Supplementary Materials

Direct Stereospecific Synthesis of Unprotected N-H/N-Me Aziridines from Olefins

Jawahar L. Jat[1], Mahesh P. Paudyal[1], Hongyin Gao[1], Qing-Long Xu[1], Muhammed Yousufuddin[2], Deepa Devararajan[3], Daniel H. Ess[3], László Kürti*[1] and J. R. Falck*[1]*

TABLE OF CONTENTS

General Methods and Materials SI-2

Catalyst Screening Results: **Tables S1, S2 & S3** ..... SI-3 – SI-5

Stereospecificity Studies: **Figures S1a - S1f** ..... SI-6 – SI-11

Epoxy-Olefin N-H Aziridination Study: **Figures S2a & S2b** ..... SI-12 – SI-13

Search for Allylic C-H Amination Side Product(s): **Figures S3a – S3c** ..... SI-14 – SI-16

Chiral Induction Studies: **Figures S4a & S4b** ..... SI-17 – SI-18

General Amino-oxyarylation Procedure SI-19

General N-H/N-Me Aziridination Procedure SI-21

Preparation and Analytical Data of Products ..... SI-19 – SI-46

X-Ray Diffraction Data for Compound **10ss** ..... SI-46 – SI-61

Tables S4 – S6 ..... SI-47 – SI-58

Tables S7 – S8 ..... SI-59 – SI-61

Computational Details ..... SI-61 – SI-63

Calculated Catalytic Cycles: **Figure S5** SI-62

XYZ Coordinates and Thermochemical Data (Energies in Hartree) ..... SI-64 – SI-101

Copies of ^{1}H- and ^{13}C-NMR Spectra ..... SI-102 – SI-213

Direct Stereospecific Synthesis of Unprotected N-H/N-Me Aziridines from Olefins

Jawahar L. Jat[1], Mahesh P. Paudyal[1], Hongyin Gao[1], Qing-Long Xu[1], Muhammed Yousufuddin[2], Deepa Devararajan[3], Daniel H. Ess[3], László Kürti*[1] and J. R. Falck*[1]*

[1]Division of Chemistry, Department of Biochemistry, UT Southwestern, Dallas, TX 75390;

[2]Center for Nanostructured Materials, The University of Texas at Arlington, TX 76019;

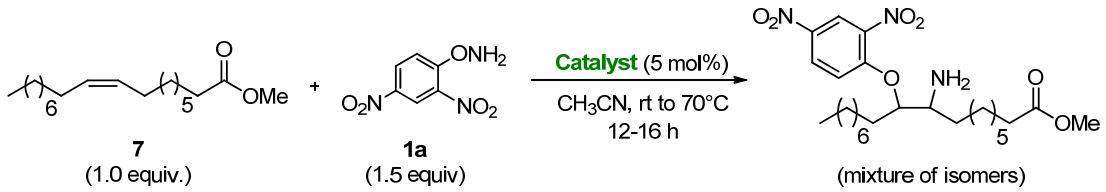
[3]Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602

Supplementary Materials

General Methods and Materials

Proton and carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded on a Varian 500 at 500 MHz and 126 MHz, respectively, or a Varian 400 at 400 MHz and 101 MHz, respectively, in $CDCl_3$ with TMS as internal standard, unless otherwise stated. ^{1}H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, app q = apparent quartet, qn = quintet, app qn = apparent quintet, m = multiplet) and coupling constant (Hz). High resolution mass spectra (HRMS) were obtained using a Shimadzu IT-TOF mass spectrometer at UT Arlington. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum 1000 Fourier transform infrared spectrometer. Melting points were measured using an OptiMelt from Stanford Research Systems and are uncorrected. Analytical thin layer chromatography (TLC) used EMD Chemicals TLC silica gel 60 F_{254} plates (0.040-0.063 mm) with visualization by UV light and/or $KMNO_4$ or phosphomolybdic acid (PMA) solution followed by heating. Chromatographic purifications utilized Et_3N basified preparative TLC or flash chromatography using pre-packed SiO_2 columns on a CombiFlash Rf200 chromatograph (Teledyne Isco). Unless otherwise noted, yields refer to isolated, purified material with spectral data consistent with assigned structures or, if known, were in agreement with published data. All reactions were conducted under an argon atmosphere in oven-dried glassware with magnetic stirring. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise noted. Anhydrous acetonitrile and 2,2,2-trifluoroethanol (Aldrich Chem. Co.) were used directly. Tetrahydrofuran (THF) was dried on a Glass Contours Solvent System by passage through a column of activated, neutral alumina under argon before use. Amination reagents were obtained from Corvinus Chemicals and Rh catalysts from Sigma-Aldrich Chem. Co. and Strem Chemicals.

Table S1: Catalyst Screening

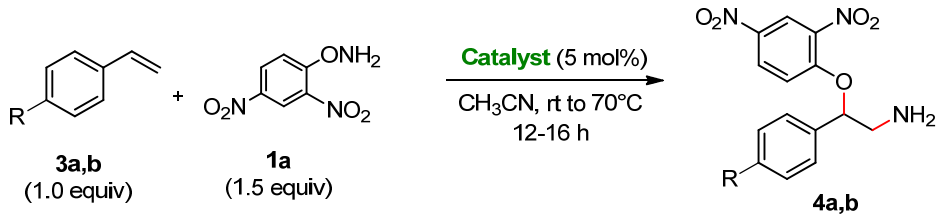


7 (1.0 equiv.) **1a** (1.5 equiv) (mixture of isomers)

Entry	Catalyst	Result[a]
1	$Cu(CH_3CN)_4PF_6$	No reaction, **1a** decomposed
2	$FeCl_3$	No reaction, **1a** decomposed
3	Fe(II)OTf	No reaction, **1a** decomposed
4	Mn(II)OTf	No reaction, **1a** decomposed
5	$(C_5H_5)(CO)_2(THF)Fe(II)BF_4$	No reaction, **1a** decomposed
6	$Pd(OAc)_2$	No reaction, **1a** decomposed
7	$Rh_2(OAc)_4$	15% isolated product

[a]Determined by NMR analysis of the crude reaction mixture.

Table S2: Catalyst Screening



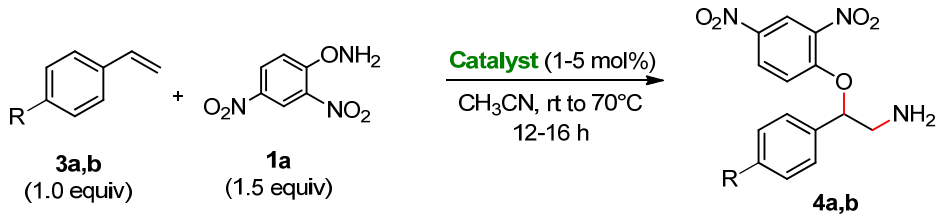
3a,b (1.0 equiv) **1a** (1.5 equiv) **4a,b**

Entry	Substrate	Catalyst	Result[a]
1	**3a**	CuI	No reaction, **1a** decomposed
2	**3a**	CuBr	No reaction, **1a** decomposed
3	**3a**	Cu(BF4)2·H2O	No reaction, **1a** decomposed
4.	**3a**	$Cu(acac)_2$	No reaction, **1a** decomposed
5.	**3a**	CuOTf	<10% of **4a**

6.	**3a**	$Rh_2(OAc)_4$	25% product isolated
7.	**3a**	$Rh_2(TFA)_4$	No reaction, **1a** decomposed
8.	**3a**	$Rh_2(Hfb)_4$	No reaction, **1a** decomposed
9	**3a**	$Rh_2(TPA)_4$	No reaction, **1a** decomposed
10	**3a**	Hydroxy(COD)Rh(I)dimer	No reaction, **1a** decomposed
11	**3a**	Chloro(COD)Rh(I)dimer	No reaction, **1a** decomposed
12	**3a**	$Cl(CO)(Ph_3P)_2Rh(I)$	No reaction, **1a** decomposed
13	**3a**	$Cl(Ph_3P)_3Rh(I)$	No reaction, **1a** decomposed
14	**3a**	$(CO)_2(acac)_2Rh(I)$	No reaction, **1a** decomposed
15	**3a**	$(Ph_3P)_3Rh(I)(CO)(H)$	No reaction, **1a** decomposed
16	**3a**	$Rh(III)(acac)_3$	No reaction, **1a** decomposed
17	**3a**	$Co_2(CO)_8$	No reaction, **1a** decomposed
18	**3b**	$[(Cy_3P)_3(COD)(pyridine)Ir(I)]PF_6$	No reaction, **1a** decomposed
19	**3b**	{Chloro(4,4-dicarboxy-2,2-bipyridine)(p-cymene) RuCl}	No reaction, **1a** decomposed
20	**3b**	$(COD)_2Ni(0)$	No reaction, **1a** decomposed
21	**3b**	$[(MeO)(COD)Ir(I)]_2$	No reaction, **1a** decomposed
22	**3b**	$Ir(III)Cl_3$	No reaction, **1a** decomposed
23	**3b**	$Cl(Ph_3P)_3Au(I)$	No reaction, **1a** decomposed
24	**3b**	$Au(III)Cl_3$	No reaction, **1a** decomposed
25	**3b**	$(COD)(Ph_3P)_2Rh(I)PF_6 \cdot CH_2Cl_2$	No reaction, **1a** decomposed
26	**3b**	1,2-Bis[(2S,5S)-2,5-diethylphospholano]benzene(COD) Rh(I)OTf	No reaction, **1a** decomposed

[a]Determined by NMR analysis of the crude reaction mixture.

Table S3: Screening of Dirhodium Catalysts



Entry	Substrate	Catalyst	Results[a]/Isolated Yield
1	**3a**	$Rh_2(TFA)_4$ (5 mol%)	No reaction, **1a** decomposed
2	**3a**	$Rh_2(Hfb)_4$ (5 mol%)	No reaction, **1a** decomposed
3	**3a**	$Rh_2(TPA)_4$ (5 mol%)	No reaction, **1a** decomposed
4	**3a**	$Rh_2(OAc)_4$ (5 mol%)	25% **4a**
5	**3a**	$Rh_2(octanoate)_4$ (5 mol%)	36% **4a**
6	**3a**	$Rh_2(esp)_2$ (1 mol%)	56% **4a**
7	**3b**	$Rh_2(OAc)_4$ (5 mol%)	42% **4b**
8	**3b**	$Rh_2(esp)_2$ (1 mol%)	75% **4b**

[a]Determined by NMR analysis of the crude reaction mixture.

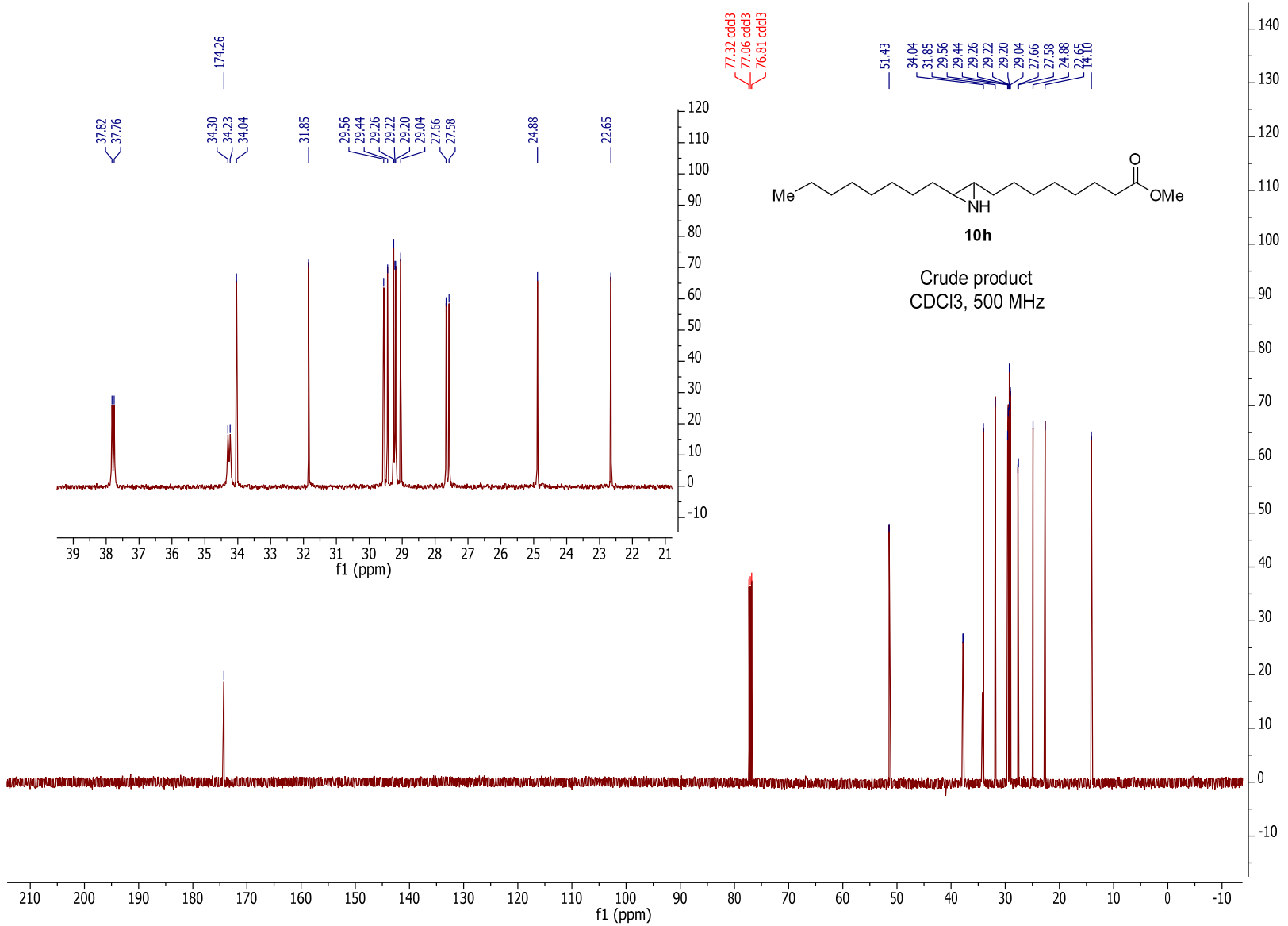


Figure S1a. Stereospecificity studies for the direct N-H aziridination of *trans*-Me-elaidate (**9h**) – Crude ^{13}C-NMR of **10h**.

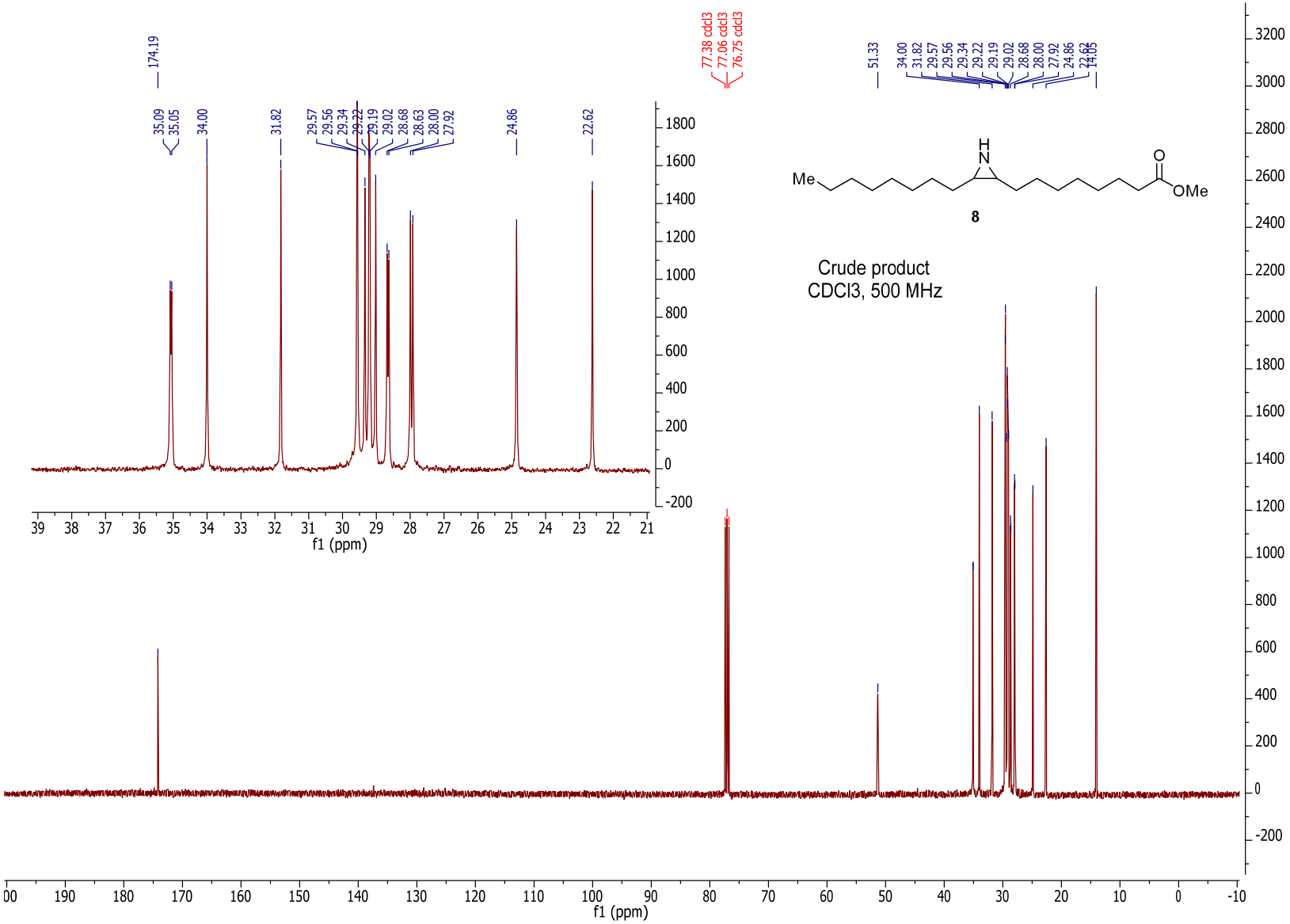


Figure S1b. Stereospecificity studies for the direct N-H aziridination of *cis*-Me-oleate (**7**) – Crude ^{13}C-NMR of **8**.

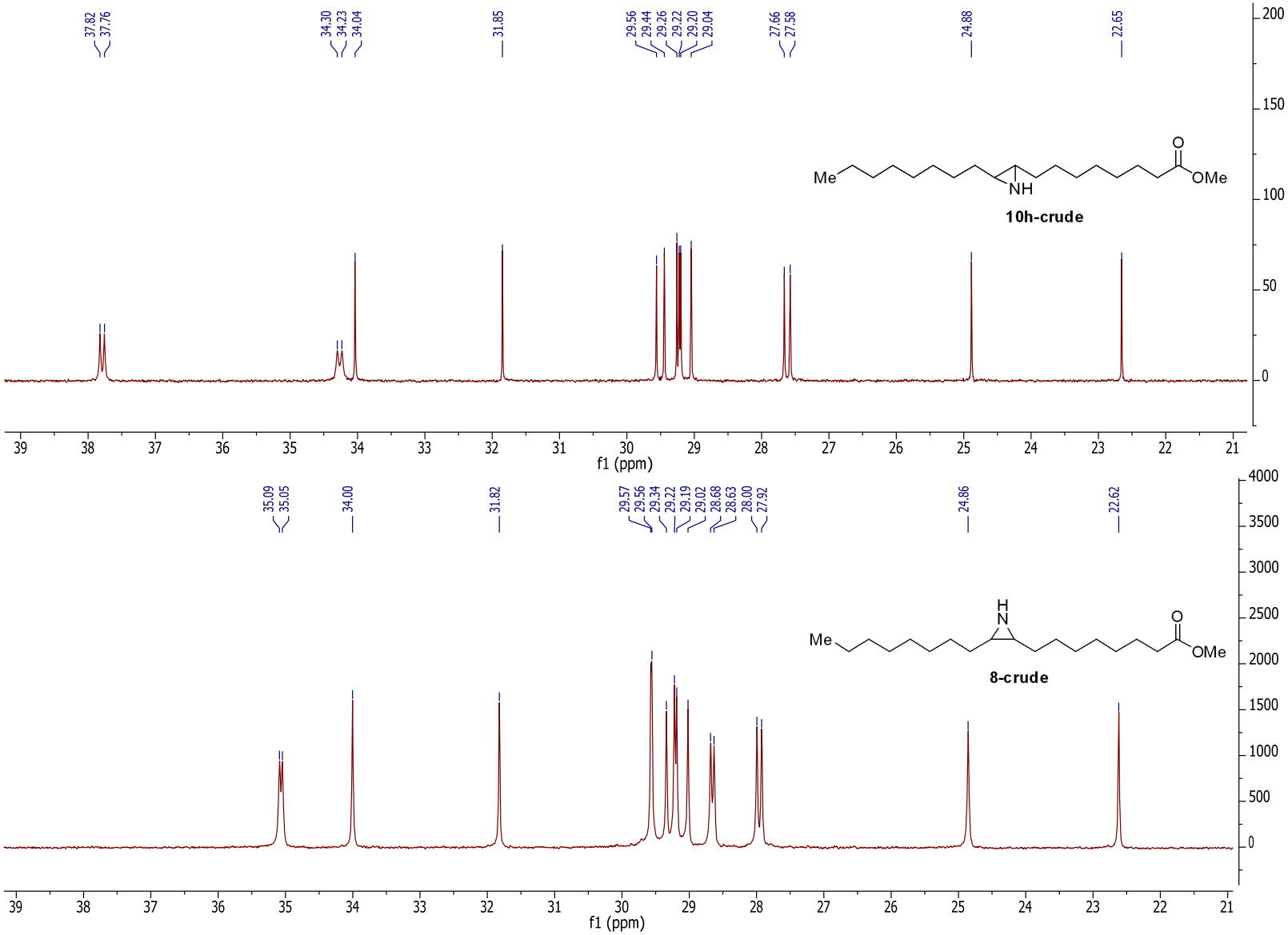


Figure S1c. Stereospecificity studies – Stacked crude ^{13}C-NMR spectra of N-H aziridines **10h** and **8**.

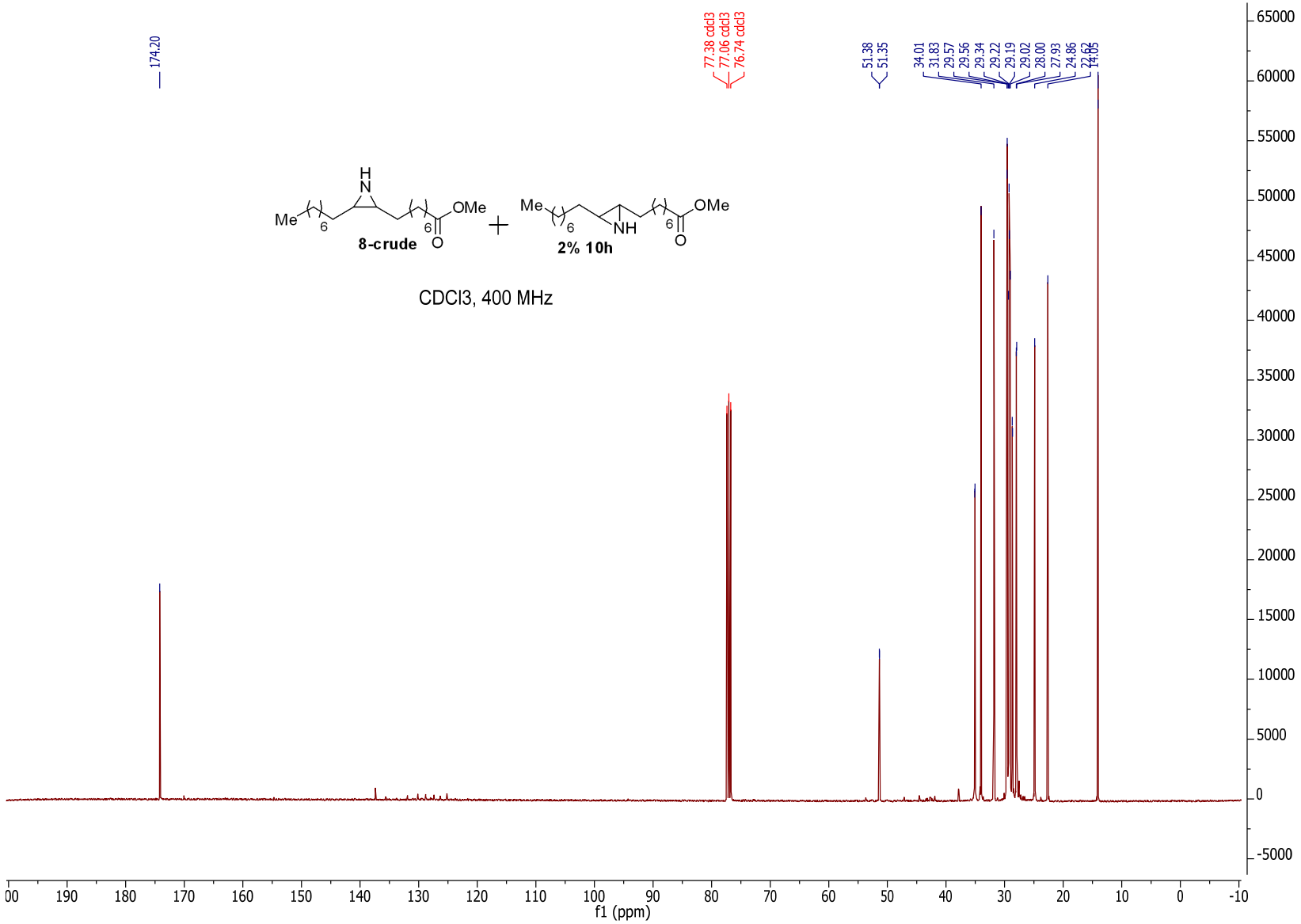


Figure S1d. Stereospecificity studies – Crude ^{13}C-NMR of **8** spiked with 2% of analytically pure **10h**.

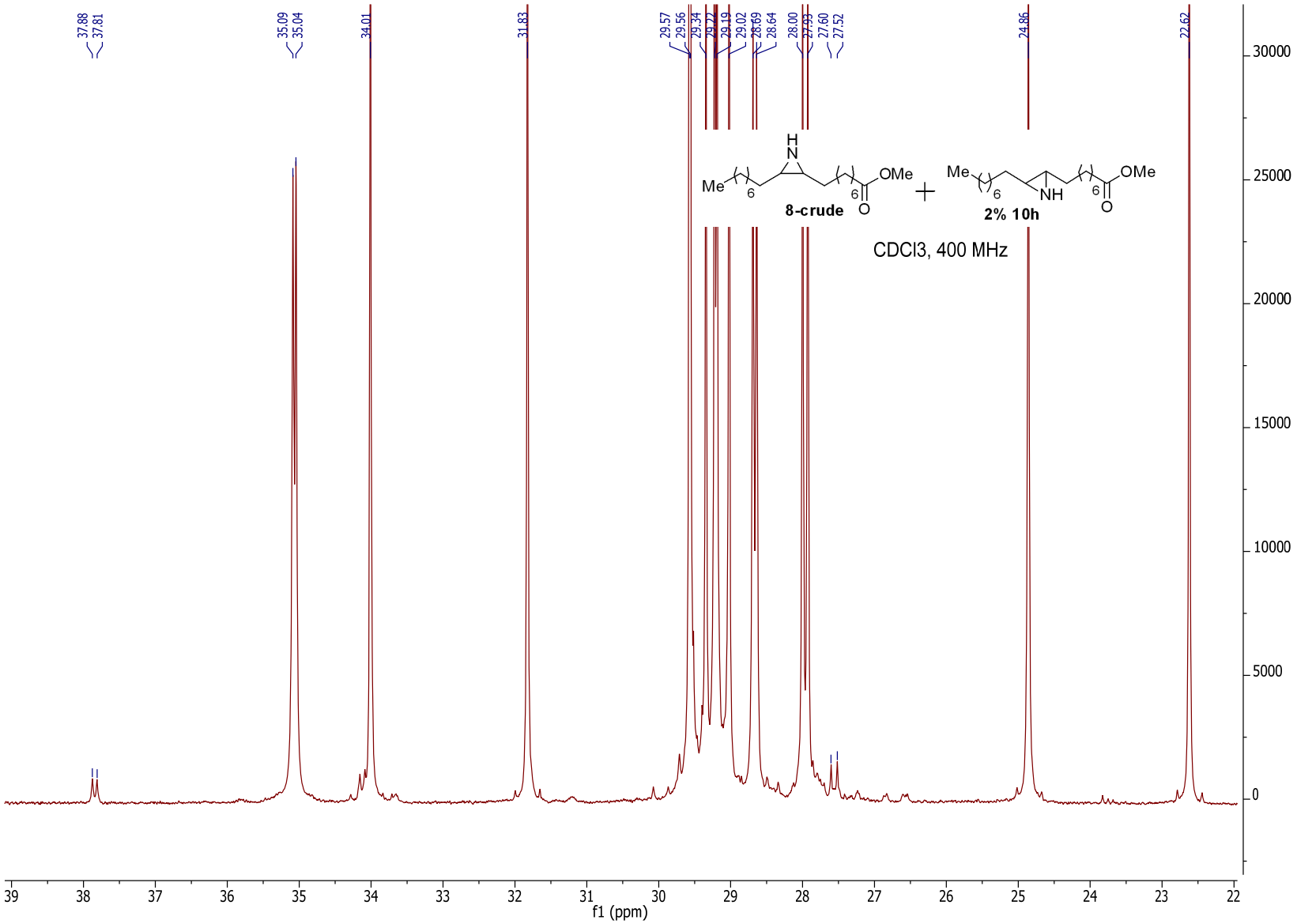


Figure S1e. Stereospecificity studies – Expanded crude ^{13}C-NMR of **8** spiked with 2% of analytically pure **10h**.

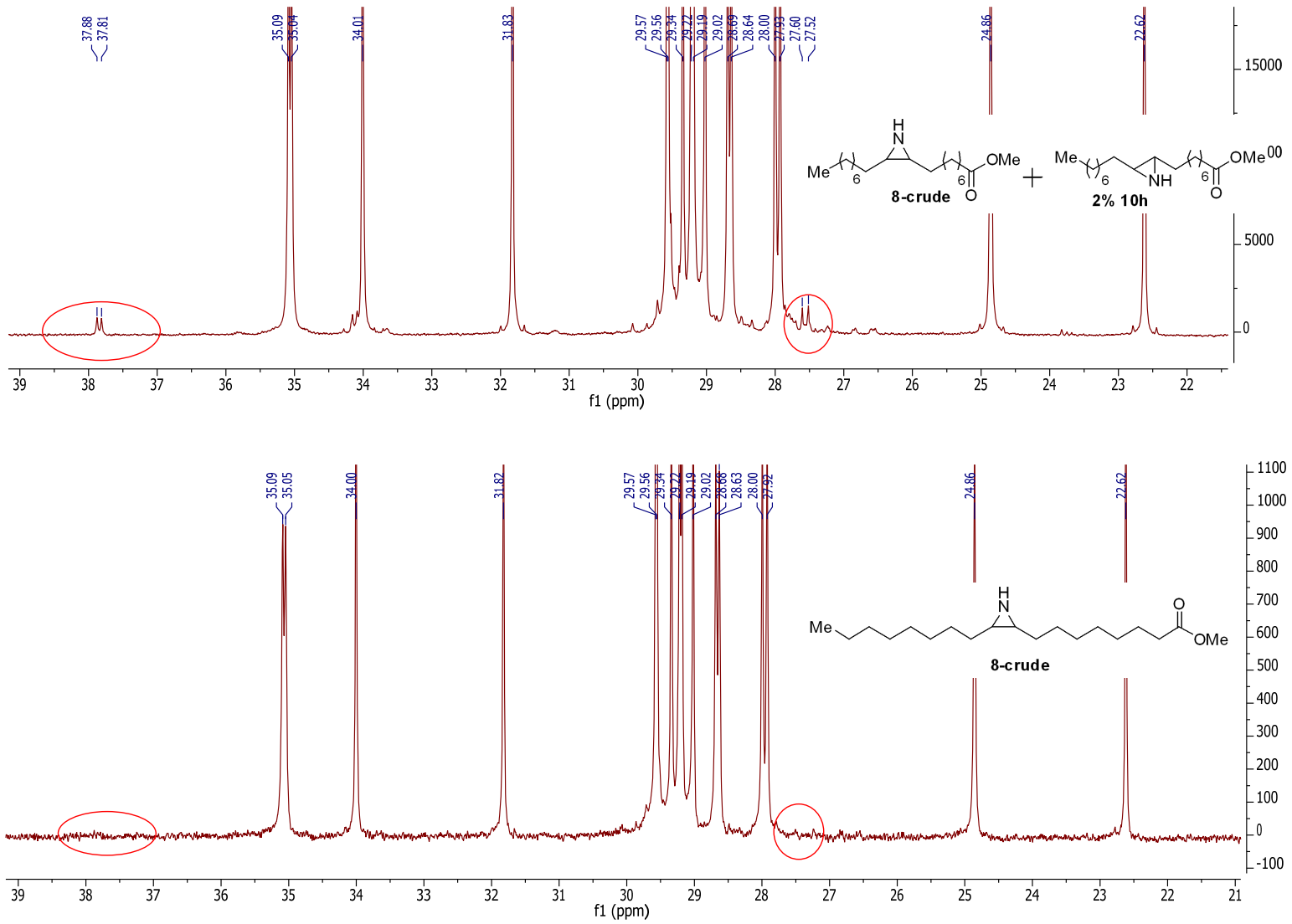


Figure S1f. Stereospecificity studies – Stacked crude ^{13}C-NMR of N-H aziridine **8** spiked with 2% of analytically pure **10h** and crude ^{13}C-NMR of N-H aziridine **8.**

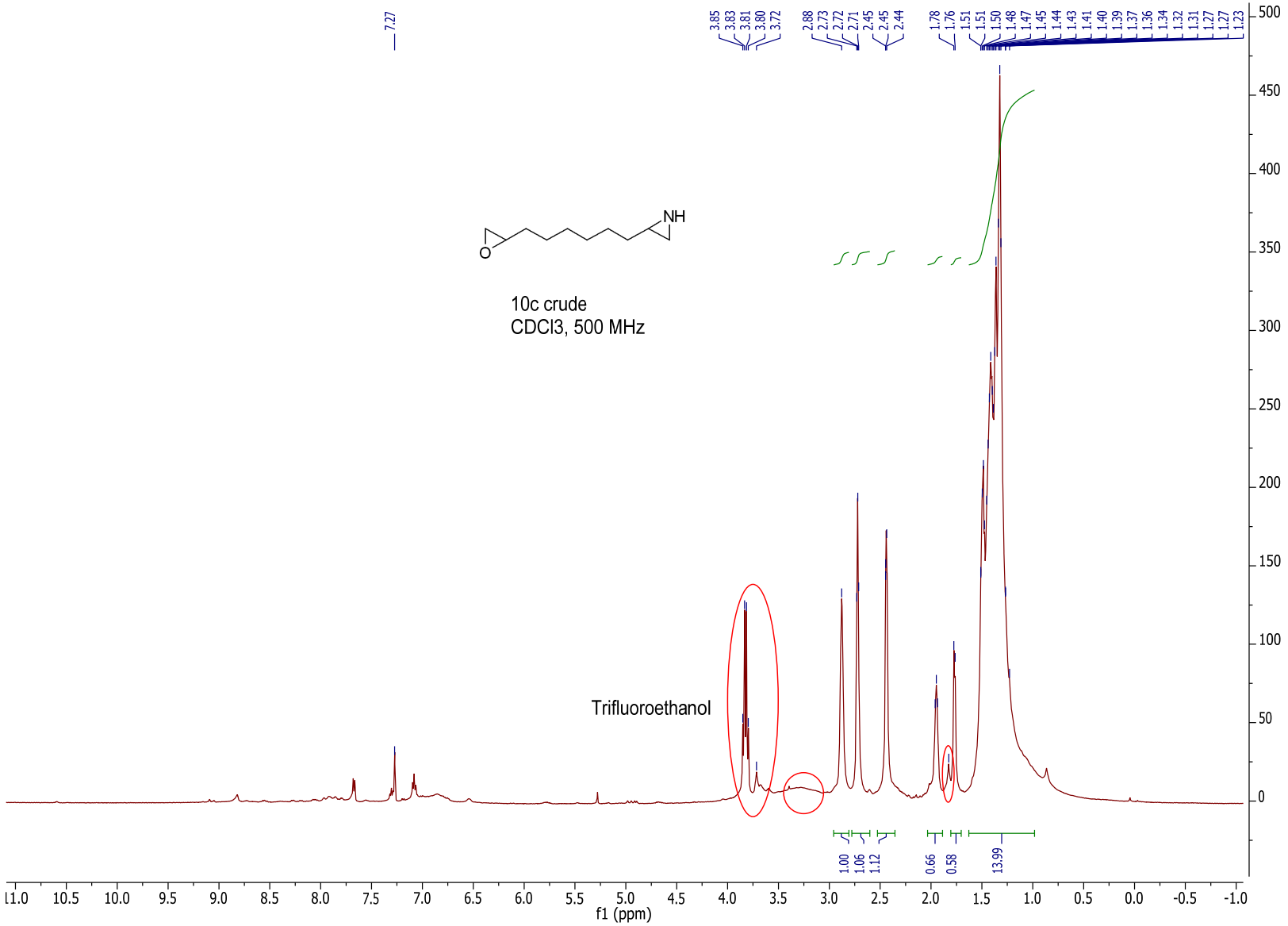


Figure S2a. Epoxy-olefin N-H aziridination study – Crude ^{1}H-NMR of N-H aziridine **10c**.

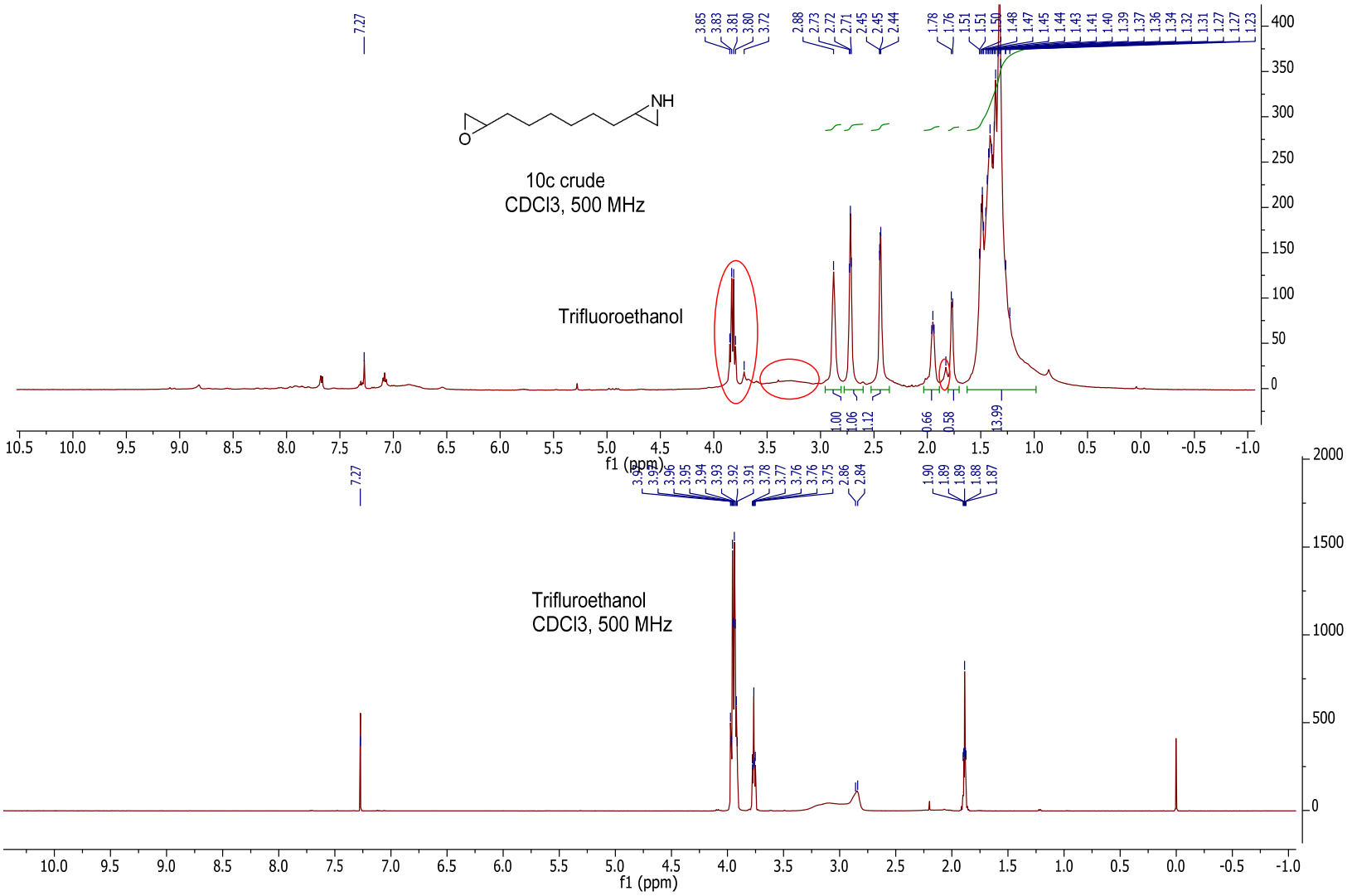


Figure S2b. Epoxy-olefin N-H aziridination study – Stacked crude ^{1}H-NMR of N-H aziridine **10c** and trifluoroethanol.

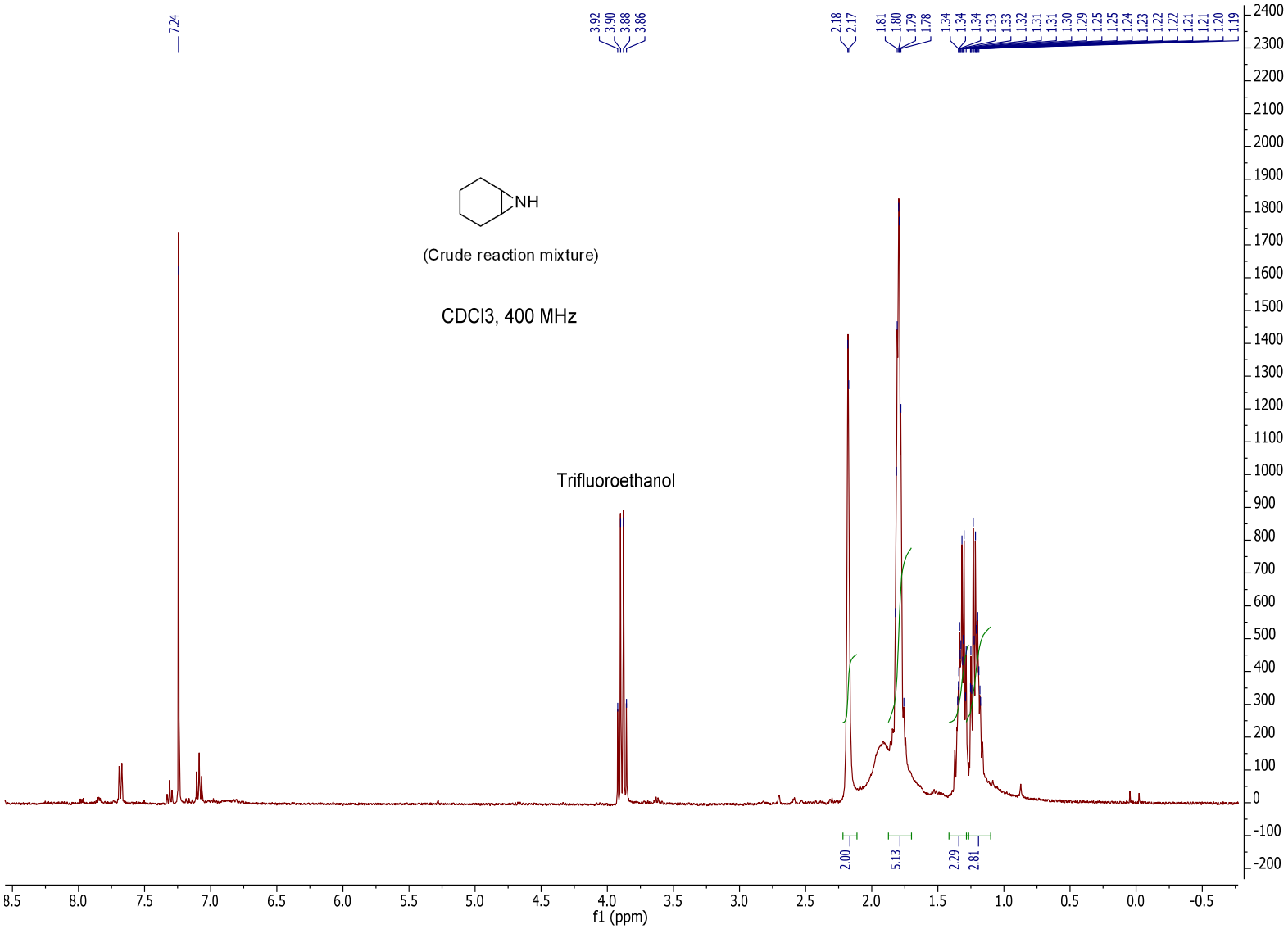


Figure S3a. Search for allylic C-H amination side product(s) during the N-H aziridination of cyclohexene **9n** – Crude ^{1}H-NMR of N-H aziridine **10n**.

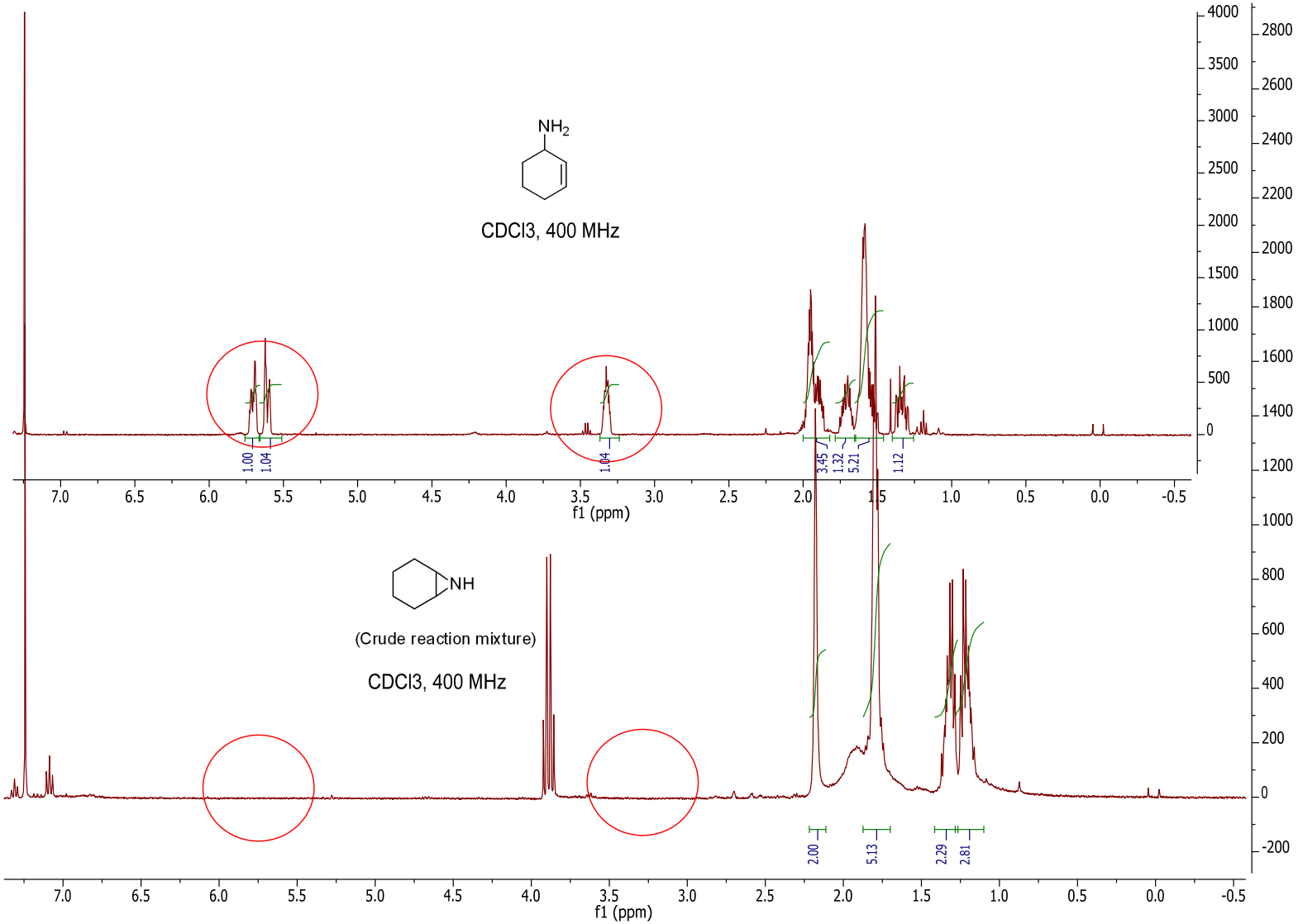


Figure S3b. Search for allylic C-H amination side product(s) during the N-H aziridination of cyclohexene **9n** – Stacked crude ^{1}H-NMR of N-H aziridine **10n** and independently prepared analytically pure cyclohex-2-enamine.

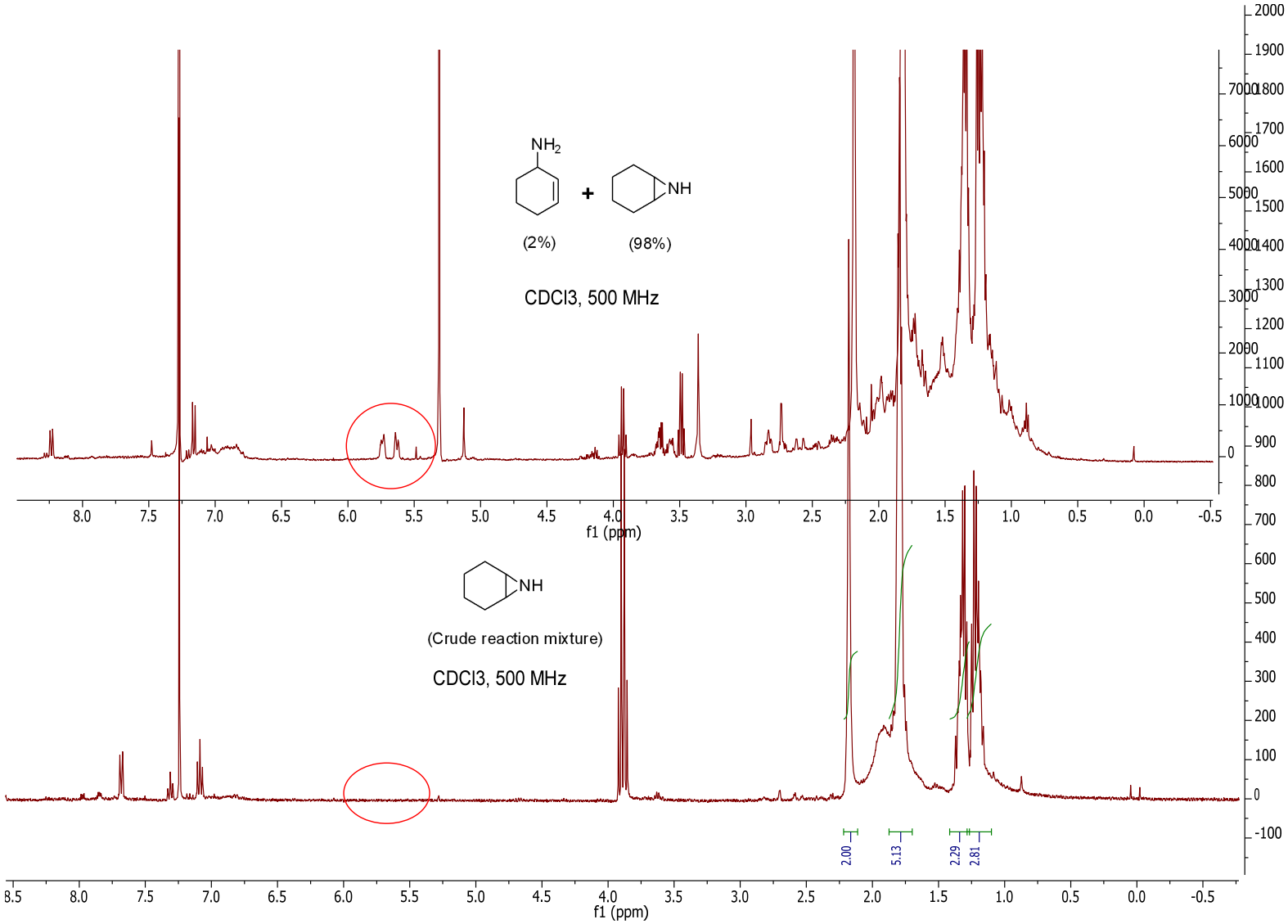
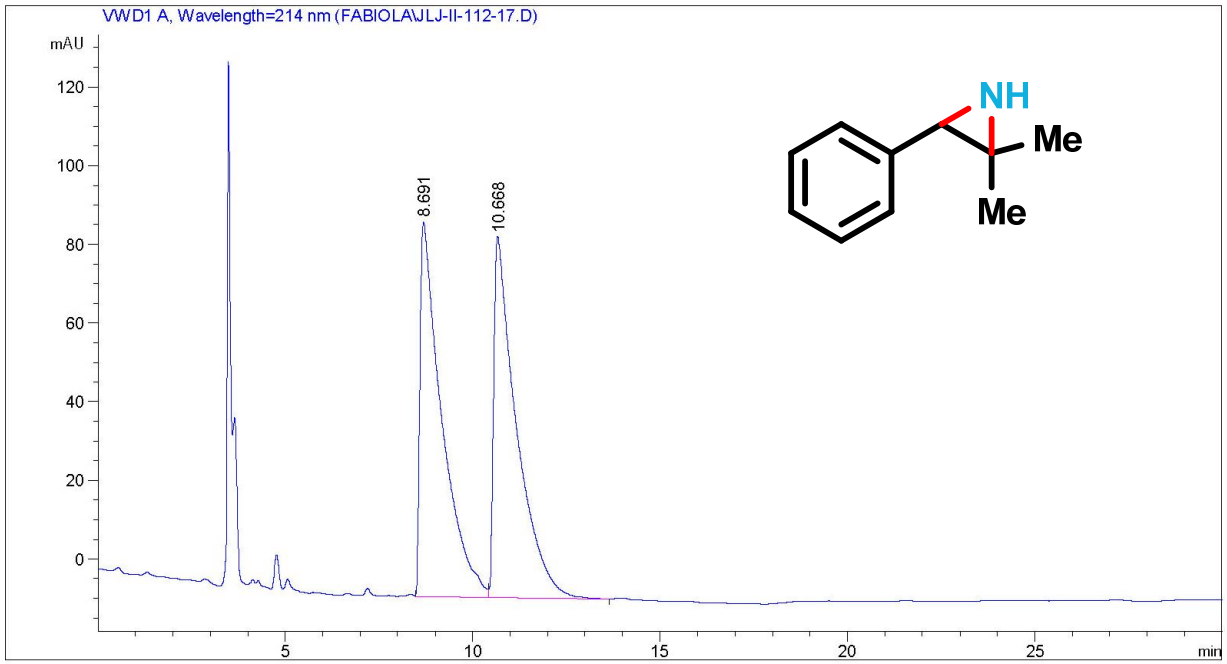


Figure S3c. Search for allylic C-H amination side product(s) during the N-H aziridination of cyclohexene **9n** – Stacked crude ^{1}H-NMR of N-H aziridine **10n** spiked with 2% of independently prepared cyclohex-2-enamine.

Column Conditions: Chiralpak IC, 5% IPA/Hexanes, 0.5 mL/min, Injection volume - 5 μL

I. Aziridine **12f** – Using Du Bois catalyst $Rh_2(esp)_2$

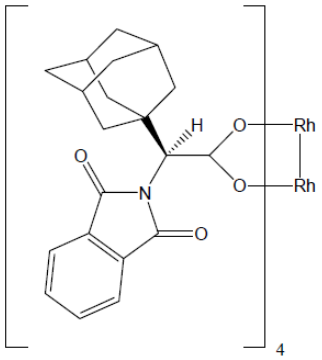


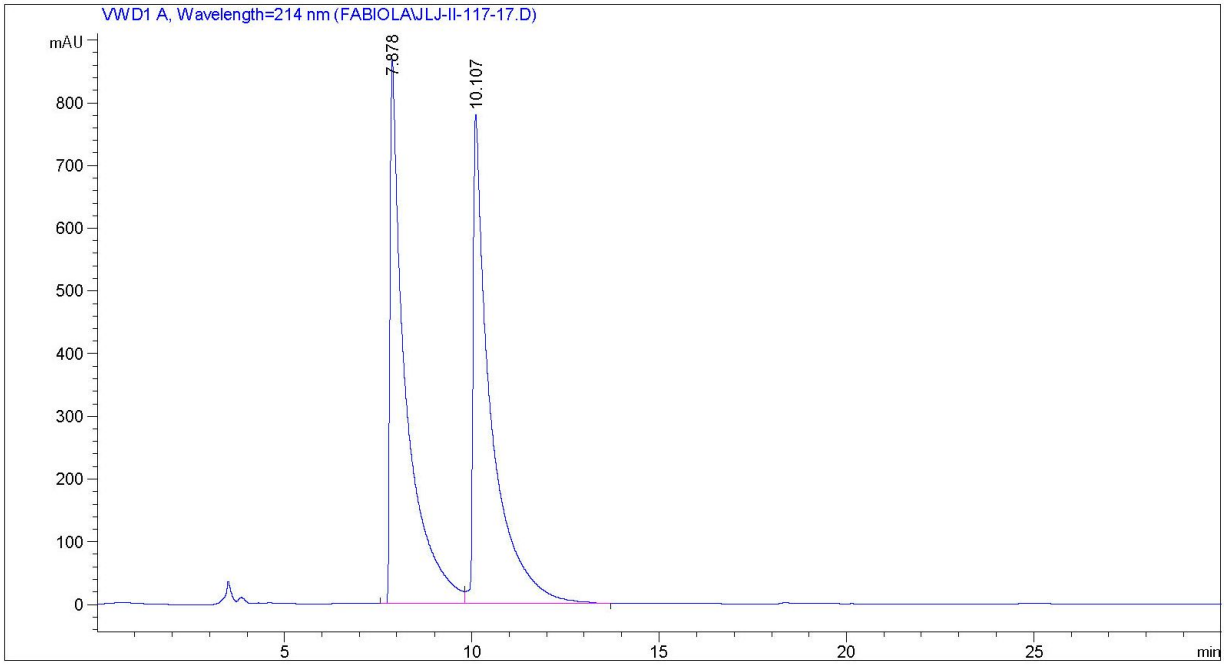
Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.691	VV	0.5435	3829.91064	95.17074	49.8774
2	10.668	VB	0.5655	3848.74243	91.72713	50.1226
Totals :				7678.65308	186.89787	

Figure S4a. Chiral induction studies – Chromatogram showing the baseline separation of the two enantiomers of N-H aziridine **12f** using chiral HPLC.

II. Aziridine **12f** – Using chiral catalyst Rh_2-(S)-PTAD





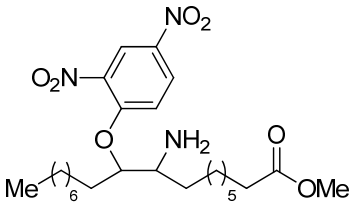
Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.878	BV	0.3776	2.52082e4	865.93591	50.0088
2	10.107	VB	0.4211	2.51993e4	779.54169	49.9912
Totals :				5.04074e4	1645.47760	

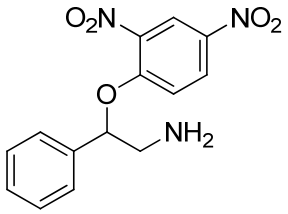
Figure S4b. Chiral induction studies – Chromatogram showing the baseline separation of the two enantiomers of N-H aziridine **12f** using chiral HPLC after the N-H aziridination of styrene **11f** using 5 mol% of Rh_2-(S)-PTAD instead of 1 mol% of catalyst **2**.

General Amino-oxyarylation Procedure

$Rh_2(OAc)_4$ or $Rh_2(esp)_2$ (Du Bois' catalyst, 1-5 mol%) and aminating agent (1.5 equiv) were added to a stirring, rt solution of alkene (1.0 equiv) in dry CH_3CN (0.1-0.5 M), unless otherwise specified. The reaction was stirred at the specified temperature and monitored by TLC. More catalyst and aminating agent were added, if required. After completion, the reaction mixture was diluted with EtOAc and washed once with 15% aqueous $NaHCO_3$ solution. The aqueous layer was extracted twice with EtOAc and the combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified on pre-packed SiO_2 columns using a CombiFlash chromatograph.

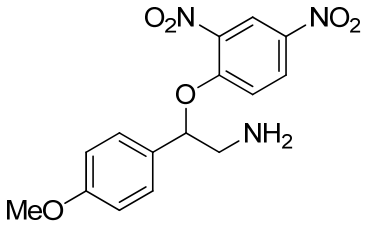


Methyl 9-amino-10-(2,4-dinitrophenoxy)octadecanoate: Following the general aminoaryloxylation procedure, methyl oleate **7** (10 mg, 34 μmol), aminating agent **1a** (10 mg, 51 μmol), and $Rh_2(OAc)_4$ (0.8 mg, 1.7 μmol) were stirred in dry CH_3CN (0.5 mL) at rt for 2 h, then at 60 °C for 10 h. Chromatographic purification of the crude product by preparative TLC using 40% EtOAc/hexanes as eluent afforded the title aminoaryloxylated product as a viscous oil (2.5 mg, 15%). TLC: $R_f \approx 0.5$ (30% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, J = 2.7 Hz, 1H), 8.93 (dd, J = 9.0, 2.4 Hz, 1H), 8.24 (dd, J = 9.6, 2.7 Hz, 1H), 6.94 (dd, J = 9.7, 3.5 Hz, 1H), 3.87–3.83 (m, 1H), 3.67 (s, 1.5H), 3.66 (s, 1.5H), 3.65–3.61 (m, 1H), 2.30 (t, J = 7.4 Hz, 1H), 2.29 (t, J = 7.4 Hz, 1H), 1.96 (br s, 1H), 1.80–1.77 (m, 1H), 1.76–1.14 (m, 30H), 0.87 (t, J = 6.9 Hz, 1.5H), 0.86 (t, J = 6.9 Hz, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.25, 174.24, 148.68, 148.66, 135.58, 130.31, 130.25, 124.77, 114.06, 114.03, 72.17, 57.40, 57.31, 51.51, 51.49, 34.50, 34.44, 33.96, 33.93, 32.13, 32.06, 31.77, 29.54, 29.43, 29.42, 29.40, 29.25, 29.17, 29.15, 29.12, 29.03, 28.96, 28.86, 26.19, 26.04, 25.79, 25.65, 24.74, 22.62, 22.61, 14.07; HRMS (ESI^+) Calcd. for $[C_{25}H_{41}N_3O_7+Na]^+$ 518.2837, Found 518.2827.



4a

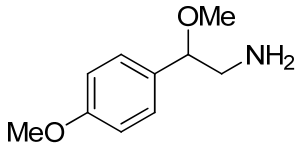
2-(2,4-Dinitrophenoxy)-2-phenylethanamine: Following the general aminoaryloxylation procedure, styrene **3a** (10 mg, 0.09 mmol), aminating agent **1a** (27 mg, 0.135 mmol), and $Rh_2(OAc)_4$ (2.0 mg, 4.5 μmol) were stirred in dry CH_3CN (0.5 mL) at rt for 1 h, then at 60 °C for 2 h. Chromatographic purification of the crude product by PTLC using EtOAc/hexanes (1:1) as eluent afforded the title aminoaryloxylated product as a foamy solid (7 mg, 25%), mp 123.6-123.9 °C. TLC: $R_f \approx 0.5$ (50% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11–9.08 (m, 1H), 8.89 (br s, 1H), 8.20 (dd, J = 9.4, 2.6 Hz, 1H), 7.52–7.31 (m, 5H), 6.89 (d, J = 9.5 Hz, 1H), 5.07 (dd, J = 7.7, 4.3 Hz, 1H), 3.72–3.56 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.33, 140.62, 136.08, 130.50, 130.19, 129.01, 128.82, 125.76, 124.27, 114.07, 72.42, 50.37; HRMS (ESI^+) Calcd. for $[C_{14}H_{13}N_3O_5+Na]^+$ 326.0747, Found 326.0741.



4b

2-(2,4-Dinitrophenoxy)-2-(4-methoxyphenyl)ethanamine: Following the general aminoaryloxylation procedure, 4-methoxystyrene **3b** (30 mg, 0.22 mmol), aminating agent **1a** (66 mg, 0.33 mmol), and $Rh_2(esp)_2$ (1.7 mg, 2.2 μmol) were stirred in dry CH_3CN (1 mL) at rt for 3 h. Chromatographic purification of the crude product by PTLC using EtOAc/hexanes (40%) as eluent afforded the title aminoaryloxylated product as a solid (57 mg, 75%), mp 114.6 °C. TLC: $R_f \approx 0.3$ (40% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, J = 2.7 Hz, 1H), 8.90 (t, J = 5.4 Hz, 1H), 8.25 (dd, J = 9.5, 2.7 Hz, 1H), 7.38 (d, J = 8.6 Hz, 2H), 6.97–6.91 (m, 3H), 5.08–5.02 (m, 1H), 3.84 (s, 3H), 3.73–3.55 (m, 2H), 2.20 (br s, 1H); ^{13}C NMR (101 MHz, CD_3CN) δ 159.37, 148.66, 135.67, 133.92, 129.83, 127.29, 123.73, 117.38, 115.22,

113.75, 70.83, 54.93, 50.23; HRMS (ESI^+) Calcd. for $[C_{15}H_{15}N_3O_6+Na]^+$ 356.0853, Found 356.0846.



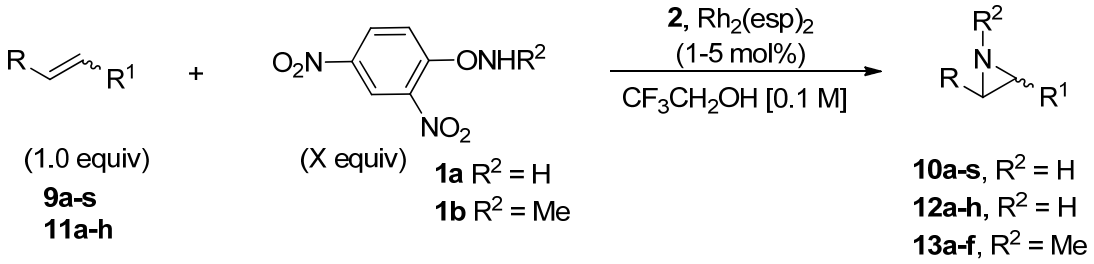
5

2-Methoxy-2-(4-methoxyphenyl)ethanamine: Following the general aminoaryloxylation procedure, 4-methoxystyrene **3b** (68 mg, 0.5 mmol), aminating agent **1a** (0.150 g, 0.75 mmol), and $Rh_2(esp)_2$ (19 mg, 25 μmol) were stirred in dry MeOH (1 mL) at rt for 4 h. Chromatographic purification of the crude product by CombiFlash using 5-10% MeOH/CH_2Cl_2 as eluent afforded the title aminomethoxylated product as a viscous liquid (52 mg, 56%) along with **4b** (36 mg, 22%). TLC: $R_f \approx 0.3$ (80% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.07 (dd, J = 7.7, 4.3 Hz, 1H), 3.79 (s, 3H), 3.22 (s, 3H), 2.88 (dd, J = 13.2, 7.7 Hz, 1H), 2.78 (dd, J = 13.2, 4.4 Hz, 1H), 1.48 (br s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) 159.21, 132.06, 127.91, 113.83, 85.30, 56.62, 55.23, 48.91; HRMS (ESI^+) Calcd. for $[C_{10}H_{15}NO_2+Na]^+$ 204.0995, Found 204.0991.

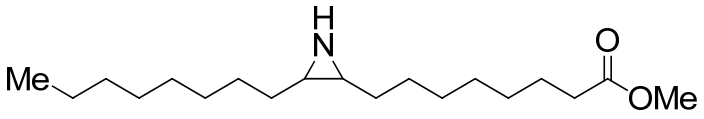
General N-H/N-Me Aziridination Procedure

A round bottom flask equipped with a magnetic stirrer was charged with alkene (0.5 mmol, 1.0 equiv) and CF_3CH_2OH (5 mL), unless otherwise specified. To this solution at the specified temperature were added $Rh_2(esp)_2$ (Du Bois' catalyst, 3.8 mg, 5 μmol, 1 mol%) and aminating agent **1a** (or **1b**) (0.119 g, 0.6 mmol, 1.2 equiv). The reaction was stirred at the specified temperature and monitored by TLC. More catalyst and aminating agent were added, if required. After completion, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed once with 15% aqueous $NaHCO_3$ solution (5 mL). The aqueous layer was extracted twice with CH_2Cl_2 (10 mL) and the combined organic portions were washed once with brine (5 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified on pre-packed SiO_2 columns using a CombiFlash chromatograph.

Scheme S1

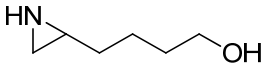


Experimental



8

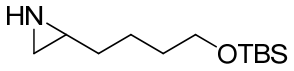
Methyl (*Z*)-8-(3-octylaziridin-2-yl)octanoate:(*42, 43*) Following the general aziridination procedure, methyl oleate **7** (0.148 g, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at rt for 3 h. Chromatographic purification of the crude product using 50–70% EtOAc/hexanes as eluent afforded the title aziridine as a viscous oil which solidified upon standing (0.130 g, 83%), mp 51.4–51.7 °C. TLC: $R_f \approx 0.3$ (60% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 3H), 2.27 (t, J = 7.5 Hz, 2H), 1.93–1.90 (m, 2H), 1.66–1.53 (m, 2H), 1.49–1.19 (m, 25H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.24, 51.39, 34.94, 34.90, 34.05, 31.84, 29.60, 29.58, 29.37, 29.24, 29.21, 29.05, 28.87, 28.82, 28.04, 27.97, 24.89, 22.63, 14.07; HRMS (ESI$^+$) Calcd. for $[C_{19}H_{37}NO_2+H]^+$ 312.2897, Found 312.2887.



10a

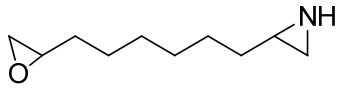
4-(Aziridin-2-yl)butan-1-ol: Following the general aziridination procedure, hex-5-en-1-ol **9a** (0.1 g, 1.0 mmol), aminating agent **1a** (0.239 g, 1.2 mmol), and $Rh_2(esp)_2$ (38 mg, 50 μmol, 5 mol%) were stirred in CF_3CH_2OH (10 mL) at rt for 2 h. Chromatographic purification on a CombiFlash system using 10-15% MeOH/CH_2Cl_2 as eluent afforded the title aziridine as a viscous oil (68 mg, 59%). TLC: $R_f \approx 0.4$ (20% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59 (td, J = 6.2, 1.7 Hz, 2H), 2.17 (br s, 2H), 1.97–1.94 (m, 1H), 1.77 (d, J = 5.9 Hz, 1H), 1.68–

1.39 (m, 5H), 1.42–1.27 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 62.01, 33.53, 32.27, 30.29, 25.02, 23.82; HRMS (ESI$^+$) Calcd. for $[C_6H_{13}NO+H]^+$ 116.1070, Found 116.1074.



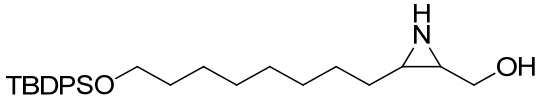
10b

2-(4-(*tert*-Butyldimethylsilyloxy)butyl)aziridine: Following the general aziridination procedure, *tert*-butyl(hex-5-en-1-yloxy)dimethylsilane(*44*) **9b** (0.107 g, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (19 mg, 25 μmol, 5 mol%) were stirred in CF_3CH_2OH (5 mL) at rt for 2 h. Chromatographic purification on a CombiFlash system using 2-3% MeOH/CH_2Cl_2 as eluent afforded the title aziridine as a viscous oil (83 mg, 72%). TLC: $R_f \approx$ 0.5 (10% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.61 (t, J = 6.3 Hz, 2H), 1.95–1.91 (m, 1H), 1.75 (d, J = 5.8 Hz, 1H), 1.62–1.34 (m, 6H), 1.32 (d, J = 3.6 Hz, 1H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 63.07, 34.21, 32.58, 30.25, 25.93, 25.05, 23.85, 18.32, -5.32; HRMS (ESI$^+$) Calcd. for $[C_{12}H_{27}NOSi+H]^+$ 230.1935, Found 230.1934.



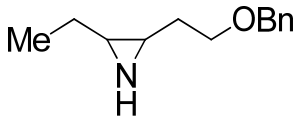
10c

2-(6-(Oxiran-2-yl)hexyl)aziridine: Following the general aziridination procedure, 2-(oct-7-en-1-yl)oxirane **9c** (77 mg, 0.5 mmol), aminating agent **1a** (0.199 g, 1.0 mmol), and $Rh_2(esp)_2$ (19 mg, 25 μmol) were stirred in CF_3CH_2OH (5 mL) at rt for 5 h. Chromatographic purification on a CombiFlash system gave the title aziridine as a viscous oil (65 mg, 77%). TLC: $R_f \approx$ 0.5 (10% MeOH/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90–2.84 (m, 1H), 2.71 (dd, J = 4.9, 4.2 Hz, 1H), 2.43 (dd, J = 5.0, 2.7 Hz, 1H), 1.93–1.87 (m, 1H), 1.72 (d, J = 5.8 Hz, 1H), 1.55–1.20 (m, 13H), 1.04 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 52.33, 47.08, 34.33, 32.41, 30.32, 29.36, 29.33, 27.44, 25.88, 25.07; HRMS (ESI$^+$) Calcd. for $[C_{10}H_{19}NO+H]^+$ 170.1539, Found 170.1544.



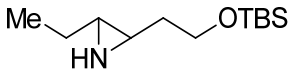
10d

(*Z*)-(3-(8-(*tert*-Butyldimethylsilyloxy)octyl)aziridin-2-yl)methanol: Following the general aziridination procedure, (*Z*)-11-(*tert*-butyldiphenylsilyloxy)undec-2-en-1-ol **9d** (21 mg, 50 μmol), aminating agent **1a** (12 mg, 60 μmol), and $Rh_2(esp)_2$ (0.4 mg, 0.5 μmol) were stirred in CF_3CH_2OH (0.5 mL) at rt. After 2 h, another portion of catalyst (0.4 mg, 0.5 μmol, 1 mol%) and aminating agent (12 mg, 60 μmol, 1.2 equiv) were added and the stirring was continued for an additional 1 h. Chromatographic purification via preparative TLC using 15% MeOH/CH_2Cl_2 as eluent afforded the title aziridine as a viscous oil (14 mg, 64%). TLC: $R_f \approx 0.4$ (15% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.66 (m, 4H), 7.49–7.33 (m, 6H), 3.77 (dd, *J* = 11.5, 4.9 Hz, 1H), 3.66 (t, *J* = 6.5 Hz, 2H), 3.52 (dd, *J* = 11.6, 7.1 Hz, 1H), 2.35 (br s, 1H), 2.15 (br s, 1H), 1.81 (br s, 2H), 1.55 (app qn, *J* = 7.0 Hz, 2H), 1.51–1.17 (m, 12H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.55, 134.16, 129.45, 127.54, 63.98, 61.11, 35.42, 35.31, 32.56, 29.69, 29.55, 29.41, 29.30, 28.80, 27.98, 26.86, 25.74, 19.21; HRMS (ESI^+) Calcd. for $[C_{27}H_{41}NO_2Si+H]^+$ 440.2979, Found 440.2980.



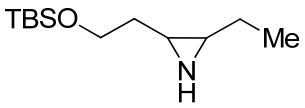
10e

(*Z*)-2-(2-(Benzyloxy)ethyl)-3-ethylaziridine: Following the general aziridination procedure, (*Z*)-((hex-3-en-1-yloxy)methyl)benzene(*45*) **9e** (38 mg, 0.2 mmol), aminating agent **1a** (48 mg, 0.24 mmol), and $Rh_2(esp)_2$ (4.5 mg, 6 μmol, 3 mol%) were stirred in CF_3CH_2OH (2 mL) at rt for 36 h. The catalyst was added in three equal portions; the remaining two at intervals of 12 h after the initial addition. The crude aziridine was purified by Et_3N basified preparative TLC using EtOAc as eluent to afford the title aziridine as an oil (32 mg, 78%). TLC: $R_f \approx 0.2$ (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.33 (m, 3H), 7.32–7.22 (m, 2H), 4.54 (s, 2H), 3.64 (dd, *J* = 7.0, 6.0 Hz, 2H), 2.26–2.13 (m, 1H), 2.20–1.90 (m, 1H), 1.85–1.78 (m, 1H), 1.64–1.57 (m, 1H), 1.44–1.38 (m, 2H), 1.26 (br s, 1H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.46, 128.37, 127.64, 127.55, 73.02, 68.93, 36.30, 32.20, 29.00, 22.07, 12.09; HRMS (ESI^+) Calcd. for $[C_{13}H_{19}NO+H]^+$ 206.1539, Found 206.1536.



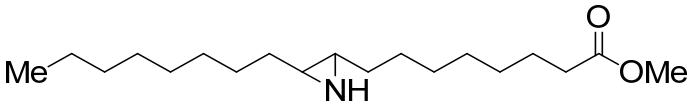
10f

(*E*)-2-(2-(*tert*-Butyldimethylsilyloxy)ethyl)-3-ethylaziridine: Following the general aziridination procedure, (*E*)-*tert*-butyl(hex-3-en-1-yloxy)dimethylsilane **9f** (54 mg, 0.25 mmol), aminating agent **1a** (60 mg, 0.3 mmol), and $Rh_2(esp)_2$ (1.9 mg, 2.5 μmol) were stirred in CF_3CH_2OH (2.5 mL) at rt for 4 h. Chromatographic purification of the crude product by Et_3N basified preparative TLC using 80% EtOAc/hexanes as eluent afforded the title aziridine as an oil (41 mg, 72%). TLC: $R_f \approx 0.3$ (80% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.74 (t, *J* = 6.2 Hz, 2H), 1.77 (br s, 1H), 1.69–1.63 (m, 2H), 1.62–1.53 (m, 1H), 1.51–1.37 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 61.49, 38.95, 37.21, 34.93, 27.21, 25.93, 18.30, 11.64, -5.34, -5.35; HRMS (ESI^+) Calcd. for $[C_{12}H_{27}NOSi+H]^+$ 230.1935, Found 230.1943.



10g

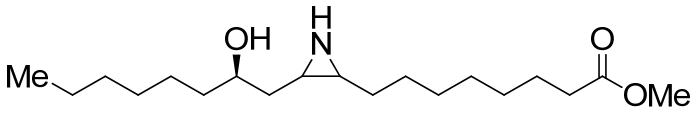
(*Z*)-2-(2-(*tert*-Butyldimethylsilyloxy)ethyl)-3-ethylaziridine: Following the general aziridination procedure, (Z)-*tert*-butyl(hex-3-en-1-yloxy)dimethylsilane(*46*) **9g** (43 mg, 0.2 mmol), aminating agent **1a** (48 mg, 0.24 mmol), and $Rh_2(esp)_2$ (1.5 mg, 2 μmol) were stirred in CF_3CH_2OH (2 mL) at rt. After 24 h, more Rh-catalyst (1.5 mg, 2 μmol, 1 mol%) was added and the stirring was continued for another 5 h. Chromatographic purification of the crude product by Et_3N basified preparative TLC using 80% EtOAc/hexanes as eluent afforded the title aziridine as an oil (25 mg, 55%). TLC: $R_f \approx 0.3$ (80% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80–3.70 (m, 2H), 2.17 (br s, 1H), 2.00 (br s, 1H), 1.75–1.65 (m, 1H), 1.57–1.45 (m, 1H), 1.42 (app qn, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 61.81, 36.34, 32.06, 31.85, 25.97, 22.15, 18.37, 12.13, -5.29; HRMS (ESI^+) Calcd. for $[C_{12}H_{27}NOSi+H]^+$ 230.1935, Found 230.1927.



10h

Methyl *E*-8-(3-octylaziridin-2-yl)octanoate: Following the general aziridination procedure, methyl elaidate **9h** (0.148 g, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at rt for 2 h. Chromatographic purification

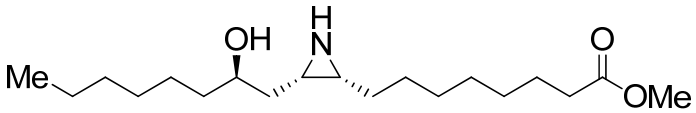
of the crude product using 50–70% EtOAc/hexanes as eluent afforded the title aziridine as a viscous, reddish brown oil which solidified upon standing (0.142 g, 91%), mp 41.1–41.4 °C. TLC: $R_f \approx$ 0.3 (60% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (s, 3H), 2.26 (t, J = 7.6 Hz, 2H), 1.60–1.54 (m, 4H), 1.43–1.15 (m, 25H), 0.84 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.20, 51.38, 37.74, 37.68, 34.34, 34.29, 34.02, 31.82, 29.53, 29.42, 29.22, 29.20, 29.16, 29.02, 27.63, 27.55, 24.86, 22.61, 14.05; HRMS (ESI$^+$) Calcd. for $[C_{19}H_{37}NO_2+H]^+$ 312.2897, Found 312.2886.



10i

Methyl (*Z*)-8-[3-(2*R*-hydroxyoctyl)aziridine-2-yl]octanoate:(*43*) Following the general aziridination procedure, methyl ricinoleate **9i** (0.156 g, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (11.4 mg, 15 μmol, 3 mol%) were stirred in CF_3CH_2OH (5 mL) at rt for 6 h. The catalyst was added in three equal portions at intervals of 2 h. Purification of the crude product using 5–10% MeOH/CH_2Cl_2 as eluent afforded the title aziridine as a viscous oil (0.135 g, 82%) obtained as a 1:1 mixture of diastereomers. TLC: $R_f \approx$ 0.5 (10% MeOH/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95–3.82 (m, 0.8H), 3.82–3.73 (m, 0.8H), 3.66 (s, 3H), 2.29 (t, J = 7.5 Hz, 2H), 2.25–2.20 (m, 1H), 2.00–1.96 (m, 1H), 1.77–1.55 (m, 3H), 1.54–1.12 (m, 22H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.334, 174.326, 72.03, 71.10, 51.49, 37.74, 37.48, 34.54, 34.32, 34.07, 33.71, 33.49, 33.09, 31.87, 31.85, 31.34, 29.41, 29.38, 29.34, 29.30, 29.26, 29.24, 29.06, 28.79, 28.61, 27.79, 27.61, 25.86, 25.49, 24.91, 22.65, 22.64, 14.13, 14.12; HRMS (ESI$^+$) Calcd. for $[C_{19}H_{37}NO_3+Na]^+$ 350.2666, Found 350.2660.

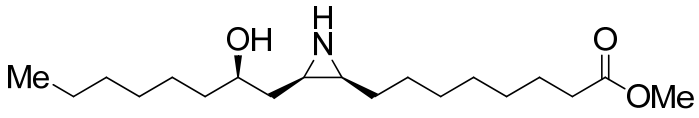
The diastereomers were resolved via preparative TLC using MeOH/EtOAc (1:5):



10i - dr A

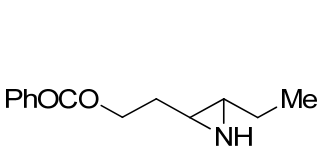
Methyl 8-[3(*S*)-(2*R*-hydroxyoctyl)aziridine-2*R*-yl]octanoate: TLC: $R_f \approx$ 0.5 (17% MeOH/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84–3.80 (m, 1H), 3.67 (s, 3H), 2.31 (t, J = 7.5

Hz, 2H), 2.27 (br s, 1H), 2.02 (br s, 1H), 1.71 (br s, 1H), 1.65–1.57 (m, 2H), 1.57–1.50 (m, 2H), 1.49–1.23 (m, 21H), 0.88 (t, *J* = 7.1 Hz, 3H).

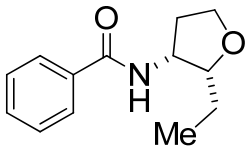


10i - dr B

Methyl 8-[3*R*-(2*R*-hydroxyoctyl)aziridine-2(*S*)-yl]octanoate: TLC: R_f ≈ 0.4 (17% MeOH/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92–3.84 (m, 1H), 3.68 (s, 3H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.26 (br s, 1H), 2.00 (br s, 1H), 1.80–1.72 (m, 1H), 1.67–1.60 (m, 2H), 1.54–1.17 (m, 23H), 0.89 (t, *J* = 7.1 H, 3H).



and rearrangement to

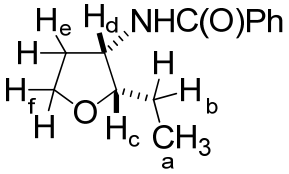


10j **10jj**

(*E*)-2-(3-Ethylaziridin-2-yl)ethyl benzoate and rearrangement product (*Z*)-*N*-(2-ethyltetrahydrofuran-3-yl)benzamide: Following the general aziridination procedure, (*E*)-hex-3-en-1-yl benzoate(*47*) **9j** (0.102 g, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at rt for 1 h. Chromatographic purification of the crude product using a CombiFlash with 50–70% EtOAc/hexanes as eluent afforded the title aziridine as a reddish brown oil (95 mg, 86%) along with **10jj**, obtained as a yellow oil (5 mg, 4%), arising from O→N benzoate migration followed by S_N2 addition of the oxygen to the now activated aziridine. **(*E*)-2-(3-ethylaziridin-2-yl)ethyl benzoate:** TLC: R_f ≈ 0.3 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–7.98 (m, 2H), 7.62–7.51 (m, 1H), 7.51–7.36 (m, 2H), 4.53–4.35 (m, 2H), 1.95–1.76 (m, 3H), 1.70 (td, *J* = 6.1, 2.5 Hz, 1H), 1.56–1.29 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.51, 132.91, 130.21, 129.52, 128.34, 63.40, 39.07, 34.44, 33.47, 27.29, 11.61; HRMS (ESI$^+$) Calcd. for $[C_{13}H_{17}NO_2+H]^+$ 220.1332, Found 220.1334; IR (neat) 3297, 3220, 2963, 1718 cm^{-1}. **(*Z*)-N-(2-ethyltetrahydrofuran-3-yl)benzamide:** TLC: R_f ≈ 0.5 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.80 (m, 2H), 7.45–7.26 (m, 3H), 4.80 (ddd, *J* = 10.7, 9.2, 3.1 Hz, 1H), 4.07 (td, *J* = 9.1, 5.5 Hz, 1H), 3.88–3.80 (m, 2H), 1.95–1.68 (m, 2H), 1.68–1.40 (m, 3H), 1.05 (t, *J* = 7.3 Hz, 3H);

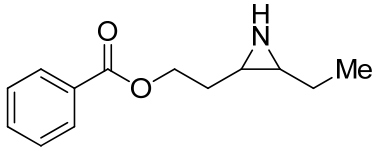
^{13}C NMR (126 MHz, $CDCl_3$) 162.43, 131.26, 128.29, 128.11, 127.96, 80.29, 69.97, 60.63, 32.05, 23.74, 11.85; HRMS (ESI^-) Calcd. for $[C_{13}H_{17}NO_2\text{-}H]^-$ 218.1187; Found 218.1180; IR (neat) 3280, 2959, 2937, 1646 cm^{-1}.

Structure confirmed by nOe: (see spectrum also)



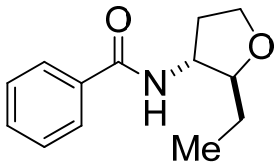
10jj

Irradiation (saturation) of proton d (H_d) leads to the enhancement of the protons e (H_e) and c (H_c). Protons a and b (H_a and H_b) of ethyl group are completely suppressed.



10k

(*Z*)-2-(3-Ethylaziridin-2-yl)ethyl benzoate: Following the general aziridination procedure, (*Z*)-hex-3-en-1-yl benzoate(*47*) **9k** (0.102 g, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (19 mg, 25 μmol, 5 mol%) were stirred in CF_3CH_2OH (5 mL) at rt for 2 h. Chromatographic purification on a CombiFlash system using 70-90% EtOAc/hexanes as eluent afforded the title aziridine as a viscous oil (76 mg, 69%). TLC: $R_f \approx 0.3$ (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.03 (m, 2H), 7.57–7.53 (m, 1H), 7.45–7.41 (m, 2H), 4.47 (t, J = 6.4 Hz, 2H), 2.22 (app q, J = 6.4 Hz, 1H), 2.05 (app q, J = 6.7 Hz, 1H), 2.01–1.92 (m, 2H), 1.82–1.73 (m, 1H), 1.45 (app qn, J = 7.3 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 132.91, 130.25, 129.54, 128.34, 63.67, 36.38, 32.05, 28.10, 21.93, 12.04. HRMS (ESI^+) Calcd. for $[C_{13}H_{17}NO_2\text{+}H]^+$ 220.1332, Found 220.1336.

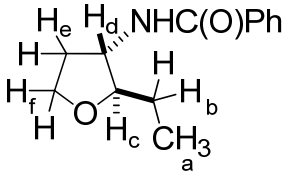


10kk

(*E*)-*N*-(2-Ethyltetrahydrofuran-3-yl)benzamide: Aminating agent **1a** (0.119 g, 0.6 mmol) was added to a stirring, rt solution of (*Z*)-hex-3-en-1-yl benzoate **9k** (0.102 g, 0.5 mmol) and

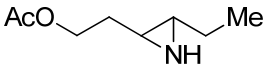
$Rh_2(esp)_2$ (3.8 mg, 5 μmol) in CF_3CH_2OH (5 mL). After 16 h, the temperature was raised to 50 °C. Following another 9 h at this higher temperature, more Rh-catalyst (3.8 mg, 5 μmol, 1 mol%) was added. Thereafter, two more portions of catalyst (3.8 mg) were added every 24 h. The substrate was completely consumed after a total of 96 h. The reaction mixture was then cooled to rt, diluted with CH_2Cl_2 (10 mL), and washed with 15% aqueous $NaHCO_3$ solution (5 mL). The layers were separated and the aqueous layer was extracted with fresh CH_2Cl_2 (10 mL ×2). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated. Chromatographic purification of the residue on a CombiFlash system to afforded the title tetrahydrofuran as a viscous liquid (92 mg, 84%). TLC: $R_f \approx 0.3$ (60% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.88 (m, 2H), 7.52–7.44 (m, 1H), 7.44–7.35 (m, 2H), 4.49 (ddd, J = 8.8, 6.4, 4.1 Hz, 1H), 3.92–3.74 (m, 3H), 2.86 (br s, 1H), 2.00–1.81 (m, 2H), 1.80–1.53 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.68, 131.35, 128.26, 128.19, 127.79, 81.84, 73.24, 59.14, 38.40, 28.34, 9.82; HRMS (ESI^+) Calcd. for $[C_{13}H_{17}NO_2+H]^+$ 220.1332, Found 220.1325; IR (neat) 3286, 2961, 2933, 1644 cm^{-1}.

Structure confirmed by nOe: (see spectrum also)



10kk

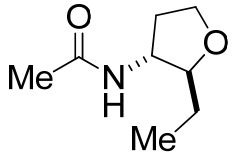
Irradiation (saturation) of proton d (H_d) leads to the enhancement of the proton e (H_e) and protons a and b (H_a and H_b) of ethyl group.



10l

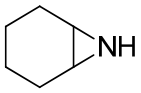
(*E*)-2-(3-Ethylaziridin-2-yl)ethyl acetate: Following the general aziridination procedure, (*E*)-hex-3-en-1-yl acetate(*48*) **9l** (0.1 g, 0.7 mmol), aminating agent **1a** (0.167 g, 0.84 mmol), and $Rh_2(esp)_2$ (5.3 mg, 7 μmol) were stirred in CF_3CH_2OH (7 mL) at rt for 1.5 h. Chromatographic purification on a CombiFlash system using 70-90% EtOAc/hexanes as eluent afforded the title aziridine as an oil (91 mg, 83%). TLC: $R_f \approx 0.3$ (90% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17–4.13 (m, 2H), 2.02 (s, 3H), 1.76–1.58 (m, 4H), 1.49–1.40 (m, 1H), 1.38–1.30 (m, 1H), 0.96 (t, J = 7.4 Hz, 3H), 0.41 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.06, 62.89,

39.00, 34.33, 33.22, 27.28, 20.96, 11.61; HRMS (ESI^+) Calcd. for $[C_8H_{15}NO_2+H]^+$ 158.1176, Found 158.1170; IR (neat) 3297, 3222, 2964, 1739 cm^{-1}.



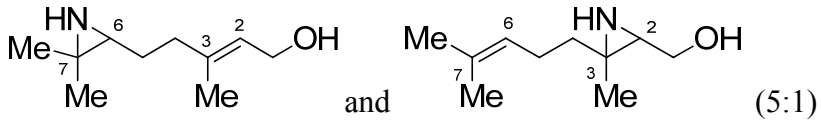
10mm

(*E*)-*N*-(2-Ethyltetrahydrofuran-3-yl)acetamide: A mixture of (*Z*)-hex-3-en-1-yl acetate(*48*) **9m** (0.124 g, 0.87 mmol), aminating agent **1a** (0.208 g, 1.04 mmol), and $Rh_2(esp)_2$ (6.6 mg, 1 mol%) was stirred at rt in CF_3CH_2OH (8 mL). Three additional portions of catalyst (6.6 mg, 1 mol %) were added every 12 h thereafter for a total of 26.4 mg (35 μmol, 4 mol%). After a total of 51 h, the reaction mixture was quenched and chromatographically purified on a CombiFlash system using 80-100% EtOAc/hexanes as eluent to afford the title tetrahydrofuran as a viscous oil (84 mg, 61%) obtained as a mixture of diastereomers (>95:5). TLC: $R_f \approx 0.3$ (80% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) (major diastereomer) δ 4.23 (ddd, J = 8.7, 6.7, 4.3 Hz, 1H), 3.77–3.67 (m, 2H), 3.58–3.50 (m, 1H), 3.19 (br s, 1H), 1.92 (s, 3H), 1.87–1.68 (m, 2H), 1.63–1.37 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.98, 82.16, 72.85, 58.89, 38.28, 28.28, 14.04, 9.84; HRMS (ESI^+) Calcd. for $[C_8H_{15}NO_2+H]^+$ 158.1176, Found 158.1173; IR (neat) 3272, 2963, 2935, 1668 cm^{-1}.



10n

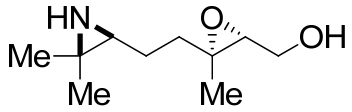
7-Azabicyclo[4.1.0]heptanes:(*49*) Following the general aziridination procedure, cyclohexene **9n** (41 mg, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at rt for 3 h. Chromatographic purification on a CombiFlash system using 60-70% EtOAc/hexanes as eluent to give the title aziridine as an oil (34 mg, 71%). TLC: $R_f \approx 0.3$ (80% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 2.15 (br s, 2H), 1.81–1.76 (m, 4H), 1.37–1.30 (m, 2H), 1.28–1.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) 29.35, 24.51, 20.02.



(5:1)

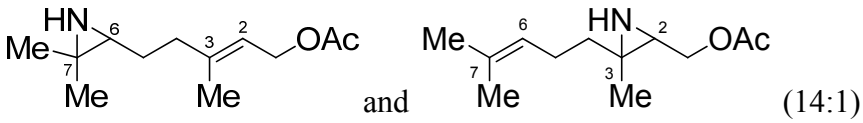
10o

5-(3,3-Dimethylaziridin-2-yl)-3-methylpent-2(*E*)-en-1-ol:(*50*) Following the general aziridination procedure, geranyl alcohol **9o** (46 mg, 0.3 mmol), aminating agent **1a** (66 mg, 0.33 mmol, 1.1 equiv), and $Rh_2(esp)_2$ (2.3 mg, 3 μmol) were combined at 0 °C in CF_3CH_2OH (3 mL), then stirred at rt for 5 h. Chromatographic purification of the crude product over Florisil using 5-10% MeOH/CH_2Cl_2 as eluent afforded the title aziridine (30 mg, 59%) as an oil accompanied by the 2,3-regioisomer (6 mg, 12%). **Major regioisomer**. TLC $R_f \approx 0.3$ (20% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44–5.42 (m, 1H), 4.15 (d, J = 6.8 Hz, 2H), 2.21–2.05 (m, 2H), 1.75 (t, J = 6.6 Hz, 1H), 1.69 (s, 3H), 1.62–1.46 (m, 2H), 1.25 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.77, 123.93, 59.12, 43.09, 37.75, 35.65, 28.11, 27.51, 19.69, 16.33. **Minor regioisomer**. **3-methyl-3-(4-methylpent-3-en-1-yl)aziridin-2 (*E*)-yl)methanol:** TLC: $R_f \approx 0.4$ (20% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12–5.08 (m, 1H), 3.74 (dd, J = 11.5, 5.4 Hz, 1H), 3.55 (dd, J = 11.5, 7.0 Hz, 1H), 2.19–2.07 (m, 3H), 1.70 (s, 3H), 1.63 (s, 3H), 1.63–1.57 (m, 1H), 1.35 (dt, J = 13.7, 8.1 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.22, 123.44, 61.48, 42.68, 41.52, 39.27, 25.69, 24.81, 17.67, 17.16.



10p

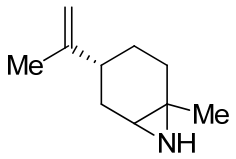
((2*R*,3*R*)-3-(2-(3,3-dimethylaziridin-2-yl)ethyl)-3-methyloxiran-2-yl)methanol: Following the general aziridination procedure, ((2*R*,3*R*)-3-methyl-3-(4-methylpent-3-en-1-yl)oxiran-2-yl)methanol(*51*) **9p** (85 mg, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at 0-5 °C for 4 h. Chromatographic purification on a CombiFlash system using 10-20% MeOH/CH_2Cl_2 as eluent to give the title aziridine (1:1 diastereomers) as an oil (78 mg, 84%). TLC: $R_f \approx 0.3$ (10% MeOH/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74–3.61 (m, 2H), 2.94 (app q, J = 5.4 Hz, 1H), 2.25 (br s, 2H), 1.83–1.68 (m, 2H), 1.65–1.35 (m, 3H), 1.28 (s, 1.5H), 1.27 (s, 1.5H), 1.23 (s, 3H), 1.14 (s, 1.5H), 1.13 (s, 1.5 H); ^{13}C NMR (101 MHz, CDCl3) δ 63.06, 62.69, 60.71, 60.67, 60.65, 60.64, 43.20, 42.97, 36.95, 36.53, 36.07, 35.92, 27.34, 27.28, 25.39, 25.30, 19.46, 19.39, 16.95, 16.57; HRMS (ESI^+) Calcd. for $[C_{10}H_{19}NO_2+H]^+$ 186.1489, Found 186.1490.



10q

5-(3,3-Dimethylaziridin-2-yl)-3-methylpent-2(*E*)-en-1-yl acetate: Following the general aziridination procedure, geranyl acetate **9q** (59 mg, 0.3 mmol), aminating agent **1a** (72 mg, 0.36 mmol), and $Rh_2(esp)_2$ (2.3 mg, 3 μmol) were stirred in CF_3CH_2OH (3 mL) at rt for 3 h. Chromatographic purification of the crude product by Et_3N basified preparative TLC using 80% EtOAc/hexanes as eluent afforded the title aziridine as an oil (48 mg, 76%) and its 2,3-regioisomer (3.5 mg, 5%). **6,7-Regioisomer**. TLC: $R_f \approx 0.3$ (80% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (tq, J = 7.1, 1.4 Hz, 1H), 4.56 (d, J = 7.2 Hz, 2H), 2.24–2.05 (m, 2H), 2.03 (s, 3H), 1.74 (t, J = 6.6 Hz, 1H), 1.69 (s, 3H), 1.60–1.51 (m, 2H), 1.24 (s, 3H), 1.14 (s, 3H), 1.01 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.08, 141.76, 118.58, 61.29, 43.02, 37.68, 35.86, 27.93, 27.40, 21.05, 19.62, 16.46; HRMS (ESI^+) Calcd. for $[C_{12}H_{21}NO_2+H]^+$ 212.1645, Found 212.1651. **2,3-Regioisomer**. TLC: $R_f \approx 0.4$ (80% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09–5.05 (m, 1H), 4.16–4.00 (m, 2H), 2.16–1.99 (m, 3H), 2.06 (s, 3H), 1.66 (s, 3H), 1.60 (s, 3H), 1.60–1.54 (m, 1H), 1.31 (ddd, J = 13.6, 9.2, 6.8 Hz, 1H), 1.17 (s, 3H), 0.46 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.01, 132.11, 123.33, 64.89, 41.31, 39.28, 38.67, 25.65, 24.72, 20.90, 17.61, 17.41; HRMS (ESI^+) Calcd. for $[C_{12}H_{21}NO_2+Na]^+$ 234.1465, Found 234.1456.

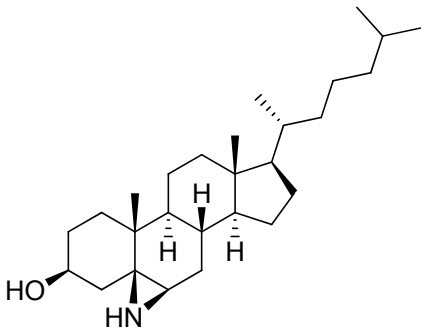
When the above aziridination was repeated using 1.18 gram (6.0 mmol) of geranyl acetate, the yield of 6,7-regioisomer was 72% and 2,3-regioisomer was 5%.



10r

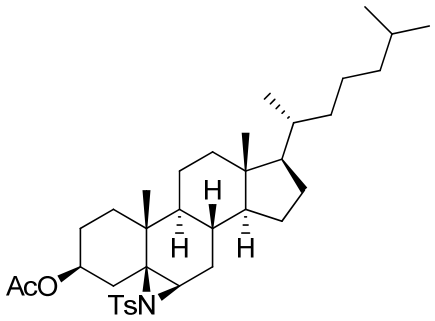
4(*R*)-1-Methyl-4-(prop-1-en-2-yl)-7-azabicyclo[4.1.0]heptanes:(*52*) (*R*)-(+)-Limonene **9r** (68 mg, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were combined at 0 °C in CH_3CF_2OH (5 mL), then stirred at rt for 12 h. Chromatographic purification on a CombiFlash system using 60-70% EtOAc/hexanes as eluent gave the title aziridine as an oil (54 mg, 72%) obtained as a 1:1 mixture of diastereomers. TLC: $R_f \approx 0.3$ (80% EtOAc/hexanes);

^{1}H NMR (400 MHz, $CDCl_3$) of 1:1 mixture of diastereomers: δ 4.68–4.66 (m, 1H), 4.65–4.63 (m, 1H), 4.62–4.60 (m, 2H), 2.09–2.02 (m, 1H), 2.01–1.96 (m, 5H), 1.93–1.73 (m, 3H), 1.67–1.63 (m, 3H), 1.66 (s, 3H), 1.65 (s, 3H), 1.51–1.37 (m, 3H), 1.26 (s, 3H), 1.24 (s, 3H), 1.20–1.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.75, 149.43, 108.81, 108.70, 41.52, 39.25, 37.65, 36.61, 35.22, 34.53, 30.98, 30.55, 30.45, 29.52, 27.47, 26.50, 26.37, 24.86, 21.08, 20.38; HRMS (ESI$^+$) Calcd. for $[C_{10}H_{17}NO+H]^+$ 152.1434, Found 152.1436.



10s

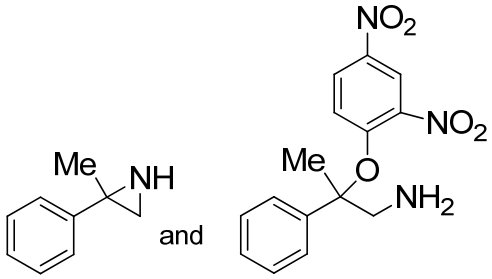
5*β*,6*β*-Aziridinylcholestan-3-*β*-ol:(*53*) Following the general aziridination procedure, cholesterol **9s** (0.193 g, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in a mixture of CH_3CF_2OH (3 mL) and THF (2 mL) at rt. After 24 h, another portion of catalyst (3.8 mg, 5 μmol, 1 mol%) and aminating agent (0.1 g, 0.5 mmol, 1.0 equiv) were added and the stirring was continued for an additional 24 h. Chromatographic purification on a CombiFlash system using 1-2% MeOH/CH_2Cl_2 as eluent afforded the title aziridine as a solid (0.14 g, 71%), mp 130-132 ^{o}C. TLC: $R_f \approx 0.3$ (10% MeOH/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of invertomers) δ 3.79–3.64 (m, 1H), 2.18 (dd, J = 12.9, 11.3 Hz, 0.5H), 2.11 (br s, 0.5H), 1.99 (dd, J = 12.8, 11.0 Hz, 0.5H), 1.91–1.85 (m, 4H), 1.80–1.70 (m, 2H), 1.62–1.59 (m, 1H), 1.50–1.47 (m, 2H), 1.34–1.26 (m, 9H), 1.09–1.06 (m, 6H), 1.03 (s, 3H), 0.93 (s, 3H), 0.85–0.80 (m, 11H), 0.60 (s, 1.5 H), 0.56 (s, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.97, 68.64, 57.08, 56.52, 56.21, 55.87, 51.13, 45.92, 45.23, 42.72, 42.65, 42.38, 42.28, 42.26, 42.19, 39.94, 39.44, 37.37, 36.93, 36.10, 36.08, 35.74, 35.68, 34.34, 34.11, 32.48, 32.31, 31.42, 30.96, 30.19, 29.92, 28.69, 28.14, 28.06, 27.95, 27.94, 24.14, 23.97, 23.84, 23.78, 22.78, 22.52, 22.23, 20.87, 18.66, 18.63, 18.60, 16.29, 11.89, 11.87; HRMS (ESI$^+$) Calcd. for $[C_{27}H_{47}NO+H]^+$ 402.3730, Found 402.3733.



10ss

(3*S*,4a*S*,5a*S*,6a*S*,6b*S*,9*R*,9a*R*,11a*S*,11b*R*)-9a,11b-dimethyl-9-((*R*)-6-methylheptan-2-yl)-5-tosylhexadecahydro-1H-cyclopenta[1,2]phenanthro[8a,9-b]azirin-3-ylacetate:(*54*)

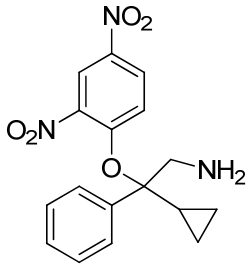
Cholesterol aziridine **10s** (80 mg, 0.2 mmol), tosyl chloride (46 mg, 0.24 mmol), acetic anhydride (0.4 mL) and pyridine (1 mL) were reacted following the literature described procedure.(*54*) Chromatographic separation of the crude product using EtOAc/hexanes (5-10%) as eluent furnished the title compound as a white solid (38 mg, 32%), m.p. 157-158 °C, lit. m.p. 148-150 °C. TLC: $R_f \approx 0.7$ (30% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), δ 7.28 (d, J = 8.1 Hz, 2H), 4.95-4.88 (1H, m), 3.15 (br s, 1H), 2.53 (dd, J = 13.3, 11.0 Hz, 1H), 2.43 (s, 3H), 2.29 (dd, J = 13.3, 5.9 Hz, 1H), 2.04 (s, 3H), 2.00–1.87 (m, 1H), 1.90–1.67 (m, 4H), 1.60–0.91 (m, 19H), 1.05 (s, 3H), 0.91–0.73 (m, 10H), 0.73–0.62 (m, 1H), 0.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.52, 143.39, 139.05, 129.33, 126.83, 70.50, 57.02, 56.03, 55.94, 50.07, 48.30, 42.16, 39.68, 39.45, 36.16, 36.05, 35.68, 34.17, 32.53, 30.46, 29.89, 28.07, 27.98, 26.57, 24.09, 23.75, 22.79, 22.54, 22.03, 21.58, 21.32, 20.63, 18.62, 11.71.



12a and **12aa**

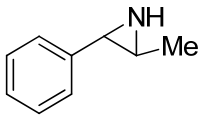
2-Methyl-2-phenylaziridine:(*55*) Following the general aziridination procedure, α-methylstyrene **11a** (59 mg, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at 0 °C for 2 h. Chromatographic purification by Et_3N basified preparative TLC using 60% EtOAc/hexanes as eluent afforded the

title aziridine as an oil (42 mg, 64%) accompanied by aminoaryloxylated product **12aa** (11 mg, 7%) as a sticky solid. **Aziridine**: TLC: $R_f \approx 0.3$ (60% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.23 (m, 5H), 1.98 (s, 1H), 1.97 (s, 1H), 1.63 (s, 3H), 1.01 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.60, 128.39, 126.82, 126.17, 36.97, 35.01, 25.17; HRMS (ESI^+) Calcd. for $[C_9H_{11}N+H]^+$ 134.0964, Found 134.0960. **2-(2,4-Dinitrophenoxy)-2-phenylpropan-1-amine:** TLC: $R_f \approx 0.7$ (60% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 2.7 Hz, 1H), 8.79 (t, J = 5.3 Hz, 1H), 8.13 (dd, J = 9.6, 2.7 Hz, 1H), 7.59–7.45 (m, 2H), 7.44–7.36 (m, 2H), 7.35–7.19 (m, 1H), 6.85 (d, J = 9.6 Hz, 1H), 3.70–3.57 (m, 2H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.51, 144.19, 135.83, 130.31, 130.08, 128.79, 127.91, 124.72, 124.18, 114.21, 74.00, 54.68, 27.79; HRMS (ESI^-) Calcd. for $[C_{15}H_{15}N_3O_5-H]^-$ 316.0939, Found 316.0929.



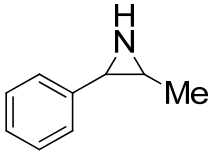
12b

2-Cyclopropyl-2-(2,4-dinitrophenoxy)-2-phenylethanamine: $Rh_2(esp)_2$ (3.8 mg, 5 μmol) and aminating agent **1a** (0.119 g, 0.6 mmol) were added successively to a stirring solution of (1-cyclopropylvinyl)benzene(*56*) **11b** (72 mg, 0.5 mmol) in CF_3CH_2OH (5 mL) at 0 °C. After 2 h, the reaction mixture was diluted with CH_2Cl_2 (10 mL) followed by 15% aqueous $NaHCO_3$ solution (5 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated. The residue was purified on a CombiFlash system over SiO_2 using 15-20% EtOAc/hexanes to furnish the title amine as an oil (0.125 g, 73%). TLC: $R_f \approx 0.5$ (30% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (d, J = 2.7 Hz, 1H), 8.87 (t, J = 4.5 Hz, 1H), 8.19 (dd, J = 9.5, 2.7 Hz, 1H), 7.64–7.50 (m, 2H), 7.44–7.39 (m, 2H), 7.36–7.31 (m, 1H), 6.92 (d, J = 9.6 Hz, 1H), 3.88–3.69 (m, 2H), 2.03 (br s, 1H), 1.52–1.46 (m, 1H), 0.76–0.62 (m, 2H), 0.61–0.49 (m, 1H), 0.39–0.33 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.52, 143.10, 135.83, 130.34, 130.15, 128.72, 128.10, 125.38, 124.27, 114.18, 74.44, 54.20, 19.24, 1.52, 0.64; HRMS (ESI^+) Calcd. for $[C_{17}H_{17}N_3O_5+Na]^+$ 366.1060, Found 366.1052.



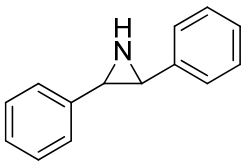
12c

(*E*)-2-Methyl-3-phenylaziridine:(*57*) Following the general aziridination procedure, *trans-β*-methylstyrene **11c** (59 mg, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at -10 °C for 14 h. Chromatographic purification by Et_3N basified preparative TLC using 60% EtOAc/hexanes as eluent afforded the title aziridine as an oil (35 mg, 53%). TLC: $R_f \approx 0.3$ (50% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.13 (m, 5H), 2.68 (d, J = 2.9 Hz, 1H), 2.18–2.14 (m, 1H), 1.38 (d, J = 5.5 Hz, 3H), 1.28 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.37, 128.48, 126.98, 125.52, 40.46, 37.15, 19.64.



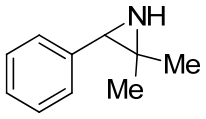
12d

(*Z*)-2-Methyl-3-phenylaziridine:(*57*) Following the general aziridination procedure, c*is-β*-methylstyrene **11d** (59 mg, 0.5 mmol), aminating agent **1a** (0.119 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol, 1 mol%) were stirred in CF_3CH_2OH (5 mL) at -10 °C. Two additional portions of catalysts (3.8 mg) were added at 24 h intervals. After a total of 68 h, the reaction was subjected to extractive isolation and the resultant crude material was chromatographically purified by Et_3N basified preparative TLC using 60% EtOAc/hexanes as eluent to give the title aziridine as an oil (51 mg, 76%). TLC: $R_f \approx 0.4$ (60% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.19 (m, 5H), 3.26 (d, J = 6.6 Hz, 1H), 2.42 (app qn, J = 5.8 Hz, 1H), 1.46 (br s, 1H), 0.93 (d, J = 5.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.53, 127.92, 127.80, 126.65, 37.17, 32.24, 13.62.



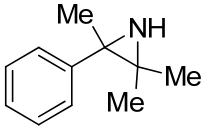
12e

(*E*)-2,3-Diphenylaziridine:(*58*) Following the general aziridination procedure, *trans*-stilbene **11e** (90 mg, 0.5 mmol), aminating agent **1a** (0.109 g, 0.55 mmol, 1.1 equiv), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in a mixture of CF_3CH_2OH (3 mL) and THF (2 mL) at rt. After 16 h, another portion of catalyst (5 μmol, 3.8 mg) and aminating agent (0.02 g, 0.1 mmol, 0.2 equiv) was added and the stirring was continued for another an additional 7 h. Chromatographic purification on a CombiFlash system over $^tBu_3N$ basified SiO_2 using 10-15% EtOAc/hexanes to afford the title aziridine as an oil (49 mg, 51%). TLC: $R_f \approx 0.4$ (30% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66–6.82 (m, 10H), 3.12 (br s, 2H), 1.50 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.60, 128.62, 127.32, 125.47, 43.70.



12f

2,2-Dimethyl-3-phenylaziridine:(*59*) Following the general procedure, (2-methylprop-1-en-1-yl)benzene **11f** (0.132 g, 1.0 mmol), aminating agent **1a** (0.219 g, 1.1 mmol, 1.1 equiv), and $Rh_2(esp)_2$ (7.6 mg, 10 μmol) were stirred in CF_3CH_2OH (10 mL) at rt for 3 h. Chromatographic purification by flash column chromatography over Florisil® using 10-25% EtOAc/hexanes as eluent afforded the title aziridine as an oil (0.135 g, 92%). TLC: $R_f \approx 0.4$ (50% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.30 (m, 4H), 7.28–7.17 (m, 1H), 3.05 (s, 1H), 1.46 (s, 3H), 0.94 (s, 3H), 0.65 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) 138.43, 127.91, 127.50, 126.51, 45.39, 38.49, 27.51, 19.43; HRMS (ESI^+) Calcd. for $[C_{10}H_{13}N+H]^+$ 148.1121, Found 148.1122.

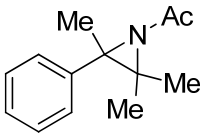


12g

2,2,3-trimethyl-3-phenylaziridine: Following the general procedure, (3-methylbut-2-en-2-yl)benzene* **11g** (50 mg, 0.34 mmol), aminating agent **1a** (82 mg, 0.41 mmol), and $Rh_2(esp)_2$ (2.6 mg, 3.4 μmol) were stirred in CF_3CH_2OH (3 mL) at rt for 1 h. Chromatographic purification by prep TLC afforded the title aziridine as an oil (38 mg, 70%) (Both the proton and carbon NMR shows some impurity that is hard to get rid of). TLC: $R_f \approx 0.2$ (50% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.14 (m, 5H), 1.54 (s, 3H), 1.40 (s, 3H), 1.28 (br s, 1H), 0.88 (s,

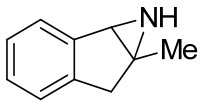
3H); ^{13}C NMR (101 MHz, $CDCl_3$) 144.03, 128.13, 127.17, 126.35, 47.41, 41.02, 23.99, 23.56, 21.89; HRMS (ESI$^+$) Calcd. for $[C_{11}H_{15}N+H]^+$ 162.1277, Found 162.1280.

* The starting olefin bought from Aldrich contains significant amount of impurities (see spectrum) which is carried through the aziridination. Repeated column chromatography could not remove the impurities completely. Conversion of the aziridine **12g** to acetate **12gg** afforded pure *N*-protected aziridine.



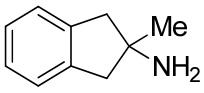
12gg

1-(2,2,3-trimethyl-3-phenylaziridin-1-yl)ethanone: 2,2,3-trimethyl-3-phenylaziridine **12g** (15 mg, 93 μmol), acetic anhydride (17 μL, 0.13 mmol), pyridine (11 μL, 0.13 mmol) were reacted in CH_2Cl_2 (1 mL) at rt for 3 h. Evaporation of volatiles and chromatographic purification by prep TLC using 40% EtOAc/hexanes as eluent afforded the title *N*-protected aziridine as a light yellow oil (18 mg, 90%). TLC: $R_f \approx 0.4$ (40% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.14 (m, 5H), 2.13 (s, 3H), 1.65 (s, 3H), 1.49 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.74, 141.40, 128.24, 126.99, 126.78, 50.91, 46.62, 24.99, 22.43, 19.47, 18.73.



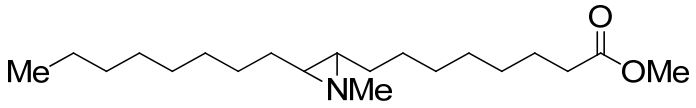
12h

6a-Methyl-1,1a,6,6a-tetrahydroindeno[1,2-b]azirine: 2-Methylindene **11h** (0.130 g, 1.0 mmol), aminating agent **1a** (0.219 g, 1.1 mmol, 1.1 equiv), and $Rh_2(esp)_2$ (7.6 mg, 10 μmol) were combined in CF_3CH_2OH (10 mL) at 0 °C with stirring. The mixture was then warmed to 5 °C and maintained at this temperature for 2.5 h. Chromatographic purification via flash column chromatography over Florisil® using 20-30% EtOAc/hexanes as eluent afforded the title aziridine as a pale yellow oil (20 mg, 14%). TLC: $R_f \approx 0.4$ (50% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, J = 6.6, 1.8 Hz, 1H), 7.27–7.07 (m, 3H), 3.24–2.91 (m, 3H), 1.57 (s, 3H); HRMS (ESI$^+$) Calcd. for $[C_{10}H_{11}N+H]^+$ 146.0964, Found 146.0964



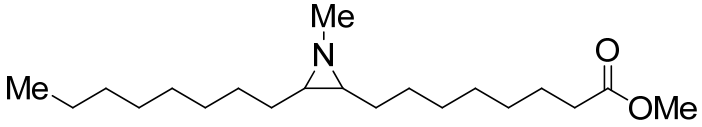
12hh

2-Methyl-2,3-dihydro-1H-inden-2-amine:(*60*) 2-Methylindene **11h** (0.130 g, 1.0 mmol), aminating agent **1a** (0.239 g, 1.2 mmol), and $Rh_2(esp)_2$ (7.6 mg, 10 μmol) in CF_3CH_2OH (10 mL) reacted exactly as above. The crude product (0.143 g), without further purification, was subjected to catalytic hydrogenation over 10% Pd/C (10 mg) in dry MeOH (5 mL) at 1 atm hydrogen pressure (balloon). After 15 h, the reaction mixture was passed through a small plug of cotton. The plug was washed with MeOH (3 mL) and the solvent was evaporated. The residue was purified by CombiFlash column chromatography over SiO_2 using 10-20% MeOH/CH_2Cl_2 as eluent to give the title amine as a pale yellow solid (88 mg, 60%), decomposes (or charring) >211 °C. TLC: $R_f \approx 0.3$ (20% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.11 (m, 4H), 3.40 (d, J = 15.9 Hz, 2H), 3.07 (d, J = 15.8 Hz, 2H), 1.62 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.24, 127.29, 124.97, 61.49, 44.66, 24.93; HRMS (ESI$^+$) Calcd. for $[C_{10}H_{13}N+H]^+$ 148.1121, Found 148.1116.



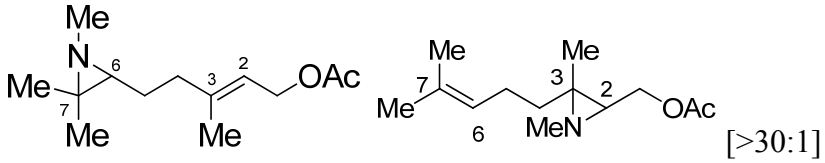
13a

Methyl (*E*)-8-(1-methyl-3-octylaziridin-2-yl)octanoate: Following the general aziridination procedure, methyl elaidate **9h** (59 mg, 0.2 mmol), *N*-methylaminating agent(*61*) **1b** (51 mg, 0.24 mmol), and $Rh_2(esp)_2$ (1.5 mg, 2 μmol) were stirred in CF_3CH_2OH (2 mL) at rt. After 2 h, another portion of catalyst (0.8 mg, 0.5 mol%) and aminating agent (9 mg, 0.04 mmol, 0.2 equiv) were added and the stirring was continued for an additional 2 h. Chromatographic purification on a CombiFlash system over SiO_2 gave the title aziridine as an oil (51 mg, 78%). TLC: $R_f \approx 0.3$ (50% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$; 1:1 mixture of invertomers) δ 3.62 (s, 3H), 2.33 (s, 3H), 2.27 (t, J = 7.5 Hz, 1H), 2.26 (t, J = 7.5 Hz, 1H), 1.65–1.50 (m, 4H), 1.45–1.11 (m, 23H), 1.04–0.91 (m, 1H), 0.84 (t, J = 6.8 Hz, 1.5H), 0.83 (t, J = 6.8 Hz, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.20, 174.17, 51.38, 51.36, 51.34, 47.08, 47.03, 42.90, 42.85, 38.78, 34.03, 34.01, 33.22, 33.18, 31.83, 29.57, 29.52, 29.49, 29.46, 29.30, 29.24, 29.20, 29.14, 29.04, 28.47, 28.40, 27.48, 27.39, 25.60, 25.58, 24.88, 24.87, 22.62, 14.05; HRMS (ESI$^+$) Calcd. for $[C_{20}H_{39}NO_2+H]^+$ 326.3054, Found 326.3049.



13b

Methyl (*Z*)-8-(1-methyl-3-octylaziridin-2-yl)octanoate: Following the general aziridination procedure, methyl oleate **7** (89 mg, 0.3 mmol), *N*-methylaminating agent **1b** (77 mg, 0.36 mmol), and $Rh_2(esp)_2$ (2.3 mg, 3 μmol) were stirred in CF_3CH_2OH (3 mL) at rt for 2 h. Thereafter, two more portions of catalyst (1.1 mg, 0.5 mol%) and aminating agent (13 mg, 0.06 mmol, 0.2 equiv) were added after every 2 h and stirred for a total of 6 h. Chromatographic purification on a CombiFlash system over SiO_2 to give the title aziridine as an oil (78 mg, 80%). TLC: $R_f \approx 0.5$ (50% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.64 (s, 3H), 2.31 (s, 3H), 2.27 (t, J = 7.6 Hz, 2H), 1.64–1.54 (m, 2H), 1.46–1.19 (m, 24H), 1.19–1.14 (m, 2H), 0.85 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.28, 51.42, 48.12, 45.46, 45.41, 34.05, 31.86, 29.62, 29.61, 29.39, 29.27, 29.26, 29.07, 28.22, 28.18, 28.12, 28.05, 24.90, 22.67, 14.11; HRMS (ESI^+) Calcd. for $[C_{20}H_{39}NO_2+Na]^+$ 348.2873, Found 348.2863.

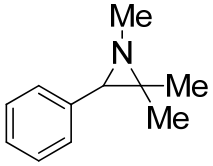


[>30:1]

13c

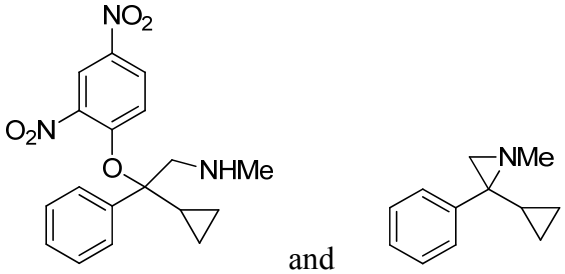
(*E*)-3-Methyl-5-(1,3,3-trimethylaziridin-2-yl)pent-2-en-1-yl acetate: Following the general aziridination procedure, geranyl acetate **9q** (98 mg, 0.5 mmol), *N*-methylaminating agent **1b** (0.128 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at rt. After 2 h, another portion of catalyst (1 mg, 0.25 mol%) and aminating agent (21 mg, 0.1 mmol, 0.2 equiv) were added and the stirring was continued for another 2 h. Chromatographic purification on a CombiFlash system over SiO_2 gave the title aziridine as an oil (91 mg, 81%) accompanied by the 2,3-regioisomer (3 mg, 3%). **Major regioisomer.** TLC: $R_f \approx 0.2$ (10% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.37–5.27 (m, 1H), 4.53 (d, J = 7.1 Hz, 2H), 2.30 (s, 3H), 2.15–2.05 (m, 2H), 1.98 (s, 3H), 1.65 (s, 3H), 1.56–1.35 (m, 2H), 1.11 (s, 3H), 1.01 (s, 3H), 0.99 (t, J = 6.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.01, 141.93, 118.50, 61.26, 51.77, 39.60, 39.13, 37.70, 27.44, 21.75, 20.98, 17.87, 16.30; HRMS (ESI^+) Calcd. for $[C_{13}H_{23}NO_2+H]^+$ 226.1802, Found 226.1801. **Minor regioisomer.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16–5.01 (m, 1H), 4.04 (d, J = 6.4 Hz, 2H), 2.43 (s, 3H), 2.20–2.01 (m, 2H), 2.06 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55–1.39 (m, 3H), 1.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.07,

131.98, 123.59, 64.74, 48.41, 39.09, 32.03, 29.68, 25.67, 25.10, 20.95, 19.19, 17.64; HRMS (ESI^+) Calcd. for $[C_{13}H_{23}NO_2+H]^+$ 226.1802, Found 226.1797.



13d

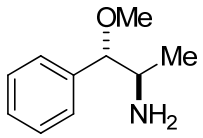
1,2,2-Trimethyl-3-phenylaziridine: Following the general aziridine procedure, 2-methyl-1-phenyl-2-propene **11f** (66 mg, 0.5 mmol), *N*-methylaminating agent **1b** (0.128 g, 0.6 mmol), and $Rh_2(esp)_2$ (3.8 mg, 5 μmol) were stirred in CF_3CH_2OH (5 mL) at rt. After 2 h, another portion of catalyst (1 mg, 0.25 mol%) and aminating agent (21 mg, 0.1 mmol, 0.2 equiv) were added to the reaction mixture. Following 2 h more, the crude reaction mixture was purified on a CombiFlash system over SiO_2 to give the title aziridine as an oil (65 mg, 81%). TLC: $R_f \approx 0.4$ (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.28 (m, 4H), 7.27–7.17 (m, 1H), 2.58 (s, 3H), 2.36 (s, 1H), 1.37 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.81, 127.89, 127.43, 126.38, 54.39, 42.70, 39.59, 21.47, 17.68; HRMS (ESI^+) Calcd. for $[C_{11}H_{15}N+H]^+$ 162.1277, Found 162.1271.



13e and **13f**

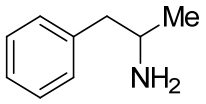
2-Cyclopropyl-2-(2,4-dinitrophenoxy)-*N*-methyl-2-phenylethanamine: (1-Cyclopropylvinyl)-benzene **11b** (72 mg, 0.5 mmol), $Rh_2(esp)_2$ (3.8 mg, 5 μmol), and *N*-Methyl aminating agent **1b** (0.128 g, 0.6 mmol) were reacted in CF_3CH_2OH (5 mL) following the procedure described above for 2-cyclopropyl-2-(2,4-dinitrophenoxy)-2-phenylethanamine **13e**. Chromatographic purification on a CombiFlash system over SiO_2 furnished the title *N*-methylamine SI-11e as a viscous oil (42 mg, 24%) accompanied by the precursor *N*-methylaziridine SI-11f (13 mg, 15%). **2-Cyclopropyl-2-(2,4-dinitrophenoxy)-*N*-methyl-2-phenylethanamine:** TLC: $R_f \approx 0.7$ (50% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, J = 2.7 Hz, 1H), 8.06 (dd, J = 9.5, 2.7

Hz, 1H), 7.54–7.45 (m, 2H), 7.39–7.30 (m, 2H), 7.32–7.24 (m, 1H), 7.13 (d, *J* = 9.6 Hz, 1H), 3.98 (d, *J* = 14.7 Hz, 1H), 3.90 (d, *J* = 14.8 Hz, 1H), 2.82 (s, 3H), 2.13 (s, 1H), 1.43–1.37 (m, 1H), 0.65–0.54 (m, 1H), 0.53–0.40 (m, 2H), 0.33–0.29 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.97, 144.07, 136.97, 136.92, 128.46, 127.68, 126.95, 125.37, 123.75, 119.08, 75.86, 64.34, 44.87, 19.38, 1.55, 1.15; HRMS (ESI$^+$) Calcd. for $[C_{18}H_{19}N_3O_5+Na]^+$ 380.1217, Found 380.1211. **2-Cyclopropyl-1-methyl-2-phenylaziridine**: TLC: $R_f \approx 0.5$ (50% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$, 1:4 mixture of invertomers) Major invertomer: δ 7.45–7.25 (m, 5 H), 2.01 (s, 3H), 1.94 (s, 1H), 1.60 (s, 1H), 1.31–1.20 (m, 1H), 0.56-0.50 (m, 1H), 0.46–0.41 (m, 1H), 0.33–0.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.86, 130.15, 128.02, 127.37, 47.36, 42.37, 38.10, 18.22, 3.45, 1.17. Minor invertomer: δ 7.45–7.25 (m, 1.0 H, overlapped with major invertomer), 2.72 (s, 0.74H), 1.86 (br s, 0.30H), 1.55 (s, 0.24H), 1.20–1.15 (m, 0.22H), 0.72-0.66 (m, 0.21H), 0.65–0.60 (m, 0.21H), 0.39–0.35 (m, 0.45H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.49, 127.85, 127.71, 126.42, 46.42, 40.59, 39.73, 10.98, 5.23, 2.92; HRMS (ESI$^+$): Calcd. for $[C_{12}H_{15}N+H]^+$ 174.1277, Found 174.1281.



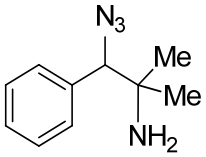
14

***erythro*-1-Methoxy-1-phenylpropan-2-amine**:(*62*) CSA (46 mg, 0.2 mmol) was added to a stirring 0 °C solution of (*E*)-2-methyl-3-phenylaziridine **12c** (27 mg, 0.2 mmol) in dry MeOH (2 mL). After 1 h, the reaction mixture was warmed to rt. After 16 h, the reaction mixture was warmed to 40 °C and held at this temperature for an additional 1 h. The reaction mixture was then cooled to rt, diluted with $CHCl_3$ (5 mL), and the pH was adjusted to 8.5 using aqueous 1.0 M NaOH. The layers were separated, and the aqueous layer was extracted with $CHCl_3$ (5 m × 3). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated to obtain the title amino-alcohol as a light yellow oil in quantitative yield (33 mg). TLC: $R_f \approx 0.2$ (10% MeOH/DCM); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.08 (m, 5H), 3.93 (d, *J* = 5.5 Hz, 1H), 3.24 (s, 3H), 3.14 (app qn, *J* = 6.0 Hz, 1H), 1.32 (br s, 2H), 1.05 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.89, 128.22, 127.73, 127.60, 88.92, 57.01, 51.67, 19.19; HRMS (ESI$^+$): Calcd. for $[C_{10}H_{15}NO+H]^+$ 166.1226, Found 166.1220.



15

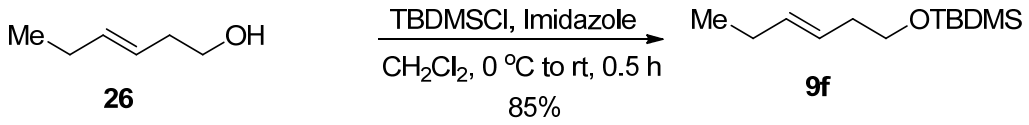
1-Phenylpropan-2-amine:(*63*) A suspension of (*E*)-2-methyl-3-phenylaziridine **12c** (20 mg, 0.15 mmol) and 10% Pd/C (10 mg) in MeOH (1 mL) was stirred under a hydrogen atmosphere (1 atm) at rt for 16 h. The reaction mixture was filtered by passage through a small pad of Celite™. The pad was washed with methanol and the combined filtrates were evaporated to furnish the title amine as an oil (19 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (br s, 2H), 7.34–7.20 (m, 5H), 3.65–3.53 (m, 1H), 3.27 (dd, *J* = 13.4, 5.1 Hz, 1H), 2.87 (dd, *J* = 13.3, 9.1 Hz, 1H), 1.39 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.83, 129.35, 128.87, 127.26, 49.80, 41.07, 18.13.



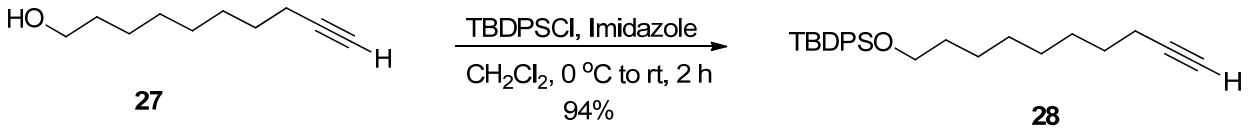
16

1-Azido-2-methyl-1-phenylpropan-2-amine: CSA (77 mg, 0.33 mmol, 1.1 equiv) was added to a stirring 0 °C solution of 2,2-dimethyl-3-phenylaziridine **12f** (44 mg, 0.3 mmol) in dry CH_3CN (3 mL). After 10 min, NaN_3 (59 mg, 0.9 mmol, 3.0 equiv) was added and the temperature was then raised to 50 °C. After 46 h, the reaction mixture was cooled to rt, diluted with $CHCl_3$ (5 mL), and the pH was adjusted to 8.5 using aqueous 1.0 M NaOH. The layers were separated and the aqueous layer was extracted with $CHCl_3$ (5 mL × 3). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated. The residue was purified on a CombiFlash system over SiO_2 using 70-80% EtOAc/hexanes as eluent to give the title azido-amine as an oil (45 mg, 79%). TLC: $R_f \approx 0.3$ (80% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.27 (m, 5H), 4.41 (s, 1H), 1.33 (br s, 2H), 1.13 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.76, 128.40, 128.26, 128.25, 76.60, 53.01, 27.67, 26.71; HRMS (ESI^+) Calcd. for $[C_{10}H_{14}N_4+H]^+$ 191.1291, Found 191.1287; IR (neat) 3366, 3320, 2971, 2102 cm^{-1}.

Starting alkenes synthesis:

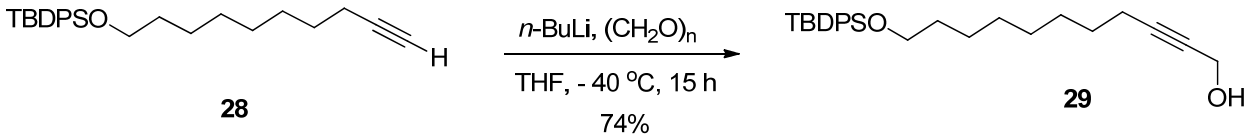


(*E*)-*tert*-butyl(hex-3-en-1-yloxy)dimethylsilane: To a stirred solution of (*E*)-hex-3-en-1-ol **26** (0.3 g, 3.0 mmol) in dry CH_2Cl_2 (6 mL) at rt was added imidazole (0.245 g, 3.6 mmol) in one portion, and the reaction mixture was cooled to 0 °C. Then *tert*-butyldimethylchlorosilane (TBDMSCl) (0.542 g, 3.6 mmol) was added in one portion; stirring was continued at that temperature for 10 minutes before warming up to rt. TLC analysis after a total of 30 min indicated the reaction was complete. The reaction mixture was then diluted with CH_2Cl_2 (10 mL) and washed once with water (10 mL). The aqueous layer was extracted once with CH_2Cl_2 (10 mL) and the combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated *in vacuo* to obtain the crude product which was purified by Combiflash column chromatography using a gradient EtOAc/hexanes (2-3%) as eluent to furnish title protected alcohol as a colorless oil (0.55 g, 85%). TLC: $R_f \approx$ 0.8 (5% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58–5.45 (m, 1H), 5.45–5.32 (m, 1H), 3.61 (t, J = 7.0 Hz, 2H), 2.26–2.15 (m, 2H), 2.06–1.94 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.14, 125.32, 63.38, 36.26, 25.95, 25.66, 18.38, 13.78, -5.24.

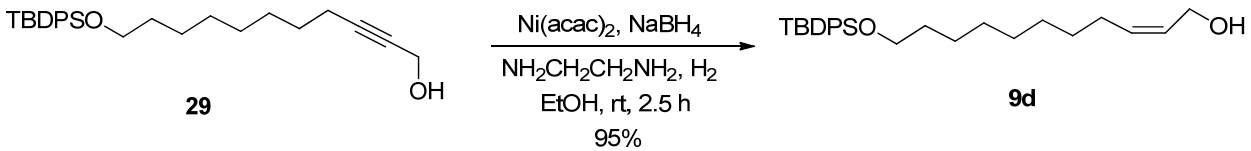


***tert*-butyl(dec-9-yn-1-yloxy)diphenylsilane:** To a stirring solution of dec-9-yn-1-ol(*64*) **27** (1.5 g, 9.7 mmol) in dry CH_2Cl_2 (20 mL) at rt was added imidazole (0.794 g, 11.6 mmol) in one portion. The reaction mixture was cooled to 0 °C. Then *tert*-butyldiphenylchlorosilane (TBDPSCl) (2.91 g, 10.6 mmol) was added dropwise and the reaction mixture was stirred for 10 minutes before warming up to rt. After stirring for a total of 2 h (TLC analysis), the reaction mixture was diluted with CH_2Cl_2 (10 mL), water (10 mL) was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by Combiflash column chromatography using a gradient EtOAc/hexanes (1-3%) as eluent to furnish the title alkyne as a colorless viscous oil (3.60 g,

94%). TLC: $R_f \approx 0.8$ (5% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.65 (m, 4H), 7.50–7.31 (m, 6H), 3.66 (t, *J* = 6.5 Hz, 2H), 2.18 (td, *J* = 7.1, 2.7 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.64–1.46 (m, 4H), 1.46–1.22 (m, 8H), 1.06 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.57, 134.15, 129.47, 127.55, 84.78, 68.06, 63.96, 32.54, 29.21, 29.06, 28.69, 28.47, 26.87, 25.71, 19.22, 18.40; HRMS (ESI$^+$) Calcd. for $[C_{26}H_{36}OSi+H]^+$ 393.2608, Found 393.2609.



11-((*tert*-butyldiphenylsilyl)oxy)undec-2-yn-1-ol: To a stirring solution of *tert*-butyl(dec-9-yn-1-yloxy)diphenylsilane **28** (0.325 g, 0.83 mmol) in dry THF(3 mL) at -40 °C was added *n*-BuLi (2.5 M in hexanes, 0.4 mL, 0.996 mmol), and the resulting light yellow solution was stirred at that temperature for 10 min. A suspension of paraformaldehyde (0.075 g, 2.49 mmol) in dry THF (1 mL) at -40 °C was then added *via* cannula, and the stirring was continued at that temperature for 15 minutes before warming up to rt. After a total of 15 h (TLC analysis), saturated aqueous NH_4Cl solution (2 mL) and EtOAc (10 mL) were added to the reaction mixture. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by Combiflash column chromatography using a gradient of EtOAc/hexanes (10-15%) as eluent to furnish the title alcohol as a thick, colorless oil (0.26 g, 74%). TLC: $R_f \approx 0.3$ (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.64 (m, 4H), 7.46–7.34 (m, 6H), 4.25 (dt, *J* = 6.0, 2.2 Hz, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.21 (tt, *J* = 7.1, 2.2 Hz, 2H), 1.64–1.43 (m, 4H), 1.42–1.21 (m, 8H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.56, 134.14, 129.47, 127.55, 86.65, 78.26, 63.97, 51.44, 32.53, 29.21, 29.07, 28.79, 28.57, 26.87, 25.71, 19.22, 18.73; HRMS (ESI$^+$) Calcd. for $[C_{27}H_{38}O_2Si+Na]^+$ 445.2533, Found 445.2524.



(*Z*)-11-((*tert*-Butyldiphenylsilyl)oxy)undec-2-en-1-ol: To a stirring solution of $Ni(acac)_2 \cdot 4H_2O$ (0.348 g, 1.4 mmol) in absolute ethanol (12 mL) at rt was added $NaBH_4$ (53 mg, 1.4 mmol). The

resulting black reaction mixture was stirred under H_2 (1 atm) for 20 minutes before adding ethylenediamine (0.19 mL, 2.9 mmol). After 15 min, a solution of 11-((*tert*-butyldiphenylsilyl)oxy)undec-2-yn-1-ol **29** (2.49 g, 5.9 mmol) in absolute ethanol (10 mL) was added and the stirring was continued for a total of 2.5 h (TLC analysis). The reaction mixture was then passed through a small pad of silica to remove the solids. The filtrate was concentrated and the crude product was purified by Combi-flash column chromatography using a gradient of EtOAc/hexanes (20-25%) as eluent to furnish the title alcohol as a viscous, colorless oil (2.38 g, 95%). TLC: $R_f \approx 0.6$ (40% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.64 (m, 4H), 7.48–7.29 (m, 6H), 5.67–5.45 (m, 2H), 4.20 (d, J = 6.2 Hz, 2H), 3.66 (t, J = 6.5 Hz, 2H), 2.07 (app q, J = 7.1 Hz, 2H), 1.68–1.45 (m, 3H), 1.46–1.16 (m, 10H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.56, 134.15, 133.27, 129.47, 128.27, 127.55, 63.97, 58.62, 32.55, 29.59, 29.42, 29.30, 29.14, 27.43, 26.87, 25.74, 19.22; HRMS (ESI^+) Calcd. for $[C_{27}H_{40}O_2Si+H]^+$ 425.2876, Found 425.2881.

X-ray Diffraction Experiment Data for Compound 10ss

The data were measured at 100(2) K on a Bruker D8 Quest system equipped with a Photon 100 CMOS detector and Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed using the Saint Plus program. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14).(*65*) Initial atomic positions were located by using XT, and the structures of the compounds were refined by the least-squares method using XL. Absorption corrections were applied by using SADABS. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons.

Table S4. Crystal data and structure refinement for $C_{36}H_{55}NO_4S$.

Empirical formula	C_{36} H_{55} N O_4 S
Formula weight	597.87
Temperature	100(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P\ 2_1$	
Unit cell dimensions	a = 14.0032(7) Å	α = 90°.
	b = 6.0260(3) Å	β = 106.216(1)°.
	c = 21.2960(11) Å	γ = 90°.
Volume	1725.53(15) $Å^3$	
Z	2	
Density (calculated)	1.151 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	652	
Crystal size	0.543 x 0.333 x 0.066 mm^3	
Theta range for data collection	2.913 to 33.141°.	
Index ranges	-21<=h<=21, -9<=k<=9, -32<=l<=32	
Reflections collected	30153	
Independent reflections	13103 [R(int) = 0.0451]	
Completeness to theta = 25.000°	99.7 %	
Absorption correction	Numerical	
Max. and min. transmission	1.000 and 0.885	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13103 / 1 / 386	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1265	
R indices (all data)	R1 = 0.0800, wR2 = 0.1352	
Absolute structure parameter	-0.01(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.774 and -0.343 $e.Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $C_{36}H_{55}NO_4S$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6370(1)	-106(1)	9144(1)	18(1)
O(1)	6767(1)	-2317(3)	9189(1)	24(1)
O(2)	6864(1)	1499(3)	9625(1)	25(1)
O(3)	9721(1)	3170(3)	8816(1)	24(1)
O(4)	9423(2)	6750(4)	8974(1)	50(1)
N(1)	6219(1)	700(3)	8381(1)	15(1)
C(1)	5115(2)	-168(4)	9137(1)	17(1)
C(2)	4702(2)	1676(4)	9361(1)	21(1)
C(3)	3702(2)	1650(5)	9336(1)	24(1)
C(4)	3112(2)	-205(5)	9105(1)	25(1)
C(5)	3542(2)	-2033(5)	8886(1)	26(1)
C(6)	4538(2)	-2034(4)	8898(1)	22(1)
C(7)	2039(2)	-228(7)	9105(1)	36(1)
C(8)	8779(2)	3035(4)	8311(1)	18(1)
C(9)	8026(2)	2033(4)	8615(1)	17(1)
C(10)	7007(2)	1714(4)	8120(1)	13(1)
C(11)	6997(2)	722(4)	7448(1)	12(1)
C(12)	7892(2)	1638(4)	7232(1)	17(1)
C(13)	8896(2)	1584(4)	7759(1)	19(1)
C(14)	6156(2)	3085(4)	8204(1)	14(1)
C(15)	5258(2)	3572(4)	7643(1)	14(1)
C(16)	5083(2)	1776(4)	7115(1)	12(1)
C(17)	6035(2)	1408(4)	6898(1)	13(1)
C(18)	4245(2)	2495(4)	6524(1)	12(1)
C(19)	3982(2)	815(4)	5955(1)	14(1)
C(20)	4929(2)	538(4)	5732(1)	18(1)

C(21)	5824(2)	-169(4)	6302(1)	17(1)
C(22)	3240(2)	3099(4)	6633(1)	16(1)
C(23)	2512(2)	3025(4)	5936(1)	17(1)
C(24)	3097(2)	2038(4)	5474(1)	16(1)
C(25)	2402(2)	751(5)	4900(1)	22(1)
C(26)	1642(2)	2371(5)	4474(1)	28(1)
C(27)	747(2)	1308(6)	3992(2)	42(1)
C(28)	62(2)	3029(5)	3557(1)	32(1)
C(29)	-942(2)	2171(7)	3149(2)	46(1)
C(30)	-1532(3)	4087(7)	2769(2)	47(1)
C(31)	-874(3)	307(9)	2713(2)	81(2)
C(32)	2958(2)	-469(5)	4479(1)	31(1)
C(33)	3636(2)	-1418(4)	6163(1)	18(1)
C(34)	7116(2)	-1798(4)	7544(1)	18(1)
C(35)	9927(2)	5121(5)	9134(1)	24(1)
C(36)	10826(2)	4964(6)	9710(1)	34(1)

Table S6. Bond lengths [Å] and angles [°] for $C_{36}H_{55}NO_4S$.

S(1)-O(1)	1.4365(19)
S(1)-O(2)	1.4379(18)
S(1)-N(1)	1.6513(18)
S(1)-C(1)	1.754(2)
O(3)-C(35)	1.348(3)
O(3)-C(8)	1.452(3)
O(4)-C(35)	1.202(3)
N(1)-C(14)	1.482(3)
N(1)-C(10)	1.497(3)
C(1)-C(6)	1.395(3)
C(1)-C(2)	1.396(3)
C(2)-C(3)	1.386(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.396(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.397(4)

C(4)-C(7)	1.503(4)
C(5)-C(6)	1.389(4)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(13)	1.510(3)
C(8)-C(9)	1.510(3)
C(8)-H(8)	1.0000
C(9)-C(10)	1.530(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(14)	1.501(3)
C(10)-C(11)	1.549(3)
C(11)-C(34)	1.535(3)
C(11)-C(12)	1.552(3)
C(11)-C(17)	1.574(3)
C(12)-C(13)	1.535(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.501(3)
C(14)-H(14)	1.0000
C(15)-C(16)	1.531(3)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(18)	1.525(3)
C(16)-C(17)	1.544(3)
C(16)-H(16)	1.0000
C(17)-C(21)	1.545(3)
C(17)-H(17)	1.0000
C(18)-C(22)	1.533(3)
C(18)-C(19)	1.541(3)
C(18)-H(18)	1.0000

C(19)-C(33)	1.537(3)
C(19)-C(20)	1.537(3)
C(19)-C(24)	1.556(3)
C(20)-C(21)	1.542(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.548(3)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.564(3)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.542(3)
C(24)-H(24)	1.0000
C(25)-C(32)	1.529(4)
C(25)-C(26)	1.539(3)
C(25)-H(25)	1.0000
C(26)-C(27)	1.522(4)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-C(28)	1.536(4)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-C(29)	1.521(4)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(31)	1.478(6)
C(29)-C(30)	1.516(5)
C(29)-H(29)	1.0000
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800

C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-C(36)	1.495(3)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800

O(1)-S(1)-O(2)	118.44(11)
O(1)-S(1)-N(1)	106.20(10)
O(2)-S(1)-N(1)	114.03(11)
O(1)-S(1)-C(1)	110.43(12)
O(2)-S(1)-C(1)	107.52(11)
N(1)-S(1)-C(1)	98.39(10)
C(35)-O(3)-C(8)	116.39(19)
C(14)-N(1)-C(10)	60.49(14)
C(14)-N(1)-S(1)	121.18(15)
C(10)-N(1)-S(1)	125.43(14)
C(6)-C(1)-C(2)	120.9(2)
C(6)-C(1)-S(1)	119.77(19)
C(2)-C(1)-S(1)	119.35(19)
C(3)-C(2)-C(1)	119.2(2)
C(3)-C(2)-H(2)	120.4
C(1)-C(2)-H(2)	120.4
C(2)-C(3)-C(4)	121.0(2)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	118.8(2)
C(3)-C(4)-C(7)	120.1(3)

C(5)-C(4)-C(7)	121.1(3)
C(6)-C(5)-C(4)	121.3(3)
C(6)-C(5)-H(5)	119.4
C(4)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	118.8(2)
C(5)-C(6)-H(6)	120.6
C(1)-C(6)-H(6)	120.6
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
O(3)-C(8)-C(13)	109.58(18)
O(3)-C(8)-C(9)	107.69(18)
C(13)-C(8)-C(9)	110.1(2)
O(3)-C(8)-H(8)	109.8
C(13)-C(8)-H(8)	109.8
C(9)-C(8)-H(8)	109.8
C(8)-C(9)-C(10)	112.57(18)
C(8)-C(9)-H(9A)	109.1
C(10)-C(9)-H(9A)	109.1
C(8)-C(9)-H(9B)	109.1
C(10)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.8
N(1)-C(10)-C(14)	59.28(14)
N(1)-C(10)-C(9)	115.98(17)
C(14)-C(10)-C(9)	117.90(18)
N(1)-C(10)-C(11)	111.59(17)
C(14)-C(10)-C(11)	121.28(17)
C(9)-C(10)-C(11)	116.81(18)
C(34)-C(11)-C(10)	106.63(18)
C(34)-C(11)-C(12)	108.97(19)
C(10)-C(11)-C(12)	109.66(17)
C(34)-C(11)-C(17)	113.42(17)
C(10)-C(11)-C(17)	111.83(17)

C(12)-C(11)-C(17)	106.29(16)
C(13)-C(12)-C(11)	115.30(18)
C(13)-C(12)-H(12A)	108.5
C(11)-C(12)-H(12A)	108.5
C(13)-C(12)-H(12B)	108.5
C(11)-C(12)-H(12B)	108.5
H(12A)-C(12)-H(12B)	107.5
C(8)-C(13)-C(12)	106.24(18)
C(8)-C(13)-H(13A)	110.5
C(12)-C(13)-H(13A)	110.5
C(8)-C(13)-H(13B)	110.5
C(12)-C(13)-H(13B)	110.5
H(13A)-C(13)-H(13B)	108.7
N(1)-C(14)-C(15)	111.68(18)
N(1)-C(14)-C(10)	60.23(14)
C(15)-C(14)-C(10)	122.03(18)
N(1)-C(14)-H(14)	116.6
C(15)-C(14)-H(14)	116.6
C(10)-C(14)-H(14)	116.6
C(14)-C(15)-C(16)	111.89(18)
C(14)-C(15)-H(15A)	109.2
C(16)-C(15)-H(15A)	109.2
C(14)-C(15)-H(15B)	109.2
C(16)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
C(18)-C(16)-C(15)	109.54(17)
C(18)-C(16)-C(17)	108.86(16)
C(15)-C(16)-C(17)	110.30(17)
C(18)-C(16)-H(16)	109.4
C(15)-C(16)-H(16)	109.4
C(17)-C(16)-H(16)	109.4
C(16)-C(17)-C(21)	110.54(16)
C(16)-C(17)-C(11)	116.48(16)
C(21)-C(17)-C(11)	112.11(17)
C(16)-C(17)-H(17)	105.6
C(21)-C(17)-H(17)	105.6

C(11)-C(17)-H(17)	105.6
C(16)-C(18)-C(22)	118.05(17)
C(16)-C(18)-C(19)	114.94(17)
C(22)-C(18)-C(19)	104.29(16)
C(16)-C(18)-H(18)	106.2
C(22)-C(18)-H(18)	106.2
C(19)-C(18)-H(18)	106.2
C(33)-C(19)-C(20)	111.24(19)
C(33)-C(19)-C(18)	112.00(17)
C(20)-C(19)-C(18)	106.08(17)
C(33)-C(19)-C(24)	110.27(18)
C(20)-C(19)-C(24)	116.43(18)
C(18)-C(19)-C(24)	100.26(17)
C(19)-C(20)-C(21)	111.61(17)
C(19)-C(20)-H(20A)	109.3
C(21)-C(20)-H(20A)	109.3
C(19)-C(20)-H(20B)	109.3
C(21)-C(20)-H(20B)	109.3
H(20A)-C(20)-H(20B)	108.0
C(20)-C(21)-C(17)	113.77(19)
C(20)-C(21)-H(21A)	108.8
C(17)-C(21)-H(21A)	108.8
C(20)-C(21)-H(21B)	108.8
C(17)-C(21)-H(21B)	108.8
H(21A)-C(21)-H(21B)	107.7
C(18)-C(22)-C(23)	103.60(17)
C(18)-C(22)-H(22A)	111.0
C(23)-C(22)-H(22A)	111.0
C(18)-C(22)-H(22B)	111.0
C(23)-C(22)-H(22B)	111.0
H(22A)-C(22)-H(22B)	109.0
C(22)-C(23)-C(24)	107.07(17)
C(22)-C(23)-H(23A)	110.3
C(24)-C(23)-H(23A)	110.3
C(22)-C(23)-H(23B)	110.3
C(24)-C(23)-H(23B)	110.3

H(23A)-C(23)-H(23B)	108.6
C(25)-C(24)-C(19)	119.62(19)
C(25)-C(24)-C(23)	111.40(18)
C(19)-C(24)-C(23)	103.10(16)
C(25)-C(24)-H(24)	107.4
C(19)-C(24)-H(24)	107.4
C(23)-C(24)-H(24)	107.4
C(32)-C(25)-C(26)	109.9(2)
C(32)-C(25)-C(24)	113.3(2)
C(26)-C(25)-C(24)	109.1(2)
C(32)-C(25)-H(25)	108.1
C(26)-C(25)-H(25)	108.1
C(24)-C(25)-H(25)	108.1
C(27)-C(26)-C(25)	115.7(2)
C(27)-C(26)-H(26A)	108.3
C(25)-C(26)-H(26A)	108.3
C(27)-C(26)-H(26B)	108.3
C(25)-C(26)-H(26B)	108.3
H(26A)-C(26)-H(26B)	107.4
C(26)-C(27)-C(28)	112.4(3)
C(26)-C(27)-H(27A)	109.1
C(28)-C(27)-H(27A)	109.1
C(26)-C(27)-H(27B)	109.1
C(28)-C(27)-H(27B)	109.1
H(27A)-C(27)-H(27B)	107.9
C(29)-C(28)-C(27)	115.9(3)
C(29)-C(28)-H(28A)	108.3
C(27)-C(28)-H(28A)	108.3
C(29)-C(28)-H(28B)	108.3
C(27)-C(28)-H(28B)	108.3
H(28A)-C(28)-H(28B)	107.4
C(31)-C(29)-C(30)	111.3(3)
C(31)-C(29)-C(28)	113.9(3)
C(30)-C(29)-C(28)	109.0(3)
C(31)-C(29)-H(29)	107.4
C(30)-C(29)-H(29)	107.4

C(28)-C(29)-H(29)	107.4
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(25)-C(32)-H(32A)	109.5
C(25)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(25)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(19)-C(33)-H(33A)	109.5
C(19)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(19)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(11)-C(34)-H(34A)	109.5
C(11)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(11)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
O(4)-C(35)-O(3)	122.9(2)
O(4)-C(35)-C(36)	125.3(3)
O(3)-C(35)-C(36)	111.8(2)
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5

H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_{36}H_{55}NO_4S$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	21(1)	21(1)	9(1)	1(1)	1(1)	2(1)
O(1)	29(1)	26(1)	17(1)	6(1)	6(1)	8(1)
O(2)	26(1)	32(1)	13(1)	-4(1)	0(1)	-3(1)
O(3)	15(1)	22(1)	26(1)	-3(1)	-8(1)	0(1)
O(4)	55(1)	29(1)	46(1)	-14(1)	-22(1)	8(1)
N(1)	17(1)	17(1)	9(1)	1(1)	2(1)	-2(1)
C(1)	21(1)	20(1)	11(1)	2(1)	5(1)	2(1)
C(2)	27(1)	22(1)	15(1)	-2(1)	5(1)	2(1)
C(3)	28(1)	29(1)	16(1)	-1(1)	7(1)	7(1)
C(4)	25(1)	35(1)	16(1)	5(1)	7(1)	1(1)
C(5)	27(1)	23(1)	28(1)	3(1)	5(1)	-5(1)
C(6)	27(1)	19(1)	21(1)	1(1)	6(1)	1(1)
C(7)	25(1)	51(2)	34(1)	10(2)	10(1)	3(2)
C(8)	12(1)	18(1)	18(1)	-1(1)	-5(1)	0(1)
C(9)	14(1)	19(1)	15(1)	-1(1)	-3(1)	1(1)
C(10)	13(1)	14(1)	12(1)	0(1)	0(1)	-1(1)
C(11)	12(1)	12(1)	11(1)	-1(1)	1(1)	1(1)
C(12)	12(1)	22(1)	15(1)	1(1)	2(1)	-1(1)
C(13)	11(1)	24(1)	20(1)	-1(1)	1(1)	0(1)
C(14)	16(1)	14(1)	12(1)	-2(1)	1(1)	0(1)
C(15)	12(1)	15(1)	14(1)	-2(1)	1(1)	0(1)
C(16)	12(1)	11(1)	11(1)	-1(1)	1(1)	0(1)
C(17)	11(1)	14(1)	11(1)	0(1)	1(1)	-1(1)
C(18)	11(1)	11(1)	12(1)	0(1)	1(1)	-1(1)

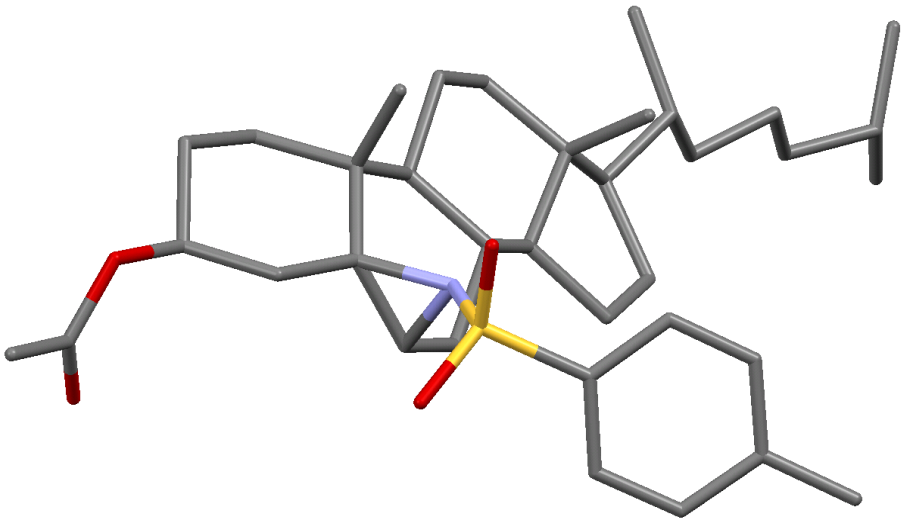
C(19)	14(1)	14(1)	11(1)	-1(1)	-2(1)	0(1)
C(20)	15(1)	25(1)	11(1)	-3(1)	0(1)	1(1)
C(21)	14(1)	21(1)	14(1)	-4(1)	1(1)	3(1)
C(22)	13(1)	17(1)	15(1)	-2(1)	2(1)	0(1)
C(23)	14(1)	18(1)	16(1)	-1(1)	-1(1)	2(1)
C(24)	15(1)	17(1)	13(1)	1(1)	0(1)	0(1)
C(25)	18(1)	27(1)	14(1)	-3(1)	-4(1)	4(1)
C(26)	24(1)	33(1)	19(1)	0(1)	-6(1)	7(1)
C(27)	31(2)	42(2)	37(2)	-2(1)	-15(1)	7(1)
C(28)	25(1)	38(2)	28(1)	3(1)	1(1)	5(1)
C(29)	30(2)	58(2)	40(2)	3(2)	-6(1)	4(2)
C(30)	38(2)	62(2)	33(2)	-9(2)	-5(1)	21(2)
C(31)	61(3)	63(3)	86(3)	-33(3)	-37(2)	25(2)
C(32)	26(1)	42(2)	17(1)	-10(1)	-6(1)	10(1)
C(33)	19(1)	13(1)	18(1)	-1(1)	-3(1)	-2(1)
C(34)	22(1)	13(1)	16(1)	-1(1)	-2(1)	2(1)
C(35)	24(1)	24(1)	20(1)	-3(1)	-1(1)	-5(1)
C(36)	27(1)	37(2)	27(1)	-2(1)	-10(1)	-7(1)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_{36}H_{55}NO_4S$.

	x	y	z	U(eq)
H(2)	5101	2934	9528	26
H(3)	3415	2914	9478	29
H(5)	3145	-3300	8726	32
H(6)	4822	-3283	8745	27
H(7A)	1995	-68	9554	55
H(7B)	1733	-1635	8922	55
H(7C)	1687	1005	8838	55
H(8)	8560	4554	8142	21
H(9A)	7952	3010	8972	21
H(9B)	8274	577	8809	21

H(12A)	7953	770	6851	20
H(12B)	7746	3193	7086	20
H(13A)	9066	47	7914	23
H(13B)	9431	2163	7582	23
H(14)	6311	4169	8574	17
H(15A)	5348	5022	7449	17
H(15B)	4665	3680	7809	17
H(16)	4894	356	7293	14
H(17)	6191	2880	6733	15
H(18)	4485	3861	6349	14
H(20A)	5083	1959	5549	21
H(20B)	4811	-594	5382	21
H(21A)	6423	-241	6143	21
H(21B)	5700	-1679	6446	21
H(22A)	3259	4598	6826	19
H(22B)	3047	2010	6924	19
H(23A)	2271	4537	5792	20
H(23B)	1931	2080	5931	20
H(24)	3379	3313	5284	19
H(25)	2030	-374	5085	26
H(26A)	1398	3362	4767	33
H(26B)	1990	3308	4226	33
H(27A)	364	459	4238	50
H(27B)	982	251	3712	50
H(28A)	-56	4244	3839	38
H(28B)	415	3675	3257	38
H(29)	-1309	1623	3459	55
H(30A)	-1218	4588	2436	71
H(30B)	-1547	5312	3069	71
H(30C)	-2213	3598	2556	71
H(31A)	-434	720	2446	122
H(31B)	-1538	-32	2427	122
H(31C)	-606	-1002	2976	122
H(32A)	3394	575	4338	46
H(32B)	2477	-1098	4094	46
H(32C)	3358	-1665	4735	46

H(33A)	3553	-2491	5805	27
H(33B)	3000	-1217	6263	27
H(33C)	4134	-1972	6551	27
H(34A)	7682	-2112	7923	28
H(34B)	7232	-2470	7152	28
H(34C)	6509	-2421	7616	28
H(36A)	11071	6460	9849	51
H(36B)	11346	4122	9589	51
H(36C)	10651	4209	10070	51



10ss m.p. = 157-158 °C

Computational Details: All the geometries were optimized using the (U)M06(*66, 67*) functional in Gaussian09 with the 6-31G(d,p) basis on the main group elements and LANL2DZ basis set and pseudopotential on Rh. Solvent effects were incorporated modeled using the CPCM implicit model for 2,2,2-trifluoroethanol (TFE). Stationary points were characterized as minima or first-order saddle points by computing the Hessian matrix. Singlet−triplet spin-crossing points, also called minimum energy crossing points (MECP), were located using the algorithm developed by Harvey et al. in conjunction with Gaussian 09.(*68, 69*) Vibrational frequency analysis on the MECP structure was performed to estimate

thermochemical data. Electronic energies were further refined using the 6-311++G(2d,2p) basis on the main group elements and LANL2TZ(f) basis set and pseudopotential on Rh.

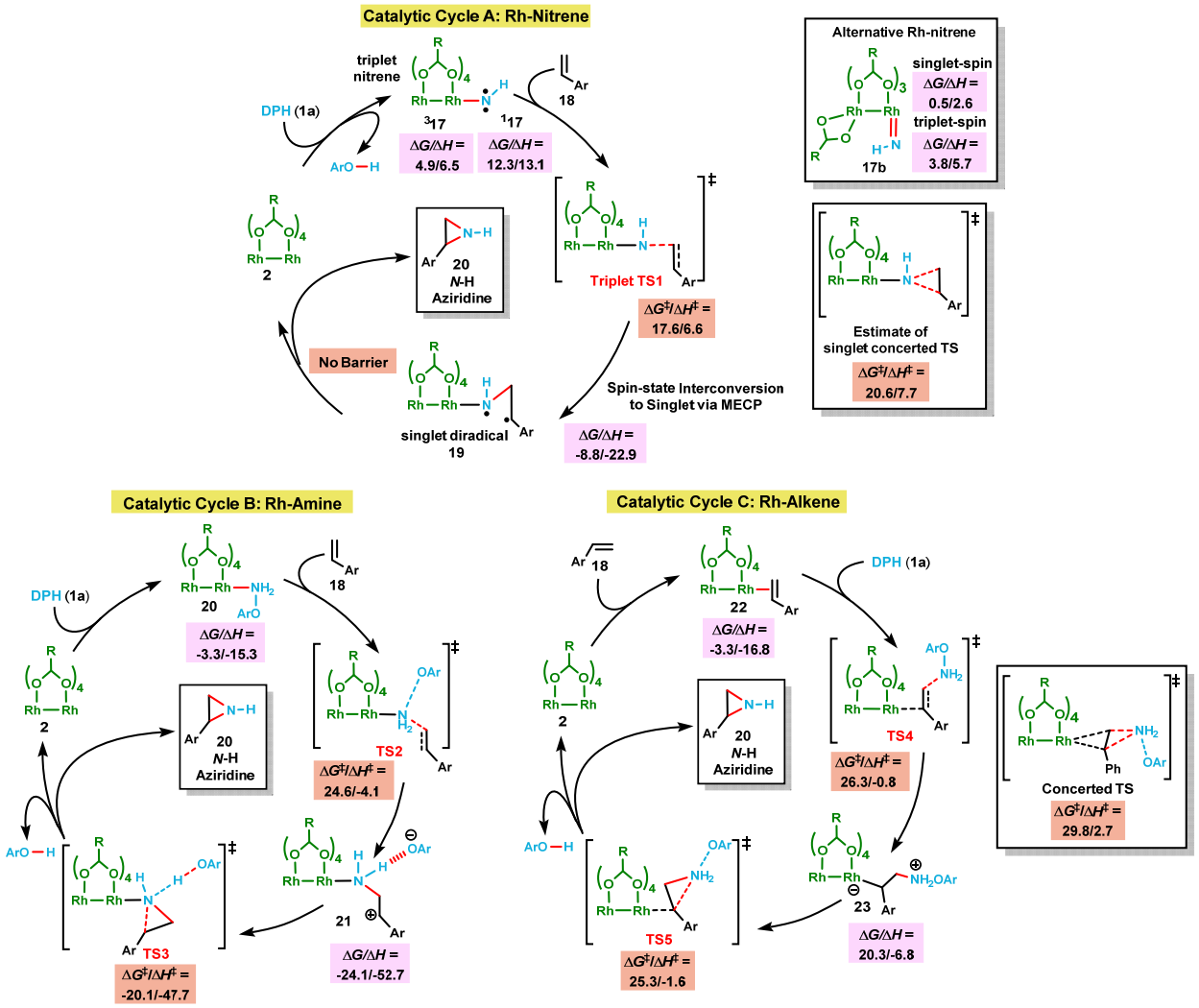


Figure S5. DFT examined pathways for N-H aziridination of styrene. R = esp ligands. Solvent = trifluoroethanol. Energies relative to **2**, **18**, and **1a**. Energies in kcal/mol. MECP = minimum energy crossing point.

Notes on the catalytic cycles shown in Figure S5.

Note 1. We also examined whether a transition state similar to **TS1** occurs on the singlet energy surface. All attempts to locate this transition state failed. We have estimated the energy of this transition state by evaluating the singlet-spin open-shell energy on the geometry of triplet-spin **TS1**. This singlet free energy is 27.5 kcal/mol, which is ~10 kcal/mol higher than the triplet-spin energy.

Note 2. The insert of Catalytic Cycle A shows the concerted transition state for the reaction between ^{1}**17** and styrene. The concerted transition state was located for a model system with formate ligands as replacements for esp ligands. When esp ligands were used we were unable to converge on the transition state. To estimate the energy of the concerted reaction pathway with esp ligands we constrained the forming C-N bond lengths to be identical to the transition state located with the model formate ligands. The free energy of this structure is 20.6 kcal/mol.

Note 3. In addition to the rhodium nitrene species ^{3}**17** we also identified an alternative rhodium nitrene species **17b** (shown in the insert of Catalytic Cycle A). While **17b** is thermodynamically feasible, esp ligand migration in catalyst **2** requires 20.5 kcal/mol of free energy and is unlikely. Interestingly, for **17b** the singlet-spin state is more stable than the triplet-spin state. So far we were unable to locate a transition state leading from singlet **17b** to aziridine **20**.

Note 4. For Catalytic Cycle B the mechanism begins with **1a** coordinating to $Rh_2(esp)_2$ to give **20**. Next, styrene acts as a π nucleophile to form the first C–N bond with expulsion of an aryl oxide leaving group that remains hydrogen-bonded. The zwitterionic intermediate **21** formed from **TS2** then undergoes ring-closure with only a few kcal/mol barrier (**TS3**).

Note 5. Catalytic Cycle C shows the possibility of initial styrene coordination to $Rh_2(esp)_2$ and electrophilic π-activation. Subsequent nitrogen atom nucleophilic addition of **1a** to **22** via **TS4** forms the first C–N bond and the corresponding rhodium-alkyl intermediate **23**. It is also possible that this nucleophilic attack involves hydrogen bonding by a second molecule of **1a**. The second C–N bond forming transition state, **TS5**, results in aziridine **20**. The insert of Catalytic Cycle C shows the possibility of concerted nitrene transfer from **1a** after styrene π-coordination to $Rh_2(esp)_2$.

XYZ Coordinates and Thermochemical Data (Energies in Hartree)

Cycle A: Rh-Nitrene

^{1}17 (Singlet 17)

Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]

Electronic Energy = -2118.58361471
Electronic and Zero-Point Energy = -2117.900287
Enthalpy = -2117.856144
Free Energy = -2117.971047

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2119.12880183

Rh	0.072291000	0.004933000	-1.302466000
C	1.850962000	-1.903999000	-0.074631000
C	2.900726000	-3.009629000	0.000929000
C	2.266489000	-4.229453000	0.674873000
H	1.903097000	-3.990015000	1.679288000
H	3.013966000	-5.027551000	0.757422000
H	1.428391000	-4.614725000	0.082419000
C	3.380388000	-3.388858000	-1.394800000
H	2.552512000	-3.759976000	-2.008198000
H	4.129958000	-4.185775000	-1.312426000
H	3.835463000	-2.540800000	-1.916140000
O	1.529822000	-1.445169000	-1.203172000
O	1.374254000	1.483628000	1.157104000
C	5.764609000	1.222427000	-0.426808000
H	6.186765000	2.172625000	-0.753073000
C	4.700358000	1.217364000	0.478463000
C	4.085113000	2.492901000	0.983608000
H	4.833850000	3.297804000	0.998032000
H	3.743236000	2.353025000	2.017268000
C	2.890639000	3.011573000	0.144279000
C	3.351035000	3.444443000	-1.242236000
H	3.802659000	2.618355000	-1.800590000
H	4.098203000	4.241617000	-1.141015000
H	2.513400000	3.833488000	-1.830919000
C	2.263270000	4.203980000	0.871214000
H	1.409636000	4.602208000	0.309906000
H	3.006383000	5.005057000	0.965099000
H	1.922162000	3.928476000	1.874096000
C	1.842830000	1.903257000	0.046713000
O	1.517016000	1.482967000	-1.096840000
O	1.364740000	-1.518372000	1.040144000
C	4.081111000	-2.518487000	0.876029000

H	3.724177000	-2.417898000	1.909237000
H	4.830938000	-3.322392000	0.871362000
C	4.699451000	-1.223714000	0.426769000
C	5.764684000	-1.191716000	-0.477041000
H	6.187504000	-2.127457000	-0.841852000
C	6.295398000	0.024580000	-0.896656000
H	7.133018000	0.038994000	-1.590488000
C	4.194115000	-0.012700000	0.903239000
H	3.379430000	-0.027466000	1.627599000
O	-1.367901000	1.494381000	-1.319624000
C	-4.099952000	2.495488000	-1.057516000
H	-3.792715000	2.360530000	-2.102766000
H	-4.848210000	3.300773000	-1.042502000
C	-4.696430000	1.217361000	-0.537490000
C	-5.728907000	1.216765000	0.403897000
H	-6.139684000	2.164740000	0.750481000
C	-6.243941000	0.015680000	0.882912000
H	-7.057219000	0.025304000	1.605159000
C	-4.205347000	-0.009458000	-0.988102000
H	-3.415930000	-0.020037000	-1.739943000
O	-1.509711000	-1.466890000	1.016006000
O	-1.372253000	-1.519321000	-1.237159000
C	-5.729686000	-1.197741000	0.435167000
H	-6.141946000	-2.135942000	0.805734000
C	-4.696431000	-1.223830000	-0.505208000
C	-4.100035000	-2.515337000	-0.991258000
H	-4.853104000	-3.316032000	-0.969056000
H	-3.779671000	-2.403066000	-2.035159000
C	-2.889748000	-3.022377000	-0.167108000
C	-3.322510000	-3.426028000	1.237100000
H	-3.763260000	-2.588992000	1.787683000
H	-4.071808000	-4.224456000	1.167034000
H	-2.474130000	-3.804649000	1.817229000
C	-2.284627000	-4.232056000	-0.883775000
H	-1.431853000	-4.634650000	-0.324785000
H	-3.039564000	-5.023912000	-0.959926000
H	-1.950012000	-3.973221000	-1.893208000
C	-1.836862000	-1.915014000	-0.134168000
O	-1.501988000	1.453589000	0.926067000
C	-1.831654000	1.901317000	-0.219484000
C	-2.877360000	3.012867000	-0.257825000
C	-2.274204000	4.205882000	-1.003607000
H	-1.963815000	3.929765000	-2.016179000
H	-3.022489000	5.004343000	-1.075029000
H	-1.405066000	4.606629000	-0.468896000
C	-3.289043000	3.440557000	1.145426000
H	-2.430525000	3.822049000	1.708593000
H	-4.033910000	4.242776000	1.072859000
H	-3.728237000	2.614701000	1.713919000
Rh	-0.062834000	-0.014023000	1.133975000
H	-0.851946000	-0.776988000	3.262306000

N	-0.171291000	-0.038586000	2.995453000

^{3}17 (Triplet 17)

Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -2118.59712915
Electronic and Zero-Point Energy = -2117.914039
Enthalpy = -2117.869849
Free Energy = -2117.986109

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2119.13918840

Rh	0.061945000	-0.006262000	-1.285911000
C	1.852736000	-1.894357000	-0.010630000
C	2.902817000	-3.001516000	0.065946000
C	2.274929000	-4.207388000	0.770220000
H	1.927356000	-3.948550000	1.775401000
H	3.019979000	-5.007616000	0.855841000
H	1.426036000	-4.599276000	0.197468000
C	3.365227000	-3.409374000	-1.327544000
H	2.529136000	-3.789894000	-1.923842000
H	4.114115000	-4.206515000	-1.239651000
H	3.815645000	-2.572640000	-1.870905000
O	1.515523000	-1.468555000	-1.151755000
O	1.379301000	1.507832000	1.144319000
C	5.768932000	1.217978000	-0.467925000
H	6.188312000	2.162223000	-0.814460000
C	4.711453000	1.228541000	0.445248000
C	4.097456000	2.511783000	0.931774000
H	4.844034000	3.318747000	0.926952000
H	3.762346000	2.389994000	1.970049000
C	2.896593000	3.013578000	0.091008000
C	3.345475000	3.415954000	-1.308404000
H	3.791705000	2.577415000	-1.852374000
H	4.094416000	4.213949000	-1.230432000
H	2.503556000	3.793702000	-1.898334000
C	2.275964000	4.221388000	0.798510000
H	1.421375000	4.612104000	0.233652000
H	3.022474000	5.021132000	0.874045000
H	1.938876000	3.965562000	1.808005000
C	1.847785000	1.907252000	0.027217000
O	1.508835000	1.459736000	-1.103940000
O	1.391339000	-1.481408000	1.101456000
C	4.096277000	-2.499072000	0.916227000
H	3.753632000	-2.379997000	1.952221000
H	4.845331000	-3.303842000	0.915116000

C	4.710743000	-1.213060000	0.437558000
C	5.768700000	-1.196889000	-0.475062000
H	6.188561000	-2.139004000	-0.826755000
C	6.296172000	0.011835000	-0.920230000
H	7.128430000	0.013831000	-1.620655000
C	4.209154000	0.006495000	0.896039000
H	3.399954000	0.003801000	1.626352000
O	-1.381455000	1.497453000	-1.252960000
C	-4.094755000	2.511943000	-1.026373000
H	-3.771985000	2.387138000	-2.068097000
H	-4.846084000	3.314541000	-1.015562000
C	-4.695997000	1.227191000	-0.528182000
C	-5.734013000	1.213669000	0.407188000
H	-6.146275000	2.156775000	0.765150000
C	-6.252674000	0.006257000	0.866006000
H	-7.069606000	0.006276000	1.584229000
C	-4.204920000	0.006413000	-0.994686000
H	-3.411117000	0.006833000	-1.741747000
O	-1.503052000	-1.441026000	0.948209000
O	-1.371821000	-1.507609000	-1.302467000
C	-5.737286000	-1.201163000	0.403443000
H	-6.151203000	-2.144417000	0.759156000
C	-4.700010000	-1.214356000	-0.532556000
C	-4.101893000	-2.498999000	-1.034490000
H	-4.851323000	-3.303151000	-1.013739000
H	-3.789854000	-2.376445000	-2.079850000
C	-2.883189000	-3.006996000	-0.223310000
C	-3.303102000	-3.416188000	1.183100000
H	-3.741594000	-2.581748000	1.739407000
H	-4.050617000	-4.216635000	1.117003000
H	-2.448650000	-3.793608000	1.755182000
C	-2.281735000	-4.212466000	-0.950176000
H	-1.418007000	-4.610536000	-0.404724000
H	-3.032912000	-5.008763000	-1.016374000
H	-1.963388000	-3.950877000	-1.964142000
C	-1.833240000	-1.897683000	-0.190914000
O	-1.489313000	1.496947000	0.999617000
C	-1.834649000	1.917994000	-0.149605000
C	-2.885831000	3.024775000	-0.204191000
C	-2.274475000	4.224404000	-0.932940000
H	-1.941312000	3.953775000	-1.939873000
H	-3.024814000	5.019830000	-1.017244000
H	-1.418980000	4.627676000	-0.378387000
C	-3.321550000	3.445195000	1.194055000
H	-2.474035000	3.829416000	1.771668000
H	-4.070496000	4.243038000	1.113504000
H	-3.763444000	2.614267000	1.753105000
Rh	-0.048181000	0.027216000	1.147084000
H	-0.823039000	-1.164277000	3.291146000
N	-0.314513000	-0.291253000	3.055490000

^{1}17b (Singlet 17b)

Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -2118.59853632
Electronic and Zero-Point Energy = -2117.915082
Enthalpy = -2117.870783
Free Energy = -2117.987822

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2119.14589136

Rh	1.139290000	1.897241000	0.703962000
C	3.040027000	3.656256000	2.039778000
C	4.239839000	3.946524000	2.940383000
C	3.736657000	4.720099000	4.161446000
H	3.239980000	5.650380000	3.868191000
H	4.583938000	4.967045000	4.812673000
H	3.029306000	4.117766000	4.744465000
C	4.920436000	2.661222000	3.395336000
H	4.229031000	2.030399000	3.964600000
H	5.769036000	2.910942000	4.044799000
H	5.295319000	2.074938000	2.550525000
O	2.842209000	2.444889000	1.708071000
O	1.953246000	4.174928000	-1.198844000
C	6.426512000	3.145979000	-1.608724000
H	6.719280000	2.715455000	-2.566052000
C	5.265960000	3.920294000	-1.528127000
C	4.373853000	4.138404000	-2.718950000
H	4.962179000	4.110673000	-3.647198000
H	3.915180000	5.133446000	-2.658664000
C	3.245538000	3.090937000	-2.882180000
C	3.822143000	1.715213000	-3.193704000
H	4.465362000	1.349212000	-2.386704000
H	4.421101000	1.775799000	-4.110814000
H	3.025891000	0.980794000	-3.353033000
C	2.326743000	3.533717000	-4.026651000
H	1.506946000	2.820126000	-4.173145000
H	2.904093000	3.579465000	-4.957812000
H	1.898538000	4.523203000	-3.835734000
C	2.400788000	3.052925000	-1.612433000
O	2.183050000	1.930844000	-1.073440000
O	2.316072000	4.619863000	1.672576000
C	5.234270000	4.843293000	2.161044000
H	4.755856000	5.816616000	1.989067000
H	6.092543000	5.017318000	2.825843000
C	5.691828000	4.266929000	0.850656000
C	6.846334000	3.487635000	0.745279000

H	7.464621000	3.321568000	1.627208000
C	7.213279000	2.937031000	-0.479615000
H	8.121155000	2.342640000	-0.555485000
C	4.928892000	4.485336000	-0.297242000
H	4.039255000	5.110470000	-0.227524000
O	1.000543000	-0.316278000	0.686440000
C	-1.543313000	-1.981435000	0.988617000
H	-0.715231000	-2.380744000	1.590345000
H	-2.160066000	-2.838275000	0.681401000
C	-2.352421000	-1.022308000	1.817519000
C	-3.732494000	-0.881731000	1.648075000
H	-4.251581000	-1.505449000	0.920554000
C	-4.442994000	0.035832000	2.415806000
H	-5.520145000	0.125508000	2.293149000
C	-1.715232000	-0.227960000	2.770307000
H	-0.641813000	-0.340135000	2.917561000
O	-0.441888000	4.145607000	2.168662000
O	0.123638000	1.983996000	2.483693000
C	-3.784452000	0.833876000	3.348252000
H	-4.352797000	1.536906000	3.956373000
C	-2.402324000	0.723722000	3.526564000
C	-1.656165000	1.577128000	4.519192000
H	-2.247066000	1.675383000	5.442001000
H	-0.724665000	1.068067000	4.797728000
C	-1.308179000	3.020527000	4.086751000
C	-2.564472000	3.872498000	3.916096000
H	-3.199123000	3.503226000	3.102663000
H	-3.148866000	3.847656000	4.844142000
H	-2.305905000	4.913399000	3.701231000
C	-0.411493000	3.640742000	5.167507000
H	-0.129747000	4.666508000	4.903609000
H	-0.950911000	3.665607000	6.121969000
H	0.503068000	3.051101000	5.306833000
C	-0.489172000	3.041028000	2.802435000
O	-0.489240000	0.998981000	-0.209423000
C	-0.097327000	-0.188183000	0.066858000
C	-0.942999000	-1.383639000	-0.313373000
C	-0.043138000	-2.437051000	-0.961421000
H	0.761761000	-2.745089000	-0.286528000
H	-0.640484000	-3.320961000	-1.214689000
H	0.406749000	-2.056841000	-1.886355000
C	-2.046829000	-0.972715000	-1.280901000
H	-1.625957000	-0.555686000	-2.202705000
H	-2.642487000	-1.855038000	-1.546241000
H	-2.715944000	-0.224892000	-0.844208000
Rh	0.593269000	4.295454000	0.368359000
H	-1.122798000	3.249379000	-0.877911000
N	-0.848717000	4.232630000	-0.668709000

^{3}17b (Triplet 17b)

Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -2118.59582357
Electronic and Zero-Point Energy = -2117.912607
Enthalpy = -2117.868387
Free Energy = -2117.985076

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2119.14057889

Rh	1.182222000	1.894858000	0.737534000
C	3.085923000	3.648007000	2.077866000
C	4.290863000	3.967431000	2.958036000
C	3.801181000	4.754335000	4.176032000
H	3.290295000	5.675700000	3.879177000
H	4.658171000	5.019106000	4.807007000
H	3.111405000	4.154087000	4.781570000
C	4.988489000	2.693521000	3.418875000
H	4.310161000	2.064556000	4.005673000
H	5.843337000	2.959284000	4.053372000
H	5.356787000	2.100034000	2.576387000
O	2.901223000	2.442506000	1.735094000
O	1.959984000	4.185150000	-1.214932000
C	6.434073000	3.137708000	-1.615178000
H	6.723532000	2.701945000	-2.571152000
C	5.272704000	3.910816000	-1.535338000
C	4.381315000	4.123839000	-2.727878000
H	4.971791000	4.088668000	-3.654625000
H	3.926399000	5.120983000	-2.674047000
C	3.247917000	3.080769000	-2.885579000
C	3.820077000	1.700704000	-3.185637000
H	4.461105000	1.338594000	-2.375152000
H	4.420059000	1.750747000	-4.102904000
H	3.021184000	0.967902000	-3.339186000
C	2.335817000	3.518332000	-4.036320000
H	1.512473000	2.807802000	-4.178448000
H	2.914853000	3.553258000	-4.967070000
H	1.911809000	4.511327000	-3.854766000
C	2.405368000	3.062265000	-1.612029000
O	2.200367000	1.942481000	-1.055641000
O	2.334379000	4.604111000	1.730864000
C	5.263289000	4.862687000	2.148476000
H	4.771881000	5.828527000	1.970462000
H	6.129077000	5.055562000	2.798092000
C	5.709398000	4.274171000	0.839374000
C	6.865356000	3.496846000	0.733710000
H	7.489667000	3.340439000	1.613119000
C	7.226677000	2.937440000	-0.488619000

H	8.135407000	2.344422000	-0.564888000
C	4.939266000	4.482107000	-0.305767000
H	4.048888000	5.106765000	-0.237409000
O	1.002011000	-0.340870000	0.691902000
C	-1.558228000	-1.964966000	0.957159000
H	-0.728171000	-2.377760000	1.546943000
H	-2.176940000	-2.814404000	0.633864000
C	-2.365961000	-1.023928000	1.807573000
C	-3.752115000	-0.914935000	1.670371000
H	-4.272428000	-1.546915000	0.950841000
C	-4.466362000	-0.018057000	2.458903000
H	-5.547771000	0.047574000	2.360829000
C	-1.724053000	-0.218039000	2.748114000
H	-0.644670000	-0.303524000	2.867555000
O	-0.493870000	4.135540000	2.147912000
O	0.159233000	2.005891000	2.523918000
C	-3.805131000	0.788667000	3.381294000
H	-4.374875000	1.474869000	4.007111000
C	-2.416764000	0.710489000	3.527537000
C	-1.674228000	1.573571000	4.514145000
H	-2.263129000	1.666250000	5.438876000
H	-0.735108000	1.077270000	4.789620000
C	-1.347747000	3.018795000	4.074008000
C	-2.618489000	3.843139000	3.880130000
H	-3.236943000	3.451386000	3.064676000
H	-3.212768000	3.818004000	4.802069000
H	-2.378522000	4.886328000	3.655230000
C	-0.479716000	3.666161000	5.162201000
H	-0.221575000	4.697360000	4.895032000
H	-1.029832000	3.683535000	6.110793000
H	0.448729000	3.102164000	5.314640000
C	-0.506433000	3.046276000	2.802331000
O	-0.451894000	1.032226000	-0.176743000
C	-0.087976000	-0.172747000	0.075320000
C	-0.962170000	-1.338951000	-0.332455000
C	-0.086931000	-2.388405000	-1.020104000
H	0.718374000	-2.729688000	-0.361893000
H	-0.701915000	-3.254068000	-1.293441000
H	0.361288000	-1.989351000	-1.937849000
C	-2.068726000	-0.882386000	-1.275573000
H	-1.650752000	-0.446707000	-2.190044000
H	-2.682368000	-1.746636000	-1.558992000
H	-2.721122000	-0.136804000	-0.810455000
Rh	0.687741000	4.297627000	0.438575000
H	-1.263622000	2.995049000	-0.808499000
N	-0.756072000	3.869340000	-0.609524000

Triplet TS1

Lowest Frequency Vibration = -302.8633 cm**-1

Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -2427.99912310
Electronic and Zero-Point Energy = -2427.182492
Enthalpy = -2427.130504
Free Energy = -2427.265878

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2428.62191107

Rh	-0.655226000	-1.905424000	0.688214000
C	1.584316000	-0.515506000	1.946186000
C	2.702211000	-0.294920000	2.963184000
C	2.428346000	1.017966000	3.701457000
H	2.390781000	1.866509000	3.009639000
H	3.225865000	1.202096000	4.431559000
H	1.477355000	0.973113000	4.246045000
C	2.762039000	-1.441942000	3.964367000
H	1.822330000	-1.527749000	4.520654000
H	3.569733000	-1.253393000	4.682795000
H	2.953954000	-2.402047000	3.474906000
O	0.917745000	-1.586722000	2.006523000
O	1.133376000	-0.787648000	-1.630501000
C	4.837952000	-3.397979000	-0.525149000
H	5.039806000	-4.211499000	-1.221580000
C	4.124738000	-2.278678000	-0.962654000
C	3.581860000	-2.181225000	-2.361451000
H	4.226531000	-2.732469000	-3.061124000
H	3.583119000	-1.131333000	-2.682006000
C	2.147827000	-2.740167000	-2.540850000
C	2.129698000	-4.252003000	-2.350820000
H	2.467024000	-4.543127000	-1.351029000
H	2.795467000	-4.717019000	-3.088808000
H	1.121673000	-4.654370000	-2.498154000
C	1.661217000	-2.395864000	-3.950857000
H	0.644037000	-2.770582000	-4.118575000
H	2.319400000	-2.867711000	-4.690583000
H	1.665419000	-1.314883000	-4.122832000
C	1.228673000	-2.053704000	-1.532759000
O	0.636355000	-2.770504000	-0.678314000
O	1.413758000	0.417958000	1.096988000
C	4.045041000	-0.162145000	2.200795000
H	4.029710000	0.781850000	1.640221000
H	4.833894000	-0.071659000	2.961440000
C	4.350744000	-1.295613000	1.261382000
C	5.060763000	-2.425997000	1.674381000
H	5.436361000	-2.480490000	2.695929000
C	5.305206000	-3.467789000	0.784116000
H	5.870901000	-4.337490000	1.111122000

C	3.905135000	-1.236084000	-0.060588000
H	3.367871000	-0.349165000	-0.397378000
O	-2.172217000	-2.064384000	-0.732349000
C	-4.801693000	-1.407626000	-1.831403000
H	-4.808276000	-2.351810000	-1.271440000
H	-5.593155000	-1.477932000	-2.591518000
C	-5.078063000	-0.267179000	-0.891430000
C	-5.750229000	0.885985000	-1.305374000
H	-6.117913000	0.955038000	-2.328896000
C	-5.968274000	1.932301000	-0.413528000
H	-6.504050000	2.820252000	-0.741900000
C	-4.644918000	-0.344586000	0.433454000
H	-4.136393000	-1.247840000	0.770994000
O	-1.388094000	1.084614000	1.071111000
O	-1.886452000	-0.896586000	2.027278000
C	-5.514802000	1.843142000	0.899602000
H	-5.697438000	2.659659000	1.597907000
C	-4.842087000	0.699833000	1.338547000
C	-4.321097000	0.575381000	2.743180000
H	-4.954117000	1.146003000	3.437981000
H	-4.364930000	-0.475746000	3.057121000
C	-2.869026000	1.077191000	2.946174000
C	-2.790277000	2.590144000	2.778953000
H	-3.111092000	2.910428000	1.782502000
H	-3.439052000	3.070914000	3.521988000
H	-1.766638000	2.949332000	2.935664000
C	-2.414875000	0.694220000	4.356404000
H	-1.390933000	1.036968000	4.547866000
H	-3.071722000	1.171296000	5.094039000
H	-2.452510000	-0.389049000	4.508100000
C	-1.972157000	0.362308000	1.936449000
O	-1.658553000	-0.057679000	-1.630477000
C	-2.336305000	-1.131175000	-1.570555000
C	-3.456701000	-1.308886000	-2.594884000
C	-3.221186000	-2.624255000	-3.341157000
H	-3.194497000	-3.474527000	-2.652510000
H	-4.031549000	-2.786148000	-4.062414000
H	-2.276305000	-2.597815000	-3.897544000
C	-3.487260000	-0.156639000	-3.591550000
H	-2.546245000	-0.093132000	-4.148703000
H	-4.299601000	-0.322623000	-4.310401000
H	-3.655036000	0.806708000	-3.099861000
Rh	-0.092532000	0.238417000	-0.312045000
H	-0.643404000	2.625578000	-1.445114000
N	0.133854000	2.081784000	-1.029669000
C	2.084976000	3.868679000	0.165211000
C	0.817549000	3.587374000	0.561780000
H	-0.025258000	4.229007000	0.310409000
H	0.635668000	2.820211000	1.309528000
H	2.891413000	3.244350000	0.557676000
C	2.488411000	4.891996000	-0.784266000

C	1.563277000	5.649512000	-1.523540000
C	3.856900000	5.131374000	-0.987458000
C	1.995505000	6.616092000	-2.419232000
C	4.288692000	6.101467000	-1.882610000
C	3.359208000	6.849015000	-2.601289000
H	0.496283000	5.469962000	-1.403312000
H	4.583084000	4.545008000	-0.425945000
H	1.266042000	7.190708000	-2.985284000
H	5.353235000	6.273659000	-2.022467000
H	3.693759000	7.606765000	-3.305637000

MECP

Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -2428.05471761
Electronic and Zero-Point Energy = -2427.234410
Enthalpy = -2427.183059
Free Energy = -2427.313661

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2428.67191494

Rh	0.683998000	0.550334000	-1.596736000
C	-1.163202000	2.277418000	-0.147732000
C	-2.069559000	3.485764000	0.086042000
C	-1.554923000	4.244929000	1.311143000
H	-1.539708000	3.602608000	2.198596000
H	-2.206378000	5.103525000	1.515587000
H	-0.540053000	4.624853000	1.141317000
C	-2.074092000	4.410827000	-1.124226000
H	-1.066385000	4.784188000	-1.337029000
H	-2.722782000	5.272369000	-0.920527000
H	-2.443063000	3.906421000	-2.022973000
O	-0.617539000	2.144181000	-1.278422000
O	-1.304423000	-1.351007000	-0.091077000
C	-5.047663000	0.174702000	-2.490585000
H	-5.446735000	-0.541614000	-3.208581000
C	-4.300060000	-0.285231000	-1.403194000
C	-3.992863000	-1.743446000	-1.204429000
H	-4.793466000	-2.362853000	-1.635699000
H	-3.958137000	-1.965235000	-0.129374000
C	-2.665113000	-2.228518000	-1.839539000
C	-2.756266000	-2.199392000	-3.360669000
H	-2.950643000	-1.191085000	-3.740094000
H	-3.574140000	-2.853891000	-3.688409000
H	-1.827786000	-2.558617000	-3.817921000
C	-2.404593000	-3.661177000	-1.368573000

H	-1.469612000	-4.052055000	-1.789109000
H	-3.222324000	-4.311796000	-1.703406000
H	-2.344888000	-3.713387000	-0.276268000
C	-1.525026000	-1.337115000	-1.342545000
O	-0.893393000	-0.653307000	-2.198392000
O	-1.037873000	1.485158000	0.839186000
C	-3.500413000	2.974868000	0.389431000
H	-3.485193000	2.487148000	1.373900000
H	-4.144909000	3.861897000	0.477735000
C	-4.060184000	2.017554000	-0.625935000
C	-4.808620000	2.452861000	-1.722305000
H	-5.019718000	3.515776000	-1.839992000
C	-5.300251000	1.535230000	-2.646991000
H	-5.893631000	1.882265000	-3.490289000
C	-3.824664000	0.649183000	-0.481371000
H	-3.253559000	0.297979000	0.378044000
O	1.932902000	-1.124216000	-1.717939000
C	4.426114000	-2.556656000	-1.278611000
H	4.364468000	-2.093467000	-2.271749000
H	5.080754000	-3.435218000	-1.373000000
C	5.011339000	-1.573499000	-0.303056000
C	5.808883000	-1.981922000	0.769521000
H	6.045039000	-3.038842000	0.891273000
C	6.314258000	-1.046511000	1.667821000
H	6.944859000	-1.372823000	2.492045000
C	4.745509000	-0.211110000	-0.452385000
H	4.137571000	0.119072000	-1.294401000
O	1.783290000	1.054938000	1.297269000
O	2.216095000	1.733271000	-0.812341000
C	6.024252000	0.305956000	1.512077000
H	6.429104000	1.036508000	2.212105000
C	5.228510000	0.739680000	0.448516000
C	4.875428000	2.188942000	0.264011000
H	5.671402000	2.829480000	0.670729000
H	4.799083000	2.413225000	-0.807686000
C	3.554677000	2.629429000	0.943193000
C	3.681412000	2.565557000	2.460362000
H	3.906872000	1.553587000	2.812190000
H	4.492127000	3.230771000	2.784273000
H	2.755919000	2.893566000	2.946249000
C	3.251640000	4.067674000	0.516038000
H	2.329248000	4.433078000	0.983247000
H	4.070922000	4.725021000	0.832185000
H	3.144054000	4.145351000	-0.570450000
C	2.423932000	1.732838000	0.435529000
O	1.536792000	-1.738688000	0.418624000
C	2.085023000	-1.883821000	-0.717404000
C	3.018317000	-3.082429000	-0.902493000
C	2.487122000	-3.927255000	-2.063763000
H	2.440364000	-3.347691000	-2.991180000
H	3.149128000	-4.787035000	-2.225014000

H	1.483427000	-4.313005000	-1.844782000
C	3.087425000	-3.939739000	0.355182000
H	2.101928000	-4.342256000	0.613149000
H	3.765484000	-4.784774000	0.178895000
H	3.459651000	-3.376041000	1.216598000
Rh	0.215495000	-0.162982000	0.692586000
H	0.844743000	-0.617592000	3.187579000
N	-0.062959000	-0.578540000	2.721061000
C	-2.379790000	0.175487000	3.190839000
C	-0.930357000	0.279428000	3.463949000
H	-0.798322000	0.110460000	4.553315000
H	-0.651693000	1.345461000	3.330889000
H	-2.952099000	1.086671000	3.380016000
C	-3.120559000	-0.961745000	2.828327000
C	-2.539035000	-2.247281000	2.650867000
C	-4.533541000	-0.841364000	2.697722000
C	-3.339904000	-3.351199000	2.425642000
C	-5.318609000	-1.947079000	2.440678000
C	-4.726390000	-3.209643000	2.314165000
H	-1.455395000	-2.329736000	2.693329000
H	-4.988032000	0.142130000	2.812359000
H	-2.886902000	-4.333936000	2.317239000
H	-6.396354000	-1.841283000	2.346701000
H	-5.345484000	-4.082588000	2.122589000

Singlet concerted TS

Lowest Frequency Vibration = -49.4218 cm**-1
Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -2427.99456675
Electronic and Zero-Point Energy = -2427.176312
Enthalpy = -2427.124772
Free Energy = -2427.257222

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2428.62136409

Rh	0.091751000	0.003562000	-1.213616000
C	1.930564000	-1.780241000	0.161499000
C	2.979481000	-2.876582000	0.325529000
C	2.340029000	-4.013072000	1.126913000
H	1.954993000	-3.657641000	2.088371000
H	3.088769000	-4.790986000	1.323997000
H	1.517217000	-4.472603000	0.566124000
C	3.439394000	-3.399731000	-1.028972000
H	2.601352000	-3.828582000	-1.588388000
H	4.187475000	-4.187731000	-0.875453000

H	3.890107000	-2.613118000	-1.642585000
O	1.541121000	-1.472123000	-0.995648000
O	1.546494000	1.777431000	0.790298000
C	5.930429000	1.164033000	-0.713670000
H	6.368592000	2.042722000	-1.186427000
C	4.848913000	1.320446000	0.157229000
C	4.246424000	2.673173000	0.421177000
H	5.008674000	3.456147000	0.299707000
H	3.893237000	2.725567000	1.458911000
C	3.069040000	3.052489000	-0.511438000
C	3.538618000	3.182278000	-1.955040000
H	3.952186000	2.243553000	-2.337406000
H	4.319666000	3.950898000	-2.011735000
H	2.715082000	3.483134000	-2.611074000
C	2.481815000	4.386809000	-0.042242000
H	1.638134000	4.688860000	-0.674458000
H	3.249274000	5.167218000	-0.111362000
H	2.137195000	4.330720000	0.995311000
C	1.979737000	1.987904000	-0.387156000
O	1.585077000	1.401371000	-1.432290000
O	1.520592000	-1.253128000	1.250920000
C	4.170367000	-2.303023000	1.134652000
H	3.814439000	-2.062320000	2.145857000
H	4.904028000	-3.115730000	1.235151000
C	4.816319000	-1.095819000	0.511245000
C	5.899423000	-1.223102000	-0.362682000
H	6.312742000	-2.211462000	-0.562387000
C	6.455778000	-0.099483000	-0.966004000
H	7.306379000	-0.208968000	-1.635092000
C	4.319101000	0.183437000	0.772493000
H	3.493513000	0.297923000	1.476058000
O	-1.317770000	1.555026000	-1.194845000
C	-4.028437000	2.607653000	-0.830082000
H	-3.808303000	2.361073000	-1.876956000
H	-4.769430000	3.419817000	-0.838379000
C	-4.586430000	1.397090000	-0.134963000
C	-5.522938000	1.506204000	0.896301000
H	-5.889927000	2.490492000	1.186050000
C	-6.000164000	0.366837000	1.537640000
H	-6.739256000	0.461252000	2.330098000
C	-4.153328000	0.123515000	-0.508847000
H	-3.439605000	0.027230000	-1.327654000
O	-1.321976000	-1.155998000	1.361044000
O	-1.367487000	-1.455578000	-0.871341000
C	-5.543400000	-0.893551000	1.163240000
H	-5.926600000	-1.783787000	1.661417000
C	-4.607502000	-1.029504000	0.134516000
C	-4.075016000	-2.373816000	-0.277555000
H	-4.829768000	-3.154201000	-0.104278000
H	-3.856858000	-2.369407000	-1.353375000
C	-2.793996000	-2.822292000	0.471203000

C	-3.089742000	-3.087642000	1.941826000
H	-3.483077000	-2.198808000	2.446850000
H	-3.836592000	-3.887072000	2.022261000
H	-2.184210000	-3.411883000	2.469517000
C	-2.266881000	-4.101759000	-0.182670000
H	-1.365188000	-4.460705000	0.327320000
H	-3.029143000	-4.886793000	-0.110031000
H	-2.031248000	-3.943397000	-1.239560000
C	-1.741212000	-1.731153000	0.298999000
O	-1.320159000	1.720664000	1.056619000
C	-1.706131000	2.066966000	-0.108973000
C	-2.741396000	3.187521000	-0.189677000
C	-2.190871000	4.283338000	-1.105218000
H	-1.962537000	3.894356000	-2.102327000
H	-2.935512000	5.082268000	-1.205409000
H	-1.279077000	4.724886000	-0.685691000
C	-3.038308000	3.773371000	1.185329000
H	-2.134240000	4.197416000	1.635627000
H	-3.777997000	4.577190000	1.082103000
H	-3.439731000	3.023331000	1.873908000
Rh	0.125105000	0.271836000	1.217920000
H	1.107573000	-0.267772000	3.285723000
N	0.624186000	0.600868000	2.978068000
C	-0.282895000	-1.145915000	5.242131000
C	-1.546749000	-0.930330000	4.850222000
H	0.232053000	-0.359916000	5.799579000
H	-2.059605000	-0.006018000	5.100267000
H	-2.103739000	-1.658369000	4.262643000
C	0.508957000	-2.354013000	4.986835000
C	-0.082873000	-3.587302000	4.677067000
C	1.905982000	-2.292199000	5.090901000
C	0.698333000	-4.719018000	4.481862000
C	2.689284000	-3.423728000	4.887029000
C	2.086679000	-4.642541000	4.588691000
H	-1.167994000	-3.666787000	4.634388000
H	2.377641000	-1.343363000	5.348077000
H	0.221495000	-5.670454000	4.258197000
H	3.771405000	-3.354719000	4.971876000
H	2.695291000	-5.531120000	4.438459000

Cycle B: Rh-Amine

20
Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -2834.73739462
Electronic and Zero-Point Energy = -2833.936749
Enthalpy = -2833.881545

Free Energy = -2834.023887

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2835.48701372

Rh	-0.718973000	-0.961882000	-0.053749000
C	1.876121000	-1.309603000	1.239328000
C	2.982349000	-2.060311000	1.979293000
C	3.207964000	-1.371600000	3.328073000
H	3.490209000	-0.321858000	3.198551000
H	4.012198000	-1.882898000	3.871243000
H	2.304065000	-1.414719000	3.947938000
C	2.596806000	-3.516110000	2.210622000
H	1.690763000	-3.589844000	2.821561000
H	3.410257000	-4.026569000	2.741769000
H	2.414359000	-4.045798000	1.270154000
O	0.834759000	-1.946124000	0.913128000
O	1.407981000	0.475421000	-1.848931000
C	3.861147000	-3.351238000	-2.900232000
H	3.749779000	-3.697869000	-3.927393000
C	3.595490000	-2.014292000	-2.593479000
C	3.113636000	-1.047244000	-3.638844000
H	3.490411000	-1.338502000	-4.629874000
H	3.518731000	-0.048903000	-3.427411000
C	1.573768000	-0.935129000	-3.760936000
C	0.986115000	-2.232479000	-4.302627000
H	1.200215000	-3.082919000	-3.647285000
H	1.417560000	-2.441352000	-5.289821000
H	-0.100685000	-2.155704000	-4.413340000
C	1.241601000	0.213918000	-4.717075000
H	0.157088000	0.319182000	-4.842286000
H	1.675294000	0.008588000	-5.703470000
H	1.641094000	1.167096000	-4.354445000
C	0.989331000	-0.596882000	-2.389512000
O	0.138992000	-1.389073000	-1.892374000
O	2.094197000	-0.078195000	1.004846000
C	4.288146000	-1.962364000	1.151461000
H	4.614292000	-0.914216000	1.148483000
H	5.052611000	-2.536878000	1.694286000
C	4.170586000	-2.458488000	-0.262892000
C	4.431475000	-3.790297000	-0.596172000
H	4.765733000	-4.480623000	0.177989000
C	4.281579000	-4.231537000	-1.907516000
H	4.499082000	-5.267322000	-2.158799000
C	3.770927000	-1.584836000	-1.276194000
H	3.583361000	-0.538400000	-1.030393000
O	-2.152025000	0.171734000	-1.052525000
C	-4.321580000	2.103741000	-1.192482000
H	-4.670911000	1.063112000	-1.183733000
H	-5.075553000	2.692883000	-1.734369000
C	-4.188244000	2.601310000	0.220071000

C	-4.433445000	3.934995000	0.557044000
H	-4.761490000	4.631459000	-0.214361000
C	-4.277174000	4.369897000	1.870145000
H	-4.482780000	5.407320000	2.124908000
C	-3.794907000	1.721556000	1.230291000
H	-3.617275000	0.675559000	0.980485000
O	-0.190348000	1.484058000	1.840375000
O	-1.445481000	-0.390603000	1.815721000
C	-3.867662000	3.481580000	2.860544000
H	-3.754330000	3.823754000	3.889032000
C	-3.616204000	2.142735000	2.549404000
C	-3.149037000	1.161550000	3.588639000
H	-3.529066000	1.447152000	4.580225000
H	-3.554742000	0.166988000	3.362184000
C	-1.610458000	1.036729000	3.718230000
C	-1.009972000	2.329399000	4.256621000
H	-1.212607000	3.180561000	3.598686000
H	-1.441969000	2.546137000	5.241953000
H	0.075712000	2.240970000	4.371770000
C	-1.294521000	-0.111879000	4.679734000
H	-0.211629000	-0.233814000	4.804319000
H	-1.723400000	0.106033000	5.665568000
H	-1.711559000	-1.058423000	4.321487000
C	-1.033948000	0.682298000	2.347676000
O	-0.880240000	2.032688000	-0.954539000
C	-1.926742000	1.396674000	-1.285288000
C	-3.018229000	2.168381000	-2.027065000
C	-3.264707000	1.475388000	-3.369681000
H	-3.563393000	0.431463000	-3.230817000
H	-4.064161000	1.996594000	-3.910576000
H	-2.364662000	1.499293000	-3.996217000
C	-2.607311000	3.615481000	-2.269975000
H	-1.699526000	3.669657000	-2.880625000
H	-3.411693000	4.135127000	-2.806122000
H	-2.417593000	4.150071000	-1.333653000
Rh	0.647982000	1.026562000	0.009565000
H	1.947812000	3.474530000	0.757235000
O	3.248314000	7.233421000	-0.459029000
O	2.159245000	5.569451000	0.382643000
H	2.964521000	2.303614000	0.151023000
O	2.009386000	3.411623000	-1.205358000
C	3.238845000	3.867126000	-1.592212000
C	3.731333000	5.136493000	-1.251382000
C	3.988556000	3.040492000	-2.422558000
C	4.946024000	5.580454000	-1.748231000
C	5.216298000	3.459498000	-2.910392000
H	3.568196000	2.065996000	-2.665232000
C	5.669733000	4.726150000	-2.562258000
H	5.318859000	6.567695000	-1.498294000
H	5.818447000	2.826268000	-3.553013000
N	2.042341000	2.740240000	0.048330000

N	2.987732000	6.046745000	-0.379918000
N	6.965704000	5.184512000	-3.076446000
O	7.588114000	4.419878000	-3.794014000
O	7.339043000	6.300152000	-2.754954000

TS2
Lowest Frequency Vibration = -432.9984 cm**-1
Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -3144.11774606
Electronic and Zero-Point Energy = -3143.184828
Enthalpy = -3143.122273
Free Energy = -3143.277309

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -3144.95029397

Rh	-0.637406000	-0.941294000	0.072976000
C	1.983495000	-1.129242000	1.338597000
C	3.138167000	-1.804096000	2.075367000
C	3.377552000	-1.056908000	3.390337000
H	3.671975000	-0.015702000	3.219387000
H	4.182105000	-1.549679000	3.949348000
H	2.478116000	-1.063393000	4.018142000
C	2.809734000	-3.262040000	2.374472000
H	1.923671000	-3.340786000	3.013567000
H	3.654364000	-3.722564000	2.901891000
H	2.619748000	-3.834789000	1.461454000
O	0.979463000	-1.825128000	1.025747000
O	1.343935000	0.608801000	-1.747003000
C	3.877935000	-3.180937000	-2.799308000
H	3.738183000	-3.553049000	-3.813882000
C	3.615176000	-1.837951000	-2.518150000
C	3.097832000	-0.901683000	-3.574184000
H	3.450915000	-1.214502000	-4.567125000
H	3.507444000	0.100300000	-3.397932000
C	1.553171000	-0.806690000	-3.662927000
C	0.978275000	-2.114696000	-4.195921000
H	1.229349000	-2.964502000	-3.553387000
H	1.386682000	-2.306201000	-5.196216000
H	-0.112566000	-2.061548000	-4.276079000
C	1.174971000	0.332694000	-4.613503000
H	0.086997000	0.389670000	-4.739735000
H	1.618188000	0.149962000	-5.599946000
H	1.525792000	1.304762000	-4.251039000
C	0.986863000	-0.489996000	-2.277991000
O	0.203492000	-1.335467000	-1.759408000
O	2.125142000	0.113070000	1.088402000

C	4.415478000	-1.696532000	1.203631000
H	4.726136000	-0.643533000	1.172353000
H	5.207488000	-2.244299000	1.734040000
C	4.263287000	-2.220697000	-0.196941000
C	4.521188000	-3.559289000	-0.504940000
H	4.883790000	-4.227973000	0.275271000
C	4.334140000	-4.034239000	-1.799184000
H	4.550503000	-5.074612000	-2.031292000
C	3.829753000	-1.372425000	-1.218567000
H	3.648078000	-0.317936000	-0.997317000
O	-2.152450000	0.096079000	-0.907252000
C	-4.439271000	1.919194000	-1.008085000
H	-4.745366000	0.865024000	-0.992853000
H	-5.227016000	2.476372000	-1.535335000
C	-4.296614000	2.420837000	0.401866000
C	-4.560407000	3.749997000	0.742792000
H	-4.915333000	4.440038000	-0.022339000
C	-4.389822000	4.188061000	2.053077000
H	-4.610209000	5.221562000	2.311114000
C	-3.871933000	1.548686000	1.405715000
H	-3.682527000	0.505062000	1.153518000
O	-0.297790000	1.492757000	1.972036000
O	-1.400802000	-0.471142000	1.944550000
C	-3.948326000	3.307734000	3.037004000
H	-3.825604000	3.652178000	4.063588000
C	-3.679642000	1.973349000	2.721732000
C	-3.179786000	0.998638000	3.751291000
H	-3.561539000	1.263973000	4.747680000
H	-3.558718000	-0.005032000	3.518278000
C	-1.637069000	0.914436000	3.872375000
C	-1.067618000	2.206018000	4.445882000
H	-1.279703000	3.070328000	3.807723000
H	-1.509569000	2.390066000	5.433128000
H	0.018991000	2.130757000	4.570975000
C	-1.284078000	-0.252174000	4.798440000
H	-0.197586000	-0.351526000	4.911133000
H	-1.709854000	-0.070581000	5.792813000
H	-1.681545000	-1.198486000	4.418661000
C	-1.064057000	0.620095000	2.487307000
O	-1.017283000	2.042374000	-0.796289000
C	-2.016775000	1.334024000	-1.133017000
C	-3.156128000	2.037295000	-1.868786000
C	-3.389418000	1.312128000	-3.196454000
H	-3.633832000	0.257054000	-3.038385000
H	-4.222563000	1.785671000	-3.729997000
H	-2.502152000	1.371537000	-3.838527000
C	-2.821290000	3.499111000	-2.140135000
H	-1.925121000	3.588198000	-2.763994000
H	-3.657600000	3.967796000	-2.673998000
H	-2.646455000	4.059041000	-1.216032000
Rh	0.585139000	1.146321000	0.131841000

H	1.416771000	3.904033000	0.390025000
O	3.895685000	7.059330000	-0.587505000
O	2.322725000	5.744463000	0.077918000
C	2.283399000	2.947307000	2.529284000
C	3.292476000	3.847808000	2.360983000
H	1.339688000	3.257166000	2.967918000
H	2.426261000	1.876255000	2.406207000
H	3.111727000	4.885279000	2.647670000
C	4.574120000	3.588880000	1.745185000
C	4.881909000	2.360060000	1.121677000
C	5.527243000	4.623674000	1.700081000
C	6.101825000	2.179787000	0.489118000
C	6.752136000	4.433085000	1.078902000
C	7.039721000	3.213474000	0.466378000
H	4.156420000	1.544474000	1.127875000
H	5.289828000	5.580165000	2.163495000
H	6.321035000	1.233617000	-0.001655000
H	7.480381000	5.239618000	1.052101000
H	7.996883000	3.067009000	-0.029224000
H	2.689056000	2.872273000	0.163061000
O	1.800064000	3.692464000	-1.668909000
C	3.053161000	3.830369000	-1.901010000
C	3.860266000	4.928378000	-1.442677000
C	3.743234000	2.834643000	-2.652312000
C	5.200773000	5.044946000	-1.776938000
C	5.077349000	2.921400000	-2.956520000
H	3.137757000	1.984833000	-2.952624000
C	5.800360000	4.036210000	-2.508375000
H	5.777482000	5.898515000	-1.437447000
H	5.584794000	2.141909000	-3.517152000
N	1.675065000	2.927493000	0.239714000
N	3.317391000	5.982012000	-0.604024000
N	7.221220000	4.127955000	-2.787840000
O	7.733785000	3.225472000	-3.437086000
O	7.836140000	5.092625000	-2.350279000

21

Temperature = 298.150 Kq
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -3144.20278694
Electronic and Zero-Point Energy = -3143.265269
Enthalpy = -3143.202737
Free Energy = -3143.358076

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -3145.03226081

Rh	-0.645157000	-0.797854000	0.118212000
C	2.134437000	-0.071546000	0.646079000
C	3.575508000	-0.293628000	1.106893000
C	3.878135000	0.673421000	2.254480000
H	3.733899000	1.718287000	1.958504000
H	4.920053000	0.549051000	2.574444000
H	3.234754000	0.472155000	3.119625000
C	3.781699000	-1.724228000	1.590335000
H	3.128292000	-1.949657000	2.439930000
H	4.822256000	-1.851150000	1.915234000
H	3.576065000	-2.455195000	0.802052000
O	1.337320000	-1.050581000	0.687928000
O	0.286844000	0.862899000	-2.354099000
C	3.633875000	-2.162763000	-3.675047000
H	3.410964000	-2.706095000	-4.593265000
C	3.001045000	-0.942272000	-3.425615000
C	1.988062000	-0.357409000	-4.369855000
H	2.202666000	-0.668582000	-5.402759000
H	2.058329000	0.738254000	-4.333247000
C	0.520943000	-0.760061000	-4.076498000
C	0.315942000	-2.252433000	-4.304685000
H	0.954559000	-2.857296000	-3.653077000
H	0.558012000	-2.496551000	-5.347059000
H	-0.724928000	-2.539232000	-4.119337000
C	-0.396845000	0.029693000	-5.012803000
H	-1.449995000	-0.220555000	-4.834844000
H	-0.163809000	-0.221891000	-6.054851000
H	-0.269382000	1.108668000	-4.879859000
C	0.188891000	-0.370409000	-2.635919000
O	-0.150832000	-1.288444000	-1.833232000
O	1.847108000	1.100731000	0.243517000
C	4.526180000	0.019882000	-0.075232000
H	4.468560000	1.095867000	-0.295667000
H	5.548851000	-0.182200000	0.275296000
C	4.239221000	-0.753681000	-1.332069000
C	4.860438000	-1.975427000	-1.602912000
H	5.594368000	-2.372466000	-0.901758000
C	4.559231000	-2.673891000	-2.768912000
H	5.056584000	-3.618660000	-2.977711000
C	3.319347000	-0.249888000	-2.255036000
H	2.855172000	0.722079000	-2.075799000
O	-2.578602000	-0.359245000	-0.537731000
C	-5.250338000	0.762978000	-0.213686000
H	-5.205545000	-0.311049000	0.008763000
H	-6.269818000	0.977527000	-0.565720000
C	-4.954341000	1.547039000	1.034636000
C	-5.548639000	2.787171000	1.282679000
H	-6.271195000	3.187575000	0.571839000
C	-5.235786000	3.500160000	2.436492000
H	-5.713237000	4.459003000	2.626531000
C	-4.053228000	1.041683000	1.973758000

H	-3.595774000	0.068146000	1.797206000
O	-0.566074000	2.008065000	1.530555000
O	-1.059562000	-0.127906000	2.059266000
C	-4.322563000	2.987232000	3.353568000
H	-4.086951000	3.544017000	4.260383000
C	-3.715683000	1.748610000	3.129633000
C	-2.710594000	1.172640000	4.088435000
H	-2.911992000	1.526436000	5.109989000
H	-2.803597000	0.078810000	4.102538000
C	-1.235814000	1.525931000	3.773865000
C	-0.985399000	3.016485000	3.970364000
H	-1.616221000	3.627363000	3.316038000
H	-1.204183000	3.287526000	5.011121000
H	0.060709000	3.269607000	3.762975000
C	-0.331672000	0.727835000	4.716054000
H	0.725659000	0.952026000	4.529258000
H	-0.553755000	0.997785000	5.755835000
H	-0.484029000	-0.349608000	4.597213000
C	-0.928050000	1.099032000	2.339051000
O	-2.058963000	1.793059000	-0.977114000
C	-2.860392000	0.809081000	-0.935942000
C	-4.296856000	1.049903000	-1.400456000
C	-4.609422000	0.060766000	-2.526059000
H	-4.485581000	-0.974497000	-2.192911000
H	-5.645864000	0.197706000	-2.858314000
H	-3.954995000	0.228192000	-3.390425000
C	-4.485997000	2.473668000	-1.909169000
H	-3.828751000	2.677399000	-2.761537000
H	-5.524460000	2.605546000	-2.238956000
H	-4.275159000	3.217422000	-1.134129000
Rh	-0.095053000	1.498744000	-0.412499000
H	1.199880000	3.526787000	-1.610966000
H	-0.279357000	4.149749000	-1.169896000
O	2.716154000	3.069056000	-2.619749000
C	3.819696000	3.625440000	-2.770413000
C	4.048768000	5.070060000	-2.853644000
C	5.032651000	2.830193000	-2.885098000
C	6.276001000	3.370551000	-2.976223000
H	4.887408000	1.751120000	-2.868072000
H	7.163294000	2.747076000	-3.028356000
N	0.505007000	3.584819000	-0.849412000
N	2.971654000	6.004545000	-2.813732000
O	3.190707000	7.189377000	-3.068871000
O	1.845463000	5.609033000	-2.481138000
C	1.128146000	4.156300000	0.352369000
C	1.958400000	5.357378000	0.078646000
H	0.335915000	4.441322000	1.056757000
H	1.712636000	3.371345000	0.840323000
H	1.436385000	6.290932000	-0.135306000
C	3.345117000	5.398911000	0.174869000
C	4.123813000	4.211412000	0.309045000

C	4.009786000	6.657435000	0.091383000
C	5.495512000	4.292181000	0.398691000
C	5.382303000	6.724056000	0.181966000
C	6.121349000	5.543213000	0.332209000
H	3.628674000	3.240607000	0.300788000
H	3.414154000	7.559024000	-0.034789000
H	6.091088000	3.388153000	0.493903000
H	5.892978000	7.680166000	0.124711000
H	7.205805000	5.599336000	0.393614000
C	5.327053000	5.611540000	-2.964070000
C	6.424256000	4.780778000	-2.985238000
H	5.453959000	6.688289000	-2.998356000
N	7.739832000	5.362903000	-3.012527000
O	8.701767000	4.607264000	-3.123678000
O	7.844475000	6.583120000	-2.911760000

TS3
Lowest Frequency Vibration = -446.5202 cm**-1
Temperature = 298.150 Kq
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -3144.19048413
Electronic and Zero-Point Energy = -3143.255792
Enthalpy = -3143.193402
Free Energy = -3143.350210

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -3145.02145549

Rh	-0.632859000	-0.756087000	-0.002437000
C	2.070921000	-0.476998000	1.026920000
C	3.398151000	-0.934981000	1.627006000
C	3.618109000	-0.187397000	2.944652000
H	3.633083000	0.897008000	2.791649000
H	4.578314000	-0.488782000	3.380901000
H	2.830680000	-0.425218000	3.669999000
C	3.396021000	-2.436279000	1.886518000
H	2.606744000	-2.711934000	2.594471000
H	4.360995000	-2.730753000	2.318184000
H	3.241479000	-3.009840000	0.967246000
O	1.198473000	-1.354372000	0.755629000
O	0.823790000	1.182103000	-1.943928000
C	3.953278000	-1.980082000	-3.369853000
H	3.808910000	-2.332798000	-4.391067000
C	3.443654000	-0.735204000	-2.992036000
C	2.661954000	0.127182000	-3.943323000
H	2.992758000	-0.045173000	-4.977974000
H	2.851824000	1.185127000	-3.713723000
C	1.129307000	-0.100576000	-3.921792000

C	0.780596000	-1.474340000	-4.480806000
H	1.237247000	-2.280257000	-3.897358000
H	1.143736000	-1.548301000	-5.513725000
H	-0.303307000	-1.633384000	-4.487216000
C	0.470455000	0.986486000	-4.774647000
H	-0.620708000	0.875315000	-4.783729000
H	0.825178000	0.905498000	-5.809520000
H	0.715860000	1.986087000	-4.400255000
C	0.635908000	0.050984000	-2.484106000
O	0.085410000	-0.948965000	-1.931021000
O	1.944235000	0.771073000	0.833267000
C	4.534572000	-0.547772000	0.646762000
H	4.606910000	0.548656000	0.624396000
H	5.470955000	-0.926836000	1.081561000
C	4.358792000	-1.062705000	-0.754943000
C	4.860633000	-2.304100000	-1.155153000
H	5.424939000	-2.910225000	-0.446476000
C	4.659718000	-2.757620000	-2.455970000
H	5.064536000	-3.719788000	-2.762481000
C	3.662740000	-0.289549000	-1.686450000
H	3.292019000	0.694554000	-1.393001000
O	-2.400300000	0.011803000	-0.801777000
C	-4.962511000	1.413177000	-0.627403000
H	-5.081005000	0.322260000	-0.594912000
H	-5.886815000	1.825408000	-1.057299000
C	-4.756179000	1.935521000	0.767077000
C	-5.205428000	3.200577000	1.155107000
H	-5.749730000	3.819052000	0.441780000
C	-4.978592000	3.662412000	2.448612000
H	-5.343994000	4.643284000	2.744809000
C	-4.087752000	1.149934000	1.707789000
H	-3.747615000	0.154760000	1.420327000
O	-0.516663000	1.708200000	1.924967000
O	-1.265695000	-0.417690000	1.957266000
C	-4.297148000	2.870336000	3.368540000
H	-4.131822000	3.230508000	4.383741000
C	-3.838790000	1.601307000	3.005306000
C	-3.081310000	0.725662000	3.964252000
H	-3.400487000	0.924127000	4.997589000
H	-3.308685000	-0.327680000	3.753996000
C	-1.542171000	0.901799000	3.929904000
C	-1.143369000	2.273362000	4.462330000
H	-1.580711000	3.085428000	3.872064000
H	-1.489447000	2.375275000	5.498663000
H	-0.054183000	2.396395000	4.451613000
C	-0.908904000	-0.188083000	4.797527000
H	0.183917000	-0.097780000	4.808551000
H	-1.264761000	-0.087335000	5.830139000
H	-1.170694000	-1.187644000	4.436634000
C	-1.067634000	0.714696000	2.490753000
O	-1.611701000	2.123644000	-0.771945000

C	-2.503994000	1.255912000	-1.020453000
C	-3.820549000	1.744691000	-1.621164000
C	-4.073415000	0.981606000	-2.923615000
H	-4.111392000	-0.098821000	-2.752855000
H	-5.031287000	1.298957000	-3.353571000
H	-3.289255000	1.189917000	-3.661437000
C	-3.774506000	3.240467000	-1.909142000
H	-2.978945000	3.479390000	-2.623535000
H	-4.731245000	3.554074000	-2.345568000
H	-3.602060000	3.828130000	-1.001950000
Rh	0.195671000	1.495482000	0.001865000
H	1.711096000	3.556733000	-0.724457000
H	0.103774000	4.157769000	-0.291090000
O	3.198647000	3.010294000	-1.275782000
C	3.897189000	3.359978000	-2.255789000
C	3.522754000	4.318548000	-3.283962000
C	5.233507000	2.824493000	-2.406131000
C	6.092887000	3.215060000	-3.387136000
H	5.529033000	2.086474000	-1.662982000
H	7.093420000	2.800274000	-3.461160000
N	0.982074000	3.743810000	0.012558000
N	2.222189000	4.930037000	-3.315268000
O	2.043789000	5.903672000	-4.045423000
O	1.321387000	4.461397000	-2.616989000
C	1.446994000	4.016834000	1.382689000
C	1.773681000	5.291309000	0.772213000
H	0.637118000	3.981945000	2.110128000
H	2.265291000	3.342964000	1.640670000
H	0.952369000	6.003059000	0.694673000
C	3.035548000	5.692297000	0.227038000
C	4.238058000	5.040245000	0.557021000
C	3.054195000	6.773749000	-0.674932000
C	5.428779000	5.466217000	-0.005744000
C	4.245081000	7.179123000	-1.253004000
C	5.430291000	6.523880000	-0.917026000
H	4.235548000	4.205496000	1.253225000
H	2.119341000	7.270826000	-0.929025000
H	6.359517000	4.968874000	0.251699000
H	4.255717000	8.000594000	-1.963661000
H	6.366993000	6.841617000	-1.368375000
C	4.411784000	4.729154000	-4.270343000
C	5.679904000	4.187742000	-4.326446000
H	4.100603000	5.469654000	-4.998618000
N	6.581082000	4.613276000	-5.357926000
O	7.704756000	4.113300000	-5.387220000
O	6.199901000	5.457644000	-6.167023000

Cycle C: Rh-Alkene

22

Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -2372.80767740
Electronic and Zero-Point Energy = -2372.001657
Enthalpy = -2371.951761
Free Energy = -2372.079183

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -2373.41025444

Rh	-0.699766000	-1.080902000	0.202007000
C	1.942535000	-1.260802000	1.388611000
C	3.098842000	-1.938431000	2.123978000
C	3.366977000	-1.161246000	3.415172000
H	3.612049000	-0.114813000	3.208181000
H	4.210154000	-1.616522000	3.949049000
H	2.494371000	-1.189215000	4.079456000
C	2.767955000	-3.386626000	2.464058000
H	1.885254000	-3.447484000	3.110033000
H	3.614917000	-3.834743000	2.999059000
H	2.573220000	-3.984762000	1.568205000
O	0.926286000	-1.971606000	1.117811000
O	1.261519000	0.386912000	-1.763254000
C	3.778749000	-3.441679000	-2.733495000
H	3.632264000	-3.834267000	-3.739510000
C	3.501918000	-2.097102000	-2.472467000
C	2.966318000	-1.177308000	-3.534138000
H	3.321446000	-1.492031000	-4.526119000
H	3.346569000	-0.161722000	-3.363551000
C	1.420938000	-1.105561000	-3.615165000
C	0.842192000	-2.432344000	-4.090666000
H	1.070663000	-3.251967000	-3.400724000
H	1.262265000	-2.680200000	-5.073737000
H	-0.247791000	-2.368817000	-4.189983000
C	1.038241000	-0.001430000	-4.603899000
H	-0.051258000	0.082972000	-4.697345000
H	1.442130000	-0.241471000	-5.595150000
H	1.436861000	0.969391000	-4.293044000
C	0.881133000	-0.724590000	-2.236699000
O	0.101847000	-1.543121000	-1.662933000
O	2.087556000	-0.036498000	1.098483000
C	4.361228000	-1.862528000	1.229060000
H	4.666337000	-0.810471000	1.156515000
H	5.161949000	-2.394835000	1.762631000
C	4.185765000	-2.430395000	-0.152107000
C	4.456666000	-3.771024000	-0.439084000
H	4.839493000	-4.421272000	0.347278000
C	4.256707000	-4.270981000	-1.722759000
H	4.482445000	-5.312967000	-1.938944000
C	3.723486000	-1.610270000	-1.183070000

H	3.524428000	-0.559090000	-0.974067000
O	-2.232135000	-0.068219000	-0.750517000
C	-4.544275000	1.597199000	-0.940031000
H	-4.764079000	0.521993000	-0.899606000
H	-5.369695000	2.078013000	-1.484805000
C	-4.449937000	2.152458000	0.454961000
C	-4.864349000	3.453185000	0.754009000
H	-5.304216000	4.068987000	-0.030297000
C	-4.729689000	3.957411000	2.044209000
H	-5.067101000	4.966869000	2.269125000
C	-3.911662000	1.373463000	1.482188000
H	-3.605098000	0.350005000	1.264346000
O	-0.223336000	1.528923000	1.929354000
O	-1.334895000	-0.424530000	2.084766000
C	-4.167800000	3.174801000	3.048368000
H	-4.063703000	3.572420000	4.057724000
C	-3.744738000	1.870887000	2.776371000
C	-3.099744000	1.017147000	3.833381000
H	-3.468743000	1.303621000	4.828879000
H	-3.373834000	-0.034526000	3.677443000
C	-1.554535000	1.111017000	3.885182000
C	-1.109819000	2.514016000	4.278940000
H	-1.443721000	3.266626000	3.557358000
H	-1.532893000	2.766413000	5.259647000
H	-0.018788000	2.574495000	4.351768000
C	-1.038008000	0.103969000	4.917076000
H	0.056745000	0.133593000	4.980474000
H	-1.438383000	0.354211000	5.907176000
H	-1.344070000	-0.917106000	4.667252000
C	-0.989180000	0.715904000	2.521595000
O	-1.058554000	1.856207000	-0.848906000
C	-2.086432000	1.152383000	-1.069367000
C	-3.267250000	1.794164000	-1.793928000
C	-3.445026000	1.056176000	-3.124796000
H	-3.620635000	-0.014235000	-2.966875000
H	-4.302919000	1.474707000	-3.665815000
H	-2.557617000	1.176582000	-3.758739000
C	-3.014828000	3.272685000	-2.059952000
H	-2.131571000	3.412999000	-2.691982000
H	-3.880563000	3.700063000	-2.581848000
H	-2.861048000	3.835361000	-1.133291000
Rh	0.567639000	0.987417000	0.097164000
C	-1.869367000	-3.247151000	-0.343291000
H	-0.977271000	-3.792696000	-0.657456000
C	-1.987111000	-2.922142000	0.974815000
H	-1.256689000	-3.274164000	1.697863000
H	-2.878962000	-2.446089000	1.378928000
C	-2.865456000	-3.032220000	-1.390886000
C	-2.560821000	-3.442254000	-2.694466000
C	-4.117524000	-2.449890000	-1.144815000
C	-3.476033000	-3.277896000	-3.727825000

H	-1.591820000	-3.899980000	-2.889713000
C	-5.035703000	-2.294684000	-2.173417000
H	-4.374063000	-2.111833000	-0.142276000
C	-4.718717000	-2.706718000	-3.468608000
H	-3.221110000	-3.603150000	-4.733783000
H	-6.004729000	-1.845255000	-1.967174000
H	-5.441146000	-2.582111000	-4.271664000

TS4

Lowest Frequency Vibration = -367.8429 cm**-1
Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -3144.11767411
Electronic and Zero-Point Energy = -3143.182064
Enthalpy = -3143.119819
Free Energy = -3143.277519

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -3144.94737130

Rh	-0.473235000	-1.176742000	0.007509000
C	2.202266000	-1.152054000	1.134468000
C	3.450415000	-1.755827000	1.783416000
C	3.674859000	-1.063157000	3.129576000
H	3.789398000	0.018447000	3.007026000
H	4.583421000	-1.457795000	3.601235000
H	2.835506000	-1.248351000	3.811401000
C	3.293881000	-3.255018000	2.007320000
H	2.442215000	-3.467636000	2.663210000
H	4.200666000	-3.647674000	2.485359000
H	3.140186000	-3.796026000	1.068148000
O	1.260522000	-1.950000000	0.837089000
O	1.249774000	0.637995000	-1.878629000
C	4.169405000	-2.799265000	-3.191798000
H	4.043822000	-3.129661000	-4.222805000
C	3.736513000	-1.523367000	-2.821241000
C	3.064449000	-0.599101000	-3.798345000
H	3.421618000	-0.799912000	-4.819001000
H	3.332368000	0.438925000	-3.561787000
C	1.519305000	-0.699483000	-3.833735000
C	1.079780000	-2.048649000	-4.389278000
H	1.433261000	-2.881811000	-3.772337000
H	1.482332000	-2.173930000	-5.402787000
H	-0.013592000	-2.111452000	-4.443818000
C	0.981779000	0.416866000	-4.732088000
H	-0.113059000	0.380928000	-4.790676000
H	1.376057000	0.294983000	-5.748672000

H	1.276828000	1.403571000	-4.361419000
C	0.985179000	-0.476944000	-2.416563000
O	0.327705000	-1.424490000	-1.889846000
O	2.210364000	0.097959000	0.940634000
C	4.668118000	-1.465575000	0.871305000
H	4.846788000	-0.382479000	0.875899000
H	5.541566000	-1.939134000	1.343056000
C	4.520379000	-1.943336000	-0.546766000
C	4.946609000	-3.213791000	-0.943205000
H	5.428547000	-3.868544000	-0.217288000
C	4.773680000	-3.636695000	-2.258204000
H	5.119792000	-4.623076000	-2.559637000
C	3.930969000	-1.112052000	-1.501087000
H	3.605966000	-0.114520000	-1.205257000
O	-2.128549000	-0.252024000	-0.847424000
C	-4.622335000	1.139540000	-0.829833000
H	-4.708072000	0.045704000	-0.878870000
H	-5.515866000	1.560557000	-1.313895000
C	-4.555366000	1.581102000	0.606057000
C	-5.105885000	2.795485000	1.025022000
H	-5.631438000	3.422078000	0.304486000
C	-4.996989000	3.199245000	2.352506000
H	-5.439738000	4.140768000	2.670548000
C	-3.908178000	0.782973000	1.552239000
H	-3.489962000	-0.174113000	1.239057000
O	-0.250488000	1.323849000	1.949829000
O	-1.149688000	-0.746219000	1.942778000
C	-4.326593000	2.401904000	3.275502000
H	-4.242787000	2.720301000	4.314496000
C	-3.767014000	1.182985000	2.882910000
C	-3.003216000	0.320138000	3.849142000
H	-3.374877000	0.476141000	4.872510000
H	-3.163869000	-0.738543000	3.604552000
C	-1.476985000	0.581237000	3.879768000
C	-1.178153000	1.980353000	4.402910000
H	-1.611482000	2.756237000	3.763354000
H	-1.598607000	2.090610000	5.410827000
H	-0.098535000	2.154924000	4.461683000
C	-0.825709000	-0.457345000	4.797826000
H	0.260921000	-0.313308000	4.844344000
H	-1.222196000	-0.352880000	5.815448000
H	-1.026117000	-1.476714000	4.449935000
C	-0.909678000	0.381931000	2.472726000
O	-1.188667000	1.801921000	-0.788233000
C	-2.131018000	1.000007000	-1.051349000
C	-3.404330000	1.559300000	-1.688869000
C	-3.548217000	0.923422000	-3.075079000
H	-3.619243000	-0.168483000	-3.006335000
H	-4.456103000	1.301567000	-3.561993000
H	-2.694075000	1.180664000	-3.714188000
C	-3.334091000	3.074575000	-1.828306000

H	-2.495991000	3.371294000	-2.467880000
H	-4.261481000	3.442071000	-2.286535000
H	-3.210966000	3.569704000	-0.859413000
Rh	0.560746000	1.051408000	0.052074000
C	-1.323181000	-3.263326000	-0.302029000
H	-0.412653000	-3.748884000	-0.662950000
C	-1.575543000	-3.385221000	1.079475000
H	-0.725681000	-3.501399000	1.749536000
H	-2.418324000	-2.858794000	1.530112000
C	-2.403761000	-3.186927000	-1.293028000
C	-2.107599000	-3.428036000	-2.642701000
C	-3.726277000	-2.856574000	-0.960296000
C	-3.088681000	-3.338754000	-3.622848000
H	-1.082450000	-3.676157000	-2.915712000
C	-4.710138000	-2.775954000	-1.938635000
H	-3.993818000	-2.644056000	0.074716000
C	-4.399171000	-3.014851000	-3.276305000
H	-2.829309000	-3.529910000	-4.662624000
H	-5.729190000	-2.520801000	-1.653349000
H	-5.171220000	-2.952079000	-4.039616000
N	-2.368570000	-5.099627000	1.518866000
H	-1.757460000	-5.900857000	1.342191000
H	-3.251669000	-5.169224000	1.002760000
O	-2.665706000	-5.033353000	2.893318000
C	-3.403539000	-6.102731000	3.342013000
C	-2.729194000	-7.135525000	3.982018000
C	-4.806302000	-6.134764000	3.270870000
C	-3.429512000	-8.200645000	4.528214000
H	-1.647003000	-7.079053000	4.051088000
C	-5.522162000	-7.180201000	3.830240000
C	-4.815283000	-8.202914000	4.437841000
H	-2.917956000	-9.018922000	5.023318000
H	-6.605793000	-7.194426000	3.786897000
N	-5.574785000	-5.067885000	2.631966000
O	-6.720517000	-4.901864000	3.003306000
O	-5.028208000	-4.411387000	1.753745000
N	-5.566374000	-9.323916000	5.015247000
O	-6.781821000	-9.297396000	4.920348000
O	-4.926379000	-10.211101000	5.553578000

23

Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -3144.13050787
Electronic and Zero-Point Energy = -3143.192639
Enthalpy = -3143.130454
Free Energy = -3143.288036

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -3144.95924142

Rh	-0.640296000	-1.083474000	-0.037061000
C	1.962383000	-1.212662000	1.273953000
C	3.105521000	-1.890246000	2.035861000
C	3.314914000	-1.142808000	3.354737000
H	3.547441000	-0.087430000	3.181122000
H	4.146261000	-1.595227000	3.909861000
H	2.418920000	-1.200593000	3.985631000
C	2.792980000	-3.352552000	2.329912000
H	1.893930000	-3.444290000	2.950300000
H	3.631681000	-3.802135000	2.877375000
H	2.631985000	-3.930462000	1.413987000
O	0.973666000	-1.942909000	0.953880000
O	1.346845000	0.468879000	-1.894211000
C	4.032104000	-3.273032000	-2.826250000
H	3.943554000	-3.646295000	-3.846457000
C	3.691679000	-1.946468000	-2.547628000
C	3.166988000	-1.023536000	-3.612596000
H	3.572909000	-1.307955000	-4.594587000
H	3.506287000	0.000213000	-3.407692000
C	1.624711000	-0.998620000	-3.750731000
C	1.111054000	-2.338368000	-4.263980000
H	1.366885000	-3.161423000	-3.588994000
H	1.555864000	-2.547888000	-5.245645000
H	0.021325000	-2.323259000	-4.378485000
C	1.245165000	0.102765000	-4.742943000
H	0.157302000	0.152490000	-4.876800000
H	1.694131000	-0.108558000	-5.721638000
H	1.596915000	1.082236000	-4.403653000
C	1.019944000	-0.648657000	-2.387003000
O	0.248555000	-1.509425000	-1.862321000
O	2.099521000	0.016660000	1.018918000
C	4.397659000	-1.768374000	1.190999000
H	4.678108000	-0.707729000	1.151326000
H	5.192808000	-2.292407000	1.741492000
C	4.291126000	-2.309799000	-0.207956000
C	4.624140000	-3.632366000	-0.512828000
H	4.998447000	-4.286218000	0.274846000
C	4.497419000	-4.108686000	-1.814766000
H	4.771583000	-5.136181000	-2.044505000
C	3.838732000	-1.483395000	-1.238698000
H	3.584630000	-0.447773000	-1.012865000
O	-2.132626000	-0.047698000	-1.073890000
C	-4.481094000	1.618119000	-1.267241000
H	-4.711061000	0.543380000	-1.256497000
H	-5.287448000	2.118433000	-1.824194000
C	-4.432706000	2.132778000	0.144930000
C	-4.842618000	3.428173000	0.472394000
H	-5.237883000	4.078977000	-0.307662000

C	-4.763347000	3.881649000	1.786167000
H	-5.096417000	4.887582000	2.033143000
C	-3.953117000	1.308034000	1.165223000
H	-3.647399000	0.291311000	0.917949000
O	-0.329741000	1.447922000	1.822190000
O	-1.420527000	-0.533477000	1.819801000
C	-4.266750000	3.051013000	2.786802000
H	-4.211711000	3.406997000	3.815592000
C	-3.849494000	1.751618000	2.485399000
C	-3.281792000	0.840917000	3.539369000
H	-3.706634000	1.088445000	4.523451000
H	-3.563610000	-0.197441000	3.318141000
C	-1.741180000	0.898371000	3.684630000
C	-1.300753000	2.261070000	4.204060000
H	-1.585846000	3.069132000	3.522625000
H	-1.770571000	2.450419000	5.178047000
H	-0.213962000	2.298548000	4.335497000
C	-1.306005000	-0.187598000	4.672249000
H	-0.215991000	-0.189193000	4.799280000
H	-1.758455000	-0.000245000	5.654207000
H	-1.615640000	-1.181938000	4.332041000
C	-1.104671000	0.589007000	2.326358000
O	-1.031235000	1.926028000	-1.005103000
C	-2.009998000	1.189820000	-1.319831000
C	-3.178558000	1.826719000	-2.079203000
C	-3.325133000	1.099409000	-3.418665000
H	-3.512003000	0.029808000	-3.268955000
H	-4.164883000	1.525522000	-3.982403000
H	-2.419779000	1.213994000	-4.028475000
C	-2.933651000	3.309199000	-2.330347000
H	-2.029009000	3.462697000	-2.928758000
H	-3.784237000	3.732029000	-2.880917000
H	-2.818397000	3.868278000	-1.395969000
Rh	0.596244000	1.071783000	-0.018173000
C	-1.673187000	-2.980301000	-0.057829000
H	-1.046519000	-3.561501000	-0.748124000
C	-1.554343000	-3.479623000	1.344961000
H	-0.515162000	-3.612813000	1.657990000
H	-2.084727000	-2.871714000	2.086460000
C	-3.034040000	-2.775737000	-0.584807000
C	-3.281233000	-2.945590000	-1.957254000
C	-4.100385000	-2.344603000	0.221118000
C	-4.533420000	-2.692707000	-2.500663000
H	-2.460129000	-3.267157000	-2.599333000
C	-5.356783000	-2.096133000	-0.321621000
H	-3.940501000	-2.169253000	1.285574000
C	-5.582903000	-2.267637000	-1.685106000
H	-4.695868000	-2.831903000	-3.567774000
H	-6.162341000	-1.756604000	0.327109000
H	-6.565613000	-2.074526000	-2.108706000
N	-2.194969000	-4.854677000	1.447700000

H	-1.731453000	-5.521208000	0.815960000
H	-3.207082000	-4.782107000	1.235968000
O	-2.086440000	-5.322501000	2.783337000
C	-2.641898000	-6.573996000	2.967889000
C	-1.765472000	-7.645638000	3.062742000
C	-4.017119000	-6.776269000	3.173181000
C	-2.244072000	-8.918555000	3.340734000
H	-0.704363000	-7.460055000	2.926826000
C	-4.506376000	-8.037837000	3.466420000
C	-3.607387000	-9.088061000	3.532221000
H	-1.575879000	-9.769821000	3.411871000
H	-5.566103000	-8.193838000	3.637142000
N	-4.986385000	-5.684008000	3.116024000
O	-6.028176000	-5.824291000	3.721215000
O	-4.699099000	-4.689863000	2.454967000
N	-4.124728000	-10.431823000	3.828699000
O	-5.327867000	-10.549312000	3.983225000
O	-3.315456000	-11.339795000	3.900546000

TS5
Lowest Frequency Vibration = -569.7282 cm**-1
Temperature = 298.150 K
Pressure = 1.00000 Atm

6-31G(d,p)[LANL2DZ]
Electronic Energy = -3144.11863196
Electronic and Zero-Point Energy = -3143.184118
Enthalpy = -3143.121738
Free Energy = -3143.279774

6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -3144.94771598

Rh	-0.713753000	-1.058055000	-0.028859000
C	1.878288000	-1.271328000	1.287586000
C	2.993923000	-1.980871000	2.056983000
C	3.221833000	-1.233130000	3.372774000
H	3.488966000	-0.186646000	3.195082000
H	4.036639000	-1.709754000	3.931772000
H	2.322912000	-1.259935000	4.001163000
C	2.628794000	-3.430139000	2.355393000
H	1.724260000	-3.488115000	2.971791000
H	3.448909000	-3.905310000	2.908891000
H	2.452744000	-4.006132000	1.441000000
O	0.865090000	-1.965319000	0.964582000
O	1.327147000	0.417632000	-1.878166000
C	3.880058000	-3.411543000	-2.795671000
H	3.779440000	-3.785041000	-3.814583000
C	3.590314000	-2.071885000	-2.522693000
C	3.101241000	-1.134015000	-3.591392000

H	3.499066000	-1.434279000	-4.571782000
H	3.474627000	-0.121854000	-3.388258000
C	1.560870000	-1.057928000	-3.735114000
C	1.003123000	-2.380257000	-4.247465000
H	1.227180000	-3.209990000	-3.569380000
H	1.445675000	-2.606631000	-5.226163000
H	-0.084664000	-2.327356000	-4.368134000
C	1.221053000	0.055480000	-4.728602000
H	0.136260000	0.140317000	-4.867756000
H	1.667472000	-0.172129000	-5.704601000
H	1.603693000	1.023223000	-4.389189000
C	0.964149000	-0.688950000	-2.374920000
O	0.160868000	-1.518626000	-1.849142000
O	2.052755000	-0.046938000	1.024896000
C	4.292880000	-1.906783000	1.216509000
H	4.612229000	-0.857249000	1.175057000
H	5.065520000	-2.457419000	1.772675000
C	4.170981000	-2.448910000	-0.180768000
C	4.453419000	-3.784441000	-0.479730000
H	4.800513000	-4.449160000	0.311198000
C	4.311363000	-4.260396000	-1.780177000
H	4.546438000	-5.298440000	-2.005503000
C	3.753327000	-1.609433000	-1.215545000
H	3.542144000	-0.563034000	-0.994758000
O	-2.168008000	0.023628000	-1.072199000
C	-4.442480000	1.795524000	-1.280177000
H	-4.722111000	0.732977000	-1.267944000
H	-5.223142000	2.332146000	-1.839529000
C	-4.369167000	2.311146000	0.130383000
C	-4.707689000	3.628149000	0.452681000
H	-5.065632000	4.296742000	-0.330254000
C	-4.605473000	4.081312000	1.764959000
H	-4.883298000	5.104807000	2.007753000
C	-3.937509000	1.465142000	1.154567000
H	-3.689604000	0.431430000	0.912760000
O	-0.322733000	1.448662000	1.816315000
O	-1.483410000	-0.489145000	1.815712000
C	-4.156028000	3.228652000	2.769366000
H	-4.082589000	3.585039000	3.796787000
C	-3.810752000	1.907280000	2.473057000
C	-3.293468000	0.969931000	3.529375000
H	-3.709096000	1.236907000	4.512072000
H	-3.624485000	-0.053536000	3.306375000
C	-1.752135000	0.953646000	3.682155000
C	-1.247908000	2.291804000	4.207314000
H	-1.494160000	3.115657000	3.529744000
H	-1.709357000	2.497929000	5.181666000
H	-0.160746000	2.277020000	4.340230000
C	-1.373047000	-0.156612000	4.666092000
H	-0.285502000	-0.207663000	4.801622000
H	-1.824451000	0.047213000	5.645018000

H	-1.724912000	-1.134273000	4.318930000
C	-1.129115000	0.620185000	2.325765000
O	-0.989980000	1.949417000	-1.005237000
C	-1.998123000	1.253598000	-1.325493000
C	-3.131348000	1.938918000	-2.092369000
C	-3.309033000	1.210177000	-3.427173000
H	-3.538821000	0.149920000	-3.271436000
H	-4.132472000	1.667206000	-3.990410000
H	-2.401748000	1.285783000	-4.039678000
C	-2.815771000	3.406657000	-2.351363000
H	-1.903613000	3.514010000	-2.948321000
H	-3.644303000	3.864200000	-2.907401000
H	-2.677864000	3.965880000	-1.420193000
Rh	0.581231000	1.027596000	-0.014968000
C	-1.859741000	-2.979270000	-0.082851000
H	-1.216592000	-3.533991000	-0.776229000
C	-1.716631000	-3.429189000	1.347175000
H	-0.674543000	-3.502651000	1.665266000
H	-2.287816000	-2.831930000	2.064135000
C	-3.187012000	-2.673756000	-0.622137000
C	-3.415108000	-2.812783000	-2.001076000
C	-4.232169000	-2.179080000	0.174880000
C	-4.638915000	-2.474698000	-2.561791000
H	-2.605943000	-3.183087000	-2.631195000
C	-5.459170000	-1.847632000	-0.386150000
H	-4.081874000	-2.038423000	1.245386000
C	-5.670699000	-1.993105000	-1.756081000
H	-4.792989000	-2.591635000	-3.632373000
H	-6.253625000	-1.463820000	0.250838000
H	-6.631991000	-1.733368000	-2.192742000
N	-2.293808000	-4.762865000	1.278542000
H	-1.733784000	-5.441591000	0.756961000
H	-3.292999000	-4.772788000	1.026379000
O	-2.454580000	-5.511119000	2.827005000
C	-2.929629000	-6.744391000	2.735336000
C	-2.037344000	-7.823712000	2.874265000
C	-4.308534000	-7.051057000	2.583660000
C	-2.481342000	-9.130394000	2.888347000
H	-0.983985000	-7.587169000	2.992202000
C	-4.770082000	-8.355680000	2.615082000
C	-3.847002000	-9.377502000	2.755135000
H	-1.792565000	-9.961131000	2.998717000
H	-5.829244000	-8.570384000	2.522948000
N	-5.313018000	-6.010121000	2.421780000
O	-6.438324000	-6.239757000	2.824878000
O	-4.988693000	-4.958390000	1.873407000
N	-4.327939000	-10.755987000	2.766916000
O	-5.529114000	-10.941661000	2.642877000
O	-3.498880000	-11.642985000	2.900912000

Concerted TS

Lowest Frequency Vibration = -654.4925 cm**-1
Temperature = 298.150 K
Pressure = 1.00000 Atm

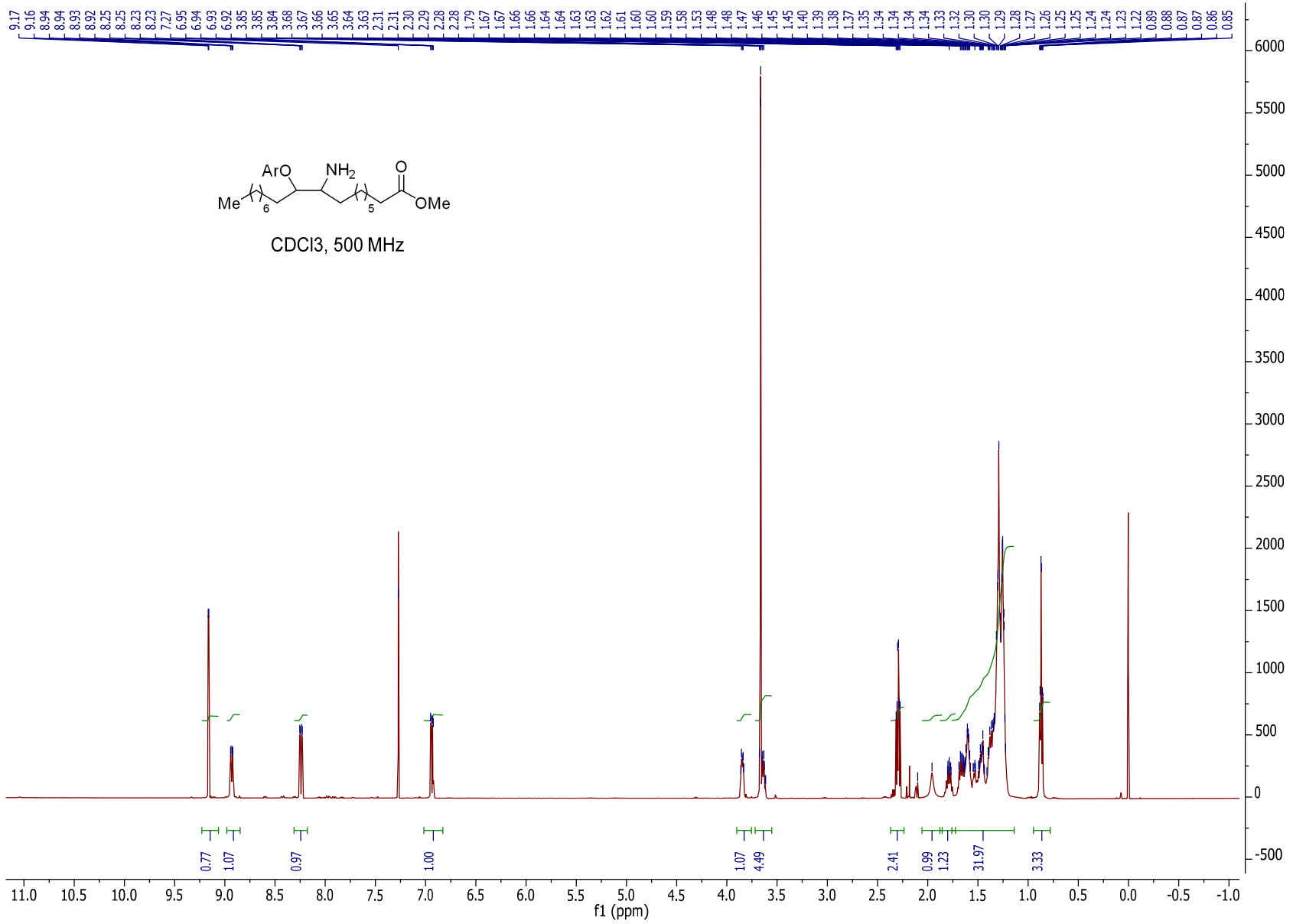
6-31G(d,p)[LANL2DZ]
Electronic Energy = -3144.10604316
Electronic and Zero-Point Energy = -3143.173210
Enthalpy = -3143.110271
Free Energy = -3143.267887

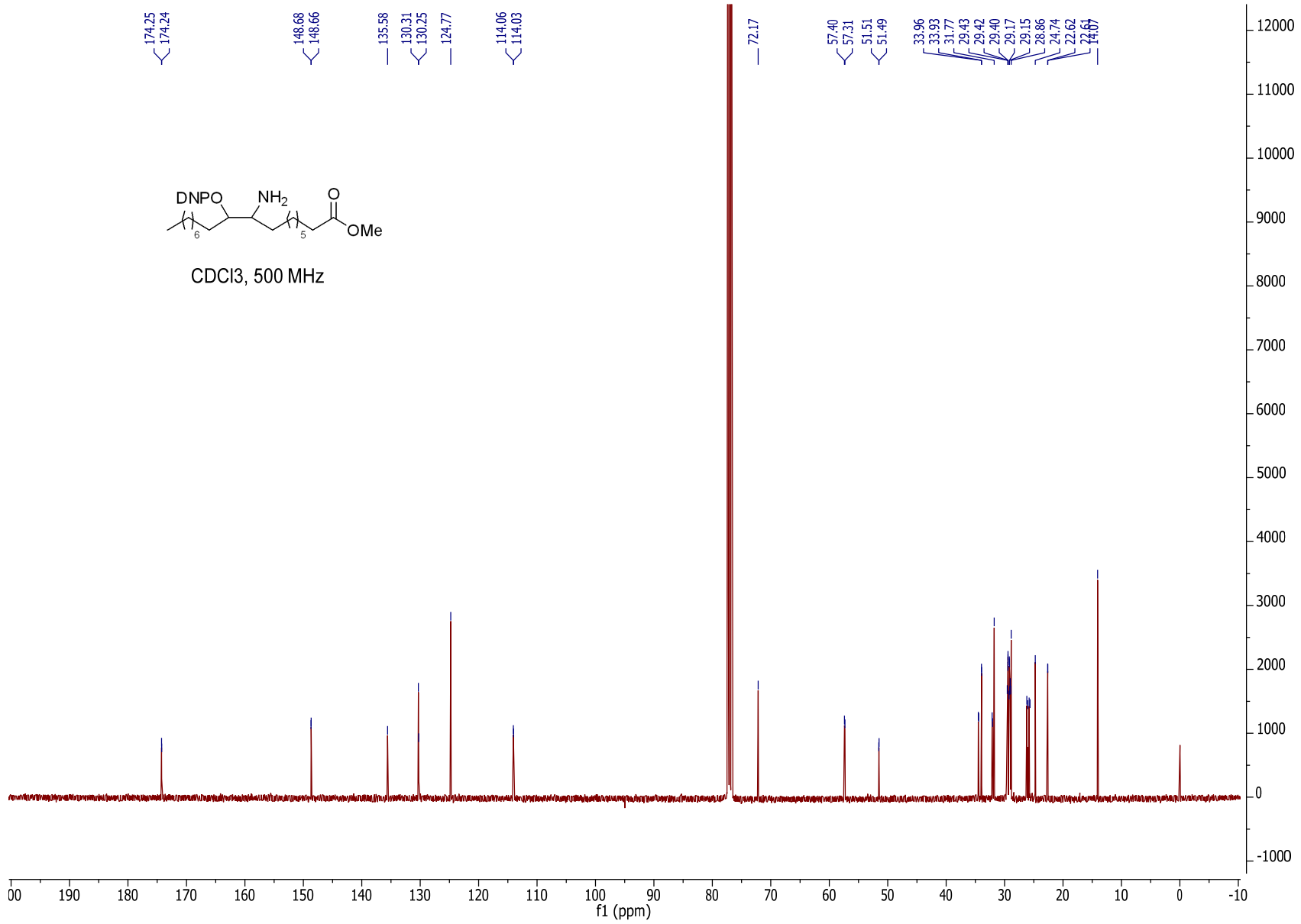
6-311++G(2d,2p)[LANL2TZ(f)]
Electronic Energy = -3144.93970009

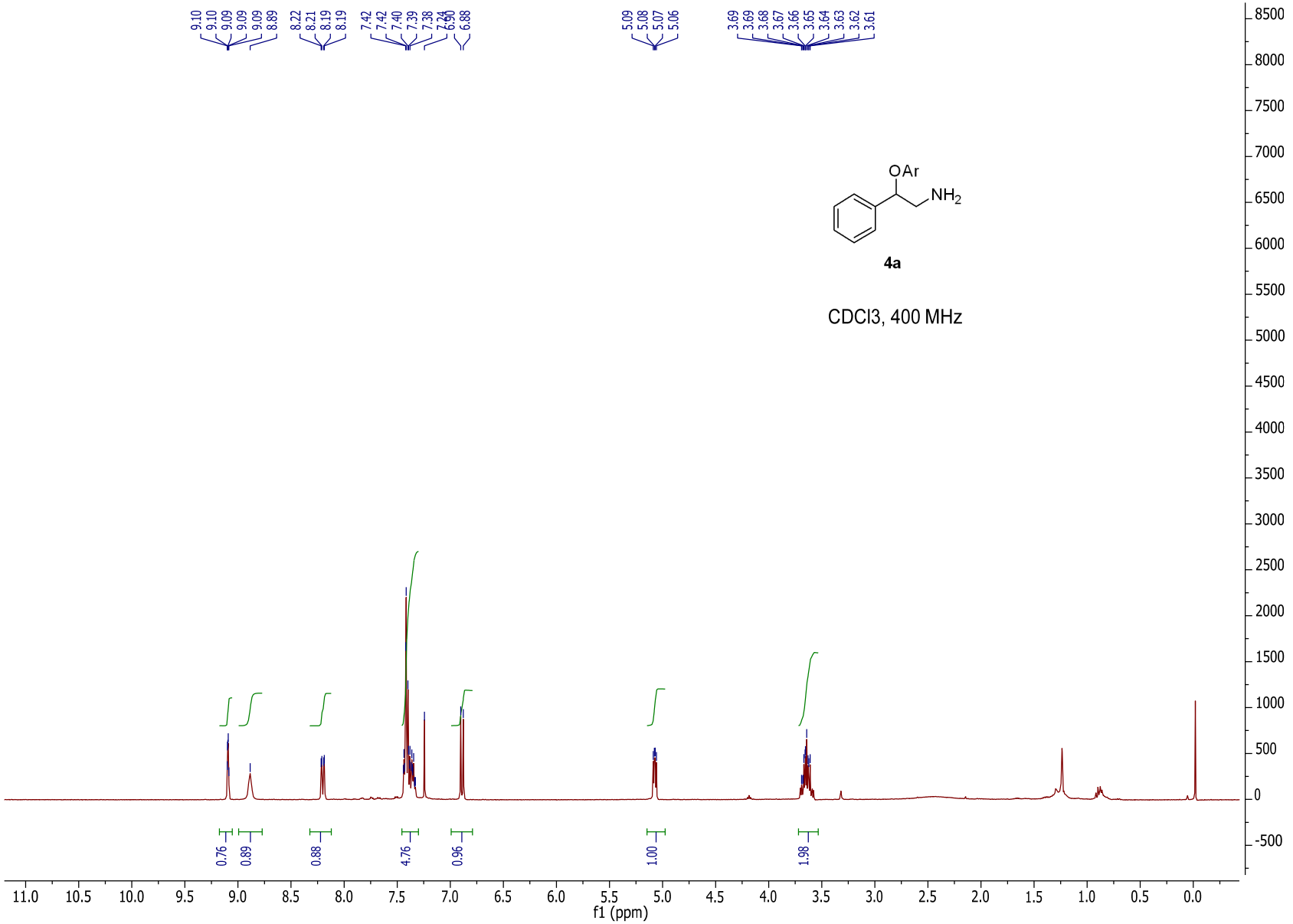
Rh	-2.490089000	-2.700380000	-2.053089000
C	0.002599000	-3.214438000	-3.479413000
C	1.383610000	-3.832385000	-3.683630000
C	2.397507000	-2.703895000	-3.884809000
H	2.133251000	-2.076623000	-4.741801000
H	3.391052000	-3.133286000	-4.062199000
H	2.460938000	-2.067445000	-2.994002000
C	1.792082000	-4.675455000	-2.481443000
H	1.834472000	-4.067017000	-1.571157000
H	2.789681000	-5.096791000	-2.658080000
H	1.096509000	-5.501447000	-2.302875000
O	-0.641326000	-3.549652000	-2.439530000
O	-3.262356000	-3.121440000	-5.031591000
C	-1.853308000	-7.577513000	-5.042471000
H	-2.664532000	-8.304701000	-5.069168000
C	-2.065911000	-6.289810000	-5.541655000
C	-3.400508000	-5.856137000	-6.080312000
H	-3.927917000	-6.709823000	-6.529734000
H	-3.249344000	-5.116011000	-6.876946000
C	-4.360073000	-5.242323000	-5.029545000
C	-4.823281000	-6.300096000	-4.034731000
H	-3.987117000	-6.736654000	-3.478576000
H	-5.337575000	-7.104990000	-4.574690000
H	-5.525543000	-5.872647000	-3.309408000
C	-5.573623000	-4.664565000	-5.761288000
H	-6.289716000	-4.228379000	-5.054769000
H	-6.086546000	-5.466448000	-6.306215000
H	-5.277971000	-3.892622000	-6.478578000
C	-3.630228000	-4.103591000	-4.319966000
O	-3.432839000	-4.224236000	-3.071692000
O	-0.411818000	-2.416233000	-4.371787000
C	1.342496000	-4.694353000	-4.971139000
H	1.235220000	-4.019324000	-5.830306000
H	2.326418000	-5.176825000	-5.060867000
C	0.247866000	-5.724151000	-5.003758000
C	0.435739000	-7.018259000	-4.511466000
H	1.411690000	-7.308857000	-4.123351000

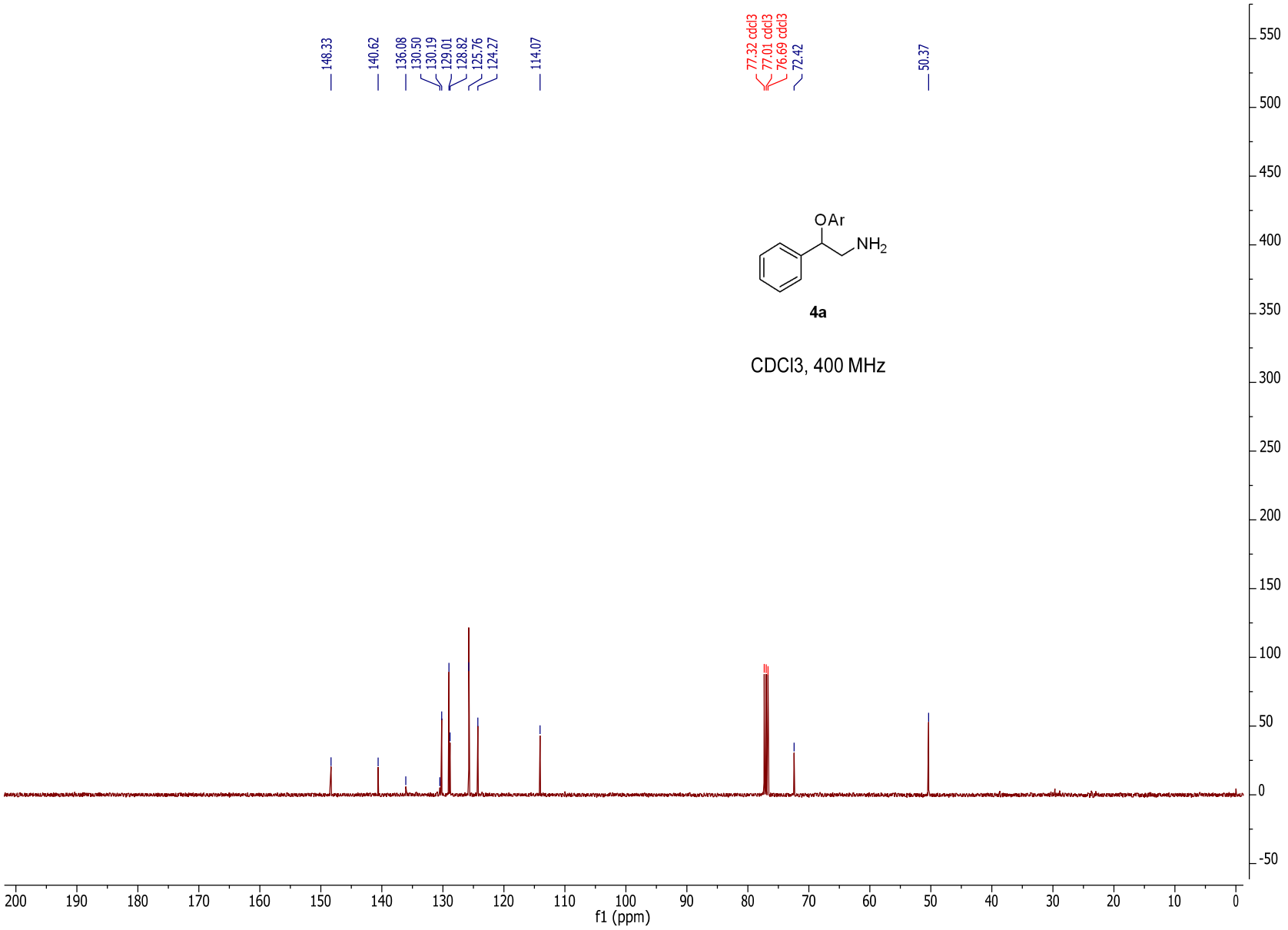
C	-0.608665000	-7.938469000	-4.534022000
H	-0.448609000	-8.947741000	-4.161135000
C	-1.002546000	-5.385545000	-5.523834000
H	-1.153473000	-4.384470000	-5.928483000
O	-4.340484000	-1.753747000	-1.879182000
C	-6.115229000	0.411807000	-1.185718000
H	-6.024487000	-0.339694000	-0.389883000
H	-7.104660000	0.878728000	-1.076615000
C	-5.032901000	1.444562000	-1.034880000
C	-5.242857000	2.782266000	-1.379601000
H	-6.224218000	3.096693000	-1.734186000
C	-4.214075000	3.711640000	-1.256771000
H	-4.391617000	4.753190000	-1.515486000
C	-3.774721000	1.070362000	-0.557748000
H	-3.606674000	0.032408000	-0.268505000
O	-1.341632000	0.003933000	-3.090754000
O	-1.495560000	-1.125188000	-1.145118000
C	-2.961176000	3.315727000	-0.798121000
H	-2.159386000	4.047000000	-0.698417000
C	-2.724618000	1.983974000	-0.447195000
C	-1.373424000	1.519062000	0.020966000
H	-0.841838000	2.339127000	0.524756000
H	-1.495630000	0.713634000	0.757161000
C	-0.439597000	1.007643000	-1.104635000
C	-0.065759000	2.138952000	-2.054175000
H	-0.944596000	2.570790000	-2.543504000
H	0.438262000	2.933008000	-1.488884000
H	0.618720000	1.787821000	-2.833767000
C	0.829240000	0.437321000	-0.464407000
H	1.517677000	0.055071000	-1.227811000
H	1.347686000	1.230420000	0.087981000
H	0.596746000	-0.374552000	0.232102000
C	-1.147400000	-0.123408000	-1.846884000
O	-4.102656000	-0.635692000	-3.818797000
C	-4.743475000	-0.949193000	-2.773134000
C	-6.118656000	-0.325801000	-2.547939000
C	-7.144680000	-1.461275000	-2.485131000
H	-6.909820000	-2.168655000	-1.681430000
H	-8.141648000	-1.043004000	-2.299419000
H	-7.182219000	-2.008615000	-3.434713000
C	-6.479915000	0.629743000	-3.678347000
H	-6.506926000	0.108460000	-4.641121000
H	-7.474737000	1.052703000	-3.489870000
H	-5.765767000	1.455765000	-3.759472000
Rh	-2.269721000	-1.518862000	-4.143148000
H	-3.348449000	-5.427690000	1.461010000
H	-2.567911000	-4.307951000	2.335908000
O	-2.861217000	-6.070719000	3.411545000
C	-4.147350000	-6.195532000	3.427749000
C	-5.095034000	-5.129309000	3.618051000
C	-4.710565000	-7.486303000	3.212825000

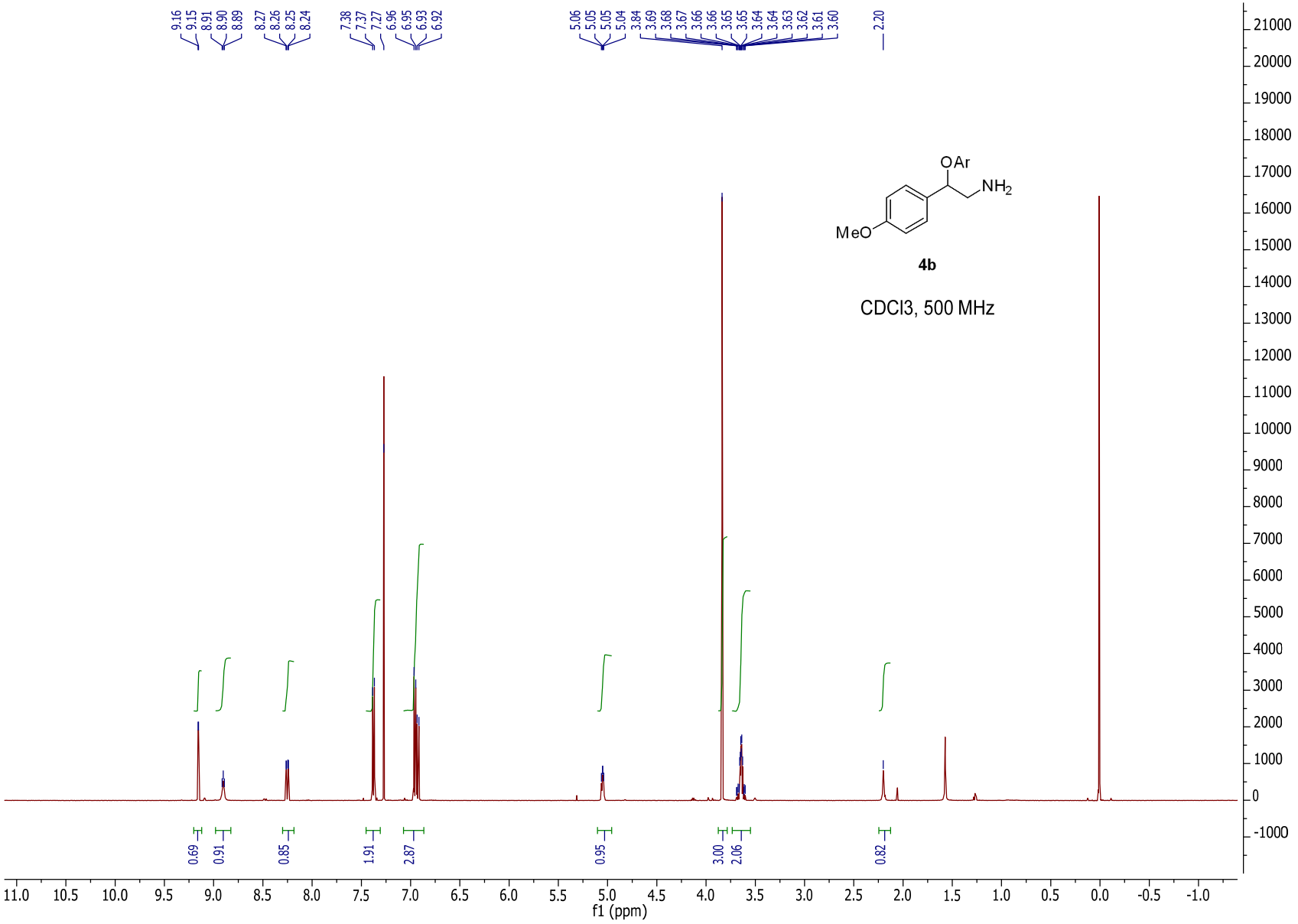
C	-6.466018000	-5.352379000	3.564230000
C	-6.063123000	-7.709042000	3.151162000
H	-4.003031000	-8.298656000	3.073430000
C	-6.935349000	-6.624015000	3.307895000
H	-7.157187000	-4.530358000	3.712337000
H	-6.466052000	-8.698325000	2.959820000
N	-2.416701000	-5.156555000	1.779475000
N	-4.698988000	-3.765868000	3.928032000
O	-5.547889000	-3.010440000	4.380951000
O	-3.537827000	-3.410789000	3.727784000
N	-8.367415000	-6.830903000	3.191386000
O	-8.766310000	-7.977043000	3.032809000
O	-9.100194000	-5.851444000	3.251642000
C	-2.148783000	-4.263324000	-0.048347000
C	-3.175411000	-3.373647000	0.258700000
H	-1.114770000	-3.948693000	0.045522000
H	-2.320734000	-5.179119000	-0.609540000
H	-2.882819000	-2.438737000	0.744416000
C	-4.598459000	-3.666061000	0.275480000
C	-5.145438000	-4.822879000	-0.307134000
C	-5.446301000	-2.788574000	0.969252000
C	-6.497819000	-5.100371000	-0.171418000
C	-6.800999000	-3.066436000	1.097580000
C	-7.327437000	-4.229070000	0.537448000
H	-4.511324000	-5.496330000	-0.881918000
H	-5.026172000	-1.890586000	1.423173000
H	-6.909965000	-6.002651000	-0.616461000
H	-7.443962000	-2.382794000	1.646783000
H	-8.383678000	-4.459499000	0.655339000

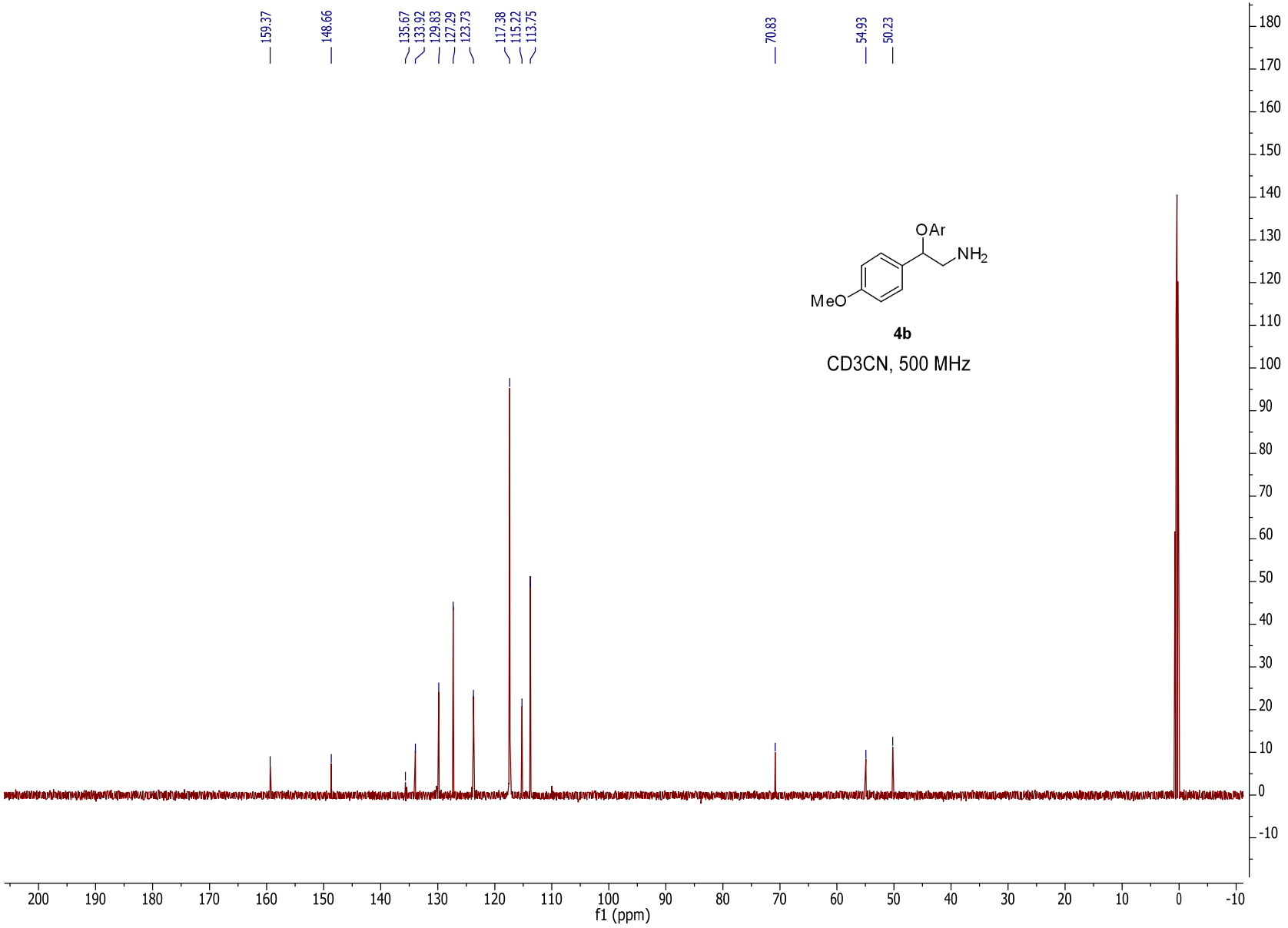

ArO
NH2
O
Me
6
5
OMe
CDCl3, 500 MHz
f1 (ppm)

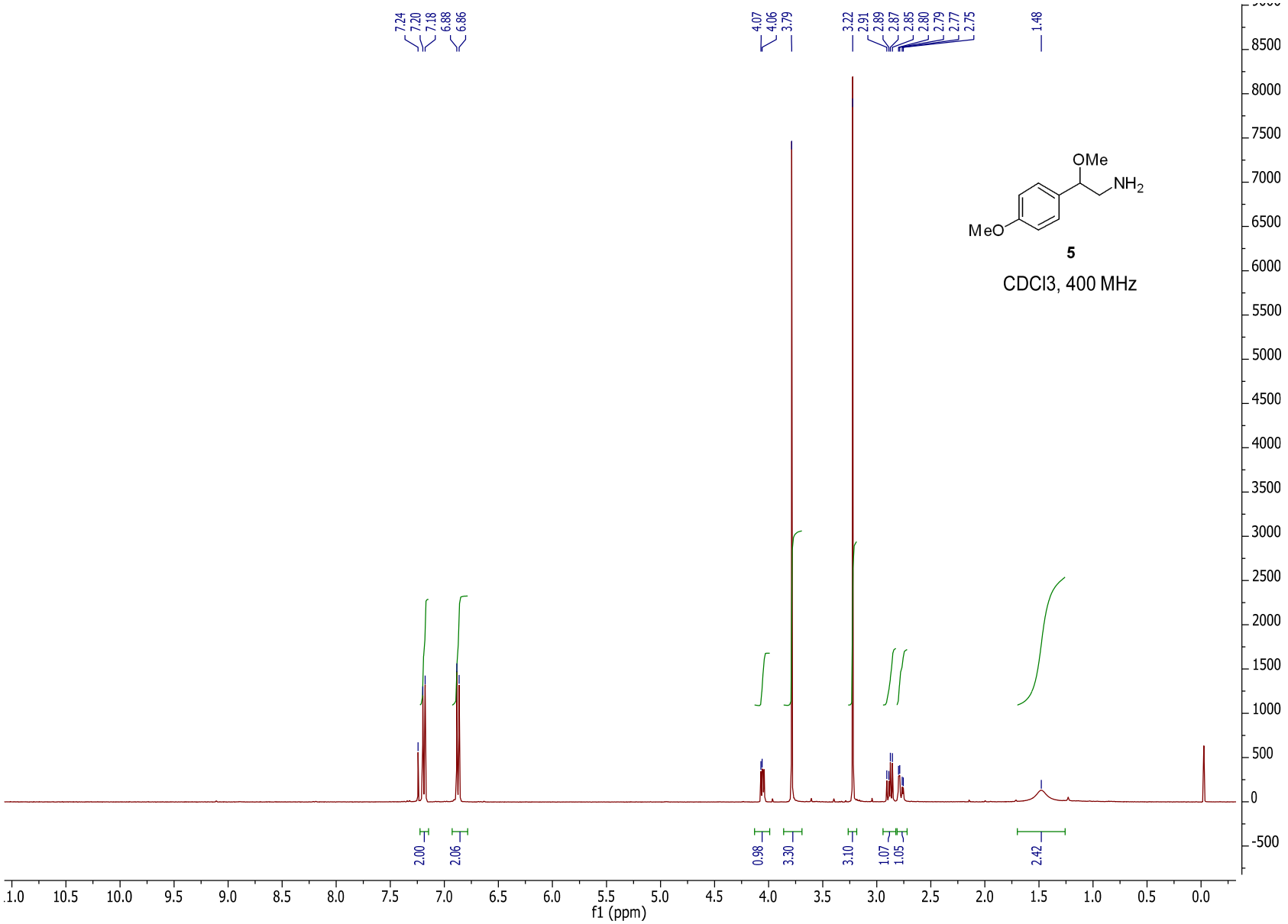

174.25
174.24
148.68
148.66
135.58
130.31
130.25
124.77
114.06
114.03
72.17
57.40
57.31
51.51
51.49
33.96
33.93
31.77
29.43
29.42
29.40
29.17
29.15
28.86
24.74
22.62
14.07
DNPO
NH2
O
OMe
6
5
CDCl3, 500 MHz
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

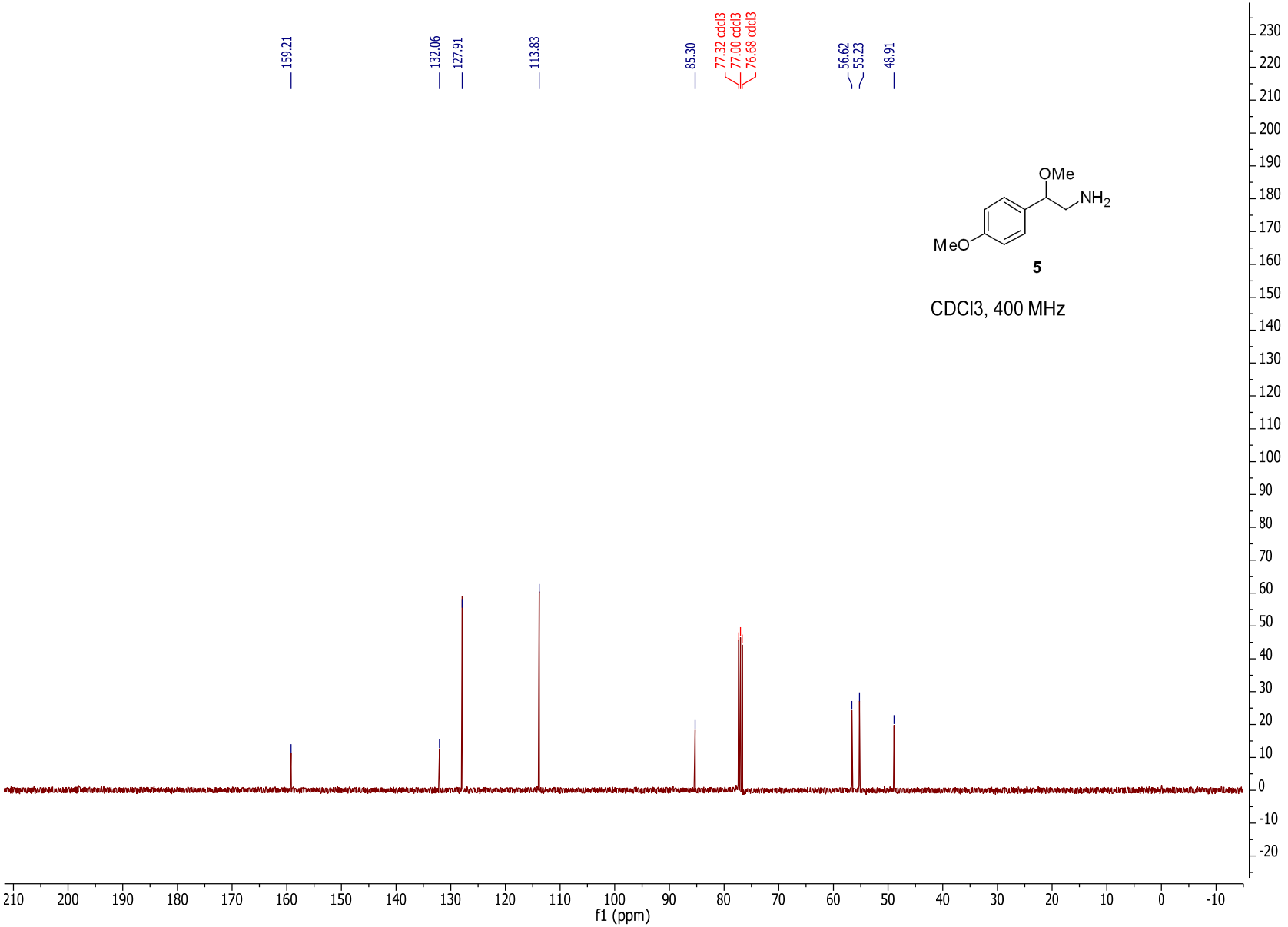

9.10
9.10
9.09
9.09
9.09
8.89
8.22
8.21
8.19
8.19
7.42
7.42
7.40
7.39
7.38
7.24
6.90
6.88
5.09
5.08
5.07
5.06
3.69
3.69
3.68
3.67
3.66
3.65
3.64
3.63
3.62
3.61
OAr
NH2
4a
CDCl3, 400 MHz
0.76
0.89
0.88
4.76
0.96
1.00
1.98
f1 (ppm)

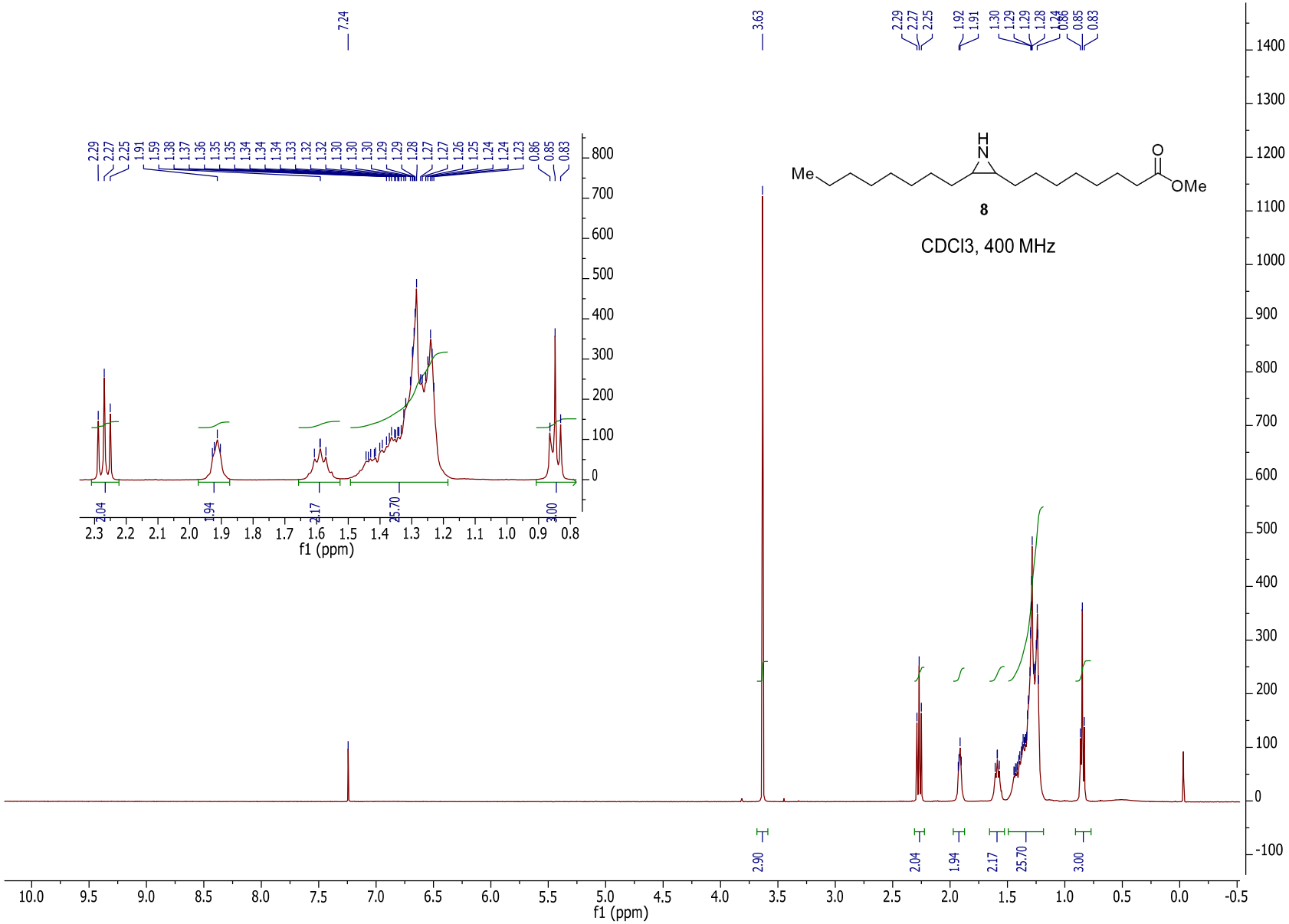

148.33
140.62
136.08
130.50
130.19
129.01
128.82
125.76
124.27
114.07
77.32 cdcl3
77.01 cdcl3
76.69 cdcl3
72.42
50.37
OAr
NH2
4a
CDCl3, 400 MHz
f1 (ppm)

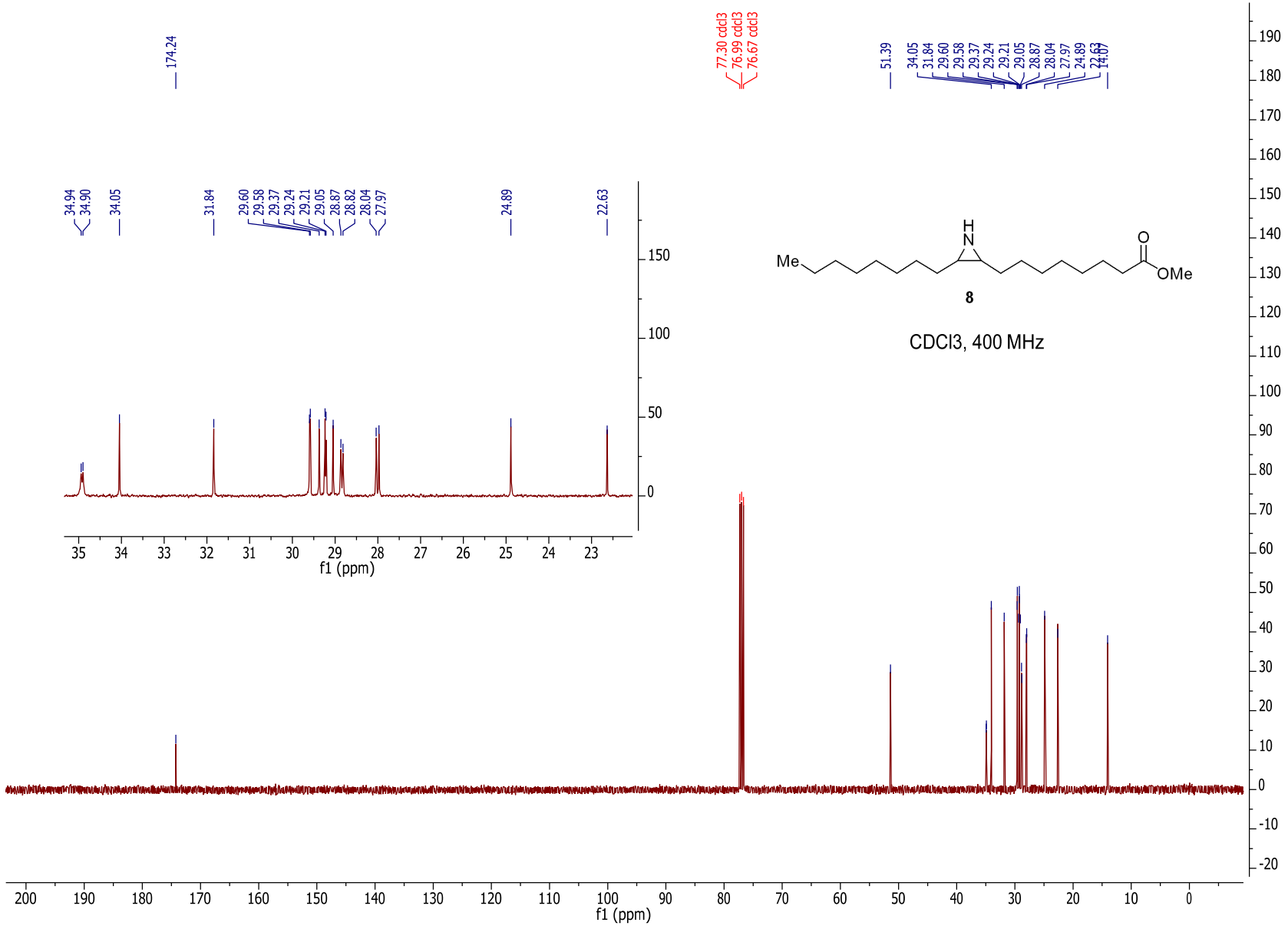

9.16
9.15
8.91
8.90
8.89
8.27
8.26
8.25
8.24
7.38
7.37
7.27
6.96
6.95
6.93
6.92
5.06
5.05
5.05
5.04
3.84
3.69
3.68
3.67
3.66
3.66
3.65
3.65
3.64
3.64
3.63
3.62
3.61
3.60
2.20
OAr
NH2
MeO
4b
CDCl3, 500 MHz
0.69
0.91
0.85
1.91
2.87
0.95
3.00
2.06
0.82
f1 (ppm)

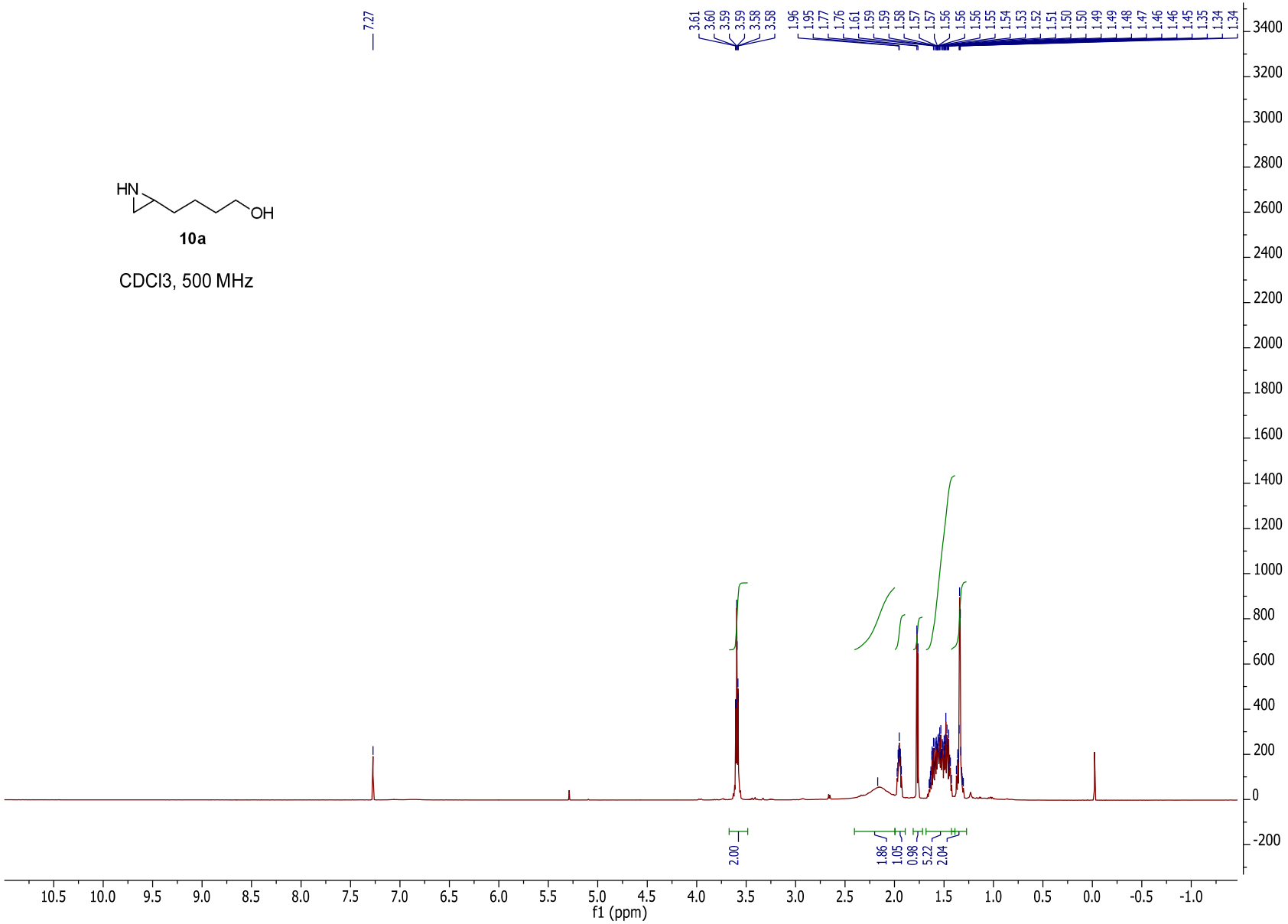

159.37
148.66
135.67
133.92
129.83
127.29
123.73
117.38
115.22
113.75
70.83
54.93
50.23
OAr
NH2
MeO
4b
CD3CN, 500 MHz
f1 (ppm)

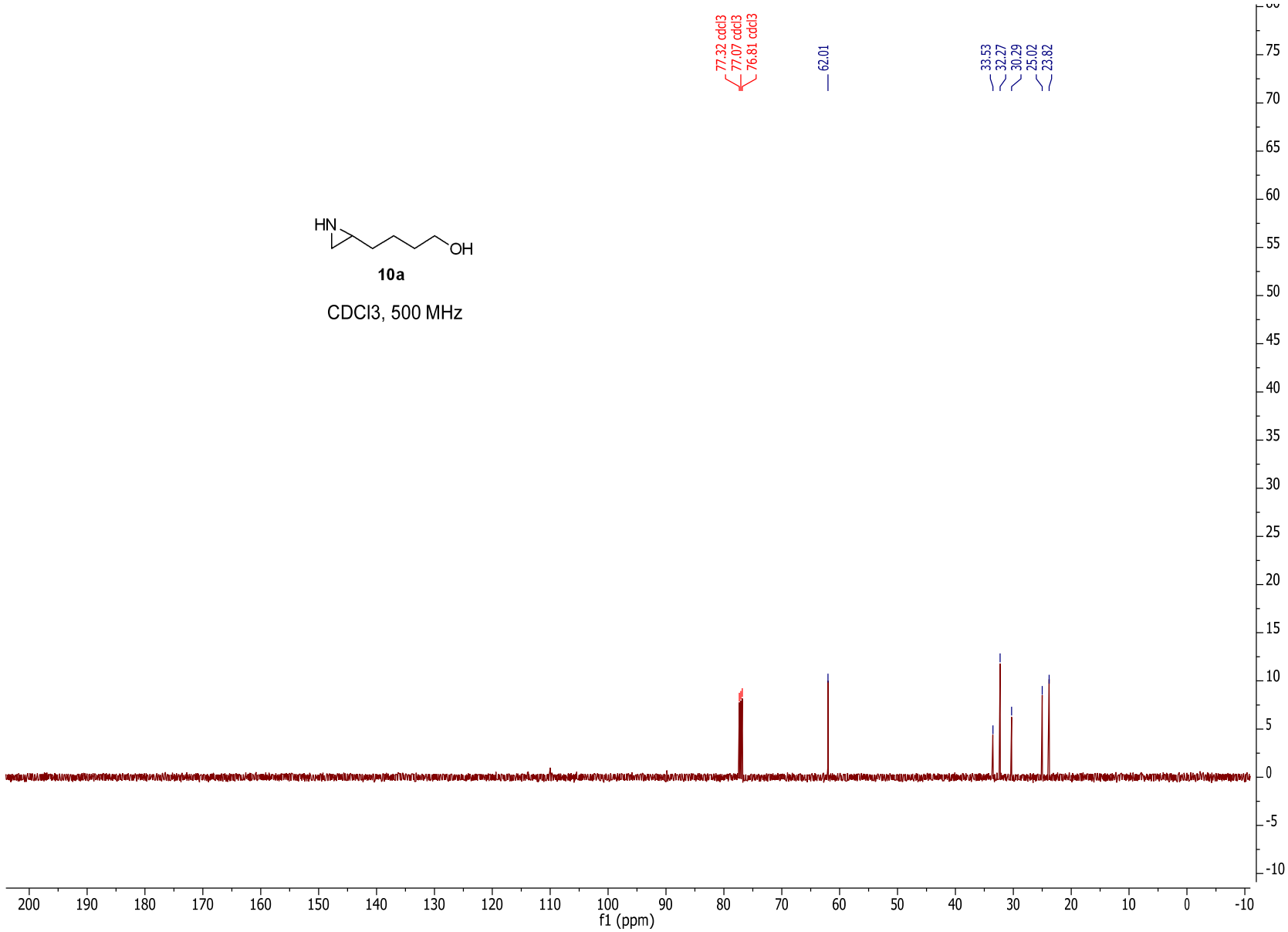

7.24
7.20
7.18
6.88
6.86
4.07
4.06
3.79
3.22
2.91
2.89
2.87
2.85
2.80
2.79
2.77
2.75
1.48
OMe
NH2
MeO
5
CDCl3, 400 MHz
2.00
2.06
0.98
3.30
3.10
1.07
1.05
2.42
f1 (ppm)

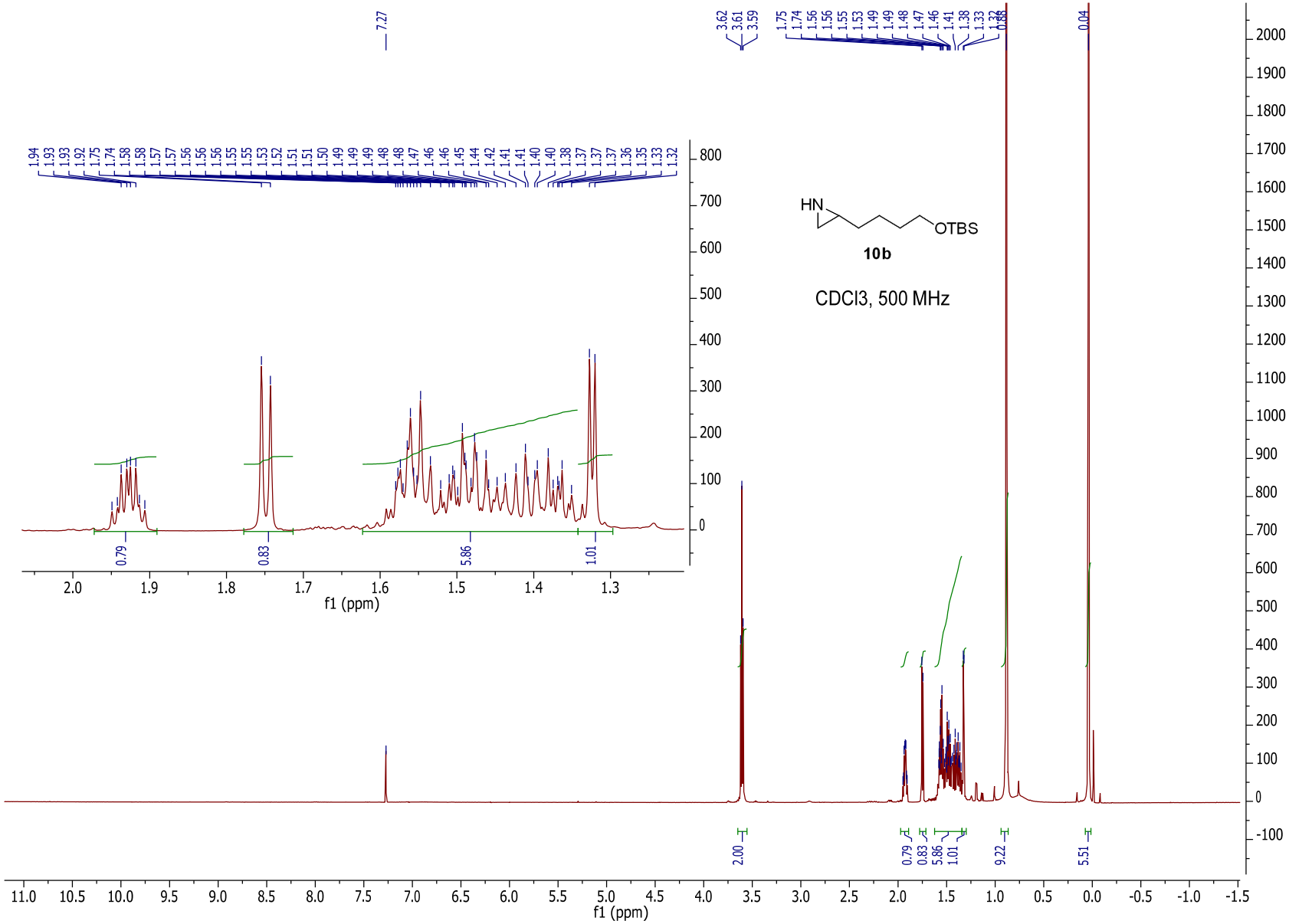

159.21
132.06
127.91
113.83
85.30
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
56.62
55.23
48.91
OMe
NH2
MeO
5
CDCl3, 400 MHz
f1 (ppm)

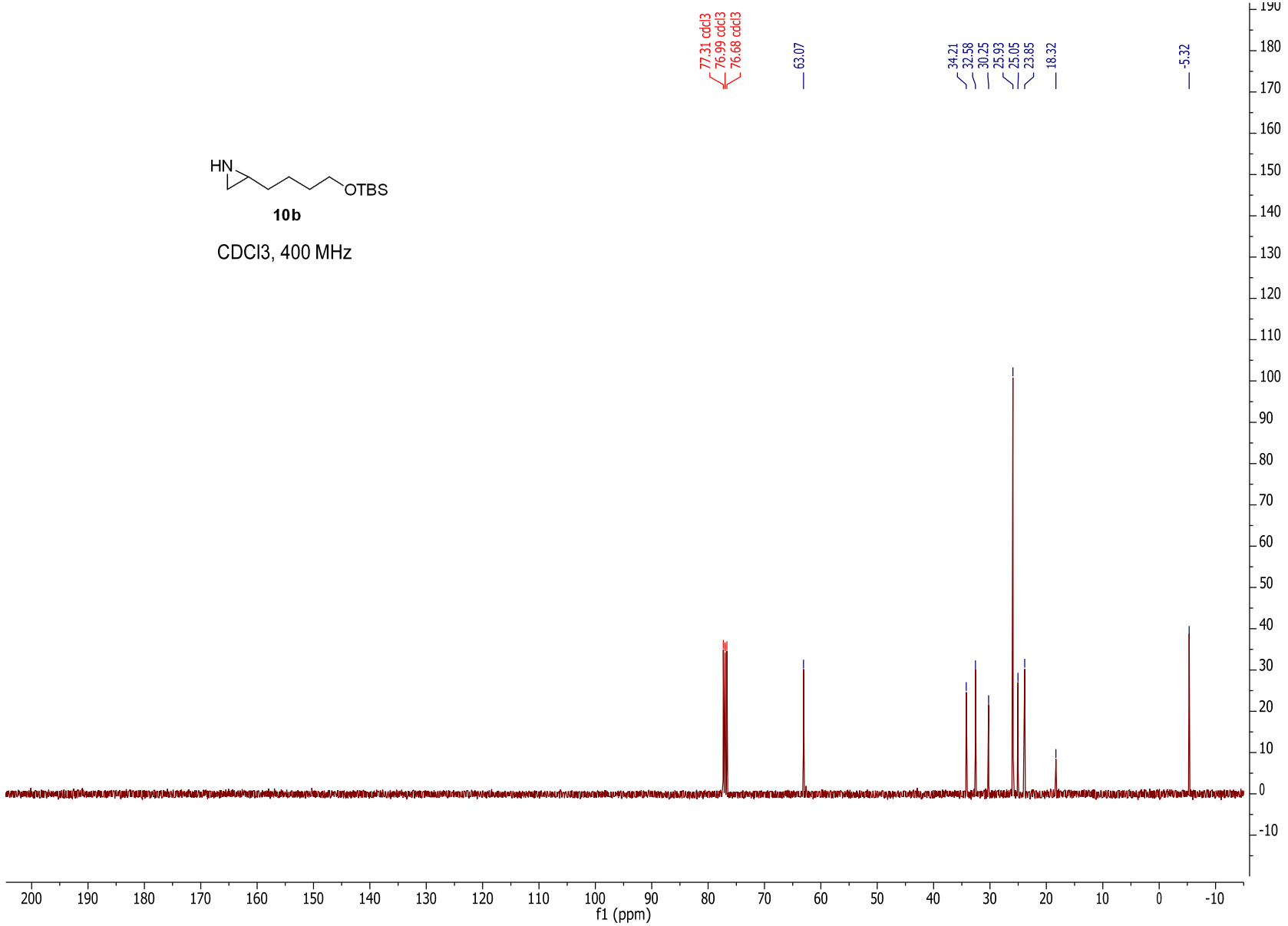

7.24
3.63
2.29
2.27
2.25
1.92
1.91
1.30
1.29
1.29
1.28
0.85
0.83
Me
H
N
O
OMe
8
CDCl3, 400 MHz
f1 (ppm)
2.90
2.04
1.94
2.17
25.70
3.00

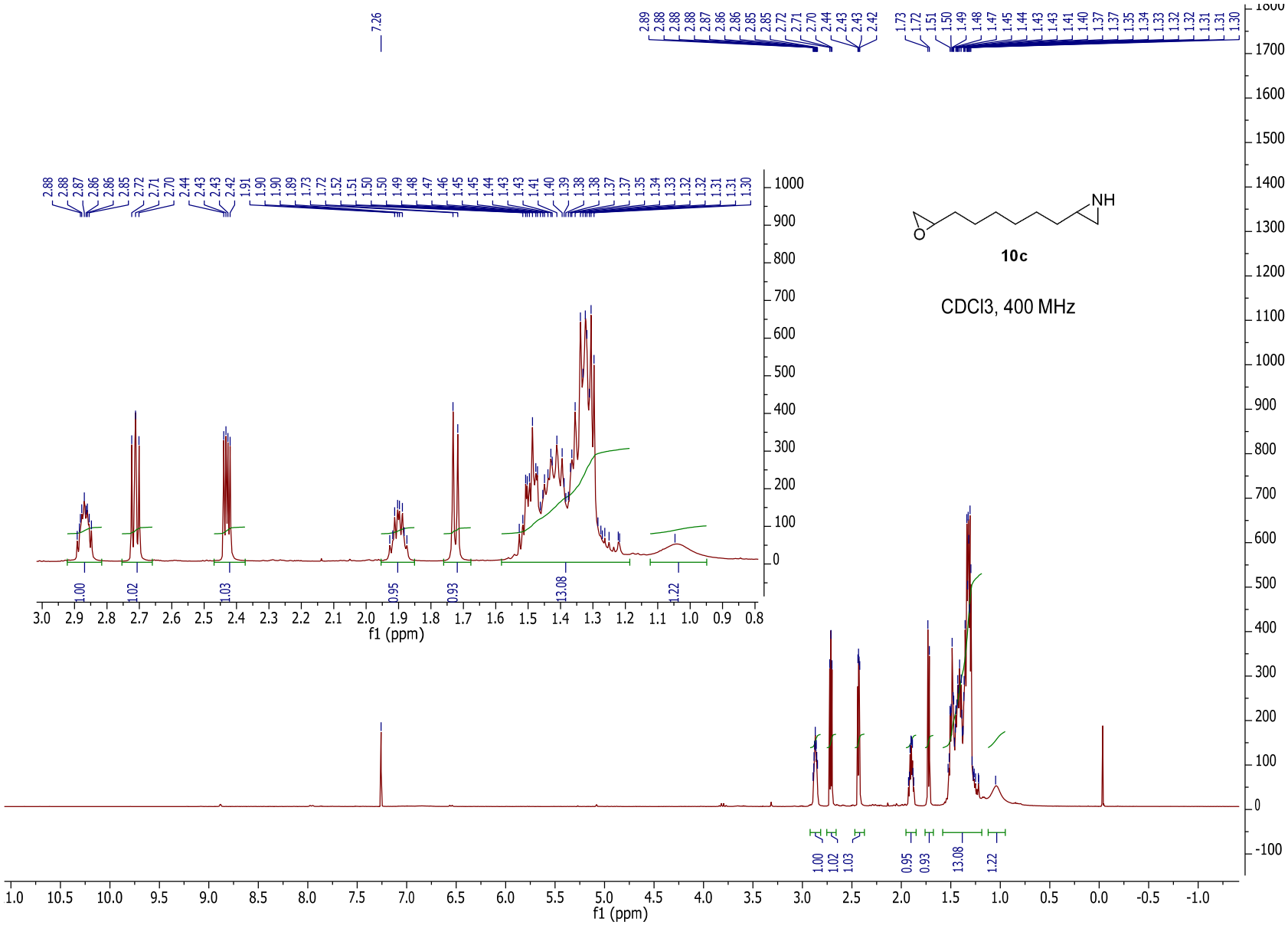

174.24
77.30 cdcl3
76.99 cdcl3
76.67 cdcl3
51.39
34.05
31.84
29.60
29.58
29.37
29.24
29.21
29.05
28.87
28.04
27.97
24.89
22.63
14.07
34.94
34.90
34.05
31.84
29.60
29.58
29.37
29.24
29.21
29.05
28.87
28.82
28.04
27.97
24.89
22.63
f1 (ppm)
Me
H
N
O
OMe
8
CDCl3, 400 MHz
f1 (ppm)

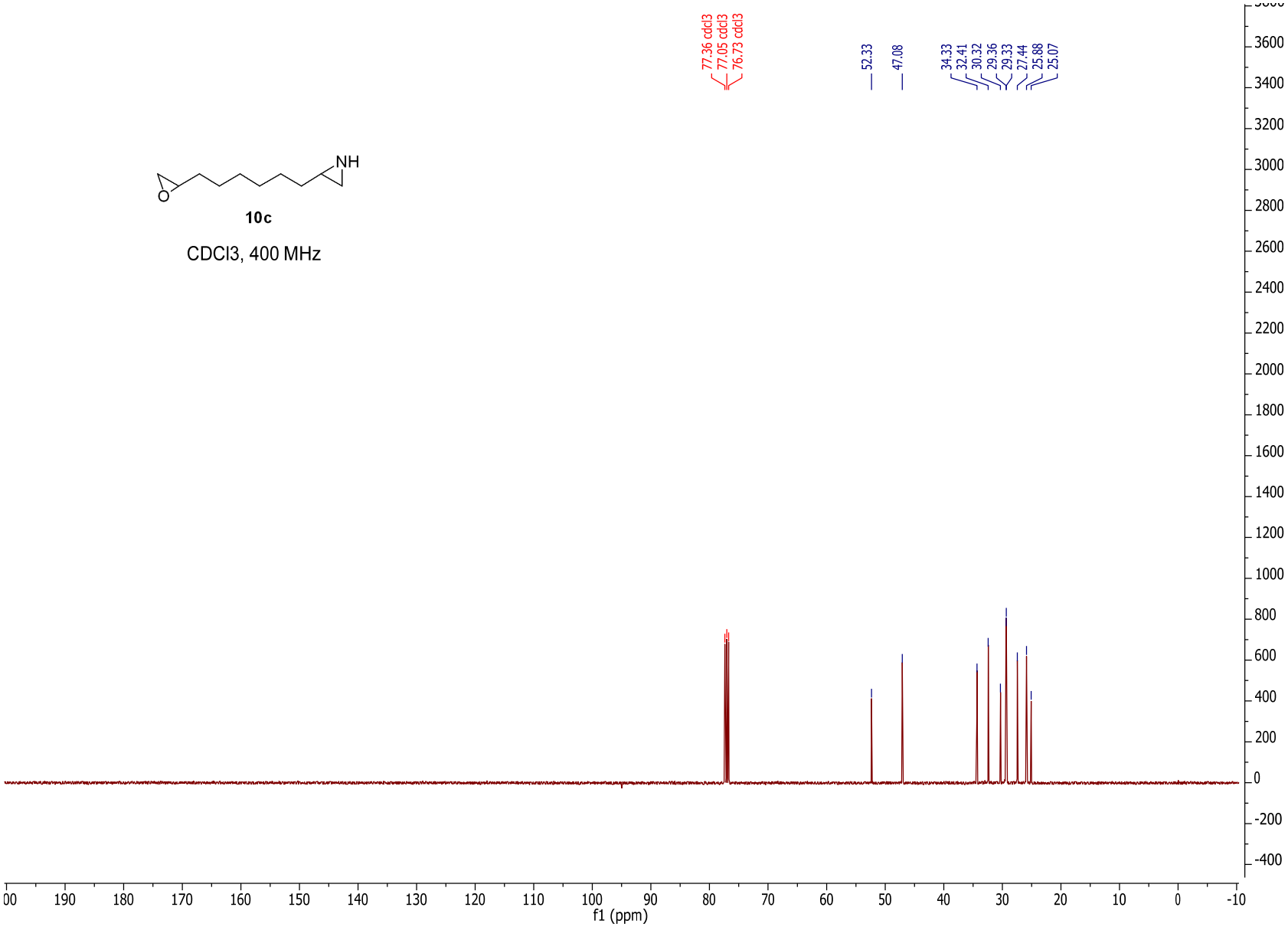

HN
OH
10a
CDCl3, 500 MHz
7.27
3.61 3.60 3.59 3.59 3.58 3.58
1.96 1.95 1.77 1.76 1.61 1.59 1.59 1.58 1.57 1.57 1.56 1.56 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.50 1.49 1.49 1.48 1.47 1.46 1.46 1.45 1.35 1.34 1.34
2.00
1.86
1.05
0.98
5.22
2.04
f1 (ppm)

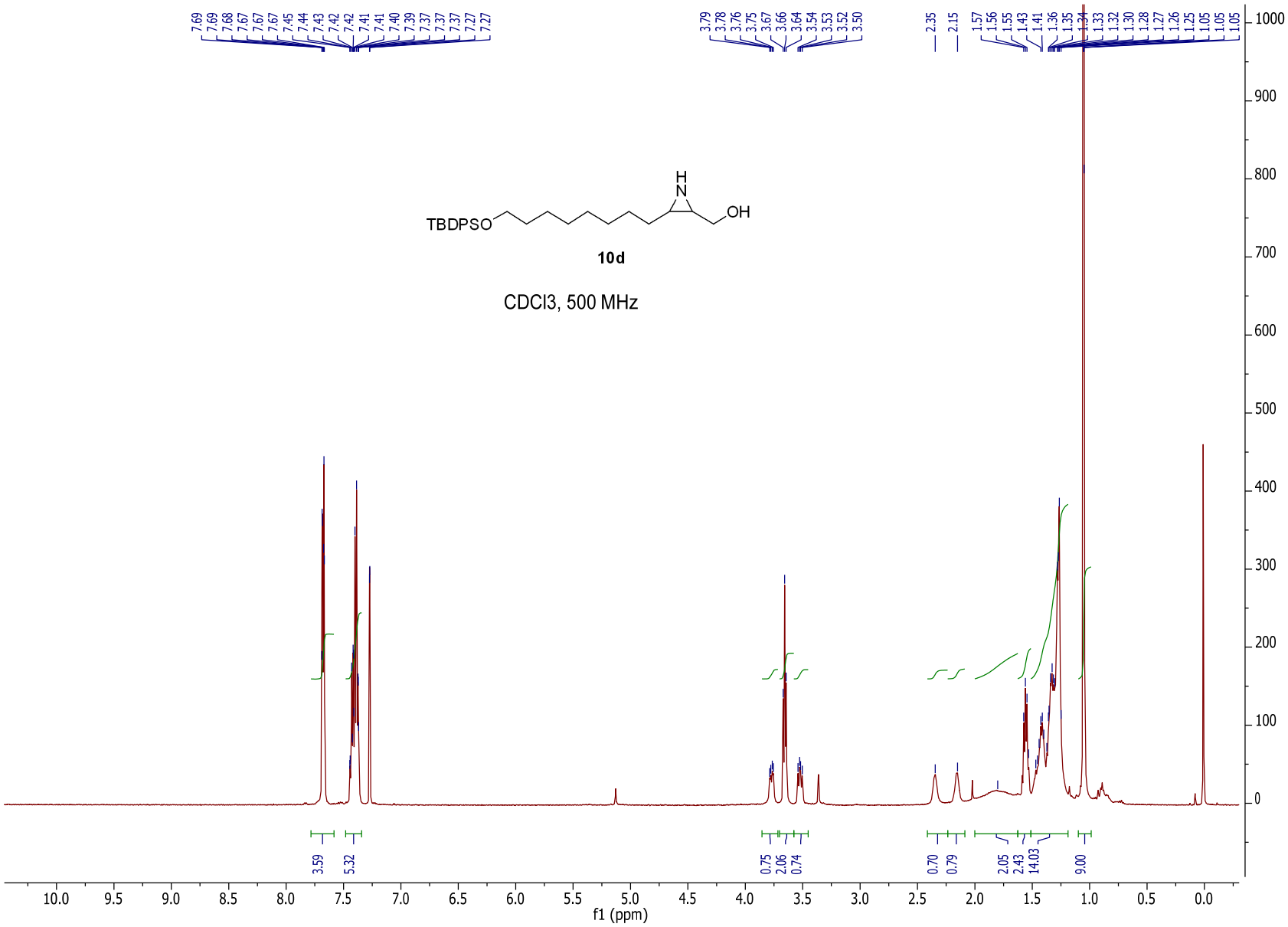

77.32 cdcl3
77.07 cdcl3
76.81 cdcl3
62.01
33.53
32.27
30.29
25.02
23.82
HN
OH
10a
CDCl3, 500 MHz
f1 (ppm)

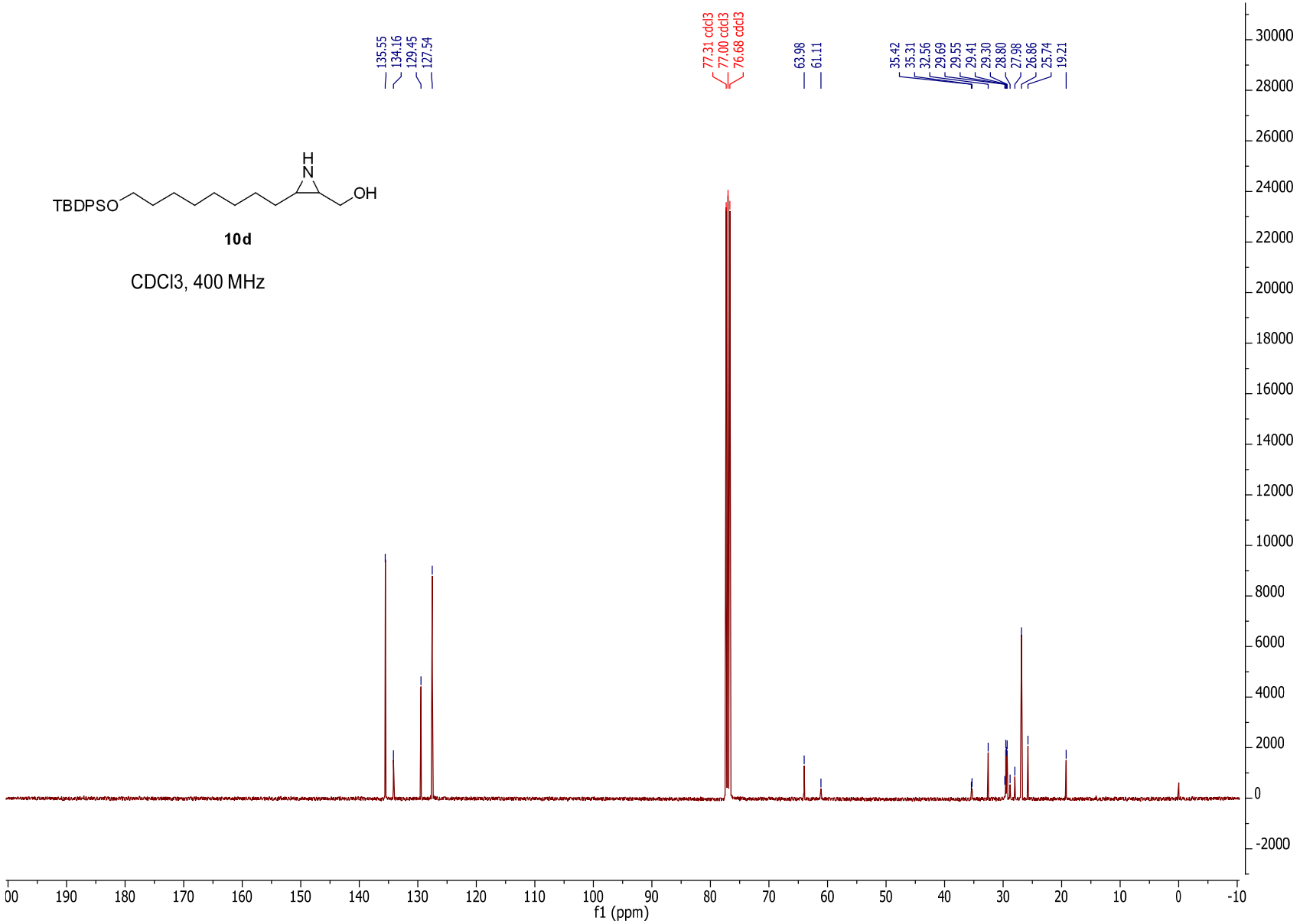

HN
OTBS
10b
CDCl3, 500 MHz
f1 (ppm)

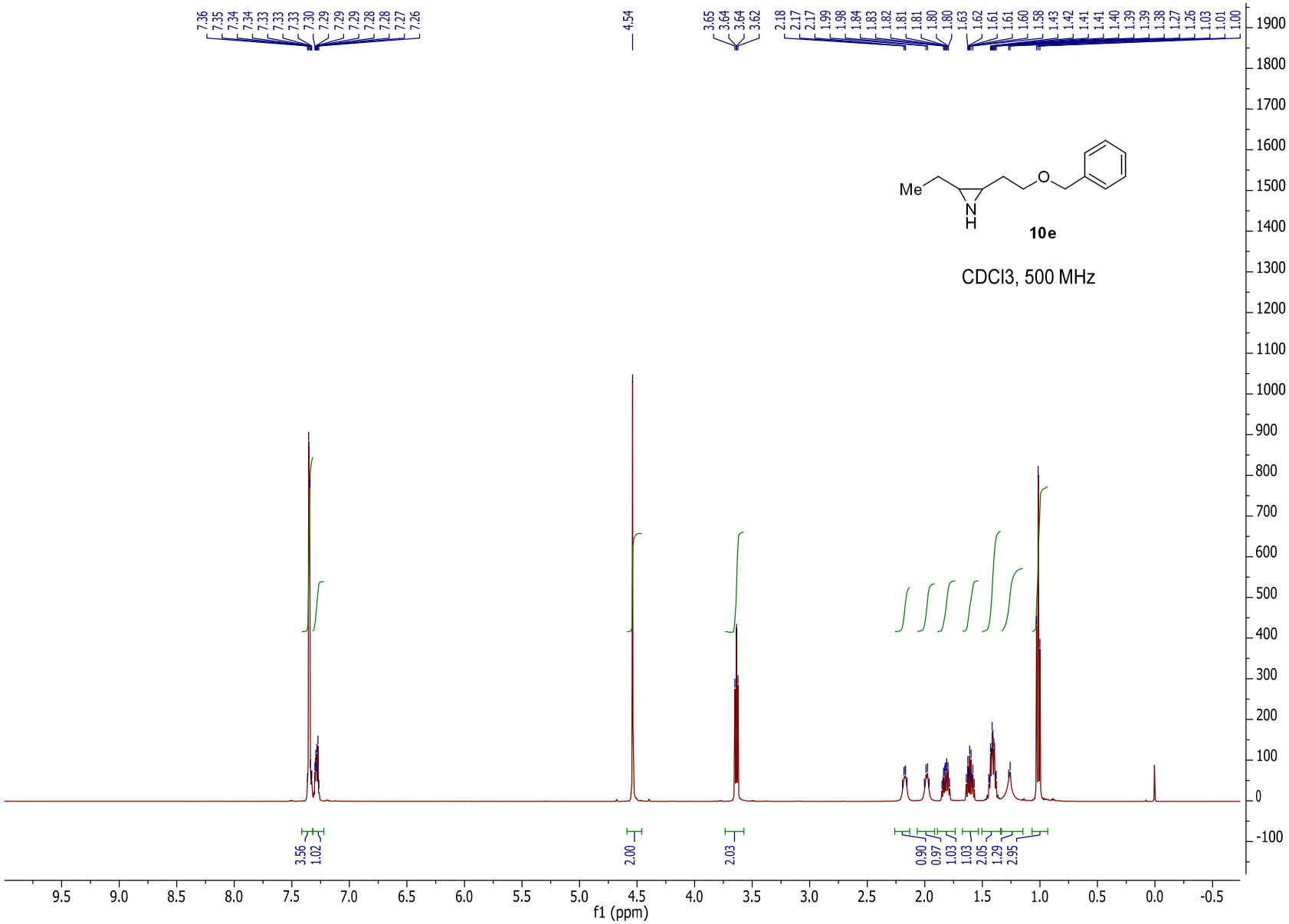

HN
OTBS
10b
CDCl3, 400 MHz
77.31 cdcl3
76.99 cdcl3
76.68 cdcl3
63.07
34.21
32.58
30.25
25.93
25.05
23.85
18.32
-5.32
f1 (ppm)

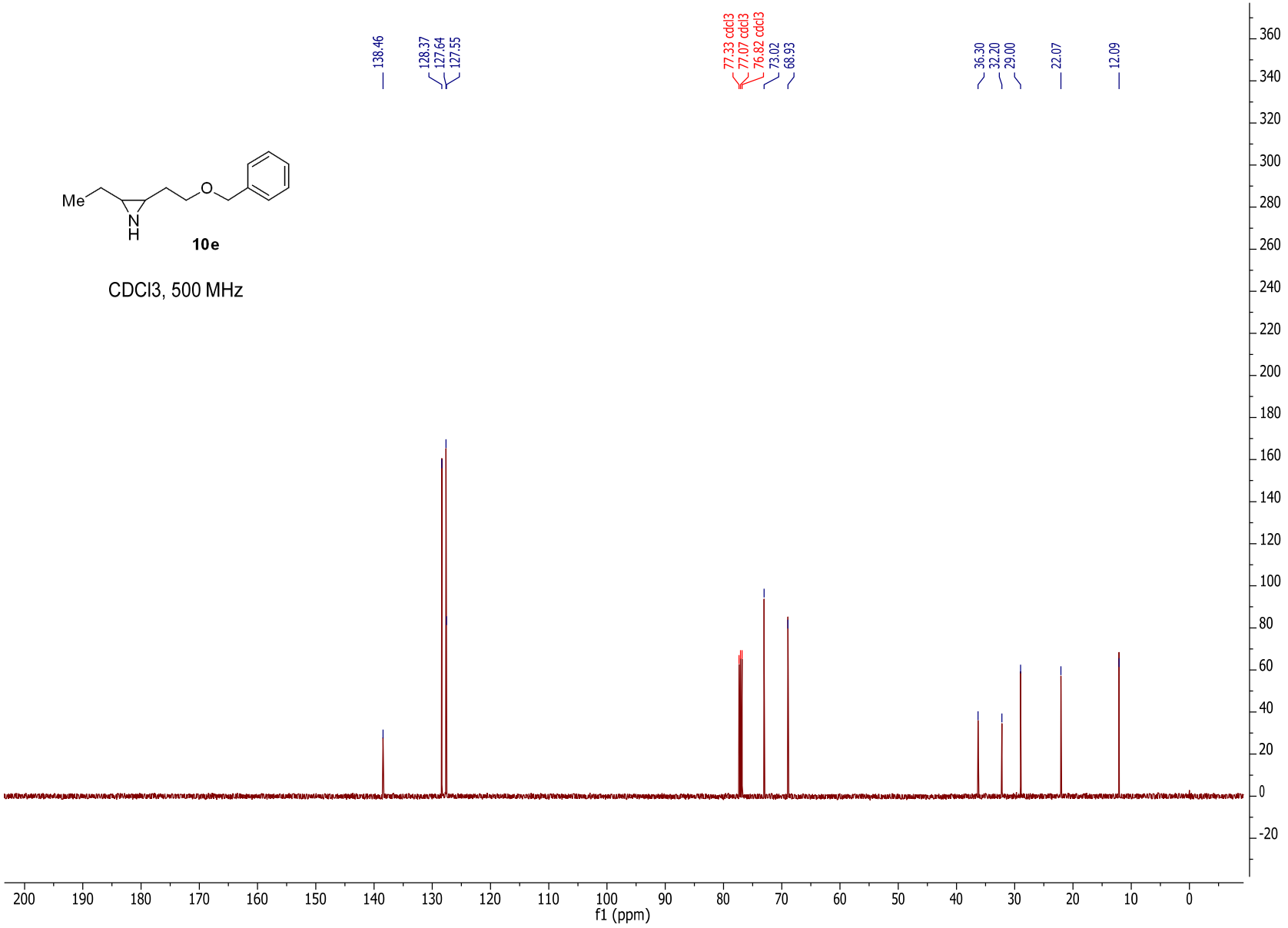

10c
CDCl3, 400 MHz
f1 (ppm)

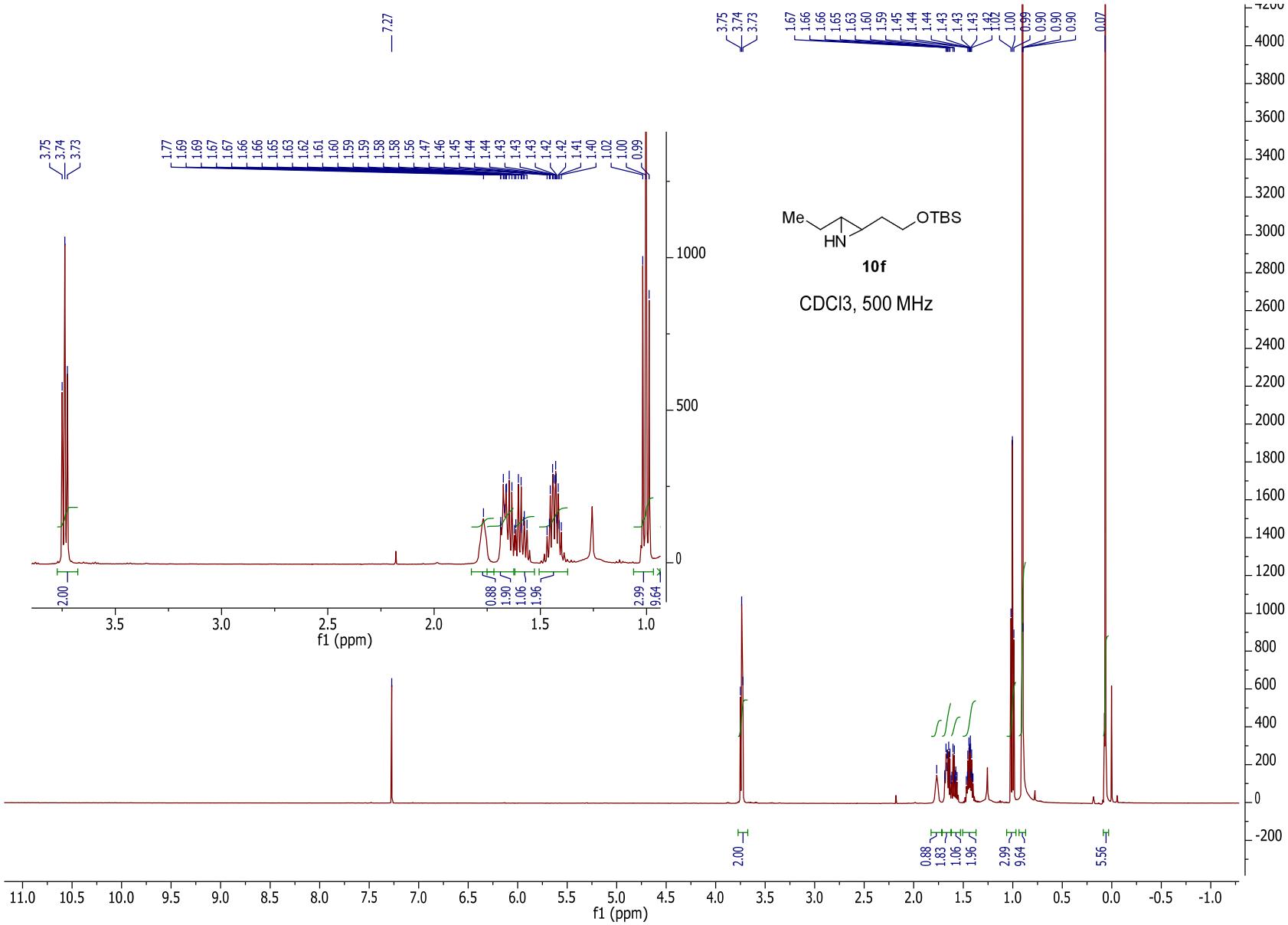

NH
O
10c
CDCl3, 400 MHz
77.36 cdcl3
77.05 cdcl3
76.73 cdcl3
52.33
47.08
34.33
32.41
30.32
29.36
29.33
27.44
25.88
25.07
f1 (ppm)

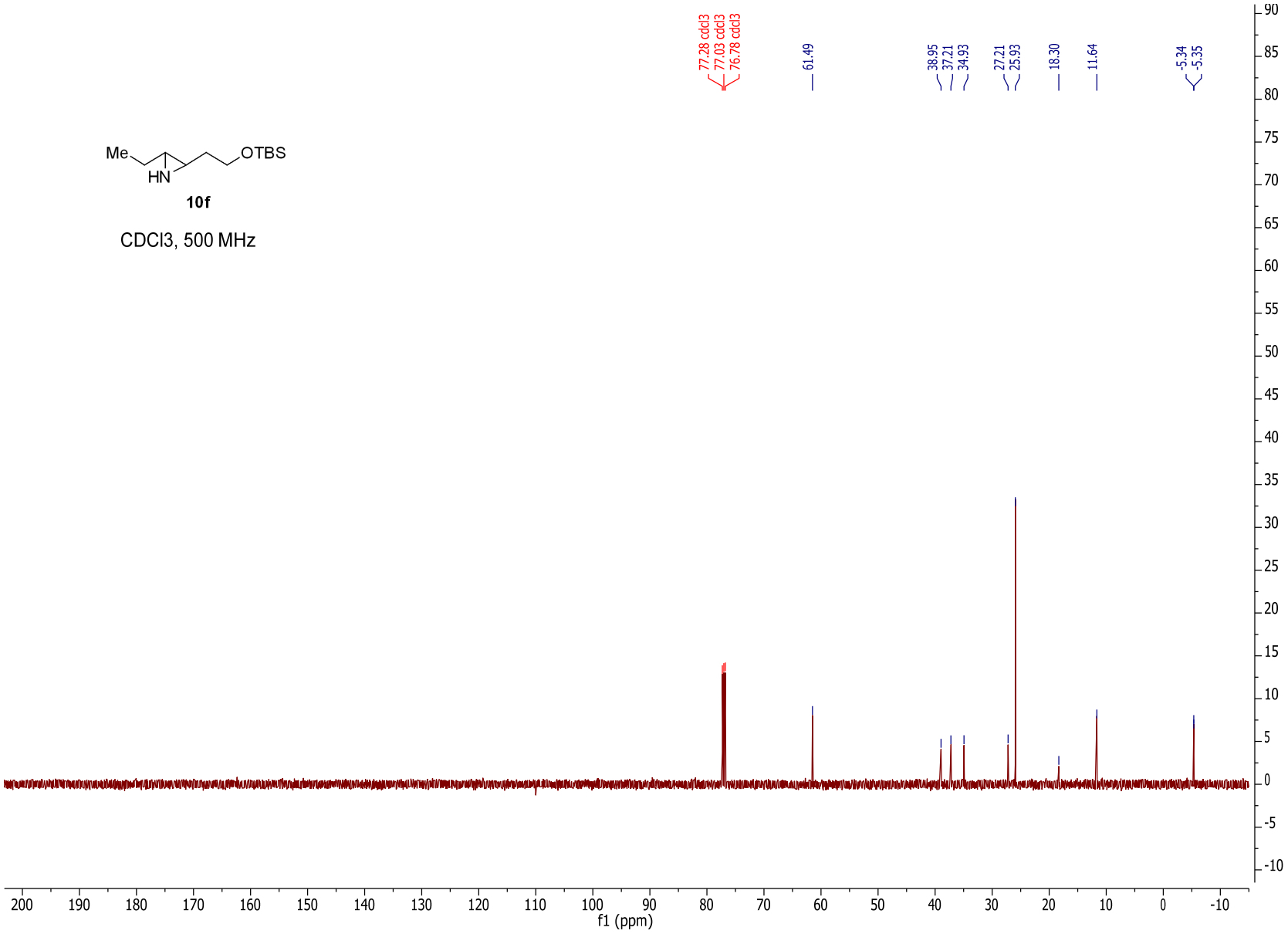

TBDPSO
H
N
OH
10d
CDCl3, 500 MHz
f1 (ppm)

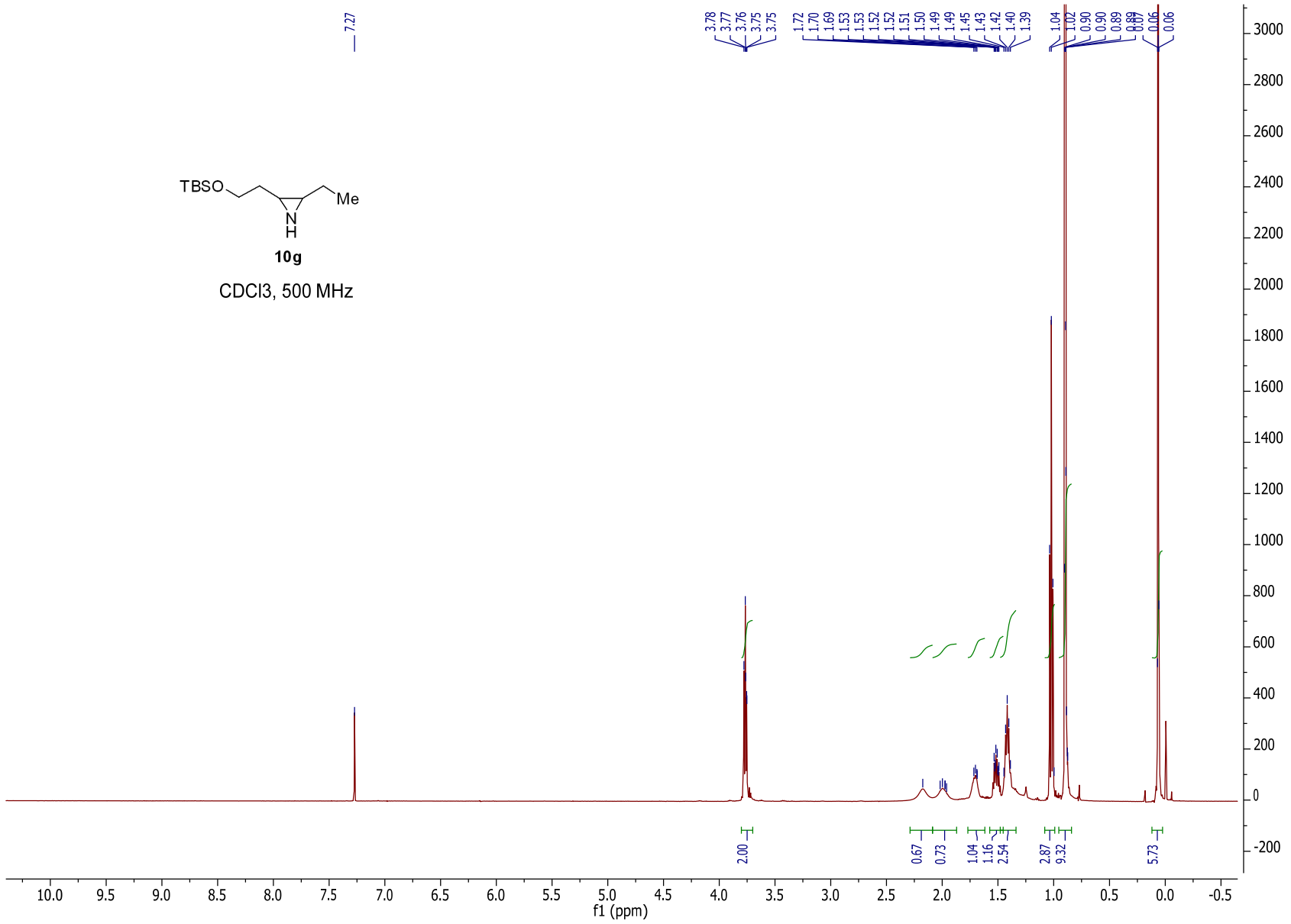

135.55
134.16
129.45
127.54
77.31 cdcl3
77.00 cdcl3
76.68 cdcl3
63.98
61.11
35.42
35.31
32.56
29.69
29.55
29.41
29.30
28.80
27.98
26.86
25.74
19.21
TBDPSO
H
N
OH
10d
CDCl3, 400 MHz
f1 (ppm)

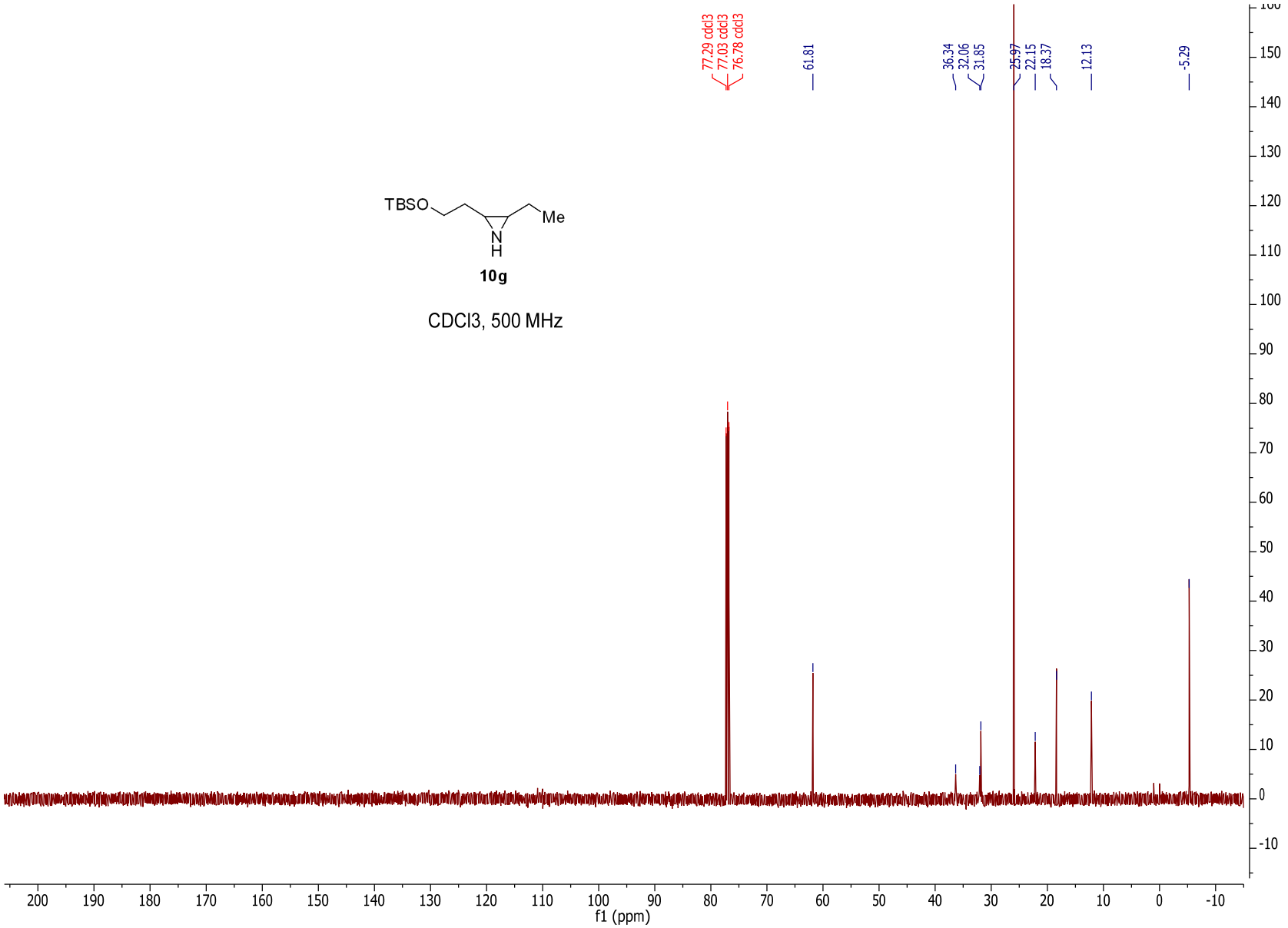

7.36
7.35
7.34
7.34
7.33
7.33
7.33
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26
4.54
3.65
3.64
3.64
3.62
2.18
2.17
2.17
1.99
1.98
1.84
1.83
1.82
1.81
1.81
1.80
1.80
1.63
1.62
1.61
1.61
1.60
1.58
1.43
1.42
1.41
1.41
1.40
1.39
1.39
1.38
1.27
1.26
1.03
1.01
1.00
Me
O
N
H
10e
CDCl3, 500 MHz
3.56
1.02
2.00
2.03
0.90
0.97
1.03
1.03
2.05
1.29
2.95
f1 (ppm)

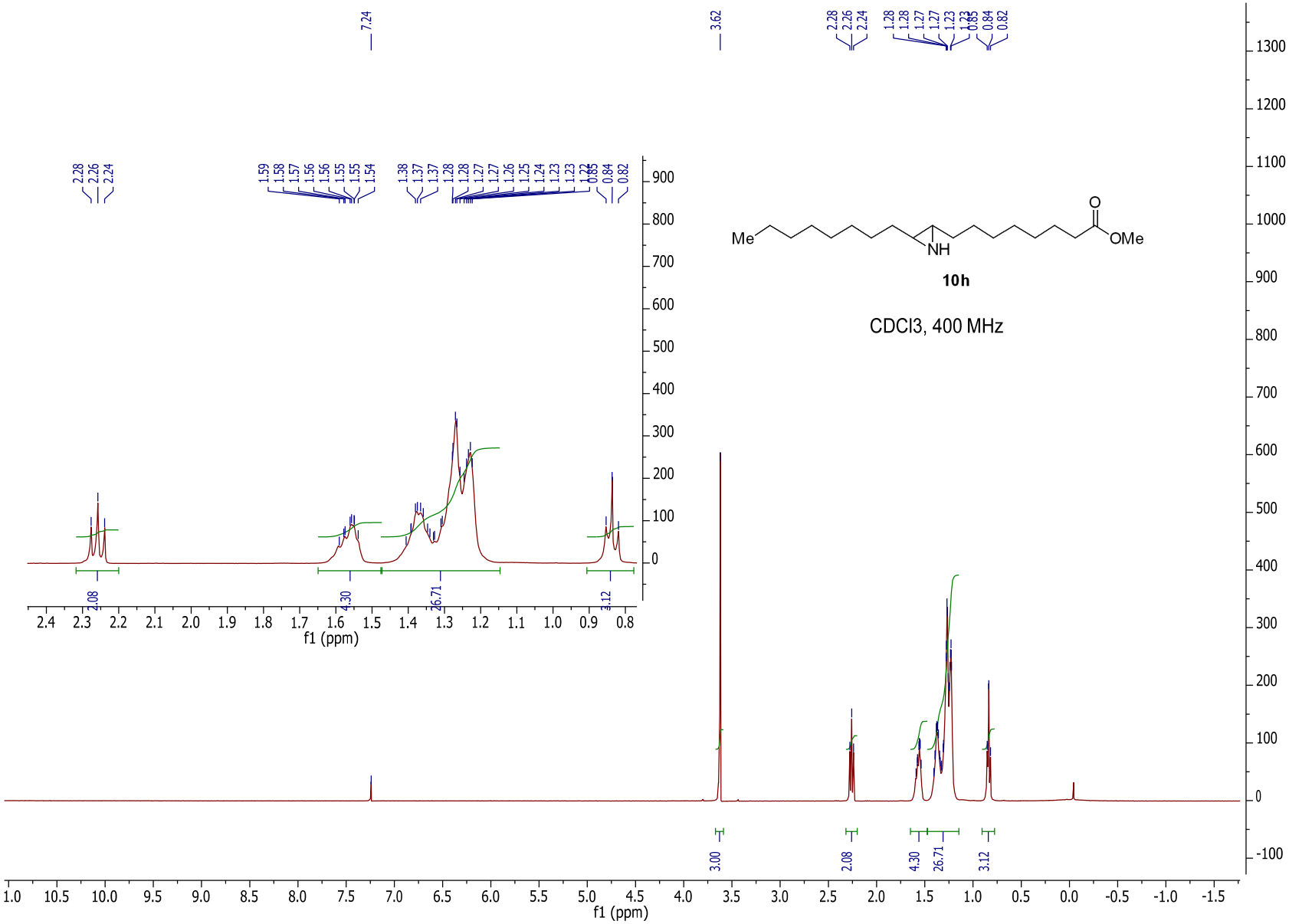

138.46
128.37
127.64
127.55
77.33 cdcl3
77.07 cdcl3
76.82 cdcl3
73.02
68.93
36.30
32.20
29.00
22.07
12.09
Me
O
N
H
10e
CDCl3, 500 MHz
f1 (ppm)

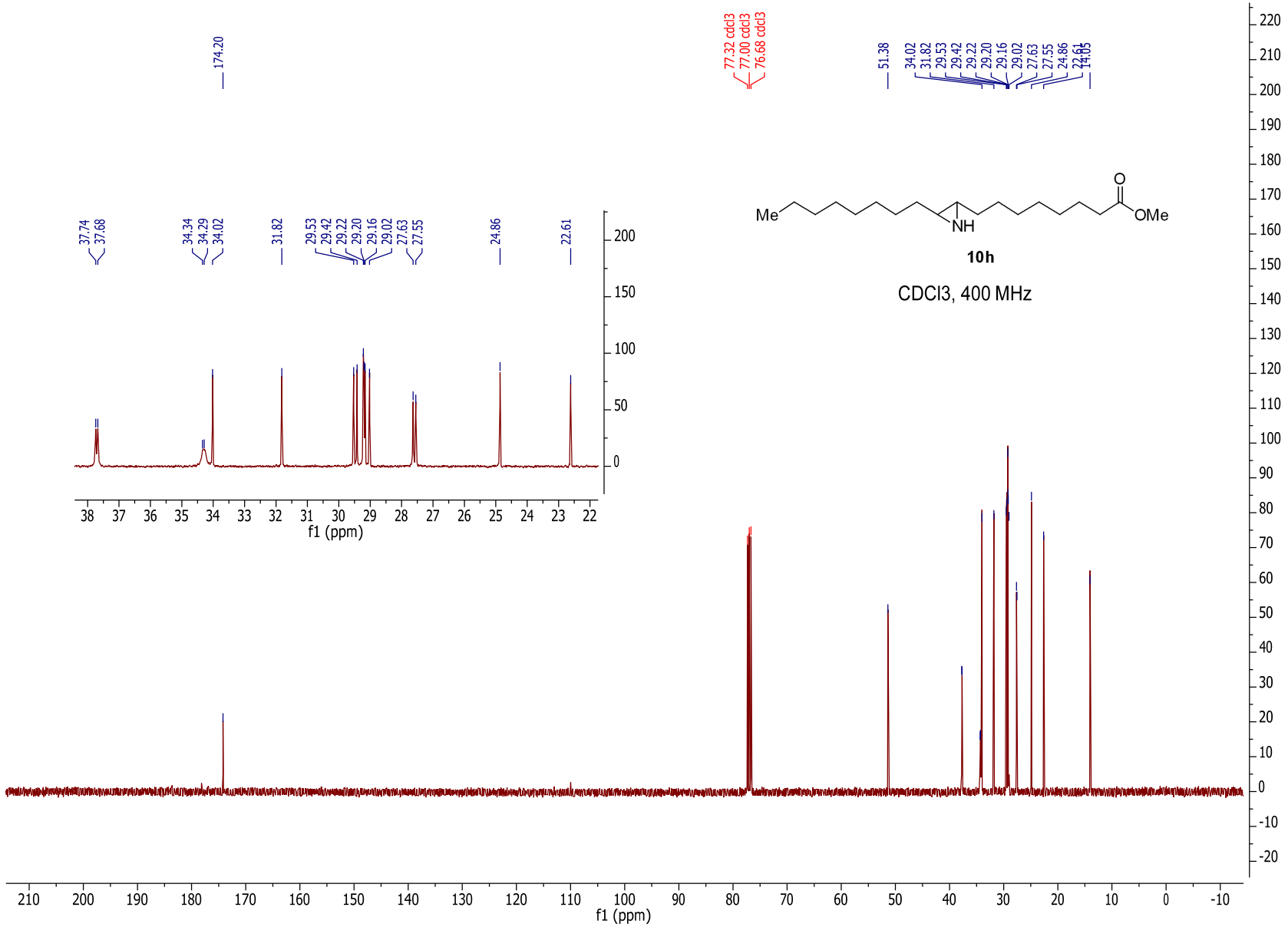

Me
OTBS
HN
10f
CDCl3, 500 MHz
f1 (ppm)

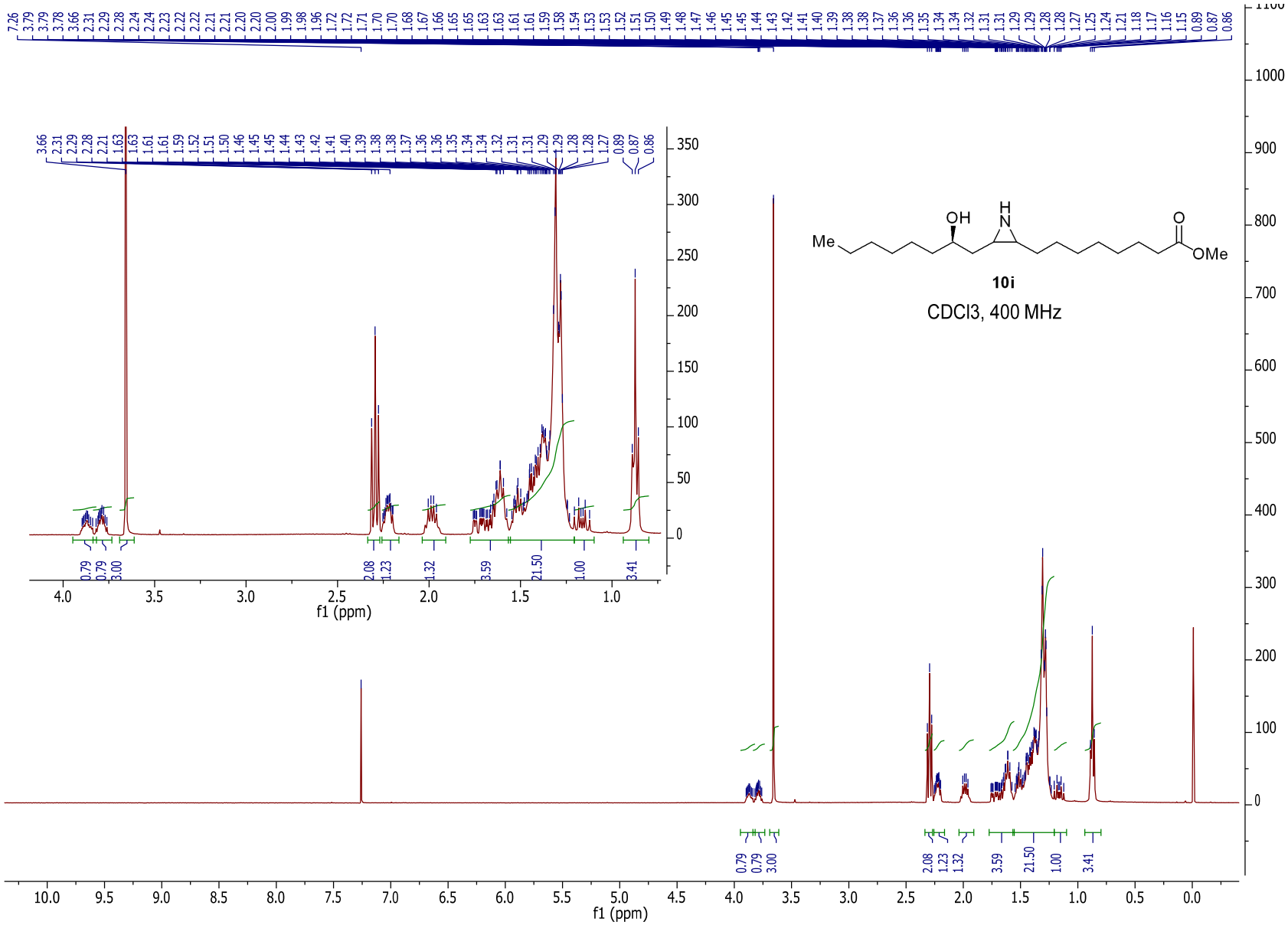

Me
HN
OTBS
10f
CDCl3, 500 MHz
77.28 cdd3
77.03 cdd3
76.78 cdd3
61.49
38.95
37.21
34.93
27.21
25.93
18.30
11.64
-5.34
-5.35
f1 (ppm)

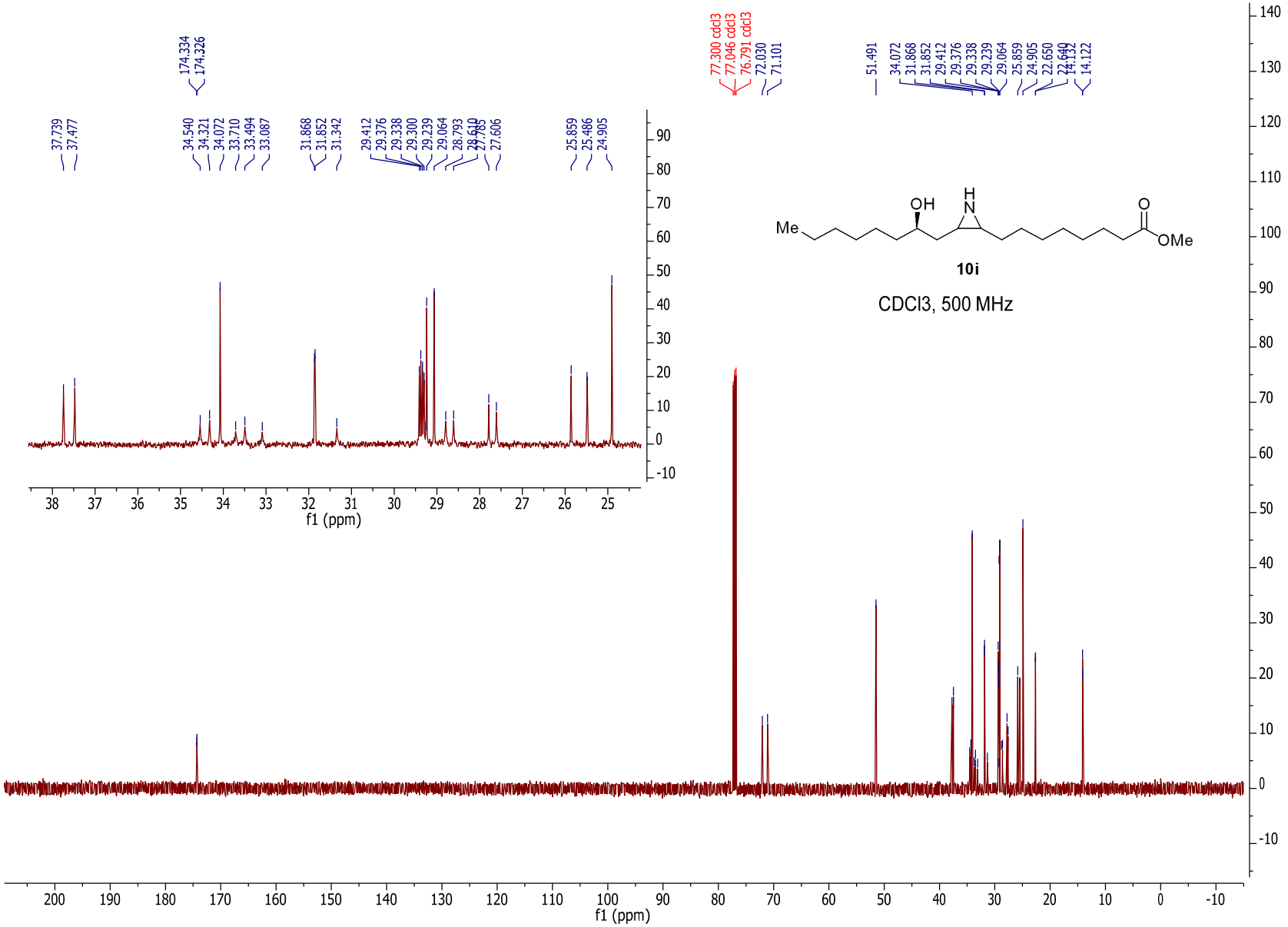

TBSO
Me
N
H
10g
CDCl3, 500 MHz
f1 (ppm)

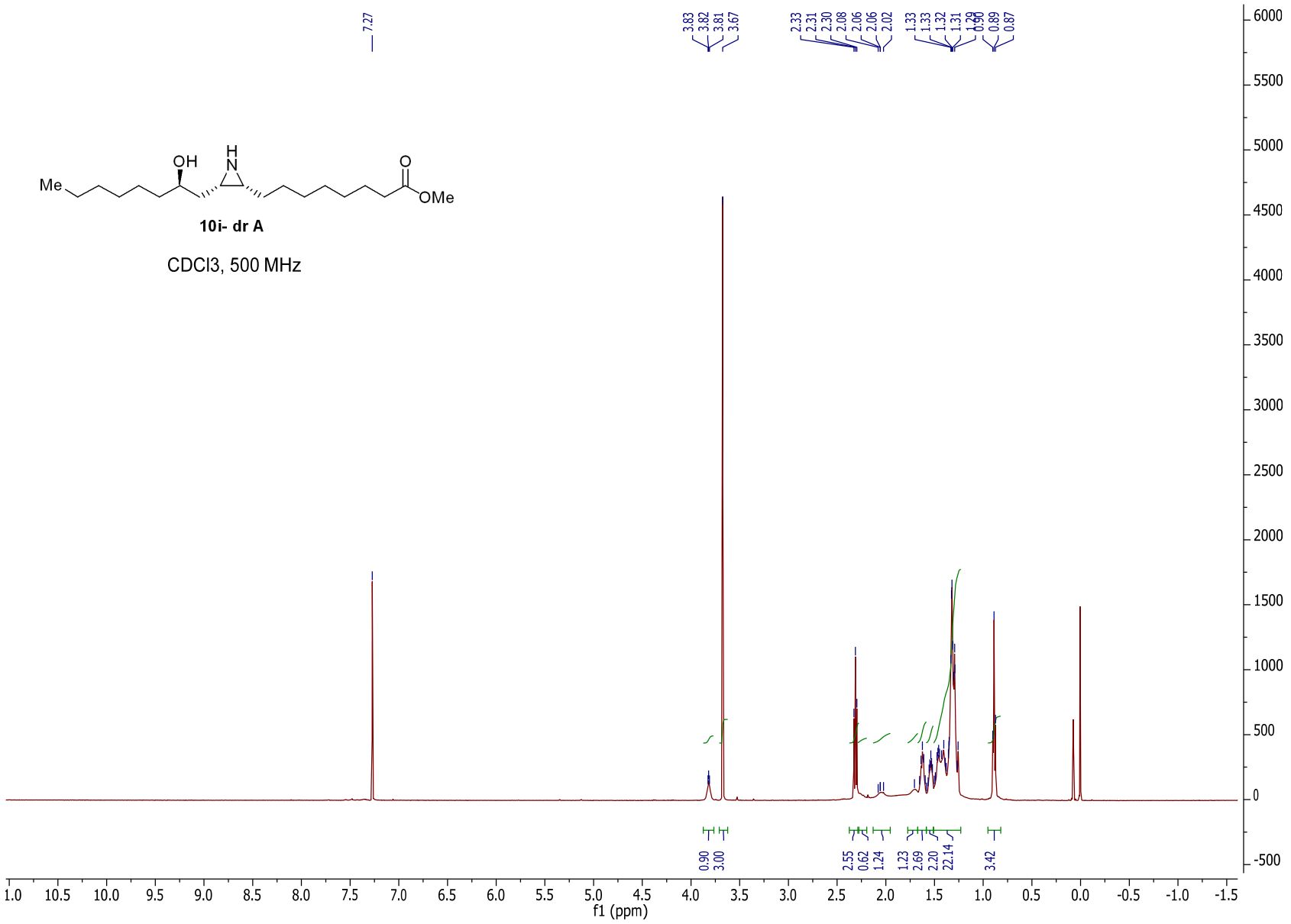

77.29 cdcl3
77.03 cdcl3
76.78 cdcl3
61.81
36.34
32.06
31.85
25.97
22.15
18.37
12.13
-5.29
TBSO
Me
N
H
10g
CDCl3, 500 MHz
f1 (ppm)

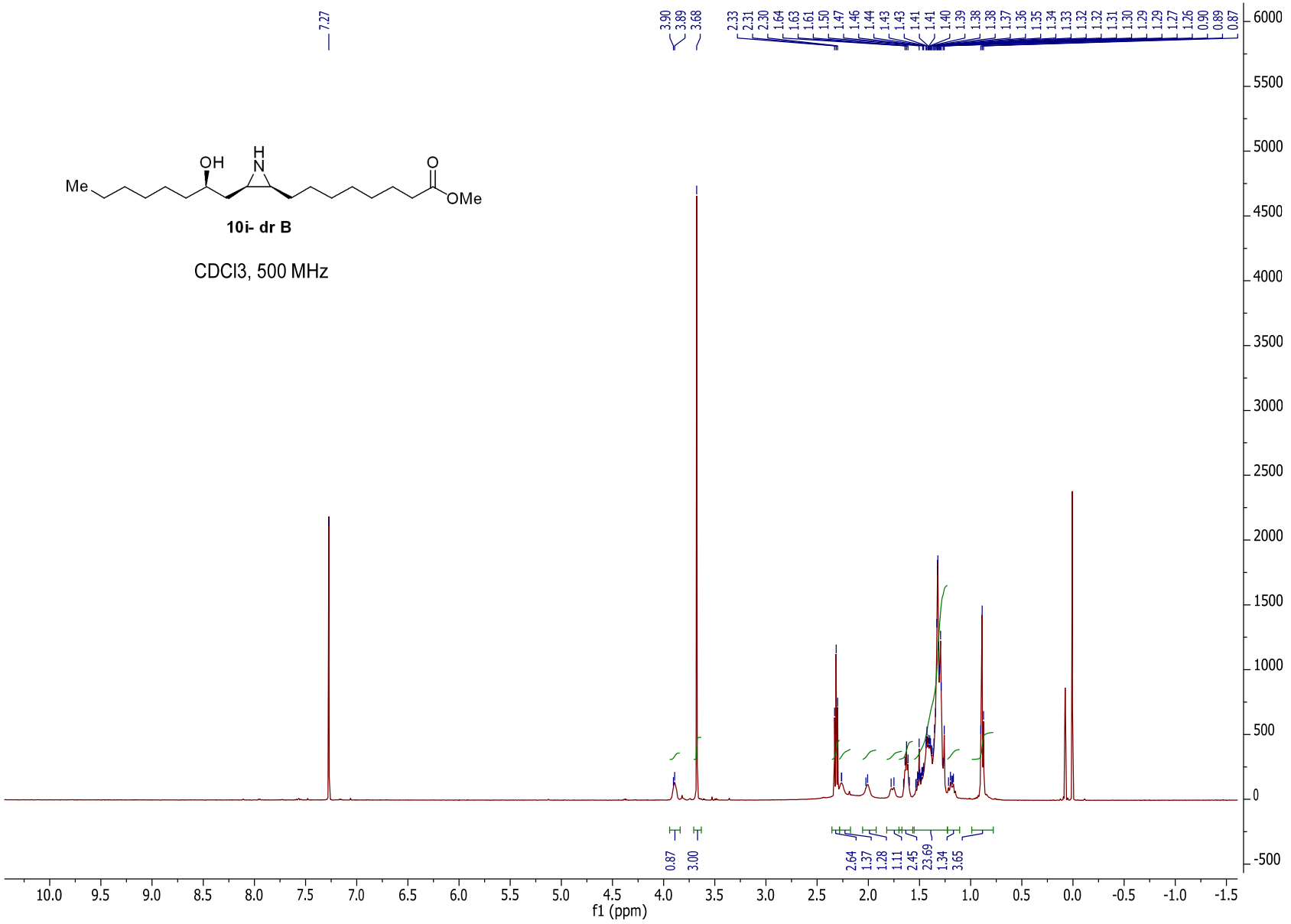

Me
NH
O
OMe
10h
CDCl3, 400 MHz
f1 (ppm)

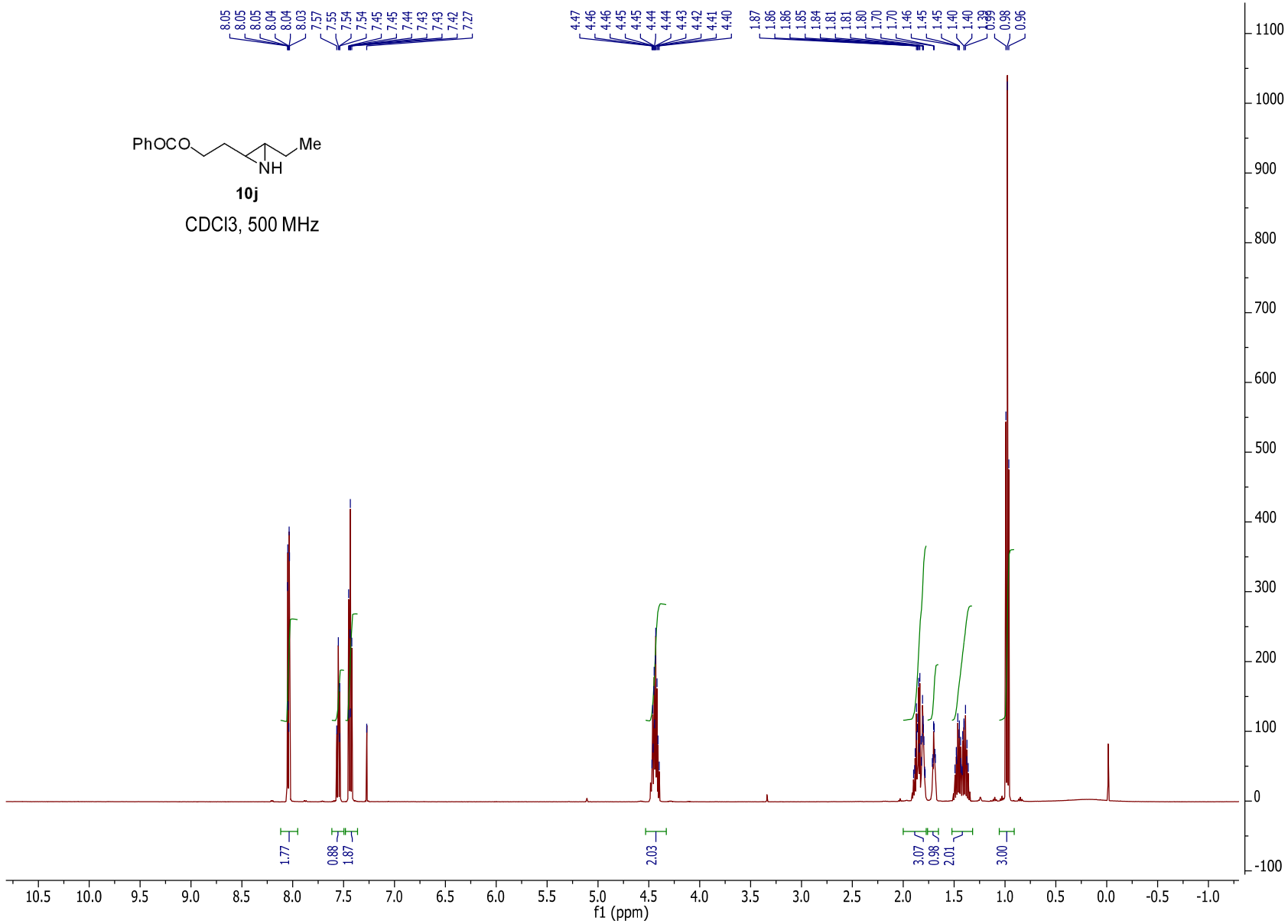

174.20
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.38
34.02
31.82
29.53
29.42
29.22
29.20
29.16
29.02
27.63
27.55
24.86
22.61
14.05
37.74
37.68
34.34
34.29
34.02
31.82
29.53
29.42
29.22
29.20
29.16
29.02
27.63
27.55
24.86
22.61
Me
NH
O
OMe
10h
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

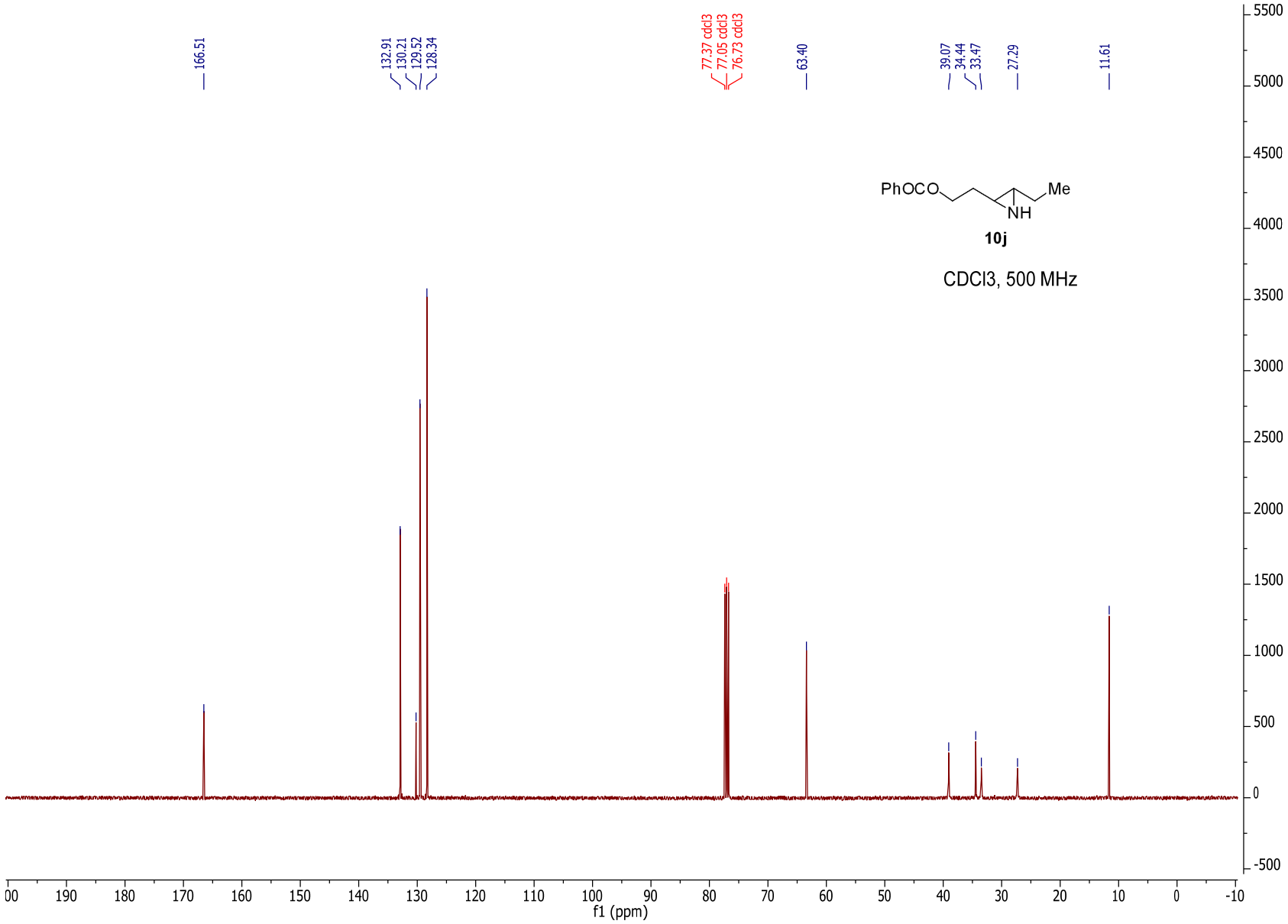

OH
H
N
O
Me
OMe
10i
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

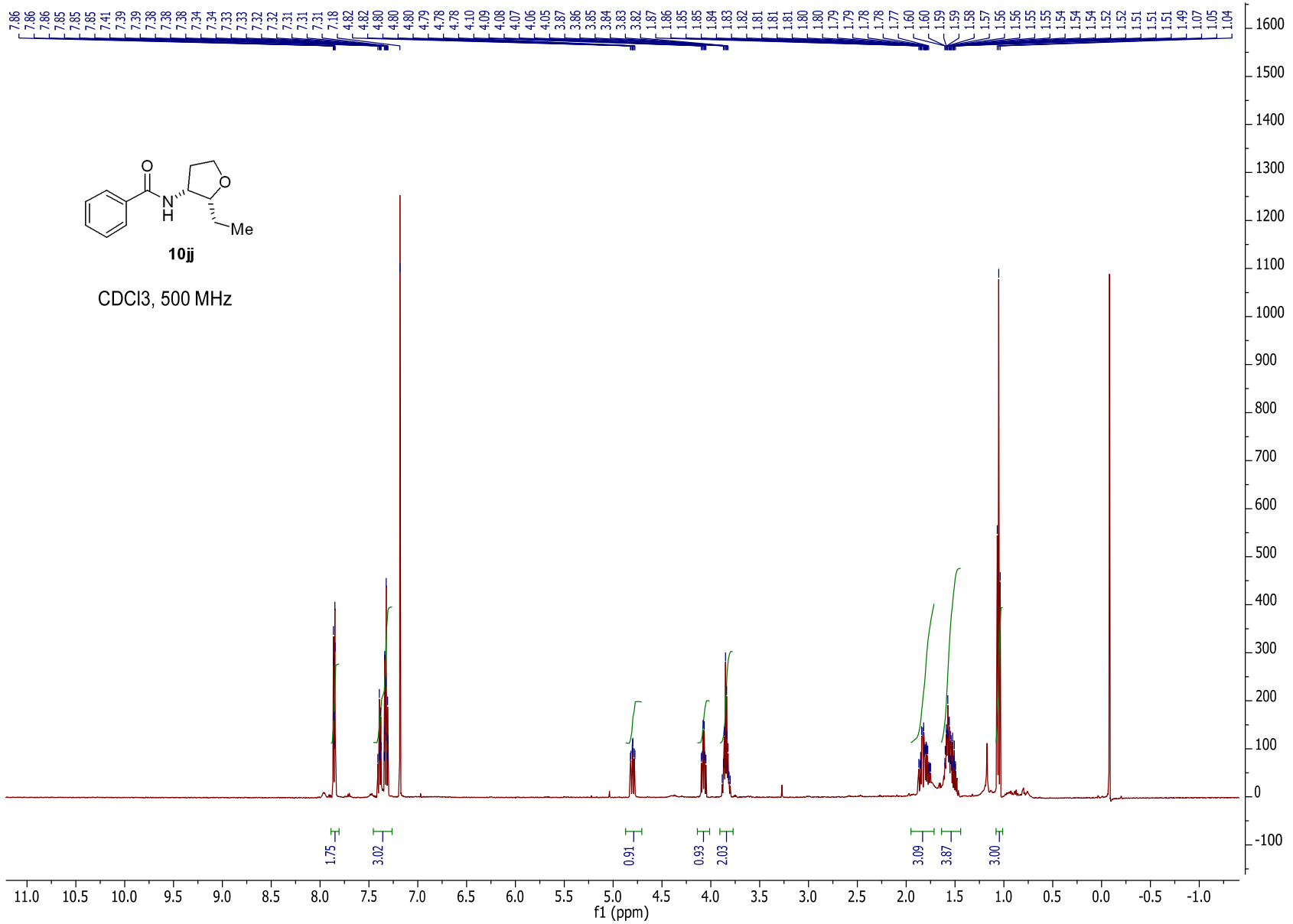

174.334
174.326
77.300 cdcl3
77.046 cdcl3
76.791 cdcl3
72.030
71.101
51.491
34.072
31.868
31.852
29.412
29.376
29.338
29.239
29.064
25.859
24.905
22.650
14.132
14.122
37.739
37.477
34.540
34.321
34.072
33.710
33.494
33.087
31.868
31.852
31.342
29.412
29.376
29.338
29.300
29.239
29.064
28.793
27.785
27.606
25.859
25.486
24.905
OH
H
N
O
Me
OMe
10i
CDCl3, 500 MHz
f1 (ppm)
f1 (ppm)

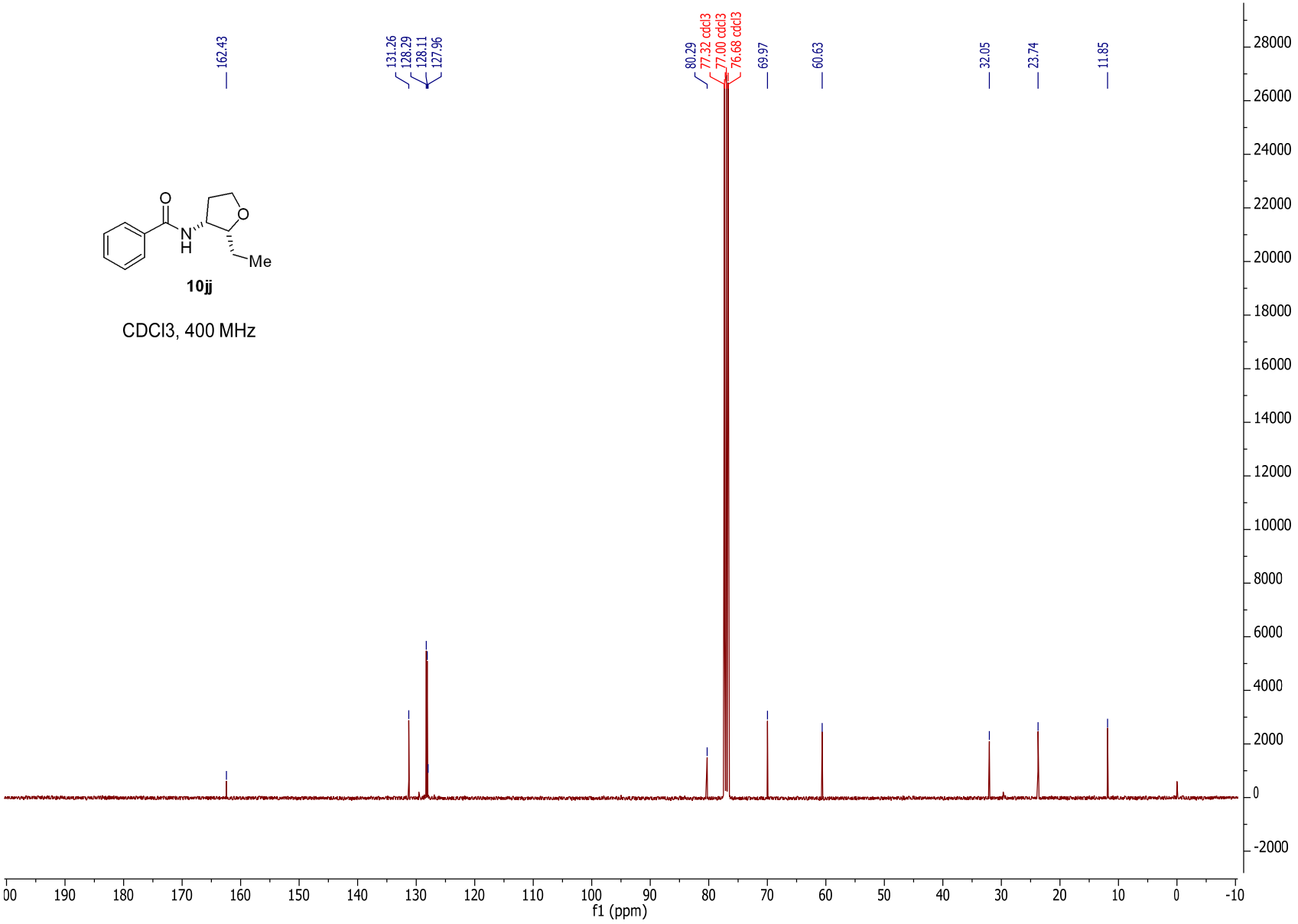

OH
H
N
O
Me
OMe
10i- dr A
CDCl3, 500 MHz
7.27
3.83
3.82
3.81
3.67
2.33
2.31
2.30
2.08
2.06
2.06
2.02
1.33
1.33
1.32
1.31
0.90
0.89
0.87
0.90
3.00
2.55
0.62
1.24
1.23
2.69
2.20
22.14
3.42
f1 (ppm)

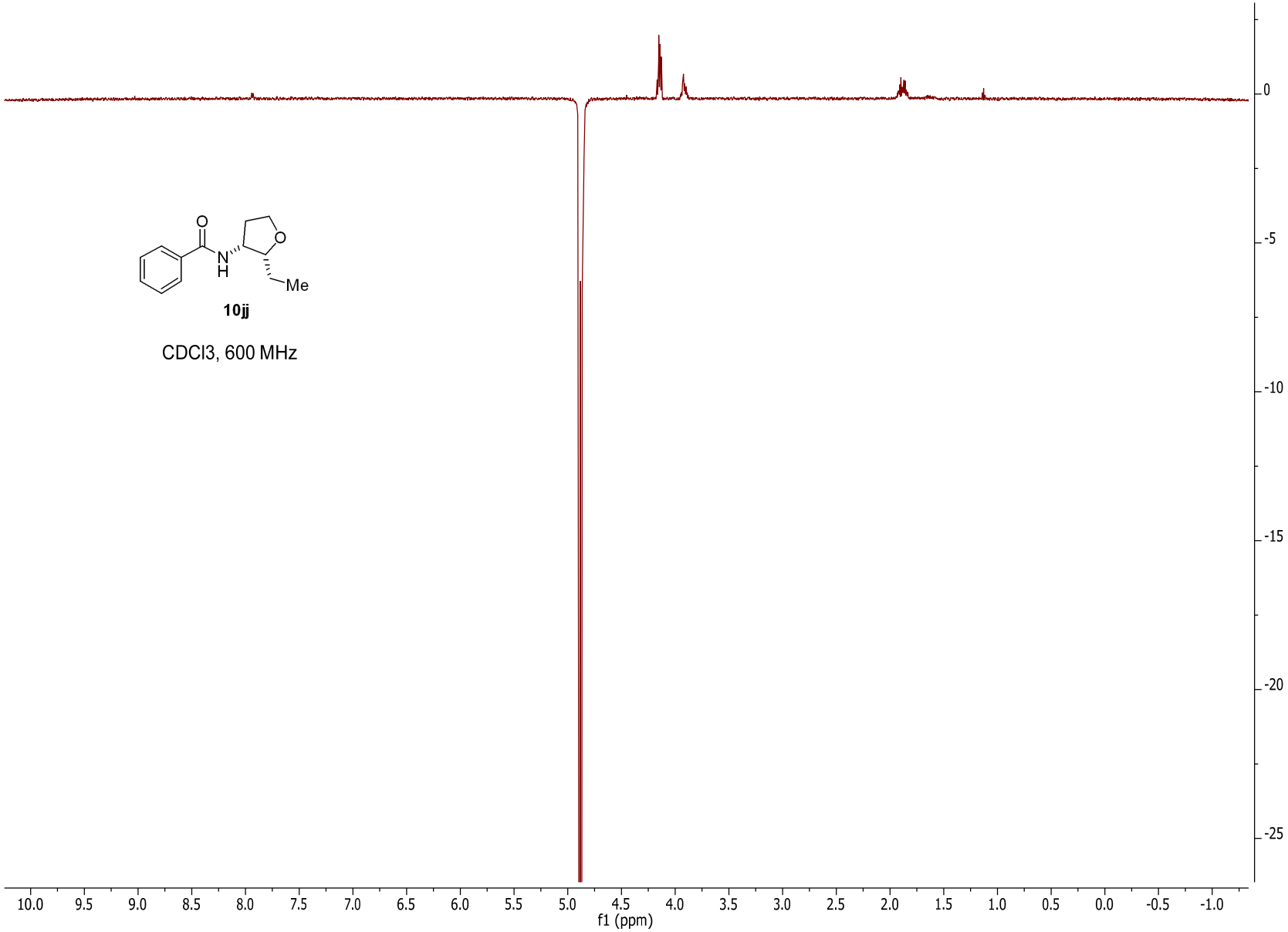

7.27
3.90
3.89
3.68
2.33
2.31
2.30
1.64
1.63
1.61
1.50
1.47
1.46
1.44
1.43
1.43
1.41
1.41
1.40
1.39
1.38
1.38
1.37
1.36
1.35
1.34
1.33
1.32
1.32
1.31
1.30
1.29
1.29
1.27
1.26
0.90
0.89
0.87
OH
H
N
O
Me
OMe
10i- dr B
CDCl3, 500 MHz
0.87
3.00
2.64
1.37
1.28
1.11
2.45
23.69
1.34
3.65
f1 (ppm)

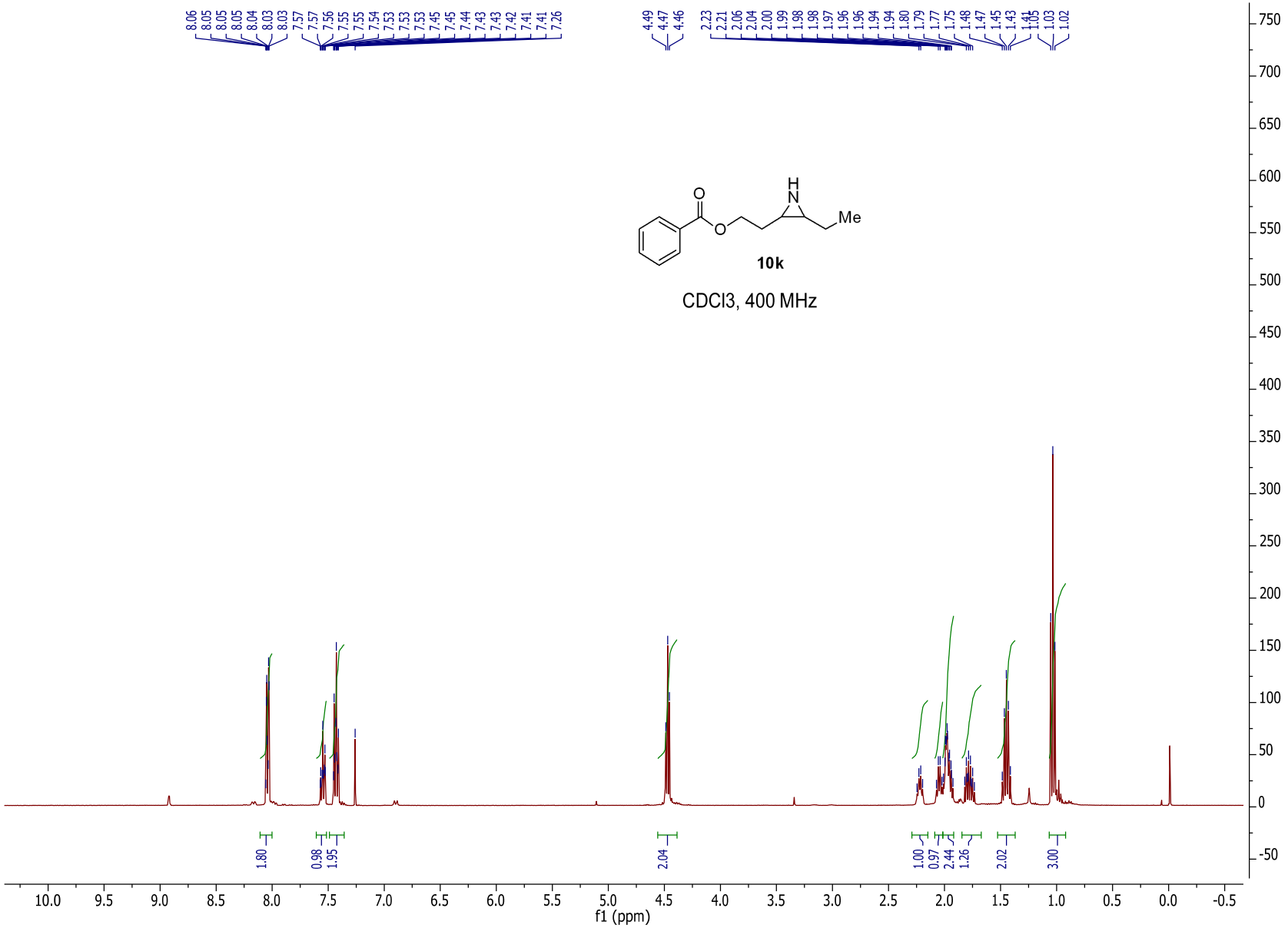

PhOCO
Me
NH
10j
CDCl3, 500 MHz
f1 (ppm)

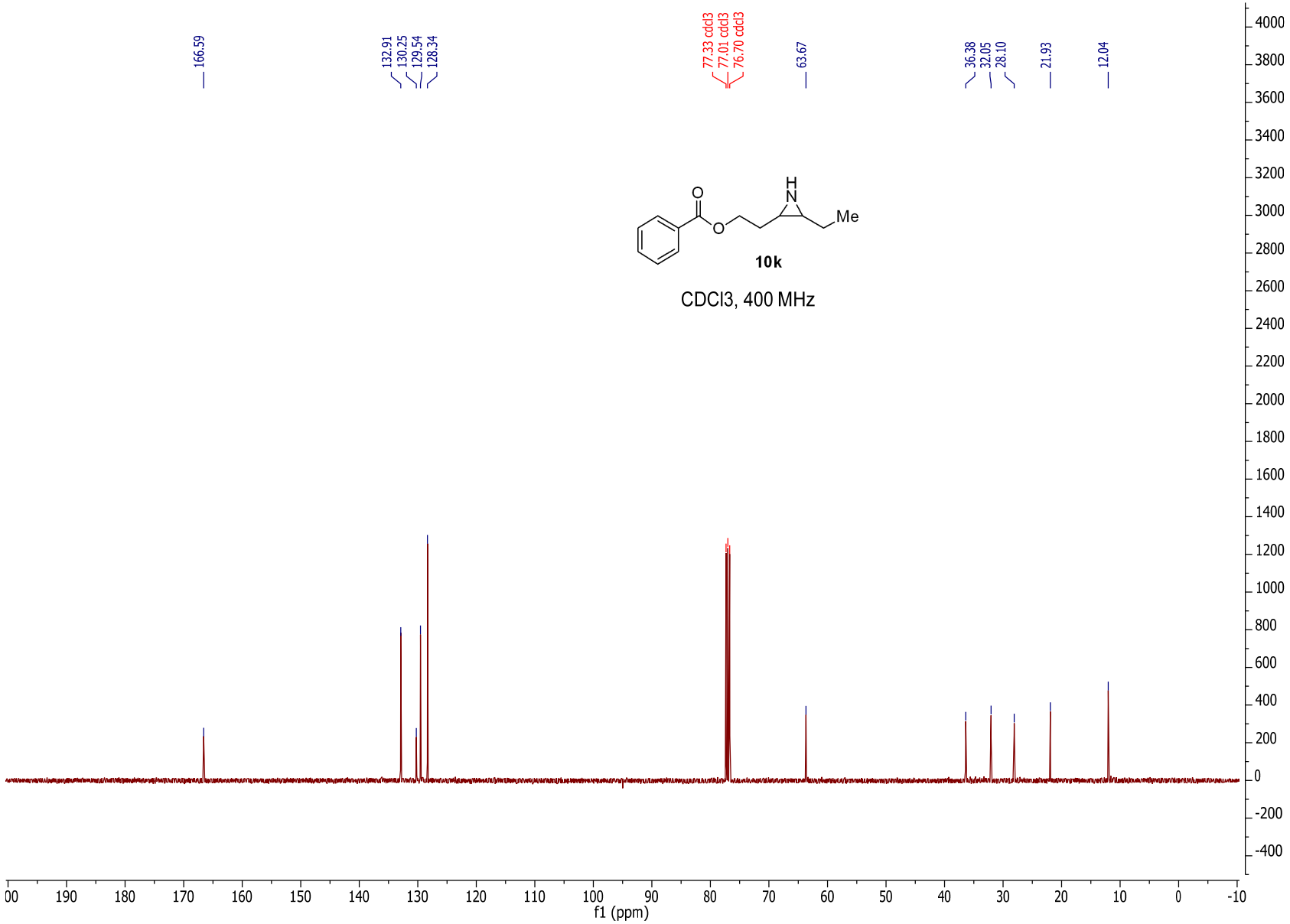

166.51
132.91
130.21
129.52
128.34
77.37 cdcl3
77.05 cdcl3
76.73 cdcl3
63.40
39.07
34.44
33.47
27.29
11.61
PhOCO
Me
NH
10j
CDCl3, 500 MHz
f1 (ppm)

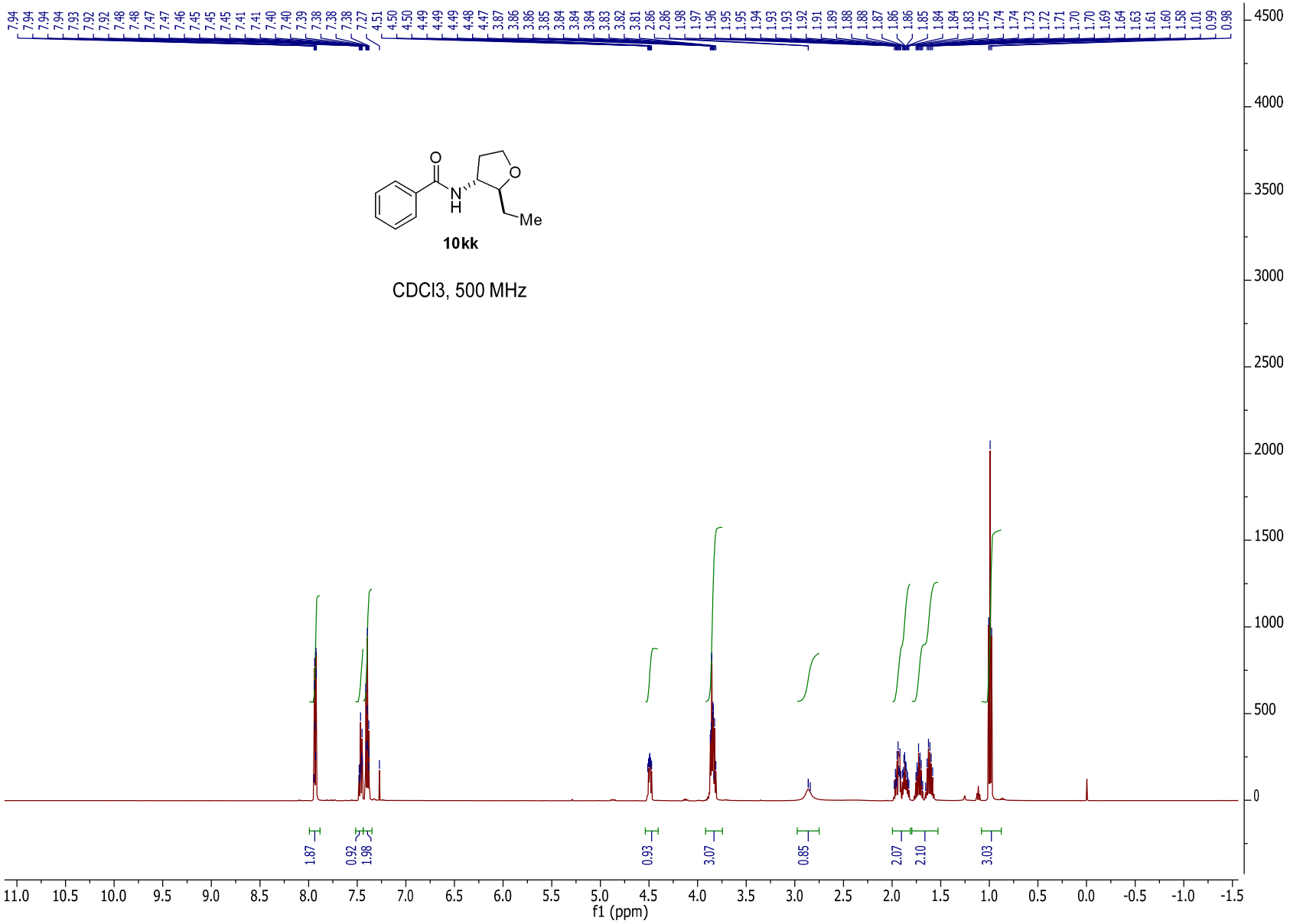

10jj
CDCl3, 500 MHz
Me
f1 (ppm)

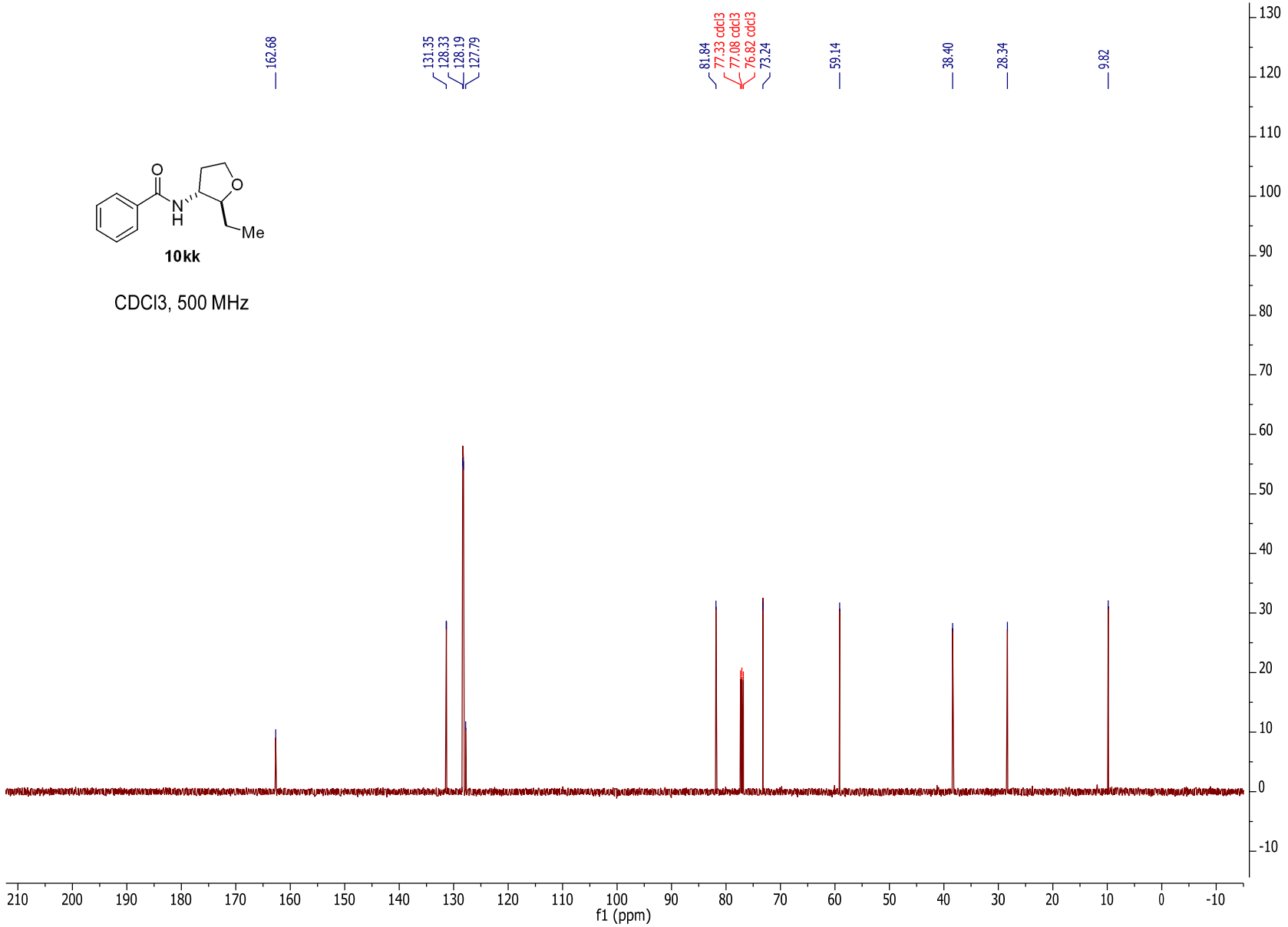

162.43
131.26
128.29
128.11
127.96
80.29
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
69.97
60.63
32.05
23.74
11.85
O
N
H
O
Me
10jj
CDCl3, 400 MHz
f1 (ppm)

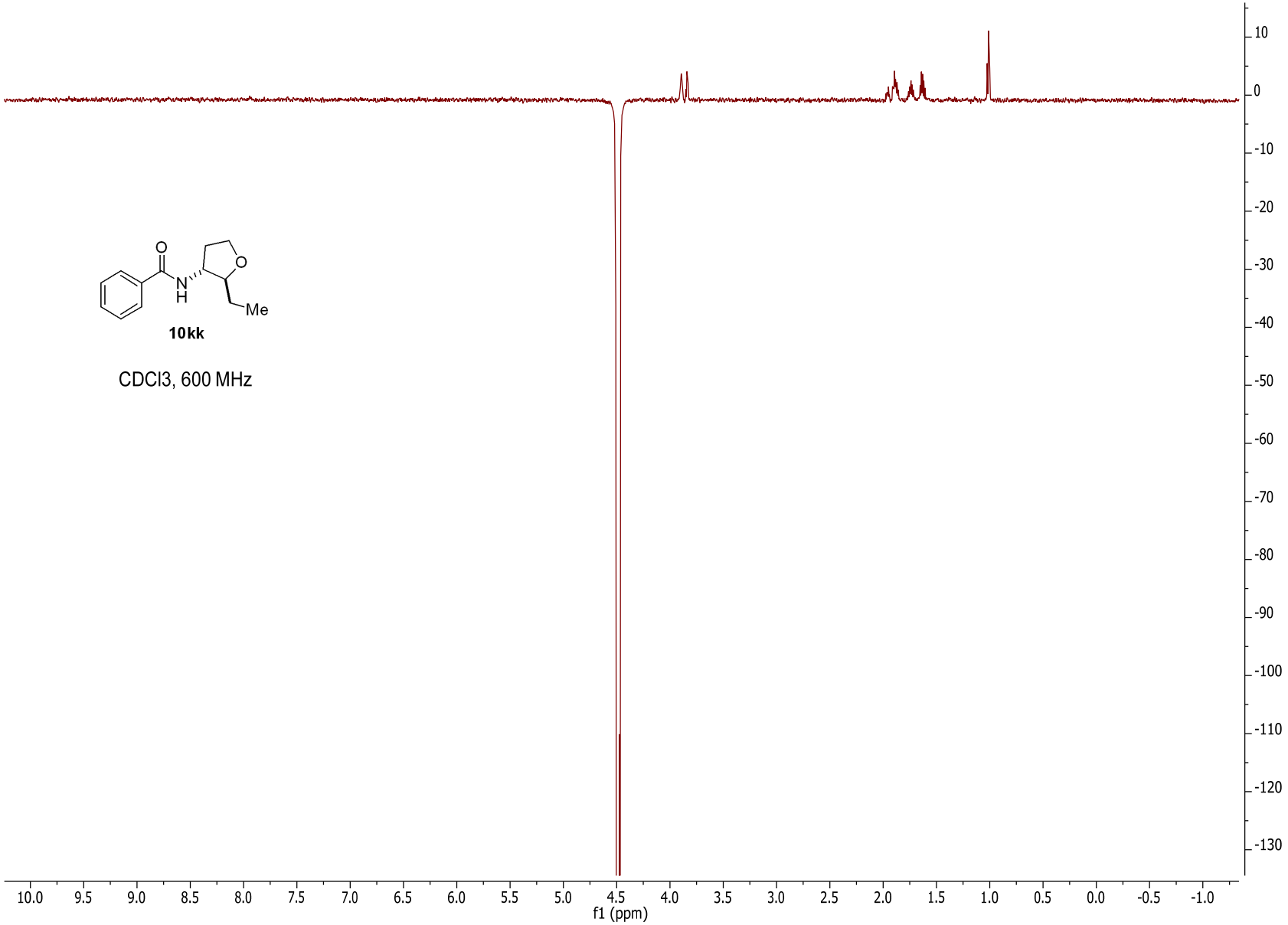

O
N
H
O
Me
10jj
CDCl3, 600 MHz
0
-5
-10
-15
-20
-25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

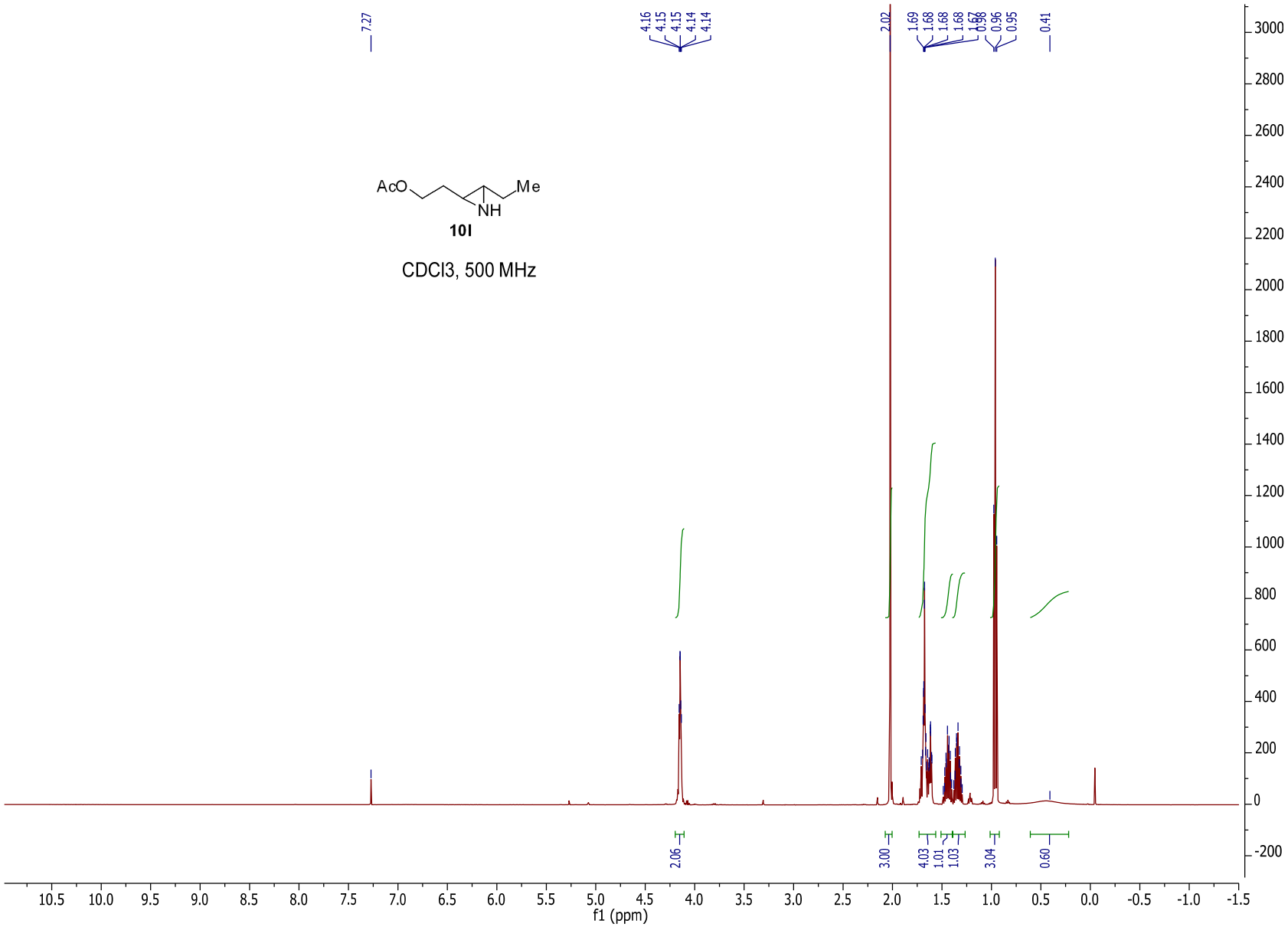

8.06 8.05 8.05 8.05 8.04 8.03 8.03 7.57 7.57 7.56 7.55 7.55 7.54 7.53 7.53 7.53 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.26
4.49 4.47 4.46 2.23 2.21 2.06 2.04 2.00 1.99 1.98 1.98 1.97 1.96 1.96 1.94 1.94 1.80 1.79 1.77 1.75 1.48 1.47 1.45 1.43 1.41 1.05 1.03 1.02
O
O
H
N
Me
10k
CDCl3, 400 MHz
1.80
0.98
1.95
2.04
1.00
0.97
2.44
1.26
2.02
3.00
f1 (ppm)

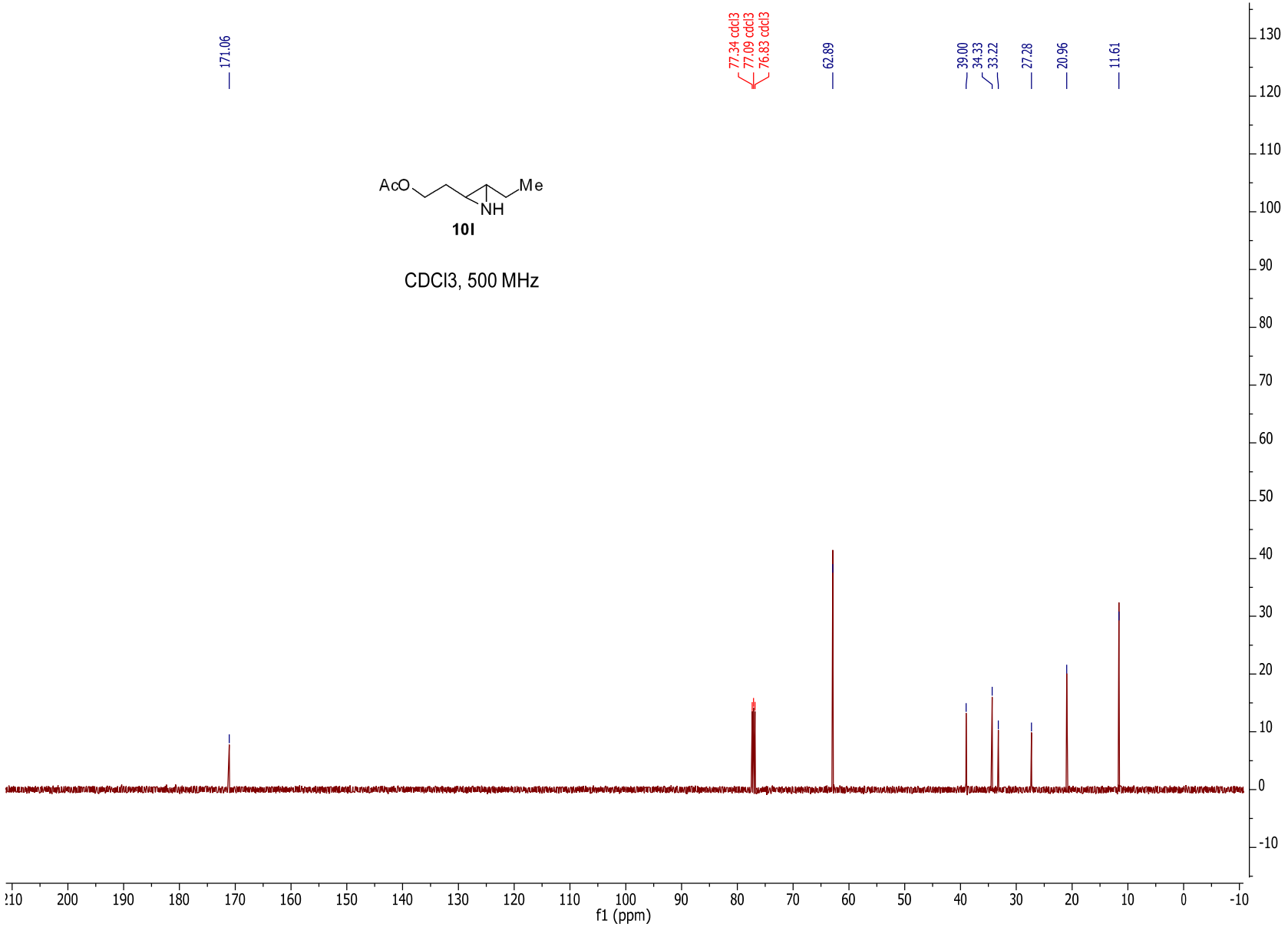

166.59
132.91
130.25
129.54
128.34
77.33 cdcl3
77.01 cdcl3
76.70 cdcl3
63.67
36.38
32.05
28.10
21.93
12.04
O
O
H
N
Me
10k
CDCl3, 400 MHz
f1 (ppm)

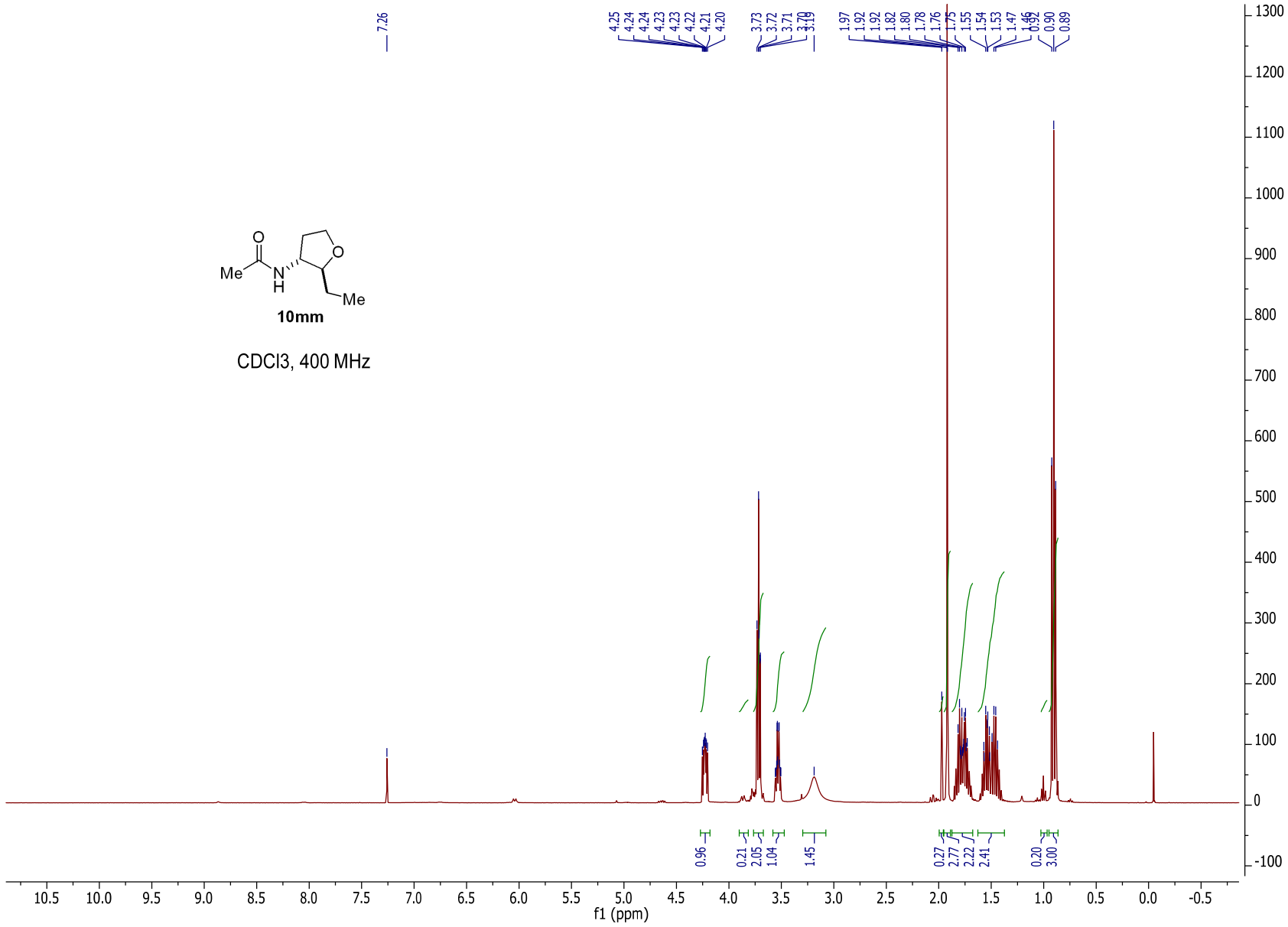

10kk
CDCl3, 500 MHz
f1 (ppm)

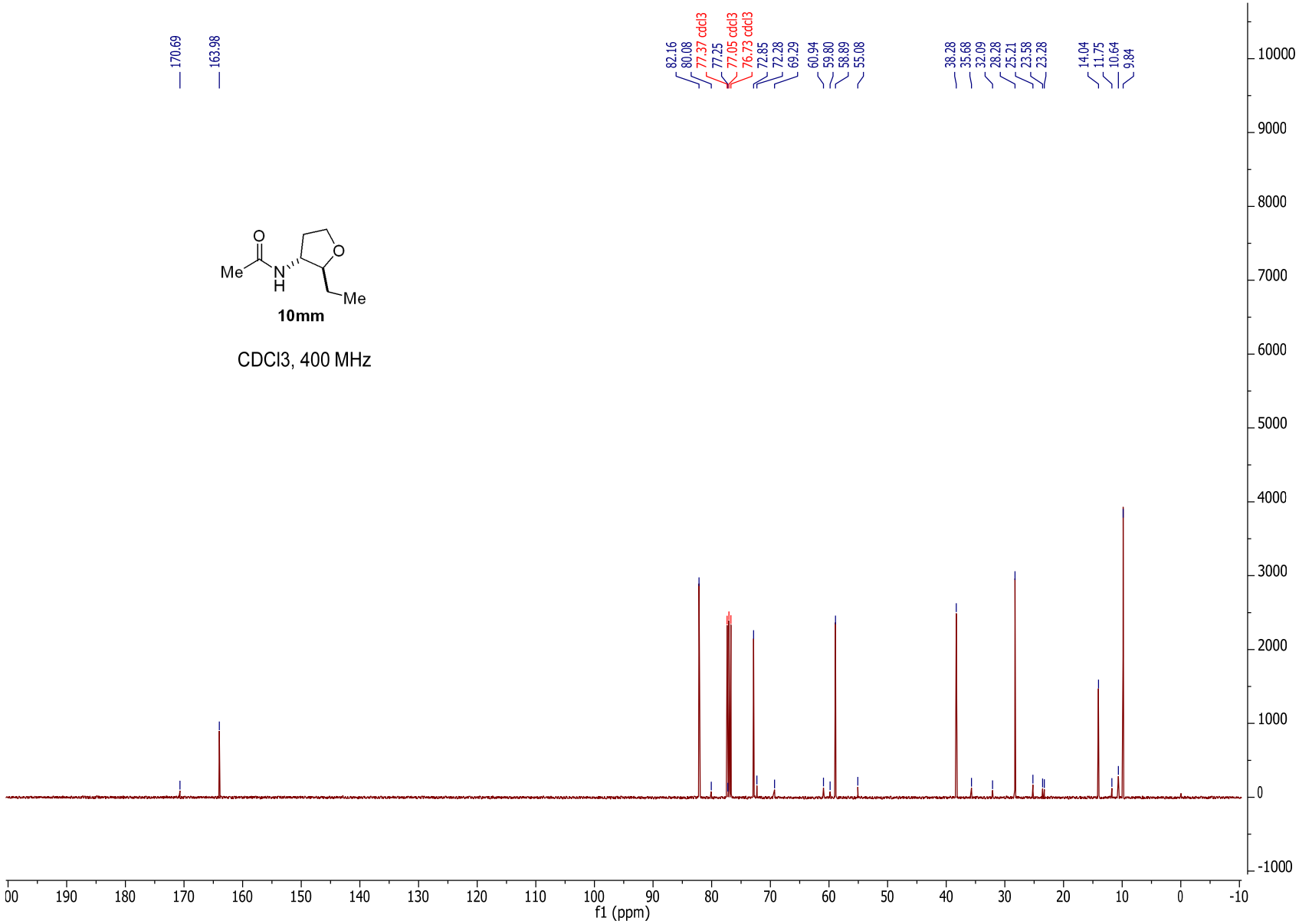

162.68
131.35
128.33
128.19
127.79
81.84
77.33 cdcl3
77.08 cdcl3
76.82 cdcl3
73.24
59.14
38.40
28.34
9.82
O
N
H
O
Me
10kk
CDCl3, 500 MHz
f1 (ppm)

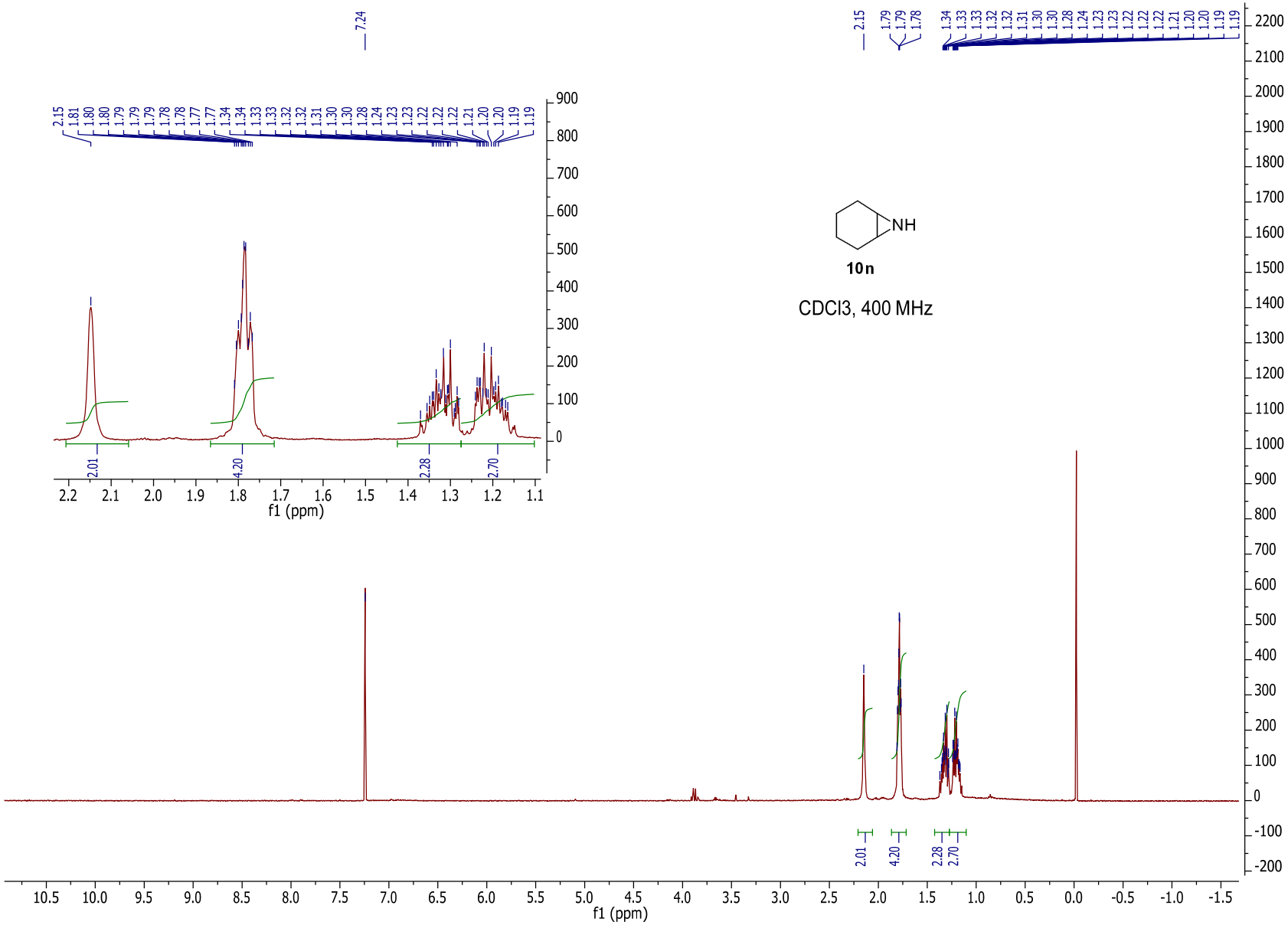

O
N
H
O
Me
10kk
CDCl3, 600 MHz
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

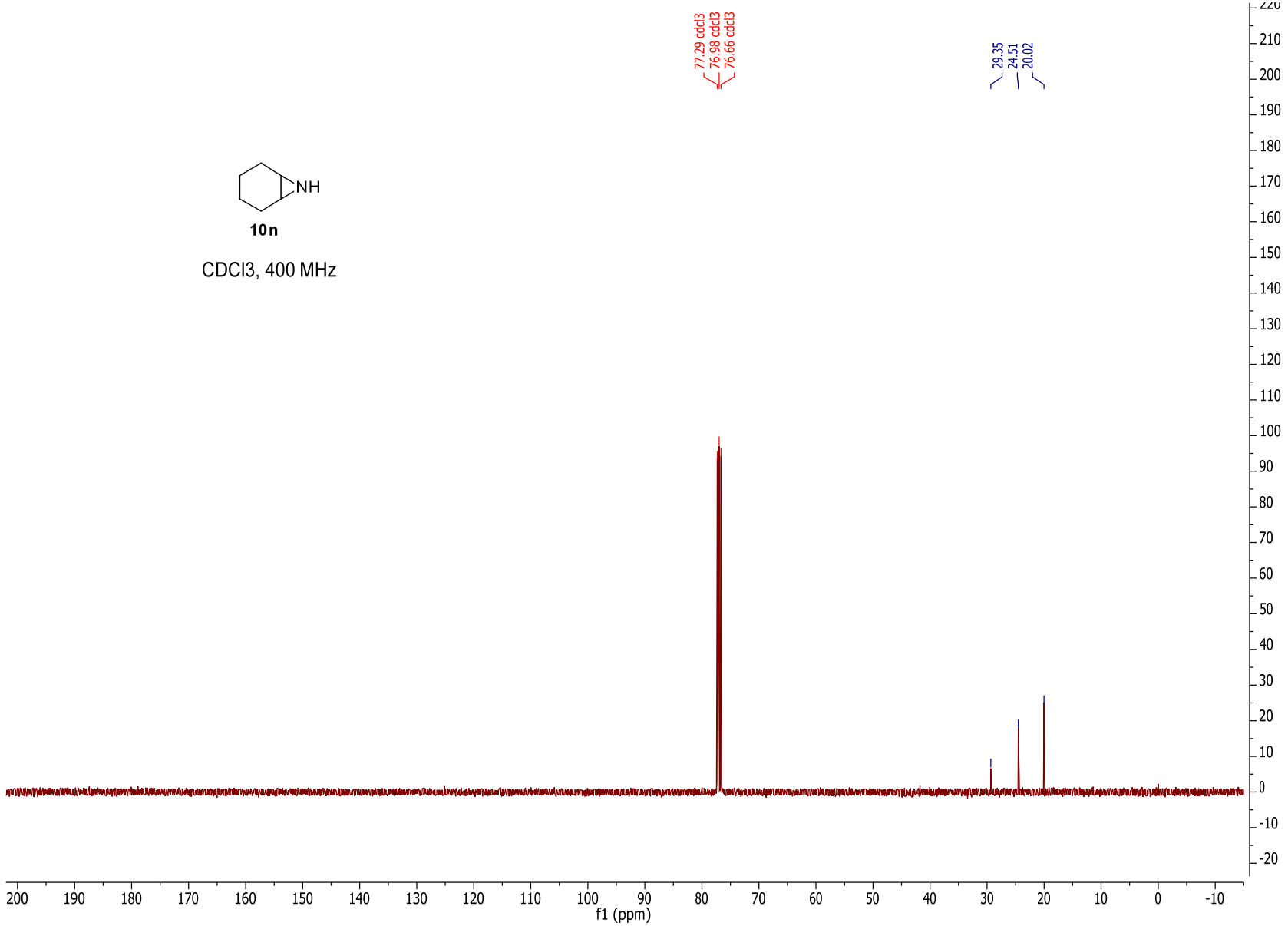

7.27
4.16
4.15
4.15
4.14
4.14
2.02
1.69
1.68
1.68
1.68
0.98
0.96
0.95
0.41
AcO
Me
NH
10l
CDCl3, 500 MHz
2.06
3.00
4.03
1.01
1.03
3.04
0.60
f1 (ppm)

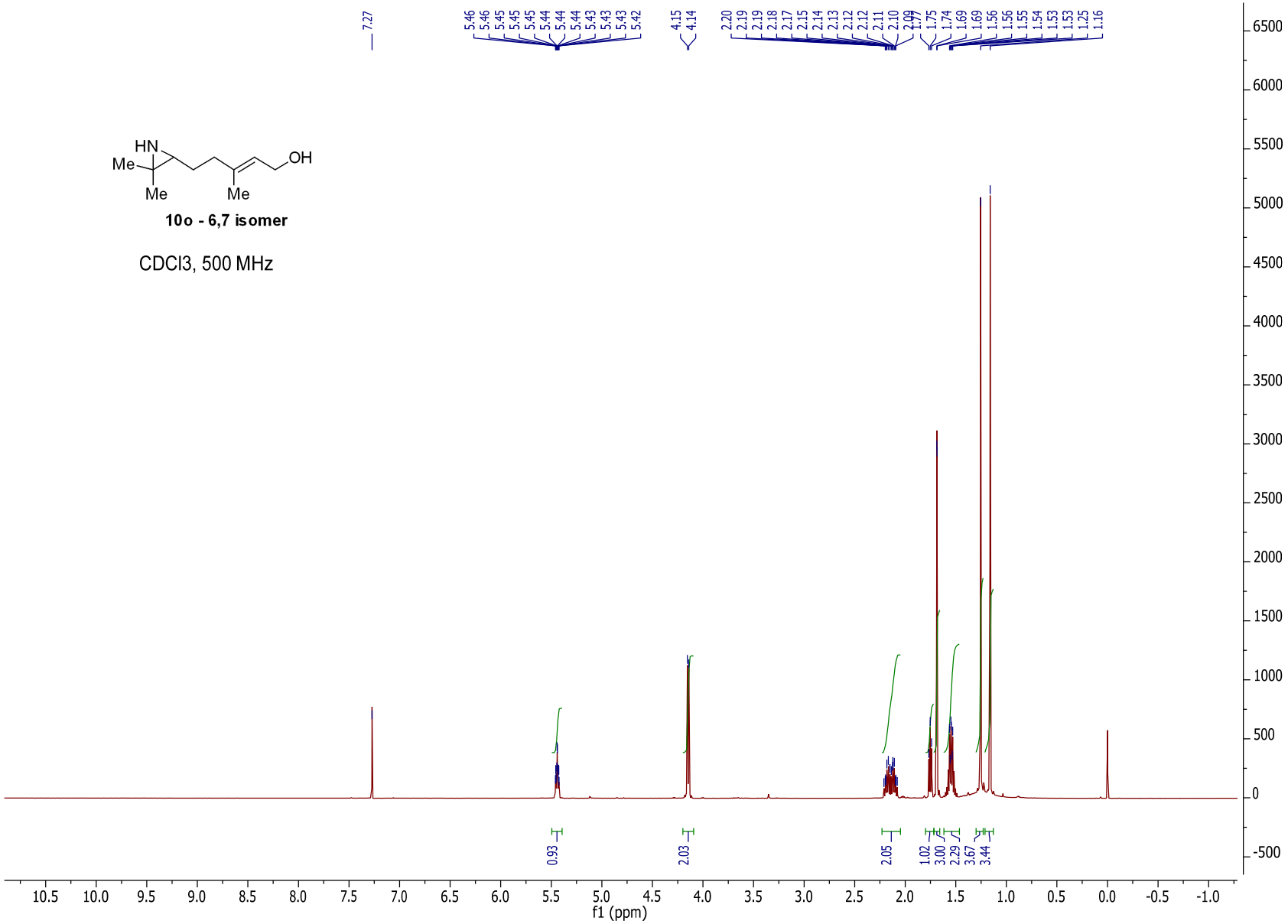

171.06
77.34 cdcl3
77.09 cdcl3
76.83 cdcl3
62.89
39.00
34.33
33.22
27.28
20.96
11.61
AcO
Me
NH
10l
CDCl3, 500 MHz
f1 (ppm)

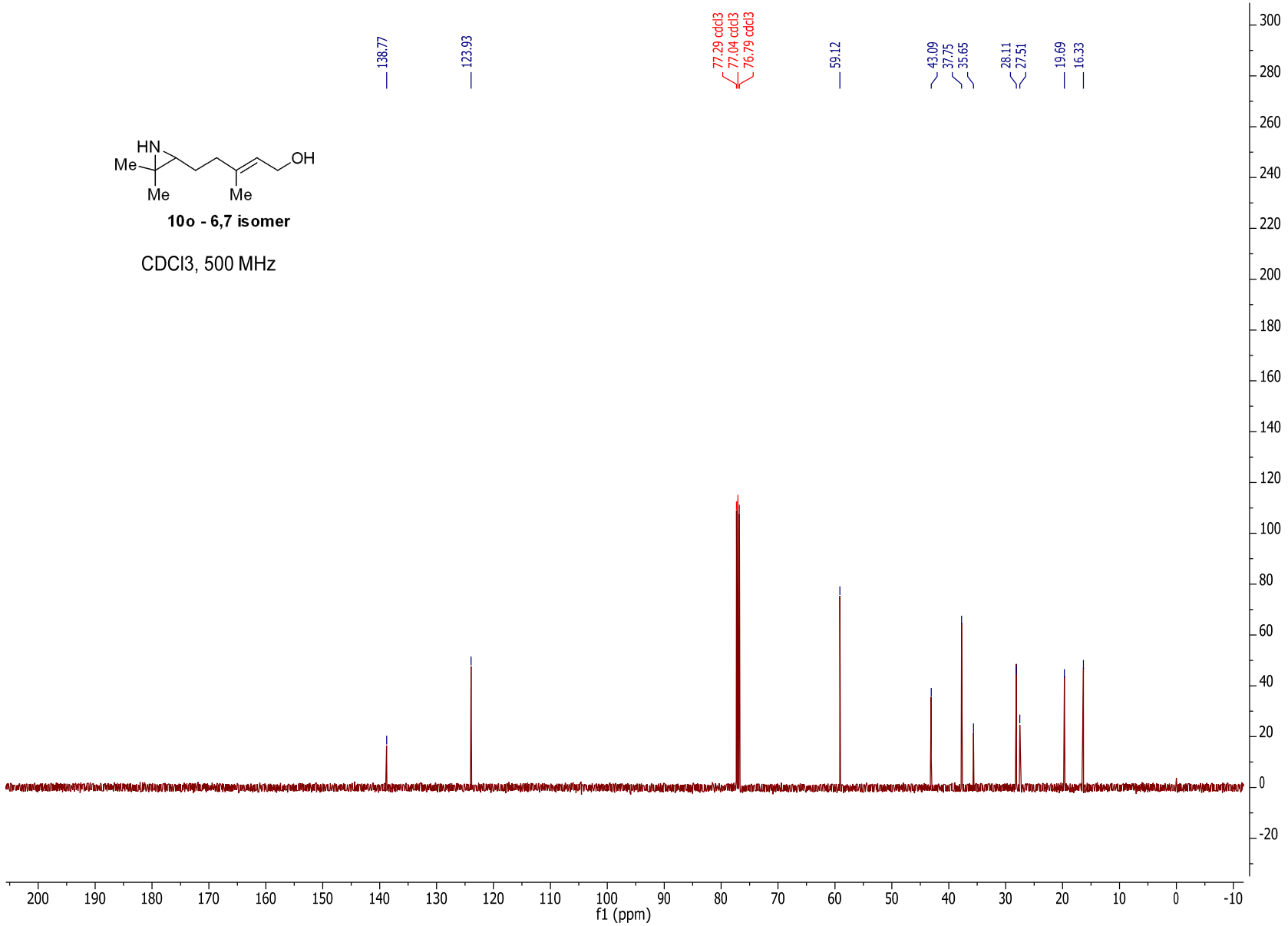

10mm
CDCl3, 400 MHz
f1 (ppm)

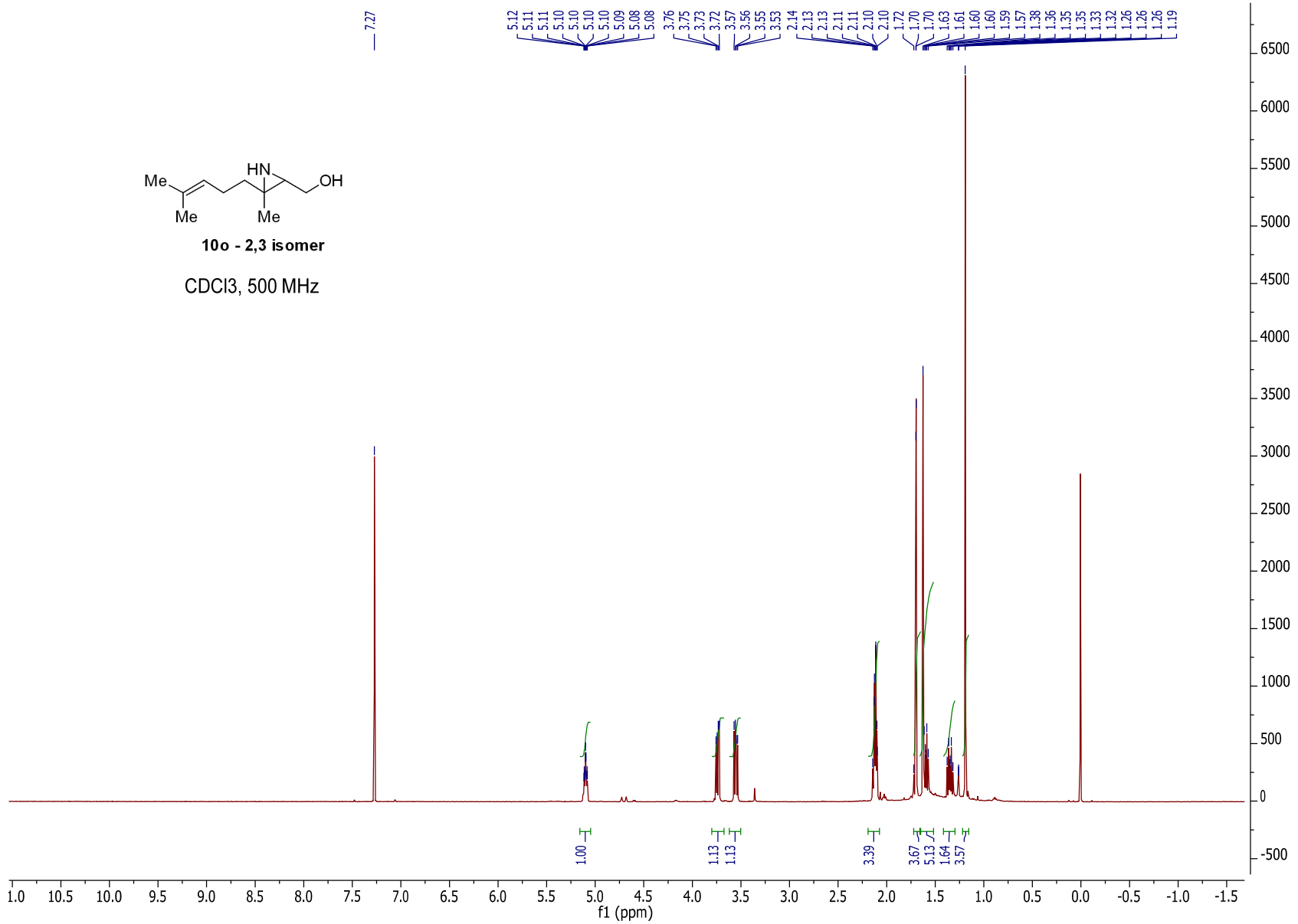

170.69
163.98
82.16
80.08
77.37 cdcl3
77.25
77.05 cdcl3
76.73 cdcl3
72.85
72.28
69.29
60.94
59.80
58.89
55.08
38.28
35.68
32.09
28.28
25.21
23.58
23.28
14.04
11.75
10.64
9.84
Me
N
H
O
O
Me
10mm
CDCl3, 400 MHz
f1 (ppm)

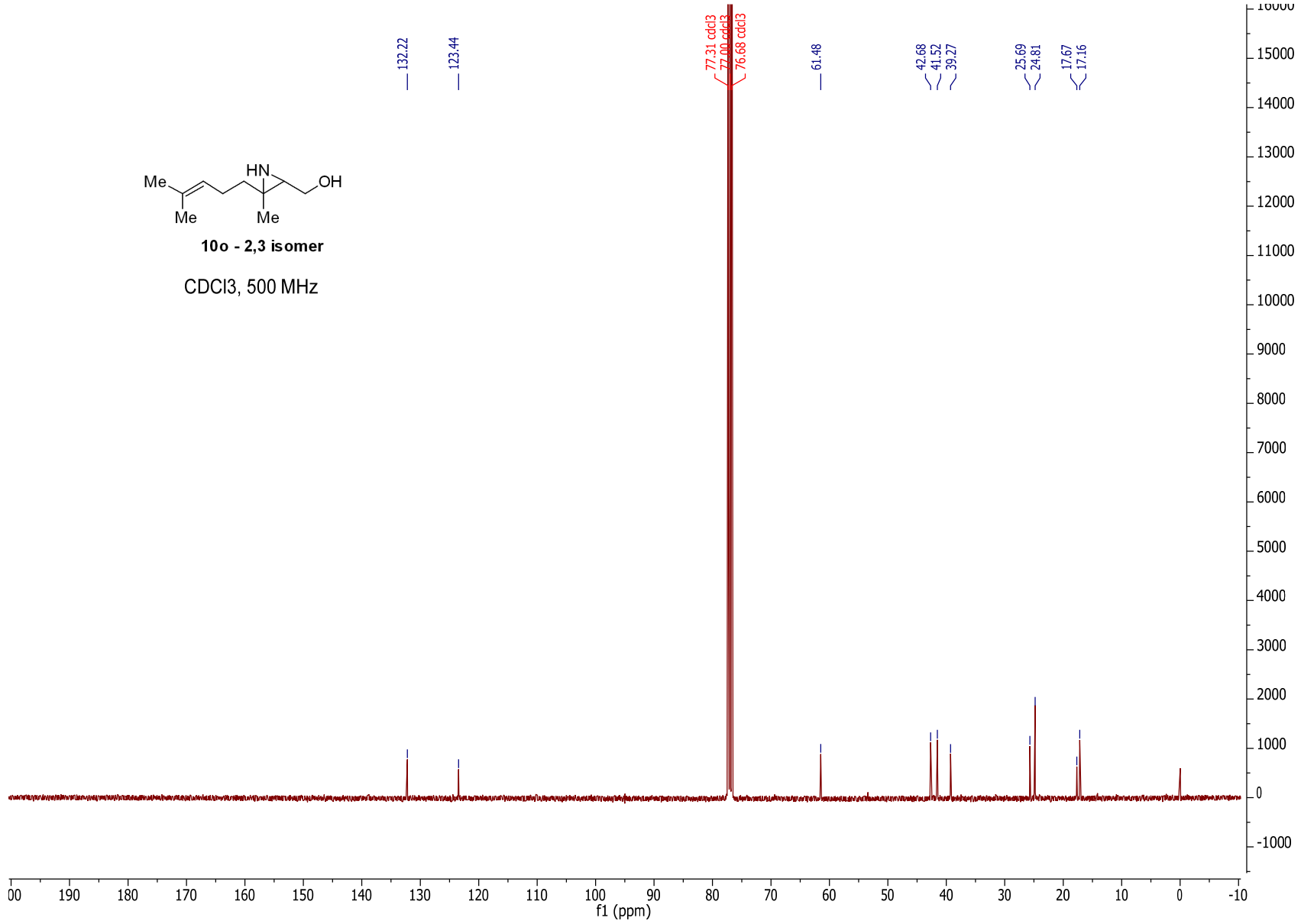

NH
10n
CDCl3, 400 MHz
f1 (ppm)

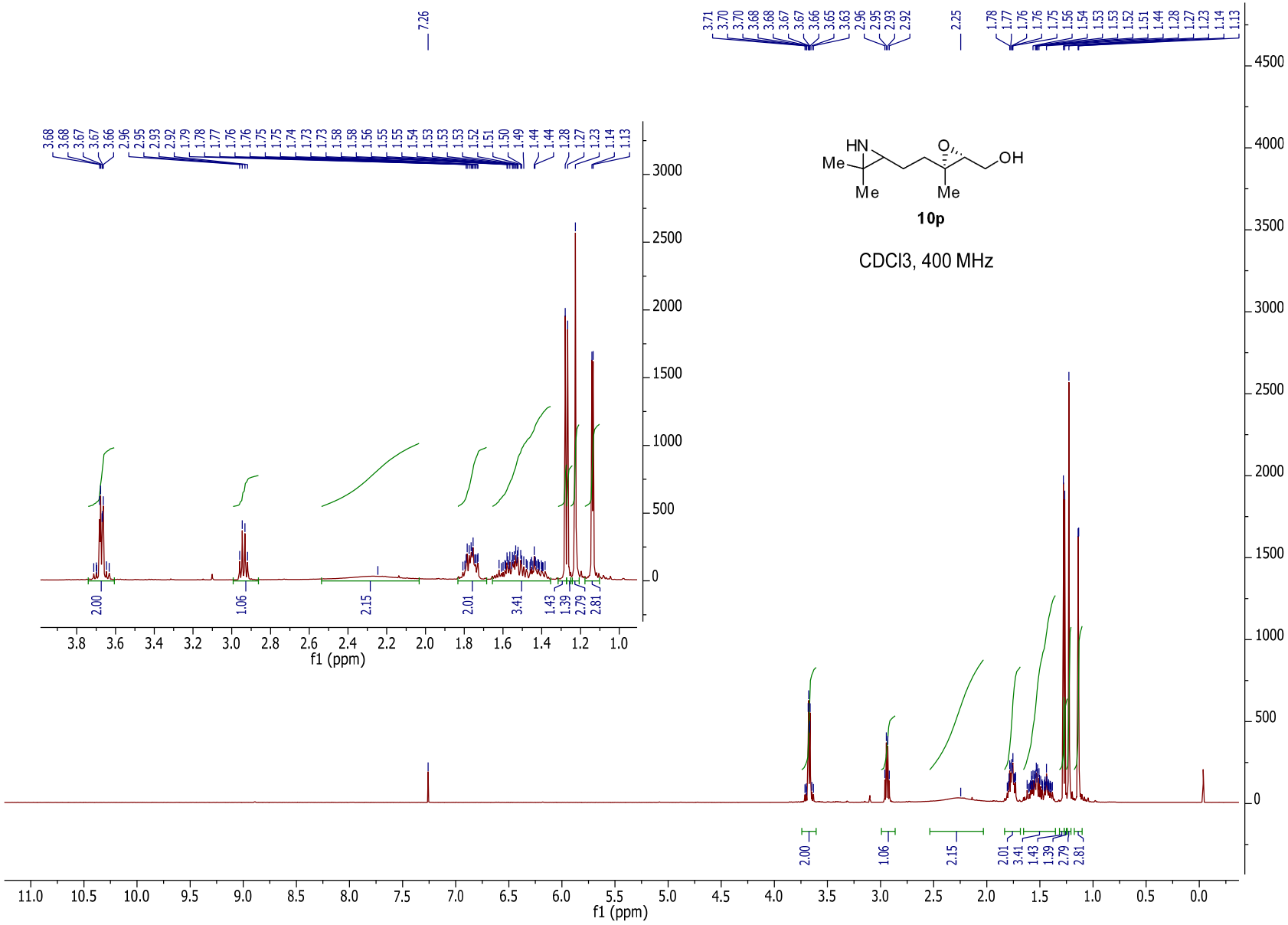

77.29 cdcl3
76.98 cdcl3
76.66 cdcl3
29.35
24.51
20.02
NH
10n
CDCl3, 400 MHz
f1 (ppm)

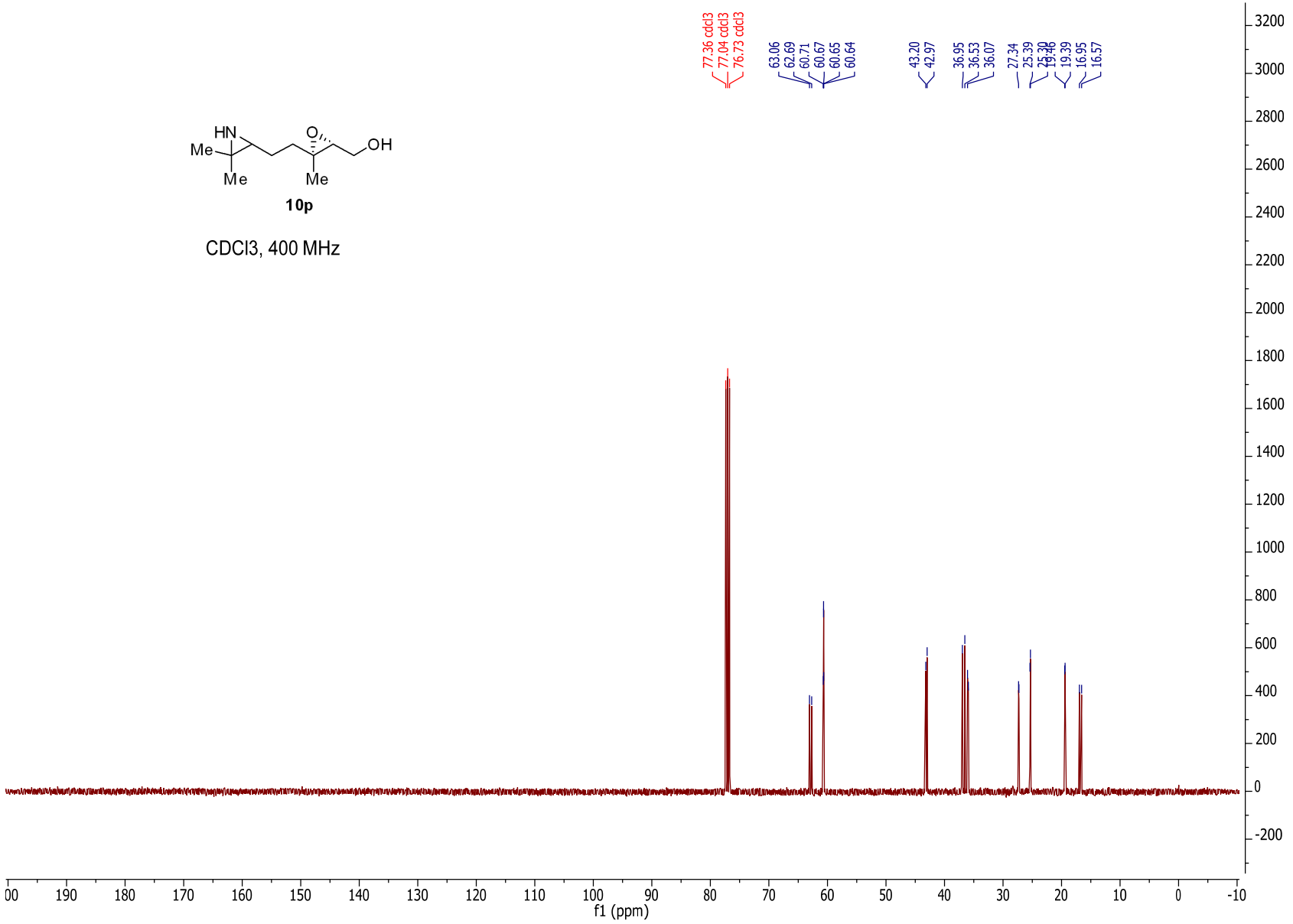

HN
Me
Me
Me
OH
10o - 6,7 isomer
CDCl3, 500 MHz
f1 (ppm)

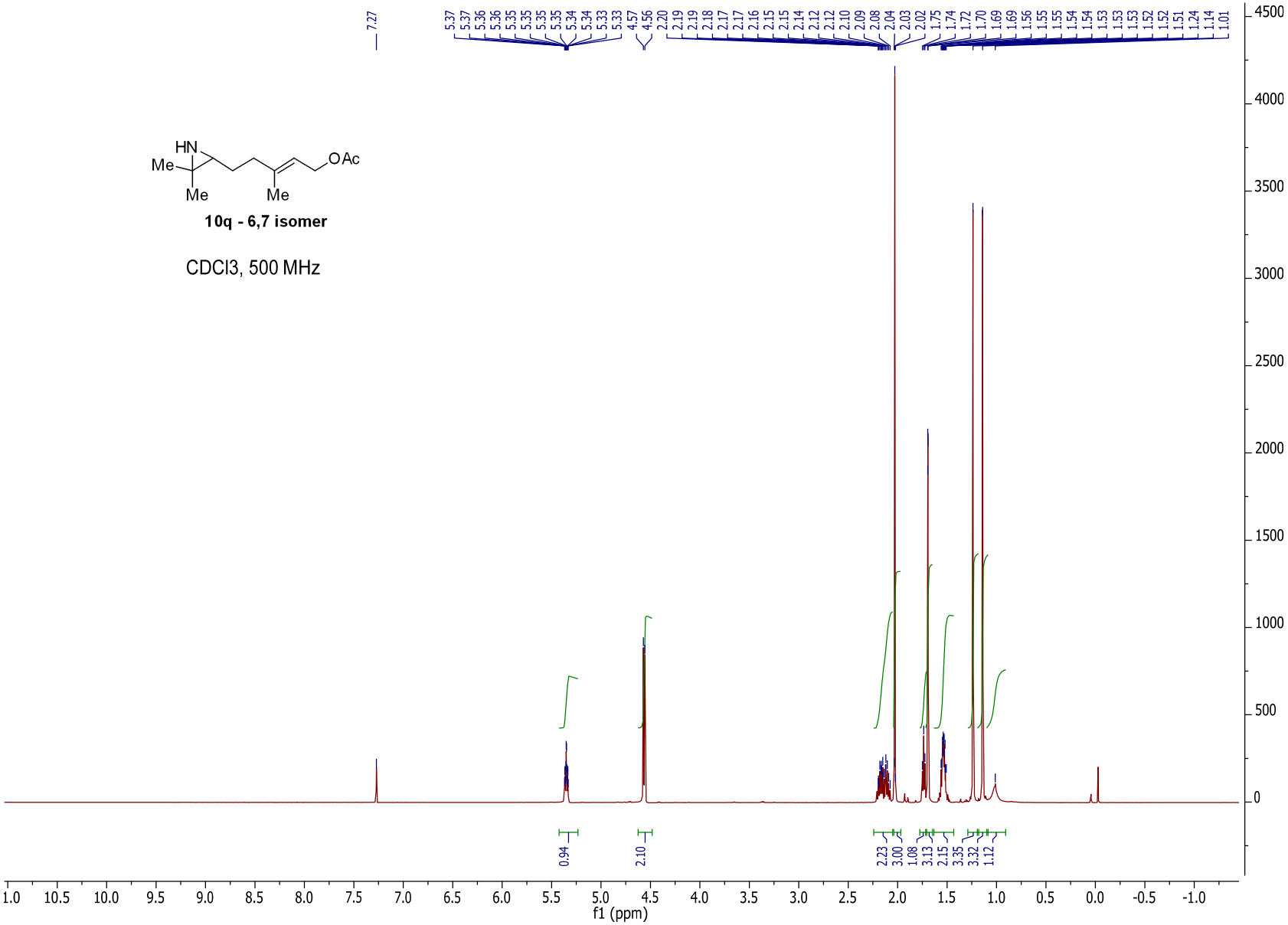

138.77
123.93
77.29 cdcl3
77.04 cdcl3
76.79 cdcl3
59.12
43.09
37.75
35.65
28.11
27.51
19.69
16.33
HN
Me
Me
Me
OH
10o - 6,7 isomer
CDCl3, 500 MHz
f1 (ppm)

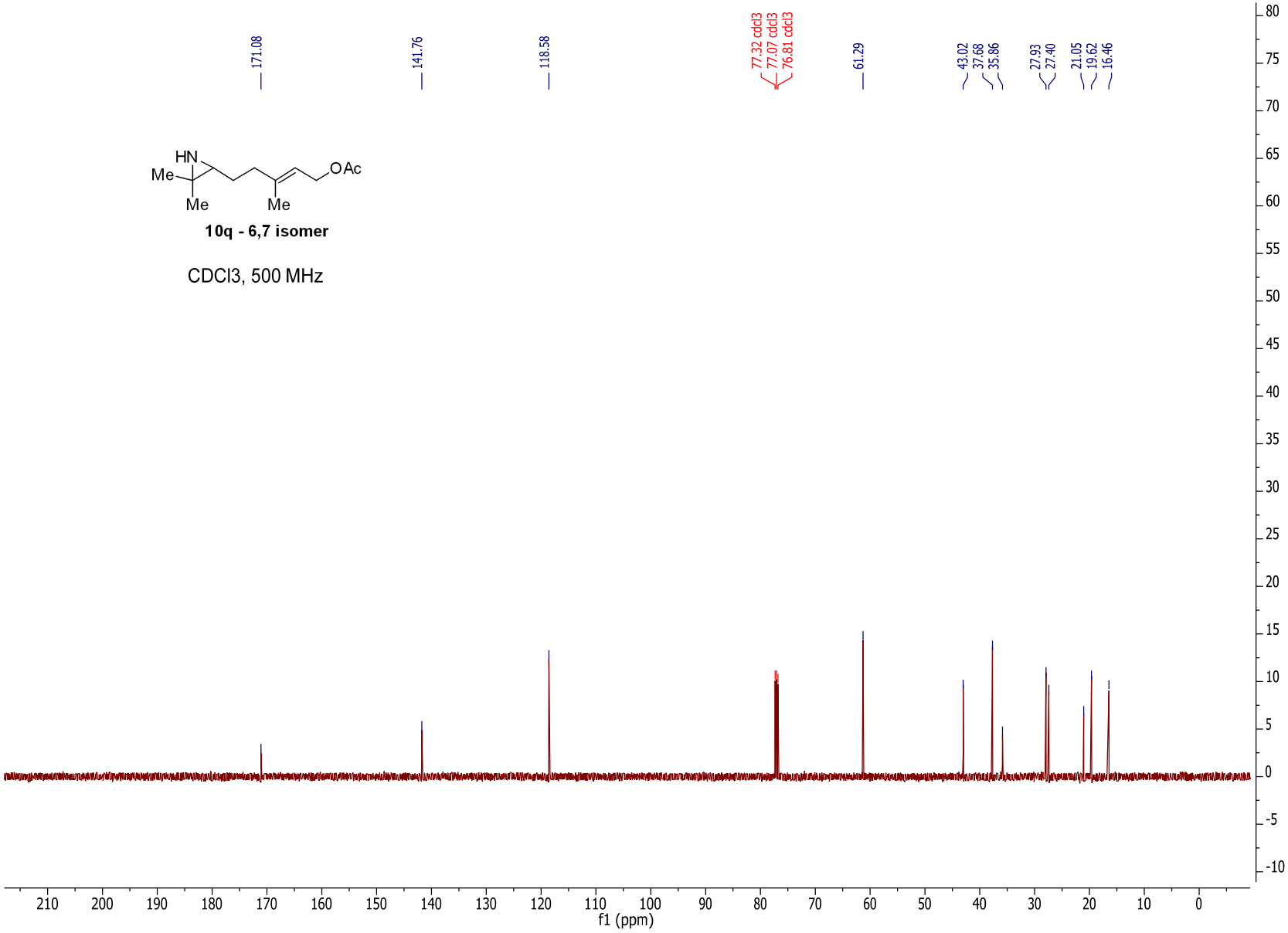

HN
Me
OH
Me
Me
10o - 2,3 isomer
CDCl3, 500 MHz
f1 (ppm)

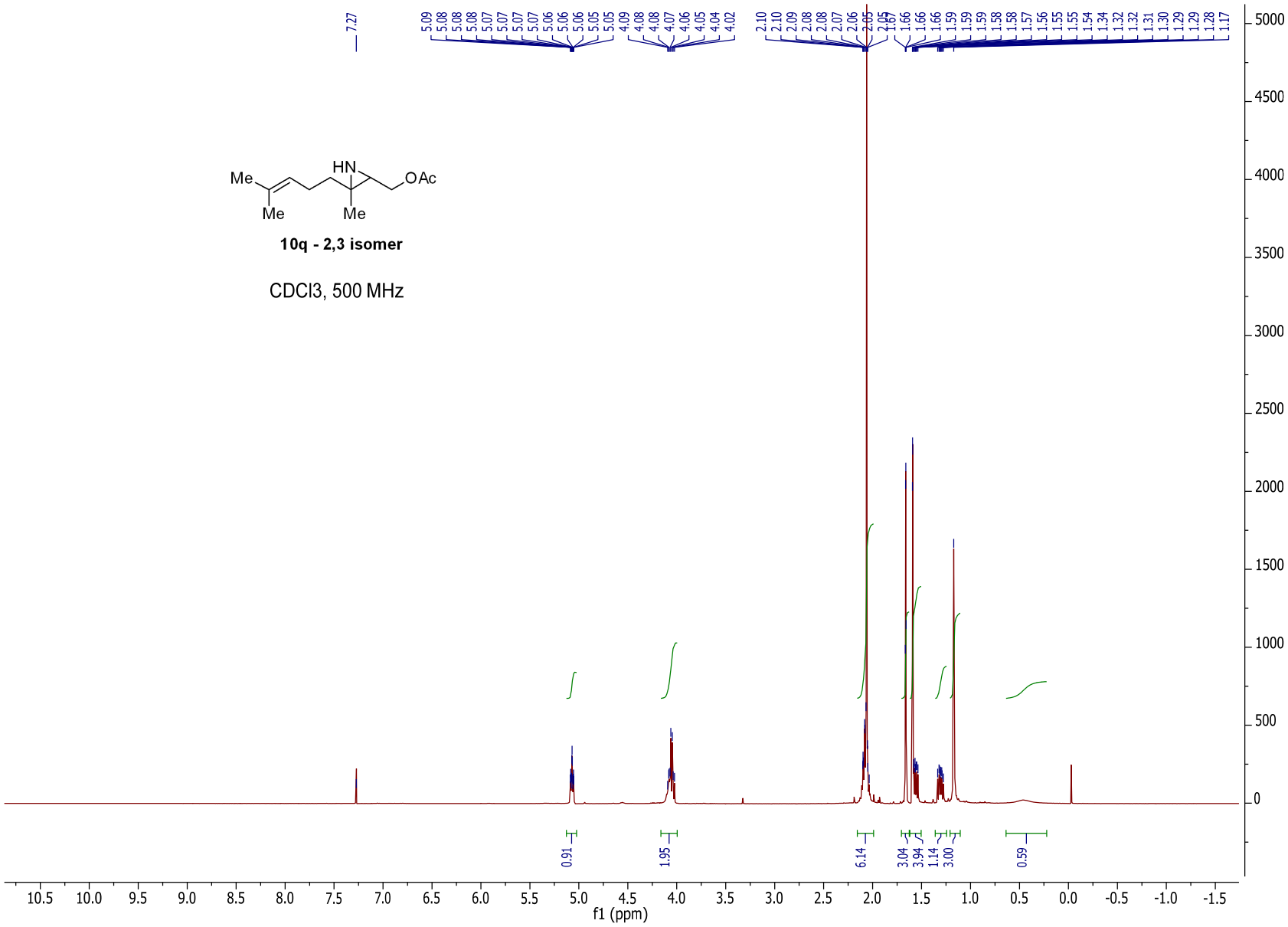

132.22
123.44
77.31 cdcl3
77.00 cdcl3
76.68 cdcl3
61.48
42.68
41.52
39.27
25.69
24.81
17.67
17.16
HN
OH
Me
Me
Me
10o - 2,3 isomer
CDCl3, 500 MHz
f1 (ppm)

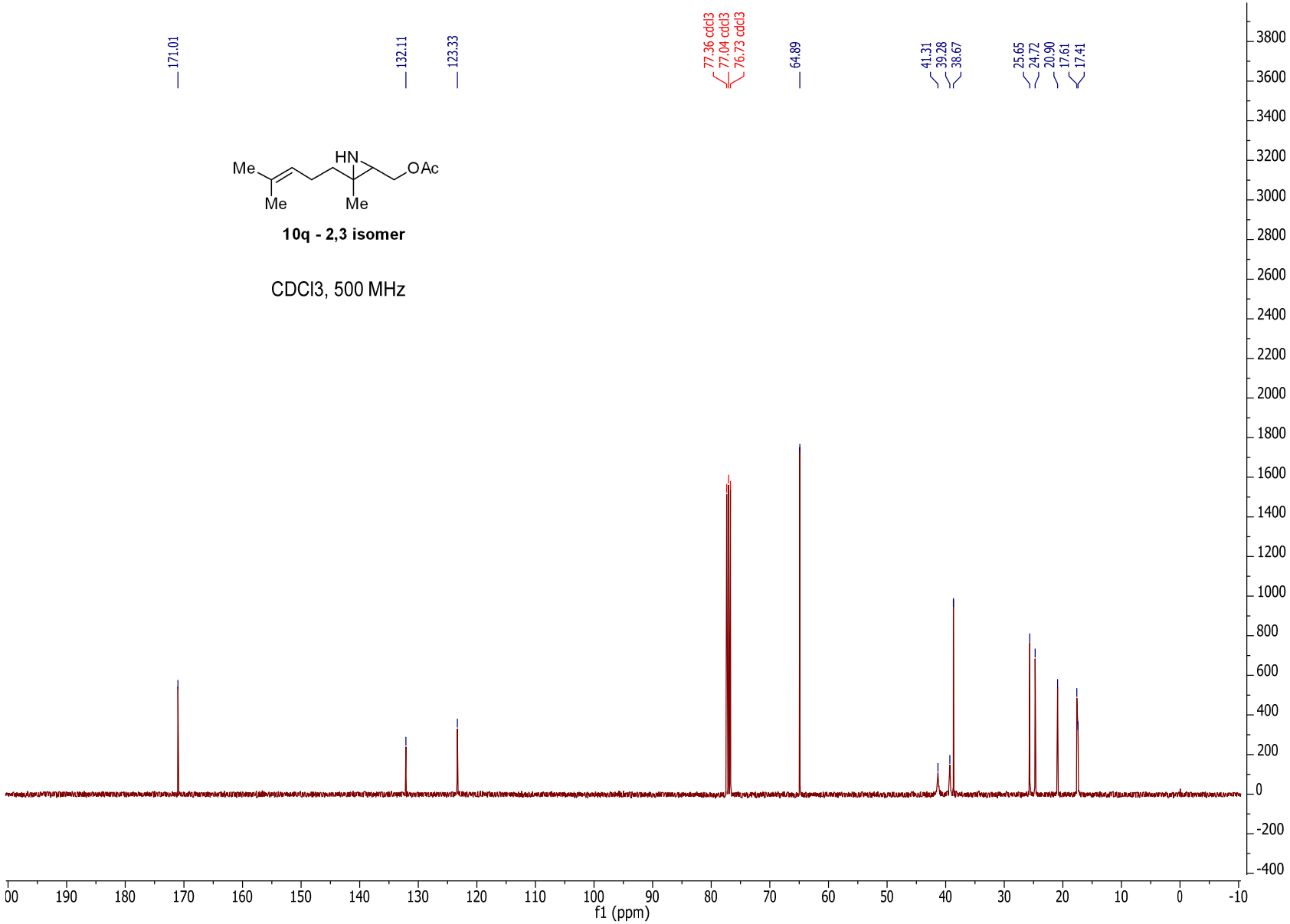

HN
Me
Me
O
OH
Me
10p
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

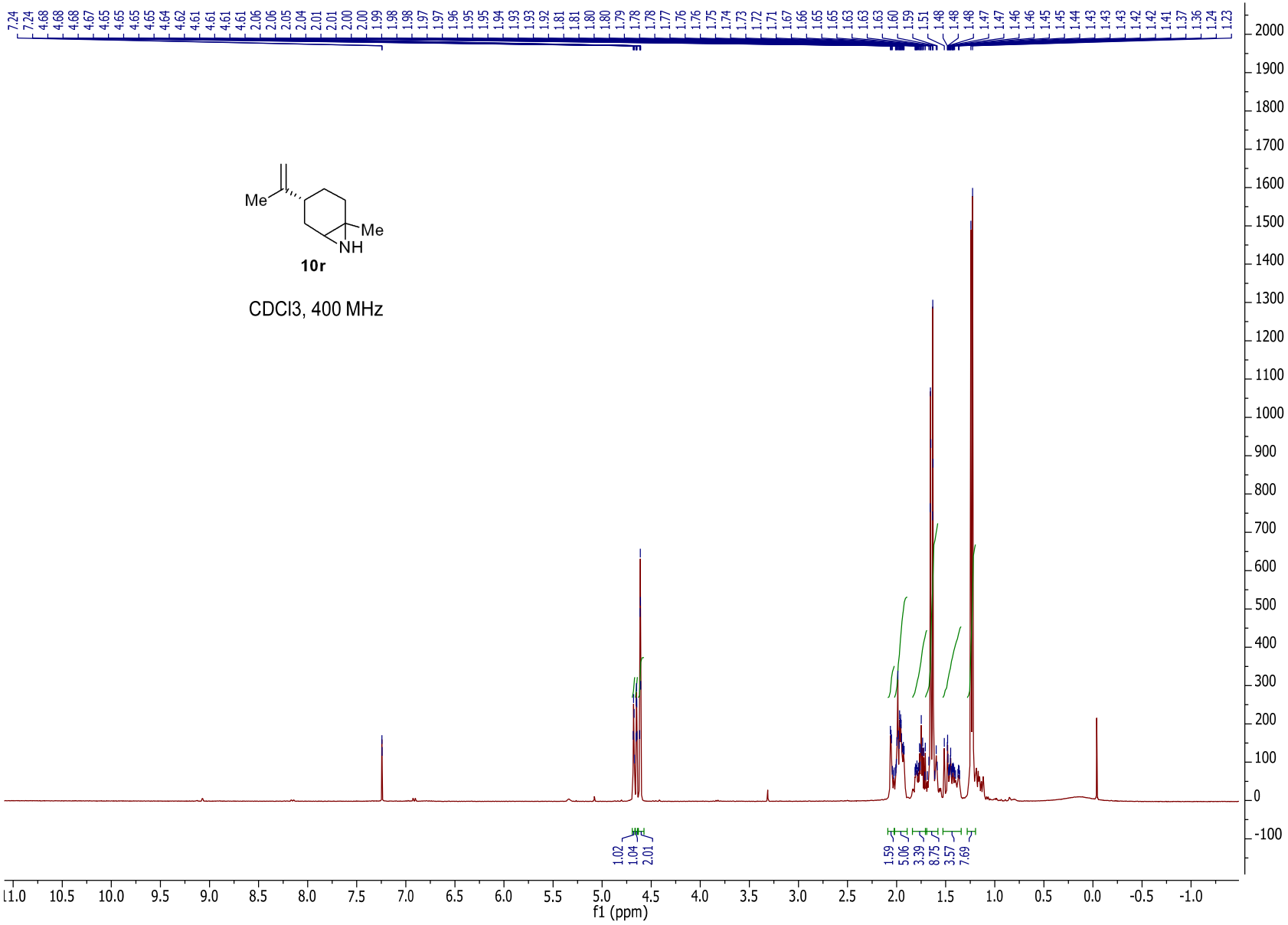

HN
Me
Me
O
Me
OH
10p
CDCl3, 400 MHz
77.36 cdcl3
77.04 cdcl3
76.73 cdcl3
63.06
62.69
60.71
60.67
60.65
60.64
43.20
42.97
36.95
36.53
36.07
27.34
25.39
19.39
16.95
16.57
f1 (ppm)

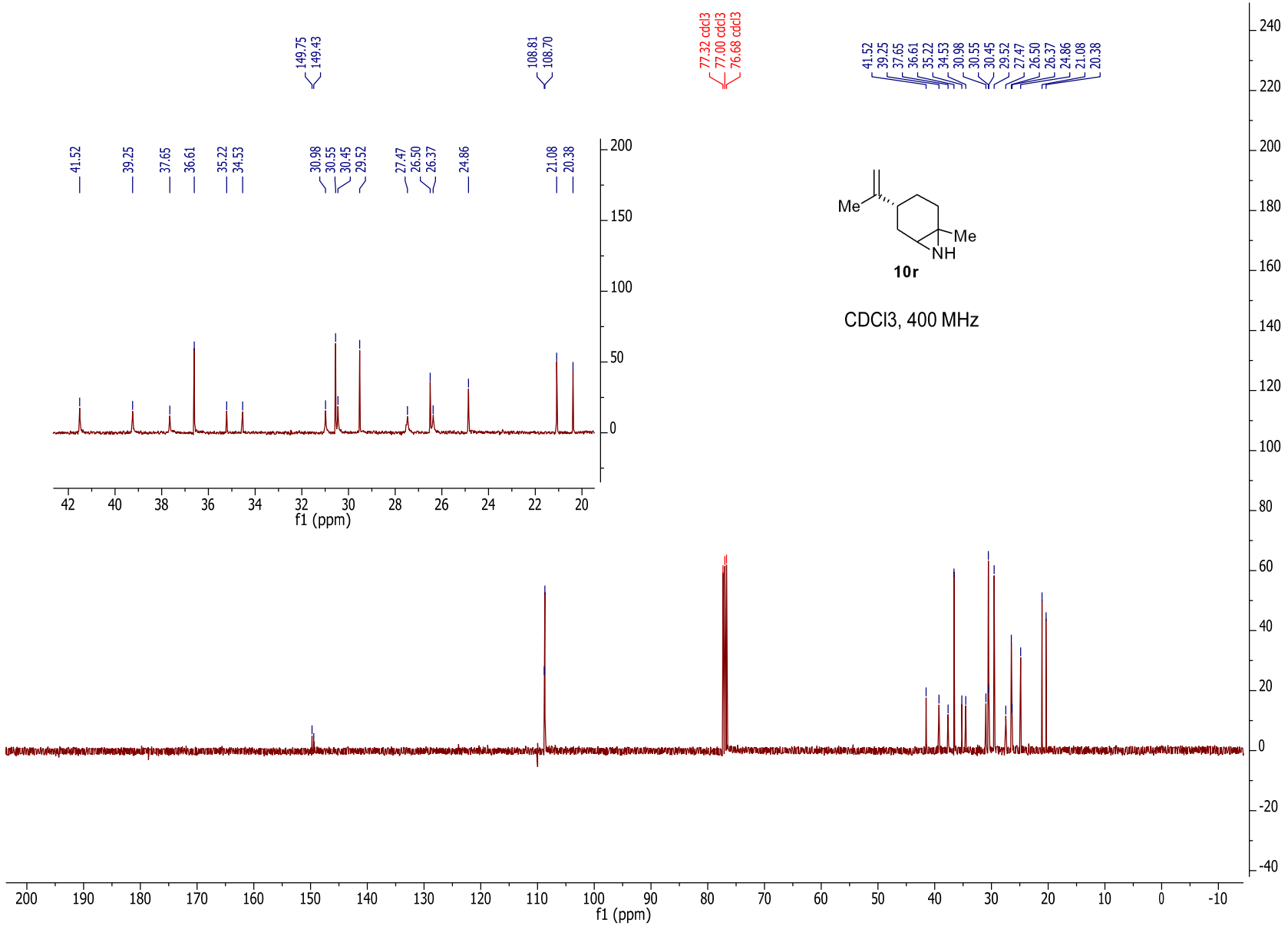

HN
Me
Me
Me
OAc
10q - 6,7 isomer
CDCl3, 500 MHz
f1 (ppm)

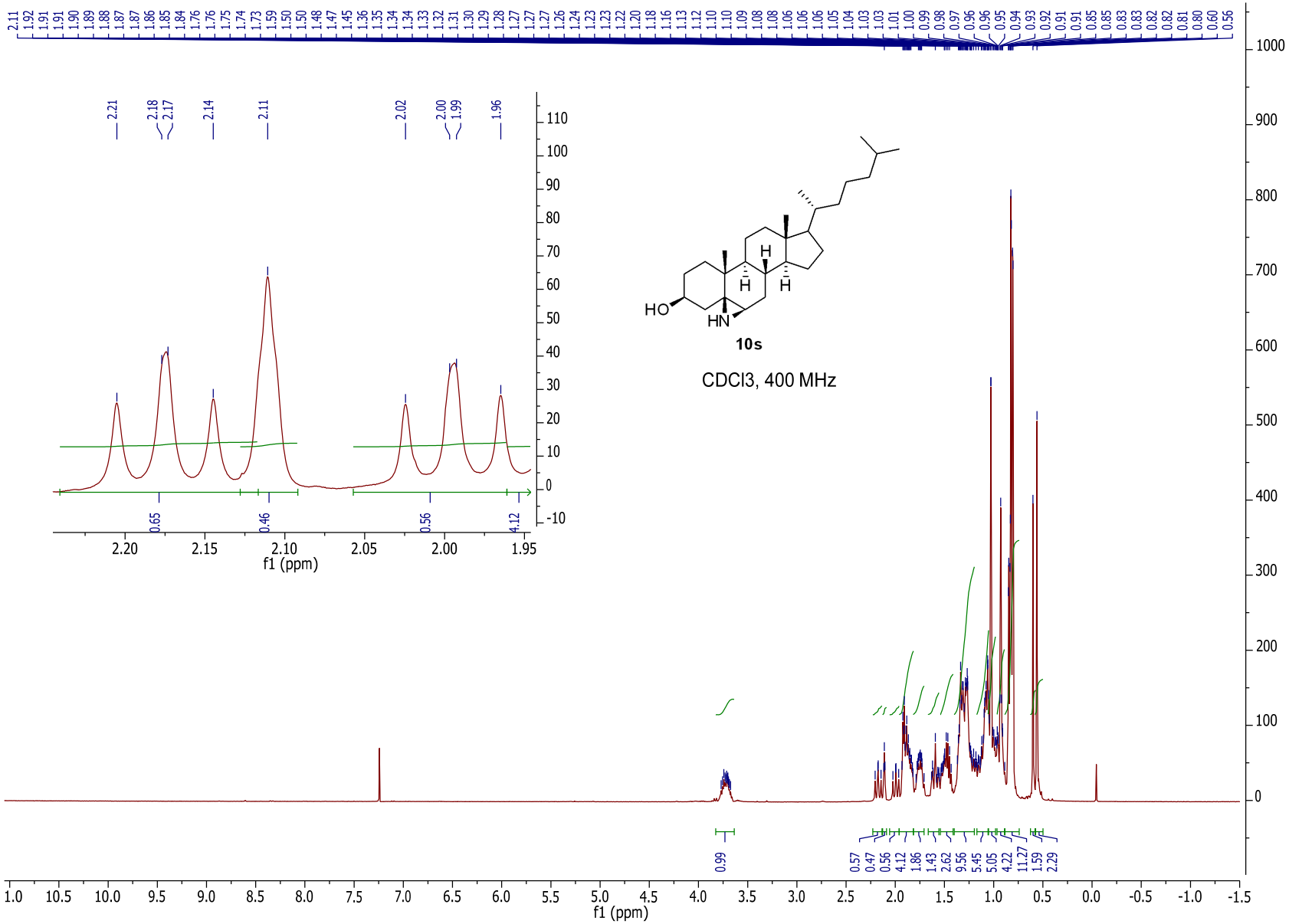

171.08
141.76
118.58
77.32 cdcl3
77.07 cdcl3
76.81 cdcl3
61.29
43.02
37.68
35.86
27.93
27.40
21.05
19.62
16.46
HN
Me
Me
Me
OAc
10q - 6,7 isomer
CDCl3, 500 MHz
f1 (ppm)

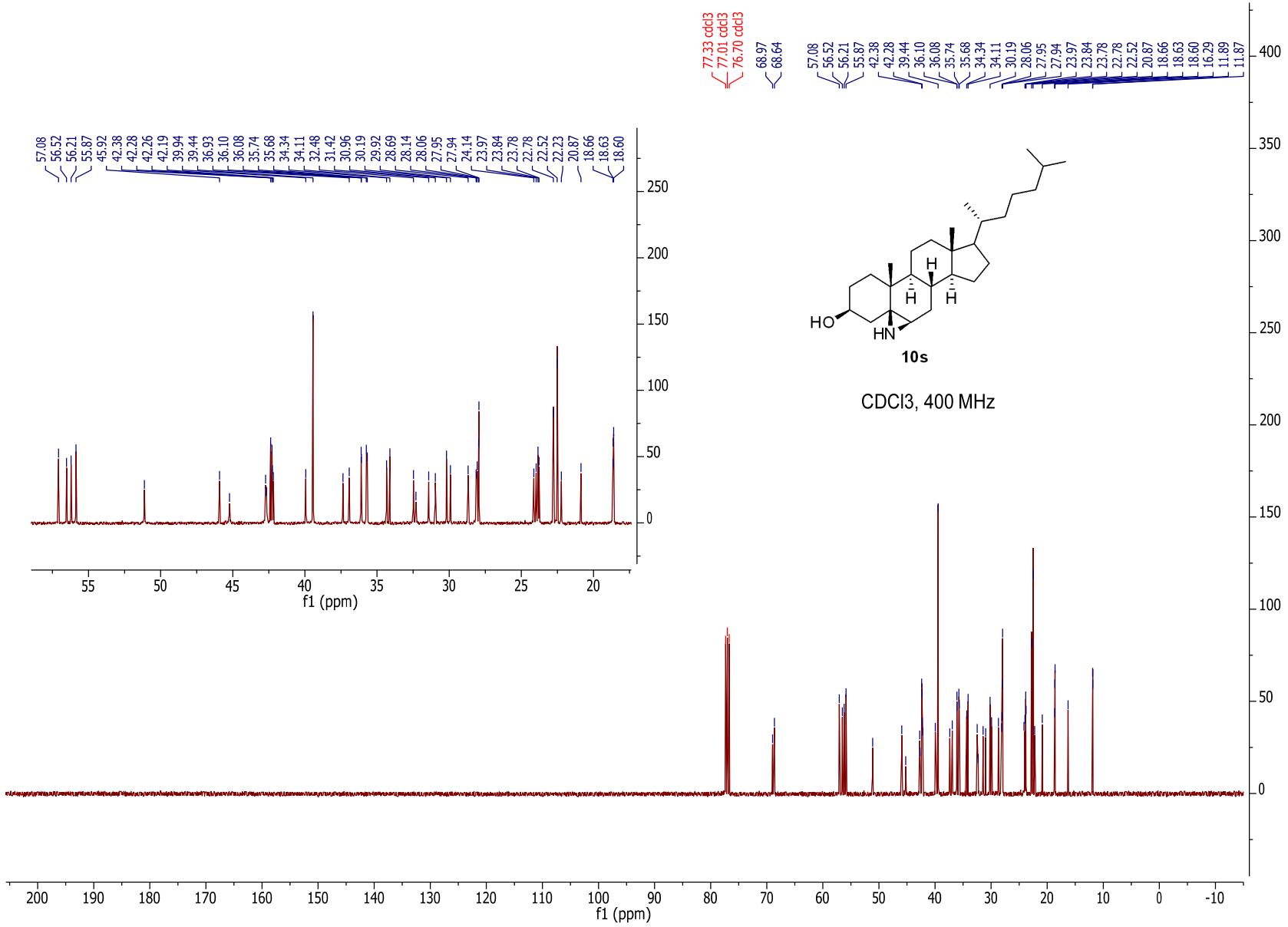

HN
Me
OAc
Me
Me
10q - 2,3 isomer
CDCl3, 500 MHz
f1 (ppm)

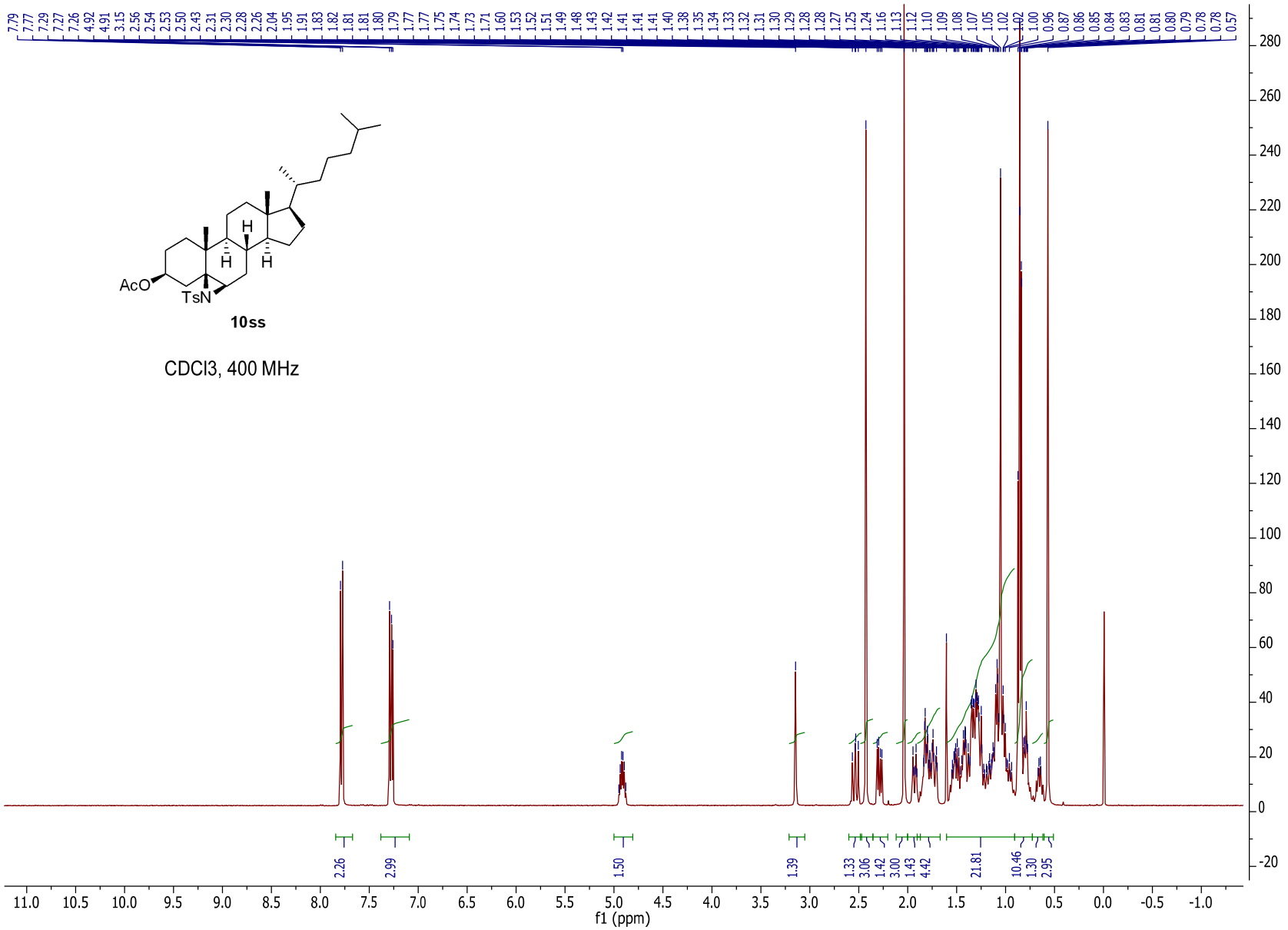

171.01
132.11
123.33
77.36 cdcl3
77.04 cdcl3
76.73 cdcl3
64.89
41.31
39.28
38.67
25.65
24.72
20.90
17.61
17.41
HN
Me
OAc
Me
Me
10q - 2,3 isomer
CDCl3, 500 MHz
f1 (ppm)

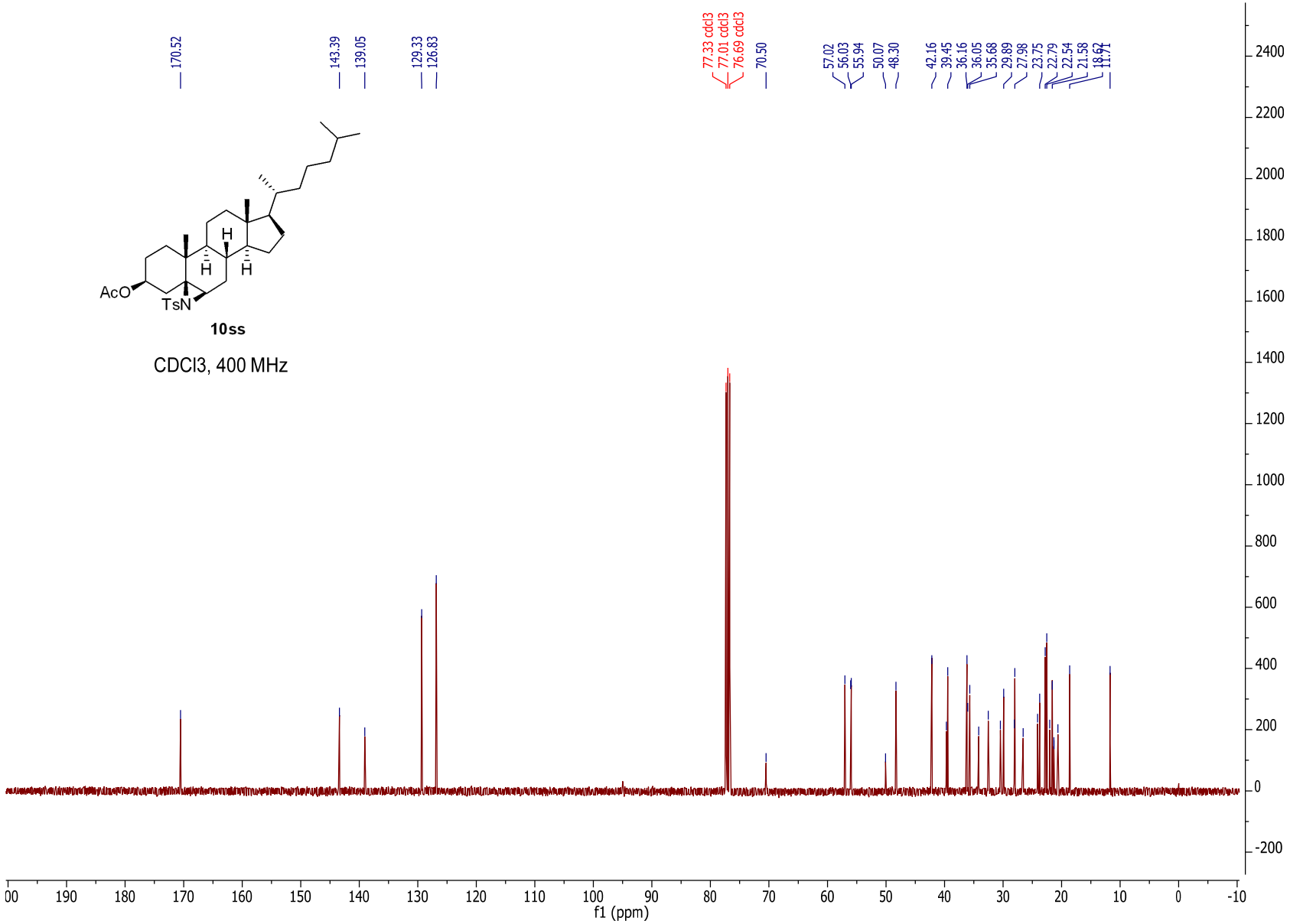

Me
Me
NH
10r
CDCl3, 400 MHz
f1 (ppm)

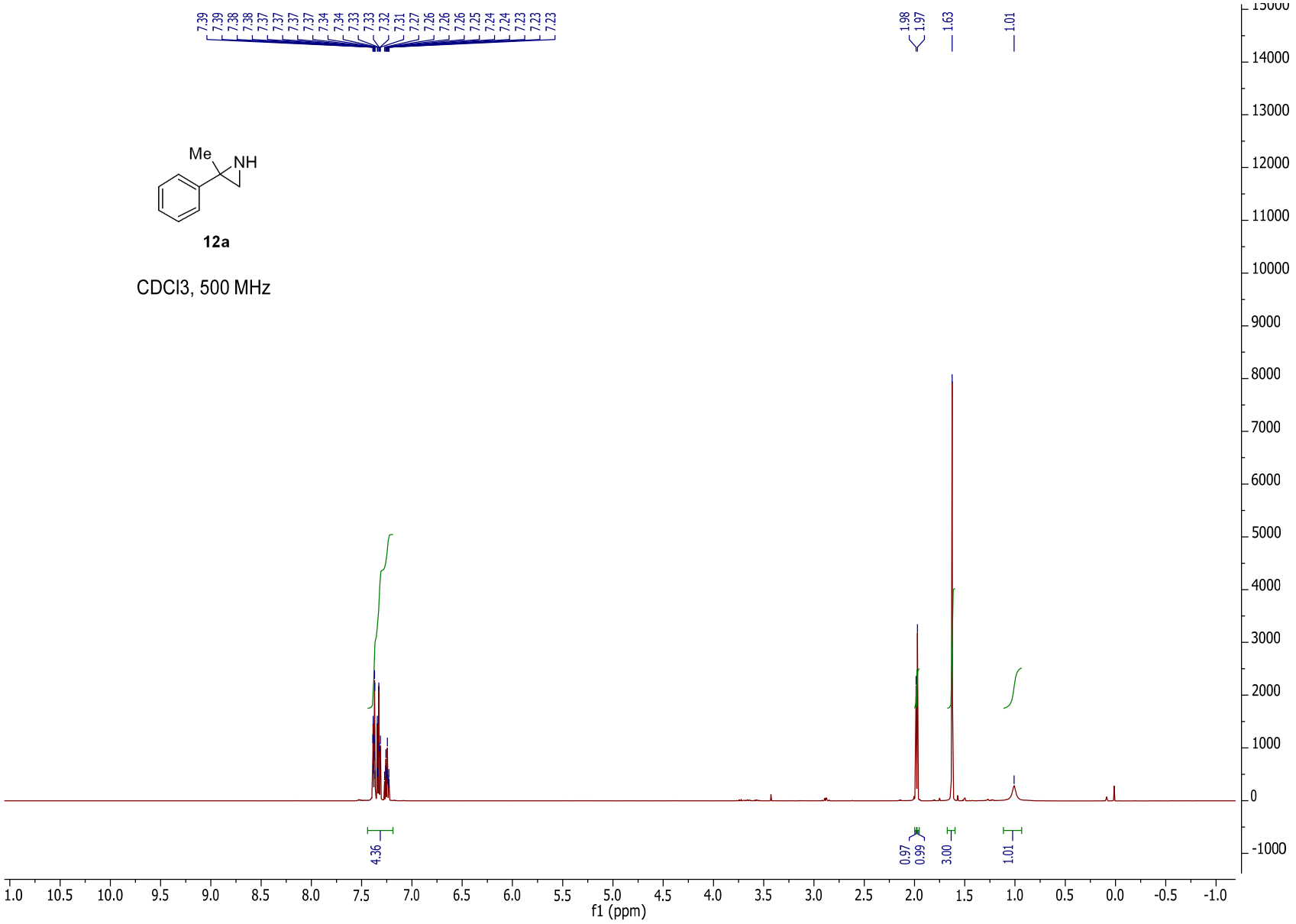

149.75
149.43
108.81
108.70
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
41.52
39.25
37.65
36.61
35.22
34.53
30.98
30.55
30.45
29.52
27.47
26.50
26.37
24.86
21.08
20.38
Me
Me
NH
10r
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

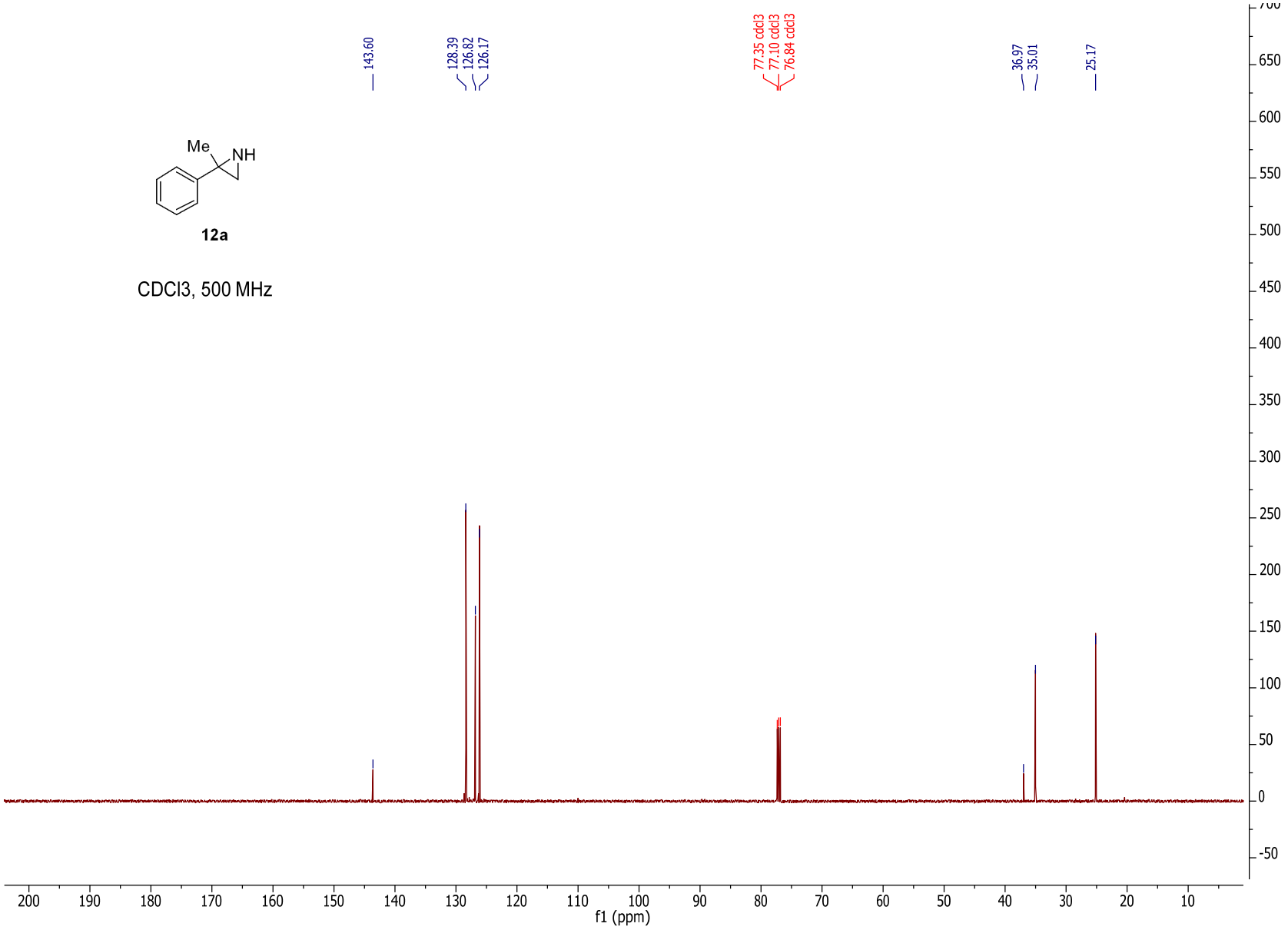

HO
HN
H
H
H
10s
CDCl3, 400 MHz
f1 (ppm)

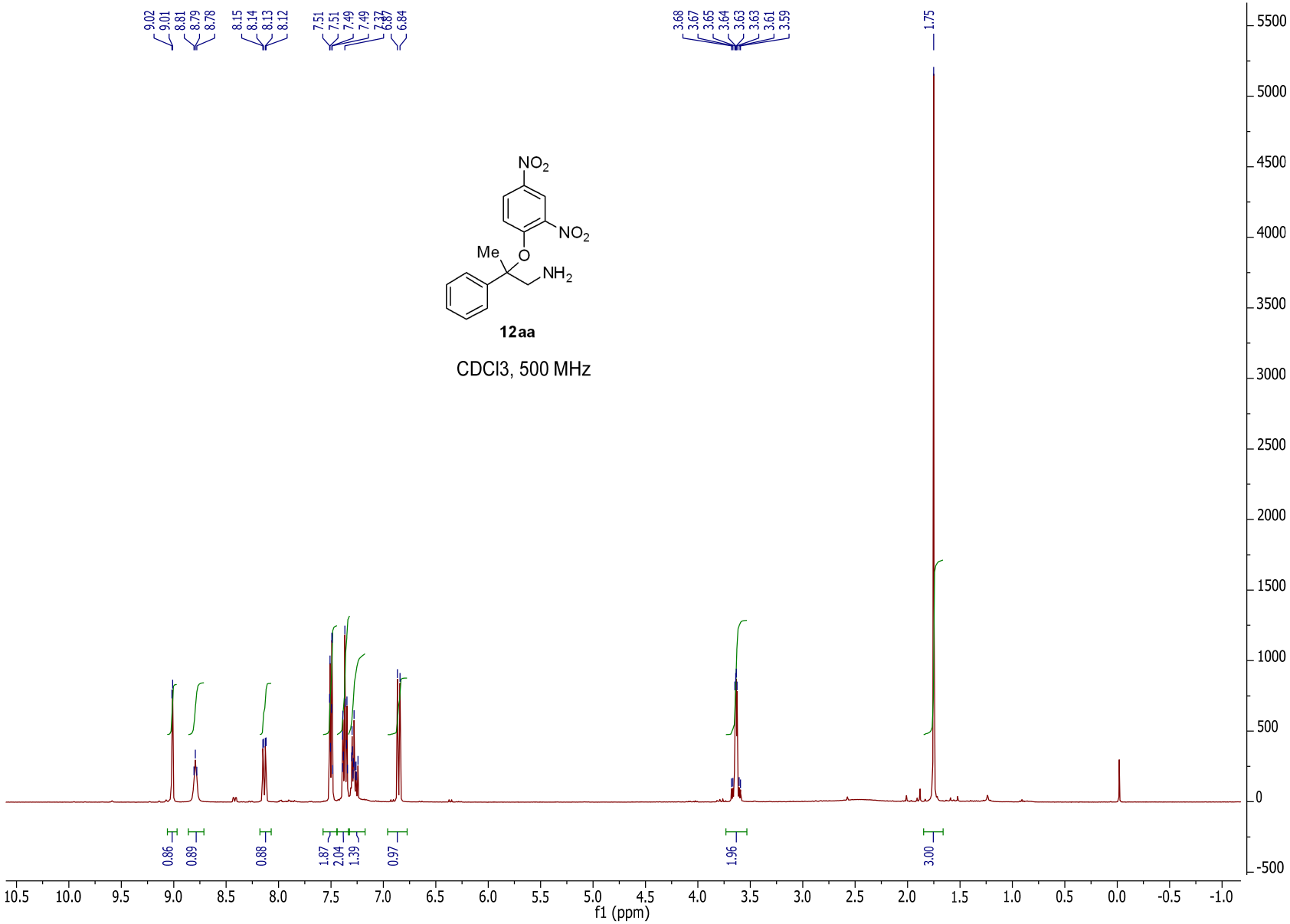

77.33 cdcl3
77.01 cdcl3
76.70 cdcl3
68.97
68.64
57.08
56.52
56.21
55.87
42.38
42.28
42.26
42.19
39.94
39.44
36.93
36.10
36.08
35.74
35.68
34.34
34.11
32.48
31.42
30.96
30.19
29.92
28.69
28.14
28.06
27.95
27.94
24.14
23.97
23.84
23.78
22.78
22.52
22.23
20.87
18.66
18.63
18.60
45.92
16.29
11.89
11.87
HO
HN
H
10s
CDCl3, 400 MHz
f1 (ppm)

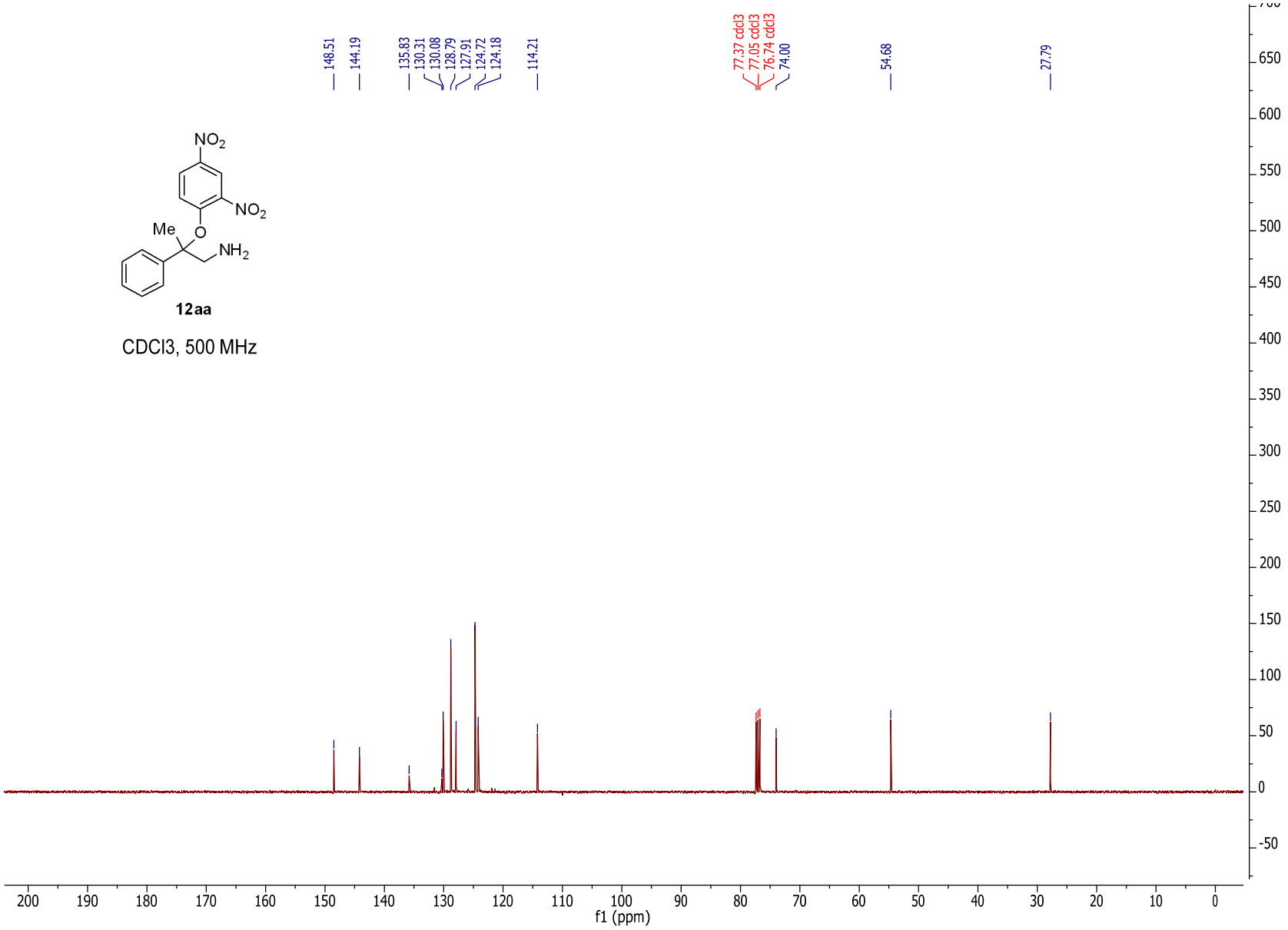

AcO
TsN
H
H
H
10ss
CDCl3, 400 MHz
f1 (ppm)

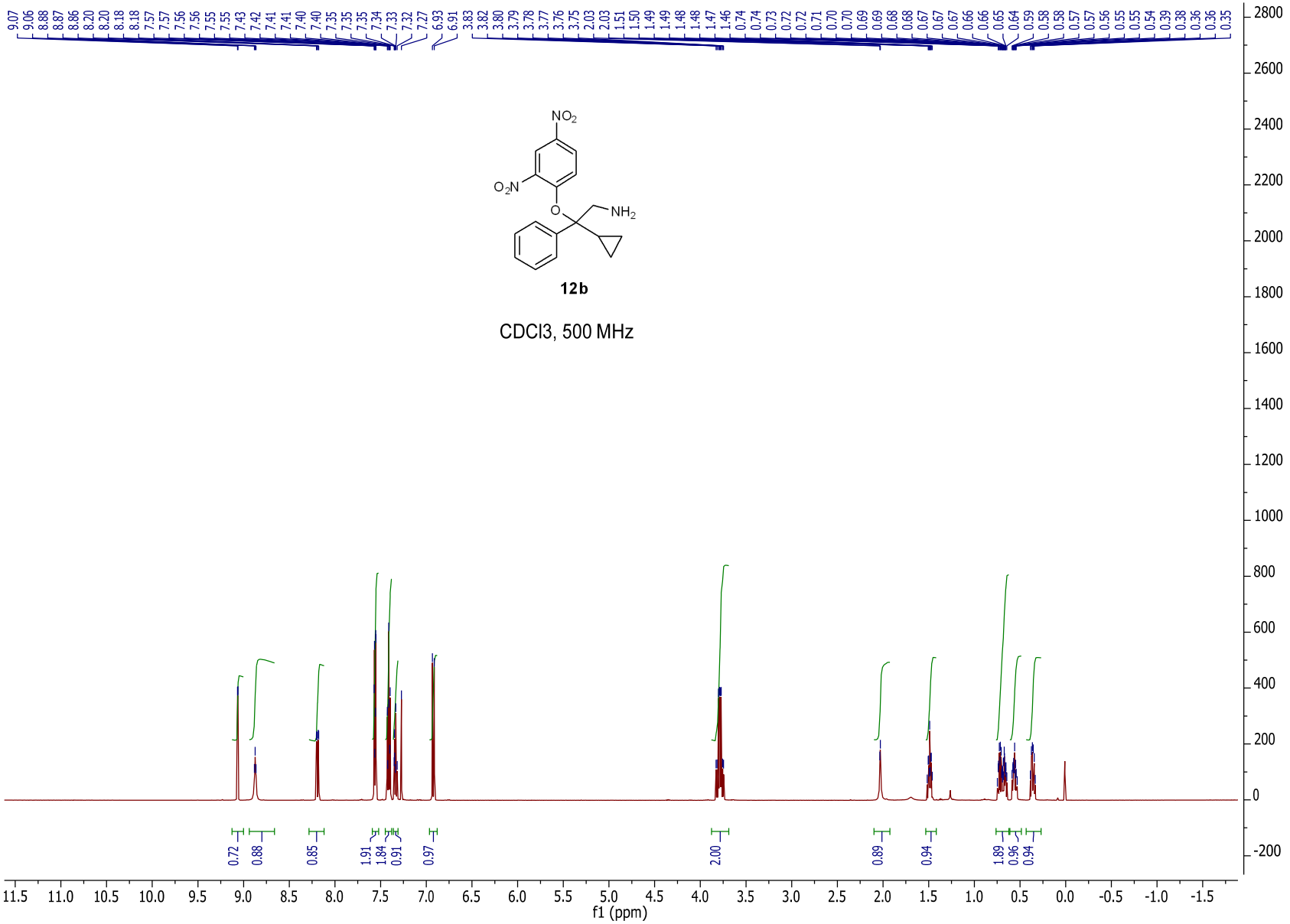

170.52
143.39
139.05
129.33
126.83
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
70.50
57.02
56.03
55.94
50.07
48.30
42.16
39.45
36.16
36.05
35.68
29.89
27.98
23.75
22.79
22.54
21.58
18.62
11.71
AcO
TsN
H
H
H
10ss
CDCl3, 400 MHz
f1 (ppm)

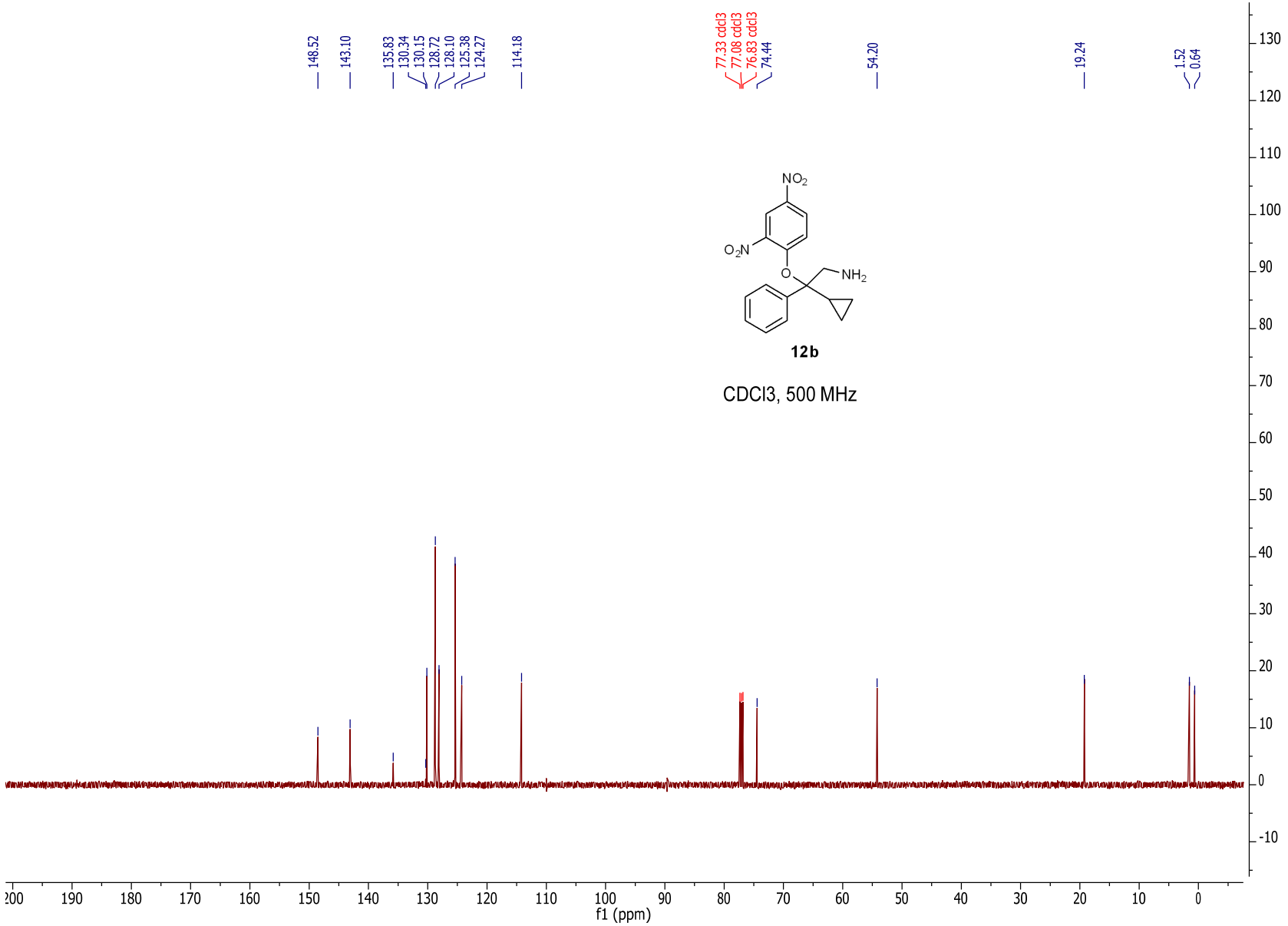

7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.37
7.34
7.34
7.33
7.33
7.32
7.31
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.23
1.98
1.97
1.63
1.01
Me
NH
12a
CDCl3, 500 MHz
4.36
0.97
0.99
3.00
1.01
f1 (ppm)

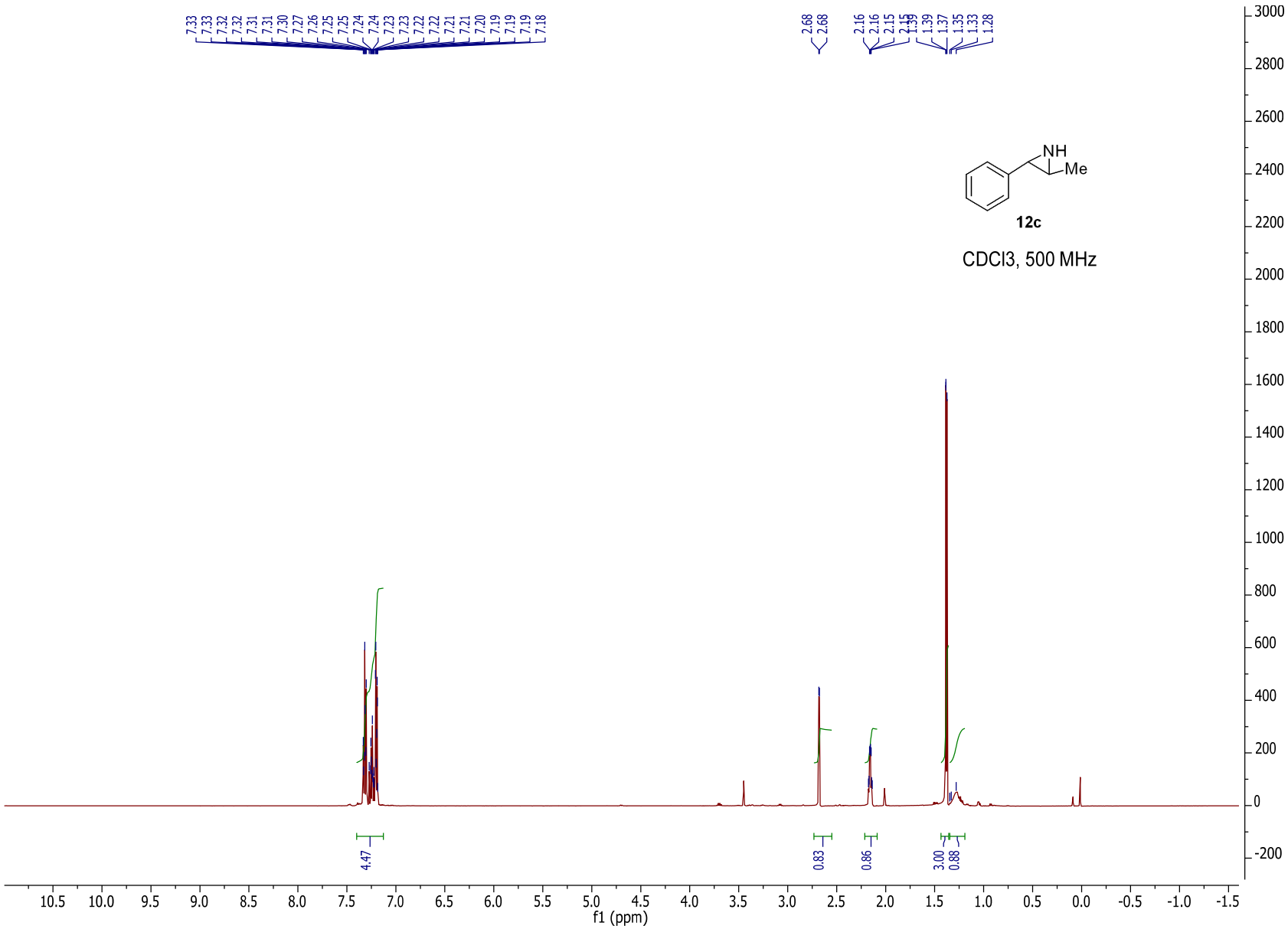

143.60
128.39
126.82
126.17
77.35 cdcl3
77.10 cdcl3
76.84 cdcl3
36.97
35.01
25.17
Me
NH
12a
CDCl3, 500 MHz
f1 (ppm)

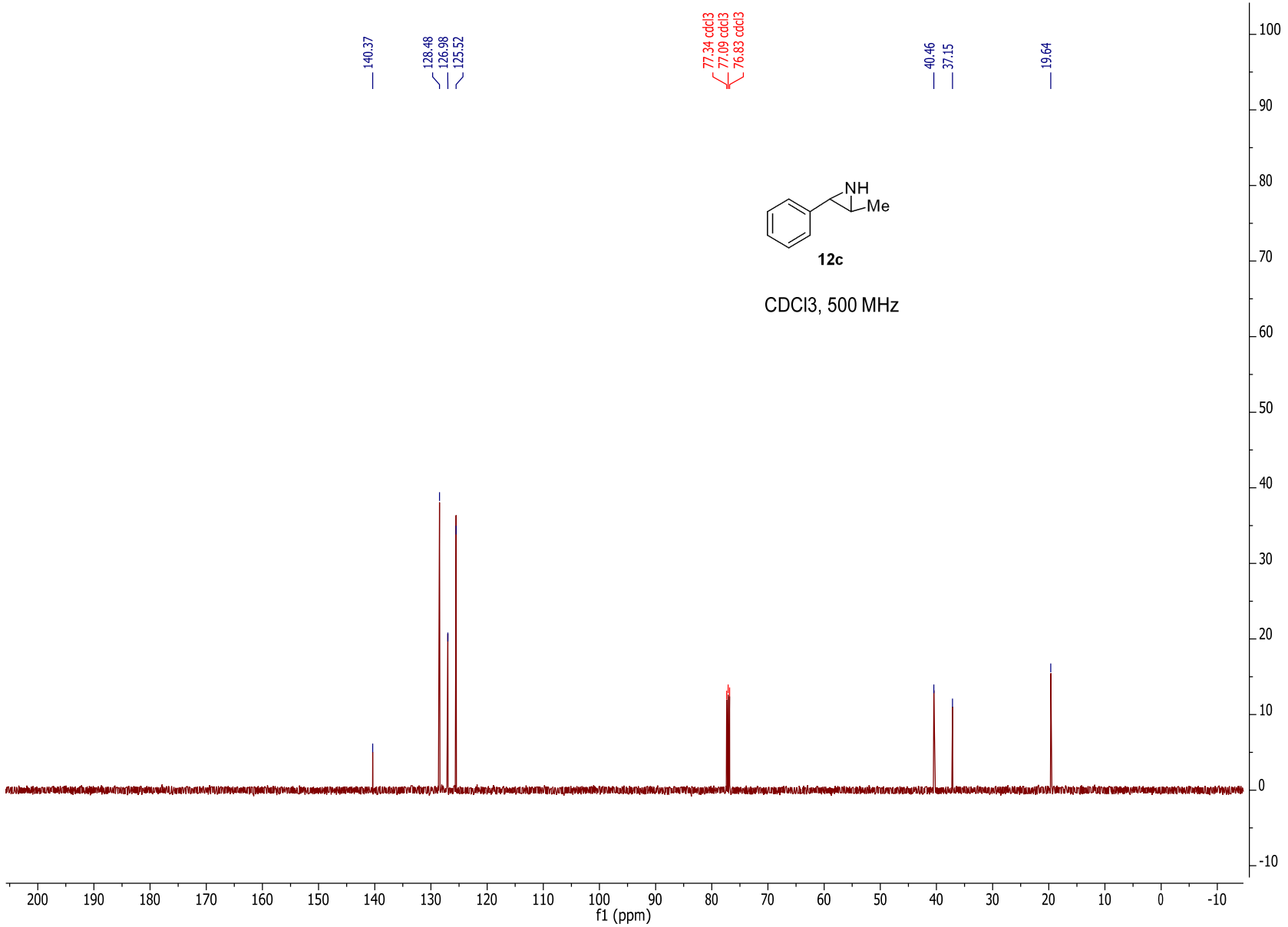

9.02
9.01
8.81
8.79
8.78
8.15
8.14
8.13
8.12
7.51
7.51
7.49
7.49
7.37
6.87
6.84
3.68
3.67
3.65
3.64
3.63
3.63
3.61
3.59
1.75
NO2
NO2
Me
O
NH2
12aa
CDCl3, 500 MHz
0.86
0.89
0.88
1.87
2.04
1.39
0.97
1.96
3.00
f1 (ppm)

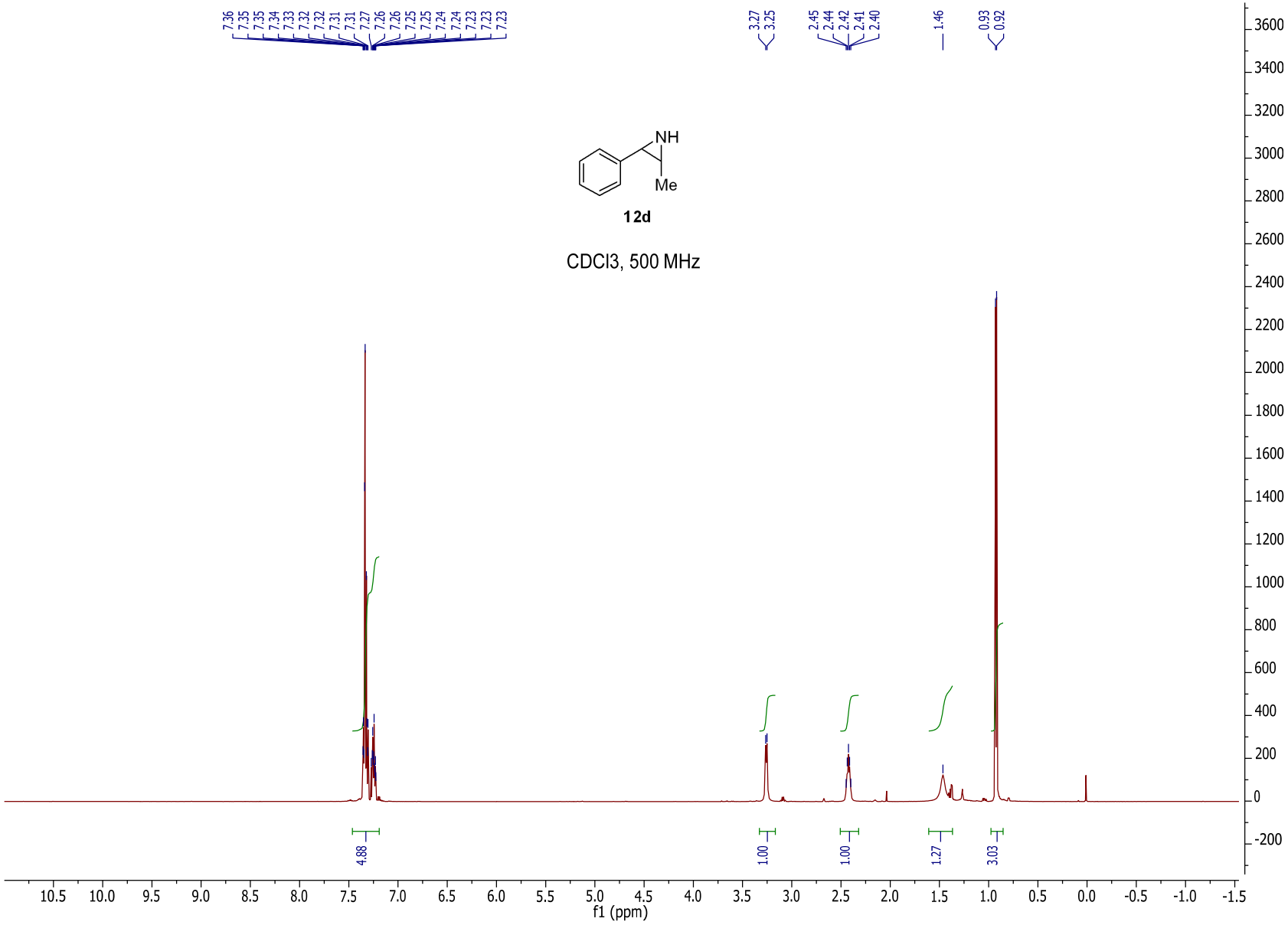

148.51
144.19
135.83
130.31
130.08
128.79
127.91
124.72
124.18
114.21
77.37 cdcl3
77.05 cdcl3
76.74 cdcl3
74.00
54.68
27.79
NO2
NO2
Me
O
NH2
12aa
CDCl3, 500 MHz
f1 (ppm)

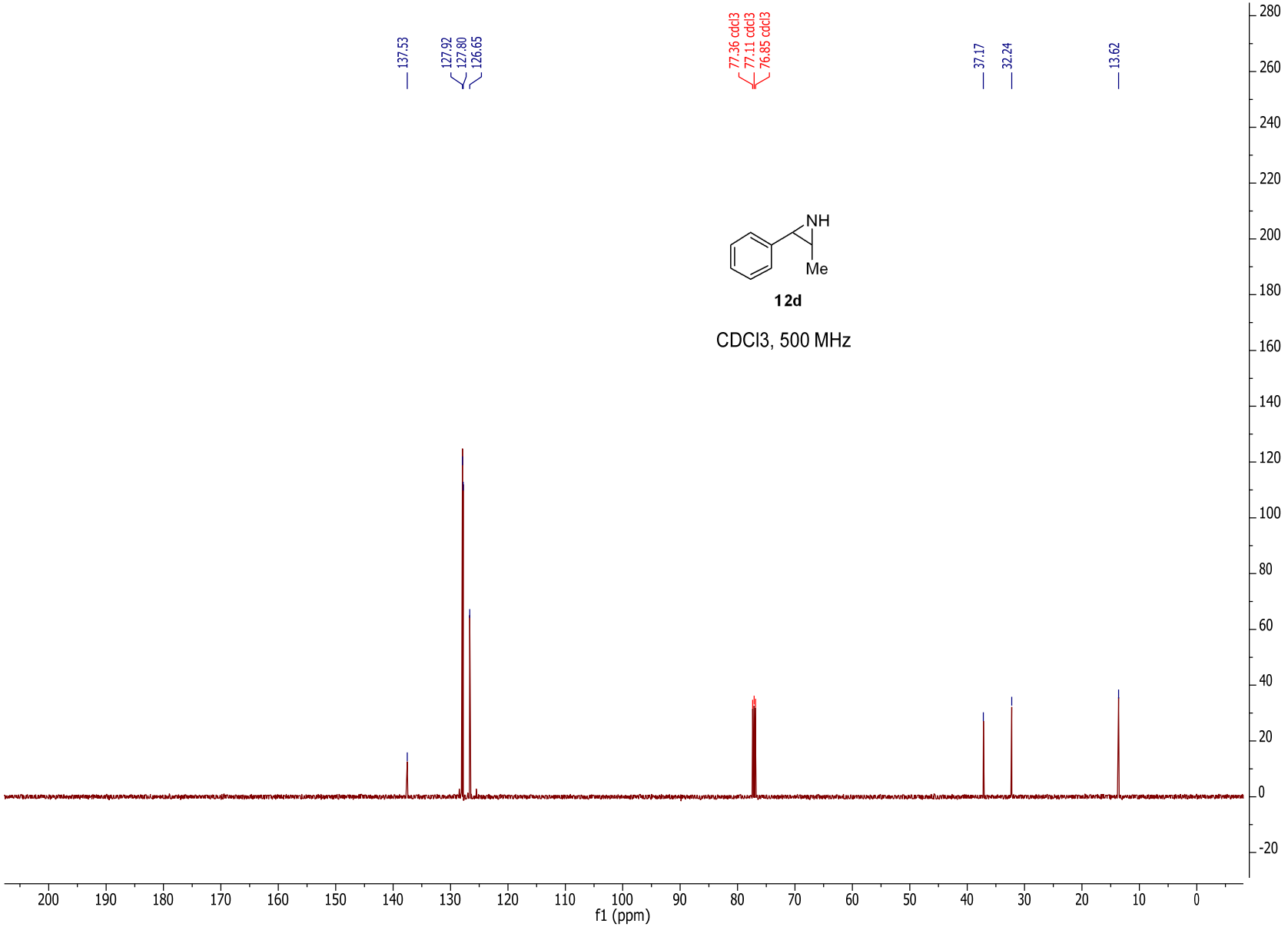

12b
CDCl3, 500 MHz
f1 (ppm)

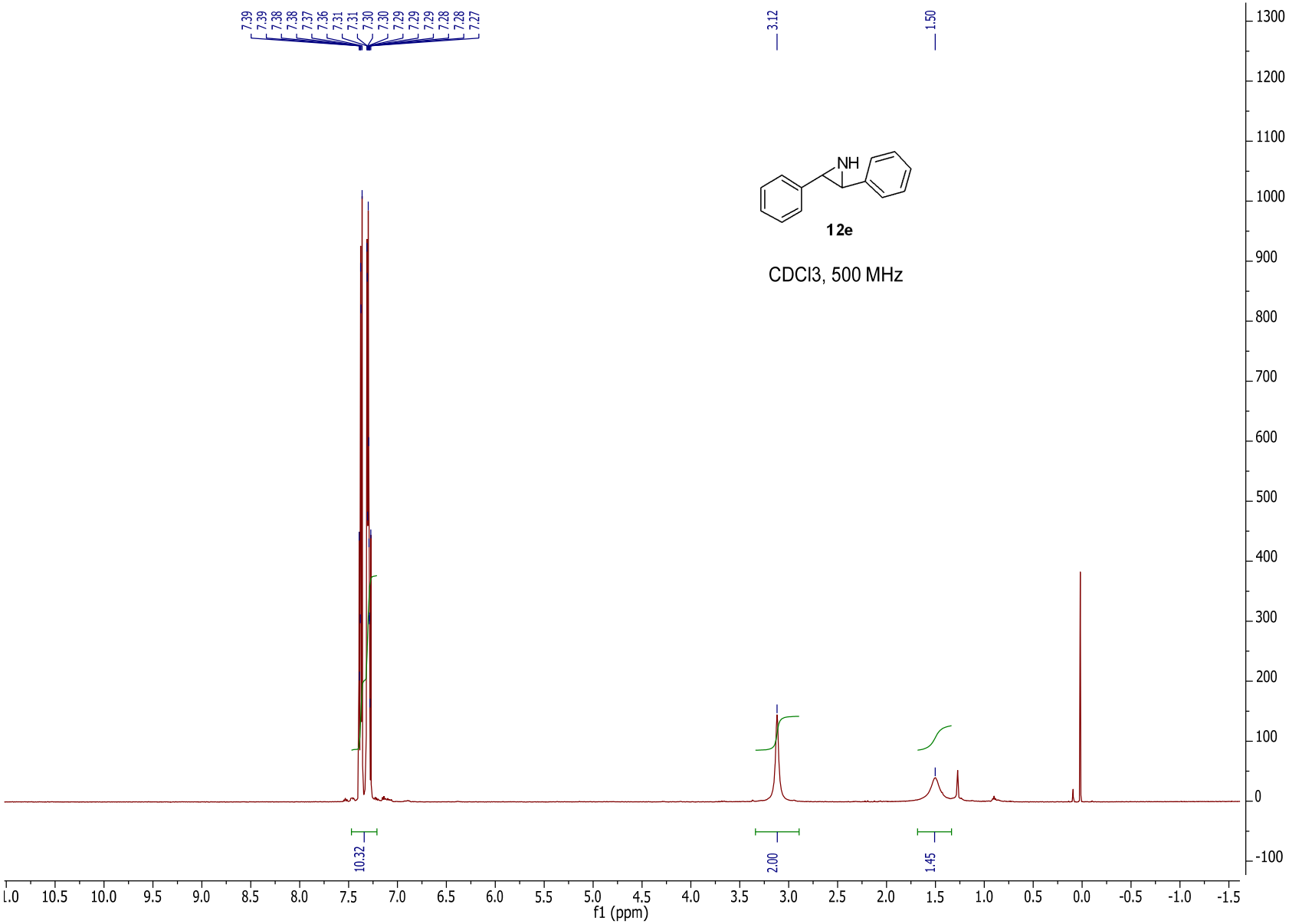

148.52
143.10
135.83
130.34
130.15
128.72
128.10
125.38
124.27
114.18
77.33 cdcl3
77.08 cdcl3
76.83 cdcl3
74.44
54.20
19.24
1.52
0.64
NO2
O2N
O
NH2
12b
CDCl3, 500 MHz
f1 (ppm)

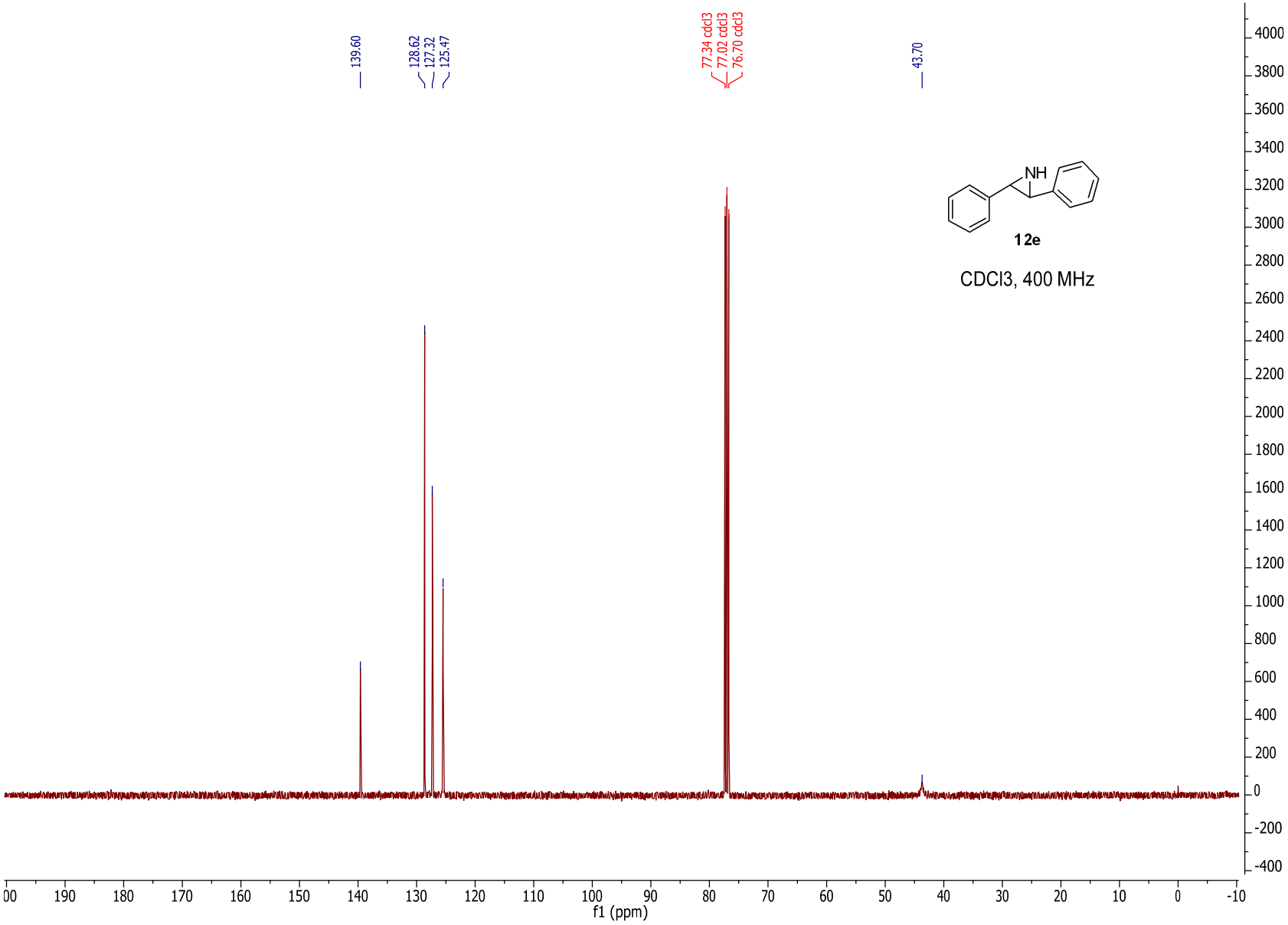

7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.19
7.18
2.68
2.68
2.16
2.16
2.15
2.15
1.39
1.37
1.35
1.33
1.28
NH
Me
12c
CDCl3, 500 MHz
4.47
0.83
0.86
3.00
0.88
f1 (ppm)

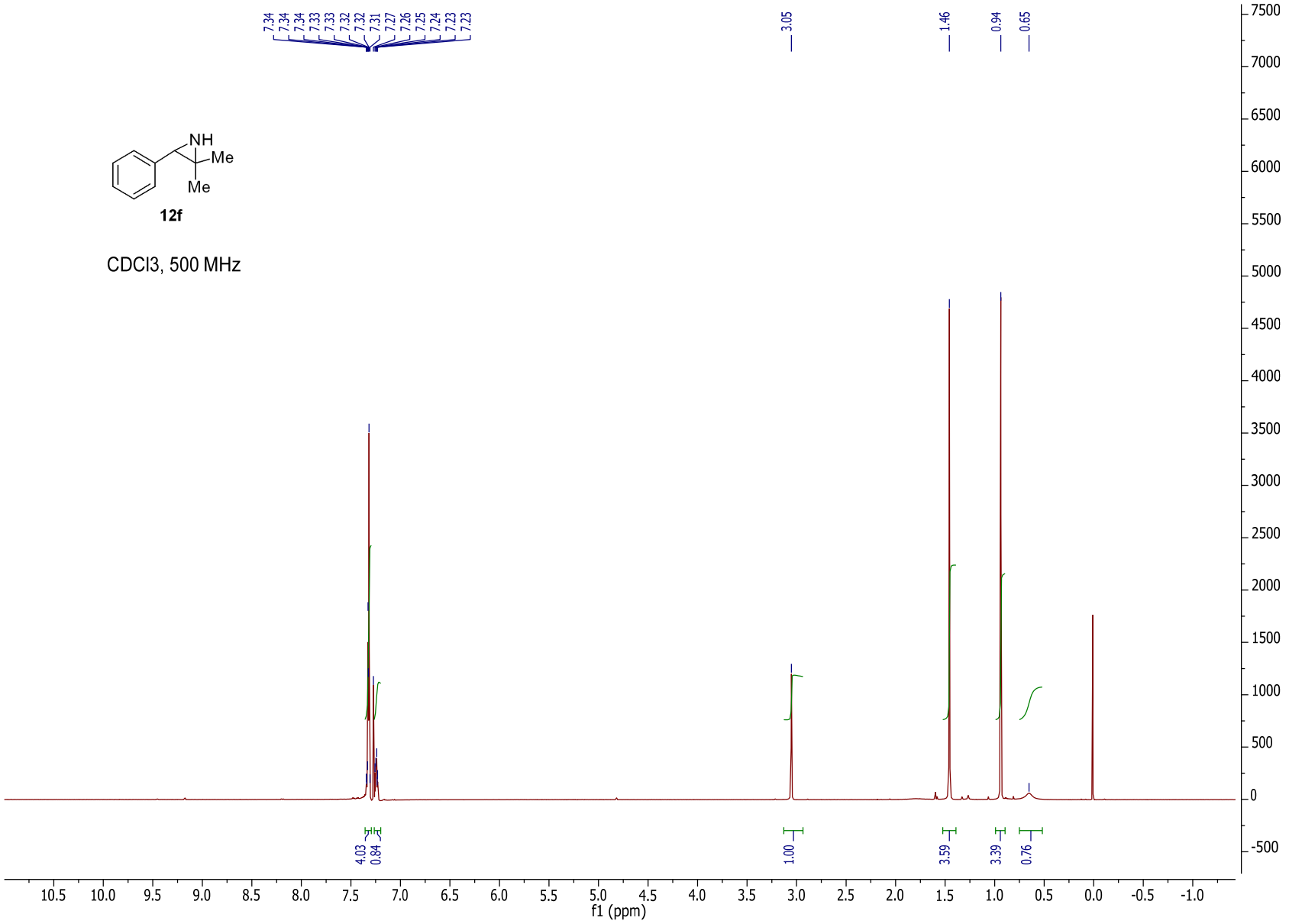

140.37
128.48
126.98
125.52
77.34 cdcl3
77.09 cdcl3
76.83 cdcl3
40.46
37.15
19.64
NH
Me
12c
CDCl3, 500 MHz
f1 (ppm)

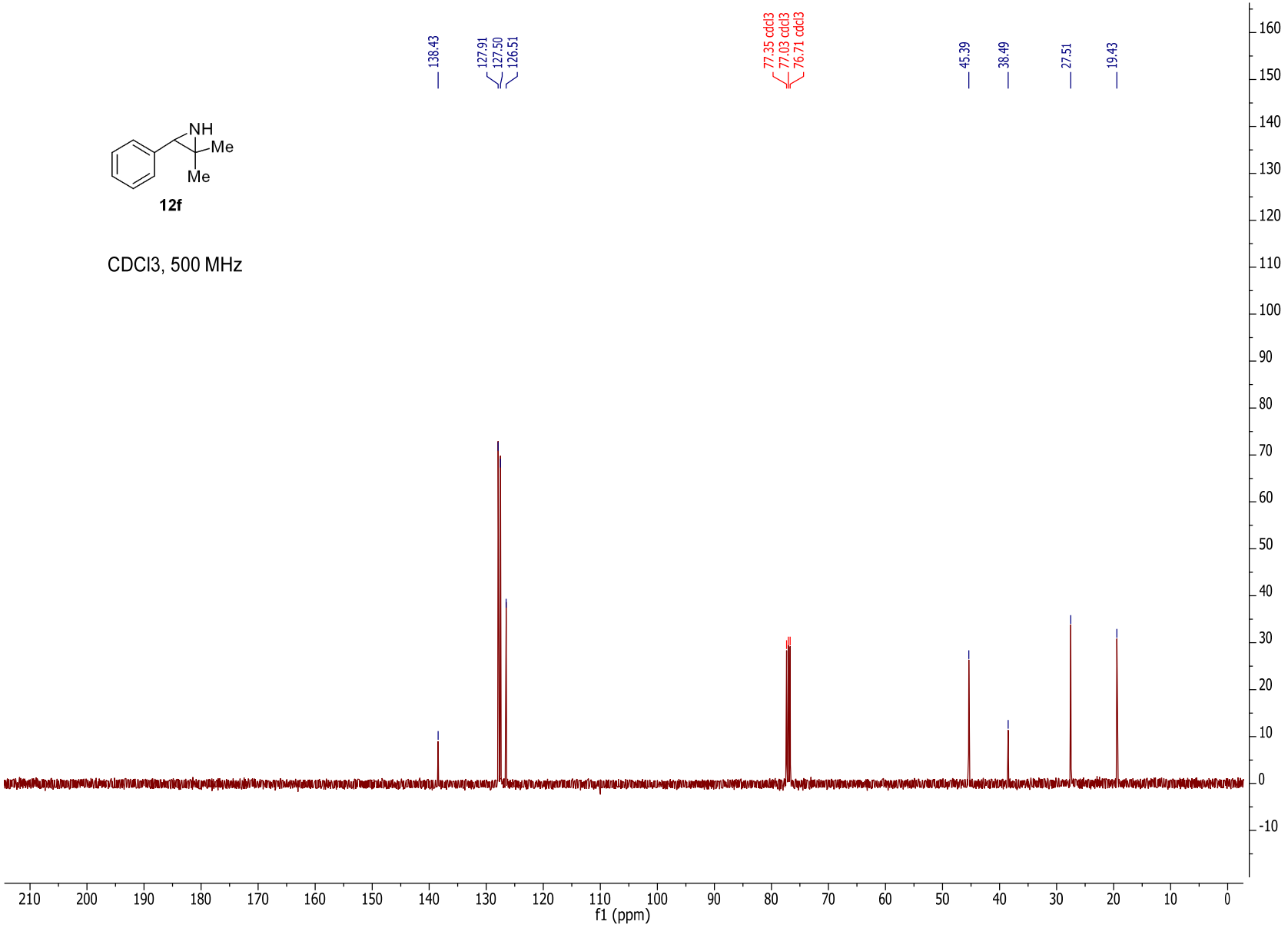

7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.23
3.27
3.25
2.45
2.44
2.42
2.41
2.40
1.46
0.93
0.92
NH
Me
12d
CDCl3, 500 MHz
4.88
1.00
1.00
1.27
3.03
f1 (ppm)

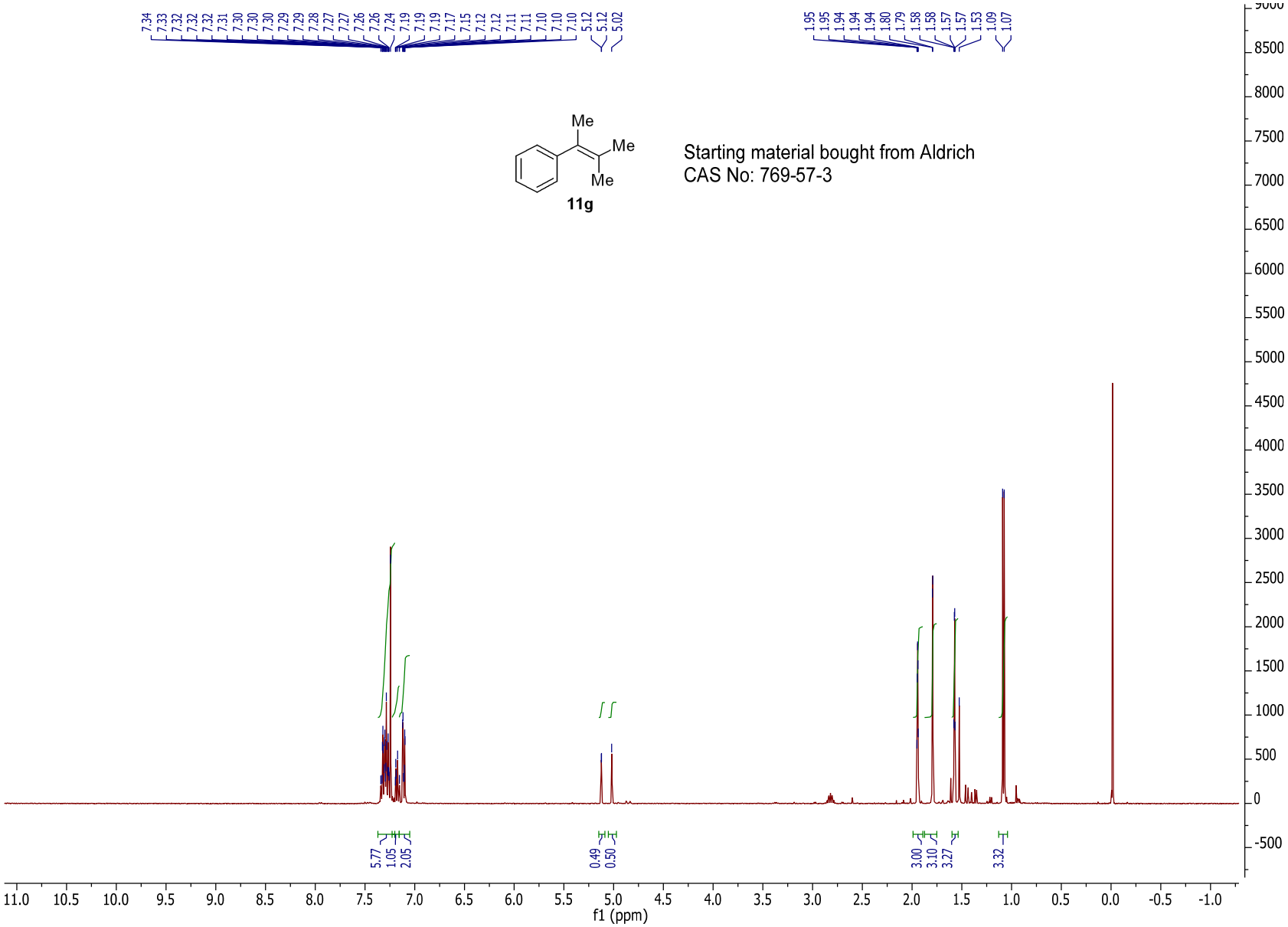

137.53
127.92
127.80
126.65
77.36 cdcl3
77.11 cdcl3
76.85 cdcl3
37.17
32.24
13.62
NH
Me
12d
CDCl3, 500 MHz
f1 (ppm)

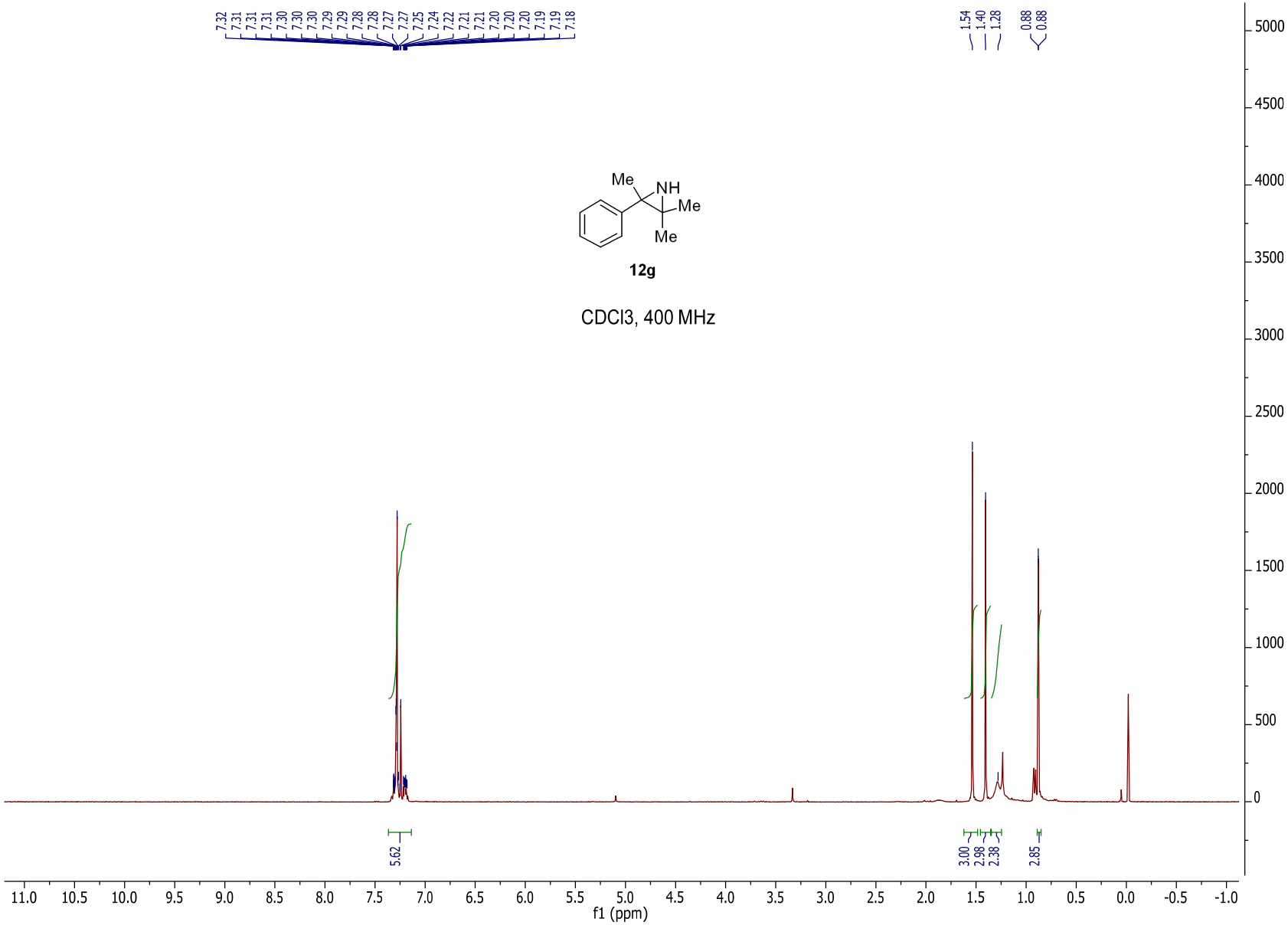

7.39
7.39
7.38
7.38
7.37
7.36
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
3.12
1.50
NH
12e
CDCl3, 500 MHz
10.32
2.00
1.45
f1 (ppm)

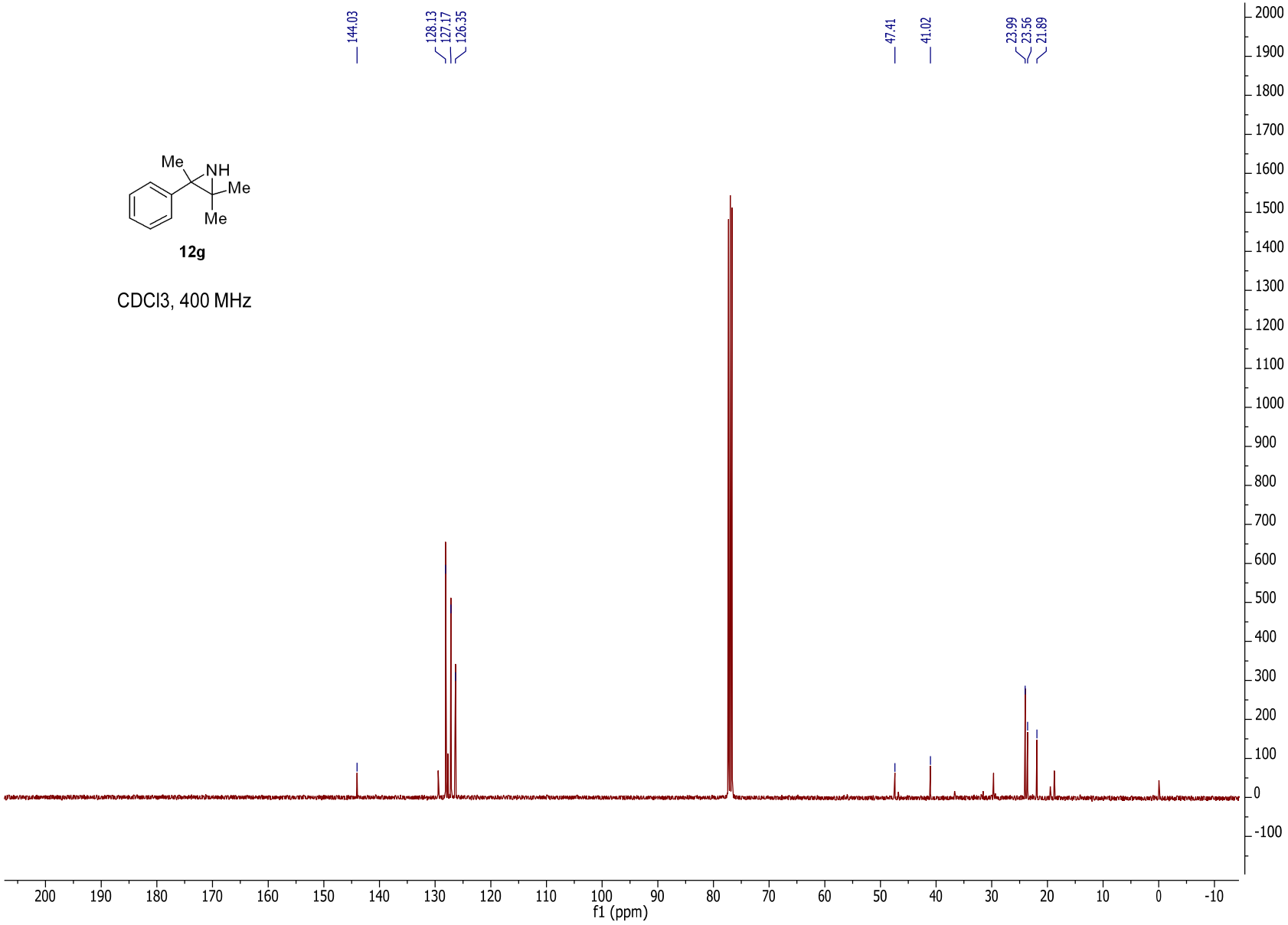

139.60
128.62
127.32
125.47
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
43.70
NH
12e
CDCl3, 400 MHz
f1 (ppm)

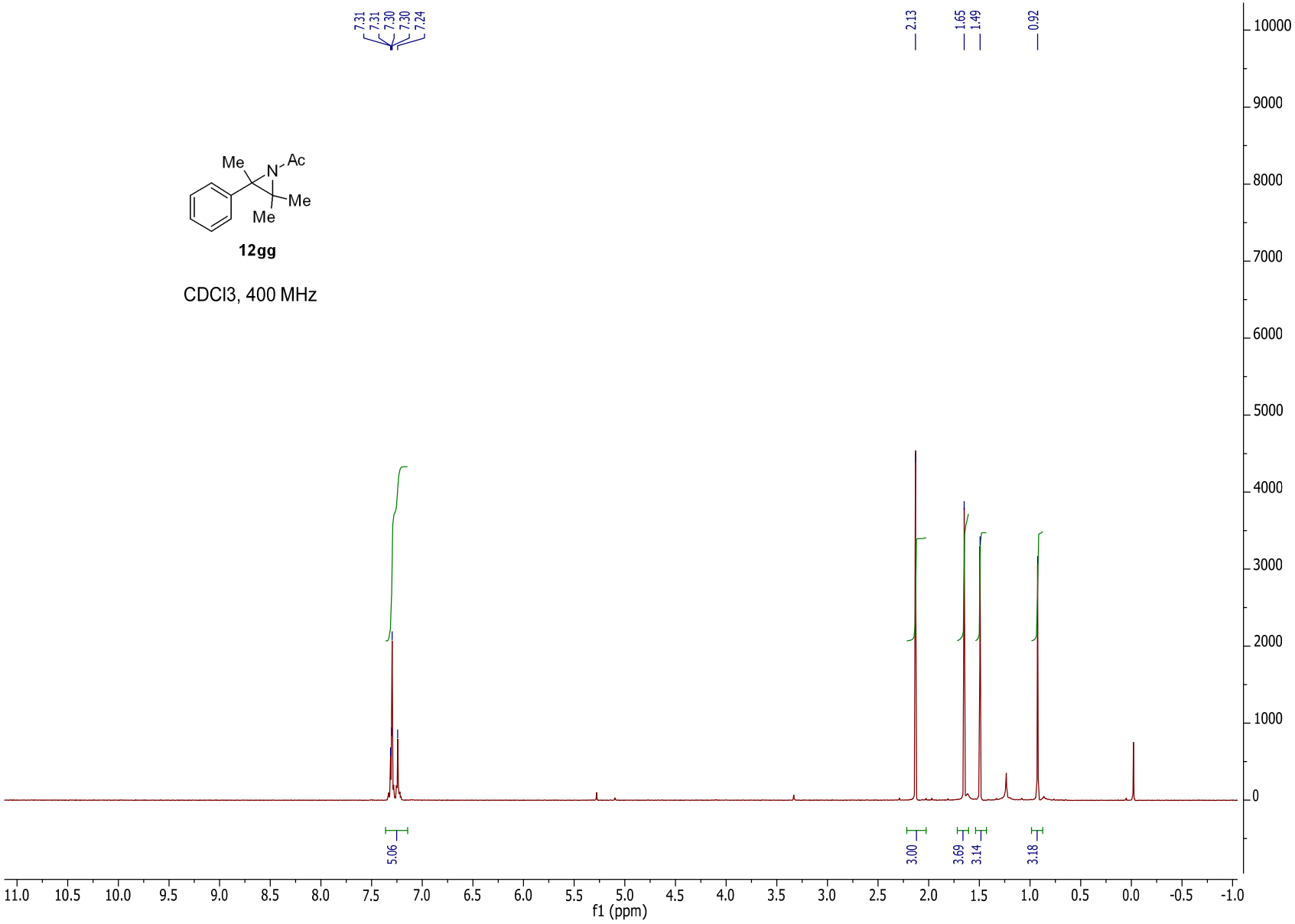

7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.27
7.26
7.25
7.24
7.23
7.23
3.05
1.46
0.94
0.65
NH
Me
Me
12f
CDCl3, 500 MHz
4.03
0.84
1.00
3.59
3.39
0.76
f1 (ppm)

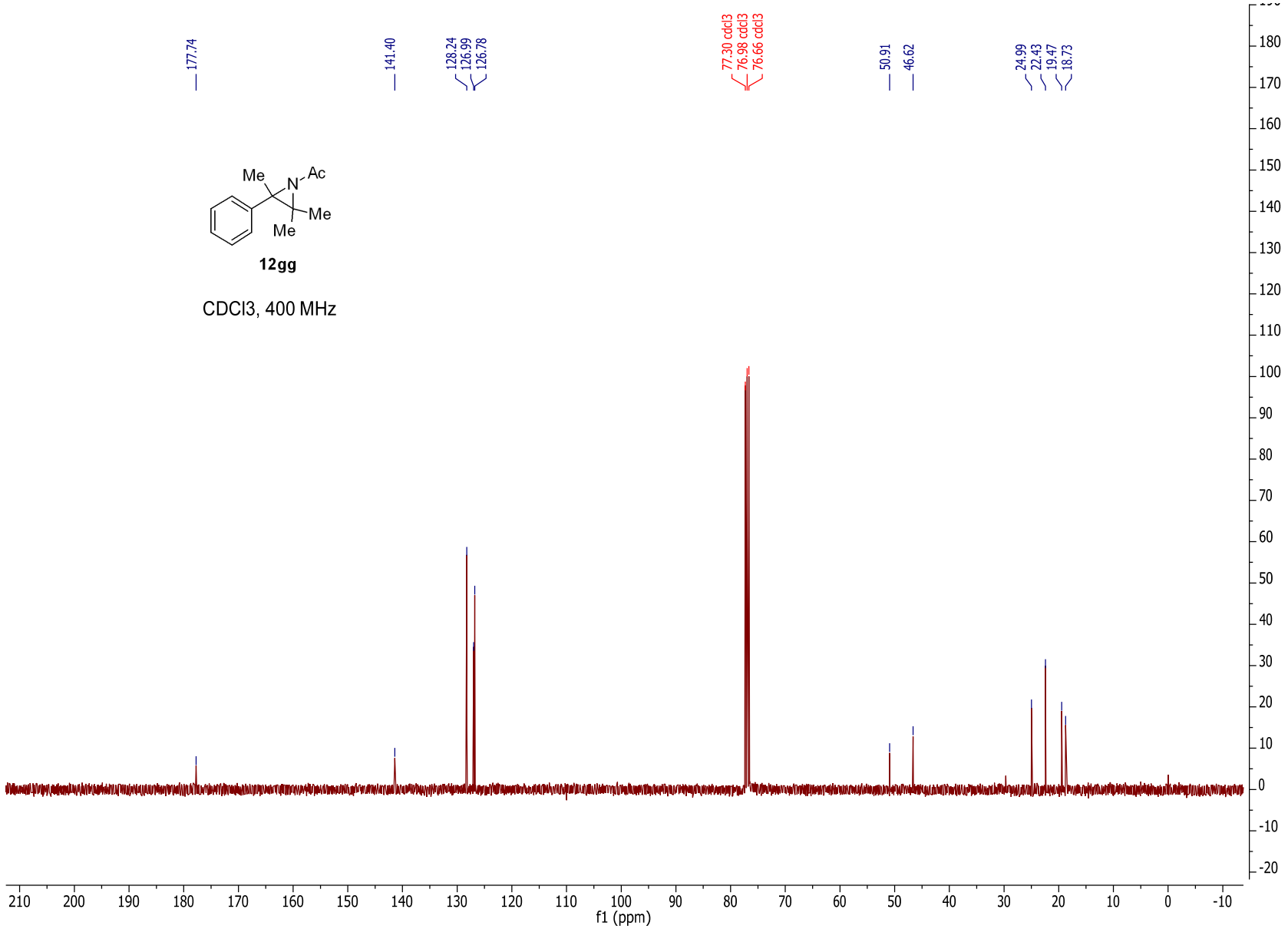

138.43
127.91
127.50
126.51
77.35 cdcl3
77.03 cdcl3
76.71 cdcl3
45.39
38.49
27.51
19.43
NH
Me
Me
12f
CDCl3, 500 MHz
f1 (ppm)

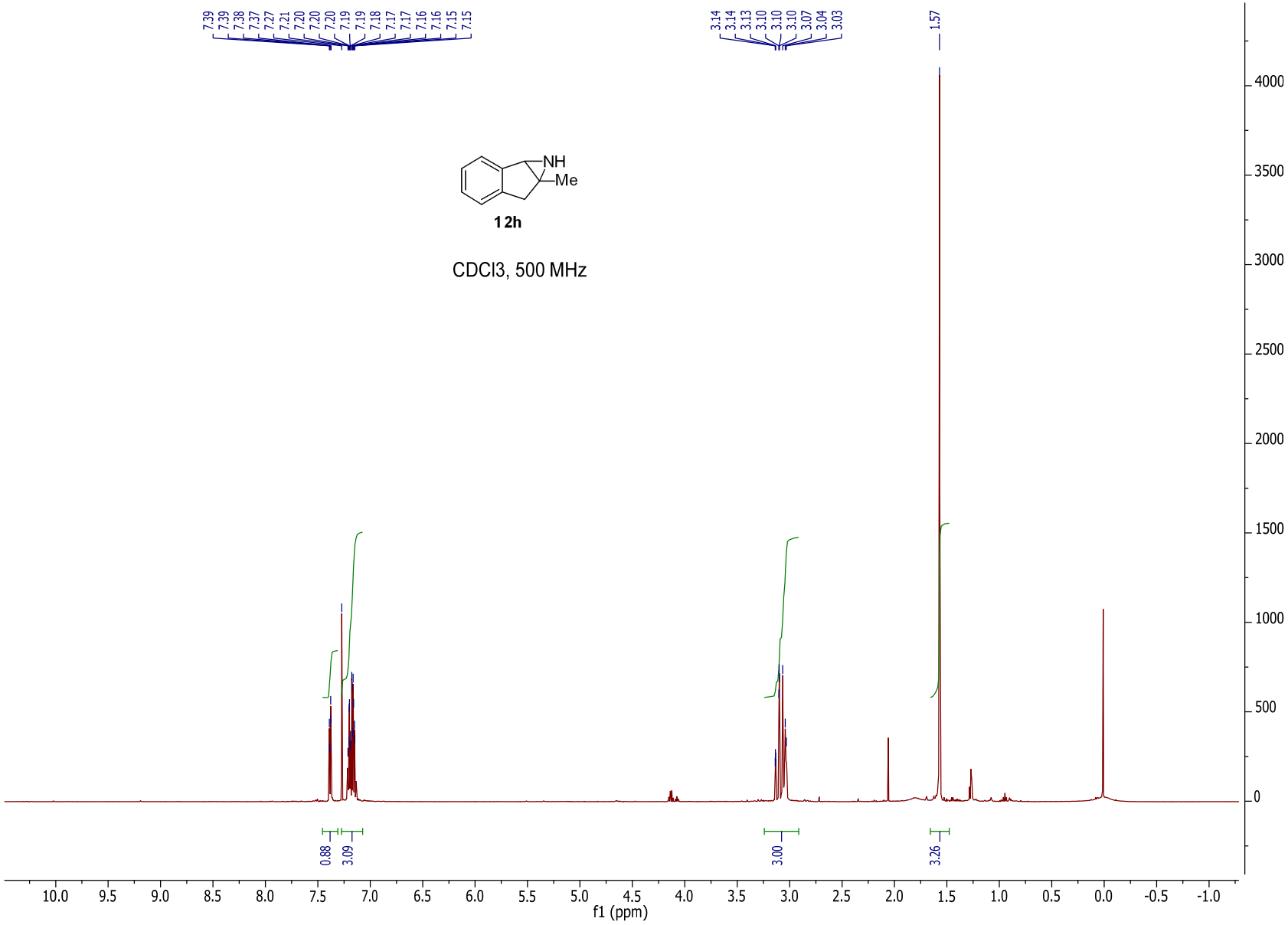

7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.24
7.19
7.19
7.19
7.17
7.15
7.12
7.12
7.11
7.11
7.10
7.10
7.10
5.12
5.12
5.02
1.95
1.95
1.94
1.94
1.94
1.80
1.79
1.58
1.58
1.57
1.57
1.53
1.09
1.07
Me
Me
Me
11g
Starting material bought from Aldrich
CAS No: 769-57-3
5.77
1.05
2.05
0.49
0.50
3.00
3.10
3.27
3.32
f1 (ppm)

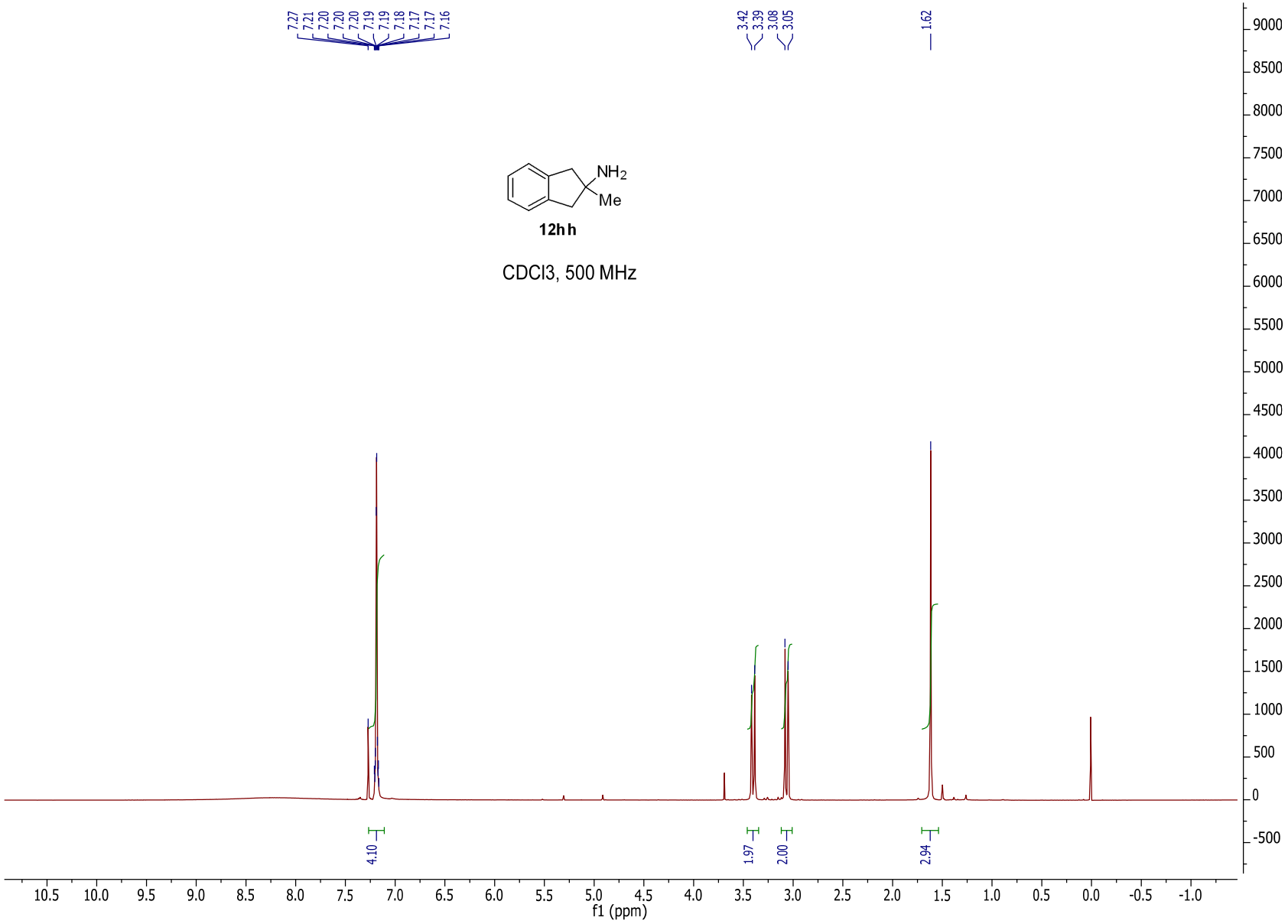

7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.25
7.24
7.22
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.18
1.54
1.40
1.28
0.88
0.88
Me
NH
Me
Me
12g
CDCl3, 400 MHz
5.62
3.00
2.98
2.38
2.85
f1 (ppm)

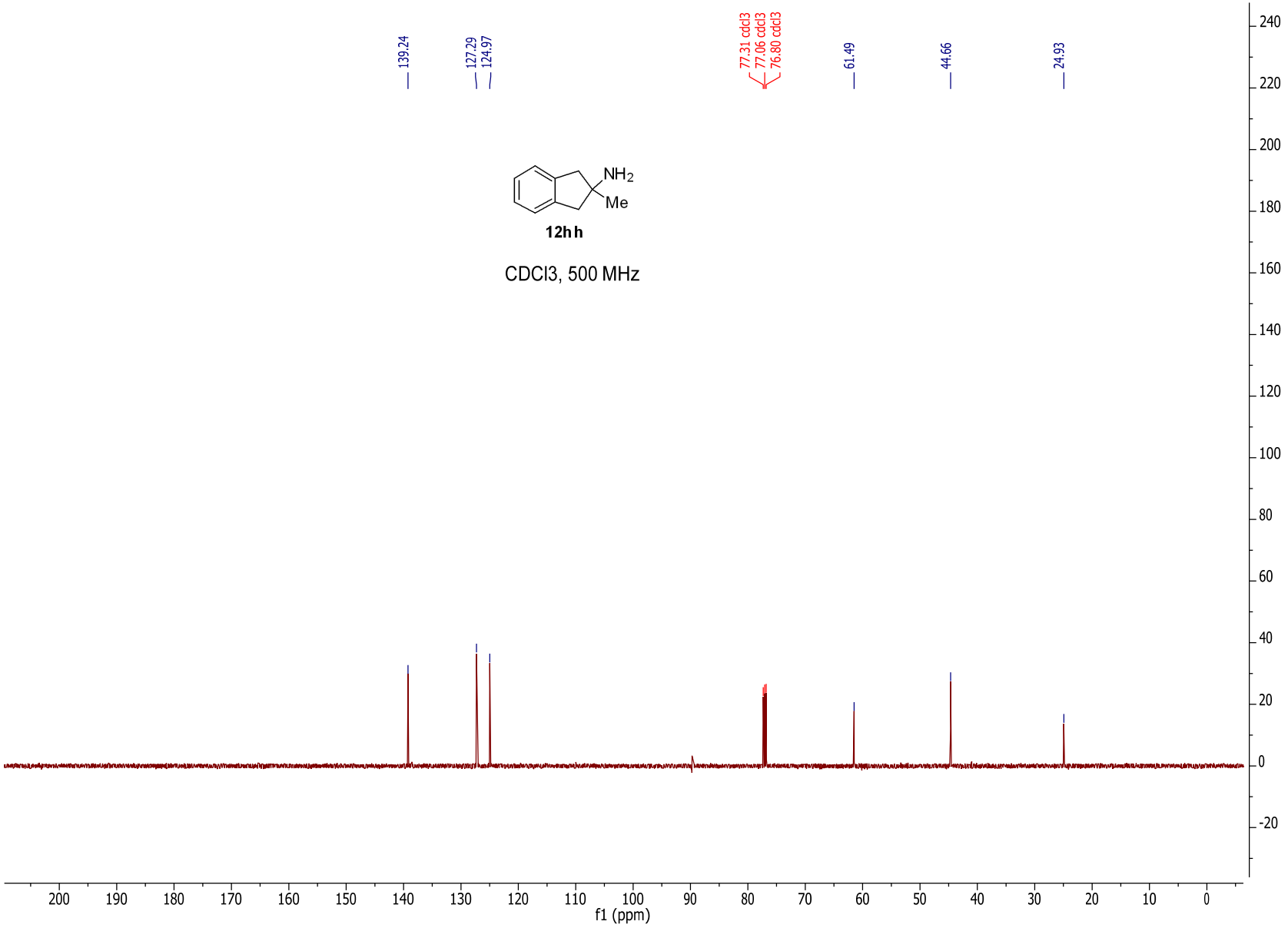

144.03
128.13
127.17
126.35
47.41
41.02
23.99
23.56
21.89
Me
NH
Me
Me
12g
CDCl3, 400 MHz
f1 (ppm)

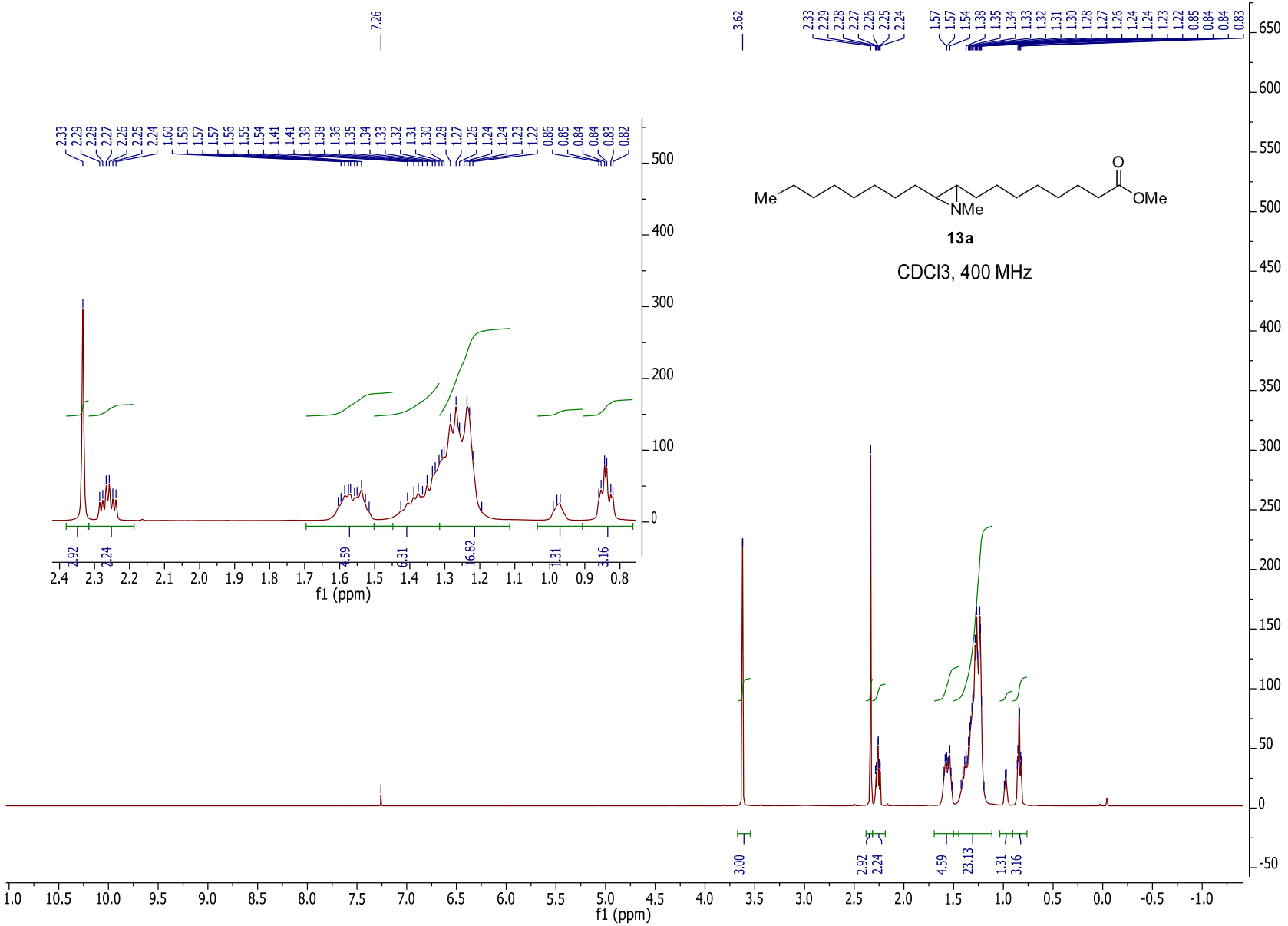

7.31
7.31
7.30
7.30
7.24
2.13
1.65
1.49
0.92
Me
N
Ac
Me
Me
12gg
CDCl3, 400 MHz
5.06
3.00
3.69
3.14
3.18
f1 (ppm)

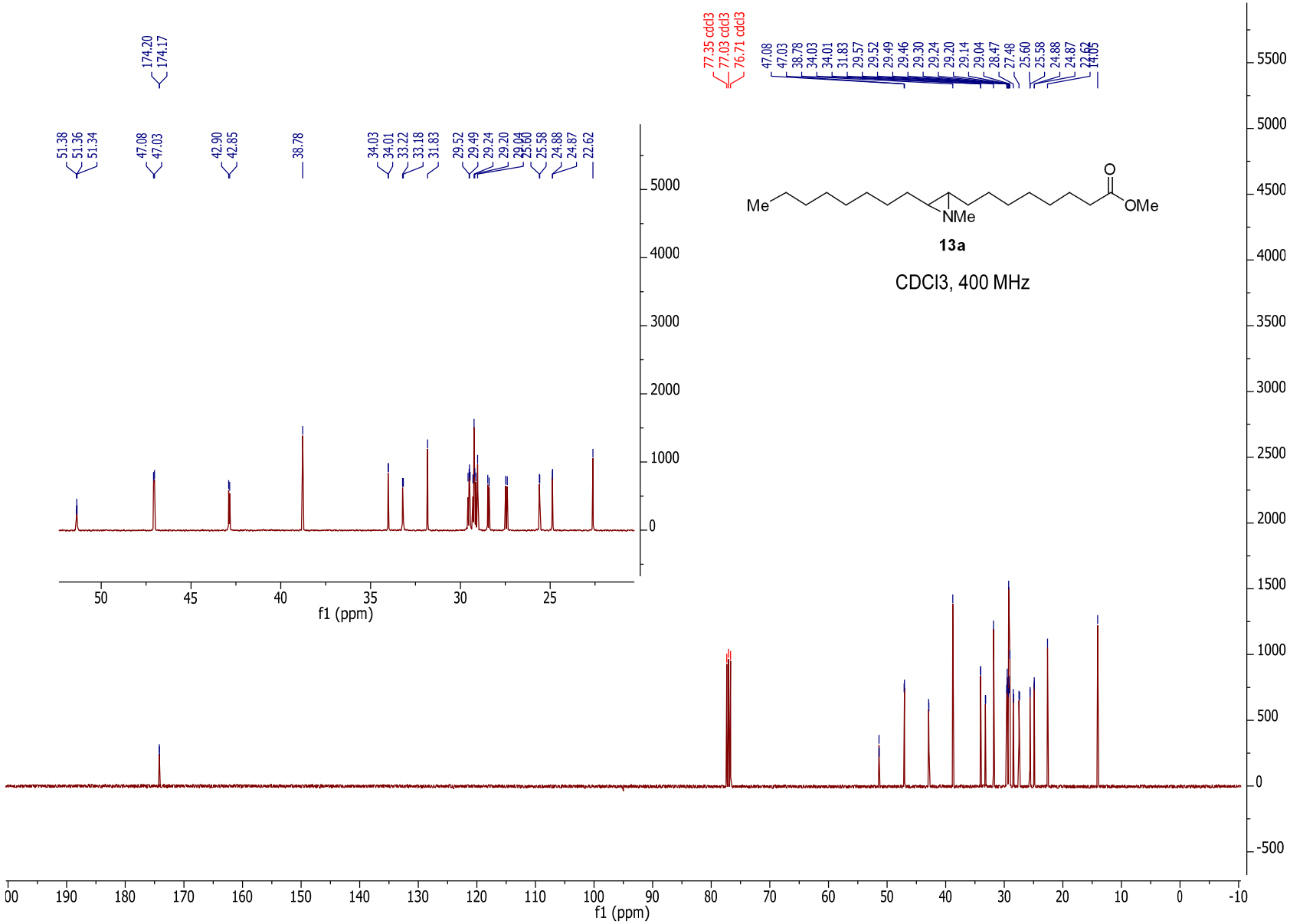

177.74
141.40
128.24
126.99
126.78
77.30 cdcl3
76.98 cdcl3
76.66 cdcl3
50.91
46.62
24.99
22.43
19.47
18.73
Me
N
Ac
Me
Me
12gg
CDCl3, 400 MHz
f1 (ppm)

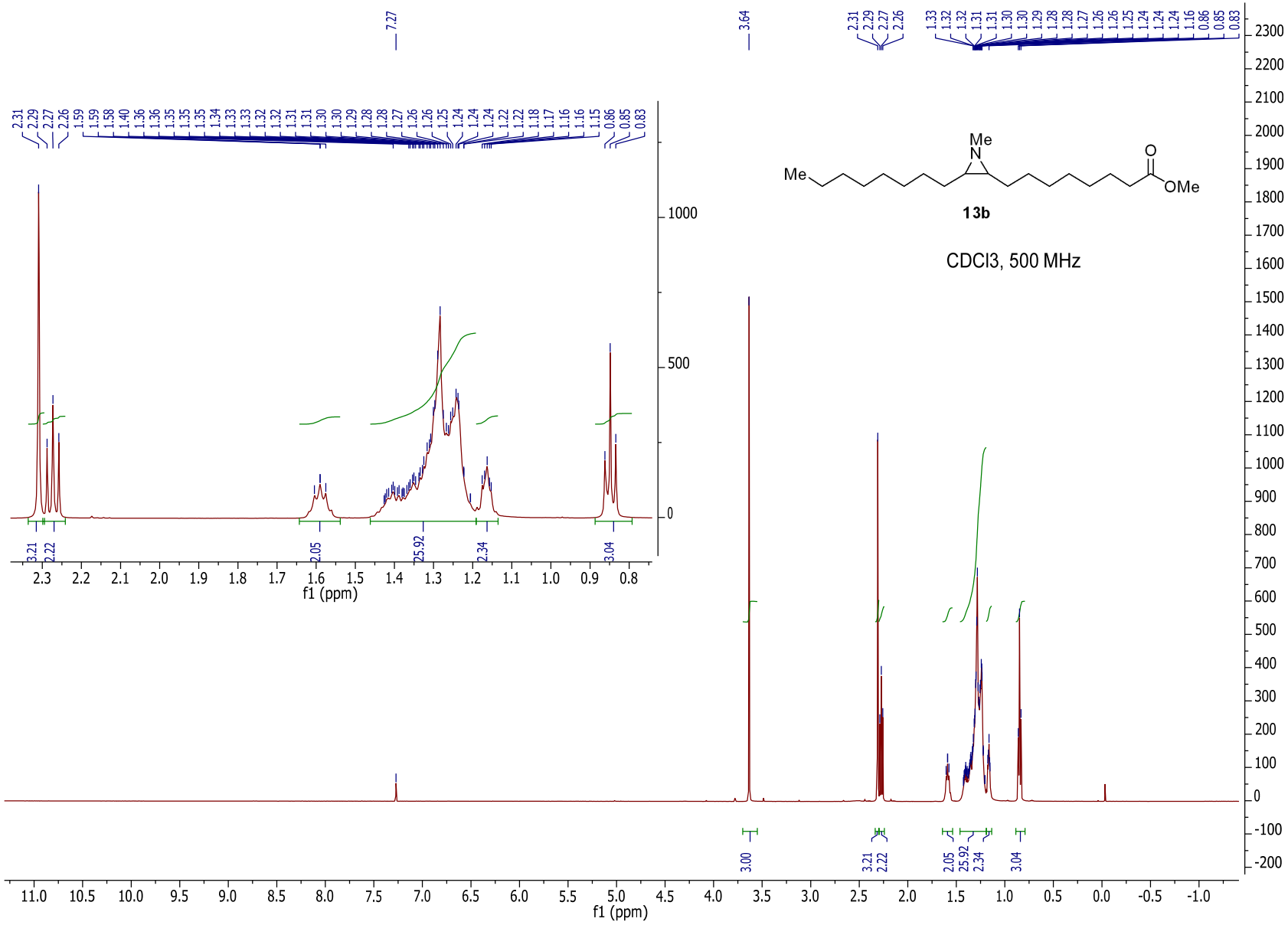

7.39
7.39
7.38
7.37
7.27
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15
3.14
3.14
3.13
3.10
3.10
3.10
3.07
3.04
3.03
1.57
NH
Me
12h
CDCl3, 500 MHz
4000
3500
3000
2500
2000
1500
1000
500
0
0.88
3.09
3.00
3.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

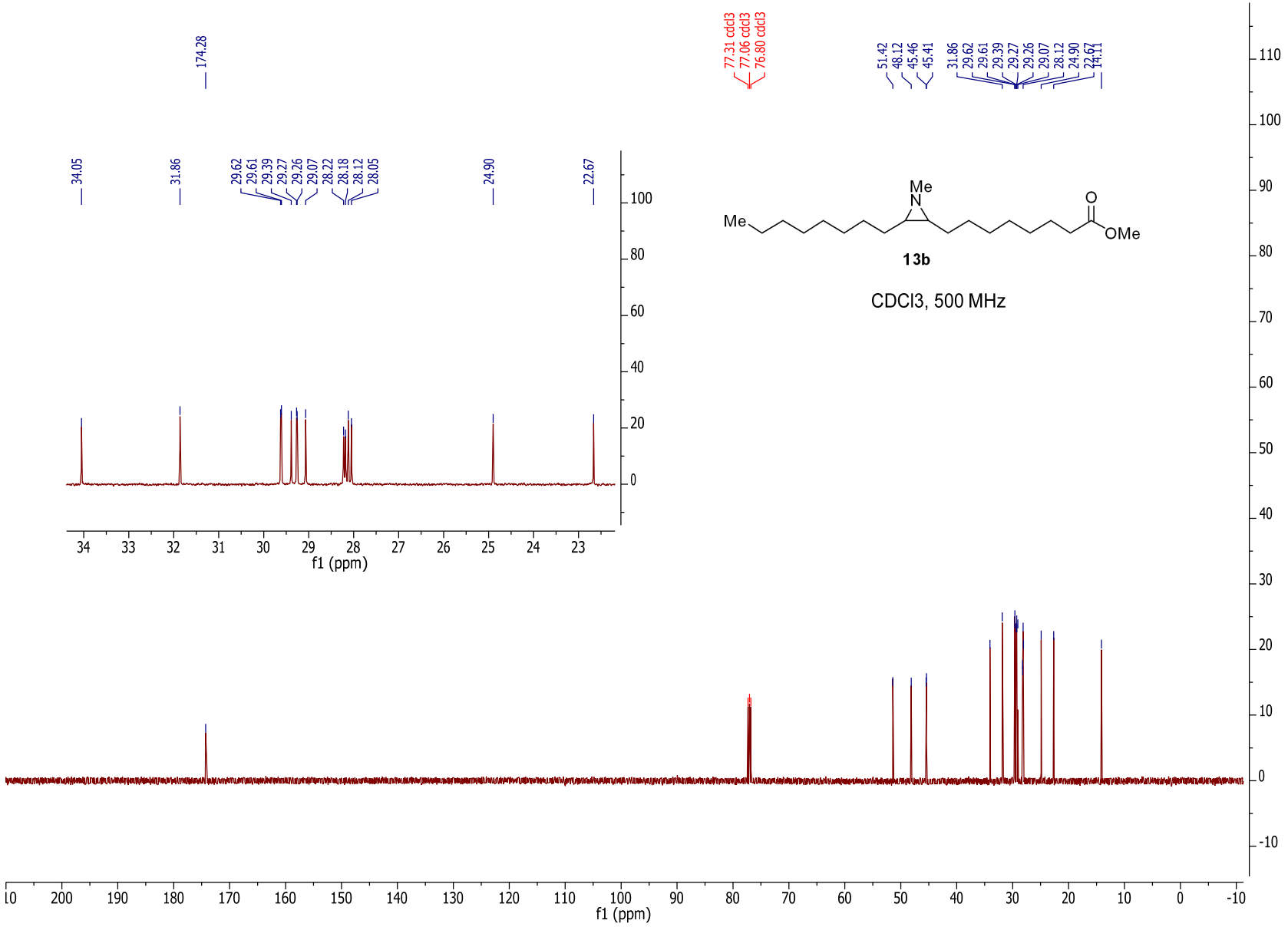

7.27
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
3.42
3.39
3.08
3.05
1.62
NH2
Me
12hh
CDCl3, 500 MHz
4.10
1.97
2.00
2.94
f1 (ppm)

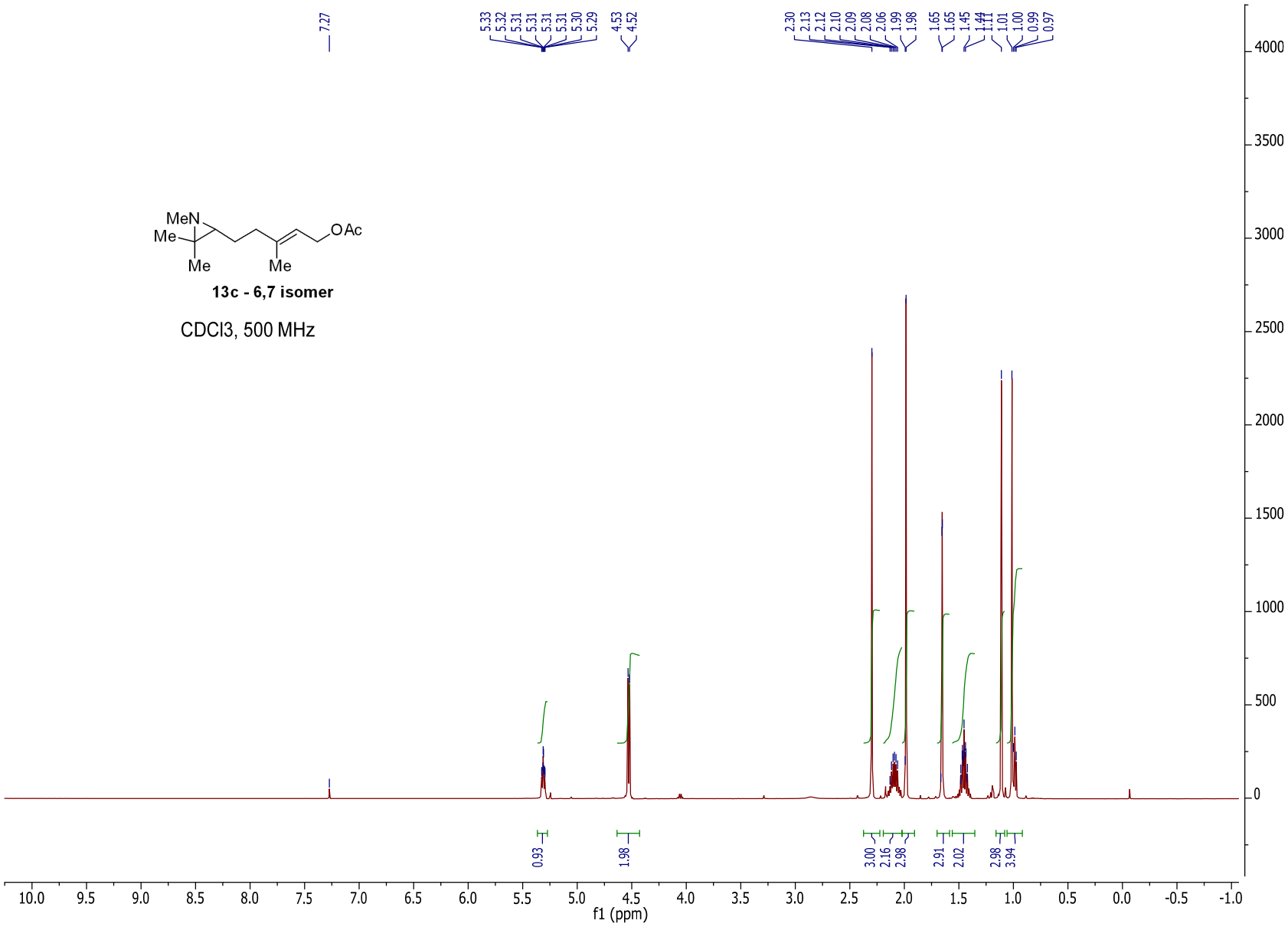

139.24
127.29
124.97
77.31 cdd3
77.06 cdd3
76.80 cdd3
61.49
44.66
24.93
NH2
Me
12hh
CDCl3, 500 MHz
f1 (ppm)

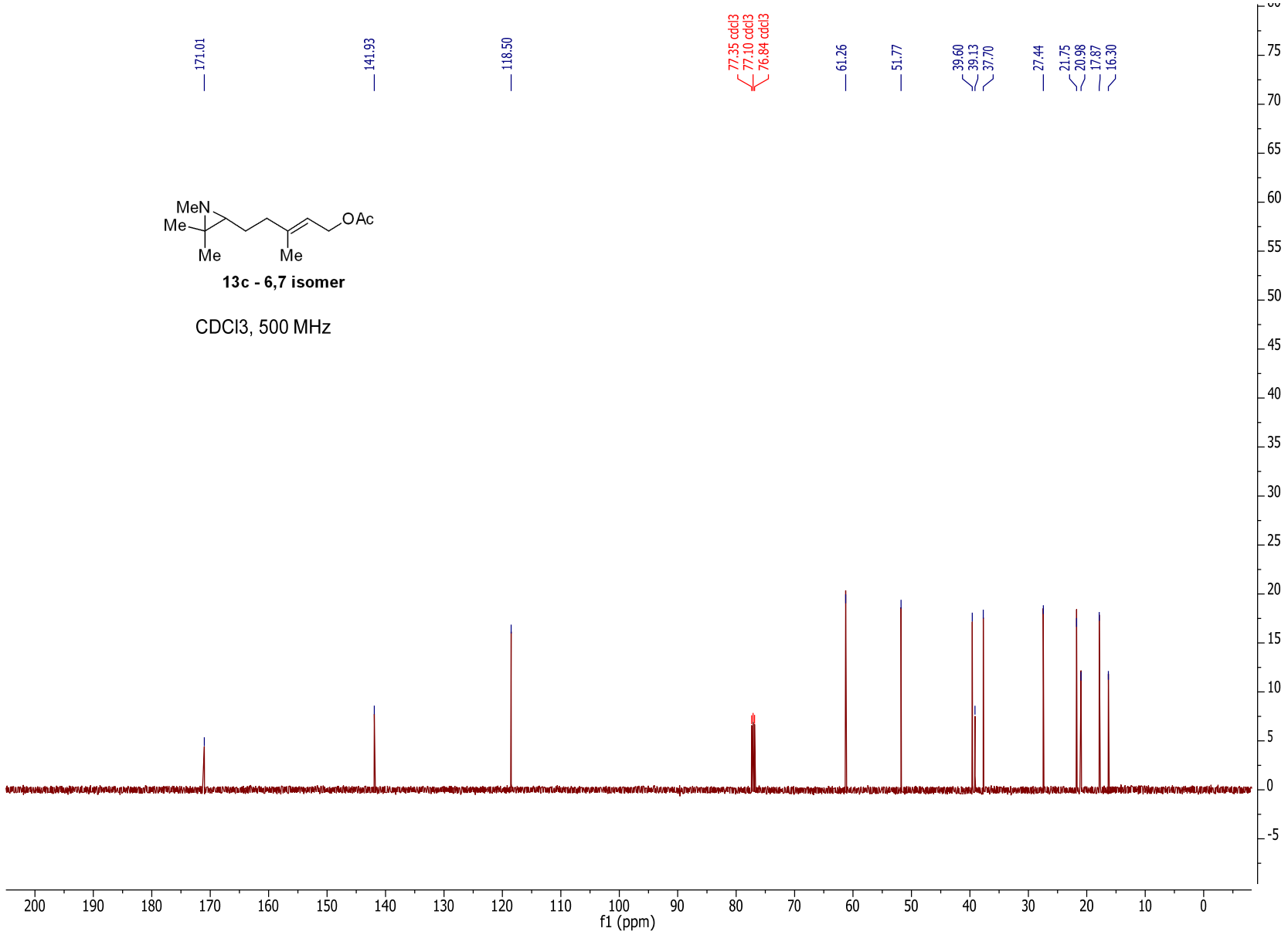

Me
NMe
O
OMe
13a
CDCl3, 400 MHz
f1 (ppm)

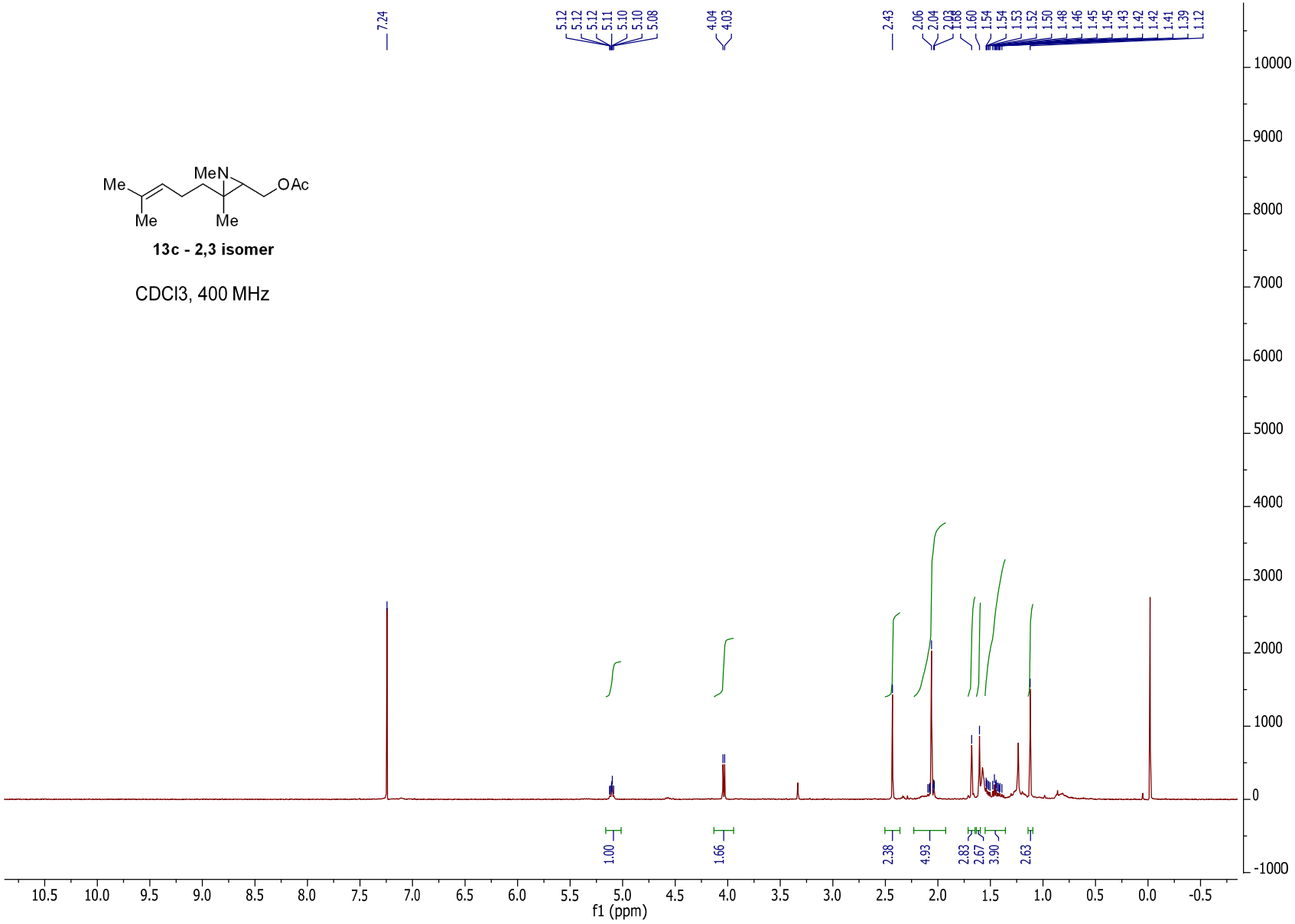

174.20
174.17
77.35 cdcl3
77.03 cdcl3
76.71 cdcl3
47.08
47.03
38.78
34.03
34.01
31.83
29.57
29.52
29.49
29.46
29.30
29.24
29.20
29.14
29.04
28.47
27.48
25.60
25.58
24.88
24.87
22.62
14.05
51.38
51.36
51.34
47.08
47.03
42.90
42.85
38.78
34.03
34.01
33.22
33.18
31.83
29.52
29.49
29.24
29.20
25.60
25.58
24.88
24.87
22.62
Me
NMe
O
OMe
13a
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

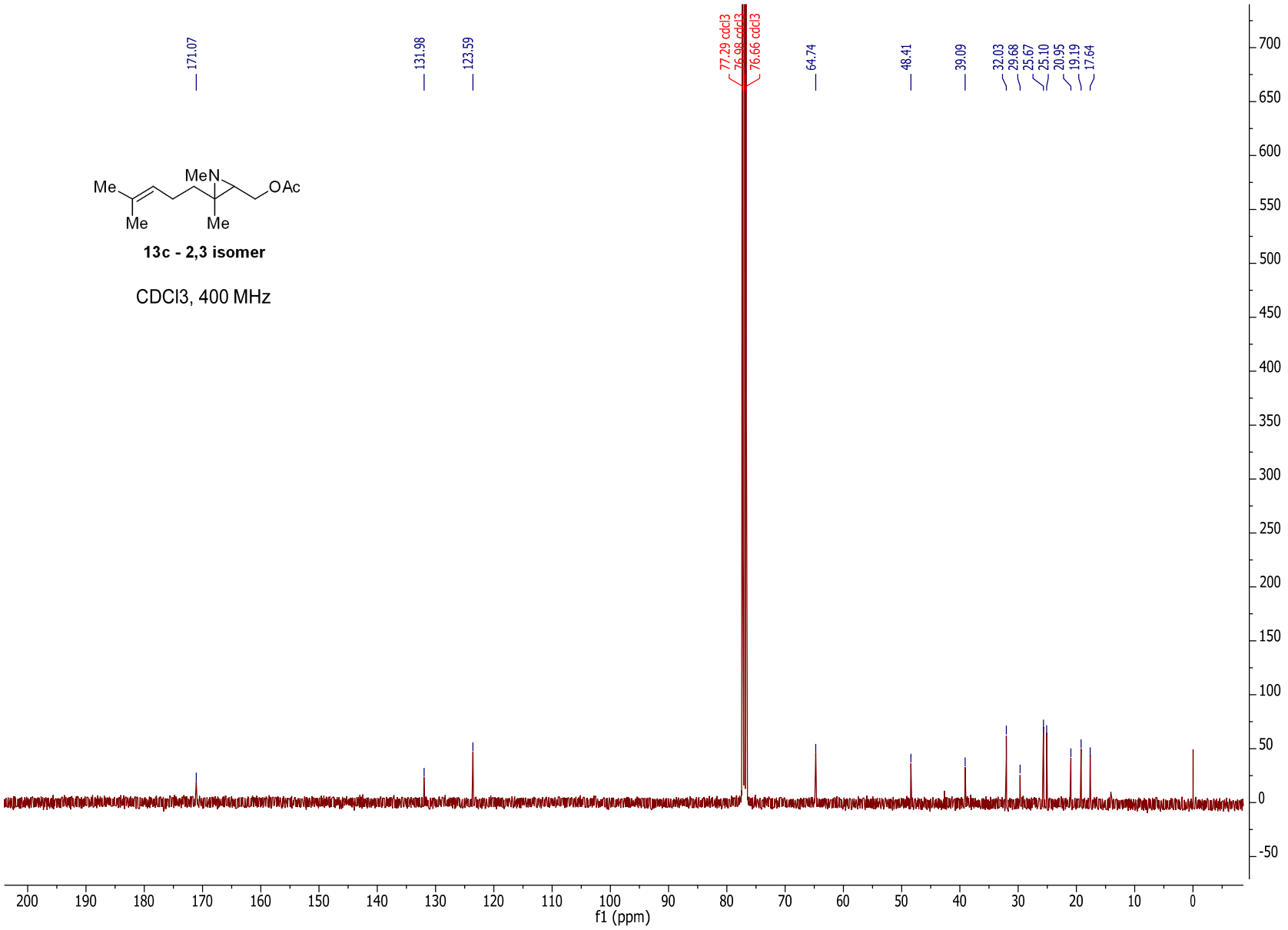

Me
N
O
Me
OMe
13b
CDCl3, 500 MHz
f1 (ppm)

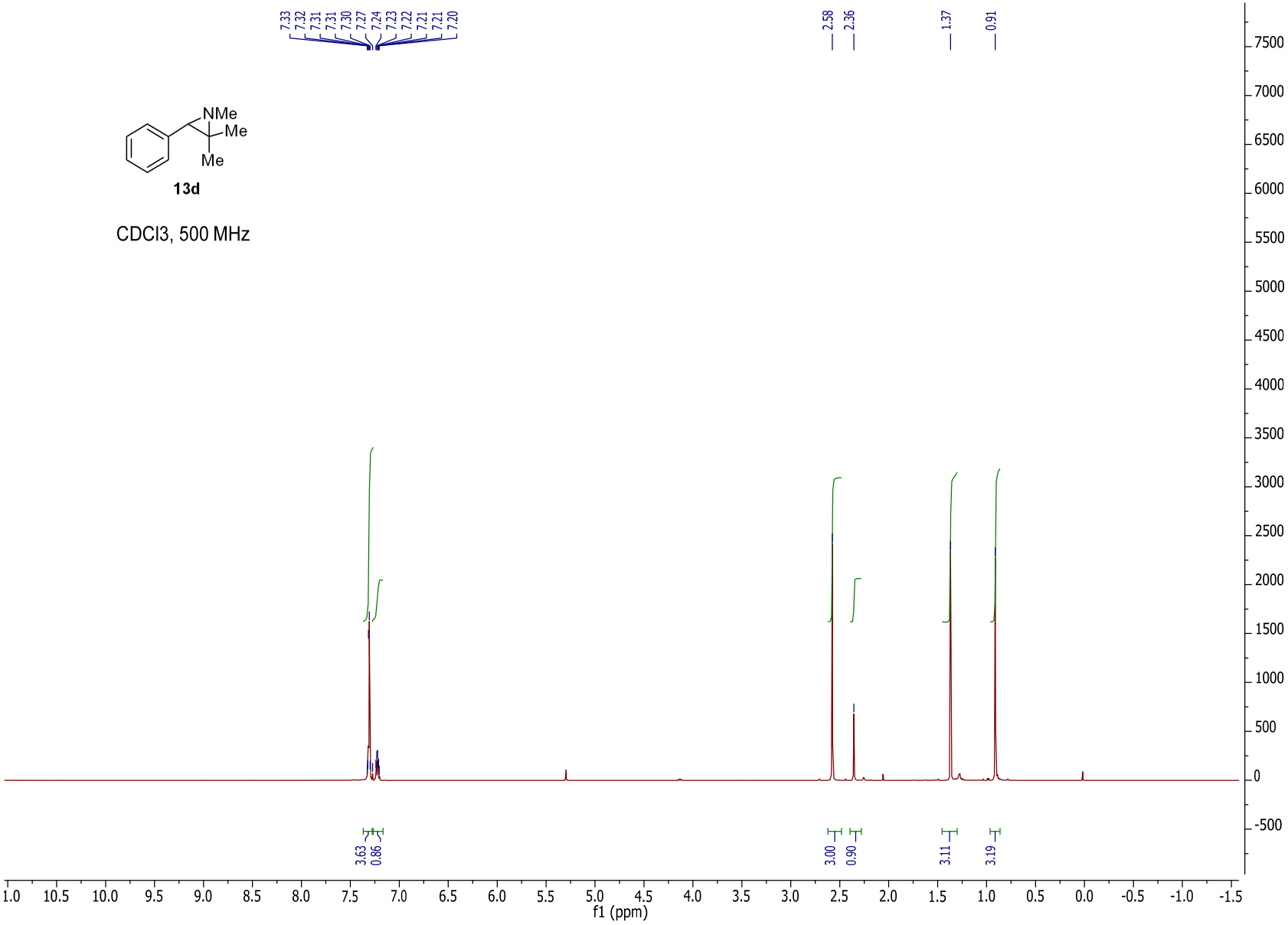

174.28
77.31 cdcl3
77.06 cdcl3
76.80 cdcl3
51.42
48.12
45.46
45.41
31.86
29.62
29.61
29.39
29.27
29.26
29.07
28.12
24.90
22.67
14.11
34.05
31.86
29.62
29.61
29.39
29.27
29.26
29.07
28.22
28.18
28.12
28.05
24.90
22.67
Me
N
Me
O
OMe
13b
CDCl3, 500 MHz
f1 (ppm)
f1 (ppm)

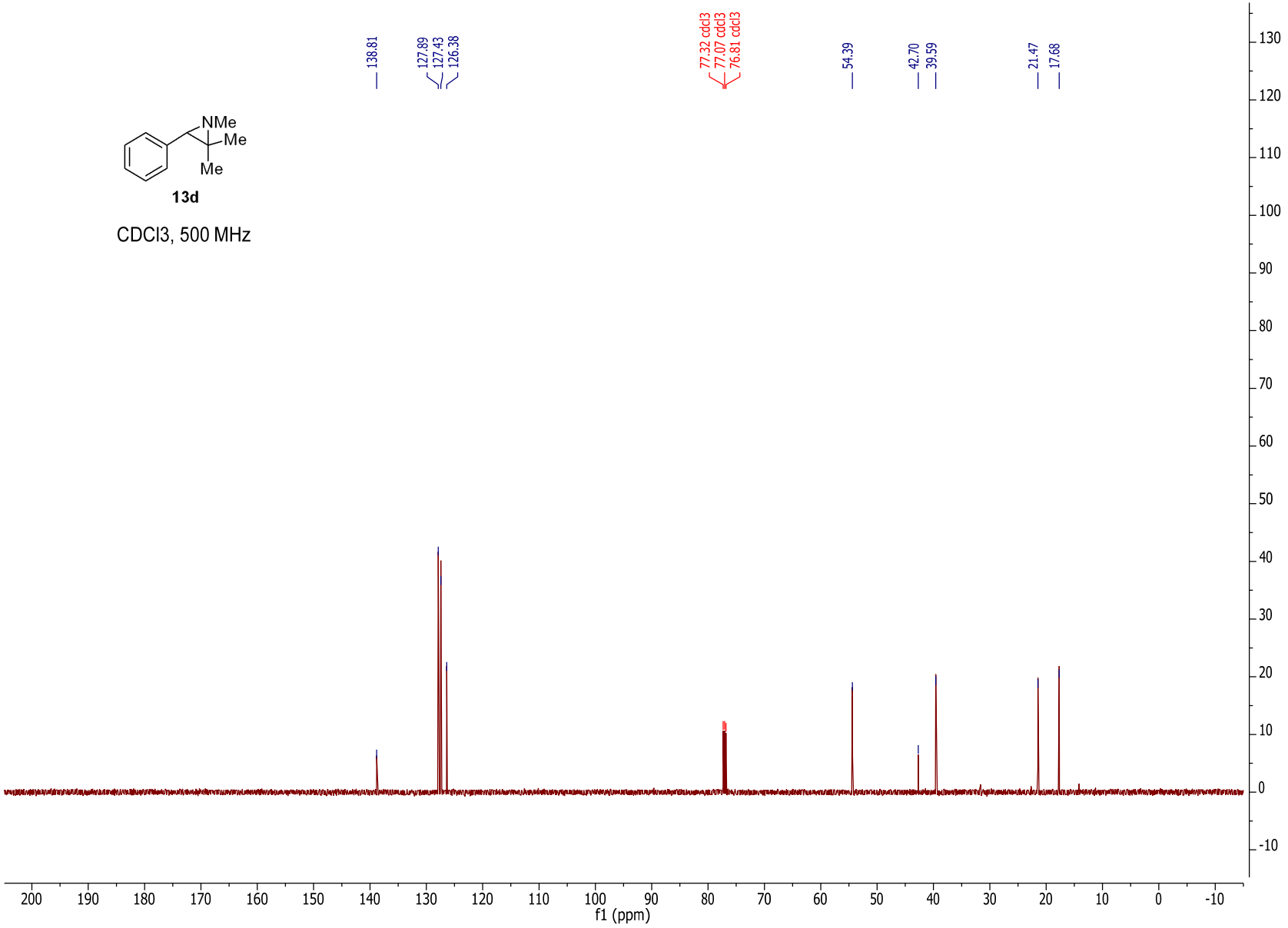

MeN
Me
Me
Me
OAc
13c - 6,7 isomer
CDCl3, 500 MHz
7.27
5.33
5.32
5.31
5.31
5.31
5.31
5.30
5.29
4.53
4.52
2.30
2.13
2.12
2.10
2.09
2.08
2.06
1.99
1.98
1.65
1.65
1.45
1.44
1.11
1.01
1.00
0.99
0.97
0.93
1.98
3.00
2.16
2.98
2.91
2.02
2.98
3.94
f1 (ppm)

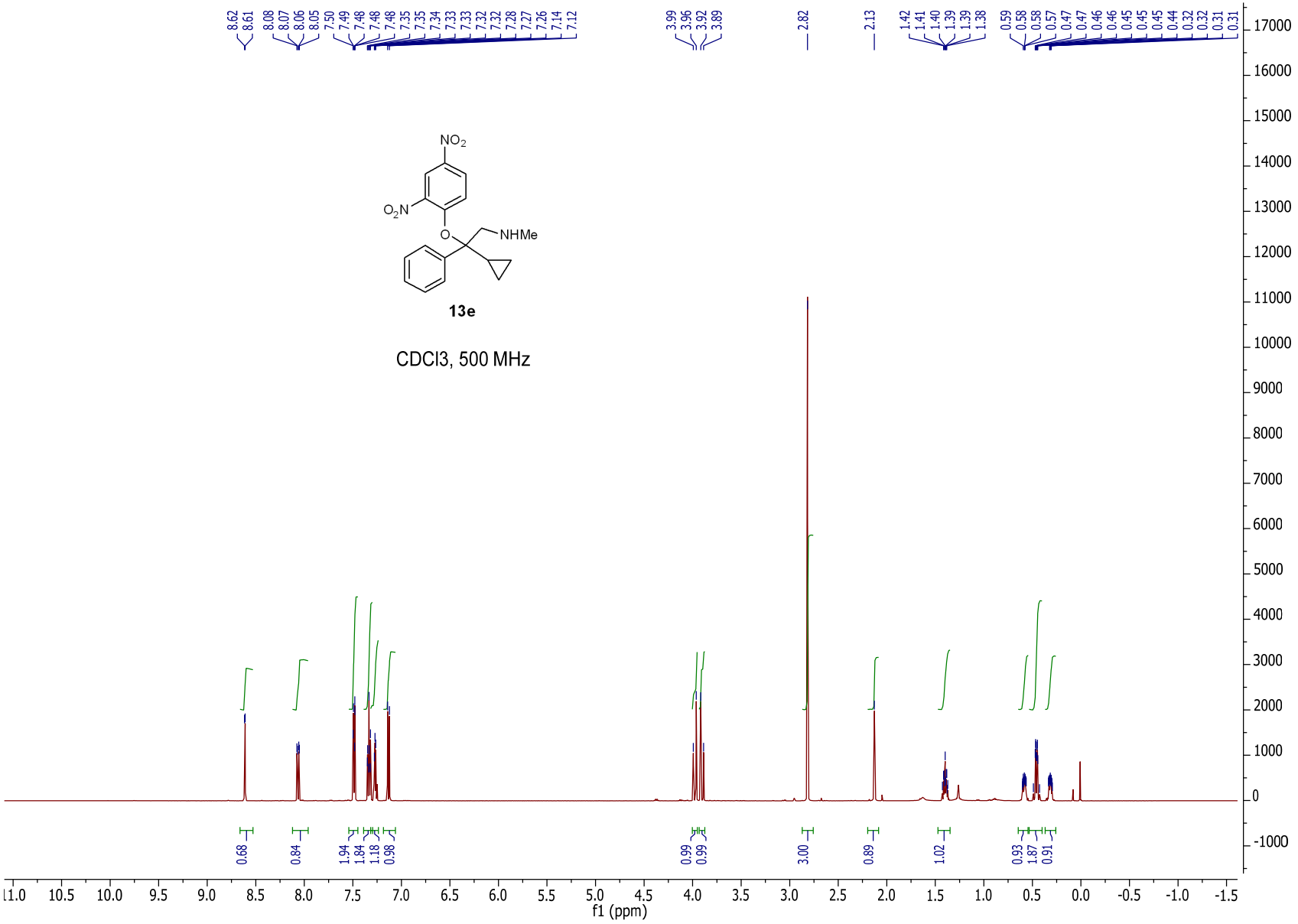

171.01
141.93
118.50
77.35 cdcl3
77.10 cdcl3
76.84 cdcl3
61.26
51.77
39.60
39.13
37.70
27.44
21.75
20.98
17.87
16.30
MeN
Me
Me
Me
OAc
13c - 6,7 isomer
CDCl3, 500 MHz
f1 (ppm)

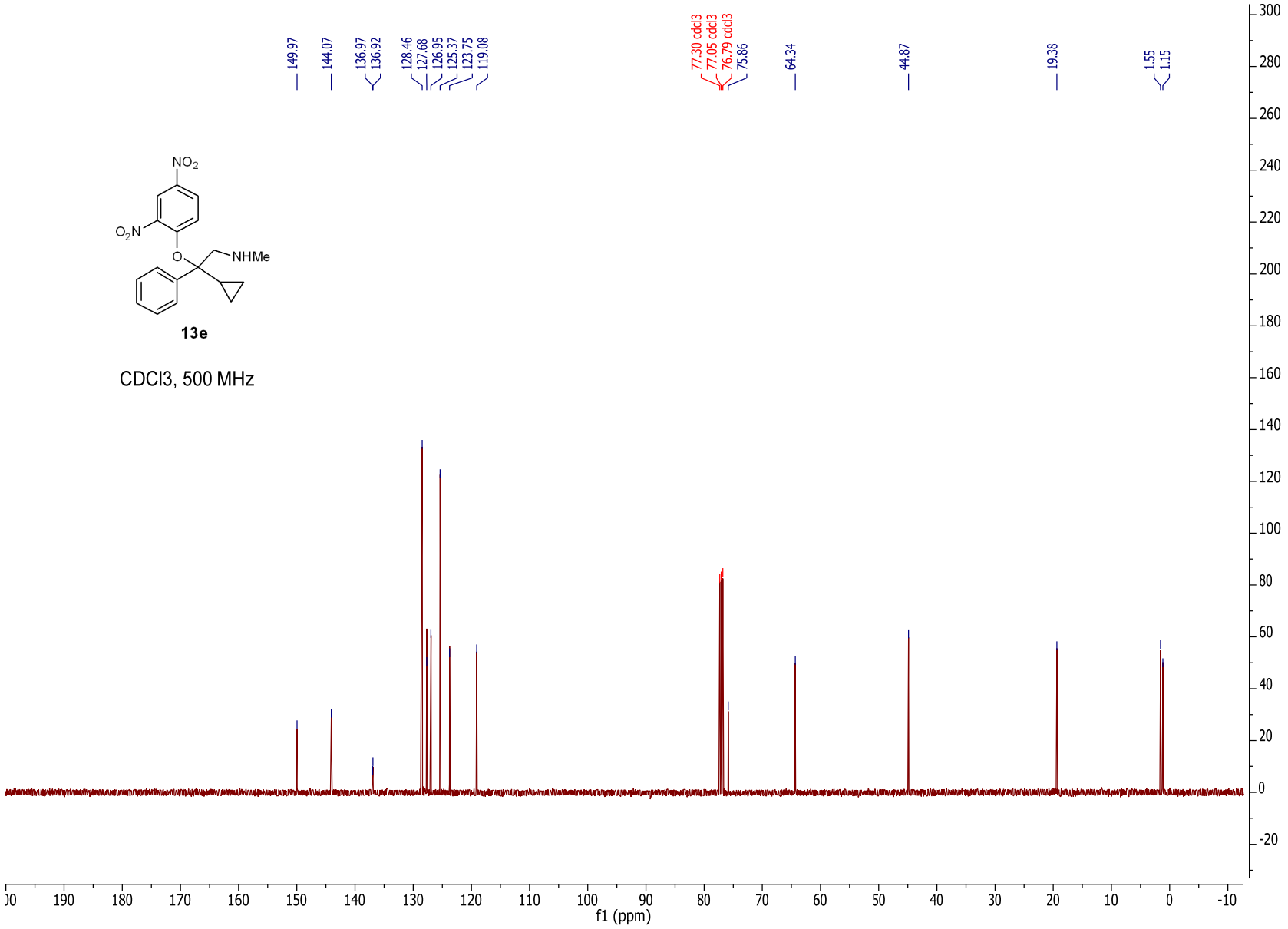

7.24
5.12
5.12
5.12
5.11
5.10
5.10
5.08
4.04
4.03
2.43
2.06
2.04
2.03
1.68
1.60
1.54
1.54
1.53
1.52
1.50
1.48
1.46
1.45
1.45
1.43
1.42
1.42
1.41
1.39
1.12
MeN
Me
OAc
Me
Me
13c - 2,3 isomer
CDCl3, 400 MHz
1.00
1.66
2.38
4.93
2.83
2.67
3.90
2.63
f1 (ppm)

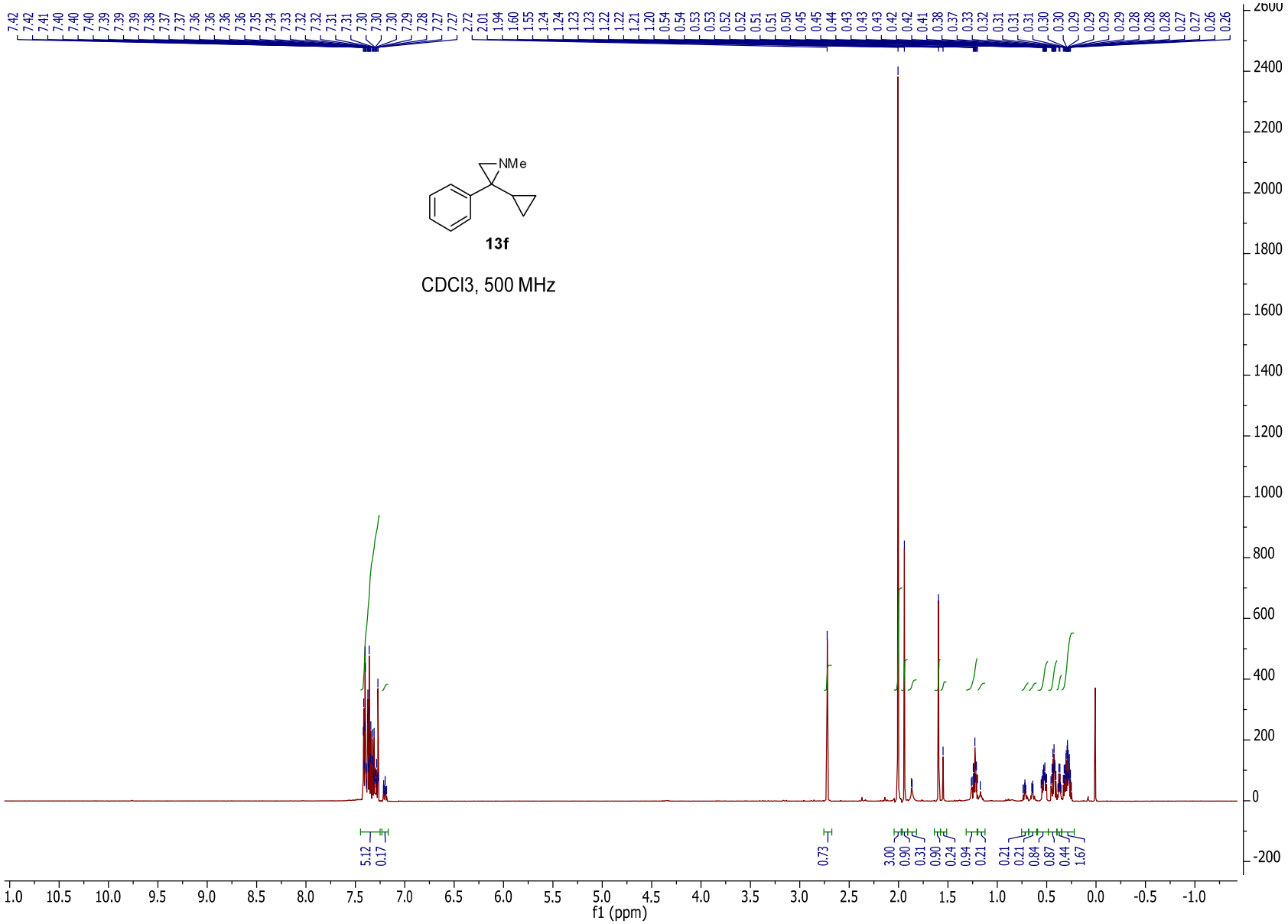

171.07
131.98
123.59
77.29 cdcl3
76.98 cdcl3
76.66 cdcl3
64.74
48.41
39.09
32.03
29.68
25.67
25.10
20.95
19.19
17.64
MeN
Me
OAc
Me
Me
13c - 2,3 isomer
CDCl3, 400 MHz
f1 (ppm)

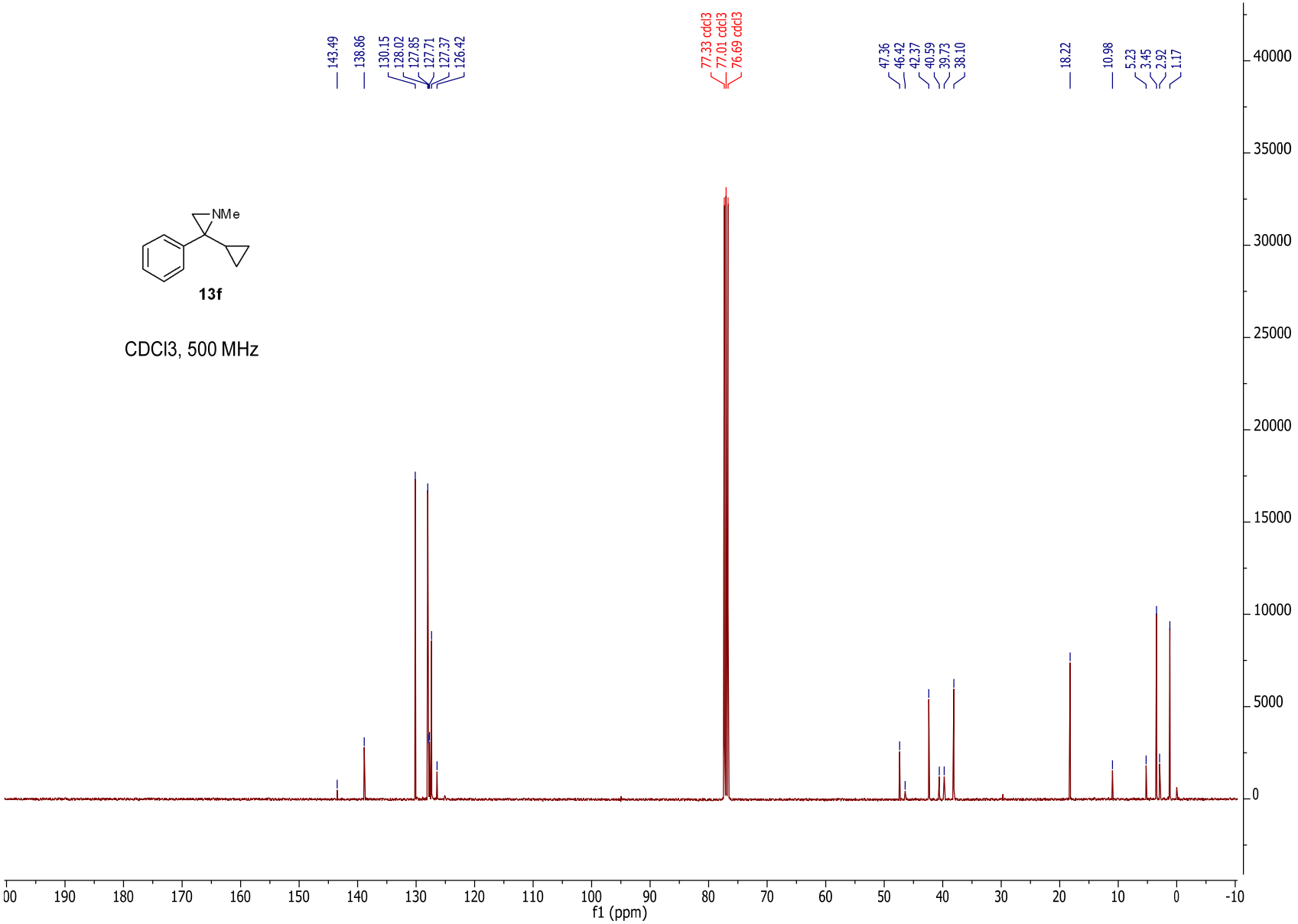

7.33
7.32
7.31
7.31
7.30
7.27
7.24
7.23
7.22
7.21
7.21
7.20
2.58
2.36
1.37
0.91
NMe
Me
Me
13d
CDCl3, 500 MHz
3.63
2.86
3.00
0.90
3.11
3.19
f1 (ppm)

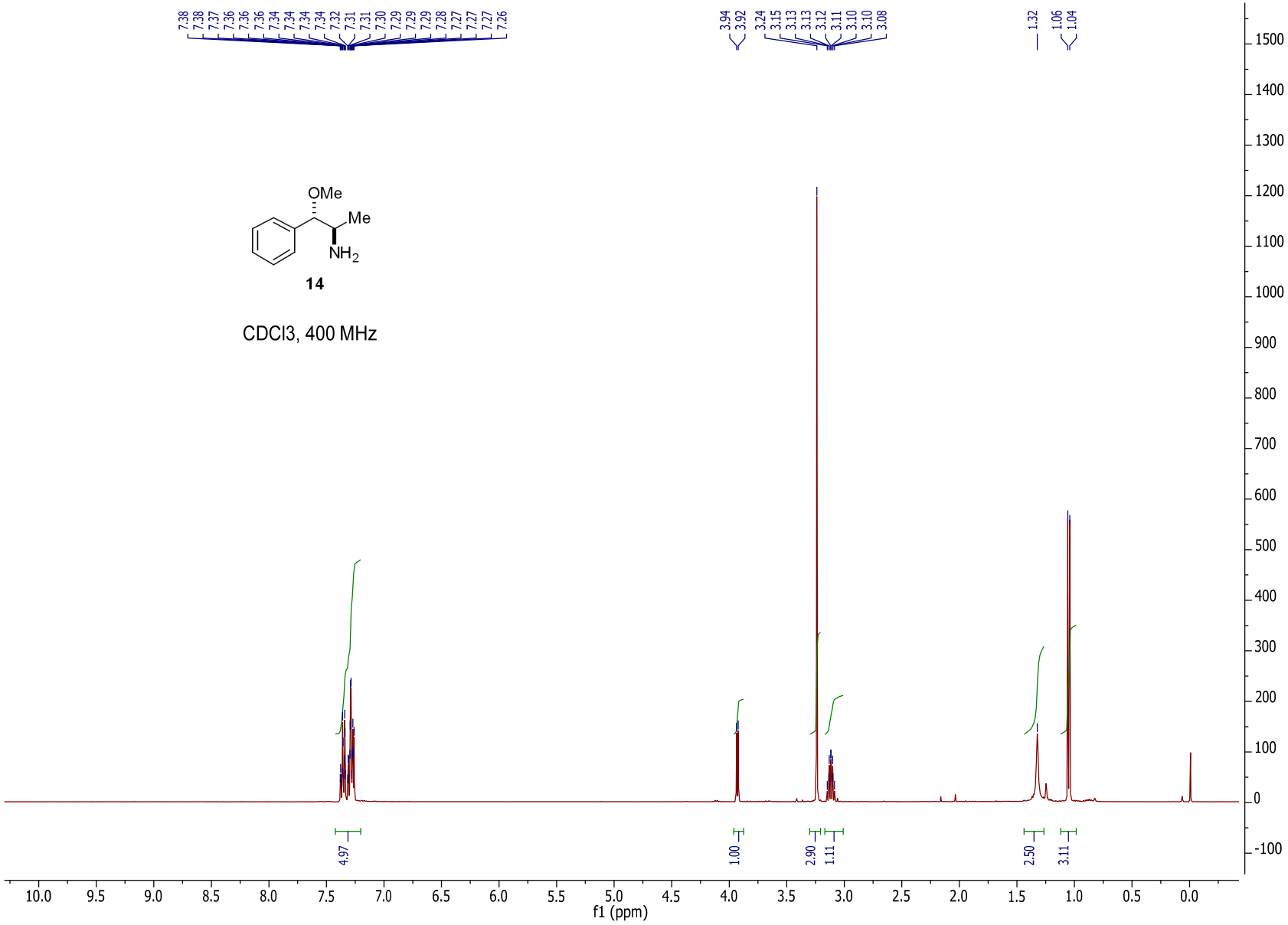

138.81
127.89
127.43
126.38
77.32 cdcl3
77.07 cdcl3
76.81 cdcl3
54.39
42.70
39.59
21.47
17.68
NMe
Me
Me
13d
CDCl3, 500 MHz
f1 (ppm)

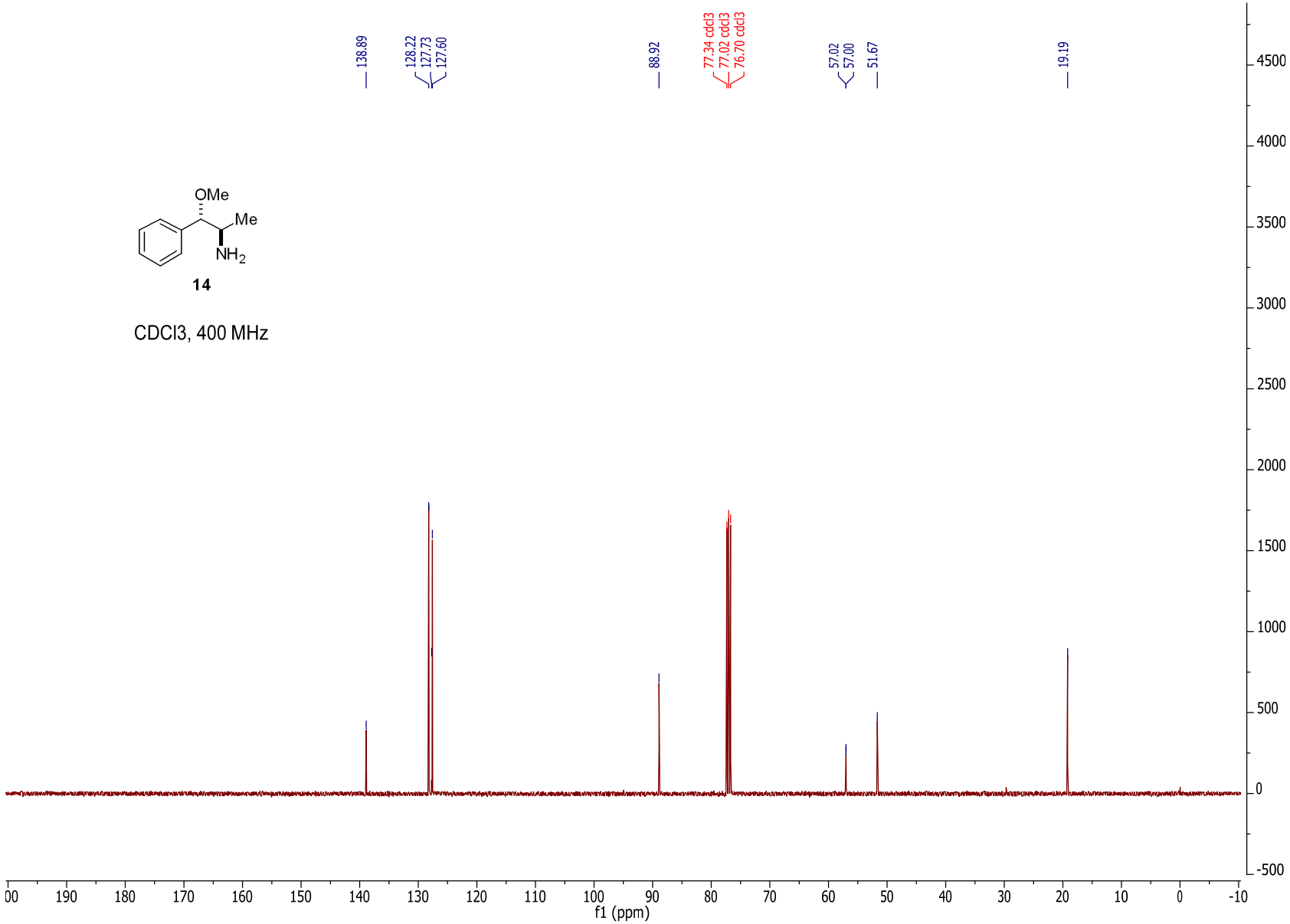

8.62
8.61
8.08
8.07
8.06
8.05
7.50
7.49
7.48
7.48
7.48
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.28
7.27
7.26
7.14
7.12
3.99
3.96
3.92
3.89
2.82
2.13
1.42
1.41
1.40
1.39
1.39
1.38
0.59
0.58
0.58
0.57
0.47
0.47
0.46
0.46
0.45
0.45
0.45
0.44
0.32
0.32
0.31
0.31
NO2
O2N
O
NHMe
13e
CDCl3, 500 MHz
0.68
0.84
1.94
1.84
1.18
0.98
0.99
0.99
3.00
0.89
1.02
0.93
1.87
0.91
f1 (ppm)

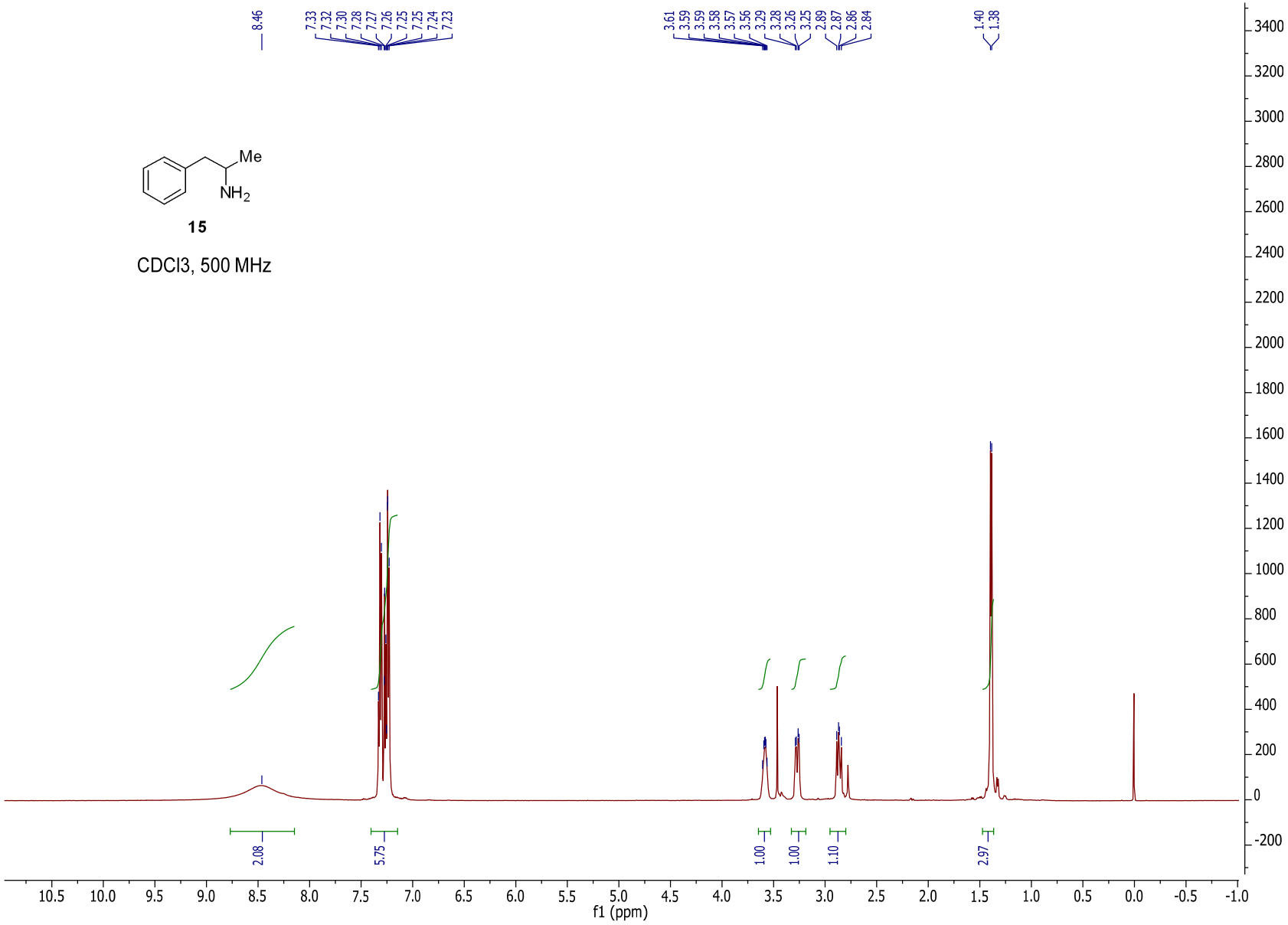

149.97
144.07
136.97
136.92
128.46
127.68
126.95
125.37
123.75
119.08
77.30 cdcl3
77.05 cdcl3
76.79 cdcl3
75.86
64.34
44.87
19.38
1.55
1.15
NO2
O2N
O
NHMe
13e
CDCl3, 500 MHz
f1 (ppm)

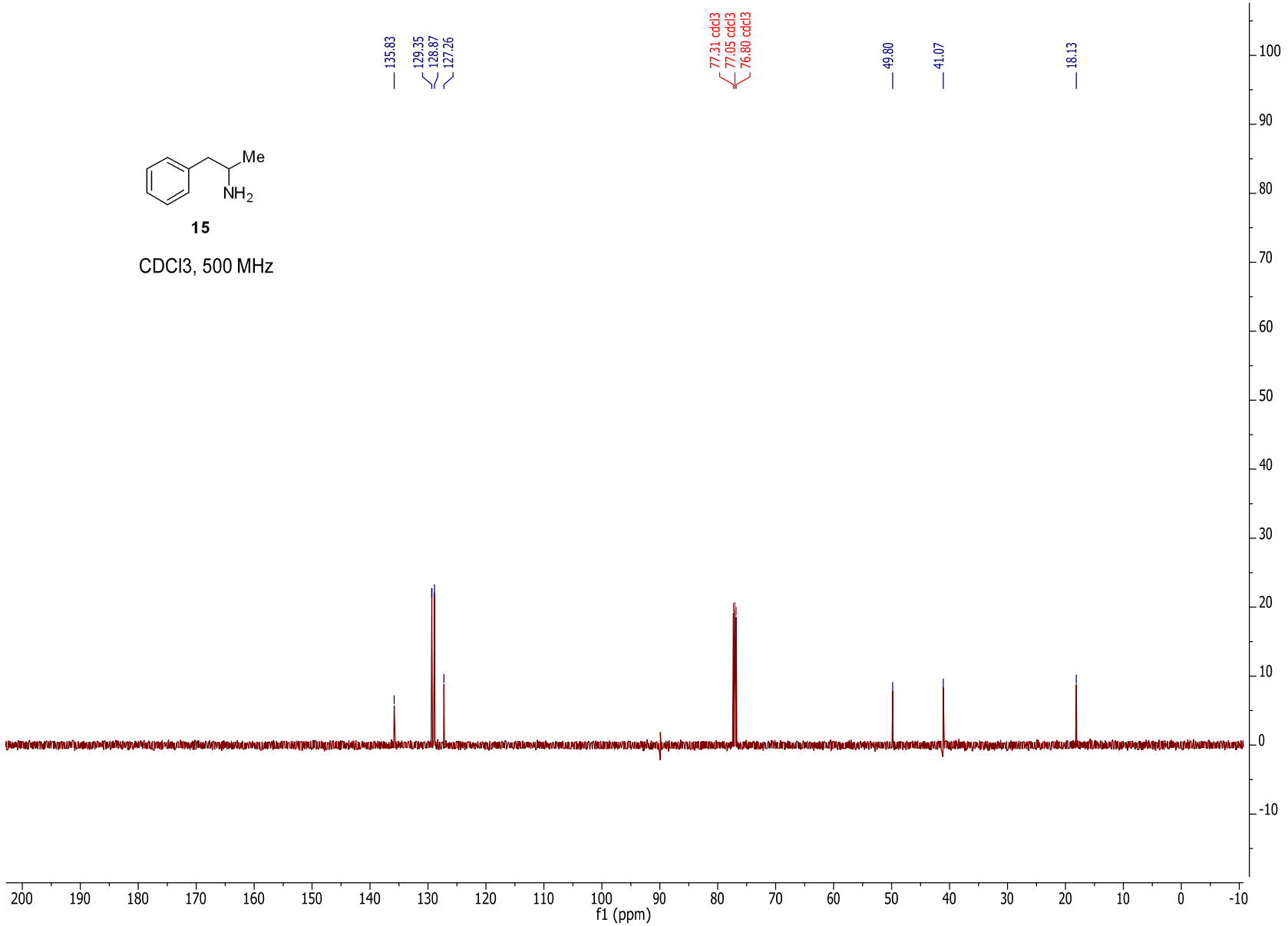

NMe
13f
CDCl3, 500 MHz
f1 (ppm)

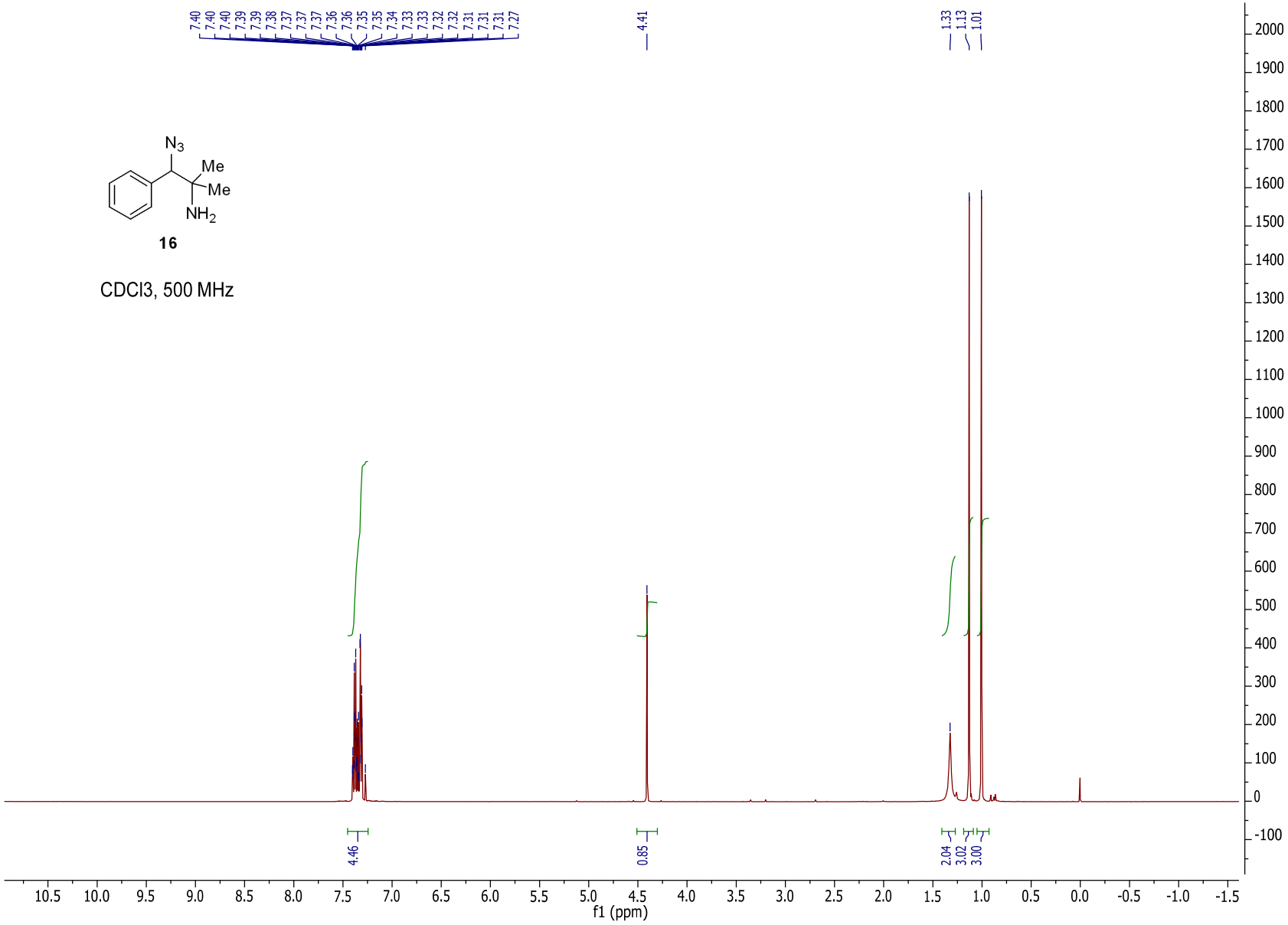

143.49
138.86
130.15
128.02
127.85
127.71
127.37
126.42
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
47.36
46.42
42.37
40.59
39.73
38.10
18.22
10.98
5.23
3.45
2.92
1.17
NMe
13f
CDCl3, 500 MHz
f1 (ppm)

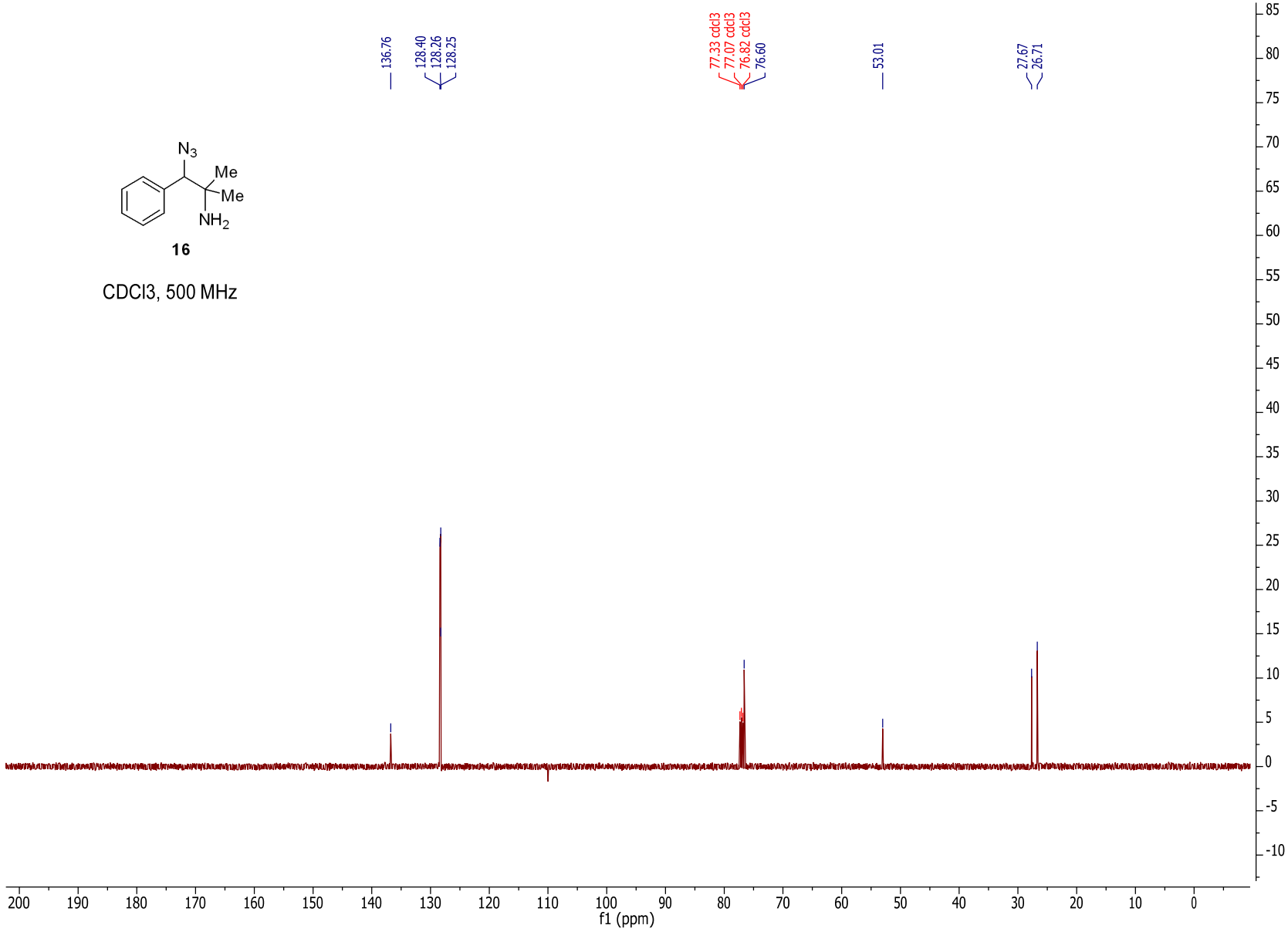

7.38
7.38
7.37
7.36
7.36
7.36
7.34
7.34
7.34
7.34
7.32
7.31
7.31
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.27
7.26
3.94
3.92
3.24
3.15
3.13
3.13
3.12
3.11
3.10
3.10
3.08
1.32
1.06
1.04
OMe
Me
NH2
14
CDCl3, 400 MHz
4.97
1.00
2.90
1.11
2.50
3.11
f1 (ppm)

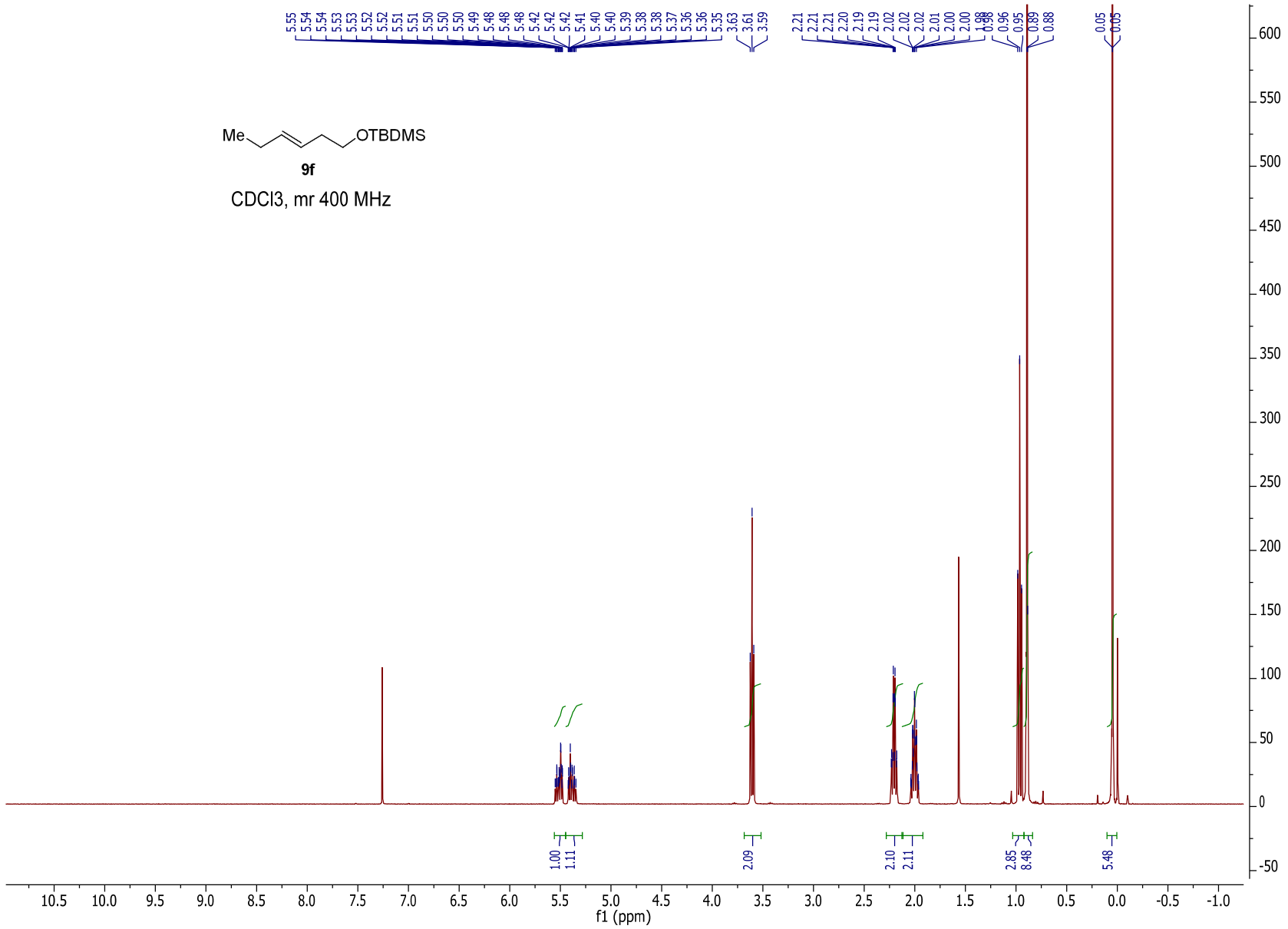

138.89
128.22
127.73
127.60
88.92
77.34 cdcl3
77.02 cdcl3
76.70 cdcl3
57.02
57.00
51.67
19.19
OMe
Me
NH2
14
CDCl3, 400 MHz
f1 (ppm)

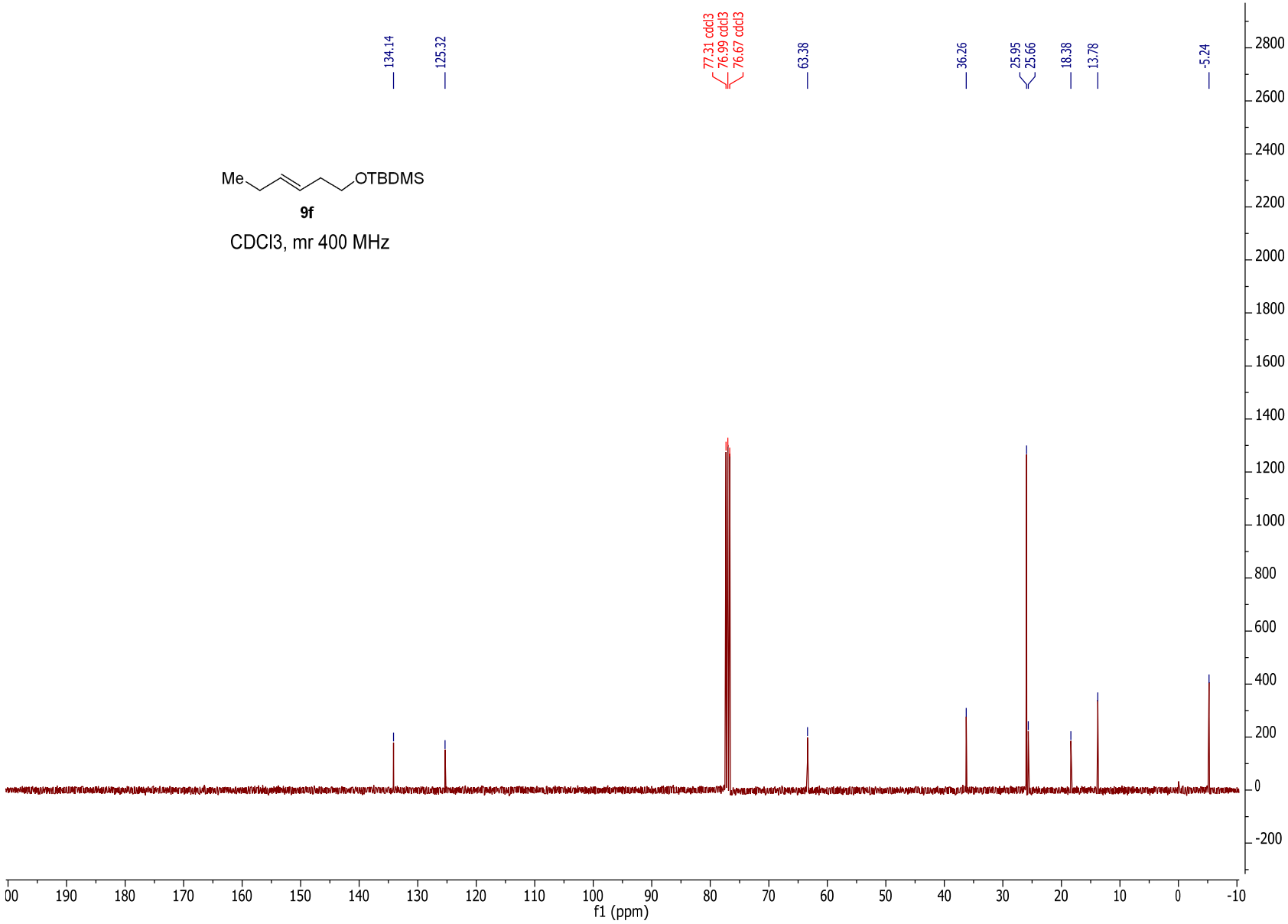

8.46
7.33
7.32
7.30
7.28
7.27
7.26
7.25
7.25
7.24
7.23
3.61
3.59
3.59
3.58
3.57
3.56
3.29
3.28
3.26
3.25
2.89
2.87
2.86
2.84
1.40
1.38
Me
NH2
15
CDCl3, 500 MHz
2.08
5.75
1.00
1.00
1.10
2.97
f1 (ppm)

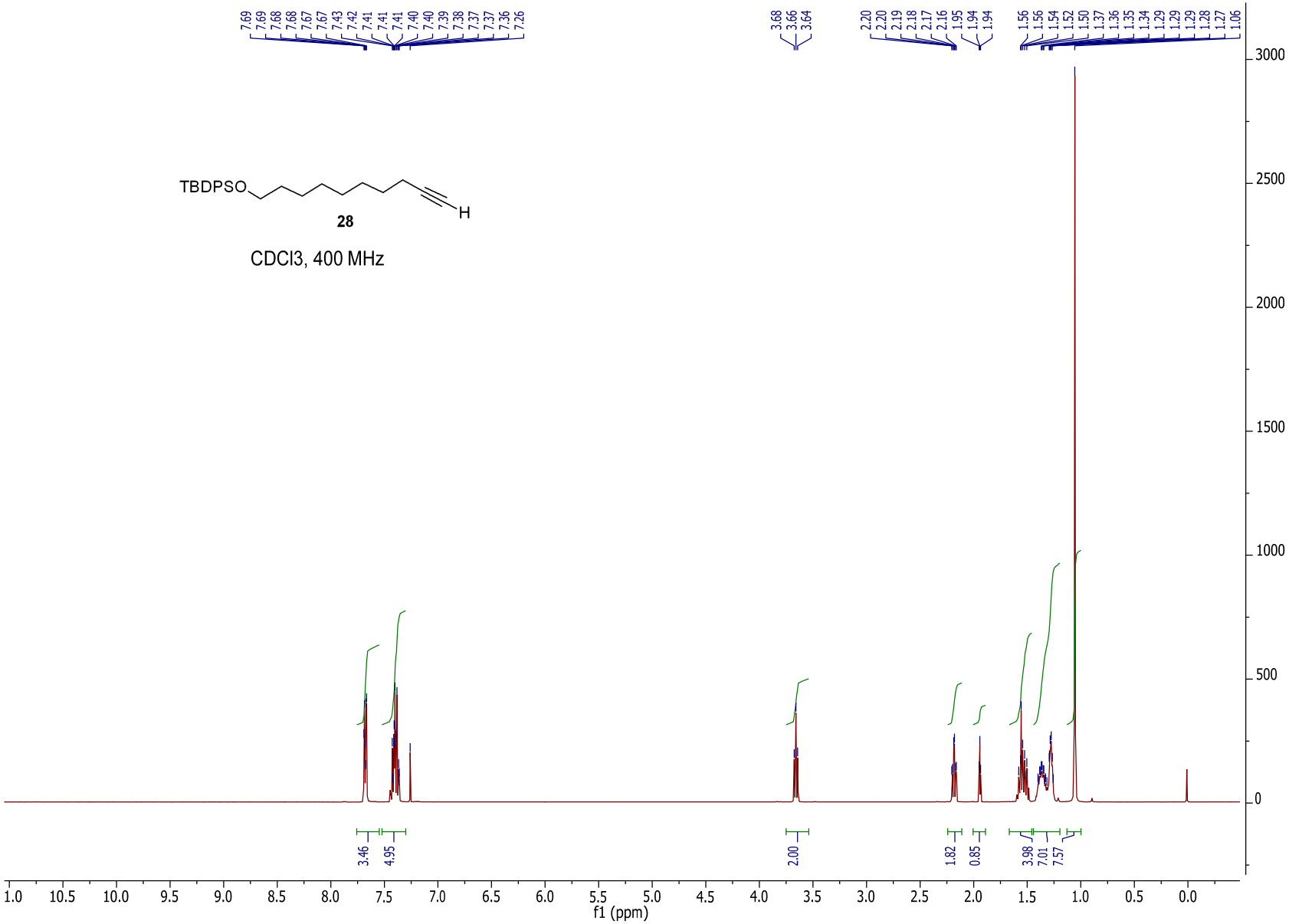

135.83
129.35
128.87
127.26
77.31 cdcl3
77.05 cdcl3
76.80 cdcl3
49.80
41.07
18.13
Me
NH2
15
CDCl3, 500 MHz
f1 (ppm)

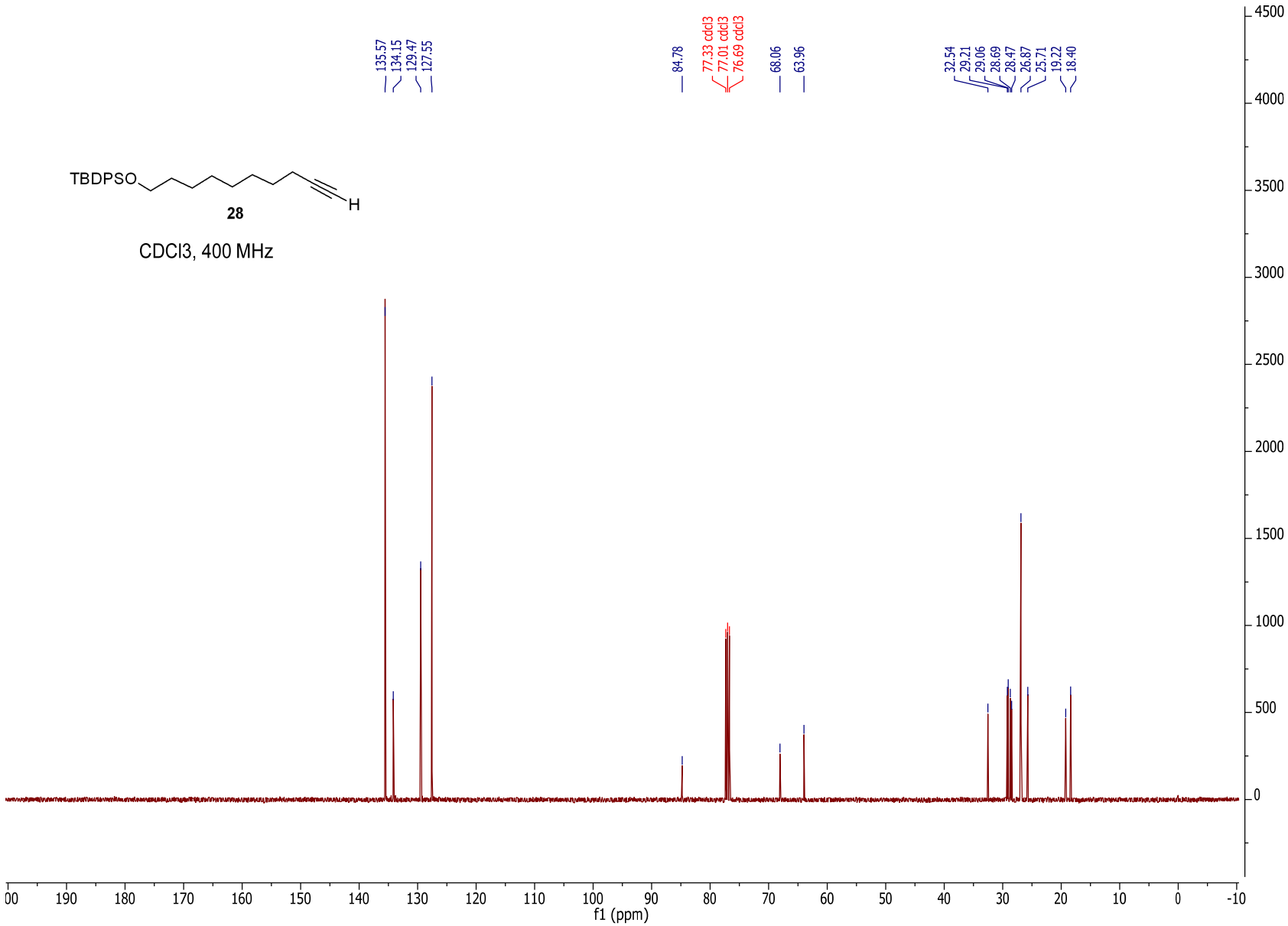

7.40
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.27
4.41
1.33
1.13
1.01
N3
Me
Me
NH2
16
CDCl3, 500 MHz
4.46
0.85
2.04
3.02
3.00
f1 (ppm)

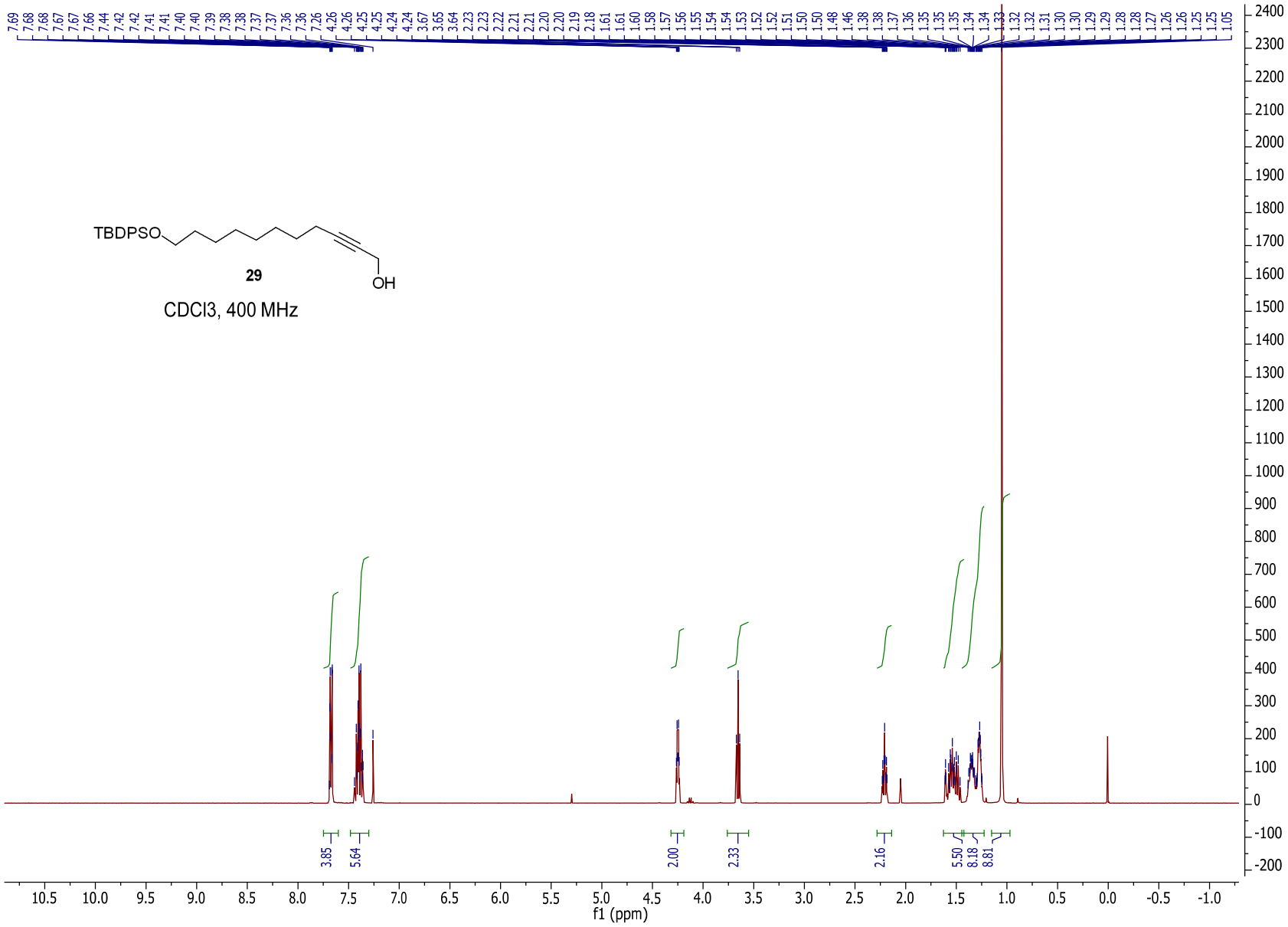

136.76
128.40
128.26
128.25
77.33 cdcl3
77.07 cdcl3
76.82 cdcl3
76.60
53.01
27.67
26.71
N3
Me
Me
NH2
16
CDCl3, 500 MHz
f1 (ppm)

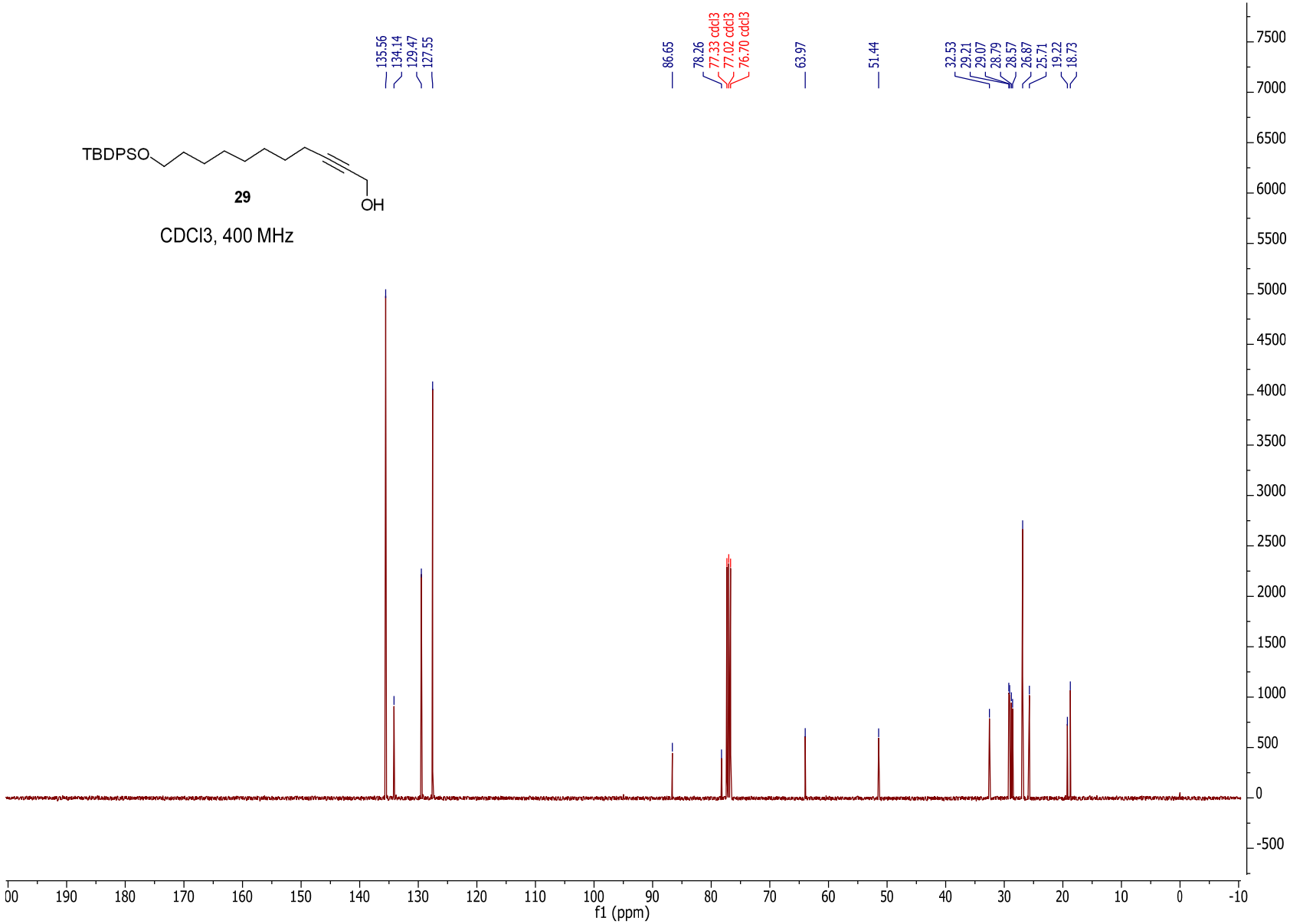

Me
OTBDMS
9f
CDCl3, mr 400 MHz
f1 (ppm)

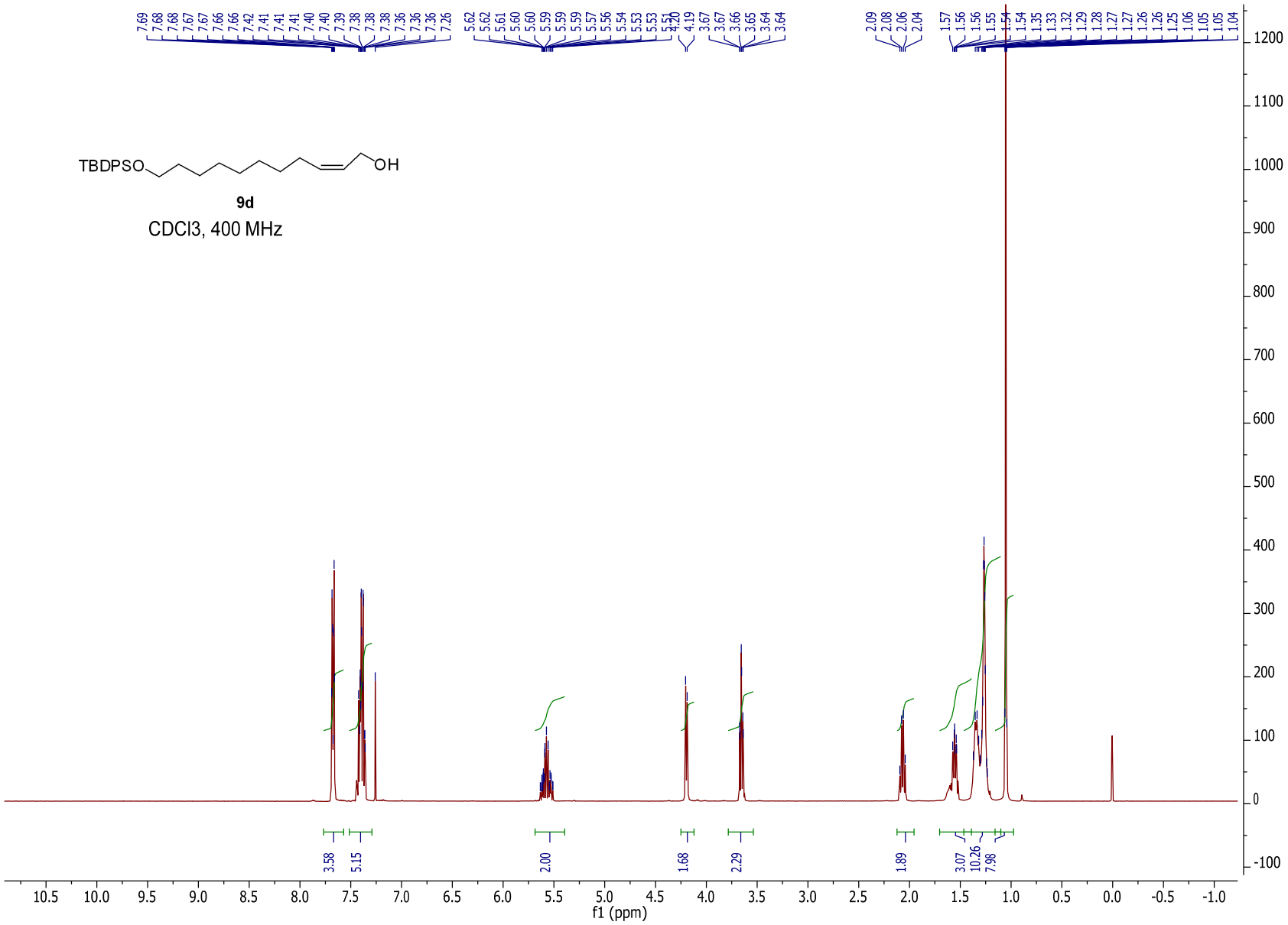

134.14
125.32
77.31 cdcl3
76.99 cdcl3
76.67 cdcl3
63.38
36.26
25.95
25.66
18.38
13.78
-5.24
Me
OTBDMS
9f
CDCl3, mr 400 MHz
f1 (ppm)

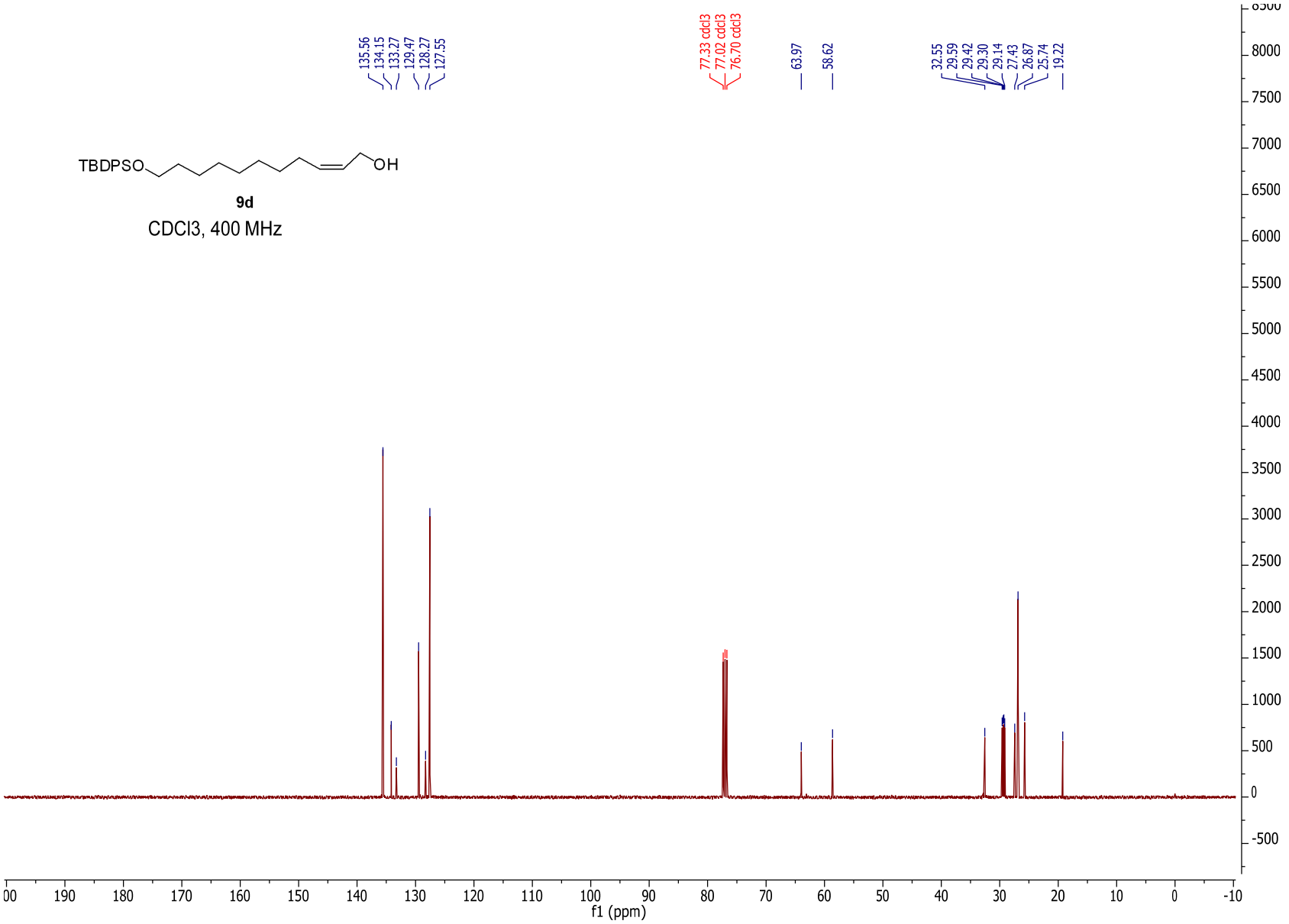

TBDPSO
H
28
CDCl3, 400 MHz
7.69 7.69 7.68 7.68 7.67 7.67 7.43 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.26
3.68 3.66 3.64
2.20 2.20 2.19 2.18 2.17 2.16 1.95 1.94 1.94
1.56 1.56 1.54 1.52 1.50 1.37 1.36 1.35 1.34 1.29 1.29 1.28 1.27 1.06
3.46 4.95 2.00 1.82 0.85 3.98 7.01 7.57
f1 (ppm)


135.57
134.15
129.47
127.55
84.78
77.33 cdcl3
77.01 cdcl3
76.69 cdcl3
68.06
63.96
32.54
29.21
29.06
28.69
28.47
26.87
25.71
19.22
18.40
TBDPSO
H
28
CDCl3, 400 MHz
f1 (ppm)


TBDPSO
29
OH
CDCl3, 400 MHz
f1 (ppm)


135.56
134.14
129.47
127.55
86.65
78.26
77.33 cdcl3
77.02 cdcl3
76.70 cdcl3
63.97
51.44
32.53
29.21
29.07
28.79
28.57
26.87
25.71
19.22
18.73
TBDPSO
OH
29
CDCl3, 400 MHz
f1 (ppm)


TBDPSO
OH
9d
CDCl3, 400 MHz
f1 (ppm)


135.56
134.15
133.27
129.47
128.27
127.55
77.33 cdcl3
77.02 cdcl3
76.70 cdcl3
63.97
58.62
32.55
29.59
29.42
29.30
29.14
27.43
26.87
25.74
19.22
TBDPSO
OH
9d
CDCl3, 400 MHz
f1 (ppm)