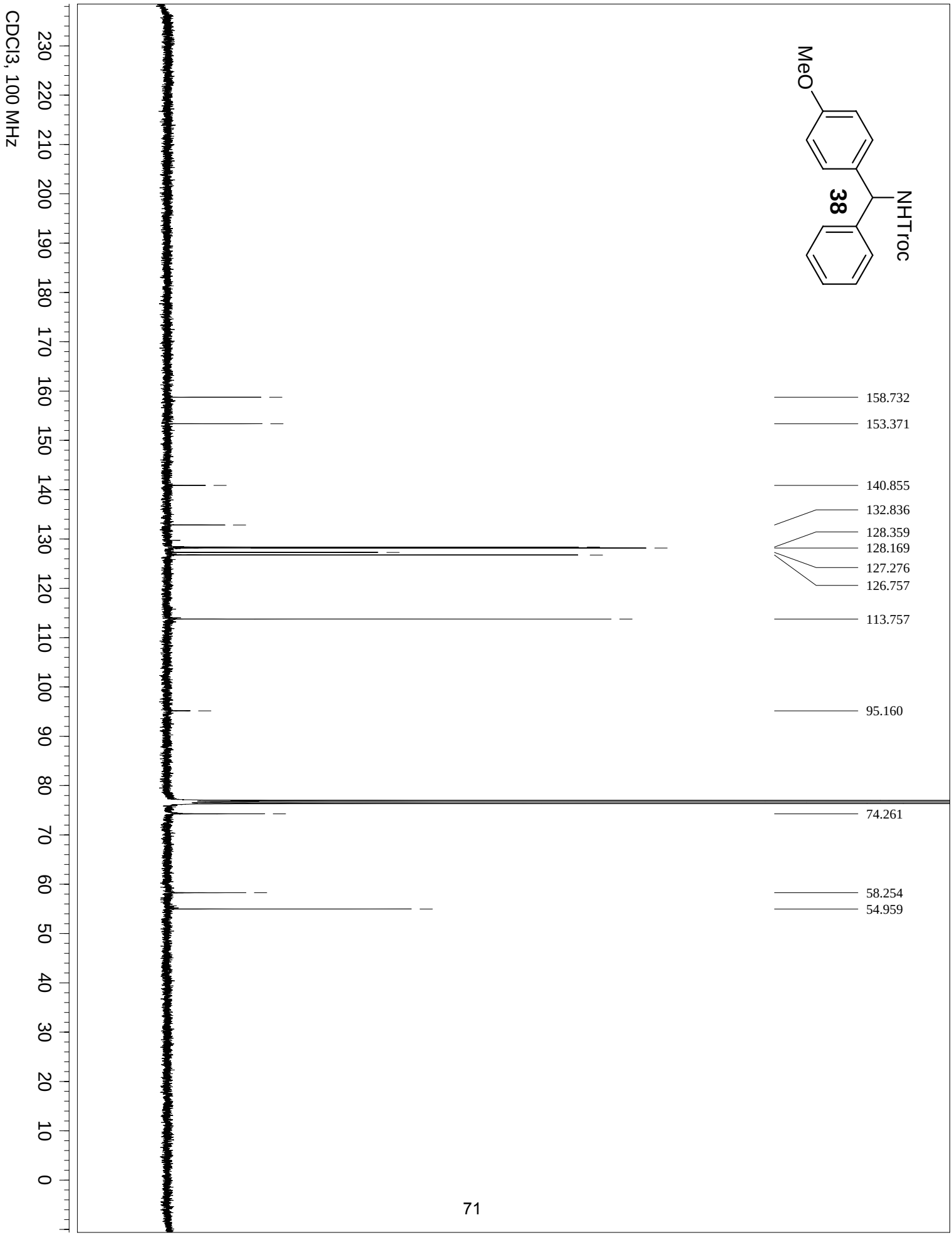
CDCl3, 100 MHz

CDCl3, 400 MHz
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.88
0.99
0.99
0.93
0.99
1.91
2.00
O_2N
8.098
8.093
8.086
8.083
7.553
7.534
7.493
7.483
7.471
7.463
7.452
7.370
7.366
7.353
7.334
7.293
7.283
7.275
7.256
7.226
7.208
4.110

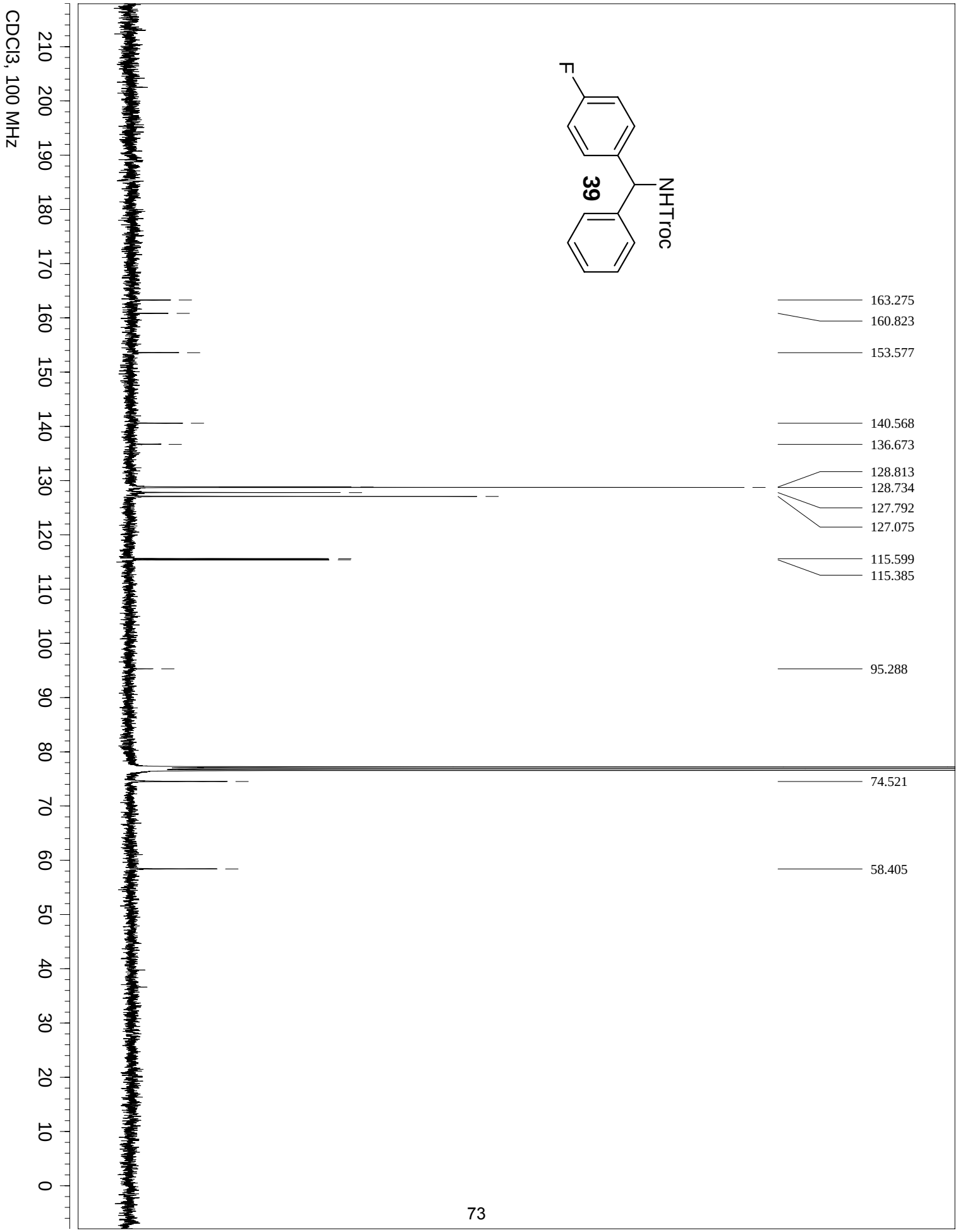
CDCl3, 400 MHz, 45 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
9.91
0.94
0.78
2.00
7.372
7.369
7.365
7.352
7.337
7.333
7.323
7.312
7.308
7.304
7.296
7.290
7.280
7.275
7.263
6.018
5.999
5.580
4.757
37
NHTroc


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
37
NHTroc
153.661
140.892
128.630
127.603
127.150
95.391
74.518
59.028

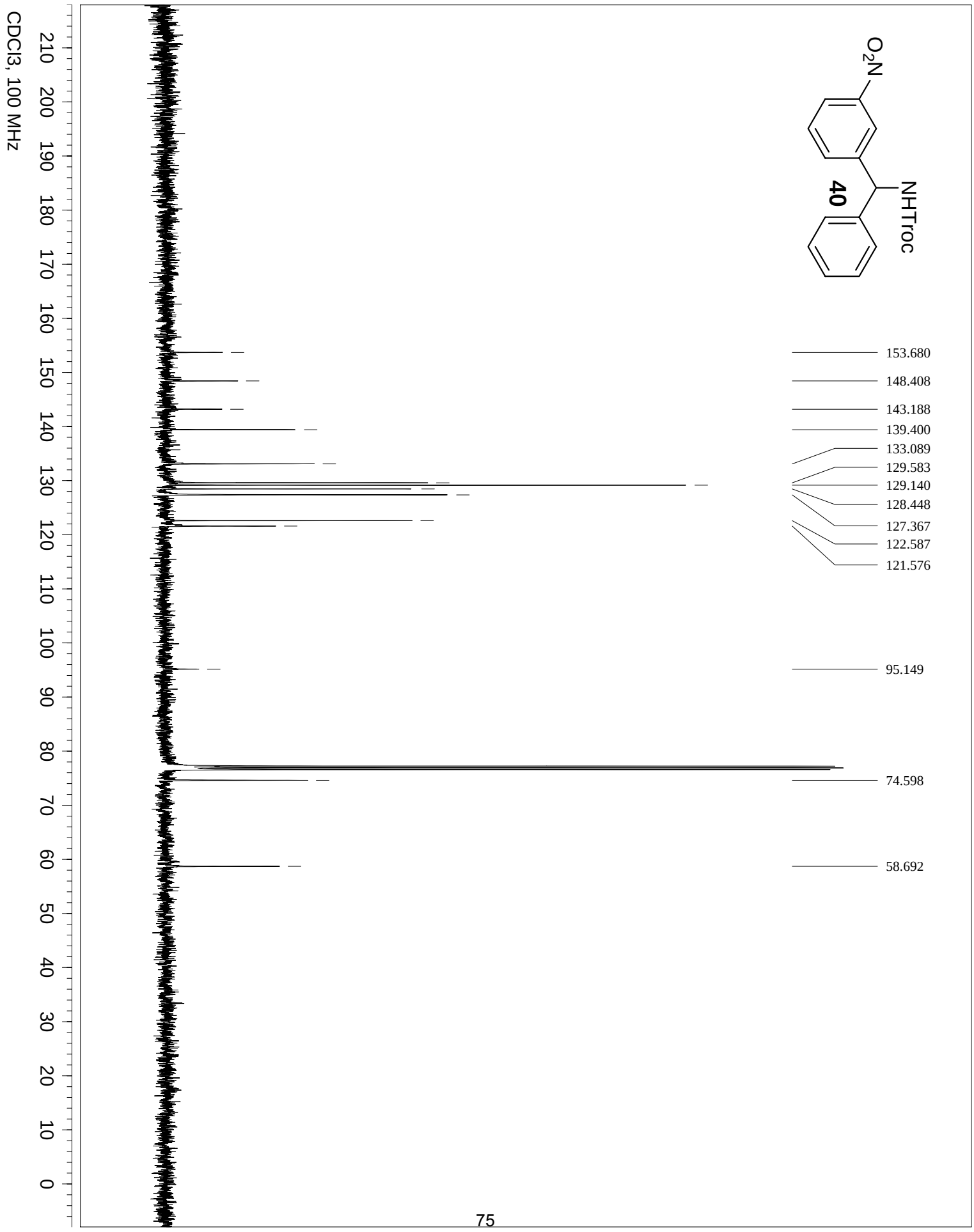

7.363
7.346
7.326
7.295
7.280
7.275
7.263
7.185
7.164
6.885
6.863
5.967
5.947
5.536
4.751
3.799
NHTroc
38
MeO
70
2.06
3.47
2.03
2.01
1.00
0.81
2.10
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CDCl3, 400 MHz, 45 °C


CDCl3, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
MeO
38
NHTroc
158.732
153.371
140.855
132.836
128.359
128.169
127.276
126.757
113.757
95.160
74.261
58.254
54.959

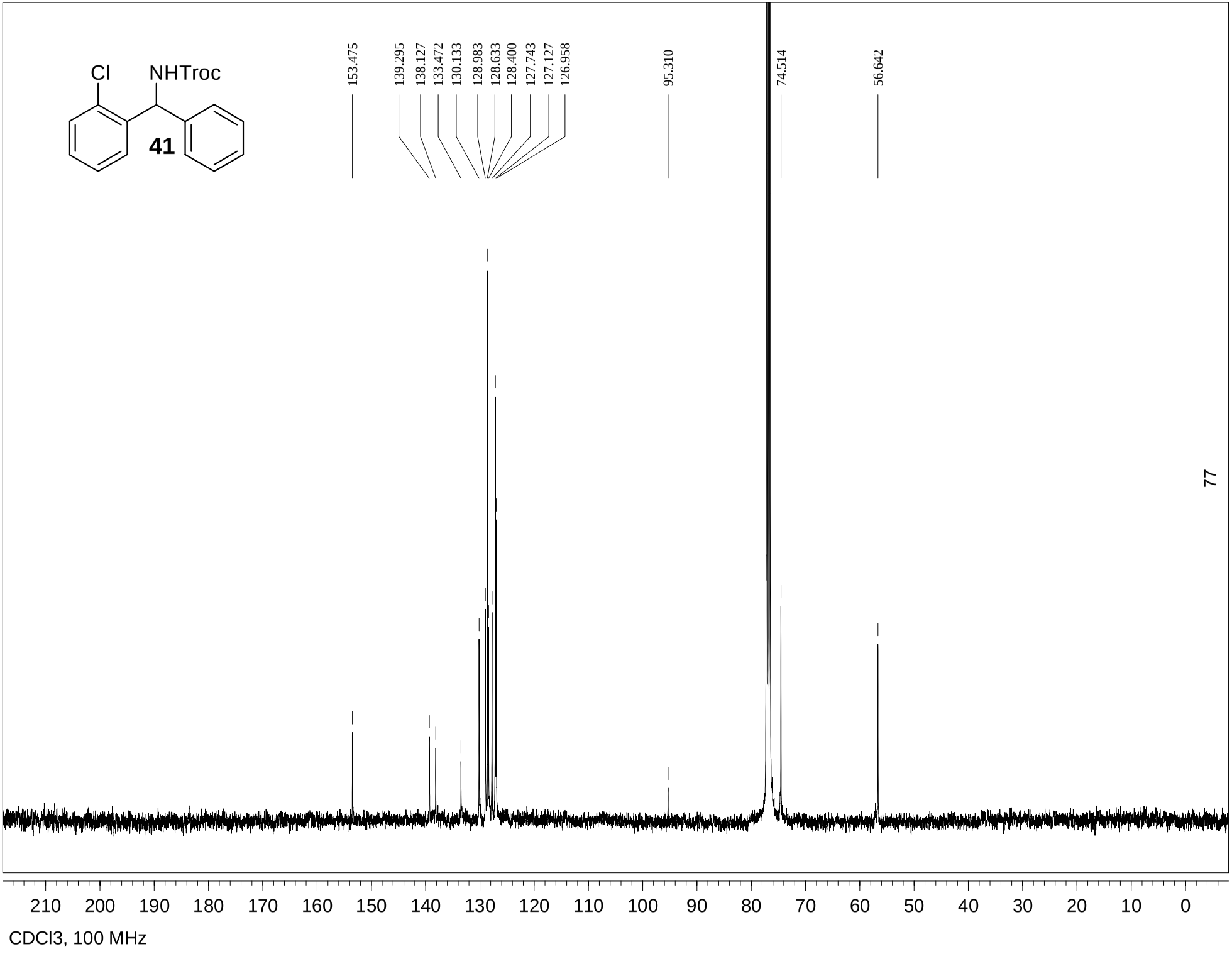
CDCl3, 400 MHz, 45 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.78
2.03
1.00
0.89
2.01
7.381
7.360
7.342
7.321
7.303
7.285
7.261
7.239
7.225
7.056
7.034
7.013
5.998
5.978
5.550
4.754
F
39
NHTroc


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
F
39
NHTroc
163.275
160.823
153.577
140.568
136.673
128.813
128.734
127.792
127.075
115.599
115.385
95.288
74.521
58.405

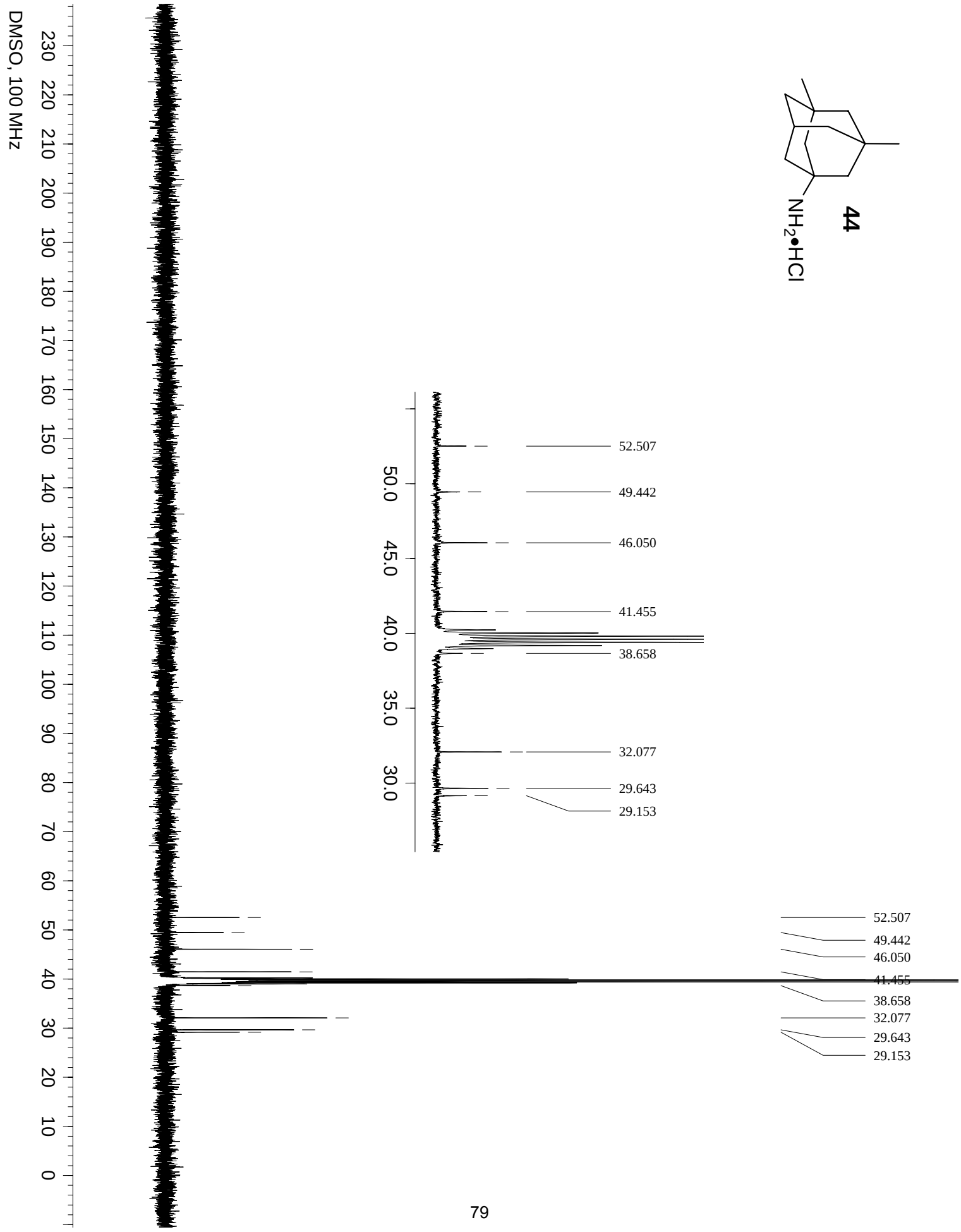
CDCl3, 400 MHz, 45 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.94
0.89
1.05
0.99
3.00
2.23
1.00
0.91
2.05
8.200
8.169
8.146
7.637
7.618
7.548
7.528
7.508
7.410
7.404
7.388
7.370
7.365
7.350
7.343
7.325
7.263
7.251
7.235
6.082
6.064
5.656
4.815
4.786
4.755
4.726
O2N
NHTroc
40

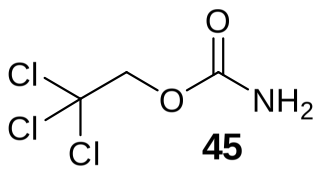

CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O2N
40
NHTroc
153.680
148.408
143.188
139.400
133.089
129.583
129.140
128.448
127.367
122.587
121.576
95.149
74.598
58.692

CDCl3, 400 MHz, 45 °C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
10.86
1.00
0.83
2.01
7.410
7.392
7.387
7.361
7.349
7.344
7.340
7.329
7.325
7.305
7.295
7.291
7.277
7.262
7.258
7.239
6.363
6.344
5.640
4.763
Cl
NHTroc
41


Cl
NHTroc
41
153.475
139.295
138.127
133.472
130.133
128.983
128.633
128.400
127.743
127.127
126.958
95.310
74.514
56.642
77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
CDCl3, 100 MHz

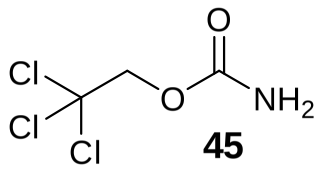
DMSO, 400 MHz
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.12
1.00
2.10
4.02
4.23
2.04
6.47
7.822
2.158
1.602
1.414
1.383
1.356
1.293
1.178
1.146
1.103
1.069
0.852
NH2•HCl
44


DMSO, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
50.0 45.0 40.0 35.0 30.0
52.507
49.442
46.050
41.455
38.658
32.077
29.643
29.153
NH2•HCl
44



45

CDCl3, 400 MHz



45

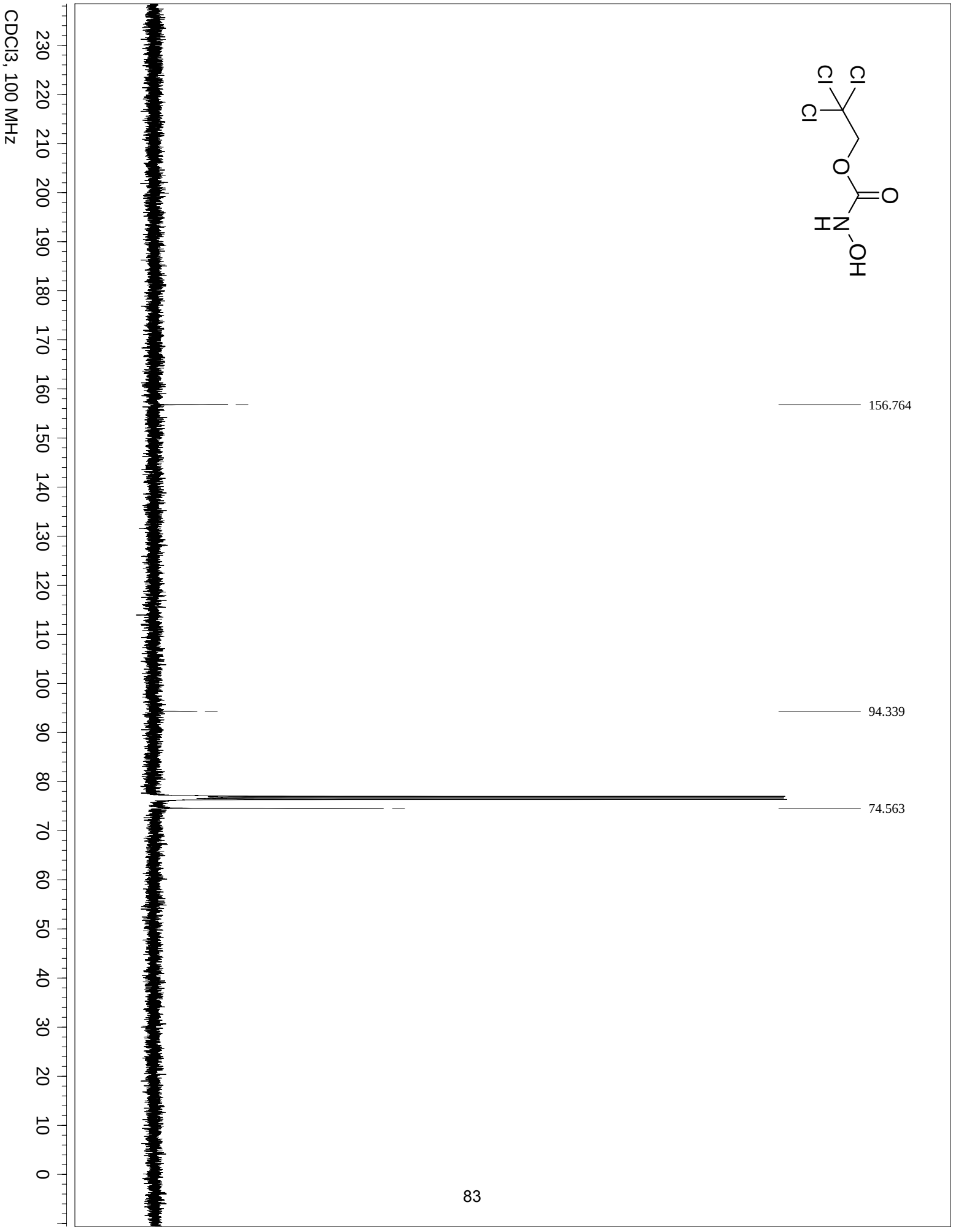
CDCl3, 100 MHz

CDCl3, 400 MHz

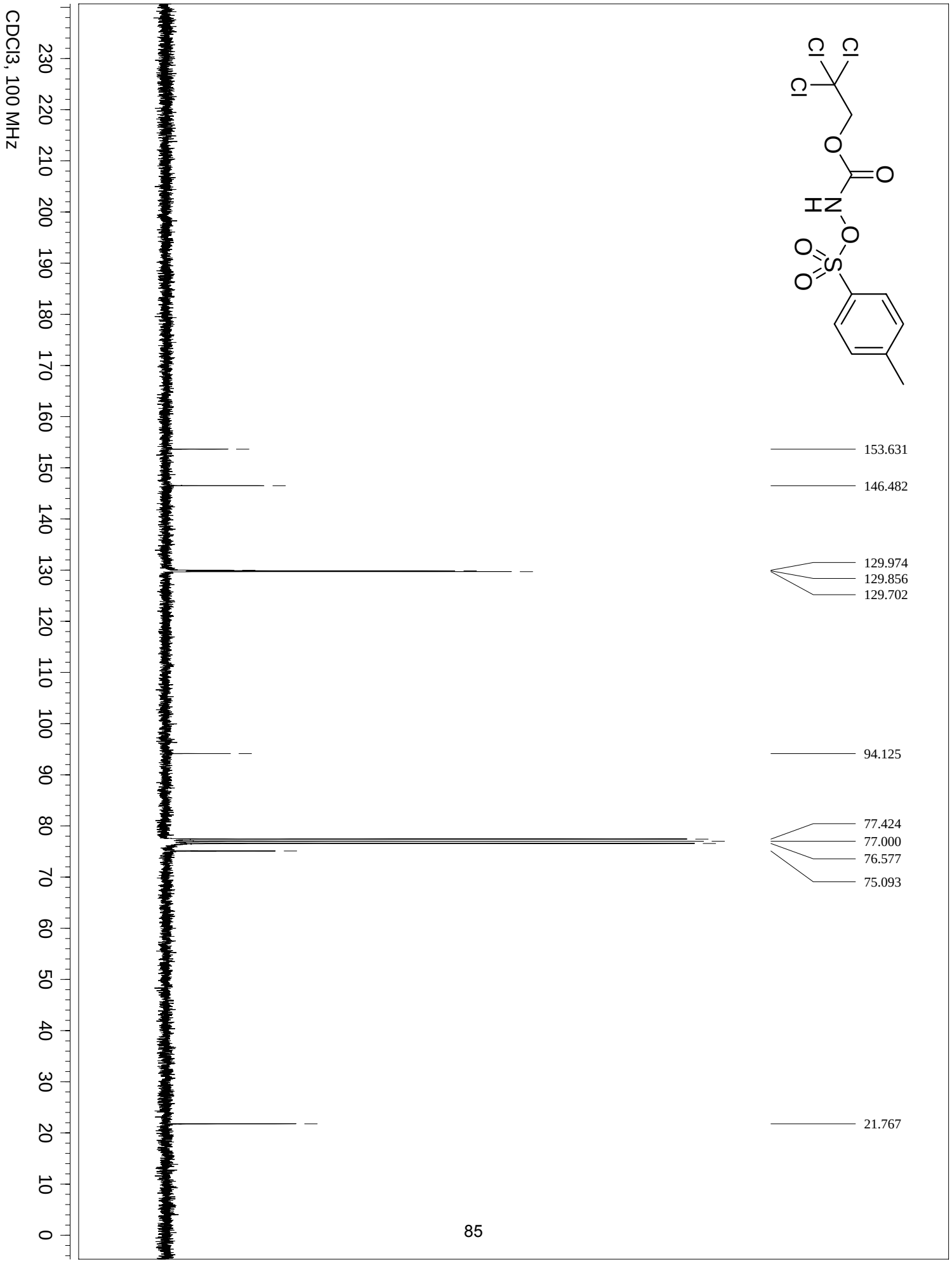
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

0.95
0.76
2.00

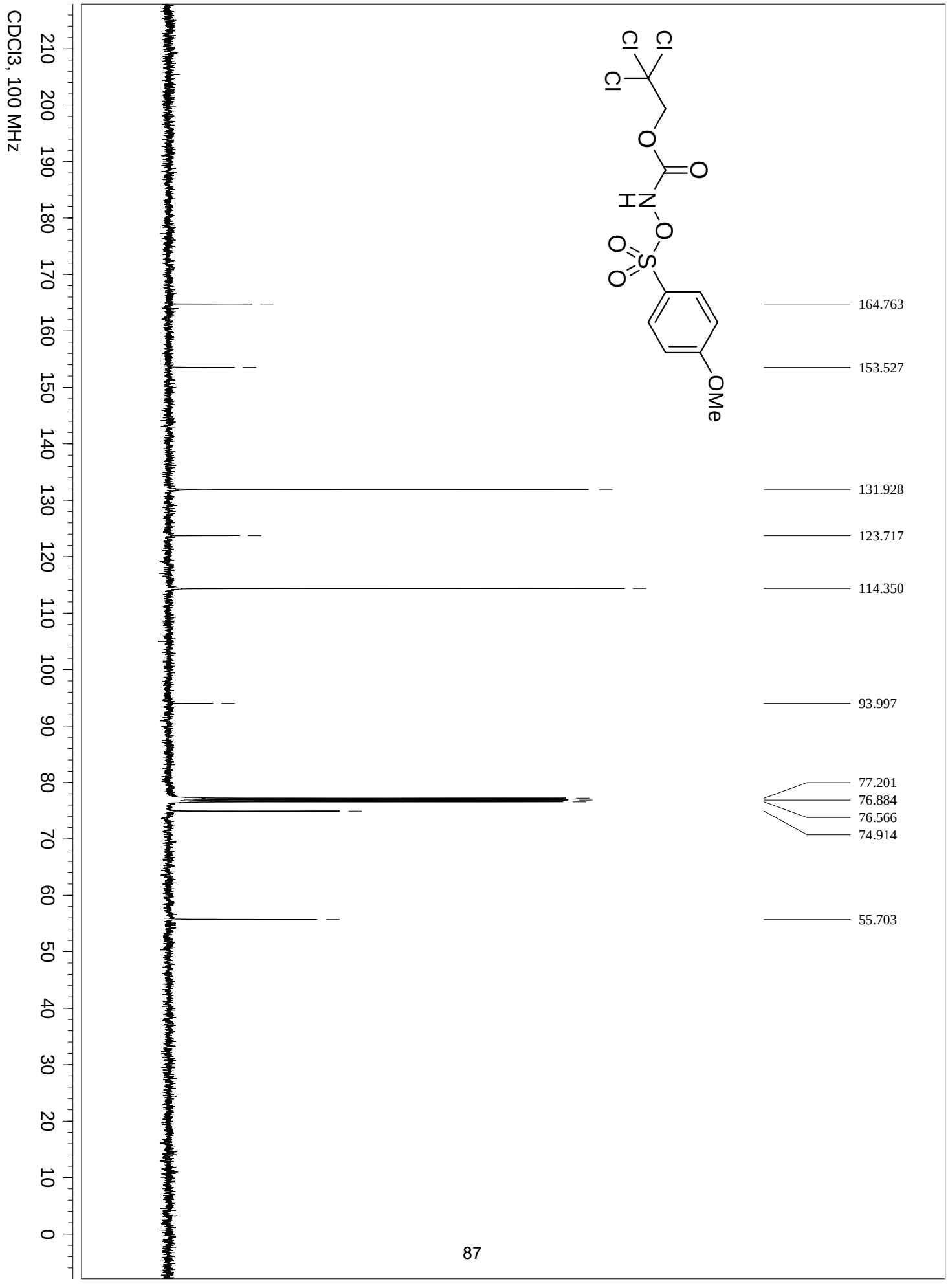
7.622
6.922
4.814

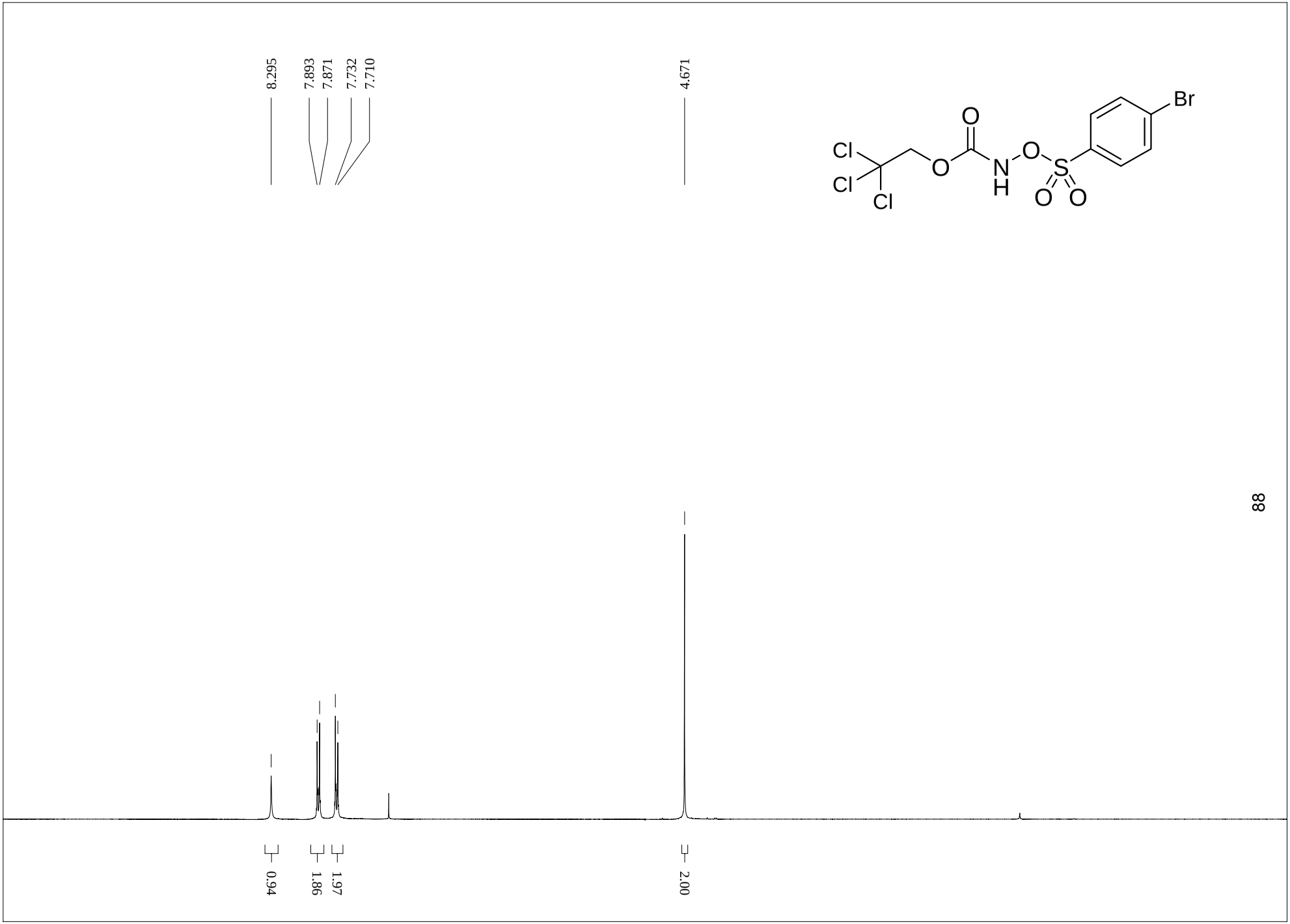

CDCl3, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
156.764
94.339
74.563
Cl
Cl
Cl
O
O
N
H
OH

CDCl3, 400 MHz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.96
1.74
1.87
2.00
3.03
8.141
7.916
7.895
7.376
7.356
4.654
2.463
Cl
Cl
Cl
O
O
H
N
O
S
O
O


CDCl3, 100 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
153.631
146.482
129.974
129.856
129.702
94.125
77.424
77.000
76.577
75.093
21.767
Cl
Cl
Cl
O
O
H
N
O
O
S
O

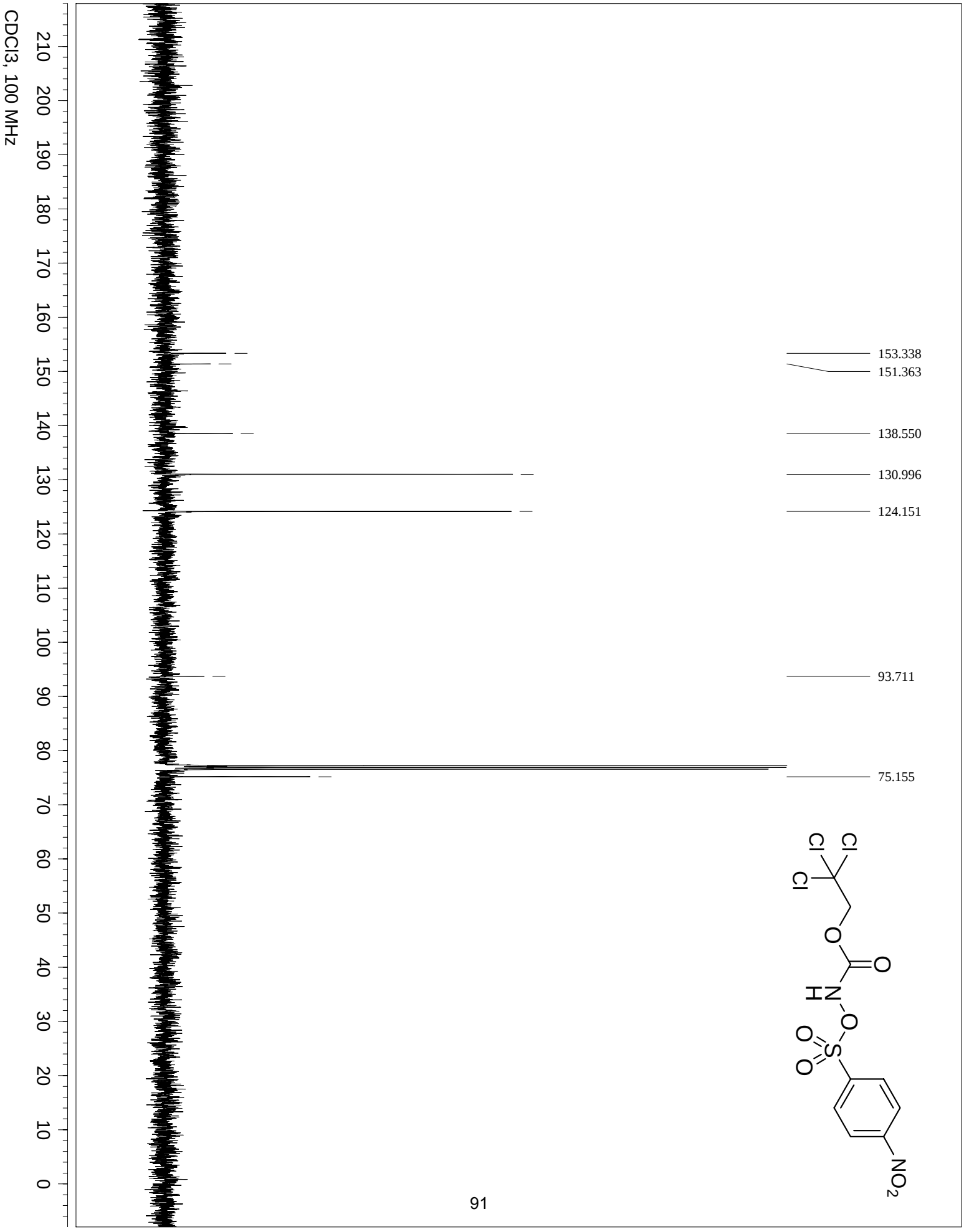
CDCl3, 400 MHz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.73
1.74
1.90
2.00
3.04
8.276
7.954
7.949
7.936
7.931
7.019
6.997
4.654
3.891
Cl
Cl
Cl
O
O
H
N
O
O
O
S
O
OMe


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Cl
Cl
Cl
O
O
H
N
O
O
S
O
OMe
164.763
153.527
131.928
123.717
114.350
93.997
77.201
76.884
76.566
74.914
55.703


8.295
7.893
7.871
7.732
7.710
4.671
Cl
Cl
Cl
O
O
N
H
O
S
O
O
Br
88
0.94
1.86
1.97
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CDCl3, 400 MHz

CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
153.447
132.494
131.738
130.939
130.671
93.857
75.046
Cl
Cl
Cl
O
O
N
H
O
S
O
O
Br

CDCl3, 400 MHz


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
153.338
151.363
138.550
130.996
124.151
93.711
75.155
Cl
Cl
Cl
O
O
N
H
O
S
O
O
NO2

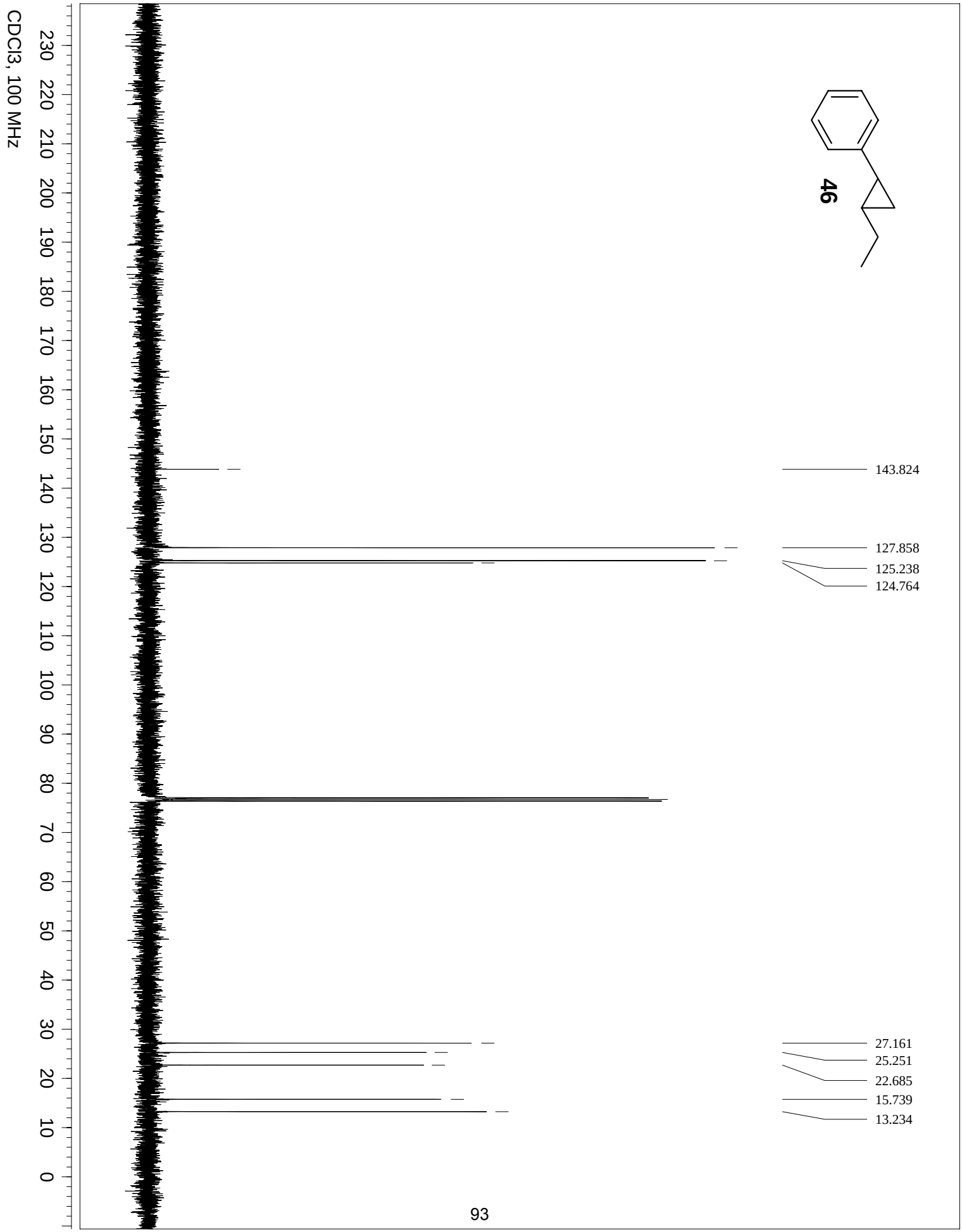
CDCl3, 400 MHz

7.299
7.284
7.281
7.262
7.180
7.161
7.143
7.099
7.096
7.078

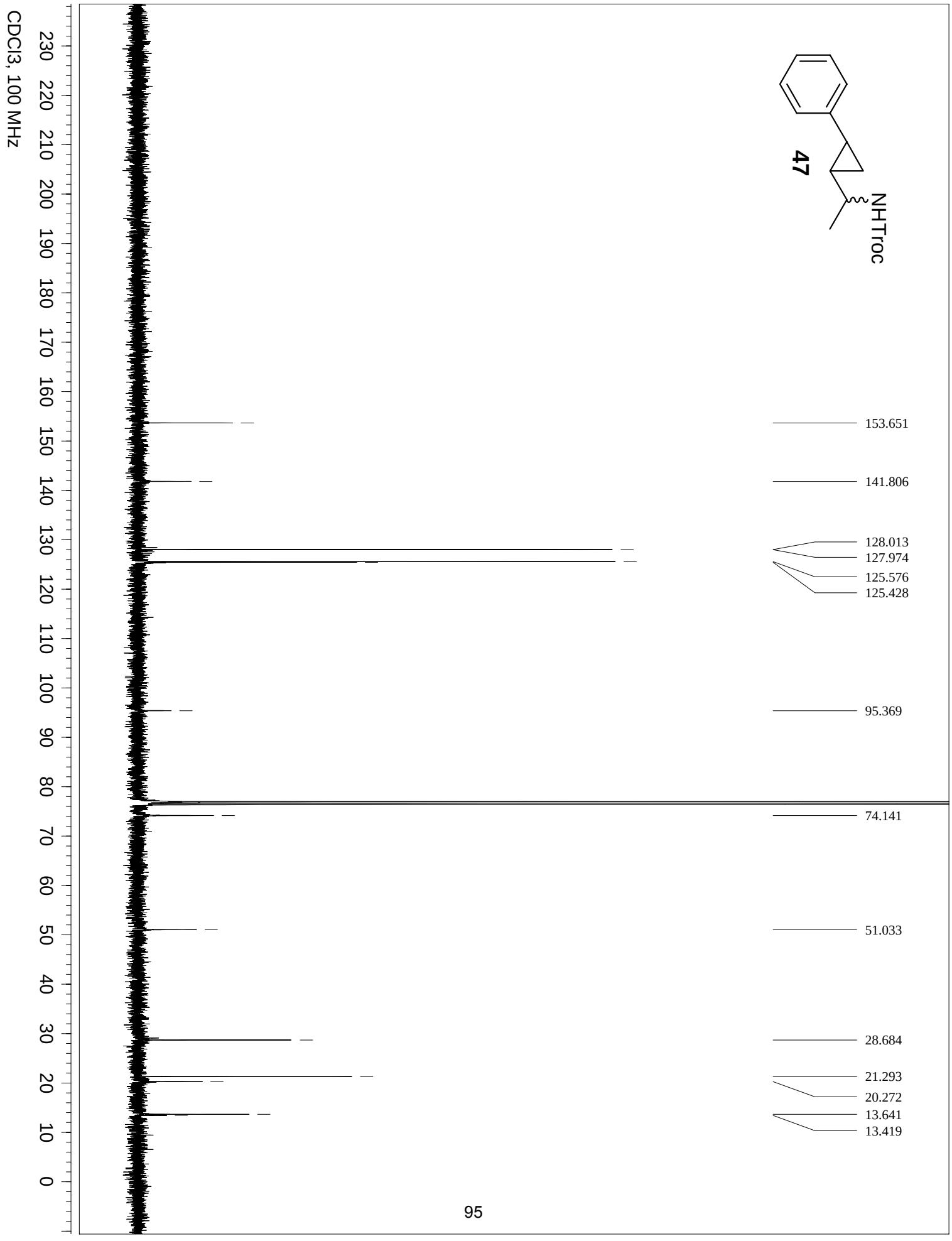
1.671
1.659
1.649
1.638
1.626
1.476
1.460
1.442
1.424
1.406
1.071
1.053
1.034
0.927
0.915
0.903
0.894
0.882
0.820
0.806
0.799
0.795

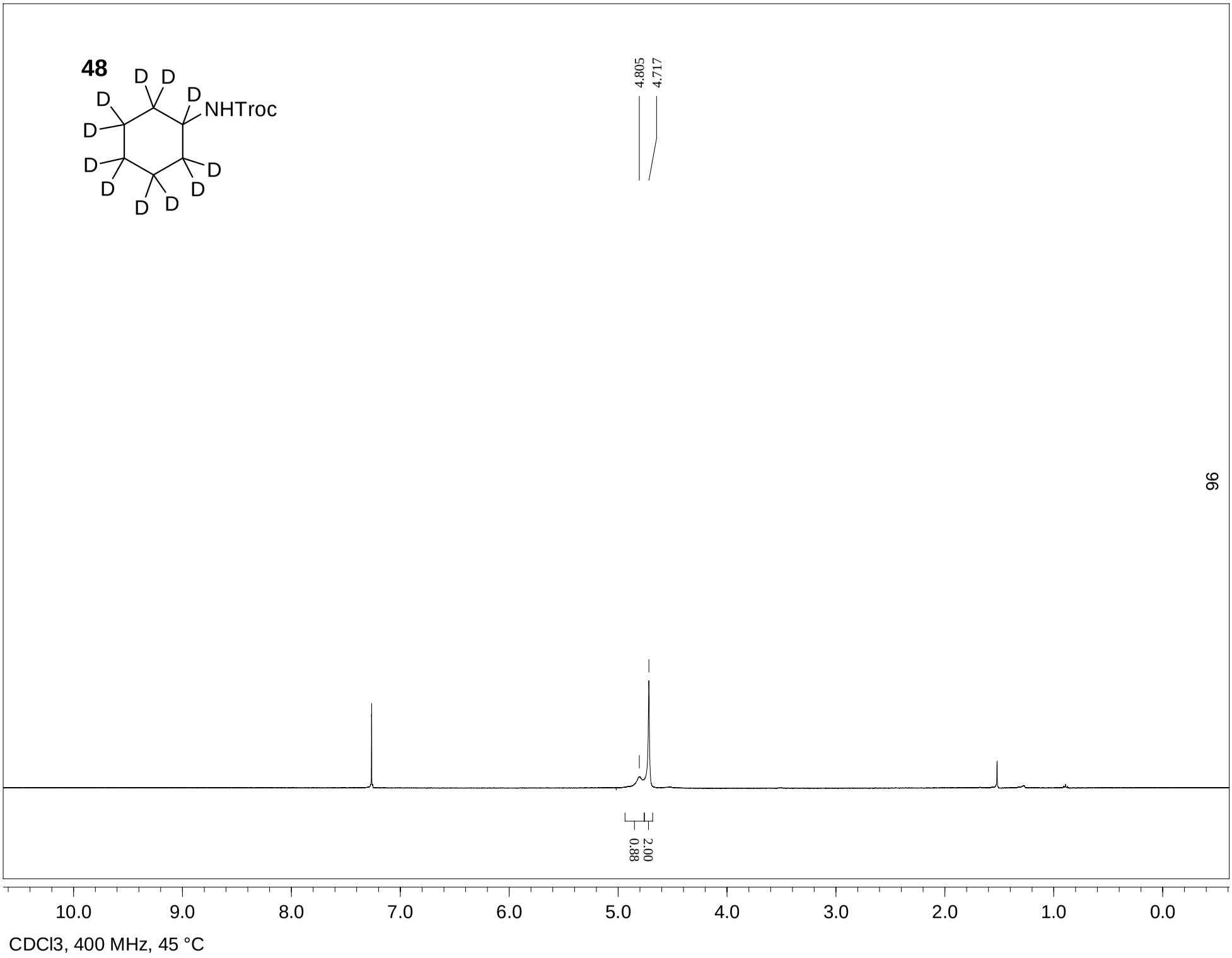
2.16
0.95
1.98
1.00
2.07
4.09
1.07
1.03

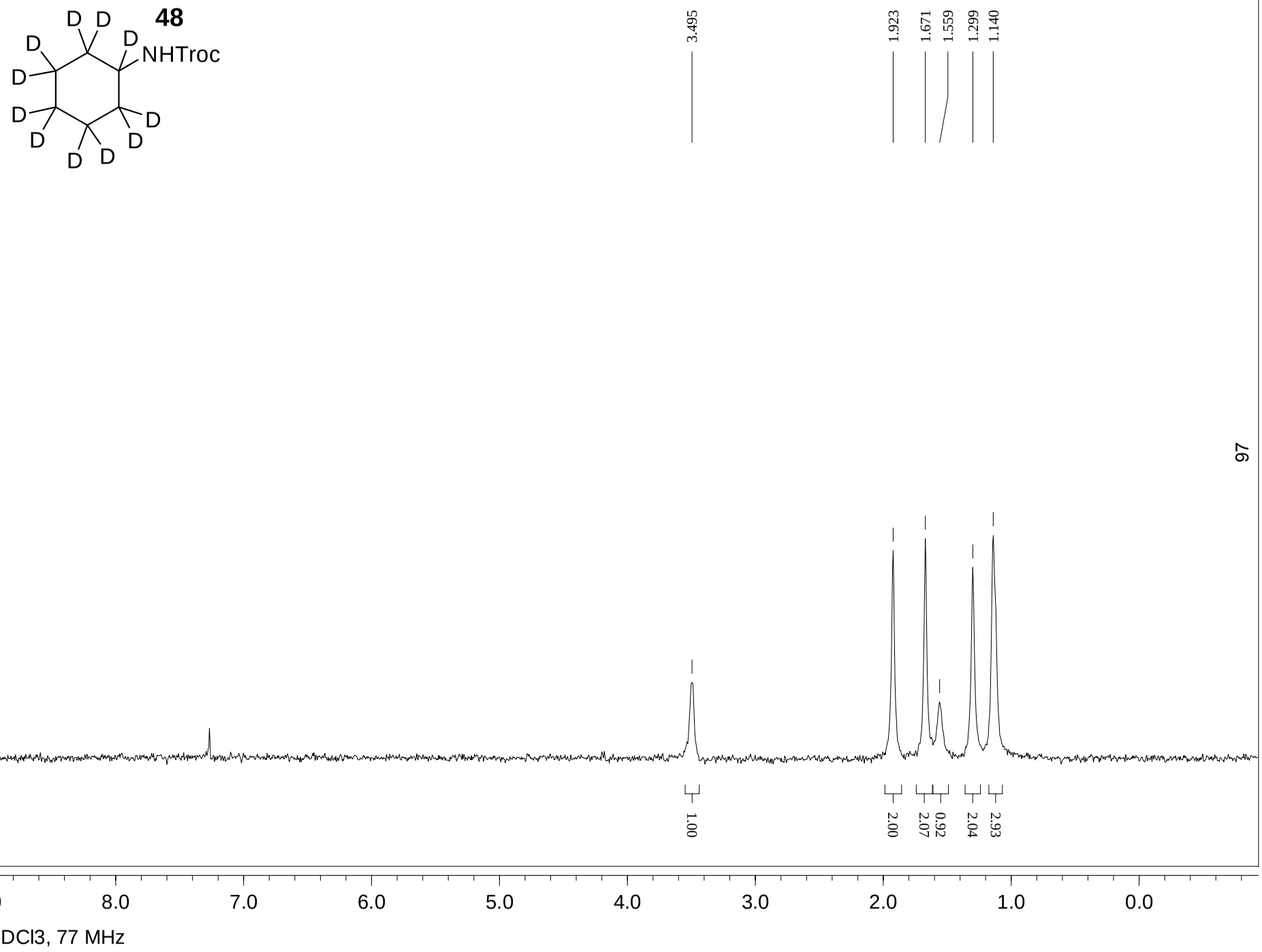
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


CDCl3, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
46
143.824
127.858
125.238
124.764
27.161
25.251
22.685
15.739
13.234

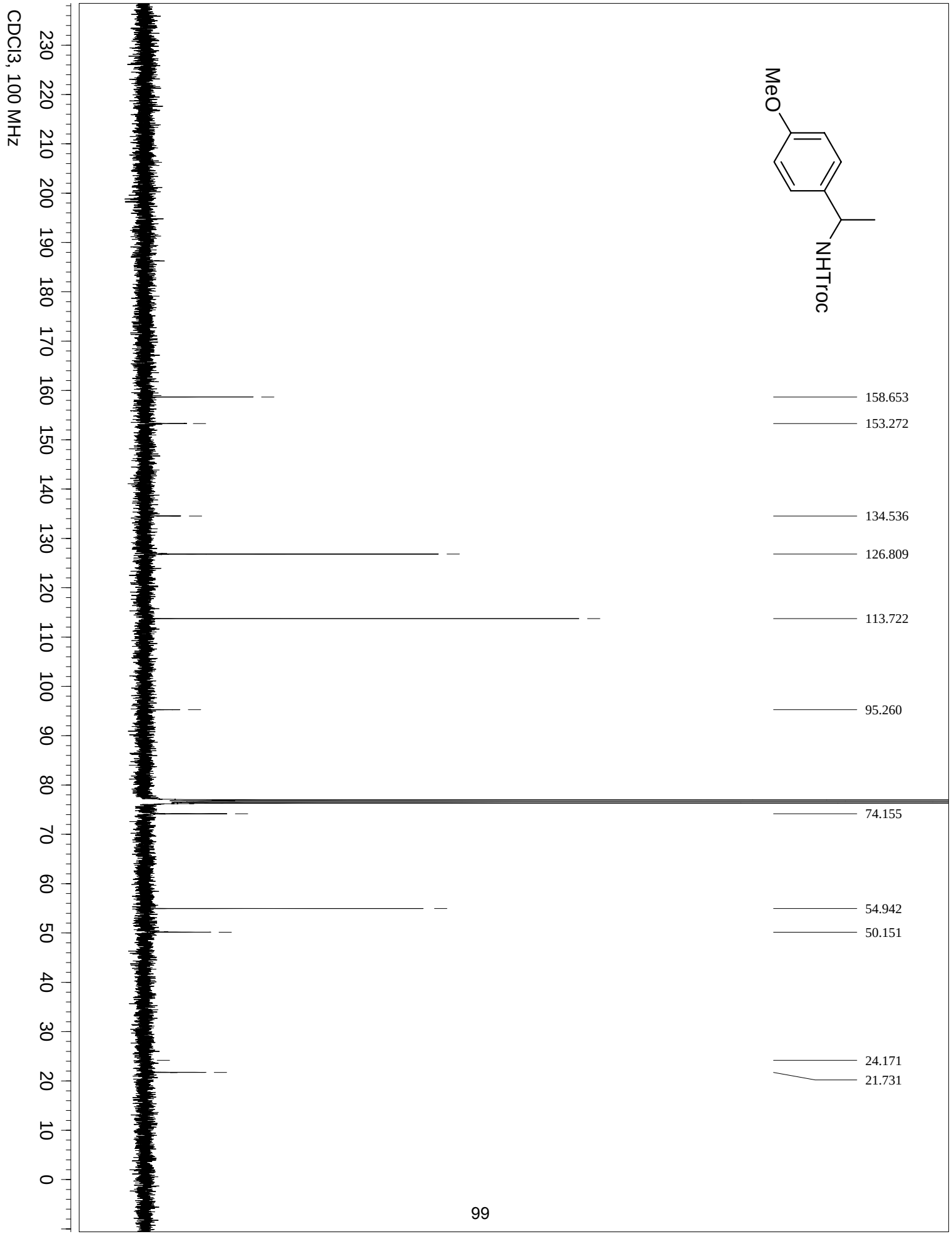
CDCl3, 400 MHz
47
NHTroc
7.308
7.289
7.271
7.255
7.209
7.191
7.176
7.099
7.081
5.026
4.765
3.488
3.470
3.451
3.434
3.414
3.397
2.087
2.073
2.062
2.053
2.038
1.896
1.884
1.873
1.862
1.850
1.360
1.344
1.246
1.232
1.211
1.200
1.179
1.147
1.125
1.112
1.098
0.999
2.33
1.02
2.03
0.86
2.04
1.00
0.16
0.85
3.06
0.92
1.01
1.04

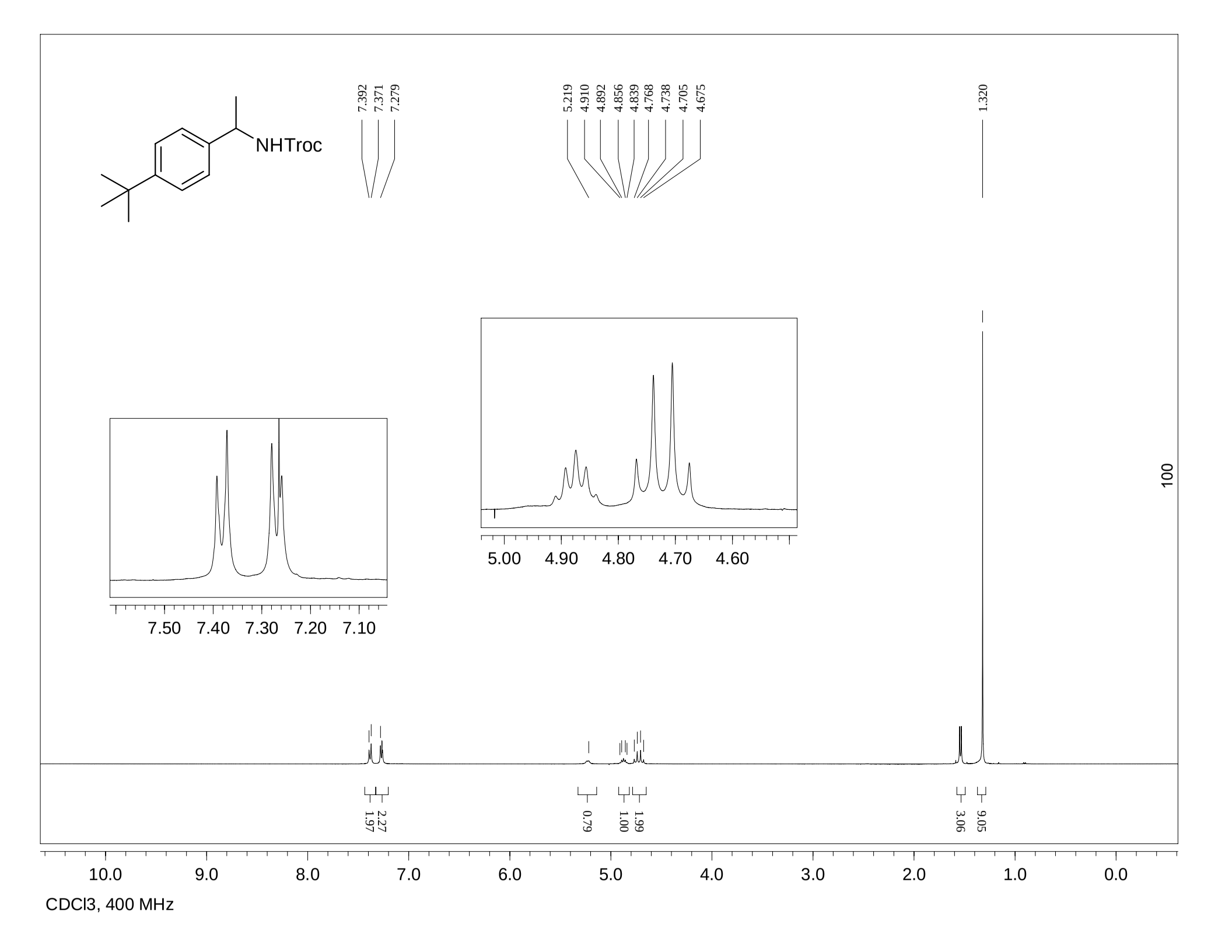

CDCl3, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
47
NHTroc
153.651
141.806
128.013
127.974
125.576
125.428
95.369
74.141
51.033
28.684
21.293
20.272
13.641
13.419

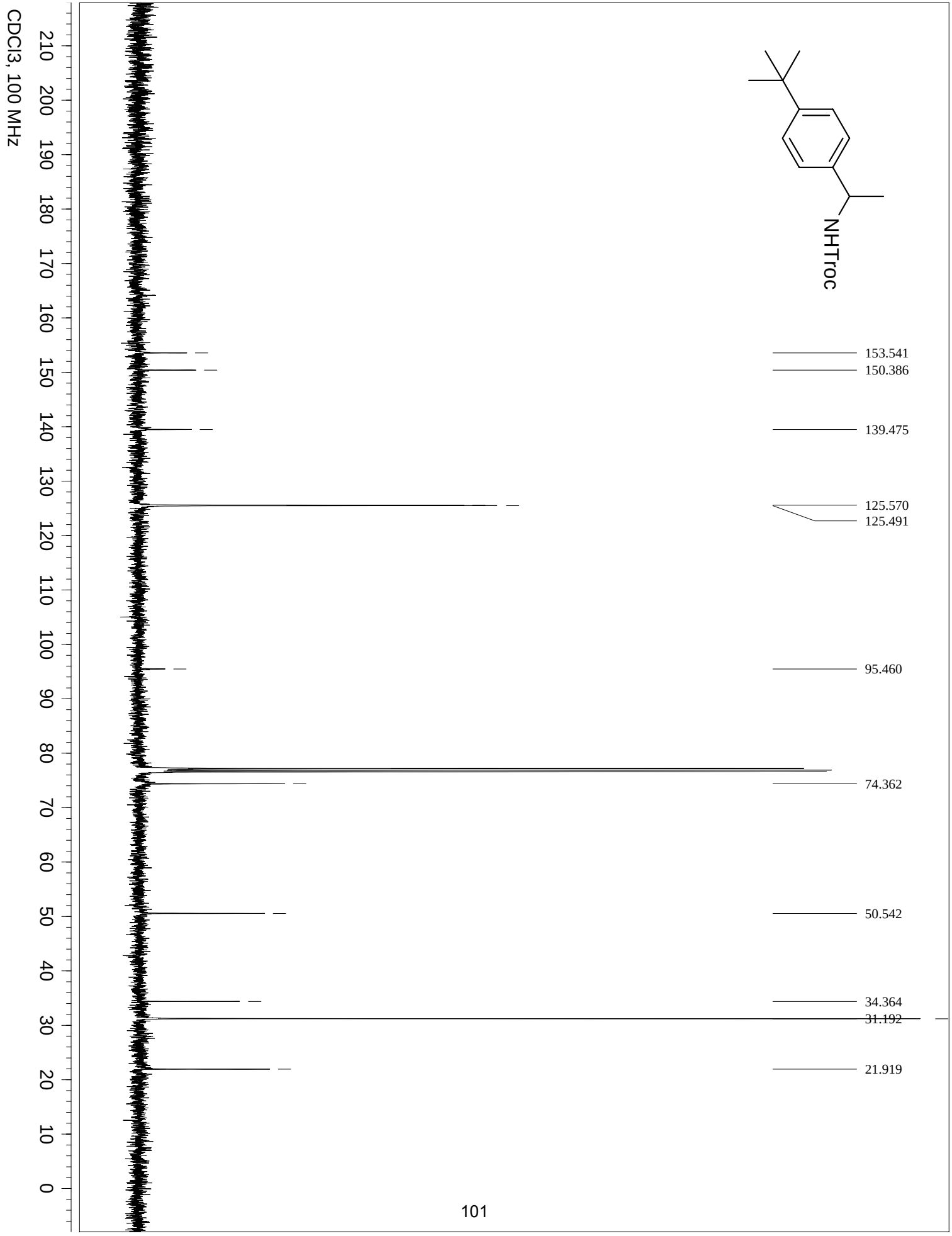

48
D
D
D
D
NHTroc
D
D
D
D
D
D
D
4.805
4.717
96
0.88
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CDCl3, 400 MHz, 45 °C


48
D
D
D
NHTroc
D
D
D
D
D
D
D
D
D
3.495
1.923
1.671
1.559
1.267
1.140
1.00
2.00
2.07
0.92
2.04
2.93
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2H, CDCl3, 77 MHz

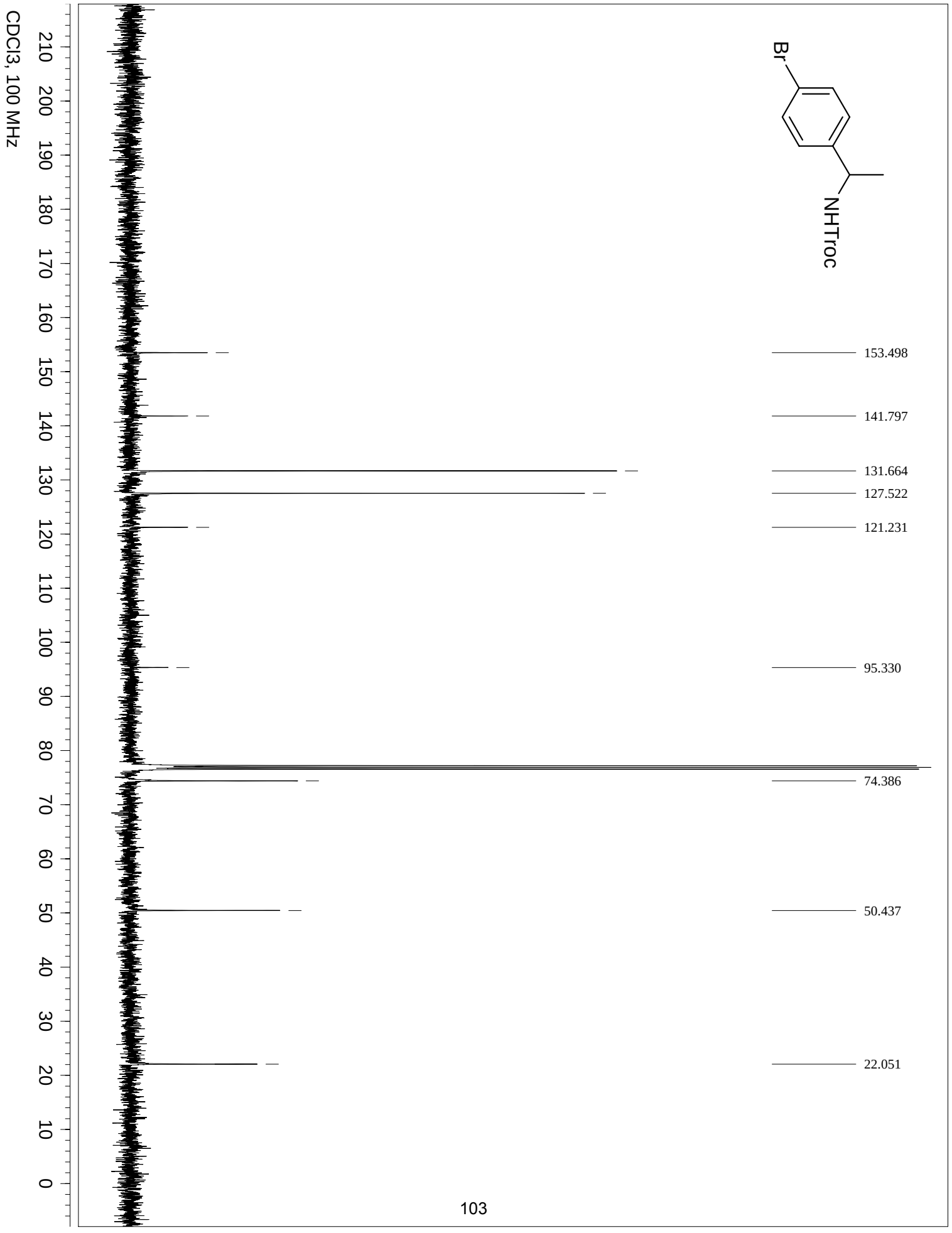
CDCl3, 400 MHz
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.42
1.95
0.76
1.08
1.92
3.00
3.00
MeO
NHTroc
7.284
7.266
6.914
6.893
5.199
4.893
4.875
4.857
4.840
4.822
4.780
4.750
4.718
4.688
3.823
1.550
1.533


CDCl3, 100 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
MeO
NHTroc
158.653
153.272
134.536
126.809
113.722
95.260
74.155
54.942
50.151
24.171
21.731

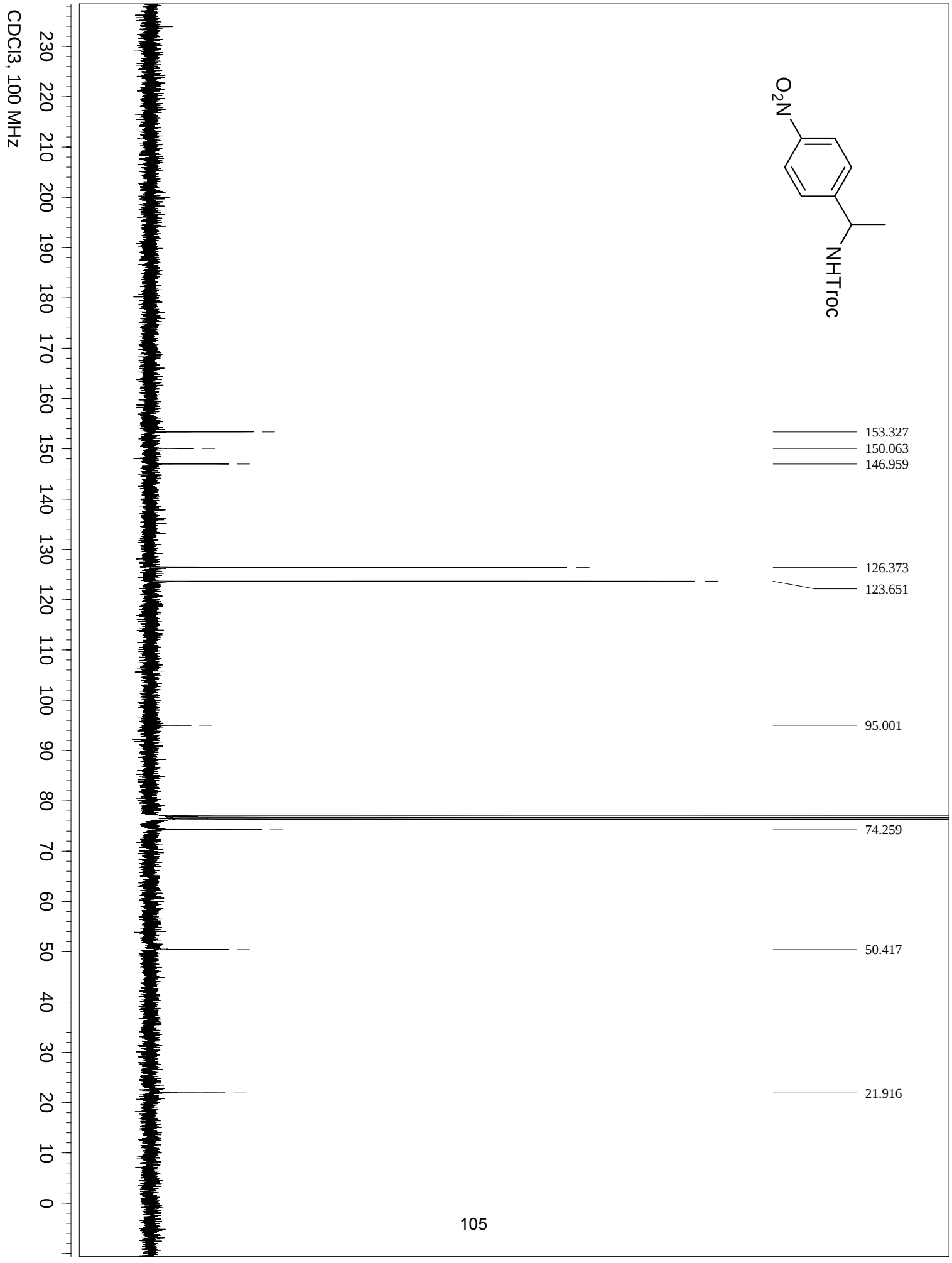

NHTroc
7.392
7.371
7.279
5.219
4.910
4.892
4.856
4.839
4.768
4.738
4.705
4.675
1.320
7.50 7.40 7.30 7.20 7.10
5.00 4.90 4.80 4.70 4.60
100
1.97
2.27
0.79
1.00
1.99
3.06
9.05
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
CDCl3, 400 MHz


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
NHTroc
153.541
150.386
139.475
125.570
125.491
95.460
74.362
50.542
34.364
31.192
21.919

CDCl3, 400 MHz
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Br
NHTroc
1.83
1.91
0.77
1.00
1.99
3.07
7.484
7.463
7.218
7.197
5.247
4.867
4.850
4.832
4.814
4.796
4.753
4.722
4.698
4.668
1.517
1.500


CDCl3, 100 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Br
NHTroc
153.498
141.797
131.664
127.522
121.231
95.330
74.386
50.437
22.051

CDCl3, 400 MHz
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.04
2.05
0.76
1.00
2.07
3.10
O2N
NHTroc
8.247
8.225
7.530
7.509
5.353
5.012
4.994
4.975
4.957
4.940
4.765
4.730
4.700
1.589
1.568


CDCl3, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
O2N
NHTroc
153.327
150.063
146.959
126.373
123.651
95.001
74.259
50.417
21.916